Supporting Information

Direct Decarboxylative Functionalization of Carboxylic Acids via O–H Hydrogen Atom Transfer

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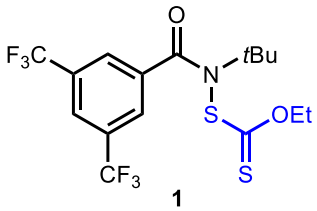
General Methods and Materials

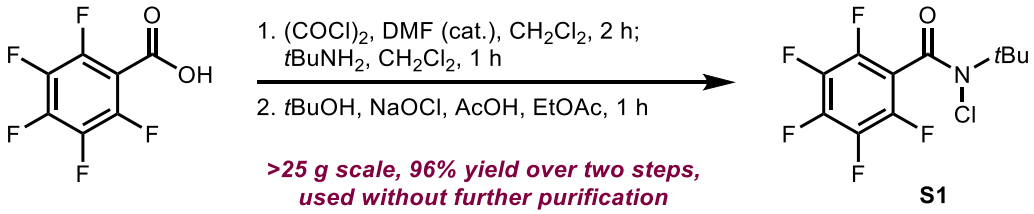
Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Bruker AVANCE III 600 CryoProbe (^{1}H NMR at 600 MHz and ^{13}C NMR at 151 MHz) spectrometer with solvent resonance as the internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.16 ppm). Fluorine magnetic resonance spectra (^{19}F NMR) was recorded on a Bruker model DRX 400 (^{19}F NMR at 376 MHz). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, tdd = triplet of doublet of doublets, qd = quartet of doublets, m = multiplet), coupling constants (Hz), and integration. Mass spectra were obtained using a Q Exactive HF-X mass spectrometer using either electrospray (ES) or atmospheric-pressure photoionization (APPI) and external calibration. Thin layer chromatography (TLC) was performed on SiliaPlate 250μm thick silica gel plates provided by Silicycle. Visualization was accomplished with short wave UV light (254 nm), iodine, aqueous basic potassium permanganate solution, or aqueous acidic ceric ammonium molybdate solution followed by heating. Flash chromatography was performed using SiliaFlash P60 silica gel (40-63 μm) purchased from Silicycle. Tetrahydrofuran, diethyl ether, and dichloromethane were dried by passage through a column of neutral alumina under nitrogen prior to use. Reactions involving blue light irradiation were performed using the PAR38 Royal Blue 21W aquarium LED lamps (Model #6851) fabricated with high-power Cree XR-E LEDs as purchased from Ecoxotic (www.ecoxotic.com) or Kessil PR160 440 nm LED Photoredox Lights. Reaction temperatures reached approximately 50 °C using the Ecoxotic lamp and 40–50 °C with the Kessil light. UV light experiments were performed in a Luzchem LZC-ORG photoreactor containing UV-A lamps. All substrates were obtained from commercial vendors (Sigma-Aldrich, Matrix Scientific, TCI Chemicals) and used without further purification unless otherwise noted.

Reagent Synthesis



1

N-(*tert*-butyl)-*N*-((ethoxycarbonothioyl)thio)-3,5-bis(trifluoromethyl)benzamide (**1**) was prepared as described in a previous report from our laboratory.[1]

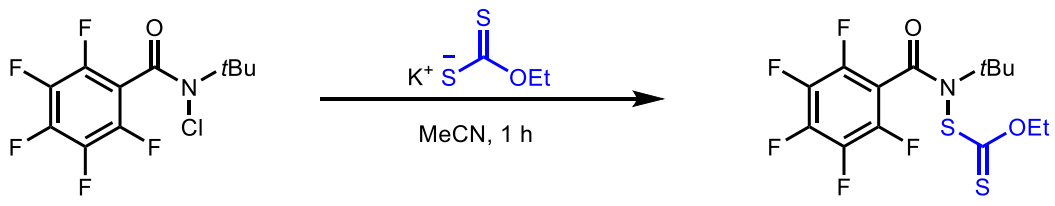


S1

***N*-(*tert*-butyl)-*N*-chloro-2,3,4,5,6-pentafluorobenzamide (S1).** To a solution of 2,3,4,5,6-pentafluorobenzoic acid (21.2 g, 100 mmol, 1.0 equiv) in CH_2Cl_2/DMF (200 mL/0.1 mL) was added oxalyl chloride (9.63 mL, 110 mmol, 1.1 equiv) dropwise. The resulting solution was stirred for 2 h, then concentrated *in vacuo* to remove excess oxalyl chloride. The resulting crude mixture was resuspended in CH_2Cl_2 and chilled to 0 ˚C. *tert*-Butylamine (27.0 mL, 250 mmol, 2.5 equiv) was added, and the mixture was warmed to rt and stirred for 1 h. The mixture was diluted with CH_2Cl_2 (300 mL), and the organic layer was washed with 10% NaOH (1 x 500 mL), 1M HCl (1 x 500 mL), brine (1 x 500 mL), dried with $MgSO_4$ and concentrated to afford the amide as a white solid, which was used directly in the next step.

With the laboratory lights off, to a solution of amide in EtOAc (200 mL) was added *t*BuOH (9.5 mL, 100 mmol, 1 equiv). To this solution was added AcOH (34 mL) and NaOCl (400 mL, 10-15% available chlorine). The mixture was stirred vigorously for 1 h, then quenched with sat. aq. $NaHCO_3$ (200 mL). The aqueous phase was extracted with EtOAc (300 mL), and the combined organic phase was washed with brine (1 x 500 mL), dried with $MgSO_4$, and concentrated *in vacuo* to yield a colorless solid (28.9 g, 96% yield), which was used without further purification.[2]

Note*:* Given the sensitivity of chloroamide **S1** to light, special care is taken by turning off the laboratory lights during workup and foil-wrapping flasks when appropriate. The compound is stored in foil-wrapped vials in the freezer when not in use. The reagent can be weighed out on the benchtop without risk of decomposition.



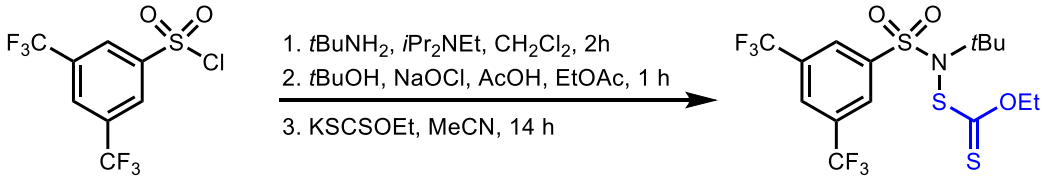
S1 **2**

***N*-(*tert*-butyl)-*N*-((ethoxycarbonothioyl)thio)-2,3,4,5,6-pentafluorobenzamide (2)**: In a 5L round-bottom flask, potassium ethyl xanthate (8.82 g, 55.0 mmol, 1.0 equiv) was suspended in MeCN (2.0 L). To this suspension was added a solution of chloroamide **S1** (16.6 g, 55.0 mmol,

1.0 equiv) in MeCN (500 mL) via cannula wire over 20 min. The flask was stirred for 1 h, at which point the suspension was concentrated *in vacuo*. The residue was taken up in CH_2Cl_2/H_2O (1:1, 1 L total volume), and the layers were separated. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The resultant solid was purified by flash column chromatography (1–5% EtOAc in hexanes) to afford the title compound as a light yellow solid (15.0 g, 70% yield):

^{1}H NMR (600 MHz, Chloroform-*d*) δ 4.75 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.58 (dq, *J* = 10.6, 7.1 Hz, 1H), 1.58 (s, 9H), 1.49 (t, *J* = 7.1 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -140.43 (dt, *J* = 24.3, 6.8 Hz, 1F), -142.52 (dt, *J* = 23.0, 6.7 Hz, 1F), -152.52 (td, *J* = 20.5, 7.3 Hz, 2F), -160.43 (td, *J* = 21.6, 8.5 Hz, 1F), -160.82 (td, *J* = 21.6, 8.5 Hz, 1F).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 211.41, 163.40, 144.25 – 135.78 (m), 113.53 (t, *J* = 21.4 Hz), 71.02, 64.69, 29.17, 13.43 (d, *J* = 1.6 Hz).
HRMS (ES+) Exact mass calcd for $C_{14}H_{14}F_5NNaO_2S_2$ $[M+Na]^+$, 410.0284. Found 410.0283.

Note*:* Xanthylamide **2** is not particularly sensitive to light under ambient laboratory lighting and may be stored on the benchtop without any special precautions.



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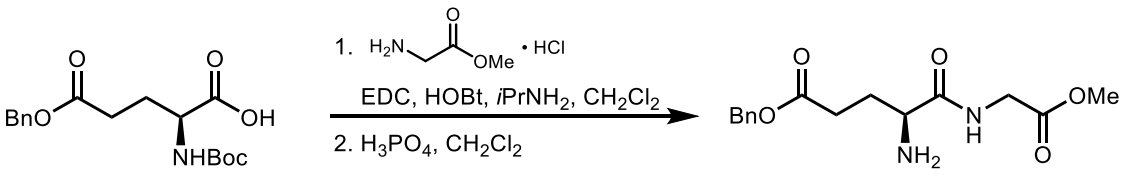
***N*-(*tert*-butyl)-*N*-((ethoxycarbonothioyl)thio)-3,5-bis(trifluoromethyl)benzenesulfonamide (36):** To a solution of 3,5-bis(trifluoromethyl)benzenesulfonyl chloride (6.10 g, 19.5 mmol, 1.3 equiv) and *N*,*N*-diisopropylethylamine (2.9 mL, 16.5 mmol, 1.1 equiv) in CH_2Cl_2 (100 mL) at 0 °C was added *tert*-butylamine (1.6 mL, 15.0 mmol, 1 equiv) dropwise. The mixture was warmed to rt and stirred for 2 h. The mixture was diluted with CH_2Cl_2 (100 mL), and the organic layer was washed with 1M HCl (200 mL), sat. aq. $NaHCO_3$ (200 mL), and brine (200 mL), dried over anhydrous $MgSO_4$, and concentrated to afford the sulfonamide as a white solid, which was used directly in the next step.

