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Supporting information

Efficient Synthesis of Chiral 2,3-Dihydro-benzo[*b*]thiophene 1,1-Dioxides *via* Rh-Catalyzed Hydrogenation

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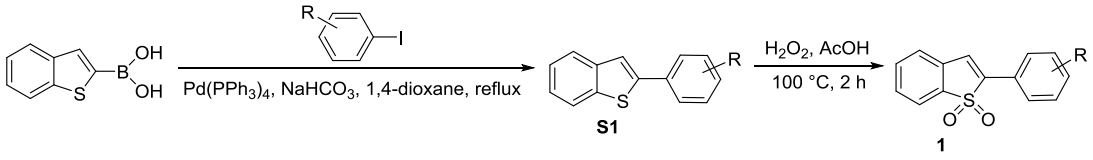
Contents

1. General remarks

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification. Anhydrous solvents were purchased from Sigma-Aldrich, J&K Chemical Technology company, and transferred by syringe. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker ADVANCE III (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts are reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the $CDCl_3$ at 7.26 ppm (for ^{1}H NMR) or 77.0 ppm (for ^{13}C NMR). Data are reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in hertz (Hz) and signal area integration in natural numbers. ^{13}C NMR analyses were run with decoupling. Enantiomeric excess values were determined by Daicel chiral column on an Agilent 1260 Series HPLC instrument. Optical rotations $[\alpha]_D$ were measured on a PERKIN ELMER polarimeter 343 instrucment. Column Chromatography was performed with silica gel (300-400 mesh).

2. General procedure for the synthesis of substrate

The substrates of aryl-substituted benzothiophene 1,1-dioxides according were synthesized to the method A:

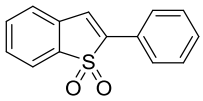


Step 1:[1-2] Aromatic iodide (10.00 mmol, 1.0 eq.) was added under argon at r.t. to a solution of $Pd(Ph_3P)_4$ (58 mg, 0.05 mmol, 0.005 eq.) in dry 1,4-dioxane (50 mL) and stirred for 20 min. After this time saturated $NaHCO_3$ (aq., 14.0 mL) and commercially available 1-benzothiophene-2-boronic acid (979 mg, 11.0 mmol, 1.1 eq.) were added and the resulting reaction mixture was refluxed overnight. The reaction mixture was then allowed to cool to r.t. and diluted with H_2O (80 mL) and extracted with CH_2Cl_2 (3×60 mL). The combined organic extracts were washed with NaOH (aq. 1 M, 40 mL)

and then with brine, dried over $MgSO_4$ and concentrated in vacuo to give a brown crystalline solid that was purified by flash chromatography to give the corresponding product **S1**.

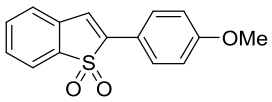
Step 2:[3] **S1** (1.00 eq.) was suspended in glacial AcOH (concentration ≈ 0.9 M) and H_2O_2 (30% aq. solution, 6.5 eq.) was slowly added. The mixture was heated to 100 °C and, at this temperature, it became a clear solution. Stirring at 100 °C was continued for 3 h and GC-MS analysis showed full conversion. The mixture was allowed to cool to r.t. and partitioned between CH_2Cl_2 and saturated $NaHCO_3$ (aq. so to bring the pH of the aq. phase to ≈ 9), the layers were separated and the aq. phase was extracted three times with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo to give the crude product that was purified by flash chromatography (silica gel, petroleum ether–EtOAc).

2-phenylbenzo[*b*]thiophene 1,1-dioxide **1a**



White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.83 (m, 2H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.52-7.45 (m, 4H), 7.44-7.40 (m, 1H), 7.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.54, 137.02, 133.76, 131.10, 130.34, 129.91, 129.22, 127.10, 126.52, 125.02, 123.66, 121.48. The characterization data of compound **1a** is in accordance with the reported data in the literature.[2]

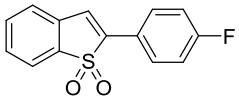
2-(4-methoxyphenyl)benzo[*b*]thiophene 1,1-dioxide **1b**



Yellow crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.79-7.77 (m, 2H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.15 (s, 1H), 7.00-6.97 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.19, 142.23, 136.70, 133.72, 131.53, 129.36, 128.10, 124.66, 121.38, 121.25, 119.54, 114.72, 55.42. The characterization data of compound **1b** is in

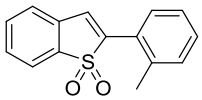
accordance with the reported data in the literature.[2]

2-(4-fluorophenyl)benzo[*b*]thiophene 1,1-dioxide **1c**



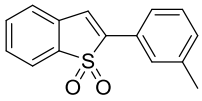
Pale yellow crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.81 (m, 2H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.60-7.56 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.23 (s, 1H), 7.20-7.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.77 (d, *J* = 251.0 Hz), 141.54, 136.76, 133.85, 131.00, 129.97, 128.65 (d, *J* = 9.0 Hz), 125.03, 123.51 (d, *J* = 2.0 Hz), 123.36 (d, *J* = 4.0 Hz), 121.54, 116.52 (d, *J* = 22.0 Hz). The characterization data of compound **1c** is in accordance with the reported data in the literature.[2]

2-(*o*-tolyl)benzo[*b*]thiophene 1,1-dioxide **1d**



White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.60-7.56 (m, 1H), 7.53-7.49 (m, 1H), 7.41-7.39 (m, 1H), 7.36-7.27 (m, 3H), 7.04 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.59, 138.06, 136.29, 133.66, 131.06, 130.09, 130.06, 129.47, 128.18, 126.40, 126.19, 125.00, 121.70, 20.67. The characterization data of compound **1d** is in accordance with the reported data in the literature.[2]

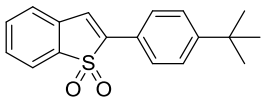
2-(*m*-tolyl)benzo[*b*]thiophene 1,1-dioxide **1e**



White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.65-7.62 (m, 2H), 7.58-7.51 (m, 1H), 7.49-7.47 (m, 1H), 7.40-7.34 (m, 2H), 7.27 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.69, 139.02, 137.04, 133.72, 131.22, 129.81, 129.10, 127.00, 124.94, 123.71, 123.50, 121.46, 21.46. The

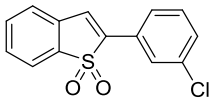
characterization data of compound **1e** is in accordance with the reported data in the literature.[2]

2-(4-(tert-butyl)phenyl)benzo[*b*]thiophene 1,1-dioxide **1f**



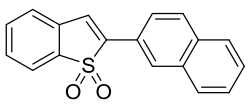
White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.75 (m, 3H), 7.59-7.55 (m, 1H), 7.51-7.47 (m, 3H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.25 (s, 1H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.85, 142.60, 136.98, 133.72, 131.37, 129.67, 126.30, 126.26, 124.86, 124.21, 122.64, 121.48, 34.93, 31.09. HRMS calculated for $C_{18}H_{18}NaO_2S^+$ [$(M+Na)^+$] = 321.0922, found: 321.0919.

2-(3-chlorophenyl)benzo[*b*]thiophene 1,1-dioxide **1g**



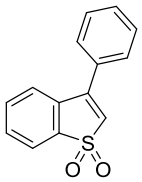
White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.73 (m, 3H), 7.61-7.57 (m, 1H), 7.57-7.51 (m, 1H), 7.44-7.42 (m, 3H), 7.32 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.24, 136.97, 135.24, 133.89, 130.70, 130.49, 130.37, 130.33, 128.80, 126.46, 125.30, 124.99, 124.66, 121.59. HRMS calculated for $C_{14}H_9ClNaO_2S^+$ [$(M+Na)^+$] = 298.9907, found: 298.9903.

2-(naphthalen-2-yl)benzo[*b*]thiophene 1,1-dioxide **1h**



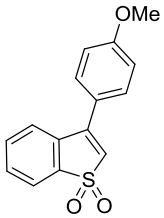
White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.91-7.80 (m, 6H), 7.68 (s, 1H), 7.54-7.47 (m, 2H), 7.39-7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.56, 137.08, 133.81, 133.10, 131.24, 129.89, 129.18, 128.97, 127.72, 127.56, 126.96, 126.73, 125.03, 124.24, 123.65, 123.05, 121.52. HRMS calculated for $C_{18}H_{12}NaO_2S^+$ [$(M+Na)^+$] = 315.0456, found: 315.0450.

3-phenylbenzo[*b*]thiophene 1,1-dioxide **1m**



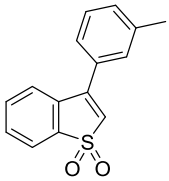
White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.79 (m, 1H), 7.60-7.48 (m, 8H), 6.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.95, 138.08, 133.29, 131.90, 130.99, 130.59, 130.47, 129.16, 127.95, 125.60, 124.28, 121.62. The characterization data of compound **1m** is in accordance with the reported data in the literature.[2]

3-(4-methoxyphenyl)benzo[*b*]thiophene 1,1-dioxide **1n**



White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.79 (m, 1H), 7.59-7.53 (m, 3H), 7.50-7.47 (m, 2H), 7.05-7.03 (m, 2H), 6.58 (s, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.35, 145.60, 138.24, 133.17, 132.06, 130.44, 129.47, 124.25, 124.22, 123.14, 121.50, 114.55, 55.43. The characterization data of compound **1n** is in accordance with the reported data in the literature.[2]

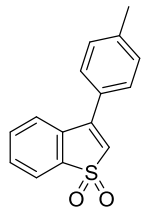
3-(*m*-tolyl)benzo[*b*]thiophene 1,1-dioxide **1o**



White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.79 (m, 1H), 7.59-7.55 (m, 2H), 7.53-7.49 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 3H), 6.63 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.12, 139.07, 138.10, 133.26, 132.01, 131.23, 130.94, 130.53, 129.01, 128.51, 125.39, 125.03,

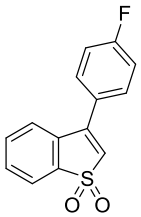
124.34, 121.57, 21.45. The characterization data of compound **1o** is in accordance with the reported data in the literature.[2]

3-(*p*-tolyl)benzo[*b*]thiophene 1,1-dioxide **1p**



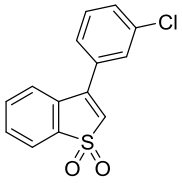
White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.79 (m, 1H), 7.58-7.56 (m, 2H), 7.53-7.50 (m, 1H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.62 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.98, 140.86, 138.16, 133.22, 132.03, 130.49, 129.82, 128.06, 127.88, 124.96, 124.29, 121.54, 21.44. The characterization data of compound **1p** is in accordance with the reported data in the literature.[2]

3-(4-fluorophenyl)benzo[*b*]thiophene 1,1-dioxide **1r**



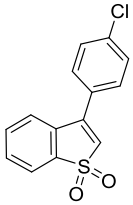
White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.80 (m, 1H), 7.60–7.58 (m, 2H), 7.54-7.46 (m, 2H), 7.47-7.46 (m, 1H), 7.25–7.21 (m, 2H), 6.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.91 (d, *J* = 250.0 Hz), 144.91, 138.07, 133.35, 131.74, 130.72, 129.98 (d, *J*= 8.0 Hz), 127.03 (d, *J* = 3.0 Hz), 125.77, 124.06, 121.71, 116.44 (d, *J* = 21.0 Hz). The characterization data of compound **1r** is in accordance with the reported data in the literature.[2]

3-(3-chlorophenyl)benzo[*b*]thiophene 1,1-dioxide **1s**



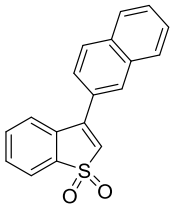
White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81-7.80 (m, 1H), 7.61-7.59 (m, 2H), 7.52-7.40 (m, 5H), 6.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.51, 137.93, 135.23, 133.44, 132.72, 131.39, 130.83, 130.55, 130.53, 127.97, 126.53, 126.12, 124.03, 121.79. HRMS calculated for $C_{14}H_9ClNaO_2S^+$ [$(M+Na)^+$] = 298.9907, found: 298.9903.

3-(4-chlorophenyl)benzo[*b*]thiophene 1,1-dioxide **1t**



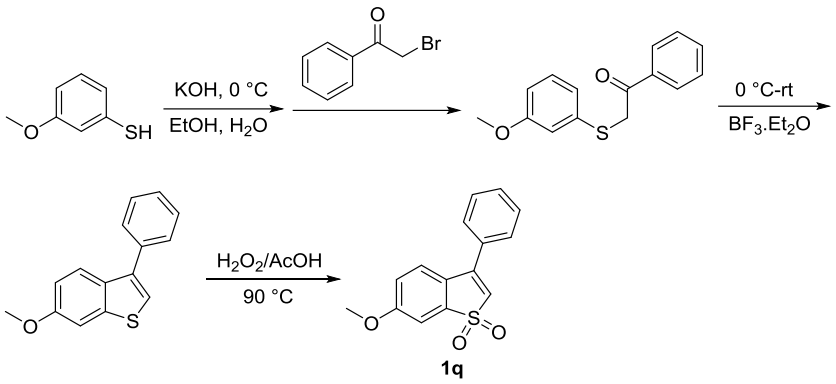
White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.82-7.80 (m, 1H), 7.60-7.58 (m, 2H), 7.53-7.44 (m, 5H), 6.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.79, 138.02, 136.68, 133.38, 131.53, 130.78, 129.52, 129.40, 129.28, 126.04, 124.02, 121.76. HRMS calculated for $C_{14}H_9ClNaO_2S^+$ [$(M+Na)^+$] = 298.9908, found: 298.9903.

3-(naphthalen-2-yl)benzo[*b*]thiophene 1,1-dioxide **1u**



White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.03 (s, 1H), 7.98 (d, *J* = 4.2 Hz, 1H), 7.93-7.91 (m, 2H), 7.85-7.81 (m, 1H), 7.61-7.55 (m, 6H), 6.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.97, 138.16, 133.93, 133.30, 132.96, 131.99, 130.60, 129.03, 128.39, 128.34, 127.87, 127.56, 127.11, 125.82, 124.81, 124.37, 121.62. HRMS calculated for $C_{18}H_{12}NaO_2S^+$ [$(M+Na)^+$] = 315.0455, found: 315.0450.

The synthesis of substrate 6-methoxy-3-phenylbenzo[*b*]thiophene 1,1-dioxide according to the method B:



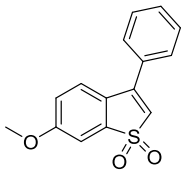
Step 1:[4] Methoxybenzenethiol (1.12 g, 8.0 mmol) was added to a round-bottom flask charged with a freshly prepared solution containing 6 mL ethanol, 14 mL water, and KOH (0.51 g, 9.0 mmol). The solution was cooled in an ice-water bath, and a solution of 2-bromo-1-phenylethan-1-one (1.59 g, 8.0 mmol) in 10 mL ethyl acetate was slowly added. The reaction mixture was monitored by TLC until completion. The solvents were evaporated under reduced pressure, and the residue mixture was partitioned between water and ethyl acetate. The combined organic phase was washed with brine, and dried by Na_2SO_4 to give 2-((4-methoxyphenyl)thio)-1-phenylethan-1-one, which was used in the next step without further purification.

Step 2:[5] $BF_3{\cdot}OEt_2$ (70 mL) was slowly added to a flask charged with 2-((4-methoxyphenyl)thio)-1-phenylethan-1-one (2.0 g) under argon atmosphere in an ice bath. The reaction mixture was stirred until starting material was consumed as monitored by TLC. The reaction mixture was poured into saturated $NaHCO_3$/ice-water, stirred 30 min, and extracted with dichloromethane. The crude product was purified by silica gel chromatography (5% dichloromethane in petroleum ether). The combined fractions from the column were concentrated and recrystallized in ethanol to give pale yellow solid (0.5 g).

Step 3: 5-methoxy-3-phenylbenzo[*b*]thiophene (1.00 eq.) was suspended in glacial AcOH (concentration ≈ 0.9 M) and H_2O_2 (30% aq. solution, 6.5 eq.) was

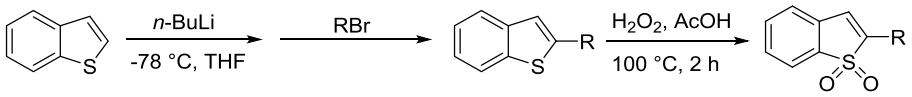
slowly added. The mixture was heated to 90 °C and, at this temperature, it became a clear solution. Stirring at 90 °C was continued for 3 h and GC-MS analysis showed full conversion. The mixture was allowed to cool to r.t. and partitioned between CH_2Cl_2 and saturated $NaHCO_3$ (aq. so to bring the pH of the aq. phase to ≈ 9), the layers were separated and the aq. phase was extracted three times with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo to give the crude product that was purified by flash chromatography (silica gel, petroleum ether–EtOAc).

6-methoxy-3-phenylbenzo[*b*]thiophene 1,1-dioxide **1q**



White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.52 (s, 5H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 1.2 Hz, 1H), 7.04-7.01 (m, 1H), 6.54 (s, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.93, 146.24, 140.00, 131.32, 130.40, 129.10, 127.89, 125.42, 123.93, 123.82, 118.48, 107.51, 56.05. HRMS calculated for $C_{15}H_{12}NaO_3S^+$ [$(M+Na)^+$] = 295.0402, found: 295.0399.

The substrates of 2-alkyl-substituted benzothiophene 1,1-dioxides 1i-l according were synthesized to the method C:

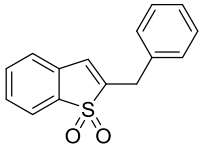


Step 1:[6] To a cold (-78 °C) solution of benzo[*b*]thiophene (2.00 mL, 17.1 mmol, 1.00 eq.) in THF (40 mL) was added *n*-BuLi (1.6 M in hexane, 21.4 mL, 34.3 mmol, 2.00 eq.) dropwise via dropping funnel (over 30 min) under Ar. The dropping funnel was rinsed twice with 5 mL Et_2O. Stirring was continued at -78 °C for 45 min and then the mixture was allowed to slowly warm to r.t. and stirred at this temperature for another 45 min (at r.t. the reaction mixture turned from colorless to yellow). After

this time the reaction mixture was cooled again to -78 °C and bromoalkanes (51.4 mmol, 3.00 eq.) was slowly added *via* dropping funnel. The mixture was stirred for 30 min at -78 °C (formation of a lump of white solid was observed) and then the temperature was slowly raised to 0 °C (vigorous gas evolution and formation of a white suspension). After 20 min of stirring at r.t., an aqueous solution of NaOH (66 mmol in 15 mL of H_2O) was added, the layers were separated and the organic phase was washed with water (10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated *in vacuo* to give a colorless oil that was purified by flash chromatography (silica gel, petroleum ether) to give 2-alkyl benzo[*b*]thiophene as white crystalline solid.

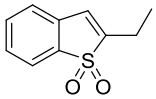
Step 2: 2-alkyl benzo[*b*]thiophene (1.00 eq.) was suspended in glacial AcOH (concentration ≈ 0.9 M) and H_2O_2 (30% aq. solution, 6.5 eq.) was slowly added. The mixture was heated to 100 °C and, at this temperature, it became a clear solution. Stirring at 100 °C was continued for 3 h and after this time GC-MS analysis showed full conversion. The mixture was allowed to cool to r.t. and partitioned between CH_2Cl_2 and $NaHCO_3$ (aq. sat. so to bring the pH of the aq. phase to ≈ 9), the layers were separated and the aq. phase was extracted three times with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo to give the crude product that was purified by flash chromatography (silica gel, petroleum ether–ethyl acetate).

2-benzylbenzo[*b*]thiophene 1,1-dioxide **1i**



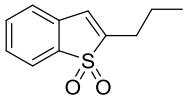
White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.49-7.31 (m, 7H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.41-6.40 (m, 1H), 3.85 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.21, 136.84, 134.99, 133.63, 131.42, 129.45, 129.41, 128.95, 127.37, 126.31, 124.52, 121.55, 29.61. The characterization data of compound **1i** is in accordance with the reported data in the literature.[2]

2-ethylbenzo[*b*]thiophene 1,1-dioxide **1j**



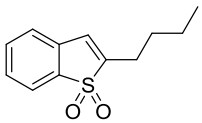
White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.6 Hz, 1H), 7.54-7.50 (m, 1H), 7.45-7.41 (m, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 6.76-6.75 (m, 1H), 2.65-2.59 (m, 2H), 1.35 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.71, 136.77, 133.57, 131.61, 129.30, 124.31, 124.27, 121.43, 17.14, 11.14. The characterization data of compound **1j** is in accordance with the reported data in the literature.[2]

2-propylbenzo[*b*]thiophene 1,1-dioxide **1k**



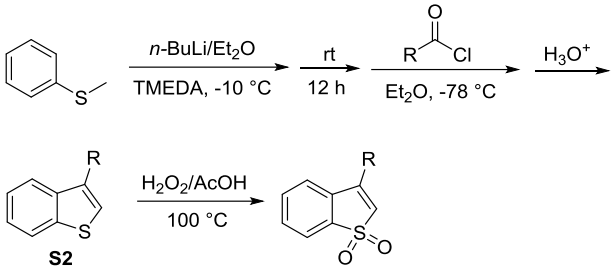
White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 1H), 7.53-7.49 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 6.76-6.75 (m, 1H), 2.58-2.53 (m, 2H), 1.81-1.74 (m, 2H), 1.05 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.00, 136.57, 133.51, 131.55, 129.25, 125.07, 124.28, 121.27, 25.82, 20.21, 13.61. The characterization data of compound **1k** is in accordance with the reported data in the literature.[2]

2-butylbenzo[*b*]thiophene 1,1-dioxide **1l**



White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.2 Hz, 1H), 7.50 (td, *J* = 7.6 Hz, 1.2Hz, 1H), 7.42 (m, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.27 (d, *J* = 5.2 Hz 1H), 6.75 (d, *J* = 0.8 Hz, 1H), 2.59-2.55 (m, 2H), 1.76-1.68 (m, 2H), 1.50-1.41 (m, 2H), 0.96 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.38, 136.65, 133.54, 131.63, 129.27, 124.89, 124.26, 121.38, 28.83, 23.56, 22.25, 13.67. HRMS calculated for $C_{12}H_{14}NaO_2S^+$ [$(M+Na)^+$] = 245.0608, found: 245.0606.

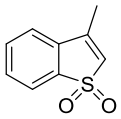
The synthesis of substrates 3-alkyl-substituted benzothiophene 1,1-dioxides 1v-x according to the method D:



Step 1:[7] To a vigorously stirred solution of methyl(phenyl)sulfane (2.48 g, 20.0 mmol), anhydrous TMEDA (2.28 g, 22.0 mmol), and anhydrous Et_2O (50 mL) cooled to -10 °C, 2.4 M solution of *n*-BuLi in hexane (60 mL) is gradually added under N_2, and stirring is continued at the room temperature for 12 h. The mixture is then cooled to -78 °C and a solution of the acyl chloride (19.0 mmol) in anhydrous Et_2O (10 mL) is gradually (30 min) added under N_2. The resultant mixture is stirred at -78 °C for 1 h, then allowed to warm to room temperature, stirred for 16 h, and poured into H_2O (50 mL). The pH is adjusted to 4-5 by addition of 10% aqueous HCl. The organic layer is separated, and the aqueous layer extracted with Et_2O (2×50 mL). The organic phases are combined, dried by Na_2SO_4, and concentrated. The crude product was purified by silica gel chromatography to obtain **S2**.

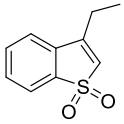
Step 2: **S2** (1.00 eq.) was suspended in glacial AcOH (concentration ≈ 0.9 M) and H_2O_2 (30% aq. solution, 6.5 eq.) was slowly added. The mixture was heated to 100 °C and, at this temperature, it became a clear solution. Stirring at 100 °C was continued for 3 h and after this time GC-MS analysis showed full conversion. The mixture was allowed to cool to r.t. and partitioned between CH_2Cl_2 and $NaHCO_3$ (aq. sat. so to bring the pH of the aq. phase to ≈ 9), the layers were separated and the aq. phase was extracted three times with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo to give the crude product that was purified by flash chromatography (silica gel, petroleum ether–EtOAc).

3-methylbenzo[*b*]thiophene 1,1-dioxide **1v**



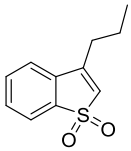
White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.71 (m, 1H), 7.62-7.58 (m, 1H), 7.56-752 (m, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 6.48-6.47 (m, 1H), 2.28 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.83, 137.48, 133.45, 133.07, 130.41, 125.71, 122.23, 120.90, 13.84. The characterization data of compound **1v** is in accordance with the reported data in the literature.[2]

3-ethylbenzo[*b*]thiophene 1,1-dioxide **1w**



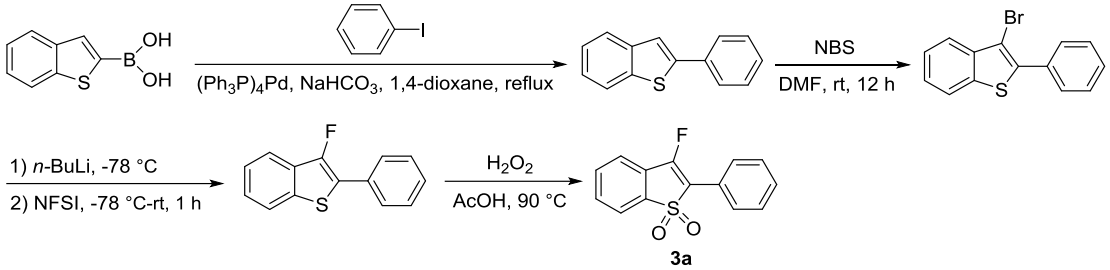
White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.72-7.70 (m, 1H), 7.60-7.52 (m, 2H), 7.43-7.41 (m, 1H), 6.45-6.44 (m, 1H), 2.67-2.61 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.72, 137.77, 133.39, 132.71, 130.43, 124.04, 122.07, 121.00, 21.15, 10.95. HRMS calculated for $C_{10}H_{10}NaO_2S^+$ $[(M+Na)^+]$ = 217.0294, found: 217.0293.

3-propylbenzo[*b*]thiophene 1,1-dioxide **1x**



White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.72-7.70 (m, 1H), 7.60-7.51 (m, 2H), 7.43-7.41 (m, 1H), 6.44-6.43 (m, 1H), 2.60-2.56 (m, 2H), 1.75-1.70 (m, 2H), 1.07 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.04, 137.72, 133.36, 132.76, 130.40, 124.61, 122.19, 121.03, 29.79, 20.12, 13.82. HRMS calculated for $C_{11}H_{12}NaO_2S^+$ $[(M+Na)^+]$ = 231.0458, found: 231.0450.

The synthesis of substrate 3-fluoro-2-phenylbenzo[b]thiophene 1,1-dioxide 3a according to the method E:



3a

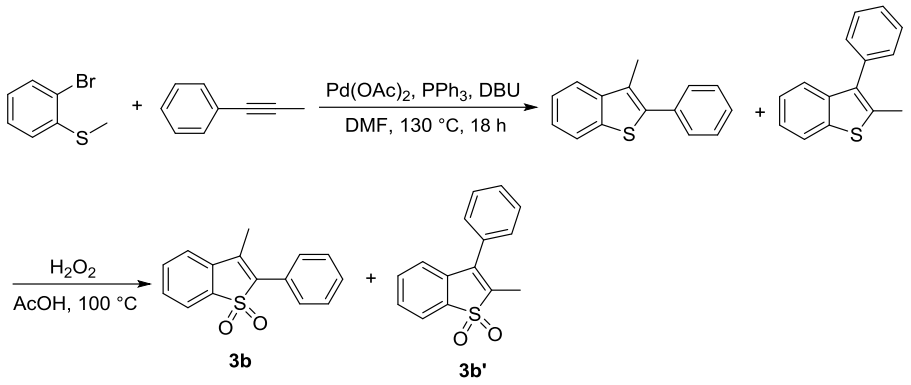
Step 1: The 2-phenylbenzo[*b*]thiophene was synthesized through the procedure according to the method A.

Step 2:[8] 2-phenylbenzo[*b*]thiophene (1.00 g, 4.76 mmol, 1.00 eq.), *N*-bromosuccinimide (933 mg, 5.24 mmol, 1.10 eq.), and DMF (10 mL) were combined in a 50 mL round-bottom flask and allowed to stir at room temperature for 12 h. Purification of the crude reaction mixture by filtration through a silica gel plug, eluting with ether, followed by recrystallization of the resulting solid from MeOH, provided 3-bromo-2-phenylbenzo[*b*]thiophene as a pale yellow solid.

Step 3:[8] 3-bromo-2-phenylbenzo[*b*]thiophene (578 mg, 2 mmol, 1.0 eq.), *n*-BuLi (2.5 M in hexanes, 0.9 mL, 2.2 mmol, 1.10 eq.), NFSI (758 mg, 2.4 mmol, 1.20 eq.), and THF (15 mL) were combined and allowed to stir at room temperature for 1 h. The 3-fluoro-2-phenylbenzo[*b*]thiophene was purified by flash chromatography (340 mg, 74% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.78-7.74 (m, 4H), 7.47-7.34 (m, 5H). The characterization data of compound is in accordance with the reported data in the literature. [8]

Step 4：The substrate **3a** was synthesized through oxidation reaction in the method A: White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.91-7.89 (m, 2H), 7.83-7.81 (m, 1H), 7.69-7.66 (m, 1H), 7.63-7.59 (m, 2H), 7.53-7.43 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 155.96 (*J* = 290.0 Hz), 137.50 (*J* = 3.0 Hz), 133.72, 131.15, 129.96 (*J* = 2.0 Hz), 129.20, 127.54 (*J* = 5.0 Hz), 126.86 (*J* = 28.0 Hz), 124.47 (*J* = 4.0 Hz), 121.18 (*J* = 3.0 Hz), 120.81 (*J* = 6.0 Hz), 120.53. HRMS calculated for $C_{14}H_9FNaO_2S^+$ [$(M+Na)^+$] = 283.0197, found:281.0199.

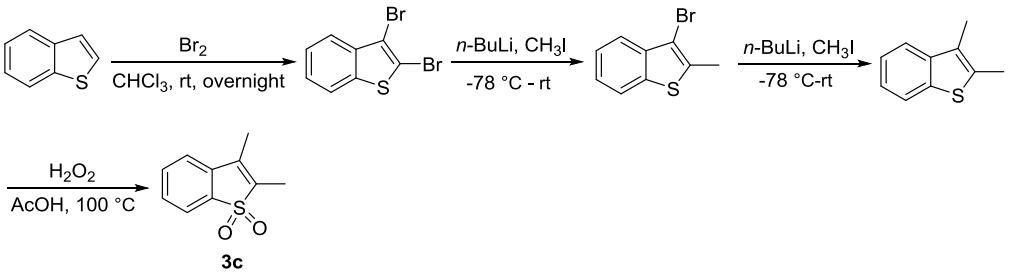
The synthesis of substrate 3-methyl-2-phenylbenzo[*b*]thiophene 1,1-dioxide 3b:



Step 1:[9] An oven-dried 50 mL screw-capped vial was charged with (2-bromophenyl)(methyl)sulfane (1.217 g, 6.0 mmol), prop-1-yn-1-ylbenzene (1.043 g, 9.0 mmol), $Pd(OAc)_2$ (133.89 mg, 0.6 mmol), PPh_3 (480 mg, 1.8 mmol), DBU (2.736 g, 18 mmol), and DMF (18 mL) under a gentle stream of nitrogen. The vessel was then sealed and heated at 130 °C for 18 h. The mixture was cooled to rt and filtered through a short pad of silica gel, eluting with EtOAc.

Step 2: The substrate **3b** was synthesized through oxidation reaction according to the method A: The mixtures of compounds **3b** and **3b'** were recrystallized several times in ethanol to get pure compound **3b**. White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.78 (d, *J* = 7.4 Hz, 1H), 7.66-7.60 (m, 3H), 7.55-7.46 (m, 5H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 137.42, 136.01, 135.38, 133.56, 133.37, 129.91, 129.75, 129.36, 128.97, 127.03, 122.26, 121.04, 12.01. HRMS calculated for $C_{15}H_{13}O_2S^+$ [$(M+H)^+$] = 257.0635, found: 257.0630.

The synthesis of substrate 2,3-dimethylbenzo[*b*]thiophene 1,1-dioxide 3c:



Step 1:[10] To a stirred solution of of 2,3-benzo[*b*]thiophene (1.01 g, 7.5 mmol, 1.0 eq.) in 20 mL $CHCl_3$, bromine (0.8 mL, 15 mmol, 2.0 eq.) in 20 mL $CHCl_3$ was added dropwise at room temperature over 1 h. After stirring for 18 h in the dark, solid

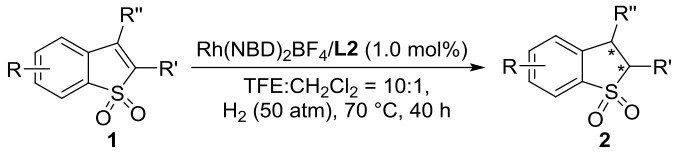
$NaHCO_3$ was added to neutralize the hydrobromic acid until gas evolution ceased. The organic phase was washed with water and 10% aqueous $Na_2S_2O_3$ solution, extracted with $CHCl_3$, and dried over $MgSO_4$. After evaporation of the solvent, crystallization from methanol gave 2,3-dibromobenzo[*b*]thiophene (2.03 g, 91% yield) as a white solid.

Step 2:[10] 2,3-dibromobenzo[*b*]thiophene (2.03 g, 7.0 mmol, 1.0 eq.) was dissolved in 10 mL dry degassed THF under argon. The solution was cooled to -78°C before *n*-BuLi (4.8 mL, 7.7 mmol, 1.6 M in hexane, 1.1 eq.) was added, and the mixture was stirred for 30 min before iodomethane (0.5 mL, 7.9 mmol, 1.1 eq.) was added. The mixture was allowed to warm to room temperature, washed with water, extracted with ethyl acetate and dried over $MgSO_4$. A short column chromatography (silica, petroleum ether 100%) gave the product as white solid.

Step 3:[11] 3-Bromo-2-methylbenzothiophene (1.0 g, 4.4 mmol) was dissolved in THF (25 mL). 3 mL *n*-BuLi (1.6 M in hexane, 4.8 mmol) was added slowly with stirring at -78 °C. Reaction mixture was stirred for 30 min and then methyl iodide (4.8 mmol) was added. After stirring for 1h, the mixture was warmed to room temperature and stirred for 2 h at room temperature. After completion of reaction, H_2O was added. The mixture was extracted with CH_2Cl_2 (2 x 25 mL), dried over $MgSO_4$, filtered and the solvents were removed. The residue was purified by chromatography on silica gel to give 2 ,3-dimethylbenzo[*b*]thiophene (642 mg, 90 % yield).

Step 4: The substrate **3c** according was synthesized through oxidation reaction according to the method A: White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.72 (d, *J* = 7.4 Hz, 1H), 7.58-7.54 (m, 1H), 7.48-7.44 (m, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 2.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 135.90, 134.09, 133.91, 133.47, 129.12, 121.50, 120.90, 10.92, 6.83. HRMS calculated for $C_{10}H_{11}O_2S^+$ [$(M+H)^+$] = 195.0476, found: 195.0474.

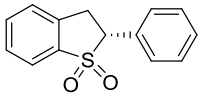
3. General procedure for asymmetric hydrogenation



A stock solution was made by mixing $Rh(NBD)_2BF_4$ with *N*-methylated ZhaoPhos **L2** in a 1:1.1 molar ratio in CH_2Cl_2 at room temperature for 40 min in a argon-filled glovebox. An aliquot of the catalyst solution (0.1 mL, 0.001 mmol) was transferred by syringe into the vials charged with different substrates (0.1 mmol for each) in anhydrous CF_3CH_2OH (1.0 mL). The vials were subsequently transferred into an autoclave into which hydrogen gas was then charged. The reaction was then stirred under H_2 (50 atm) at 70°C for 40 h. After completed, the hydrogen gas was released slowly and carefully. The solution was concentrated and passed through a short column of silica gel (eluant: EA) to remove the metal complex. The ee values of all compounds were determined by HPLC analysis on a chiral stationary phase.

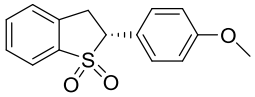
The absolute configurations of products **2a**, **2n** and **2v** were determined by comparison of analytical data with the literatures (optical rotation data). [2] The absolute configuration of others was assigned by analogy.

(*R*)-2-phenyl-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2a**



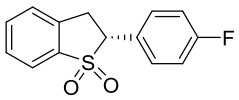
Colorless crystalline solid; >99% conv., 98% yield, 24.0 mg, >99% ee; $[\alpha]_D^{20}$ = -75.0 (c = 0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 54.6 min (major), 74.7 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80 (d, *J* = 8.0 Hz, 1H), 7.64-7.60 (m, 1H), 7.53-7.50 (m, 1H), 7.49-7.42 (m, 6H), 4.68 (t, *J* = 8.4 Hz, 1H), 3.65 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 138.30, 136.30, 133.42, 129.99, 129.39, 129.31, 129.05, 128.97, 127.01, 122.32, 67.33, 32.78. The characterization data of compound **2a** is in accordance with the reported data in the literature.[2]

(*R*)-2-(4-methoxyphenyl)-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2b**



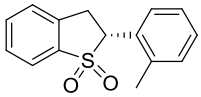
Colorless crystalline solid; >99% conv., 98% yield, 26.8 mg, 97% ee; $[\alpha]_D^{20}$ = -57.8 (c = 0.6, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 36.6 min (minor), 54.5 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.79 (d, *J* = 7.7 Hz, 1H), 7.63-7.59 (m, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.41-7.38 (m, 2H), 6.98-6.94 (m, 2H), 4.63 (t, *J* = 8.5 Hz, 1H), 3.83 (s, 3H), 3.61-3.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.39, 138.25, 136.36, 133.34, 130.50, 128.99, 126.97, 122.33, 121.57, 114.40, 66.82, 55.30, 32.82. The characterization data of compound **2b** is in accordance with the reported data in the literature.[2]

(*R*)-2-(4-fluorophenyl)-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2c**



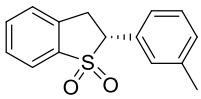
Colorless crystalline solid; >99% conv., 99% yield, 25.9 mg, 97% ee; $[\alpha]_D^{20}$ = -57.9 (c = 0.62, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 47.9 min (minor), 55.2 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80 (d, *J* = 7.7 Hz, 1H), 7.65-7.61 (m, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.48-7.44 (m, 3H), 7.16-7.11 (m, 2H), 4.68-4.64 (m, 1H), 3.69-3.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.35 (d, *J* = 248.0 Hz), 138.10, 136.06, 133.51, 131.12 (d, *J* = 8.0 Hz), 129.16, 127.01, 125.76 (d, *J* = 3.0 Hz), 122.36, 116.07 (d, *J* = 21.0 Hz), 66.54, 32.97. The characterization data of compound **2c** is in accordance with the reported data in the literature.[2]

(*R*)-2-(*o*-tolyl)-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2d**



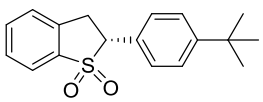
Colorless crystalline solid; >99% conv., 98% yield, 25.3 mg, 97% ee; $[\alpha]_D^{20}$ = -191.8 (c = 0.44, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 30.0 min (minor), 35.0 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.78 (d, *J* = 7.7 Hz, 1H), 7.64-7.60 (m, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.30-7.22 (m, 3H), 5.06 (t, *J* = 7.9 Hz, 1H), 3.65 (d, *J* = 7.5 Hz, 2H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 138.54, 138.32, 136.69, 133.40, 130.92, 129.04, 129.00, 128.85, 127.84, 126.91, 126.47, 122.29, 62.93, 33.10, 20.24. The characterization data of compound **2d** is in accordance with the reported data in the literature.[2]

(*R*)-2-(*m*-tolyl)-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2e**



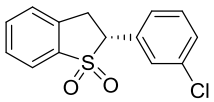
Colorless crystalline solid; >99% conv., 98% yield, 25.3 mg, 97% ee; $[\alpha]_D^{20}$ = -71.7 (c = 0.67, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 40.4 min (major), 56.9 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80 (d, *J* = 7.7 Hz, 1H), 7.63-7.59 (m, 1H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.5 Hz , 1H), 7.28-7.23 (m, 3H), 4.65 (t, *J* = 8.5 Hz, 1H), 3.64 (d, *J* = 8.1 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 138.67, 138.31, 136.33, 133.37, 130.19, 130.04, 129.75, 128.99, 128.82, 126.99, 126.24, 122.28, 67.29, 32.65, 21.41. The characterization data of compound **2e** is in accordance with the reported data in the literature.[2]

(*R*)-2-(4-(tert-butyl)phenyl)-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2f**



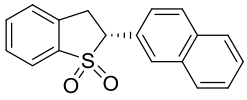
Colorless crystalline solid; >99% conv., 98% yield, 29.4 mg, 96% ee; $[\alpha]_D^{20}$ = -26.7 (c = 0.80, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 29.1 min (minor), 31.1 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.79 (d, *J* = 7.6 Hz, 1H), 7.62-7.58 (m, 1H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.47-7.39 (m, 5H), 4.66 (t, *J* = 8.5 Hz, 1H), 3.62 (d, *J* = 8.4 Hz, 2H), 1.33 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 152.42, 138.35, 136.42, 133.34, 129.01, 128.98, 127.00, 126.74, 125.96, 122.30, 67.09, 34.66, 32.78, 31.20. HRMS calculated for $C_{18}H_{20}NaO_2S^+$ [$(M+Na)^+$] = 323.1078, found: 323.1076.

(*R*)-2-(3-chlorophenyl)-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2g**



Colorless crystalline solid; >99% conv., 98% yield, 27.2 mg, 98% ee; $[\alpha]_D^{20}$ = -58.8 (c = 0.53, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 42.3 min (major), 48.3 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80 (d, *J* = 7.7 Hz, 1H), 7.65-7.61 (m, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.46-7.44 (m, 2H), 7.42-7.36 (m, 3H), 4.64 (t, *J* = 8.0 Hz, 1H), 3.69-3.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 138.04, 135.89, 134.83, 133.60, 132.03, 130.17, 129.59, 129.39, 129.21, 127.56, 127.04, 122.32, 66.67, 32.70. HRMS calculated for $C_{14}H_{11}ClNaO_2S^+$ [$(M+Na)^+$] = 301.0059, found: 301.0060.

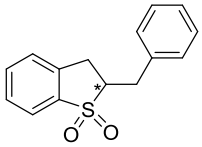
(*R*)-2-(naphthalen-2-yl)-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2h**



Colorless crystalline solid; >99% conv., 98% yield, 28.8 mg, 95% ee; $[\alpha]_D^{20}$ = -79.1 (c = 0.67, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 85:15; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 35.4 min (major), 52.5 min (minor). ^{1}H NMR (400 MHz,

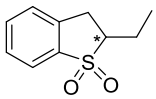
$CDCl_3$) δ (ppm) 7.94-7.81 (m, 5H), 7.64 (t, *J* = 7.1 Hz, 1H), 7.58-7.47 (m, 5H), 4.85 (t, *J* = 8.4 Hz, 1H), 3.82-3.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 138.33, 136.29, 133.57, 133.47, 133.13, 129.23, 129.08, 128.78, 128.08, 127.71, 127.41, 127.04, 126.79, 126.54, 126.03, 122.33, 67.45, 32.78. HRMS calculated for $C_{18}H_{14}NaO_2S^+$ [$(M+Na)^+$] = 317.0610, found: 317.0606.

(+)-2-benzyl-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2i**



Colorless crystalline solid; >99% conv., 98% yield, 25.3 mg, 83% ee; $[\alpha]_D^{20}$ = +27.2 (c = 0.66, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 53.8 min (major), 68.0 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J* = 7.7 Hz, 1H), 7.57-7.53 (m, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.38-7.35 (m, 2H), 7.31-7.27 (m, 4H), 3.77-3.69 (m, 1H), 3.54 (dd, *J* = 14.0, 4.7 Hz 1H), 3.22 (dd, *J* = 16.3, 7.5 Hz 1H), 3.05 (dd, *J* = 16.3, 8.1 Hz, 1H), 2.90 (dd, *J* = 14.0, 10.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 138.85, 136.53, 136.31, 133.41, 128.98, 128.93, 128.79, 127.17, 127.10, 121.93, 62.37, 33.15, 31.83. The characterization data of compound **2i** is in accordance with the reported data in the literature.[2]

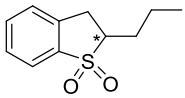
(+)-2-ethyl-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2j**



White solid; >99% conv., 99% yield, 19.4 mg, 88% ee; $[\alpha]_D^{20}$ = +20.0 (c =0.58, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 28.9 min (major), 65.0 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.74 (d, *J* = 7.7 Hz, 1H), 7.55 (td, *J* = 7.5, 1.0 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.34

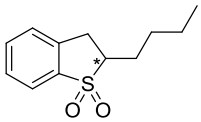
(d, *J* = 7.7 Hz, 1H), 3.45-3.35 (m, 2H), 3.00-2.93 (m, 1H), 2.23-2.12 (m, 1H), 1.85-1.74 (m, 1H), 1.19 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 139.17, 136.41, 133.26, 128.69, 126.98, 121.79, 62.94, 32.19, 21.08, 11.60. The characterization data of compound **2j** is in accordance with the reported data in the literature.[2]

(+)-2-propyl-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2k**



White solid; >99% conv., 98% yield, 20.6 mg, 92% ee; $[\alpha]_D^{20}$ = +19.2 (c =0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 27.2 min (major), 50.6 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.58-7.54 (m, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 3.51-3.38 (m, 2H), 3.02–2.96 (m, 1H), 2.17-2.08 (m, 1H), 1.78–1.71 (m, 1H), 1.64-1.60 (m, 2H), 1.04 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 139.10, 136.46, 133.22, 128.64, 126.97, 121.74, 61.24, 32.37, 29.48, 20.27, 13.88. The characterization data of compound **2k** is in accordance with the reported data in the literature.[2]

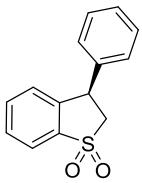
(+)-2-butyl-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2l**



White solid; >99% conv., 98% yield, 22.0 mg, 91% ee; $[\alpha]_D^{20}$ = +20.8 (c =0.72, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 30.2 min (major), 47.7 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.74 (d, *J* = 7.7 Hz, 1H), 7.57-7.52 (m, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 3.46-3.38 (m, 2H), 3.02–2.94 (m, 1H), 2.16-2.10 (m, 1H), 1.76-1.71 (m, 1H), 1.61-1.51 (m, 2H), 1.45-1.39 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz,

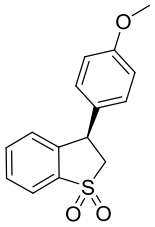
$CDCl_3$) δ (ppm) 139.14, 136.47, 133.23, 128.66, 126.97, 121.79, 61.57, 32.44, 29.07, 27.20, 22.54, 13.78. HRMS calculated for $C_{12}H_{16}NaO_2S^+$ [$(M+Na)^+$] = 247.0766, found: 247.0763.

(*R*)-3-phenyl-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2m**



Colorless crystalline solid; >99% conv., 99% yield, 24.2 mg, >99% ee; $[\alpha]_D^{20}$ = +9.4 (c = 0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 58.9 min (major), t_R = 39.6 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.82-7.80 (m, 1H), 7.57-7.50 (m, 2H), 7.41-7.32 (m, 3H), 7.26-7.24 (m, 2H), 7.10 (d, *J* = 7.4 Hz, 1H), 4.79 (t, *J* = 7.8 Hz, 1H), 3.93 (dd, *J* = 13.5, 8.0 Hz, 1H), 3.51 (dd, *J* = 13.5, 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 141.00, 139.70, 139.02, 133.71, 129.29, 129.11, 128.21, 128.10, 127.21, 121.15, 58.93, 43.96. The characterization data of compound **2m** is in accordance with the reported data in the literature.[2]

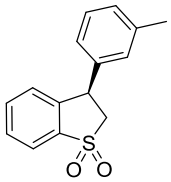
(*R*)-3-(4-methoxyphenyl)-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2n**



Colorless crystalline solid; >99% conv., 99% yield, 27.2 mg, >99% ee; $[\alpha]_D^{20}$ = +6.7 (c = 0.7, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 82.7 min (major), t_R = 55.4 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81-7.78 (m, 1H), 7.56-7.48 (m, 2H), 7.17-7.14 (m, 2H), 7.11-7.10

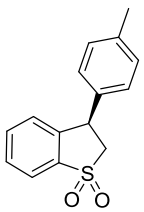
(m, 1H), 6.92-6.88 (m, 2H), 4.75 (t, *J* = 7.9 Hz, 1H), 3.89 (dd, *J* = 13.5, 7.9 Hz, 1H), 3.82 (s, 3H), 3.46 (dd, *J* = 13.5, 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.28, 141.39, 138.97, 133.66, 131.59, 129.28, 129.01, 127.14, 121.08, 114.58, 59.06, 55.31, 43.22. The characterization data of compound **2n** is in accordance with the reported data in the literature.[2]

(*R*)-3-(*m*-tolyl)-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2o**



Colorless crystalline solid; >99% conv., 99% yield, 25.6 mg, >99% ee; $[\alpha]_D^{20}$ = +6.26 (c = 0.33 $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 41.4 min (major), t_R = 28.0 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81-7.79 (m, 1H), 7.56-7.49 (m, 2H), 7.28-7.25 (m, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.04-7.02 (m, 2H), 4.75 (t, *J* = 7.9 Hz, 1H), 3.91 (dd, *J* =13.5, 8.0 Hz, 1H), 3.50 (dd, *J* = 13.5, 7.9 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 141.13, 139.61, 139.11, 138.99, 133.69, 129.14, 129.04, 128.84, 127.23, 125.27, 121.10, 58.94, 43.90, 21.38. The characterization data of compound **2o** is in accordance with the reported data in the literature.[2]

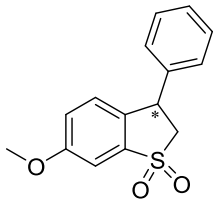
(*R*)-3-(*p*-tolyl)-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2p**



Colorless crystalline solid; >99% conv., 99% yield, 25.6 mg, >99% ee; $[\alpha]_D^{20}$ = +8.5 (c = 0.75, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV

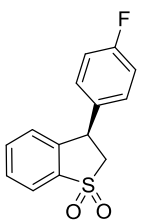
detection at 220 nm; t_R = 40.3 min (major), t_R = 33.9 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80-7.78 (m, 1H), 7.56-7.48 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.13-7.09 (m, 3H), 4.75 (t, *J* = 7.9 Hz, 1H), 3.90 (dd, *J* =13.5, 7.9 Hz, 1H), 3.48 (dd, *J* = 13.5, 7.9 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 141.27, 139.01, 137.93, 136.64, 133.66, 129.93, 129.02, 128.07, 127.17, 121.11, 59.02, 43.60, 21.07. The characterization data of compound **2p** is in accordance with the reported data in the literature.[2]

(-)-6-methoxy-3-phenyl-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2q**



Colorless crystalline solid; >99% conv., 99% yield, 27.1 mg, >99% ee; $[\alpha]_D^{20}$ = -10.56 (c =3.00, CH_3OH); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 36.8 min (minor), t_R = 39.5 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.39-7.30 (m, 3H), 7.24-7.22 (m, 3H), 7.08 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 4.72 (t, *J* = 7.7 Hz, 1H), 3.93 (dd, *J* = 13.5, 8.0 Hz, 1H), 3.87 (s, 3H), 3.50 (dd, *J* = 13.5, 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.31, 140.11, 139.98, 132.74, 129.23, 128.13, 128.07, 128.00, 122.24, 103.37, 59.60, 55.83, 43.22. HRMS calculated for $C_{15}H_{14}NaO_3S^+$ $[(M+Na)^+]$ = 297.0558, found: 297.0555.

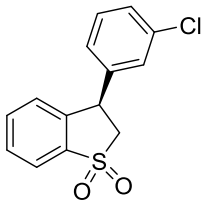
(*R*)-3-(4-fluorophenyl)-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2r**



Colorless crystalline solid; >99% conv., 99% yield, 26.0 mg, >99% ee; $[\alpha]_D^{20}$ =

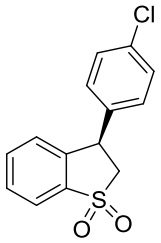
+7.7 (c = 0.7, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 43.8 min (minor), t_R = 63.9 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.82-7.80 (m, 1H), 7.59-7.51 (m, 2H), 7.24-7.20 (m, 2H), 7.11-7.05 (m, 3H), 4.79 (t, *J* = 7.7 Hz, 1H), 3.92 (dd, *J* = 13.5, 8.0 Hz, 1H), 3.46 (dd, *J* =13.5, 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.35 (d, *J* = 246.0 Hz), 140.71, 139.03, 135.60 (d, *J* = 3.0 Hz), 133.81, 129.84 (d, *J* = 8.0 Hz), 129.27, 127.11, 121.24, 116.25 (d, *J* = 21.0 Hz), 58.88, 43.23. The characterization data of compound **2r** is in accordance with the reported data in the literature.[2]

(*R*)-3-(3-chlorophenyl)-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2s**



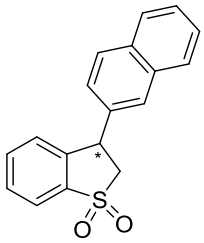
Colorless crystalline solid; >99% conv., 99% yield, 27.5 mg, >99% ee; $[\alpha]_D^{20}$ = +2.03 (c = 0.59, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 35.5 min (minor), t_R = 61.5 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.83-7.80 (m, 1H), 7.60-7.52 (m, 2H), 7.34-7.30 (m, 2H), 7.25 (d, *J* = 0.8 Hz, 1H), 7.15-7.11 (m, 2H), 4.77 (t, *J* = 7.8 Hz, 1H), 3.92 (dd, *J* = 13.5, 8.1 Hz, 1H), 3.48 (dd, *J* = 13.5, 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 141.81, 140.08, 139.09, 135.13, 133.90, 130.63, 129.43, 128.40, 128.37, 127.15, 126.39, 121.34, 58.62, 43.59. HRMS calculated for $C_{14}H_{11}ClNaO_2S^+$ [$(M+Na)^+$] = 301.0063, found: 301.0060.

(*R*)-3-(4-chlorophenyl)-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2t**



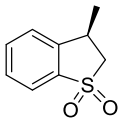
Colorless crystalline solid; >99% conv., 98% yield, 27.2 mg, 94% ee; $[\alpha]_D^{20}$ = +1.60 (c = 0.56, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 54.8 min (minor), t_R = 59.5 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81-7.79 (m, 1H), 7.58-7.50 (m, 2H), 7.37-7.33 (m, 2H), 7.20-7.17 (m, 2H), 7.10-7.08 (m, 1H), 4.77 (t, *J* = 7.7 Hz, 1H), 3.91 (dd, *J* = 13.5, 8.1 Hz, 1H), 3.45 (dd, *J* = 13.5, 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 140.37, 139.04, 138.33, 134.06, 133.84, 129.54, 129.48, 129.34, 127.10, 121.28, 58.69, 43.33. HRMS calculated for $C_{14}H_{11}ClNaO_2S^+$ $[(M+Na)^+]$ = 301.0062, found: 301.0060.

(-)-3-(naphthalen-2-yl)-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2u**



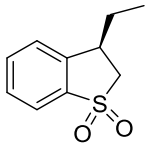
Colorless crystalline solid; >99% conv., 99% yield, 29.1 mg, >99% ee; $[\alpha]_D^{20}$ = -49.64 (c = 0.56, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 37.5 min (minor), t_R = 56.2 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.87-7.82 (m, 4H), 7.77 (d, *J* = 1.3 Hz, 1H), 7.55-7.51 (m, 4H), 7.27-7.25 (m, 1H), 7.12-7.10 (m, 1H), 4.96 (t, *J* = 7.9 Hz, 1H), 3.98 (dd, *J* = 13.6, 8.0 Hz, 1H), 3.61 (dd, *J* = 13.6, 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 140.89, 139.12, 136.85, 133.75, 133.31, 132.83, 129.48, 129.19, 127.75, 127.73, 127.70, 127.31, 126.75, 126.51, 125.16, 121.21, 58.75, 44.14. HRMS calculated for $C_{18}H_{14}NaO_2S^+$ $[(M+Na)^+]$ = 317.0609, found: 317.0606.

(*R*)-3-methyl-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2v**



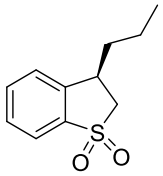
Colorless crystalline solid; >99% conv., 97% yield, 17.7 mg, 97% ee; $[\alpha]_D^{20}$ = +30.7 (c = 0.41, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 26.1 min (major), 27.7 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.73 (d, *J*= 7.8 Hz, 1H), 7.64-7.60 (m, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 3.74-3.65 (m, 2H), 3.17-3.10 (m, 1H), 1.54 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 142.34, 138.63, 133.64, 128.79, 125.52, 121.28, 57.90, 32.57, 19.83. The characterization data of compound **2v** is in accordance with the reported data in the literature.[2]

(*R*)-3-ethyl-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2w**

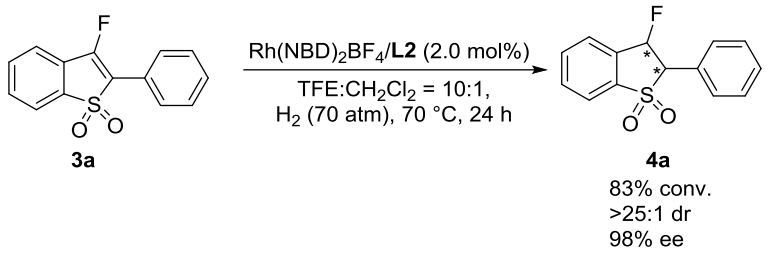


Colorless crystalline solid; >99% conv., 98% yield, 19.0 mg, 98% ee; $[\alpha]_D^{20}$ = +81.73 (c = 0.46, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 95:5; flow rate = 0.3 mL/min; UV detection at 220 nm; t_R = 83.0 min (major), t_R = 87.2 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.72 (d, *J* = 7.8 Hz, 1H), 7.62-7.58 (m, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.43-7.41 (m, 1H), 3.62 (dd, *J* = 13.0, 7.8 Hz, 1H), 3.56-3.50 (m, 1H), 3.20 (dd, *J* = 13.0, 5.3 Hz, 1H), 2.08-2.05 (m, 1H), 1.76-1.74 (m, 1H), 1.04 (t, *J*= 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 141.17, 138.99, 133.45, 128.89, 125.99, 121.41, 55.47, 39.40, 27.32, 11.55. HRMS calculated for $C_{10}H_{12}NaO_2S^+$ [$(M+Na)^+$] = 219.0450, found: 219.0450.

(*R*)-3-propyl-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide **2x**

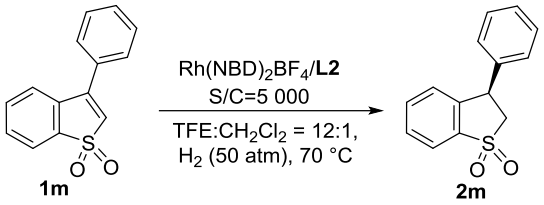


Colorless crystalline solid; >99% conv., 98% yield, 20.6 mg, 96% ee; $[\alpha]_D^{20}$ = +36.87 (c = 1.33, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 95:5; flow rate = 0.3 mL/min; UV detection at 220 nm; t_R = 69.1 min (major), t_R = 73.2 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.72 (d, *J* = 7.8 Hz, 1H), 7.62-7.58 (m, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 3.64-3.56 (m, 2H), 3.22-3.17 (m, 1H), 2.03-1.95 (m, 1H), 1.71-1.63 (m, 1H), 1.50-1.41 (m, 2H), 1.00 (t, *J* =7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 141.48, 138.85, 133.45, 128.86, 125.98, 121.42, 55.88, 37.80, 36.67, 20.57, 13.85. HRMS calculated for $C_{11}H_{14}NaO_2S^+$ [$(M+Na)^+$] = 233.0609, found: 233.0606.



Colorless crystalline solid; 83% conv., >25:1 dr, 98% ee; $[\alpha]_D^{20}$ = +56.00 (c = 0.35, $CHCl_3$); The dr value was analyzed by ^{1}H NMR spectroscopy; The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 35.0 min (major), t_R = 71.3 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.93 (d, *J* = 7.5 Hz, 1H), 7.79-7.73 (m, 3H), 7.58-7.55 (m, 2H), 7.50-7.43 (m, 3H), 6.11 (dd, *J* = 53.3, 5.1Hz, 1H), 4.70 (dd, *J* = 24.0, 5.1Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 139.80 (d, *J* = 3.0 Hz), 134.00 (d, *J* = 3.0 Hz), 133.60 (d, *J* = 18.0 Hz), 132.43 (d, *J* = 3.0 Hz), 131.78 (d, *J* = 3.0 Hz), 129.75, 128.72, 128.15, 126.32, 122.45, 87.11 (d, *J* = 190.0 Hz), 69.87 (d, *J* = 20.0 Hz). HRMS calculated for $C_{14}H_{11}FNaO_2S^+$ [$(M+Na)^+$] = 285.0356, found: 285.0355.

4. General procedure for the high TON experiment



1.21g

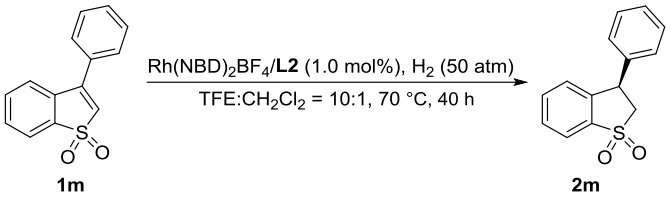
>99% conv.
99% yied
99% ee

A stock solution was made by mixing $[Rh(NBD)_2]BF_4$ with *N*-methylated ZhaoPhos **L2** in a 1:1.1 molar ratio in CH_2Cl_2 at room temperature for 40 min in a nitrogen-filled glovebox. An aliquot of the catalyst solution (0.001 mmol) was transferred by syringe into a hydrogenated vial charged with **1m** (5.0 mmol, 1.21 g) in anhydrous CF_3CH_2OH :CH_2Cl_2 = 12:1 (8 mL). The cup was subsequently transferred into an autoclave into which hydrogen gas was charged. The reaction was then stirred under H_2 (50 atm) at 70 ^oC for 120 h. After completed, the hydrogen gas was released slowly and carefully. The product **2m** was obtained by a column of silica gel (petroleum ether–EtOAc).

5. General procedure for Job plot

In order to inspect the possible catalytic model, the experiments for the investigation of the nonlinear effect and ^1H NMR titration were conducted. The asymmetric hydrogenation of substrate **1m** was performed in the presence of ligand **L2** with different ee values (Table S1). As shown in Figure S1, no nonlinear effect was observed in this Rh-catalyzed asymmetric hydrogenation, which displayed that it should be no catalyst self-aggregation or ligand-substrate agglomeration in this catalytic system.

Table S1. Nonlinear effect for Rh/ligand **L2**-catalyzed asymmetric hydrogenation of **1m**.



entry	ee of **L2** (%)	conv. (%)	ee (%)
1	0	>99	0
2	10	>99	11
3	20	>99	20
4	40	>99	40
5	60	>99	60
6	80	>99	80
7	90	>99	91
8	100	>99	>99

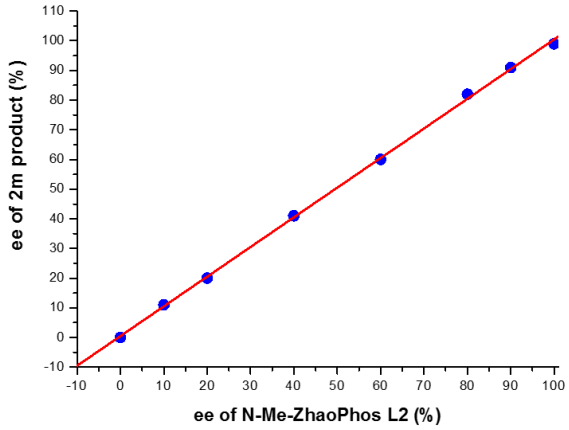


Figure S1. Nonlinear effect of the hydrogenation of substrate **1m** using ligand **L2** with different ee values

A series of ^{1}H NMR titration experiments were conducted in chloroform-d, which was dried with potassium carbonate and degassed. The total concentration of the host (**1m**) and the guest (ligand **L2**) was 0.02 M. The proportion of the concentration of the host *vs* the total concentration varied, the chemical shifts of the proton on the 2-position of **1m** were recorded (Table S2). A Job plot was drawn (Figure S2) and the curve suggests a 1:1 binding pattern between ligand **L2** and substrate **1m**.

Table S2. Data for Job plot.

NO.	c_1 (**1m**)	c_2 (**L2**)	δ (H-**1m**)	Δδ (H-**1m**)	$\Delta\delta*10^4*c_1/0.02$
1	0.02	0	6.6569	0	0
2	0.016	0.004	6.6556	0.0013	10.4
3	0.014	0.006	6.6551	0.0018	12.6
4	0.012	0.008	6.6547	0.0022	13.2
5	0.01	0.01	6.6542	0.0027	13.5
6	0.008	0.012	6.6538	0.0031	12.4
7	0.006	0.014	6.6532	0.0037	11.1
8	0.004	0.016	6.6527	0.0042	8.4

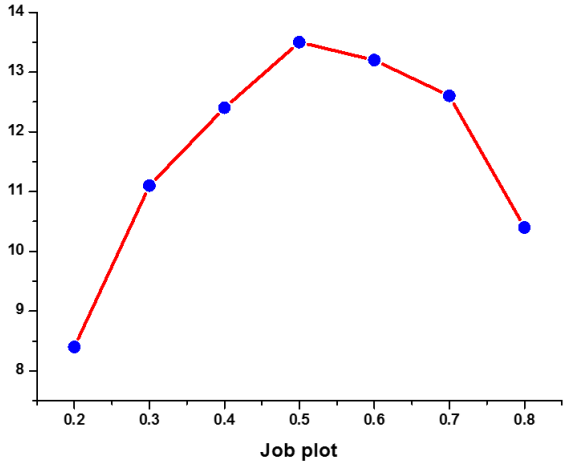
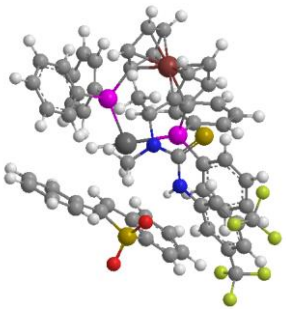


Figure S2. Job plot of ligand **L2** and **1m**, x = c (**1m**)/[c (ligand **L2**)+c (**1m**)], y = $\Delta\delta*10^4*$c (**1m**)/[c (ligand **L2**)+c (**1m**)]

6. General computational calculation (DFT) details

DFT calculations were performed using the M06-L method [12] with the Gaussian09 program [13]. The 6-31G(d) basis set was used for the C, H, N, O, F, S and P, and the SDD basis set was used for the Rh and Fe. Solvent effect and Grimme's dispersion correction [14] were applied during geometry optimization. The parameter of int=ultrafine was used. Mixture of 2,2,2-trifluoroethanol and dichloromethane (10:1) was employed as the solvents. The solvent effects were considered using SMD continuum solvation model [15]. Frequency calculations at the same level of theory

have been performed to identify all of the stationary points as minima (zero imaginary frequencies) and to provide free energies at 298.15 K.



