SUPPORTING INFORMATION

Synthetic and Mechanistic Studies of a Versatile Heteroaryl Thioether Directing Group for Pd(II) Catalysis

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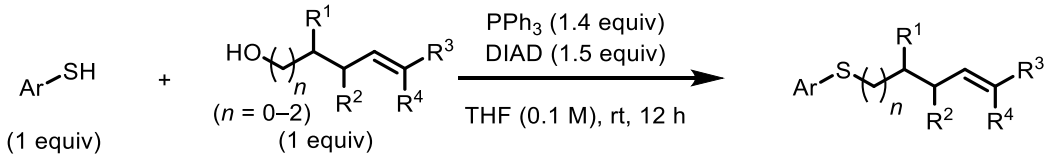
GENERAL INFORMATION

Except where otherwise stated, all materials were used as received from commercial sources without further purification. All reactants, reagents, and solvents unless otherwise mentioned were purchased from Aldrich, Alfa Aesar, Oakwood, and Combi-Blocks. Grubbs *Z*-selective catalyst (C675) was donated by Umicore.[1] NMR spectra were recorded on AV-600 or Bruker AV-400 machines. Spectra were internally referenced to $SiMe_4$, solvent signals, or internal standard. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet. High-resolution mass spectra (HRMS) for new compounds were obtained with an Agilent LC/MSD TOF mass spectrometer.

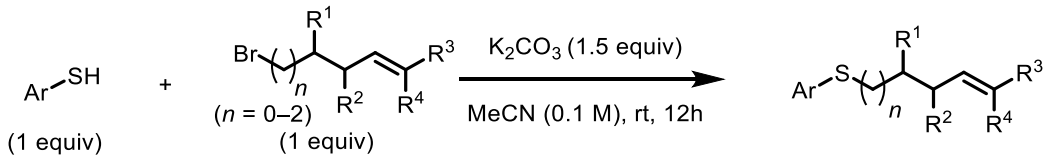
SYNTHETIC PROCEDURES

Starting Material Synthesis for Oxidative Heck Reaction



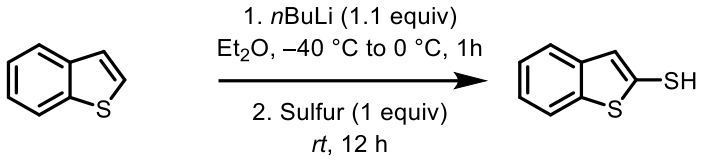
Scheme S1. General Procedure 1.

General Procedure 1: To a 50-mL round-bottom flask equipped with a magnetic stir bar and containing the alcohol (1.0 mmol, 1 equiv), thiol (1.0 mmol, 1 equiv), PPh_3 (1.4 mmol, 1.4 equiv), and THF (10 mL, 0.1 M) was added DIAD (1.5 mmol, 1.5 equiv) dropwise in air. The reaction was stirred at room temperature for 12 h. The organic materials were separated by addition of H_2O (25 mL), followed by extraction with EtOAc (3 × 10 mL) and dried with Na_2SO_4. The solvent was removed *in vacuo*, and the crude residue was purified by SiO_2 gel column chromatography or preparative TLC.



Scheme S2. General Procedure 2.

General Procedure 2: To a 50-mL round-bottom flask equipped with a magnetic stir bar were added the bromide (1.0 mmol, 1 equiv), thiol (1.0 mmol, 1 equiv), K_2CO_3 (1.5 mmol, 1.5 equiv) and MeCN (10 mL, 0.1 M) in air. The reaction was stirred at room temperature for 12 h. The organic materials were separated by addition of H_2O (25 mL), followed by extraction with EtOAc (3 × 10 mL) and dried with Na_2SO_4. The solvent was removed *in vacuo*, and the crude residue was purified by SiO_2 gel column chromatography or preparative TLC.



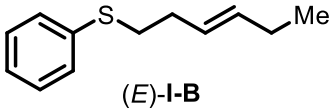
Scheme S3. Synthesis of Benzothiophene-2-thiol

Synthesis of Benzothiophene-2-thiol

A flame dried 50-mL round-bottom flask equipped with a magnetic stir bar was charged with benzothiophene (5.0 mmol, 1 equiv) in dry diethyl ether (10 mL, 0.5 M) under nitrogen. The solution was cooled to –40 ° C and *n*BuLi (2.2 mL, 1.1 equiv; 2.5 M sol. in hexanes) was added and the reaction was allowed to warm in an ice bath at 0 ° C for 1 h. Sulfur (5.0 mmol, 1 equiv) was added in one portion, and the reaction was allowed to slowly warm to room temperature over 12 h. 1 N HCl (10 mL) was added, and the reaction was stirred for 1 h. The organic material was extracted with ether, washed with brine, and dried over Na_2SO_4. The solvent was then removed *in vacuo* to give the desired benzothiophene-2-thiol.[2]

Characterization Data for Starting Materials for Oxidative Heck Reaction

(***E***)**-hex-3-en-1-yl(phenyl)sulfane** ((*E*)-**I-B**)**:** A flame dried 50-mL round-bottom flask equipped with a magnetic stir bar was charged with *p*-toluenesulfonyl chloride (10.00 mmol, 1 equiv) and sealed with a rubber septum. Chloroform (5 mL) and pyridine (1.3 mL) were added via syringe. The mixture was stirred for 5 min until the *p*-toluenesulfonyl chloride fully dissolved and the mixture turned yellow. (*E*)-Hex-3-en-1-ol (10 mmol, 1 equiv) was dissolved in chloroform (4 mL), and the resulting solution was added dropwise to the reaction. The reaction was allowed to stir at room temperature for 12 h. Diethyl ether (10 mL) was added, and the mixture was washed sequentially with 1 N HCl (50 mL), saturated aqueous $NaHCO_3$ (50 mL), and brine (50 mL). The organic layer was dried over $MgSO_4$. After filtration the solvent was removed *in vacuo,* and the crude residue was purified by SiO_2 gel column chromatography (10% EtOAc/hexanes) to give (*E*)-hex-3-en-1-yl 4-methylbenzenesulfonate, which was directly brought on to the next step.

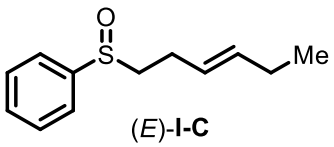


(*E*)-**I-B**

To a flame-dried, 25-mL round-bottom flask equipped with a magnetic stir bar were added NaH (60% oil dispersion, 3.0 mmol, 3 equiv) and DMF (10 mL, 0.1 M) under nitrogen. The mixture was cooled to 0 ° C. Thiophenol (0.900 mmol, 0.9 equiv) was added via syringe, followed by (*E*)-hex-3-en-1-yl 4-methylbenzenesulfonate (1.000 mmol, 1 equiv) in DMF (5 mL). The reaction was allowed to warm to room temperature and stirred for 20 h. The reaction was cooled to 0 ° C and quenched with the addition of water and diethyl ether (5 mL, 1:1 mixture). The organic materials were separated by addition to H_2O (25 mL), followed by extraction with EtOAc (3 × 10 mL). The organic layer was dried with Na_2SO_4. After filtration the solvent was removed *in vacuo,* and the crude residue was purified by SiO_2 gel column chromatography (10% EtOAc/hexanes). Purification afforded (*E*)-**I-B** as a clear liquid (96 mg, 50%).[4] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.2, 1.4 Hz, 2H),

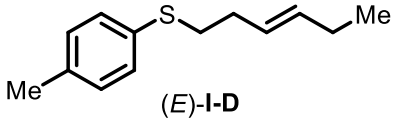
7.28 (t, *J* = 7.8 Hz, 2H), 7.20–7.14 (m, 1H), 5.54 (dtt, *J* = 15.2, 6.2, 1.3 Hz, 1H), 5.44 (dtt, *J* = 15.0, 6.7, 1.5 Hz, 1H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.33 (q, *J* = 7.1 Hz, 2H), 2.01 (p, *J* = 6.5 Hz, 2H), 0.97 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 136.89, 134.21, 129.23, 128.96, 126.78, 125.90, 33.82, 32.48, 25.70, 13.86. **HRMS** calcd. for $C_{12}H_{17}S^+$ $[M+H]^+$: 193.1046, Found: 193.1040.

(***E***)**-(hex-3-en-1-ylsulfinyl)benzene ((*E*)-I-C):** A 25-mL round-bottom flask equipped with a magnetic stir bar was charged with (*E*)-hex-3-en-1-yl(phenyl)sulfane (0.5 mmol, 1 equiv) and DCM (5 mL, 0.1 M). The mixture was cooled to 0 ° C. A solution of mCPBA (0.5 mmol, 1 equiv) in DCM (5 mL, 0.1 M) was then added dropwise. The reaction was stirred for 4 h. The organic materials were separated by addition of NaOH in H_2O (0.2 M, 25 mL), followed by extraction with EtOAc (3 × 10 mL). The organic layer was dried over Na_2SO_4, and after filtration the solvent was removed *in vacuo*. The crude residue was purified by SiO_2 gel column chromatography (40% EtOAc/hexanes). Purification afforded (*E*)-**I-C** as a white solid (84 mg, 81%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.55 (dt, *J* = 15.2, 6.5 Hz, 1H), 5.36 (dt, *J* = 15.1, 6.6 Hz, 1H), 2.82 (dd, *J* = 8.6, 6.8 Hz, 2H), 2.46 (dq, *J* = 15.2, 7.6 Hz, 1H), 2.28 (dq, *J* = 14.5, 7.4 Hz, 1H), 1.99 (p, *J* = 7.9, 7.4 Hz, 2H), 0.94 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.01, 135.13, 131.06, 129.33, 125.17, 124.19, 57.17, 25.65, 25.36, 13.75. **HRMS** calcd. for $C_{12}H_{17}OS^+$ $[M+H]^+$: 209.0995, Found: 209.1007.



(*E*)-**I-C**

(***E***)**-hex-3-en-1-yl(*p*-tolyl)sulfane ((*E*)-I-D):** A flame dried 50-mL round-bottom flask equipped with a magnetic stir bar was charged with *p*-toluenesulfonyl chloride (10.00 mmol, 1 equiv) and sealed with a rubber septum. Chloroform (5 mL) and pyridine (1.3 mL) were added via syringe. The mixture was stirred for 5 min until the *p*-toluenesulfonyl chloride fully dissolved and the mixture turned yellow. (*E*)-Hex-3-en-1-ol (10 mmol, 1 equiv) was dissolved in chloroform (4 mL), and the resulting solution was added dropwise to the reaction. The reaction was allowed to stir at room temperature for 12 h. Diethyl ether (10 mL) was added, and the mixture was washed sequentially with 1 N HCl (50 mL), saturated aqueous $NaHCO_3$ (50 mL), and brine (50 mL). The organic layer was dried over $MgSO_4$. After filtration the solvent was removed *in vacuo*, and the crude residue was purified by SiO_2 gel column chromatography (10% EtOAc/hexanes) to give (*E*)-hex-3-en-1-yl 4-methylbenzenesulfonate, which was directly carried on to the next step.

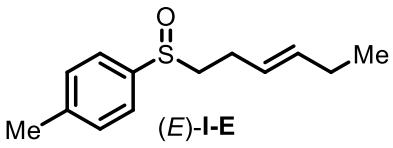


(*E*)-**I-D**

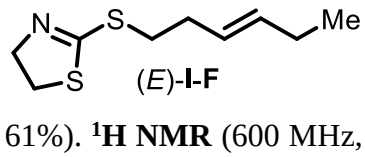
To a flame-dried, 25-mL round-bottom flask equipped with a magnetic stir bar were added NaH (60% oil dispersion, 3.0 mmol, 3 equiv) and DMF (10 mL, 0.1 M) under nitrogen. The mixture was cooled to 0 ° C. 4-Methylbenzenethiol (0.900 mmol, 0.9 equiv) was added followed by (*E*)-hex-3-en-1-yl 4-methylbenzenesulfonate (1.000 mmol, 1 equiv) in DMF (5 mL). The reaction was allowed to warm to room temperature and stirred for 20 h. The reaction was cooled to 0 ° C and quenched with the addition of water and diethyl ether (5 mL, 1:1 mixture). The organic materials were separated by addition to H_2O (25 mL), followed by extraction with EtOAc (3 × 10 mL). The organic layer was dried with Na_2SO_4. After filtration the solvent was removed *in vacuo*, and the crude residue

was purified by SiO_2 gel column chromatography (10% EtOAc/hexanes). Purification afforded (*E*)-**I-D** as a clear liquid (99 mg, 48%).[4] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 6.8, 1.6 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 5.54 (dtt, *J* = 15.1, 6.1, 1.3 Hz, 1H), 5.45 (dtt, *J* = 15.0, 6.6, 1.5 Hz, 1H), 2.99–2.84 (m, 2H), 2.34 (s, 3H), 2.33–2.29 (m, 2H), 2.03 (p, *J* = 6.5 Hz, 2H), 0.99 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 136.12, 134.09, 132.97, 130.16, 129.75, 126.89, 34.57, 32.59, 25.70, 21.15, 13.88. **HRMS** calcd. for $C_{13}H_{19}S^+$ $[M+H]^+$: 207.1202, Found: 207.1202.

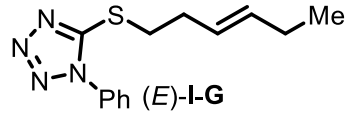
(*E*)-1-(hex-3-en-1-ylsulfinyl)-4-methylbenzene ((*E*)-I-E): To a 25-mL round-bottom flask equipped with a magnetic stir bar was charged (*E*)-hex-3-en-1-yl(*p*-tolyl)sulfane (0.5 mmol, 1 equiv) and DCM (5 mL, 0.1 M). The mixture was cooled to 0 ° C. A solution of mCPBA (0.5 mmol, 1 equiv) in DCM (5 mL, 0.1 M) was then added dropwise. The reaction was stirred for 4 h. The organic materials were separated by addition of NaOH in H_2O (0.2 M, 25 mL), followed by extraction with EtOAc (3 × 10 mL). The solvent was removed *in vacuo*, and the crude residue was purified by SiO_2 gel column chromatography. The organic layer was dried over Na_2SO_4, and after filtration the crude residue was purified by SiO_2 gel column chromatography (40% EtOAc/hexanes). Purification afforded (*E*)-**I-E** as a white solid (89 mg, 80%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 5.55 (dtt, *J* = 15.5, 6.4, 1.4 Hz, 1H), 5.36 (dtt, *J* = 15.1, 6.8, 1.6 Hz, 1H), 2.86–2.73 (m, 2H), 2.48–2.36 (m, 4H), 2.28 (tt, *J* = 14.6, 8.4 Hz, 1H), 1.99 (p, *J* = 6.6 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 141.54, 140.72, 135.02, 130.03, 125.26, 124.26, 57.20, 25.66, 25.40, 21.55, 13.76. **HRMS** calcd. for $C_{13}H_{19}OS^+$ $[M+H]^+$: 223.1151, Found: 223.1166.



(*E*)-2-(hex-3-en-1-ylthio)-4,5-dihydrothiazole ((*E*)-I-F): The title compound was prepared on a 0.300 mmol scale according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded (*E*)-**I-F** as a clear liquid (37 mg, 61%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.55 (dtt, *J* = 15.3, 6.2, 1.4 Hz, 1H), 5.40 (dtt, *J* = 15.1, 6.7, 1.6 Hz, 1H), 4.21 (t, *J* = 7.9 Hz, 2H), 3.37 (t, *J* = 7.9 Hz, 2H), 3.13 (t, *J* = 7.4 Hz, 2H), 2.38 (q, *J* = 6.5 Hz, 2H), 2.01 (dq, *J* = 7.7, 6.1 Hz, 2H), 0.96 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.80, 134.60, 126.33, 64.48, 35.49, 32.88, 32.43, 25.67, 13.82. **HRMS** calcd. for $C_9H_{16}NS_2^+$ $[M+H]^+$: 202.0719, Found: 202.0725.

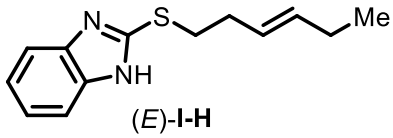


(*E*)-5-(hex-3-en-1-ylthio)-1-phenyl-1H-tetrazole ((*E*)-I-G): The title compound was prepared according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (10% Et_2O/hexanes). Purification afforded (*E*)-**I-G** as a clear liquid (96 mg, 37%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63–7.52 (m, 5H), 5.61 (dtt, *J* = 15.4, 6.3, 1.4 Hz, 1H), 5.44 (dtt, *J* = 15.2, 6.8, 1.6 Hz, 1H), 3.45 (t, *J* = 7.3 Hz, 2H), 2.54 (qd, *J* = 7.2, 1.2 Hz, 2H), 2.03 (dtdd, *J* = 8.9, 7.5, 6.2, 1.3 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.54, 135.47, 133.89, 130.20, 129.90,



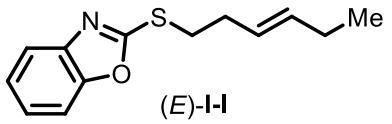
125.56, 124.00, 33.49, 32.23, 25.65, 13.77. **HRMS** calcd. for $C_{13}H_{17}N_4S$ $[M+H]^+$: 261.1169, Found: 261.1157.

(***E***)**-2-(hex-3-en-1-ylthio)-1H-benzoimidazole (**(*E*)**-I-H):** The title compound was prepared according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (10% EtOAc/hexanes). Purification afforded (*E*)-**I-H** as a white solid (34 mg, 49%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.60–7.45 (m, 2H), 7.22–7.15 (m, 2H), 5.58–5.50 (m, 1H), 5.44–5.36 (m, 1H), 3.36 (td, *J* = 7.3, 1.4 Hz, 2H), 2.50–2.41 (m, 2H), 2.03–1.88 (m, 2H), 0.93 (td, *J* = 7.3, 2.8 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.65, 150.57, 134.84, 126.17, 126.16, 122.42, 32.85, 32.72, 25.65, 13.78. **HRMS** calcd. for $C_{13}H_{17}N_2S^+$ $[M+H]^+$: 233.1107, Found: 233.1114.



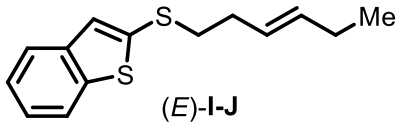
(*E*)-**I-H**

(*E*)-2-(hex-3-en-1-ylthio)benzooxazole ((*E*)**-I-I):** The title compound was prepared according to General Procedure 1 on a 0.500 mmol scale. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded (*E*)-**I-I** as a clear liquid (53 mg, 45%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 1.2 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.23 (td, *J* = 7.7, 1.4 Hz, 1H), 5.61 (dtt, *J* = 15.2, 6.3, 1.2 Hz, 1H), 5.50 – 5.41 (m, 1H), 3.34 (t, *J* = 7.3 Hz, 2H), 2.52 (qd, *J* = 7.1, 1.1 Hz, 2H), 2.07 – 1.88 (m, 2H), 0.97 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.28, 151.95, 142.16, 135.24, 125.87, 124.36, 123.90, 118.49, 109.96, 32.43, 25.68, 13.78. **HRMS** calcd. for $C_{13}H_{15}NOS^+$ $[M+H]^+$: 234.0953, Found: 234.0958.



(*E*)-**I-I**

(*E*)-2-(hex-3-en-1-ylthio)benzothiophene ((*E*)**-I-J):** A flame dried 50-mL round-bottom flask equipped with a magnetic stir bar was charged with *p*-toluenesulfonyl chloride (10.00 mmol, 1 equiv) and sealed with a rubber septum. Chloroform (5 mL) and pyridine (1.3 mL) were added via syringe. The mixture was stirred for 5 min until the *p*-toluenesulfonyl chloride fully dissolved and the mixture turned yellow. (*Z*)-Hex-3-en-1-ol (10 mmol, 1 equiv) was dissolved in chloroform (4 mL), and the resulting solution was added dropwise to the reaction. The reaction was allowed to stir at room temperature for 12 h. Diethyl ether (10 mL) was added, and the mixture was washed sequentially with 1 N HCl (50 mL), saturated aqueous $NaHCO_3$ (50 mL), and brine (50 mL). The organic layer was dried over $MgSO_4$. After filtration the solvent was removed *in vacuo,* and the crude residue was purified by SiO_2 gel column chromatography (10% EtOAc/hexanes) to give (*E*)-hex-3-en-1-yl 4-methylbenzenesulfonate, which was directly carried on to the next step.

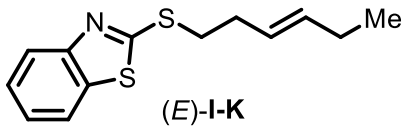


(*E*)-**I-J**

To a flame-dried, 25-mL round-bottom flask equipped with a magnetic stir bar were added NaH (60% oil dispersion, 2.0 mmol, 3 equiv) and DMF (10 mL, 0.2 M) under nitrogen. The mixture was cooled to 0 ° C. Benzothiophene-2-thiol (2.00 mmol, 1 equiv) was added followed by (*E*)-hex-3-en-

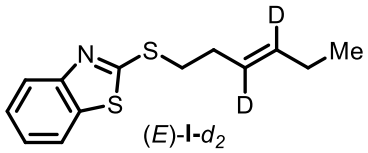
1-yl 4-methylbenzenesulfonate (2.45 mmol, 1.2 equiv) in DMF (5 mL). The reaction was allowed to warm to room temperature and stirred for 20 h. The reaction was cooled to 0 ° C and quenched with the addition of water and diethyl ether (5 mL, 1:1 mixture). The organic materials were separated by addition to H_2O (25 mL), followed by extraction with EtOAc (3 × 10 mL). The organic layer was dried with Na_2SO_4. After filtration the solvent was removed *in vacuo*, and the crude residue was purified by SiO_2 gel column chromatography (10% EtOAc/hexanes). Purification afforded (*E*)-**I-J** as a pink liquid (190 mg, 38%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.68 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.35 – 7.27 (m, 3H), 5.55 (dtt, *J* = 15.2, 6.2, 1.4 Hz, 1H), 5.42 (dtt, *J* = 15.1, 6.8, 1.6 Hz, 1H), 2.96 (t, *J* = 7.5 Hz, 2H), 2.43 – 2.31 (m, 2H), 2.02 (qdd, *J* = 7.6, 6.2, 1.4 Hz, 2H), 0.97 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 141.75, 139.97, 137.51, 134.59, 128.07, 126.34, 124.56, 124.41, 123.09, 121.96, 37.61, 32.81, 25.70, 13.84. **HRMS** calcd. for $C_{14}H_{17}S_2^+$ $[M+H]^+$: 249.0772, Found: 249.0770.

(*E*)-2-(hex-3-en-1-ylthio)benzothiazole ((*E*)-I-K): The title compound was prepared according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded (*E*)-**I-K** as a clear liquid (249 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 5.61 (dt, *J* = 15.1, 6.3 Hz, 1H), 5.47 (dt, *J* = 15.0, 6.7 Hz, 1H), 3.38 (t, *J* = 7.4 Hz, 2H), 2.52 (q, *J* = 7.2 Hz, 2H), 2.03 (p, *J* = 7.0 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.31, 153.50, 135.33, 135.01, 126.12, 126.10, 124.25, 121.60, 121.04, 33.75, 32.41, 25.69, 13.80. **HRMS** calcd. for $C_{13}H_{16}NS_2^+$ $[M+H]^+$: 250.0719, Found: 250.0724.



(*E*)-**I-K**

(*E*)-2-((hex-3-en-1-yl-3,4-*d*$_2$)thio)benzothiazole ((*E*)-I-*d*$_2$): To a dry 2-necked, 250 mL round-bottom flask equipped with a stir bar was added lithium aluminum deuteride (10.2 mmol, 2 equiv). The flask was fitted with an addition funnel and a reflux condenser. The apparatus was purged with nitrogen and dry THF (50 mL, 0.1 M) was added. The solution was then cooled to 0 °C while stirring. To the closed addition funnel under nitrogen was added 3-hexyn-1-ol (5.1 mmol, 1 equiv) and THF (10 mL, 0.5 M). The addition funnel was then opened and washed with THF (5 mL). The reaction was allowed to warm to room temperature over 1 h. The reaction was then heated to 70 °C for 72 h. The reaction was cooled in an ice bath and then quenched by addition of D_2O (10 mL). Et_2O (10 mL) was added and the layers were separated. The aqueous layer was extracted with Et_2O (3 × 10 mL). The organic solution was washed with brine (10 mL) and dried over Na_2SO_4.[3] After filtration, the solvent was removed *in vacuo* to afford the crude material that was used directly in the next step.

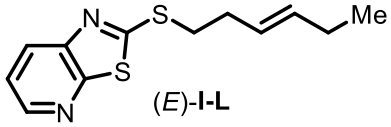


(*E*)-**I-***d*$_2$

The title compound was then prepared according to General Procedure 1 on a 5.1 mmol scale using the crude material from above as the alcohol. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded (*E*)-**I-*d*$_2$** as a clear liquid (120 mg, 10%). **^{1}H NMR** (600 MHz, $CDCl_3$ δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.75 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.41 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.31 – 7.27 (m, 1H), 3.38 (t, *J* = 7.3 Hz, 2H), 2.51 (t, *J* = 7.4 Hz, 2H), 2.02

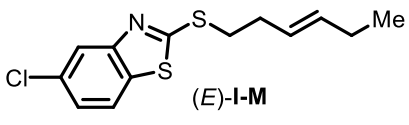
(q, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.34, 153.50, 135.33, 134.70, 134.55, 134.40, 126.13, 125.80, 125.65, 125.50, 124.25, 121.60, 121.05, 33.72, 32.24, 25.51, 13.75. **HRMS** calcd. for $C_{13}H_{14}D_2NS_2^+$ $[M+H]^+$: 252.0850, Found: 252.0851.

(***E***)**-2-(hex-3-en-1-ylthio)thiazolo[5,4-b]pyridine ((*E*)-I-L):** The title compound was prepared on an 0.300 mmol scale according to General Procedure 1. The crude residue was purified by preparative TLC (10% EtOAc/hexanes). Purification afforded (*E*)-**I-L** as a yellow liquid (74 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.05 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.34 (dd, *J* = 8.2, 4.7 Hz, 1H), 5.62 (dtt, *J* = 15.3, 6.2, 1.4 Hz, 1H), 5.46 (dtt, *J* = 15.3, 6.9, 1.6 Hz, 1H), 3.39 (t, *J* = 7.3 Hz, 2H), 2.52 (q, *J* = 7.1, 6.7 Hz, 2H), 2.03 (ddd, *J* = 12.4, 7.0, 3.8 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.99, 158.88, 146.61, 145.67, 135.22, 127.94, 125.92, 121.23, 33.09, 32.30, 25.69, 13.79. **HRMS** calcd. for $C_{12}H_{15}N_2S_2^+$ $[M+H]^+$: 251.0671, Found: 251.0687



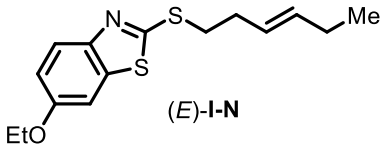
(*E*)-**I-L**

(***E***)**-5-chloro-2-(hex-3-en-1-ylthio)benzothiazole ((*E*)-I-M):** The title compound was prepared on a 0.300 mmol scale according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded (*E*)-**I-M** as a clear liquid (82 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 2.0 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.26 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.61 (dtt, *J* = 15.3, 6.3, 1.4 Hz, 1H), 5.46 (dtt, *J* = 15.2, 6.8, 1.6 Hz, 1H), 3.37 (t, *J* = 7.3 Hz, 2H), 2.51 (qd, *J* = 7.1, 1.2 Hz, 2H), 2.03 (qdq, *J* = 7.4, 6.3, 1.2 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 4H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.60, 154.31, 135.15, 133.56, 132.20, 125.96, 124.58, 121.64, 121.49, 33.75, 32.34, 25.69, 13.79. **HRMS** calcd. for $C_{13}H_{15}ClNS_2^+$ $[M+H]^+$: 284.0329, Found: 284.0337.



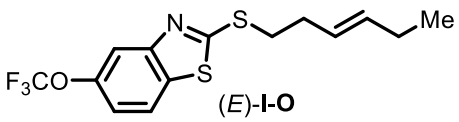
(*E*)-**I-M**

(***E***)**-6-ethoxy-2-(hex-3-en-1-ylthio)benzothiazole ((*E*)-I-N):** The title compound was prepared on a 0.300 mmol scale according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded (*E*)-**I-N** as a clear liquid (85 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.9 Hz, 1H), 7.22 (d, *J* = 2.6 Hz, 1H), 7.00 (dd, *J* = 8.9, 2.6 Hz, 1H), 5.60 (dtt, *J* = 15.3, 6.2, 1.3 Hz, 1H), 5.46 (dtt, *J* = 15.1, 6.8, 1.6 Hz, 1H), 4.07 (q, *J* = 7.0 Hz, 2H), 3.33 (t, *J* = 7.4 Hz, 2H), 2.49 (q, *J* = 7.2, 6.7 Hz, 2H), 2.03 (q, *J* = 6.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H), 0.97 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.89, 156.47, 148.01, 136.68, 134.93, 126.16, 122.08, 115.34, 104.97, 64.27, 33.94, 32.50, 25.70, 15.00, 13.81. **HRMS** calcd. for $C_{15}H_{20}NOS_2^+$ $[M+H]^+$: 294.0981, Found: 294.0985.



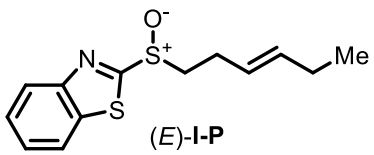
(*E*)-**I-N**

(***E***)**-2-(hex-3-en-1-ylthio)-5-(trifluoromethoxy)benzothiazole (**(*E*)**-I-O):** The title compound was prepared on a 0.300 mmol scale according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded (*E*)-**I-O** as a clear liquid (99 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81–7.66 (m, 2H), 7.17 (dd, *J* = 8.8, 2.3 Hz, 1H), 5.61 (dtt, *J* = 15.3, 6.3, 1.3 Hz, 1H), 5.46 (dtt, *J* = 15.2, 6.9, 1.6 Hz, 1H), 3.39 (t, *J* = 7.3 Hz, 2H), 2.52 (q, *J* = 7.1, 6.6 Hz, 2H), 2.03 (p, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.38, 154.12, 147.96, 135.18, 134.75, 133.65, 125.94, 125.69, 121.61, 121.56, 119.85, 117.67, 114.10, 33.75, 32.32, 25.69, 13.79. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.99. **HRMS** calcd. for $C_{14}H_{15}F_3NOS_2^+$ $[M+H]^+$: 334.0542, Found: 334.0556.



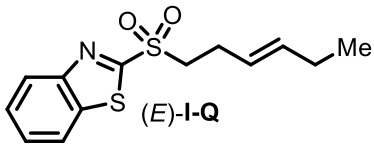
(*E*)-**I-O**

(***E***)**-2-(hex-3-en-1-ylsulfinyl)benzothiazole (**(*E*)**-I-P):** To a 25-mL round-bottom flask equipped with a magnetic stir bar was charged (*E*)-2-(hex-3-en-1-ylsulfinyl)benzothiazole (0.5 mmol, 1 equiv) and DCM (5 mL, 0.1 M) The mixture was cooled to 0 ° C. A solution of mCPBA (0.5 mmol, 1 equiv) in DCM (5 mL, 0.1 M) was then added dropwise. The reaction was stirred for 4 h. The organic materials were separated by addition of H_2O (25 mL), followed by extraction with EtOAc (3 × 10 mL). The organic layer was dried over Na_2SO_4, and after filtration the solvent was removed *in vacuo.* The crude residue was purified by SiO_2 gel column chromatography (40% EtOAc/hexanes). Purification afforded (*E*)-**I-P** as a white solid (111 mg, 80%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 7.2 Hz, 1H), 7.56 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.49 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 5.61 (dtt, *J* = 15.4, 6.3, 1.4 Hz, 1H), 5.39 (dtt, *J* = 15.1, 6.7, 1.6 Hz, 1H), 3.29 (ddd, *J* = 13.2, 9.2, 6.8 Hz, 1H), 3.22 (ddd, *J* = 13.3, 9.0, 5.5 Hz, 1H), 2.79–2.57 (m, 1H), 2.49–2.37 (m, 1H), 1.97 (p, *J* = 6.6 Hz, 2H), 0.93 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 177.88, 154.08, 136.14, 135.85, 127.05, 126.27, 124.47, 124.05, 122.41, 56.58, 25.62, 24.79, 13.62. **HRMS** calcd. for $C_{13}H_{16}NOS_2^+$ $[M+H]^+$: 266.0668, Found: 266.0682.



(*E*)-**I-P**

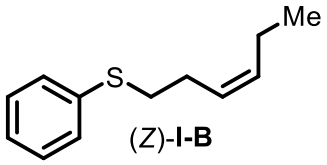
(***E***)**-2-(hex-3-en-1-ylsulfonyl)benzothiazole (**(*E*)**-I-Q):** To a 100-mL round-bottom flask equipped with a magnetic stir bar were added (*E*)-2-(hex-3-en-1-ylthio)benzothiazole (0.300 mmol, 1 equiv), 30% aqueous H_2O_2 (0.6 mL, 6 equiv), ammonium heptamolybdate tetrahydrate (0.006 mmol, 1 mol%), and ethanol (5.0 mL, 0.06 M). The reaction was stirred at room temperature for 12 h. The organic materials were separated by addition of H_2O (20 mL), followed by extraction with EtOAc (3 × 10 mL). The organic solution was washed with brine (10 mL) and dried over Na_2SO_4. After filtration, the solvent was removed *in vacuo,* and (*E*)-**I-Q** was obtained as a white solid (81 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.2 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.62 (dt, *J* = 27.8, 7.2 Hz, 2H), 5.55 (dtt, *J* = 15.4, 6.3, 1.4 Hz, 1H), 5.31 (dddd, *J* = 15.2, 6.7, 5.0, 1.6 Hz, 1H), 3.59–3.51 (m, 2H), 2.58 (q, *J* = 6.9 Hz, 2H), 1.91 (p, *J* = 6.6 Hz, 2H), 0.87 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.01,



(*E*)-**I-Q**

152.89, 136.95, 135.78, 128.15, 127.78, 125.60, 123.57, 122.46, 54.73, 25.72, 25.49, 13.47. **HRMS** calcd. for $C_{13}H_{16}NO_2S_2^+$ $[M+H]^+$: 282.0617, Found: 282.0622.

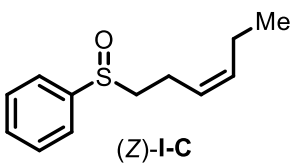
(*Z*)-hex-3-en-1-yl(phenyl)sulfane ((*Z*)-I-B): A flame dried 50-mL round-bottom flask equipped with a magnetic stir bar was charged with *p*-toluenesulfonyl chloride (10.00 mmol, 1 equiv) and sealed with a rubber septum. Chloroform (5 mL) and pyridine (1.3 mL) were added via syringe. The mixture was stirred for 5 min until the *p*-toluenesulfonyl chloride fully dissolved and the mixture turned yellow. (*E*)-Hex-3-en-1-ol (10 mmol, 1 equiv) was dissolved in chloroform (4 mL), and the resulting solution was added dropwise to the reaction. The reaction was allowed to stir at room temperature for 12 h. Diethyl ether (10 mL) was added, and the mixture was washed sequentially with 1 N HCl (50 mL), saturated aqueous $NaHCO_3$ (50 mL), and brine (50 mL). The organic layer was dried over $MgSO_4$. After filtration the solvent was removed *in vacuo*, and the crude residue was purified by SiO_2 gel column chromatography (10% EtOAc/hexanes) to give (*Z*)-hex-3-en-1-yl 4-methylbenzenesulfonate, which was directly carried on to the next step.



(*Z*)-**I-B**

To a flame-dried, 25-mL round-bottom flask equipped with a magnetic stir bar were added NaH (60% oil dispersion, 3.0 mmol, 3 equiv) and DMF (10 mL, 0.1 M) under nitrogen. The mixture was cooled to 0 ° C. Thiophenol (0.900 mmol, 0.9 equiv) was added via syringe, followed by (*Z*)-hex-3-en-1-yl 4-methylbenzenesulfonate (1.000 mmol, 1 equiv) in DMF (5 mL). The reaction was allowed to warm to room temperature and stirred for 20 h. The reaction was cooled to 0 ° C and quenched with the addition of water and diethyl ether (5 mL, 1:1 mixture). The organic materials were separated by addition to H_2O (25 mL), followed by extraction with EtOAc (3 × 10 mL). The organic layer was dried with Na_2SO_4. After filtration the solvent was removed *in vacuo*, and the crude residue was purified by SiO_2 gel column chromatography (10% EtOAc/hexanes). Purification afforded (*Z*)-**I-B** as a clear liquid (67 mg, 35%).[4] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 5.47 (dd, *J* = 12.2, 5.7 Hz, 1H), 5.38 (dt, *J* = 10.1, 7.4 Hz, 1H), 2.94 (t, *J* = 7.5 Hz, 2H), 2.38 (q, *J* = 7.4 Hz, 2H), 2.02 (p, *J* = 7.5 Hz, 2H), 0.96 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 136.74, 133.77, 129.23, 128.98, 126.54, 125.96, 33.73, 27.04, 20.78, 14.38. **HRMS** calcd. for $C_{12}H_{17}S^+$ $[M+H]^+$: 193.1046, Found: 193.1041.

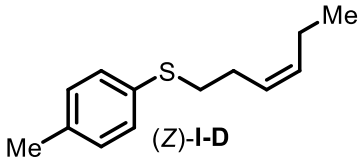
(*Z*)-(hex-3-en-1-ylsulfinyl)benzene ((*Z*)-I-C): To a 25-mL round-bottom flask equipped with a magnetic stir bar was charged (*Z*)-hex-3-en-1-yl(phenyl)sulfane (0.5 mmol, 1 equiv) and DCM (5 mL, 0.1 M). The mixture was cooled to 0 °C. A solution of mCPBA (0.5 mmol, 1 equiv) in DCM (5 mL, 0.1 M) was then added dropwise. The reaction was stirred for 4 h. The organic materials were separated by addition of NaOH in H_2O (0.2 M, 25 mL), followed by extraction with EtOAc (3 × 10 mL). The organic layer was dried over Na_2SO_4, and after filtration the solvent was removed *in vacuo*. The crude residue was purified by SiO_2 gel column chromatography (40% EtOAc/hexanes). Purification afforded (*Z*)-**I-C** as a white solid (87 mg, 84%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.67–7.59 (m, 2H), 7.55–7.45 (m, 3H), 5.48 (dtt, *J* = 10.6, 7.3, 1.6



(*Z*)-**I-C**

Hz, 1H), 5.31 (dtt, *J* = 10.8, 7.3, 1.7 Hz, 1H), 2.81 (t, *J* = 7.6 Hz, 2H), 2.53 (dq, *J* = 15.3, 7.8 Hz, 1H), 2.32 (dq, *J* = 14.1, 7.0 Hz, 1H), 2.01 (p, *J* = 7.5 Hz, 2H), 0.94 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.91, 134.74, 131.10, 129.35, 124.85, 124.18, 57.15, 20.69, 20.27, 14.22. **HRMS** calcd. for $C_{12}H_{17}OS^+$ $[M+H]^+$: 209.0995, Found: 209.1010.

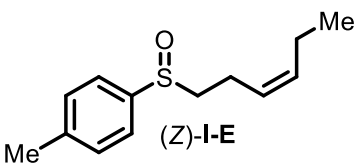
(*Z*)-hex-3-en-1-yl(*p*-tolyl)sulfane ((*Z*)-I-D): A flame dried 50-mL round-bottom flask equipped with a magnetic stir bar was charged with *p*-toluenesulfonyl chloride (10.00 mmol, 1 equiv) and sealed with a rubber septum. Chloroform (5 mL) and pyridine (1.3 mL) were added via syringe. The mixture was stirred for 5 min until the *p*-toluenesulfonyl chloride fully dissolved and the mixture turned yellow. (*E*)-Hex-3-en-1-ol (10 mmol, 1 equiv) was dissolved in chloroform (4 mL), and the resulting solution was added dropwise to the reaction. The reaction was allowed to stir at room temperature for 12 h. Diethyl ether (10 mL) was added, and the mixture was washed sequentially with 1 N HCl (50 mL), saturated aqueous $NaHCO_3$ (50 mL), and brine (50 mL). The organic layer was dried over $MgSO_4$. After filtration the solvent was removed *in vacuo,* and the crude residue was purified by SiO_2 gel column chromatography (10% EtOAc/hexanes) to give (*Z*)-hex-3-en-1-yl 4-methylbenzenesulfonate, which was directly carried on to the next step.



(*Z*)-**I-D**

To a flame-dried, 25-mL round-bottom flask equipped with a magnetic stir bar were added NaH (60% oil dispersion, 3.0 mmol, 3 equiv) and DMF (10 mL, 0.1 M) under nitrogen. The mixture was cooled to 0 ° C. 4-Methylbenzenethiol (0.900 mmol, 0.9 equiv) was added followed by (*Z*)-hex-3-en-1-yl 4-methylbenzenesulfonate (1.000 mmol, 1 equiv) in DMF (5 mL). The reaction was allowed to warm to room temperature and stirred for 20 h. The reaction was cooled to 0 ° C and quenched with the addition of water and diethyl ether (5 mL, 1:1 mixture). The organic materials were separated by addition to H_2O (25 mL), followed by extraction with EtOAc (3 × 10 mL). The organic layer was dried with Na_2SO_4. After filtration the solvent was removed *in vacuo,* and the crude residue was purified by SiO_2 gel column chromatography (10% EtOAc/hexanes). Purification afforded (*Z*)-**I-D** as a clear liquid (76 mg, 37%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 5.46 (dtt, *J* = 10.2, 7.1, 1.5 Hz, 1H), 5.37 (dtt, *J* = 10.6, 7.3, 1.5 Hz, 1H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.35 (q, *J* = 9.9, 8.6 Hz, 2H), 2.32 (s, 3H), 2.01 (pd, *J* = 7.4, 1.4 Hz, 2H), 0.95 (t, *J* = 7.5 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 136.16, 133.65, 132.85, 130.15, 130.12, 129.77, 126.67, 34.47, 27.15, 21.15, 20.78, 14.39. **HRMS** calcd. for $C_{13}H_{19}S^+$ $[M+H]^+$: 207.1202, Found: 207.1215.

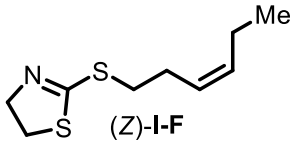
(*Z*)-1-(hex-3-en-1-ylsulfinyl)-4-methylbenzene ((*Z*)-I-E): To a 25-mL round-bottom flask equipped with a magnetic stir bar was charged (*Z*)-hex-3-en-1-yl(*p*-tolyl)sulfane (0.5 mmol, 1 equiv) and DCM (5 mL, 0.1 M) M). The mixture was cooled to 0 ° C. A solution of mCPBA (0.5 mmol, 1 equiv) in DCM (5 mL, 0.1 M) was then added dropwise. The reaction was stirred for 4 h. The organic materials were separated by addition of NaOH in H_2O (0.2 M, 25 mL), followed by extraction with EtOAc (3 × 10 mL). The organic layer was dried over Na_2SO_4, and after filtration the solvent was removed *in vacuo*. The crude residue was purified by SiO_2 gel column chromatography (40% EtOAc/hexanes). Purification afforded (*Z*)-**I-E**



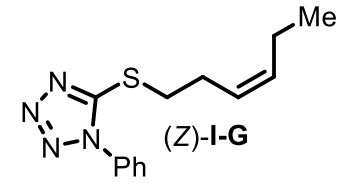
(*Z*)-**I-E**

as a white solid (92 mg, 83%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 5.47 (dtt, *J* = 10.5, 7.3, 1.5 Hz, 1H), 5.30 (dtt, *J* = 10.7, 7.4, 1.6 Hz, 1H), 2.79 (qdd, *J* = 13.0, 9.1, 6.2 Hz, 2H), 2.49 (tt, *J* = 19.5, 9.7 Hz, 1H), 2.41 (s, 3H), 2.31 (dq, *J* = 14.8, 7.0 Hz, 1H), 2.00 (h, *J* = 7.0, 6.6 Hz, 2H), 0.94 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 141.57, 140.64, 134.64, 130.03, 124.95, 124.23, 57.19, 21.54, 20.69, 20.33, 14.23. **HRMS** calcd. for $C_{13}H_{19}OS^+$ $[M+H]^+$: 223.1151, Found: 223.1162.

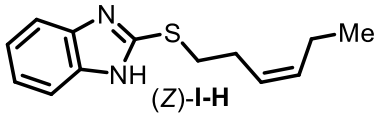
(*Z*)-1-(hex-3-en-1-ylsulfinyl)-4-methylbenzene ((*Z*)-I-F): The title compound was prepared on a 0.300 mmol scale according to General Procedure 1. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded (*Z*)-**I-F** as a clear liquid (39 mg, 64%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.51–5.44 (m, 1H), 5.34 (dtt, *J* = 10.6, 7.4, 1.6 Hz, 1H), 4.21 (t, *J* = 7.9 Hz, 2H), 3.37 (t, *J* = 7.9 Hz, 2H), 3.11 (t, *J* = 7.4 Hz, 2H), 2.44 (qd, *J* = 7.4, 1.4 Hz, 2H), 2.05 (pd, *J* = 7.5, 1.6 Hz, 2H), 0.96 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.70, 134.19, 126.12, 64.49, 35.51, 32.85, 27.11, 20.81, 14.36. **HRMS** calcd. for $C_9H_{16}NS_2^+$ $[M+H]^+$: 202.0719, Found: 202.0723.



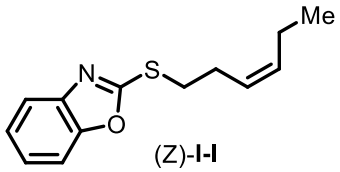
(*Z*)-5-(hex-3-en-1-ylthio)-1-phenyl-1H-tetrazolemethylbenzene ((*Z*)-I-G): The title compound was prepared according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (10% Et_2O/hexanes). Purification afforded (*Z*)-**I-G** as a clear liquid (110 mg, 41%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.65–7.46 (m, 5H), 5.51 (dt, *J* = 10.7, 7.1 Hz, 1H), 5.41–5.26 (m, 1H), 3.41 (t, *J* = 7.2 Hz, 2H), 2.58 (q, *J* = 7.3 Hz, 2H), 2.03 (p, *J* = 6.7, 6.3 Hz, 2H), 0.94 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.27, 134.80, 133.66, 130.00, 129.69, 125.08, 123.77, 33.19, 26.67, 20.62, 14.07. **HRMS** calcd. for $C_{13}H_{17}N_4S^+$ $[M+H]^+$: 261.1169, Found: 261.1157.



(*Z*)-2-(hex-3-en-1-ylthio)-1H-benzoimidazole ((*Z*)-I-H): The title compound was prepared according to General Procedure 1. The crude residue was purified by preparative TLC (10% EtOAc/hexanes). Purification afforded (*Z*)-**I-H** as a white solid (33 mg, 47%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.51 (s, 2H), 7.20 (dd, *J* = 6.0, 3.1 Hz, 2H), 5.47 (dtt, *J* = 10.5, 7.3, 1.5 Hz, 1H), 5.36 (dtt, *J* = 10.6, 7.3, 1.6 Hz, 1H), 3.36 (t, *J* = 7.3 Hz, 2H), 2.52 (q, *J* = 7.1 Hz, 2H), 2.02 (pd, *J* = 7.5, 1.5 Hz, 2H), 0.94 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.60, 134.35, 125.99, 122.39, 32.82, 27.34, 20.82, 14.31. **HRMS** calcd. for $C_{13}H_{17}N_2S^+$ $[M+H]^+$: 233.1107, Found: 233.1115.

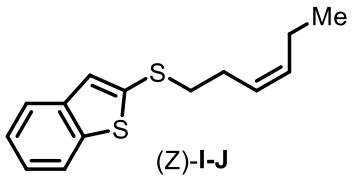


(*Z*)-2-(hex-3-en-1-ylthio)benzooxazole ((*Z*)-I-I): The title compound was prepared according to General Procedure 1 on a 0.500 mmol scale. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded (*Z*)-**I-I** as a clear liquid (47 mg, 40%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 1H), 7.47 – 7.41 (m, 1H), 7.28 (td, *J* = 7.6, 1.2 Hz, 1H), 7.24 (td, *J* = 7.7, 1.3 Hz, 1H), 5.58 – 5.49 (m, 1H), 5.44 – 5.39 (m, 1H), 3.33 (t, *J* = 7.3 Hz, 2H), 2.71 – 2.48 (m, 2H), 2.08 (pd, *J* = 7.5, 1.5 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.21, 151.96, 142.17, 134.75, 125.63, 124.37, 123.92, 118.51, 109.97, 32.37, 27.15, 20.85, 14.32. **HRMS** calcd. for $C_{13}H_{15}NOS^+$ $[M+H]^+$: 234.0953, Found: 234.0957.



(Z)-**I-I**

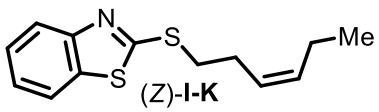
(*Z*)-2-(hex-3-en-1-ylthio)benzothiophene ((*Z*)-I-J): A flame dried 50-mL round-bottom flask equipped with a magnetic stir bar was charged with *p*-toluenesulfonyl chloride (10.00 mmol, 1 equiv) and sealed with a rubber septum. Chloroform (5 mL) and pyridine (1.3 mL) were added via syringe. The mixture was stirred for 5 min until the *p*-toluenesulfonyl chloride fully dissolved and the mixture turned yellow. (*Z*)-Hex-3-en-1-ol (10 mmol, 1 equiv) was dissolved in chloroform (4 mL), and the resulting solution was added dropwise to the reaction. The reaction was allowed to stir at room temperature for 12 h. Diethyl ether (10 mL) was added, and the mixture was washed sequentially with 1 N HCl (50 mL), saturated aqueous $NaHCO_3$ (50 mL), and brine (50 mL). The organic layer was dried over $MgSO_4$. After filtration the solvent was removed *in vacuo,* and the crude residue was purified by SiO_2 gel column chromatography (10% EtOAc/hexanes) to give (*E*)-hex-3-en-1-yl 4-methylbenzenesulfonate, which was directly carried on to the next step.



(Z)-**I-J**

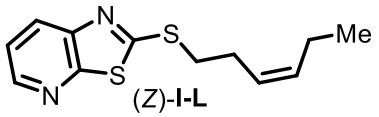
To a flame-dried, 25-mL round-bottom flask equipped with a magnetic stir bar were added NaH (60% oil dispersion, 2.0 mmol, 3 equiv) and DMF (10 mL, 0.2 M) under nitrogen. The mixture was cooled to 0 ° C. Benzothiophene-2-thiol (2.00 mmol, 1 equiv) was added followed by (*Z*)-hex-3-en-1-yl 4-methylbenzenesulfonate (2.45 mmol, 1.2 equiv) in DMF (5 mL). The reaction was allowed to warm to room temperature and stirred for 20 h. The reaction was cooled to 0 ° C and quenched with the addition of water and diethyl ether (5 mL, 1:1 mixture). The organic materials were separated by addition to H_2O (25 mL), followed by extraction with EtOAc (3 × 10 mL). The organic layer was dried with Na_2SO_4. After filtration the solvent was removed *in vacuo,* and the crude residue was purified by SiO_2 gel column chromatography (10% EtOAc/hexanes). Purification afforded (*Z*)-**I-J** as a pink liquid (162 mg, 32%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.7 Hz, 1H), 7.68 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.38 – 7.28 (m, 3H), 5.53 – 5.43 (m, 1H), 5.37 (dtt, *J* = 10.5, 7.2, 1.6 Hz, 1H), 2.96 (t, *J* = 7.4 Hz, 2H), 2.42 (qd, *J* = 7.4, 1.4 Hz, 2H), 2.03 (pd, *J* = 7.4, 1.6 Hz, 2H), 0.96 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 141.74, 139.95, 137.42, 134.10, 128.02, 126.12, 124.58, 124.42, 123.10, 121.98, 37.52, 27.45, 20.84, 14.37. **HRMS** calcd. for $C_{14}H_{17}S_2^+$ $[M+H]^+$: 249.0772, Found: 249.0768.

(*Z*)-2-(hex-3-en-1-ylthio)benzothiazole ((*Z*)-I-K): The title compound was prepared according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded (*Z*)-**I-K** as a clear liquid (250 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 5.57–5.48 (m, 1H), 5.46–5.38 (m, 1H), 3.36 (t, *J* = 7.4 Hz, 2H), 2.58 (q, *J* = 7.2 Hz, 2H), 2.09 (p, *J* = 7.2 Hz, 2H), 0.99 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.14, 153.47, 135.34, 134.56, 126.11, 125.85, 124.24, 121.57, 121.05, 33.58, 27.17, 20.84, 14.37. **HRMS** calcd. for $C_{13}H_{16}NS_2^+$ $[M+H]^+$: 250.0719, Found: 250.0724.



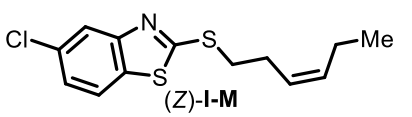
(*Z*)-**I-K**

(*Z*)-2-(hex-3-en-1-ylthio)thiazolo[5,4-b]pyridine ((*Z*)-I-L): The title compound was prepared on an 0.300 mmol scale according to General Procedure 1. The crude residue was purified by SiO_2 (10% EtOAc/hexanes). Purification afforded (*Z*)-**I-L** as a clear liquid (74 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.04 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.34 (dd, *J* = 8.2, 4.7 Hz, 1H), 5.60–5.49 (m, 1H), 5.41 (dtt, *J* = 10.7, 7.3, 1.6 Hz, 1H), 3.38 (t, *J* = 7.4 Hz, 2H), 2.58 (qd, *J* = 7.4, 1.4 Hz, 2H), 2.09 (pd, *J* = 7.5, 1.5 Hz, 2H), 0.99 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.85, 158.90, 146.58, 145.69, 134.76, 127.93, 125.67, 121.24, 32.95, 27.08, 20.86, 14.37. **HRMS** calcd. for $C_{12}H_{15}N_2S_2^+$ $[M+H]^+$: 251.0671, Found: 251.0688.



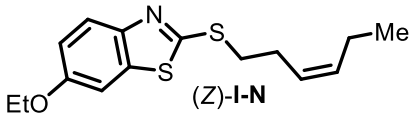
(*Z*)-**I-L**

(*Z*)-5-chloro-2-(hex-3-en-1-ylthio)benzothiazole ((*Z*)-I-M): The title compound was prepared on a 0.300 mmol scale according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded (*Z*)-**I-M** as a clear liquid (81 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 2.1 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.26 (dd, *J* = 8.5, 1.9 Hz, 1H), 5.57–5.48 (m, 1H), 5.41 (dtt, *J* = 10.6, 7.3, 1.6 Hz, 1H), 3.36 (t, *J* = 7.4 Hz, 2H), 2.58 (qd, *J* = 7.3, 1.4 Hz, 2H), 2.08 (pd, *J* = 7.5, 1.5 Hz, 2H), 0.99 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.45, 154.30, 134.71, 133.59, 132.21, 125.72, 124.60, 121.67, 121.48, 33.62, 27.11, 20.86, 14.38. **HRMS** calcd. for $C_{13}H_{15}ClNS_2^+$ $[M+H]^+$: 284.0329, Found: 284.0333.



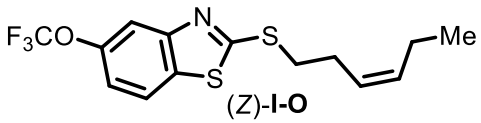
(*Z*)-**I-M**

(*Z*)-6-ethoxy-2-(hex-3-en-1-ylthio)benzothiazole ((*Z*)-I-N): The reaction was carried out according to General Procedure 1 on a 0.300 mmol scale. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded (*Z*)-**I-N** as a clear liquid (86 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.9 Hz, 1H), 7.22 (d, *J* = 2.5 Hz, 1H), 7.00 (dd, *J* = 8.9, 2.5 Hz, 1H), 5.51 (dtt, *J* = 10.2, 7.2, 1.5 Hz, 1H), 5.45–5.34 (m, 1H), 4.07 (q, *J* = 7.0 Hz, 2H), 3.32 (t, *J* = 7.4 Hz, 2H), 2.56 (q, *J* = 6.8, 6.2 Hz, 2H), 2.08 (pd, *J* = 7.5, 1.5 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H), 0.98 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.73, 156.47, 147.99, 136.68, 134.50, 125.93, 122.06, 115.35, 104.98, 27.25, 20.85, 14.99, 14.38. **HRMS** calcd. for $C_{15}H_{20}NOS_2^+$ $[M+H]^+$: 294.0981, Found: 294.0987.



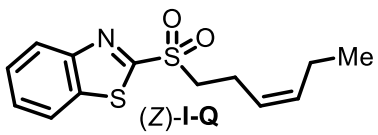
(*Z*)-**I-N**

(*Z*)-2-(hex-3-en-1-ylthio)-5-(trifluoromethoxy)benzothiazole ((*Z*)-I-O): The title compound was prepared on an 0.300 mmol scale according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded (*Z*)-**I-O** as a clear liquid (100 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80–7.66 (m, 2H), 7.18 (dd, *J* = 8.7, 2.3 Hz, 1H), 5.54 (dtt, *J* = 10.5, 7.3, 1.5 Hz, 1H), 5.41 (dtt, *J* = 10.6, 7.3, 1.6 Hz, 1H), 3.37 (t, *J* = 7.4 Hz, 2H), 2.58 (qd, *J* = 7.4, 1.4 Hz, 2H), 2.09 (pd, *J* = 7.5, 1.5 Hz, 2H), 0.99 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.29, 154.08, 147.97, 134.75, 133.65, 125.68, 123.26, 121.64, 121.55, 119.85, 118.14, 117.69, 114.09, 33.64, 27.08, 20.86, 14.36. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.99. **HRMS** calcd. for $C_{14}H_{15}F_3NOS_2^+$ $[M+H]^+$: 334.0542, Found: 334.0550.



(*Z*)-**I-O**

(*Z*)-2-(hex-3-en-1-ylsulfinyl)benzothiazole ((*Z*)-I-P): To a 25-mL round-bottom flask equipped with a magnetic stir bar was charged (*E*)-2-(hex-3-en-1-ylsulfinyl)benzothiazole (0.5 mmol, 1 equiv) and DCM (5 mL, 0.1 M). The mixture was cooled to 0 ° C. A solution of mCPBA (0.5 mmol, 1 equiv) in DCM (5 mL, 0.1 M) was then added dropwise. The reaction was stirred for 4 h. The organic materials were separated by addition of H_2O (0.2 M, 25 mL), followed by extraction with EtOAc (3 × 10 mL). The organic layer was dried over Na_2SO_4, and after filtration the solvent was removed *in vacuo.* The mixture was purified by SiO_2 gel column chromatography (40% EtOAc/hexanes). Purification afforded (*Z*)-**I-P** as a white solid (105 mg, 79%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 5.51 (dtt, *J* = 10.5, 7.3, 1.5 Hz, 1H), 5.38–5.31 (m, 1H), 3.24 (dddd, *J* = 35.7, 13.3, 9.1, 6.2 Hz, 2H), 2.73 (dq, *J* = 14.9, 7.9, 7.2 Hz, 1H), 2.50–2.40 (m, 1H), 2.04 (h, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 177.80, 154.07, 136.13, 135.40, 127.06, 126.28, 124.15, 124.04, 122.42, 56.54, 20.73, 19.80, 14.19. **HRMS** calcd. for $C_{13}H_{16}NOS_2^+$ $[M+H]^+$: 266.0668, Found: 266.0682.



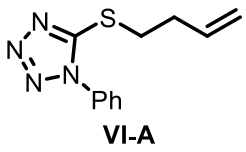
(*Z*)-**I-P**

(*Z*)-2-(hex-3-en-1-ylsulfonyl)benzothiazole ((*Z*)-I-Q): To a 100-mL round-bottom flask equipped with a magnetic stir bar were added (*E*)-2-(hex-3-en-1-ylthio)benzothiazole (0.300 mmol, 1 equiv), 30% aqueous H_2O_2 (0.6 mL, 6 equiv), ammonium heptamolybdate tetrahydrate (0.006 mmol, 1 mol%), and ethanol (5.0 mL, 0.06 M). The reaction was stirred at room temperature for 12 h. The organic materials were separated by addition of H_2O (20 mL), followed by extraction with EtOAc (3 × 10 mL). The organic solution was washed with brine (10 mL) and dried over Na_2SO_4. After filtration, the solvent was removed *in vacuo* to afford (*Z*)-**I-Q** as a white solid (82 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.62 (dt, *J* = 27.1, 7.2 Hz, 2H), 5.51–5.41 (m, 1H), 5.26 (dddd, *J* = 14.4, 7.4, 5.2, 3.6 Hz, 1H), 3.57–3.50 (m, 2H), 2.63 (q, *J* = 7.4 Hz, 2H), 2.02 (p, *J* = 7.1 Hz, 2H), 0.94 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.97, 152.84, 136.89, 135.49, 128.17, 127.81, 125.58,

(*Z*)-**I-Q**

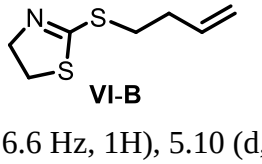
123.22, 122.48, 54.56, 20.68, 20.58, 14.14. **HRMS** calcd. for $C_{13}H_{16}NO_2S_2^+$ $[M+H]^+$: 282.0617, Found: 282.0624.

5-(but-3-en-1-ylthio)-1-phenyl-1H-tetrazole (VI-A): The title compound was prepared according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (10% Et_2O/hexanes). Purification afforded **VI-A** as a yellow solid (232.3 mg, 35%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.66–7.51 (m, 5H), 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.12 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.09 (d, *J* = 9.0 Hz, 1H), 3.46 (t, *J* = 7.2 Hz, 2H), 2.59 (q, *J* = 7.1 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.36, 135.23, 133.81, 130.23, 129.91, 123.97, 117.53, 33.25, 32.69. **HRMS** calcd. for $C_{11}H_{13}N_4S^+$ $[M+H]^+$: 233.0856, Found: 233.0863.



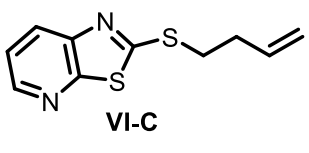
VI-A

2-(but-3-en-1-ylthio)-4,5-dihydrothiazole (VI-B): The title compound was prepared according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (10% Et_2O/hexanes). Purification afforded **IV-B** as a clear liquid (173 mg, 43%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.81 (ddt, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.10 (d, *J* = 18.9 Hz, 1H), 5.05 (d, *J* = 12.2 Hz, 0H), 4.21 (t, *J* = 8.0 Hz, 2H), 3.37 (t, *J* = 8.0 Hz, 2H), 3.16 (t, *J* = 7.3 Hz, 2H), 2.45 (q, *J* = 7.1 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 136.05, 116.70, 64.45, 35.52, 33.52, 32.06. **HRMS** calcd. for $C_7H_{12}NS_2^+$ $[M+H]^+$: 174.0406, Found: 174.0408.



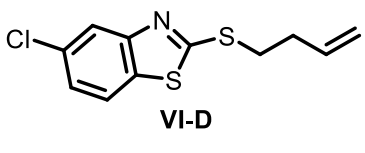
VI-B

2-(but-3-en-1-ylthio)thiazolo[5,4-b]pyridine (VI-C): The title compound was prepared according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (10% Et_2O/hexanes). Purification afforded **VI-C** as a clear liquid (171 mg, 77%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.52–8.36 (m, 1H), 8.04 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.38–7.30 (m, 1H), 5.88 (ddt, *J* = 17.0, 10.6, 6.7 Hz, 1H), 5.16 (d, *J* = 17.7 Hz, 1H), 5.11 (d, *J* = 10.2 Hz, 1H), 3.43 (t, *J* = 7.3 Hz, 2H), 2.59 (q, *J* = 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.52, 158.79, 146.45, 145.63, 135.57, 127.88, 121.15, 117.19, 33.30, 32.11. **HRMS** calcd. for $C_{10}H_{11}N_2S_2^+$ $[M+H]^+$: 223.0358, Found: 223.0364.



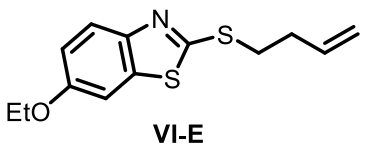
VI-C

2-(but-3-en-1-ylthio)-5-chlorobenzothiazole (VI-D): The title compound was prepared according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded **VI-D** as a clear liquid (255 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 2.1 Hz, 1H), 7.63 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.28–7.21 (m, 1H), 5.88 (ddt, *J* = 16.9, 10.3, 6.7 Hz, 1H), 5.16 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.11 (dd, *J* = 10.2, 1.6 Hz, 1H), 3.41 (t, *J* = 7.3 Hz, 2H), 2.58 (q, *J* = 7.1 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.21, 154.21, 135.67, 133.54, 132.18, 124.59, 121.63, 121.47, 117.18, 33.39, 32.86. **HRMS** calcd. for $C_{11}H_{11}ClNS_2^+$ $[M+H]^+$: 256.0016, Found: 256.0025.



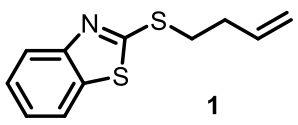
VI-D

2-(but-3-en-1-ylthio)-6-ethoxybenzothiazole (VI-E): The title compound was prepared according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded **VI-E** as a clear liquid (264 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.9 Hz, 1H), 7.21 (d, *J* = 2.6 Hz, 1H), 7.00 (dd, *J* = 8.9, 2.6 Hz, 1H), 5.88 (ddt, *J* = 16.9, 10.3, 6.6 Hz, 1H), 5.15 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.09 (dd, *J* = 10.2, 1.6 Hz, 1H), 4.06 (q, *J* = 7.0 Hz, 2H), 3.37 (t, *J* = 7.4 Hz, 2H), 2.57 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.47, 156.45, 147.90, 136.63, 135.85, 122.05, 116.96, 115.32, 104.90, 64.19, 33.52, 33.02, 14.94. **HRMS** calcd. for $C_{13}H_{16}NOS_2^+$ $[M+H]^+$: 266.0668, Found: 266.0679.



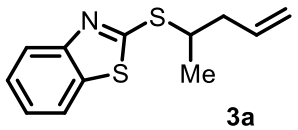
VI-E

2-(but-3-en-1-ylthio)benzothiazole (1): The title compound was prepared on 18 mmol scale according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (10% Et_2O/hexanes). Purification afforded **1** as a clear liquid (3.98 g, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.44–7.40 (m, 1H), 7.32–7.28 (m, 1H), 5.89 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.16 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.11 (dd, *J* = 10.2, 1.5 Hz, 1H), 3.43 (t, *J* = 7.3 Hz, 2H), 2.60 (q, *J* = 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.91, 153.41, 135.80, 135.31, 126.10, 124.26, 121.59, 121.03, 117.05, 33.45, 32.84. **HRMS** calcd. for $C_{11}H_{12}NS_2^+$ $[M+H]^+$: 222.0406, Found: 222.0411.



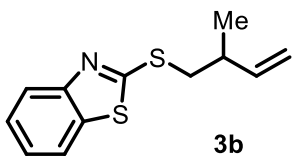
1

2-(pent-4-en-2-ylthio)benzothiazole (3a): The title compound was prepared according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded **3a** as a yellow liquid (233 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.41 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.30 (td, *J* = 7.7, 1.2 Hz, 1H), 5.88 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.18–5.10 (m, 2H), 4.07 (td, *J* = 7.1, 6.0 Hz, 1H), 2.61 (dddt, *J* = 12.7, 7.1, 5.8, 1.3 Hz, 1H), 2.48 (dtt, *J* = 14.4, 7.3, 1.3 Hz, 1H), 1.50 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.36, 153.54, 135.46, 134.63, 126.11, 124.39, 121.76, 121.06, 118.15, 43.68, 41.02, 20.77. **HRMS** calcd. for $C_{12}H_{14}NS_2^+$ $[M+H]^+$: 236.0562, Found: 236.0551.



3a

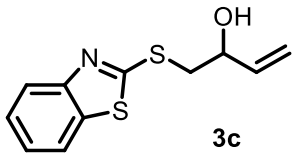
2-((2-methylbut-3-en-1-yl)thio)benzothiazole (3b): The title compound was prepared according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded **3b** as a yellow liquid (231 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 5.83 (ddd, *J* = 17.2, 10.3, 6.9 Hz, 1H), 5.13 (d, *J* = 17.6 Hz, 1H), 5.07 (d, *J* = 10.2 Hz, 1H), 3.37 (qd, *J* = 12.8, 6.9 Hz, 2H), 2.68 (h, *J* = 6.9, 6.3 Hz, 1H), 1.20 (d, *J* = 6.6 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.39, 153.43, 141.62, 135.33, 126.13, 124.27, 121.59,



3b

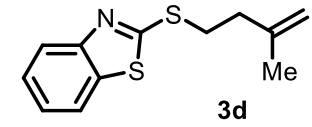
121.06, 114.99, 39.84, 37.69, 19.49. **HRMS** calcd. for $C_{12}H_{14}NS_2^+$ $[M+H]^+$: 236.0562, Found: 236.0552.

1-(benzothiazol-2-ylthio)but-3-en-2-ol (3c): The title compound was prepared according to General Procedure 2. The crude residue was purified by SiO_2 gel column chromatography (20% EtOAc/hexanes). Purification afforded **3c** as a white solid (159 mg, 67%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.1, 1.2 Hz, 1H), 7.42 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.34–7.28 (m, 1H), 5.98 (ddd, *J* = 17.2, 10.4, 5.5 Hz, 1H), 5.47–5.38 (m, 1H), 5.24 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.63–4.58 (m, 2H), 3.59 (dd, *J* = 14.4, 3.2 Hz, 1H), 3.42 (dd, *J* = 14.4, 7.3 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.85, 152.52, 138.87, 135.61, 126.41, 124.78, 121.49, 121.21, 116.32, 72.39, 40.73. **HRMS** calcd. for $C_{11}H_{12}NOS_2^+$ $[M+H]^+$: 238.0355, Found: 238.0337.



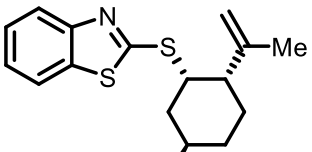
3c

2-((3-methylbut-3-en-1-yl)thio)benzothiazole (3d): The title compound was prepared according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded **3d** as a yellow liquid (232 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 1.1 Hz, 1H), 7.45–7.39 (m, 1H), 7.31–7.27 (m, 1H), 4.84 (d, *J* = 21.5 Hz, 2H), 3.48 (t, *J* = 7.6 Hz, 2H), 2.54 (t, *J* = 7.5 Hz, 2H), 1.81 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.08, 153.46, 143.25, 135.34, 126.13, 124.29, 121.62, 121.07, 112.24, 37.30, 31.81, 22.36. **HRMS** calcd. for $C_{12}H_{14}NS_2^+$ $[M+H]^+$: 236.0562, Found: 236.0569.



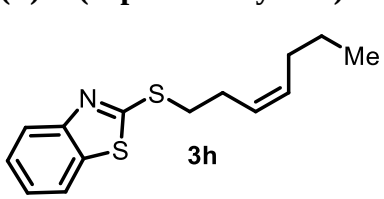
3d

2-(1*S*,2*S*,5*R*)-5-methyl-2-(prop-1-en-2-yl)cyclohexyl)thio)benzothiazole (3e): The title compound was prepared according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (10% Et_2O/hexanes). Purification afforded **3e** as a yellow liquid (247 mg, 81%). **^{1}H NMR** (600 MHz, Benzene-d_6) δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 5.01 (d, *J* = 3.8 Hz, 1H), 4.85 (d, *J* = 44.4 Hz, 2H), 2.39 (dt, *J* = 13.9, 2.8 Hz, 1H), 2.03 (d, *J* = 12.2 Hz, 1H), 1.85–1.79 (m, 1H), 1.77 (s, 3H), 1.58 (d, *J* = 11.1 Hz, 2H), 1.47 (qd, *J* = 13.5, 12.9, 3.6 Hz, 1H), 1.29 (ddd, *J* = 14.5, 12.1, 3.3 Hz, 1H), 0.81–0.69 (m, 4H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.89, 152.83, 145.91, 134.77, 125.39, 123.56, 120.89, 120.40, 110.60, 48.95, 46.53, 40.48, 34.30, 27.31, 26.04, 21.93, 21.57. **HRMS** calcd. for $C_{17}H_{22}NS_2^+$ $[M+H]^+$: 304.1188, Found: 304.1206.



3e

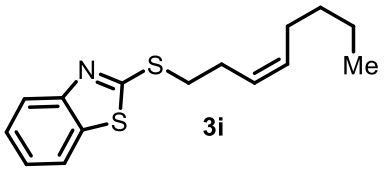
(*Z*)-2-(hept-3-en-1-ylthio)benzothiazole (3h): The title compound was prepared according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded **3h** as a clear liquid (261 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.75 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.41 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.29 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1H),



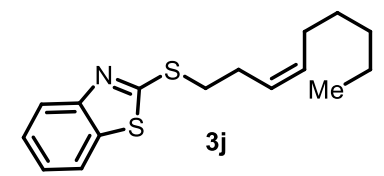
3h

5.53 (dtt, *J* = 12.0, 7.1, 1.3 Hz, 1H), 5.49–5.42 (m, 1H), 3.36 (t, *J* = 7.4 Hz, 2H), 2.59 (qd, *J* = 7.3, 1.3 Hz, 2H), 2.06 (qd, *J* = 7.4, 1.4 Hz, 2H), 1.40 (h, *J* = 7.4 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.17, 153.48, 135.35, 132.76, 126.61, 126.13, 124.26, 121.59, 121.06, 33.58, 29.58, 27.30, 22.88, 13.94. **HRMS** calcd. for $C_{14}H_{18}NS_2^+$ $[M+H]^+$: 264.0875, Found: 264.0877.

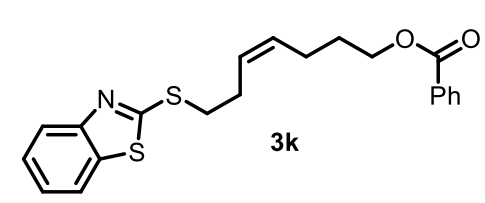
(*Z*)-2-(oct-3-en-1-ylthio)benzothiazole (3i): The title compound was prepared according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded **3i** as a clear liquid (275 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.41 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.31–7.27 (m, 1H), 5.58–5.49 (m, 1H), 5.49–5.42 (m, 1H), 3.36 (t, *J* = 7.4 Hz, 2H), 2.59 (q, *J* = 7.0 Hz, 2H), 2.05 (qd, *J* = 7.3, 1.4 Hz, 2H), 1.40 (h, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.89–0.71 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.18, 153.49, 135.35, 132.99, 126.41, 126.13, 124.27, 121.59, 121.06, 33.59, 31.92, 27.27, 22.50, 14.13. **HRMS** calcd. for $C_{15}H_{20}NS_2^+$ $[M+H]^+$: 278.1032, Found: 278.1045.



(*Z*)-2-(non-3-en-1-ylthio)benzothiazole (3j): The title compound was prepared according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded **3j** as a clear liquid (290 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.78 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.43 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.36–7.30 (m, 1H), 5.59–5.51 (m, 1H), 5.51–5.42 (m, 1H), 3.39 (t, *J* = 7.4 Hz, 2H), 2.61 (qd, *J* = 7.3, 1.3 Hz, 2H), 2.12–2.05 (m, 2H), 1.39 (p, *J* = 7.3 Hz, 2H), 1.30 (tdd, *J* = 9.5, 7.3, 5.6 Hz, 4H), 0.90 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.16, 153.49, 135.34, 133.05, 126.38, 126.12, 124.26, 121.59, 121.05, 33.59, 31.65, 29.42, 27.52, 27.26, 22.69, 14.20. **HRMS** calcd. for $C_{16}H_{22}NS_2^+$ $[M+H]^+$: 292.1188, Found: 292.1211.



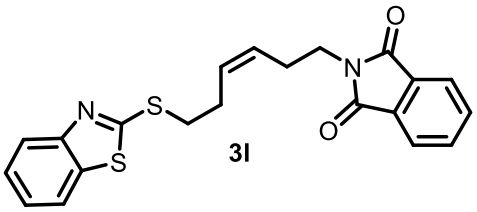
(*Z*)-7-(benzothiazol-2-ylthio)hept-4-en-1-yl benzoate (3k): The initial cross coupling was performed following a literature procedure.[5] To a 20-mL flame-dried vial with a magnetic stir bar in a glovebox under nitrogen atmosphere were added 2-(but-3-en-1-ylthio)benzothiazole (**1**) (1.0 mmol, 1 equiv) and pent-4-en-1-ol (2.0 mmol, 2 equiv). To this mixture was added Grubbs *Z*-selective catalyst (Grubbs C675) dissolved in THF (2.5 mol%, 2.5 mL, 0.01 M). The solution was allowed to stir in an uncapped vial in the glovebox under nitrogen atmosphere for 24 h. The crude reaction mixture was filtered through a pad of Celite and the solvent was removed *in vacuo*. MeCN (1 mL) was added to the crude mixture, and the crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min,



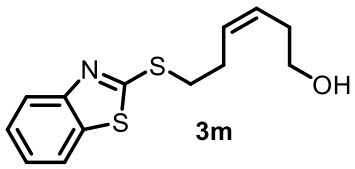
main segment of gradient at 45–65% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z =280.1 [M+H], cone voltage 15V). Purification afforded (*Z*)-7-(benzothiazol-2-ylthio)hept-4-en-1-ol as a yellow solid (84 mg, 30%), which was directly brought on to the next step.

A 4-mL vial equipped with a magnetic stir bar was charged with benzoyl chloride (0.150 mmol, 1.5 equiv), (*Z*)-7-(benzothiazol-2-ylthio)hept-4-en-1-ol (0.100 mmol, 1 equiv), pyridine (0.042 mL, 5 equiv), and *N*,*N*-dimethylaminopyridine (1.3 mg, 0.1 equiv). The reagents were disolved in DCM (1 mL, 0.1 M) at 0 ° C and allowed to stir for 1 h. Water (1 mL) was added to the solution, and the solution was allowed to warm to room temperature. The organic materials were separated by addition of H_2O (25 mL), followed by extraction with EtOAc (3 × 10 mL). The organic layer was dried over Na_2SO_4, and, after filtration, the solvent was removed *in vacuo,* and the crude residue was purified by SiO_2 gel column chromatography (10% Et_2O/hexanes). Purification afforded **3k** as a clear liquid (32 mg, 80%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06–7.95 (m, 2H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.43–7.34 (m, 3H), 7.30–7.27 (m, 1H), 5.55 (tq, *J* = 11.1, 5.6, 4.3 Hz, 2H), 4.32 (t, *J* = 6.5 Hz, 2H), 3.36 (t, *J* = 7.4 Hz, 2H), 2.61 (q, *J* = 7.1 Hz, 2H), 2.26 (q, *J* = 7.1 Hz, 2H), 1.86 (p, *J* = 6.9 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.98, 166.74, 153.43, 135.32, 132.98, 131.26, 130.48, 129.65, 128.46, 127.79, 126.16, 124.30, 121.59, 121.08, 64.46, 33.38, 28.72, 27.33, 24.04. **HRMS** calcd. for $C_{21}H_{22}NO_2S_2^+$ $[M+H]^+$: 384.1087, Found: 384.1099.

(*Z*)-2-(6-(benzothiazol-2-ylthio)hex-3-en-1-yl)isoindoline-1,3-dione (3l): The title compound was prepared following a literature procedure.[5] To a 20-mL flame- dried vial with a magnetic stir bar in a glovebox under nitrogen atmosphere were added 2-(but-3-en-1-ylthio)benzothiazole (**1**) (4.0 mmol, 1 equiv) and 2-(but-3-en-1-yl)isoindoline-1,3-dione (6.0 mmol, 1.5 equiv). To this mixture was added Grubbs *Z*-selective catalyst (Grubbs C675) dissolved in THF (3.0 mol%, 12 mL, 0.01 M). The solution was allowed to stir in an uncapped vial in the glovebox under nitrogen atmosphere for 24 h. The crude reaction mixture was filtered through a pad of Celite and the solvent was removed *in vacuo*. MeCN (1 mL) was added to the crude mixture, and the crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 395.1 [M+H], cone voltage 15V). Purification afforded **3l** as a clear liquid (47 mg, 3%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86–7.78 (m, 3H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.66 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 5.55 (dtd, *J* = 14.7, 11.1, 5.5 Hz, 2H), 3.76 (t, *J* = 7.1 Hz, 2H), 3.29 (t, *J* = 7.3 Hz, 2H), 2.52 (dq, *J* = 23.7, 7.0 Hz, 4H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.47, 166.90, 153.40, 135.33, 134.03, 132.18, 129.79, 127.96, 126.08, 124.24, 123.35, 121.61, 121.05, 37.59, 33.29, 27.18, 26.82. **HRMS** calcd. for $C_{21}H_{19}N_2O_2S_2^+$ $[M+H]^+$: 395.0883, Found: 395.0899.

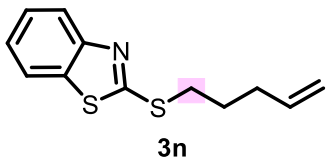


(*Z*)-**6-(benzothiazol-2-ylthio)hex-3-en-1-ol (3m):** The title compound was prepared following a literature procedure.[5] To a 20-mL flame-dried vial with a magnetic stir bar in a glovebox under nitrogen atmosphere were added 2-(but-3-en-1- ylthio)benzothiazole (**1**) (1.0 mmol, 1 equiv) and but-3-en-1-ol (2.0 mmol, 2 equiv). To this mixture was added Grubbs *Z*-selective catalyst (Grubbs C675) dissolved in THF (2.5 mol%, 2.5 mL, 0.01 M). The solution was allowed to stir in an uncapped vial in the glovebox under nitrogen atmosphere for 24 h. The crude reaction mixture was filtered through a pad of Celite and the solvent was removed *in vacuo*. MeCN (1 mL) was added to the crude mixture, and the crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 55–75% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 266.1 [M+H], cone voltage 15V). Purification afforded **3m** as a clear liquid (35 mg, 30%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.75 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.42 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.30 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 1H), 5.65 (ddt, *J* = 12.5, 7.4, 1.5 Hz, 1H), 5.55 (dtt, *J* = 10.5, 7.5, 1.4 Hz, 1H), 3.71 (t, *J* = 6.3 Hz, 2H), 3.39 (t, *J* = 7.4 Hz, 2H), 2.62 (qd, *J* = 7.5, 1.3 Hz, 2H), 2.38 (td, *J* = 7.7, 7.0, 5.6 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.18, 153.28, 135.31, 129.67, 128.63, 126.22, 124.40, 121.49, 121.13, 62.16, 33.23, 31.18, 27.57. **HRMS** calcd. for $C_{13}H_{15}NOS_2^+$ $[M+H]^+$: 266.0668, Found: 266.0682.



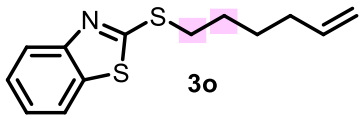
3m

2-(pent-4-en-1-ylthio)benzothiazole (3n): The title compound was prepared according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded **3n** as a yellow liquid (234 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.92–7.81 (m, 1H), 7.75 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.41 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.33–7.26 (m, 1H), 5.83 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.09 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.03 (dd, *J* = 10.2, 1.6 Hz, 1H), 3.36 (t, *J* = 7.3 Hz, 2H), 2.26 (q, *J* = 6.7 Hz, 2H), 1.94 (p, *J* = 7.3 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.21, 153.48, 137.33, 135.33, 126.14, 124.28, 121.63, 121.06, 115.88, 33.03, 32.77, 28.52. **HRMS** calcd. for $C_{12}H_{14}NS_2^+$ $[M+H]^+$: 236.0569, Found: 236.0562.



3n

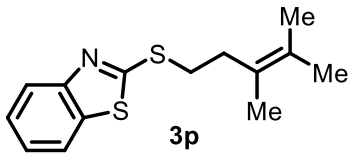
2-(hex-5-en-1-ylthio)benzothiazole (3o): The title compound was prepared according to General Procedure 2. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded **3o** as a clear liquid (244 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.75 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.03 (dd, *J* = 17.2, 1.8 Hz, 1H), 4.97 (dd, *J* = 10.2, 1.8 Hz, 1H), 3.36 (t, *J* = 7.4 Hz, 2H), 2.12 (q, *J* = 7.1 Hz, 2H), 1.85 (p, *J* = 7.4 Hz, 2H), 1.63–1.56 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.38, 153.49, 138.35, 135.31, 126.14, 124.26, 121.60, 121.06,



3o

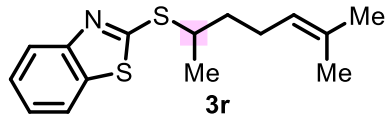
115.08, 33.57, 33.31, 28.82, 28.09. **HRMS** calcd. for $C_{13}H_{16}NS_2^+$ $[M+H]^+$: 250.0719, Found: 250.0712.

2-(hex-5-en-1-ylthio)benzothiazole (3p): The title compound was prepared from 5-bromo-2,3-dimethylpent-2-ene[6] according to General Procedure 2. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded **3p** as an orange liquid (256 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.45–7.38 (m, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 3.39–3.29 (m, 2H), 2.56 (t, *J* = 7.9 Hz, 2H), 1.73 (s, 6H), 1.67 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.44, 153.51, 135.35, 127.44, 126.10, 125.26, 124.21, 121.57, 121.06, 34.37, 32.32, 20.82, 20.56, 18.43. **HRMS** calcd. for $C_{14}H_{18}NS_2^+$ $[M+H]^+$: 264.0875, Found: 264.0873.



3p

(***E***)**-2-((3-methylpent-3-en-1-yl)thio)benzothiazole (3q):** The title compound was prepared from (*E*)-5-bromo-3-methylpent-2-ene[7] according to General Procedure 2. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded **3q** as a white solid (249 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (m, 1H), 7.79–7.73 (m, 1H), 7.47–7.37 (m, 1H), 7.32–7.26 (m, 1H), 5.41–5.30 (m, 1H), 3.43 (t, *J* = 7.6 Hz, 2H), 2.49 (t, *J* = 7.6 Hz, 2H), 1.69 (s, 3H), 1.63–1.58 (m, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.42, 153.50, 135.31, 133.29, 126.11, 124.23, 121.59, 121.31, 121.04, 39.11, 32.46, 15.59, 13.56. **HRMS** calcd. for $C_{13}H_{16}NS_2^+$ $[M+H]^+$: 250.0719, Found: 250.0706.



3q

2-((6-methylhept-5-en-2-yl)thio)benzothiazole (3r): The title compound was prepared according to General Procedure 1. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/hexanes). Purification afforded **3r** as a yellow liquid (274 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.41 (t, *J* = 8.1 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 5.13 (tt, *J* = 7.0, 1.6 Hz, 1H), 3.96 (h, *J* = 6.8 Hz, 1H), 2.31–2.08 (m, 2H), 1.84 (ddt, *J* = 13.8, 8.5, 6.8 Hz, 1H), 1.77–1.70 (m, 1H), 1.70 (s, 3H), 1.61 (s, 3H), 1.52 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.77, 153.58, 135.47, 132.77, 126.09, 124.31, 123.33, 121.73, 121.02, 44.27, 36.92, 25.88, 25.72, 21.70, 17.87. **HRMS** calcd. for $C_{15}H_{20}NS_2^+$ $[M+H]^+$: 278.1032, Found: 278.1037.

3r

Oxidative Heck Reaction Design of Experiment

During reaction optimization, other product isomers were occasionally observed by ^{1}H-NMR analysis of the crude reaction mixture. Below is a representative example of a ^{1}H-NMR spectrum of the mixture of products from a concentrated (0.1 mM), unoptimized oxidative Heck reaction of (*Z*)-2-(hex-3-en-1-ylthio)benzothiazole ((*Z*)-**I**).

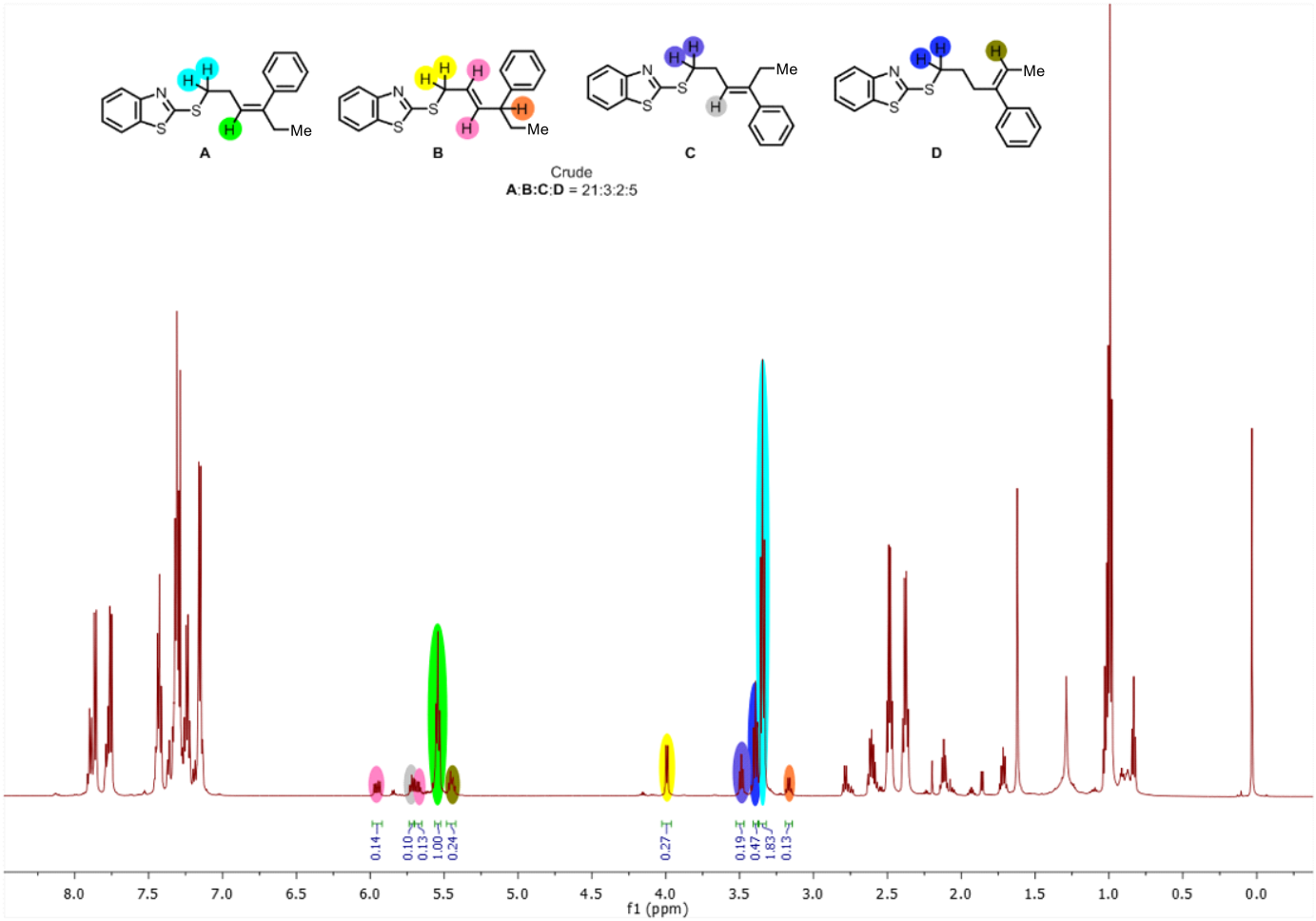
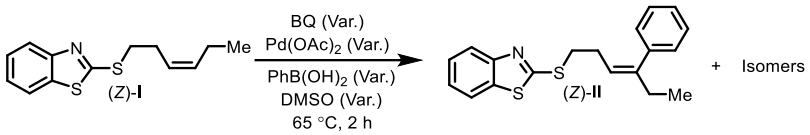


Table S1. Model Reaction under Investigation



	DMSO	Benzoquinone	$Pd(OAc)_2$	Phenylboronic Acid
Low	0.100 M	0.7 equiv	2.5 mol%	1.0 equiv
Medium	0.075M	1.0 equiv	5.0 mol%	1.2 equiv
High	0.050 M	1.3 equiv	7.5 mol%	1.4 equiv

A. Design of Experiment Setup: Concentrated stock solutions of benzoquinone, palladium(II) acetate, phenylboronic acid, and (*Z*)-2-(hex-3-en-1-yl-thio)benzothiazole were prepared in DMSO. (*Z*)-2-(hex-3-en-1-yl-thio)benzothiazole (0.1 mmol) was loaded into 81 reaction vessels from the stock solution using a multichannel pipette. The reaction vessels in metal heating block were placed on the Unchained Labs Freeslate robotic platform and charged with every combination of the above high, medium, and low values for each reagent noted reagent to build a response-surface reaction space. The reaction was heated at 65 ^{O}C and sampling was performed at 2 h. Relative yields were measured using and LCMS. The data was then processed through JMP statistical software to build a reaction space.

B. Photography of Setup:

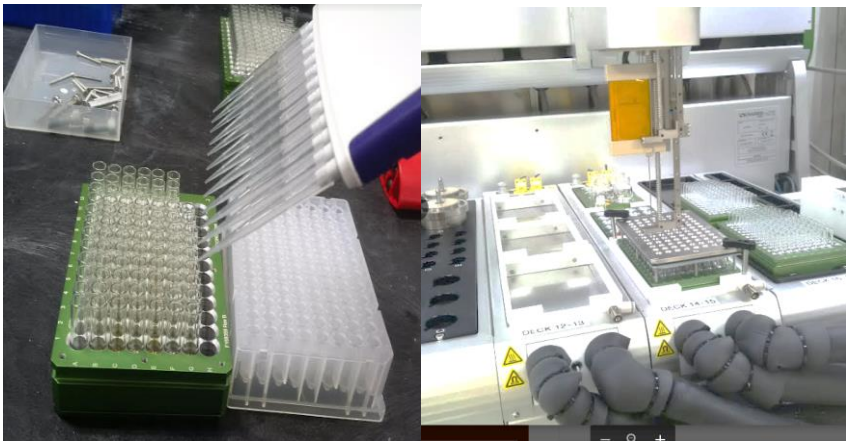


Figure S1. Photographic depiction of setup described in section A above displaying preparation of starting material using multichannel pipette (left) and sampling of the reaction at 2 h (right).

Table S2. Log-Worth Values of Reagents

2 hour run

Substrate	Log-Worth
Palladium acetate (mol%)	18.1
DMSO (concentration)	13.9
Palladium acetate (mol%) * DMSO (concentration)	7.2
Palladium acetate (mol%) * Phenylboronic acid (equiv)	2.6

C. JMP Statistical Software Analysis

Through use of JMP statistical software, the value of each reagent as it pertains to yield was determined for the 2 hour time point. The reagents, or combinations thereof, that statistically provide the greatest leverage are displayed along with their log-worth values (Table S2).

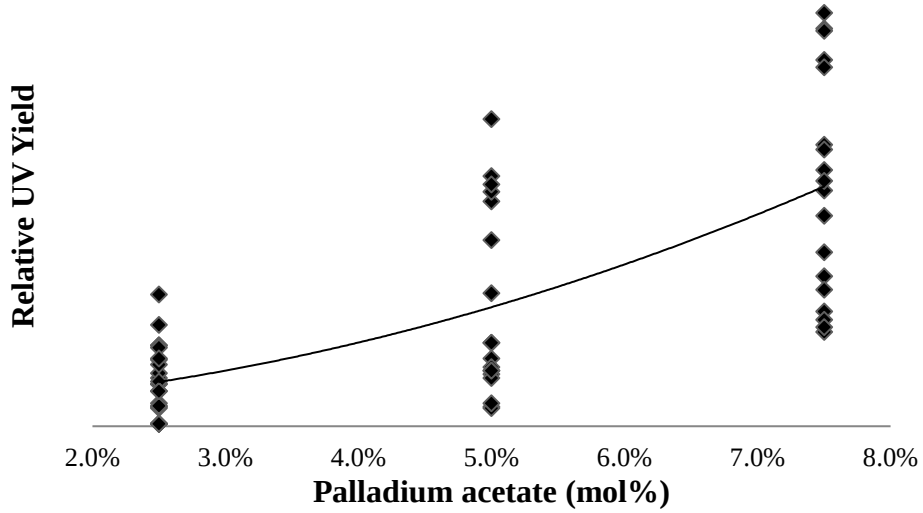


Figure S2. Palladium acetate (mol%) is plotted against the Relative UV-yield at 2 h. As could be anticipated, an increase in catalyst generally provides an increase in yield.

f

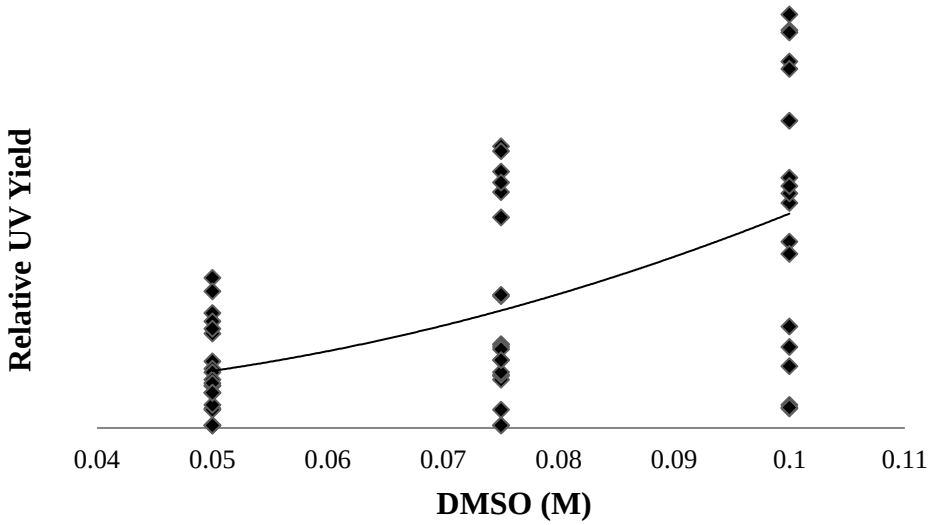


Figure S3. DMSO (M) is plotted against the Relative UV-yield at 2 h. There is slightly greater spread in this data giving the DMSO variable a bit less log-worth in the reaction space meaning that it has somewhat less effect on yield.

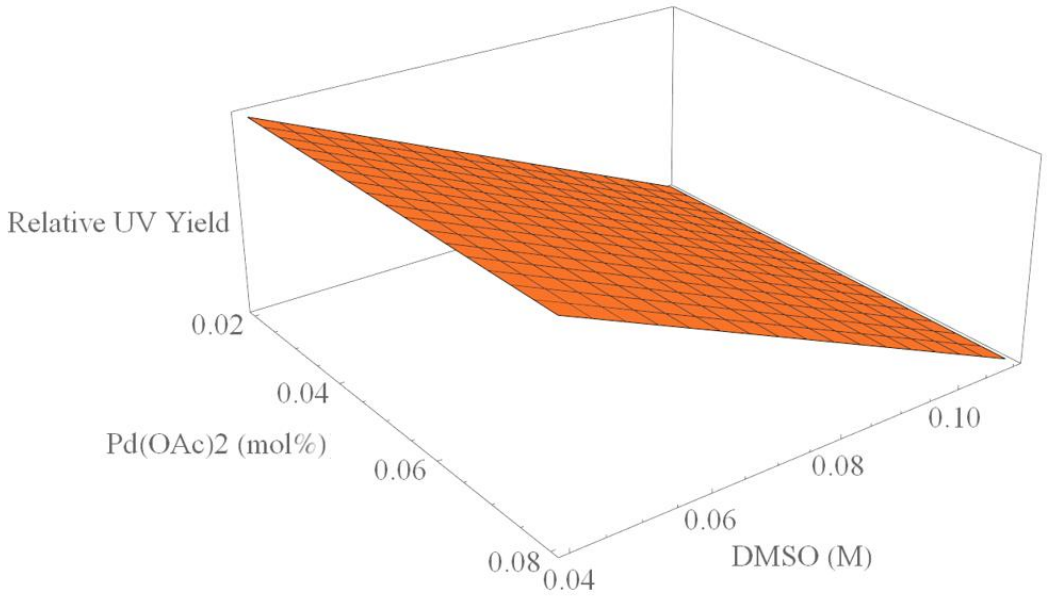


Figure S4. Relative UV Yield is plotted in relation to palladium acetate loading and concentration of reaction in DMSO, as measured by molarity, using Wolfram Mathematica 11.1. This graph shows a representation of the reaction space based on the design of experiment results.

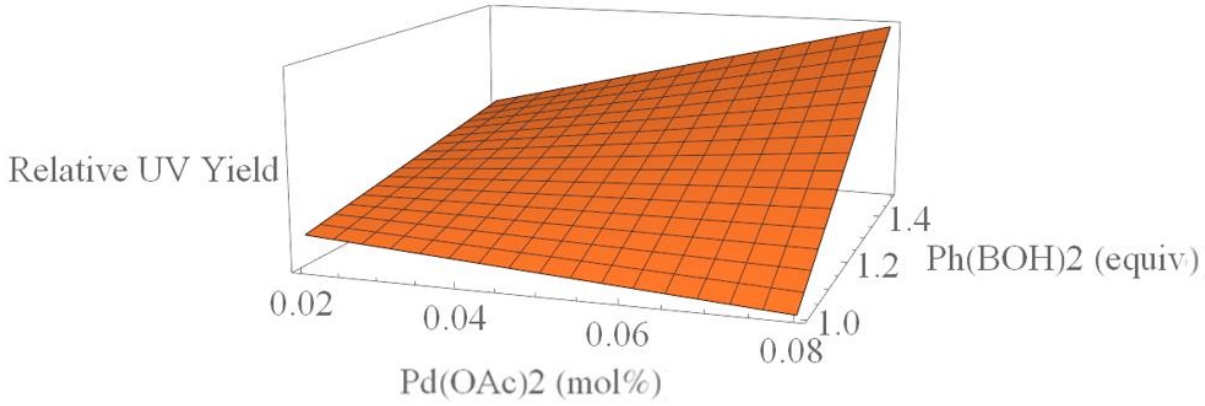
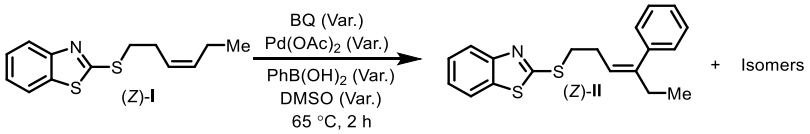


Figure S5. UV yield is plotted in relation to palladium acetate loading and phenylboronic acid loading using Wolfram Mathematica 11.1. This graph shows a representation of the reaction space based on the design of experiment results.

Table S3. Design-of-Experiment-Guided Reactions

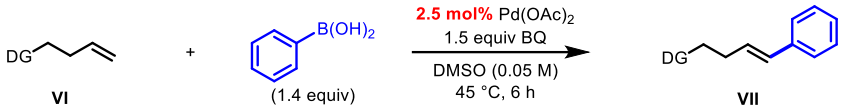


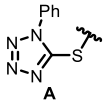
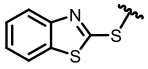
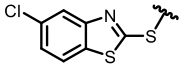
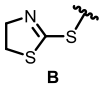
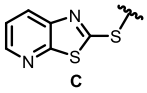
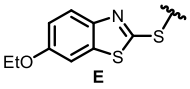
	Benzoquinone (equiv)	$Pd(OAc)_2$ (mol%)	Phenylboronic acid (equiv)	DMSO (M)	Conversion (NMR)	Desired Product (NMR)
1	1.5	7.5	1.1	0.1	99%	50%
2	1.5	2.5	1.4	0.1	94%	58%
3	1.5	7.5	1.4	0.05	99%	84%*

*Isolated yield: 91%

Directing Group Optimization for Oxidative Heck Reaction

Table S4. Optimization of Directing Group for Terminal Alkene in Oxidative Heck Reaction[a]

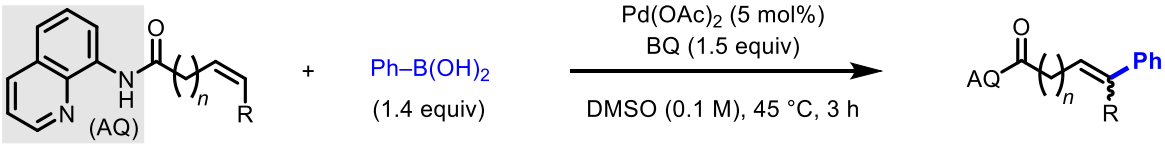


Directing Group (DG)	Yield (**VII**)	Directing Group (DG)	Yield (**VII**)	Directing Group (DG)	Yield (**VII**)
 **A**	76%	 **1**[c]; **2a**[d] (BT)S	50%	 **D**	54%
 **B**	<15%[b]	 **C**	50%	 **E**	44%

[a]Isolated yields except where otherwise noted. [b]Determined by ^{1}H-NMR of the crude reaction using 1,3,5-trimethoxybenzene as internal standard. [c]Starting material. [d]Product.

Control Experiments on 8-Aminoquinoline Directed Oxidative Heck Reaction

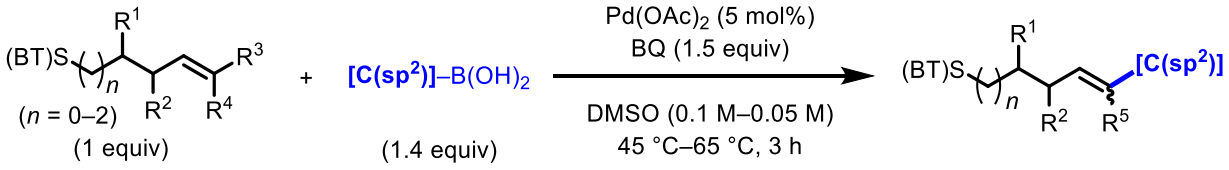
Table S5. Control Experiments on 8-Aminoquinoline Directed Oxidative Heck Reaction



R	***n***	**Temp.**	**Yield**[a]
H	1	45	*n.r.*[b]
H	1	65	*n.r.*[b]
H	1	110	< 5%
H	2	45	*n.r.*[b]
H	2	65	< 5%
H	2	110	< 5%
Et	1	45	*n.r.*[b]
Et	1	65	*n.r.*[b]
Et	1	110	< 5%

[a]Determined by LCMS. [b]n.r.=no reaction.

General Procedures for Oxidative Heck Reaction



Scheme S4. General Procedure for Oxidative Heck Reaction.

General Procedure for Oxidative Heck Reaction: To a 1-dram (4 mL) vial equipped with magnetic stir bar were added alkene (0.10 mmol, 1 equiv), boronic acid (0.14 mmol, 1.4 equiv), benzoquinone (0.15 mmol, 1.5 equiv), $Pd(OAc)_2$ (0.005 mmol, 5 mol%), and DMSO in air. The reaction was placed on a hot plate that was pre-heated to the correct temperature. Except for when otherwise mentioned, after 3 h, the reaction was brought to room temperature. The organic materials were separated from the DMSO by addition of 5% LiCl in H_2O (10 mL), followed by extraction with EtOAc (3 × 5 mL) and dried with Na_2SO_4. The solvent was removed *in vacuo*, and the crude residue was purified by SiO_2 gel column chromatography, preparative TLC, or mass-directed prep LC.

- **General Procedure 3:**
  DMSO (1 mL, 0.1 M), 45 ° C
- **General Procedure 4:**
  DMSO (2 mL, 0.05 M), 6 h, 45 ° C
- **General Procedure 5:**
  DMSO (2 mL, 0.05M), 65 ° C

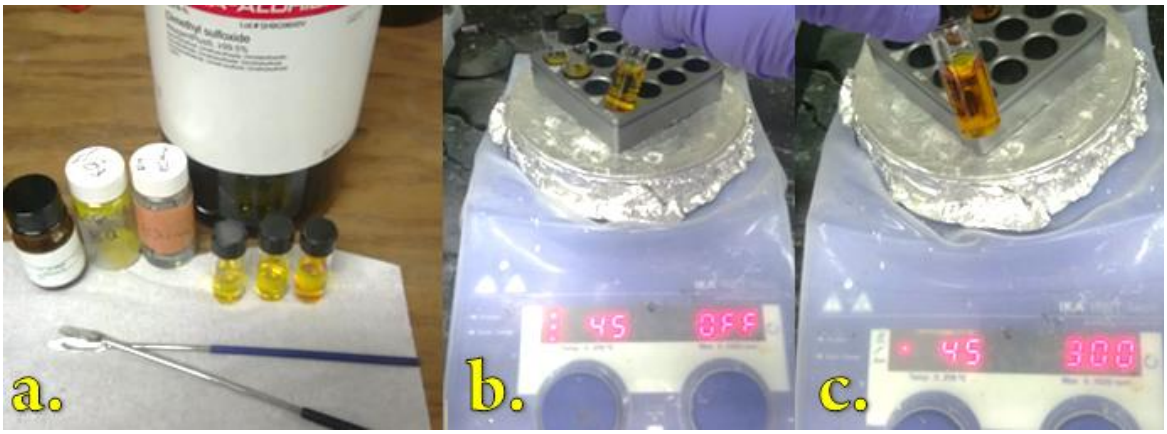
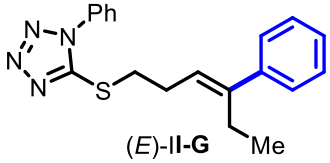


Figure S6. Photographic depiction of reaction setup according to General Procedure 3. From left to right: a) preparation of materials. b) reaction at 0 min before heating. c) reaction at 3 h after heating.

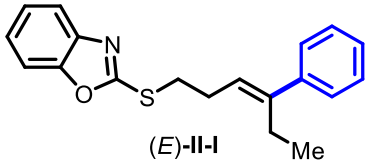
Characterization Data for Oxidative Heck Products

(*E*)-1-phenyl-5-((4-phenylhex-3-en-1-yl)thio)-1H-tetrazole ((*E*)-II-G): The title compound was prepared according to General Procedure 4. The crude residue was purified by preparative TLC (10% Et_2O/hexanes). Purification afforded (*E*)-**II-G** as a clear liquid (24 mg, 67%) containing 22% inseparable isomers. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.65–7.48 (m, 5H), 7.32–7.04 (m, 5H), 5.63 (t, *J* = 7.2 Hz, 1H), 3.51 (t, *J* = 7.3 Hz, 2H), 2.76 (q, *J* = 7.2 Hz, 2H), 2.51 (q, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.50, 144.93, 142.48, 140.52, 133.87, 130.24, 129.93, 128.44, 126.49, 124.05, 124.00, 33.50, 28.19, 23.28, 13.67. **HRMS** calcd. for $C_{19}H_{21}N_4S^+$ $[M+H]^+$: 337.1482, Found: 337.1485.



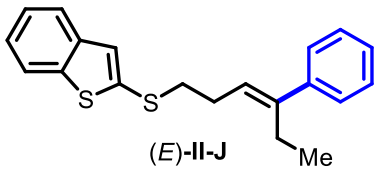
(*E*)-**II-G**

(*E*)-2-((4-phenylhex-3-en-1-yl)thio)benzooxazole ((*E*)-II-I): The title compound was prepared according to General Procedure 4. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded (*E*)-**II-I** as a yellow liquid (10 mg, 32%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.32 (m, 1H), 7.29 – 7.08 (m, 7H), 5.61 (d, *J* = 7.9 Hz, 1H), 3.72 – 3.20 (m, 2H), 2.79 – 2.56 (m, 2H), 2.56 – 2.35 (m, 2H), 0.92 (dt, *J* = 8.1, 4.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.14, 152.00, 144.67, 142.60, 142.17, 128.36, 127.03, 126.54, 124.53, 124.41, 123.96, 118.53, 109.99, 32.44, 28.49, 23.30, 13.69. **HRMS** calcd. for $C_{19}H_{20}NOS_2$ $[M+H]^+$: 310.1266, Found: 310.1269.



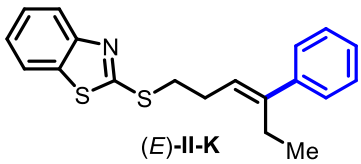
(*E*)-**II-I**

(*E*)-2-((4-phenylhex-3-en-1-yl)thio)benzothiophene ((*E*)-II-J): The title compound was prepared according to General Procedure 4. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded (*E*)-**II-J** as a yellow liquid (28 mg, 86%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.31 (dq, *J* = 14.8, 7.9, 7.4 Hz, 7H), 7.25 – 7.21 (m, 1H), 5.65 (t, *J* = 7.3 Hz, 1H), 3.05 (t, *J* = 7.4 Hz, 2H), 2.59 (q, *J* = 7.4 Hz, 2H), 2.49 (q, *J* = 7.5 Hz, 2H), 0.96 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.90, 142.68, 141.79, 139.97, 137.36, 128.34, 128.21, 126.93, 126.49, 125.05, 124.61, 124.48, 123.15, 122.00, 37.61, 28.83, 23.24, 13.70. **HRMS** calcd. for $C_{20}H_{21}S_2^+$ $[M+H]^+$: 325.1085, Found: 325.1088.



(*E*)-**II-J**

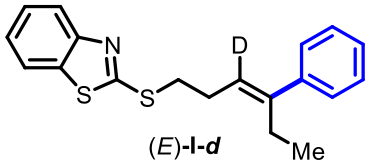
(*E*)-2-((4-phenylhex-3-en-1-yl)thio)benzothiazole ((*E*)-II-K): The title compound was prepared according to General Procedure 4. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded (*E*)-**II-K** as a yellow liquid (28 mg, 85%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.76 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.42 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.36–7.32 (m, 2H), 7.30 (td, *J* = 7.6, 1.3 Hz, 3H), 7.25–7.21 (m, 1H), 5.69 (t, *J* = 7.4 Hz, 1H), 3.51–3.43 (m, 2H), 2.76 (q, *J* = 7.4 Hz, 2H), 2.56 (q, *J* = 7.6 Hz, 2H), 1.00 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.07, 153.48, 144.46,



(*E*)-**II-K**

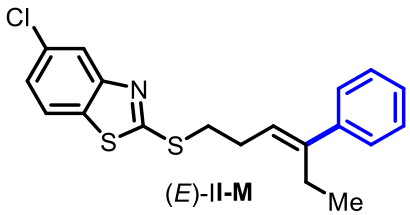
142.64, 135.40, 128.35, 126.99, 126.53, 126.16, 124.79, 124.30, 121.61, 121.10, 33.64, 28.58, 23.28, 13.76. **HRMS** calcd. for $C_{19}H_{20}NS_2$ $[M+H]^+$: 326.1037, Found: 326.1034.

(*E*)-2-((4-phenylhex-3-en-1-yl-3-*d*)thio)benzothiazole ((*E*)-I-*d*): The title compound was prepared according to General Procedure 4. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded (*E*)- **I-*d*** as a yellow liquid (17 mg, 52%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.78 – 7.71 (m, 1H), 7.47 – 7.39 (m, 1H), 7.38 – 7.32 (m, 2H), 7.32 – 7.28 (m, 3H), 7.25 – 7.21 (m, 1H), 3.46 (t, *J* = 7.4 Hz, 2H), 2.75 (t, *J* = 7.4 Hz, 2H), 2.56 (q, *J* = 7.5 Hz, 2H), 1.00 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.08, 153.49, 144.37, 142.61, 135.40, 128.35, 126.99, 126.53, 126.16, 124.31, 121.62, 121.11, 33.62, 28.48, 23.23, 13.76. **HRMS** calcd. for $C_{19}H_{19}DNS_2$ $[M+H]^+$: 327.1100, Found: 327.1106.



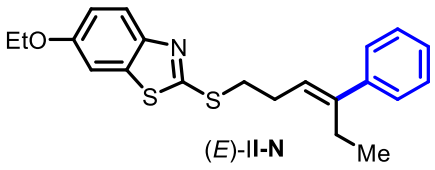
(*E*)-**I-*d***

(***E***)-5-chloro-2-((4-phenylhex-3-en-1-yl)thio)benzothiazole ((*E*)-II-M):** The title compound was prepared according to General Procedure 4. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded (*E*)-**II-M** as a yellow solid (21 mg, 59%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 2.1 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.41–7.01 (m, 6H), 5.68 (t, *J* = 7.3 Hz, 1H), 3.46 (t, *J* = 7.4 Hz, 2H), 2.75 (q, *J* = 7.4 Hz, 2H), 2.56 (q, *J* = 7.5 Hz, 2H), 1.00 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.35, 154.29, 144.59, 142.57, 133.62, 132.23, 128.36, 127.04, 126.52, 124.64, 124.62, 121.69, 121.49, 33.66, 28.50, 23.28, 13.77. **HRMS** calcd. for $C_{19}H_{19}ClNS_2^+$ $[M+H]^+$: 360.0642, Found: 360.0651.



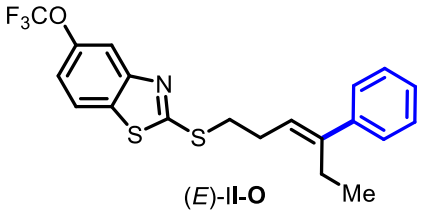
(*E*)-**II-M**

(***E***)-6-ethoxy-2-((4-phenylhex-3-en-1-yl)thio)benzothiazole ((*E*)-II-N):** The title compound was prepared according to General Procedure 4. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded (*E*)-**II-N** as a yellow liquid (24 mg, 65%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.9 Hz, 1H), 7.35–7.32 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.25–7.21 (m, 2H), 7.01 (dd, *J* = 8.9, 2.5 Hz, 1H), 5.68 (t, *J* = 7.3 Hz, 1H), 4.07 (q, *J* = 6.9 Hz, 2H), 3.42 (t, *J* = 7.4 Hz, 2H), 2.73 (q, *J* = 7.4 Hz, 2H), 2.55 (q, *J* = 7.5 Hz, 2H), 1.45 (t, *J* = 7.0 Hz, 4H), 0.99 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.64, 156.50, 147.99, 144.36, 142.66, 136.72, 128.34, 126.97, 126.53, 124.87, 122.08, 115.39, 105.00, 64.28, 33.82, 28.65, 23.27, 15.00, 13.76. **HRMS** calcd. for $C_{21}H_{24}NOS_2^+$ $[M+H]^+$: 370.1294, Found: 370.1299.



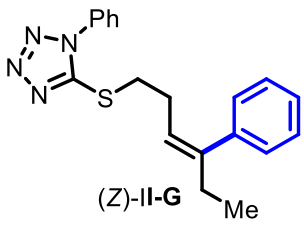
(*E*)-**II-N**

(*E*)-2-((4-phenylhex-3-en-1-yl)thio)-5-(trifluoromethoxy)benzothiazole ((*E*)-II-O): The title compound was prepared according to General Procedure 4. The crude residue was purified by preparative TLC (10% Et_2O/hexanes). Purification afforded (*E*)-**II-O** as a clear liquid (16 mg, 40%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78–7.67 (m, 2H), 7.37–7.12 (m, 6H), 5.68 (t, *J* = 7.3 Hz, 1H), 3.47 (t, *J* = 7.4 Hz, 2H), 2.76 (q, *J* = 7.4 Hz, 2H), 2.56 (q, *J* = 7.5 Hz, 2H), 1.00 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.15, 154.09, 147.99, 144.63, 142.57, 133.71, 128.37, 127.05, 126.52, 124.59, 121.67, 117.72, 114.10, 33.67, 28.49, 23.28, 13.75. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.99. **HRMS** calcd. for $C_{20}H_{19}F_3NOS_2^+$ $[M+H]^+$: 410.0855, Found: 410.0858.



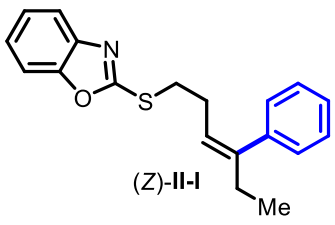
(*E*)-**II-O**

(*Z*)-1-phenyl-5-((4-phenylhex-3-en-1-yl)thio)-1H-tetrazole ((*Z*)-II-G): The title compound was prepared according to General Procedure 4. The crude residue was purified by preparative TLC (10% Et_2O/hexanes). Purification afforded (*Z*)-**II-G** as a clear liquid (19 mg, 56%) containing 26% inseparable isomers. Because all of the peaks belonging to each of the two isomers could not be clearly resolved for the ^{13}C NMR spectrum, the analytical data below correspond to the mixture. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.61–7.47 (m, 5H), 7.33–7.04 (m, 5H), 5.46 (tt, *J* = 7.3, 1.4 Hz, 1H), 3.38 (t, *J* = 7.3 Hz, 2H), 2.44 (qt, *J* = 7.3, 1.1 Hz, 2H), 1.69 (p, *J* = 7.3 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.44, 154.43, 153.95, 146.22, 144.00, 140.88, 140.47, 133.89, 130.23, 130.17, 129.92, 129.88, 128.62, 128.46, 128.39, 128.27, 127.67, 127.11, 126.87, 126.49, 126.43, 126.38, 124.07, 124.00, 123.94, 122.87, 122.05, 62.25, 50.49, 35.82, 34.21, 33.62, 32.28, 32.08, 29.86, 29.64, 29.52, 29.43, 29.28, 28.71, 28.51, 25.02, 22.85, 14.27, 13.00, 12.24, 0.15. **HRMS** calcd. for $C_{19}H_{21}N_4S^+$ $[M+H]^+$: 337.1482, Found: 337.1489.



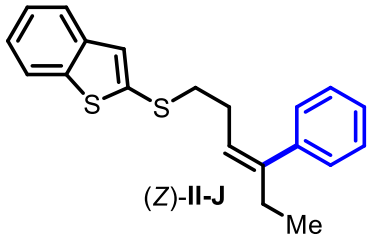
(*Z*)-**II-G**

(*Z*)-2-((4-phenylhex-3-en-1-yl)thio)benzooxazole ((*Z*)-II-I): The title compound was prepared according to General Procedure 5. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded (*Z*)-**II-I** as a yellow liquid (7 mg, 23%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.47 – 7.33 (m, 1H), 7.29 – 7.25 (m, 3H), 7.22 (td, *J* = 7.7, 1.4 Hz, 1H), 7.20 – 7.16 (m, 1H), 7.14 – 7.10 (m, 2H), 5.50 (tt, *J* = 7.4, 1.5 Hz, 1H), 3.29 (t, *J* = 7.3 Hz, 2H), 2.46 (q, *J* = 7.3 Hz, 2H), 2.37 – 2.31 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.12, 151.89, 146.03, 142.13, 141.04, 128.34, 128.21, 126.74, 124.32, 123.85, 122.35, 118.47, 109.92, 32.56, 32.31, 28.60, 12.99. **HRMS** calcd. for $C_{19}H_{20}NOS_2^+$ $[M+H]^+$: 310.1266, Found: 310.1265.

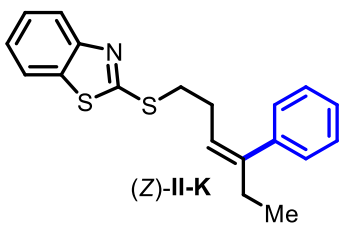


(*Z*)-**II-I**

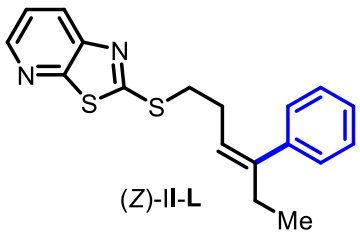
(*Z*)-2-((4-phenylhex-3-en-1-yl)thio)benzothiophene ((*Z*)-II-J): The title compound was prepared according to General Procedure 5. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded (*Z*)-**II-J** as a yellow liquid (26 mg, 80%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.35 – 7.16 (m, 5H), 7.12 (s, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 5.47 (t, *J* = 7.4 Hz, 1H), 2.90 (t, *J* = 7.4 Hz, 2H), 2.33 (dq, *J* = 19.1, 7.4 Hz, 4H), 0.96 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.34, 141.70, 141.14, 139.94, 137.42, 128.36, 128.20, 127.92, 126.68, 124.47, 124.33, 123.07, 122.83, 121.91, 37.79, 32.27, 29.04, 13.04. **HRMS** calcd. for $C_{20}H_{21}S_2^+$ $[M+H]^+$: 325.1085, Found: 325.1078.



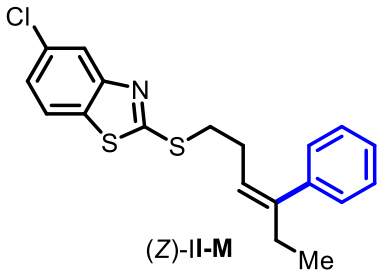
(*Z*)-2-((4-phenylhex-3-en-1-yl)thio)benzothiazole ((*Z*)-II-K): The title compound was prepared according to General Procedure 5. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded (*Z*)-**II-K** as a yellow liquid (30 mg, 91%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.43 (ddd, *J* = 8.2, 7.2, 1.3 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 3H), 7.26–7.20 (m, 1H), 7.17–7.14 (m, 2H), 5.54 (tt, *J* = 7.3, 1.5 Hz, 1H), 3.34 (t, *J* = 7.4 Hz, 2H), 2.48 (q, *J* = 7.3 Hz, 2H), 2.38 (q, *J* = 7.4, 6.8 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.26, 153.46, 145.78, 141.08, 135.32, 128.39, 128.23, 126.73, 126.08, 124.21, 122.59, 121.58, 121.00, 33.87, 32.33, 28.66, 13.01. **HRMS** calcd. for $C_{19}H_{20}NS_2^+$ $[M+H]^+$: 326.1037, Found: 326.1038.



(*Z*)-2-((4-phenylhex-3-en-1-yl)thio)thiazolo[5,4-b]pyridine ((*Z*)-II-L): The title compound was prepared according to General Procedure 5. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 327.1 [M+H], cone voltage 15V). Purification afforded (*Z*)-**II-L** as a yellow liquid (8 mg, 25%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.42 (d, *J* = 4.8 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.33 (dd, *J* = 8.1, 4.7 Hz, 1H), 7.31–7.17 (m, 4H), 7.12 (d, *J* = 7.5 Hz, 2H), 5.50 (t, *J* = 7.4 Hz, 1H), 3.33 (t, *J* = 7.2 Hz, 2H), 2.46 (q, *J* = 7.3 Hz, 2H), 2.35 (q, *J* = 7.5 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.89, 158.83, 146.54, 146.03, 145.61, 141.02, 128.35, 128.22, 127.89, 126.76, 122.38, 121.17, 33.23, 32.33, 28.49, 12.99. **HRMS** calcd. for $C_{18}H_{19}N_2S_2^+$ $[M+H]^+$: 327.0984, Found: 327.0989.

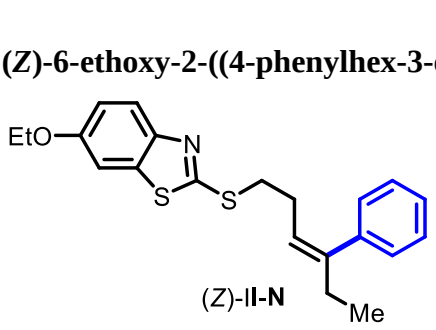


(*Z*)-5-chloro-2-((4-phenylhex-3-en-1-yl)thio)benzothiazole ((*Z*)-II-M): The title compound was prepared according to General Procedure 5. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded (*Z*)-**II-M** as a yellow solid (30 mg, 84%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 2.0 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.33–7.17 (m, 4), 7.12 (dd, *J* = 8.2, 1.4 Hz, 2H), 5.50 (tt, *J* = 7.3, 1.5 Hz, 1H), 3.30 (t, *J* = 7.3 Hz, 2H), 2.46 (q, *J* = 7.3 Hz, 2H), 2.35 (q, *J* = 7.6 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.50, 154.25, 145.96, 141.04, 133.54, 132.14, 128.37, 128.24, 126.76, 124.52, 122.43, 121.59, 121.47, 33.86, 32.34, 28.57, 13.00. **HRMS** calcd. for $C_{19}H_{19}ClNS_2^+$ $[M+H]^+$: 360.0642, Found: 360.0650.



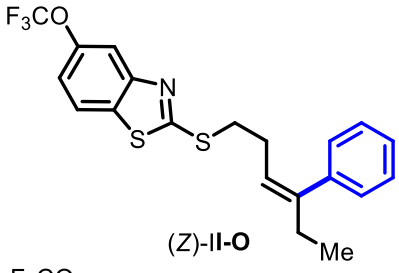
(*Z*)-II-M

(*Z*)-6-ethoxy-2-((4-phenylhex-3-en-1-yl)thio)benzothiazole ((*Z*)-II-N): The title compound was prepared according to General Procedure 5. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded (*Z*)-**II-N** as a yellow solid (30 mg, 82%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.9 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.23 (td, *J* = 6.2, 5.2, 2.0 Hz, 2H), 7.20–7.11 (m, 2H), 7.02 (dd, *J* = 8.9, 2.6 Hz, 1H), 5.53 (t, *J* = 7.4 Hz, 1H), 4.09 (q, *J* = 7.0 Hz, 2H), 3.30 (t, *J* = 7.3 Hz, 2H), 2.46 (q, *J* = 7.3 Hz, 2H), 2.37 (q, *J* = 6.8 Hz, 2H), 1.47 (t, *J* = 7.0 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.24, 155.82, 147.37, 145.06, 140.50, 136.05, 127.79, 127.62, 126.11, 122.06, 121.45, 114.68, 104.35, 63.66, 33.45, 31.71, 28.15, 14.39, 12.40. **HRMS** calcd. for $C_{21}H_{24}NOS_2^+$ $[M+H]^+$: 370.1294, Found: 370.1295.

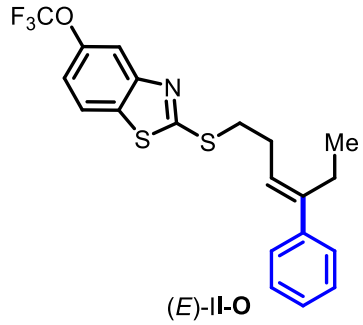


(*Z*)-II-N

(*Z*)-2-((4-phenylhex-3-en-1-yl)thio)-5-(trifluoromethoxy)benzothiazole ((*Z*)-II-O): The title compound was prepared according to General Procedure 5. The crude residue was purified by preparative TLC (10% Et_2O/hexanes). Purification afforded a 7:1 mixture of (*Z*)-2-((4-phenylhex-3-en-1-yl)thio)-5-(trifluoromethoxy)benzothiazole((*Z*)-**II-O**) to (*E*)-2-((4-phenylhex-3-en-1-yl)thio)-5-(trifluoromethoxy)benzothiazole **(**(*E*)-**II-O**) as a clear liquid (30 mg, 74%). In this case, it was possible to distinguish NMR peaks corresponding to each of the isomers, so their data are reported separately. (*Z*)-**2-((4-phenylhex-3-en-1-yl)thio)-5-(trifluoromethoxy)benzothiazole (**(*Z*)-**II-O**): **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 2.1 Hz, 1H), 7.38–7.05 (m, 6H), 5.50 (tt, *J* = 7.4, 1.5 Hz, 1H), 3.31 (t, *J* = 7.3 Hz, 2H), 2.47 (q, *J* = 7.3 Hz, 2H), 2.35 (q, *J* = 7.3 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.25, 154.06, 146.03, 141.05, 133.63, 128.37, 128.23,



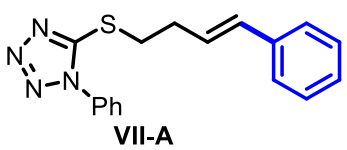
(*Z*)-II-O



(*E*)-II-O

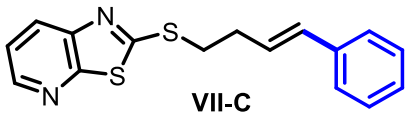
126.75, 122.40, 121.55, 117.63, 114.07, 33.84, 32.35, 28.56, 13.00. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.99. (*E*)**-2-((4-phenylhex-3-en-1-yl)thio)-5-(trifluoromethoxy)benzothiazole ((*E*)-II-O)**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78–7.67 (m, 2H), 7.37–7.12 (m, 6H), 5.68 (t, *J* = 7.3 Hz, 1H), 3.47 (t, *J* = 7.4 Hz, 2H), 2.76 (q, *J* = 7.4 Hz, 2H), 2.56 (q, *J* = 7.5 Hz, 2H), 1.00 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.15, 154.09, 147.99, 144.63, 142.57, 133.71, 128.37, 127.05, 126.52, 124.59, 121.67, 117.72, 114.10, 33.67, 28.49, 23.28, 13.75. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.99. **HRMS** calcd. for $C_{20}H_{19}F_3NOS_2^+$ $[M+H]^+$: 410.0855, Found: 410.0860.

(*E*)**-1-phenyl-5-((4-phenylbut-3-en-1-yl)thio)-1H-tetrazole (VII-A):** The title compound was prepared with 2.50 μmol $Pd(OAc)_2$ according to General Procedure 3. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded **VII-A** as a yellow liquid (18 mg, 76%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.60–7.51 (m, 5H), 7.37–7.28 (m, 4H), 7.24–7.19 (m, 1H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.21 (dt, *J* = 15.8, 7.0 Hz, 1H), 3.55 (t, *J* = 7.1 Hz, 2H), 2.76 (qd, *J* = 7.1, 1.5 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.79, 136.46, 133.21, 132.20, 129.65, 129.32, 128.11, 127.01, 126.15, 125.70, 123.42, 32.60, 32.13. **HRMS** calcd. for $C_{17}H_{17}N_4S^+$ $[M+H]^+$: 309.1168, Found: 309.1168.



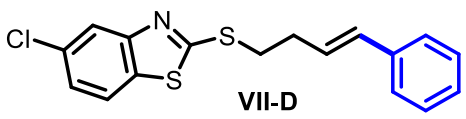
VII-A

(*E*)**-2-((4-phenylbut-3-en-1-yl)thio)thiazolo[5,4-b]pyridine (VII-C):** The title compound was prepared with 2.50 μmol $Pd(OAc)_2$ according to General Procedure 3. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 299.1 [M+H], cone voltage 15V). Purification afforded **VII-C** as a yellow liquid (15 mg, 50%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 4.7, 1.5 Hz, 1H), 8.06 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.35 (dt, *J* = 8.3, 2.4 Hz, 3H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.27 (dt, *J* = 15.7, 7.0 Hz, 1H), 3.51 (t, *J* = 7.3 Hz, 2H), 2.76 (q, *J* = 7.0 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.58, 158.88, 146.56, 145.73, 137.18, 132.49, 128.68, 127.99, 127.53, 127.23, 126.28, 121.24, 32.83, 32.70. **HRMS** calcd. for $C_{16}H_{15}N_2S_2^+$ $[M+H]^+$: 299.0671, Found: 299.0682.



VII-C

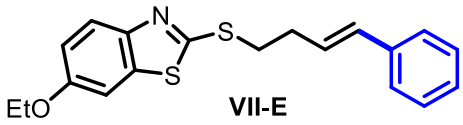
(*E*)**-5-chloro-2-((4-phenylbut-3-en-1-yl)thio)benzothiazole (VII-D):** The title compound was prepared with 2.50 μmol $Pd(OAc)_2$ according to General Procedure 3. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded **VII-D** as a yellow liquid (18 mg, 54%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 2.0 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.39–7.32 (m, 2H), 7.32–7.26 (m, 3H), 7.24–7.20 (m, 1H), 6.54–6.47 (m, 1H), 6.26 (dt, *J* = 15.8, 7.0 Hz, 1H), 3.50 (t, *J* = 7.3 Hz, 2H), 2.75 (qd, *J* = 7.2, 1.5 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.18, 154.26, 137.20, 133.61, 132.43, 132.23, 128.67, 127.51, 127.30, 126.28, 124.66,



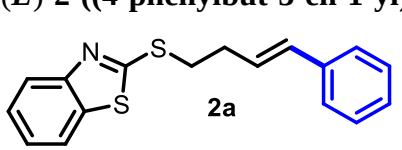
VII-D

124.64, 121.68, 121.66, 121.52, 33.38, 32.87. **HRMS** calcd. for $C_{17}H_{15}ClNS_2^+$ $[M+H]^+$: 332.0329, Found: 332.0335.

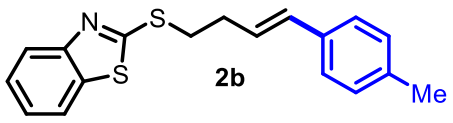
(***E***)**-6-ethoxy-2-((4-phenylbut-3-en-1-yl)thio)benzothiazole (VII-E):** The title compound was prepared with 2.50 µmol $Pd(OAc)_2$ according to General Procedure 3. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded **VII-E** as a yellow liquid (15 mg, 44%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.9 Hz, 1H), 7.37–7.32 (m, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.22 (q, *J* = 3.0, 2.3 Hz, 2H), 7.01 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.27 (dt, *J* = 15.8, 7.0 Hz, 1H), 4.07 (q, *J* = 7.0 Hz, 2H), 3.45 (t, *J* = 7.3 Hz, 2H), 2.74 (qd, *J* = 7.2, 1.5 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 4H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.47, 156.52, 147.96, 137.30, 136.73, 132.24, 128.65, 127.56, 127.43, 126.28, 122.12, 115.40, 104.97, 64.26, 33.57, 33.02, 14.99. **HRMS** calcd. for $C_{19}H_{20}NOS_2^+$ $[M+H]^+$: 342.0981, Found: 342.0986.



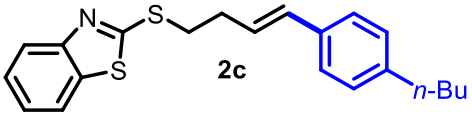
(***E***)**-2-((4-phenylbut-3-en-1-yl)thio)benzothiazole (2a):** The title compound was prepared according to General Procedure 3. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded **2a** as a yellow liquid (29 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.78–7.74 (m, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 7.1 Hz, 2H), 7.32–7.28 (m, 3H), 7.24–7.19 (m, 1H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.28 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.50 (t, *J* = 7.3 Hz, 2H), 2.76 (qd, *J* = 7.2, 1.5 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.89, 153.44, 137.26, 135.36, 132.30, 128.65, 127.46, 127.45, 126.27, 126.14, 124.32, 121.62, 121.07, 33.35, 32.91. **HRMS** calcd. for $C_{17}H_{16}NS_2^+$ $[M+H]^+$: 298.0719, Found: 298.0726.



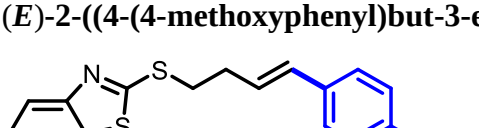
(***E***)**-2-((4-(*p*-tolyl)but-3-en-1-yl)thio)benzothiazole (2b):** The title compound was prepared according to General Procedure 3. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 312.1 [M+H], cone voltage 15V). Purification afforded **2b** as a clear liquid (30 mg, 97%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.76 (dt, *J* = 8.0, 0.6 Hz, 1H), 7.42 (ddd, *J* = 8.3, 7.3, 1.3 Hz, 1H), 7.30 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.47 (dt, *J* = 15.8, 1.5 Hz, 1H), 6.22 (dt, *J* = 15.8, 7.0 Hz, 1H), 3.49 (t, *J* = 7.3 Hz, 2H), 2.74 (qd, *J* = 7.2, 1.5 Hz, 2H), 2.33 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.98, 153.47, 137.23, 135.38, 134.49, 132.16, 129.36, 126.41, 126.18, 126.14, 124.30, 121.63, 121.08, 33.46, 32.92, 21.31. **HRMS** calcd. for $C_{18}H_{18}NS_2$ $[M+H]^+$: 312.0875, Found: 312.0875.



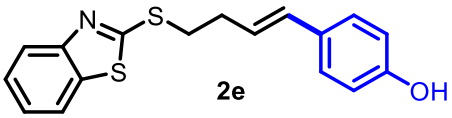
(***E***)**-2-((4-(4-butylphenyl)but-3-en-1-yl)thio)benzothiazole (2c):** The title compound was prepared according to General Procedure 3. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 354.1 [M+H], cone voltage 15V). Purification afforded **2b** as a yellow liquid (34 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 1H), 7.78–7.70 (m, 1H), 7.45–7.39 (m, 1H), 7.33–7.24 (m, 3H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.7, 7.0 Hz, 1H), 3.49 (t, *J* = 7.3 Hz, 2H), 2.74 (qd, *J* = 7.1, 1.4 Hz, 2H), 2.59 (t, *J* = 7.8 Hz, 2H), 1.58 (tt, *J* = 9.9, 7.2 Hz, 2H), 1.35 (h, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.98, 153.46, 142.33, 135.37, 134.69, 132.21, 128.73, 126.43, 126.17, 126.13, 124.30, 121.63, 121.07, 35.48, 33.73, 33.48, 32.92, 22.46, 14.10. **HRMS** calcd. for $C_{21}H_{24}NS_2^+$ $[M+H]^+$: 354.1350, Found: 354.1352.



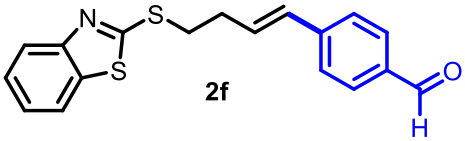
(***E***)**-2-((4-(4-methoxyphenyl)but-3-en-1-yl)thio)benzothiazole (2d):** The title compound was prepared according to General Procedure 3. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 328.1 [M+H], cone voltage 15V). Purification afforded **2d** as a yellow liquid (32 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.76 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.42 (ddd, *J* = 8.4, 7.3, 1.3 Hz, 1H), 7.32–7.27 (m, 3H), 6.86–6.80 (m, 2H), 6.49–6.42 (m, 1H), 6.13 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.80 (s, 3H), 3.48 (t, *J* = 7.3 Hz, 2H), 2.73 (qd, *J* = 7.2, 1.4 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.02, 159.15, 153.47, 135.38, 131.71, 130.11, 127.42, 126.15, 125.26, 124.31, 121.63, 121.11, 114.09, 55.43, 33.57, 32.93. **HRMS** calcd. for $C_{18}H_{18}NOS_2$ $[M+H]^+$: 328.0824, Found: 328.0825.



(***E***)**-4-(4-(benzothiazol-2-ylthio)but-1-en-1-yl)phenol (2e):** The title compound was prepared according to General Procedure 3. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded **2e** as a yellow liquid (31 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.79–7.72 (m, 1H), 7.46–7.38 (m, 1H), 7.33–7.28 (m, 1H), 7.21 (d, *J* = 8.6 Hz, 2H), 6.81–6.72 (m, 2H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.09 (dt, *J* = 15.8, 7.0 Hz, 1H), 5.38 (s, 1H), 3.48 (t, *J* = 7.3 Hz, 2H), 2.72 (qd, *J* = 7.2, 1.4 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.65, 155.45, 153.24, 135.18, 131.79, 130.01, 127.64, 126.31, 124.95, 124.46, 121.52, 121.12, 115.66, 33.69, 32.80. **HRMS** calcd. for $C_{17}H_{16}NOS_2^+$ $[M+H]^+$: 314.0668, Found: 314.0669.

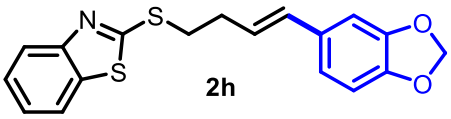


(***E***)**-4-(4-(benzothiazol-2-ylthio)but-1-en-1-yl)benzaldehyde (2f):** The title compound was prepared according to General Procedure 3. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 326.1 [M+H], cone voltage 15V). Purification afforded **2f** as a clear liquid (32 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.90–7.85 (m, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.75 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.42 (ddd, *J* = 8.4, 7.3, 1.3 Hz, 1H), 7.30 (td, *J* = 7.7, 7.3, 1.2 Hz, 1H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.46 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.53 (t, *J* = 7.2 Hz, 2H), 2.81 (qd, *J* = 7.1, 1.3 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 191.82, 166.55, 153.38, 143.31, 135.38, 135.35, 131.55, 131.37, 130.25, 126.75, 126.21, 124.43, 121.63, 121.12, 33.11, 32.95. **HRMS** calcd. for $C_{18}H_{16}NOS_2^+$ $[M+H]^+$: 326.0668, Found: 326.0670.

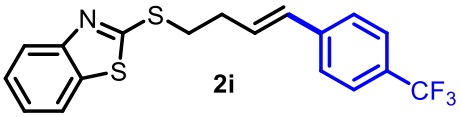


(***E***)**-2-((4-(3-isopropylphenyl)but-3-en-1-yl)thio)benzothiazole (2g):** The title compound was prepared according to General Procedure 3. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded **2g** as a clear liquid (34 mg, >95%) with 8% inseparable isomer. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.42 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.32–7.27 (m, 1H), 7.26–7.15 (m, 3H), 7.10 (dt, *J* = 7.5, 1.6 Hz, 1H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.27 (dt, *J* = 15.8, 7.0 Hz, 1H), 3.50 (t, *J* = 7.3 Hz, 2H), 2.88 (p, *J* = 6.9 Hz, 1H), 2.76 (qd, *J* = 7.2, 1.4 Hz, 2H), 1.25 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.96, 153.46, 149.23, 137.22, 135.37, 132.58, 128.65, 127.16, 126.14, 125.67, 124.49, 124.31, 123.81, 121.63, 121.08, 34.24, 33.39, 32.96, 24.12. **HRMS** calcd. for $C_{20}H_{22}NS_2^+$ $[M+H]^+$: 340.1188, Found: 312.0875.

(***E***)**-2-((4-(benzo[d][1,3]dioxol-5-yl)but-3-en-1-yl)thio)benzothiazole (2h):** The title compound was prepared according to General Procedure 3. The crude residue was purified by preparative TLC (10% Et_2O/hexanes). Purification afforded **2h** as a yellow liquid (25 mg, 72%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.48–7.37 (m, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 1.6 Hz, 1H), 6.83–6.66 (m, 2H), 6.41 (d, *J* = 15.7 Hz, 1H), 6.09 (dt, *J* = 15.7, 7.0 Hz, 1H), 5.94 (s, 2H), 3.48 (t, *J* = 7.3 Hz, 2H), 2.72 (qd, *J* = 7.2, 1.4 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.36, 152.85, 147.51, 146.52, 134.77, 131.30, 131.19, 125.57, 125.11, 123.73, 121.03, 120.49, 120.21, 107.78, 105.07, 100.54, 32.88, 32.24. **HRMS** calcd. for $C_{18}H_{16}NO_2S_2^+$ $[M+H]^+$: 342.0619, Found: 342.0617.

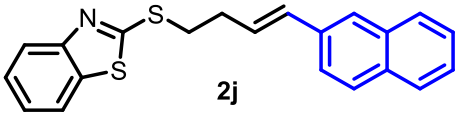


(***E***)**-2-((4-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)thio)benzothiazole (2i):** The title compound



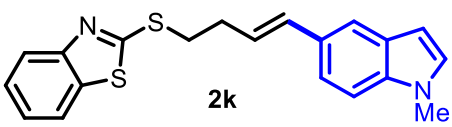
was prepared according to General Procedure 3. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 366.1 [M+H], cone voltage 15V). Purification afforded **2i** as a clear liquid (20 mg, 55%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91–7.85 (m, 1H), 7.75 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.42 (ddd, *J* = 8.5, 7.3, 1.3 Hz, 3H), 7.30 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 1H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.38 (dt, *J* = 15.9, 7.0 Hz, 1H), 3.52 (t, *J* = 7.2 Hz, 2H), 2.79 (qd, *J* = 7.1, 1.4 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.62, 153.40, 140.72, 135.40, 131.07, 130.37, 126.41, 126.21, 125.64, 125.61, 125.59, 125.56, 124.43, 121.64, 121.12, 33.06, 33.01. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.47. **HRMS** calcd. for $C_{18}H_{15}F_3NS_2$ $[M+H]^+$: 366.0593, Found: 366.0604.

(***E***)**-2-((4-(naphthalen-2-yl)but-3-en-1-yl)thio)benzothiazole (2j):** The title compound was



prepared according to General Procedure 3. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 348.1 [M+H], cone voltage 15V). Purification afforded **2j** as a yellow solid (34 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.82–7.73 (m, 4H), 7.69 (d, *J* = 1.7 Hz, 1H), 7.57 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.49–7.40 (m, 3H), 7.33–7.28 (m, 1H), 6.67 (d, *J* = 15.8 Hz, 1H), 6.41 (dt, *J* = 15.8, 7.0 Hz, 1H), 3.54 (t, *J* = 7.3 Hz, 2H), 2.82 (qd, *J* = 7.2, 1.5 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.91, 153.46, 135.40, 134.74, 133.75, 133.00, 132.43, 128.28, 128.05, 127.94, 127.77, 126.34, 126.17, 126.02, 125.85, 124.35, 123.62, 121.65, 121.11, 33.39, 33.10. **HRMS** calcd. for $C_{21}H_{18}NS_2^+$ $[M+H]^+$: 348.0875, Found: 348.0877.

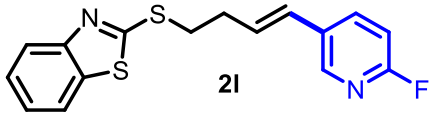
(***E***)**-2-((4-(1-methyl-1H-indol-5-yl)but-3-en-1-yl)thio)benzothiazole (2k):** The title compound



was prepared according to General Procedure 3. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 351.1 [M+H], cone voltage 15V). Purification afforded **2k** as a red solid (56 mg, 80%) as a 10:1 mixture of isomers. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.1 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.57 (d, *J* = 1.6 Hz, 1H), 7.45–7.40 (m, 1H), 7.32–7.28

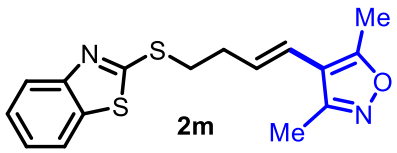
(m, 2H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.02 (d, *J* = 3.2 Hz, 1H), 6.62 (d, *J* = 15.7 Hz, 1H), 6.44 (d, *J* = 3.1 Hz, 1H), 6.21 (dt, *J* = 15.7, 7.0 Hz, 1H), 3.78 (s, 3H), 3.51 (t, *J* = 7.3 Hz, 2H), 2.76 (qd, *J* = 7.1, 1.4 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.24, 153.52, 136.48, 135.39, 133.41, 129.39, 128.93, 128.80, 126.14, 124.39, 124.28, 121.65, 121.08, 120.03, 119.18, 109.41, 101.34, 33.77, 33.06, 33.05. **HRMS** calcd. for $C_{20}H_{18}N_2S_2$ $[M+H]^+$: 351.0984, Found: 351.0991.

(***E***)**-2-((4-(6-fluoropyridin-3-yl)but-3-en-1-yl)thio)benzothiazole (2l):** The title compound was prepared according to General Procedure 3. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 317.1 [M+H], cone voltage 15V). Purification afforded **2l** as a clear liquid (20 mg, 65%) as a 25:2 mixture of isomers. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.5 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.75 (dd, *J* = 8.0, 2.9 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 6.84 (dd, *J* = 8.5, 3.0 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.26 (dt, *J* = 15.9, 6.9 Hz, 1H), 3.51 (t, *J* = 7.1 Hz, 2H), 2.77 (q, *J* = 7.1 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.53, 163.67, 162.09, 153.36, 145.73, 145.64, 137.90, 137.85, 135.36, 129.81, 129.80, 127.39, 126.21, 124.44, 121.62, 121.12, 109.60, 109.35, 33.01. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.93. **HRMS** calcd. for $C_{16}H_{14}FN_2S_2^+$ $[M+H]^+$: 317.0577, Found: 317.0574.



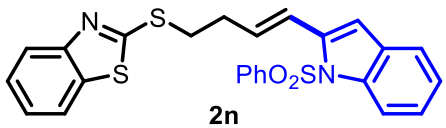
2l

(***E***)**-4-(4-(benzothiazol-2-ylthio)but-1-en-1-yl)-3,5-dimethylisoxazole (2m):** The title compound was prepared according to General Procedure 3. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 317.1 [M+H], cone voltage 15V). Purification afforded **2m** as a white solid (16 mg, 49%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 6.15 (d, *J* = 16.1 Hz, 1H), 5.91 (dt, *J* = 16.0, 6.9 Hz, 1H), 3.50 (t, *J* = 7.1 Hz, 2H), 2.73 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.67, 165.26, 158.38, 153.37, 135.36, 129.16, 126.23, 124.45, 121.61, 121.13, 120.21, 112.67, 33.52, 33.29, 11.79, 11.53. **HRMS** calcd. for $C_{16}H_{17}N_2OS_2^+$ $[M+H]^+$: 317.0777, Found: 317.0777.



2m

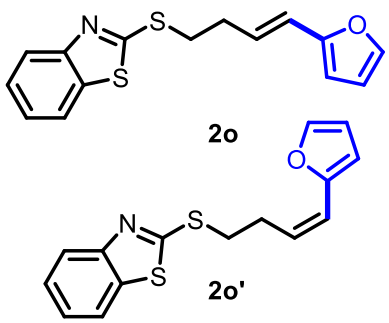
(***E***)**-2-((4-(1-(phenylsulfonyl)-1H-indol-2-yl)but-3-en-1-yl)thio)benzothiazole (2n):** The title compound was prepared according to General Procedure 3. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a



2n

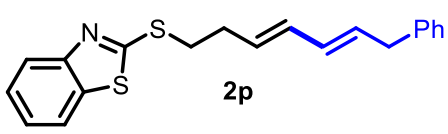
0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 477.1 [M+H], cone voltage 15V). Purification afforded **2n** as an orange solid (17 mg, 35%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.77 (dt, *J* = 8.6, 1.6 Hz, 3H), 7.51–7.45 (m, 1H), 7.47–7.40 (m, 1H), 7.37 (t, *J* = 7.9 Hz, 3H), 7.33–7.27 (m, 2H), 7.23–7.15 (m, 2H), 6.58 (s, 1H), 6.20 (dt, *J* = 15.7, 7.0 Hz, 1H), 3.55 (t, *J* = 7.1 Hz, 2H), 2.83 (qd, *J* = 7.1, 1.5 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.60, 153.43, 139.22, 138.58, 137.30, 135.41, 133.82, 132.21, 130.08, 129.17, 126.80, 126.25, 124.76, 124.45, 124.07, 122.96, 121.70, 121.17, 120.70, 115.23, 108.79, 33.12, 32.95. **HRMS** calcd. for $C_{25}H_{21}N_2O_2S_3^+$ $[M+H]^+$: 477.0760, Found: 477.0765.

(***E***)**-2-((4-(furan-2-yl)but-3-en-1-yl)thio)benzothiazole (2o)** and (***E***)**-2-((4-(furan-2-yl)but-3-en-1-yl)thio)benzothiazole (2o'):** The title compound was prepared according to General Procedure 3.



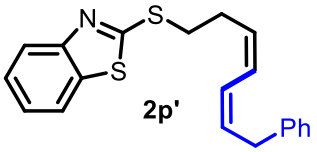
The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 288.1 [M+H], cone voltage 15V). Purification afforded **2o** and **2o'** as an orange liquid (6 mg, 21%) in a 6:1 ratio of *E* and *Z* isomers (**2o**:**2o'**). In this case, it was possible to distinguish NMR peaks corresponding to each of the isomers, so their data are reported separately. (***E***)**-2-((4-(furan-2-yl)but-3-en-1-yl)thio)benzothiazole**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.35–7.28 (m, 2H), 6.44–6.13 (m, 4H), 3.47 (t, *J* = 7.3 Hz, 2H), 2.73 (q, *J* = 7.1 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.82, 153.46, 152.74, 141.84, 135.39, 126.33, 126.16, 124.34, 121.66, 121.09, 120.83, 111.33, 107.28, 33.24, 32.70. (*Z*)**-2-((4-(furan-2-yl)but-3-en-1-yl)thio)benzothiazole: ^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.35–7.28 (m, 2H), 6.44–6.13 (m, 4H), 3.48 (t, *J* = 7.3 Hz, 2H), 3.03 (qd, *J* = 7.4, 1.7 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.82, 153.46, 152.93, 141.93, 135.39, 126.93, 126.16, 124.33, 121.64, 121.09, 119.31, 111.26, 109.94, 33.24, 32.70. **HRMS** calcd. for $C_{15}H_{14}NOS_2^+$ $[M+H]^+$: 288.0511, Found: 288.0513.

2-(3*E*,5*E*)-7-phenylhepta-3,5-dien-1-yl)thio)benzothiazole (2p): The title compound was prepared according to General Procedure 3. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 338.1 [M+H], cone voltage 15V). Purification afforded **2p** as a yellow solid (13



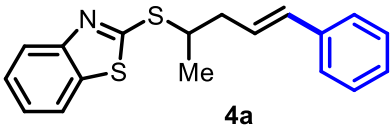
mg, 38%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 3H), 7.22–7.16 (m, 3H), 6.15 (dd, *J* = 15.1, 10.3 Hz, 1H), 6.07 (dd, *J* = 15.0, 10.4 Hz, 1H), 5.79 (dt, *J* = 14.5, 7.0 Hz, 1H), 5.66 (dt, *J* = 14.6, 7.0 Hz, 1H), 3.40 (t, *J* = 7.6 Hz, 4H), 2.60 (q, *J* = 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.99, 153.46, 140.34, 135.36, 132.52, 132.30, 131.13, 129.58, 128.74, 128.59, 126.24, 126.15, 124.31, 121.64, 121.08, 39.12, 33.37, 32.47. **HRMS** calcd. for $C_{20}H_{20}NS_2^+$ $[M+H]^+$: 338.1032, Found: 338.1032.

2-(3*Z*,5*Z*)-7-phenylhepta-3,5-dien-1-yl)thio)benzothiazole (2p'): The reaction was carried out according to General Procedure 3. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 338.1 [M+H], cone voltage 15V). Purification afforded **2p'** as a yellow solid (9 mg, 26%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.44–7.38 (m, 1H), 7.29 (q, *J* = 7.6 Hz, 3H), 7.21–7.16 (m, 3H), 6.40 (ddd, *J* = 14.9, 10.9, 1.5 Hz, 1H), 6.11 (t, *J* = 10.9 Hz, 1H), 5.86 (dt, *J* = 14.6, 7.1 Hz, 1H), 5.44 (dt, *J* = 10.7, 7.6 Hz, 1H), 3.43 (d, *J* = 7.2 Hz, 2H), 3.40 (t, *J* = 7.4 Hz, 2H), 2.73 (qd, *J* = 7.5, 1.4 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.94, 153.46, 140.24, 135.38, 134.30, 130.90, 128.67, 128.60, 127.02, 126.58, 126.27, 126.16, 124.33, 121.62, 121.10, 39.41, 33.42, 27.74. **HRMS** calcd. for $C_{20}H_{20}NS_2^+$ $[M+H]^+$: 338.1032, Found: 338.1034.



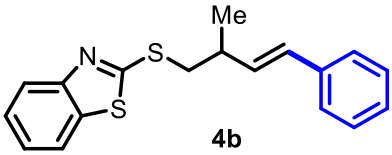
2p'

(***E***)**-2-((5-phenylpent-4-en-2-yl)thio)benzothiazole (4a):** The title compound was prepared according to General Procedure 3. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded **4a** as a yellow liquid (30 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.78–7.68 (m, 1H), 7.46–7.39 (m, 1H), 7.35 (d, *J* = 7.3 Hz, 2H), 7.32–7.28 (m, 3H), 7.23–7.19 (m, 1H), 6.50 (d, *J* = 15.7 Hz, 1H), 6.28 (dt, *J* = 15.8, 7.3 Hz, 1H), 4.16 (p, *J* = 6.8 Hz, 1H), 2.90–2.70 (m, 1H), 2.65 (dtd, *J* = 14.4, 7.3, 1.3 Hz, 1H), 1.55 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.33, 153.54, 137.31, 135.48, 133.21, 128.65, 127.44, 126.33, 126.31, 126.13, 124.41, 121.76, 121.07, 44.19, 40.35, 20.84. **HRMS** calcd. for $C_{18}H_{18}NS_2$ $[M+H]^+$: 312.0876, Found: 312.0876.



4a

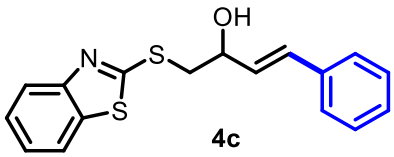
(***E***)**-2-((2-methyl-4-phenylbut-3-en-1-yl)thio)benzothiazole (4b):** The title compound was prepared according to General Procedure 3. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 312.1 [M+H], cone voltage 15V). Purification afforded **4b** as a yellow liquid (30 mg, >95%).



4b

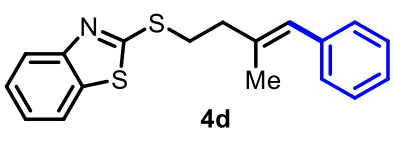
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.77–7.71 (m, 1H), 7.44–7.39 (m, 1H), 7.34 (d, *J* = 7.1 Hz, 2H), 7.29 (td, *J* = 7.4, 2.3 Hz, 3H), 7.23–7.19 (m, 1H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.19 (dd, *J* = 15.8, 7.7 Hz, 1H), 3.46 (qd, *J* = 12.8, 6.9 Hz, 2H), 2.86 (p, *J* = 7.0 Hz, 1H), 1.30 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.33, 153.43, 137.30, 135.37, 133.35, 130.29, 128.75, 128.64, 127.43, 126.34, 126.13, 124.30, 121.59, 121.07, 40.32, 37.39, 19.99. **HRMS** calcd. for $C_{18}H_{18}NS_2^+$ $[M+H]^+$: 312.0875, Found: 312.0876.

(***E***)**-1-(benzothiazol-2-ylthio)-4-phenylbut-3-en-2-ol (4c):** The title compound was prepared according to General Procedure 3. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded **4c** as a yellow liquid (14 mg, 63%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.32 (q, *J* = 7.2 Hz, 3H), 7.24 (d, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 15.8 Hz, 1H), 6.32 (dd, *J* = 15.8, 5.9 Hz, 1H), 4.77 (d, *J* = 31.4 Hz, 2H), 3.67 (dd, *J* = 14.4, 3.3 Hz, 1H), 3.51 (dd, *J* = 14.4, 7.2 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.88, 152.53, 136.62, 135.64, 131.45, 130.17, 128.71, 127.93, 126.74, 126.43, 124.81, 121.50, 121.23, 72.30, 41.10. **HRMS** calcd. for $C_{17}H_{16}NOS_2^+$ $[M+H]^+$: 314.0668, Found: 314.0668.



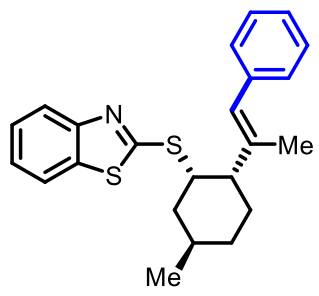
4c

(***E***)**-2-((3-methyl-4-phenylbut-3-en-1-yl)thio)benzothiazole (4d):** The title compound was prepared according to General Procedure 3. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 312.1 [M+H], cone voltage 15V). Purification afforded **4d** as a yellow liquid (21 mg, 68%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.46–7.39 (m, 1H), 7.31 (dt, *J* = 12.6, 7.6 Hz, 3H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.40 (s, 1H), 3.57 (t, *J* = 7.6 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 1.95 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.08, 153.47, 138.05, 136.17, 135.38, 128.99, 128.22, 127.37, 126.39, 126.16, 124.32, 121.63, 121.10, 40.21, 32.33, 17.75. **HRMS** calcd. for $C_{18}H_{18}NS_2^+$ $[M+H]^+$: 312.0875, Found: 312.0876.



4d

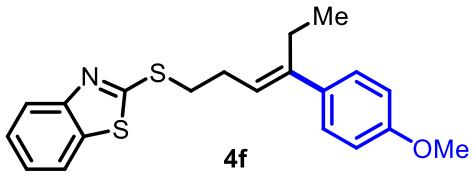
2-(1*S*,2*S*,5*R*)-5-methyl-2-((*E*)-1-phenylprop-1-en-2-yl)cyclohexyl)thio)benzothiazole (4e): The title compound was prepared from **3e** according to General Procedure 3. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 380.2 [M+H], cone voltage 15V). Purification afforded **4e** as a yellow



4e

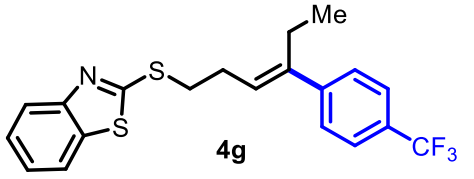
liquid (38 mg, >95%) as a 10:1 mixture of isomers. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 2H), 6.28 (s, 1H), 4.85 (d, *J* = 3.7 Hz, 1H), 2.47 (dd, *J* = 12.2, 3.4 Hz, 1H), 2.34 (dd, *J* = 13.5, 3.1 Hz, 1H), 1.90 (s, 3H), 1.88–1.72 (m, 4H), 1.71–1.55 (m, 2H), 1.10 (qd, *J* = 12.6, 3.7 Hz, 1H), 0.95 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.59, 153.39, 139.69, 138.49, 135.42, 129.11, 127.94, 126.03, 126.01, 125.50, 124.18, 121.44, 121.00, 50.65, 49.47, 41.43, 35.06, 28.21, 26.61, 22.23, 18.45. **HRMS** calcd. for $C_{23}H_{26}NS_2^+$ $[M+H]^+$: 380.1501, Found: 380.1509.

(***E***)**-2-((4-(4-methoxyphenyl)hex-3-en-1-yl)thio)benzothiazole (4f):** The title compound was prepared according to General Procedure 4. The crude residue was purified by preparative TLC (10% Et_2O/hexanes). Purification afforded **4f** as a clear liquid (31 mg, 86%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.45–7.38 (m, 1H), 7.32–7.27 (m, 3H), 6.84 (d, *J* = 8.7 Hz, 2H), 5.63 (t, *J* = 7.3 Hz, 1H), 3.81 (s, 3H), 3.45 (t, *J* = 7.4 Hz, 2H), 2.74 (q, *J* = 7.4 Hz, 2H), 2.53 (q, *J* = 7.5 Hz, 2H), 0.99 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.14, 158.79, 153.49, 143.77, 135.39, 135.04, 127.52, 126.15, 124.29, 123.36, 121.60, 121.09, 113.72, 55.41, 33.74, 28.56, 23.24, 13.78. **HRMS** calcd. for $C_{20}H_{22}NOS_2^+$ $[M+H]^+$: 356.1137, Found: 356.1150.



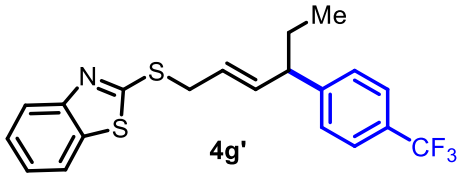
4f

(***E***)**-2-((4-(4-(trifluoromethyl)phenyl)hex-3-en-1-yl)thio)benzothiazole (4g):** The title compound was prepared according to General Procedure 4. The crude residue was purified by preparative TLC (10% EtOAc/hexanes). Purification afforded **4g** as a clear liquid (20 mg, 50%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.79–7.72 (m, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.42 (td, *J* = 8.3, 1.7 Hz, 3H), 7.35–7.29 (m, 1H), 5.75 (t, *J* = 7.3 Hz, 1H), 3.48 (t, *J* = 7.3 Hz, 2H), 2.78 (q, *J* = 7.3 Hz, 2H), 2.57 (q, *J* = 7.6 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.81, 153.43, 146.25, 143.44, 135.40, 126.81, 126.79, 126.21, 125.34, 125.31, 125.29, 125.26, 124.40, 121.61, 121.14, 33.40, 28.65, 23.18, 13.60. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.36. **HRMS** calcd. for $C_{20}H_{19}F_3NS_2^+$ $[M+H]^+$: 394.0906, Found: 394.0929.



4g

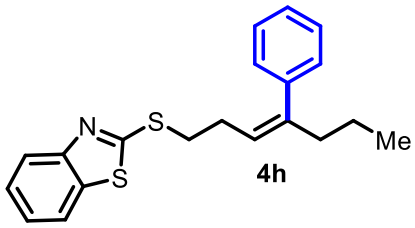
(***E***)**-2-((4-(4-(trifluoromethyl)phenyl)hex-2-en-1-yl)thio)benzothiazole (4g'):** The title compound was prepared according to General Procedure 4. The crude residue was purified by preparative TLC (10% EtOAc/hexanes). Purification afforded **4g'** as a clear liquid (6 mg, 15%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.44 (td, *J* = 8.1, 1.7 Hz, 3H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.9 Hz, 2H), 5.91 (dd, *J* = 15.2, 7.8 Hz, 1H), 5.69 (dt, *J* = 14.8, 7.1 Hz, 1H), 3.98 (d, *J* = 7.1 Hz, 2H), 3.22 (q, *J* = 7.5 Hz, 1H), 1.72 (dtd, *J* = 17.3, 13.8, 7.0 Hz,



4g'

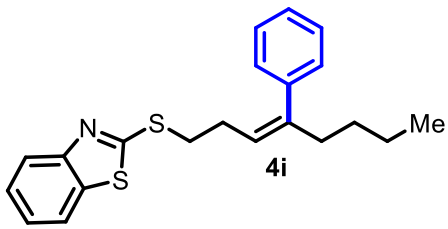
2H), 0.83 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.97, 153.32, 148.27, 138.24, 135.52, 127.96, 126.21, 125.46, 125.44, 125.41, 125.39, 124.63, 124.51, 121.76, 121.10, 50.20, 35.99, 28.50, 12.11, 0.15. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.29. **HRMS** calcd. for $C_{20}H_{19}F_3NS_2^+$ $[M+H]^+$: 394.0906, Found: 394.0917.

(*Z*)-2-((4-phenylhept-3-en-1-yl)thio)benzothiazole (4h): The title compound was prepared according to General Procedure 5. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded **4h** as a white solid (31 mg, 90%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.31–7.26 (m, 3H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.1 Hz, 2H), 5.52 (t, *J* = 7.3 Hz, 1H), 3.31 (t, *J* = 7.3 Hz, 2H), 2.46 (q, *J* = 7.3 Hz, 2H), 2.31 (t, *J* = 7.6 Hz, 2H), 1.32 (q, *J* = 7.4 Hz, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.27, 153.47, 144.08, 140.96, 135.33, 128.40, 128.22, 126.72, 126.09, 124.21, 123.90, 121.59, 121.01, 41.60, 33.88, 28.67, 21.15, 13.75. **HRMS** calcd. for $C_{20}H_{22}NS_2^+$ $[M+H]^+$: 340.1188, Found: 340.1204.



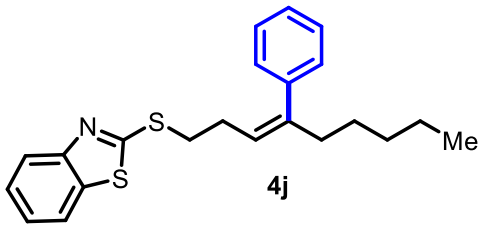
4h

(*Z*)-2-((4-phenyloct-3-en-1-yl)thio)benzothiazole (4i): The title compound was prepared according to General Procedure 5. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded **4i** as a clear liquid (32 mg, 91%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 8.1 Hz, 1H), 7.31–7.25 (m, 3H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.0 Hz, 2H), 5.52 (t, *J* = 7.3 Hz, 1H), 3.32 (t, *J* = 7.3 Hz, 2H), 2.46 (q, *J* = 7.3 Hz, 2H), 2.39–2.27 (m, 2H), 1.27 (dt, *J* = 8.1, 3.9 Hz, 4H), 0.88–0.80 (m, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.27, 153.46, 144.33, 141.02, 135.32, 128.40, 128.22, 126.71, 126.09, 124.21, 123.65, 121.59, 121.01, 39.23, 33.88, 30.27, 28.70, 22.40, 14.06. **HRMS** calcd. for $C_{21}H_{24}NS_2^+$ $[M+H]^+$: 354.1345, Found: 354.1356.



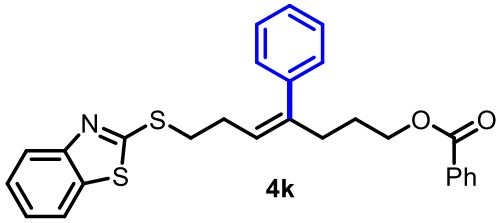
4i

(*Z*)-2-((4-phenylnon-3-en-1-yl)thio)benzothiazole (4j): The title compound was prepared according to General Procedure 5. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded **4j** as a white solid (31 mg, 85%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.28 (td, *J* = 8.1, 3.6 Hz, 3H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 2H), 5.52 (t, *J* = 7.3 Hz, 1H), 3.32 (t, *J* = 7.3 Hz, 2H), 2.46 (q, *J* = 7.3 Hz, 2H), 2.32 (t, *J* = 7.3 Hz, 2H), 1.30 (t, *J* = 6.7 Hz, 1H), 1.26–1.22 (m, 4H), 0.90–0.65 (m, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.29, 153.45, 144.36, 141.02, 135.31, 128.39, 128.21, 126.70, 126.09, 124.21, 123.64, 121.59, 121.00, 39.48, 33.89, 31.53, 28.68, 27.74, 22.61, 14.21. **HRMS** calcd. for $C_{22}H_{26}NS_2^+$ $[M+H]^+$: 368.1501, Found: 368.1519.

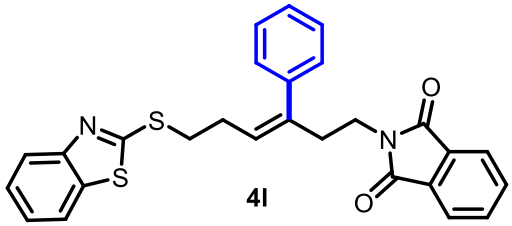


4j

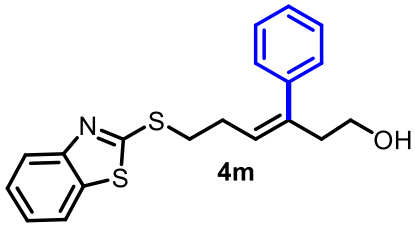
(*Z*)-7-(benzothiazol-2-ylthio)-4-phenylhept-4-en-1-yl benzoate (4k): The reaction was carried out according to General Procedure 5. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 460.1[M+H], cone voltage 15V). Purification afforded **4k** as a yellow liquid (28 mg, 61%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.7 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 3H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 2H), 5.59 (t, *J* = 7.3 Hz, 1H), 4.29 (t, *J* = 6.6 Hz, 2H), 3.32 (t, *J* = 7.3 Hz, 2H), 2.50 (dq, *J* = 14.6, 7.4 Hz, 4H), 1.78 (p, *J* = 6.8 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.07, 166.71, 153.41, 142.74, 140.25, 135.31, 132.98, 130.53, 129.68, 128.47, 128.47, 128.41, 127.02, 126.09, 124.86, 124.23, 121.58, 121.01, 64.46, 35.81, 33.69, 28.70, 27.16. **HRMS** calcd. for $C_{27}H_{26}NO_2S_2^+$ $[M+H]^+$: 460.1400, Found: 460.1409.



(*Z*)-2-(6-(benzothiazol-2-ylthio)-3-phenylhex-3-en-1-yl)isoindoline-1,3-dione (4l): The title compound was prepared according to General Procedure 5. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 471.1 [M+H], cone voltage 15V). Purification afforded **4l** as a yellow liquid (28 mg, 60%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84–7.76 (m, 3H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.65 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.26 (dd, *J* = 24.2, 7.5 Hz, 3H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 5.55 (t, *J* = 7.4 Hz, 1H), 3.72 (t, *J* = 6.9 Hz, 2H), 3.22 (t, *J* = 7.3 Hz, 2H), 2.77 (t, *J* = 7.0 Hz, 2H), 2.45 (q, *J* = 7.3 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.45, 166.90, 153.39, 140.24, 139.48, 135.29, 133.94, 132.18, 128.57, 128.34, 127.11, 126.82, 126.09, 124.23, 123.24, 121.59, 121.01, 37.64, 37.24, 33.51, 28.57. **HRMS** calcd. for $C_{27}H_{23}N_2O_2S_2^+$ $[M+H]^+$: 471.1196, Found: 471.1191.

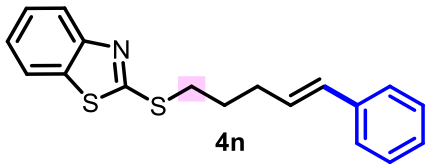


(*Z*)-6-(benzothiazol-2-ylthio)-3-phenylhex-3-en-1-ol (4m): The title compound was prepared according to General Procedure 5. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 55–75% acetonitrile over 8 min) at ambient temperature.

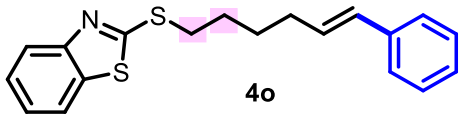


Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 342.1 [M+H], cone voltage 15V). Purification afforded **4m** as a yellow liquid (18 mg, 53%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.45–7.38 (m, 1H), 7.33–7.26 (m, 4H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.18–7.10 (m, 2H), 5.64 (t, *J* = 7.3 Hz, 1H), 3.57 (t, *J* = 6.3 Hz, 2H), 3.34 (t, *J* = 7.2 Hz, 2H), 2.62 (t, *J* = 6.3 Hz, 2H), 2.51 (q, *J* = 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.88, 153.38, 140.45, 139.81, 135.31, 128.47, 128.37, 127.16, 127.03, 126.13, 124.30, 121.62, 121.04, 60.52, 42.59, 33.61, 28.66. **HRMS** calcd. for $C_{19}H_{20}NOS_2^+$ $[M+H]^+$: 342.0981, Found: 342.0997.

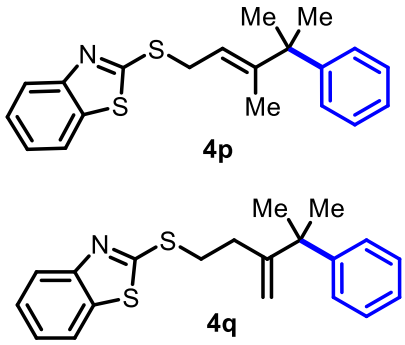
(***E***)**-2-((5-phenylpent-4-en-1-yl)thio)benzothiazole (4n):** The title compound was prepared according to General Procedure 3. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 312.1 [M+H], cone voltage 15V). Purification afforded **4n** as a white solid (29 mg, 94%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.78–7.70 (m, 1H), 7.46–7.38 (m, 1H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.32–7.28 (m, 3H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.41 (t, *J* = 7.2 Hz, 2H), 2.42 (qd, *J* = 7.1, 1.5 Hz, 2H), 2.03 (p, *J* = 7.3 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.13, 153.47, 137.62, 135.35, 131.25, 129.15, 128.65, 127.21, 126.15, 124.30, 121.64, 121.07, 33.06, 32.01, 29.03. **HRMS** calcd. for $C_{18}H_{18}NS_2$ $[M+H]^+$: 312.0875, Found: 312.0874.



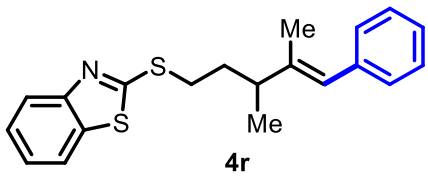
(***E***)**-2-((6-phenylhex-5-en-1-yl)thio)benzothiazole (4o):** The title compound was prepared according to General Procedure 3. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded **4o** as a yellow liquid (18 mg, 54%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.41 (t, *J* = 8.1 Hz, 1H), 7.35–7.27 (m, 5H), 7.22–7.16 (m, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.21 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.39 (t, *J* = 7.3 Hz, 2H), 2.29 (qd, *J* = 7.2, 1.5 Hz, 2H), 1.90 (p, *J* = 7.5 Hz, 2H), 1.68 (p, *J* = 7.5 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.32, 153.48, 137.80, 135.33, 130.56, 130.23, 128.63, 127.06, 126.14, 126.10, 124.27, 121.62, 121.06, 33.57, 32.55, 28.90, 28.52. **HRMS** calcd. for $C_{19}H_{20}NS_2^+$ $[M+H]^+$: 326.1032, Found: 326.1046.



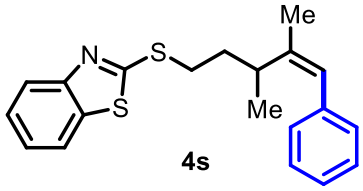
(***E***)**-2-((3,4-dimethyl-4-phenylpent-2-en-1-yl)thio)benzothiazole (4p)** and **2-((4-methyl-3-methylene-4-phenylpentyl)thio)benzothiazole (4q):** The title compound was prepared according to General Procedure 5. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 340.1 [M+H], cone voltage 15V). Purification afforded a 5:2 mixture of **4p** and **4q** as a yellow liquid (8 mg, 12%). In this case, it was possible to distinguish NMR peaks corresponding to each of the isomers, so their data are reported separately. **^{1}H NMR** (600 MHz, $CDCl_3$) **(4p):** δ 7.87 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.40 (m, *J* = 7.5 Hz, 1H), 7.29–7.06 (m, 6H), δ 5.75 (t, *J* = 7.8 Hz, 1H), 4.08 (d, *J* = 7.7 Hz, 2H), 1.55 (s, 3H), 1.39 (s, 6H); **(4q):** δ 7.82 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.40 (m, *J* = 7.5 Hz, 1H), 7.29–7.06 (m, 6H), 5.29 (s, 1H), 5.11 (s, 1H), 3.31 (t, *J* = 7.7 Hz, 2H), 2.30 (t, *J* = 8.0 Hz, 2H), 1.46 (s, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) **4p:** δ 166.96, 153.51, 148.70, 148.19, 135.55, 128.25, 126.23, 126.17, 125.87, 124.35, 121.73, 121.09, 116.85, 45.03, 32.33, 28.29, 14.66; **4q:** δ 167.21, 154.68, 153.45, 147.71, 135.31, 128.35, 126.33, 126.07, 126.07, 124.19, 121.59, 121.01, 109.63, 44.56, 33.13, 32.26, 28.48. **HRMS** calcd. for $C_{20}H_{22}NS_2^+$ $[M+H]^+$: 340.1188, Found: 340.1189.



(***E***)**-2-((3,4-dimethyl-5-phenylpent-4-en-1-yl)thio)benzothiazole (4r):** The title compound was prepared according to General Procedure 5. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 340.1 [M+H], cone voltage 15V). Purification afforded **4r** as a yellow liquid (3 mg, 5%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0, 1H), 7.40 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.34–7.15 (m, 6H), 6.38 (s, 1H), 3.39 (ddd, *J* = 13.0, 9.1, 5.4 Hz, 1H), 3.25 (ddd, *J* = 13.1, 9.1, 6.8 Hz, 1H), 2.63–2.47 (m, 1H), 2.08–1.97 (m, 1H), 1.90 (dddd, *J* = 14.1, 9.1, 6.8, 5.5 Hz, 1H), 1.83 (d, *J* = 1.4 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.31, 153.51, 141.40, 138.40, 135.35, 129.11, 128.18, 126.18, 126.14, 125.89, 124.26, 121.63, 121.06, 43.11, 34.49, 31.99, 19.74, 14.04. **HRMS** calcd. for $C_{20}H_{22}NS_2^+$ $[M+H]^+$: 340.1188, Found: 340.1191.

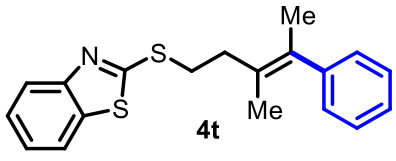


(*Z*)-2-((3,4-dimethyl-5-phenylpent-4-en-1-yl)thio)benzothiazole (4s): The title compound was prepared according to General Procedure 5. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 340.1 [M+H], cone voltage 15V). Purification afforded **4s** as a yellow liquid (5 mg, 7%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 8.0, 1.2 Hz, 1H), 7.46–7.38 (m, 1H), 7.30 (q, *J* = 7.2, 6.7 Hz, 3H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 6.39 (s, 1H), 3.27 (ddd, *J* = 13.1, 9.9, 5.4 Hz, 1H), 3.11–2.98 (m, 2H), 1.96 (dtd, *J* = 14.5, 9.5, 5.4 Hz, 1H), 1.84 (d, *J* = 1.5 Hz, 3H), 1.78 (dtd, *J* = 13.7, 9.9, 6.1 Hz, 1H), 1.11 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.30, 153.48, 141.68, 138.40, 135.34, 128.86, 128.29, 127.05, 126.23, 126.11, 124.22, 121.59, 121.05, 34.60, 33.93, 31.80, 19.35, 18.26. **HRMS** calcd. for $C_{20}H_{22}NS_2^+$ $[M+H]^+$: 340.1188, Found: 340.1194.



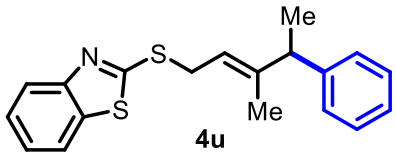
4s

(*E*)-2-((3-methyl-4-phenylpent-3-en-1-yl)thio)benzothiazole (4t): The title compound was prepared according to General Procedure 3. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 326.1 [M+H], cone voltage 15V). Purification afforded **4t** as a yellow liquid (6 mg, 17%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.79–7.75 (m, 1H), 7.46–7.39 (m, 1H), 7.33–7.27 (m, 3H), 7.23–7.17 (m, 1H), 7.13–7.08 (m, 2H), 3.54–3.47 (m, 2H), 2.76–2.69 (m, 2H), 2.03 (s, 3H), 1.65 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.63, 152.88, 144.38, 134.77, 133.10, 128.04, 127.70, 127.58, 125.59, 125.55, 123.69, 120.99, 120.50, 33.65, 31.48, 20.44, 19.35. **HRMS** calcd. for $C_{19}H_{20}NS_2^+$ $[M+H]^+$: 326.1032, Found: 326.1037.

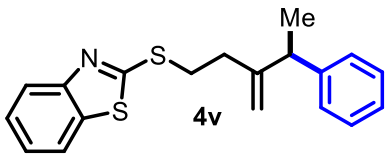


4t

(*E*)-2-((3-methyl-4-phenylpent-2-en-1-yl)thio)benzothiazole (4u) and **2-((3-methylene-4-phenylpentyl)thio)benzothiazole (4v):** The title compound was prepared according to General Procedure 3. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 326.1 [M+H], cone voltage 15V). Purification afforded a 2:1 mixture of **4u** and **4v** as a yellow liquid (15 mg, 14%). In this case, it was possible to distinguish



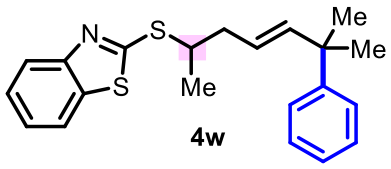
4u



4v

NMR peaks corresponding to each of the isomers, so their data are reported separately. **^{1}H NMR** (600 MHz, $CDCl_3$) (***E***)**-2-((3-methyl-4-phenylpent-2-en-1-yl)thio)benzothiazole (4u):** δ 7.86 (m, J = 8.2, 0.8 Hz, 1H), 7.75 (m, J = 7.9, 0.9 Hz, 1H), 7.41 (m, J = 8.3, 7.2, 1.2 Hz, 1H), 7.32–7.27 (m, 2H), 7.24–7.09 (m, 4H), 5.65 (tt, *J* = 7.7, 1.4 Hz, 1H), 4.06 (dd, *J* = 7.7, 4.3 Hz, 2H), 3.44–3.31 (m, 1H), 1.62 (s, *J* = 1.2 Hz, 3H), 1.35 (d, *J* = 7.1 Hz, 3H); **2-((3-methylene-4-phenylpentyl)thio)benzothiazole (4v):** δ 7.85 (m, J = 8.2, 0.8 Hz, 1H), 7.74 (m, J = 7.9, 0.9 Hz, 1H), 7.41 (m, J = 8.3, 7.2, 1.2 Hz, 1H), 7.32–7.27 (m, 2H), 7.24–7.09 (m, 4H), 5.11 (s, 1H), 5.06 (s, 1H), 3.49 (q, *J* = 7.0 Hz, 1H), 3.44–3.31 (m, 2H), 2.52–2.31 (m, 2H), 1.40 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) **4u:** 166.93, 153.47, 145.34, 144.59, 135.53, 128.40, 127.57, 126.28, 126.16, 124.33, 121.70, 121.09, 117.94, 47.77, 32.03, 19.56, 15.34; **4v:** δ 167.12, 153.44, 150.69, 144.84, 135.33, 128.59, 127.68, 126.47, 126.12, 124.25, 121.60, 121.05, 111.09, 45.34, 34.76, 32.35, 20.75. **HRMS** calcd. for $C_{19}H_{20}NS_2^+$ $[M+H]^+$: 326.1032, Found: 326.1034.

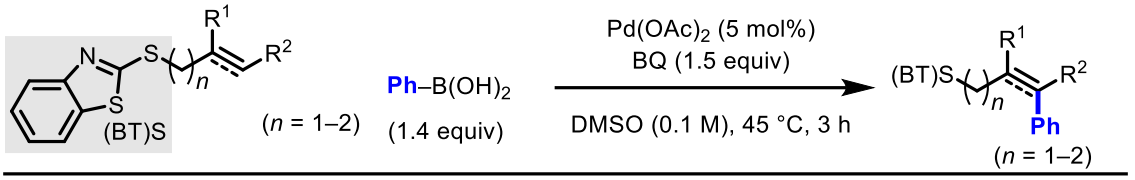
(***E***)**-2-((6-methyl-6-phenylhept-4-en-2-yl)thio)benzothiazole (4w):** The title compound was prepared according to General Procedure 5. The crude residue was purified by preparative TLC (5% Et_2O/hexanes). Purification afforded **4w** as a yellow liquid (16 mg, 45%) as a 9:1 mixture of 2-((6-methylhept-5-en-2-yl)thio)benzothiazole to an inseparable isomer. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.36–7.27 (m, 5H), 7.18 (q, *J* = 7.5 Hz, 1H), 5.76 (d, *J* = 15.5 Hz, 1H), 5.52 (dt, *J* = 15.0, 7.1 Hz, 1H), 4.08 (h, *J* = 6.8 Hz, 1H), 2.58 (dt, *J* = 13.2, 6.4 Hz, 1H), 2.49 (dt, *J* = 14.2, 7.2 Hz, 1H), 1.50 (d, *J* = 6.8 Hz, 3H), 1.38 (s, 5H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.63, 153.55, 148.99, 143.85, 135.45, 128.20, 126.29, 126.12, 125.88, 124.36, 122.35, 121.73, 121.05, 44.43, 40.74, 40.11, 28.93, 28.91, 20.94. **HRMS** calcd. for $C_{21}H_{24}NS_2^+$ $[M+H]^+$: 354.1345, Found: 354.1360.

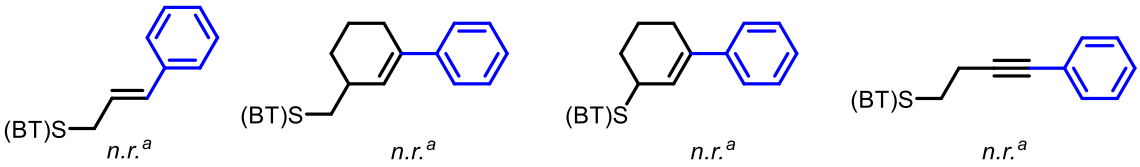


4w

Unsuccessful Substrates in Oxidative Heck Reaction Substrates

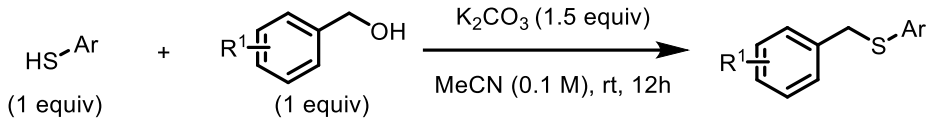
Table S6. Unsuccessful Substrates in Oxidative Heck Reaction Substrates





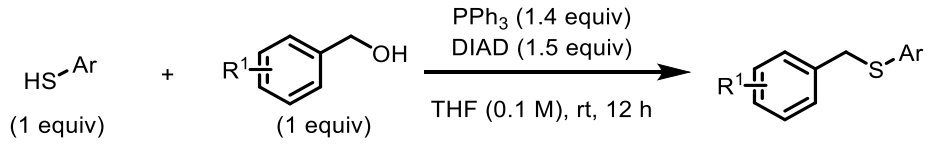
[a]n.r.=no reaction.

Starting Material Synthesis for C−H Functionalization



Scheme S5. General Procedure 6.

General Procedure 6: To a 50-mL round-bottom flask equipped with a magnetic stir bar were added the bromide (1.0 mmol, 1 equiv), thiol (1.0 mmol, 1 equiv), K_2CO_3 (1.5 mmol, 1.5 equiv) and MeCN (10 mL, 0.1 M) in air. The reaction was stirred at room temperature for 12 h. The organic materials were separated by addition of H_2O (25 mL), followed by extraction with EtOAc (3 × 10 mL) and dried with Na_2SO_4. The solvent was removed *in vacuo,* and the crude residue was purified by SiO_2 gel column chromatography or preparative TLC.

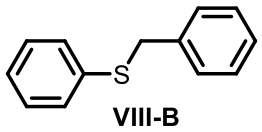


Scheme S6. General Procedure 7.

General Procedure 7: To a 50-mL round-bottom flask equipped with a magnetic stir bar nd containing the alcohol (1.0 mmol, 1 equiv), thiol (1.0 mmol, 1 equiv), PPh_3 (1.4 mmol, 1.4 equiv), and THF (10 mL, 0.1 M) was added DIAD (1.5 mmol, 1.5 equiv) dropwise in air. The reaction was stirred at room temperature for 12 h. The organic materials were separated by addition of H_2O (25 mL), followed by extraction with EtOAc (3 × 10 mL) and dried with Na_2SO_4. The solvent was removed *in vacuo*, and the crude residue was purified by SiO_2 gel column chromatography or preparative TLC.

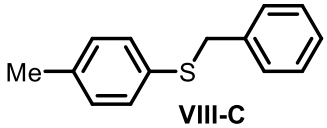
Characterization Data for Starting Materials for C−H Functionalization

benzyl(phenyl)sulfane (VIII-B): The title compound was prepared according to General Procedure 7. The crude residue was purified by SiO_2 gel column chromatography (5% EtOAc/hexanes). Purification afforded **VII-B** as a yellow solid (162 mg, 81%). Characterization data were consistent with previously reported data.[8]



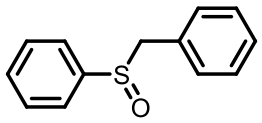
VIII-B

benzyl(*p*-tolyl)sulfane (VIII-C): The title compound was prepared according to General Procedure 7. The crude residue was purified by SiO_2 gel column chromatography (5% EtOAc/hexanes). Purification afforded **VII-C** as a yellow liquid (171 mg, 80%). Characterization data were consistent with previously reported data.[9]



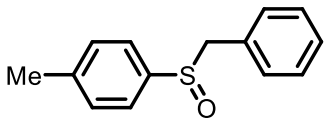
VIII-C

(benzylsulfinyl)benzene (VIII-D): In a 10-mL round-bottom flask equipped with a stir bar were added benzyl(phenyl)sulfane (**VIII-B**) (0.500 mmol, 1 equiv) and DCM (5 mL, 0.1 M). The mixture was cooled in an ice-water bath and then *m*-CPBA (0.500 mmol, 1 equiv) was added. The mixture was stirred for 1 h and then washed with NaOH (3 mL, 0.2 M). The organic layer was removed and the solvent was removed *in vacuo.* Ether was then added and the mixture was cooled to -5 ° C for 12 h. Solvent was removed and white precipitate was isolated. Purification afforded **VIII-D** as a white solid (87 mg, 80%). Characterization data were consistent with previously reported data.[10]



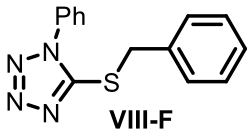
VIII-D

1-(benzylsulfinyl)-4-methylbenzene (VIII-E): In a 10-mL round-bottom flask equipped with a stir bar were added benzyl(*p*-tolyl)sulfane (**VIII-C**) (0.500 mmol, 1 equiv) and DCM (5 mL, 0.1 M). The mixture was cooled in an ice-water bath and then *m*-CPBA (0.500 mmol, 1 equiv) was added. The mixture was stirred for 1 h and then washed with NaOH (3 mL, 0.2 M). The organic layer was removed and the solvent was removed *in vacuo.* Ether was then added and the mixture was cooled to -5 ° C for 12 h. Solvent was removed and white precipitate was isolated. Purification afforded **VIII-E** as a white solid (97 mg, 84%). Characterization data were consistent with previously reported data.[10]



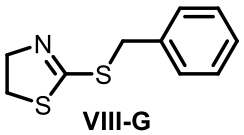
VIII-E

5-(benzylthio)-1-phenyl-1H-tetrazole (VIII-F): The title compound was prepared according to General Procedure 7. The crude residue was purified by SiO_2 gel column chromatography (20% EtOAc/hexanes). Purification afforded **VIII-F** as a white solid (134 mg, 50%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.60–7.49 (m, 5H), 7.48–7.42 (m, 2H), 7.38–7.30 (m, 3H), 4.66 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.05, 135.35, 133.77, 130.25, 129.90, 129.39, 128.99, 128.35, 123.96, 37.81. **HRMS** calcd. for $C_{14}H_{13}N_4S^+$ $[M+H]^+$: 269.0855, Found: 269.0866.



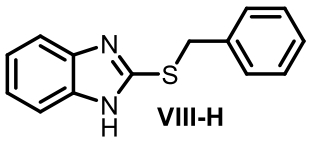
VIII-F

2-(benzylthio)-4,5-dihydrothiazole (VIII-G): The title compound was prepared according to General Procedure 7. The crude residue was purified by SiO_2 gel column chromatography (20% EtOAc/hexanes). Purification afforded **VIII-G** as an orange solid (168 mg, 80%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38–7.34 (m, 2H), 7.33–7.29 (m, 2H), 7.27 (d, *J* = 7.4 Hz, 1H), 4.36 (s, 2H), 4.24 (t, *J* = 8.0 Hz, 2H), 3.41 (t, *J* = 8.0 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 136.73, 129.17, 128.75, 127.64, 64.40, 37.14, 35.81. **HRMS** calcd. for $C_{10}H_{12}NS_2^+$ $[M+H]^+$: 210.0406, Found: 210.0409.



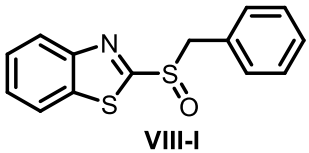
VIII-G

2-(benzylthio)-1H-benzoimidazole (VIII-H): The title compound was prepared according to General Procedure 6. The crude residue was purified by SiO_2 gel column chromatography (40% EtOAc/hexanes). Purification afforded **VIII-H** as a white solid (157 mg, 64%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 11.00 (s, 1H), 7.37 (d, *J* = 7.1 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.29–7.26 (m, 2H), 7.21–7.16 (m, 1H), 7.12 (td, *J* = 7.8, 1.1 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 5.55 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.14, 135.48, 132.84, 130.64, 128.95, 128.05, 127.67, 123.66, 123.15, 110.19, 110.04, 47.93. **HRMS** calcd. for $C_{14}H_{13}N_2S^+$ $[M+H]^+$: 241.0794, Found: 241.0799.



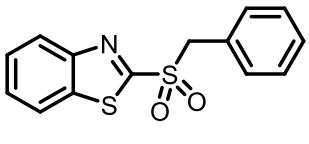
VIII-H

2-(benzylsulfinyl)benzothiazole (VIII-I): To a 25-mL round-bottom flask equipped with a magnetic stir bar was charged 2-(benzylthio)benzothiazole (0.5 mmol, 1 equiv) and DCM (5 mL, 0.1 M). The mixture was cooled to 0 ° C. A solution of mCPBA (0.5 mmol, 1 equiv) in DCM (5 mL, 0.1 M) was then added dropwise. The reaction was stirred for 4 h. The organic materials were separated by addition of H_2O (0.2 M, 25 mL), followed by extraction with EtOAc (3 × 10 mL). The organic layer was dried over Na_2SO_4, and after filtration the solvent was removed *in vacuo*. The crude residue was purified by SiO_2 gel column chromatography (40% EtOAc/hexanes). Purification afforded **VIII-I** as a white solid (114 mg, 81%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.61–7.54 (m, 1H), 7.52–7.46 (m, 1H), 7.34–7.29 (m, 1H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.20–7.16 (m, 2H), 4.52 (d, *J* = 13.2 Hz, 1H), 4.34 (d, *J* = 13.2 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 177.10, 153.87, 136.16, 130.60, 128.88, 128.84, 128.51, 127.05, 126.28, 124.05, 122.39, 62.98. **HRMS** calcd. for $C_{14}H_{12}NOS_2^+$ $[M+H]^+$: 274.0355, Found: 274.0359.



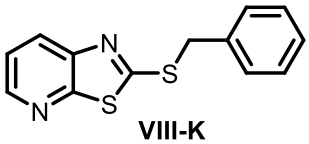
VIII-I

2-(benzylsulfonyl)benzothiazole (VIII-J): To a 10-mL round-bottom flask equipped with a magnetic stir bar were added 2-(benzylthio)benzothiazole (0.1 mmol, 1 equiv), 30% aqueous H_2O_2 (0.2 mL, 6 equiv), ammonium heptamolybdate tetrahydrate (0.001 mmol, 1 mol%), and ethanol (2 mL, 0.05 M). The reaction was stirred at room temperature for 12 h. The organic materials were separated by addition of H_2O (25 mL), followed by extraction with EtOAc (3 × 10 mL). The organic solution was washed with brine (10 mL) and dried over Na_2SO_4. After filtration, the solvent was removed *in vacuo,* and **VIII-J** was obtained as a white solid (29 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.1 Hz, 1H), 7.94 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.65 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.58 (ddd, *J* = 8.3, 7.2, 1.1 Hz, 1H), 7.35–7.29 (m, 1H), 7.30–7.25 (m, 4H), 4.76 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.31, 152.70, 137.18, 131.24, 129.35, 129.03, 128.13, 127.77, 126.46, 125.61, 122.41, 61.14. **HRMS** calcd. for $C_{14}H_{12}NO_2S_2^+$ $[M+H]^+$: 290.0304, Found: 290.0305.



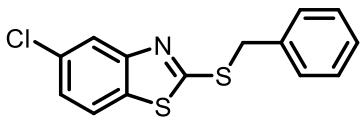
VIII-J

2-(benzylthio)thiazolo[5,4-b]pyridine (VIII-K): The title compound was prepared according to General Procedure 7. The crude residue was purified by SiO_2 gel column chromatography (10% EtOAc/hexanes). Purification afforded **VIII-K** as a white solid (244 mg, 95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 4.7, 1.5 Hz, 1H), 8.08 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.49–7.43 (m, 2H), 7.40–7.32 (m, 3H), 7.32–7.27 (m, 1H), 4.62 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.18, 158.98, 146.42, 145.87, 135.97, 129.31, 128.92, 128.08, 128.03, 121.30, 37.13. **HRMS** calcd. for $C_{13}H_{11}N_2S_2$ $[M+H]^+$: 259.0358, Found: 259.0365.



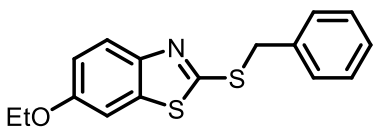
VIII-K

2-(benzylthio)-5-chlorobenzothiazole (VIII-L): The title compound was prepared according to General Procedure 6. The crude residue was purified by SiO_2 gel column chromatography (20% EtOAc/hexanes). Purification afforded **VIII-L** as a white solid (120 mg, 41%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 2.0 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.45 (dd, *J* = 7.3, 1.8 Hz, 2H), 7.34 (dd, *J* = 8.3, 6.6 Hz, 2H), 7.31–7.25 (m, 2H), 4.60 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.77, 154.10, 136.14, 133.71, 132.28, 129.28, 128.88, 127.99, 124.77, 121.75, 121.59, 37.82. **HRMS** calcd. for $C_{14}H_{11}ClNS_2^+$ $[M+H]^+$: 292.0016, Found: 292.0026.



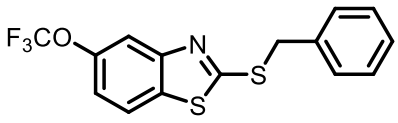
VIII-L

2-(benzylthio)-6-ethoxybenzothiazole (VIII-M): The title compound was prepared according to General Procedure 6. The crude residue was purified by SiO_2 gel column chromatography (20% EtO_2/hexanes). Purification afforded **VIII-M** as a white solid (272 mg, 91%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.8 Hz, 1H), 7.44 (d, *J* = 7.0 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.21 (d, *J* = 2.5 Hz, 1H), 7.01 (dd, *J* = 8.9, 2.5 Hz, 1H), 4.56 (s, 2H), 4.07 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.09, 156.60, 147.82, 136.84, 136.47, 129.26, 128.83, 127.85, 122.20, 115.49, 104.96, 64.27, 38.13, 14.98. **HRMS** calcd. for $C_{16}H_{16}NOS_2^+$ $[M+H]^+$: 302.0668, Found: 302.0679.



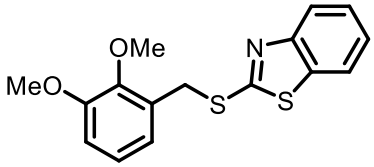
VIII-M

2-(benzylthio)-5-(trifluoromethoxy)benzothiazole (VIII-N): The title compound was prepared according to General Procedure 7. The crude residue was purified by SiO_2 gel column chromatography (5% EtOAc/hexanes). Purification afforded **VIII-N** as a yellow solid (245 mg, 95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 2.4, 1.2 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.46 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.37–7.32 (m, 2H), 7.31–7.27 (m, 1H), 7.20–7.17 (m, 1H), 4.62 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.59, 153.92, 148.01, 148.00, 136.04, 133.77, 129.28, 128.91, 128.03, 121.73, 121.55, 119.85, 117.86, 114.20, 37.83. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.99. **HRMS** calcd. for $C_{15}H_{11}F_3NOS_2^+$ $[M+H]^+$: 342.0229, Found: 342.0234.



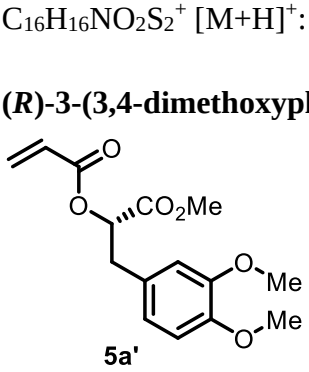
VIII-N

2-((2,3-dimethoxybenzyl)thio)benzothiazole (5a): The title compound was prepared on a 10 mmol scale according to General Procedure 6. The crude residue was purified by SiO_2 gel column chromatography (15% EtOAc/hexanes). Purification afforded **5a** as a yellow liquid (3.174 g, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.45–7.40 (m, 1H), 7.32–7.27 (m, 1H), 7.08 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.87 (dd, *J* = 8.2, 1.5 Hz, 1H), 4.65 (s, 2H), 3.94 (s, 3H), 3.87 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.89, 153.20, 152.72, 147.57, 135.31, 130.02, 125.99, 124.17, 123.96, 122.46, 121.46, 120.97, 112.31, 61.10, 55.75, 32.30. **HRMS** calcd. for $C_{16}H_{16}NO_2S_2^+$ $[M+H]^+$: 318.0617, Found: 318.0631.



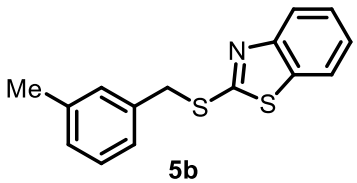
5a

(*R*)-3-(3,4-dimethoxyphenyl)-1-methoxy-1-oxopropan-2-yl acrylate (5a'): The title compound was prepared following a literature procedure.[11] To a 50-mL round-bottom flask with methyl (*R*)-3-(3,4-dimethoxyphenyl)-2-hydroxypropanoate (4.5 mmol, 1 equiv), DMAP (9.0 mmol, 2 equiv) and acrylic acid (6.75 mmol, 1.5 equiv) in CH_2Cl_2 (15 mL, 27 mM) at 0 ° C was added EDC•HCl (9.0 mmol, 2 equiv). The reaction mixture was slowly warmed up to room temperature and stirred overnight. After cooling the reaction mixture to 0 ° C, 2.0 N HCl solution (25 mL) was added. The aqueous layer was extracted with Et_2O (3 × 20 mL) and dried with Na_2SO_4. The crude residue was purified by SiO_2 gel column chromatography (1−10% Et_2O/CH_2Cl_2). Purification afforded **5a'** as a yellow liquid (1.20 g, 90%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.82–6.74 (m, 3H), 6.44 (dd, *J* = 17.3, 1.3 Hz, 1H), 6.15 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.88 (dd, *J* = 10.5, 1.3 Hz, 1H), 5.28 (dd, *J* = 8.4, 4.6 Hz, 1H), 3.86 (s, 6H), 3.73 (s, 3H), 3.18–3.07 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.20, 165.42, 148.93, 148.23, 132.11, 128.40, 127.71, 121.57, 112.58, 111.29, 73.35, 56.00, 55.97, 52.51, 37.20. **HRMS** calcd. for $C_{15}H_{18}O_6Na^+$ $[M+Na]^+$: 317.0996, Found: 317.0996.



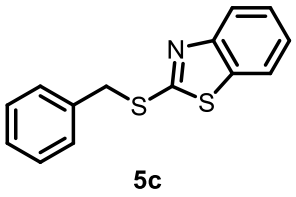
5a'

2-((3-methylbenzyl)thio)benzothiazole (5b): The title compound was prepared according to General Procedure 6. The crude residue was purified by SiO_2 gel column chromatography (15% EtOAc/hexanes). Purification afforded **5b** as a yellow liquid (260 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.43 (td, *J* = 7.7, 1.2 Hz, 1H), 7.30 (ddd, *J* = 8.2, 7.4, 1.1 Hz, 1H), 7.28–7.24 (m, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 4.58 (s, 2H), 2.35 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.56, 153.19, 138.38, 135.91, 135.31, 129.85, 128.61, 128.56, 126.21, 126.05, 124.24, 121.53, 121.00, 37.74, 21.38. **HRMS** calcd. for $C_{15}H_{14}NS_2^+$ $[M+H]^+$: 272.0562, Found: 272.0573.



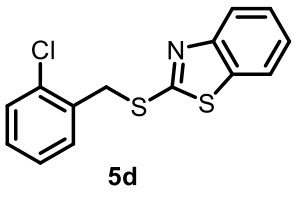
5b

2-(benzylthio)benzothiazole (5c): The title compound was prepared on a 10 mmol scale according to General Procedure 6. The crude residue was purified by SiO_2 gel column chromatography (20% EtOAc/hexanes). Purification afforded **5c** as a white solid (2.57 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (ddd, *J* = 8.2, 1.2, 0.6 Hz, 1H), 7.75 (ddd, *J* = 8.0, 1.3, 0.6 Hz, 1H), 7.49–7.40 (m, 3H), 7.36–7.28 (m, 4H), 4.61 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.50, 153.26, 136.28, 135.43, 129.24, 128.81, 127.86, 126.16, 124.39, 121.66, 121.11, 37.82. **HRMS** calcd. for $C_{14}H_{12}NS_2^+$ $[M+H]^+$: 258.0406, Found: 258.0417.



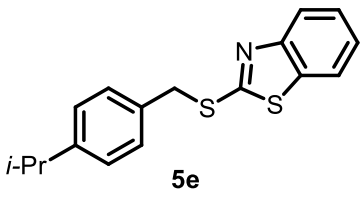
5c

2-((2-chlorobenzyl)thio)benzothiazole (5d): The title compound was prepared according to General Procedure 6. The crude residue was purified by SiO_2 gel column chromatography (15% EtOAc/hexanes). Purification afforded **5d** as a yellow liquid (186 mg, 64%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.94–7.89 (m, 1H), 7.75 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.60 (dd, *J* = 7.2, 2.1 Hz, 1H), 7.43 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 7.40 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.30 (td, *J* = 7.7, 7.3, 1.2 Hz, 1H), 7.22 (pd, *J* = 7.4, 1.8 Hz, 2H), 4.74 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.99, 153.03, 135.40, 134.34, 134.26, 131.22, 129.62, 129.12, 126.93, 125.99, 124.25, 121.50, 120.98, 35.18. **HRMS** calcd. for $C_{14}H_{11}ClNS_2^+$ $[M+H]^+$: 292.0016, Found: 292.0024.



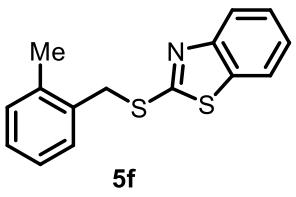
5d

2-((4-isopropylbenzyl)thio)benzothiazole (5e): The title compound was prepared according to General Procedure 7. The crude residue was purified by SiO_2 gel column chromatography (15% EtOAc/hexanes). Purification afforded **5e** as a white solid (268 mg, 89%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.43 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.32–7.28 (m, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 4.59 (s, 2H), 2.90 (p, *J* = 6.9 Hz, 1H), 1.24 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.77, 153.30, 148.60, 135.40, 133.42, 129.21, 126.90, 126.14, 124.33, 121.63, 121.09, 37.63, 33.93, 24.05. **HRMS** calcd. for $C_{17}H_{18}NS_2^+$ $[M+H]^+$: 300.0875, Found: 300.0885.



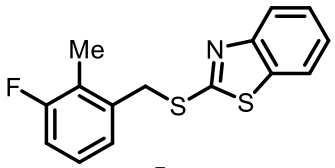
5e

2-((2-methylbenzyl)thio)benzothiazole (5f): The title compound was prepared according to General Procedure 7. The crude residue was purified by SiO_2 gel column chromatography (10% EtOAc/hexanes). Purification afforded **5f** as a clear liquid (252 mg, 97%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1, 0.8 Hz, 1H), 7.76 (d, *J* = 8.0, 0.8 Hz, 1H), 7.46–7.39 (m, 2H), 7.31 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 1H), 7.24–7.15 (m, 3H), 4.64 (s, 2H), 2.46 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.74, 153.35, 137.31, 135.43, 133.79, 130.78, 130.37, 128.32, 126.46, 126.20, 124.43, 121.67, 121.16, 36.16, 19.44. **HRMS** calcd. for $C_{15}H_{14}NS_2^+$ $[M+H]^+$: 272.0562, Found: 272.0573.



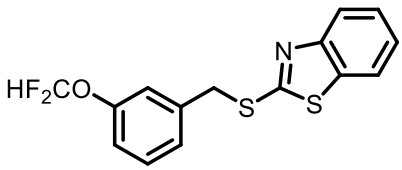
5f

2-((3-fluoro-2-methylbenzyl)thio)benzothiazole (5g): The title compound was prepared according to General Procedure 7. The crude residue was purified by SiO_2 gel column chromatography (8% EtOAc/hexanes). Purification afforded **5g** as a yellow liquid (288 mg, >95%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.11 (q, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 8.9 Hz, 1H), 4.65 (s, 2H), 2.35 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.14, 162.32, 160.70, 153.26, 136.44, 136.41, 135.47, 127.07, 127.01, 126.25, 125.86, 125.84, 124.56, 124.53, 124.44, 121.71, 121.19, 115.02, 114.86, 35.64, 10.71. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.24. **HRMS** calcd. for $C_{15}H_{13}FNS_2^+$ $[M+H]^+$: 290.0468, Found: 290.0474.



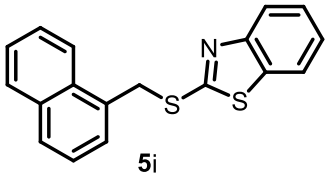
5g

2-((3-(difluoromethoxy)benzyl)thio)benzothiazole (5h): The title compound was prepared according to General Procedure 7. The crude residue was purified by SiO_2 gel column chromatography (15% EtOAc/hexanes). Purification afforded **5h** as a white solid (299 mg, 92%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.65 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.50 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.36–7.30 (m, 1H), 7.22–7.17 (m, 2H), 7.08–7.03 (m, 2H), 6.49 (t, *J* = 73.7 Hz, 1H), 4.57 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.08, 153.12, 149.65, 149.63, 149.61, 135.46, 131.47, 129.31, 128.34, 126.09, 125.57, 124.35, 121.55, 121.05, 118.79, 117.97, 116.25, 116.23, 114.52, 31.75. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.22. **HRMS** calcd. for $C_{15}H_{12}F_2NOS_2^+$ $[M+H]^+$: 324.0323, Found: 324.0334.



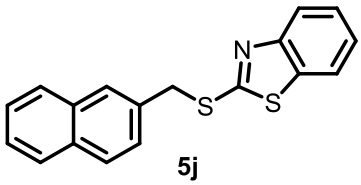
5h

2-((naphthalen-1-ylmethyl)thio)benzothiazole (5i): The title compound was prepared according to General Procedure 6. The crude residue was purified by SiO_2 gel column chromatography (15% EtOAc/hexanes). Purification afforded **5i** as a white solid (264 mg, 85%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.89 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.80–7.76 (m, 1H), 7.65 (d, *J* = 6.9 Hz, 1H), 7.57 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.53 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.48–7.44 (m, 1H), 7.42 (dd, *J* = 8.3, 7.0 Hz, 1H), 7.35–7.30 (m, 1H), 5.13 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.51, 153.15, 135.28, 133.86, 131.47, 131.33, 128.85, 128.05, 126.52, 126.03, 125.97, 125.34, 124.24, 123.59, 121.49, 121.00, 35.55. **HRMS** calcd. for $C_{18}H_{14}NS_2^+$ $[M+H]^+$: 308.0562, Found: 308.0571.



5i

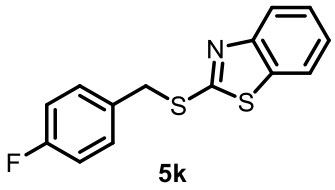
2-((naphthalen-2-ylmethyl)thio)benzothiazole (5j): The title compound was prepared according to General Procedure 6. The crude residue was purified by SiO_2 gel column chromatography (15% EtOAc/hexanes). Purification afforded **5j** as a yellow solid (248 mg, 81%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 6.2 Hz, 2H), 7.82 (t, *J* = 7.8 Hz, 3H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.57 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.48 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.45–7.41 (m, 1H), 7.32–7.28 (m, 1H), 4.78 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.40, 153.23, 135.42, 133.60, 133.34, 132.86, 128.63, 128.14, 127.87, 127.77, 126.99, 126.40, 126.22,



5j

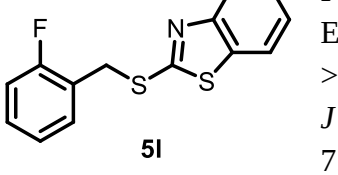
126.15, 124.37, 121.64, 121.09, 38.07. **HRMS** calcd. for $C_{18}H_{14}NS_2^+$ $[M+H]^+$: 308.0562, Found: 308.0574.

2-((4-fluorobenzyl)thio)benzothiazole (5k): The title compound was prepared according to General Procedure 7. The crude residue was purified by SiO_2 plug (50% EtOAc/hexanes). Purification afforded **5k** as a yellow solid (262 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.43 (td, *J* = 6.2, 5.4, 1.3 Hz, 3H), 7.33–7.28 (m, 1H), 7.01 (t, *J* = 8.7 Hz, 2H), 4.58 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.05, 163.13, 161.50, 153.16, 135.41, 132.20, 132.18, 130.89, 130.83, 126.16, 124.43, 121.63, 121.10, 115.71, 115.57, 36.91. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.78. **HRMS** calcd. for $C_{14}H_{11}FNS_2^+$ $[M+H]^+$: 276.0312, Found: 276.0316.



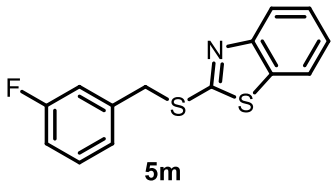
5k

2-((2-fluorobenzyl)thio)benzothiazole (5l): The title compound was prepared according to General Procedure 7. The crude residue was purified by SiO_2 plug (8% EtOAc/hexanes). Purification afforded **5l** as a yellow liquid (269 mg, >95%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.75 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.53 (td, *J* = 7.7, 1.8 Hz, 1H), 7.48–7.41 (m, 1H), 7.34–7.26 (m, 2H), 7.13–7.03 (m, 2H), 4.66 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.12, 161.98, 160.34, 153.26, 135.57, 131.43, 131.40, 129.78, 129.72, 126.20, 124.47, 124.45, 124.40, 124.37, 123.91, 123.81, 121.74, 121.16, 115.76, 115.62, 30.82. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.24. **HRMS** calcd. for $C_{14}H_{11}FNS_2^+$ $[M+H]^+$: 276.0312, Found: 276.0317.



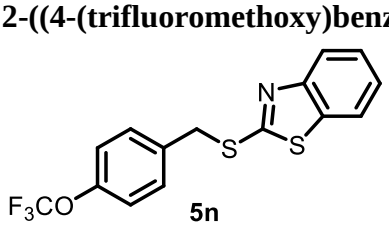
5l

2-((3-fluorobenzyl)thio)benzothiazole (5m): The title compound was prepared according to General Procedure 7. The crude residue was purified by SiO_2 plug (50% EtOAc/hexanes). Purification afforded **5m** as a yellow solid (268 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.34–7.26 (m, 2H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.22–7.17 (m, 1H), 6.97 (td, *J* = 8.5, 2.3 Hz, 1H), 4.59 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.83, 163.67, 162.03, 153.13, 139.05, 139.00, 135.45, 130.25, 130.19, 126.19, 126.18, 124.85, 124.84, 124.47, 121.68, 121.11, 116.25, 116.10, 114.85, 114.70, 37.04. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.09. **HRMS** calcd. for $C_{14}H_{11}FNS_2^+$ $[M+H]^+$: 276.0312, Found: 276.0335.



5m

2-((4-(trifluoromethoxy)benzyl)thio)benzothiazole (5m): The title compound was prepared according to General Procedure 7. The crude residue was purified by SiO_2 gel column chromatography (20% EtOAc/hexanes). Purification afforded **5m** as a white solid (340 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.51–7.48 (m, 2H), 7.44 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 1H), 7.34–7.28 (m, 1H), 7.17 (d, *J* = 8.2 Hz, 2H), 4.60 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.83,

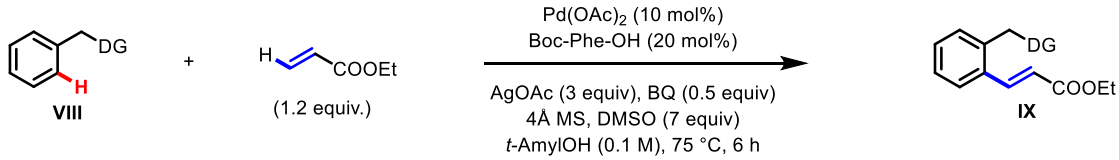


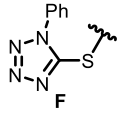
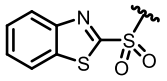
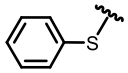
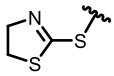
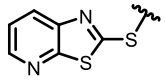
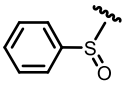
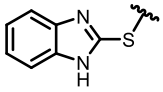
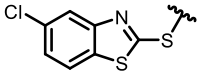
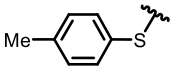
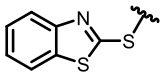
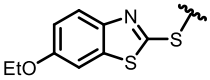
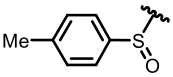
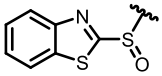
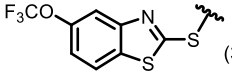
5n

153.17, 148.79, 148.78, 148.76, 148.75, 135.51, 135.41, 130.85, 130.67, 126.24, 126.06, 124.54, 123.11, 121.71, 121.41, 121.22, 121.17, 120.95, 119.70, 118.00, 36.76. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.93. **HRMS** calcd. for $C_{15}H_{11}F_3NOS_2^+$ $[M+H]^+$: 342.0229, Found: 342.0256.

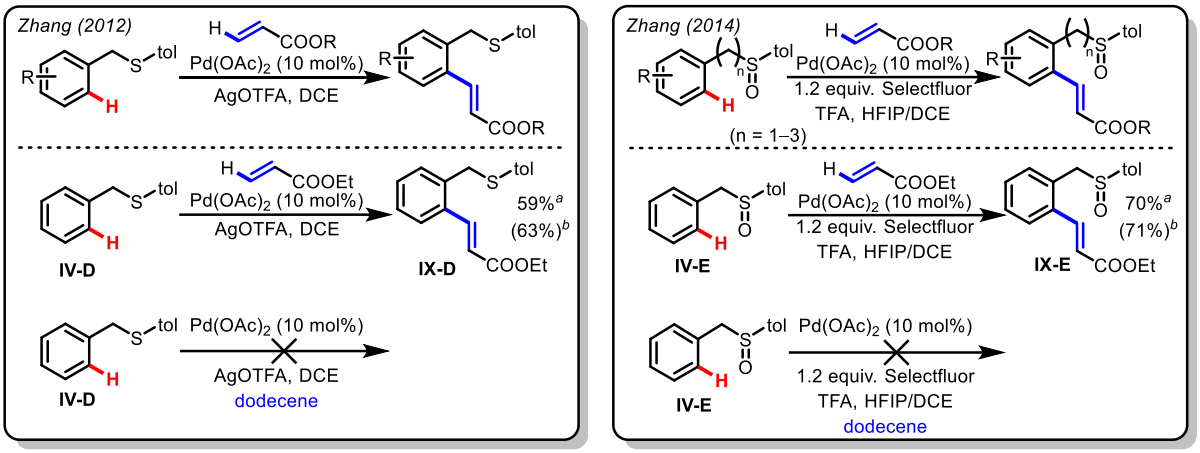
Directing Group Optimization for C−H Functionalization

Table S7. Optimization of Directing Group in C–H Functionalization Reaction[a]



Directing Group (DG)	Yield (**IX**)[b]	Directing Group (DG)	Yield (**IX**)[b]	Directing Group (DG)	Yield (**IX**)[b]
 **A**	n.r.[d]	 **F**	<15%[c]	 **J**	n.r.[d]
 **B**	<15%[c]	 **G**	<15%[c]	 **K**	<15%[c]
 **C**	<15%[c]	 **H**	n.r.[d]	 **L**	43% (34%+9%[b])
 **D**	<15%[c]	 **5c**[e]; **6c**[f] (BT)S	**76%** (**44% + 32%**)	 **M**	69% (40%+29%)
 **E**	<15%[c]	 **I**	n.r.[d]	 **N**	34% (30%+4%[b])

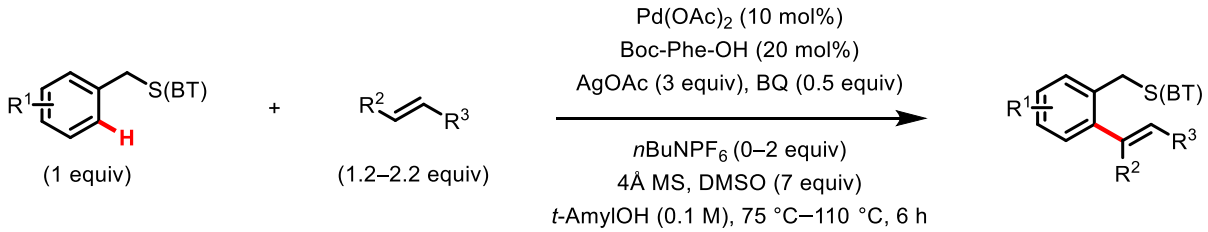
[a]Isolated yields except where otherwise noted. [b]Values inside of parentheses are yield of mono- and bis-functionalized products, respectively. Values outside of parentheses are combined yields of mono- and bis-functionalized products. [c]Determined by ^{1}H-NMR of the crude reaction using 1,3,5-trimethoxybenzene as internal standard. [d]n.r.=no reaction. [e]Starting material. [f]Product.



[a]Isolated Yield. [b]Determined by ^{1}H-NMR of the crude reaction using 1,3,5-trimethoxybenzene as internal standard.

Scheme S7. Comparative Reactivity of Dodecene Using Alternative Directing Groups[12]

General Procedures for C–H Functionalization



Scheme S8. General Procedure for C–H Functionalization.

General Procedure for C–H Functionalization: To a 1-dram (4 mL) vial equipped with magnetic stir bar were added arene (0.10 mmol, 1 equiv), alkene, silver acetate (0.30 mmol, 3 equiv) benzoquinone (0.05 mmol, 0.5 equiv), Boc-L-phenylalanine (0.02 mmol, 0.2 equiv), 4 Å molecular sieves (5 mg), DMSO (0.70 mmol, 7 equiv), $Pd(OAc)_2$ (0.01 mmol, 10 mol%), and *tert*-amyl alcohol (1 mL, 0.1 M). The reaction was placed on a hot plate that was pre-heated to the correct temperature. Except for when otherwise mentioned, after 6 h, the reaction was brought to room temperature. The organic materials were separated by addition of H_2O (10 mL), followed by extraction with EtOAc (3 × 5 mL) and dried with Na_2SO_4. The solvent was removed *in vacuo*, and the crude residue was purified by SiO_2 gel column chromatography, preparative TLC, or mass-directed prep LC.

- **General Procedure 8:**

  Alkene (0.12 mmol, 1.2 equiv), 75 ° C
- **General Procedure 9:**

  Alkene (0.12 mmol, 1.2 equiv), *n*BuNPF$_6$ (0.20 mmol, 2 equiv), 110 ° C
- **General Procedure 10:**

  Alkene (0.22 mmol, 2.2 equiv), 75 ° C

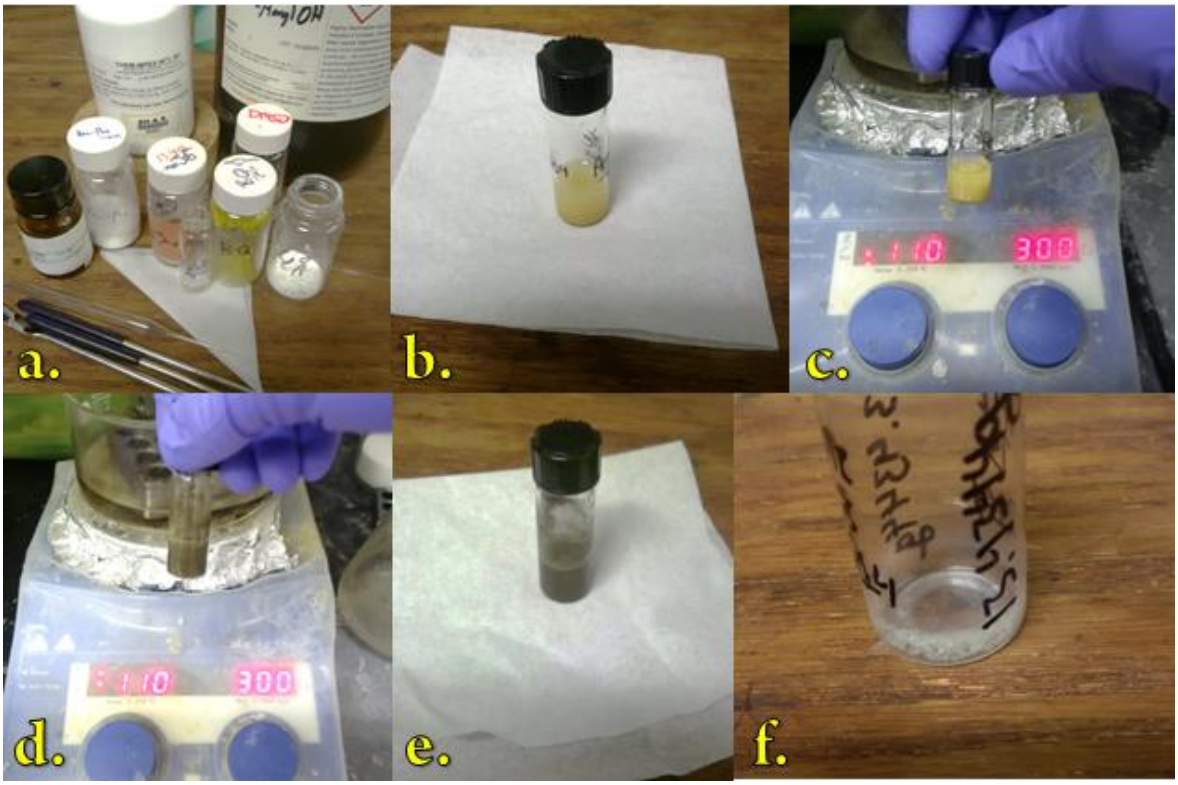
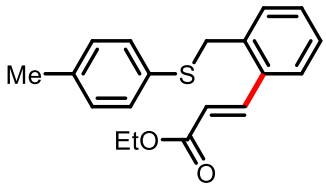


Figure S7. Photographic depiction of reaction setup according to General Procedure 9. From left to right: a) preparation of materials. b) reaction at 0 min before heating. c) vial being placed on hot plate. d) vial at 6 h after heating. e) crude reaction mixture after heating. f) pure product (**6a**)

Characterization Data for C−H Functionalization Products

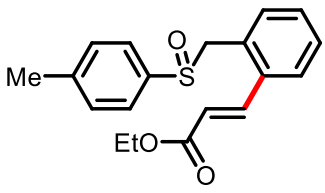
2-(benzylthio)-5-(trifluoromethoxy)benzothiazole (IX-D): The title compound was prepared following a literature procedure.[12b] Benzyl(*p*-tolyl)sulfane (**VIII-C**) (0.3 mmol, 1.0 equiv), ethyl acrylate (0.36 mmol, 1.2 equiv), $Pd(OAc)_2$ (6.7 mg, 10 mol%) and AgOTFA (0.6 mmol, 2.0 equiv) in DCE (2 mL, 0.15 M) were stirred at 100 ° C for 12 h. The organic materials were separated by addition of H_2O (25 mL), followed by extraction with EtOAc (3 × 10 mL). The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 299.1 [M+H], cone voltage 15V). Purification afforded **IX-D** as a colorless liquid (54 mg, 58%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 15.8 Hz, 1H), 7.59–7.52 (m, 1H), 7.29–7.24 (m, 2H), 7.24–7.22 (m, 2H), 7.21–7.17 (m, 1H), 7.06 (d, *J* = 7.7 Hz, 2H), 4.27 (q, *J* = 7.2 Hz, 2H), 4.14 (s, 2H), 2.31 (s, 3H), 1.35 (t, *J*



IX-D

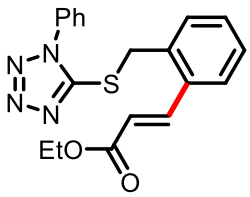
= 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.28, 140.84, 136.97, 136.32, 133.20, 131.81, 131.02, 130.22, 129.41, 129.21, 127.31, 126.30, 119.59, 60.05, 37.61, 20.64, 13.89. **HRMS** calcd. for $C_{19}H_{21}O_2S^+$ $[M+H]^+$: 313.1257, Found: 312.1260.

ethyl (*E*)-3-(2-((*p*-tolylsulfinyl)methyl)phenyl)acrylate (IX-E): The title compound was prepared following a literature procedure. [12a] 1-(benzylsulfinyl)-4-methylbenzene (**VIII-E**) (0.2 mmol, 1 equiv), ethyl acrylate (0.4 mmol, 2 equiv), $Pd(OAc)_2$ (4 mg, 10 mol%), TFA (2 mmol, 10 equiv) and Selectfluor (0.24 mmol, 1.2 equiv) in DCE (2 mL, 0.1 M) were stirred at 100 ° C for 24 h. Afterward, the reaction mixture was allowed to cool to room temperature and filtered through a pad of Celite. The solvent was removed *in vacuo*. The crude residue was purified by preparative TLC (30% EtOAc/hexanes). Purification afforded **IX-E** as white solid (10 mg, 70%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 15.7 Hz, 1H), 7.50–7.46 (m, 1H), 7.34–7.29 (m, 2H), 7.21–7.10 (m, 5H), 6.07 (d, *J* = 15.6 Hz, 1H), 4.30–4.22 (m, 3H), 4.15 (d, *J* = 12.8 Hz, 1H), 2.37 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.42, 142.18, 140.26, 139.12, 134.96, 132.65, 129.88, 129.77, 128.93, 128.55, 126.83, 124.58, 120.44, 60.70, 60.65, 21.56, 14.52. **HRMS** calcd. for $C_{19}H_{21}O_3S^+$ $[M+H]^+$: 329.1206, Found: 329.1218.



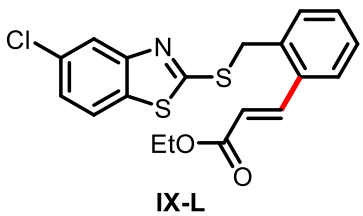
IX-E

ethyl (*E*)-3-(2-(1-phenyl-1H-tetrazol-5-yl)thio)methyl)phenyl)acrylate (IX-E): The title compound was prepared according to General Procedure 8. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 55–75% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 367.1 [M+H], cone voltage 15V). Purification afforded **IX-E** as a yellow solid (5 mg, 13%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 15.7 Hz, 1H), 7.58 (dd, *J* = 5.5, 3.7 Hz, 1H), 7.55-7.47 (m, 6H), 7.34 (dd, *J* = 5.7, 3.4 Hz, 2H), 6.38 (d, *J* = 15.7 Hz, 1H), 4.77 (s, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.62, 153.68, 140.52, 134.20, 134.08, 133.68, 131.45, 130.43, 130.29, 129.93, 129.17, 127.34, 123.95, 121.54, 60.88, 35.43, 14.44. **HRMS** calcd. for $C_{19}H_{19}N_4O_2S^+$ $[M+H]^+$: 367.1223, Found: 367.1237.



IX-F

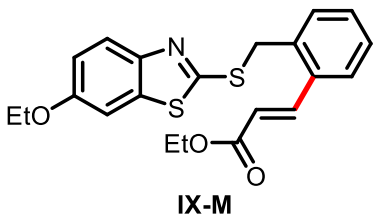
ethyl (*E*)-3-(2-(5-chlorobenzothiazol-2-yl)thio)methyl)phenyl)acrylate (IX-L): The title compound was prepared according to General Procedure 8. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded **IX-L** as a yellow solid (13 mg, 34%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 15.7 Hz, 1H), 7.90 (d, *J* = 2.0 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.59 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.51 (dd, *J* = 7.1, 1.8 Hz, 1H), 7.33 (pd, *J* = 7.4, 1.7 Hz, 2H), 7.28 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.41 (d, *J* = 15.7 Hz, 1H), 4.74 (s, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.1 Hz,



IX-L

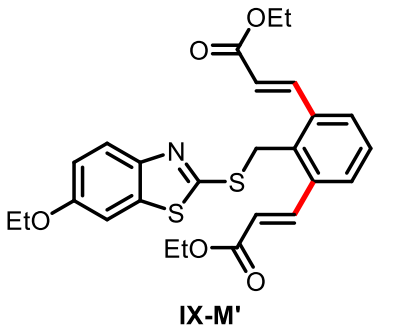
3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.17, 166.95, 154.19, 141.33, 135.38, 134.38, 134.00, 132.49, 131.40, 130.50, 128.89, 127.43, 125.05, 121.97, 121.87, 121.38, 60.99, 35.38, 14.62. **HRMS** calcd. for $C_{19}H_{17}ClNO_2S_2^+$ $[M+H]^+$: 390.0384, Found: 390.0388.

ethyl (*E*)-3-(2-(5-chlorobenzothiazol-2-yl)thio)methyl)phenyl)acrylate (IX-M): The title compound was prepared according to General Procedure 8. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded **IX-M** as a yellow liquid (16 mg, 40%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 15.8 Hz, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.58 (dd, *J* = 7.0, 2.1 Hz, 1H), 7.48 (dd, *J* = 7.2, 1.9 Hz, 1H), 7.32 (tt, *J* = 7.5, 5.6 Hz, 2H), 7.21 (d, *J* = 2.5 Hz, 1H), 7.02 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.39 (d, *J* = 15.7 Hz, 1H), 4.70 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.07 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.76, 162.27, 156.65, 147.75, 141.21, 136.95, 135.46, 134.17, 131.16, 130.25, 128.56, 127.19, 122.28, 121.08, 115.53, 104.93, 64.26, 60.74, 35.54, 14.97, 14.42. **HRMS** calcd. for $C_{21}H_{22}NO_3S_2^+$ $[M+H]^+$: 400.1036, Found: 400.1033.



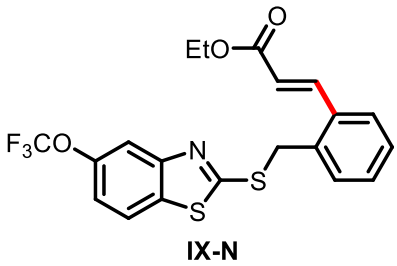
IX-M

diethyl 3,3'-(2-(6-ethoxybenzothiazol-2-yl)thio)methyl)-1,3-phenylene)(2*E*,2'*E*)-diacrylate (IX-M'): The title compound was prepared according to General Procedure 8. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded **IX-M'** as a yellow solid (14 mg, 29%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 15.7 Hz, 2H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 2.5 Hz, 1H), 7.03 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.36 (d, *J* = 15.7 Hz, 2H), 4.82 (s, 2H), 4.22 (q, *J* = 7.2 Hz, 4H), 4.08 (q, *J* = 6.9 Hz, 2H), 1.45 (t, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 161.55, 156.72, 147.75, 141.42, 137.11, 135.83, 133.76, 128.83, 128.75, 122.51, 115.59, 104.89, 64.27, 60.83, 29.85, 14.98, 14.38. **HRMS** calcd. for $C_{26}H_{28}NO_5S_2^+$ $[M+H]^+$: 498.1403, Found: 498.1409.



IX-M'

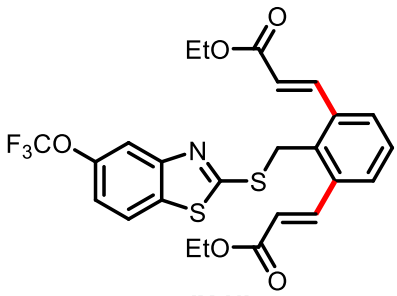
ethyl (*E*)-3-(2-(5-(trifluoromethoxy)benzothiazol-2-yl)thio)methyl)phenyl)acrylate (IX-N): The title compound was prepared according to General Procedure 8. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded **IX-N** as a yellow solid (13 mg, 30%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 15.7 Hz, 1H), 7.80 (dd, *J* = 2.4, 1.2 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.60 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.51 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.34 (pd, *J* = 7.4, 1.7 Hz, 2H), 7.22–7.16 (m, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 4.76 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.80, 166.74, 153.82, 148.01, 141.10, 135.07, 134.20, 133.85, 131.20, 130.32, 128.73, 127.25,



IX-N

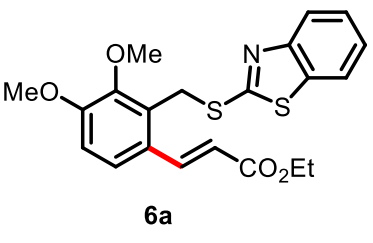
123.25, 121.75, 121.55, 121.20, 119.85, 118.14, 117.94, 114.29, 60.78, 35.20, 14.38. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.98. **HRMS** calcd. for $C_{20}H_{17}F_3NO_3S_2^+$ $[M+H]^+$: 440.0597, Found: 440.0601.

diethyl 3,3'-(2-(5-(trifluoromethoxy)benzothiazol-2-yl)thio)methyl)-1,3-phenylene)(2*E*,2'*E*)-diacrylate (IX-N'): The title compound was prepared according to General Procedure 8. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded **IX-N'** as a yellow solid (2.0 mg, 4%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 15.7 Hz, 2H), 7.90–7.83 (m, 1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.20 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.39 (d, *J* = 15.7 Hz, 2H), 4.90 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 4H), 1.27 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.17, 166.46, 153.76, 148.05, 141.32, 135.84, 133.93, 133.42, 128.92, 128.88, 122.63, 121.75, 121.56, 119.86, 118.04, 114.51, 60.87, 31.54, 14.35. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.98. **HRMS** calcd. for $C_{25}H_{22}F_3NO_5S_2^+$ $[M+H]^+$: 538.0964, Found: 538.0977.



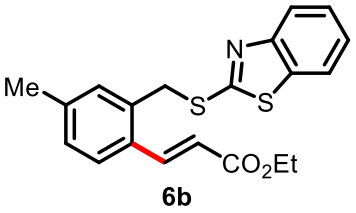
IX-N'

ethyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)-3,4-dimethoxyphenyl)acrylate (6a): The title compound was prepared according to General Procedure 9 on a 9.0 mmol scale. The crude residue was purified by SiO_2 gel column chromatography (20% EtOAc/hexanes). Purification afforded **6a** as a yellow liquid (3.71 g, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 15.7 Hz, 1H), 7.96 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.76 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.43 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 1H), 7.30 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 1H), 6.29 (d, *J* = 15.7 Hz, 1H), 4.85 (s, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 3H), 3.91 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.96, 166.36, 154.08, 153.34, 148.08, 141.33, 135.57, 129.56, 127.54, 126.17, 124.40, 123.08, 121.86, 121.10, 119.28, 112.38, 61.54, 60.55, 55.97, 29.08, 14.41. **HRMS** calcd. for $C_{21}H_{22}NO_4S_2^+$ $[M+H]^+$: 416.0985, Found: 416.0991.

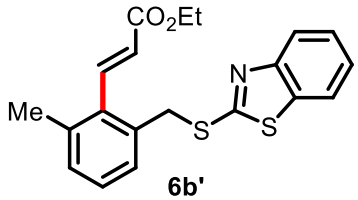


6a

ethyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)-4-methylphenyl)acrylate (6b) and **ethyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)-6-methylphenyl)acrylate (6b'):** The title compound was prepared according to General Procedure 10. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded a 2:1 mixture of **(6b)** and **(6b')** as an orange solid (15.1 mg, 41%). In this case, it was possible to distinguish NMR peaks corresponding to each of the isomers, so their data are reported separately. **(6b): ^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 15.7 Hz, 1H), 7.95–7.90 (m, 1H), 7.78–7.73 (m, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.47–7.10 (m, 4H), 6.37 (d, *J* = 15.8 Hz, 1H), 4.73 (s, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.94, 165.91, 153.25, 142.44,



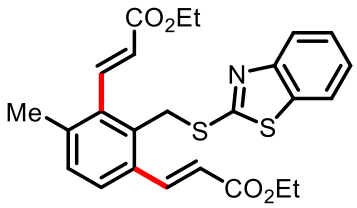
6b



6b'

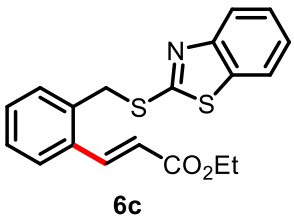
141.05, 140.70, 135.54, 135.10, 131.90, 129.51, 127.13, 126.21, 124.49, 121.76, 121.16, 120.04, 60.66, 35.29, 21.44, 14.43. **(6b'): ^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 15.7 Hz, 1H), 7.95–7.90 (m, 1H), 7.78–7.73 (m, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.47–7.10 (m, 4H), 6.17 (d, *J* = 16.3 Hz, 1H), 4.66 (s, 2H), 4.18 (q, *J* = 6.9 Hz, 2H), 2.33 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.33, 166.22, 153.25, 137.09, 135.54, 135.10, 134.22, 131.32, 130.21, 128.58, 128.43, 125.46, 124.45, 121.71, 121.16, 120.04, 60.79, 36.12, 21.06, 14.34. **HRMS** calcd. for $C_{20}H_{20}NO_2S_2^+$ $[M+H]^+$: 370.0930, Found: 370.0937.

diethyl 3,3'-(2-((benzothiazol-2-ylthio)methyl)-4-methyl-1,3-phenylene)(2*E*,2'*E*)-diacrylate (6b''): The title compound was prepared according to General Procedure 10. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded **6b''** as a yellow solid (15 mg, 32%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 15.7 Hz, 1H), 7.94–7.88 (m, 2H), 7.77–7.74 (m, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.43 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 7.31 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 6.36 (d, *J* = 15.7 Hz, 1H), 6.15 (d, *J* = 16.3 Hz, 1H), 4.79 (s, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.66, 166.03, 165.46, 153.20, 142.30, 141.39, 138.88, 136.80, 135.56, 133.02, 132.59, 130.54, 127.01, 126.23, 126.20, 124.51, 121.85, 121.25, 121.12, 60.84, 60.71, 32.96, 21.24, 14.35, 14.25. **HRMS** calcd. for $C_{25}H_{26}NO_4S_2^+$ $[M+H]^+$: 468.1298, Found: 468.1306.



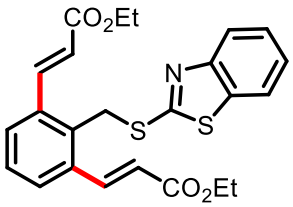
6b''

ethyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)phenyl)acrylate (6c): The title compound was prepared on a 3.885 mmol scale according to General Procedure 8. The crude residue was purified by SiO_2 gel column chromatography (20% EtOAc/hexanes). Purification afforded **6c** as a white solid (605 mg, 44%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 15.7 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.75 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.59 (dd, *J* = 7.1, 2.0 Hz, 1H), 7.52 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.43 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 7.36–7.29 (m, 3H), 6.41 (d, *J* = 15.7 Hz, 1H), 4.76 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.68, 165.68, 153.15, 141.12, 135.50, 135.27, 134.13, 131.13, 130.22, 128.55, 127.15, 126.16, 124.47, 121.72, 121.12, 121.09, 60.68, 35.18, 14.37. **HRMS** calcd. for $C_{19}H_{18}NO_2S_2^+$ $[M+H]^+$: 356.0774, Found: 356.0780.



6c

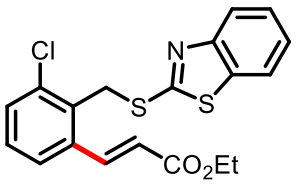
diethyl 3,3'-(2-((benzothiazol-2-ylthio)methyl)-1,3-phenylene)(2*E*,2'*E*)-diacrylate (6c'): The title compound was prepared on a 3.885 mmol scale according to General Procedure 8. The crude residue was purified by SiO_2 gel column chromatography (20% EtOAc/hexanes). Purification afforded **6c'** as a white solid (575 mg, 33%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 15.7 Hz, 2H), 7.97 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.76 (dt, *J* = 7.9, 0.8 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.44 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.31 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 1H), 6.38 (d, *J* = 15.7 Hz, 2H), 4.88 (s,



6c'

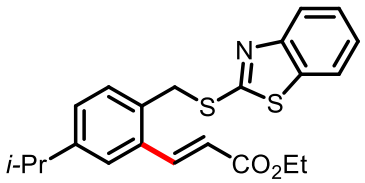
2H), 4.21 (q, *J* = 7.2 Hz, 4H), 1.26 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.45, 165.09, 153.18, 141.38, 135.87, 135.65, 133.58, 128.85, 128.81, 126.24, 124.60, 122.60, 121.97, 121.16, 60.83, 31.64, 14.37. **HRMS** calcd. for $C_{24}H_{24}NO_4S_2^+$ $[M+H]^+$: 454.1141, Found: 454.1147. **X-ray** (single-crystal) Colorless blocks of X-ray diffraction quality were obtained by vapor diffusion of ether into a saturated solution of **6c'** in acetonitrile (CCDC 1905653).[23]

ethyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)-3-chlorophenyl)acrylate (6d): The title compound was prepared according to General Procedure 10 with a reaction time of 24 h. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 390.0 [M+H], cone voltage 15V). Purification afforded **6d** as a brown solid (28 mg, 71%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.29 (d, *J* = 15.7 Hz, 1H), 7.99 (dt, *J* = 8.1, 0.8 Hz, 1H), 7.76 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.48–7.42 (m, 3H), 7.31 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 1H), 7.27 (t, *J* = 7.9 Hz, 1H), 6.34 (d, *J* = 15.7 Hz, 1H), 4.93 (s, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.34, 165.58, 153.21, 141.46, 136.86, 136.29, 135.72, 133.11, 131.13, 129.31, 126.22, 125.94, 124.54, 122.80, 121.99, 121.13, 60.83, 32.52, 14.38. **HRMS** calcd. for $C_{19}H_{17}ClNO_2S_2^+$ $[M+H]^+$: 390.0384, Found: 390.0391. **X-ray** (single-crystal) Brown blocks of X-ray diffraction quality were obtained by vapor diffusion of ether into a saturated solution of **6d** in acetonitrile (CCDC 1905643).[23]



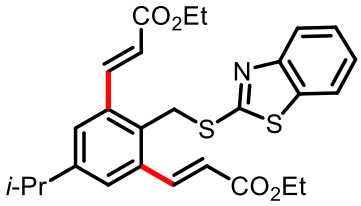
6d

ethyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)-5-isopropylphenyl)acrylate (6e): The title compound was prepared according to General Procedure 10. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded **6e** as a yellow solid (16.7 mg, 42%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 15.7 Hz, 1H), 7.92 (dt, *J* = 8.1, 0.8 Hz, 1H), 7.75 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.46–7.40 (m, 3H), 7.30 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 1H), 7.21 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 4.73 (s, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.90 (p, *J* = 6.9 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.25 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.84, 166.03, 153.25, 149.34, 141.54, 135.53, 134.00, 132.64, 131.24, 128.66, 126.19, 125.24, 124.47, 121.75, 121.16, 120.79, 60.71, 35.07, 34.03, 23.95, 14.42. **HRMS** calcd. for $C_{22}H_{24}NO_2S_2^+$ $[M+H]^+$: 398.1243, Found: 398.1246. **X-ray** (single-crystal) Yellow blocks of X-ray diffraction quality were obtained by vapor diffusion of ether into a saturated solution of **6e** in acetonitrile (CCDC 1905647).[23]



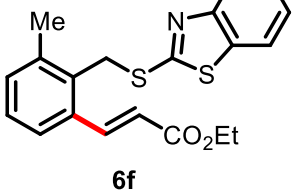
6e

diethyl 3,3'-(2-((benzothiazol-2-ylthio)methyl)-5-isopropyl-1,3-phenylene)(2*E*,2'*E*)-diacrylate (6e'): The title compound was prepared according to General Procedure 10. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded **6e'** as a yellow solid (14 mg, 28%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 15.7 Hz, 2H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.78–7.74 (m, 1H), 7.47–7.41 (m, 3H), 7.34–7.29 (m, 1H), 6.39 (d, *J* = 15.7 Hz, 2H), 4.85 (s, 2H), 4.22 (q, *J* = 7.2 Hz, 4H), 2.92 (p, *J* = 6.9 Hz, 1H), 1.30–1.23 (m, 12H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.53, 165.34, 153.21, 149.44, 141.75, 135.76, 135.61, 130.99, 127.15, 126.22, 124.56, 122.26, 121.94, 121.14, 60.80, 34.09, 31.53, 23.86, 14.38. **HRMS** calcd. for $C_{27}H_{30}NO_4S_2^+$ $[M+H]^+$: 496.1611, Found: 496.1610.



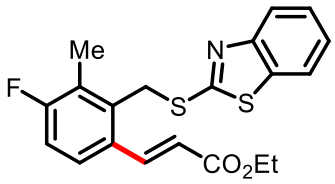
6e'

ethyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)-3-methylphenyl)acrylate (6f): The title compound was prepared according to General Procedure 8. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 370.1 [M+H], cone voltage 15V). Purification afforded **6f** as a yellow solid (26 mg, 69%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 15.7 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.47–7.41 (m, 2H), 7.34–7.29 (m, 1H), 7.24 (d, *J* = 5.4 Hz, 2H), 6.37 (d, *J* = 15.7 Hz, 1H), 4.79 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.49 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.74, 166.15, 153.30, 142.02, 138.63, 135.51, 135.15, 132.58, 132.37, 128.46, 126.23, 125.27, 124.53, 121.79, 121.63, 121.18, 60.69, 32.36, 19.96, 14.39. **HRMS** calcd. for $C_{20}H_{20}NO_2S_2^+$ $[M+H]^+$: 370.0930, Found: 370.0937.



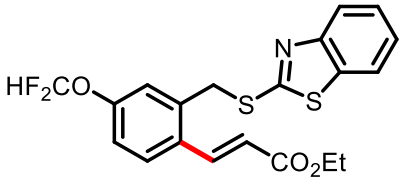
6f

ethyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)-4-fluoro-3-methylphenyl)acrylate (6g): The title compound was prepared according to General Procedure 8. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded **6g** as a yellow solid (25 mg, 64%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 15.7 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.77 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.47–7.39 (m, 2H), 7.35–7.30 (m, 1H), 7.02 (t, *J* = 8.8 Hz, 1H), 6.31 (d, *J* = 15.6 Hz, 1H), 4.79 (s, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.38 (d, *J* = 2.2 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.53, 163.01, 161.36, 153.21, 141.26, 141.25, 135.54, 135.32, 135.29, 131.04, 131.02, 126.34, 126.28, 125.68, 125.57, 124.63, 121.84, 121.26, 121.25, 121.20, 115.63, 115.48, 60.72, 32.16, 14.39, 11.09. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.79. **HRMS** calcd. for $C_{20}H_{19}FNO_2S_2^+$ $[M+H]^+$: 388.0836, Found: 388.0837. **X-ray** (single-crystal) Yellow blocks of X-ray diffraction quality were obtained by vapor diffusion of ether into a saturated solution of **6g** in acetonitrile (CCDC 1905650).[23]



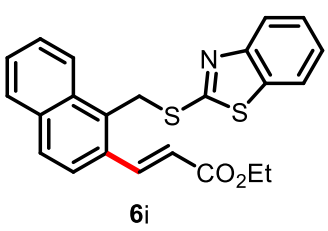
6g

ethyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)-4-(difluoromethoxy)phenyl)acrylate (6h): The title compound was prepared according to General Procedure 8. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded **6h** as a yellow solid (22.7 mg, 54%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.28 (d, *J* = 15.8 Hz, 1H), 7.97 (dt, *J* = 8.1, 0.8 Hz, 1H), 7.80–7.71 (m, 1H), 7.46–7.40 (m, 2H), 7.36–7.29 (m, 2H), 7.20 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.58 (t, *J* = 73.3 Hz, 1H), 6.37 (d, *J* = 15.7 Hz, 1H), 4.83 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.40, 165.54, 153.20, 150.48, 150.46, 150.44, 140.97, 136.73, 135.70, 129.34, 127.40, 126.23, 124.54, 124.10, 122.60, 121.95, 121.13, 119.87, 117.85, 116.12, 114.39, 60.84, 28.71, 14.38. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.49. **HRMS** calcd. for $C_{20}H_{18}F_2NO_3S_2^+$ $[M+H]^+$: 422.0691, Found: 422.0693.



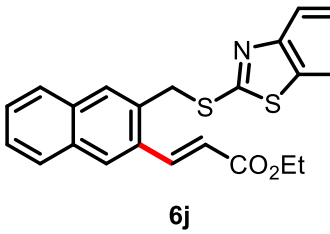
6h

ethyl (*E*)-3-(1-((benzothiazol-2-ylthio)methyl)naphthalen-2-yl)acrylate (6i): The title compound was prepared according to General Procedure 8. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded **6i** as a yellow solid (20.4 mg, 50%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.40 (d, *J* = 15.7 Hz, 1H), 8.24–8.21 (m, 1H), 8.00 (dt, *J* = 8.1, 0.8 Hz, 1H), 7.88–7.84 (m, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.78 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.59 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.54 (ddd, *J* = 7.9, 6.8, 1.2 Hz, 1H), 7.47 (ddd, *J* = 8.3, 7.3, 1.3 Hz, 1H), 7.34 (ddd, *J* = 8.2, 7.4, 1.2 Hz, 1H), 6.52 (d, *J* = 15.7 Hz, 1H), 5.30 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.79, 166.04, 153.27, 141.63, 135.59, 134.44, 132.21, 132.12, 131.09, 129.35, 128.95, 127.59, 127.22, 126.27, 124.61, 124.58, 123.93, 122.08, 121.87, 121.22, 60.80, 31.04, 14.44. **HRMS** calcd. for $C_{23}H_{20}NO_2S_2^+$ $[M+H]^+$: 406.0930, Found: 406.0934.

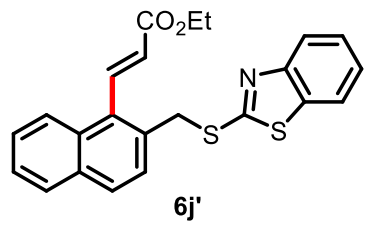


6i

ethyl (*E*)-3-(3-((benzothiazol-2-ylthio)methyl)naphthalen-2-yl)acrylate (6j) and **ethyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)naphthalen-1-yl)acrylate (6j'):** The title compound was prepared according to General Procedure 8. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded a 5:3 ratio of **(6j)** to **(6j')** as a yellow liquid (15.4 mg, 38%). Because all of the peaks belonging to each of the two isomers could not be clearly resolved, the analytical data below correspond to the mixture: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.32 (d, *J* = 16.2 Hz, 1H), 8.20 (d, *J* = 15.7 Hz, 2H), 8.09 (s, 2H), 8.03–7.98 (m, 3H), 7.94 (dd, *J* = 8.1, 3.5 Hz, 3H), 7.85–7.76 (m, 6H), 7.75 (d, *J* = 7.9 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.54–7.47 (m, 5H), 7.44 (ddt, *J* = 9.4, 8.2, 1.6 Hz, 3H), 7.33–7.28 (m, 3H), 6.55 (d, *J* = 15.7 Hz, 2H), 6.34 (d, *J* = 16.3 Hz, 1H), 4.91 (s, 3H), 4.83 (s, 2H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 5H). **^{13}C NMR**



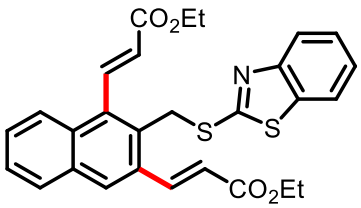
6j



6j'

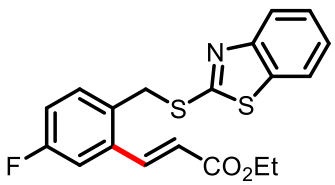
(150 MHz, $CDCl_3$) δ 166.69, 166.21, 165.98, 165.75, 153.24, 153.21, 141.73, 141.61, 135.58, 135.54, 133.88, 133.00, 132.95, 132.92, 132.27, 132.12, 131.65, 131.50, 130.19, 129.24, 128.47, 128.30, 127.88, 127.71, 127.50, 127.34, 127.08, 127.01, 126.51, 126.22, 125.43, 124.51, 124.50, 121.76, 121.48, 121.18, 121.17, 60.95, 60.75, 36.20, 35.90, 14.41, 14.40. **HRMS** calcd. for $C_{23}H_{20}NO_2S_2^+$ $[M+H]^+$: 406.0930, Found: 406.0936.

diethyl 3,3'-(2-((benzothiazol-2-ylthio)methyl)naphthalene-1,3-diyl)(2*E*,2'*E*)-diacrylate (6j''): The title compound was prepared according to General Procedure 8. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded **6j''** as a yellow solid (5.4 mg, 10%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.30 (d, *J* = 16.3 Hz, 1H), 8.23 (d, *J* = 15.6 Hz, 1H), 8.07 (s, 1H), 7.98–7.93 (m, 2H), 7.88–7.84 (m, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.54 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.46–7.42 (m, 1H), 7.34–7.30 (m, 1H), 6.52 (d, *J* = 15.6 Hz, 1H), 6.31 (d, *J* = 16.3 Hz, 1H), 4.96 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.49, 165.97, 165.36, 153.20, 141.92, 141.64, 135.59, 134.72, 132.82, 132.79, 132.01, 129.51, 128.93, 127.95, 127.92, 127.71, 127.27, 126.24, 125.67, 124.56, 122.39, 121.88, 121.16, 61.01, 33.55, 14.34. **HRMS** calcd. for $C_{28}H_{26}NO_4S_2^+$ $[M+H]^+$: 504.1298, Found: 504.1308. **X-ray** (single-crystal) Yellow blocks of X-ray diffraction quality were obtained by vapor diffusion of ether into a saturated solution of **6j''** in acetonitrile (CCDC 1905652).[23]



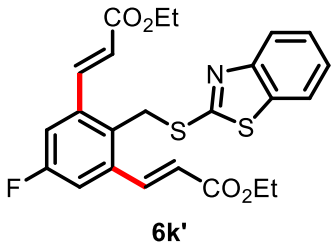
6j''

ethyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)-5-fluorophenyl)acrylate (6k): The title compound was prepared according to General Procedure 8. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 374.1 [M+H], cone voltage 15V). Purification afforded **6k** as a yellow solid (11.4 mg, 30%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 15.8, 1.4 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.50 (dd, *J* = 8.6, 5.6 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.29–7.23 (m, 1H), 7.03 (td, *J* = 8.2, 2.7 Hz, 1H), 6.38 (d, *J* = 15.7 Hz, 1H), 4.71 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.40, 165.38, 163.35, 161.71, 153.15, 140.12, 140.11, 136.19, 136.14, 135.57, 133.03, 132.98, 131.37, 131.35, 126.26, 124.60, 122.25, 121.80, 121.20, 117.28, 117.14, 113.78, 113.63, 60.92, 34.49, 14.39. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.51. **HRMS** calcd. for $C_{19}H_{17}FNO_2S_2^+$ $[M+H]^+$: 374.0679, Found: 374.0688.