With the laboratory lights off, to a solution of the sulfonamide in EtOAc (30 mL) was added *t*BuOH (1.4 mL, 15.0 mmol, 1 equiv). To this solution was added AcOH (2.6 mL) and NaOCl (60 mL, 10-15% available chlorine). The mixture was stirred vigorously for 1 h, then quenched with sat. aq. $NaHCO_3$ (30 mL). The aqueous phase was extracted with EtOAc (30 mL), and the combined organic phase was washed with brine (1 x 50 mL), dried with $MgSO_4$, and concentrated *in vacuo* to yield a colorless oil (5.28 g, 92% yield over two steps), which was used without further purification (the chlorosulfonamide intermediate is prone to decomposition on silica gel.)

In a 1L round-bottom flask, potassium ethyl xanthate (2.21 g, 13.8 mmol, 1.0 equiv) was suspended in MeCN (250 mL). To this suspension was added a solution of chlorosulfonamide (5.28 g. 13.8 mmol, 1 equiv) in MeCN (250 mL) via cannula wire over 20 min. The flask was stirred overnight, at which point the suspension was concentrated *in vacuo*. The residue was taken up in CH_2Cl_2/H_2O (1:1, 250 mL total volume) and the layers were separated. The organic layer was washed with brine, dried with $MgSO_4$, and concentrated in vacuo. The resultant solid was purified by flash column chromatography (1–5% EtOAc in hexanes) to afford the title compound as a light yellow solid (1.76 g, 27% yield):

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.36 (t, *J* = 2.2 Hz, 2H), 8.05 (d, *J* = 3.2 Hz, 1H), 4.63 (dt, *J* = 6.8, 3.2 Hz, 1H), 4.27 (dt, *J* = 7.2, 3.7 Hz, 1H), 1.57 (s, 9H), 1.32 (td, *J* = 7.2, 3.0 Hz, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 212.03, 143.56, 132.74 (q, *J* = 34.5 Hz), 128.35 (d, *J* = 4.2 Hz), 126.44 – 126.25 (m), 122.52 (q, *J* = 273.3 Hz), 70.70, 68.60, 30.84, 13.59.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.88.
HRMS (ES+) Exact mass calcd for $C_{15}H_{18}F_6NO_3S_3$ $[M+H]^+$, 492.0172. Found 492.0172.

Tripeptide Synthesis

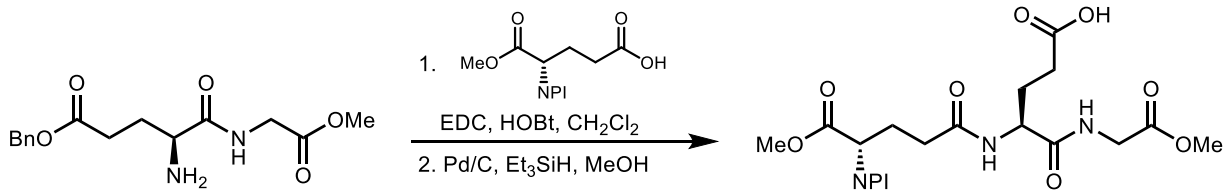


S2

H-Glu(OBn)-Gly-OMe (S2): A 250 mL round-bottom flask was charged with a solution of *N*-(*tert*-butyloxycarbonyl)-γ-benzyl-L-glutamic acid (5.16 g, 15.3 mmol), glycine methyl ester hydrochloride (2.11 g, 16.8 mmol) and hydroxybenzotriazole (HOBt: 2.07 g, 15.3 mmol) in CH_2Cl_2 (150 mL) and cooled to 0 °C. To this solution was added *i*Pr_2NEt (2.9 mL, 16.8 mmol) dropwise over 5 min, and the resulting mixture was stirred at 0 °C for 10 min. To this solution was added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC: 3.22 g, 16.8 mmol), and the resulting mixture was warmed to room temperature. After 16 h, the reaction mixture was cooled to 0 °C and quenched with 1 M HCl (50 mL). The precipitate was filtered off, and the phases were separated. The aqueous phase was further extracted with CH_2Cl_2 (30 mL × 3). The combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by column chromatography (SiO_2, 40% EtOAc/ hexanes) to provide the amide (6.26 g, quantitative yield) as a white solid:

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 5H), 7.00 (t, *J* = 5.4 Hz, 1H), 5.44 (d, *J* = 8.1 Hz, 1H), 5.11 (s, 2H), 4.27 (q, *J* = 7.6 Hz, 1H), 4.01 (qd, *J* = 18.2, 5.5 Hz, 2H), 3.71 (s, 3H), 2.64 – 2.42 (m, 2H), 2.16 (ddd, *J* = 15.3, 7.8, 5.8 Hz, 1H), 1.96 (ddd, *J* = 14.4, 8.1, 6.8 Hz, 1H), 1.41 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 173.28, 172.05, 170.15, 155.80, 135.77, 128.65, 128.37, 128.32, 80.22, 77.16, 66.64, 53.53, 52.44, 41.20, 30.44, 28.37, 28.01.
HRMS (ES+) Exact mass calcd for $C_{20}H_{28}N_2NaO_7$ $[M+Na]^+$, 431.1794. Found 431.1796.

N-Boc deprotection: To a solution of the dipeptide (6.26 g, 15.3 mmol, 1 equiv) in CH_2Cl_2 (5 mL) at room temperature was added aqueous phosphoric acid (85 wt %, 2.6 mL). The mixture was stirred vigorously for 3 h. Then 15 mL of water was added and the mixture was cooled to 0 °C. A 50 wt % NaOH solution was added slowly to adjust the pH to 8. The mixture was then extracted with CH_2Cl_2 (3 x 30 mL). The combined organic phase was dried over $MgSO_4$ and concentrated in vacuo to give **S2** (3.99 g, 84% yield) as a white solid, which was used directly in the next step without further purification.



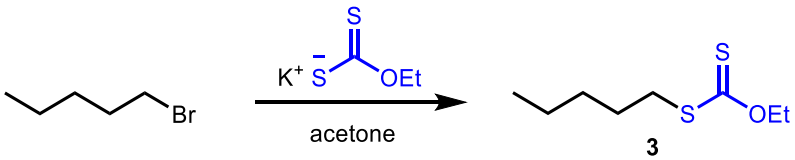
S2 **S3**

Phth-Glu(OMe)-Glu(OH)-Gly-OMe (S3): A 50 mL round-bottom flask was charged with a solution of H-Glu(OBn)-Gly-OMe (**S2**) (0.50 g, 1.6 mmol, 1 equiv), *N*,*N*-phthaloyl-L-glutamic acid-1-methyl ester (0.58 g, 2.0 mmol) and hydroxybenzotriazole (HOBt: 0.27 g, 2.0 mmol, 1.2 equiv) in CH_2Cl_2 (10 mL) and cooled to 0 °C. To this solution was added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC: 0.31 g, 1.6 mmol, 1 equiv) and the resulting mixture was warmed to room temperature. After 16 h, the reaction mixture was cooled to 0 °C and quenched with 1 M HCl (10 mL). The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (10 mL x 3). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to provide the amide (0.63 g, 67% yield) as a pale-yellow oil, which was used directly in the next step.

OBn deprotection: To a stirred solution of the tripeptide (0.63 g, 1.1 mmol, 1 equiv) and 10% palladium on carbon (0.12 g, 0.11 mmol, 0.1 equiv) in MeOH (2 mL) under an Ar-filled balloon was added triethylsilane (1.7 mL, 11 mmol, 10 equiv) dropwise over 10 min. When the reaction was complete (TLC), the mixture was filtered through celite and the solvent was removed in vacuo. The residue was basified with saturated bicarbonate solution (10 mL), and the aqueous layer was washed with pentane (10 mL x 2). The aqueous layer was then acidified to pH = 2 with 6 M HCl and extracted with CH_2Cl_2 (20 mL x 3). The combined organic layer was washed with brine (30 mL), dried over $MgSO_4$, concentrated to give a white solid (0.49 g, 92% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 2H), 7.74 (dd, J = 5.5, 3.0 Hz, 2H), 7.70 (t, J = 5.7 Hz, 1H), 7.04 (d, J = 8.3 Hz, 1H), 4.87 (dd, J = 10.2, 4.8 Hz, 1H), 4.71 (td, J = 8.2, 6.0 Hz, 1H), 4.07 (dd, J = 18.0, 6.0 Hz, 1H), 3.93 (dd, J = 18.0, 5.4 Hz, 1H), 3.71 (s, 3H), 3.69 (s, 3H), 2.65 – 2.54 (m, 1H), 2.54 – 2.35 (m, 3H), 2.35 – 2.22 (m, 2H), 2.12 – 2.02 (m, 1H), 1.91 (dq, J = 14.2, 7.1 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 176.15, 172.34, 172.23, 170.23, 169.46, 167.78, 134.48, 131.74, 123.79, 52.99, 52.43, 51.96, 51.28, 41.29, 32.48, 29.93, 28.09, 24.75.
HRMS (ES+) Exact mass calcd for $C_{22}H_{25}N_3NaO_{10}$ $[M+Na]^+$, 514.1438. Found 514.1438.

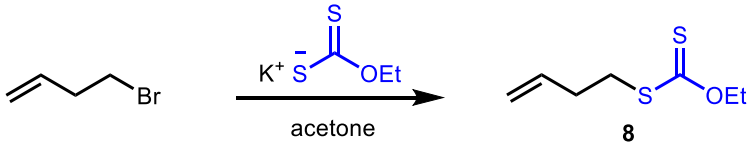
Standard syntheses for GC analysis



3

***O*-ethyl *S*-pentyl carbonodithioate (3):** To a suspension of potassium ethyl xanthate (0.48 g, 3.0 mmol, 1.5 equiv) in acetone (4 mL) was added 1-bromopentane (0.25 mL, 2.0 mmol, 1 equiv). The mixture was stirred overnight at rt and then concentrated. The residue was taken up in CH_2Cl_2 (20 mL) and washed with H_2O (20 mL), brine (20 mL), dried with $MgSO_4$, and concentrated to afford alkyl xanthate **3** (0.36 g, 94% yield) as a pale-yellow oil.