Rh(III)HH-**1a**-pro-(*S*) **I**:

Thermal correction to Gibbs Free Energy= 0.852493

Sum of electronic and thermal Free Energies= -4887.807460

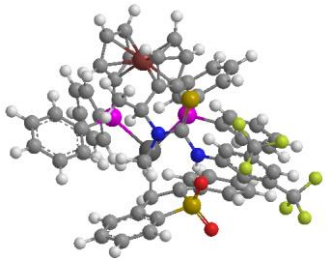
Fe	2.42478900	-3.29284100	-0.46493600
S	-2.37544200	-3.34083100	1.17685000
N	-0.71879400	-1.31952700	1.79913300
N	-2.84536300	-0.67979800	1.31749800
F	-5.53705100	2.33804900	-1.45188100
F	-7.11988100	1.02373800	-2.14819800
F	-7.44382800	2.27296300	-0.41196400
F	-7.53634000	-2.55549300	2.91741500
F	-6.88382000	-3.89657400	1.35078400
F	-8.58921800	-2.59159300	1.01899300
C	0.49554100	-2.16166100	1.69788600
C	-1.96880800	-1.73402200	1.44467700
C	-4.20819800	-0.69686200	0.99626000
C	-6.01663600	0.41187800	-0.16062100
C	-6.44170900	-1.59913200	1.06322200
C	-6.52050300	1.51364800	-1.03853800
C	-7.36751300	-2.65649400	1.57946100
C	0.63905200	-2.91215700	0.39735600
C	0.84556500	-4.32081000	0.29792900

C	1.03949300	-4.66873900	-1.06493700
C	0.95086200	-3.48158800	-1.83797300
C	0.70964300	-2.37537300	-0.95188800
C	3.86182600	-1.92386400	-0.05943900
C	3.87529600	-2.99731700	0.90439300
C	4.10787400	-4.21708600	0.20999500
C	4.22294800	-3.92460000	-1.17938700
C	4.05692800	-2.52205500	-1.35910400
H	-2.41516600	0.22941900	1.15669800
H	1.27855200	-5.65653700	-1.44347000
H	1.10386200	-3.40545700	-2.90916100
H	3.73179300	-2.88663700	1.97430900
H	4.12963000	-5.20360100	0.65991200
H	4.35020100	-4.65010100	-1.97539800
H	4.08551600	-1.99608600	-2.30744600
C	0.66496000	-3.03749400	2.93133700
H	0.62358300	-2.42492700	3.83874600
H	-0.12802700	-3.78963600	2.98464200
H	1.63526000	-3.54645400	2.91432600
H	1.30941900	-1.41783000	1.72053400
C	-0.52604700	-0.07928200	2.53926400
H	-0.26182000	0.76795900	1.88518300
H	-1.43404600	0.19049800	3.08481800
H	0.27906100	-0.21997800	3.26849700
H	0.89349300	-5.00495400	1.13822000
P	0.61641600	-0.64642400	-1.49618600
P	3.73328200	-0.15979700	0.34140500
C	1.35413100	-0.69326200	-3.18369900
C	0.62698900	-1.21344700	-4.26466200
C	2.64680200	-0.20996400	-3.41988300

C	1.18611100	-1.26096200	-5.53827300
H	-0.38600500	-1.58429300	-4.11045700
C	3.20771100	-0.25775400	-4.69418600
H	3.23028300	0.20886400	-2.60070500
C	2.47773500	-0.78390600	-5.75680900
H	0.60702700	-1.66949300	-6.36375500
H	4.21494900	0.12347300	-4.85125500
H	2.91058800	-0.81687500	-6.75435100
C	5.16731900	0.58636400	-0.50949100
C	6.26758700	-0.20425100	-0.87307400
C	5.20855700	1.96636700	-0.75317900
C	7.38033000	0.37724400	-1.47479300
H	6.25920600	-1.27702200	-0.69087600
C	6.32392800	2.54110200	-1.35350000
H	4.36304900	2.59221000	-0.47231900
C	7.40974200	1.74775000	-1.71928700
H	8.22456500	-0.24845700	-1.75549700
H	6.34030500	3.61255000	-1.54015400
H	8.27772000	2.19784900	-2.19612000
C	-1.15345000	-0.44162700	-1.92756200
C	-1.58592000	0.78373900	-2.45360800
C	-2.04946600	-1.51595100	-1.87726000
C	-2.88283400	0.91907000	-2.94106500
H	-0.89458800	1.62841900	-2.50635800
C	-3.35259400	-1.36958900	-2.34754100
H	-1.73167300	-2.47376600	-1.47038900
C	-3.76707400	-0.15777200	-2.89282400
H	-3.20679000	1.86923200	-3.36096200
H	-4.04326800	-2.20969000	-2.28503300
H	-4.78366100	-0.04487100	-3.26565800

C	4.14329500	-0.16577100	2.12460400
C	3.26277800	0.33739800	3.08745500
C	5.34934400	-0.75145800	2.53742600
C	3.56349000	0.22073300	4.44362600
H	2.34815100	0.84912200	2.78556600
C	5.65681100	-0.84370000	3.88963000
H	6.04689200	-1.14504900	1.79810700
C	4.75709800	-0.37082000	4.84558000
H	2.86279400	0.60541200	5.18204100
H	6.59780400	-1.29381400	4.19779600
H	4.99309000	-0.45710400	5.90395200
Rh	1.81463300	0.89782600	-0.03977500
H	2.70665000	1.94566700	0.79395800
H	2.50620200	1.53102100	-1.24652500
C	-1.36644600	3.96053900	-0.96667000
C	0.00094100	4.02747500	-1.26446500
C	0.20926400	3.63843000	1.07740200
C	0.85375900	3.86545900	-0.09614900
S	-1.56893800	3.59952200	0.75950800
O	-2.24412600	4.67971700	1.48276600
O	-2.09541600	2.23140400	0.92856700
C	-6.91262900	-0.57412500	0.25298500
H	-7.95482200	-0.53976100	-0.05156300
C	-4.68154200	0.35988700	0.20729400
H	-3.98804600	1.12193200	-0.13993200
C	-5.10269000	-1.66630300	1.44874300
H	-4.76129900	-2.46991100	2.09137200
C	-2.35746400	4.12064100	-1.91398500
H	-3.41111000	4.06708500	-1.64841000
C	-1.95277500	4.35173500	-3.23396100

H	-2.70409700	4.48968400	-4.00768400
C	-0.59783100	4.39861000	-3.56267400
H	-0.30362600	4.56817100	-4.59552400
C	0.38852400	4.24051200	-2.58677900
H	1.44421000	4.28679900	-2.84754400
C	0.71816700	3.51264800	2.42902300
C	-0.10486900	3.07790800	3.48283300
C	2.06260500	3.82574200	2.70801800
C	0.40440200	2.94791900	4.77020600
H	-1.14788600	2.82750600	3.29571000
C	2.56337400	3.69848600	3.99482400
H	2.71135100	4.17878300	1.90835600
C	1.73685700	3.25915700	5.03132000
H	-0.24614700	2.60567200	5.57188700
H	3.60462900	3.94352500	4.19275300
H	2.13302200	3.16235000	6.04000400
H	1.93361300	3.97413600	-0.16895000



Rh(III)HH-**1a**-pro-(*R*) **II**:

Thermal correction to Gibbs Free Energy= 0.860058

Sum of electronic and thermal Free Energies= -4887.800670

Fe	2.07779300	-2.57936200	-2.16863700
S	-2.83940600	-3.14830900	-1.01451700
N	-1.13541300	-2.07720900	0.77621900
N	-3.19818000	-1.13528100	0.75469500
F	-5.68749000	3.08071500	0.28774400

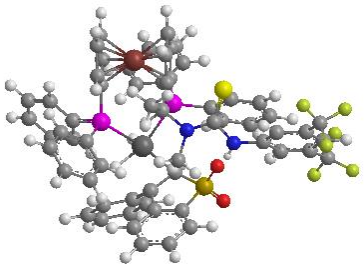
F	-6.90541500	2.48062600	-1.40461200
F	-7.77036500	2.52611500	0.57910700
F	-8.43638700	-2.87969700	1.07338600
F	-7.30997300	-3.77804300	-0.54437300
F	-8.82764600	-2.28138000	-0.97161900
C	0.06670200	-2.71555400	0.19022600
C	-2.37741400	-2.10292800	0.21495100
C	-4.54295000	-0.87847000	0.46690100
C	-6.24880700	0.78964100	0.09237700
C	-6.81460200	-1.53673700	0.01200300
C	-6.64625700	2.21942000	-0.10075700
C	-7.84304900	-2.61790500	-0.11404900
C	0.27130400	-2.47971400	-1.28663600
C	0.28305500	-3.52856000	-2.25715900
C	0.60495200	-2.99071200	-3.52862500
C	0.79698700	-1.59371500	-3.37674300
C	0.60831000	-1.24699700	-1.99148800
C	3.57886400	-2.02752700	-0.95149900
C	3.36396200	-3.45047700	-0.87863700
C	3.54552000	-3.99680900	-2.17904100
C	3.87133800	-2.93287800	-3.06801900
C	3.88696000	-1.71711100	-2.32750300
H	-2.69937000	-0.31938400	1.11045300
H	0.74588900	-3.55396400	-4.44454800
H	1.10744200	-0.90951700	-4.15856600
H	3.10121700	-4.00298000	0.01660900
H	3.40501000	-5.03750800	-2.44975100
H	4.02324300	-3.01890100	-4.13835300
H	4.09452100	-0.73193000	-2.73100500
C	0.12667000	-4.18785100	0.58030500

H	0.09754500	-4.29558600	1.67005500
H	-0.72616200	-4.72850400	0.15839300
H	1.04922600	-4.65465800	0.22145600
H	0.88936300	-2.19407500	0.70930900
C	-0.95421100	-1.67479000	2.16499100
H	-0.49889300	-0.68339100	2.24901200
H	-1.91254000	-1.66119200	2.68774500
H	-0.30304300	-2.39987800	2.66786500
H	0.11346000	-4.57682500	-2.03803600
P	0.77824100	0.47415700	-1.41141000
P	3.53161300	-0.87636400	0.44835800
C	1.82550300	1.28160300	-2.69365600
C	1.27720200	1.62283300	-3.94032000
C	3.17265900	1.58416600	-2.45969000
C	2.05388500	2.24225500	-4.91463000
H	0.23089100	1.40784800	-4.15060900
C	3.95164300	2.20466200	-3.43317100
H	3.63891100	1.32894400	-1.50950600
C	3.39249900	2.53834900	-4.66354600
H	1.60685000	2.49786100	-5.87280700
H	4.99525500	2.42842300	-3.22063800
H	3.99569200	3.03041500	-5.42336500
C	5.17997700	-0.07932800	0.34803300
C	6.22927500	-0.72036000	-0.32819400
C	5.43310700	1.14888900	0.97505400
C	7.49331800	-0.14005100	-0.38007200
H	6.06246000	-1.67462400	-0.82345800
C	6.69800800	1.72622800	0.91901200
H	4.64161900	1.66220600	1.51686300
C	7.72994400	1.08544300	0.23767600

H	8.29381500	-0.64991900	-0.91134100
H	6.87216500	2.68216200	1.40770100
H	8.71663900	1.54057100	0.18793200
C	-0.86900200	1.15440900	-1.81883700
C	-1.02733900	2.53683300	-1.96783800
C	-1.97521400	0.31890400	-1.99549900
C	-2.28108800	3.07798700	-2.23415700
H	-0.16170300	3.19194000	-1.89993600
C	-3.22526100	0.86178500	-2.28287000
H	-1.86629300	-0.76211400	-1.93292200
C	-3.38745000	2.24209600	-2.38130400
H	-2.38938200	4.15651900	-2.33812800
H	-4.07585400	0.19651200	-2.42719100
H	-4.36967000	2.66354400	-2.58687000
C	3.61570400	-2.00285600	1.88582300
C	2.65636400	-1.93483200	2.90108000
C	4.64065200	-2.95508800	1.97711600
C	2.70108900	-2.81544600	3.97943200
H	1.86952700	-1.18100100	2.86116000
C	4.69103500	-3.82597400	3.05975700
H	5.39972300	-3.01737500	1.19743000
C	3.71779700	-3.76262100	4.05800900
H	1.94176700	-2.75385900	4.75678400
H	5.49250300	-4.55845200	3.12337200
H	3.75782900	-4.45037000	4.89974200
Rh	1.83493300	0.74917400	0.80345600
H	2.88618700	0.66674500	2.00927600
H	2.83078900	1.69601600	0.17387400
C	-0.39214800	1.50837700	3.52036300
C	0.99821200	1.56872000	3.60044100

C	0.71897100	2.67372100	1.44159800
C	1.62517600	2.23353200	2.44297100
S	-0.96848700	2.32081900	2.05376200
O	-1.69719100	1.37446700	1.18973200
O	-1.65536400	3.56647700	2.41623300
C	-7.20328600	-0.20573000	-0.10643000
H	-8.23063900	0.05170100	-0.35076900
C	-4.93156500	0.46347800	0.38457400
H	-4.18750900	1.24556600	0.51594100
C	-5.49773900	-1.88384300	0.30344400
H	-5.21458100	-2.92581300	0.39753900
C	-1.18193500	0.89026900	4.47790100
H	-2.26538200	0.85724700	4.38181600
C	-0.53218700	0.30954600	5.56611400
H	-1.11559000	-0.18422400	6.33897300
C	0.86116500	0.36341400	5.67283600
H	1.35016700	-0.09534900	6.52894600
C	1.63532700	0.98610300	4.69668600
H	2.72150600	1.00404000	4.77262000
C	0.95562700	3.86819400	0.60089500
C	-0.08926500	4.66602800	0.11029400
C	2.27349200	4.24706000	0.28447000
C	0.17488400	5.78602700	-0.67372100
H	-1.12191700	4.41452800	0.32956600
C	2.53312100	5.35725000	-0.50724100
H	3.11461600	3.66080100	0.65363000
C	1.48252300	6.13483400	-0.99451400
H	-0.65784900	6.38244900	-1.04133800
H	3.56359000	5.61440300	-0.74322000
H	1.68491800	7.00366100	-1.61667900

H	2.56490600	2.76248700	2.59413000



Rh(III)HH-**1m**-pro-(*S*) **III**:

Thermal correction to Gibbs Free Energy= 0.856984

Sum of electronic and thermal Free Energies= -4887.806304

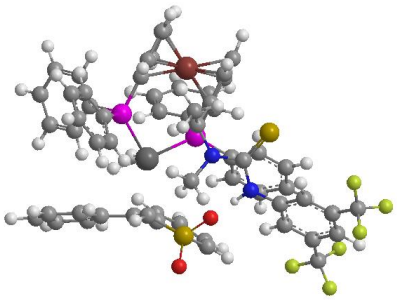
Fe	-1.54599200	-3.56938500	0.59663800
S	3.29097800	-2.88152200	-0.63516500
N	1.41556100	-1.19075800	-1.58445300
N	3.44443700	-0.24485500	-1.17125200
F	5.83109800	3.23665800	1.41969400
F	6.75696800	1.74299800	2.68931100
F	7.95208900	2.79611800	1.22042400
F	8.78870900	-1.09874500	-2.44351600
F	7.73892900	-2.84753100	-1.71084100
F	9.17042300	-1.82013600	-0.43753900
C	0.32259700	-2.18110800	-1.43675700
C	2.69477100	-1.40134300	-1.15900200
C	4.78582500	-0.10197600	-0.79454200
C	6.42820900	1.17204600	0.43340100
C	7.10588400	-0.74740400	-0.83014900
C	6.74126700	2.24403800	1.42845600
C	8.19563200	-1.63248200	-1.35094800
C	0.18995600	-2.80460800	-0.06899100
C	0.33369200	-4.20457700	0.17832500
C	0.02886700	-4.47678600	1.53579000
C	-0.30978600	-3.25058600	2.16308000

C	-0.22358000	-2.19310600	1.18798200
C	-3.16194400	-2.62996800	-0.14458400
C	-2.78217100	-3.72872000	-0.99280200
C	-2.82965200	-4.92438500	-0.22349600
C	-3.23868400	-4.58735900	1.09883400
C	-3.44065000	-3.17977700	1.16064100
H	2.89397100	0.60163300	-1.03102400
H	-0.00607900	-5.45642900	1.99954100
H	-0.64103400	-3.13361300	3.18890500
H	-2.49975800	-3.64900400	-2.03679300
H	-2.54875900	-5.91093600	-0.57574800
H	-3.32649900	-5.27331600	1.93420700
H	-3.74897500	-2.62141800	2.03776400
C	0.39030900	-3.20977800	-2.56087900
H	0.33295600	-2.71584100	-3.53680800
H	1.33113400	-3.76662100	-2.50938000
H	-0.43807500	-3.92133800	-2.49680300
H	-0.58094400	-1.56657600	-1.59359800
C	1.10243500	-0.14938400	-2.55791700
H	0.49470800	0.65440100	-2.12568500
H	2.01589500	0.28662100	-2.96492700
H	0.53942800	-0.59217600	-3.38867400
H	0.59459300	-4.94176100	-0.57265700
P	-0.61844600	-0.46894800	1.61214400
P	-3.34255800	-0.89687800	-0.65293600
C	-1.63160800	-0.61205300	3.13954300
C	-1.01201600	-0.88599800	4.36849500
C	-3.02268100	-0.45895300	3.11417700
C	-1.76732300	-1.01164000	5.53051000
H	0.06973900	-1.00162500	4.41814200

C	-3.77956900	-0.58379700	4.27652000
H	-3.53638200	-0.24602900	2.17805500
C	-3.15249000	-0.86028100	5.48850400
H	-1.26836100	-1.22537100	6.47319100
H	-4.85969100	-0.45930900	4.22726300
H	-3.73989500	-0.95271900	6.39937100
C	-5.05170700	-0.54719100	-0.09591700
C	-6.00103200	-1.58134600	-0.07141800
C	-5.44285500	0.73774700	0.29758400
C	-7.30976600	-1.32530600	0.32379100
H	-5.71708300	-2.59538000	-0.34752900
C	-6.75213100	0.98944400	0.69828000
H	-4.72249200	1.55289900	0.29880800
C	-7.68844300	-0.04078800	0.71041000
H	-8.03352800	-2.13712800	0.33677300
H	-7.03396200	1.99459300	1.00571800
H	-8.71073500	0.15371200	1.02737100
C	0.95218700	0.17586700	2.28274500
C	0.94139100	1.37113200	3.01538100
C	2.16208500	-0.49260700	2.07986200
C	2.12742200	1.90441200	3.50727600
H	-0.00226400	1.87258200	3.23041300
C	3.34702100	0.04014900	2.58429800
H	2.18659100	-1.43570700	1.53418200
C	3.33581000	1.24452300	3.28372600
H	2.10693700	2.83391500	4.07249300
H	4.28456500	-0.49176300	2.42493400
H	4.26452100	1.66282300	3.66587700
C	-3.40213200	-1.02078200	-2.47827400
C	-2.55702600	-0.23322900	-3.26902900

C	-4.28043200	-1.91517100	-3.10598800
C	-2.57313400	-0.34586100	-4.65725900
H	-1.88444200	0.48903300	-2.80460600
C	-4.30427200	-2.01851200	-4.49240800
H	-4.94670600	-2.53789200	-2.51046000
C	-3.44672800	-1.23959000	-5.26989600
H	-1.90410400	0.27158900	-5.25376600
H	-4.99386000	-2.71265300	-4.96725800
H	-3.46441400	-1.32843600	-6.35381900
Rh	-1.82541200	0.83678200	-0.05643700
H	-2.95372500	1.36260200	-1.07714700
H	-2.79832900	1.21803600	1.04594500
C	0.28684300	3.24546900	-1.78136100
C	-1.10983500	3.24177200	-1.82074000
C	-0.77801900	2.66267200	0.50000700
C	-1.73857800	3.05006900	-0.47857800
H	-0.89755900	2.93286600	1.54592400
C	-2.95328900	3.83265200	-0.11472300
C	-4.16432400	3.71824200	-0.81028800
C	-2.85790300	4.77896800	0.91417700
C	-5.25011700	4.52252800	-0.48463400
H	-4.27404200	2.96058700	-1.58633500
C	-3.94748300	5.58133600	1.24301800
H	-1.91452900	4.90809700	1.44242700
C	-5.14601700	5.45571700	0.54624000
H	-6.18522700	4.40686900	-1.02862500
H	-3.85314300	6.31000900	2.04505900
H	-5.99839200	6.07950200	0.80609000
S	0.86777400	2.98270800	-0.12548600
O	1.77238900	1.82235100	-0.12028000

O	1.35013200	4.21788700	0.50383900
C	7.43660500	0.30818700	0.01708100
H	8.46175200	0.45331500	0.34683700
C	5.11289200	0.98006600	0.02641400
H	4.32659000	1.64881300	0.36936800
C	5.79422500	-0.95865600	-1.24317700
H	5.55250400	-1.78198900	-1.90587300
C	1.08078100	3.38250200	-2.91009700
H	2.16654800	3.36868800	-2.83838900
C	0.43696600	3.52732800	-4.13711300
H	1.02467400	3.63528600	-5.04504900
C	-0.95873700	3.53649600	-4.20393500
H	-1.44864800	3.64861900	-5.16816400
C	-1.73799600	3.39981500	-3.05745700
H	-2.82258700	3.39984200	-3.13563300



Rh(III)HH-**1m**-pro-(*R*) **IV**:

Thermal correction to Gibbs Free Energy= 0.855831

Sum of electronic and thermal Free Energies= -4887.790620

Fe	1.63346300	3.29458000	1.49130300
S	-3.15750800	3.29098400	-0.19192500
N	-1.26996100	1.84388300	-1.45788900
N	-3.29064200	0.82758800	-1.29871500
F	-5.52707900	-3.30789400	0.12406900
F	-6.99279100	-2.43980500	1.47105700

F	-7.58264100	-3.02817600	-0.52537500
F	-8.74962000	1.89518300	-2.17613400
F	-7.63826600	3.38835800	-1.06275100
F	-8.98742600	2.03369900	-0.02920200
C	-0.15492800	2.70773200	-1.00214900
C	-2.55579100	1.95624600	-1.01370900
C	-4.63324400	0.55742400	-1.01117700
C	-6.25102400	-1.09447600	-0.31224400
C	-6.96512600	1.13115300	-0.83884600
C	-6.57912000	-2.46837100	0.18212800
C	-8.07775100	2.11649400	-1.02282100
C	-0.07366900	2.89755800	0.49142400
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C	0.02145500	3.98056600	2.54091200
C	0.24253400	2.59803700	2.77617300
C	0.20172700	1.90215300	1.51766600
C	3.27823100	2.53456500	0.61061400
C	3.05063800	3.89267900	0.18380400
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C	3.30396200	3.91311800	2.47653500
C	3.42095300	2.56089700	2.04639800
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H	0.47961200	2.14991400	3.73477900
H	2.88744300	4.21378400	-0.83935100
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H	3.58628200	1.70136300	2.68762200
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7. Reference

(1) Kuhn, M.; Falk, F. C.; Paradies, J. *Org. Lett.* **2011**, *13*, 4100.

(2) Tosatti, P.; Pfaltz, A. *Angew. Chem. Int. Ed.* **2017**, *56*, 4579.

(3) Antonow, D.; Marrafa, T.; Dawood, I.; Ahmed, T.; Haque, M. R.; Thurston, D. E.; Zinzalla, G. *Chem. Commun.*, **2010**, *46*, 2289.

(4) Xiong, R.; Patel, H. K.; Gutgesell, L. M.; Zhao, J.; Delgado-Rivera, L.; Pham, T. N. D.; Zhao, H.; Carlson, K.; Martin, T.; Katzenellenbogen, J. A.; Moore, T. W.; Tonetti, D. A.; Thatcher, G. R. J. *J. Med. Chem.* **2016**, *59*, 219.

(5) Kim, S.; Yang, J.; Dininno, F. *Tetrahedron Lett.* **1999**, *40*, 2909.

(6) Urban, S.; Beiring, B.; Ortega, N.; Paul, D.; Glorius, F. *J. Am. Chem. Soc.* **2012**, *134*, 15241.

(7) Cabiddu, S.; Cancellu, D.; Floris, G.; Gelli, G.; Melis, S. *Synthesis* **1988**, 888.

(8) Milner, P. J.; Yang, Y.; Buchwald, S. L. *Organometallics* **2015**, *34*, 4775.

(9) Masuya, Y.; Tobisu, M.; Chatani, N. *Org. Lett.* **2016**, *18*, 4312.

(10) Fredrich, S.; A.; Bonasera, V.; Valderrey, Hecht, S. *J. Am. Chem. Soc.* **2018**, *140*, 6432.

(11) Jeong, Y.-C.; Park, D. G.; Kim, E.; Yang, S. I.; Ahn, K.-H. *Macromolecules* **2006**, *39*, 3106.

(12) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.*, **2006**, *125*, 194101.

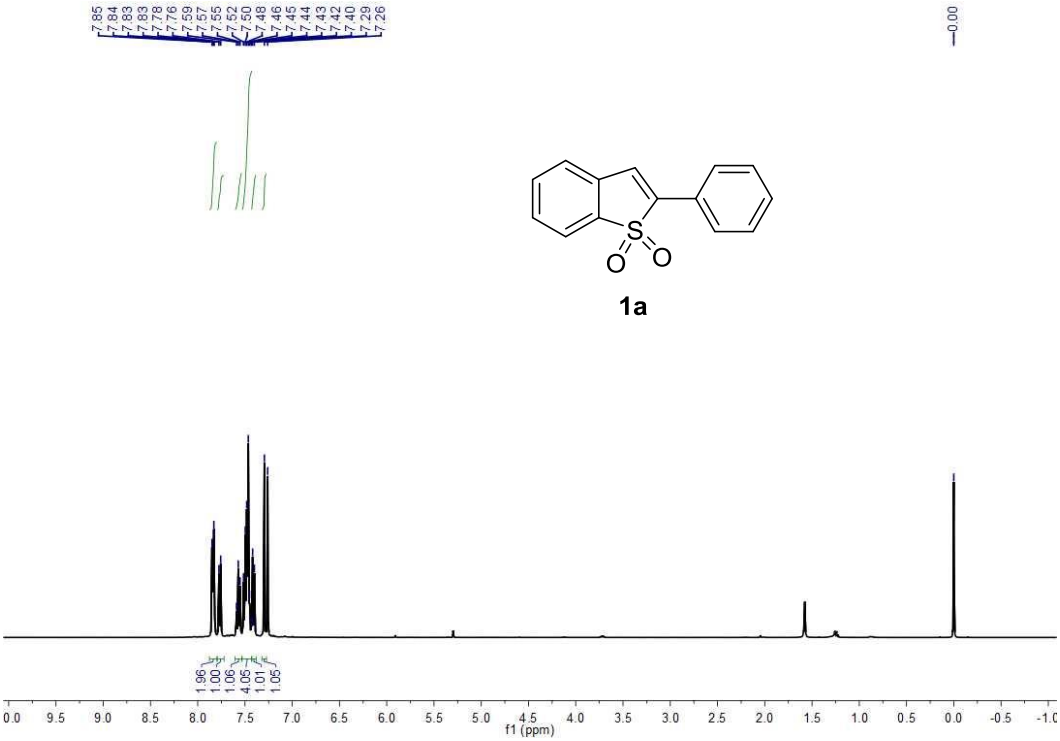
(13) Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, Jr., J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.;

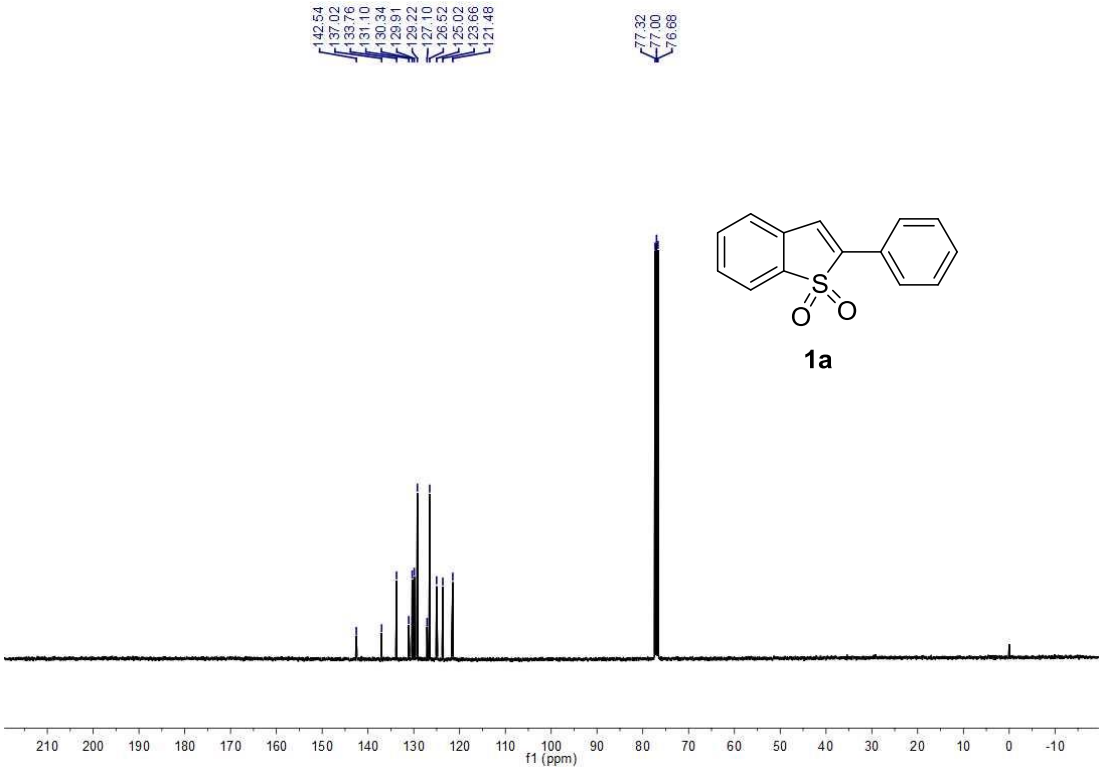
Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc., Wallingford CT, 2013.

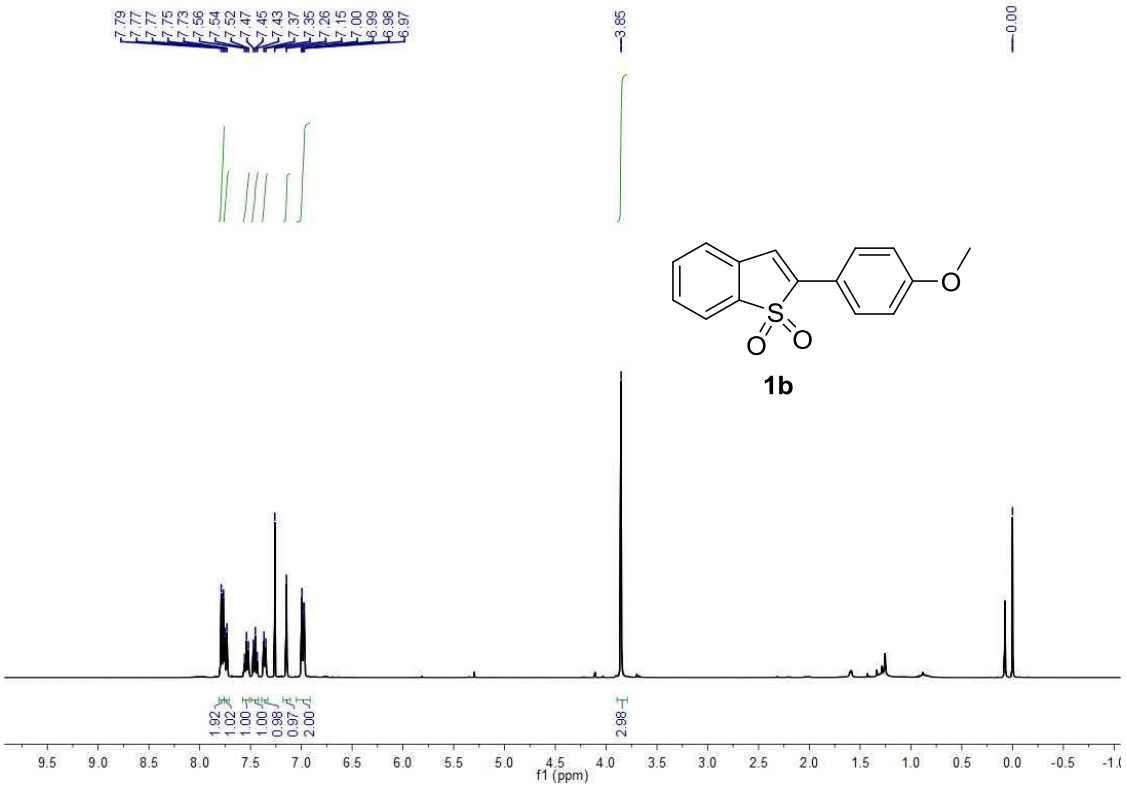
(14) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

(15) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378.

8. NMR spectra



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6.99
6.98
6.97
3.85
0.00
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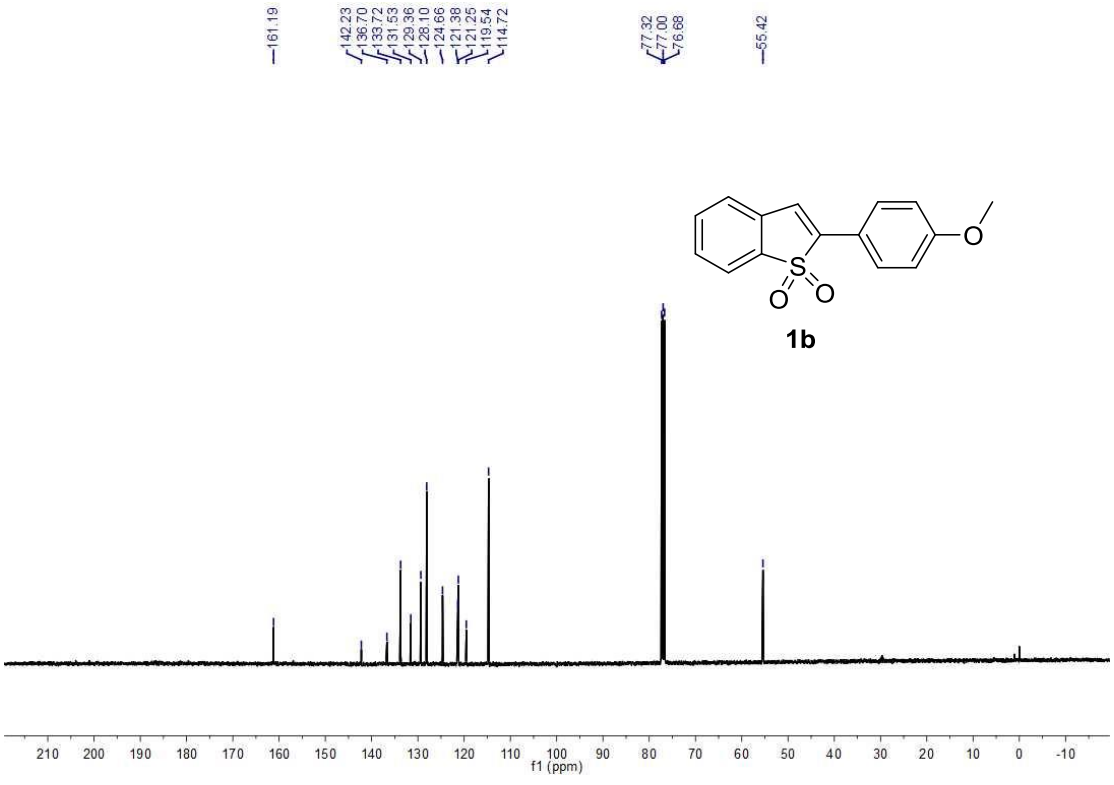
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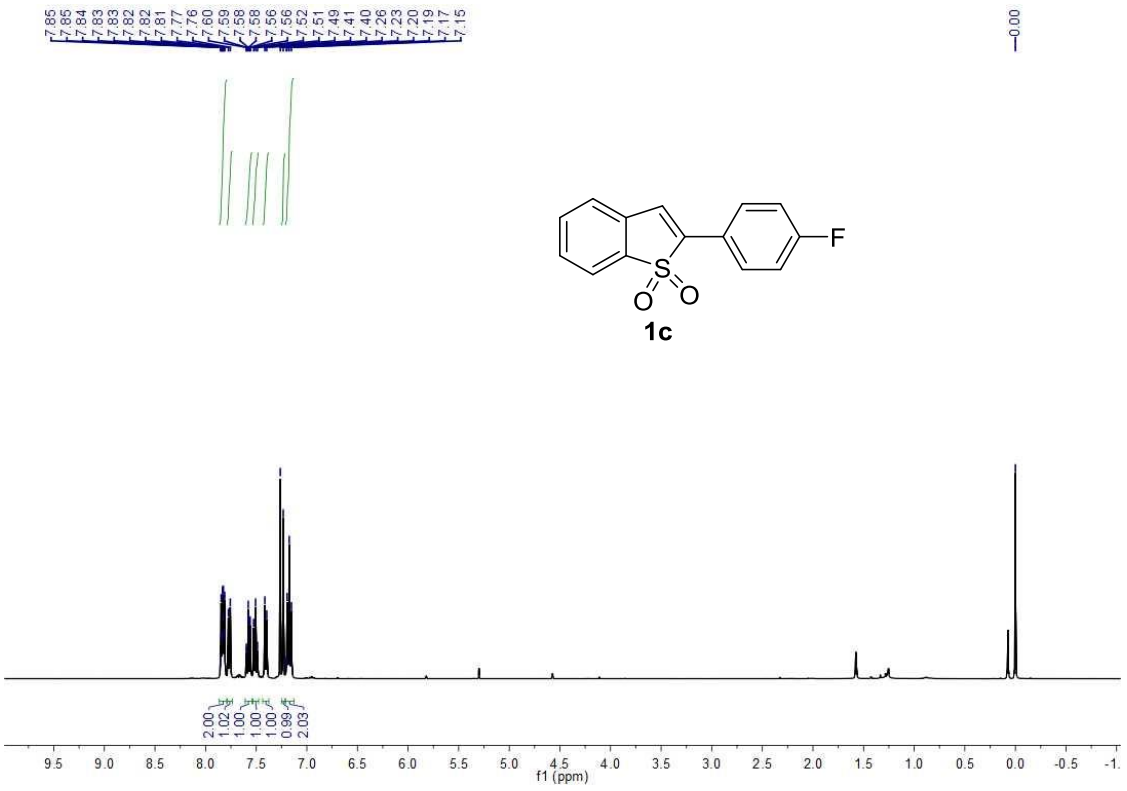
O
O
1b
f1 (ppm)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7.58
7.56
7.56
7.52
7.51
7.49
7.41
7.40
7.26
7.23
7.20
7.19
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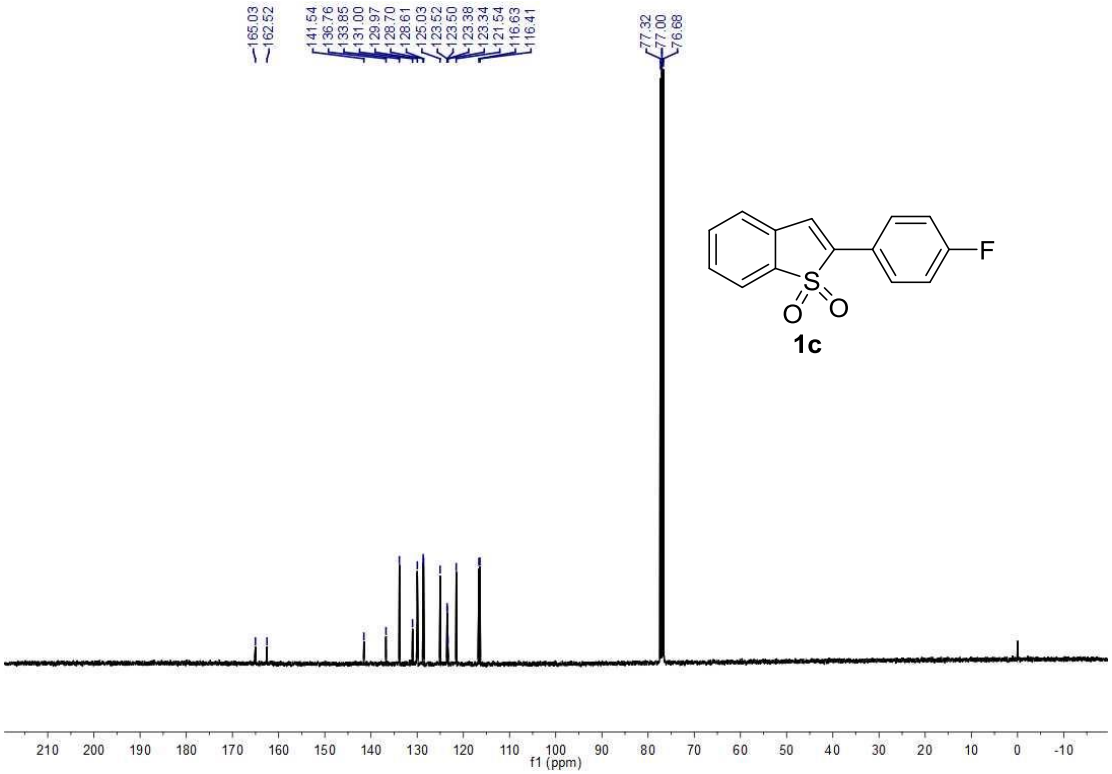
f1 (ppm)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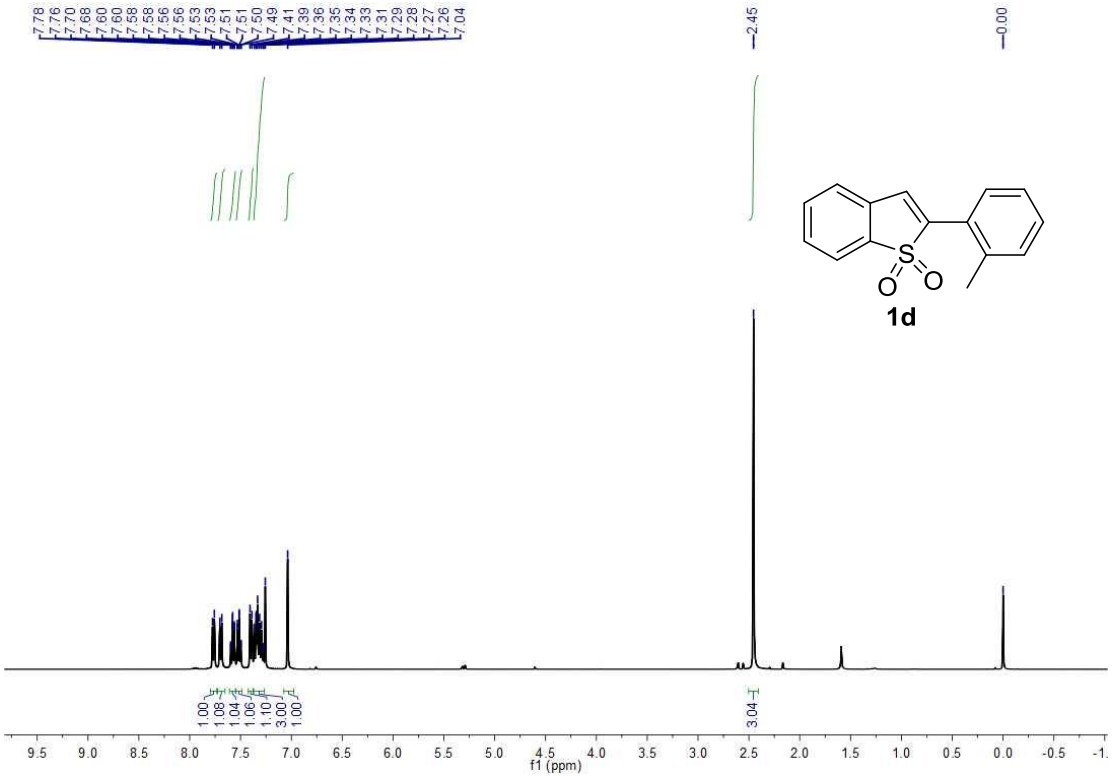
F
S
O
O
1c
f1 (ppm)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7.49
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7.34
7.33
7.31
7.29
7.28
7.27
7.26
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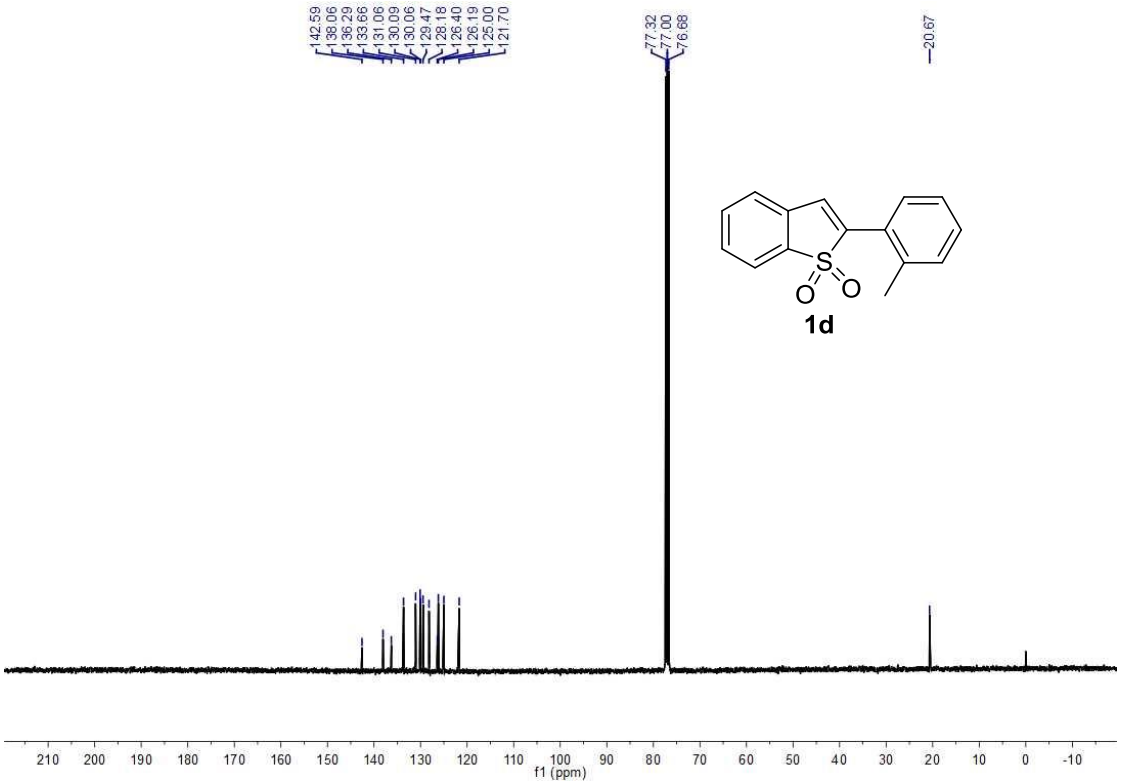
f1 (ppm)

1d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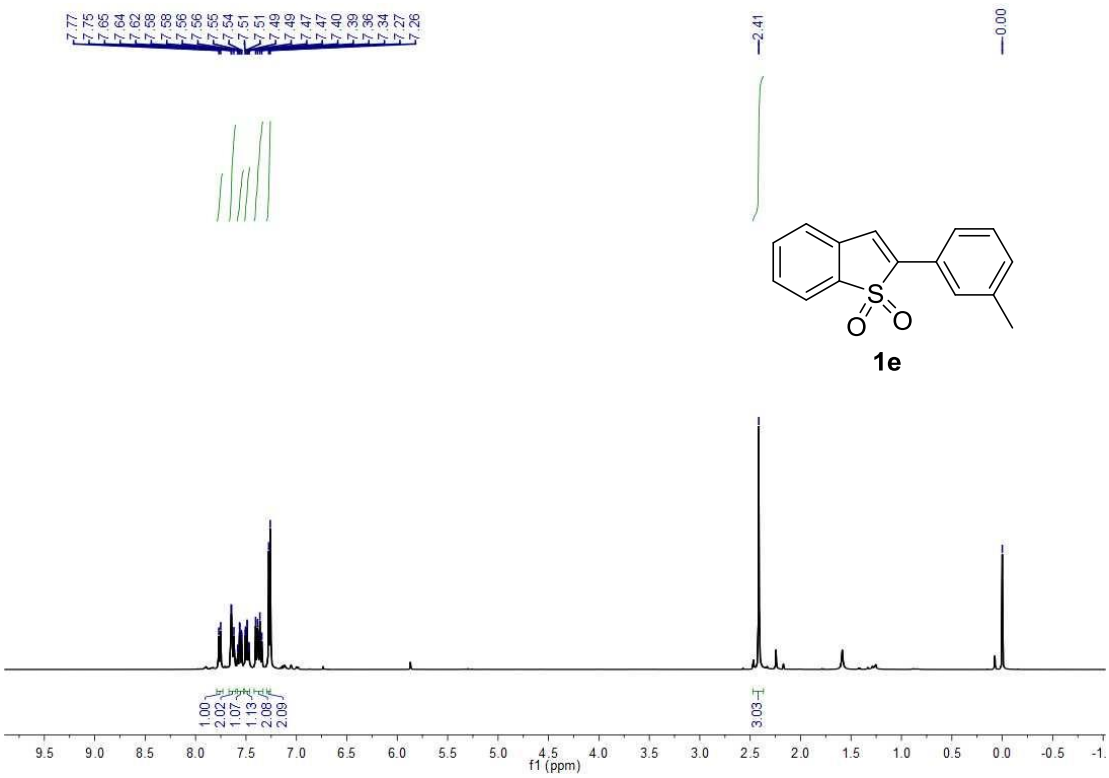
f1 (ppm)

1d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7.49
7.47
7.47
7.40
7.39
7.36
7.34
7.27
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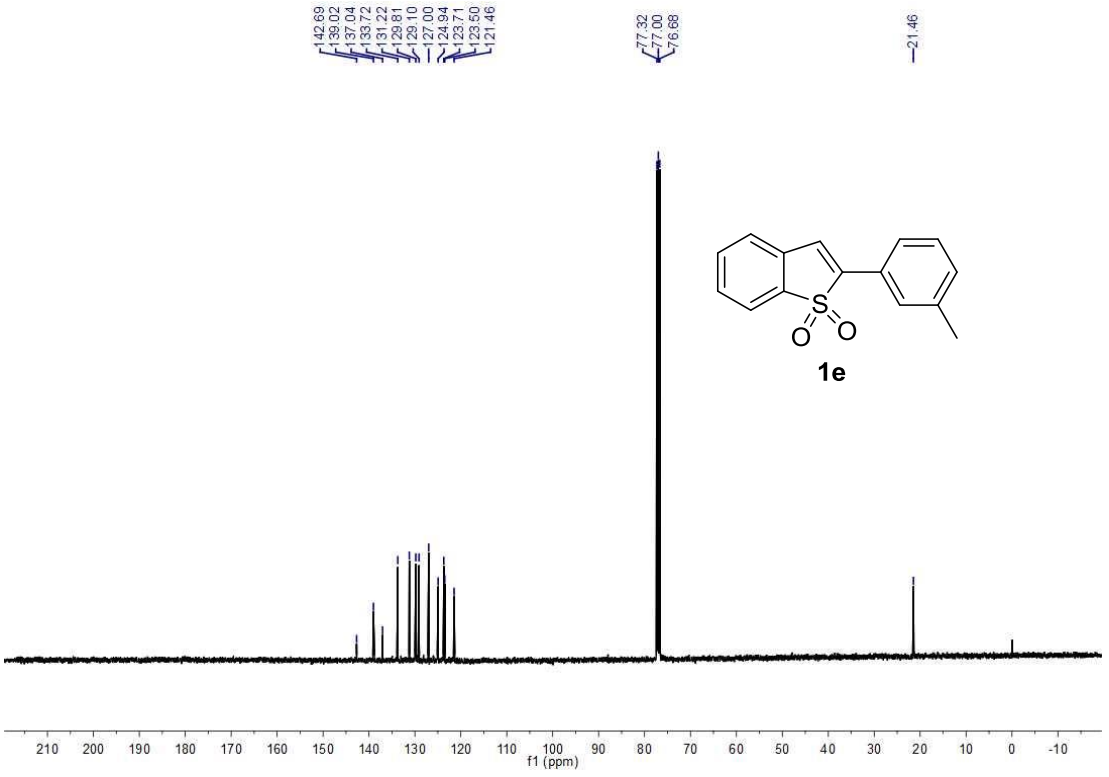
f1 (ppm)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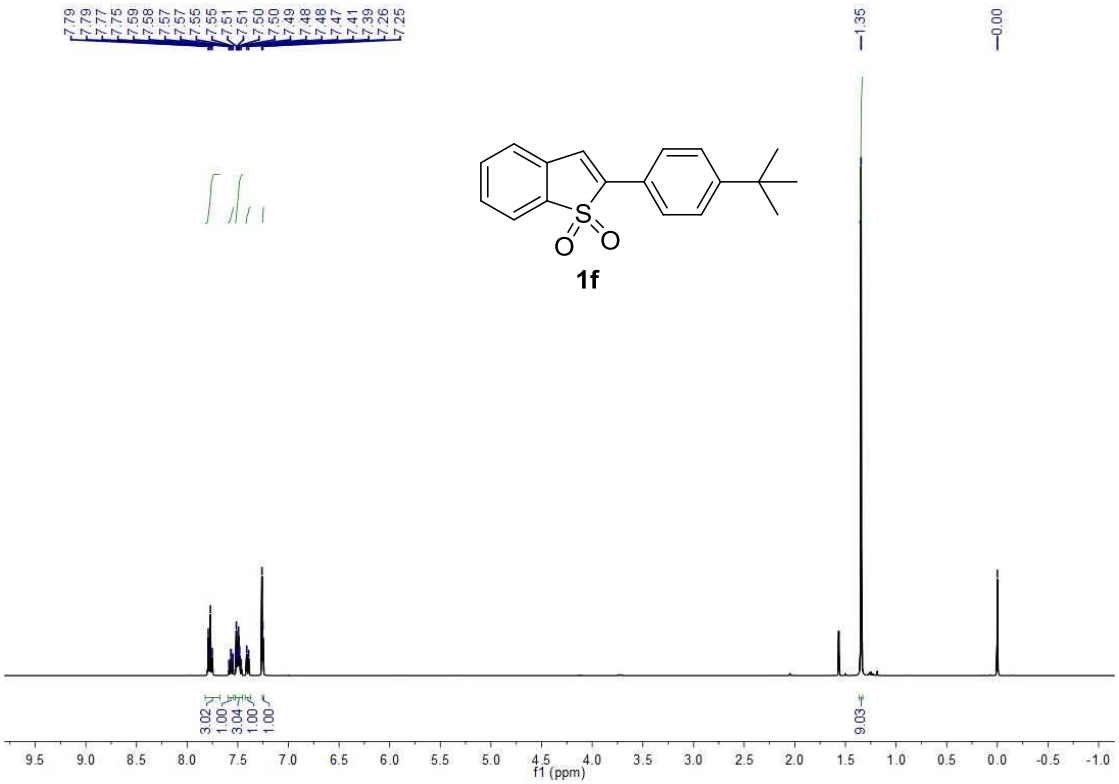
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7.39
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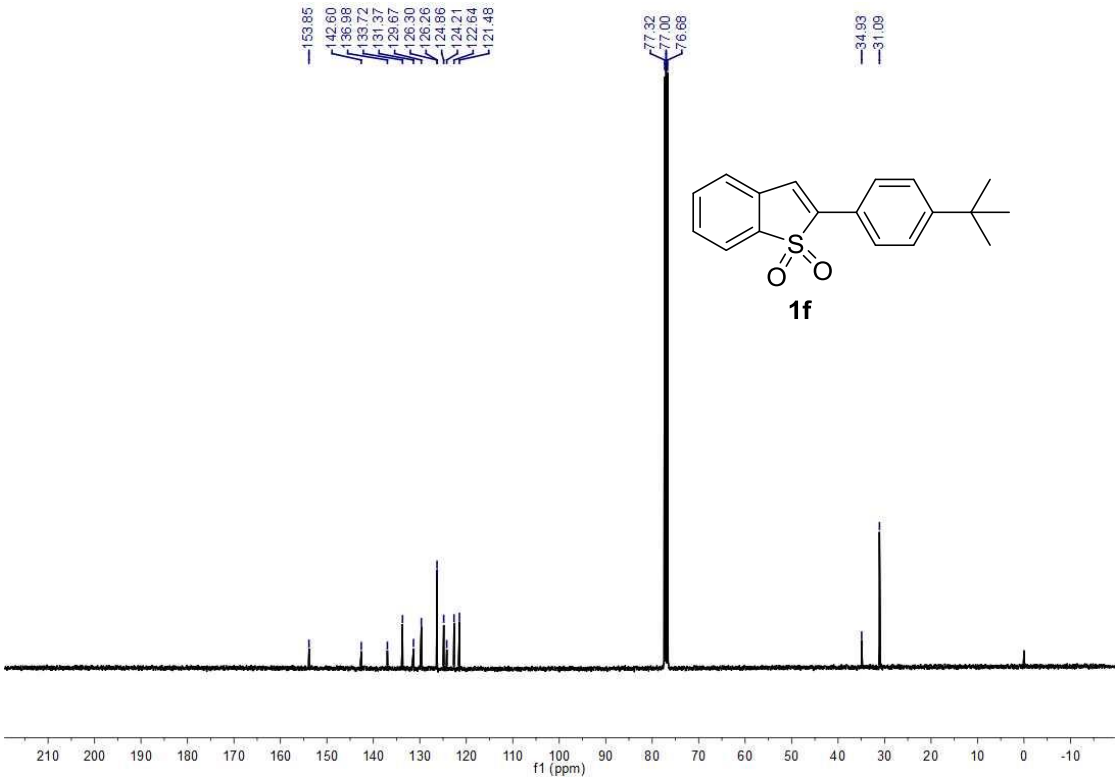
1f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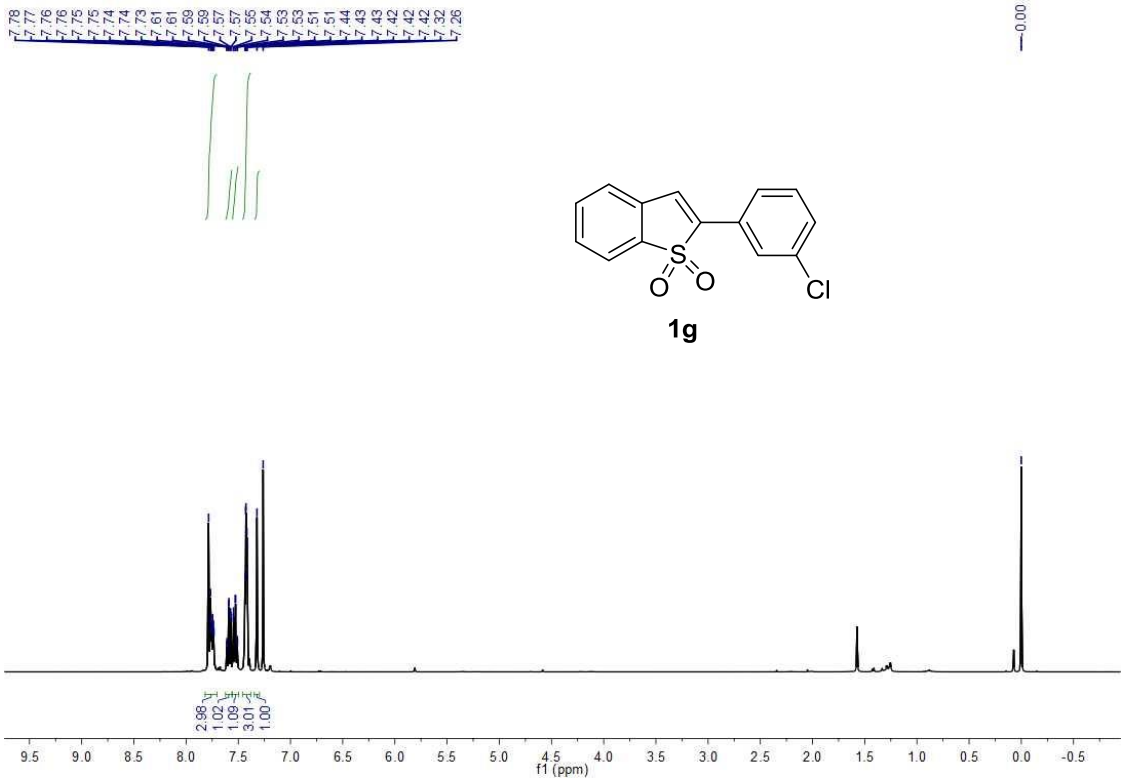
1f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7.51
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S
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O
Cl
2.98
1.02
1.09
3.01
1.00
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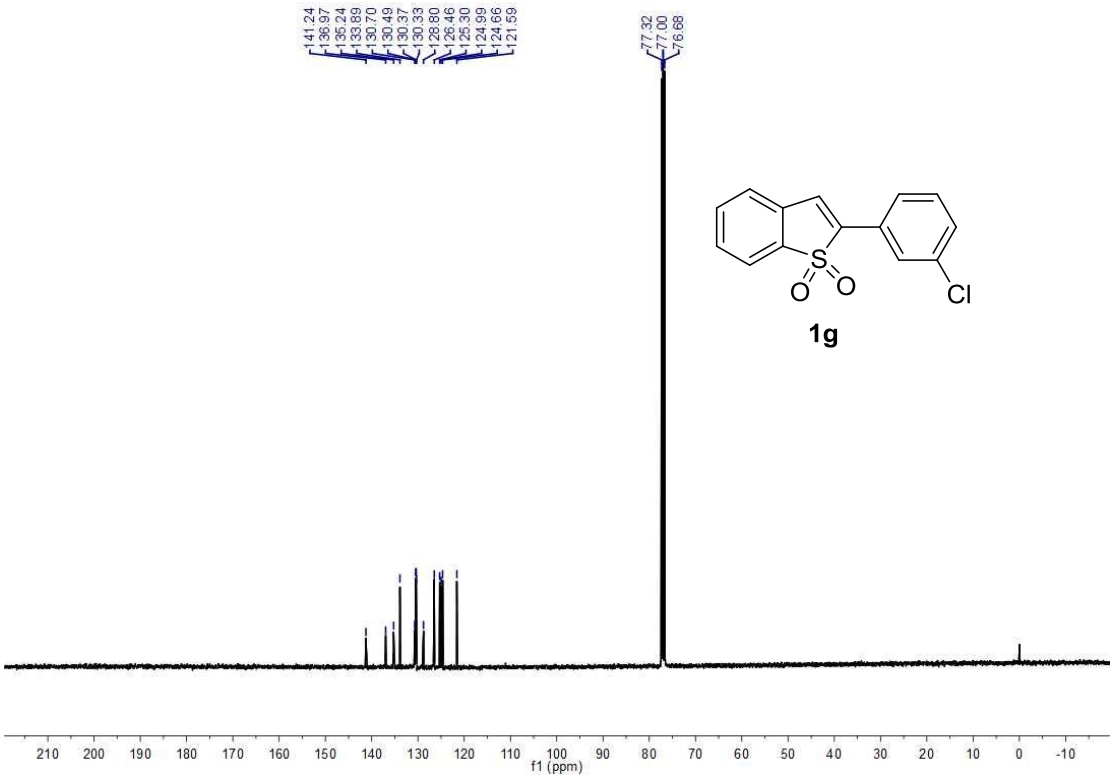
1g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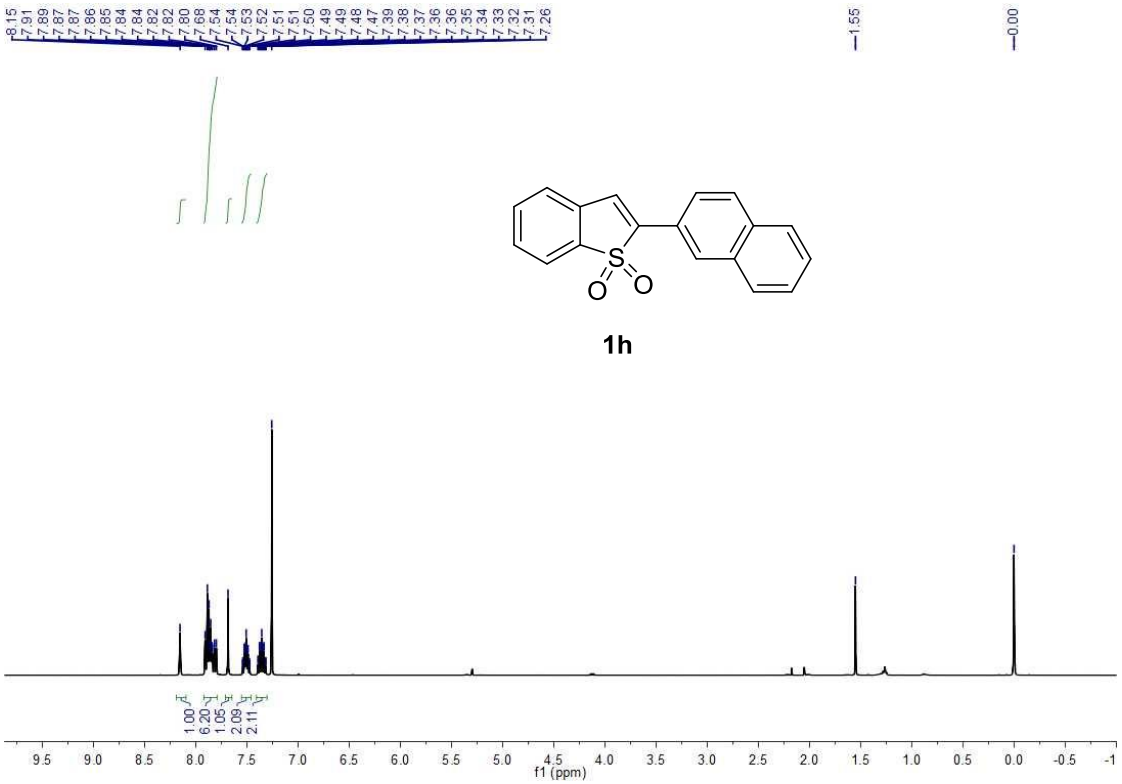
1g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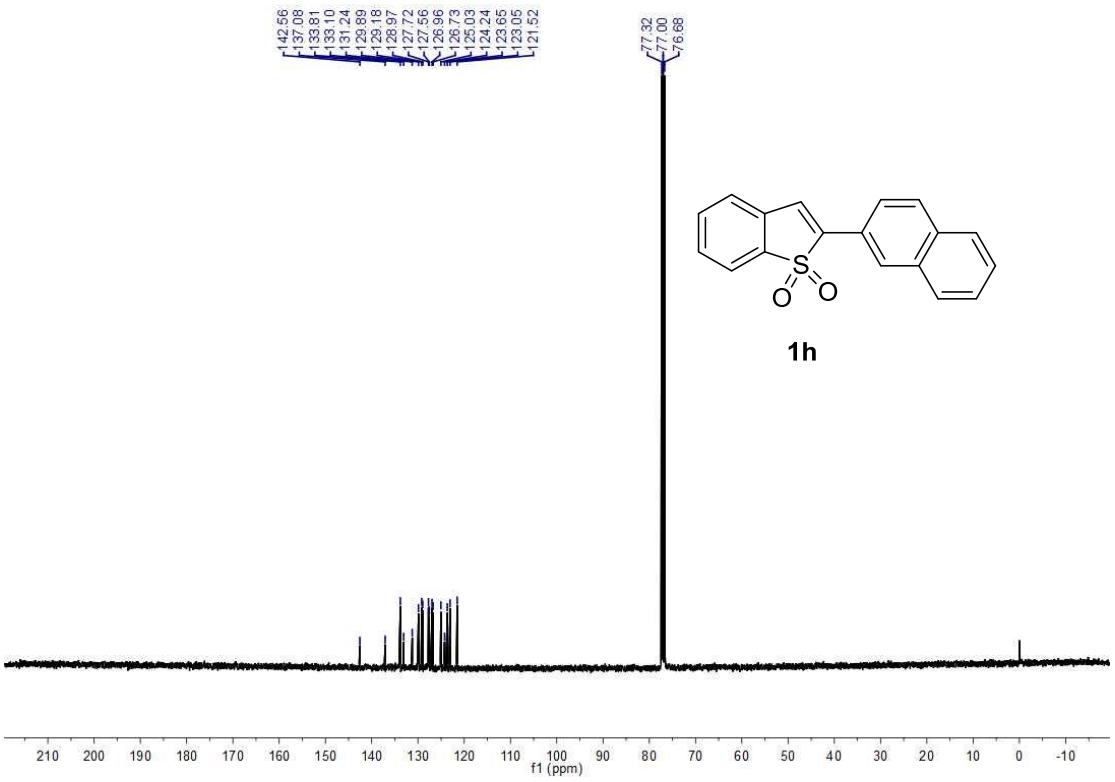
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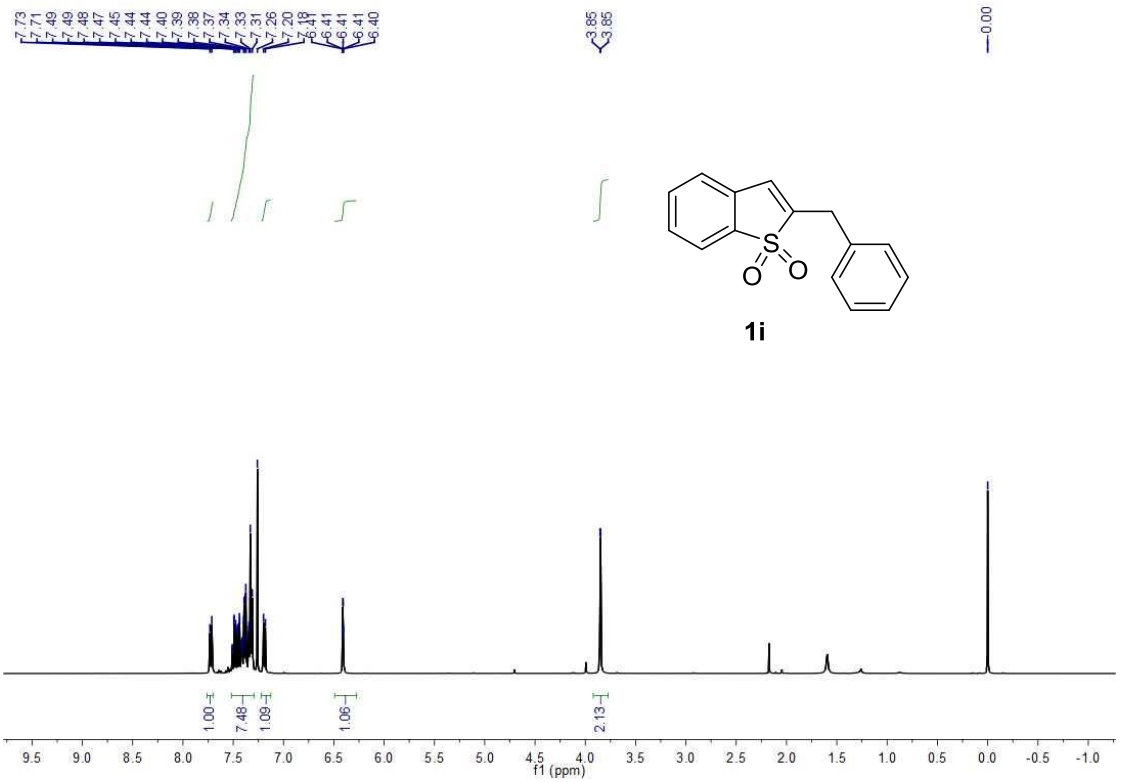
125.03
124.24
123.65
123.05
121.52
77.32
77.00
76.68
f1 (ppm)