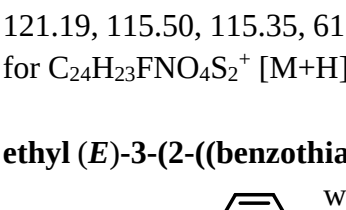
6k

diethyl 3,3'-(2-((benzothiazol-2-ylthio)methyl)-5-fluoro-1,3-phenylene)(2*E*,2'*E*)-diacrylate (6k'): The title compound was prepared according to General Procedure 8. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 472.1 [M+H], cone voltage 15V). Purification afforded **6k'** as a yellow liquid (4 mg, 9%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 15.9, 4.7 Hz, 2H), 7.96 (t, *J* = 6.7 Hz, 1H), 7.76 (t, *J* = 6.8 Hz, 1H), 7.44 (d, *J* = 6.9 Hz, 1H), 7.37–7.22 (m, 3H), 6.50–6.23 (m, 2H), 4.84 (s, 2H), 4.23 (t, *J* = 6.8 Hz, 4H), 1.27 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.12, 164.77, 163.09, 161.44, 153.12, 140.39, 140.37, 138.08, 138.03, 135.66, 129.75, 129.73, 126.29, 124.69, 123.59, 122.00, 121.19, 115.50, 115.35, 61.00, 31.16, 14.35. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.60. **HRMS** calcd. for $C_{24}H_{23}FNO_4S_2^+$ $[M+H]^+$: 472.1047, Found: 472.1050.



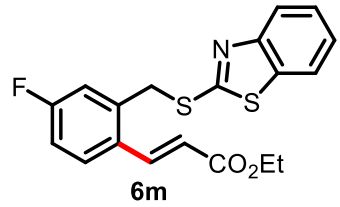
6k'

ethyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)-3-fluorophenyl)acrylate (6l): The title compound was prepared according to General Procedure 10. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded **6l** as an orange solid (13.9 mg, 37%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 15.8 Hz, 1H), 7.96 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.75 (ddd, *J* = 8.0, 1.3, 0.6 Hz, 1H), 7.43 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 7.40–7.35 (m, 1H), 7.34–7.27 (m, 2H), 7.11 (ddd, *J* = 9.5, 8.2, 1.2 Hz, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 4.81 (d, *J* = 1.8 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.44, 165.42, 162.54, 160.89, 153.21, 140.53, 140.50, 136.57, 136.55, 135.68, 129.66, 129.60, 126.22, 124.56, 123.08, 122.98, 122.84, 122.82, 122.40, 121.95, 121.14, 116.88, 116.73, 60.84, 27.76, 14.39. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.53. **HRMS** calcd. for $C_{19}H_{17}FNO_2S_2^+$ $[M+H]^+$: 374.0679, Found: 374.0686.

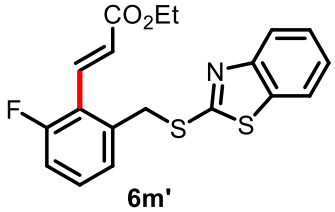


6l

ethyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)-4-fluorophenyl)acrylate (6m) and **ethyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)-6-fluorophenyl)acrylate (6m'):** The title compound was prepared according to General Procedure 9. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded a 7:2 mixture of **(6m)** to **(6m')** as a brown solid (11 mg, 29%). Because all of the peaks belonging to each of the two isomers could not be clearly resolved, the analytical data below correspond to the mixture: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 15.7 Hz, 3H), 7.92 (d, *J* = 8.2 Hz, 4H), 7.87 (d, *J* = 16.2 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 4H), 7.57 (dd, *J* = 8.7, 5.7 Hz, 3H), 7.43 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 4H), 7.37–7.27 (m, 9H), 7.09–7.03 (m, 1H), 7.01 (td, *J* = 8.3, 2.7 Hz, 3H), 6.62 (dd, *J* = 16.2, 1.2 Hz, 1H), 6.34 (d,



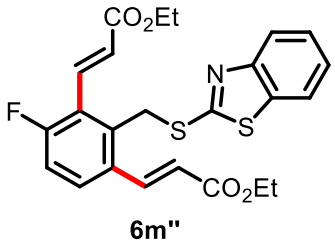
6m



6m'

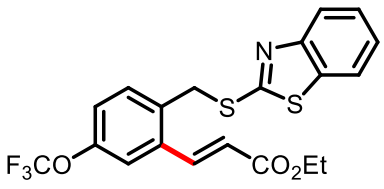
J = 15.7 Hz, 3H), 4.75 (s, 2H), 4.72 (s, 6H), 4.27–4.20 (m, 8H), 1.33–1.25 (m, 12H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.88, 166.65, 165.31, 165.12, 164.34, 162.68, 162.56, 160.88, 153.14, 153.10, 140.12, 138.21, 138.16, 137.83, 135.61, 134.94, 130.64, 130.57, 130.32, 130.29, 129.19, 129.14, 126.99, 126.81, 126.78, 126.28, 126.26, 125.69, 125.60, 124.63, 124.60, 124.23, 122.46, 122.18, 121.84, 121.82, 121.20, 120.90, 120.89, 117.98, 117.83, 116.13, 115.97, 115.88, 115.73, 60.84, 60.80, 35.21, 35.19, 34.66, 14.42, 14.38. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.39, -110.41, -110.41, -110.43, -110.44, -110.45, -110.66, -110.68, -110.69, -110.70. **HRMS** calcd. for $C_{19}H_{17}FNO_2S_2^+$ $[M+H]^+$: 374.0679, Found: 374.0683

diethyl 3,3'-(2-((benzothiazol-2-ylthio)methyl)-4-fluoro-1,3-phenylene)(2*E*,2'*E*)-diacrylate (6m''): The title compound was prepared according to General Procedure 9. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded **6m''** as a yellow solid (1.1 mg, 2%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 15.6 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 16.2 Hz, 1H), 7.78–7.74 (m, 1H), 7.54 (dd, *J* = 8.7, 5.3 Hz, 1H), 7.48–7.41 (m, 1H), 7.36–7.29 (m, 1H), 7.15–7.08 (m, 1H), 6.55 (dd, *J* = 16.2, 1.4 Hz, 1H), 6.32 (d, *J* = 15.7 Hz, 1H), 4.86 (s, 2H), 4.20 (qd, *J* = 7.1, 2.6 Hz, 4H), 1.25 (dt, *J* = 7.2, 3.6 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.46, 166.37, 164.64, 162.72, 161.02, 153.10, 140.64, 136.09, 136.07, 135.67, 134.85, 131.86, 131.84, 129.55, 129.48, 126.94, 126.87, 126.29, 124.69, 123.89, 123.80, 122.28, 122.02, 121.18, 116.62, 116.46, 60.93, 32.02, 29.85, 14.35. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.05. **HRMS** calcd. for $C_{24}H_{23}FNO_4S_2^+$ $[M+H]^+$: 472.1047, Found: 472.1052.



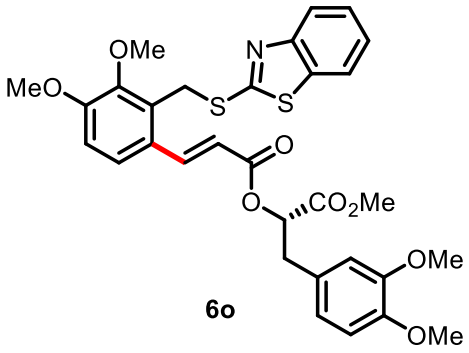
6m"

ethyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)-5-(trifluoromethoxy)phenyl)acrylate (6n): The title compound was prepared according to General Procedure 10. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded **6n** as a yellow solid (11.5 mg, 26%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 15.7 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.47–7.41 (m, 1H), 7.41–7.39 (m, 1H), 7.34–7.29 (m, 1H), 7.17 (dt, *J* = 8.3, 1.9 Hz, 1H), 6.40 (d, *J* = 15.7 Hz, 1H), 4.73 (s, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.29, 165.13, 153.10, 149.14, 139.90, 136.06, 135.61, 134.24, 132.73, 130.72, 126.29, 124.66, 123.08, 122.68, 122.29, 121.83, 121.37, 121.22, 119.66, 119.36, 117.95, 60.98, 34.31, 14.39. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.75. **HRMS** calcd. for $C_{20}H_{17}F_3NO_3S_2^+$ $[M+H]^+$: 440.0597, Found: 440.0605.



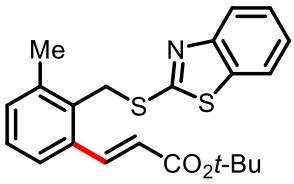
6n

(*R*)-3-(3,4-dimethoxyphenyl)-1-methoxy-1-oxopropan-2-yl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)-3,4-dimethoxyphenyl)acrylate (6o): The title compound was prepared on a 3.780 mmol scale according to General Procedure 9. The crude residue was purified by SiO_2 gel column chromatography (2.5% Et_2O/CH_2Cl_2). Purification afforded **6o** as a yellow solid (1.975 g, 86%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 15.6 Hz, 1H), 7.95–7.92 (m, 1H), 7.74 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.44–7.36 (m, 2H), 7.31–7.27 (m, 1H), 6.91 (d, *J* = 8.7 Hz, 1H), 6.78–6.71 (m, 3H), 6.34 (d, *J* = 15.7 Hz, 1H), 5.28 (dd, *J* = 8.4, 4.6 Hz, 1H), 4.83 (d, *J* = 1.1 Hz, 2H), 3.93 (s, 3H), 3.91 (s, 3H), 3.83 (s, 3H), 3.81 (s, 3H), 3.72 (s, 3H), 3.13–3.01 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.48, 166.22, 166.13, 154.39, 153.32, 148.91, 148.17, 148.12, 142.83, 135.50, 129.68, 128.52, 127.11, 126.20, 124.42, 123.20, 121.90, 121.70, 121.09, 117.66, 112.48, 112.40, 111.29, 73.35, 61.54, 56.00, 55.98, 55.96, 52.45, 37.24, 28.98. **HRMS** calcd. for $C_{31}H_{32}NO_8S_2^+$ $[M+H]^+$: 610.1564, Found: 610.1566.



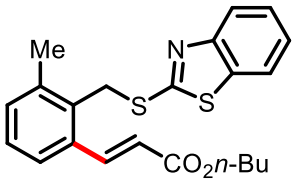
6o

***tert*-butyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)-3-methylphenyl)acrylate (6p):** The title compound was prepared according to General Procedure 8 with a reaction time of 24 h. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 398.1 [M+H], cone voltage 15V). Purification afforded **6p** as a brown solid (33 mg, 82%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 15.6 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.46–7.42 (m, 2H), 7.33–7.29 (m, 1H), 7.23 (d, *J* = 4.7 Hz, 2H), 6.31 (d, *J* = 15.7 Hz, 1H), 4.79 (s, 2H), 2.49 (s, 3H), 1.47 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.25, 166.08, 153.32, 140.94, 138.58, 135.45, 135.29, 132.36, 132.15, 128.40, 126.21, 125.22, 124.47, 123.41, 121.79, 121.15, 80.72, 32.37, 28.28, 19.95. **HRMS** calcd. for $C_{22}H_{24}NO_2S_2^+$ $[M+H]^+$: 398.1243, Found: 398.1256.



6p

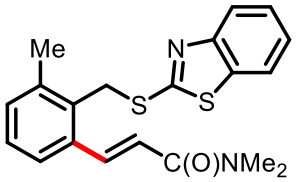
***n*-butyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)-3-methylphenyl)acrylate (6q):** The title compound was prepared according to General Procedure 10 with a reaction time of 24 h. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 398.1 [M+H], cone voltage 15V). Purification afforded **6q** as a yellow solid (25 mg, 63%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 15.7 Hz, 1H), 7.94 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.77 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.48–7.42 (m, 2H), 7.32 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 7.24 (d, *J* = 5.2 Hz, 2H), 6.37 (d, *J* = 15.7 Hz, 1H), 4.79 (s, 2H),



6q

4.15 (t, *J* = 6.7 Hz, 2H), 2.49 (s, 3H), 1.65–1.57 (m, 2H), 1.39–1.31 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.83, 166.14, 153.31, 141.96, 138.62, 135.48, 135.16, 132.51, 132.37, 128.46, 126.23, 125.25, 124.53, 121.79, 121.61, 121.18, 64.61, 32.35, 30.82, 19.96, 19.29, 13.82. **HRMS** calcd. for $C_{22}H_{24}NO_2S_2^+$ $[M+H]^+$: 398.1243, Found: 398.1256.

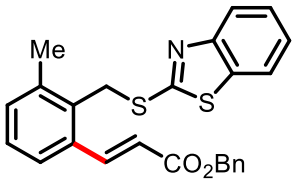
(***E***)**-3-(2-((benzothiazol-2-ylthio)methyl)-3-methylphenyl)-*N*,*N*-dimethylacrylamide (6r):** The



6r

title compound was prepared according to General Procedure 10. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 369.1 [M+H], cone voltage 15V). Purification afforded **6r** as a yellow solid (23 mg, 62%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 15.2 Hz, 1H), 7.95–7.90 (m, 1H), 7.79–7.75 (m, 1H), 7.43 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.39 (dd, *J* = 7.2, 1.9 Hz, 1H), 7.31 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 7.25–7.19 (m, 2H), 6.80 (d, *J* = 15.2 Hz, 1H), 4.78 (s, 2H), 3.09 (s, 3H), 3.02 (s, 3H), 2.50 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.55, 166.28, 153.32, 139.85, 138.66, 136.47, 135.42, 132.05, 131.64, 128.32, 126.19, 125.52, 124.43, 121.78, 121.59, 121.13, 37.53, 35.98, 32.78, 19.91. **HRMS** calcd. for $C_{20}H_{21}N_2OS_2^+$ $[M+H]^+$: 369.1090, Found: 369.1100.

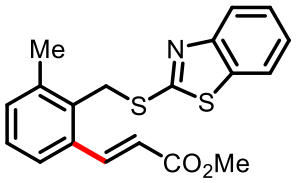
(***E***)**-3-(2-((benzothiazol-2-ylthio)methyl)-3-methylphenyl)-*N*,*N*-dimethylacrylamide (6s):** The



6s

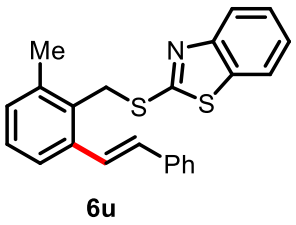
title compound was prepared according to General Procedure 10. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 398.1 [M+H], cone voltage 15V). Purification afforded **6s** as a brown solid (26 mg, 60%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 15.7 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.82–7.73 (m, 1H), 7.47–7.40 (m, 2H), 7.38–7.21 (m, 8H), 6.42 (d, *J* = 15.7 Hz, 1H), 5.20 (s, 2H), 4.79 (s, 2H), 2.49 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.52, 166.06, 153.30, 142.62, 138.66, 136.11, 135.50, 134.99, 132.61, 132.50, 128.65, 128.47, 128.29, 126.24, 125.25, 124.53, 121.82, 121.17, 121.12, 66.48, 32.34, 19.96. **HRMS** calcd. for $C_{25}H_{22}NO_2S_2^+$ $[M+H]^+$: 432.1086, Found: 432.1090.

methyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)-3-methylphenyl)acrylate (6t): The title compound was prepared according to General Procedure 10. The crude residue was purified by preparative TLC (10% EtOAc/hexanes). Purification afforded **6t** as a yellow liquid (18 mg, 50%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 15.7 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.50–7.40 (m, 2H), 7.35–7.29 (m, 1H), 7.26–7.22 (m, 2H), 6.37 (d, *J* = 15.7 Hz, 1H), 4.79 (s, 2H), 3.74 (s, 3H), 2.49 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.15, 166.13, 153.29, 142.29, 138.64, 135.52, 135.06, 132.65, 132.44, 128.47, 126.24, 125.27, 124.54, 121.79, 121.18, 51.86, 32.31, 19.95. **HRMS** calcd. for $C_{19}H_{18}NO_2S_2^+$ $[M+H]^+$: 356.0774, Found: 356.0788.



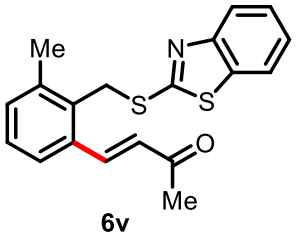
6t

(*E*)-2-((2-methyl-6-styrylbenzyl)thio)benzothiazole (6u): The title compound was prepared according to General Procedure 10 with a reaction time of 24 h. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 55–75% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 374.1 [M+H], cone voltage 15V). Purification afforded **6u** as a yellow solid (19 mg, 50%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.96–7.91 (m, 1H), 7.80–7.75 (m, 1H), 7.54 (d, *J* = 16.0 Hz, 1H), 7.52–7.49 (m, 1H), 7.45 (ddd, *J* = 8.3, 5.5, 1.5 Hz, 3H), 7.33 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 1H), 7.30–7.19 (m, 4H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 16.0 Hz, 1H), 4.86 (s, 2H), 2.50 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.85, 153.35, 138.08, 137.43, 135.52, 132.07, 131.19, 130.07, 128.76, 128.34, 127.90, 126.88, 126.24, 126.14, 124.48, 121.72, 121.21, 32.74, 20.06. **HRMS** calcd. for $C_{23}H_{20}NS_2^+$ $[M+H]^+$: 374.1032, Found: 374.1041. **X-ray** (single-crystal) Yellow blocks of X-ray diffraction quality were obtained by vapor diffusion of ether into a saturated solution of **6u** in acetonitrile (CCDC 1905649).[23]



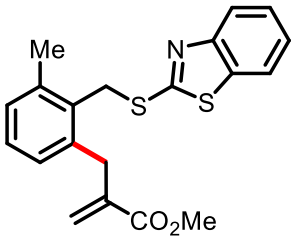
6u

(*E*)-4-(2-((benzothiazol-2-ylthio)methyl)-3-methylphenyl)but-3-en-2-one (6v): The title compound was prepared according to General Procedure 10 with a reaction time of 24 h. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 340.1 [M+H], cone voltage 15V). Purification afforded **6v** as a yellow solid (15.5 mg, 46%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 16.0 Hz, 1H), 7.95–7.89 (m, 1H), 7.78 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.45 (ddd, *J* = 8.0, 5.8, 2.2 Hz, 2H), 7.33 (td, *J* = 7.7, 1.1 Hz, 1H), 7.26 (d, *J* = 5.9 Hz, 2H), 6.61 (d, *J* = 16.0 Hz, 1H), 4.83 (s, 2H), 2.50 (s, 3H), 2.30 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.53, 165.93, 153.19, 140.90, 138.56, 135.49, 135.01, 132.92, 132.57, 130.44, 128.52, 126.33, 125.23, 124.65, 121.72, 121.24, 32.22, 27.41, 20.00. **HRMS** calcd. for $C_{19}H_{18}NOS_2^+$ $[M+H]^+$: 340.0824, Found: 340.0836.



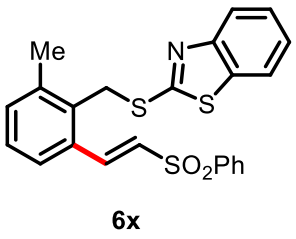
6v

methyl 2-(2-((benzothiazol-2-ylthio)methyl)-3-methylbenzyl)acrylate (6w): The title compound was prepared according to General Procedure 10 using methyl methacrylate as the alkene. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 370.1 [M+H], cone voltage 15V). Purification afforded **6w** as a yellow solid (16 mg, 44%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.80–7.69 (m, 1H), 7.45–7.40 (m, 1H), 7.35–7.28 (m, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.26 (d, *J* = 1.6 Hz, 1H), 5.27 (d, *J* = 1.6 Hz, 1H), 4.67 (s, 2H), 3.80 (s, 2H), 3.70 (s, 3H), 2.47 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.41, 167.01, 153.34, 139.79, 138.53, 138.19, 135.39, 132.03, 129.46, 128.66, 128.32, 126.72, 126.20, 124.40, 121.63, 121.15, 52.10, 35.32, 32.55, 20.08. **HRMS** calcd. for $C_{20}H_{20}NO_2S_2^+$ $[M+H]^+$: 370.0930, Found: 370.0938.



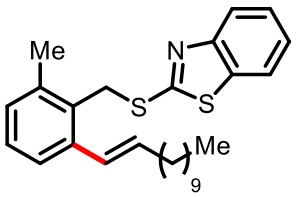
6w

methyl 2-(2-((benzothiazol-2-ylthio)methyl)-3-methylbenzyl)acrylate (6x): The title compound was prepared according to General Procedure 8 with a reaction time of 24 h. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 438.1 [M+H], cone voltage 15V). Purification afforded **6x** as a yellow solid (18.5 mg, 44%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 15.1 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.91–7.86 (m, 2H), 7.82–7.78 (m, 1H), 7.53–7.41 (m, 4H), 7.38–7.30 (m, 2H), 7.26 (d, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 15.1 Hz, 1H), 4.77 (s, 2H), 2.48 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.52, 153.26, 140.48, 140.40, 138.89, 135.42, 133.46, 133.16, 133.11, 133.08, 130.78, 129.37, 128.57, 127.89, 126.37, 125.69, 124.67, 121.97, 121.19, 32.10, 19.97. **HRMS** calcd. for $C_{23}H_{20}NO_2S_3^+$ $[M+H]^+$: 438.0651, Found: 438.0660. **X-ray** (single-crystal) Yellow blocks of X-ray diffraction quality were obtained by vapor diffusion of ether into a saturated solution of **6x** in acetonitrile (CCDC 1905646).[23]



6x

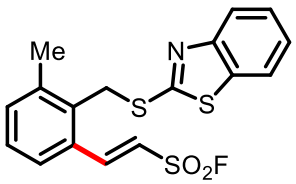
(***E***)**-2-((2-(dodec-1-en-1-yl)-6-methylbenzyl)thio)benzothiazole (6y):** The title compound was prepared according to General Procedure 10. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 24 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 438.2 [M+H], cone voltage 15V). Purification afforded **6y** as



6y

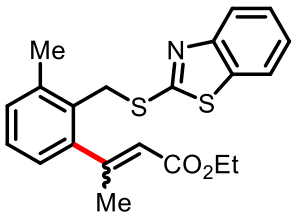
a yellow solid (16.5 mg, 38%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 2H), 5.56–5.45 (m, 2H), 4.71 (s, 2H), 3.55 (d, *J* = 5.1 Hz, 2H), 2.47 (s, 3H), 2.10 (q, *J* = 7.0 Hz, 2H), 1.36–1.10 (m, 14H), 0.87 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.14, 153.45, 141.13, 138.32, 135.35, 131.63, 131.22, 128.80, 128.32, 127.74, 127.70, 127.62, 126.20, 124.38, 121.64, 121.12, 32.70, 32.05, 31.42, 29.74, 29.72, 29.65, 29.52, 29.45, 27.60, 22.83, 19.98, 14.28. **HRMS** calcd. for $C_{27}H_{36}NS_2^+$ $[M+H]^+$: 438.2284, Found: 438.2295.

(***E***)**-2-(2-((benzothiazol-2-ylthio)methyl)-3-methylphenyl)ethene-1-sulfonyl fluoride (6z):** The title compound was prepared according to General Procedure 10. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 380.0 [M+H], cone voltage 15V). Purification afforded **6z** as a yellow solid (11.4 mg, 30%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.55 (d, *J* = 15.2 Hz, 1H), 8.01–7.96 (m, 1H), 7.77 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.46 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.35–7.28 (m, 2H), 6.83 (dd, *J* = 15.2, 2.3 Hz, 1H), 4.79 (s, 2H), 2.52 (s, 3H). **^{13}C NMR** δ 164.97, 153.11, 147.06, 147.04, 139.35, 135.54, 134.62, 134.54, 131.42, 128.75, 126.39, 125.79, 124.75, 122.03, 121.19, 120.85, 120.67, 31.72, 20.10. **^{19}F NMR** (376 MHz, $CDCl_3$) δ 61.01. **HRMS** calcd. for $C_{17}H_{15}FNO_2S_3^+$ $[M+H]^+$: 380.0244, Found: 380.0253.



6z

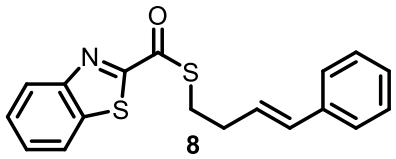
ethyl 3-(2-((benzothiazol-2-ylthio)methyl)-3-methylphenyl)but-2-enoate (6aa): The title compound was prepared according to General Procedure 10 with a reaction time of 24 h. The crude residue was purified by preparative TLC (20% EtOAc/hexanes). Purification afforded **6aa** as a yellow solid (7.4 mg, 19%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.46–7.40 (m, 1H), 7.33–7.29 (m, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 6.98 (dd, *J* = 7.5, 1.5 Hz, 1H), 5.84 (q, *J* = 1.5 Hz, 1H), 4.66 (s, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.52 (d, *J* = 1.5 Hz, 3H), 2.49 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.63, 166.38, 156.87, 153.29, 145.51, 138.76, 135.36, 130.28, 129.46, 128.11, 126.21, 125.55, 124.42, 121.66, 121.13, 120.38, 60.00, 33.57, 21.92, 19.94, 14.35. **HRMS** calcd. for $C_{21}H_{22}NO_2S_2^+$ $[M+H]^+$: 384.1087, Found: 384.1087.



6aa

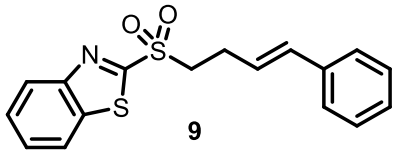
Characterization Data for Productive (BT)S Removal/Transformation

(***E***)**-S-(4-phenylbut-3-en-1-yl) benzothiazole-2-carbothioate (8):** The title compound was prepared following a literature procedure.[13] To a 25-mL round-bottom flask equipped with a magnetic stir bar were added (*E*)-2-((4-phenylbut-3-en-1-yl)thio)benzothiazole (**2a**) (0.500 mmol, 1 equiv), $Pd(PPh_3)_4$ (5 mol%), 1,1'-bis(diphenylphosphino)ferrocene (5 mol%), $Zn(OAc)_2$ (0.125 mmol, 0.25 equiv), and K_3PO_4 (0.125 mmol, 0.25 equiv). The flask was sealed with a rubber septum and filled with N_2. To a 4-mL vial charged with MeCN (1 mL) was added *t*BuCN (1.0 mmol, 2 equiv). The *t*BuCN solution was then added via syringe into the 25-mL round-bottom flask. The reaction was heated to 90 ° C and allowed to stir for 24 h. The reaction was cooled to room temperature and quenched with 1 N HCl (5 mL) and allowed to stir at room temperature for 1 h. The organic materials were separated by addition of H_2O (25 mL), followed by extraction with EtOAc (3 × 10 mL). The organic layer was dried over Na_2SO_4, and after filtration the solvent was removed *in vacuo,* and the crude residue was purified by preparative TLC (10% Et_2O/hexanes). Purification afforded **8** as a yellow solid (83 mg, 51%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.58 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.53 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.38–7.33 (m, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.24–7.19 (m, 1H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.26 (dt, *J* = 15.8, 7.0 Hz, 1H), 3.29 (t, *J* = 7.3 Hz, 2H), 2.65 (qd, *J* = 7.2, 1.5 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 186.74, 164.35, 153.09, 137.28, 136.66, 132.36, 128.66, 127.78, 127.46, 127.32, 126.32, 125.56, 122.45, 32.84, 29.05. **HRMS** calcd. for $C_{18}H_{16}NOS_2^+$ $[M+H]^+$: 326.0668, Found: 326.0668.



8

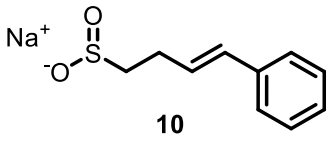
(***E***)**-2-((4-phenylbut-3-en-1-yl)sulfonyl)benzothiazole (9):** The title compound was prepared following a literature procedure.[14] To a 100-mL round-bottom flask equipped with a magnetic stir bar were added (*E*)-2-((4-phenylbut-3-en-1-yl)thio)benzothiazole (**2a**) (3.00 mmol, 1 equiv), 30% aqueous H_2O_2 (6.0 mL, 6 equiv), ammonium heptamolybdate tetrahydrate (0.060 mmol, 1 mol%), and ethanol (50 mL, 0.06 M). The reaction was stirred at room temperature for 12 h. The organic materials were separated by addition of H_2O (40 mL), followed by extraction with EtOAc (3 × 20 mL). The organic solution was washed with brine (20 mL) and dried over Na_2SO_4. After filtration, the solvent was removed *in vacuo,* and **9** was obtained as a yellow solid (962 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.3 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.63 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.57 (td, *J* = 7.6, 7.1, 1.2 Hz, 1H), 7.21 (dtd, *J* = 15.2, 8.2, 7.8, 6.2 Hz, 5H), 6.43 (d, *J* = 15.9 Hz, 1H), 6.07 (dt, *J* = 15.7, 7.0 Hz, 1H), 3.69 (dd, *J* = 8.7, 6.8 Hz, 2H), 2.82 (qd, *J* = 7.5, 1.5 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.97, 152.87, 136.97, 136.57, 133.10, 128.64, 128.20, 127.80, 127.75, 126.22, 125.59, 124.53, 122.46, 54.40, 26.32. **HRMS** calcd. for $C_{17}H_{16}NO_2S_2^+$ $[M+H]^+$: 330.0617, Found: 330.0622. **X-ray** (single-crystal)



9

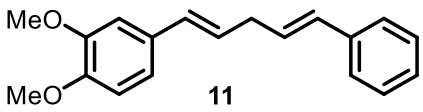
Colorless blocks of X-ray diffraction quality were obtained by vapor diffusion of ether into a saturated solution of **9** in acetonitrile (CCDC 1905644).[23]

Sodium (*E*)-5-phenylpent-4-enoate (10): The title compound was prepared following a literature procedure.[14] To a 10-mL round-bottom flask equipped with a stir bar was added (*E*)-2-((4-phenylbut-3-en-1-yl)sulfonyl)benzothiazole (**9**) (0.500 mmol, 1 equiv) in ethanol (1 mL, 0.1 M). $NaBH_4$ (1.0 mmol, 2 equiv) was added and allowed to stir at room temperature for 6 h. The solution was then concentrated *in vacuo,* and hexanes were added to the crude product leading to formation of the desired product as a crystal. The crystal was washed with hexanes then dried *in vacuo,* and **10** was obtained as a white solid (10.9 mg, >95%).[13] **^{1}H NMR** (600 MHz, D_2O) δ 7.46 (d, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 6.55 (dd, *J* = 16.1, 3.6 Hz, 1H), 6.43–6.34 (m, 1H), 2.51 (s, 3H). **^{13}C NMR** (150 MHz, Deuterium Oxide) δ 138.09, 130.99, 129.88, 129.52, 128.02, 126.67, 60.62, 26.19. **HRMS** calcd. for $C_{10}H_{13}O_2S^+$ $[M+2H–Na]^+$: 197.0636, Found: 197.0635.



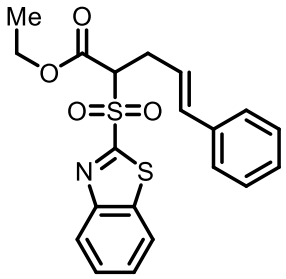
10

1,2-dimethoxy-4-((1*E*,4*E*)-5-phenylpenta-1,4-dien-1-yl)benzene (11): In a 50-mL round-bottom flask, solution of LDA in THF (1.800 mmol, 2.5M) was cooled to –78 ° C and added dropwise to a precooled solution of (*E*)-2-((4-phenylbut-3-en-1-yl)sulfonyl)benzothiazole (**9**) (1.500 mmol, 1.0 equiv) and 3,4-dimethoxybenzaldehyde (1.500 mmol, 1.0 equiv) in THF (15 mL, 0.1 M). The reaction was stirred for 90 min at –78 ° C, during which it turned a bright orange color. The reaction was then warmed to room temperature and stirred for 30 min, at which point it turned yellow. The organic solution was diluted with Et_2O (5 mL) and washed with brine (5 mL). The aqueous layer was extracted with Et_2O (3 × 5 mL), combined with the organic layer, and dried with Na_2SO_4. The solvent was removed *in vacuo*. The crude residue was purified by SiO_2 gel column chromatography (15% EtO_2/hexanes). Purification afforded **11** as a yellow solid (228 mg, 54%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.94 (s, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.42 (d, *J* = 15.7 Hz, 1H), 6.34–6.27 (m, 1H), 6.23–6.09 (m, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.12 (t, *J* = 6.1 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.12, 148.55, 137.68, 131.07, 130.83, 130.76, 128.65, 128.52, 127.21, 126.43, 126.18, 119.14, 111.27, 108.71, 56.05, 55.92, 36.29. **HRMS** calcd. for $C_{19}H_{20}O_2Na^+$ $[M+Na]^+$: 303.1356, Found: 303.1360.



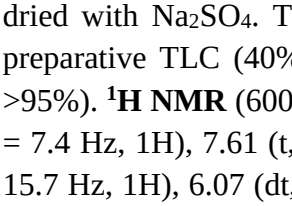
11

ethyl (*E*)-2-(benzothiazol-2-ylsulfonyl)-5-phenylpent-4-enoate (12-I): The title compound was prepared following a literature procedure.[16] To a flame-dried 10-mL round-bottom flask equipped with a stir bar was added (*E*)-2-((4-phenylbut-3-en-1-yl)sulfonyl)benzothiazole (**9**) (0.100 mmol, 1 equiv) in THF (1 mL, 0.1 M) and cooled to –78 ° C. LiHMDS (0.1 mL, 2.2 equiv; 1 M sol. in THF) was added followed quickly by ethyl carbonocyanidate (0.120 mmol, 1.2 equiv). The reaction was allowed to stir at –78 ° C for 30 min. The solution was warmed to 0 ° C in an ice bath within 1 h and stirred for an additional 1 h before addition of a saturated aqueous solution of NH_4Cl (10 mL) was added. The aqueous layer was extracted with Et_2O (3 × 5 mL), and the combined organic layers were dried with Na_2SO_4. The solvent was removed *in vacuo*, and the crude residue was purified by preparative TLC (40% EtOAc/hexanes). Purification afforded **12-I** as a yellow solid (40.1 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 1.8 Hz, 4H), 7.24–7.19 (m, 1H), 6.53 (d, *J* = 15.7 Hz, 1H), 6.07 (dt, *J* = 15.2, 7.2 Hz, 1H), 4.60 (dd, *J* = 9.6, 5.2 Hz, 1H), 4.16 (qq, *J* = 7.4, 3.7 Hz, 2H), 3.21–3.09 (m, 2H), 1.09 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.52, 164.39, 152.79, 137.33, 136.56, 134.81, 128.69, 128.43, 127.95, 127.92, 126.41, 125.85, 122.58, 122.43, 69.40, 62.89, 29.93, 13.98. **HRMS** calcd. for $C_{20}H_{20}NO_4S_2^+$ $[M+H]^+$: 402.0834, Found: 402.0833.



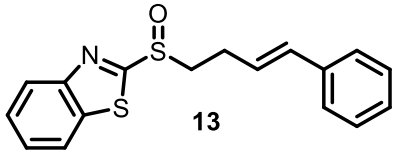
12-I

ethyl (*E*)-5-phenylpent-4-enoate (12): The title compound was prepared following a literature procedure.[16] To a 10-mL round-bottom flask equipped with a stirbar was added ethyl (*E*)-2-(benzothiazol-2-ylsulfonyl)-5-phenylpent-4-enoate (**12-I**) (0.100 mmol, 1 equiv) in THF (1 mL, 0.1 M). Zinc dust (0.500 mmol, 5 equiv) was added, and the reaction mixture was cooled to 0 ° C. AcOH (0.5 mL, excess) was added, and the reaction was allowed to warm to room temperature and stir for 8 h. EtOAc (10 mL) was added, and the crude mixture was filtered through a pad of Celite, which was washed with EtOAc. The combined filtrates were washed with brine (10 mL) and the organic layer was dried with Na_2SO_4. The solvent was removed *in vacuo*, and the crude residue was purified by preparative TLC (5% EtOAc/hexanes). Purification afforded **12** as a yellow oil (17.4 mg, 85%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.21 (dt, *J* = 15.8, 6.7 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.54 (q, *J* = 7.2 Hz, 2H), 2.48 (t, *J* = 7.0 Hz, 2H), 1.29–1.22 (m, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.14, 137.54, 131.08, 128.65, 127.27, 126.20, 60.55, 34.23, 29.86, 28.46, 14.42. **HRMS** calcd. for $C_{13}H_{17}O_2^+$ $[M+H]^+$: 205.1229, Found: 205.1230.



12

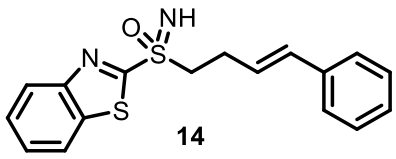
(***E***)**-2-((4-phenylbut-3-en-1-yl)sulfinyl)benzothiazole (13):** To a 25-mL round-bottom flask equipped with a magnetic stir bar was charged (*E*)-2-((4-phenylbut-3-en-1-yl)thio)benzothiazole (**2a**) (0.500 mmol, 1 equiv) and DCM (5 mL, 0.1 M). The mixture was cooled to 0 ° C. A solution of mCPBA (0.5 mmol, 1 equiv) in DCM (5 mL, 0.1 M) was then added dropwise. The reaction was stirred for 4 h. The organic materials were separated by



13

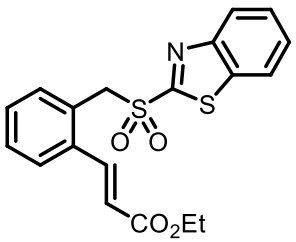
addition of H_2O (25 mL), followed by extraction with EtOAc (3 × 10 mL). The organic layer was dried over Na_2SO_4, and after filtration the crude residue was purified by SiO_2 gel column chromatography (40% EtOAc/hexanes). Purification afforded **13** as a white solid (131 mg, 82%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.59–7.55 (m, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.27–7.17 (m, 5H), 6.49 (d, *J* = 15.7 Hz, 1H), 6.15 (dt, *J* = 15.7, 7.0 Hz, 1H), 3.42 (ddd, *J* = 13.3, 9.1, 6.6 Hz, 1H), 3.35 (ddd, *J* = 13.8, 8.9, 5.7 Hz, 1H), 2.88 (h, *J* = 8.5, 7.8 Hz, 1H), 2.66 (dt, *J* = 14.9, 8.1 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 177.56, 154.10, 136.86, 136.19, 133.09, 128.66, 127.64, 127.09, 126.33, 126.25, 125.67, 124.07, 122.42, 55.91, 25.10. **HRMS** calcd. for $C_{17}H_{16}NOS_2^+$ $[M+H]^+$: 314.0668, Found: 314.0672.

(***E***)**-benzothiazol-2-yl(imino)(4-phenylbut-3-en-1-yl)-λ^6-sulfanone (14):** The title compound was prepared following a literature procedure.[17] To a 4-mL vial equipped with a magnetic stir bar were added (*E*)-2-((4-phenylbut-3-en-1-yl)sulfinyl)benzothiazole (**13**) (0.100 mmol, 1 equiv), $PhI(OAc)_2$ (0.300 mmol, 3 equiv), and ammonium acetate (0.600 mmol, 6 equiv). The reagents were dissolved in MeOH (1 mL, 0.1 M) and allowed to stir at room temperature for 30 min. The solvent was removed *in vacuo*, and the crude residue was purified by preparative TLC (5% EtOAc/hexanes). Purification afforded **14** as a yellow solid (20 mg, 61%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.60 (dt, *J* = 38.0, 7.5 Hz, 2H), 7.23 (td, *J* = 12.5, 11.3, 7.4 Hz, 5H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.10 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.70 (qdd, *J* = 14.5, 9.7, 6.0 Hz, 2H), 3.45 (s, 1H), 2.86 (dh, *J* = 30.9, 8.1, 7.4 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.68, 153.15, 137.73, 136.70, 132.91, 128.63, 127.81, 127.66, 127.58, 126.21, 125.46, 124.90, 122.39, 55.57, 26.67. **HRMS** calcd. for $C_{17}H_{17}N_2OS_2^+$ $[M+H]^+$: 329.0782, Found: 329.0780.



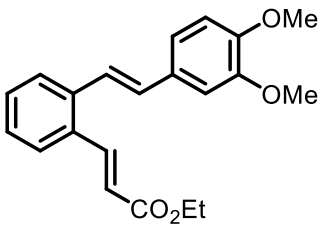
14

ethyl (*E*)-3-(2-((benzothiazol-2-ylsulfonyl)methyl)phenyl)acrylate (15): To a 10-mL round-bottom flask equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)phenyl)acrylate (**6a**) (0.1 mmol, 1 equiv), 30% aqueous H_2O_2 (0.2 mL, 6 equiv), ammonium heptamolybdate tetrahydrate (0.005 mmol, 5 mol%), and ethanol (2 mL, 0.05 M). The reaction was stirred at room temperature for 12 h. The organic materials were separated by addition of H_2O (25 mL), followed by extraction with EtOAc (3 × 10 mL). The organic solution was washed with brine (10 mL) and dried over Na_2SO_4. After filtration, the solvent was removed *in vacuo*, and **15** was obtained as a white solid (29 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.2 Hz, 1H), 7.93 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.83 (d, *J* = 15.7 Hz, 1H), 7.63 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.57 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 7.50 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.40–7.32 (m, 3H), 6.07 (d, *J* = 15.6 Hz, 1H), 4.91 (s, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.04, 164.56, 152.79, 140.25, 137.52, 135.72, 133.21, 130.27, 130.01, 128.18, 127.74, 127.43, 125.90, 125.80, 125.77, 122.31, 121.75, 60.73, 58.17, 14.42. **HRMS** calcd. for $C_{19}H_{18}NO_4S_2^+$ $[M+H]^+$: 388.0672, Found: 388.0681.



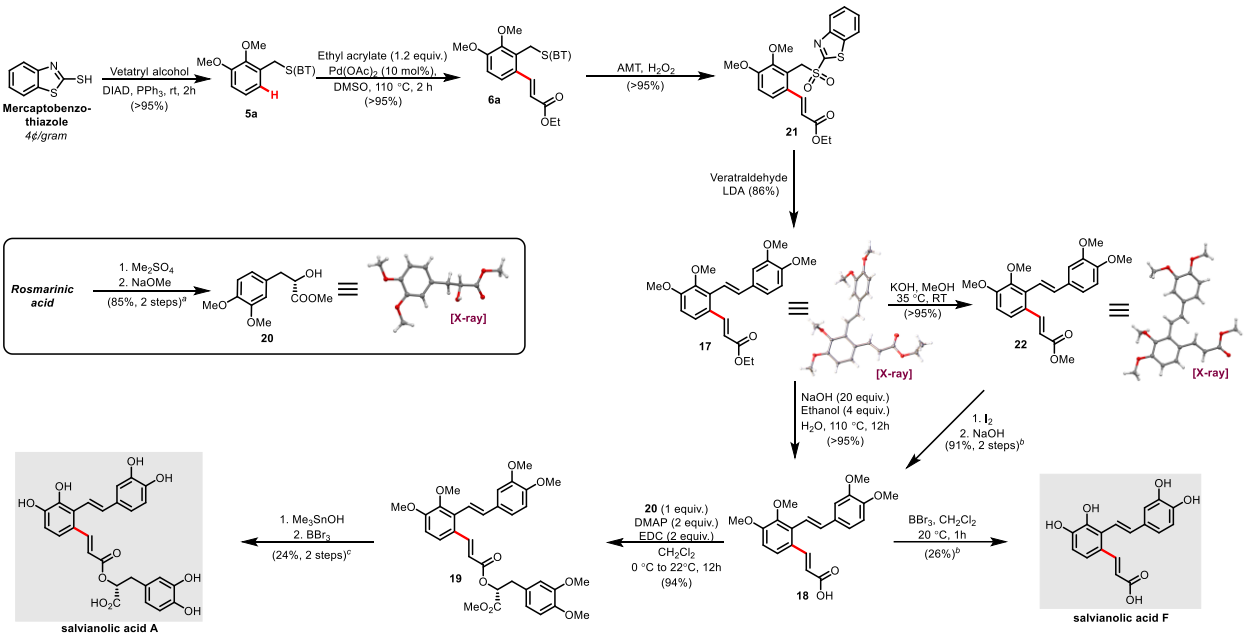
15

ethyl (*E*)**-3-(2-((benzothiazol-2-ylsulfonyl)methyl)phenyl)acrylate (16):** A solution of LDA in THF (0.100 mmol, 2.5M) was cooled to −78 ° C and added dropwise to a precooled solution of ethyl (*E*)-3-(2-((benzothiazol-2-ylsulfonyl)methyl)phenyl)acrylate (**15**) (0.100 mmol, 1 equiv) and 3,4-dimethoxybenzaldehyde (0.090 mmol, 0.9 equiv) in THF (0.9 mL, 0.2 M). The reaction was stirred for 90 min at −78 ° C, during which time it turned a bright orange color. The reaction was then warmed to room temperature and stirred for 30 min, at which point it turned yellow. The organic solution was diluted with Et_2O (5 mL) and washed with brine (5 mL). The aqueous layer was extracted with Et_2O (3 × 5 mL), combined with the organic layer, and dried with Na_2SO_4. The solvent was removed *in vacuo*. The crude residue was purified by mass-directed prep LC. The crude material was purified on a Waters Autopurification LC with a Waters BEH C18 column (19×160 mm, 5 mm) using a 0.1% aqueous formic acid:acetonitrile gradient (30 mL/min, main segment of gradient at 65–95% acetonitrile over 8 min) at ambient temperature. Fractionation was triggered by a Waters QDa single quadrupole mass spec in ESI+ (m/z = 339.2 [M+H], cone voltage 15V). Purification afforded **16** as a yellow solid (47.6 mg, 78%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 15.8 Hz, 1H), 7.59 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.56 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H), 7.31–7.26 (m, 3H), 7.11–7.06 (m, 2H), 6.93 (d, *J* = 16.0 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 3.96 (s, 3H), 3.92 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.07, 149.45, 149.31, 142.61, 137.94, 132.79, 132.64, 130.42, 130.16, 127.61, 127.41, 127.00, 123.79, 120.40, 120.35, 111.39, 109.31, 60.67, 56.13, 14.49. **HRMS** calcd. for $C_{21}H_{23}O_4^+$ $[M+H]^+$: 339.1591, Found: 339.1599.



16

Formal Synthesis of (+)-Salvianolic Acid A and Salvianolic Acid F

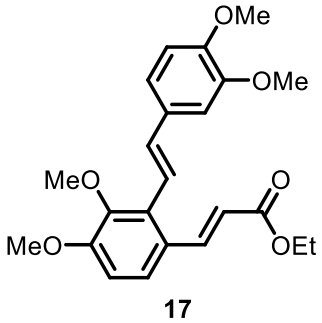


Scheme S9. Total Synthesis of (+)-salvianolic acid A and salvianolic acid F

[a]Rosmarinic acid global methylation and hydrolysis was performed according to a literature procedure (Ref. 18). [b]Ester demethylation and global salvianolic acid F demethylation were performed according to a literature procedure (Ref. 19) [c]Global salvianolic acid A demethylation was performed according to a literature procedure (Ref. 20).

Characterization Data for Total Synthesis

ethyl (*E*)-3-(2-((*E*)-3,4-dimethoxystyryl)-3,4-dimethoxyphenyl)acrylate (17): In a 100-mL round-bottom flask, solution of LDA in THF (4.830 mmol, 2.5M) was cooled to −78 ° C and added dropwise to a precooled solution of ethyl (*E*)-3-(2-((benzothiazol-2-ylsulfonyl)methyl)-3,4-dimethoxyphenyl)acrylate (**21**) (4.830 mmol, 1.0 equiv) and 3,4-dimethoxybenzaldehyde (4.830 mmol, 1.0 equiv) in THF (48 mL, 0.1 M). The reaction was stirred for 90 min at −78 ° C, during which it turned a bright orange color. The reaction was then warmed to room temperature and stirred for 30 min, at which point it turned yellow. The organic solution was diluted with Et_2O (5 mL) and washed with brine (5 mL). The aqueous layer was



17

extracted with Et_2O (3 × 5 mL), combined with the organic layer, and dried with Na_2SO_4. The solvent was removed *in vacuo*. The crude residue was purified by SiO_2 gel column chromatography (25% EtO_2/toluene). Purification afforded **17** as a yellow solid (1.66 g, 86%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 15.8 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 1H), 7.19 (d, *J* = 16.4 Hz, 1H), 7.13–7.04 (m, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 16.4 Hz, 1H), 6.32 (d, *J* = 15.8 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 3.94 (s, 3H), 3.94 (s, 3H), 3.81 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.27, 153.97, 149.42, 149.27, 147.08, 144.03, 137.19, 133.36, 130.72, 126.80, 123.98, 120.31, 119.83, 117.75, 111.33, 111.24, 109.19, 60.61, 60.40, 56.14, 56.10, 56.04, 14.50. **HRMS** calcd. for $C_{23}H_{27}O_6^+$ $[M+H]^+$: 399.1802, Found: 399.1812. **X-ray** (single-crystal) Yellow blocks of X-ray diffraction quality were obtained by vapor diffusion of ether into a saturated solution of **17** in acetonitrile (CCDC 1905651).[23]

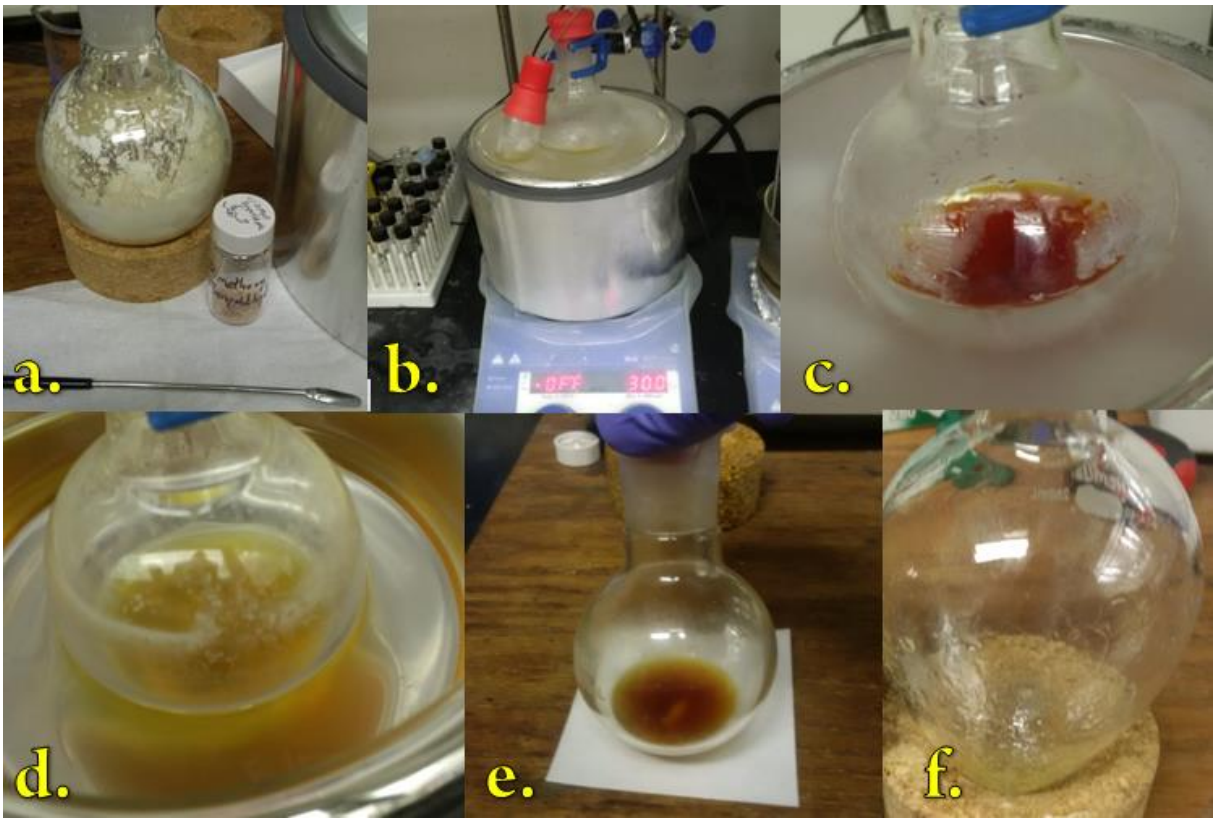
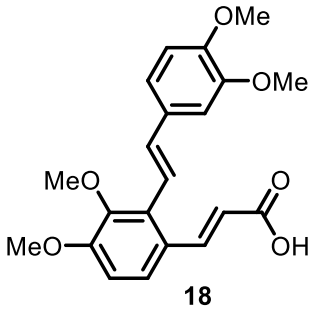


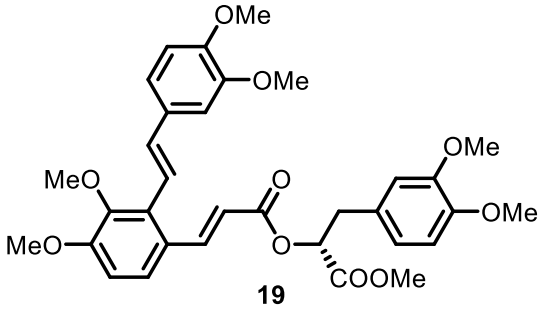
Figure S8. From left to right: a) preparation of materials. b) reaction at 0 min before mixing LDA and starting materials. c) reaction at 10m. d) reaction at 2h after warming to room temperature. e) crude reaction mixture after heating. f) pure product (**17**).

(***E***)**-3-(2-((*E*)-3,4-dimethoxystyryl)-3,4-dimethoxyphenyl)acrylic acid (18):** To a 50-mL round-bottom flask were added ethyl (*E*)-3-(2-((*E*)-3,4-dimethoxystyryl)-3,4-dimethoxyphenyl)acrylate (**17**) (0.440 mmol, 1 equiv), NaOH (8.8 mmol, 20 equiv), and ethanol (2 mL, 1M). The mixture was quenched with water (18 mL) and acidified to pH = 2 with hydrochloric acid. The solution was then extracted with ethyl acetate (3 × 50 mL) and dried with $NaSO_4$. After filtration, the solvent was removed *in vacuo*. Workup afforded **18** as a yellow solid (163 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 15.8 Hz, 1H), 7.40 (d, *J* = 8.7 Hz, 1H), 7.18 (d, *J* = 16.4 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 2H), 6.88 (dd, *J* = 11.3, 8.4 Hz, 2H), 6.68 (d, *J* = 16.4 Hz, 1H), 6.30 (d, *J* = 15.7 Hz, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.91 (s, 3H), 3.80 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.19, 154.30, 149.50, 149.30, 147.08, 146.51, 137.57, 133.80, 130.59, 126.32, 124.31, 120.32, 119.75, 116.44, 111.38, 111.29, 109.25, 60.66, 56.14, 56.11, 56.06. **HRMS** calcd. for $C_{21}H_{23}O_6^+$ $[M+H]^+$: 371.1489, Found: 371.1499.



18

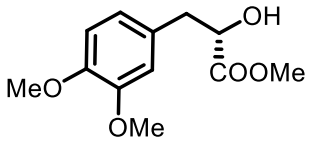
(*R*)-3-(3,4-dimethoxyphenyl)-1-methoxy-1-oxopropan-2-yl (*E*)-3-(2-((*E*)-3,4-dimethoxystyryl)-3,4-dimethoxyphenyl)acrylate (19): To a 100-mL round-bottom flask with (*E*)-3-(2-((*E*)-3,4-dimethoxystyryl)-3,4-dimethoxyphenyl)acrylic acid (**18**) (0.270 mmol, 1 equiv), DMAP (0.540 mmol, 2 equiv) and methyl (*R*)-3-(3,4-dimethoxyphenyl)-2-hydroxypropanoate (**20**) (0.540 mmol, 2 equiv) in CH_2Cl_2 (10 mL, 27 mM) at 0° C was added EDC•HCl (0.540 mmol, 2 equiv). The reaction mixture was slowly warmed up to room temperature and stirred overnight. After cooling the reaction mixture to 0° C, 2.0 N HCl solution (20 mL) was added. The aqueous layer was extracted with Et_2O (3 × 20 mL) and dried with Na_2SO_4. The crude residue was purified by SiO_2 gel column chromatography (5% Et_2O/CH_2Cl_2). Purification afforded **19** as a white foam (151 mg, 94%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 15.9 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.17 (d, *J* = 16.4 Hz, 1H), 7.08 (dd, *J* = 4.4, 2.5 Hz, 2H), 6.87 (dd, *J* = 10.4, 8.7 Hz, 2H), 6.76–6.66 (m, 4H), 6.32 (d, *J* = 15.8 Hz, 1H), 5.30 (dd, *J* = 8.2, 4.6 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.90 (s, 3H), 3.81 (s, 6H), 3.79 (s, 3H), 3.71 (s, 3H), 3.16–3.05 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.39, 166.26, 154.10, 149.34, 149.15, 148.77, 148.04, 146.94, 145.39, 137.35, 133.49, 130.48, 128.39, 126.26, 123.98, 121.47, 120.07, 119.52, 116.09, 112.45, 111.23, 111.16, 111.13, 109.27, 73.07, 60.51, 55.99, 55.97, 55.91, 55.90, 55.82, 52.27, 37.19. **HRMS** calcd. for $C_{33}H_{36}O_{10}Na^+$ $[M+Na]^+$: 615.2201, Found: 615.2208.



19

Figure S9. From left to right: a) Reaction at 0 h and at 0 °C. b) reaction at 12 h and room temperature. c) pure product (**19**) under normal light. d) pure product (**19**) under UV-light.

methyl (*R*)-3-(3,4-dimethoxyphenyl)-2-hydroxypropanoate (20): The title compound was prepared following a literature procedure.[18] To a 500-mL round-bottom flask equipped with a magnetic stir bar and reflux condenser were added rosmarinic acid (2.8 mmol, 1 equiv), acetone (100 mL), dimethyl sulfate (30.2 mmol, 10.8 equiv), and potassium carbonate (30.200 mmol, 10.8 equiv). The reaction mixture was heated at reflux under N_2. After 16 h, the reaction was cooled to room temperature and diluted with Et_2O (50 mL) and saturated NH_4Cl (50 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with brine and dried with Na_2SO_4. The solvent was removed *in vacuo*, and the crude residue was purified by SiO_2 gel column chromatography (10−40% Et_2O/benzene) to afford pentamethyl rosmarinic acid as a light yellow foam. To the pentamethyl rosmarinic acid in a 50-mL round-bottom flask were added MeOH (20 mL) and NaOMe (2.800 mmol, 1 equiv) at room temperature under N_2. After 2 h, saturated aqueous NH_4Cl (20 mL) was added followed by extraction with EtOAc (3 × 50 mL). The combined organic layers were washed with brine and dried with Na_2SO_4. The solvent was removed *in vacuo*, and the crude residue was purified by SiO_2 gel column chromatography (1−10% Et_2O/CH_2Cl_2) to afford **20** as a yellow solid (577 mg, 86%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.83–6.63 (m, 3H), 4.42 (td, *J* = 6.3, 4.0 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.77 (d, *J* = 2.6 Hz, 3H), 3.06 (dt, *J* = 14.1, 3.4 Hz, 1H), 2.91 (dd, *J* = 14.1, 6.6 Hz, 1H), 2.74 (t, *J* = 4.6 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 174.62, 148.89, 148.12, 128.83, 121.58, 112.79, 111.26, 71.48, 55.95, 55.92, 52.53, 40.21. **HRMS** calcd. for $C_{12}H_{17}O_5^+$ $[M+H]^+$: 241.1071, Found: 241.1077. **X-ray** (single-crystal) Yellow blocks of X-ray diffraction quality were obtained by vapor diffusion of ether into a saturated solution of **20** in acetonitrile (CCDC 1905645).[23]



20

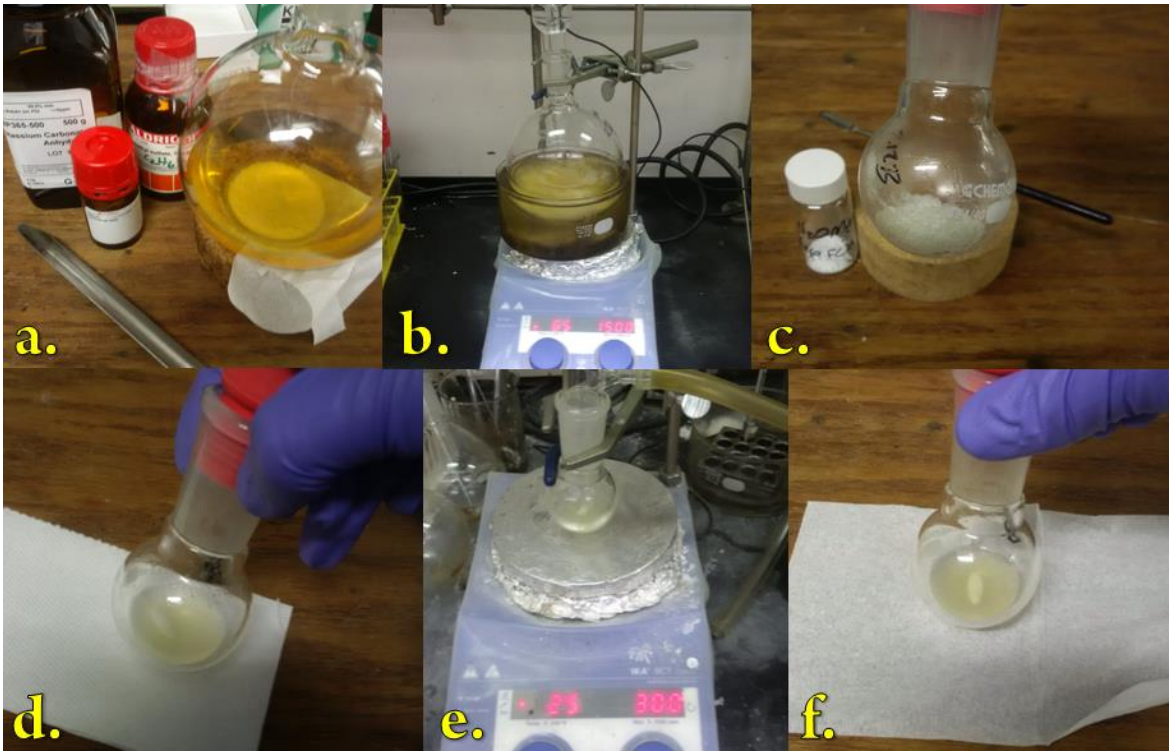
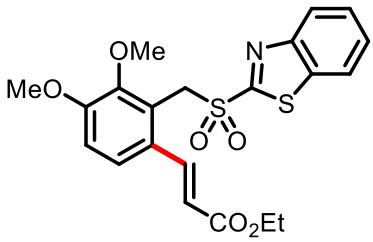


Figure S10. From left to right: a) preparation of materials. b) reaction at 16 h after heating. c) isolated pentamethylated rosmarinic acid. d) ester hydrolysis reaction at 0 h. e) ester hydrolysis at 1 h. f) crude reaction after 2 h containing **20**.

ethyl (*E*)-3-(2-((benzothiazol-2-ylsulfonyl)methyl)-3,4-dimethoxyphenyl)acrylate (21): To a 50-mL round-bottom flask equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-((benzothiazol-2-ylthio)methyl)-3,4-dimethoxyphenyl)acrylate (**6a**) (5.2 mmol, 1 equiv), 30% aqueous H_2O_2 (2.7 mL, 5 equiv), ammonium heptamolybdate tetrahydrate (0.26 mmol, 5 mol%), and ethanol (10.4 mL, 0.500 M). The reaction was stirred at room temperature for 12 h. The organic materials were separated by addition of H_2O (100 mL), followed by extraction with EtOAc (3 × 50 mL). The organic solution was washed with brine (50 mL) and dried over Na_2SO_4. After filtration, the solvent was removed *in vacuo*, and **21** was obtained as a yellow solid (2.33 g, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.22 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.96 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.65–7.60 (m, 2H), 7.57 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 5.96 (d, *J* = 15.5 Hz, 1H), 5.09 (s, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 3.89 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.21, 165.36, 153.93, 152.97, 149.26, 140.30, 137.73, 128.39, 128.02, 127.61, 125.88, 122.77, 122.29, 120.52, 119.12, 113.94, 61.49, 60.47, 55.98, 52.90, 14.40. **HRMS** calcd. for $C_{21}H_{22}NO_6S_2^+$ $[M+H]^+$: 448.0883, Found: 448.0898.



21

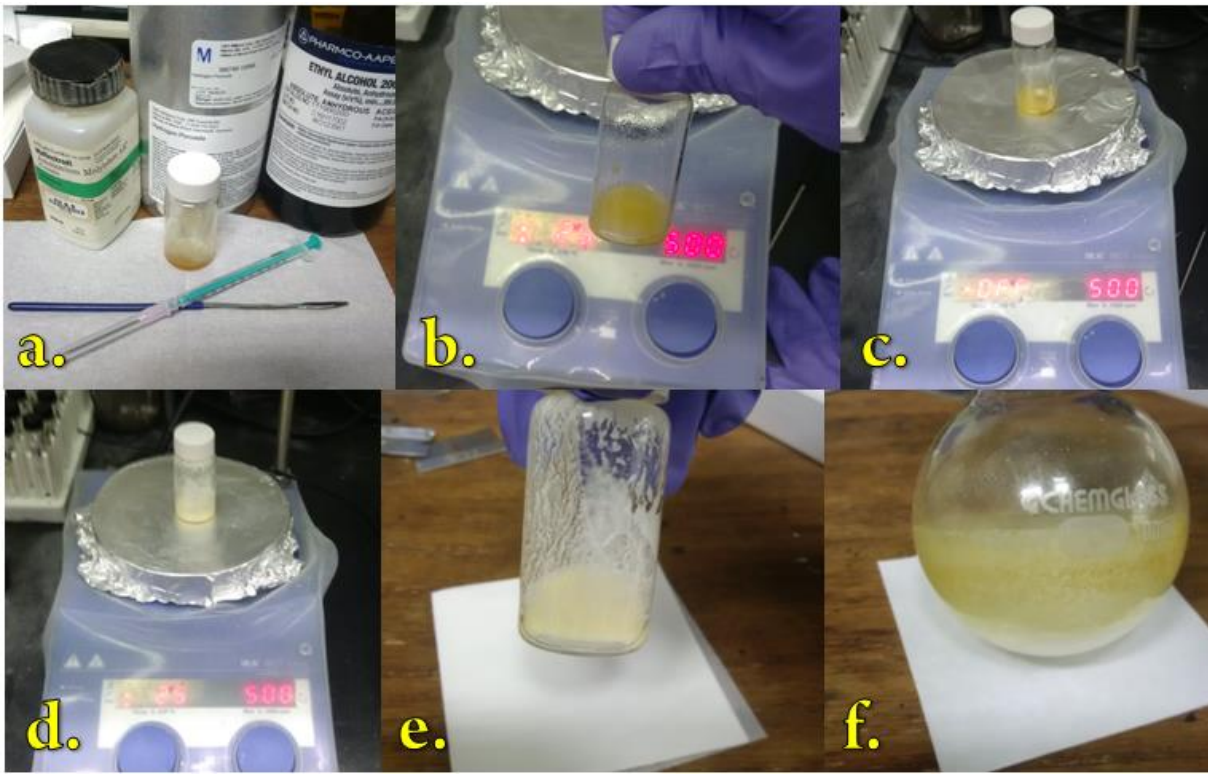
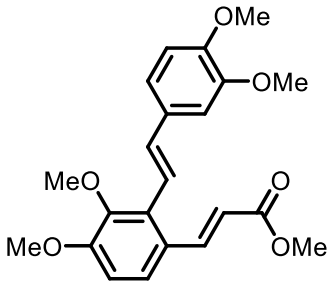


Figure S11. From left to right: a) preparation of materials for small-scale reaction (1 mmol). b) reaction at 0 m. c) vial being placed on stir plate. d) vial at 12 h. e) crude reaction mixture. f) pure product **21.**

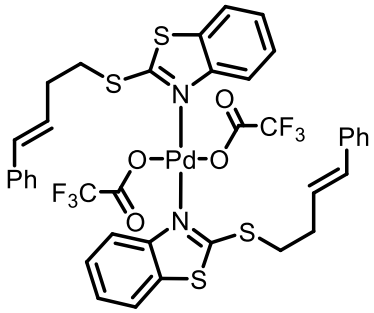
methyl (*E*)-3-(2-((*E*)-3,4-dimethoxystyryl)-3,4-dimethoxyphenyl)acrylate (22): To a 1-dram (4 mL) vial equipped with a stir bar were added ethyl (*E*)-3-(2-((*E*)-3,4-dimethoxystyryl)-3,4-dimethoxyphenyl)acrylate (**17**) (0.100 mmol, 1 equiv), KOH (0.300 mmol, 3 equiv), and MeOH (1 mL, 0.1 M). The reaction was placed on a heating block that was pre-heated to 35 ° C for 12 h. After 12 h, the reaction was brought to room temperature and treated with HCl until the solution reached pH = 2. The aqueous layer was extracted with ether (3 × 10 mL). The mixture was run through a pad of SiO_2 and the solvent was removed *in vacuo*. Workup afforded **22** as a yellow solid (37 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 15.8 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 7.17 (d, *J* = 16.4 Hz, 1H), 7.10–7.05 (m, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 16.4 Hz, 1H), 6.30 (d, *J* = 15.8 Hz, 1H), 3.96 (s, 3H), 3.91 (s, 6H), 3.79 (s, 3H), 3.77 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.68, 154.01, 149.43, 149.27, 147.08, 144.28, 137.22, 133.40, 130.71, 126.72, 124.01, 120.30, 119.86, 117.29, 111.34, 111.25, 109.23, 60.61, 56.14, 56.11, 56.03, 51.69. **HRMS** calcd. for $C_{22}H_{25}O_6^+$ $[M+H]^+$: 385.1646, Found: 385.1663. **X-ray** (single-crystal) Yellow blocks of X-ray diffraction quality were obtained by vapor diffusion of ether into a saturated solution of **22** in acetonitrile (CCDC 1905648).[23]



22

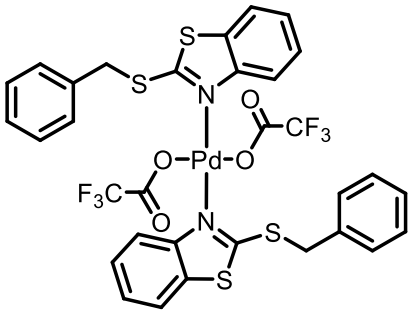
Preparation of Palladium Complexes

Pd-1: To a 1-dram (4 mL) vial equipped with a stir bar were added (*E*)-2-((4-phenylbut-3-en-1-yl)thio)benzothiazole (**2a**) (0.100 mmol, 1 equiv), palladium(II) trifluoroacetate (0.050 mmol, 0.5 equiv) in DCE (1 mL, 0.1 M). The reaction was placed on a heating block that was preheated to 45 ° C for 4 h. After 4 h, the reaction was brought to room temperature and filtered through a 0.2 μm PTFE filter into a new 1-dram (4 mL) vial. The uncapped vial containing the crude mixture was placed inside a scintillation vial (20 mL) containing diethyl ether (2 mL). The scintillation vial was capped and allowed to sit undisturbed for 72 h. **X-ray** (single-crystal) Yellow blocks of X-ray diffraction quality were obtained by vapor diffusion of ether into a saturated solution of **Pd-1** in dichloroethane (CCDC 1905654).[23]



Pd-1

Pd-2: To a 1-dram (4 mL) vial equipped with a stir bar were added 2-(benzylthio)benzothiazole (**5c**) (0.100 mmol, 1 equiv), palladium(II) trifluoroacetate (0.050 mmol, 0.5 equiv) in DCE (1 mL, 0.1 M). The reaction was placed on a heating block that was preheated to 45 ° C for 4 h. After 4 h, the reaction was brought to room temperature and filtered through a 0.2 μm PTFE filter into a new 1-dram (4 mL) vial. The uncapped vial containing the crude mixture was placed inside a scintillation vial (20 mL) containing diethyl ether (2 mL). The scintillation vial was capped and allowed to sit undisturbed for 72 h. **X-ray** (single-crystal) Yellow blocks of X-ray diffraction quality were obtained by vapor diffusion of ether into a saturated solution of **Pd-2** in dichloroethane (CCDC 1905655).[23]

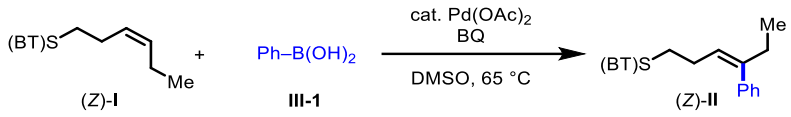


Pd-2

KINETICS PROCEDURES

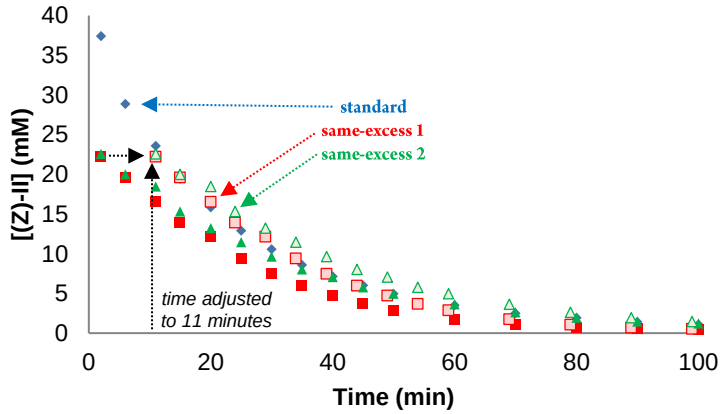
Kinetic Analysis of Oxidative Heck Reaction

The kinetics trials for both (*E*)-**I** and (*Z*)-**I** same-excess experiments were performed with (1) a standard reaction under optimized conditions, (2) a reaction prepared as though 20 mM conversion had already occurred with no product present, and (3) a reaction at 20 mM conversion with 20 mM of the corresponding product present. Each of these reactions was set up from stock solutions in vials open to air and at the appropriate temperature (45 ° C or 65 ° C). At designated time intervals 40 μL samples were removed from each reaction using a pipette and subsequently diluted in acetonitrile (0.5 mL) and filtered through a 0.2 μm PTFE filter into 96-well plates. Within an hour of sampling the last time point, the 96-well plates were sampled via LCMS. The concentration of each reaction component (except the Pd-catalyst, which was not directly monitored during the reaction) was then determined from LCMS based on the internal standard (1,3,5-trimethoxybenzene).



A[a]

	[(*Z*)-**I**]	[**III-1**]	[**BQ**]	[(*Z*)-**II**]
standard	**50.0 mM**	**70.0 mM**	**75.0 mM**	**0 mM**
same-excess 1	**30.0 mM**	**50.0 mM**	**55.0 mM**	0 mM
same-excess 2	30.0 mM	50.0 mM	55.0 mM	**20.0 mM**



B[b]

	[(*Z*)-**I**]	[**III-1**]	[**BQ**]	[(*Z*)-**II**]
standard	**50.0 mM**	**70.0 mM**	**75.0 mM**	**0 mM**
diff.-excess (*Z*)-I	**30.0 mM**	70.0 mM	75.0 mM	0 mM
diff.-excess III-1	50.0 mM	**50.0 mM**	75.0 mM	0 mM
diff.-excess BQ	50.0 mM	70.0 mM	**55.0 mM**	0 mM

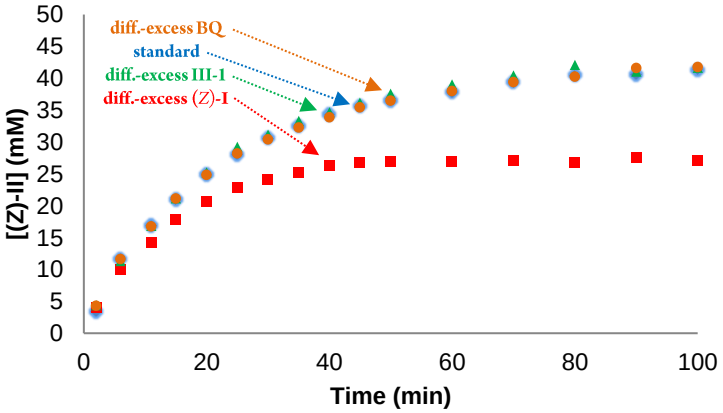
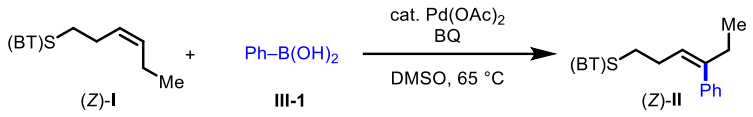
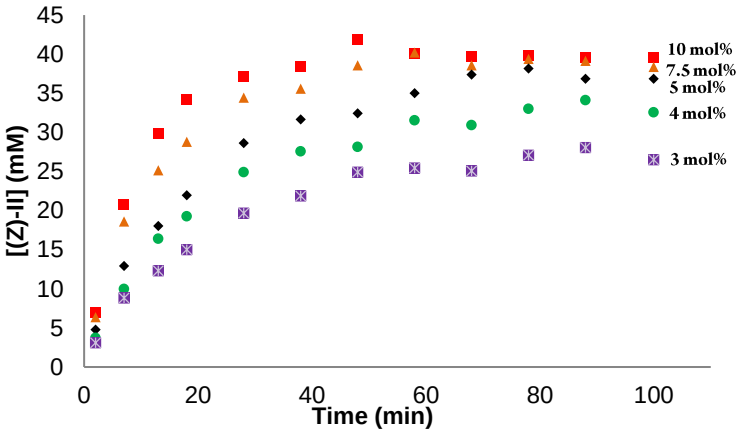


Figure S12. (A) Same-excess experiments with and without product. (B) Different-excess experiments of starting material, phenylboronic acid, and benzoquinone. [a]Due to the consumption of 1 equivalent of benzoquinone per turnover, reactions were set up with $Pd(OAc)_2$ (2.5 mM) and with (*Z*)-**I** (*variable*), **III**, BQ, and (*Z*)-**II** (for same-excess 3) corresponding to the expected amounts at time=80min for the standard reaction in DMSO (2.0 mL), at 65 °C, an in air. [b]Reaction conditions: (*Z*)-**I** (*variable*), **III** (*variable*), Benzoquinone (*variable*), $Pd(OAc)_2$ (*variable*), DMSO (2.0 mL), 65 °C, air.



A[a]

	[(*Z*)-**I**]	[**III-1**]	[**BQ**]	[$Pd(OAc)_2$]
10 mol%	**50.0 mM**	**70.0 mM**	**75.0 mM**	**5.00 mM**
7.5 mol%	50.0 mM	70.0 mM	75.0 mM	**3.75 mM**
5 mol%	50.0 mM	70.0 mM	75.0 mM	**2.50 mM**
4 mol%	50.0 mM	70.0 mM	75.0 mM	**2.00 mM**
3 mol%	50.0 mM	70.0 mM	75.0 mM	**2.50 mM**



B[b]

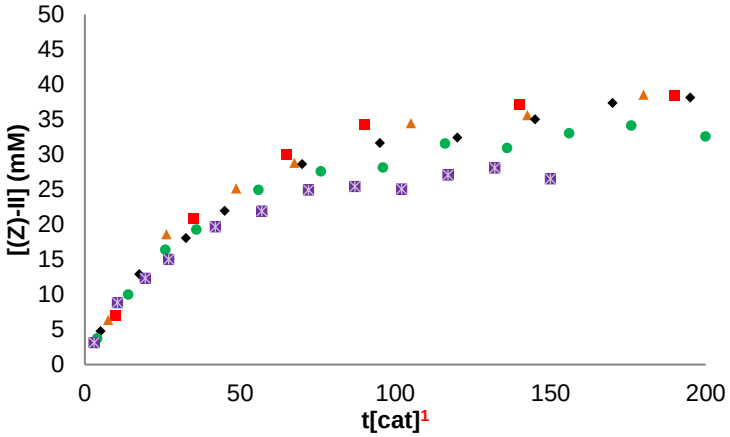


Figure S13. Reaction conditions (*Z*)-**I** (50 mM), **III-1** (70 mM), Benzoquinone (75 mM), $Pd(OAc)_2$ (*variable*), DMSO (2.0 mL), 65 °C, air.

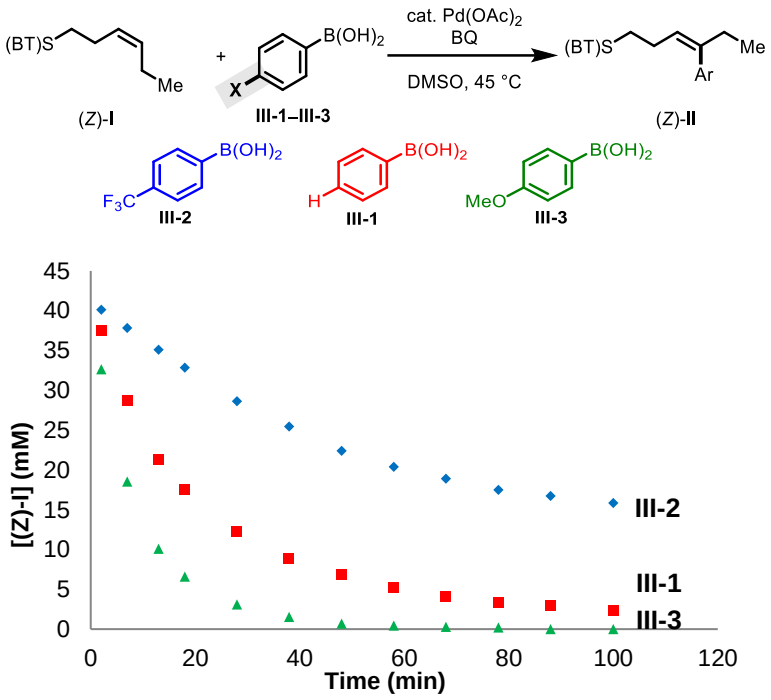


Figure S14. Reaction conditions (*Z*)-**I** (50 mM), **III-1–3** (70 mM), Benzoquinone (75 mM), $Pd(OAc)_2$ (5 mol%), DMSO (2.0 mL), 65 °C, air.

Kinetic Isotope Effect Experiment

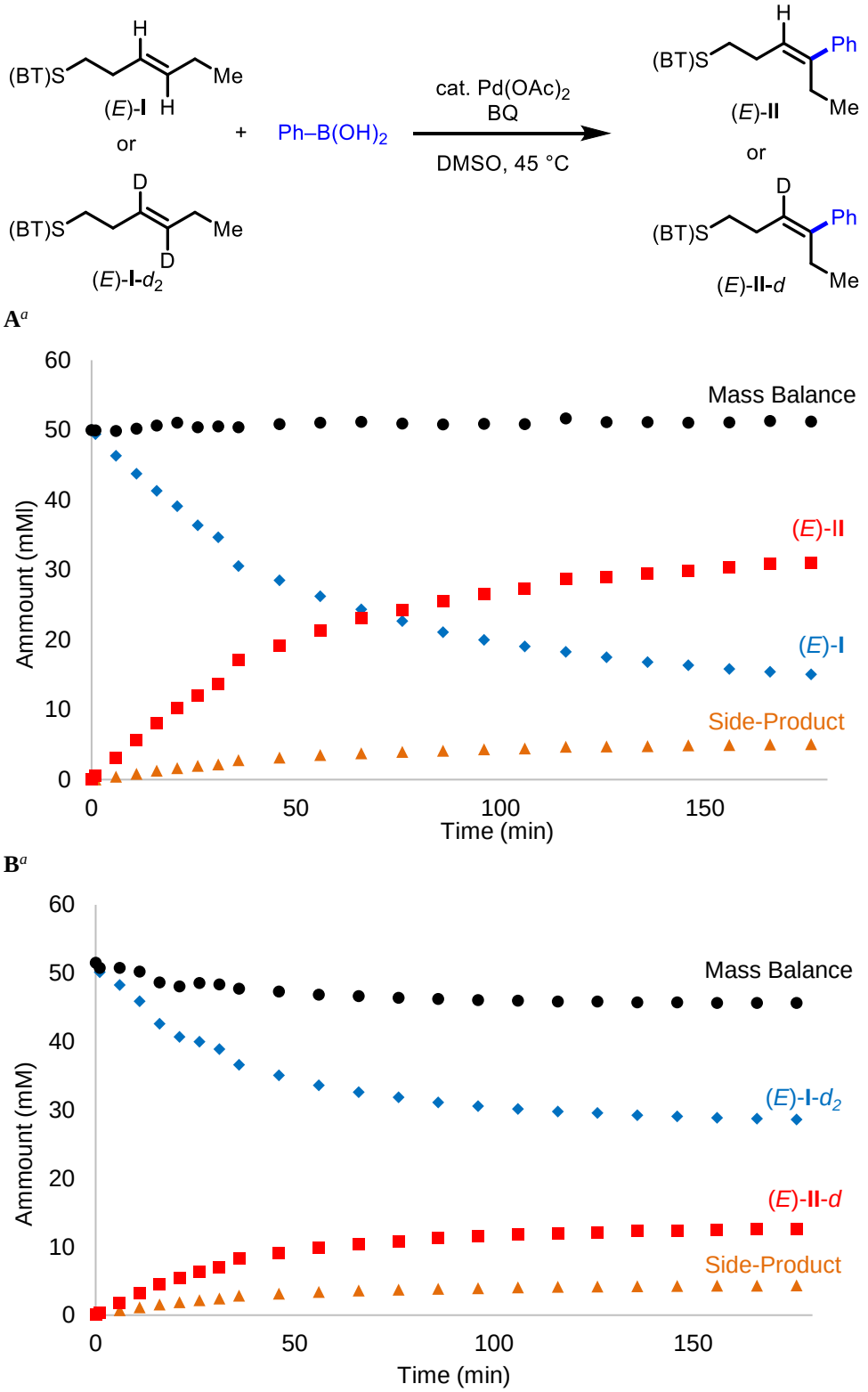
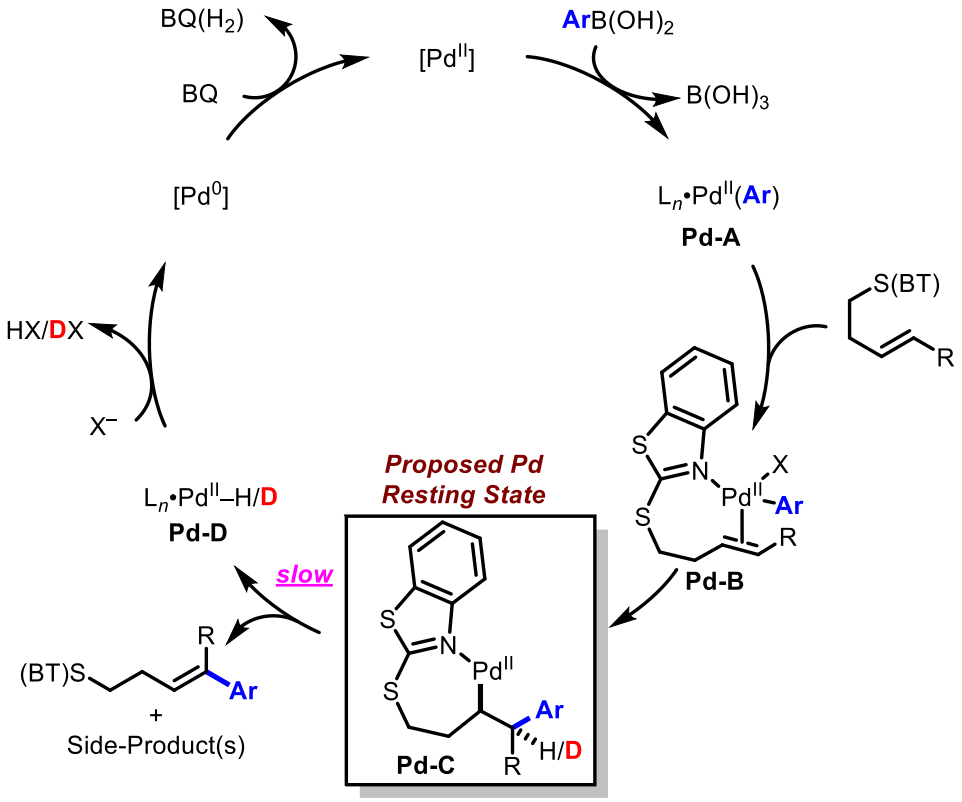


Figure S15. (A) Standard reaction run with (*E*)-**I**. (B) Reaction run with deuterated starting material ((*E*)-**IV**). [a]Reaction conditions (*E*)-**I** or (*E*)-**IV** (50 mM), **III-1**(70 mM), Benzoquinone (75 mM), $Pd(OAc)_2$ (5 mol%), DMSO (2.0 mL), 45 °C, air. Reactions observed by LCMS with 1,3,5-trimethoxybenzene as internal standard.

By running the standard oxidative Heck reaction with and without deuterium across the alkene, we were able to better probe the rate-determining step (Figure S15) and calculate a Kinetic Isotope Effect, KIE, equal to 2 for the initial regime of the reaction. Formation of a side-product, where β-hydride elimination occurs to create the olefin out of conjugation in both cases, was observed in to occur at similar rates. This is consistent with our proposed cycle as a hydride is being eliminated in both cases so no effect from the deuteride should be observed. For this reason, we also suggest that the secondary KIE during migratory insertion is negligible. We do observe a small decrease in mass balance for the reaction with the deuterated starting material, (*E*)-**IV**, suggesting that another untraced side-product was being produced. Finally, we observed that in the initial regime of the reaction, that the decay of either starting material, (*E*)-**I** and (*E*)-**IV**, occur at similar rates. This initial regime represents 4 turn-overs of Pd. We suggest that this is due to the resting state being **Pd-C** since the rate-determining step is β-hydride/deuteride elimination (Scheme S9). With this in mind, we rationalized that the free Pd^{II} catalyst in solution should react in both cases at the same rate with $PhB(OH)_2$ and the corresponding starting material, leading to a similar initial decay in starting material for both reactions. This rate of decay of starting material will, of course, decrease in the case of (*E*)-**IV** over time as the Pd-catalyst is being sequestered longer in the resting state than in the reaction with the standard starting material, (*E*)-**I**, reflected in the KIE. We do, indeed, see that after 4 turn-overs of Pd the difference in rate for starting material decay becomes obvious.



Scheme S10. Catalytic Cycle for (BT)S-directed Oxidative Heck Reaction

Kinetic Analysis of C–H Olefination

Same-Excess Setup

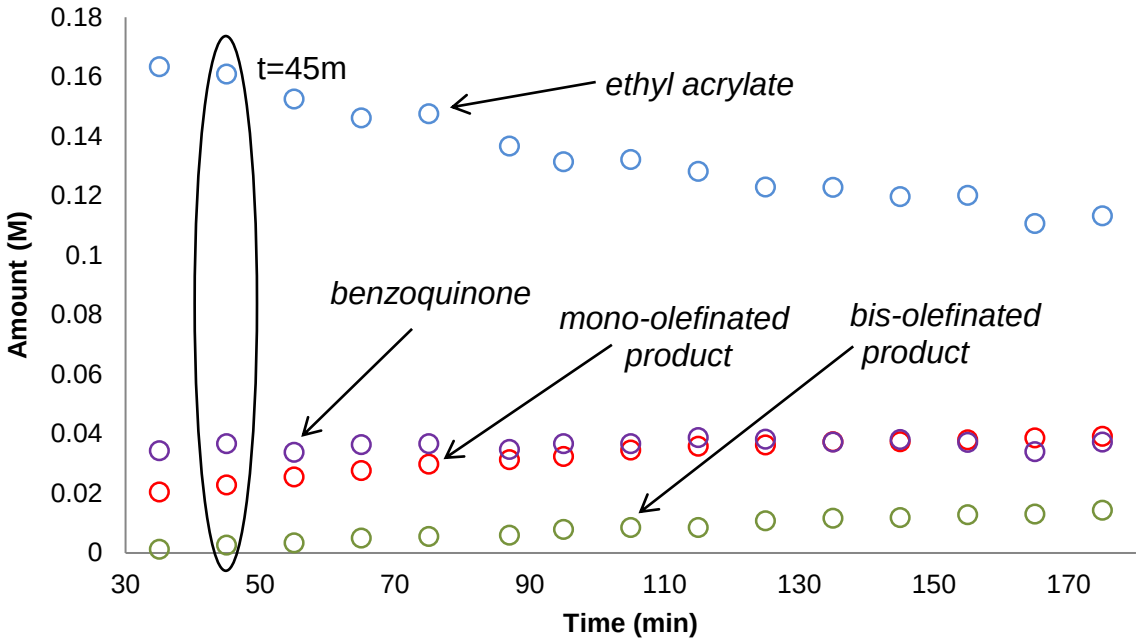


Figure S16. Reaction from *different-excess 2* in **Figure 7A** plotted from 35 min to 175 min showing the concentrations of ethyl acrylate (blue), benzoquinone (purple), mono-olefinated product (red), and bis-olefinated product (green) present as measured by ^{1}H-NMR. The values at t=45m for each are used in **Figure 7B**.

COMPUTATIONAL DETAILS

All calculations were performed with Gaussian 09.[21] The B3LYP density functional and LANL2DZ basis set were used in geometry optimizations. Single-point energies were calculated with M06 and a mixed basis set of SDD for Pd and 6-311+G(d,p) for other atoms. Solvation energy corrections were calculated using the SMD model.[22] In accordance with the experimental conditions, DMSO (ε = 46.826) was used as solvent in the single point calculations. To confirm the nature of the stationary points, vibrational frequency calculations were performed for all optimized structures. All optimized transition state structures have only one imaginary (negative) frequency, and all minima (reactants, products, and intermediates) have no imaginary frequencies. The imaginary frequencies of all transition states are provided in the "Cartesian Coordinates and Energies of the Optimized Structures" section below. The reported Gibbs free energies and enthalpies include zero-point vibrational energies and thermal corrections at 298 K.

Probing the energy profile for the terminal alkene

The energy profile for the migratory insertion and β-hydride elimination was also calculated for the terminal alkene, **1** (Figure S17). Similar to the internal alkene, the migratory insertion step (**TS1**) has a lower activation free energy barrier of 12.4 kcal/mol with respect to the π-alkene complex **INT1'** while the subsequent β-hydride elimination step has a higher activation energy barrier indicating that the β-hydride elimination is the rate-determining step. As in the case of the for the internal alkene, the coordination of the (BT)S group is weakened at both the migratory insertion and β-hydride elimination steps. The transition state leading to the *E*-isomer (**TS2_E**) has an activation energy of 13.8 kcal/mol, lower than 17.8 kcal/mol for the *Z*-isomer (**TS2_Z**). This indicates that the formation of the *E*-isomer is kinetically favored at the rate-determining step, consistent with experimental selectivity.

The optimized structures of **TS2_Z** and **TS2_E** are shown in figure **S18**. In the less stable transition state **TS2_Z**, the steric repulsions between of the phenyl group and the acetate group as well as with the methylene group *cis* to it is evidenced by the short O···H distance of 2.46 Å, C···C distance of 3.36 Å and C···H distances of and 2.58 Å and 2.64 Å respectively. In **TS2_E**, such steric repulsions are absent as the phenyl group is oriented away from the acetate group and is *trans* to the corresponding methylene group.

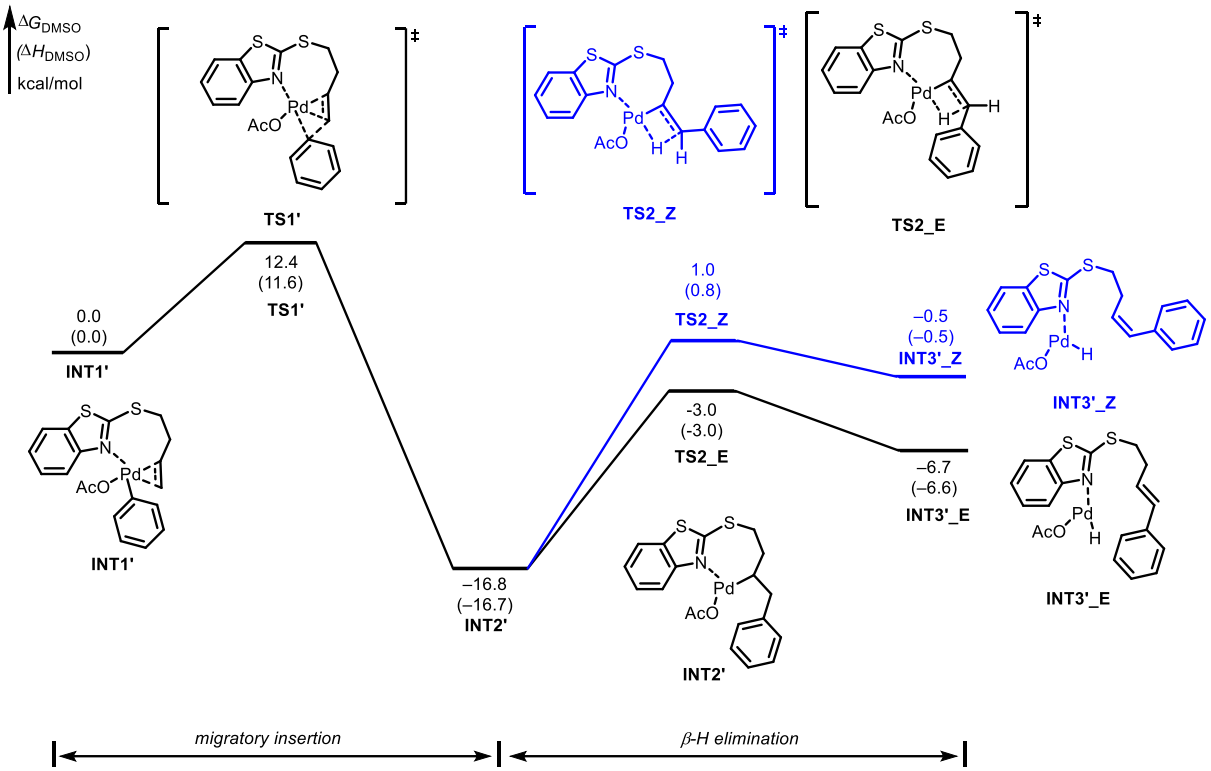


Figure S17. Computed energy profile for migratory insertion and β-hydride elimination steps for the terminal alkene **1**.

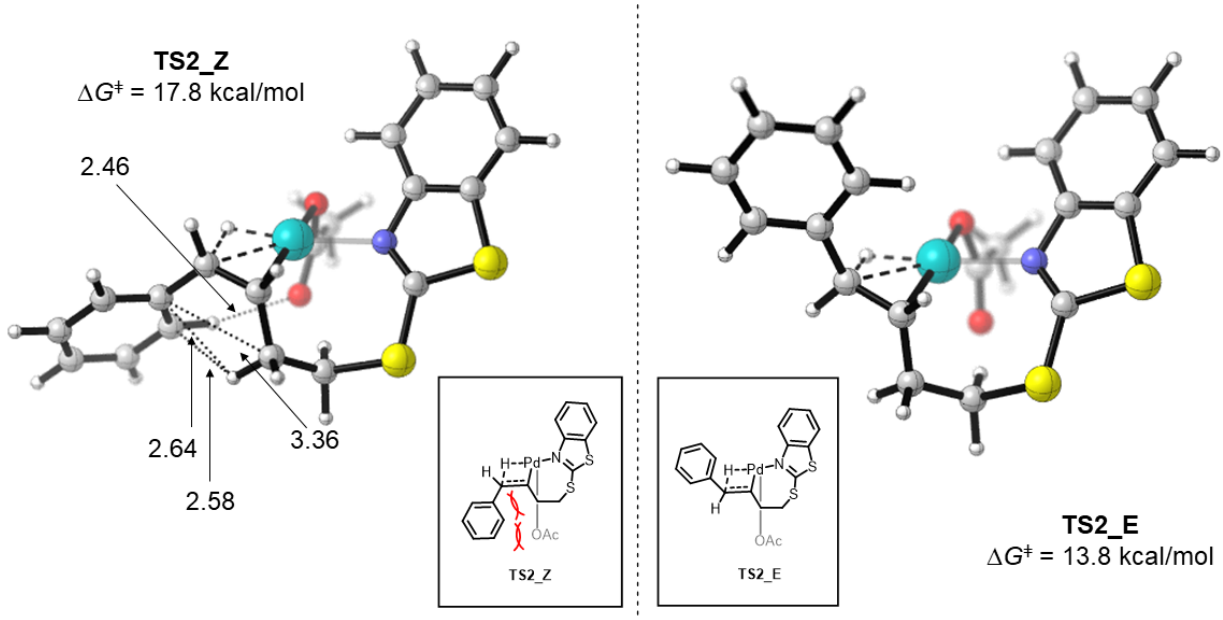


Figure S18. Computed transition states of the β-hydride elimination step leading to the *Z* and *E* isomers.

Probing transition states for alternative coordination modes

Even though the N-coordinated intermediates were lower in energy for the system, there was a concern whether the thermodynamic energy difference between the N- and S-coordinated intermediates were small enough for the S-coordinated high energy intermediates to be still kinetically favored. Therefore, the transition states for the S-coordination modes were calculated for the migratory insertion step using the terminal alkene. The S-coordinated transition states (**TS1'_S5** for the 5-membered metallacycle and **TS1'_S7** for the 7-membered metallacycle) were energetically higher than that for the N-coordinated transition state (Figure S19). Therefore, S-coordinated modes are not favored energetically for this directing group. However, the difference in energy for the transition states between the N- and S- coordination modes are minimal indicating that the S-coordination modes could be viable and operating under the reaction conditions in similar directing groups especially in the absence of potential N-coordination modes.

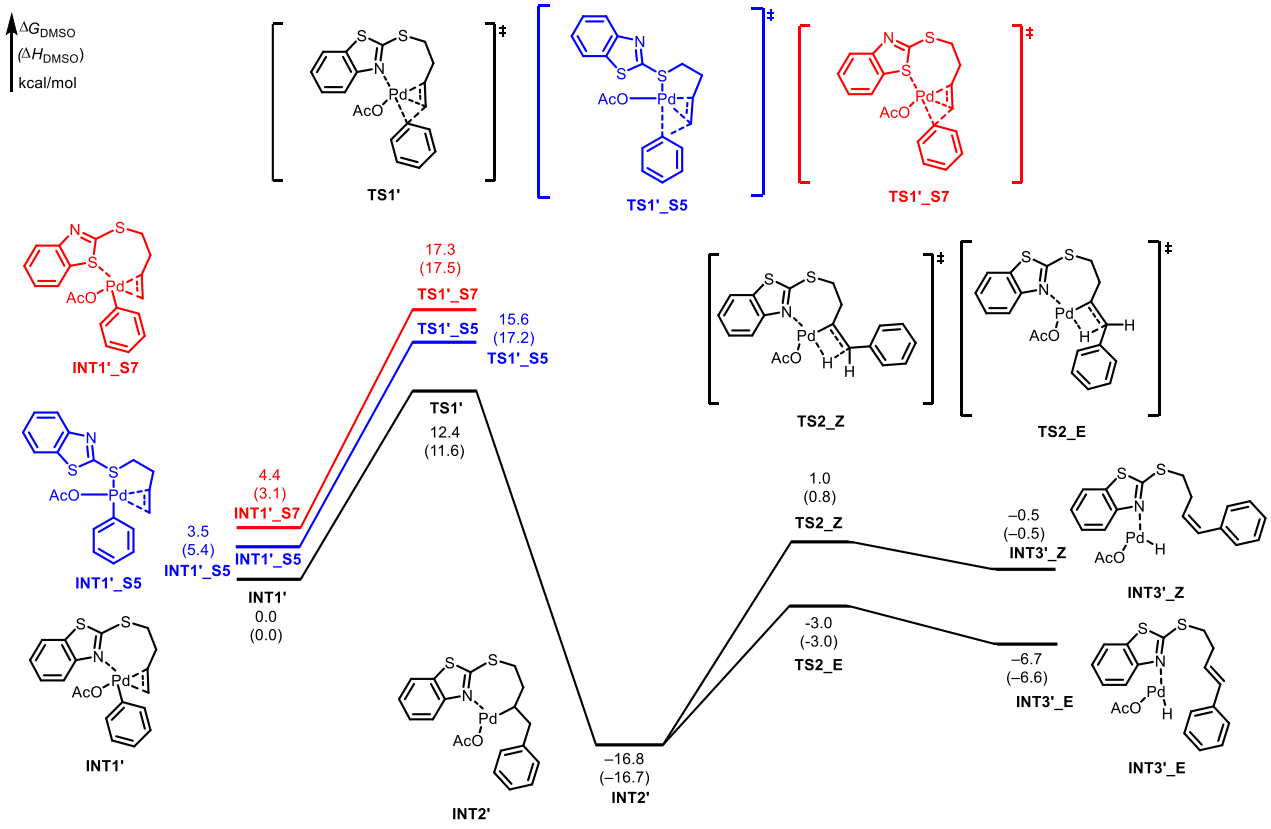


Figure S19. Comparison of the transition states (N-coordinated vs S-coordinated) for the terminal alkene.

Cartesian Coordinates and Energies of the Optimized Structures

INT1_N

B3LYP SCF energy: -1087.47077077 a.u.
B3LYP enthalpy: -1087.106164 a.u.
B3LYP free energy: -1087.190662 a.u.
M06 SCF energy in solution: -1864.539847 a.u.
M06 enthalpy in solution: -1864.175240 a.u.
M06 free energy in solution: -1864.259738 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.74136000	3.29923200	-0.49307200
H	1.22332200	4.18593800	-0.94150000
C	1.33581000	2.10263300	-1.21493600
H	2.41941900	2.05575000	-1.12376000
C	0.74934200	1.29662900	-2.18888800
H	-0.28694300	1.41116900	-2.49400000
H	1.07117900	3.28386500	0.55382800
H	1.37819400	0.70144600	-2.84506200
O	0.52450400	-1.42976400	1.10614800
C	0.72165600	-1.07278000	2.37868200
O	0.99903700	0.10664400	2.74208400
C	0.60470800	-2.22405300	3.37021100
H	-0.25545200	-2.85533600	3.12376000
H	1.50582400	-2.84750500	3.30349500
H	0.51411800	-1.83377600	4.38735900
C	-0.77772500	3.52105000	-0.55544800
H	-1.00888100	4.58851800	-0.48313900
H	-1.23759300	3.13814500	-1.46984800
S	-1.76548000	2.80740800	0.92223000
C	-2.26893800	1.18627100	0.31486400
C	-2.22966900	-0.92359500	-0.54615100
C	-3.61856000	-0.86637800	-0.25665000
C	-1.67380200	-2.09214600	-1.10281900
C	-4.47011400	-1.95040600	-0.51748700
C	-2.52146500	-3.17327300	-1.37452400
H	-0.60534300	-2.15066400	-1.27763600
C	-3.90704800	-3.10505400	-1.08762900
H	-5.53083400	-1.90472800	-0.28981400
H	-2.10639000	-4.08412200	-1.79679000
H	-4.54396900	-3.95886200	-1.30327000
S	-4.03965500	0.74606400	0.45958200
N	-1.50901900	0.24766000	-0.19955400
Pd	0.73043300	0.10356200	-0.28618000
C	2.69240700	-0.33504700	-0.35208700

C	3.20760500	-1.07846400	-1.43499600
C	3.54898100	0.06082500	0.69724700
C	4.57715600	-1.42030200	-1.47102300
H	2.55755700	-1.41304600	-2.24203500
C	4.91723200	-0.27905800	0.65139100
H	3.14635500	0.59931400	1.55080600
C	5.43596500	-1.01730000	-0.43115600
H	4.96471900	-2.00126100	-2.30613200
H	5.57130600	0.02520800	1.46651800
H	6.49105300	-1.28080600	-0.45964000

INT1_S

B3LYP SCF energy: -1087.45200476 a.u.
B3LYP enthalpy: -1087.087888 a.u.
B3LYP free energy: -1087.174323 a.u.
M06 SCF energy in solution: -1864.522482 a.u.
M06 enthalpy in solution: -1864.158365 a.u.
M06 free energy in solution: -1864.244800 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.31244100	3.23789000	-0.06360200
H	0.21596900	4.20004700	-0.14224000
C	0.47962900	2.25475100	-0.92518900
H	1.53424200	2.50777000	-1.02487600
C	-0.02893800	1.29407300	-1.79897900
H	-1.09690700	1.11877500	-1.90612300
H	-0.23524900	2.96217100	0.99704400
H	0.60214900	0.87940800	-2.57886400
O	1.12814000	-1.37784500	1.34500600
C	1.69090600	-0.94383900	2.48188800
O	1.89528600	0.28076400	2.72405000
C	2.08118800	-2.04754600	3.45368500
H	1.26325300	-2.76778400	3.56484200
H	2.94799000	-2.58918000	3.05398600
H	2.34057300	-1.61740500	4.42421300
C	-1.78859800	3.48910800	-0.45171300
H	-2.03048100	4.55179600	-0.34359600
H	-2.01024700	3.19450400	-1.47996700
S	-3.13692200	2.70330100	0.66403800
C	-2.95937100	0.94574200	0.25327500
C	-2.23616900	-1.48744000	0.17408500
C	-3.28661100	-1.08427000	-0.69871500
C	-1.73719400	-2.79559600	0.17918700
C	-3.87311900	-2.02321900	-1.56902300
C	-2.33236600	-3.72189100	-0.69787500
H	-0.90165200	-3.06745500	0.81603200

C	-3.39268400	-3.34159500	-1.55671000
H	-4.67730800	-1.71121300	-2.22801300
H	-1.96554000	-4.74467500	-0.71845800
H	-3.83441700	-4.08055000	-2.21990100
Pd	0.70360200	0.18375800	0.01527200
C	2.55363500	0.01681300	-0.74015500
C	2.77789100	-0.73386000	-1.91014300
C	3.62359900	0.62411800	-0.05494100
C	4.09246400	-0.86330700	-2.40859400
H	1.95834300	-1.23151300	-2.42359700
C	4.93207800	0.49211000	-0.56711200
H	3.44774800	1.15740100	0.87513800
C	5.16896800	-0.24641500	-1.74316100
H	4.26822000	-1.44806700	-3.30939100
H	5.76119000	0.95750100	-0.03787100
H	6.18020100	-0.34767000	-2.13046900
N	-3.64694700	0.28164600	-0.62538400
S	-1.70743900	-0.07613500	1.19831100

INT1_S'

B3LYP SCF energy: -1087.46127389 a.u.
B3LYP enthalpy: -1087.096654 a.u.
B3LYP free energy: -1087.183156 a.u.
M06 SCF energy in solution: -1864.528713 a.u.
M06 enthalpy in solution: -1864.164093 a.u.
M06 free energy in solution: -1864.250595 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.89120600	-3.04936100	1.75269900
H	-0.79644100	-4.13029400	1.95104400
C	-1.44106200	-2.85735900	0.34721400
H	-2.52137000	-2.95569100	0.24294400
C	-0.69126300	-2.63484300	-0.77824400
H	0.39576200	-2.58383000	-0.76807900
H	-1.62859300	-2.67793200	2.47649100
H	-1.16766600	-2.59990900	-1.75367700
S	0.38458000	-0.51284000	1.75074400
C	0.48177800	-2.42050500	2.01827300
H	0.80503000	-2.55455900	3.05307900
H	1.26164400	-2.76480600	1.33645500
C	1.94130900	-0.23186300	0.82613900
C	3.95018200	0.75097300	-0.29102000
C	3.82274600	-0.66687100	-0.33142900
C	5.03500800	1.40508400	-0.89260000
C	4.79957000	-1.44516100	-0.98140600
C	6.00459100	0.61575600	-1.53776000
H	5.13220000	2.48608900	-0.86614800
C	5.88754800	-0.79506500	-1.58156800
H	4.69360100	-2.52514400	-1.00810600
H	6.85573900	1.09898300	-2.01003300
H	6.65076700	-1.37933800	-2.08830800
S	2.55021300	1.48421500	0.61197500
N	2.67315100	-1.17401400	0.31046400
O	-2.78309700	-0.25231800	-1.48982500
C	-3.94476600	-0.90693100	-1.36956600
O	-4.22756400	-1.70674300	-0.43357400
C	-4.93142800	-0.58160800	-2.48631300
H	-5.34576800	0.42014700	-2.31503100
H	-4.42312300	-0.56963200	-3.45610000
H	-5.74526700	-1.31128000	-2.48855700
Pd	-1.37180600	-0.39440300	-0.00261600
C	-1.59140200	1.59664100	0.23912700
C	-1.68098400	2.40212500	-0.91526900
C	-1.64339400	2.19448400	1.51724200
C	-1.79034900	3.80190200	-0.79022300

H	-1.69910600	1.93829000	-1.89716800
C	-1.77160400	3.59616000	1.63504200
H	-1.59905400	1.59216500	2.42143700
C	-1.83603500	4.40300900	0.48386100
H	-1.85351000	4.41731000	-1.68584300
H	-1.82052800	4.04832900	2.62401700
H	-1.93015200	5.48283000	0.57717300

INT2_N

B3LYP SCF energy: -1087.49574227 a.u.
B3LYP enthalpy: -1087.129181 a.u.
B3LYP free energy: -1087.213320 a.u.
M06 SCF energy in solution: -1864.558736 a.u.
M06 enthalpy in solution: -1864.192174 a.u.
M06 free energy in solution: -1864.276314 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.67338400	0.10822800	1.59167000
H	-2.66308000	-0.37724400	1.69583300
C	-1.37080800	0.16982900	0.08804800
H	-2.17572700	0.73097800	-0.39762200
H	-1.80464600	1.13424300	1.95111900
O	-1.05017000	2.97020700	-0.90879100
C	-2.01996700	3.55689200	-0.19076500
O	-2.42502300	3.15081800	0.93201300
C	-2.60579700	4.78936900	-0.87202200
H	-1.82950800	5.55828700	-0.97014300
H	-2.94378900	4.53352700	-1.88287700
H	-3.43924600	5.18167200	-0.28397400
C	-0.73607100	-0.68984600	2.50289900
H	-1.17699400	-0.79754300	3.50011500
H	-0.49744500	-1.68676000	2.12327800
S	0.95951600	0.12675600	2.94257900
C	1.93129100	-0.25572100	1.47574100
C	2.64156400	-0.28597900	-0.70236000
C	3.68362900	-1.07528600	-0.15122700
C	2.62487800	0.00580400	-2.08051100
C	4.72075600	-1.57905700	-0.95091600
C	3.65502900	-0.50073200	-2.88345800
H	1.82344700	0.61321300	-2.49129200
C	4.69450100	-1.28553800	-2.32526500
H	5.52012500	-2.17984600	-0.52780900
H	3.65849500	-0.28625700	-3.94838400
H	5.48390800	-1.66657000	-2.96742600

Pd	0.17328400	1.49607800	-0.26005000
C	-1.13318900	-1.16762600	-0.65149100
H	-0.85980800	-0.93909100	-1.68994800
H	-0.29014300	-1.71614100	-0.21499300
C	-2.37916900	-2.05538700	-0.64398500
C	-3.52904600	-1.68159900	-1.37740100
C	-2.41472100	-3.25890600	0.09323500
C	-4.68212800	-2.48635600	-1.37115200
H	-3.51861700	-0.76131500	-1.95895500
C	-3.56734900	-4.06865300	0.10274500
H	-1.53499300	-3.57229700	0.65362900
C	-4.70672600	-3.68383800	-0.62844200
H	-5.55627800	-2.18358100	-1.94312000
H	-3.57452300	-4.99430700	0.67409300
H	-5.59780100	-4.30712100	-0.62324400
N	1.69129200	0.16794900	0.24642000
S	3.42600300	-1.28806000	1.63250000

INT2_S

B3LYP SCF energy: -1087.46447376 a.u.
B3LYP enthalpy: -1087.098474 a.u.
B3LYP free energy: -1087.183936 a.u.
M06 SCF energy in solution: -1864.53638 a.u.
M06 enthalpy in solution: -1864.17038 a.u.
M06 free energy in solution: -1864.255843 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.52357600	-0.44820200	1.61368500
H	-2.24176200	-1.28835700	1.68432100
C	-1.21678400	-0.30780000	0.11323900
H	-2.16795500	-0.33345500	-0.42538000
H	-2.09460700	0.43102300	1.93121200
O	-2.58790500	1.94921000	-1.20871200
C	-3.72300100	1.96449600	-0.48842900
O	-3.80339400	1.62223400	0.72124000
C	-4.93052100	2.43807100	-1.29001900
H	-4.76886400	3.46951300	-1.62558300
H	-5.05168400	1.81710200	-2.18523100
H	-5.83098900	2.38718200	-0.67287800
C	-0.41612200	-0.79646800	2.61598300
H	-0.86224300	-1.06886100	3.57853900
H	0.23034700	-1.61540200	2.29333900
S	0.76908400	0.63620500	3.12952800
C	1.86549100	0.60370500	1.70044400
C	2.89678800	1.06389300	-0.60091000
C	3.40720400	-0.03098000	0.15328600

C	3.41448600	1.39269300	-1.85881800
C	4.45149800	-0.81638600	-0.36785300
C	4.45449900	0.59389100	-2.37277100
H	3.02626300	2.23011300	-2.43035700
C	4.96815900	-0.49750700	-1.63359900
H	4.83669500	-1.64639200	0.21583200
H	4.86660800	0.82203700	-3.35199900
H	5.77331000	-1.09500700	-2.05201100
Pd	-0.74045900	1.65338800	-0.40498400
N	2.79514200	-0.24668400	1.41114900
S	1.60440900	1.92144100	0.36213000
C	-0.20913200	-1.27470500	-0.53857600
H	-0.05665700	-0.95992600	-1.57974800
H	0.76496700	-1.23322300	-0.04207900
C	-0.71497800	-2.72150300	-0.52048500
C	-1.87184100	-3.08895400	-1.24562500
C	-0.03452700	-3.71704000	0.21380900
C	-2.33816800	-4.41556400	-1.23214500
H	-2.40363400	-2.33895800	-1.82852000
C	-0.49826200	-5.04689900	0.22923700
H	0.86888600	-3.45720200	0.76347100
C	-1.65417500	-5.40041600	-0.49162400
H	-3.22818400	-4.68156100	-1.79779800
H	0.04129000	-5.80119900	0.79754700
H	-2.01439900	-6.42634300	-0.48118400

INT2_S’

B3LYP SCF energy: -1087.48739901 a.u.
B3LYP enthalpy: -1087.120831 a.u.
B3LYP free energy: -1087.206165 a.u.
M06 SCF energy in solution: -1864.552828 a.u.
M06 enthalpy in solution: -1864.18626 a.u.
M06 free energy in solution: -1864.271594 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.68911700	-1.48243300	0.22253500
H	-1.34328100	-2.30691000	0.55344800
H	0.05864000	-1.33255600	1.00990600
S	0.94472400	-0.39381900	-1.79759000
C	0.01872300	-1.91344700	-1.06258600
H	0.78236700	-2.67573100	-0.89974400
H	-0.66014800	-2.21281000	-1.86469400
C	2.49910500	-0.47567400	-0.83021300
C	4.76299700	-0.06076700	0.15908300
C	4.10196100	-1.26328900	0.54061100

C	6.02955700	0.26983200	0.66070400
C	4.72033700	-2.15203600	1.43997900
C	6.63630200	-0.62757800	1.55917900
H	6.53362500	1.18725200	0.37286400
C	5.98799700	-1.82591500	1.94428500
H	4.20870200	-3.06549500	1.72618300
H	7.61761200	-0.39357200	1.96316500
H	6.47959100	-2.49979200	2.64056200
S	3.72787800	0.88424200	-1.00436700
N	2.83101700	-1.45314200	-0.04450400
O	-1.27690300	2.92105800	0.20820800
C	-2.35849300	3.07543600	0.97717900
O	-3.11827700	2.13927000	1.34706100
C	-2.60207700	4.52722700	1.37830800
H	-1.73574400	4.90851500	1.93170800
H	-2.71784700	5.14555700	0.48034500
H	-3.49988200	4.59757700	1.99732400
Pd	-0.36382100	1.32971700	-0.63816200
C	-1.54838500	-0.21285900	0.06736900
H	-1.84561300	0.19980200	1.03487500
C	-2.78467200	-0.32403800	-0.85168000
H	-3.20021600	0.68114700	-0.97652100
H	-2.51306100	-0.69973700	-1.84720800
C	-3.84492700	-1.23028000	-0.22168500
C	-4.12056000	-2.51116300	-0.74693100
C	-4.55898100	-0.78730300	0.91767300
C	-5.09092900	-3.34094200	-0.15064300
H	-3.58956200	-2.85687500	-1.63340800
C	-5.52712900	-1.61640600	1.51213000
H	-4.35150200	0.20288900	1.31703500
C	-5.79595400	-2.89566900	0.98341400
H	-5.29829100	-4.32286800	-0.57091400
H	-6.07429000	-1.26423100	2.38389400
H	-6.54715800	-3.53272900	1.44507400

INT1

B3LYP SCF energy: -1126.78852395 a.u.
B3LYP enthalpy: -1126.393877 a.u.
B3LYP free energy: -1126.480367 a.u.
M06 SCF energy in solution: -1903.838928 a.u.
M06 enthalpy in solution: -1903.444281 a.u.
M06 free energy in solution: -1903.530772 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.93211200	3.00894000	-0.47397200
H	-2.00598800	2.95014600	-0.24967900
C	-0.54049800	1.93453500	-1.47447400
H	0.50348600	1.95776400	-1.78742400
C	-1.41081100	1.15906300	-2.22656900
H	-2.48024100	1.26800100	-2.06157800
H	-0.74974100	3.99360100	-0.93245100
O	-0.50221700	-1.45267000	1.19542100
C	-0.55222800	-0.95142600	2.42999200
O	-0.64738800	0.28837600	2.68272500
C	-0.50658400	-1.99776500	3.53399500
H	-1.49588400	-2.46525400	3.62317200
H	0.21310200	-2.78442200	3.28584500
H	-0.24800500	-1.52724800	4.48618900
C	-0.16495600	2.91557200	0.86067600
H	-0.35098800	3.79389100	1.48867100
H	-0.38859900	2.01065800	1.43727000
S	1.73384800	2.98559600	0.64844900
C	2.24392900	1.30199900	0.25799600
C	2.34277200	-0.89618300	-0.35476800
C	3.73509300	-0.68961200	-0.18239100
C	1.86548600	-2.16213800	-0.74563200
C	4.66786300	-1.71175500	-0.40809500
C	2.79300300	-3.18833100	-0.97407500
H	0.79852700	-2.33319700	-0.82738500
C	4.18153100	-2.96825700	-0.81137200
H	5.73271900	-1.54556600	-0.27536600
H	2.43720700	-4.17141300	-1.27002200
H	4.88176700	-3.77958000	-0.99178200
S	4.05662400	1.01401700	0.35624800
Pd	-0.67740400	-0.00580500	-0.29268000
C	-2.65349500	-0.41182800	-0.20711900
C	-3.47498100	0.29762400	0.69396200
C	-3.20546300	-1.45753600	-0.97595200
C	-4.84376600	-0.02742100	0.80877400
H	-3.05182000	1.06938200	1.33201000

C	-4.57362700	-1.78026500	-0.85661800
H	-2.58024500	-2.03359200	-1.65601800
C	-5.39843400	-1.06233100	0.03153100
H	-5.46765600	0.52028500	1.51287200
H	-4.98915500	-2.59169800	-1.45161000
H	-6.45305000	-1.31250500	0.12344500
N	1.54153600	0.25385100	-0.11307600
C	-1.01068600	0.38776600	-3.46633400
H	-1.50731900	-0.58883100	-3.50269900
H	-1.32425600	0.94240800	-4.36415100
H	0.07307100	0.23390000	-3.52215200

TS1

B3LYP SCF energy: -1126.76259526 a.u.
B3LYP enthalpy: -1126.369584 a.u.
B3LYP free energy: -1126.454439 a.u.
M06 SCF energy in solution: -1903.816166 a.u.
M06 enthalpy in solution: -1903.423155 a.u.
M06 free energy in solution: -1903.50801 a.u.
Imaginary frequency: -332.9875 cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
C	-0.75210900	3.11502700	0.03504400
H	-1.77510900	3.16843900	0.43787000
C	-0.69644100	2.05495900	-1.07072400
H	0.17544300	2.10447300	-1.72825300
C	-1.92963500	1.60062300	-1.67699700
H	-2.83146600	2.12754700	-1.36611800
H	-0.53169100	4.10465200	-0.39605000
O	-0.70135300	-1.59855100	1.05266700
C	-0.72355800	-1.22984900	2.32592500
O	-0.64647400	-0.01346000	2.70584400
C	-0.86316000	-2.36526700	3.33256400
H	-1.84110600	-2.84677700	3.20613700
H	-0.09571800	-3.12609200	3.14754800
H	-0.77253900	-1.98134900	4.35193900
C	0.17988600	2.86299000	1.23451100
H	0.11719900	3.68012500	1.96190800
H	-0.01981600	1.91376300	1.74569100
S	2.02436700	2.89810700	0.75643800
C	2.39340000	1.21329900	0.25236100
C	2.28827800	-0.98644500	-0.35997300
C	3.69681600	-0.83717500	-0.42879500
C	1.70266200	-2.23515900	-0.64823700
C	4.53804100	-1.89367600	-0.80491500

C	2.54003300	-3.29571600	-1.02472100
H	0.63531600	-2.36828100	-0.51601600
C	3.94251300	-3.13052500	-1.10986400
H	5.61542000	-1.76749800	-0.85658400
H	2.10072500	-4.26566900	-1.24192100
H	4.56982300	-3.96850400	-1.40253500
S	4.17910400	0.84854000	0.04000900
Pd	-0.58154700	0.17283400	-0.16768100
C	-2.64267500	-0.02151900	-0.60076000
C	-3.50970200	0.34741700	0.45827600
C	-2.97716900	-1.13626800	-1.40437400
C	-4.66639100	-0.40446400	0.72564600
H	-3.26852100	1.19805400	1.09145300
C	-4.13654100	-1.88665500	-1.13623900
H	-2.32480000	-1.43462200	-2.22202200
C	-4.98562400	-1.52221100	-0.07306200
H	-5.31193900	-0.12393400	1.55501700
H	-4.37222500	-2.75330400	-1.75014800
H	-5.88333200	-2.10103800	0.13212400
N	1.58885500	0.20262500	0.00586500
C	-1.93585800	1.19710000	-3.14475400
H	-2.85397100	0.66986400	-3.41931600
H	-1.87366900	2.10861400	-3.75788000
H	-1.07835400	0.56360800	-3.39731000

INT2

B3LYP SCF energy: -1126.81681727 a.u.
B3LYP enthalpy: -1126.420744 a.u.
B3LYP free energy: -1126.506305 a.u.
M06 SCF energy in solution: -1903.860285 a.u.
M06 enthalpy in solution: -1903.46421 a.u.
M06 free energy in solution: -1903.549773 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.30216800	3.35224400	0.60640300
H	0.46949000	2.77287100	1.51849400
H	0.36695000	4.42203600	0.83389700
C	-1.07421600	1.53726300	-0.59029500
C	-2.47724700	1.05238800	-1.03272100
H	-3.10698500	0.99353600	-0.13624500
H	-0.35281000	1.39589600	-1.40695300
C	2.23260500	1.34182500	-0.31779900
S	1.83274200	3.08627800	-0.50628900
C	-1.02318300	2.98290600	-0.07414500
H	-1.20512000	3.68487700	-0.90383100

H	-1.82355600	3.14329800	0.66459700
C	2.22896700	-0.88999700	0.20847600
C	3.51284800	-0.83687800	-0.38569900
C	1.75002700	-2.09852300	0.75032400
C	4.32820700	-1.97250200	-0.48535600
C	2.56432500	-3.23647000	0.65846200
H	0.78658300	-2.13107100	1.24903200
C	3.83683400	-3.18009600	0.04244100
H	5.30987700	-1.92650400	-0.94724900
H	2.21071700	-4.17556100	1.07463600
H	4.44797100	-4.07674500	-0.01737900
N	1.52959100	0.35385800	0.20248700
S	3.88652800	0.85478500	-0.93256000
Pd	-0.42283300	0.32353100	0.93761600
O	-0.63251600	-1.09488800	2.87257700
C	-1.86281100	-0.70044600	2.88779500
O	-2.27832400	0.13199200	1.94819000
C	-2.83072300	-1.13838200	3.96069000
H	-3.86271500	-1.01602200	3.62118100
H	-2.63796100	-2.17969100	4.23675600
H	-2.68175400	-0.52003300	4.85579700
C	-2.41492700	-0.34361700	-1.66066500
C	-1.74307100	-0.56804900	-2.88471500
C	-3.04689100	-1.43989000	-1.03499900
C	-1.70409000	-1.84830400	-3.46556400
H	-1.24994200	0.25905000	-3.39306700
C	-3.01388100	-2.72309100	-1.61381600
H	-3.55376900	-1.28424300	-0.08556000
C	-2.34175600	-2.93363600	-2.83262000
H	-1.18122500	-1.99951800	-4.40775300
H	-3.50810100	-3.55383500	-1.11427000
H	-2.31433900	-3.92392900	-3.28182300
C	-3.15522400	2.05757700	-2.01407200
H	-2.53580400	2.23863900	-2.90268200
H	-4.11780500	1.65510200	-2.35322600
H	-3.34589000	3.02261500	-1.52938500

TS2

B3LYP SCF energy: -1126.77559828 a.u.
B3LYP enthalpy: -1126.384987 a.u.
B3LYP free energy: -1126.470581 a.u.
M06 SCF energy in solution: -1903.82977 a.u.
M06 enthalpy in solution: -1903.439159 a.u.
M06 free energy in solution: -1903.524753 a.u.
Imaginary frequency: -604.4603 cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
C	-0.14959300	-2.57776900	-1.86421700
H	-0.58188500	-2.66379100	-0.86117600
H	-0.28137900	-3.52958600	-2.39024000
C	1.63427300	-0.82616600	-1.17031900
C	2.67891800	-0.66296800	-0.18016700
H	1.83300900	-0.83655600	1.24022200
H	1.41880300	0.04916000	-1.78415600
C	-1.83178800	-0.19081900	-1.69659600
S	-1.23543700	-1.39467000	-2.88964900
C	1.33566700	-2.16887500	-1.83964200
H	1.72149000	-2.13910000	-2.87089600
H	1.86336900	-2.98285900	-1.32935200
C	-2.17566400	1.09347900	0.16026100
C	-3.16694400	1.68355800	-0.66607900
C	-1.99861600	1.55745200	1.47930300
C	-3.96979200	2.74321200	-0.22155400
C	-2.80026900	2.61781700	1.92841600
H	-1.29219000	1.05712200	2.13265500
C	-3.77256700	3.21149100	1.08978400
H	-4.72367100	3.18930900	-0.86339600
H	-2.67618900	2.98048600	2.94531200
H	-4.38159100	4.03096400	1.46243900
N	-1.42862600	0.05284400	-0.46971100
S	-3.21156000	0.86547700	-2.28565300
Pd	0.40470600	-0.64569200	0.56037300
O	-0.62252400	-0.95515000	2.40395600
C	-1.17141500	-2.16536000	2.37250000
O	-1.06164800	-2.95477400	1.37886200
C	-1.95691100	-2.55185800	3.61881600
H	-2.33994500	-3.57078600	3.52243100
H	-1.31292600	-2.47543000	4.50287000
H	-2.79247000	-1.85494500	3.75938500
C	3.29699700	0.71559600	-0.04499800
C	4.70022000	0.87365700	-0.12781700
C	2.50122900	1.87547600	0.10587800
C	5.28607100	2.15257600	-0.08330500

H	5.34516800	0.00740800	-0.23936200
C	3.08385000	3.15198400	0.14949200
H	1.42463700	1.76675700	0.22100300
C	4.48177500	3.29826500	0.05250900
H	6.36689600	2.25043400	-0.15305600
H	2.45102500	4.02721600	0.27410000
H	4.93492100	4.28566300	0.09389900
C	3.58783300	-1.84513900	0.19363800
H	4.31017100	-2.03268200	-0.61347800
H	4.14464700	-1.63251500	1.11152700
H	3.01770400	-2.76150400	0.35697800

INT3

B3LYP SCF energy: -1126.78663553 a.u.
B3LYP enthalpy: -1126.393435 a.u.
B3LYP free energy: -1126.478771 a.u.
M06 SCF energy in solution: -1903.838962 a.u.
M06 enthalpy in solution: -1903.445761 a.u.
M06 free energy in solution: -1903.531098 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.42709400	-2.76528500	1.70547800
H	0.88381800	-2.76332400	0.70891100
H	0.70304000	-3.69128600	2.22196500
C	-1.53567500	-1.21878100	1.15944100
C	-2.59889700	-0.92440400	0.28915100
H	-1.27835100	-1.78894100	-1.68267500
H	-1.16989800	-0.40087500	1.77653300
C	1.64718200	-0.07294500	1.62562800
S	1.33940600	-1.44737000	2.74965700
C	-1.10432100	-2.58098200	1.67816800
H	-1.50768500	-2.71014200	2.69580900
H	-1.50885300	-3.39523200	1.06560900
C	1.59857700	1.43284700	-0.09050700
C	2.59026400	2.07741700	0.69260900
C	1.19385200	1.99783800	-1.31545500
C	3.18196400	3.28282100	0.28899700
C	1.78208400	3.20311800	-1.72425800
H	0.46420800	1.48446200	-1.93079800
C	2.76513600	3.84286600	-0.93198600
H	3.94062700	3.77123000	0.89321700
H	1.48288300	3.64700900	-2.66969000
H	3.20965800	4.77478200	-1.27137800
N	1.08436000	0.23488500	0.47753900
S	2.93024600	1.11406400	2.19333900

Pd	-0.41585300	-0.93169900	-0.74210100
O	0.97672700	-0.97810700	-2.27902900
C	1.88323200	-1.94961200	-2.15743400
O	1.91941700	-2.76622500	-1.18919500
C	2.89022400	-2.00147100	-3.29939300
H	3.65950700	-2.74790600	-3.08701300
H	2.37296900	-2.25987200	-4.23154700
H	3.34847100	-1.01585400	-3.43939300
C	-3.12253800	0.48452100	0.17716600
C	-4.43524200	0.72259600	-0.29800600
C	-2.35011100	1.61244800	0.56178100
C	-4.96088100	2.02557400	-0.37232100
H	-5.06427600	-0.10500100	-0.60725000
C	-2.87195600	2.91138100	0.48800900
H	-1.32611900	1.48325300	0.89684600
C	-4.18464800	3.12850400	0.02185600
H	-5.97422700	2.17461800	-0.73767900
H	-2.25268800	3.75497100	0.78297900
H	-4.58766800	4.13644700	-0.03796700
C	-3.48864400	-2.02802800	-0.27510400
H	-4.39059900	-2.12478100	0.34841700
H	-3.80711300	-1.81033100	-1.29852200
H	-2.98278100	-2.99424100	-0.28757200

INT1’

B3LYP SCF energy: -1087.47632148 a.u.
B3LYP enthalpy: -1087.111470 a.u.
B3LYP free energy: -1087.194417 a.u.
M06 SCF energy in solution: -1864.541159 a.u.
M06 enthalpy in solution: -1864.176308 a.u.
M06 free energy in solution: -1864.259254 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.93535200	3.02622000	-0.73481000
H	-2.01505900	2.99003200	-0.53725200
C	-0.53127600	1.90958800	-1.67902400
H	0.52137300	1.90563000	-1.95824700
C	-1.38423800	1.08112200	-2.38949100
H	-2.46176600	1.17259100	-2.31566100
H	-0.72337800	3.98978300	-1.22359800
H	-1.00403000	0.45227000	-3.19133500
O	-0.55515600	-1.39541300	1.10224800
C	-0.61639500	-0.84331300	2.31411300

O	-0.70768500	0.40681000	2.51268600
C	-0.58850600	-1.84197200	3.46147700
H	-1.57829900	-2.30797700	3.55245200
H	0.13667000	-2.63666500	3.25907700
H	-0.34732600	-1.33153600	4.39747900
C	-0.20091400	2.96362100	0.62080200
H	-0.39520400	3.86005300	1.21962800
H	-0.44627300	2.07647300	1.21603100
S	1.70299000	3.00945900	0.45396200
C	2.20930800	1.30802800	0.13713900
C	2.31080100	-0.90698100	-0.41119900
C	3.69688500	-0.70787400	-0.18792100
C	1.83746500	-2.17814900	-0.78944600
C	4.62780400	-1.74419000	-0.34678200
C	2.76306200	-3.21844800	-0.95155000
H	0.77349800	-2.34136000	-0.91561000
C	4.14570200	-3.00672300	-0.73580700
H	5.68787500	-1.58414000	-0.17426000
H	2.41010700	-4.20560400	-1.23699100
H	4.84443400	-3.82908500	-0.86455800
S	4.01302800	1.00715200	0.31621700
Pd	-0.70804900	-0.01082000	-0.44734800
C	-2.68608400	-0.41475000	-0.36969000
C	-3.50977400	0.30658000	0.51876300
C	-3.23429000	-1.46409100	-1.13613300
C	-4.87984300	-0.01617600	0.62887900
H	-3.08990000	1.08517000	1.15061500
C	-4.60311100	-1.78436900	-1.01947000
H	-2.60761200	-2.03855300	-1.81566300
C	-5.43110200	-1.05831700	-0.14070400
H	-5.50696200	0.53995000	1.32337400
H	-5.01721400	-2.59828300	-1.61191800
H	-6.48653300	-1.30618400	-0.05225600
N	1.51163300	0.25562100	-0.23150400

TS1'

B3LYP SCF energy: -1087.45379570 a.u.
B3LYP enthalpy: -1087.090396 a.u.
B3LYP free energy: -1087.171992 a.u.
M06 SCF energy in solution: -1864.521301 a.u.
M06 enthalpy in solution: -1864.157901 a.u.
M06 free energy in solution: -1864.239498 a.u.
Imaginary frequency: -331.4135 cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
C	-0.64955900	3.19258900	-0.50069600
H	-1.68370500	3.38082700	-0.17413300
C	-0.63220400	1.98804400	-1.44529800
H	0.24576700	1.88867200	-2.08651700
C	-1.87515700	1.46463200	-1.94727900
H	-2.78324100	2.04096000	-1.78690500
H	-0.32134500	4.09037100	-1.04695200
H	-1.85625300	0.92614700	-2.89201400
O	-0.82731500	-1.38624400	1.11249600
C	-0.92337300	-0.85369400	2.32303700
O	-0.86595300	0.40281900	2.54144100
C	-1.12738400	-1.84774400	3.45895900
H	-2.11754400	-2.31135400	3.36288600
H	-0.38168900	-2.64844500	3.39519100
H	-1.05452600	-1.34064700	4.42450100
C	0.19276900	3.03971700	0.77971900
H	0.13359300	3.94206400	1.39865600
H	-0.09346100	2.17261000	1.38650500
S	2.06193000	2.92738600	0.42921400
C	2.37019400	1.18587500	0.11230800
C	2.19176400	-1.05870000	-0.28562900
C	3.60692800	-0.97340700	-0.30815500
C	1.56381700	-2.30521500	-0.47819300
C	4.41503800	-2.09429000	-0.54456100
C	2.36755800	-3.42984200	-0.71606300
H	0.48768900	-2.38410700	-0.38208000
C	3.77813400	-3.32999200	-0.75576100
H	5.49809300	-2.01695800	-0.56190800
H	1.89459400	-4.39764400	-0.85940500
H	4.37881100	-4.21677900	-0.94039300
S	4.14449600	0.73007200	0.01358600
Pd	-0.62708500	0.20956600	-0.31380400
C	-2.67465500	-0.02118900	-0.78259200
C	-3.57403200	0.40800900	0.22431400
C	-3.01331400	-1.13638100	-1.58410800
C	-4.77067600	-0.29488500	0.44790400

H	-3.32583100	1.25982800	0.85244100
C	-4.21409400	-1.83487800	-1.35847500
H	-2.33933200	-1.46632700	-2.37242000
C	-5.09668900	-1.41572400	-0.34389200
H	-5.44350700	0.02784700	1.23944800
H	-4.45847000	-2.69956700	-1.97172800
H	-6.02629300	-1.95349700	-0.17213800
N	1.53221600	0.18807100	-0.06679500

INT2'

B3LYP SCF energy: -1087.51247577 a.u.
B3LYP enthalpy: -1087.146059 a.u.
B3LYP free energy: 1087.229194 a.u.
M06 SCF energy in solution: -1864.569309 a.u.
M06 enthalpy in solution: -1864.202892 a.u.
M06 free energy in solution: -1864.286027 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.52660500	-3.39433700	-0.33956600
H	-0.68470700	-3.07355700	0.69353900
H	-0.68766300	-4.47508600	-0.41644800
C	1.03837400	-1.45048600	-0.97475000
C	2.49691700	-1.05339200	-1.28555600
H	3.11989600	-1.25378100	-0.40637300
H	0.36430800	-1.03094000	-1.73364100
C	-2.24968000	-1.04575400	-0.69529600
S	-1.97830100	-2.69426700	-1.36463300
C	0.85129700	-2.97035000	-0.86324600
H	1.02683200	-3.43328700	-1.84991500
H	1.60434700	-3.38644800	-0.17675200
C	-2.10070700	0.93925200	0.44305600
C	-3.36274100	1.15907800	-0.15971700
C	-1.55792200	1.90190200	1.31648700
C	-4.08980800	2.33770400	0.05601700
C	-2.28471100	3.08007900	1.54110400
H	-0.61561000	1.71539000	1.82200700
C	-3.53324600	3.30304300	0.91405500
H	-5.05408300	2.50257500	-0.41524800
H	-1.88112100	3.83055300	2.21494900
H	-4.07536000	4.22579000	1.10283900
N	-1.49242200	-0.30369300	0.09114000
S	-3.84045600	-0.27413600	-1.16747100
Pd	0.44971500	-0.61097100	0.80307300
O	0.76492800	0.25627900	3.04438500
C	1.96057900	-0.21525700	2.92843700

O	2.30825500	-0.80575500	1.79581000
C	2.96969800	-0.14112800	4.04897200
H	3.97842100	-0.00976800	3.64553200
H	2.71819400	0.67686200	4.72932300
H	2.95261500	-1.08213100	4.61472000
C	2.65936700	0.39167700	-1.73260300
C	2.36282800	0.77028500	-3.06172900
C	3.09914100	1.38685400	-0.83226200
C	2.49638600	2.10706400	-3.48117300
H	2.03403200	0.01380600	-3.77365600
C	3.23656300	2.72500000	-1.24755400
H	3.33129600	1.10480100	0.19186600
C	2.93445500	3.09132300	-2.57349100
H	2.26681400	2.37881300	-4.50945600
H	3.57922700	3.47763600	-0.54049100
H	3.04209800	4.12462500	-2.89591900
H	2.85404700	-1.72043500	-2.09119800

TS2_Z

B3LYP SCF energy: -1087.46960920 a.u.
B3LYP enthalpy: -1087.108470 a.u.
B3LYP free energy: -1087.191062 a.u.
M06 SCF energy in solution: -1864.536177 a.u.
M06 enthalpy in solution: -1864.175037 a.u.
M06 free energy in solution: -1864.25763 a.u.
Imaginary frequency: -430.7933 cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
C	0.74799800	-2.09053900	1.41997000
H	0.66488700	-1.04298200	1.72746700
H	1.17555300	-2.66649800	2.24847100
C	1.23913900	-1.37797000	-1.04195400
C	2.14437600	-0.37044600	-1.51899200
H	1.57789600	1.15026200	-0.93442000
H	0.54627900	-1.78923200	-1.77773600
C	-2.02411000	-1.58476700	0.53521700
S	-1.00029900	-2.84057100	1.31125200
C	1.58453000	-2.28468500	0.14086500
H	1.50687700	-3.33254400	-0.18125600
H	2.63054900	-2.11805500	0.42835900
C	-2.82591000	0.29079200	-0.49470200
C	-4.06102800	-0.39163700	-0.35559100
C	-2.79492300	1.56637400	-1.09188900
C	-5.26683800	0.15422700	-0.81723800
C	-3.99815400	2.11680200	-1.55701900
H	-1.86346900	2.11732100	-1.13637000

C	-5.22277200	1.42037200	-1.42759000
H	-6.20731100	-0.37745800	-0.70771400
H	-3.98798800	3.10255200	-2.01405600
H	-6.14202300	1.86938100	-1.79445100
N	-1.69905400	-0.42725900	0.00560200
S	-3.81443800	-1.98518500	0.47879000
Pd	0.26875000	0.44373800	-0.41794300
O	-0.31333400	2.26988200	0.49746700
C	0.23947900	2.34603400	1.70371300
O	0.99259100	1.43867800	2.18797400
C	-0.07881300	3.61801100	2.47817400
H	0.25627800	3.52294600	3.51401100
H	0.43209800	4.46804400	2.00792800
H	-1.15506400	3.81962300	2.44365600
C	3.53026100	-0.14549000	-0.97267900
C	4.62505600	-0.37094000	-1.83799900
C	3.77490700	0.25942500	0.36010200
C	5.94504700	-0.22275500	-1.37435800
H	4.44646900	-0.66770100	-2.87014300
C	5.09618900	0.40979400	0.81867300
H	2.94027800	0.49656100	1.01873100
C	6.18444400	0.16529300	-0.04196700
H	6.77844700	-0.40205000	-2.04947900
H	5.27151200	0.73146400	1.84221400
H	7.20389700	0.28802400	0.31595000
H	2.02416700	-0.09455000	-2.56762900

TS2_E

B3LYP SCF energy: 1087.47278607 a.u.
B3LYP enthalpy: 1087.111829 a.u.
B3LYP free energy: -1087.194739 a.u.
M06 SCF energy in solution: -1864.542117 a.u.
M06 enthalpy in solution: -1864.18116 a.u.
M06 free energy in solution: -1864.26407 a.u.
Imaginary frequency: -669.1739 cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
C	-0.33036500	-2.88668400	-1.42495400
H	-0.69742300	-2.79001500	-0.39701200
H	-0.54091800	-3.89987200	-1.78427700
C	1.55745700	-1.12783700	-1.16878700
C	2.64298100	-0.90867400	-0.24568700
H	1.92470500	-0.94353900	1.21184300
H	1.36885700	-0.36043700	-1.91917800
C	-1.86389800	-0.38657300	-1.55808600
S	-1.43562200	-1.82023600	-2.55583500

C	1.16880000	-2.55531200	-1.55843300
H	1.49727600	-2.74791500	-2.59146400
H	1.70171300	-3.26940600	-0.91275700
C	-1.97336700	1.23821300	0.04577300
C	-3.00761700	1.72848500	-0.79226400
C	-1.65030100	1.92306500	1.23411800
C	-3.71359100	2.90116900	-0.48983800
C	-2.35479200	3.09672100	1.54125400
H	-0.90904900	1.50698900	1.90725000
C	-3.37212700	3.58747400	0.68926700
H	-4.50196700	3.27031500	-1.13901900
H	-2.11930600	3.63091300	2.45777500
H	-3.90399100	4.49859200	0.95060800
N	-1.33975700	0.05477200	-0.43583800
S	-3.24110200	0.63003500	-2.21862200
Pd	0.47945300	-0.62377500	0.58392500
O	-0.44520800	-0.55064600	2.50366700
C	-1.11516400	-1.68343800	2.68957700
O	-1.15825100	-2.61822100	1.82533100
C	-1.84684000	-1.79107400	4.02102000
H	-2.31906800	-2.77223800	4.11380300
H	-1.14312100	-1.63297400	4.84657900
H	-2.61138000	-1.00675600	4.08574000
C	3.48632400	0.32927500	-0.23982700
C	4.86497500	0.20684600	0.04337100
C	2.96240400	1.60915700	-0.53573300
C	5.70887800	1.33226500	0.01152600
H	5.28022300	-0.77003700	0.28531400
C	3.80381000	2.73217700	-0.57064300
H	1.89546600	1.72766000	-0.71002600
C	5.18142100	2.59888700	-0.29955100
H	6.76791600	1.22054000	0.23061600
H	3.38741100	3.71107400	-0.79523400
H	5.82948600	3.47156800	-0.32026700
H	3.17796900	-1.80490000	0.07675500

INT3'_Z

B3LYP SCF energy: -1087.47543758 a.u.
B3LYP enthalpy: -1087.112152 a.u.
B3LYP free energy: -1087.195082 a.u.
M06 SCF energy in solution: -1864.540342 a.u.
M06 enthalpy in solution: -1864.177057 a.u.
M06 free energy in solution: -1864.259987 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.53317200	2.34166700	1.43714900
H	-0.31407500	1.38390900	1.92351900
H	-0.77281200	3.08474300	2.20566500
C	-1.33512200	1.29619200	-0.75138200
C	-2.15382800	0.29845600	-1.29497900
H	-1.71600300	-1.38692200	0.43117700
H	-0.49349100	1.60151200	-1.37283200
C	1.97205600	1.61265100	0.03126600
S	1.11019200	3.02579000	0.74043900
C	-1.65082300	2.26084100	0.37811100
H	-1.81035000	3.25909800	-0.05858900
H	-2.57751000	1.98588100	0.89161800
C	2.55546800	-0.42303900	-0.82232100
C	3.80294800	0.22362900	-1.01650400
C	2.39737800	-1.76915200	-1.20554200
C	4.89495500	-0.43482300	-1.59927200
C	3.48559700	-2.43286000	-1.78997100
H	1.46018500	-2.27803200	-1.01302600
C	4.72252900	-1.77500100	-1.98942600
H	5.84654200	0.06755500	-1.74533200
H	3.37790300	-3.47310500	-2.08470700
H	5.55257100	-2.31080100	-2.44230500
N	1.54842700	0.39962600	-0.24488300
S	3.72924000	1.93146500	-0.40501400
Pd	-0.45982100	-0.57386400	0.09933900
O	0.50938100	-1.97769400	1.28274500
C	0.67561400	-1.56758800	2.54195900
O	0.29801700	-0.43538400	2.96951900
C	1.37211600	-2.58282900	3.43798900
H	1.50517200	-2.16889800	4.44039000
H	0.77355000	-3.50007300	3.49014800
H	2.34585800	-2.84935100	3.01054800
C	-3.57997000	-0.01549400	-0.97774400
C	-4.43728700	-0.25532500	-2.07881900
C	-4.13388500	-0.06310900	0.32476800
C	-5.80921700	-0.50267600	-1.89200500
H	-4.02888800	-0.24146700	-3.08776700

C	-5.50321700	-0.31181700	0.51264400
H	-3.48660600	0.03405000	1.19116900
C	-6.35008700	-0.52626500	-0.59347500
H	-6.44772200	-0.68231200	-2.75356600
H	-5.90604600	-0.35656300	1.52156300
H	-7.40833800	-0.72510400	-0.44325400
H	-1.82956700	-0.09598600	-2.25945100

INT3'_E

B3LYP SCF energy: -1087.48434621 a.u.
B3LYP enthalpy: 1087.121000 a.u.
B3LYP free energy: -1087.204141 a.u.
M06 SCF energy in solution: -1864.550149 a.u.
M06 enthalpy in solution: -1864.186803 a.u.
M06 free energy in solution: -1864.269943 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.88609500	-2.81557600	-1.54093900
H	-1.23760200	-2.71412100	-0.50773600
H	-1.31925300	-3.72187000	-1.97821400
C	1.28817300	-1.48786900	-1.28601100
C	2.39760600	-1.34075400	-0.44935500
H	1.21585600	-1.94699700	1.60390900
H	1.01281200	-0.65293700	-1.92762800
C	-1.71614200	0.02865700	-1.52281800
S	-1.73821900	-1.44186400	-2.56539200
C	0.65149100	-2.81238500	-1.67087800
H	0.93334700	-3.05002900	-2.70898200
H	1.03611200	-3.61998800	-1.03255300
C	-1.26091900	1.60870300	0.06328400
C	-2.21477500	2.35611300	-0.67363500
C	-0.64944800	2.17447000	1.19851400
C	-2.56827800	3.66352800	-0.31120800
C	-0.99811600	3.48195000	1.56530700
H	0.05242300	1.58916400	1.78123100
C	-1.94635200	4.22241800	0.81980900
H	-3.29967400	4.23057700	-0.87928700
H	-0.53727000	3.92936500	2.44158600
H	-2.20309500	5.23323200	1.12563400
N	-1.00176400	0.311069^{i}00	-0.45558600
S	-2.84892600	1.37163600	-2.06163400
Pd	0.39911000	-1.00011900	0.69777500
O	-0.83081000	-0.77267400	2.35292800
C	-1.87031100	-1.60900100	2.36625700
O	-2.10806700	-2.45355600	1.45161100
C	-2.76221700	-1.47070500	3.59303800

H	-3.66825700	-2.06838400	3.46658100
H	-2.21691500	-1.81600100	4.48029600
H	-3.02042000	-0.41815500	3.75333400
C	3.25904800	-0.13671800	-0.33014000
C	4.41433700	-0.21591700	0.48337800
C	2.99693200	1.07828600	-1.01106800
C	5.28330800	0.87998600	0.61700200
H	4.62564100	-1.13953000	1.01943400
C	3.86415100	2.17366500	-0.87835800
H	2.11742400	1.17505500	-1.64195000
C	5.01202000	2.08142700	-0.06459600
H	6.16443000	0.79794500	1.24857100
H	3.64758300	3.09903800	-1.40673900
H	5.68122100	2.93236700	0.03592100
H	2.80776900	-2.23892600	0.00864200

INT1'_S5

B3LYP SCF energy: -1087.46170710 a.u.
B3LYP enthalpy: -1087.097245 a.u.
B3LYP free energy: -1087.183117 a.u.
M06 SCF energy in solution: -1864.53222942 a.u.
M06 enthalpy in solution: -1864.167767 a.u.
M06 free energy in solution: -1864.253639 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.07581200	3.09913300	1.22857900
H	-1.27515600	3.39666100	2.26698700
H	-0.98990300	4.02528300	0.64420200
S	0.67025700	1.92283100	-0.59894600
C	0.28012000	2.36578500	1.22358900
H	1.09379100	2.99641500	1.58596000
H	0.26150000	1.41148100	1.75563800
C	2.19088600	0.96045200	-0.37393500
C	4.21023500	-0.49118300	-0.66914400
C	4.09998900	0.22240900	0.55908100
C	5.30199900	-1.33107200	-0.93206400
C	5.10019100	0.08997200	1.54117400
C	6.29502200	-1.45265700	0.05754100
H	5.38624200	-1.87674200	-1.86707300
C	6.19374500	-0.74929100	1.28241900
H	5.00442100	0.63383300	2.47563600
H	7.15036200	-2.09863300	-0.12271500
H	6.97326200	-0.86379700	2.03099200
S	2.77156200	-0.14569600	-1.72795500
N	2.95337500	1.03410000	0.67472300

Pd	-1.59583800	0.45916500	-0.44728600
C	-3.26891800	-0.56880400	-0.04225600
C	-4.25593700	-0.74348800	-1.03091600
C	-3.41635000	-1.14943300	1.23252400
C	-5.41161000	-1.49732300	-0.73222200
H	-4.13242800	-0.32116500	-2.02594600
C	-4.57831800	-1.89628900	1.52158900
H	-2.63068800	-1.05021000	1.97717300
C	-5.57745300	-2.06926300	0.54380300
H	-6.17234200	-1.63754100	-1.49772300
H	-4.69239900	-2.34808400	2.50501900
H	-6.46916600	-2.64934400	0.77028800
O	-0.64648500	-1.36716800	-0.73655700
C	-0.01899600	-1.78653600	0.36439800
C	0.60688200	-3.16671000	0.24745600
H	1.28988700	-3.34285700	1.08239000
H	-0.18814700	-3.92334700	0.26445900
H	1.13491900	-3.26260200	-0.70669900
O	0.03959600	-1.10104000	1.43277800
C	-2.78023300	2.38170900	-0.57468100
H	-3.77694300	2.02111200	-0.80872900
H	-2.31262200	3.03250500	-1.31176400
C	-2.27060500	2.28311300	0.72141000
H	-2.88267100	1.80513000	1.48456800

INT1'_S7

B3LYP SCF energy: -1087.45391057 a.u.
B3LYP enthalpy: -1087.089645 a.u.
B3LYP free energy: -1087.174631 a.u.
M06 SCF energy in solution: -1864.52327231 a.u.
M06 enthalpy in solution: -1864.159007 a.u.
M06 free energy in solution: -1864.243992 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.53869700	2.78706400	-0.79142900
H	-1.63588000	2.82104400	-0.75650900
C	-0.08044300	1.55475800	-1.55000300
H	0.99835500	1.40682700	-1.58194800
C	-0.84560500	0.78779200	-2.41581200
H	-1.88880900	1.01425200	-2.60736600
H	-0.20395000	3.67530600	-1.34932400
H	-0.37073100	0.07924000	-3.09090100
O	-1.16196500	-1.59284600	1.20964400
C	-1.35317700	-0.94909900	2.36615000
O	-1.25389600	0.31080000	2.48202300

C	-1.71037500	-1.84849800	3.53732900
H	-2.74513400	-2.19548900	3.42125000
H	-1.06489900	-2.73302600	3.54959500
H	-1.61847400	-1.29653100	4.47607500
C	-0.00633900	2.87657700	0.65749200
H	-0.36725200	3.79099700	1.13989000
H	-0.30857300	2.02483100	1.27530500
S	1.88962200	3.10093700	0.77090900
C	2.53605800	1.46040600	0.37880100
C	3.03198200	-1.01920000	0.10160200
C	4.00075200	-0.09603600	-0.38385300
C	3.20743100	-2.40287000	-0.02182200
C	5.17297200	-0.57024100	-1.00096300
C	4.38470200	-2.86444900	-0.64296400
H	2.46470000	-3.10241300	0.34932200
C	5.35688900	-1.95688300	-1.12528100
H	5.90724700	0.14053300	-1.36659500
H	4.54640600	-3.93384100	-0.74916000
H	6.25758100	-2.33899600	-1.59826200
Pd	-0.81477800	-0.28658000	-0.37036800
C	-2.80451700	-0.36564400	-0.66844100
C	-3.63224100	0.50861000	0.05908600
C	-3.35253600	-1.33591800	-1.52740400
C	-5.03315500	0.41714700	-0.09408400
H	-3.20700100	1.21996000	0.76151200
C	-4.75414700	-1.42070600	-1.66775400
H	-2.71230600	-2.02474300	-2.07308900
C	-5.59572600	-0.54227500	-0.95734700
H	-5.67666500	1.08744600	0.47222200
H	-5.18121700	-2.17292700	-2.32794900
H	-6.67533000	-0.61102900	-1.06860100
S	1.65319400	-0.12649100	0.89465400
N	3.67151100	1.26760800	-0.22010200

TS1'_S5

B3LYP SCF energy: -1087.43339427 a.u.
B3LYP enthalpy: -1087.070447 a.u.
B3LYP free energy: -1087.155813 a.u.
M06 SCF energy in solution: -1864.51192366 a.u.
M06 enthalpy in solution: -1864.148976 a.u.
M06 free energy in solution: -1864.234342 a.u.
Imaginary frequency: -332.3360 cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
C	0.63718600	-3.35079200	-0.21321300
H	0.56703200	-4.33421400	0.28385700

H	1.41067400	-3.44378300	-0.98767200
S	-0.72956400	-1.27933200	-1.58602900
C	-0.73259100	-3.06040000	-0.84472800
H	-0.98251400	-3.73718200	-1.66510700
H	-1.53637300	-3.04727000	-0.10394900
C	-2.21817700	-0.58711000	-0.77890500
C	-4.15080700	0.84048000	-0.09018800
C	-3.97599400	-0.38634400	0.61183700
C	-5.19378800	1.72252700	0.22724200
C	-4.86545500	-0.74000500	1.64432200
C	-6.07543000	1.35691200	1.26077000
H	-5.32259700	2.66226900	-0.30107800
C	-5.91275600	0.13705500	1.96174500
H	-4.72336000	-1.67595700	2.17564200
H	-6.89141500	2.02430600	1.52533800
H	-6.60698900	-0.11904000	2.75767400
S	-2.86289400	1.02614900	-1.35959500
N	-2.87310200	-1.15665600	0.18895600
Pd	1.28599700	-0.47387500	-0.25615600
C	3.16861100	-0.22228800	0.68478500
C	4.30729500	-0.37508700	-0.13922500
C	3.17843000	0.73426200	1.72775400
C	5.43737600	0.43857800	0.06309200
H	4.30867100	-1.10947700	-0.94192000
C	4.30959700	1.54682100	1.92130100
H	2.30050900	0.86769900	2.35389300
C	5.44242700	1.39868200	1.09439200
H	6.30532100	0.32538700	-0.58271000
H	4.30288500	2.29642600	2.70931800
H	6.31699100	2.02602400	1.25088000
O	1.55100100	1.34324000	-1.30402900
C	1.00030700	2.35202100	-0.63456300
C	1.22216200	3.72983900	-1.24712900
H	0.53242500	4.45474500	-0.80597100
H	2.25360800	4.04992200	-1.04892100
H	1.09145500	3.68797100	-2.33376300
O	0.35042900	2.19623700	0.44826100
C	2.38380000	-2.05485200	1.21540600
H	2.57254500	-1.82870400	2.26079200
H	3.16608100	-2.64545800	0.74136000
C	1.02308000	-2.27480600	0.80289800
H	0.24718000	-2.05664900	1.54335300

TS1'_S7

B3LYP SCF energy: -1087.43237100 a.u.
B3LYP enthalpy: -1087.069363 a.u.

B3LYP free energy: -1087.152617 a.u.
M06 SCF energy in solution: -1864.51140184 a.u.
M06 enthalpy in solution: -1864.148394 a.u.
M06 free energy in solution: -1864.231648 a.u.
Imaginary frequency: -318.5045 cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
C	-0.04080000	3.27335700	-0.20659400
H	-1.01025900	3.45955300	0.27999800
C	-0.15401200	2.05068700	-1.11596400
H	0.75315500	1.79972200	-1.67135800
C	-1.40153700	1.76661800	-1.77625100
H	-2.23145800	2.45301200	-1.62280800
H	0.17118700	4.15150000	-0.83768900
H	-1.36087600	1.33659700	-2.77311200
O	-1.09040200	-1.49469500	1.06226100
C	-1.58968600	-1.11914300	2.23986700
O	-1.66133900	0.09862700	2.60248600
C	-2.09911900	-2.24955500	3.12396900
H	-3.06350900	-2.60201900	2.73493700
H	-1.40502000	-3.09676000	3.10260200
H	-2.23605100	-1.89564100	4.14928300
C	1.01662700	3.21968300	0.91430100
H	1.08794500	4.18817600	1.41937900
H	0.78061100	2.46505400	1.66891800
S	2.80374200	2.92907300	0.31066700
C	2.83725000	1.13834500	0.10803800
C	2.42360000	-1.37186100	0.17464200
C	3.51139000	-0.90278500	-0.61204800
C	2.07310400	-2.72322500	0.23760400
C	4.29133600	-1.82290500	-1.33500800
C	2.86273000	-3.63323800	-0.49407300
H	1.20632800	-3.04632500	0.80500000
C	3.96210600	-3.18746700	-1.26423000
H	5.12265500	-1.46426400	-1.93359600
H	2.61577200	-4.69116500	-0.46904300
H	4.55609200	-3.91069700	-1.81688100
Pd	-0.62066800	0.26436200	-0.07389100
C	-2.51990400	0.21999700	-0.99821700
C	-3.58920700	0.61813700	-0.16186900
C	-2.72230800	-0.78890400	-1.96723200
C	-4.84125500	-0.01165100	-0.28103400
H	-3.43637300	1.38041800	0.59707600
C	-3.97754600	-1.41474500	-2.07939400
H	-1.90723700	-1.09424600	-2.61990600
C	-5.04041800	-1.02590600	-1.24019000

H	-5.65454600	0.28476300	0.37751600
H	-4.12327500	-2.19989500	-2.81789500
H	-6.01157100	-1.50674800	-1.33153000
S	1.62603900	0.02548300	1.04266600
N	3.68863900	0.50162200	-0.63015900

X-RAY CRYSTALLOGRAPHY

Experimental Summary for Crystal **6c'** (CCDC 1905653)

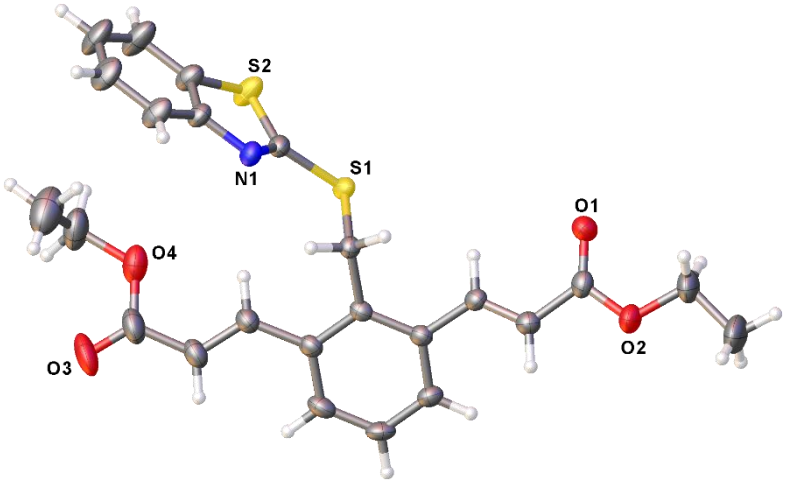


Table S8. Crystal data and structure refinement for **6c'.**

Empirical formula	C24 H23 N O4 S2	
Formula weight	453.55	
Temperature	200 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 15.796 Å	□= 90°.
	b = 15.246 Å	□= 105.81°.
	c = 9.849 Å	□ = 90°.
Volume	2282.1 $Å^3$	
Z	4	
Density (calculated)	1.320 Mg/m^3	
Absorption coefficient	2.367 mm^{-1}	
F(000)	952	
Crystal size	0.26 x 0.26 x 0.06 mm^3	
Theta range for data collection	4.107 to 68.155°.	
Index ranges	-18<=h<=19, -14<=k<=17, -11<=l<=11	
Reflections collected	13943	
Independent reflections	4121 [R(int) = 0.0385]	
Completeness to theta = 67.684°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7530 and 0.6063	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4121 / 33 / 311	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.1180	
R indices (all data)	R1 = 0.0631, wR2 = 0.1300	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.320 and -0.226 $e.Å^{-3}$	

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6c'**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	5486(1)	3911(1)	4683(1)	37(1)
S(2)	6678(1)	4952(1)	7001(1)	57(1)
O(1)	2851(1)	4112(1)	-323(2)	56(1)
O(2)	2313(1)	3043(1)	-1879(2)	57(1)
O(3)	8600(2)	1002(2)	7384(3)	84(1)
N(1)	7192(1)	4310(1)	4918(2)	38(1)
C(00E)	6600(2)	1873(2)	5210(3)	43(1)
C(1)	7771(2)	5104(2)	7013(3)	50(1)
C(2)	8449(2)	5511(3)	8030(4)	74(1)
C(3)	9270(2)	5522(3)	7826(4)	74(1)
C(4)	9429(2)	5145(2)	6640(4)	64(1)
C(5)	8762(2)	4749(2)	5629(3)	55(1)
C(6)	7919(2)	4717(2)	5821(3)	41(1)
C(7)	6525(2)	4376(2)	5411(3)	36(1)
C(8)	5705(2)	3236(1)	3275(2)	32(1)
C(9)	5306(2)	2339(1)	3250(2)	31(1)
C(10)	4494(2)	2139(1)	2280(2)	32(1)
C(11)	4165(2)	1285(2)	2207(3)	39(1)
C(12)	4624(2)	639(2)	3072(3)	45(1)
C(13)	5411(2)	832(2)	4036(3)	43(1)
C(14)	5766(2)	1677(2)	4150(3)	35(1)
C(15)	3970(2)	2813(2)	1350(2)	35(1)
C(16)	3412(2)	2659(2)	104(3)	41(1)
C(17)	2850(2)	3360(2)	-685(3)	42(1)
C(18)	1680(2)	3656(2)	-2735(4)	73(1)
C(19)	1112(3)	3145(3)	-3907(5)	105(2)
C(20)	7204(2)	1289(2)	5831(3)	50(1)
C(21)	8019(2)	1514(2)	6905(4)	66(1)
O(4)	7949(4)	2325(5)	7544(7)	68(2)
C(22)	8684(5)	2648(7)	8750(8)	85(3)
C(23)	9451(7)	2931(7)	8256(10)	112(4)

O(4')	8174(5)	2360(5)	7008(11)	70(2)
C(23')	8977(7)	2582(9)	8004(14)	105(5)
C(24')	8843(8)	3097(12)	9078(16)	158(9)

Table S10. Bond lengths [Å] and angles [°] for **6c'**.

S(1)-C(7)	1.753(2)
S(1)-C(8)	1.834(2)
S(2)-C(1)	1.738(3)
S(2)-C(7)	1.753(2)
O(1)-C(17)	1.201(3)
O(2)-C(17)	1.338(3)
O(2)-C(18)	1.458(4)
O(3)-C(21)	1.199(4)
N(1)-C(6)	1.392(3)
N(1)-C(7)	1.279(3)
C(00E)-C(14)	1.471(3)
C(00E)-C(20)	1.325(4)
C(1)-C(2)	1.397(4)
C(1)-C(6)	1.390(4)
C(2)-C(3)	1.365(5)
C(3)-C(4)	1.385(5)
C(4)-C(5)	1.376(4)
C(5)-C(6)	1.395(4)
C(8)-C(9)	1.504(3)
C(9)-C(10)	1.407(3)
C(9)-C(14)	1.408(3)
C(10)-C(11)	1.398(3)
C(10)-C(15)	1.471(3)
C(11)-C(12)	1.372(4)
C(12)-C(13)	1.375(4)
C(13)-C(14)	1.397(3)
C(15)-C(16)	1.321(3)
C(16)-C(17)	1.470(4)
C(18)-C(19)	1.477(5)
C(20)-C(21)	1.468(4)
C(21)-O(4)	1.405(8)
C(21)-O(4')	1.312(9)
O(4)-C(22)	1.4998(10)
C(22)-C(23)	1.487(12)

O(4')-C(23')	1.416(10)
C(23')-C(24')	1.380(14)

C(7)-S(1)-C(8)	100.80(11)
C(1)-S(2)-C(7)	88.17(12)
C(17)-O(2)-C(18)	116.5(2)
C(7)-N(1)-C(6)	110.1(2)
C(20)-C(00E)-C(14)	125.7(3)
C(2)-C(1)-S(2)	129.1(2)
C(6)-C(1)-S(2)	109.45(19)
C(6)-C(1)-C(2)	121.4(3)
C(3)-C(2)-C(1)	118.3(3)
C(2)-C(3)-C(4)	121.1(3)
C(5)-C(4)-C(3)	120.8(3)
C(4)-C(5)-C(6)	119.3(3)
N(1)-C(6)-C(5)	125.5(2)
C(1)-C(6)-N(1)	115.4(2)
C(1)-C(6)-C(5)	119.1(2)
S(1)-C(7)-S(2)	117.00(14)
N(1)-C(7)-S(1)	126.12(19)
N(1)-C(7)-S(2)	116.84(18)
C(9)-C(8)-S(1)	110.94(16)
C(10)-C(9)-C(8)	120.5(2)
C(10)-C(9)-C(14)	119.4(2)
C(14)-C(9)-C(8)	120.0(2)
C(9)-C(10)-C(15)	121.7(2)
C(11)-C(10)-C(9)	119.6(2)
C(11)-C(10)-C(15)	118.7(2)
C(12)-C(11)-C(10)	120.7(2)
C(11)-C(12)-C(13)	120.1(2)
C(12)-C(13)-C(14)	121.3(2)
C(9)-C(14)-C(00E)	120.7(2)
C(13)-C(14)-C(00E)	120.4(2)
C(13)-C(14)-C(9)	118.9(2)
C(16)-C(15)-C(10)	125.0(2)
C(15)-C(16)-C(17)	121.0(2)

O(1)-C(17)-O(2)	123.7(2)
O(1)-C(17)-C(16)	125.8(2)
O(2)-C(17)-C(16)	110.4(2)
O(2)-C(18)-C(19)	106.8(3)
C(00E)-C(20)-C(21)	123.8(3)
O(3)-C(21)-C(20)	124.0(4)
O(3)-C(21)-O(4)	122.8(4)
O(3)-C(21)-O(4')	120.2(4)
O(4)-C(21)-C(20)	111.5(3)
O(4')-C(21)-C(20)	113.2(4)
C(21)-O(4)-C(22)	120.3(7)
C(23)-C(22)-O(4)	111.1(8)
C(21)-O(4')-C(23')	113.6(8)
C(24')-C(23')-O(4')	111.8(11)

Symmetry transformations used to generate equivalent atoms:

Table S11. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6c'**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	29(1)	33(1)	49(1)	-8(1)	10(1)	-2(1)
S(2)	41(1)	71(1)	62(1)	-32(1)	19(1)	-13(1)
O(1)	57(1)	40(1)	59(1)	-2(1)	-1(1)	7(1)
O(2)	53(1)	51(1)	52(1)	1(1)	-13(1)	1(1)
O(3)	50(1)	94(2)	96(2)	42(2)	1(1)	25(1)
N(1)	32(1)	40(1)	42(1)	-5(1)	8(1)	-7(1)
C(00E)	43(1)	35(1)	49(2)	5(1)	7(1)	6(1)
C(1)	40(1)	53(2)	57(2)	-17(1)	13(1)	-10(1)
C(2)	54(2)	97(3)	70(2)	-46(2)	17(2)	-25(2)
C(3)	49(2)	95(3)	74(2)	-33(2)	7(2)	-29(2)
C(4)	41(2)	79(2)	72(2)	-17(2)	16(1)	-21(2)
C(5)	42(2)	68(2)	58(2)	-16(2)	20(1)	-18(1)
C(6)	37(1)	40(1)	44(1)	-6(1)	8(1)	-10(1)
C(7)	34(1)	28(1)	42(1)	1(1)	7(1)	-2(1)
C(8)	34(1)	30(1)	33(1)	1(1)	9(1)	1(1)
C(9)	34(1)	27(1)	34(1)	0(1)	13(1)	2(1)
C(10)	35(1)	28(1)	36(1)	-5(1)	13(1)	1(1)
C(11)	44(1)	33(1)	41(1)	-5(1)	12(1)	-4(1)
C(12)	60(2)	26(1)	52(2)	-5(1)	17(1)	-6(1)
C(13)	53(2)	26(1)	53(2)	6(1)	17(1)	9(1)
C(14)	36(1)	32(1)	38(1)	1(1)	12(1)	6(1)
C(15)	31(1)	31(1)	41(1)	-4(1)	9(1)	-3(1)
C(16)	43(1)	34(1)	43(1)	-4(1)	7(1)	-1(1)
C(17)	35(1)	45(2)	43(1)	1(1)	5(1)	-3(1)
C(18)	60(2)	68(2)	70(2)	8(2)	-18(2)	9(2)
C(19)	84(3)	94(3)	98(3)	3(3)	-42(2)	4(2)
C(20)	44(2)	47(2)	57(2)	13(1)	10(1)	13(1)
C(21)	50(2)	70(2)	69(2)	23(2)	1(2)	13(2)
O(4)	50(3)	95(3)	51(3)	2(2)	0(2)	8(2)
C(22)	57(4)	126(7)	57(5)	-11(4)	-8(3)	12(4)
C(23)	95(6)	131(8)	93(7)	21(6)	-5(5)	-25(6)

O(4')	50(4)	70(3)	69(5)	-8(3)	-19(3)	7(3)
C(23')	47(5)	137(9)	105(8)	-54(7)	-21(5)	8(5)
C(24')	58(7)	244(19)	145(11)	-130(12)	-16(7)	2(9)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **6c'**.

	x	y	z	U(eq)
H(00E)	6715	2469	5472	52
H(2)	8343	5772	8843	88
H(3)	9740	5794	8508	89
H(4)	10007	5159	6522	76
H(5)	8873	4501	4810	66
H(8A)	5457	3527	2353	39
H(8B)	6348	3180	3425	39
H(11)	3618	1149	1552	47
H(12)	4398	59	3004	55
H(13)	5721	381	4637	52
H(15)	4038	3403	1669	42
H(16)	3375	2086	-287	49
H(18A)	1988	4125	-3106	88
H(18B)	1324	3929	-2163	88
H(19A)	1470	2896	-4484	158
H(19B)	660	3529	-4492	158
H(19C)	829	2669	-3524	158
H(20)	7102	691	5565	60
H(22A)	8474	3148	9212	102
H(22B)	8868	2175	9456	102
H(23A)	9255	3349	7477	169
H(23B)	9714	2419	7929	169
H(23C)	9888	3212	9035	169
H(23D)	9286	2037	8409	126
H(23E)	9357	2900	7520	126
H(24A)	8454	3587	8675	236
H(24B)	9409	3326	9646	236
H(24C)	8571	2744	9677	236

Experimental Summary for Crystal **6d** (CCDC 1905643)

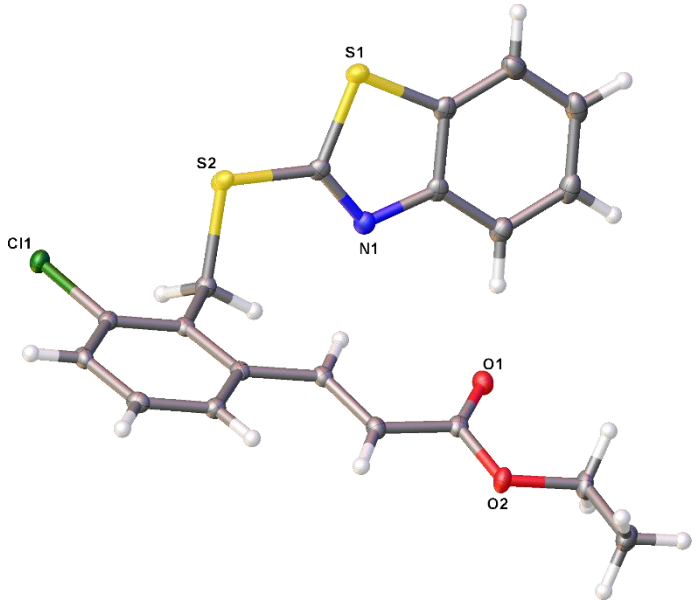


Table S13. Crystal data and structure refinement for **6d**.

Empirical formula	C19 H16 Cl N O2 S2
Formula weight	389.90
Temperature	100.0 K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 6.56960(10) Å □= 79.9110(10)°. b = 10.4589(2) Å □= 84.1890(10)°. c = 13.1664(3) Å □ = 81.3560(10)°.
Volume	877.96(3) $Å^3$
Z	2
Density (calculated)	1.475 Mg/m^3
Absorption coefficient	4.255 mm^{-1}
F(000)	404
Crystal size	0.3 x 0.28 x 0.26 mm^3
Theta range for data collection	3.420 to 68.330°.
Index ranges	-7<=h<=7, -12<=k<=12, -15<=l<=15
Reflections collected	10384
Independent reflections	3141 [R(int) = 0.0225]
Completeness to theta = 67.679°	98.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7531 and 0.5864
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3141 / 0 / 227
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0279, wR2 = 0.0736
R indices (all data)	R1 = 0.0295, wR2 = 0.0751
Extinction coefficient	n/a
Largest diff. peak and hole	0.346 and -0.217 e.$Å^{-3}$

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	14164(1)	3208(1)	9144(1)	20(1)
S(1)	7011(1)	-220(1)	9036(1)	22(1)
S(2)	10146(1)	1578(1)	8809(1)	22(1)
O(2)	2966(2)	6451(1)	5973(1)	20(1)
O(1)	4213(2)	4300(1)	6168(1)	21(1)
N(1)	7625(2)	1406(1)	7327(1)	18(1)
C(11)	10675(2)	4152(1)	8155(1)	15(1)
C(19)	6053(2)	710(1)	7180(1)	18(1)
C(9)	12008(2)	5609(2)	9113(1)	18(1)
C(6)	8981(2)	5124(1)	7918(1)	15(1)
C(7)	8856(2)	6322(2)	8276(1)	17(1)
C(5)	7337(2)	4880(2)	7322(1)	16(1)
C(10)	12127(2)	4423(2)	8767(1)	16(1)
C(3)	4313(2)	5399(2)	6311(1)	17(1)
C(4)	5904(2)	5785(2)	6876(1)	18(1)
C(14)	5504(2)	-222(2)	8023(1)	21(1)
C(8)	10357(2)	6561(2)	8857(1)	18(1)
C(18)	5031(3)	877(2)	6276(1)	23(1)
C(13)	8235(2)	1015(1)	8243(1)	17(1)
C(12)	10964(2)	2856(2)	7777(1)	18(1)
C(2)	1338(2)	6192(2)	5397(1)	22(1)
C(16)	2986(3)	-828(2)	7093(2)	28(1)
C(17)	3512(3)	97(2)	6245(1)	26(1)
C(1)	-172(3)	7423(2)	5225(1)	28(1)
C(15)	3971(3)	-996(2)	7993(1)	27(1)

Table S15. Bond lengths [Å] and angles [°] for **6d**.

Cl(1)-C(10)	1.7477(15)
S(1)-C(14)	1.7391(16)
S(1)-C(13)	1.7534(16)
S(2)-C(13)	1.7448(15)
S(2)-C(12)	1.8307(16)
O(2)-C(3)	1.3446(19)
O(2)-C(2)	1.4546(18)
O(1)-C(3)	1.2087(19)
N(1)-C(19)	1.396(2)
N(1)-C(13)	1.288(2)
C(11)-C(6)	1.409(2)
C(11)-C(10)	1.398(2)
C(11)-C(12)	1.504(2)
C(19)-C(14)	1.400(2)
C(19)-C(18)	1.397(2)
C(9)-H(9)	0.9500
C(9)-C(10)	1.384(2)
C(9)-C(8)	1.384(2)
C(6)-C(7)	1.402(2)
C(6)-C(5)	1.474(2)
C(7)-H(7)	0.9500
C(7)-C(8)	1.384(2)
C(5)-H(5)	0.9500
C(5)-C(4)	1.333(2)
C(3)-C(4)	1.482(2)
C(4)-H(4)	0.9500
C(14)-C(15)	1.391(2)
C(8)-H(8)	0.9500
C(18)-H(18)	0.9500
C(18)-C(17)	1.388(2)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900

C(2)-C(1)	1.501(2)
C(16)-H(16)	0.9500
C(16)-C(17)	1.396(3)
C(16)-C(15)	1.379(3)
C(17)-H(17)	0.9500
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(15)-H(15)	0.9500

C(14)-S(1)-C(13)	88.22(8)
C(13)-S(2)-C(12)	101.77(7)
C(3)-O(2)-C(2)	115.31(12)
C(13)-N(1)-C(19)	109.67(13)
C(6)-C(11)-C(12)	122.63(13)
C(10)-C(11)-C(6)	117.80(13)
C(10)-C(11)-C(12)	119.57(13)
N(1)-C(19)-C(14)	115.43(14)
N(1)-C(19)-C(18)	125.29(15)
C(18)-C(19)-C(14)	119.27(15)
C(10)-C(9)-H(9)	120.8
C(10)-C(9)-C(8)	118.45(14)
C(8)-C(9)-H(9)	120.8
C(11)-C(6)-C(5)	120.74(13)
C(7)-C(6)-C(11)	119.08(13)
C(7)-C(6)-C(5)	120.17(14)
C(6)-C(7)-H(7)	119.4
C(8)-C(7)-C(6)	121.22(14)
C(8)-C(7)-H(7)	119.4
C(6)-C(5)-H(5)	117.0
C(4)-C(5)-C(6)	126.01(14)
C(4)-C(5)-H(5)	117.0
C(11)-C(10)-Cl(1)	119.25(12)
C(9)-C(10)-Cl(1)	117.72(12)
C(9)-C(10)-C(11)	123.01(14)
O(2)-C(3)-C(4)	110.39(13)

O(1)-C(3)-O(2)	123.96(14)
O(1)-C(3)-C(4)	125.65(14)
C(5)-C(4)-C(3)	120.37(14)
C(5)-C(4)-H(4)	119.8
C(3)-C(4)-H(4)	119.8
C(19)-C(14)-S(1)	109.49(12)
C(15)-C(14)-S(1)	128.34(13)
C(15)-C(14)-C(19)	122.17(15)
C(9)-C(8)-C(7)	120.41(14)
C(9)-C(8)-H(8)	119.8
C(7)-C(8)-H(8)	119.8
C(19)-C(18)-H(18)	120.8
C(17)-C(18)-C(19)	118.46(16)
C(17)-C(18)-H(18)	120.8
S(2)-C(13)-S(1)	115.10(9)
N(1)-C(13)-S(1)	117.18(12)
N(1)-C(13)-S(2)	127.72(12)
S(2)-C(12)-H(12A)	109.6
S(2)-C(12)-H(12B)	109.6
C(11)-C(12)-S(2)	110.22(10)
C(11)-C(12)-H(12A)	109.6
C(11)-C(12)-H(12B)	109.6
H(12A)-C(12)-H(12B)	108.1
O(2)-C(2)-H(2A)	110.2
O(2)-C(2)-H(2B)	110.2
O(2)-C(2)-C(1)	107.54(13)
H(2A)-C(2)-H(2B)	108.5
C(1)-C(2)-H(2A)	110.2
C(1)-C(2)-H(2B)	110.2
C(17)-C(16)-H(16)	119.7
C(15)-C(16)-H(16)	119.7
C(15)-C(16)-C(17)	120.62(16)
C(18)-C(17)-C(16)	121.49(16)
C(18)-C(17)-H(17)	119.3
C(16)-C(17)-H(17)	119.3
C(2)-C(1)-H(1A)	109.5

C(2)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(14)-C(15)-H(15)	121.0
C(16)-C(15)-C(14)	117.98(16)
C(16)-C(15)-H(15)	121.0

Symmetry transformations used to generate equivalent atoms:

Table S16. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	17(1)	21(1)	21(1)	-3(1)	-5(1)	0(1)
S(1)	26(1)	18(1)	22(1)	1(1)	-5(1)	-4(1)
S(2)	31(1)	16(1)	21(1)	-2(1)	-11(1)	-4(1)
O(2)	16(1)	24(1)	22(1)	-7(1)	-6(1)	0(1)
O(1)	20(1)	22(1)	21(1)	-6(1)	-2(1)	-5(1)
N(1)	21(1)	16(1)	19(1)	-6(1)	-3(1)	-1(1)
C(11)	16(1)	18(1)	12(1)	-4(1)	2(1)	-4(1)
C(19)	18(1)	14(1)	24(1)	-8(1)	-3(1)	3(1)
C(9)	18(1)	21(1)	16(1)	-4(1)	-2(1)	-7(1)
C(6)	16(1)	18(1)	12(1)	-3(1)	1(1)	-4(1)
C(7)	17(1)	18(1)	16(1)	-3(1)	0(1)	-1(1)
C(5)	16(1)	18(1)	15(1)	-5(1)	2(1)	-4(1)
C(10)	15(1)	18(1)	14(1)	-1(1)	0(1)	-2(1)
C(3)	15(1)	21(1)	14(1)	-4(1)	2(1)	-2(1)
C(4)	17(1)	19(1)	18(1)	-5(1)	0(1)	-4(1)
C(14)	20(1)	16(1)	26(1)	-7(1)	-4(1)	3(1)
C(8)	22(1)	16(1)	17(1)	-5(1)	1(1)	-4(1)
C(18)	25(1)	21(1)	24(1)	-7(1)	-6(1)	0(1)
C(13)	20(1)	12(1)	19(1)	-6(1)	-2(1)	2(1)
C(12)	18(1)	19(1)	17(1)	-5(1)	-2(1)	-1(1)
C(2)	16(1)	35(1)	18(1)	-9(1)	-5(1)	-3(1)
C(16)	22(1)	21(1)	45(1)	-13(1)	-6(1)	-2(1)
C(17)	24(1)	24(1)	33(1)	-14(1)	-10(1)	3(1)
C(1)	20(1)	37(1)	26(1)	1(1)	-5(1)	-2(1)
C(15)	24(1)	20(1)	37(1)	-3(1)	-2(1)	-4(1)

Table S17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **6d**.

	x	y	z	U(eq)
H(9)	13036	5765	9517	21
H(7)	7721	6981	8116	21
H(5)	7296	3997	7248	19
H(4)	5902	6682	6920	21
H(8)	10252	7385	9082	22
H(18)	5367	1510	5696	28
H(12A)	12436	2620	7551	22
H(12B)	10142	2925	7175	22
H(2A)	640	5464	5793	27
H(2B)	1926	5944	4725	27
H(16)	1939	-1348	7050	34
H(17)	2814	196	5632	32
H(1A)	524	8129	4811	42
H(1B)	-712	7674	5894	42
H(1C)	-1314	7270	4857	42
H(15)	3614	-1620	8575	32

Experimental Summary for Crystal **6e** (CCDC 1905647)

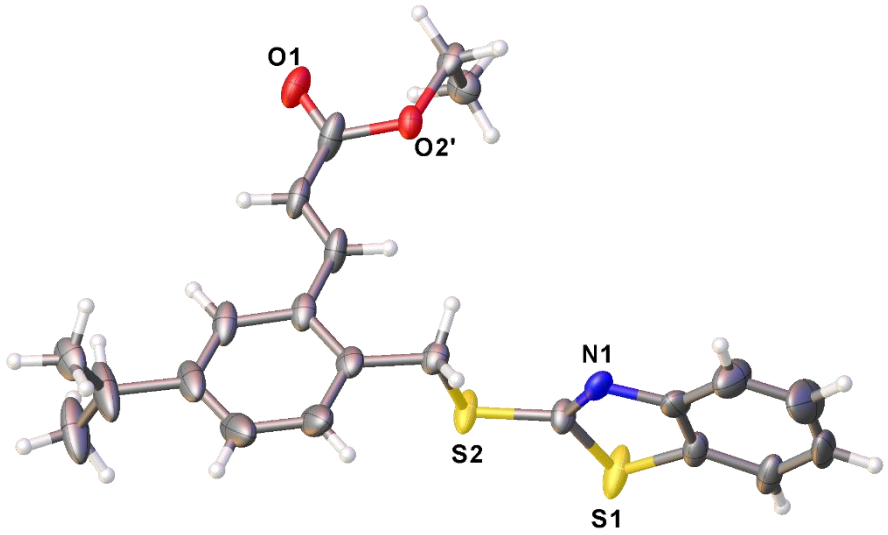


Table S18. Crystal data and structure refinement for **6e**.

Empirical formula	C22 H23 N O2 S2
Formula weight	397.53
Temperature	100.0 K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 8.6349(6) Å □= 70.251(5)°. b = 9.3163(4) Å □= 85.755(5)°. c = 13.5605(9) Å □ = 83.165(5)°.
Volume	1018.75(11) Å^3
Z	2
Density (calculated)	1.296 Mg/m^3
Absorption coefficient	2.496 mm^{-1}
F(000)	420
Crystal size	0.28 x 0.27 x 0.22 mm^3
Theta range for data collection	3.465 to 65.996°.
Index ranges	-10<=h<=10, -9<=k<=11, -16<=l<=16
Reflections collected	10983
Independent reflections	3493 [R(int) = 0.0399]
Completeness to theta = 65.996°	98.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7531 and 0.5935
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3493 / 3 / 296
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0757, wR2 = 0.1763
R indices (all data)	R1 = 0.0943, wR2 = 0.1909
Extinction coefficient	n/a
Largest diff. peak and hole	1.034 and -0.939 e.Å^{-3}

Table S19. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6e**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(2)	6709(2)	4372(1)	4539(1)	54(1)
S(1)	5306(2)	1925(1)	6299(1)	70(1)
O(1)	3694(4)	8297(3)	-214(2)	57(1)
N(1)	7230(4)	1337(4)	4869(3)	43(1)
C(15)	5701(5)	7738(4)	990(3)	46(1)
C(006)	6512(5)	2428(4)	5154(3)	38(1)
C(13)	7858(5)	7067(4)	2237(3)	42(1)
C(6)	6806(5)	-64(5)	5576(3)	45(1)
C(1)	5796(5)	24(5)	6388(3)	44(1)
C(7)	8164(5)	4312(5)	3511(3)	40(1)
C(8)	8656(5)	5908(5)	3044(3)	41(1)
C(14)	6497(5)	6774(5)	1778(4)	50(1)
C(12)	8381(6)	8528(5)	1893(4)	54(1)
C(16)	4342(5)	7427(5)	541(4)	59(1)
C(11)	9642(7)	8878(6)	2306(4)	66(2)
C(2)	5286(5)	-1263(5)	7169(4)	54(1)
C(9)	9924(7)	6253(6)	3463(4)	63(1)
C(3)	5834(8)	-2661(5)	7079(5)	76(2)
C(10)	10407(8)	7716(8)	3100(4)	79(2)
C(5)	7282(9)	-1485(6)	5504(4)	81(2)
C(4)	6781(11)	-2763(6)	6257(6)	100(3)
C(19)	11570(40)	10610(40)	1180(40)	64(8)
C(20)	10171(8)	10484(6)	1897	107(3)
C(21)	9300(40)	11550(20)	2230(30)	89(9)
O(2')	4077(7)	5848(7)	821(7)	39(3)
O(2)	3685(8)	6294(8)	1320(7)	36(3)
C(1A)	11110(50)	10730(40)	1010(40)	60(9)
C(22)	9920(30)	11350(30)	2559(16)	55(5)
C(17)	2225(9)	5942(11)	952(7)	51(2)
C(17')	2714(15)	5364(18)	402(12)	38(3)
C(18)	2650(30)	5200(30)	129(14)	82(8)

C(18')	1267(10)	5744(11)	985(7)	46(2)

Table S20. Bond lengths [Å] and angles [°] for **6e**.

S(2)-C(006)	1.742(4)
S(2)-C(7)	1.818(4)
S(1)-C(006)	1.761(4)
S(1)-C(1)	1.736(4)
O(1)-C(16)	1.198(6)
N(1)-C(006)	1.283(5)
N(1)-C(6)	1.405(5)
C(15)-C(14)	1.317(6)
C(15)-C(16)	1.462(7)
C(13)-C(8)	1.405(6)
C(13)-C(14)	1.464(7)
C(13)-C(12)	1.400(6)
C(6)-C(1)	1.371(6)
C(6)-C(5)	1.372(7)
C(1)-C(2)	1.397(6)
C(7)-C(8)	1.505(5)
C(8)-C(9)	1.388(7)
C(12)-C(11)	1.380(8)
C(16)-O(2')	1.431(8)
C(16)-O(2)	1.360(7)
C(11)-C(10)	1.384(9)
C(11)-C(20)	1.522(6)
C(2)-C(3)	1.374(8)
C(9)-C(10)	1.387(7)
C(3)-C(4)	1.355(10)
C(5)-C(4)	1.372(9)
C(19)-C(20)	1.48(4)
C(20)-C(21)	1.35(2)
C(20)-C(1A)	1.37(5)
C(20)-C(22)	1.39(2)
O(2')-C(17')	1.52(2)
O(2)-C(17)	1.4996(10)
C(17)-C(18)	1.4999(10)
C(17')-C(18')	1.5000(10)

C(006)-S(2)-C(7)	101.16(18)
C(1)-S(1)-C(006)	87.4(2)
C(006)-N(1)-C(6)	108.6(4)
C(14)-C(15)-C(16)	126.3(4)
S(2)-C(006)-S(1)	116.9(2)
N(1)-C(006)-S(2)	125.4(3)
N(1)-C(006)-S(1)	117.6(3)
C(8)-C(13)-C(14)	121.3(4)
C(12)-C(13)-C(8)	118.1(4)
C(12)-C(13)-C(14)	120.6(4)
C(1)-C(6)-N(1)	116.1(4)
C(1)-C(6)-C(5)	118.2(4)
C(5)-C(6)-N(1)	125.6(5)
C(6)-C(1)-S(1)	110.2(3)
C(6)-C(1)-C(2)	123.3(4)
C(2)-C(1)-S(1)	126.5(4)
C(8)-C(7)-S(2)	106.2(3)
C(13)-C(8)-C(7)	123.1(4)
C(9)-C(8)-C(13)	119.0(4)
C(9)-C(8)-C(7)	117.9(4)
C(15)-C(14)-C(13)	126.9(4)
C(11)-C(12)-C(13)	123.2(5)
O(1)-C(16)-C(15)	124.7(4)
O(1)-C(16)-O(2')	116.4(5)
O(1)-C(16)-O(2)	125.7(5)
O(2')-C(16)-C(15)	116.1(4)
O(2)-C(16)-C(15)	105.9(5)
C(12)-C(11)-C(10)	117.5(4)
C(12)-C(11)-C(20)	121.0(5)
C(10)-C(11)-C(20)	121.5(5)
C(3)-C(2)-C(1)	116.2(5)
C(10)-C(9)-C(8)	121.1(5)
C(4)-C(3)-C(2)	121.1(5)
C(11)-C(10)-C(9)	121.1(5)
C(4)-C(5)-C(6)	119.4(6)

C(3)-C(4)-C(5)	121.7(5)
C(19)-C(20)-C(11)	113.4(15)
C(21)-C(20)-C(11)	115.9(9)
C(21)-C(20)-C(19)	130.7(17)
C(1A)-C(20)-C(11)	112.9(14)
C(1A)-C(20)-C(22)	128.6(16)
C(22)-C(20)-C(11)	117.0(10)
C(16)-O(2')-C(17')	121.5(7)
C(16)-O(2)-C(17)	110.0(6)
O(2)-C(17)-C(18)	109.2(13)
C(18')-C(17')-O(2')	107.1(11)

Symmetry transformations used to generate equivalent atoms:

Table S21. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6e**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(2)	73(1)	26(1)	54(1)	-8(1)	36(1)	-9(1)
S(1)	75(1)	32(1)	76(1)	3(1)	42(1)	-1(1)
O(1)	65(2)	37(2)	51(2)	6(1)	4(2)	-1(2)
N(1)	51(2)	38(2)	33(2)	3(2)	-12(2)	-6(2)
C(15)	51(3)	25(2)	48(2)	2(2)	18(2)	-3(2)
C(006)	41(2)	25(2)	43(2)	-10(2)	12(2)	0(2)
C(13)	45(2)	31(2)	45(2)	-12(2)	23(2)	-7(2)
C(6)	60(3)	35(2)	38(2)	-6(2)	-20(2)	0(2)
C(1)	42(2)	31(2)	50(2)	1(2)	-12(2)	-4(2)
C(7)	42(2)	37(2)	35(2)	-9(2)	12(2)	-4(2)
C(8)	50(2)	39(2)	33(2)	-13(2)	19(2)	-13(2)
C(14)	42(2)	26(2)	65(3)	4(2)	12(2)	-4(2)
C(12)	66(3)	31(2)	58(3)	-13(2)	37(2)	-11(2)
C(16)	42(3)	35(2)	72(3)	14(2)	9(2)	1(2)
C(11)	95(4)	58(3)	57(3)	-32(3)	47(3)	-45(3)
C(2)	48(3)	40(3)	58(3)	12(2)	-15(2)	-12(2)
C(9)	79(4)	74(3)	36(2)	-12(2)	9(2)	-38(3)
C(3)	113(5)	30(3)	70(4)	15(2)	-46(4)	-23(3)
C(10)	106(5)	98(5)	47(3)	-30(3)	23(3)	-69(4)
C(5)	138(6)	45(3)	53(3)	-15(2)	-3(3)	13(3)
C(4)	179(8)	31(3)	87(5)	-22(3)	-25(5)	15(4)
C(19)	64(15)	68(11)	70(14)	-34(8)	33(10)	-35(9)
C(20)	146(6)	68(4)	130(6)	-63(4)	100(5)	-73(4)
C(21)	91(15)	42(8)	140(20)	-47(12)	58(14)	-30(10)
O(2')	41(3)	27(3)	44(4)	-6(3)	5(3)	-5(2)
O(2)	38(4)	28(3)	36(4)	-5(3)	7(3)	-4(3)
C(1A)	80(20)	36(9)	72(16)	-33(9)	45(15)	-40(11)
C(22)	57(11)	66(9)	56(8)	-37(7)	26(7)	-21(8)
C(17)	42(6)	48(5)	46(6)	1(5)	11(5)	-1(5)
C(17')	42(6)	35(6)	29(6)	-4(5)	17(5)	-4(5)
C(18)	84(12)	79(12)	86(16)	-36(10)	13(9)	-6(9)

C(18')	33(5)	56(6)	51(5)	-19(4)	5(4)	-7(4)

Table S22. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **6e**.

	x	y	z	U(eq)
H(15)	6044	8730	683	56
H(7A)	9070	3570	3805	48
H(7B)	7715	4005	2970	48
H(14)	6150	5782	2082	60
H(12)	7843	9315	1350	65
H(2)	4600	-1177	7731	65
H(9)	10471	5475	4008	75
H(3)	5544	-3572	7601	91
H(10)	11276	7924	3402	94
H(5)	7954	-1583	4938	97
H(4)	7106	-3744	6201	120
H(19A)	12480	10041	1583	96
H(19B)	11755	11694	862	96
H(19C)	11406	10189	634	96
H(20)	10852	10222	2510	129
H(20A)	9201	10953	1502	129
H(21A)	8315	11838	1865	133
H(21B)	9873	12450	2073	133
H(21C)	9091	11119	2985	133
H(1AA)	11944	9881	1118	90
H(1AB)	11578	11693	858	90
H(1AC)	10494	10784	418	90
H(22A)	8889	11208	2911	83
H(22B)	9969	12438	2149	83
H(22C)	10725	11023	3085	83
H(17A)	1532	6899	657	61
H(17B)	1660	5243	1550	61
H(17C)	2628	5920	-360	46
H(17D)	2865	4250	515	46
H(18A)	3223	5892	-455	123

H(18B)	1694	4996	-127	123
H(18C)	3302	4237	432	123
H(18D)	371	5380	771	70
H(18E)	1089	6857	826	70
H(18F)	1397	5244	1741	70

Experimental Summary for Crystal **6g** (CCDC 1905650)

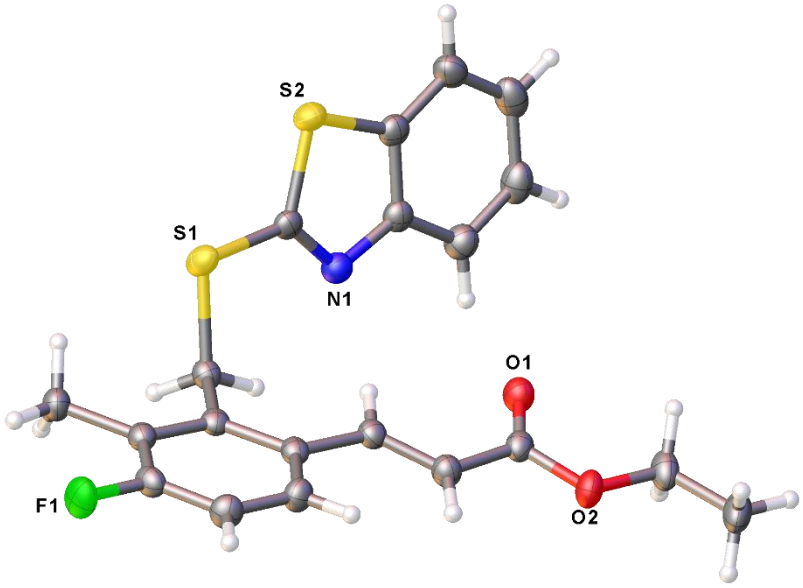


Table S23. Crystal data and structure refinement for **6g**.

Empirical formula	C20 H18 F N O2 S2	
Formula weight	387.47	
Temperature	200 K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.0055(2) Å	□= 79.220(2)°.
	b = 10.2801(3) Å	□= 84.888(2)°.
	c = 13.1310(3) Å	□ = 80.238(2)°.
Volume	913.91(4) $Å^3$	
Z	2	
Density (calculated)	1.408 Mg/m^3	
Absorption coefficient	2.851 mm^{-1}	
F(000)	404	
Crystal size	0.29 x 0.28 x 0.27 mm^3	
Theta range for data collection	4.433 to 68.311°.	
Index ranges	-8<=h<=8, -12<=k<=10, -15<=l<=15	
Reflections collected	8744	
Independent reflections	3247 [R(int) = 0.0260]	
Completeness to theta = 67.679°	97.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.6344	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3247 / 0 / 237	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0371, wR2 = 0.0969	
R indices (all data)	R1 = 0.0410, wR2 = 0.1009	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.365 and -0.381 $e.Å^{-3}$	

Table S24. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6g**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	9930(1)	1628(1)	8803(1)	38(1)
S(2)	6869(1)	-83(1)	9097(1)	38(1)
F(1)	13101(2)	5996(1)	9478(1)	48(1)
O(2)	2987(2)	6510(1)	5949(1)	39(1)
O(1)	4237(2)	4321(1)	6196(1)	40(1)
N(1)	7549(2)	1433(2)	7326(1)	33(1)
C(7)	8105(3)	1076(2)	8262(1)	30(1)
C(16)	7226(2)	4959(2)	7276(1)	29(1)
C(9)	10443(2)	4233(2)	8084(1)	26(1)
C(1)	6035(3)	767(2)	7200(2)	32(1)
C(14)	11916(2)	4481(2)	8647(1)	29(1)
C(6)	5458(3)	-110(2)	8080(2)	34(1)
C(17)	5813(3)	5862(2)	6836(2)	34(1)
C(8)	10682(2)	2896(2)	7738(1)	31(1)
C(10)	8797(2)	5216(2)	7847(1)	28(1)
C(15)	13656(3)	3445(2)	8954(2)	37(1)
C(2)	5093(3)	912(2)	6283(2)	42(1)
C(11)	8677(3)	6442(2)	8181(2)	34(1)
C(12)	10123(3)	6708(2)	8723(2)	37(1)
C(3)	3635(3)	160(2)	6273(2)	47(1)
C(18)	4309(2)	5446(2)	6303(1)	32(1)
C(13)	11696(3)	5723(2)	8939(1)	33(1)
C(20)	-36(3)	7468(3)	5224(2)	55(1)
C(5)	3981(3)	-854(2)	8066(2)	43(1)
C(19)	1446(3)	6225(2)	5398(2)	43(1)
C(4)	3089(3)	-707(2)	7152(2)	48(1)

Table S25. Bond lengths [Å] and angles [°] for **6g**.

S(1)-C(7)	1.7375(18)
S(1)-C(8)	1.8307(19)
S(2)-C(7)	1.7505(19)
S(2)-C(6)	1.738(2)
F(1)-C(13)	1.357(2)
O(2)-C(18)	1.346(2)
O(2)-C(19)	1.449(2)
O(1)-C(18)	1.201(2)
N(1)-C(7)	1.290(2)
N(1)-C(1)	1.393(2)
C(16)-H(16)	0.9500
C(16)-C(17)	1.329(3)
C(16)-C(10)	1.471(2)
C(9)-C(14)	1.404(2)
C(9)-C(8)	1.506(2)
C(9)-C(10)	1.414(2)
C(1)-C(6)	1.401(3)
C(1)-C(2)	1.396(3)
C(14)-C(15)	1.507(2)
C(14)-C(13)	1.380(3)
C(6)-C(5)	1.391(3)
C(17)-H(17)	0.9500
C(17)-C(18)	1.476(2)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(10)-C(11)	1.397(3)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(2)-H(2)	0.9500
C(2)-C(3)	1.384(3)
C(11)-H(11)	0.9500
C(11)-C(12)	1.379(3)
C(12)-H(12)	0.9500

C(12)-C(13)	1.375(3)
C(3)-H(3)	0.9500
C(3)-C(4)	1.388(3)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(20)-C(19)	1.498(3)
C(5)-H(5)	0.9500
C(5)-C(4)	1.374(3)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(4)-H(4)	0.9500

C(7)-S(1)-C(8)	101.81(8)
C(6)-S(2)-C(7)	88.63(9)
C(18)-O(2)-C(19)	115.66(15)
C(7)-N(1)-C(1)	109.96(16)
S(1)-C(7)-S(2)	115.69(10)
N(1)-C(7)-S(1)	127.58(14)
N(1)-C(7)-S(2)	116.72(14)
C(17)-C(16)-H(16)	116.6
C(17)-C(16)-C(10)	126.76(17)
C(10)-C(16)-H(16)	116.6
C(14)-C(9)-C(8)	117.91(15)
C(14)-C(9)-C(10)	120.72(16)
C(10)-C(9)-C(8)	121.36(15)
N(1)-C(1)-C(6)	115.48(16)
N(1)-C(1)-C(2)	125.15(18)
C(2)-C(1)-C(6)	119.37(18)
C(9)-C(14)-C(15)	122.57(16)
C(13)-C(14)-C(9)	117.20(16)
C(13)-C(14)-C(15)	120.22(16)
C(1)-C(6)-S(2)	109.20(14)
C(5)-C(6)-S(2)	128.88(17)
C(5)-C(6)-C(1)	121.92(19)
C(16)-C(17)-H(17)	119.7

C(16)-C(17)-C(18)	120.59(17)
C(18)-C(17)-H(17)	119.7
S(1)-C(8)-H(8A)	109.6
S(1)-C(8)-H(8B)	109.6
C(9)-C(8)-S(1)	110.07(12)
C(9)-C(8)-H(8A)	109.6
C(9)-C(8)-H(8B)	109.6
H(8A)-C(8)-H(8B)	108.2
C(9)-C(10)-C(16)	121.23(16)
C(11)-C(10)-C(16)	120.31(16)
C(11)-C(10)-C(9)	118.45(16)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(1)-C(2)-H(2)	120.8
C(3)-C(2)-C(1)	118.4(2)
C(3)-C(2)-H(2)	120.8
C(10)-C(11)-H(11)	119.2
C(12)-C(11)-C(10)	121.51(17)
C(12)-C(11)-H(11)	119.2
C(11)-C(12)-H(12)	120.9
C(13)-C(12)-C(11)	118.15(17)
C(13)-C(12)-H(12)	120.9
C(2)-C(3)-H(3)	119.3
C(2)-C(3)-C(4)	121.4(2)
C(4)-C(3)-H(3)	119.3
O(2)-C(18)-C(17)	110.68(16)
O(1)-C(18)-O(2)	123.58(16)
O(1)-C(18)-C(17)	125.73(16)
F(1)-C(13)-C(14)	118.59(16)
F(1)-C(13)-C(12)	117.45(16)
C(12)-C(13)-C(14)	123.96(16)
H(20A)-C(20)-H(20B)	109.5

H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
C(6)-C(5)-H(5)	121.1
C(4)-C(5)-C(6)	117.7(2)
C(4)-C(5)-H(5)	121.1
O(2)-C(19)-C(20)	107.67(18)
O(2)-C(19)-H(19A)	110.2
O(2)-C(19)-H(19B)	110.2
C(20)-C(19)-H(19A)	110.2
C(20)-C(19)-H(19B)	110.2
H(19A)-C(19)-H(19B)	108.5
C(3)-C(4)-H(4)	119.4
C(5)-C(4)-C(3)	121.22(19)
C(5)-C(4)-H(4)	119.4

Symmetry transformations used to generate equivalent atoms:

Table S26. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6g**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	45(1)	35(1)	37(1)	-1(1)	-17(1)	-11(1)
S(2)	41(1)	35(1)	37(1)	2(1)	-8(1)	-9(1)
F(1)	47(1)	49(1)	56(1)	-15(1)	-24(1)	-13(1)
O(2)	32(1)	45(1)	40(1)	-8(1)	-14(1)	0(1)
O(1)	35(1)	41(1)	44(1)	-9(1)	-10(1)	-7(1)
N(1)	35(1)	34(1)	32(1)	-7(1)	-6(1)	-7(1)
C(7)	31(1)	25(1)	33(1)	-7(1)	-4(1)	0(1)
C(16)	26(1)	35(1)	28(1)	-7(1)	0(1)	-7(1)
C(9)	24(1)	32(1)	23(1)	-4(1)	1(1)	-7(1)
C(1)	32(1)	28(1)	38(1)	-10(1)	-6(1)	-2(1)
C(14)	26(1)	35(1)	26(1)	-3(1)	-3(1)	-8(1)
C(6)	32(1)	27(1)	43(1)	-8(1)	-6(1)	0(1)
C(17)	31(1)	35(1)	39(1)	-8(1)	-6(1)	-6(1)
C(8)	27(1)	35(1)	32(1)	-10(1)	-2(1)	-5(1)
C(10)	26(1)	35(1)	23(1)	-4(1)	-1(1)	-7(1)
C(15)	29(1)	40(1)	43(1)	-3(1)	-9(1)	-6(1)
C(2)	45(1)	43(1)	41(1)	-9(1)	-12(1)	-7(1)
C(11)	32(1)	34(1)	37(1)	-9(1)	-6(1)	-1(1)
C(12)	42(1)	34(1)	39(1)	-13(1)	-6(1)	-7(1)
C(3)	44(1)	46(1)	56(1)	-20(1)	-18(1)	-2(1)
C(18)	26(1)	40(1)	28(1)	-5(1)	-1(1)	-3(1)
C(13)	32(1)	42(1)	30(1)	-8(1)	-7(1)	-14(1)
C(20)	34(1)	75(2)	49(1)	2(1)	-11(1)	1(1)
C(5)	39(1)	35(1)	58(1)	-6(1)	-5(1)	-11(1)
C(19)	30(1)	65(1)	34(1)	-12(1)	-10(1)	-4(1)
C(4)	37(1)	41(1)	72(2)	-20(1)	-10(1)	-10(1)

Table S27. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **6g**.

	x	y	z	U(eq)
H(16)	7221	4053	7217	35
H(17)	5771	6783	6864	41
H(8A)	12056	2624	7514	37
H(8B)	9884	2968	7138	37
H(15A)	13227	2664	9407	56
H(15B)	14519	3827	9323	56
H(15C)	14354	3168	8329	56
H(2)	5444	1513	5680	50
H(11)	7574	7109	8031	41
H(12)	10035	7548	8941	45
H(3)	2995	239	5651	56
H(20A)	558	8196	4792	82
H(20B)	-515	7724	5894	82
H(20C)	-1120	7295	4872	82
H(5)	3601	-1445	8669	52
H(19A)	850	5473	5812	51
H(19B)	1969	5972	4724	51
H(4)	2080	-1208	7122	58

Experimental Summary for Crystal **6j''** (CCDC 1905652)

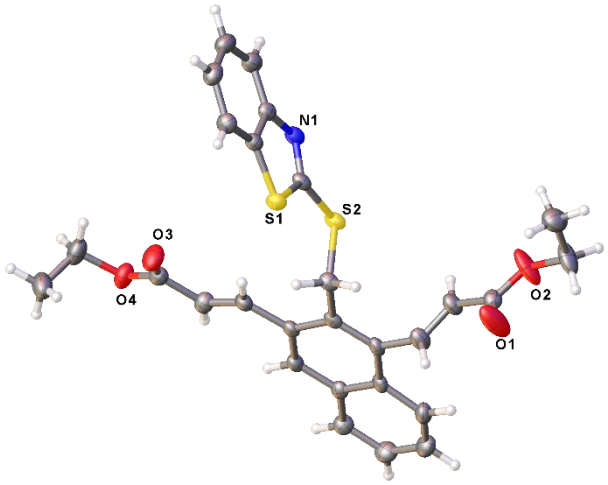


Table S28. Crystal data and structure refinement for **6j''**.

Empirical formula	C28 H25 N O4 S2	
Formula weight	503.61	
Temperature	200 K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.4844(7) Å	□= 112.337(6)°.
	b = 12.3314(9) Å	□= 94.171(5)°.
	c = 12.7997(11) Å	□ = 98.558(6)°.
Volume	1212.59(18) $Å^3$	
Z	2	
Density (calculated)	1.379 Mg/m^3	
Absorption coefficient	2.286 mm^{-1}	
F(000)	528	
Crystal size	0.3 x 0.29 x 0.28 mm^3	
Theta range for data collection	3.771 to 68.433°.	
Index ranges	-10<=h<=10, -14<=k<=14, -15<=l<=15	
Reflections collected	13527	
Independent reflections	4305 [R(int) = 0.0410]	
Completeness to theta = 67.679°	97.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.5788	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4305 / 0 / 318	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0515, wR2 = 0.1293	
R indices (all data)	R1 = 0.0597, wR2 = 0.1403	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.622 and -0.318 $e.Å^{-3}$	

Table S29. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6j''**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	4488(1)	4185(1)	8096(1)	34(1)
S(2)	2712(1)	5950(1)	7564(1)	34(1)
O(1)	8143(3)	9354(3)	8027(2)	94(1)
O(4)	-1243(2)	1259(2)	3667(2)	51(1)
O(3)	968(3)	1654(2)	4921(2)	64(1)
O(2)	6412(3)	10350(2)	8968(2)	79(1)
N(1)	1975(2)	4910(2)	8980(2)	33(1)
C(17)	1798(3)	5294(2)	3819(2)	31(1)
C(16)	2400(3)	6356(2)	3695(2)	30(1)
C(11)	3668(3)	7197(2)	4506(2)	31(1)
C(9)	3615(3)	5923(2)	5576(2)	29(1)
C(21)	6804(3)	9477(2)	8112(2)	36(1)
C(26)	131(3)	1939(2)	4309(2)	39(1)
C(13)	3693(4)	8431(3)	3423(3)	48(1)
C(6)	3752(3)	3636(2)	9065(2)	33(1)
C(1)	2398(3)	4117(2)	9441(2)	32(1)
C(24)	1754(3)	3902(2)	4798(2)	34(1)
C(19)	5523(3)	7878(2)	6335(2)	42(1)
C(12)	4317(3)	8240(2)	4334(2)	42(1)
C(20)	5404(3)	8661(2)	7306(2)	40(1)
C(8)	4212(3)	5675(2)	6589(2)	31(1)
C(2)	1589(3)	3775(3)	10213(2)	43(1)
C(15)	1770(3)	6597(2)	2760(2)	38(1)
C(3)	2173(4)	2996(3)	10606(2)	49(1)
C(14)	2402(3)	7619(3)	2635(2)	45(1)
C(4)	3531(4)	2533(3)	10236(2)	47(1)
C(25)	517(3)	3070(2)	4153(2)	38(1)
C(5)	4329(3)	2846(2)	9455(2)	41(1)
C(23)	8108(4)	10727(3)	10716(3)	64(1)
C(27)	-1729(4)	103(3)	3734(3)	60(1)
C(22)	7728(5)	11175(3)	9836(3)	69(1)

C(28)	-1018(6)	-825(3)	2928(3)	71(1)
C(10)	4240(3)	6971(2)	5475(2)	31(1)
C(7)	2957(3)	5017(2)	8278(2)	30(1)
C(18)	2370(3)	5044(2)	4720(2)	29(1)

Table S30. Bond lengths [Å] and angles [°] for **6j''**.

S(1)-C(6)	1.736(3)
S(1)-C(7)	1.747(2)
S(2)-C(8)	1.825(2)
S(2)-C(7)	1.745(2)
O(1)-C(21)	1.176(4)
O(4)-C(26)	1.336(3)
O(4)-C(27)	1.460(4)
O(3)-C(26)	1.201(4)
O(2)-C(21)	1.316(3)
O(2)-C(22)	1.463(4)
N(1)-C(1)	1.394(3)
N(1)-C(7)	1.299(3)
C(17)-H(17)	0.9500
C(17)-C(16)	1.403(4)
C(17)-C(18)	1.377(3)
C(16)-C(11)	1.413(3)
C(16)-C(15)	1.426(4)
C(11)-C(12)	1.425(4)
C(11)-C(10)	1.438(3)
C(9)-C(8)	1.511(3)
C(9)-C(10)	1.378(4)
C(9)-C(18)	1.441(3)
C(21)-C(20)	1.471(3)
C(26)-C(25)	1.476(4)
C(13)-H(13)	0.9500
C(13)-C(12)	1.360(4)
C(13)-C(14)	1.402(4)
C(6)-C(1)	1.403(3)
C(6)-C(5)	1.383(4)
C(1)-C(2)	1.398(4)
C(24)-H(24)	0.9500
C(24)-C(25)	1.321(4)
C(24)-C(18)	1.470(4)
C(19)-H(19)	0.9500

C(19)-C(20)	1.274(4)
C(19)-C(10)	1.475(3)
C(12)-H(12)	0.9500
C(20)-H(20)	0.9500
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(2)-H(2)	0.9500
C(2)-C(3)	1.376(4)
C(15)-H(15)	0.9500
C(15)-C(14)	1.366(4)
C(3)-H(3)	0.9500
C(3)-C(4)	1.395(4)
C(14)-H(14)	0.9500
C(4)-H(4)	0.9500
C(4)-C(5)	1.386(4)
C(25)-H(25)	0.9500
C(5)-H(5)	0.9500
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(23)-C(22)	1.467(5)
C(27)-H(27A)	0.9900
C(27)-H(27B)	0.9900
C(27)-C(28)	1.462(5)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800

C(6)-S(1)-C(7)	88.59(11)
C(7)-S(2)-C(8)	103.64(11)
C(26)-O(4)-C(27)	116.5(2)
C(21)-O(2)-C(22)	116.9(3)
C(7)-N(1)-C(1)	110.1(2)
C(16)-C(17)-H(17)	118.7

C(18)-C(17)-H(17)	118.7
C(18)-C(17)-C(16)	122.6(2)
C(17)-C(16)-C(11)	119.4(2)
C(17)-C(16)-C(15)	121.3(2)
C(11)-C(16)-C(15)	119.3(2)
C(16)-C(11)-C(12)	118.6(2)
C(16)-C(11)-C(10)	118.7(2)
C(12)-C(11)-C(10)	122.7(2)
C(10)-C(9)-C(8)	120.7(2)
C(10)-C(9)-C(18)	120.7(2)
C(18)-C(9)-C(8)	118.6(2)
O(1)-C(21)-O(2)	122.6(3)
O(1)-C(21)-C(20)	124.0(2)
O(2)-C(21)-C(20)	113.3(2)
O(4)-C(26)-C(25)	111.7(2)
O(3)-C(26)-O(4)	124.2(3)
O(3)-C(26)-C(25)	124.1(3)
C(12)-C(13)-H(13)	119.3
C(12)-C(13)-C(14)	121.5(3)
C(14)-C(13)-H(13)	119.3
C(1)-C(6)-S(1)	109.69(19)
C(5)-C(6)-S(1)	128.6(2)
C(5)-C(6)-C(1)	121.7(2)
N(1)-C(1)-C(6)	114.9(2)
N(1)-C(1)-C(2)	125.7(2)
C(2)-C(1)-C(6)	119.4(2)
C(25)-C(24)-H(24)	116.2
C(25)-C(24)-C(18)	127.6(2)
C(18)-C(24)-H(24)	116.2
C(20)-C(19)-H(19)	115.6
C(20)-C(19)-C(10)	128.7(2)
C(10)-C(19)-H(19)	115.6
C(11)-C(12)-H(12)	119.9
C(13)-C(12)-C(11)	120.3(2)
C(13)-C(12)-H(12)	119.9
C(21)-C(20)-H(20)	118.4

C(19)-C(20)-C(21)	123.1(2)
C(19)-C(20)-H(20)	118.4
S(2)-C(8)-H(8A)	110.2
S(2)-C(8)-H(8B)	110.2
C(9)-C(8)-S(2)	107.72(15)
C(9)-C(8)-H(8A)	110.2
C(9)-C(8)-H(8B)	110.2
H(8A)-C(8)-H(8B)	108.5
C(1)-C(2)-H(2)	120.6
C(3)-C(2)-C(1)	118.8(3)
C(3)-C(2)-H(2)	120.6
C(16)-C(15)-H(15)	119.8
C(14)-C(15)-C(16)	120.5(2)
C(14)-C(15)-H(15)	119.8
C(2)-C(3)-H(3)	119.3
C(2)-C(3)-C(4)	121.3(3)
C(4)-C(3)-H(3)	119.3
C(13)-C(14)-H(14)	120.1
C(15)-C(14)-C(13)	119.9(3)
C(15)-C(14)-H(14)	120.1
C(3)-C(4)-H(4)	119.7
C(5)-C(4)-C(3)	120.6(3)
C(5)-C(4)-H(4)	119.7
C(26)-C(25)-H(25)	119.9
C(24)-C(25)-C(26)	120.1(2)
C(24)-C(25)-H(25)	119.9
C(6)-C(5)-C(4)	118.2(3)
C(6)-C(5)-H(5)	120.9
C(4)-C(5)-H(5)	120.9
H(23A)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
O(4)-C(27)-H(27A)	109.2

O(4)-C(27)-H(27B)	109.2
O(4)-C(27)-C(28)	111.9(3)
H(27A)-C(27)-H(27B)	107.9
C(28)-C(27)-H(27A)	109.2
C(28)-C(27)-H(27B)	109.2
O(2)-C(22)-C(23)	111.1(3)
O(2)-C(22)-H(22A)	109.4
O(2)-C(22)-H(22B)	109.4
C(23)-C(22)-H(22A)	109.4
C(23)-C(22)-H(22B)	109.4
H(22A)-C(22)-H(22B)	108.0
C(27)-C(28)-H(28A)	109.5
C(27)-C(28)-H(28B)	109.5
C(27)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(11)-C(10)-C(19)	118.1(2)
C(9)-C(10)-C(11)	120.3(2)
C(9)-C(10)-C(19)	121.6(2)
S(2)-C(7)-S(1)	123.05(13)
N(1)-C(7)-S(1)	116.66(19)
N(1)-C(7)-S(2)	120.28(18)
C(17)-C(18)-C(9)	118.2(2)
C(17)-C(18)-C(24)	121.0(2)
C(9)-C(18)-C(24)	120.8(2)

Symmetry transformations used to generate equivalent atoms:

Table S31. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6j''**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	30(1)	40(1)	35(1)	16(1)	9(1)	16(1)
S(2)	34(1)	42(1)	29(1)	13(1)	6(1)	19(1)
O(1)	37(1)	113(2)	69(2)	-26(2)	0(1)	-4(1)
O(4)	40(1)	38(1)	74(1)	24(1)	5(1)	1(1)
O(3)	79(2)	50(1)	62(1)	33(1)	-9(1)	-4(1)
O(2)	73(2)	68(2)	54(1)	-23(1)	-26(1)	32(1)
N(1)	28(1)	39(1)	30(1)	9(1)	3(1)	7(1)
C(17)	25(1)	31(1)	29(1)	5(1)	0(1)	3(1)
C(16)	27(1)	29(1)	33(1)	8(1)	5(1)	8(1)
C(11)	31(1)	26(1)	32(1)	6(1)	7(1)	10(1)
C(9)	25(1)	34(1)	25(1)	6(1)	4(1)	12(1)
C(21)	42(1)	33(1)	32(1)	14(1)	-1(1)	5(1)
C(26)	41(1)	36(1)	41(1)	15(1)	12(1)	10(1)
C(13)	56(2)	37(1)	56(2)	23(1)	11(1)	10(1)
C(6)	30(1)	34(1)	30(1)	9(1)	1(1)	4(1)
C(1)	26(1)	34(1)	30(1)	7(1)	-2(1)	2(1)
C(24)	41(1)	32(1)	28(1)	9(1)	6(1)	9(1)
C(19)	28(1)	42(2)	43(1)	2(1)	5(1)	8(1)
C(12)	42(1)	29(1)	47(2)	9(1)	6(1)	2(1)
C(20)	35(1)	42(1)	35(1)	5(1)	1(1)	10(1)
C(8)	25(1)	39(1)	29(1)	11(1)	4(1)	12(1)
C(2)	35(1)	48(2)	42(1)	15(1)	7(1)	1(1)
C(15)	34(1)	42(1)	40(1)	16(1)	2(1)	10(1)
C(3)	50(2)	50(2)	44(2)	23(1)	4(1)	-6(1)
C(14)	48(2)	48(2)	49(2)	28(1)	5(1)	16(1)
C(4)	53(2)	40(2)	49(2)	23(1)	-2(1)	3(1)
C(25)	35(1)	37(1)	45(1)	19(1)	5(1)	9(1)
C(5)	41(1)	40(1)	44(1)	19(1)	2(1)	9(1)
C(23)	66(2)	68(2)	46(2)	16(2)	-3(2)	0(2)
C(27)	54(2)	44(2)	84(2)	29(2)	15(2)	-2(1)
C(22)	91(3)	43(2)	49(2)	-4(1)	-31(2)	16(2)

C(28)	109(3)	43(2)	55(2)	17(2)	7(2)	5(2)
C(10)	26(1)	29(1)	30(1)	4(1)	7(1)	8(1)
C(7)	25(1)	33(1)	26(1)	5(1)	0(1)	8(1)
C(18)	28(1)	30(1)	26(1)	7(1)	6(1)	9(1)

Table S32. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **6j''**.

	x	y	z	U(eq)
H(17)	964	4726	3259	37
H(13)	4142	9129	3318	58
H(24)	2311	3743	5379	41
H(19)	6582	7878	6139	50
H(12)	5190	8806	4858	50
H(20)	4361	8720	7520	49
H(8A)	5260	6206	6975	38
H(8B)	4358	4836	6337	38
H(2)	654	4076	10462	51
H(15)	904	6043	2219	46
H(3)	1640	2769	11140	58
H(14)	1967	7779	2015	54
H(4)	3911	1999	10522	56
H(25)	-126	3200	3589	46
H(5)	5247	2527	9195	49
H(23A)	8622	10033	10394	96
H(23B)	7114	10492	10986	96
H(23C)	8843	11356	11356	96
H(27A)	-2917	-132	3571	72
H(27B)	-1394	176	4519	72
H(22A)	7420	11964	10194	83
H(22B)	8696	11280	9470	83
H(28A)	-1321	-883	2153	107
H(28B)	-1413	-1593	2972	107
H(28C)	157	-621	3121	107

Experimental Summary for Crystal **6u** (CCDC 1905649)

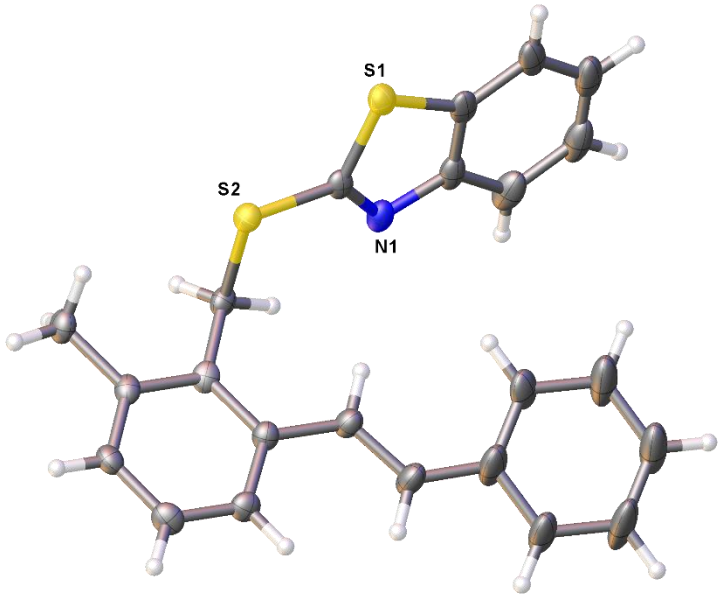


Table S33. Crystal data and structure refinement for **6u**.

Empirical formula	C23 H19 N S2
Formula weight	373.51
Temperature	100.0 K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 10.584(2) Å □= 90°. b = 4.3460(12) Å □= 95.273(9)°. c = 40.473(8) Å □ = 90°.
Volume	1853.8(7) Å^3
Z	4
Density (calculated)	1.338 Mg/m^3
Absorption coefficient	2.631 mm^{-1}
F(000)	784
Crystal size	0.2 x 0.16 x 0.07 mm^3
Theta range for data collection	2.192 to 68.386°.
Index ranges	-11<=h<=12, -5<=k<=5, -48<=l<=46
Reflections collected	7925
Independent reflections	3200 [R(int) = 0.0797]
Completeness to theta = 67.679°	94.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7531 and 0.4511
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3200 / 258 / 260
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0996, wR2 = 0.2305
R indices (all data)	R1 = 0.1292, wR2 = 0.2467
Extinction coefficient	n/a
Largest diff. peak and hole	0.682 and -0.682 e.Å^{-3}

Table S34. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6u**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(2)	7146(1)	5200(4)	7001(1)	29(1)
S(1)	4502(1)	5463(4)	6682(1)	34(1)
C(7)	6066(5)	4091(14)	6669(1)	27(1)
N(1)	6302(5)	2441(12)	6420(1)	33(1)
C(9)	9685(5)	5339(13)	6901(1)	27(1)
C(12)	11412(5)	8016(15)	7203(1)	31(1)
C(15)	10029(5)	6657(14)	6604(1)	28(1)
C(10)	10386(5)	6088(15)	7203(1)	28(1)
C(11)	10016(6)	4814(16)	7527(1)	35(1)
C(8)	8600(6)	3159(15)	6905(1)	29(1)
C(14)	11075(6)	8640(15)	6615(1)	32(1)
C(16)	9285(6)	6010(15)	6286(1)	33(1)
C(6)	4117(6)	3584(16)	6306(1)	38(1)
C(13)	11768(6)	9313(15)	6913(2)	35(1)
C(1)	5189(6)	2112(16)	6205(1)	37(1)
C(00G)	9590(30)	6880(80)	5974(4)	43(6)
C(5)	2935(7)	3472(18)	6119(2)	47(2)
C(18)	8825(8)	6400(20)	5667(2)	63(4)
C(25)	9388(9)	7080(40)	5378(2)	63(4)
C(26)	8714(11)	6660(40)	5070(2)	89(7)
C(21)	7477(10)	5550(30)	5051(2)	79(5)
C(22)	6914(8)	4870(30)	5339(3)	79(5)
C(23)	7588(8)	5290(30)	5647(2)	51(4)
C(2)	5120(8)	411(18)	5911(2)	52(2)
C(4)	2877(8)	1820(20)	5826(2)	59(2)
C(3)	3921(8)	390(19)	5727(2)	58(2)
C(17)	9390(40)	7310(130)	6028(8)	26(6)
C(24)	8712(14)	6550(30)	5679(3)	34(4)
C(19)	8796(19)	8630(30)	5421(4)	44(6)
C(20)	8130(20)	8090(40)	5114(3)	62(7)
C(27)	7378(18)	5480(40)	5065(3)	62(7)

C(28)	7290(20)	3400(40)	5323(4)	70(10)
C(29)	7960(19)	3930(40)	5630(3)	34(4)

Table S35. Bond lengths [Å] and angles [°] for **6u**.

S(2)-C(7)	1.750(6)
S(2)-C(8)	1.849(6)
S(1)-C(7)	1.764(6)
S(1)-C(6)	1.742(7)
C(7)-N(1)	1.283(8)
N(1)-C(1)	1.406(7)
C(9)-C(15)	1.409(8)
C(9)-C(10)	1.409(7)
C(9)-C(8)	1.490(9)
C(12)-H(12)	0.9500
C(12)-C(10)	1.372(9)
C(12)-C(13)	1.384(8)
C(15)-C(14)	1.401(8)
C(15)-C(16)	1.472(8)
C(10)-C(11)	1.508(8)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(8)-H(8A)	1.04(7)
C(8)-H(8B)	0.95(6)
C(14)-H(14)	0.9500
C(14)-C(13)	1.383(8)
C(16)-H(16)	0.9500
C(16)-H(00H)	0.9500
C(16)-C(00G)	1.384(19)
C(16)-C(17)	1.20(4)
C(6)-C(1)	1.396(10)
C(6)-C(5)	1.402(9)
C(13)-H(13)	0.9500
C(1)-C(2)	1.397(9)
C(00G)-H(00G)	0.9500
C(00G)-C(18)	1.44(2)
C(5)-H(5)	0.9500
C(5)-C(4)	1.380(11)

C(18)-C(25)	1.3900
C(18)-C(23)	1.3900
C(25)-H(25)	0.9500
C(25)-C(26)	1.3900
C(26)-H(26)	0.9500
C(26)-C(21)	1.3900
C(21)-H(21)	0.9500
C(21)-C(22)	1.3900
C(22)-H(22)	0.9500
C(22)-C(23)	1.3900
C(23)-H(23)	0.9500
C(2)-H(2)	0.9500
C(2)-C(3)	1.411(11)
C(4)-H(4)	0.9500
C(4)-C(3)	1.362(12)
C(3)-H(3)	0.9500
C(17)-H(0AA)	0.9500
C(17)-C(24)	1.56(4)
C(24)-C(19)	1.3900
C(24)-C(29)	1.3900
C(19)-H(00T)	0.9500
C(19)-C(20)	1.3900
C(20)-H(5AA)	0.9500
C(20)-C(27)	1.3900
C(27)-H(4AA)	0.9500
C(27)-C(28)	1.3900
C(28)-H(3AA)	0.9500
C(28)-C(29)	1.3900
C(29)-H(2AA)	0.9500

C(7)-S(2)-C(8)	101.8(3)
C(6)-S(1)-C(7)	87.8(3)
S(2)-C(7)-S(1)	115.7(3)
N(1)-C(7)-S(2)	126.7(5)
N(1)-C(7)-S(1)	117.6(4)
C(7)-N(1)-C(1)	109.3(5)

C(15)-C(9)-C(8)	121.9(5)
C(10)-C(9)-C(15)	119.3(6)
C(10)-C(9)-C(8)	118.8(5)
C(10)-C(12)-H(12)	119.1
C(10)-C(12)-C(13)	121.9(5)
C(13)-C(12)-H(12)	119.1
C(9)-C(15)-C(16)	120.5(5)
C(14)-C(15)-C(9)	119.2(5)
C(14)-C(15)-C(16)	120.2(5)
C(9)-C(10)-C(11)	120.8(6)
C(12)-C(10)-C(9)	119.5(5)
C(12)-C(10)-C(11)	119.7(5)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
S(2)-C(8)-H(8A)	106(4)
S(2)-C(8)-H(8B)	106(3)
C(9)-C(8)-S(2)	110.8(4)
C(9)-C(8)-H(8A)	114(4)
C(9)-C(8)-H(8B)	112(3)
H(8A)-C(8)-H(8B)	108(5)
C(15)-C(14)-H(14)	119.6
C(13)-C(14)-C(15)	120.8(6)
C(13)-C(14)-H(14)	119.6
C(15)-C(16)-H(16)	116.8
C(15)-C(16)-H(00H)	117.1
C(00G)-C(16)-C(15)	126.5(14)
C(00G)-C(16)-H(16)	116.8
C(17)-C(16)-C(15)	126(2)
C(17)-C(16)-H(00H)	117.1
C(1)-C(6)-S(1)	109.9(4)
C(1)-C(6)-C(5)	122.3(6)
C(5)-C(6)-S(1)	127.8(6)

C(12)-C(13)-H(13)	120.4
C(14)-C(13)-C(12)	119.2(6)
C(14)-C(13)-H(13)	120.4
C(6)-C(1)-N(1)	115.4(5)
C(6)-C(1)-C(2)	120.8(6)
C(2)-C(1)-N(1)	123.8(7)
C(16)-C(00G)-H(00G)	116.8
C(16)-C(00G)-C(18)	126(2)
C(18)-C(00G)-H(00G)	116.8
C(6)-C(5)-H(5)	121.7
C(4)-C(5)-C(6)	116.6(8)
C(4)-C(5)-H(5)	121.7
C(25)-C(18)-C(00G)	116.5(12)
C(25)-C(18)-C(23)	120.0
C(23)-C(18)-C(00G)	123.5(12)
C(18)-C(25)-H(25)	120.0
C(26)-C(25)-C(18)	120.0
C(26)-C(25)-H(25)	120.0
C(25)-C(26)-H(26)	120.0
C(25)-C(26)-C(21)	120.0
C(21)-C(26)-H(26)	120.0
C(26)-C(21)-H(21)	120.0
C(22)-C(21)-C(26)	120.0
C(22)-C(21)-H(21)	120.0
C(21)-C(22)-H(22)	120.0
C(21)-C(22)-C(23)	120.0
C(23)-C(22)-H(22)	120.0
C(18)-C(23)-H(23)	120.0
C(22)-C(23)-C(18)	120.0
C(22)-C(23)-H(23)	120.0
C(1)-C(2)-H(2)	122.3
C(1)-C(2)-C(3)	115.3(8)
C(3)-C(2)-H(2)	122.3
C(5)-C(4)-H(4)	119.4
C(3)-C(4)-C(5)	121.2(7)
C(3)-C(4)-H(4)	119.4

C(2)-C(3)-H(3)	118.2
C(4)-C(3)-C(2)	123.7(7)
C(4)-C(3)-H(3)	118.2
C(16)-C(17)-H(0AA)	116.0
C(16)-C(17)-C(24)	128(4)
C(24)-C(17)-H(0AA)	116.0
C(19)-C(24)-C(17)	119(2)
C(19)-C(24)-C(29)	120.0
C(29)-C(24)-C(17)	121(2)
C(24)-C(19)-H(00T)	120.0
C(20)-C(19)-C(24)	120.0
C(20)-C(19)-H(00T)	120.0
C(19)-C(20)-H(5AA)	120.0
C(19)-C(20)-C(27)	120.0
C(27)-C(20)-H(5AA)	120.0
C(20)-C(27)-H(4AA)	120.0
C(20)-C(27)-C(28)	120.0
C(28)-C(27)-H(4AA)	120.0
C(27)-C(28)-H(3AA)	120.0
C(29)-C(28)-C(27)	120.0
C(29)-C(28)-H(3AA)	120.0
C(24)-C(29)-H(2AA)	120.0
C(28)-C(29)-C(24)	120.0
C(28)-C(29)-H(2AA)	120.0

Symmetry transformations used to generate equivalent atoms:

Table S36. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6u**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(2)	34(1)	25(1)	28(1)	-4(1)	2(1)	-2(1)
S(1)	37(1)	30(1)	35(1)	6(1)	-1(1)	-1(1)
C(7)	35(3)	18(3)	28(2)	5(2)	-1(2)	-5(2)
N(1)	44(3)	27(3)	27(2)	2(2)	0(2)	-9(2)
C(9)	38(3)	14(3)	28(2)	-5(2)	2(2)	5(2)
C(12)	26(3)	32(4)	34(3)	-3(3)	-2(2)	3(2)
C(15)	33(3)	23(3)	28(2)	0(2)	1(2)	-1(2)
C(10)	32(3)	27(3)	25(2)	-4(2)	1(2)	8(2)
C(11)	45(3)	33(4)	26(3)	-3(3)	-3(2)	-2(3)
C(8)	36(3)	25(3)	25(3)	4(3)	3(2)	4(2)
C(14)	37(3)	24(3)	35(3)	4(3)	4(2)	-2(3)
C(16)	38(3)	33(4)	28(3)	0(3)	4(2)	-7(3)
C(6)	45(3)	35(4)	33(3)	17(3)	-4(2)	-18(3)
C(13)	38(3)	22(3)	44(3)	-3(3)	0(2)	-4(3)
C(1)	52(3)	30(4)	27(3)	9(2)	-5(2)	-17(3)
C(00G)	52(11)	52(14)	26(5)	4(7)	4(5)	-16(10)
C(5)	49(4)	48(4)	41(3)	25(3)	-11(3)	-20(3)
C(18)	77(6)	76(9)	34(4)	24(5)	-9(4)	-36(6)
C(25)	77(6)	76(9)	34(4)	24(5)	-9(4)	-36(6)
C(26)	125(11)	106(16)	32(5)	30(8)	-17(6)	-67(12)
C(21)	102(7)	85(10)	45(5)	29(6)	-30(5)	-45(8)
C(22)	102(7)	85(10)	45(5)	29(6)	-30(5)	-45(8)
C(23)	58(6)	49(9)	41(5)	24(6)	-12(4)	-10(6)
C(2)	75(4)	46(5)	35(3)	-2(3)	2(3)	-30(4)
C(4)	71(4)	65(6)	38(3)	25(3)	-15(3)	-31(4)
C(3)	88(5)	50(5)	31(3)	8(3)	-8(3)	-37(4)
C(17)	27(11)	24(12)	29(6)	0(7)	4(6)	-1(9)
C(24)	49(9)	28(9)	25(5)	5(5)	2(5)	-9(7)
C(19)	60(13)	34(11)	38(7)	11(7)	-4(7)	-13(10)
C(20)	91(14)	66(13)	27(6)	13(8)	-7(7)	-31(11)
C(27)	91(14)	66(13)	27(6)	13(8)	-7(7)	-31(11)

C(28)	110(20)	62(16)	32(8)	7(9)	-11(9)	-54(15)
C(29)	49(9)	28(9)	25(5)	5(5)	2(5)	-9(7)

Table S37. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **6u**.

	x	y	z	U(eq)
H(12)	11892	8474	7407	37
H(11A)	9120	5264	7549	53
H(11B)	10540	5767	7712	53
H(11C)	10148	2582	7532	53
H(14)	11312	9534	6416	38
H(16)	8520	4883	6297	39
H(00H)	8664	4430	6286	39
H(13)	12480	10649	6918	42
H(00G)	10377	7898	5963	52
H(5)	2211	4479	6190	56
H(25)	10233	7835	5392	76
H(26)	9099	7124	4874	107
H(21)	7017	5263	4840	95
H(22)	6069	4112	5326	95
H(23)	7203	4822	5844	61
H(2)	5830	-657	5840	63
H(4)	2094	1689	5692	71
H(3)	3838	-685	5521	69
H(0AA)	9962	9002	6038	32
H(00T)	9310	10413	5454	53
H(5AA)	8187	9516	4938	74
H(4AA)	6922	5118	4856	74
H(3AA)	6780	1616	5290	84
H(2AA)	7903	2513	5806	41
H(8A)	8360(60)	2040(170)	6682(17)	50(20)
H(8B)	8750(50)	1640(150)	7073(14)	23(15)

Experimental Summary for Crystal **6x** (CCDC 1905646)

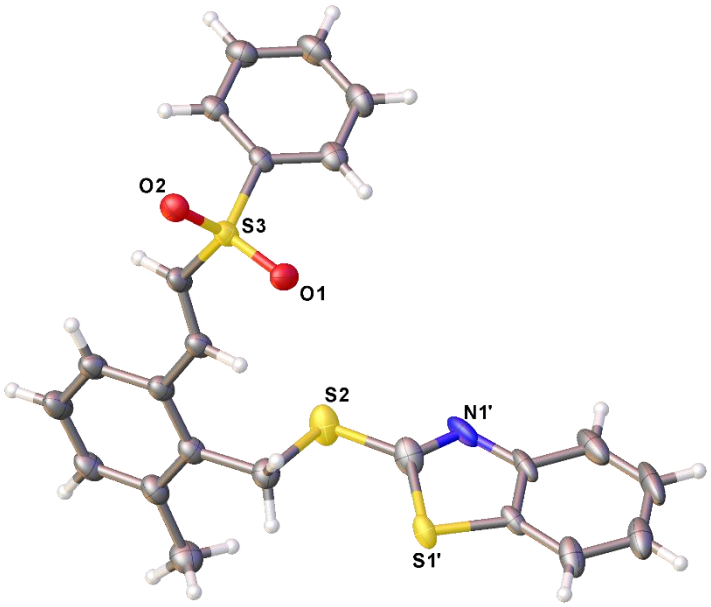


Table S38. Crystal data and structure refinement for **6x**.

Empirical formula	C23 H19 N O2 S3	
Formula weight	437.57	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 6.9999(12) Å	□= 90°.
	b = 10.6761(15) Å	□= 92.750(10)°.
	c = 27.063(3) Å	□ = 90°.
Volume	2020.1(5) Å^3	
Z	4	
Density (calculated)	1.439 Mg/m^3	
Absorption coefficient	3.519 mm^{-1}	
F(000)	912	
Crystal size	0.22 x 0.08 x 0.04 mm^3	
Theta range for data collection	3.270 to 68.234°.	
Index ranges	-8<=h<=8, -12<=k<=12, -32<=l<=23	
Reflections collected	11679	
Independent reflections	3664 [R(int) = 0.0682]	
Completeness to theta = 67.679°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.6198	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3664 / 0 / 288	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0584, wR2 = 0.1444	
R indices (all data)	R1 = 0.0900, wR2 = 0.1621	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.822 and -0.540 e.Å^{-3}	

Table S39. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6x**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(3)	2551(1)	4033(1)	5480(1)	31(1)
S(2)	6872(2)	7452(1)	6660(1)	52(1)
S(1')	11108(2)	6534(1)	6649(1)	35(1)
O(2)	1581(4)	3628(2)	5026(1)	37(1)
O(1)	4465(4)	3592(2)	5594(1)	38(1)
C(4)	808(7)	2918(4)	6801(1)	44(1)
C(5)	1944(7)	3140(3)	6404(1)	37(1)
C(1)	-834(6)	3921(3)	5934(1)	32(1)
C(3)	-1101(8)	3221(4)	6771(2)	47(1)
C(11)	2727(7)	9704(4)	5381(2)	45(1)
C(6)	1101(6)	3643(3)	5978(1)	29(1)
C(9)	4235(6)	7718(3)	5579(1)	33(1)
N(1')	8873(9)	6400(5)	7389(2)	44(1)
C(23')	11990(7)	5843(4)	7184(1)	31(2)
C(18')	10621(6)	5861(4)	7539(2)	42(2)
C(19')	11031(7)	5340(4)	8003(1)	60(2)
C(20')	12810(8)	4803(4)	8111(1)	71(3)
C(21')	14180(6)	4786(5)	7756(2)	58(2)
C(22')	13769(7)	5306(4)	7292(1)	50(2)
C(13)	5907(7)	9671(4)	5775(1)	39(1)
C(15)	7642(8)	10383(4)	5978(2)	51(1)
C(8)	4116(6)	6336(3)	5581(1)	34(1)
C(16)	7519(6)	7648(4)	6020(1)	37(1)
C(2)	-1938(7)	3719(4)	6341(1)	40(1)
C(7)	2531(6)	5670(3)	5481(1)	34(1)
C(10)	2667(6)	8412(4)	5376(2)	39(1)
C(14)	5855(6)	8349(4)	5775(1)	35(1)
C(12)	4337(7)	10321(4)	5584(2)	42(1)
N(1)	10140(30)	6462(13)	6787(6)	35(1)
S(1)	8353(7)	5825(5)	7559(2)	38(2)
C(23)	11390(20)	5851(16)	7144(6)	90(15)

C(18)	10682(16)	5415(15)	7584(6)	29(5)
C(19)	11880(20)	4777(14)	7922(4)	39(3)
C(20)	13780(20)	4573(15)	7821(5)	39(3)
C(21)	14488(17)	5009(14)	7381(6)	39(3)
C(22)	13290(20)	5647(13)	7043(4)	39(3)
C(17)	8858(7)	6729(4)	6943(1)	45(1)

Table S40. Bond lengths [Å] and angles [°] for **6x**.

S(3)-O(2)	1.442(3)
S(3)-O(1)	1.440(3)
S(3)-C(6)	1.775(3)
S(3)-C(7)	1.747(4)
S(2)-C(16)	1.822(4)
S(2)-C(17)	1.736(5)
S(1')-C(23')	1.712(3)
S(1')-C(17)	1.809(5)
C(4)-C(5)	1.389(6)
C(4)-C(3)	1.373(7)
C(5)-C(6)	1.377(6)
C(1)-C(6)	1.386(6)
C(1)-C(2)	1.392(5)
C(3)-C(2)	1.382(7)
C(11)-C(10)	1.380(6)
C(11)-C(12)	1.394(7)
C(9)-C(8)	1.478(5)
C(9)-C(10)	1.413(6)
C(9)-C(14)	1.401(6)
N(1')-C(18')	1.395(7)
N(1')-C(17)	1.257(7)
C(23')-C(18')	1.3900
C(23')-C(22')	1.3900
C(18')-C(19')	1.3900
C(19')-C(20')	1.3900
C(20')-C(21')	1.3900
C(21')-C(22')	1.3900
C(13)-C(15)	1.513(7)
C(13)-C(14)	1.412(5)
C(13)-C(12)	1.380(6)
C(8)-C(7)	1.334(6)
C(16)-C(14)	1.511(6)
N(1)-C(23)	1.429(18)
N(1)-C(17)	1.05(2)

S(1)-C(18)	1.686(12)
S(1)-C(17)	1.973(7)
C(23)-C(18)	1.3900
C(23)-C(22)	1.3900
C(18)-C(19)	1.3900
C(19)-C(20)	1.3900
C(20)-C(21)	1.3900
C(21)-C(22)	1.3900

O(2)-S(3)-C(6)	108.31(17)
O(2)-S(3)-C(7)	107.32(18)
O(1)-S(3)-O(2)	118.64(16)
O(1)-S(3)-C(6)	108.73(17)
O(1)-S(3)-C(7)	109.53(19)
C(7)-S(3)-C(6)	103.22(16)
C(17)-S(2)-C(16)	103.9(2)
C(23')-S(1')-C(17)	88.0(2)
C(3)-C(4)-C(5)	120.3(4)
C(6)-C(5)-C(4)	118.4(4)
C(6)-C(1)-C(2)	118.4(4)
C(4)-C(3)-C(2)	120.9(4)
C(10)-C(11)-C(12)	120.0(4)
C(5)-C(6)-S(3)	119.2(3)
C(5)-C(6)-C(1)	122.2(3)
C(1)-C(6)-S(3)	118.4(3)
C(10)-C(9)-C(8)	118.8(4)
C(14)-C(9)-C(8)	121.6(4)
C(14)-C(9)-C(10)	119.6(4)
C(17)-N(1')-C(18')	111.2(5)
C(18')-C(23')-S(1')	110.2(3)
C(18')-C(23')-C(22')	120.0
C(22')-C(23')-S(1')	129.8(3)
C(23')-C(18')-N(1')	115.4(4)
C(23')-C(18')-C(19')	120.0
C(19')-C(18')-N(1')	124.6(4)
C(20')-C(19')-C(18')	120.0

C(19')-C(20')-C(21')	120.0
C(22')-C(21')-C(20')	120.0
C(21')-C(22')-C(23')	120.0
C(14)-C(13)-C(15)	121.5(4)
C(12)-C(13)-C(15)	119.6(4)
C(12)-C(13)-C(14)	118.8(4)
C(7)-C(8)-C(9)	125.3(4)
C(14)-C(16)-S(2)	104.6(3)
C(3)-C(2)-C(1)	119.7(4)
C(8)-C(7)-S(3)	121.8(3)
C(11)-C(10)-C(9)	119.8(5)
C(9)-C(14)-C(13)	120.1(4)
C(9)-C(14)-C(16)	121.4(3)
C(13)-C(14)-C(16)	118.4(4)
C(13)-C(12)-C(11)	121.6(4)
C(17)-N(1)-C(23)	111.0(16)
C(18)-S(1)-C(17)	87.0(6)
C(18)-C(23)-N(1)	120.1(15)
C(18)-C(23)-C(22)	120.0
C(22)-C(23)-N(1)	119.9(15)
C(23)-C(18)-S(1)	105.2(10)
C(19)-C(18)-S(1)	134.8(10)
C(19)-C(18)-C(23)	120.0
C(18)-C(19)-C(20)	120.0
C(21)-C(20)-C(19)	120.0
C(20)-C(21)-C(22)	120.0
C(21)-C(22)-C(23)	120.0
S(2)-C(17)-S(1')	123.5(2)
S(2)-C(17)-S(1)	114.7(3)
N(1')-C(17)-S(2)	121.2(4)
N(1')-C(17)-S(1')	115.0(4)
N(1)-C(17)-S(2)	128.7(8)
N(1)-C(17)-S(1)	113.5(9)

Symmetry transformations used to generate equivalent atoms:

Table S41. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6x**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(3)	35(1)	23(1)	36(1)	2(1)	7(1)	4(1)
S(2)	73(1)	48(1)	35(1)	-6(1)	7(1)	21(1)
S(1')	61(1)	26(1)	19(1)	-1(1)	3(1)	9(1)
O(2)	40(2)	38(1)	34(1)	-2(1)	9(1)	3(1)
O(1)	33(2)	27(1)	54(2)	1(1)	6(1)	6(1)
C(4)	65(3)	38(2)	28(2)	1(2)	0(2)	-3(2)
C(5)	51(3)	24(2)	36(2)	-5(2)	0(2)	-3(2)
C(1)	42(2)	22(2)	32(2)	-1(1)	8(2)	-2(2)
C(3)	66(3)	42(2)	34(2)	0(2)	16(2)	-7(2)
C(11)	43(3)	31(2)	61(3)	10(2)	13(2)	9(2)
C(6)	40(2)	17(2)	30(2)	-1(1)	5(2)	0(1)
C(9)	34(2)	26(2)	41(2)	3(2)	9(2)	4(2)
N(1')	78(4)	33(2)	22(2)	3(2)	11(2)	-18(3)
C(23')	59(4)	16(2)	18(2)	-1(2)	7(2)	-1(2)
C(18')	80(5)	24(4)	20(3)	5(2)	-4(3)	-14(3)
C(19')	104(6)	45(4)	31(3)	8(3)	-7(3)	-28(4)
C(20')	130(8)	42(3)	38(3)	18(3)	-31(4)	-25(4)
C(21')	94(6)	31(3)	47(4)	4(3)	-28(4)	-2(4)
C(22')	90(6)	25(3)	35(3)	-2(2)	-14(3)	6(3)
C(13)	51(3)	28(2)	39(2)	3(2)	7(2)	3(2)
C(15)	65(3)	32(2)	57(3)	-4(2)	0(2)	-3(2)
C(8)	34(2)	28(2)	41(2)	4(2)	9(2)	4(2)
C(16)	45(2)	28(2)	38(2)	-5(2)	0(2)	4(2)
C(2)	45(3)	37(2)	40(2)	-4(2)	11(2)	-4(2)
C(7)	32(2)	24(2)	46(2)	7(2)	7(2)	5(2)
C(10)	35(2)	32(2)	53(2)	6(2)	11(2)	3(2)
C(14)	42(2)	25(2)	39(2)	0(2)	8(2)	3(2)
C(12)	55(3)	22(2)	51(2)	4(2)	14(2)	4(2)
N(1)	61(1)	26(1)	19(1)	-1(1)	3(1)	9(1)
S(1)	41(3)	47(3)	25(2)	1(2)	2(2)	7(2)
C(23)	26(13)	63(19)	180(40)	-40(20)	-27(17)	19(12)

C(18)	29(10)	31(14)	25(10)	17(8)	-7(7)	-11(8)
C(19)	56(7)	30(6)	30(5)	3(4)	-2(4)	-4(5)
C(20)	56(7)	30(6)	30(5)	3(4)	-2(4)	-4(5)
C(21)	56(7)	30(6)	30(5)	3(4)	-2(4)	-4(5)
C(22)	56(7)	30(6)	30(5)	3(4)	-2(4)	-4(5)
C(17)	73(3)	33(2)	28(2)	-11(2)	3(2)	10(2)

Table S42. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **6x**.

	x	y	z	U(eq)
H(4)	1354	2554	7096	52
H(5)	3271	2949	6424	45
H(1)	-1394	4242	5634	38
H(3)	-1856	3086	7048	57
H(11)	1671	10172	5247	54
H(19')	10095	5352	8245	72
H(20')	13091	4447	8428	85
H(21')	15396	4418	7830	70
H(22')	14705	5294	7049	61
H(15A)	7882	10173	6328	77
H(15B)	7409	11285	5945	77
H(15C)	8758	10152	5793	77
H(8)	5260	5885	5660	41
H(16A)	8717	8135	6002	45
H(16B)	7692	6824	5860	45
H(2)	-3261	3922	6324	48
H(7)	1361	6097	5409	41
H(10)	1576	7990	5236	47
H(12)	4353	11210	5590	51
H(19)	11397	4479	8223	47
H(20)	14601	4137	8052	47
H(21)	15789	4870	7312	47
H(22)	13773	5945	6742	47

Experimental Summary for Crystal **9** (CCDC 1905644)

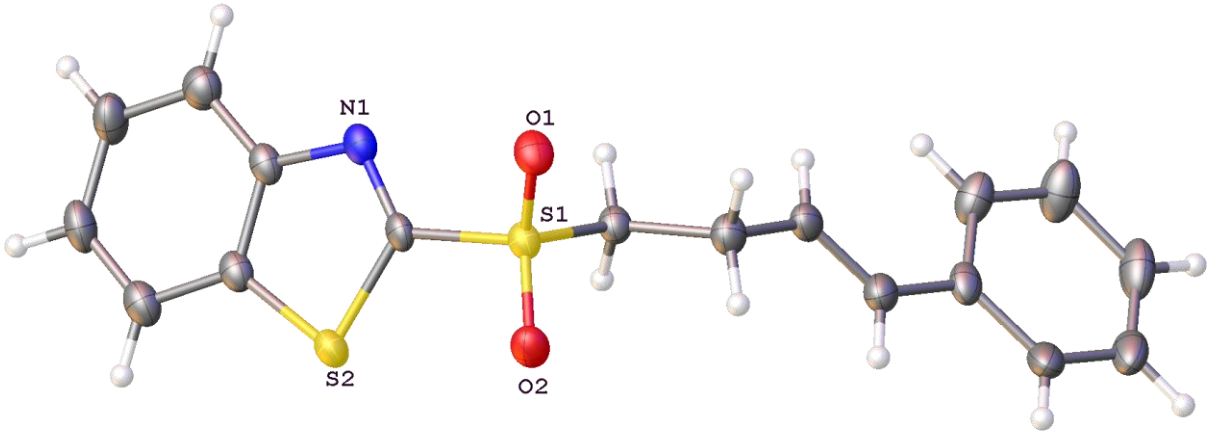


Table S43. Crystal data and structure refinement for **9**.