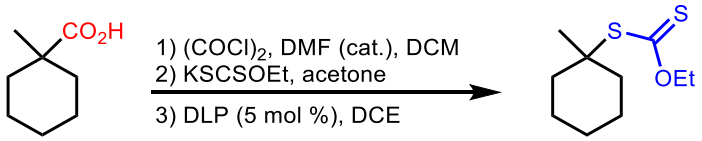
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.66 (q, J = 7.1 Hz, 2H), 3.13 (t, J = 7.7 Hz, 2H), 1.76 – 1.64 (m, 2H), 1.47 – 1.32 (m, 6H), 0.92 (t, J = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 215.34, 69.85, 35.98, 31.14, 28.17, 22.32, 14.05, 13.92.
HRMS (ES+) Exact mass calcd for $C_8H_{16}NaOS_2$ $[M+Na]^+$, 215.0540. Found 215.0538.



8

***S*-(but-3-en-1-yl) *O*-ethyl carbonodithioate (8):** To a suspension of potassium ethyl xanthate (0.48 g, 3.0 mmol, 1.5 equiv) in acetone (4 mL) was added 4-bromo-1-butene (0.20 mL, 2.0 mmol, 1 equiv). The mixture was stirred overnight at rt and then concentrated. The residue was taken up in CH_2Cl_2 (20 mL) and washed with H_2O (20 mL), brine (20 mL), dried with $MgSO_4$, and concentrated to afford alkyl xanthate **4** (0.31 g, 88% yield) as a pale-yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.82 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H), 5.14 – 5.05 (m, 2H), 4.64 (q, J = 7.1 Hz, 2H), 3.18 (t, J = 7.4 Hz, 2H), 2.51 – 2.31 (m, 2H), 1.42 (t, J = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.88, 135.95, 116.80, 69.97, 35.14, 32.62, 13.92.
HRMS (ES+) Exact mass calcd for $C_7H_{13}OS_2$ $[M+H]^+$, 177.0408. Found 177.0403.



17

***O*-ethyl *S*-(1-methylcyclohexyl) carbonodithioate (17):** To a solution of 1-methylcyclohexane-1-carboxylic acid (1.42 g, 10.0 mmol, 1 equiv) in CH_2Cl_2 (20 mL) was added dimethylformamide (DMF; 1 drop). The solution was cooled to 0 °C, and oxalyl chloride (0.96 mL, 11.0 mmol, 1.1 equiv) was added in dropwise. The solution was warmed to rt and stirred for 2 h. Afterward, the mixture was concentrated *in vacuo*, resuspended in THF (20 mL), and cooled to 0 °C. Potassium ethyl xanthate salt (1.52 g, 9.50 mmol, 0.95 equiv) was added in one portion, and the mixture was allowed to stir for 3 h. The mixture was then concentrated *in vacuo* and redissolved in CH_2Cl_2 (50 mL) and washed with H_2O (50 mL). The aqueous layer was extracted once with CH_2Cl_2 (50 mL). The combined organic phase was washed with brine (75 mL), then dried over anhydrous $MgSO_4$. The solid was filtered, and the filtrate was concentrated *in vacuo.* The crude was resuspended in DCE (20 mL) with dilauroyl peroxide (0.20 g, 0.050 mmol, 0.05 equiv) and stirred overnight under reflux. Upon concentrating, the residue was purified by flash column chromatography (0–5% Et_2O/hexanes) to afford xanthate **17** as a yellow oil (1.64 g, 75% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.65 (q, *J* = 7.1 Hz, 2H), 2.07 – 1.96 (m, 2H), 1.65 – 1.58 (m, 1H), 1.57 (s, 3H), 1.55 – 1.47 (m, 5H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.30 (qd, *J* = 9.3, 5.7 Hz, 1H), 1.24 (s, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.49, 69.40, 56.79, 37.65, 29.79, 25.73, 22.48, 13.84.
HRMS (APPI+) Exact mass calcd for $C_{10}H_{19}OS_2$ $[M+H]^+$, 219.0877. Found 219.0877.

Functionalized Products

General Procedure A – *Product functionalization using heat and initiator*

A 1 dram vial equipped with a stir bar was charged with substrate (1 equiv), xanthylamide **2** (1–2 equiv), and dilauroyl peroxide (DLP; 10 mol % wrt to xanthylamide **2**), fitted with a PTFE lined screw cap, and taken into the glovebox. The contents were dissolved in $PhCF_3$ (0.1 M wrt substrate), and the resulting solution was sealed with Teflon tape and removed from the glovebox. Alternatively, reactions may be prepared using other air-sensitive techniques, such as with a Schlenk line. The vial was placed on a block plate at 80 °C and stirred for 4 h. If necessary, additional DLP (10 mol %) was added for full conversion of xanthylamide **2** as monitored by TLC. Upon completion, the reaction was concentrated *in vacuo*, and the crude residue was purified by flash column chromatography to afford the desired product.

General Procedure B – *Product functionalization using blue LEDs*

A 1 dram vial equipped with a stir bar was charged with substrate (1 equiv) and xanthylamide **2** (1.2 equiv), fitted with a PTFE lined screw cap, and taken into the glovebox. The contents were dissolved in $PhCF_3$ (0.1 M wrt substrate), and the resulting solution was sealed with Teflon tape and removed from the glovebox. Alternatively, reactions may be prepared using other air-sensitive techniques, such as with a Schlenk line. The vial was centered approximately 4 cm away from a 440 nm Kessil PR160 LED light at max (100%) intensity. After 4 h, the light was turned off. The reaction was concentrated *in vacuo*, and the crude residue was purified by flash column chromatography to afford the desired product.

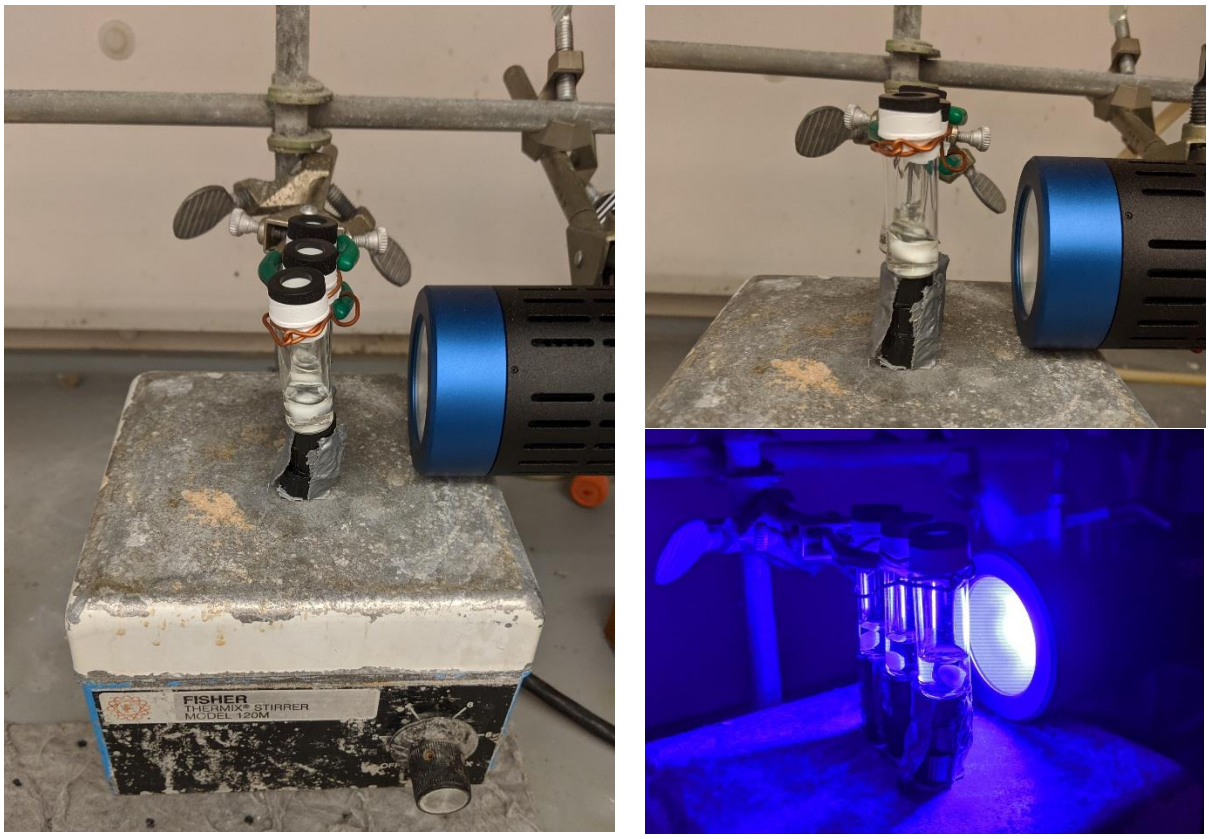
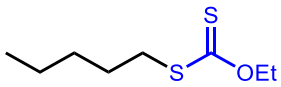
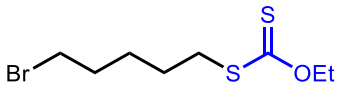


Figure S1. Pictures of the light setup used in General Procedure B. Up to three reactions may be run at a time by using copper wiring to hold the vials together.



3

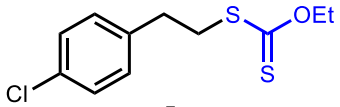
***O*-ethyl *S*-pentyl carbonodithioate (3):** Prepared according to General Procedure A using hexanoic acid (12.5 µL, 0.100 mmol, 1 equiv), xanthylamide **2** (77.4 mg, 0.200 mmol, 2 equiv), and dilauroyl peroxide (8.0 mg, 0.020 mmol, 0.2 equiv), giving 70% NMR yield. Alternatively prepared according to General Procedure B using hexanoic acid (12.5 µL, 0.100 mmol, 1 equiv) and xanthylamide **2** (46.4 mg, 0.120 mmol, 1.2 equiv), giving 86% NMR yield using a glovebox and 71% NMR yield using a Schlenk line.