1h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7.44
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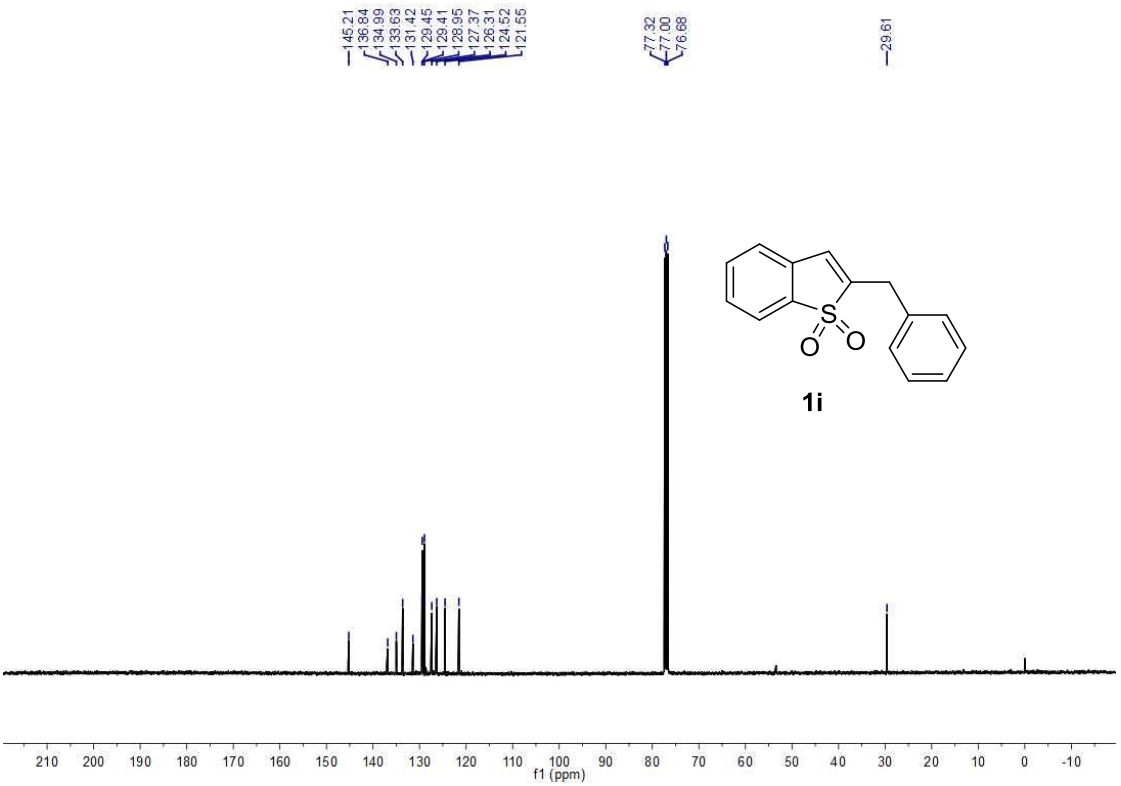
7.39
7.38
7.37
7.34
7.33
7.31
7.26
7.20
6.41
6.41
6.41
6.40
3.85
3.85
0.00
1.00
7.48
1.09
1.06
2.13
f1 (ppm)

1i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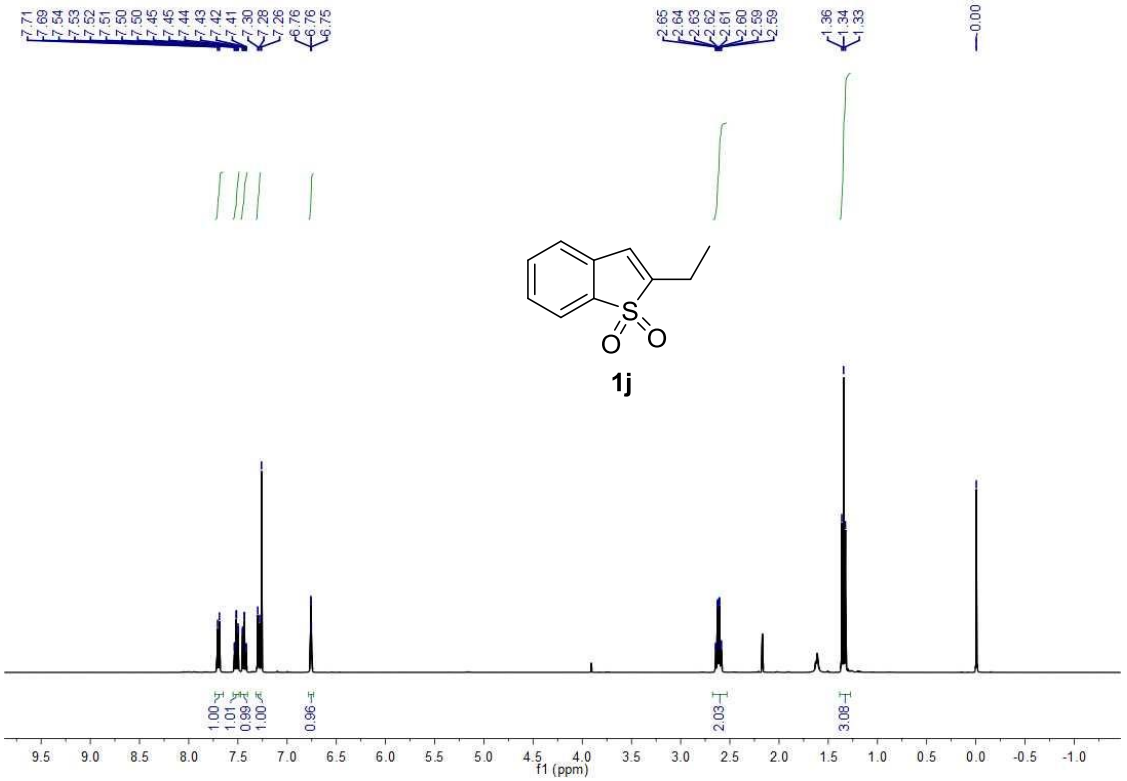
134.99
133.63
131.42
129.45
129.41
128.95
127.37
126.31
124.52
121.55
77.32
77.00
76.68
29.61
f1 (ppm)

1i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7.53
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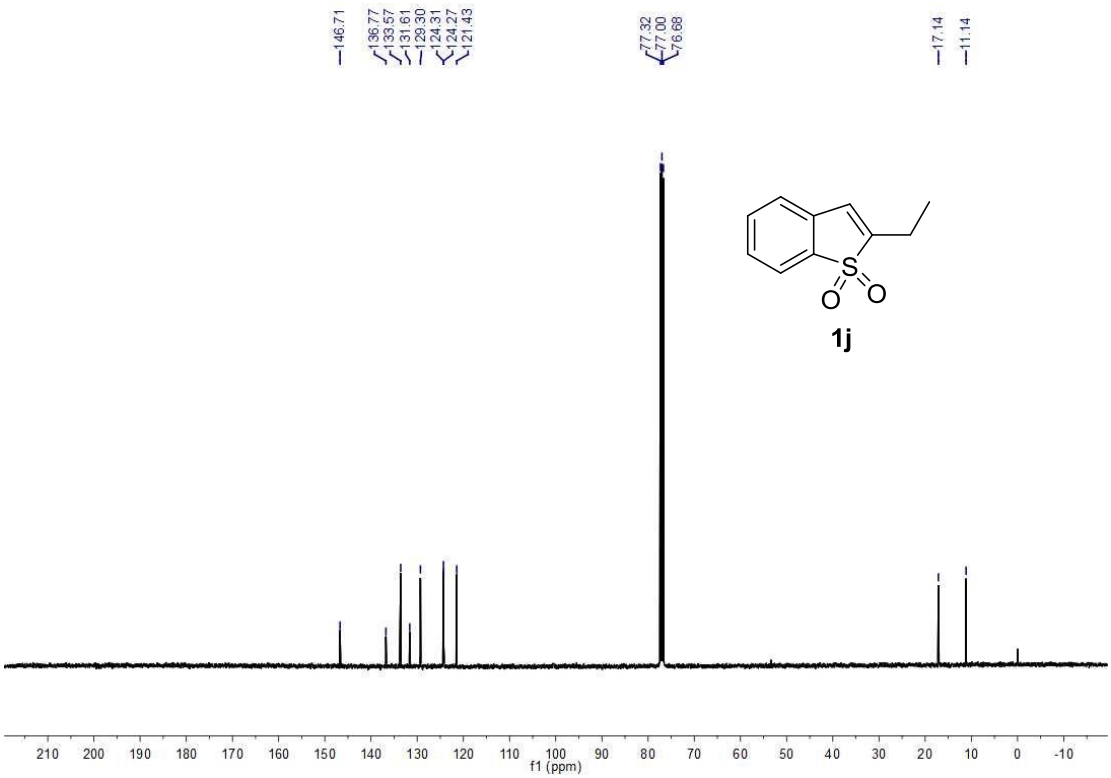
7.51
7.50
7.50
7.45
7.45
7.44
7.43
7.42
7.41
7.30
7.28
7.26
6.76
6.76
6.75
2.65
2.64
2.63
2.62
2.61
2.60
2.59
2.59
1.36
1.34
1.33
0.00
1j
1.00
1.01
0.99
1.00
0.96
2.03
3.08
f1 (ppm)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136.77
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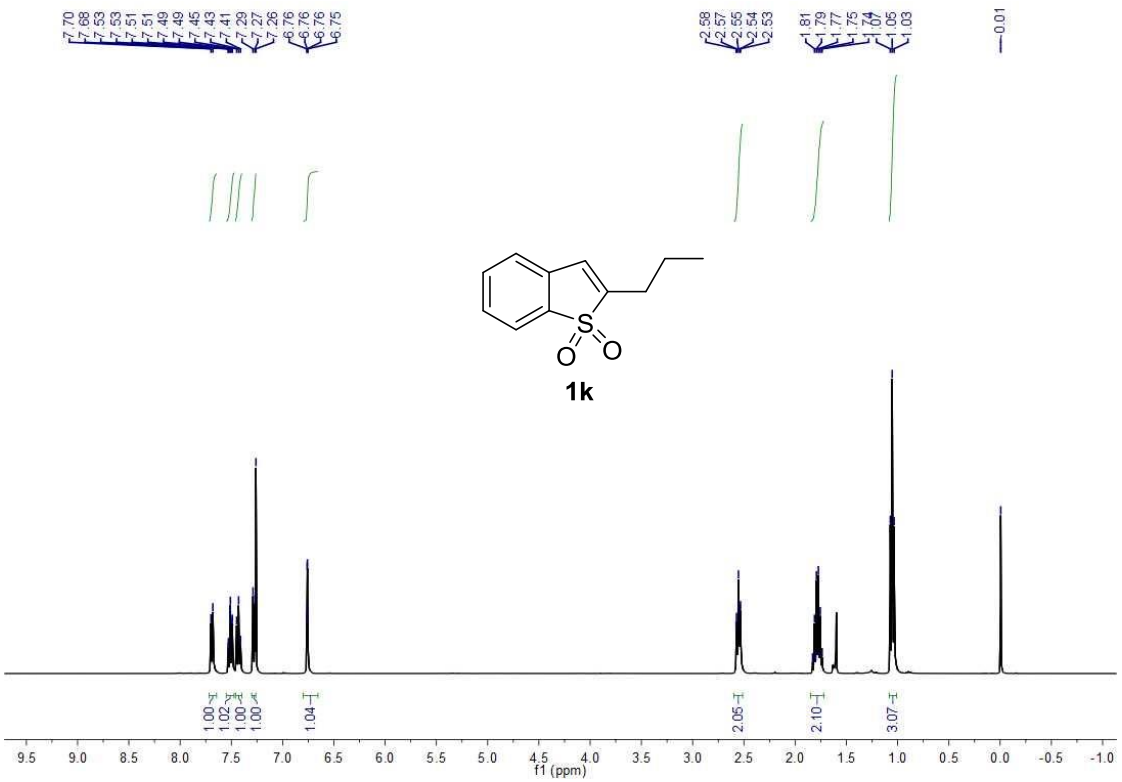
124.31
124.27
121.43
77.32
77.00
76.68
17.14
11.14
1j
f1 (ppm)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7.49
7.49
7.45
7.43
7.41
7.29
7.27
7.26
6.76
6.76
6.76
6.75
2.58
2.57
2.55
2.54
2.53
1.81
1.79
1.77
1.75
1.74
1.07
1.06
1.03
0.01
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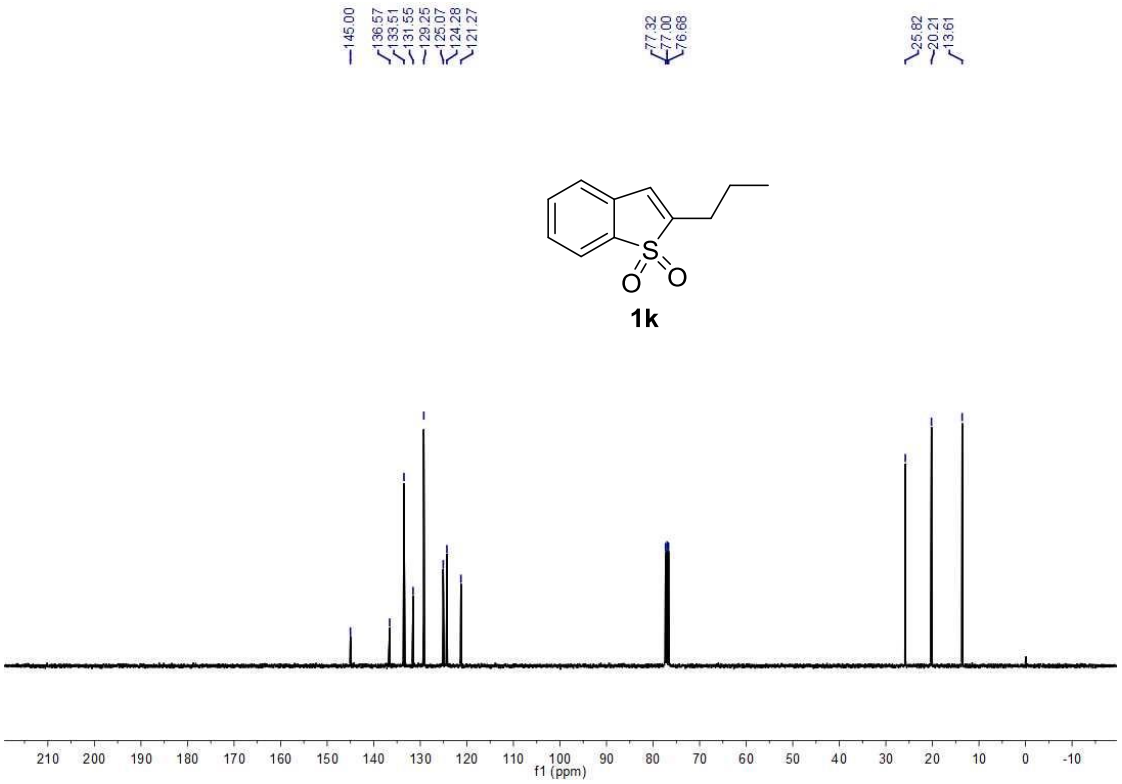
1.02
1.00
1.00
1.04
2.05
2.10
3.07
f1 (ppm)

1k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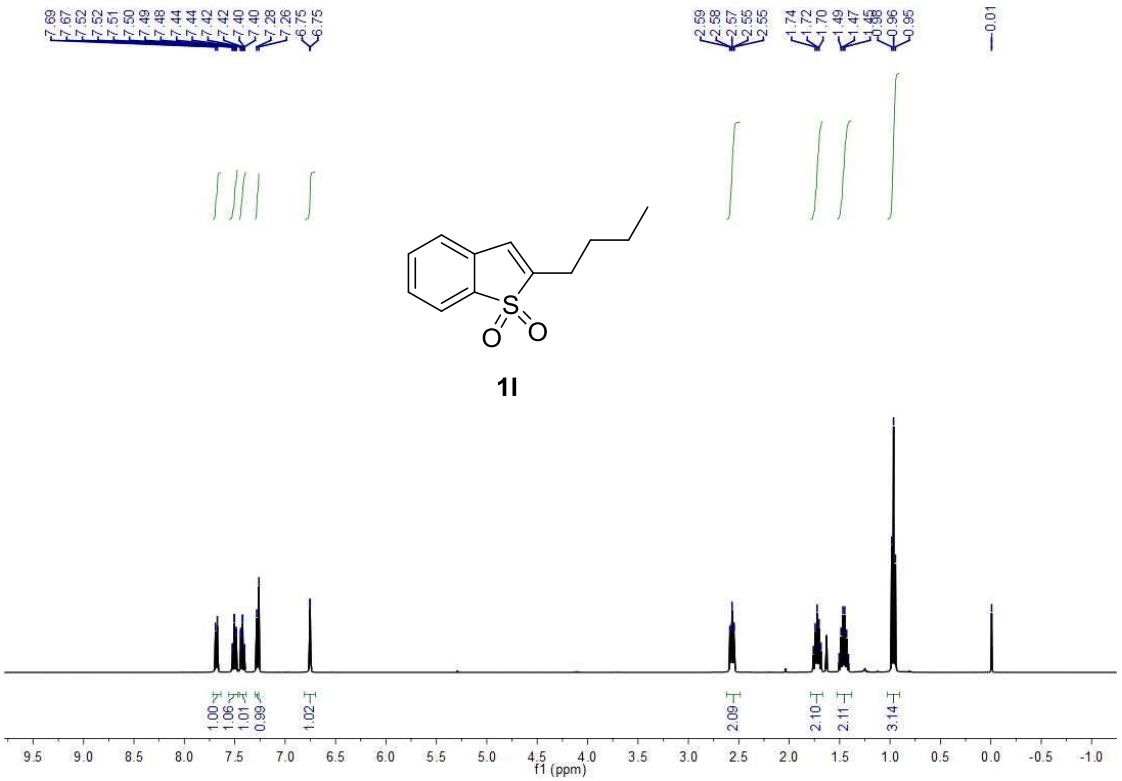
136.57
133.51
131.55
129.25
125.07
124.28
121.27
77.32
77.00
76.68
25.82
20.21
13.61
f1 (ppm)

1k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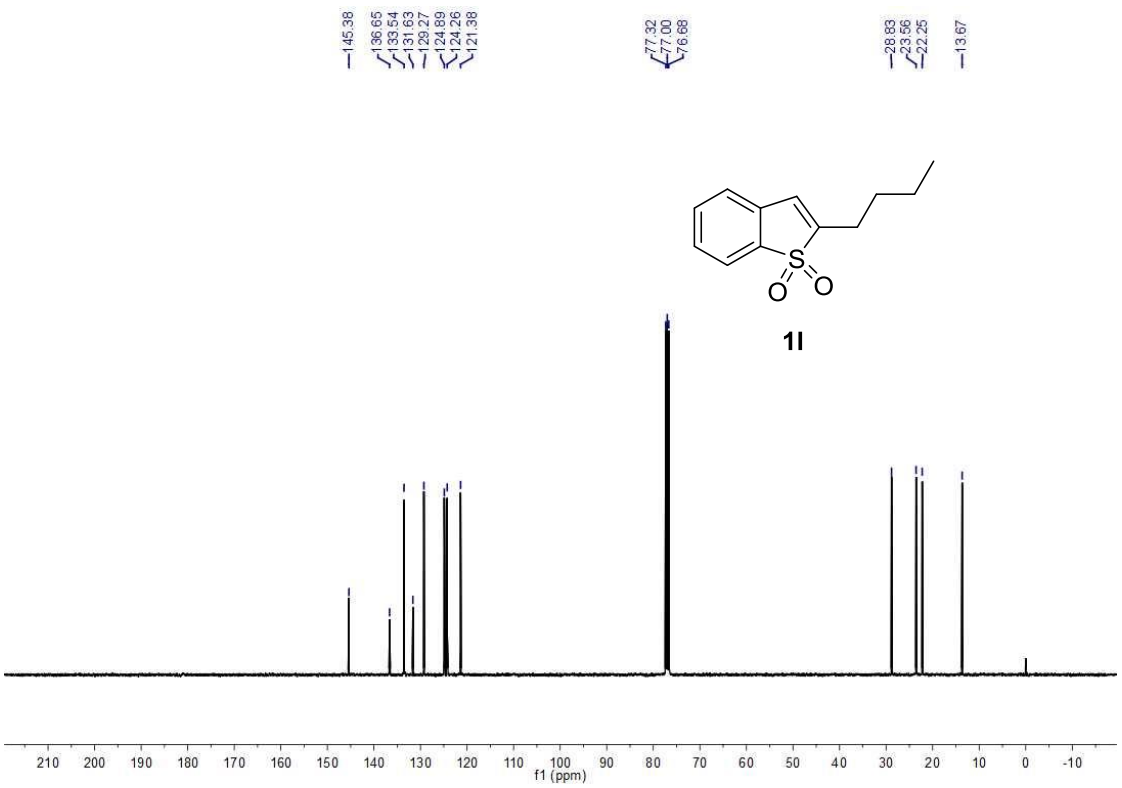
7.67
7.52
7.52
7.51
7.50
7.49
7.48
7.44
7.44
7.42
7.42
7.40
7.40
7.28
6.75
6.75
2.59
2.58
2.57
2.55
2.55
1.74
1.72
1.70
1.49
1.47
0.96
0.96
0.01
1.00
1.06
1.01
0.99
1.02
2.09
2.10
2.11
3.14
f1 (ppm)

1l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136.65
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129.27
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124.26
121.38
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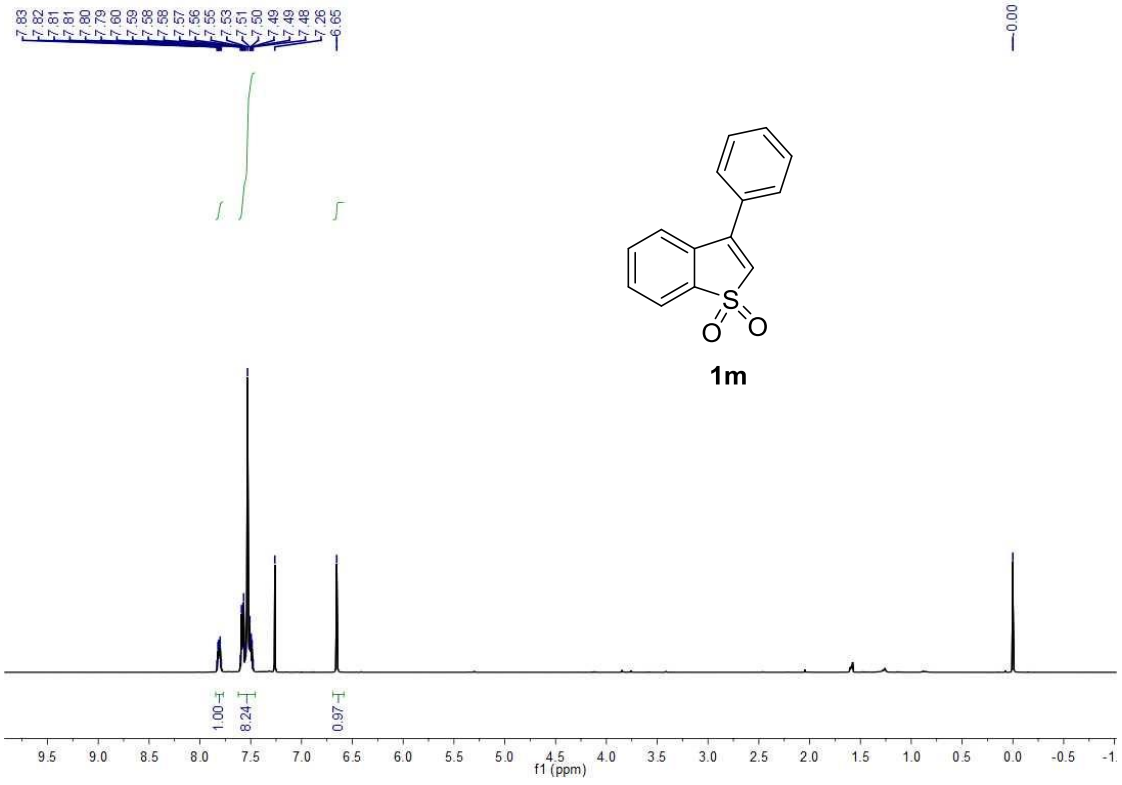
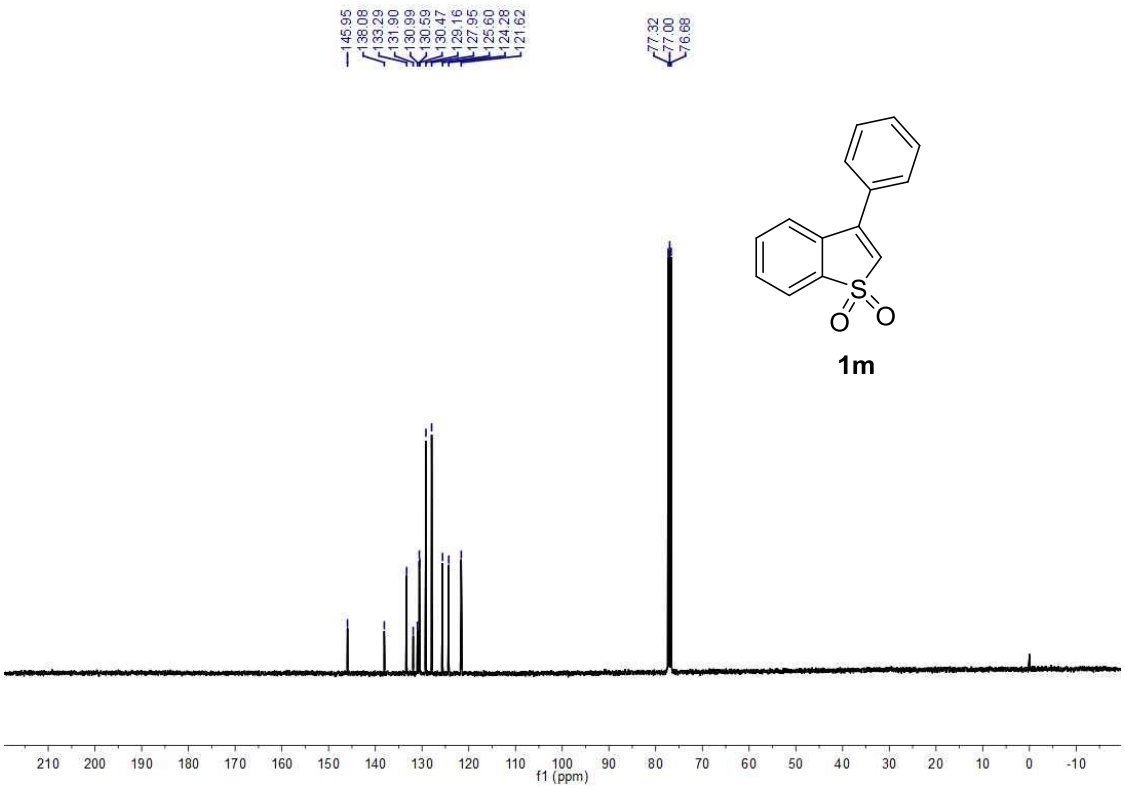
77.00
76.68
28.83
23.56
22.25
13.67
f1 (ppm)

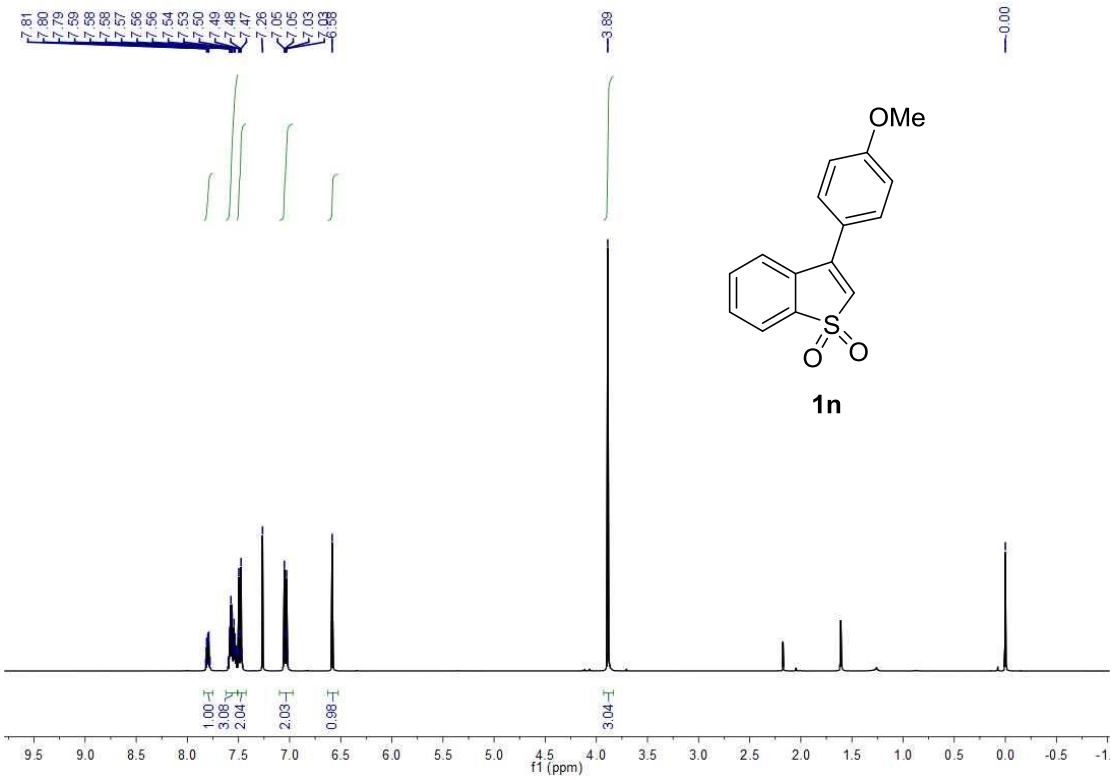
1l

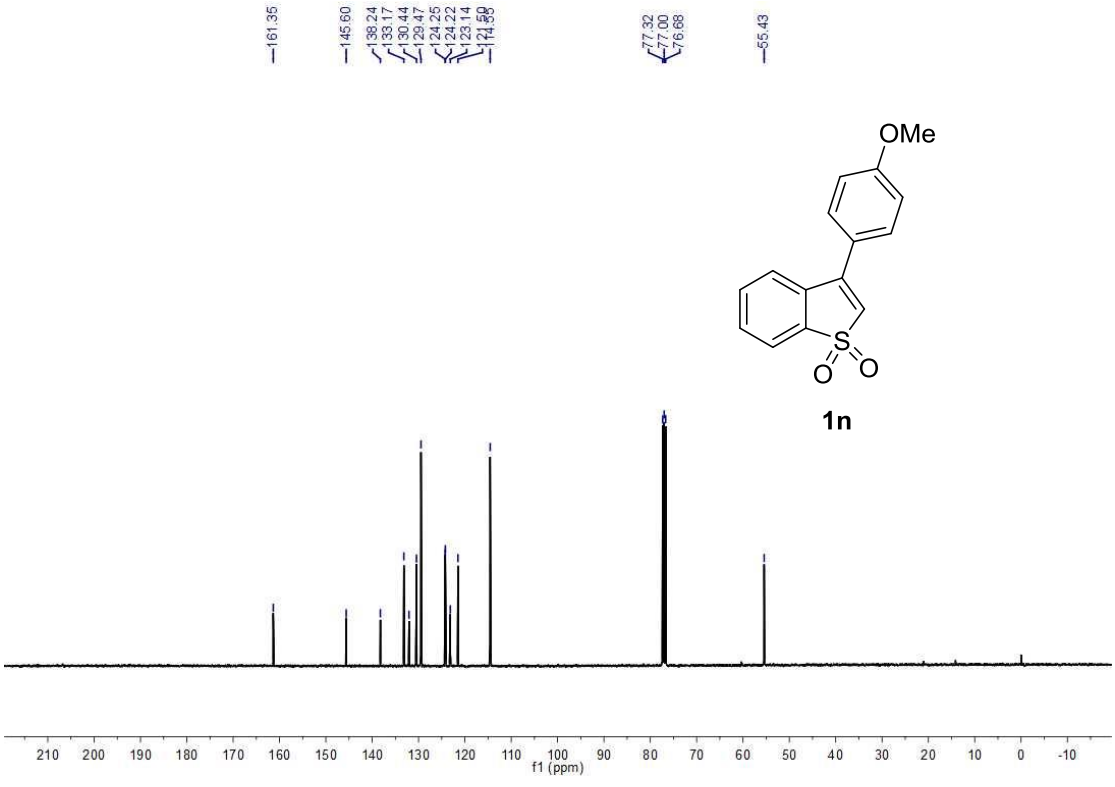

7.83
7.82
7.81
7.81
7.80
7.79
7.60
7.59
7.58
7.58
7.57
7.56
7.55
7.53
7.51
7.50
7.49
7.49
7.48
7.26
6.65
0.00
1.00
8.24
0.97
f1 (ppm)

1m


145.95
138.08
133.29
131.90
130.99
130.59
130.47
129.16
127.95
125.60
124.28
121.62
77.32
77.00
76.68
f1 (ppm)

1m


7.81
7.80
7.79
7.59
7.58
7.58
7.57
7.56
7.56
7.54
7.53
7.50
7.49
7.48
7.47
7.26
7.05
7.05
7.03
6.98
3.89
0.00
OMe
S
O
O
1n
1.00
3.08
2.04
2.03
0.98
3.04
f1 (ppm)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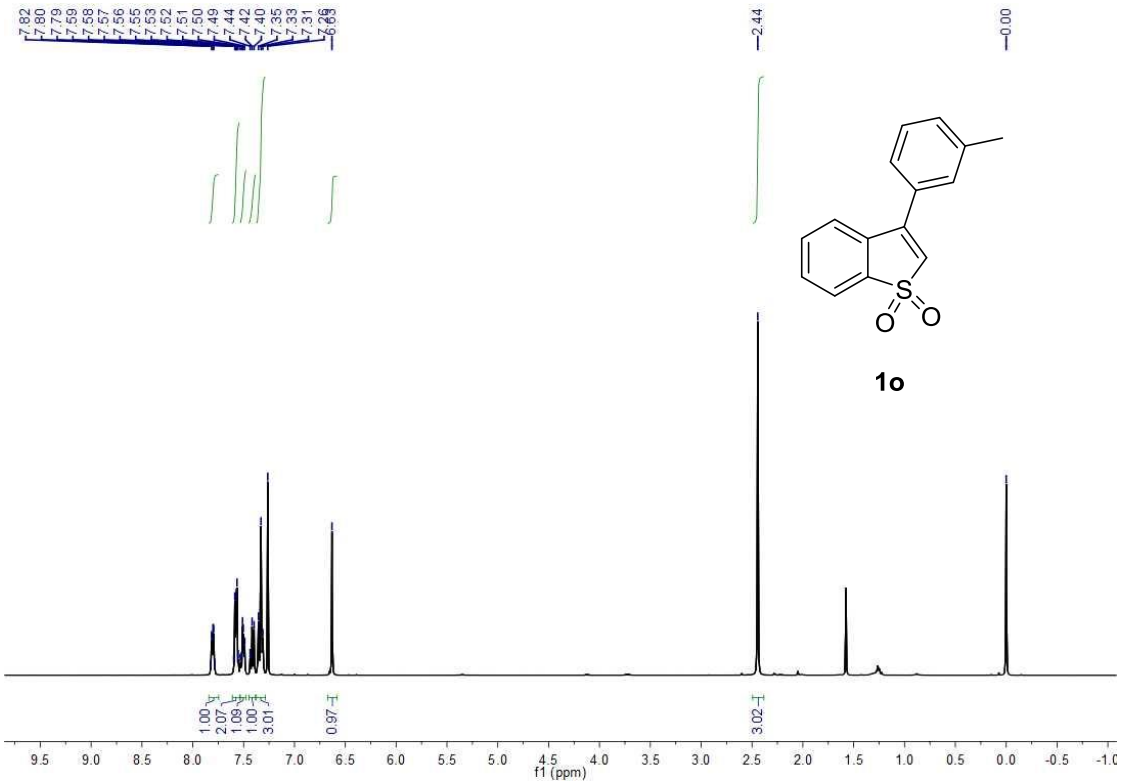
145.60
138.24
133.17
130.44
129.47
124.25
124.22
123.14
77.32
77.00
76.68
55.43
OMe
S
O
O
1n
f1 (ppm)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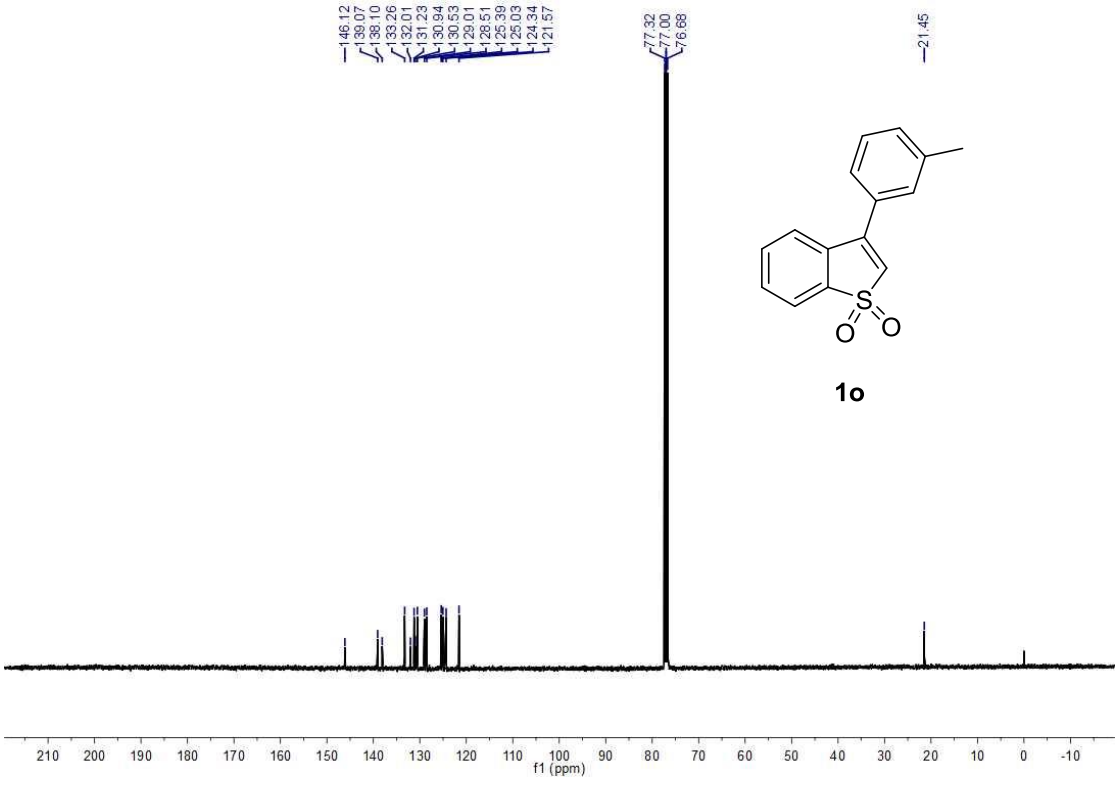
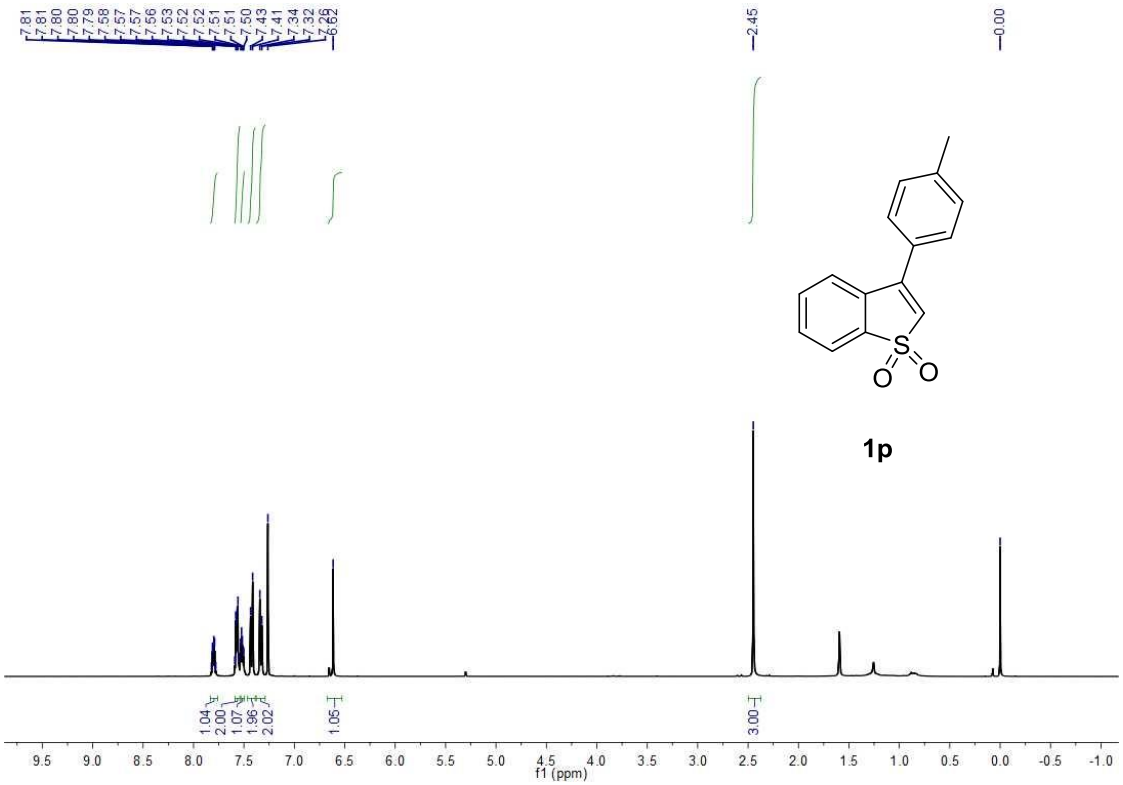
7.80
7.79
7.59
7.58
7.57
7.56
7.55
7.53
7.52
7.51
7.50
7.49
7.44
7.42
7.40
7.35
7.33
7.31
7.26
6.63
2.44
0.00
1.00
2.07
1.09
1.00
3.01
0.97
3.02
f1 (ppm)

1o


146.12
139.07
138.10
133.26
132.01
131.23
130.94
130.53
129.01
128.51
125.39
125.03
124.34
121.57
77.32
77.00
76.68
21.45
f1 (ppm)

1o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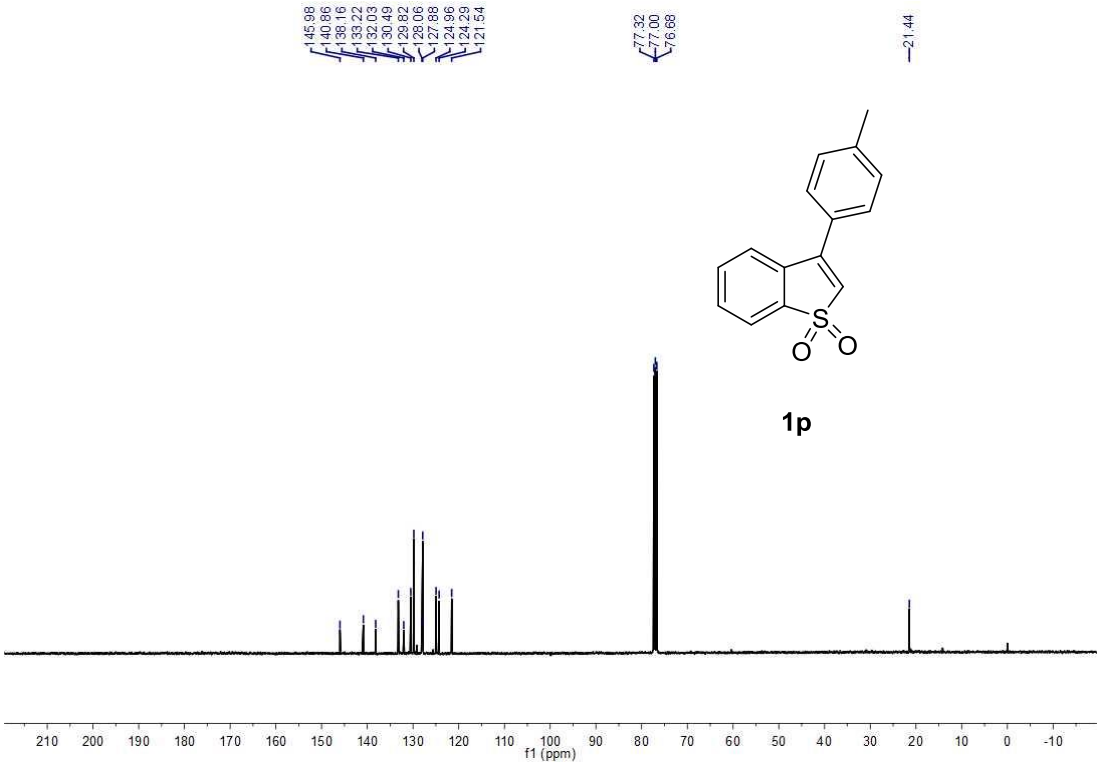
7.81
7.80
7.80
7.79
7.58
7.57
7.57
7.56
7.53
7.52
7.52
7.51
7.51
7.50
7.43
7.41
7.34
7.32
6.62
2.45
0.00
1p
1.04
2.00
1.07
1.96
2.02
1.05
3.00
f1 (ppm)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140.86
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133.22
132.03
130.49
129.82
128.06
127.88
124.96
124.29
121.54
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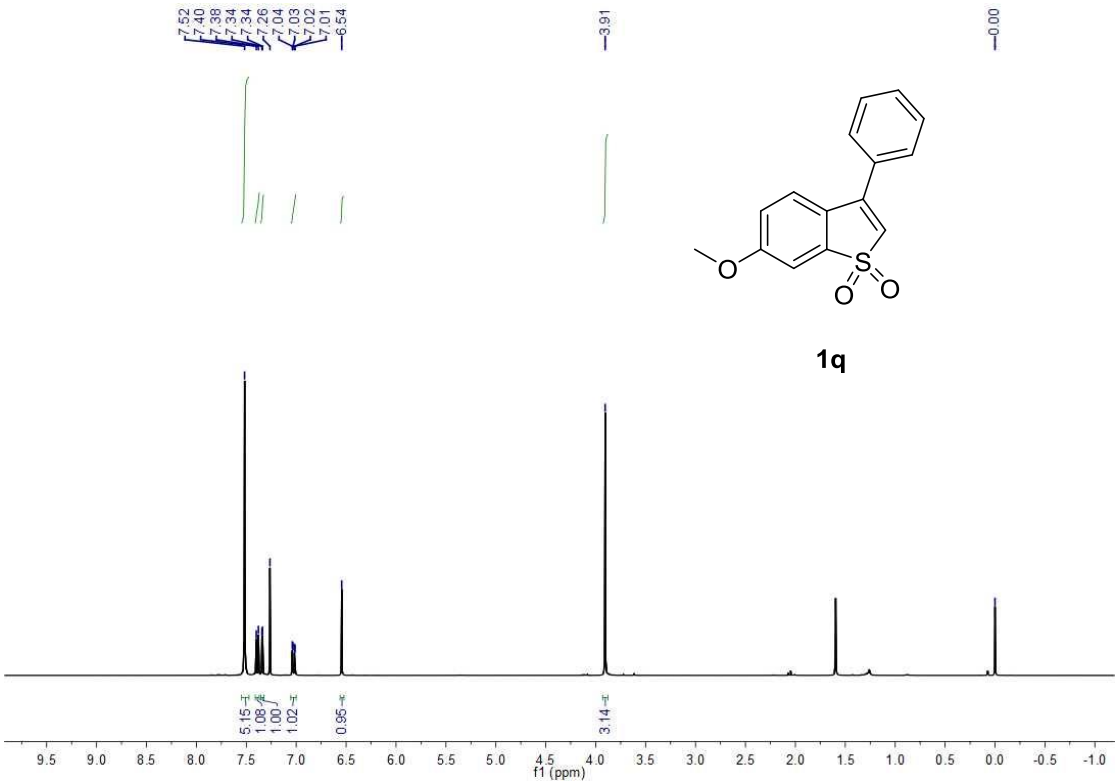
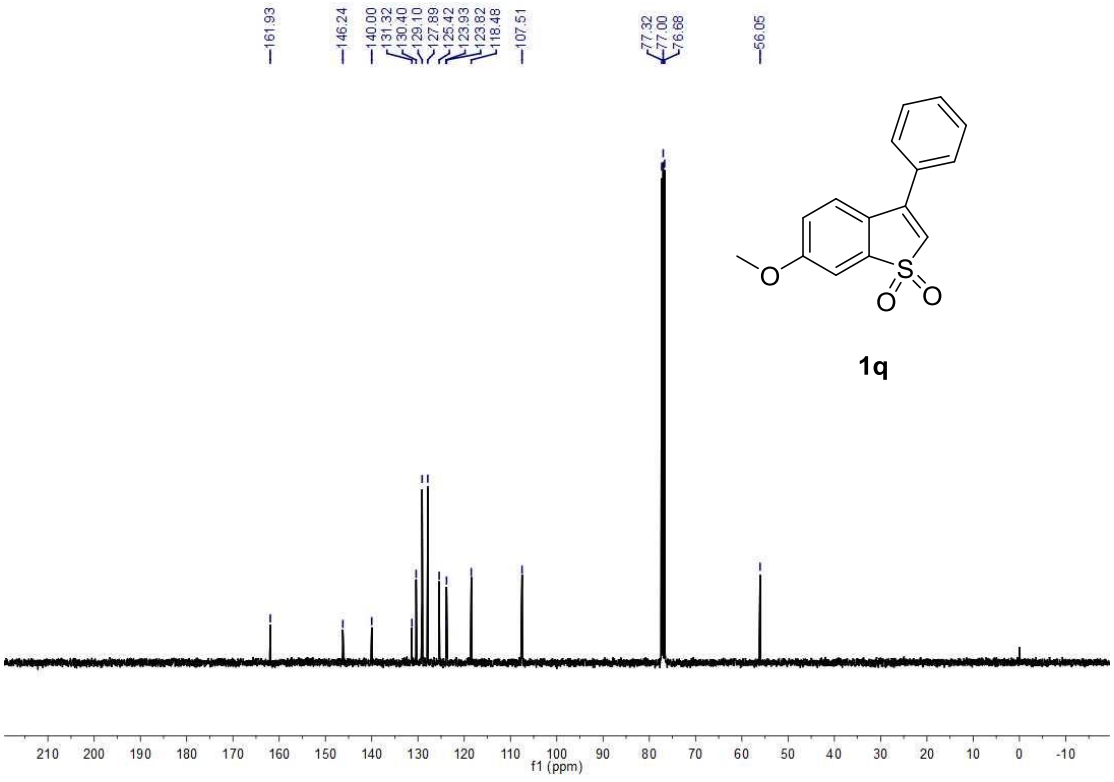
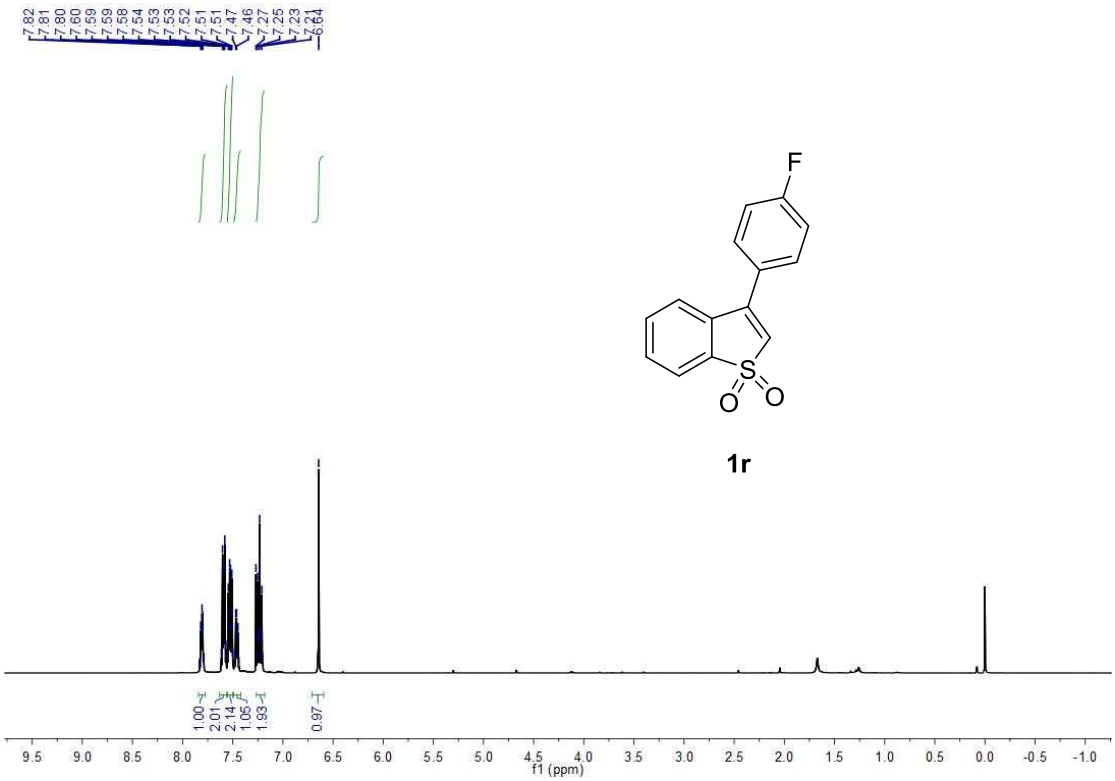
77.00
76.68
21.44
1p
f1 (ppm)


7.52
7.40
7.38
7.34
7.34
7.26
7.04
7.03
7.02
7.01
6.54
3.91
0.00
O
S
O
O
5.15
1.08
1.00
1.02
0.95
3.14
f1 (ppm)

1q


161.93
146.24
140.00
131.32
130.40
129.10
127.89
125.42
123.93
123.62
118.48
107.51
77.32
77.00
76.68
56.05
O
S
O
O
f1 (ppm)

1q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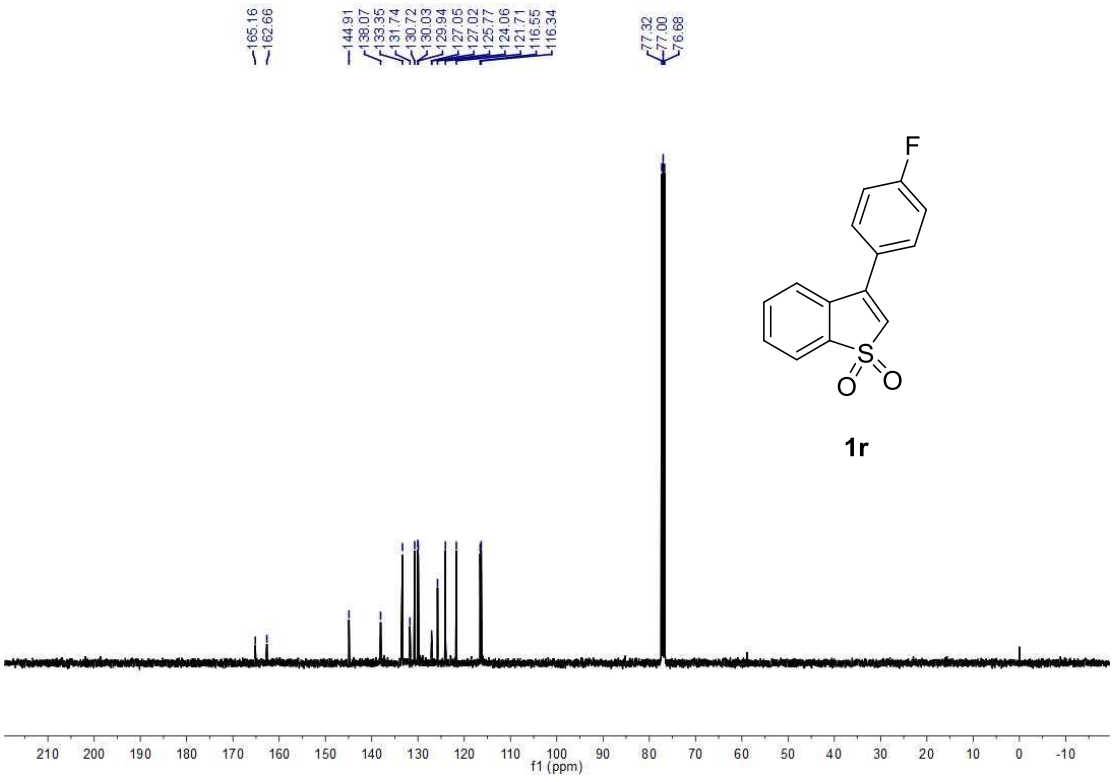
7.80
7.60
7.59
7.59
7.58
7.54
7.53
7.53
7.52
7.51
7.51
7.47
7.46
7.27
7.25
7.23
7.21
6.64
F
S
O
O
1r
1.00
2.01
2.14
1.05
1.93
0.97
f1 (ppm)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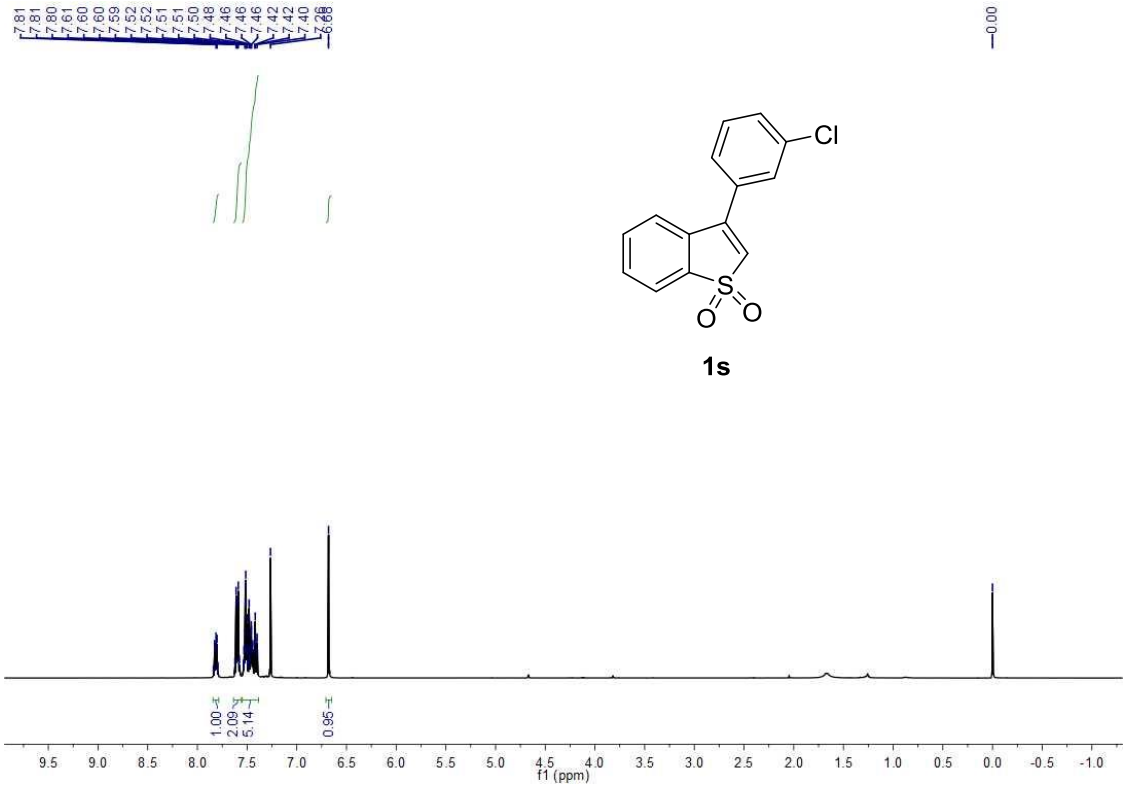
162.66
144.91
138.07
133.35
131.74
130.72
130.03
129.94
127.05
127.02
125.77
124.06
121.71
116.55
116.34
77.32
77.00
76.68
F
S
O
O
1r
f1 (ppm)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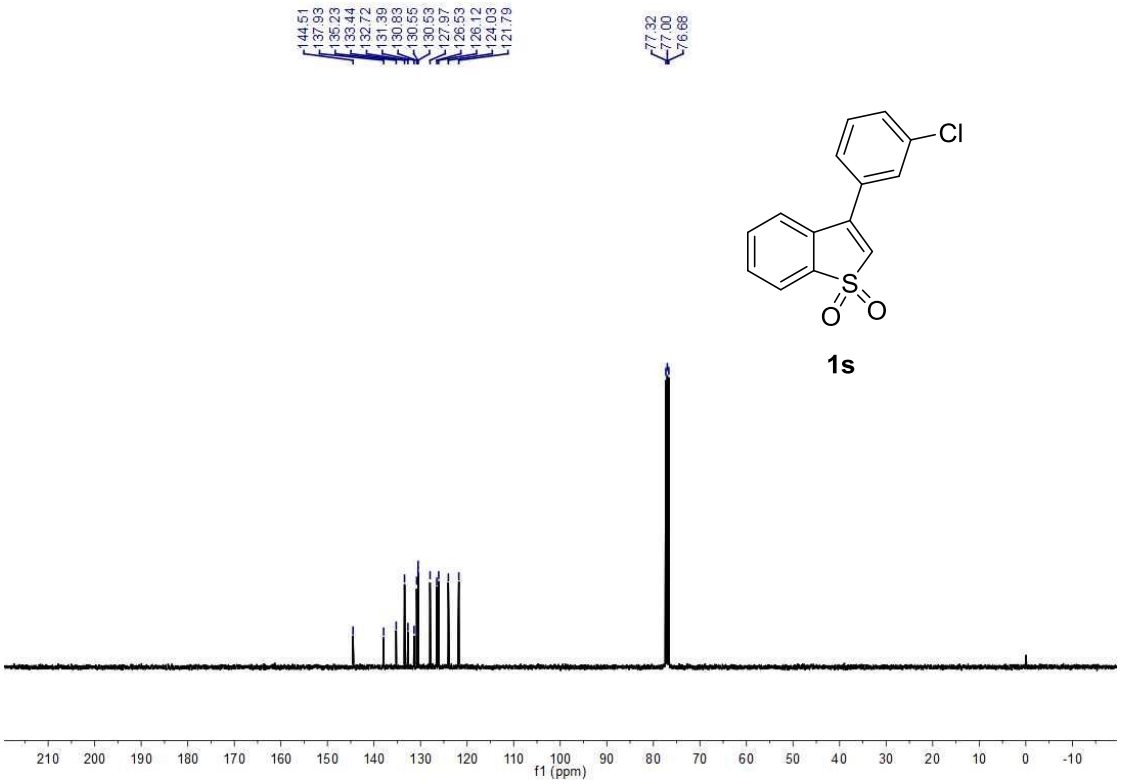
7.81
7.80
7.61
7.60
7.60
7.59
7.52
7.52
7.51
7.51
7.50
7.48
7.46
7.46
7.46
7.42
7.42
7.40
7.26
6.68
0.00
Cl
S
O
O
1s
1.00
2.09
5.14
0.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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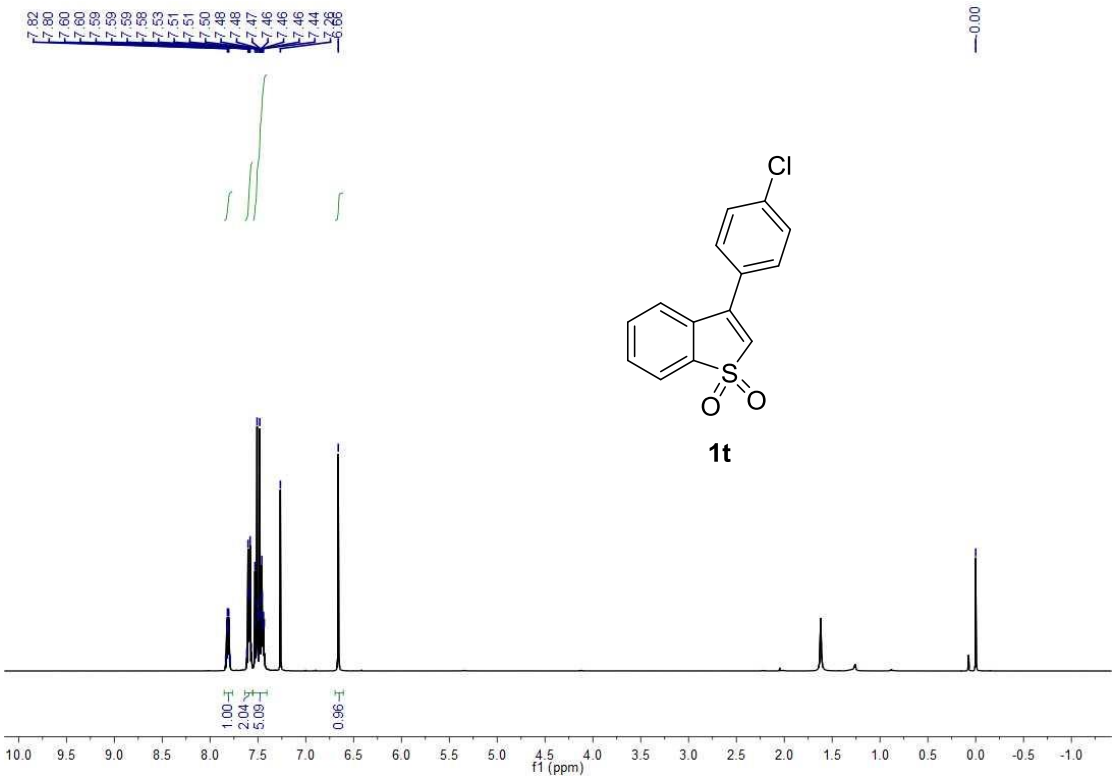
133.44
132.72
131.39
130.83
130.55
130.53
127.97
126.53
126.12
124.03
121.79
77.32
77.00
76.68
Cl
S
O
O
1s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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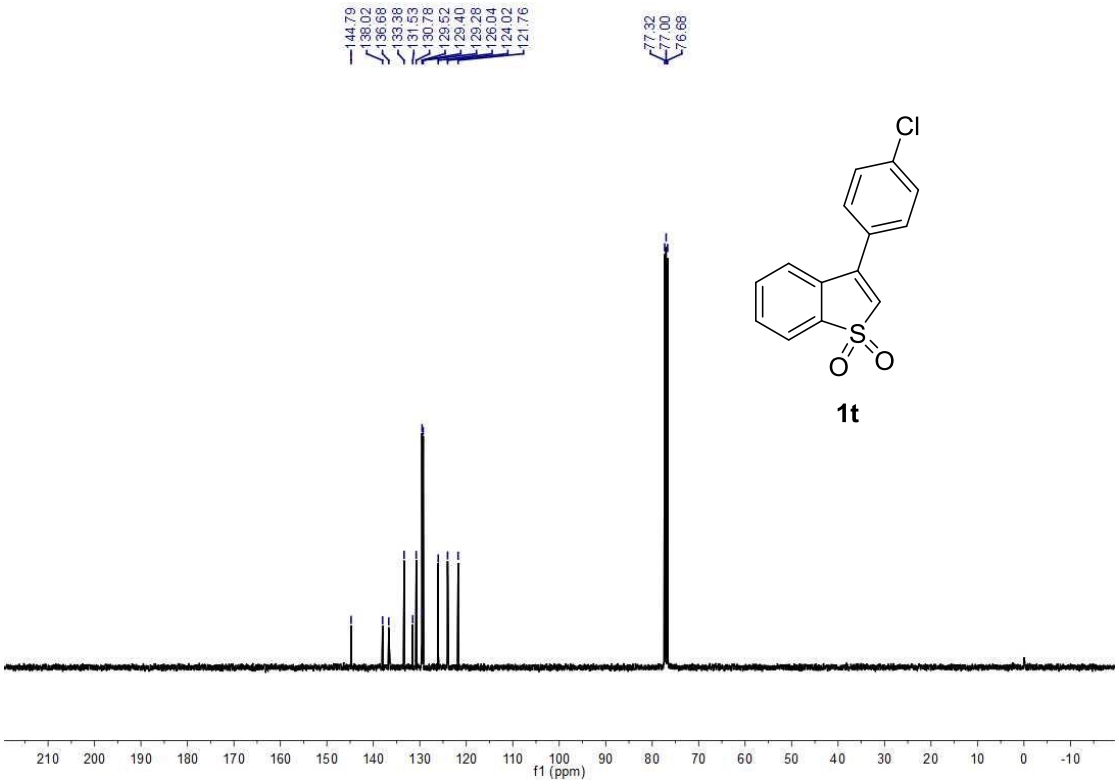
7.80
7.60
7.60
7.59
7.59
7.59
7.58
7.53
7.51
7.51
7.50
7.48
7.48
7.47
7.46
7.46
7.46
7.44
6.68
0.00
Cl
S
O
O
1t
1.00
2.04
5.09
0.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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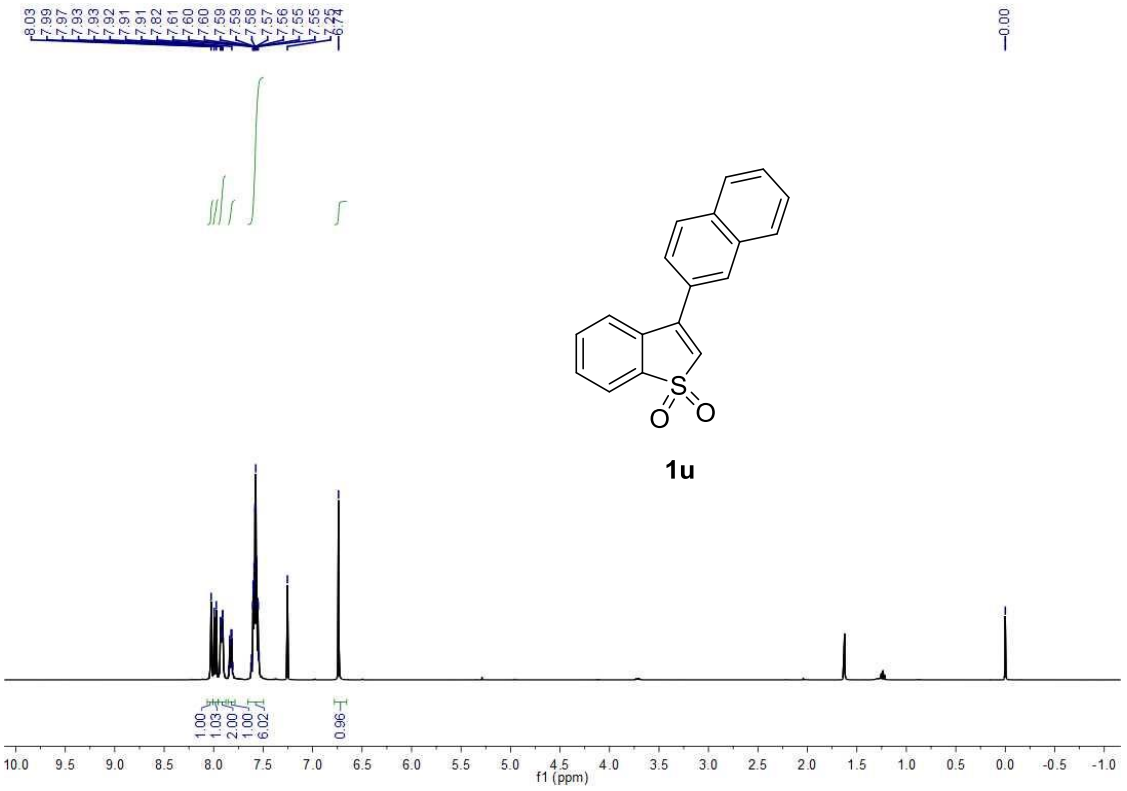
138.02
136.68
133.38
131.53
130.78
129.52
129.40
129.28
126.04
124.02
121.76
77.32
77.00
76.68
Cl
S
O
O
1t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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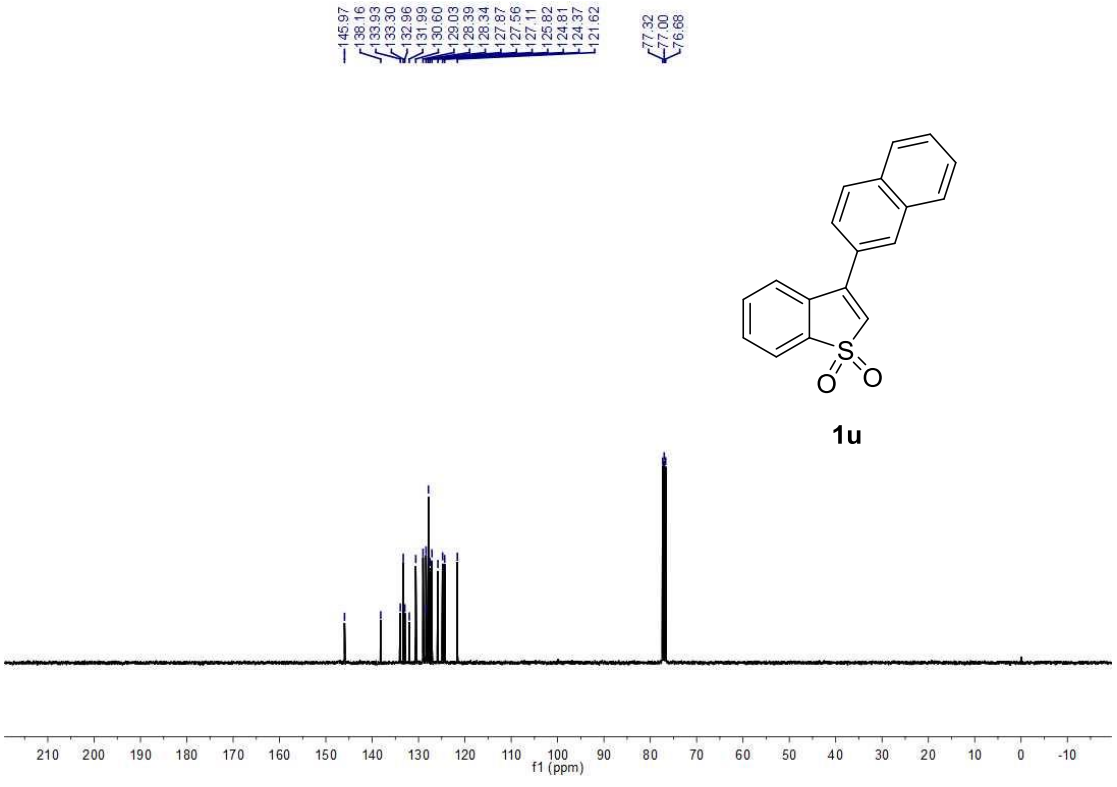
7.93
7.92
7.91
7.91
7.82
7.61
7.60
7.60
7.59
7.59
7.58
7.57
7.56
7.55
7.55
7.25
7.24
0.00
1.00
1.03
2.00
1.00
6.02
0.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