Empirical formula	C17 H15 N O2 S2	
Formula weight	329.42	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 32.753(3) Å	□= 90°.
	b = 4.8880(4) Å	□= 124.967(8)°.
	c = 23.981(2) Å	□ = 90°.
Volume	3146.2(5) Å^3	
Z	8	
Density (calculated)	1.391 Mg/m^3	
Absorption coefficient	3.117 mm^{-1}	
F(000)	1376	
Crystal size	0.24 x 0.07 x 0.03 mm^3	
Theta range for data collection	3.293 to 68.760°.	
Index ranges	-38<=h<=36, -5<=k<=5, -28<=l<=28	
Reflections collected	10051	
Independent reflections	2898 [R(int) = 0.0465]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.5787	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2898 / 0 / 199	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0439, wR2 = 0.1151	
R indices (all data)	R1 = 0.0548, wR2 = 0.1220	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.507 and -0.353 e.Å^{-3}	

Table S44. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **9**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	3331(1)	2977(1)	3565(1)	20(1)
S(2)	4356(1)	5597(1)	4352(1)	24(1)
N(1)	3686(1)	6437(4)	3057(1)	23(1)
O(1)	3061(1)	1501(4)	2933(1)	28(1)
O(2)	3603(1)	1473(4)	4197(1)	28(1)
C(7)	3778(1)	5121(5)	3583(1)	20(1)
C(6)	4095(1)	8059(5)	3242(1)	23(1)
C(1)	4502(1)	7840(5)	3930(1)	23(1)
C(8)	2925(1)	5362(5)	3569(1)	21(1)
C(9)	2522(1)	3857(5)	3585(1)	27(1)
C(13)	1624(1)	6965(7)	4570(1)	35(1)
C(2)	4943(1)	9303(6)	4185(1)	29(1)
C(11)	2084(1)	5851(6)	4067(1)	28(1)
C(12)	1720(1)	7533(6)	4083(1)	28(1)
C(10)	2178(1)	5836(5)	3596(1)	26(1)
C(3)	4961(1)	11000(6)	3742(2)	33(1)
C(17)	1443(1)	9610(6)	3613(2)	33(1)
C(5)	4124(1)	9821(5)	2806(1)	30(1)
C(4)	4554(1)	11290(6)	3058(2)	34(1)
C(16)	1089(1)	11055(6)	3635(2)	42(1)
C(15)	1004(1)	10463(6)	4128(2)	40(1)
C(14)	1269(1)	8406(7)	4589(1)	39(1)

Table S45. Bond lengths [Å] and angles [°] for **9**.

S(1)-O(1)	1.4362(18)
S(1)-O(2)	1.4433(18)
S(1)-C(7)	1.782(2)
S(1)-C(8)	1.773(2)
S(2)-C(7)	1.742(2)
S(2)-C(1)	1.736(3)
N(1)-C(7)	1.288(3)
N(1)-C(6)	1.393(3)
C(6)-C(1)	1.409(3)
C(6)-C(5)	1.398(4)
C(1)-C(2)	1.400(4)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(8)-C(9)	1.531(3)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(9)-C(10)	1.497(4)
C(13)-H(13)	0.9500
C(13)-C(12)	1.403(4)
C(13)-C(14)	1.379(4)
C(2)-H(2)	0.9500
C(2)-C(3)	1.375(4)
C(11)-H(11)	0.9500
C(11)-C(12)	1.466(4)
C(11)-C(10)	1.330(4)
C(12)-C(17)	1.398(4)
C(10)-H(10)	0.9500
C(3)-H(3)	0.9500
C(3)-C(4)	1.407(4)
C(17)-H(17)	0.9500
C(17)-C(16)	1.385(4)
C(5)-H(5)	0.9500
C(5)-C(4)	1.377(4)
C(4)-H(4)	0.9500

C(16)-H(16)	0.9500
C(16)-C(15)	1.392(4)
C(15)-H(15)	0.9500
C(15)-C(14)	1.373(5)
C(14)-H(14)	0.9500

O(1)-S(1)-O(2)	119.22(11)
O(1)-S(1)-C(7)	108.71(11)
O(1)-S(1)-C(8)	109.01(11)
O(2)-S(1)-C(7)	105.67(11)
O(2)-S(1)-C(8)	110.11(11)
C(8)-S(1)-C(7)	102.83(11)
C(1)-S(2)-C(7)	87.79(11)
C(7)-N(1)-C(6)	109.2(2)
S(2)-C(7)-S(1)	118.85(14)
N(1)-C(7)-S(1)	122.81(18)
N(1)-C(7)-S(2)	118.26(18)
N(1)-C(6)-C(1)	114.9(2)
N(1)-C(6)-C(5)	125.2(2)
C(5)-C(6)-C(1)	119.9(2)
C(6)-C(1)-S(2)	109.82(18)
C(2)-C(1)-S(2)	128.9(2)
C(2)-C(1)-C(6)	121.3(2)
S(1)-C(8)-H(8A)	109.6
S(1)-C(8)-H(8B)	109.6
H(8A)-C(8)-H(8B)	108.1
C(9)-C(8)-S(1)	110.13(17)
C(9)-C(8)-H(8A)	109.6
C(9)-C(8)-H(8B)	109.6
C(8)-C(9)-H(9A)	109.4
C(8)-C(9)-H(9B)	109.4
H(9A)-C(9)-H(9B)	108.0
C(10)-C(9)-C(8)	111.0(2)
C(10)-C(9)-H(9A)	109.4
C(10)-C(9)-H(9B)	109.4
C(12)-C(13)-H(13)	119.3

C(14)-C(13)-H(13)	119.3
C(14)-C(13)-C(12)	121.4(3)
C(1)-C(2)-H(2)	121.3
C(3)-C(2)-C(1)	117.4(3)
C(3)-C(2)-H(2)	121.3
C(12)-C(11)-H(11)	116.1
C(10)-C(11)-H(11)	116.1
C(10)-C(11)-C(12)	127.8(3)
C(13)-C(12)-C(11)	119.1(3)
C(17)-C(12)-C(13)	117.6(3)
C(17)-C(12)-C(11)	123.3(2)
C(9)-C(10)-H(10)	117.9
C(11)-C(10)-C(9)	124.2(2)
C(11)-C(10)-H(10)	117.9
C(2)-C(3)-H(3)	119.0
C(2)-C(3)-C(4)	122.0(2)
C(4)-C(3)-H(3)	119.0
C(12)-C(17)-H(17)	119.7
C(16)-C(17)-C(12)	120.7(3)
C(16)-C(17)-H(17)	119.7
C(6)-C(5)-H(5)	120.5
C(4)-C(5)-C(6)	118.9(3)
C(4)-C(5)-H(5)	120.5
C(3)-C(4)-H(4)	119.8
C(5)-C(4)-C(3)	120.4(3)
C(5)-C(4)-H(4)	119.8
C(17)-C(16)-H(16)	119.8
C(17)-C(16)-C(15)	120.4(3)
C(15)-C(16)-H(16)	119.8
C(16)-C(15)-H(15)	120.2
C(14)-C(15)-C(16)	119.5(3)
C(14)-C(15)-H(15)	120.2
C(13)-C(14)-H(14)	119.9
C(15)-C(14)-C(13)	120.3(3)
C(15)-C(14)-H(14)	119.9

Symmetry transformations used to generate equivalent atoms:

Table S46. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **9**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	17(1)	17(1)	24(1)	-1(1)	11(1)	0(1)
S(2)	16(1)	26(1)	25(1)	1(1)	9(1)	0(1)
N(1)	18(1)	20(1)	30(1)	-2(1)	14(1)	0(1)
O(1)	26(1)	25(1)	31(1)	-8(1)	16(1)	-5(1)
O(2)	24(1)	26(1)	31(1)	9(1)	14(1)	3(1)
C(7)	14(1)	19(1)	26(1)	-2(1)	12(1)	2(1)
C(6)	20(1)	20(1)	29(1)	-1(1)	15(1)	2(1)
C(1)	18(1)	22(1)	29(1)	-1(1)	13(1)	3(1)
C(8)	20(1)	20(1)	24(1)	-1(1)	12(1)	1(1)
C(9)	24(1)	26(1)	32(1)	4(1)	17(1)	0(1)
C(13)	22(1)	60(2)	21(1)	-3(1)	10(1)	-7(1)
C(2)	19(1)	30(1)	34(1)	-3(1)	12(1)	-2(1)
C(11)	22(1)	36(2)	25(1)	0(1)	12(1)	-4(1)
C(12)	22(1)	35(2)	27(1)	-10(1)	15(1)	-11(1)
C(10)	20(1)	29(1)	27(1)	0(1)	13(1)	-4(1)
C(3)	21(1)	31(2)	50(2)	-1(1)	22(1)	-3(1)
C(17)	41(2)	27(1)	45(2)	-4(1)	32(2)	-5(1)
C(5)	26(1)	29(1)	35(2)	5(1)	18(1)	4(1)
C(4)	30(2)	30(2)	48(2)	7(1)	26(1)	2(1)
C(16)	50(2)	29(2)	68(2)	1(1)	46(2)	1(1)
C(15)	38(2)	41(2)	60(2)	-21(2)	39(2)	-14(1)
C(14)	28(2)	67(2)	28(1)	-14(1)	19(1)	-14(1)

Table S47. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **9**.

	x	y	z	U(eq)
H(8A)	3118	6565	3972	25
H(8B)	2767	6522	3156	25
H(9A)	2328	2669	3179	32
H(9B)	2681	2677	3994	32
H(13)	1806	5558	4894	42
H(2)	5220	9129	4646	35
H(11)	2275	4624	4437	34
H(10)	2017	7168	3245	31
H(3)	5257	12007	3903	40
H(17)	1498	10036	3274	40
H(5)	3850	10002	2344	36
H(4)	4577	12508	2768	41
H(16)	903	12459	3311	50
H(15)	764	11476	4146	48
H(14)	1208	7973	4921	47

Experimental Summary for Crystal **17** (CCDC 1905651)

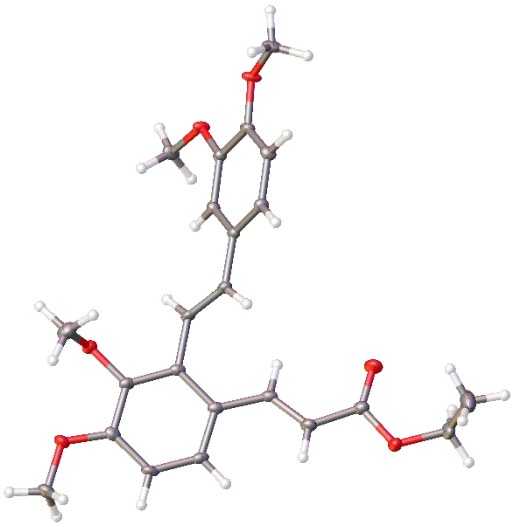


Table S48. Crystal data and structure refinement for **17**.

Empirical formula	C23 H26 O6	
Molecular formula	C23 H26 O6	
Formula weight	398.44	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.7261(18) Å	□= 65.750(6)°.
	b = 10.890(2) Å	□= 69.528(6)°.
	c = 11.528(2) Å	□ = 86.877(7)°.
Volume	1037.2(4) $Å^3$	
Z	2	
Density (calculated)	1.276 Mg/m^3	
Absorption coefficient	0.092 mm^{-1}	
F(000)	424	
Crystal size	0.27 x 0.175 x 0.125 mm^3	
Crystal color, habit	colorless irregular	
Theta range for data collection	2.062 to 26.370°.	
Index ranges	-12<=h<=12, -13<=k<=13, -14<=l<=9	
Reflections collected	12189	
Independent reflections	4247 [R(int) = 0.0316]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.6883	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4247 / 0 / 267	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.0937	
R indices (all data)	R1 = 0.0484, wR2 = 0.0993	
Largest diff. peak and hole	0.265 and -0.219 $e.Å^{-3}$	

Table S49. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **17**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3065(1)	4128(1)	9445(1)	23(1)
O(2)	3312(1)	5785(1)	7386(1)	28(1)
O(3)	3067(1)	-189(1)	4490(1)	19(1)
O(4)	3041(1)	2429(1)	2943(1)	18(1)
O(5)	3814(1)	9398(1)	-360(1)	16(1)
O(6)	1505(1)	10530(1)	459(1)	18(1)
C(1)	1576(2)	5646(2)	10344(2)	40(1)
C(2)	3075(2)	5155(2)	9941(2)	27(1)
C(3)	3180(2)	4593(1)	8129(1)	18(1)
C(4)	3115(1)	3465(1)	7754(1)	17(1)
C(5)	3340(1)	3714(1)	6460(1)	16(1)
C(6)	3270(1)	2703(1)	5952(1)	14(1)
C(7)	3340(1)	1330(1)	6732(1)	16(1)
C(8)	3275(1)	340(1)	6292(1)	16(1)
C(9)	3148(1)	692(1)	5030(1)	15(1)
C(10)	3102(1)	2063(1)	4223(1)	15(1)
C(11)	3147(1)	3075(1)	4661(1)	13(1)
C(12)	3057(1)	4478(1)	3738(1)	14(1)
C(13)	2213(1)	5367(1)	4094(1)	14(1)
C(14)	2073(1)	6741(1)	3164(1)	13(1)
C(15)	3115(1)	7418(1)	1828(1)	14(1)
C(16)	2891(1)	8672(1)	957(1)	13(1)
C(17)	1620(1)	9290(1)	1406(1)	14(1)
C(18)	609(1)	8644(1)	2721(1)	16(1)
C(19)	845(1)	7376(1)	3591(1)	15(1)
C(20)	1638(2)	2071(2)	2961(2)	27(1)
C(21)	2989(2)	-1608(1)	5337(1)	21(1)

C(22)	5085(2)	8792(1)	-890(1)	19(1)
C(23)	131(2)	11093(1)	792(1)	21(1)

Table S50. Bond lengths [Å] and angles [°] for **17**.

1)-C(2)	1.4515(17)
O(1)-C(3)	1.3523(16)
O(2)-C(3)	1.2097(16)
O(3)-C(9)	1.3592(16)
O(3)-C(21)	1.4382(15)
O(4)-C(10)	1.3840(16)
O(4)-C(20)	1.4298(17)
O(5)-C(16)	1.3687(15)
O(5)-C(22)	1.4321(16)
O(6)-C(17)	1.3731(14)
O(6)-C(23)	1.4333(16)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(1)-C(2)	1.507(2)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.4699(19)
C(4)-H(4)	0.9500
C(4)-C(5)	1.3389(19)
C(5)-H(5)	0.9500
C(5)-C(6)	1.4576(19)
C(6)-C(7)	1.4056(17)
C(6)-C(11)	1.4213(18)
C(7)-H(7)	0.9500
C(7)-C(8)	1.3788(19)

C(8)-H(8)	0.9500
C(8)-C(9)	1.3933(19)
C(9)-C(10)	1.4068(17)
C(10)-C(11)	1.3949(19)
C(11)-C(12)	1.4803(16)
C(12)-H(12)	0.9500
C(12)-C(13)	1.3355(18)
C(13)-H(13)	0.9500
C(13)-C(14)	1.4727(17)
C(14)-C(15)	1.4143(17)
C(14)-C(19)	1.3876(18)
C(15)-H(15)	0.9500
C(15)-C(16)	1.3834(17)
C(16)-C(17)	1.4134(18)
C(17)-C(18)	1.3843(18)
C(18)-H(18)	0.9500
C(18)-C(19)	1.3982(17)
C(19)-H(19)	0.9500
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800

C(3)-O(1)-C(2)	115.78(11)

C(9)-O(3)-C(21)	117.09(10)
C(10)-O(4)-C(20)	114.17(10)
C(16)-O(5)-C(22)	117.39(10)
C(17)-O(6)-C(23)	116.84(10)
H(1A)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
O(1)-C(2)-C(1)	111.76(12)
O(1)-C(2)-H(2A)	109.3
O(1)-C(2)-H(2B)	109.3
C(1)-C(2)-H(2A)	109.3
C(1)-C(2)-H(2B)	109.3
H(2A)-C(2)-H(2B)	107.9
O(1)-C(3)-C(4)	110.92(11)
O(2)-C(3)-O(1)	123.13(13)
O(2)-C(3)-C(4)	125.95(12)
C(3)-C(4)-H(4)	120.0
C(5)-C(4)-C(3)	120.07(12)
C(5)-C(4)-H(4)	120.0
C(4)-C(5)-H(5)	117.0
C(4)-C(5)-C(6)	125.95(12)
C(6)-C(5)-H(5)	117.0
C(7)-C(6)-C(5)	120.34(12)
C(7)-C(6)-C(11)	118.37(12)
C(11)-C(6)-C(5)	121.29(11)
C(6)-C(7)-H(7)	118.9
C(8)-C(7)-C(6)	122.25(12)
C(8)-C(7)-H(7)	118.9
C(7)-C(8)-H(8)	120.1

C(7)-C(8)-C(9)	119.89(12)
C(9)-C(8)-H(8)	120.1
O(3)-C(9)-C(8)	125.35(11)
O(3)-C(9)-C(10)	115.86(11)
C(8)-C(9)-C(10)	118.78(12)
O(4)-C(10)-C(9)	119.17(12)
O(4)-C(10)-C(11)	118.79(11)
C(11)-C(10)-C(9)	122.03(12)
C(6)-C(11)-C(12)	124.11(12)
C(10)-C(11)-C(6)	118.66(11)
C(10)-C(11)-C(12)	117.23(11)
C(11)-C(12)-H(12)	116.9
C(13)-C(12)-C(11)	126.24(11)
C(13)-C(12)-H(12)	116.9
C(12)-C(13)-H(13)	116.9
C(12)-C(13)-C(14)	126.10(12)
C(14)-C(13)-H(13)	116.9
C(15)-C(14)-C(13)	122.43(11)
C(19)-C(14)-C(13)	118.93(11)
C(19)-C(14)-C(15)	118.59(11)
C(14)-C(15)-H(15)	119.8
C(16)-C(15)-C(14)	120.49(12)
C(16)-C(15)-H(15)	119.8
O(5)-C(16)-C(15)	125.07(12)
O(5)-C(16)-C(17)	114.98(10)
C(15)-C(16)-C(17)	119.95(11)
O(6)-C(17)-C(16)	115.09(11)
O(6)-C(17)-C(18)	125.04(12)
C(18)-C(17)-C(16)	119.86(11)
C(17)-C(18)-H(18)	120.2
C(17)-C(18)-C(19)	119.69(12)
C(19)-C(18)-H(18)	120.2

C(14)-C(19)-C(18)	121.39(12)
C(14)-C(19)-H(19)	119.3
C(18)-C(19)-H(19)	119.3
O(4)-C(20)-H(20A)	109.5
O(4)-C(20)-H(20B)	109.5
O(4)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
O(3)-C(21)-H(21A)	109.5
O(3)-C(21)-H(21B)	109.5
O(3)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
O(5)-C(22)-H(22A)	109.5
O(5)-C(22)-H(22B)	109.5
O(5)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
O(6)-C(23)-H(23A)	109.5
O(6)-C(23)-H(23B)	109.5
O(6)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

Table S51. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **17**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	40(1)	16(1)	19(1)	-7(1)	-17(1)	5(1)
O(2)	44(1)	13(1)	25(1)	-2(1)	-17(1)	1(1)
O(3)	27(1)	11(1)	19(1)	-5(1)	-9(1)	4(1)
O(4)	23(1)	16(1)	13(1)	-5(1)	-7(1)	3(1)
O(5)	17(1)	14(1)	11(1)	-1(1)	-2(1)	4(1)
O(6)	16(1)	12(1)	18(1)	0(1)	-5(1)	5(1)
C(1)	53(1)	41(1)	57(1)	-37(1)	-37(1)	22(1)
C(2)	42(1)	22(1)	31(1)	-16(1)	-25(1)	8(1)
C(3)	20(1)	16(1)	17(1)	-4(1)	-9(1)	1(1)
C(4)	20(1)	12(1)	16(1)	-2(1)	-7(1)	0(1)
C(5)	15(1)	13(1)	15(1)	-2(1)	-6(1)	2(1)
C(6)	12(1)	14(1)	13(1)	-3(1)	-3(1)	2(1)
C(7)	15(1)	17(1)	12(1)	-2(1)	-5(1)	3(1)
C(8)	15(1)	11(1)	15(1)	0(1)	-4(1)	3(1)
C(9)	12(1)	14(1)	16(1)	-5(1)	-2(1)	2(1)
C(10)	13(1)	15(1)	11(1)	-2(1)	-3(1)	2(1)
C(11)	10(1)	13(1)	11(1)	-2(1)	-2(1)	2(1)
C(12)	15(1)	13(1)	9(1)	-1(1)	-4(1)	0(1)
C(13)	16(1)	14(1)	10(1)	-2(1)	-5(1)	-1(1)
C(14)	16(1)	11(1)	13(1)	-4(1)	-7(1)	0(1)
C(15)	13(1)	13(1)	14(1)	-6(1)	-5(1)	3(1)
C(16)	14(1)	13(1)	11(1)	-3(1)	-4(1)	-1(1)
C(17)	16(1)	10(1)	16(1)	-2(1)	-8(1)	2(1)
C(18)	13(1)	15(1)	18(1)	-7(1)	-4(1)	3(1)
C(19)	15(1)	15(1)	12(1)	-3(1)	-3(1)	-1(1)
C(20)	28(1)	31(1)	24(1)	-10(1)	-14(1)	3(1)

C(21)	24(1)	11(1)	23(1)	-4(1)	-7(1)	2(1)
C(22)	18(1)	16(1)	15(1)	-5(1)	0(1)	3(1)
C(23)	18(1)	16(1)	23(1)	-3(1)	-8(1)	7(1)

Table S52. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **17**.

	x	y	z	U(eq)
H(1A)	1303	6099	9537	60
H(1B)	1606	6285	10737	60
H(1C)	845	4873	11020	60
H(2A)	3800	5931	9219	32
H(2B)	3388	4776	10738	32
H(4)	2914	2559	8431	20
H(5)	3566	4634	5814	19
H(7)	3435	1075	7591	19
H(8)	3318	-579	6848	20
H(12)	3657	4776	2802	16
H(13)	1650	5087	5037	17
H(15)	3975	7010	1526	16
H(18)	-241	9061	3031	20
H(19)	151	6940	4494	18
H(20A)	1694	2319	2026	41
H(20B)	890	2556	3377	41
H(20C)	1369	1093	3493	41
H(21A)	2921	-2137	4844	31
H(21B)	2115	-1864	6173	31
H(21C)	3877	-1790	5573	31
H(22A)	5642	9401	-1840	28
H(22B)	4770	7929	-847	28
H(22C)	5711	8630	-346	28
H(23A)	145	11929	11	31
H(23B)	-12	11293	1579	31
H(23C)	-679	10441	1015	31

Experimental Summary for Crystal **20** (CCDC 1905645)

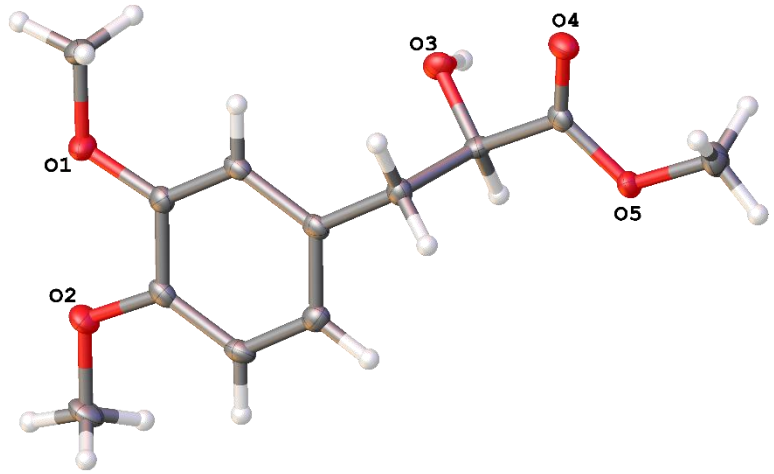


Table S53. Crystal data and structure refinement for **20**.

Empirical formula	C24 H32 O10	
Formula weight	480.49	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 11.200(2) Å	□= 90°.
	b = 5.0559(9) Å	□= 115.351(5)°.
	c = 11.554(2) Å	□ = 90°.
Volume	591.26(19) $Å^3$	
Z	1	
Density (calculated)	1.349 Mg/m^3	
Absorption coefficient	0.105 mm^{-1}	
F(000)	256	
Crystal size	0.3 x 0.2 x 0.08 mm^3	
Theta range for data collection	1.950 to 25.351°.	
Index ranges	-13<=h<=13, -6<=k<=6, -13<=l<=13	
Reflections collected	9807	
Independent reflections	2156 [R(int) = 0.0543]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.5315	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2156 / 1 / 158	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0340, wR2 = 0.0733	
R indices (all data)	R1 = 0.0439, wR2 = 0.0772	
Absolute structure parameter	-0.2(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.152 and -0.190 $e.Å^{-3}$	

Table S54. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **20**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-11306(2)	-11614(4)	-11962(2)	21(1)
O(2)	-11113(2)	-14746(4)	-13657(2)	23(1)
O(3)	-14395(2)	-16629(4)	-10450(2)	19(1)
O(4)	-17019(2)	-16121(4)	-10792(2)	21(1)
O(5)	-17458(2)	-19711(4)	-12052(2)	18(1)
C(1)	-18648(3)	-20137(6)	-11856(3)	24(1)
C(2)	-16702(3)	-17679(5)	-11408(2)	16(1)
C(3)	-15449(2)	-17500(5)	-11594(2)	15(1)
C(4)	-15646(2)	-15466(5)	-12647(2)	17(1)
C(5)	-14453(2)	-15279(5)	-12937(2)	16(1)
C(6)	-13444(3)	-13459(5)	-12294(2)	15(1)
C(7)	-12346(3)	-13318(5)	-12546(2)	16(1)
C(8)	-12243(2)	-15016(5)	-13469(2)	17(1)
C(9)	-13235(2)	-16812(6)	-14094(2)	18(1)
C(10)	-14340(3)	-16939(5)	-13833(2)	18(1)
C(11)	-11396(3)	-9851(6)	-11033(2)	21(1)
C(12)	-10985(3)	-16507(6)	-14556(2)	25(1)

Table S55. Bond lengths [Å] and angles [°] for **20**.

O(1)-C(7)	1.372(3)
O(1)-C(11)	1.431(3)
O(2)-C(8)	1.379(3)
O(2)-C(12)	1.422(3)
O(3)-H(3)	0.8400
O(3)-C(3)	1.414(3)
O(4)-C(2)	1.212(3)
O(5)-C(1)	1.461(3)
O(5)-C(2)	1.337(3)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.511(4)
C(3)-H(3A)	1.0000
C(3)-C(4)	1.535(3)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(4)-C(5)	1.514(4)
C(5)-C(6)	1.398(4)
C(5)-C(10)	1.380(3)
C(6)-H(6)	0.9500
C(6)-C(7)	1.382(3)
C(7)-C(8)	1.412(4)
C(8)-C(9)	1.376(4)
C(9)-H(9)	0.9500
C(9)-C(10)	1.396(4)
C(10)-H(10)	0.9500
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800

C(7)-O(1)-C(11)	116.2(2)
C(8)-O(2)-C(12)	116.1(2)
C(3)-O(3)-H(3)	109.5
C(2)-O(5)-C(1)	115.41(19)
O(5)-C(1)-H(1A)	109.5
O(5)-C(1)-H(1B)	109.5
O(5)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(4)-C(2)-O(5)	123.5(2)
O(4)-C(2)-C(3)	124.6(2)
O(5)-C(2)-C(3)	111.9(2)
O(3)-C(3)-C(2)	109.9(2)
O(3)-C(3)-H(3A)	109.9
O(3)-C(3)-C(4)	108.15(19)
C(2)-C(3)-H(3A)	109.9
C(2)-C(3)-C(4)	109.0(2)
C(4)-C(3)-H(3A)	109.9
C(3)-C(4)-H(4A)	109.2
C(3)-C(4)-H(4B)	109.2
H(4A)-C(4)-H(4B)	107.9
C(5)-C(4)-C(3)	112.1(2)
C(5)-C(4)-H(4A)	109.2
C(5)-C(4)-H(4B)	109.2
C(6)-C(5)-C(4)	120.8(2)
C(10)-C(5)-C(4)	120.1(2)
C(10)-C(5)-C(6)	119.1(2)
C(5)-C(6)-H(6)	119.6
C(7)-C(6)-C(5)	120.7(2)
C(7)-C(6)-H(6)	119.6
O(1)-C(7)-C(6)	125.0(2)
O(1)-C(7)-C(8)	115.2(2)
C(6)-C(7)-C(8)	119.7(2)
O(2)-C(8)-C(7)	115.9(2)
C(9)-C(8)-O(2)	124.8(2)

C(9)-C(8)-C(7)	119.3(2)
C(8)-C(9)-H(9)	119.7
C(8)-C(9)-C(10)	120.5(2)
C(10)-C(9)-H(9)	119.7
C(5)-C(10)-C(9)	120.6(2)
C(5)-C(10)-H(10)	119.7
C(9)-C(10)-H(10)	119.7
O(1)-C(11)-H(11A)	109.5
O(1)-C(11)-H(11B)	109.5
O(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
O(2)-C(12)-H(12A)	109.5
O(2)-C(12)-H(12B)	109.5
O(2)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S56. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **20**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	23(1)	21(1)	23(1)	-7(1)	14(1)	-6(1)
O(2)	24(1)	27(1)	24(1)	-5(1)	17(1)	-2(1)
O(3)	21(1)	21(1)	13(1)	1(1)	4(1)	-1(1)
O(4)	27(1)	19(1)	20(1)	-2(1)	15(1)	-1(1)
O(5)	18(1)	22(1)	17(1)	-3(1)	10(1)	-6(1)
C(1)	20(2)	29(2)	25(2)	1(1)	12(1)	-4(1)
C(2)	19(1)	15(1)	13(1)	4(1)	8(1)	1(1)
C(3)	18(1)	14(1)	14(1)	-4(1)	7(1)	-2(1)
C(4)	18(1)	18(1)	15(1)	2(1)	7(1)	-2(1)
C(5)	20(2)	16(1)	12(1)	3(1)	8(1)	1(1)
C(6)	21(2)	15(1)	13(1)	2(1)	10(1)	3(1)
C(7)	19(2)	16(1)	15(1)	2(1)	8(1)	-1(1)
C(8)	20(1)	20(2)	15(1)	4(1)	10(1)	3(1)
C(9)	25(2)	20(2)	13(1)	0(1)	10(1)	2(1)
C(10)	21(1)	18(2)	15(1)	1(1)	6(1)	-2(1)
C(11)	26(2)	20(2)	19(1)	-6(1)	11(1)	-4(1)
C(12)	32(2)	30(2)	21(1)	-2(1)	19(1)	3(1)

Table S57. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **20**.

	x	y	z	U(eq)
H(3)	-13974	-17944	-10027	29
H(1A)	-18398	-20690	-10969	36
H(1B)	-19189	-21517	-12441	36
H(1C)	-19155	-18488	-12025	36
H(3A)	-15234	-19268	-11844	18
H(4A)	-16428	-15969	-13436	21
H(4B)	-15820	-13710	-12373	21
H(6)	-13515	-12307	-11677	18
H(9)	-13166	-17974	-14709	22
H(10)	-15021	-18179	-14276	22
H(11A)	-11426	-10877	-10326	32
H(11B)	-12201	-8785	-11435	32
H(11C)	-10623	-8684	-10702	32
H(12A)	-11053	-18336	-14309	38
H(12B)	-10125	-16241	-14570	38
H(12C)	-11690	-16159	-15410	38

Experimental Summary for Crystal **22** (CCDC 1905648)

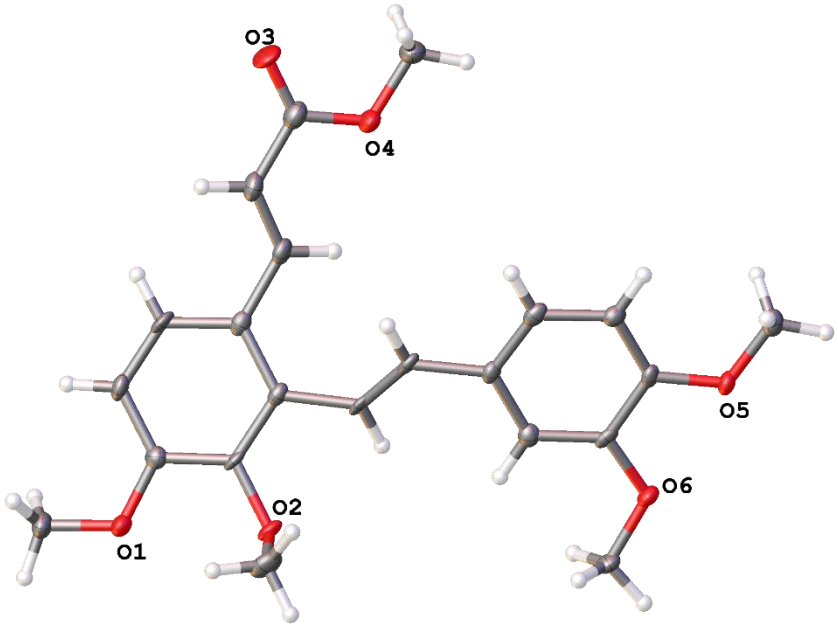


Table S58. Crystal data and structure refinement for **22**.

Empirical formula	C22 H24 O6	
Formula weight	384.41	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 19.271(5) Å	□= 90°.
	b = 4.5166(9) Å	□= 107.803(9)°.
	c = 23.345(7) Å	□ = 90°.
Volume	1934.6(9) Å^3	
Z	4	
Density (calculated)	1.320 Mg/m^3	
Absorption coefficient	0.096 mm^{-1}	
F(000)	816	
Crystal size	0.29 x 0.26 x 0.08 mm^3	
Theta range for data collection	1.829 to 25.387°.	
Index ranges	-23<=h<=19, -5<=k<=5, -28<=l<=26	
Reflections collected	12378	
Independent reflections	3529 [R(int) = 0.0632]	
Completeness to theta = 25.242°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.6249	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3529 / 0 / 258	
Goodness-of-fit on F^2	1.004	
Final R indices [I>2sigma(I)]	R1 = 0.0511, wR2 = 0.1209	
R indices (all data)	R1 = 0.0836, wR2 = 0.1394	
Extinction coefficient	n/a	

Largest diff. peak and hole	0.300 and -0.285 e.Å^{-3}

Table S59. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **22**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1224(1)	11665(3)	3585(1)	22(1)
O(2)	2551(1)	9716(3)	4180(1)	18(1)
O(3)	838(1)	1961(4)	6750(1)	35(1)
O(4)	2013(1)	3204(3)	6946(1)	27(1)
O(5)	6103(1)	3094(3)	7036(1)	19(1)
O(6)	5828(1)	6651(3)	6140(1)	20(1)
C(1)	533(1)	12979(5)	3279(1)	28(1)
C(2)	1298(1)	10311(4)	4123(1)	17(1)
C(3)	734(1)	9880(4)	4372(1)	20(1)
C(4)	882(1)	8441(5)	4921(1)	20(1)
C(5)	1576(1)	7433(4)	5242(1)	16(1)
C(6)	2152(1)	7868(4)	4990(1)	15(1)
C(7)	1994(1)	9294(4)	4433(1)	15(1)
C(8)	2567(1)	7431(5)	3757(1)	28(1)
C(9)	1696(1)	6045(4)	5834(1)	18(1)
C(10)	1190(1)	4568(5)	6008(1)	23(1)
C(11)	1315(1)	3151(5)	6596(1)	23(1)
C(12)	2152(2)	1614(5)	7512(1)	33(1)
C(13)	2915(1)	7020(4)	5288(1)	16(1)
C(14)	3172(1)	4673(4)	5634(1)	15(1)
C(15)	3941(1)	4084(4)	5961(1)	14(1)
C(16)	4110(1)	2012(4)	6423(1)	17(1)
C(17)	4827(1)	1611(4)	6793(1)	16(1)
C(18)	5388(1)	3245(4)	6699(1)	15(1)
C(19)	5229(1)	5246(4)	6210(1)	15(1)
C(20)	4523(1)	5662(4)	5855(1)	15(1)
C(21)	5717(1)	8385(4)	5608(1)	21(1)
C(22)	6282(1)	1047(5)	7524(1)	22(1)

Table S60. Bond lengths [Å] and angles [°] for **22**.

O(1)-C(1)	1.435(3)
O(1)-C(2)	1.364(3)
O(2)-C(7)	1.387(2)
O(2)-C(8)	1.435(3)
O(3)-C(11)	1.209(3)
O(4)-C(11)	1.344(3)
O(4)-C(12)	1.454(3)
O(5)-C(18)	1.365(3)
O(5)-C(22)	1.424(3)
O(6)-C(19)	1.370(2)
O(6)-C(21)	1.427(2)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.393(3)
C(2)-C(7)	1.394(3)
C(3)-H(3)	0.9500
C(3)-C(4)	1.386(3)
C(4)-H(4)	0.9500
C(4)-C(5)	1.394(3)
C(5)-C(6)	1.419(3)
C(5)-C(9)	1.471(3)
C(6)-C(7)	1.399(3)
C(6)-C(13)	1.472(3)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9)	0.9500
C(9)-C(10)	1.341(3)
C(10)-H(10)	0.9500
C(10)-C(11)	1.467(3)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800

C(13)-H(13)	0.9500
C(13)-C(14)	1.334(3)
C(14)-H(14)	0.9500
C(14)-C(15)	1.469(3)
C(15)-C(16)	1.389(3)
C(15)-C(20)	1.414(3)
C(16)-H(16)	0.9500
C(16)-C(17)	1.399(3)
C(17)-H(17)	0.9500
C(17)-C(18)	1.379(3)
C(18)-C(19)	1.414(3)
C(19)-C(20)	1.374(3)
C(20)-H(20)	0.9500
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800

C(2)-O(1)-C(1)	117.62(18)
C(7)-O(2)-C(8)	112.12(16)
C(11)-O(4)-C(12)	114.57(18)
C(18)-O(5)-C(22)	116.65(16)
C(19)-O(6)-C(21)	116.76(17)
O(1)-C(1)-H(1A)	109.5
O(1)-C(1)-H(1B)	109.5
O(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(1)-C(2)-C(3)	124.9(2)
O(1)-C(2)-C(7)	116.0(2)
C(3)-C(2)-C(7)	119.1(2)
C(2)-C(3)-H(3)	120.5
C(4)-C(3)-C(2)	119.0(2)

C(4)-C(3)-H(3)	120.5
C(3)-C(4)-H(4)	118.5
C(3)-C(4)-C(5)	122.9(2)
C(5)-C(4)-H(4)	118.5
C(4)-C(5)-C(6)	118.3(2)
C(4)-C(5)-C(9)	119.6(2)
C(6)-C(5)-C(9)	122.0(2)
C(5)-C(6)-C(13)	124.35(19)
C(7)-C(6)-C(5)	118.2(2)
C(7)-C(6)-C(13)	117.36(19)
O(2)-C(7)-C(2)	118.75(19)
O(2)-C(7)-C(6)	118.85(19)
C(2)-C(7)-C(6)	122.4(2)
O(2)-C(8)-H(8A)	109.5
O(2)-C(8)-H(8B)	109.5
O(2)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(5)-C(9)-H(9)	117.4
C(10)-C(9)-C(5)	125.1(2)
C(10)-C(9)-H(9)	117.4
C(9)-C(10)-H(10)	117.5
C(9)-C(10)-C(11)	125.0(2)
C(11)-C(10)-H(10)	117.5
O(3)-C(11)-O(4)	122.5(2)
O(3)-C(11)-C(10)	123.3(2)
O(4)-C(11)-C(10)	114.1(2)
O(4)-C(12)-H(12A)	109.5
O(4)-C(12)-H(12B)	109.5
O(4)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(6)-C(13)-H(13)	115.7
C(14)-C(13)-C(6)	128.6(2)

C(14)-C(13)-H(13)	115.7
C(13)-C(14)-H(14)	117.0
C(13)-C(14)-C(15)	125.9(2)
C(15)-C(14)-H(14)	117.0
C(16)-C(15)-C(14)	119.1(2)
C(16)-C(15)-C(20)	117.7(2)
C(20)-C(15)-C(14)	123.08(19)
C(15)-C(16)-H(16)	119.4
C(15)-C(16)-C(17)	121.3(2)
C(17)-C(16)-H(16)	119.4
C(16)-C(17)-H(17)	119.8
C(18)-C(17)-C(16)	120.4(2)
C(18)-C(17)-H(17)	119.8
O(5)-C(18)-C(17)	125.69(19)
O(5)-C(18)-C(19)	115.36(18)
C(17)-C(18)-C(19)	118.9(2)
O(6)-C(19)-C(18)	114.29(19)
O(6)-C(19)-C(20)	125.42(19)
C(20)-C(19)-C(18)	120.3(2)
C(15)-C(20)-H(20)	119.4
C(19)-C(20)-C(15)	121.18(19)
C(19)-C(20)-H(20)	119.4
O(6)-C(21)-H(21A)	109.5
O(6)-C(21)-H(21B)	109.5
O(6)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
O(5)-C(22)-H(22A)	109.5
O(5)-C(22)-H(22B)	109.5
O(5)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S61. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **22**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	16(1)	33(1)	21(1)	8(1)	8(1)	2(1)
O(2)	16(1)	23(1)	22(1)	-1(1)	13(1)	-1(1)
O(3)	21(1)	54(1)	34(1)	11(1)	12(1)	-10(1)
O(4)	18(1)	43(1)	21(1)	11(1)	7(1)	-2(1)
O(5)	12(1)	24(1)	19(1)	4(1)	5(1)	2(1)
O(6)	15(1)	26(1)	20(1)	5(1)	9(1)	0(1)
C(1)	18(1)	38(1)	26(1)	13(1)	6(1)	5(1)
C(2)	18(1)	21(1)	14(1)	1(1)	7(1)	-1(1)
C(3)	11(1)	26(1)	22(1)	0(1)	4(1)	3(1)
C(4)	15(1)	28(1)	22(1)	2(1)	14(1)	1(1)
C(5)	16(1)	18(1)	16(1)	-2(1)	8(1)	1(1)
C(6)	13(1)	16(1)	18(1)	-4(1)	7(1)	0(1)
C(7)	11(1)	18(1)	19(1)	-3(1)	9(1)	-4(1)
C(8)	28(2)	33(1)	31(1)	-7(1)	21(1)	-1(1)
C(9)	14(1)	23(1)	20(1)	-1(1)	8(1)	5(1)
C(10)	17(1)	31(1)	22(1)	3(1)	5(1)	0(1)
C(11)	19(1)	27(1)	24(1)	-1(1)	10(1)	-1(1)
C(12)	28(2)	47(2)	25(1)	17(1)	12(1)	2(1)
C(13)	13(1)	21(1)	18(1)	-5(1)	10(1)	-3(1)
C(14)	13(1)	19(1)	16(1)	-5(1)	8(1)	-2(1)
C(15)	14(1)	16(1)	15(1)	-4(1)	7(1)	1(1)
C(16)	19(1)	16(1)	18(1)	-3(1)	11(1)	-1(1)
C(17)	19(1)	16(1)	16(1)	3(1)	9(1)	1(1)
C(18)	14(1)	18(1)	13(1)	-2(1)	6(1)	4(1)
C(19)	15(1)	15(1)	18(1)	-3(1)	11(1)	-2(1)
C(20)	19(1)	16(1)	13(1)	0(1)	7(1)	2(1)
C(21)	19(1)	26(1)	21(1)	3(1)	10(1)	-3(1)
C(22)	21(1)	23(1)	21(1)	4(1)	5(1)	4(1)

Table S62. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **22**.

	x	y	z	U(eq)
H(1A)	556	13911	2906	42
H(1B)	415	14478	3538	42
H(1C)	155	11444	3183	42
H(3)	256	10562	4169	24
H(4)	494	8128	5085	24
H(8A)	2101	7395	3435	42
H(8B)	2648	5511	3963	42
H(8C)	2963	7827	3586	42
H(9)	2168	6209	6117	22
H(10)	715	4429	5728	28
H(12A)	1983	-435	7431	49
H(12B)	1890	2578	7761	49
H(12C)	2676	1627	7725	49
H(13)	3273	8318	5224	19
H(14)	2825	3252	5673	19
H(16)	3732	845	6490	20
H(17)	4929	205	7110	20
H(20)	4424	7035	5531	18
H(21A)	5468	7186	5255	32
H(21B)	6189	9046	5578	32
H(21C)	5417	10113	5626	32
H(22A)	6166	-966	7367	33
H(22B)	6000	1515	7797	33
H(22C)	6804	1184	7742	33

Experimental Summary for Crystal **Pd-1** (CCDC 1905654)

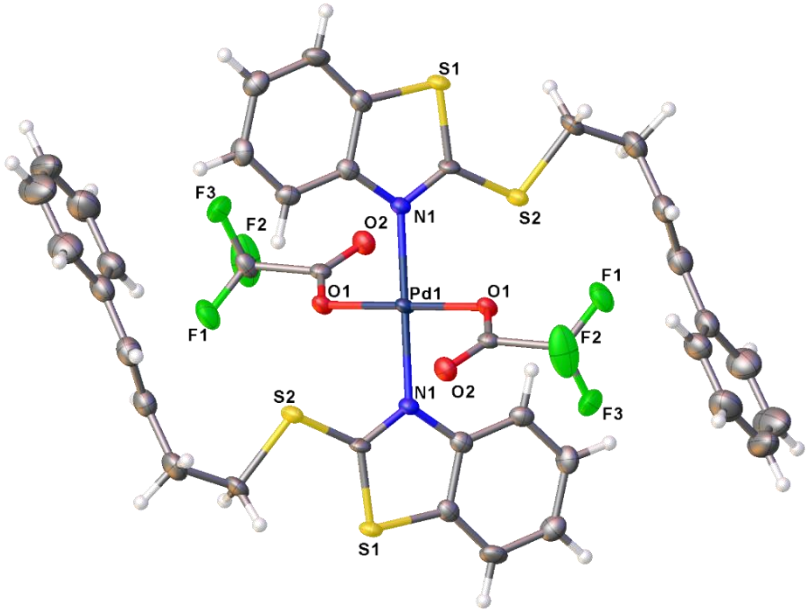


Table S63. Crystal data and structure refinement for **Pd-1**.

Empirical formula	C38 H30 F6 N2 O4 Pd S4	
Formula weight	927.28	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 15.3360(10) Å	□= 90°.
	b = 10.1947(7) Å	□= 98.408(2)°.
	c = 24.0955(13) Å	□ = 90°.
Volume	3726.7(4) Å^3	
Z	4	
Density (calculated)	1.653 Mg/m^3	
Absorption coefficient	0.797 mm^{-1}	
F(000)	1872	
Crystal size	0.25 x 0.22 x 0.18 mm^3	
Theta range for data collection	1.709 to 28.293°.	
Index ranges	-16<=h<=20, -13<=k<=11, -32<=l<=32	
Reflections collected	12876	
Independent reflections	4617 [R(int) = 0.0345]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6536	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4617 / 0 / 250	
Goodness-of-fit on F^2	1.361	
Final R indices [I>2sigma(I)]	R1 = 0.0674, wR2 = 0.1369	
R indices (all data)	R1 = 0.0805, wR2 = 0.1418	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.242 and -1.118 e.Å^{-3}	

Table S64. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **Pd-1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	5000	5000	5000	17(1)
S(1)	2322(1)	3299(1)	4334(1)	23(1)
S(2)	4197(1)	2485(1)	4210(1)	25(1)
F(1)	5004(2)	4500(4)	6900(1)	38(1)
O(1)	4972(2)	4637(3)	5815(1)	20(1)
O(2)	4652(2)	2470(4)	5734(1)	25(1)
N(1)	3724(2)	4453(4)	4823(2)	17(1)
F(3)	3712(2)	3795(5)	6604(2)	54(1)
F(2)	4769(4)	2432(4)	6857(2)	63(1)
C(2)	4763(3)	3509(5)	5978(2)	18(1)
C(9)	3460(3)	3501(5)	4477(2)	20(1)
C(3)	3016(3)	5087(5)	5025(2)	21(1)
C(4)	3080(3)	6079(5)	5422(2)	23(1)
C(8)	2189(3)	4605(5)	4785(2)	20(1)
C(1)	4576(4)	3566(5)	6598(2)	27(1)
C(6)	1476(4)	6135(5)	5309(2)	29(1)
C(7)	1408(3)	5140(6)	4920(2)	28(1)
C(5)	2305(4)	6598(5)	5564(2)	26(1)
C(12)	4817(4)	1218(6)	3228(2)	33(1)
C(10)	3470(3)	1536(6)	3691(2)	29(1)
C(13)	5644(4)	807(6)	3354(2)	34(1)
C(14)	6410(4)	1444(6)	3180(2)	35(1)
C(19)	6415(4)	2759(6)	3039(3)	39(1)
C(11)	4051(4)	558(6)	3428(3)	38(1)
C(15)	7173(4)	725(8)	3153(3)	50(2)
C(18)	7147(5)	3309(8)	2863(3)	52(2)
C(17)	7894(5)	2574(9)	2827(4)	65(2)
C(16)	7896(5)	1297(9)	2975(4)	71(3)

Table S65. Bond lengths [Å] and angles [°] for **Pd-1**.

Pd(1)-O(1)#1	2.005(3)
Pd(1)-O(1)	2.005(3)
Pd(1)-N(1)#1	2.020(4)
Pd(1)-N(1)	2.020(4)
S(1)-C(9)	1.740(5)
S(1)-C(8)	1.748(5)
S(2)-C(9)	1.726(5)
S(2)-C(10)	1.825(5)
F(1)-C(1)	1.313(6)
O(1)-C(2)	1.271(6)
O(2)-C(2)	1.211(6)
N(1)-C(9)	1.305(6)
N(1)-C(3)	1.410(6)
F(3)-C(1)	1.348(7)
F(2)-C(1)	1.326(7)
C(2)-C(1)	1.565(6)
C(3)-C(4)	1.386(7)
C(3)-C(8)	1.403(6)
C(4)-C(5)	1.389(7)
C(8)-C(7)	1.398(7)
C(6)-C(7)	1.374(8)
C(6)-C(5)	1.410(8)
C(12)-C(13)	1.328(8)
C(12)-C(11)	1.494(8)
C(10)-C(11)	1.535(8)
C(13)-C(14)	1.456(9)
C(14)-C(19)	1.384(9)
C(14)-C(15)	1.390(9)
C(19)-C(18)	1.376(9)
C(15)-C(16)	1.376(11)
C(18)-C(17)	1.382(11)
C(17)-C(16)	1.350(13)
O(1)#1-Pd(1)-O(1)	180.0

O(1)#1-Pd(1)-N(1)	90.16(14)
O(1)#1-Pd(1)-N(1)#1	89.84(14)
O(1)-Pd(1)-N(1)	89.84(14)
O(1)-Pd(1)-N(1)#1	90.16(14)
N(1)#1-Pd(1)-N(1)	180.0
C(9)-S(1)-C(8)	89.6(2)
C(9)-S(2)-C(10)	101.9(2)
C(2)-O(1)-Pd(1)	120.8(3)
C(9)-N(1)-Pd(1)	122.7(3)
C(9)-N(1)-C(3)	112.3(4)
C(3)-N(1)-Pd(1)	124.9(3)
O(1)-C(2)-C(1)	110.5(4)
O(2)-C(2)-O(1)	131.7(4)
O(2)-C(2)-C(1)	117.6(4)
S(2)-C(9)-S(1)	123.2(3)
N(1)-C(9)-S(1)	115.0(4)
N(1)-C(9)-S(2)	121.7(3)
C(4)-C(3)-N(1)	126.3(4)
C(4)-C(3)-C(8)	120.6(5)
C(8)-C(3)-N(1)	113.1(4)
C(3)-C(4)-C(5)	118.1(5)
C(3)-C(8)-S(1)	110.0(4)
C(7)-C(8)-S(1)	128.6(4)
C(7)-C(8)-C(3)	121.4(5)
F(1)-C(1)-F(3)	106.4(5)
F(1)-C(1)-F(2)	108.2(4)
F(1)-C(1)-C(2)	114.1(4)
F(3)-C(1)-C(2)	109.5(4)
F(2)-C(1)-F(3)	107.3(5)
F(2)-C(1)-C(2)	111.0(4)
C(7)-C(6)-C(5)	121.2(5)
C(6)-C(7)-C(8)	117.7(5)
C(4)-C(5)-C(6)	121.0(5)
C(13)-C(12)-C(11)	123.6(6)
C(11)-C(10)-S(2)	107.1(4)
C(12)-C(13)-C(14)	125.2(6)

C(19)-C(14)-C(13)	122.5(6)
C(19)-C(14)-C(15)	117.6(6)
C(15)-C(14)-C(13)	119.8(6)
C(18)-C(19)-C(14)	120.3(7)
C(12)-C(11)-C(10)	111.8(5)
C(16)-C(15)-C(14)	120.9(8)
C(19)-C(18)-C(17)	121.3(7)
C(16)-C(17)-C(18)	118.4(7)
C(17)-C(16)-C(15)	121.3(8)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

Table S66. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **Pd-1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	13(1)	25(1)	15(1)	-3(1)	2(1)	-7(1)
S(1)	12(1)	31(1)	24(1)	-7(1)	2(1)	-7(1)
S(2)	15(1)	31(1)	29(1)	-13(1)	4(1)	-6(1)
F(1)	42(2)	50(2)	20(2)	-8(1)	1(1)	-7(2)
O(1)	20(2)	23(2)	18(2)	-2(1)	3(1)	-8(1)
O(2)	26(2)	24(2)	26(2)	-6(2)	6(1)	-1(2)
N(1)	12(2)	22(2)	16(2)	-3(2)	2(1)	-4(2)
F(3)	34(2)	95(3)	39(2)	-23(2)	25(2)	-21(2)
F(2)	122(4)	40(2)	31(2)	10(2)	22(2)	4(2)
C(2)	10(2)	27(3)	17(2)	-3(2)	2(2)	-2(2)
C(9)	10(2)	31(3)	17(2)	0(2)	0(2)	-4(2)
C(3)	19(2)	24(2)	19(2)	3(2)	3(2)	-4(2)
C(4)	21(2)	24(3)	24(2)	2(2)	2(2)	-3(2)
C(8)	22(2)	20(2)	18(2)	0(2)	4(2)	-3(2)
C(1)	33(3)	29(3)	19(2)	0(2)	4(2)	-7(2)
C(6)	24(3)	30(3)	34(3)	2(2)	12(2)	6(2)
C(7)	22(2)	31(3)	31(2)	0(2)	4(2)	-11(2)
C(5)	32(3)	22(3)	26(2)	-3(2)	9(2)	5(2)
C(12)	35(3)	38(3)	26(3)	-9(2)	7(2)	-1(3)
C(10)	23(3)	36(3)	28(3)	-14(2)	2(2)	-11(2)
C(13)	37(3)	35(3)	30(3)	-5(2)	4(2)	2(3)
C(14)	33(3)	39(3)	33(3)	-12(3)	3(2)	1(3)
C(19)	34(3)	37(4)	45(3)	-11(3)	6(3)	-4(3)
C(11)	38(3)	40(3)	38(3)	-17(3)	9(3)	-11(3)
C(15)	35(4)	53(4)	61(4)	-6(4)	2(3)	8(3)
C(18)	55(4)	45(4)	57(4)	-9(3)	13(3)	-17(4)
C(17)	43(4)	73(6)	84(6)	-43(5)	30(4)	-21(4)
C(16)	36(4)	72(6)	106(7)	-40(5)	18(4)	-1(4)

Table S67. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **Pd-1**.

	x	y	z	U(eq)
H(4)	3639	6394	5593	28
H(6)	955	6519	5407	34
H(7)	849	4826	4750	33
H(5)	2333	7275	5837	31
H(12)	4706	1974	2998	40
H(10A)	3024	1064	3873	35
H(10B)	3160	2124	3400	35
H(13)	5744	35	3575	41
H(19)	5911	3286	3063	46
H(11A)	4270	-119	3708	46
H(11B)	3691	113	3107	46
H(15)	7195	-173	3260	60
H(18)	7139	4211	2764	62
H(17)	8394	2957	2700	78
H(16)	8407	782	2957	85

Experimental Summary for Crystal **Pd-2** (CCDC 1905655)

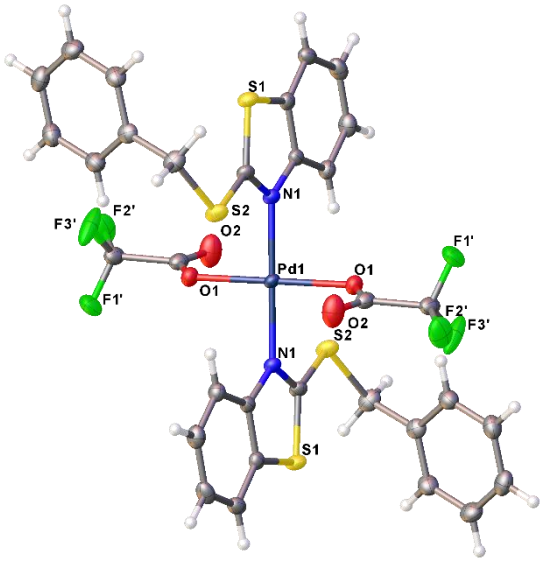


Table S68. Crystal data and structure refinement for **Pd-2**.

Empirical formula	C34 H26 Cl2 F6 N2 O4 Pd S4
Formula weight	946.11
Temperature	100.0 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.0381(9) Å □= 68.768(3)°. b = 10.3207(12) Å □= 89.673(5)°. c = 10.3832(11) Å □ = 88.327(3)°.
Volume	902.40(17) Å^3
Z	1
Density (calculated)	1.741 Mg/m^3
Absorption coefficient	0.967 mm^{-1}
F(000)	474
Crystal size	0.30 x 0.29 x 0.28 mm^3
Theta range for data collection	2.104 to 28.308°.
Index ranges	-12<=h<=12, -13<=k<=13, -13<=l<=13
Reflections collected	10713
Independent reflections	4397 [R(int) = 0.0384]
Completeness to theta = 25.242°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6793
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4397 / 15 / 269
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0317, wR2 = 0.0773
R indices (all data)	R1 = 0.0369, wR2 = 0.0825
Extinction coefficient	n/a
Largest diff. peak and hole	1.071 and -0.431 e.Å^{-3}

Table S69. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **Pd-2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	5000	5000	5000	15(1)
S(1)	4956(1)	2545(1)	2169(1)	21(1)
S(2)	3748(1)	5452(1)	1865(1)	24(1)
Cl(1)	7101(1)	981(1)	9776(1)	35(1)
O(1)	2887(2)	4436(2)	5369(2)	22(1)
N(1)	5258(2)	3679(2)	3981(2)	17(1)
F(2')	846(3)	1627(3)	7388(4)	48(1)
F(3')	461(3)	2996(4)	5329(2)	57(2)
F(1')	242(3)	3700(3)	7025(4)	47(1)
O(2)	3546(2)	2537(2)	7209(2)	42(1)
C(6)	5991(2)	1635(2)	3639(2)	18(1)
C(1)	6047(2)	2407(2)	4501(2)	17(1)
C(8)	1700(3)	3918(2)	983(2)	22(1)
C(15)	1016(3)	2929(2)	6499(2)	26(1)
C(5)	6675(3)	323(2)	4006(3)	23(1)
C(19)	4654(3)	3891(2)	2774(2)	18(1)
C(2)	6822(3)	1893(2)	5747(2)	21(1)
C(9)	777(3)	3742(3)	2105(3)	26(1)
C(13)	1573(3)	3041(3)	247(3)	26(1)
C(14)	2669(3)	3309(3)	6386(2)	22(1)
C(11)	-367(3)	1831(3)	1748(3)	30(1)
C(10)	-256(3)	2701(3)	2478(3)	28(1)
C(3)	7519(3)	604(3)	6102(3)	26(1)
C(20)	5597(3)	23(3)	9501(3)	35(1)
C(12)	547(3)	2000(3)	625(3)	30(1)
C(4)	7452(3)	-169(3)	5244(3)	26(1)
C(7)	2807(3)	5060(3)	509(2)	26(1)
F(3)	806(15)	1765(15)	6340(30)	72(10)
F(1)	96(12)	3901(17)	5670(30)	99(14)
F(2)	300(20)	2760(40)	7624(18)	117(16)

Table S70. Bond lengths [Å] and angles [°] for **Pd-2**.

Pd(1)-O(1)#1	2.0065(16)
Pd(1)-O(1)	2.0065(16)
Pd(1)-N(1)#1	2.0142(18)
Pd(1)-N(1)	2.0142(18)
S(1)-C(6)	1.736(2)
S(1)-C(19)	1.734(2)
S(2)-C(19)	1.728(2)
S(2)-C(7)	1.820(2)
Cl(1)-C(20)	1.787(3)
O(1)-C(14)	1.276(3)
N(1)-C(1)	1.400(3)
N(1)-C(19)	1.311(3)
F(2')-C(15)	1.340(3)
F(3')-C(15)	1.295(3)
F(1')-C(15)	1.304(3)
O(2)-C(14)	1.213(3)
C(6)-C(1)	1.399(3)
C(6)-C(5)	1.392(3)
C(1)-C(2)	1.392(3)
C(8)-C(9)	1.389(4)
C(8)-C(13)	1.387(3)
C(8)-C(7)	1.509(4)
C(15)-C(14)	1.549(3)
C(15)-F(3)	1.288(7)
C(15)-F(1)	1.330(7)
C(15)-F(2)	1.288(7)
C(5)-H(5)	0.9500
C(5)-C(4)	1.386(4)
C(2)-H(2)	0.9500
C(2)-C(3)	1.379(3)
C(9)-H(9)	0.9500
C(9)-C(10)	1.390(4)
C(13)-H(13)	0.9500
C(13)-C(12)	1.385(4)

C(11)-H(11)	0.9500
C(11)-C(10)	1.375(4)
C(11)-C(12)	1.386(4)
C(10)-H(10)	0.9500
C(3)-H(3)	0.9500
C(3)-C(4)	1.398(4)
C(20)-C(20)#2	1.480(6)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(12)-H(12)	0.9500
C(4)-H(4)	0.9500
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900

O(1)#1-Pd(1)-O(1)	180.0
O(1)#1-Pd(1)-N(1)	90.86(7)
O(1)-Pd(1)-N(1)	89.14(7)
O(1)#1-Pd(1)-N(1)#1	89.14(7)
O(1)-Pd(1)-N(1)#1	90.86(7)
N(1)-Pd(1)-N(1)#1	180.00(7)
C(19)-S(1)-C(6)	90.03(11)
C(19)-S(2)-C(7)	102.35(11)
C(14)-O(1)-Pd(1)	116.19(15)
C(1)-N(1)-Pd(1)	124.09(15)
C(19)-N(1)-Pd(1)	123.57(16)
C(19)-N(1)-C(1)	112.29(19)
C(1)-C(6)-S(1)	109.85(17)
C(5)-C(6)-S(1)	128.55(19)
C(5)-C(6)-C(1)	121.6(2)
C(6)-C(1)-N(1)	113.42(19)
C(2)-C(1)-N(1)	126.0(2)
C(2)-C(1)-C(6)	120.6(2)
C(9)-C(8)-C(7)	122.2(2)
C(13)-C(8)-C(9)	119.1(2)
C(13)-C(8)-C(7)	118.7(2)
F(2')-C(15)-C(14)	110.6(2)

F(3')-C(15)-F(2')	106.9(3)
F(3')-C(15)-F(1')	111.0(3)
F(3')-C(15)-C(14)	112.5(2)
F(1')-C(15)-F(2')	104.5(2)
F(1')-C(15)-C(14)	110.9(2)
F(3)-C(15)-C(14)	112.5(7)
F(3)-C(15)-F(1)	109.4(14)
F(3)-C(15)-F(2)	101.6(16)
F(1)-C(15)-C(14)	115.5(6)
F(2)-C(15)-C(14)	120.0(8)
F(2)-C(15)-F(1)	96.0(16)
C(6)-C(5)-H(5)	121.4
C(4)-C(5)-C(6)	117.1(2)
C(4)-C(5)-H(5)	121.4
S(2)-C(19)-S(1)	124.82(13)
N(1)-C(19)-S(1)	114.40(17)
N(1)-C(19)-S(2)	120.65(17)
C(1)-C(2)-H(2)	121.0
C(3)-C(2)-C(1)	117.9(2)
C(3)-C(2)-H(2)	121.0
C(8)-C(9)-H(9)	119.9
C(8)-C(9)-C(10)	120.2(2)
C(10)-C(9)-H(9)	119.9
C(8)-C(13)-H(13)	119.7
C(12)-C(13)-C(8)	120.7(2)
C(12)-C(13)-H(13)	119.7
O(1)-C(14)-C(15)	111.3(2)
O(2)-C(14)-O(1)	129.8(2)
O(2)-C(14)-C(15)	118.9(2)
C(10)-C(11)-H(11)	120.1
C(10)-C(11)-C(12)	119.9(3)
C(12)-C(11)-H(11)	120.1
C(9)-C(10)-H(10)	119.8
C(11)-C(10)-C(9)	120.4(2)
C(11)-C(10)-H(10)	119.8
C(2)-C(3)-H(3)	119.3

C(2)-C(3)-C(4)	121.4(2)
C(4)-C(3)-H(3)	119.3
Cl(1)-C(20)-H(20A)	109.8
Cl(1)-C(20)-H(20B)	109.8
C(20)#2-C(20)-Cl(1)	109.4(3)
C(20)#2-C(20)-H(20A)	109.8
C(20)#2-C(20)-H(20B)	109.8
H(20A)-C(20)-H(20B)	108.2
C(13)-C(12)-C(11)	119.9(2)
C(13)-C(12)-H(12)	120.1
C(11)-C(12)-H(12)	120.1
C(5)-C(4)-C(3)	121.4(2)
C(5)-C(4)-H(4)	119.3
C(3)-C(4)-H(4)	119.3
S(2)-C(7)-H(7A)	108.3
S(2)-C(7)-H(7B)	108.3
C(8)-C(7)-S(2)	116.12(17)
C(8)-C(7)-H(7A)	108.3
C(8)-C(7)-H(7B)	108.3
H(7A)-C(7)-H(7B)	107.4

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+1,-y,-z+2

Table S71. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **Pd-2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	17(1)	13(1)	17(1)	-6(1)	-1(1)	-2(1)
S(1)	28(1)	16(1)	18(1)	-8(1)	-3(1)	-1(1)
S(2)	34(1)	14(1)	23(1)	-5(1)	-8(1)	2(1)
Cl(1)	33(1)	28(1)	44(1)	-12(1)	-11(1)	-1(1)
O(1)	19(1)	20(1)	26(1)	-8(1)	0(1)	-3(1)
N(1)	19(1)	14(1)	18(1)	-6(1)	-1(1)	-2(1)
F(2')	36(1)	32(1)	64(2)	-3(1)	12(1)	-11(1)
F(3')	40(2)	106(4)	28(1)	-27(2)	7(1)	-44(2)
F(1')	29(1)	49(2)	77(3)	-41(2)	14(1)	1(1)
O(2)	33(1)	40(1)	38(1)	5(1)	-2(1)	-7(1)
C(6)	16(1)	18(1)	21(1)	-6(1)	2(1)	-3(1)
C(1)	15(1)	15(1)	21(1)	-6(1)	2(1)	-2(1)
C(8)	24(1)	21(1)	17(1)	-4(1)	-7(1)	3(1)
C(15)	26(1)	26(1)	29(1)	-14(1)	9(1)	-6(1)
C(5)	22(1)	18(1)	28(1)	-10(1)	5(1)	-2(1)
C(19)	21(1)	12(1)	21(1)	-6(1)	1(1)	-3(1)
C(2)	19(1)	23(1)	22(1)	-8(1)	-1(1)	-1(1)
C(9)	25(1)	30(1)	25(1)	-13(1)	-2(1)	3(1)
C(13)	26(1)	33(1)	20(1)	-12(1)	-1(1)	1(1)
C(14)	25(1)	23(1)	22(1)	-12(1)	4(1)	-5(1)
C(11)	23(1)	31(1)	30(1)	-5(1)	-7(1)	-3(1)
C(10)	21(1)	38(1)	25(1)	-10(1)	0(1)	1(1)
C(3)	22(1)	26(1)	25(1)	-3(1)	-4(1)	1(1)
C(20)	35(2)	42(2)	36(2)	-23(1)	-7(1)	-5(1)
C(12)	32(1)	32(1)	28(1)	-16(1)	-6(1)	0(1)
C(4)	22(1)	19(1)	32(1)	-2(1)	2(1)	4(1)
C(7)	32(1)	25(1)	17(1)	-3(1)	-6(1)	-2(1)
F(3)	37(7)	51(11)	160(30)	-70(17)	2(10)	-4(6)
F(1)	12(6)	41(10)	180(30)	42(13)	0(9)	-2(5)
F(2)	85(15)	240(40)	40(10)	-63(17)	35(10)	-100(20)

Table S72. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **Pd-2**.

	x	y	z	U(eq)
H(5)	6611	-211	3432	27
H(2)	6870	2414	6335	26
H(9)	852	4336	2617	31
H(13)	2195	3157	-525	31
H(11)	-1069	1115	2012	35
H(10)	-889	2589	3242	34
H(3)	8055	233	6948	31
H(20A)	5215	474	8546	42
H(20B)	5942	-934	9626	42
H(12)	470	1403	116	36
H(4)	7951	-1051	5514	32
H(7A)	2289	5919	-103	31
H(7B)	3566	4801	-54	31

CYCLIC VOLTAMMETRY

A. General Procedure

Solutions of 2-(butylthio)benzothiazole, 2-(but-3-en-1-ylthio)benzothiazole, (*E*)-2-((4-phenylbut-3-en-1-yl)thio)benzothiazole, and (*E*)-2-((4-phenylbut-3-en-1-yl)sulfonyl)benzothiazole—which was tested after an oxidation method was developed—were prepared in acetonitrile at 0.05M with tetrabutylammonium tetrafluoroborate present as an electrolyte at 0.1M. These solutions were each placed on an ElectraSyn 2.0 by IKA and run on the Cyclic Voltammetry setting with 2 segments, an initial and final voltage of 0V, an overall direction of 0, an upper voltage of 25V, a final voltage of 0V, and a sweep rate of 200 mv/s.

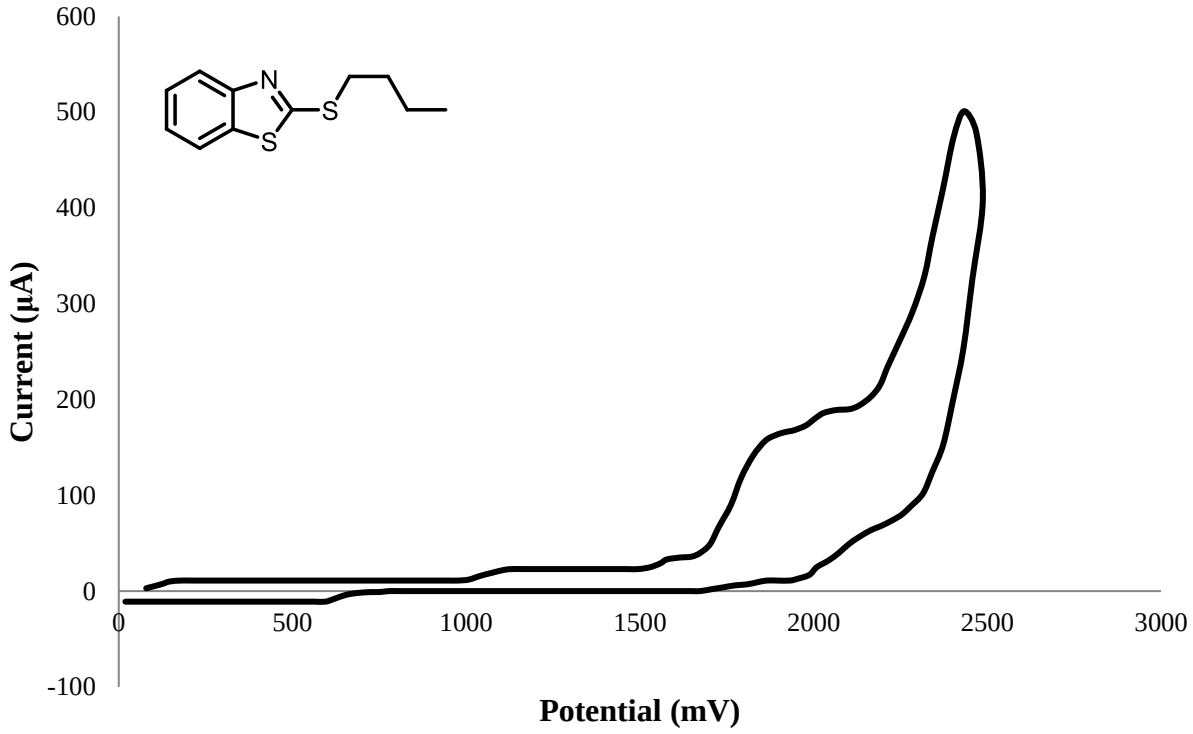


Figure S20. Cyclic voltammetry data for 2-(butylthio)benzothiazole.

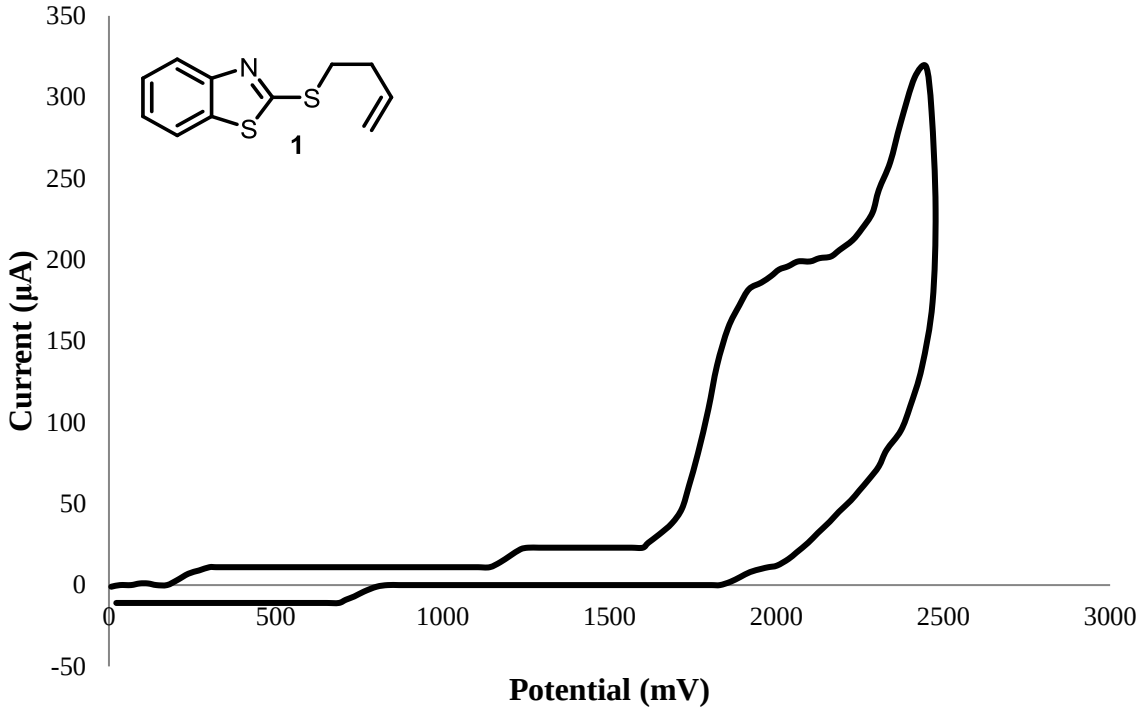


Figure S21. Cyclic voltammetry data for 2-(but-3-en-1-ylthio)benzothiazole.

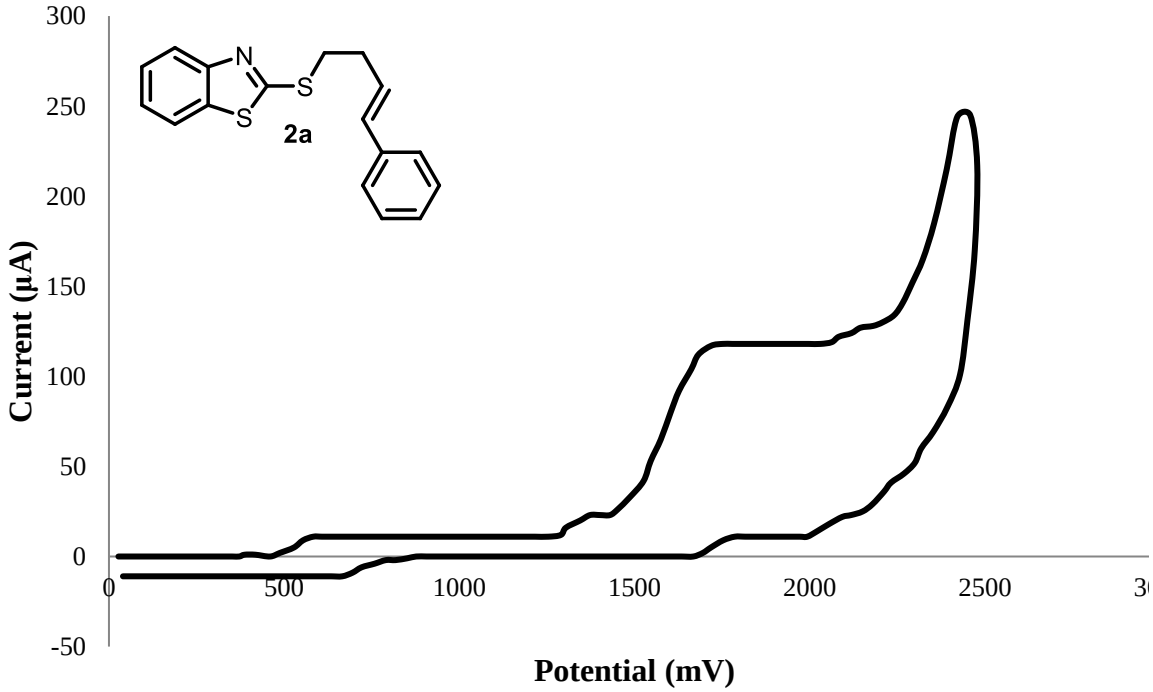


Figure S22. Cyclic voltammetry data for (*E*)-2-((4-phenylbut-3-en-1-yl)thio)benzothiazole.

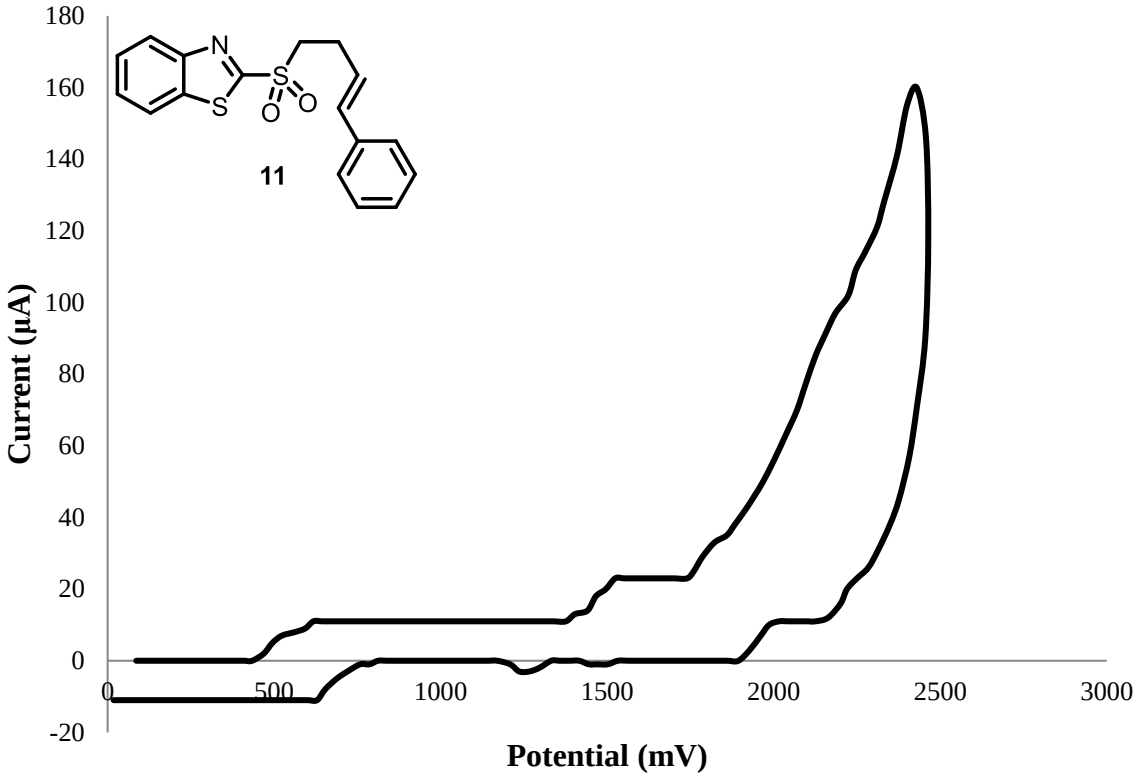


Figure S23. Cyclic voltammetry data for (*E*)-2-((4-phenylbut-3-en-1-yl)sulfonyl)benzothiazole.

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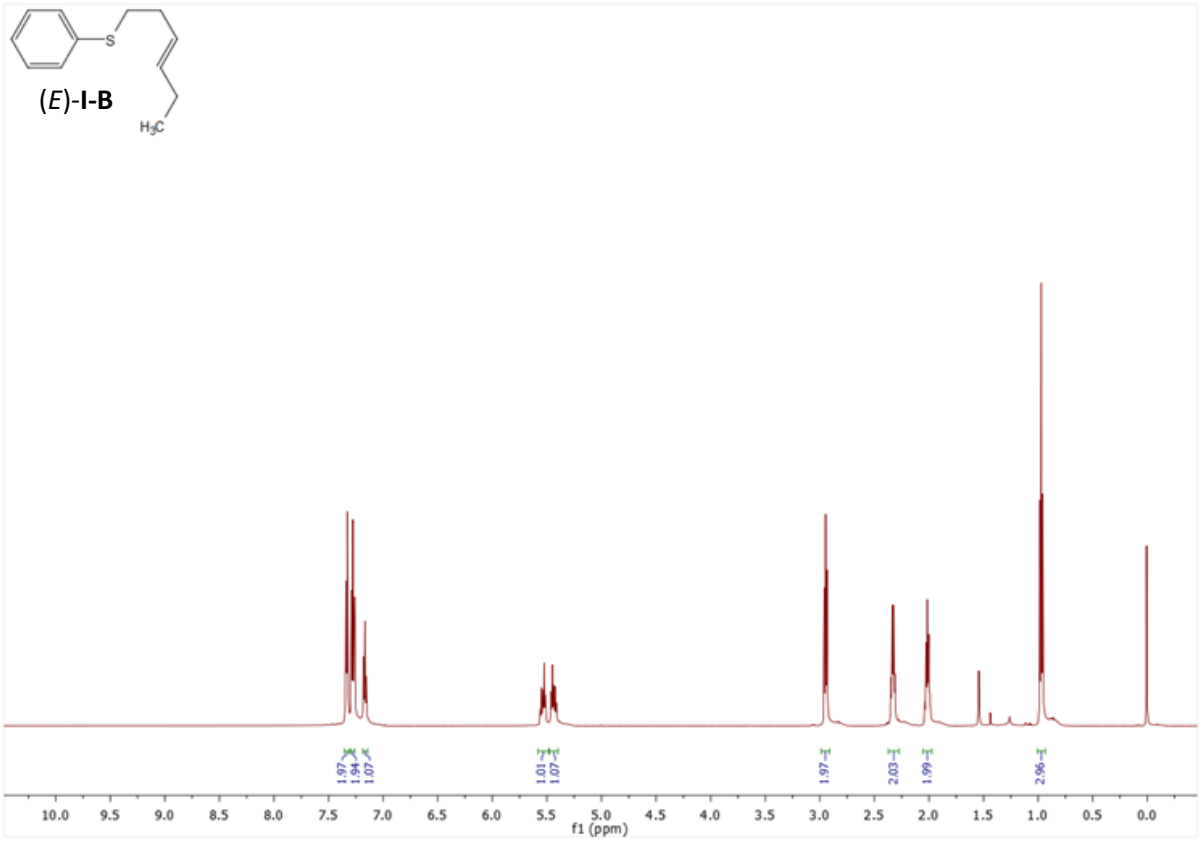
NMR SPECTRA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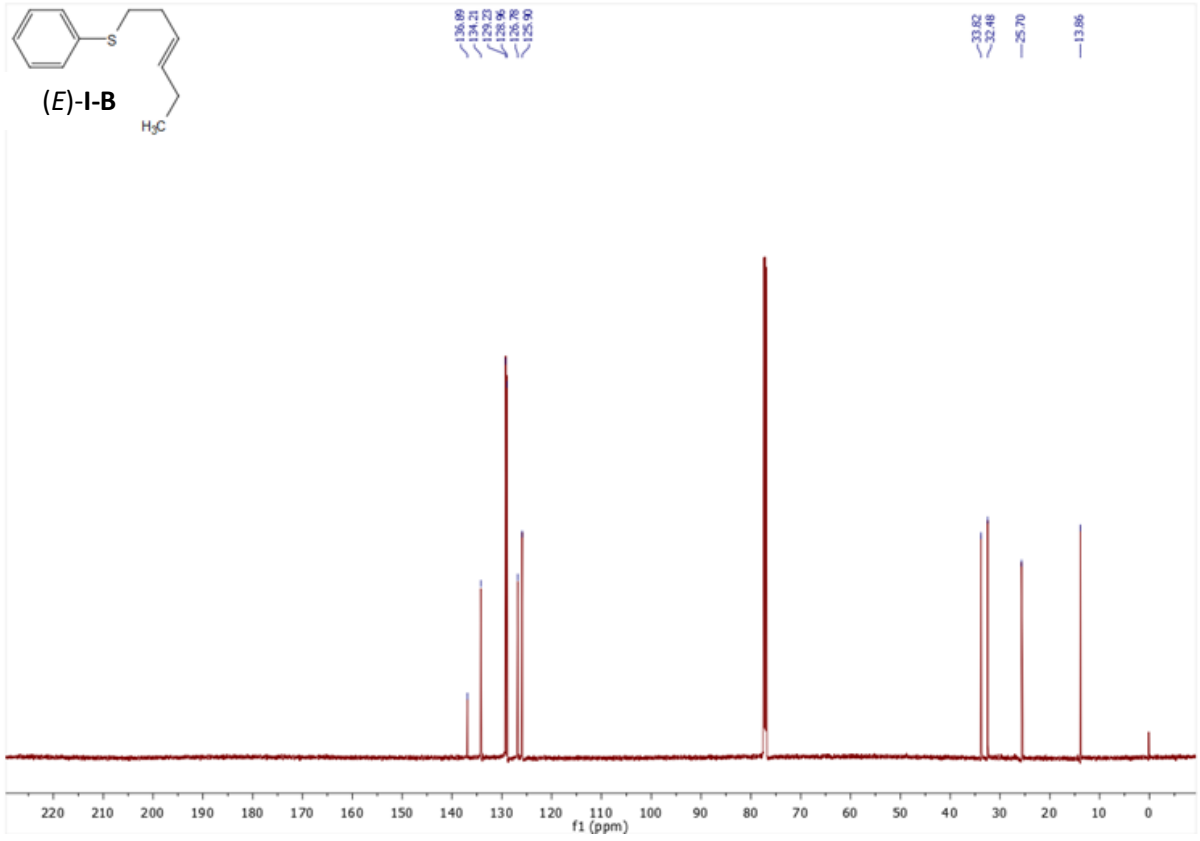
1.07
1.97
2.03
1.99
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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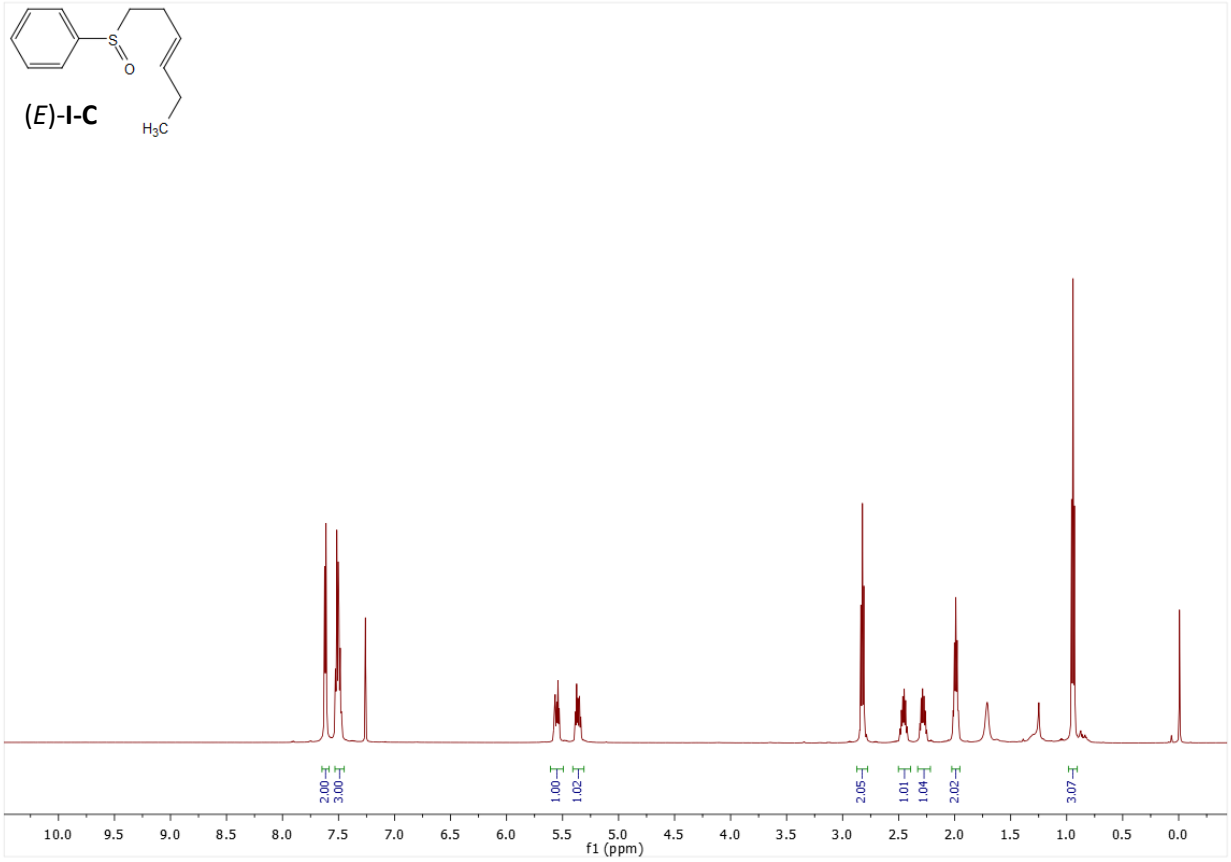
f1 (ppm)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O
H3C
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1.01
1.04
2.02
3.07
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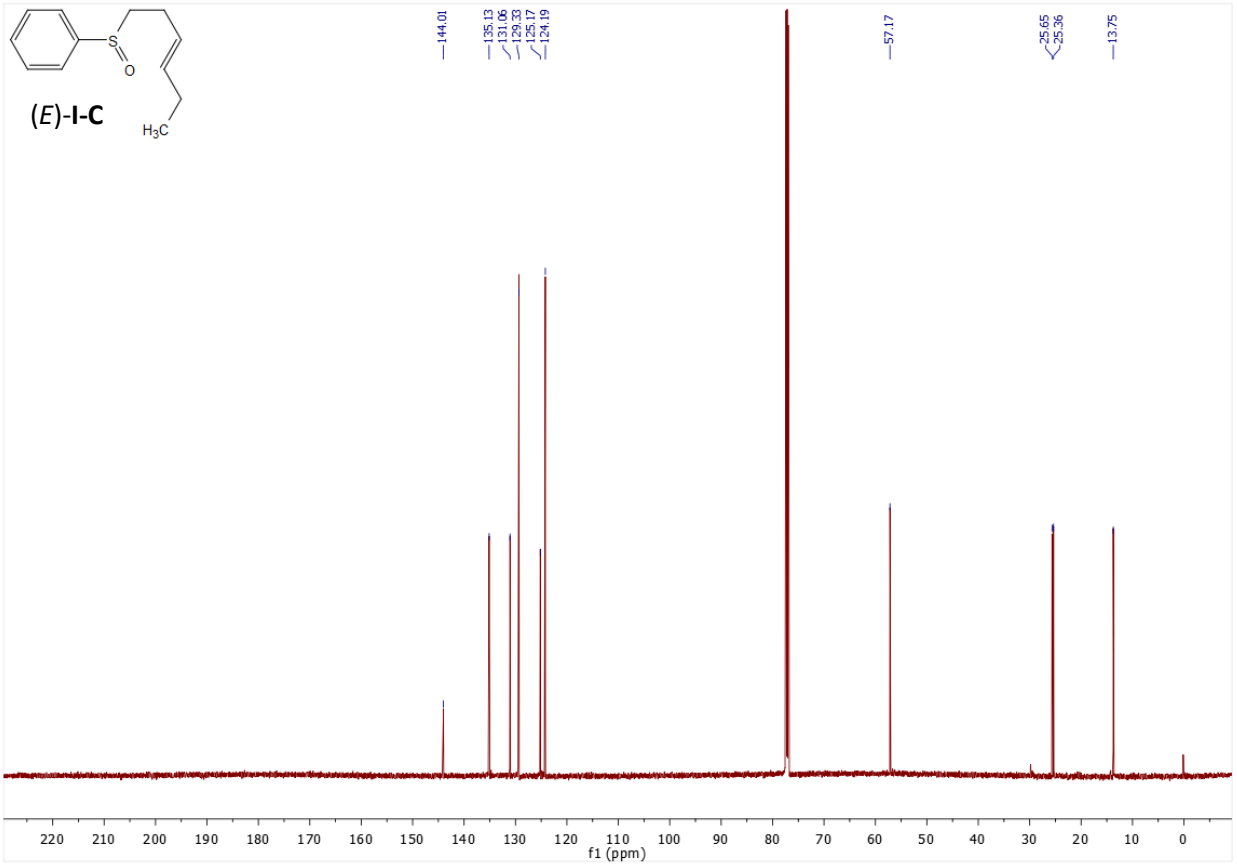
f1 (ppm)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O
H3C
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129.33
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25.36
13.75
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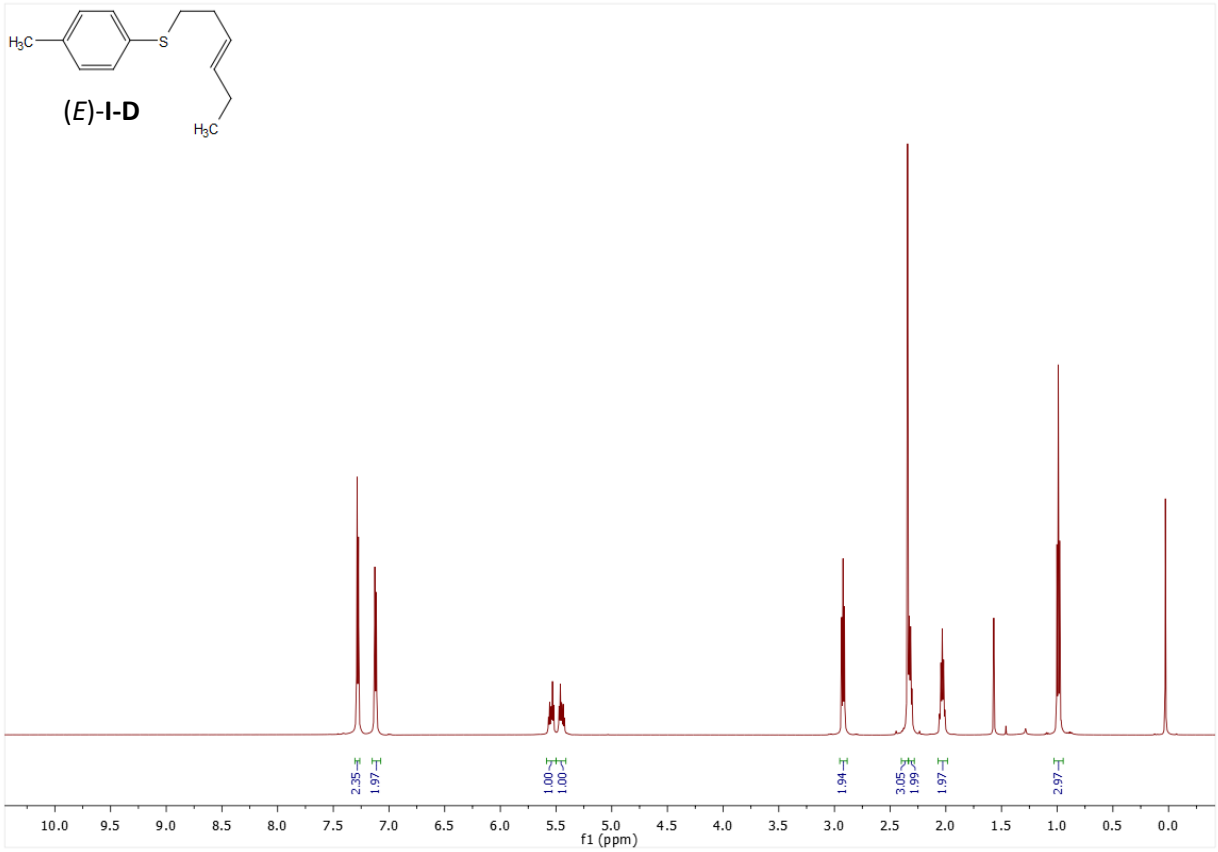
f1 (ppm)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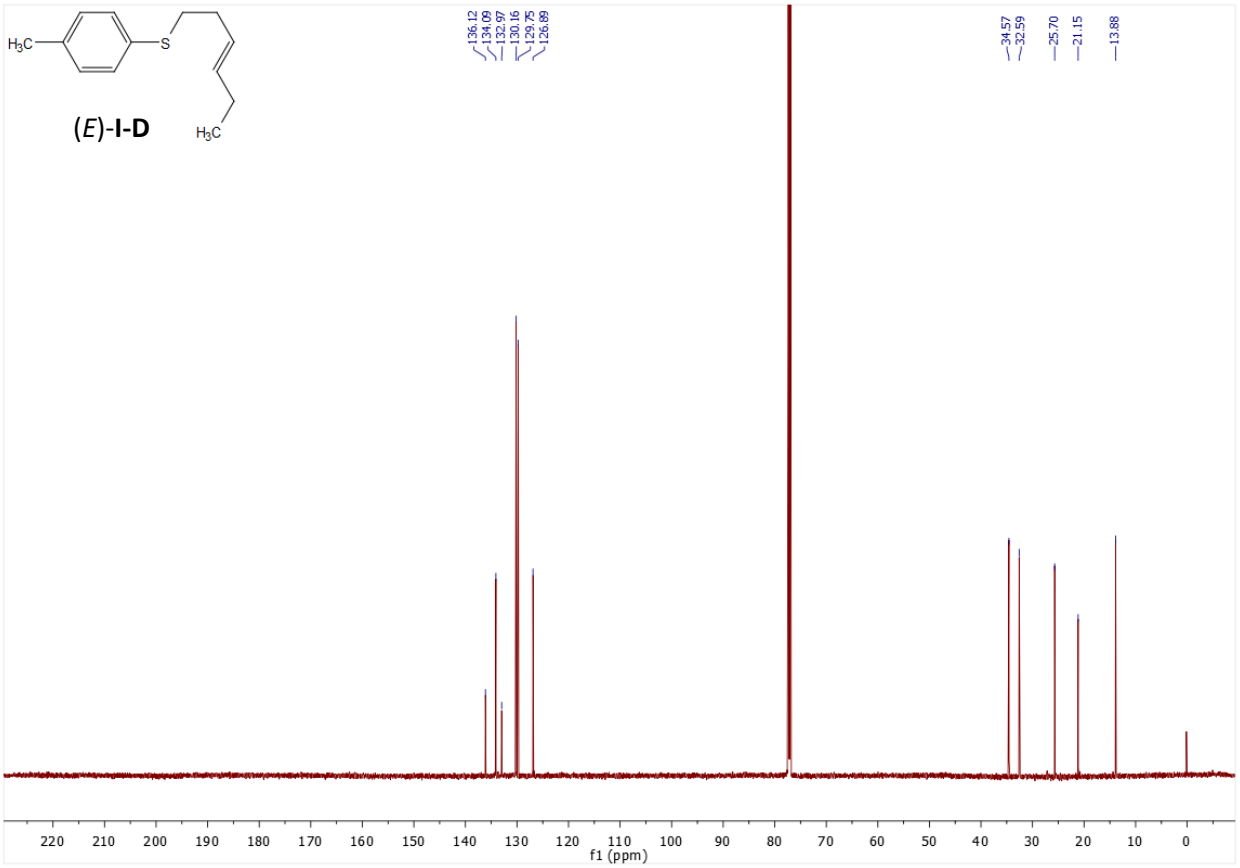
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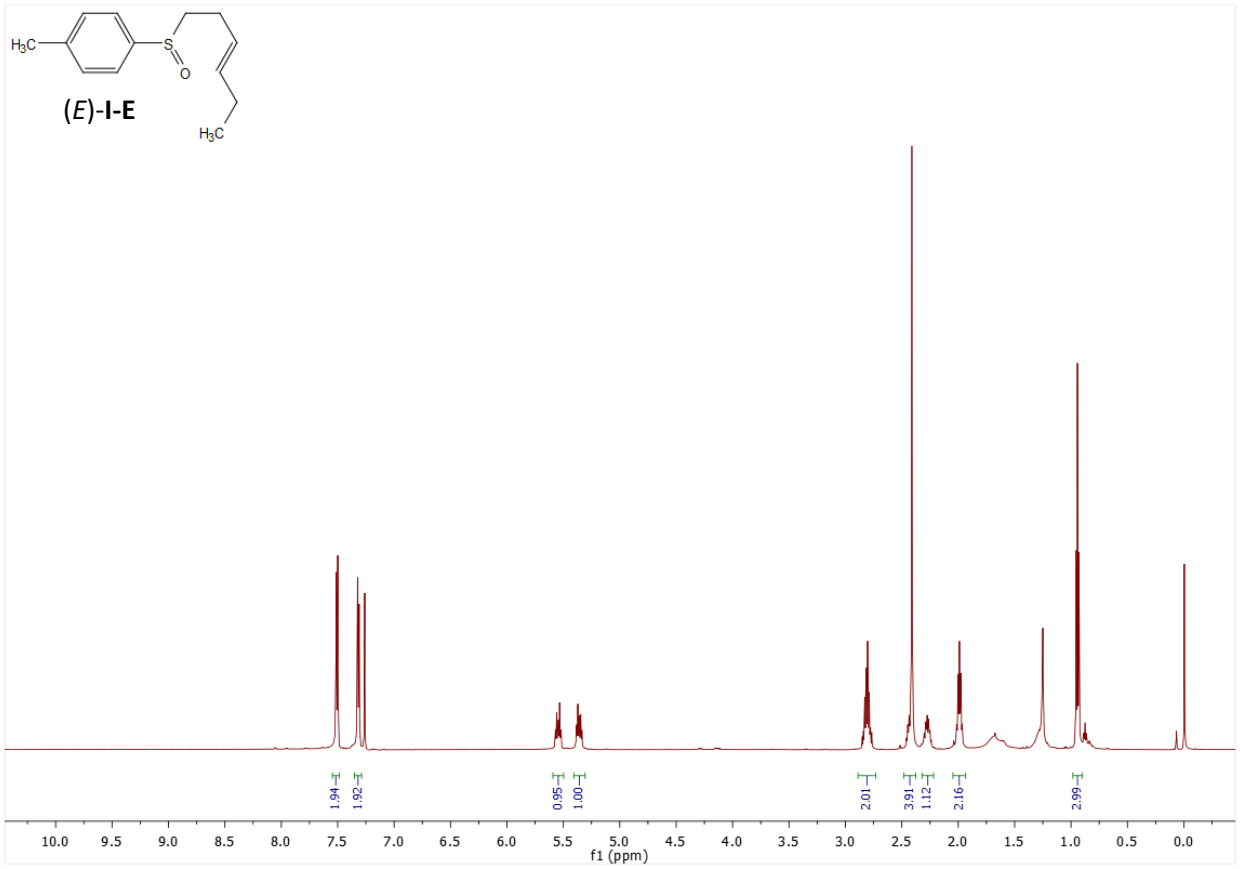
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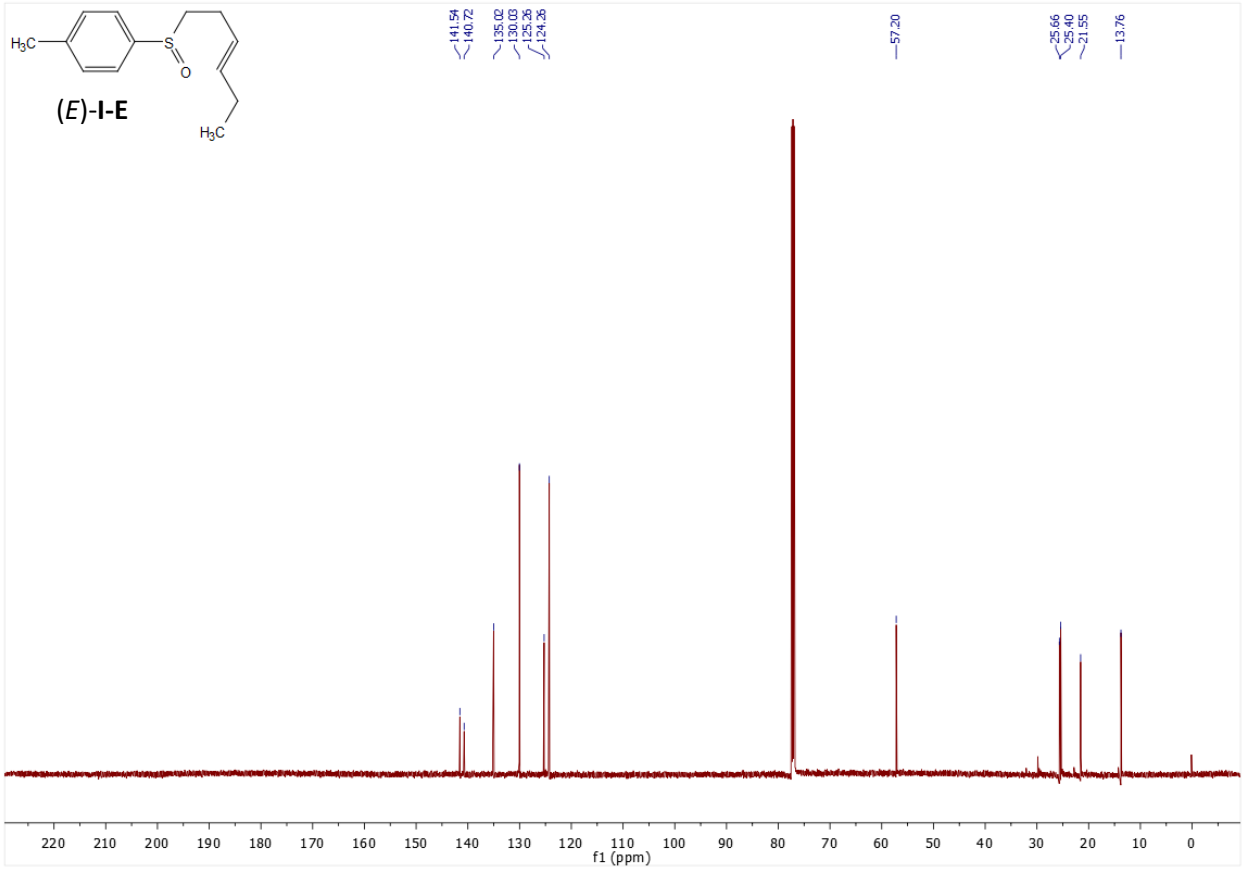
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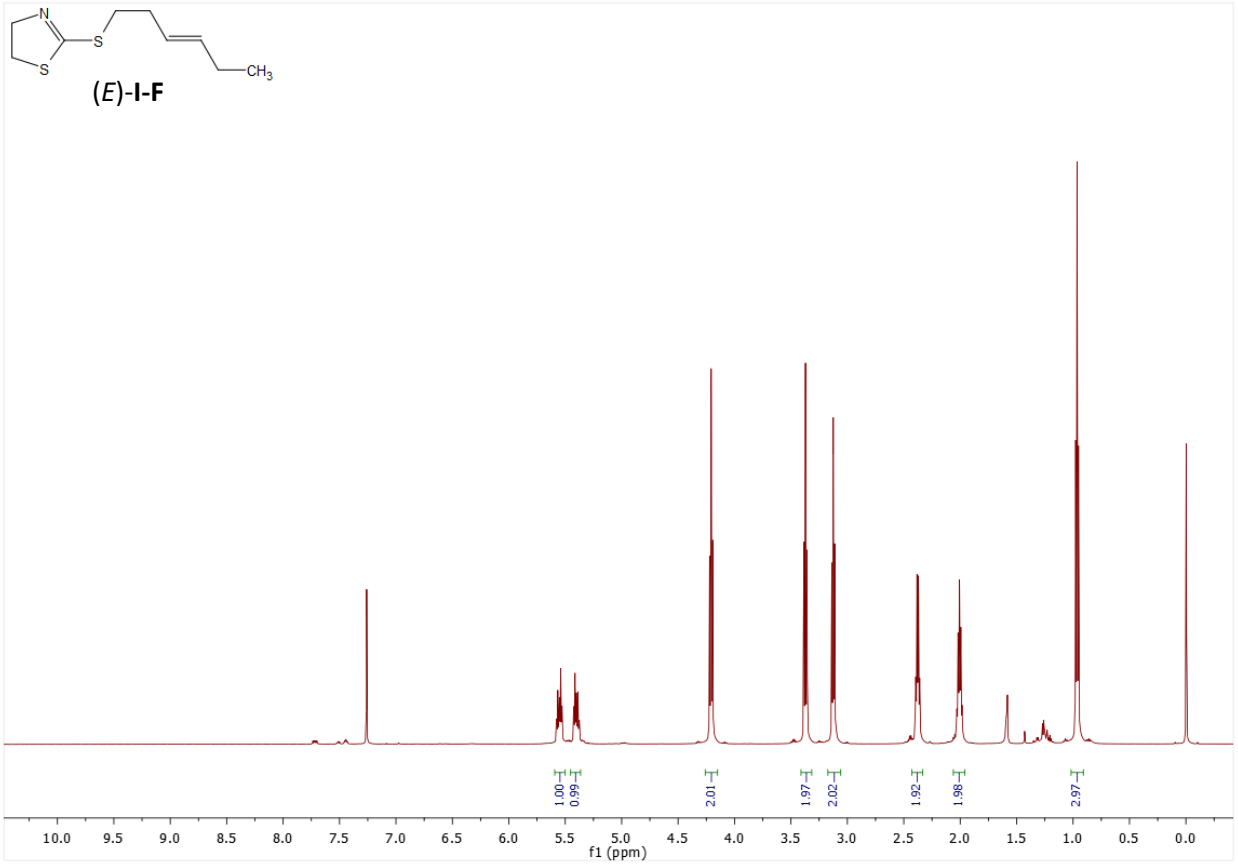
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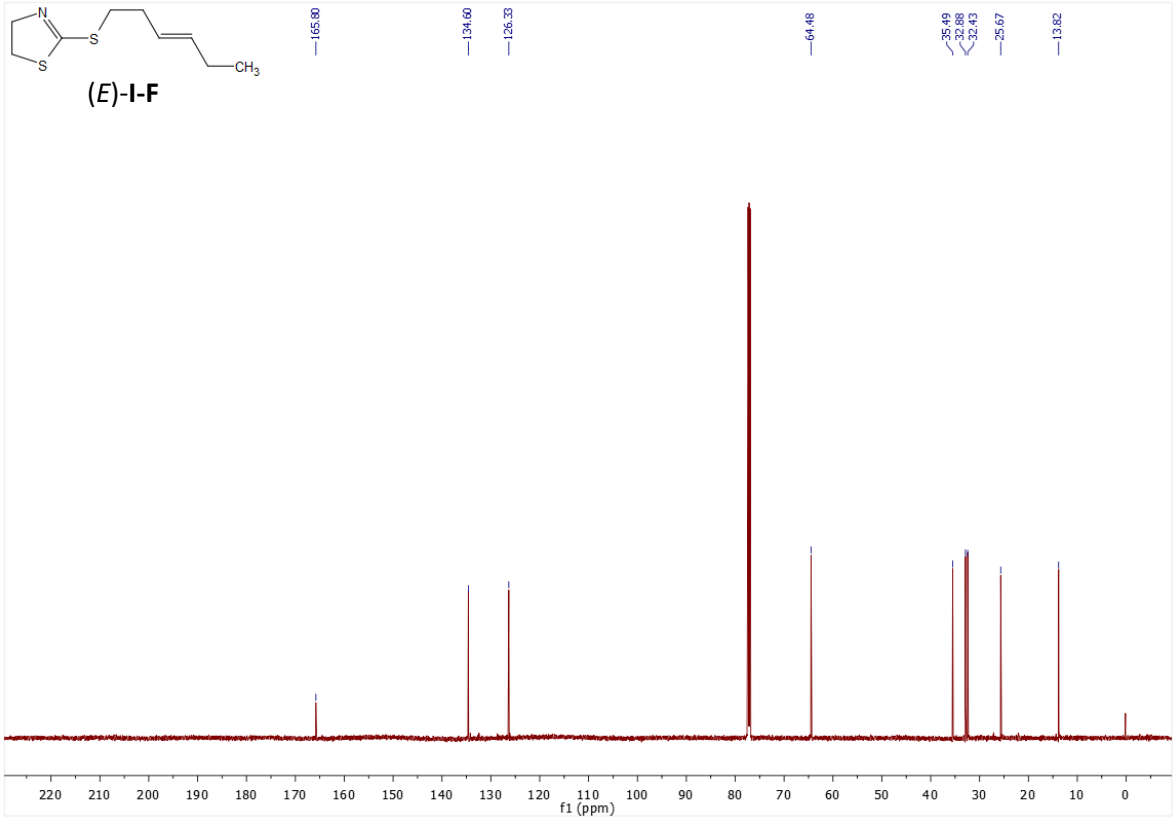
2.97
f1 (ppm)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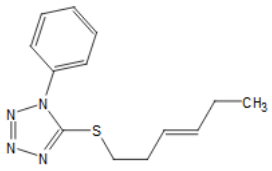
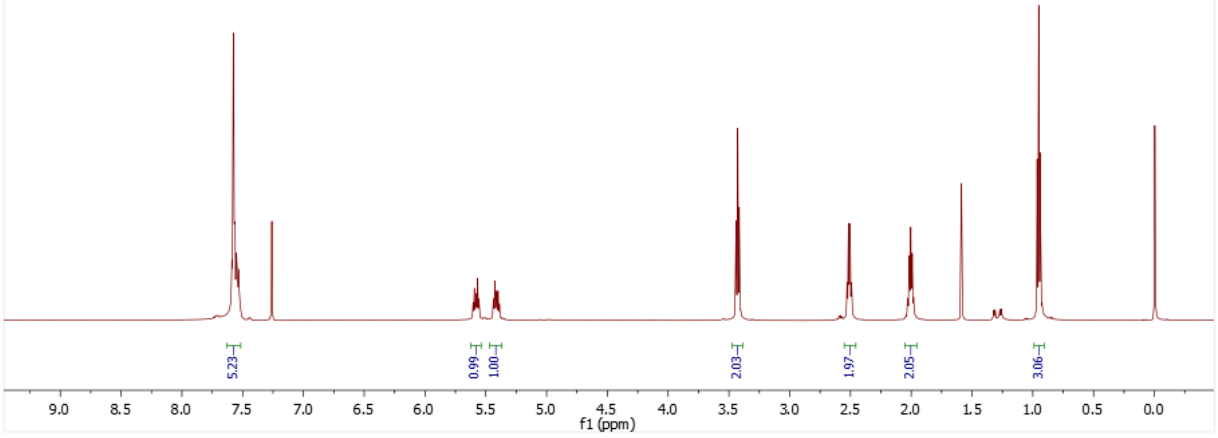
f1 (ppm)



(*E*)-**I-G**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2.05
3.06
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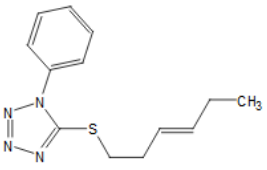

(*E*)-**I-G**

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125.56
124.00
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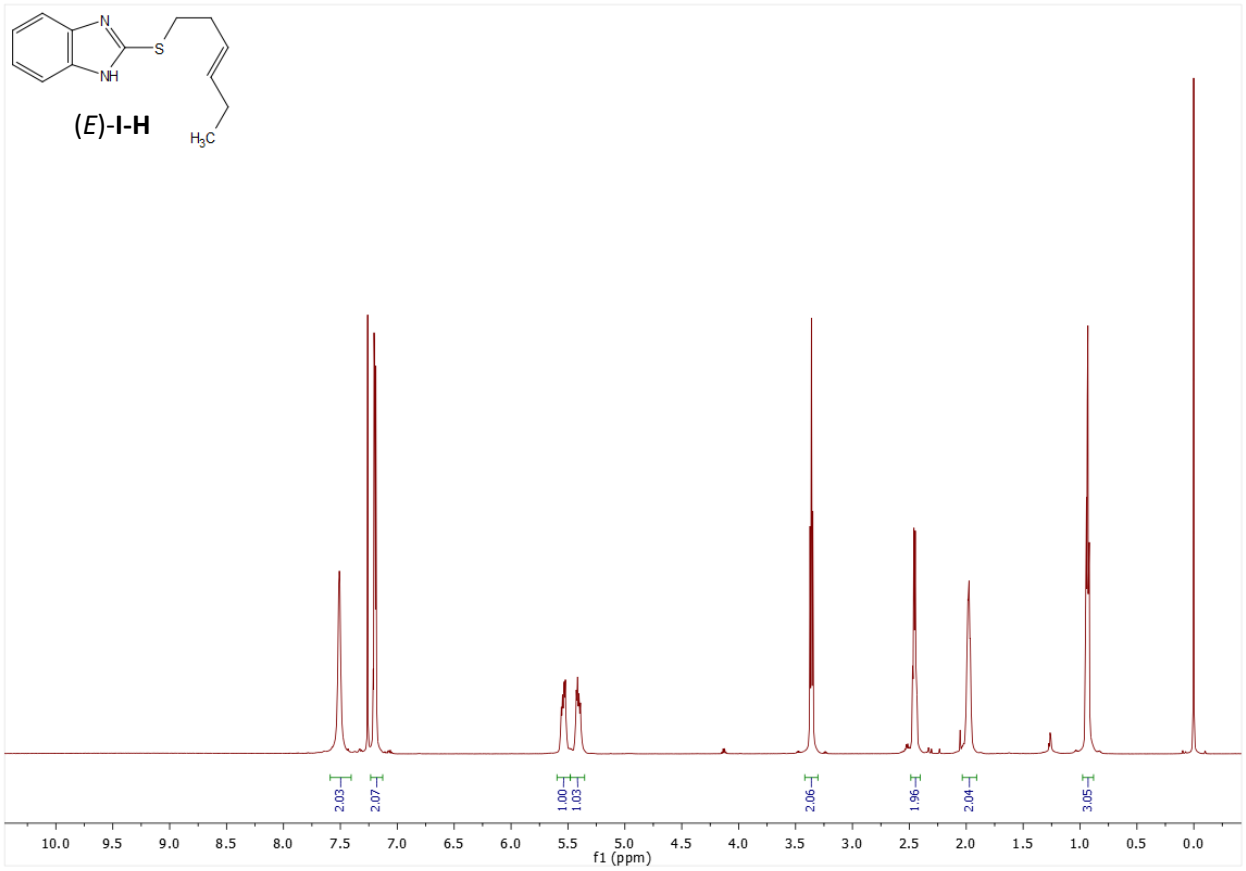
32.23
25.65
13.77
f1 (ppm)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1.03
2.06
1.96
2.04
3.05
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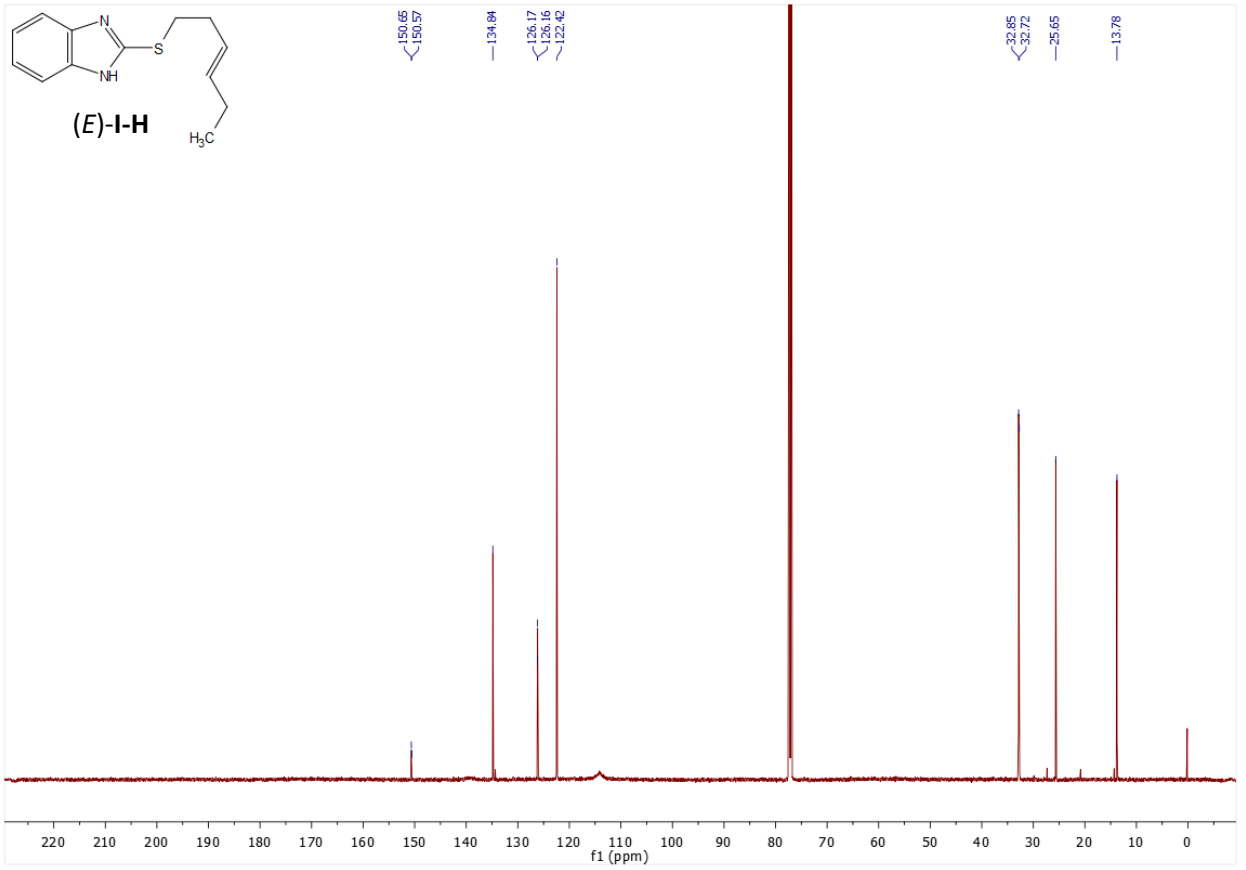
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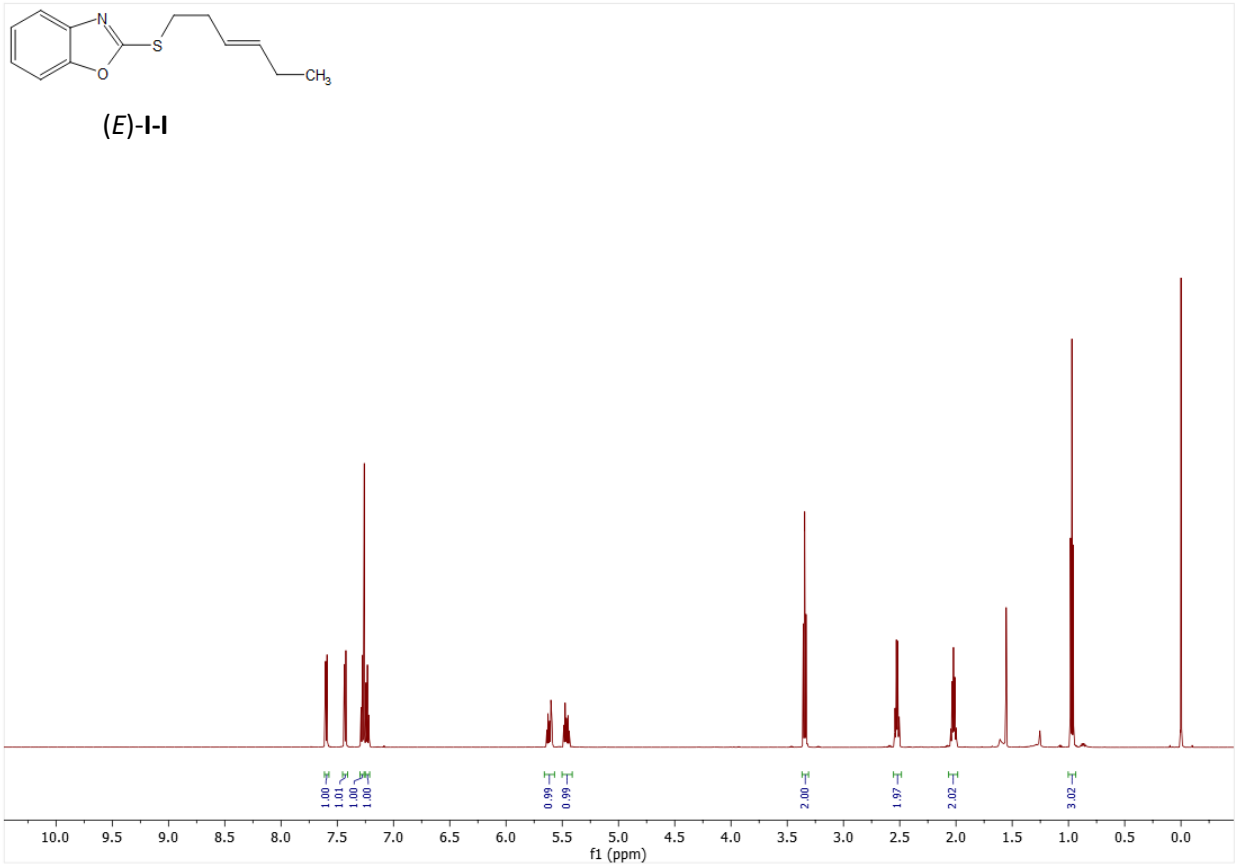
f1 (ppm)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O
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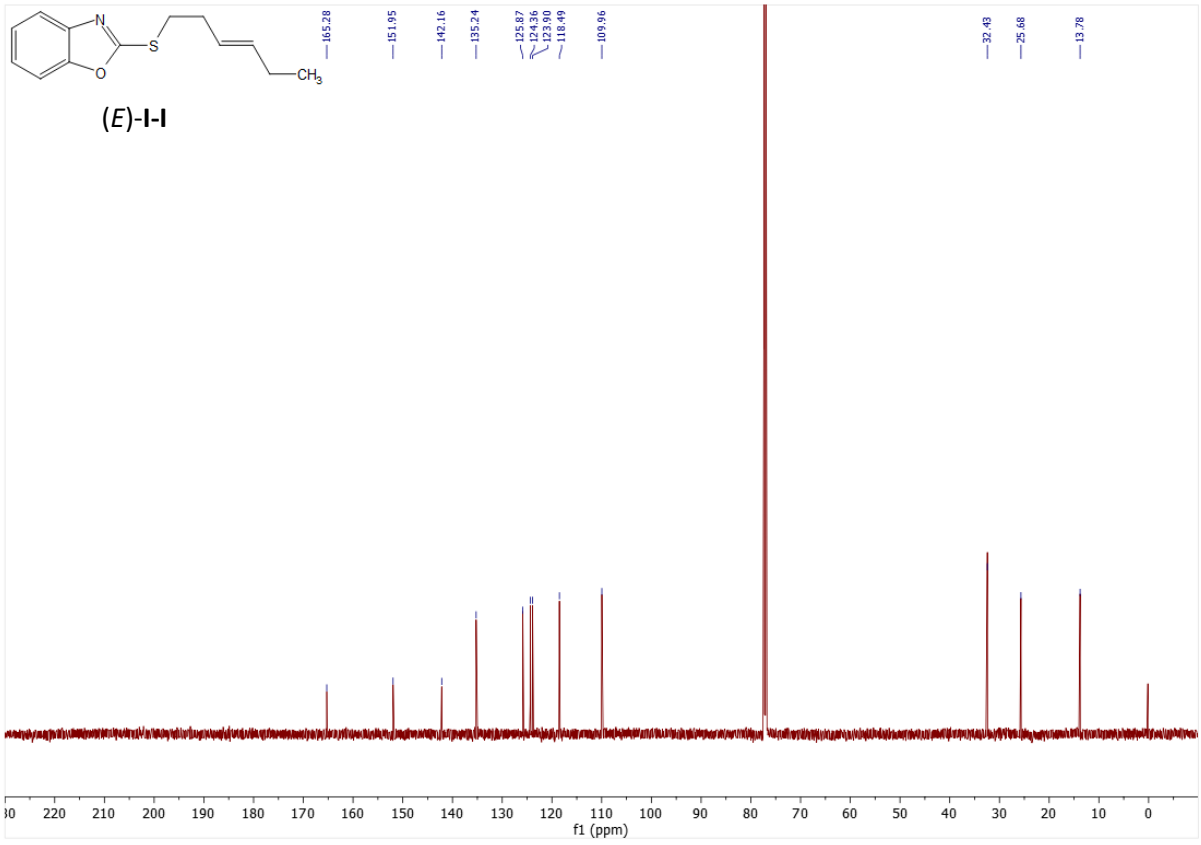
1.00
1.00
0.99
0.99
2.00
1.97
2.02
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

(*E*)-**I-l**


N
S
O
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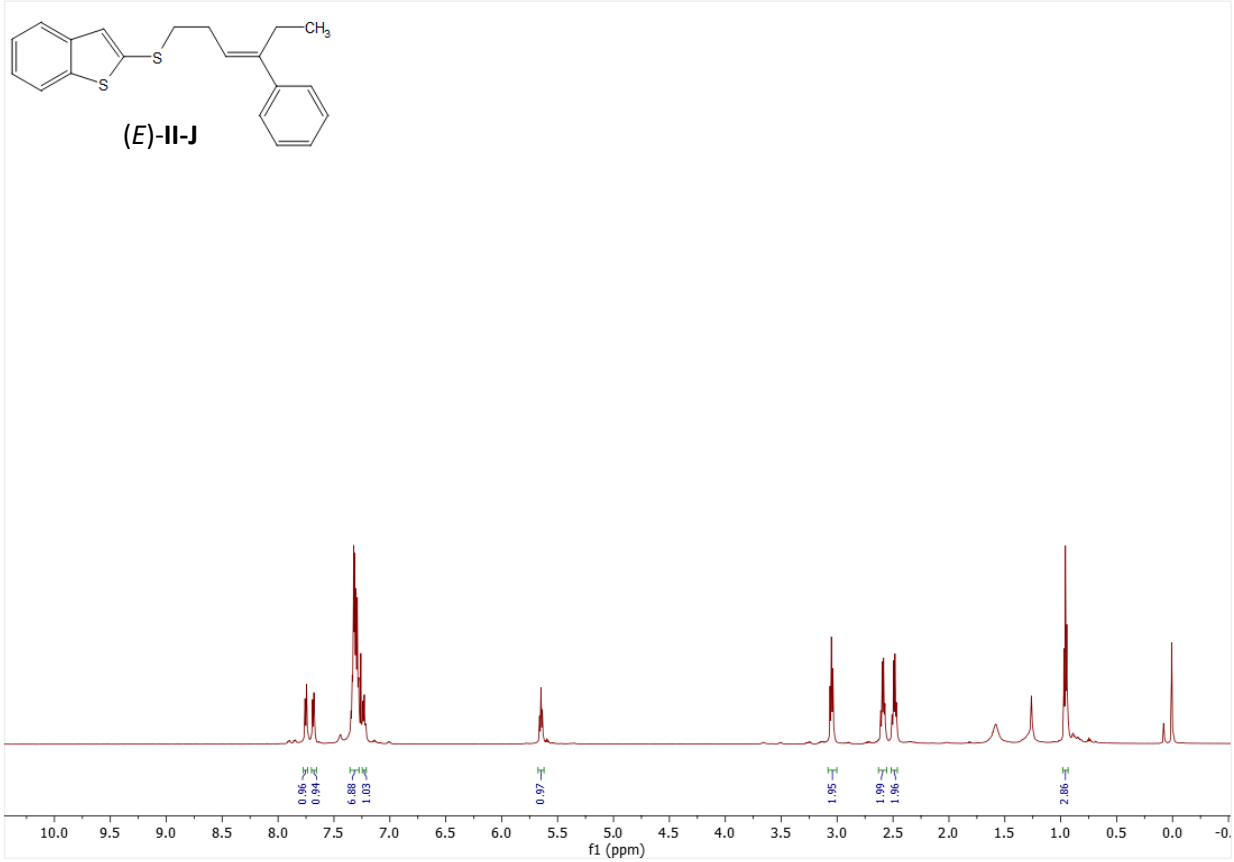
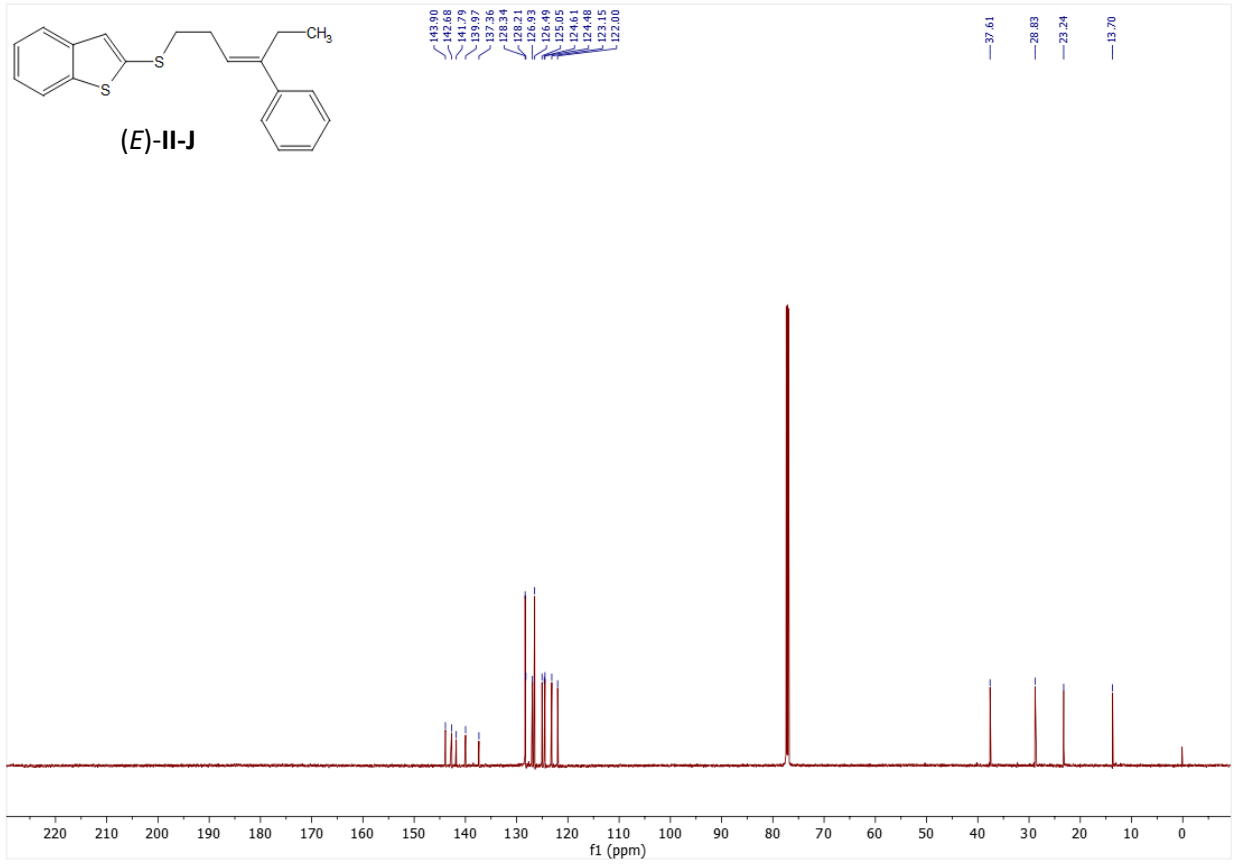
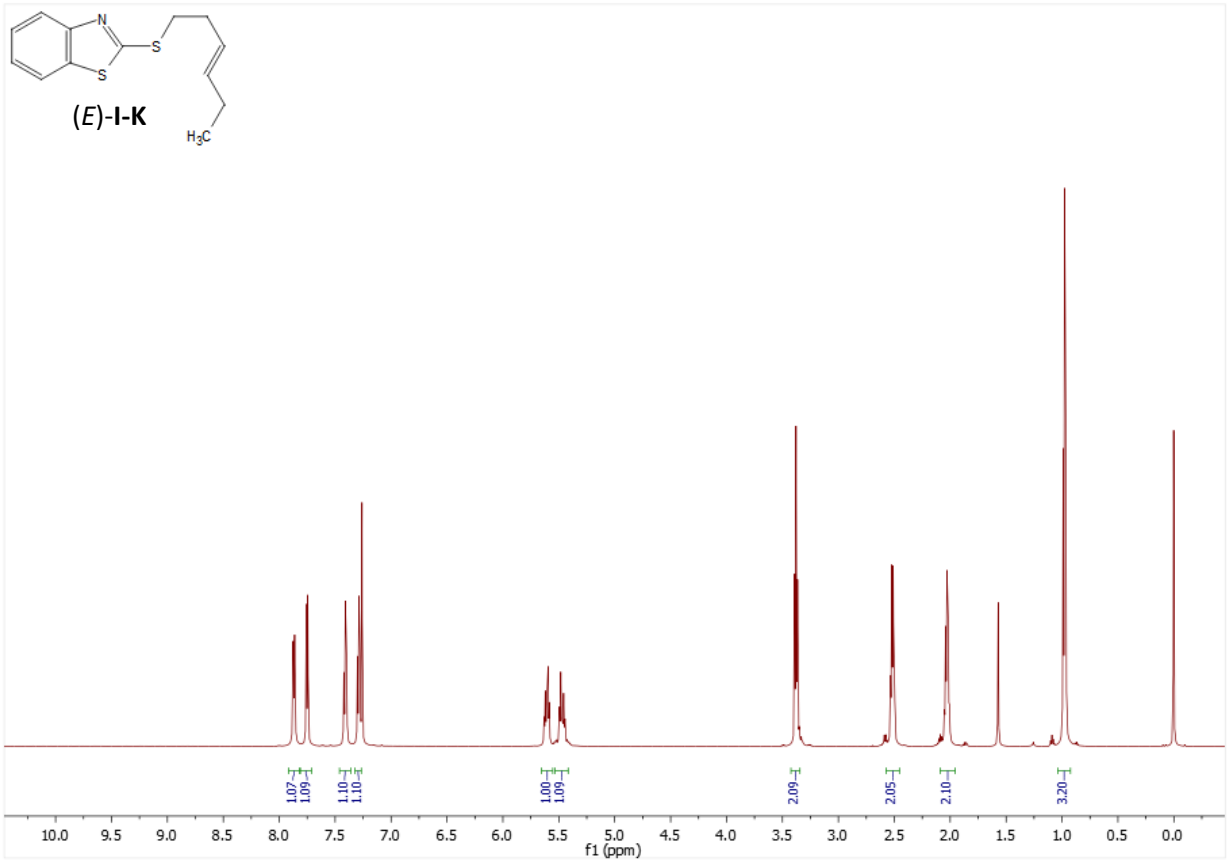
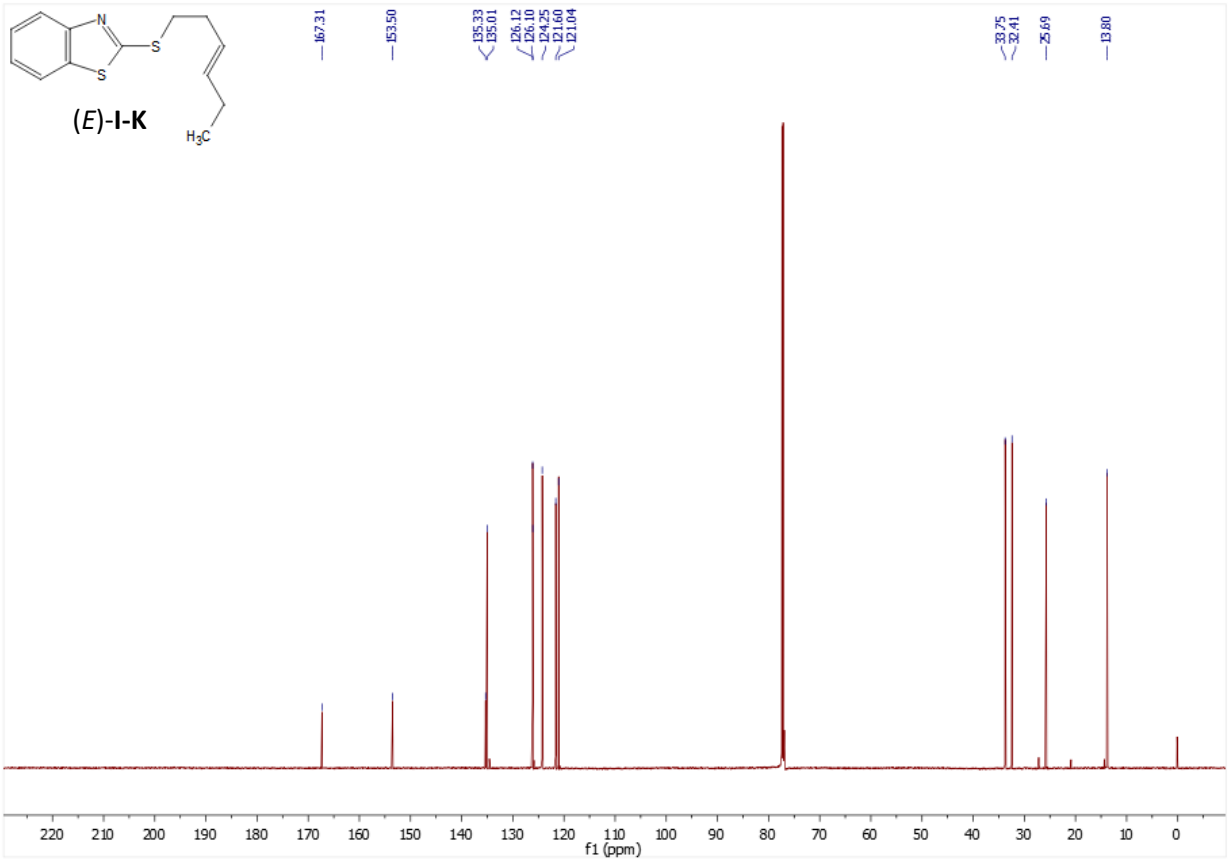
125.87
124.36
123.90
118.49
109.96
32.43
25.68
13.78
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

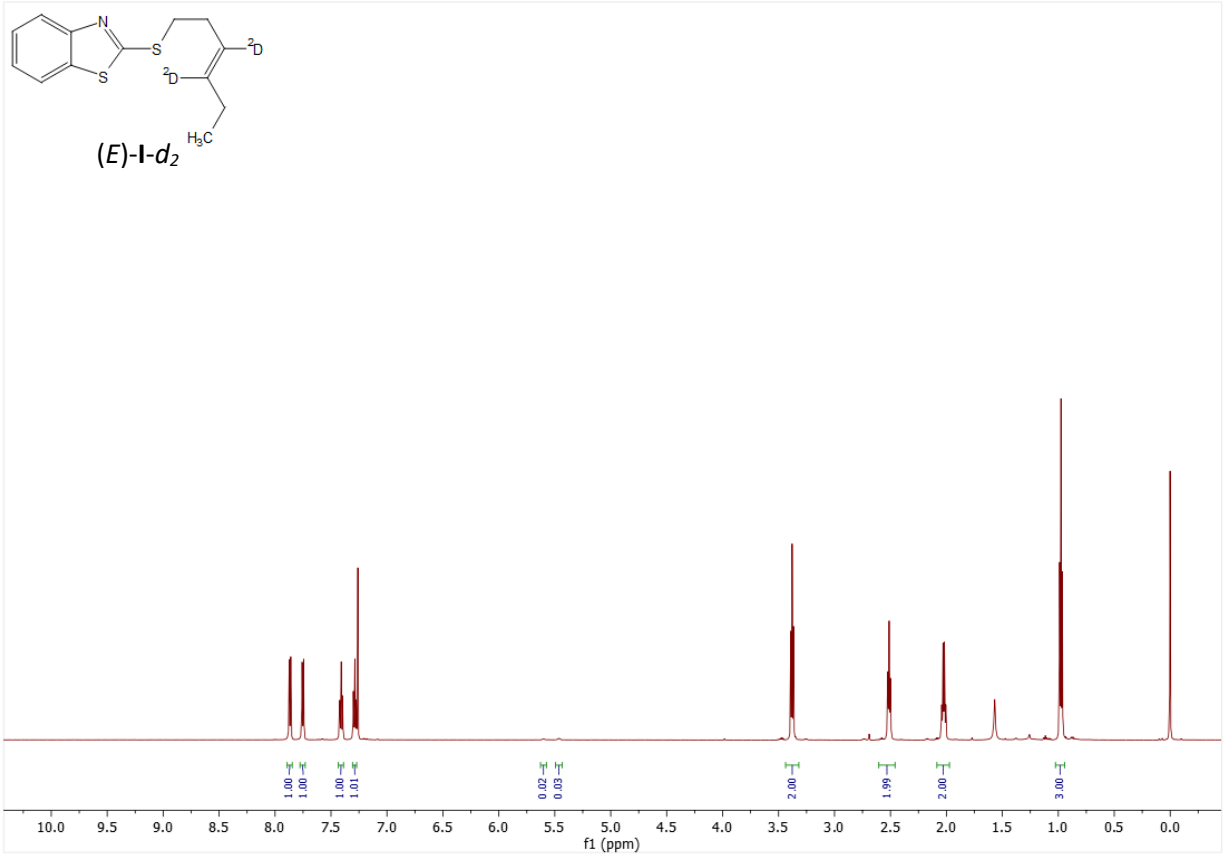
(*E*)-**I-l**

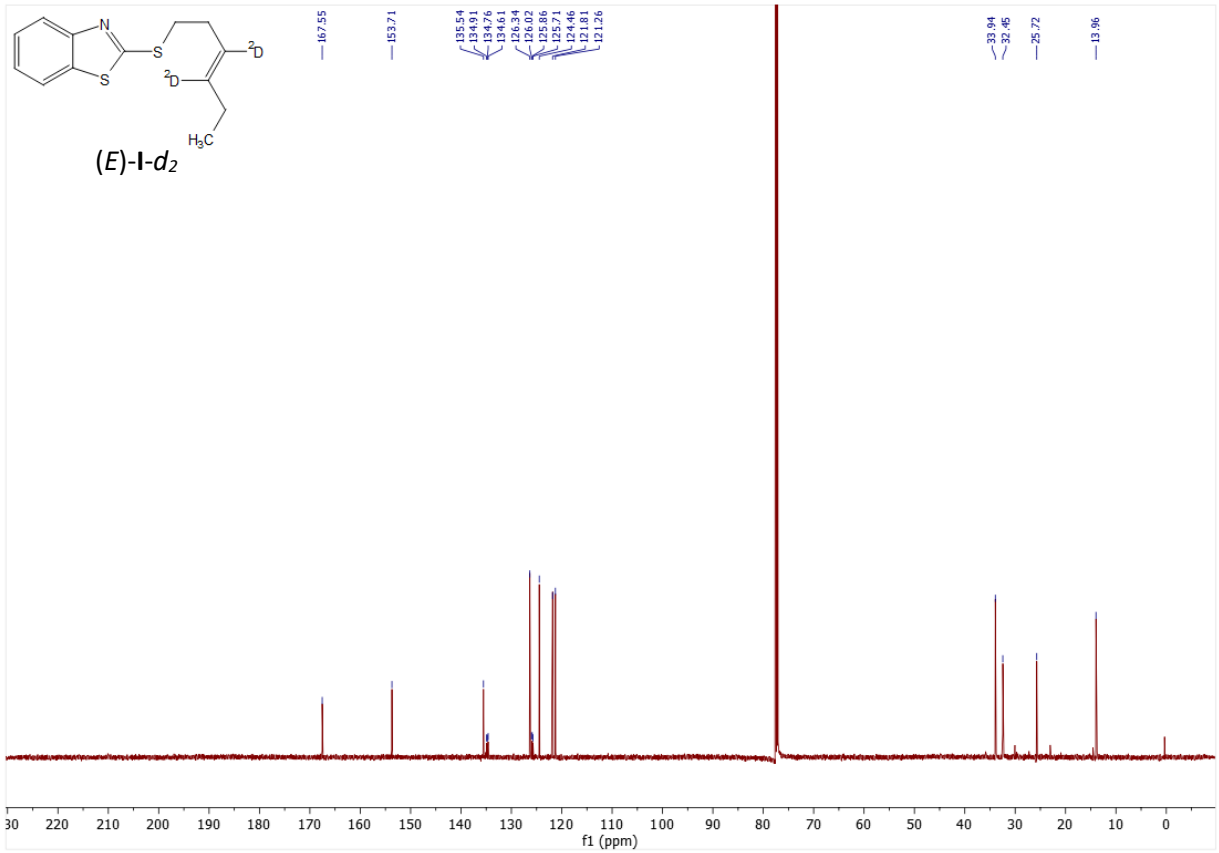

CH3
S
S
(E)-II-J
0.96
0.94
6.88
1.03
0.97
1.95
1.99
1.96
2.86
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

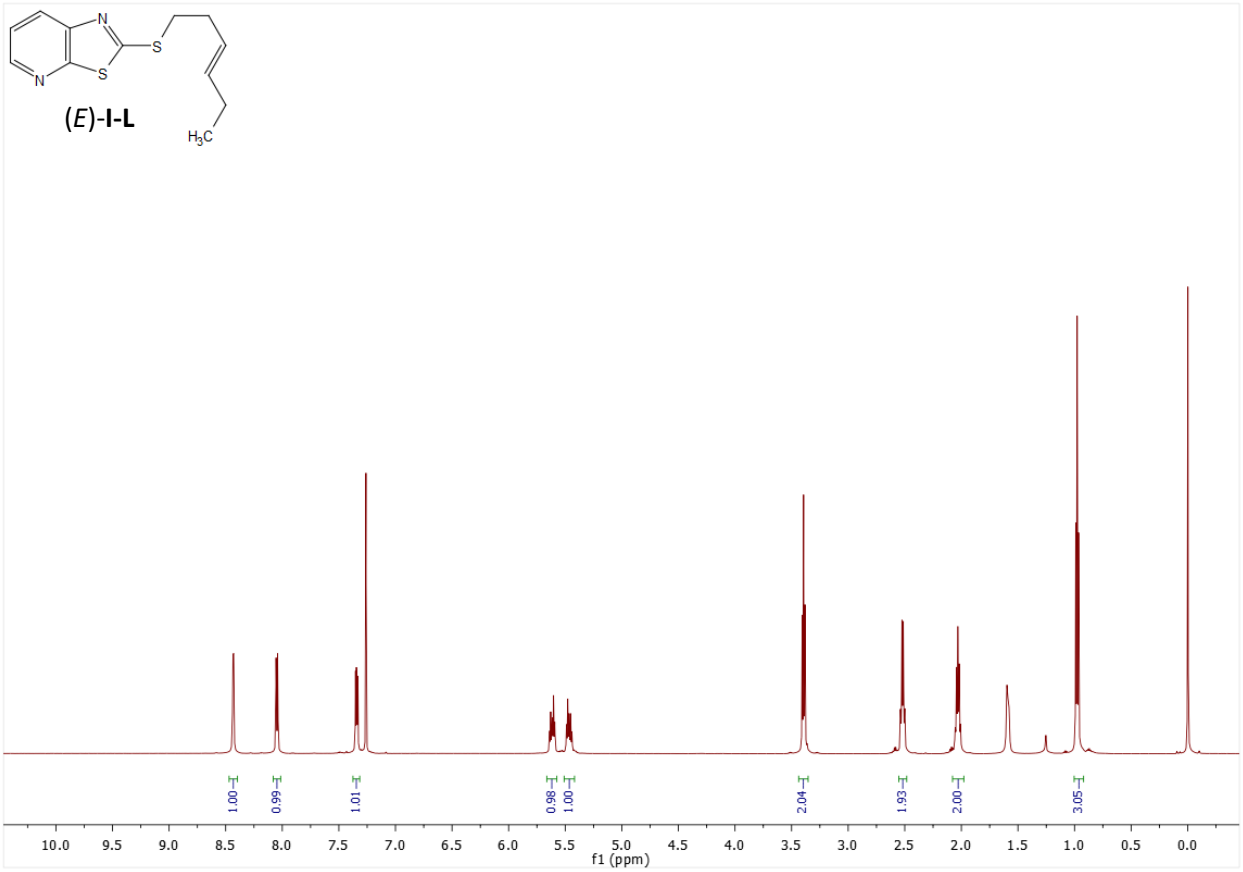

CH3
S
S
(E)-II-J
143.90
142.68
141.79
139.97
137.36
128.34
128.21
126.93
126.49
125.05
124.61
124.48
123.15
122.00
37.61
28.83
23.24
13.70
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

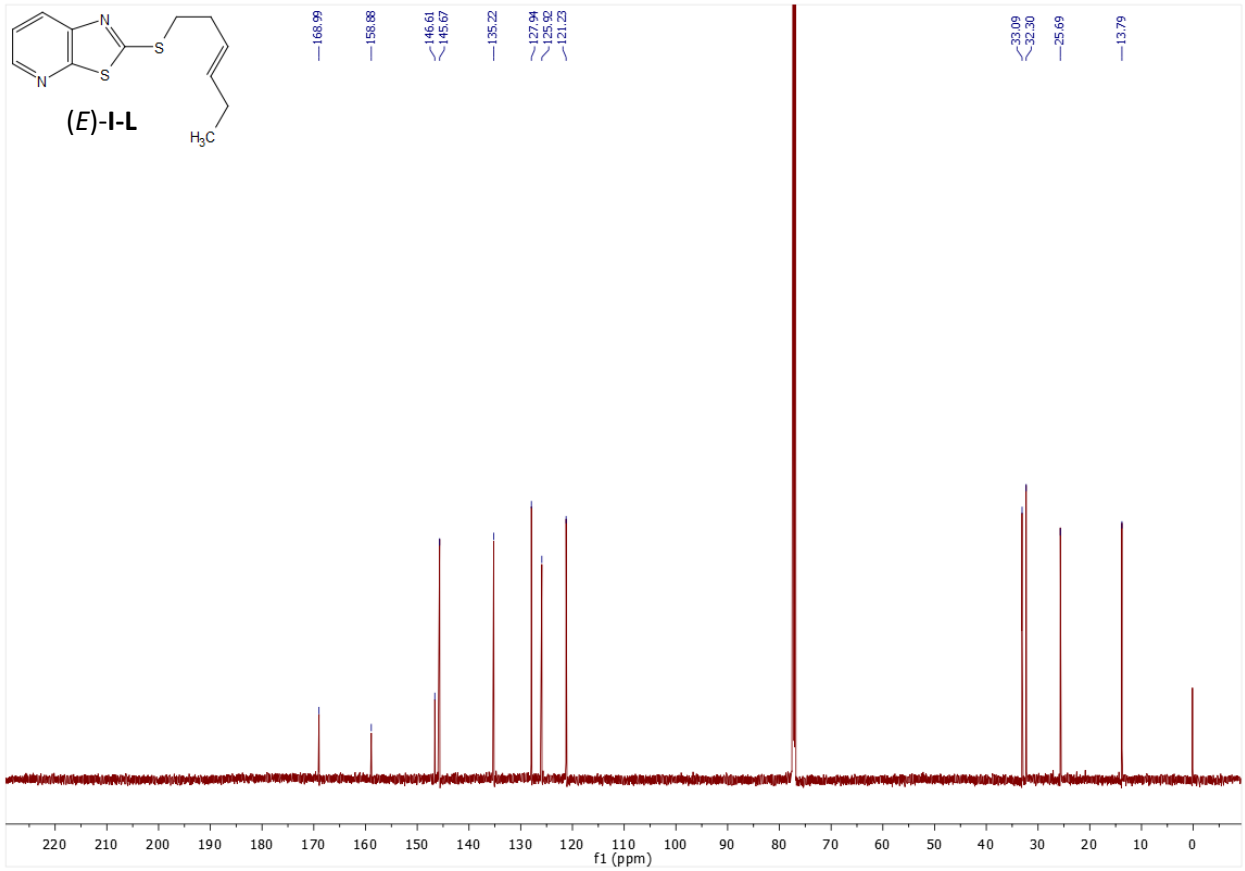

(E)-I-K
1.07
1.09
1.10
1.10
1.00
1.09
2.09
2.05
2.10
3.20
f1 (ppm)

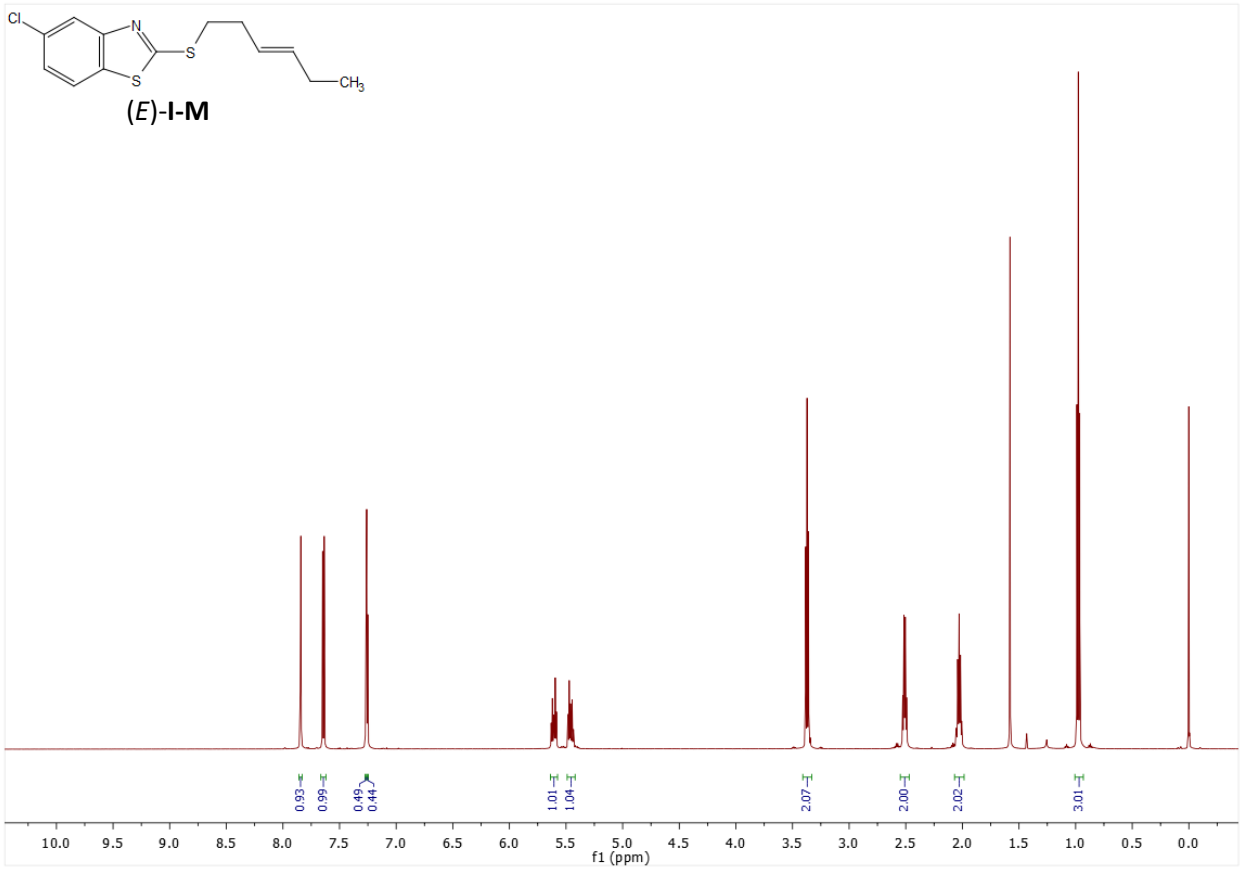

(E)-I-K
167.31
153.50
135.33
135.01
126.12
126.10
124.25
121.60
121.04
33.75
32.41
25.69
13.80
f1 (ppm)

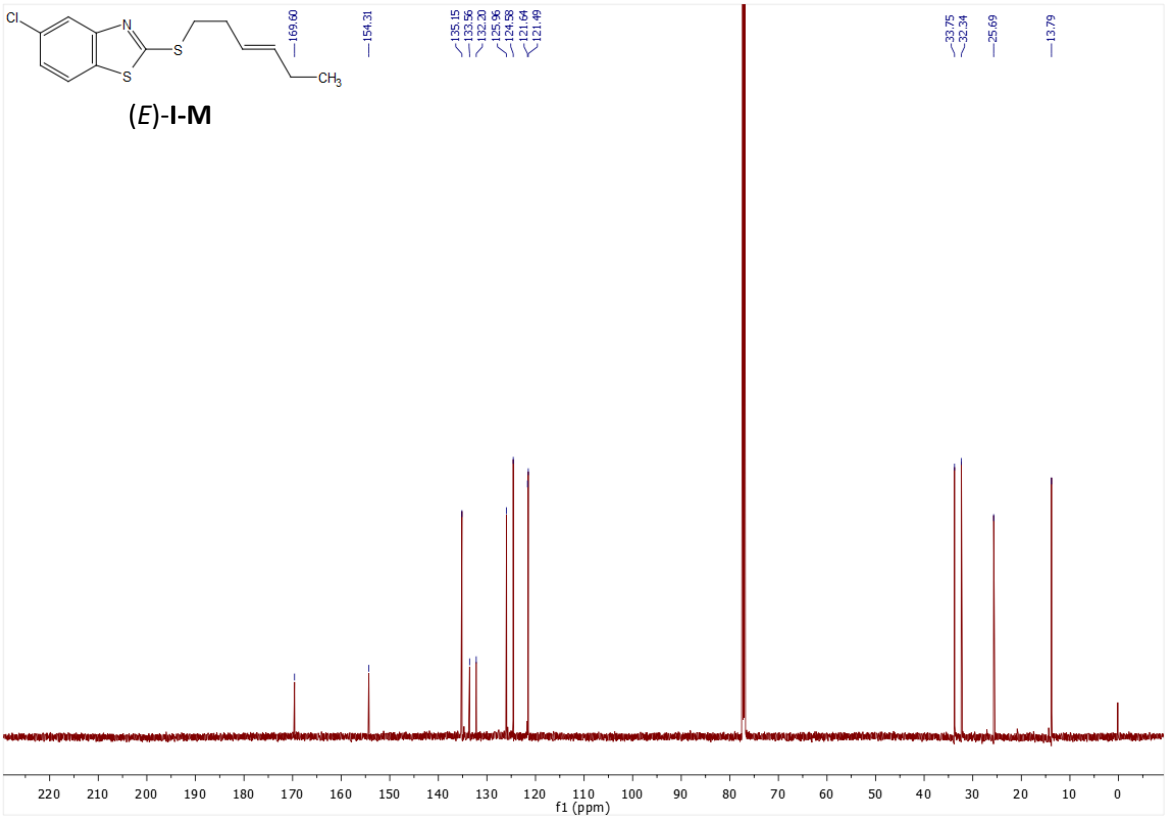

N
S
S
^{2}D
^{2}D
H$_3$C
(*E*)-**I**-*d*$_2$
1.00
1.00
1.00
1.01
0.02
0.03
2.00
1.99
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

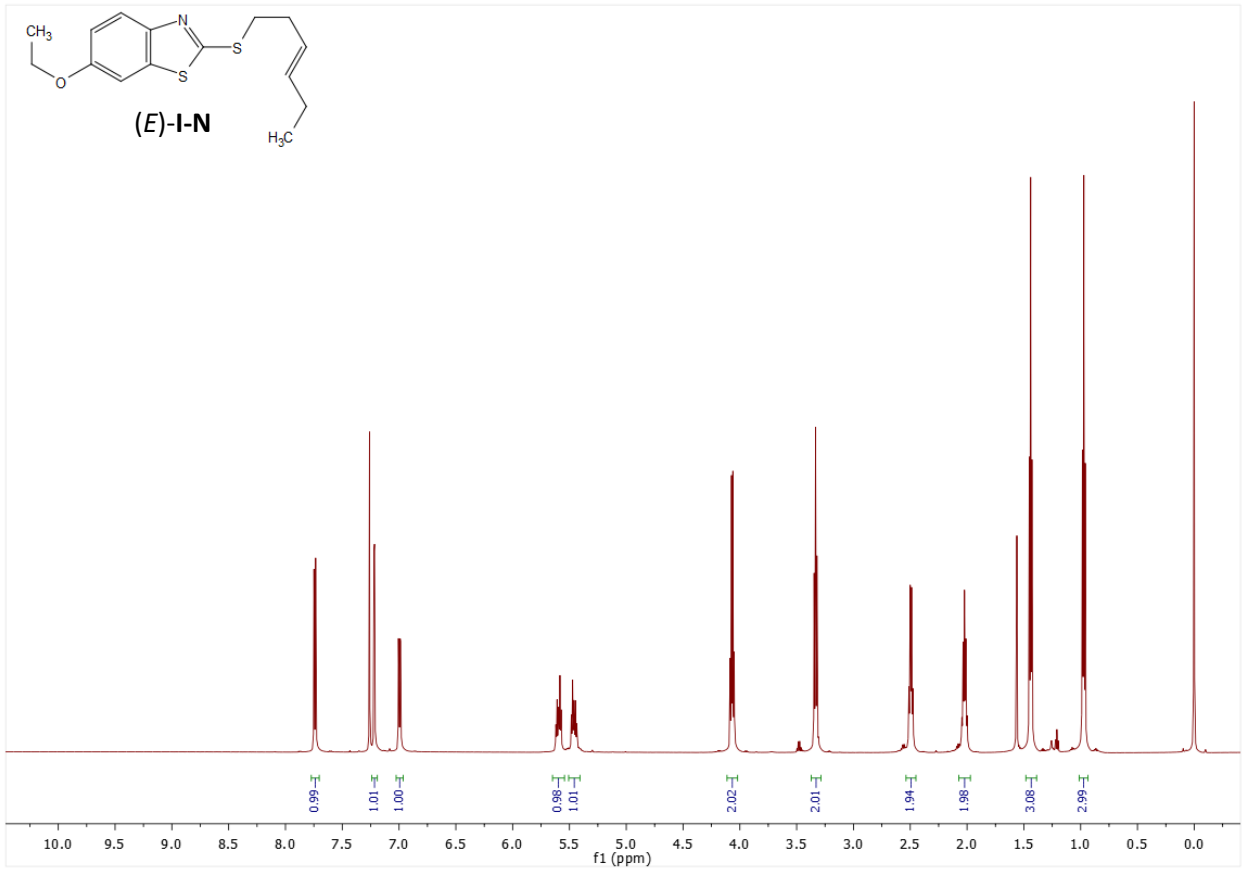

N
S
S
^{2}D
^{2}D
H$_3$C
(*E*)-**I**-*d*$_2$
167.55
153.71
135.54
134.91
134.76
134.61
126.34
126.02
125.86
125.71
124.46
121.81
121.26
33.94
32.45
25.72
13.96
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

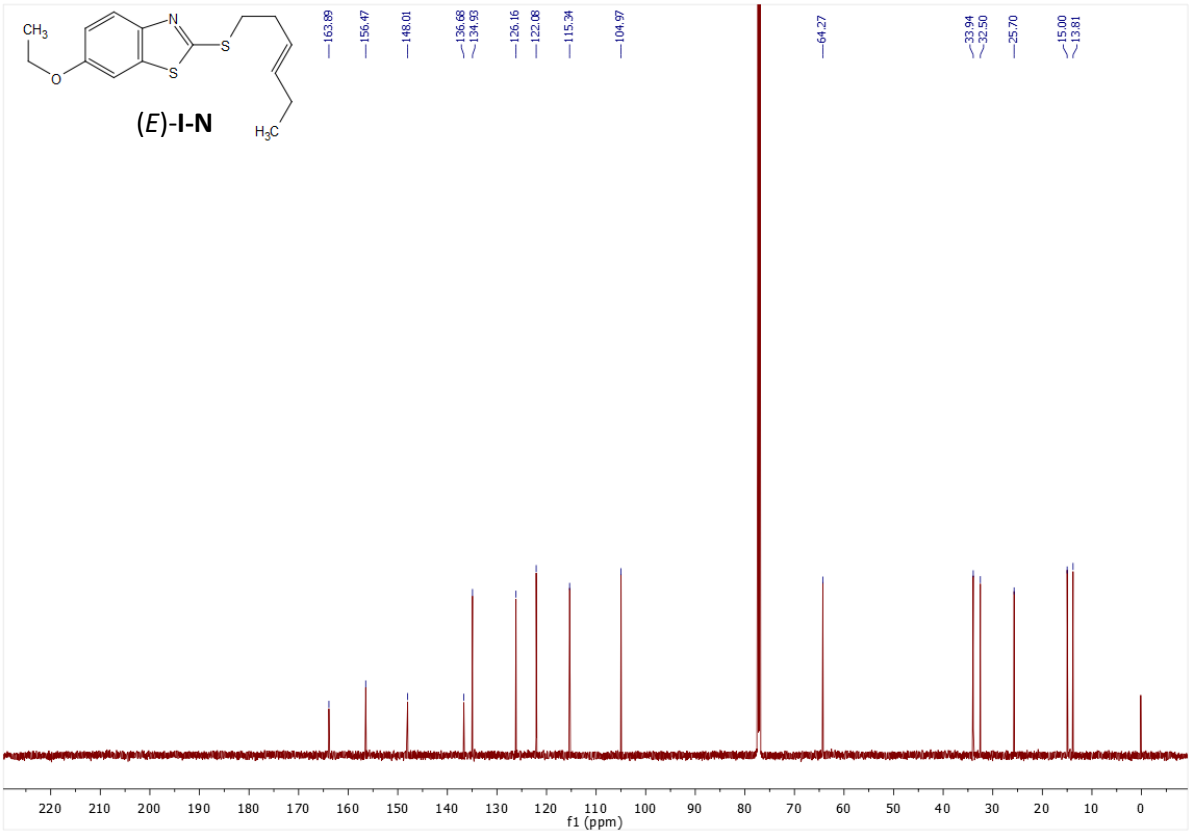

(E)-I-L
1.00
0.99
1.01
0.98
1.00
2.04
1.93
2.00
3.05
f1 (ppm)

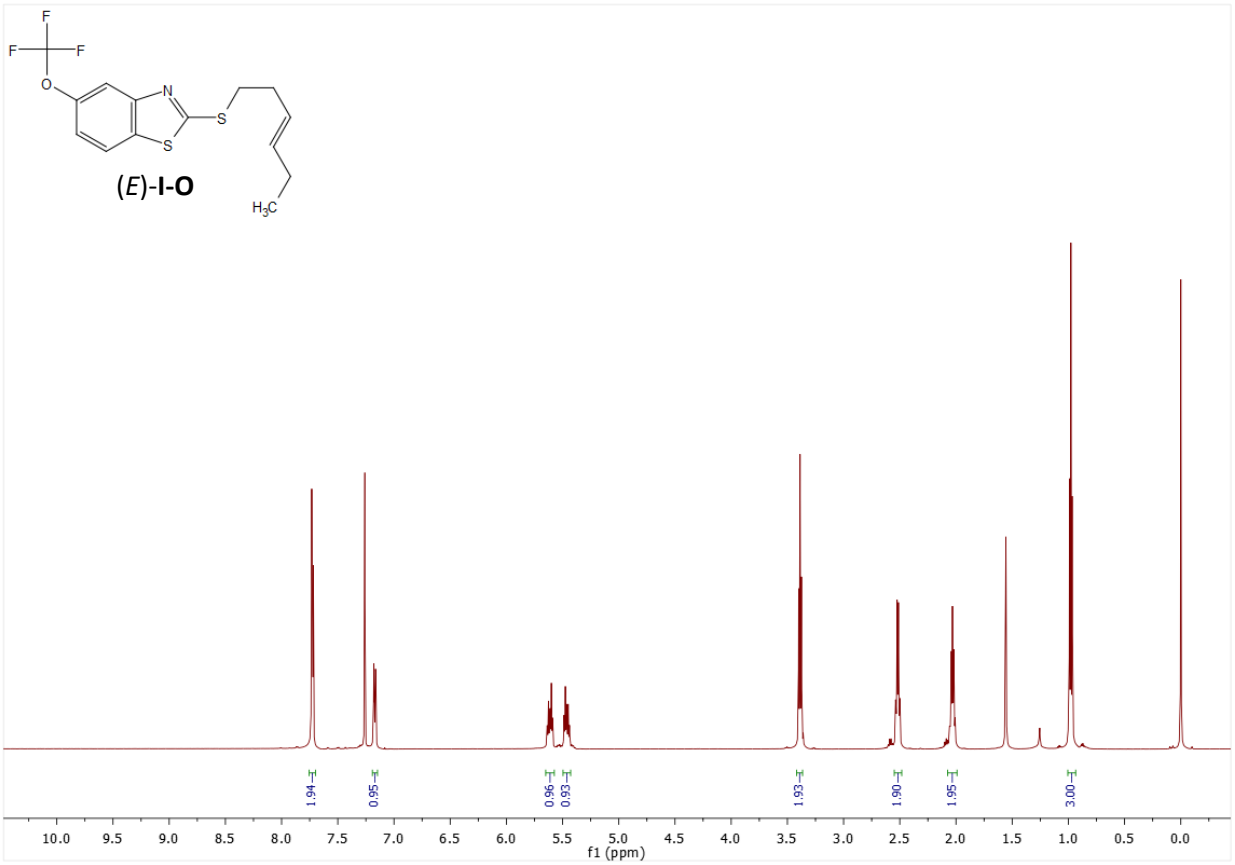

(E)-I-L
168.99
158.88
146.61
145.67
135.22
127.94
125.92
121.23
33.09
32.30
25.69
13.79
f1 (ppm)

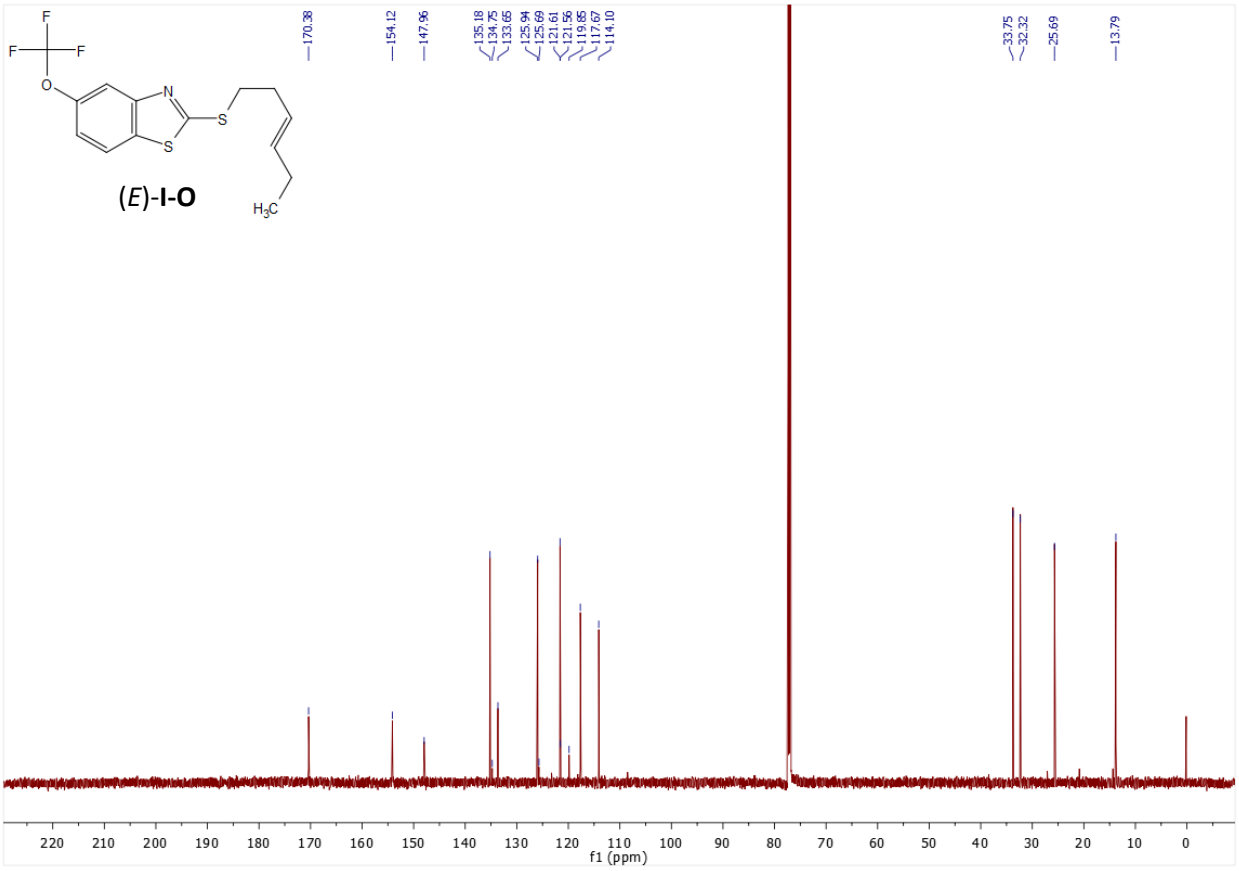

Cl
N
S
S
CH3
(E)-I-M
0.93
0.99
0.49
0.44
1.01
1.04
2.07
2.00
2.02
3.01
f1 (ppm)

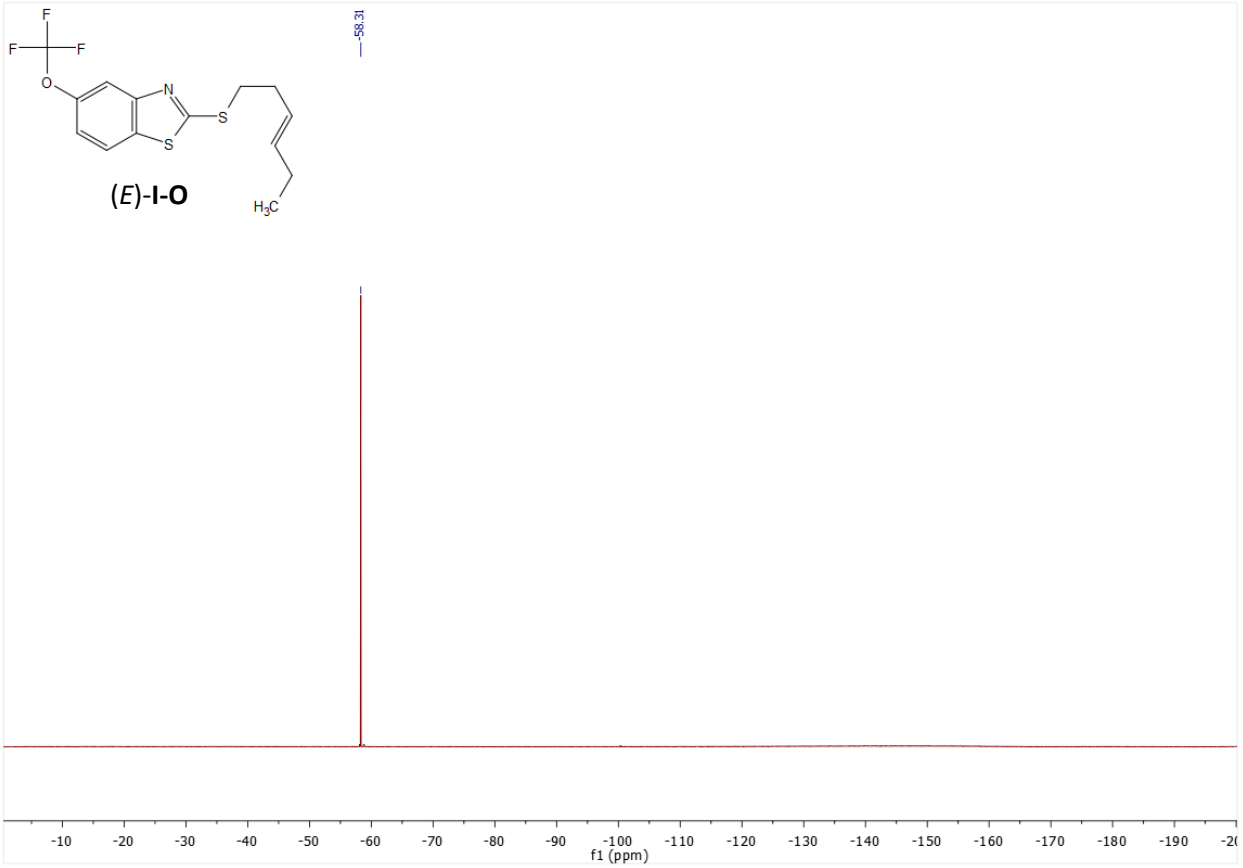

Cl
N
S
S
CH3
(E)-I-M
169.60
154.31
135.15
133.56
132.20
125.96
124.58
121.64
121.49
33.75
32.34
25.69
13.79
f1 (ppm)

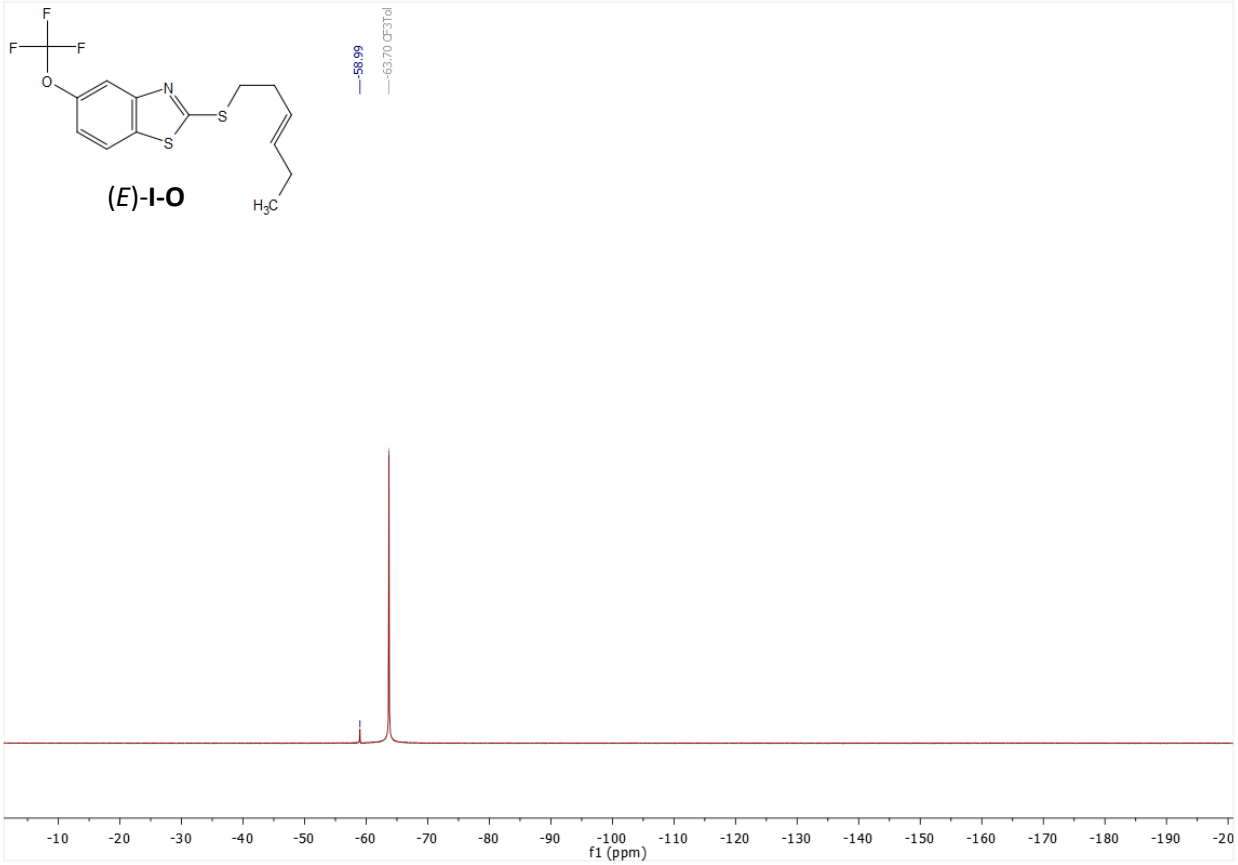

(E)-I-N
0.99
1.01
1.00
0.98
1.01
2.02
2.01
1.94
1.98
3.08
2.99
f1 (ppm)

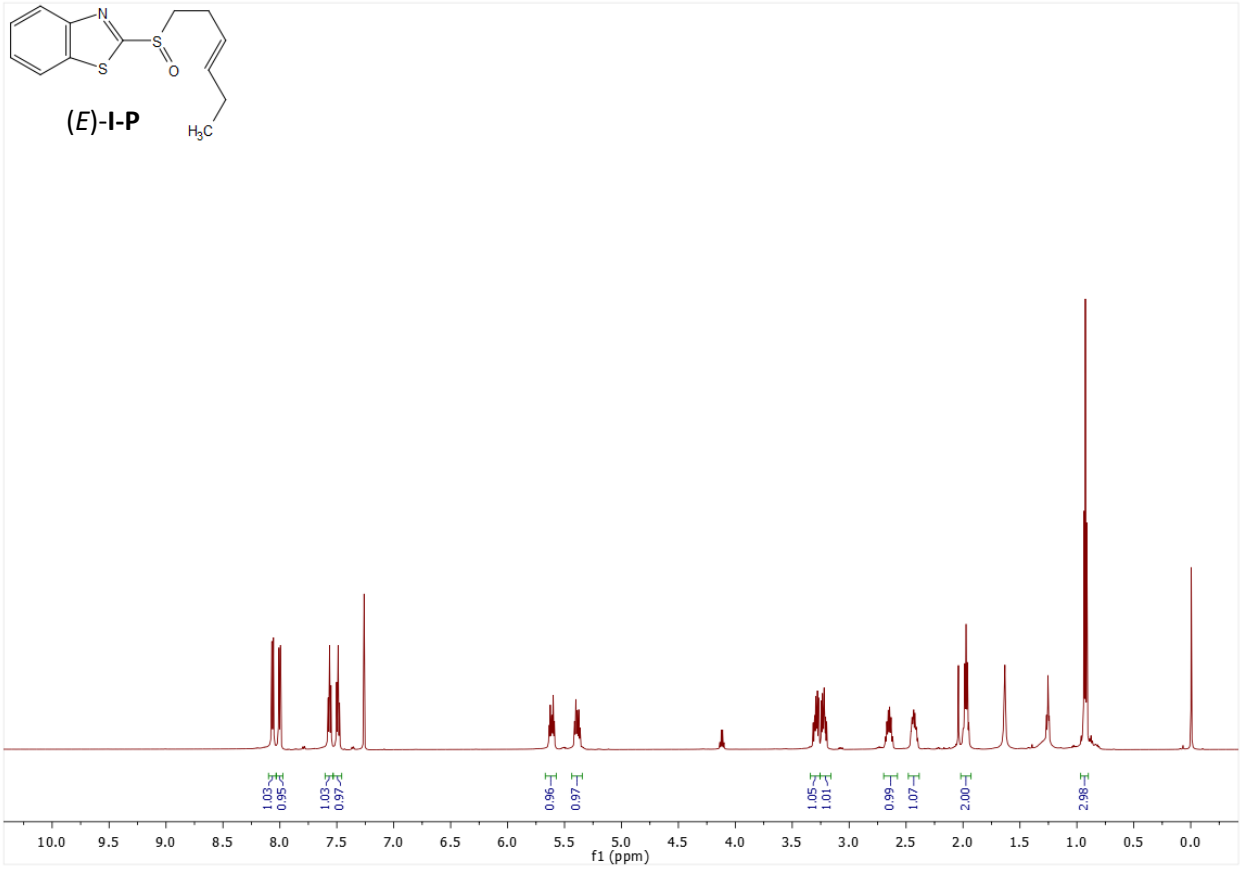

(E)-I-N
163.89
156.47
148.01
136.68
134.93
126.16
122.08
115.94
104.97
64.27
33.94
32.50
25.70
15.00
13.81
f1 (ppm)

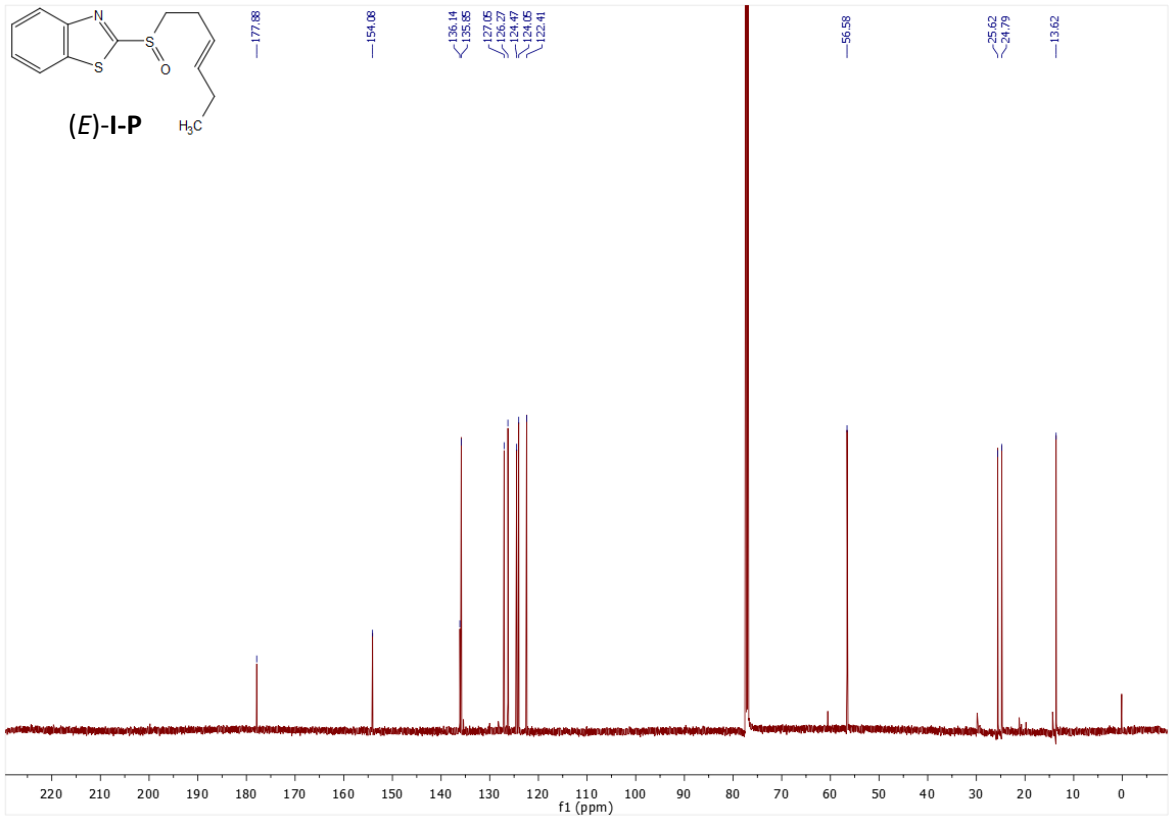

F
F
F
O
N
S
S
H3C
(E)-I-O
1.94
0.95
0.96
0.93
1.93
1.90
1.95
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

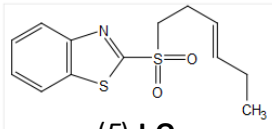

F
F
F
O
N
S
S
H3C
(E)-I-O
170.38
154.12
147.96
135.18
134.75
133.65
125.94
125.69
121.61
121.56
119.85
117.67
114.10
33.75
32.32
25.69
13.79
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
O
N
S
S
H3C
(E)-I-O
-58.31
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

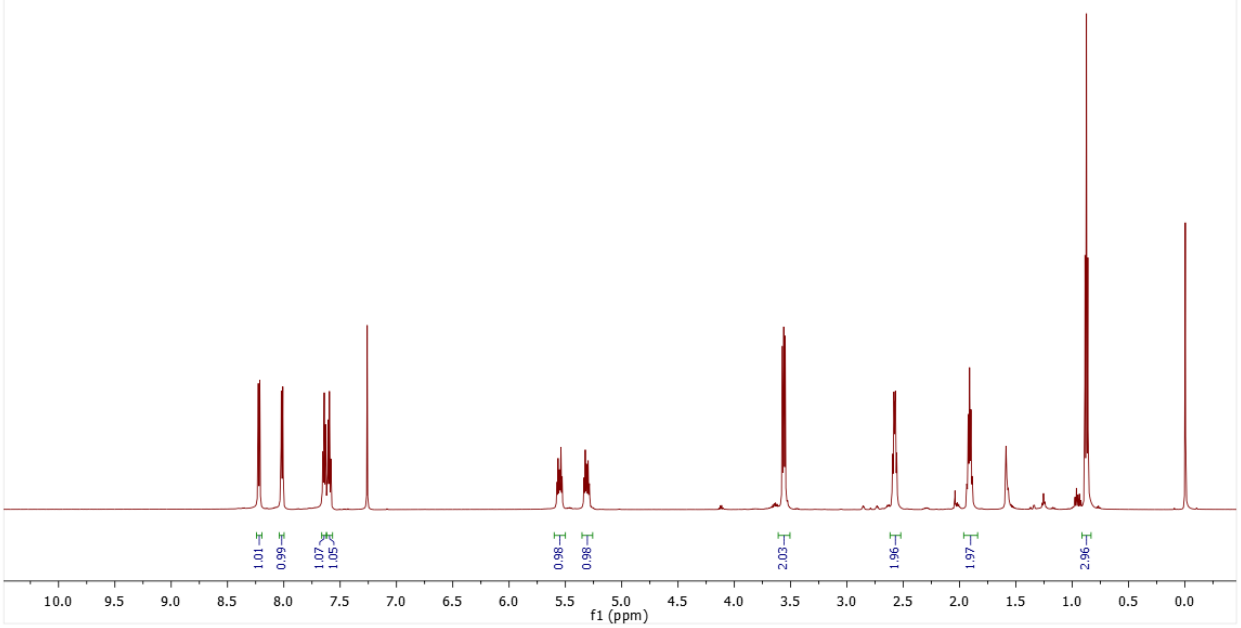

F
F
F
O
N
S
S
H3C
(E)-I-O
-58.99
-63.70 CF3Tol
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

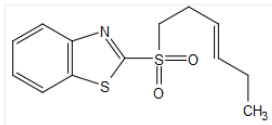

(E)-I-P
1.03
0.95
1.03
0.97
0.96
0.97
1.05
1.01
0.99
1.07
2.00
2.98
f1 (ppm)


(E)-I-P
177.88
154.08
136.14
135.85
127.05
126.27
124.47
124.05
122.41
56.58
25.62
24.79
13.62
f1 (ppm)



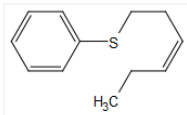
(*E*)-**I-Q**


1.01
0.99
1.07
1.05
0.98
0.98
2.03
1.96
1.97
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

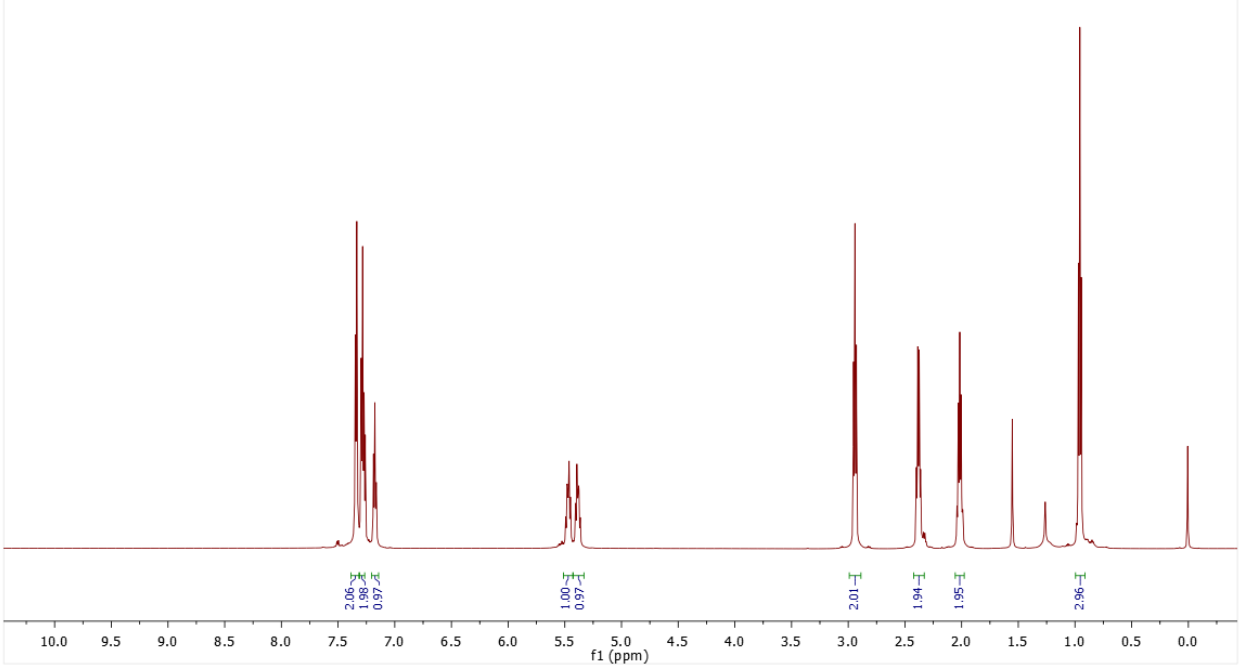


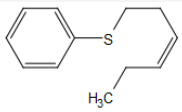
(*E*)-**I-Q**

166.01
152.89
136.95
135.78
128.15
127.78
125.60
123.57
122.46
54.73
25.72
25.49
13.47
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


S
H3C

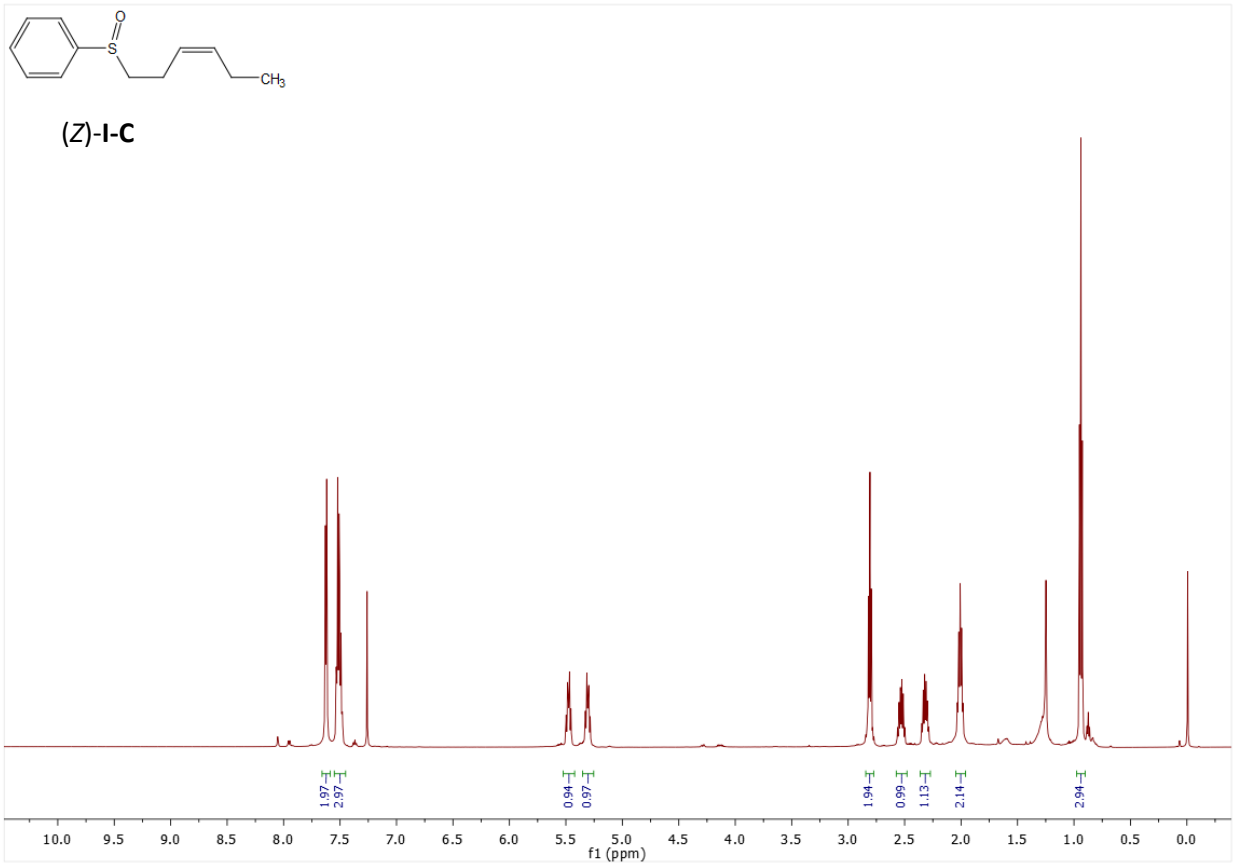
(*Z*)-**I-B**

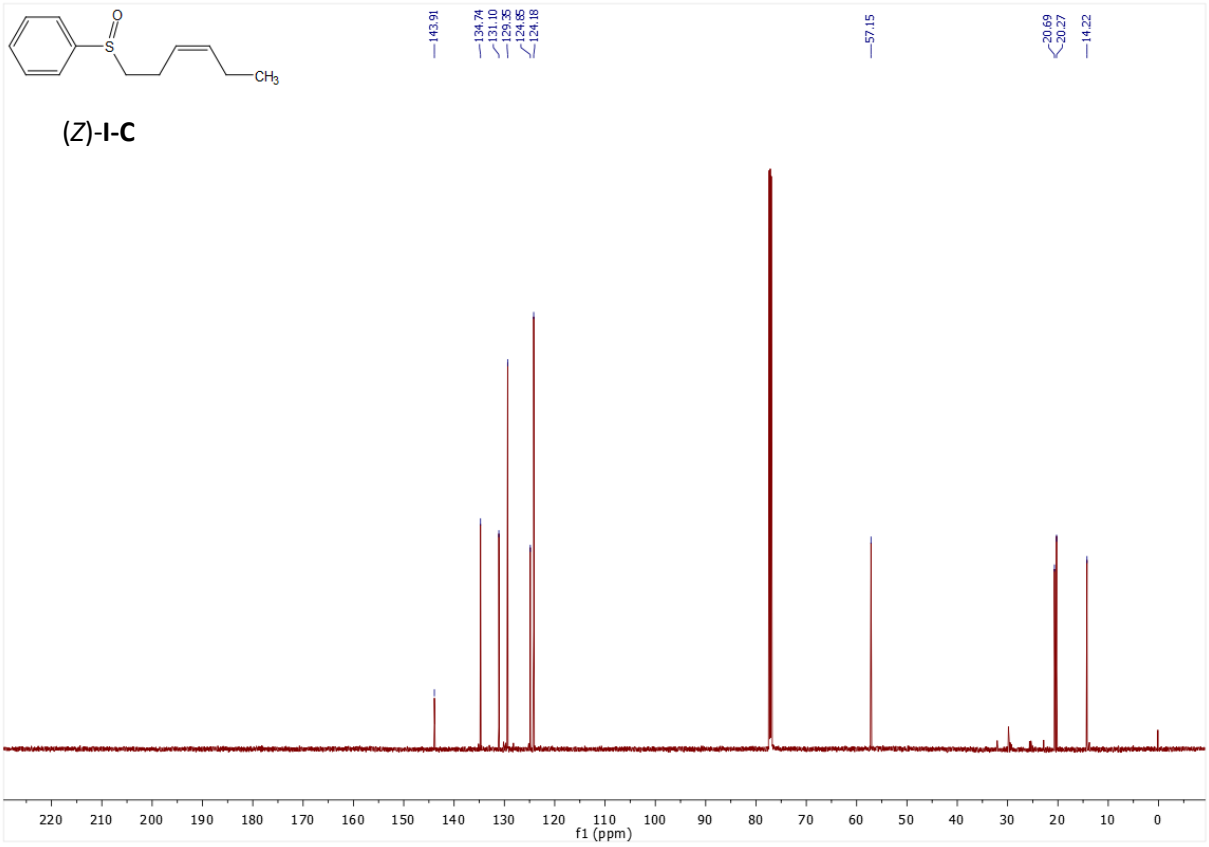

2.06
1.98
0.97
1.00
0.97
2.01
1.94
1.95
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

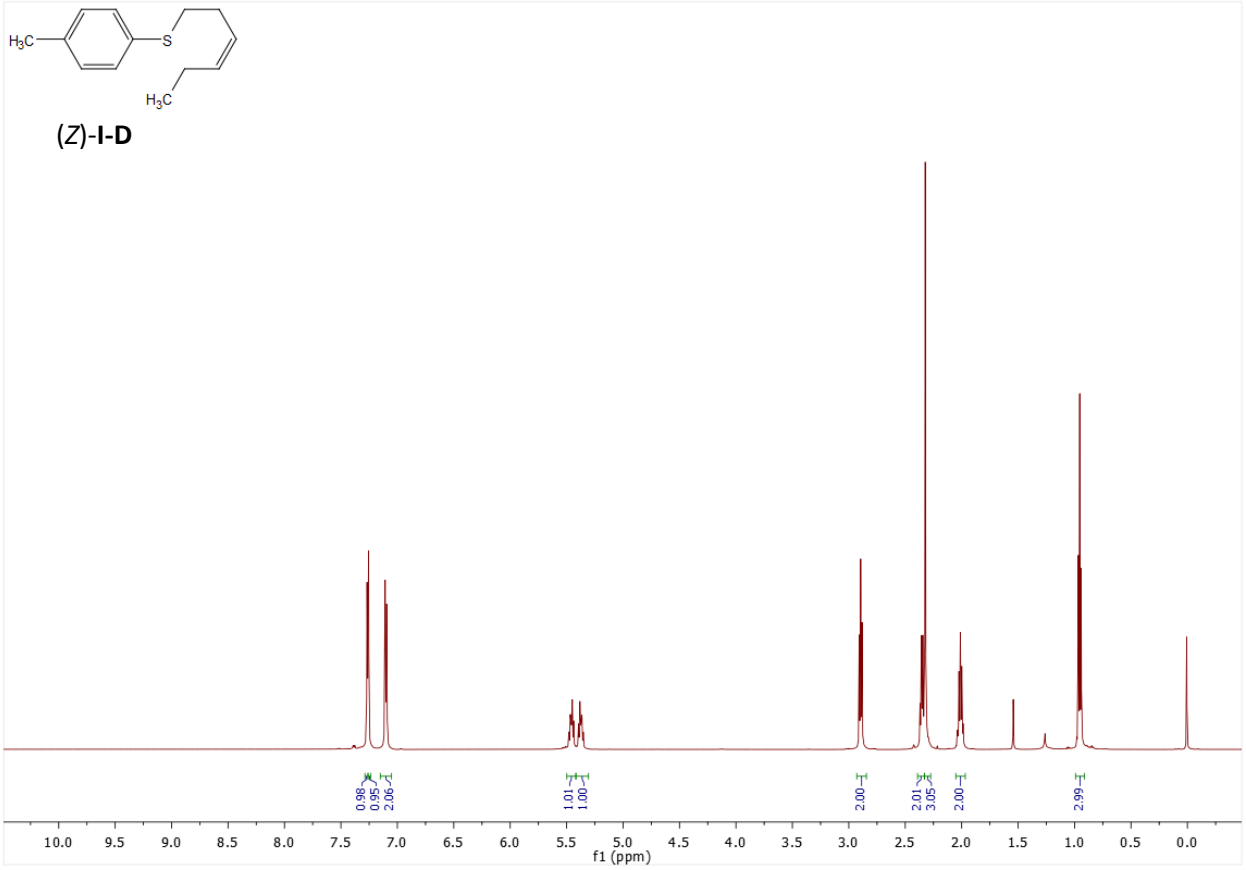

S
H3C

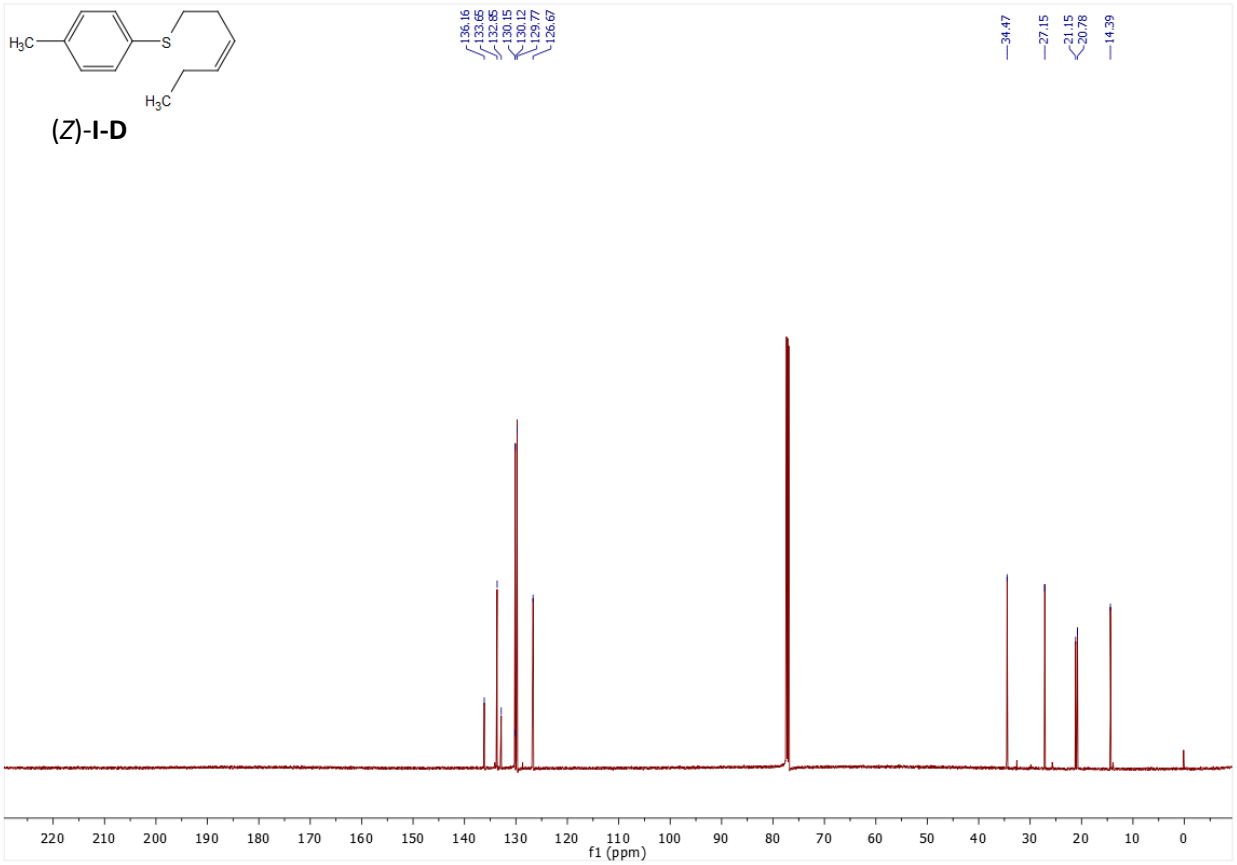
(*Z*)-**I-B**

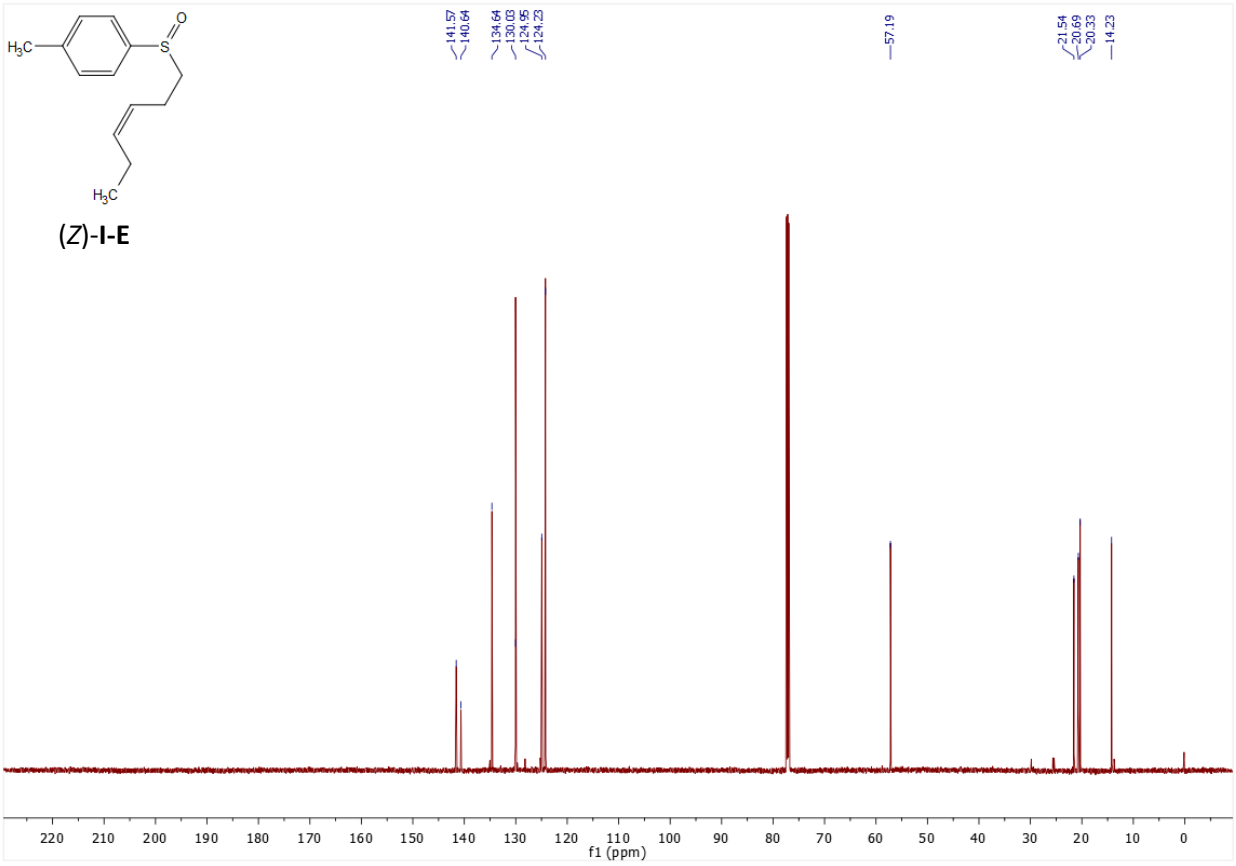
136.74
133.77
129.23
128.98
126.54
125.96
33.73
27.04
20.78
14.38
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


(Z)-I-C
1.97
2.97
0.94
0.97
1.94
0.99
1.13
2.14
2.94
f1 (ppm)

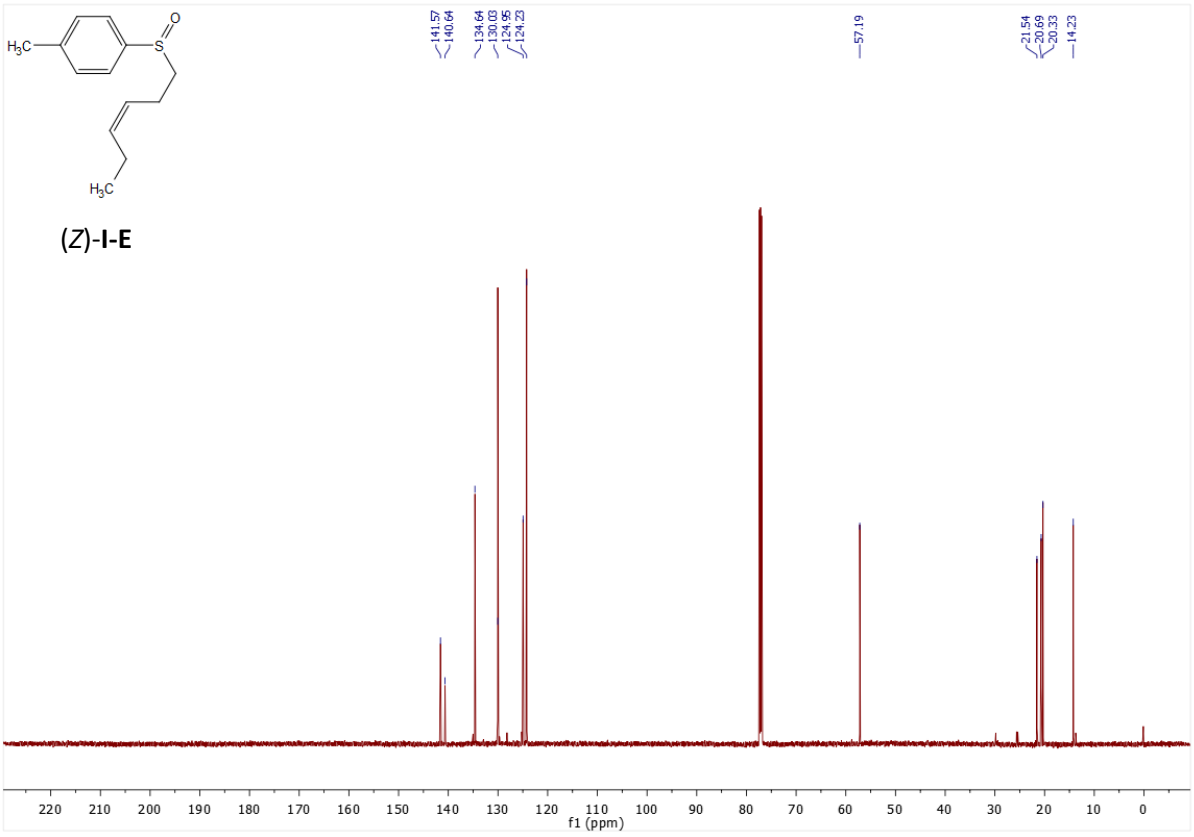

(Z)-I-C
143.91
134.74
131.10
129.35
124.85
124.18
57.15
20.69
20.27
14.22
f1 (ppm)


H3C
S
H3C
(Z)-I-D
0.98
0.95
2.08
1.01
1.00
2.00
2.01
3.05
2.00
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

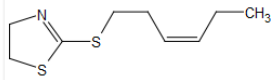

H3C
S
H3C
(Z)-I-D
136.16
133.65
132.85
130.15
130.12
129.77
126.67
34.47
27.15
21.15
20.78
14.39
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


141.57
140.64
134.64
130.03
124.95
124.23
57.19
21.54
20.69
20.33
14.23
f1 (ppm)

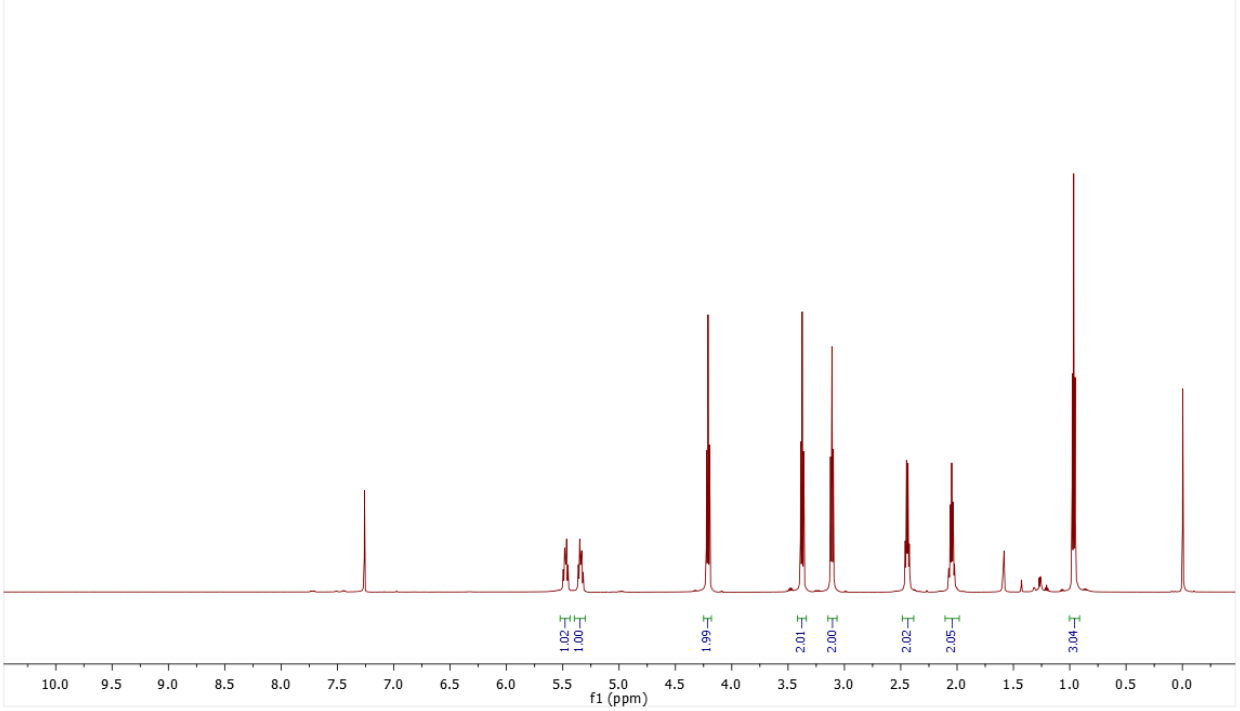
(*Z*)-**I-E**

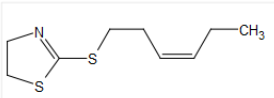

141.57
140.64
134.64
130.03
124.95
124.23
57.19
21.54
20.69
20.33
14.23
f1 (ppm)

(*Z*)-**I-E**



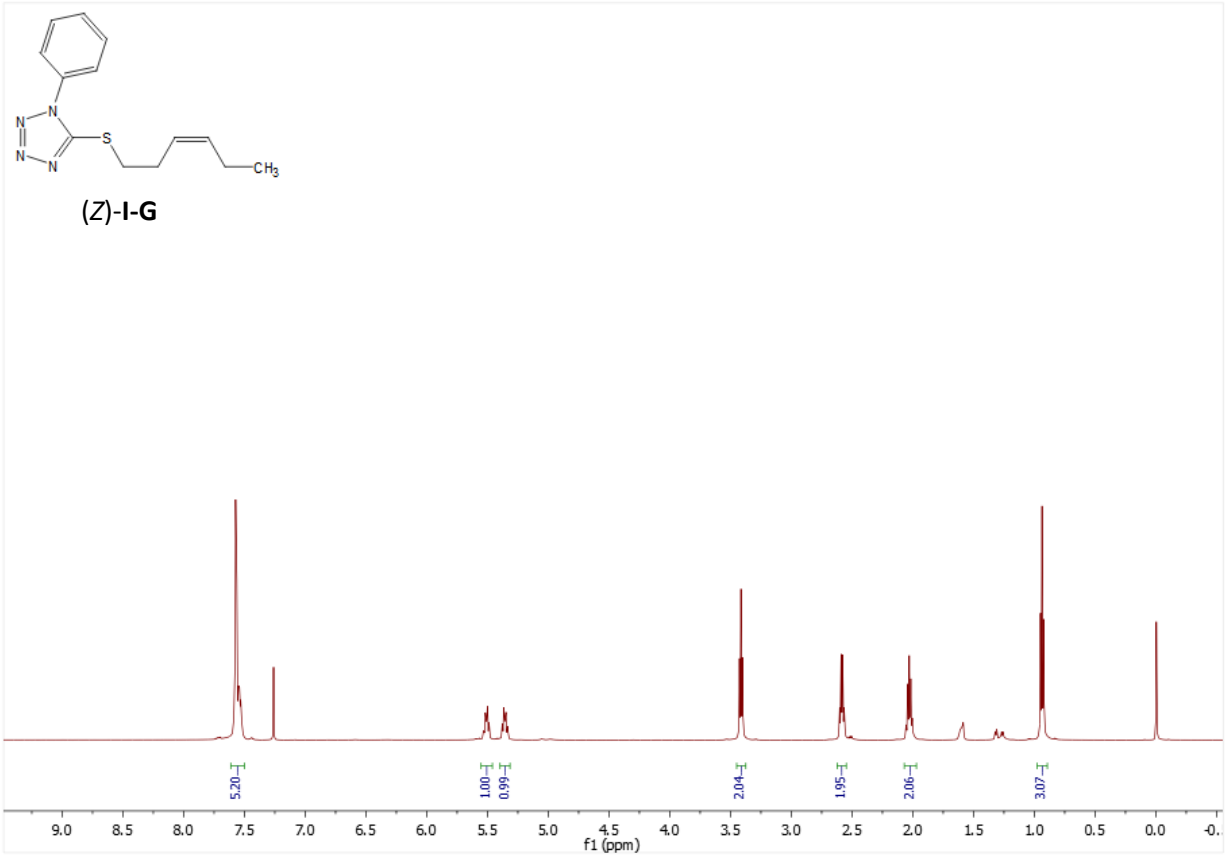
(*Z*)-**I-F**

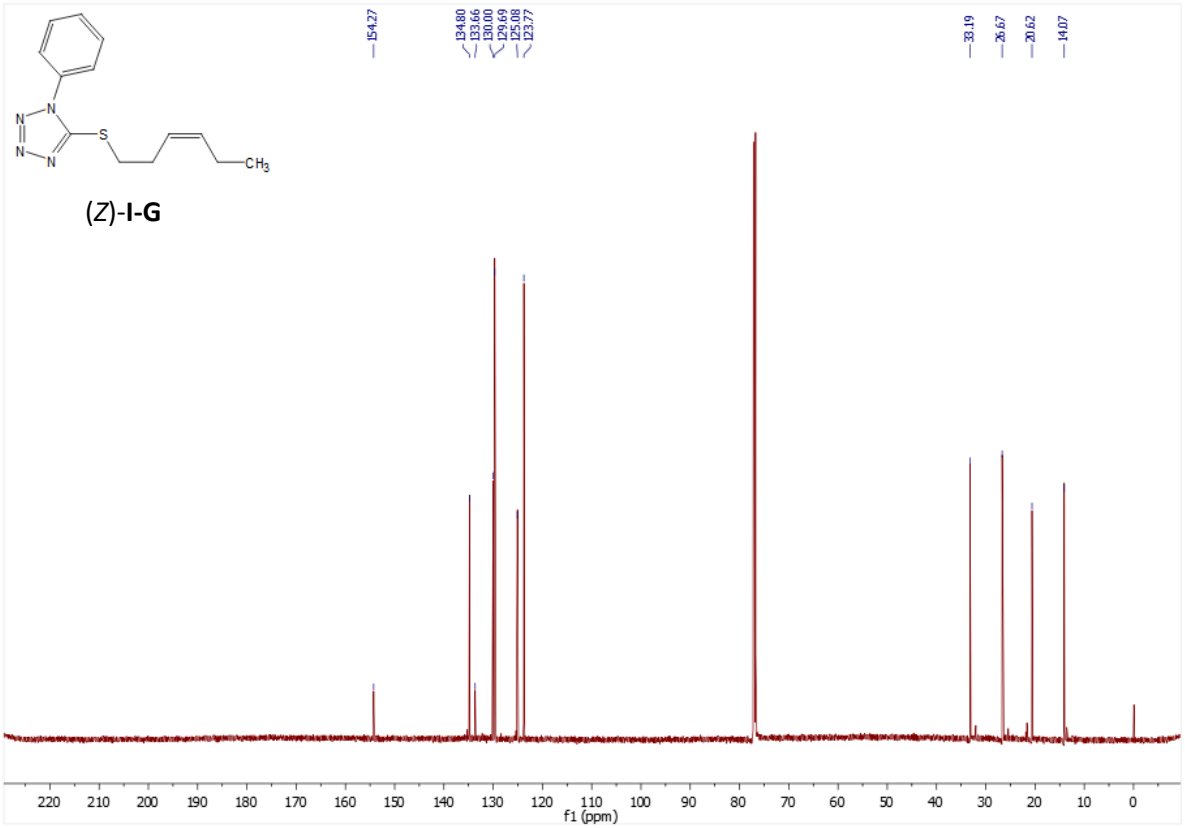

1.02
1.00
1.99
2.01
2.00
2.02
2.05
3.04
f1 (ppm)

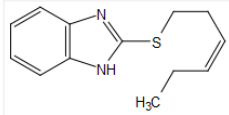


(*Z*)-**I-F**

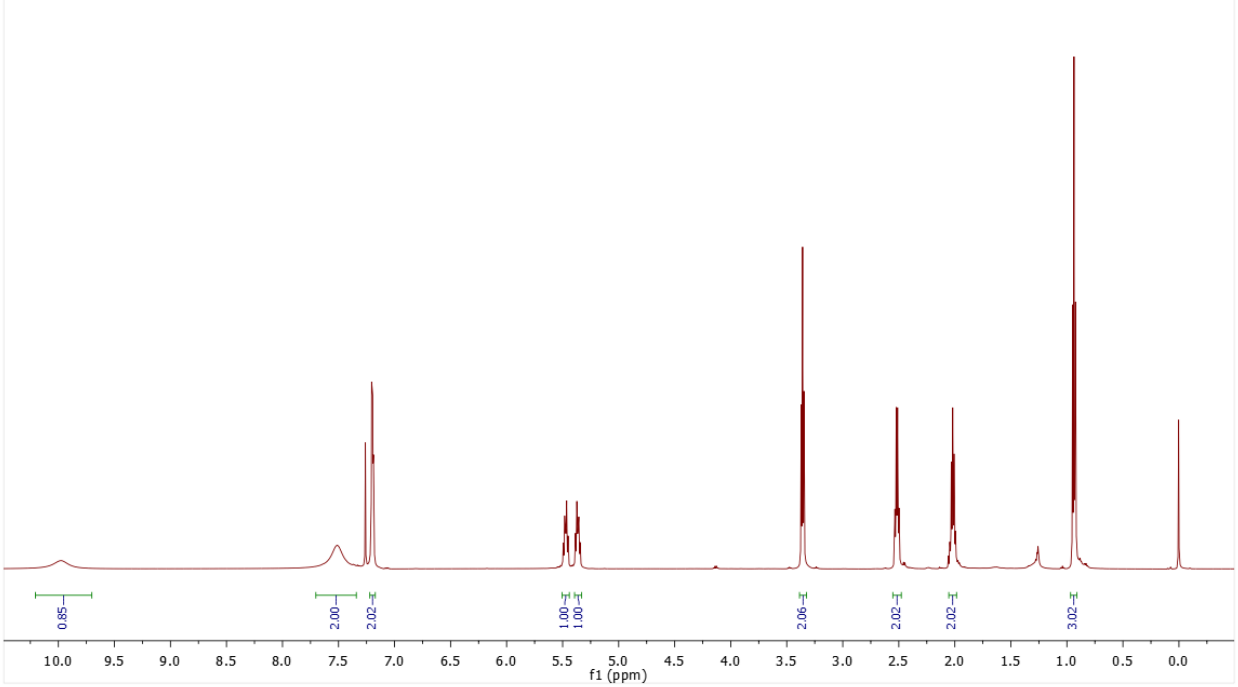
165.70
134.19
126.12
64.49
35.51
32.85
27.11
20.81
14.36
f1 (ppm)

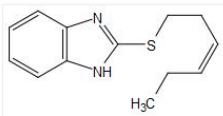

(Z)-I-G
5.20
1.00
0.99
2.04
1.95
2.06
3.07
f1 (ppm)


(Z)-I-G
154.27
134.80
133.66
130.00
129.69
125.08
123.77
33.19
26.67
20.62
14.07
f1 (ppm)


N
S
NH
H3C

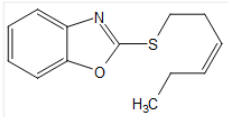
(*Z*)-**I-H**


0.85
2.00
2.02
1.00
1.00
2.06
2.02
2.02
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

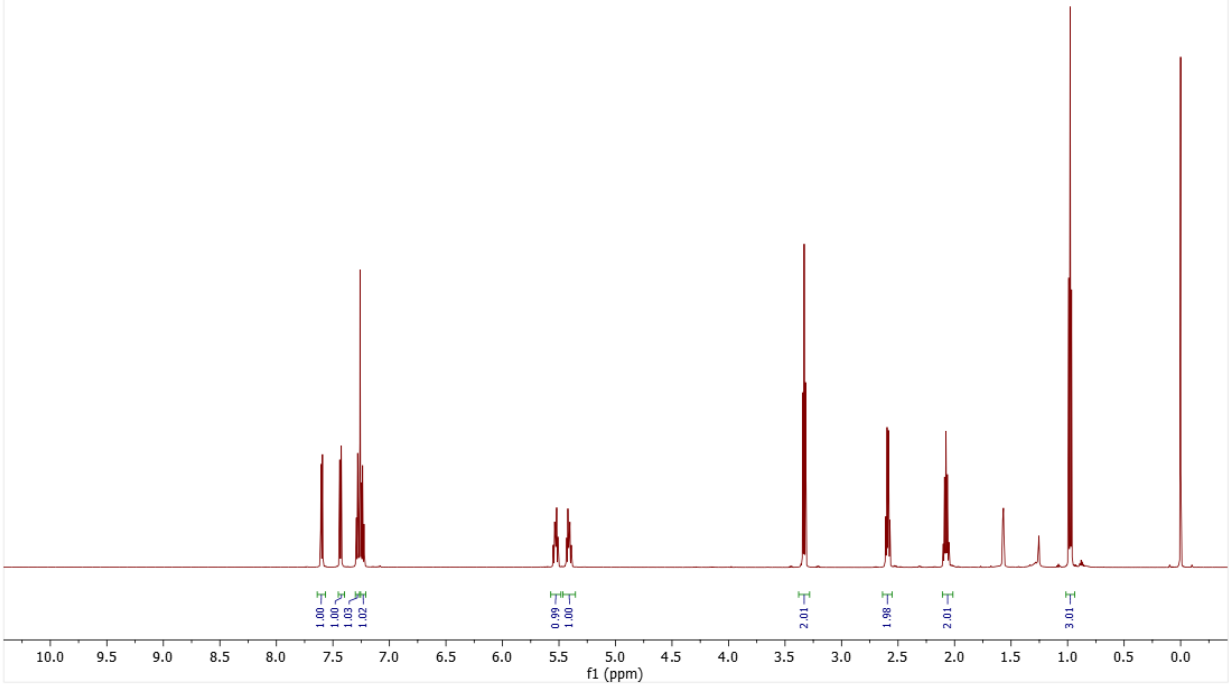

N
S
NH
H3C

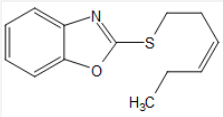
(*Z*)-**I-H**

150.60
134.35
125.99
122.39
32.82
27.34
20.82
14.31
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


N
S
O
H3C

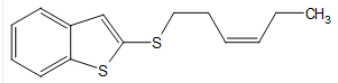
(*Z*)-**I-l**


1.00
1.00
1.03
1.02
0.99
1.00
2.01
1.98
2.01
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

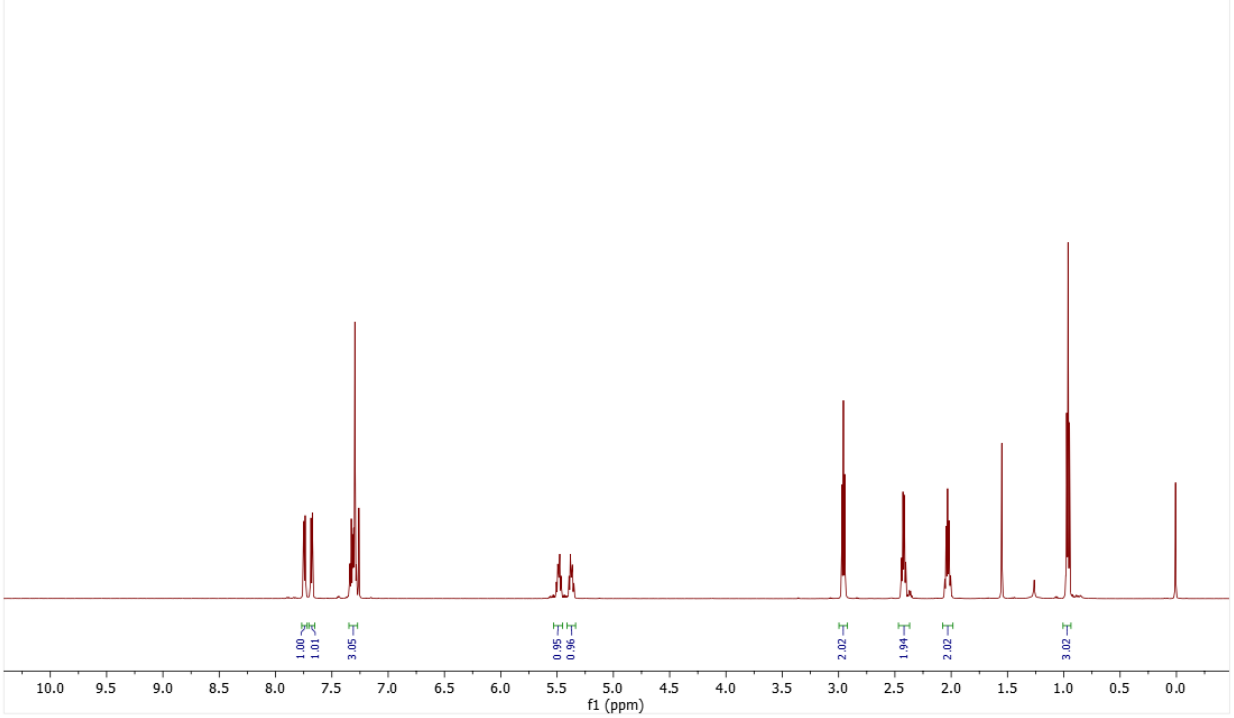

N
S
O
H3C

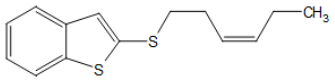
(*Z*)-**I-l**

165.21
151.96
142.17
134.75
125.63
124.37
123.92
118.51
109.97
32.37
27.15
20.85
14.32
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



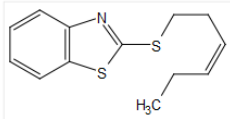
(*Z*)-**I-J**


1.00
1.01
3.05
0.95
0.96
2.02
1.94
2.02
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

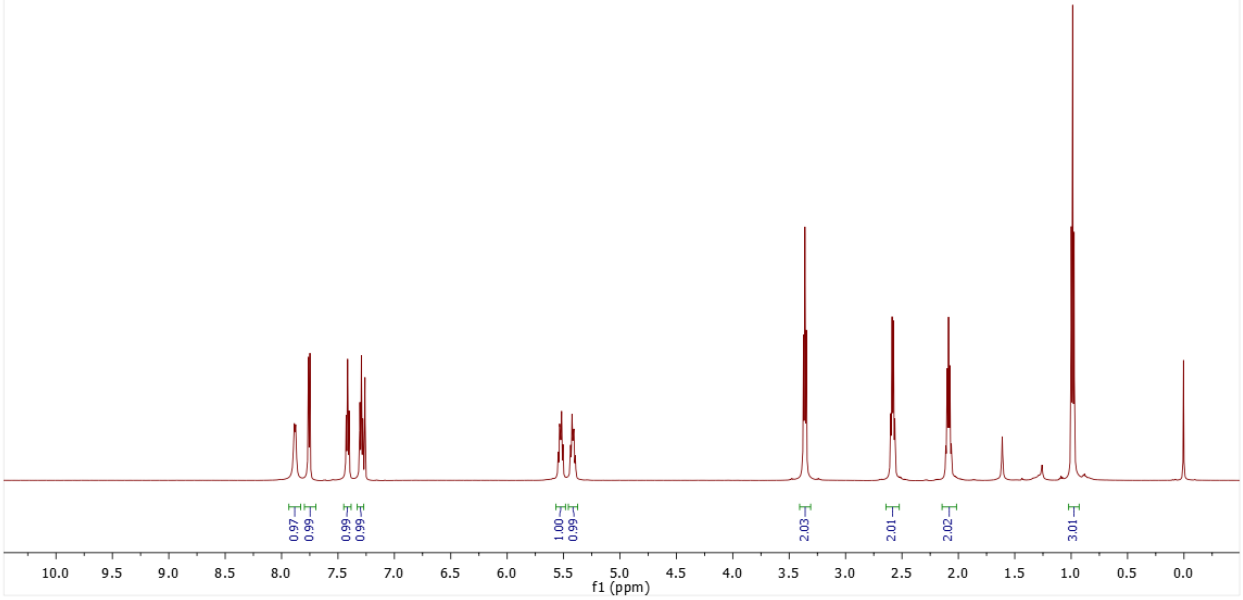


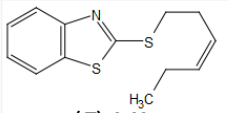
(*Z*)-**I-J**

141.74
139.95
137.42
134.10
128.02
126.12
124.58
124.42
123.10
121.98
37.52
27.45
20.84
14.37
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



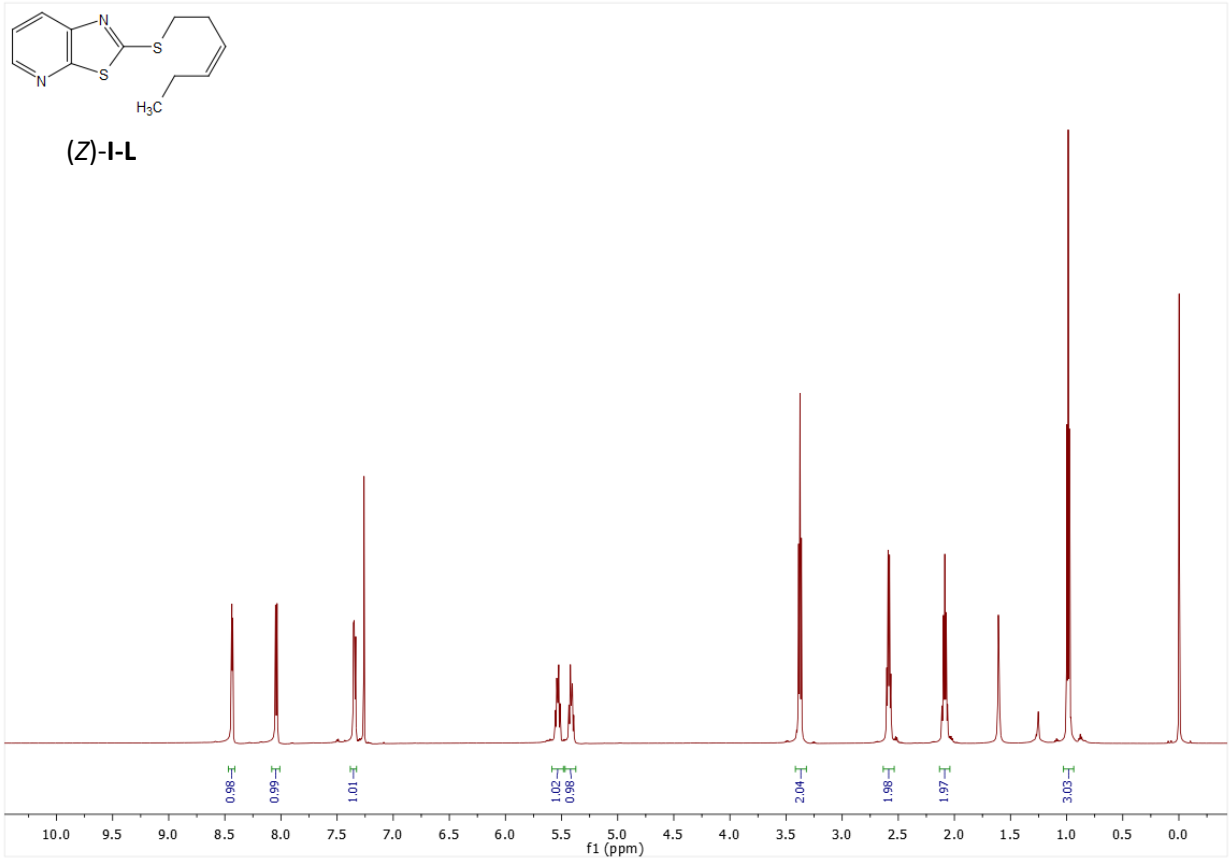
(*Z*)-**I-K**

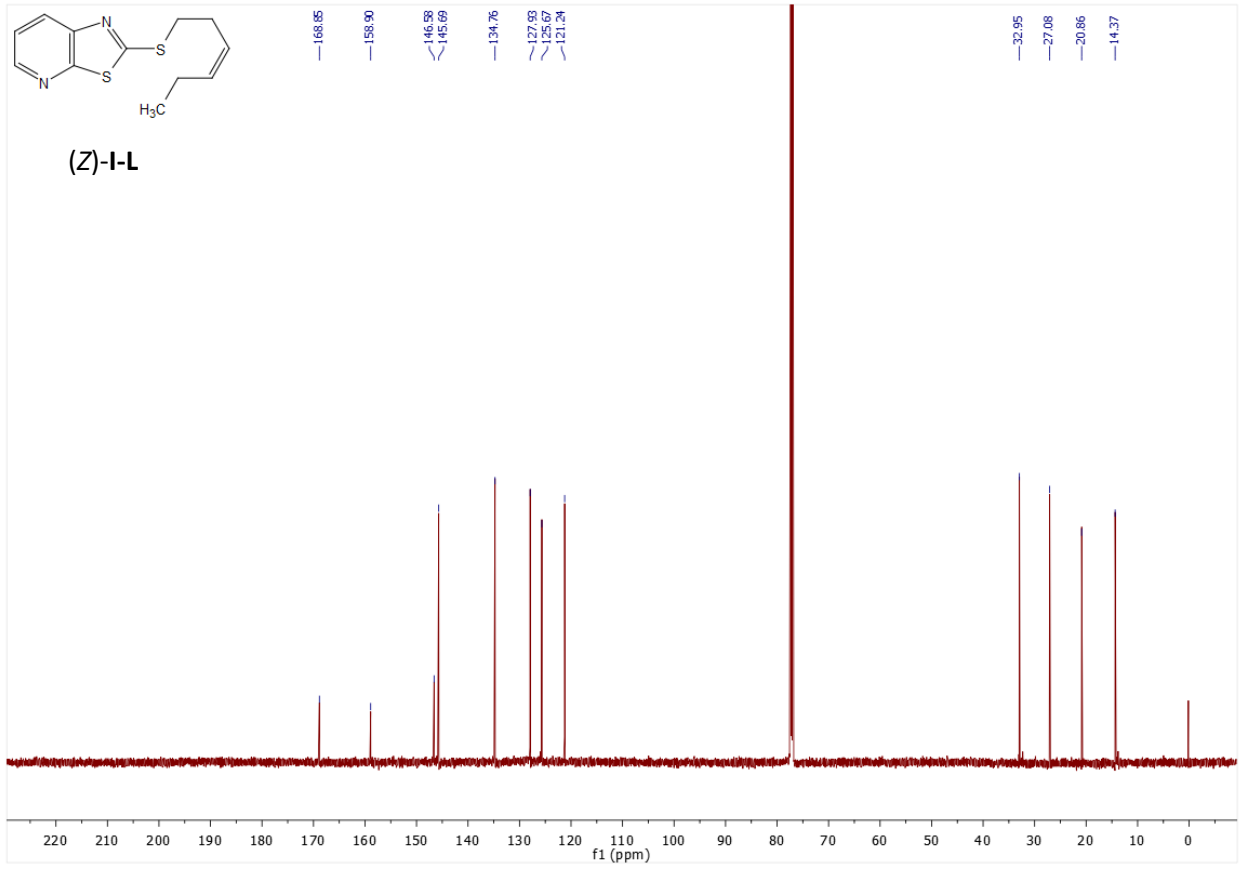

0.97
0.99
0.99
0.99
1.00
0.99
2.03
2.01
2.02
3.01
f1 (ppm)

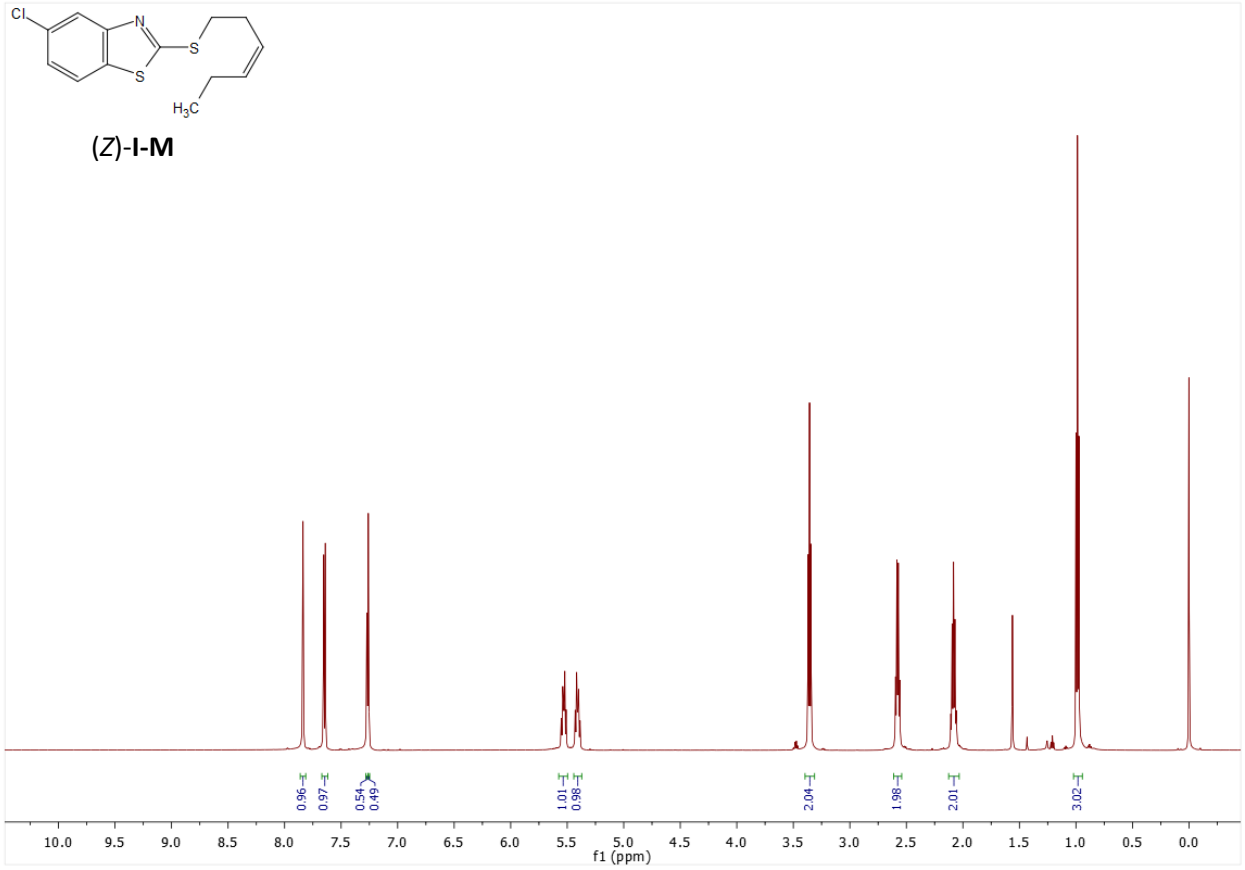


(*Z*)-**I-K**

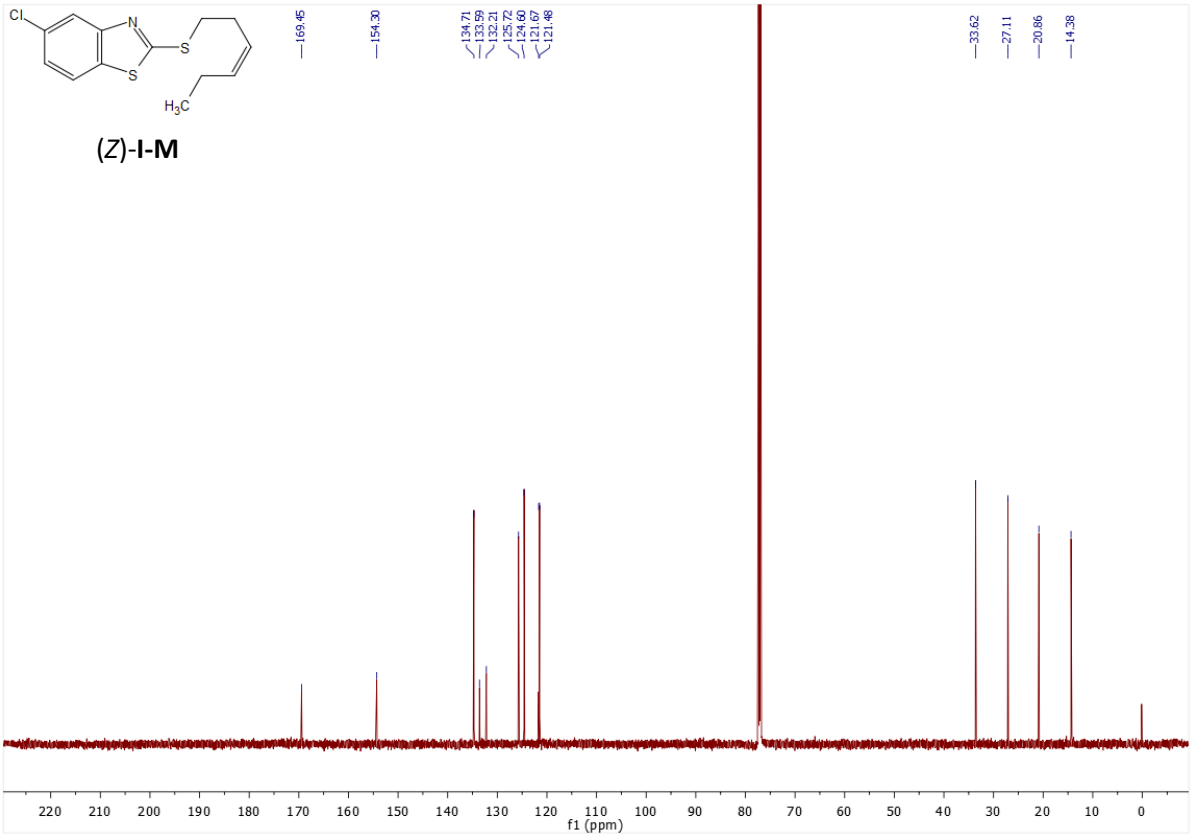
167.14
153.47
135.34
134.56
126.11
125.85
124.24
121.57
121.05
33.58
27.17
20.84
14.37
f1 (ppm)


(Z)-I-L
0.98
0.99
1.01
1.02
0.98
2.04
1.98
1.97
3.03
f1 (ppm)

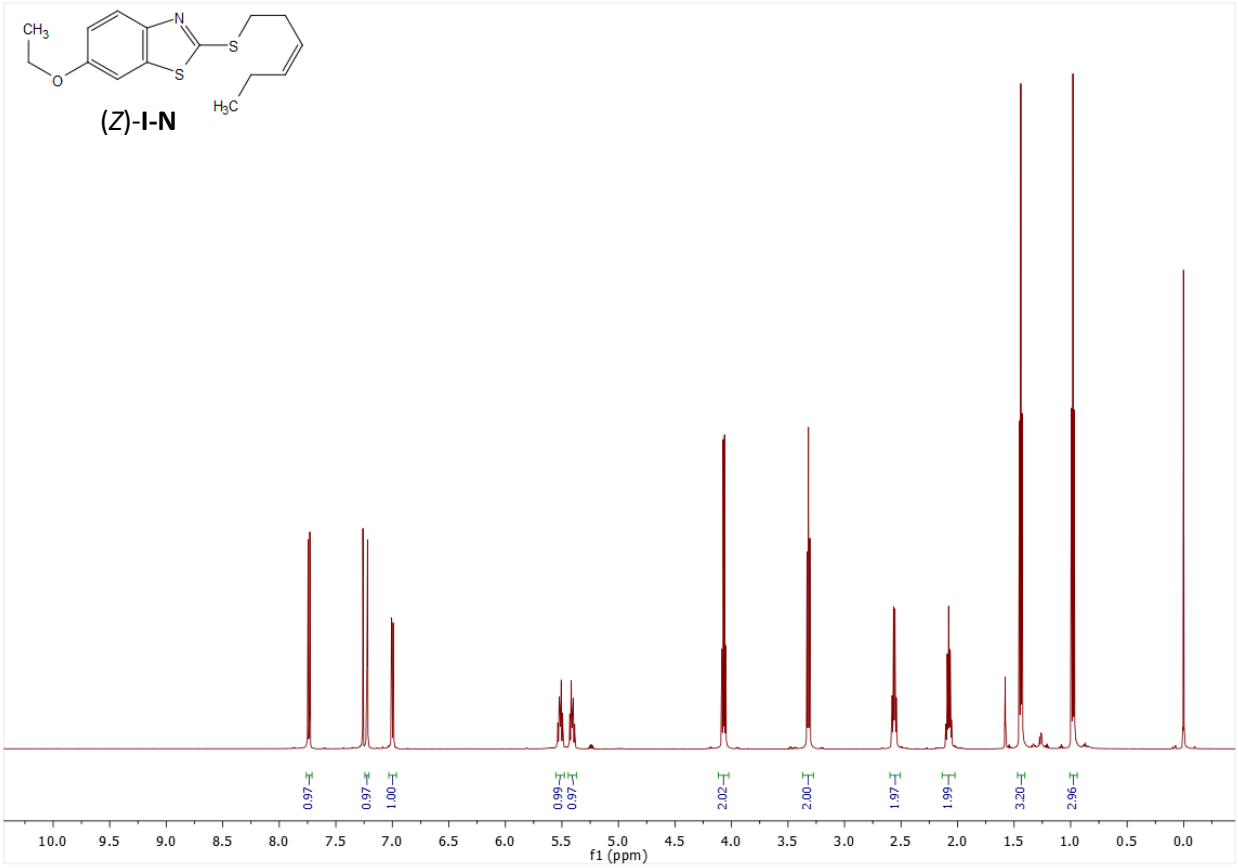

(Z)-I-L
168.85
158.90
146.58
145.69
134.76
127.93
125.67
121.24
32.95
27.08
20.86
14.37
f1 (ppm)

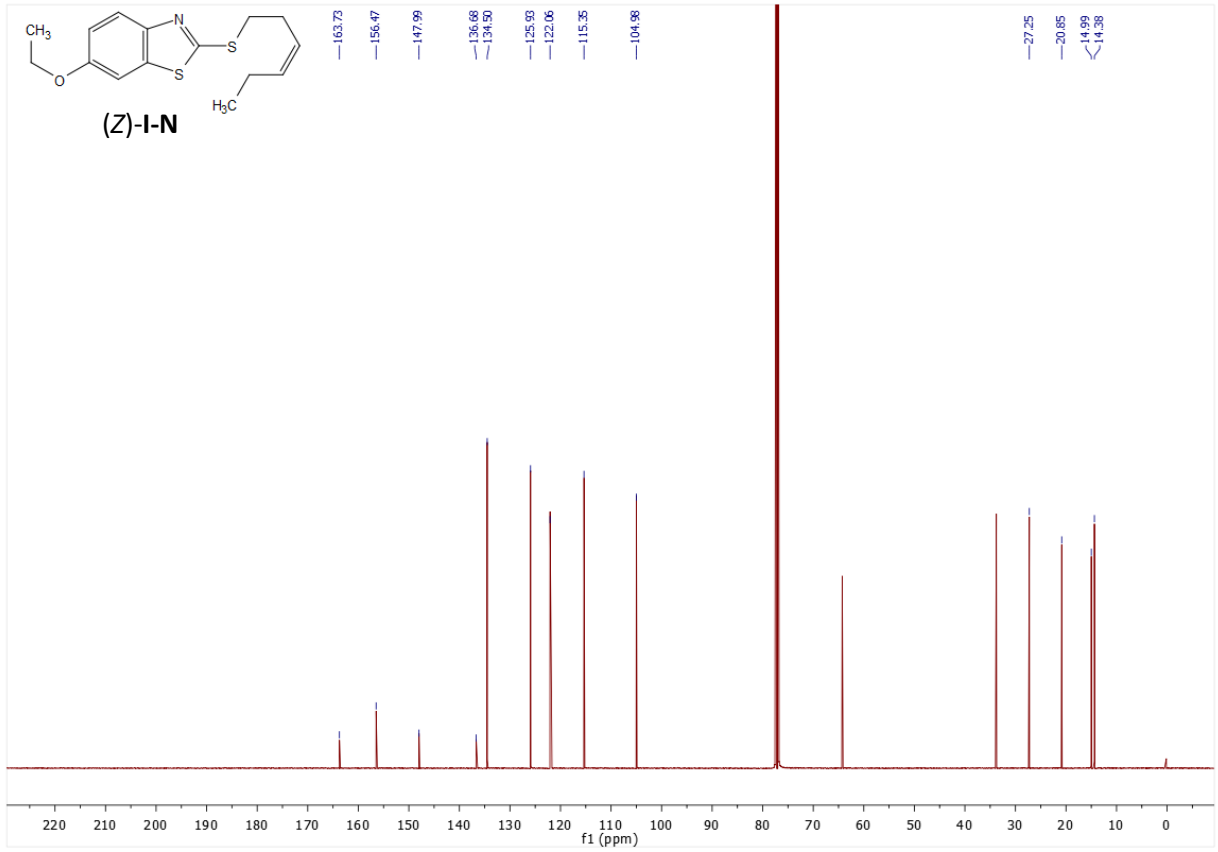

Cl
N
S
S
H3C
0.96
0.97
0.54
0.49
1.01
0.98
2.04
1.98
2.01
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