4

***S*-(5-bromopentyl) *O*-ethyl carbonodithioate (4)**: Prepared according to General Procedure A using 6-bromohexanoic acid (19.5 mg, 0.100 mmol, 1 equiv), xanthylamide **2** (77.4 mg, 0.200 mmol, 2 equiv), and dilauroyl peroxide (8.0 mg, 0.020 mmol, 0.2 equiv). Alternatively prepared according to General Procedure B using 6-bromohexanoic acid (19.5 mg, 0.100 mmol, 1 equiv) and xanthylamide **2** (46.4 mg, 0.120 mmol, 1.2 equiv). The crude residue was purified by flash column chromatography (0.1–1% EtOAc/hex) to afford **4** as a pale yellow oil (A: 20.4 mg, 75% yield; B: 27.1 mg, 100% yield):

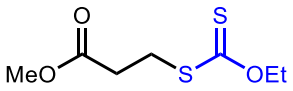
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.64 (q, *J* = 7.1 Hz, 2H), 3.41 (t, *J* = 6.7 Hz, 2H), 3.13 (t, *J* = 7.4 Hz, 2H), 1.89 (p, *J* = 6.9 Hz, 2H), 1.73 (p, *J* = 7.5 Hz, 2H), 1.57 (q, *J* = 7.9 Hz, 3H), 1.42 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 215.09, 70.05, 35.68, 33.60, 32.30, 27.77, 27.52, 13.96.
HRMS (APPI+) Exact mass calcd for $C_8H_{16}BrOS_2$ $[M+H]^+$, 270.9826. Found 270.9826.



5

***S*-(4-chlorophenethyl) *O*-ethyl carbonodithioate (5):** Prepared according to General Procedure A using 3-(4-chlorophenyl)propanoic acid (18.5 mg, 0.100 mmol, 1 equiv), xanthylamide **2** (77.4 mg, 0.20 mmol, 2 equiv), and dilauroyl peroxide (8.0 mg, 0.020 mmol, 0.2 equiv). Alternatively prepared according to General Procedure B using 3-(4-chlorophenyl)propanoic acid (18.5 mg, 0.100 mmol, 1 equiv) and xanthylamide **2** (46.4 mg, 0.120 mmol, 1.2 equiv). The crude residue was purified by flash column chromatography (0.1–1% EtOAc/hex) to afford **5** as a colorless oil (A: 18.2 mg, 70% yield; B: 26.0 mg, 99% yield):

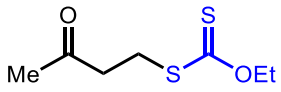
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 2H), 7.21 – 7.16 (m, 2H), 4.65 (q, *J* = 7.1 Hz, 2H), 3.37 – 3.29 (m, 2H), 3.01 – 2.91 (m, 2H), 1.43 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.66, 138.31, 132.54, 130.11, 128.82, 70.19, 37.05, 34.33, 13.97.
HRMS (APPI+) Exact mass calcd for $C_{11}H_{14}ClOS_2$ $[M+H]^+$, 261.0175. Found 261.0175.



6

Methyl 3-((ethoxycarbonothioyl)thio)propanoate (6): Prepared according to General Procedure A using monomethyl succinate (6.6 mg, 50 µmol, 1 equiv), xanthylamide **2** (38.7 mg, 100 µmol, 2 equiv), and dilauroyl peroxide (4.0 mg, 10 µmol, 0.2 equiv). Alternatively prepared according to General Procedure B using monomethyl succinate (13.2 mg, 0.100 mmol, 1 equiv) and xanthylamide **2** (46.4 mg, 0.120 mmol, 1.2 equiv). The crude residue was purified by flash column chromatography (2.5–5% EtOAc/hex) to afford **6** as a colorless oil (A: 10.1 mg, 97% yield; B: 15.5 mg, 74% yield):

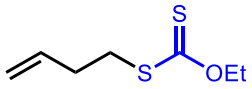
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.64 (q, *J* = 7.1 Hz, 1H), 3.71 (s, 1H), 3.37 (t, *J* = 7.1 Hz, 1H), 2.78 (t, *J* = 7.0 Hz, 1H), 1.42 (t, *J* = 7.1 Hz, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.36, 172.18, 70.29, 52.13, 33.33, 30.67, 13.94.
HRMS (ES+) Exact mass calcd for $C_7H_{12}NaO_3S_2$ $[M+Na]^+$, 231.0126. Found 231.0124.



7

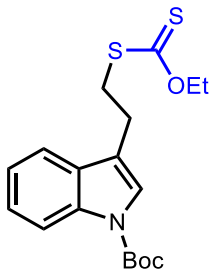
***O*-ethyl *S*-(3-oxobutyl) carbonodithioate (7):** Prepared according to General Procedure A using levulinic acid (11.6 mg, 0.100 mmol, 1 equiv), xanthylamide **2** (77.4 mg, 0.200 mmol, 2 equiv), and dilauroyl peroxide (8.0 mg, 0.020 mmol, 0.2 equiv), giving 80% NMR yield. Alternatively prepared according to General Procedure B using levulinic acid (11.6 mg, 0.100 mmol, 1 equiv) and xanthylamide **2** (46.4 mg, 0.120 mmol, 1.2 equiv), giving 88% NMR yield. Due to difficulties in isolation from inseparable byproducts, an analytical sample of **7** was obtained from reaction of levulinic acid with xanthylamide **1** and purification by flash column chromatography (2.5–5% EtOAc/hex):

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.64 (q, *J* = 7.4, 6.7, 6.1 Hz, 2H), 3.32 (t, *J* = 6.9 Hz, 2H), 2.90 (t, *J* = 6.8 Hz, 2H), 2.17 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.99, 206.44, 70.21, 42.46, 30.10, 29.47, 13.95.
HRMS (ES+) Exact mass calcd for $C_7H_{12}NaO_2S_2$ $[M+Na]^+$, 215.0176. Found 215.0173.



8

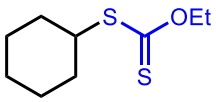
***S*-(but-3-en-1-yl) *O*-ethyl carbonodithioate (8):** Prepared according to General Procedure A using 4-pentenoic acid (10.2 µL, 0.100 mmol, 1 equiv), xanthylamide **2** (77.4 mg, 0.20 mmol, 2 equiv), and dilauroyl peroxide (8.0 mg, 0.020 mmol, 0.2 equiv). After 4 h, additional DLP (8.0 mg, 0.020 mmol, 0.2 equiv) was added to the reaction mixture under an inert atmosphere, and the reaction vial was stirred at 80 °C for another 4 h, giving 45% NMR yield. Alternatively prepared according to General Procedure B using 4-pentenoic acid (10.2 µL, 0.100 mmol, 1 equiv) and xanthylamide **2** (38.7 mg, 0.100 mmol, 1 equiv), giving 47% NMR yield.



9

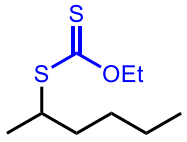
***Tert*-butyl 3-(2-((ethoxycarbonothioyl)thio)ethyl)-1H-indole-1-carboxylate (9):** Prepared according to General Procedure A using 3-(1-(*tert*-butoxycarbonyl)-1H-indol-3-yl)propanoic acid[3] (43.5 mg, 0.150 mmol, 1 equiv), xanthylamide **2** (116 mg, 0.300 mmol, 2 equiv), and dilauroyl peroxide (30.0 mg, 0.075 mmol, 0.5 equiv). After 4 h, additional DLP (30.0 mg, 0.075 mmol, 0.5 equiv) was added to the reaction mixture under an inert atmosphere, and the reaction vial was stirred at 80 °C for another 4 h. The crude residue was purified by flash column chromatography (1–2.5% EtOAc/hex) to afford **9** as a white solid (34.0 mg, 62% yield). Alternatively prepared according to General Procedure B using 3-(1-(*tert*-butoxycarbonyl)-1H-indol-3-yl)propanoic acid (43.5 mg, 0.150 mmol, 1 equiv) and xanthylamide **2** (46.4 mg, 0.120 mmol, 1.2 equiv), giving 36% NMR yield:

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (br s, 1H), 7.67 – 7.61 (m, 1H), 7.47 (br s, 1H), 7.39 – 7.33 (m, 1H), 7.31 – 7.27 (m, 1H), 4.69 (q, *J* = 7.1 Hz, 2H), 3.49 – 3.43 (m, 2H), 3.17 – 3.08 (m, 2H), 1.70 (s, 9H), 1.45 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.84, 124.61, 123.29, 122.62, 119.07, 118.78, 115.45, 70.19, 35.50, 29.30, 28.35, 24.61, 13.97.
HRMS (ES+) Exact mass calcd for $C_{18}H_{23}NNaO_3S_2$ $[M+Na]^+$, 388.1017. Found 388.1017.