1u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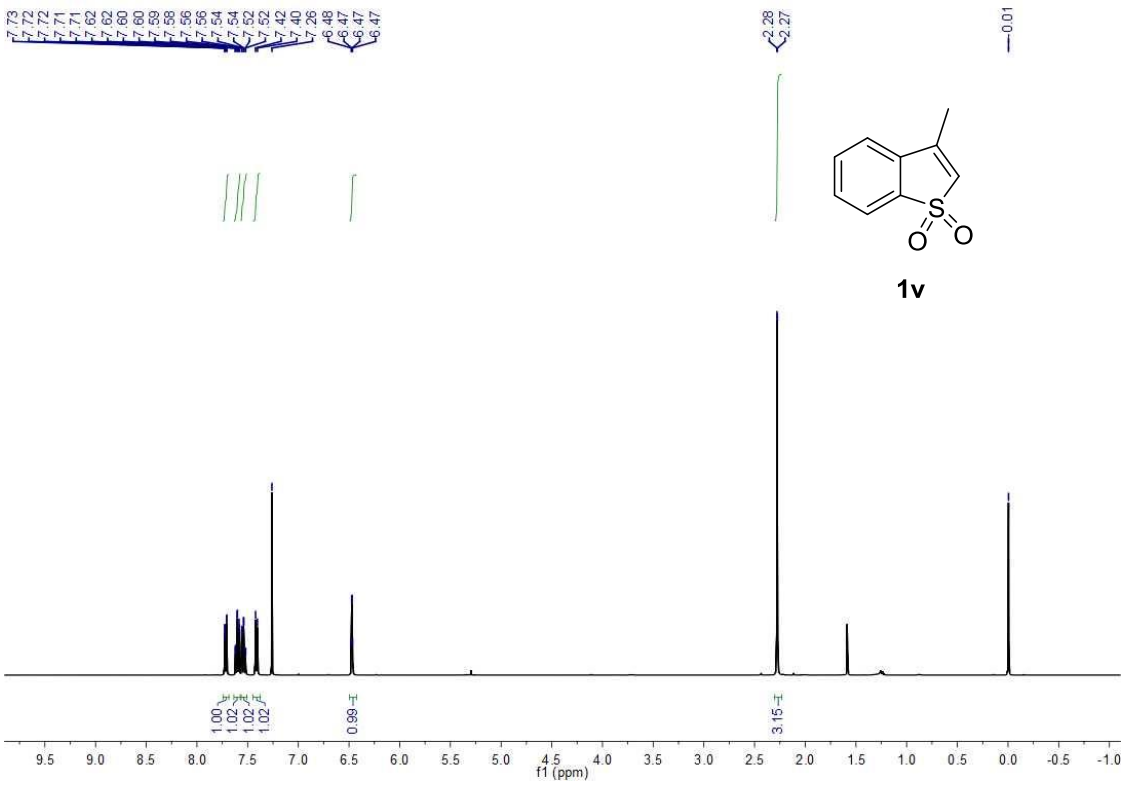
133.93
133.30
132.96
131.99
130.60
129.03
128.39
128.34
127.87
127.56
127.11
125.82
124.81
124.37
121.62
77.32
77.00
76.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1u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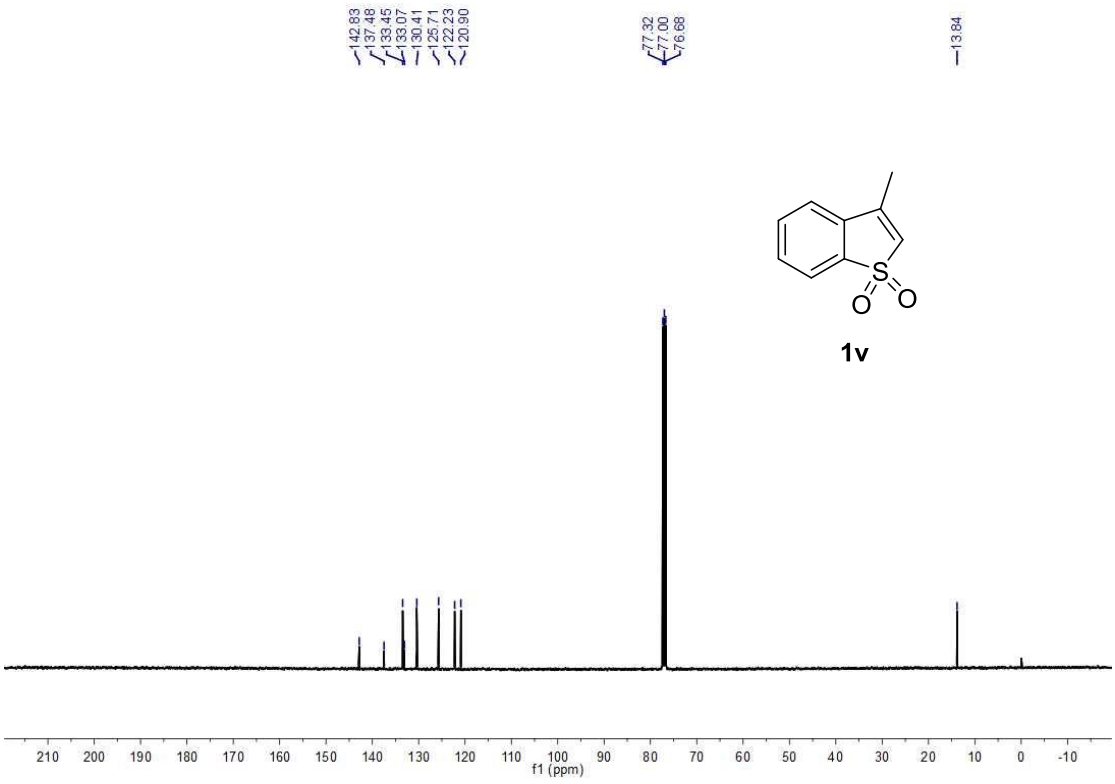
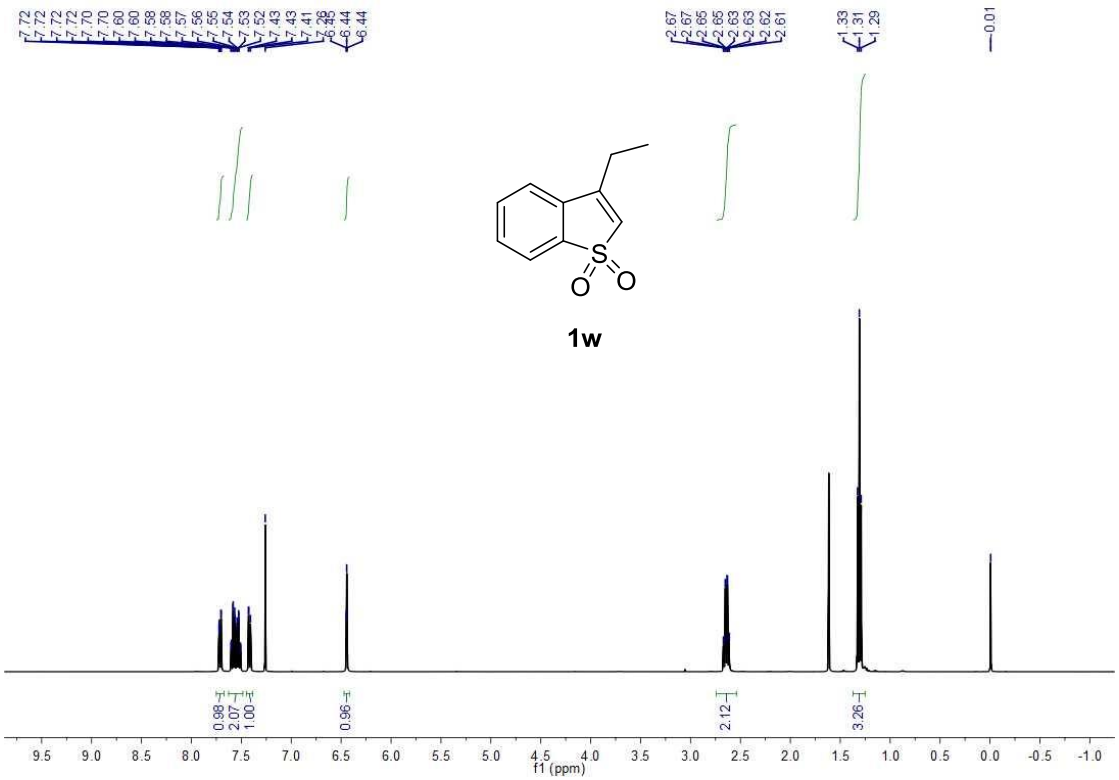
7.72
7.71
7.71
7.62
7.62
7.60
7.60
7.59
7.58
7.56
7.56
7.54
7.54
7.52
7.52
7.42
7.40
7.26
6.48
6.47
6.47
6.47
2.28
2.27
0.01
1.00
1.02
1.02
1.02
0.99
3.15
f1 (ppm)

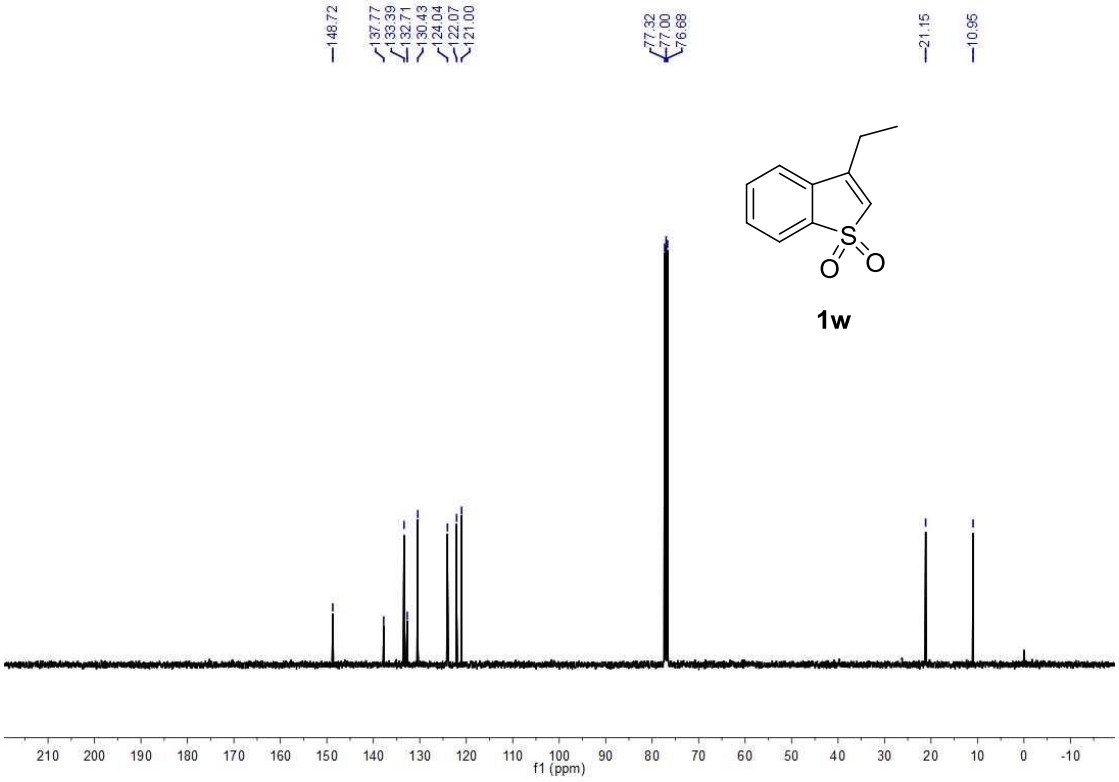
1v


142.83
137.48
133.45
133.07
130.41
125.71
122.23
120.90
77.32
77.00
76.68
13.84
f1 (ppm)

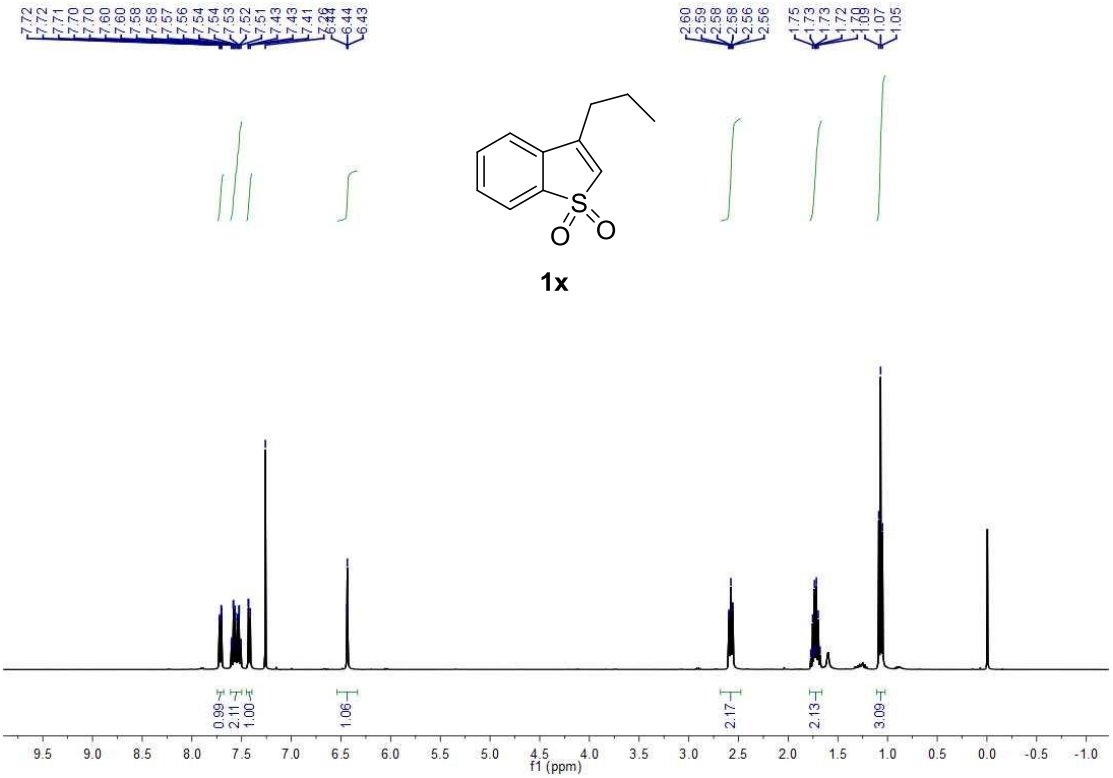
1v


7.72
7.72
7.72
7.72
7.70
7.70
7.60
7.60
7.58
7.58
7.57
7.56
7.55
7.54
7.53
7.52
7.43
7.43
7.41
7.38
6.45
6.44
6.44
2.67
2.67
2.65
2.65
2.63
2.63
2.62
2.61
1.33
1.31
1.29
0.01
0.98
2.07
1.00
0.96
2.12
3.26
f1 (ppm)

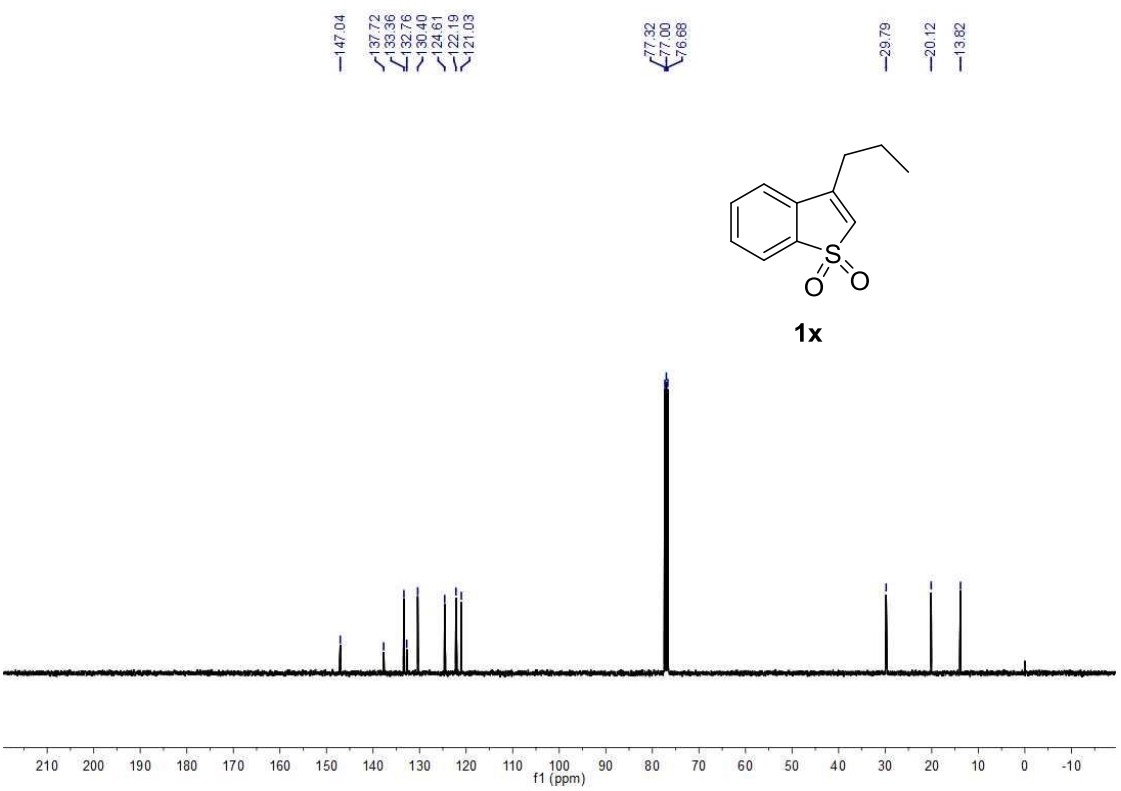
1w


148.72
137.77
133.39
132.71
130.43
124.04
122.07
121.00
77.32
77.00
76.68
21.15
10.95
f1 (ppm)

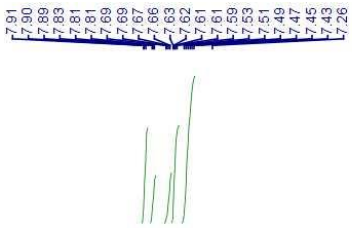
1w

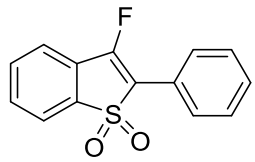

7.72
7.72
7.71
7.70
7.70
7.60
7.60
7.58
7.58
7.57
7.56
7.54
7.54
7.53
7.52
7.51
7.43
7.43
7.41
6.44
6.43
2.60
2.59
2.58
2.58
2.56
2.56
1.75
1.73
1.73
1.72
1.09
1.07
1.05
S
O
O
0.99
2.11
1.00
1.06
2.17
2.13
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

1x

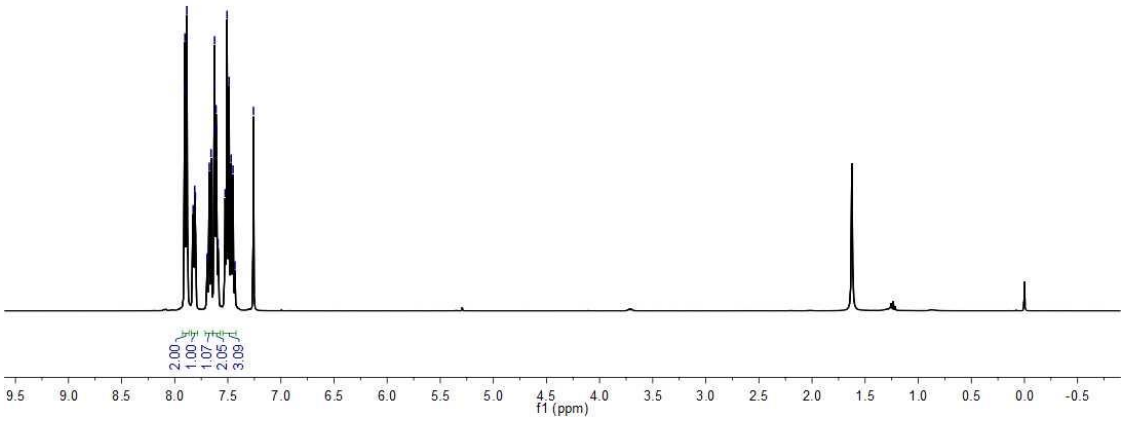

147.04
137.72
133.36
132.76
130.40
124.61
122.19
121.03
77.32
77.00
76.68
29.79
20.12
13.82
S
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1x

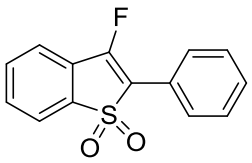

7.91
7.90
7.89
7.83
7.81
7.81
7.69
7.69
7.67
7.66
7.63
7.62
7.61
7.61
7.59
7.53
7.51
7.49
7.47
7.45
7.43
7.26


F
S
O
O

3a

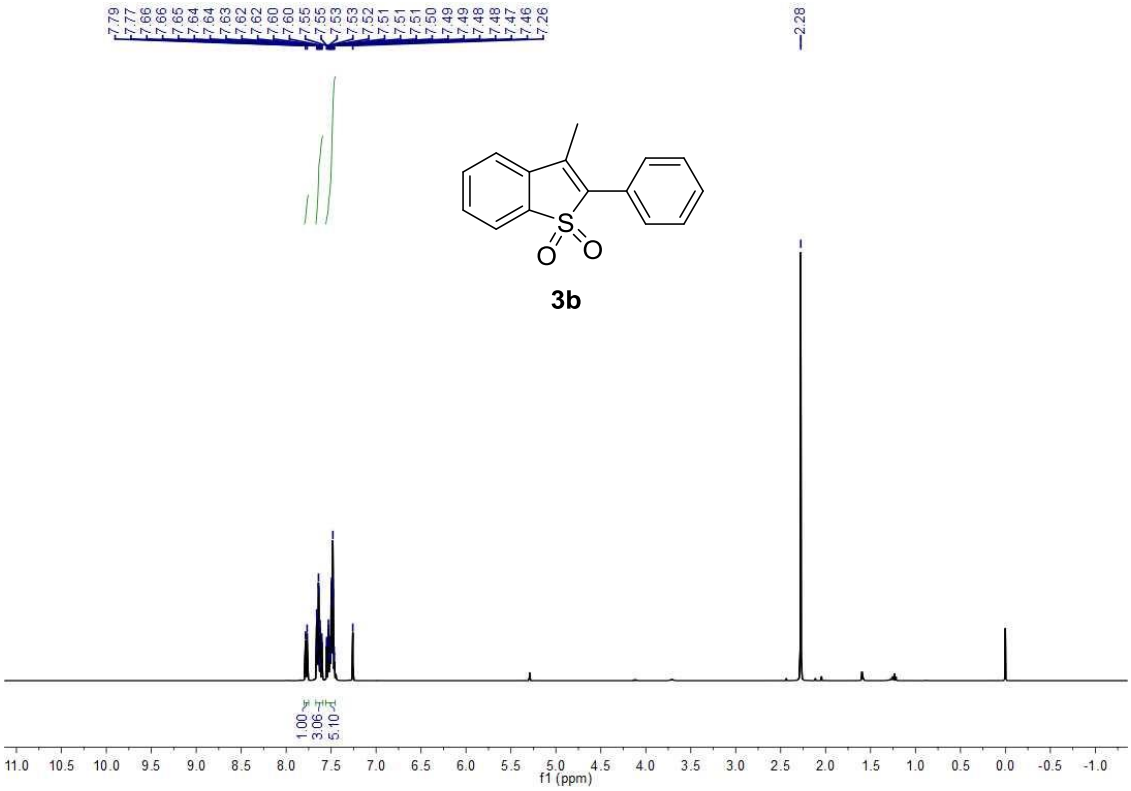

2.00
1.00
1.07
2.05
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


157.41
154.51
137.51
137.48
133.72
131.15
129.97
129.95
129.20
127.57
127.52
127.00
126.72
124.49
124.45
121.19
121.16
120.84
120.78
120.53
77.32
77.00
76.68


F
S
O
O

3a

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.77
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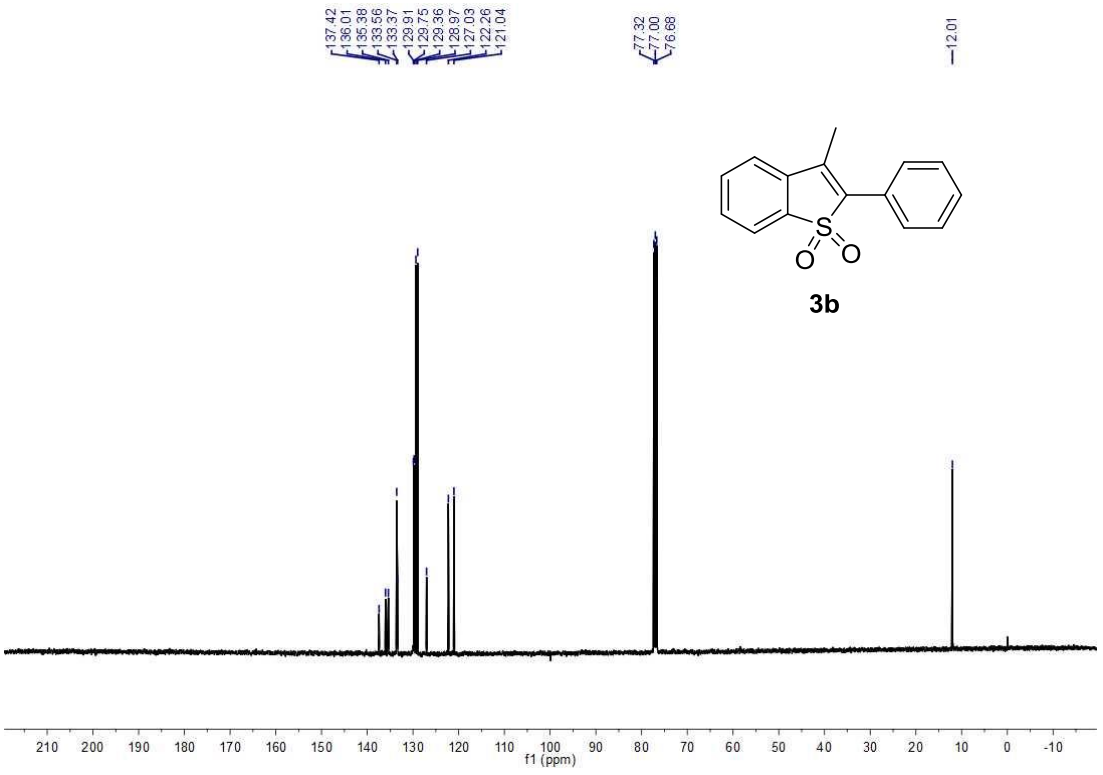
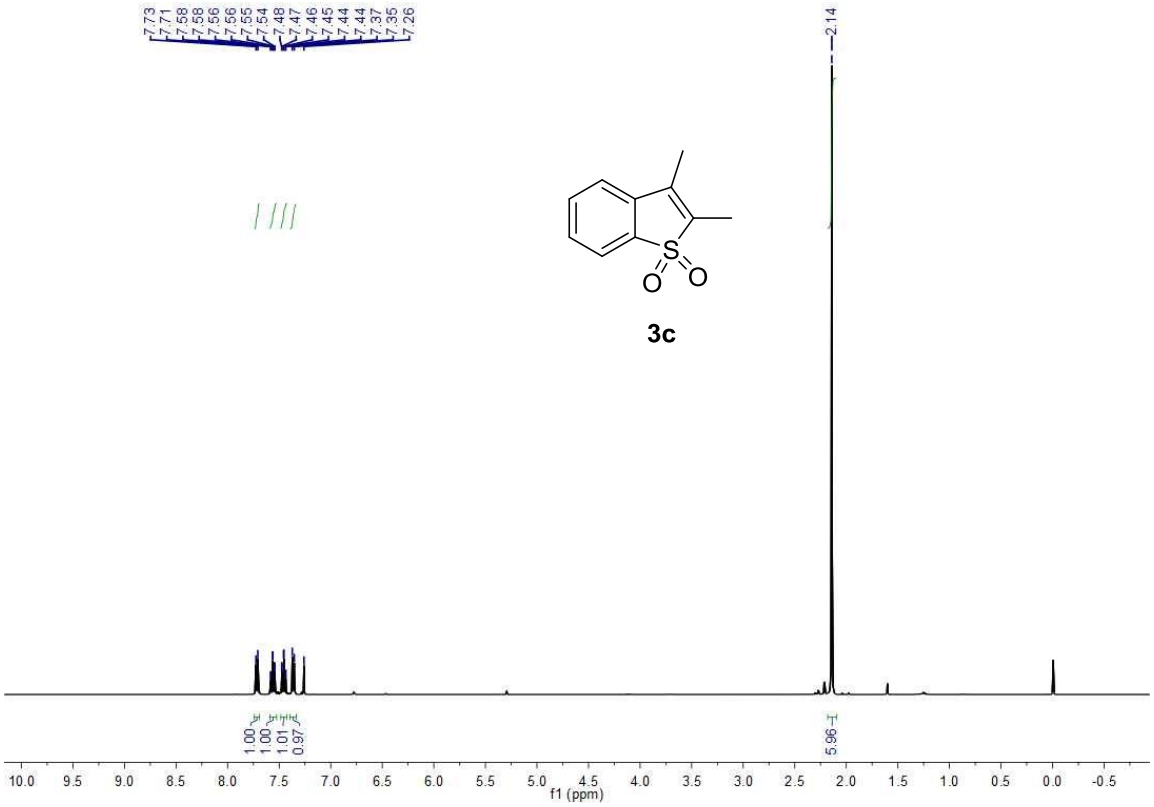
7.66
7.65
7.64
7.64
7.63
7.62
7.62
7.60
7.60
7.55
7.55
7.53
7.53
7.52
7.51
7.51
7.51
7.50
7.49
7.49
7.48
7.48
7.47
7.46
7.26
2.28
1.00
3.06
5.10
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

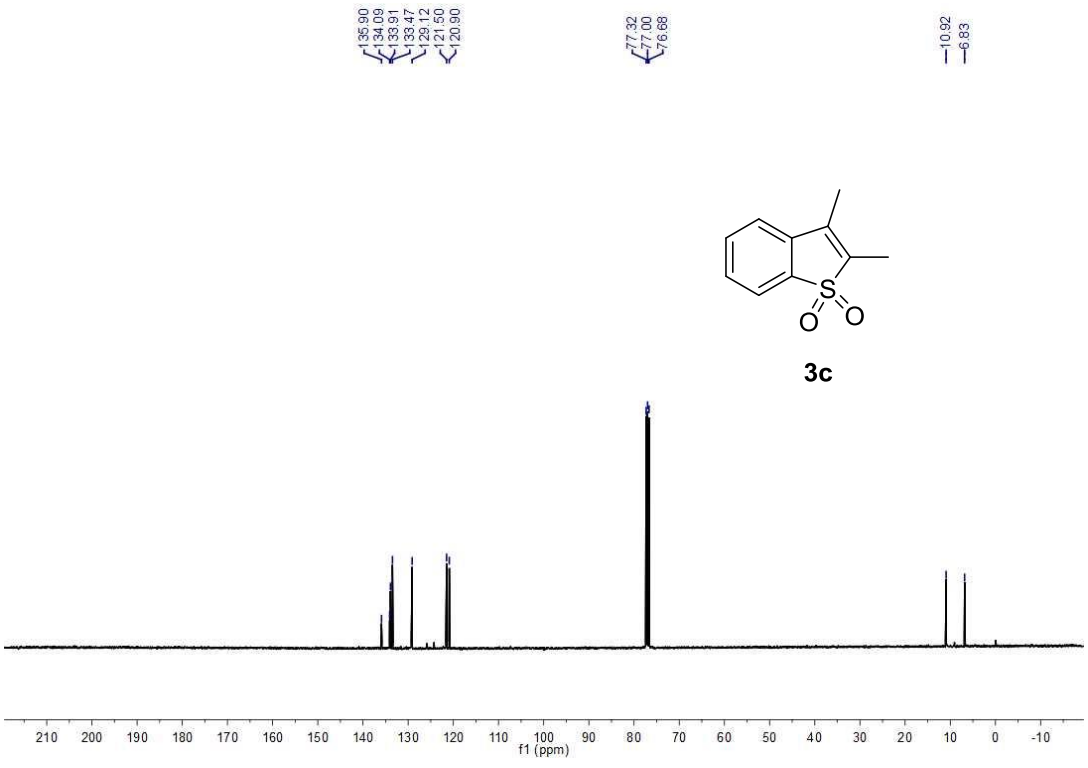
3b


137.42
136.01
135.38
133.56
133.37
129.91
129.75
129.36
128.97
127.03
122.26
121.04
77.32
77.00
76.68
12.01
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

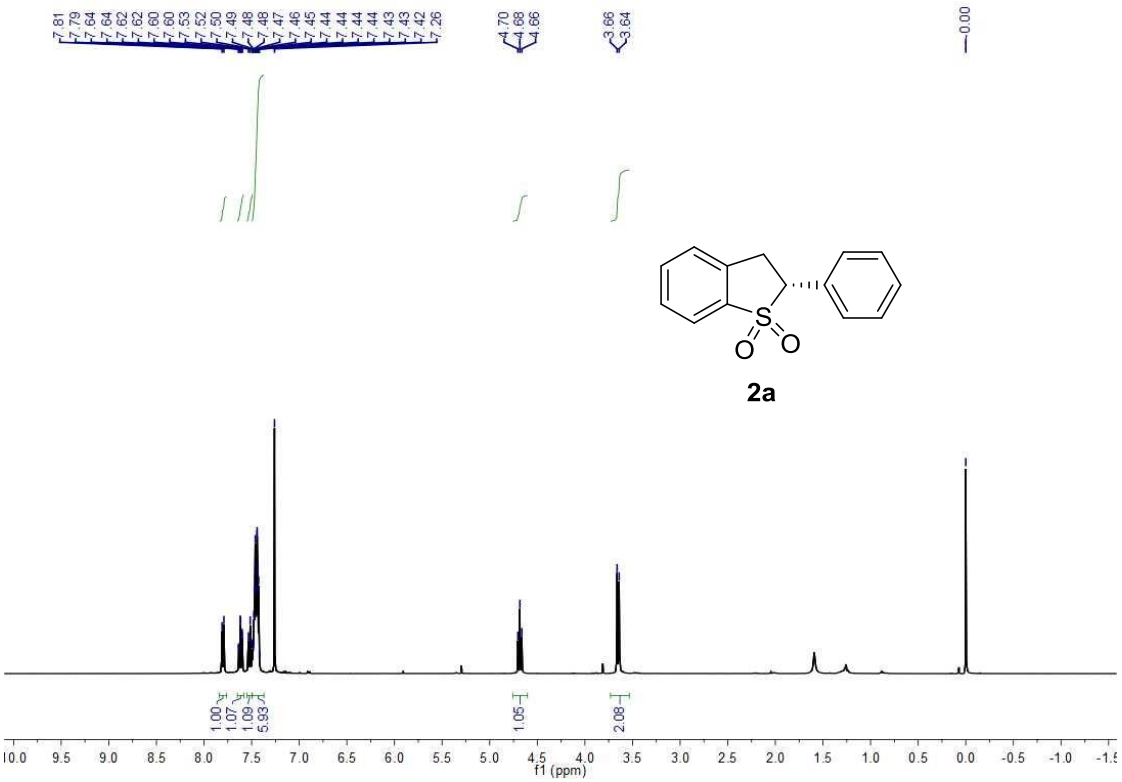
3b


7.73
7.71
7.58
7.58
7.56
7.56
7.55
7.54
7.48
7.47
7.46
7.45
7.44
7.44
7.37
7.35
7.26
2.14
1.00
1.00
1.01
0.97
5.96
f1 (ppm)

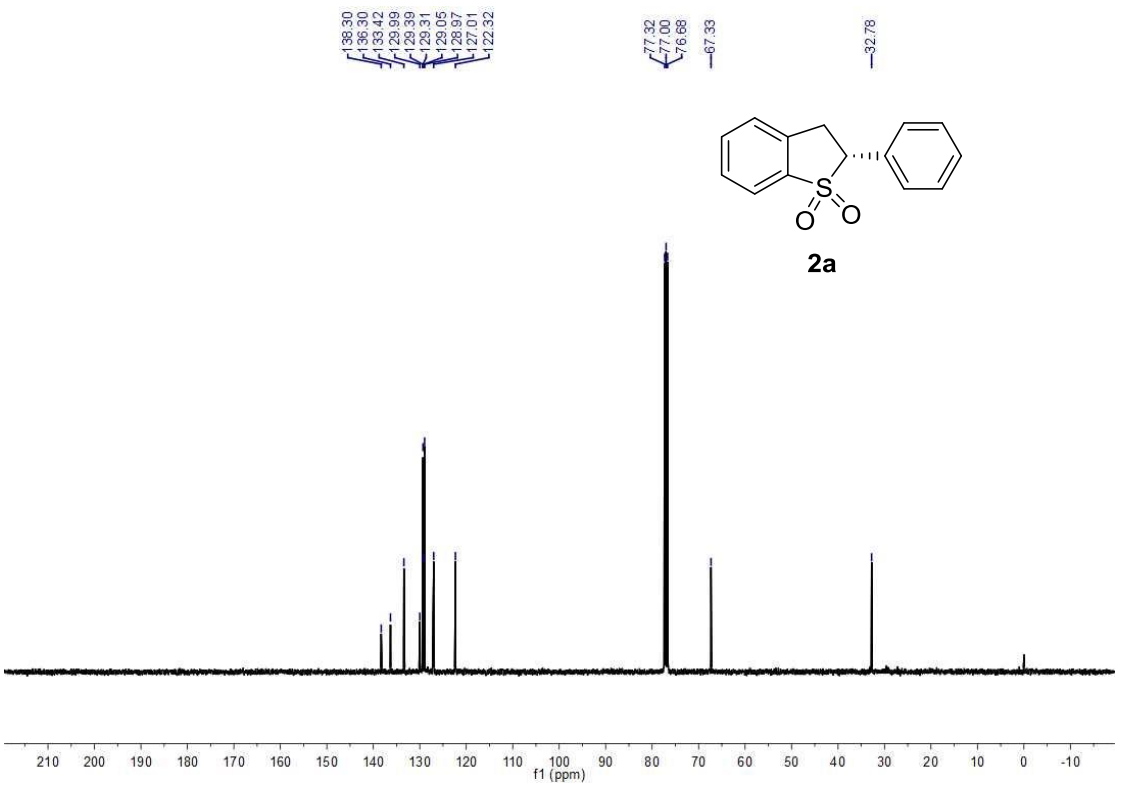
3c


135.90
134.09
133.91
133.47
129.12
121.50
120.90
77.32
77.00
76.68
10.92
6.83
f1 (ppm)

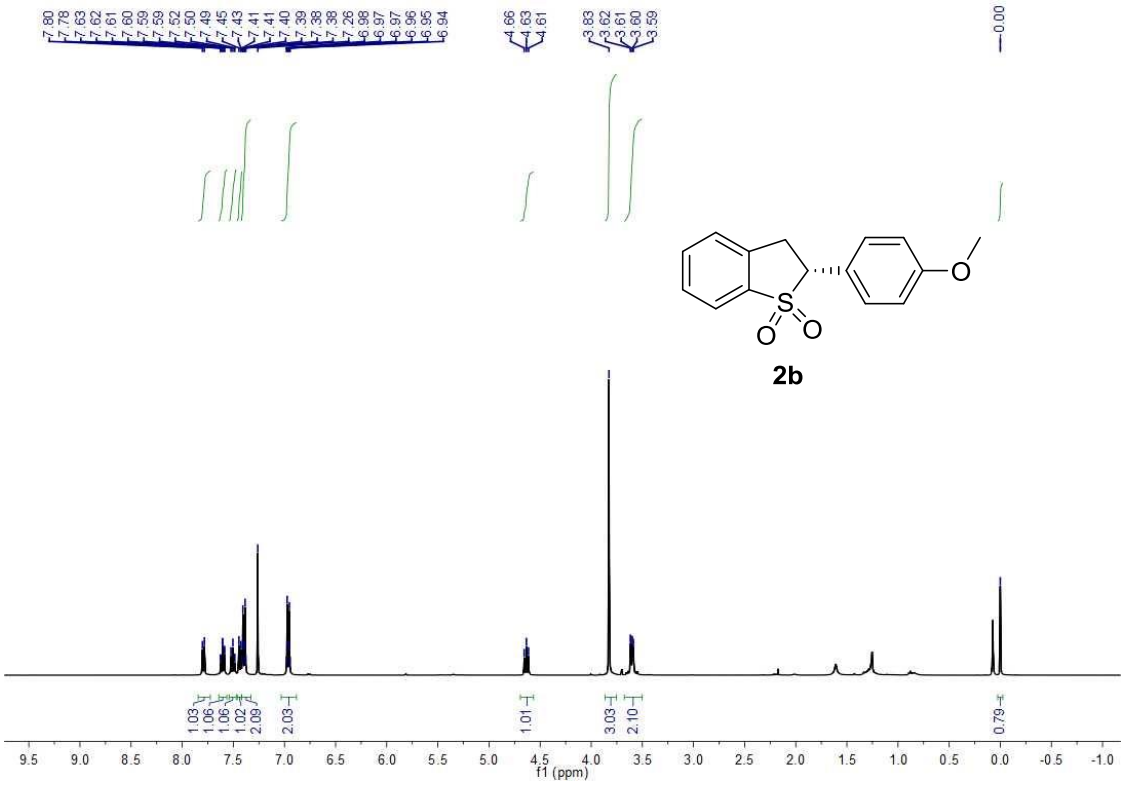
3c


7.81
7.79
7.64
7.64
7.62
7.62
7.60
7.60
7.53
7.52
7.50
7.49
7.48
7.48
7.47
7.46
7.45
7.44
7.44
7.44
7.44
7.43
7.43
7.42
7.26
4.70
4.68
4.66
3.66
3.64
0.00
1.00
1.07
1.09
5.93
1.05
2.08
f1 (ppm)

2a


138.30
136.30
133.42
129.99
129.39
129.31
129.05
128.97
127.01
122.32
77.32
77.00
76.68
67.33
32.78
f1 (ppm)

2a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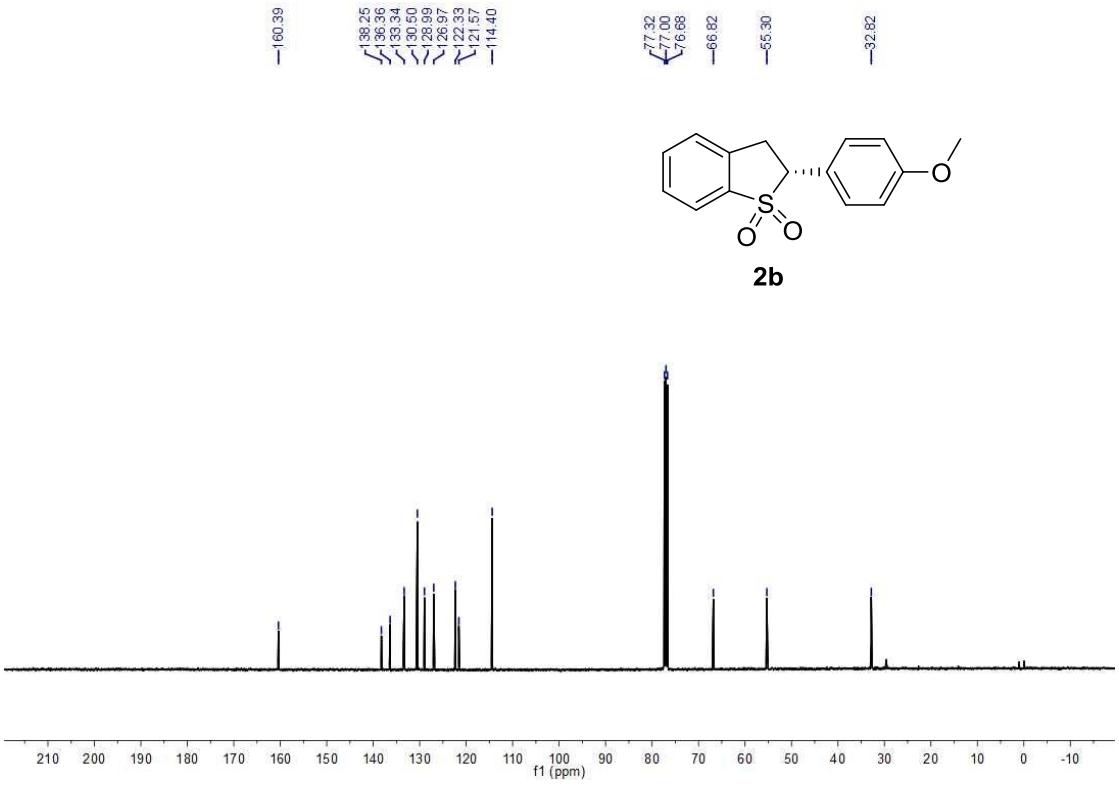
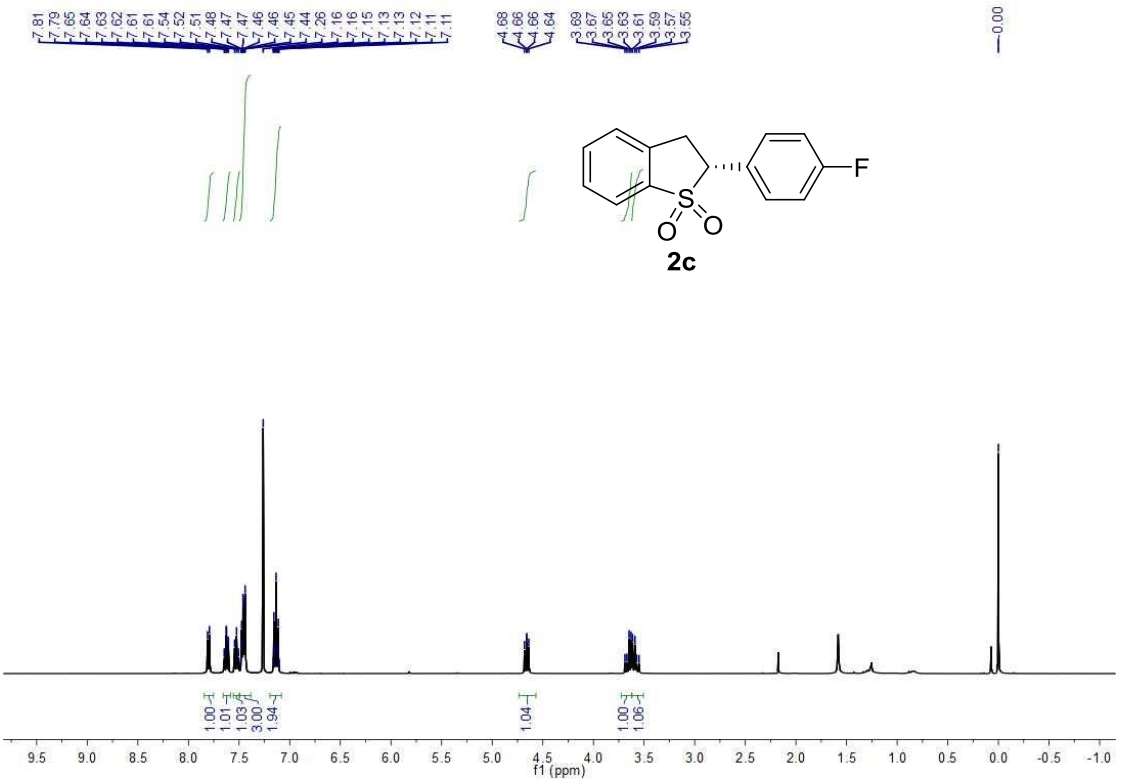
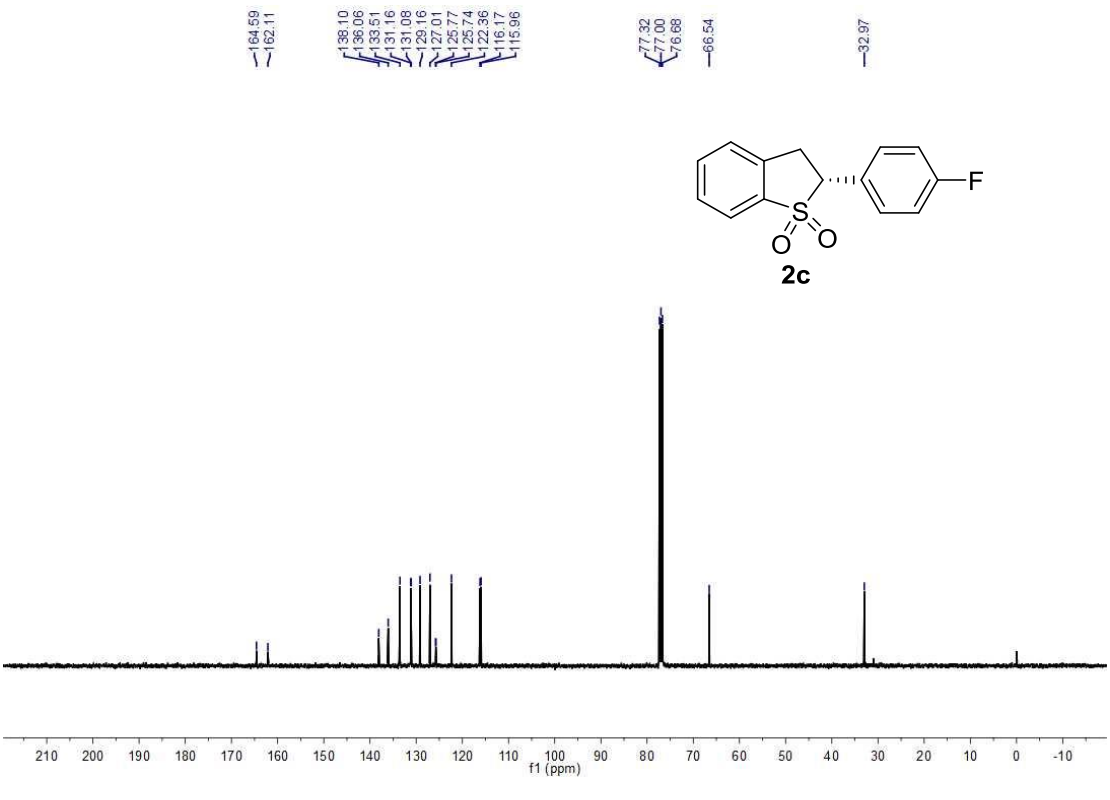
7.78
7.63
7.62
7.61
7.60
7.59
7.59
7.52
7.50
7.49
7.45
7.43
7.41
7.41
7.40
7.39
7.38
7.38
7.26
6.98
6.97
6.97
6.96
6.95
6.94
4.66
4.63
4.61
3.83
3.62
3.61
3.60
3.59
0.00
O
S
O
O
1.03
1.06
1.06
1.02
2.09
2.03
1.01
3.03
2.10
0.79
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

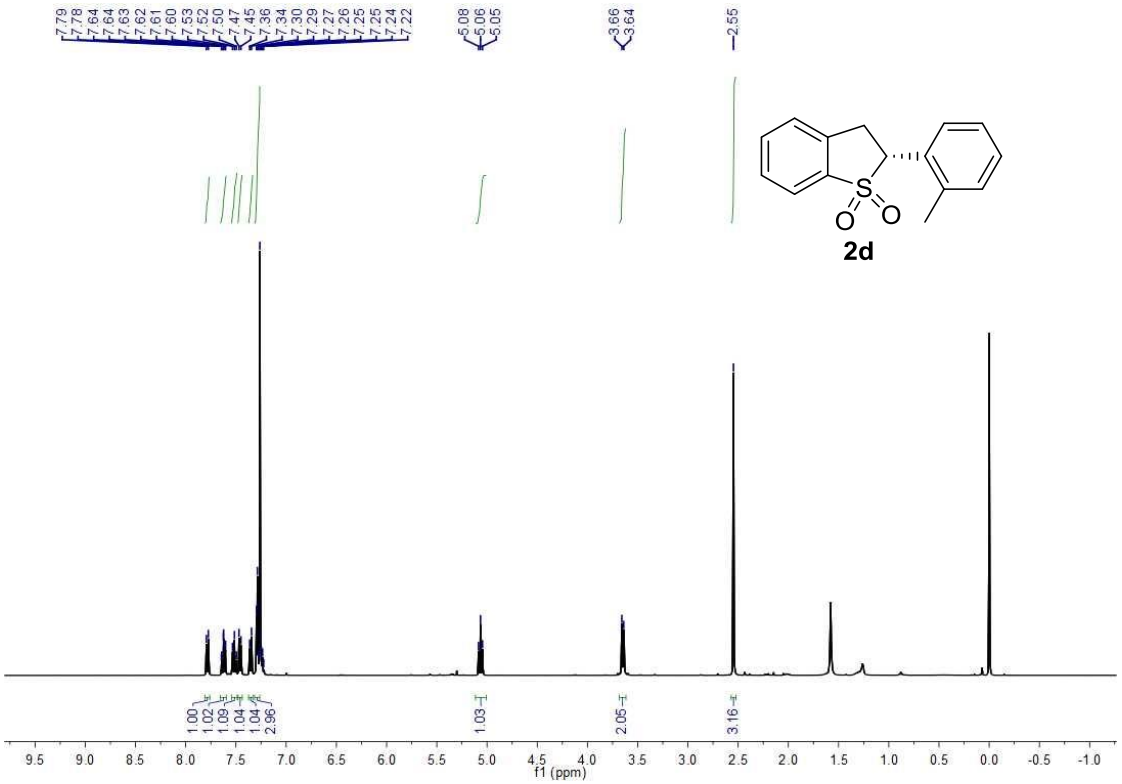
2b


160.39
138.25
136.36
133.34
130.50
128.99
126.97
122.33
121.57
114.40
77.32
77.00
76.68
66.82
55.30
32.82
O
S
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

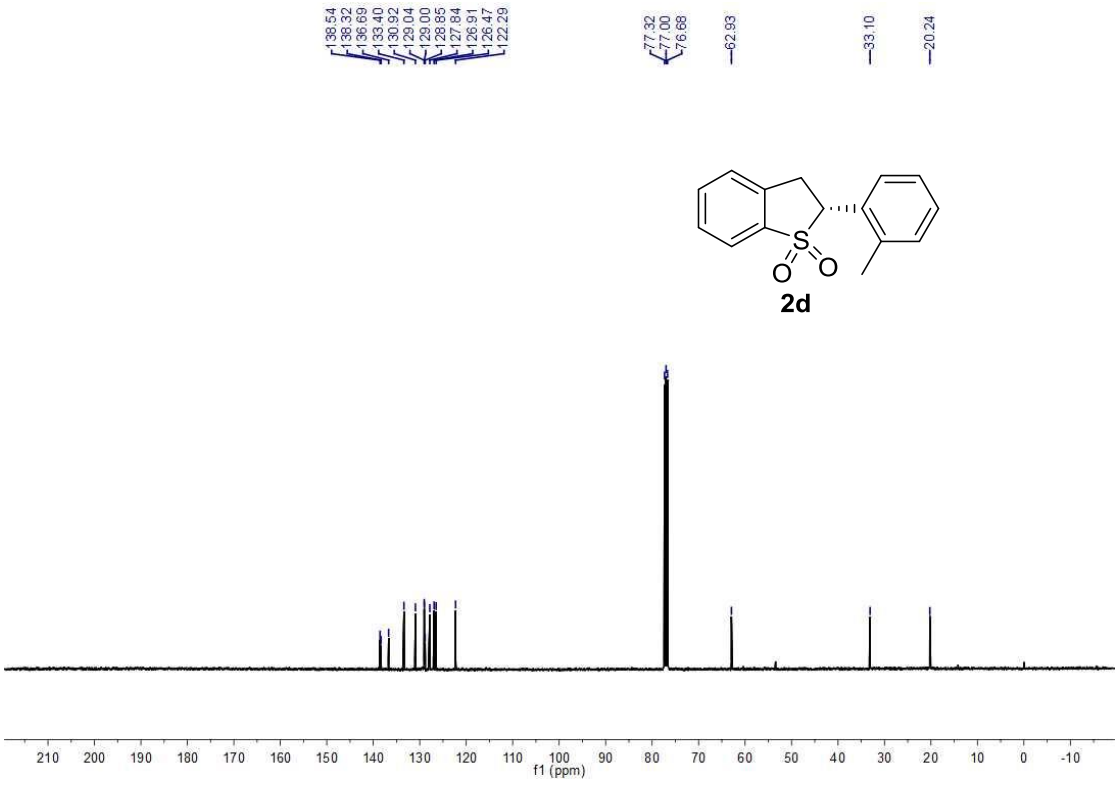
2b


7.81
7.79
7.65
7.64
7.63
7.62
7.61
7.61
7.54
7.52
7.51
7.48
7.47
7.47
7.46
7.46
7.45
7.44
7.26
7.16
7.16
7.15
7.13
7.12
7.11
7.11
4.68
4.66
4.66
4.64
3.69
3.67
3.65
3.63
3.61
3.59
3.57
3.55
0.00
F
S
O
O
2c
1.00
1.01
3.00
1.94
1.04
1.00
1.06
f1 (ppm)

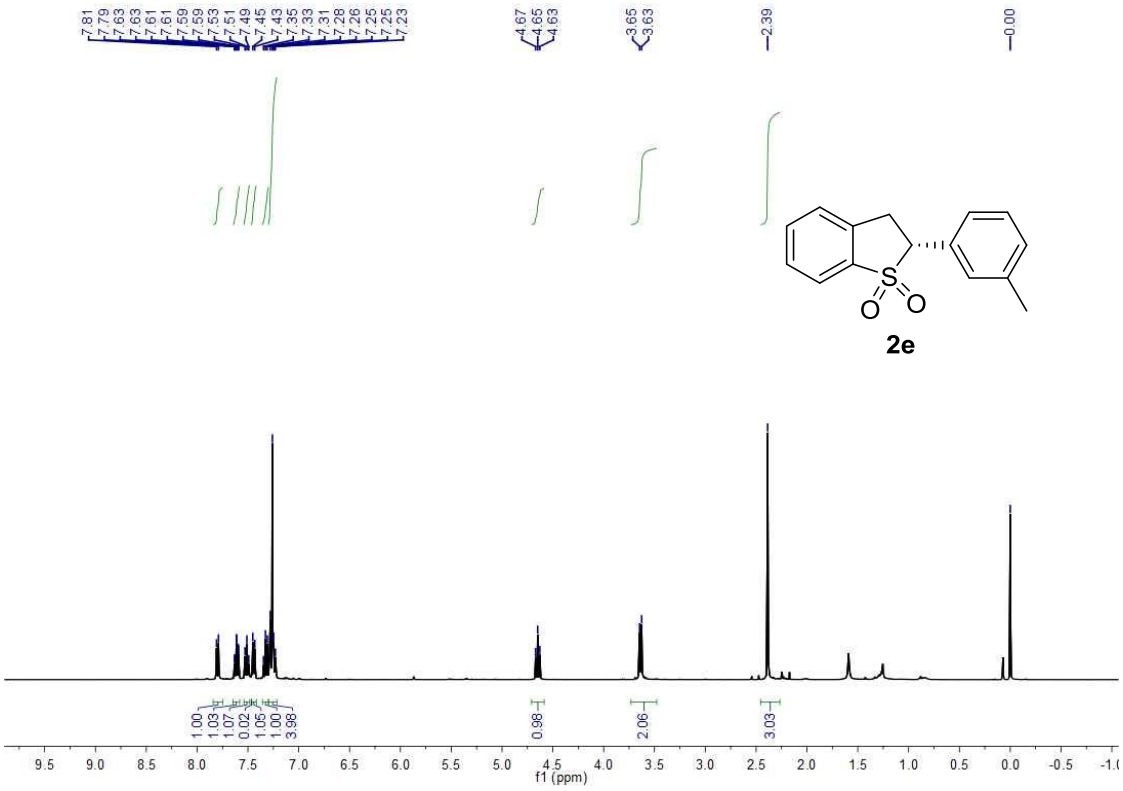

164.59
162.11
138.10
136.06
133.51
131.16
131.08
129.16
127.01
125.77
125.74
122.36
116.17
115.96
77.32
77.00
76.68
66.54
32.97
F
S
O
O
2c
f1 (ppm)


7.79
7.78
7.64
7.64
7.63
7.62
7.61
7.60
7.53
7.52
7.50
7.47
7.45
7.36
7.34
7.30
7.29
7.27
7.26
7.25
7.25
7.24
7.22
5.08
5.06
5.05
3.66
3.64
2.55
1.00
1.02
1.09
1.04
1.04
2.96
1.03
2.05
3.16
f1 (ppm)

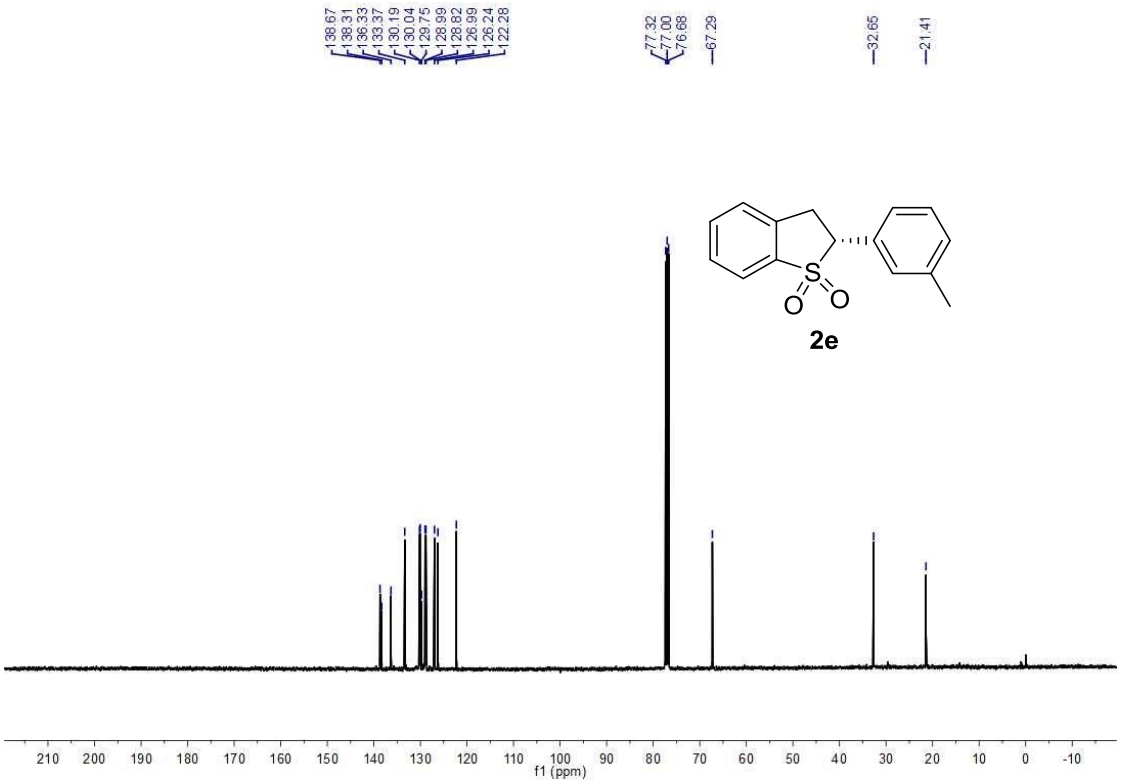
2d


138.54
138.32
136.69
133.40
130.92
129.04
129.00
128.85
127.84
126.91
126.47
122.29
77.32
77.00
76.68
62.93
33.10
20.24
f1 (ppm)