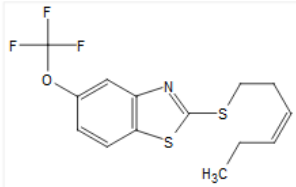
(*Z*)-**I-M**


Cl
N
S
S
H3C
169.45
154.30
134.71
133.59
132.21
125.72
124.60
121.67
121.48
33.62
27.11
20.86
14.38
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

(*Z*)-**I-M**

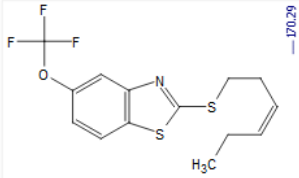

CH3
O
N
S
S
H3C
(Z)-I-N
0.97
0.97
1.00
0.99
0.97
2.02
2.00
1.97
1.99
3.20
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


CH3
O
N
S
S
H3C
(Z)-I-N
163.73
156.47
147.99
136.68
134.50
125.93
122.06
115.35
104.98
27.25
20.85
14.99
14.38
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



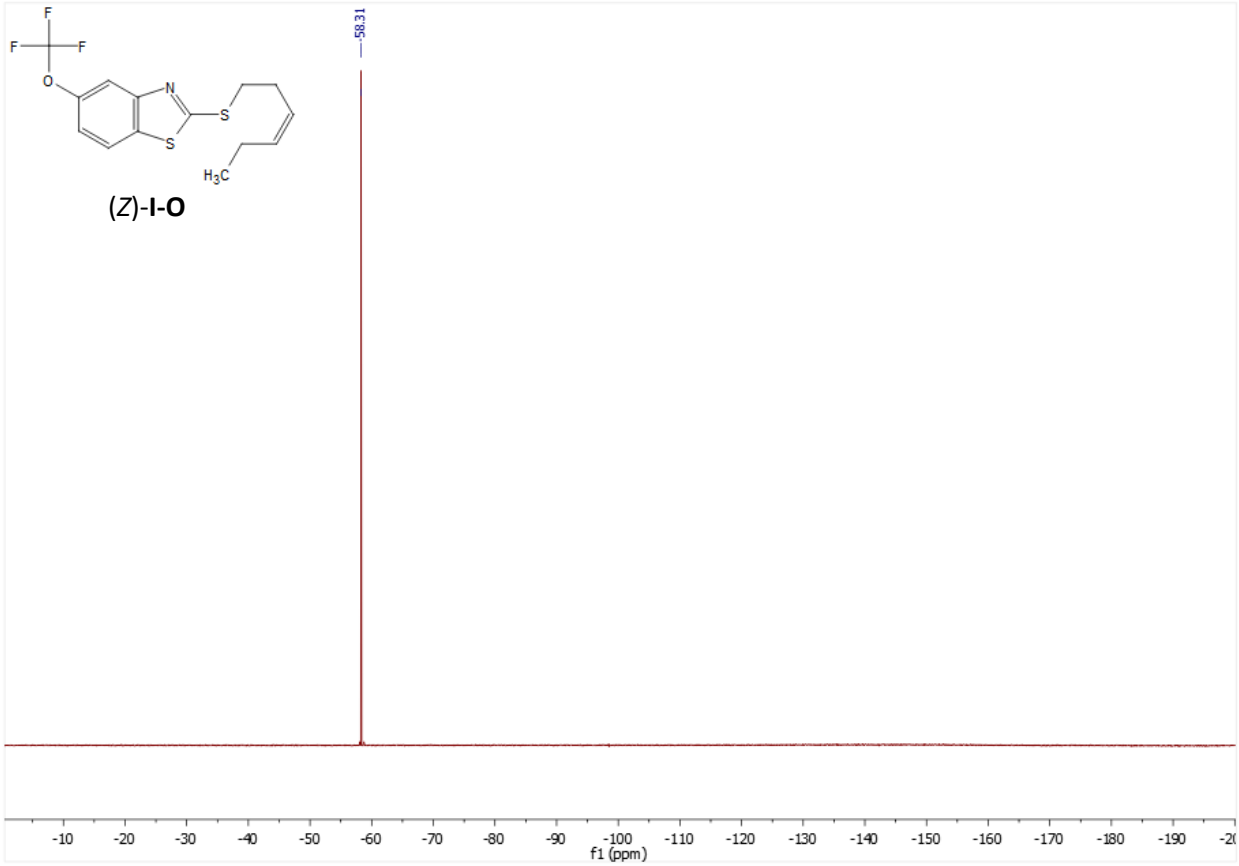
(*Z*)-**I-O**

2.02
1.02
0.99
0.99
2.03
1.97
1.98
3.00
f1 (ppm)

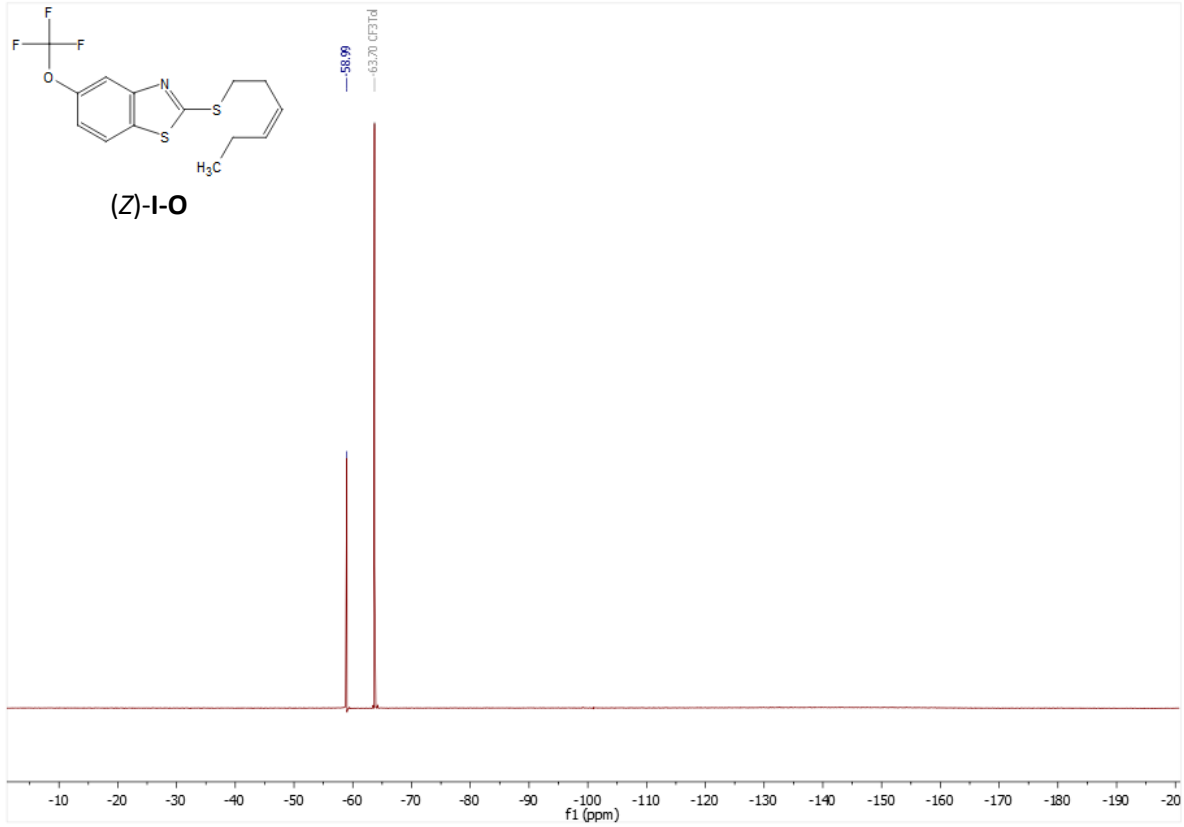


(*Z*)-**I-O**

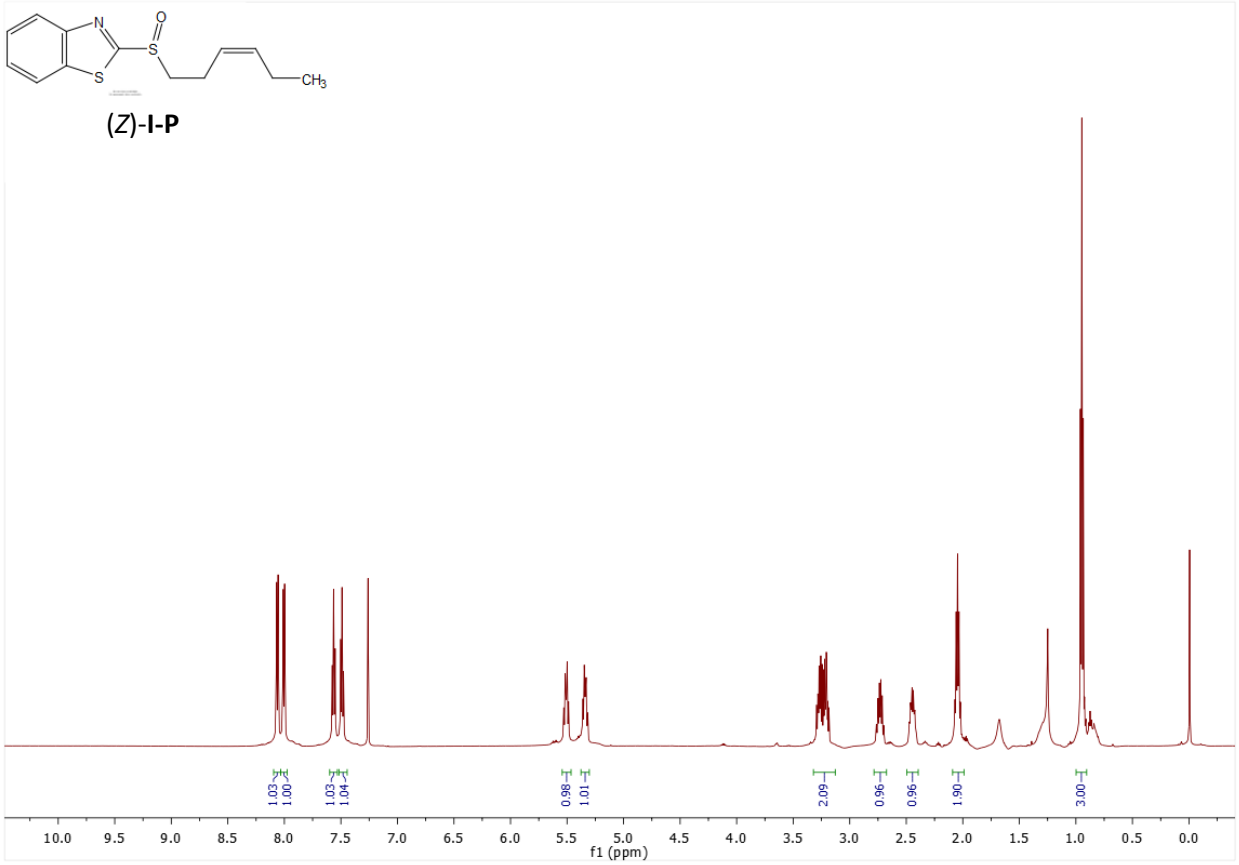
170.29
154.08
147.97
134.75
133.65
125.68
123.26
121.64
121.55
119.85
118.14
117.69
114.09
33.64
27.08
20.86
14.36
f1 (ppm)

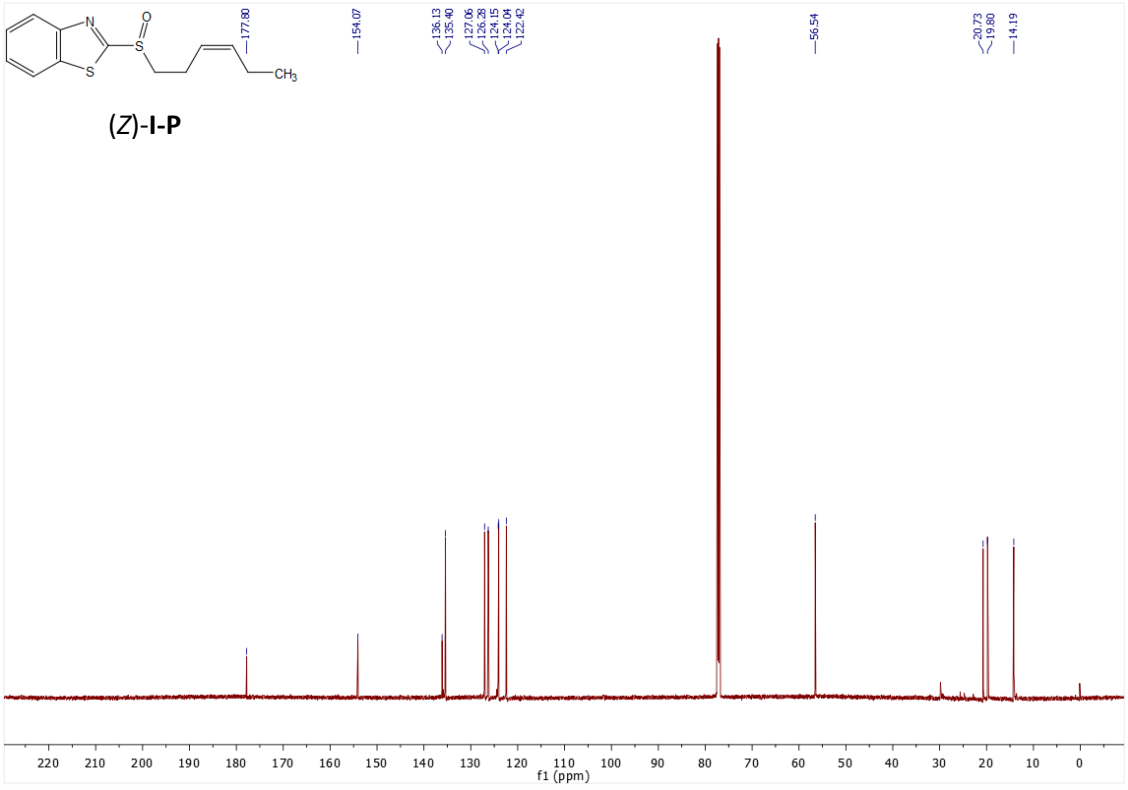

F
F
F
O
N
S
S
H3C
58.31
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

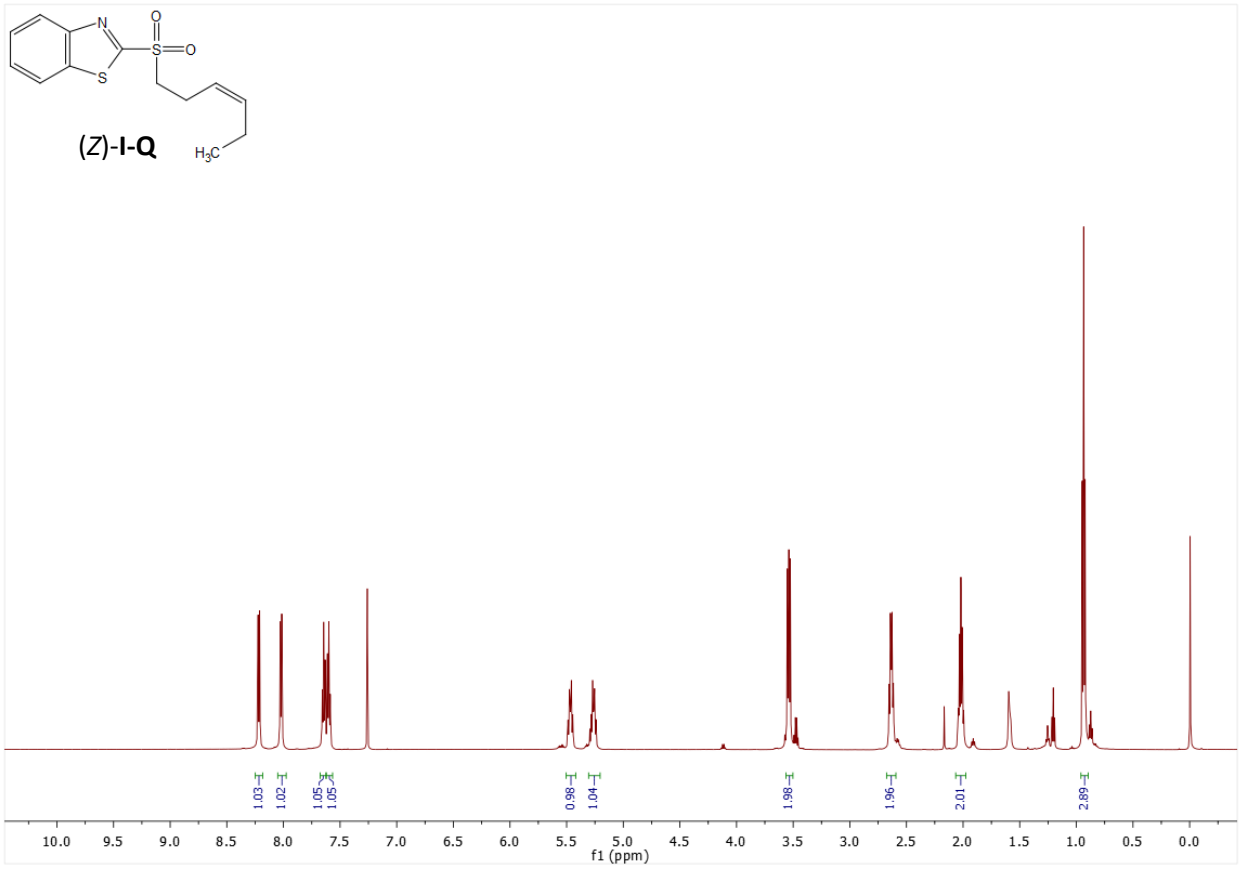
(*Z*)-**I-O**

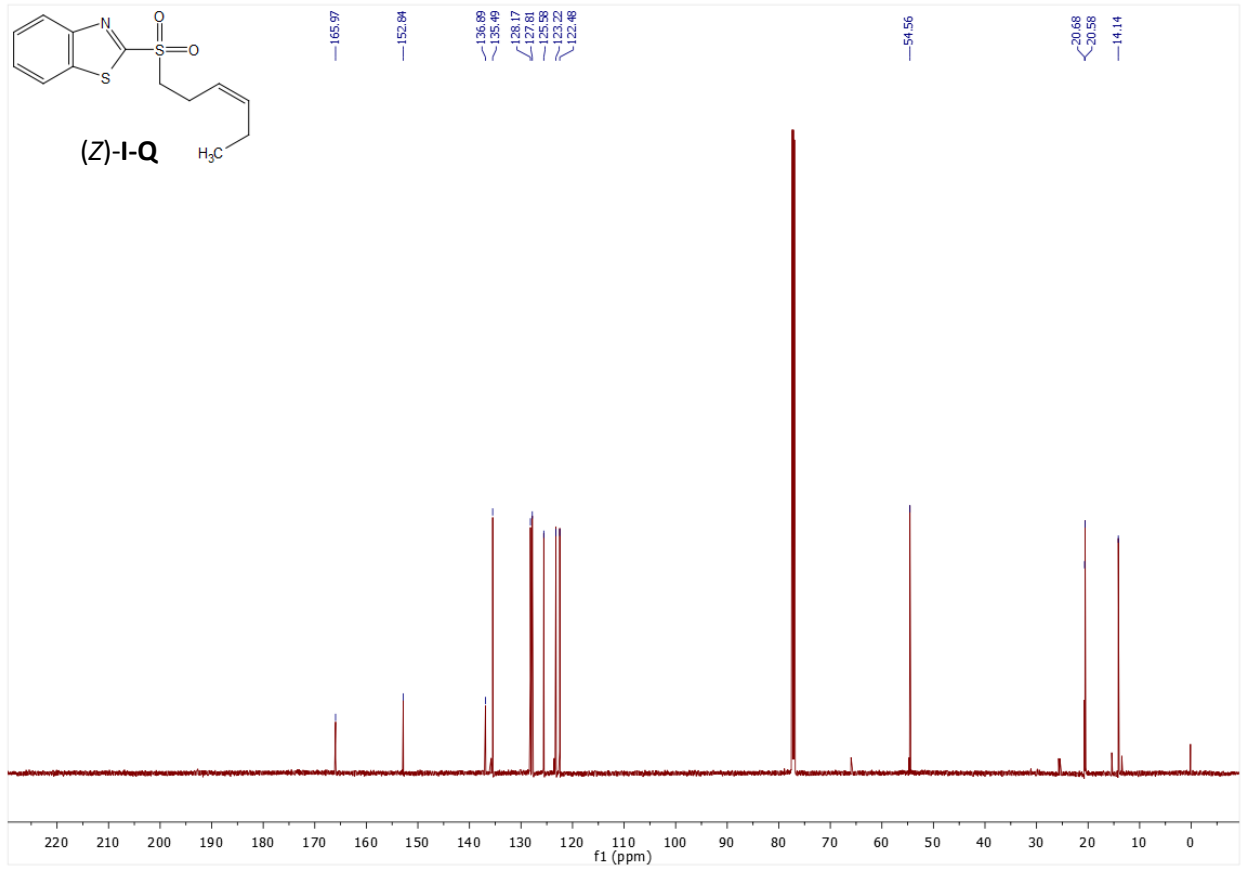

F
F
F
O
N
S
S
H3C
58.99
63.70 CF3'd
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

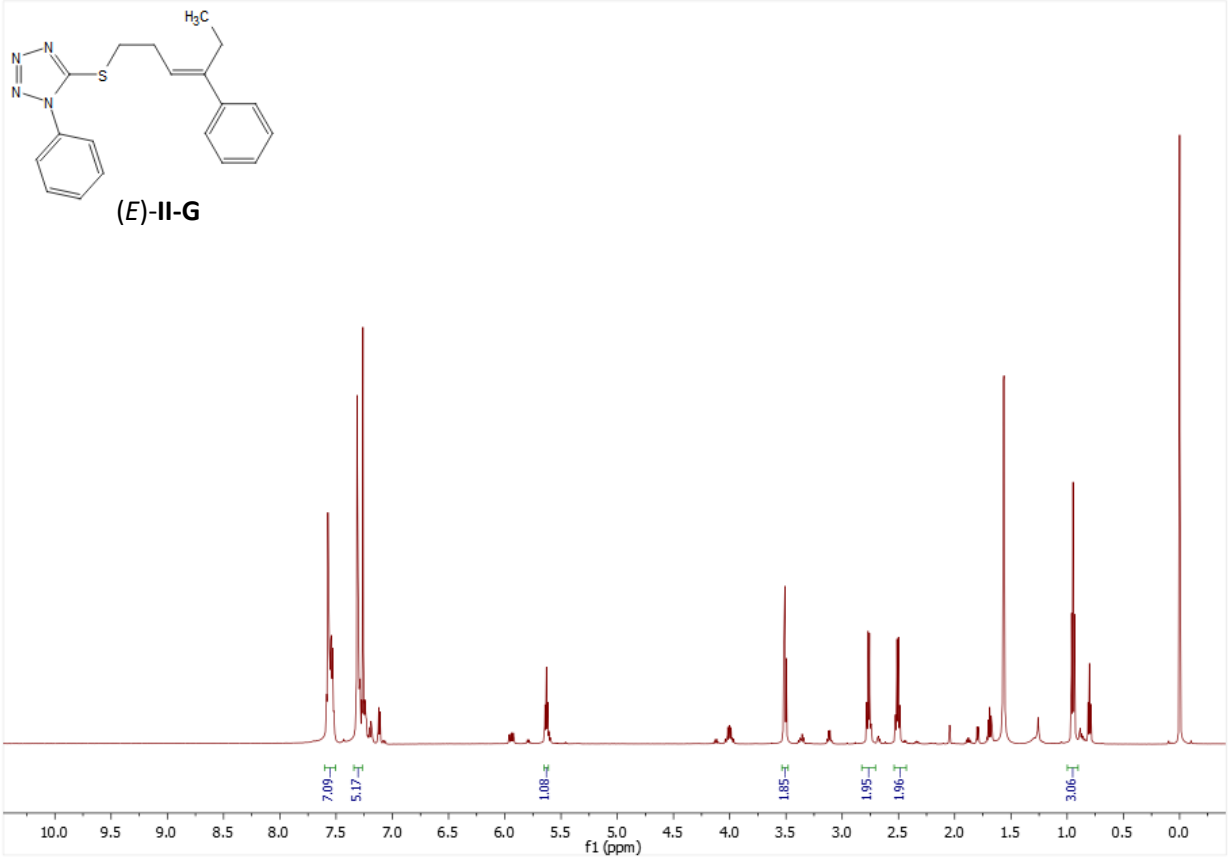
(*Z*)-**I-O**


(Z)-I-P
1.03
1.00
1.03
1.04
0.98
1.01
2.09
0.96
0.96
1.90
3.00
f1 (ppm)

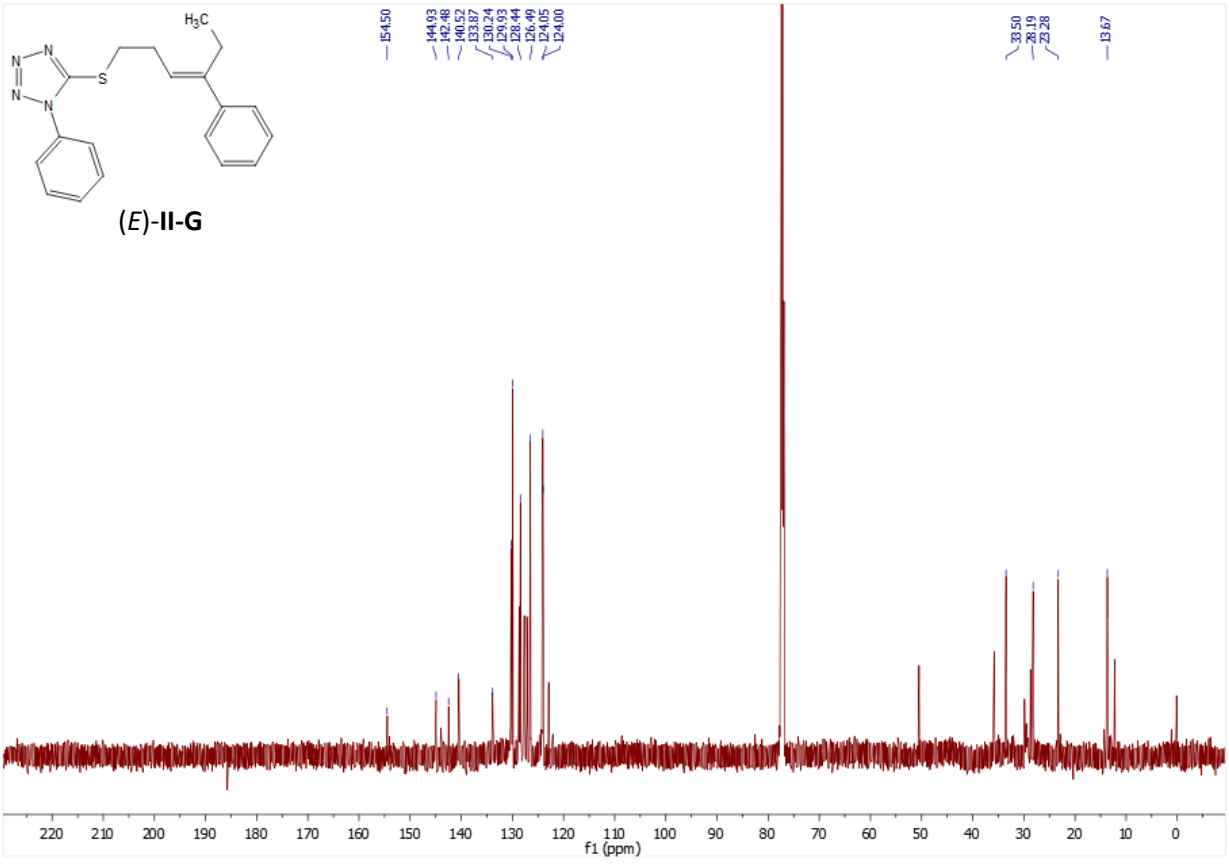

(Z)-I-P
177.80
154.07
136.13
135.40
127.06
126.28
124.15
124.04
122.42
56.54
20.73
19.80
14.19
f1 (ppm)


(Z)-I-Q
H3C
1.03
1.02
1.05
1.05
0.98
1.04
1.98
1.96
2.01
2.89
f1 (ppm)

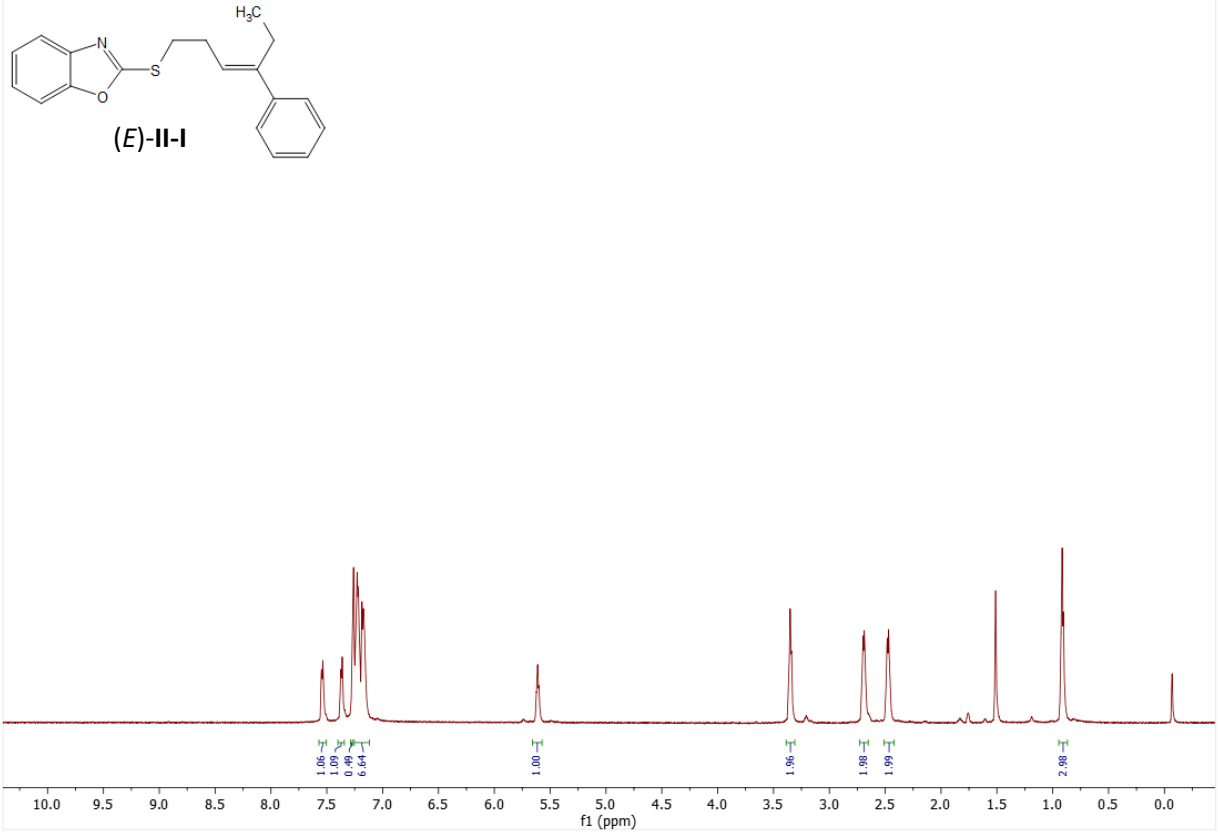

(Z)-I-Q
H3C
165.97
152.04
136.89
135.49
128.17
127.81
125.58
123.22
122.48
54.56
20.68
20.58
14.14
f1 (ppm)

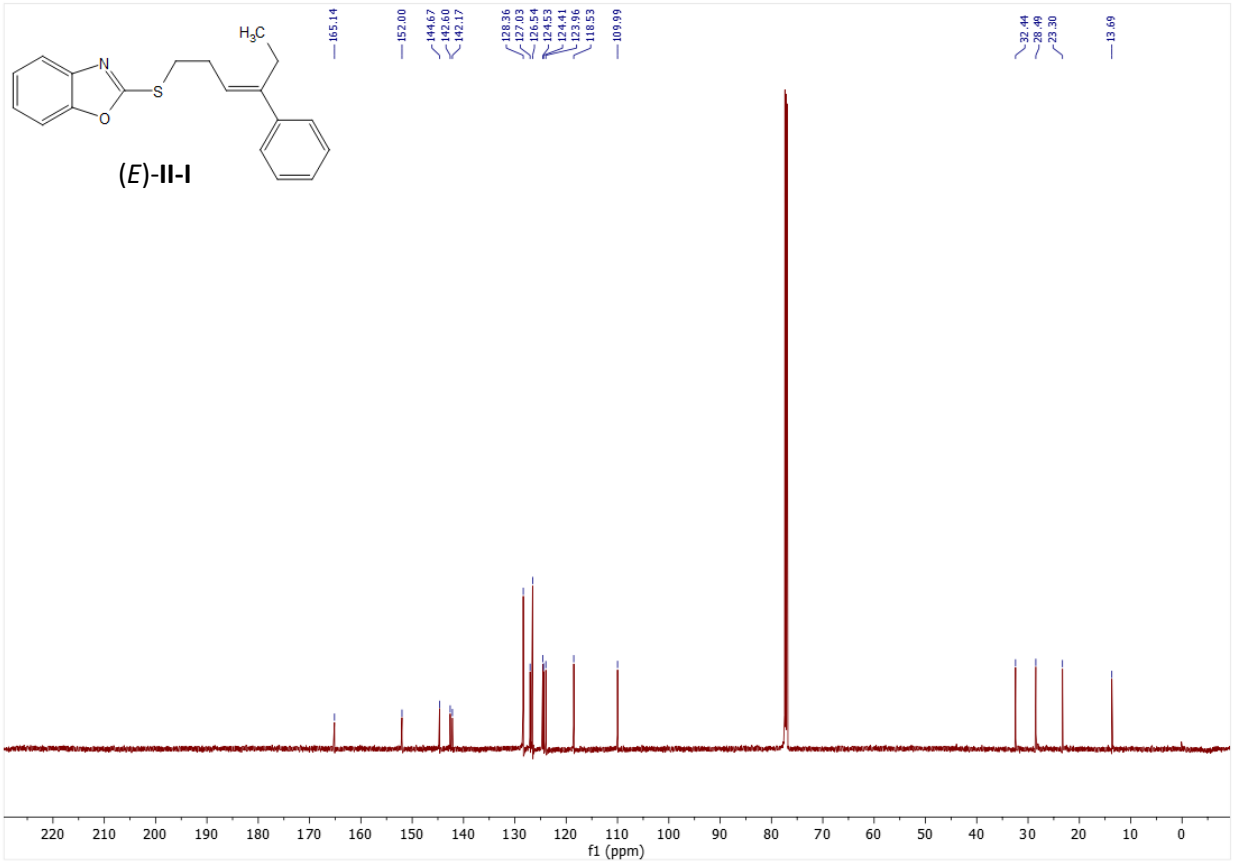

H3C
N
N
N
S
7.09
5.17
1.08
1.85
1.95
1.96
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

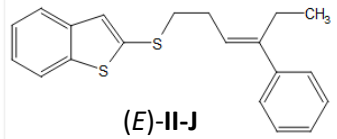
(*E*)-**II-G**


H3C
N
N
N
S
154.50
144.93
142.48
140.52
133.87
130.24
129.93
128.44
126.49
124.05
124.00
33.50
28.19
23.28
13.67
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

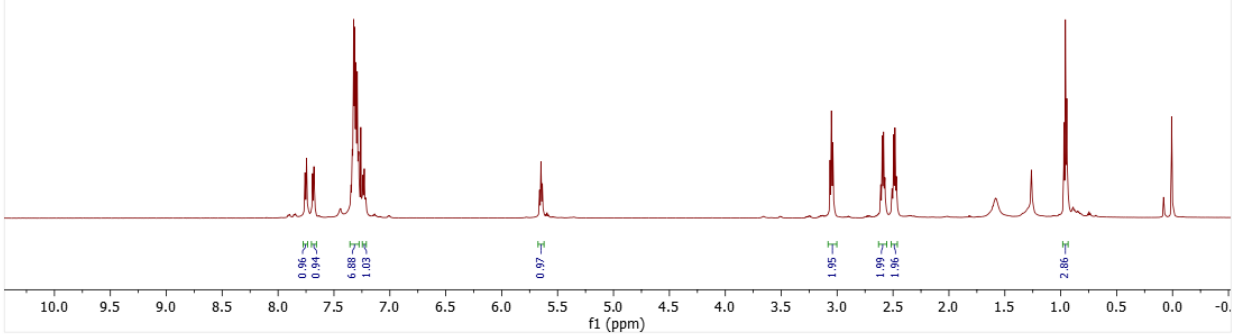
(*E*)-**II-G**

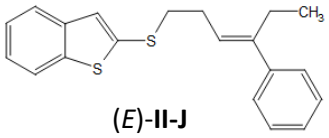

H3C
N
S
O
(E)-II-I
1.06
1.09
0.49
6.64
1.00
1.96
1.98
1.99
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


H3C
N
S
O
(E)-II-I
165.14
152.00
144.67
142.60
142.17
128.36
127.03
126.54
124.53
124.41
123.96
118.53
109.99
32.44
28.49
23.30
13.69
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



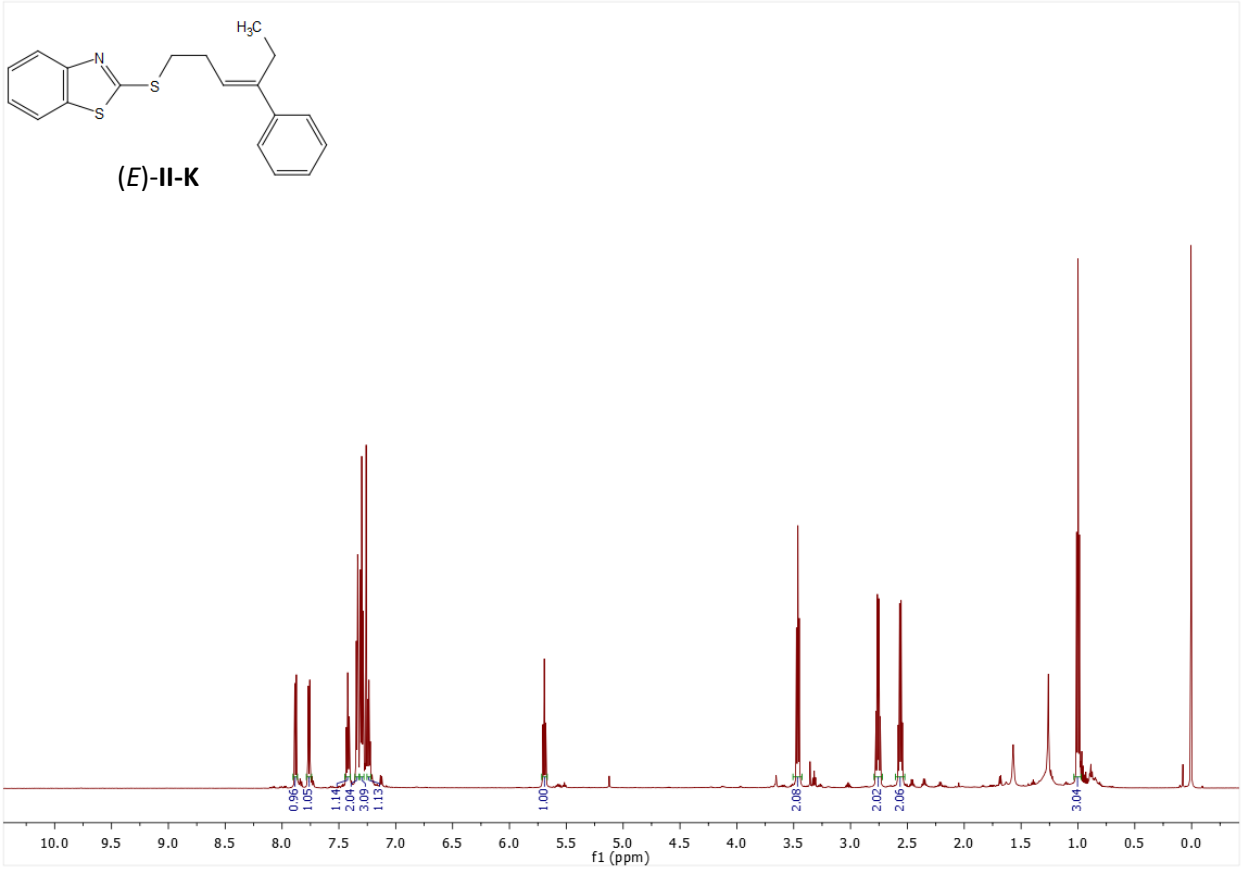
(*E*)-**II-J**

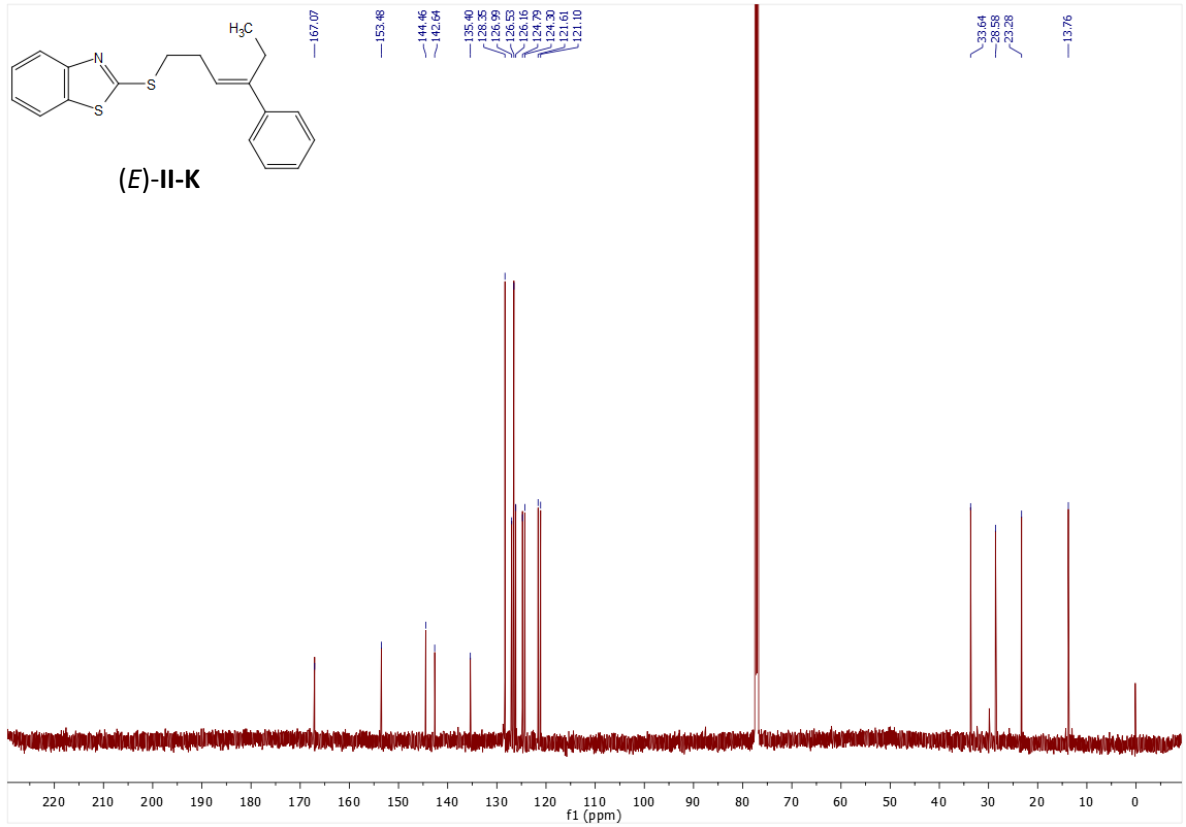

0.96
0.94
6.88
1.03
0.97
1.95
1.99
1.96
2.86
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

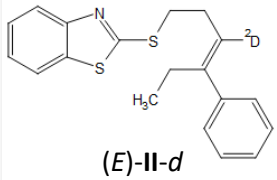


(*E*)-**II-J**

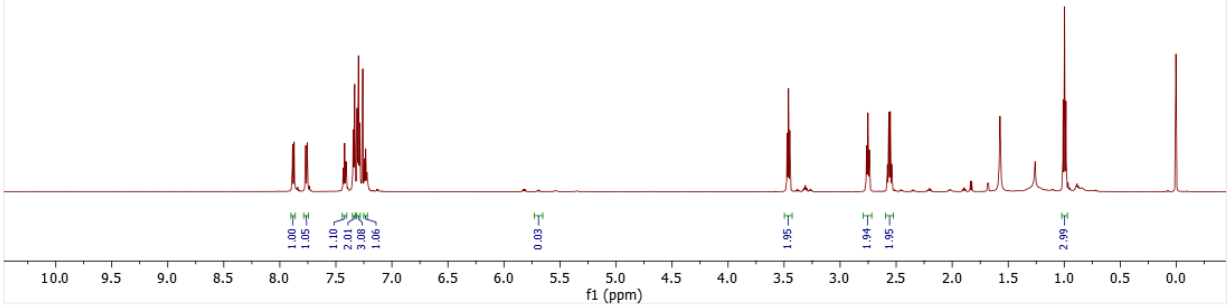
143.90
142.68
141.79
139.97
137.36
128.34
128.21
126.93
126.49
125.05
124.61
124.48
123.15
122.00
37.61
28.83
23.24
13.70
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

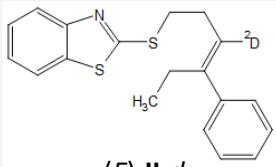

H3C
N
S
S
(E)-II-K
0.96
1.05
1.14
2.04
3.09
1.13
1.00
2.08
2.02
2.06
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


H3C
N
S
S
(E)-II-K
167.07
153.48
144.46
142.64
135.40
128.35
126.99
126.53
126.16
124.79
124.30
121.61
121.10
33.64
28.58
23.28
13.76
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


N
S
S
^{2}D
H_3C

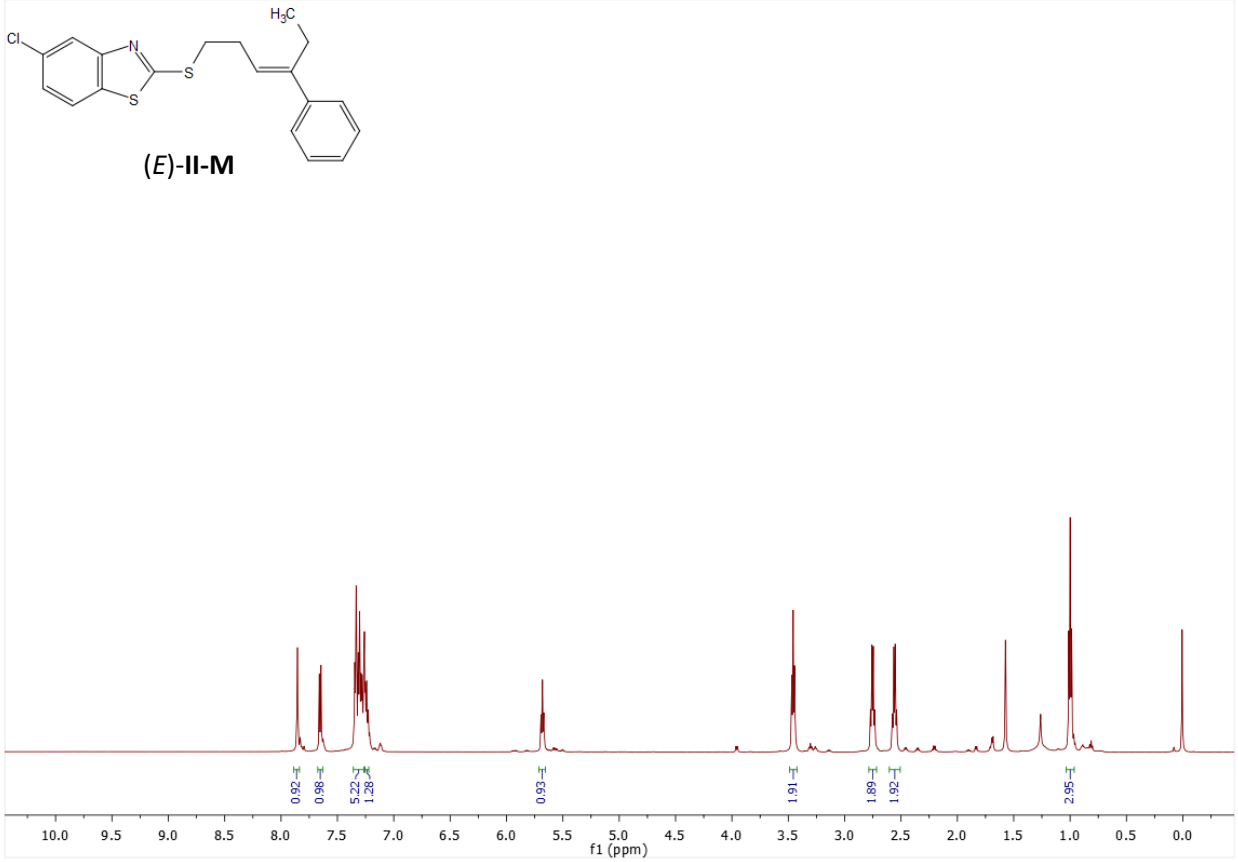
(*E*)-**II**-*d*


1.00
1.05
1.10
2.01
3.08
1.06
0.03
1.95
1.94
1.95
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

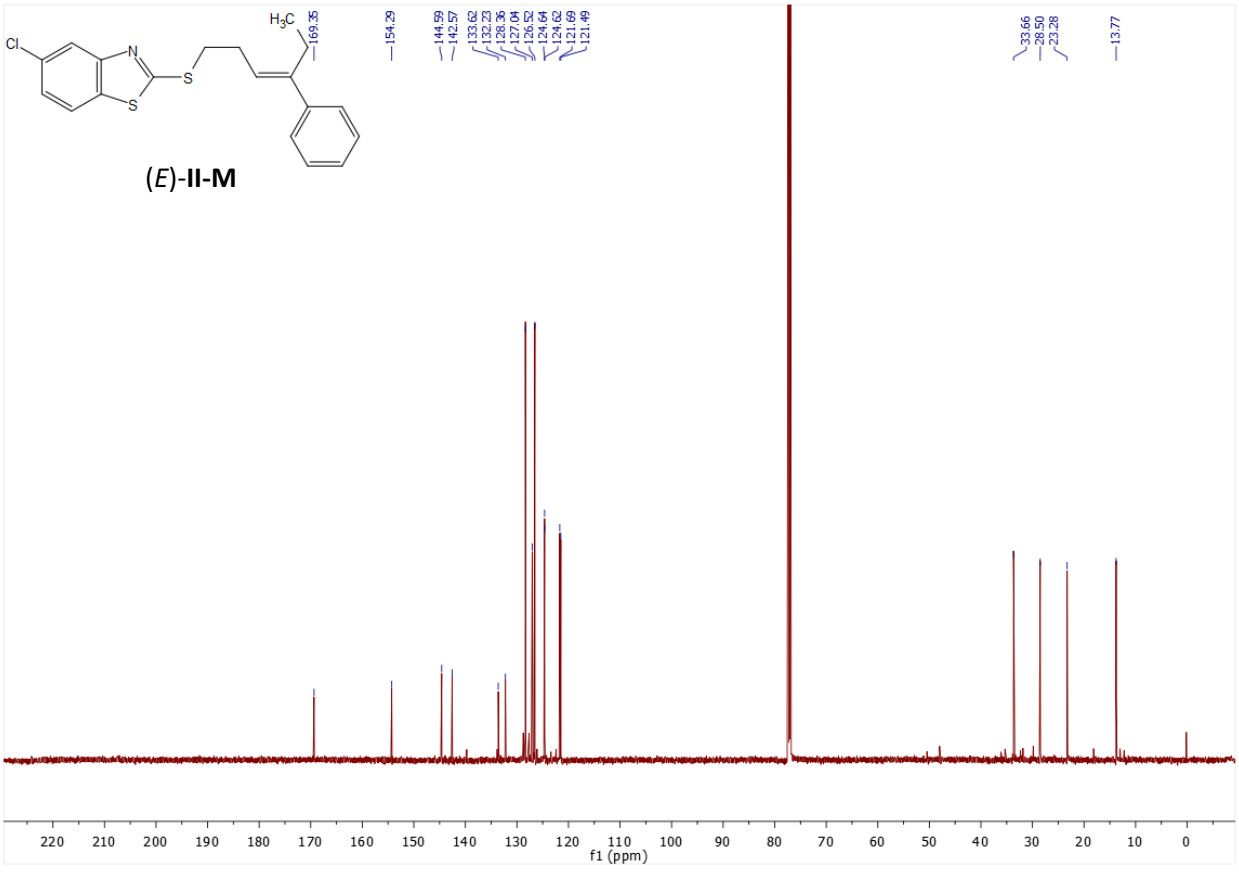

N
S
S
^{2}D
H_3C

(*E*)-**II**-*d*

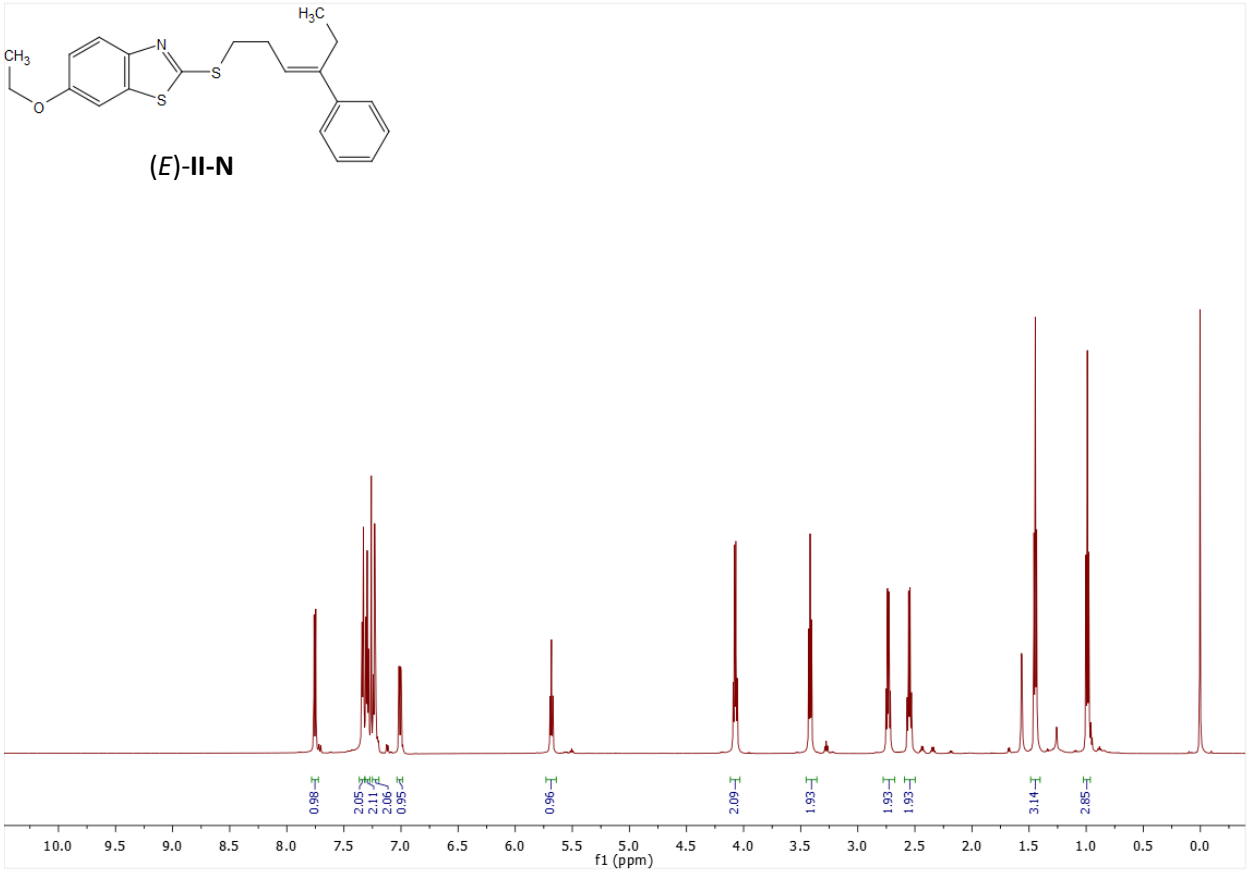
167.08
153.49
144.37
142.61
135.40
128.35
126.99
126.53
126.16
124.31
121.62
121.11
33.62
28.48
23.23
13.76
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

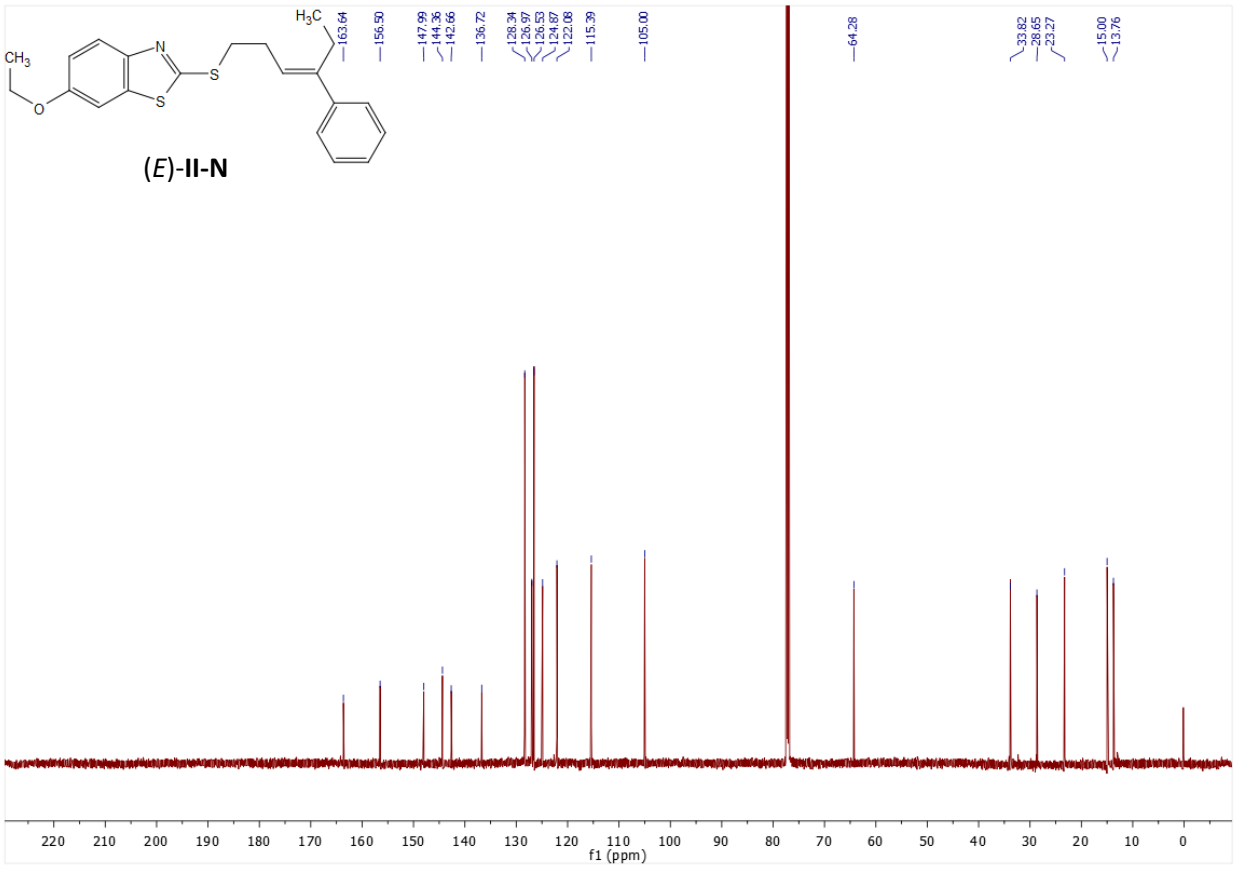

Cl
N
S
S
H3C
0.92
0.98
5.22
1.28
0.93
1.91
1.89
1.92
2.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

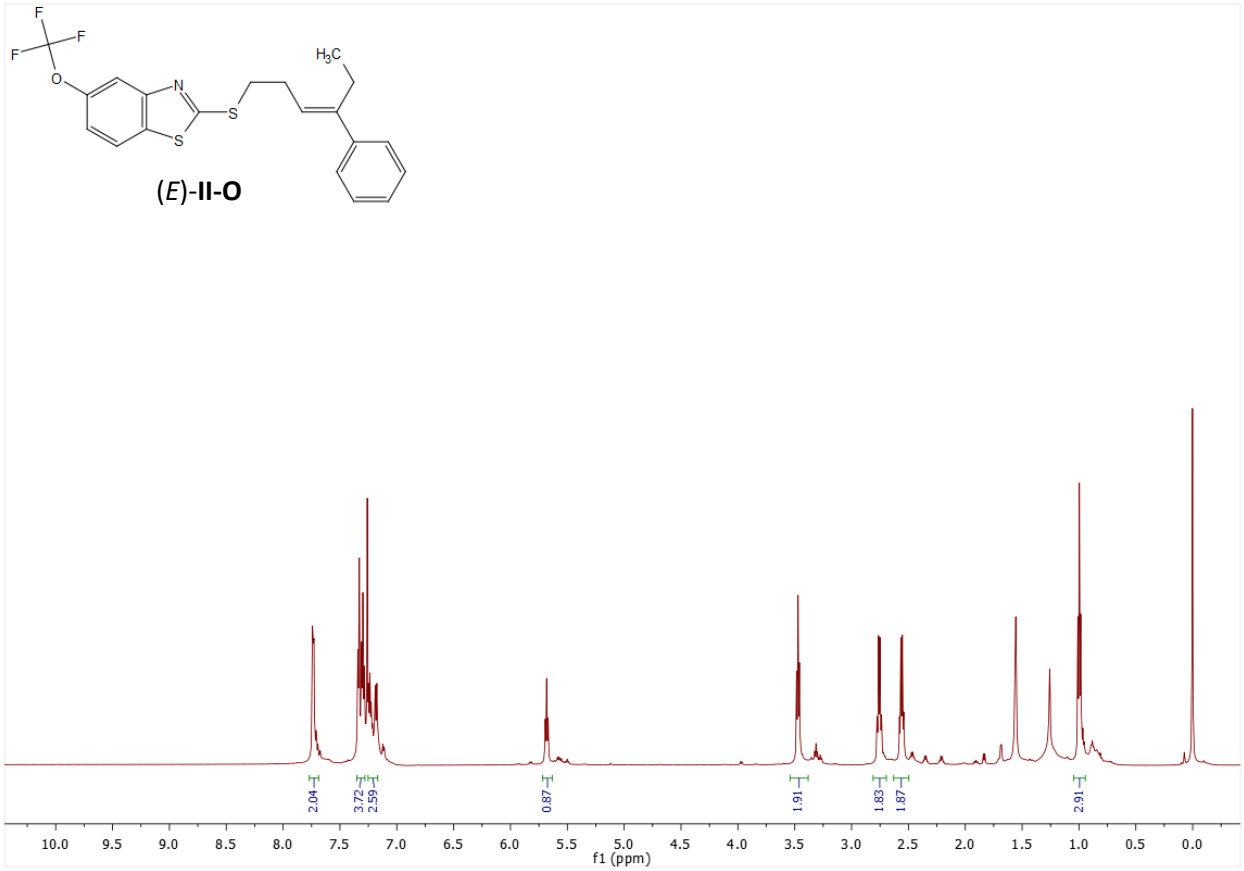
(*E*)-**II-M**

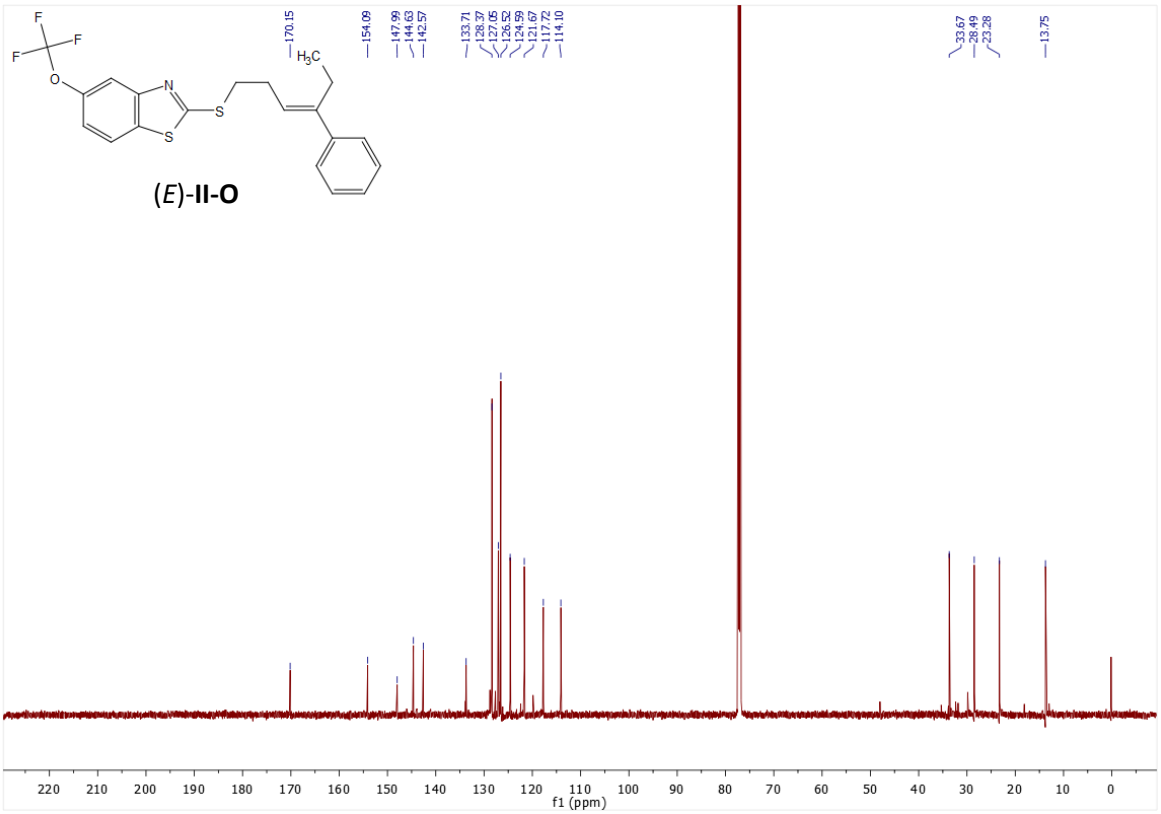

Cl
N
S
S
H3C
169.35
154.29
144.59
142.57
133.62
132.23
128.36
127.04
126.52
124.64
124.62
121.69
121.49
33.66
28.50
23.28
13.77
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

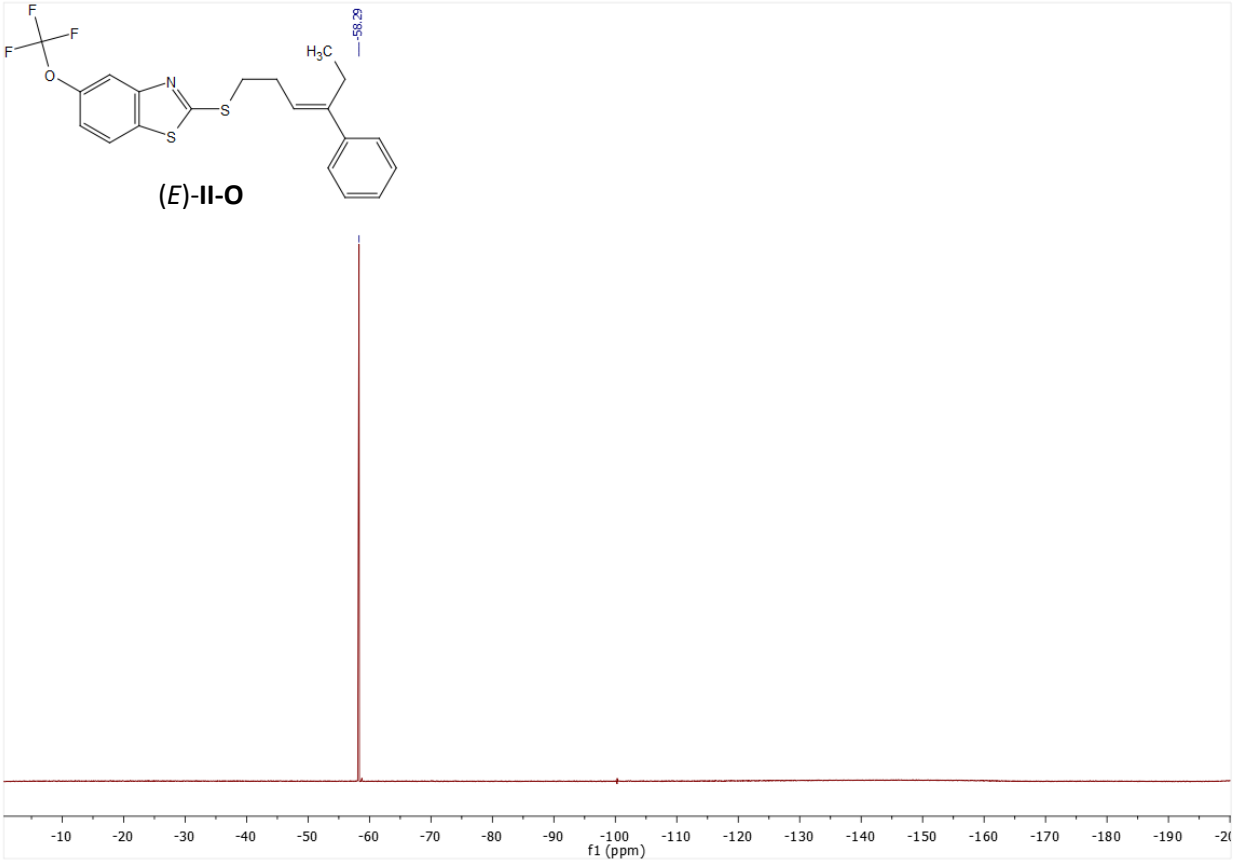
(*E*)-**II-M**


(E)-II-N
0.98
2.05
2.11
2.06
0.95
0.96
2.09
1.93
1.93
1.93
3.14
2.85
f1 (ppm)

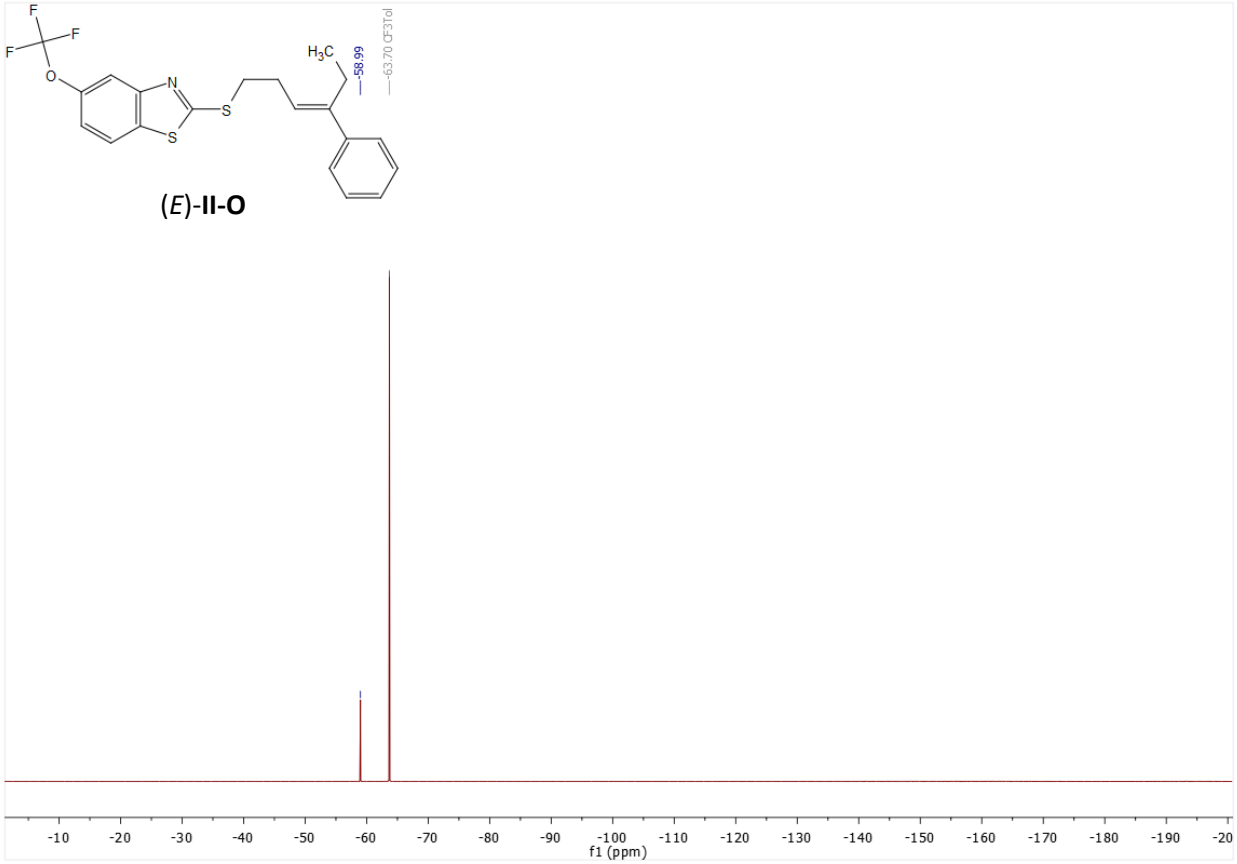

(E)-II-N
163.64
156.50
147.99
144.36
142.66
136.72
128.34
126.97
126.53
124.87
122.08
115.39
105.00
64.28
33.82
28.65
23.27
15.00
13.76
f1 (ppm)


F
F
F
O
N
S
S
H3C
(E)-II-O
2.04
3.72
2.59
0.87
1.91
1.83
1.87
2.91
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

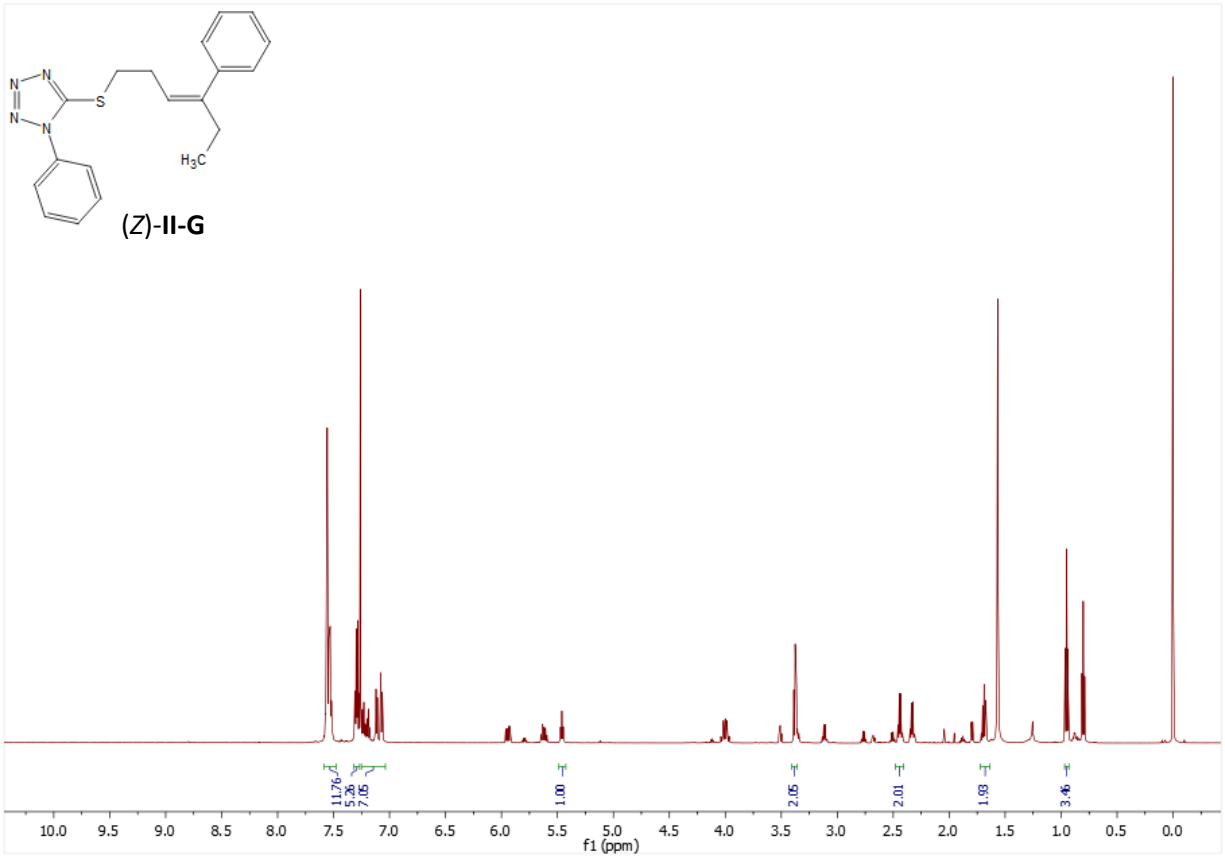

F
F
F
O
N
S
S
H3C
(E)-II-O
170.15
154.09
147.99
144.63
142.57
133.71
128.37
127.05
126.52
124.59
121.67
117.72
114.10
33.67
28.49
23.28
13.75
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

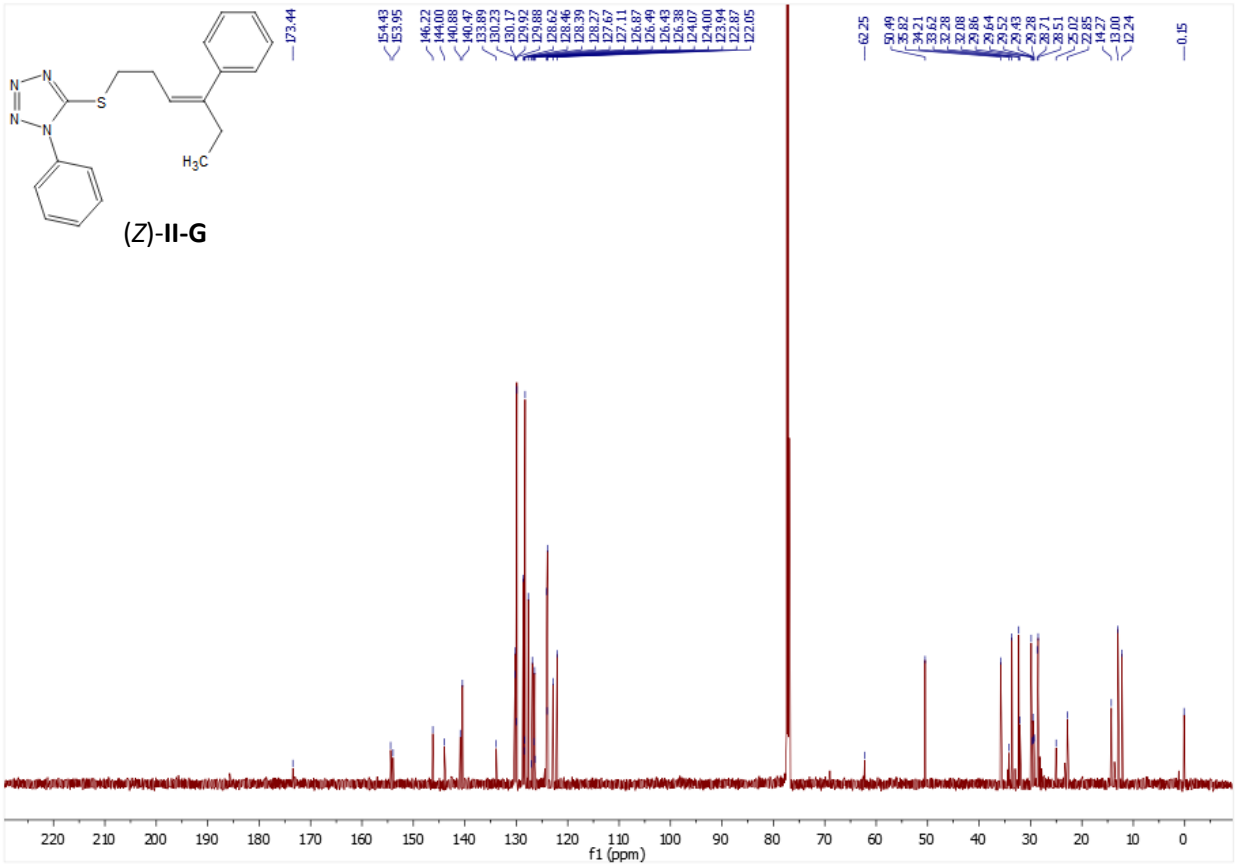

F
F
F
O
N
S
S
H3C
-58.29
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

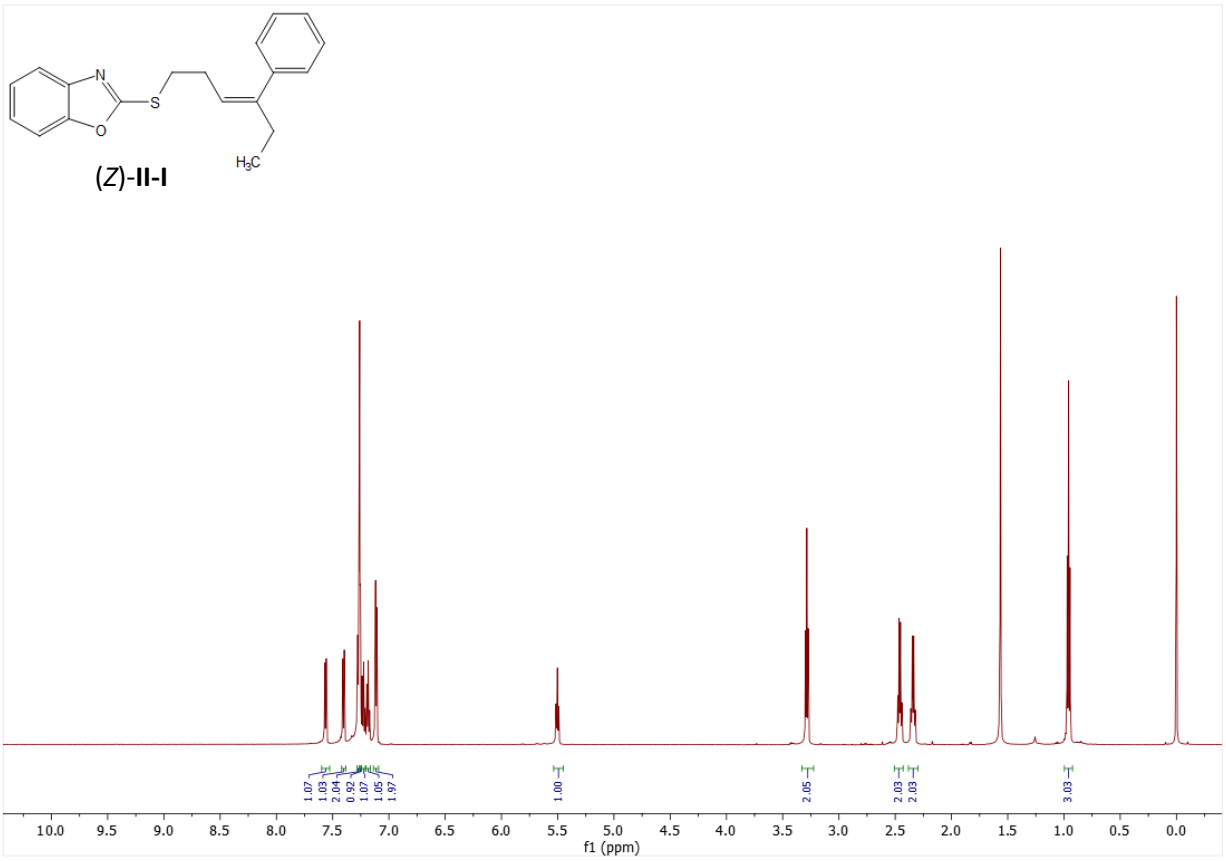
(*E*)-**II-O**


F
F
F
O
N
S
S
H3C
-58.99
-63.70 CF3Tol
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

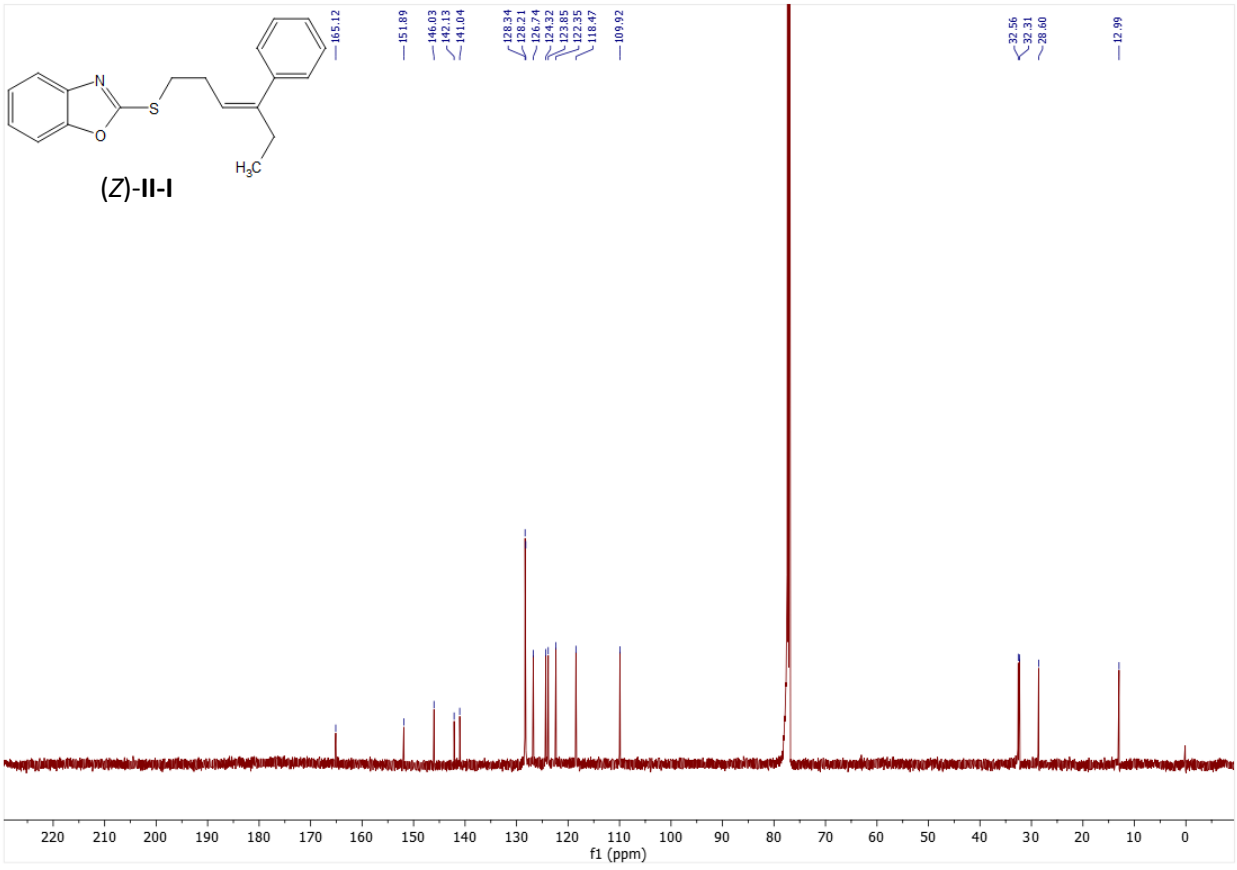
(*E*)-**II-O**


(Z)-II-G
11.76
5.26
7.05
1.00
2.05
2.01
1.93
3.46
f1 (ppm)

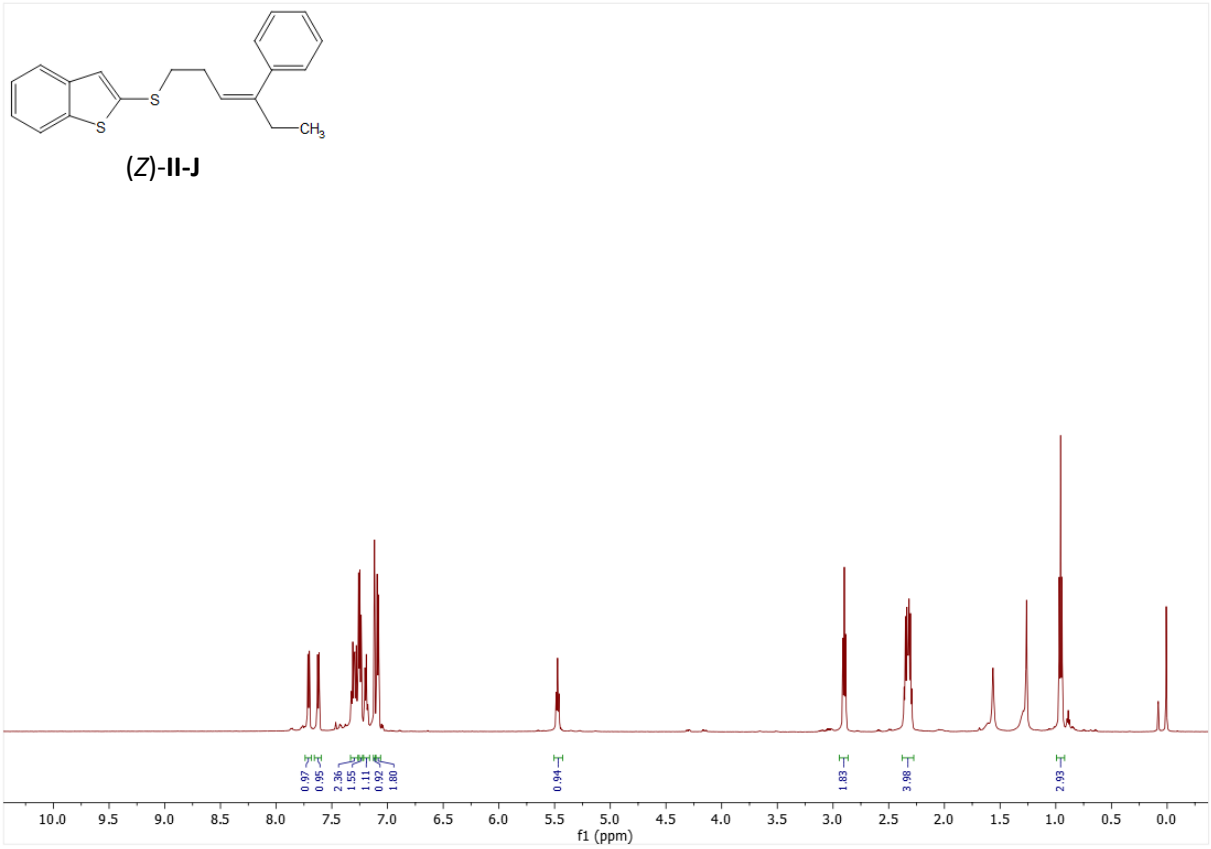

(Z)-II-G
f1 (ppm)


N
S
O
H3C
1.07
1.03
2.04
0.92
1.07
1.05
1.97
1.00
2.05
2.03
2.03
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

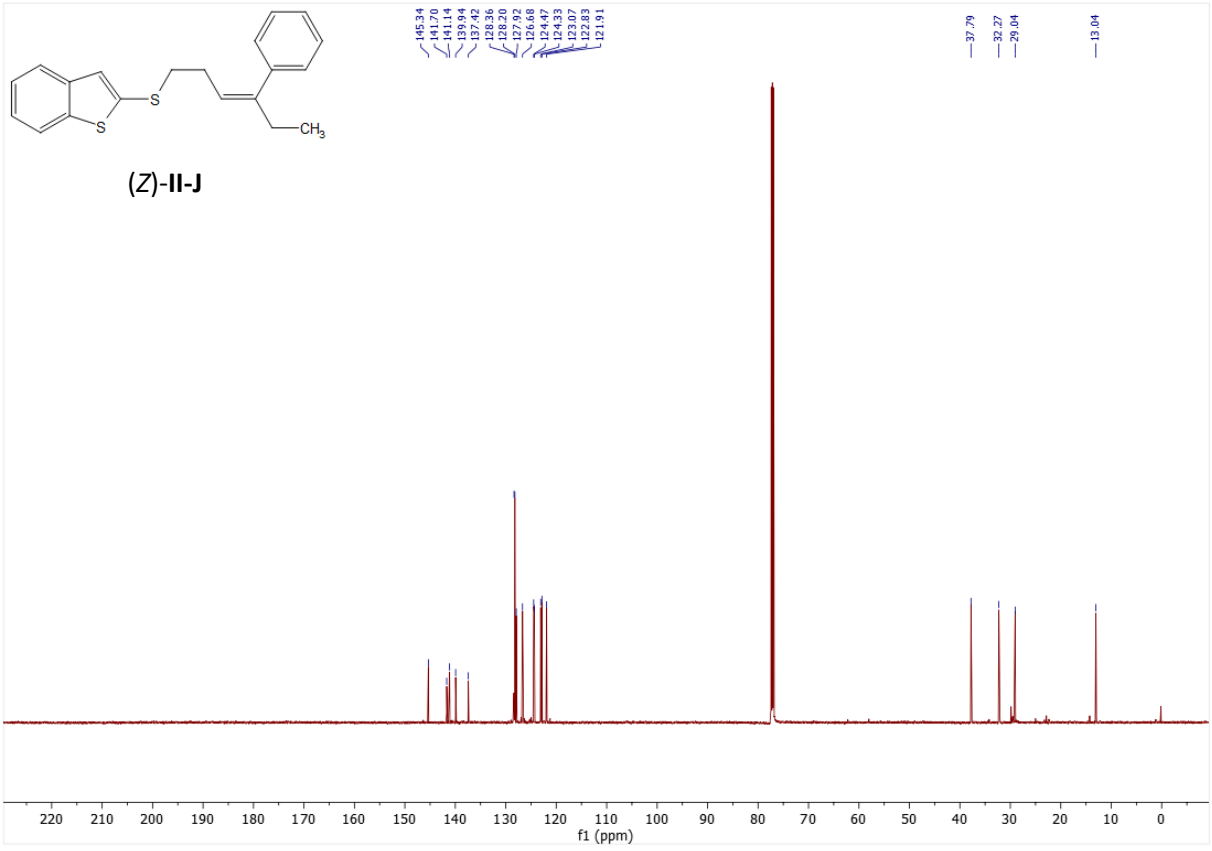
(*Z*)-**II-I**


165.12
151.89
146.03
142.13
141.04
128.34
128.21
126.74
124.32
123.85
122.35
118.47
109.92
32.56
32.31
28.60
12.99
N
S
O
H3C
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

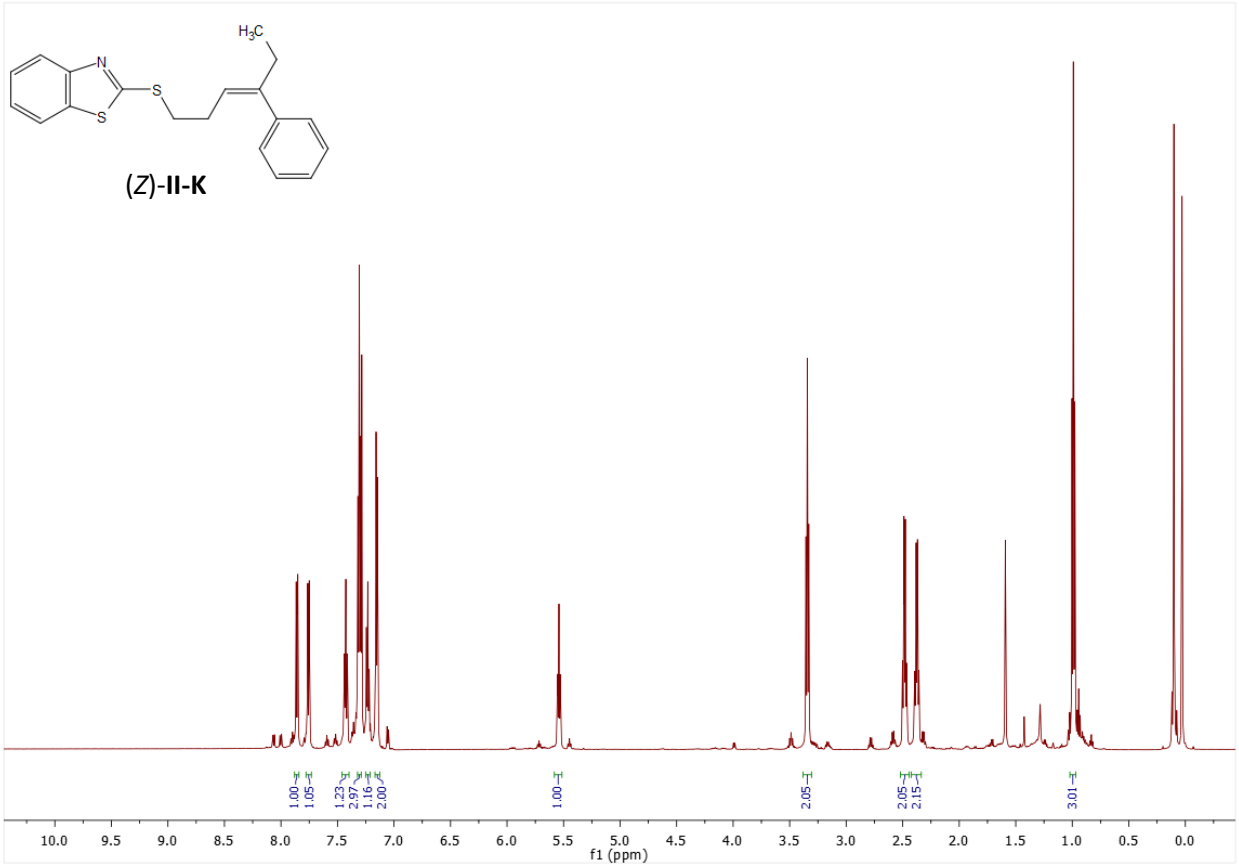
(*Z*)-**II-I**

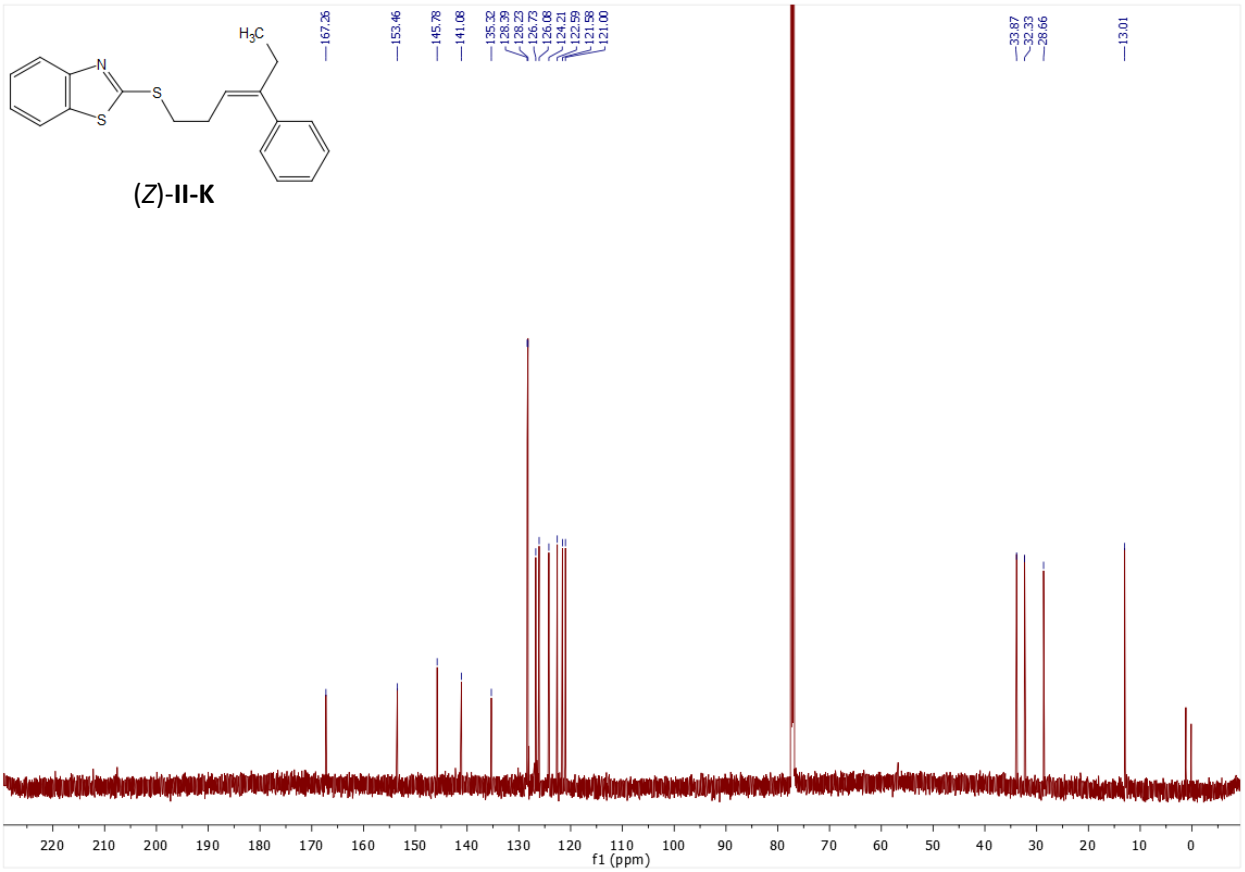

S
S
CH3
0.97
0.95
2.36
1.55
1.11
0.92
1.80
0.94
1.83
3.98
2.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

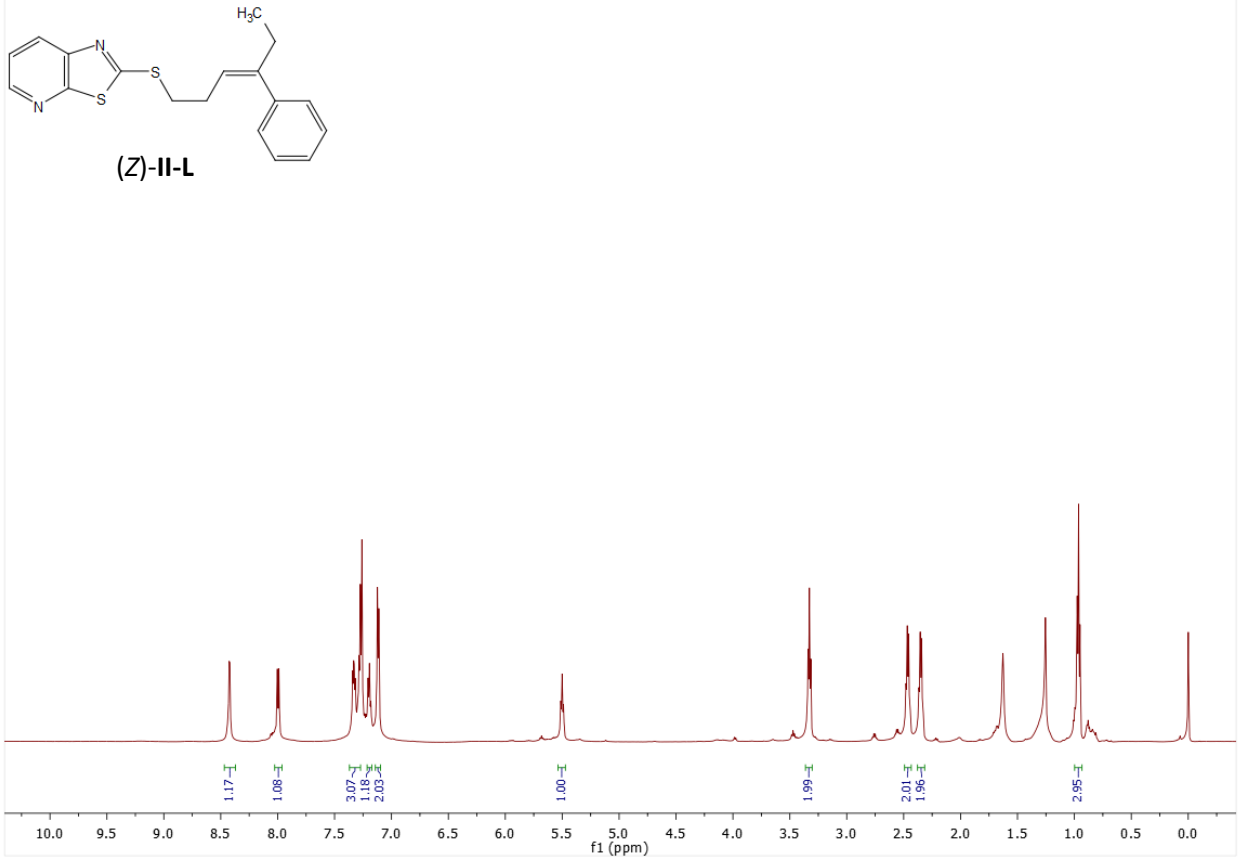
(*Z*)-**II-J**


S
S
CH3
145.34
141.70
141.14
139.94
137.42
128.36
128.20
127.92
126.68
124.47
124.33
123.07
122.83
121.91
37.79
32.27
29.04
13.04
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

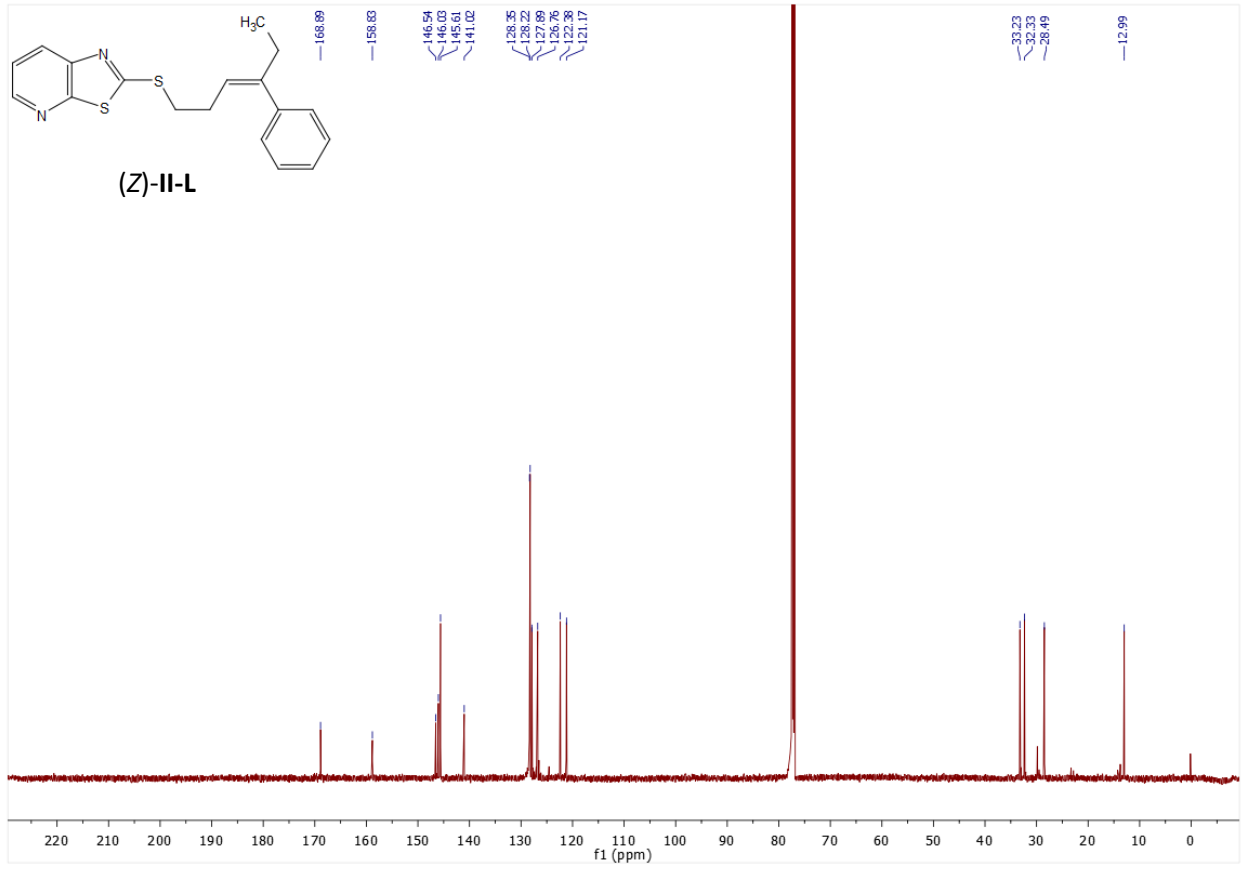
(*Z*)-**II-J**


H3C
N
S
S
(Z)-II-K
1.00
1.05
1.23
2.97
1.16
2.00
1.00
2.05
2.05
2.15
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

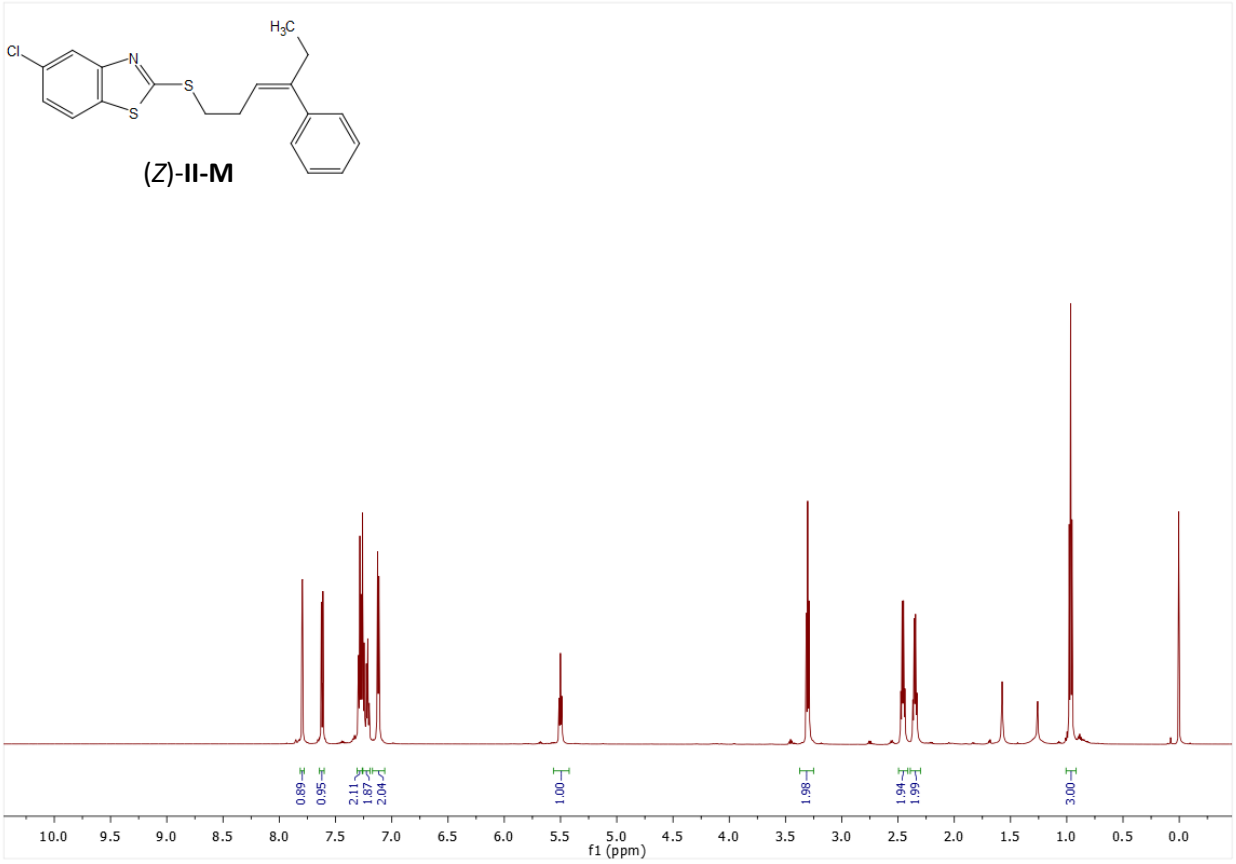

H3C
N
S
S
(Z)-II-K
167.26
153.46
145.78
141.08
135.32
128.39
128.23
126.73
126.08
124.21
122.59
121.38
121.00
33.87
32.33
28.66
13.01
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

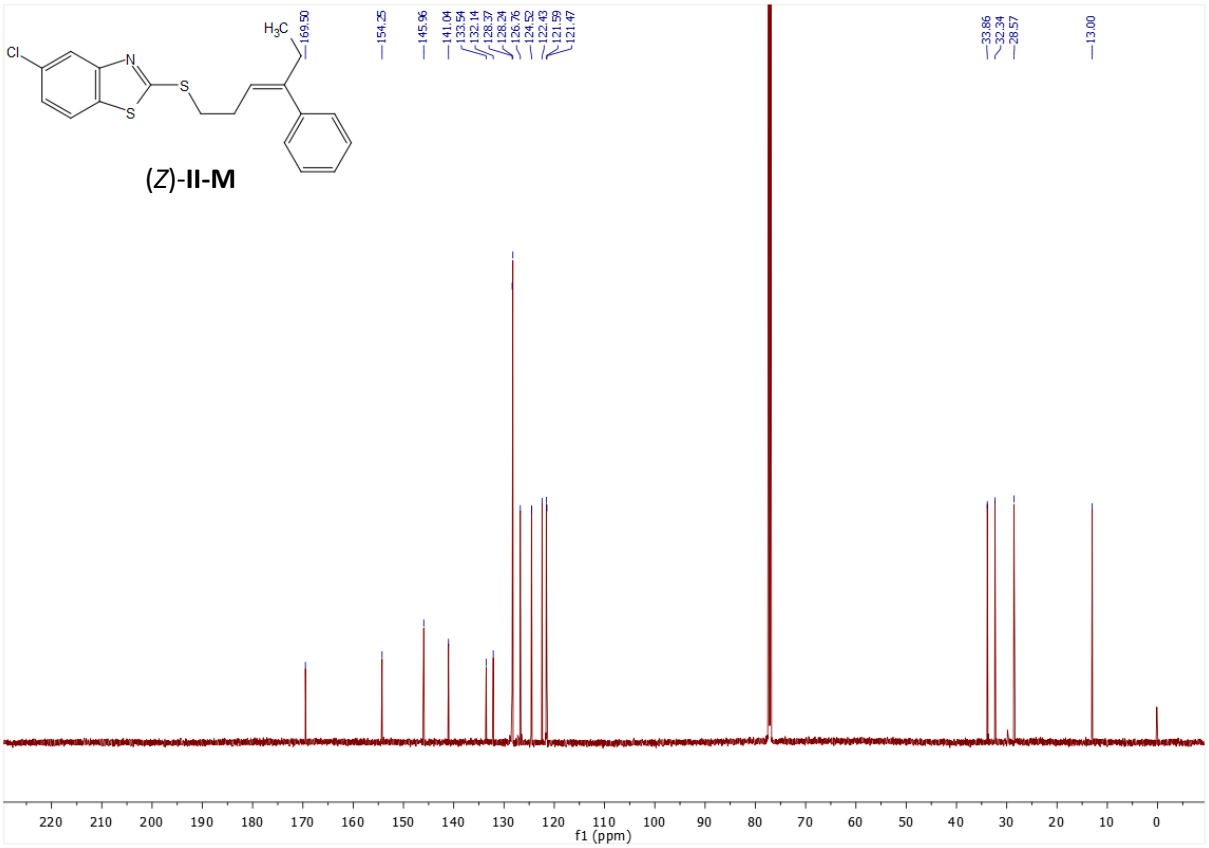

H3C
N
S
S
N
1.17
1.08
3.07
1.18
2.03
1.00
1.99
2.01
1.96
2.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

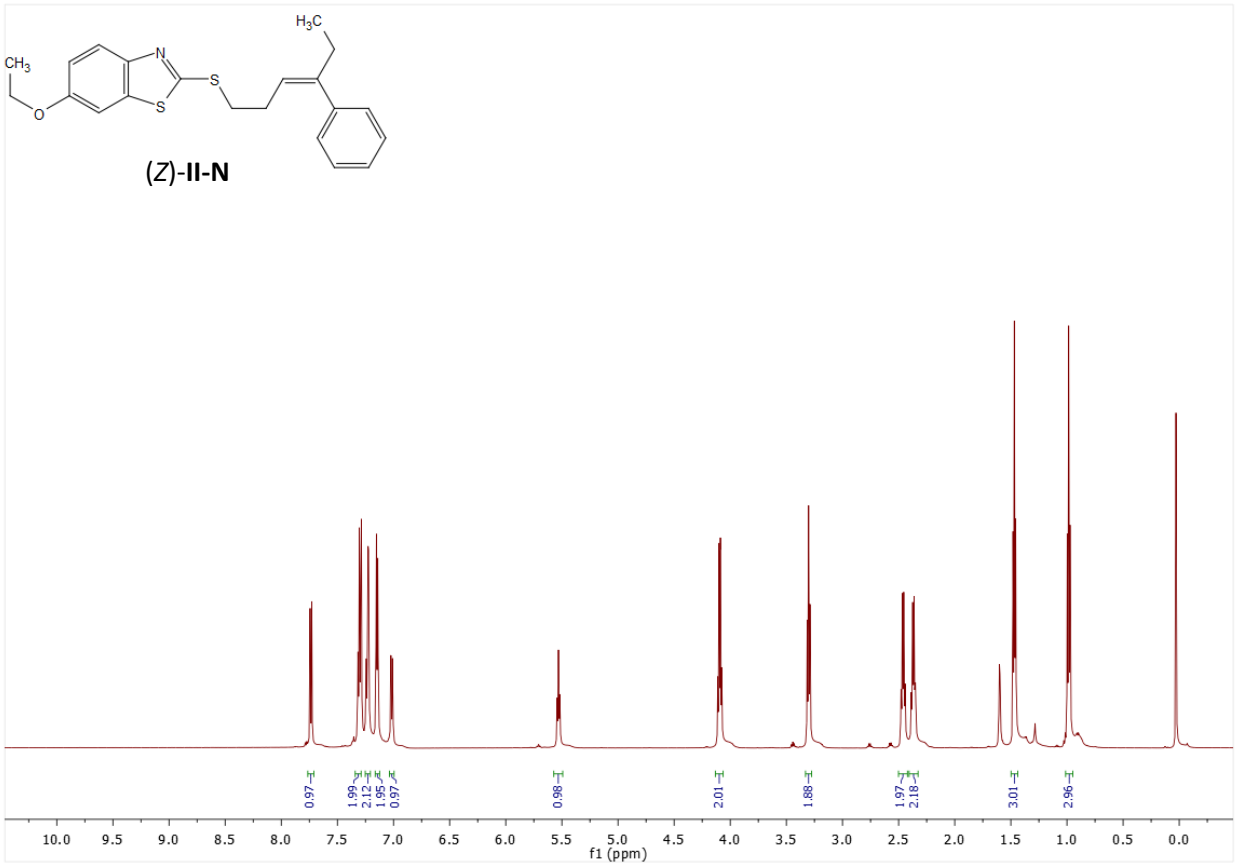
(*Z*)-**II-L**

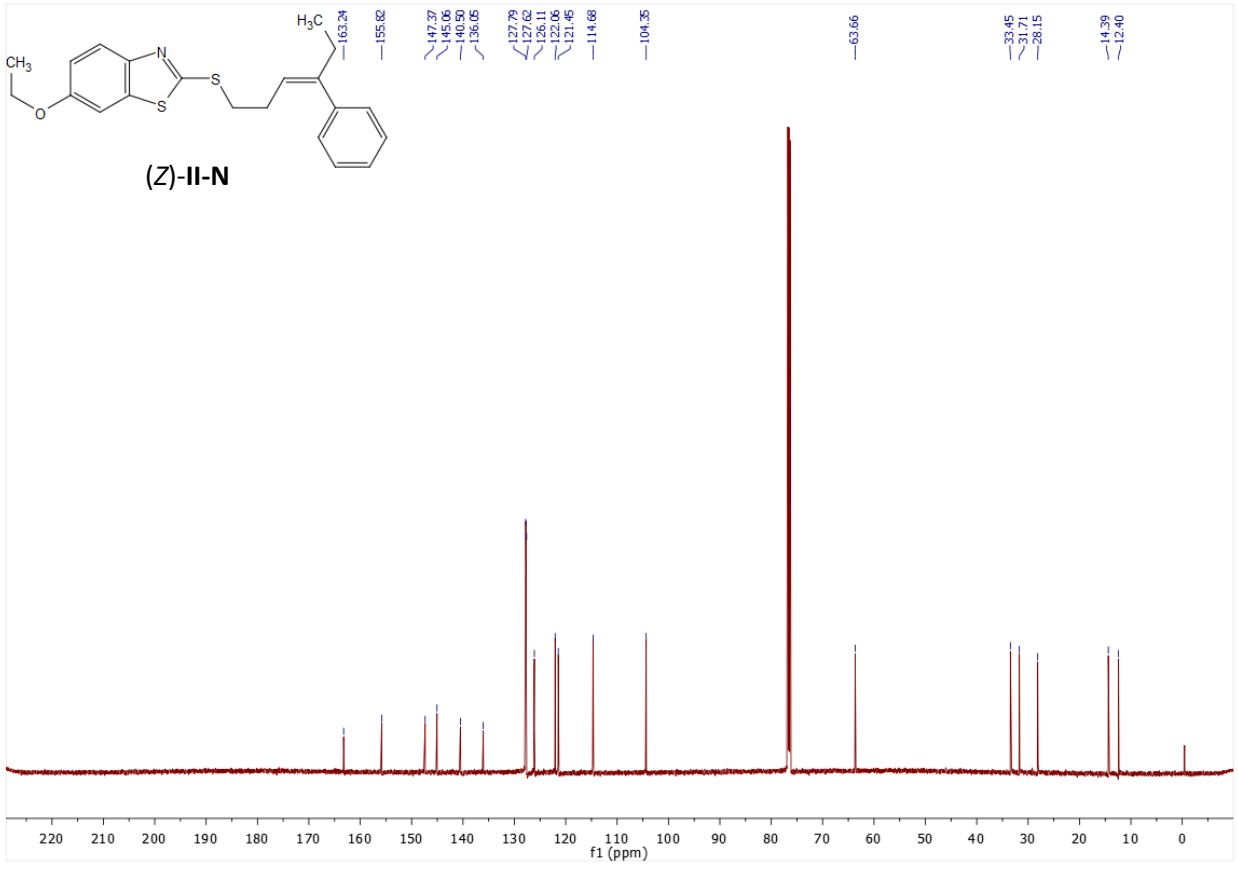

H3C
N
S
S
N
168.89
158.83
146.54
146.03
145.61
141.02
128.35
128.22
127.89
126.76
122.38
121.17
33.23
32.33
28.49
12.99
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

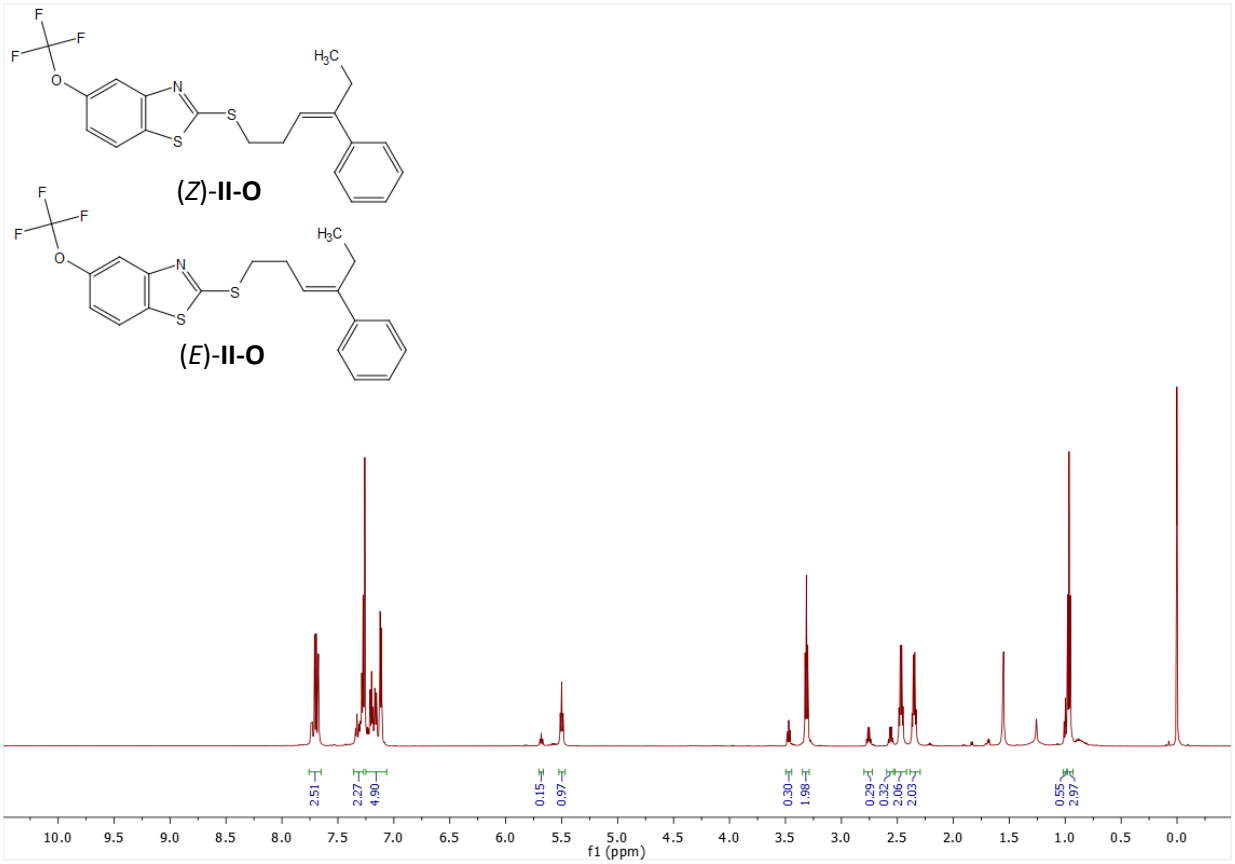
(*Z*)-**II-L**

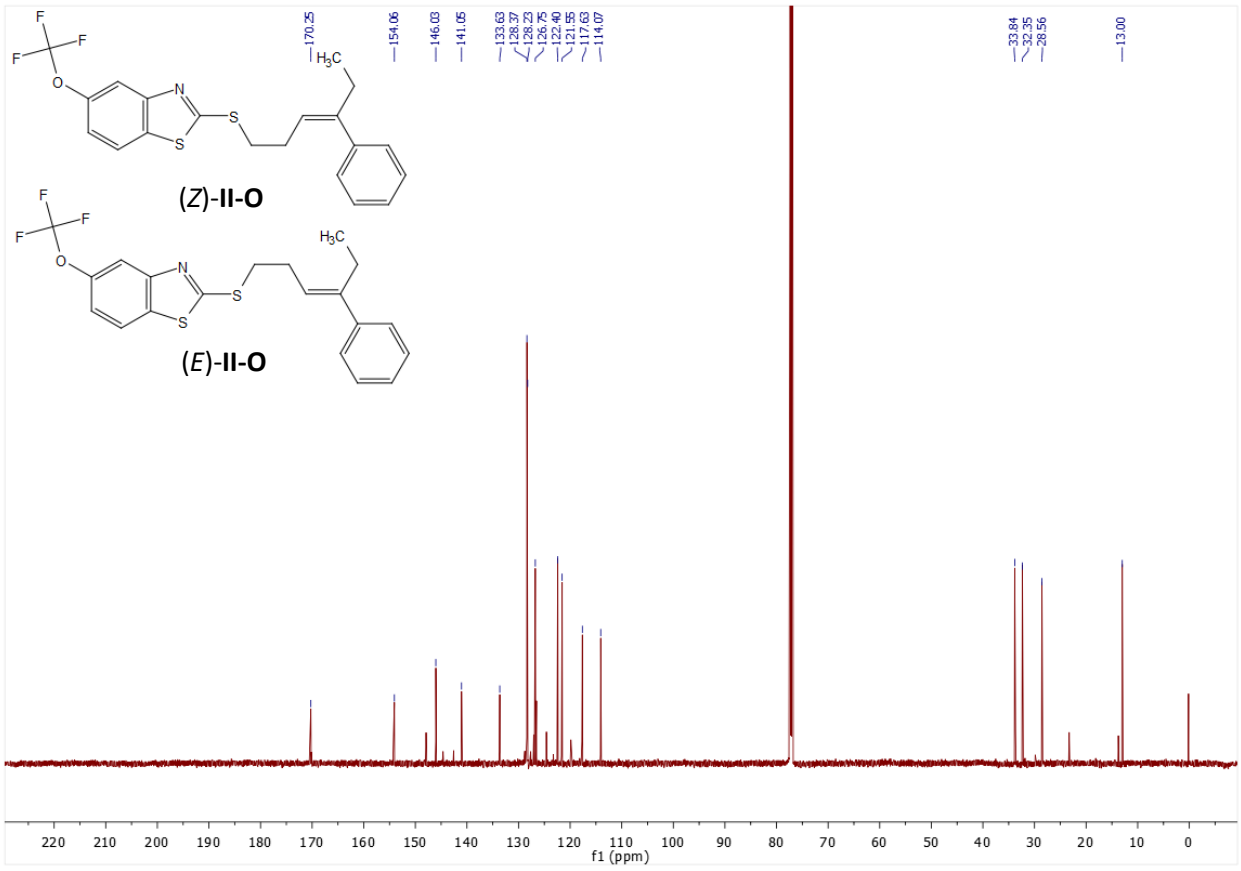

Cl
N
S
S
H3C
(Z)-II-M
0.89
0.95
2.11
1.87
2.04
1.00
1.98
1.94
1.99
3.00
f1 (ppm)

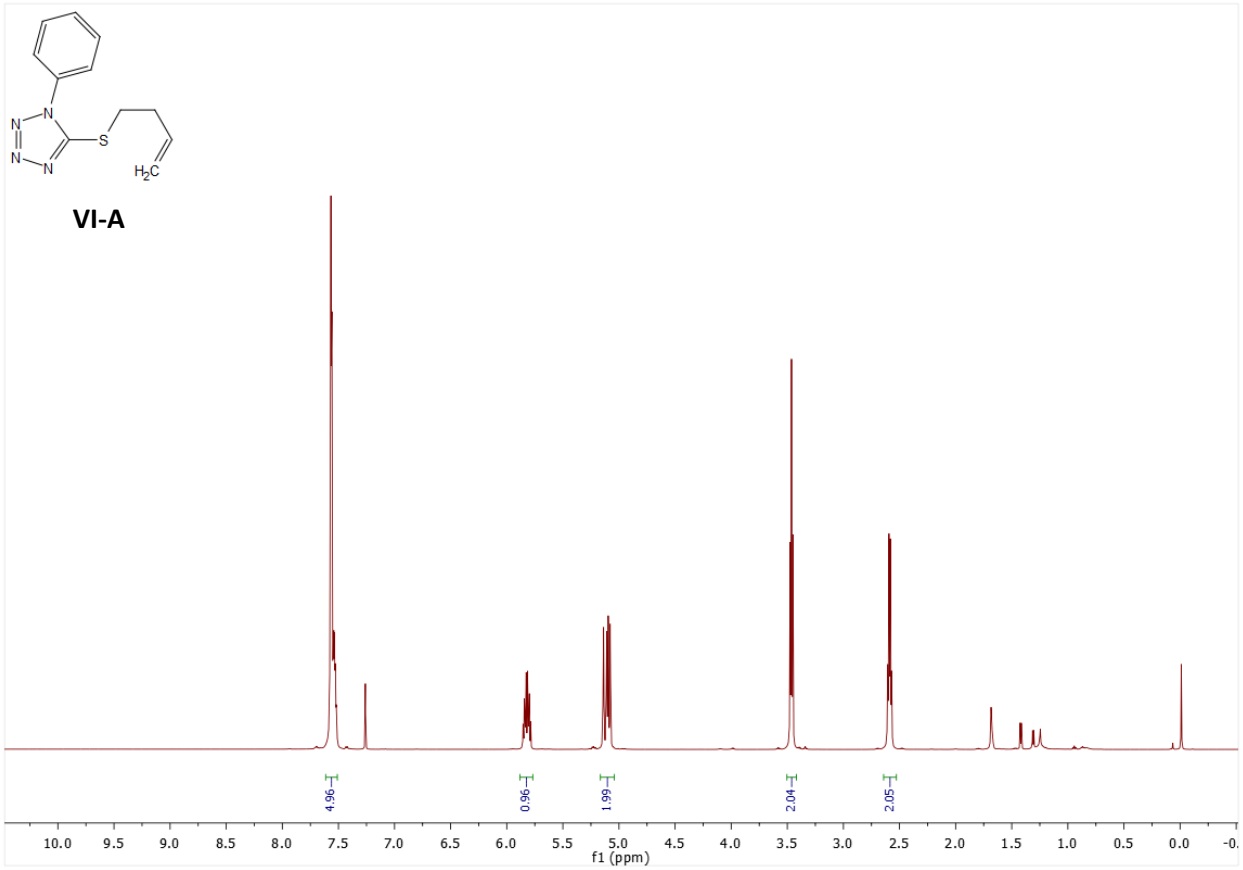

Cl
N
S
S
H3C
(Z)-II-M
169.50
154.25
145.96
141.04
133.54
132.14
128.37
128.24
126.76
124.52
122.43
121.59
121.47
33.86
32.34
28.57
13.00
f1 (ppm)

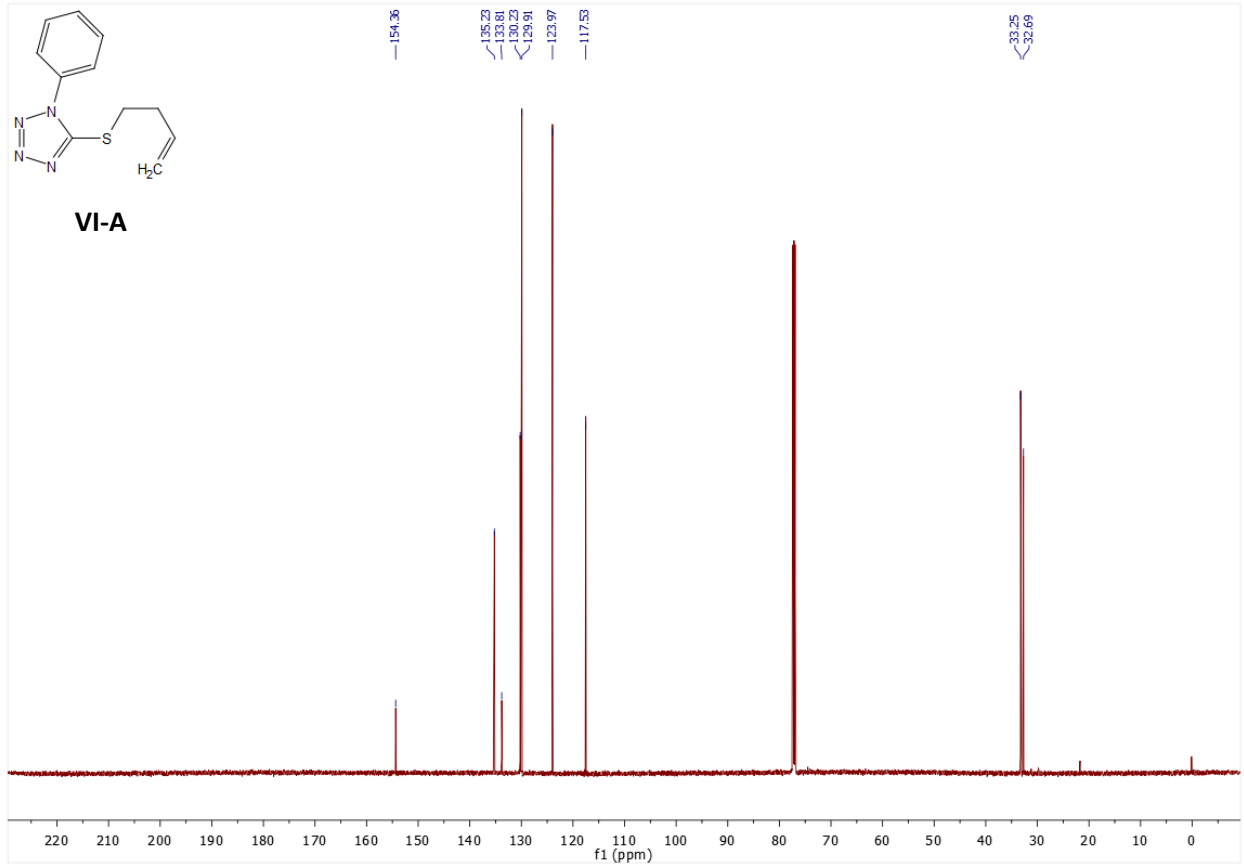

H3C
CH3
N
S
S
O
(Z)-II-N
0.97
1.99
2.12
1.95
0.97
0.98
2.01
1.88
1.97
2.18
3.01
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

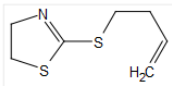

H3C
CH3
N
S
S
O
(Z)-II-N
163.24
155.82
147.37
145.06
140.50
136.05
127.79
127.62
126.11
122.06
121.45
114.68
104.35
63.66
33.45
31.71
28.15
14.39
12.40
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


(Z)-II-O
(E)-II-O
2.51
2.27
4.90
0.15
0.97
0.30
1.98
0.29
0.32
2.06
2.03
0.55
2.97
f1 (ppm)

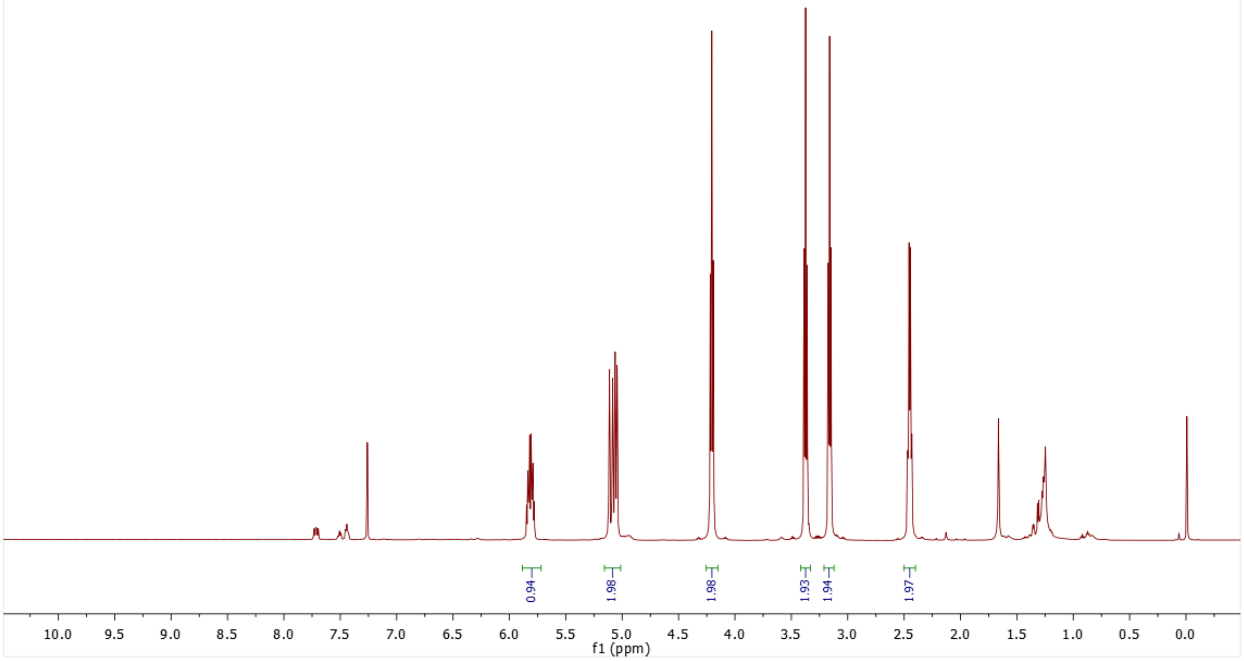

(Z)-II-O
(E)-II-O
170.25
154.06
146.03
141.05
133.63
128.37
128.23
126.75
122.40
121.55
117.63
114.07
33.84
32.35
28.56
13.00
f1 (ppm)

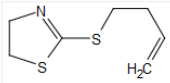

VI-A
4.96
0.96
1.99
2.04
2.05
f1 (ppm)


VI-A
154.36
135.23
133.81
130.23
129.91
123.97
117.53
33.25
32.69
f1 (ppm)



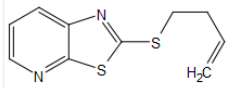
VI-B


0.94
1.98
1.98
1.93
1.94
1.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

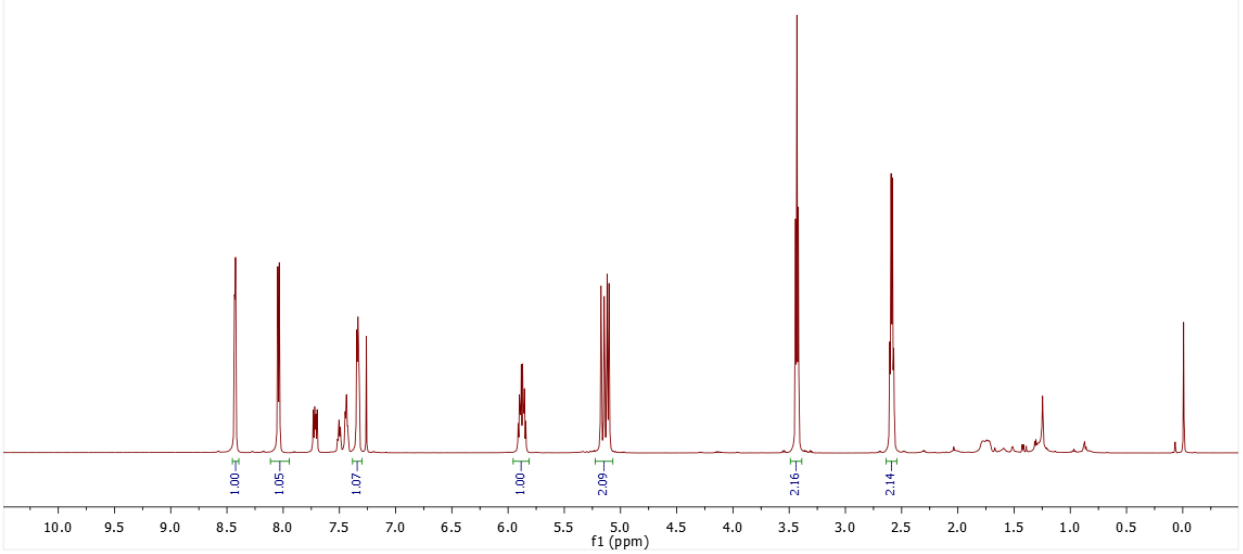


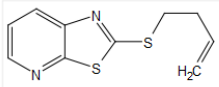
VI-B

136.05
116.70
64.45
35.52
33.52
32.06
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



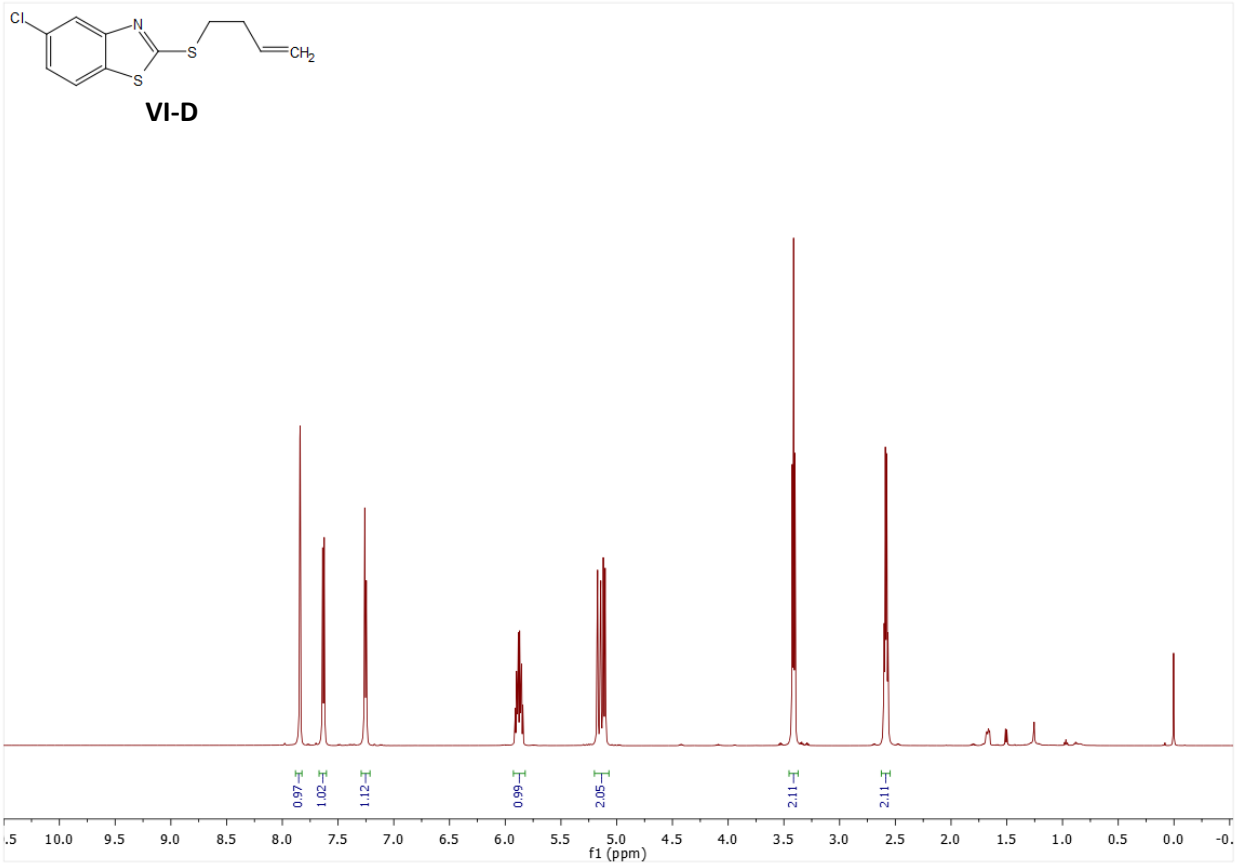
VI-C

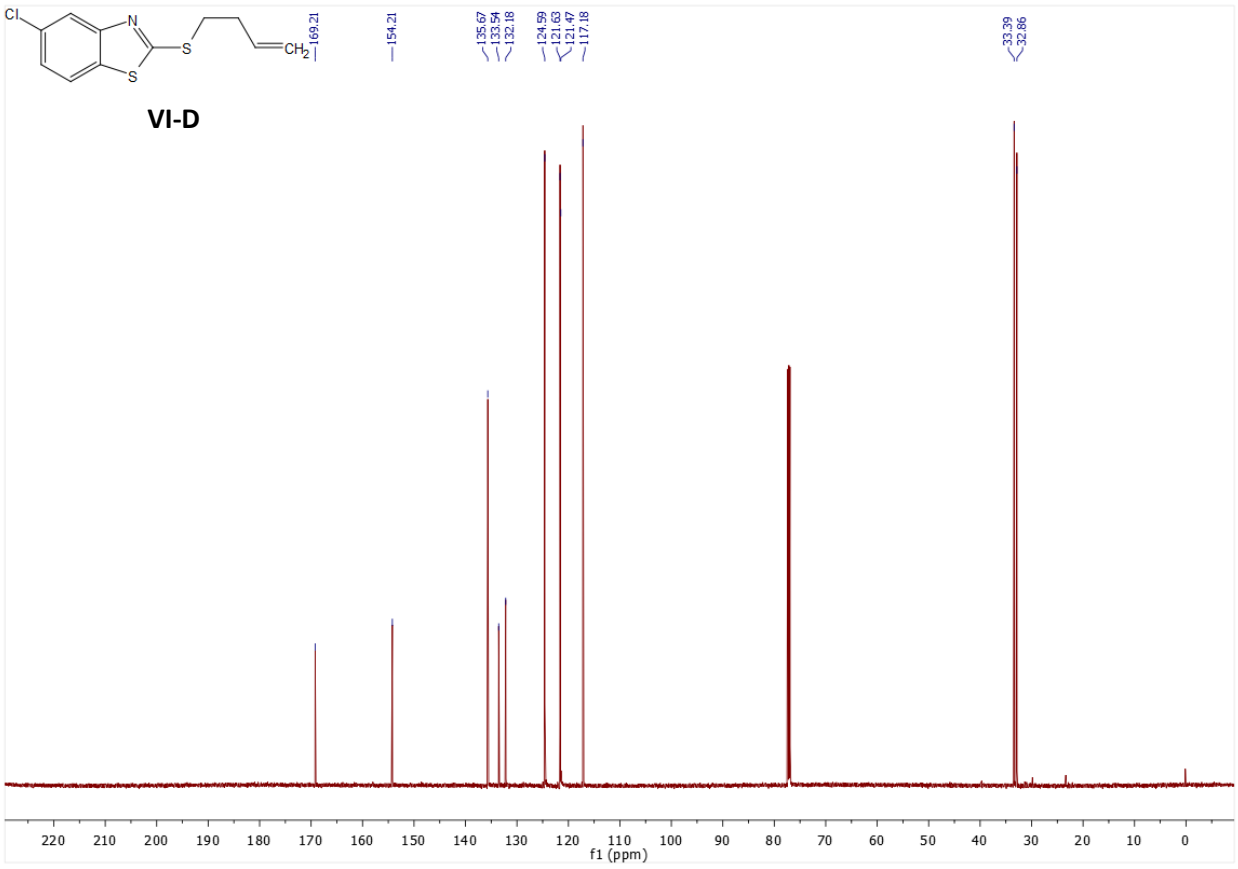

1.00
1.05
1.07
1.00
2.09
2.16
2.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

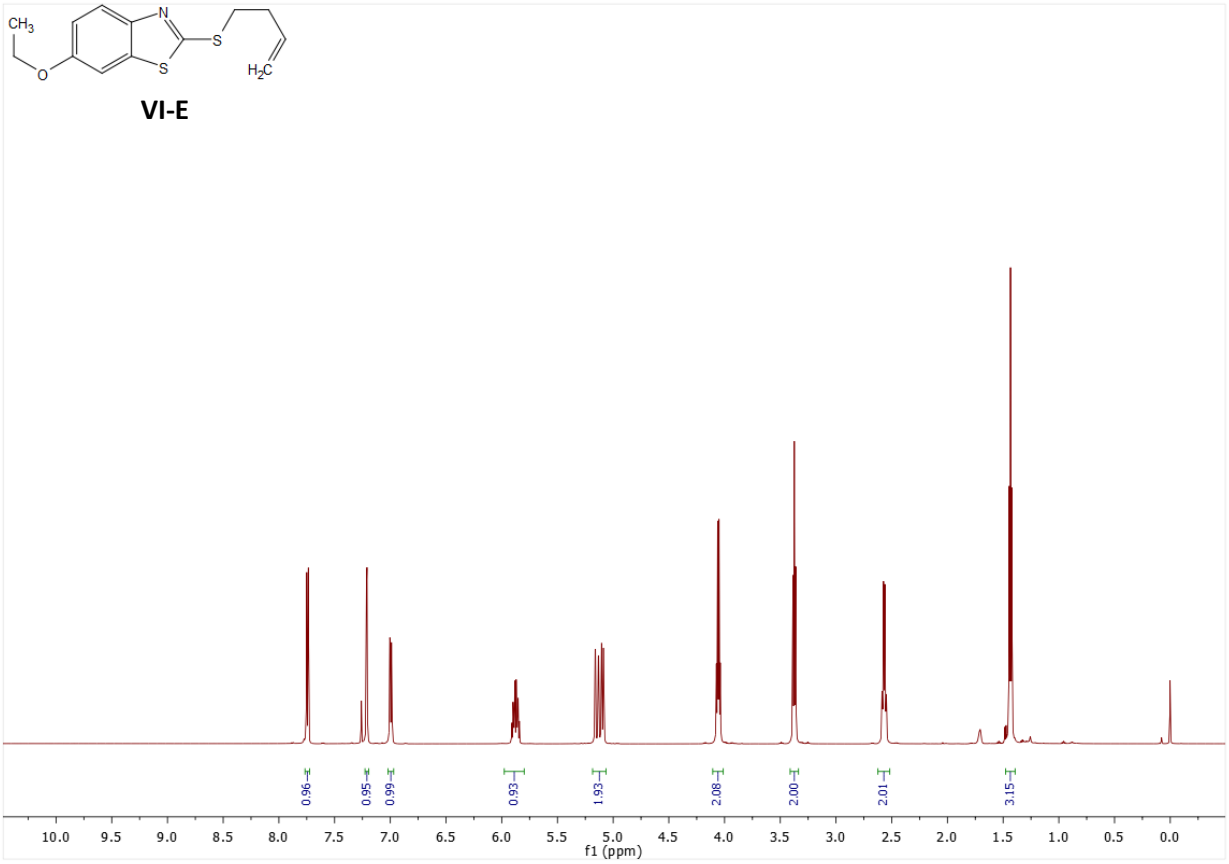


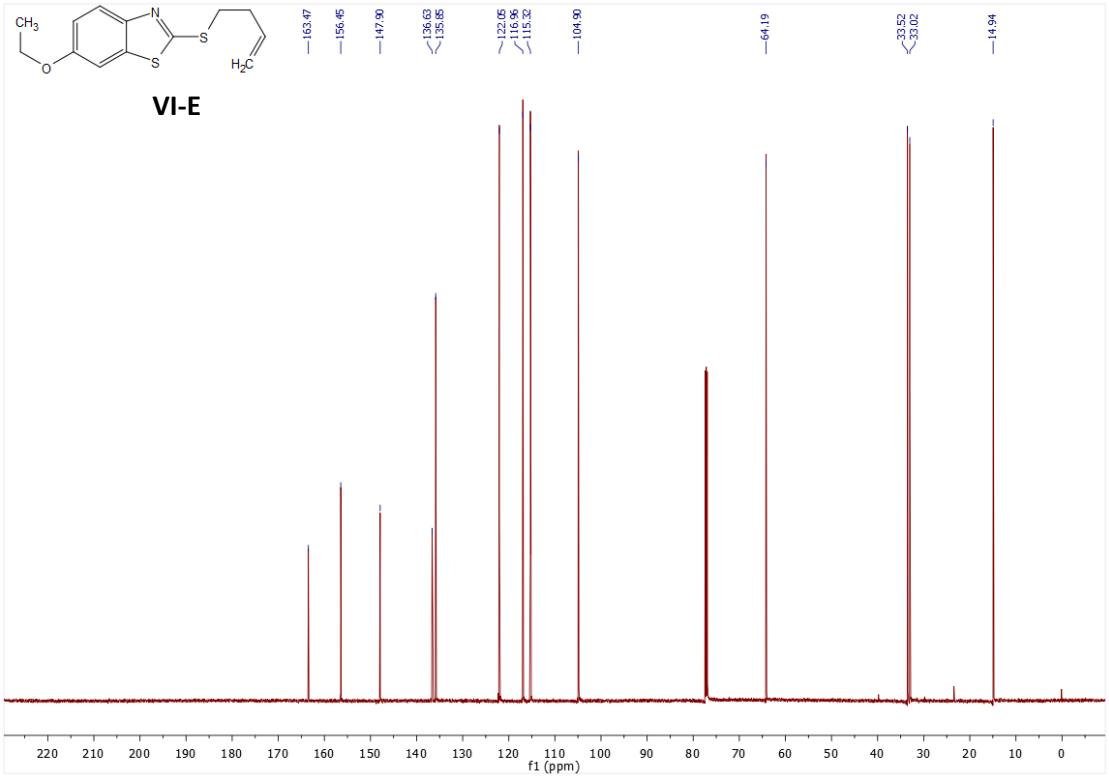
VI-C

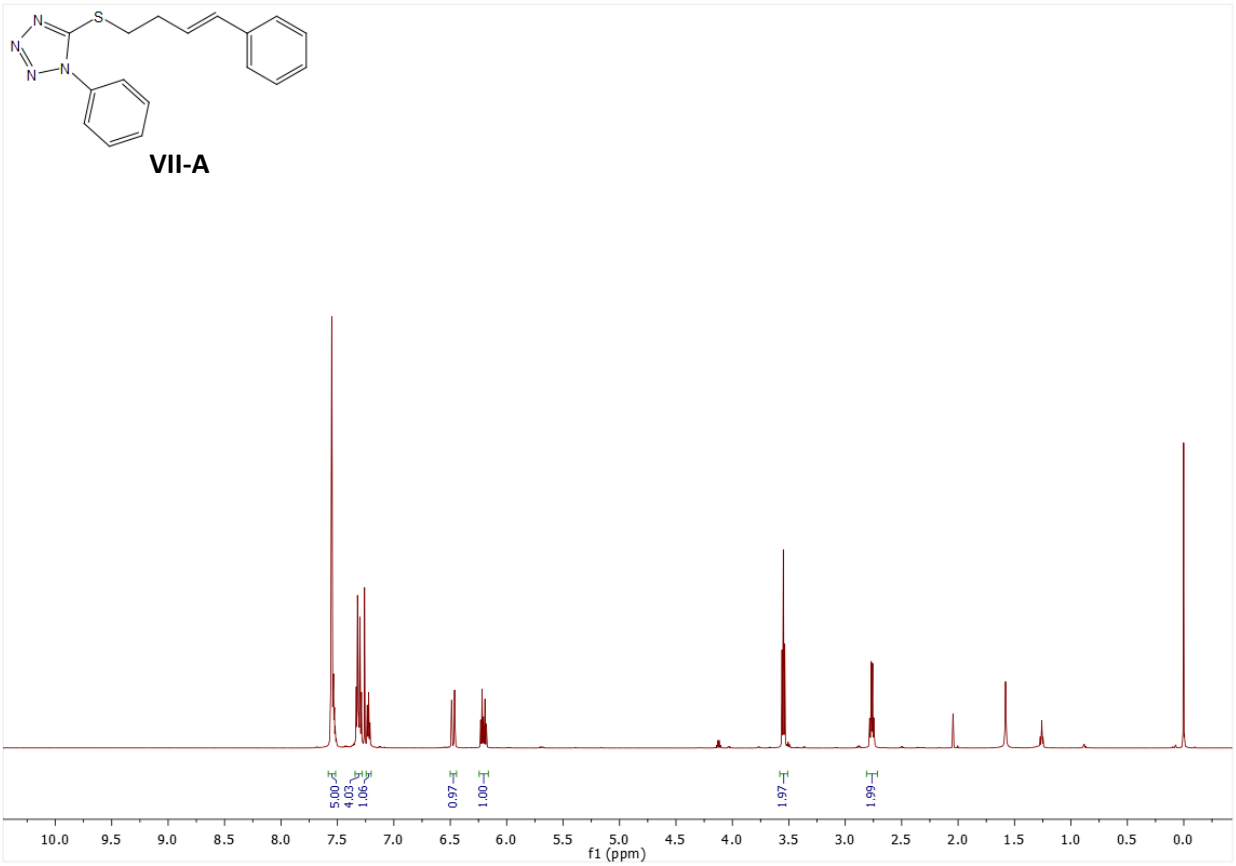
168.52
158.79
146.45
145.63
135.57
127.88
121.15
117.19
33.30
32.11
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
N
S
S
CH2
VI-D
0.97
1.02
1.12
0.99
2.05
2.11
2.11
f1 (ppm)

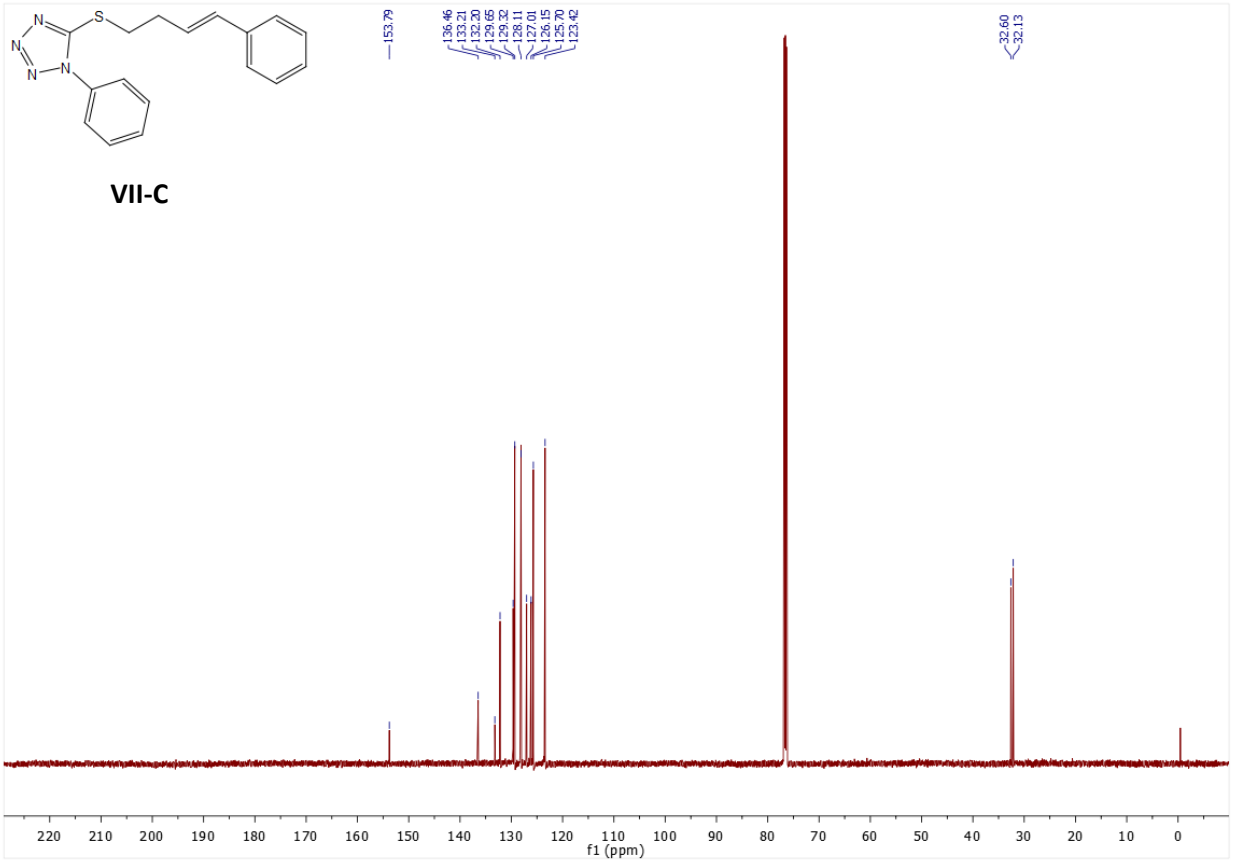

Cl
N
S
S
CH2
VI-D
169.21
154.21
135.67
133.54
132.18
124.99
121.63
121.47
117.18
33.39
32.86
f1 (ppm)


VI-E
0.96
0.95
0.99
0.93
1.93
2.08
2.00
2.01
3.15
f1 (ppm)

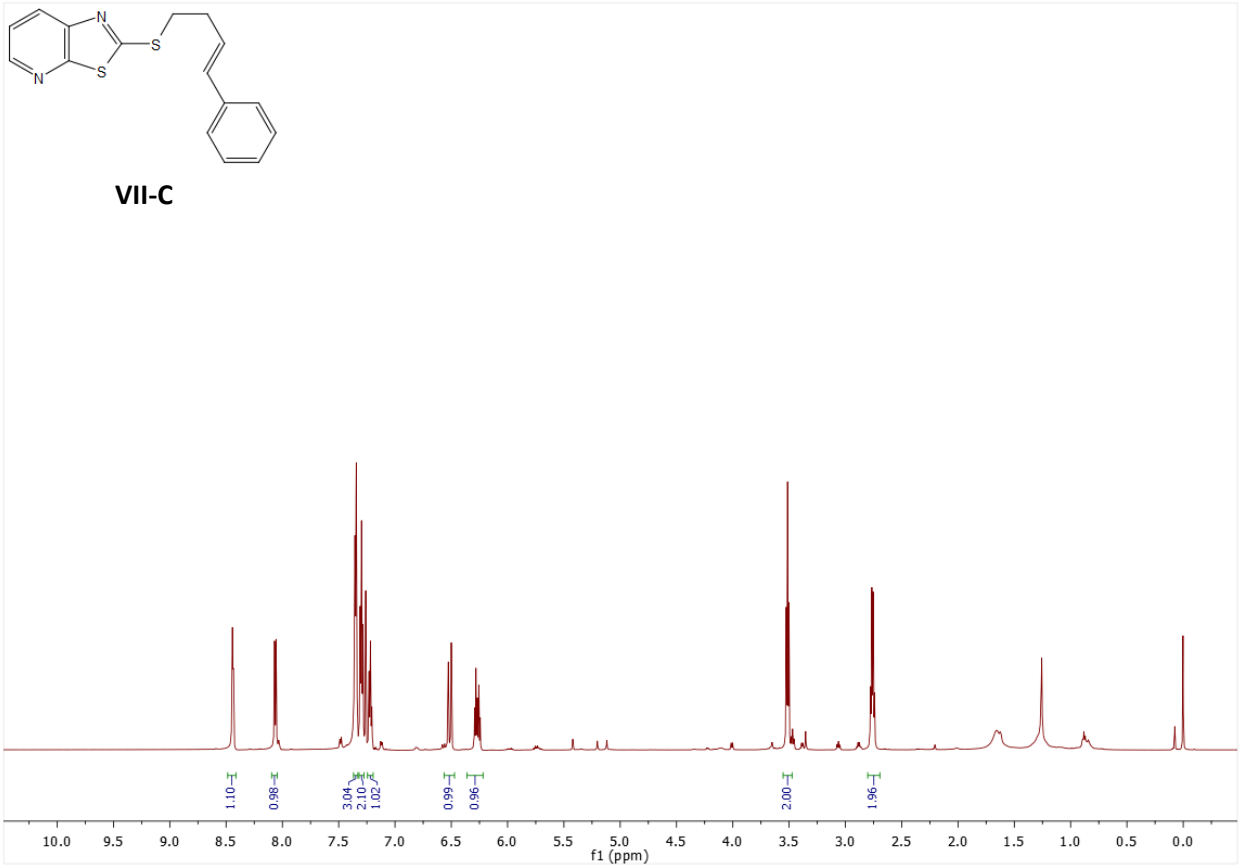

VI-E
163.47
156.45
147.90
136.63
135.85
122.05
116.96
115.32
104.90
64.19
33.52
33.02
14.94
f1 (ppm)


VII-A
5.00
4.03
1.06
0.97
1.00
1.97
1.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

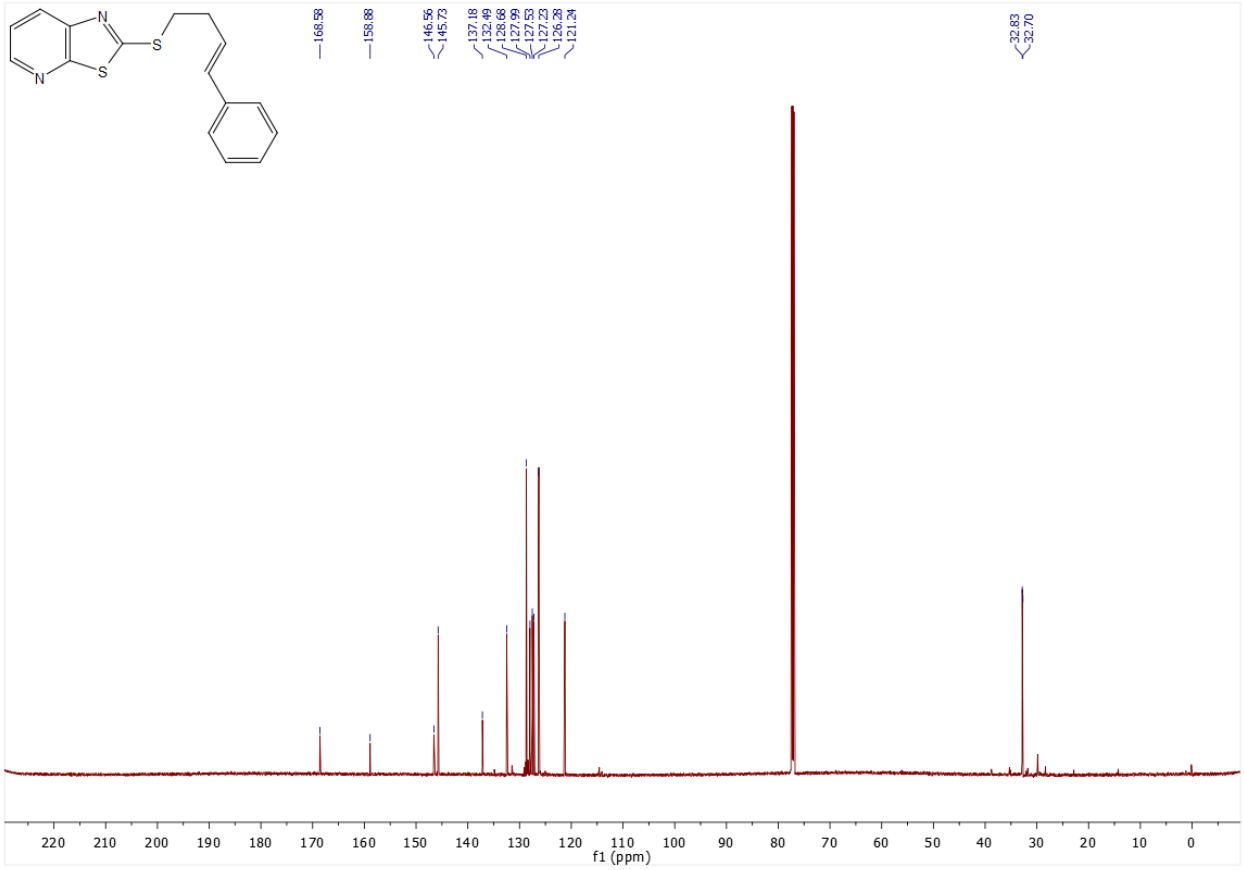
VII-A

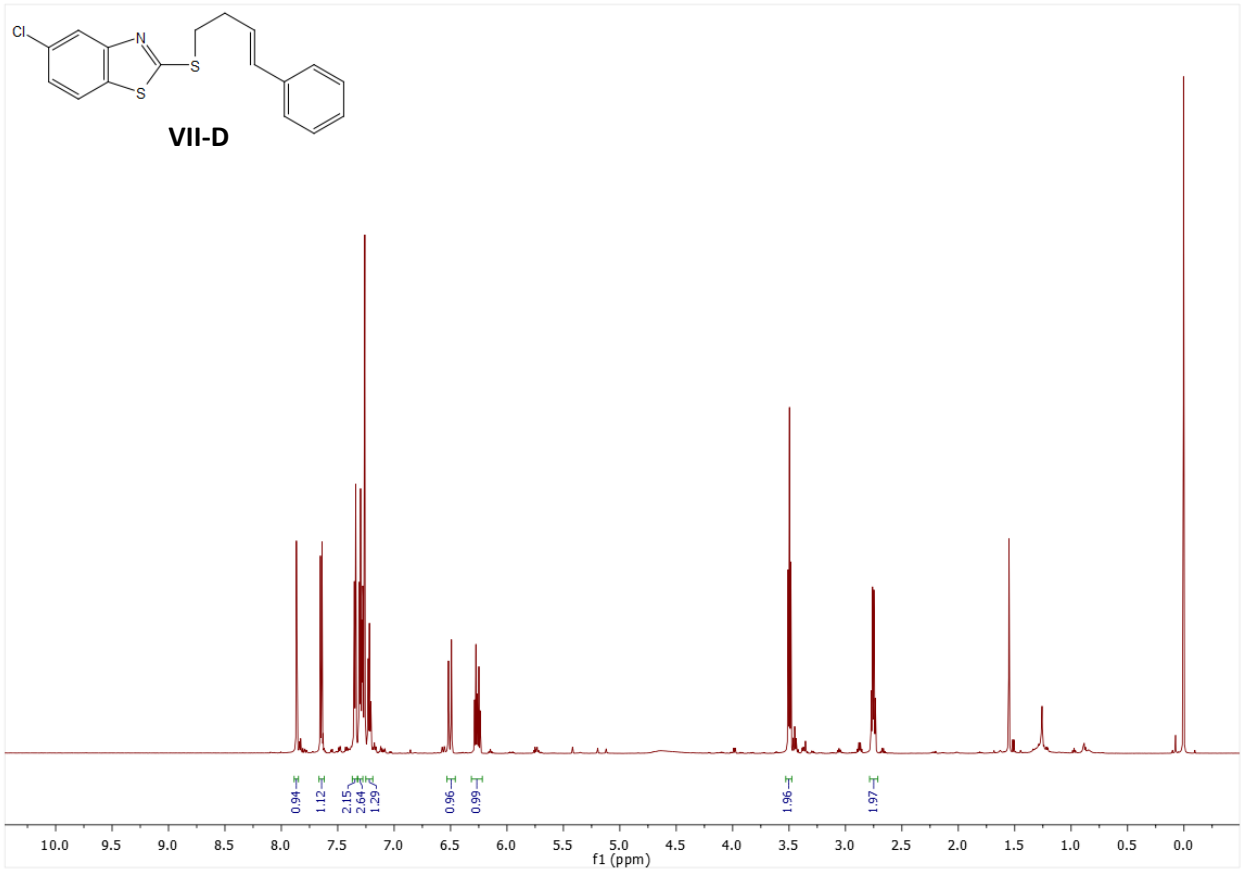

153.79
136.46
133.21
132.20
129.65
129.32
128.11
127.01
126.15
125.70
123.42
32.60
32.13
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

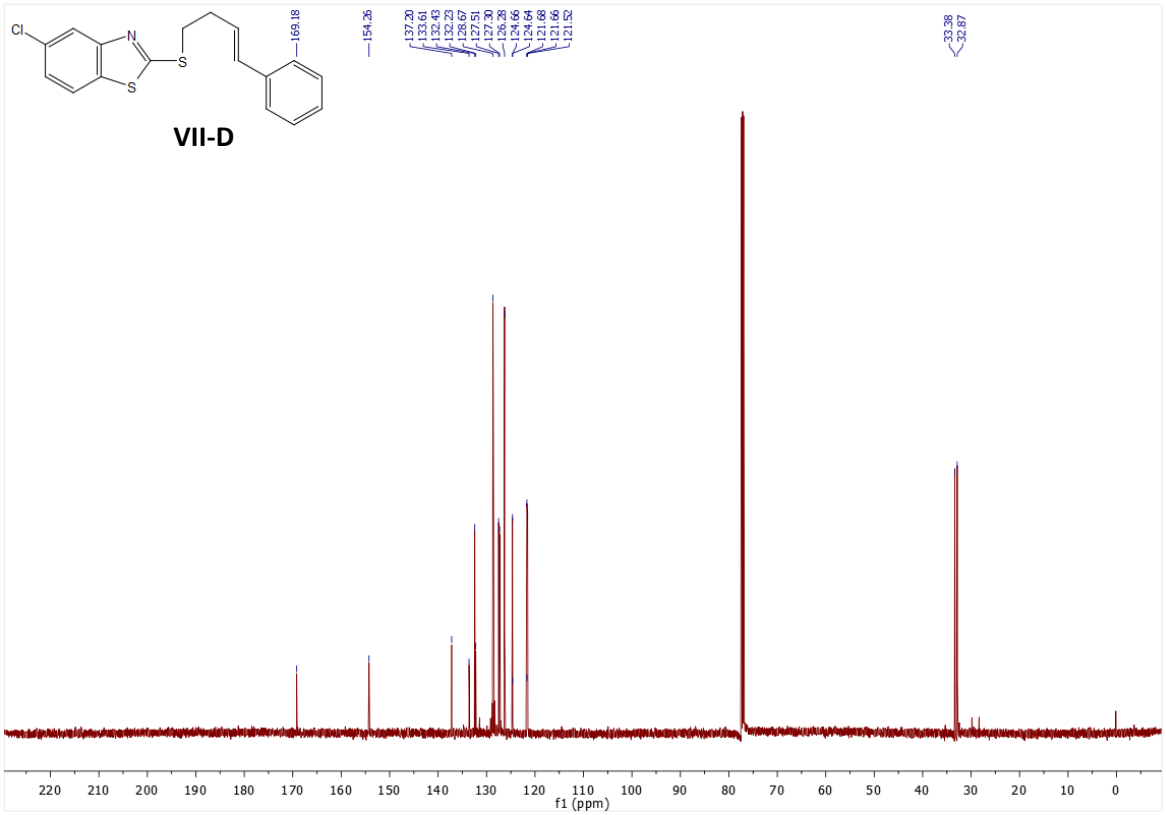
VII-C

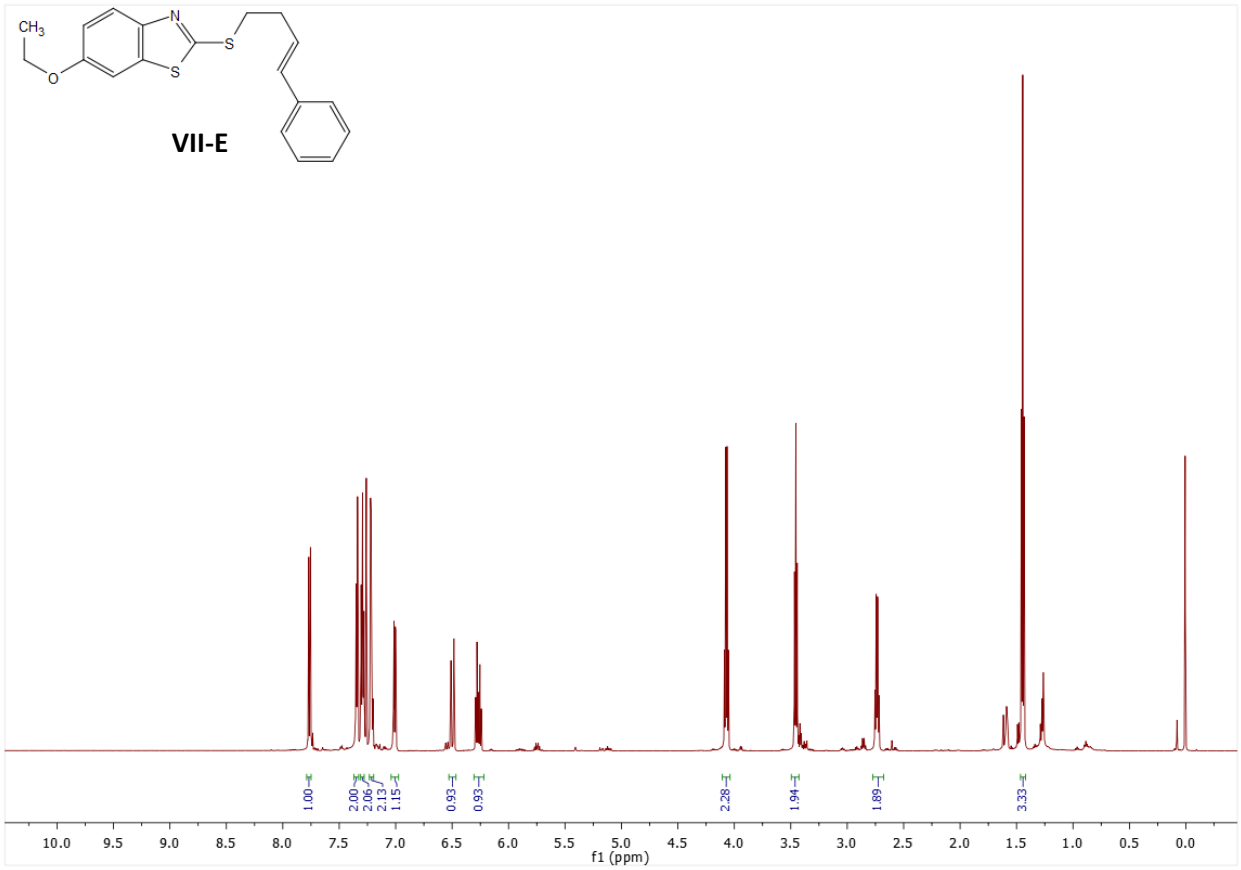

1.10
0.98
3.04
2.10
1.02
0.99
0.96
2.00
1.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

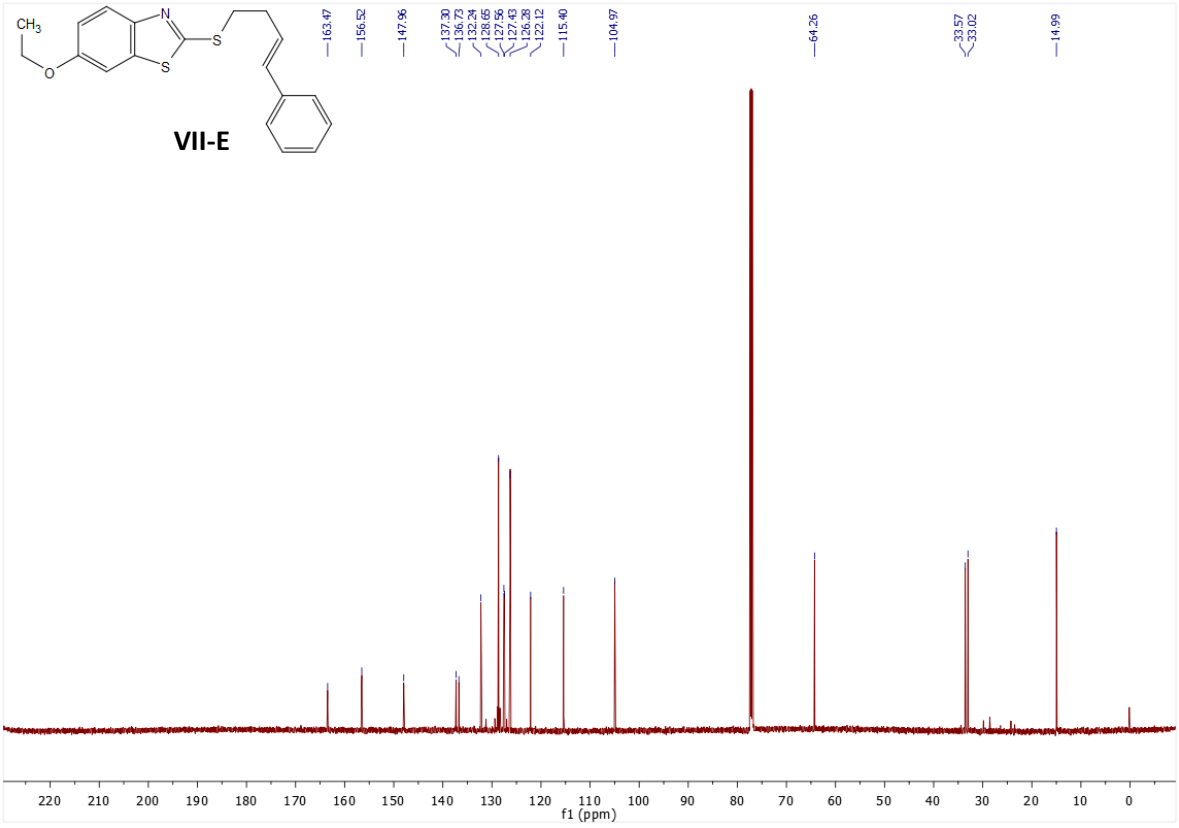
VII-C

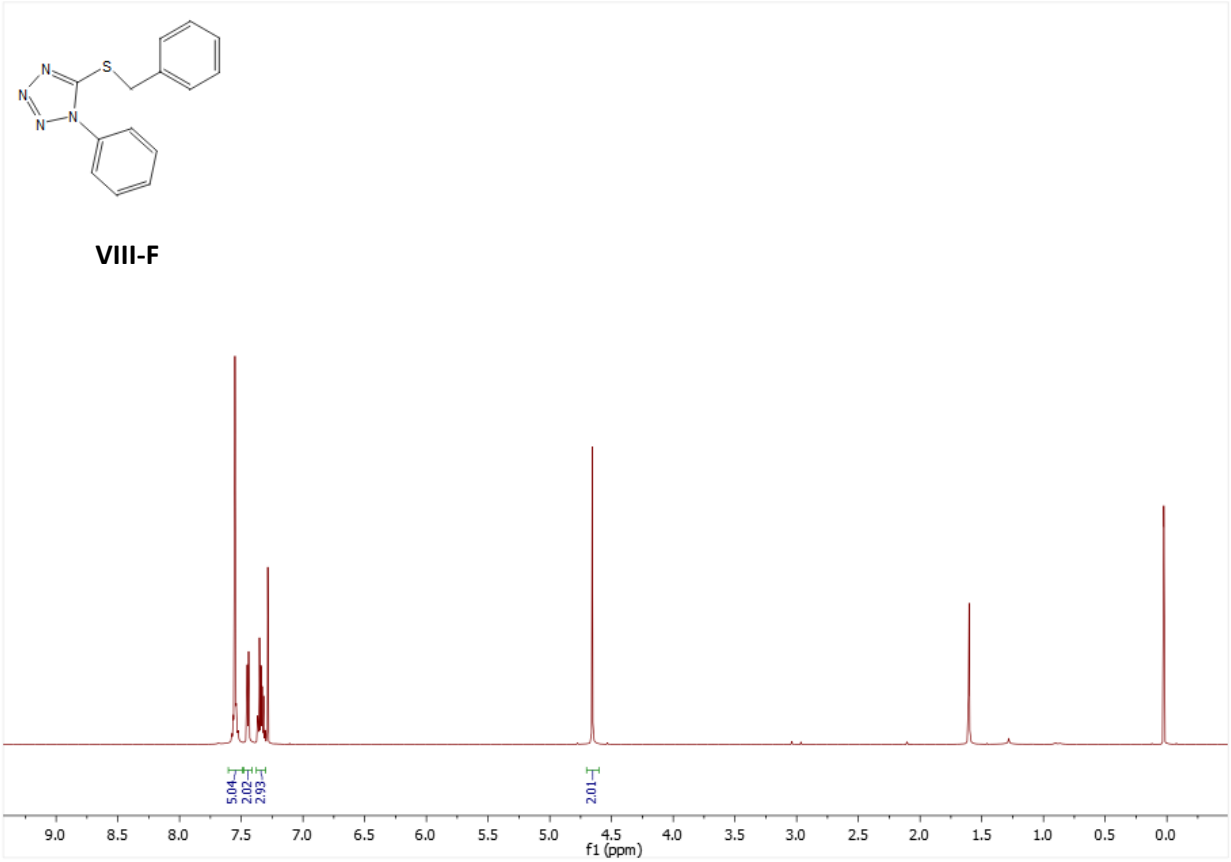

N
S
N
S
168.58
158.88
146.56
145.73
137.18
132.49
128.68
127.99
127.53
127.23
126.26
121.24
32.83
32.70
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

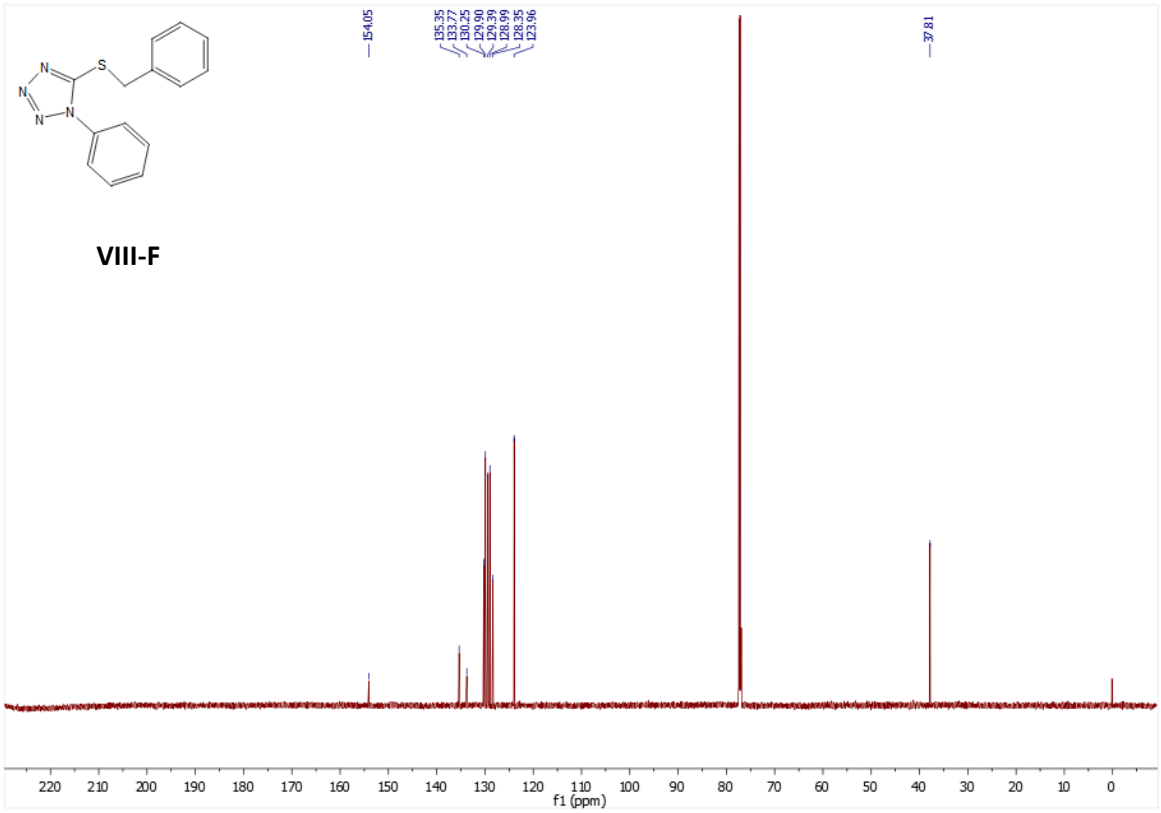

Cl
N
S
S
VII-D
0.94
1.12
2.15
2.64
1.29
0.96
0.99
1.96
1.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

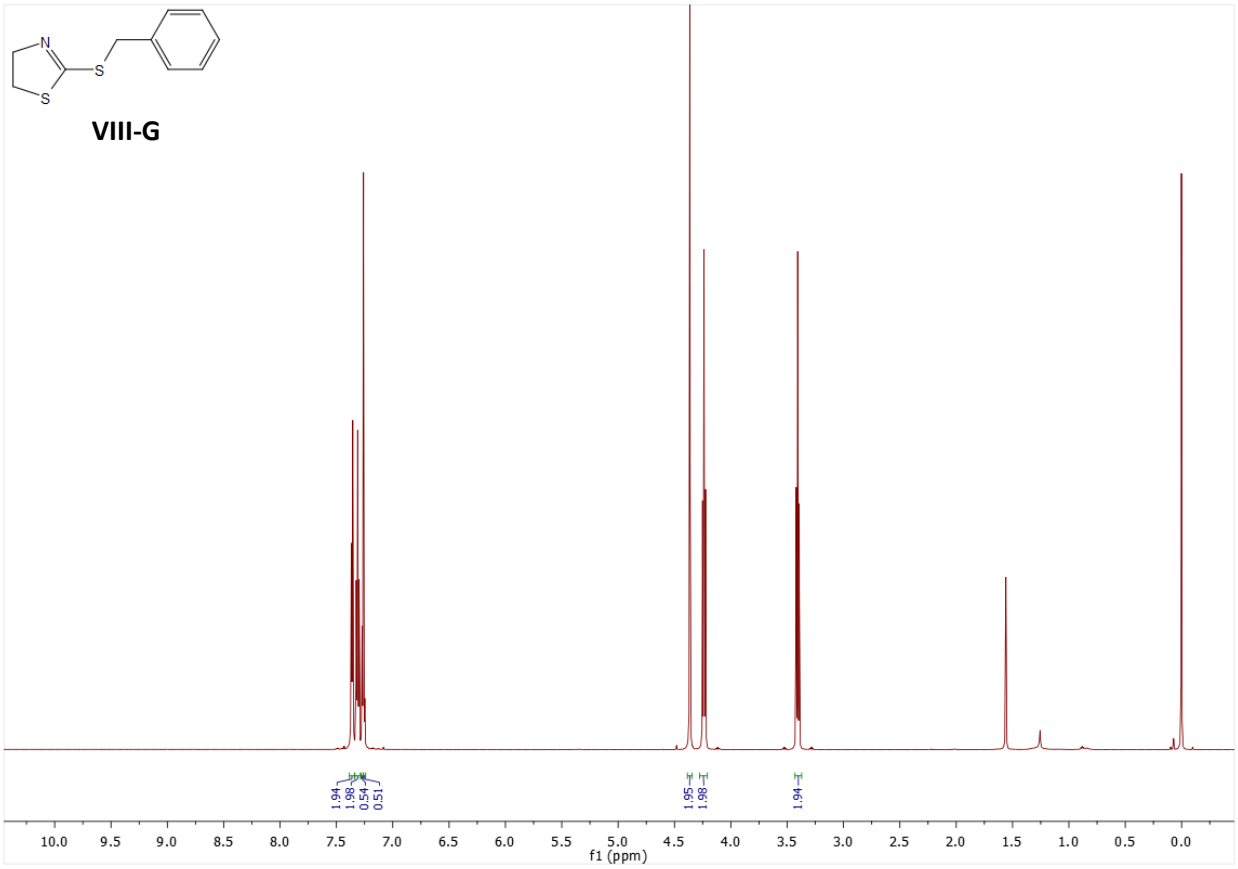

Cl
N
S
S
VII-D
169.18
154.26
137.20
133.61
132.43
132.23
128.67
127.51
127.30
126.38
124.66
124.64
121.68
121.66
121.52
33.38
32.87
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

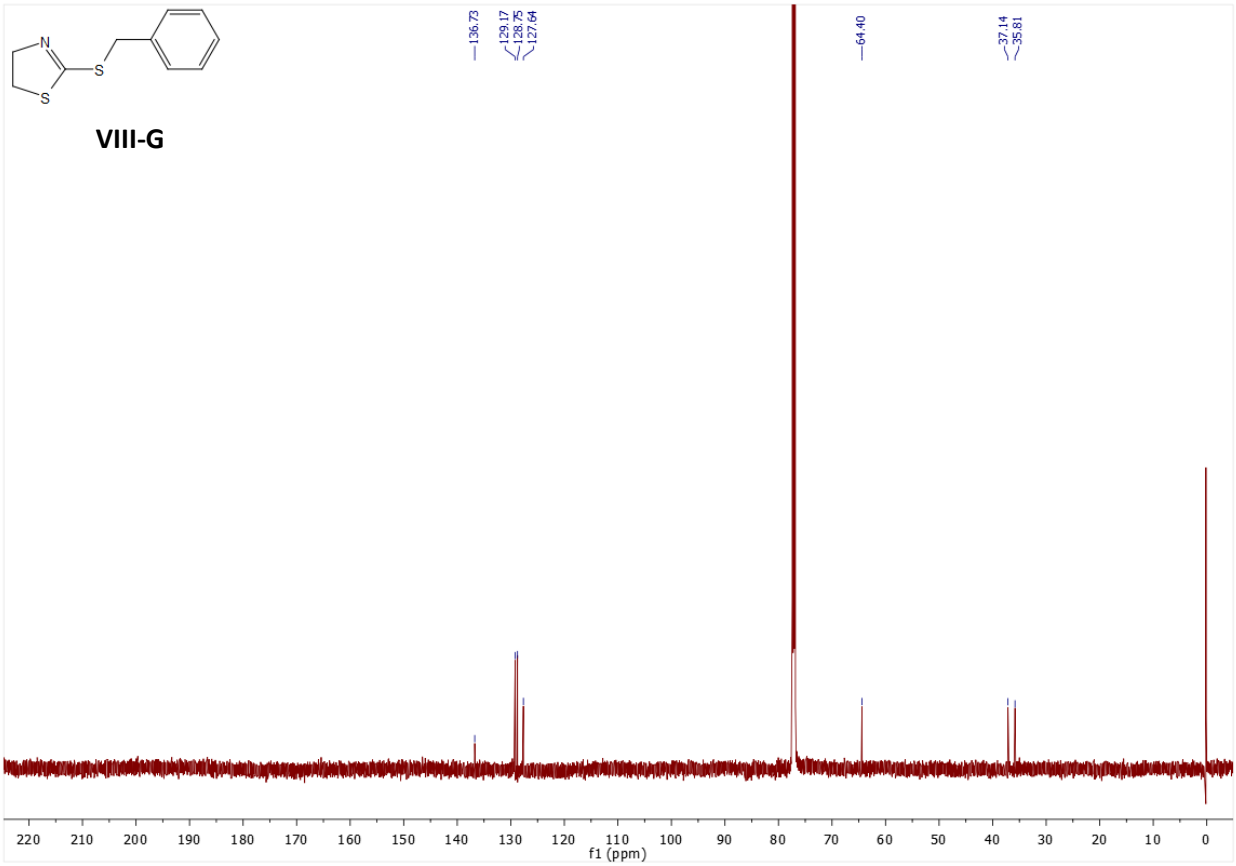

VII-E
1.00
2.00
2.06
2.13
1.15
0.93
0.93
2.28
1.94
1.89
3.33
f1 (ppm)

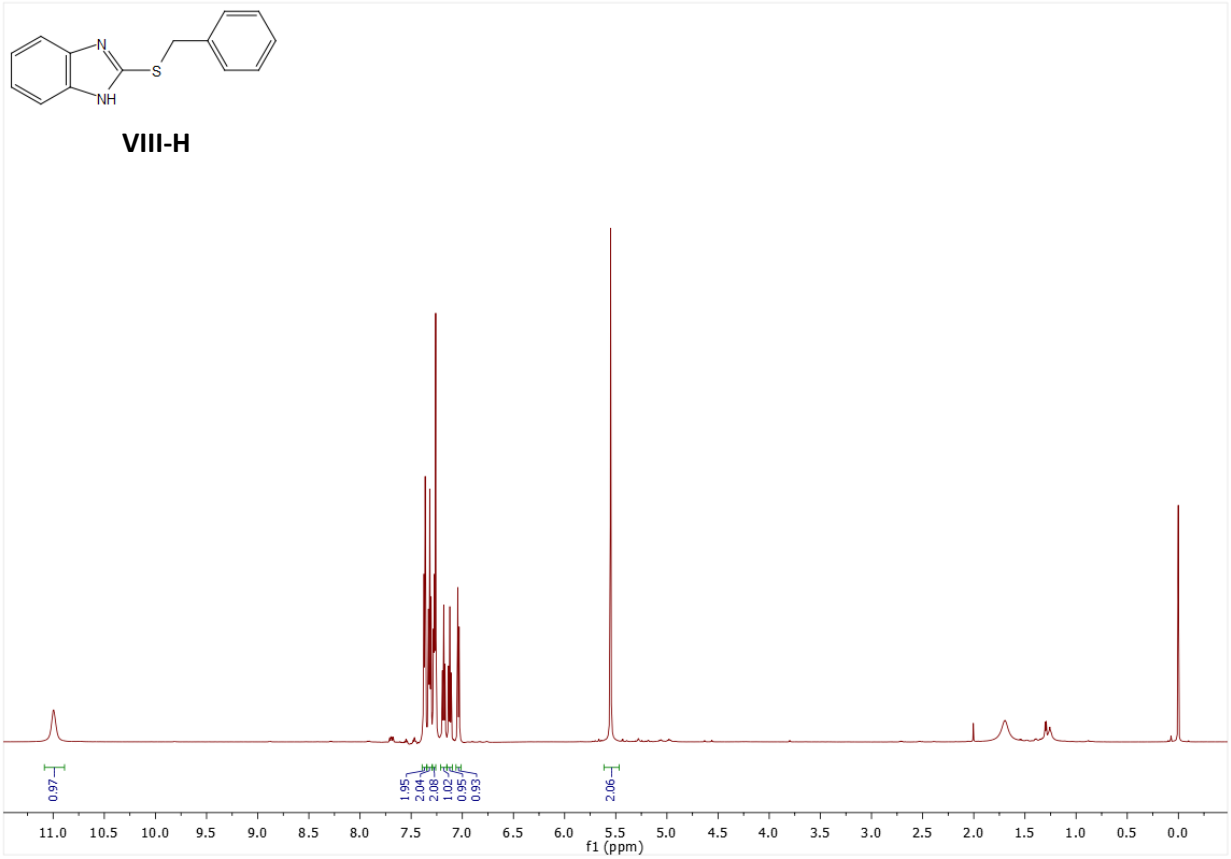

VII-E
163.47
156.52
147.96
137.30
136.73
132.24
128.65
127.55
127.43
126.28
122.12
115.40
104.97
64.26
33.57
33.02
14.99
f1 (ppm)

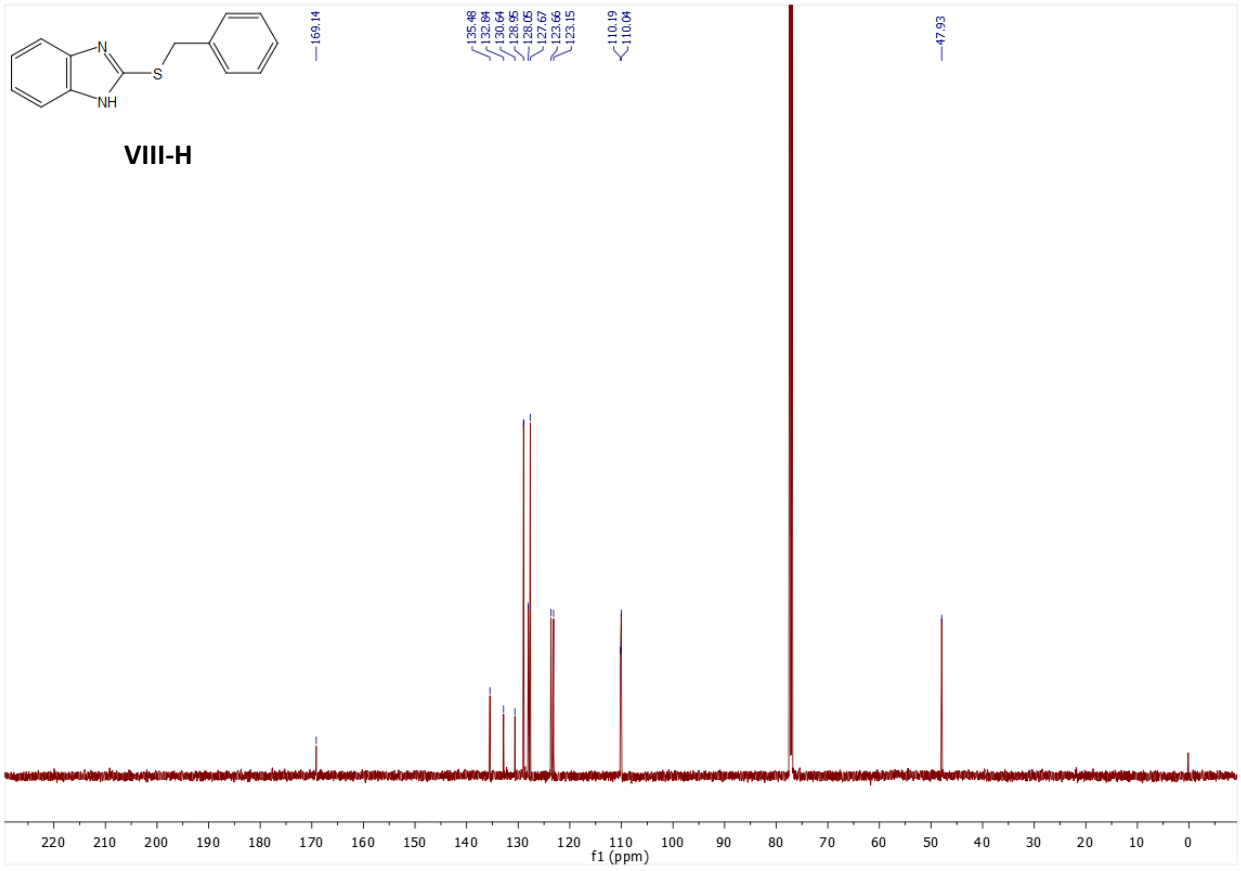

VIII-F
5.04
2.02
2.93
2.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

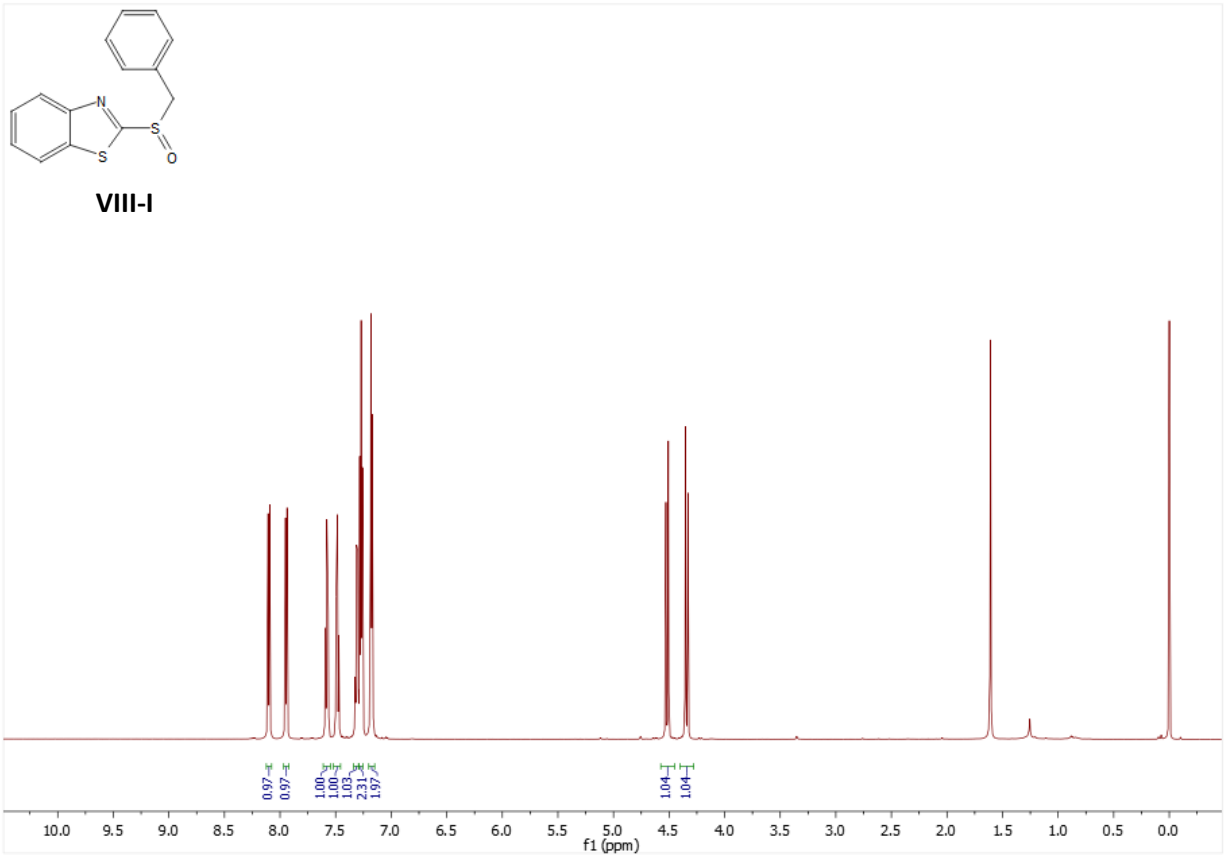

VIII-F
154.05
135.35
133.77
130.25
129.90
129.39
128.99
128.35
123.96
37.81
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

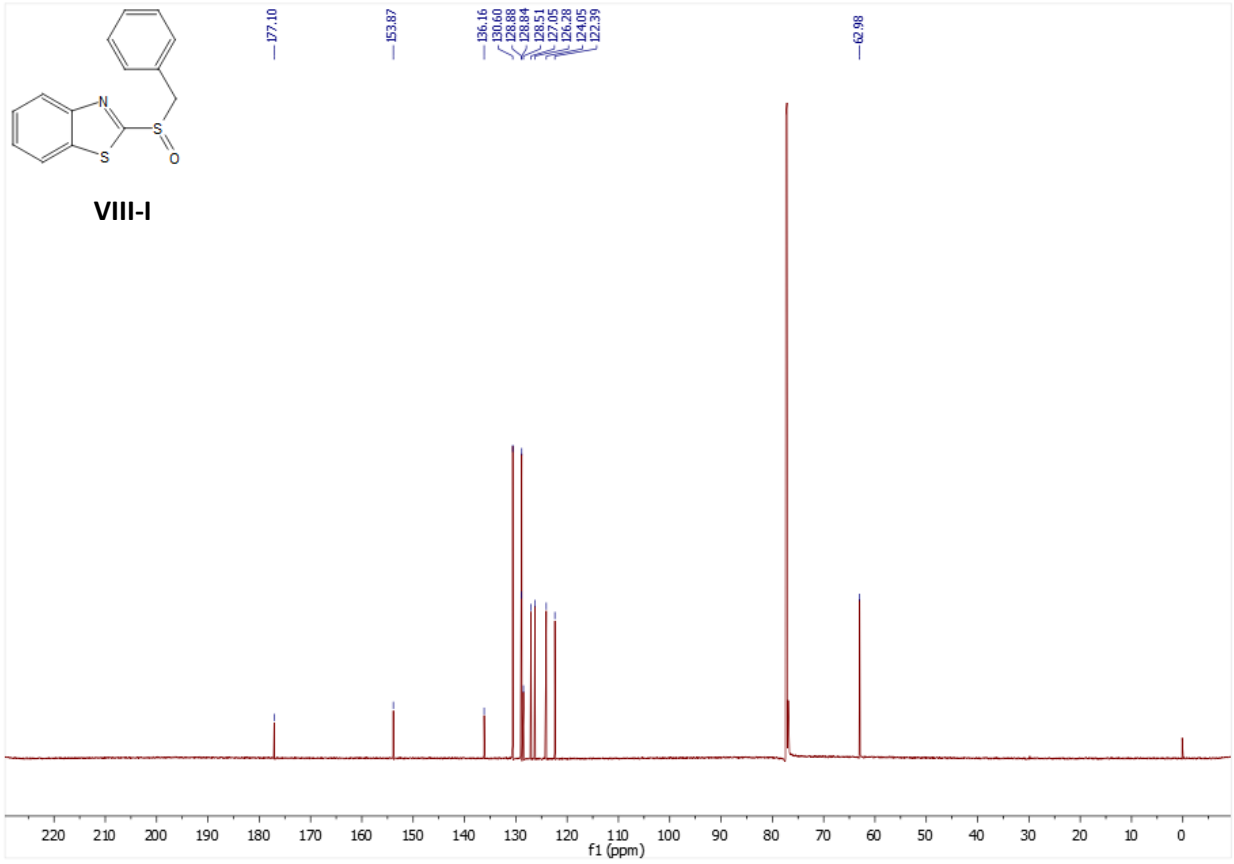

VIII-G
1.94
1.98
0.54
0.51
1.95
1.98
1.94
f1 (ppm)

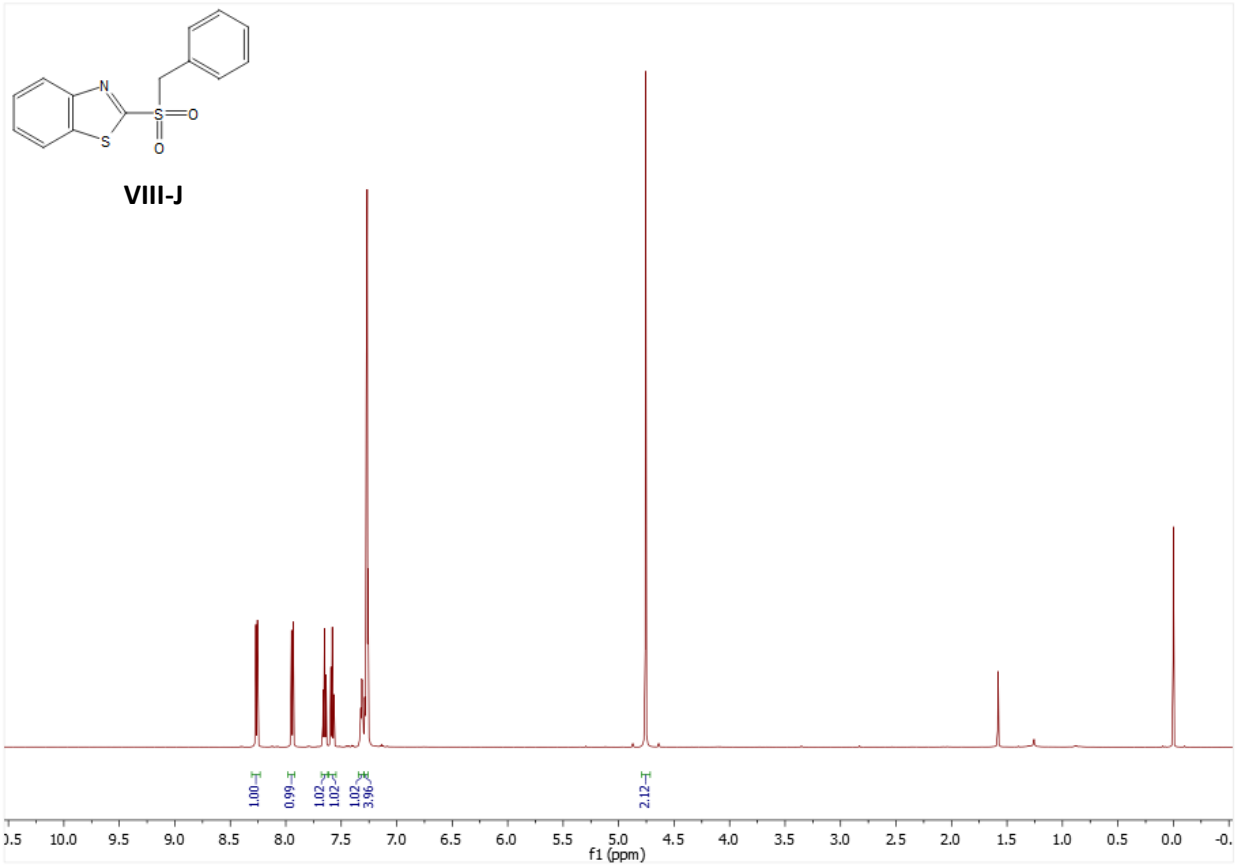

VIII-G
136.73
129.17
128.75
127.64
64.40
37.14
35.81
f1 (ppm)

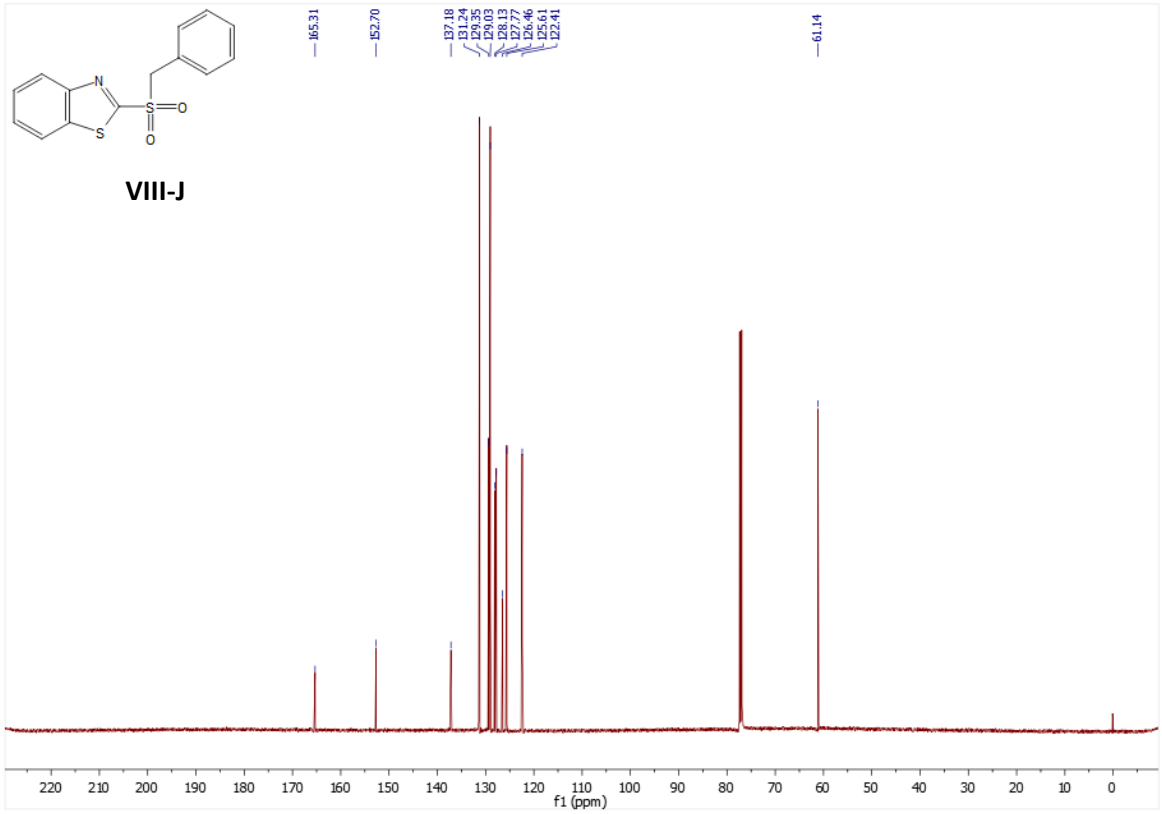

VIII-H
0.97
1.95
2.04
2.08
1.02
0.95
0.93
2.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

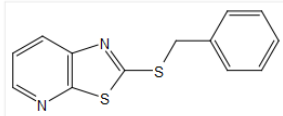

VIII-H
169.14
135.48
132.94
130.64
128.95
128.05
127.67
123.66
123.15
110.19
110.04
47.93
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


VIII-I
0.97
0.97
1.00
1.00
1.03
2.31
1.97
1.04
1.04
f1 (ppm)

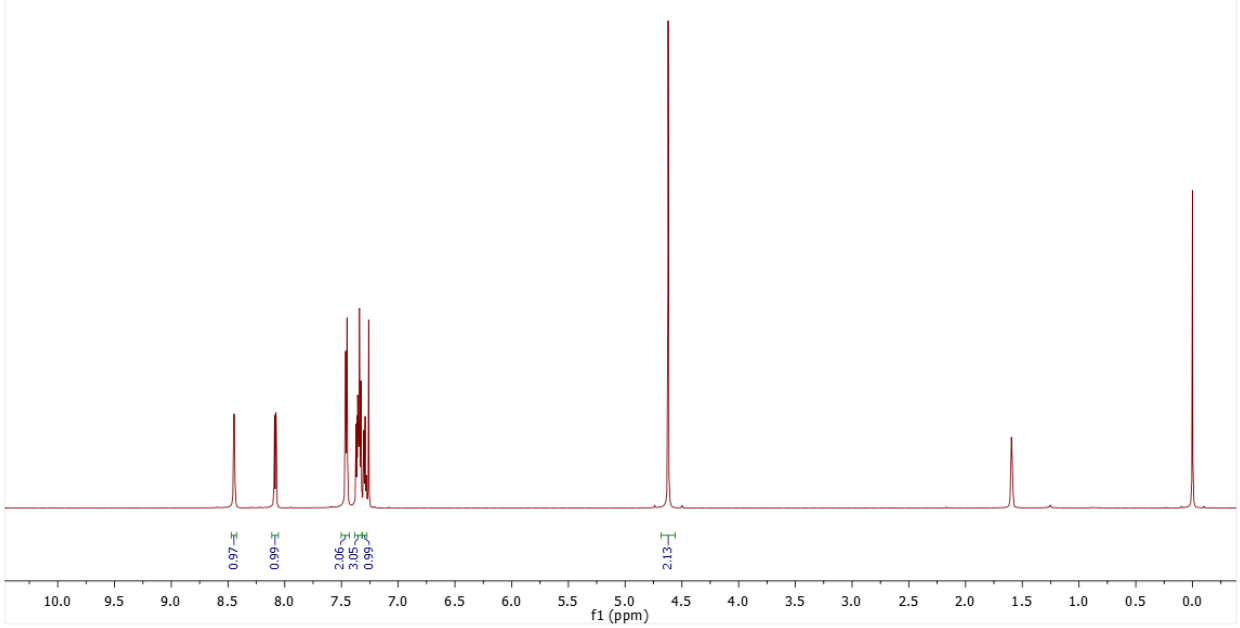

VIII-I
177.10
153.87
136.16
130.60
128.88
128.84
128.51
127.05
126.28
124.05
122.39
62.98
f1 (ppm)

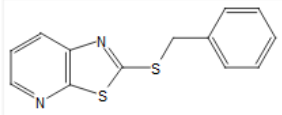

VIII-J
1.00
0.99
1.02
1.02
3.96
2.12
f1 (ppm)


VIII-J
165.31
152.70
137.18
131.24
129.35
129.03
128.13
127.77
126.46
125.61
122.41
61.14
f1 (ppm)



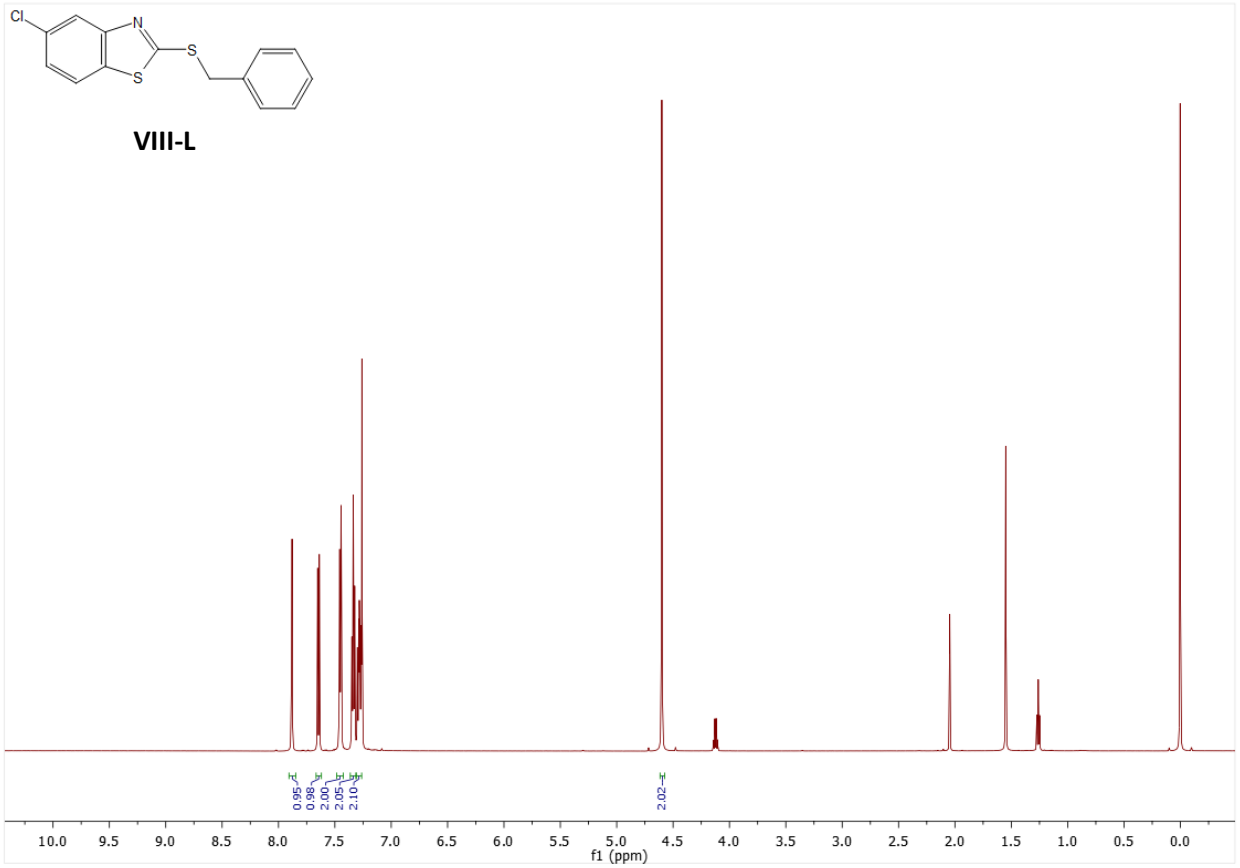
VIII-K

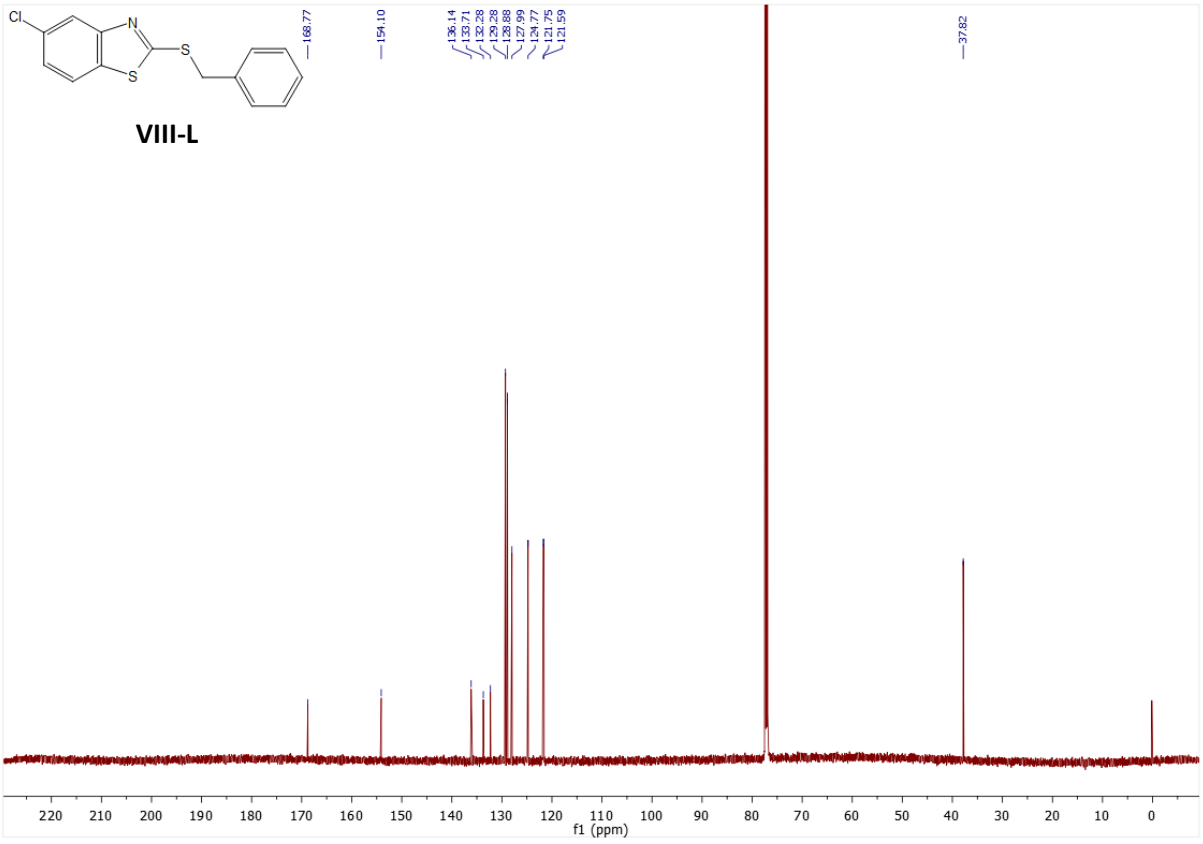

0.97
0.99
2.06
3.05
0.99
2.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

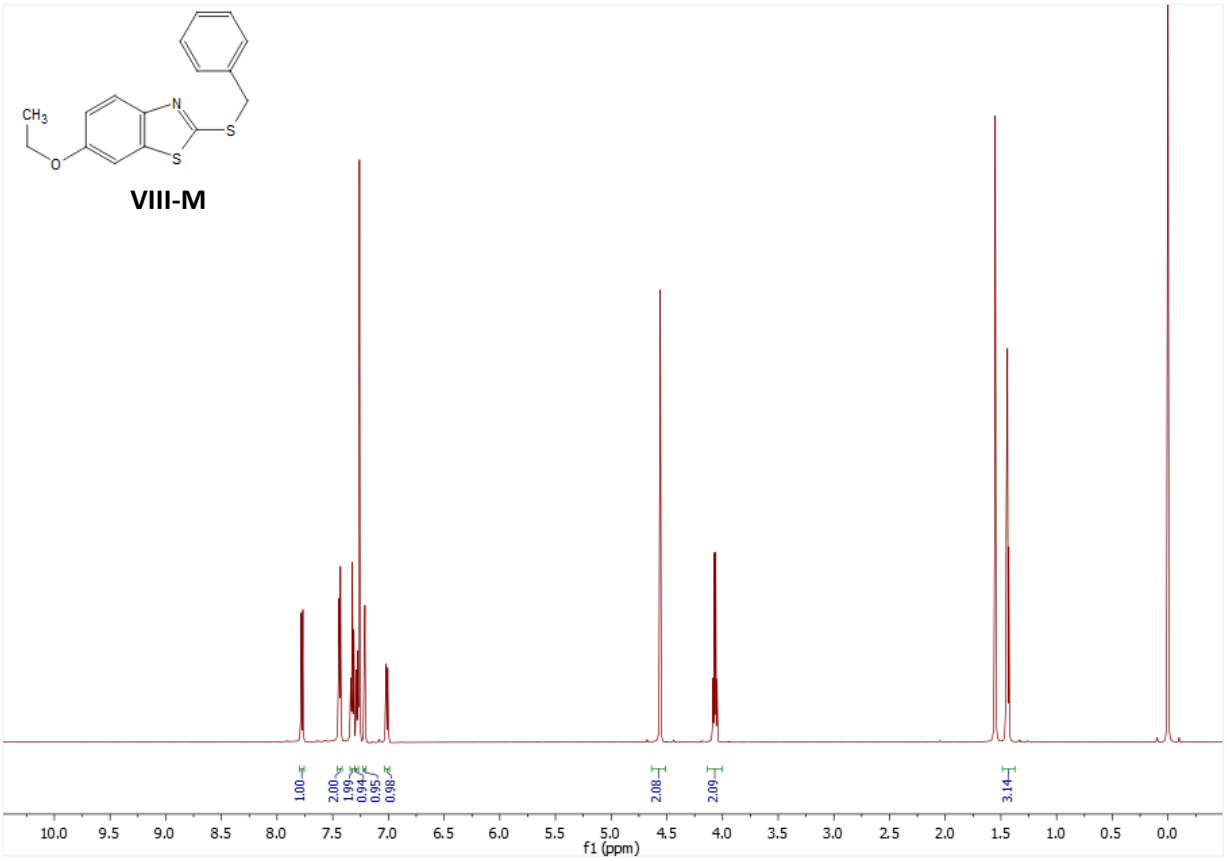


VIII-K

168.18
158.98
146.42
145.87
135.97
129.31
128.92
128.08
128.03
121.30
37.13
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

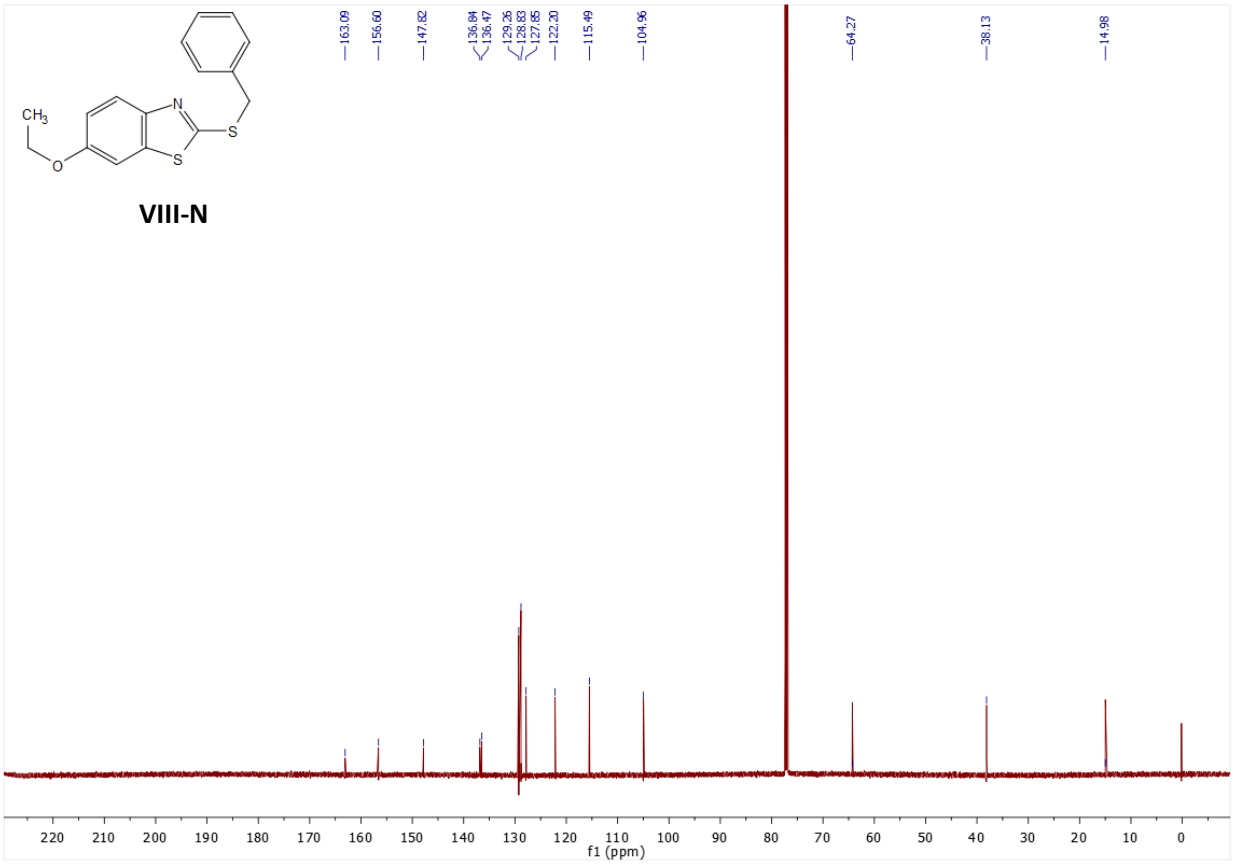

Cl
N
S
S
VIII-L
0.95
0.98
2.00
2.05
2.10
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Cl
N
S
S
VIII-L
168.77
154.10
136.14
133.71
132.28
129.28
128.88
127.99
124.77
121.75
121.59
37.82
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

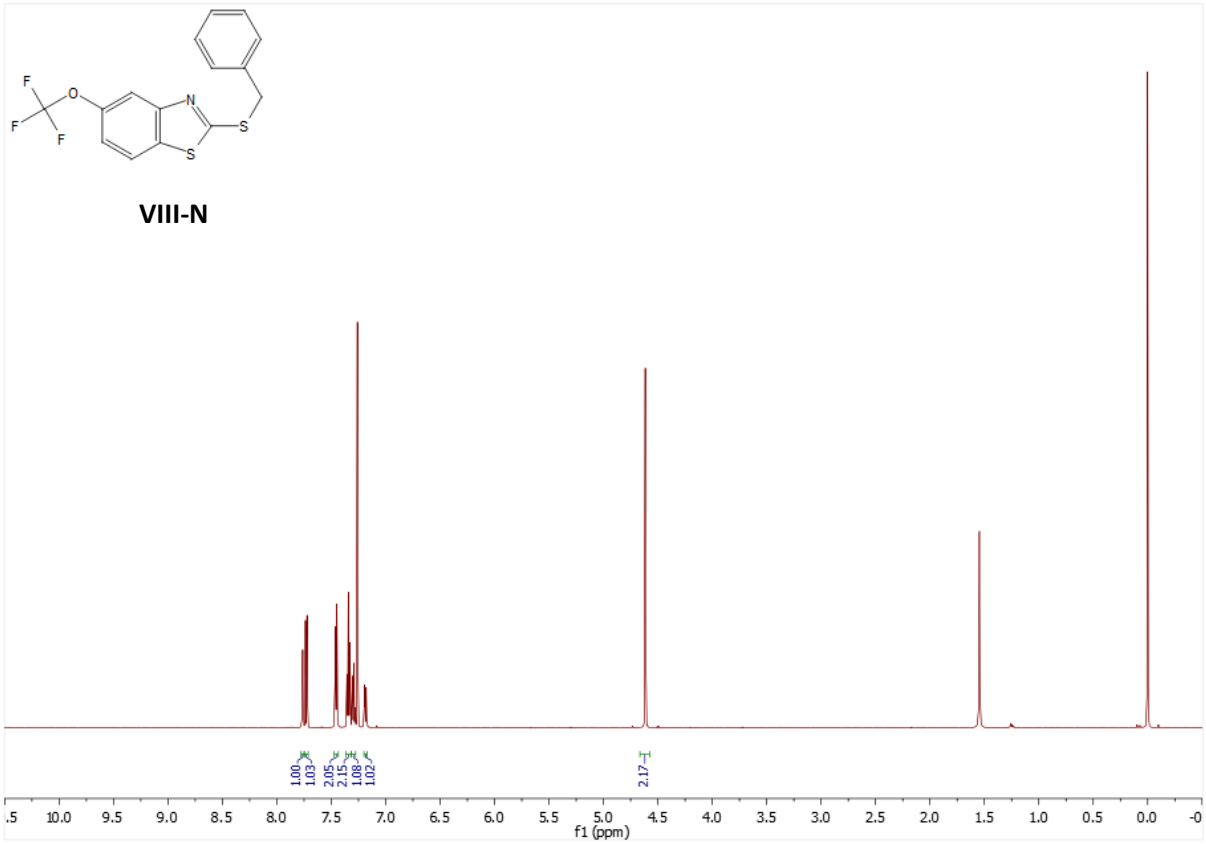

CH3
O
N
S
S
1.00
2.00
1.99
0.94
0.95
0.98
2.08
2.09
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

VIII-M

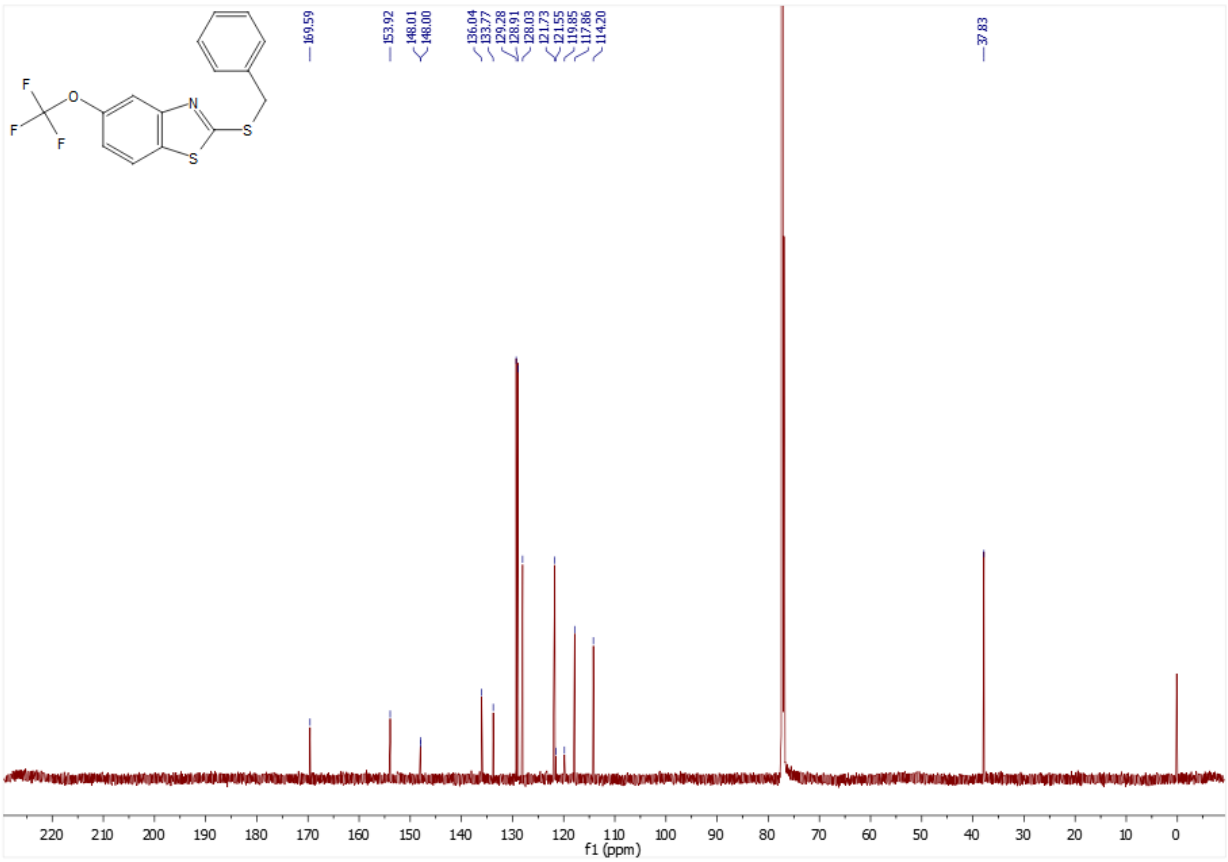
VIII-M

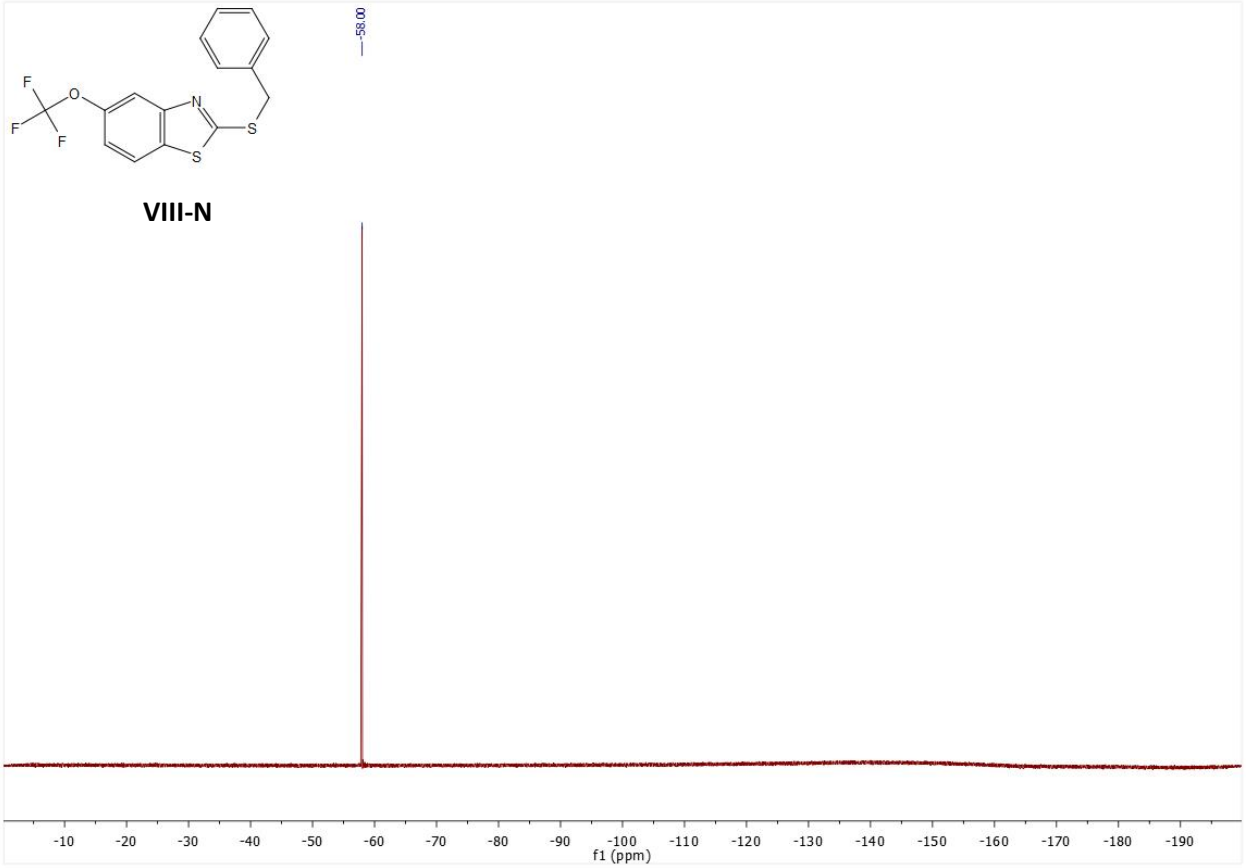

163.09
156.60
147.82
136.84
136.47
129.26
128.83
127.85
122.20
115.49
104.96
64.27
38.13
14.98
CH3
O
N
S
S
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

VIII-N

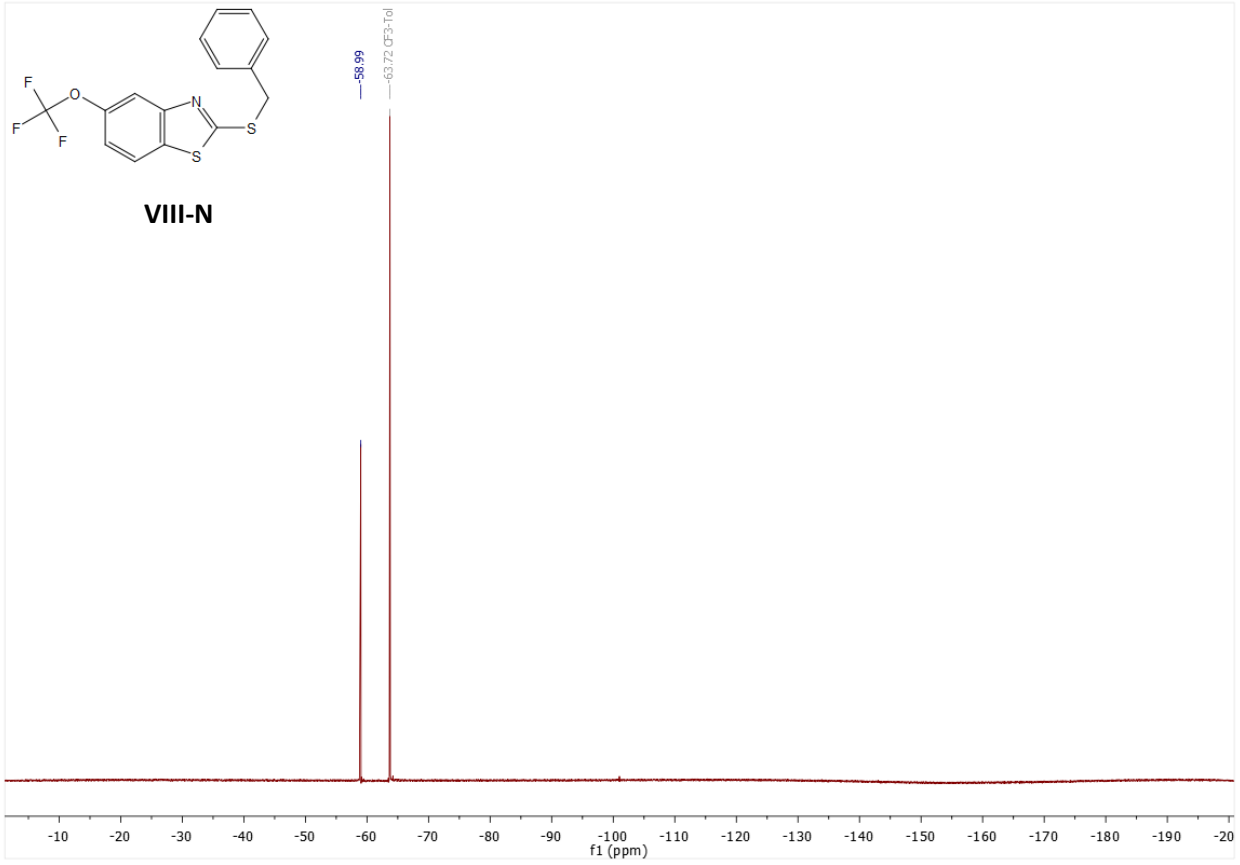

F
F
F
O
N
S
S
1.00
1.03
2.05
2.15
1.08
1.02
2.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

VIII-N

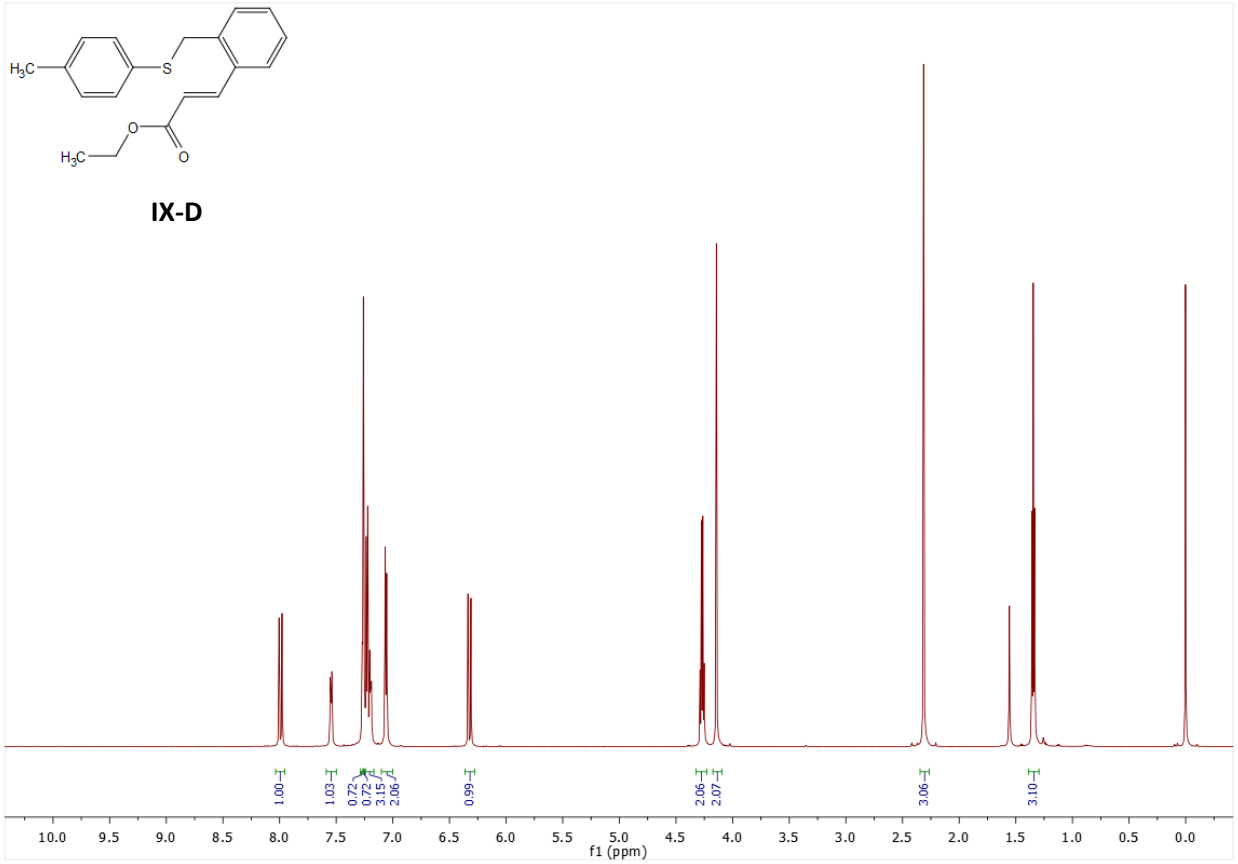

F
F
F
O
N
S
S
169.59
153.92
148.01
148.00
136.04
133.77
129.28
128.91
128.03
121.73
121.55
119.85
117.86
114.20
37.83
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

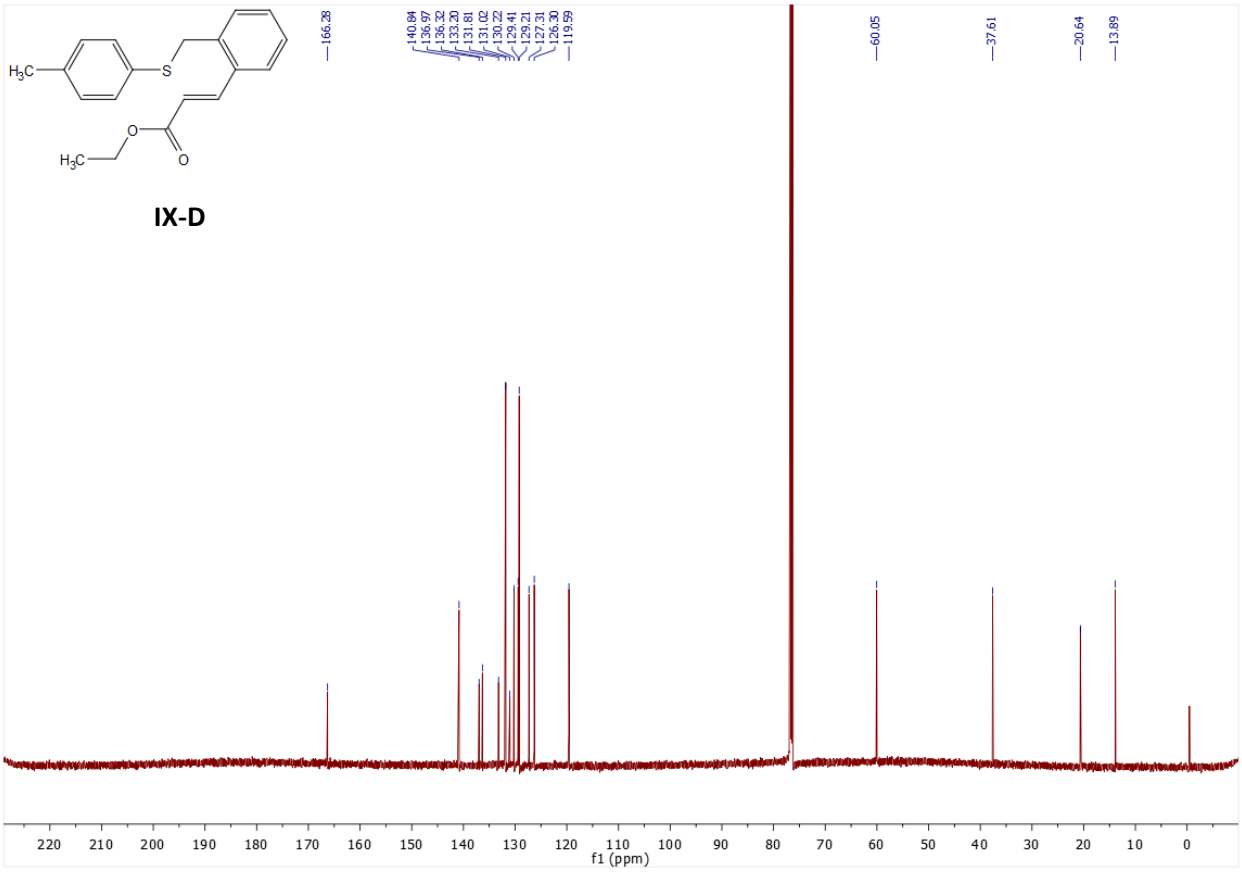

-58.00
F
O
F
F
N
S
S
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

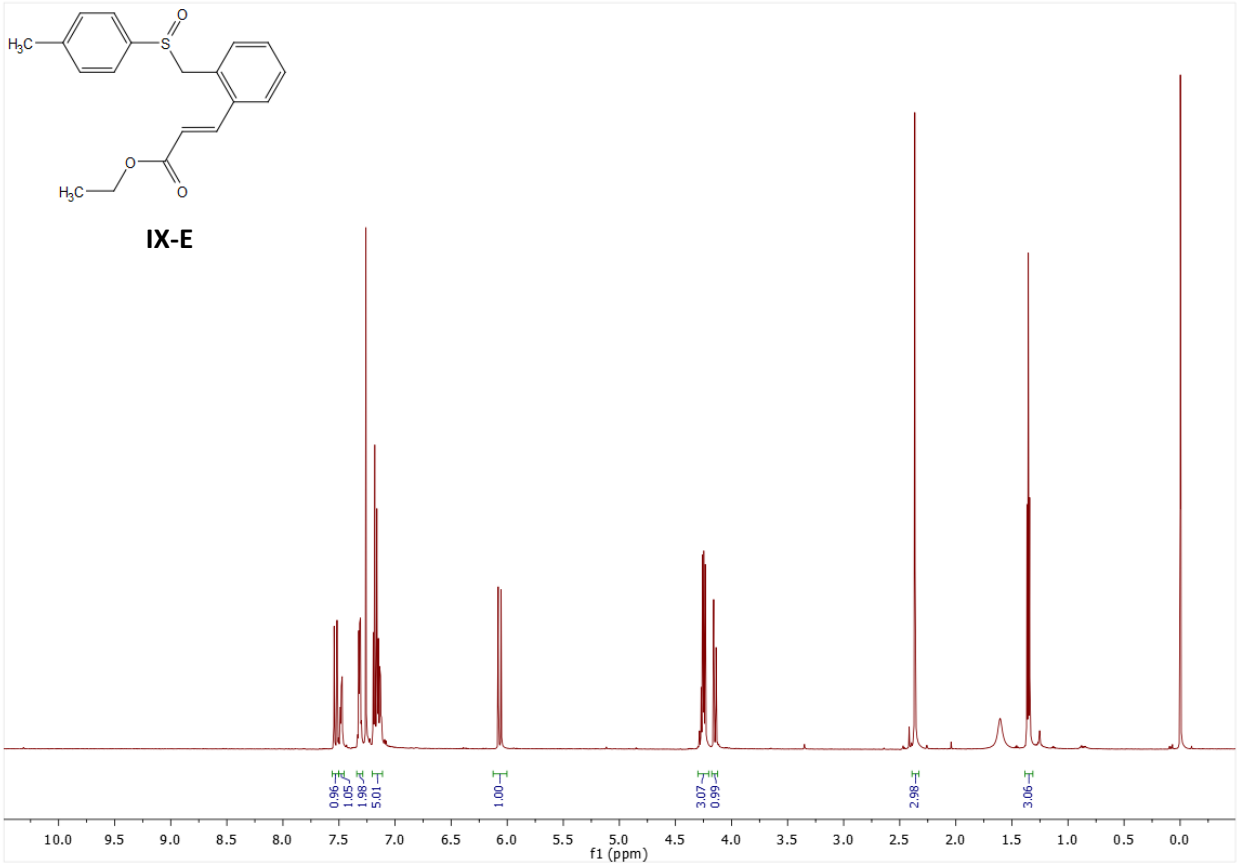
VIII-N

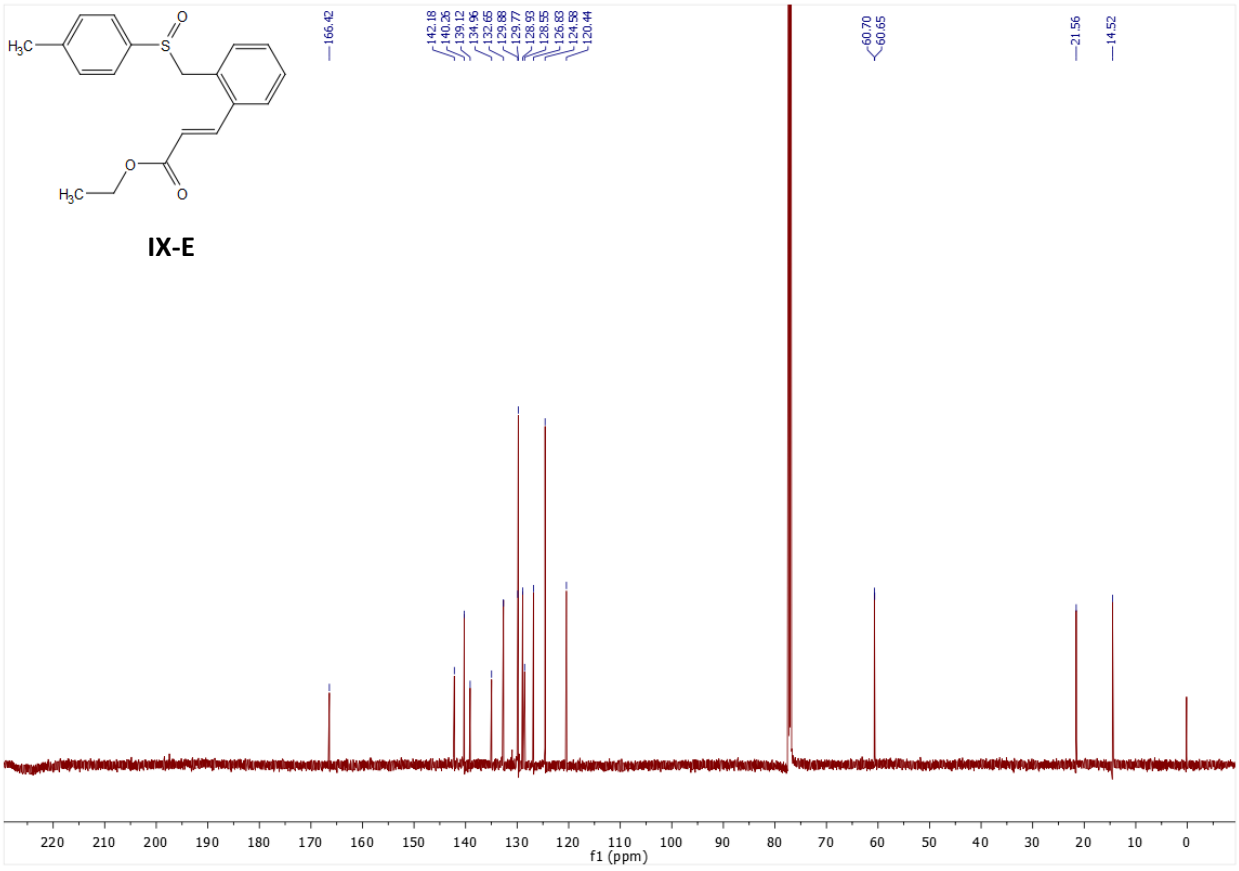

-58.99
-63.72 CF3-Tol
F
O
F
F
N
S
S
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)