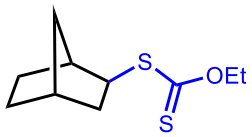
10

***S*-cyclohexyl *O*-ethyl carbonodithioate (10):** Prepared according to General Procedure A using cyclohexanecarboxylic acid (12.8 mg, 0.100 mmol, 1 equiv), xanthylamide **2** (58.1 mg, 0.150 mmol, 1.5 equiv), and dilauroyl peroxide (6.0 mg, 0.015 mmol, 0.15 equiv), giving 99% GC yield. Spectral data was in accordance with literature values.[4]



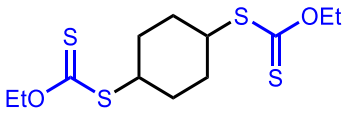
11

***O*-ethyl *S*-(hexan-2-yl) carbonodithioate (11):** Prepared according to General Procedure A using 2-methylhexanoic acid (14.1 µL, 0.100 mmol, 1 equiv), xanthylamide **2** (58.1 mg, 0.150 mmol, 1.5 equiv), and dilauroyl peroxide (6.0 mg, 0.015 mmol, 0.15 equiv), giving 99% GC yield. Spectral data was in accordance with literature values.[1]



12

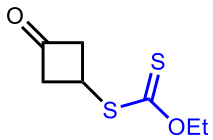
***S*-((1*S*,2*S*,4*R*)-bicyclo[2.2.1]heptan-2-yl) *O*-ethyl carbonodithioate (12):** Prepared according to General Procedure A using norbornane-2-carboxylic acid (predominantly endo isomer) (14.0 mg, 0.100 mmol, 1 equiv), xanthylamide **2** (58.1 mg, 0.150 mmol, 1.5 equiv), and dilauroyl peroxide (6.0 mg, 0.015 mmol, 0.15 equiv). Alternatively prepared according to General Procedure B using norbornane-2-carboxylic acid (predominantly endo isomer) (14.0 mg, 0.100 mmol, 1 equiv) and xanthylamide **2** (43.5 mg, 0.120 mmol, 1.2 equiv). The crude residue was purified by flash column chromatography (0.1–1% EtOAc/hex) to afford **12** as a pale yellow oil (A: 19.9 mg, 92% yield; B: 15.7 mg, 73% yield). Spectral data was in accordance with literature values.[1]



13

***S,S'*-(cyclohexane-1,4-diyl) *O,O'*-diethyl bis(carbonodithioate) (13)**: Prepared according to General Procedure A using cyclohexane-1,4-dicarboxylic acid (25.8 mg, 0.150 mmol, 1 equiv), xanthylamide **2** (174 mg, 0.450 mmol, 3 equiv), and dilauroyl peroxide (18.0 mg, 0.045 mmol, 0.45 equiv). Alternatively prepared according to General Procedure B using cyclohexane-1,4-dicarboxylic acid (17.2 mg, 0.100 mmol, 1 equiv) and xanthylamide **2** (93.0 mg, 0.240 mmol, 2.4 equiv). The crude residue was purified by flash column chromatography (1–2.5% EtOAc/hex) to afford **13** as a pale-yellow oil (A: 38.5 mg, 79% yield; B: 30.4 mg, 94% yield):

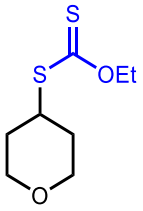
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.63 (q, *J* = 7.1 Hz, 4H), 3.90 – 3.82 (m, 1H), 3.64 – 3.57 (m, 1H), 2.33 – 2.14 (m, 1H), 2.07 – 1.97 (m, 2H), 1.93 – 1.80 (m, 2H), 1.62 – 1.55 (m, 2H), 1.44 – 1.40 (m, 6H), 1.31 – 1.22 (m, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.08, 213.95, 69.87, 69.85, 47.44, 47.31, 29.80, 29.31, 13.94, 13.93.
HRMS (ES+) Exact mass calcd for $C_{12}H_{21}O_2S_4$ $[M+H]^+$, 325.0424. Found 325.0424.



14

***O*-ethyl *S*-(3-oxocyclobutyl) carbonodithioate (14)**: Prepared according to General Procedure A using 3-oxocyclobutane-1-carboxylic acid (11.4 mg, 0.100 mmol, 1 equiv), xanthylamide **2** (58.1 mg, 0.150 mmol, 1.5 equiv), and dilauroyl peroxide (6.0 mg, 0.015 mmol, 0.15 equiv). Altenatively prepared according to General Procedure B using 3-oxocyclobutane-1-carboxylic acid (11.4 mg, 0.100 mmol, 1 equiv) and xanthylamide **2** (46.4 mg, 0.120 mmol, 1.2 equiv). The crude residue was purified by flash column chromatography (1–2.5% EtOAc/hex) to afford **14** as a colorless amorphous solid (A: 16.1 mg, 85% yield; B: 14.7 mg, 77% yield):

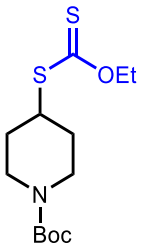
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.64 (q, J = 7.1 Hz, 2H), 4.18 – 4.12 (m, 1H), 3.71 – 3.56 (m, 2H), 3.18 – 3.10 (m, 2H), 1.43 (t, J = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 213.22, 203.96, 70.21, 54.36, 30.75, 13.92.
HRMS (ES+) Exact mass calcd for $C_7H_{10}NaOS_2$ $[M+Na]^+$, 197.0071. Found 197.0068.



15

***O*-ethyl *S*-(tetrahydro-2*H*-pyran-4-yl) carbonodithioate (15):** Prepared according to General Procedure A using tetrahydro-2*H*-pyran-4-carboxylic acid (13.0 mg, 0.100 mmol, 1 equiv), xanthylamide **2** (58.1 mg, 0.150 mmol, 1.5 equiv), and dilauroyl peroxide (6.0 mg, 0.015 mmol, 0.15 equiv). Alternatively prepared according to General Procedure B using tetrahydro-2*H*-pyran-4-carboxylic acid (13.0 mg, 0.100 mmol, 1 equiv) and xanthylamide **2** (46.4 mg, 0.120 mmol, 1.2 equiv). The crude residue was purified by flash column chromatography (1–2.5% EtOAc/hex) to afford **15** as a pale yellow oil (A: 15.0 mg, 73% yield; B: 14.4 mg, 70% yield):

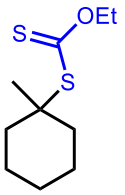
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.63 (q, *J* = 7.1 Hz, 2H), 3.94 (dt, *J* = 11.9, 3.9 Hz, 2H), 3.85 (tt, *J* = 10.7, 4.1 Hz, 1H), 3.55 (ddd, *J* = 11.7, 10.4, 2.5 Hz, 2H), 2.10 – 2.03 (m, 2H), 1.80 – 1.70 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 213.58, 69.88, 67.49, 45.45, 32.11, 13.93.
HRMS (ES+) Exact mass calcd for $C_8H_{15}O_2S_2$ $[M+H]^+$, 207.0513. Found 207.0508.



16

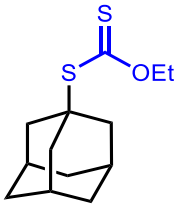
***Tert*-butyl 4-((ethoxycarbonothioyl)thio)piperidine-1-carboxylate (16):** Prepared according to General Procedure A using 1-(*tert*-butoxycarbonyl)piperidine-4-carboxylic acid[5] (34.4 mg, 0.150 mmol, 1 equiv), xanthylamide **2** (87.2 mg, 0.225 mmol, 1.5 equiv), and dilauroyl peroxide (9.0 mg, 0.023 mmol, 0.15 equiv). After 4 h, additional DLP (9.0 mg, 0.023 mmol, 0.15 equiv) was added to the reaction mixture under an inert atmosphere, and the reaction vial was stirred at 80 °C for another 4 h. Alternatively prepared according to General Procedure B using 1-(*tert*-butoxycarbonyl)piperidine-4-carboxylic acid (22.9 mg, 0.100 mmol, 1 equiv) and xanthylamide **2** (46.5 mg, 0.120 mmol, 1.2 equiv). The crude residue was purified by flash column chromatography (1–2.5% EtOAc/hex) to afford **16** as a white solid (A: 31.8 mg, 69% yield; B: 19.0 mg, 62% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.64 (q, *J* = 7.1 Hz, 2H), 3.91 (br s, 2H), 3.78 (tt, *J* = 10.4, 4.0 Hz, 1H), 3.05 (br s, 2H), 2.08 – 2.00 (m, 2H), 1.67 – 1.57 (m, 3H), 1.45 (s, 9H), 1.42 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 213.56, 154.74, 79.90, 69.96, 46.56, 28.54, 13.94.
HRMS (ES+) Exact mass calcd for $C_{13}H_{23}NNaO_3S_2$ $[M+Na]^+$, 328.1015. Found 328.1017.



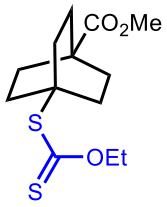
17

***O*-ethyl *S*-(1-methylcyclohexyl) carbonodithioate (17):** Prepared according to General Procedure A using 1-methylcyclohexanecarboxylic acid (14.2 mg, 0.100 mmol, 1 equiv), xanthylamide **2** (58.1 mg, 0.150 mmol, 1.5 equiv), and dilauroyl peroxide (6.0 mg, 0.015 mmol, 0.15 equiv), giving 95% GC yield.



18

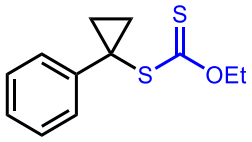
***S*-((3*s*,5*s*,7*s*)-adamantan-1-yl) *O*-ethyl carbonodithioate (18):** Prepared according to General Procedure A using 1-adamantanecarboxylic acid (18.0 mg, 0.100 mmol, 1 equiv), xanthylamide **2** (58.1 mg, 0.150 mmol, 1.5 equiv) and dilauroyl peroxide (6.0 mg, 0.015 mmol, 0.15 equiv). Alternatively prepared according to General Procedure B using 1-adamantanecarboxylic acid (18.0 mg, 0.100 mmol, 1 equiv) and xanthylamide **2** (46.5 mg, 0.120 mmol, 1.2 equiv). The crude residue was purified by flash column chromatography (0.1–1% EtOAc/hex) to afford **18** as a white solid (A: 20.6 mg, 80% yield; B: 25.4 mg, 99% yield). Spectral data was in accordance with literature values.[1]



19

Methyl 4-((ethoxycarbonothioyl)thio)bicyclo[2.2.2]octane-1-carboxylate (19): Prepared according to General Procedure A using 4-(methoxycarbonyl)bicyclo[2.2.2]octane-1-carboxylic acid (21.2 mg, 0.100 mmol, 1 equiv), xanthylamide **2** (58.1 mg, 0.150 mmol, 1.5 equiv) and dilauroyl peroxide (6.0 mg, 0.015 mmol, 0.15 equiv). Alternatively prepared according to General Procedure B using 4-(methoxycarbonyl)bicyclo[2.2.2]octane-1-carboxylic acid (21.2 mg, 0.100 mmol, 1 equiv) and xanthylamide **2** (48.5 mg, 0.120 mmol, 1.2 equiv). The crude residue was purified by flash column chromatography (1–2.5% EtOAc/hex) to afford **19** as an off-white solid (A: 26.9 mg, 93% yield; B: 29.0 mg, quantitative yield):

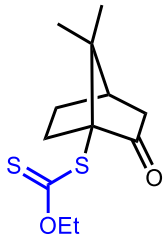
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.65 (q, *J* = 7.1 Hz, 2H), 3.63 (s, 3H), 2.10 – 1.93 (m, 6H), 1.93 – 1.84 (m, 6H), 1.45 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 213.52, 177.41, 69.47, 51.97, 51.21, 37.95, 30.29, 29.06, 13.88.
HRMS (ES+) Exact mass calcd for $C_{13}H_{21}O_3S_2$ $[M+H]^+$, 289.0932. Found 289.0931.