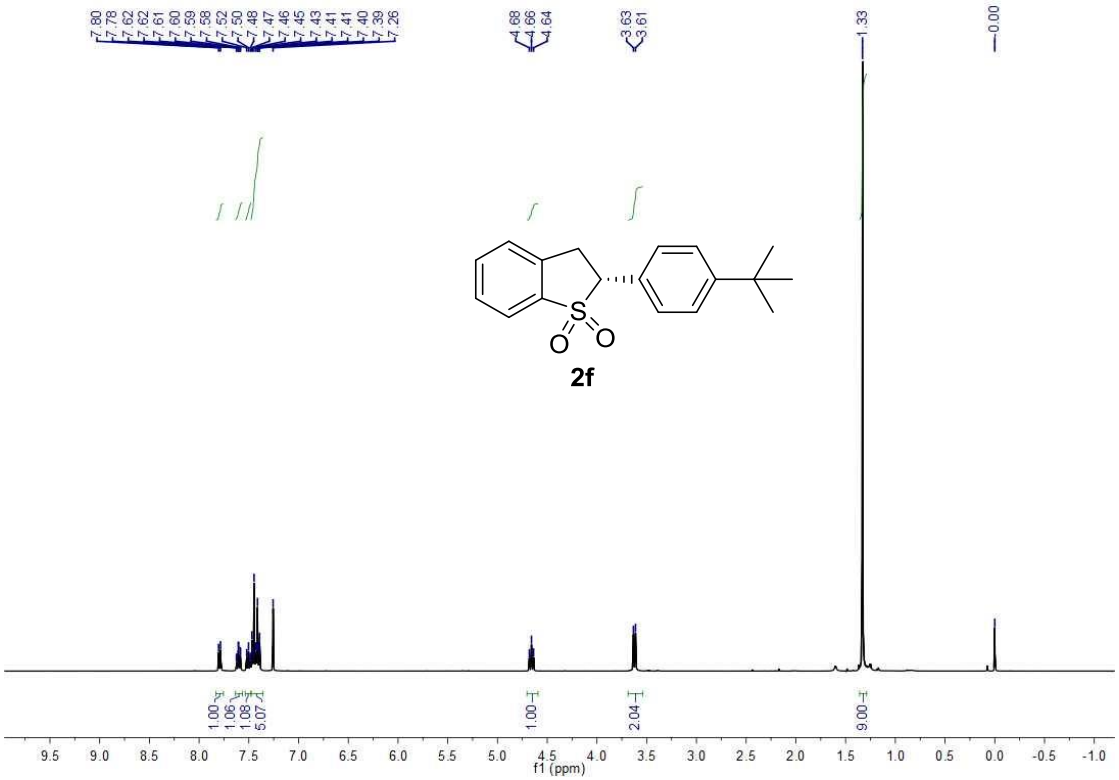
2d


7.81
7.79
7.63
7.63
7.61
7.61
7.59
7.59
7.53
7.51
7.49
7.45
7.43
7.35
7.33
7.31
7.28
7.26
7.25
7.25
7.23
4.67
4.65
4.63
3.65
3.63
2.39
0.00
1.00
1.03
1.07
0.02
1.05
1.00
3.98
0.98
2.06
3.03
f1 (ppm)

2e


138.67
138.31
136.33
133.37
130.19
130.04
129.75
128.99
128.82
126.99
126.24
122.28
77.32
77.00
76.68
67.29
32.65
21.41
f1 (ppm)

2e


7.80
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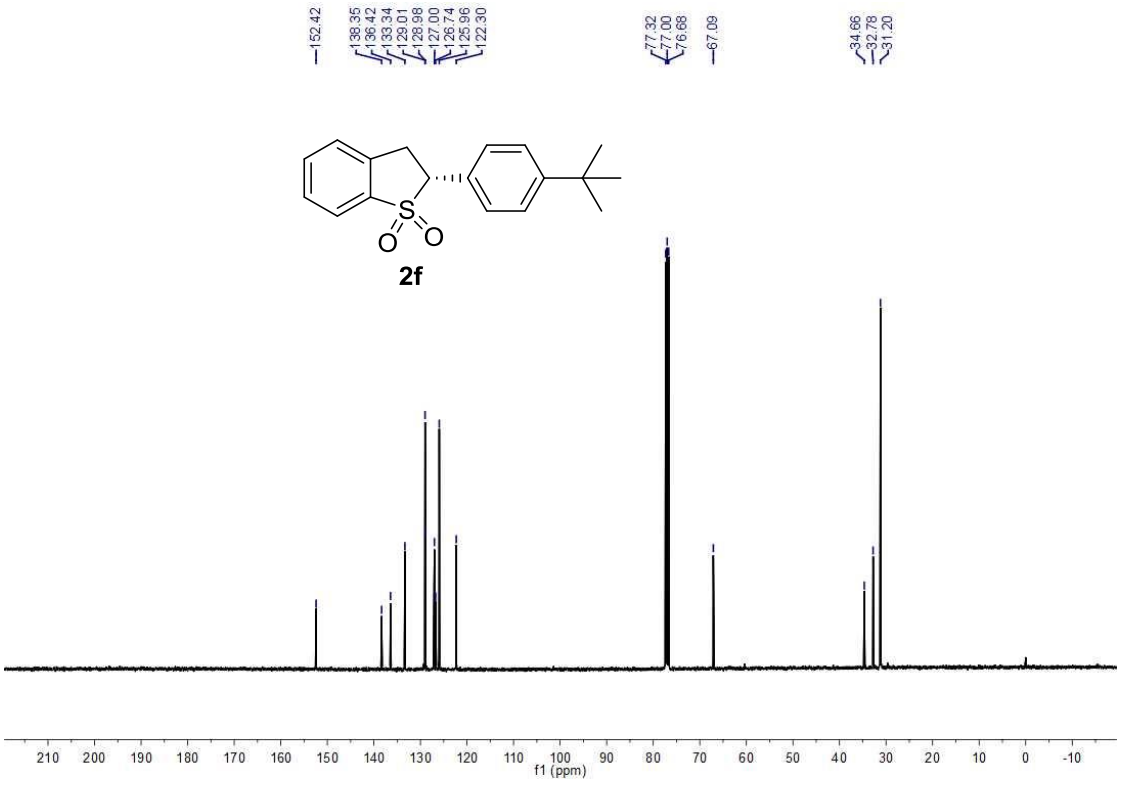
7.62
7.62
7.61
7.60
7.59
7.58
7.52
7.50
7.48
7.47
7.46
7.45
7.43
7.41
7.41
7.40
7.39
7.26
4.68
4.66
4.64
3.63
3.61
1.33
0.00
1.00
1.06
1.08
5.07
1.00
2.04
9.00
f1 (ppm)

2f


152.42
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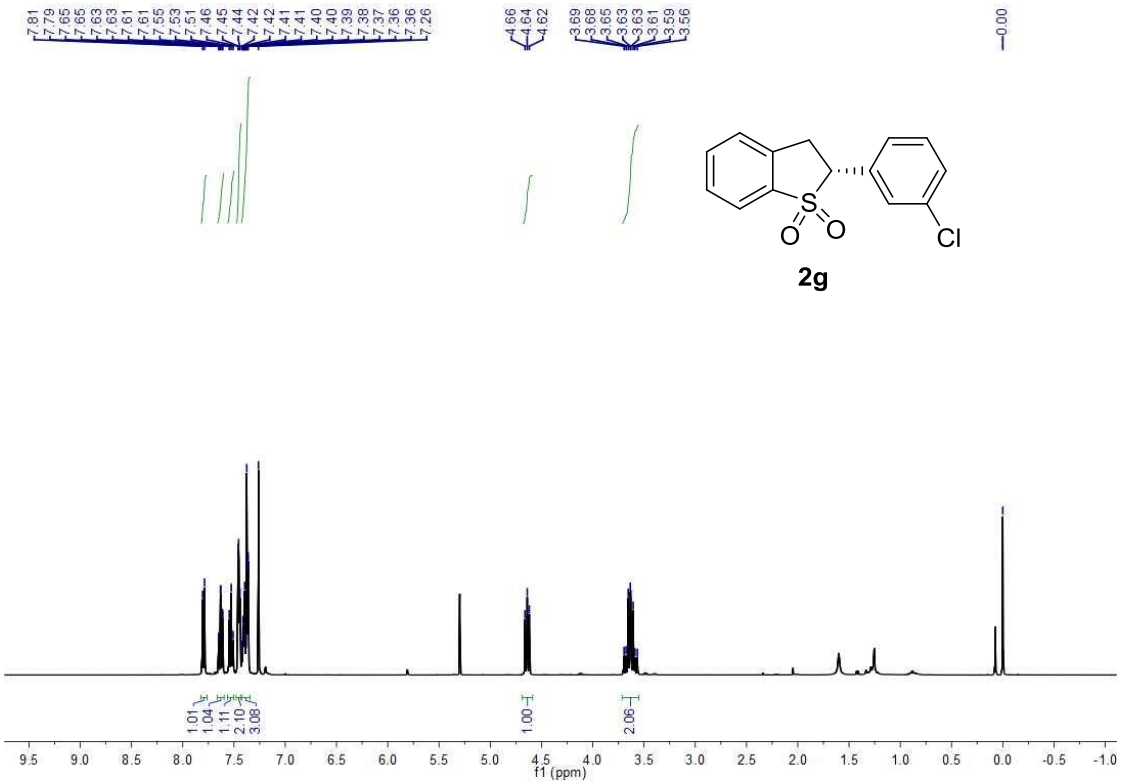
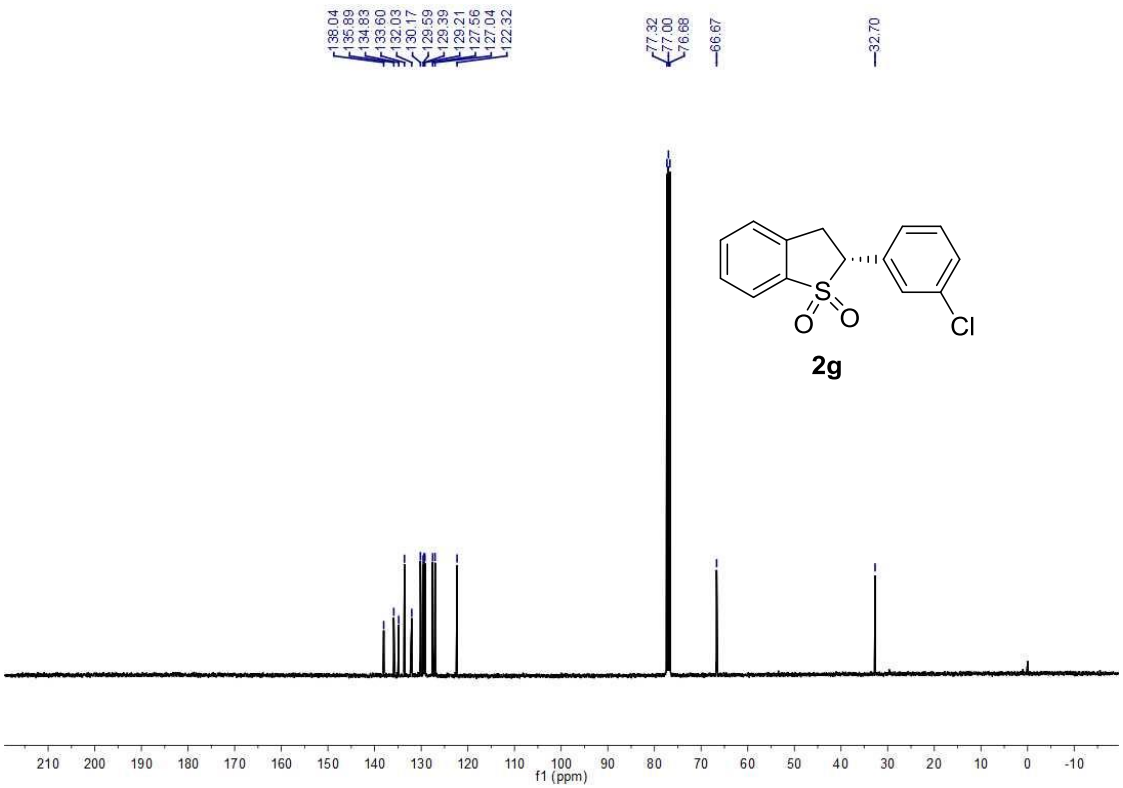
133.34
129.01
128.98
127.00
126.74
125.96
122.30
77.32
77.00
76.68
67.09
34.66
32.78
31.20
f1 (ppm)

2f


7.81
7.79
7.65
7.65
7.63
7.63
7.61
7.61
7.55
7.53
7.51
7.46
7.45
7.44
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.38
7.37
7.36
7.36
7.26
4.66
4.64
4.62
3.69
3.68
3.65
3.63
3.63
3.61
3.59
3.56
0.00
S
O
O
Cl
1.01
1.04
1.11
2.10
3.08
1.00
2.06
f1 (ppm)

2g


138.04
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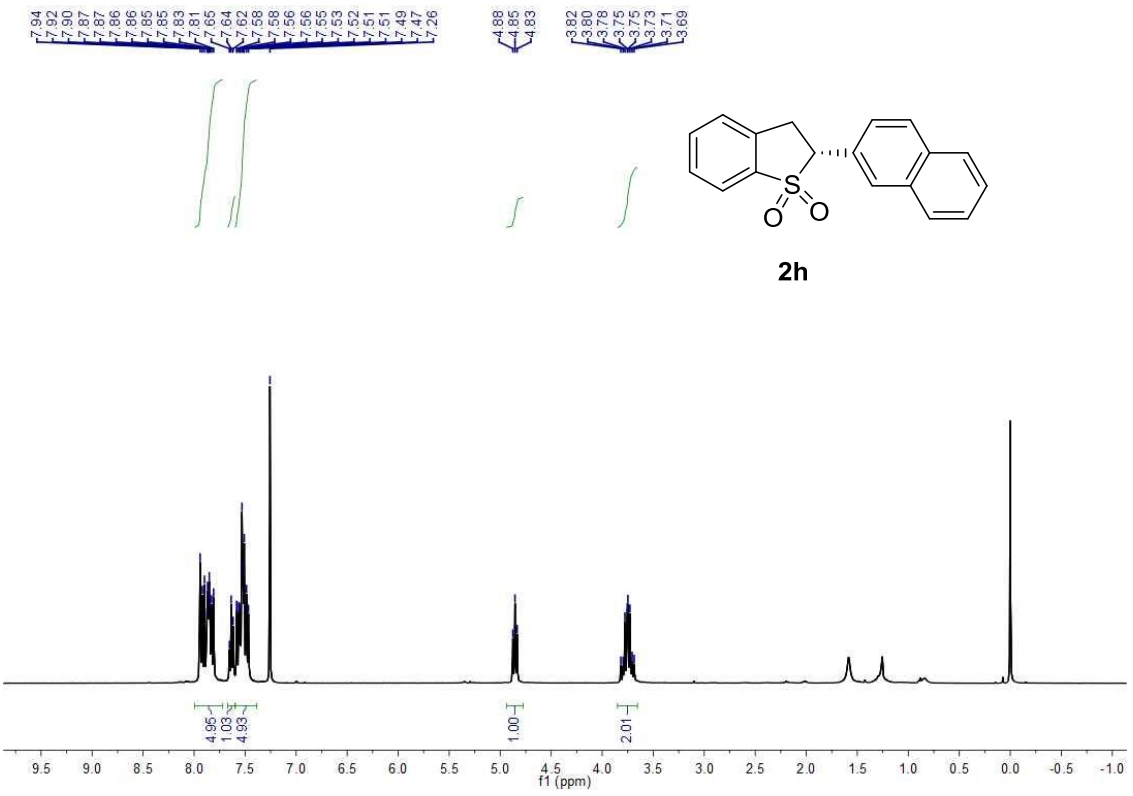
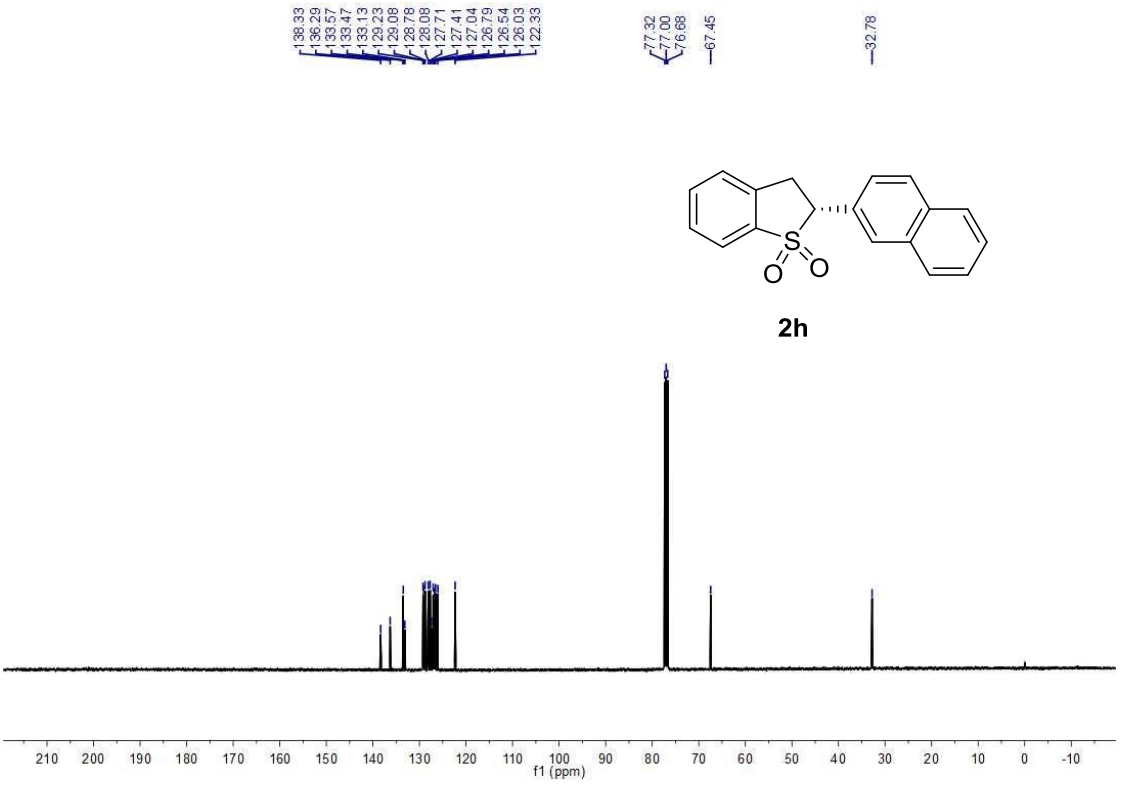
134.83
133.60
132.03
130.17
129.59
129.39
129.21
127.56
127.04
122.32
77.32
77.00
76.68
66.67
32.70
S
O
O
Cl
f1 (ppm)

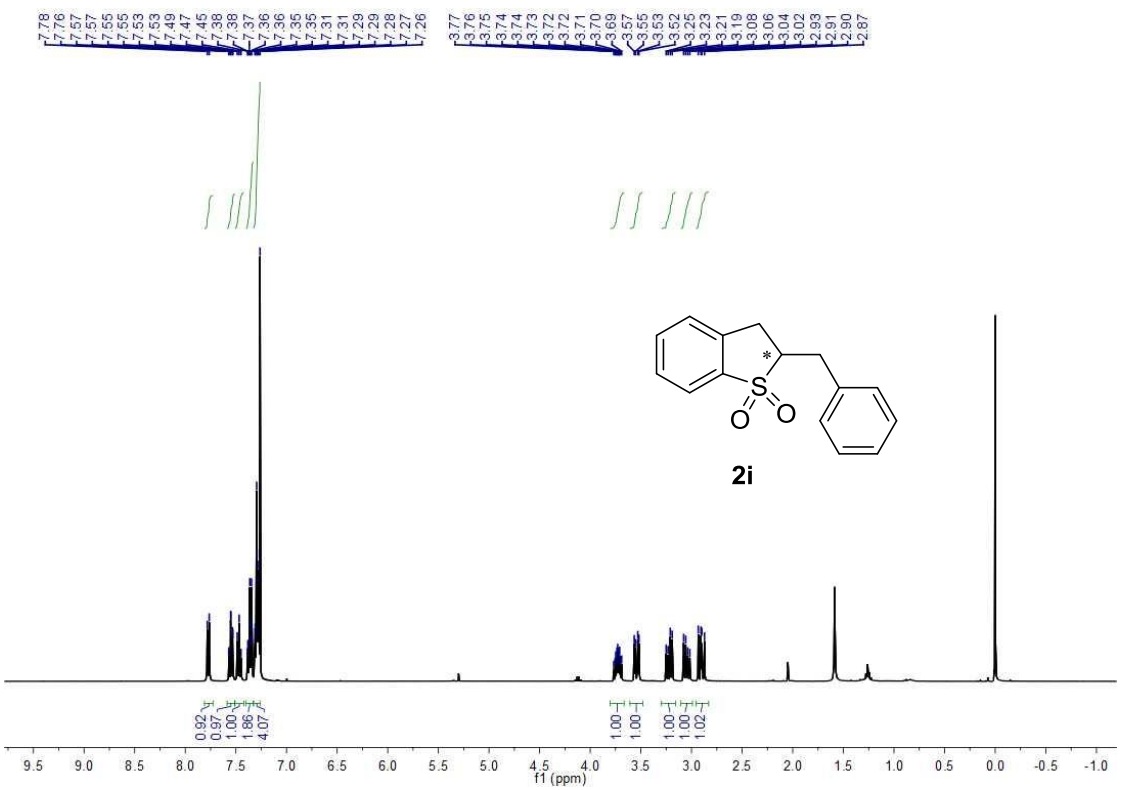
2g


7.94
7.92
7.90
7.87
7.87
7.86
7.86
7.85
7.85
7.83
7.81
7.65
7.64
7.62
7.58
7.58
7.56
7.56
7.55
7.53
7.52
7.51
7.51
7.49
7.47
7.26
4.88
4.85
4.83
3.82
3.80
3.78
3.75
3.75
3.73
3.71
3.69
S
O
O
4.95
1.03
4.93
1.00
2.01
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 -1.0
f1 (ppm)

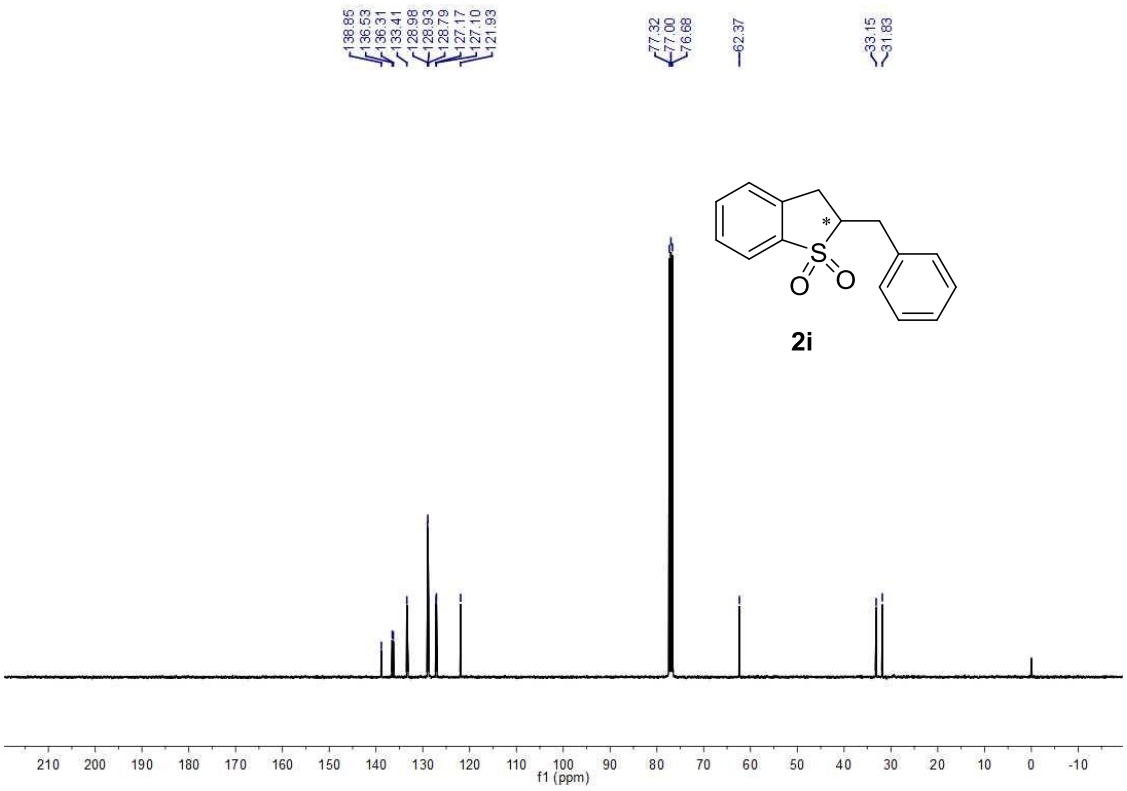
2h


138.33
136.29
133.57
133.47
133.13
129.23
129.08
128.78
128.08
127.71
127.41
127.04
126.79
126.54
126.03
122.33
77.32
77.00
76.68
67.45
32.78
S
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

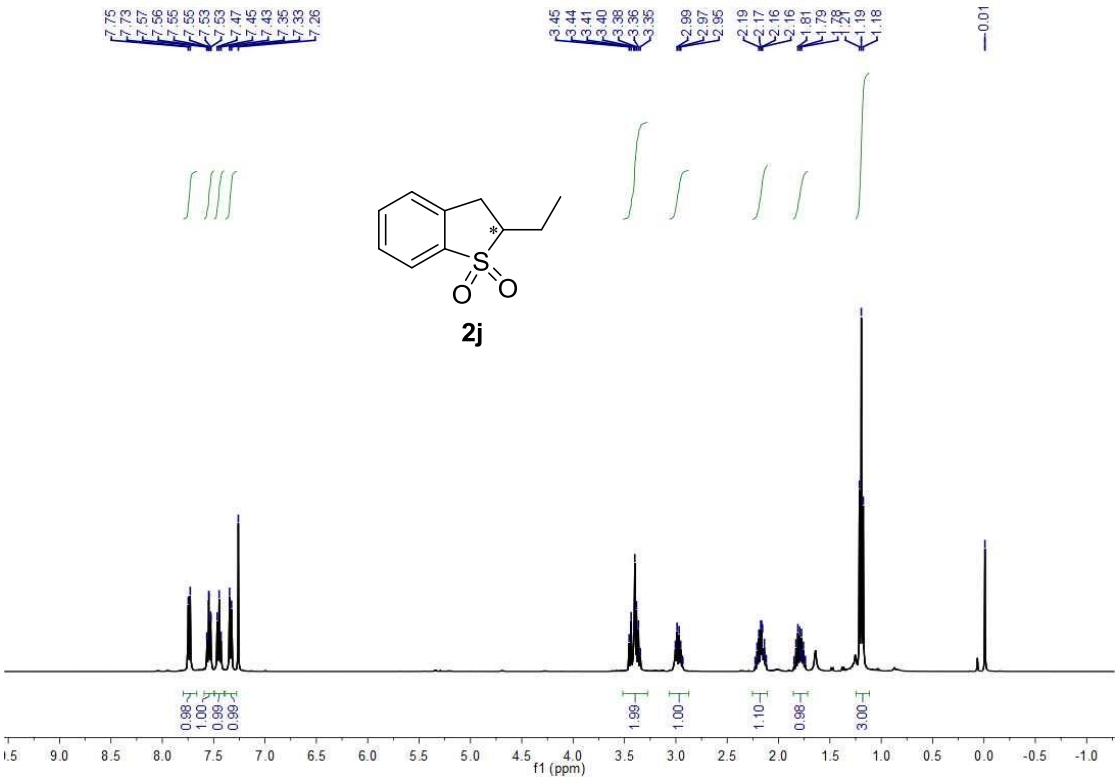
2h


7.78
7.76
7.57
7.57
7.55
7.55
7.53
7.53
7.49
7.47
7.45
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.31
7.29
7.29
7.28
7.27
7.26
3.77
3.76
3.75
3.74
3.74
3.73
3.72
3.72
3.71
3.70
3.69
3.57
3.55
3.53
3.52
3.25
3.23
3.21
3.19
3.08
3.06
3.04
3.02
2.93
2.91
2.90
2.87
0.92
0.97
1.00
1.86
4.07
1.00
1.00
1.00
1.00
1.02
f1 (ppm)

2i


138.85
136.53
136.31
133.41
128.98
128.93
128.79
127.17
127.10
121.93
77.32
77.00
76.68
62.37
33.15
31.83
f1 (ppm)

2i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7.26
3.45
3.44
3.41
3.40
3.38
3.36
3.35
2.99
2.97
2.95
2.19
2.17
2.16
1.81
1.79
1.78
1.21
1.19
1.18
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0.99
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1.99
1.00
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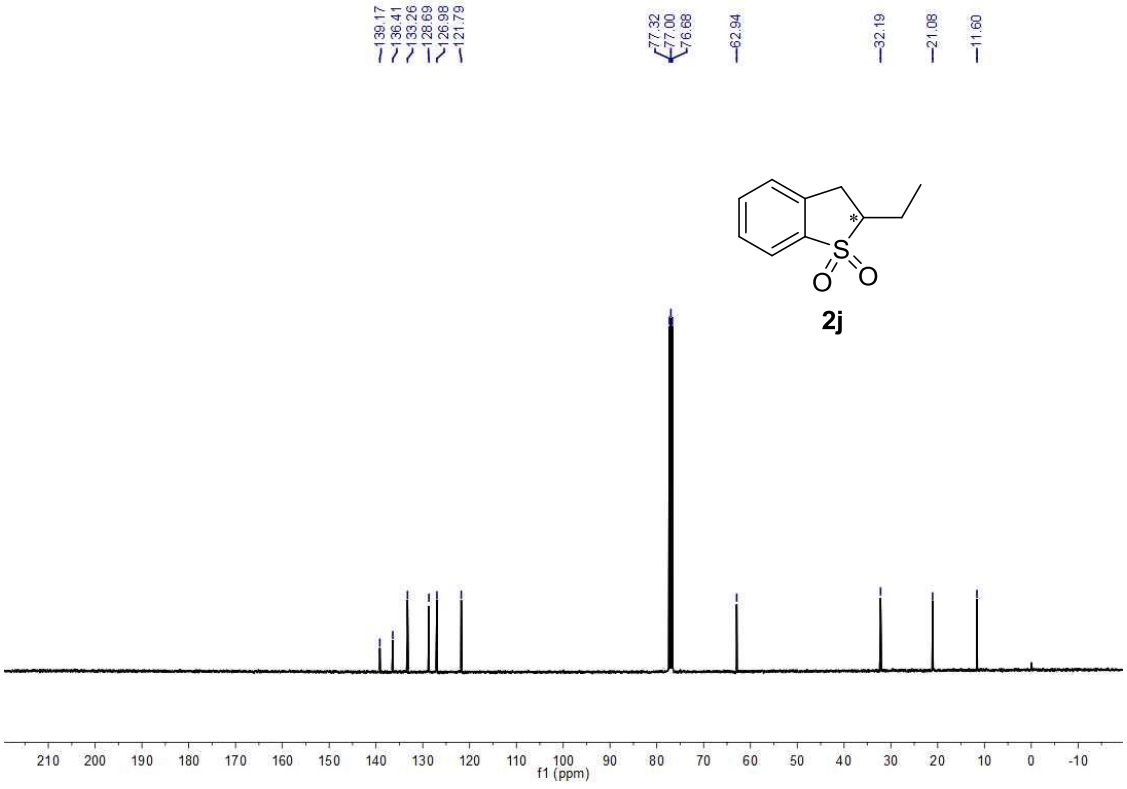
0.98
3.00
f1 (ppm)

2j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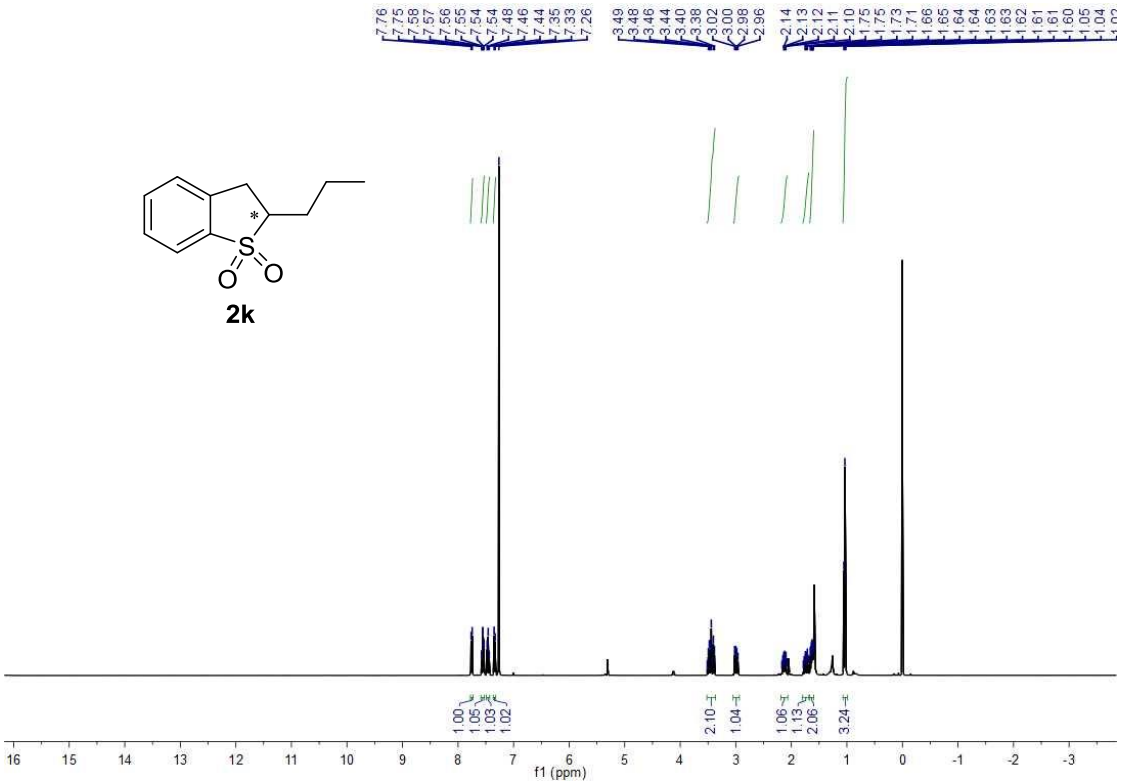
11.60
f1 (ppm)

2j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7.26
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3.48
3.46
3.44
3.40
3.38
3.02
3.00
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1.64
1.63
1.63
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1.60
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1.04
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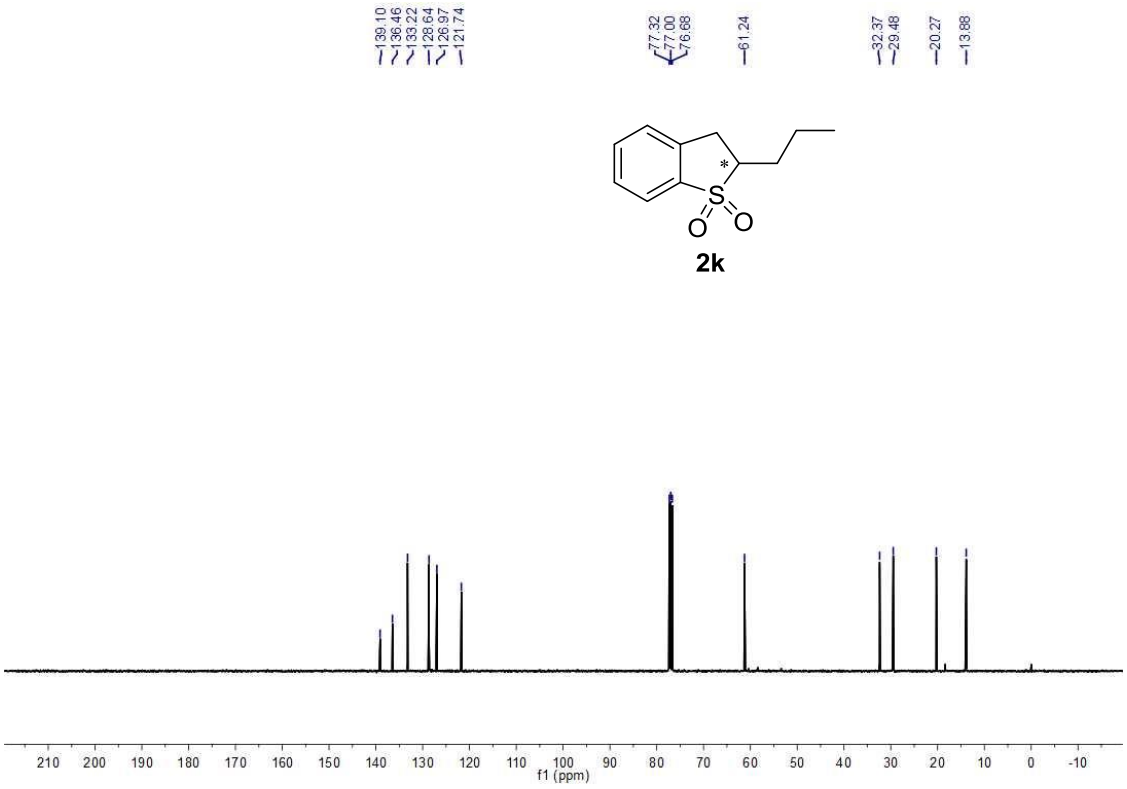
f1 (ppm)

2k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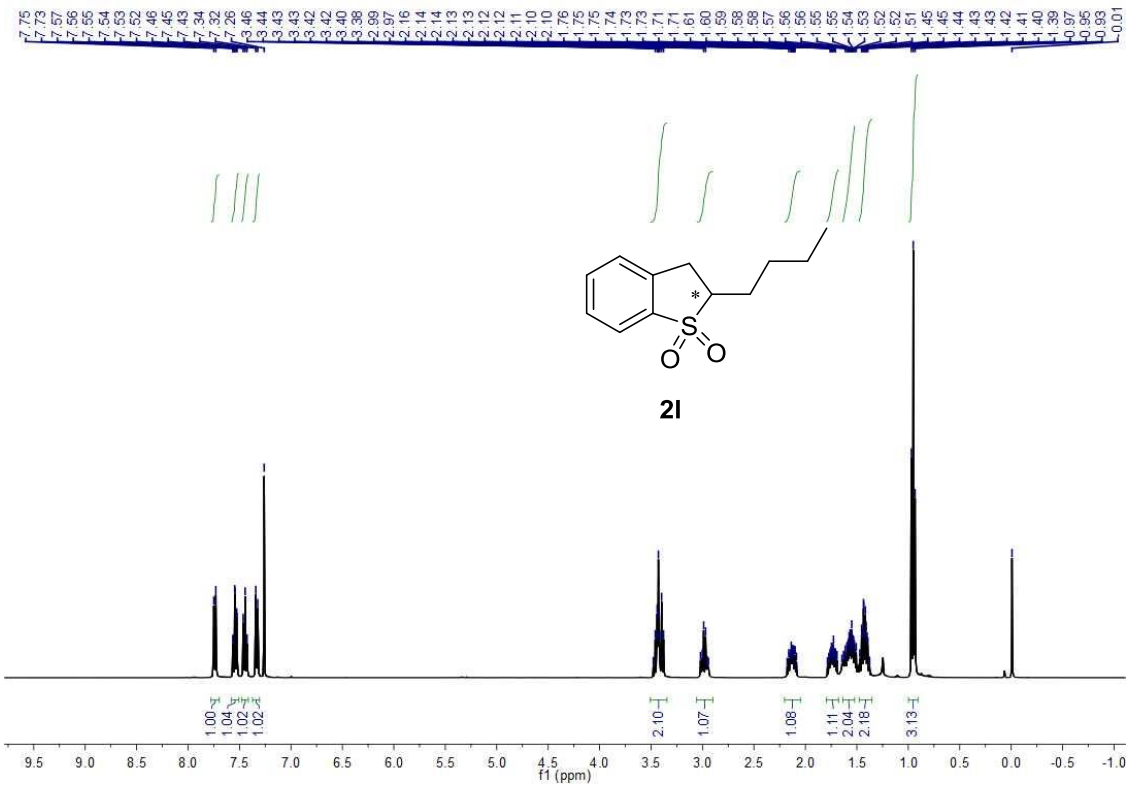
f1 (ppm)

2k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2.10
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1.75
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1.73
1.73
1.71
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1.43
1.42
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1.40
1.39
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0.95
0.93
0.01
1.00
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1.02
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1.08
1.11
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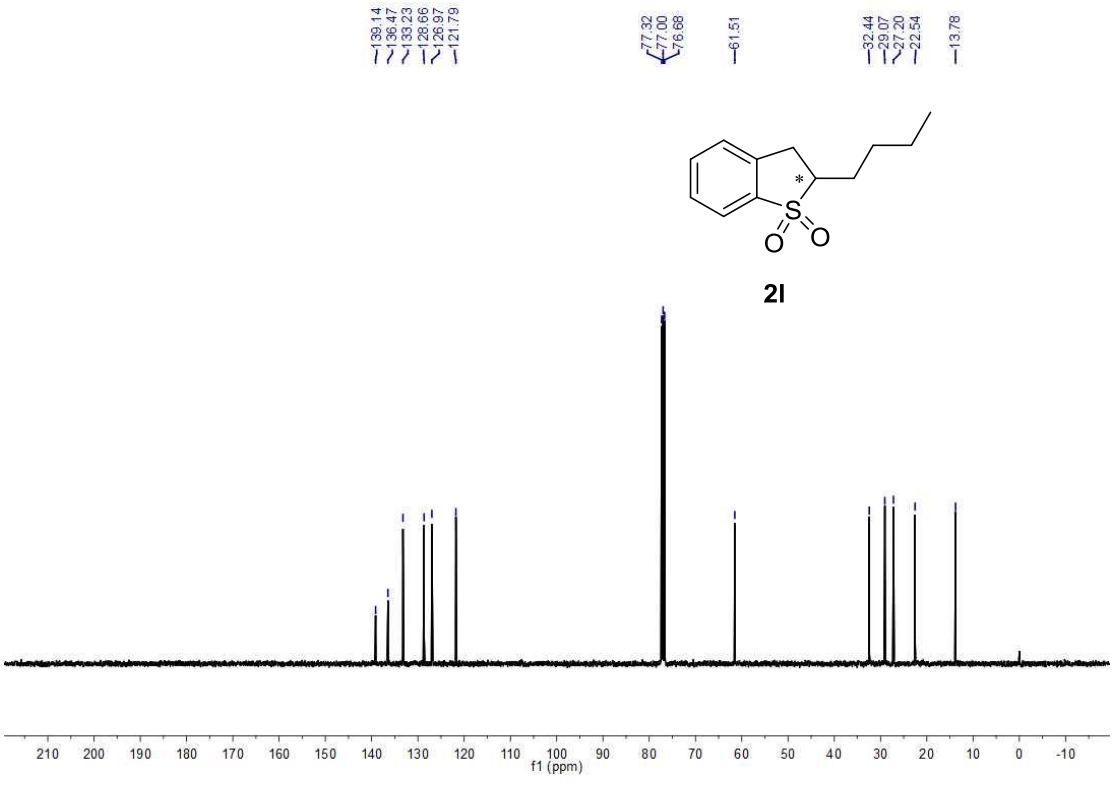
3.13
f1 (ppm)

2l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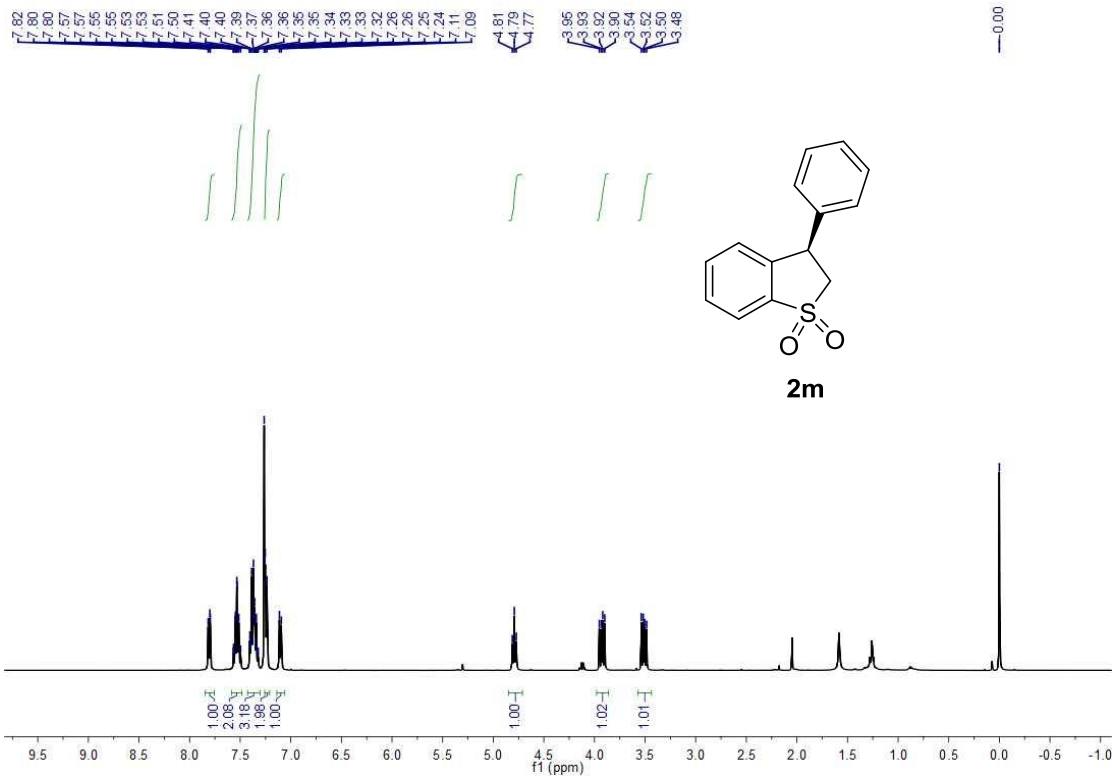
32.44
29.07
27.20
22.54
13.78
f1 (ppm)

2l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7.40
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7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.26
7.26
7.25
7.24
7.11
7.09
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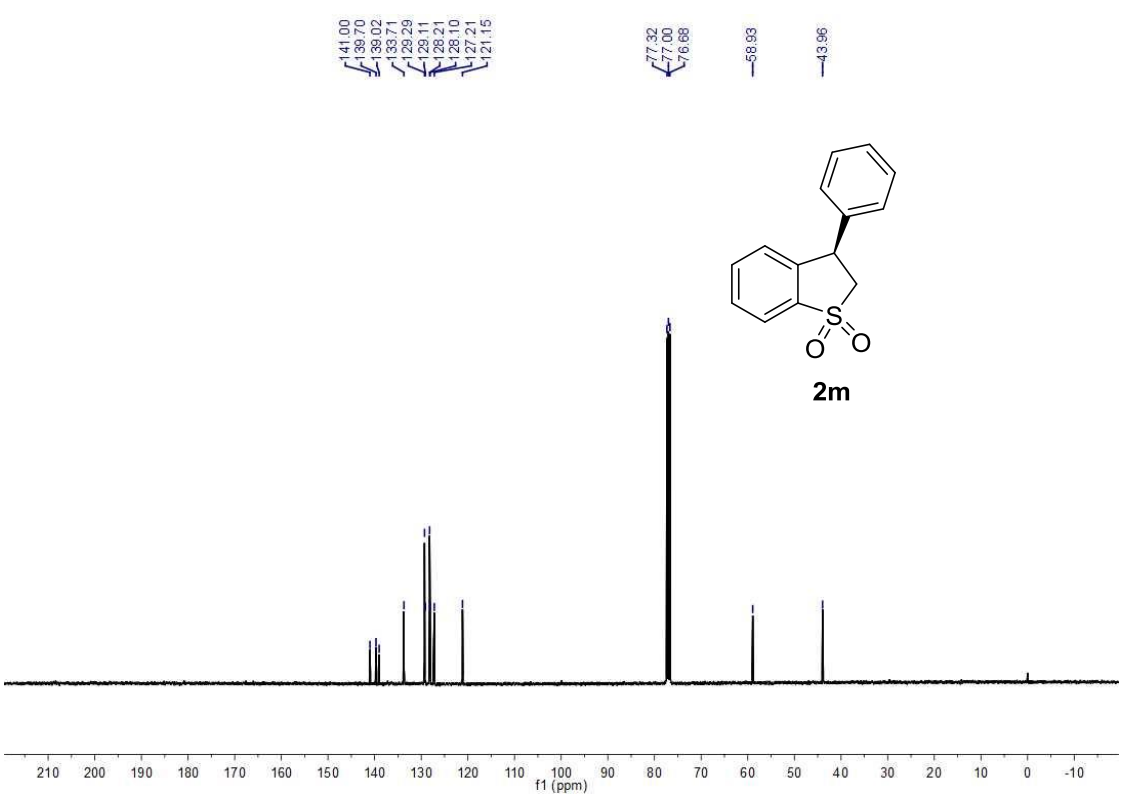
4.79
4.77
3.95
3.93
3.92
3.90
3.54
3.52
3.50
3.48
0.00
1.00
2.08
3.18
1.98
1.00
1.00
1.02
1.01
f1 (ppm)

2m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128.21
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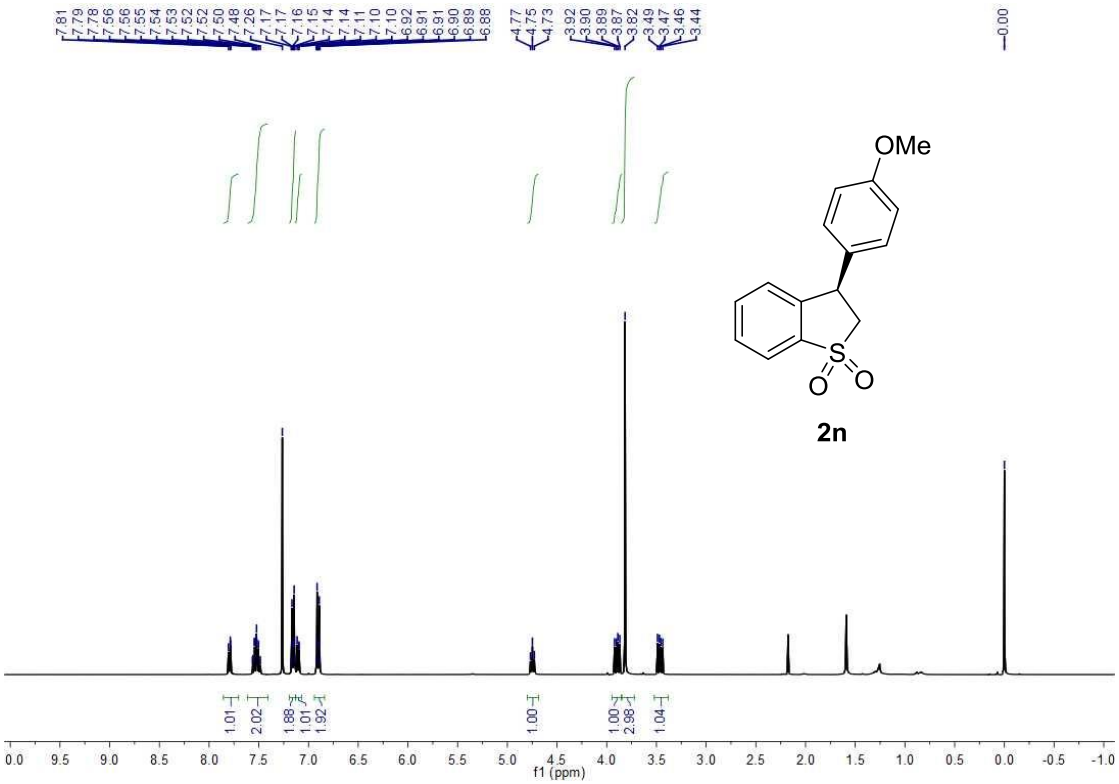
121.15
77.32
77.00
76.68
58.93
43.96
f1 (ppm)

2m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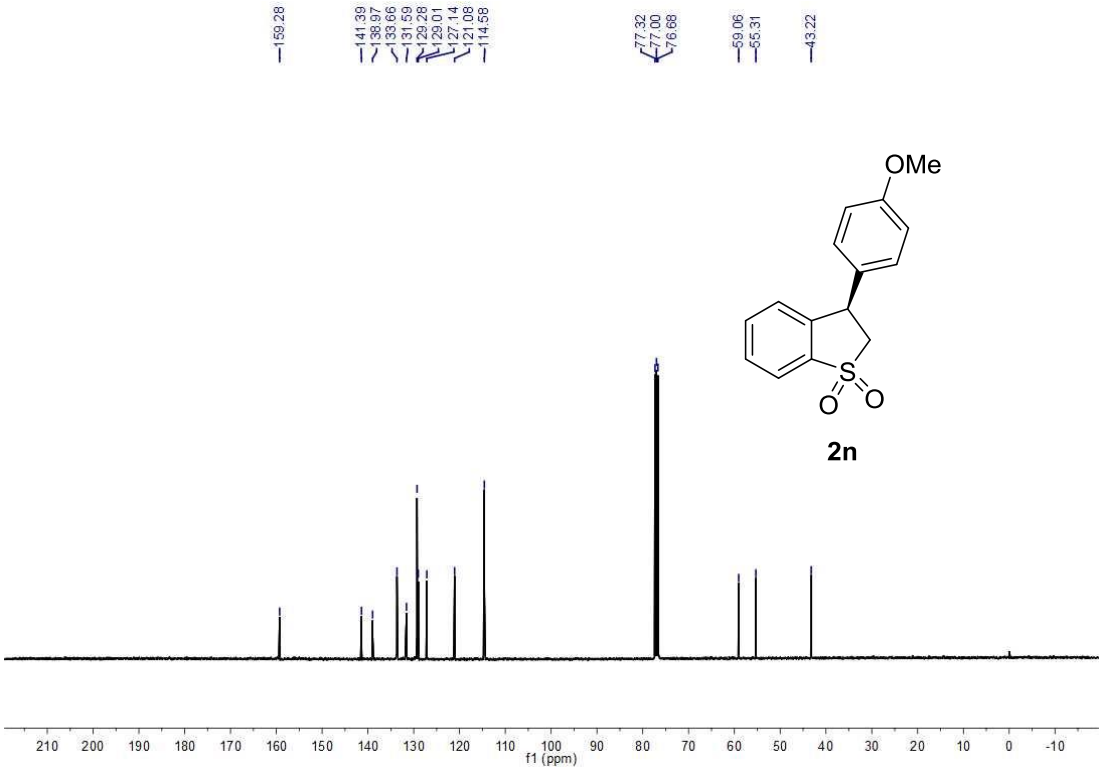
7.52
7.50
7.48
7.26
7.17
7.17
7.16
7.15
7.14
7.14
7.11
7.10
7.10
6.92
6.91
6.91
6.90
6.89
6.88
4.77
4.75
4.73
3.92
3.90
3.89
3.87
3.82
3.49
3.47
3.46
3.44
0.00
OMe
S
O
O
2n
1.01
2.02
1.88
1.01
1.92
1.00
1.00
2.98
1.04
f1 (ppm)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127.14
121.08
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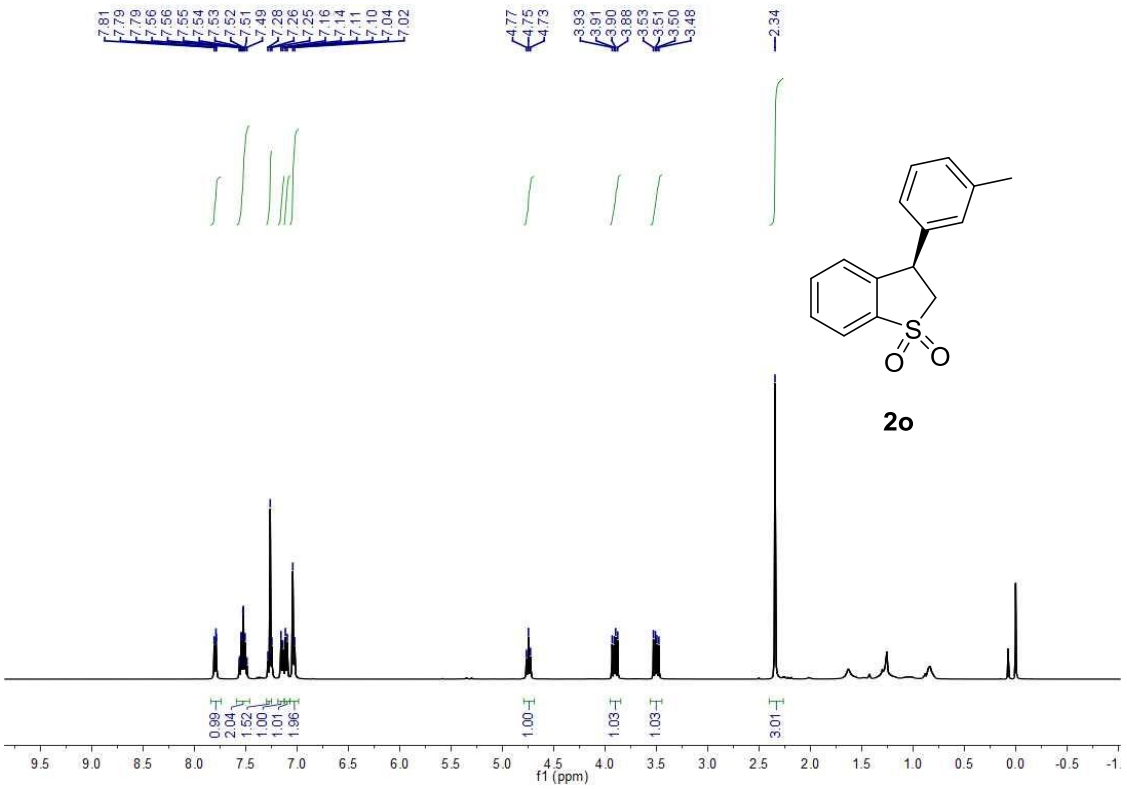
77.00
76.68
59.06
55.31
43.22
OMe
S
O
O
2n
f1 (ppm)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7.25
7.16
7.14
7.11
7.10
7.04
7.02
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4.73
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3.91
3.90
3.88
3.53
3.51
3.50
3.48
2.34
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2.04
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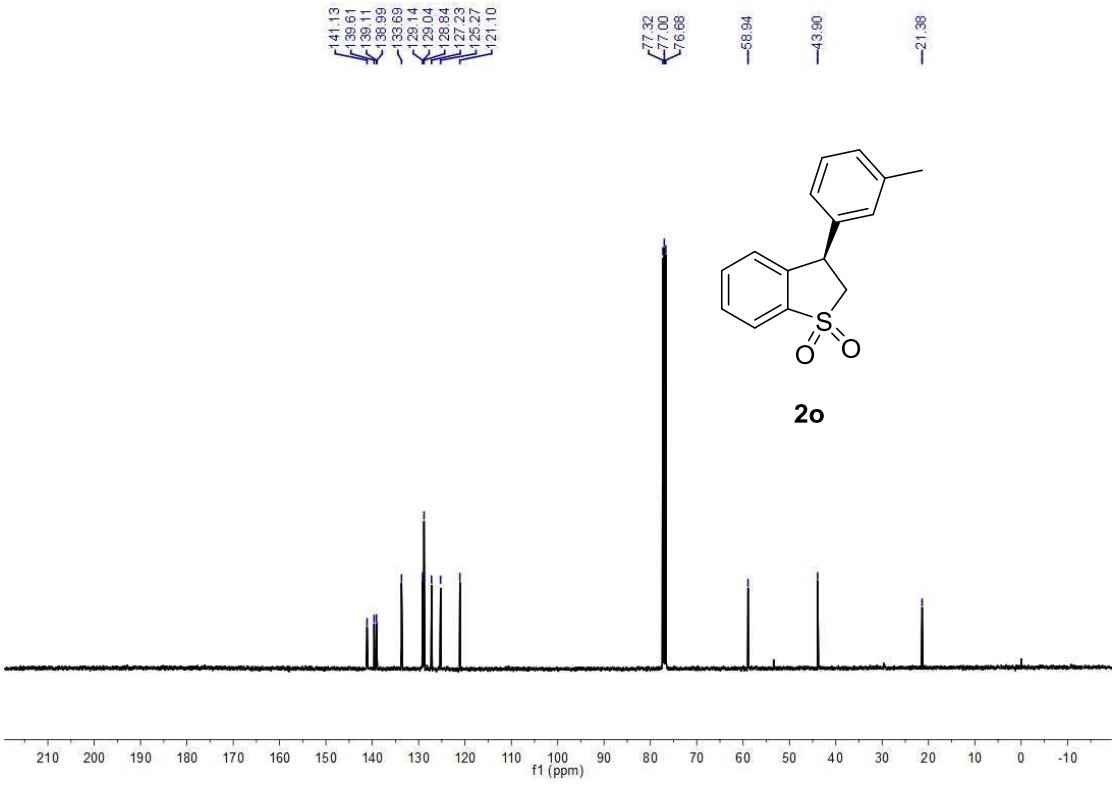
1.00
1.01
1.96
1.00
1.03
1.03
3.01
f1 (ppm)

2o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121.10
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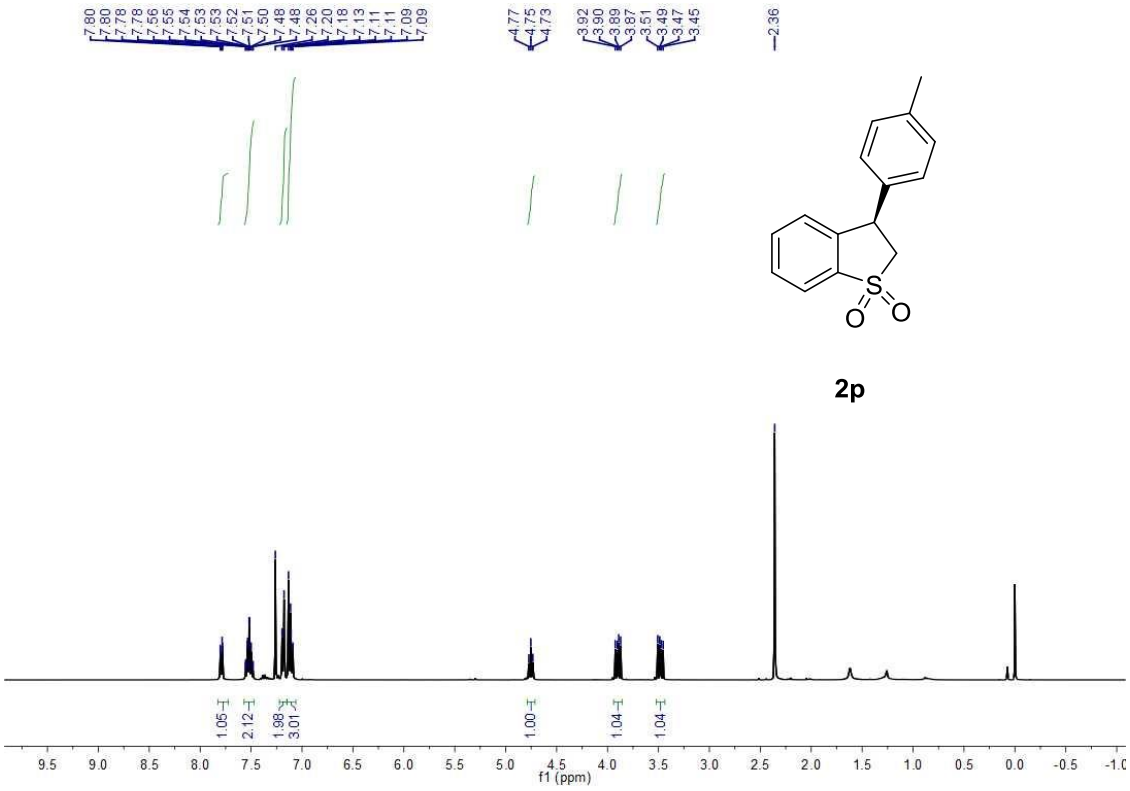
77.00
76.68
58.94
43.90
21.38
f1 (ppm)

2o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7.51
7.50
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7.48
7.26
7.20
7.18
7.13
7.11
7.11
7.09
7.09
4.77
4.75
4.73
3.92
3.90
3.89
3.87
3.51
3.49
3.47
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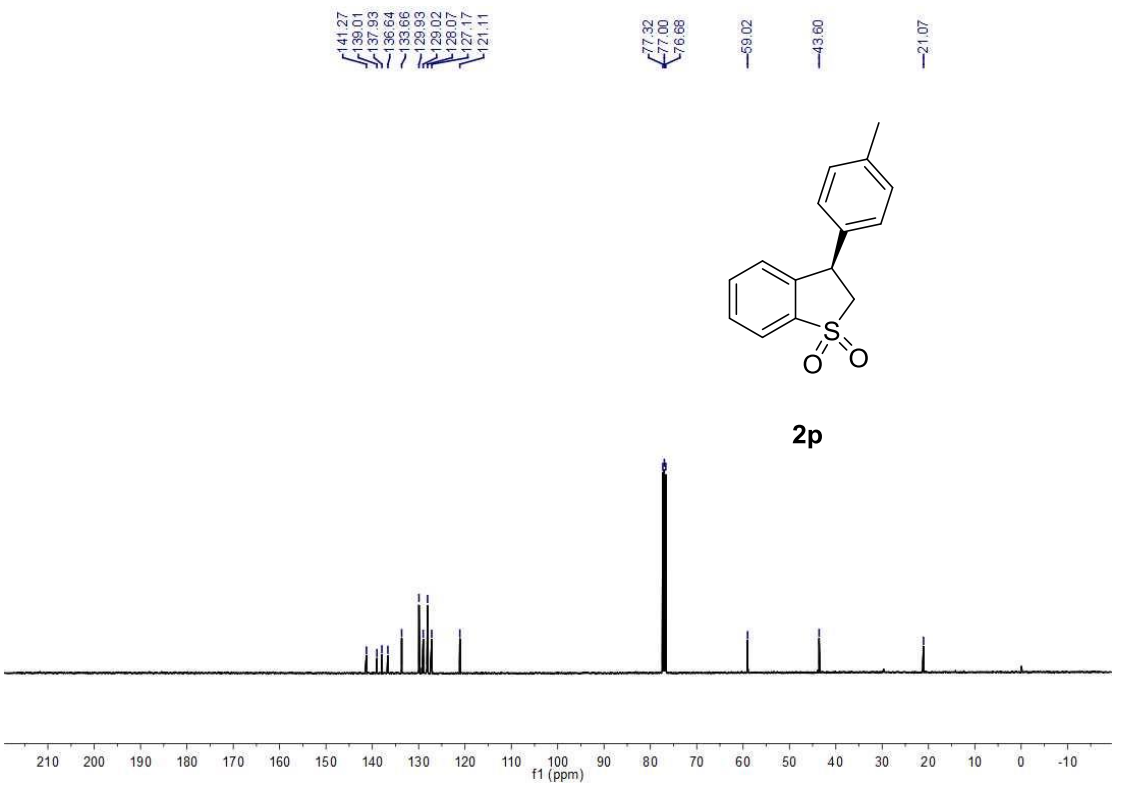
1.98
3.01
1.00
1.04
1.04
f1 (ppm)

2p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121.11
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77.00
76.68
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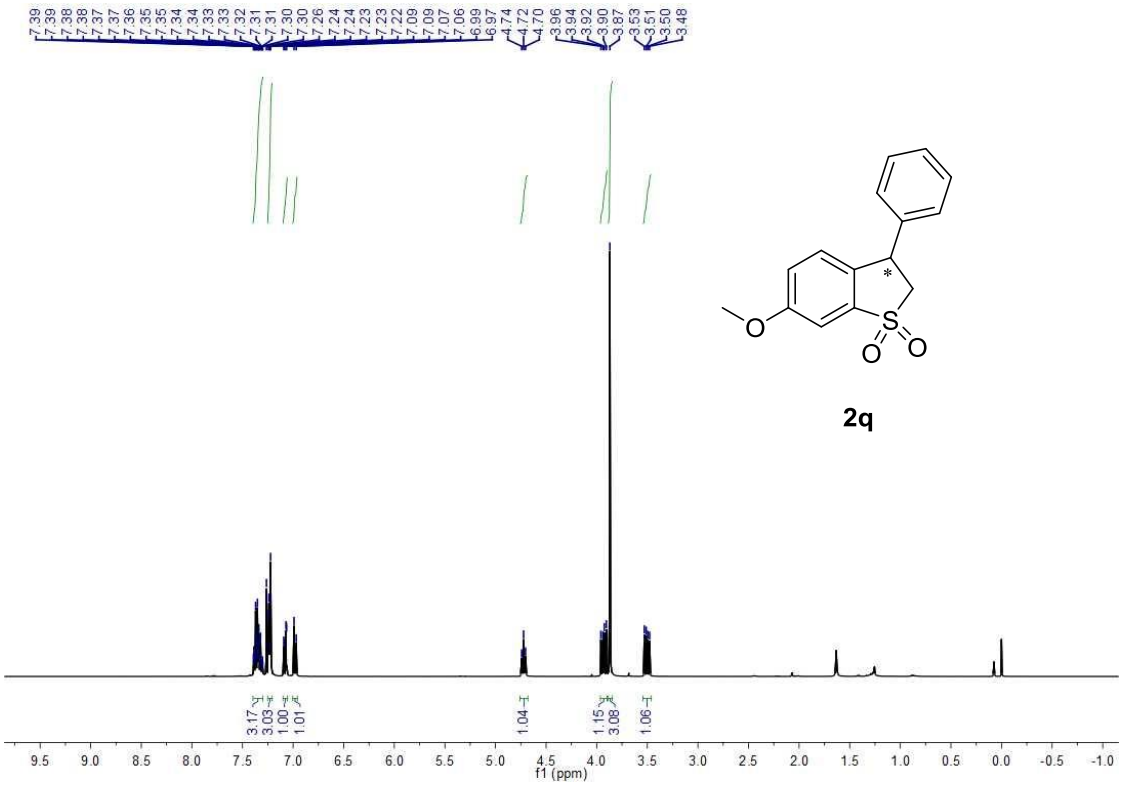
43.60
21.07
f1 (ppm)