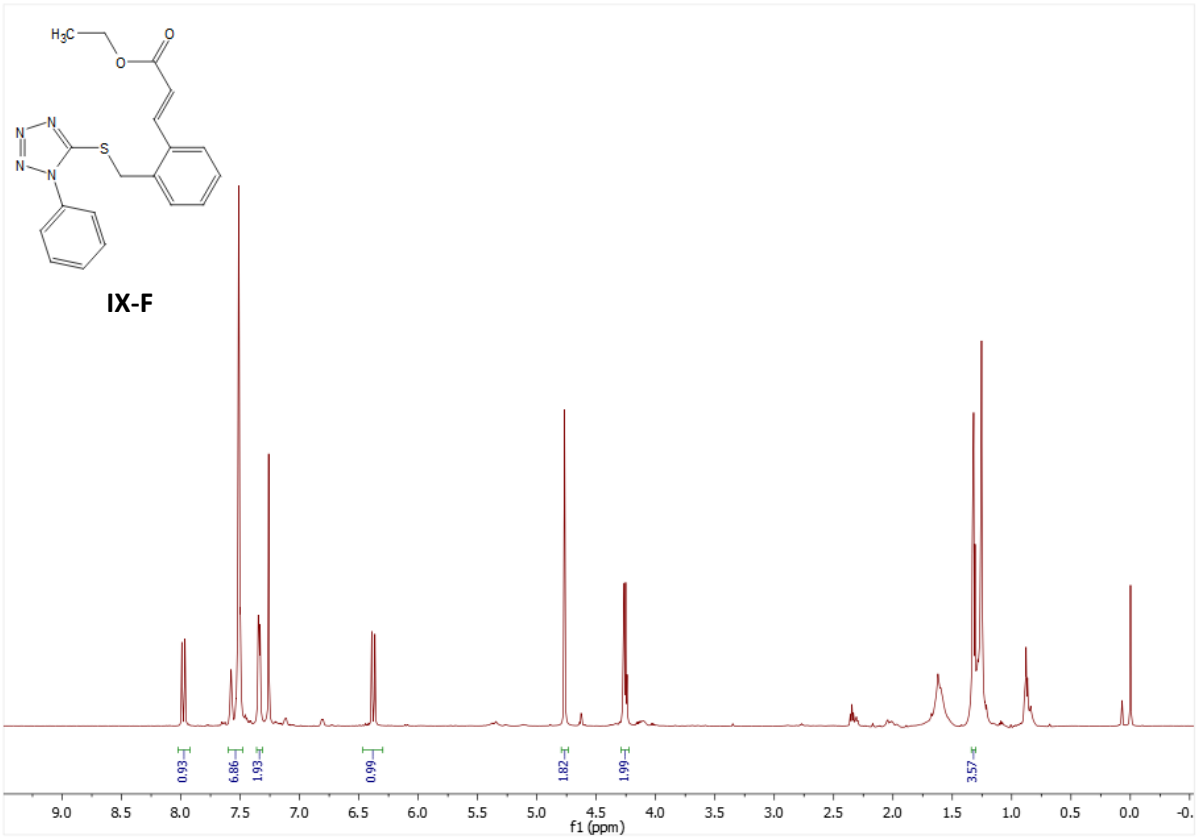
VIII-N

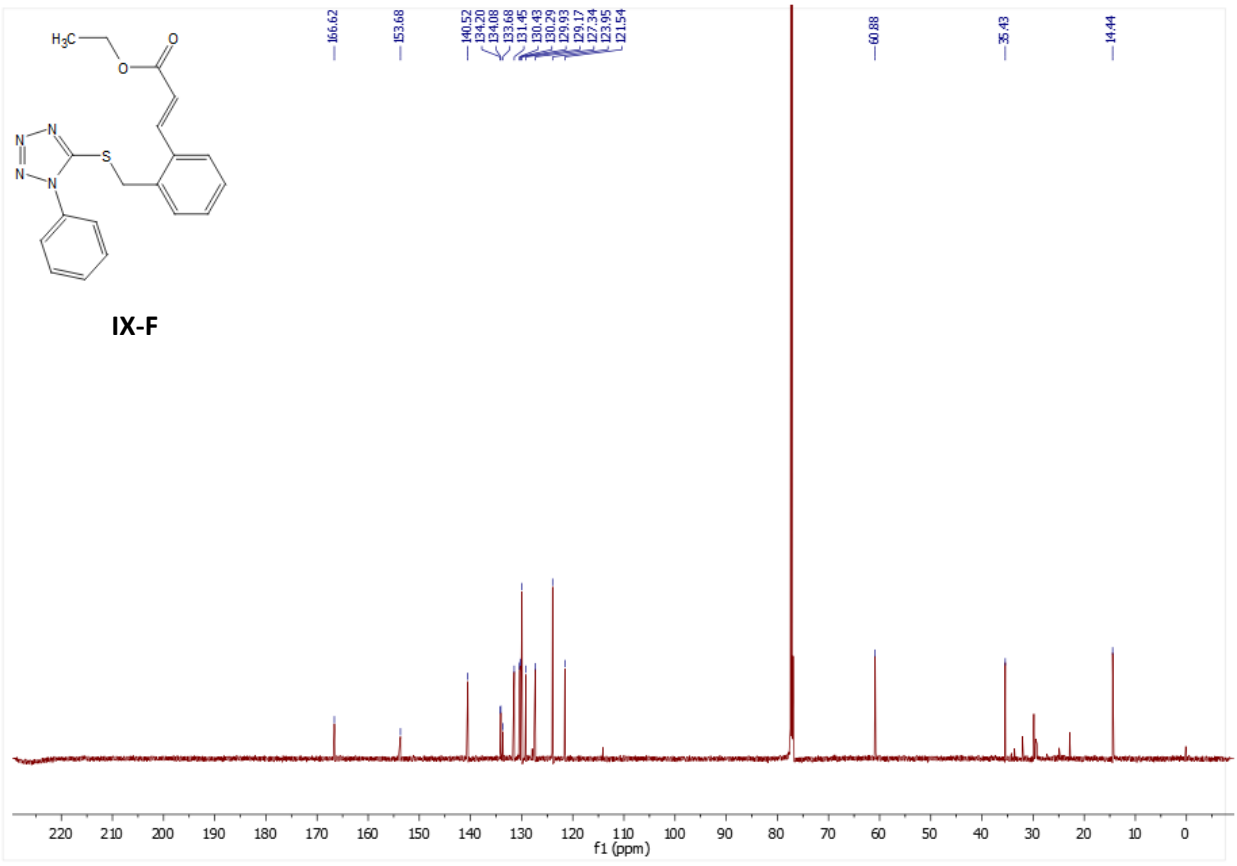

IX-D
1.00
1.03
0.72
0.72
3.15
2.06
0.99
2.06
2.07
3.06
3.10
f1 (ppm)

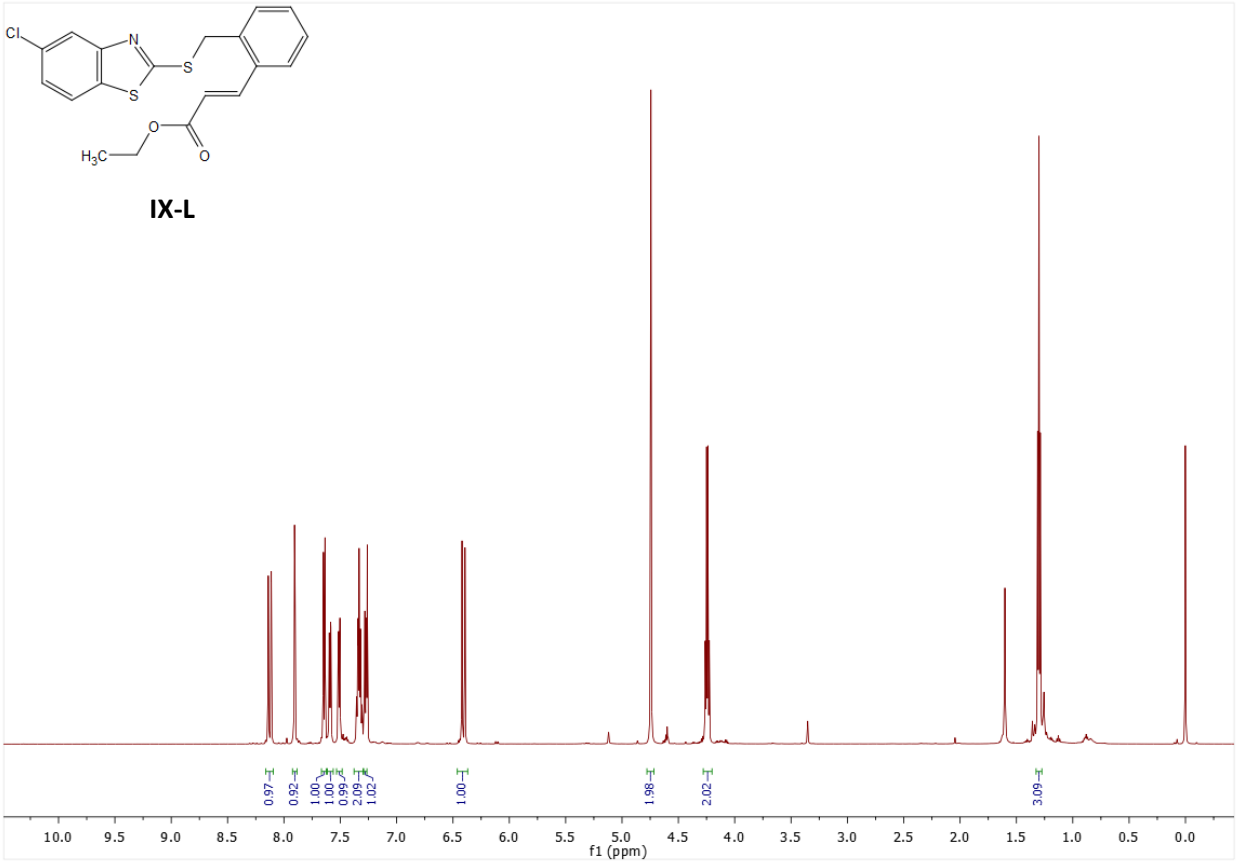

IX-D
166.28
140.84
136.97
136.32
133.20
131.81
131.02
130.22
129.41
129.21
127.31
126.30
119.99
60.05
37.61
20.64
13.89
f1 (ppm)


IX-E
0.96
1.05
1.98
5.01
1.00
3.07
0.99
2.98
3.06
f1 (ppm)


IX-E
166.42
142.18
140.26
139.12
134.96
132.65
129.88
129.77
128.93
128.55
126.83
124.58
120.44
60.70
60.65
21.56
14.52
f1 (ppm)

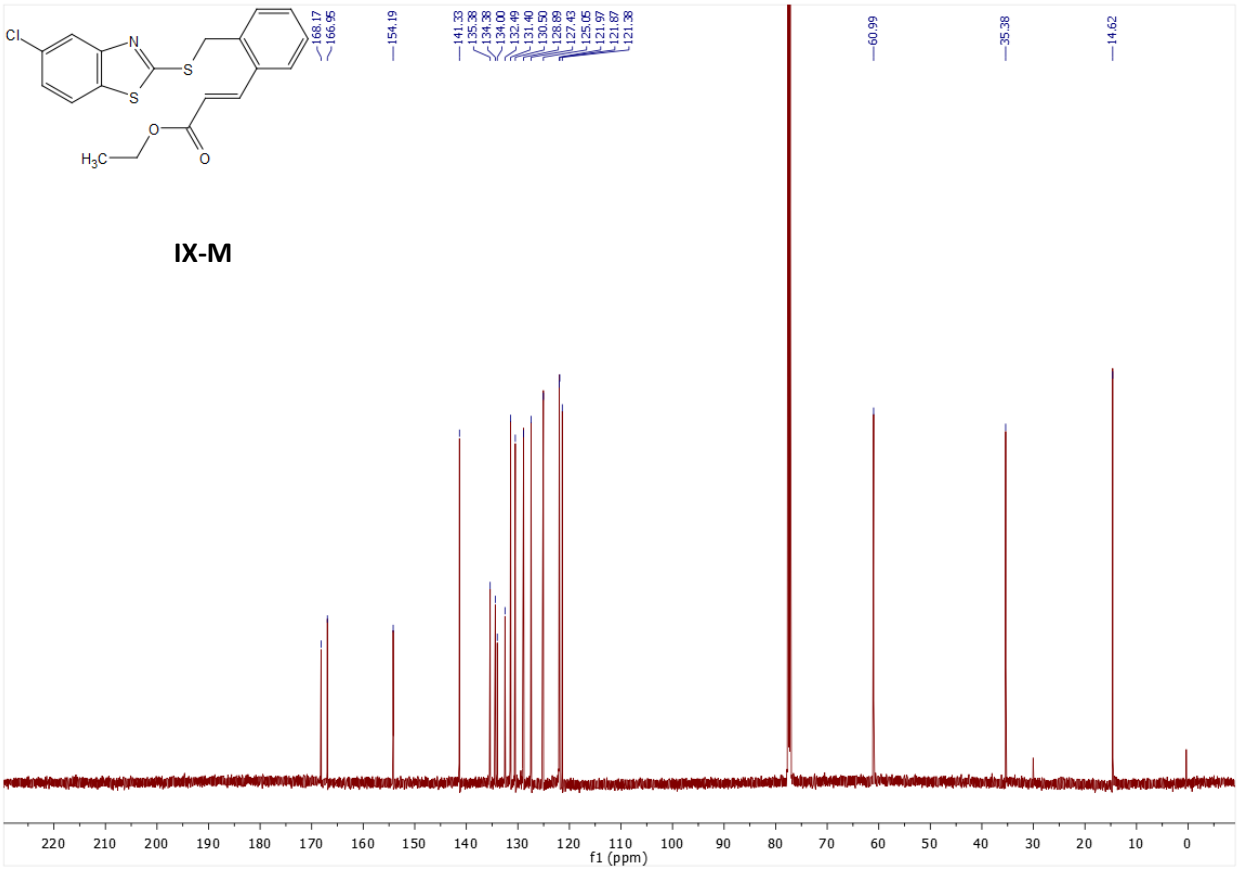

IX-F
0.93
6.86
1.93
0.99
1.82
1.99
3.57
f1 (ppm)


IX-F
166.62
153.68
140.52
134.20
134.08
133.68
131.45
130.43
130.29
129.93
129.17
127.34
123.95
121.54
60.88
35.43
14.44
f1 (ppm)

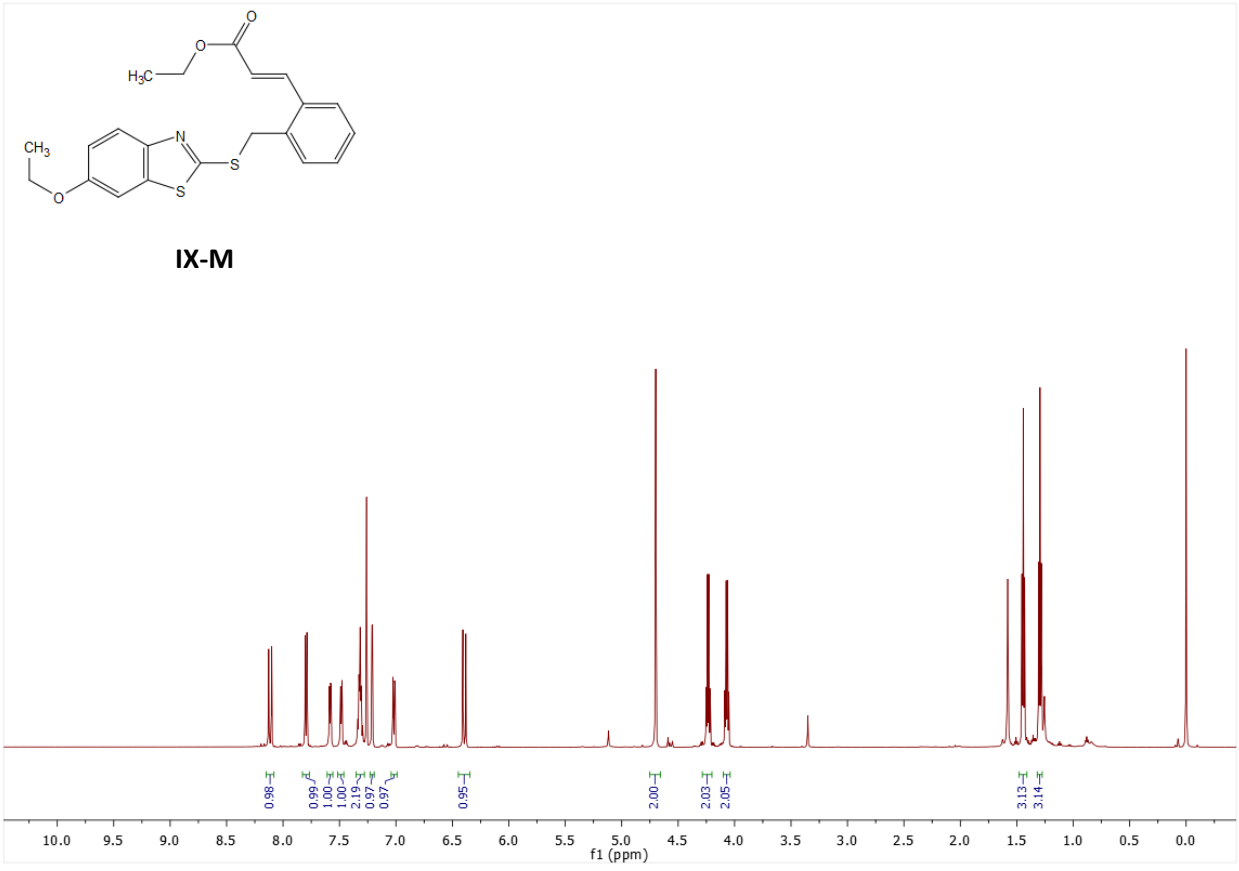

Cl
N
S
S
O
O
H3C
0.97
0.92
1.00
1.00
0.99
2.09
1.02
1.00
1.98
2.02
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

IX-L

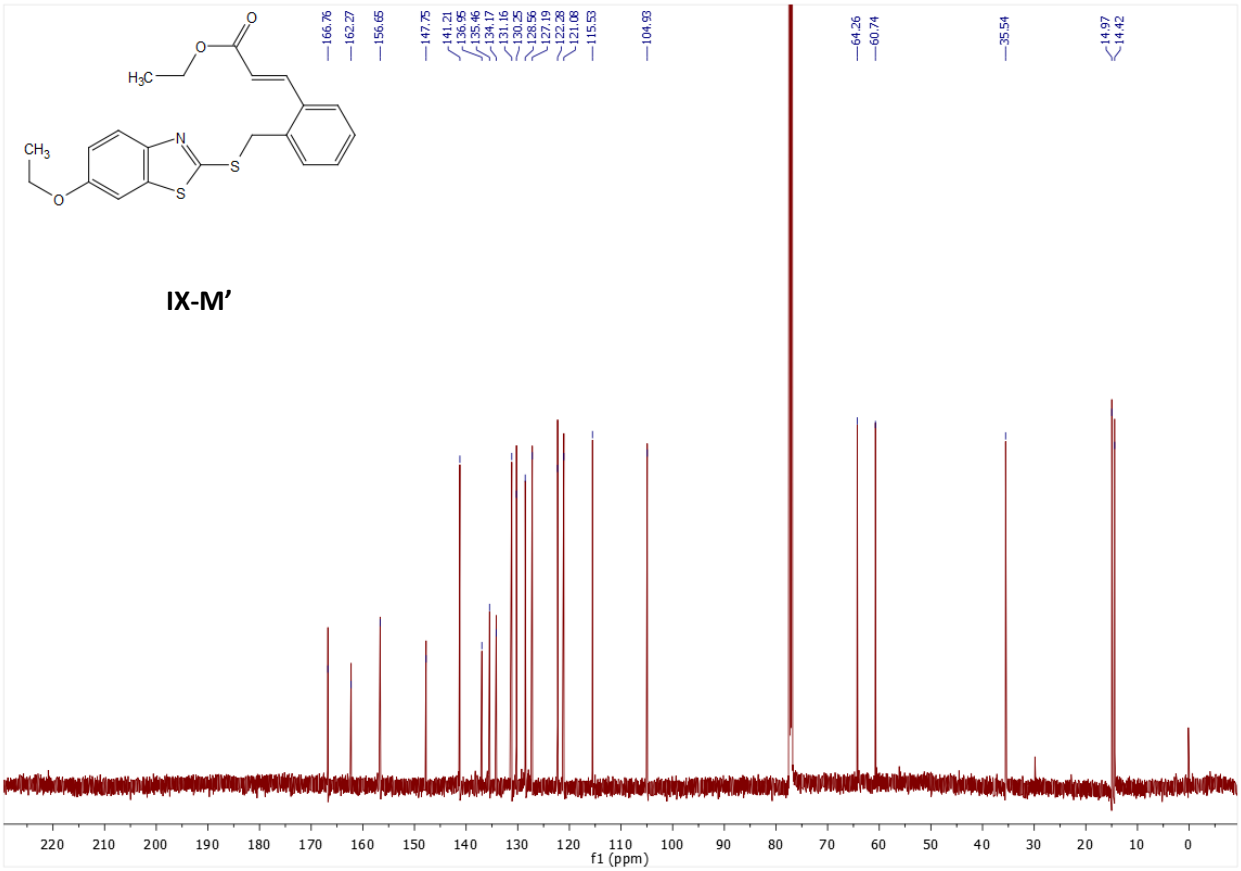
IX-L


Cl
N
S
S
O
O
H3C
168.17
166.95
154.19
141.33
135.38
134.38
134.00
132.49
131.40
130.50
128.89
127.43
125.05
121.97
121.67
121.38
60.99
35.38
14.62
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

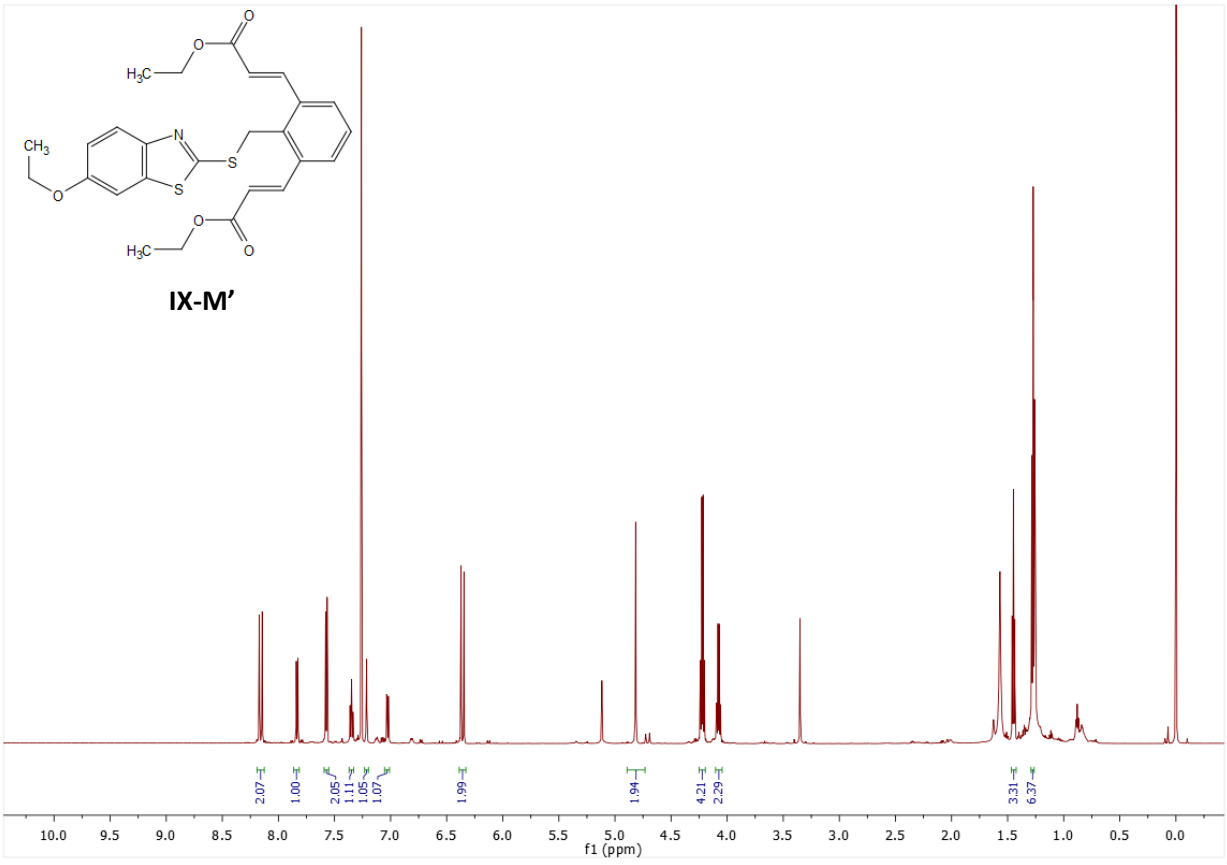
IX-M


O
O
H3C
CH3
N
S
S
O
0.98
0.99
1.00
1.00
2.19
0.97
0.97
0.95
2.00
2.03
2.05
3.13
3.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

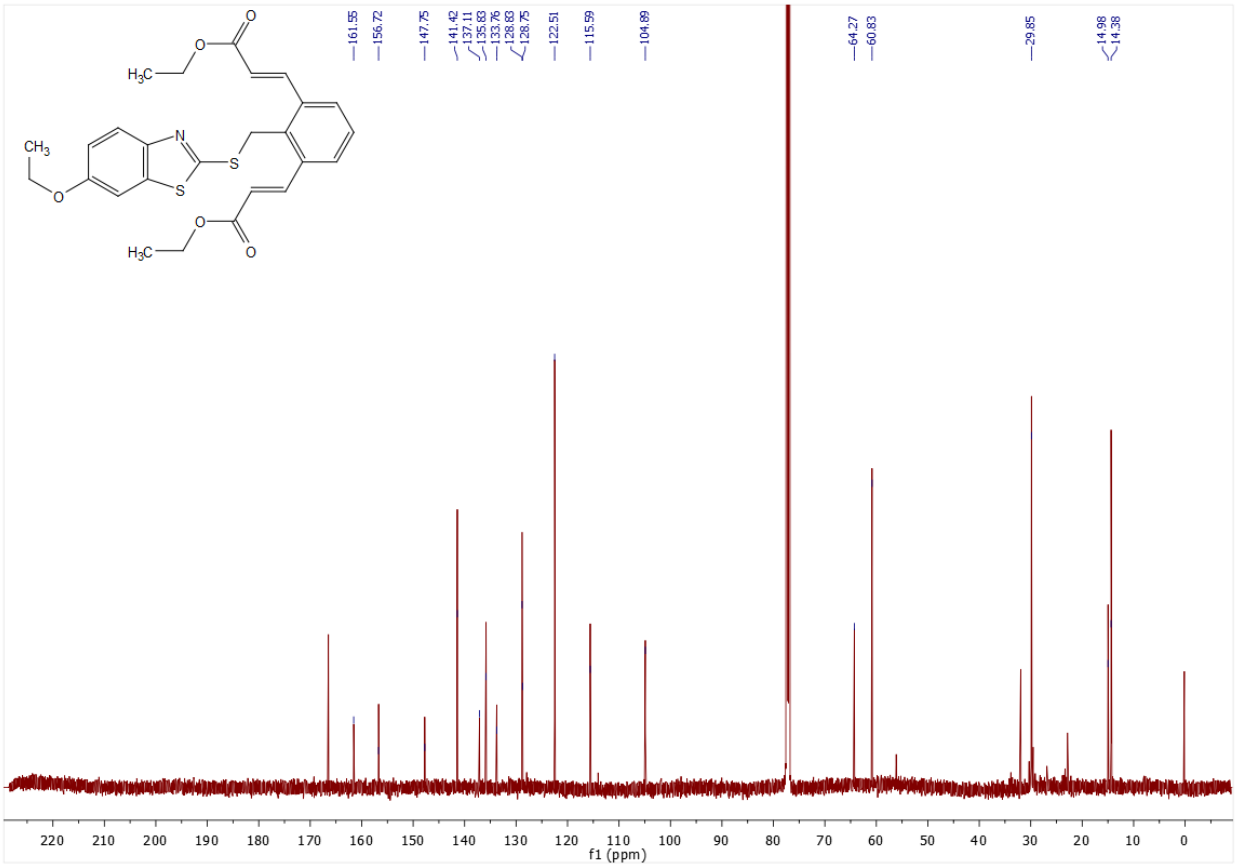
IX-M

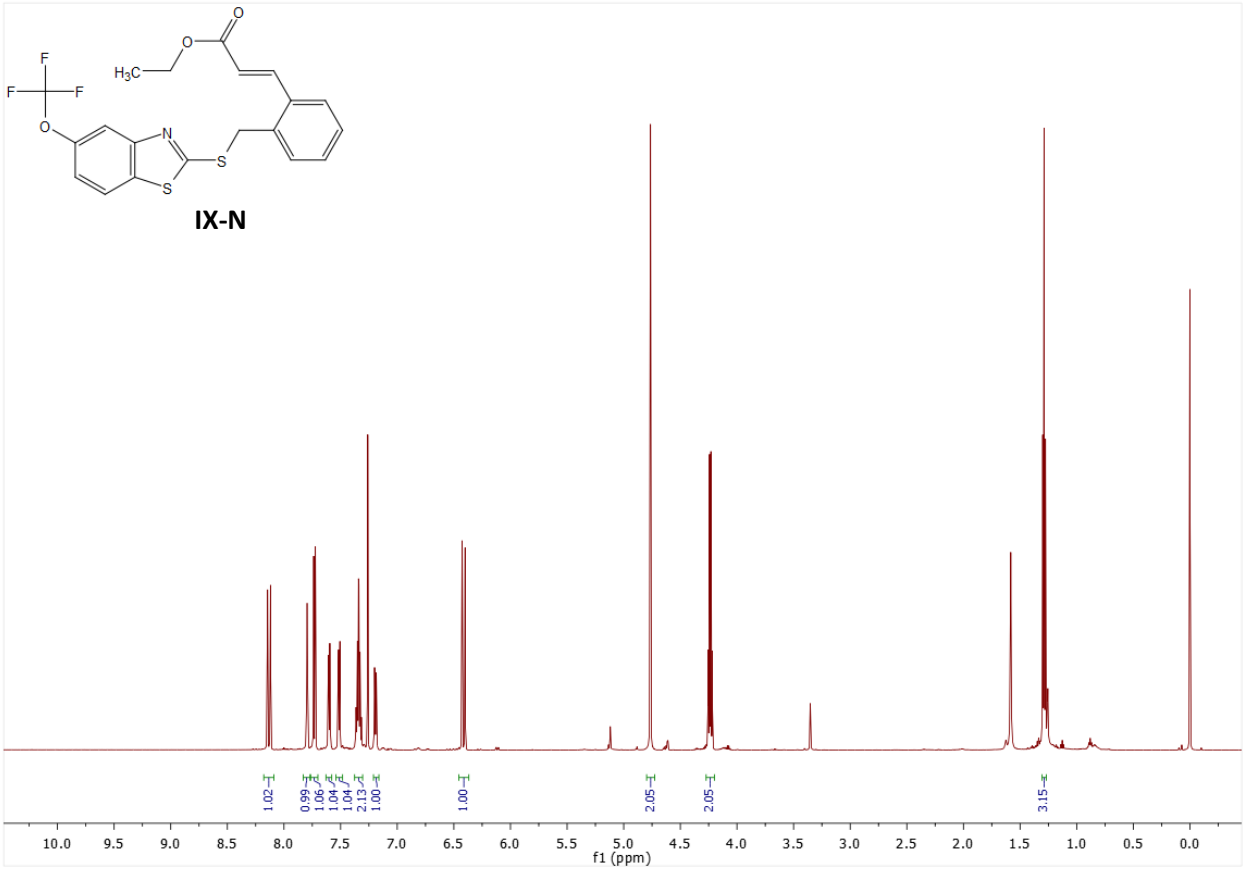

166.76
162.27
156.65
147.75
141.21
136.95
135.46
134.17
131.16
130.25
128.56
127.19
122.28
121.08
115.53
104.93
64.26
60.74
35.54
14.97
14.42
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

IX-M'


2.07
1.00
2.05
1.11
1.05
1.07
1.99
1.94
4.21
2.29
3.31
6.37
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

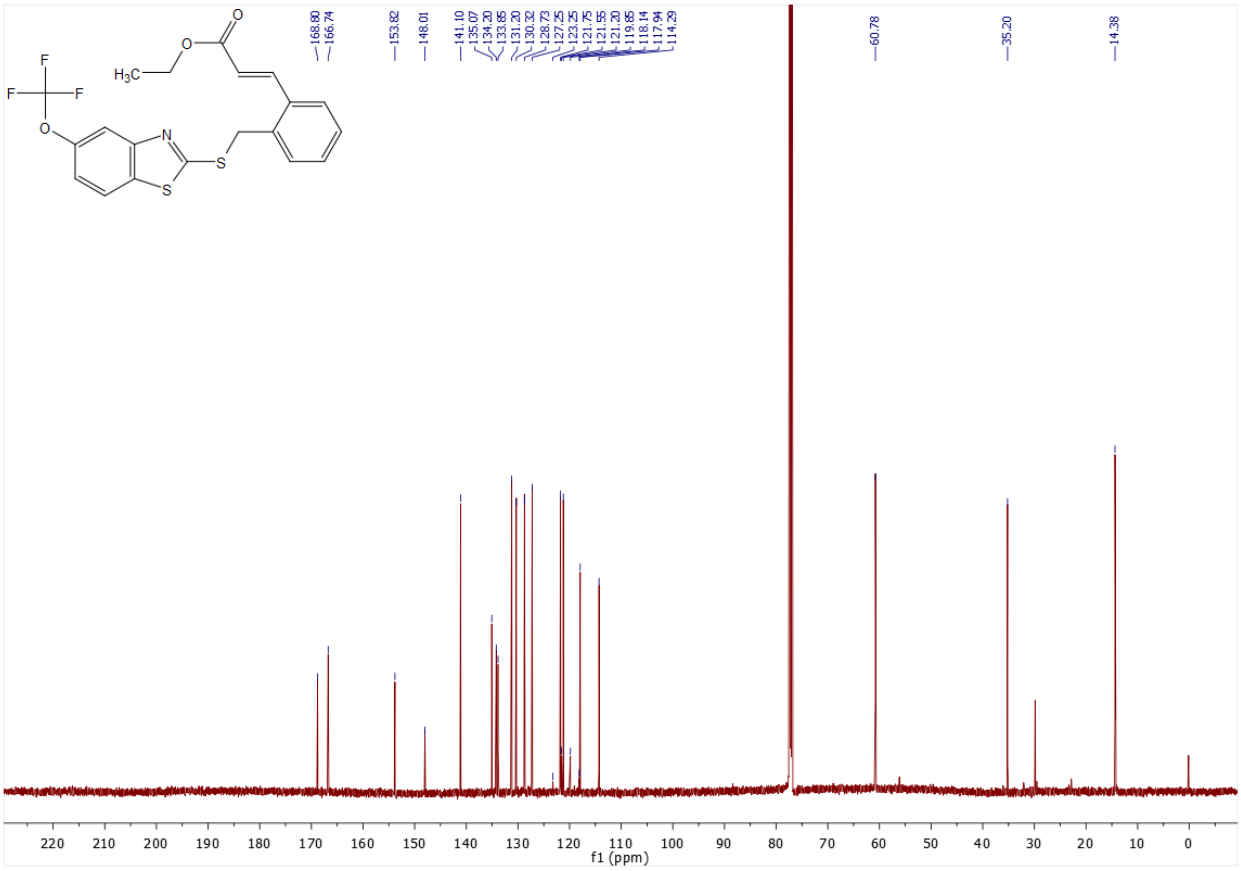
IX-M'

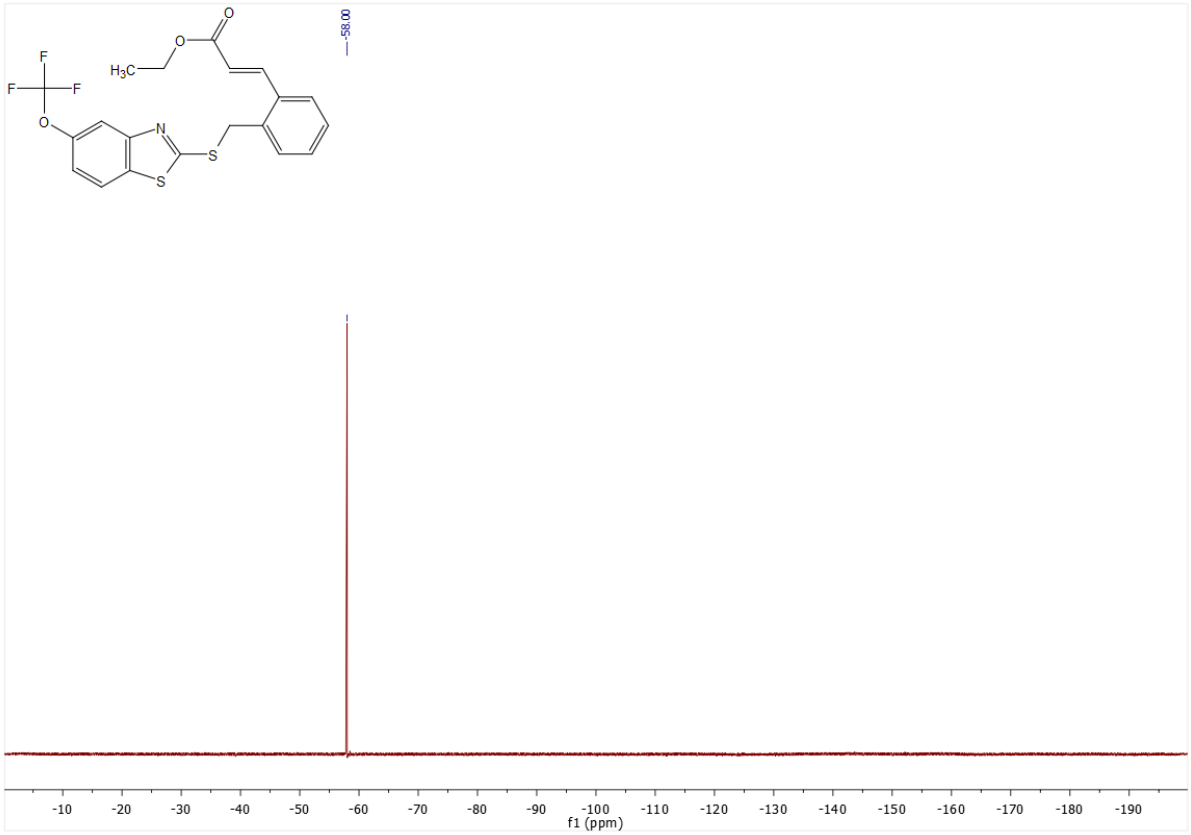

161.55
156.72
147.75
141.42
137.11
135.83
133.76
128.83
128.75
122.51
115.59
104.89
64.27
60.83
29.85
14.98
14.38
f1 (ppm)

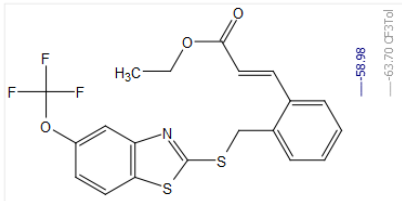

F
F
F
O
O
O
H3C
N
S
S
1.02
0.99
1.06
1.04
1.04
2.13
1.00
1.00
2.05
2.05
3.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

IX-N

IX-N

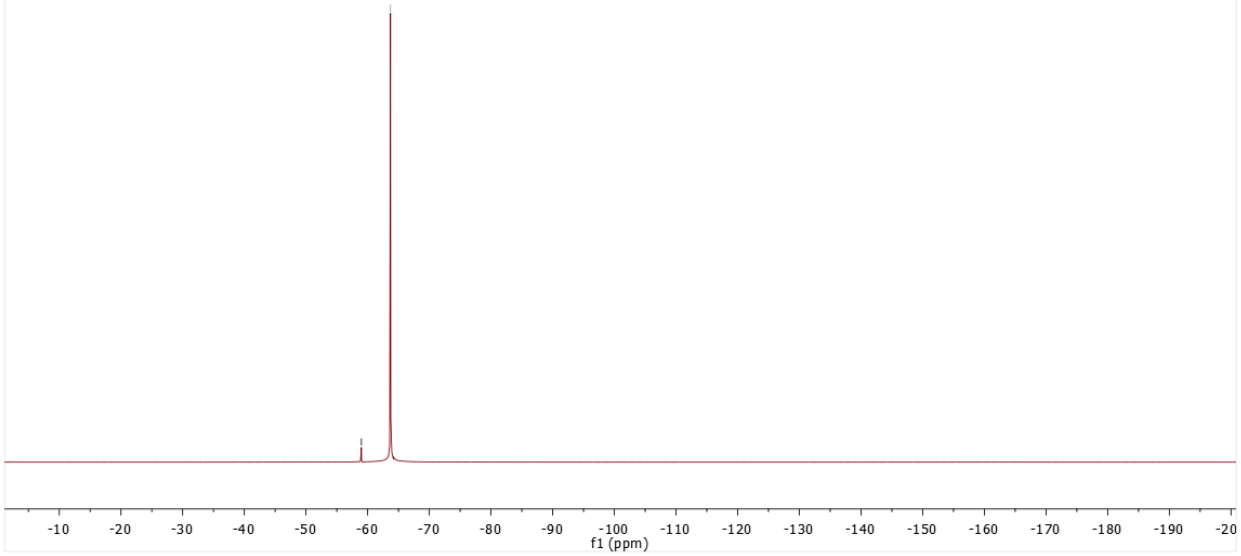

168.80
166.74
153.82
148.01
141.10
135.07
134.20
133.85
131.20
130.32
128.73
127.25
123.25
121.75
121.55
121.20
119.85
118.14
117.94
114.29
60.78
35.20
14.38
f1 (ppm)

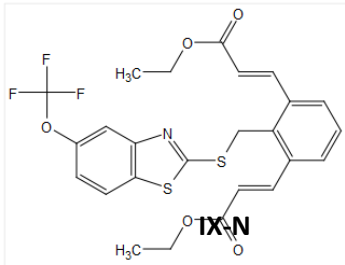

-58.00
f1 (ppm)



IX-N

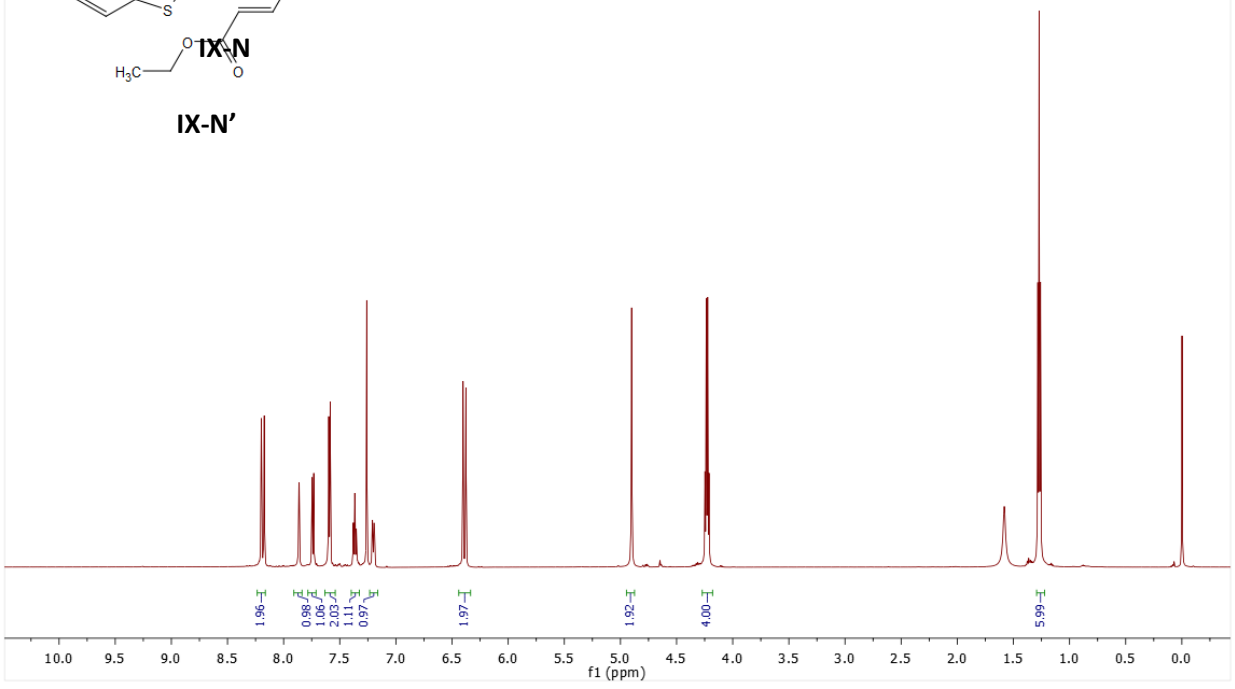
IX-N’

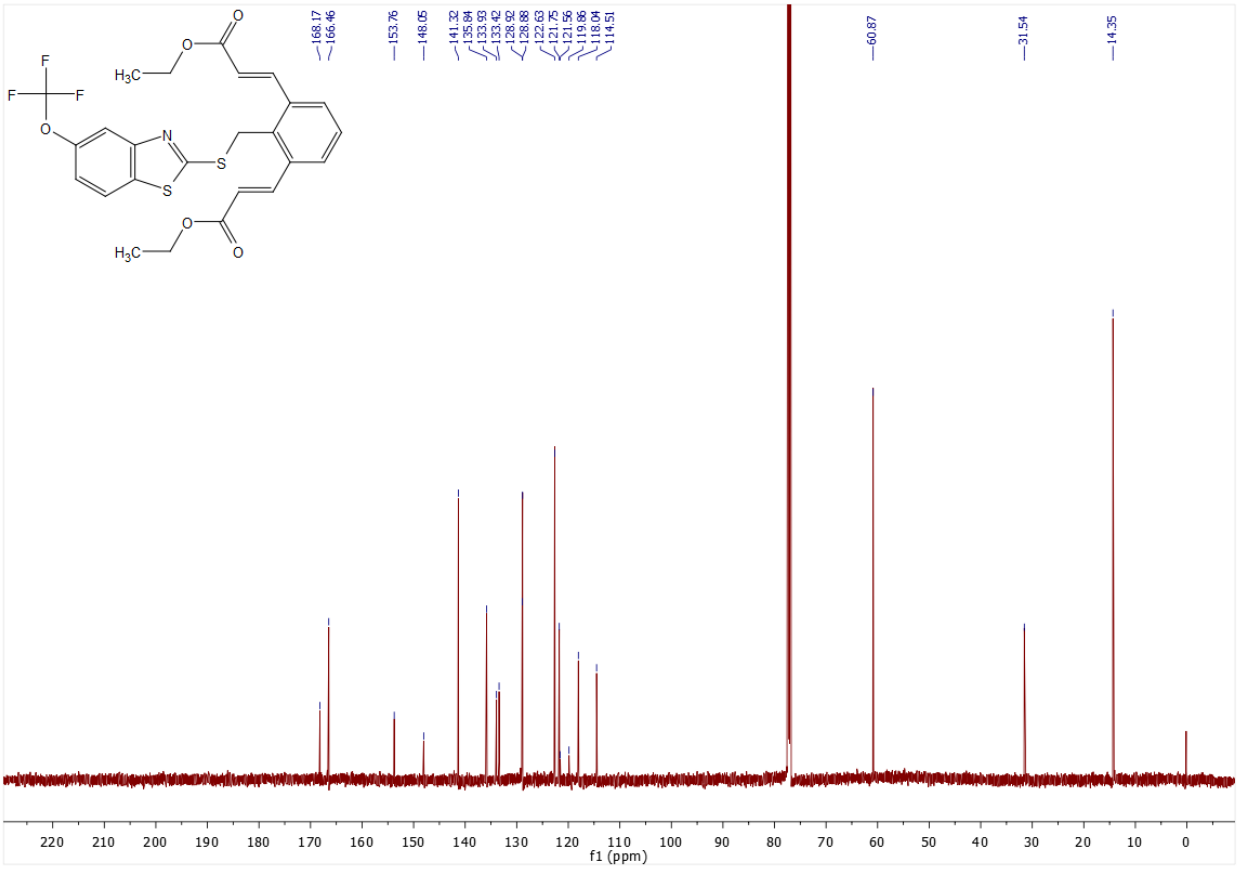


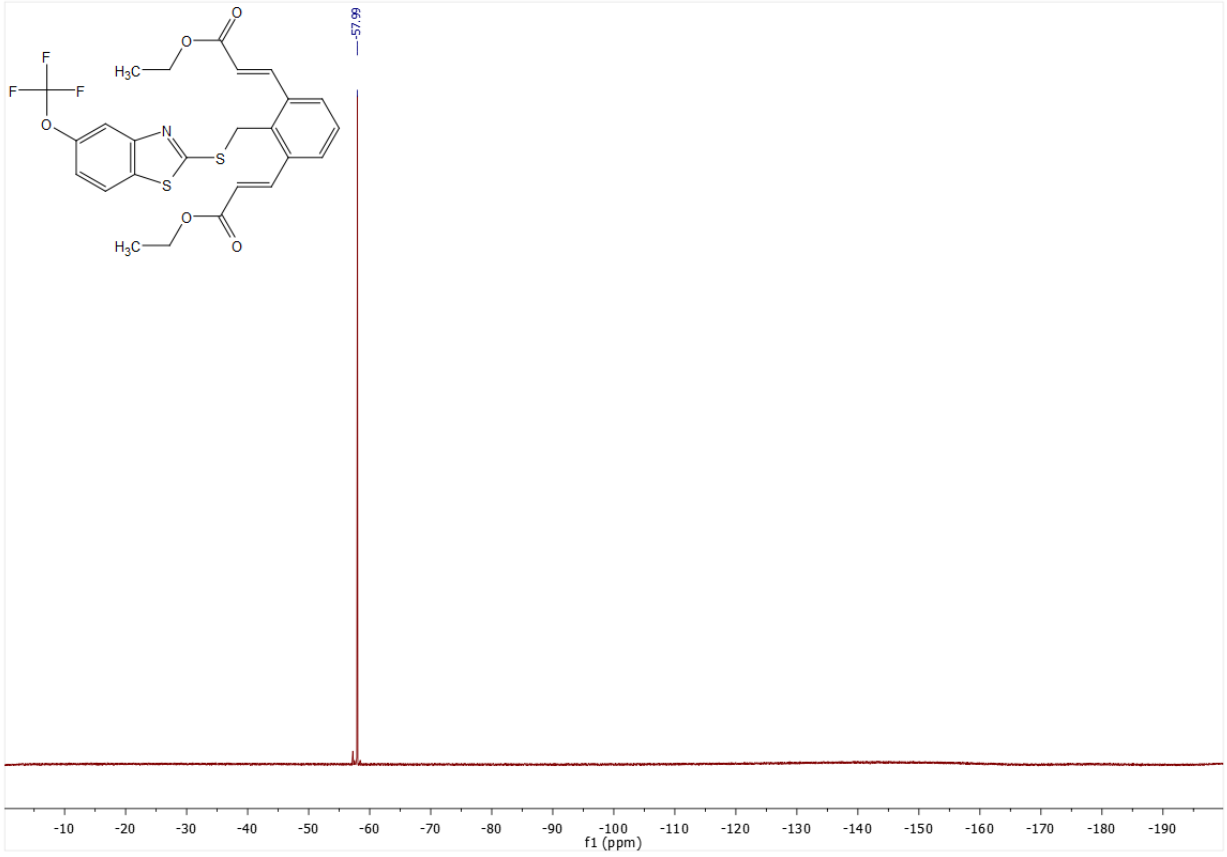


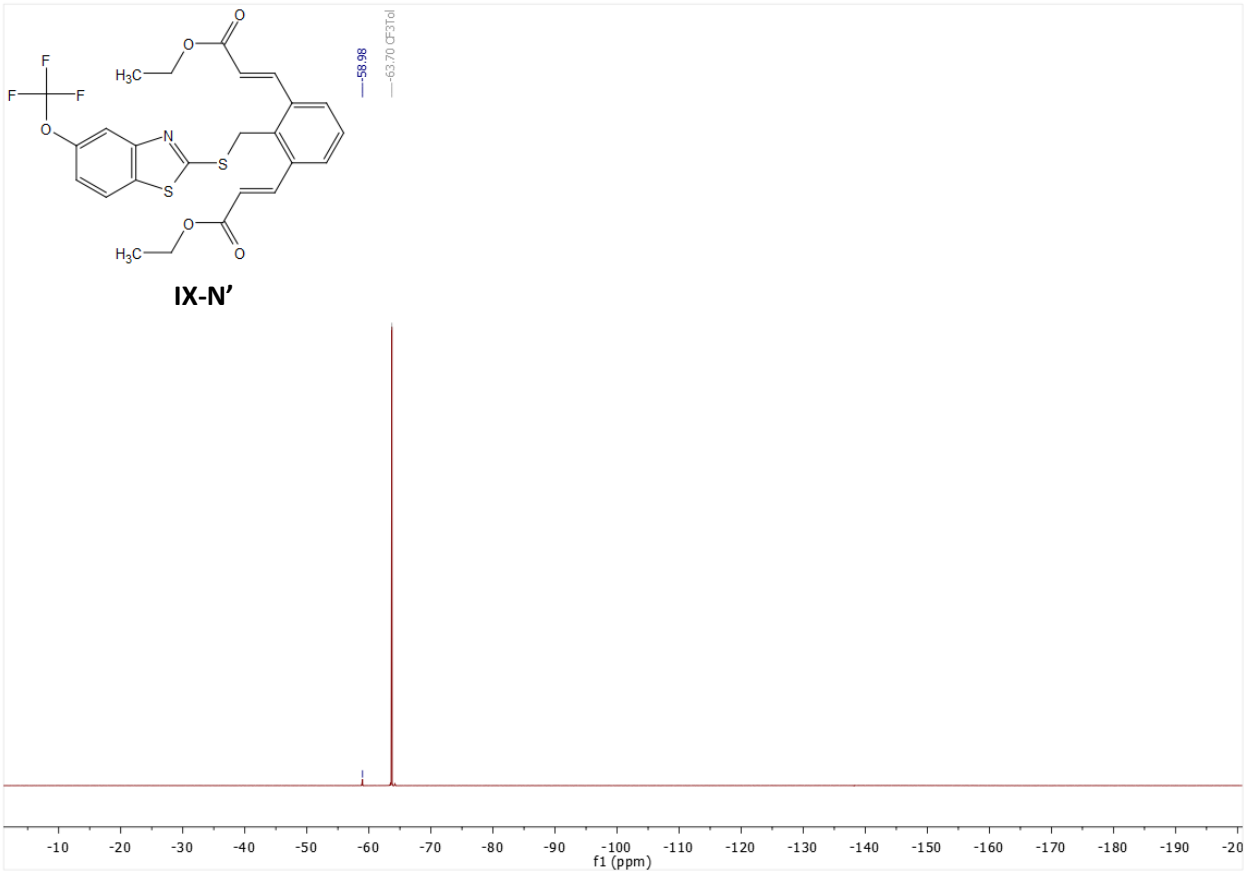
IX-N

IX-N’



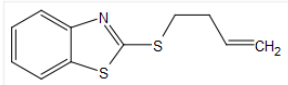

168.17
166.46
153.76
148.05
141.32
135.84
133.93
133.42
128.92
128.88
122.63
121.75
121.56
119.86
118.04
114.51
60.87
31.54
14.35
f1 (ppm)


-57.99
f1 (ppm)

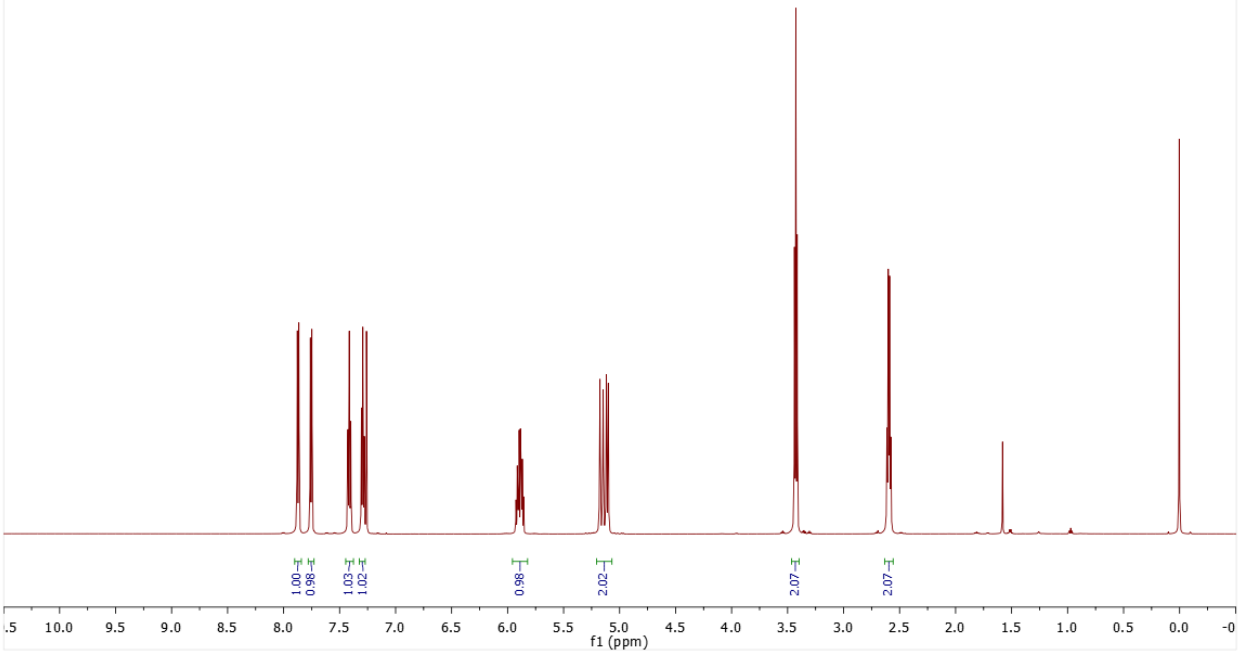

F
F
F
O
O
H3C
O
O
N
S
S
O
H3C
O
-58.98
-63.70 CF3Tol
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
f1 (ppm)

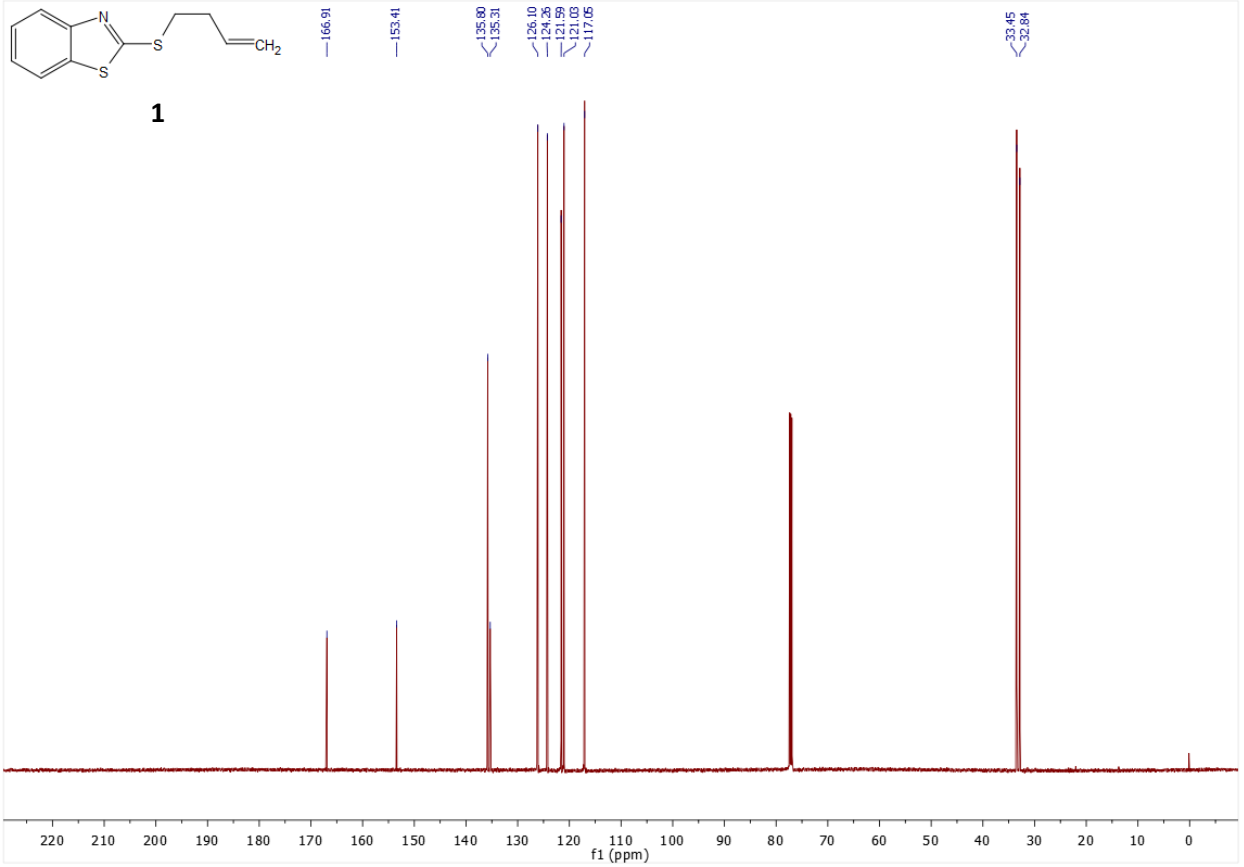
IX-N’

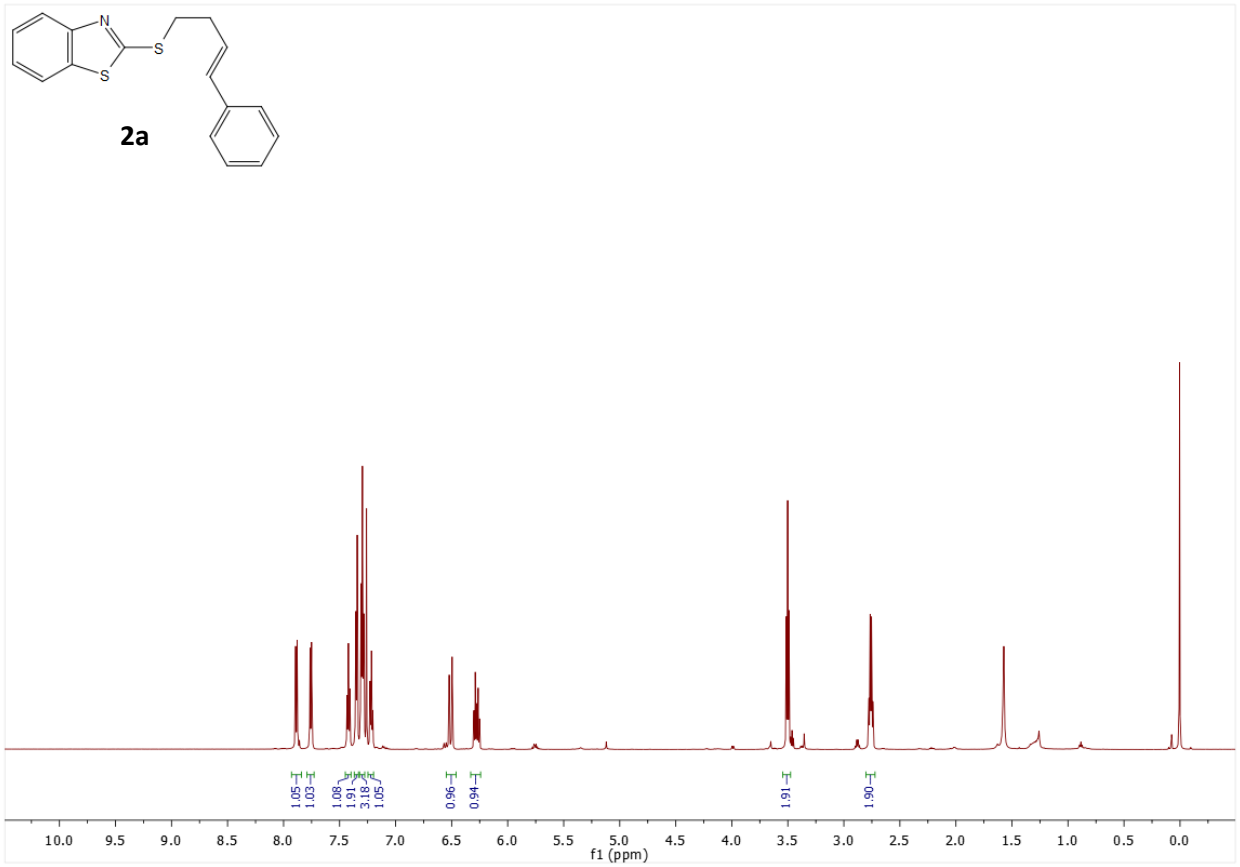
IX-N’

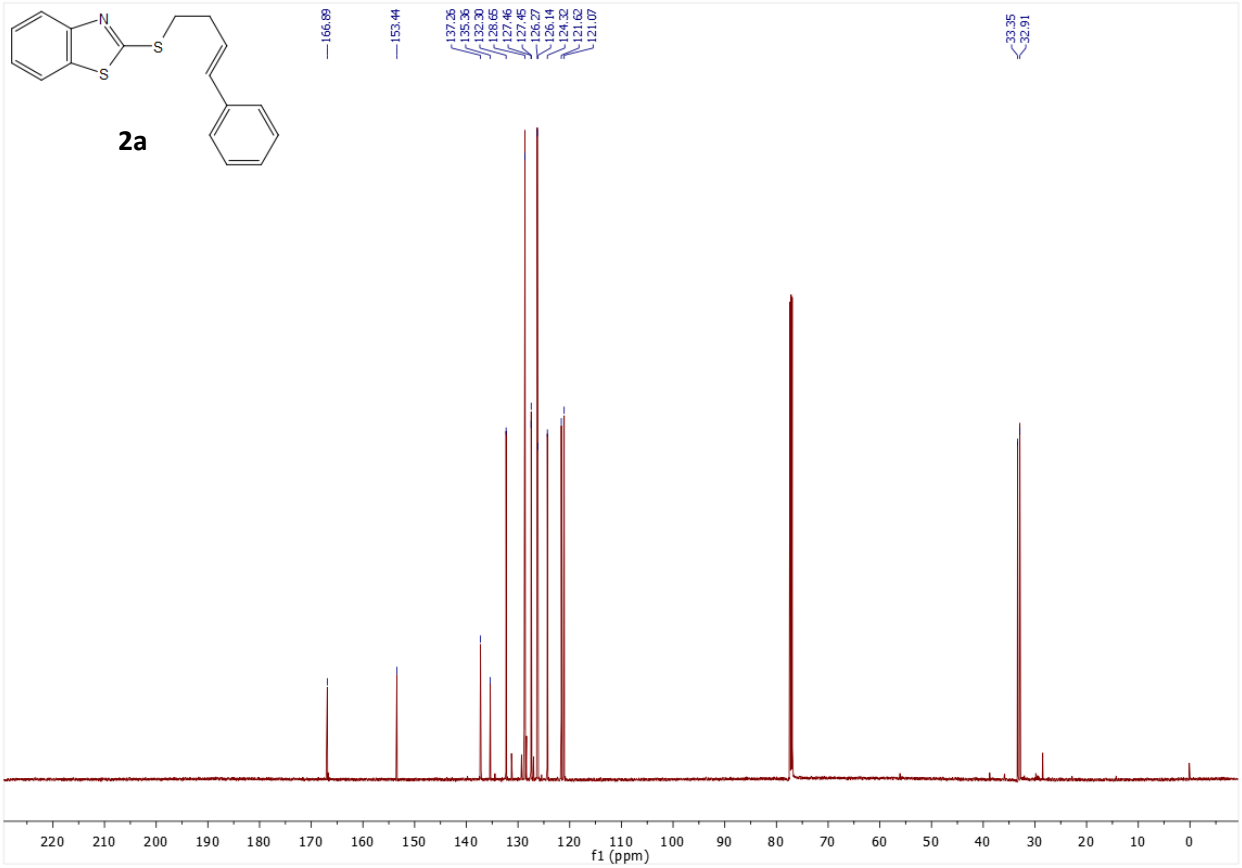

N
S
S
CH2

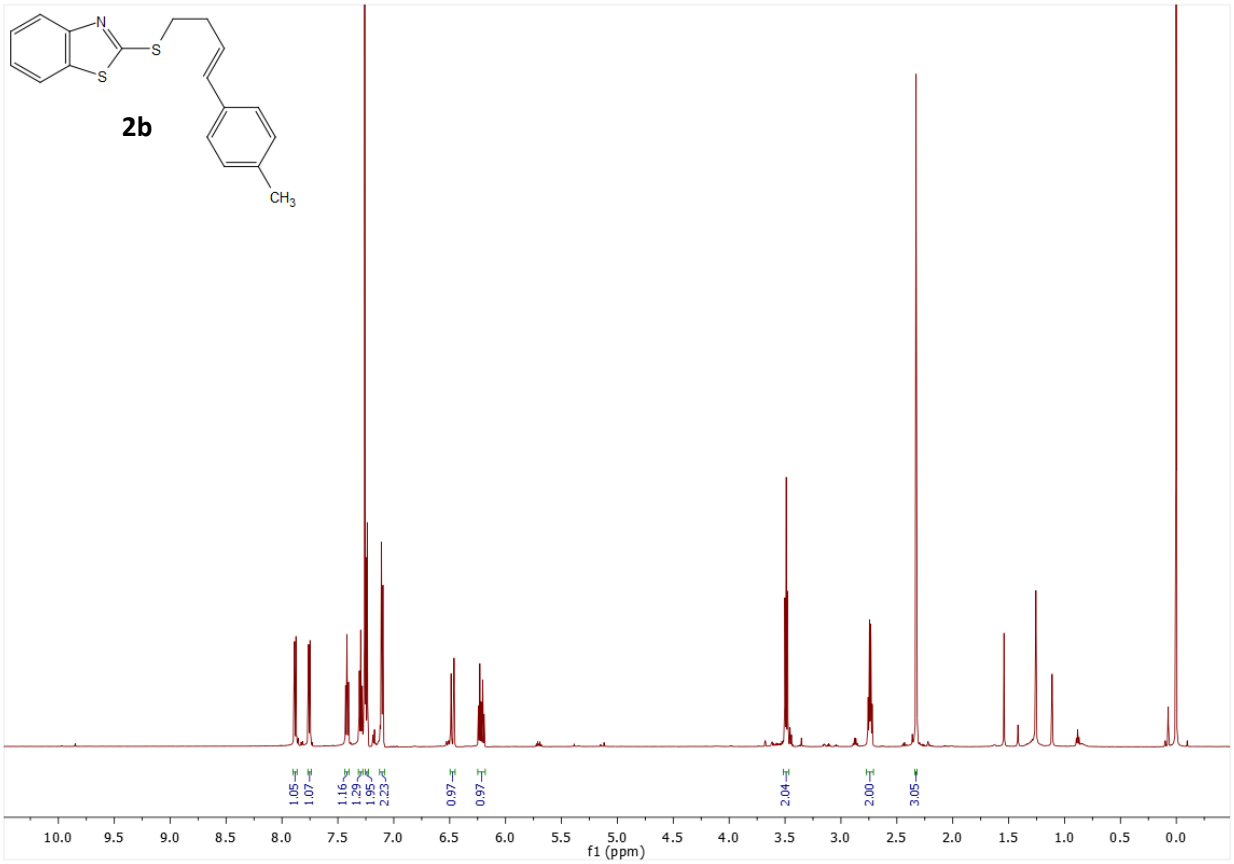
1

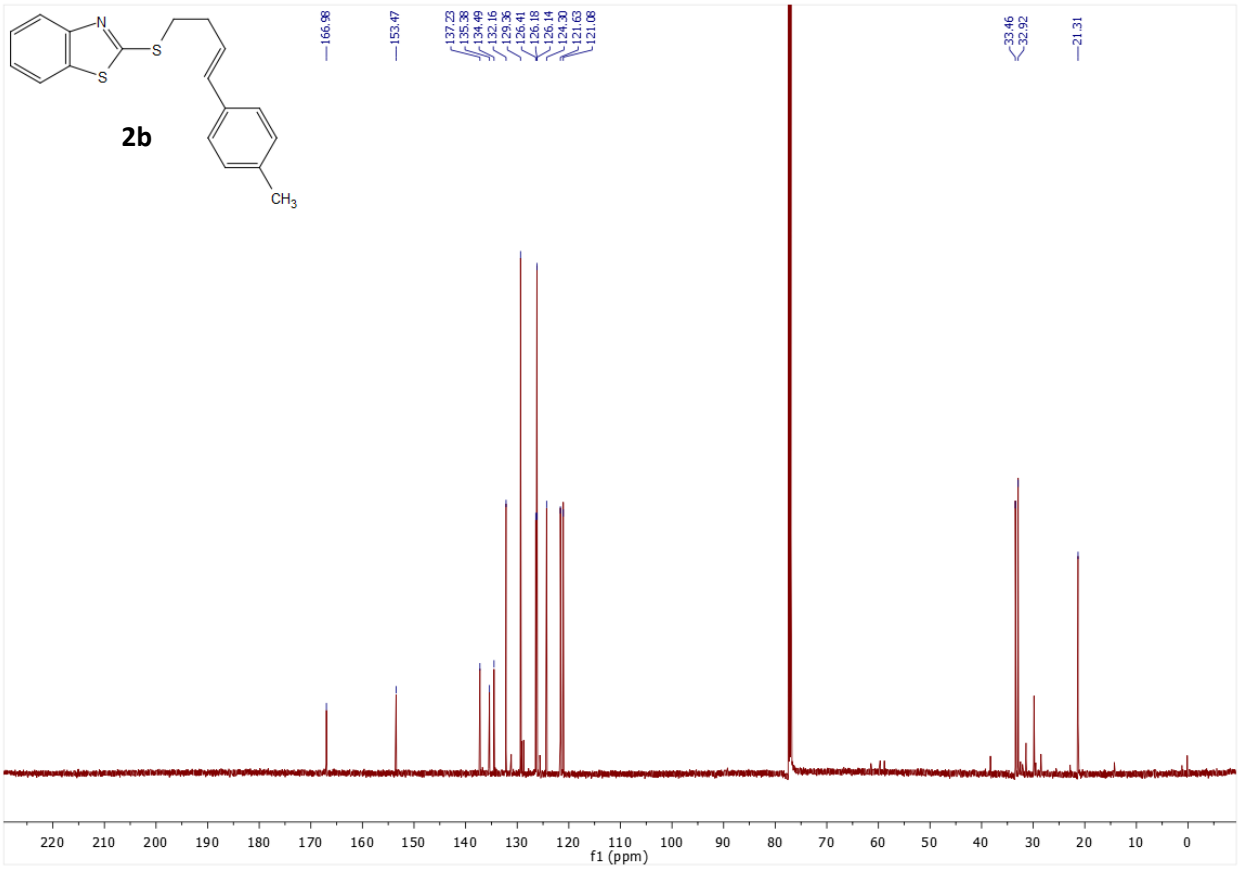

1.00
0.98
1.03
1.02
0.98
2.02
2.07
2.07
f1 (ppm)

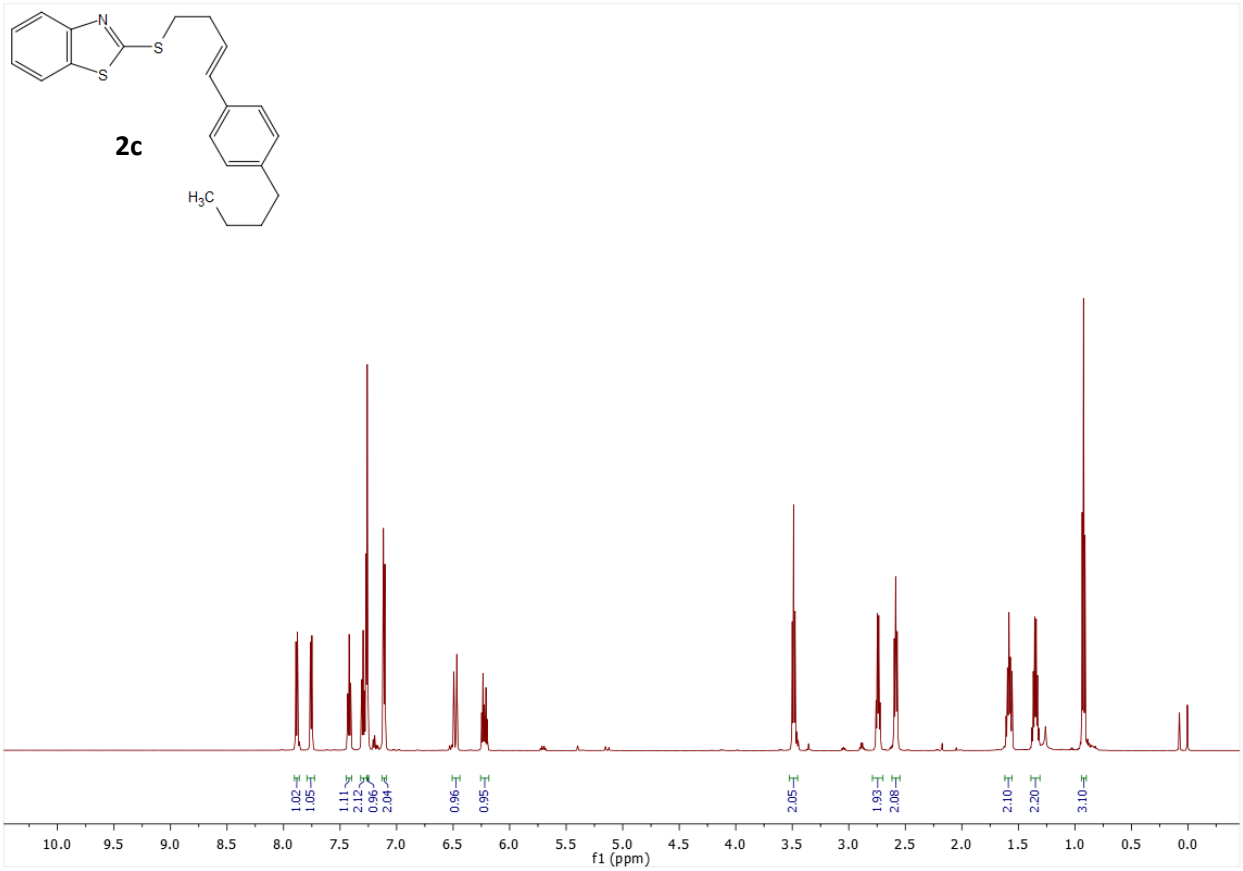

166.91
153.41
135.80
135.31
126.10
124.26
121.59
121.03
117.05
33.45
32.84
f1 (ppm)

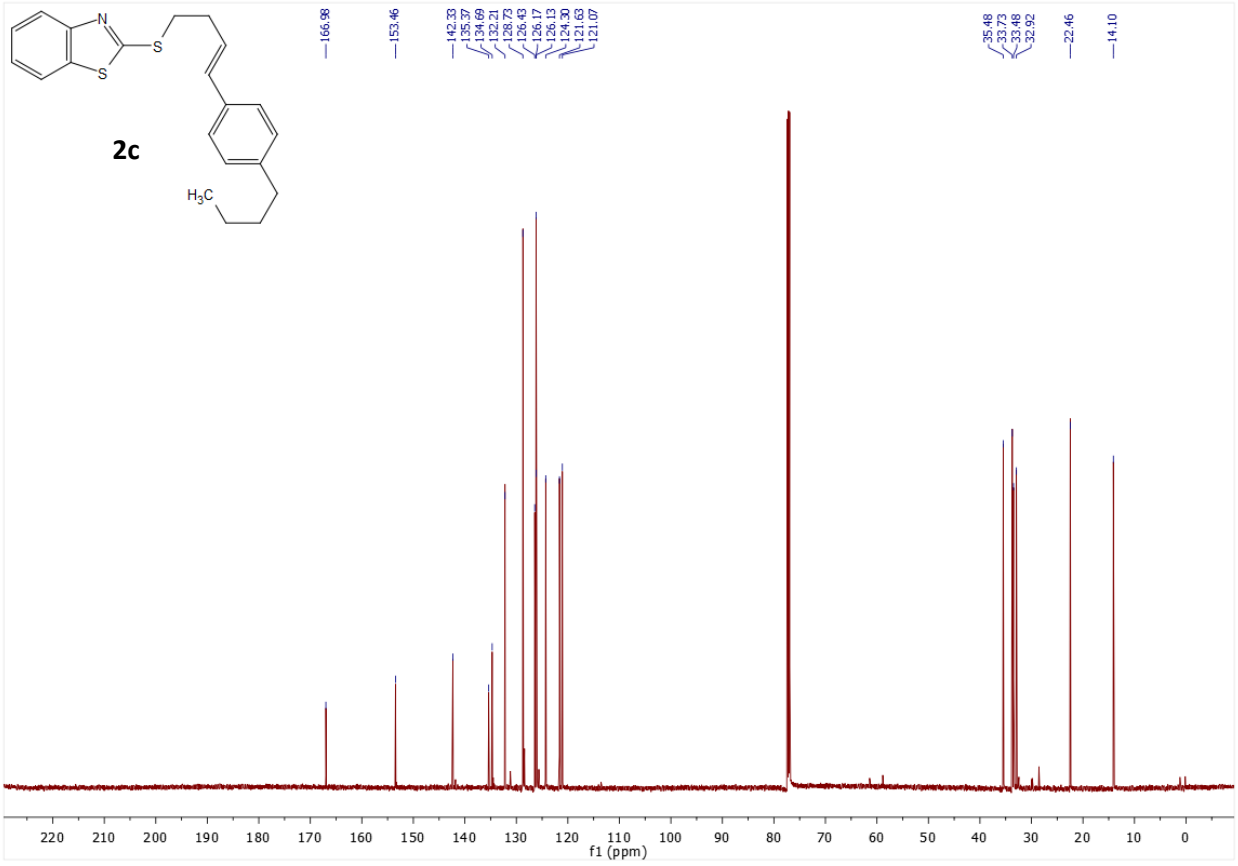

2a
1.05
1.03
1.08
1.91
3.18
1.05
0.96
0.94
1.91
1.90
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

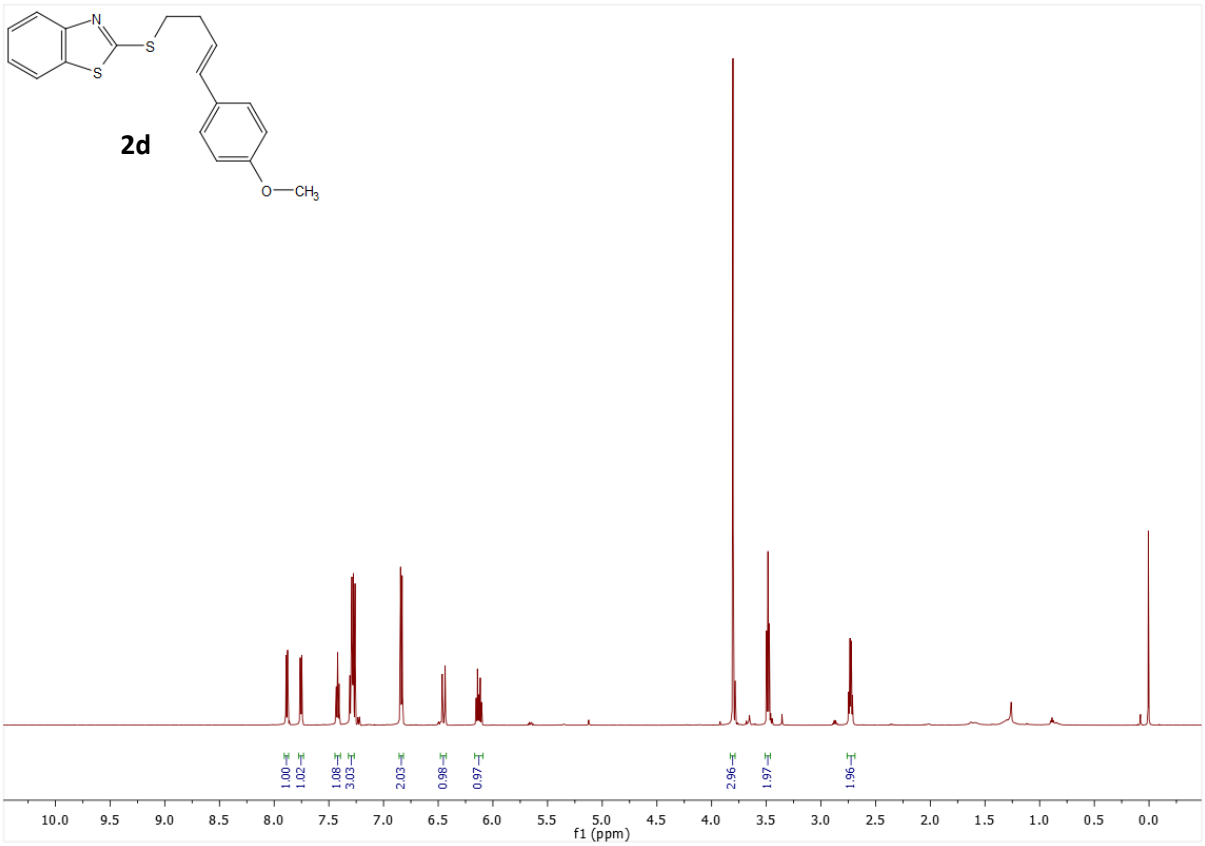

2a
166.89
153.44
137.26
135.36
132.30
128.65
127.46
127.45
126.27
126.14
124.32
121.62
121.07
33.35
32.91
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

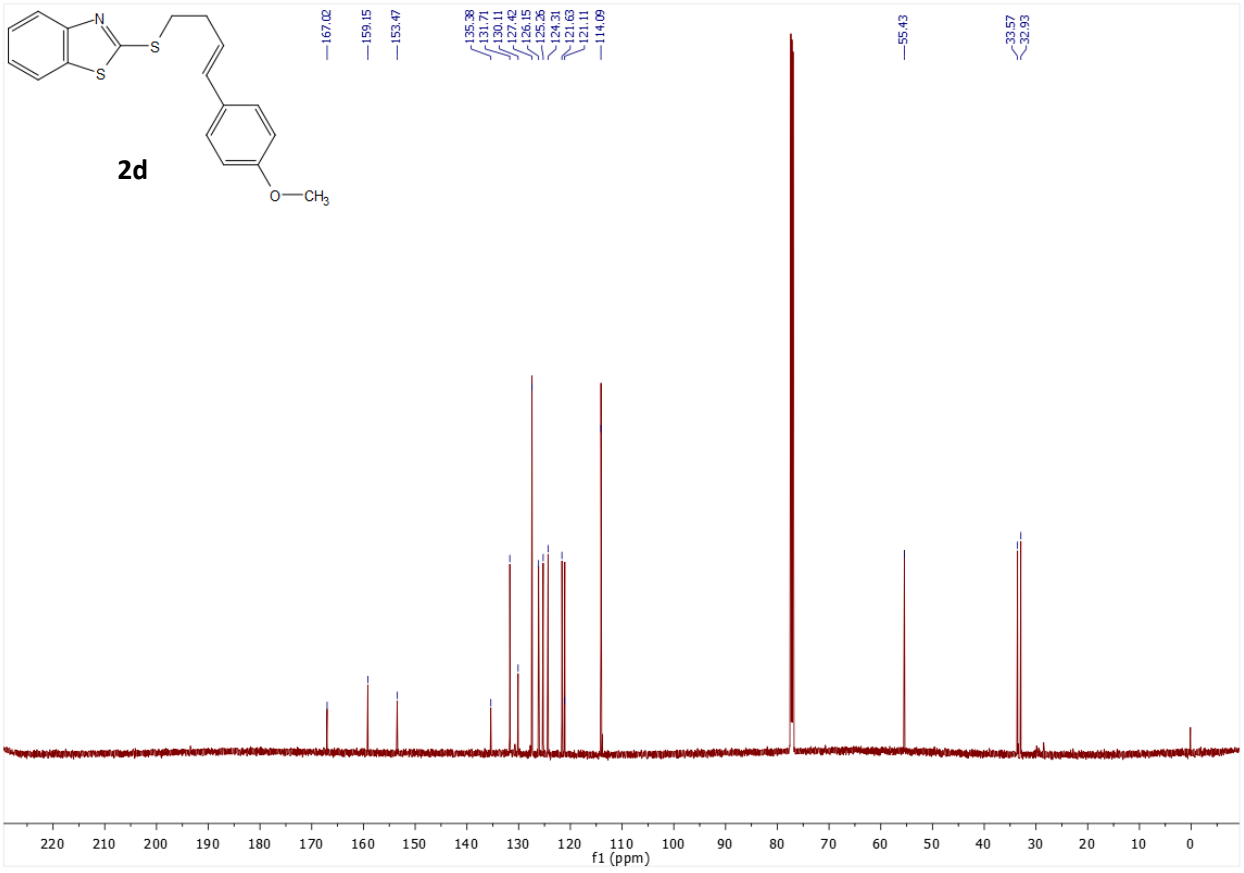

2b
N
S
S
CH3
1.05
1.07
1.16
1.29
1.95
2.23
0.97
0.97
2.04
2.00
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

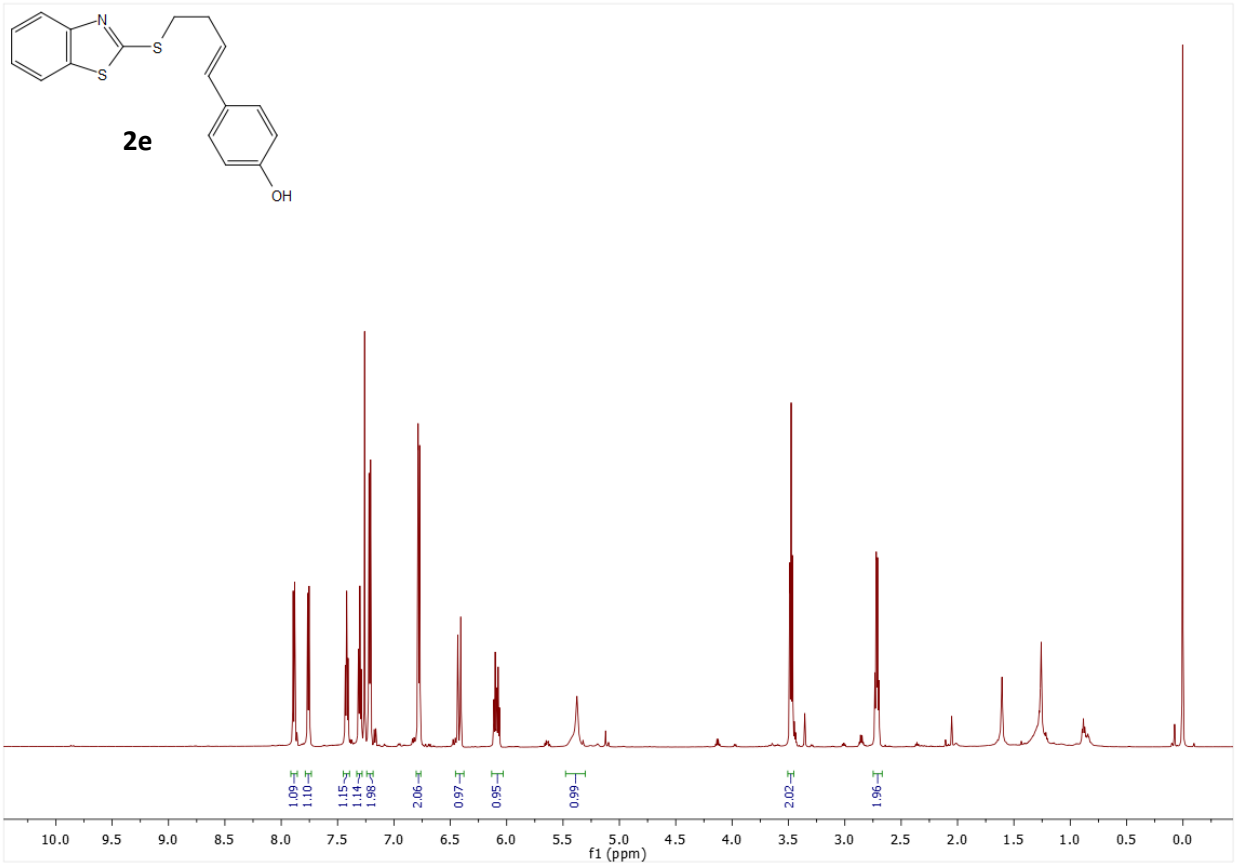

2b
N
S
S
CH3
166.98
153.47
137.23
135.38
134.49
132.16
129.36
126.41
126.18
126.14
124.30
121.63
121.08
33.46
32.92
21.31
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

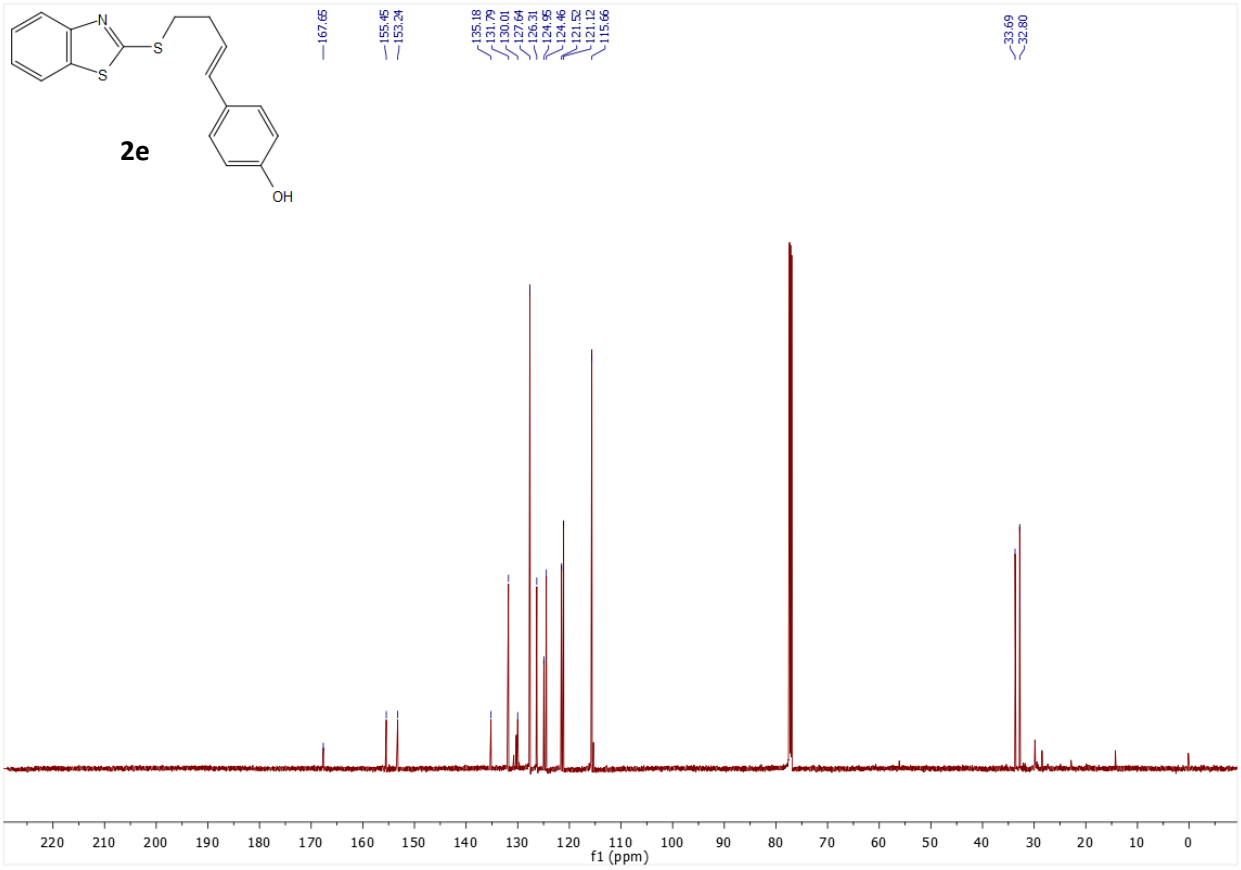

2c
H3C
1.02
1.05
1.11
2.12
0.96
2.04
0.96
0.95
2.05
1.93
2.08
2.10
2.20
3.10
f1 (ppm)

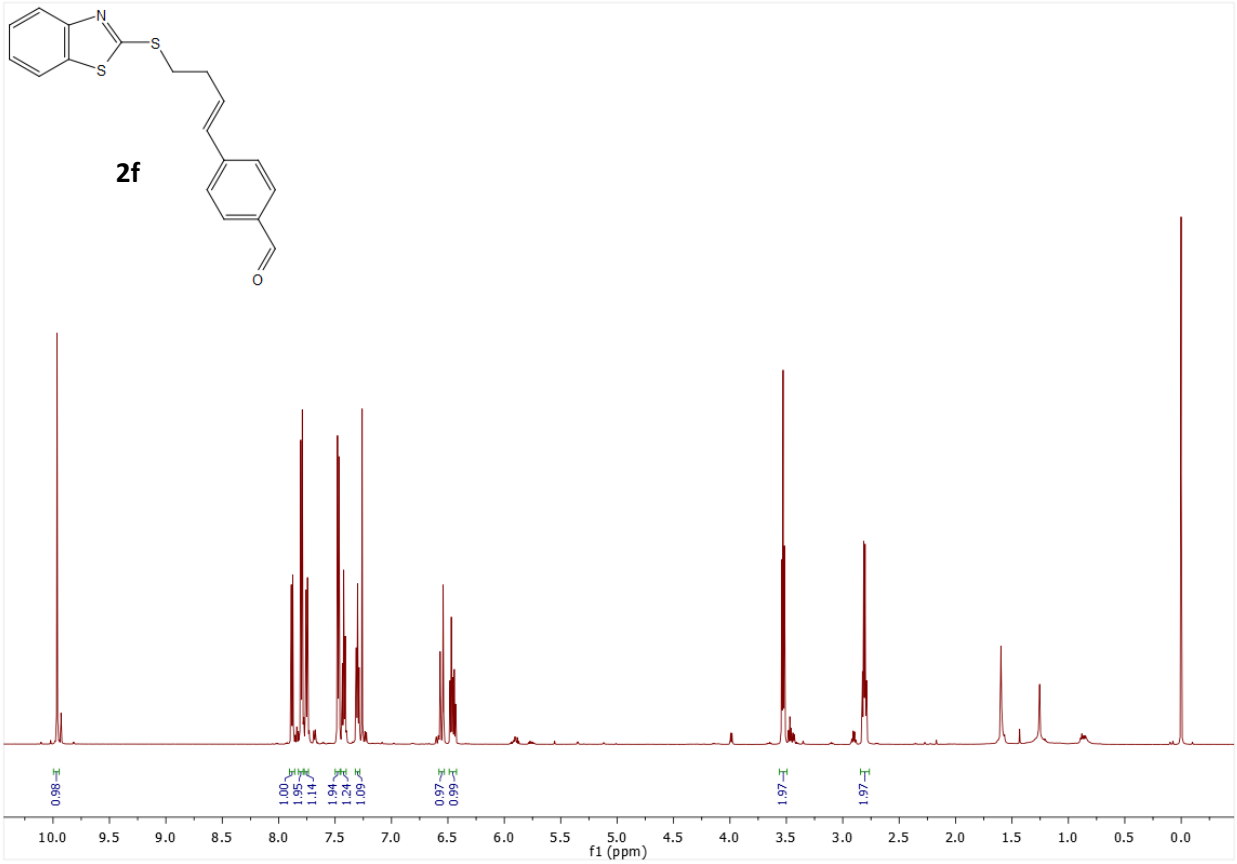

2c
H3C
166.88
153.46
142.33
135.37
134.69
132.21
128.73
126.43
126.17
126.13
124.30
121.63
121.07
35.48
33.73
33.48
32.92
22.46
14.10
f1 (ppm)

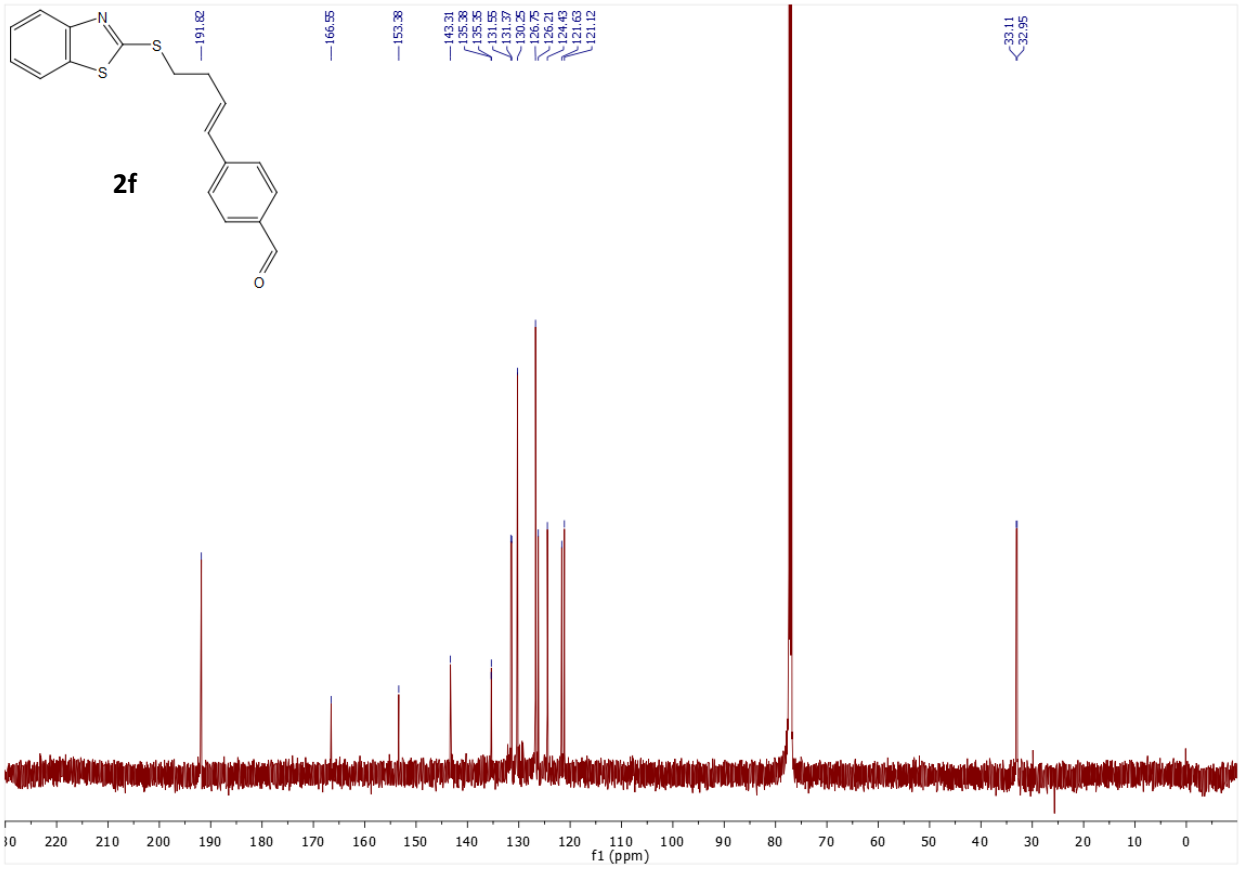

2d
N
S
S
O—CH3
1.00
1.02
1.08
3.03
2.03
0.98
0.97
2.96
1.97
1.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

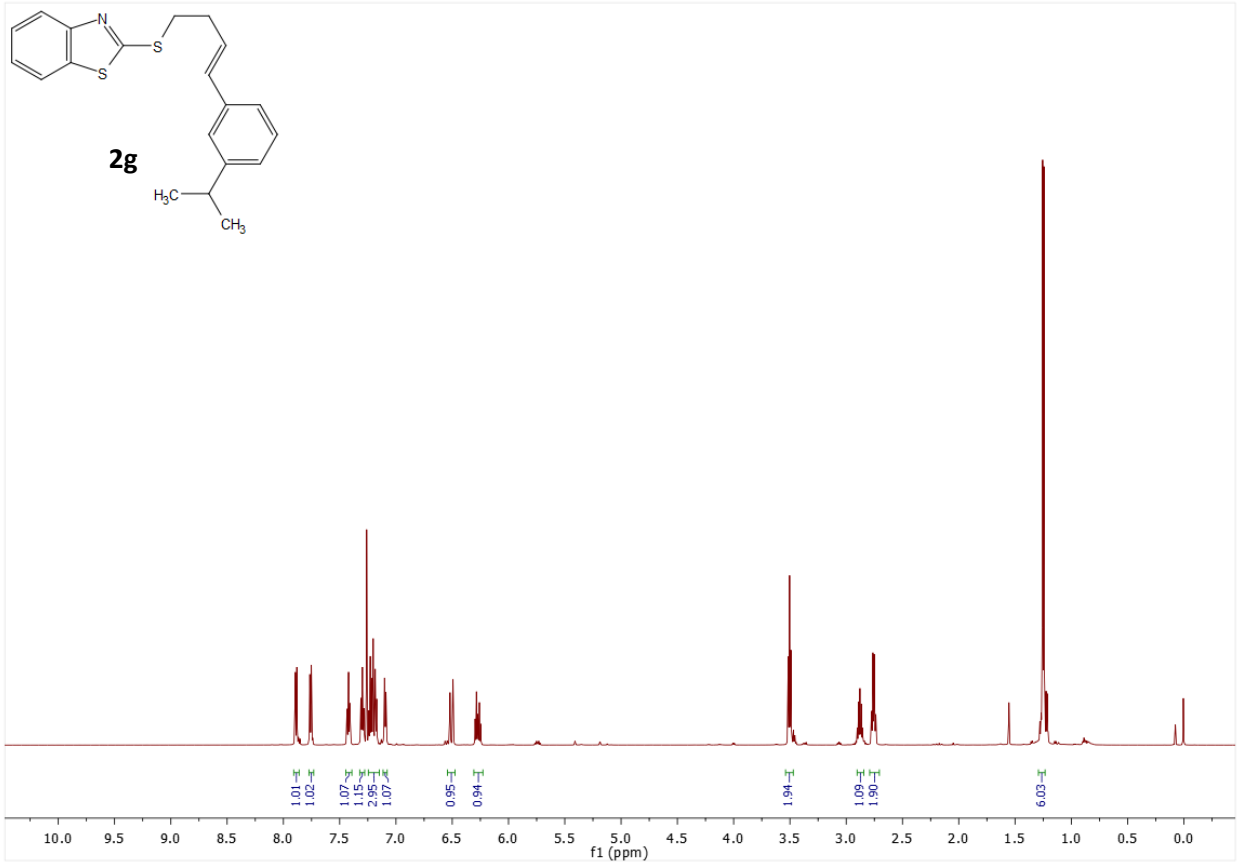

2d
N
S
S
O—CH3
167.02
159.15
153.47
135.38
131.71
130.11
127.42
126.15
125.26
124.31
121.63
121.11
114.09
55.43
33.57
32.93
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

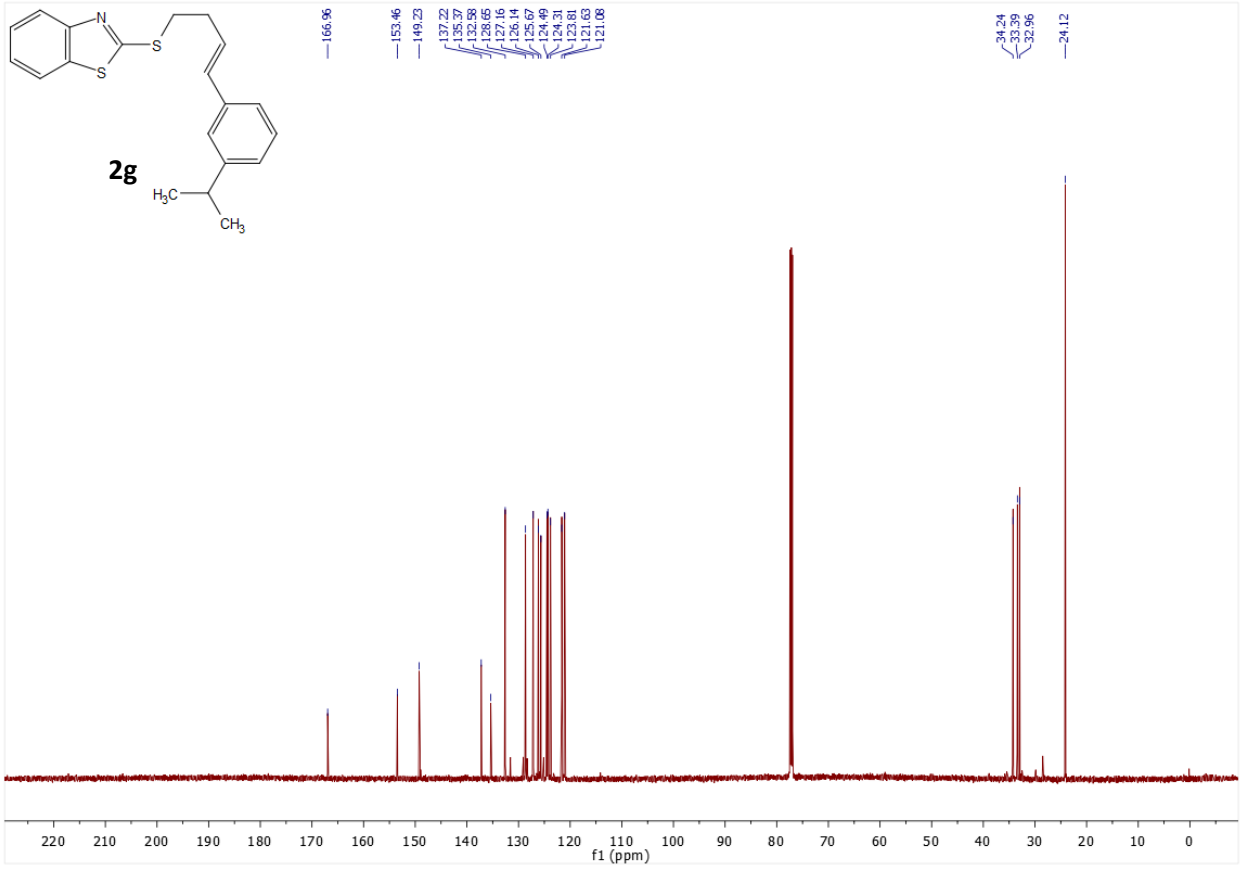

2e
N
S
S
OH
1.09
1.10
1.15
1.14
1.98
2.06
0.97
0.95
0.99
2.02
1.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

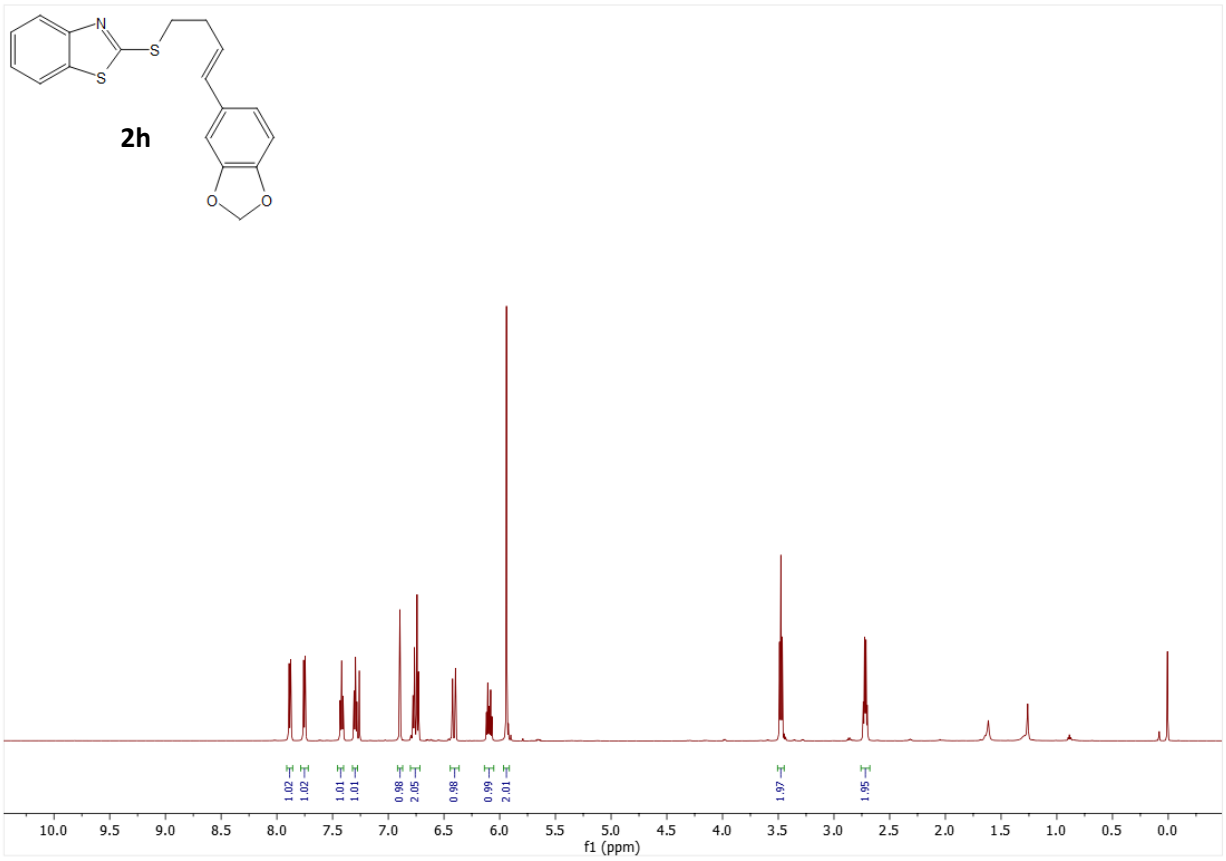

2e
N
S
S
OH
167.65
155.45
153.24
135.18
131.79
130.01
127.64
126.31
124.95
124.46
121.52
121.12
115.66
33.69
32.80
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

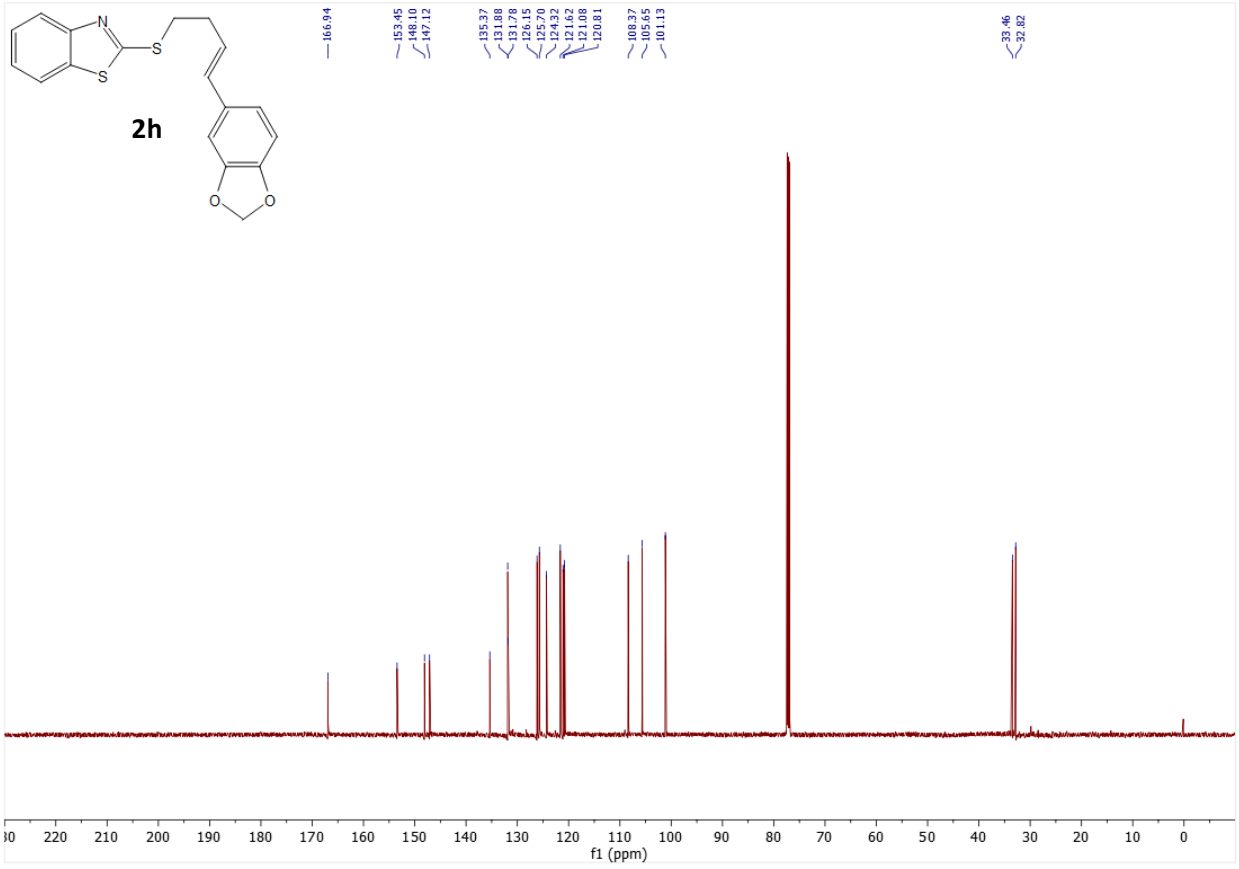

2f
0.98
1.00
1.95
1.14
1.94
1.24
1.09
0.97
0.99
1.97
1.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

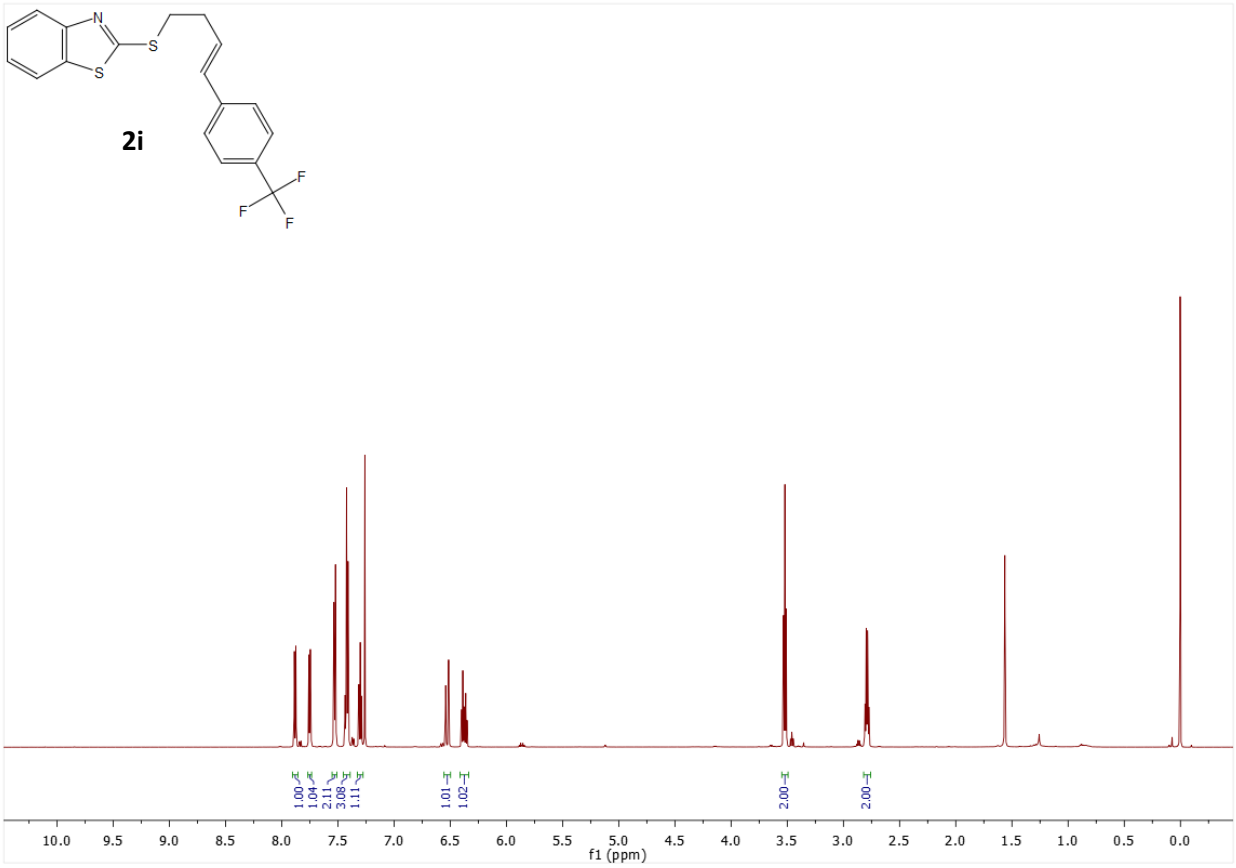

2f
191.82
166.55
153.38
143.31
135.38
135.35
131.55
131.37
130.25
126.75
126.21
124.43
121.63
121.12
33.11
32.95
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

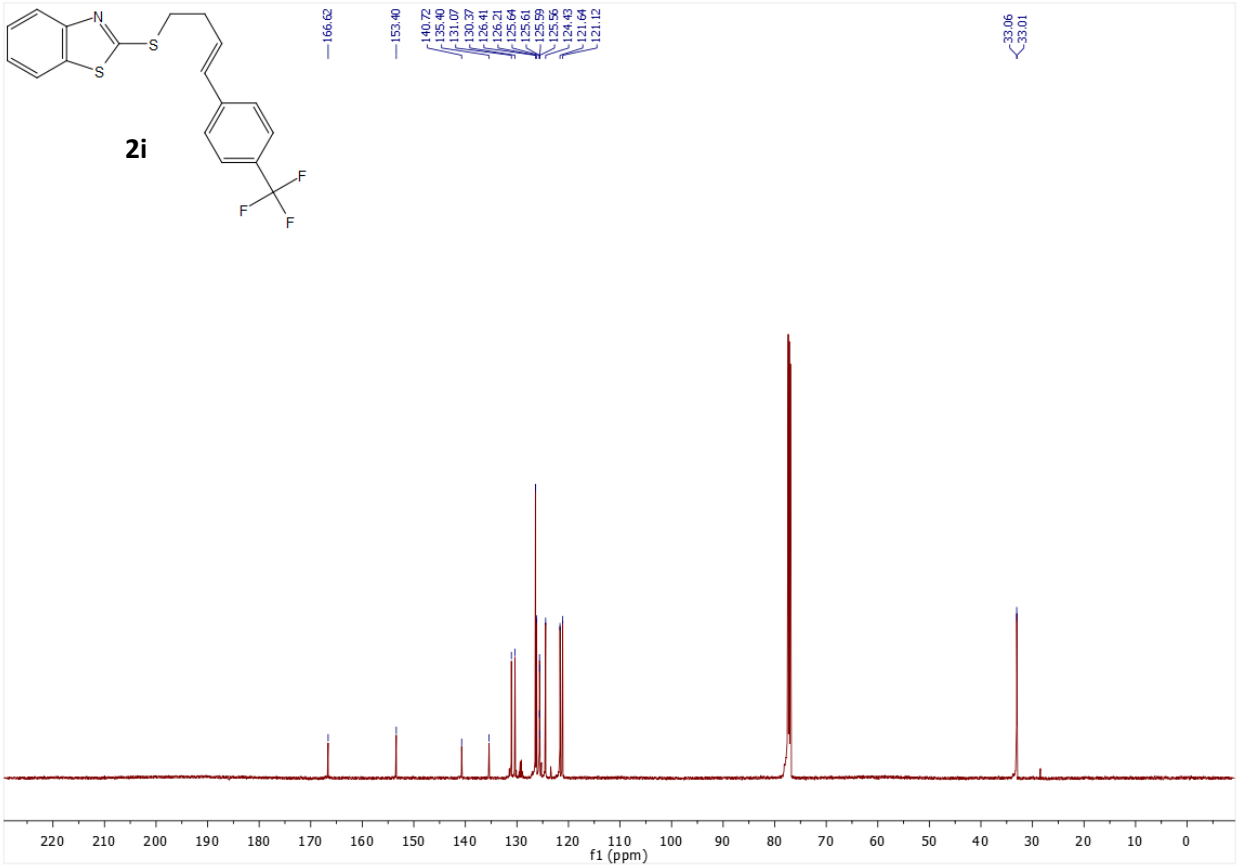

2g
1.01
1.02
1.07
1.15
2.95
1.07
0.95
0.94
1.94
1.09
1.90
6.03
f1 (ppm)

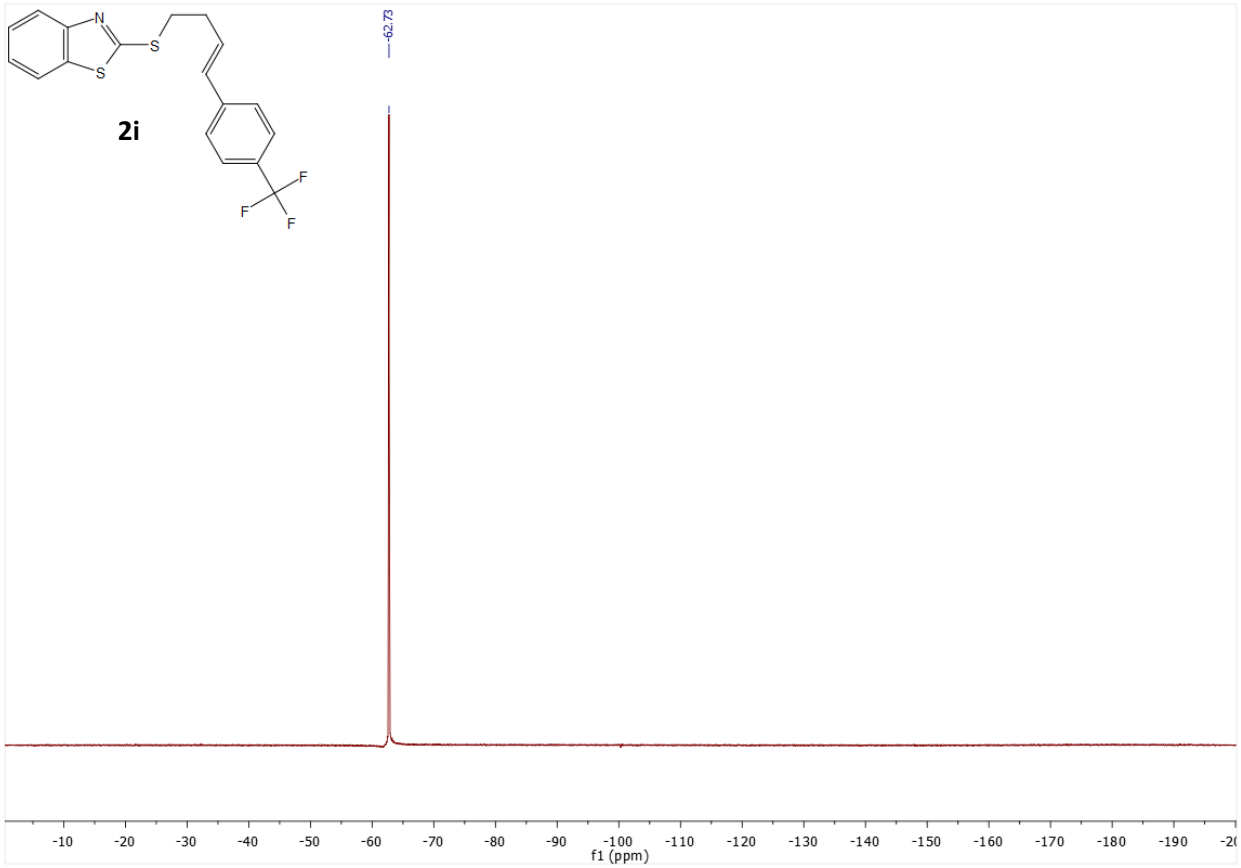

2g
166.96
153.46
149.23
137.22
135.37
132.58
128.65
127.16
126.14
125.67
124.49
124.31
123.81
121.63
121.08
34.24
33.39
32.96
24.12
f1 (ppm)

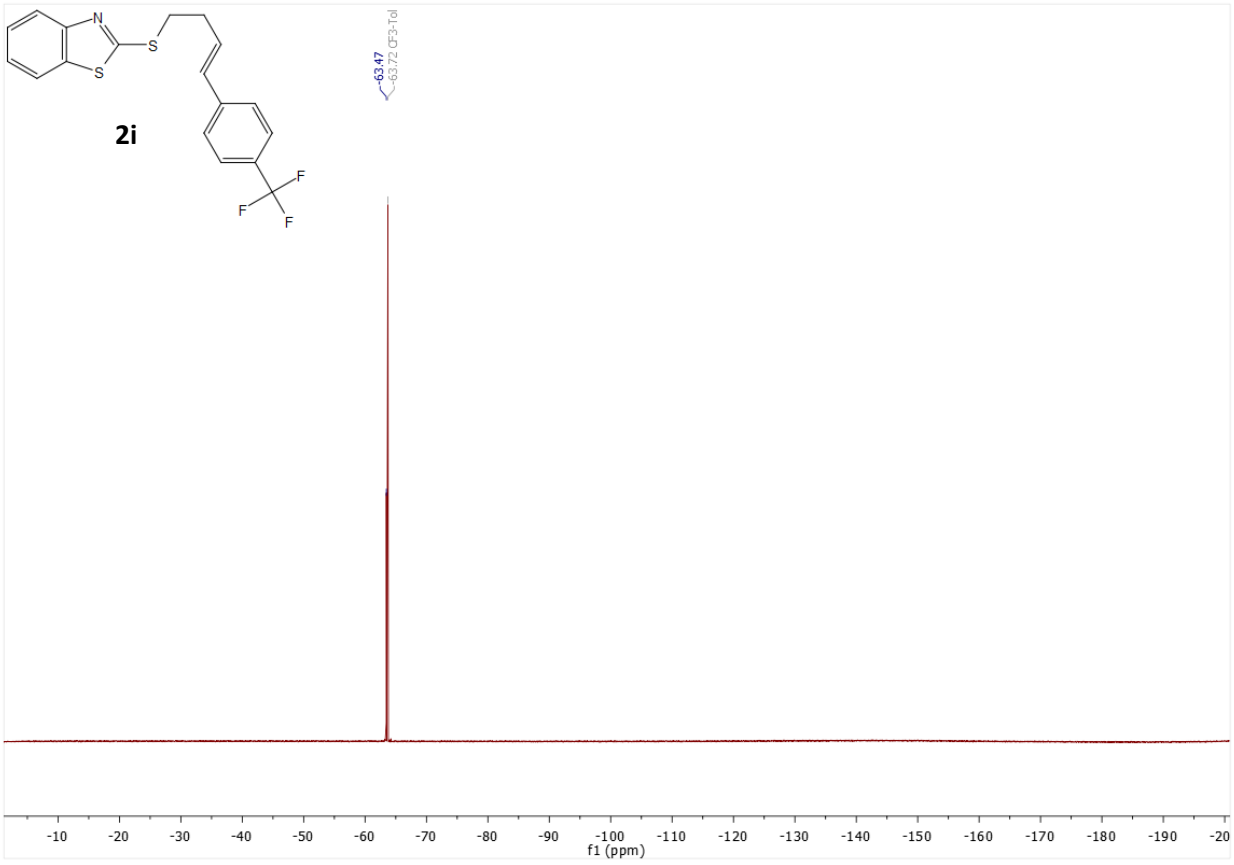

2h
1.02
1.02
1.01
1.01
0.98
2.05
0.98
0.99
2.01
1.97
1.95
f1 (ppm)

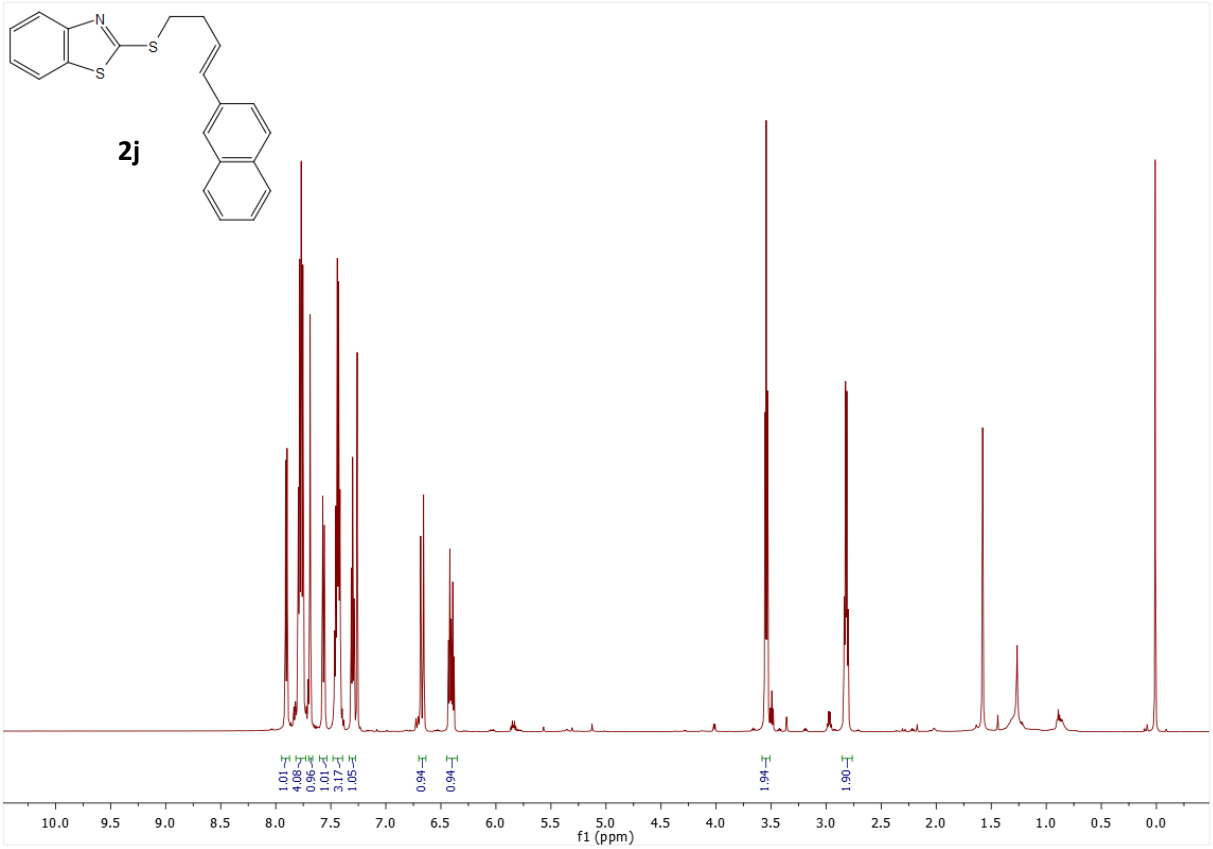

2h
166.94
153.45
148.10
147.12
135.37
131.88
131.78
126.15
125.70
124.32
121.62
121.08
120.81
108.37
105.65
101.13
33.46
32.82
f1 (ppm)

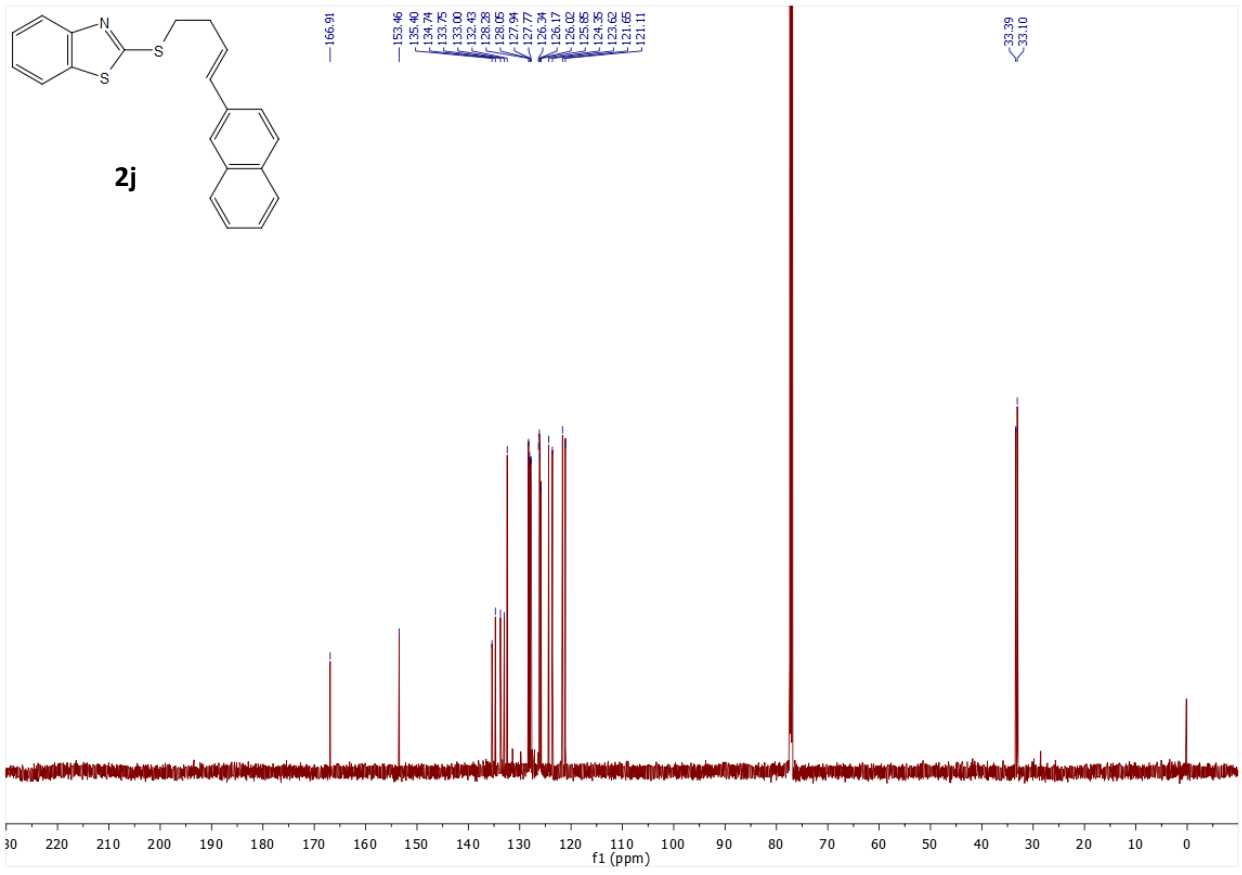

2i
1.00
1.04
2.11
3.08
1.11
1.01
1.02
2.00
2.00
f1 (ppm)

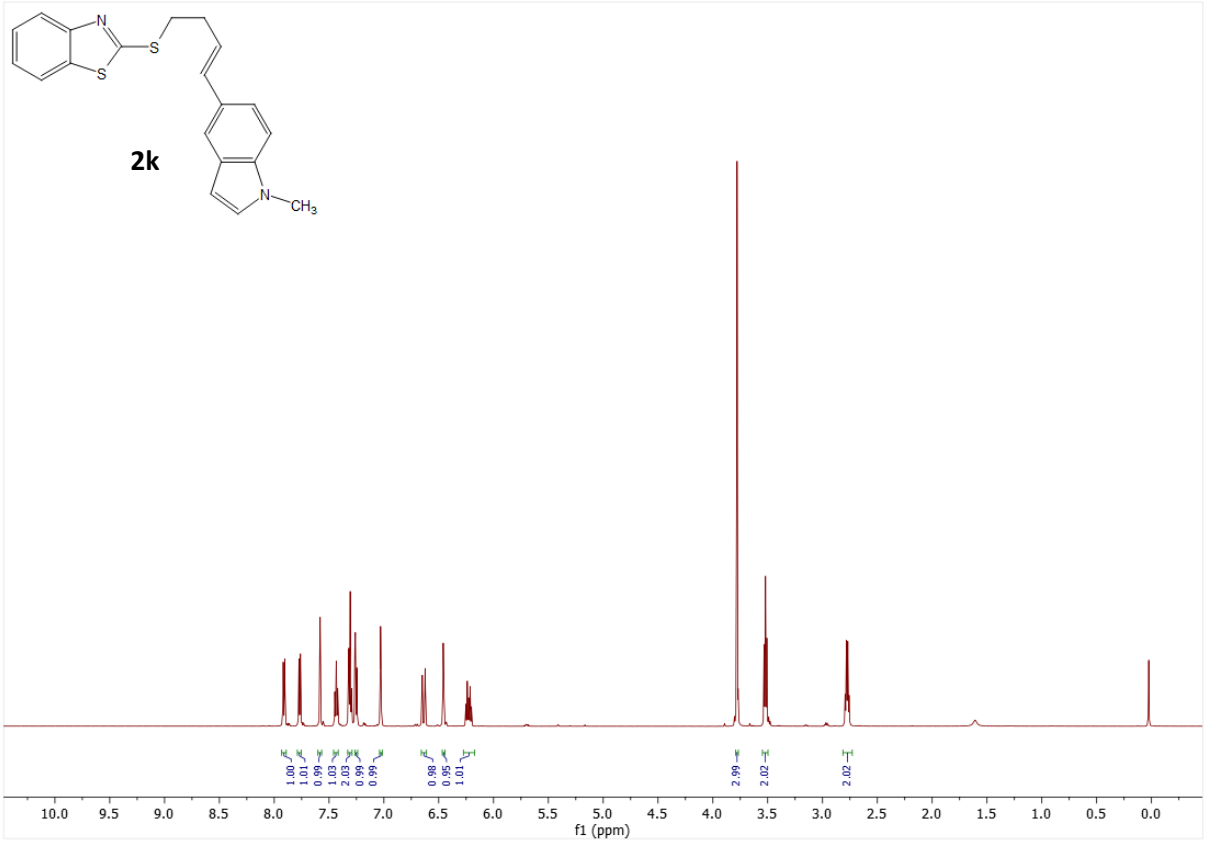

2i
166.62
153.40
140.72
135.40
131.07
130.37
126.41
126.21
125.64
125.61
125.59
125.56
124.43
121.64
121.12
33.06
33.01
f1 (ppm)

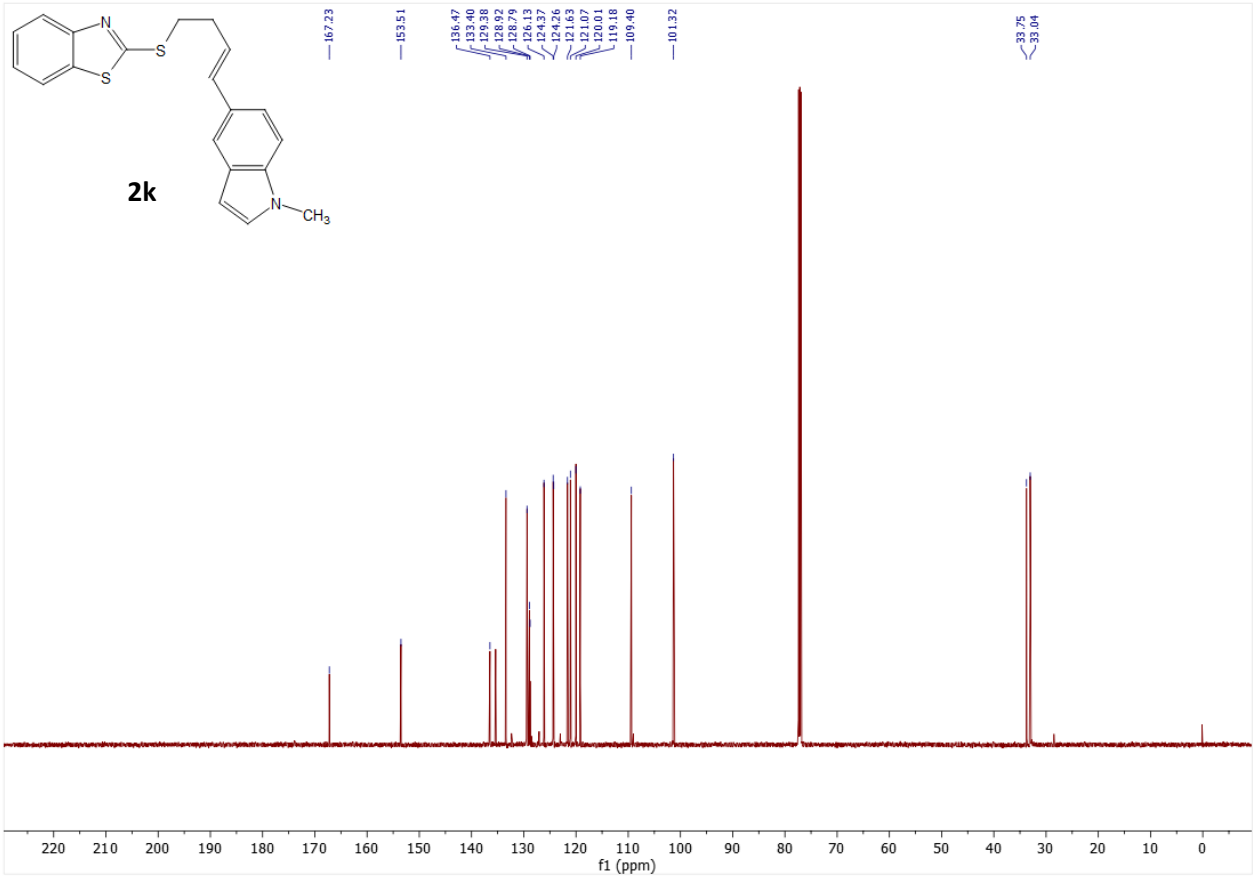

2i
-62.73
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

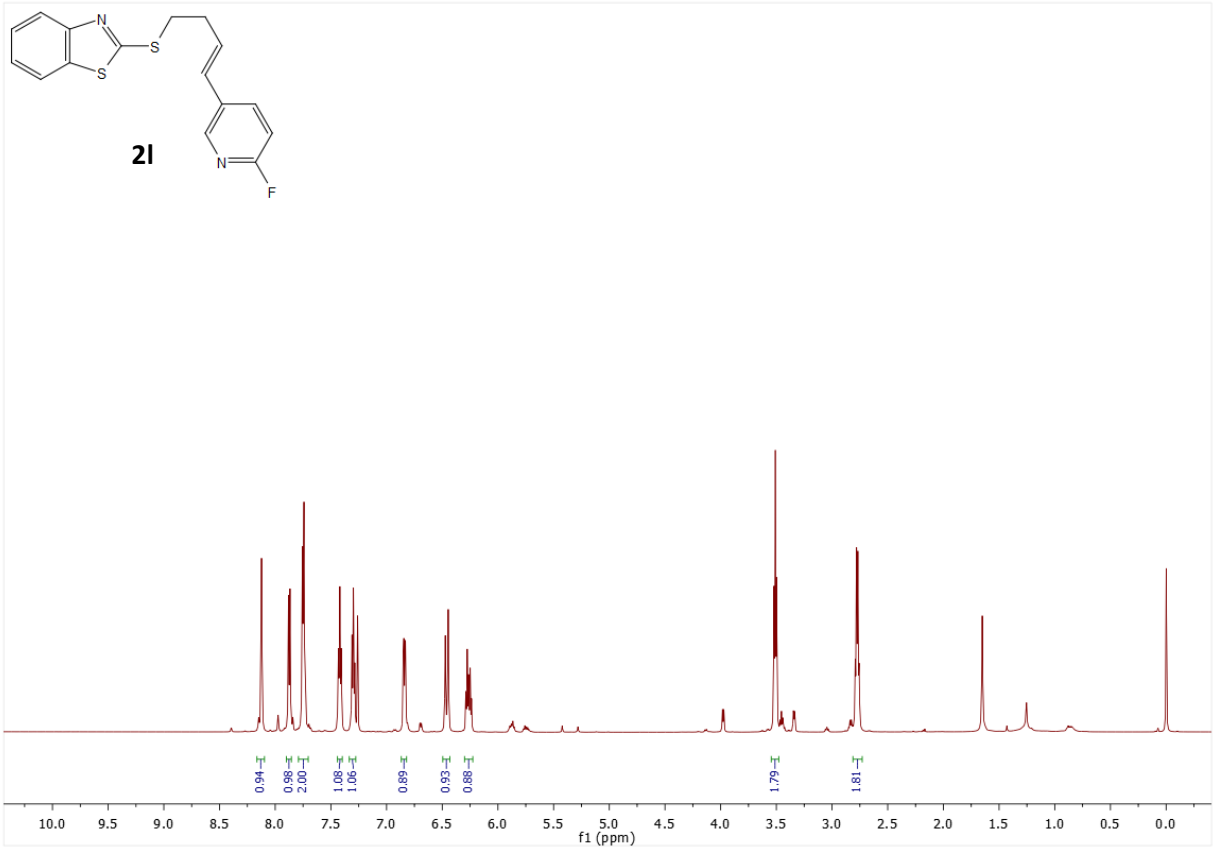

2i
-63.47
-63.72 CF3-Tol
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

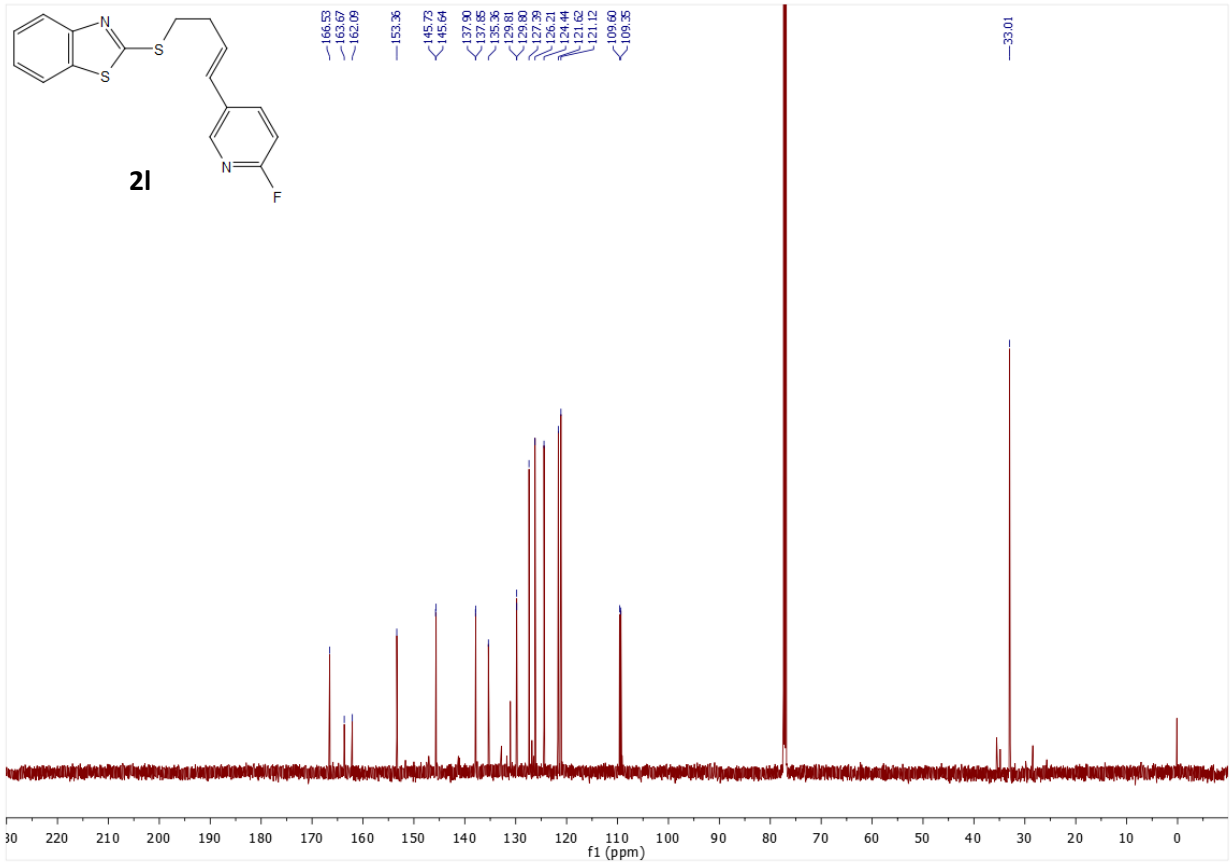

2j
1.01
4.08
0.96
1.01
3.17
1.05
0.94
0.94
1.94
1.90
f1 (ppm)

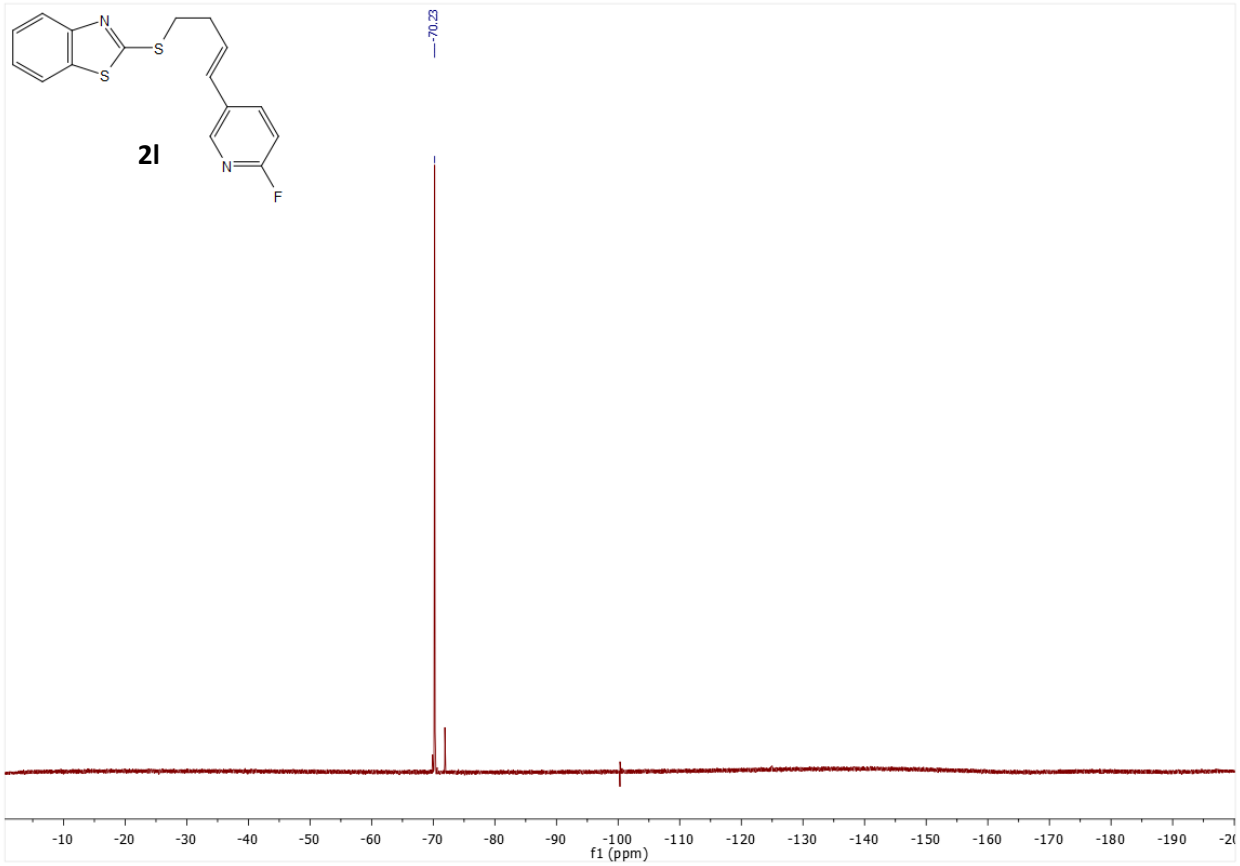

2j
166.91
153.46
135.40
134.74
133.75
133.00
132.43
128.28
128.05
127.94
127.77
126.34
126.17
126.02
125.85
124.35
123.62
121.65
121.11
33.39
33.10
f1 (ppm)

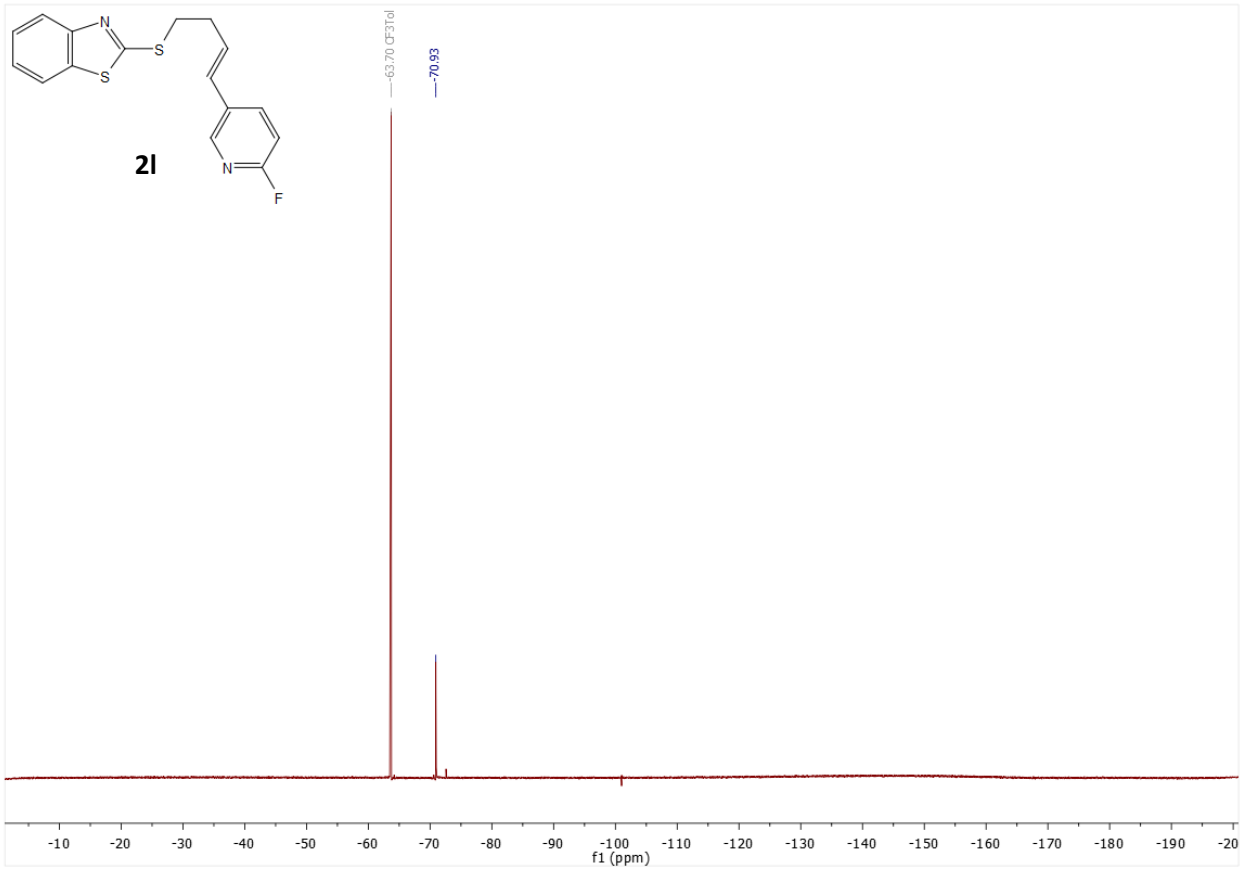

2k
1.00
1.01
0.99
1.03
2.03
0.99
0.99
0.98
0.95
1.01
2.99
2.02
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

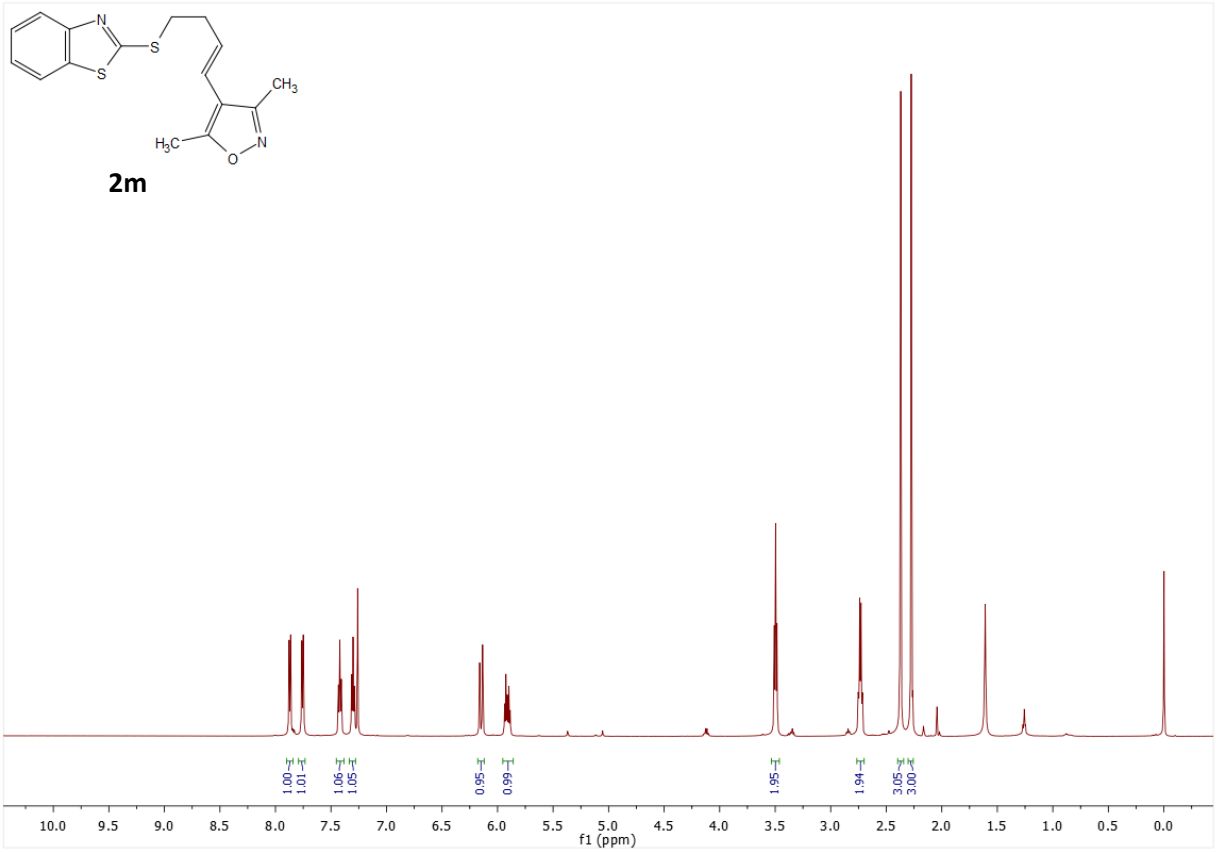

2k
167.23
153.51
136.47
133.40
129.38
128.92
128.79
126.13
124.37
124.26
121.63
121.07
120.01
119.18
109.40
101.32
33.75
33.04
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

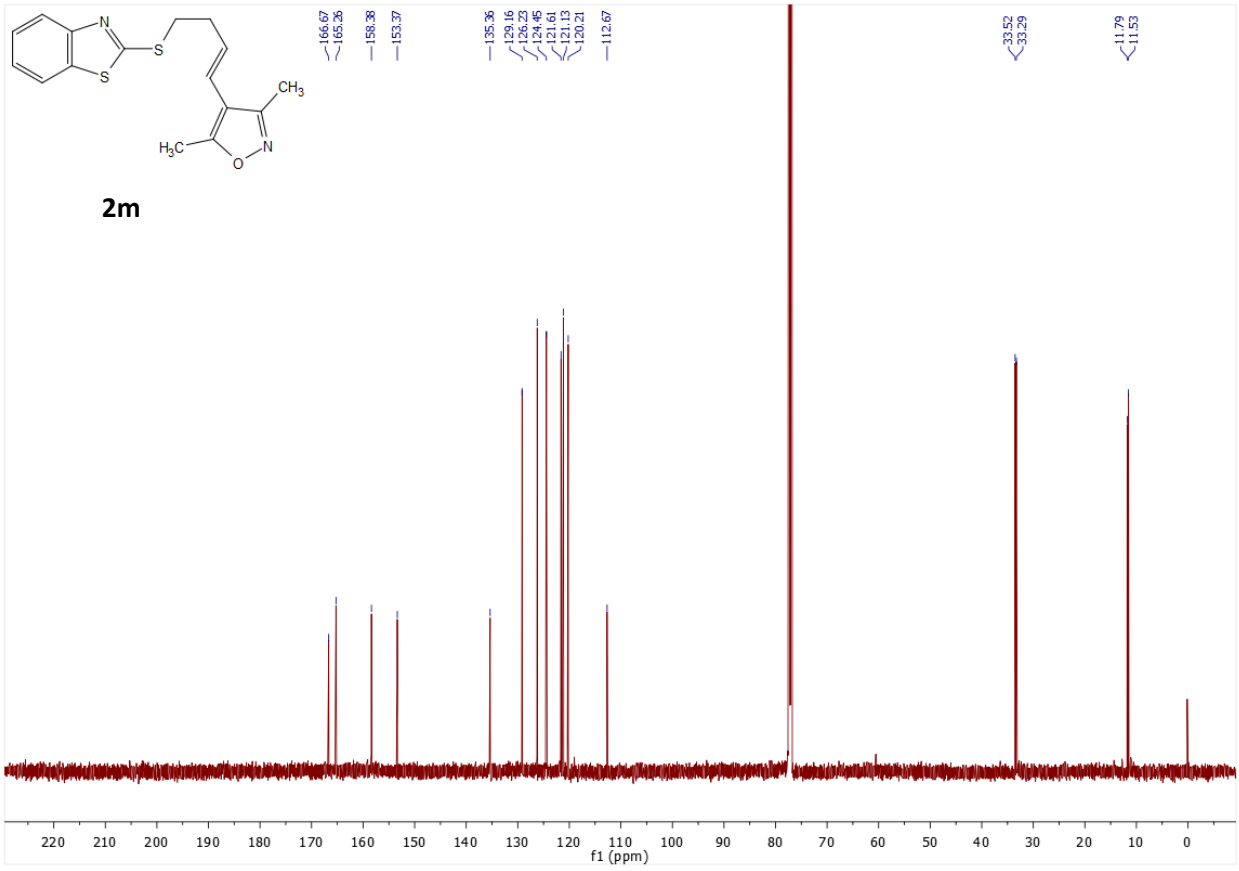

2l
0.94
0.98
2.00
1.08
1.06
0.89
0.93
0.88
1.79
1.81
f1 (ppm)

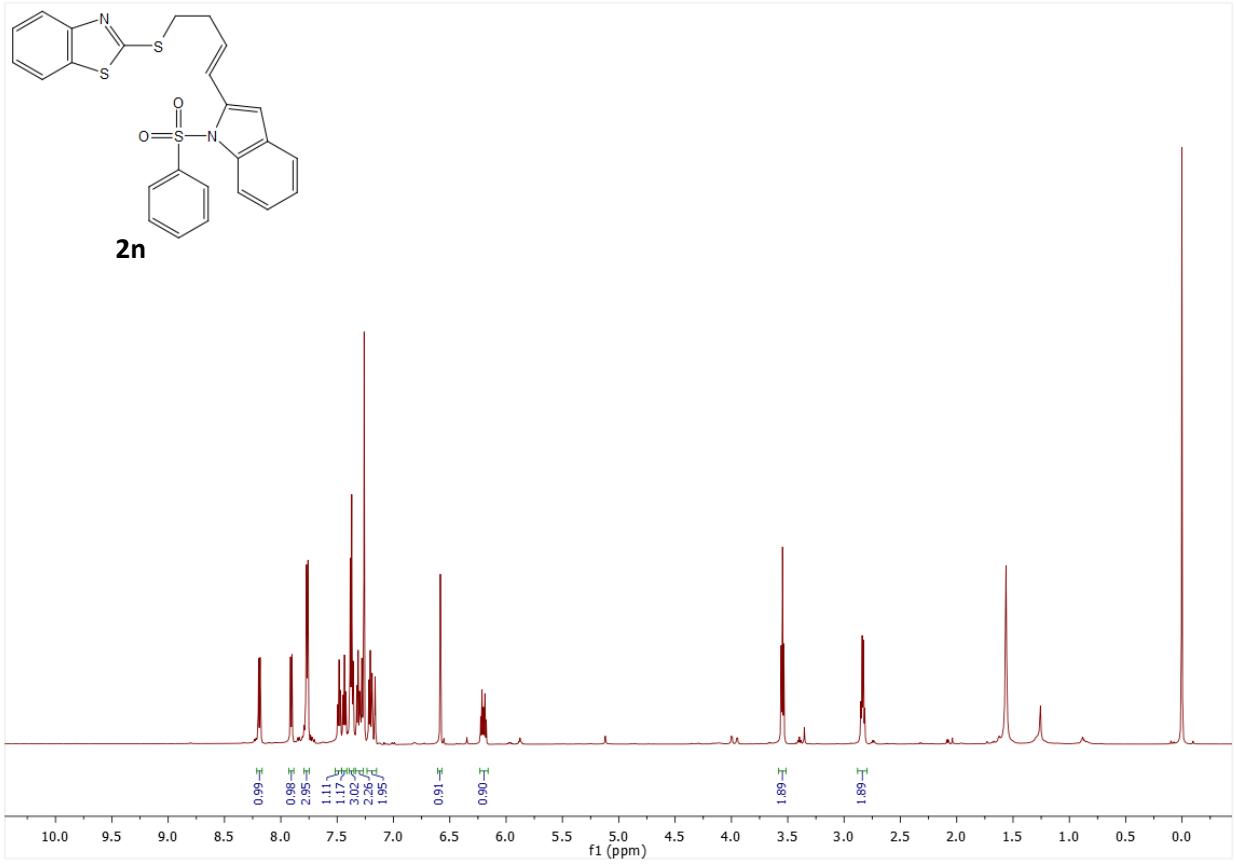

2l
166.53
163.67
162.09
153.36
145.73
145.64
137.90
137.85
135.36
129.81
129.80
127.39
126.21
124.44
121.62
121.12
109.60
109.35
33.01
f1 (ppm)

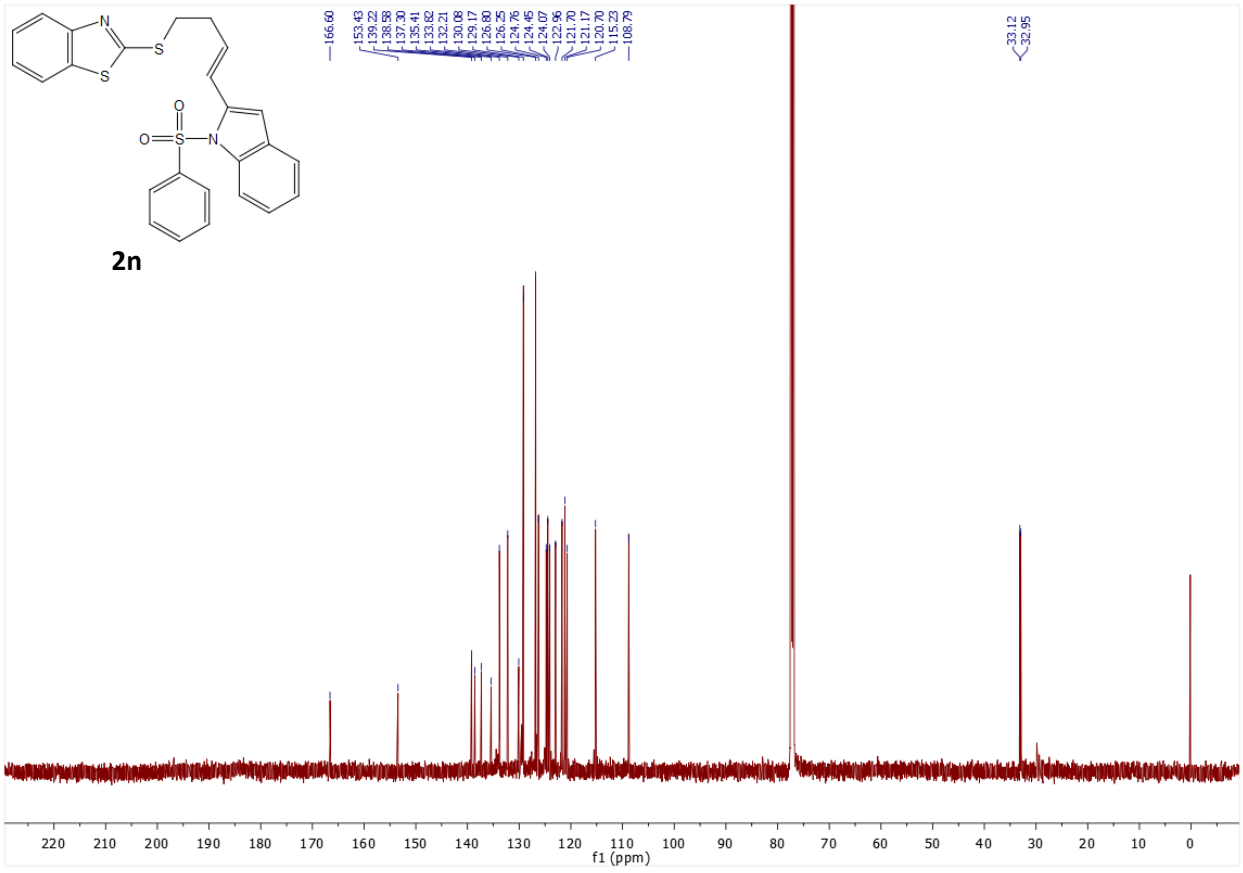

2l
-70.23
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

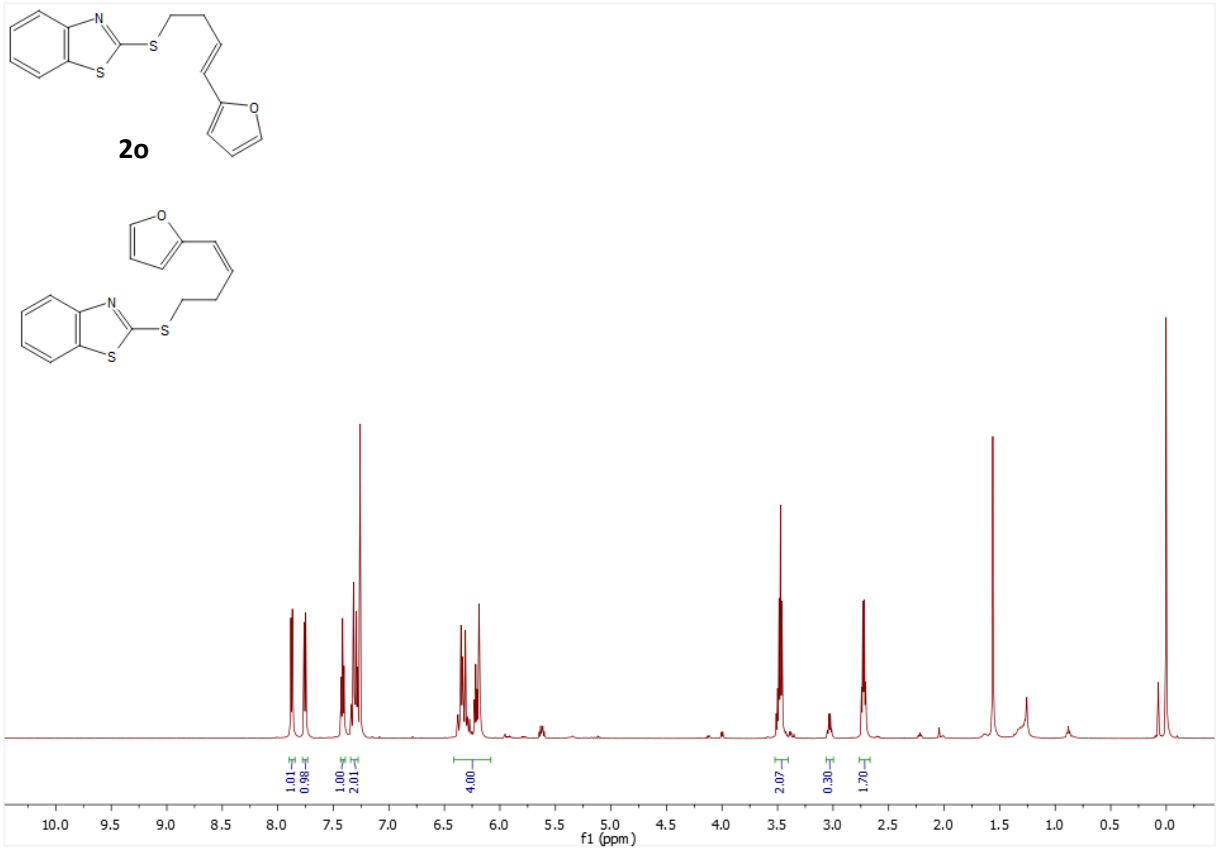

2l
-63.70 CF3Tol
-70.93
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

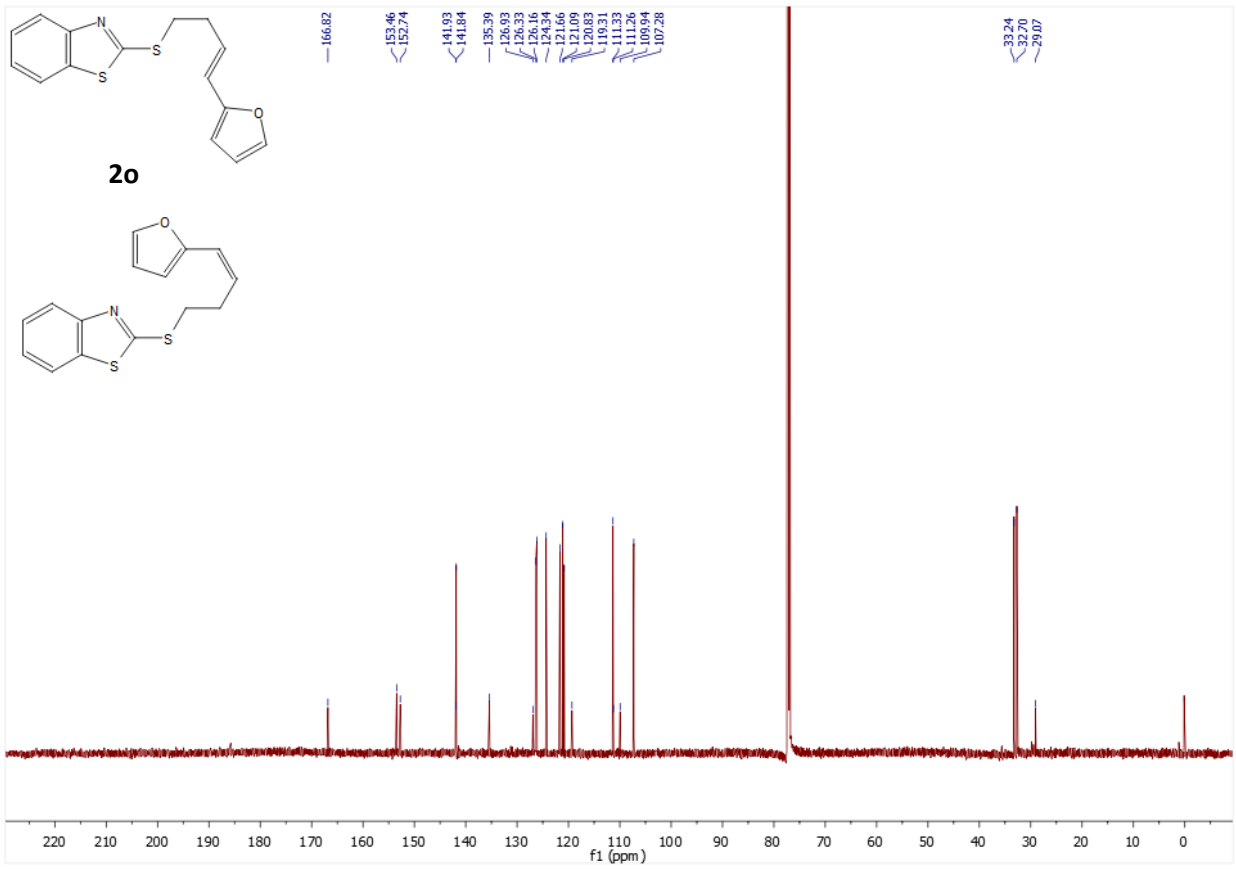

2m
1.00
1.01
1.06
1.05
0.95
0.99
1.95
1.94
3.05
3.00
f1 (ppm)

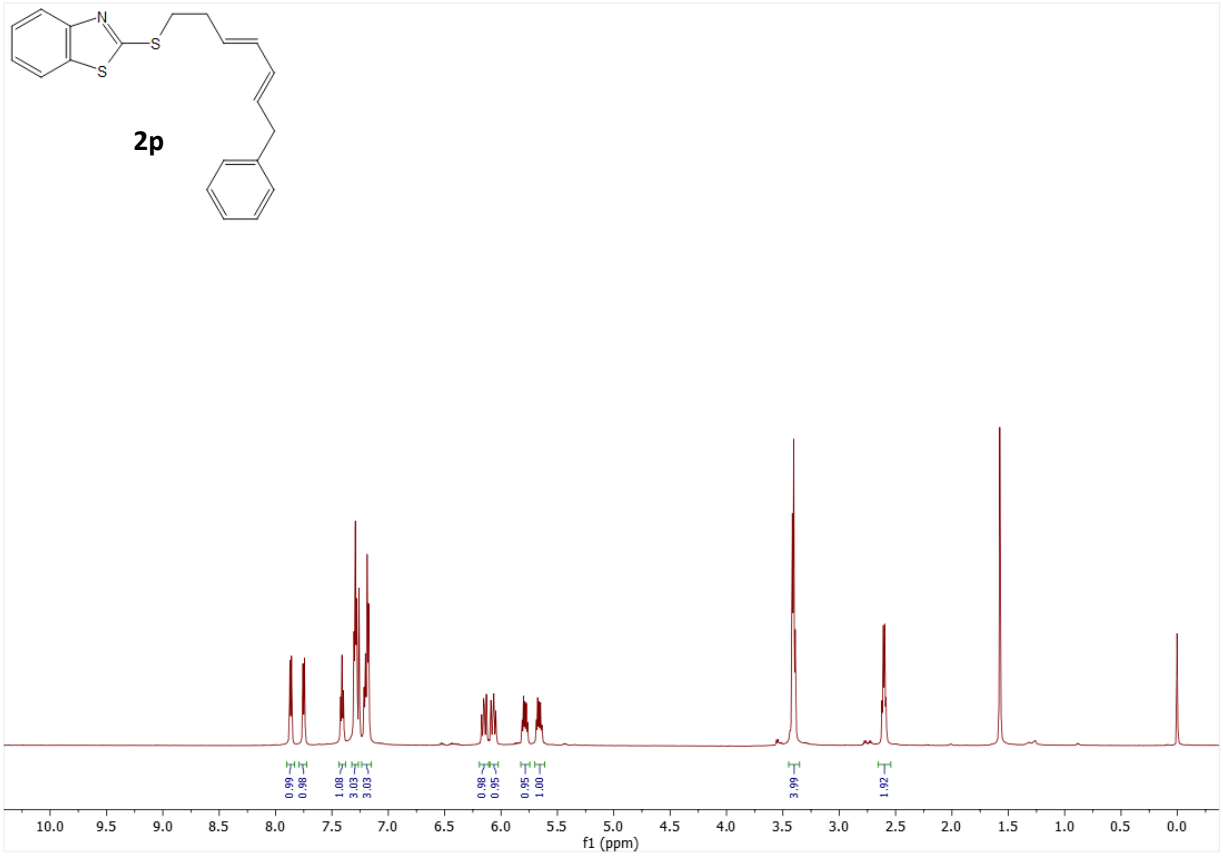

2m
166.67
165.36
158.38
153.37
135.36
129.16
126.23
124.45
121.61
121.13
120.21
112.67
33.52
33.29
11.79
11.53
f1 (ppm)

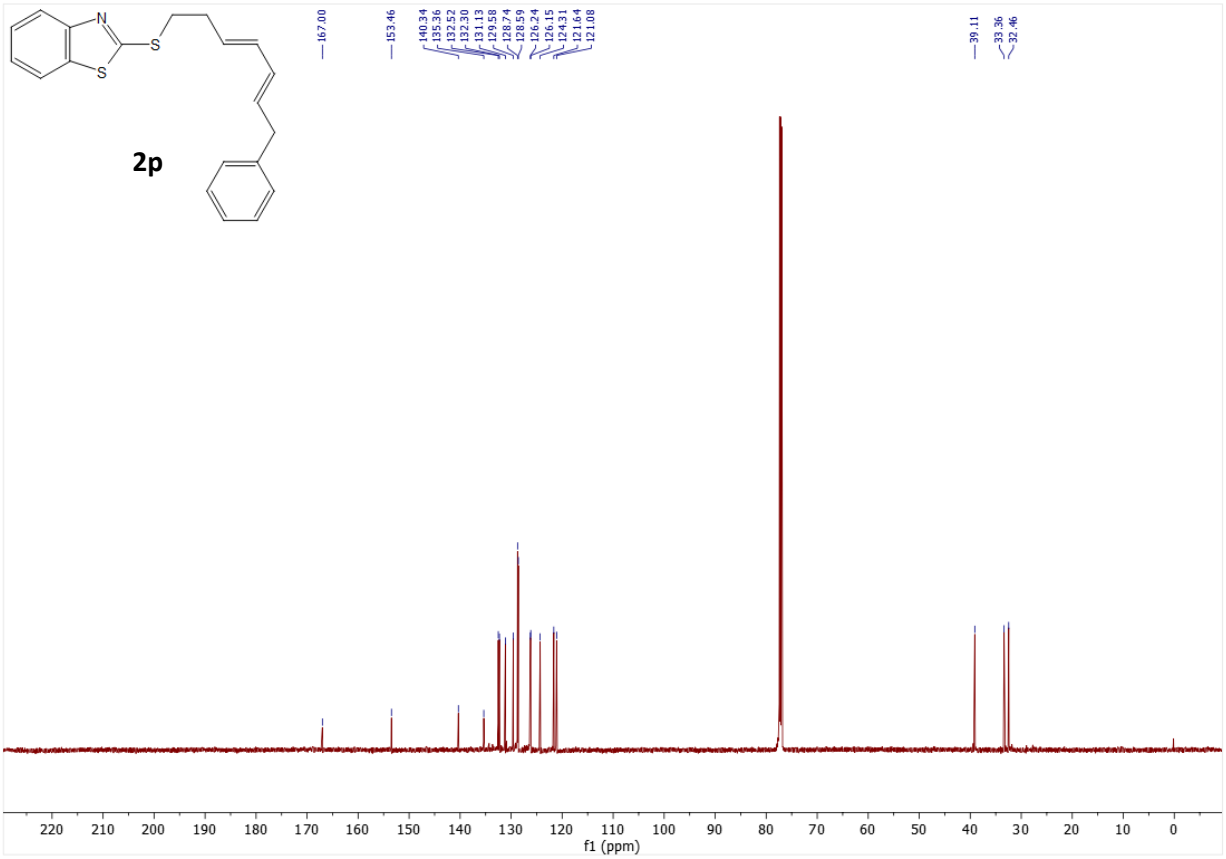

2n
0.99
0.98
2.95
1.11
1.17
3.02
2.26
1.95
0.91
0.90
1.89
1.89
f1 (ppm)

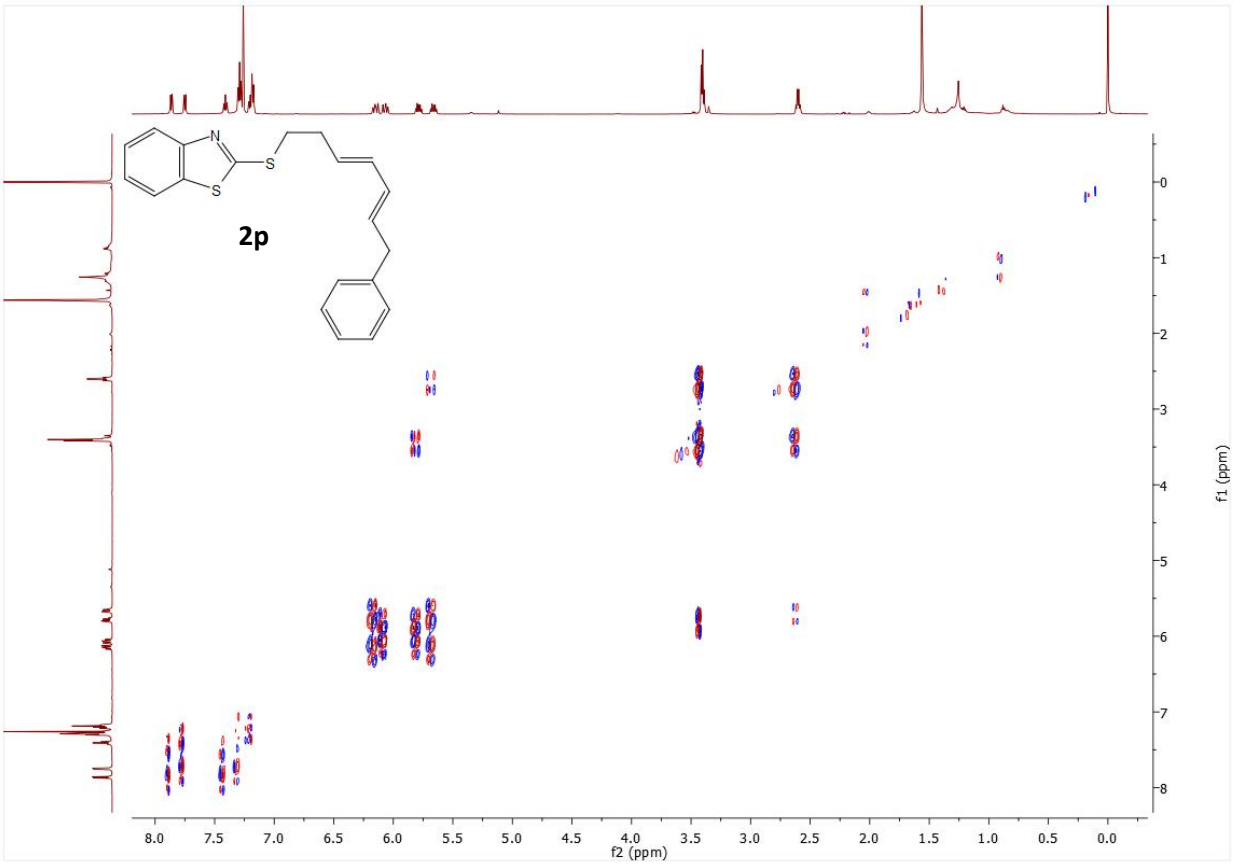

2n
166.60
153.43
139.22
138.58
137.30
135.41
133.82
132.21
130.08
129.17
126.80
126.25
124.76
124.45
124.07
122.96
121.70
121.17
120.70
115.23
108.79
33.12
32.95
f1 (ppm)

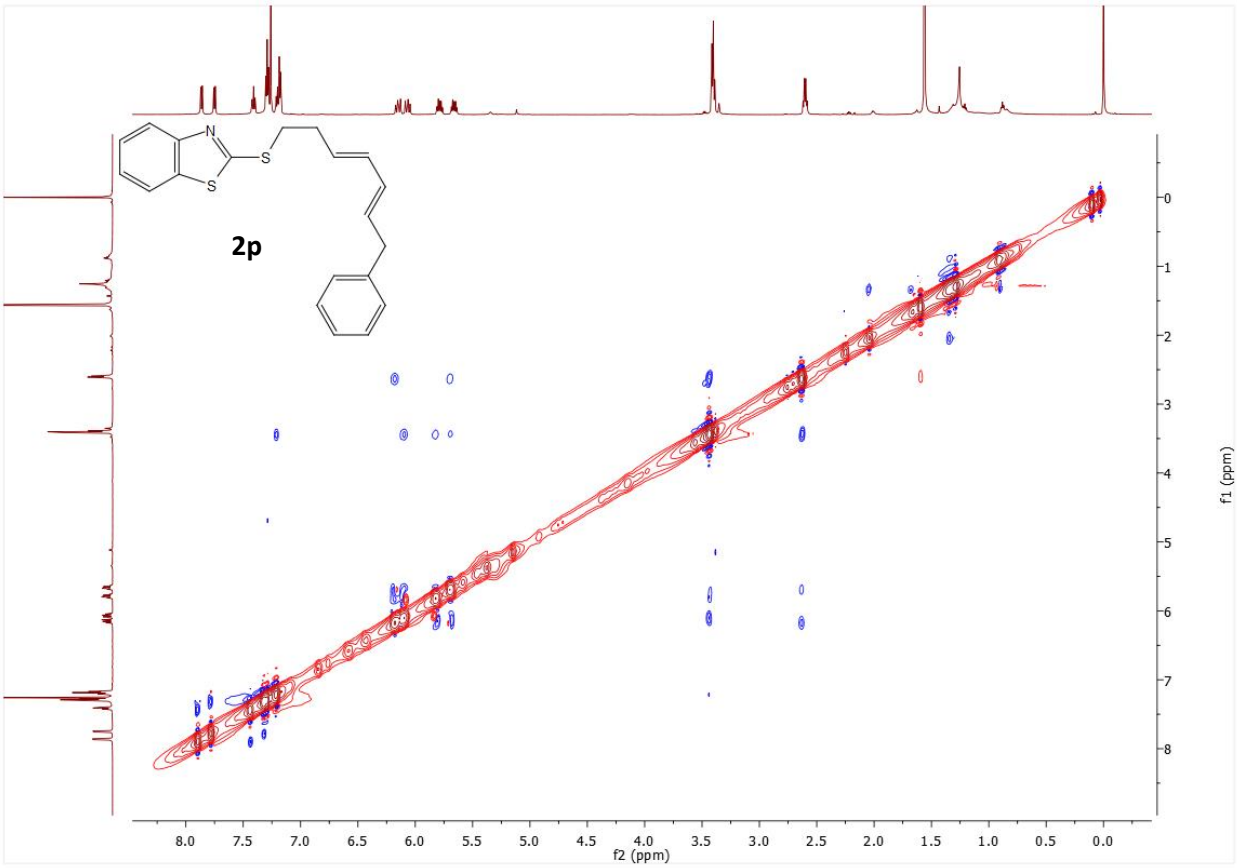

2o
1.01
0.98
1.00
2.01
4.00
2.07
0.30
1.70
f1 (ppm)

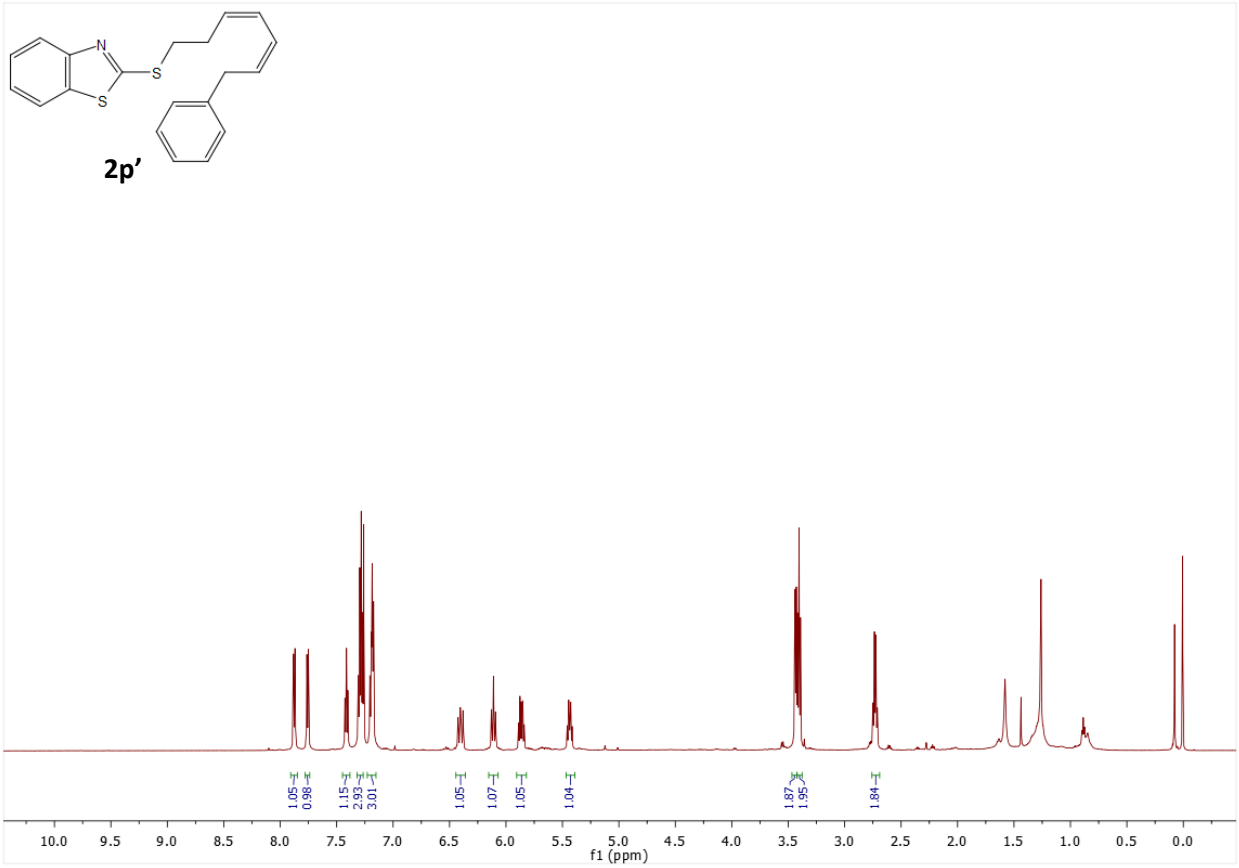

2o
166.82
153.46
152.74
141.93
141.84
135.39
126.93
126.33
126.16
124.34
121.66
121.09
120.83
119.31
111.33
111.26
109.94
107.28
33.24
32.70
29.07
f1 (ppm)

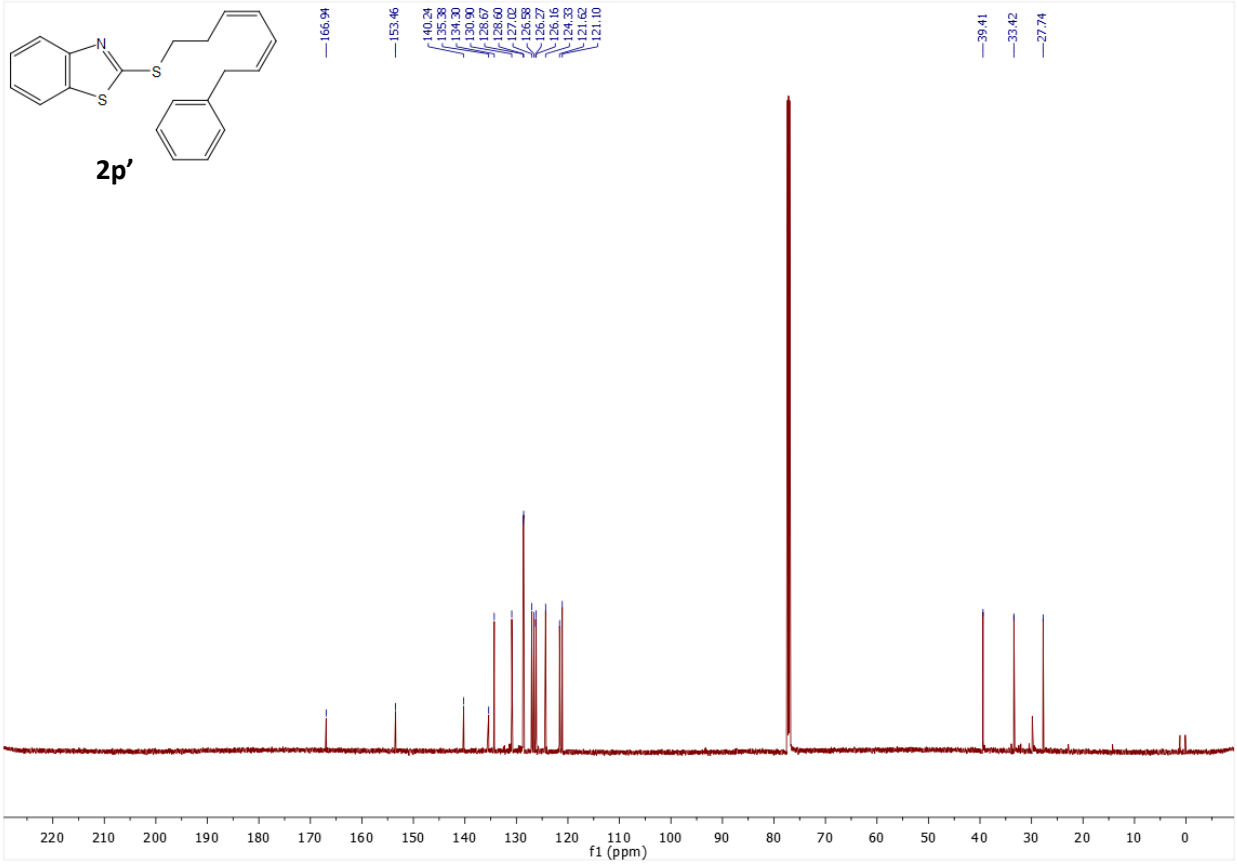

2p
0.99
0.98
1.08
3.03
3.03
0.98
0.95
0.95
1.00
3.99
1.92
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

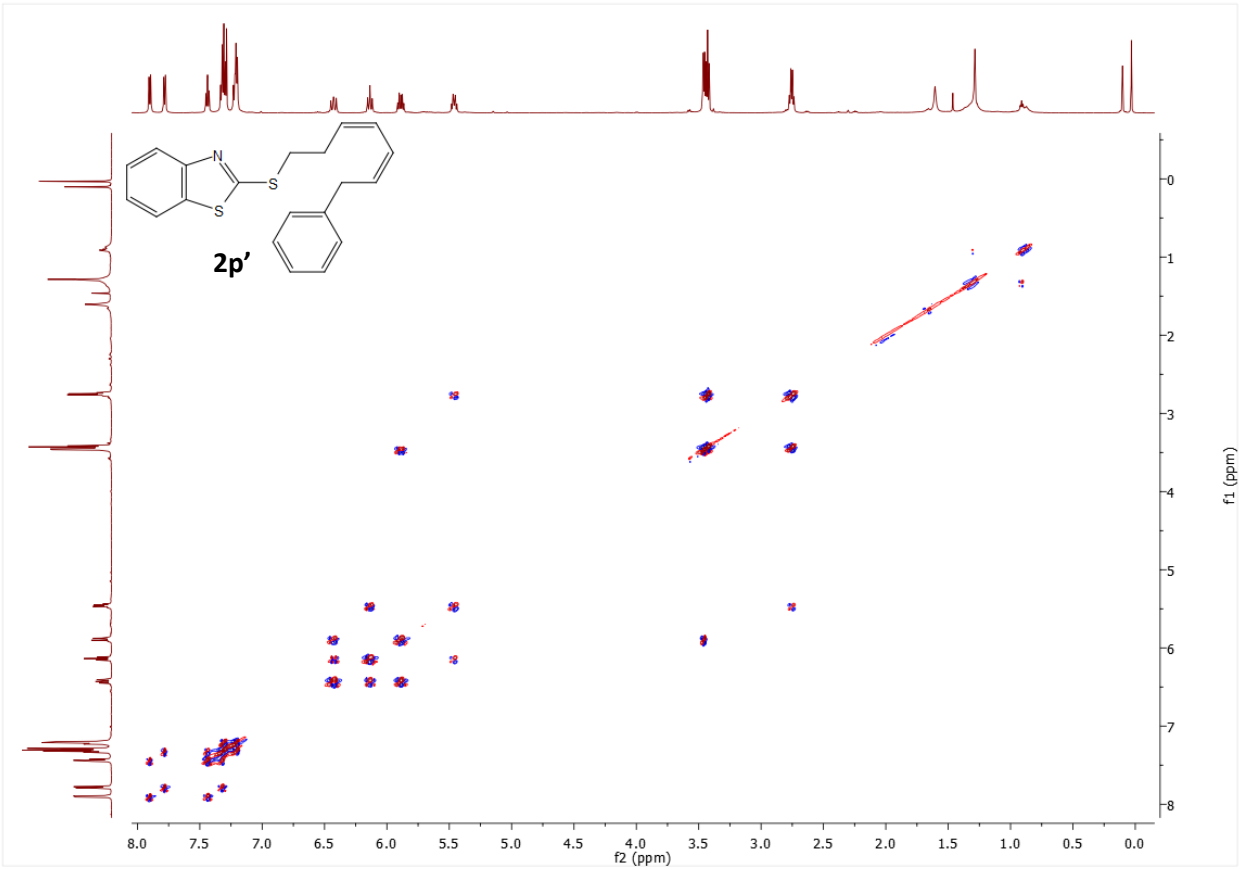

2p
167.00
153.46
140.34
135.56
132.52
132.30
131.13
129.58
128.74
128.59
126.44
126.15
124.91
121.64
121.08
39.11
33.36
32.46
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

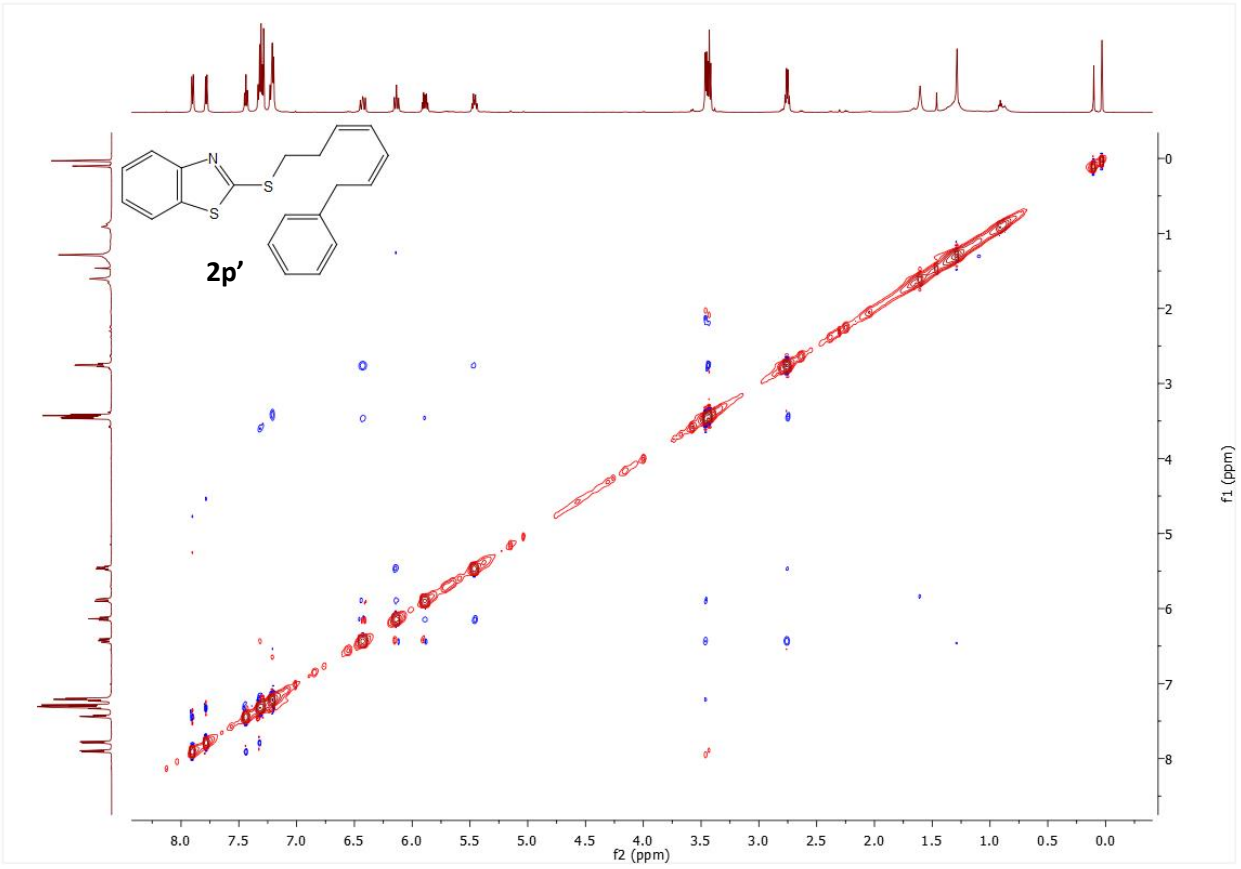

N
S
S
2p
f2 (ppm)
f1 (ppm)

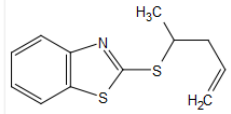

N
S
S
2p
f2 (ppm)
f1 (ppm)


2p’
1.05
0.98
1.15
2.93
3.01
1.05
1.07
1.05
1.04
1.87
1.95
1.84
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


2p’
166.94
153.46
140.24
135.38
134.30
130.90
128.67
128.60
127.02
126.58
126.27
126.16
124.33
121.62
121.10
39.41
33.42
27.74
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

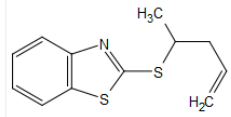

N
S
S
2p’
f2 (ppm)
f1 (ppm)


N
S
S
2p’
f2 (ppm)
f1 (ppm)



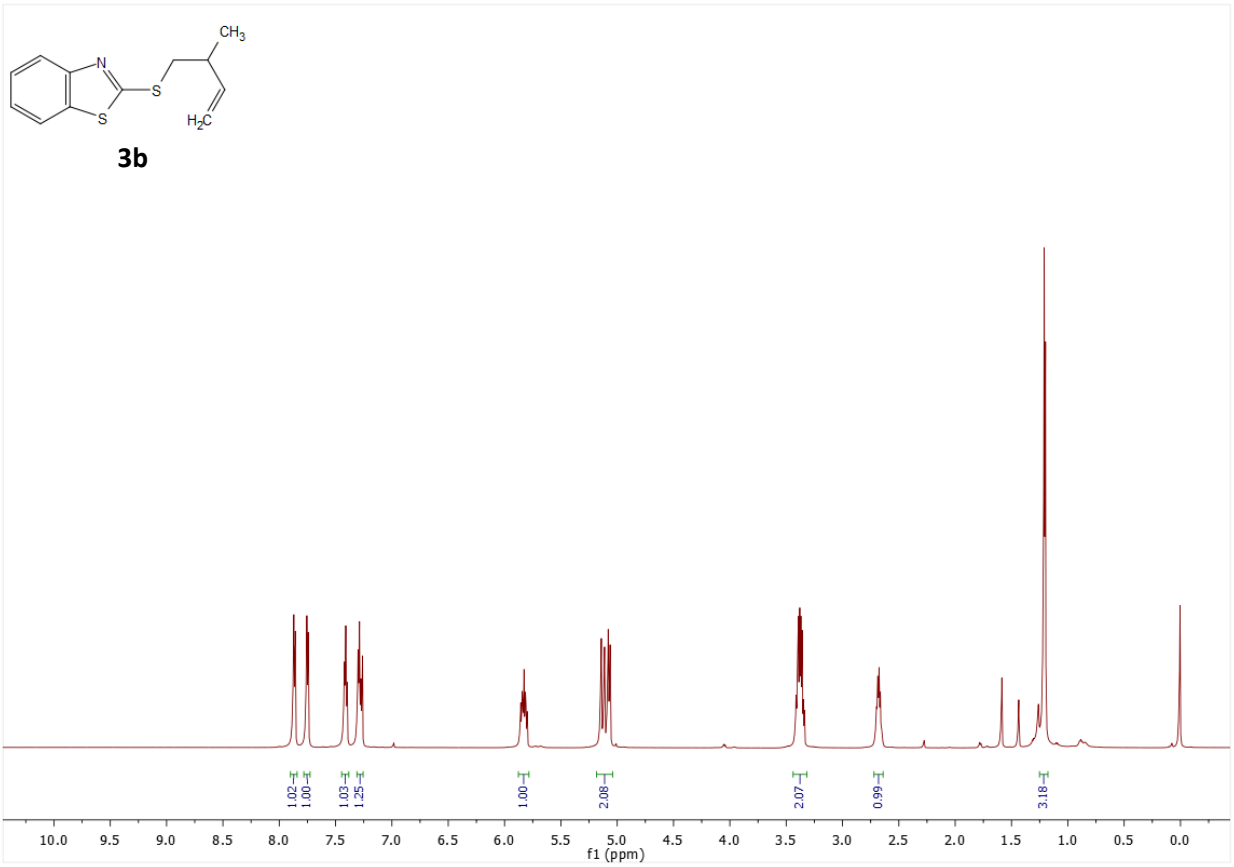
3a

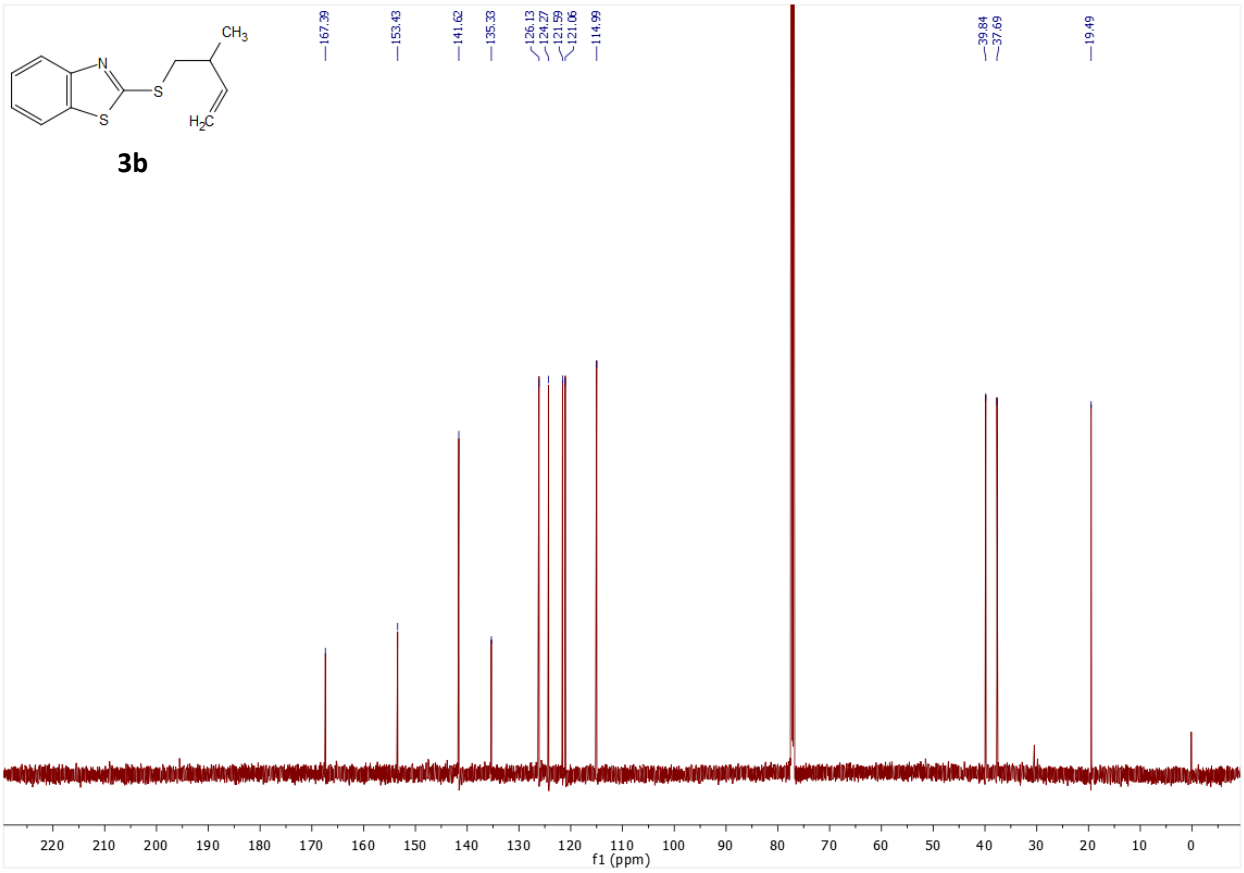
1.00
1.00
1.05
1.01
1.04
2.10
1.05
2.11
3.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

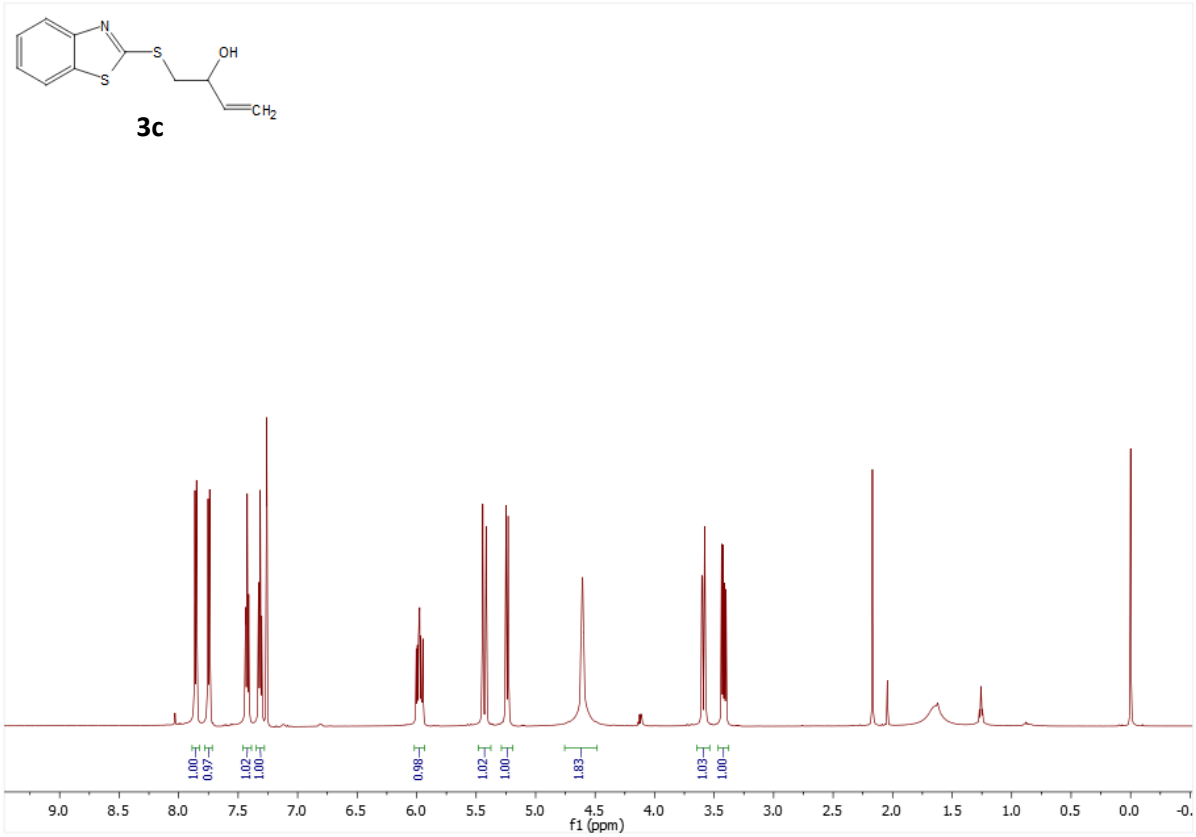


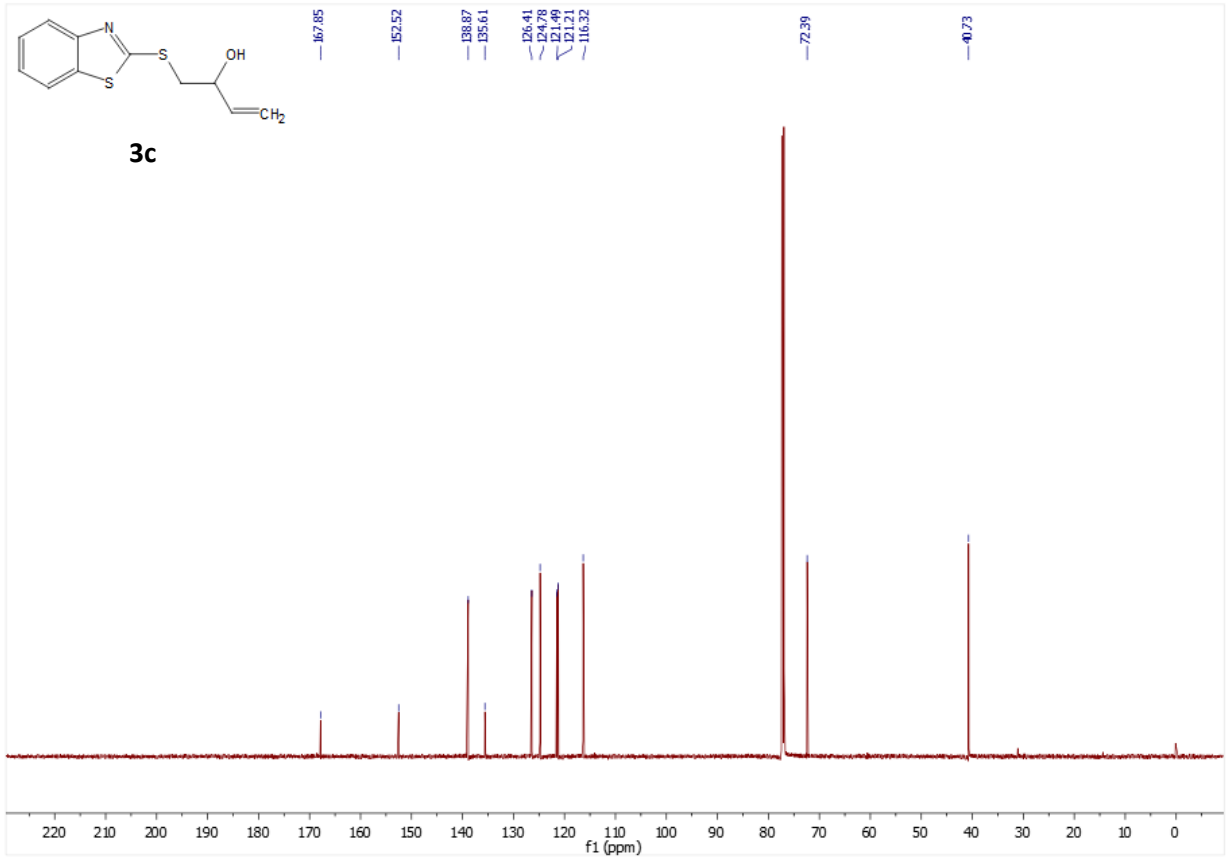
3a

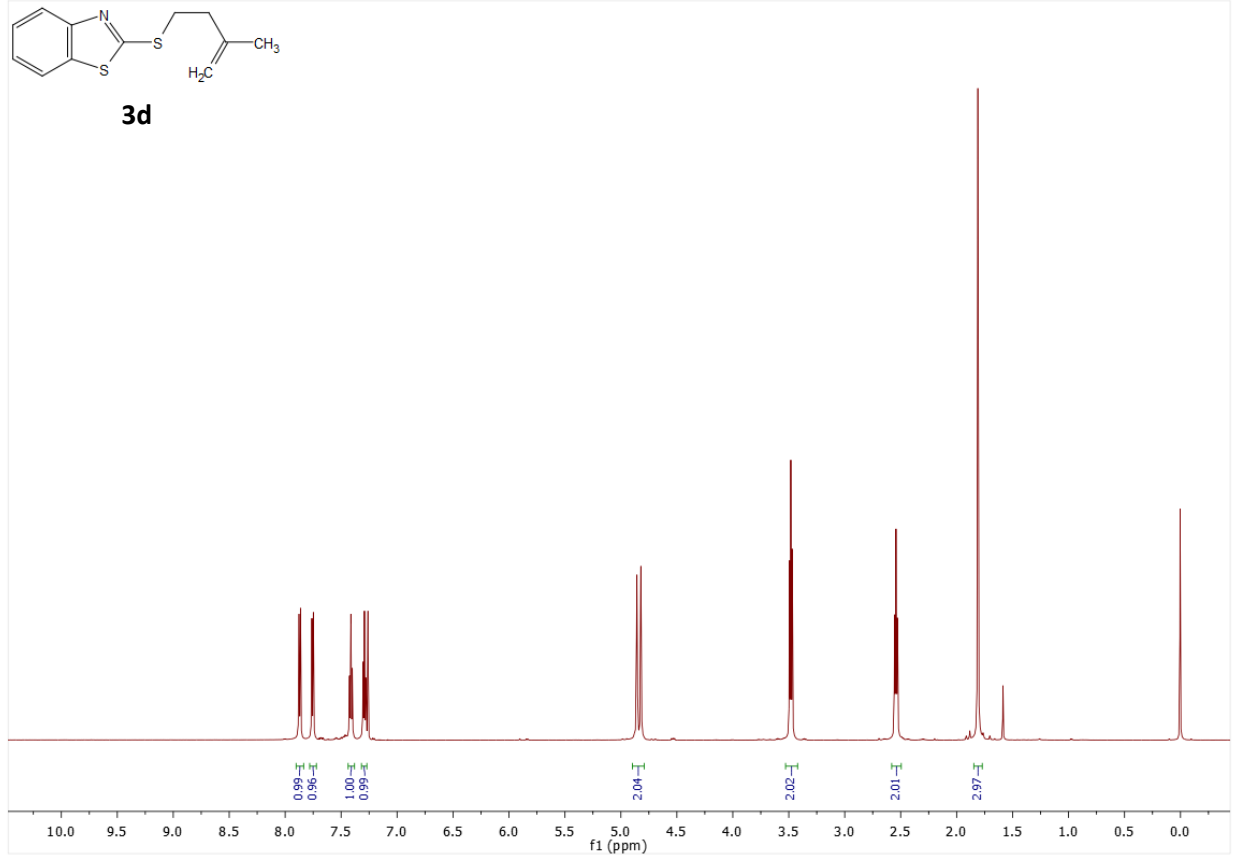
166.36
153.54
135.46
134.63
126.11
124.39
121.76
121.06
118.15
43.68
41.02
20.77
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

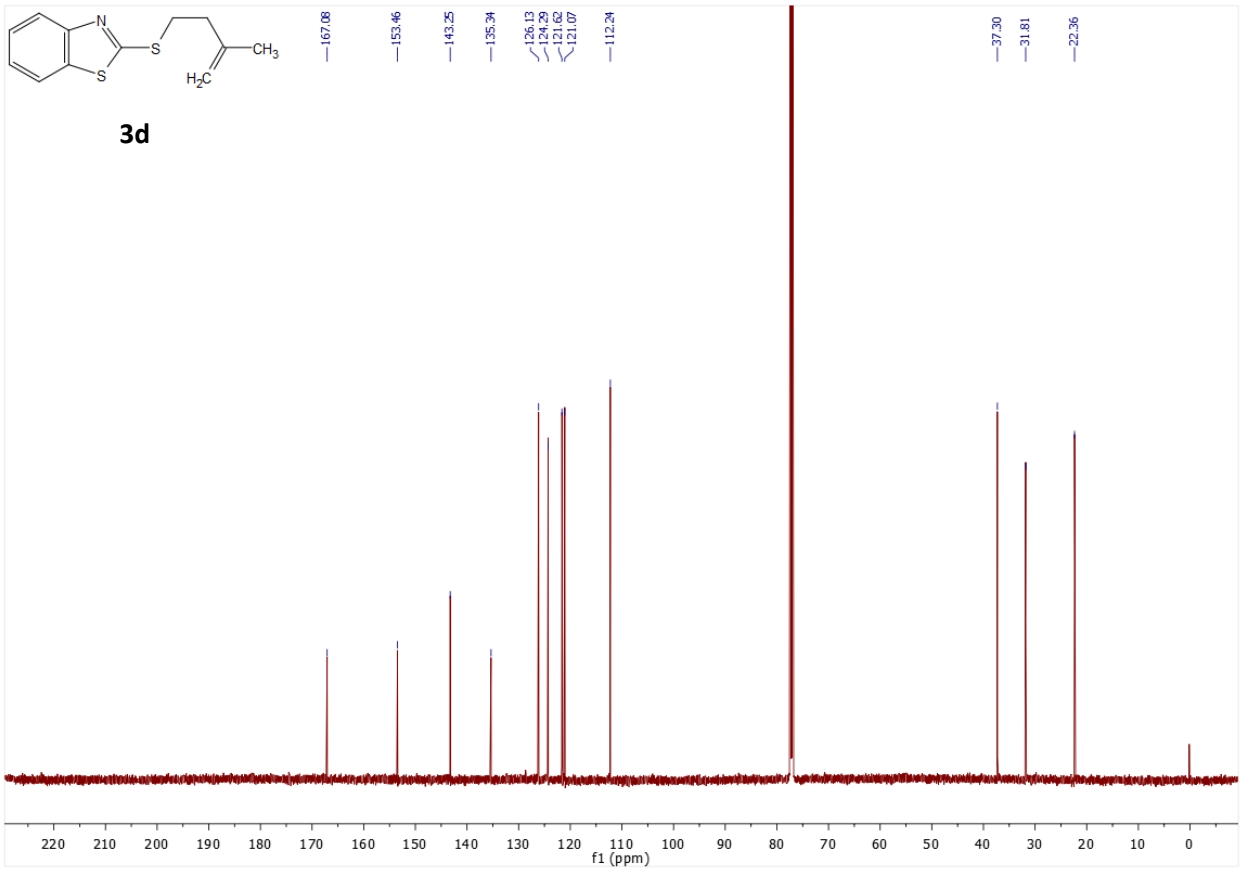

CH3
N
S
S
H2C
3b
1.02
1.00
1.03
1.25
1.00
2.08
2.07
0.99
3.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

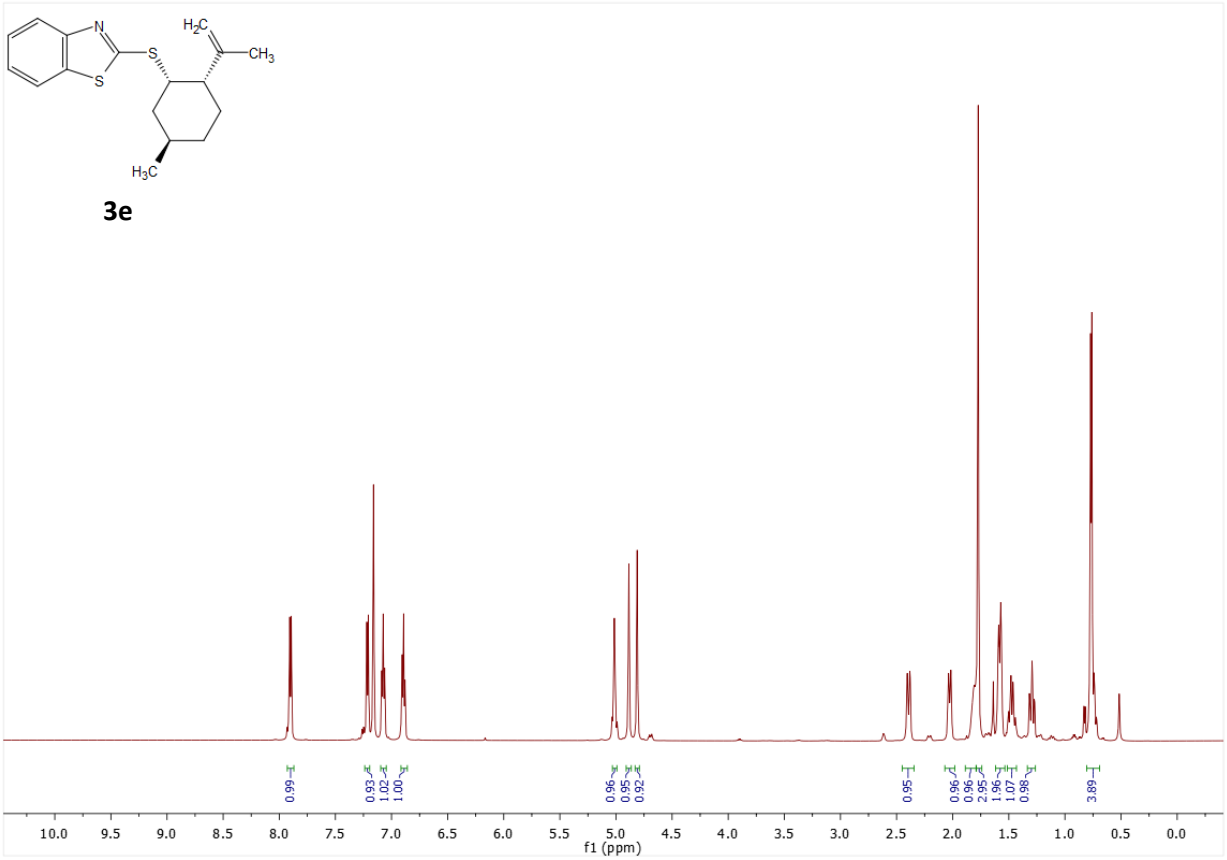

CH3
N
S
S
H2C
3b
167.39
153.43
141.62
135.33
126.13
124.27
121.59
121.06
114.99
39.84
37.69
19.49
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

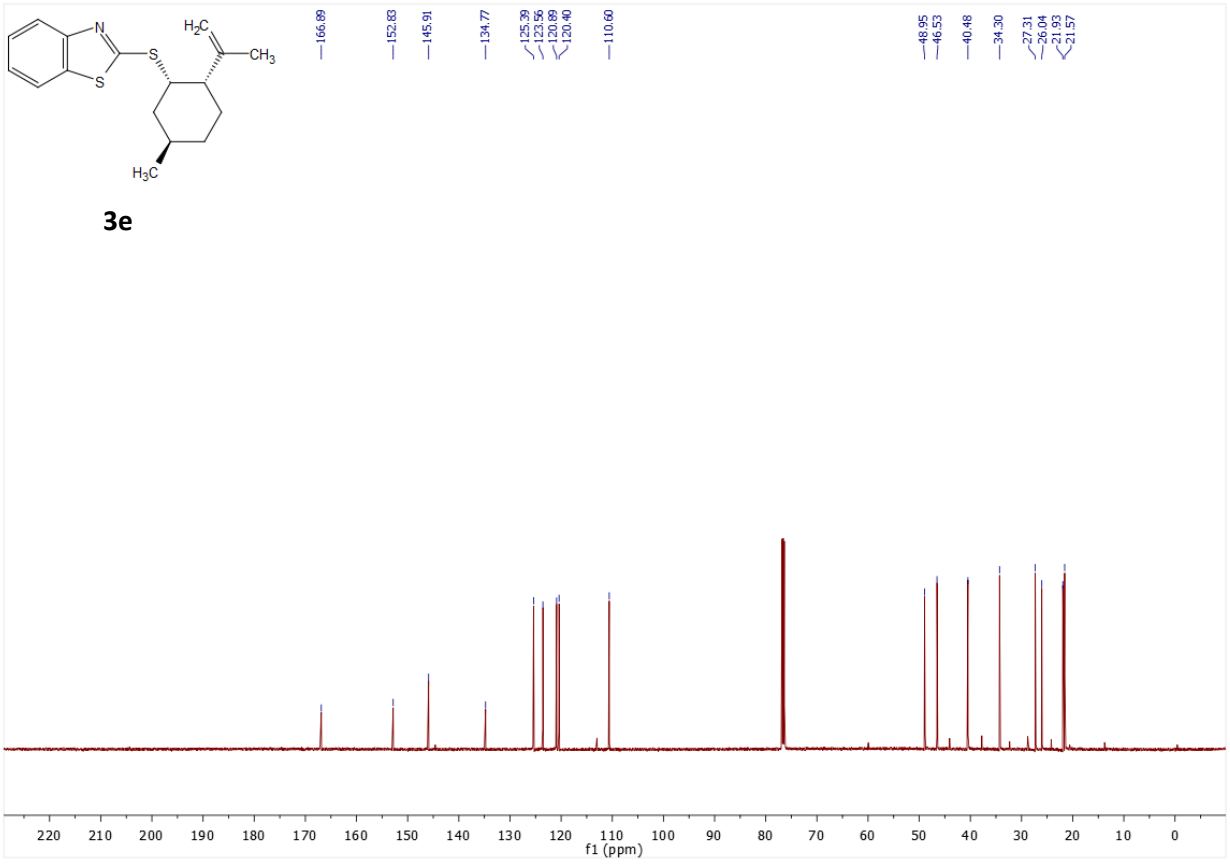

N
S
S
OH
CH2
3c
1.00
0.97
1.02
1.00
0.98
1.02
1.00
1.83
1.03
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

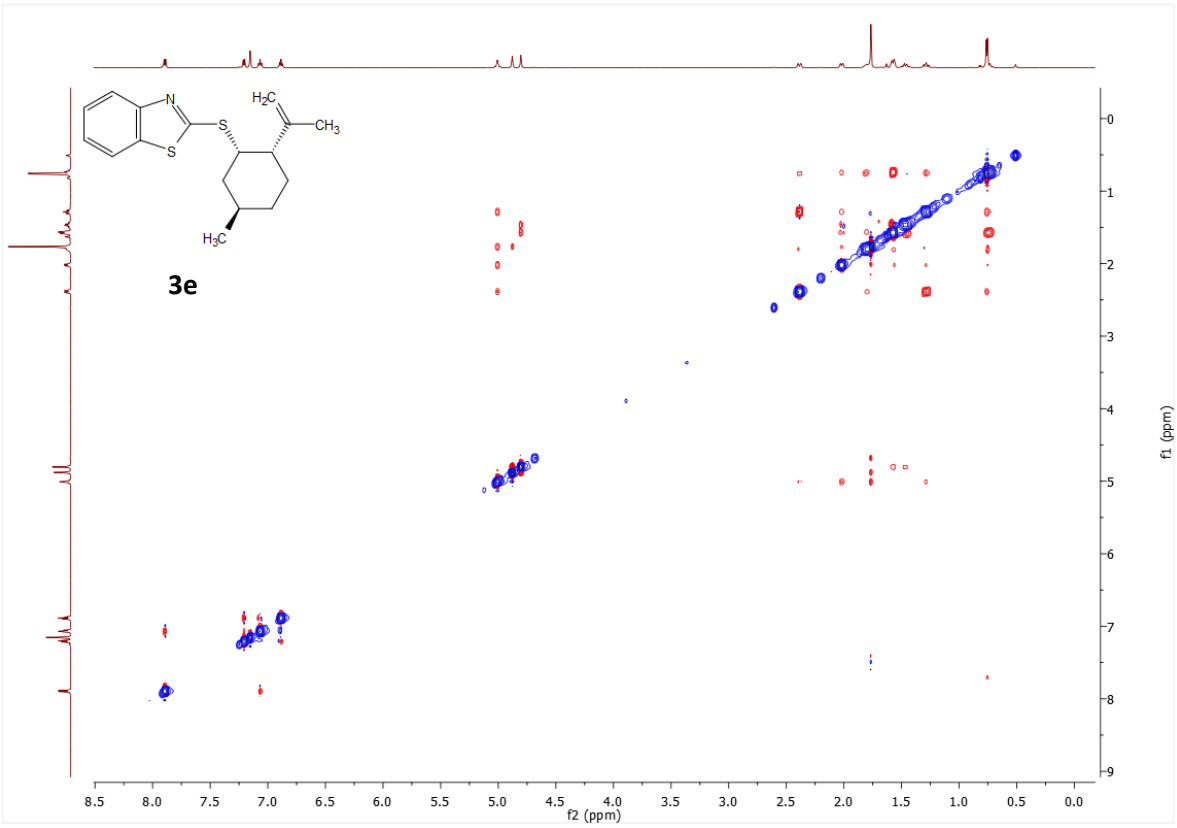

N
S
S
OH
CH2
3c
167.85
152.52
138.87
135.61
126.41
124.78
121.49
121.21
116.32
72.39
40.73
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

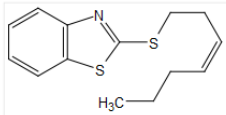

3d
0.99
0.96
1.00
0.99
2.04
2.02
2.01
2.97
f1 (ppm)


3d
167.08
153.46
143.25
135.34
126.13
124.29
121.62
121.07
112.24
37.30
31.81
22.36
f1 (ppm)


3e
0.99
0.93
1.02
1.00
0.96
0.95
0.92
0.95
0.96
0.96
2.95
1.96
1.07
0.98
3.89
f1 (ppm)

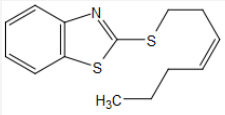

3e
166.89
152.83
145.91
134.77
125.39
123.56
120.89
120.40
110.60
48.95
46.53
40.48
34.30
27.31
26.04
21.93
21.57
f1 (ppm)


3e
f2 (ppm)
f1 (ppm)


N
S
S
H3C

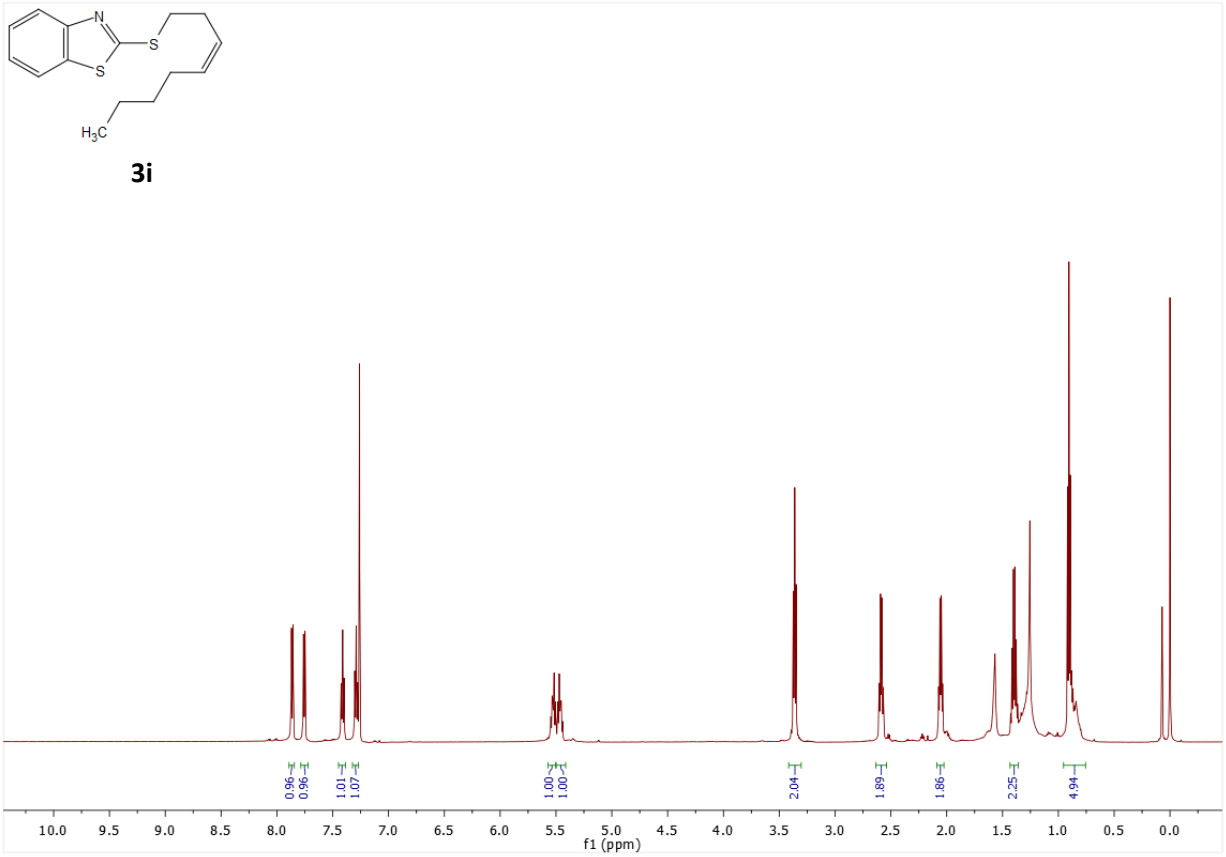
3h

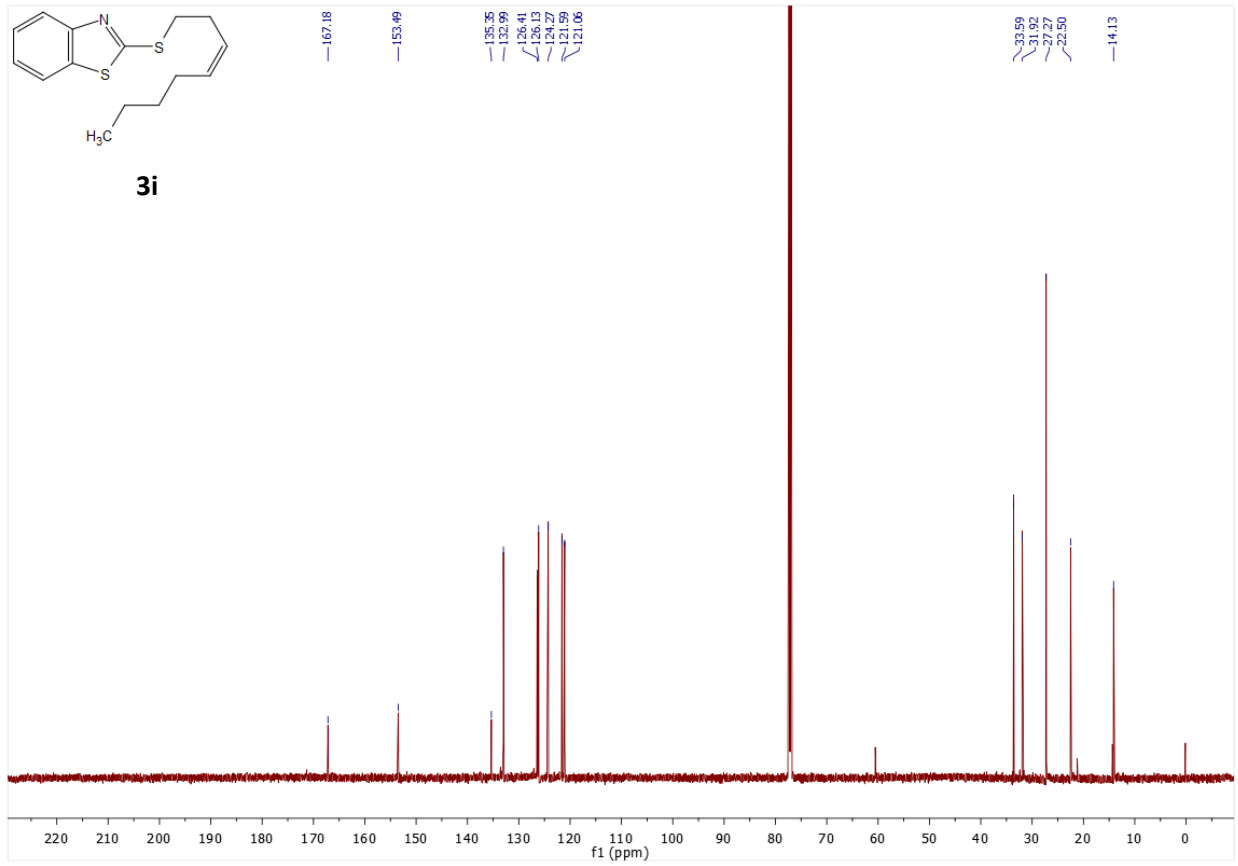
1.01
0.97
1.01
1.00
1.00
1.05
2.04
2.00
2.05
2.03
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

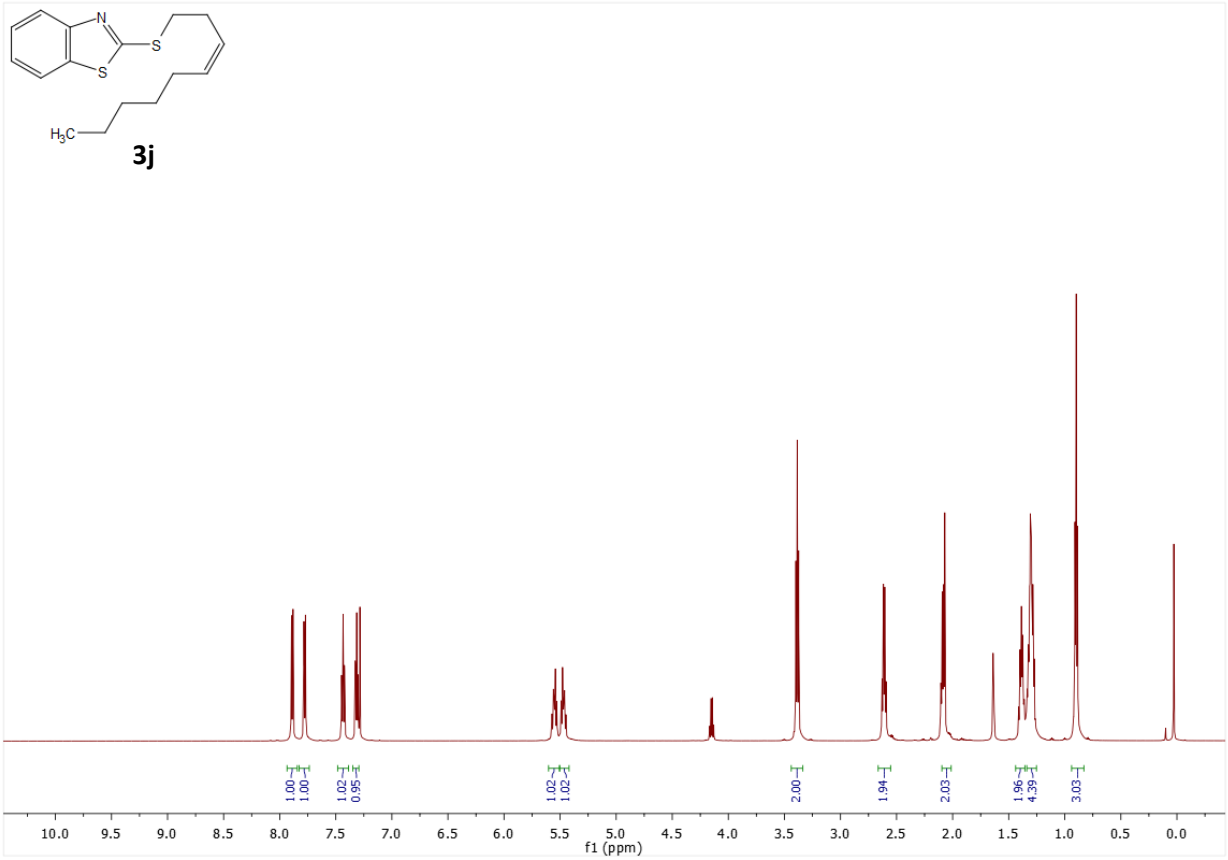

N
S
S
H3C

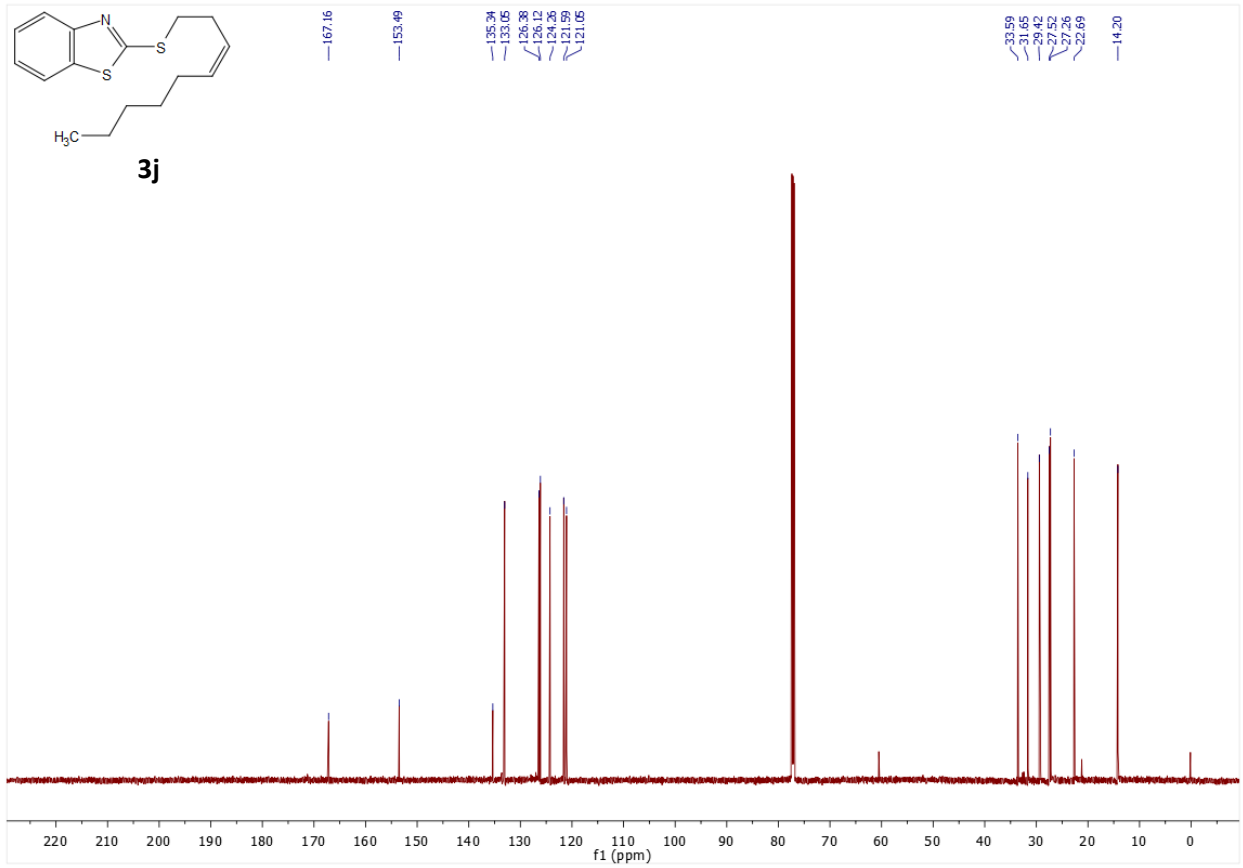
3h

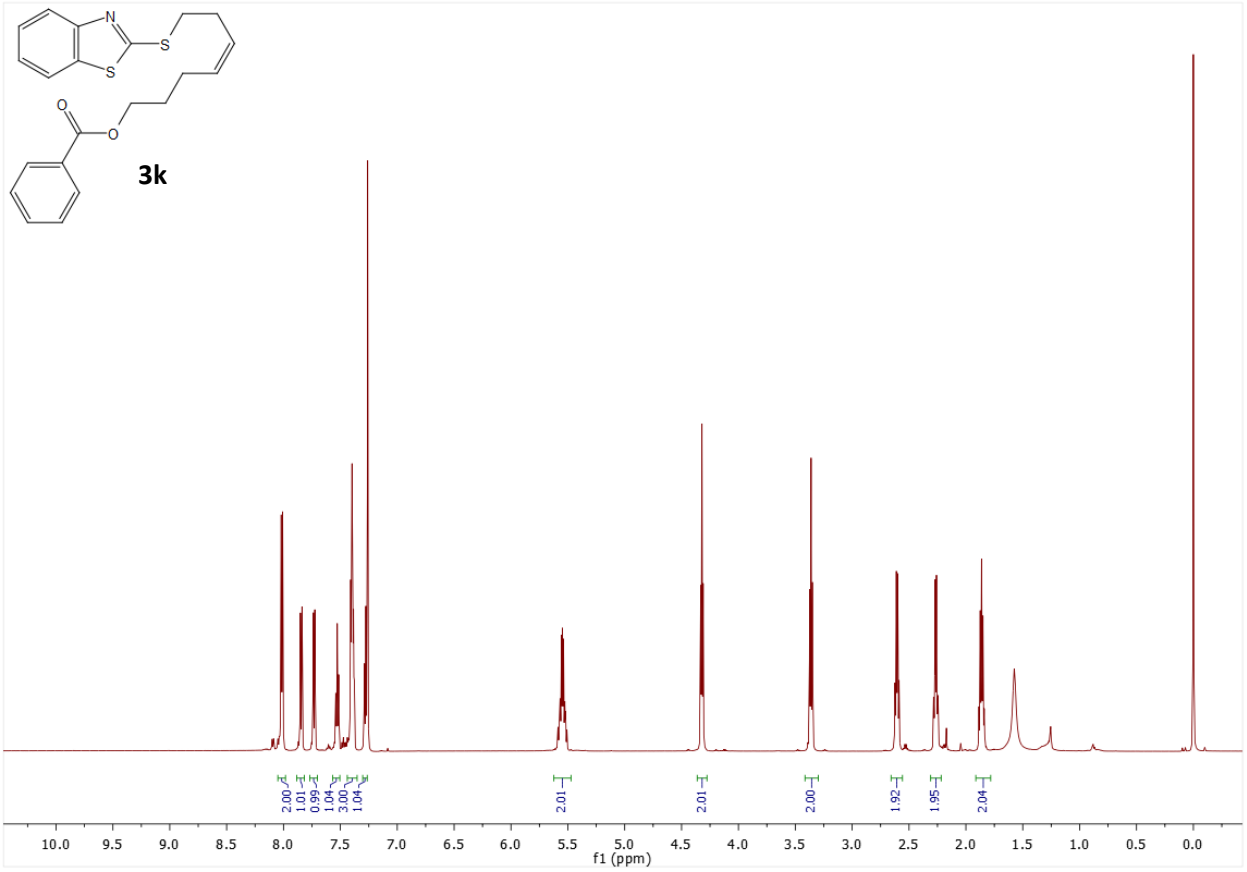
167.17
153.48
135.35
132.76
126.61
126.13
124.26
121.59
121.06
33.58
29.58
27.30
22.88
13.94
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

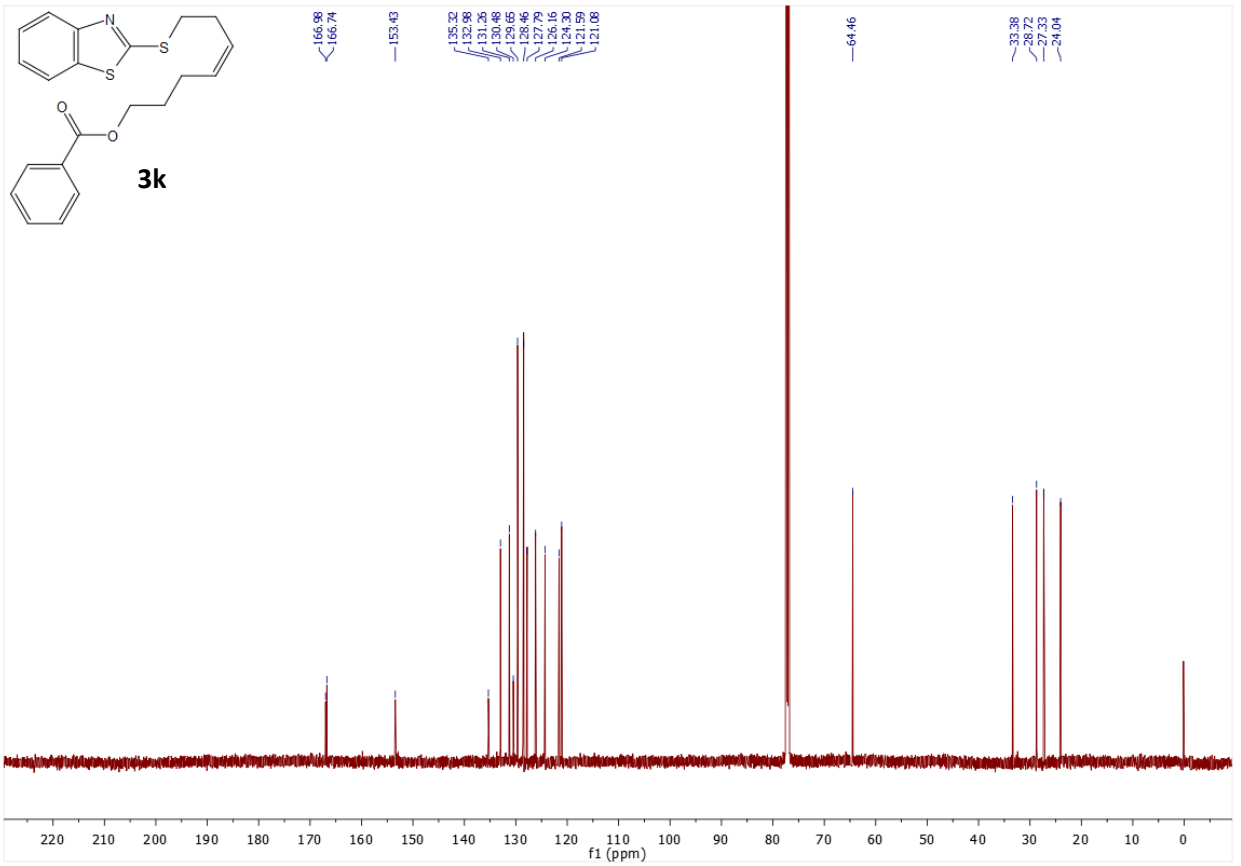

N
S
S
H3C
3i
0.96
0.96
1.01
1.07
1.00
1.00
2.04
1.89
1.86
2.25
4.94
f1 (ppm)