20

***O*-ethyl *S*-(1-phenylcyclopropyl) carbonodithioate (20):** Prepared according to General Procedure A using 1-phenylcyclopropane-1-carboxylic acid (16.2 mg, 0.100 mmol, 1 equiv), xanthylamide **2** (58.1 mg, 0.150 mmol, 1.5 equiv) and dilauroyl peroxide (6.0 mg, 0.015 mmol, 0.15 equiv). The crude residue was purified by flash column chromatography (0.1–1% EtOAc/hex) to afford **20** as a pale yellow oil (23.8 mg, quantitative yield):

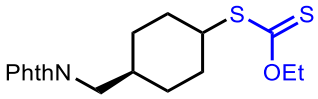
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 2H), 7.29 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.23 – 7.19 (m, 1H), 4.59 (q, *J* = 7.1 Hz, 2H), 1.48 – 1.45 (m, 2H), 1.45 – 1.41 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 213.82, 142.44, 128.46, 128.12, 126.86, 69.75, 30.60, 17.49, 13.84.
HRMS (APPI+) Exact mass calcd for $C_{12}H_{15}OS_2$ $[M+H]^+$, 239.0564. Found 239.0560.



21

***S*-((1*S*,2*S*,4*R*)-bicyclo[2.2.1]heptan-2-yl) *O*-ethyl carbonodithioate (21)**: Prepared according to General Procedure A using ketopinic acid (27.3 mg, 0.150 mmol, 1 equiv), xanthylamide **2** (87.2 mg, 0.225 mmol, 1.5 equiv) and dilauroyl peroxide (9.0 mg, 0.023 mmol, 0.15 equiv). After 4 h, additional DLP (9.0 mg, 0.023 mmol, 0.15 equiv) was added to the reaction mixture under an inert atmosphere. Alternatively prepared according to General Procedure B using ketopinic acid (18.2 mg, 0.100 mmol, 1 equiv) and xanthylamide **2** (46.5 mg, 0.120 mmol, 1.2 equiv). The crude residue was purified by flash column chromatography (5–10% EtOAc/hex) to afford **21** as a white solid (A: 25.8 mg, 67% yield; B: 15.4 mg, 60% yield):

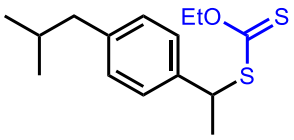
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.62 (qd, *J* = 7.1, 1.5 Hz, 2H), 2.50 (ddd, *J* = 18.3, 4.9, 3.1 Hz, 1H), 2.33 (ddd, *J* = 14.1, 9.3, 5.0 Hz, 1H), 2.24 – 2.16 (m, 2H), 2.10 (ttd, *J* = 12.2, 4.8, 3.2 Hz, 1H), 2.03 (d, *J* = 18.3 Hz, 1H), 1.54 (ddd, *J* = 12.8, 9.3, 3.7 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.07 (s, 3H), 0.98 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 211.92, 209.00, 71.45, 70.17, 49.98, 43.18, 42.75, 29.80, 27.68, 20.61, 20.07, 13.82.
HRMS (ES+) Exact mass calcd for $C_{12}H_{19}O_2S_2$ $[M+H]^+$, 259.0826. Found 259.0824.



22

***S*-(4-((1,3-dioxoisoindolin-2-yl)methyl)cyclohexyl) *O*-ethyl carbonodithioate (22):** Prepared according to General Procedure A using 4-((1,3-dioxoisoindolin-2-yl)methyl)cyclohexane-1-carboxylic acid[6] (36.3 mg, 0.126 mmol, 1 equiv), xanthylamide **2** (73.4 mg, 0.190 mmol, 1.5 equiv) and dilauroyl peroxide (7.6 mg, 0.019 mmol, 0.15 equiv). Alternatively prepared according to General Procedure B using 4-((1,3-dioxoisoindolin-2-yl)methyl)cyclohexane-1-carboxylic acid (28.7 mg, 0.100 mmol, 1 equiv) and xanthylamide **2** (48.5 mg, 0.120 mmol, 1.2 equiv). The crude residue was purified by flash column chromatography (5–10% EtOAc/hex) to afford **22** as a white solid (A: 41.1 mg, 90% yield; B: 32.1 mg, 88% yield):

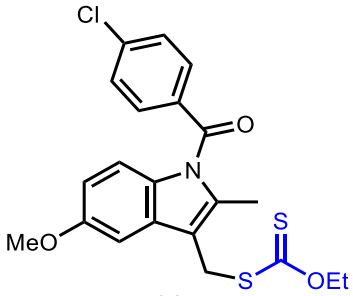
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 2H), 7.76 – 7.67 (m, 2H), 4.65 – 4.57 (m, 2H), 4.01 (p, *J* = 3.9 Hz, 0.6H), 3.59 – 3.45 (m, 2.4H), 2.19 – 2.10 (m, 0.8H), 1.99 (dq, *J* = 13.2, 4.0 Hz, 1.2H), 1.88 (dqt, *J* = 10.5, 6.9, 3.6 Hz, 0.6H), 1.84 – 1.74 (m, 2.6H), 1.62 (dq, *J* = 12.7, 3.9 Hz, 1.2H), 1.43 – 1.36 (m, 3H), 1.36 – 1.28 (m, 2.6H), 1.25 – 1.17 (m, 1.2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.38, 214.04, 168.63, 134.04, 134.01, 131.93, 131.91, 123.29, 123.27, 69.65, 69.61, 48.13, 47.53, 43.49, 43.02, 36.15, 35.83, 31.44, 30.62, 29.64, 28.68, 13.85, 13.82.
HRMS (ES+) Exact mass calcd for $C_{18}H_{21}NNaO_3S_2$ $[M+Na]^+$, 386.0861. Found 386.0860.



23

***O*-ethyl *S*-(1-(4-isobutylphenyl)ethyl) carbonodithioate (23):** Prepared according to General Procedure A using ibuprofen (20.6 mg, 0.100 mmol, 1 equiv), xanthylamide **1** (43.5 mg, 0.100 mmol, 1 equiv) and dilauroyl peroxide (4.0 mg, 0.010 mmol, 0.10 equiv). The crude residue was purified by flash column chromatography (0.1–1% EtOAc/hex) to afford **23** as a pale yellow oil (13.5 mg, 48% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.14 – 7.09 (m, 2H), 4.90 (q, *J* = 7.1 Hz, 1H), 4.64 (q, *J* = 7.1 Hz, 2H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.86 (dh, *J* = 13.6, 6.9 Hz, 1H), 1.74 (d, *J* = 7.1 Hz, 3H), 1.41 (t, *J* = 7.1 Hz, 3H), 0.92 (dd, *J* = 6.6, 1.4 Hz, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 213.76, 141.19, 138.87, 129.41, 127.31, 69.81, 49.18, 45.18, 30.33, 22.53, 22.51, 21.83, 13.87.
HRMS (APPI+) Exact mass calcd for $C_{15}H_{23}OS_2$ $[M+H]^+$, 283.1990. Found 283.1990.

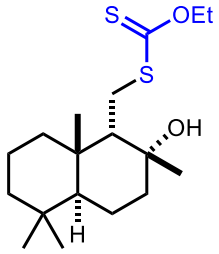


24

***S*-((1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)methyl) *O*-ethyl carbonodithioate (24):** Prepared according to General Procedure A using indomethacin (53.7 mg, 0.150 mmol, 1 equiv), xanthylamide **1** (116 mg, 0.300 mmol, 2 equiv), and dilauroyl peroxide (30 mg, 0.075

mmol, 0.5 equiv). After 4 h, additional DLP (30.0 mg, 0.075 mmol, 0.5 equiv) was added to the reaction mixture under an inert atmosphere, and the reaction vial was stirred at 80 °C for another 4 h. Alternatively prepared according to General Procedure B using indomethacin (35.8 mg, 0.100 mmol, 1 equiv) and xanthylamide **2** (48.5 mg, 0.120 mmol, 1.2 equiv). The crude residue was purified by flash column chromatography (2.5–10% EtOAc/hex) to afford **24** as a yellow amorphous solid (A: 25.0 mg, 38% yield; B: 21.1 mg, 49% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 – 7.58 (m, 2H), 7.53 – 7.41 (m, 2H), 6.98 (d, *J* = 2.5 Hz, 1H), 6.85 (d, *J* = 9.0 Hz, 1H), 6.68 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.71 (q, *J* = 7.1 Hz, 2H), 4.51 (s, 2H), 3.83 (s, 3H), 2.42 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.73, 168.31, 156.13, 139.56, 136.80, 133.72, 131.33, 130.90, 130.03, 129.27, 115.13, 112.64, 112.10, 101.33, 70.26, 55.86, 31.07, 14.00, 13.59.
HRMS (ES+) Exact mass calcd for $C_{21}H_{20}ClNaNO_3S_2$ $[M+Na]^+$, 456.0471. Found 456.0471.