2p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7.33
7.32
7.31
7.31
7.30
7.30
7.26
7.24
7.24
7.23
7.23
7.22
7.09
7.09
7.07
7.06
6.99
6.97
4.74
4.72
4.70
3.96
3.94
3.92
3.90
3.87
3.53
3.51
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3.48
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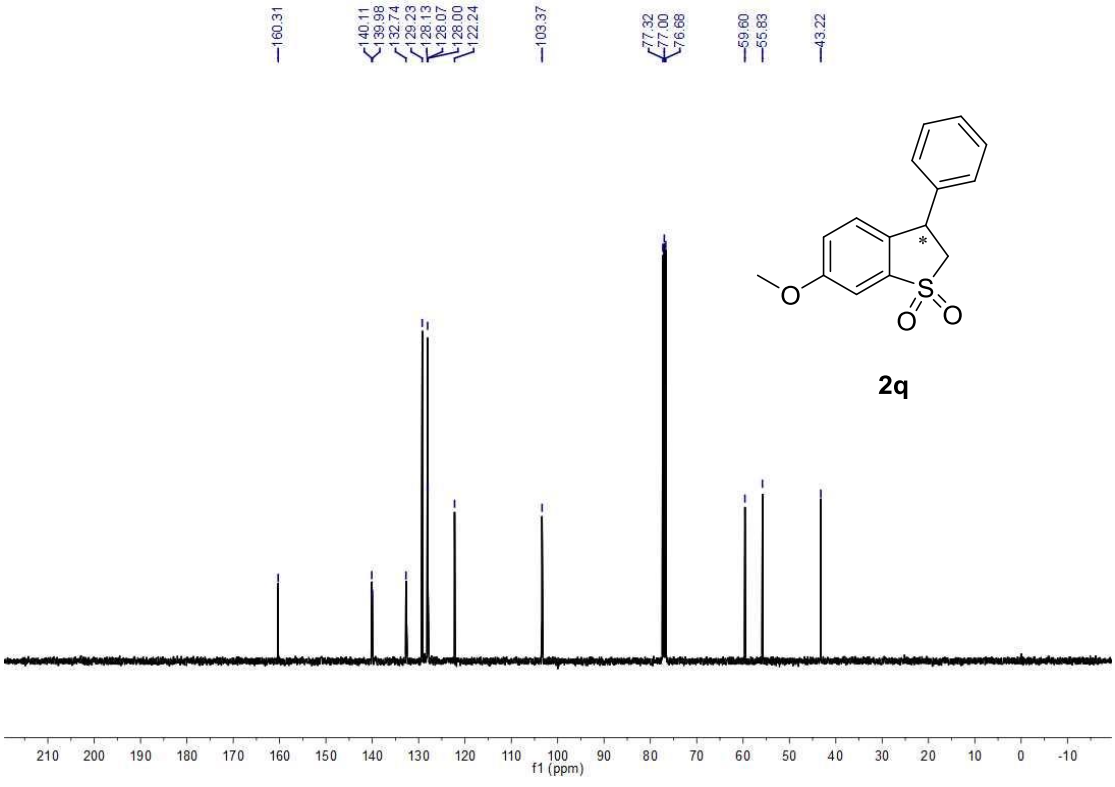
3.03
1.00
1.01
1.04
1.15
3.08
1.06
f1 (ppm)

2q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103.37
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77.00
76.68
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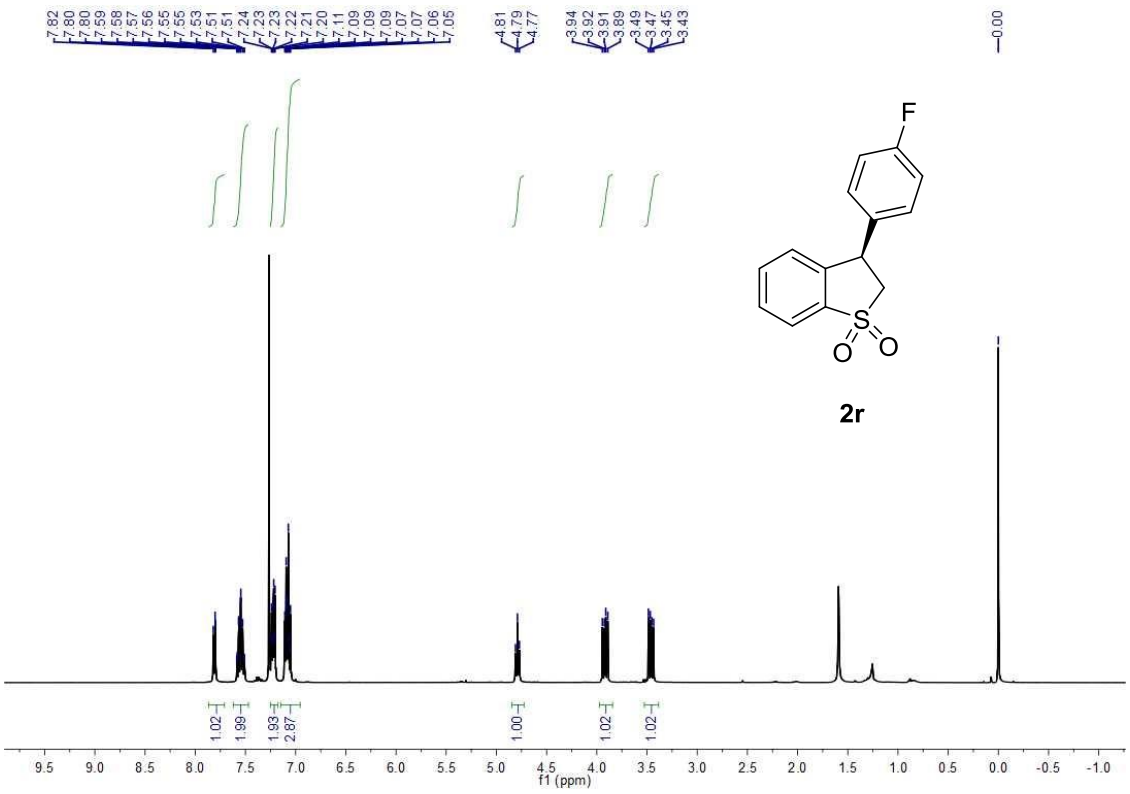
55.83
43.22
f1 (ppm)

2q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7.51
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7.23
7.23
7.22
7.21
7.20
7.11
7.09
7.09
7.09
7.07
7.07
7.06
7.05
4.81
4.79
4.77
3.94
3.92
3.91
3.89
3.49
3.47
3.45
3.43
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F
S
O
O
2r
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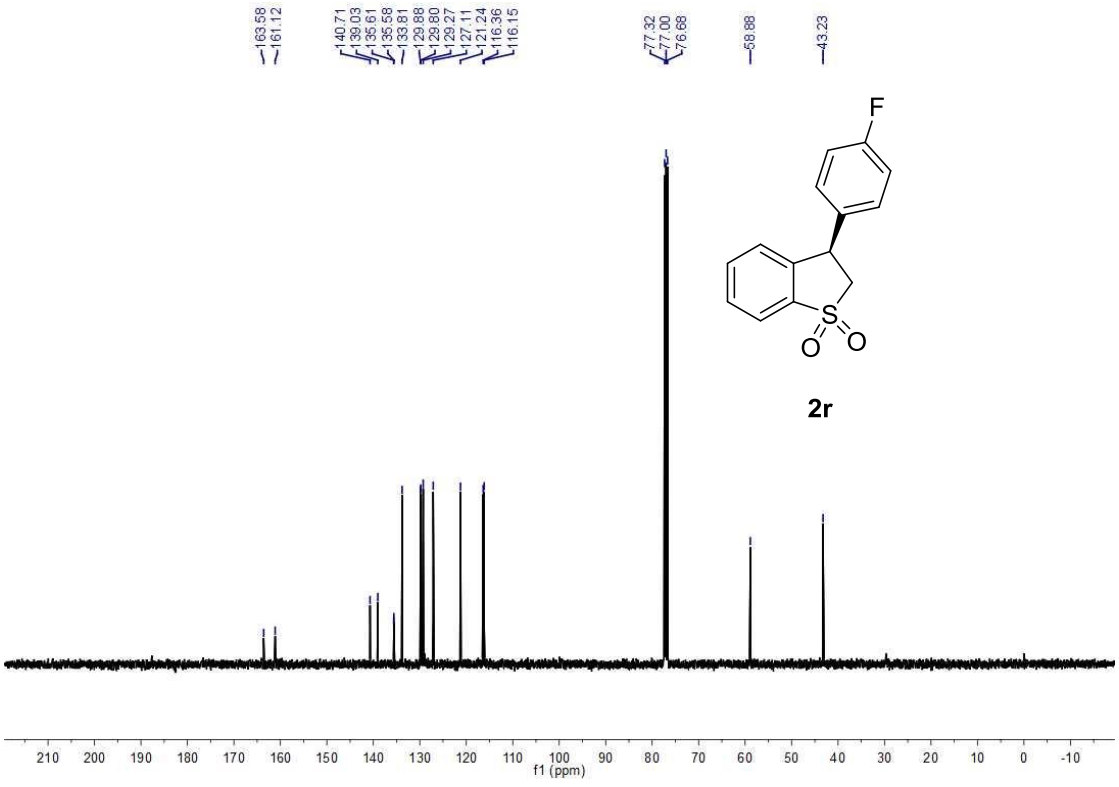
1.99
1.93
2.87
1.00
1.02
1.02
f1 (ppm)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135.58
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129.88
129.80
129.27
127.11
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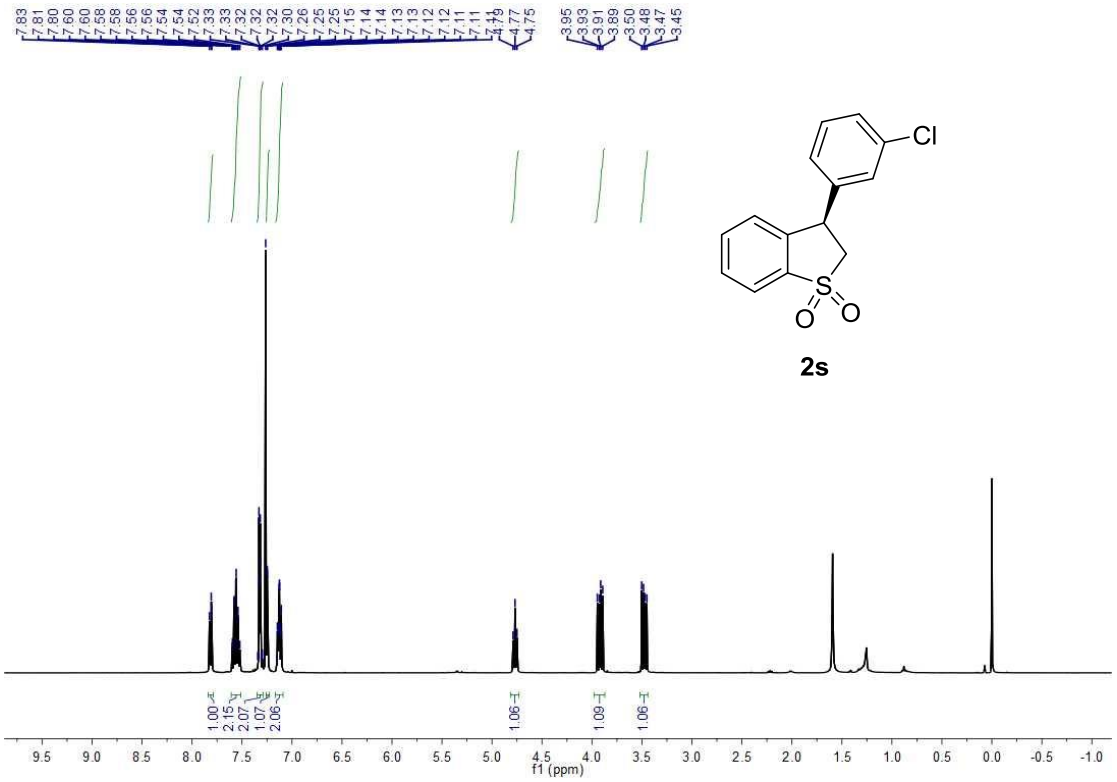
77.00
76.68
58.88
43.23
F
S
O
O
2r
f1 (ppm)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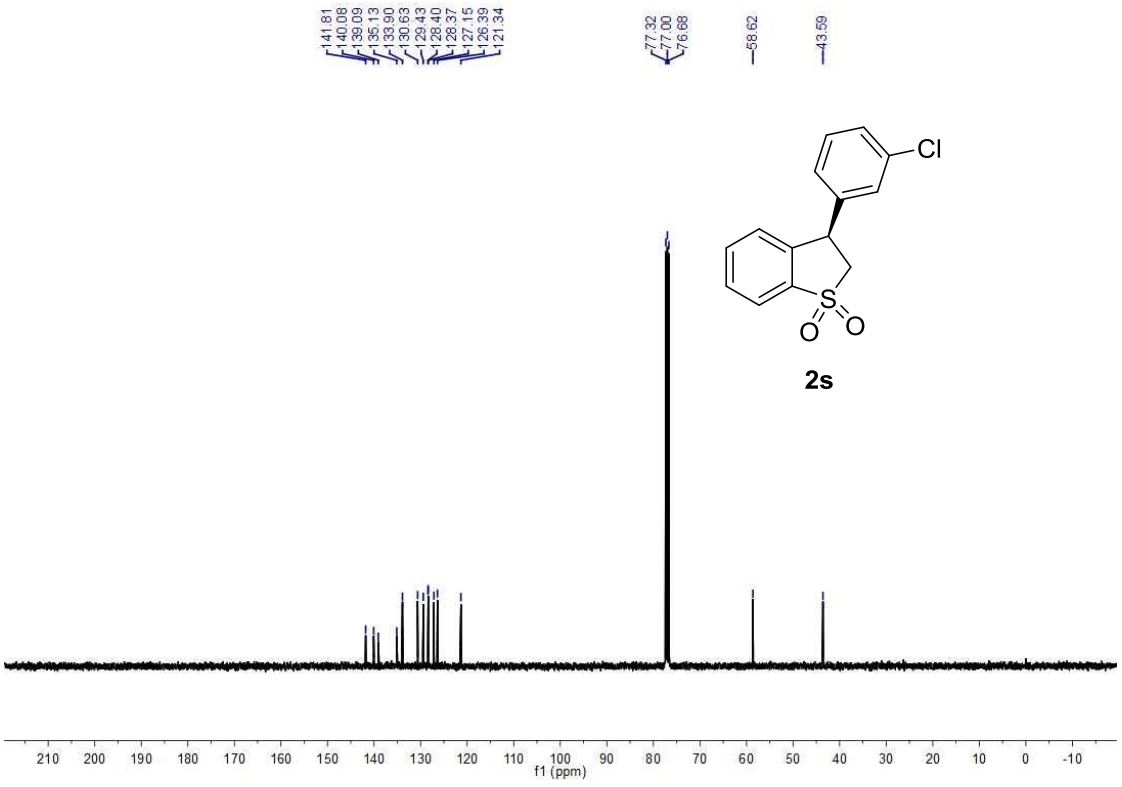
7.12
7.11
7.11
4.79
4.77
4.75
3.95
3.93
3.91
3.89
3.50
3.48
3.47
3.45
Cl
S
O
O
1.00
2.15
2.07
1.07
2.06
1.06
1.09
1.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

2s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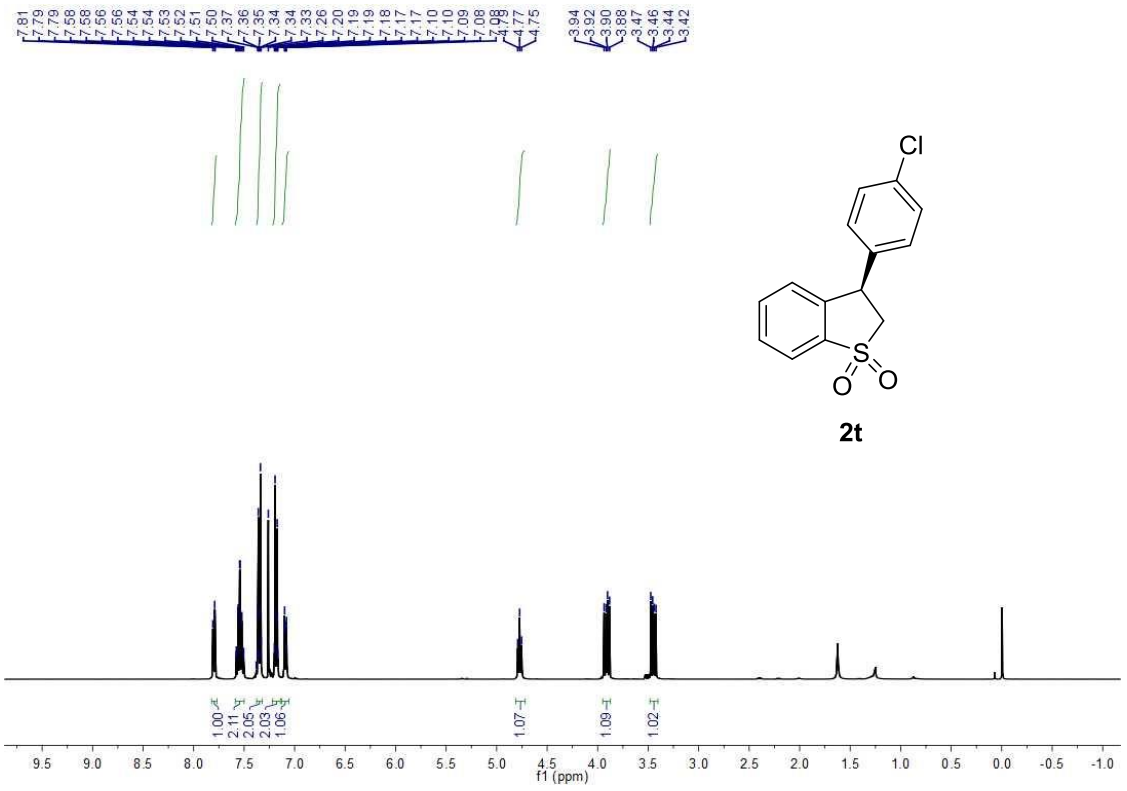
128.37
127.15
126.39
121.34
77.32
77.00
76.68
58.62
43.59
Cl
S
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2s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7.36
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7.26
7.20
7.19
7.19
7.18
7.17
7.10
7.09
7.08
4.77
4.75
3.94
3.92
3.90
3.88
3.47
3.46
3.44
3.42
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O
O
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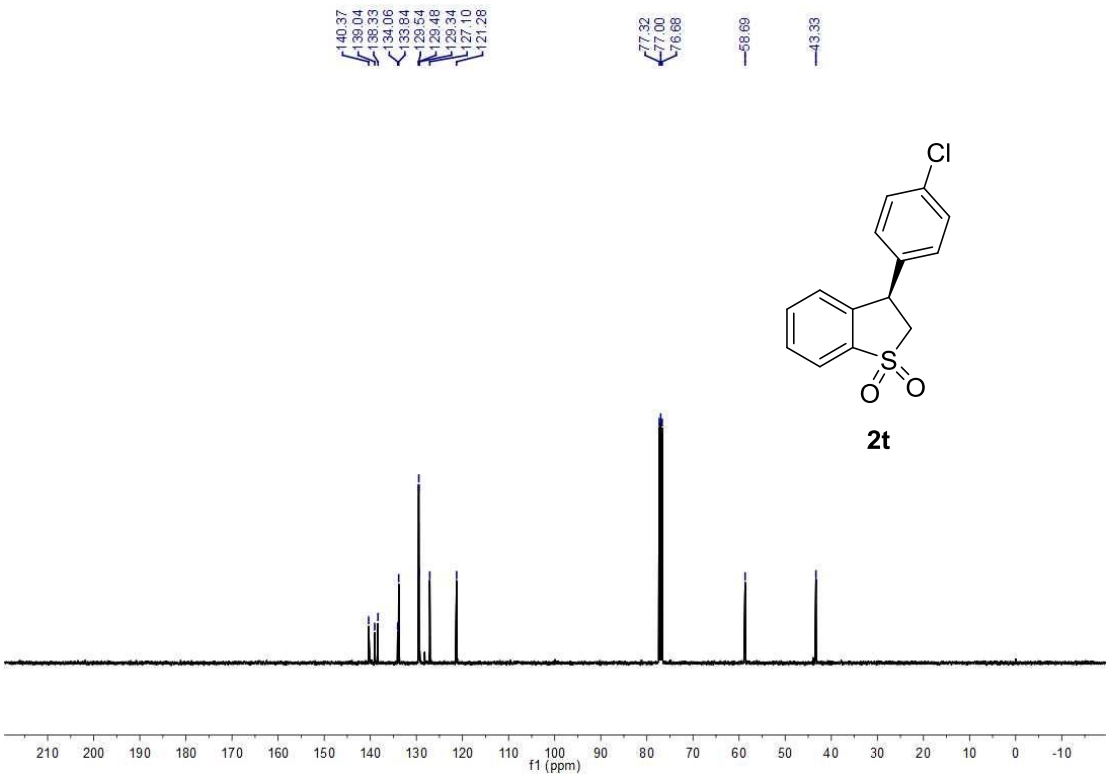
2.11
2.05
2.03
1.06
1.07
1.09
1.02
f1 (ppm)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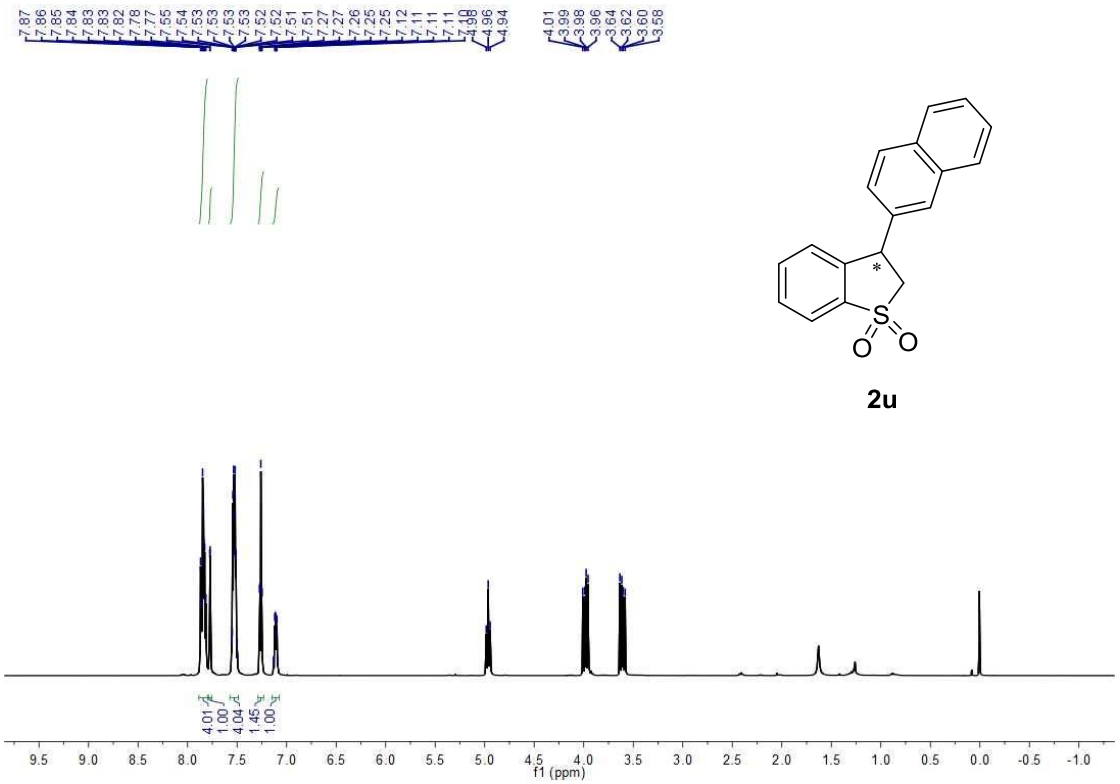
77.32
77.00
76.68
58.69
43.33
Cl
S
O
O
2t
f1 (ppm)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7.25
7.12
7.11
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7.10
4.98
4.96
4.94
4.01
3.99
3.98
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2u
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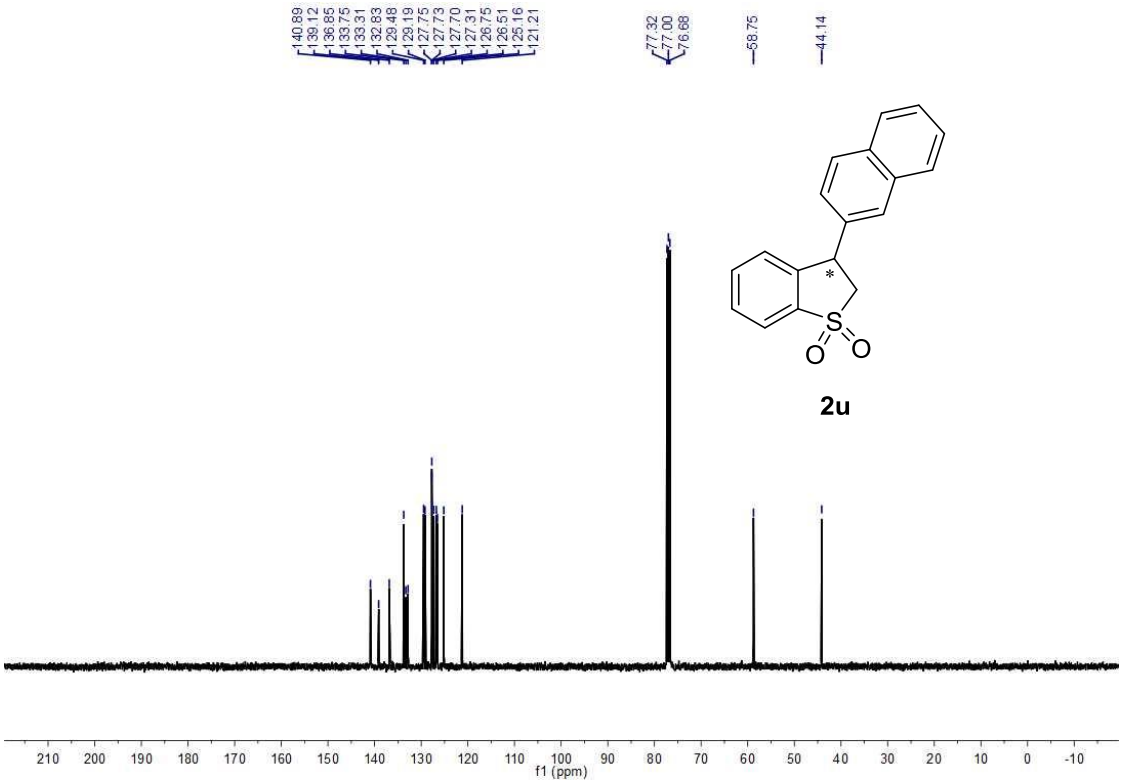
4.04
1.45
1.00
f1 (ppm)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127.75
127.73
127.70
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125.16
121.21
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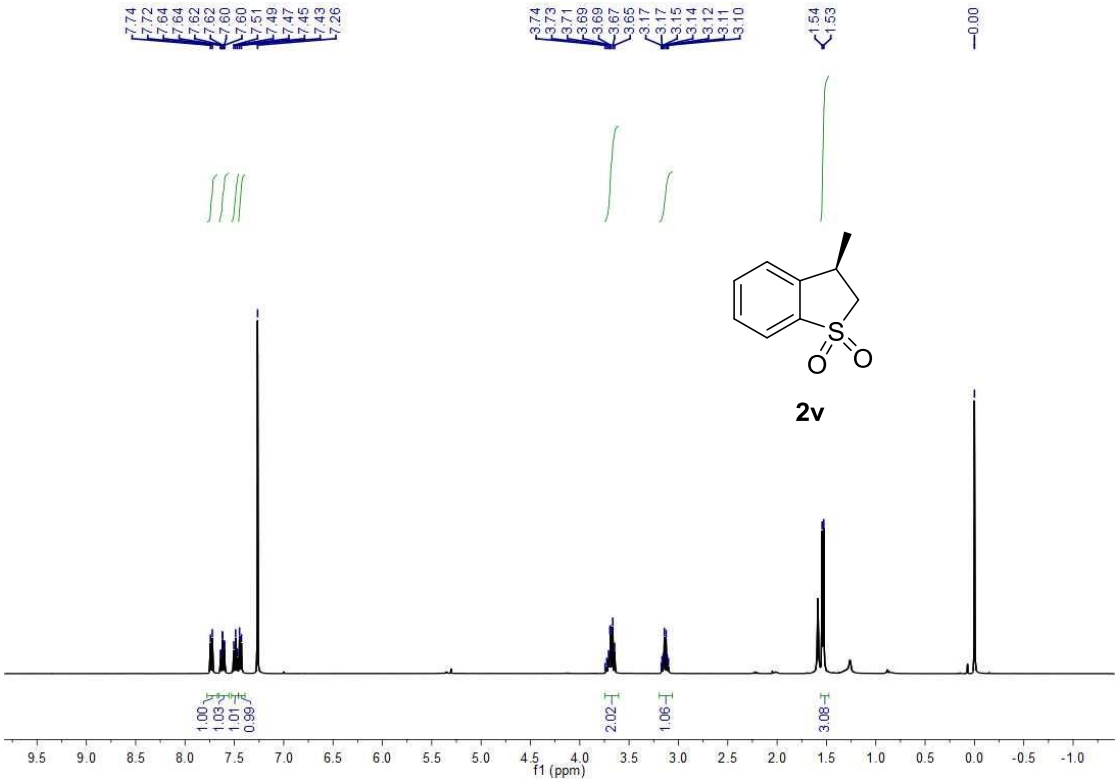
77.00
76.68
58.75
44.14
2u
f1 (ppm)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7.62
7.62
7.60
7.60
7.51
7.49
7.47
7.45
7.43
7.26
3.74
3.73
3.71
3.69
3.69
3.67
3.65
3.17
3.17
3.15
3.14
3.12
3.11
3.10
1.54
1.53
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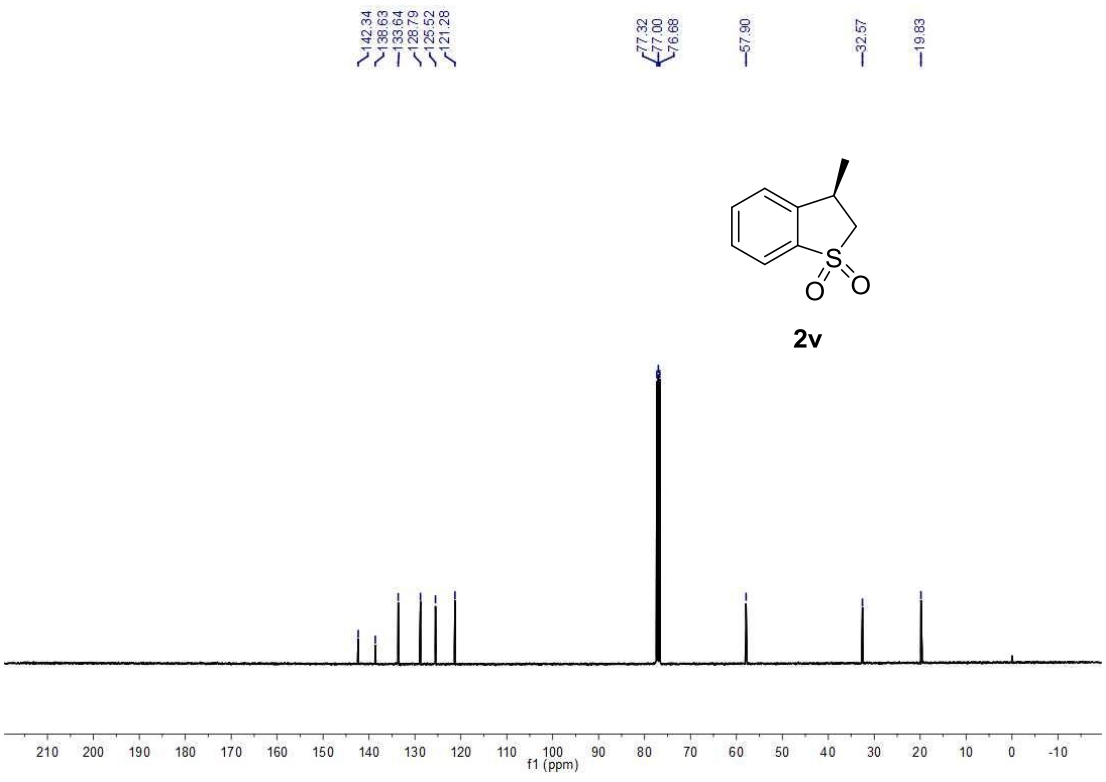
1.00
1.03
1.01
0.99
2.02
1.06
3.08
f1 (ppm)

2v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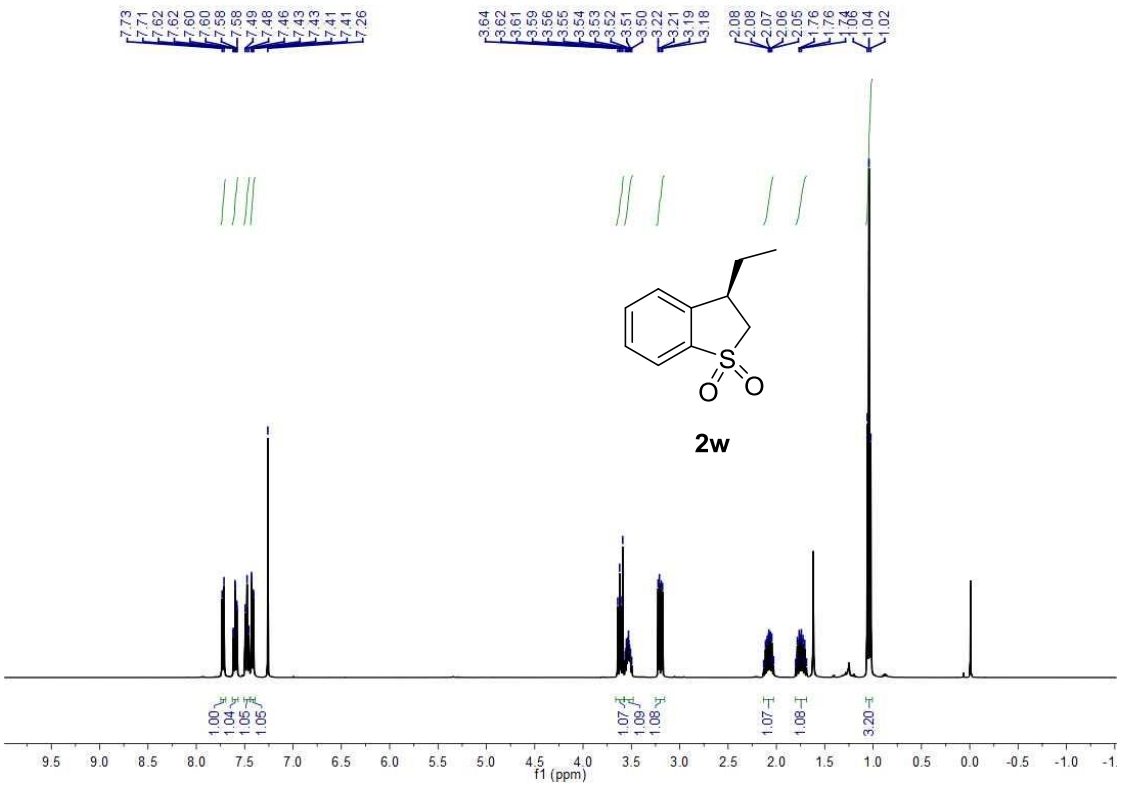
121.28
77.32
77.00
76.68
57.90
32.57
19.83
f1 (ppm)

2v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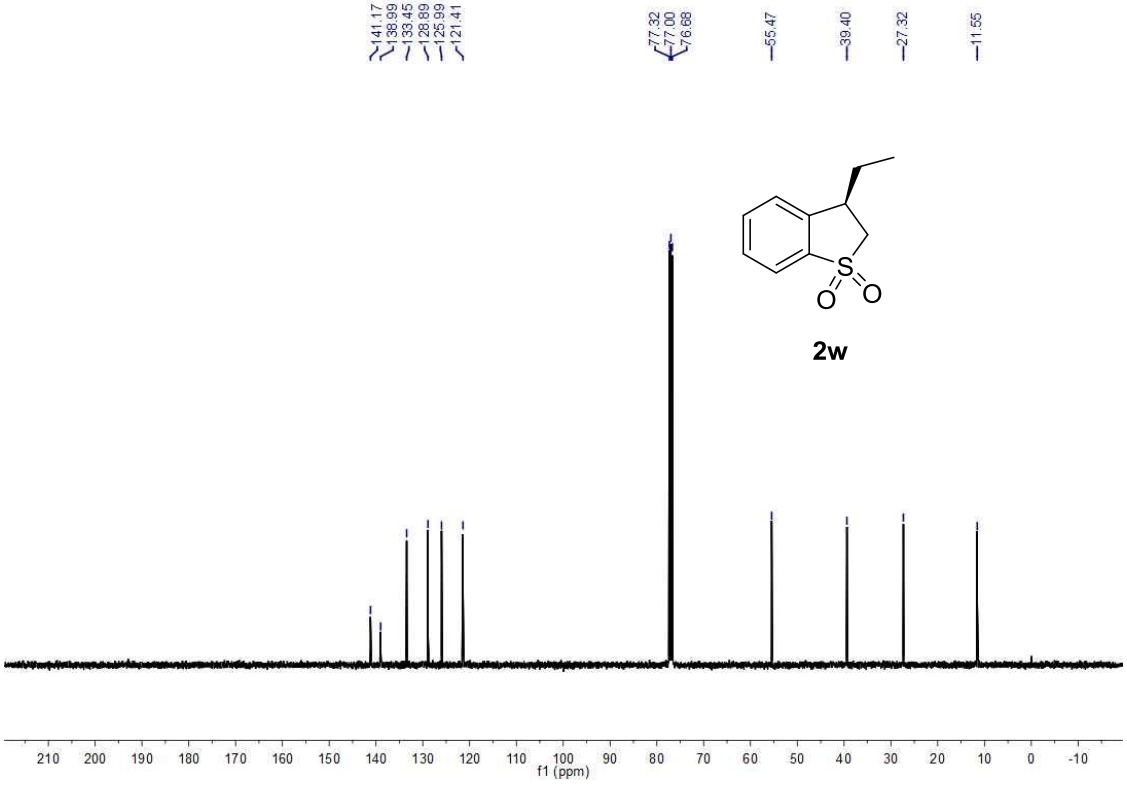
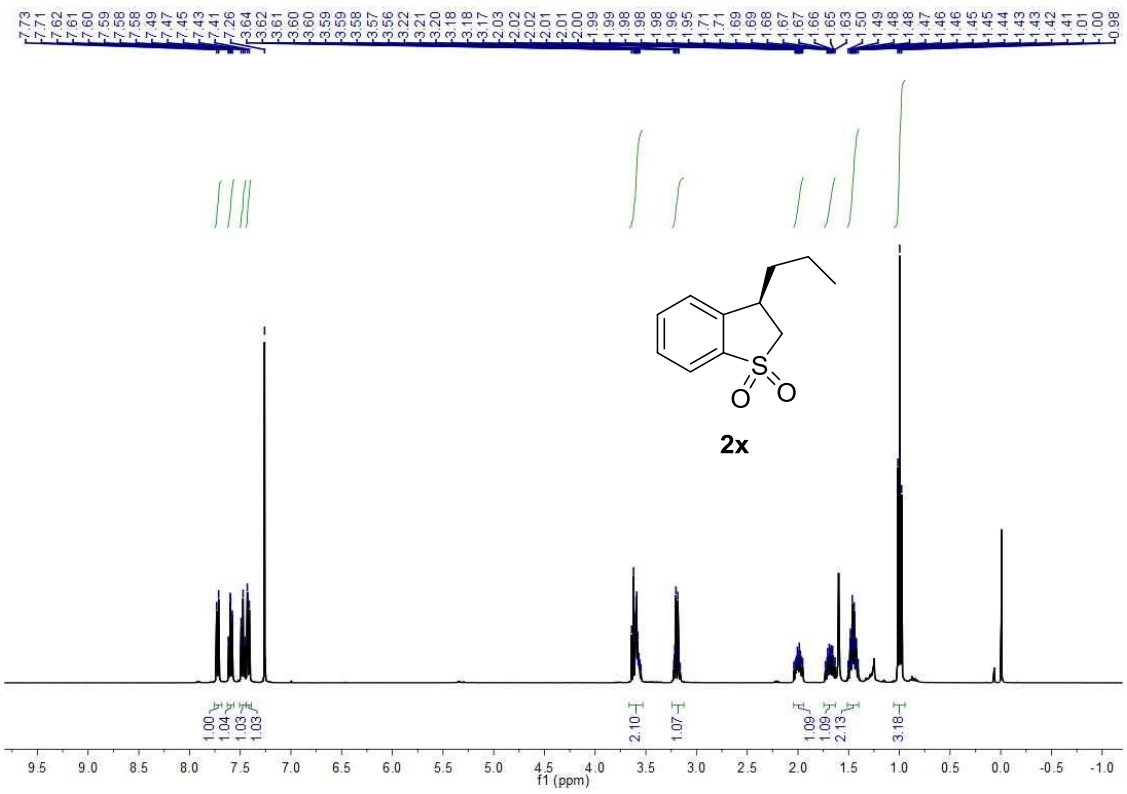
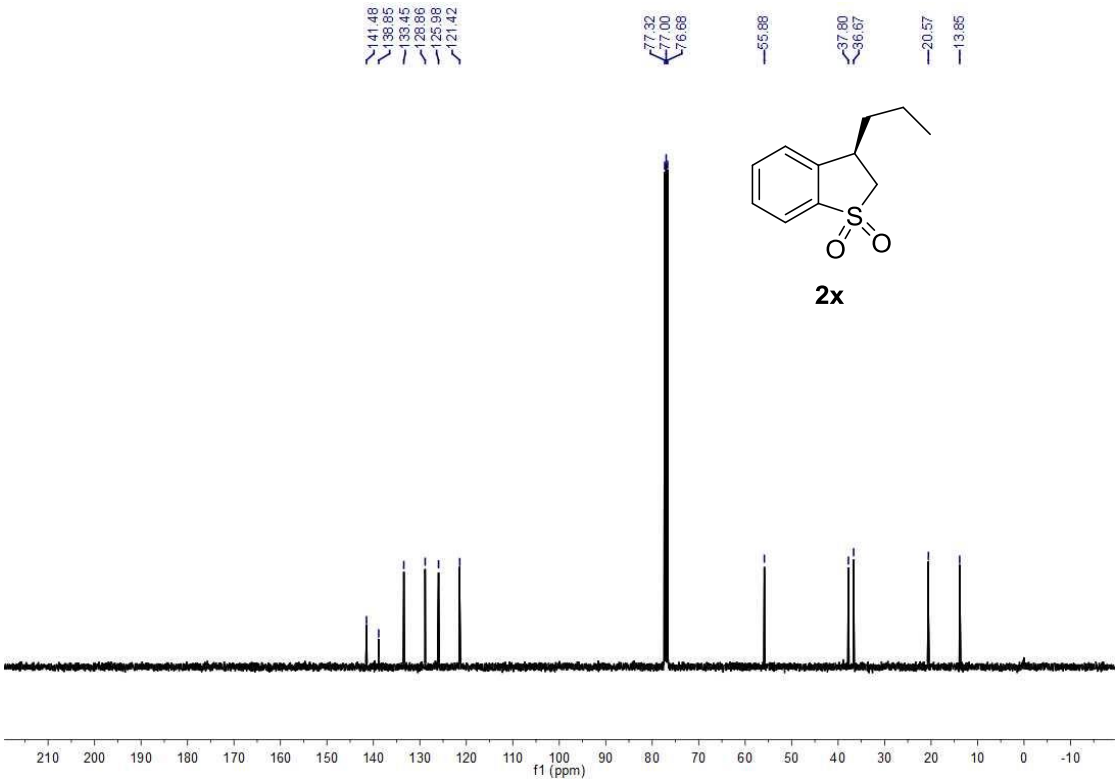
7.41
7.26
3.64
3.62
3.61
3.59
3.56
3.55
3.54
3.53
3.52
3.51
3.50
3.22
3.21
3.19
3.18
2.08
2.08
2.07
2.06
2.05
1.76
1.76
1.04
1.04
1.02
1.00
1.04
1.05
1.05
1.07
1.09
1.08
1.07
1.08
3.20
f1 (ppm)

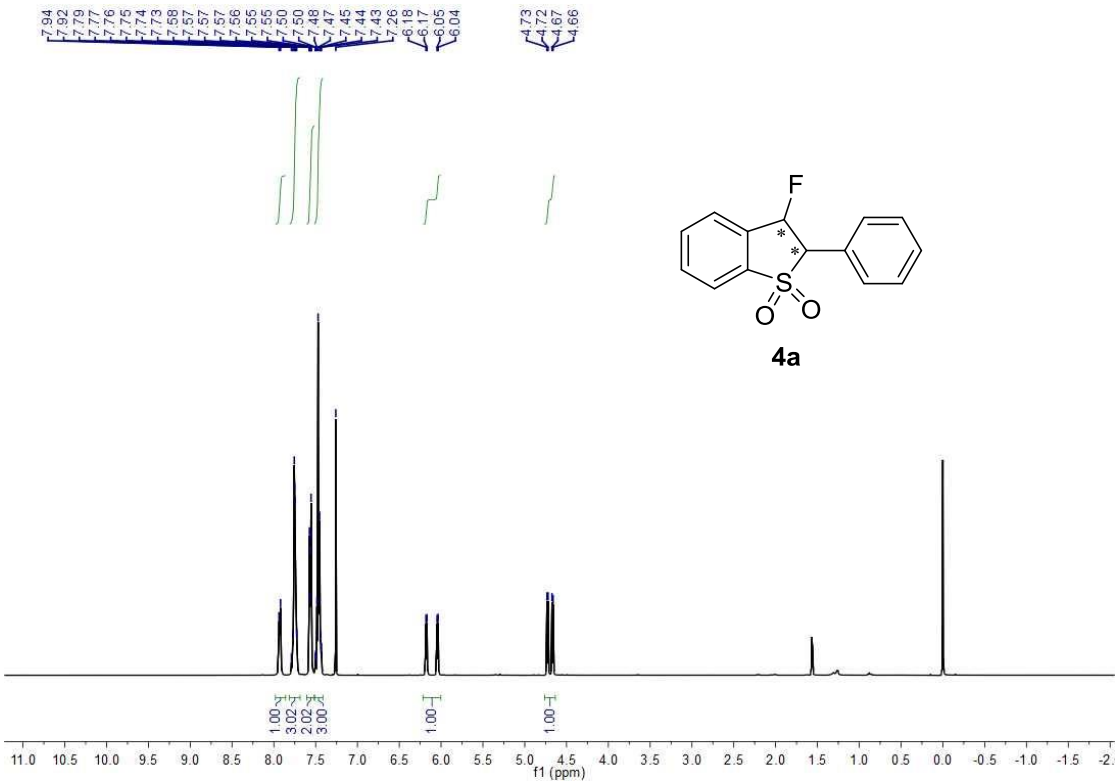
2w


141.17
138.99
133.45
128.89
125.99
121.41
77.32
77.00
76.68
55.47
39.40
27.32
11.55
f1 (ppm)

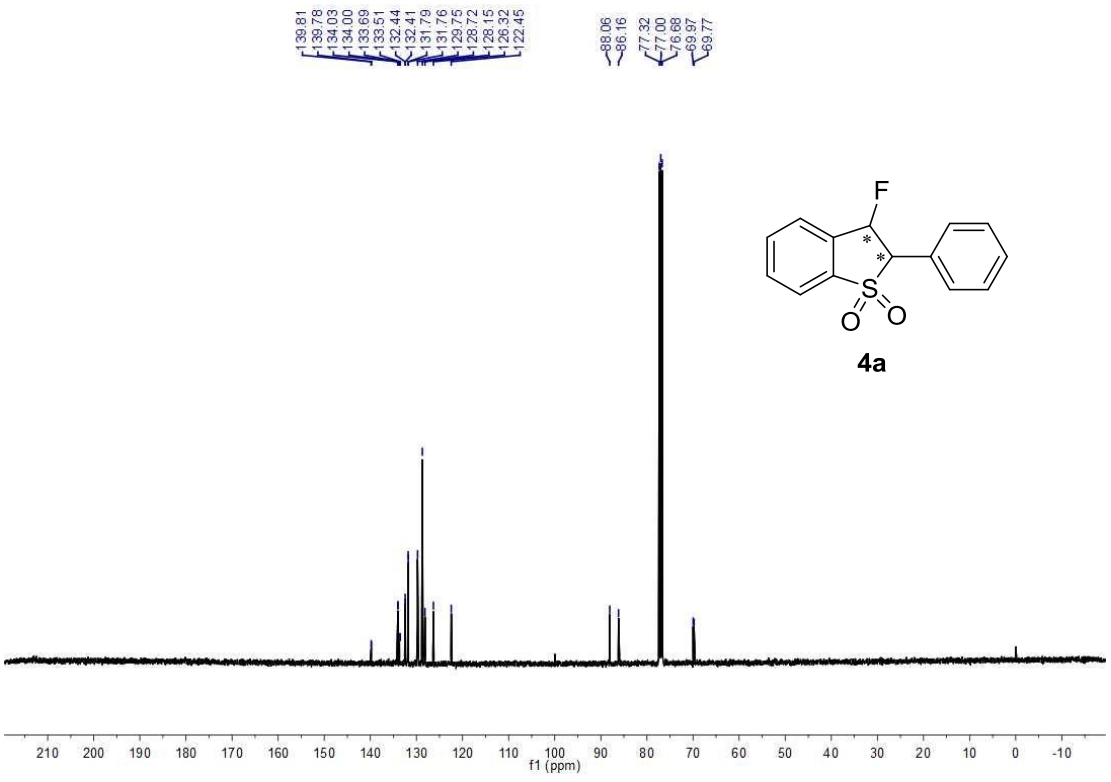
2w


2x
f1 (ppm)


2x
f1 (ppm)


7.94
7.92
7.79
7.77
7.76
7.75
7.74
7.73
7.58
7.57
7.57
7.57
7.56
7.55
7.55
7.50
7.50
7.48
7.47
7.45
7.44
7.43
7.26
6.18
6.17
6.05
6.04
4.73
4.72
4.67
4.66
F
S
O
O
1.00
3.02
2.02
3.00
1.00
1.00
f1 (ppm)

4a


139.81
139.78
134.03
134.00
133.69
133.51
132.44
132.41
131.79
131.76
129.75
128.72
128.15
126.32
122.45
88.06
86.16
77.32
77.00
76.68
69.97
69.77
F
S
O
O
f1 (ppm)

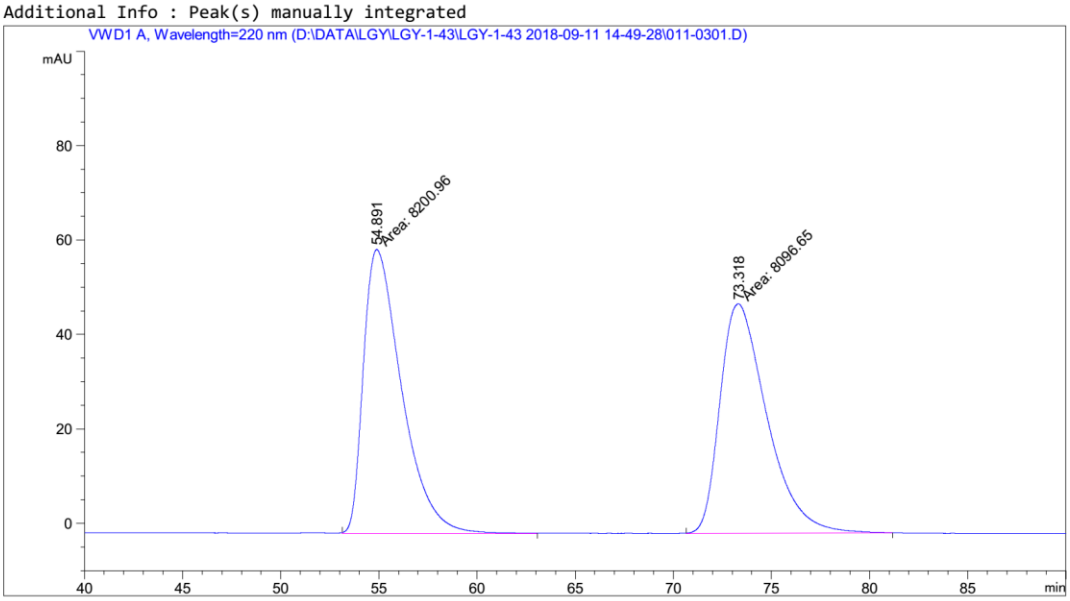
4a

9. HPLC spectra

HPLC of racemic-**2a**

Data File D:\DATA\LGY\LGY-1-43\LGY-1-43 2018-09-11 14-49-28\011-0301.D
Sample Name: LGY-1-43-1

```
======================================================================
Acq. Operator   :                                Seq. Line :   3
Acq. Instrument : Instrument 1                    Location : Vial 11
Injection Date  : 9/11/2018 3:15:08 PM                 Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : D:\DATA\LGY\LGY-1-43\LGY-1-43 2018-09-11 14-49-28\VWD-AS(1-6)-80-20-1ML-5UL
                  -220NM-80MIN.M
Last changed    : 9/11/2018 4:37:46 PM
                  (modified after loading)
Analysis Method : D:\METHOD\LG\VWD-AD(1-2)-99-1-0.2ML-2UL-220NM-10MIN.M
Last changed    : 9/12/2018 9:50:51 AM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

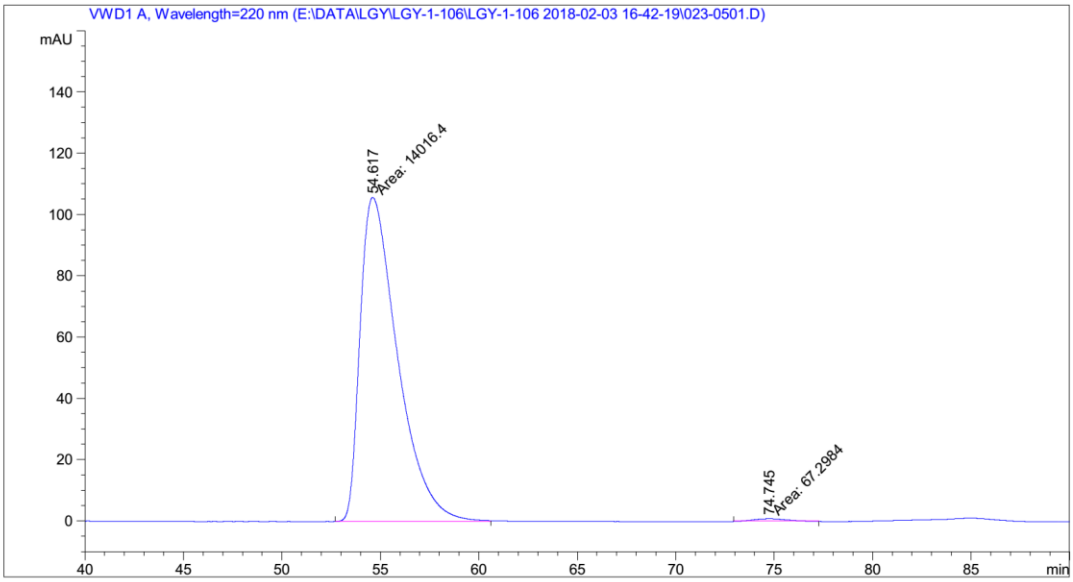



```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Retention Time
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Sig Type    Area      Height     Area
  #   [min]            [mAU*s]     [mAU]       %
----|-------|---|----|----------|----------|--------|
   1  54.891  1  MM   8200.96387   60.20780  50.3200
   2  73.318  1  MP   8096.65479   48.65597  49.6800

Totals :              1.62976e4   108.86377
```

HPLC of **2a**

Data File E:\DATA\LGY\LGY-1-106\LGY-1-106 2018-02-03 16-42-19\023-0501.D
Sample Name: LGY-1-106-3

```
==================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   5
Acq. Instrument : 1260HPLC-VWD                   Location : Vial 23
Injection Date  : 2/3/2018 8:47:02 PM                Inj :   1
                                               Inj Volume : 5.000 µl
Acq. Method     : E:\DATA\LGY\LGY-1-106\LGY-1-106 2018-02-03 16-42-19\VWD-AS(1-6)-80-20-1ML-
                  5UL-220NM-90MIN.M
Last changed    : 2/3/2018 4:42:20 PM by SYSTEM
Analysis Method : E:\DATA\LGY\LGY-1-106\LGY-1-106 2018-02-03 16-42-19\VWD-AS(1-6)-80-20-1ML-
                  5UL-220NM-90MIN.M (Sequence Method)
Last changed    : 9/14/2018 3:37:19 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

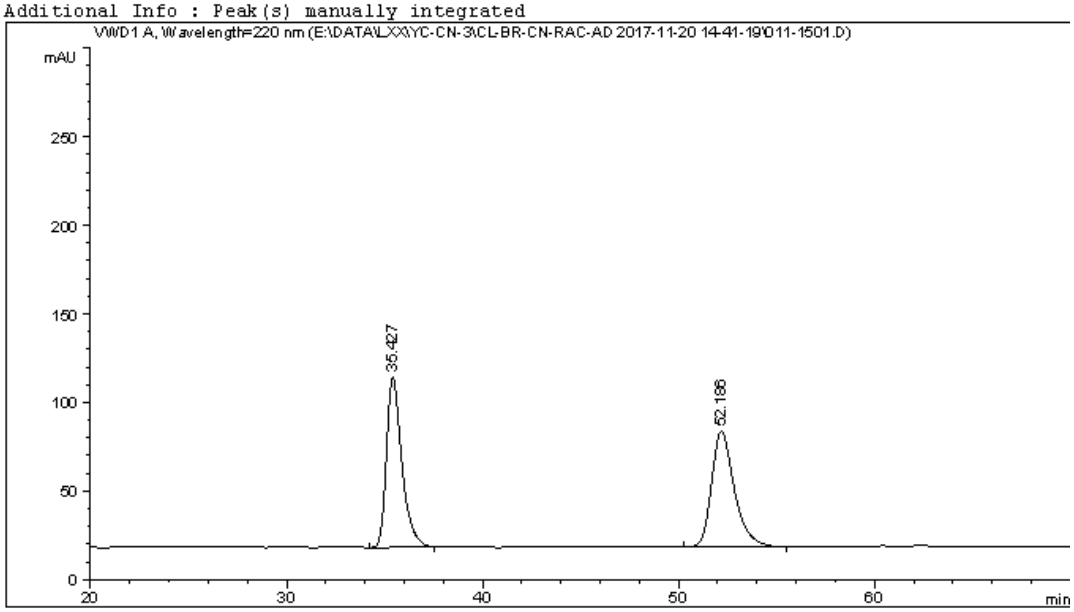



```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  54.617 MM    2.2089 1.40164e4   105.75460  99.5222
   2  74.745 MM    1.6222   67.29838 6.91447e-1   0.4778

Totals :                  1.40837e4   106.44605
```

HPLC of racemic-**2b**

Data File E:\DATA\LXX\YC-CN-3\CL-BR-CN-RAC-AD 2017-11-20 14-41-19\011-1501.D
Sample Name: LGY-1-30-1-RE-2

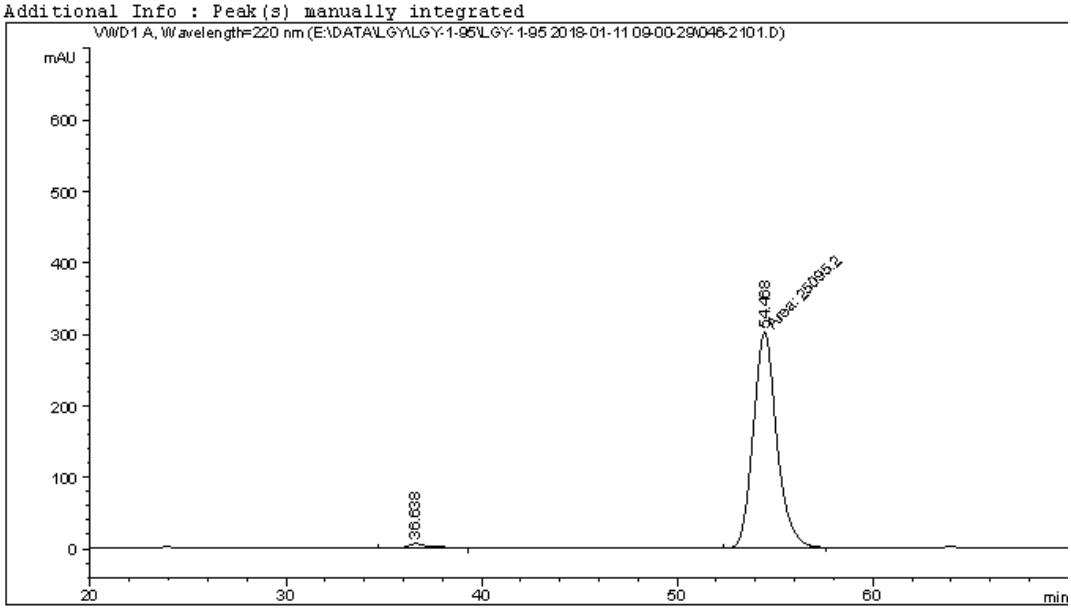
```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  15
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 11
    Injection Date  : 11/21/2017 12:11:03 AM               Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LXX\YC-CN-3\CL-BR-CN-RAC-AD 2017-11-20 14-41-19\VWD-AD(1-2)-80-
                      20-1ML-5UL-220NM-120MIN.M
    Last changed    : 11/20/2017 7:15:44 PM by SYSTEM
    Analysis Method : E:\DATA\LXX\YC-CN-3\CL-BR-CN-RAC-AD 2017-11-20 14-41-19\VWD-AD(1-2)-80-
                      20-1ML-5UL-220NM-120MIN.M (Sequence Method)
    Last changed    : 4/13/2018 10:38:59 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  35.427 BB    0.8183 5244.05957   96.45979  49.9569
       2  52.186 BB    1.2062 5253.11182   65.18310  50.0431

    Totals :                  1.04972e4   161.64289


    ======================================================================
                            *** End of Report ***

1260HPLC-VWD 4/13/2018 10:39:03 AM SYSTEM                    Page 1 of 1
```

HPLC of **2b**

```
Data File E:\DATA\LGY\LGY-1-95\LGY-1-95 2018-01-11 09-00-29\046-2101.D
Sample Name: LGY-1-95-6

    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :  21
    Acq. Instrument : 1260HPLC-VWD                   Location : Vial 46
    Injection Date  : 1/11/2018 10:48:07 PM               Inj :  1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-95\LGY-1-95 2018-01-11 09-00-29\VWD-AD(1-2)-80-20-1ML-
                      5UL-220NM-70MIN.M
    Last changed    : 1/11/2018 9:32:22 AM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-95\LGY-1-95 2018-01-11 09-00-29\VWD-AD(1-2)-80-20-1ML-
                      5UL-220NM-70MIN.M (Sequence Method)
    Last changed    : 4/13/2018 11:11:59 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

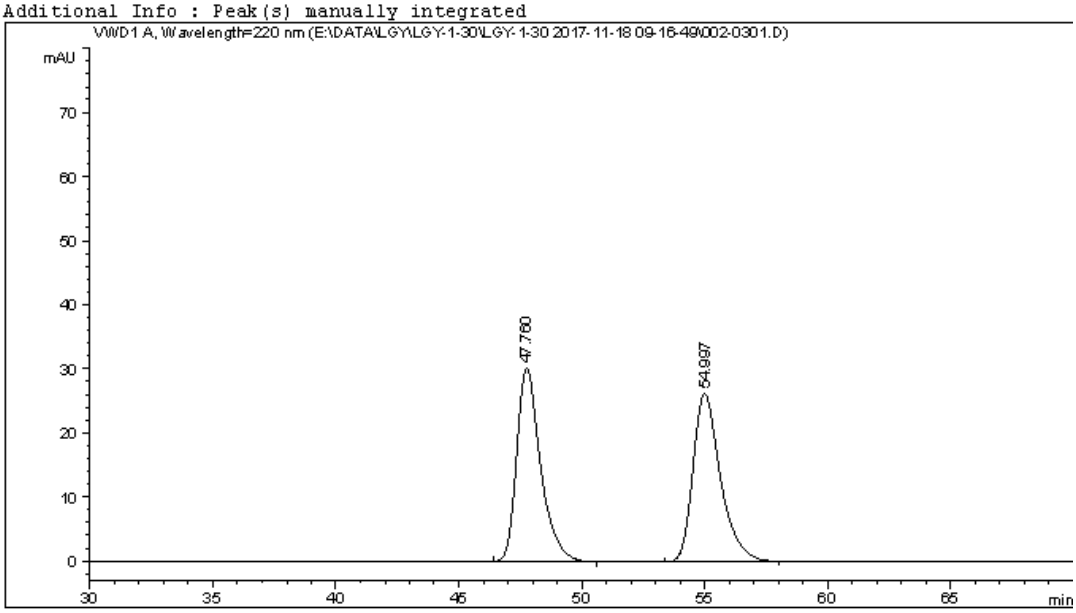



```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  36.638 BB    0.9879  444.26672    6.31377   1.7395
       2  54.468 MM    1.3885 2.50952e4   301.22711  98.2605

    Totals :                  2.55395e4   307.54088


    ======================================================================
                              *** End of Report ***

1260HPLC-VWD 4/13/2018 11:12:06 AM SYSTEM                    Page 1 of 1
```

HPLC of racemic-**2c**

Data File E:\DATA\LGY\LGY-1-30\LGY-1-30 2017-11-18 09-16-49\002-0301.D
Sample Name: LGY-1-30-2-RE

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   3
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 2
    Injection Date  : 11/18/2017 11:29:08 AM               Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-30\LGY-1-30 2017-11-18 09-16-49\VWD-AD1-2)-90-10-1ML-
                      5UL-220NM-120MIN.M
    Last changed    : 11/18/2017 9:16:49 AM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-30\LGY-1-30 2017-11-18 09-16-49\VWD-AD1-2)-90-10-1ML-
                      5UL-220NM-120MIN.M (Sequence Method)
    Last changed    : 4/13/2018 11:15:55 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

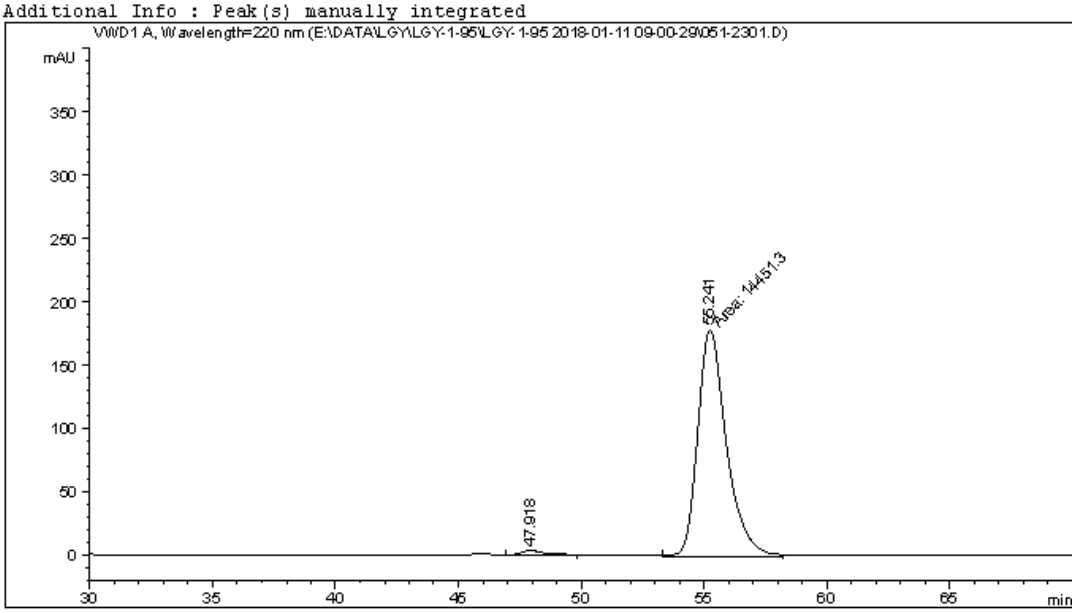



```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  47.760 BB    1.0081 2028.27917   30.18014  49.8963
       2  54.997 BB    1.1583 2036.71033   26.21724  50.1037