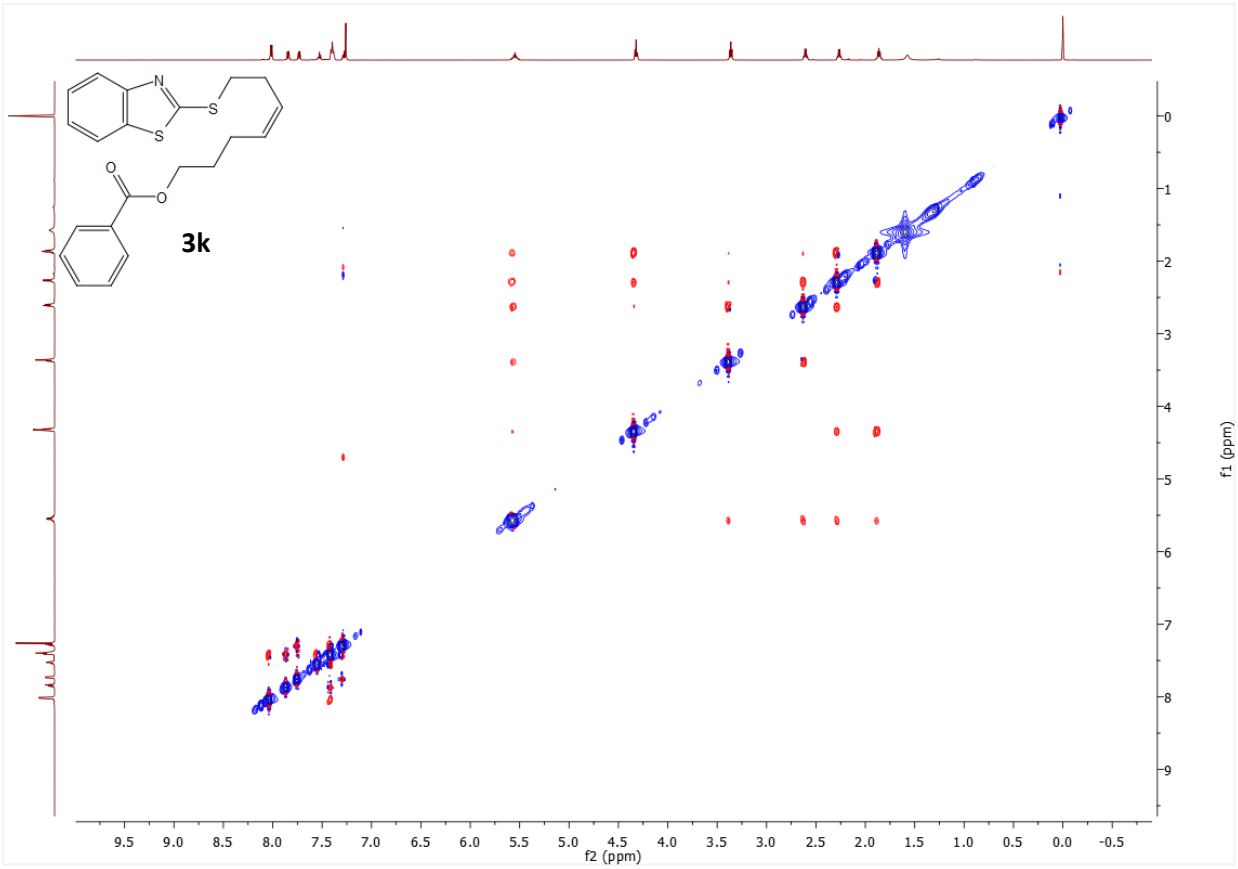

N
S
S
H3C
3i
167.18
153.49
135.35
132.99
126.41
126.13
124.27
121.59
121.06
33.59
31.92
27.27
22.50
14.13
f1 (ppm)

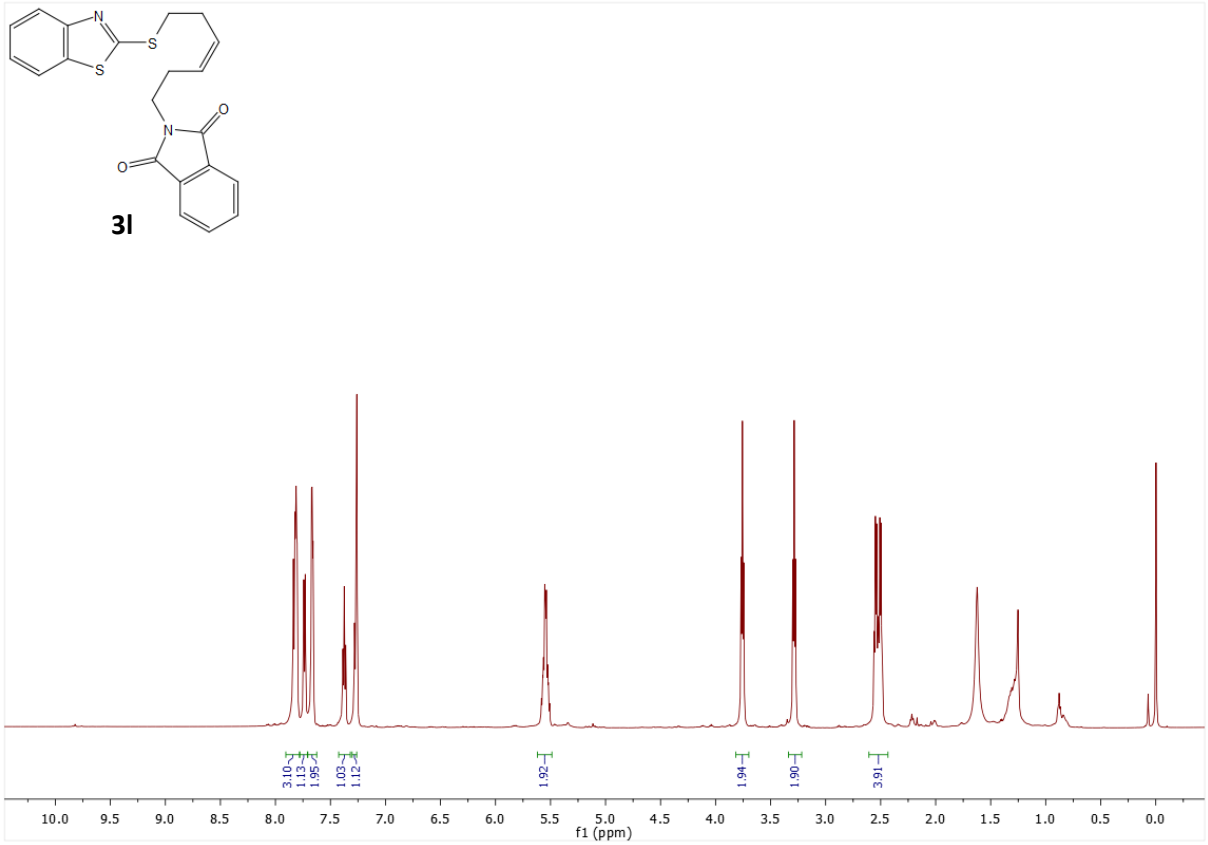

N
S
S
H3C
3j
1.00
1.00
1.02
0.95
1.02
1.02
2.00
1.94
2.03
1.96
4.39
3.03
f1 (ppm)

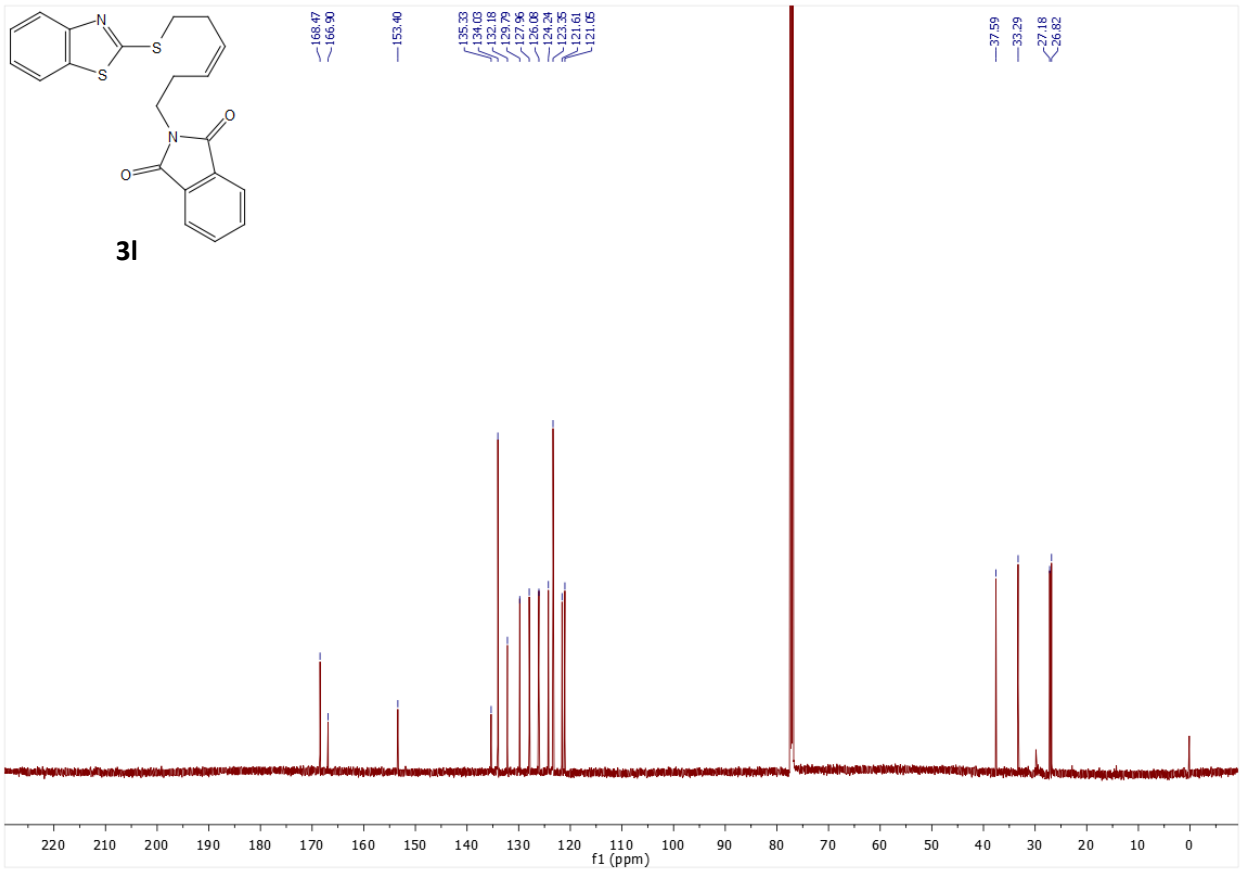

N
S
S
H3C
3j
167.16
153.49
135.34
133.05
126.38
126.12
124.26
121.59
121.05
33.59
31.65
29.42
27.52
27.26
22.69
14.20
f1 (ppm)

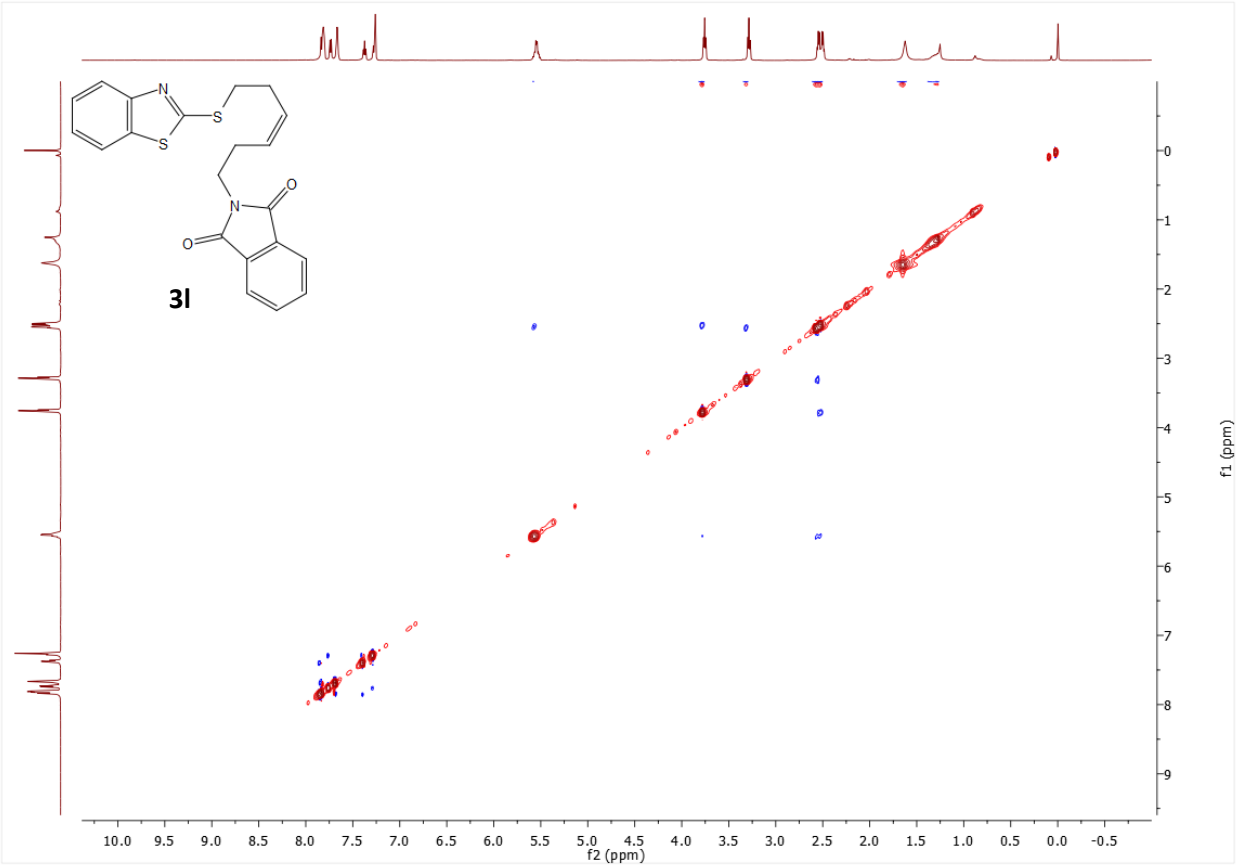

3k
2.00
1.01
0.99
1.04
3.00
1.04
2.01
2.01
2.00
1.92
1.95
2.04
f1 (ppm)

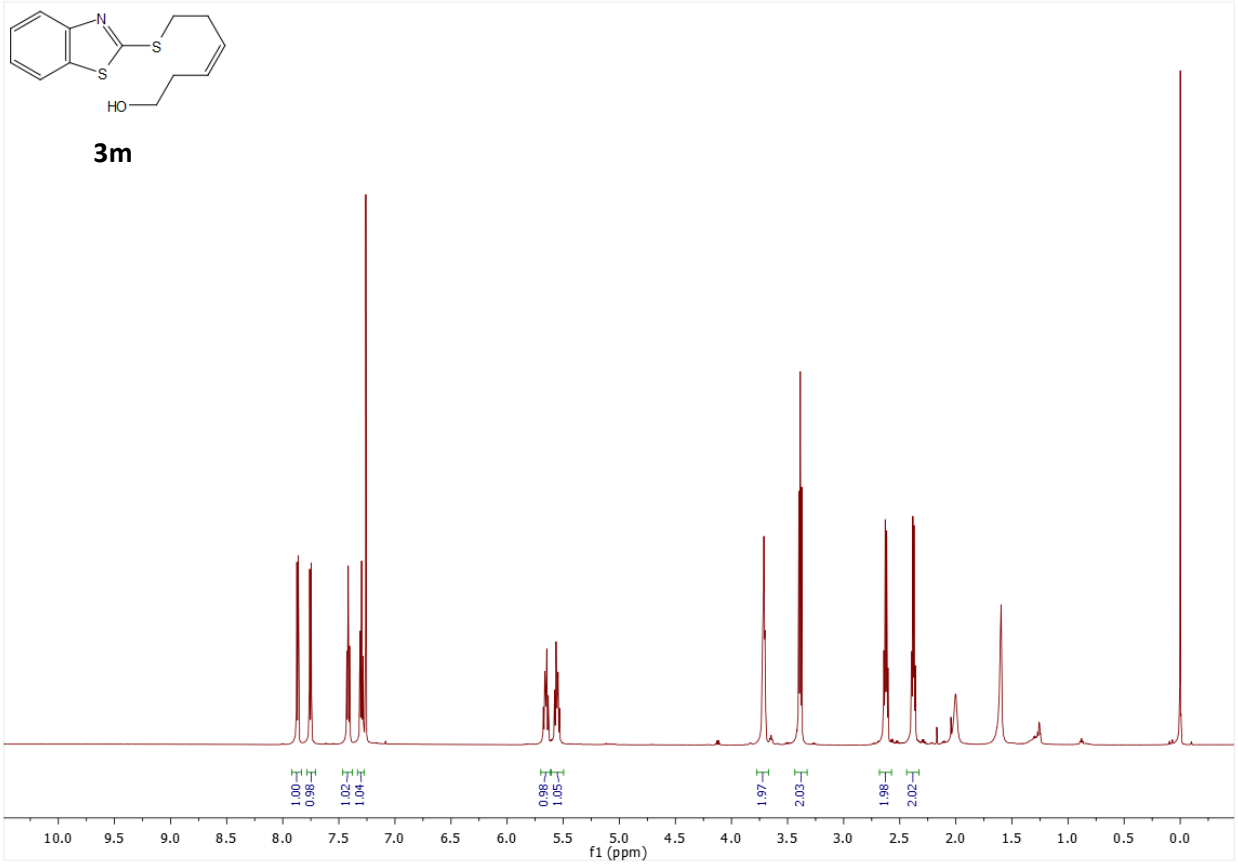

3k
166.98
166.74
153.43
135.32
132.98
131.26
130.48
129.65
128.46
127.79
126.16
124.30
121.59
121.08
64.46
33.38
28.72
27.33
24.04
f1 (ppm)

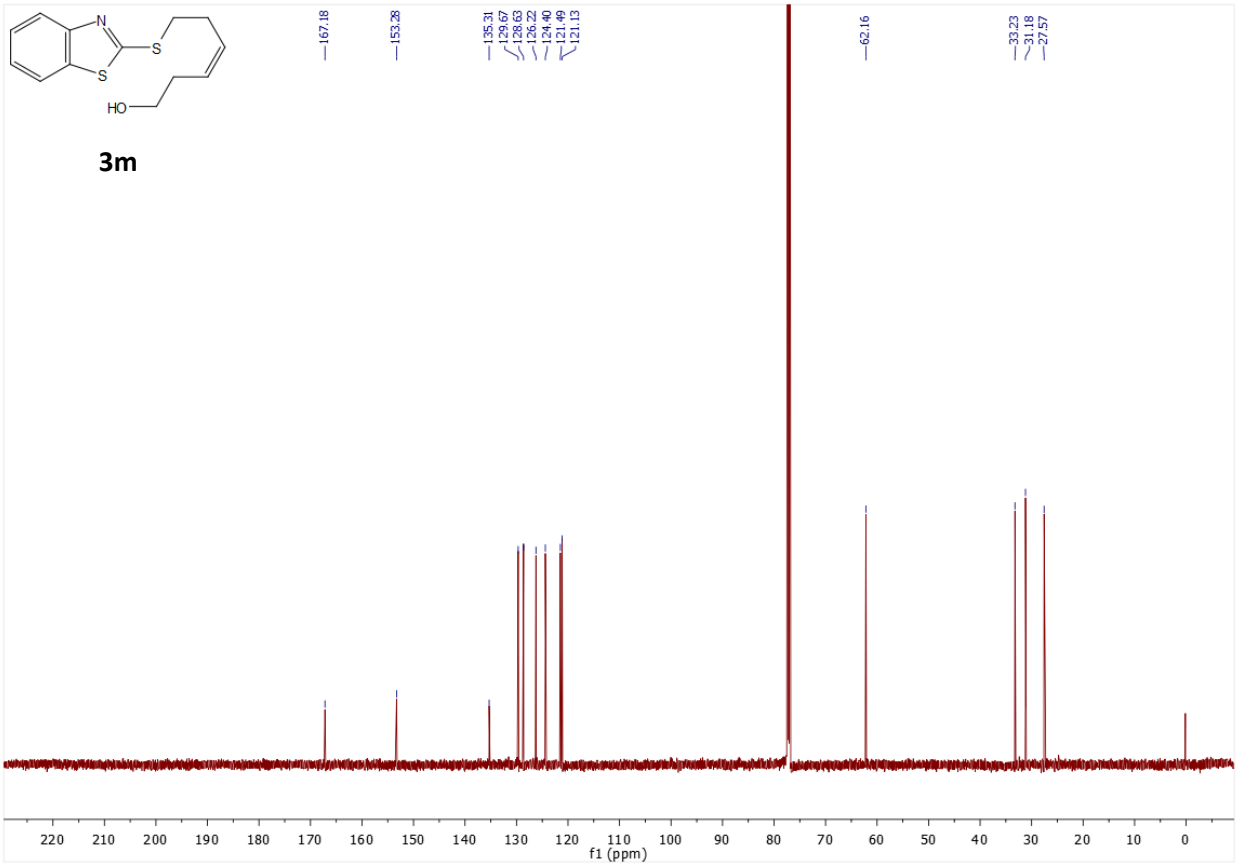

N
S
S
O
O
3k
f2 (ppm)
f1 (ppm)

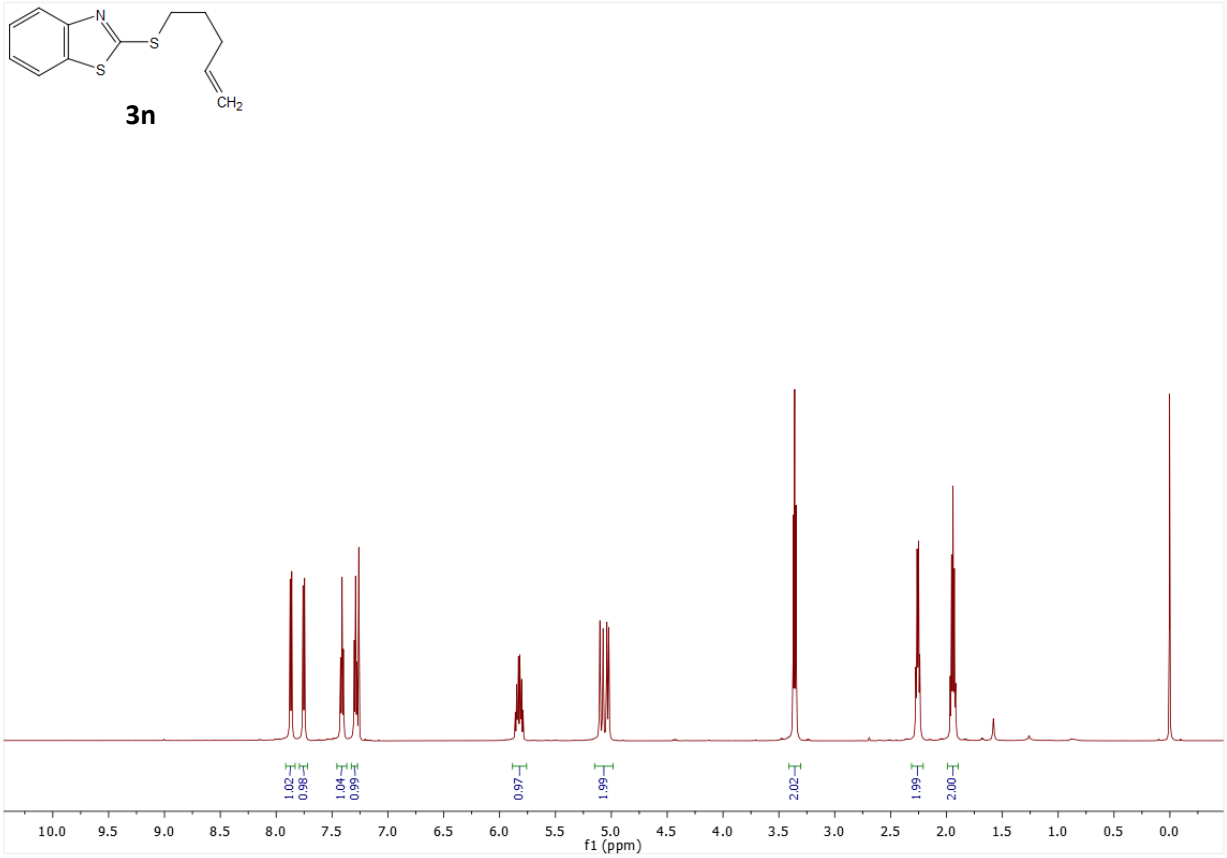

3l
3.10
1.13
1.95
1.03
1.12
1.92
1.94
1.90
3.91
f1 (ppm)

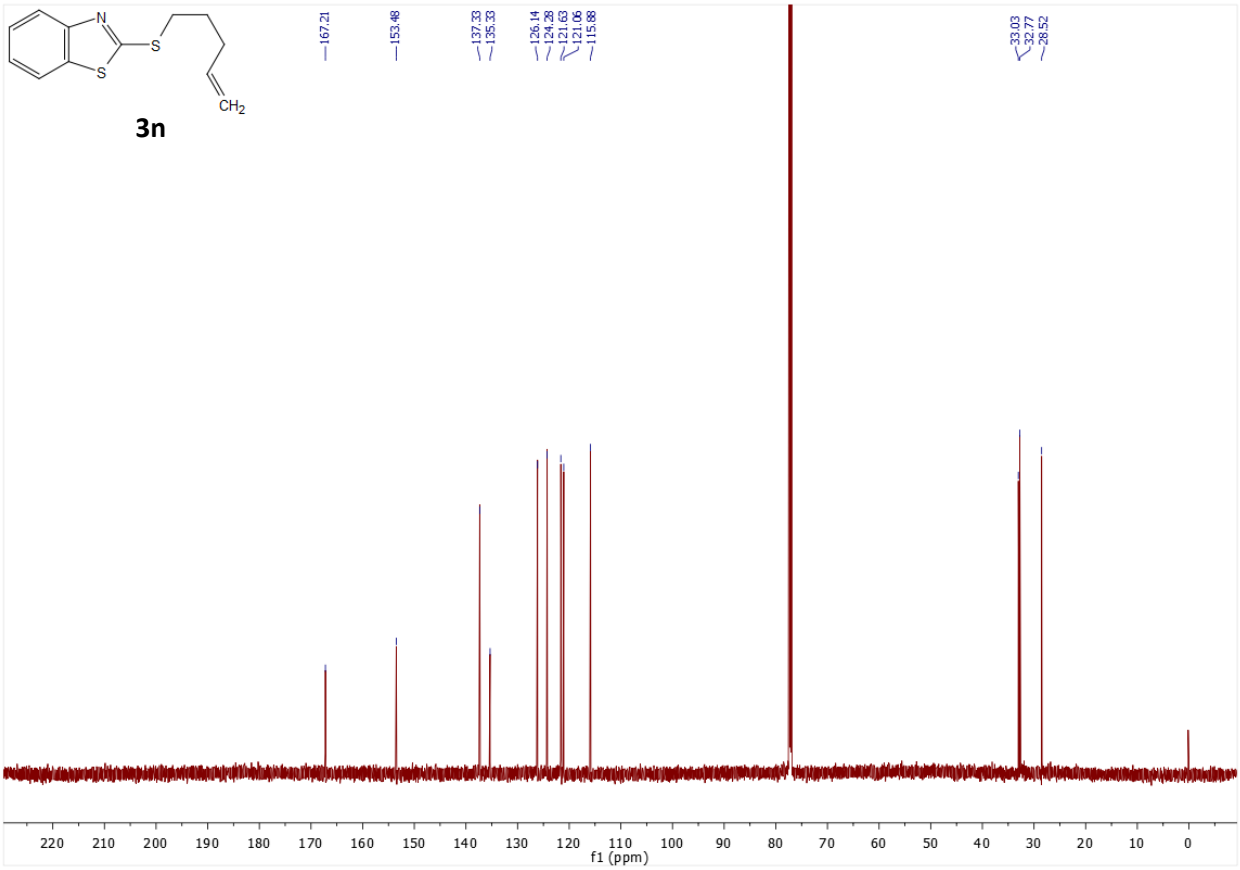

3l
168.47
166.90
153.40
135.33
134.03
132.18
129.79
127.96
126.08
124.24
123.35
121.61
121.05
37.59
33.29
27.18
26.82
f1 (ppm)

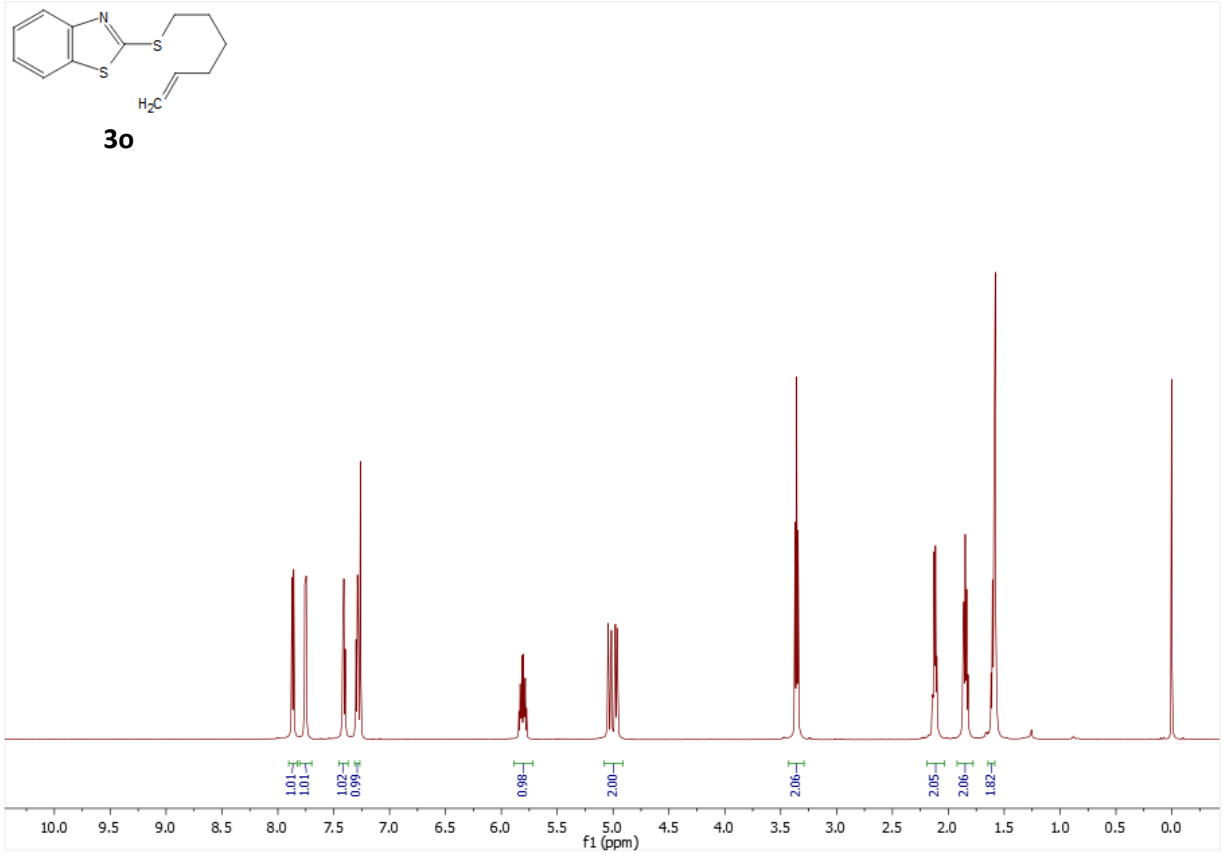

N
S
S
N
O
O
3l
f2 (ppm)
f1 (ppm)

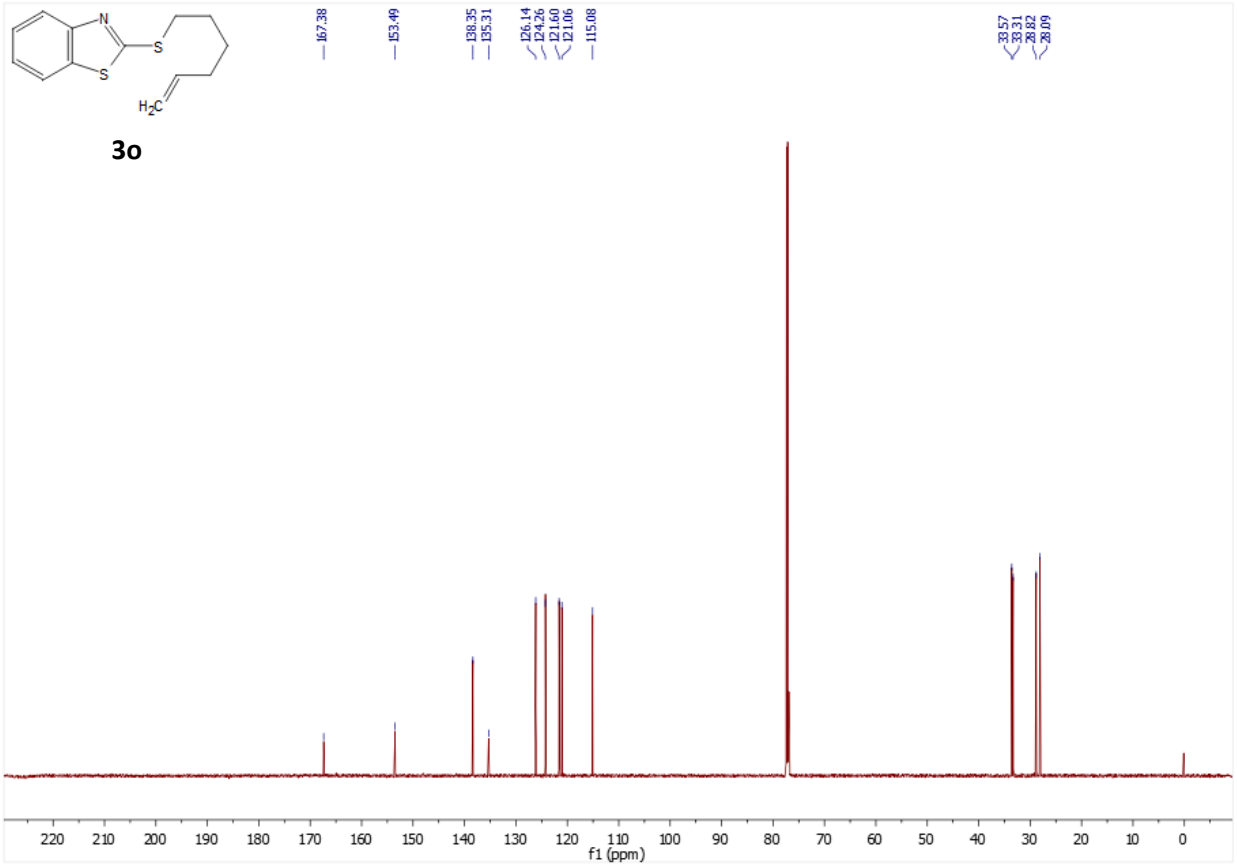

N
S
S
HO
3m
1.00
0.98
1.02
1.04
0.98
1.05
1.97
2.03
1.98
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

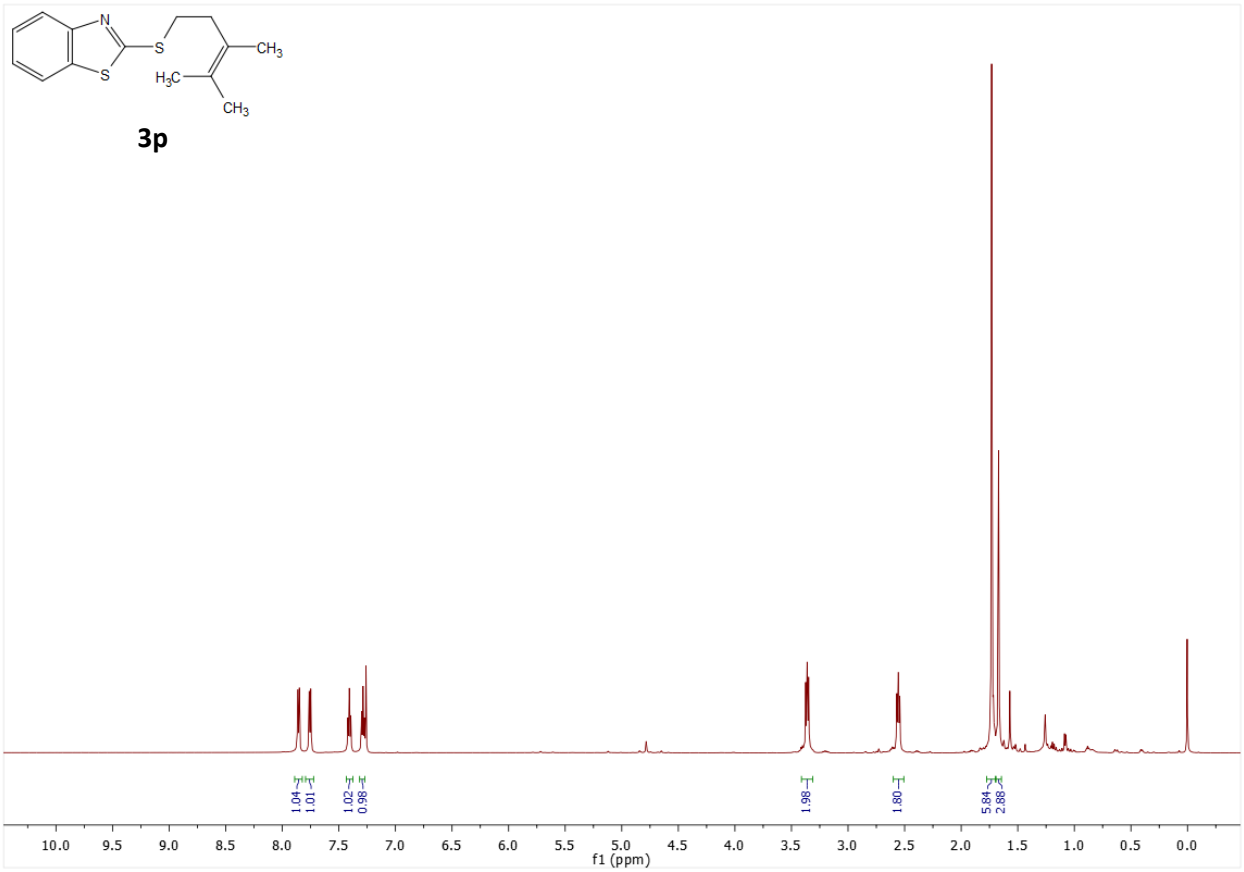

N
S
S
HO
3m
167.18
153.28
135.31
129.67
128.63
126.22
124.40
121.49
121.13
62.16
33.23
31.18
27.57
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

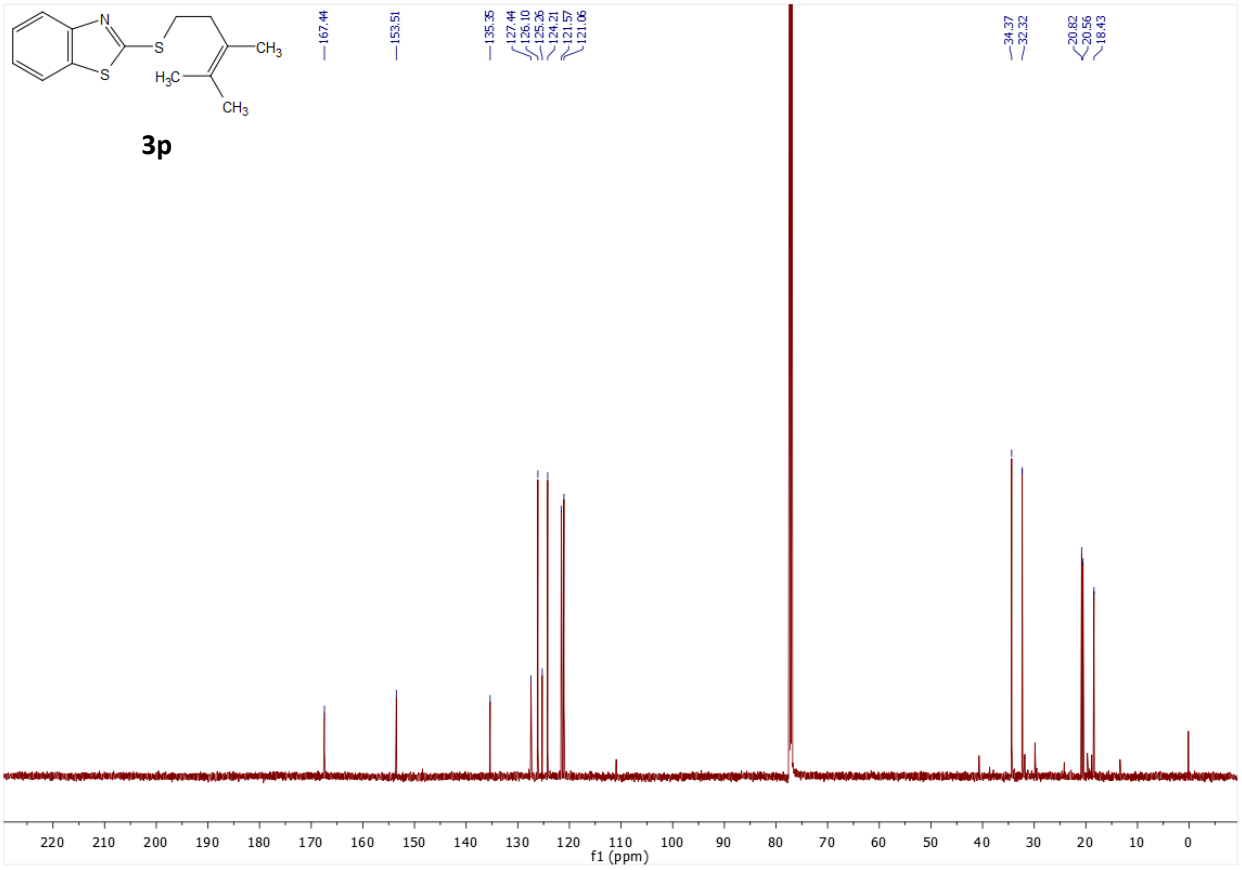

3n
1.02
0.98
1.04
0.99
0.97
1.99
2.02
1.99
2.00
f1 (ppm)

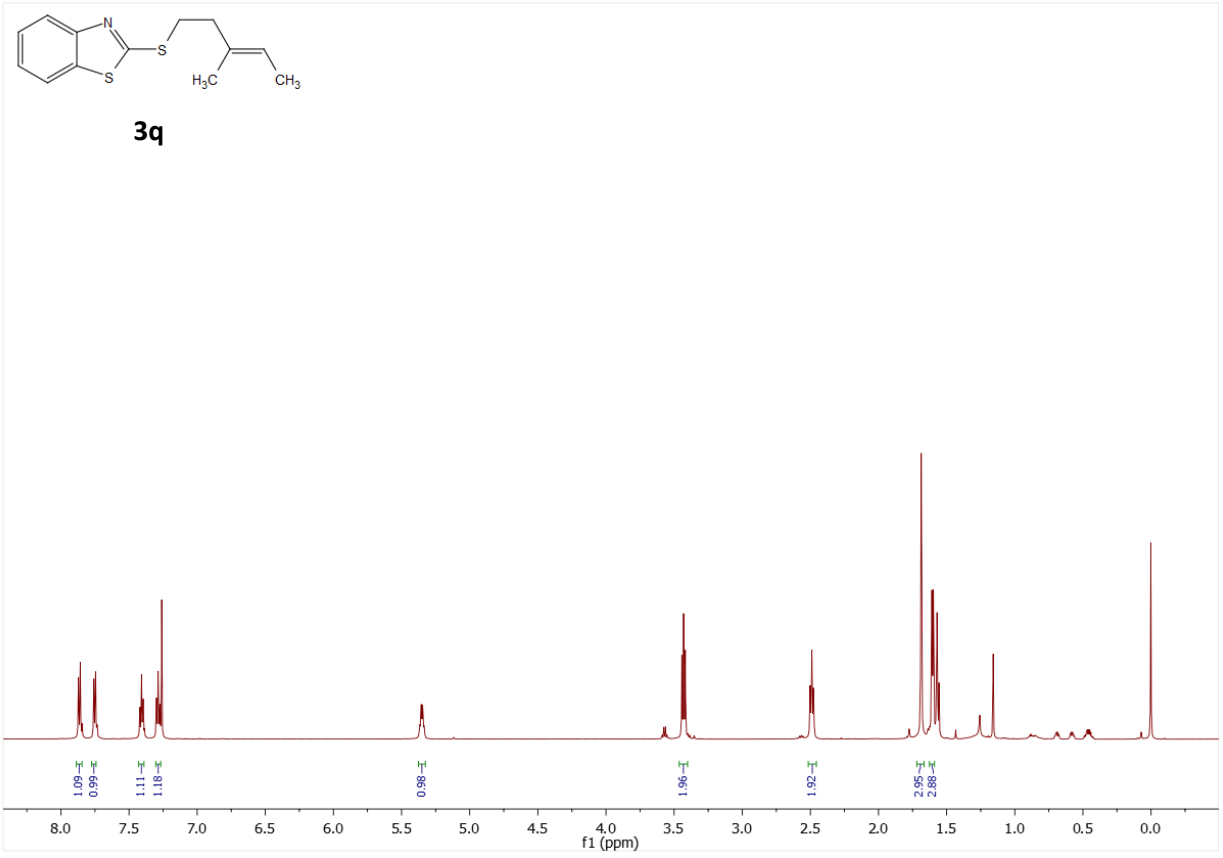

3n
167.21
153.48
137.33
135.33
126.14
124.28
121.63
121.06
115.88
33.03
32.77
28.52
f1 (ppm)

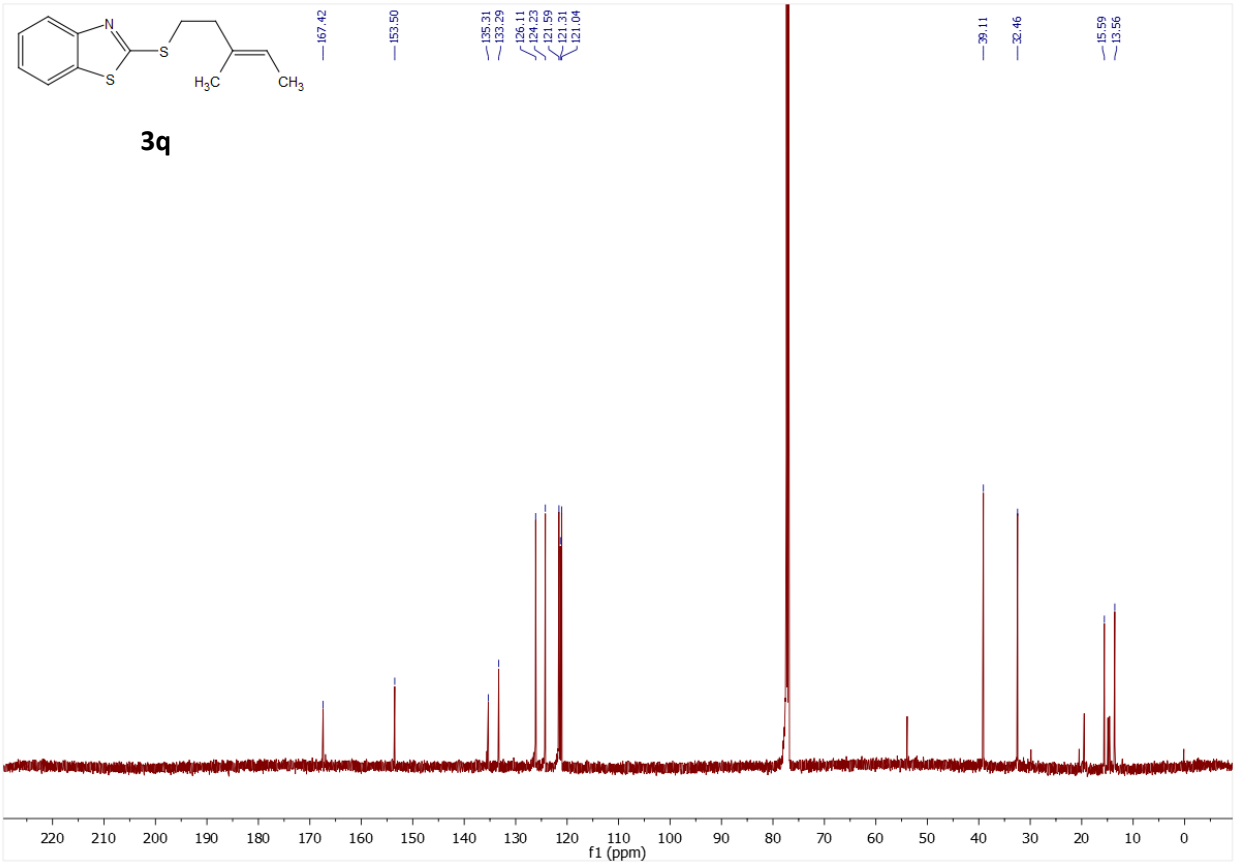

N
S
S
H2C
3o
1.01
1.01
1.02
0.99
0.98
2.00
2.06
2.05
2.06
1.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

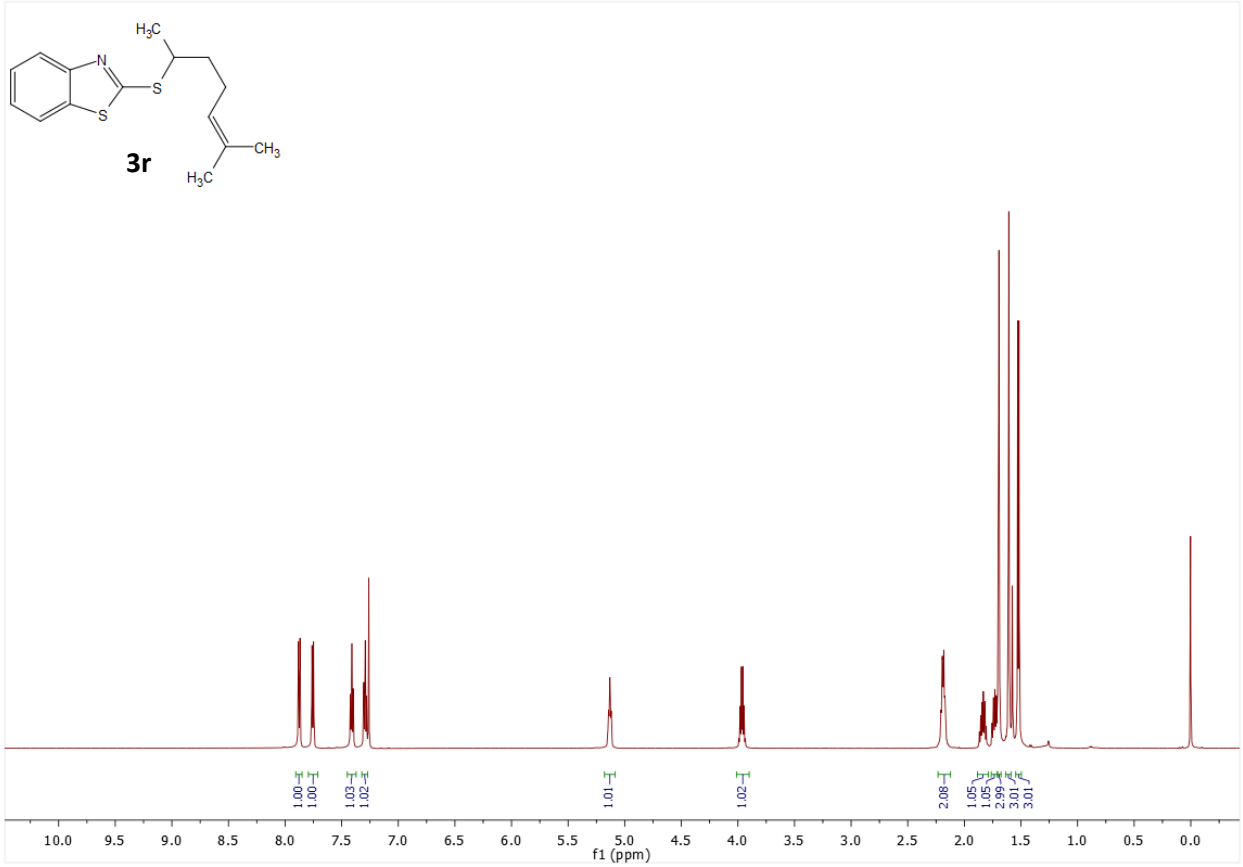

N
S
S
H2C
3o
167.38
153.49
138.35
135.31
126.14
124.26
121.60
121.06
115.08
33.57
33.31
28.82
28.09
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

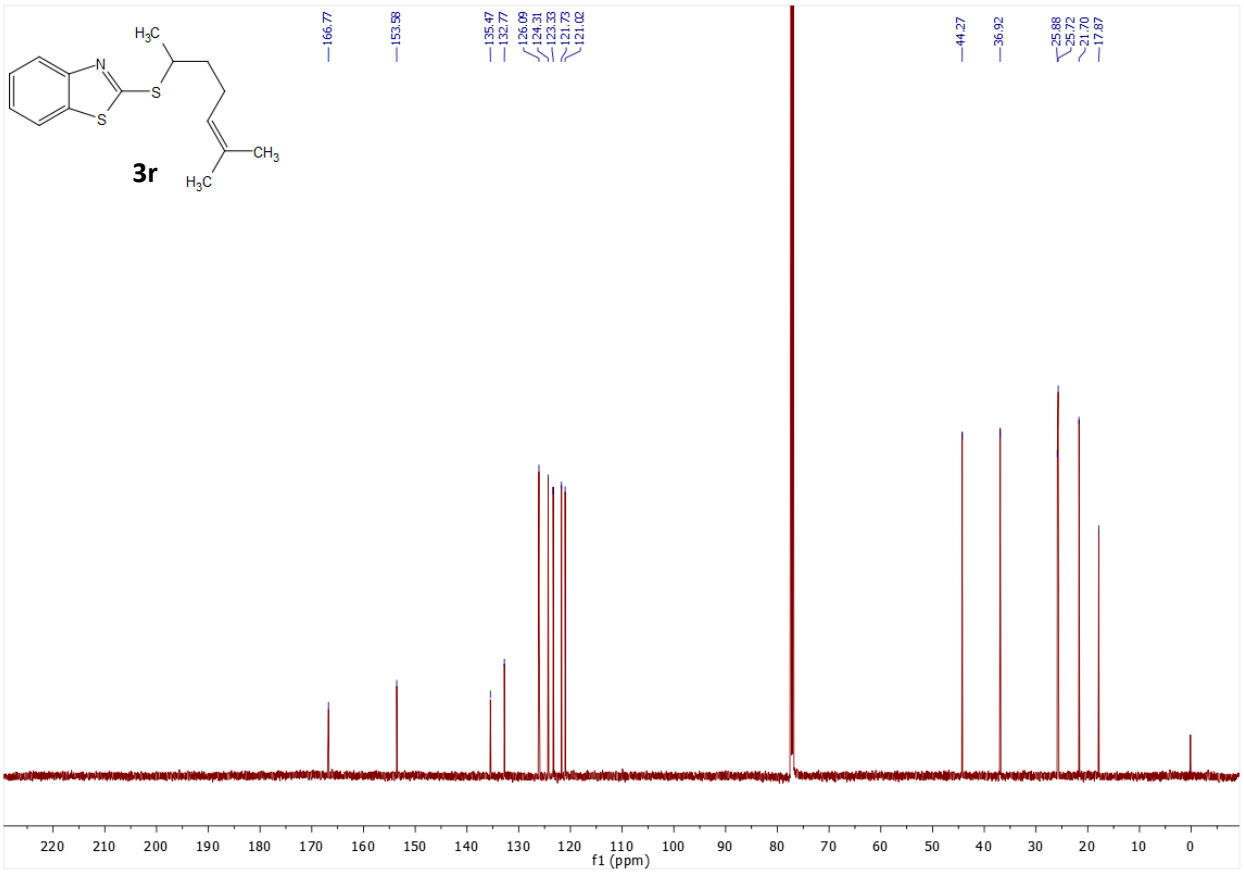

3p
1.04
1.01
1.02
0.98
1.98
1.80
5.84
2.88
f1 (ppm)

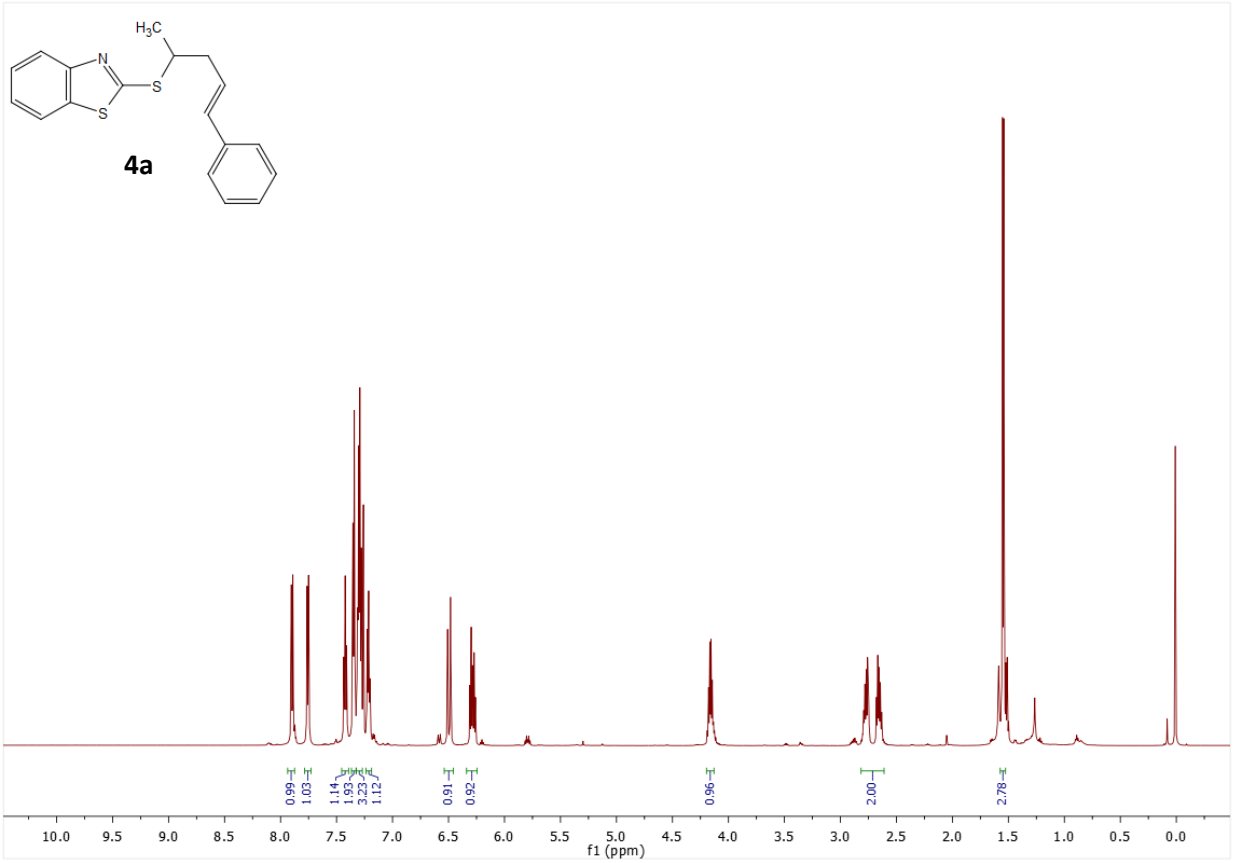

3p
167.44
153.51
135.35
127.44
126.10
125.26
124.21
121.57
121.06
34.37
32.32
20.82
20.56
18.43
f1 (ppm)

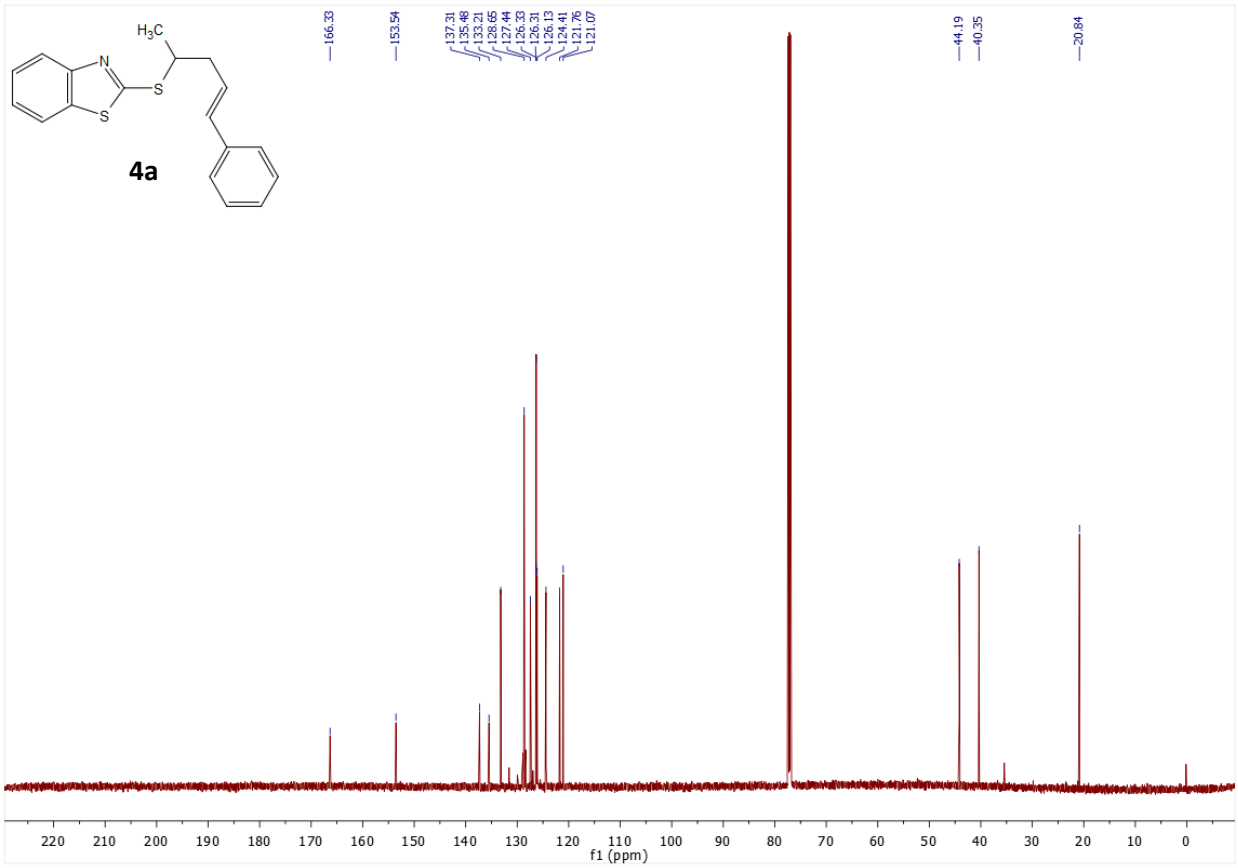

3q
1.09
0.99
1.11
1.18
0.98
1.96
1.92
2.95
2.88
f1 (ppm)

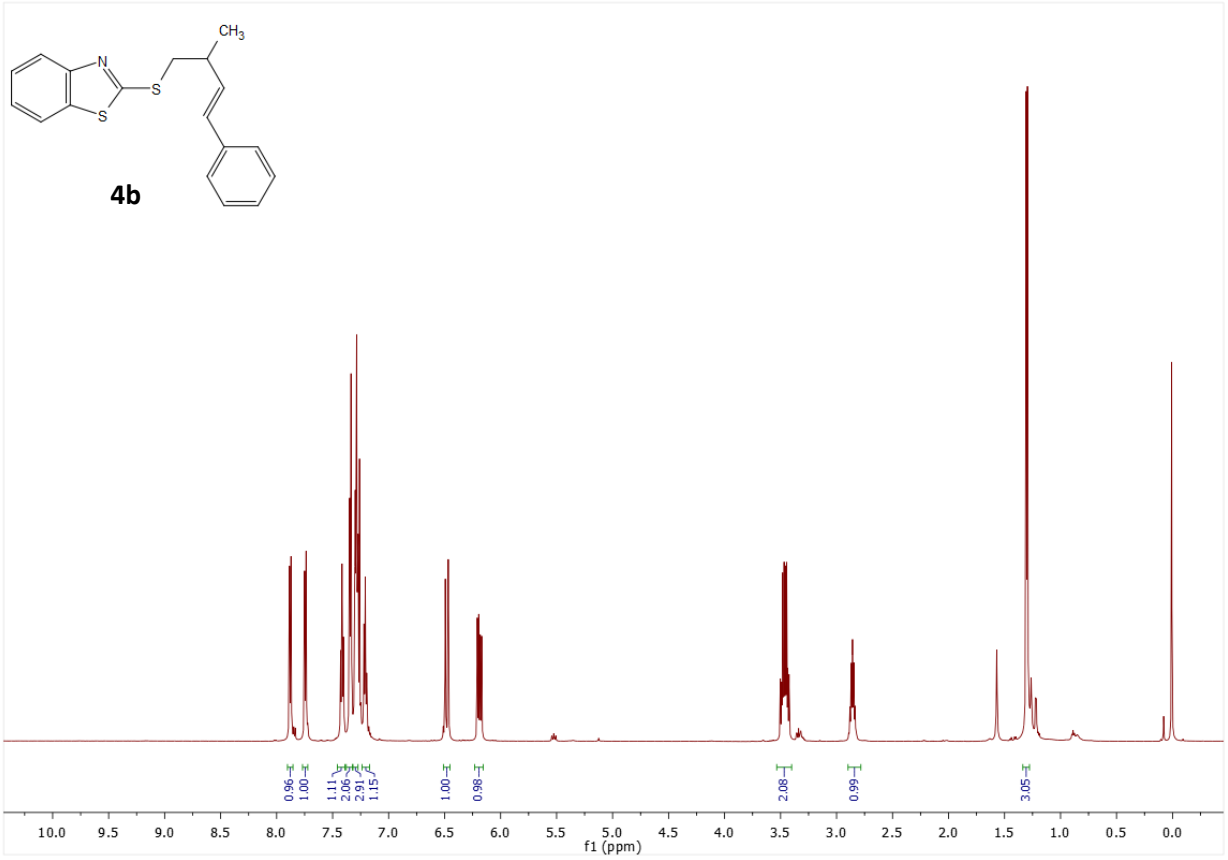

3q
167.42
153.50
135.31
133.29
126.11
124.23
121.59
121.31
121.04
39.11
32.46
15.59
13.56
f1 (ppm)

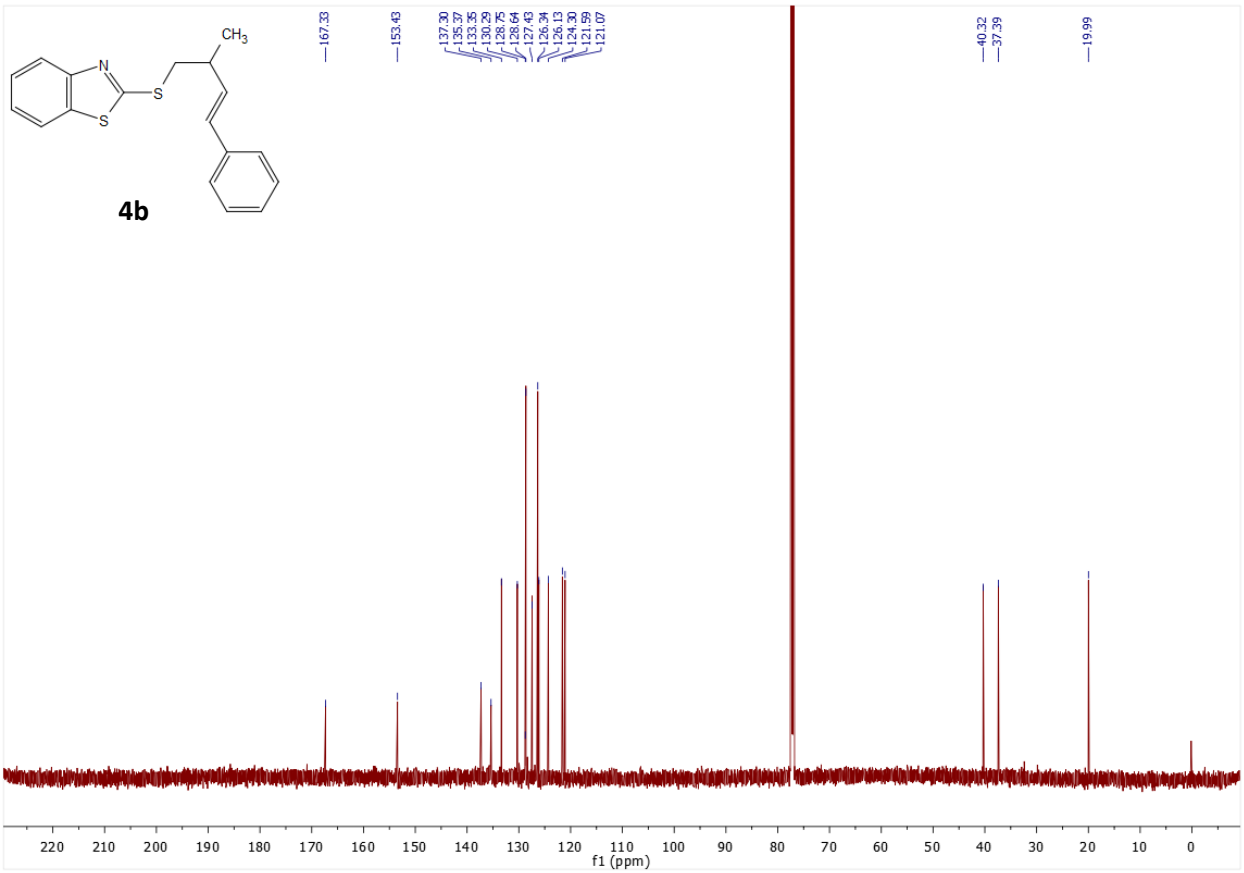

3r
1.00
1.00
1.03
1.02
1.01
1.02
2.08
1.05
2.99
3.01
3.01
f1 (ppm)

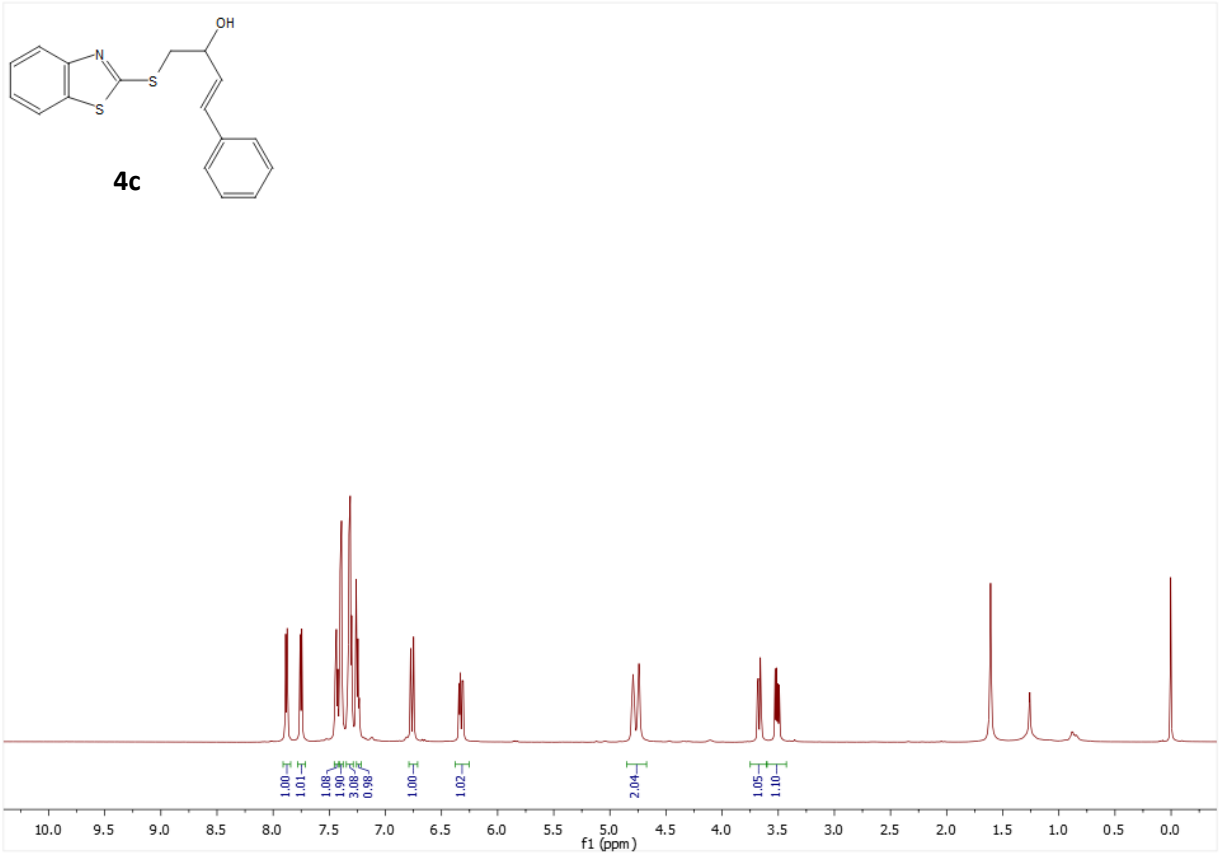

3r
166.77
153.58
135.47
132.77
126.09
124.31
123.33
121.73
121.02
44.27
36.92
25.88
25.72
21.70
17.87
f1 (ppm)

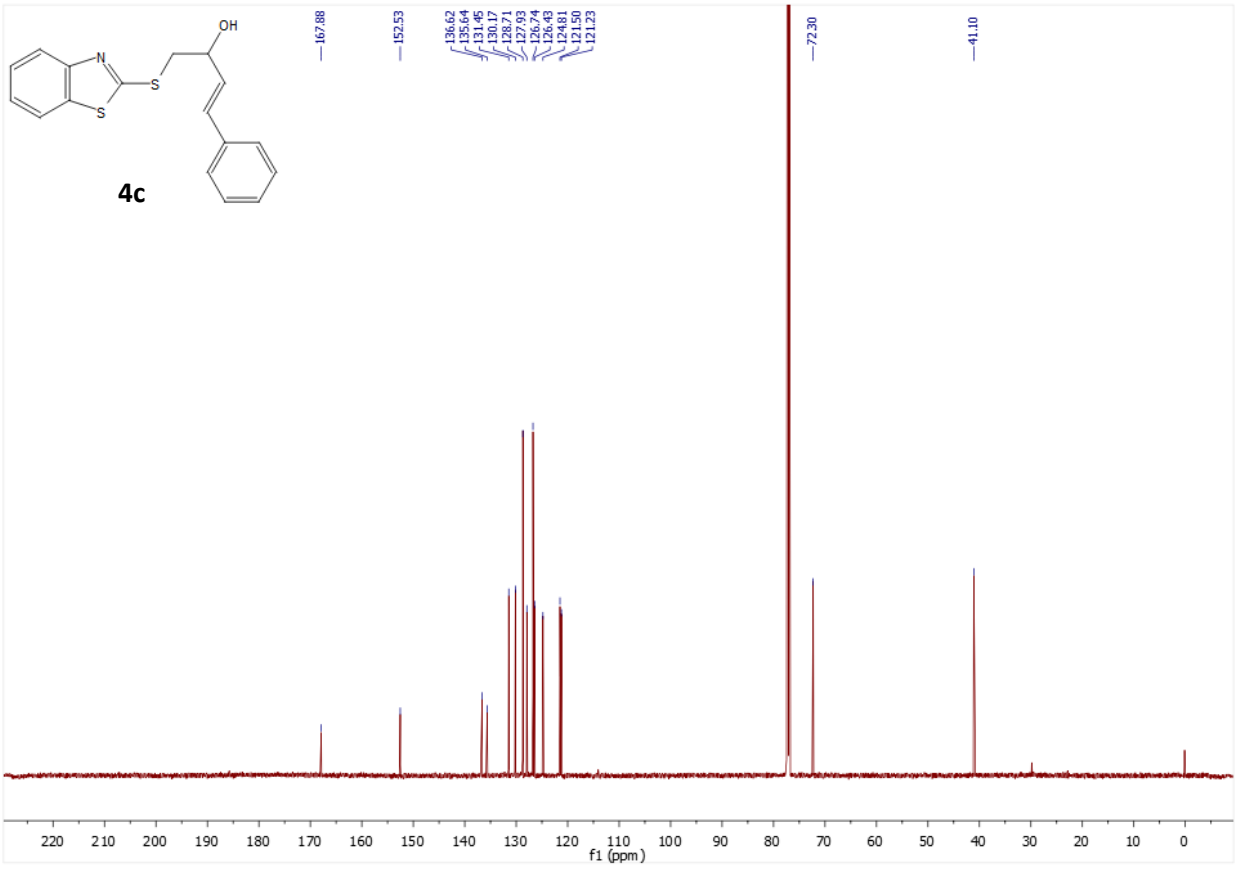

H3C
N
S
S
4a
0.99
1.03
1.14
1.93
3.23
1.12
0.91
0.92
0.96
2.00
2.78
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

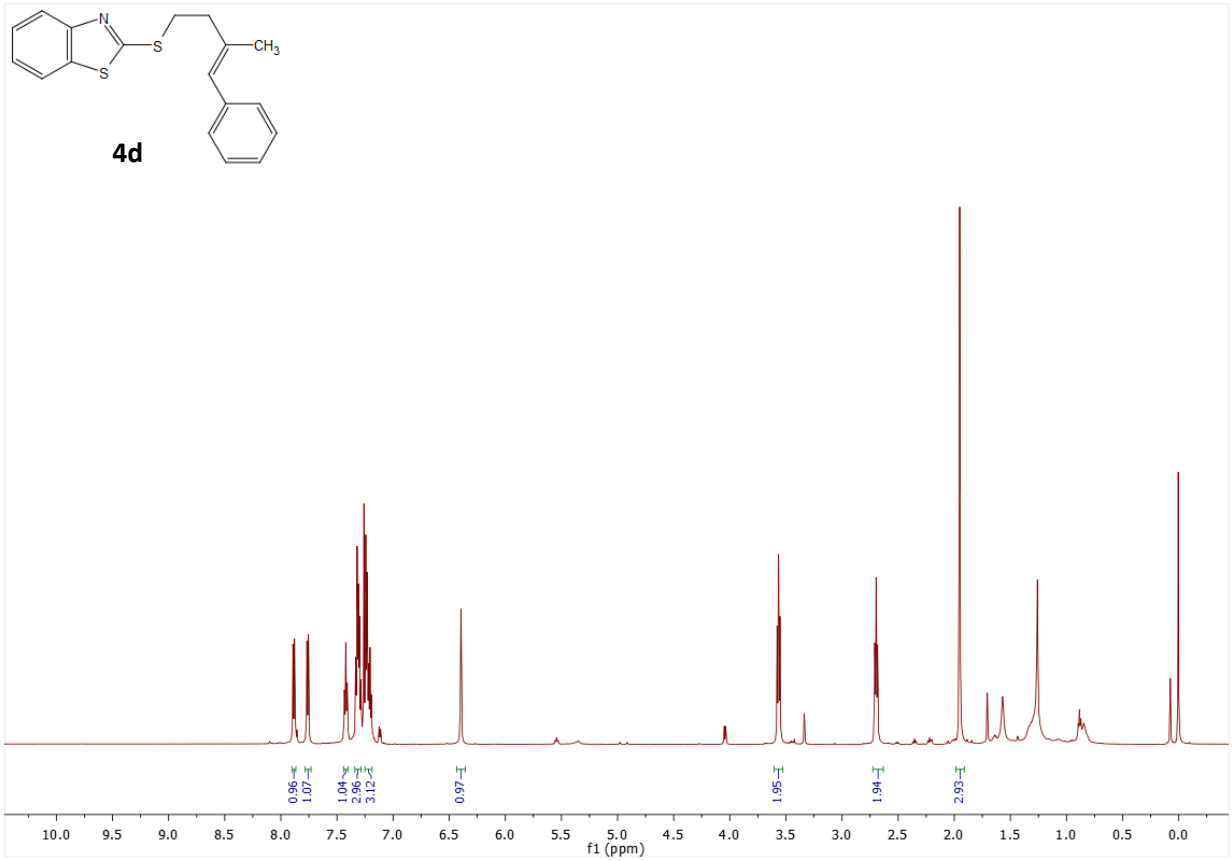

H3C
N
S
S
4a
166.33
153.54
137.31
135.48
133.21
128.65
127.44
126.33
126.31
126.13
124.41
121.76
121.07
44.19
40.35
20.84
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

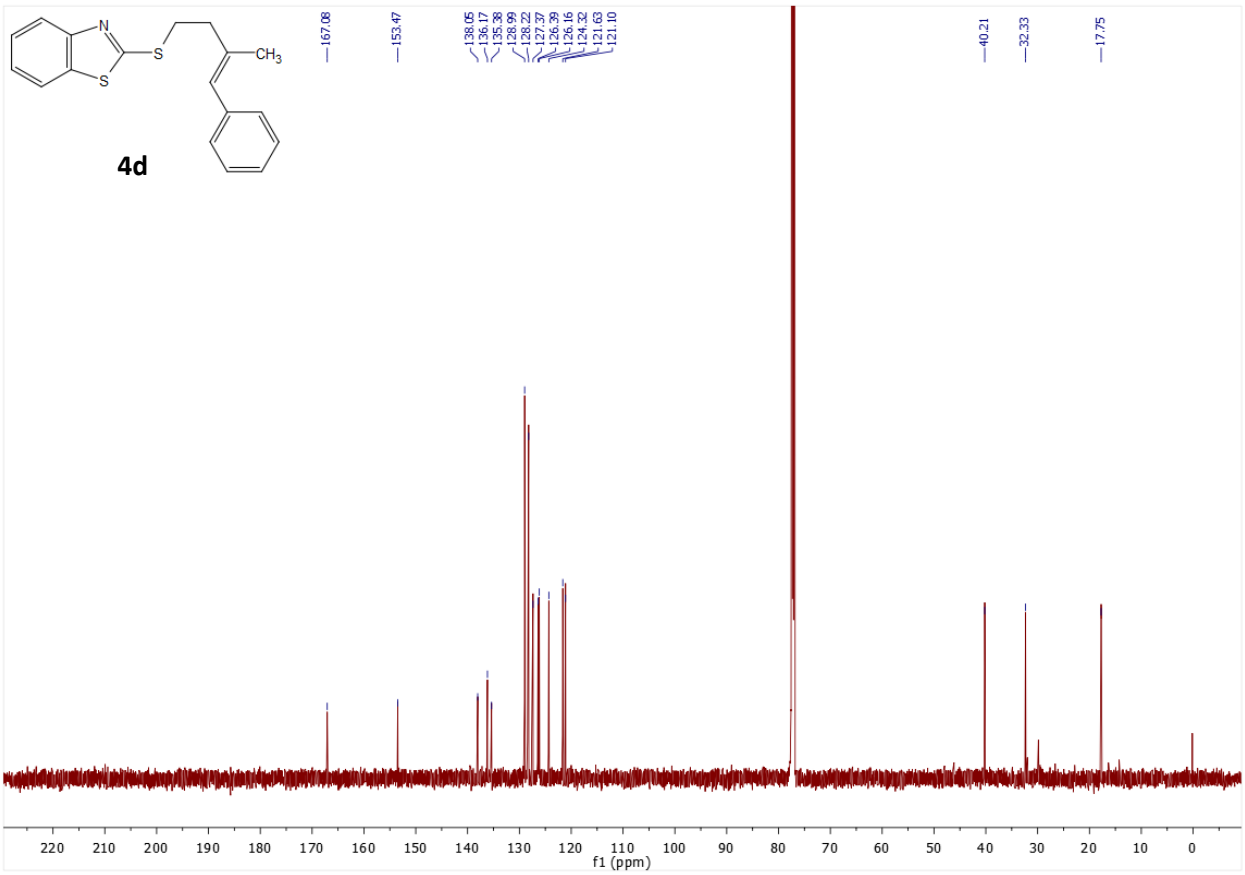

4b
0.96
1.00
1.11
2.06
2.91
1.15
1.00
0.98
2.08
0.99
3.05
f1 (ppm)

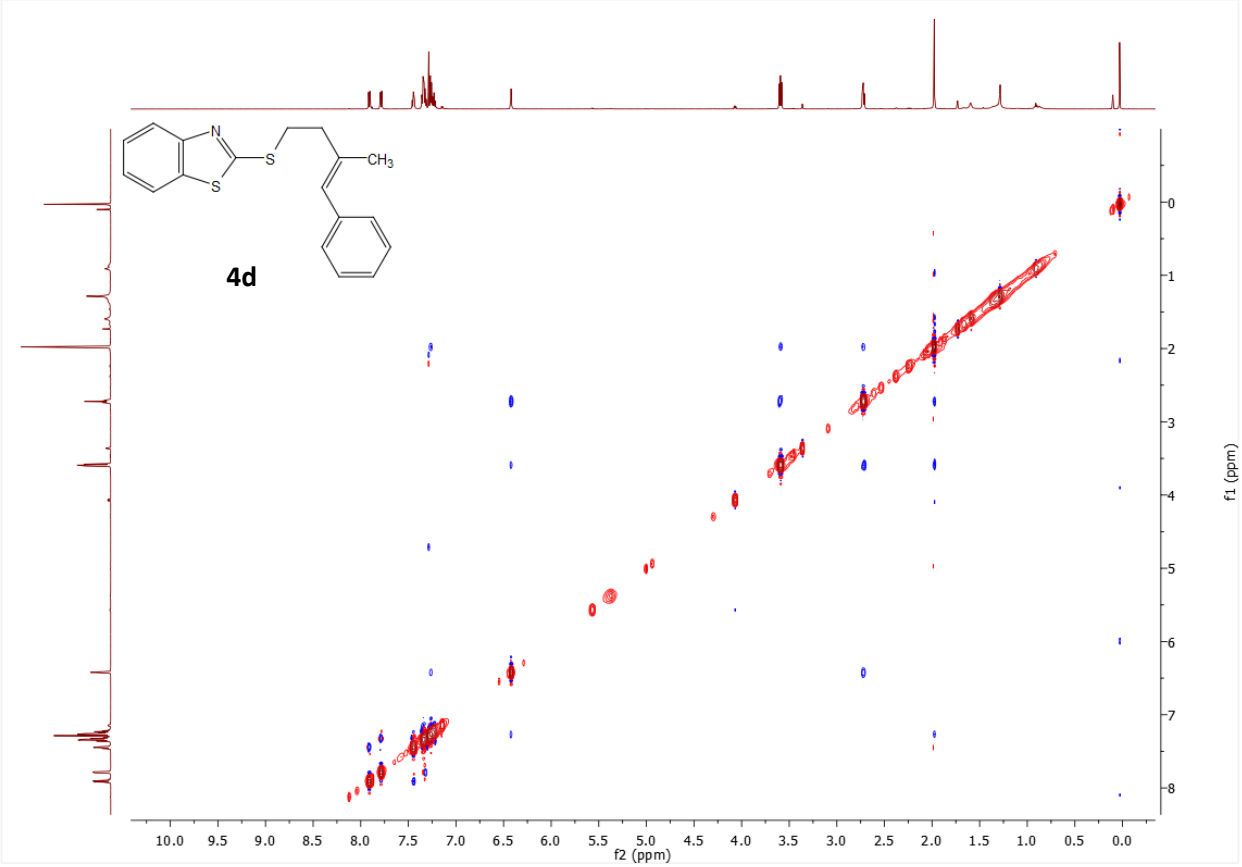

4b
167.33
153.43
137.30
135.37
133.35
130.29
128.75
128.64
127.43
126.34
126.13
124.30
121.59
121.07
40.32
37.39
19.99
f1 (ppm)

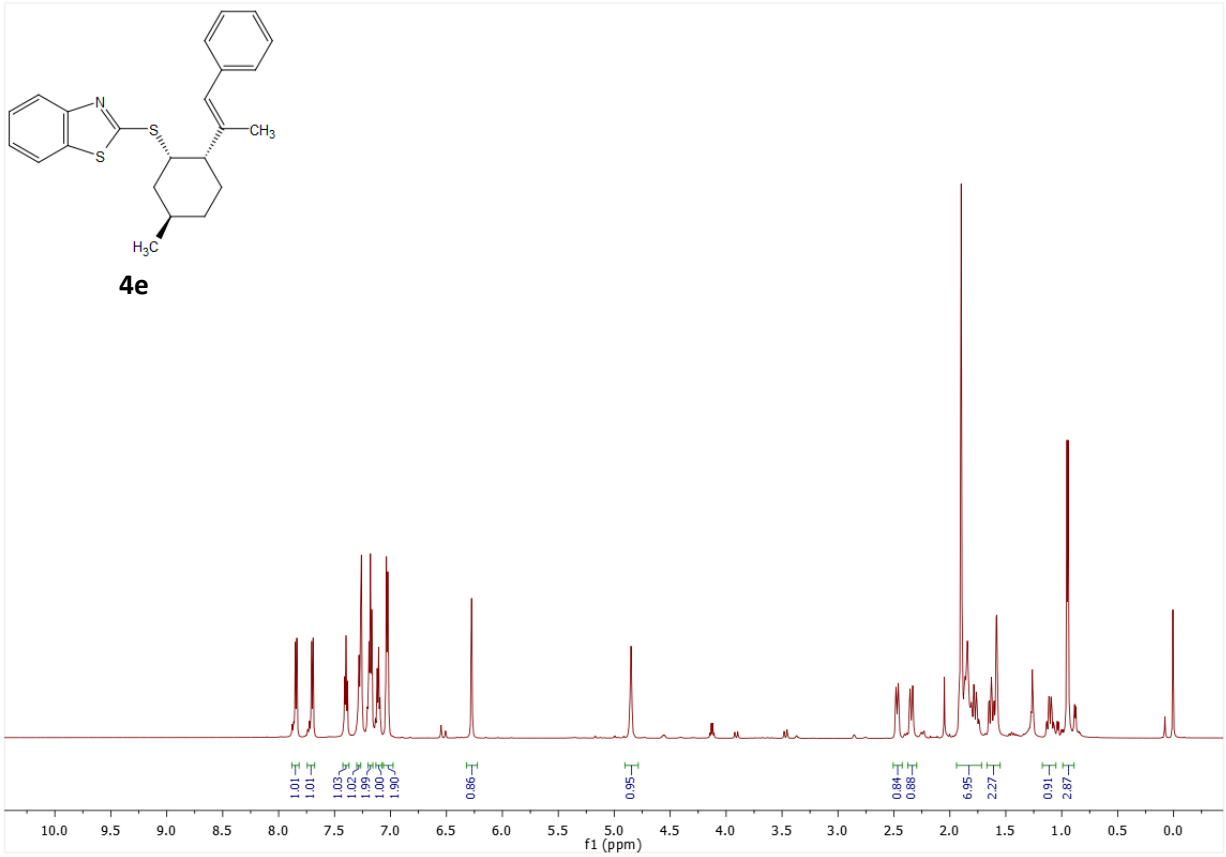

OH
N
S
S
4c
1.00
1.01
1.08
1.90
3.08
0.98
1.00
1.02
2.04
1.05
1.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

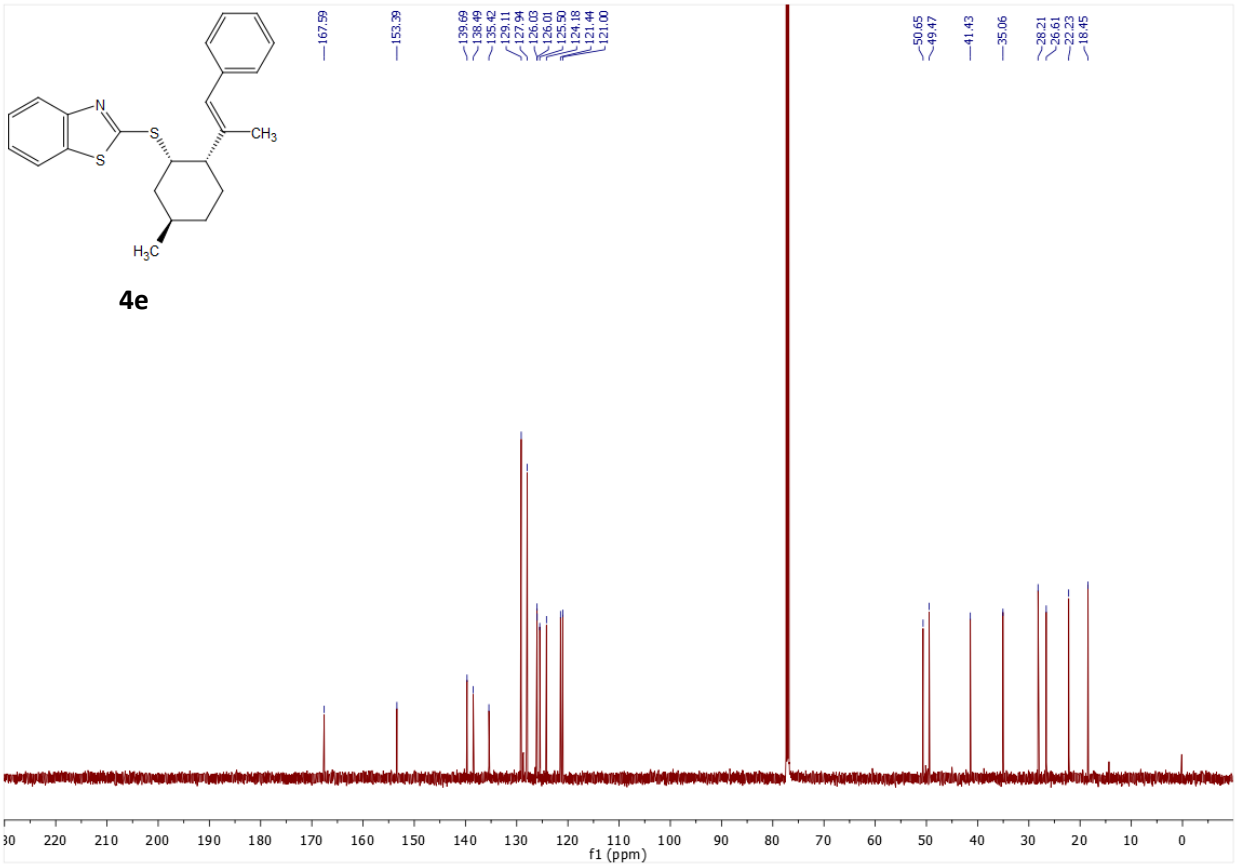

OH
N
S
S
4c
167.88
152.53
136.62
135.64
131.45
130.17
128.71
127.93
126.74
126.43
124.81
121.50
121.23
72.30
41.10
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

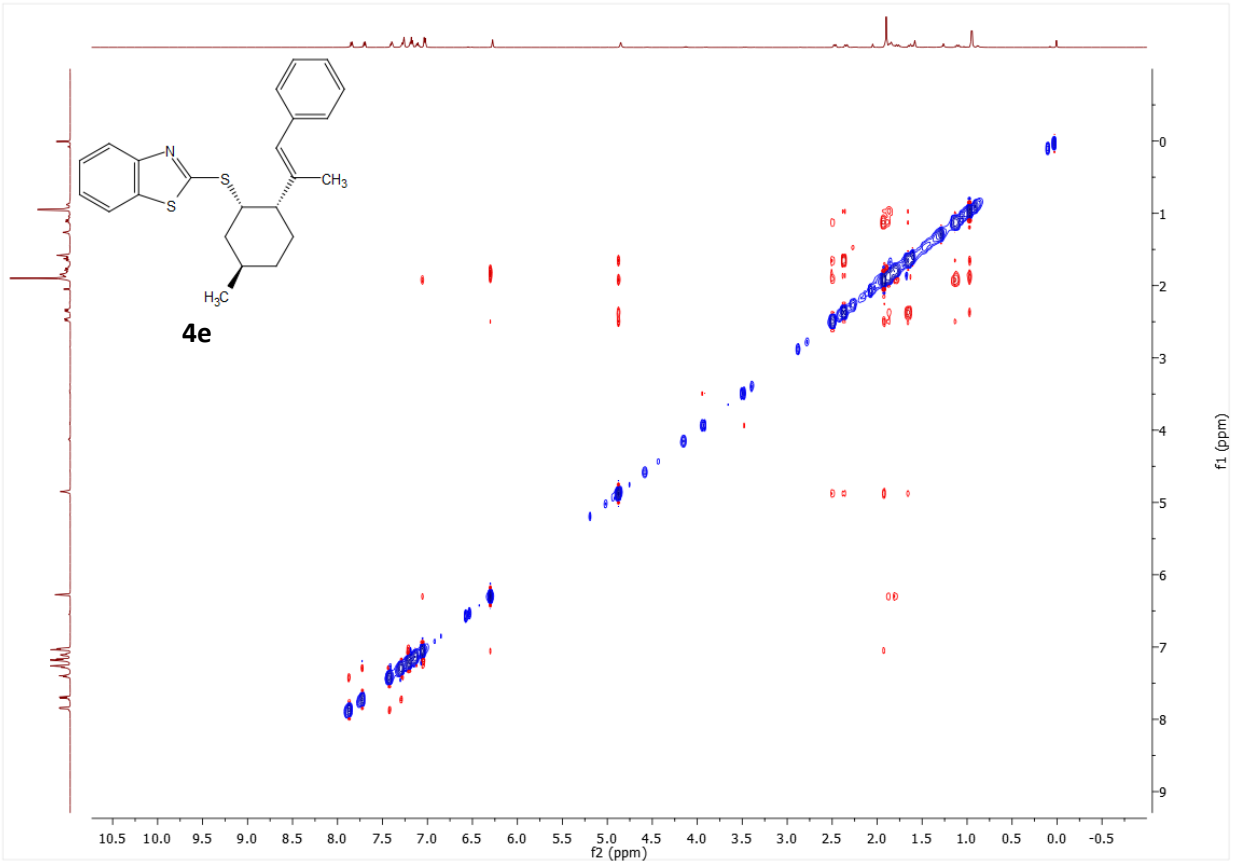

4d
0.96
1.07
1.04
2.96
3.12
0.97
1.95
1.94
2.93
f1 (ppm)

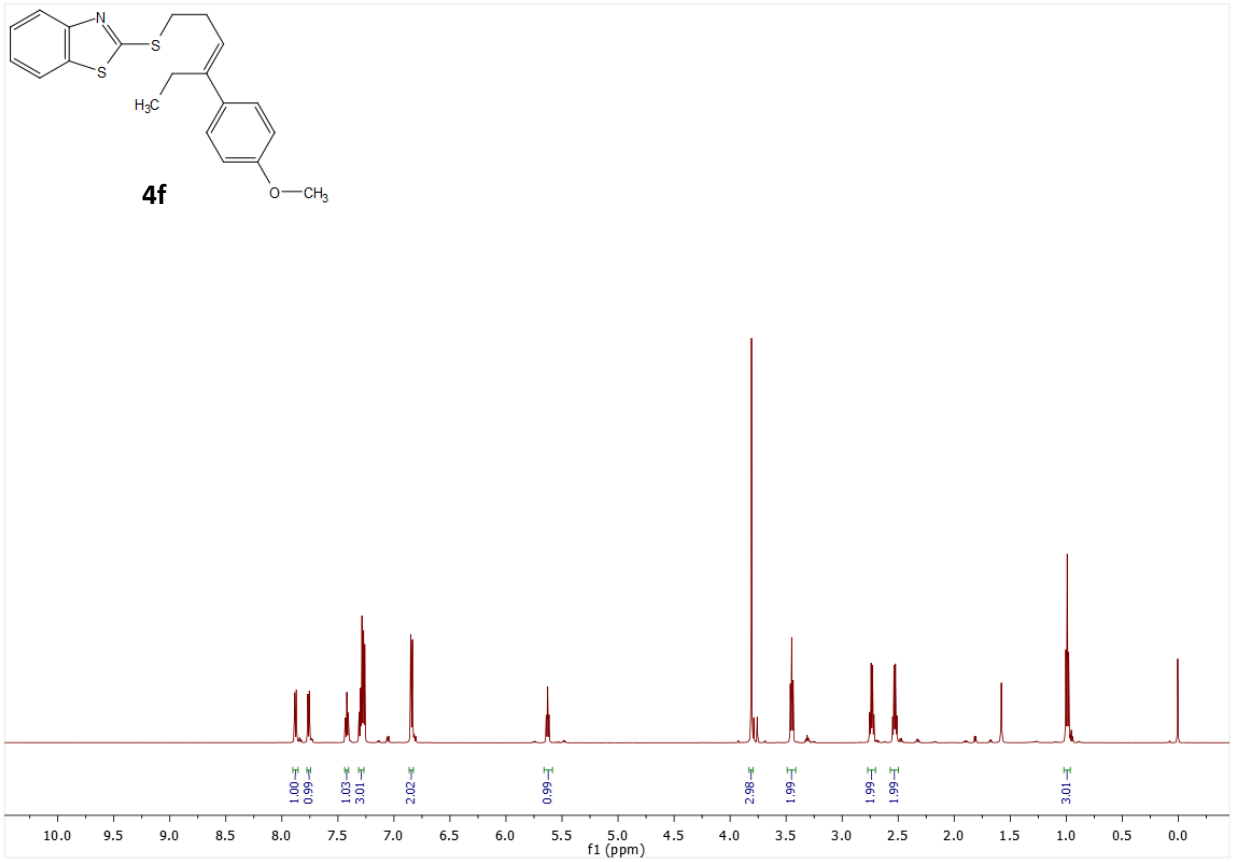

4d
167.08
153.47
138.05
136.17
135.38
128.99
128.22
127.37
126.39
126.16
124.32
121.63
121.10
40.21
32.33
17.75
f1 (ppm)

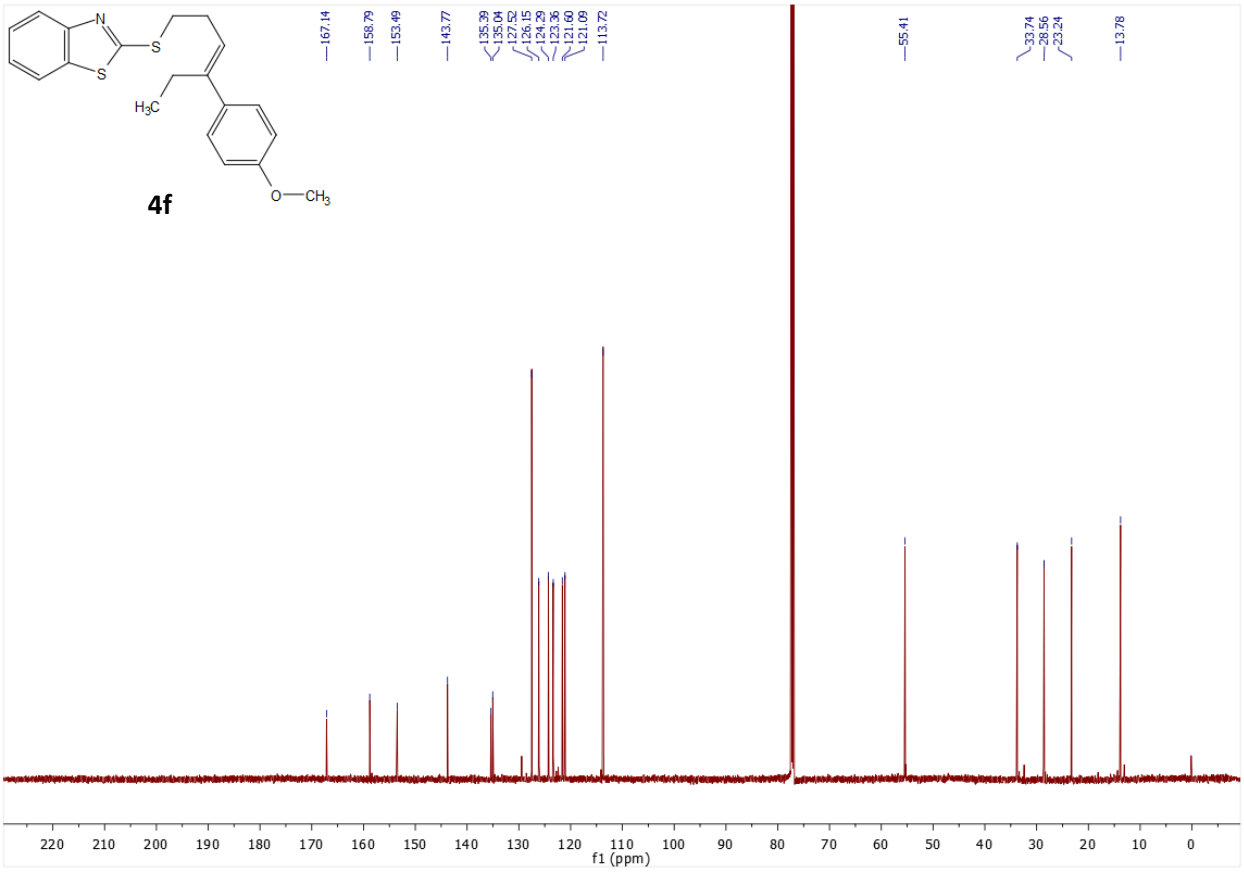

4d
N
S
S
CH3
f2 (ppm)
f1 (ppm)

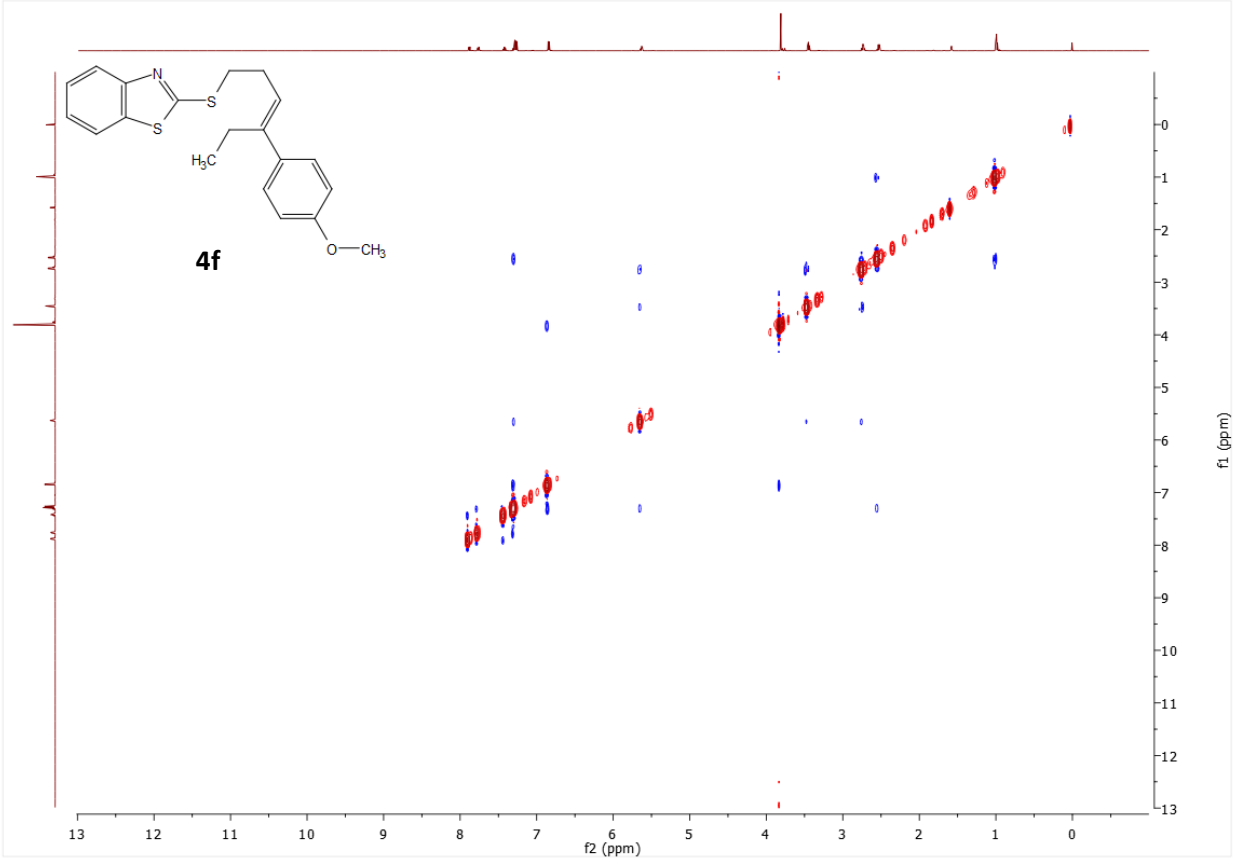

N
S
S
CH3
H3C
4e
1.01
1.01
1.03
1.02
1.99
1.00
1.90
0.86
0.95
0.84
0.88
6.95
2.27
0.91
2.87
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

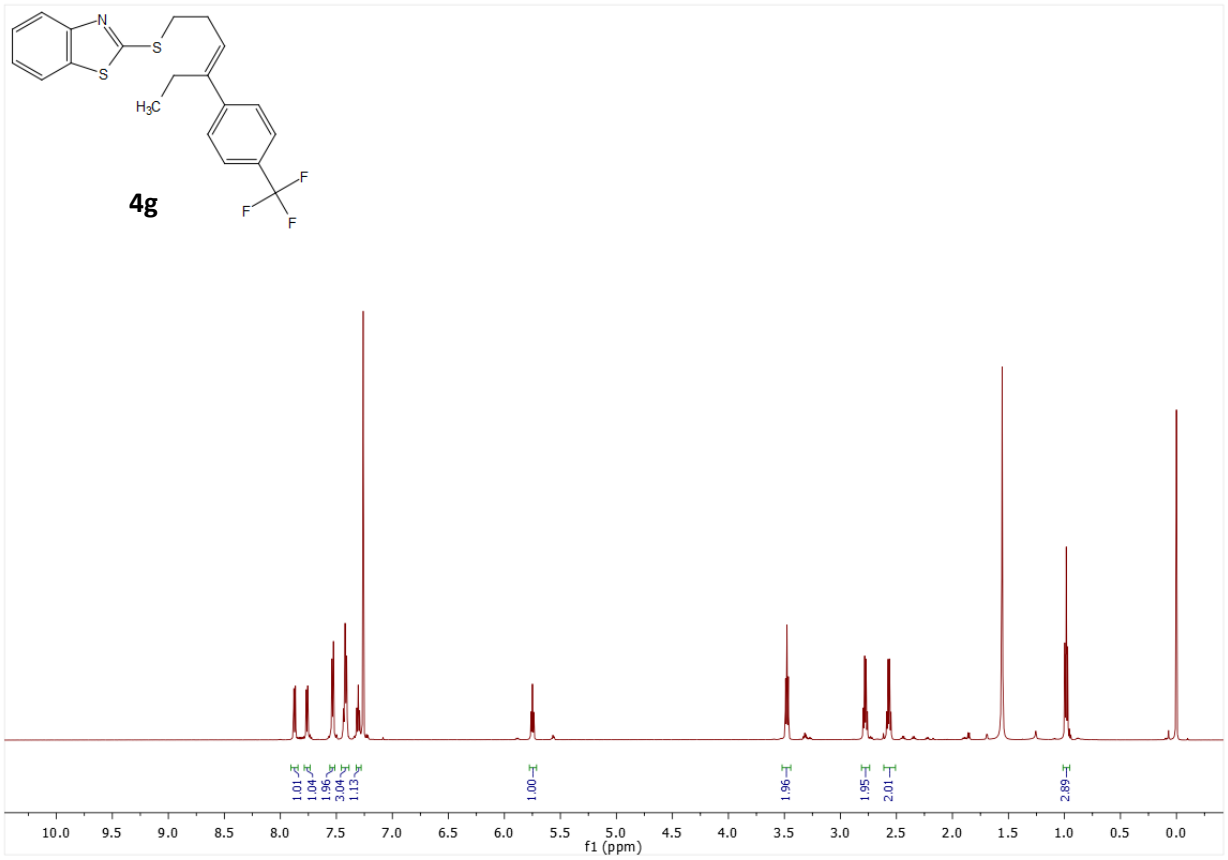

N
S
S
CH3
H3C
4e
167.59
153.39
139.69
138.49
135.42
129.11
127.94
126.03
126.01
125.50
124.18
121.44
121.00
50.65
49.47
41.43
35.06
28.21
26.61
22.23
18.45
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

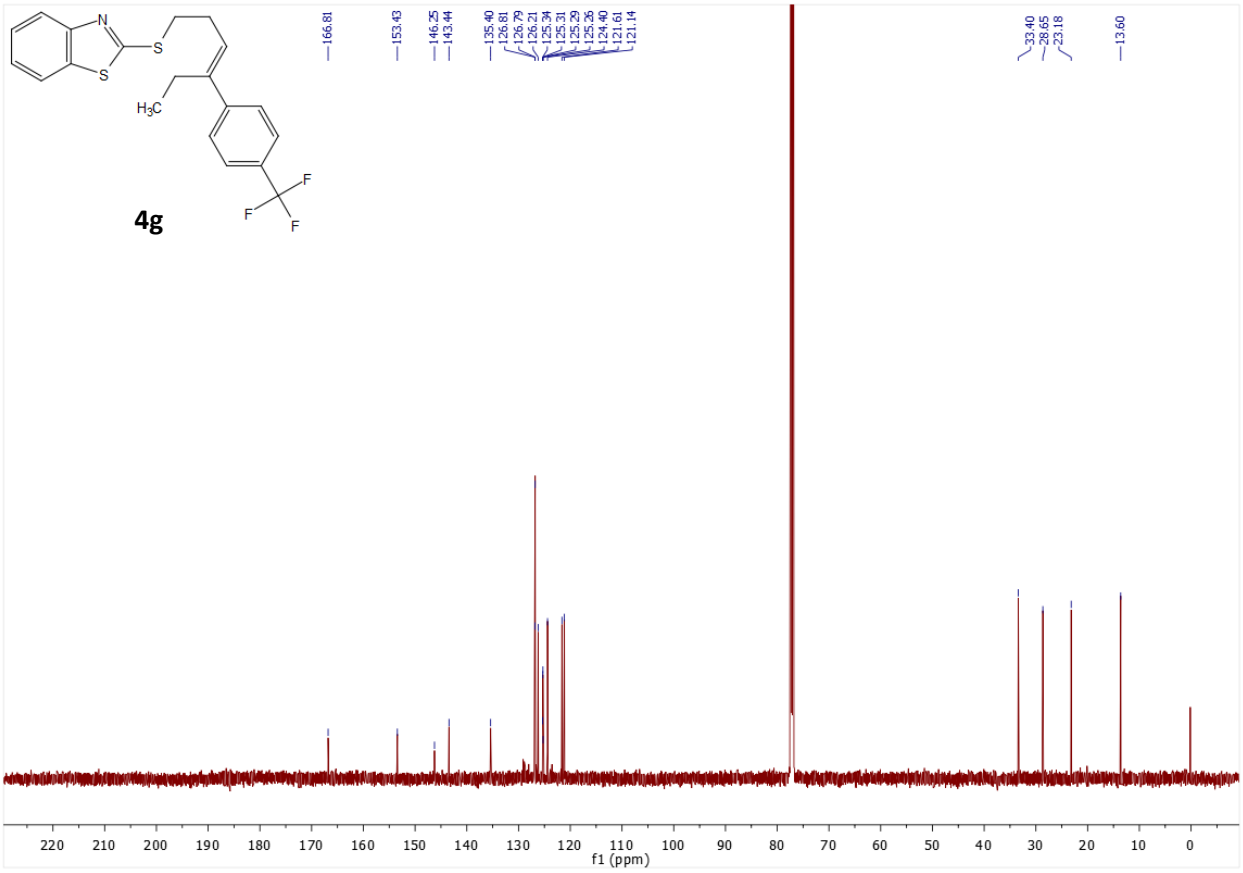

N
S
S
CH3
H3C
4e
f2 (ppm)
f1 (ppm)

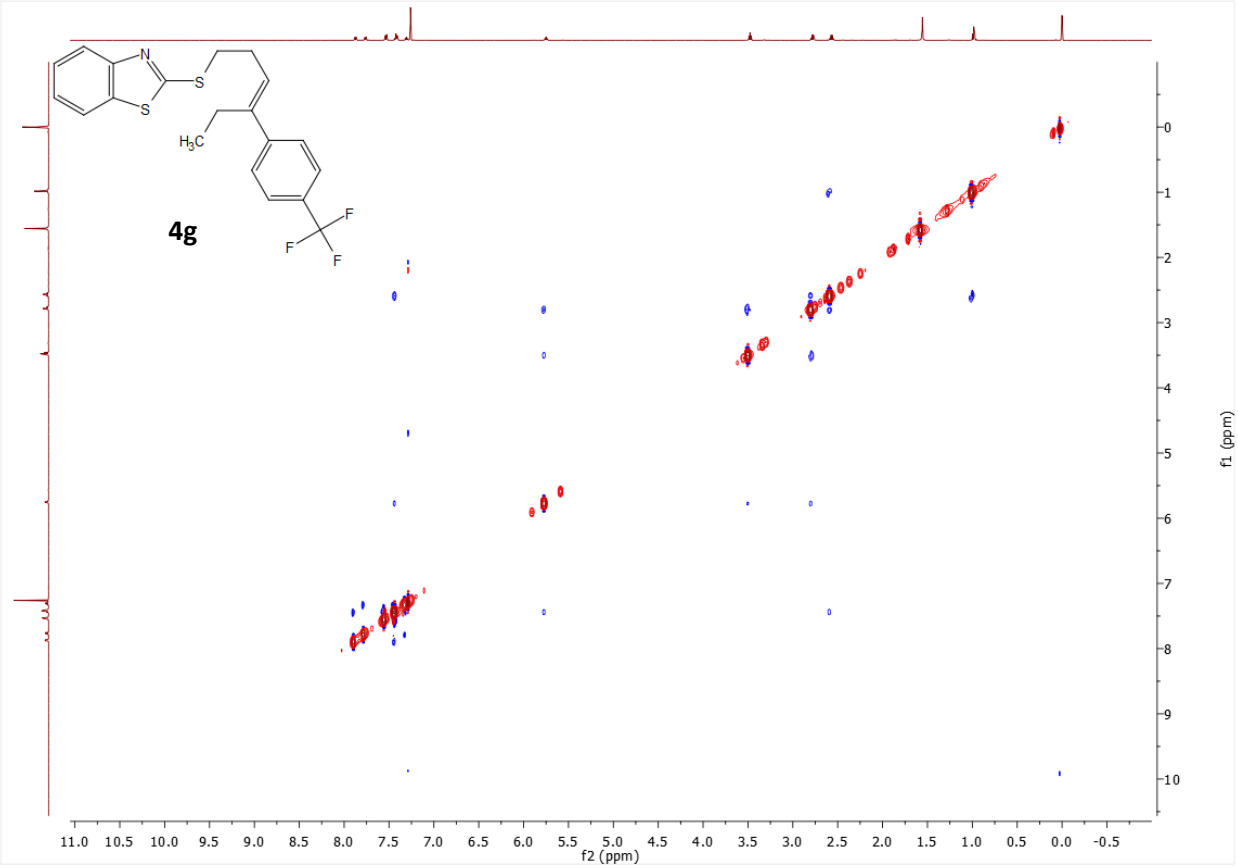

4f
1.00
0.99
1.03
3.01
2.02
0.99
2.98
1.99
1.99
1.99
3.01
f1 (ppm)

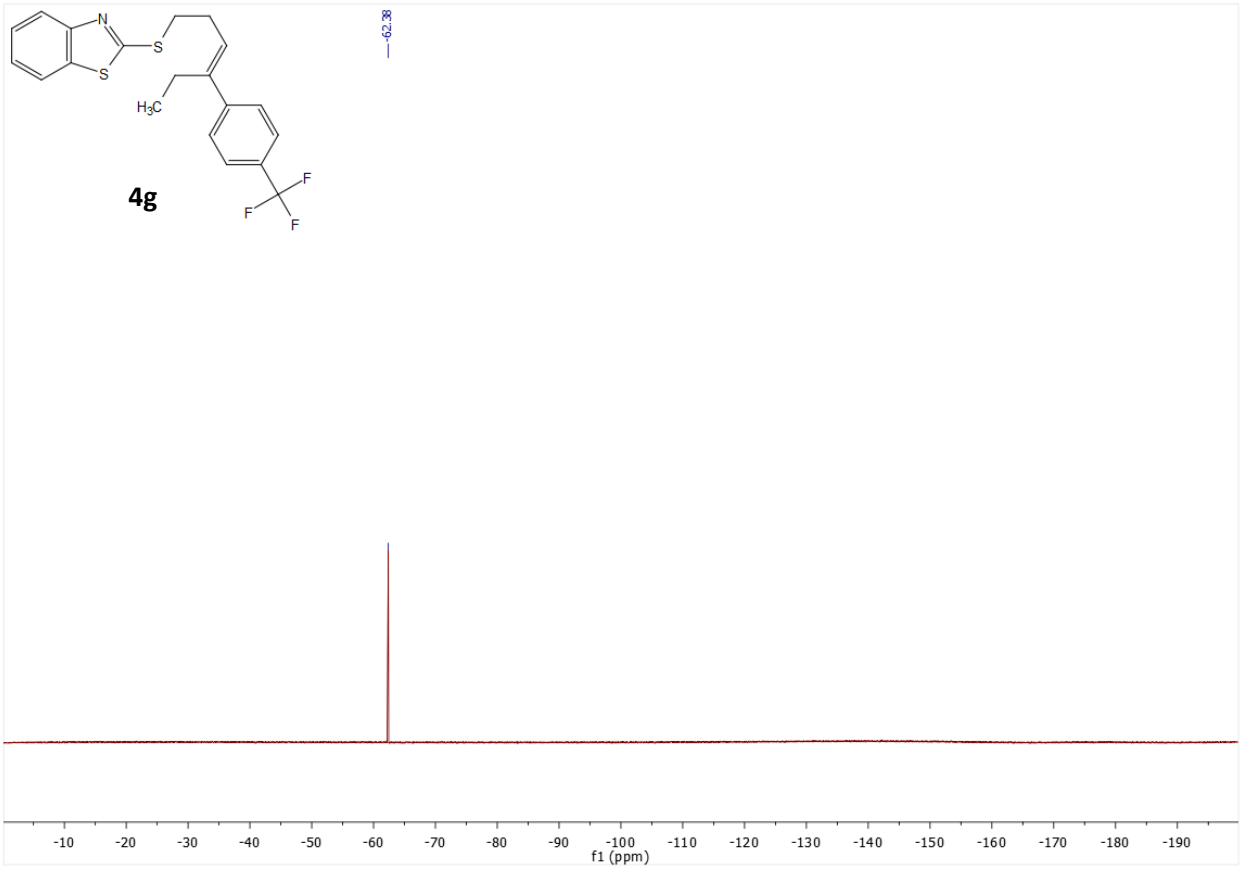

4f
167.14
158.79
153.49
143.77
135.39
135.04
127.52
126.15
124.29
123.36
121.60
121.09
113.72
55.41
33.74
28.56
23.24
13.78
f1 (ppm)

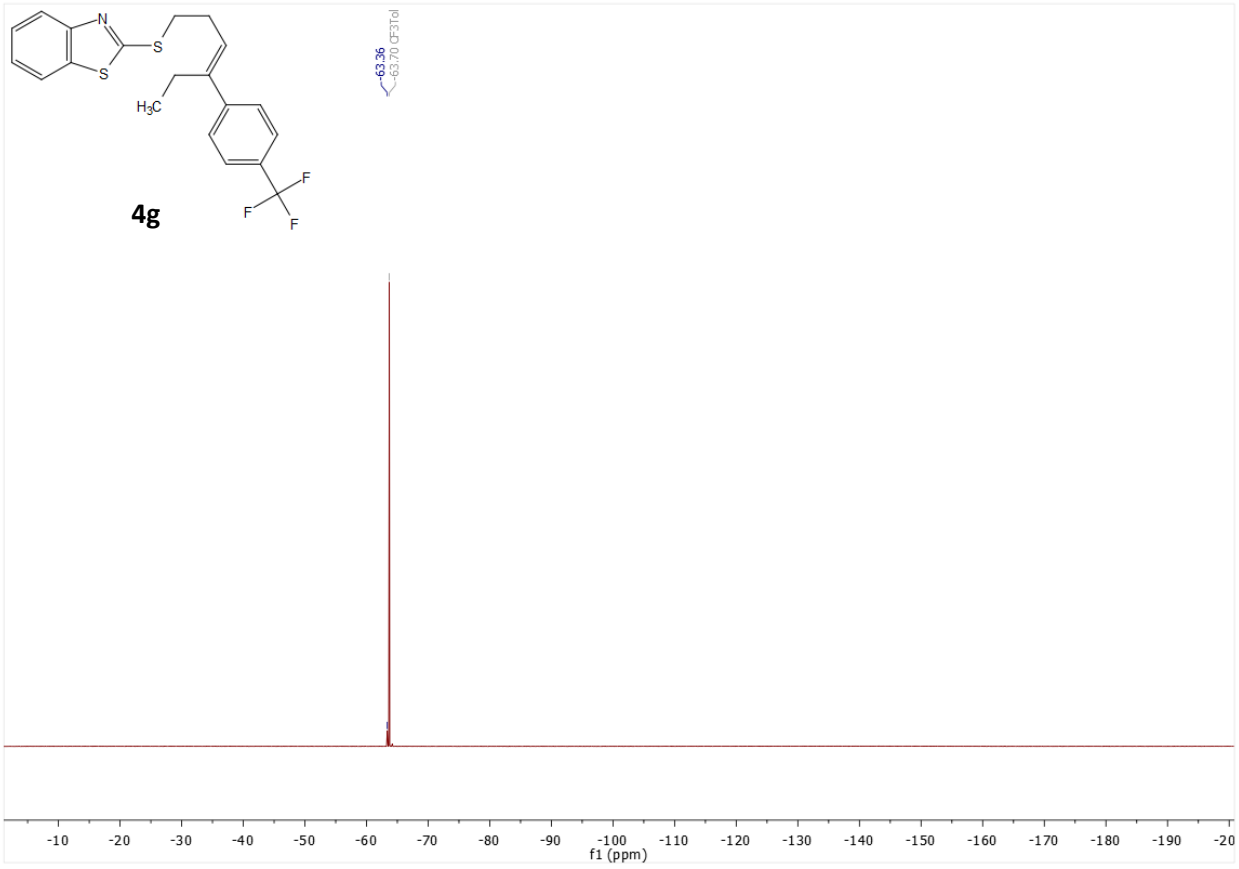

N
S
S
H3C
O—CH3
4f
f2 (ppm)
f1 (ppm)

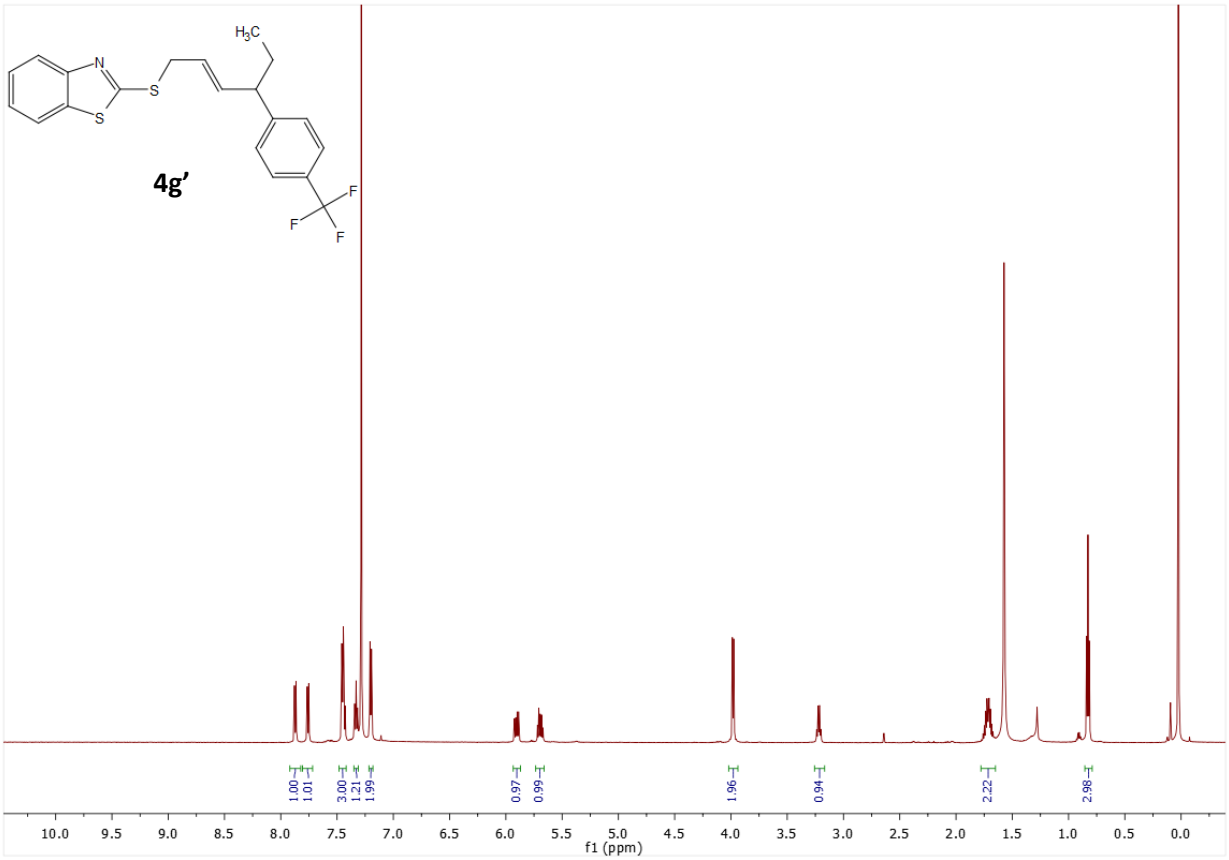

4g
1.01
1.04
1.96
3.04
1.13
1.00
1.96
1.95
2.01
2.89
f1 (ppm)

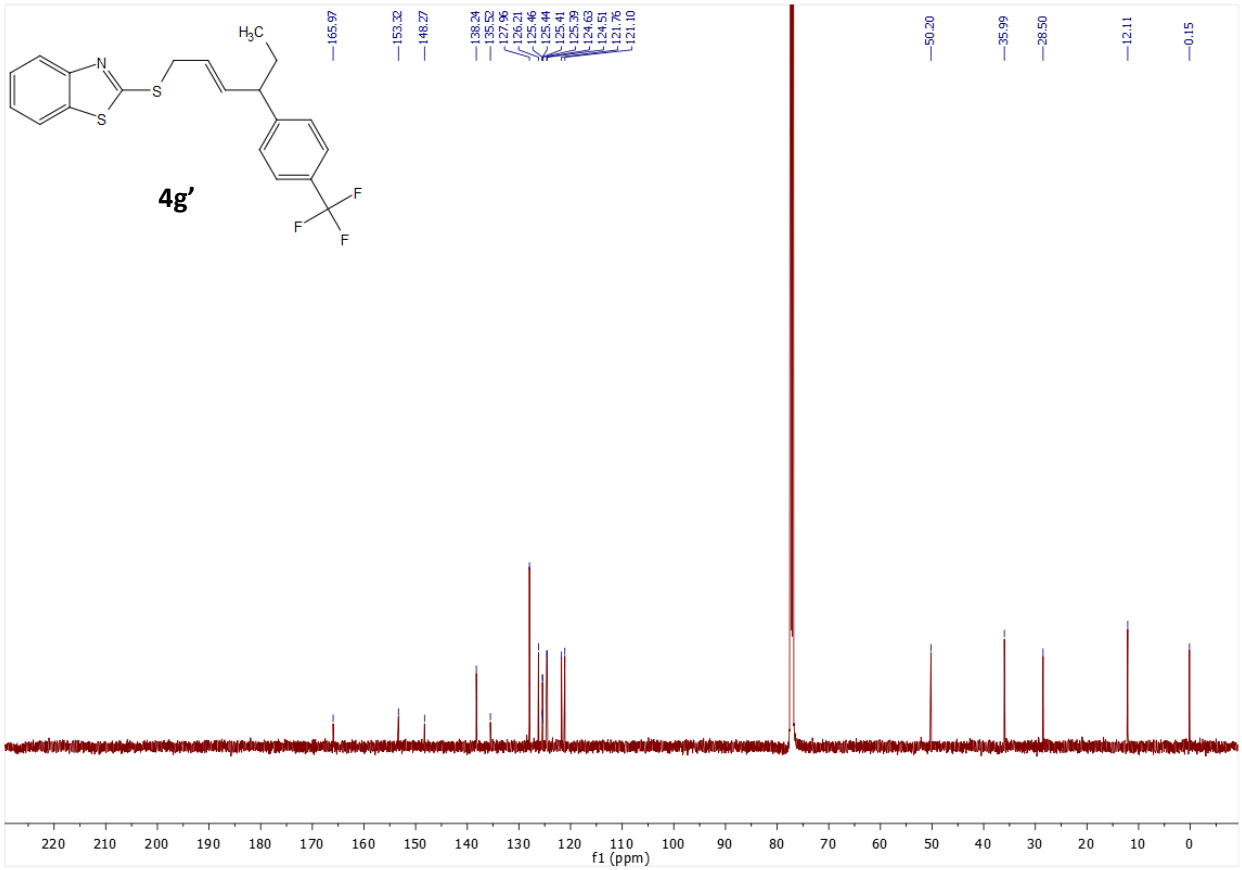

4g
166.81
153.43
146.25
143.44
135.40
126.81
126.79
126.21
125.34
125.31
125.29
125.26
124.40
121.61
121.14
33.40
28.65
23.18
13.60
f1 (ppm)

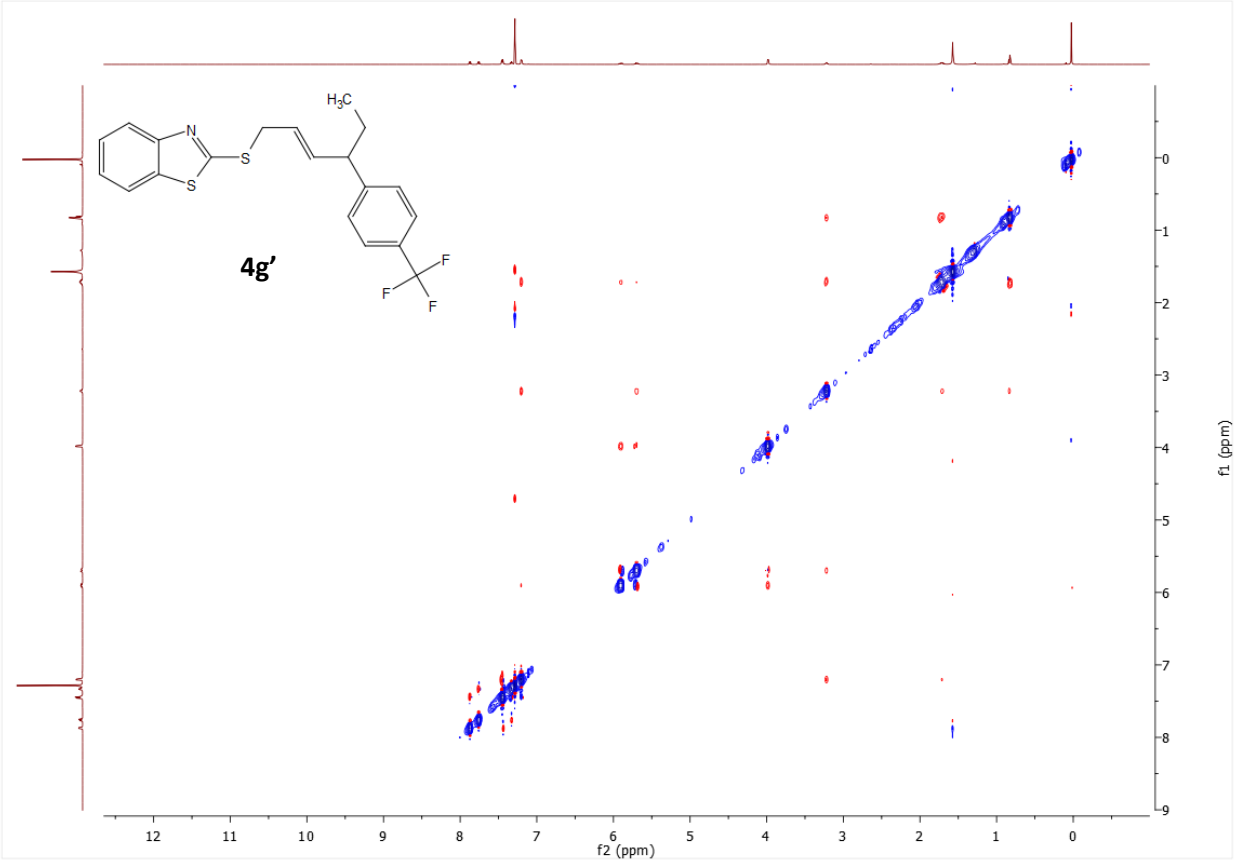

4g
N
S
S
H3C
F
F
F
f2 (ppm)
f1 (ppm)

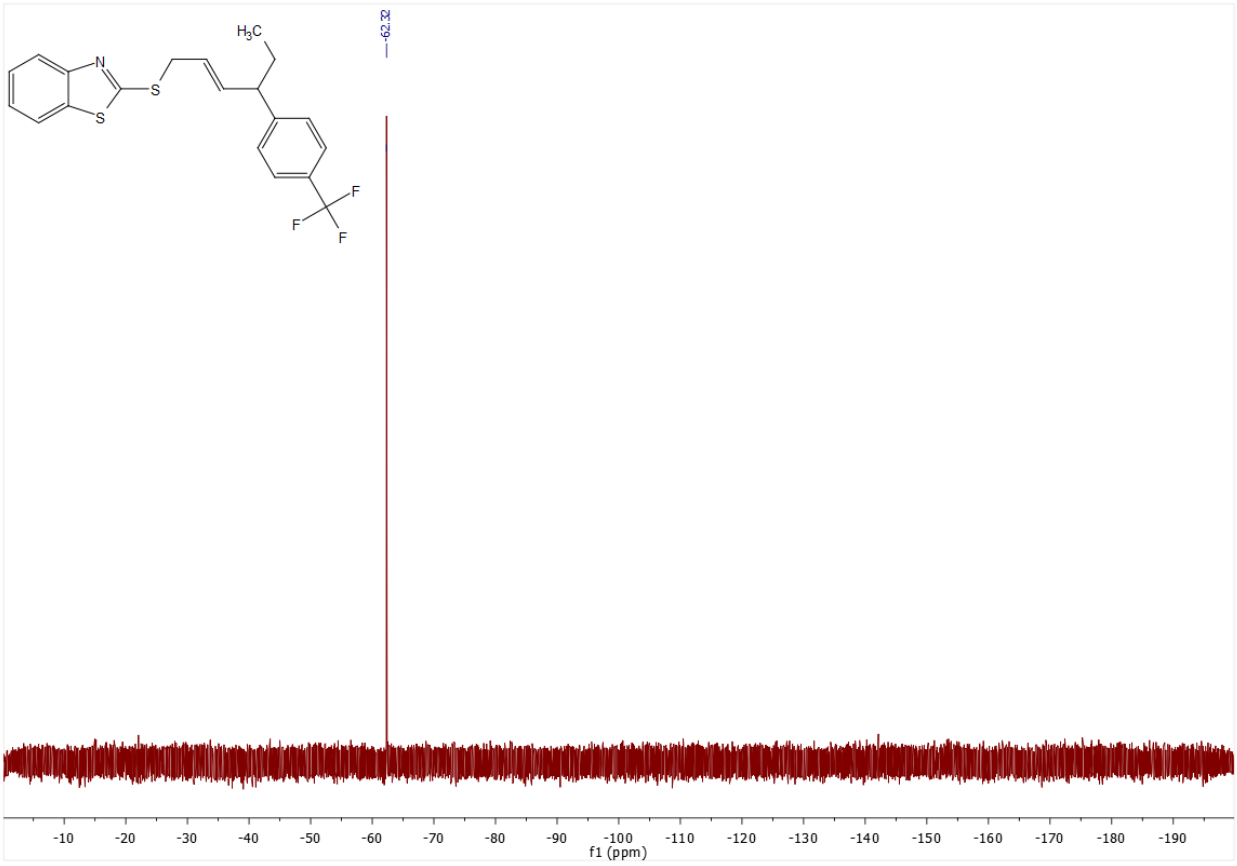

-62.38
4g
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

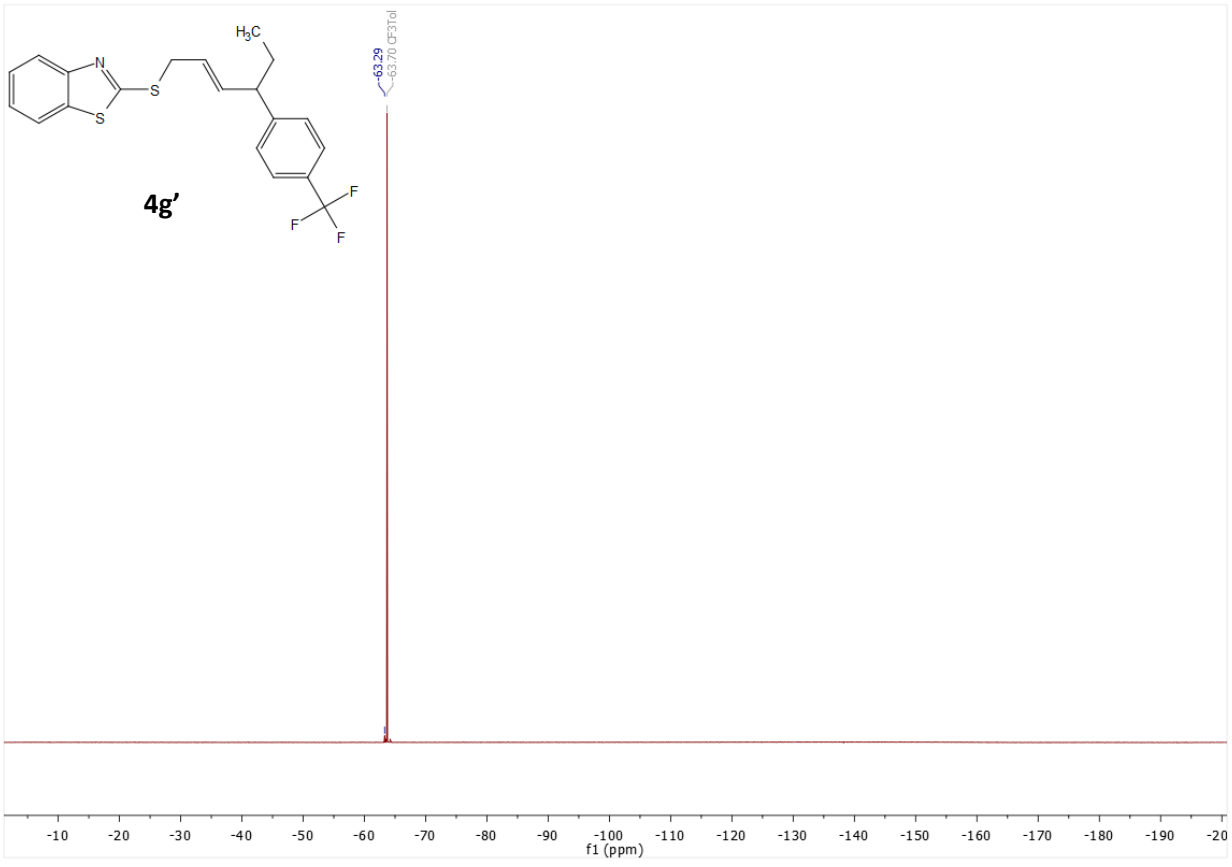

-63.36
-63.70 CF3Tol
4g
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)

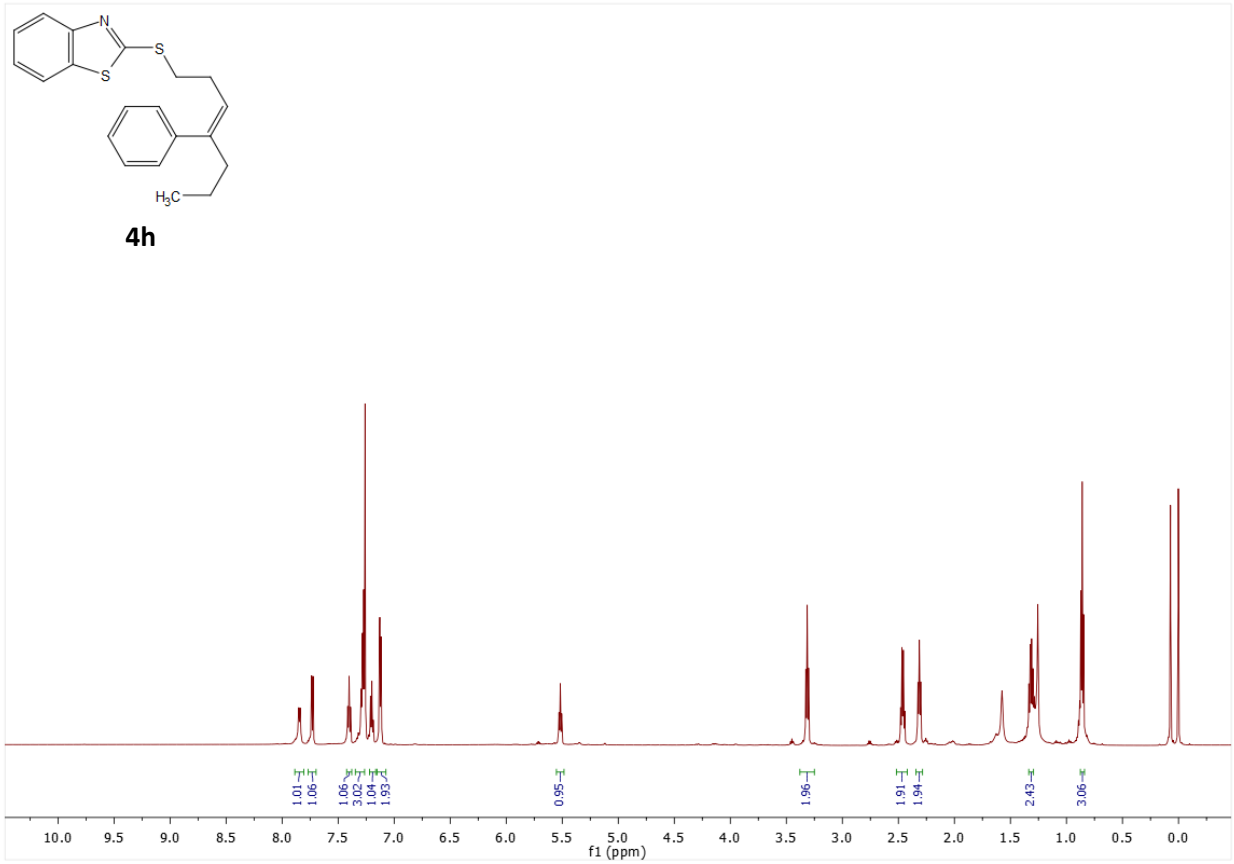

4g'
1.00
1.01
3.00
1.21
1.99
0.97
0.99
1.96
0.94
2.22
2.98
f1 (ppm)

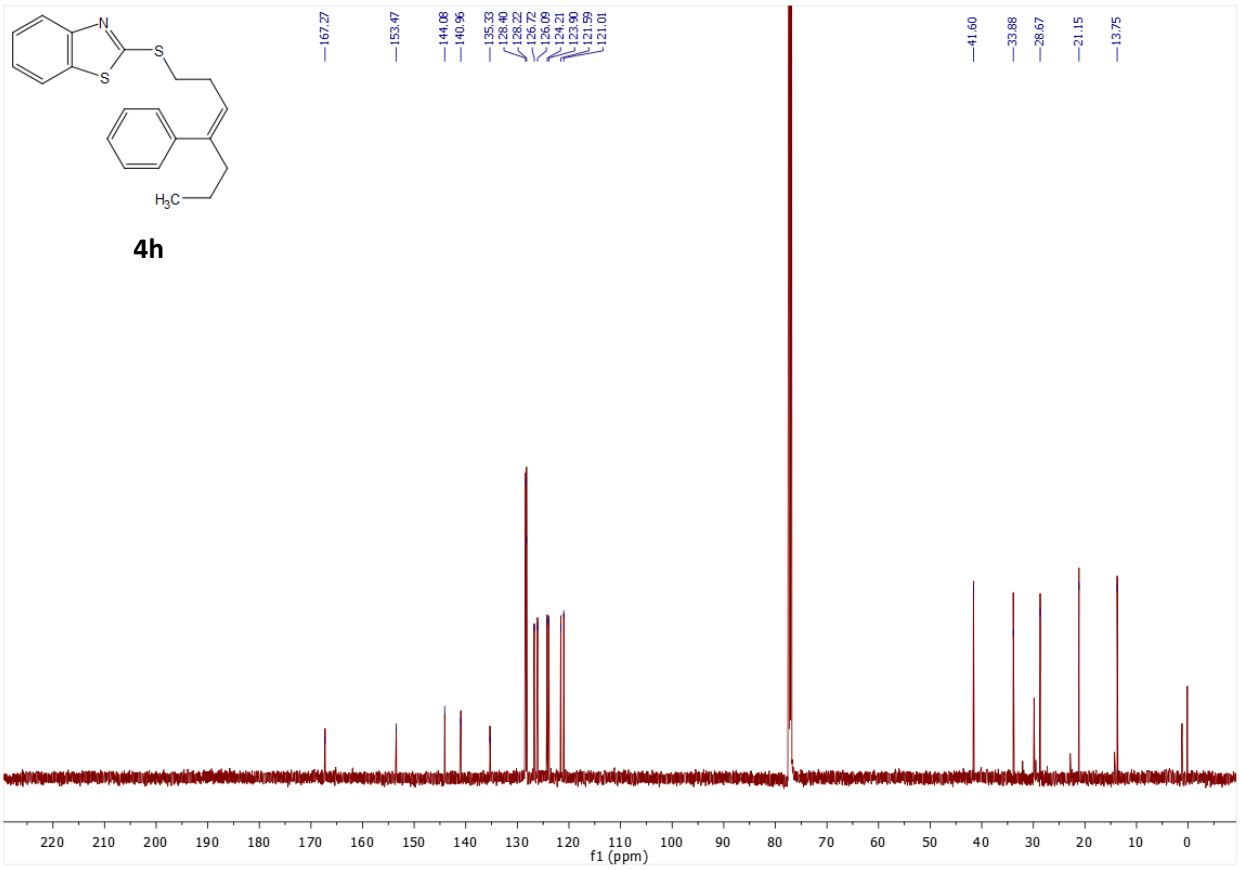

4g'
165.97
153.32
148.27
138.24
135.52
127.96
126.21
125.46
125.44
125.41
125.39
124.63
124.51
121.76
121.10
50.20
35.99
28.50
12.11
0.15
f1 (ppm)

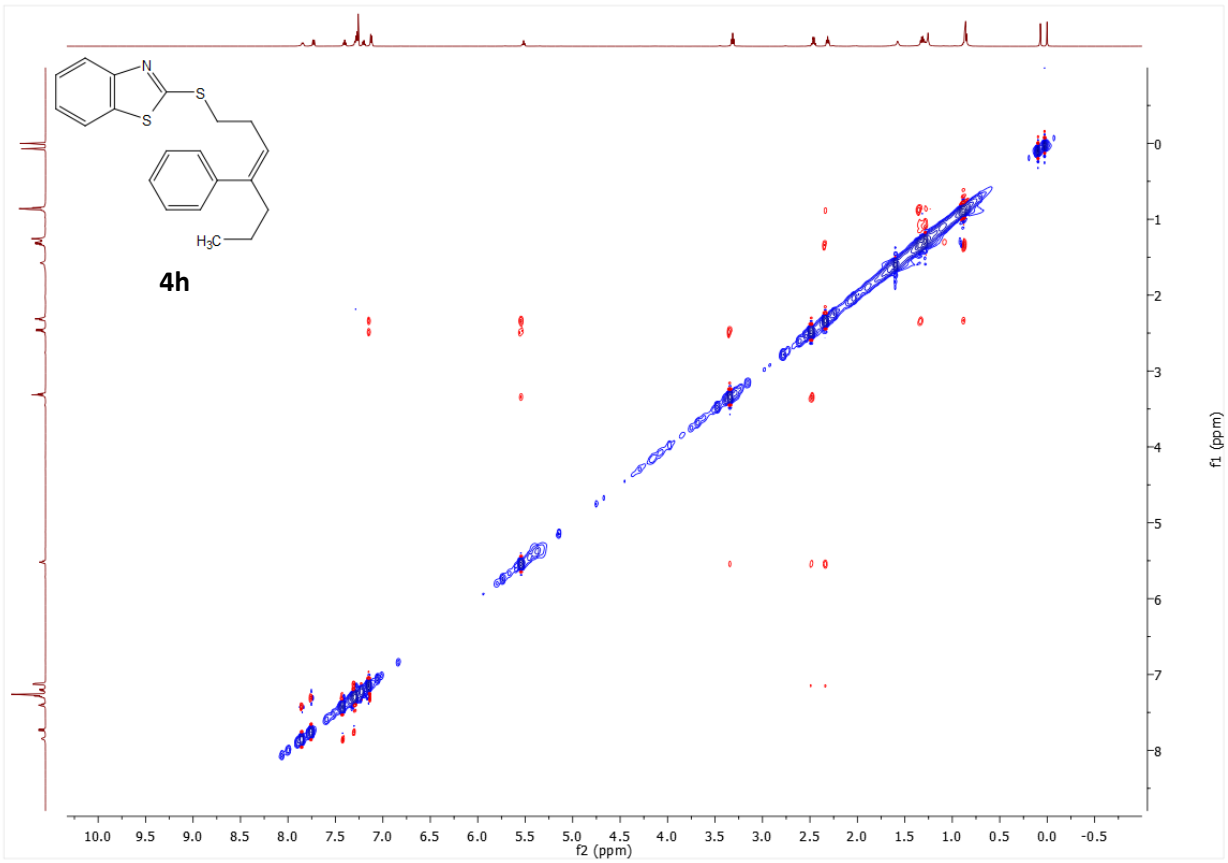

H3C
N
S
S
F
F
F
4g'
f2 (ppm)
f1 (ppm)

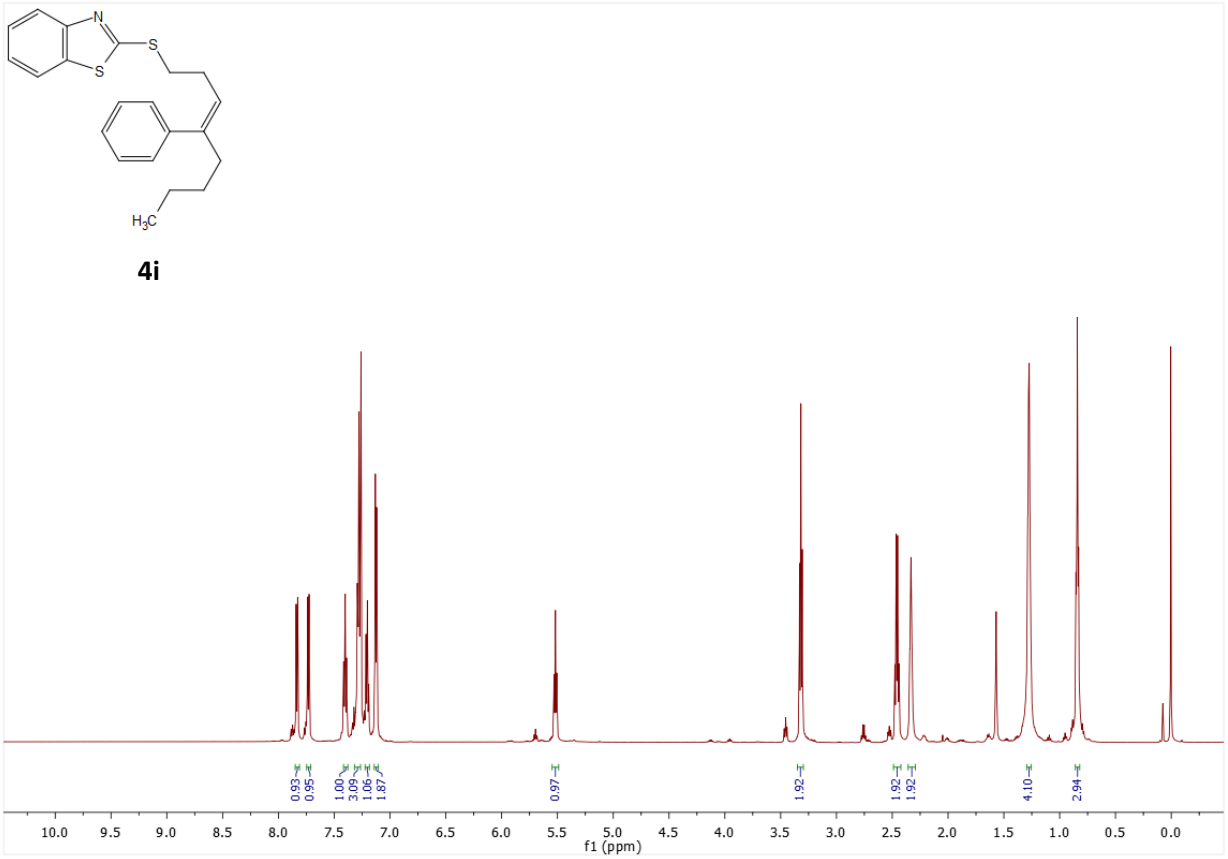

H3C
N
S
S
F
F
F
-62.32
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

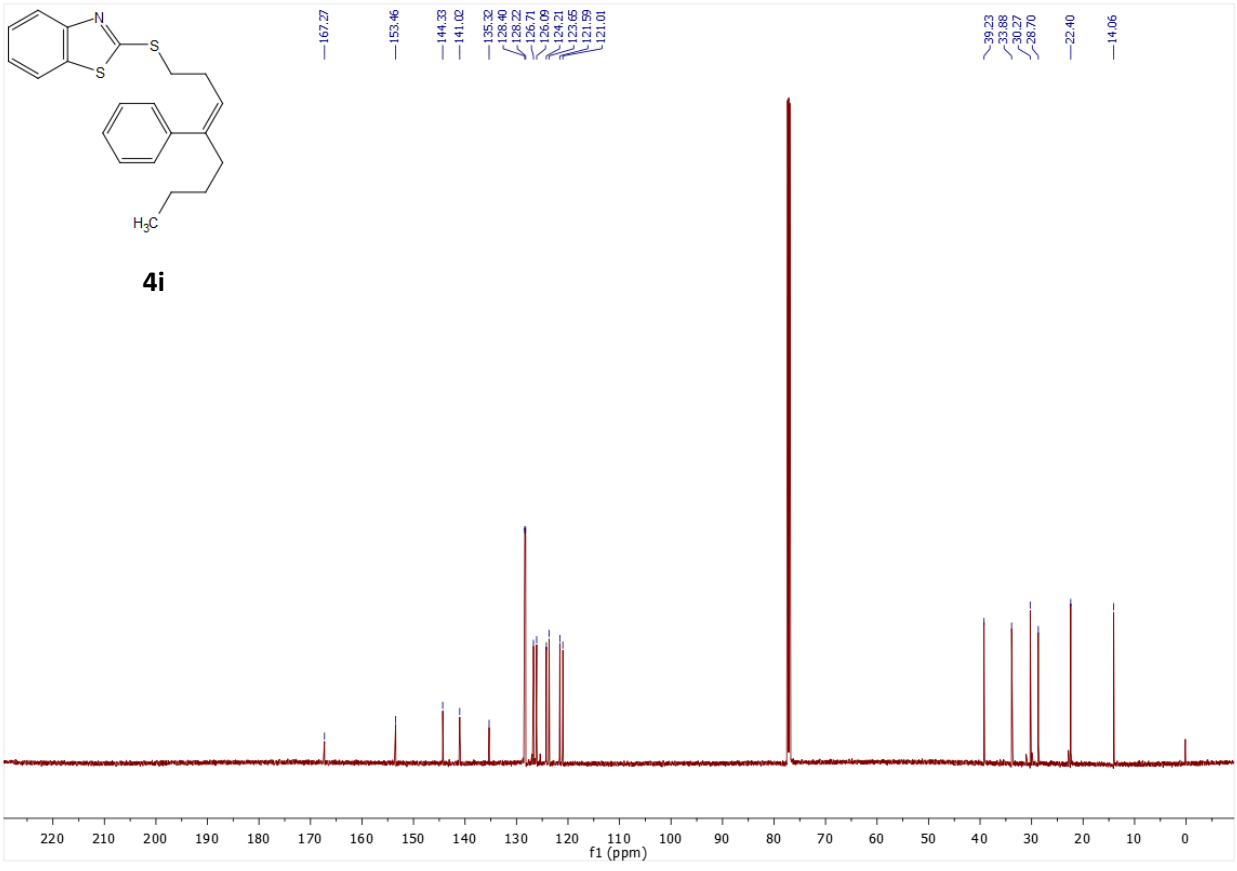

H3C
N
S
S
F
F
F
4g'
-63.29
-63.70 CF3Tol
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)

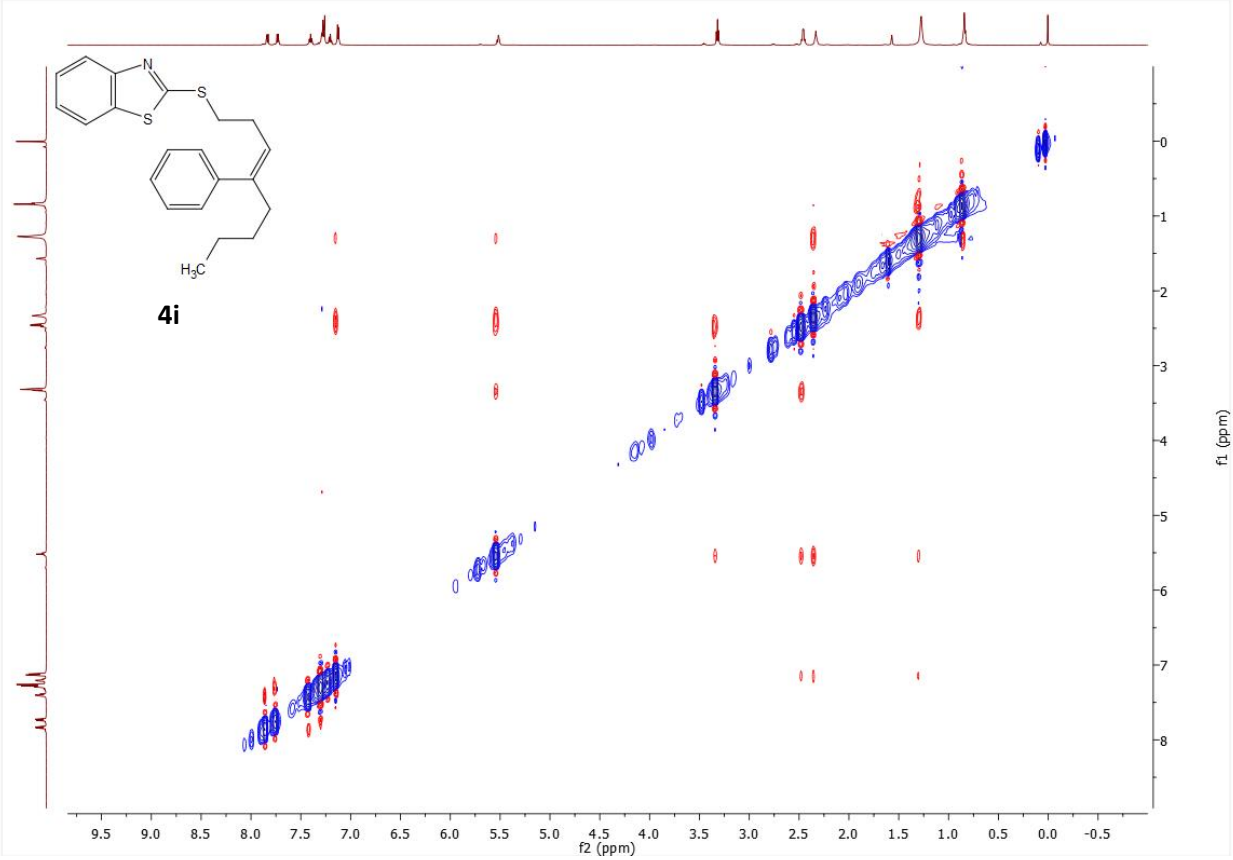

N
S
S
H3C
4h
1.01
1.06
1.06
3.02
1.04
1.93
0.95
1.96
1.91
1.94
2.43
3.06
f1 (ppm)

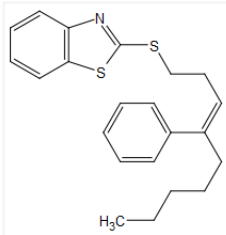

N
S
S
H3C
4h
167.27
153.47
144.08
140.96
135.33
128.40
128.22
126.72
126.09
124.21
123.90
121.59
121.01
41.60
33.88
28.67
21.15
13.75
f1 (ppm)


N
S
S
H3C
4h
f1 (ppm)
f2 (ppm)

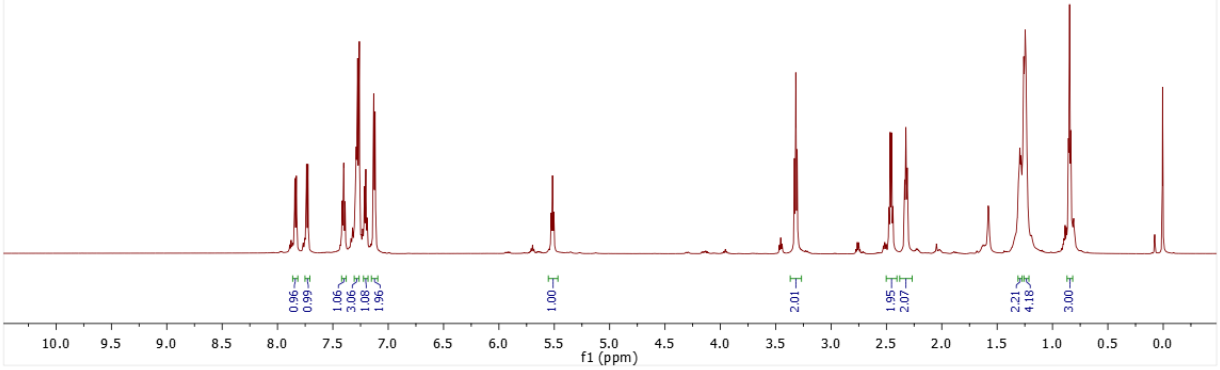

N
S
S
H3C
4i
0.93
0.95
1.00
3.09
1.06
1.87
0.97
1.92
1.92
1.92
4.10
2.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

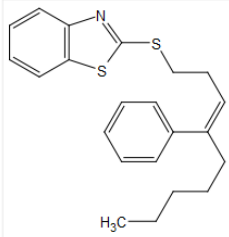

N
S
S
H3C
4i
167.27
153.46
144.33
141.02
135.32
128.40
128.22
126.71
126.09
124.21
123.65
121.59
121.01
39.23
33.88
30.27
28.70
22.40
14.06
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


N
S
S
H3C
4i
f2 (ppm)
f1 (ppm)



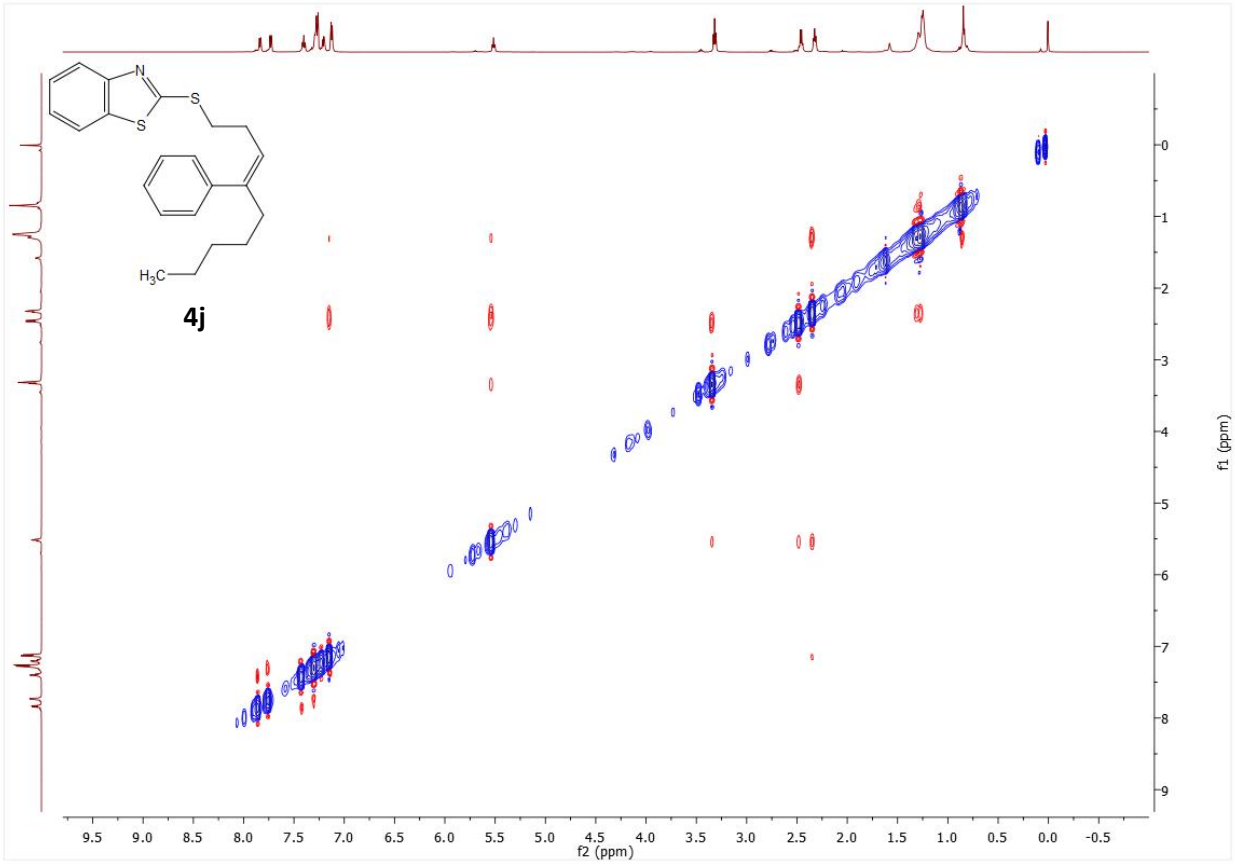
4j

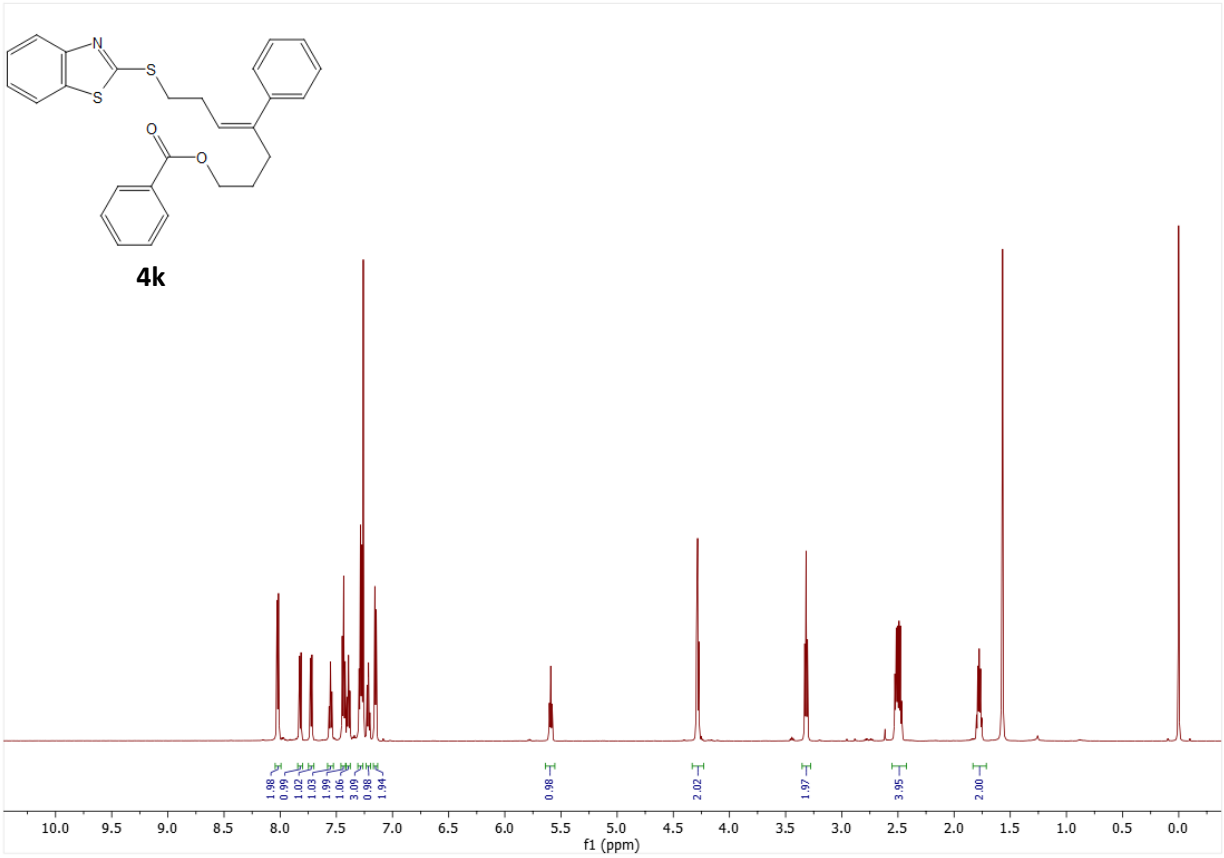

0.96
0.99
1.06
3.06
1.08
1.96
1.00
2.01
1.95
2.07
2.21
4.18
3.00
f1 (ppm)

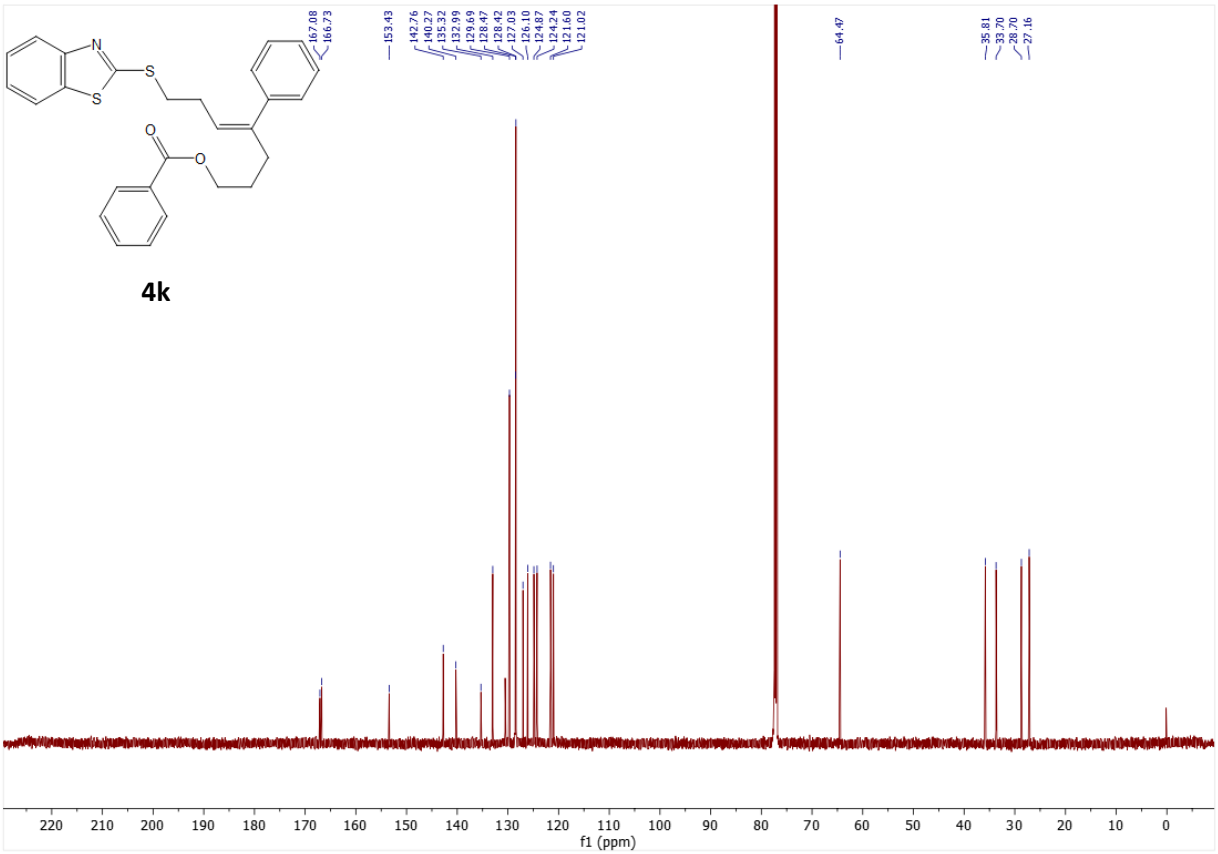


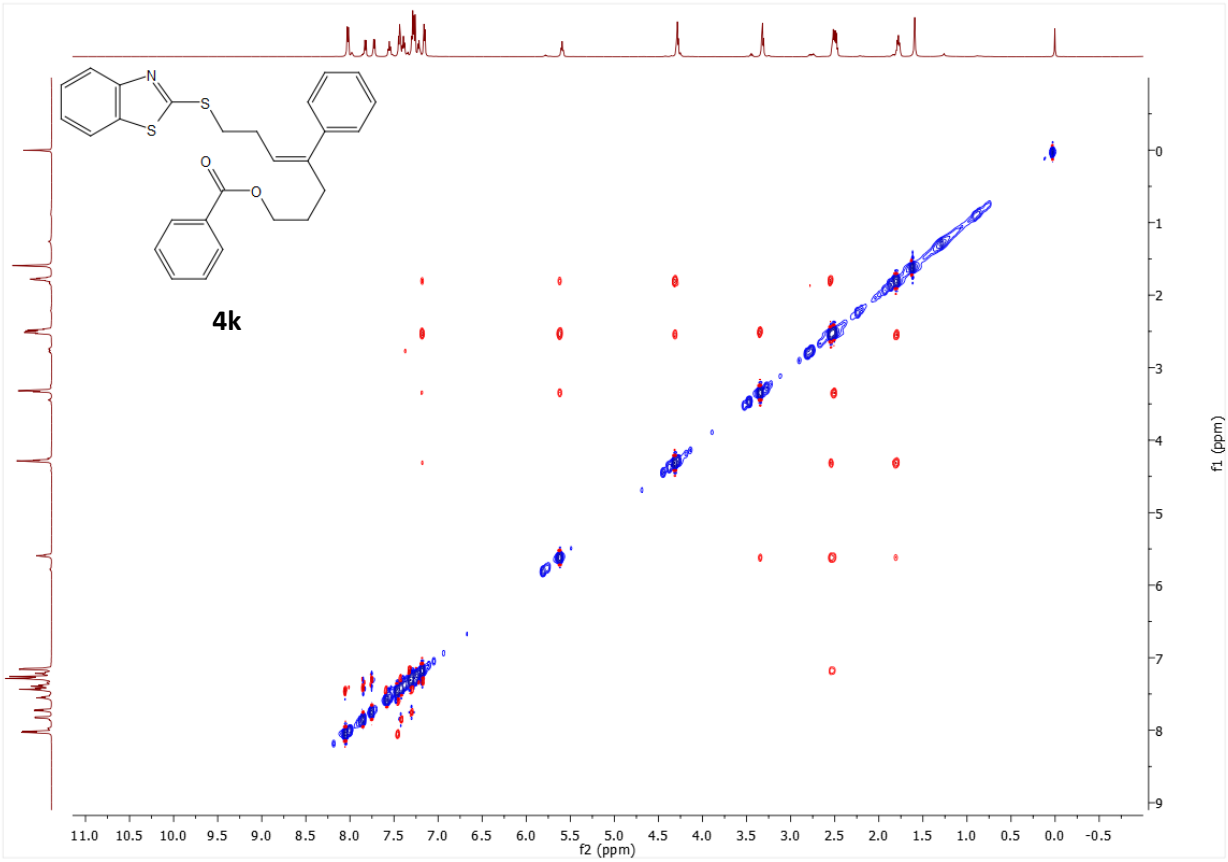
4j

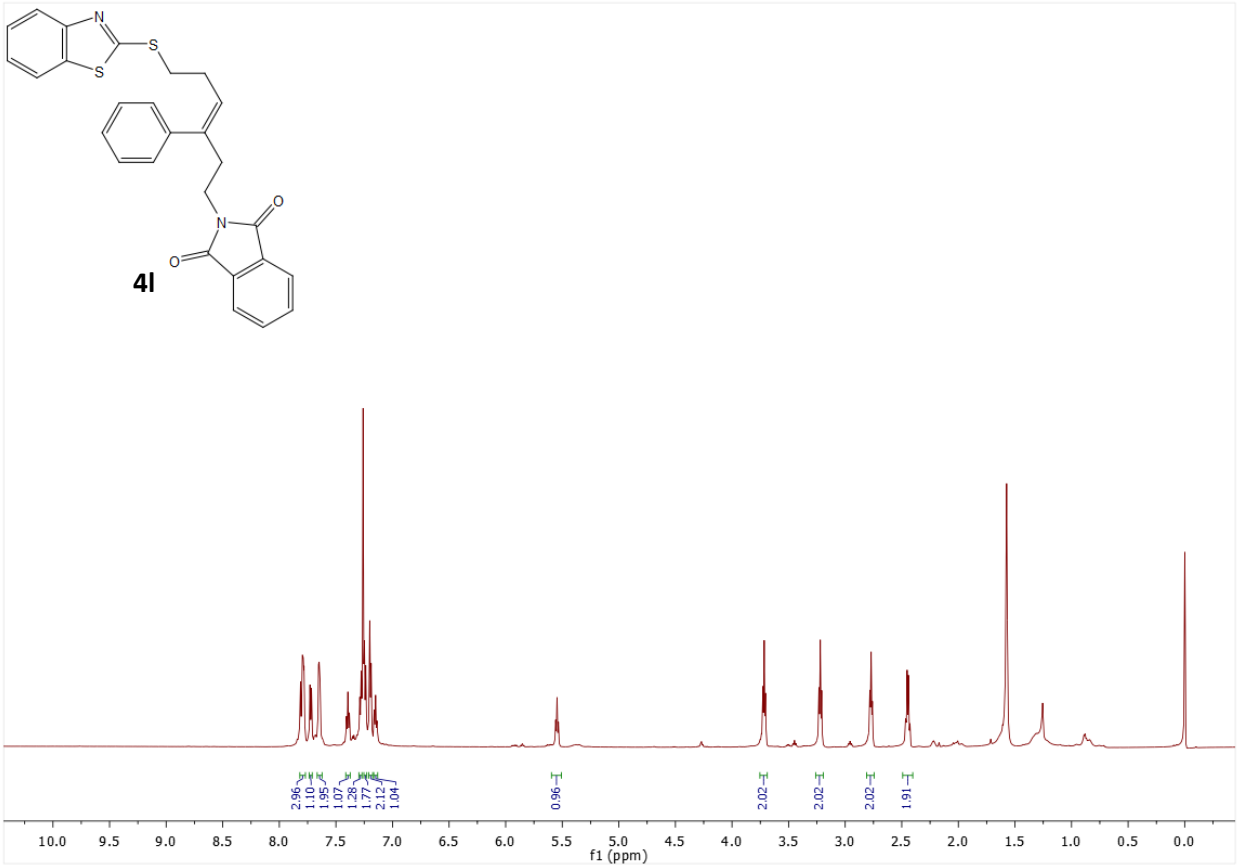
167.29
153.45
144.36
141.02
135.31
128.39
128.21
126.70
126.09
124.21
123.64
121.59
121.00
39.48
33.89
31.53
28.68
27.74
22.61
14.21
f1 (ppm)

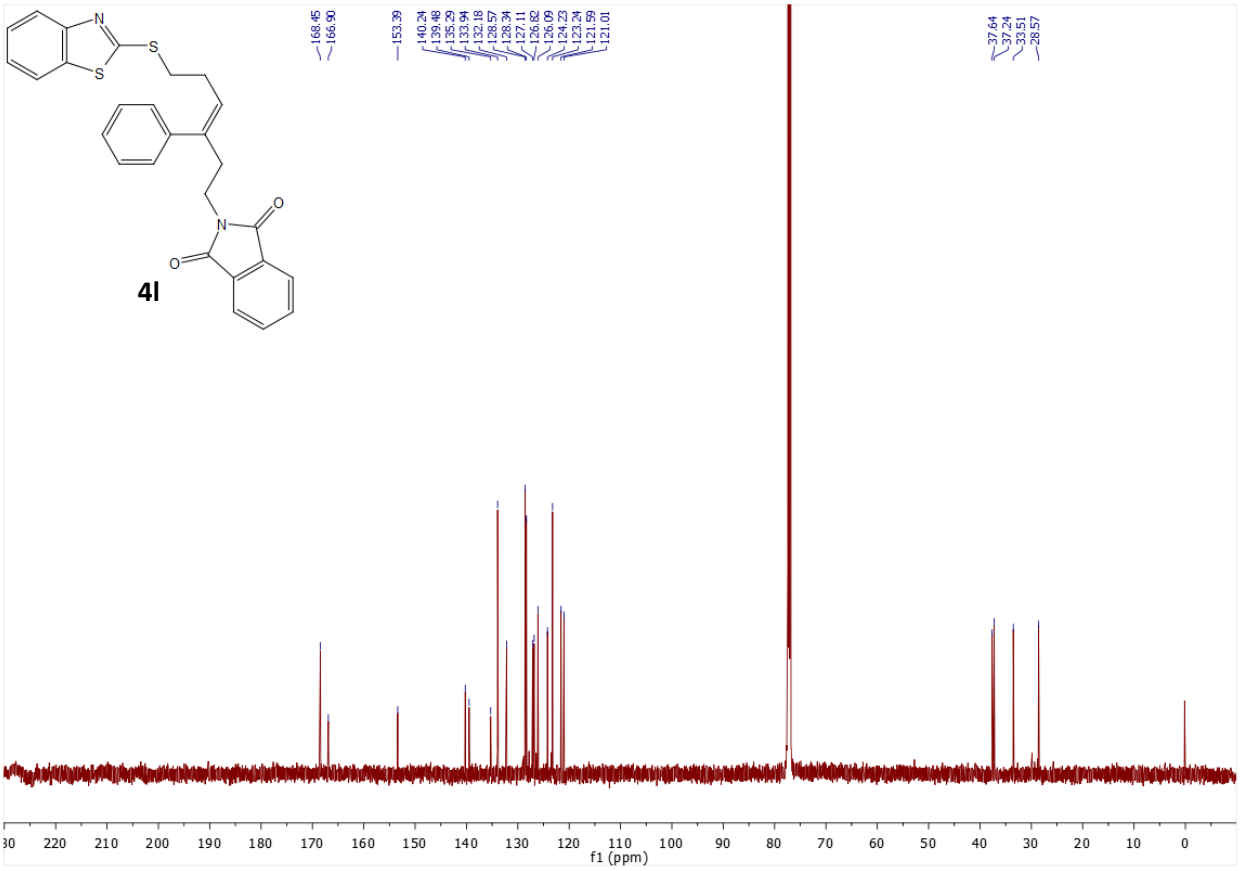

N
S
S
H3C
4j
f2 (ppm)
f1 (ppm)

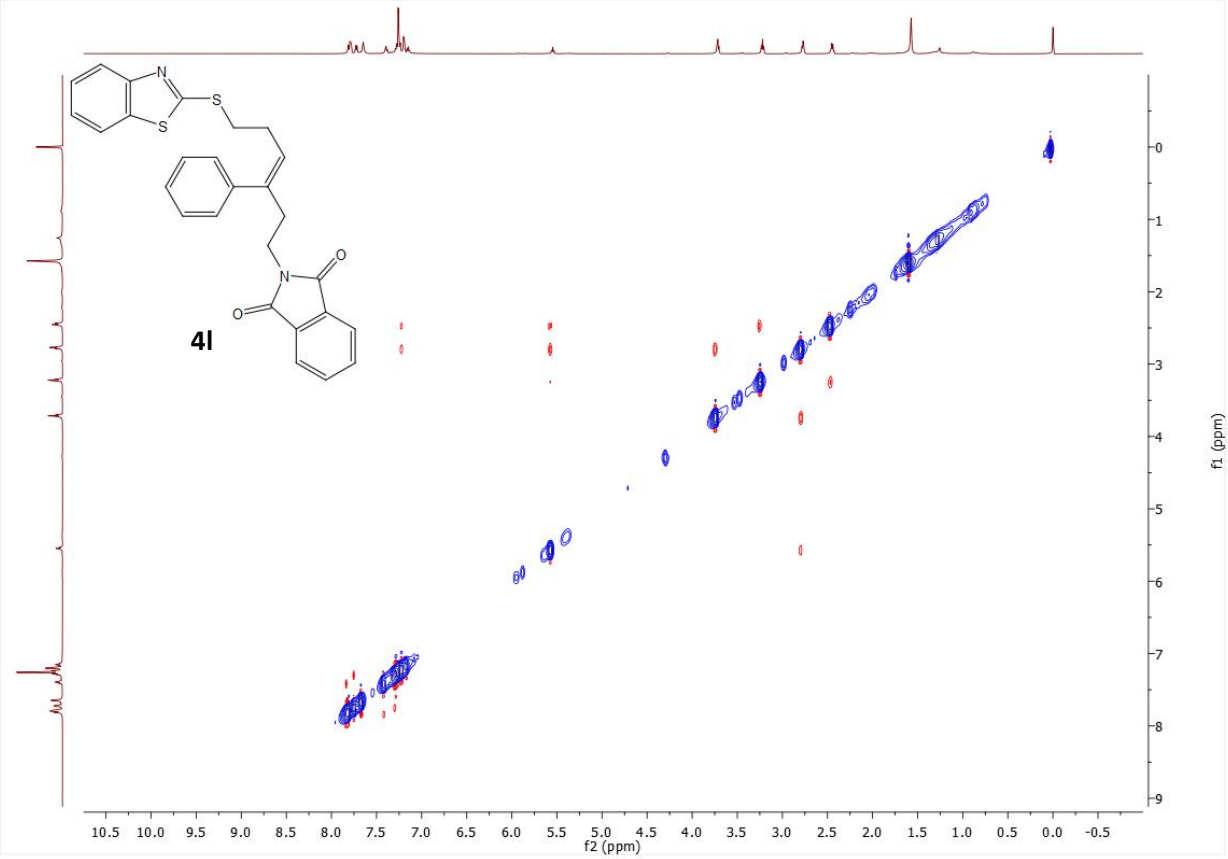

4k
1.98
0.99
1.02
1.03
1.99
1.06
3.09
0.98
1.94
0.98
2.02
1.97
3.95
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

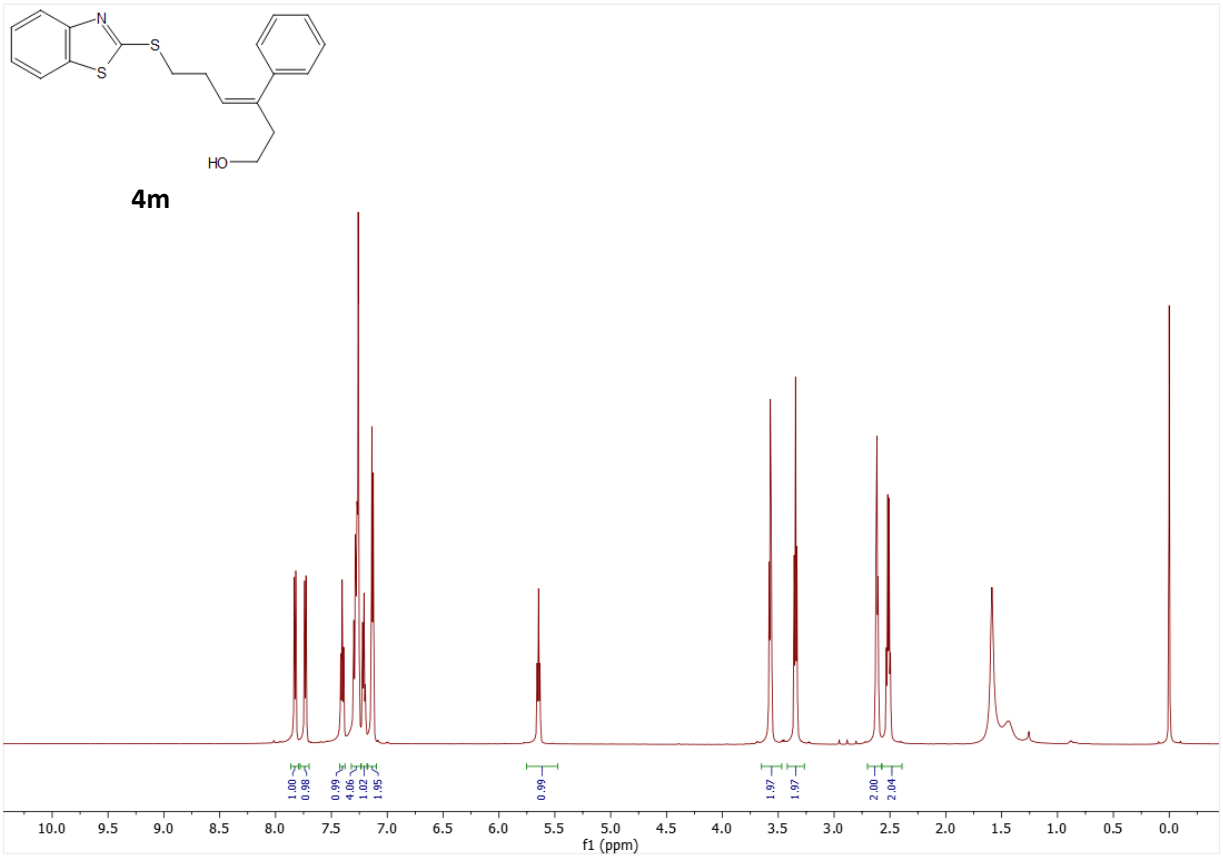

4k
167.08
166.73
153.43
142.76
140.27
135.32
132.99
129.69
128.47
128.42
127.03
126.10
124.87
124.24
121.60
121.02
64.47
35.81
33.70
29.70
27.16
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

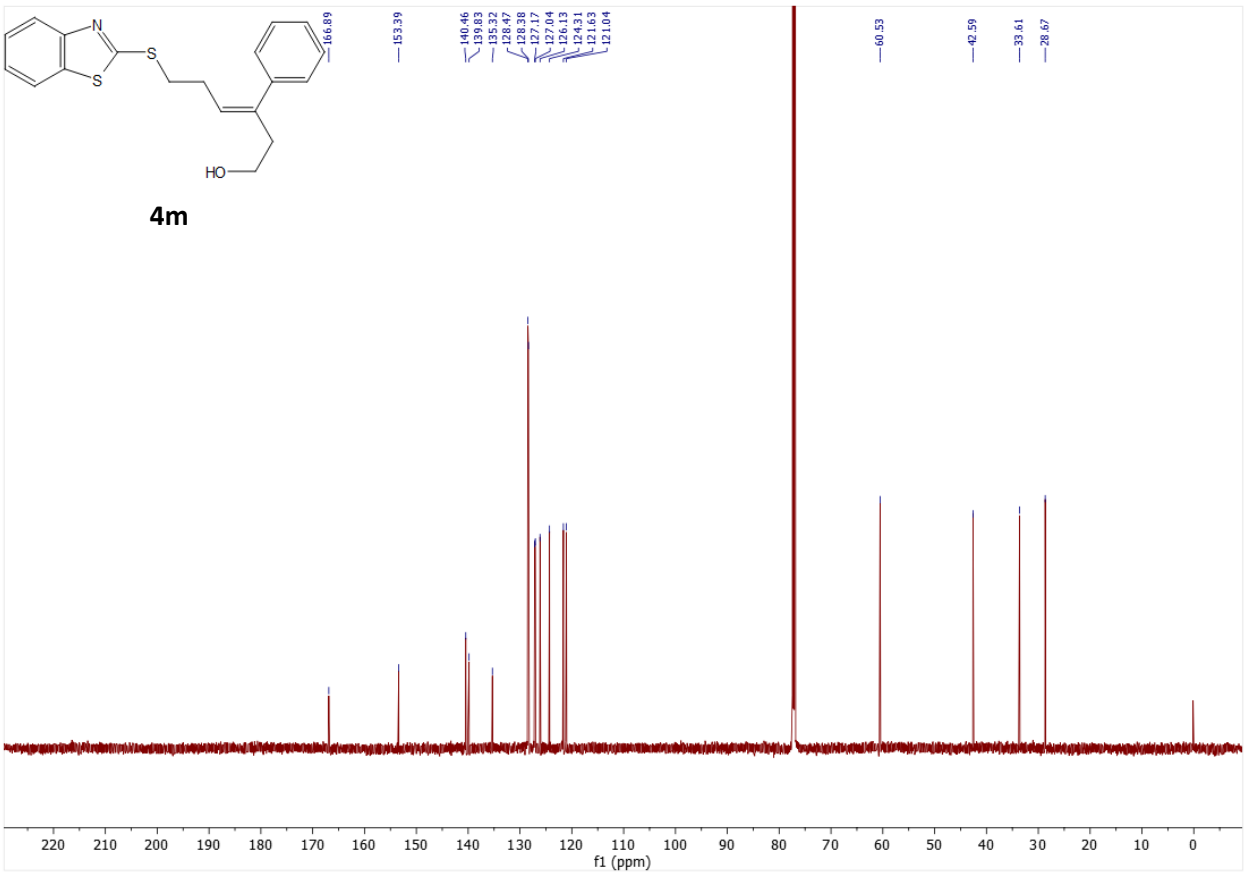

N
S
S
O
O
4k
f2 (ppm)
f1 (ppm)

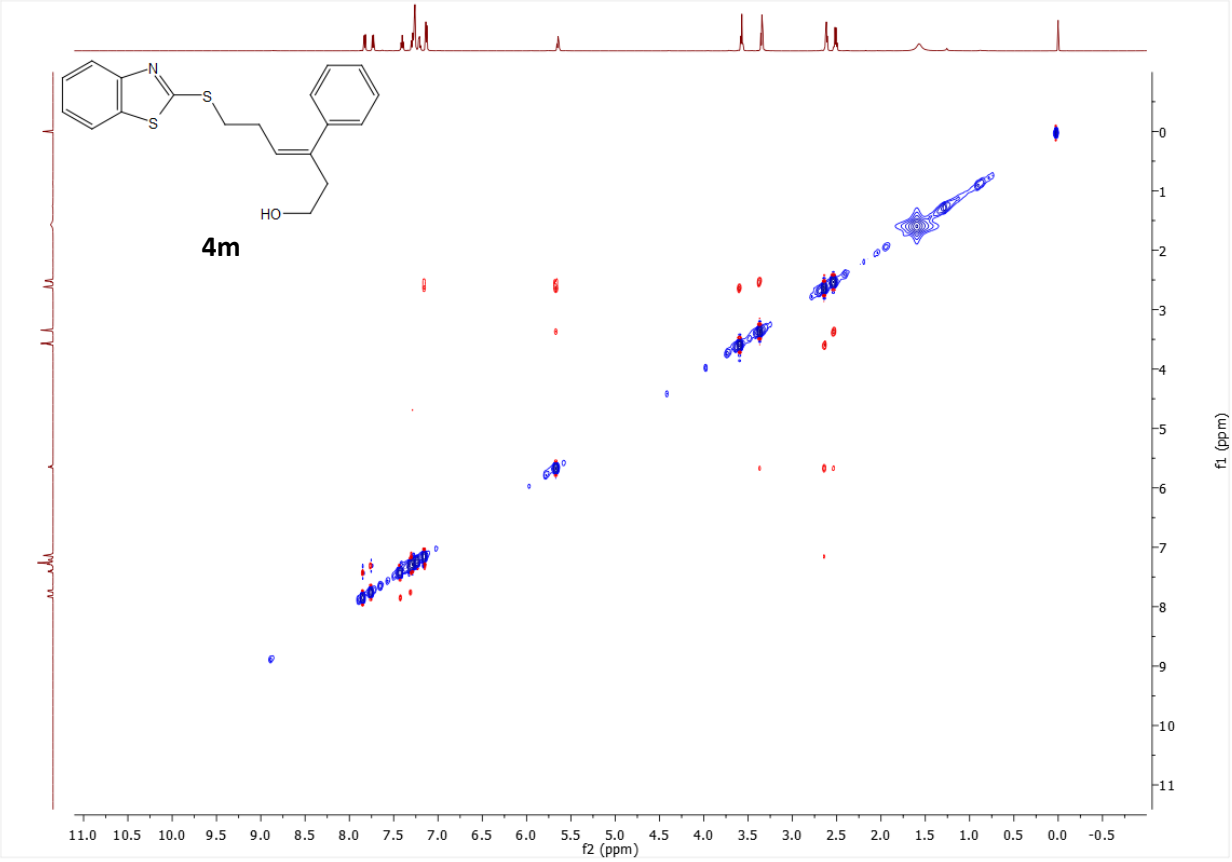

4l
2.96
1.10
1.95
1.07
1.28
1.77
2.12
1.04
0.96
2.02
2.02
2.02
1.91
f1 (ppm)

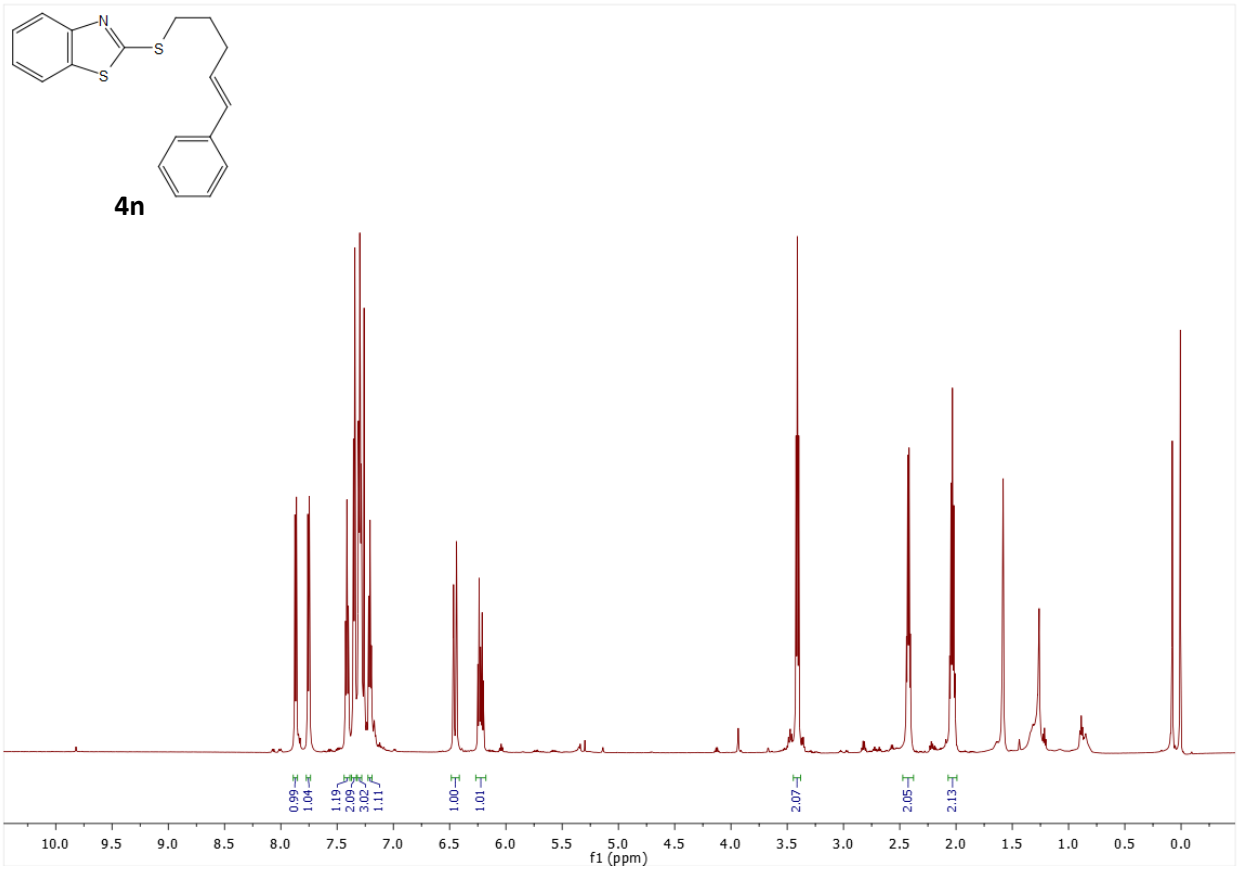

4l
168.45
166.90
153.39
140.24
139.48
135.29
133.94
132.18
128.57
128.34
127.11
126.82
126.09
124.23
123.24
121.59
121.01
37.64
37.24
33.51
28.57
f1 (ppm)

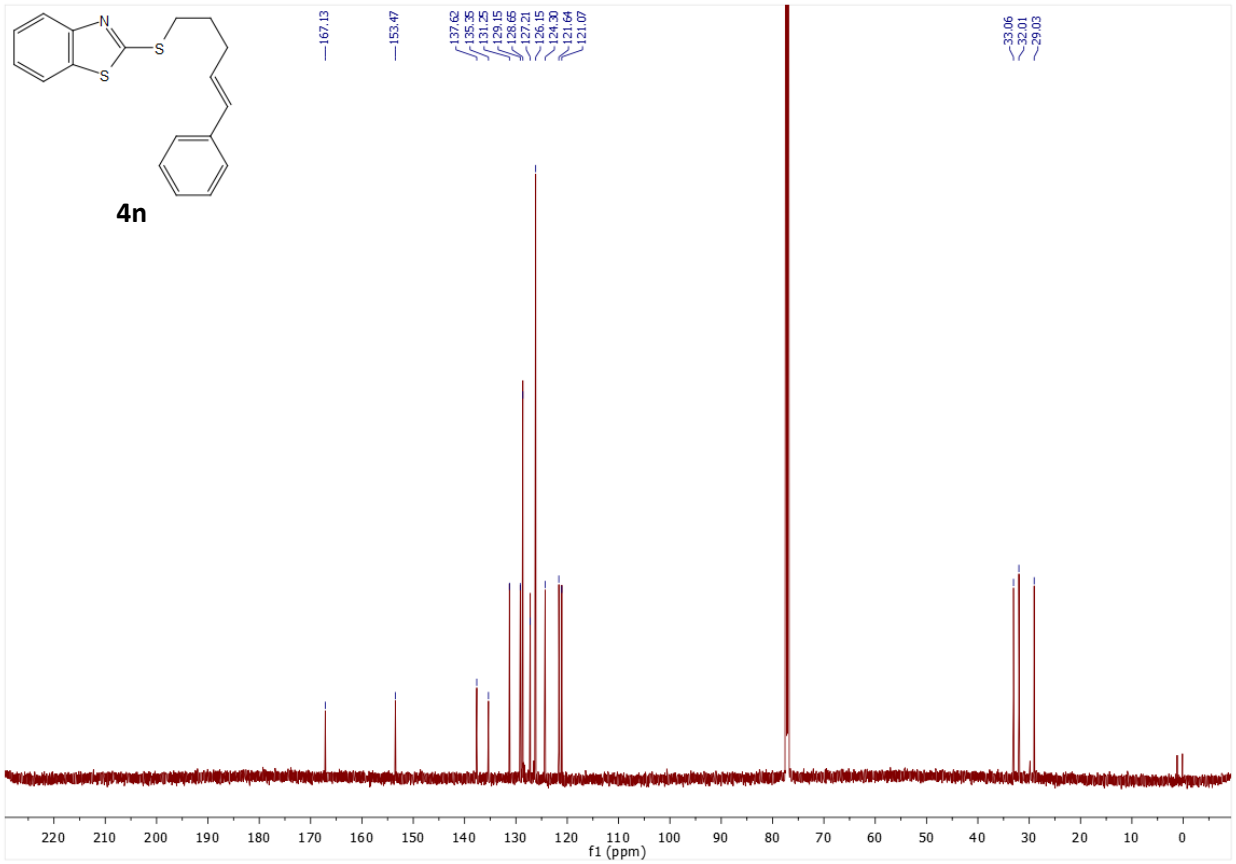

4l
f2 (ppm)
f1 (ppm)

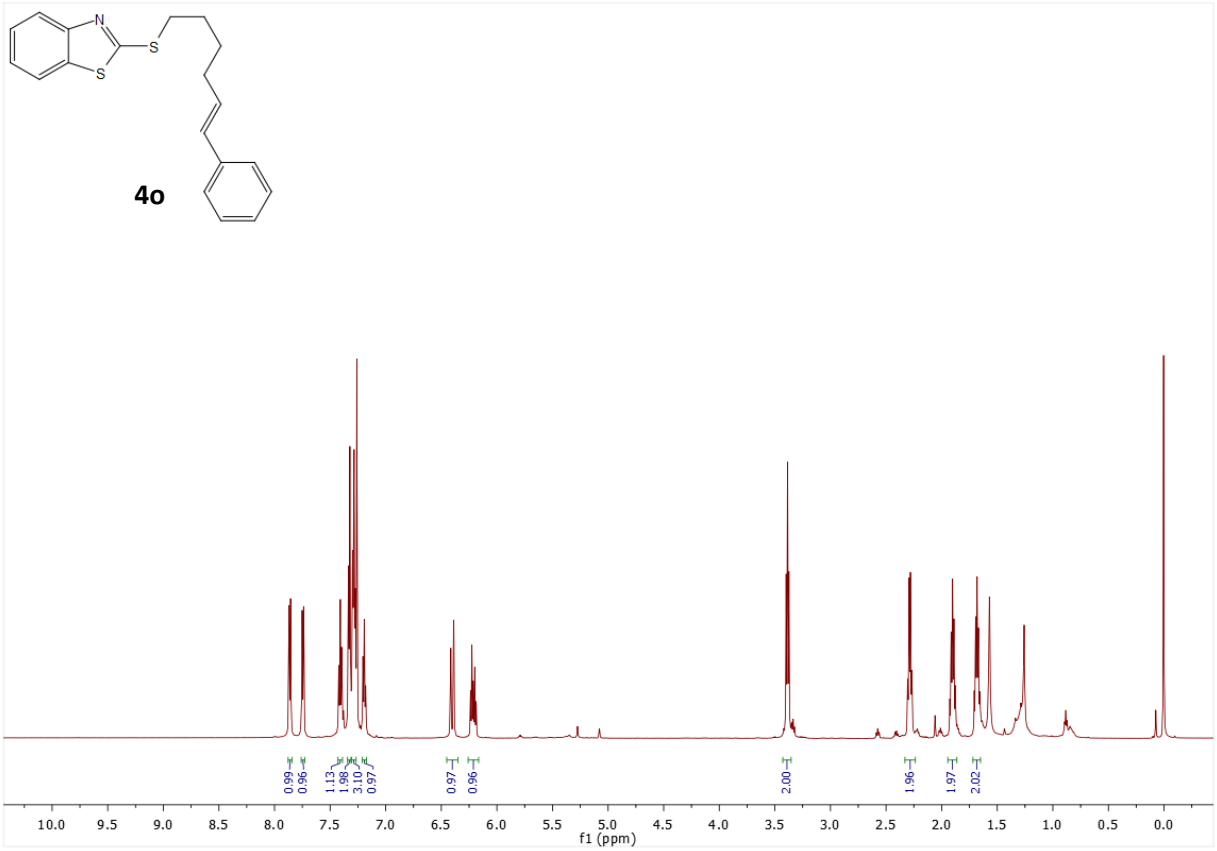

4m
1.00
0.98
0.99
4.06
1.02
1.95
0.99
1.97
1.97
2.00
2.04
f1 (ppm)

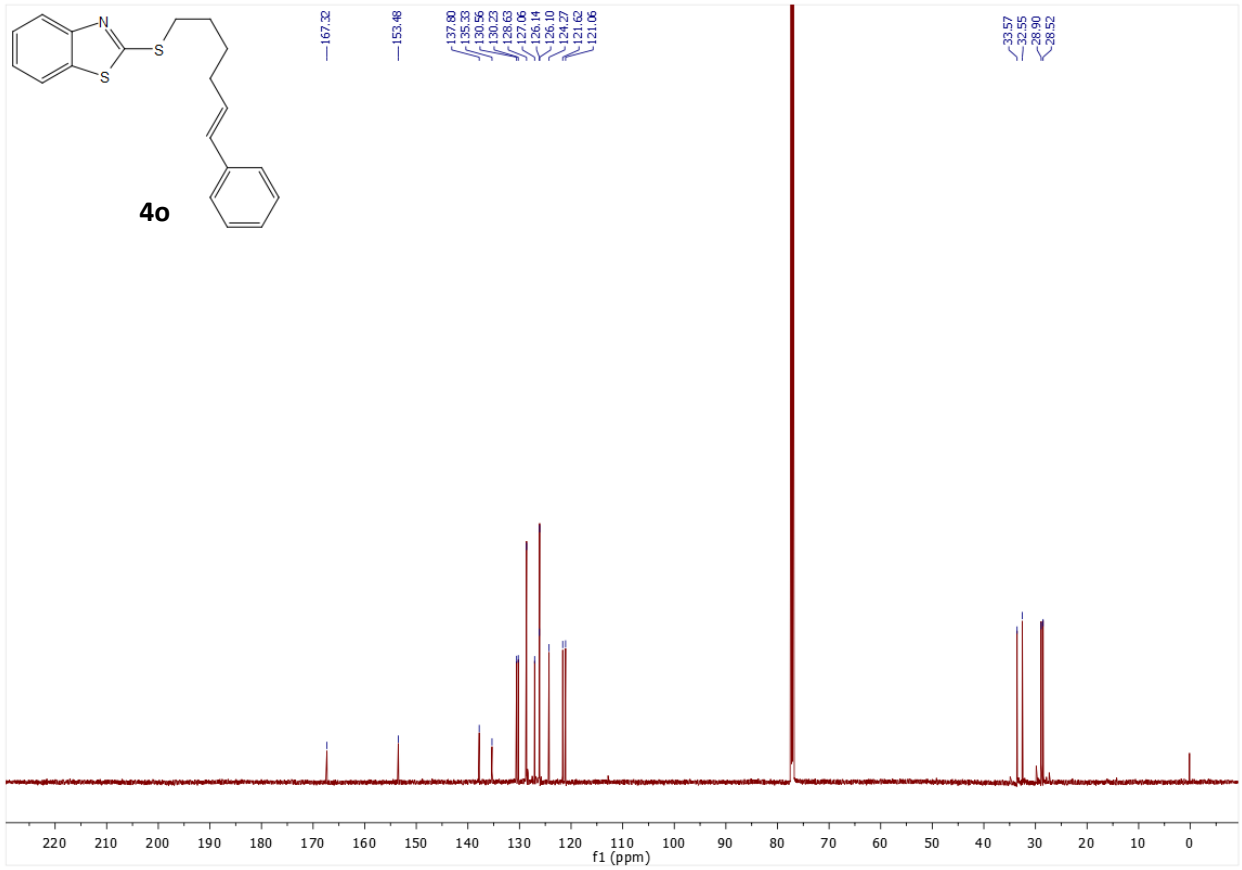

4m
166.89
153.39
140.46
139.83
135.32
128.47
128.38
127.17
127.04
126.13
124.31
121.63
121.04
60.53
42.59
33.61
28.67
f1 (ppm)

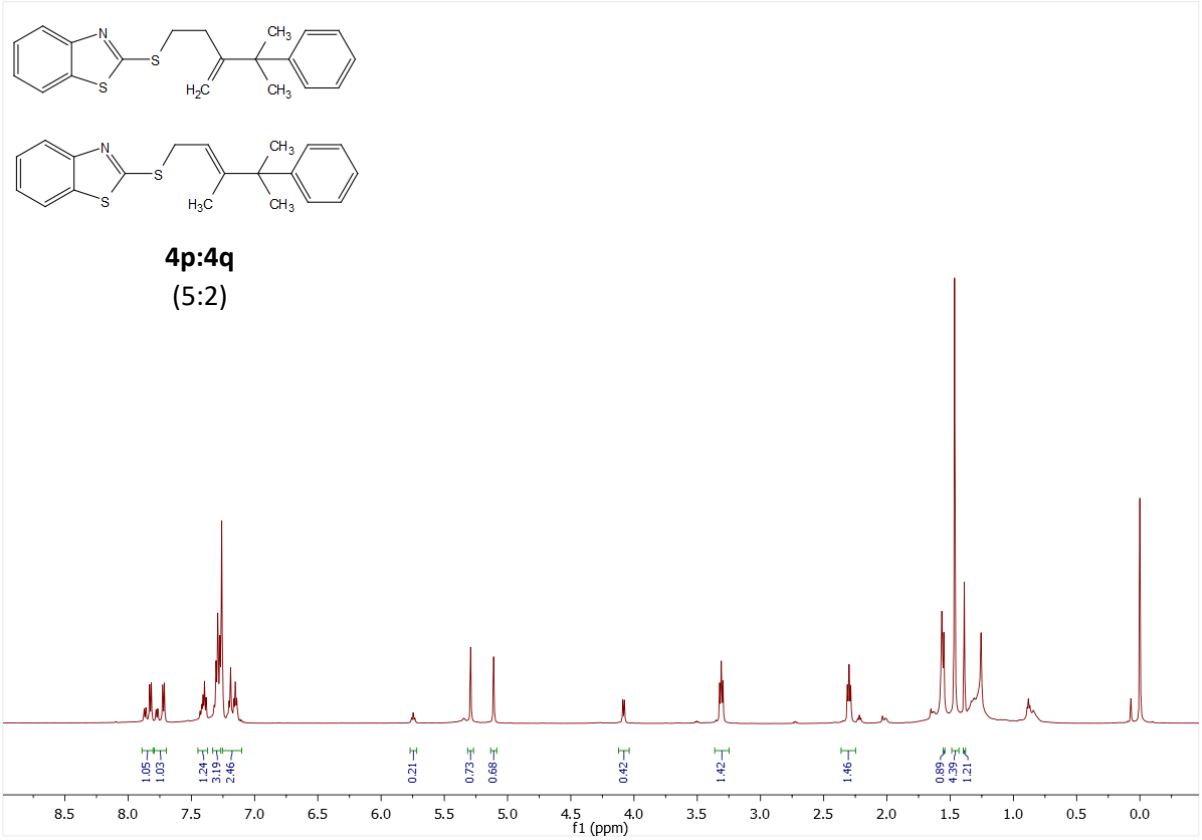

N
S
S
HO
4m
f2 (ppm)
f1 (ppm)

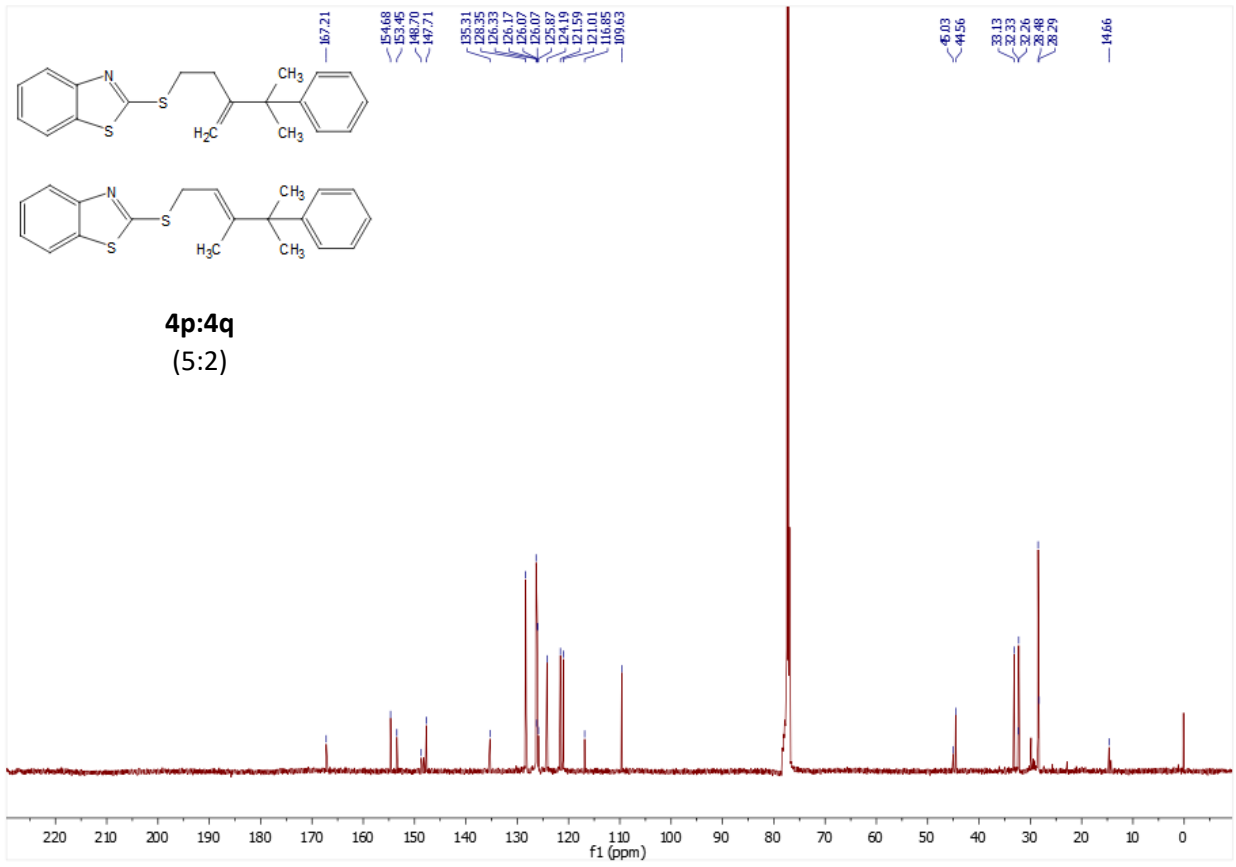

4n
0.99
1.04
1.19
2.09
3.02
1.11
1.00
1.01
2.07
2.05
2.13
f1 (ppm)

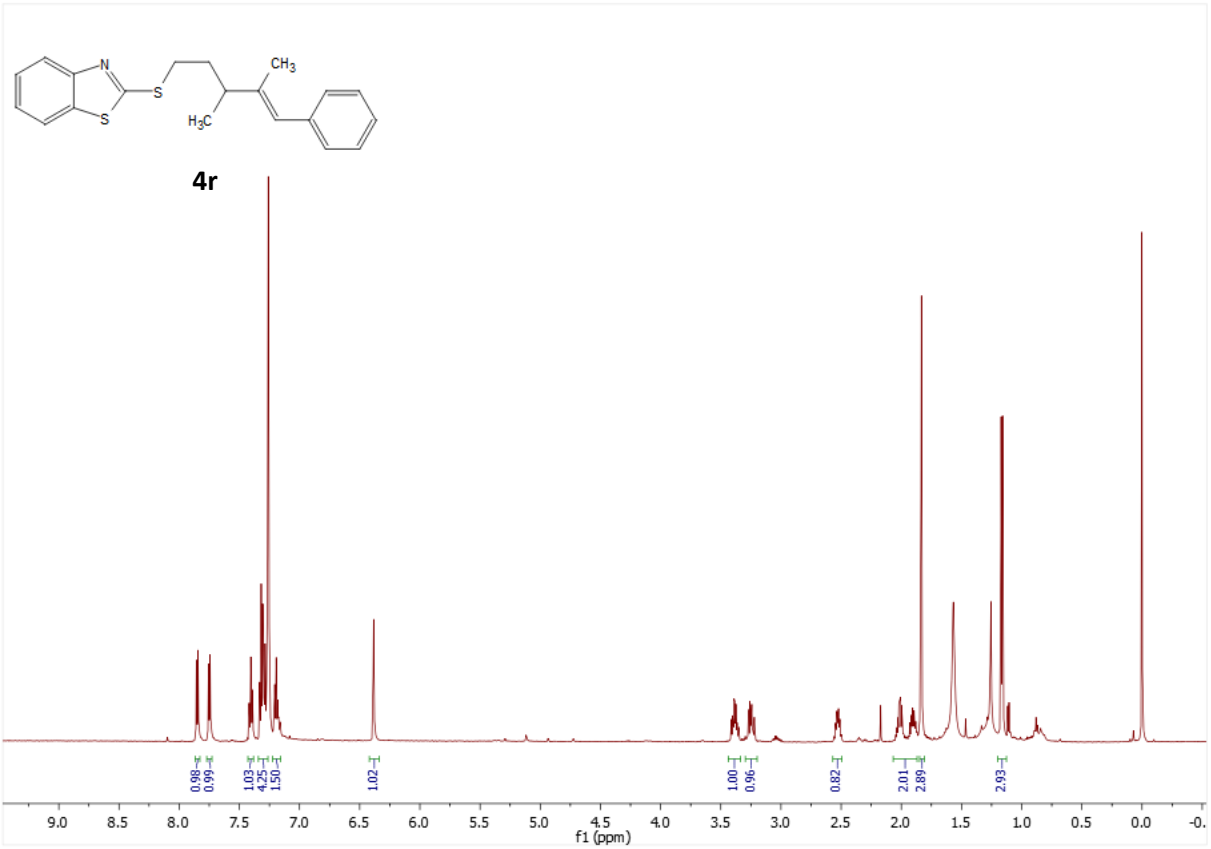

4n
167.13
153.47
137.62
135.35
131.35
129.15
128.65
128.21
127.15
124.30
121.64
121.07
33.06
32.01
29.03
f1 (ppm)

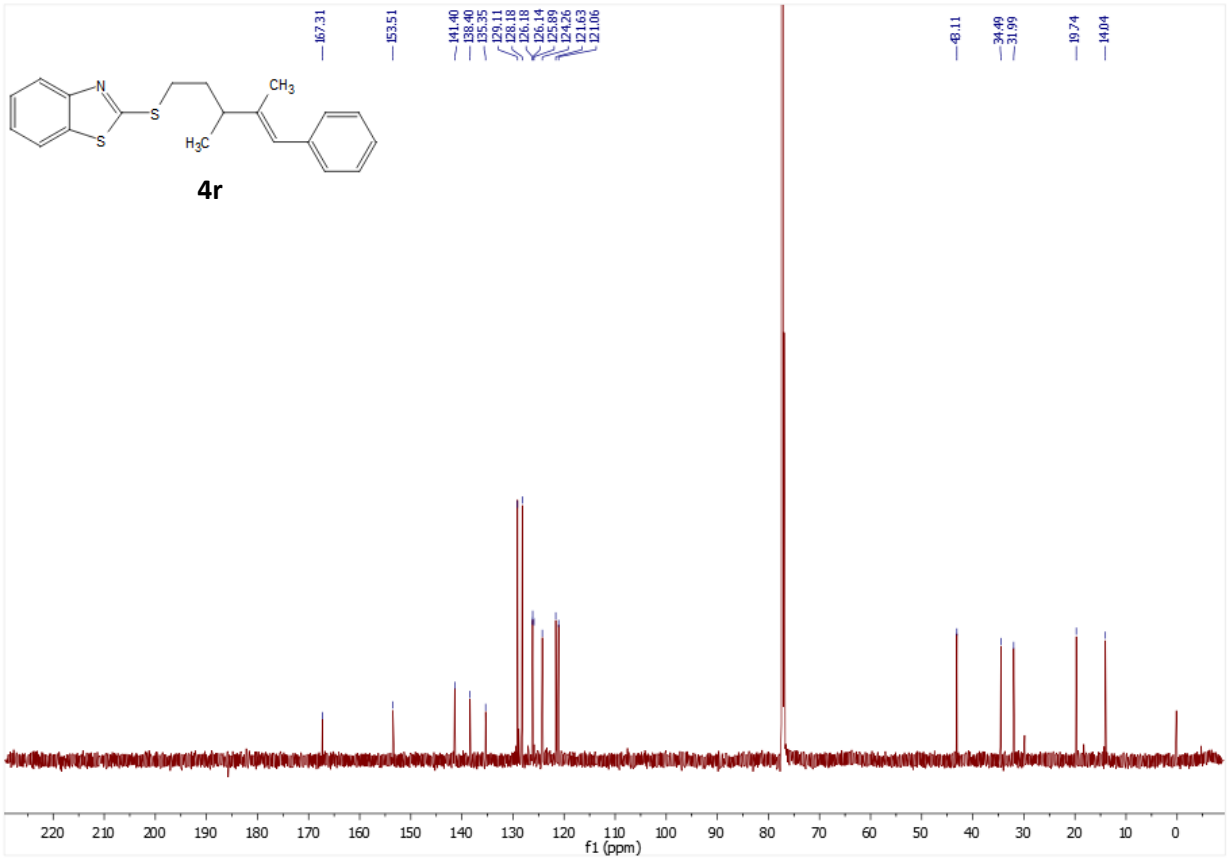

4o
0.99
0.96
1.13
1.98
3.10
0.97
0.97
0.96
2.00
1.96
1.97
2.02
f1 (ppm)

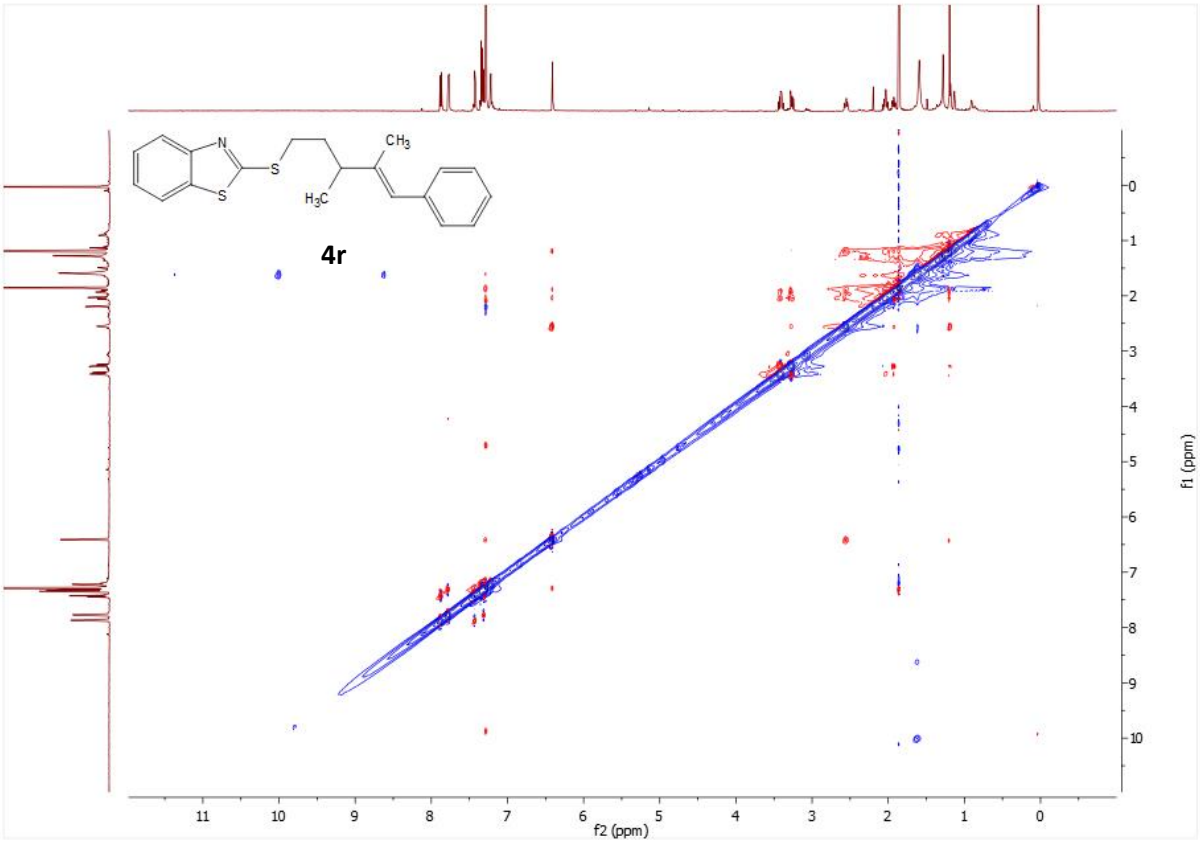

4o
167.32
153.48
137.80
135.33
130.56
130.23
128.63
127.06
126.14
126.10
124.27
121.62
121.06
33.57
32.55
28.90
28.52
f1 (ppm)

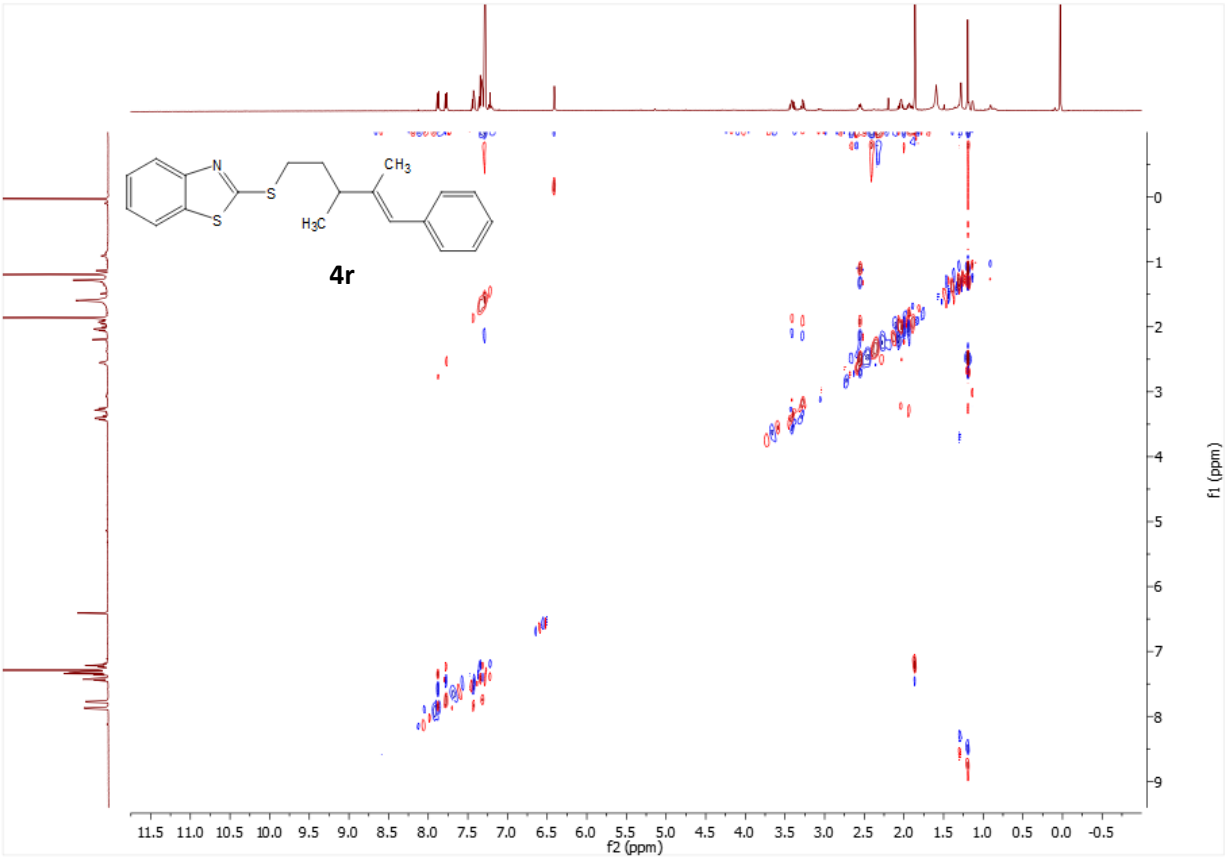

4p:4q
(5:2)
f1 (ppm)

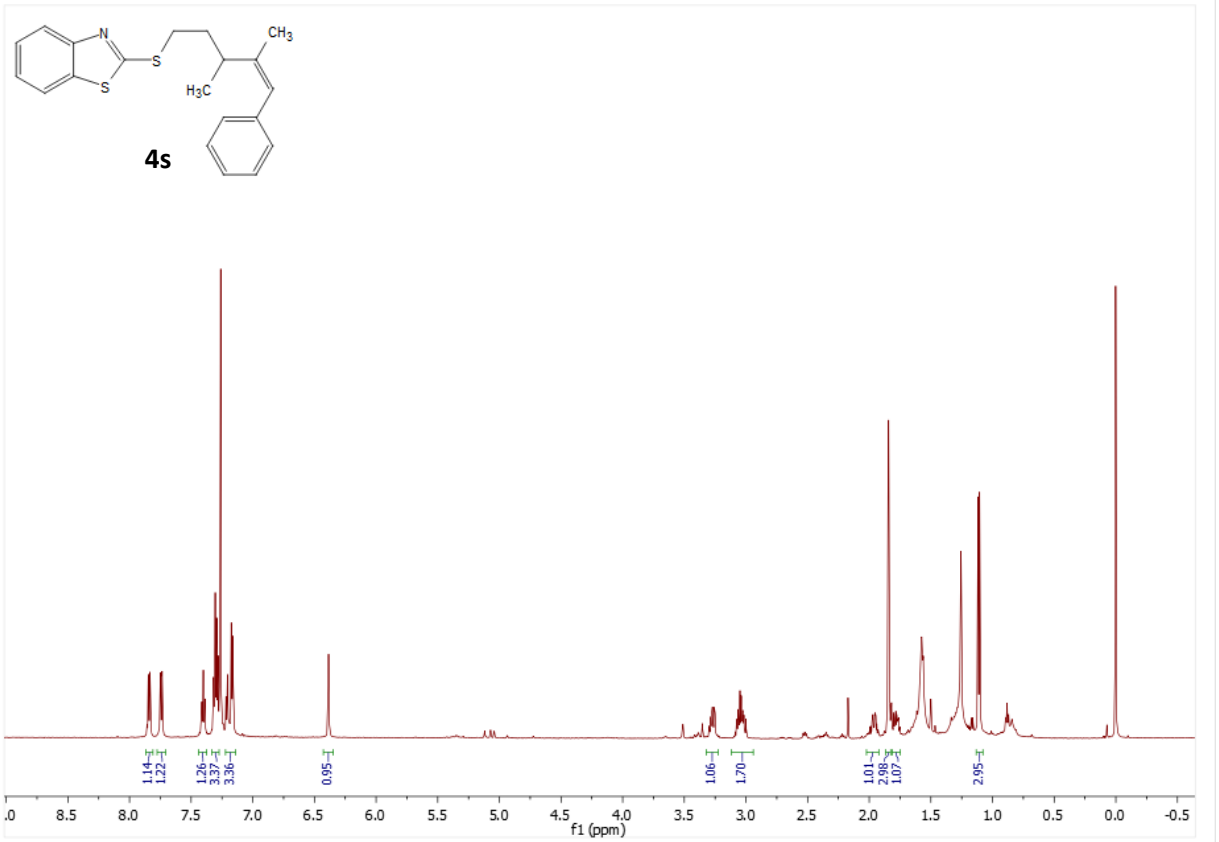

4p:4q
(5:2)
f1 (ppm)

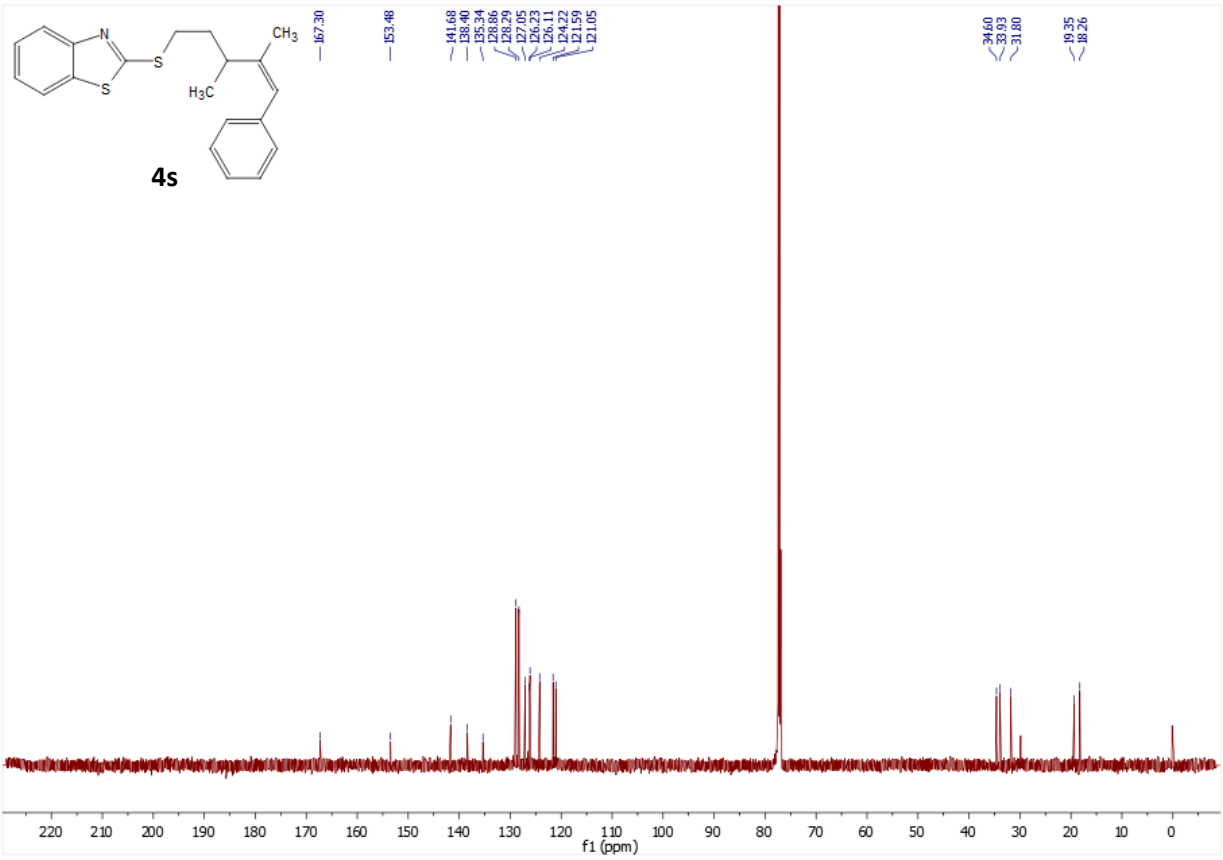

4r
0.98
0.99
1.03
4.25
1.50
1.02
1.00
0.96
0.82
2.01
2.89
2.93
f1 (ppm)

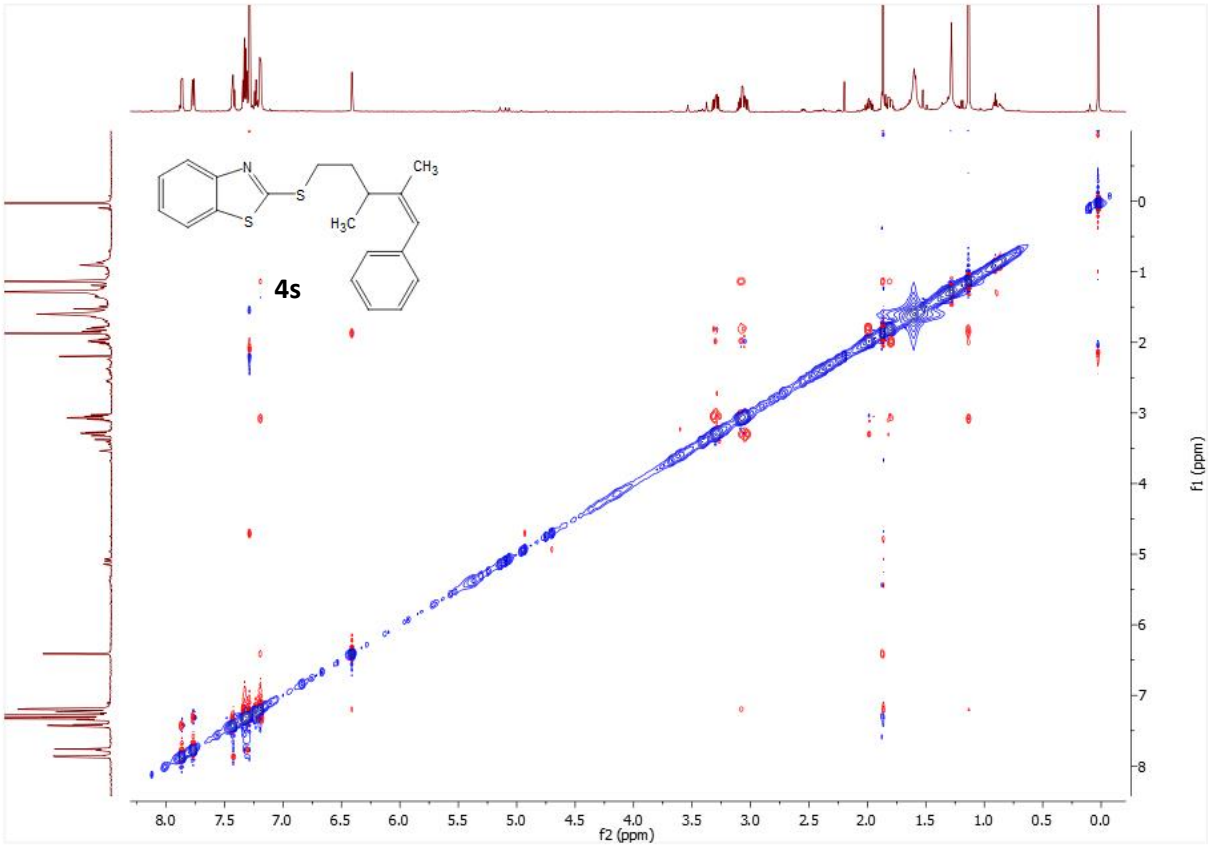

167.31
153.51
141.40
138.40
135.35
129.11
128.18
126.14
125.89
124.26
121.63
121.06
48.11
34.49
31.99
19.74
14.04
4r
f1 (ppm)

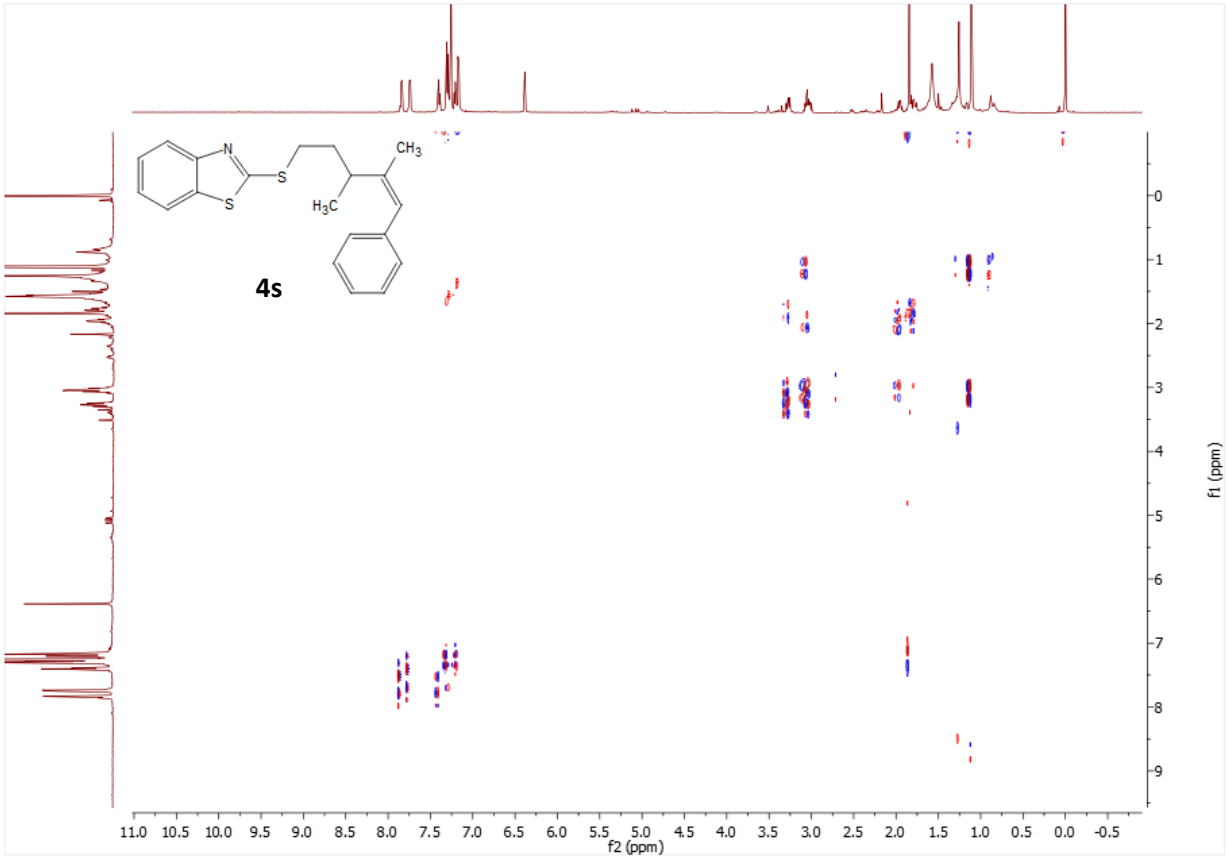

4r
f2 (ppm)
f1 (ppm)

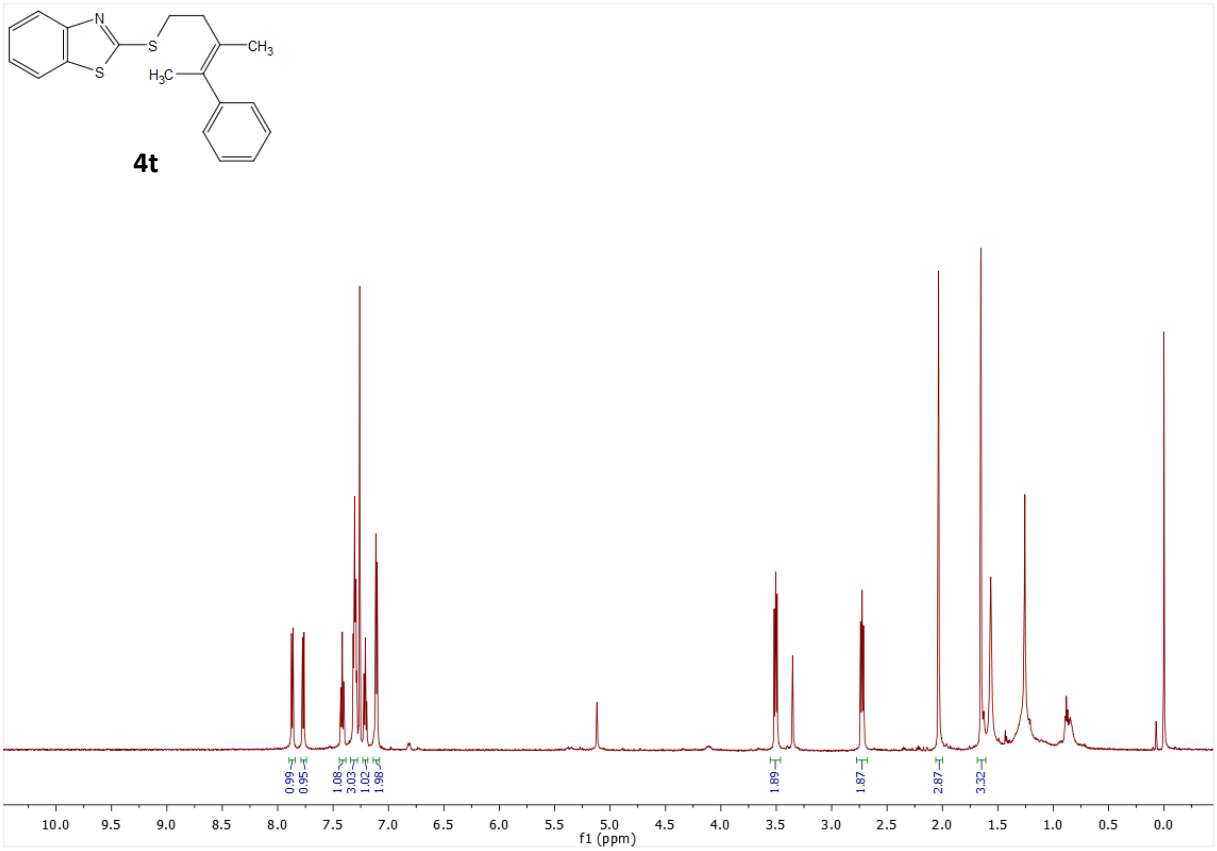

4r
f2 (ppm)
f1 (ppm)

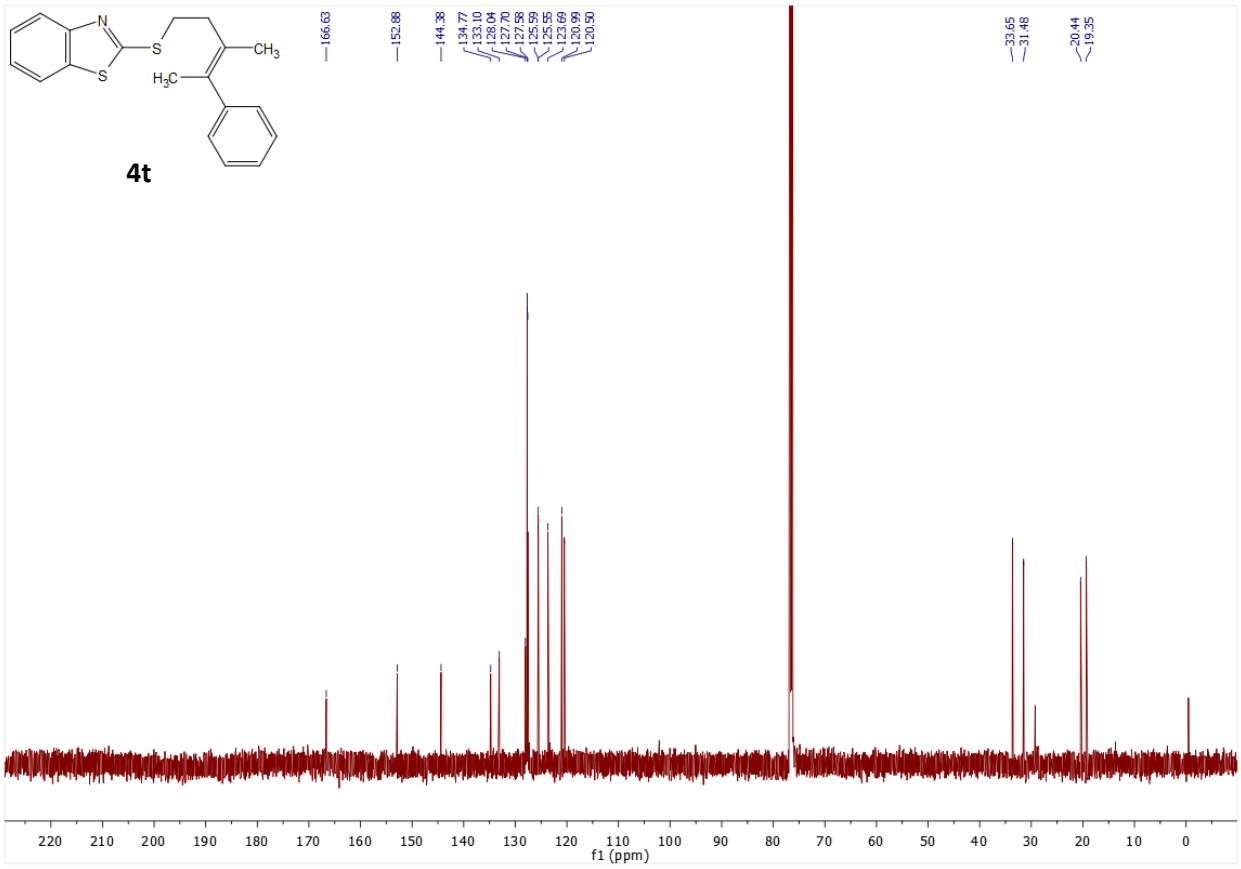

4s
1.14
1.22
1.26
3.37
3.36
0.95
1.06
1.70
1.01
2.98
1.07
2.95
f1 (ppm)

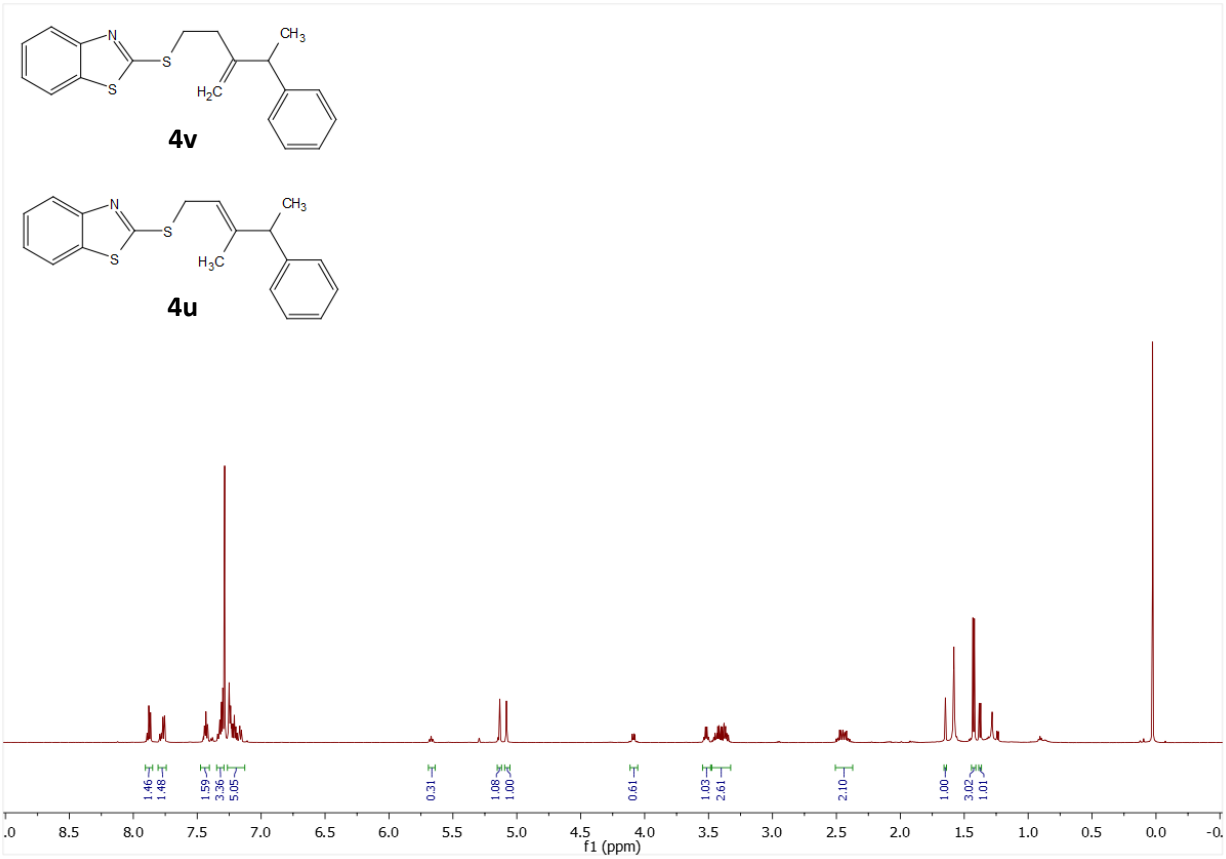

4s
167.30
153.48
141.68
138.40
135.34
128.86
128.29
127.05
126.23
126.11
124.22
121.59
121.05
34.60
33.93
31.80
19.35
18.26
f1 (ppm)

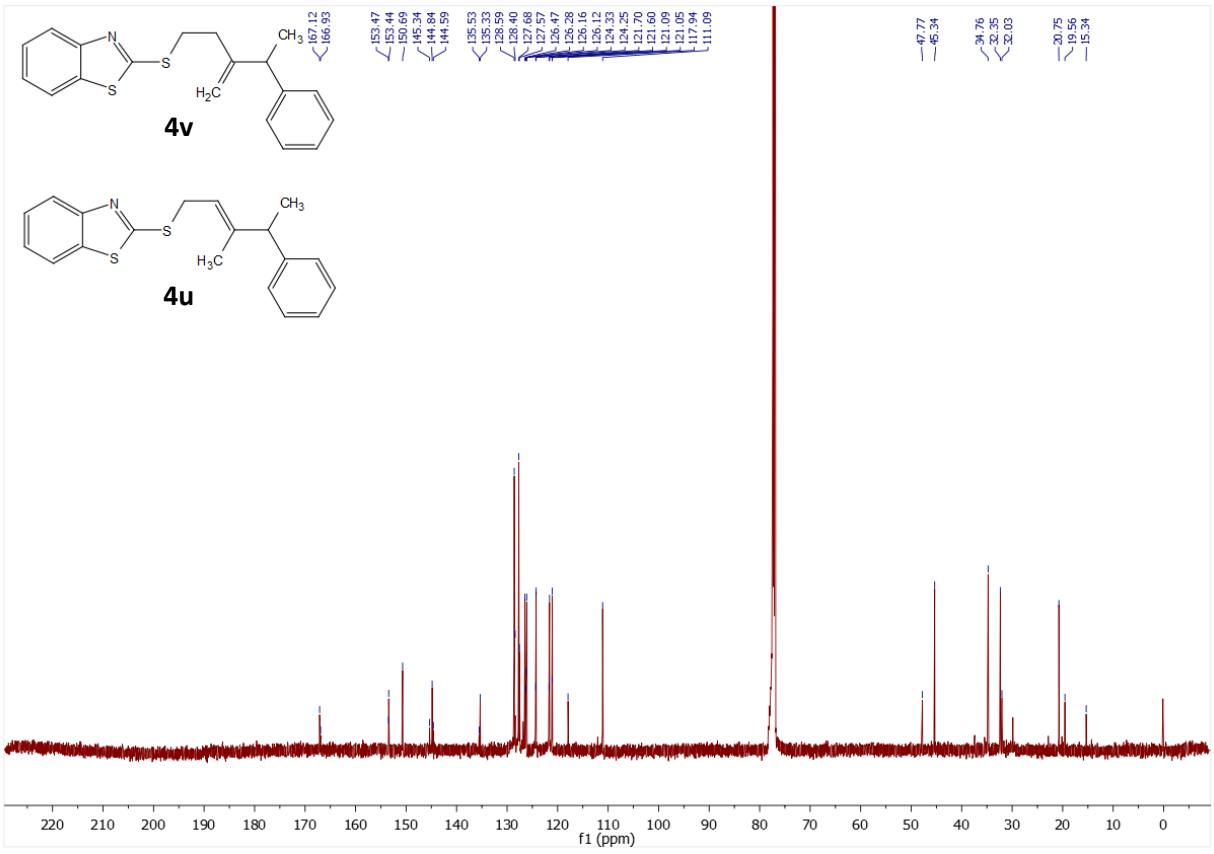

4s
f2 (ppm)
f1 (ppm)