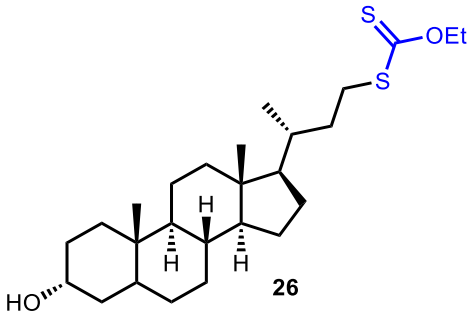


25

***O*-ethyl *S*-(((1*S*,2*R*,4*aS*,8*aS*)-2-hydroxy-2,5,5,8*a*-tetramethyldecahydronaphthalen-1-yl)methyl) carbonodithioate (25):** Prepared according to General Procedure B using 2-((1*S*,2*R*,4*aS*,8*aS*)-2-hydroxy-2,5,5,8*a*-tetramethyldecahydronaphthalen-1-yl)acetic acid[7] (53.6 mg, 0.200 mmol, 1 equiv) and xanthylamide **2** (77.4 mg, 0.200 mmol, 1 equiv) using fan cooling. The crude residue was purified by flash column chromatography (2.5–10% EtOAc/hex) to afford **25** as an off-white solid (73.5 mg, 71% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.63 (qd, *J* = 7.1, 2.5 Hz, 2H), 3.34 (dd, *J* = 13.7, 4.9 Hz, 1H), 3.19 (dd, *J* = 13.6, 5.0 Hz, 1H), 1.90 (dt, *J* = 12.6, 3.2 Hz, 1H), 1.75 – 1.63 (m, 4H), 1.57 (tt, *J* = 13.5, 3.6 Hz, 1H), 1.48 (t, *J* = 5.0 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.33 – 1.22 (m, 2H), 1.22 – 1.18 (m, 3H), 1.13 (td, *J* = 13.5, 4.2 Hz, 1H), 1.04 – 0.98 (m, 1H), 0.96 – 0.89 (m, 1H), 0.86 (s, 6H), 0.79 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 216.12, 73.45, 69.89, 61.05, 55.92, 44.13, 41.77, 40.16, 39.16, 33.47, 33.37, 32.00, 23.99, 21.59, 20.43, 18.51, 15.52, 13.96.
HRMS (ES+) Exact mass calcd for $C_{18}H_{33}O_2S_2$ $[M+H]^+$, 345.1922. Found 345.1920.

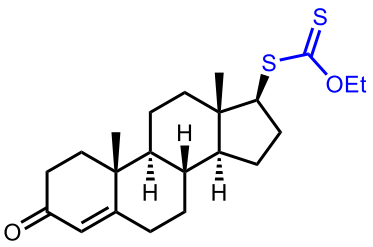
Note: Using General Procedure A promotes an undesired lactonization pathway to provide (3aR)-(+)-sclareolide.



26

***O*-ethyl *S*-((3*R*)-3-((3*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)butyl) carbonodithioate (26):** Prepared according to General Procedure A using lithocholic acid (18.8 mg, 0.050 mmol, 1 equiv), xanthylamide **2** (38.7 mg, 0.100 mmol, 2 equiv) and dilauroyl peroxide (4.0 mg, 0.010 mmol, 0.2 equiv). After 4 h, additional DLP (4.0 mg, 0.010 mmol, 0.2 equiv) was added to the reaction mixture under an inert atmosphere. The crude residue was purified by flash column chromatography (20% EtOAc/hex) to afford **26** as a white solid (18.1 mg, 80% yield):

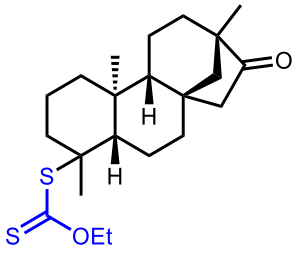
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.63 (q, *J* = 7.1 Hz, 2H), 3.61 (tt, *J* = 10.8, 4.8 Hz, 1H), 3.18 (ddd, *J* = 12.6, 10.4, 4.7 Hz, 1H), 2.97 (ddd, *J* = 13.0, 10.0, 6.5 Hz, 1H), 1.95 (dt, *J* = 12.6, 3.2 Hz, 1H), 1.87 – 1.70 (m, 5H), 1.68 – 1.62 (m, 1H), 1.55 (tt, *J* = 9.6, 4.0 Hz, 1H), 1.52 – 1.46 (m, 2H), 1.43 – 1.01 (m, 20H), 0.97 (d, zf*J* = 6.5 Hz, 3H), 0.90 (s, 3H), 0.63 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 215.35, 71.99, 69.91, 56.55, 56.06, 42.88, 42.15, 40.48, 40.21, 36.50, 35.91, 35.86, 35.42, 34.69, 34.67, 33.48, 30.61, 30.28, 27.28, 26.51, 24.33, 23.50, 20.91, 18.52, 13.98, 12.15.
HRMS (ES+) Exact mass calcd for $C_{26}H_{45}O_2S_2$ $[M+H]^+$, 453.2861. Found 453.2862.



27

***O*-ethyl *S*-((3*R*)-3-((3*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)butyl) carbonodithioate (27):** Prepared according to General Procedure A using androst-4-en-3-one-17β-carboxylic acid[8] (47.5 mg, 0.150 mmol, 1 equiv), xanthylamide **2** (87.2 mg, 0.225 mmol, 1.5 equiv), and dilauroyl peroxide (9.0 mg, 0.015 mmol, 0.15 equiv). After 4 h, additional DLP (9.0 mg, 0.023 mmol, 0.15 equiv) was added to the reaction mixture under an inert atmosphere. Alternatively prepared according to General Procedure B using androst-4-en-3-one-17β-carboxylic acid (31.6 mg, 0.100 mmol, 1 equiv), xanthylamide **2** (48.5 mg, 0.120 mmol, 1.2 equiv), The crude residue was purified by flash column chromatography (10–20% EtOAc/hex) to afford **27** as an off-white solid (A: 50.0 mg, 85% yield; B: 25.7 mg, 65% yield):

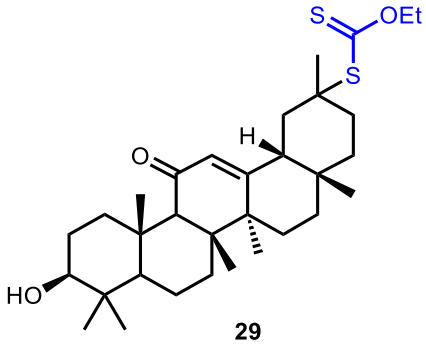
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.71 – 5.69 (m, 1H), 4.59 (q, *J* = 7.1 Hz, 2H), 3.91 (dd, *J* = 8.7, 2.3 Hz, 1H), 2.52 – 2.20 (m, 5H), 2.00 (ddd, *J* = 13.4, 5.1, 3.2 Hz, 1H), 1.89 – 1.81 (m, 1H), 1.76 (dddd, *J* = 11.8, 9.4, 6.9, 2.5 Hz, 1H), 1.72 – 1.62 (m, 3H), 1.61 – 1.46 (m, 3H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.25 (tdd, *J* = 11.9, 10.5, 7.0 Hz, 1H), 1.20 – 1.10 (m, 5H), 1.10 – 0.99 (m, 1H), 0.95 (s, 3H), 0.93 – 0.89 (m, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.75, 199.56, 171.04, 124.01, 123.97, 69.68, 58.55, 53.24, 51.03, 45.30, 38.60, 36.10, 35.71, 34.00, 33.80, 32.83, 32.14, 29.70, 24.98, 20.92, 19.32, 17.51, 13.88.
HRMS (ES+) Exact mass calcd for $C_{22}H_{33}O_2S_2$ $[M+H]^+$, 393.1922. Found 393.1920.



28

***O*-ethyl *S*-((2*S*,3*S*)-2-ethyl-1,3-dimethyl-3-((1*R*,2*R*,5*S*)-5-methyl-6-oxobicyclo[3.2.1]octan-2-yl)cyclohexyl) carbonodithioate (28):** Prepared according to General Procedure A using isosteviol[9] (15.9 mg, 0.050 mmol, 1 equiv), xanthylamide **2** (32.5 mg, 0.075 mmol, 1.5 equiv) and dilauroyl peroxide (3.0 mg, 7.5 µmol, 0.15 equiv). Alternatively prepared according to General Procedure B using isosteviol (15.9 mg, 0.100 mmol, 1 equiv) and xanthylamide **2** (46.5 mg, 0.120 mmol, 1.2 equiv). The crude residue was purified by flash column chromatography (2.5–5% EtOAc/hex) to afford **28** as a white solid (A: 16.3 mg, 82% yield; B: 23.5 mg, 60% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.71 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.65 (dq, *J* = 10.8, 7.1 Hz, 1H), 2.65 (dd, *J* = 18.6, 3.8 Hz, 1H), 2.29 – 2.23 (m, 1H), 2.19 (td, *J* = 13.1, 4.8 Hz, 1H), 1.94 – 1.90 (m, 1H), 1.87 (dd, *J* = 12.0, 1.8 Hz, 1H), 1.79 (d, *J* = 18.6 Hz, 1H), 1.68 – 1.59 (m, 7H), 1.59 – 1.52 (m, 3H), 1.48 (t, *J* = 7.1 Hz, 3H), 1.45 – 1.39 (m, 2H), 1.38 (s, 3H), 1.28 – 1.17 (m, 2H), 0.97 (s, 3H), 0.90 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.41, 69.46, 63.26, 55.76, 54.44, 52.19, 48.86, 48.82, 40.87, 39.69, 39.58, 39.10, 38.42, 37.22, 29.84, 21.60, 20.87, 20.09, 19.95, 18.93, 15.44, 14.03.
HRMS (ES+) Exact mass calcd for $C_{22}H_{34}NaO_2S_2$ $[M+Na]^+$, 417.1898. Found 417.1897.