    Totals :                  4064.98950   56.39738


    ======================================================================
                            *** End of Report ***
```

HPLC of **2c**

Data File E:\DATA\LGY\LGY-1-95\LGY-1-95 2018-01-11 09-00-29\051-2301.D
Sample Name: LGY-1-95-7

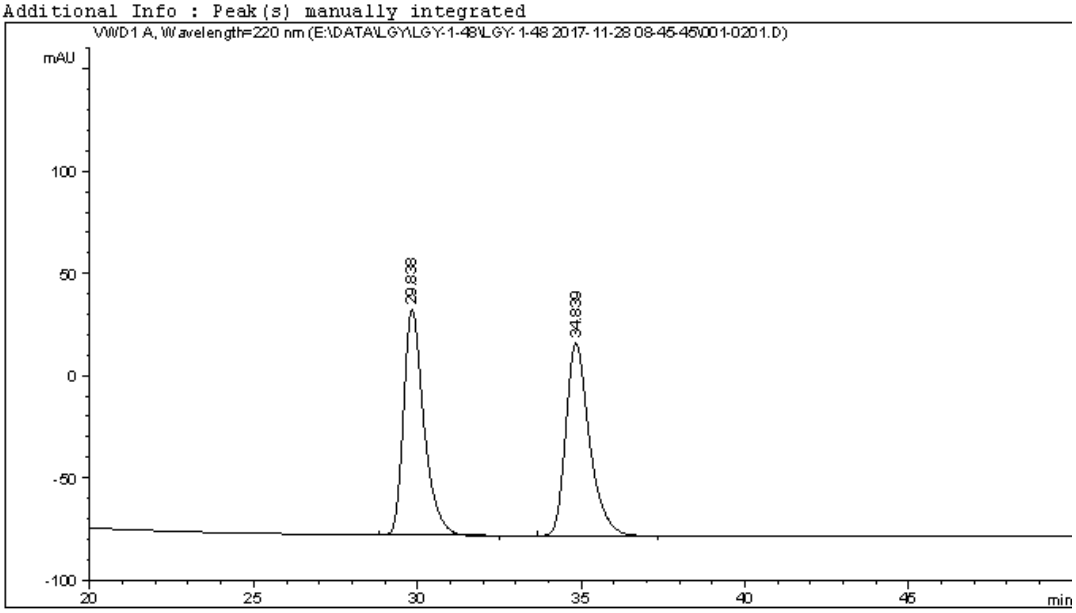
```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  23
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 51
    Injection Date  : 1/12/2018 12:09:48 AM                 Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-95\LGY-1-95 2018-01-11 09-00-29\VWD-AD(1-2)-90-10-1ML-
                      5UL-220NM-70MIN.M
    Last changed    : 1/11/2018 9:57:00 AM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-95\LGY-1-95 2018-01-11 09-00-29\VWD-AD(1-2)-90-10-1ML-
                      5UL-220NM-70MIN.M (Sequence Method)
    Last changed    : 4/13/2018 11:25:57 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  47.918 BB    0.8864  201.08961    3.24308   1.3724
       2  55.241 MM    1.3502 1.44513e4   178.37892  98.6276

    Totals :                  1.46524e4   181.62200


    ======================================================================
                            *** End of Report ***
```

HPLC of racemic-**2d**

```
Data File E:\DATA\LGY\LGY-1-48\LGY-1-48 2017-11-28 08-45-45\001-0201.D
Sample Name: LGY-1-48

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 1
    Injection Date  : 11/28/2017 8:59:18 AM                 Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-48\LGY-1-48 2017-11-28 08-45-45\VWD-AD(1-2)-90-10-1ML-
                      5UL-220NM-60MIN.M
    Last changed    : 11/28/2017 8:45:45 AM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-48\LGY-1-48 2017-11-28 08-45-45\VWD-AD(1-2)-90-10-1ML-
                      5UL-220NM-60MIN.M (Sequence Method)
    Last changed    : 4/13/2018 2:34:27 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

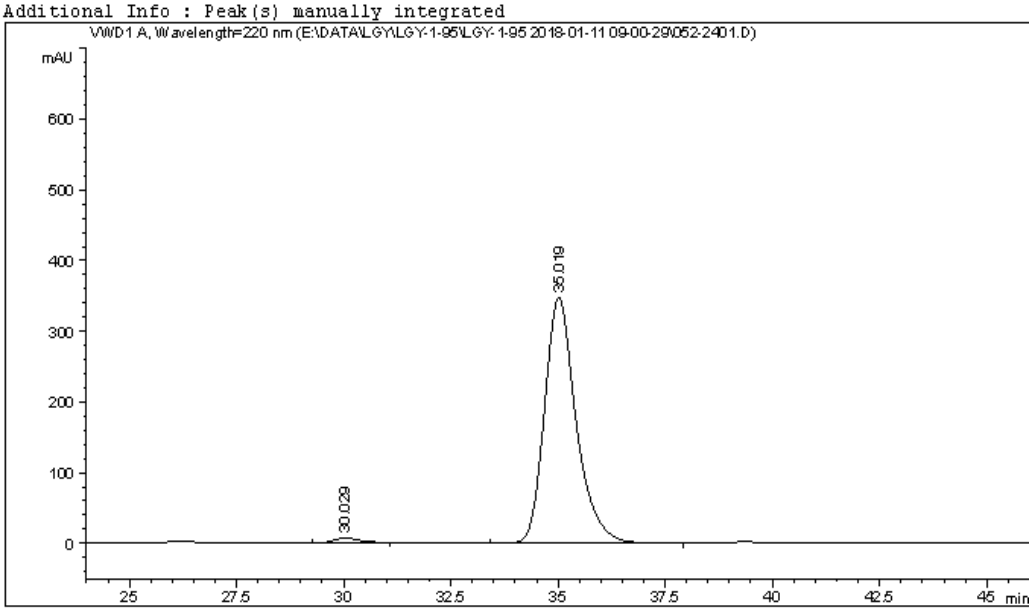



```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  29.838 BB    0.6488 4745.69092  110.33386  50.0321
       2  34.839 BB    0.7594 4739.59814   94.30391  49.9679

    Totals :                  9485.28906  204.63777


    ======================================================================
                            *** End of Report ***

1260HPLC-VWD 4/13/2018 2:34:39 PM SYSTEM                       Page 1 of 1
```

HPLC of **2d**

Data File E:\DATA\LGY\LGY-1-95\LGY-1-95 2018-01-11 09-00-29\052-2401.D
Sample Name: LGY-1-95-8

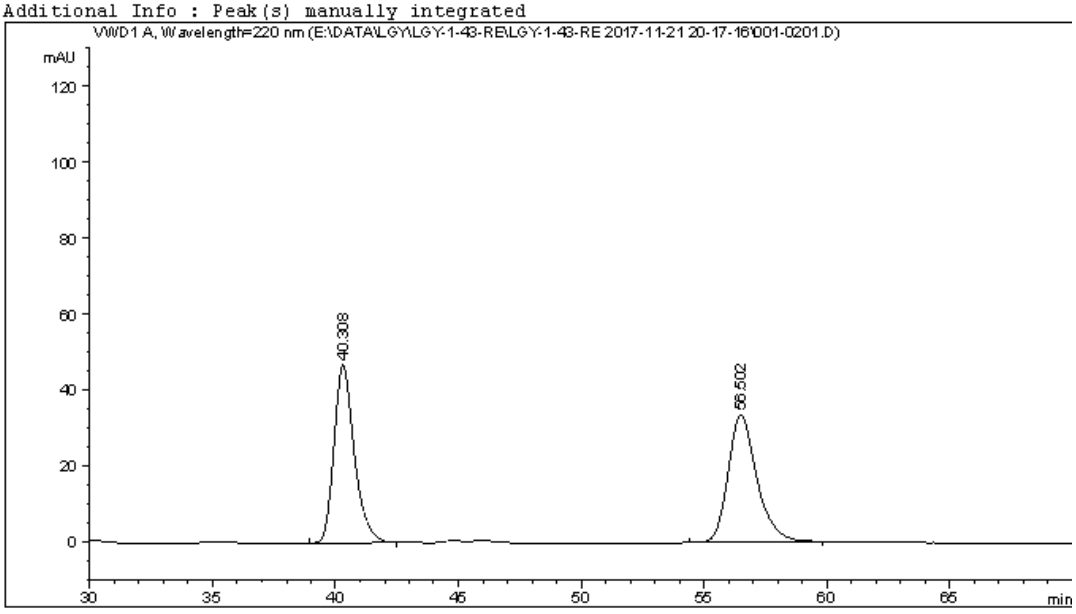
```
    ==================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :  24
    Acq. Instrument : 1260HPLC-VWD                   Location : Vial 52
    Injection Date  : 1/12/2018 1:20:36 AM                Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-95\LGY-1-95 2018-01-11 09-00-29\VWD-AD(1-2)-90-10-1ML-
                      5UL-220NM-60MIN.M
    Last changed    : 1/11/2018 9:58:22 AM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-95\LGY-1-95 2018-01-11 09-00-29\VWD-AD(1-2)-90-10-1ML-
                      5UL-220NM-60MIN.M (Sequence Method)
    Last changed    : 4/13/2018 2:41:55 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                           Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  30.029 BB    0.6273  273.22952    6.62337   1.5151
       2  35.019 BB    0.7703 1.7761le4   347.47638  98.4849

    Totals :                  1.80343e4   354.09975


    ==================================================================
                           *** End of Report ***
```

HPLC of racemic-**2e**

```
Data File E:\DATA\LGY\LGY-1-43-RE\LGY-1-43-RE 2017-11-21 20-17-16\001-0201.D
Sample Name: LGY-1-43-2

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260HPLC-VWD                    Location : Vial 1
    Injection Date  : 11/21/2017 8:28:50 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-43-RE\LGY-1-43-RE 2017-11-21 20-17-16\VWD-AD(1-2)-90-
                      10-1ML-5UL-220NM-80MIN.M
    Last changed    : 11/21/2017 8:17:16 PM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-43-RE\LGY-1-43-RE 2017-11-21 20-17-16\VWD-AD(1-2)-90-
                      10-1ML-5UL-220NM-80MIN.M (Sequence Method)
    Last changed    : 4/13/2018 2:45:27 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

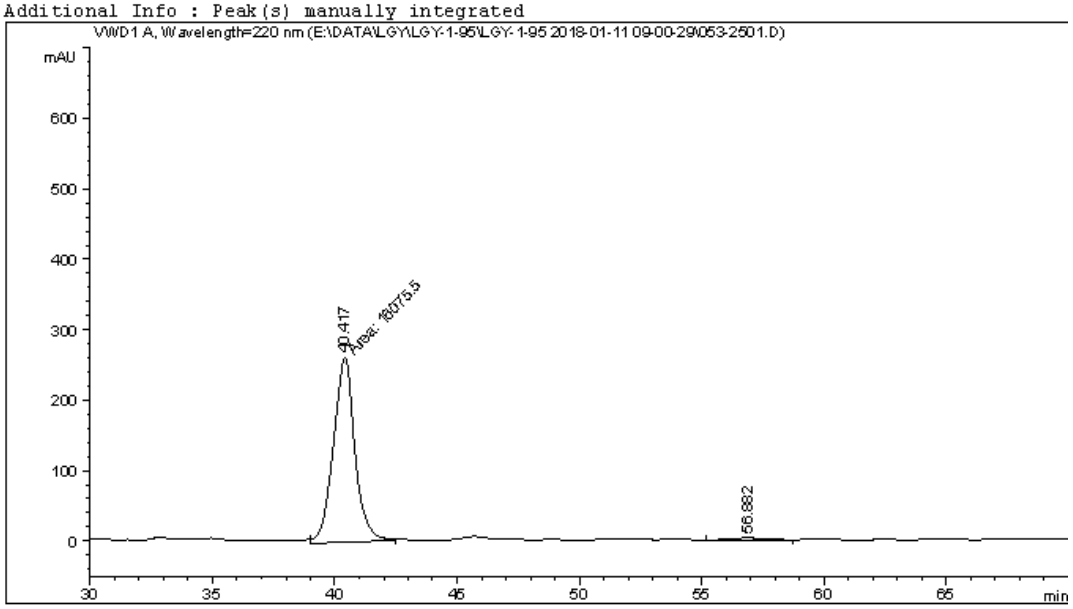



```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  40.308 BB    0.8700 2698.65698   46.85027  49.7331
       2  56.502 BB    1.2107 2727.62354   33.54262  50.2669

    Totals :                  5426.28052   80.39289


    ======================================================================
                            *** End of Report ***

1260HPLC-VWD 4/13/2018 2:45:37 PM SYSTEM                    Page 1 of 1
```

HPLC of **2e**

Data File E:\DATA\LGY\LGY-1-95\LGY-1-95 2018-01-11 09-00-29\053-2501.D
Sample Name: LGY-1-95-9

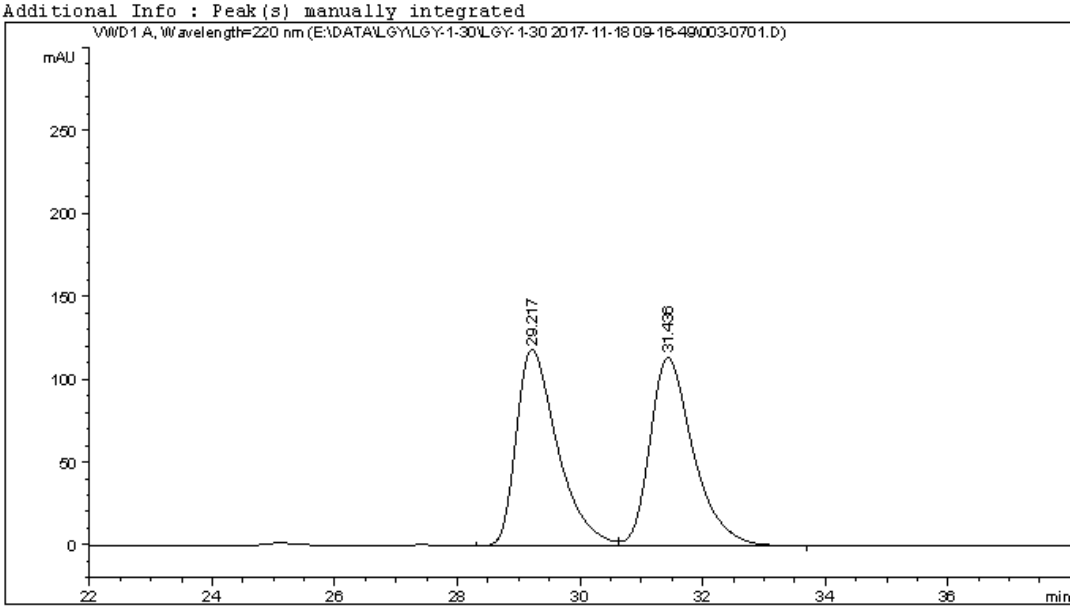
```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :  25
    Acq. Instrument : 1260HPLC-VWD                  Location : Vial 53
    Injection Date  : 1/12/2018 2:21:26 AM               Inj :  1
                                                 Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-95\LGY-1-95 2018-01-11 09-00-29\VWD-AD(1-2)-90-10-1ML-
                      5UL-220NM-70MIN.M
    Last changed    : 1/11/2018 9:57:00 AM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-95\LGY-1-95 2018-01-11 09-00-29\VWD-AD(1-2)-90-10-1ML-
                      5UL-220NM-70MIN.M (Sequence Method)
    Last changed    : 4/13/2018 2:52:00 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  40.417 MM    1.0239 1.60755e4   261.68359  98.2730
       2  56.882 BB    1.1743  282.50827    2.90835   1.7270

    Totals :                  1.63580e4   264.59194


    ======================================================================
                               *** End of Report ***
```

HPLC of racemic-**2f**

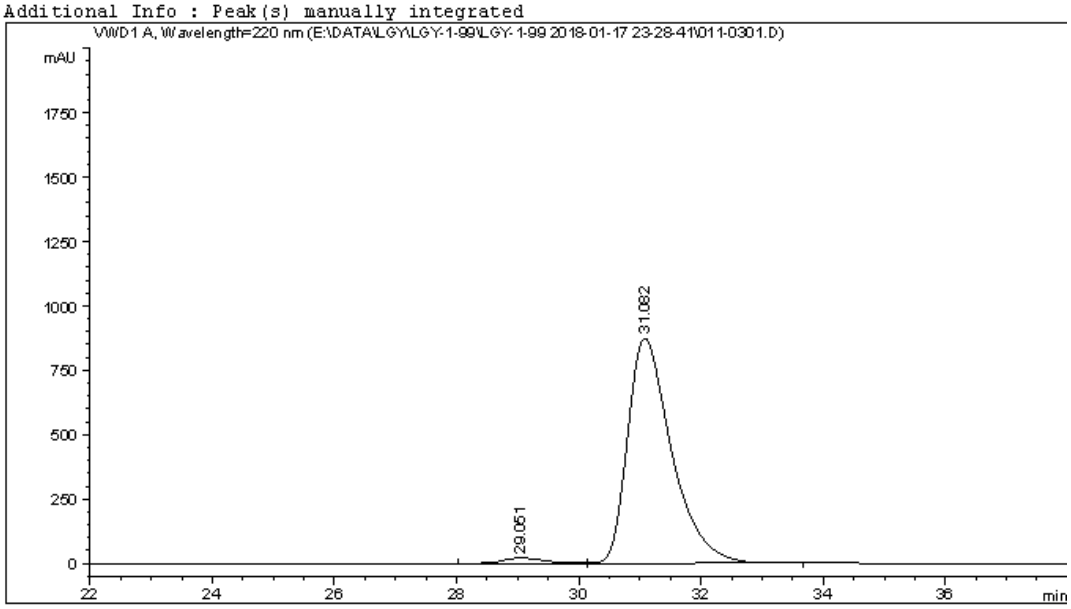
```
Data File E:\DATA\LGY\LGY-1-30\LGY-1-30 2017-11-18 09-16-49\003-0701.D
Sample Name: LGY-1-30-3

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   7
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 3
    Injection Date  : 11/18/2017 2:32:24 PM                 Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-30\LGY-1-30 2017-11-18 09-16-49\VWD-AD1-2)-90-10-1ML-
                      5UL-220NM-120MIN.M
    Last changed    : 11/18/2017 3:20:37 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\LGY\LGY-1-30\LGY-1-30 2017-11-18 09-16-49\VWD-AD1-2)-90-10-1ML-
                      5UL-220NM-120MIN.M (Sequence Method)
    Last changed    : 4/13/2018 2:55:30 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  29.217 BV    0.7098 5531.45459  118.23405  49.8168
       2  31.436 VB    0.7460 5572.14600  113.45072  50.1832

    Totals :                  1.11036e4   231.68477

    ======================================================================

1260HPLC-VWD 4/13/2018 2:55:40 PM SYSTEM                    Page 1 of 1
```

HPLC of **2f**

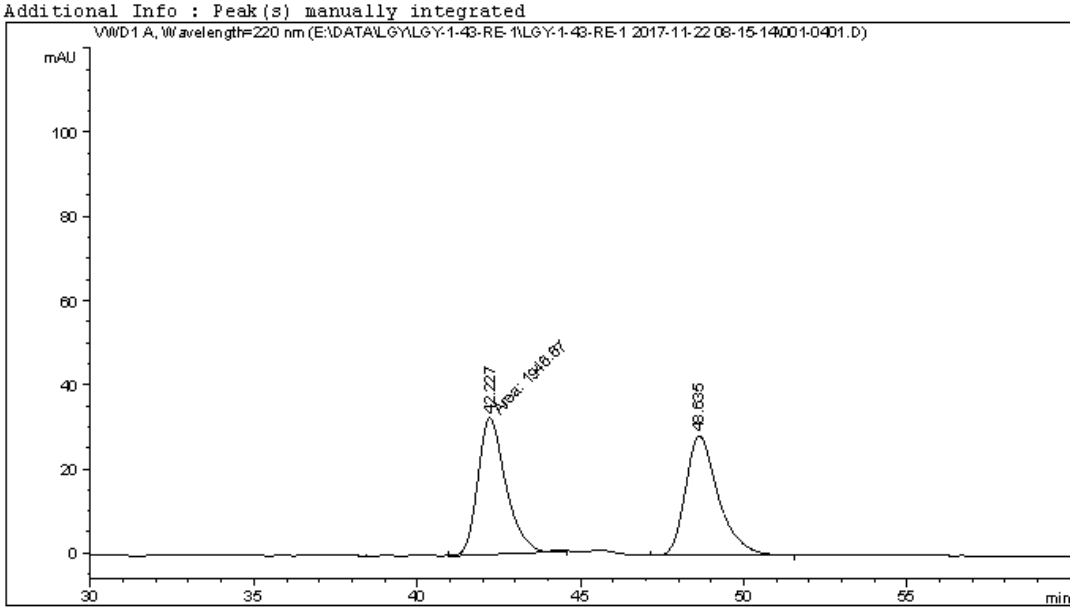
```
Data File E:\DATA\LGY\LGY-1-99\LGY-1-99 2018-01-17 23-28-41\011-0301.D
Sample Name: LGY-1-99-1

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   3
    Acq. Instrument : 1260HPLC-VWD                    Location : Vial 11
    Injection Date  : 1/18/2018 12:11:03 AM                Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-99\LGY-1-99 2018-01-17 23-28-41\VWD-AD(1-2)-90-10-1ML-
                      5UL-220NM-40MIN.M
    Last changed    : 1/17/2018 11:28:41 PM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-99\LGY-1-99 2018-01-17 23-28-41\VWD-AD(1-2)-90-10-1ML-
                      5UL-220NM-40MIN.M (Sequence Method)
    Last changed    : 4/13/2018 3:01:00 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  29.051 BV    0.6723  909.31097   20.34970   2.0434
       2  31.082 VB    0.7529 4.35909e4   873.90997  97.9566

    Totals :                  4.45002e4   894.25967


    ======================================================================
                               *** End of Report ***

1260HPLC-VWD 4/13/2018 3:01:09 PM SYSTEM                    Page 1 of 1
```

HPLC of racemic-**2g**

```
Data File E:\DATA\LGY\LGY-1-43-RE-1\LGY-1-43-RE-1 2017-11-22 08-15-14\001-0401.D
Sample Name: LGY-1-43-3--RE

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   4
    Acq. Instrument : 1260HPLC-VWD                    Location : Vial 1
    Injection Date  : 11/22/2017 10:40:29 AM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-43-RE-1\LGY-1-43-RE-1 2017-11-22 08-15-14\VWD-AD1-2)-
                      90-10-1ML-5UL-220NM-120MIN.M
    Last changed    : 11/22/2017 10:25:44 AM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-43-RE-1\LGY-1-43-RE-1 2017-11-22 08-15-14\VWD-AD1-2)-
                      90-10-1ML-5UL-220NM-120MIN.M (Sequence Method)
    Last changed    : 4/13/2018 3:11:26 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

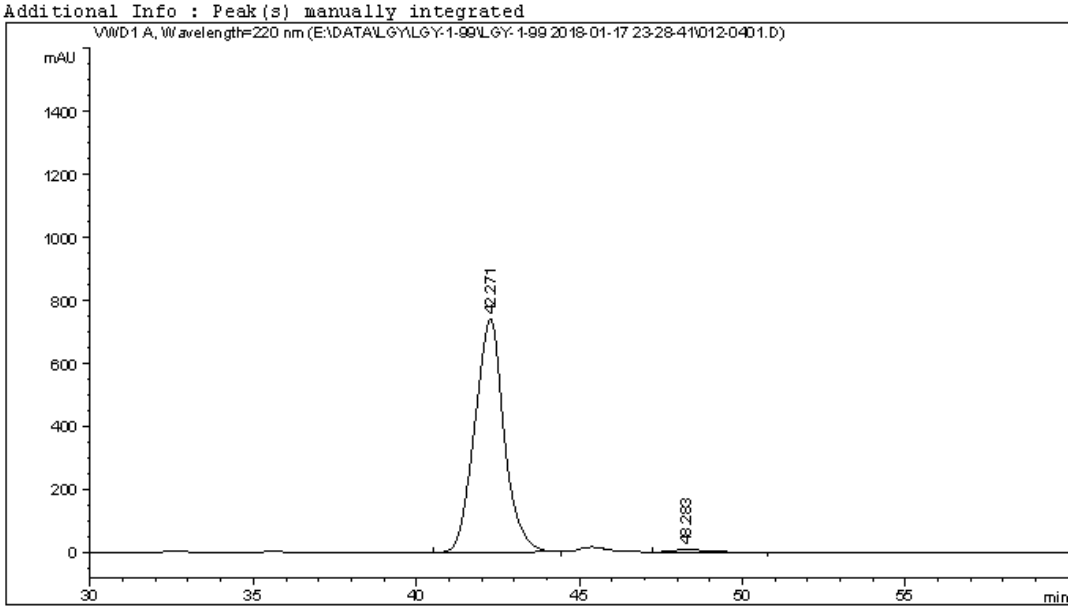



```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  42.227 MM    0.9985 1946.67358   32.49449  49.5317
       2  48.635 BB    1.0459 1983.48608   28.43331  50.4683

    Totals :                  3930.15967   60.92780


    ======================================================================
                            *** End of Report ***

1260HPLC-VWD 4/13/2018 3:11:31 PM SYSTEM                    Page 1 of 1
```

HPLC of **2g**

Data File E:\DATA\LGY\LGY-1-99\LGY-1-99 2018-01-17 23-28-41\012-0401.D
Sample Name: LGY-1-99-2

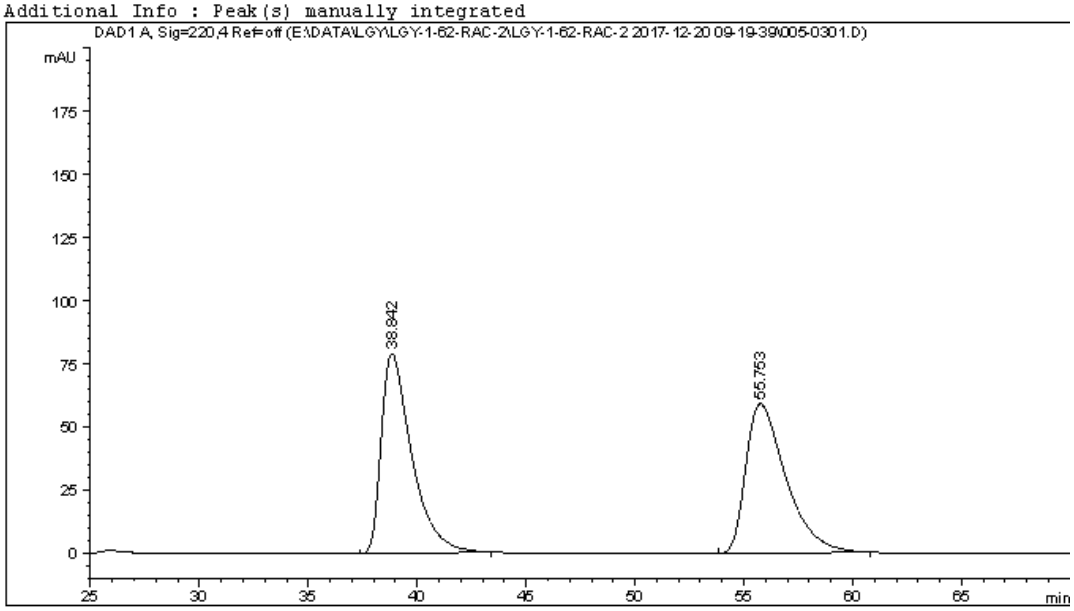
```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   4
    Acq. Instrument : 1260HPLC-VWD                   Location : Vial 12
    Injection Date  : 1/18/2018 12:51:51 AM               Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-99\LGY-1-99 2018-01-17 23-28-41\VWD-AD(1-2)-90-10-1ML-
                      5UL-220NM-60MIN.M
    Last changed    : 1/17/2018 11:28:42 PM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-99\LGY-1-99 2018-01-17 23-28-41\VWD-AD(1-2)-90-10-1ML-
                      5UL-220NM-60MIN.M (Sequence Method)
    Last changed    : 4/13/2018 3:16:25 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  42.271 BB    0.9493 4.63086e4   739.79163  98.8203
       2  48.283 BB    0.9826  552.80939    8.31575   1.1797

    Totals :                  4.68614e4   748.10738


    ======================================================================
                               *** End of Report ***
```

HPLC of racemic-**2h**

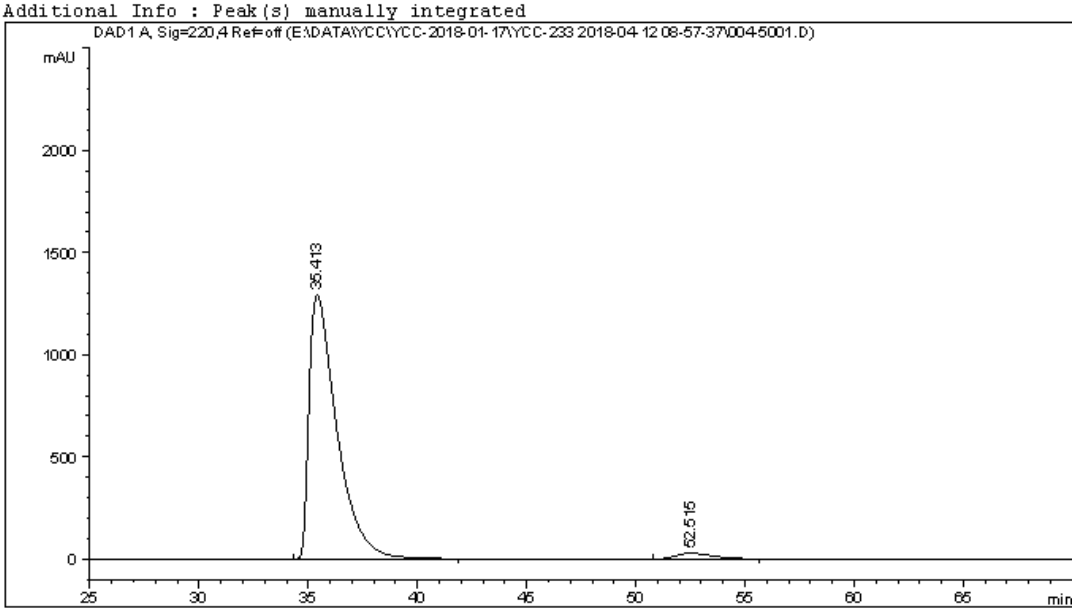
```
Data File E:\DATA\LGY\LGY-1-62-RAC-2\LGY-1-62-RAC-2 2017-12-20 09-19-39\005-0301.D
Sample Name: LGY-1-62-1

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   3
    Acq. Instrument : 1260HPLC-DAD                    Location : Vial 5
    Injection Date  : 12/20/2017 10:48:46 AM               Inj :   1
                                                   Inj Volume : 7.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-62-RAC-2\LGY-1-62-RAC-2 2017-12-20 09-19-39\DAD-OD(1-2
                      )-85-15-1ML-7UL-ALL-70MIN.M
    Last changed    : 12/20/2017 9:19:39 AM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-62-RAC-2\LGY-1-62-RAC-2 2017-12-20 09-19-39\DAD-OD(1-2
                      )-85-15-1ML-7UL-ALL-70MIN.M (Sequence Method)
    Last changed    : 4/13/2018 3:25:12 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=220,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  38.842 BB    1.3572 7681.99365   79.09193  50.3339
       2  55.753 BB    1.5096 7580.08252   59.13079  49.6661

    Totals :                  1.5262le4   138.22271


    ======================================================================
                            *** End of Report ***

1260HPLC-VWD 4/13/2018 3:25:17 PM SYSTEM                    Page 1 of 1
```

HPLC of **2h**

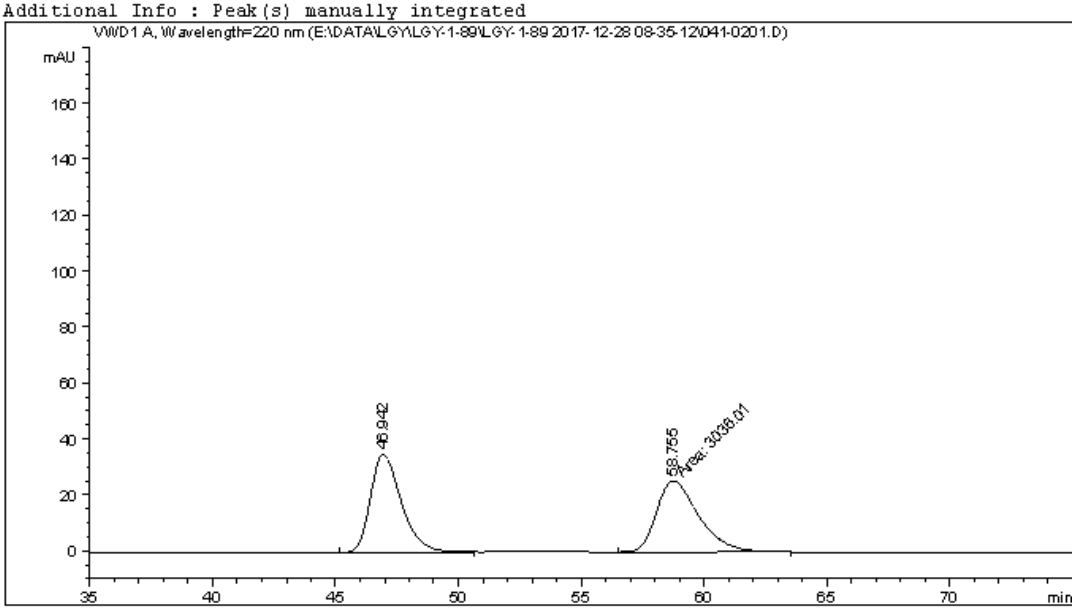
```
Data File E:\DATA\YCC\YCC-2018-01-17\YCC-233 2018-04-12 08-57-37\004-5001.D
Sample Name: LGY-1-99-3

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  50
    Acq. Instrument : 1260HPLC-DAD                    Location : Vial 4
    Injection Date  : 4/13/2018 8:38:57 AM                 Inj :   1
                                                   Inj Volume : 7.000 µl
    Acq. Method     : E:\DATA\YCC\YCC-2018-01-17\YCC-233 2018-04-12 08-57-37\DAD-0D(1-2)-85-15
                      -1ML-7UL-ALL-70MIN.M
    Last changed    : 4/12/2018 8:57:25 PM by SYSTEM
    Analysis Method : E:\DATA\YCC\YCC-2018-01-17\YCC-233 2018-04-12 08-57-37\DAD-0D(1-2)-85-15
                      -1ML-7UL-ALL-70MIN.M (Sequence Method)
    Last changed    : 4/13/2018 3:30:25 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=220,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  35.413 BB    1.2040 1.13739e5  1290.86548  97.4011
       2  52.515 BB    1.2788 3034.80859   27.77357   2.5989

    Totals :                  1.16774e5  1318.63905


    ======================================================================
                              *** End of Report ***

1260HPLC-VWD 4/13/2018 3:30:36 PM SYSTEM                       Page 1 of 1
```

HPLC of racemic-**2i**

```
Data File E:\DATA\LGY\LGY-1-89\LGY-1-89 2017-12-28 08-35-12\041-0201.D
Sample Name: LGY-1-89-RAC

    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Acq. Instrument : 1260HPLC-VWD                   Location : Vial 41
    Injection Date  : 12/28/2017 9:09:00 AM               Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-89\LGY-1-89 2017-12-28 08-35-12\VWD-AS(1-6)-80-20-1ML-
                      5UL-220NM-90MIN.M
    Last changed    : 12/28/2017 10:31:49 AM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\LGY\LGY-1-89\LGY-1-89 2017-12-28 08-35-12\VWD-AS(1-6)-80-20-1ML-
                      5UL-220NM-90MIN.M (Sequence Method)
    Last changed    : 4/13/2018 3:35:12 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

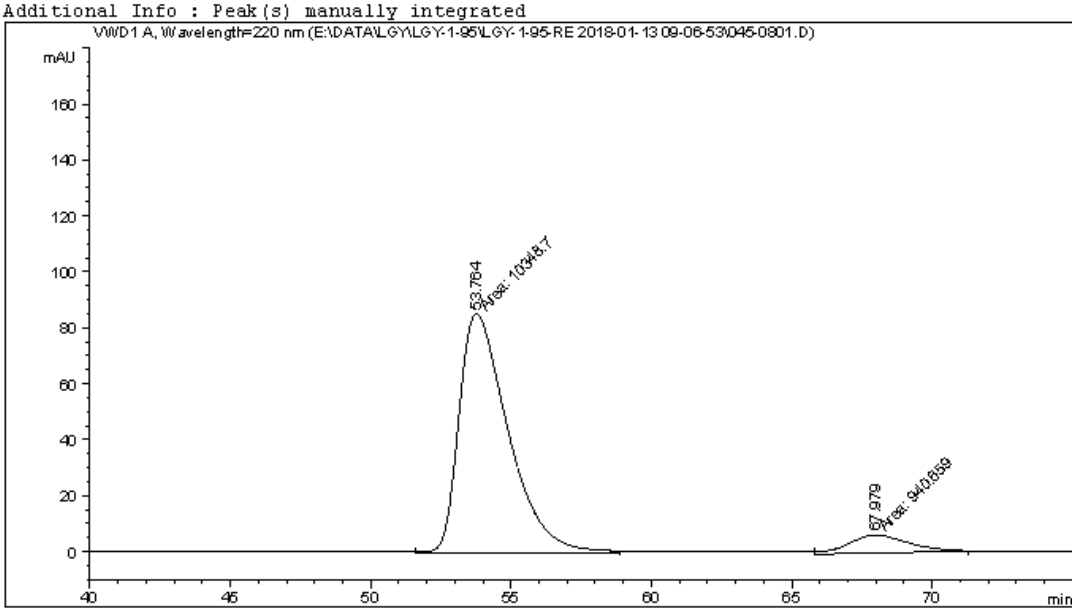



```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|-------|
       1  46.942 BB    1.3121 3043.56836   34.98038  50.0622
       2  58.755 MM    1.9840 3036.00806   25.50352  49.9378

    Totals :                  6079.57642   60.48391

    ======================================================================

1260HPLC-VWD 4/13/2018 3:35:23 PM SYSTEM                       Page 1 of 1
```

HPLC of **2i**

Data File E:\DATA\LGY\LGY-1-95\LGY-1-95-RE 2018-01-13 09-06-53\045-0801.D
Sample Name: LGY-1-95-11-RE

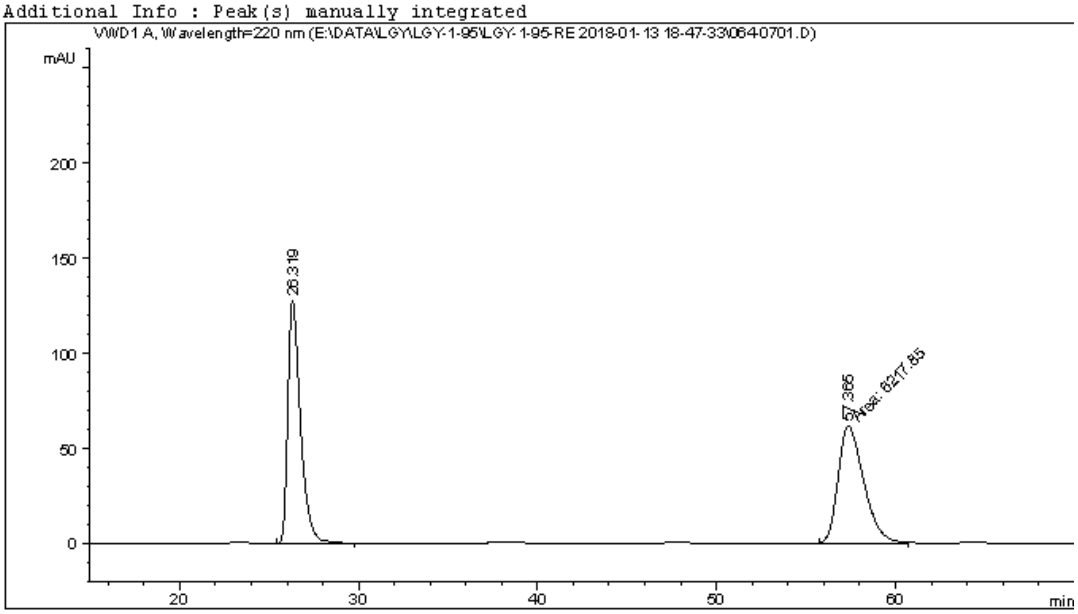
```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   8
    Acq. Instrument : 1260HPLC-VWD                   Location : Vial 45
    Injection Date  : 1/13/2018 3:01:51 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-95\LGY-1-95-RE 2018-01-13 09-06-53\VWD-AS(1-6)-80-20-
                      1ML-5UL-220NM-75MIN.M
    Last changed    : 1/13/2018 9:06:54 AM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-95\LGY-1-95-RE 2018-01-13 09-06-53\VWD-AS(1-6)-80-20-
                      1ML-5UL-220NM-75MIN.M (Sequence Method)
    Last changed    : 4/13/2018 3:50:00 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  53.764 MM    2.0249 1.03487e4    85.17876  91.6677
       2  67.979 MM    2.4811  940.65881    6.31878   8.3323

    Totals :                  1.12894e4    91.49755


    ======================================================================
                            *** End of Report ***
```

HPLC of racemic-**2j**

```
Data File E:\DATA\LGY\LGY-1-95\LGY-1-95-RE 2018-01-13 18-47-33\064-0701.D
Sample Name: LGY-1-94-1-RA

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   7
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 64
    Injection Date  : 1/14/2018 2:53:48 AM                 Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-95\LGY-1-95-RE 2018-01-13 18-47-33\VWD-AS(1-6)-80-20-
                      1ML-5UL-220NM-90MIN.M
    Last changed    : 1/13/2018 6:47:33 PM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-95\LGY-1-95-RE 2018-01-13 18-47-33\VWD-AS(1-6)-80-20-
                      1ML-5UL-220NM-90MIN.M (Sequence Method)
    Last changed    : 4/13/2018 5:11:04 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

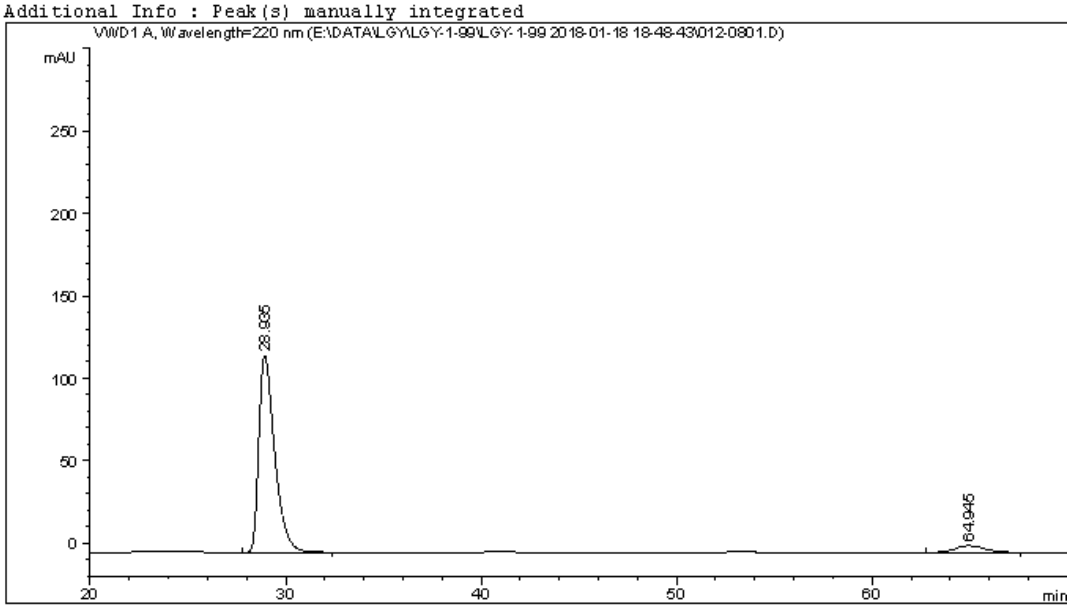



```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  26.319 BB    0.7423 6276.41748  127.73354  50.2344
       2  57.365 MM    1.6722 6217.85449   61.97150  49.7656

    Totals :                  1.24943e4   189.70504


    ======================================================================
                               *** End of Report ***

1260HPLC-VWD 4/13/2018 5:11:14 PM SYSTEM                    Page 1 of 1
```

HPLC of **2j**

Data File E:\DATA\LGY\LGY-1-99\LGY-1-99 2018-01-18 18-48-43\012-0801.D
Sample Name: LGY-1-99-5-RE-1

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   8
    Acq. Instrument : 1260HPLC-VWD                    Location : Vial 12
    Injection Date  : 1/19/2018 12:35:40 AM               Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-99\LGY-1-99 2018-01-18 18-48-43\VWD-AS(1-6)-80-20-1ML-
                      5UL-220NM-70MIN.M
    Last changed    : 1/18/2018 6:48:44 PM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-99\LGY-1-99 2018-01-18 18-48-43\VWD-AS(1-6)-80-20-1ML-
                      5UL-220NM-70MIN.M (Sequence Method)
    Last changed    : 4/13/2018 5:15:55 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

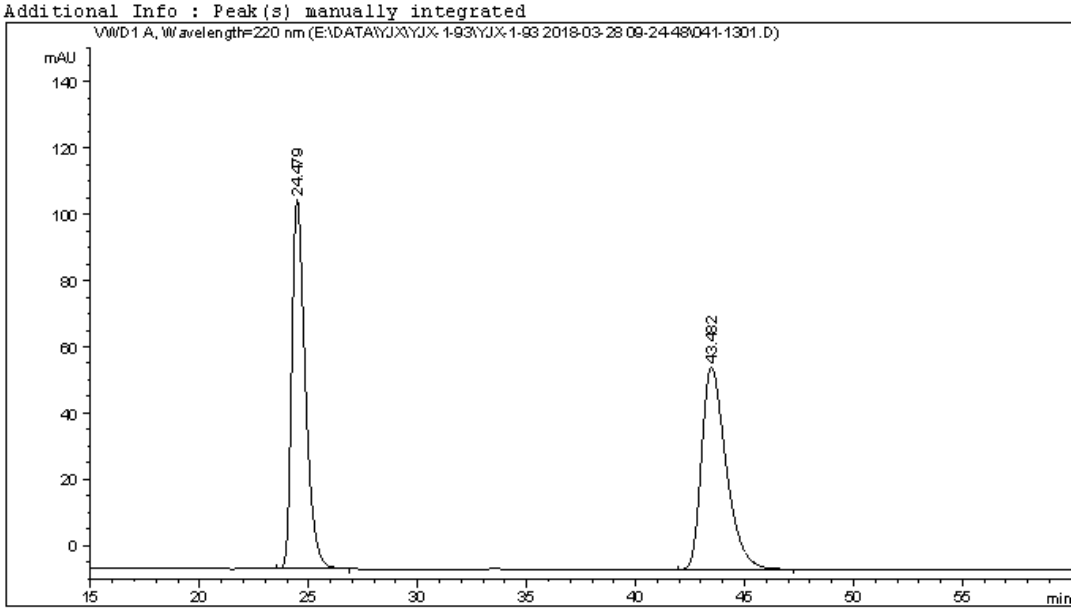



```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  28.935 BB    0.8552 6747.79639  119.24654  93.9898
       2  64.945 BB    1.2595  431.48953    4.03849   6.0102

    Totals :                  7179.28592  123.28502


    ======================================================================
                               *** End of Report ***

1260HPLC-VWD 4/13/2018 5:16:41 PM SYSTEM                    Page 1 of 1
```

HPLC of racemic-**2k**

Data File E:\DATA\YJX\YJX-1-93\YJX-1-93 2018-03-28 09-24-48\041-1301.D
Sample Name: LGY-1-130-RA

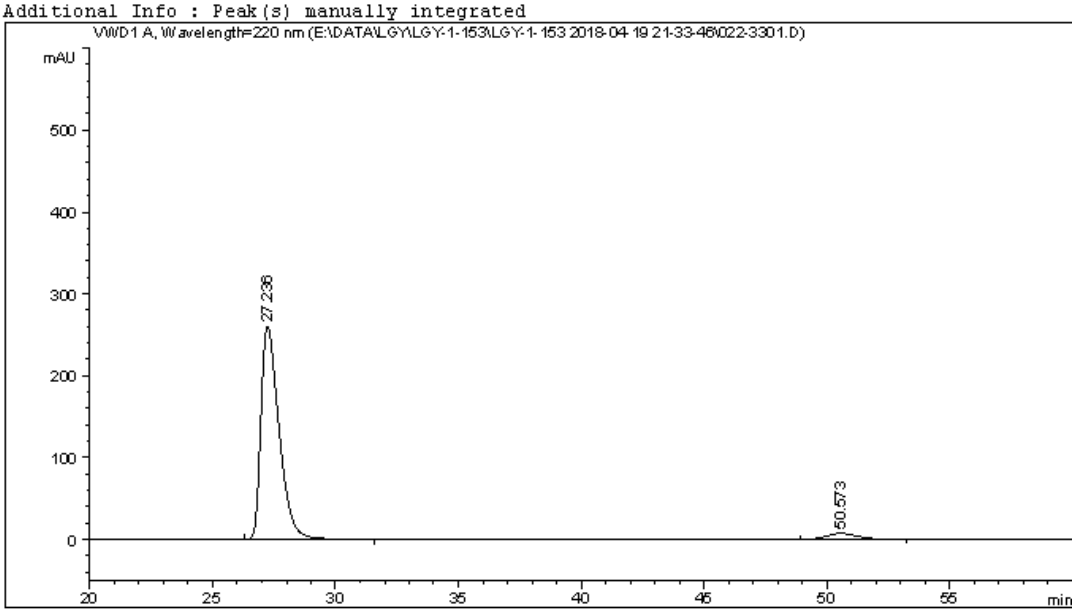
```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  13
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 41
    Injection Date  : 3/28/2018 3:52:49 PM                  Inj :  1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\YJX\YJX-1-93\YJX-1-93 2018-03-28 09-24-48\VWD-AS(1-6)-80-20-1ML-
                      5UL-220NM-90MIN.M
    Last changed    : 3/28/2018 9:59:05 AM by SYSTEM
    Analysis Method : E:\DATA\YJX\YJX-1-93\YJX-1-93 2018-03-28 09-24-48\VWD-AS(1-6)-80-20-1ML-
                      5UL-220NM-90MIN.M (Sequence Method)
    Last changed    : 4/26/2018 9:45:39 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  24.479 BB    0.6556 4785.61572  111.09396  49.9677
       2  43.482 BB    1.1908 4791.80518   60.91084  50.0323

    Totals :                  9577.42090  172.00481


    ======================================================================
                              *** End of Report ***

1260HPLC-VWD 4/26/2018 9:45:50 PM SYSTEM                    Page 1 of 1
```

HPLC of **2k**

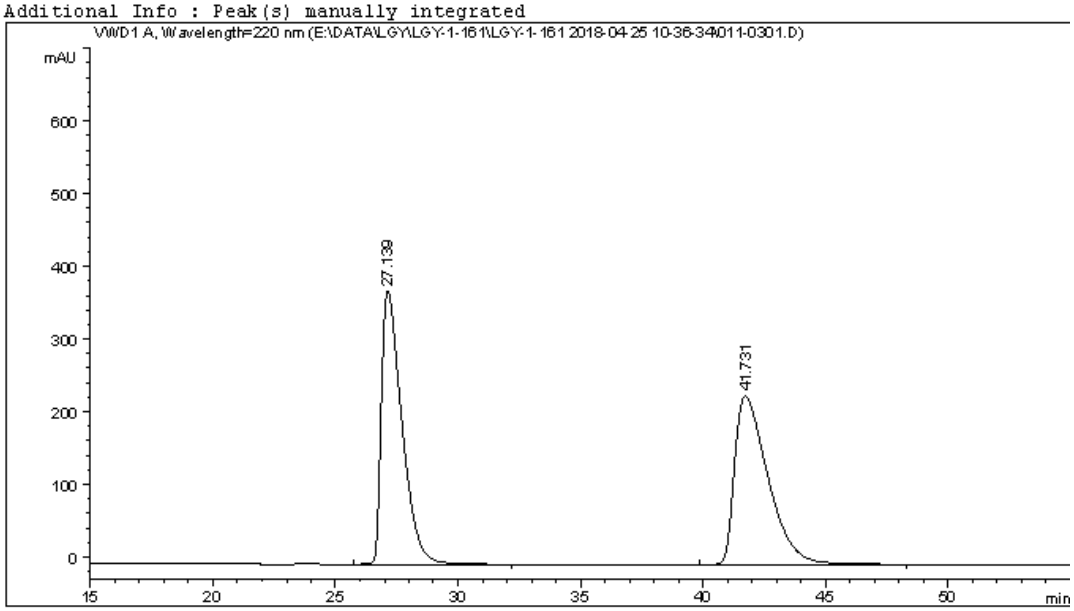
```
Data File E:\DATA\LGY\LGY-1-153\LGY-1-153 2018-04-19 21-33-46\022-3301.D
Sample Name: LGY-1-154-2

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  33
    Acq. Instrument : 1260HPLC-VWD                    Location : Vial 22
    Injection Date  : 4/21/2018 12:45:12 AM               Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-153\LGY-1-153 2018-04-19 21-33-46\VWD-AS(1-6)-80-20-
                      1ML-5UL-220NM-90MIN.M
    Last changed    : 4/19/2018 9:33:47 PM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-153\LGY-1-153 2018-04-19 21-33-46\VWD-AS(1-6)-80-20-
                      1ML-5UL-220NM-90MIN.M (Sequence Method)
    Last changed    : 4/26/2018 9:53:18 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  27.236 BB    0.7804 1.32302e4   259.66959  95.8221
       2  50.573 BB    1.1083  576.84888    7.01531   4.1779

    Totals :                  1.3807le4   266.68490


    ======================================================================
                            *** End of Report ***

1260HPLC-VWD 4/26/2018 9:53:26 PM SYSTEM                    Page 1 of 1
```

HPLC of racemic-**2l**

```
Data File E:\DATA\LGY\LGY-1-161\LGY-1-161 2018-04-25 10-36-34\011-0301.D
Sample Name: LGY-1-161

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   3
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 11
    Injection Date  : 4/25/2018 11:21:38 AM                 Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-161\LGY-1-161 2018-04-25 10-36-34\VWD-AS(1-6)-80-20-
                      1ML-5UL-220NM-90MIN.M
    Last changed    : 4/25/2018 10:36:35 AM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-161\LGY-1-161 2018-04-25 10-36-34\VWD-AS(1-6)-80-20-
                      1ML-5UL-220NM-90MIN.M (Sequence Method)
    Last changed    : 4/26/2018 9:55:57 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

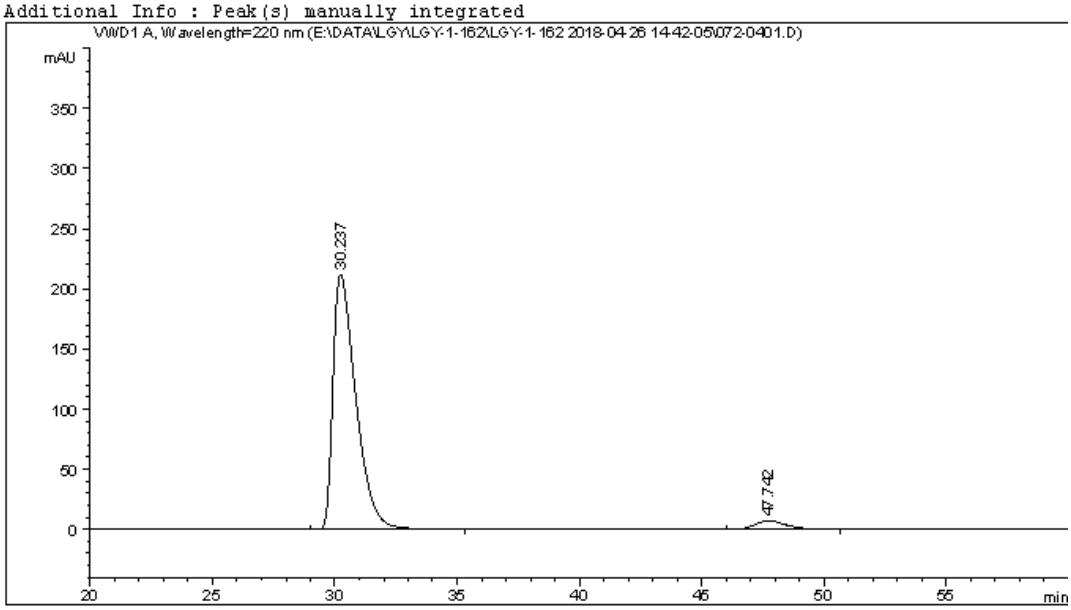



```
    ==================================================================
                            Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  27.139 BB    0.8775 2.18521e4   375.71609  49.9349
       2  41.731 BB    1.4134 2.19090e4   231.87233  50.0651

    Totals :                  4.37611e4   607.58842


    ==================================================================
                            *** End of Report ***

1260HPLC-VWD 4/26/2018 9:56:06 PM SYSTEM                    Page 1 of 1
```

HPLC of **2l**

Data File E:\DATA\LGY\LGY-1-162\LGY-1-162 2018-04-26 14-42-05\072-0401.D
Sample Name: LGY-1-162-2

```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   4
    Acq. Instrument : 1260HPLC-VWD                   Location : Vial 72
    Injection Date  : 4/26/2018 4:25:20 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-162\LGY-1-162 2018-04-26 14-42-05\VWD-AS(1-6)-80-20-
                      1ML-5UL-220NM-60MIN.M
    Last changed    : 4/26/2018 2:42:05 PM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-162\LGY-1-162 2018-04-26 14-42-05\VWD-AS(1-6)-80-20-
                      1ML-5UL-220NM-60MIN.M (Sequence Method)
    Last changed    : 4/26/2018 10:00:14 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

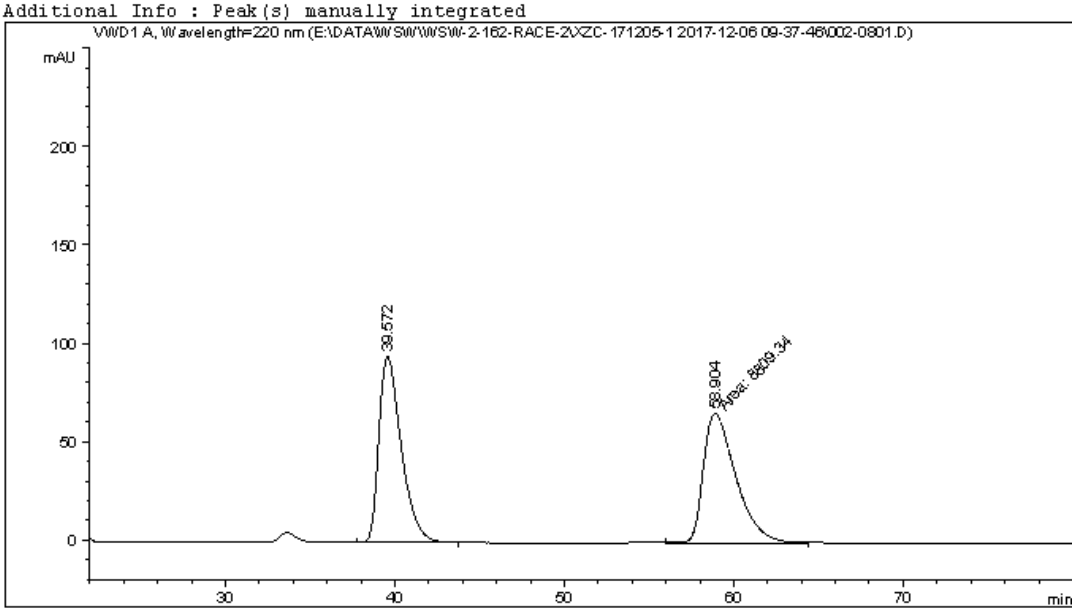



```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  30.237 BB    0.9804 1.37557e4   212.17484  95.6042
       2  47.742 BB    1.2271  632.47974    7.19835   4.3958

    Totals :                  1.4388le4   219.37319


    ======================================================================
                               *** End of Report ***
```

HPLC of racemic-**2m**

Data File E:\DATA\WSW\WSW-2-162-RACE-2\XZC-171205-1 2017-12-06 09-37-46\002-0801.D
Sample Name: LGY-1-47

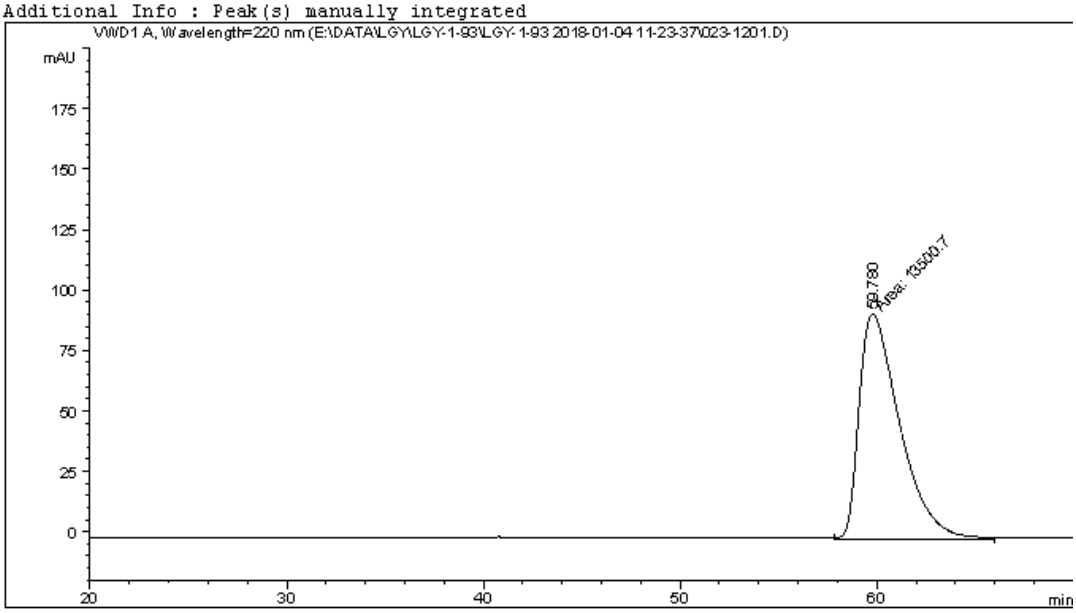
```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   8
    Acq. Instrument : 1260HPLC-VWD                    Location : Vial 2
    Injection Date  : 12/6/2017 1:15:36 PM                 Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\WSW\WSW-2-162-RACE-2\XZC-171205-1 2017-12-06 09-37-46\VWD-AS(1-6
                      )-80-20-1ML-5UL-220NM-100MIN.M
    Last changed    : 12/6/2017 9:52:57 AM by SYSTEM
    Analysis Method : E:\DATA\WSW\WSW-2-162-RACE-2\XZC-171205-1 2017-12-06 09-37-46\VWD-AS(1-6
                      )-80-20-1ML-5UL-220NM-100MIN.M (Sequence Method)
    Last changed    : 4/13/2018 5:20:12 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  39.572 BB    1.3921 8682.41602   94.48367  49.6372
       2  58.904 MM    2.2334 8809.33691   65.74026  50.3628

    Totals :                  1.74918e4   160.22394


    ======================================================================
                            *** End of Report ***
```

HPLC of **2m**

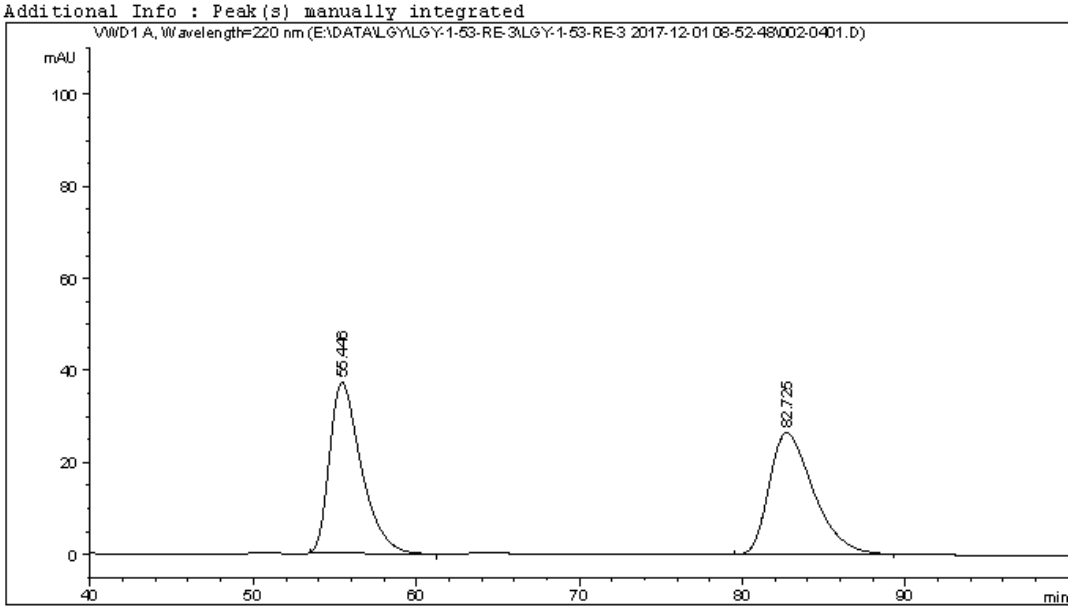
```
Data File E:\DATA\LGY\LGY-1-93\LGY-1-93 2018-01-04 11-23-37\023-1201.D
Sample Name: LGY-1-92-4

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  12
    Acq. Instrument : 1260HPLC-VWD                    Location : Vial 23
    Injection Date  : 1/4/2018 7:00:13 PM                  Inj :  1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-93\LGY-1-93 2018-01-04 11-23-37\VWD-AS(1-6)-80-20-1ML-
                      5UL-220NM-70MIN.M
    Last changed    : 1/4/2018 11:27:15 AM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-93\LGY-1-93 2018-01-04 11-23-37\VWD-AS(1-6)-80-20-1ML-
                      5UL-220NM-70MIN.M (Sequence Method)
    Last changed    : 4/13/2018 5:25:11 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  59.780 MM    2.4132 1.35007e4    93.24097 100.0000

    Totals :                  1.35007e4    93.24097


    ======================================================================
                            *** End of Report ***

1260HPLC-VWD 4/13/2018 5:25:17 PM SYSTEM                    Page 1 of 1
```

HPLC of racemic-**2n**

```
Data File E:\DATA\LGY\LGY-1-53-RE-3\LGY-1-53-RE-3 2017-12-01 08-52-48\002-0401.D
Sample Name: LGY-1-54

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   4
    Acq. Instrument : 1260HPLC-VWD                    Location : Vial 2
    Injection Date  : 12/1/2017 11:08:34 AM                Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-53-RE-3\LGY-1-53-RE-3 2017-12-01 08-52-48\VWD-AS(1-6)-
                      80-20-1ML-5UL-220NM-120MIN.M
    Last changed    : 12/1/2017 8:52:49 AM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-53-RE-3\LGY-1-53-RE-3 2017-12-01 08-52-48\VWD-AS(1-6)-
                      80-20-1ML-5UL-220NM-120MIN.M (Sequence Method)
    Last changed    : 4/13/2018 5:26:51 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

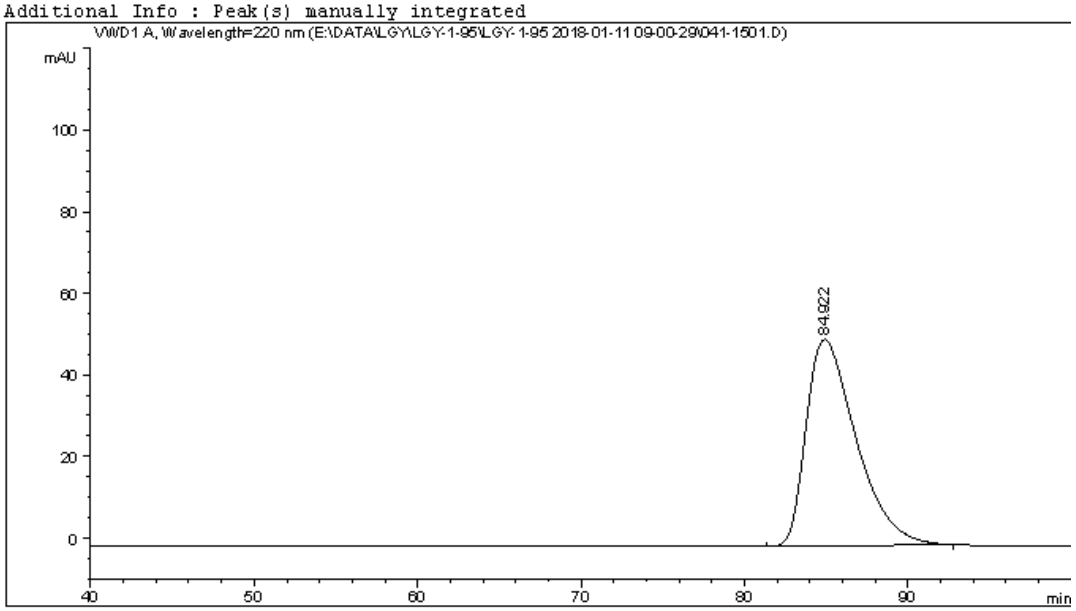



```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  55.446 BB    1.8387 5016.63232   37.12011  49.9658
       2  82.725 BB    2.5774 5023.49561   26.50241  50.0342

    Totals :                  1.00401e4    63.62252


    ======================================================================
                               *** End of Report ***