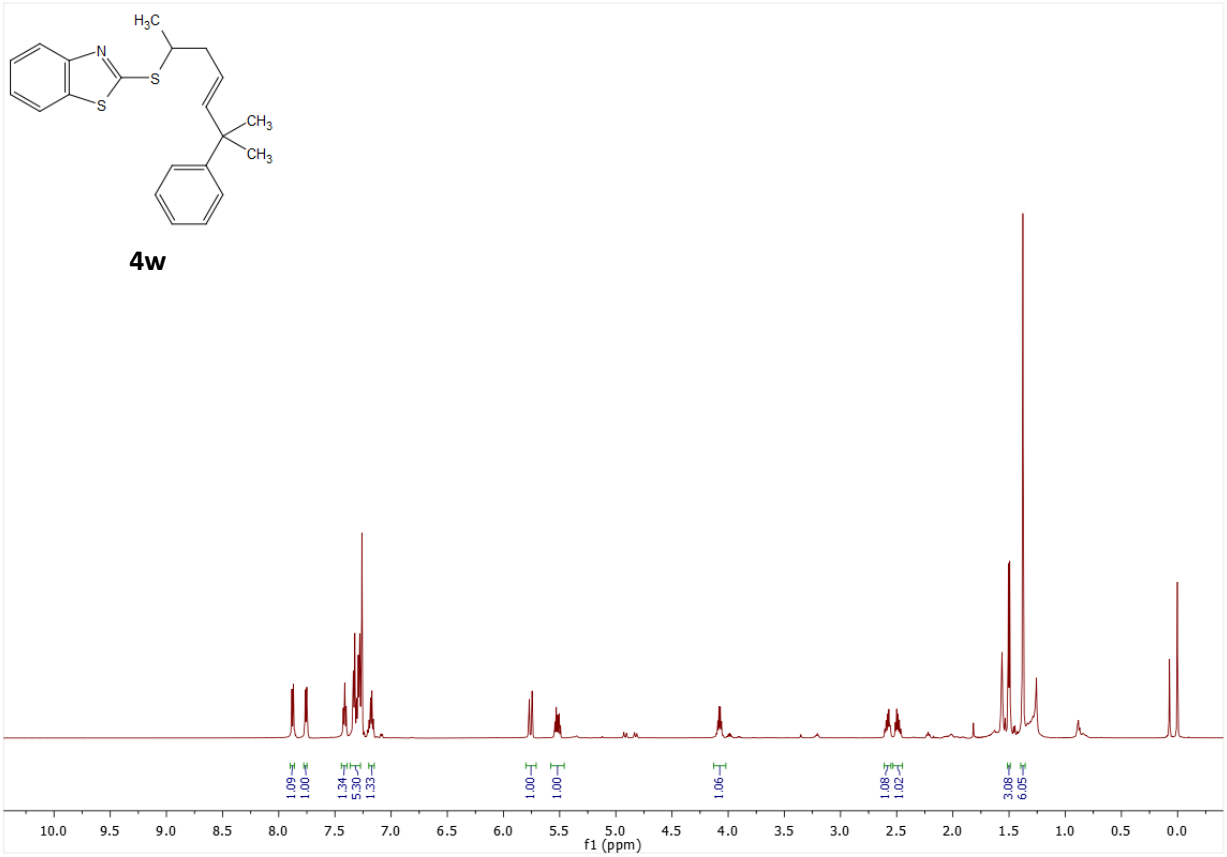

4s
f2 (ppm)
f1 (ppm)

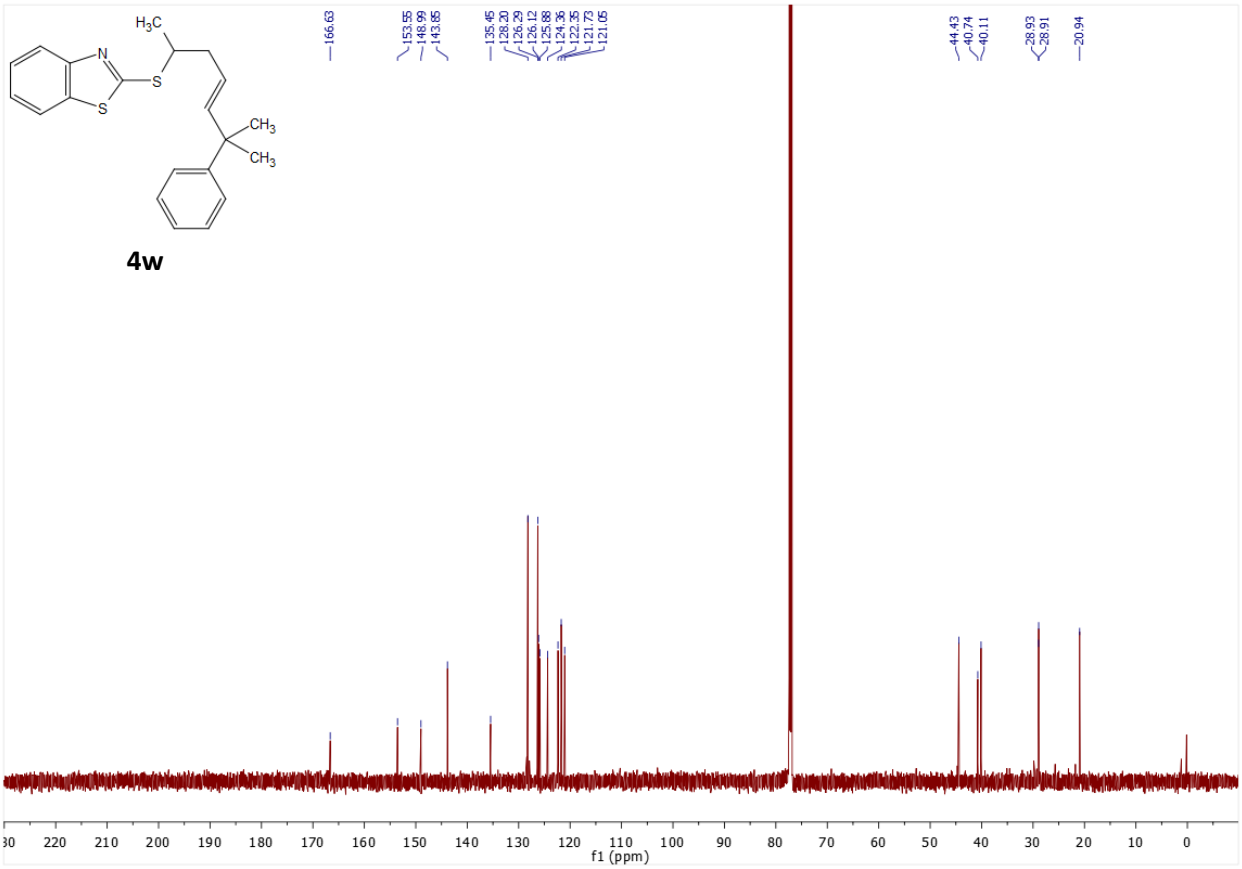

4t
0.99
0.95
1.08
3.03
1.02
1.98
1.89
1.87
2.87
3.32
f1 (ppm)

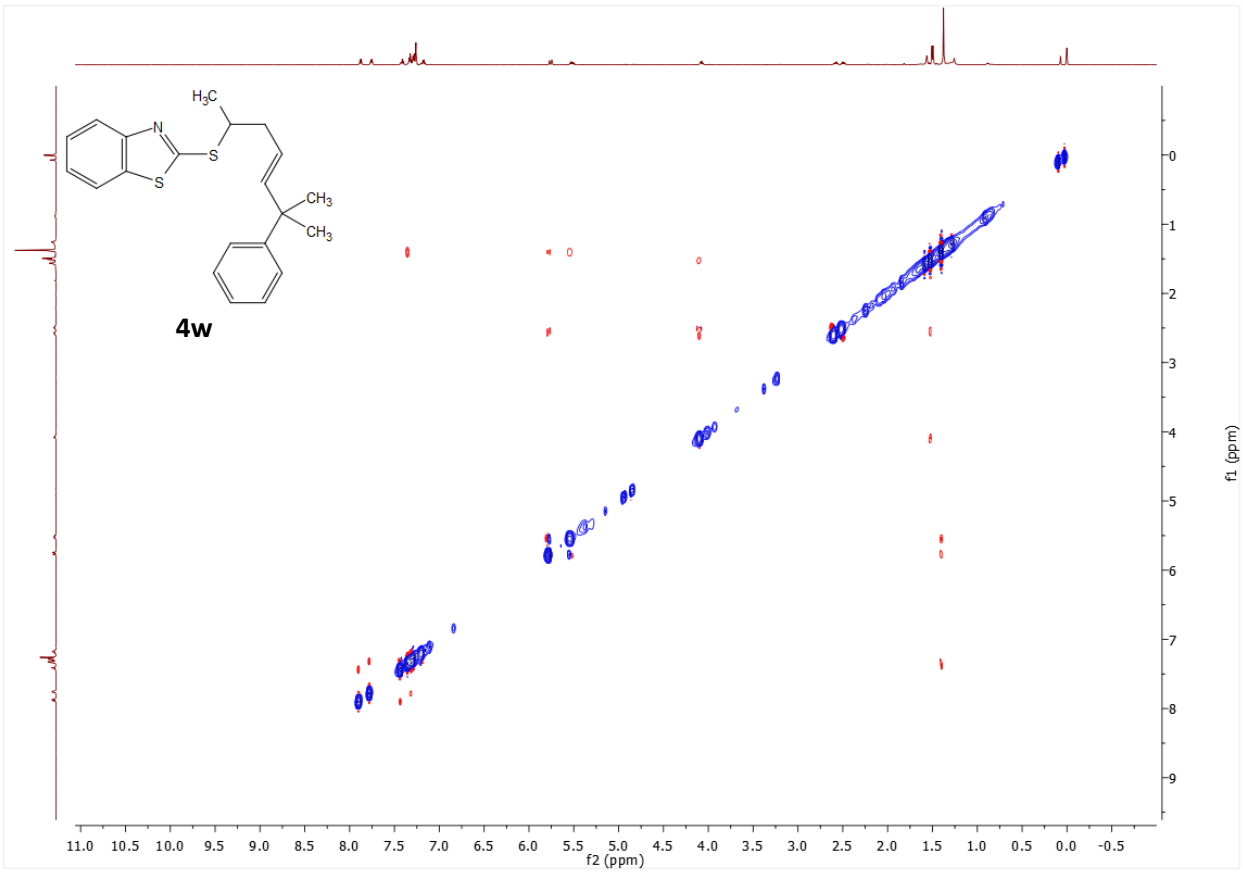

4t
166.63
152.88
144.38
134.77
133.10
128.04
127.70
127.58
125.59
125.55
123.69
120.99
120.50
33.65
31.48
20.44
19.35
f1 (ppm)

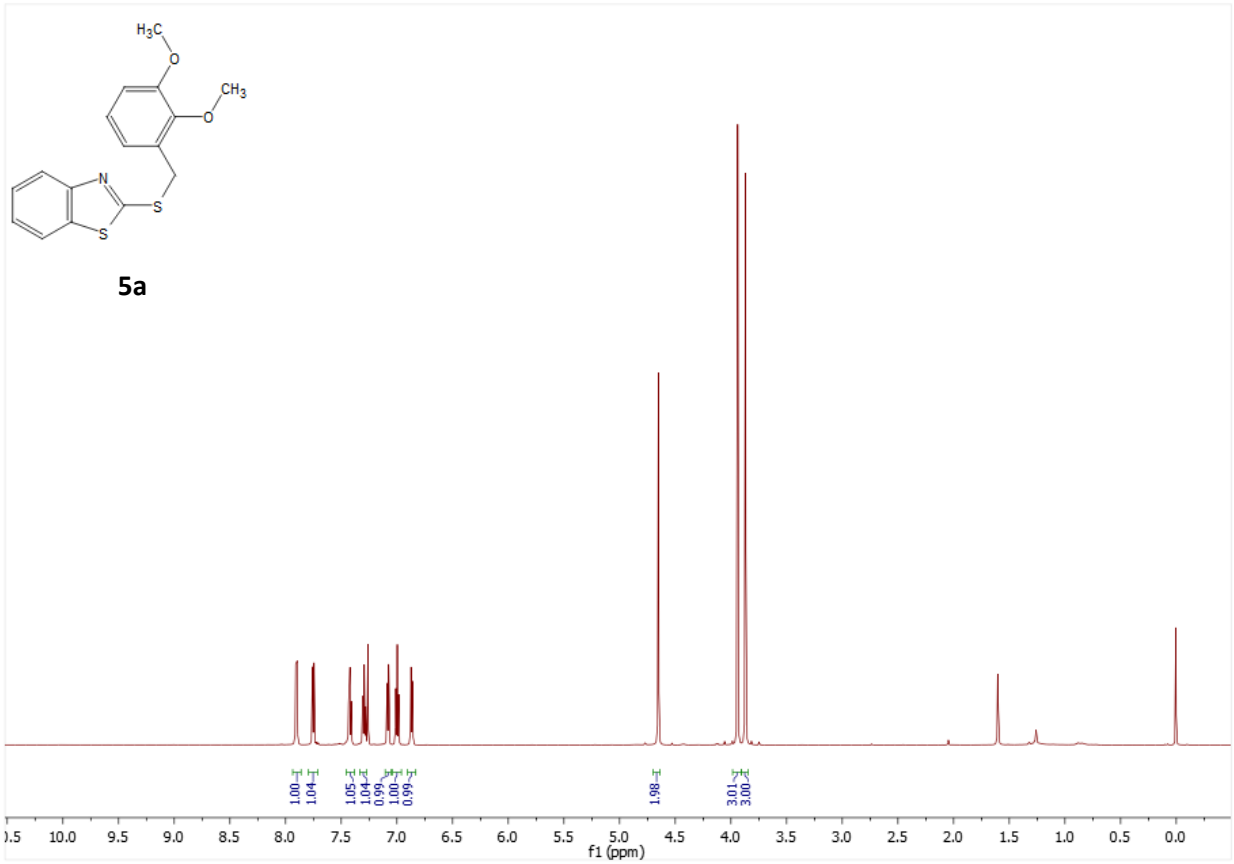

4v
4u
1.46
1.48
1.59
3.36
5.05
0.31
1.08
1.00
0.61
1.03
2.61
2.10
1.00
3.02
1.01
f1 (ppm)

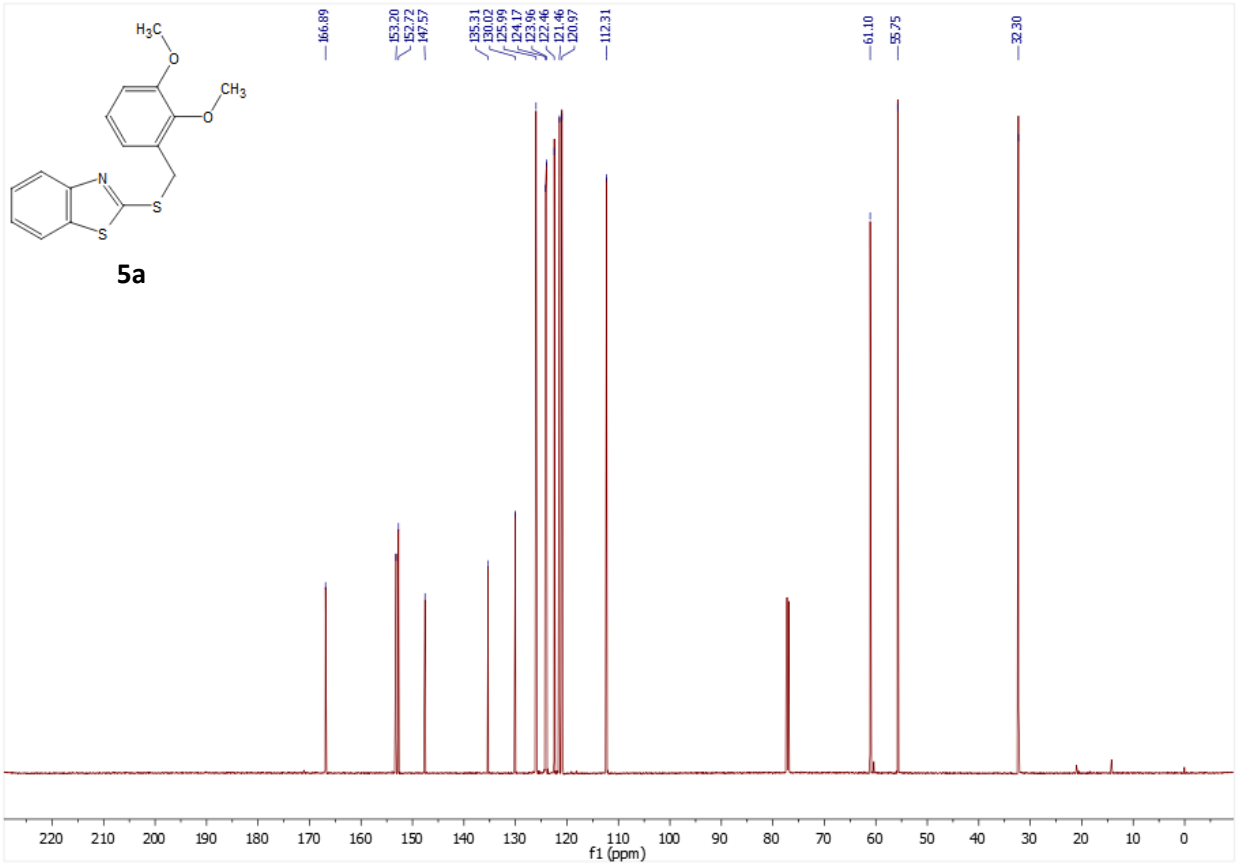

4v
4u
167.12
166.93
153.47
153.44
150.69
145.34
144.84
144.59
135.53
135.33
128.59
128.40
127.68
127.57
126.47
126.28
126.16
126.12
124.33
124.25
121.70
121.60
121.09
121.05
117.94
111.09
47.77
45.34
34.76
32.35
32.03
20.75
19.56
15.34
f1 (ppm)

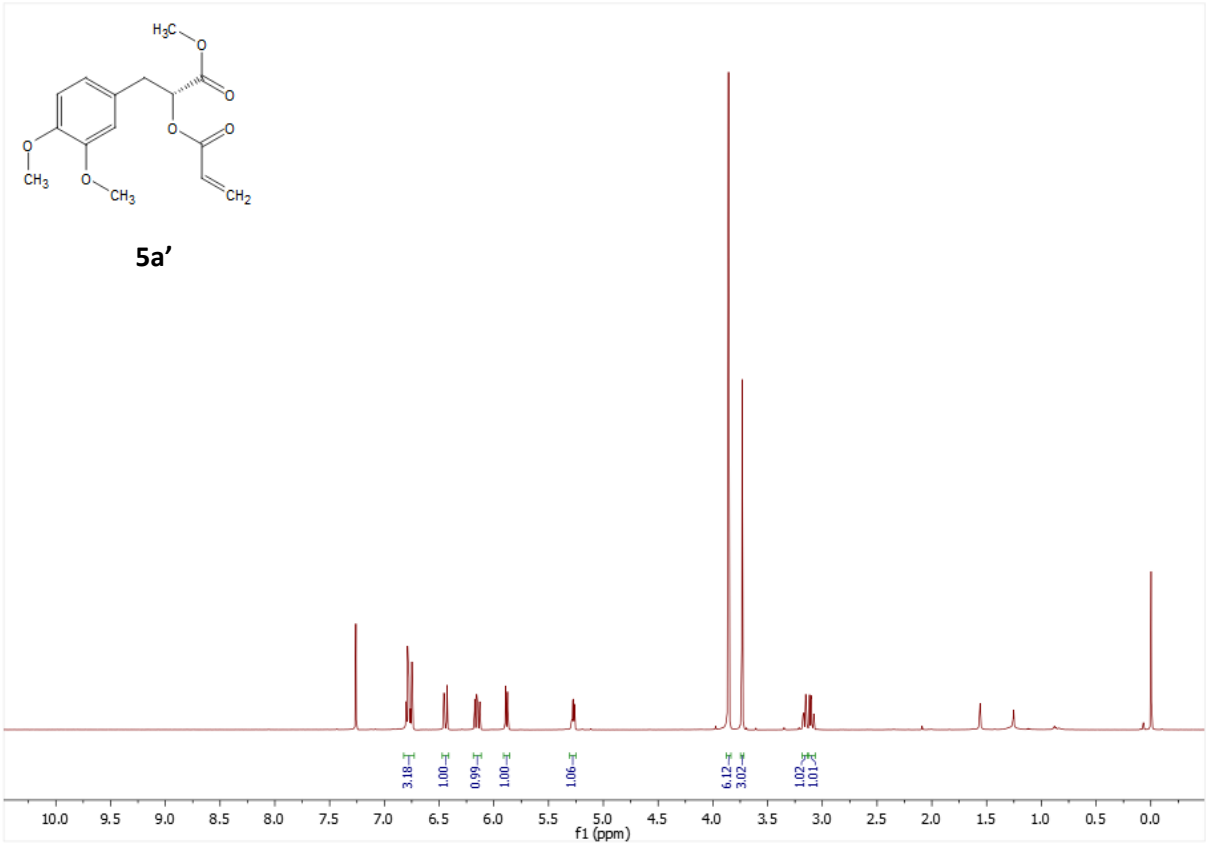

4w
1.09
1.00
1.34
5.30
1.33
1.00
1.00
1.06
1.08
1.02
3.08
6.05
f1 (ppm)


4w
166.63
153.55
148.99
143.85
135.45
128.20
126.29
126.12
125.88
124.36
122.35
121.73
121.05
44.43
40.74
40.11
28.93
28.91
20.94
f1 (ppm)

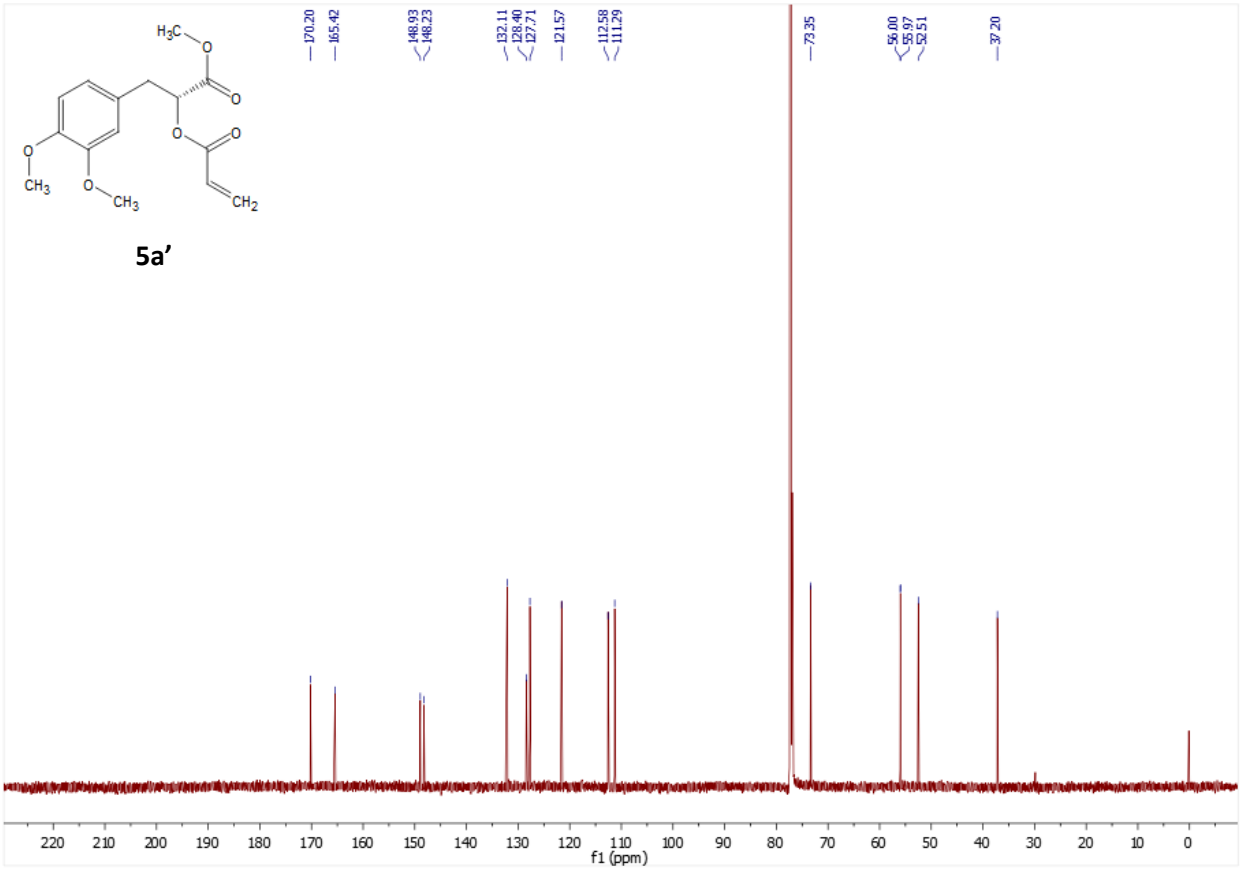

H3C
N
S
S
CH3
CH3
4w
f2 (ppm)
f1 (ppm)


5a
1.00
1.04
1.05
1.04
0.99
1.00
0.99
1.98
3.01
3.00
f1 (ppm)

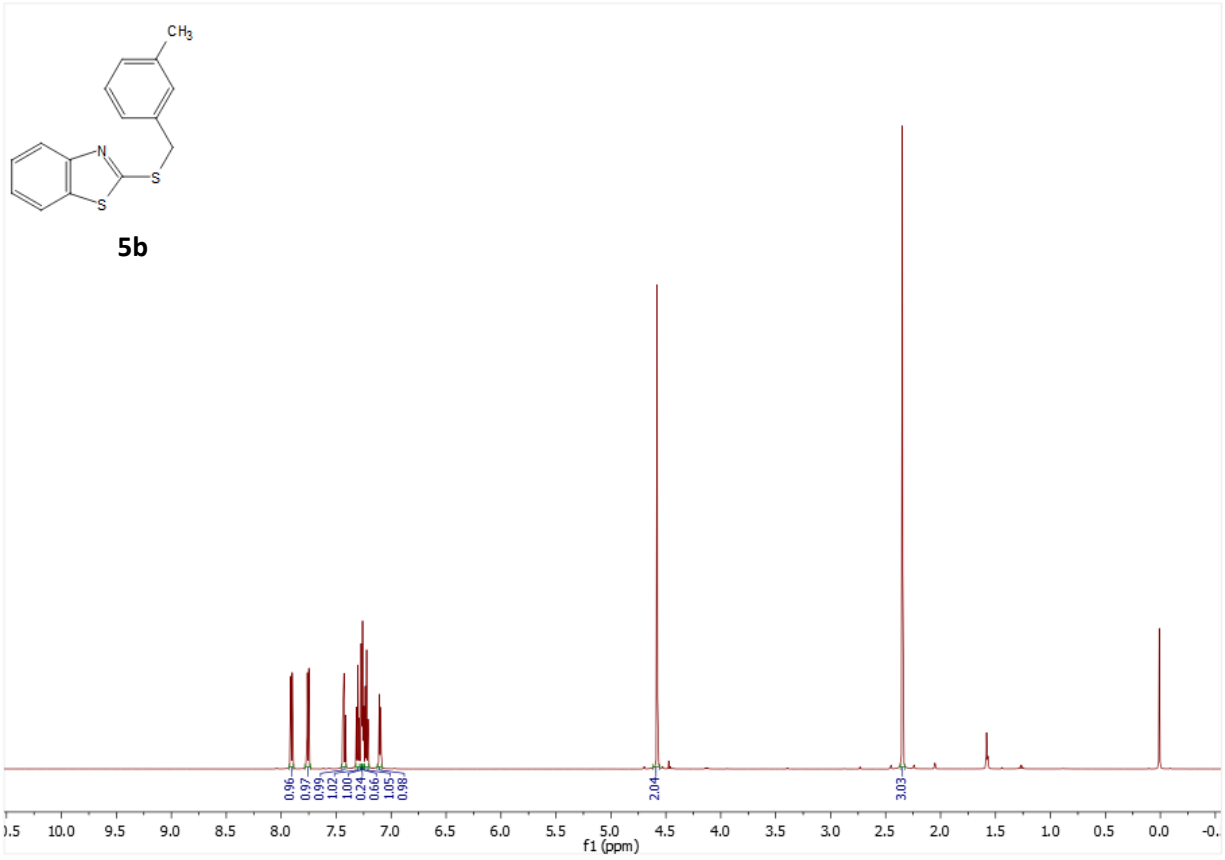

5a
166.89
153.20
152.72
147.57
135.31
130.02
125.99
124.17
123.96
122.46
121.46
120.97
112.31
61.10
55.75
32.30
f1 (ppm)

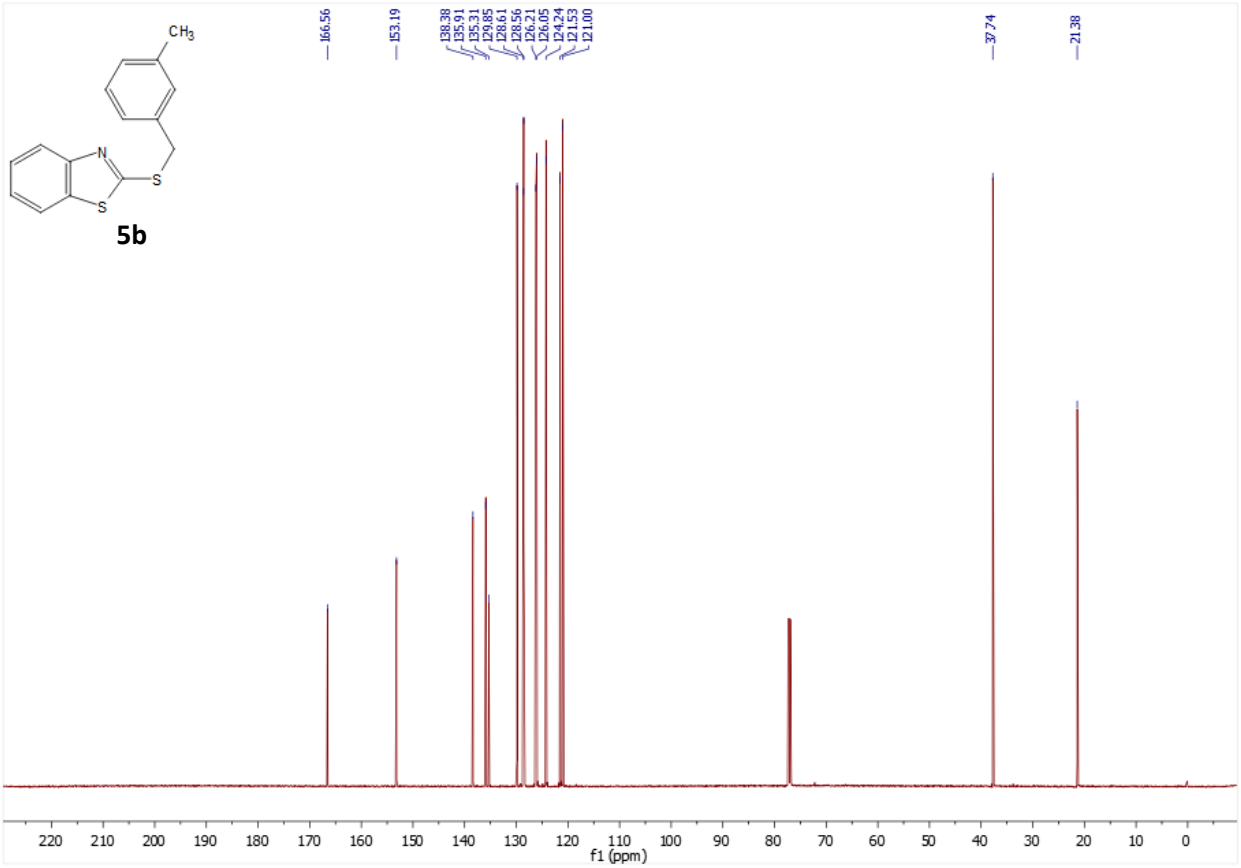

H3C
O
O
O
O
O
O
CH3
O
CH3
CH2
3.18
1.00
0.99
1.00
1.06
6.12
3.02
1.02
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

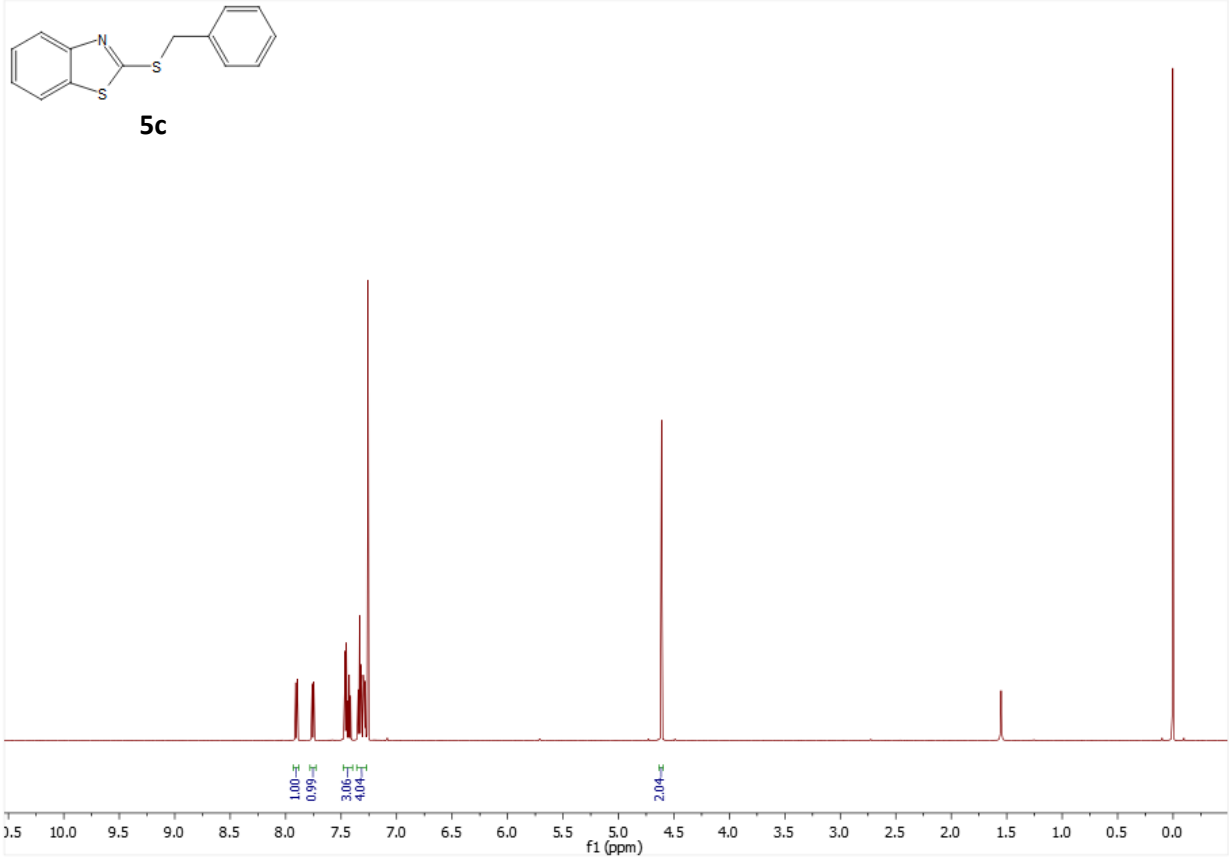
5a'

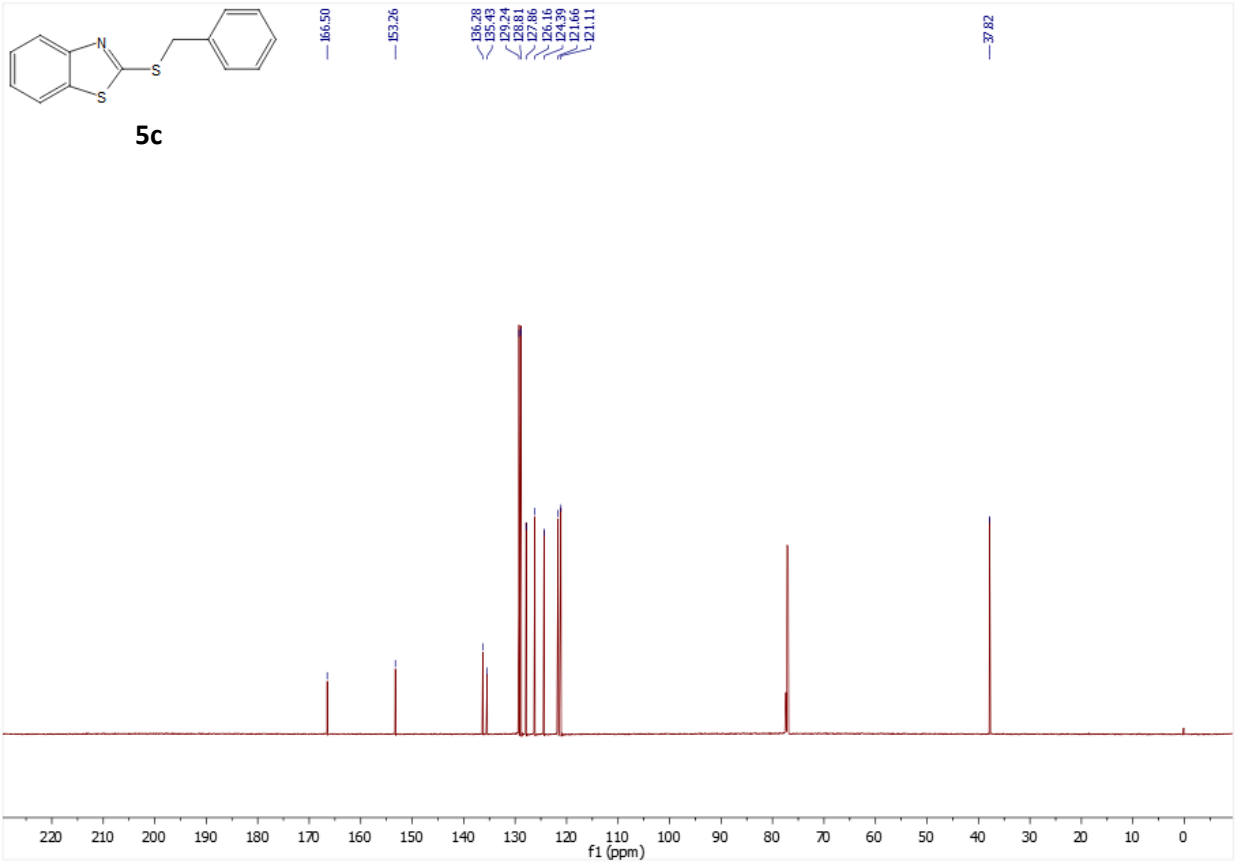

170.20
165.42
148.93
148.23
132.11
128.40
127.71
121.57
112.58
111.29
73.35
56.00
55.97
52.51
37.20
H3C
O
O
O
O
O
O
CH3
O
CH3
CH2
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

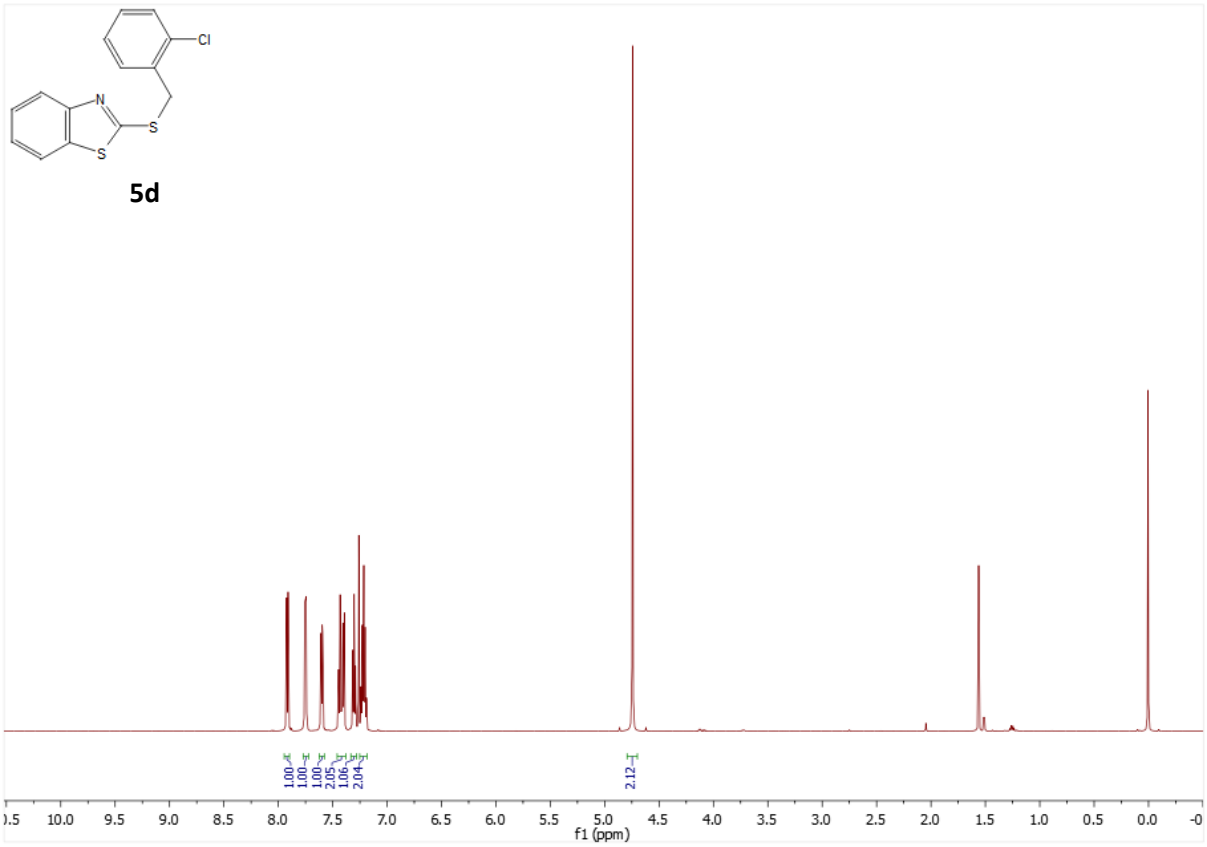
5a'

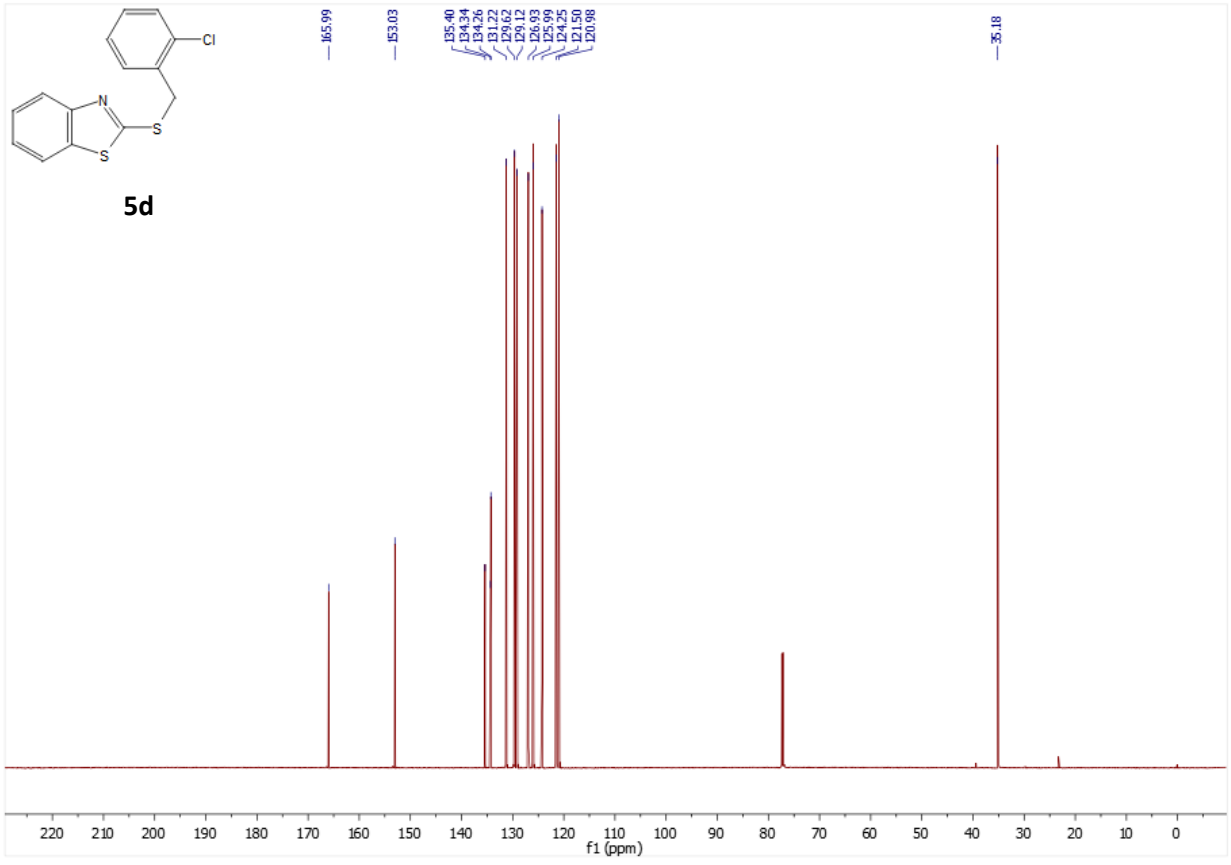

CH3
N
S
S
5b
0.96
0.97
0.99
1.02
1.00
0.24
0.66
1.05
0.98
2.04
3.03
f1 (ppm)

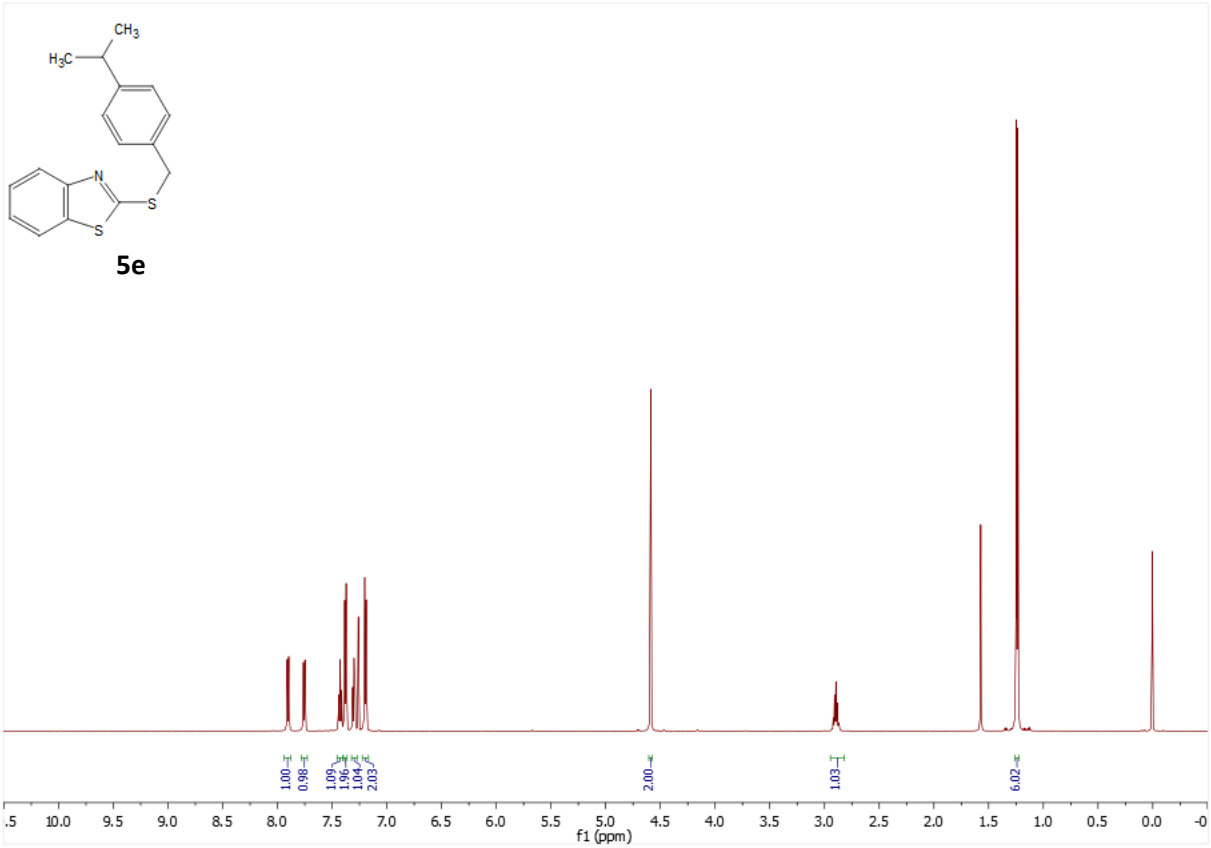

CH3
N
S
S
5b
166.56
153.19
138.38
135.91
135.31
129.85
128.61
128.56
126.21
126.05
124.24
121.53
121.00
37.74
21.38
f1 (ppm)

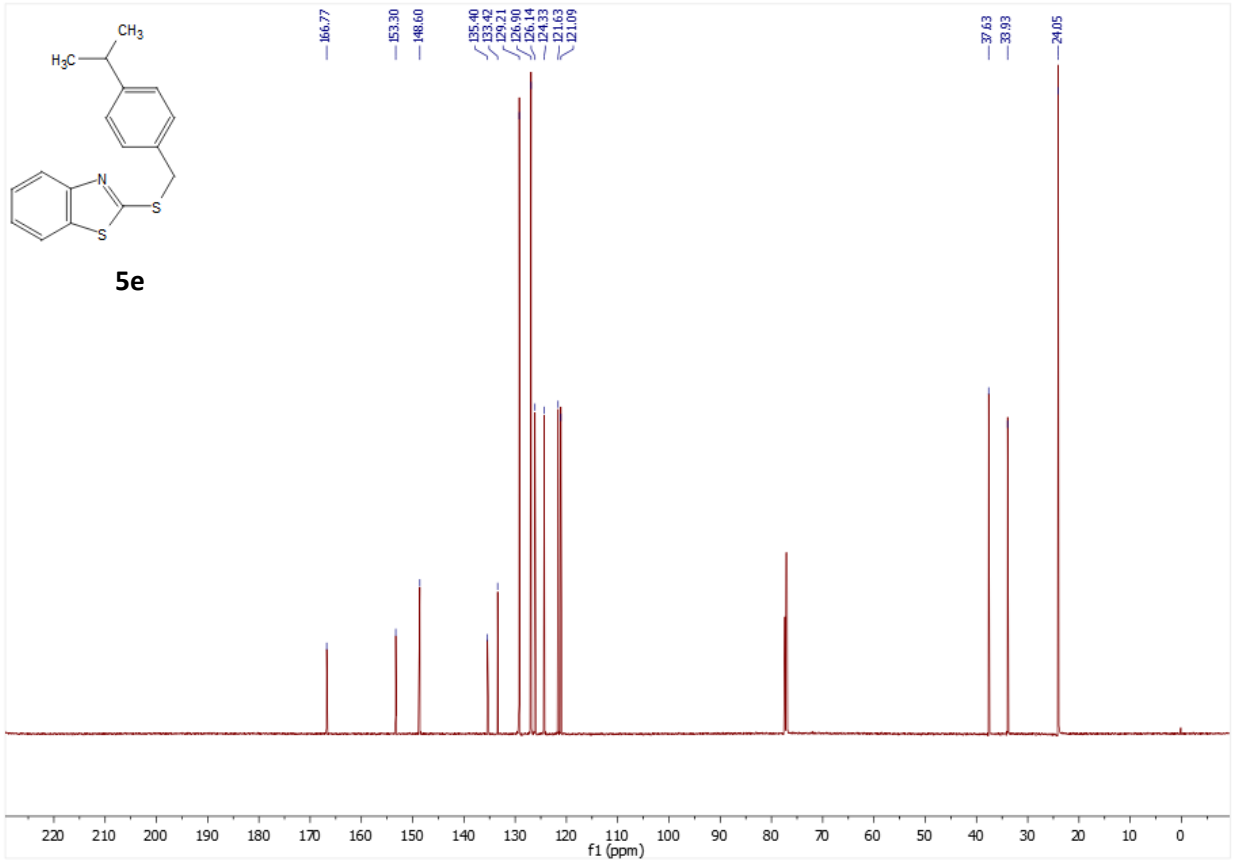

5c
1.00
0.99
3.06
4.04
2.04
f1 (ppm)

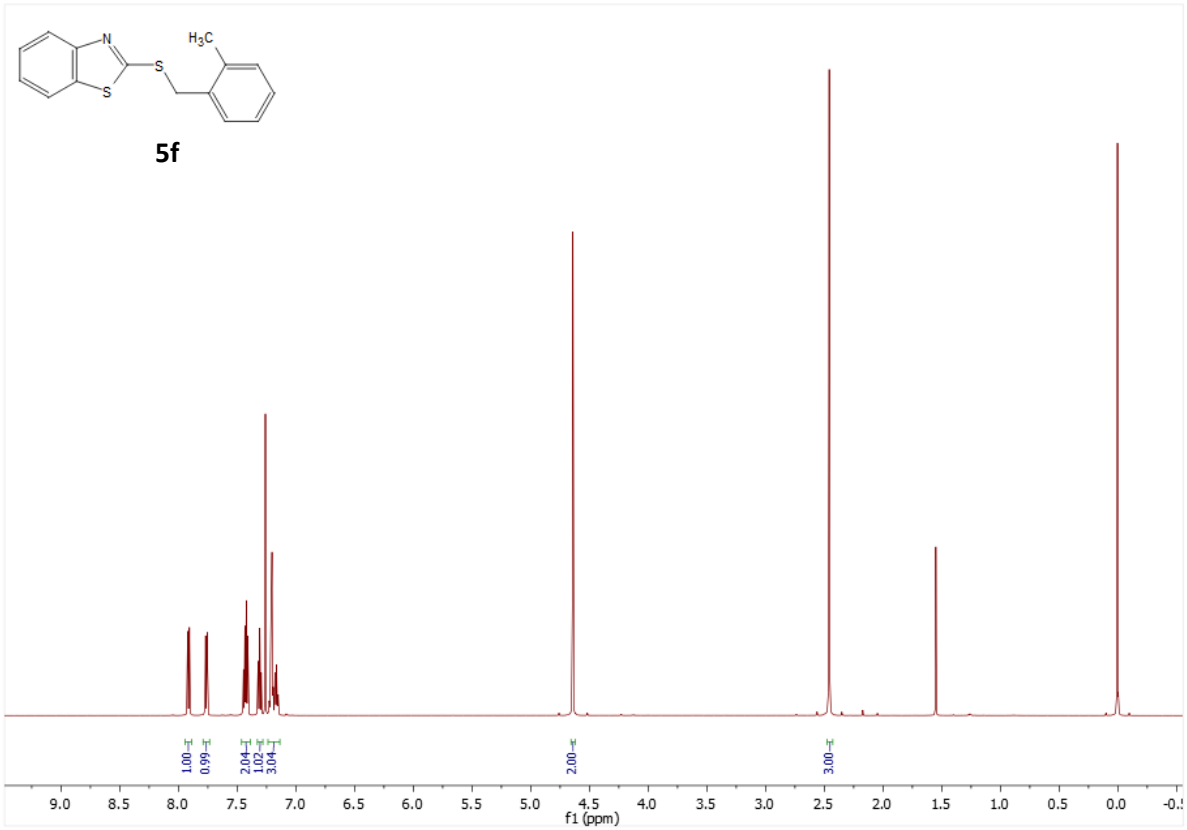

5c
166.50
153.26
136.28
135.43
129.24
128.81
127.86
126.16
124.39
121.66
121.11
37.82
f1 (ppm)

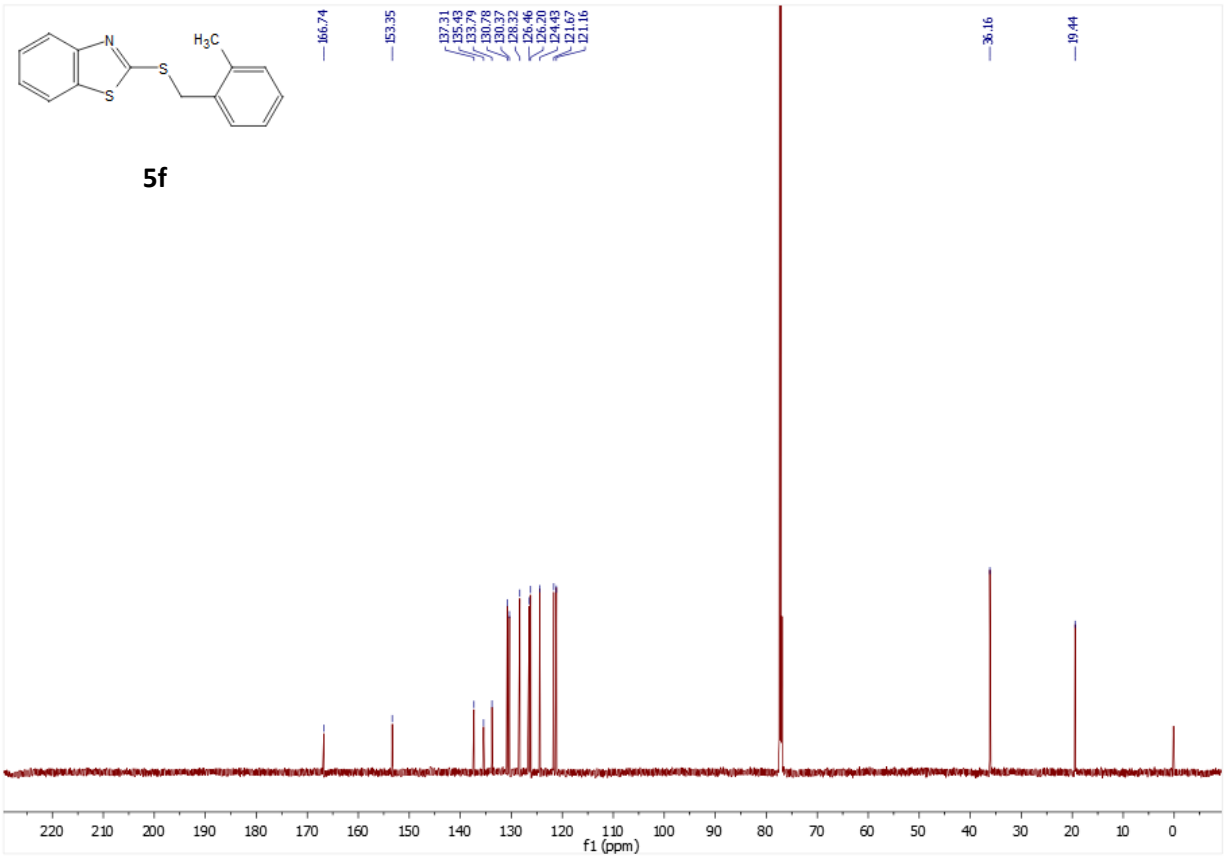

Cl
N
S
S
5d
1.00
1.00
1.00
2.05
1.06
2.04
2.12
f1 (ppm)

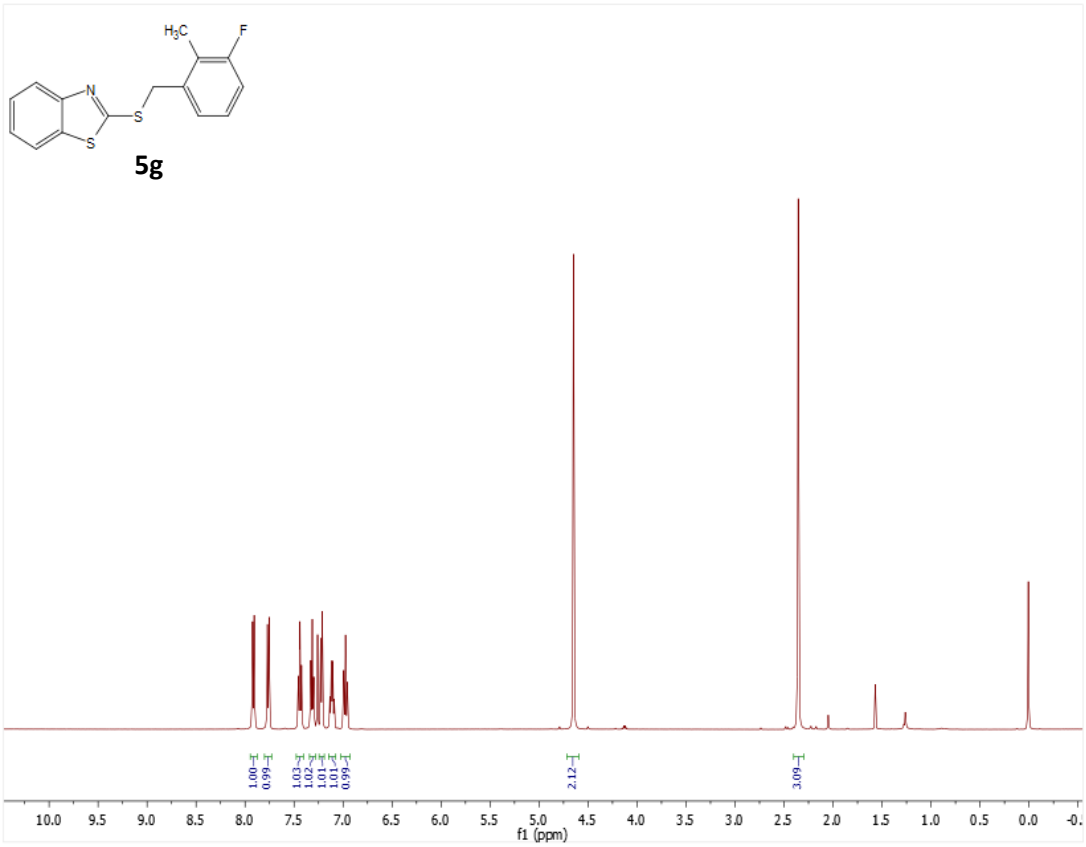

Cl
N
S
S
5d
165.99
153.03
135.40
134.34
134.26
131.22
129.62
129.12
126.93
125.99
124.25
121.50
120.98
35.18
f1 (ppm)

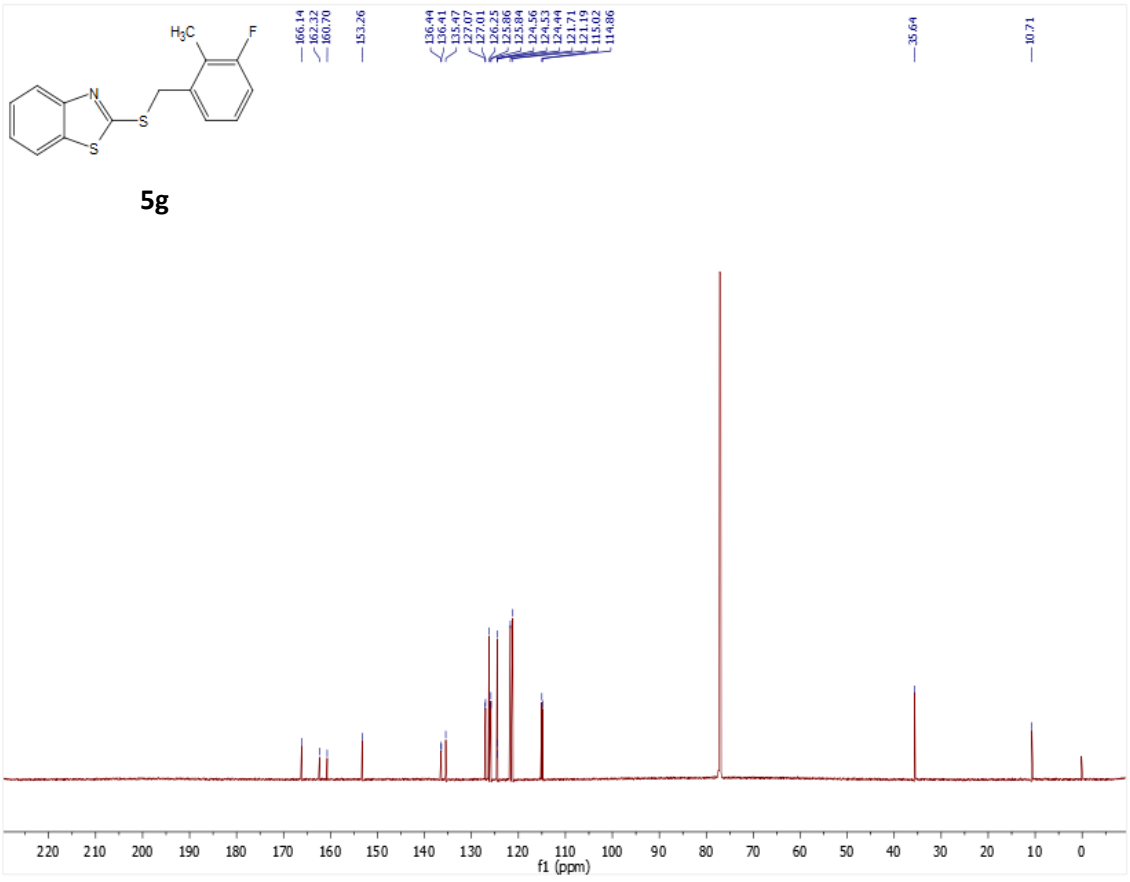

CH3
H3C
N
S
S
5e
1.00
0.98
1.09
1.96
1.04
2.03
2.00
1.03
6.02
f1 (ppm)

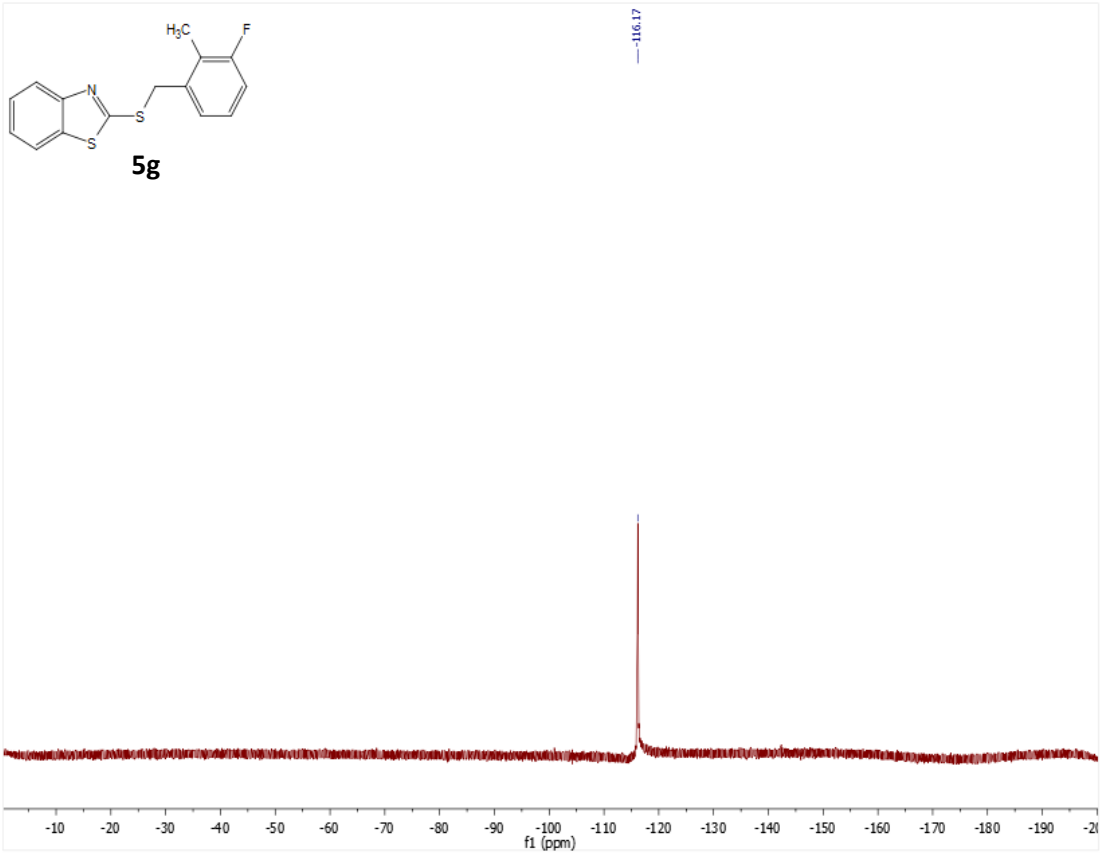

CH3
H3C
N
S
S
5e
166.77
153.30
148.60
135.40
133.42
129.21
126.90
126.14
124.33
121.63
121.09
37.63
33.93
24.05
f1 (ppm)


5f
1.00
0.99
2.04
1.02
3.04
2.00
3.00
f1 (ppm)

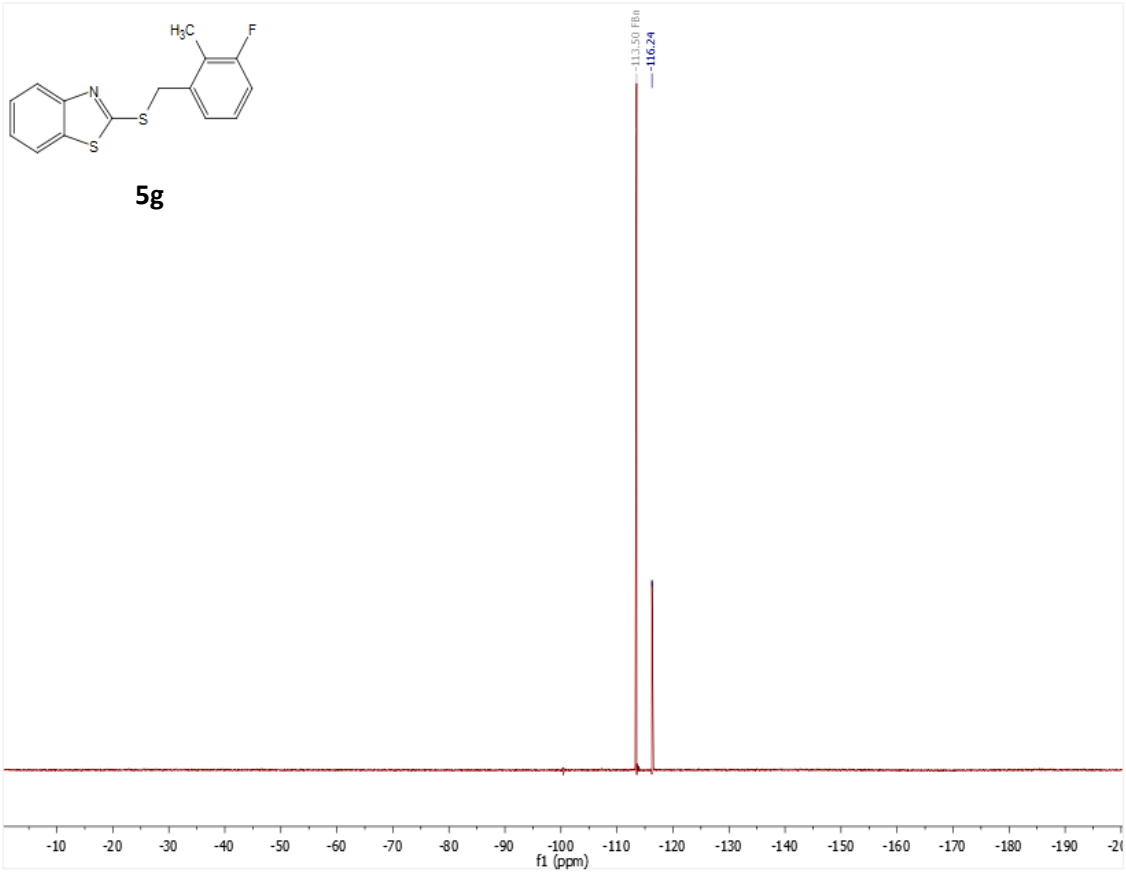

5f
166.74
153.35
137.31
135.43
133.79
130.78
130.37
128.32
126.46
126.20
124.43
121.67
121.16
36.16
19.44
f1 (ppm)


H3C
F
N
S
S
5g
1.00
0.99
1.03
1.02
1.01
1.01
0.99
2.12
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

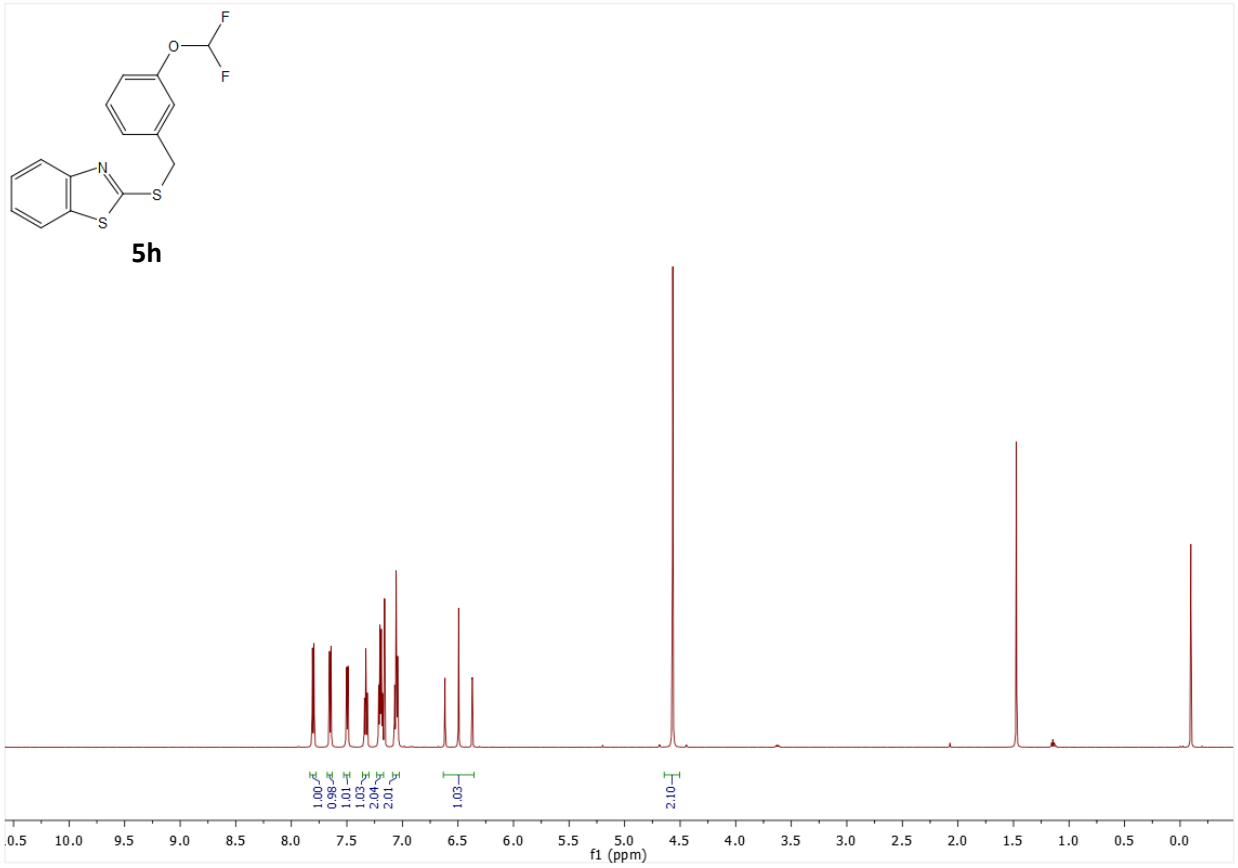

H3C
F
N
S
S
5g
166.14
162.32
160.70
153.26
136.44
136.41
135.47
127.07
127.01
126.25
125.86
125.84
124.56
124.53
124.44
121.71
121.19
115.02
114.86
35.64
10.71
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

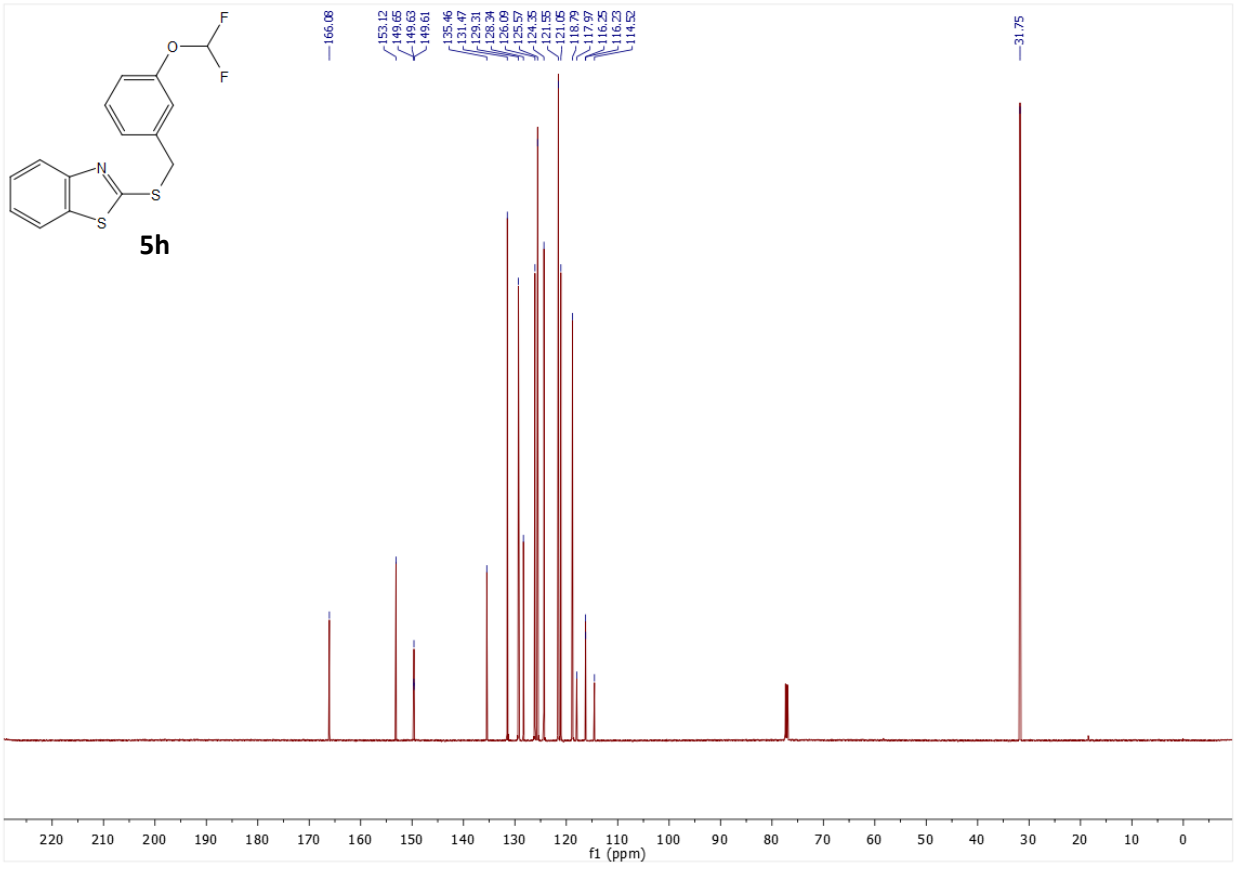

H3C
F
N
S
S
-116.17
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

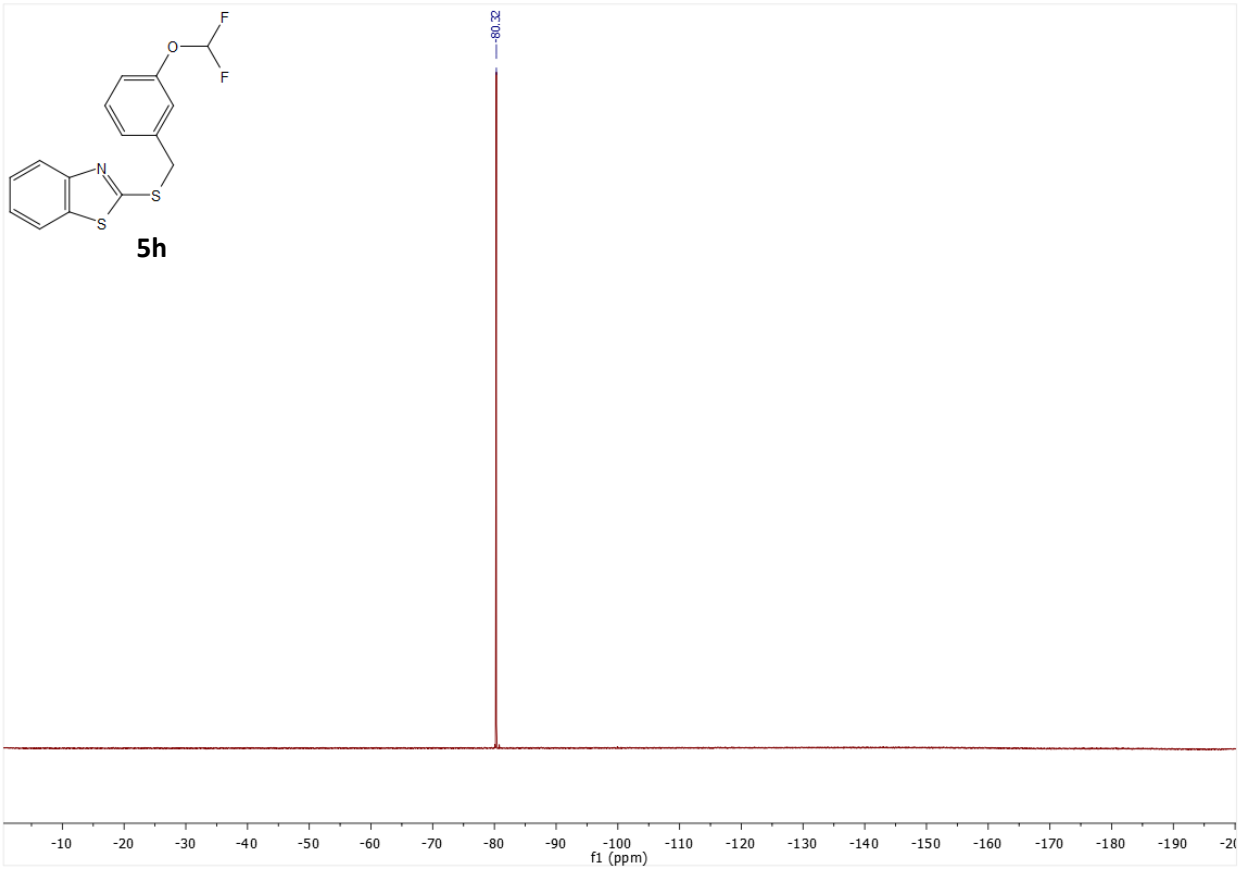
5g


H3C
F
N
S
S
-113.50 FBn
-116.24
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

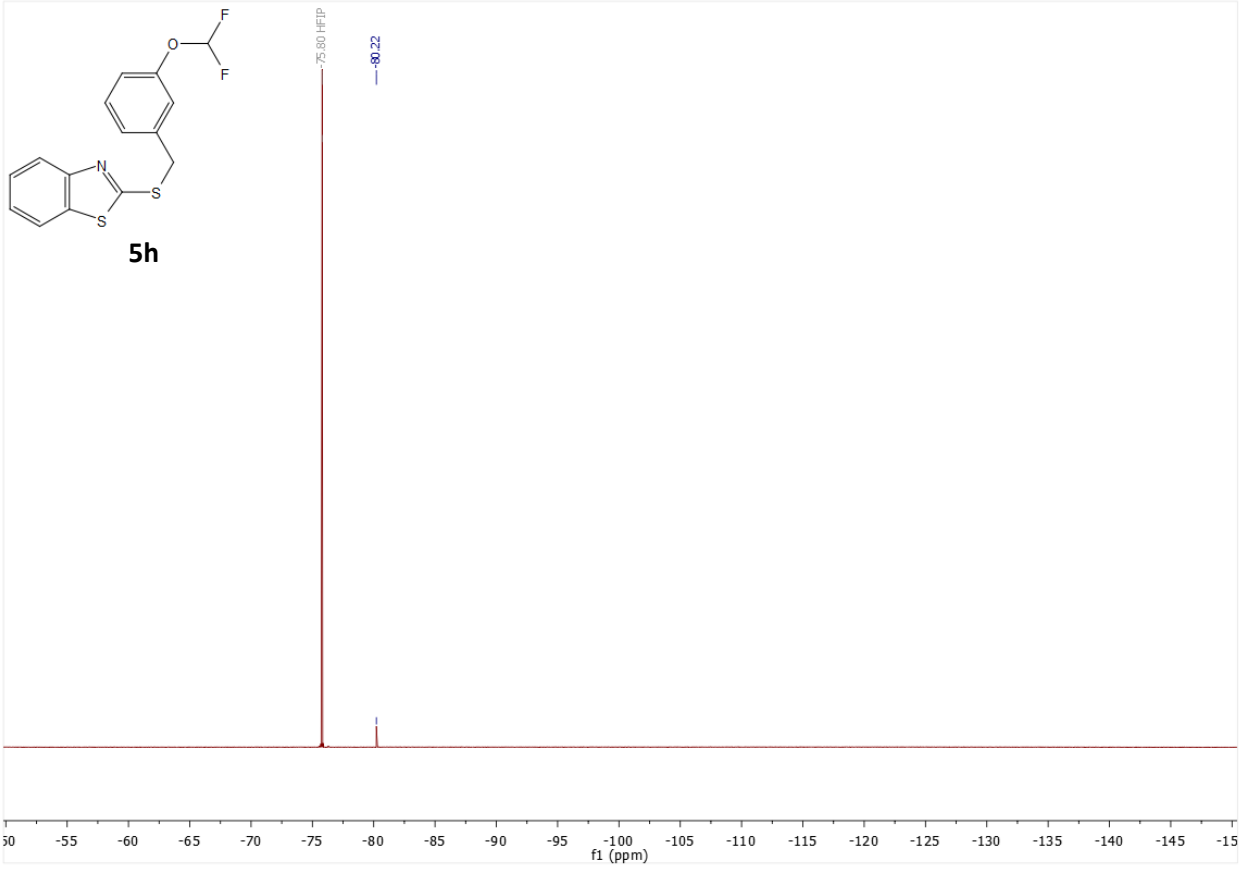
5g


F
O
F
N
S
S
5h
1.00
0.98
1.01
1.03
2.04
2.01
1.03
2.10
f1 (ppm)

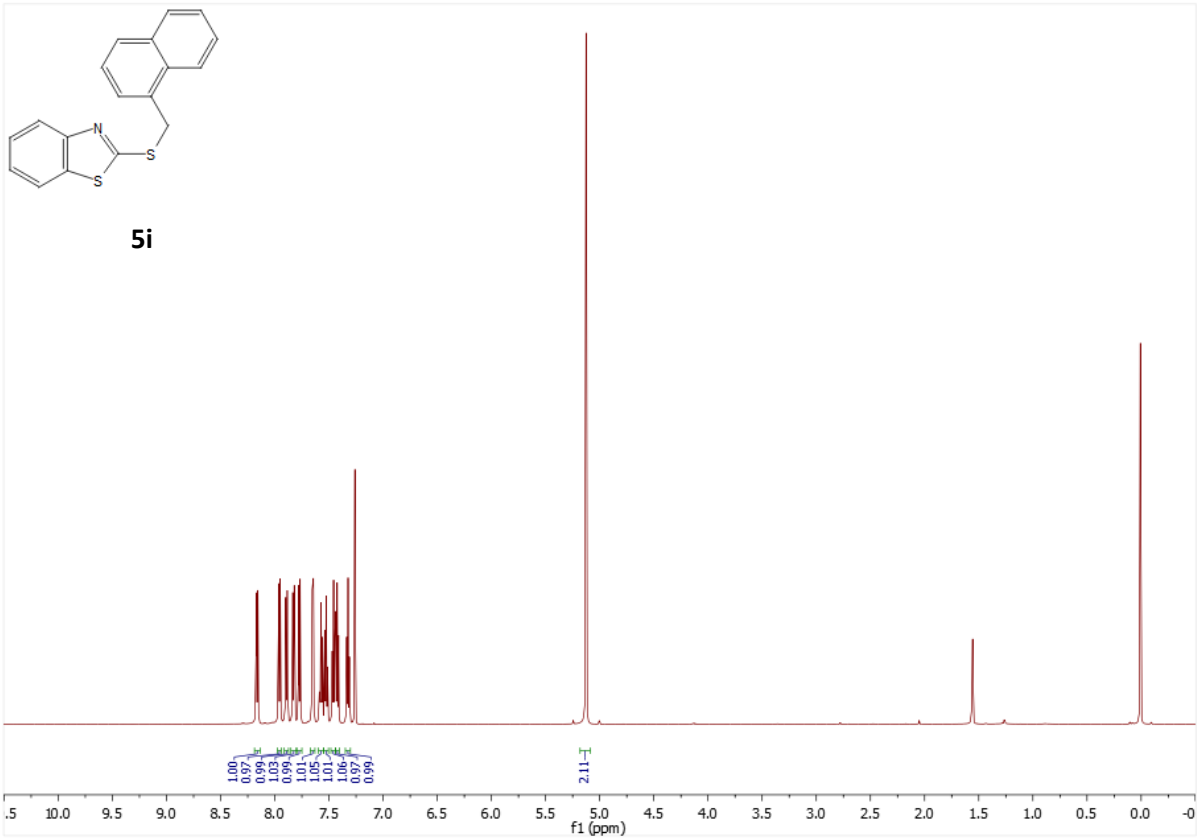

F
O
F
N
S
S
5h
166.08
153.12
149.65
149.63
149.61
135.46
131.47
129.31
128.34
126.09
125.57
124.35
121.55
121.05
118.79
117.97
116.25
116.23
114.52
31.75
f1 (ppm)

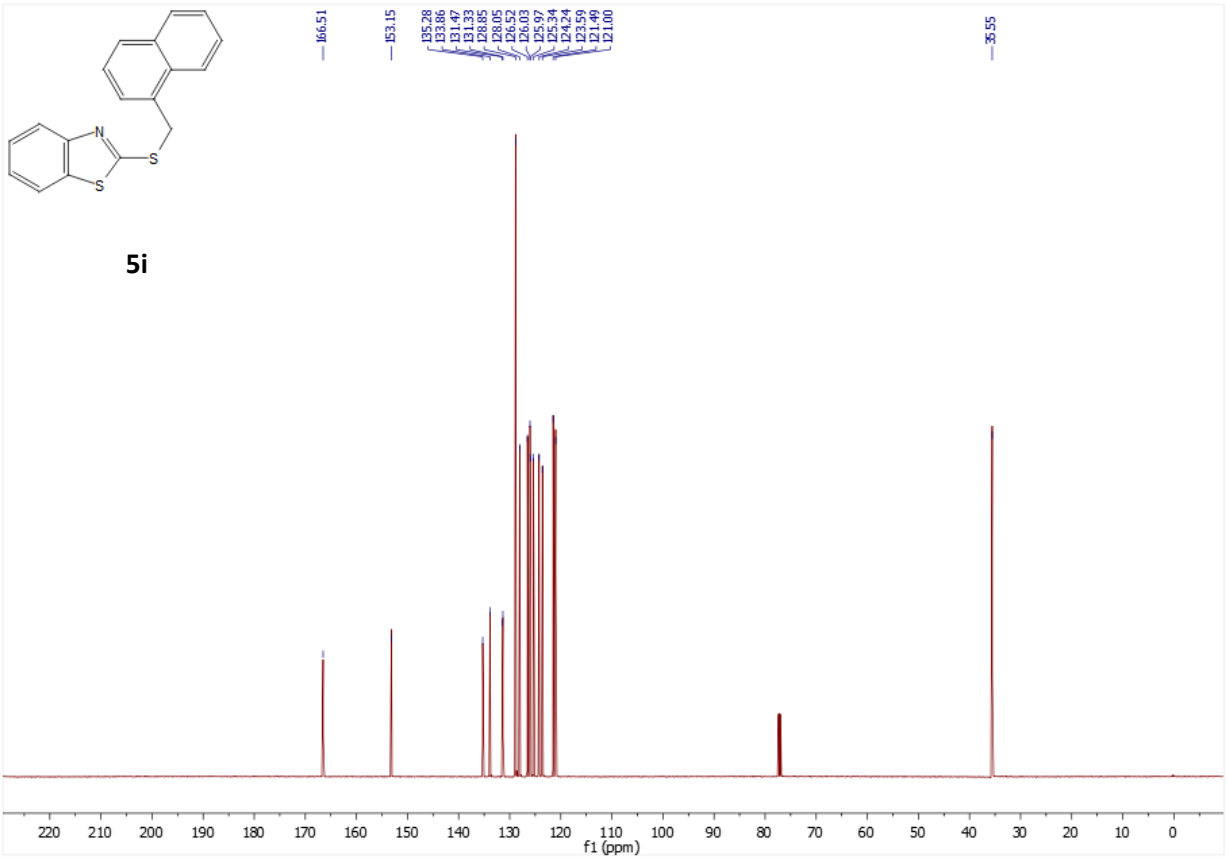

F
O
F
N
S
S
-80.32
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

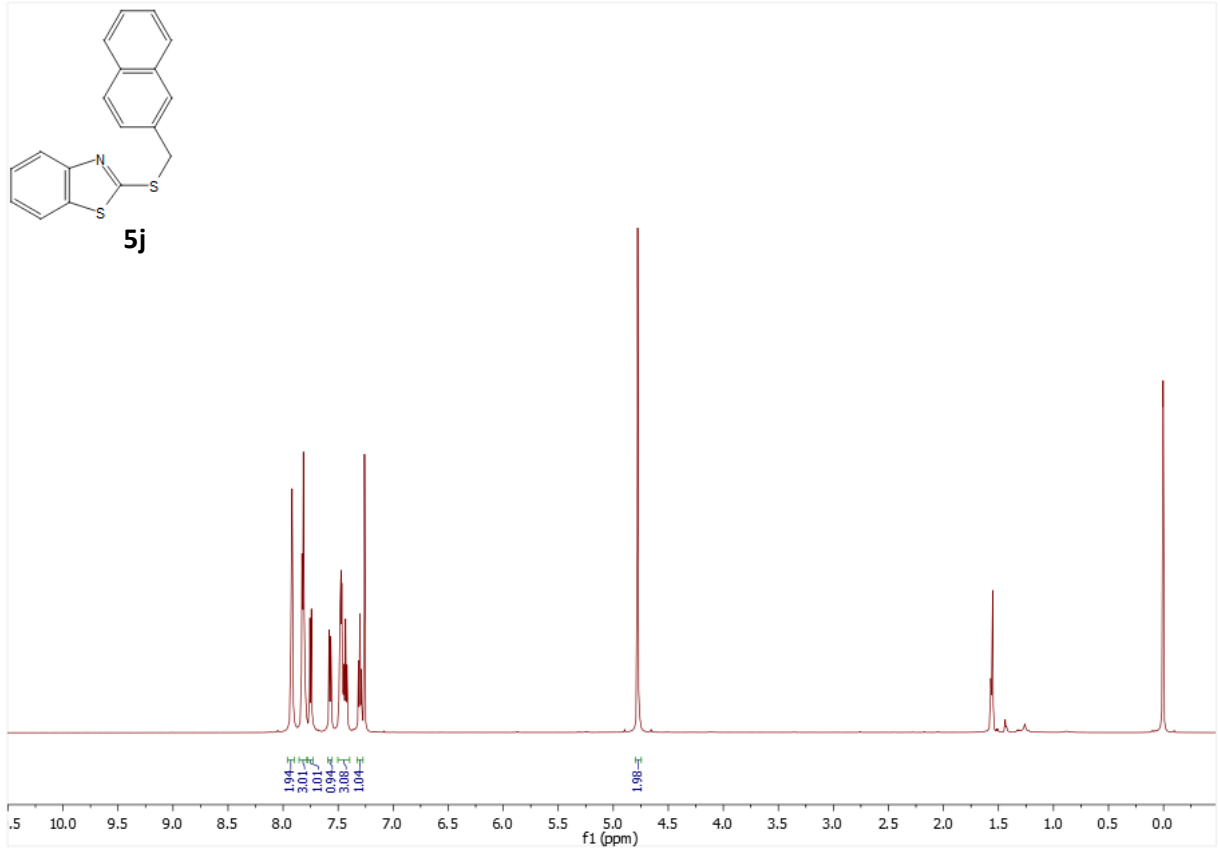
5h

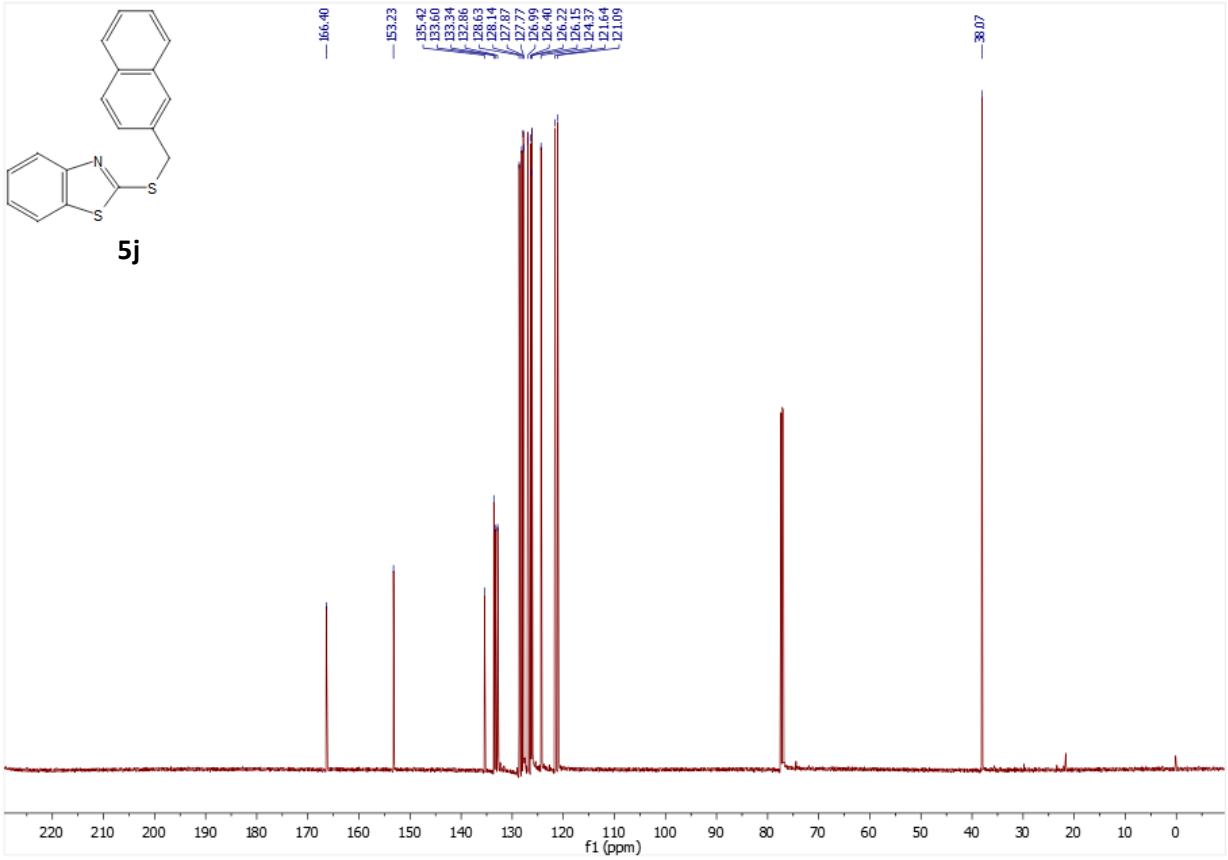

F
O
F
N
S
S
-75.80 HFIP
-80.22
-55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145
f1 (ppm)

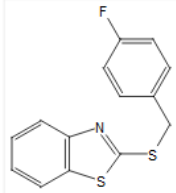
5h


5i
1.00
0.97
0.99
1.03
0.99
1.01
1.05
1.01
1.06
0.97
0.99
2.11
f1 (ppm)

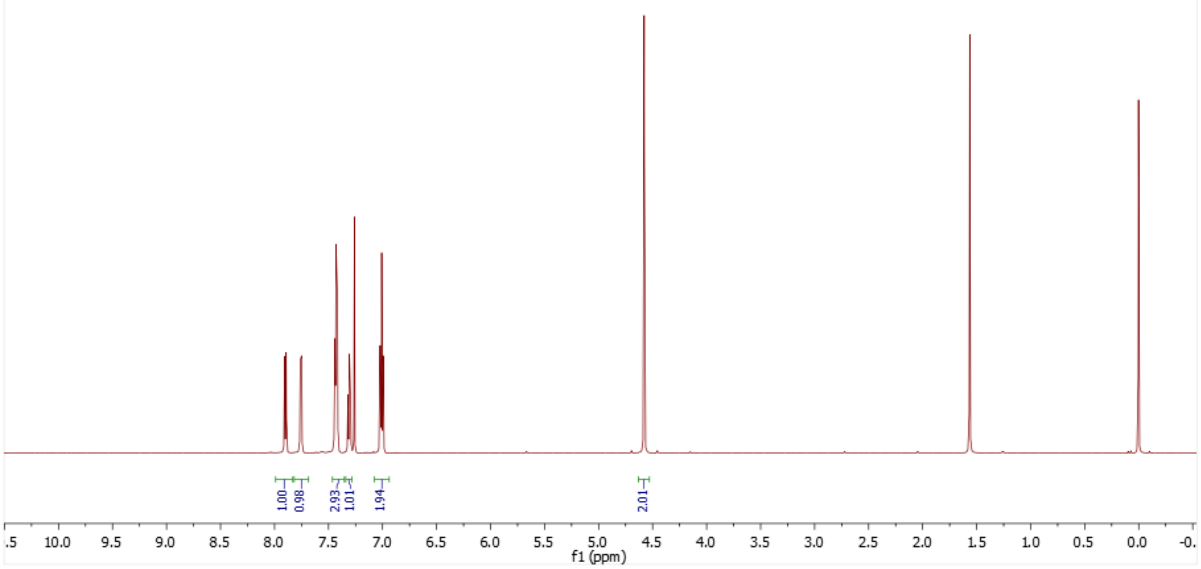

5i
166.51
153.15
135.28
133.86
131.47
131.33
128.85
128.05
126.52
126.03
125.97
125.34
124.24
123.59
121.49
121.00
35.55
f1 (ppm)

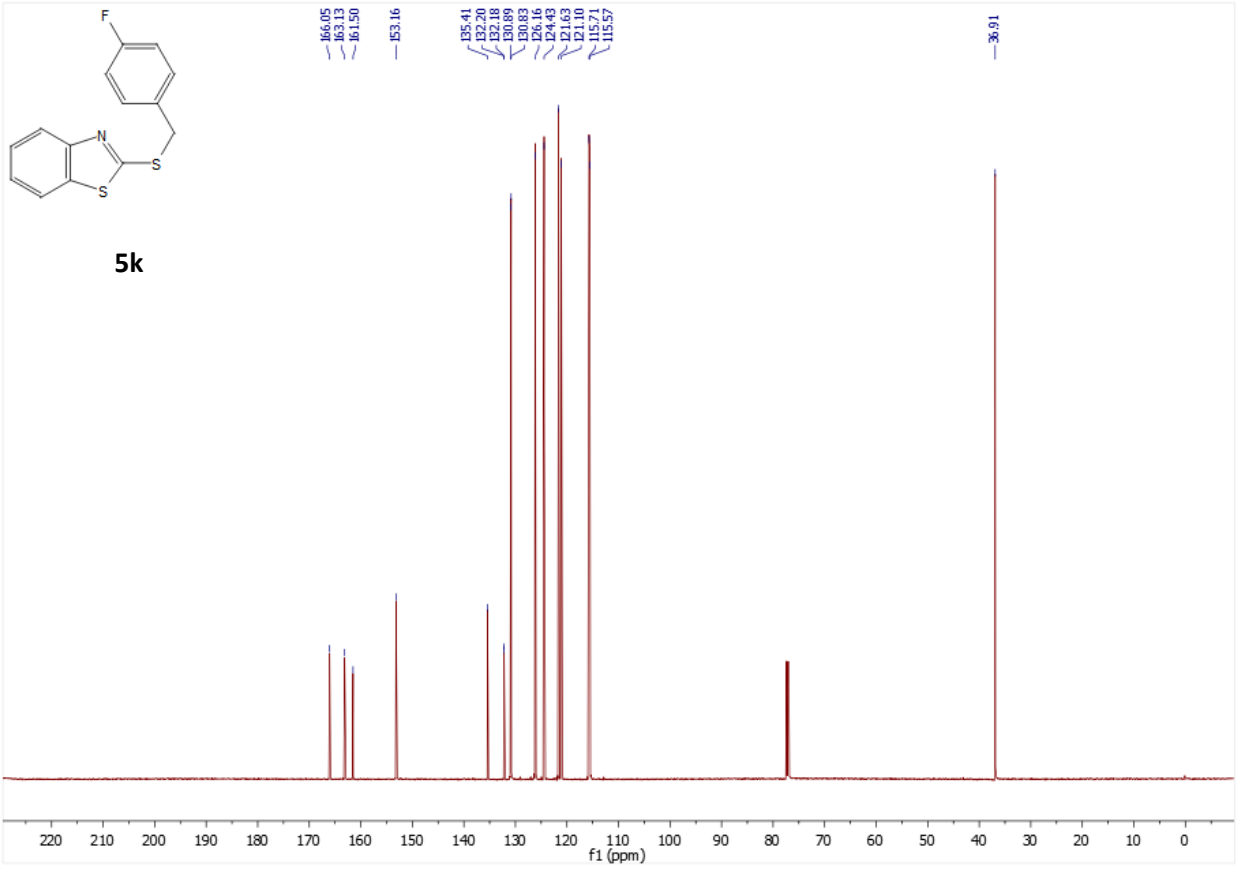

5j
1.94
3.01
1.01
0.94
3.08
1.04
1.98
f1 (ppm)


5j
166.40
153.23
135.42
133.60
133.34
132.86
128.63
128.14
127.87
127.77
126.99
126.40
126.22
126.15
124.37
121.64
121.09
38.07
f1 (ppm)

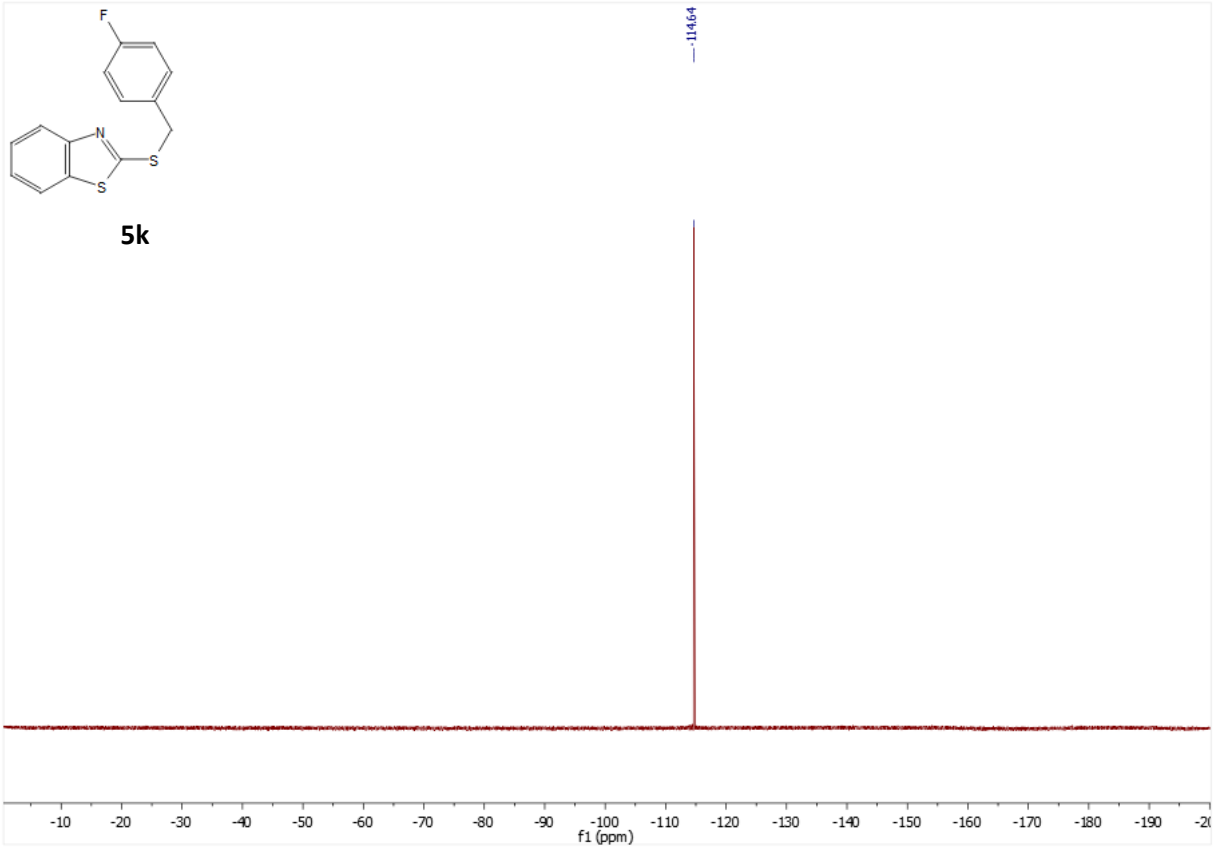

F
N
S
S

5k

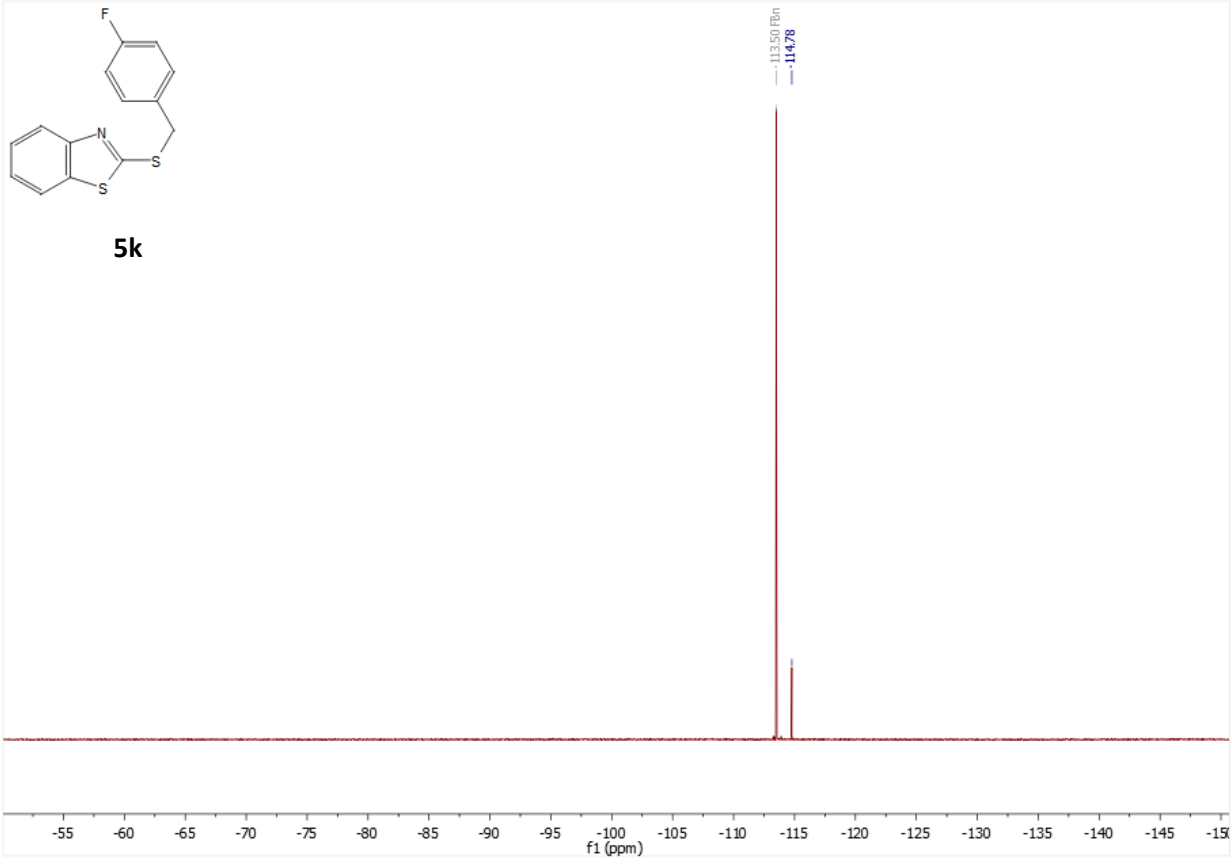

1.00
0.98
2.93
1.01
1.94
2.01
f1 (ppm)


F
N
S
S
166.05
163.13
161.50
153.16
135.41
132.20
132.18
130.89
130.83
126.16
124.43
121.63
121.10
115.71
115.57
36.91
f1 (ppm)

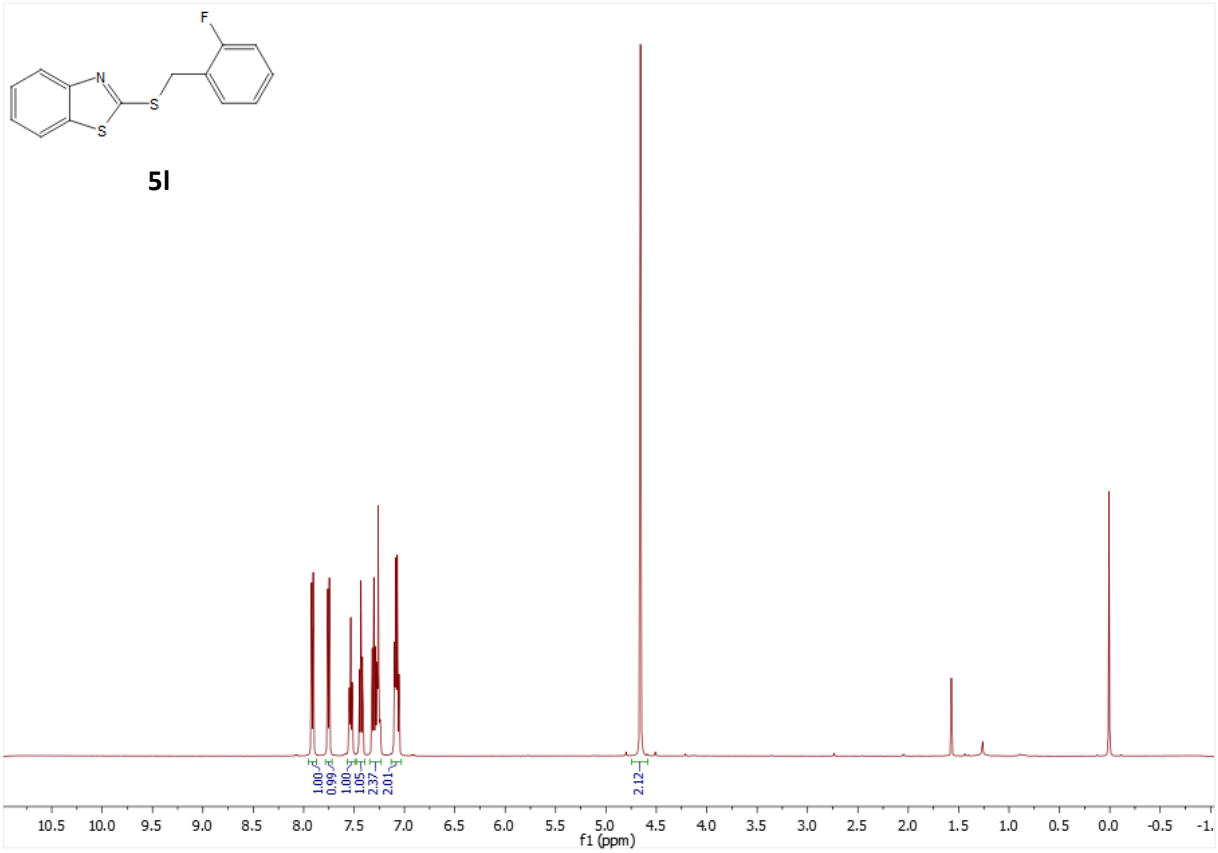
5k

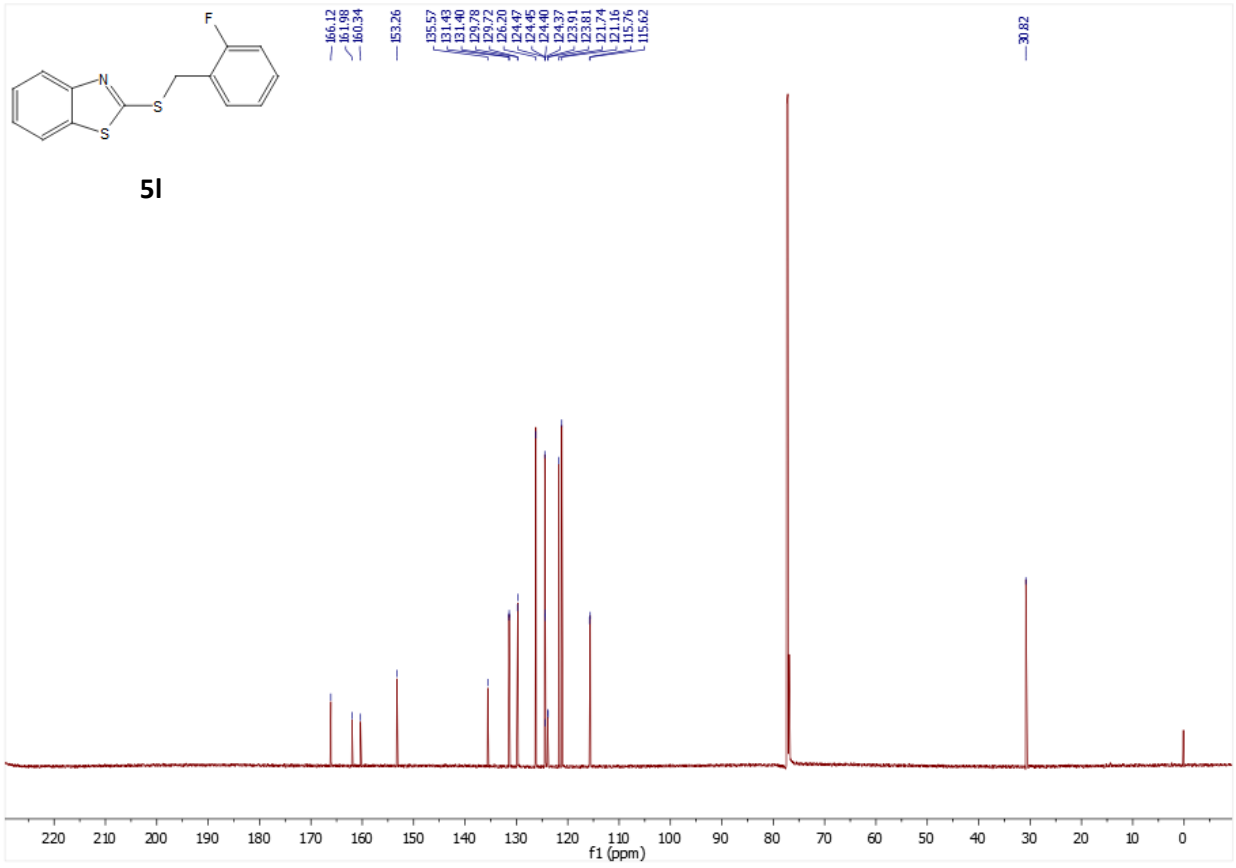

F
N
S
S
-114.64
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

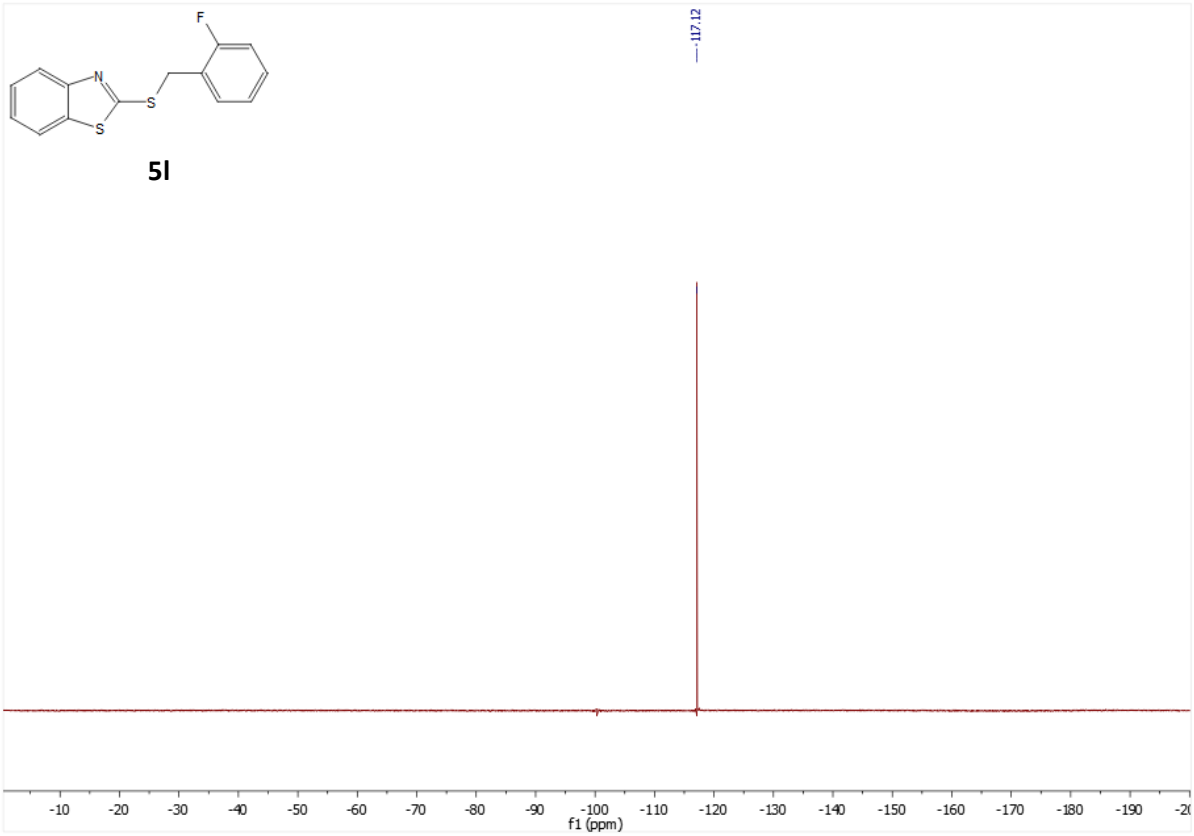
5k


F
N
S
S
-113.50 FBn
-114.78
-55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145
f1 (ppm)

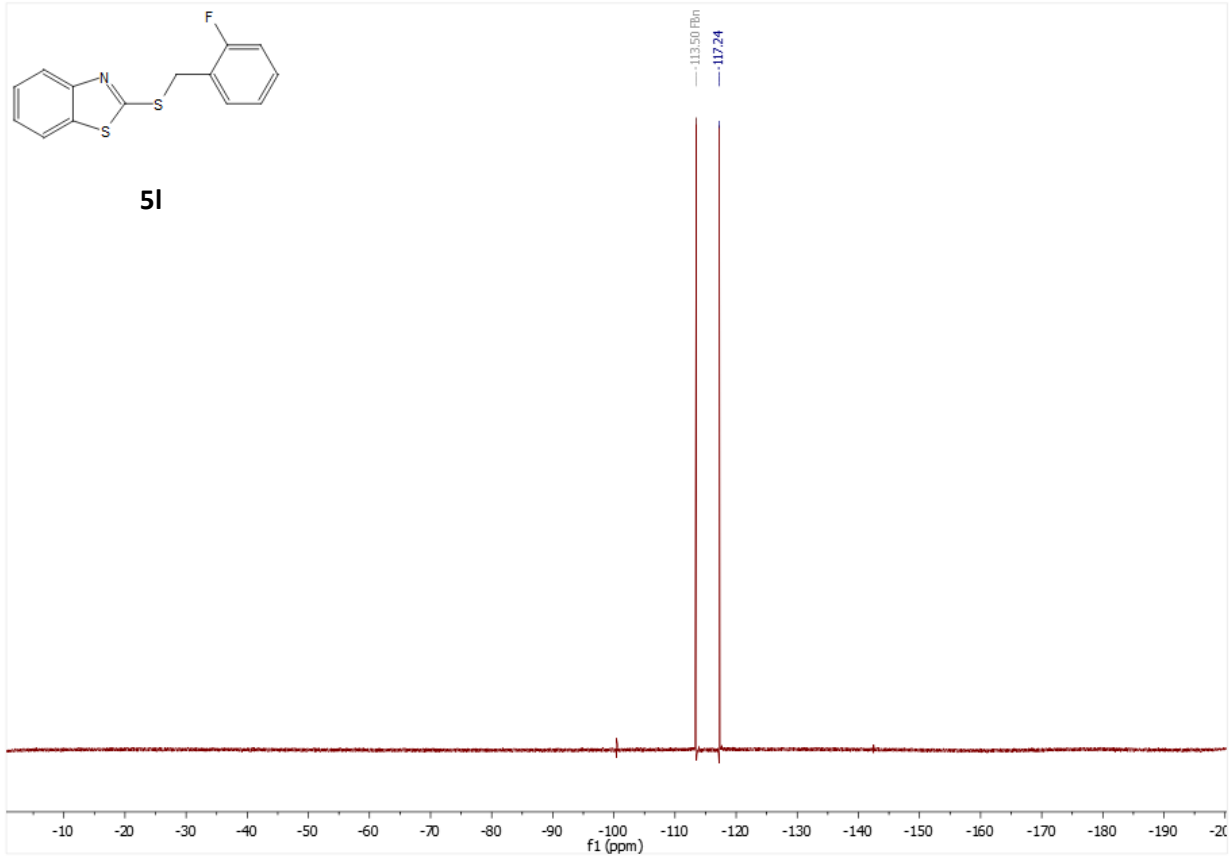
5k


F
N
S
S
5l
1.00
0.99
1.00
1.05
2.37
2.01
2.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

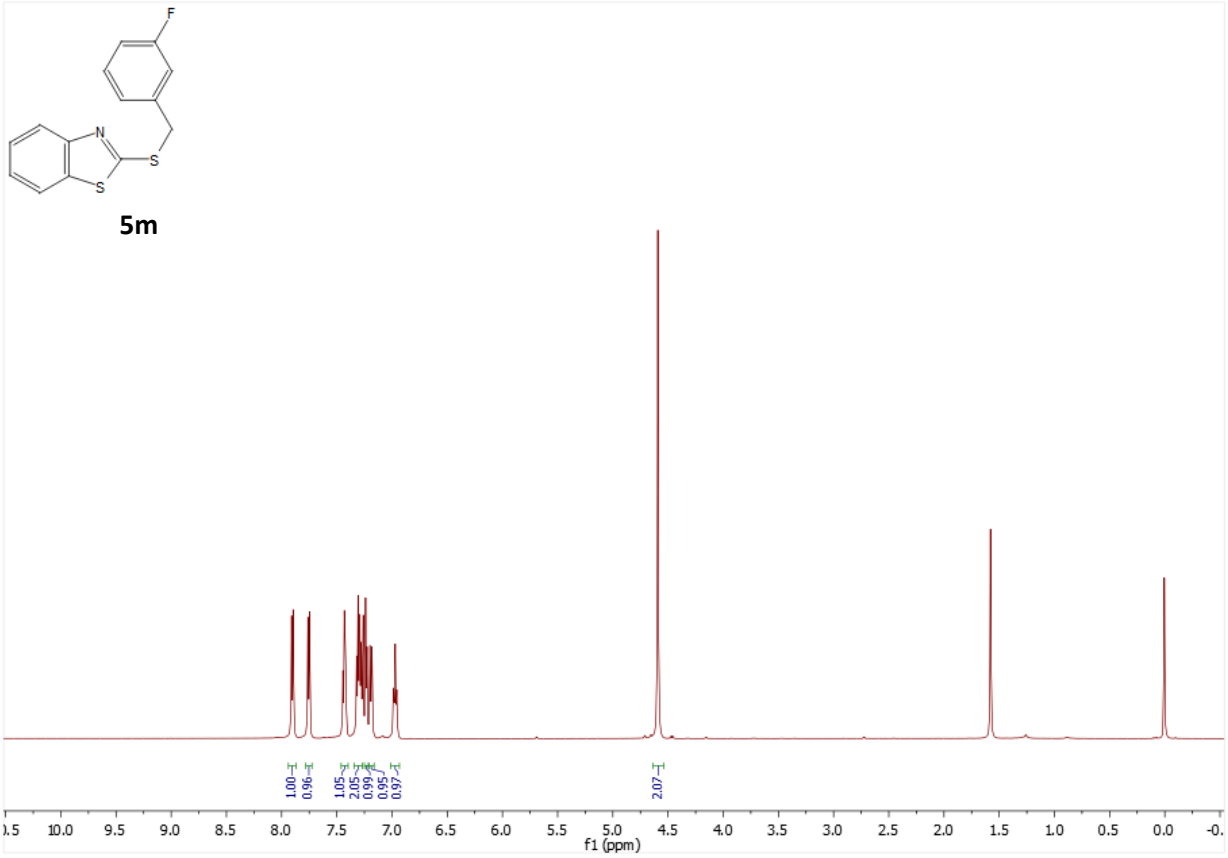

F
N
S
S
5l
166.12
161.98
160.34
153.26
135.57
131.43
131.40
129.78
129.72
126.20
124.47
124.45
124.40
124.37
123.91
123.81
121.74
121.16
115.76
115.62
30.82
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

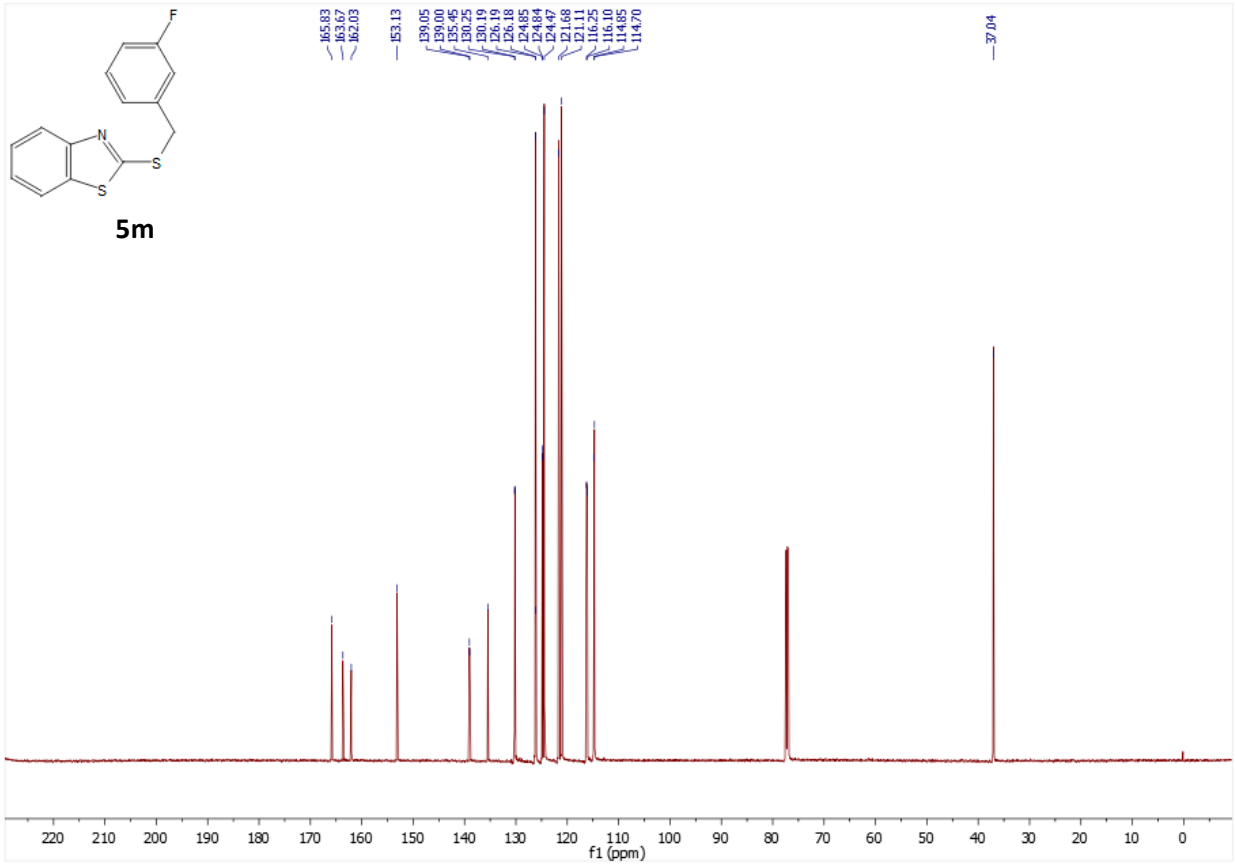

F
N
S
S
-117.12
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

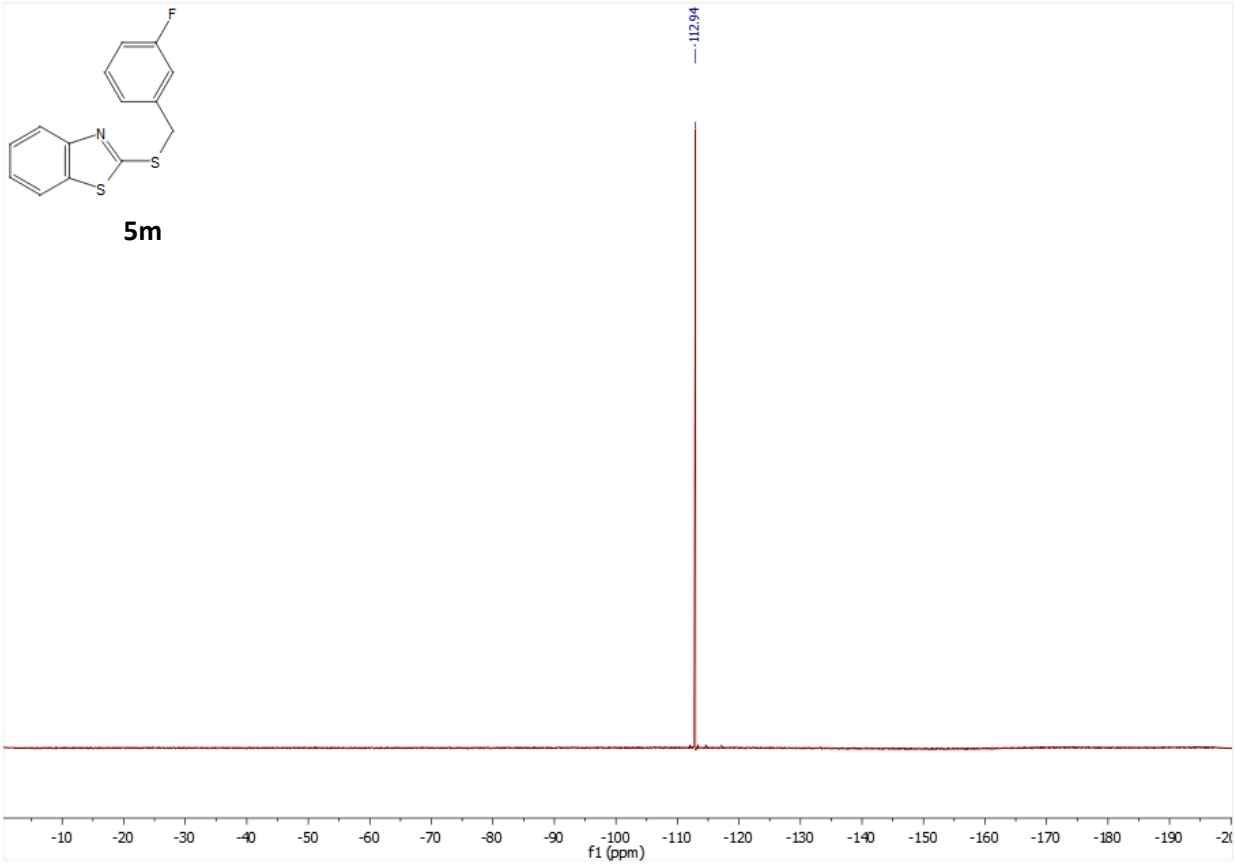
5l


F
N
S
S
-113.50 FBn
-117.24
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

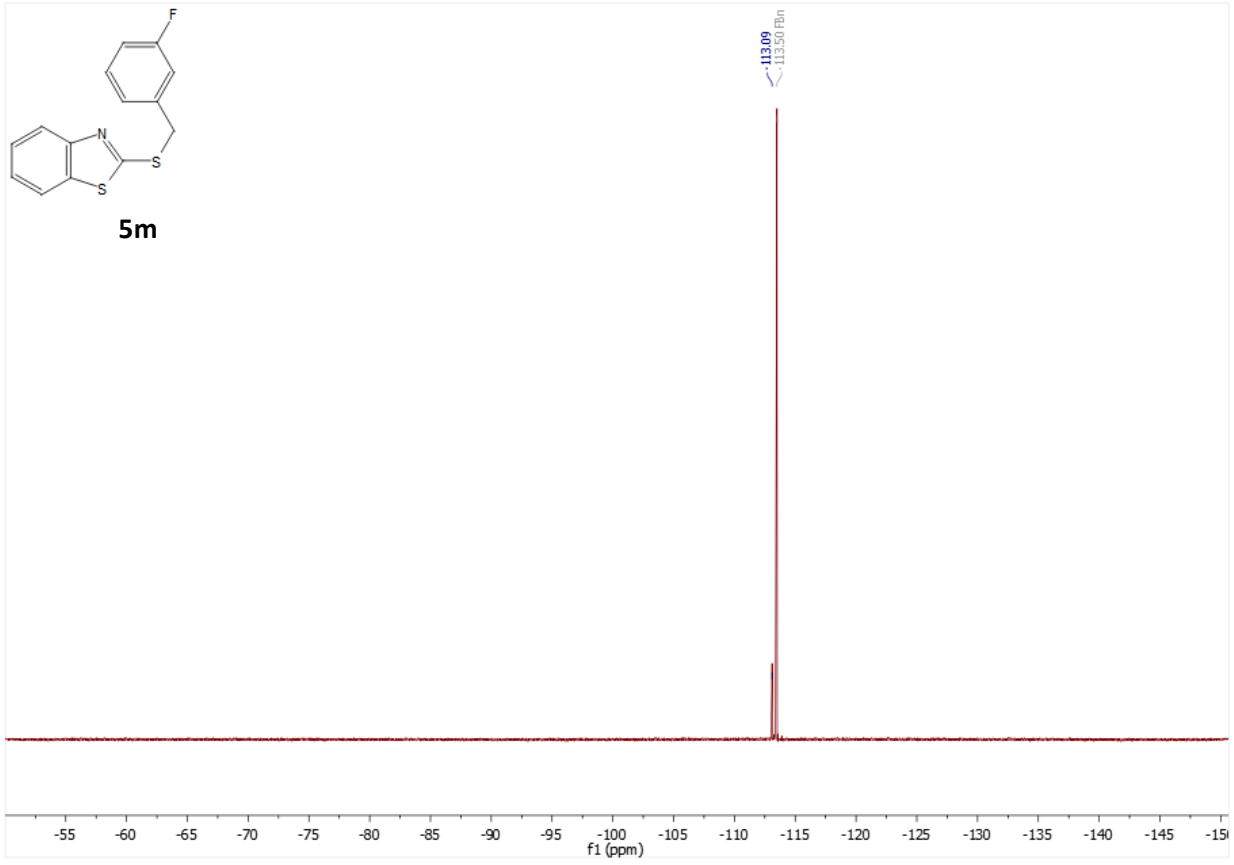
5l


F
N
S
S
5m
1.00
0.96
1.05
2.05
0.99
0.95
0.97
2.07
f1 (ppm)

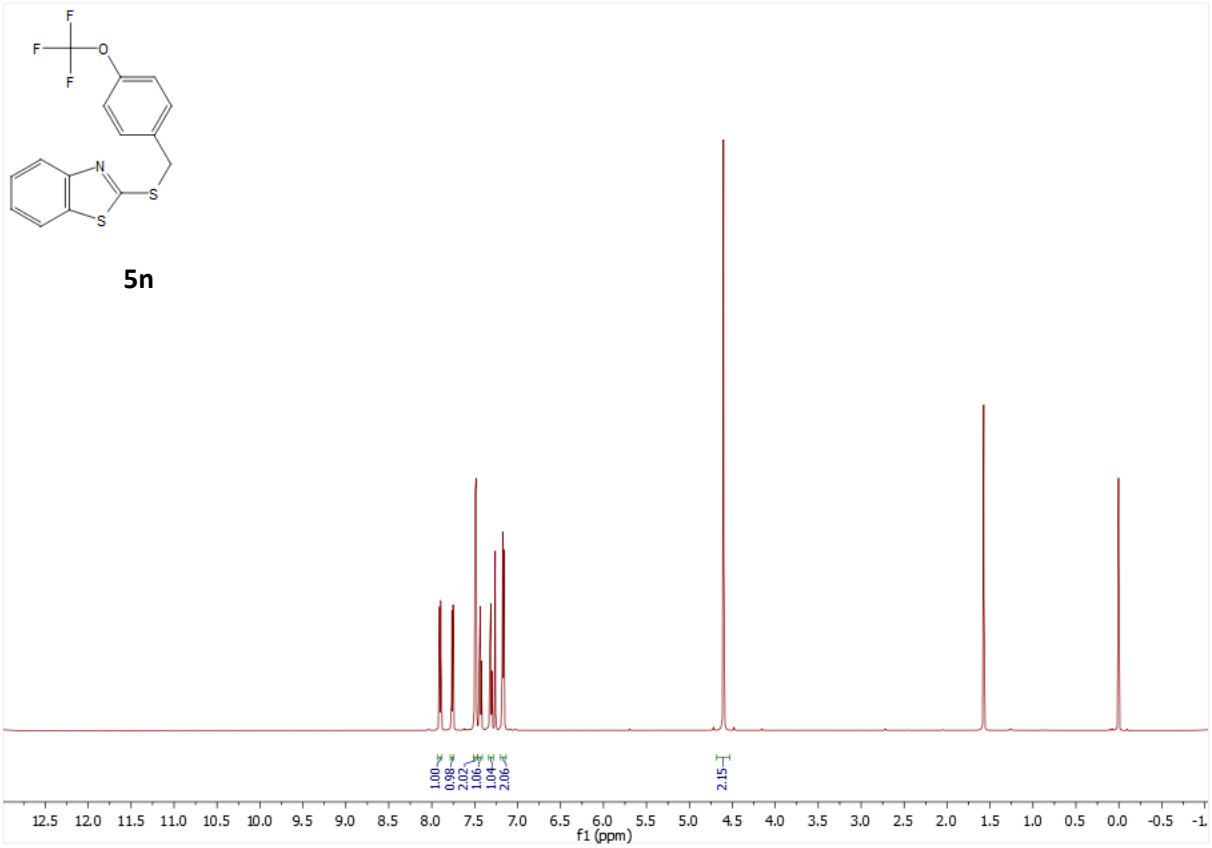

F
N
S
S
5m
165.83
163.67
162.03
153.13
139.05
139.00
135.45
130.25
130.19
126.19
126.18
124.85
124.84
124.47
121.68
121.11
116.25
116.10
114.85
114.70
37.04
f1 (ppm)

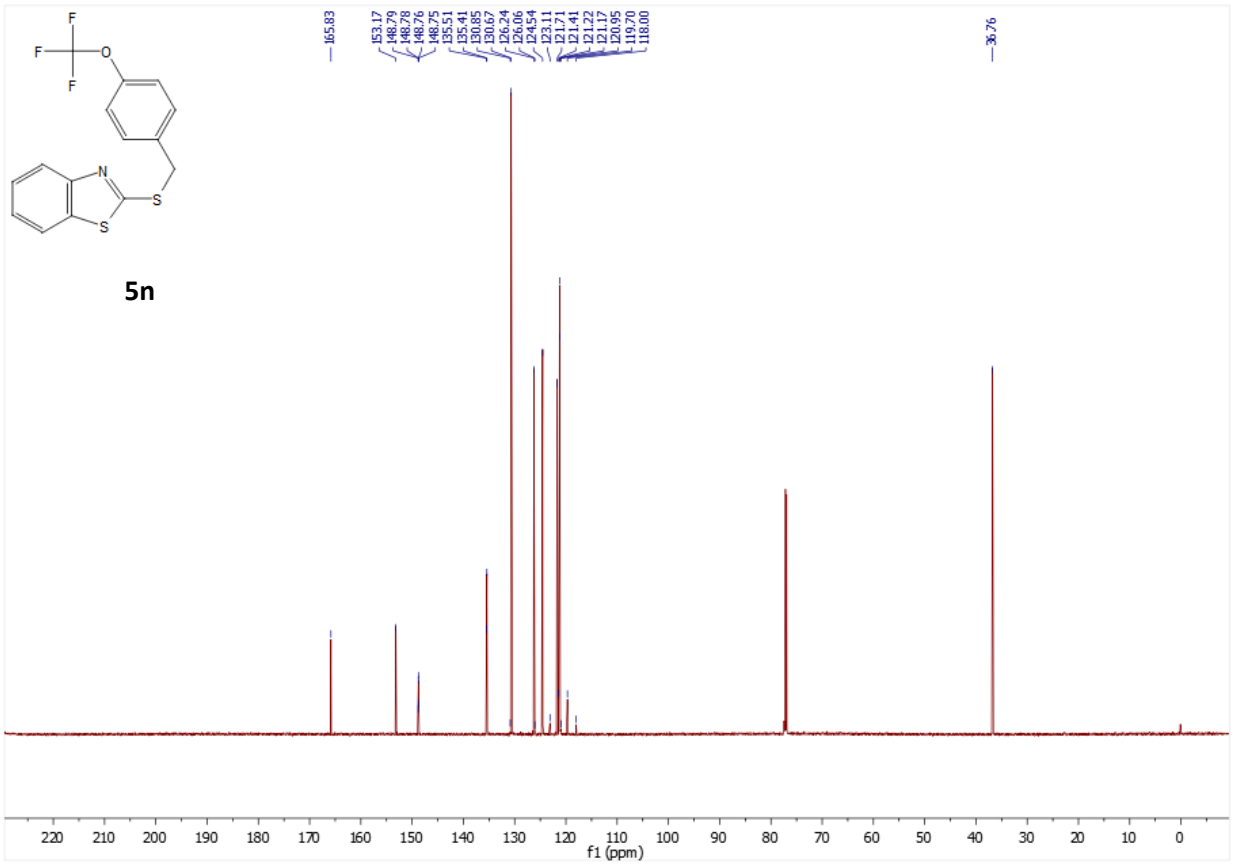

F
N
S
S
-112.94
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

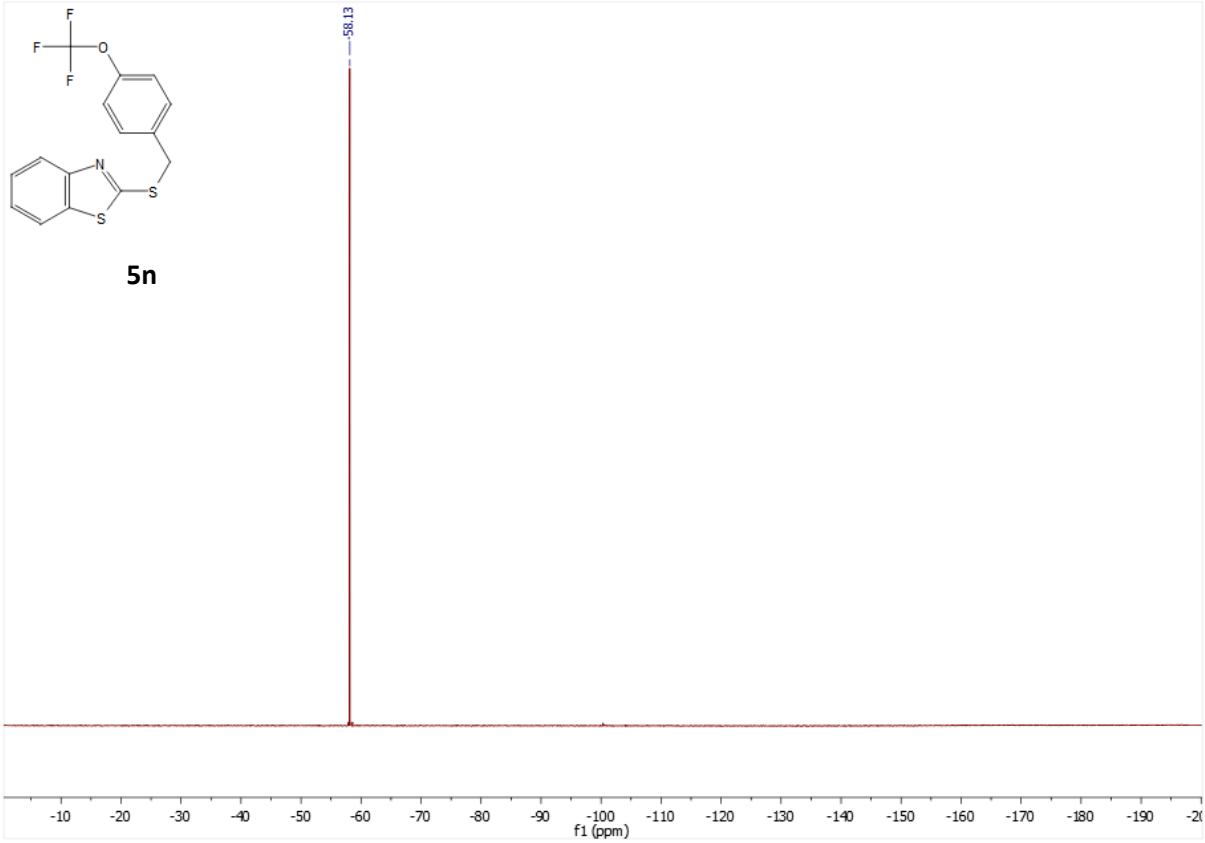
5m


F
N
S
S
113.09
113.50 fBn
-55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145
f1 (ppm)

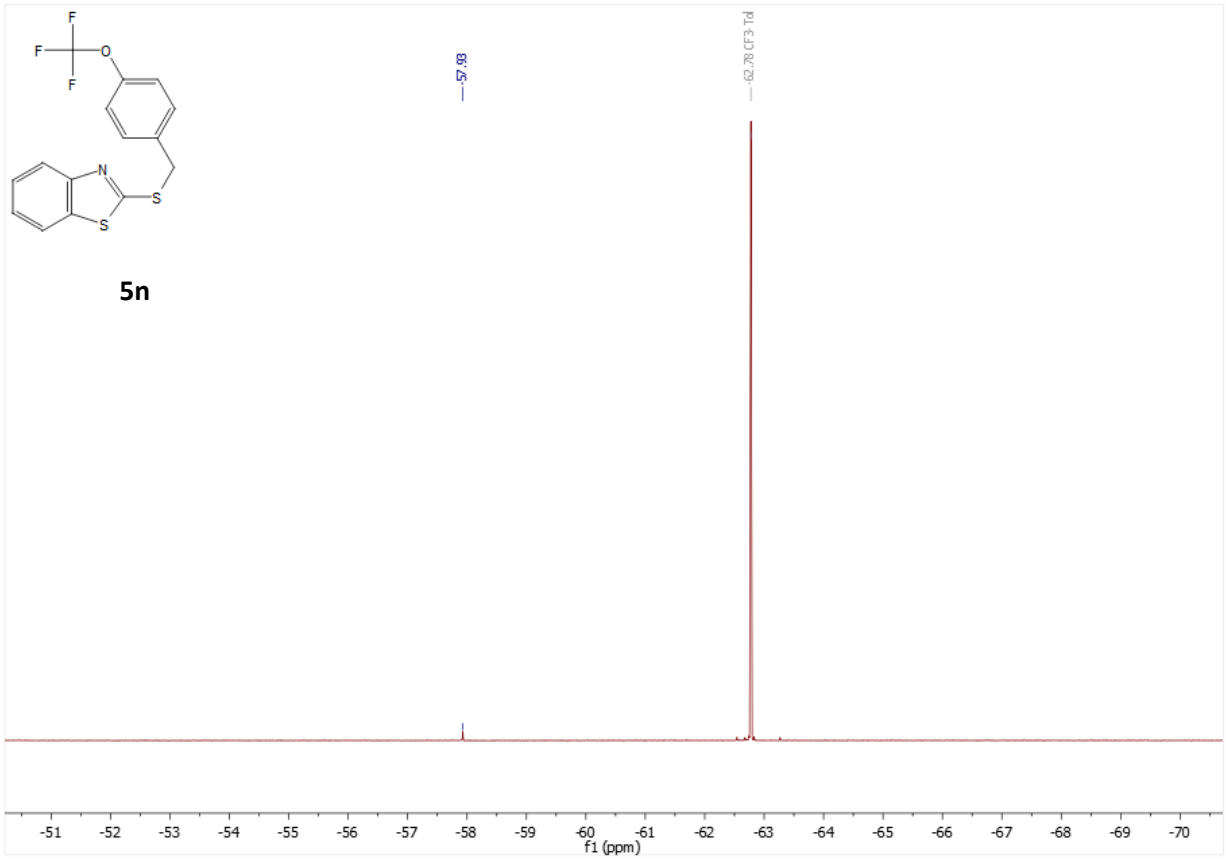
5m


5n
1.00
0.98
2.02
1.06
1.04
2.06
2.15
f1 (ppm)

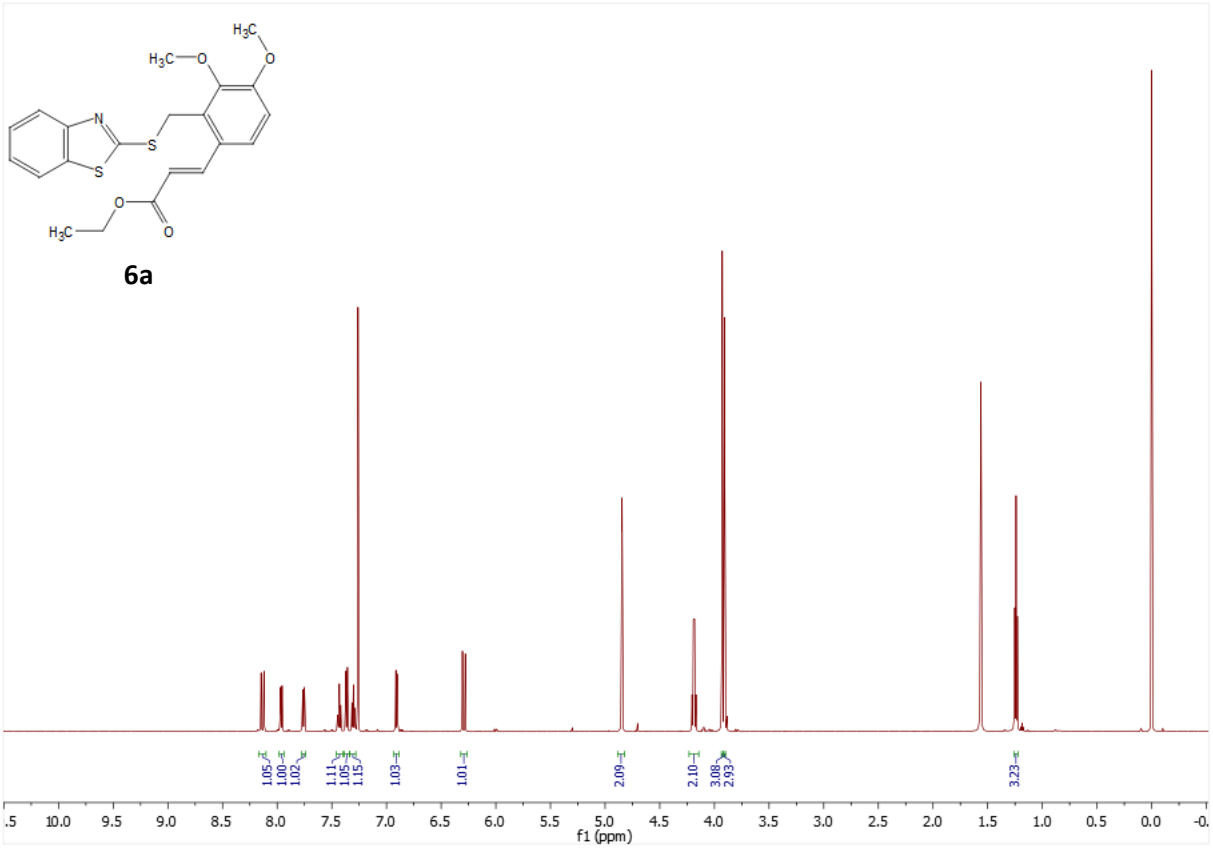

5n
165.83
153.17
148.79
148.78
148.76
148.75
135.51
135.41
130.85
130.67
126.24
126.06
124.54
123.11
121.71
121.41
121.22
121.17
120.95
119.70
118.00
36.76
f1 (ppm)

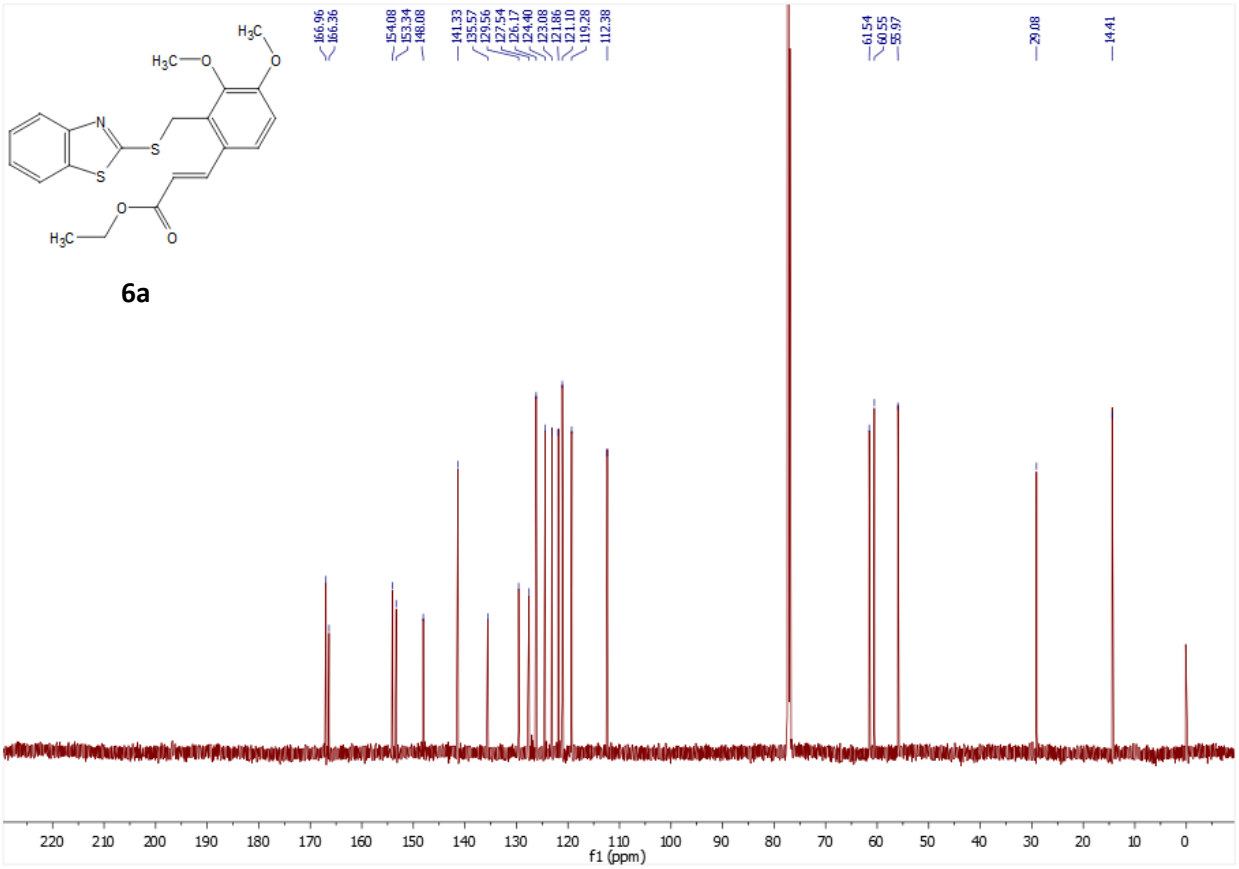

F
F
O
F
N
S
S
-58.13
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

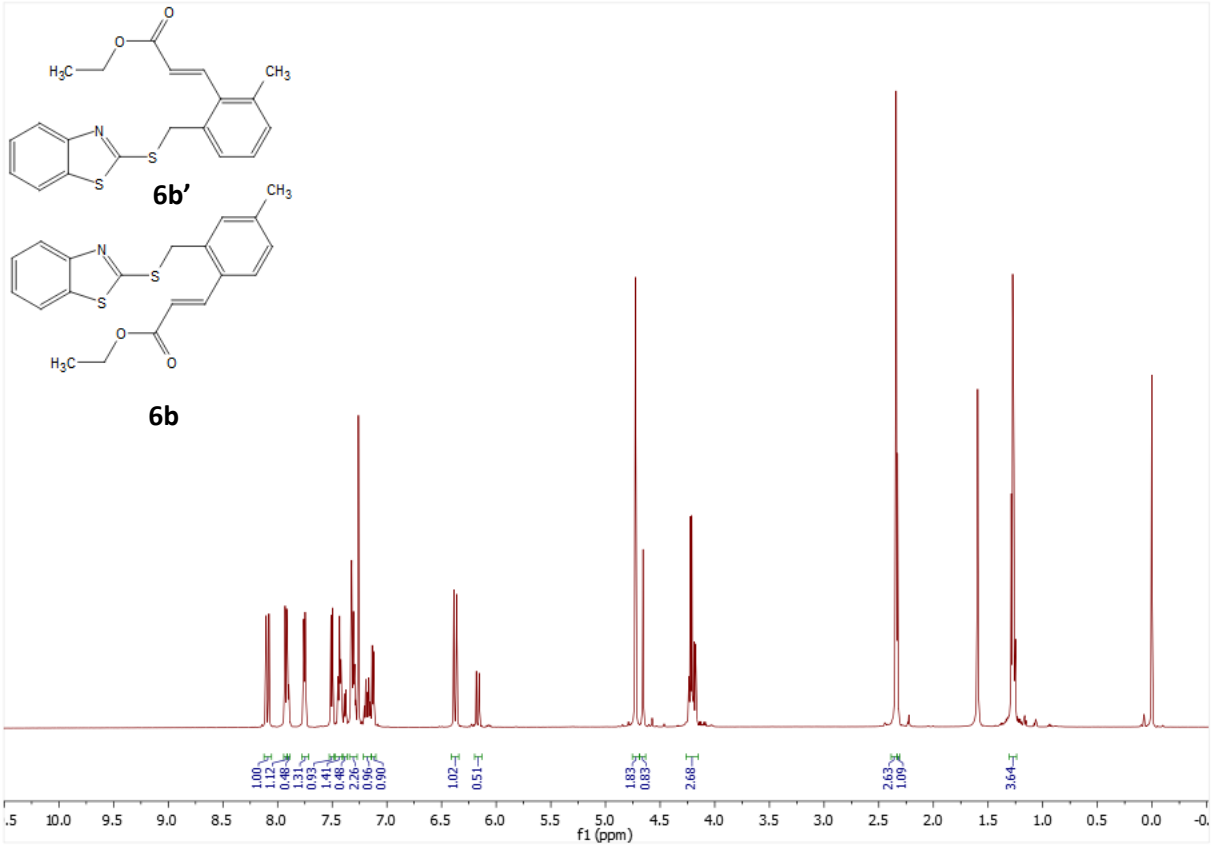
5n

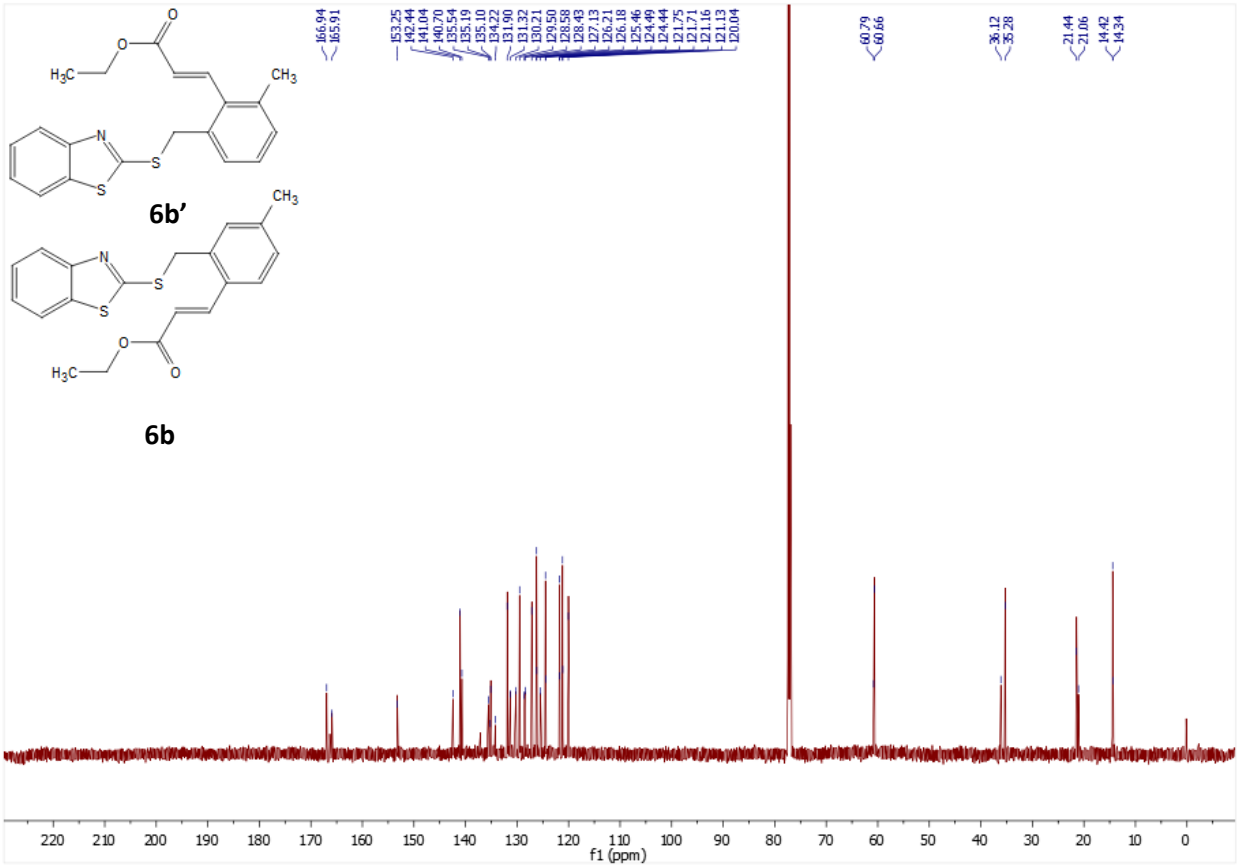

F
F
O
F
N
S
S
-57.93
-62.78 CF3 Td
-51
-52
-53
-54
-55
-56
-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
f1 (ppm)

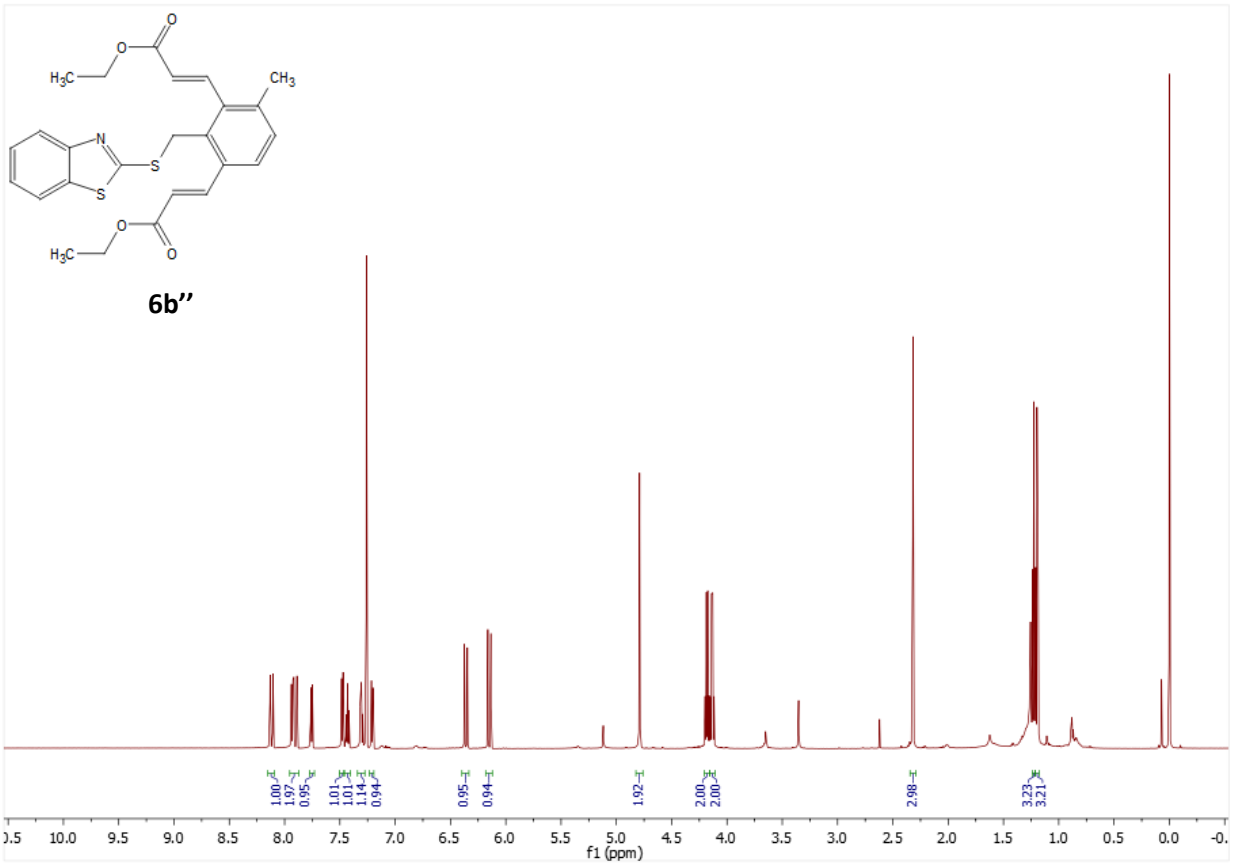
5n

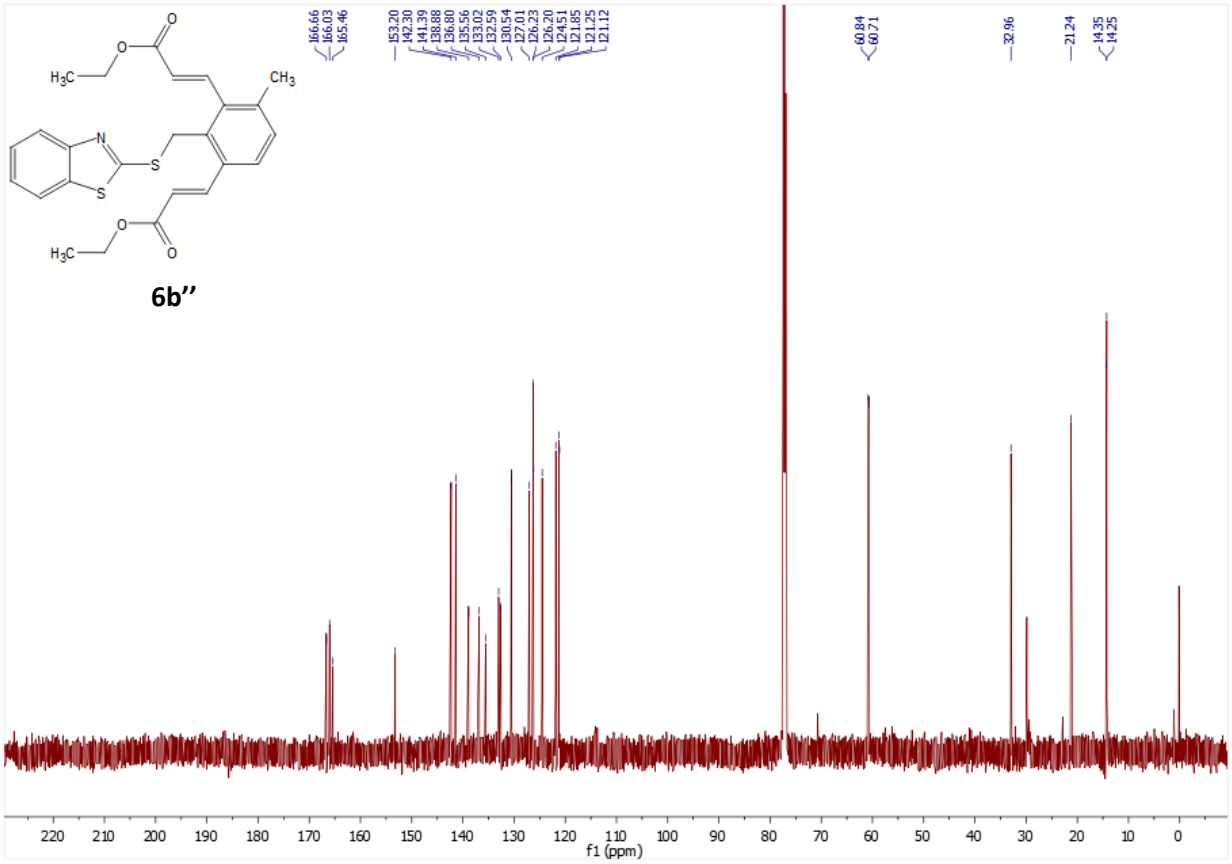

6a
1.05
1.00
1.02
1.11
1.05
1.15
1.03
1.01
2.09
2.10
3.08
2.93
3.23
f1 (ppm)

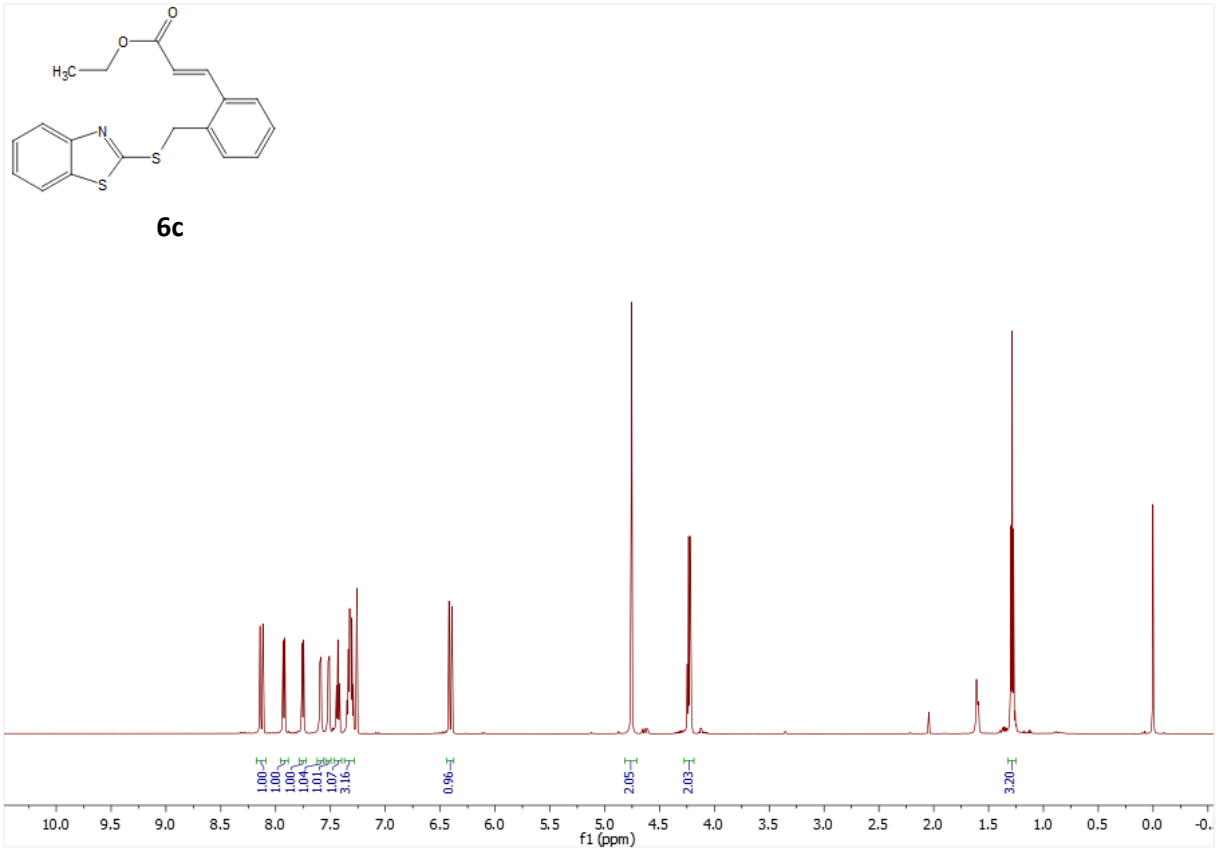

6a
166.96
166.36
154.08
153.34
148.08
141.33
135.57
129.56
127.54
126.17
124.40
123.08
121.86
121.10
119.28
112.38
61.54
60.55
55.97
29.08
14.41
f1 (ppm)

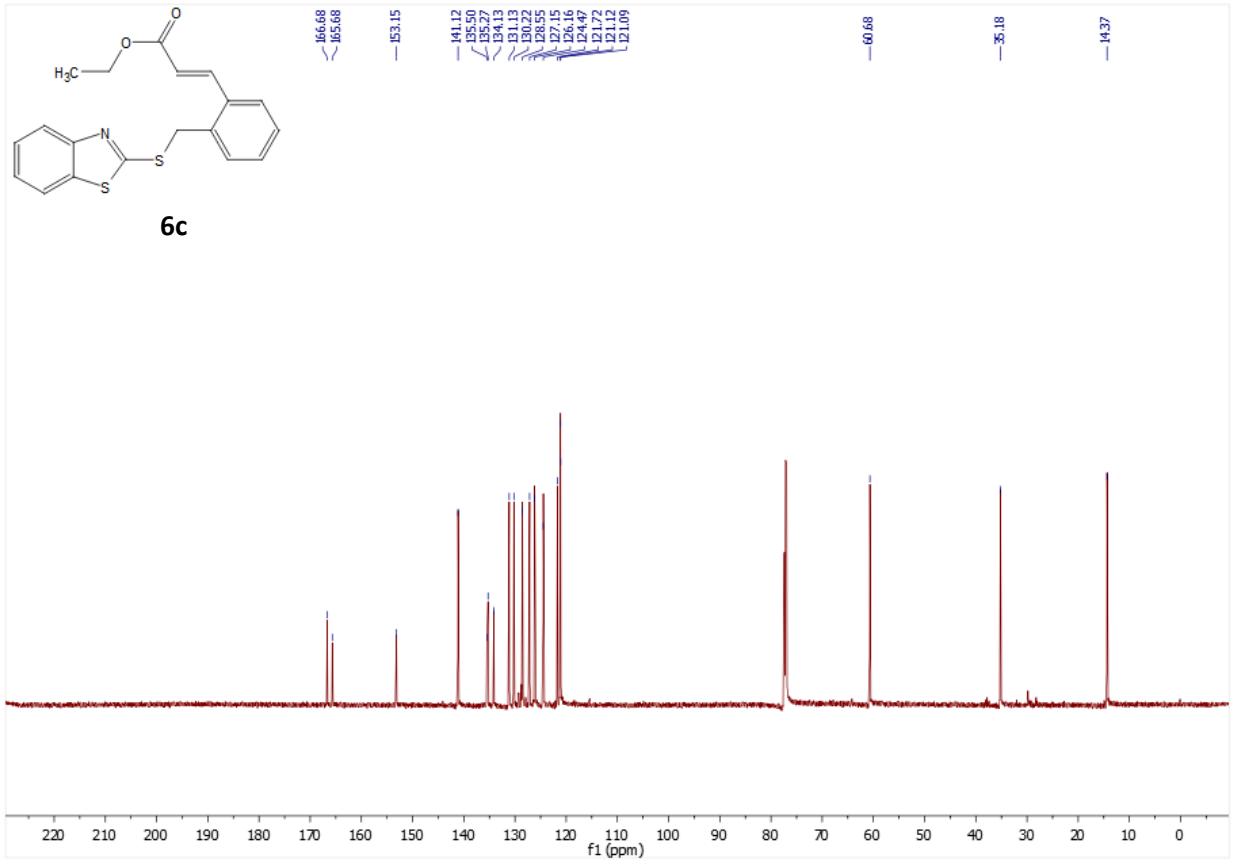

6b'
6b
1.00
1.12
0.48
1.31
0.93
1.41
0.48
2.26
0.96
0.90
1.02
0.51
1.83
0.83
2.68
2.63
1.09
3.64
f1 (ppm)

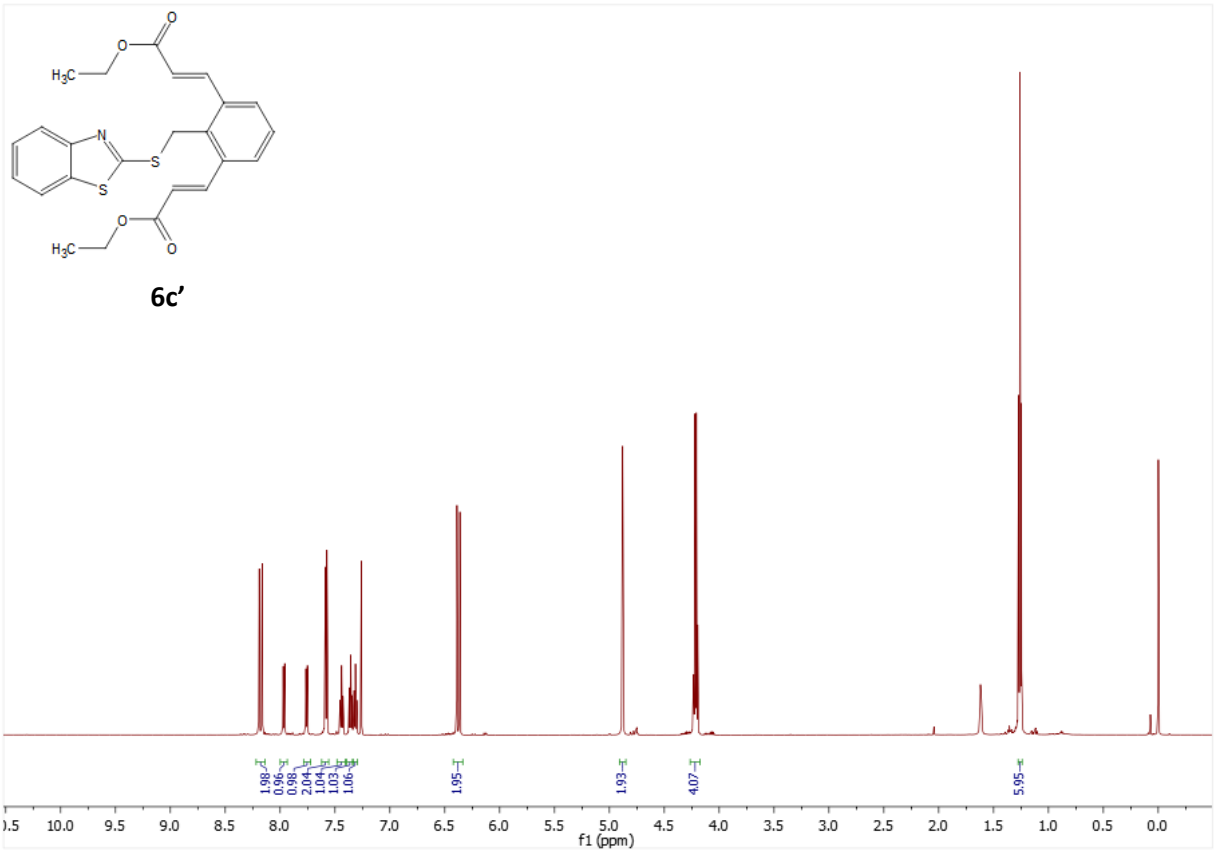

6b'
6b
166.94
165.91
153.25
142.44
141.04
140.70
135.54
135.19
135.10
134.22
131.90
131.32
130.21
129.50
128.58
128.43
127.13
126.21
126.18
125.46
124.49
124.44
121.75
121.71
121.16
121.13
120.04
60.79
60.66
36.12
35.28
21.44
21.06
14.42
14.34
f1 (ppm)

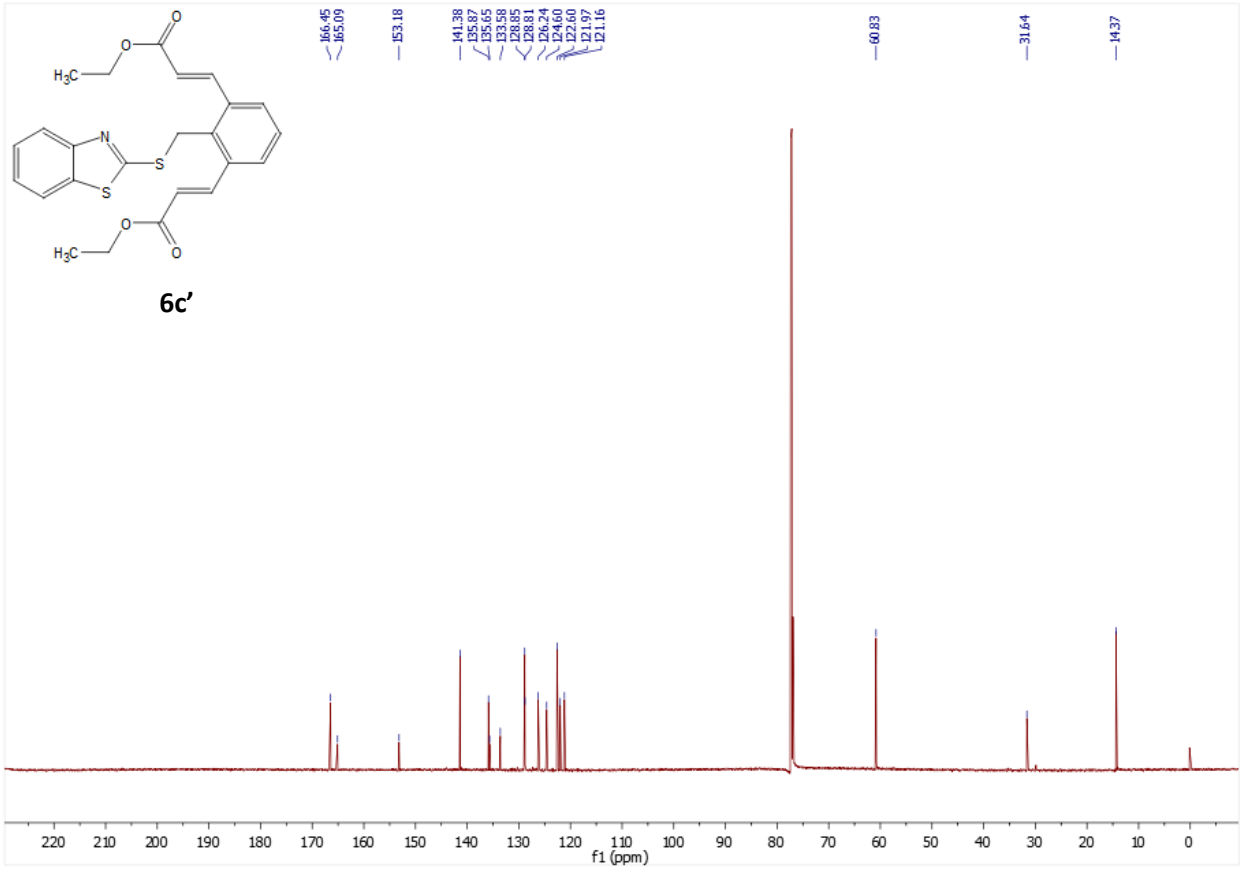

6b''
1.00
1.97
0.95
1.01
1.01
1.14
0.94
0.95
0.94
1.92
2.00
2.00
2.98
3.23
3.21
f1 (ppm)

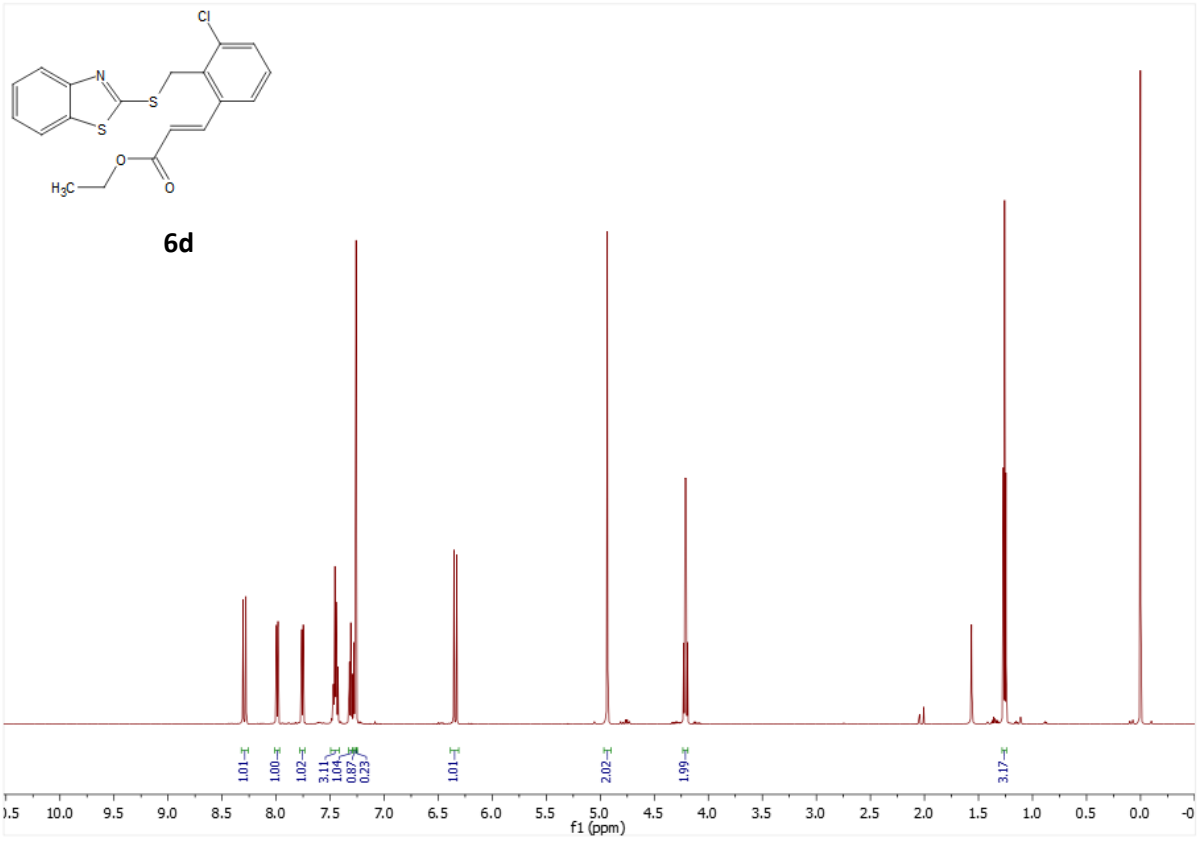

6b''
166.66
166.03
165.46
153.20
142.30
141.39
138.88
136.80
135.56
133.02
132.59
130.54
127.01
126.23
126.20
124.51
121.85
121.25
121.12
60.84
60.71
32.96
21.24
14.35
14.25
f1 (ppm)

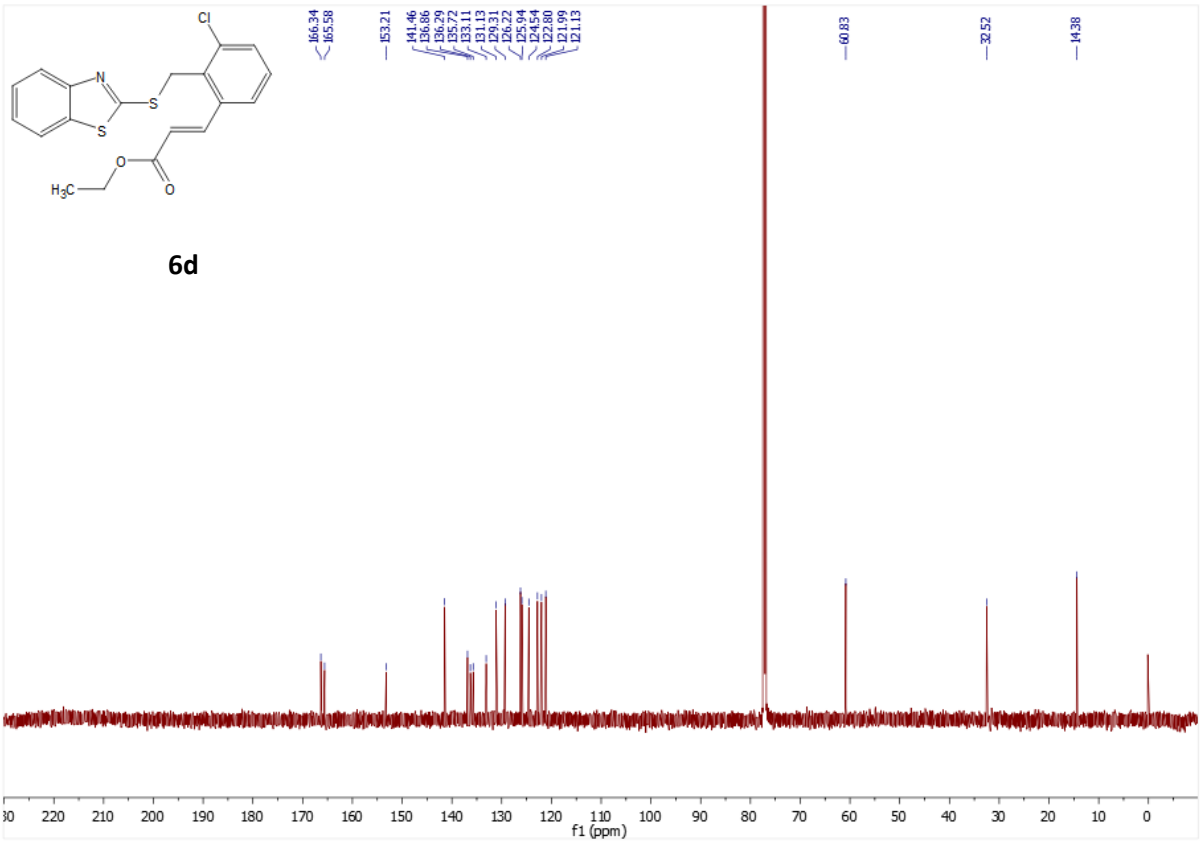

O
O
H3C
N
S
S
6c
1.00
1.00
1.00
1.04
1.01
1.07
3.16
0.96
2.05
2.03
3.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

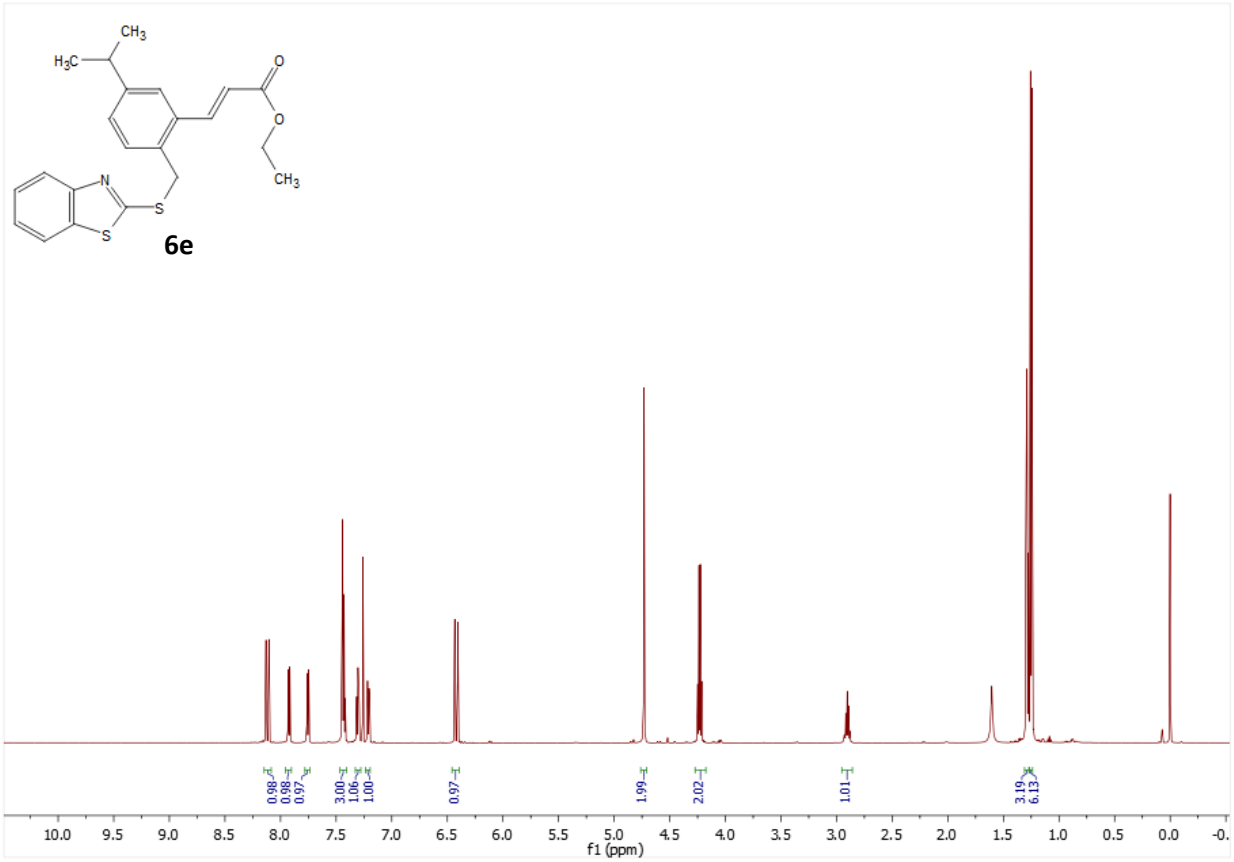

O
O
H3C
N
S
S
6c
166.68
165.68
153.15
141.12
135.50
135.27
134.13
131.13
130.22
128.55
127.15
126.16
124.47
121.72
121.12
121.09
60.68
35.18
14.37
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

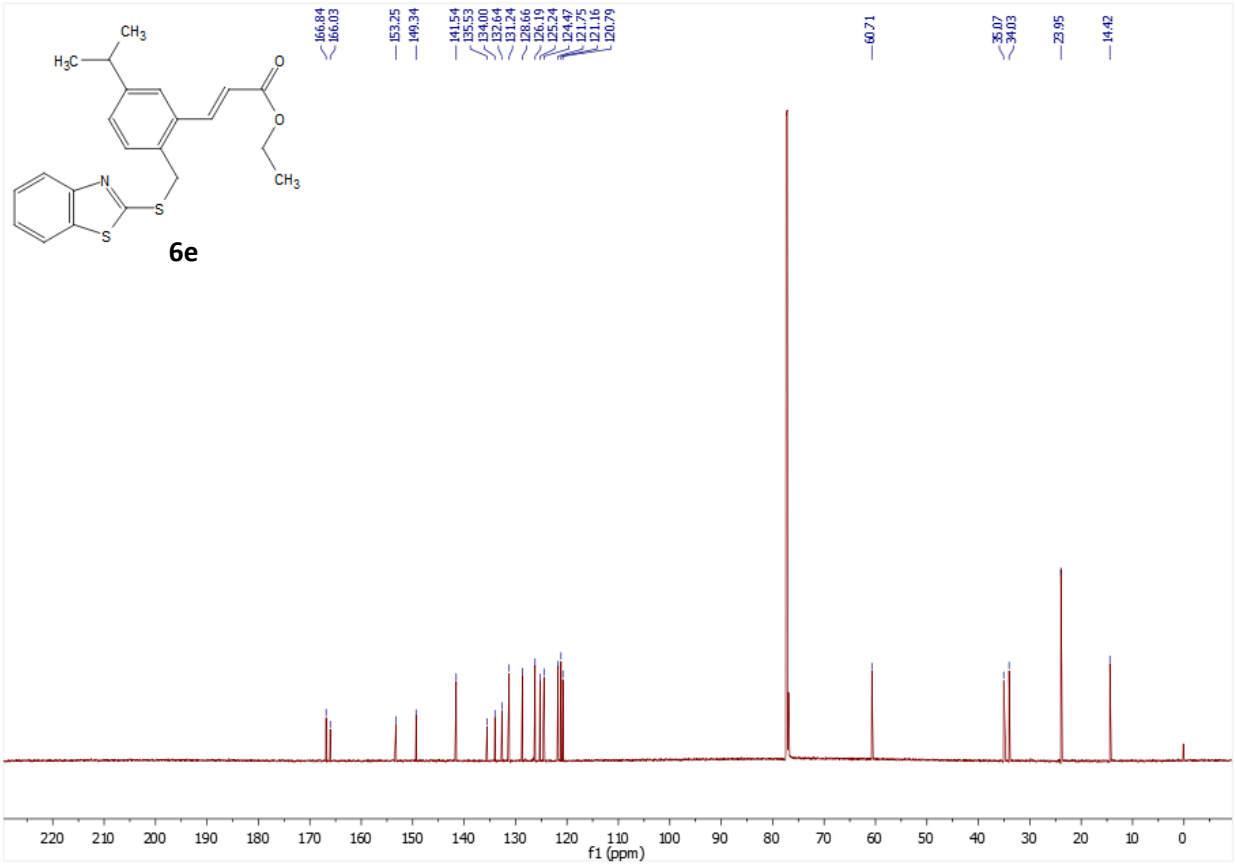

6c’
1.98
0.96
0.98
2.04
1.03
1.06
1.95
1.93
4.07
5.95
f1 (ppm)

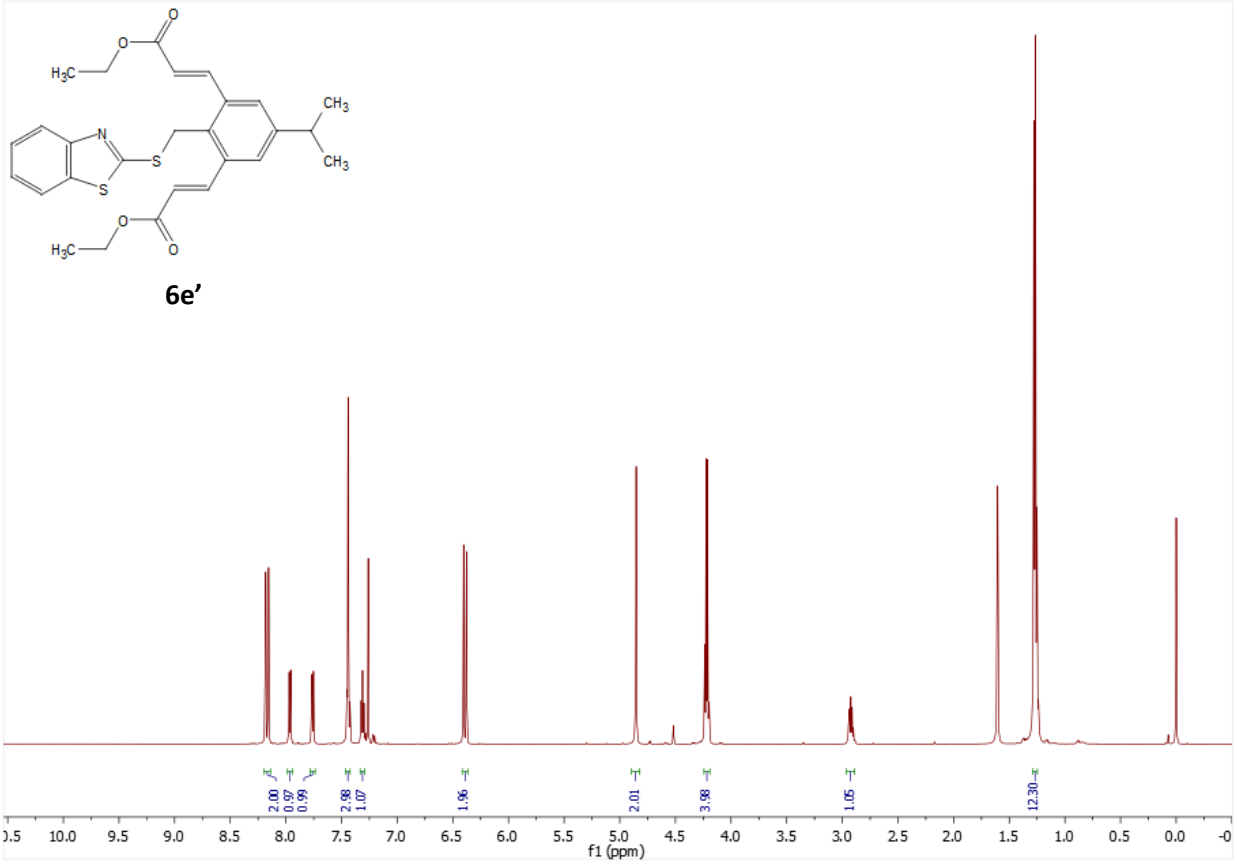

6c’
166.45
165.09
153.18
141.38
135.87
135.65
133.58
128.85
128.81
126.24
124.60
122.60
121.97
121.16
60.83
31.64
14.37
f1 (ppm)

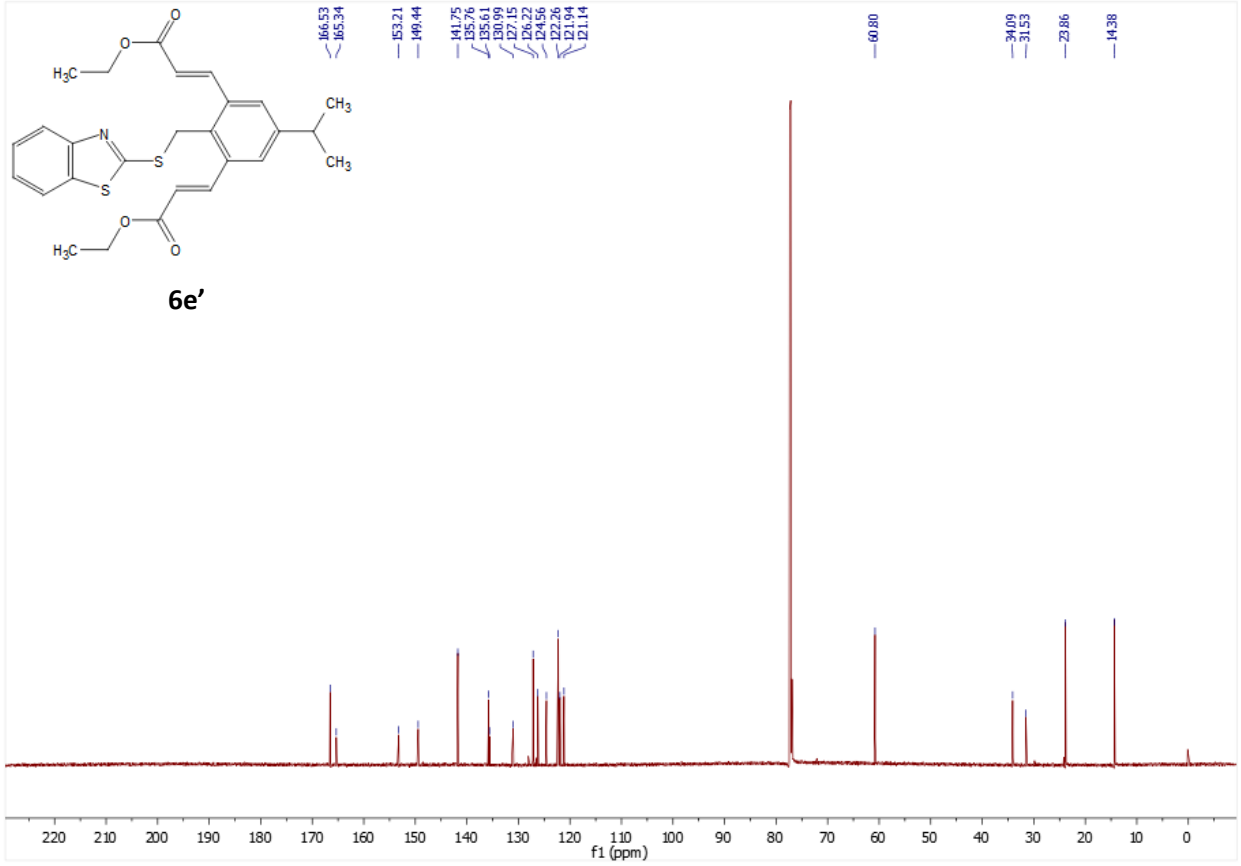

Cl
N
S
S
O
O
H3C
6d
1.01
1.00
1.02
3.11
1.04
0.87
0.23
1.01
2.02
1.99
3.17
f1 (ppm)

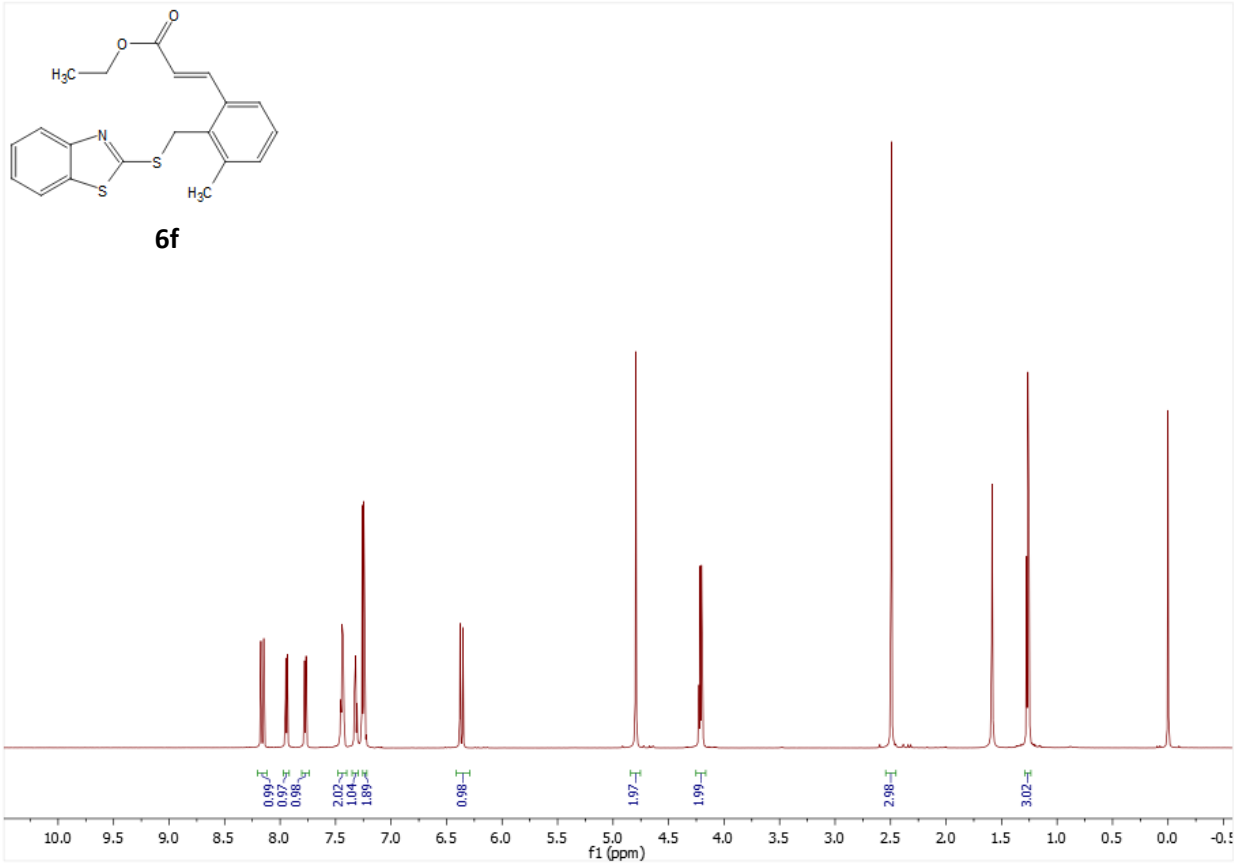

Cl
N
S
S
O
O
H3C
6d
166.34
165.58
153.21
141.46
136.86
136.29
135.72
133.11
131.13
129.31
126.22
125.94
124.54
122.80
121.99
121.13
60.83
32.52
14.38
f1 (ppm)

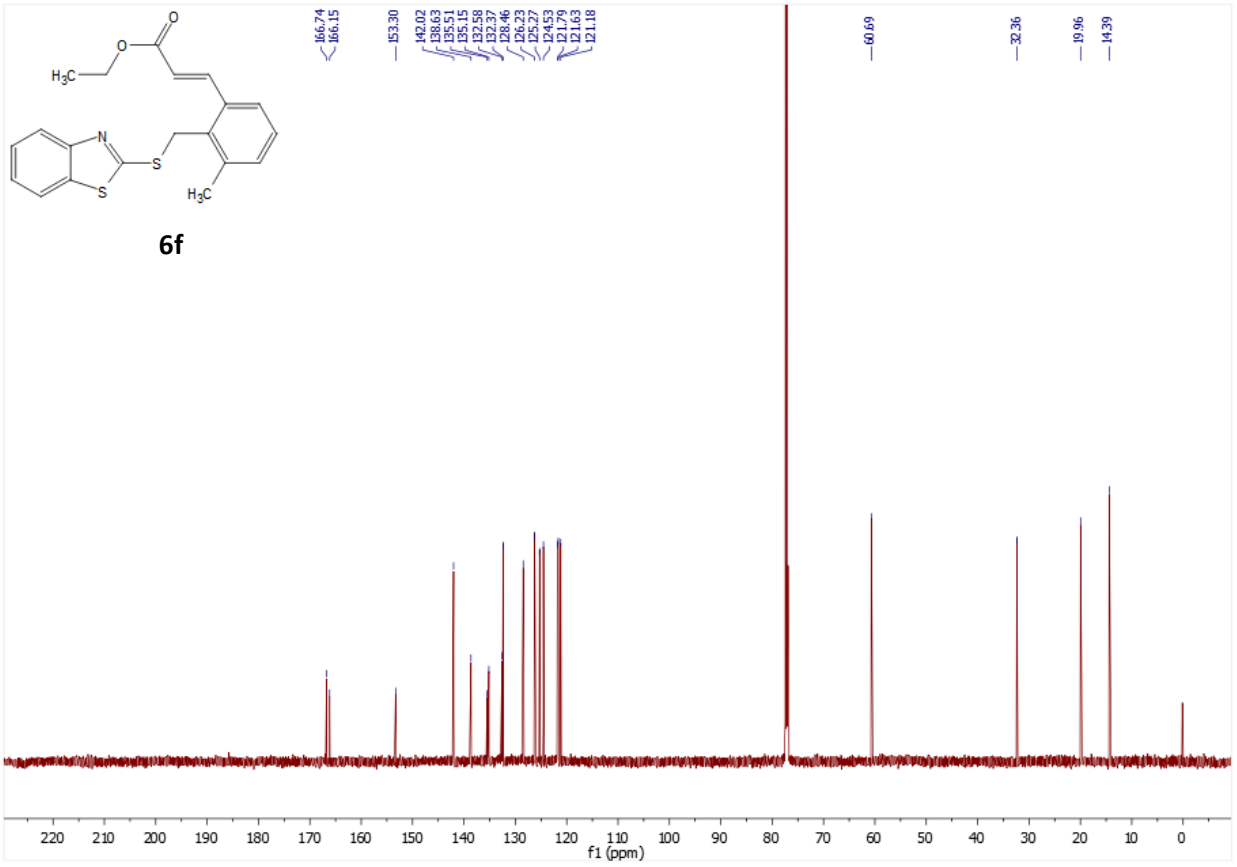

6e
f1 (ppm)

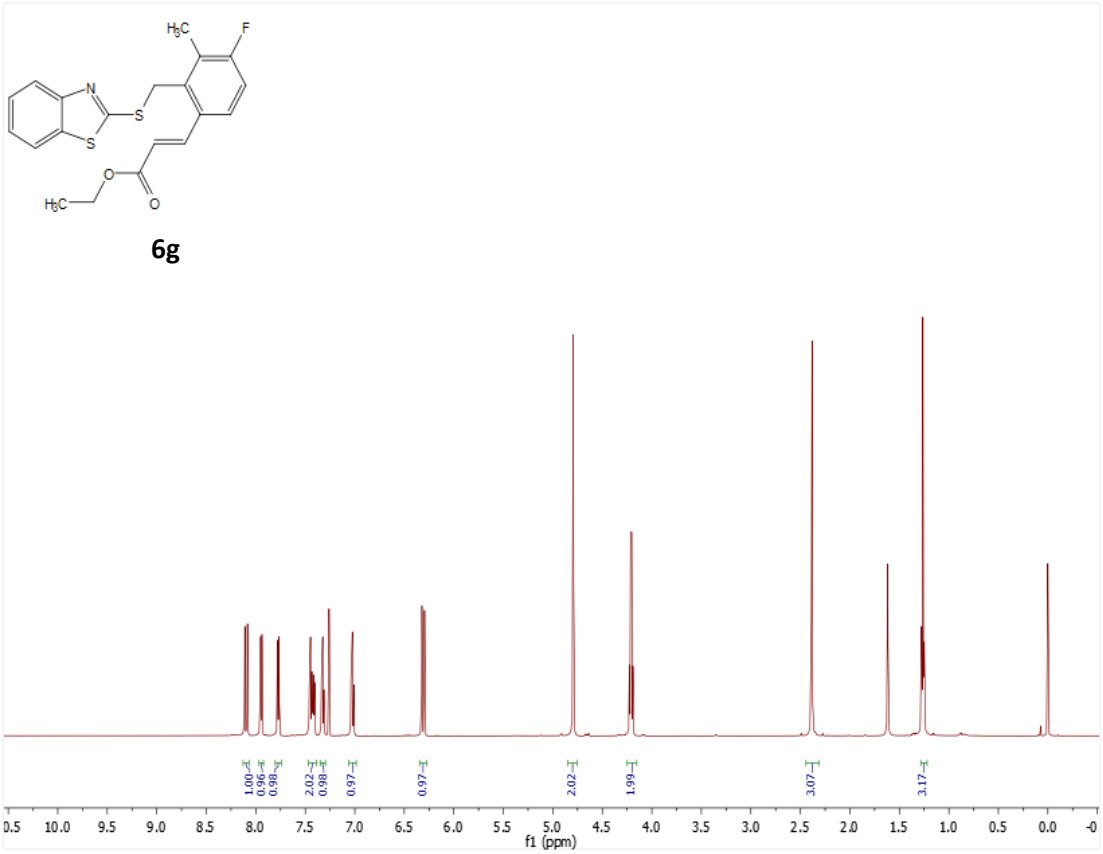

6e
f1 (ppm)


6e’
2.00
0.97
0.99
2.98
1.07
1.96
2.01
3.98
1.05
12.30
f1 (ppm)

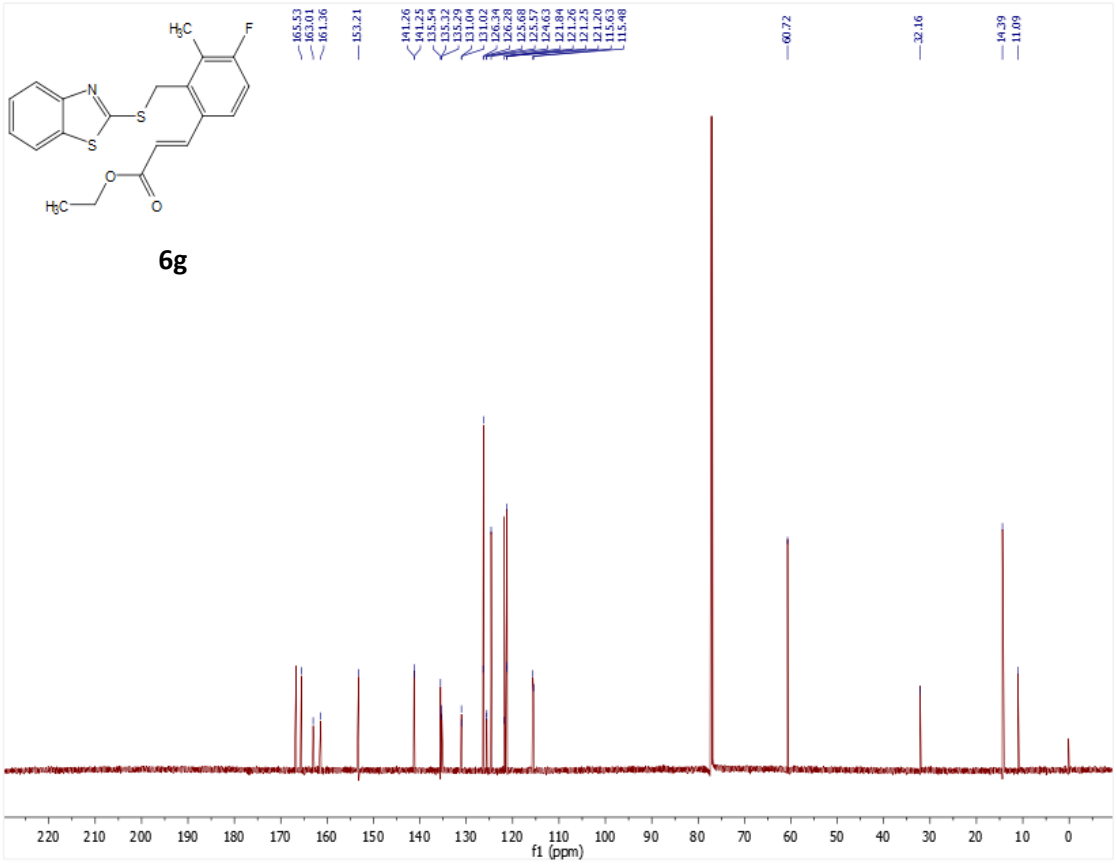

6e’
166.53
165.34
153.21
149.44
141.75
135.76
135.61
130.99
127.15
126.22
124.56
122.26
121.94
121.14
60.80
34.09
31.53
23.86
14.38
f1 (ppm)


6f
0.99
0.97
0.98
2.02
1.04
1.89
0.98
1.97
1.99
2.98
3.02
f1 (ppm)

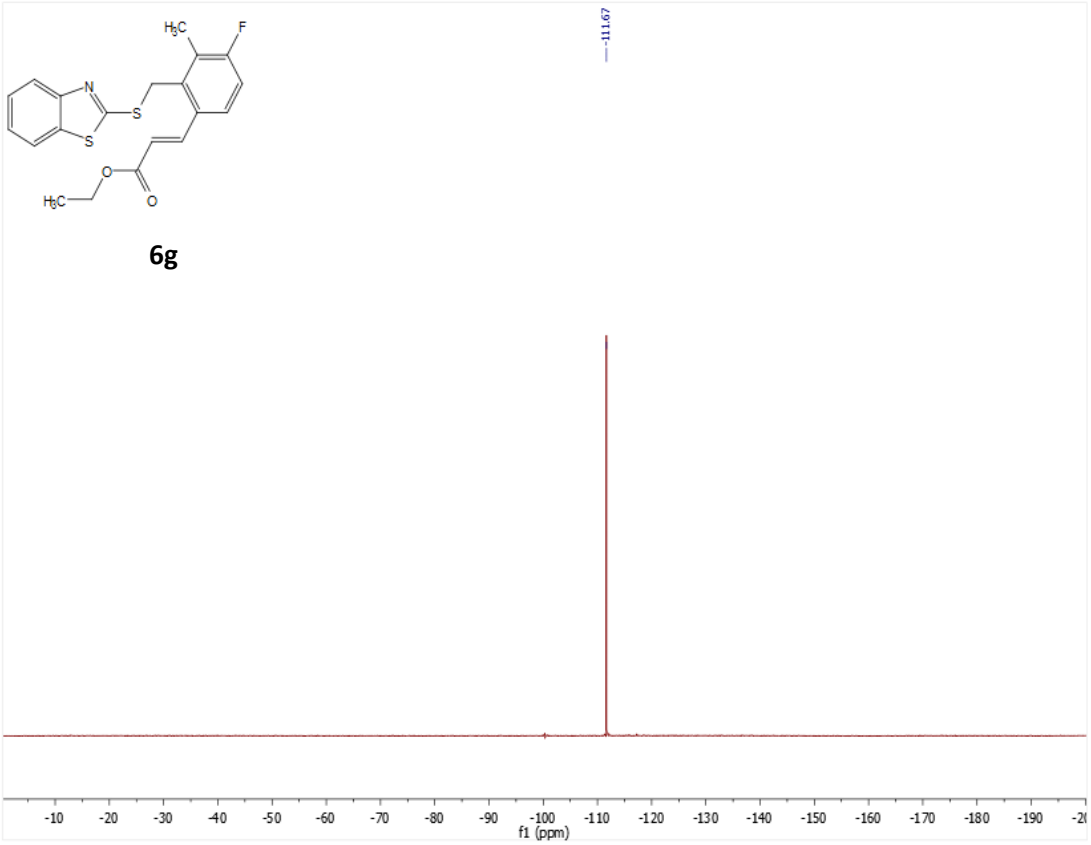

6f
166.74
166.15
153.30
142.02
138.63
135.51
135.15
132.58
132.37
128.46
126.23
125.27
124.53
121.79
121.63
121.18
60.69
32.36
19.96
14.39
f1 (ppm)


H3C
F
N
S
S
O
H3C
O
1.00
0.96
0.98
2.02
0.98
0.97
0.97
2.02
1.99
3.07
3.17
f1 (ppm)

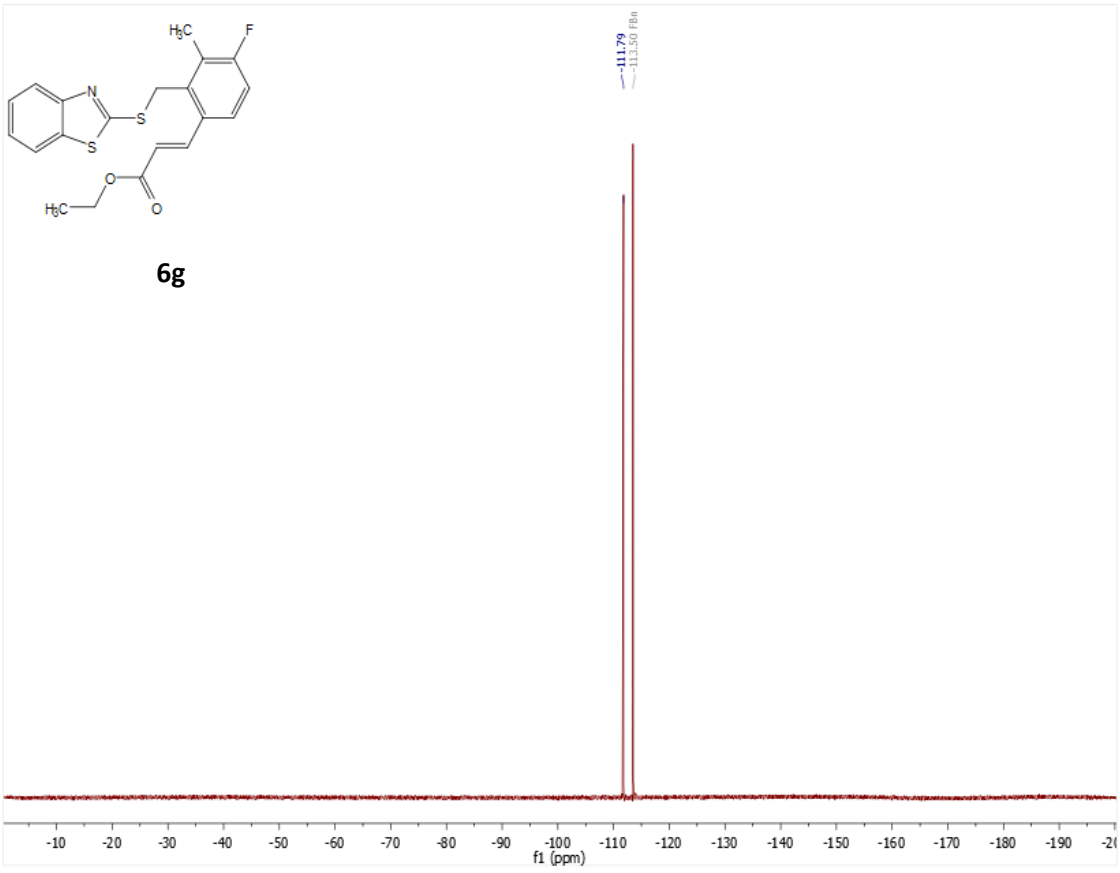
6g


H3C
F
N
S
S
O
H3C
O
165.53
163.01
161.36
153.21
141.26
141.25
135.54
135.32
135.29
131.04
131.02
126.34
126.28
125.68
125.57
124.63
121.94
121.26
121.25
121.20
115.63
115.48
60.72
32.16
14.39
11.09
f1 (ppm)

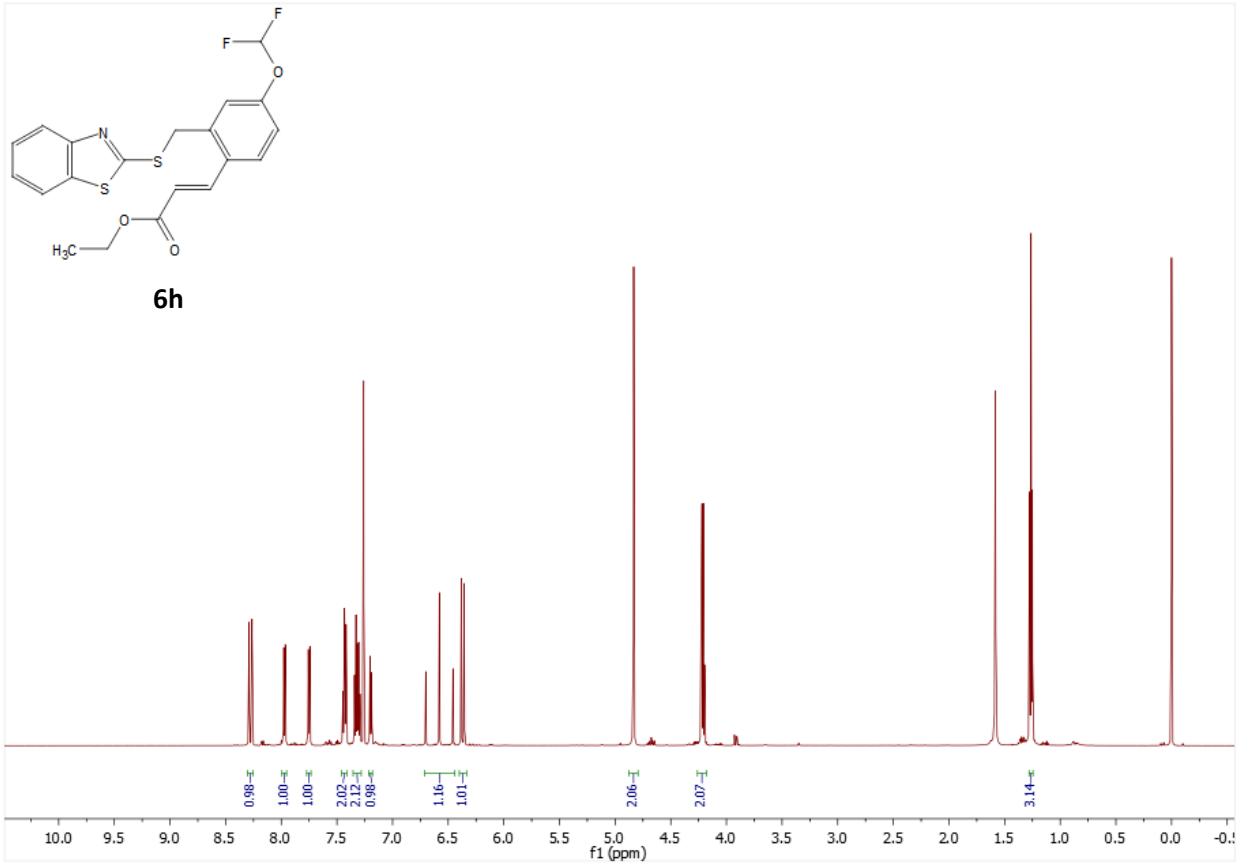
6g

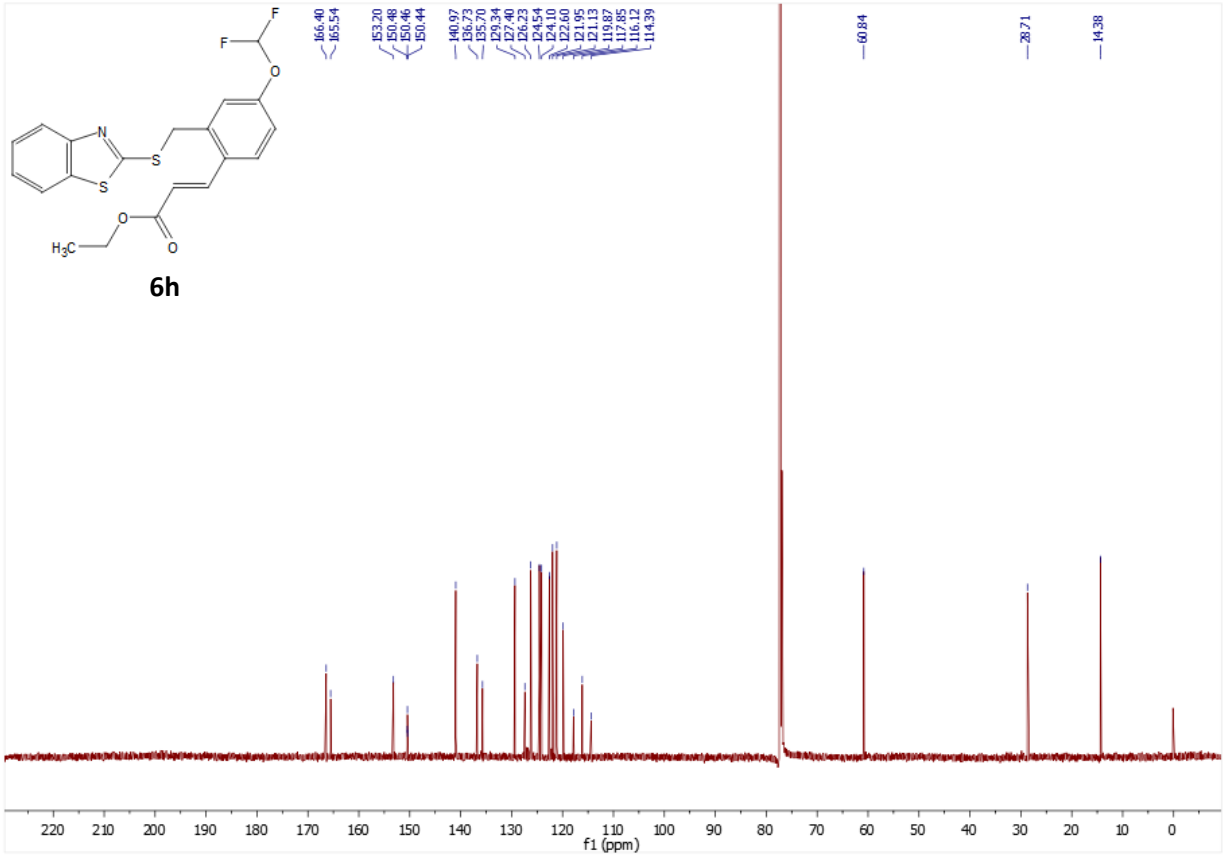

H3C
F
N
S
S
O
H3C
O
-111.67
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

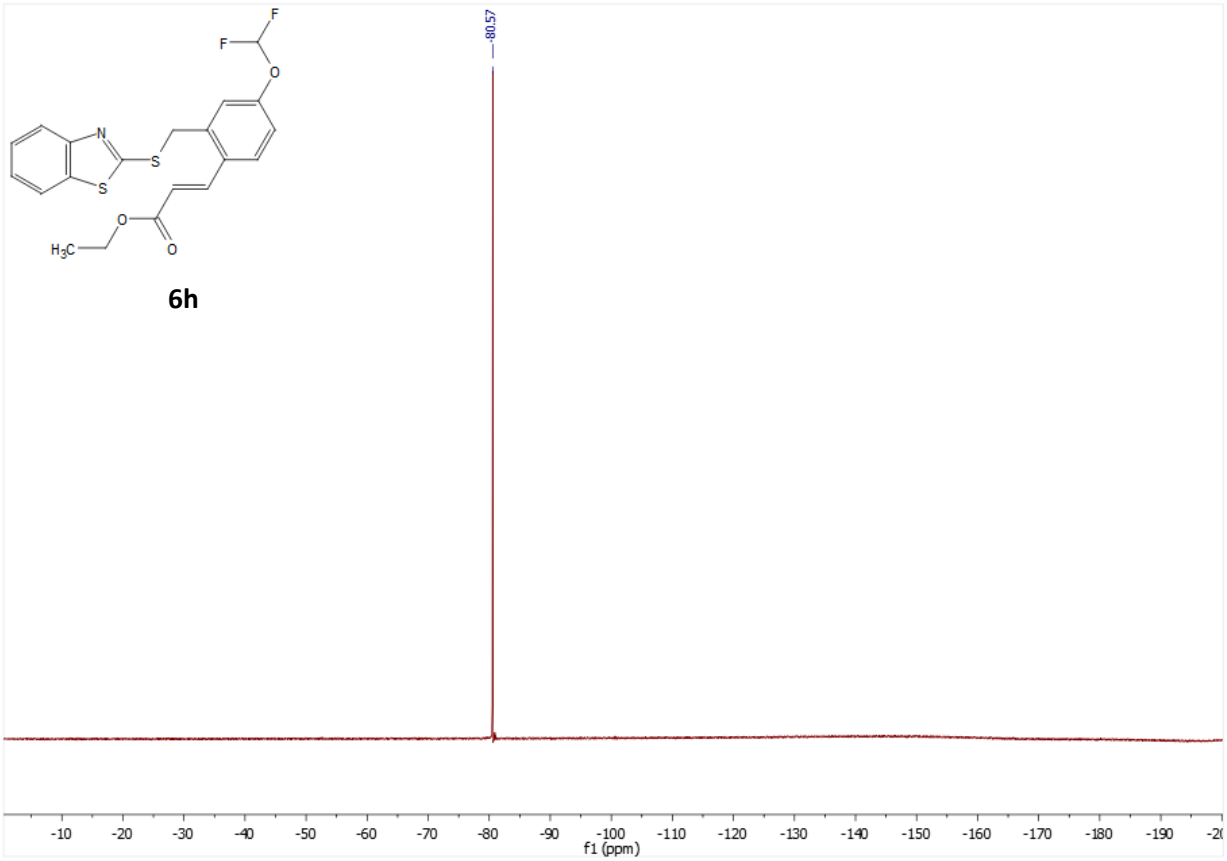
6g


H3C
F
N
S
S
O
H3C
O
-111.79
-113.50 FBn
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

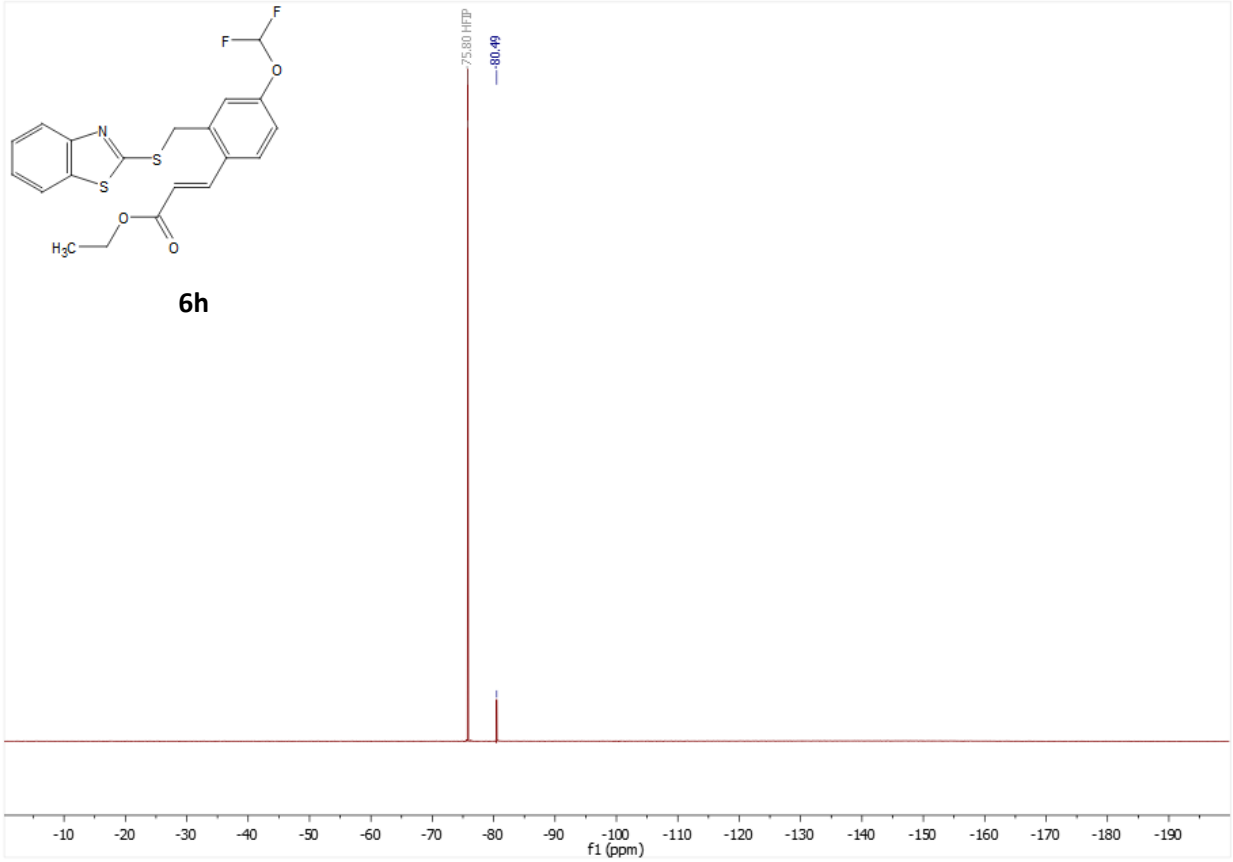
6g


F
F
O
N
S
S
O
O
H3C
6h
0.98
1.00
1.00
2.02
2.12
0.98
1.16
1.01
2.06
2.07
3.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

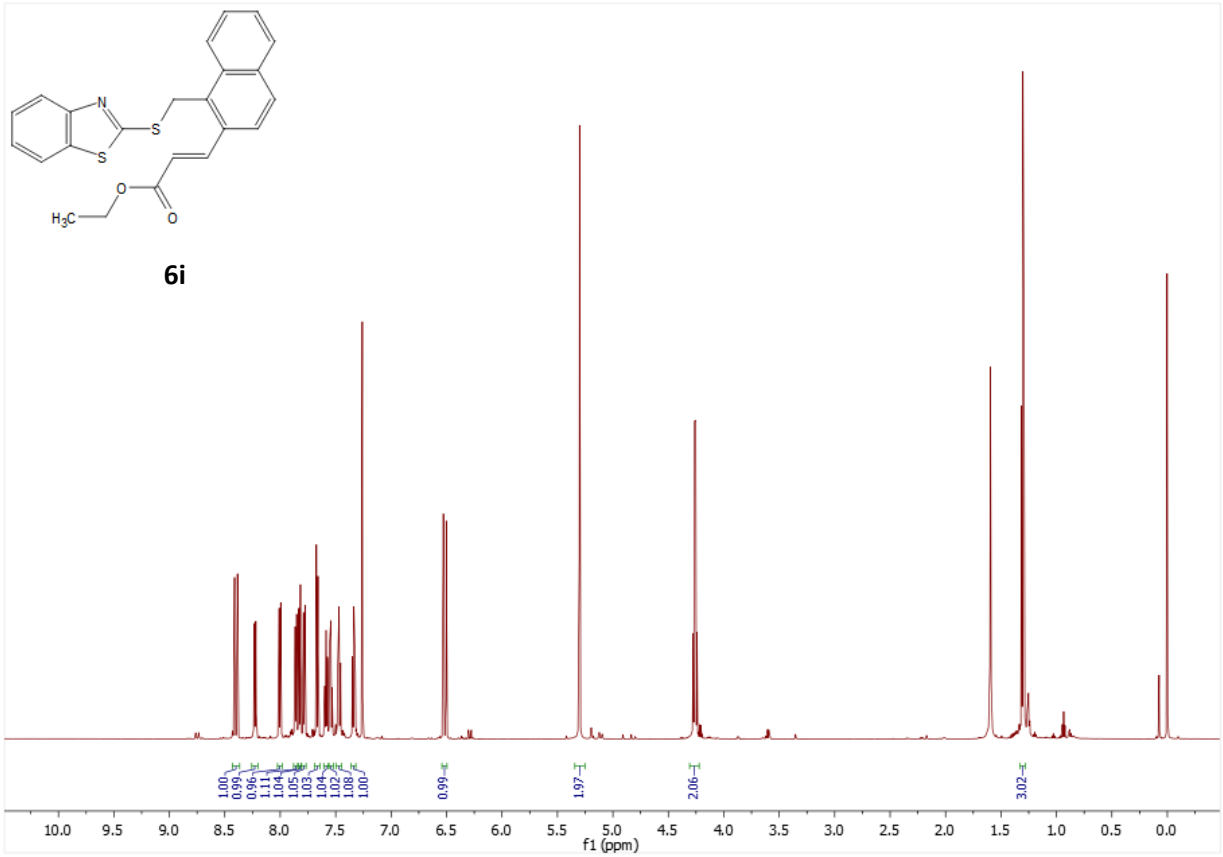

F
F
O
N
S
S
O
O
H3C
6h
166.40
165.54
153.20
150.48
150.46
150.44
140.97
136.73
135.70
129.34
127.40
126.23
124.54
124.10
122.60
121.95
121.13
119.87
117.85
116.12
114.39
60.84
28.71
14.38
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

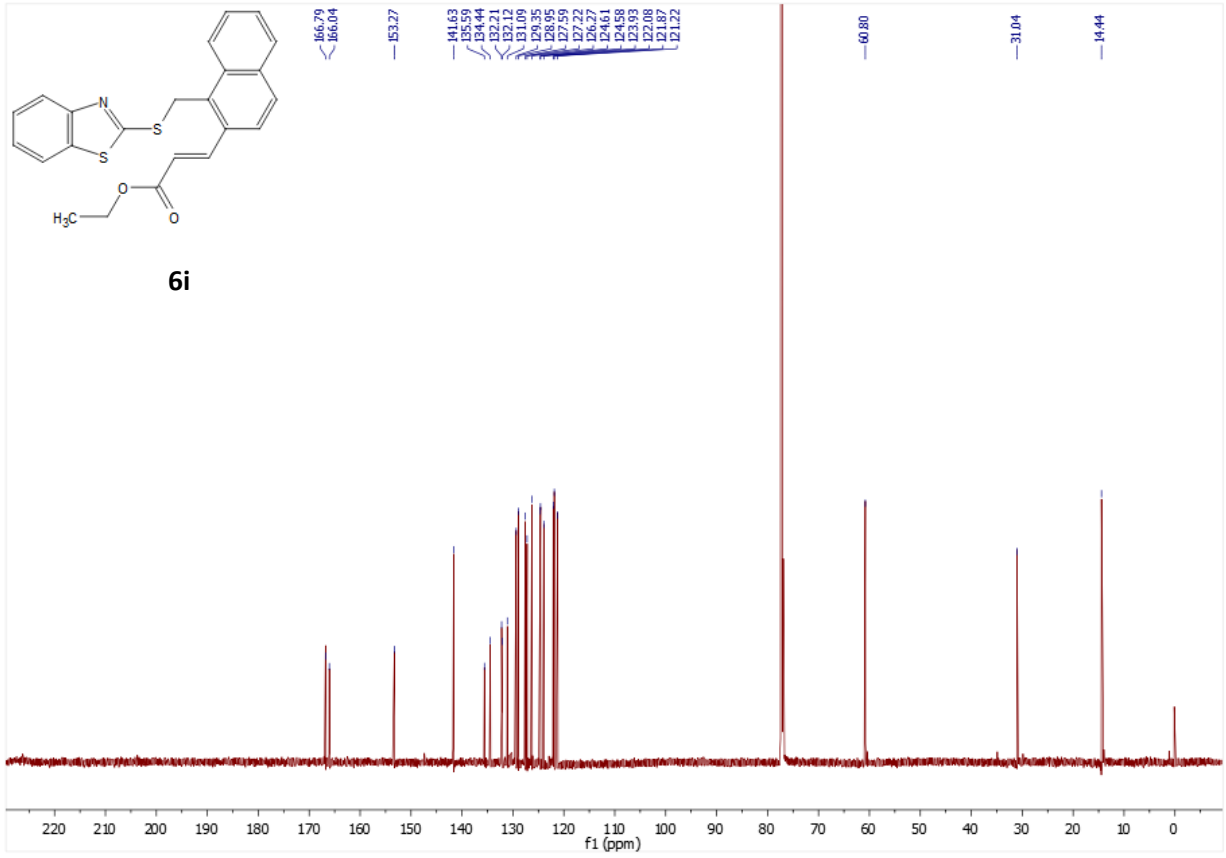

F
F
O
N
S
S
O
O
H3C
-80.57
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

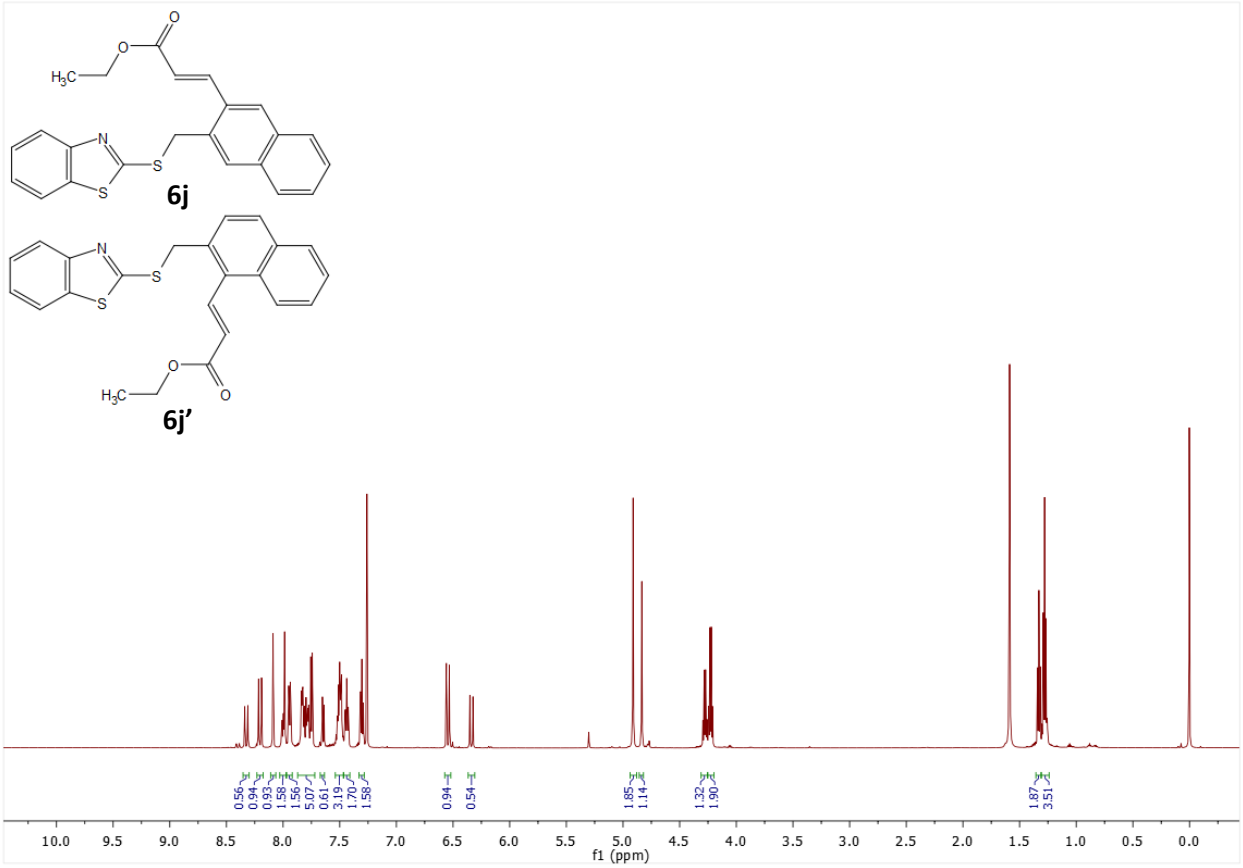
6h

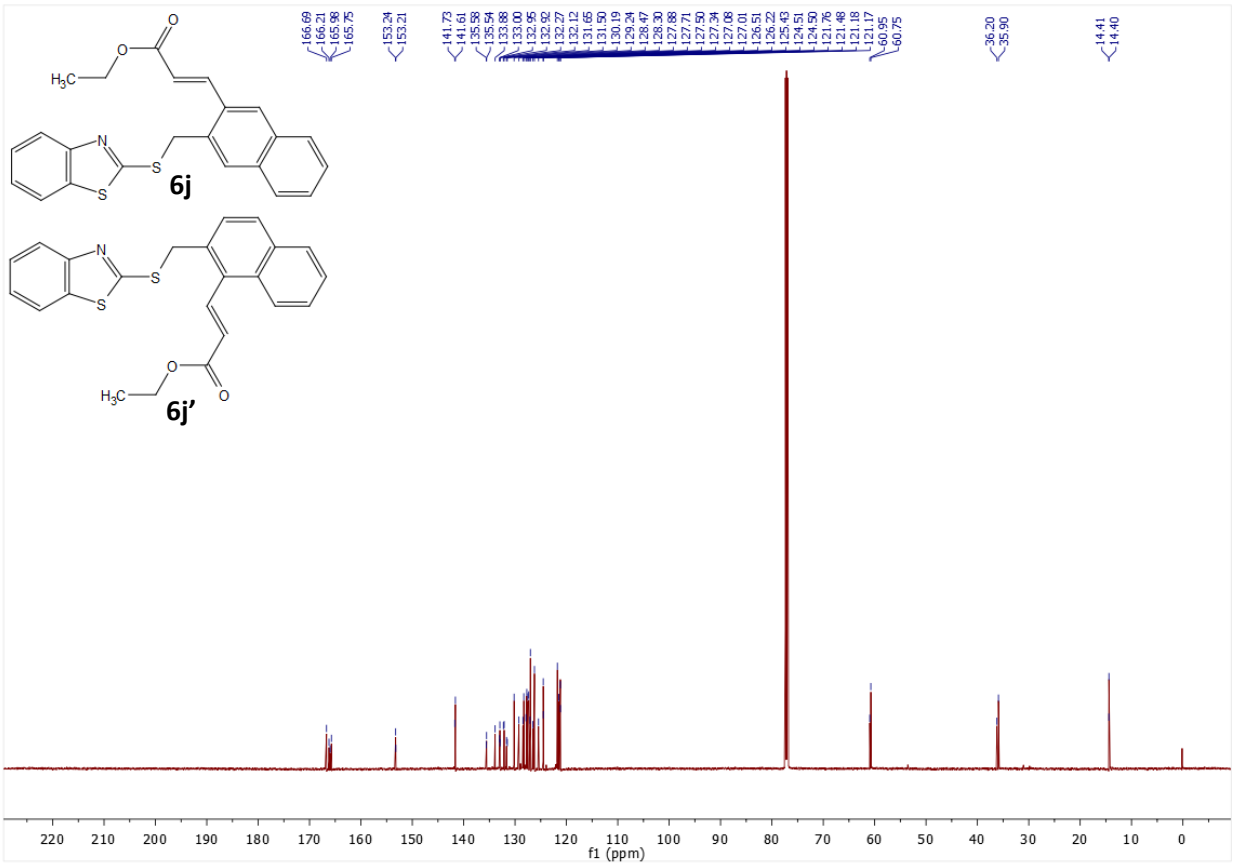

F
F
O
N
S
S
O
O
H3C
75.80 HFIP
-80.49
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

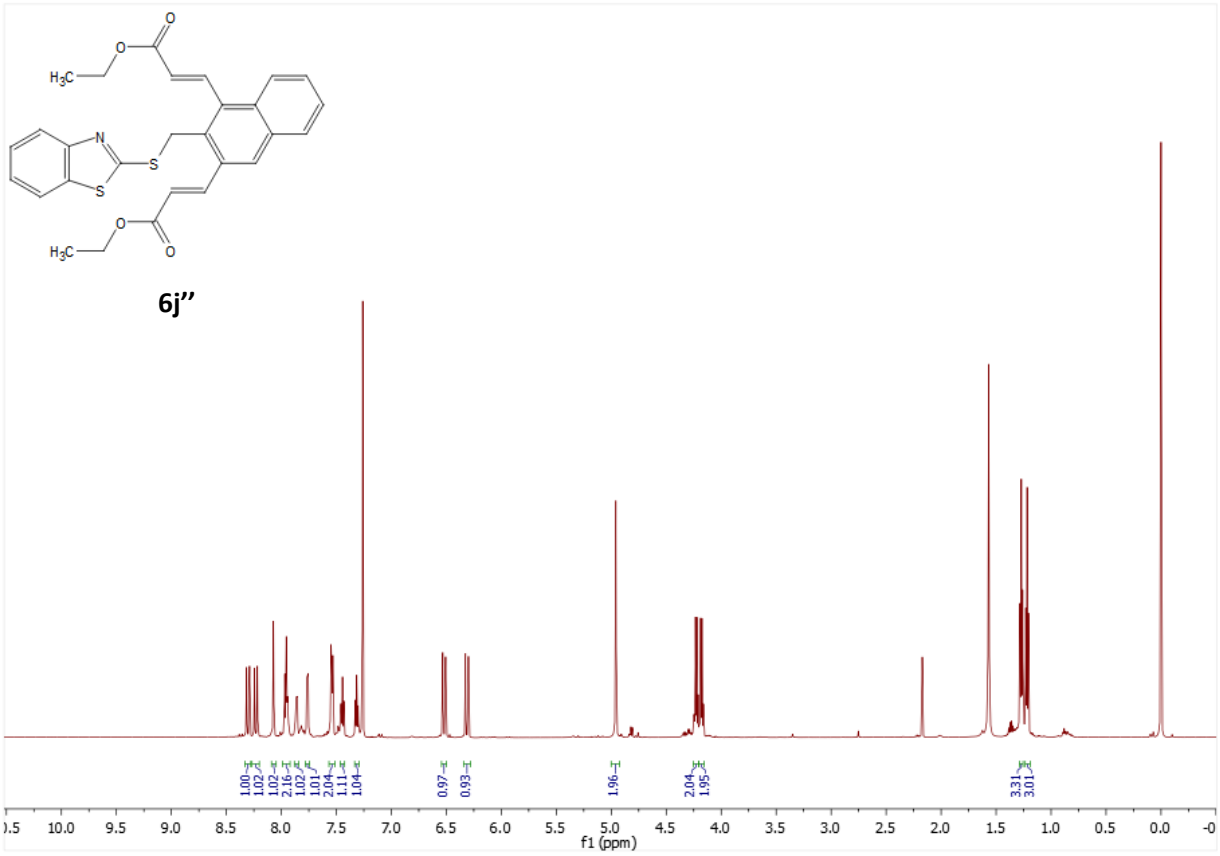
6h

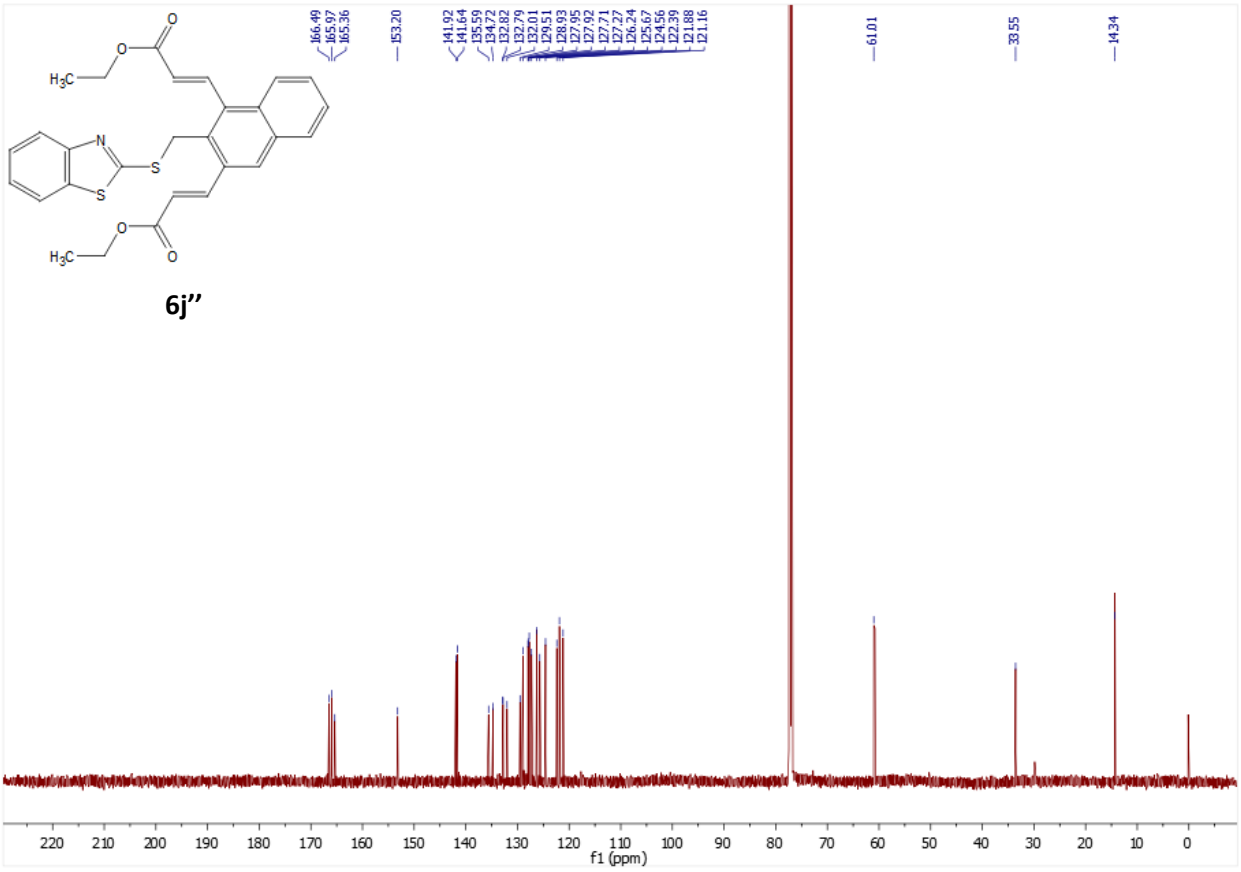

6i
1.00
0.99
0.96
1.11
1.04
1.05
1.03
1.04
1.02
1.08
1.00
0.99
1.97
2.06
3.02
f1 (ppm)