1260HPLC-VWD 4/13/2018 5:26:59 PM SYSTEM                    Page 1 of 1
```

HPLC of **2n**

Data File E:\DATA\LGY\LGY-1-95\LGY-1-95 2018-01-11 09-00-29\041-1501.D
Sample Name: LGY-1-95-1

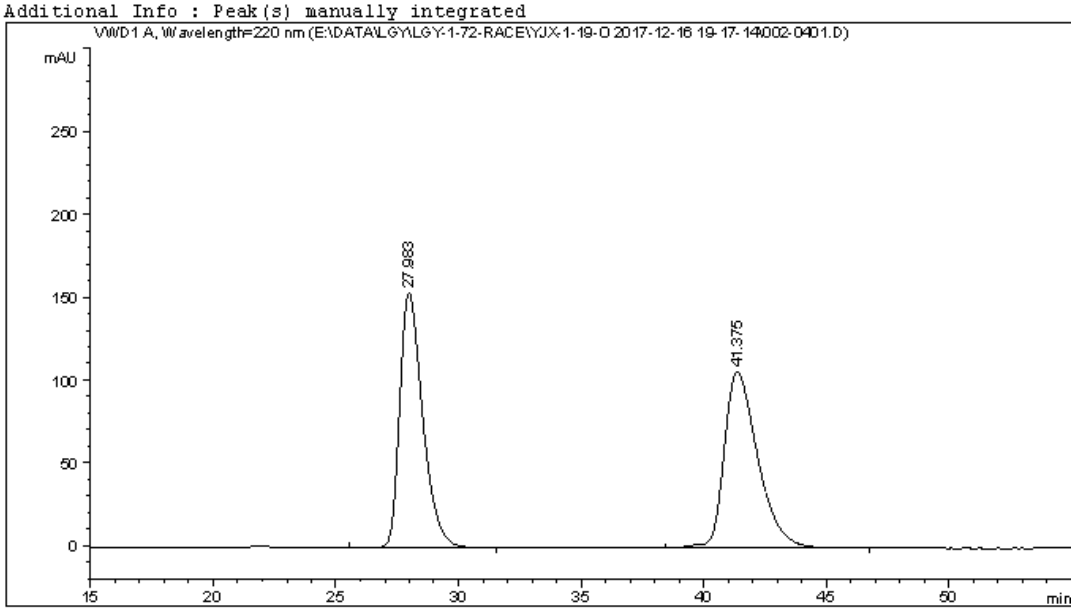
```
    ====================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :  15
    Acq. Instrument : 1260HPLC-VWD                   Location : Vial 41
    Injection Date  : 1/11/2018 3:18:34 PM                Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-95\LGY-1-95 2018-01-11 09-00-29\VWD-AS(1-6)-80-20-1ML-
                      5UL-220NM-100MIN.M
    Last changed    : 1/11/2018 9:00:30 AM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-95\LGY-1-95 2018-01-11 09-00-29\VWD-AS(1-6)-80-20-1ML-
                      5UL-220NM-100MIN.M (Sequence Method)
    Last changed    : 4/13/2018 5:44:37 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ====================================================================
                           Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  84.922 BB    2.6560 1.07293e4    50.53551 100.0000

    Totals :                  1.07293e4    50.53551


    ====================================================================
                           *** End of Report ***
```

HPLC of racemic-**2o**

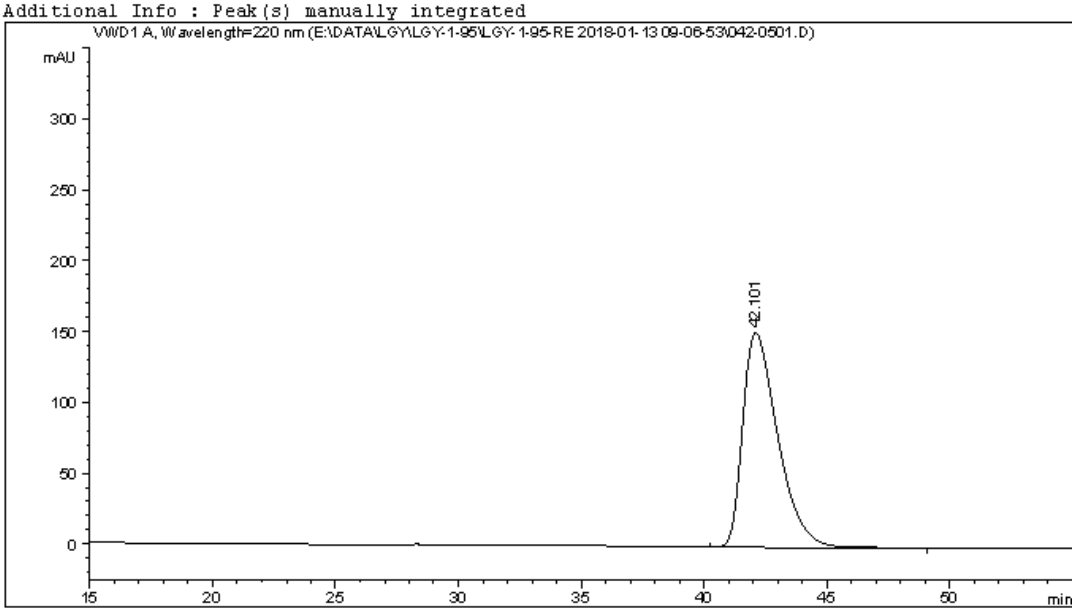
```
Data File E:\DATA\LGY\LGY-1-72-RACE\YJX-1-19-0 2017-12-16 19-17-14\002-0401.D
Sample Name: LGY-1-72-2

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   4
    Acq. Instrument : 1260HPLC-VWD                    Location : Vial 2
    Injection Date  : 12/16/2017 9:11:48 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-72-RACE\YJX-1-19-0 2017-12-16 19-17-14\VWD-AS(1-6)-80-
                      20-1ML-5UL-220NM-70MIN.M
    Last changed    : 12/16/2017 7:17:15 PM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-72-RACE\YJX-1-19-0 2017-12-16 19-17-14\VWD-AS(1-6)-80-
                      20-1ML-5UL-220NM-70MIN.M (Sequence Method)
    Last changed    : 4/14/2018 7:46:00 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  27.983 BB    0.9959 9999.52246  153.72369  49.6051
       2  41.375 BB    1.4506 1.01587e4   106.13880  50.3949

    Totals :                  2.01583e4   259.86250


    ======================================================================
                            *** End of Report ***

1260HPLC-DAD 4/14/2018 7:46:12 PM SYSTEM                       Page 1 of 1
```

HPLC of **2o**

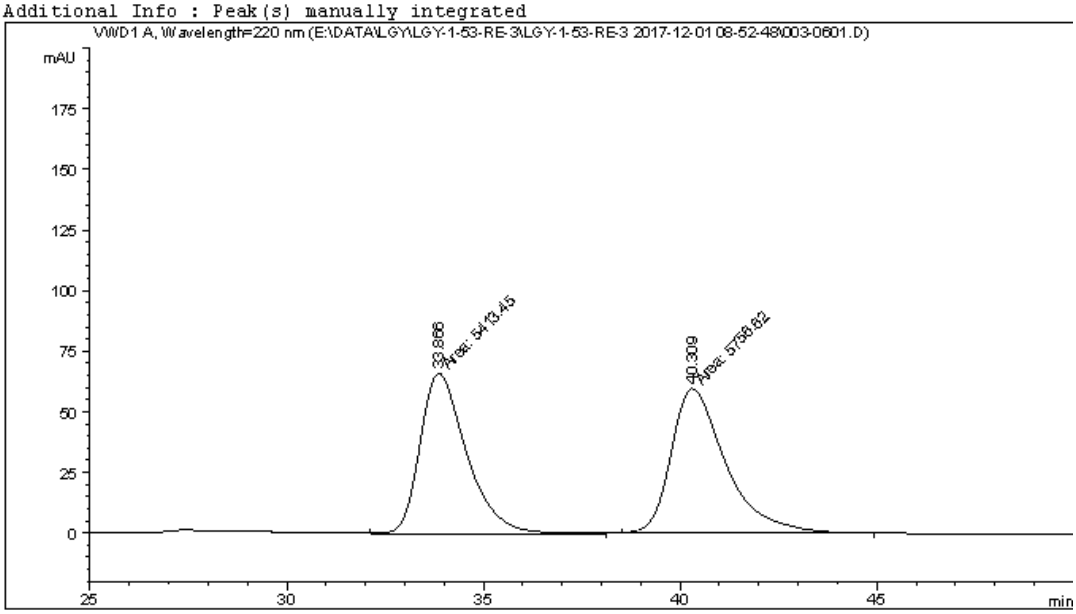
```
Data File E:\DATA\LGY\LGY-1-95\LGY-1-95-RE 2018-01-13 09-06-53\042-0501.D
Sample Name: LGY-1-95-4-RE

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   5
    Acq. Instrument : 1260HPLC-VWD                    Location : Vial 42
    Injection Date  : 1/13/2018 11:55:11 AM               Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-95\LGY-1-95-RE 2018-01-13 09-06-53\VWD-AS(1-6)-80-20-
                      1ML-5UL-220NM-60MIN.M
    Last changed    : 1/13/2018 9:06:54 AM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-95\LGY-1-95-RE 2018-01-13 09-06-53\VWD-AS(1-6)-80-20-
                      1ML-5UL-220NM-60MIN.M (Sequence Method)
    Last changed    : 4/14/2018 7:50:03 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  42.101 BB    1.5028 1.50565e4   151.58403 100.0000

    Totals :                  1.50565e4   151.58403


    ======================================================================
                            *** End of Report ***

1260HPLC-DAD 4/14/2018 7:50:09 PM SYSTEM                    Page 1 of 1
```

HPLC of racemic-**2p**

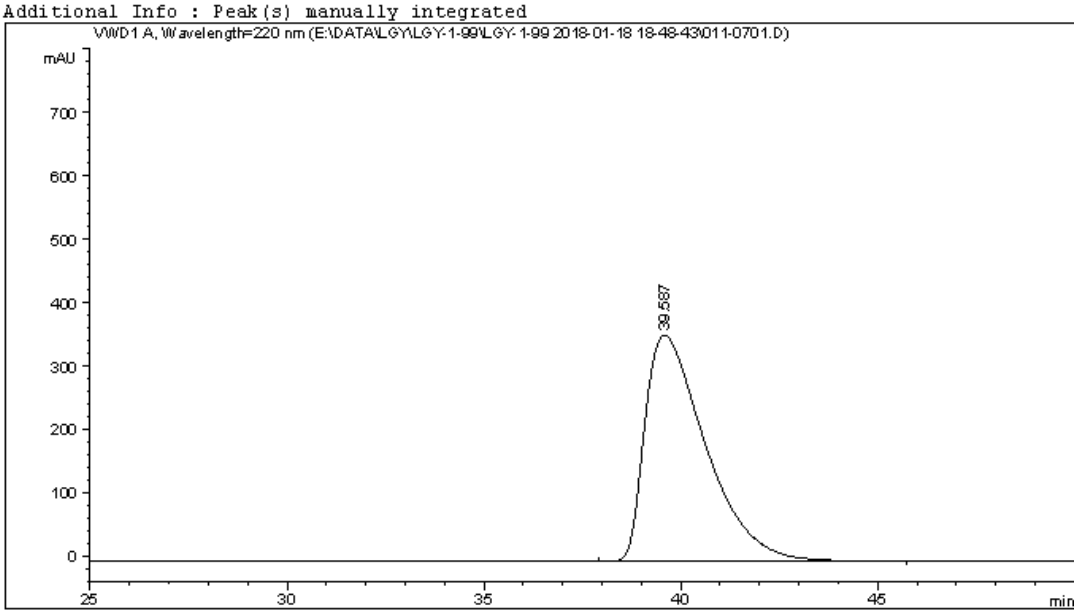
```
Data File E:\DATA\LGY\LGY-1-53-RE-3\LGY-1-53-RE-3 2017-12-01 08-52-48\003-0601.D
Sample Name: LGY-1-55

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   6
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 3
    Injection Date  : 12/1/2017 1:20:12 PM                  Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-53-RE-3\LGY-1-53-RE-3 2017-12-01 08-52-48\VWD-AS(1-6)-
                      80-20-1ML-5UL-220NM-120MIN.M
    Last changed    : 12/1/2017 8:52:49 AM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-53-RE-3\LGY-1-53-RE-3 2017-12-01 08-52-48\VWD-AS(1-6)-
                      80-20-1ML-5UL-220NM-120MIN.M (Sequence Method)
    Last changed    : 4/14/2018 7:53:32 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  33.866 MM    1.3651 5413.44727   66.09346  48.4639
       2  40.309 MM    1.6109 5756.62109   59.55768  51.5361

    Totals :                  1.11701e4   125.65114


    ======================================================================
                            *** End of Report ***

1260HPLC-DAD 4/14/2018 7:53:39 PM SYSTEM                       Page 1 of 1
```

HPLC of **2p**

```
Data File E:\DATA\LGY\LGY-1-99\LGY-1-99 2018-01-18 18-48-43\011-0701.D
Sample Name: LGY-1-99-4-RE-1

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   7
    Acq. Instrument : 1260HPLC-VWD                      Location : Vial 11
    Injection Date  : 1/18/2018 11:34:54 PM                 Inj :   1
                                                      Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-99\LGY-1-99 2018-01-18 18-48-43\VWD-AS(1-6)-80-20-1ML-
                      5UL-220NM-60MIN.M
    Last changed    : 1/18/2018 6:48:44 PM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-99\LGY-1-99 2018-01-18 18-48-43\VWD-AS(1-6)-80-20-1ML-
                      5UL-220NM-60MIN.M (Sequence Method)
    Last changed    : 4/14/2018 7:57:47 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

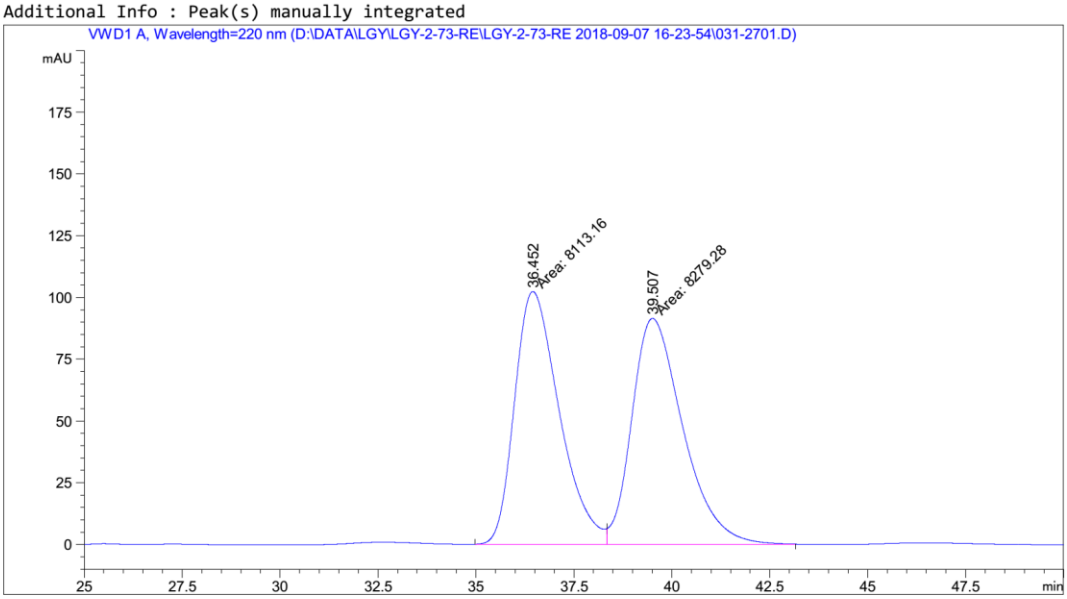



```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  39.587 BB    1.6551 3.82501e4   356.39026 100.0000

    Totals :                  3.82501e4   356.39026


    ======================================================================
                            *** End of Report ***

1260HPLC-DAD 4/14/2018 7:58:00 PM SYSTEM                    Page 1 of 1
```

HPLC of racemic-**2q**

Data File D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\031-2701.D
Sample Name: LGY-2-32-RE

```
======================================================================
Acq. Operator   :                                Seq. Line :  27
Acq. Instrument : Instrument 1                    Location : Vial 31
Injection Date  : 9/8/2018 2:57:05 PM                  Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\VWD-AS(1-6)-80-20-
                  1ML-5UL-220NM-60MIN.M
Last changed    : 5/31/2018 10:45:35 AM
Analysis Method : D:\METHOD\LG\VWD-AD(1-2)-99-1-0.2ML-2UL-220NM-10MIN.M
Last changed    : 9/10/2018 10:22:01 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```



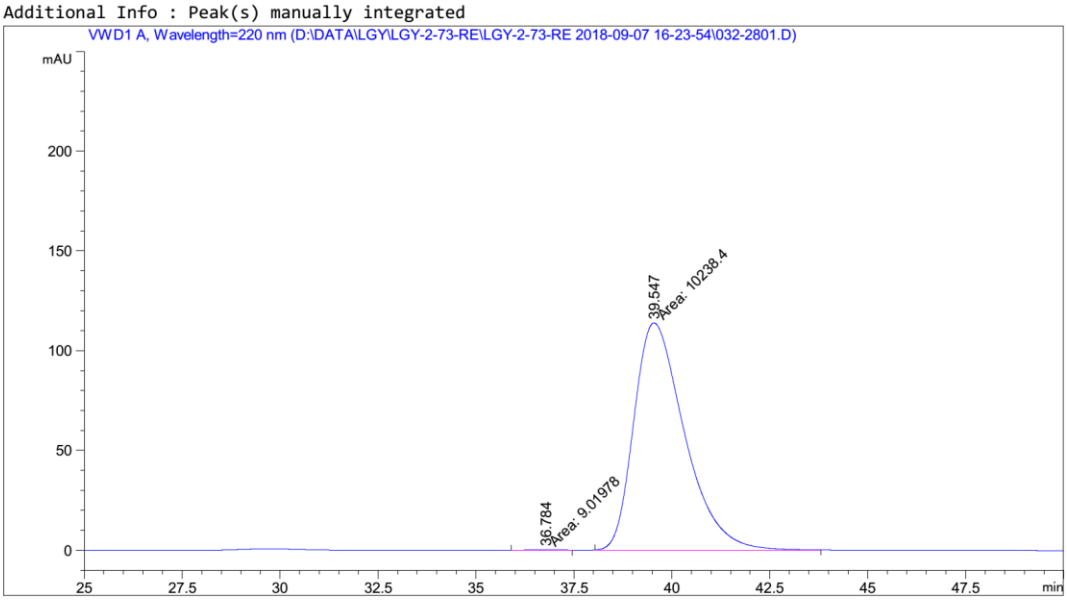

```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Retention Time
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Sig Type    Area      Height     Area
  #   [min]            [mAU*s]     [mAU]       %
----|-------|---|----|----------|----------|--------|
   1  36.452  1  MF   8113.15771  102.32407  49.4933
   2  39.507  1  FM   8279.27539   91.44144  50.5067

Totals :              1.63924e4   193.76551


======================================================================
```

Instrument 1 9/10/2018 10:22:03 PM Page 1 of 1

HPLC of **2q**

Data File D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\032-2801.D
Sample Name: LGY-2-73-7

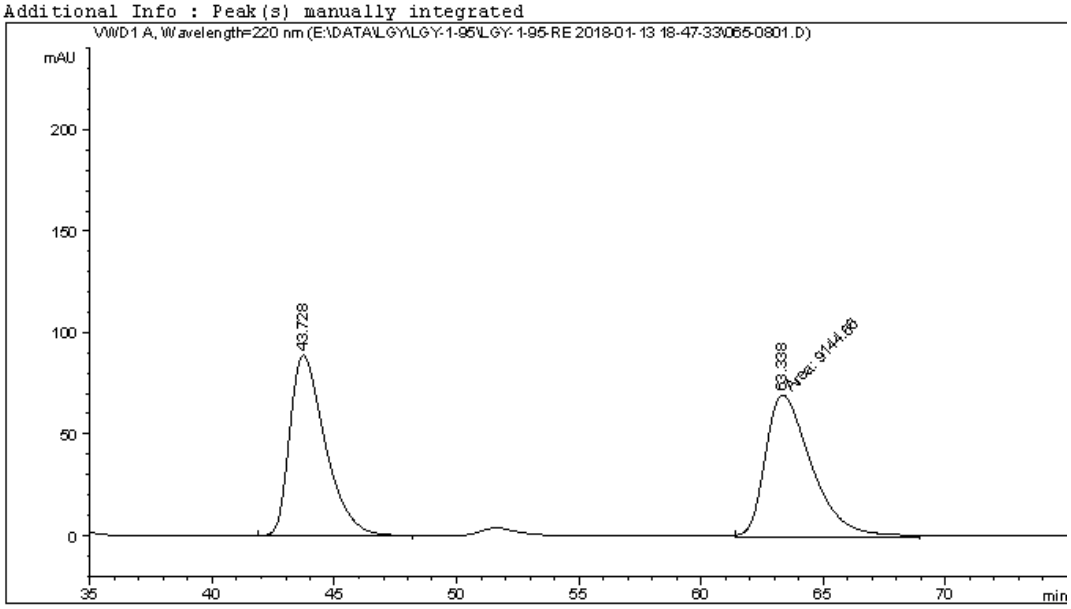
```
======================================================================
Acq. Operator   :                                Seq. Line :  28
Acq. Instrument : Instrument 1                    Location : Vial 32
Injection Date  : 9/8/2018 3:57:57 PM                  Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\VWD-AS(1-6)-80-20-
                  1ML-5UL-220NM-60MIN.M
Last changed    : 9/8/2018 4:51:09 PM
                  (modified after loading)
Analysis Method : D:\METHOD\LG\VWD-AD(1-2)-99-1-0.2ML-2UL-220NM-10MIN.M
Last changed    : 9/10/2018 10:24:16 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Retention Time
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Sig Type    Area      Height     Area
  #   [min]            [mAU*s]     [mAU]       %
----|-------|---|----|----------|----------|--------|
   1  36.784  1  MM      9.01978 1.69177e-1   0.0880
   2  39.547  1  MM   1.02384e4   113.83140  99.9120

Totals :              1.02474e4   114.00058
```

HPLC of racemic-**2r**

```
Data File E:\DATA\LGY\LGY-1-95\LGY-1-95-RE 2018-01-13 18-47-33\065-0801.D
Sample Name: LGY-1-53-RA

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   8
    Acq. Instrument : 1260HPLC-VWD                    Location : Vial 65
    Injection Date  : 1/14/2018 4:24:33 AM                 Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-95\LGY-1-95-RE 2018-01-13 18-47-33\VWD-AS(1-6)-80-20-
                      1ML-5UL-220NM-90MIN.M
    Last changed    : 1/13/2018 6:47:33 PM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-95\LGY-1-95-RE 2018-01-13 18-47-33\VWD-AS(1-6)-80-20-
                      1ML-5UL-220NM-90MIN.M (Sequence Method)
    Last changed    : 4/13/2018 9:31:55 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

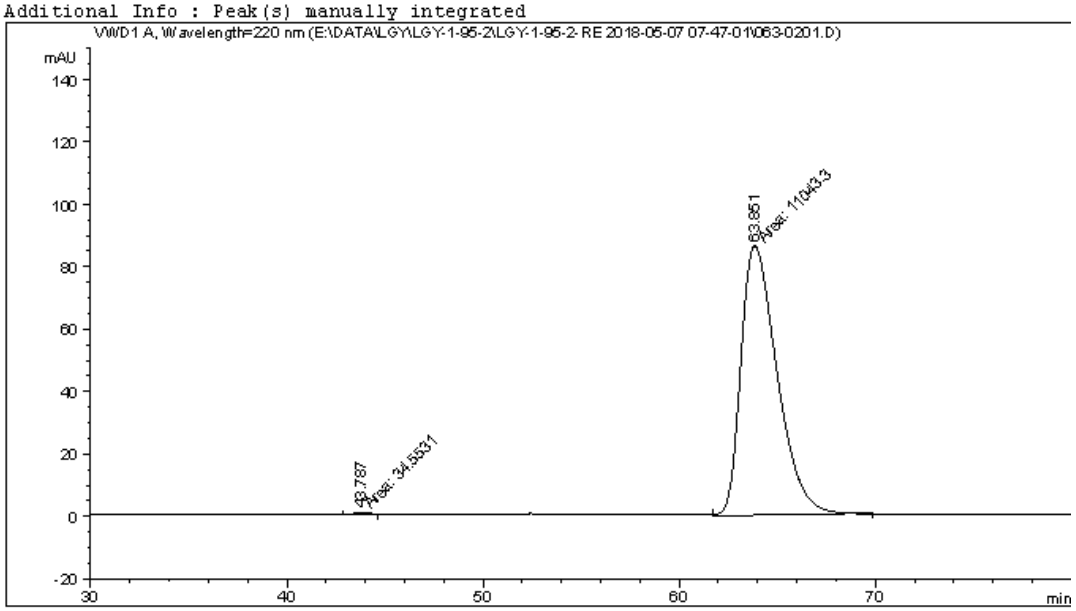



```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  43.728 BB    1.5127 8898.92871   88.68528  49.3191
       2  63.338 MM    2.1875 9144.65723   69.67457  50.6809

    Totals :                  1.80436e4   158.35985


    ======================================================================
                               *** End of Report ***

1260HPLC-VWD 4/13/2018 9:32:08 PM SYSTEM                    Page 1 of 1
```

HPLC of **2r**

Data File E:\DATA\LGY\LGY-1-95-2\LGY-1-95-2-RE 2018-05-07 07-47-01\063-0201.D
Sample Name: LGY-1-95-2-RE

```
    ====================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 63
    Injection Date  : 5/7/2018 8:01:28 AM                   Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-95-2\LGY-1-95-2-RE 2018-05-07 07-47-01\VWD-AS(1-6)-80-
                      20-1ML-5UL-220NM-90MIN.M
    Last changed    : 5/7/2018 7:47:01 AM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-95-2\LGY-1-95-2-RE 2018-05-07 07-47-01\VWD-AS(1-6)-80-
                      20-1ML-5UL-220NM-90MIN.M (Sequence Method)
    Last changed    : 5/7/2018 7:15:25 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

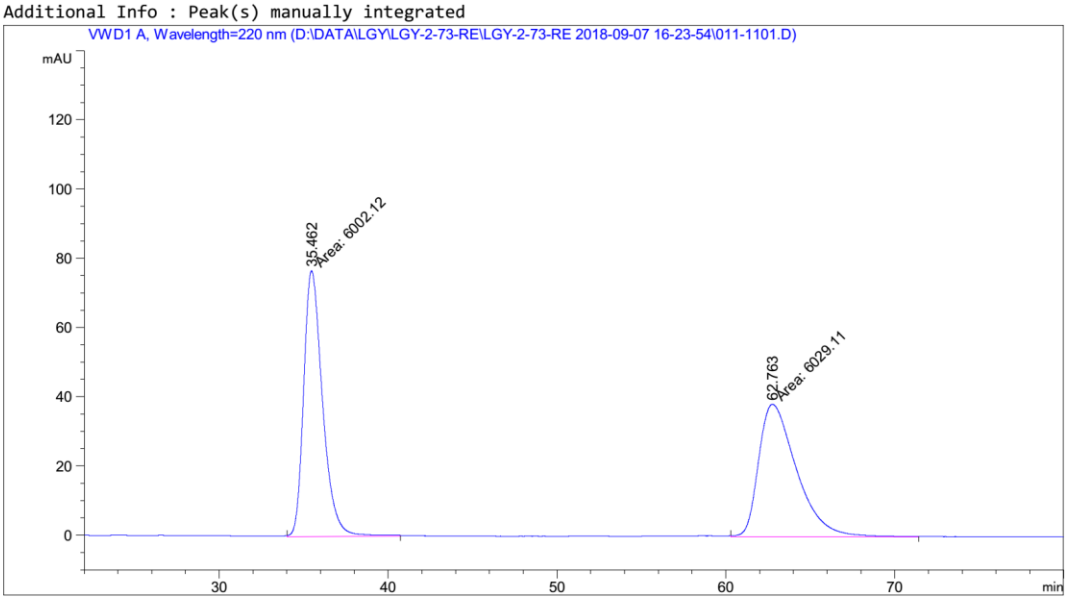



```
    ====================================================================
                            Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  43.787 MM    0.6485   34.55308 6.31873e-1   0.3119
       2  63.851 MM    2.1334 1.10433e4    86.27399  99.6881

    Totals :                  1.10778e4    86.90586


    ====================================================================
                            *** End of Report ***
```

HPLC of racemic-**2s**

Data File D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\011-1101.D
Sample Name: LGY-2-62-2

```
======================================================================
Acq. Operator   :                                Seq. Line :  11
Acq. Instrument : Instrument 1                    Location : Vial 11
Injection Date  : 9/8/2018 1:33:26 AM                  Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\VWD-AS(1-6)-80-20-
                  1ML-5UL-220NM-80MIN.M
Last changed    : 5/26/2018 3:44:58 PM
Analysis Method : D:\METHOD\LGY\VWD-AD(1-2)-95-5-0.3ML-5UL-220NM-100MIN.M
Last changed    : 9/10/2018 9:48:14 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

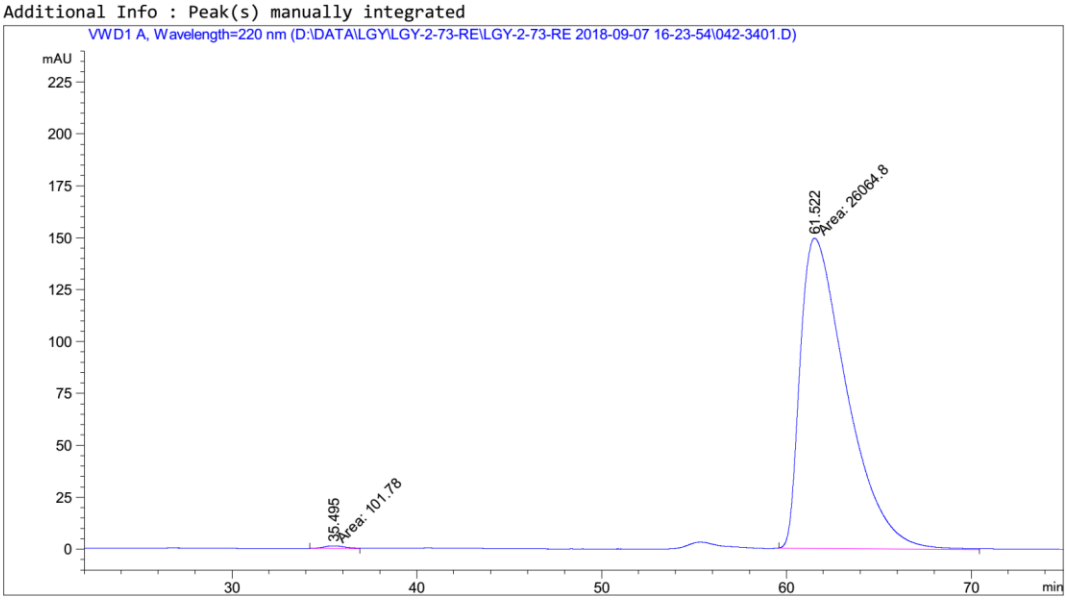



```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Retention Time
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Sig Type    Area      Height     Area
  #   [min]            [mAU*s]     [mAU]       %
----|-------|---|----|----------|----------|--------|
   1  35.462  1  MM   6002.12256   76.84860  49.8878
   2  62.763  1  MM   6029.10986   38.34726  50.1122

Totals :              1.20312e4   115.19587


======================================================================
```

HPLC of **2s**

Data File D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\042-3401.D
Sample Name: LGY-2-73-10

```
    ======================================================================
    Acq. Operator   :                                Seq. Line :  34
    Acq. Instrument : Instrument 1                    Location : Vial 42
    Injection Date  : 9/8/2018 11:41:08 PM                 Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\VWD-AS(1-6)-80-20-
                      1ML-5UL-220NM-80MIN.M
    Last changed    : 9/8/2018 10:08:46 PM
                      (modified after loading)
    Analysis Method : D:\METHOD\LG\VWD-AD(1-2)-99-1-0.2ML-2UL-220NM-10MIN.M
    Last changed    : 9/10/2018 10:32:41 PM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

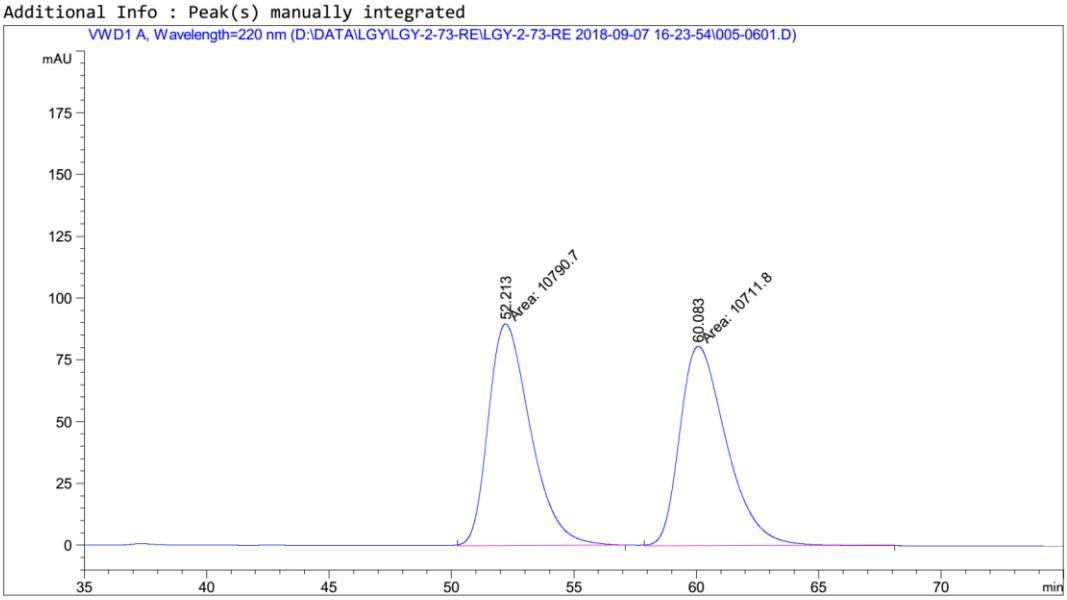



```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Retention Time
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs

    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Sig Type    Area      Height     Area
      #   [min]            [mAU*s]     [mAU]       %
    ----|-------|---|----|----------|----------|--------|
       1  35.495  1  MM    101.77962    1.28853   0.3890
       2  61.522  1  MM   2.60648e4   149.35780  99.6110

    Totals :              2.61665e4   150.64634
```

HPLC of racemic-**2t**

Data File D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\005-0601.D
Sample Name: LGY-2-62-1

```
======================================================================
Acq. Operator   :                                  Seq. Line :   6
Acq. Instrument : Instrument 1                      Location : Vial 5
Injection Date  : 9/7/2018 9:19:02 PM                    Inj :   1
                                                  Inj Volume : 5.000 µl
Acq. Method     : D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\VWD-AS(1-6)-80-20-
                  1ML-5UL-220NM-80MIN.M
Last changed    : 5/26/2018 3:44:58 PM
Analysis Method : D:\METHOD\LGY\VWD-AD(1-2)-95-5-0.3ML-5UL-220NM-100MIN.M
Last changed    : 9/10/2018 9:42:43 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

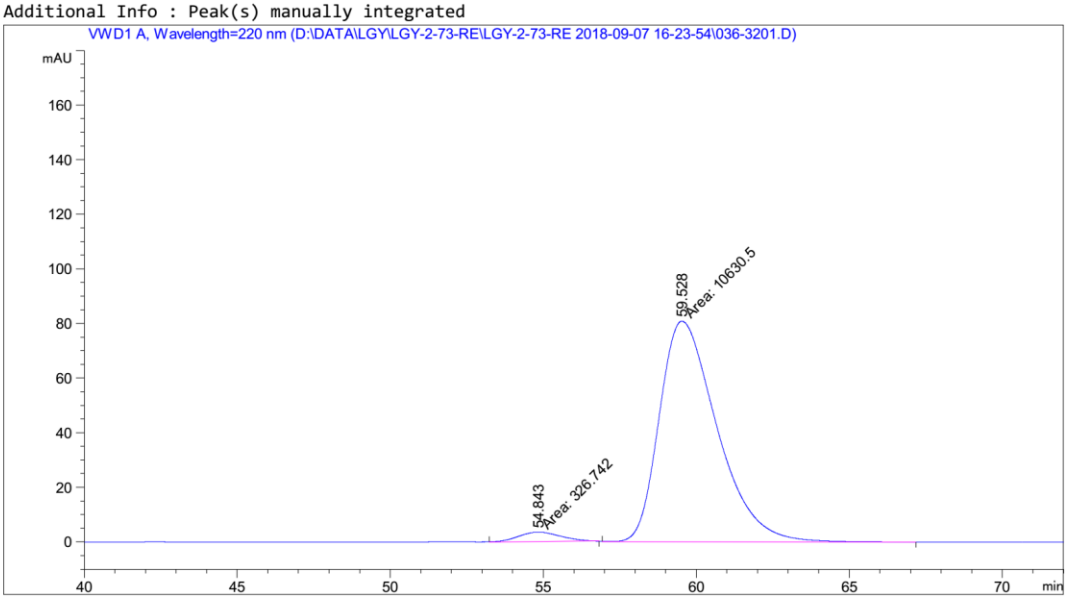



```
======================================================================
                          Area Percent Report
======================================================================

Sorted By             :      Retention Time
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Sig Type    Area      Height     Area
  #   [min]            [mAU*s]     [mAU]       %
----|-------|---|----|----------|----------|--------|
   1  52.213  1  MM   1.07907e4    89.78436  50.1836
   2  60.083  1  MM   1.07118e4    80.76544  49.8164

Totals :              2.15025e4   170.54980


======================================================================
```

HPLC of **2t**

Data File D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\036-3201.D
Sample Name: LGY-2-73-9

```
======================================================================
Acq. Operator   :                                Seq. Line :  32
Acq. Instrument : Instrument 1                    Location : Vial 36
Injection Date  : 9/8/2018 8:39:25 PM                  Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\VWD-AS(1-6)-80-20-
                  1ML-5UL-220NM-80MIN.M
Last changed    : 9/8/2018 8:41:54 PM
                  (modified after loading)
Analysis Method : D:\METHOD\LG\VWD-AD(1-2)-99-1-0.2ML-2UL-220NM-10MIN.M
Last changed    : 9/10/2018 10:30:13 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

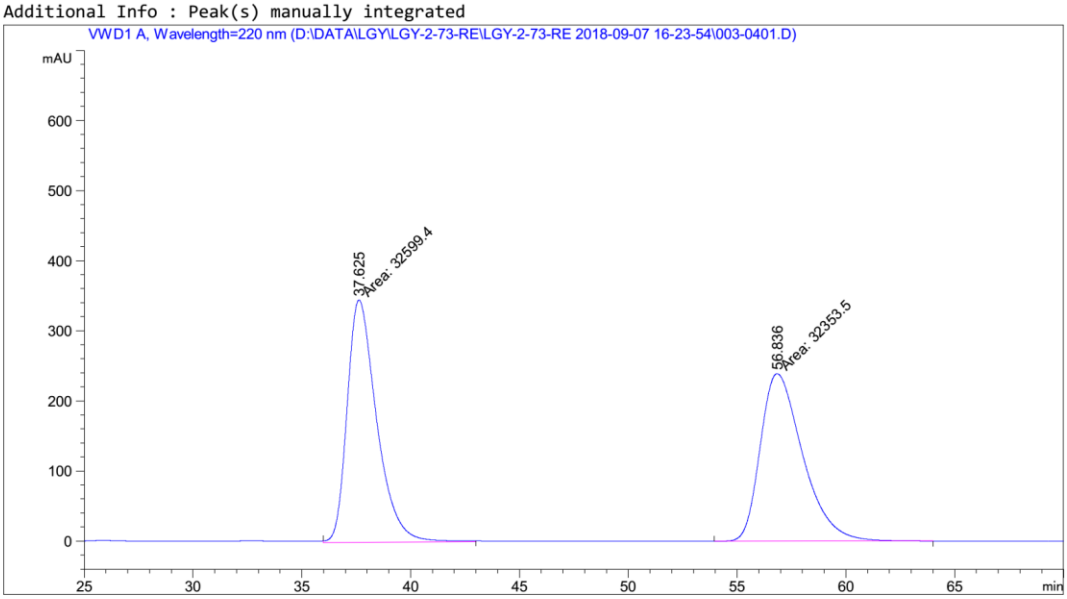



```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Retention Time
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Sig Type    Area      Height     Area
  #   [min]            [mAU*s]     [mAU]       %
----|-------|---|----|----------|----------|--------|
   1  54.843  1  MM    326.74197    3.44832   2.9820
   2  59.528  1  MM   1.06305e4    80.87628  97.0180

Totals :              1.09572e4    84.32460
```

HPLC of racemic-**2u**

Data File D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\003-0401.D
Sample Name: LGY-2-53-4

```
======================================================================
Acq. Operator   :                                Seq. Line :   4
Acq. Instrument : Instrument 1                    Location : Vial 3
Injection Date  : 9/7/2018 6:37:24 PM                  Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\VWD-AS(1-6)-80-20-
                  1ML-5UL-220NM-80MIN.M
Last changed    : 5/26/2018 3:44:58 PM
Analysis Method : D:\METHOD\LGY\VWD-AD(1-2)-95-5-0.3ML-5UL-220NM-100MIN.M
Last changed    : 9/10/2018 9:36:41 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

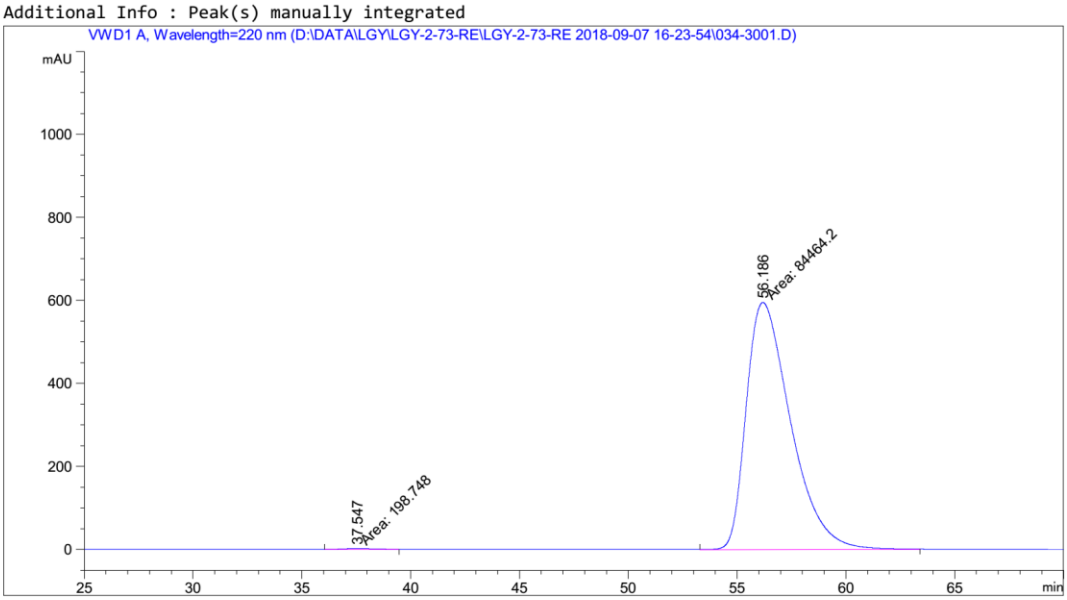



```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Retention Time
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Sig Type    Area      Height     Area
  #   [min]            [mAU*s]     [mAU]       %
----|-------|---|----|----------|----------|--------|
   1  37.625  1  MM   3.25994e4   345.56903  50.1893
   2  56.836  1  MM   3.23535e4   238.93916  49.8107

Totals :              6.49529e4   584.50819


======================================================================
```

HPLC of **2u**

Data File D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\034-3001.D
Sample Name: LGY-2-73-8

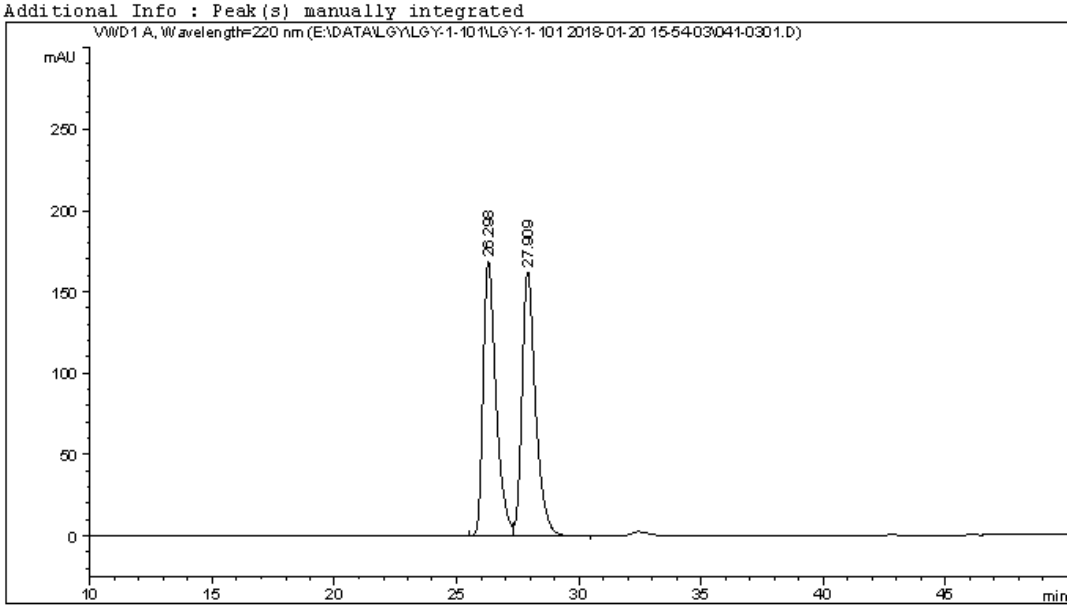
```
======================================================================
Acq. Operator   :                                Seq. Line :  30
Acq. Instrument : Instrument 1                    Location : Vial 34
Injection Date  : 9/8/2018 6:13:42 PM                  Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\VWD-AS(1-6)-80-20-
                  1ML-5UL-220NM-80MIN.M
Last changed    : 9/8/2018 6:39:09 PM
                  (modified after loading)
Analysis Method : D:\METHOD\LG\VWD-AD(1-2)-99-1-0.2ML-2UL-220NM-10MIN.M
Last changed    : 9/10/2018 10:26:57 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Retention Time
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Sig Type    Area      Height     Area
  #   [min]            [mAU*s]     [mAU]       %
----|-------|---|----|----------|----------|--------|
   1  37.547  1  MM    198.74828    2.21174   0.2348
   2  56.186  1  MM   8.44642e4   595.49066  99.7652

Totals :              8.46630e4   597.70240
```

HPLC of racemic-**2v**

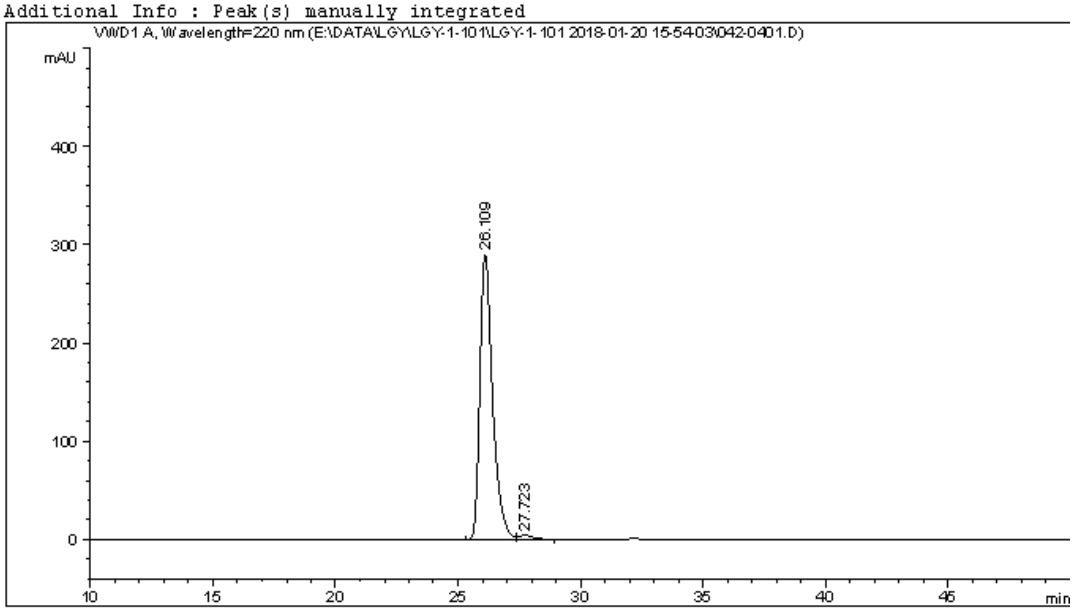
```
Data File E:\DATA\LGY\LGY-1-101\LGY-1-101 2018-01-20 15-54-03\041-0301.D
Sample Name: LGY-1-101

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   3
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 41
    Injection Date  : 1/20/2018 4:36:17 PM                  Inj :   1
                                                   Inj Volume : 3.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-101\LGY-1-101 2018-01-20 15-54-03\VWD-AD(1-2)-95-5-1ML
                      -3UL-220NM-60MIN.M
    Last changed    : 1/20/2018 3:54:03 PM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-101\LGY-1-101 2018-01-20 15-54-03\VWD-AD(1-2)-95-5-1ML
                      -3UL-220NM-60MIN.M (Sequence Method)
    Last changed    : 4/14/2018 8:00:08 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  26.298 BV    0.5487 6153.86182  168.66835  49.6834
       2  27.909 VB    0.5753 6232.27979  162.20204  50.3166

    Totals :                  1.2386le4   330.87039


    ======================================================================
                               *** End of Report ***

1260HPLC-DAD 4/14/2018 8:00:32 PM SYSTEM                    Page 1 of 1
```

HPLC of **2v**

```
Data File E:\DATA\LGY\LGY-1-101\LGY-1-101 2018-01-20 15-54-03\042-0401.D
Sample Name: LGY-1-99-6

    ====================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   4
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 42
    Injection Date  : 1/20/2018 5:37:01 PM                  Inj :   1
                                                   Inj Volume : 3.000 µl
    Acq. Method     : E:\DATA\LGY\LGY-1-101\LGY-1-101 2018-01-20 15-54-03\VWD-AD(1-2)-95-5-1ML
                      -3UL-220NM-60MIN.M
    Last changed    : 1/20/2018 3:54:03 PM by SYSTEM
    Analysis Method : E:\DATA\LGY\LGY-1-101\LGY-1-101 2018-01-20 15-54-03\VWD-AD(1-2)-95-5-1ML
                      -3UL-220NM-60MIN.M (Sequence Method)
    Last changed    : 4/14/2018 8:06:25 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

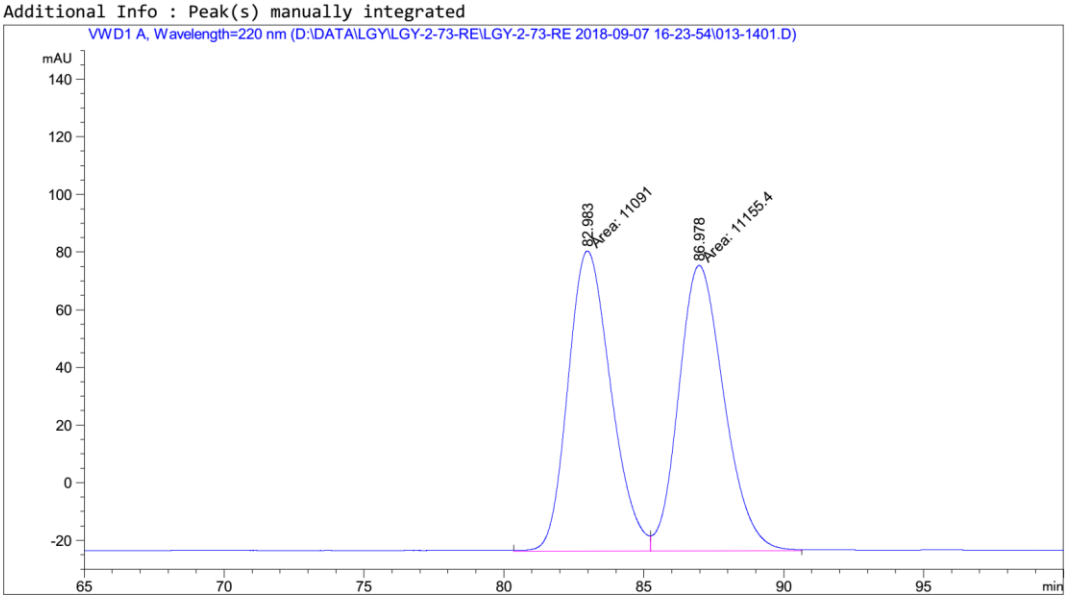



```
    ====================================================================
                            Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  26.109 BV    0.5409 1.04457e4   290.20370  98.5545
       2  27.723 VB    0.5486  153.20755    4.02011   1.4455

    Totals :                  1.05989e4   294.22382


    ====================================================================
                            *** End of Report ***

1260HPLC-DAD 4/14/2018 8:06:42 PM SYSTEM                    Page 1 of 1
```

HPLC of racemic-**2w**

Data File D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\013-1401.D
Sample Name: LGY-2-35-1

```
======================================================================
Acq. Operator   :                                Seq. Line :  14
Acq. Instrument : Instrument 1                    Location : Vial 13
Injection Date  : 9/8/2018 4:36:06 AM                  Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\VWD-AD(1-2)-95-5-0.
                  3ML-5UL-220NM-100MIN.M
Last changed    : 9/7/2018 3:24:25 PM
Analysis Method : D:\METHOD\LGY\VWD-AD(1-2)-95-5-0.3ML-5UL-220NM-100MIN.M
Last changed    : 9/10/2018 9:53:01 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

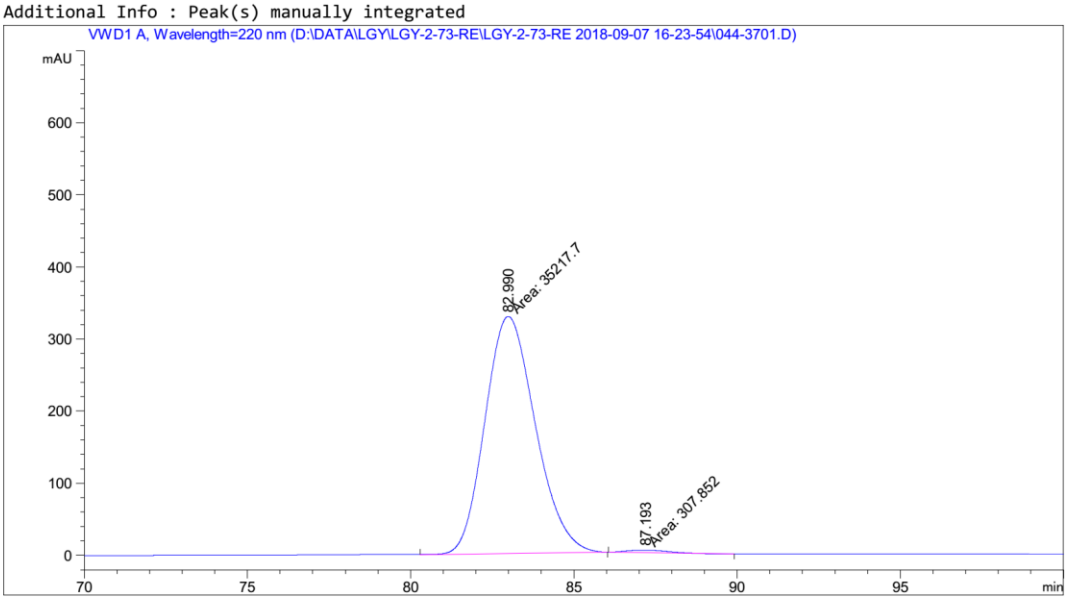



```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Retention Time
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Sig Type    Area      Height     Area
  #   [min]            [mAU*s]     [mAU]       %
----|-------|---|----|----------|----------|--------|
   1  82.983  1  MF   1.10910e4   104.12796  49.8553
   2  86.978  1  FM   1.11554e4    99.01752  50.1447

Totals :              2.22464e4   203.14548


======================================================================
```

HPLC of **2w**

Data File D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\044-3701.D
Sample Name: LGY-2-73-11

```
======================================================================
Acq. Operator   :                                Seq. Line :  37
Acq. Instrument : Instrument 1                    Location : Vial 44
Injection Date  : 9/9/2018 3:13:50 AM                  Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\VWD-AD(1-2)-95-5-0.
                  3ML-5UL-220NM-100MIN.M
Last changed    : 9/7/2018 3:24:25 PM
Analysis Method : D:\METHOD\LG\VWD-AD(1-2)-99-1-0.2ML-2UL-220NM-10MIN.M
Last changed    : 9/10/2018 10:35:32 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

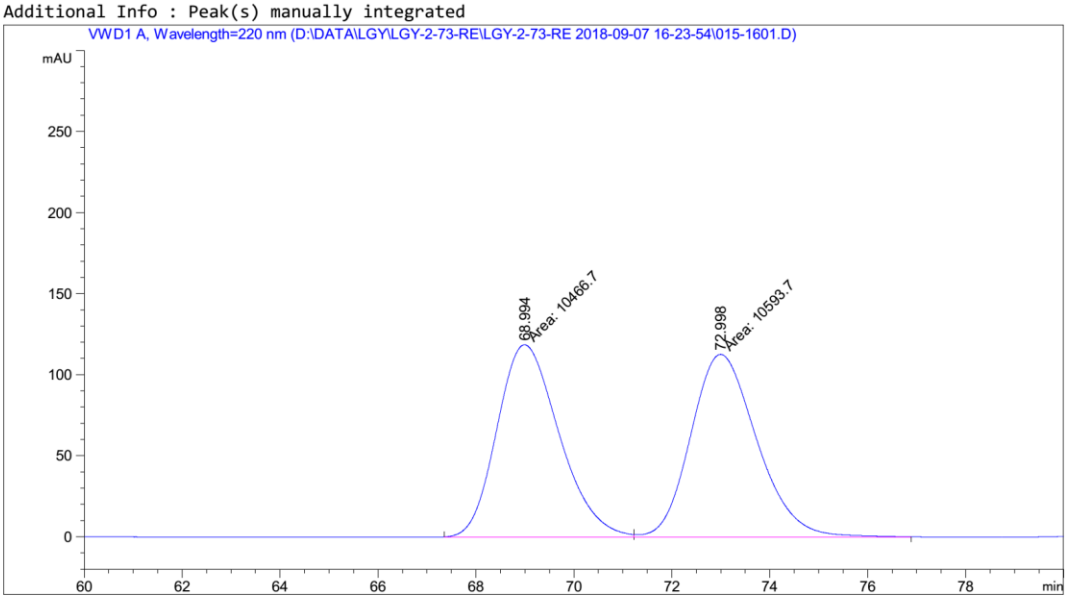



```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Retention Time
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Sig Type    Area      Height     Area
  #   [min]            [mAU*s]     [mAU]       %
----|-------|---|----|----------|----------|--------|
   1  82.990  1  MM   3.52177e4   328.70041  99.1334
   2  87.193  1  MM    307.85239    3.58854   0.8666

Totals :              3.55255e4   332.28895


======================================================================
```

HPLC of racemic-**2x**

Data File D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\015-1601.D
Sample Name: LGY-2-64

```
======================================================================
Acq. Operator   :                                Seq. Line :  16
Acq. Instrument : Instrument 1                    Location : Vial 15
Injection Date  : 9/8/2018 7:57:49 AM                  Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\VWD-AD(1-2)-95-5-0.
                  3ML-5UL-220NM-90MIN.M
Last changed    : 6/14/2018 9:07:28 PM
Analysis Method : D:\METHOD\LG\VWD-AD(1-2)-99-1-0.2ML-2UL-220NM-10MIN.M
Last changed    : 9/10/2018 10:17:07 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

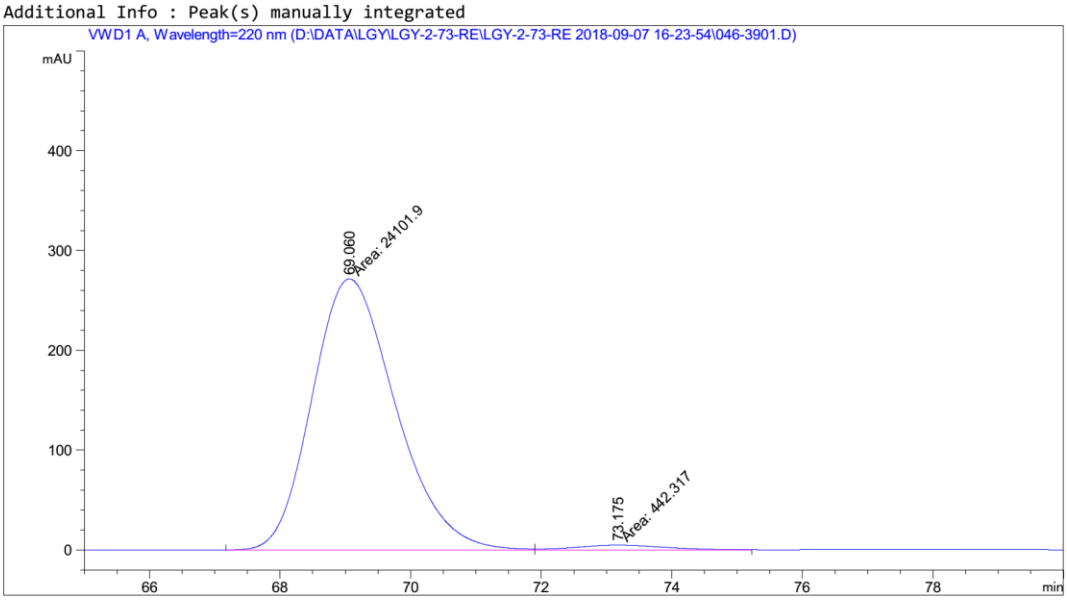



```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Retention Time
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Sig Type    Area      Height     Area
  #   [min]            [mAU*s]     [mAU]       %
----|-------|---|----|----------|----------|--------|
   1  68.994  1  MF   1.04667e4   118.64645  49.6986
   2  72.998  1  FM   1.05937e4   112.75227  50.3014

Totals :              2.10604e4   231.39873


======================================================================
```

HPLC of **2x**

Data File D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\046-3901.D
Sample Name: LGY-2-73-12

```
======================================================================
Acq. Operator   :                                Seq. Line :  39
Acq. Instrument : Instrument 1                    Location : Vial 46
Injection Date  : 9/9/2018 6:25:37 AM                  Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : D:\DATA\LGY\LGY-2-73-RE\LGY-2-73-RE 2018-09-07 16-23-54\VWD-AD(1-2)-95-5-0.
                  3ML-5UL-220NM-90MIN.M
Last changed    : 6/14/2018 9:07:28 PM
Analysis Method : D:\METHOD\LG\VWD-AD(1-2)-99-1-0.2ML-2UL-220NM-10MIN.M
Last changed    : 9/10/2018 10:38:13 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```



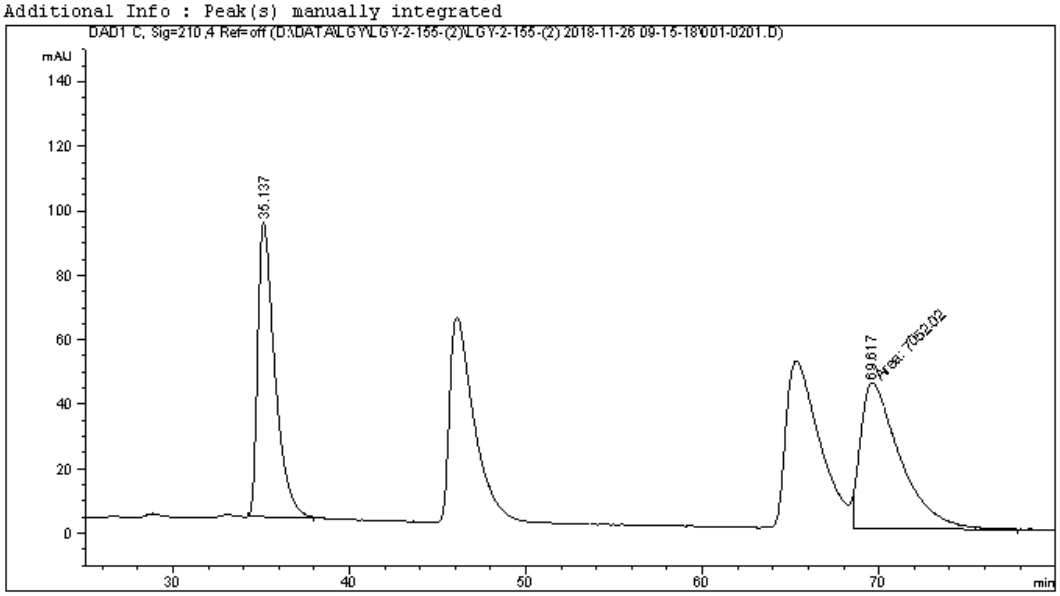

```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Retention Time
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Sig Type    Area      Height     Area
  #   [min]            [mAU*s]     [mAU]       %
----|-------|---|----|----------|----------|--------|
   1  69.060  1  MF   2.41019e4   271.55933  98.1979
   2  73.175  1  FM    442.31656    4.69764   1.8021

Totals :              2.45442e4   276.25696


======================================================================
```

Instrument 1 9/10/2018 10:38:16 PM Page 1 of 1

HPLC of racemic-**4a**

Data File D:\DATA\LGY\LGY-2-155-(2)\LGY-2-155-(2) 2018-11-26 09-15-18\001-0201.D
Sample Name: LGY-2-155

```
    ======================================================================
    Acq. Operator   :                                 Seq. Line :   2
    Acq. Instrument : Instrument 2                     Location : Vial 1
    Injection Date  : 11/26/2018 9:28:20 AM                 Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : D:\DATA\LGY\LGY-2-155-(2)\LGY-2-155-(2) 2018-11-26 09-15-18\DAD-OD(1-2)-90-
                      10-1ML-5UL-ALL-80MIN.M
    Last changed    : 5/26/2018 3:40:32 PM
    Analysis Method : D:\METHOD\TL\DAD-OJ(1-6)-80-20-1ML-3UL-ALL-10MIN.M
    Last changed    : 12/4/2018 9:40:39 AM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

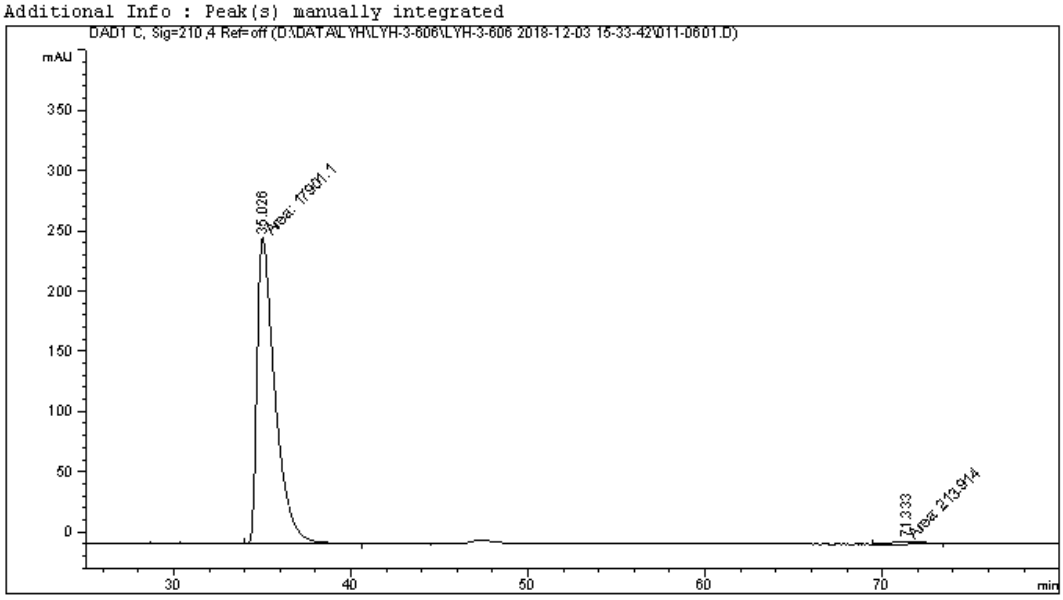



```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  35.137 BB    0.8992 6142.91992   91.04142  46.5551
       2  69.617 FM    2.6029 7052.02148   45.15573  53.4449

    Totals :                  1.31949e4   136.19715
```

HPLC of **4a**

Data File D:\DATA\LYH\LYH-3-606\LYH-3-606 2018-12-03 15-33-42\011-0601.D
Sample Name: LGY-3-14-1

```
    ======================================================================
    Acq. Operator   :                                Seq. Line :   6
    Acq. Instrument : Instrument 2                    Location : Vial 11
    Injection Date  : 12/3/2018 5:16:10 PM                 Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\DATA\LYH\LYH-3-606\LYH-3-606 2018-12-03 15-33-42\DAD-0D(1-2)-90-10-1ML-
                      5UL-ALL-80MIN.M
    Last changed    : 5/26/2018 3:40:32 PM
    Analysis Method : D:\METHOD\TL\DAD-0J(1-6)-80-20-1ML-3UL-ALL-10MIN.M
    Last changed    : 12/3/2018 8:08:37 PM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  35.026 MM    1.1786 1.79011e4   253.14673  98.8191
       2  71.333 MM    1.9375  213.91446    1.84013   1.1809

    Totals :                  1.81150e4   254.98685
```