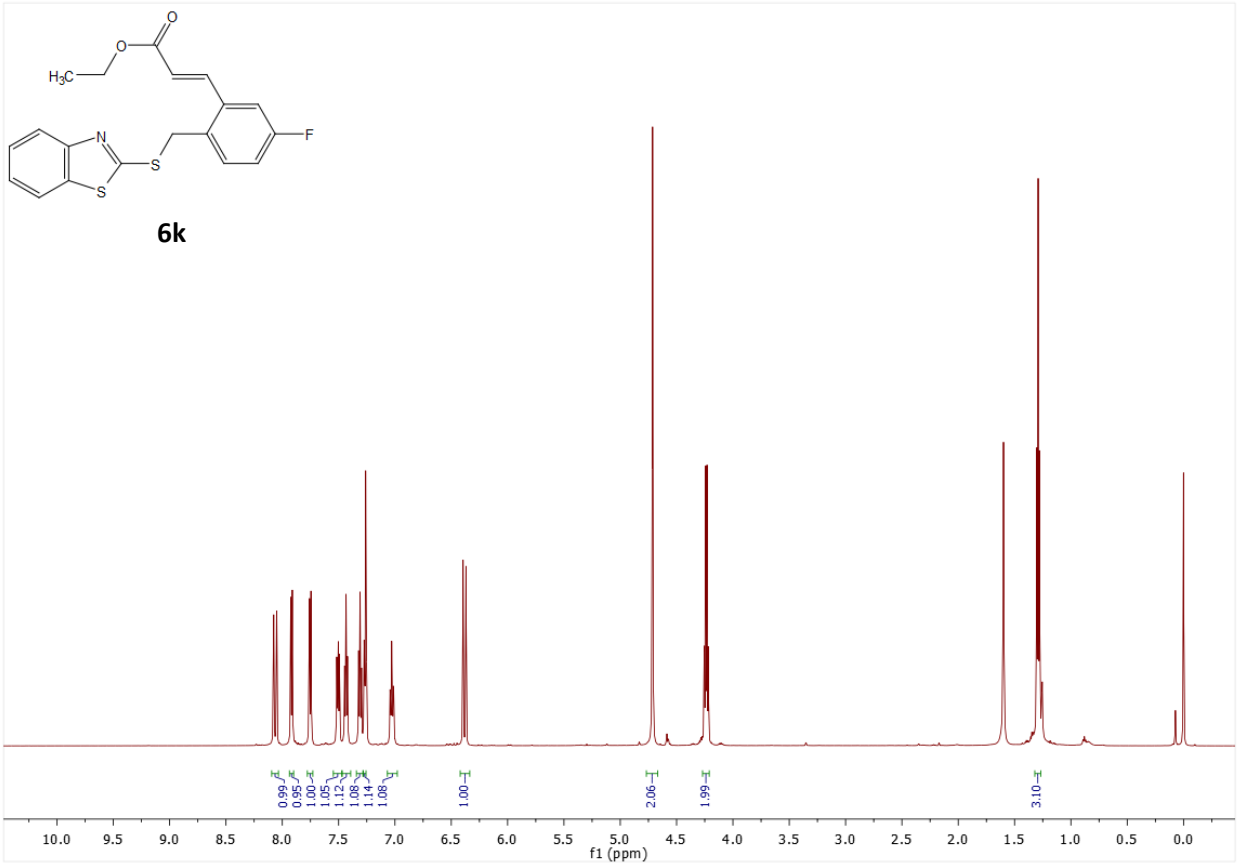

6i
166.79
166.04
153.27
141.63
135.59
134.44
132.21
132.12
131.09
129.35
128.95
127.59
127.22
126.27
124.61
124.58
123.93
122.08
121.87
121.22
60.80
31.04
14.44
f1 (ppm)

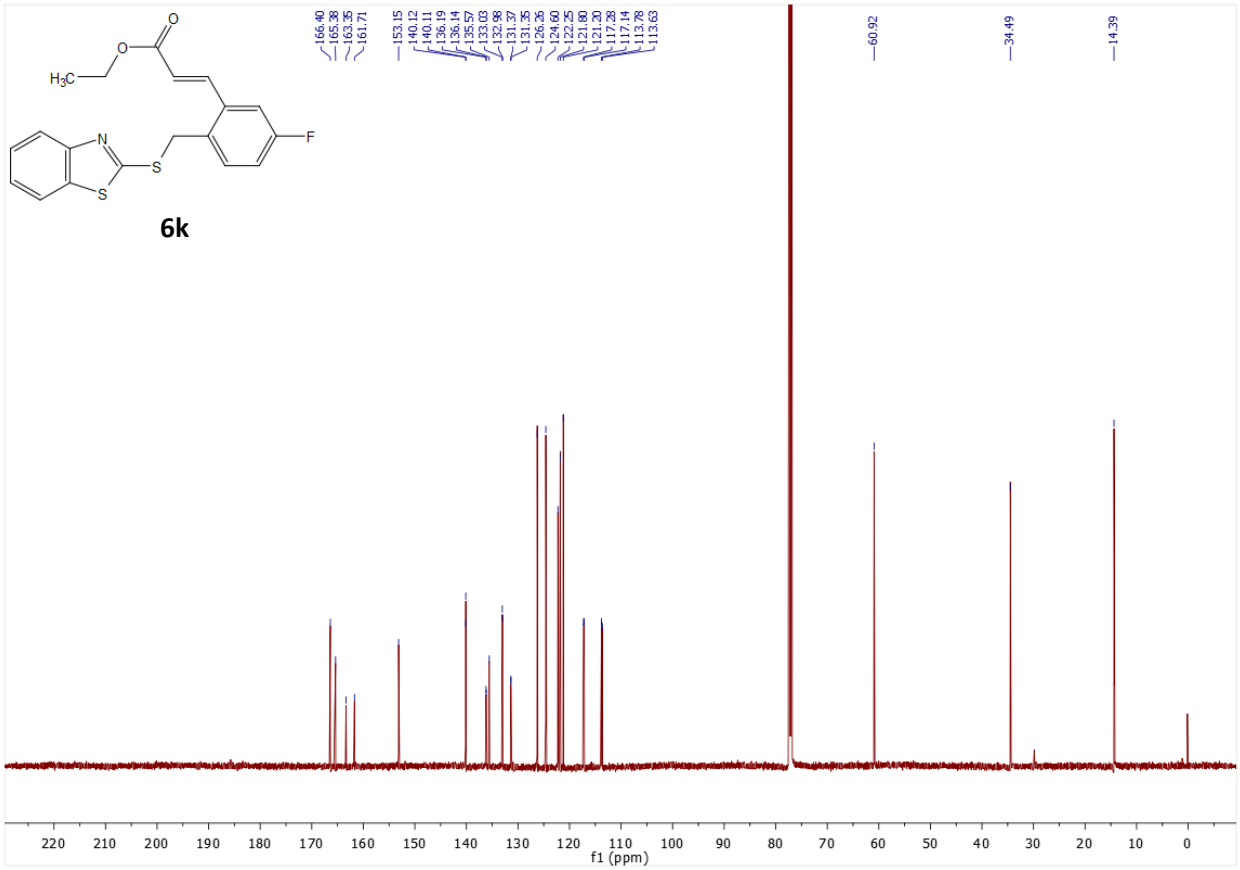

6j
6j'
0.56
0.94
0.93
1.58
1.56
5.07
0.61
3.19
1.70
1.58
0.94
0.54
1.85
1.14
1.32
1.90
1.87
3.51
f1 (ppm)

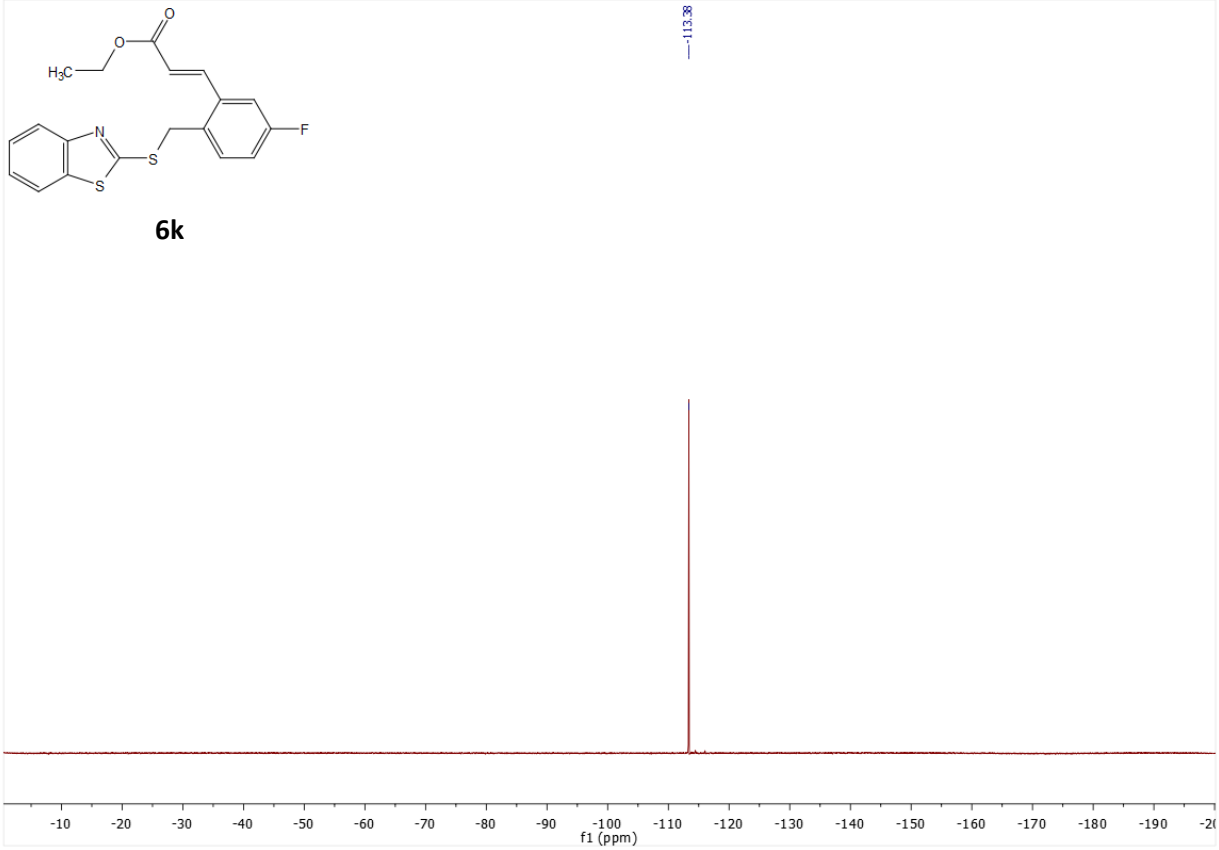

6j
6j'
166.69
166.21
165.98
165.75
153.34
153.21
141.73
141.61
135.58
135.54
133.88
133.00
132.95
132.92
132.27
132.12
131.65
131.50
130.19
129.24
128.47
128.30
127.88
127.71
127.50
127.34
127.08
127.01
126.51
126.22
125.43
124.51
124.50
121.76
121.48
121.18
121.17
60.95
60.75
36.20
35.90
14.41
14.40
f1 (ppm)


6j''
1.00
1.02
1.02
2.16
1.02
1.01
2.04
1.11
1.04
0.97
0.93
1.96
2.04
1.95
3.31
3.01
f1 (ppm)

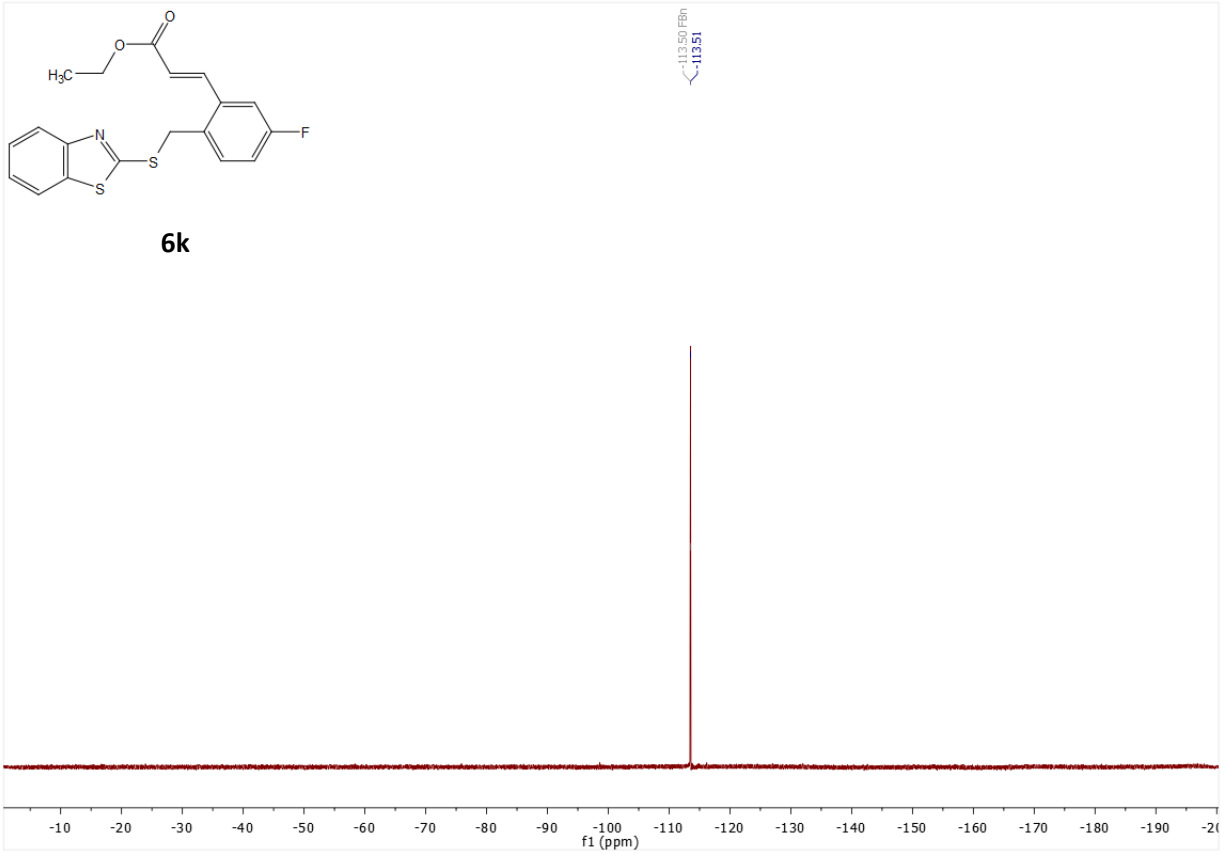

6j''
166.49
165.97
165.36
153.20
141.92
141.64
135.59
134.72
132.82
132.79
132.01
129.51
128.93
127.95
127.92
127.71
127.27
126.24
125.67
124.56
122.39
121.88
121.16
61.01
33.55
14.34
f1 (ppm)


6k
0.99
0.95
1.00
1.05
1.12
1.08
1.14
1.08
1.00
2.06
1.99
3.10
f1 (ppm)

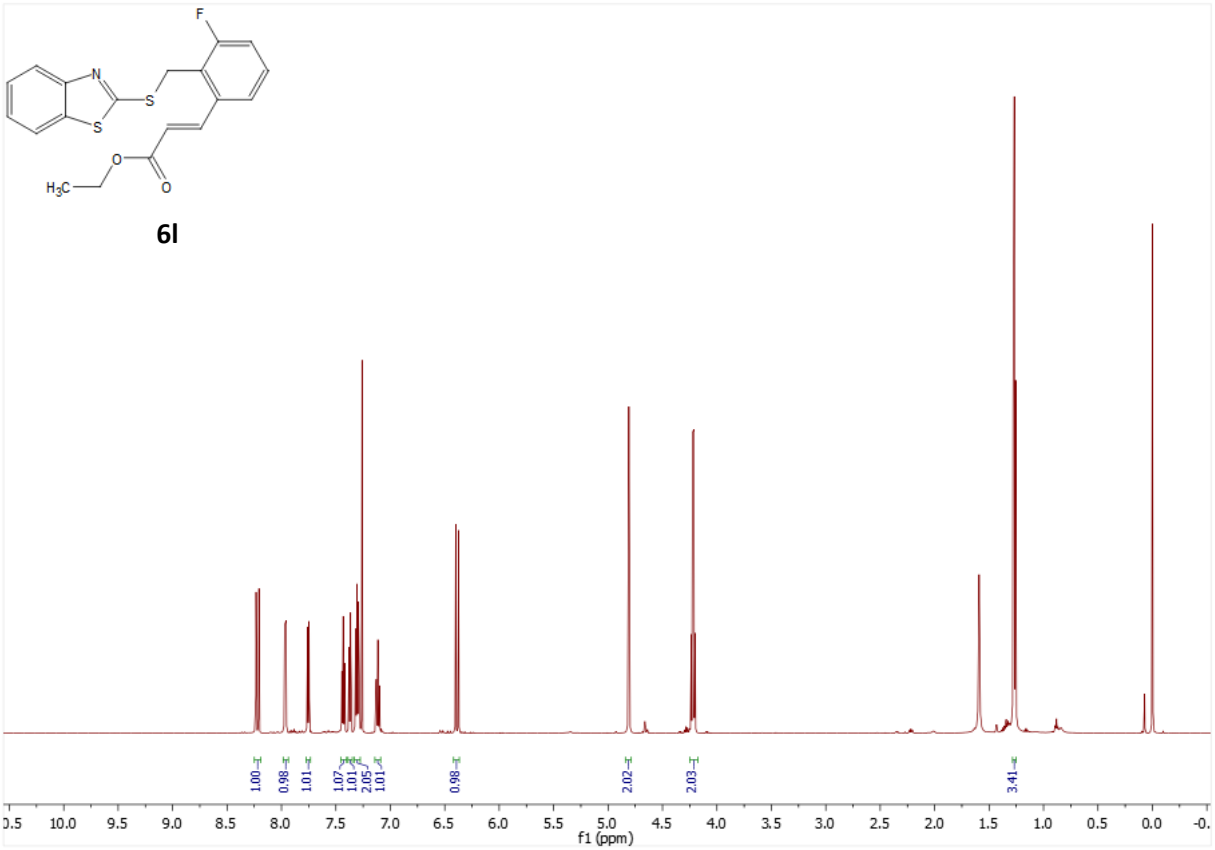

6k
166.40
165.38
163.35
161.71
153.15
140.12
140.11
136.19
136.14
135.57
133.03
132.98
131.37
131.35
126.26
124.60
122.25
121.80
121.20
117.28
117.14
113.78
113.63
60.92
34.49
14.39
f1 (ppm)

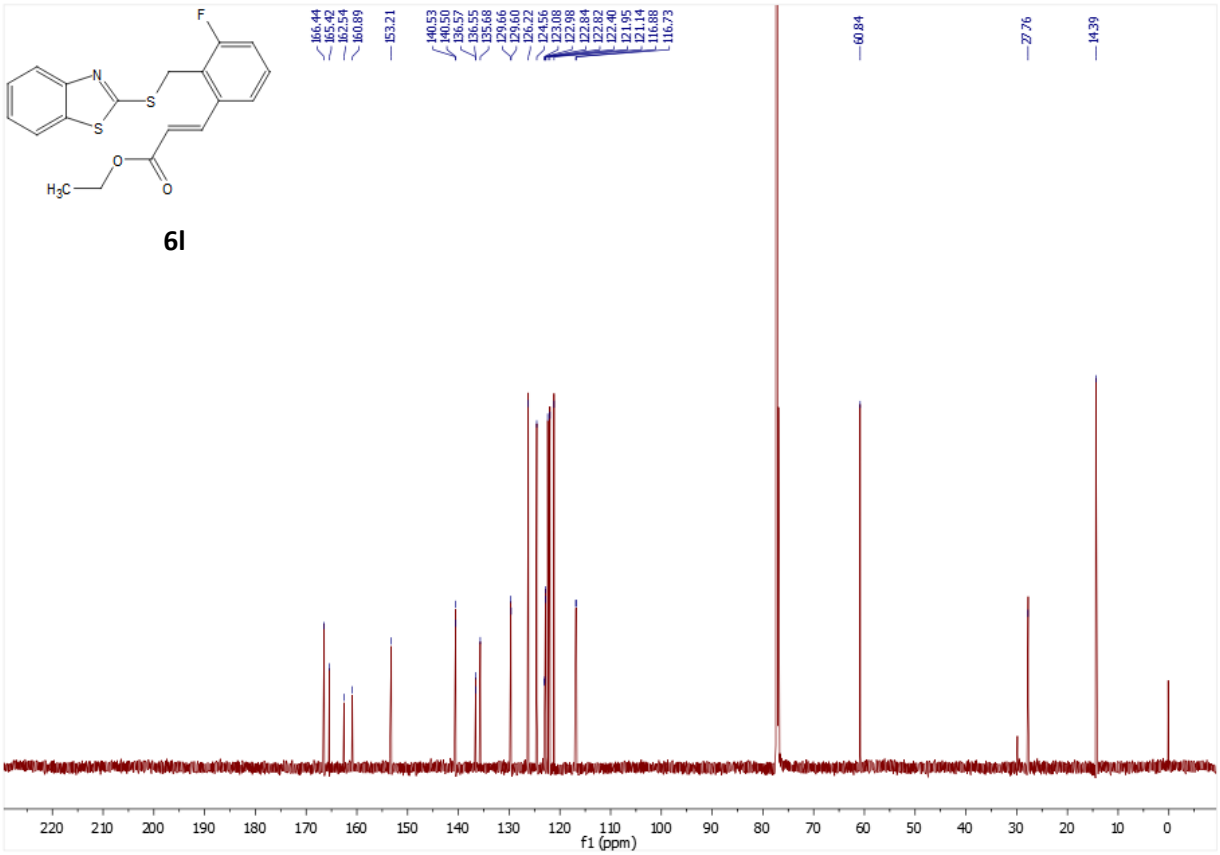

-113.38
O
O
H3C
N
S
S
F
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

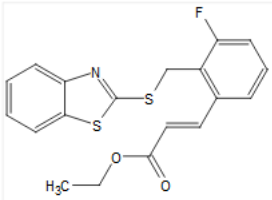
6k


-113.50 FBn
-113.51
O
O
H3C
N
S
S
F
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

6k

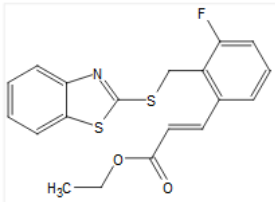

F
N
S
S
O
O
H3C
6l
1.00
0.98
1.01
1.07
1.01
2.05
1.01
0.98
2.02
2.03
3.41
f1 (ppm)


F
N
S
S
O
O
H3C
6l
166.44
165.42
162.54
160.89
153.21
140.53
140.50
136.57
136.55
135.68
129.66
129.60
129.22
124.56
123.08
122.98
122.84
122.82
122.46
121.95
121.14
116.88
116.73
60.84
27.76
14.39
f1 (ppm)


F
N
S
S
O
O
H3C

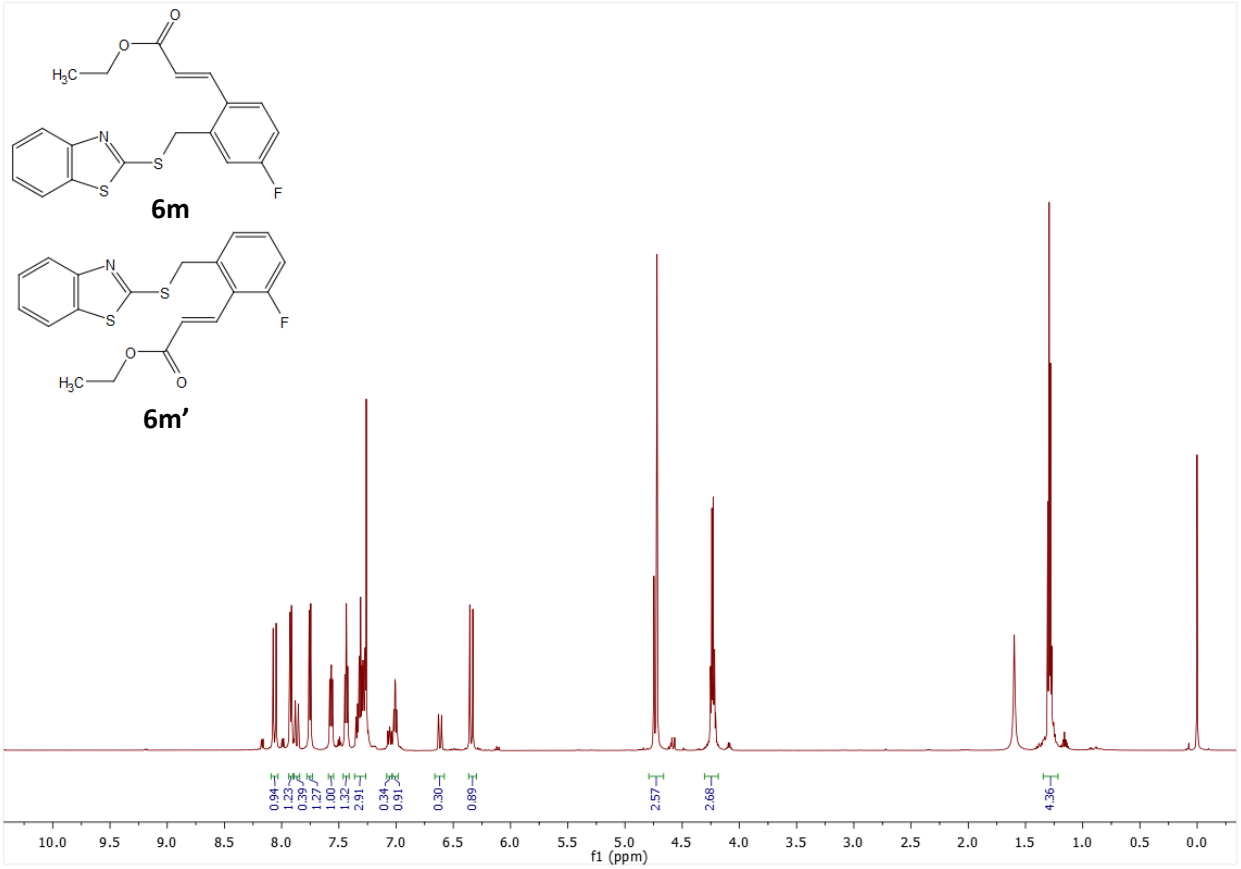
6l

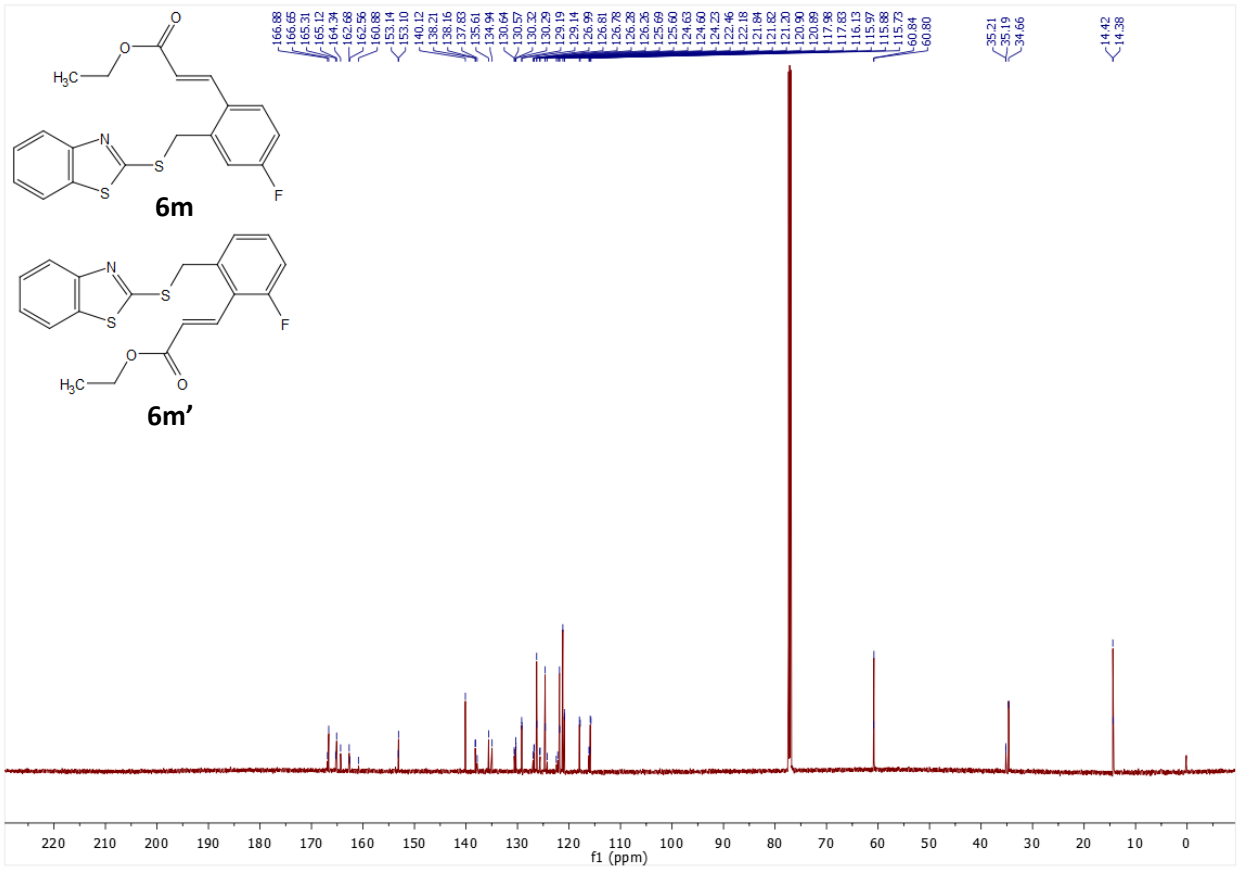
-114.41
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

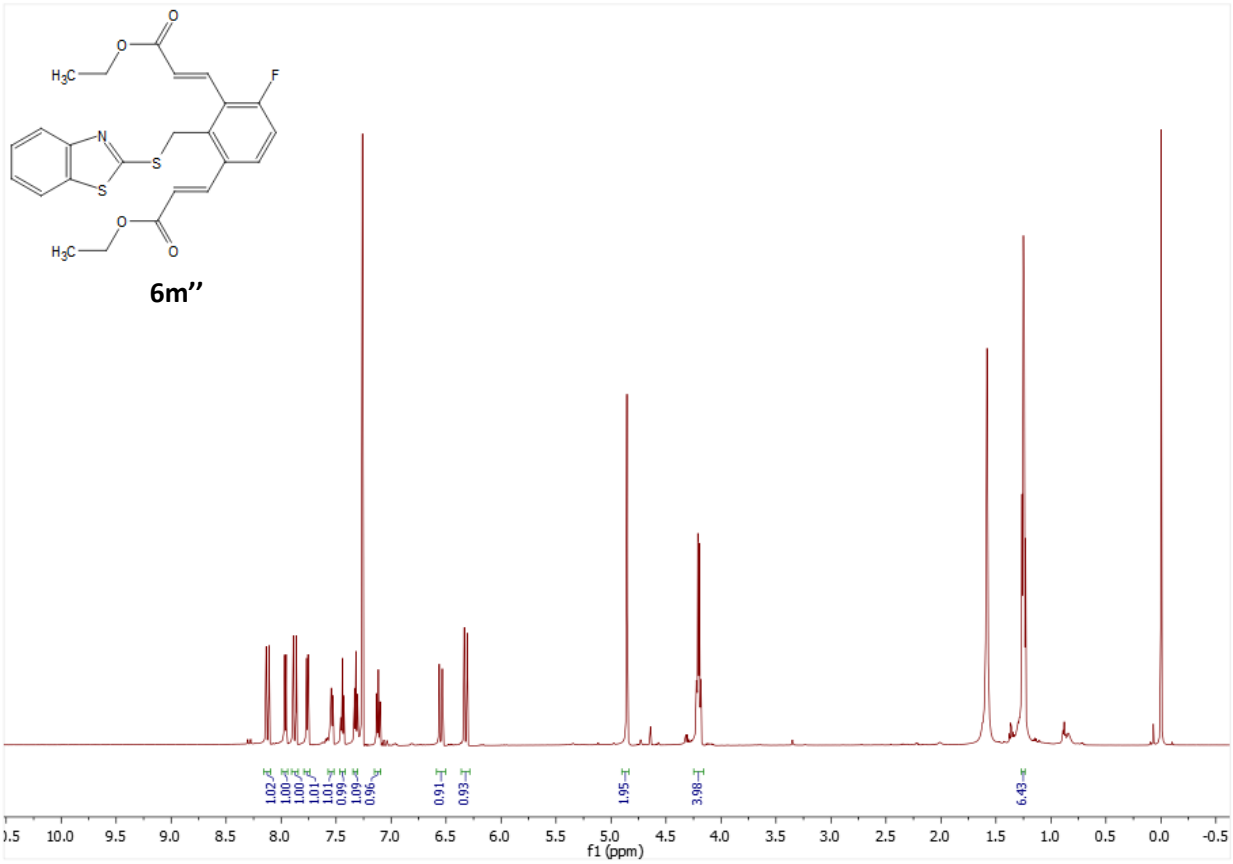

F
N
S
S
O
O
H3C

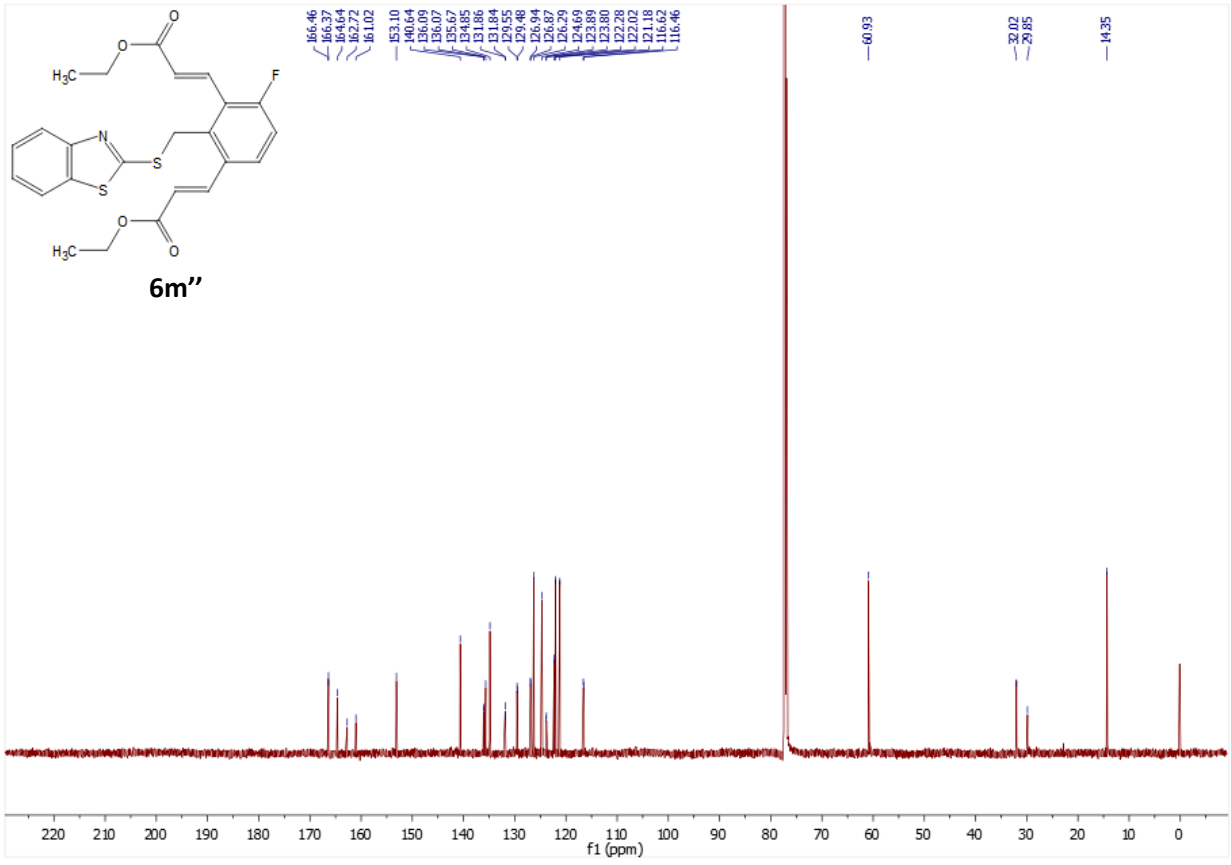
6l

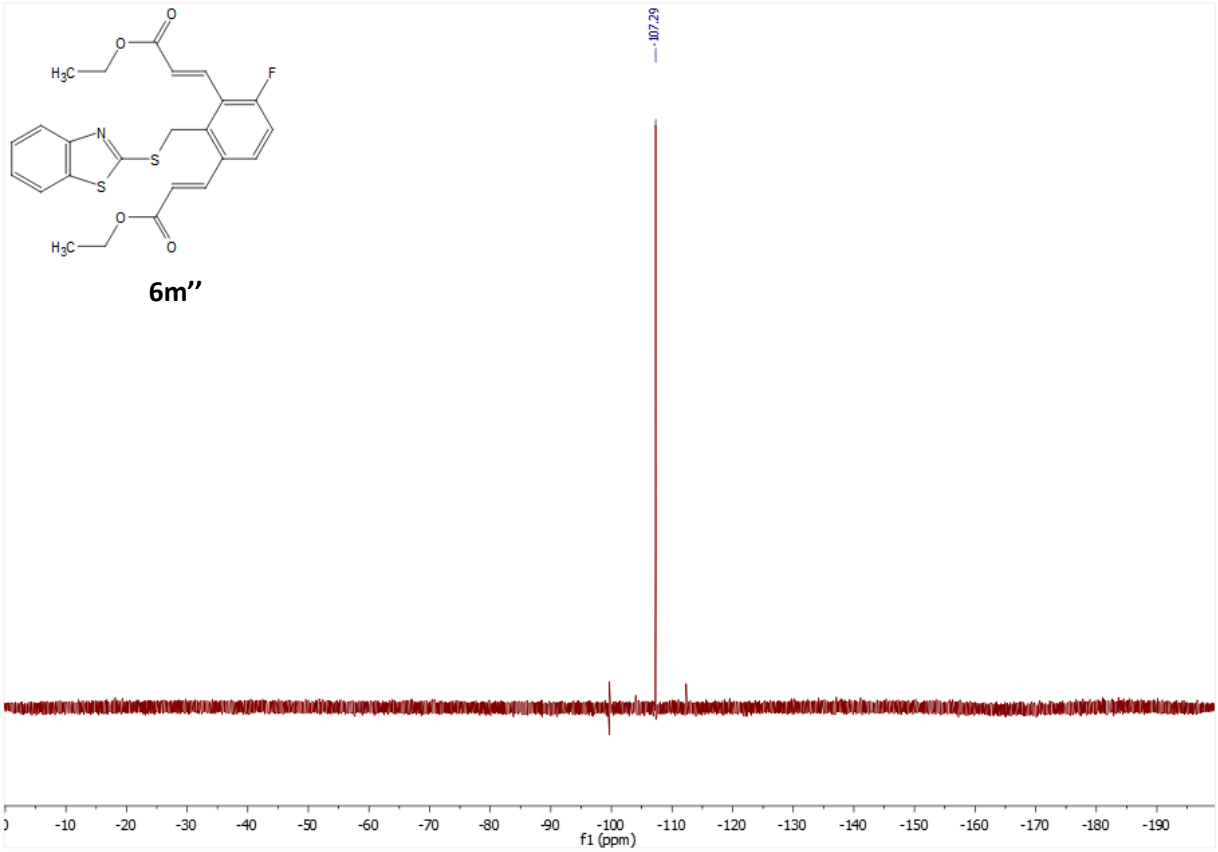
113.50 fbn
-114.53
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


6m
6m’
0.94
1.23
0.39
1.27
1.00
1.32
2.91
0.34
0.91
0.30
0.89
2.57
2.68
4.36
f1 (ppm)

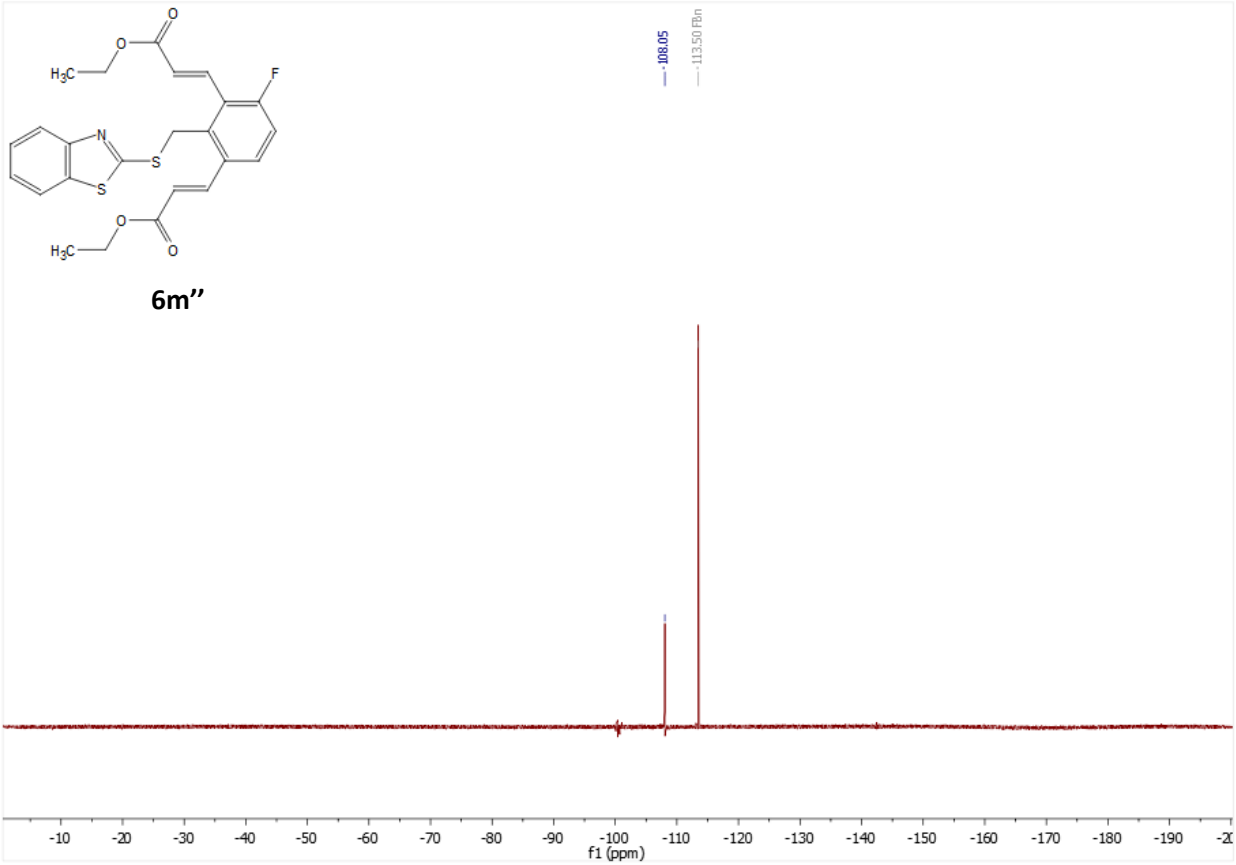

6m
6m’
166.88
166.65
165.31
165.12
164.34
162.68
162.56
160.88
153.14
153.10
140.12
138.21
138.16
137.83
135.61
134.94
130.64
130.57
130.32
130.29
129.19
129.14
126.99
126.81
126.78
126.28
126.26
125.69
125.60
124.63
124.60
124.23
122.46
122.18
121.84
121.82
121.20
120.90
120.89
117.98
117.83
116.13
115.97
115.88
115.73
60.84
60.80
35.21
35.19
34.66
14.42
14.38
f1 (ppm)


6m''
1.02
1.00
1.00
1.01
1.01
0.99
1.09
0.96
0.91
0.93
1.95
3.98
6.43
f1 (ppm)

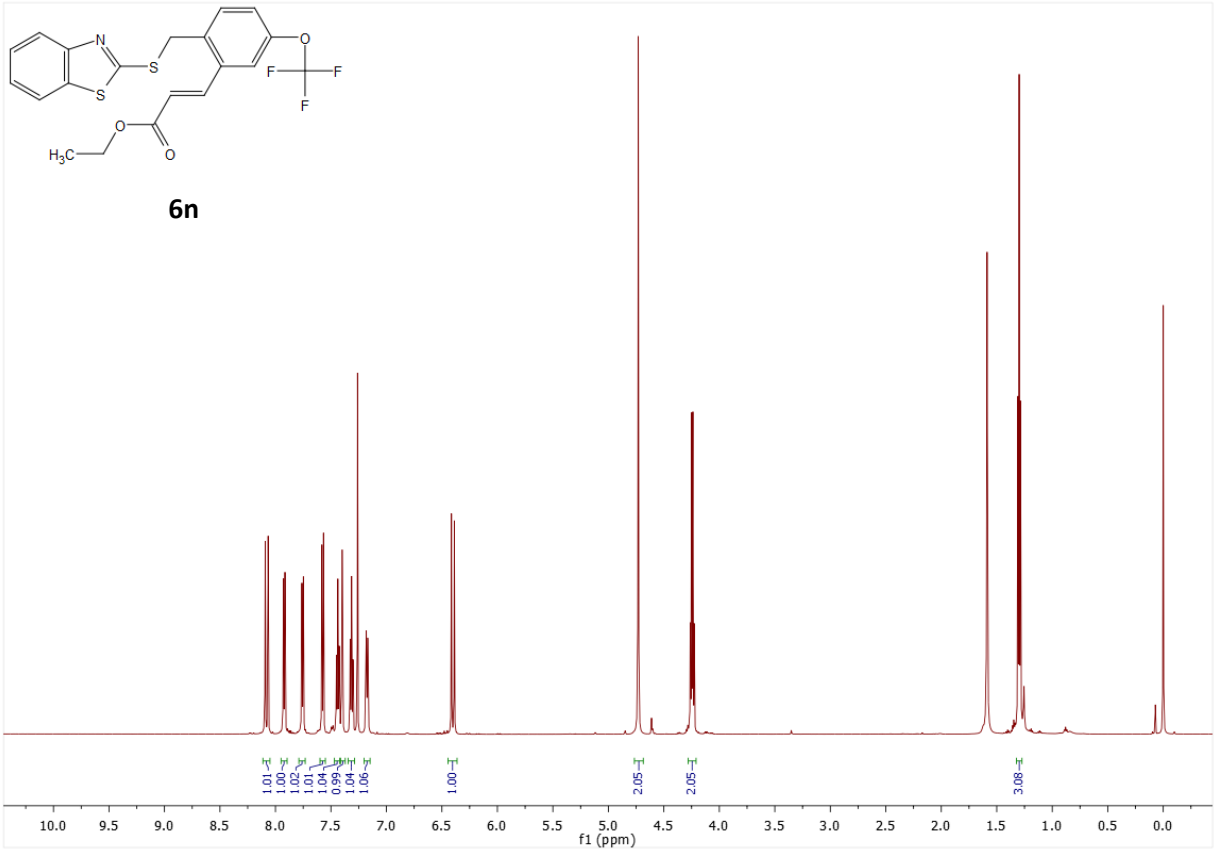

6m''
166.46
166.37
164.64
162.72
161.02
153.10
140.64
136.09
136.07
135.67
134.85
131.86
131.84
129.55
129.48
126.94
126.87
126.29
124.69
123.89
123.80
122.28
122.02
121.18
116.62
116.46
60.93
32.02
29.85
14.35
f1 (ppm)

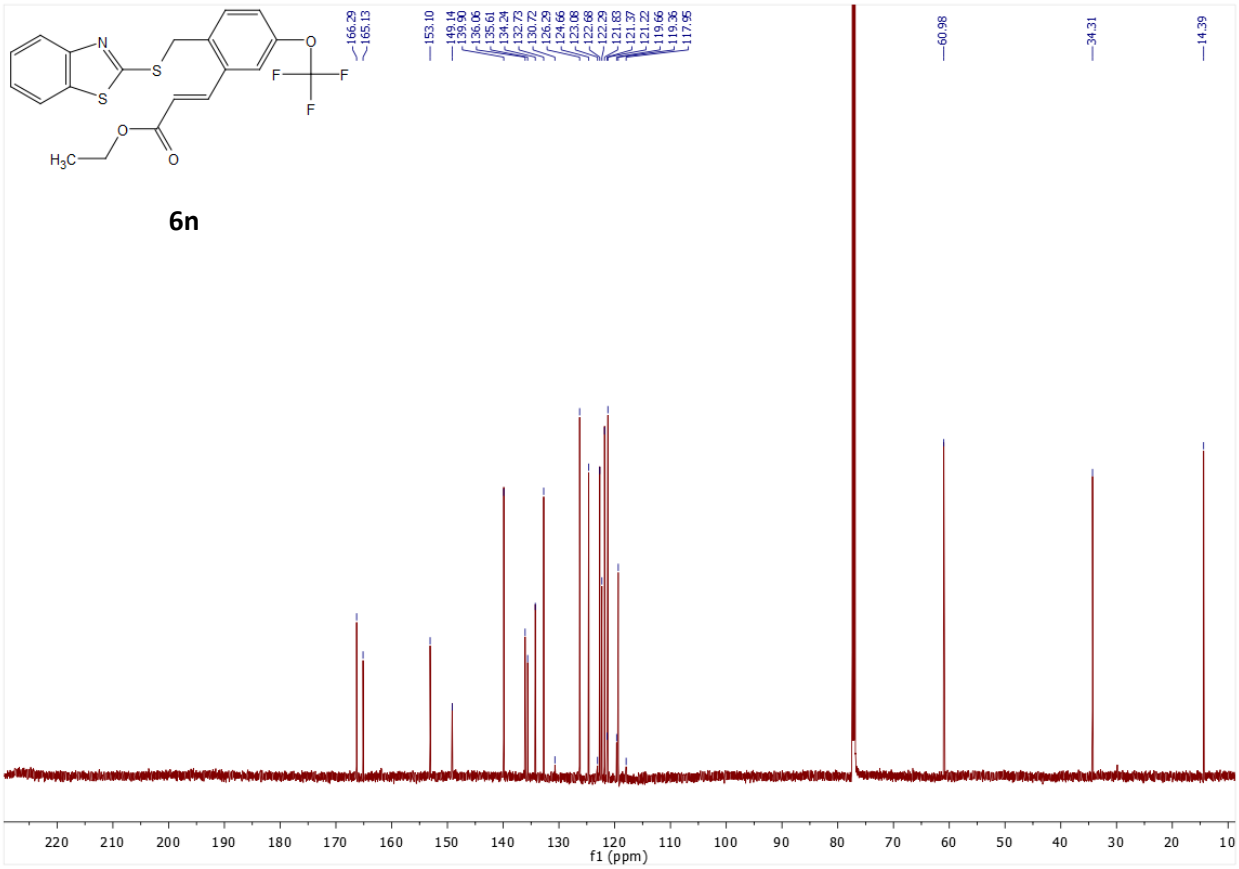

-107.29
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

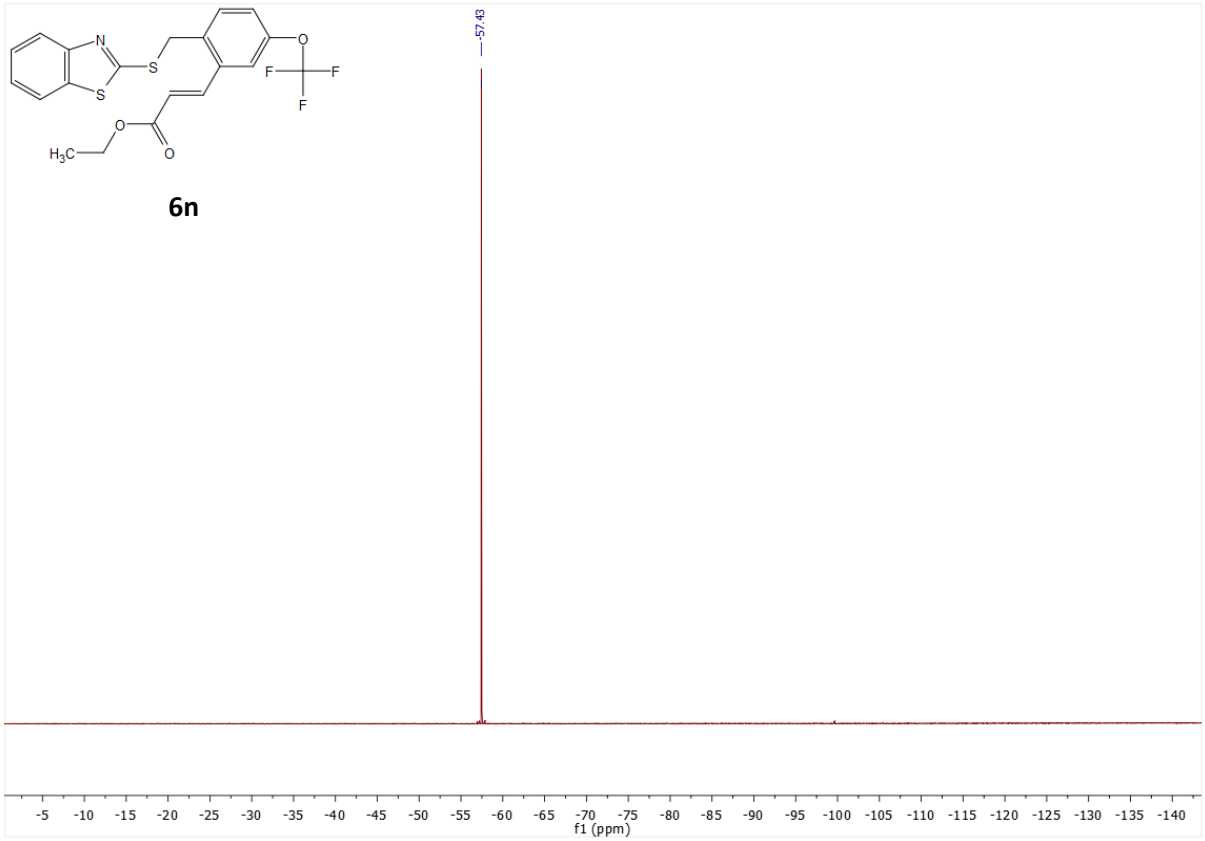
6m''


-108.05
113.50 Hz
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

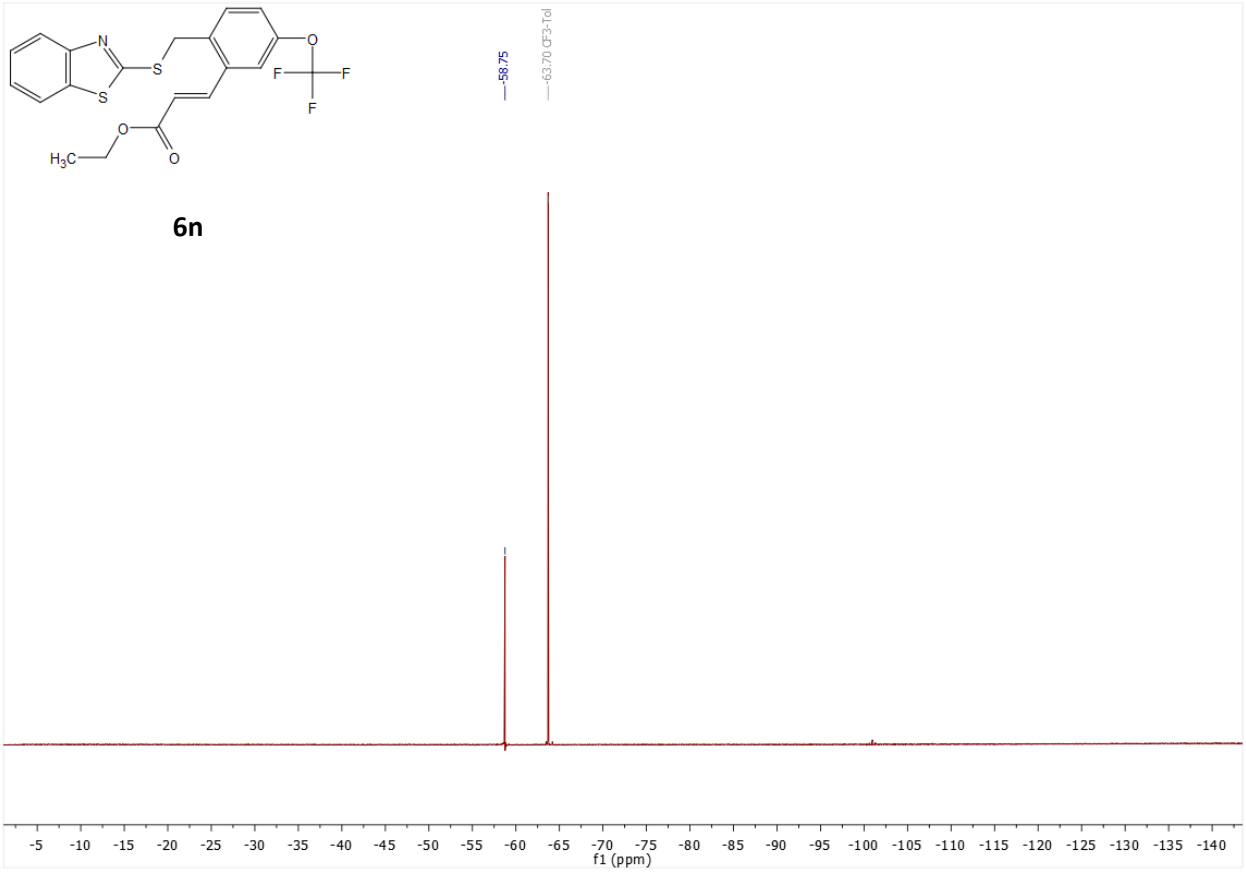
6m''


6n
1.01
1.00
1.02
1.01
1.04
0.99
1.04
1.06
1.00
2.05
2.05
3.08
f1 (ppm)

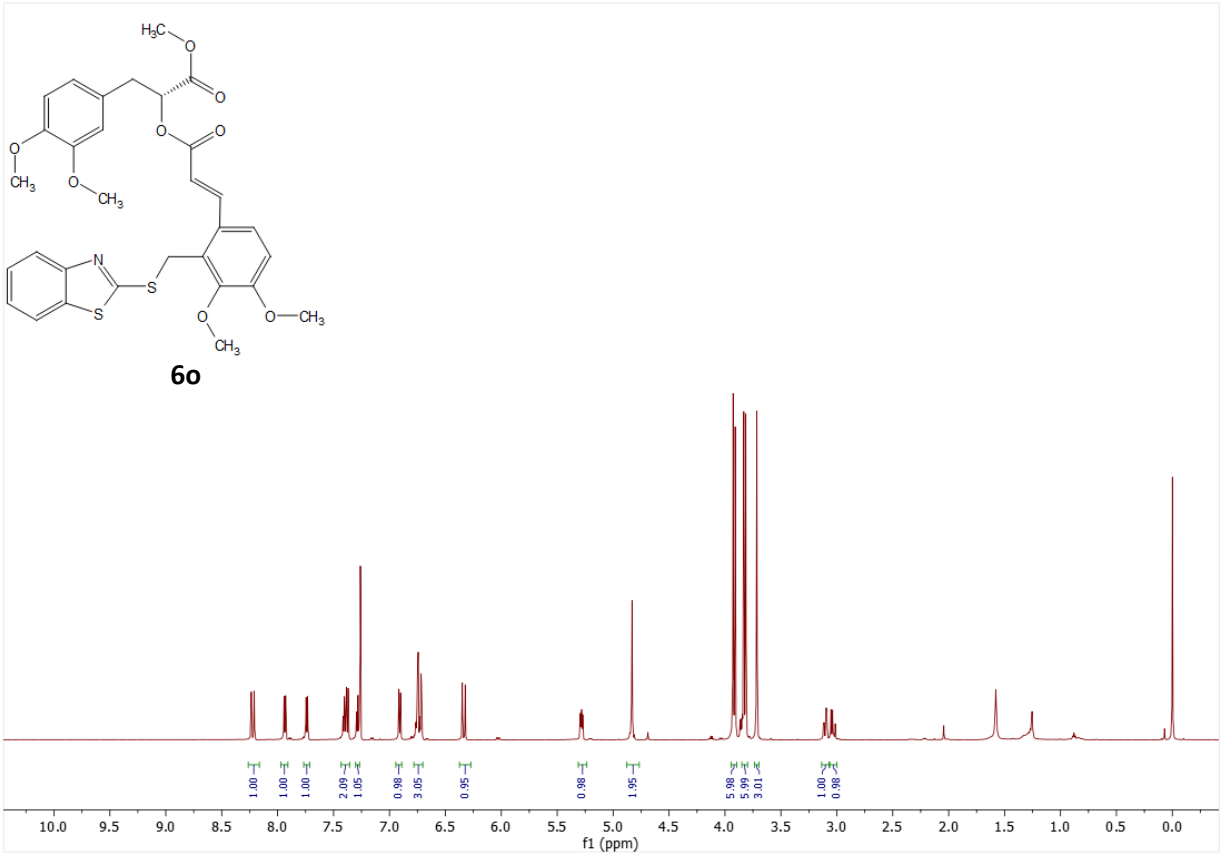

6n
166.29
165.13
153.10
149.14
139.90
136.06
135.61
134.24
132.73
130.72
126.29
124.66
123.08
122.68
122.29
121.83
121.37
121.22
119.66
119.36
117.95
60.98
34.31
14.39
f1 (ppm)

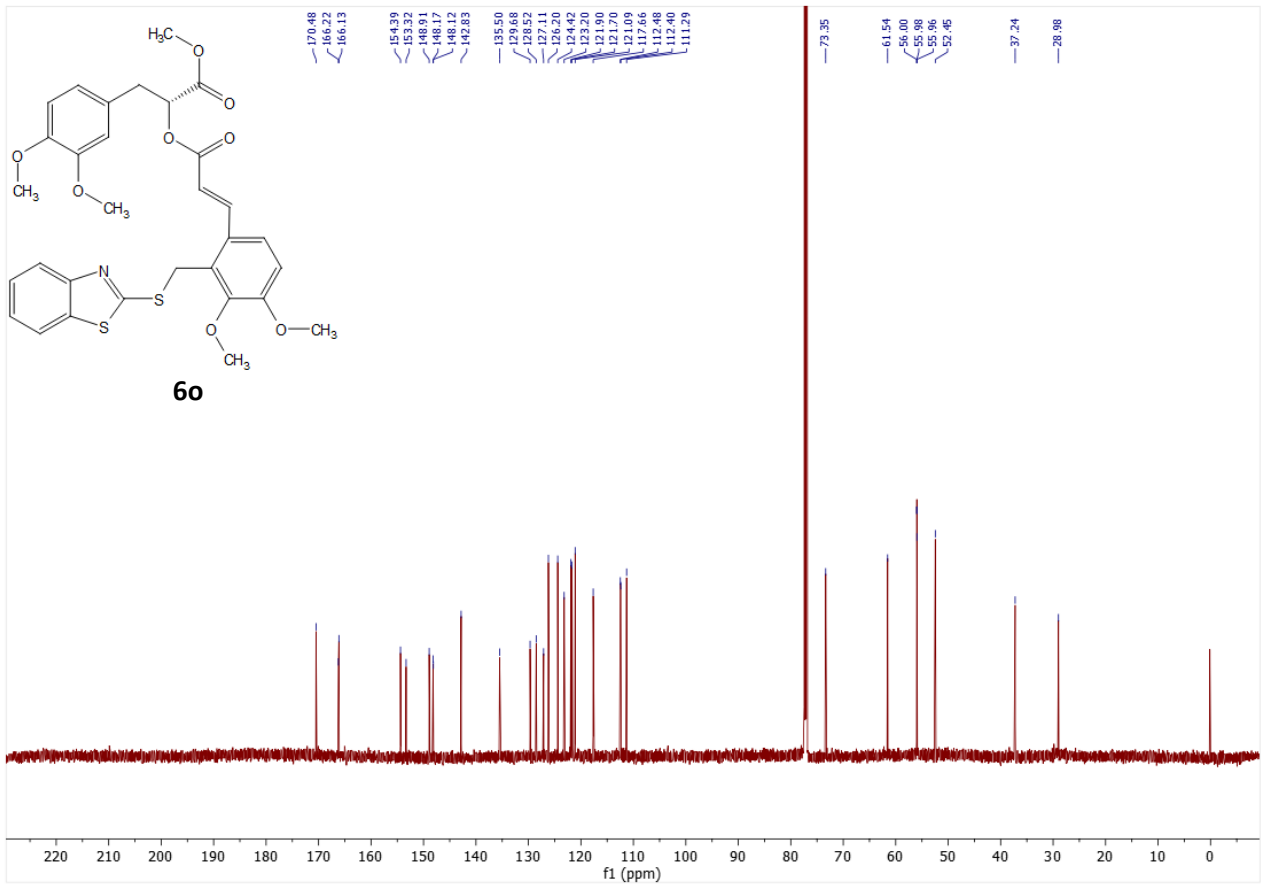

-57.43
-5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140
f1 (ppm)

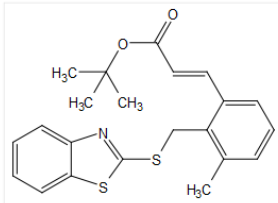
6n


-58.75
-63.70 CF3-Tol
-5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140
f1 (ppm)

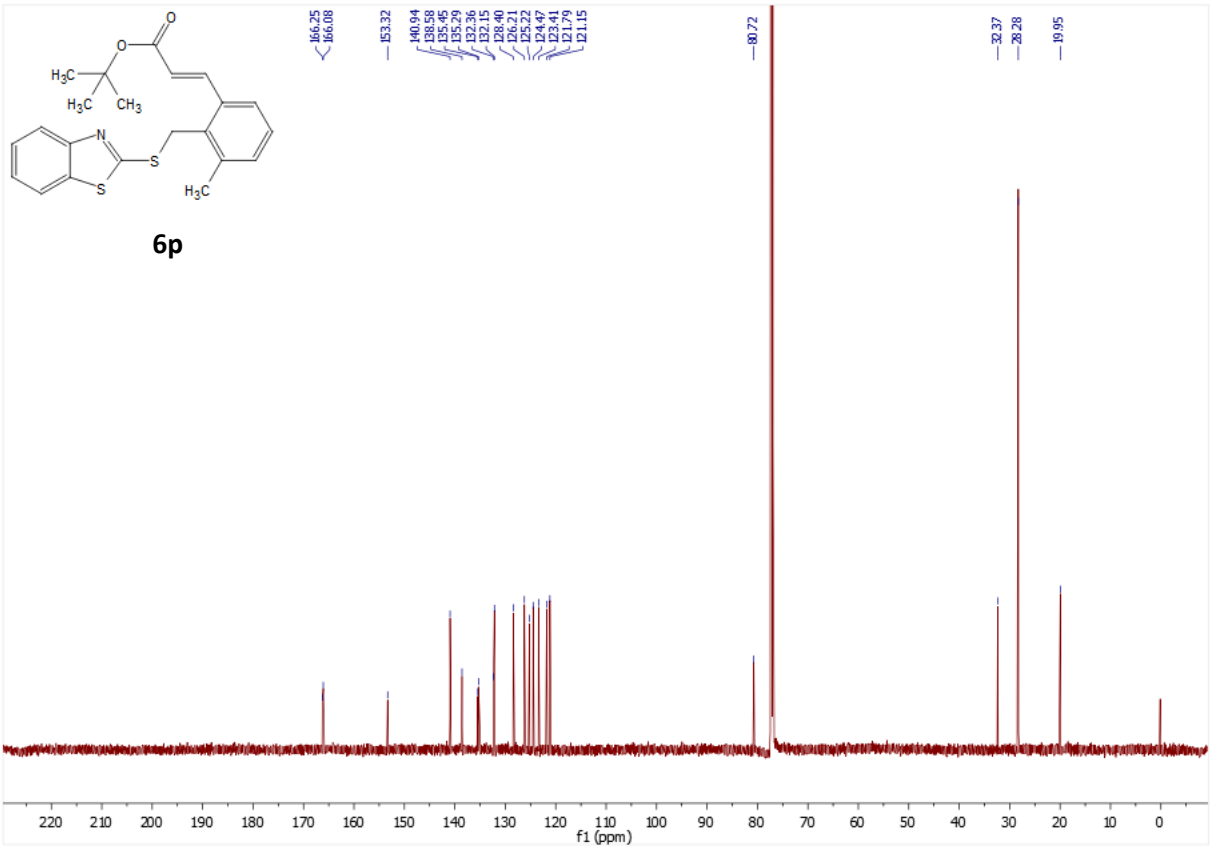
6n


6o
1.00
1.00
1.00
2.09
1.05
0.98
3.05
0.95
0.98
1.95
5.98
5.99
3.01
1.00
0.98
f1 (ppm)

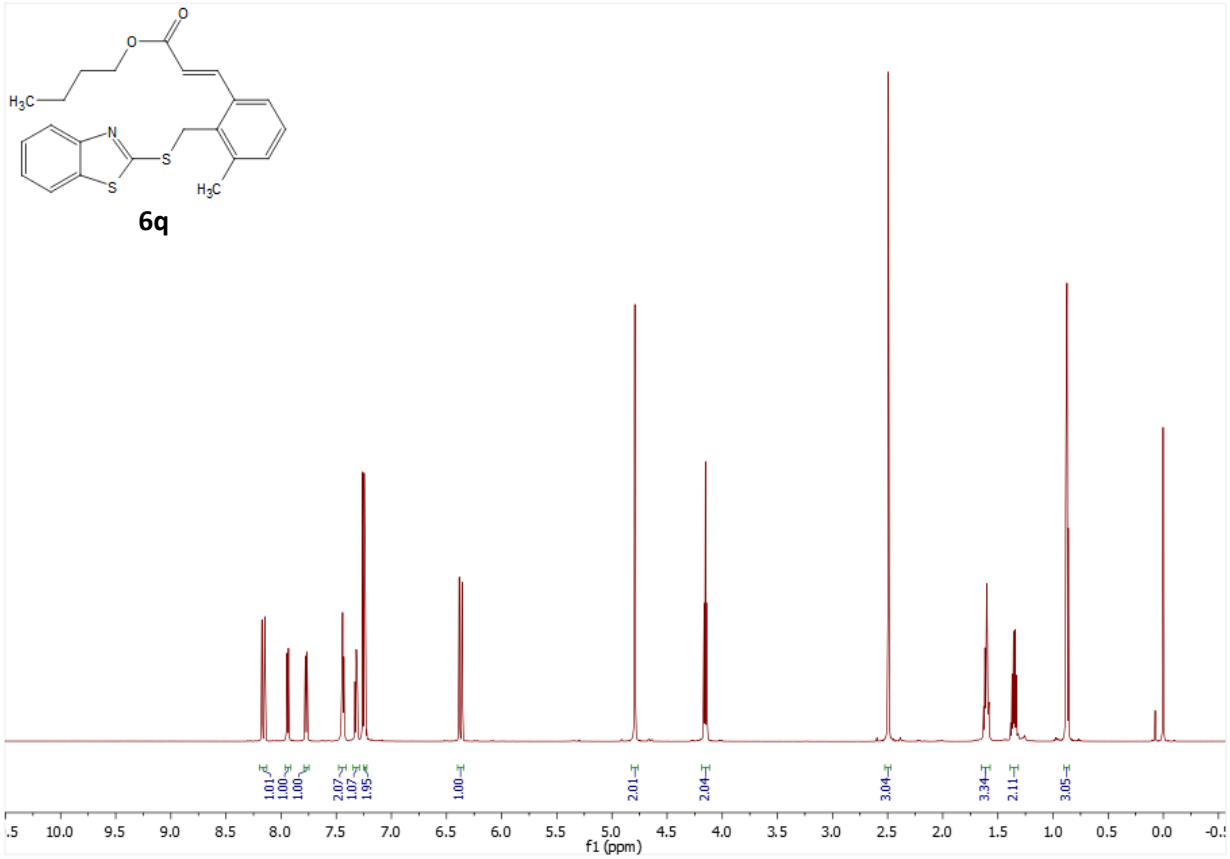

6o
170.48
166.22
166.13
154.39
153.32
148.91
148.17
148.12
142.83
135.50
129.68
128.52
127.11
126.20
124.42
123.20
121.90
121.70
121.09
117.66
112.48
112.40
111.29
73.35
61.54
56.00
55.98
55.96
52.45
37.24
28.98
f1 (ppm)



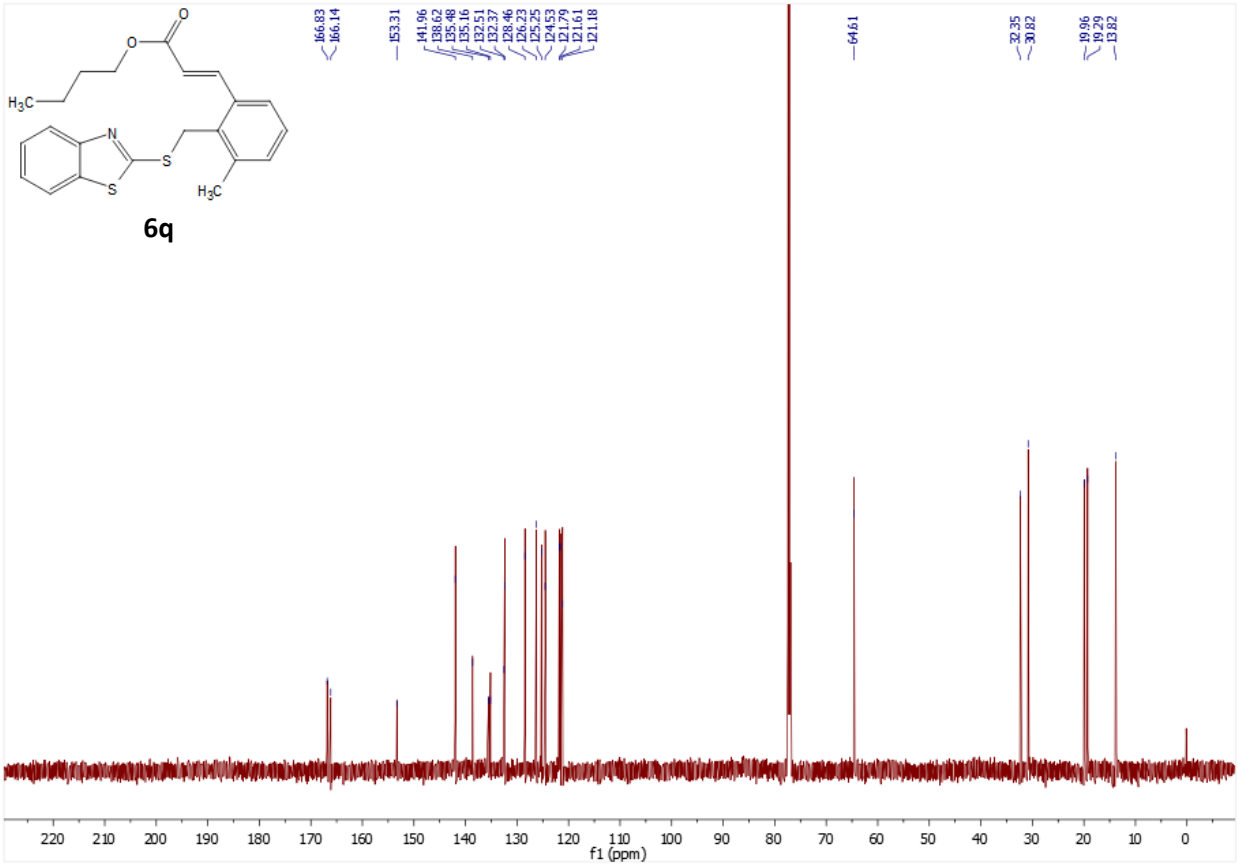
6p



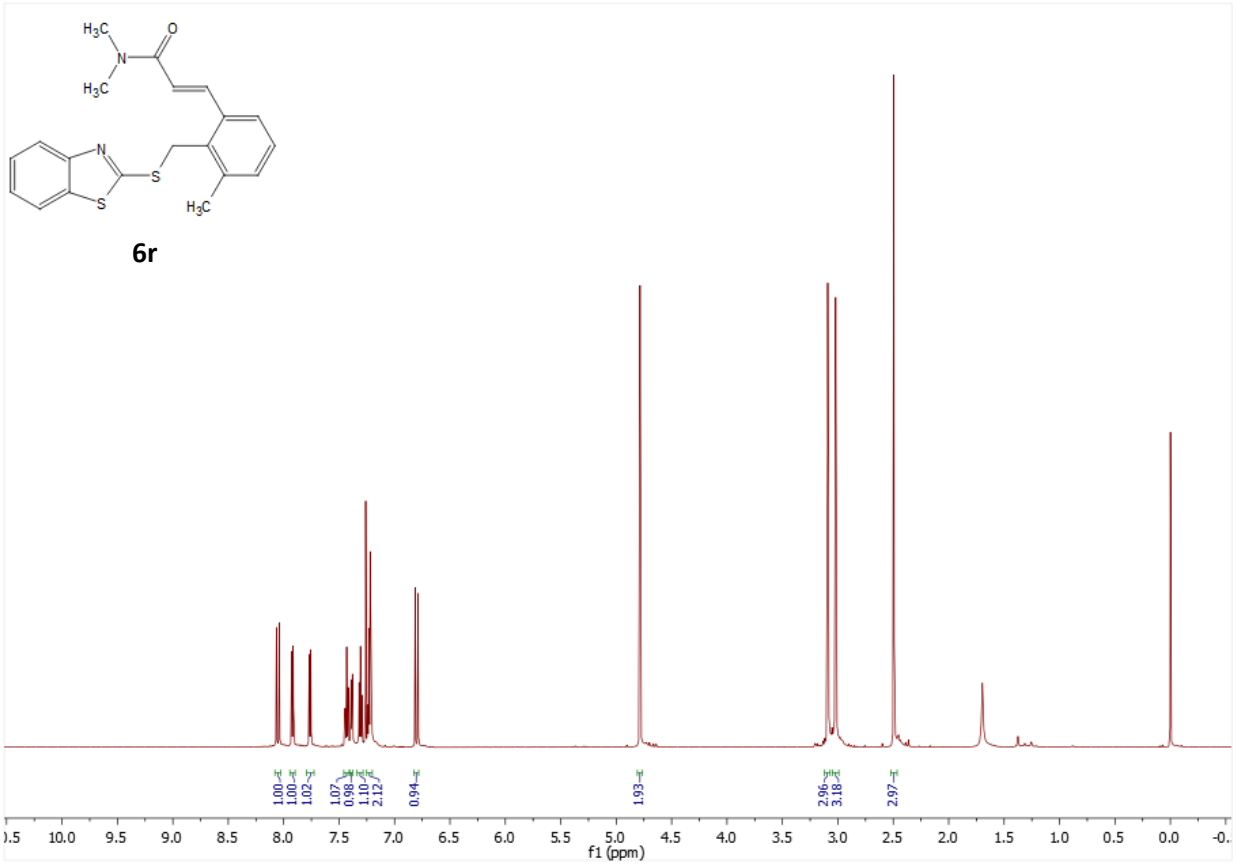
6p

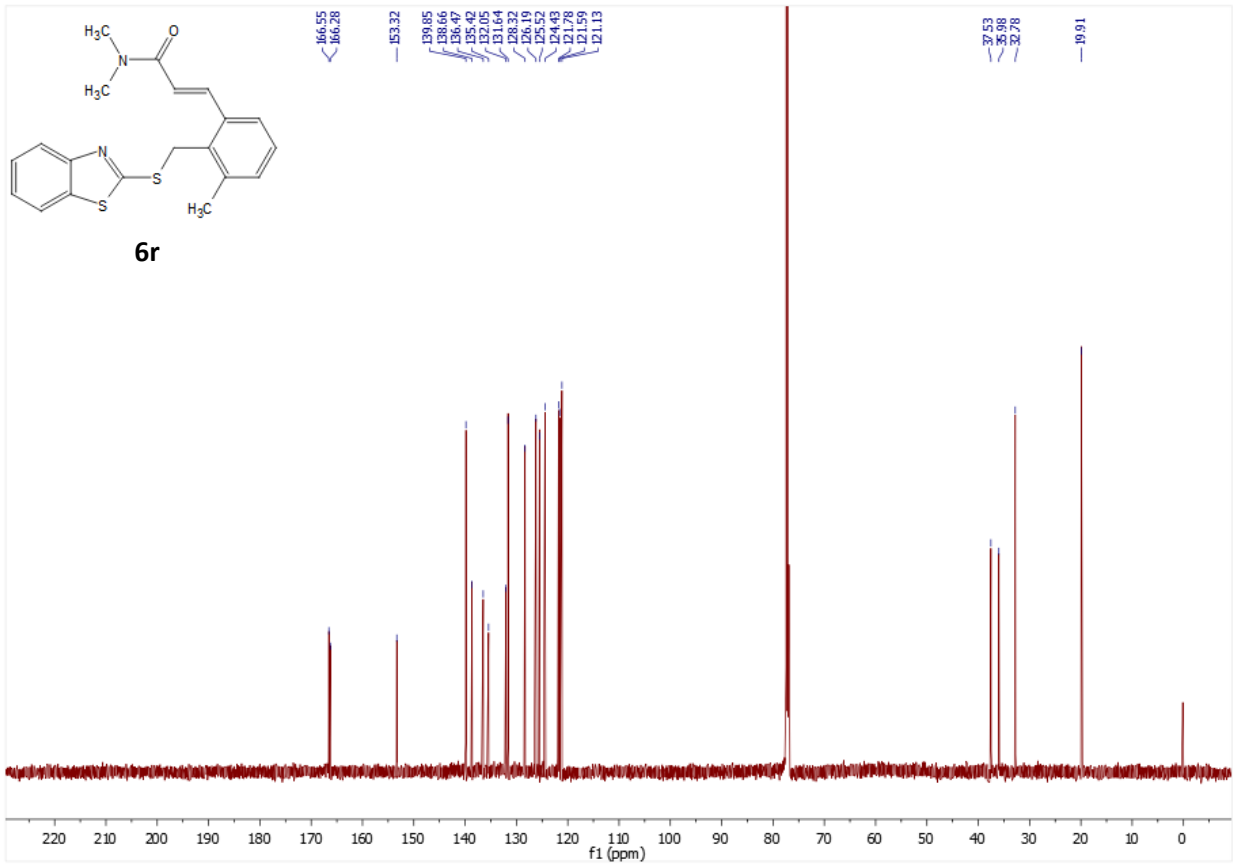

O
O
H3C
N
S
S
H3C
1.01
1.00
1.00
2.07
1.07
1.95
1.00
2.01
2.04
3.04
3.34
2.11
3.05
f1 (ppm)

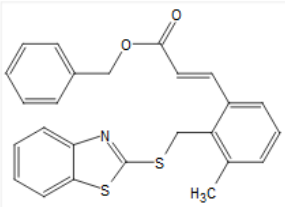
6q


O
O
H3C
N
S
S
H3C
166.83
166.14
153.31
141.96
138.62
135.48
135.16
132.51
132.37
128.46
126.23
125.25
124.53
121.79
121.61
121.18
64.61
32.35
30.82
19.96
19.29
13.82
f1 (ppm)

6q

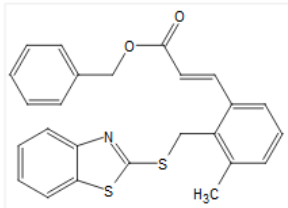

6r
1.00
1.00
1.02
1.07
0.98
1.10
2.12
0.94
1.93
2.96
3.18
2.97
f1 (ppm)


6r
166.55
166.28
153.32
139.85
138.66
136.47
135.42
132.05
131.64
128.32
126.19
125.52
124.43
121.78
121.59
121.13
37.53
36.98
32.78
19.91
f1 (ppm)


O
O
N
S
S
H3C

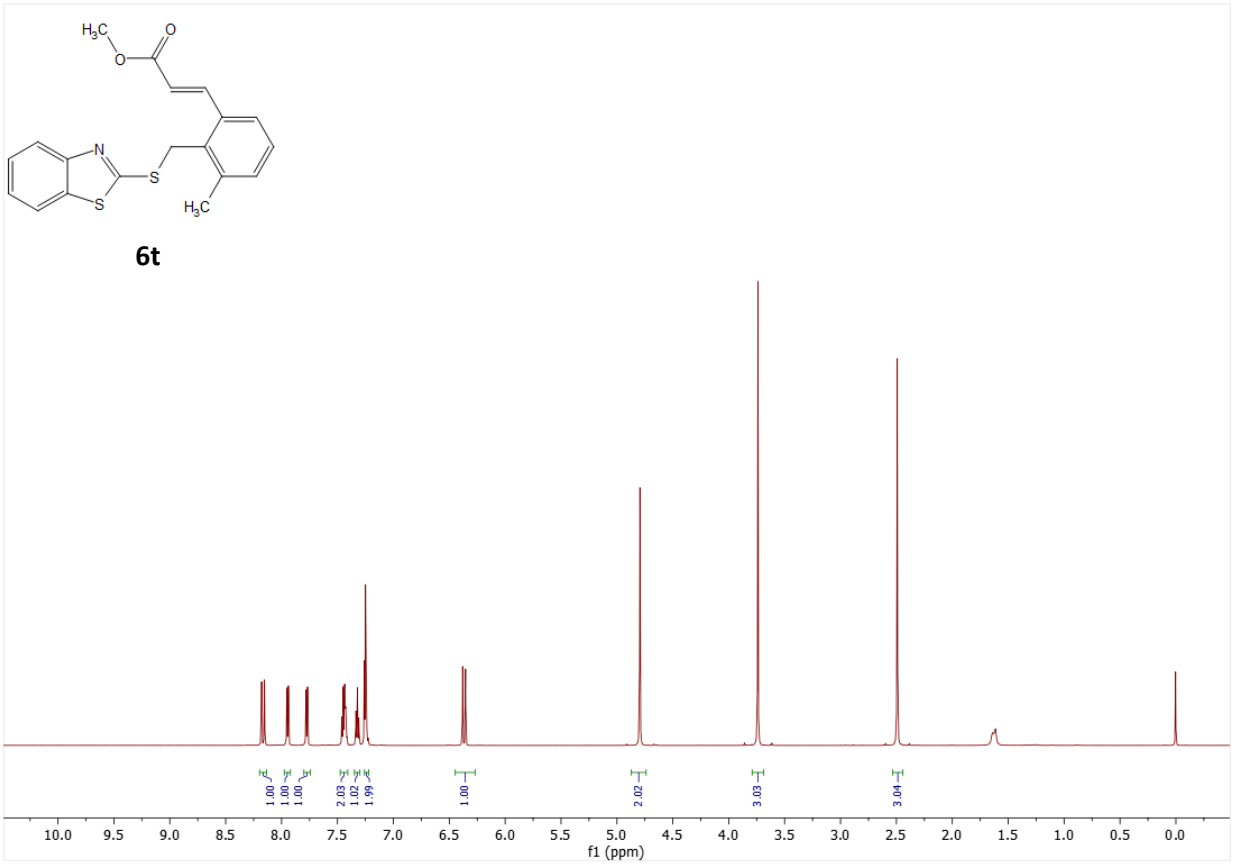
6s

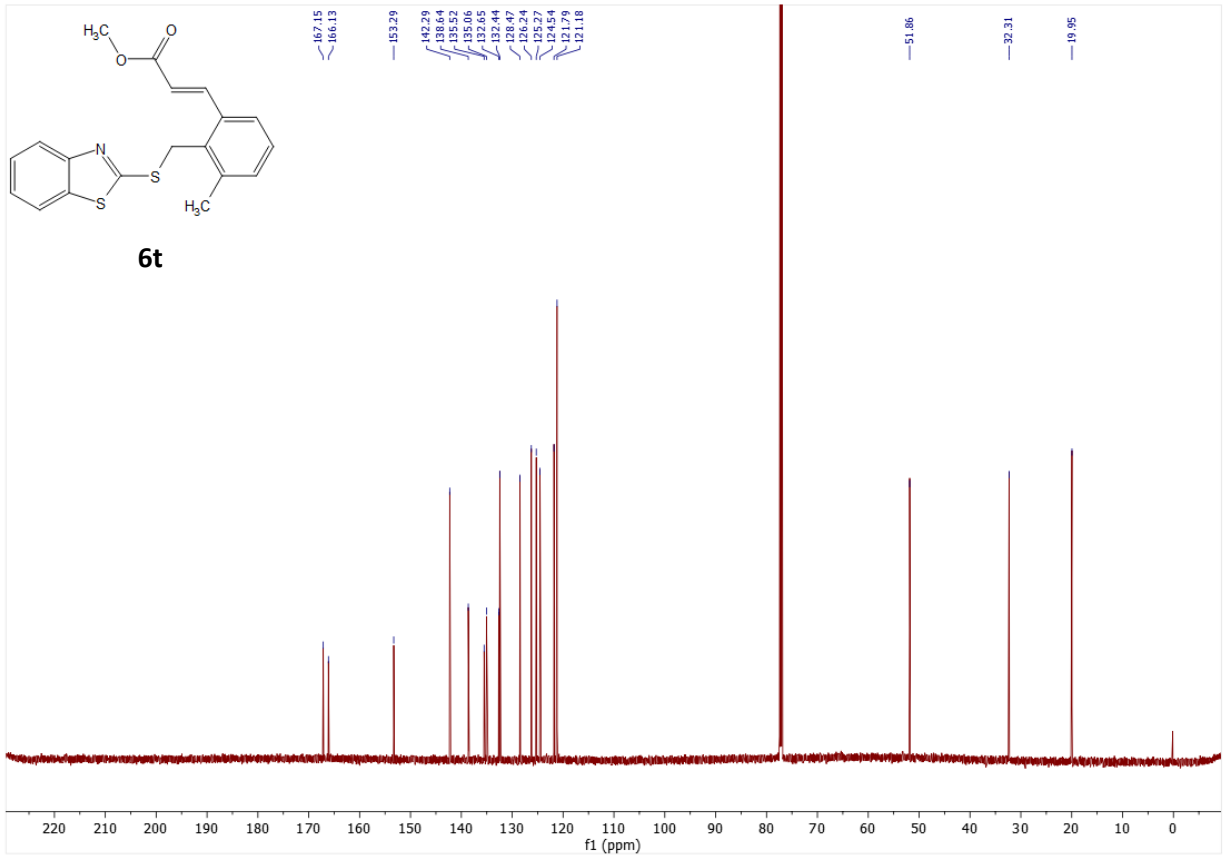
1.00
1.03
0.99
1.98
6.19
2.24
0.97
2.01
1.92
3.10
f1 (ppm)

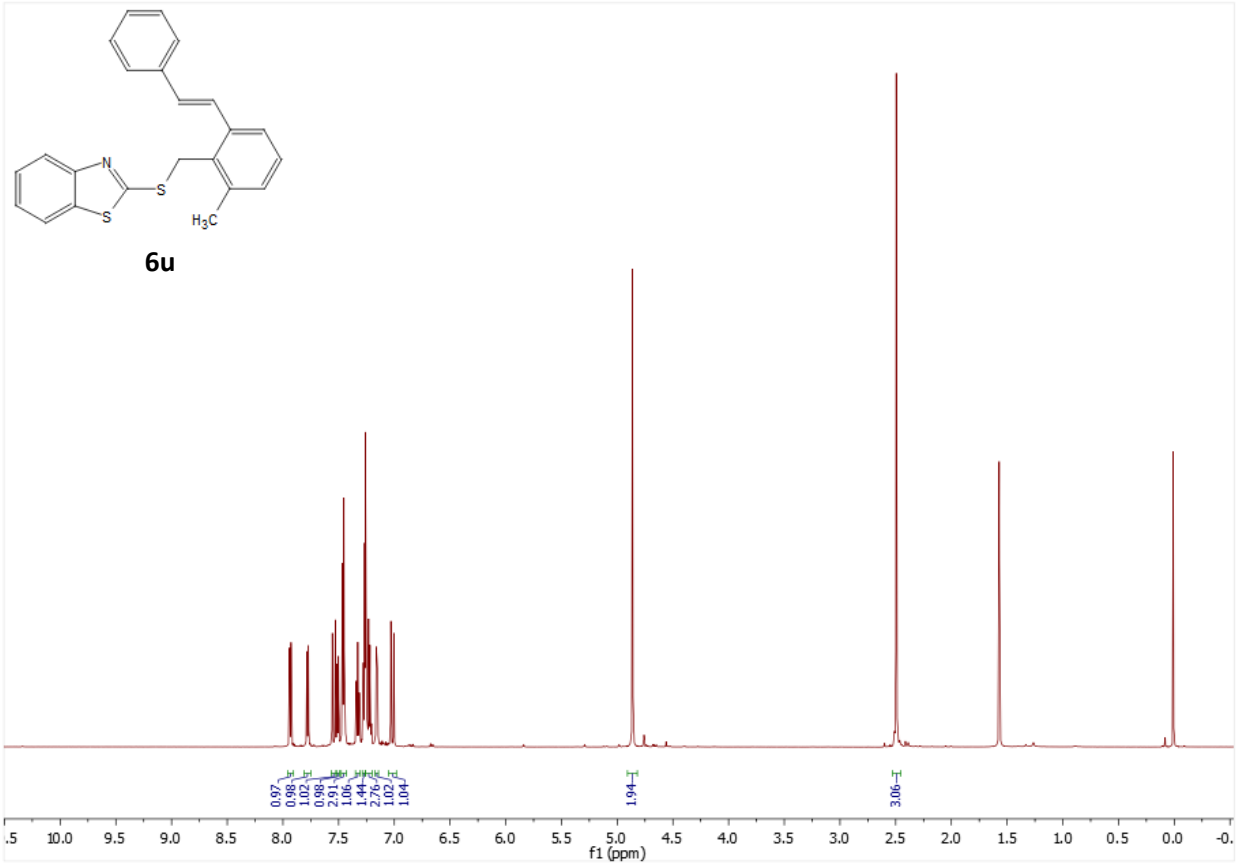

O
O
N
S
S
H3C

6s

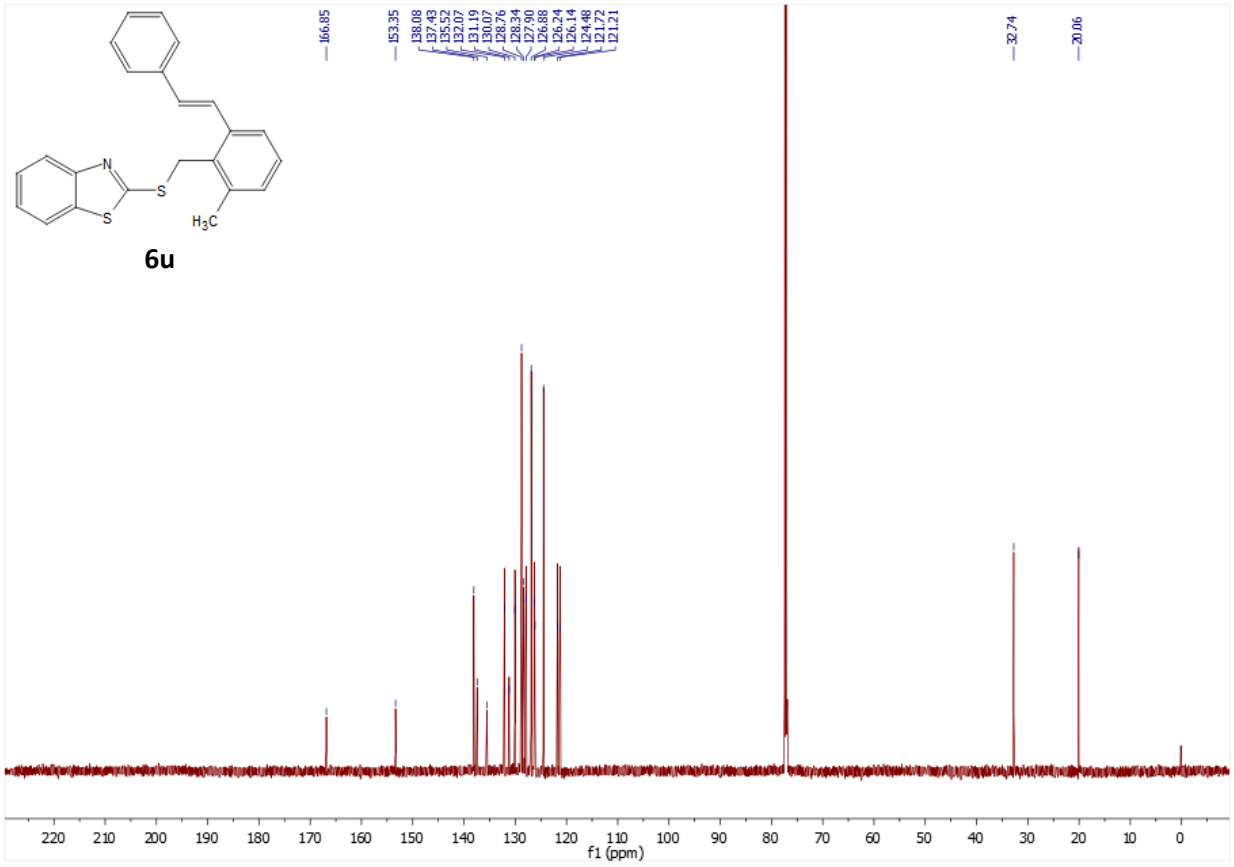
166.52
166.06
153.30
142.62
138.66
136.11
135.50
134.99
132.61
132.50
128.65
128.47
128.29
126.24
125.25
124.53
121.82
121.17
121.12
66.48
32.34
19.96
f1 (ppm)


6t
1.00
1.00
1.00
2.03
1.02
1.99
1.00
2.02
3.03
3.04
f1 (ppm)

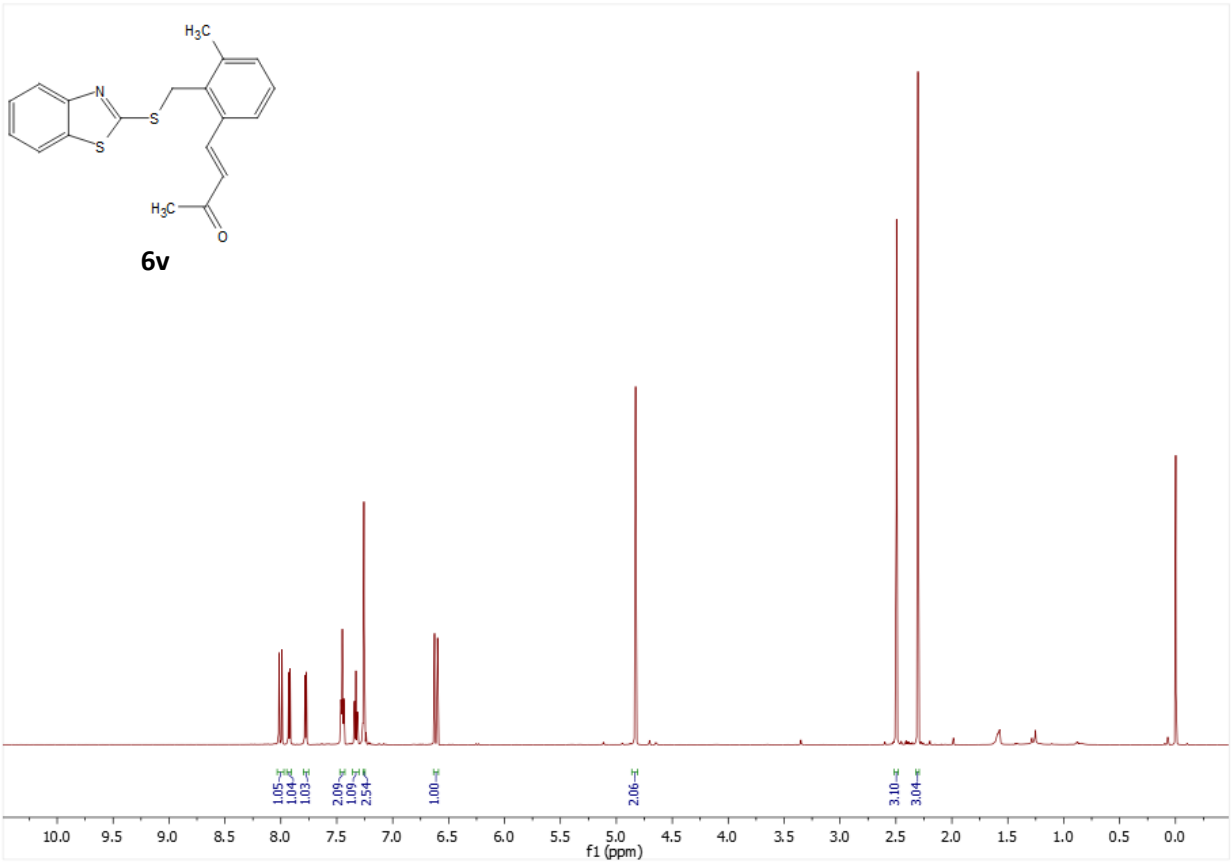

6t
167.15
166.13
153.29
142.29
138.64
135.52
135.06
132.65
132.44
128.47
126.24
125.27
124.54
121.79
121.18
51.86
32.31
19.95
f1 (ppm)

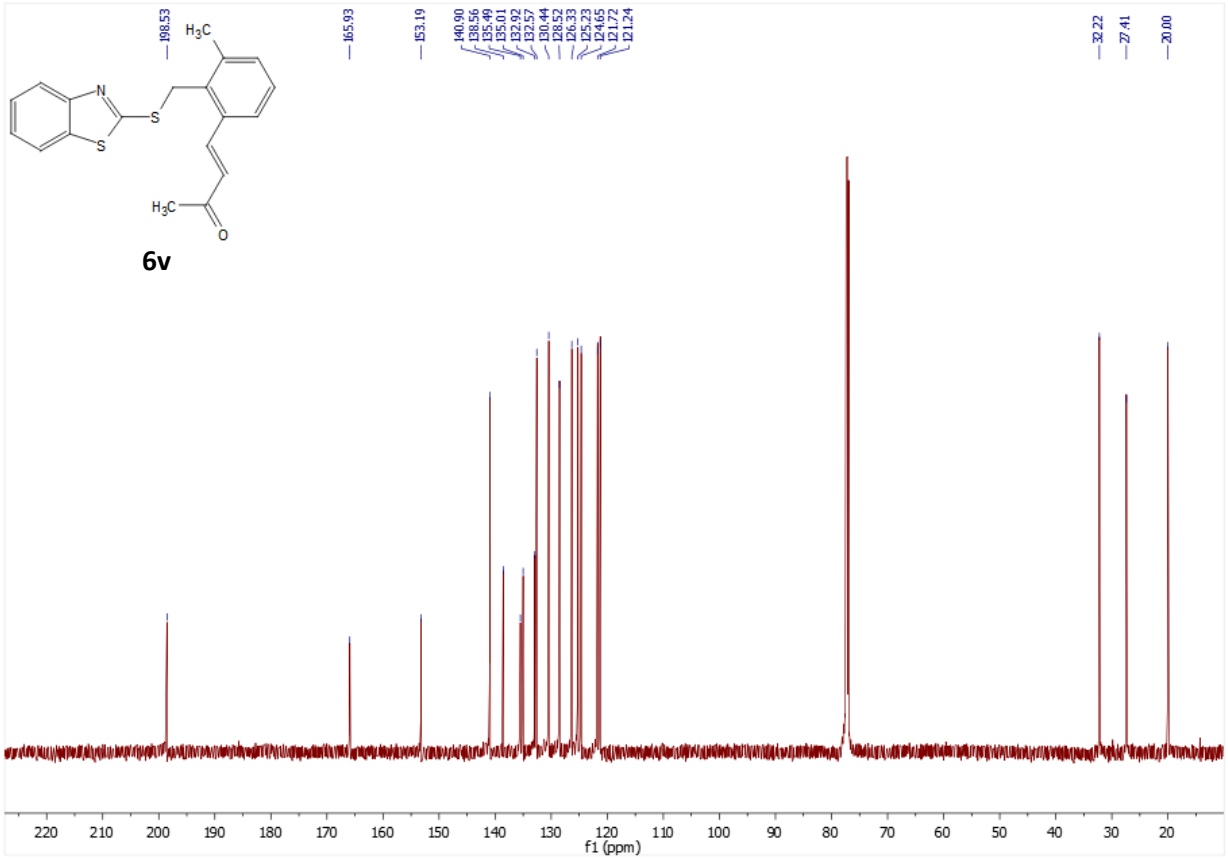

N
S
S
H3C
0.97
0.98
1.02
0.98
2.91
1.06
1.44
2.76
1.02
1.04
1.94
3.06
f1 (ppm)

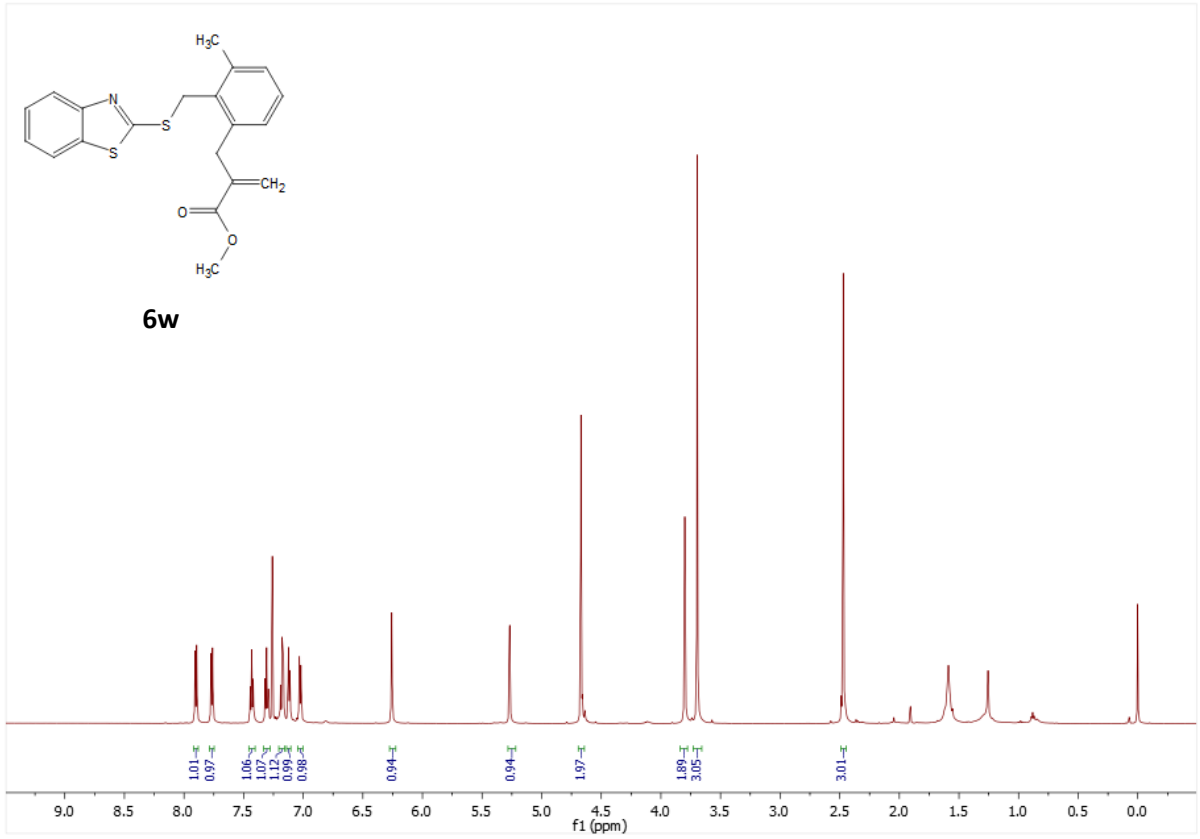
6u

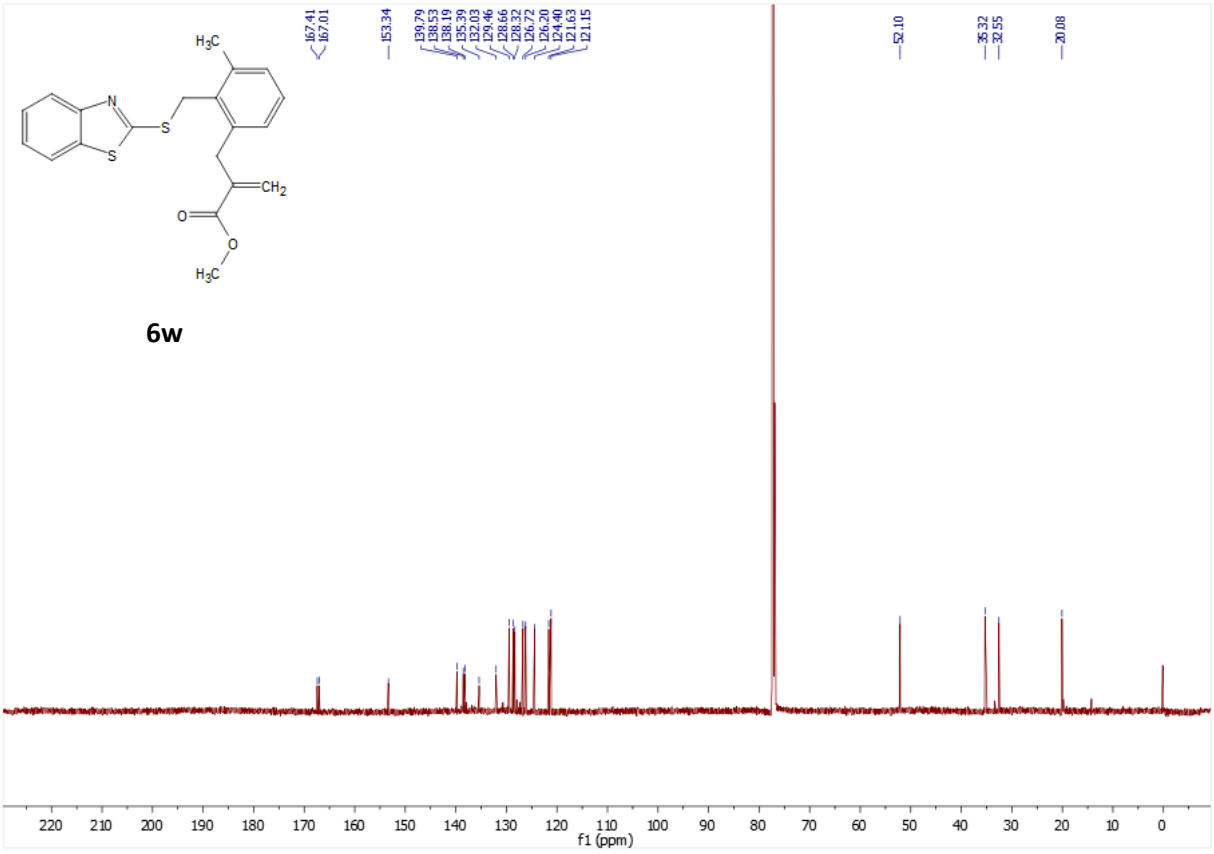

N
S
S
H3C
166.85
153.35
138.08
137.43
135.52
132.07
131.19
130.07
128.76
128.34
127.90
126.88
126.24
126.14
124.48
121.72
121.21
32.74
20.06
f1 (ppm)

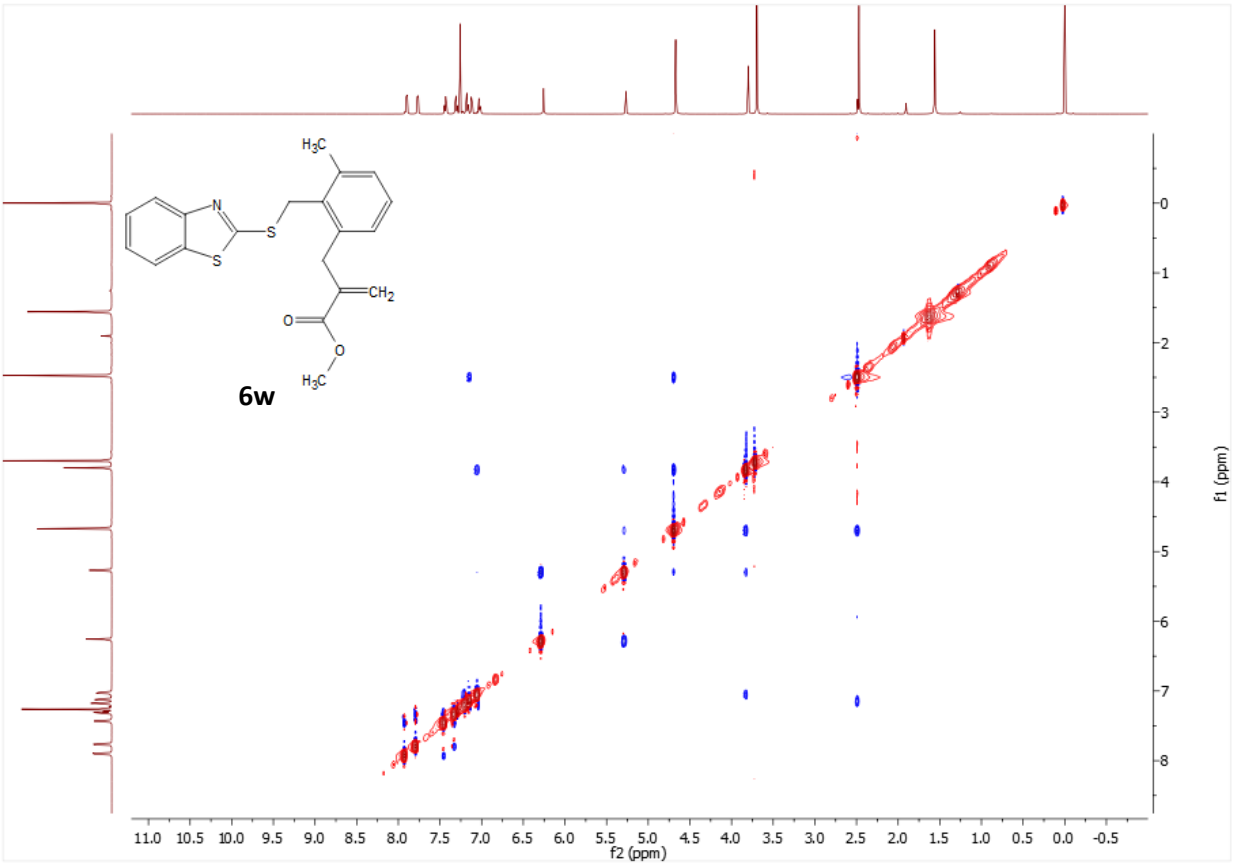
6u

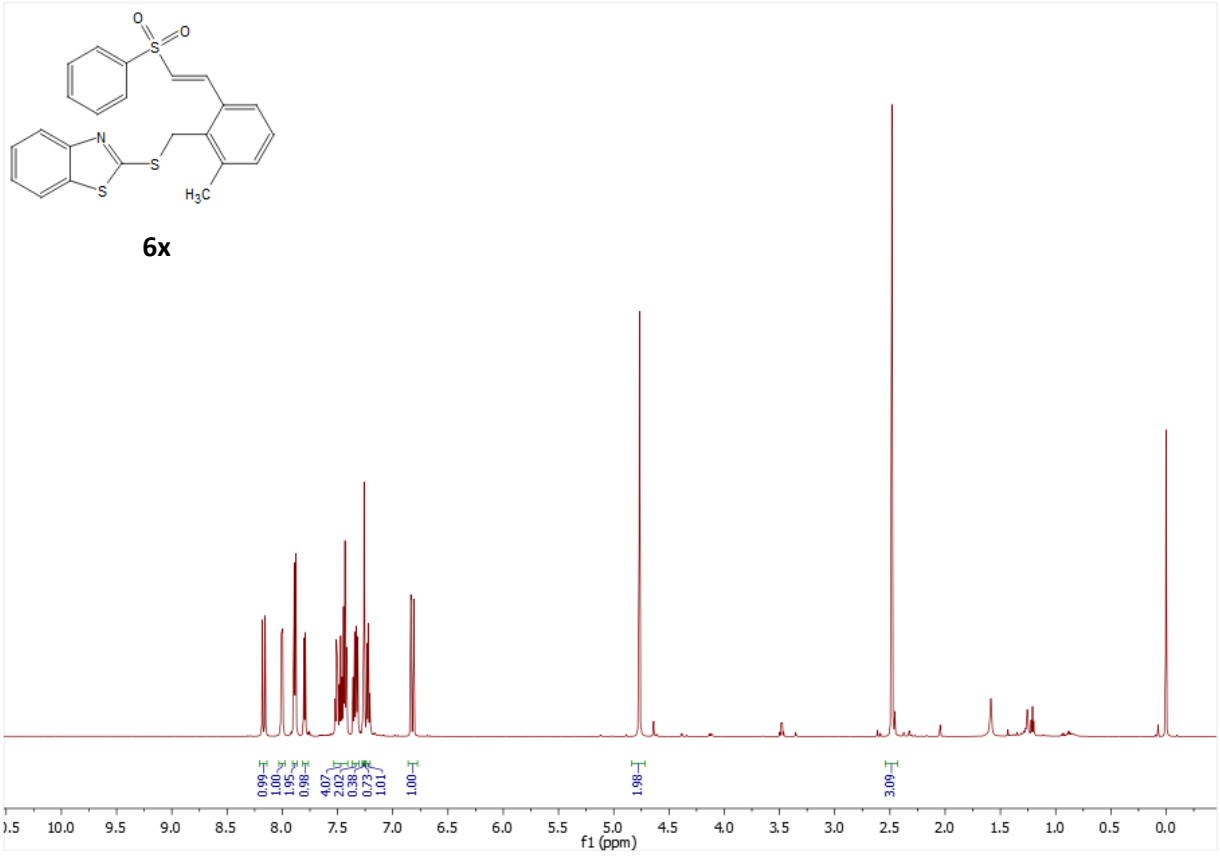

H3C
N
S
S
H3C
O
6v
1.05
1.04
1.03
2.09
1.09
2.54
1.00
2.06
3.10
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

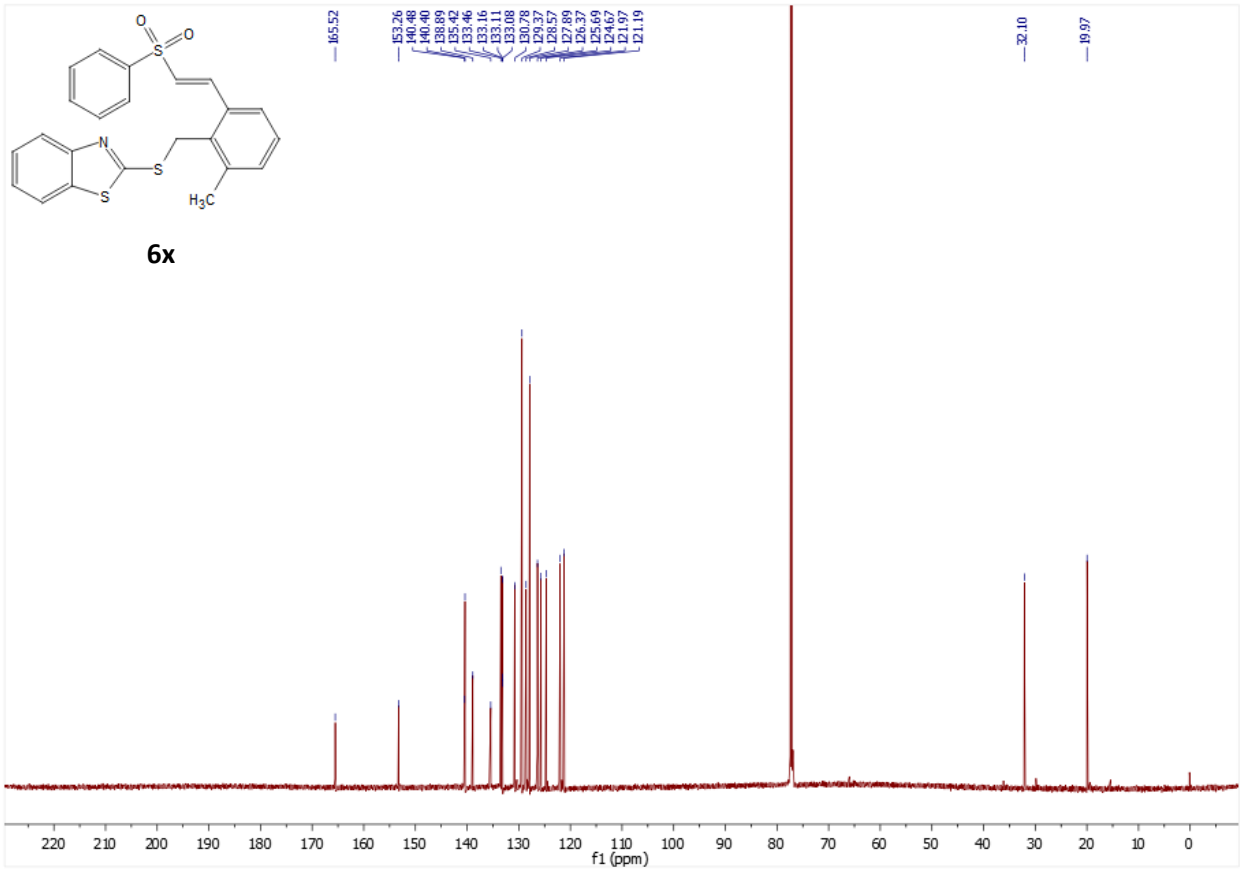

198.53
165.93
153.19
140.90
138.56
135.49
135.01
132.92
132.57
130.44
128.52
126.33
125.23
124.65
121.72
121.24
32.22
27.41
20.00
H3C
N
S
S
H3C
O
6v
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

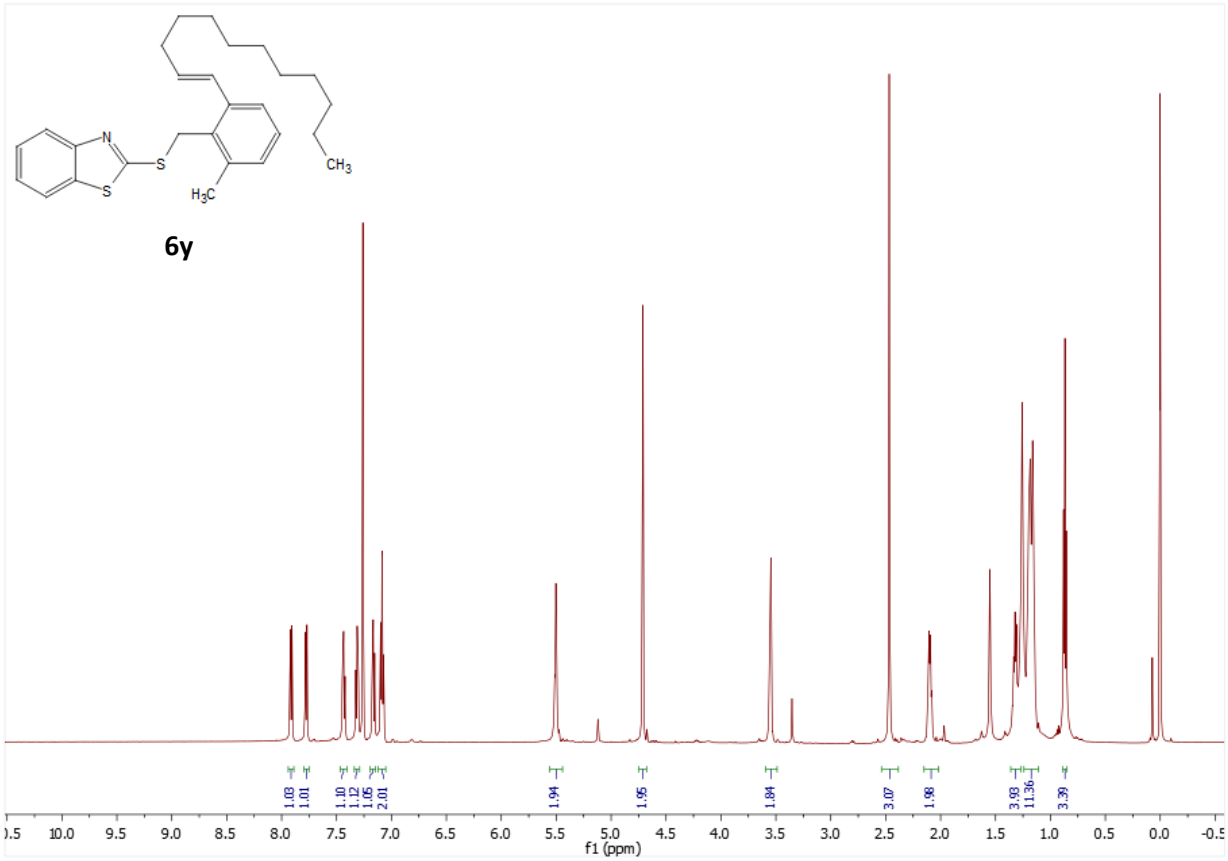

6w
1.01
0.97
1.06
1.07
1.12
0.99
0.98
0.94
0.94
1.97
1.89
3.05
3.01
f1 (ppm)


6w
167.41
167.01
153.34
139.79
138.53
138.19
135.39
132.03
129.46
128.66
128.32
126.72
126.20
124.40
121.63
121.15
52.10
35.32
32.55
20.08
f1 (ppm)

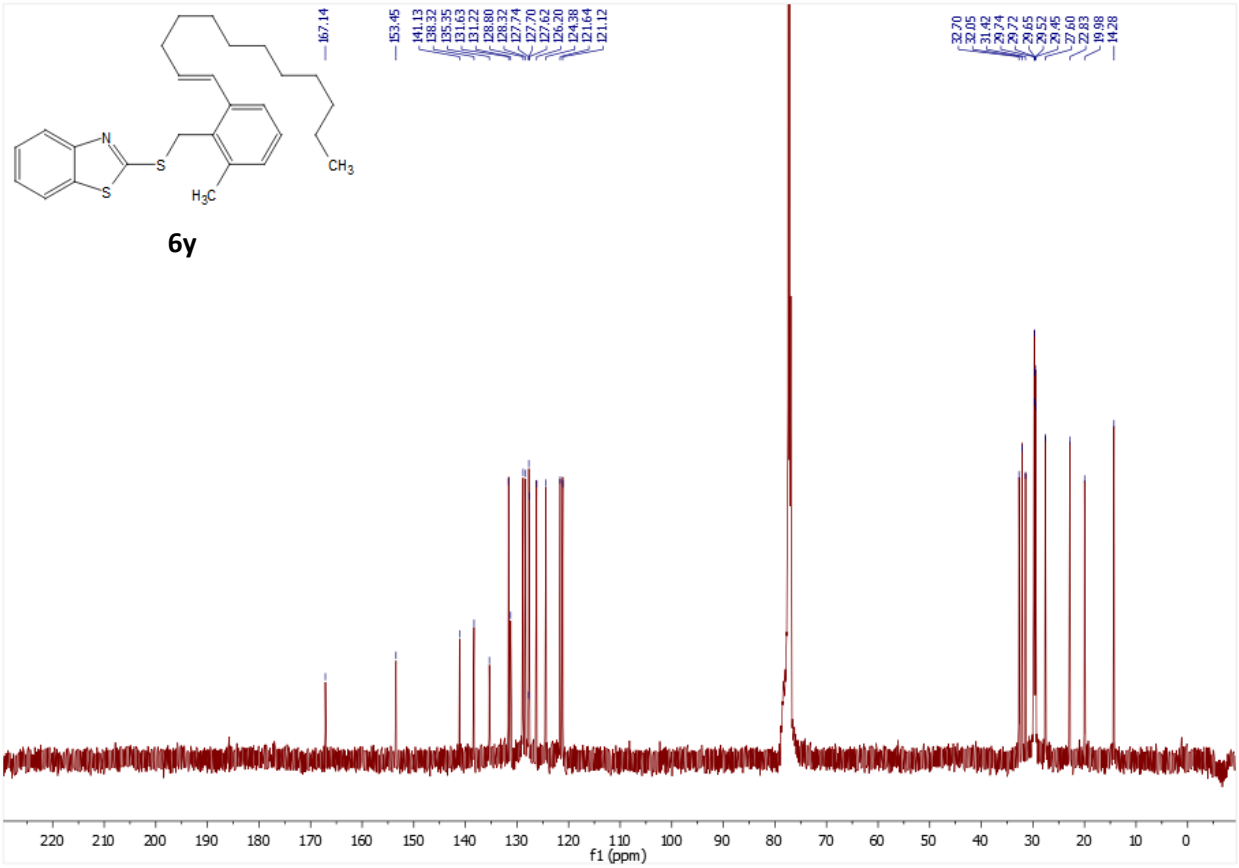

6w
f2 (ppm)
f1 (ppm)


6x
0.99
1.00
1.95
0.98
4.07
2.02
0.38
0.73
1.01
1.00
1.98
3.09
f1 (ppm)

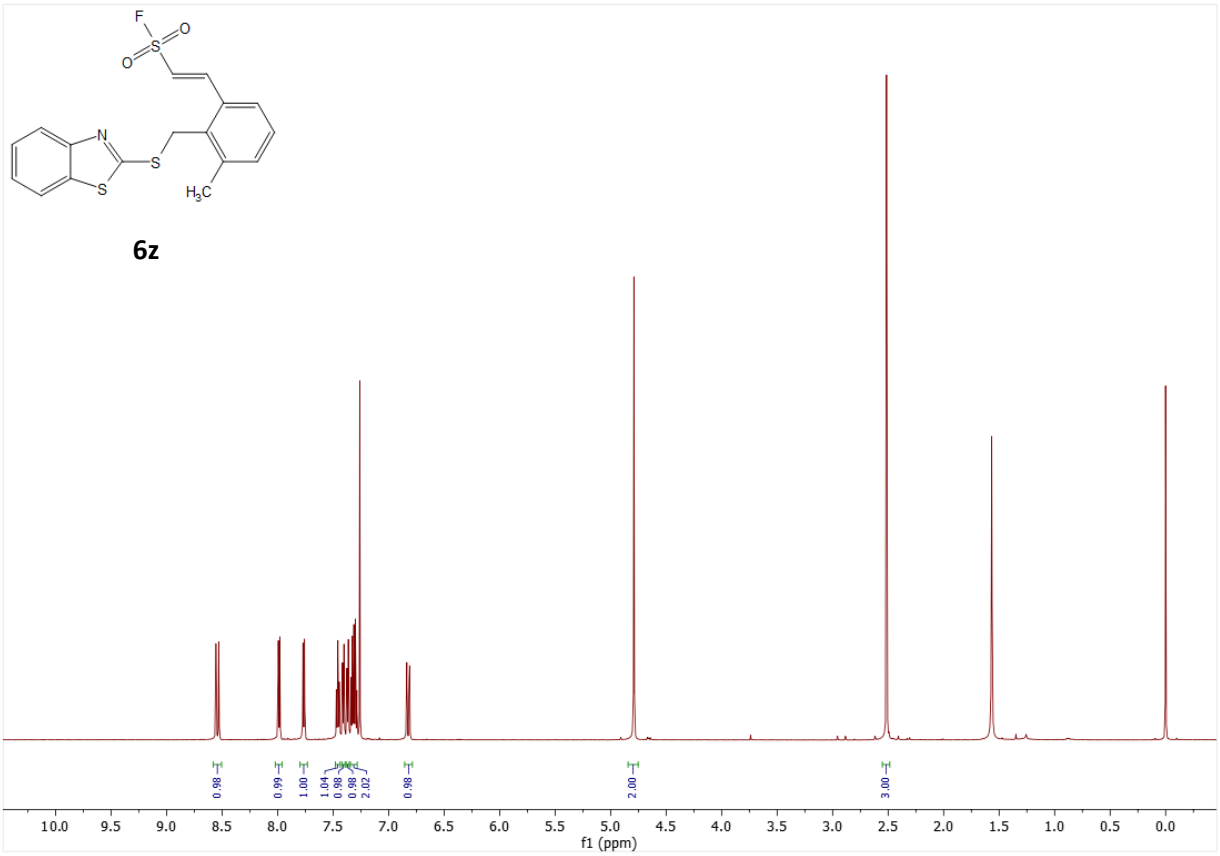

6x
165.52
153.26
140.48
140.40
138.89
135.42
133.46
133.16
133.11
133.08
130.78
129.37
128.57
127.89
126.37
125.69
124.67
121.97
121.19
32.10
19.97
f1 (ppm)

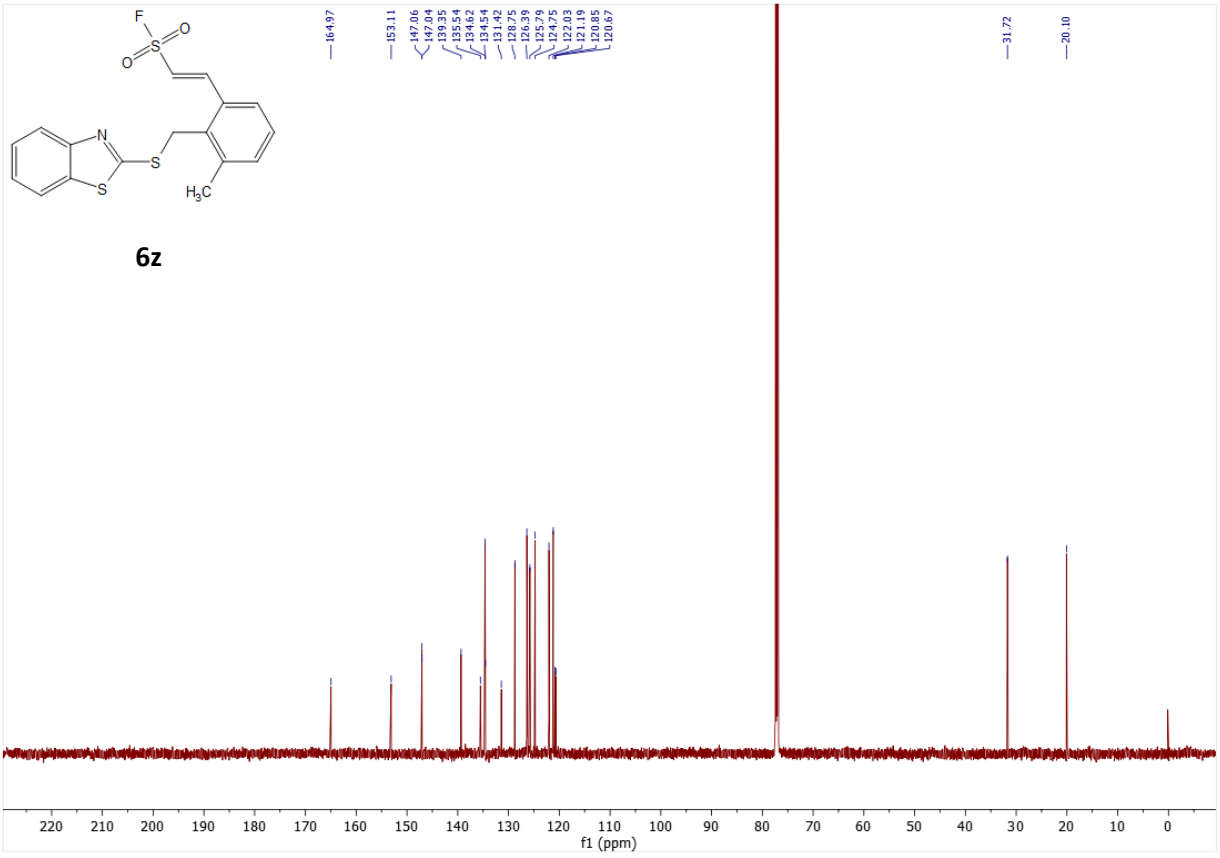

N
S
S
CH3
H3C
1.03
1.01
1.10
1.12
1.05
2.01
1.94
1.95
1.84
3.07
1.98
3.93
11.36
3.39
f1 (ppm)

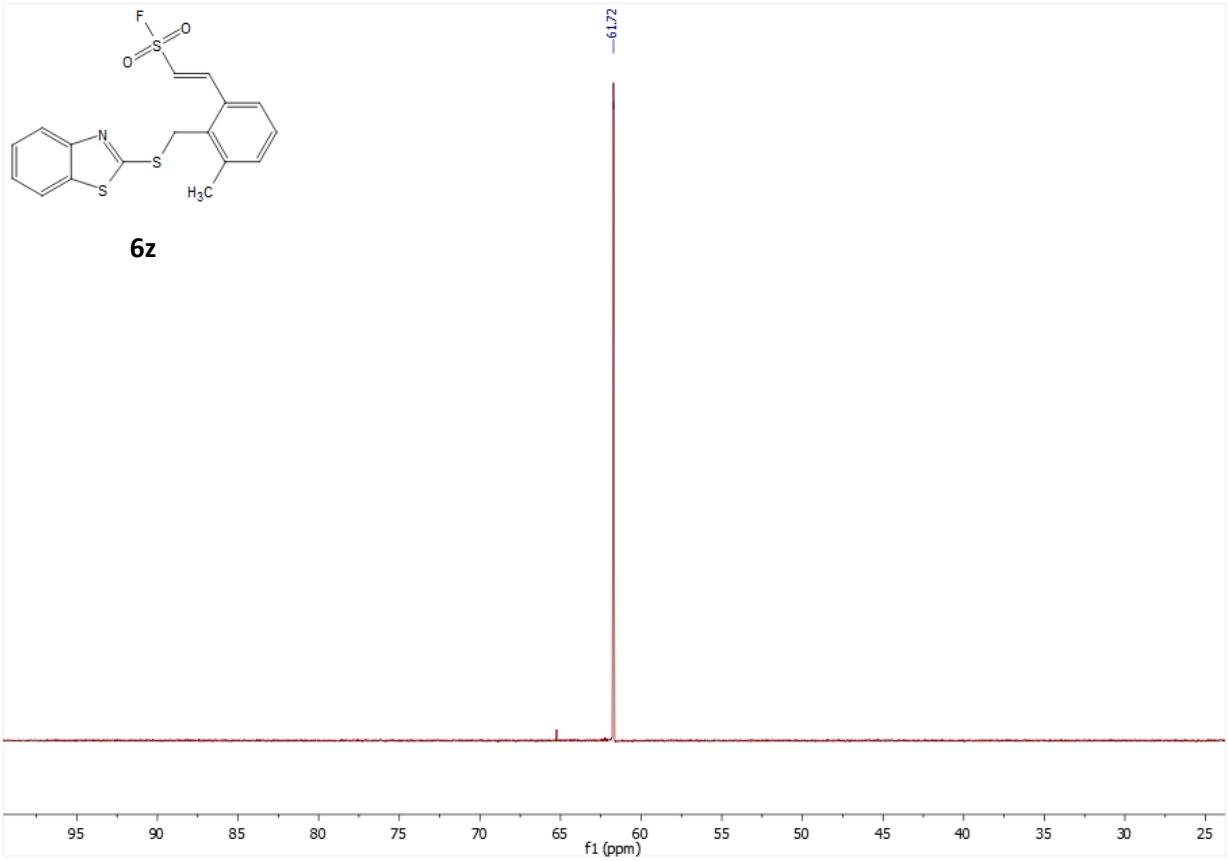
6y


N
S
S
CH3
H3C
167.14
153.45
141.13
138.32
135.35
131.63
131.22
128.80
128.32
127.74
127.70
127.62
126.20
124.38
121.64
121.12
32.70
32.05
31.42
29.74
29.72
29.65
29.52
29.45
27.60
22.83
19.98
14.28
f1 (ppm)

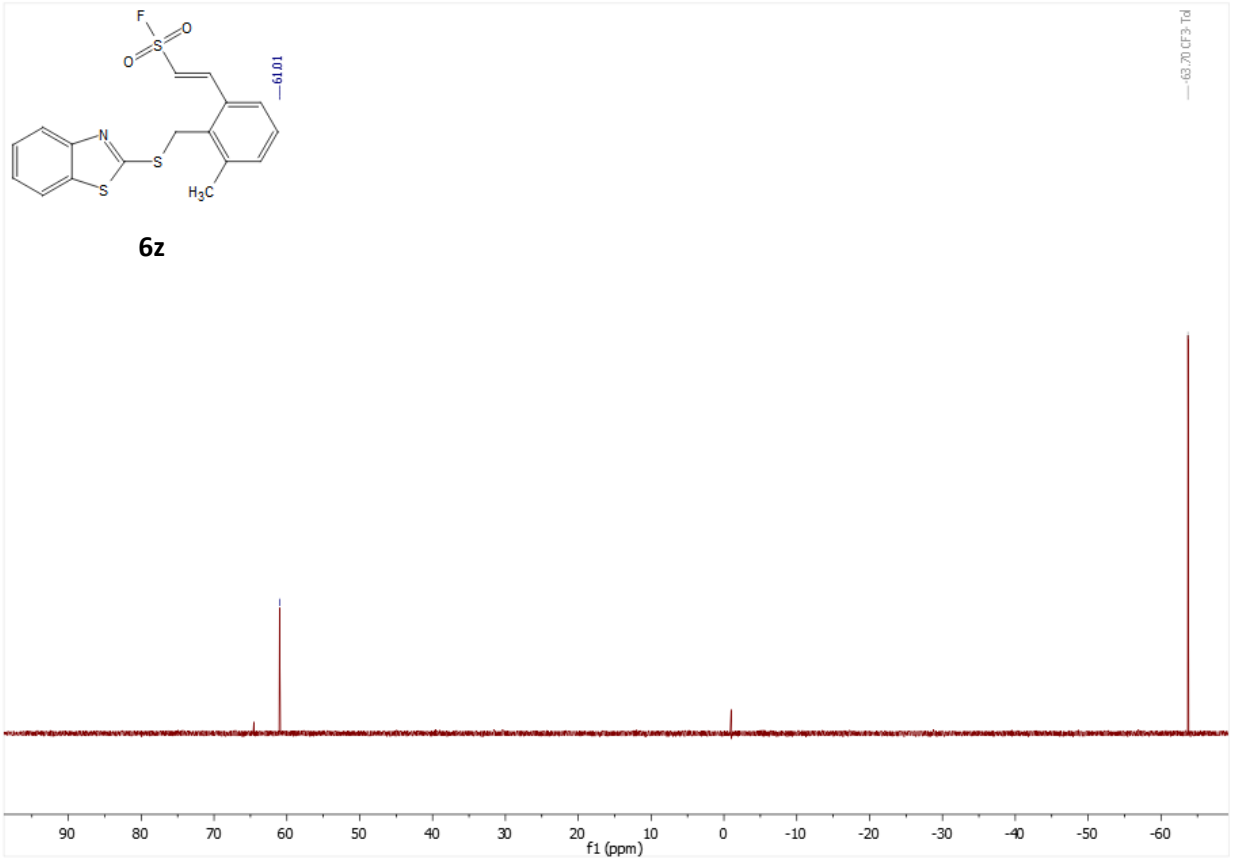
6y


F
O
O
S
N
S
S
H3C
6z
0.98
0.99
1.00
1.04
0.98
0.98
2.02
0.98
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

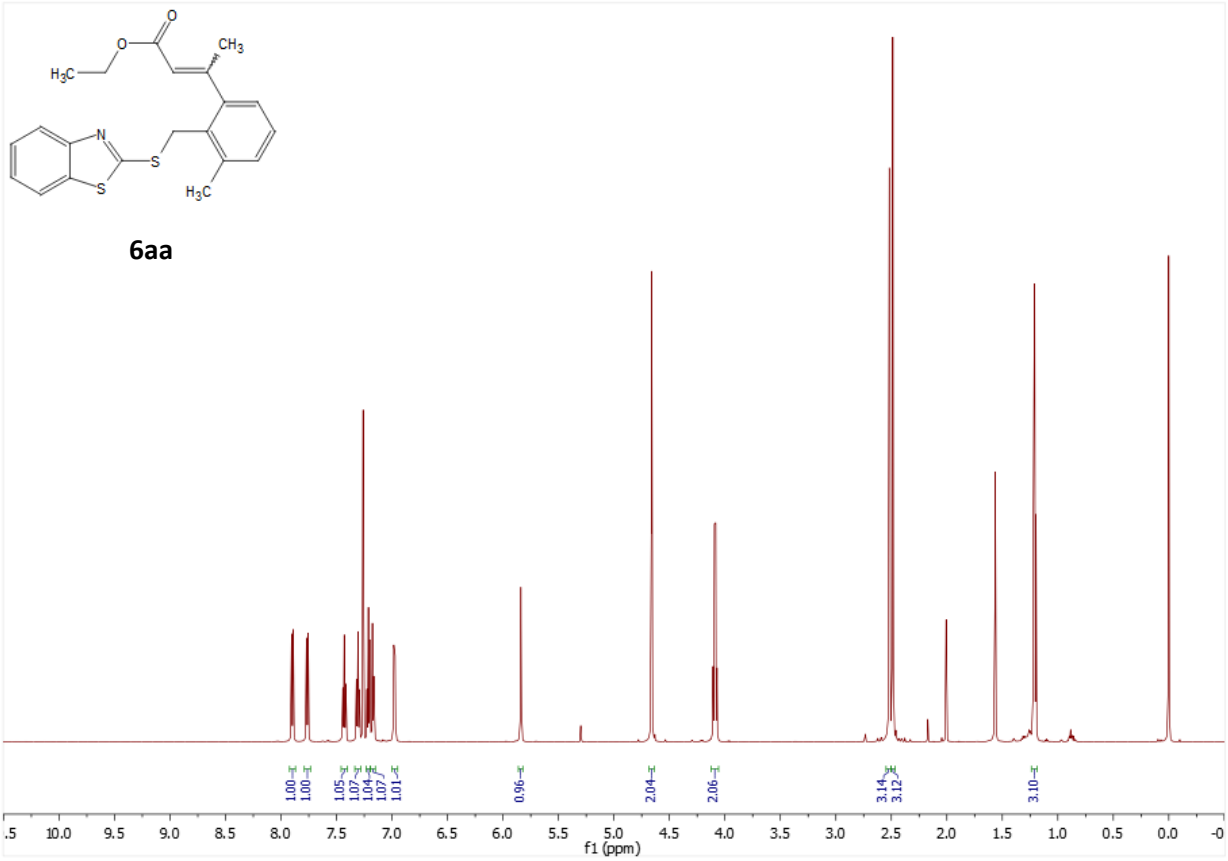

F
O
O
S
N
S
S
H3C
6z
164.97
153.11
147.06
147.04
139.35
135.54
134.62
134.54
134.42
131.75
126.39
125.79
124.75
122.03
121.19
120.85
120.67
31.72
20.10
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

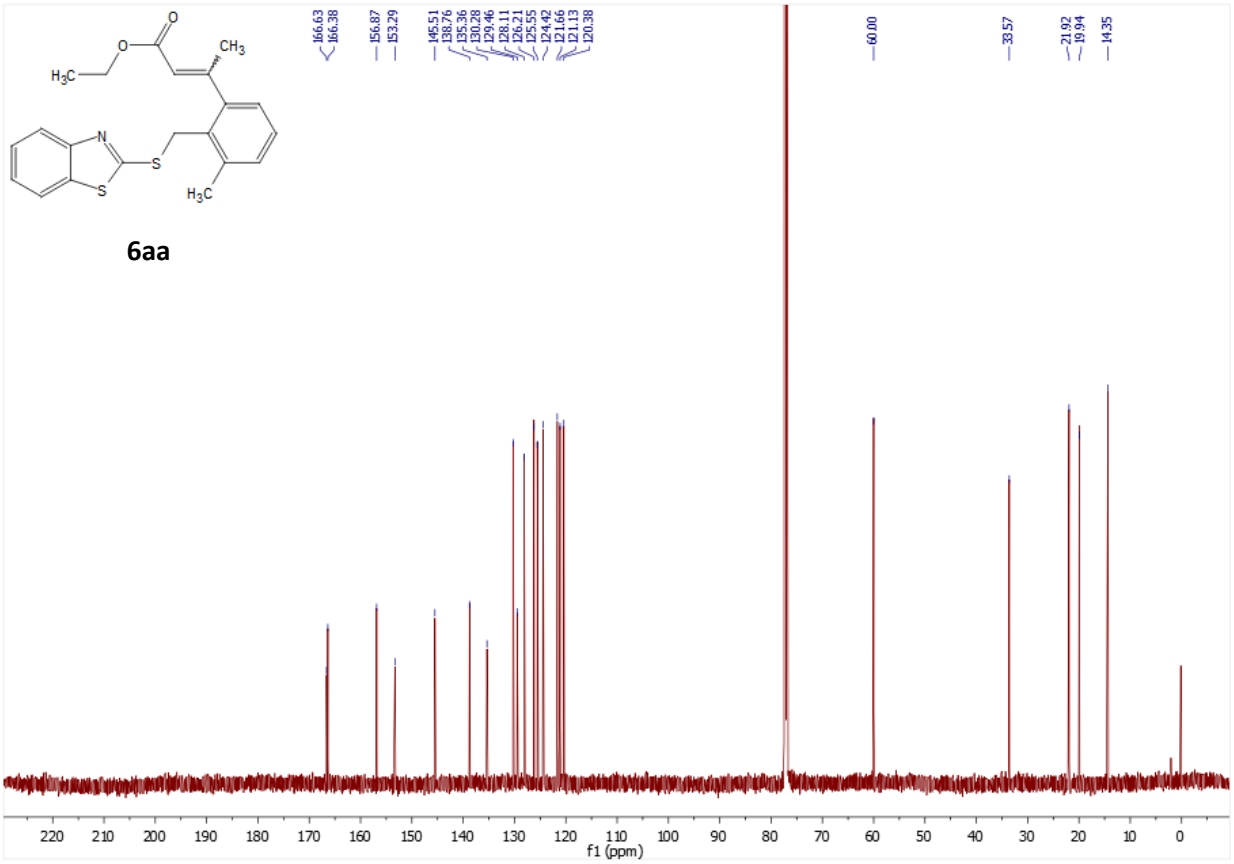

F
O
O
S
N
S
S
H3C
61.72
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
f1 (ppm)

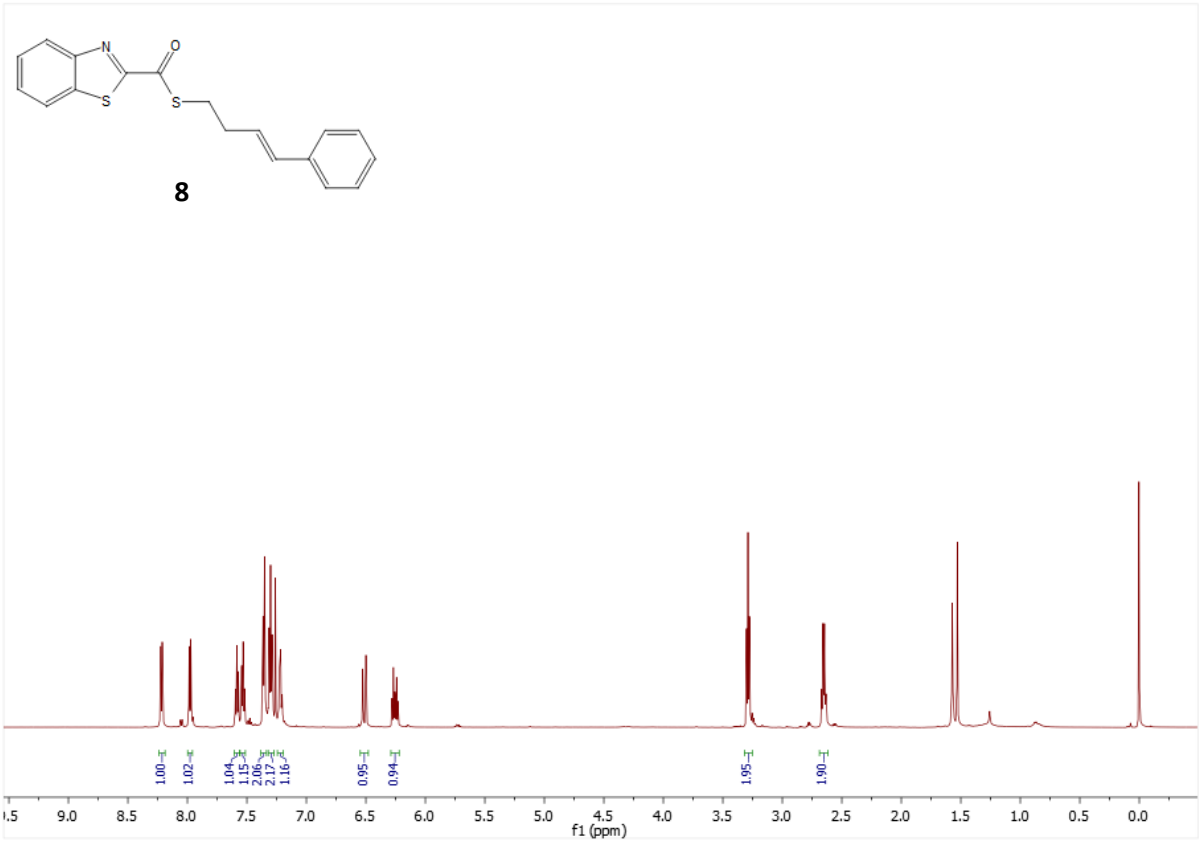
6z

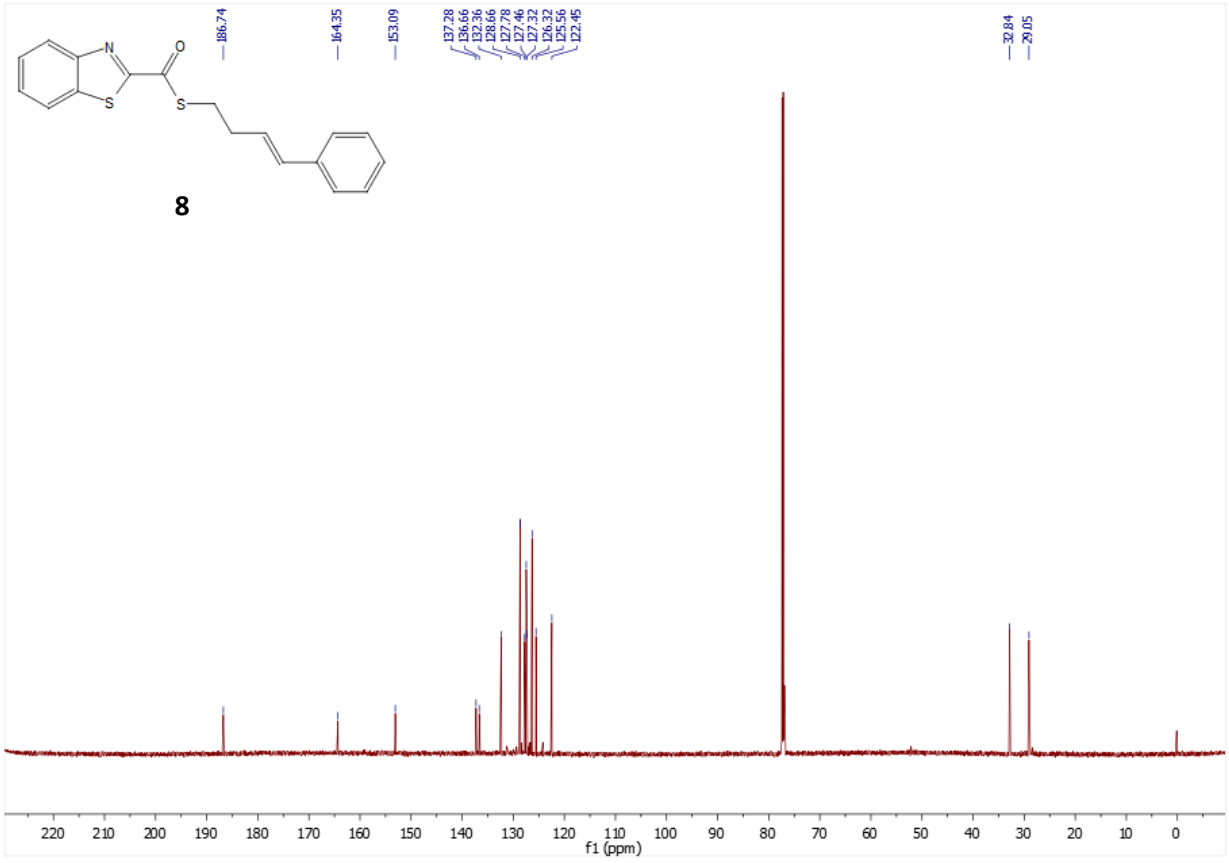

F
O
O
S
N
S
S
H3C
61.01
63.70 CF3 Td
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
f1 (ppm)

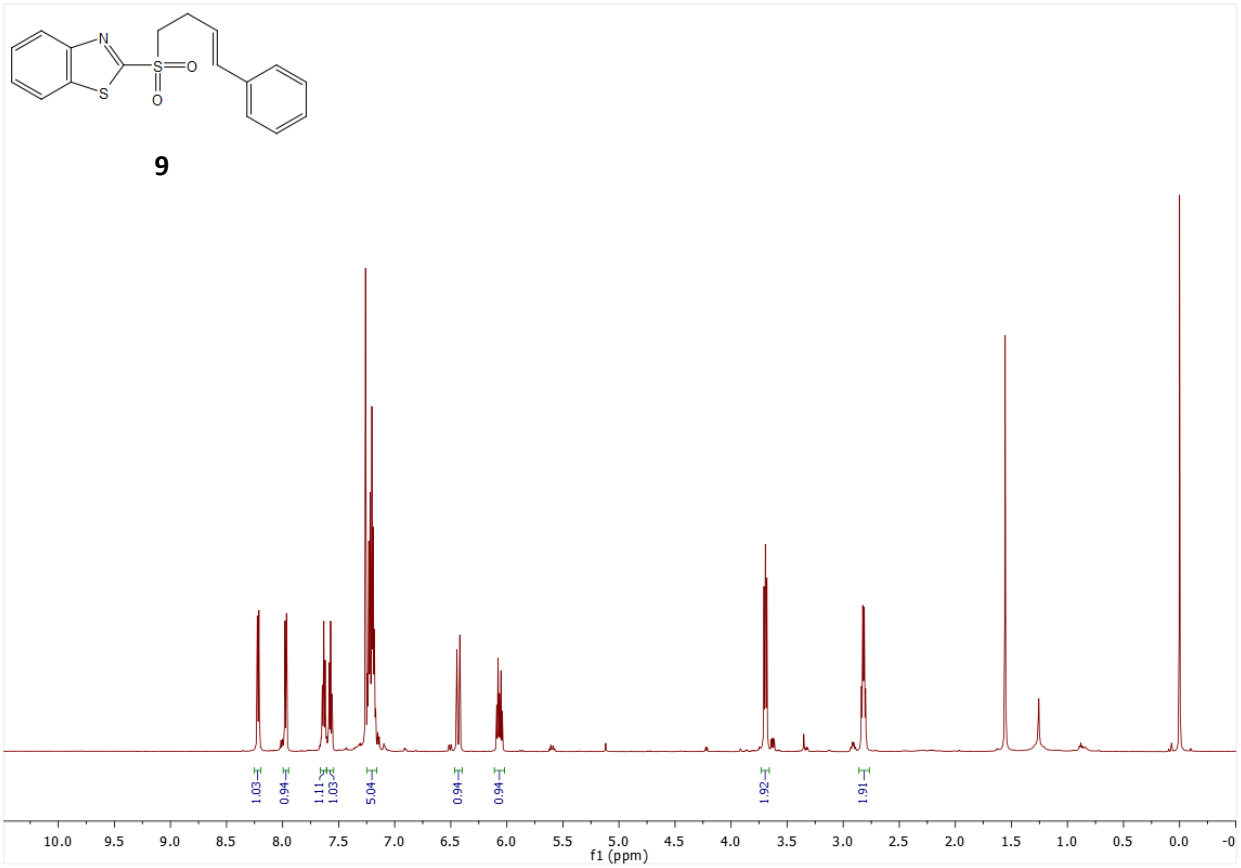
6z

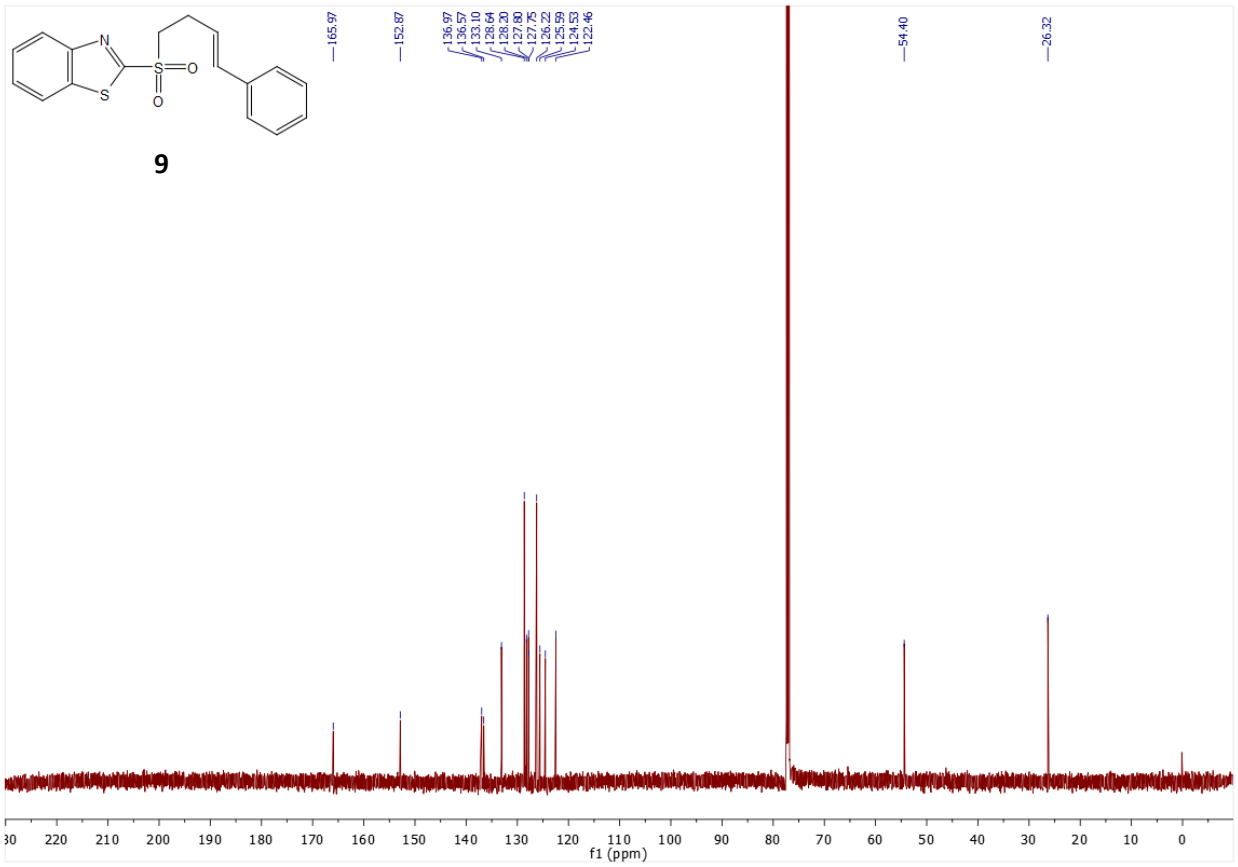

6aa
1.00
1.00
1.05
1.07
1.04
1.07
1.01
0.96
2.04
2.06
3.14
3.12
3.10
f1 (ppm)

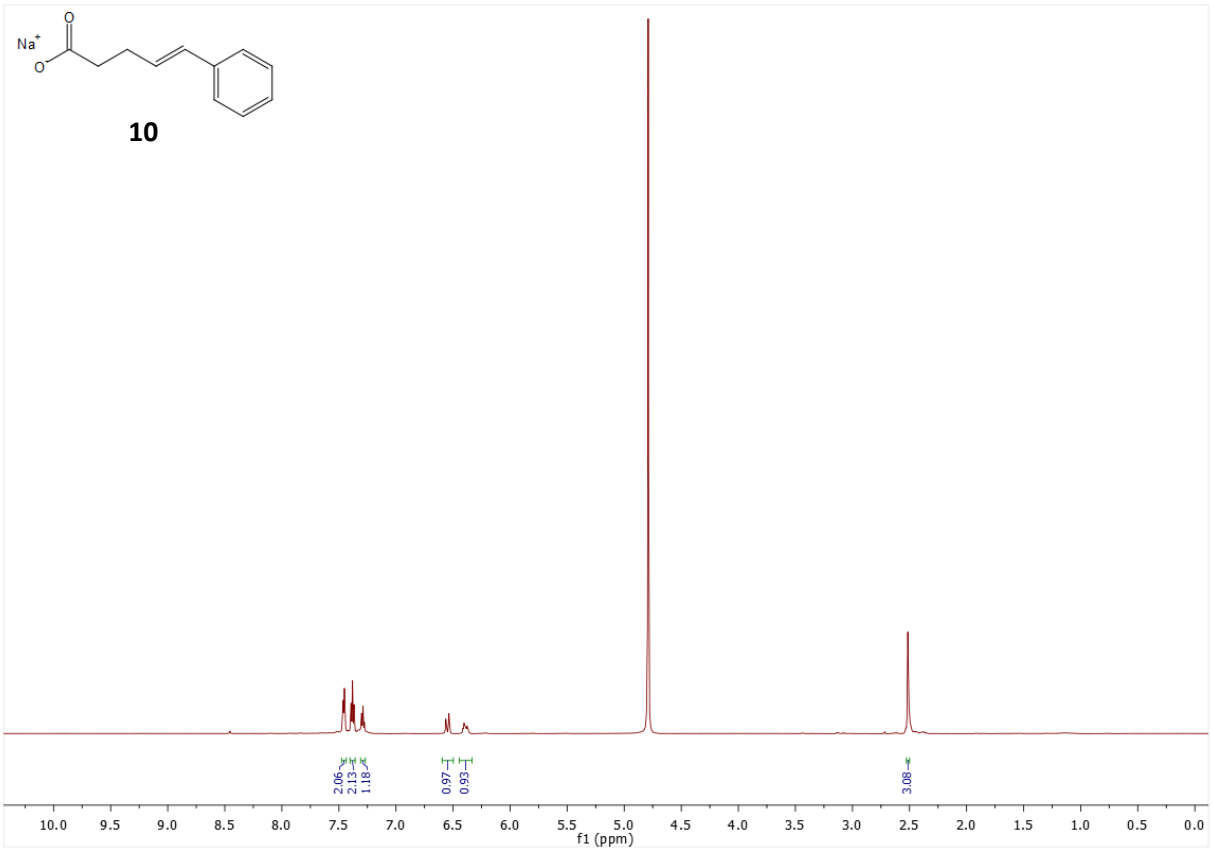

6aa
166.63
166.38
156.87
153.29
145.51
138.76
135.36
130.28
129.46
128.11
126.21
125.55
124.42
121.66
121.13
120.38
60.00
33.57
21.92
19.94
14.35
f1 (ppm)

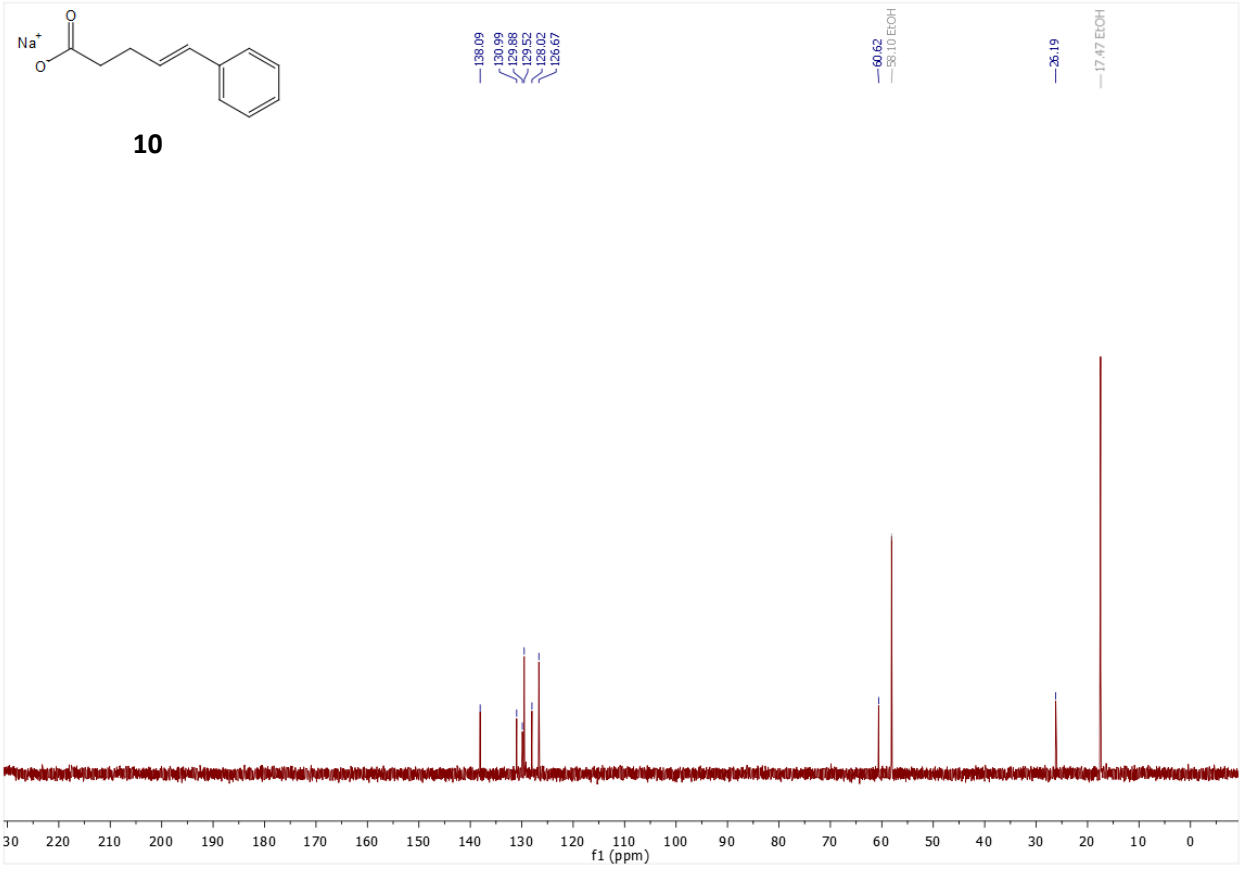

8
1.00
1.02
1.04
1.15
2.06
2.17
1.16
0.95
0.94
1.95
1.90
f1 (ppm)

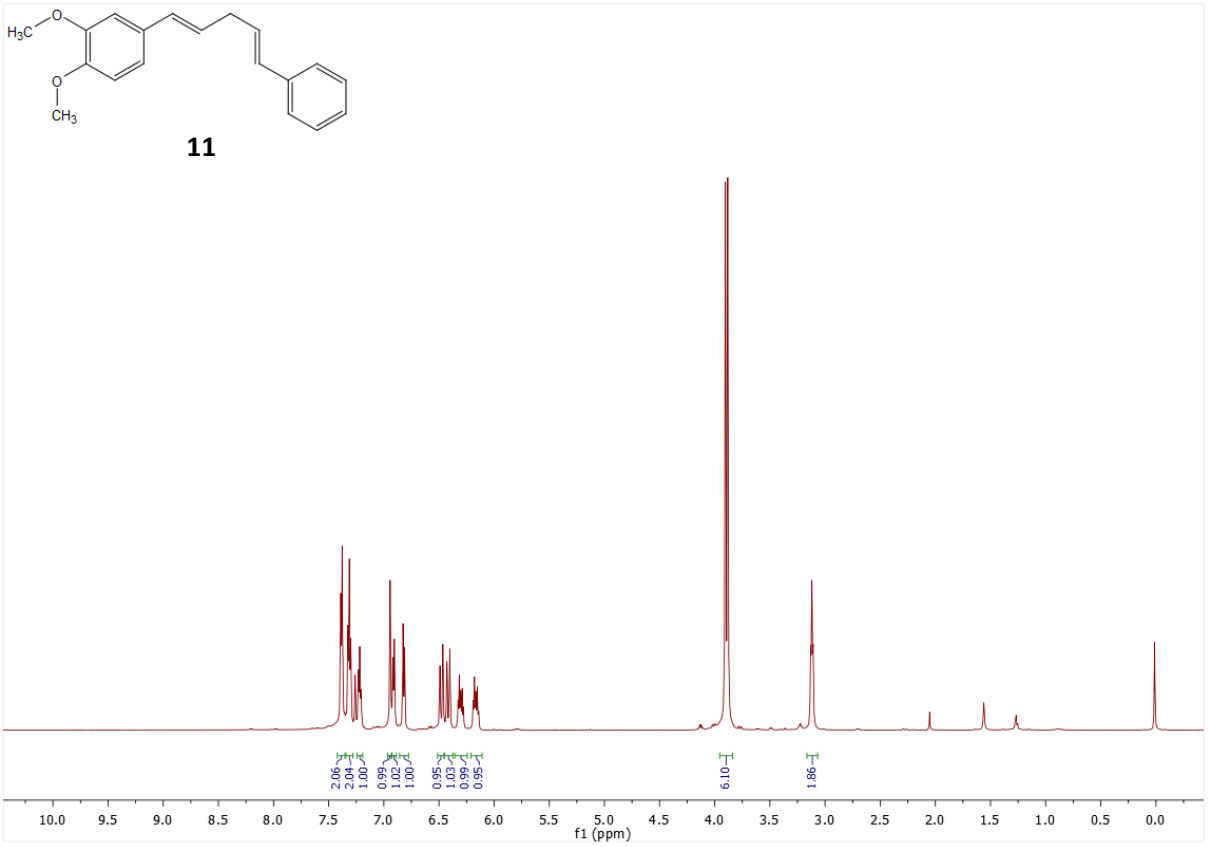

8
186.74
164.35
153.09
137.28
136.66
132.36
128.66
127.78
127.46
127.32
126.32
125.56
122.45
32.84
29.05
f1 (ppm)

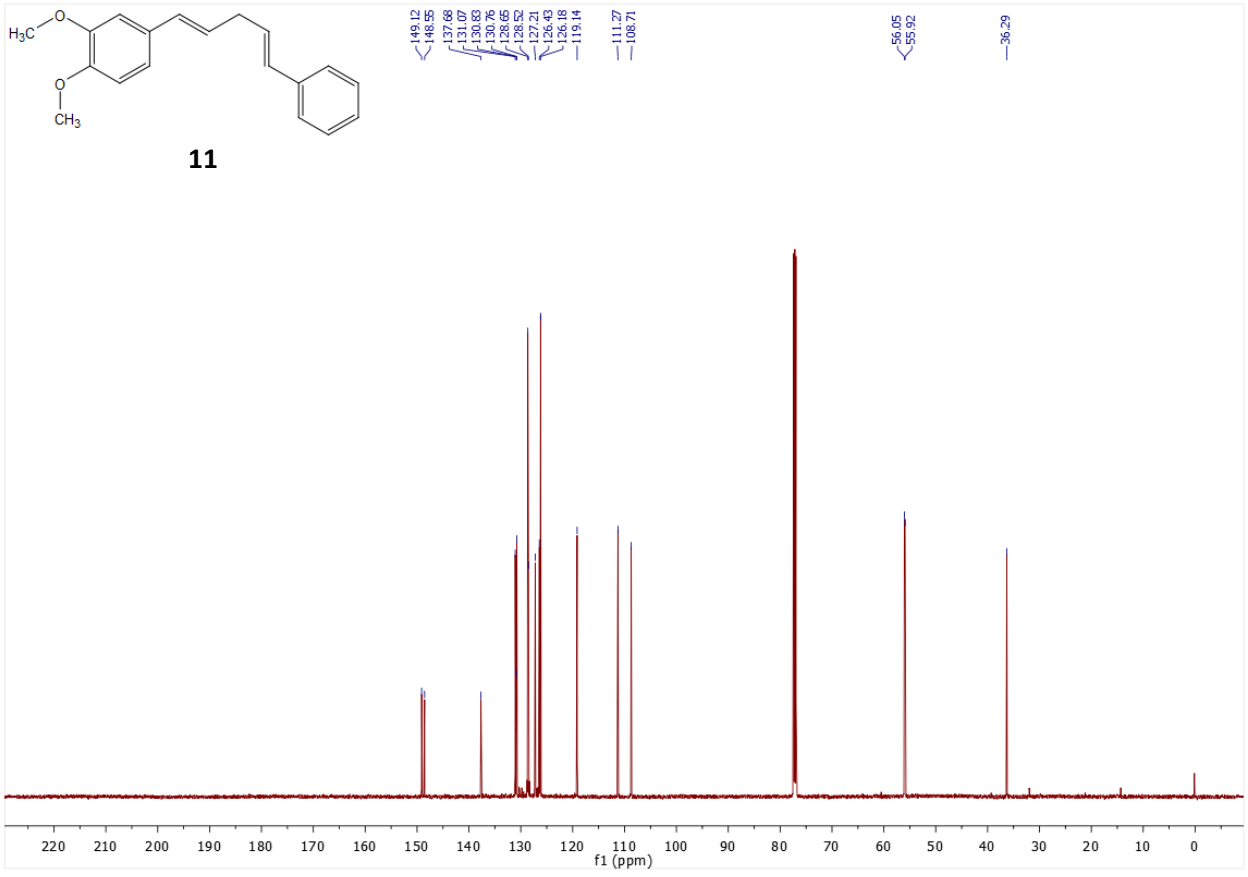

9
1.03
0.94
1.11
1.03
5.04
0.94
0.94
1.92
1.91
f1 (ppm)

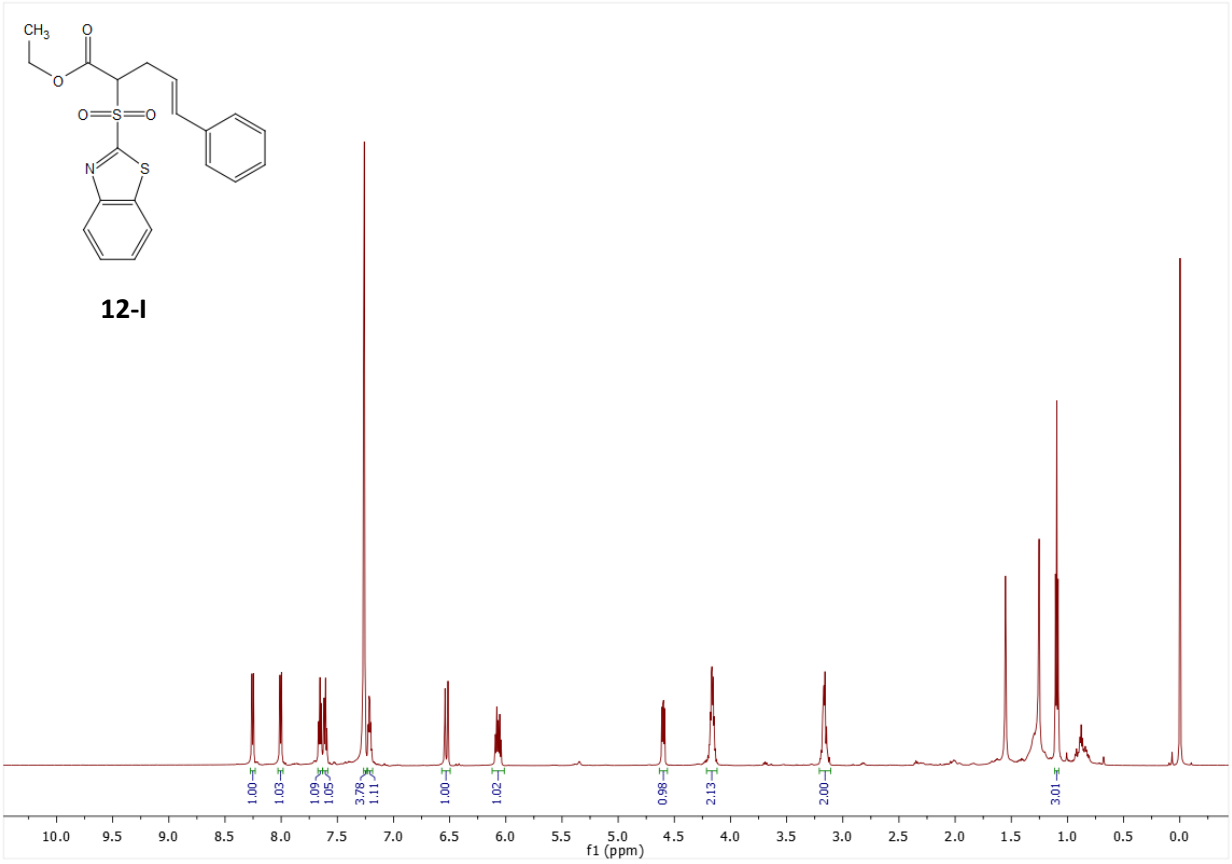

9
165.97
152.87
136.97
136.57
133.10
128.64
128.20
127.80
127.75
126.22
125.99
124.53
122.46
54.40
26.32
f1 (ppm)

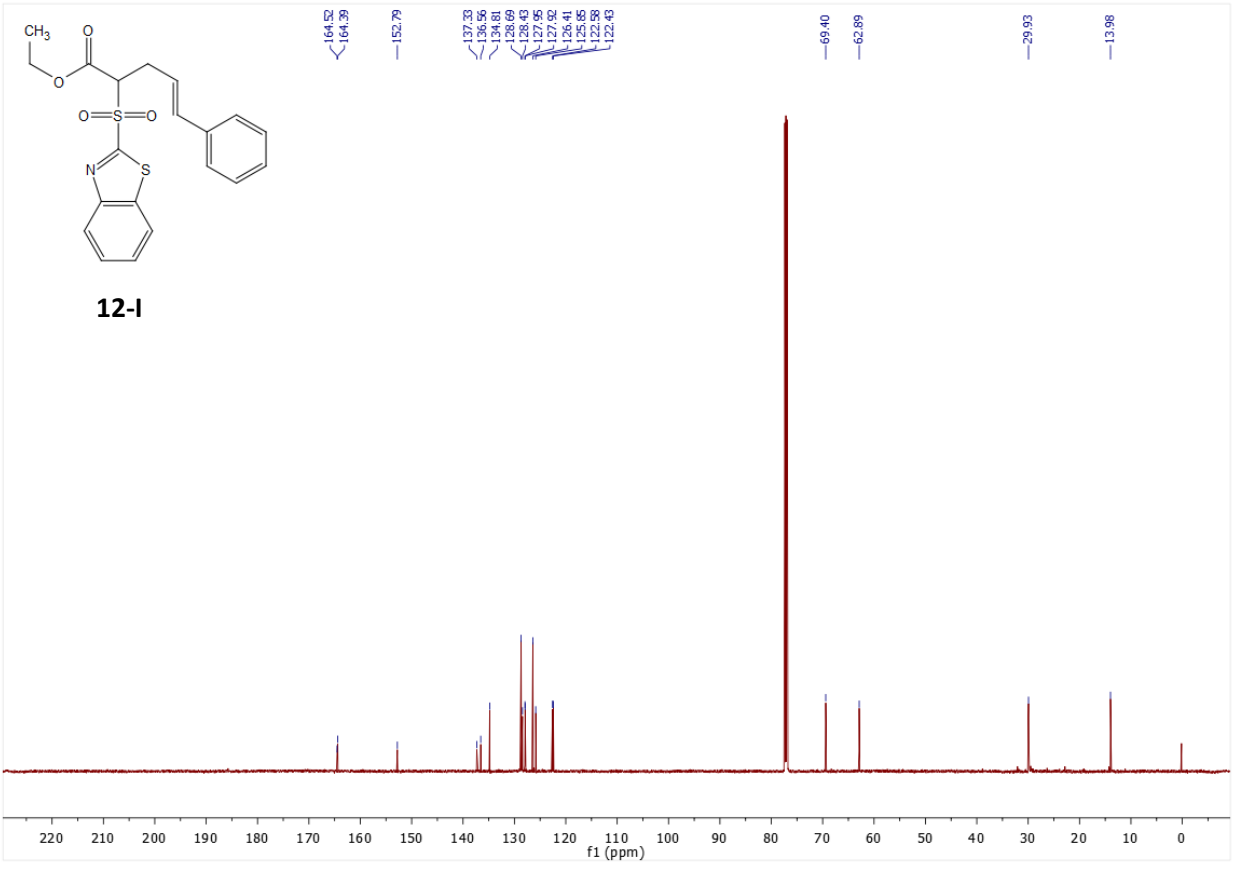

Na+
O
O
10
2.06
2.13
1.18
0.97
0.93
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

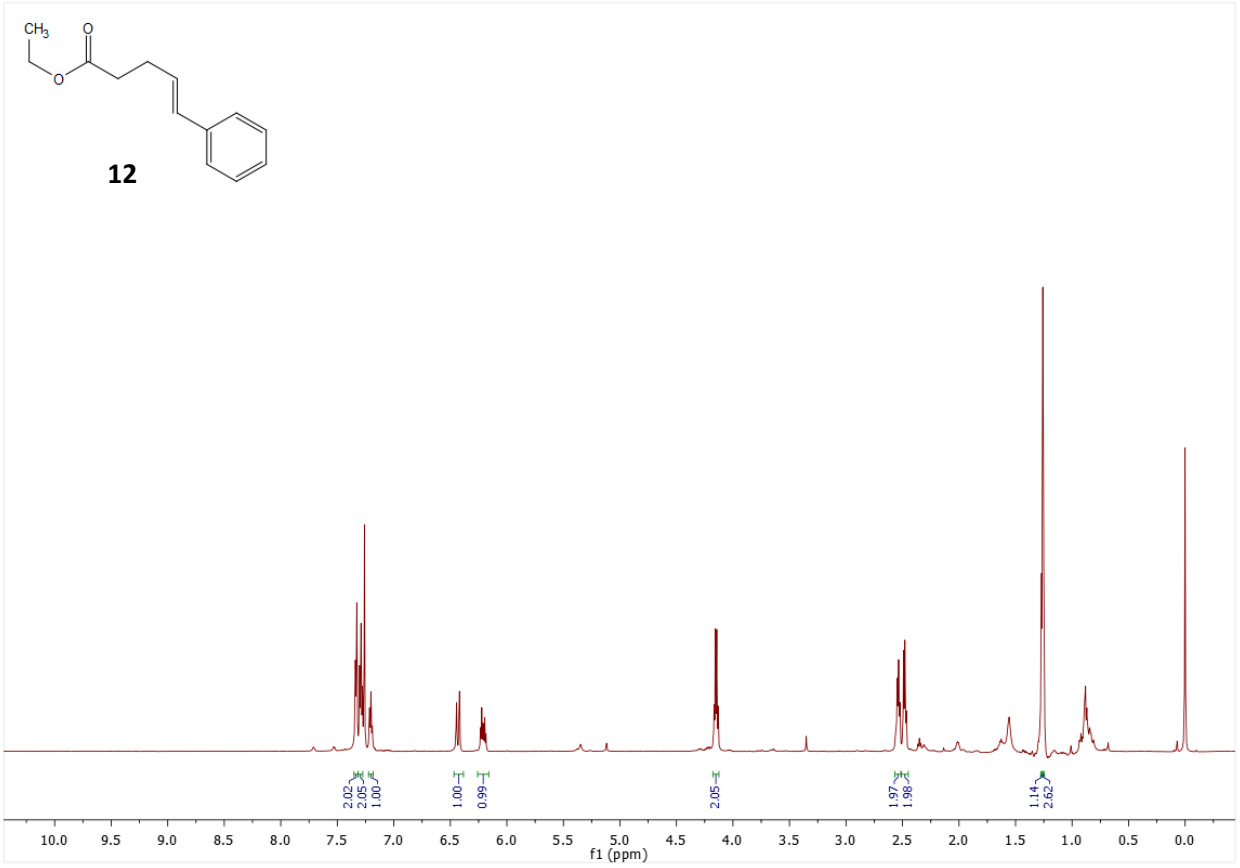

Na+
O
O
10
138.09
130.99
129.88
129.52
128.02
126.67
60.62
56.10 EtOH
26.19
17.47 EtOH
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

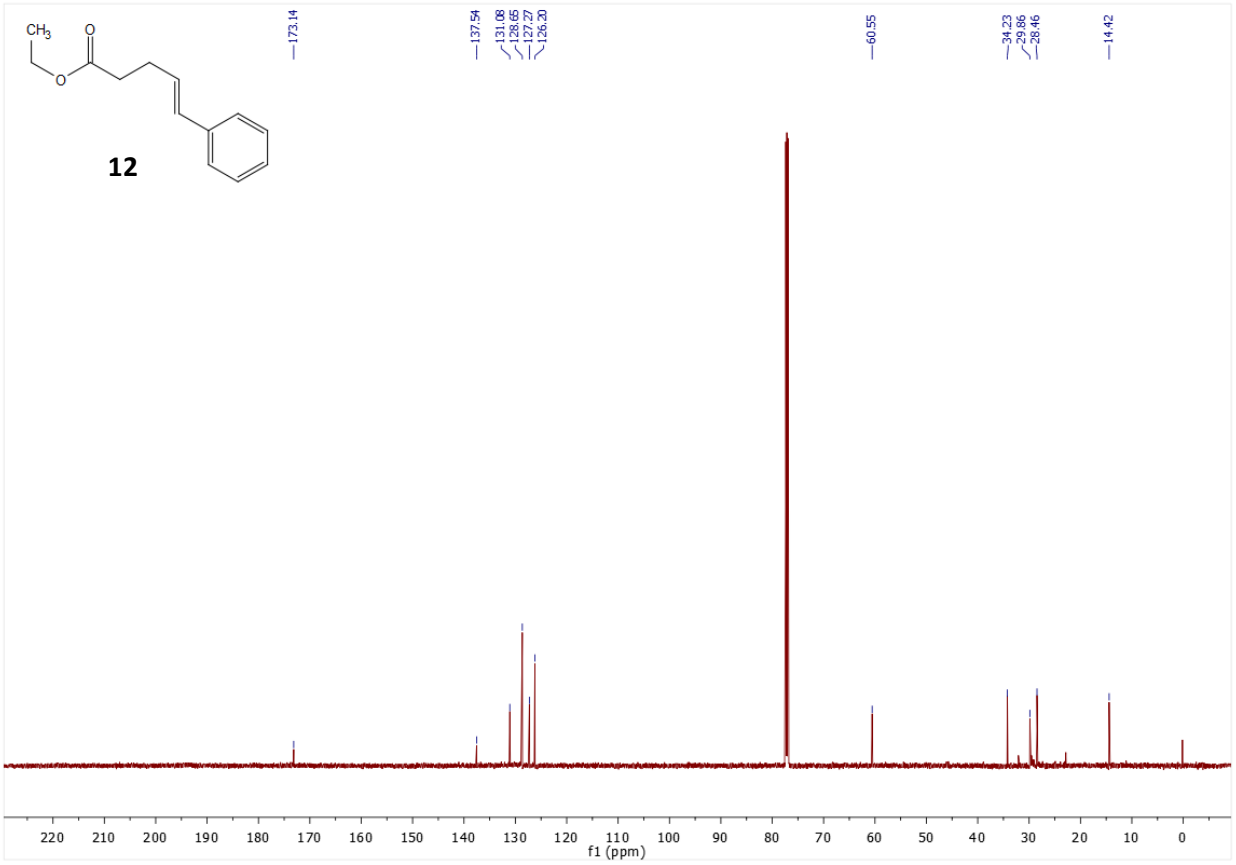

H3C
O
O
CH3
11
2.06
2.04
1.00
0.99
1.02
1.00
0.95
1.03
0.99
0.95
6.10
1.86
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

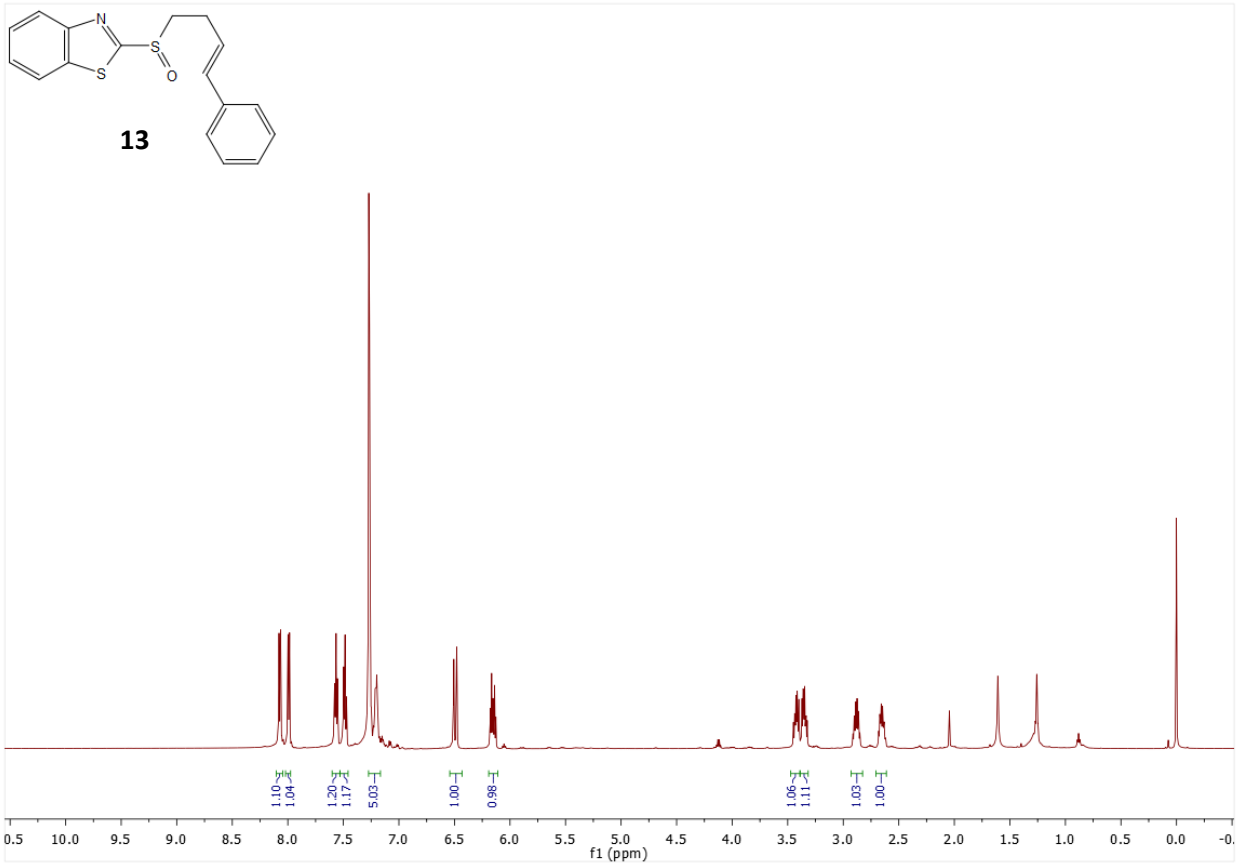

H3C
O
O
CH3
11
149.12
148.55
137.68
131.07
130.83
130.76
128.65
128.52
127.21
126.43
126.18
119.14
111.27
108.71
56.05
55.92
36.29
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

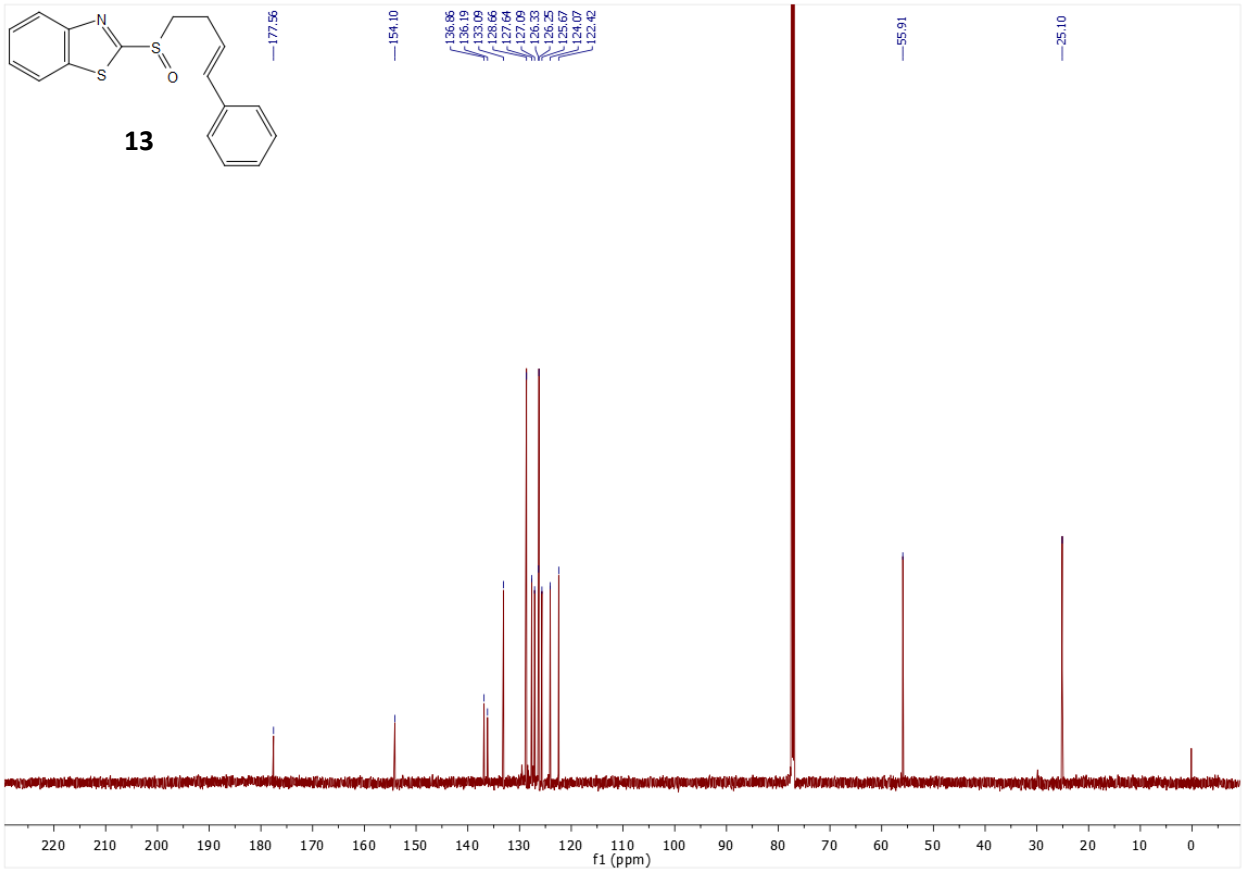

12-I
1.00
1.03
1.09
1.05
3.78
1.11
1.00
1.02
0.98
2.13
2.00
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

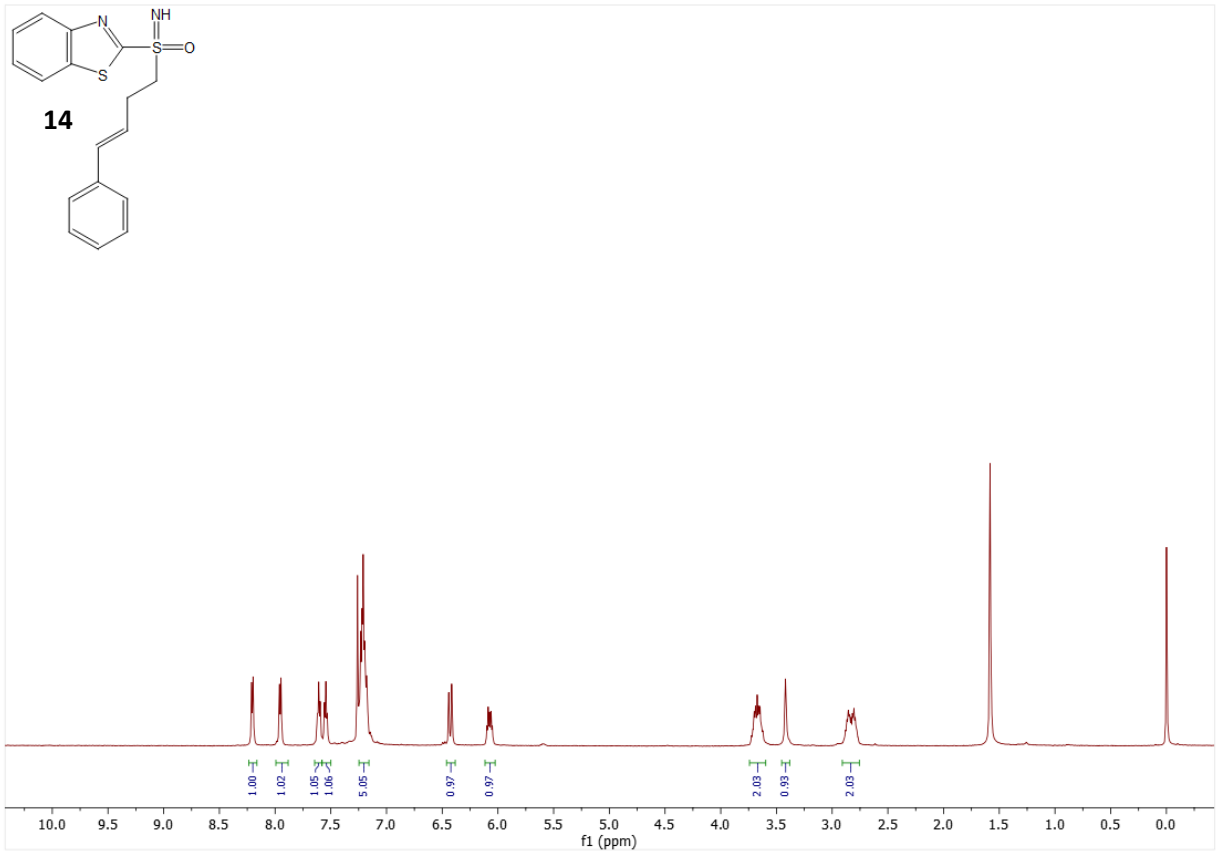

12-I
164.52
164.39
152.79
137.33
136.56
134.81
128.69
128.43
127.95
127.92
126.41
125.85
122.38
122.43
69.40
62.89
29.93
13.98
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

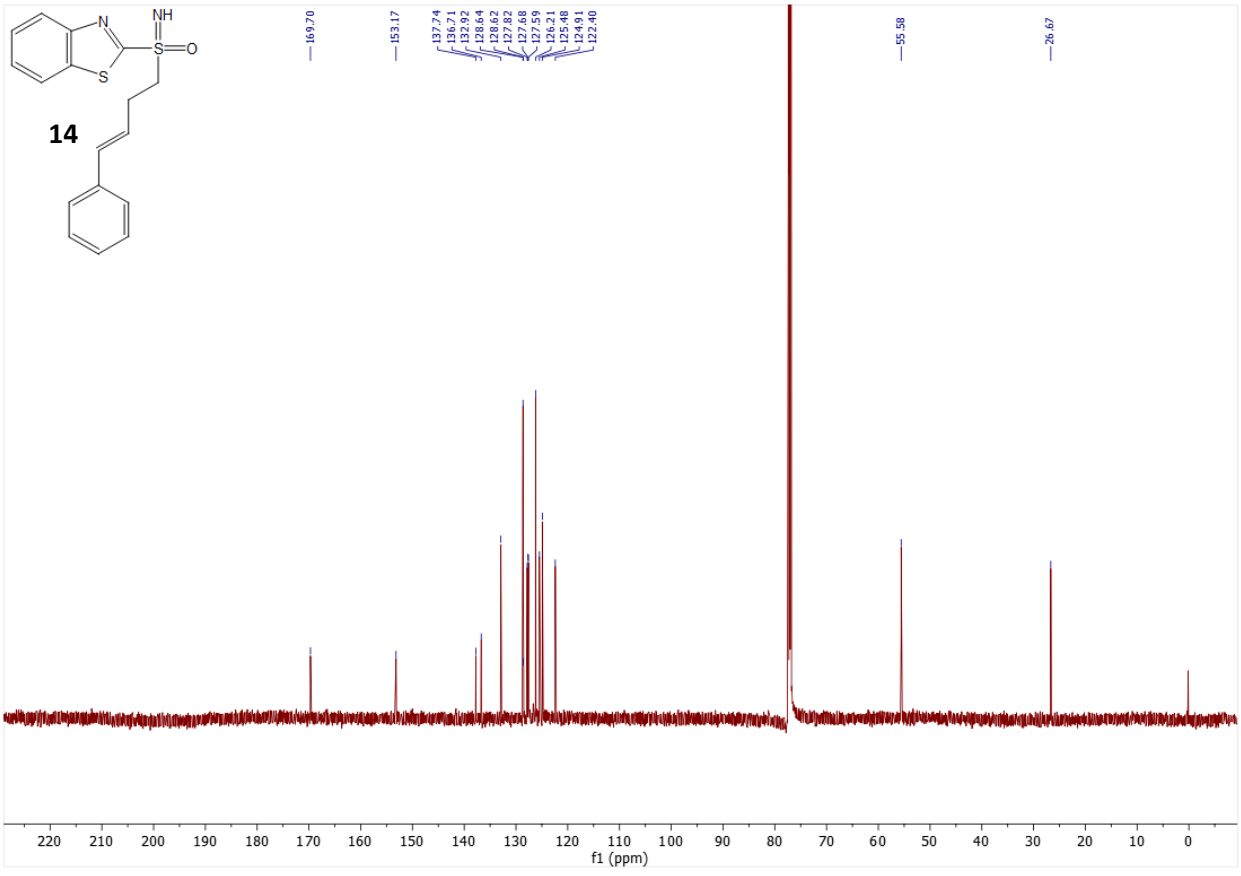

CH3
O
O
12
2.02
2.05
1.00
1.00
0.99
2.05
1.97
1.98
1.14
2.62
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

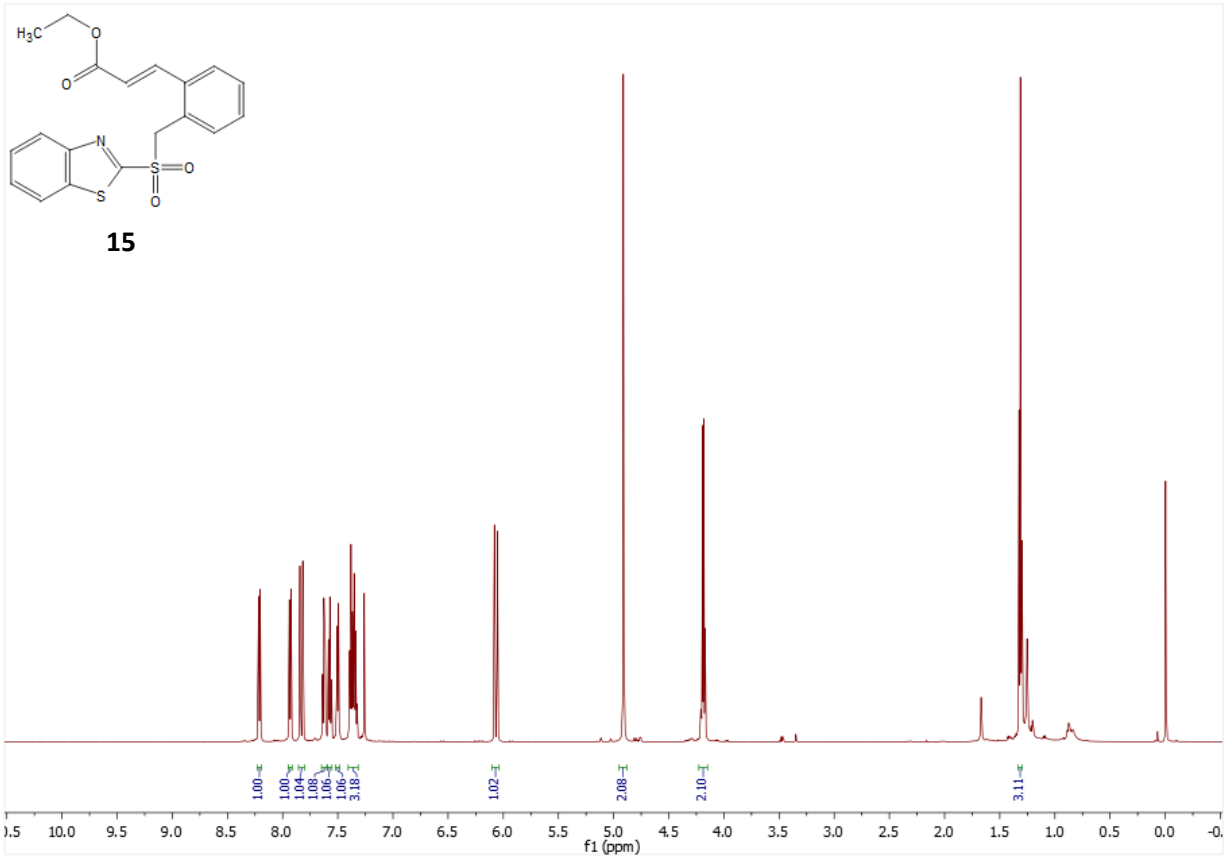

CH3
O
O
12
173.14
137.54
131.08
128.65
127.27
126.20
60.55
34.23
29.86
28.46
14.42
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

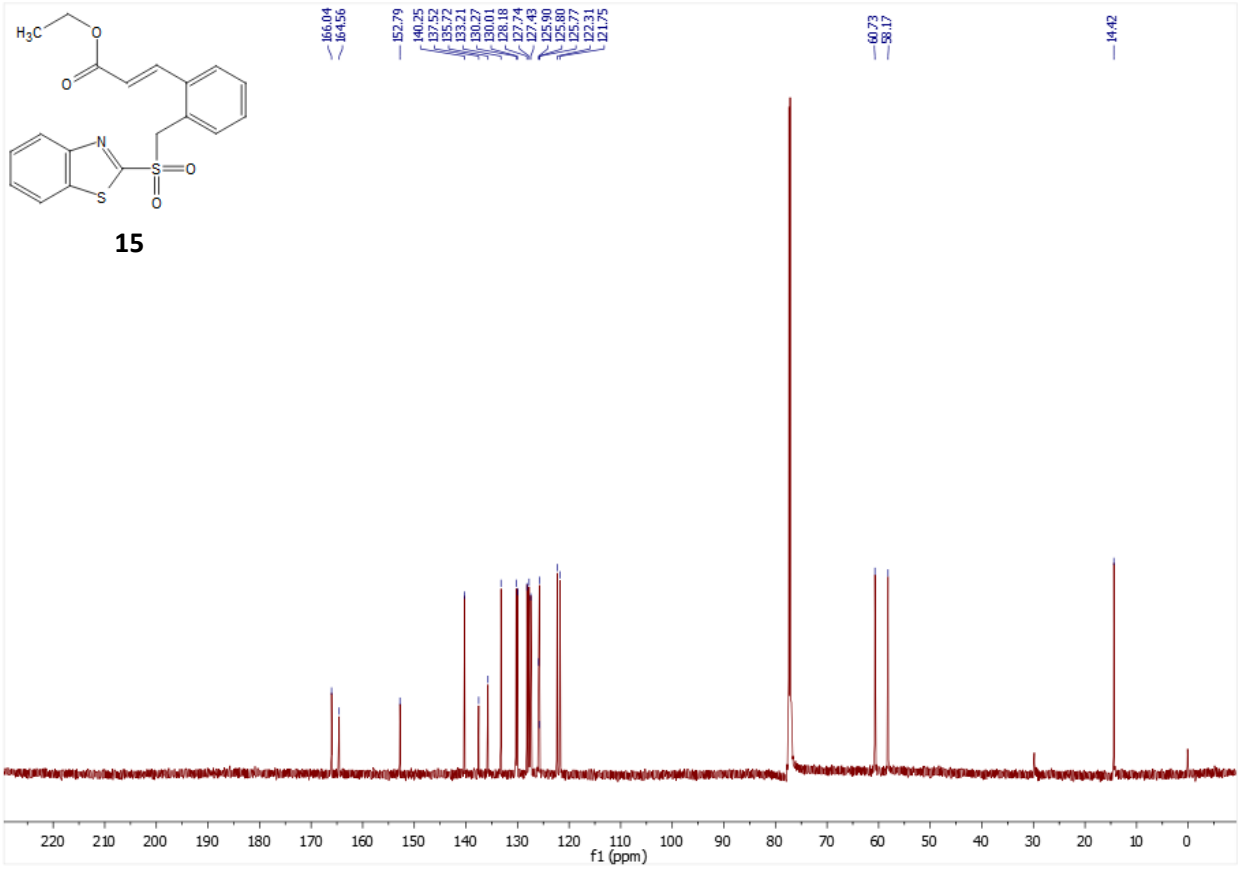

13
1.10
1.04
1.20
1.17
5.03
1.00
0.98
1.06
1.11
1.03
1.00
f1 (ppm)

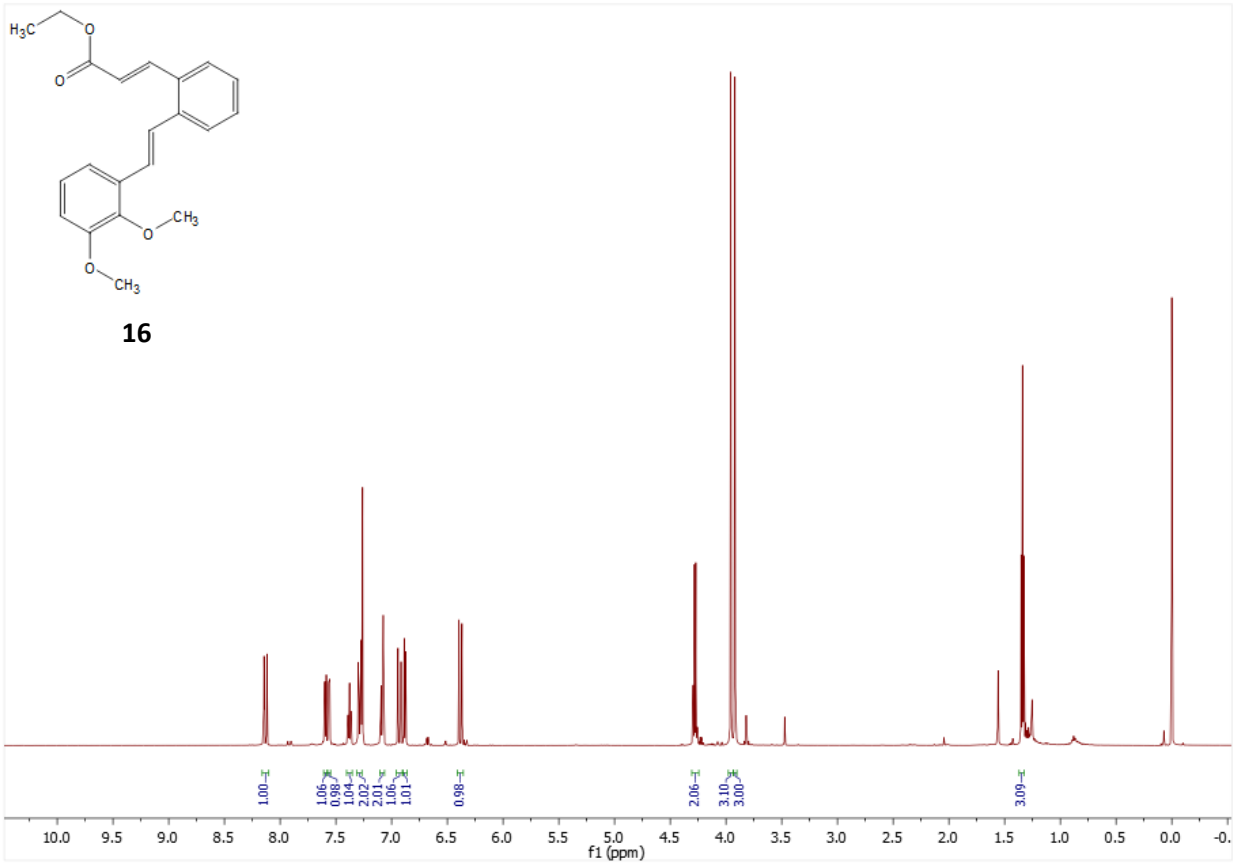

13
177.56
154.10
136.86
136.19
133.09
128.66
127.64
127.09
126.33
126.25
125.67
124.07
122.42
55.91
25.10
f1 (ppm)


14
1.00
1.02
1.05
1.06
5.05
0.97
0.97
2.03
0.93
2.03
f1 (ppm)

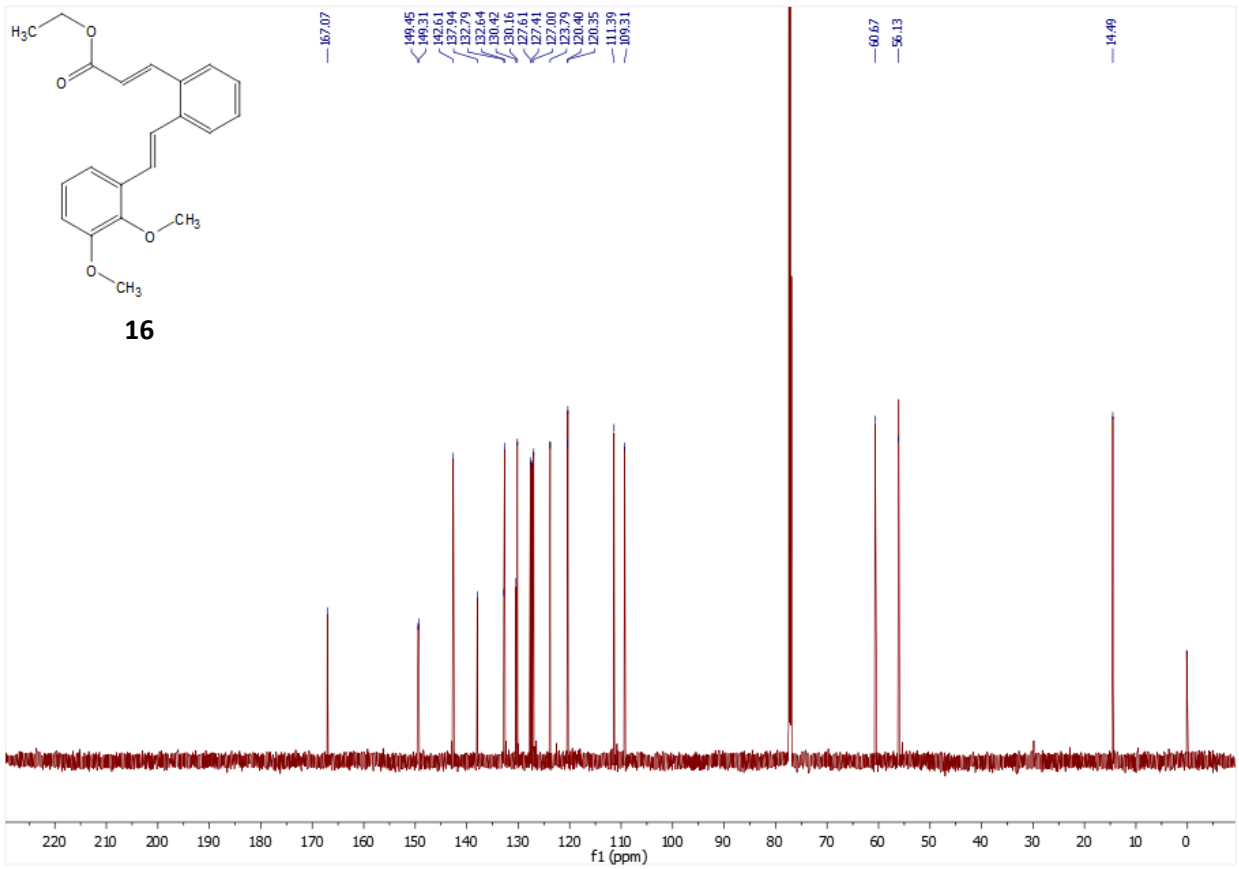

14
169.70
153.17
137.74
136.71
132.92
128.64
128.62
127.82
127.68
127.59
126.21
125.48
124.91
122.40
55.58
26.67
f1 (ppm)


H3C
O
O
N
S
S
O
O
15
1.00
1.00
1.04
1.08
1.06
1.06
3.18
1.02
2.08
2.10
3.11
f1 (ppm)

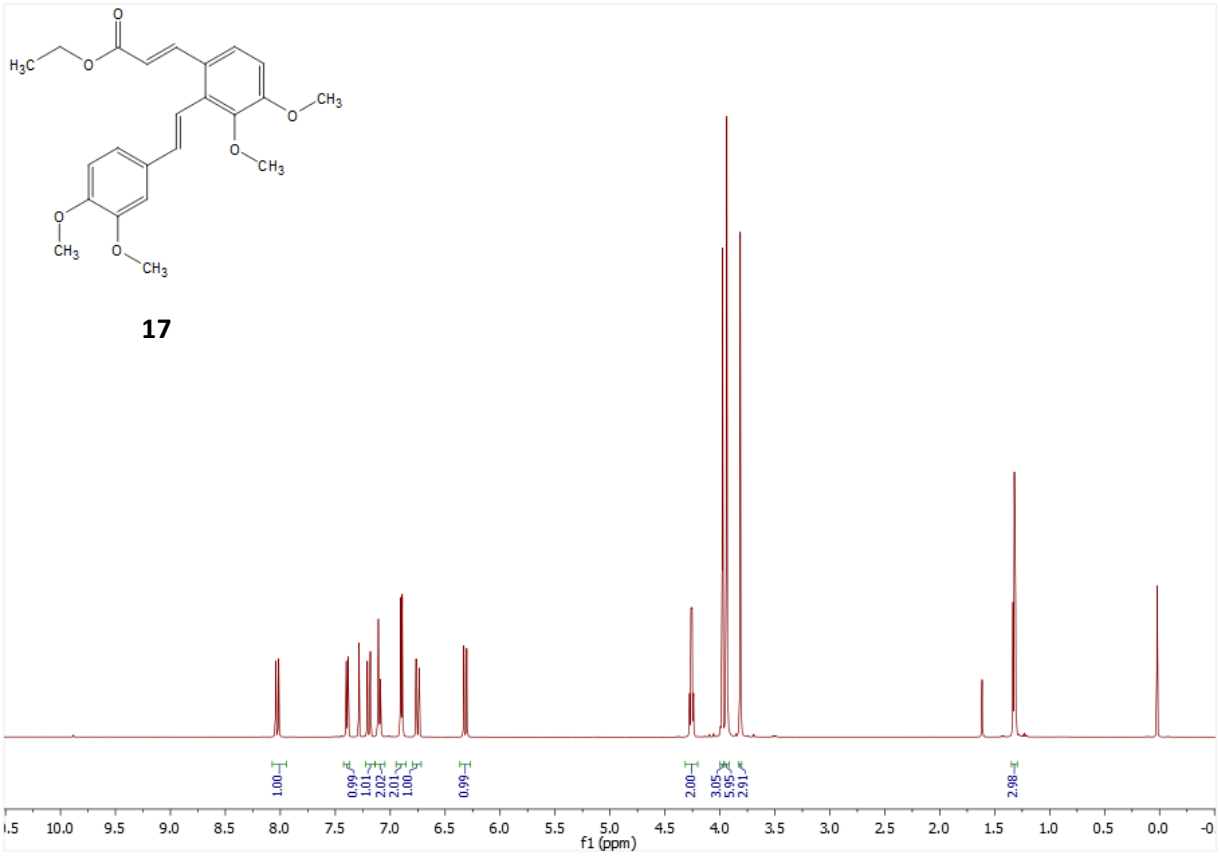

H3C
O
O
N
S
S
O
O
15
166.04
164.56
152.79
140.25
137.52
135.72
133.21
130.27
130.01
128.18
127.74
127.43
125.90
125.80
125.77
122.31
121.75
60.73
58.17
14.42
f1 (ppm)


H3C
O
O
CH3
O
O
CH3
1.00
1.06
0.98
1.04
2.02
2.01
1.06
1.01
0.98
2.06
3.10
3.00
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

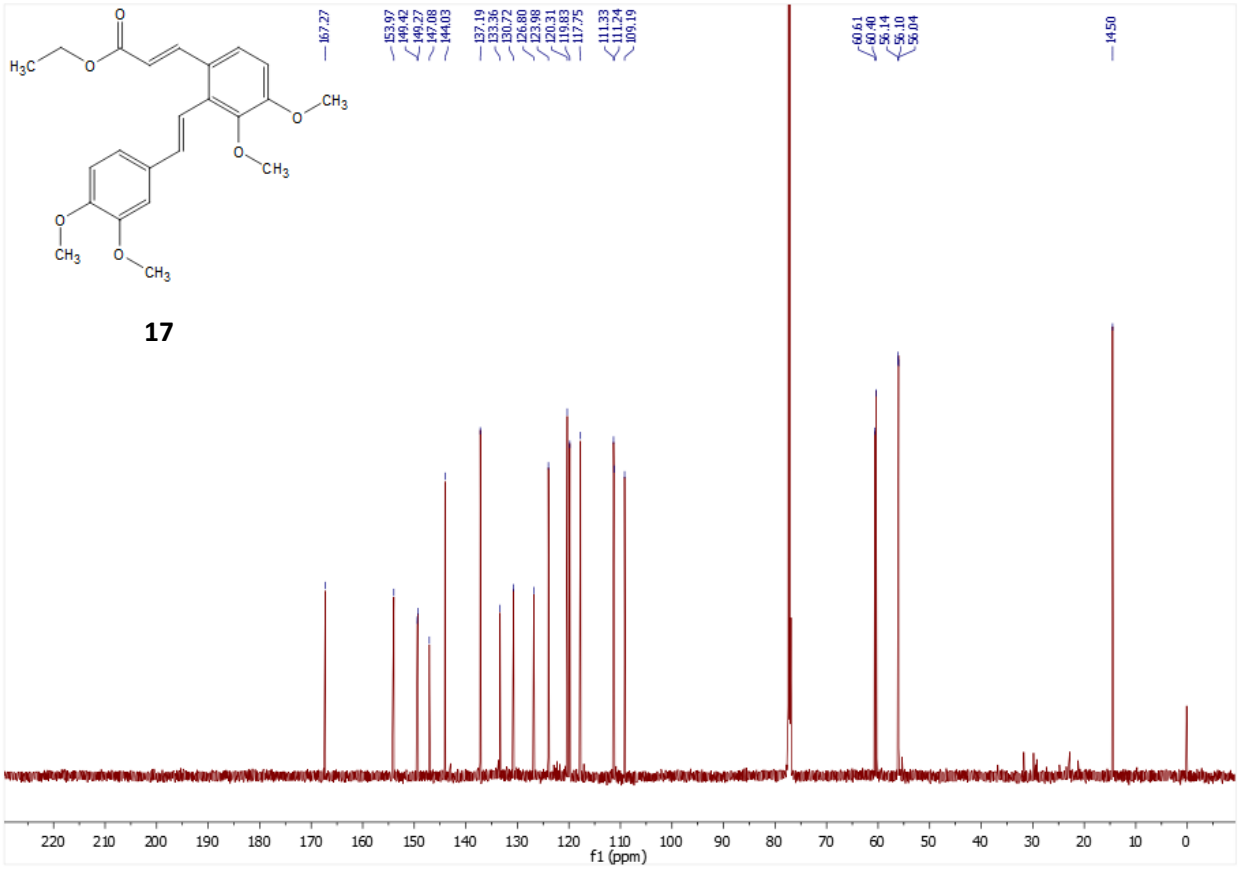
16


H3C
O
O
CH3
O
O
CH3
167.07
149.45
149.31
142.61
137.94
132.79
132.64
130.42
130.16
127.61
127.41
127.00
123.79
120.40
120.35
111.39
109.31
60.67
56.13
14.49
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

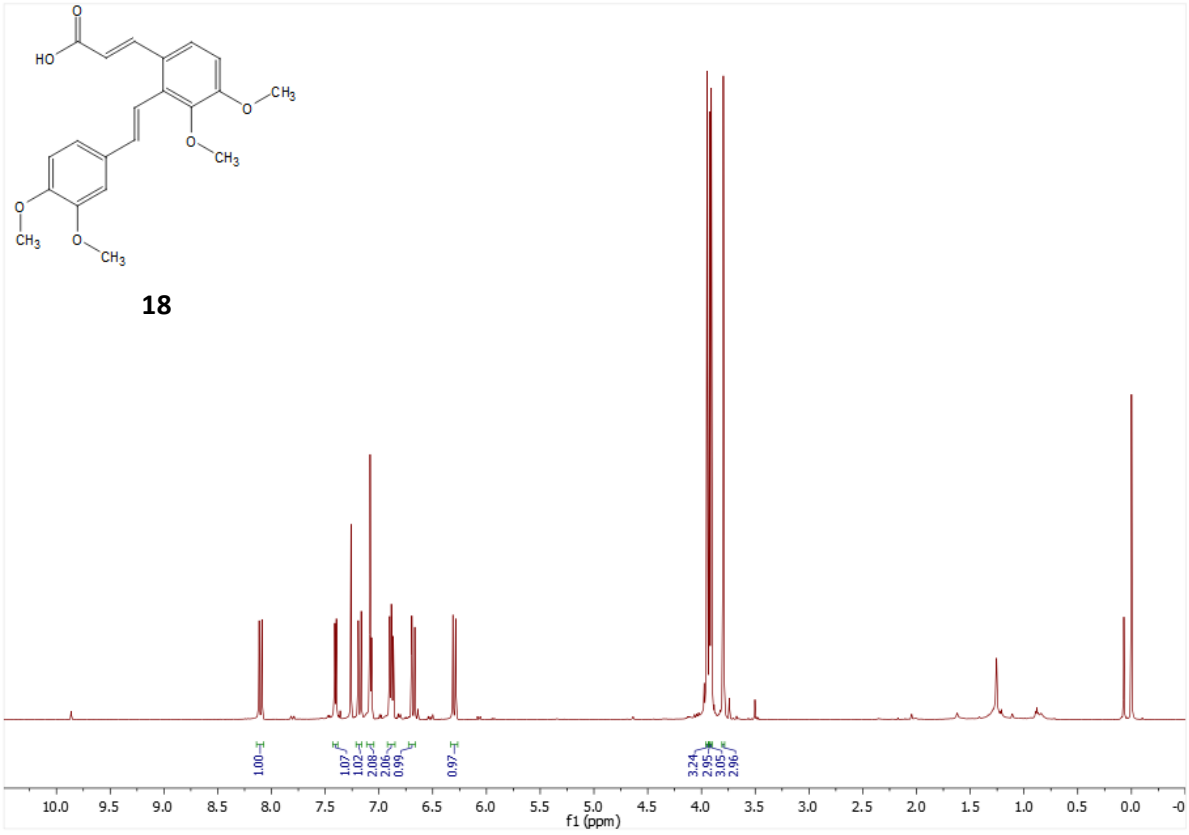
16

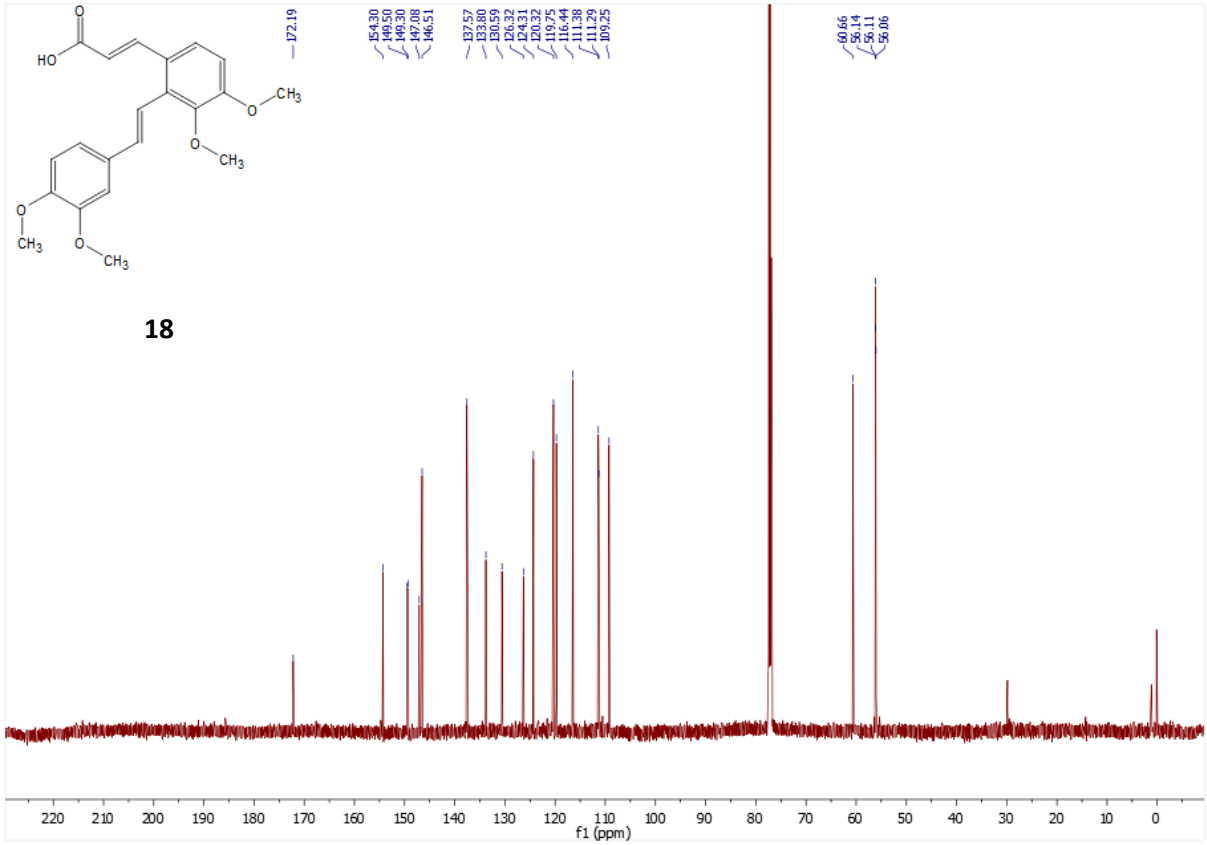


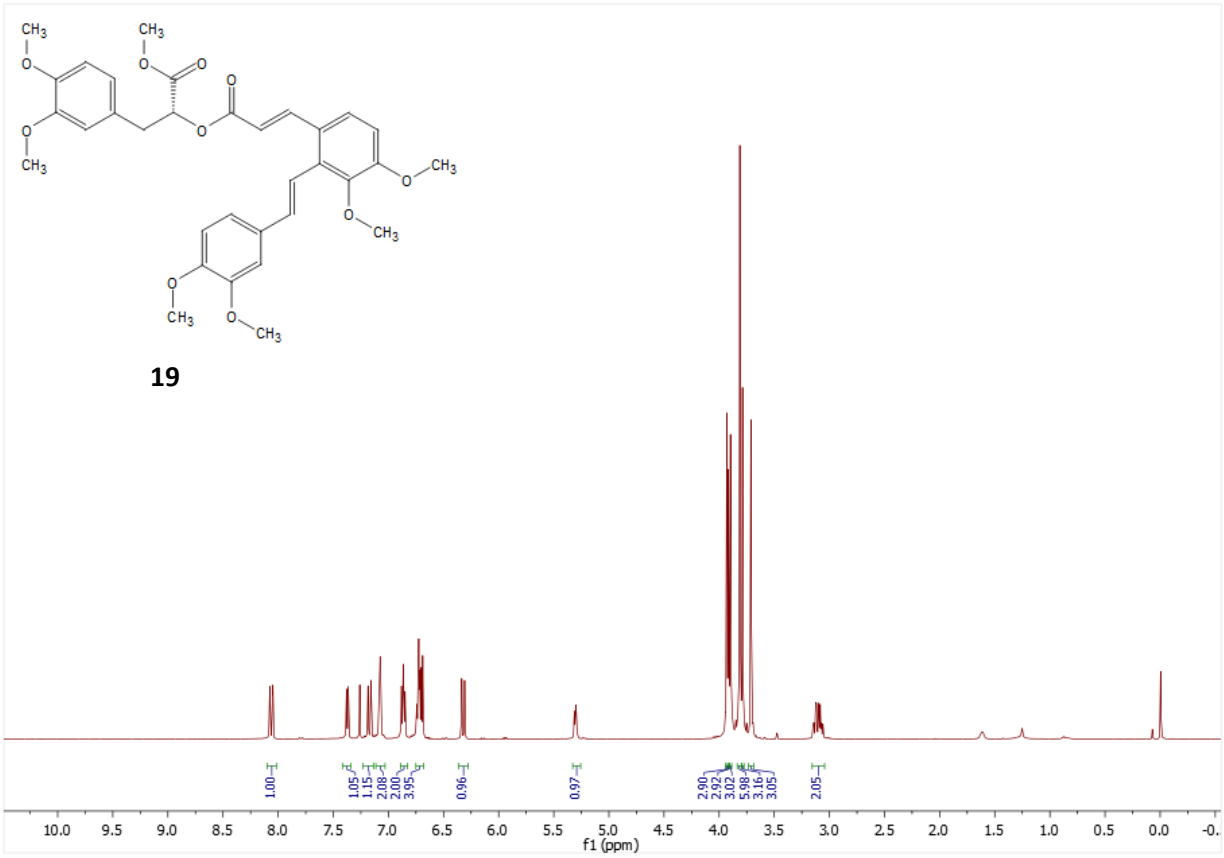
17



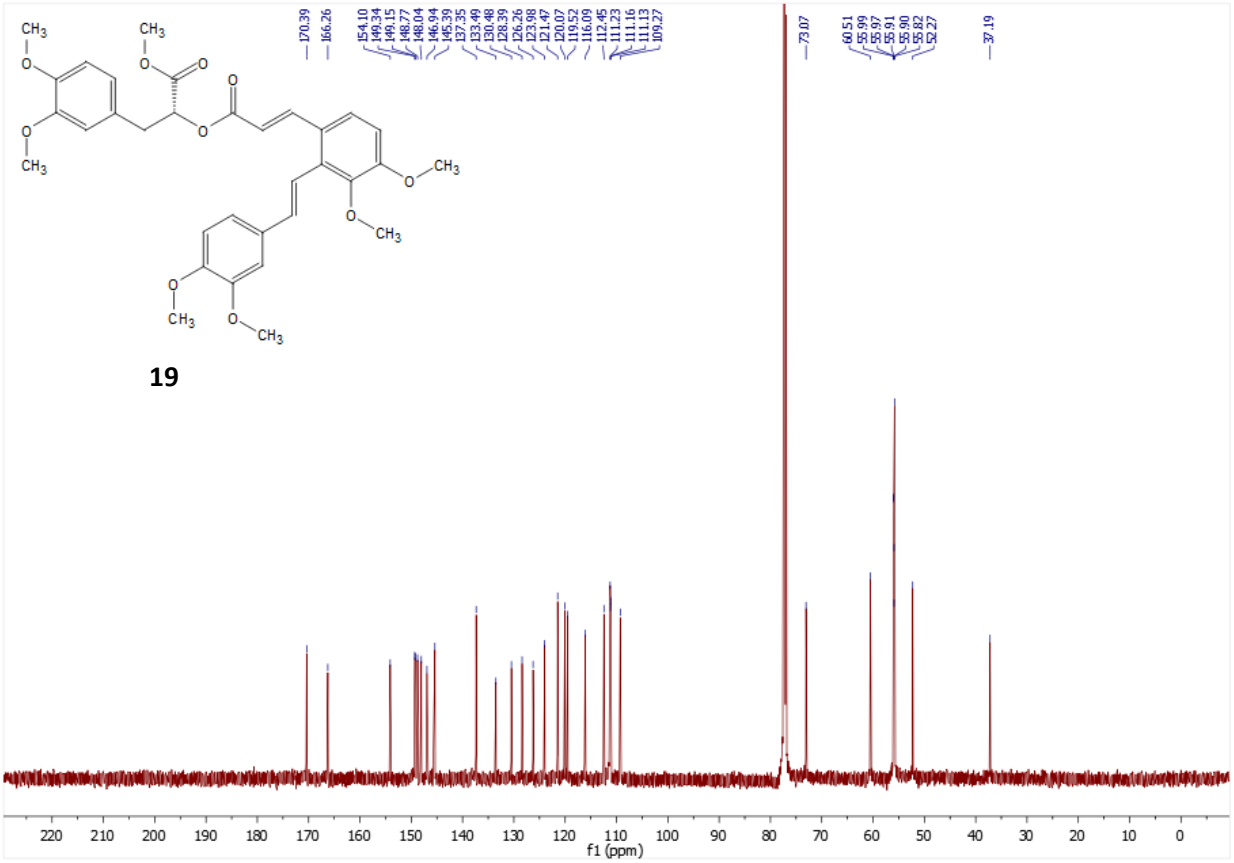
17


HO
O
CH3
O
CH3
O
CH3
O
CH3
18
1.00
1.07
1.02
2.08
2.06
0.99
0.97
3.24
2.95
3.05
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

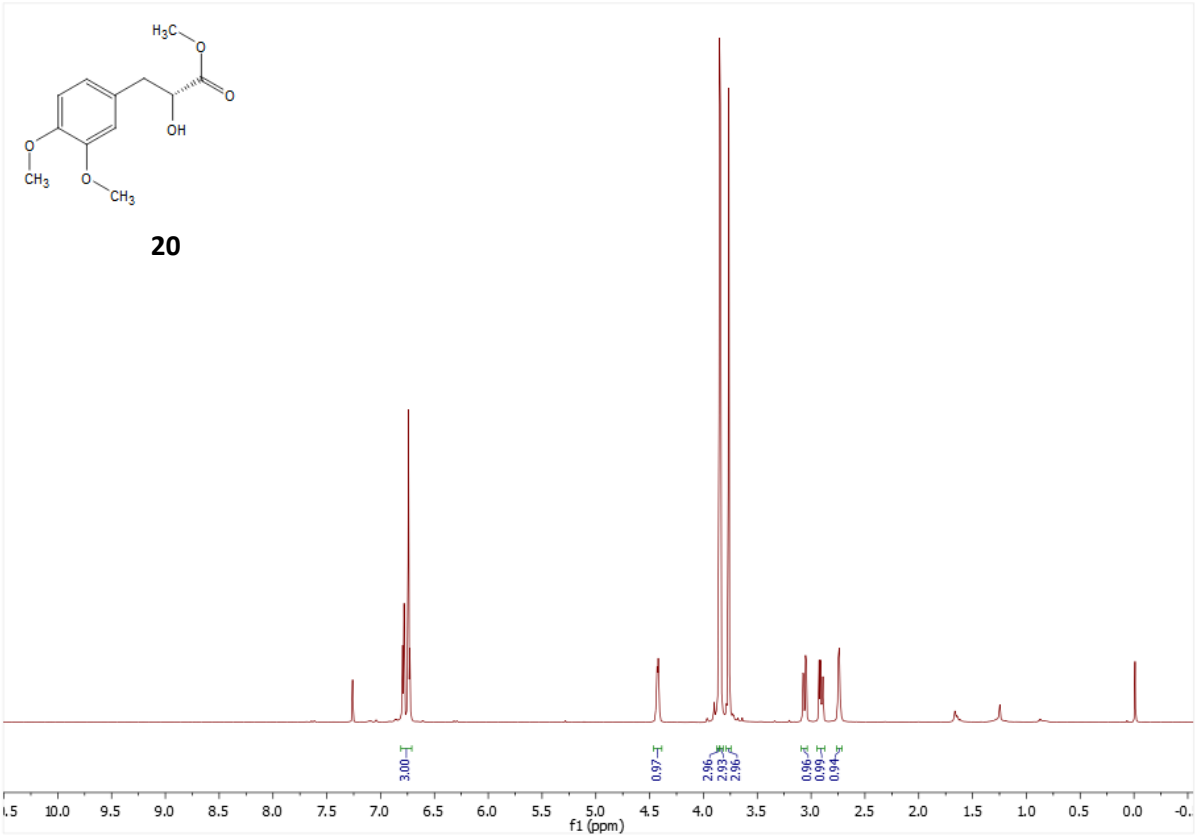

HO
O
CH3
O
CH3
O
CH3
O
CH3
18
172.19
154.30
149.50
149.30
147.08
146.51
137.57
133.80
130.59
126.32
124.31
120.32
119.75
116.44
111.38
111.29
109.25
60.66
56.14
56.11
56.06
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



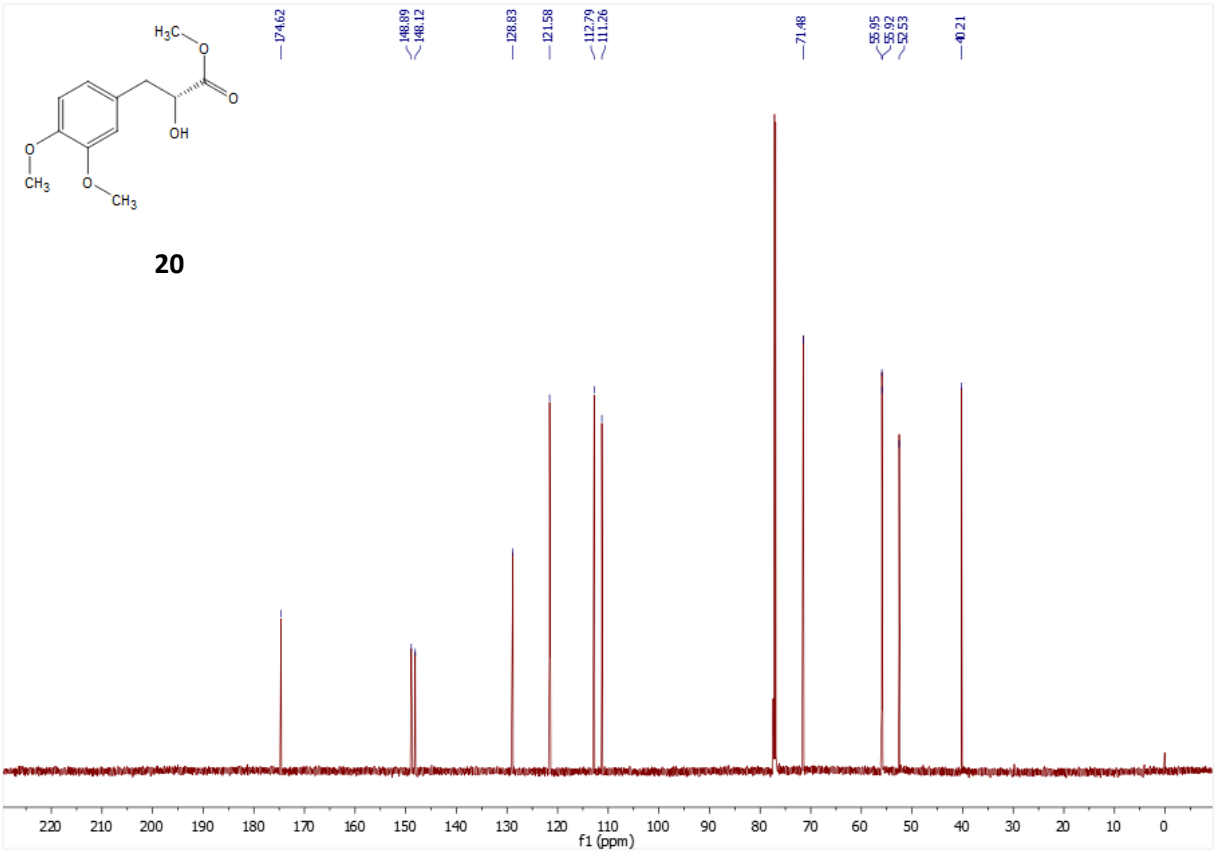
19



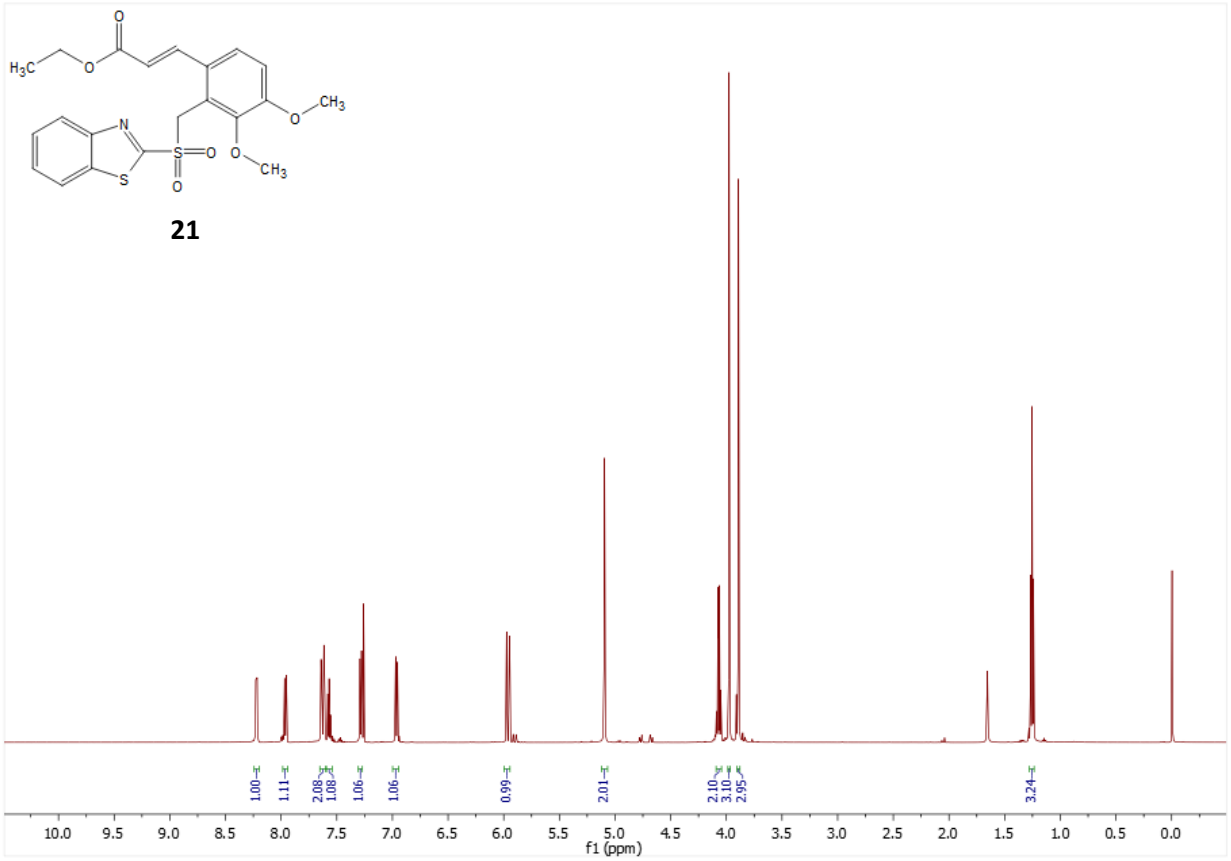
19

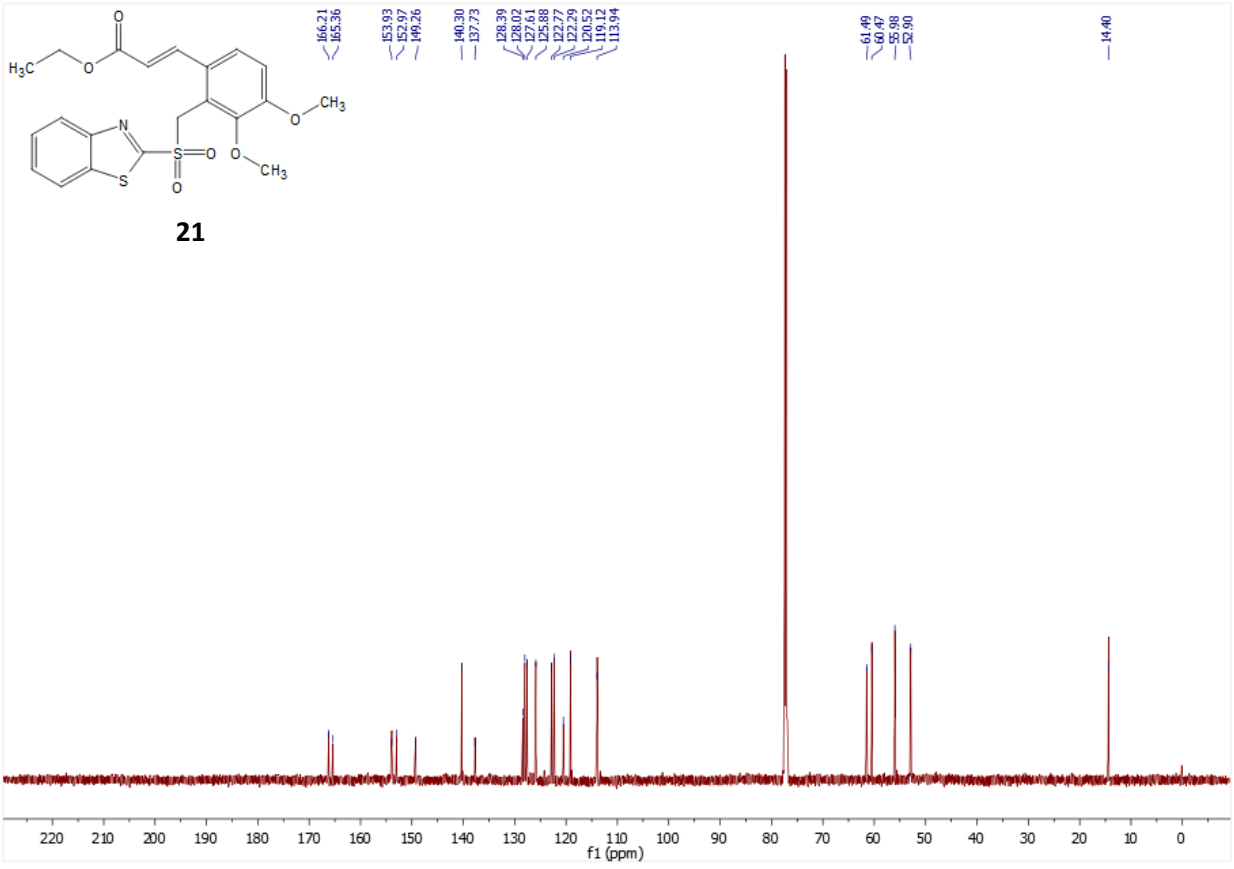

H3C
O
O
OH
O
CH3
O
CH3
3.00
0.97
2.96
2.93
2.96
0.96
0.99
0.94
f1 (ppm)

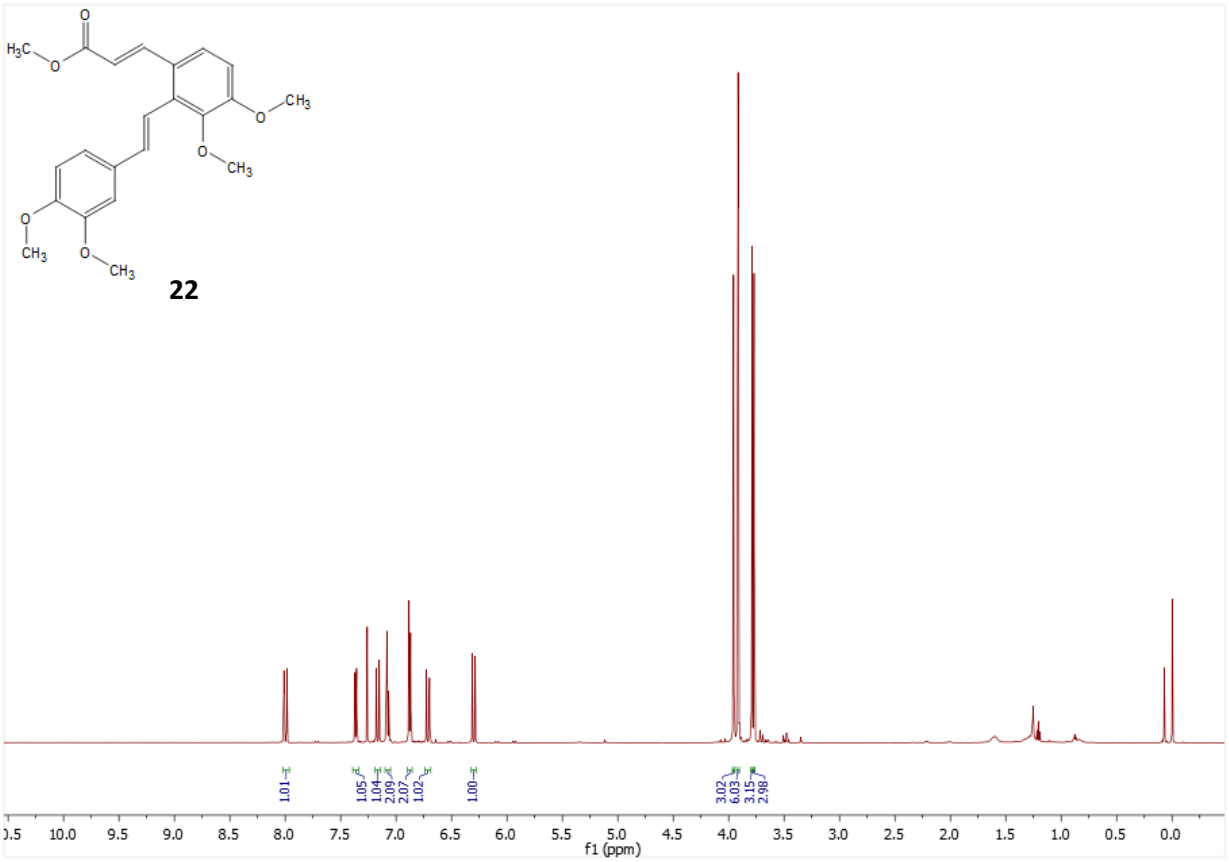
20

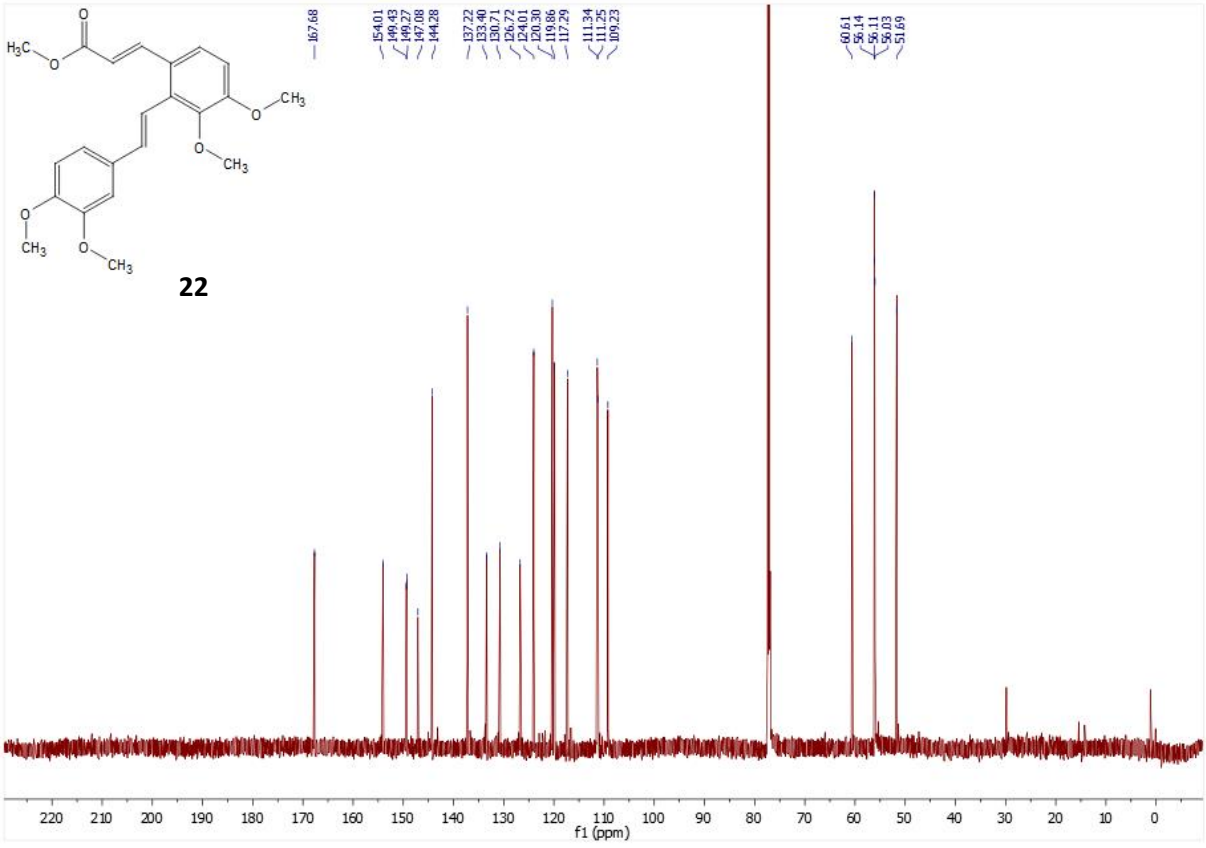

H3C
O
O
OH
O
CH3
O
CH3
174.62
148.89
148.12
128.83
121.58
112.79
111.26
71.48
55.95
55.92
52.53
40.21
f1 (ppm)

20


21
1.00
1.11
2.08
1.08
1.06
1.06
0.99
2.01
2.10
3.10
2.95
3.24
f1 (ppm)


21
166.21
165.36
153.93
152.97
149.26
140.30
137.73
128.39
128.02
127.61
125.88
122.77
122.29
120.52
119.12
113.94
61.49
60.47
55.98
52.90
14.40
f1 (ppm)


22
1.01
1.05
1.04
2.09
2.07
1.02
1.00
3.02
6.03
3.15
2.98
f1 (ppm)


22
167.68
154.01
149.43
149.27
147.08
144.28
137.22
133.40
130.71
126.72
124.01
120.30
119.86
117.29
111.34
111.25
109.23
60.61
56.14
56.11
56.03
51.69
f1 (ppm)