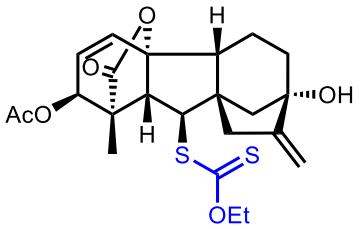
29

***O*-ethyl *S*-((4a*S*,6a*S*,6b*R*,10*S*,12a*S*,14b*R*)-10-hydroxy-2,4a,6a,6b,9,9,12a-heptamethyl-13-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicen-2-yl) carbonodithioate (29):** Prepared according to General Procedure A using 18β-glycyrrhetinic acid (70.6 mg, 0.150 mmol, 1 equiv), xanthylamide **2** (87.2 mg, 0.225 mmol, 1.5 equiv) and dilauroyl peroxide (9.0 mg, 0.023 mmol, 0.15 equiv) in DCE. The crude residue was purified by flash column chromatography (10–30% EtOAc/hex) to afford **29** as a white solid (76.5 mg, 93% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.58 – 5.50 (m, 1H), 4.64 (dq, *J* = 7.8, 4.5 Hz, 2H), 3.19 (dtd, *J* = 12.4, 7.6, 6.5, 3.6 Hz, 1H), 2.73 (ddt, *J* = 14.0, 9.9, 3.9 Hz, 1H), 2.46 – 2.23 (m, 2H), 2.15 – 2.00 (m, 1H), 2.00 – 1.89 (m, 2H), 1.86 – 1.73 (m, 2H), 1.73 – 1.53 (m, 7H), 1.53 – 1.46 (m, 2H), 1.46 – 1.35 (m, 6H), 1.35 – 1.28 (m, 4H), 1.25 – 1.12 (m, 1H), 1.09 (d, *J* = 3.4 Hz, 6H), 1.02 – 0.92 (m, 5H), 0.85 (dd, *J* = 10.0, 3.0 Hz, 3H), 0.80 – 0.74 (m, 3H), 0.66 (d, *J* = 11.3 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 213.50, 213.22, 200.18, 200.05, 168.74, 168.37, 128.71, 128.59, 78.73, 78.69, 69.46, 69.40, 61.83, 61.82, 56.79, 55.32, 54.92, 54.87, 47.40, 47.15, 45.44, 45.38,

43.32, 43.30, 42.70, 41.62, 39.14, 39.13, 39.10, 37.10, 37.06, 36.28, 36.00, 33.20, 32.73, 32.71, 32.26, 32.11, 31.55, 30.18, 28.26, 28.16, 28.10, 27.27, 27.24, 26.58, 26.45, 26.32, 26.27, 23.52, 23.47, 22.21, 18.68, 17.47, 16.40, 15.61, 13.90, 13.88.
HRMS (ES+) Exact mass calcd for $C_{32}H_{51}O_3S_2$ $[M+H]^+$, 547.3280. Found 547.3282.

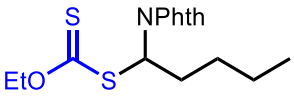
A gram-scale reaction was run using the following procedure: A 100-mL single-necked, round-bottomed flask was equipped with a 2-cm, Teflon-coated magnetic stir bar. The flask was charged sequentially with 18β-glycyrrhetinic acid (1.00 g, 2.12 mmol, 1 equiv), xanthylamide **2** (0.988 g, 2.54 mmol, 1.2 equiv), and dilauroyl peroxide (102 mg, 0.254 mmol, 0.12 equiv). A rubber septum was attached to the flask, and DCE (25 mL) was added by syringe. The heterogenous solution was degassed with nitrogen for 1 h. The septum was then removed and replaced with a reflux condenser, and was heated under reflux. The reaction was monitored by TLC, adding additional dilauroyl peroxide (102 mg, 0.254 mmol, 0.12 equiv) every 3 h until full xanthylamide **2** conversion was observed (3 additional additions were made).The resulting yellow solution was concentrated, and the crude material was dry loaded onto silica and purified by flash column chromatography to yield **29** as a white solid (0.916 g, 79% yield).



30

(1*S*,2*S*,4a*R*,4b*R*,7*S*,9a*S*,10*S*,10a*R*)-10-((ethoxycarbonothioyl)thio)-7-hydroxy-1-methyl-8-methylene-13-oxo-1,2,4b,5,6,7,8,9,10,10a-decahydro-4a,1-(epoxymethano)-7,9a-methanobenzo[*a*]azulen-2-yl acetate (30): Prepared according to General Procedure A using gibberellin A_3-3-acetate[10] (58.3 mg, 0.150 mmol, 1 equiv), xanthylamide **2** (87.2 mg, 0.225 mmol, 1.5 equiv) and dilauroyl peroxide (9.0 mg, 0.023 mmol, 0.15 equiv). After 4 h, additional DLP (9.0 mg, 0.023 mmol, 0.15 equiv) was added to the reaction mixture under an inert atmosphere. The crude residue was purified by flash column chromatography (15–35% EtOAc/hex) to afford **30** as an amorphous pale-yellow solid (50.3 mg, 72% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.37 (d, *J* = 9.3 Hz, 1H), 5.84 (dd, *J* = 9.3, 3.8 Hz, 1H), 5.33 (d, *J* = 3.7 Hz, 1H), 5.24 (t, *J* = 2.3 Hz, 1H), 4.97 (d, *J* = 2.6 Hz, 1H), 4.64 (q, *J* = 7.1 Hz, 2H), 4.23 (d, *J* = 11.1 Hz, 1H), 2.86 – 2.65 (m, 2H), 2.15 – 2.10 (m, 1H), 2.09 (s, 3H), 2.08 – 1.87 (m, 4H), 1.82 – 1.69 (m, 4H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.27 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 212.13, 176.97, 169.99, 156.74, 134.36, 129.25, 107.35, 89.04, 78.46, 70.98, 70.88, 55.03, 53.35, 52.48, 51.92, 50.21, 45.12, 44.09, 38.14, 20.93, 17.33, 14.36, 13.92.
HRMS (ES+) Exact mass calcd for $C_{23}H_{29}O_6S_2$ $[M+H]^+$, 465.1406. Found 465.1407.

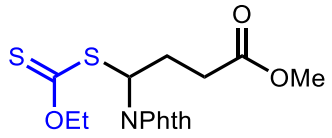


31

***S*-(1-(1,3-dioxoisoindolin-2-yl)pentyl) *O*-ethyl carbonodithioate (31):** Prepared according to General Procedure A using 2-(1,3-dioxoisoindolin-2-yl)hexanoic acid[11] (13.1 mg, 50.0 μmol, 1 equiv), xanthylamide **2** (21.7 mg, 50.0 μmol, 1 equiv) and dilauroyl peroxide (2.0 mg, 5.0 μmol,

0.1 equiv). The crude residue was purified by flash column chromatography (2.5–10% EtOAc/hex) to afford **31** as a white solid (12.9 mg, 77% yield):

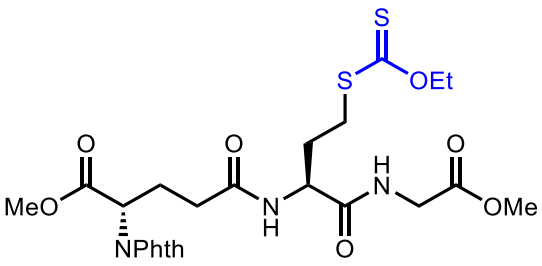
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.23 (dd, *J* = 9.5, 6.7 Hz, 1H), 4.62 (q, *J* = 7.1 Hz, 2H), 2.30 – 2.22 (m, 1H), 2.11 (dddd, *J* = 13.9, 9.7, 6.7, 5.3 Hz, 1H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.37 – 1.26 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 211.50, 167.02, 134.45, 131.70, 123.70, 70.47, 57.79, 32.91, 28.77, 22.05, 13.99, 13.88.
HRMS (ES+) Exact mass calcd for $C_{16}H_{19}NaNO_3S_2$ $[M+Na]^+$, 360.0704. Found 360.0703.



32

Methyl 4-(1,3-dioxoisoindolin-2-yl)-4-((ethoxycarbonothioyl)thio)butanoate (32): Prepared according to General Procedure A using (*S*)-2-(1,3-dioxoisoindolin-2-yl)-5-methoxy-5-oxopentanoic acid[12] (14.6 mg, 50.0 µmol, 1 equiv), xanthylamide **2** (38.7 mg, 100 µmol, 2 equiv) and dilauroyl peroxide (4.0 mg, 10 µmol, 0.2 equiv). The crude residue was purified by flash column chromatography (5–10% EtOAc/hex) to afford **32** as a white solid (13.2 mg, 72% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.32 (dd, *J* = 8.8, 7.1 Hz, 1H), 4.62 (q, *J* = 7.1 Hz, 2H), 3.63 (s, 3H), 2.60 – 2.39 (m, 4H), 1.40 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 210.87, 172.34, 166.86, 134.58, 131.59, 123.80, 70.73, 57.02, 52.04, 31.13, 28.69, 13.85.
HRMS (ES+) Exact mass calcd for $C_{16}H_{17}NNaO_5S_2$ $[M+Na]^+$, 390.0446. Found 390.0446.



33

Methyl (*S*)-5-(((*S*)-3,6-dioxo-11-thioxo-2,12-dioxa-10-thia-5-azatetradecan-7-yl)amino)-2-(1,3-dioxoisoindolin-2-yl)-5-oxopentanoate (33): Prepared according to General Procedure A using tripeptide **S3** (49.2 mg, 0.100 mmol, 1 equiv), xanthylamide **2** (77.4 mg, 0.200 mmol, 2 equiv) and dilauroyl peroxide (8.0 mg, 20 µmol, 0.2 equiv) in DCE. After 4 h, additional DLP (8.0 mg, 20 µmol, 0.2 equiv) was added to the reaction mixture under an inert atmosphere, and the reaction vial was stirred again at 80 °C. After 4 h, the vial was cooled to room temperature. The mixture was diluted with CH_2Cl_2 (20 mL), and the organic layer was washed with sat. $NaHCO_3$ (20 mL). The aqueous layer was further extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layer was concentrated to give a crude residue that was purified by flash column chromatography (30–60% EtOAc/hex) to afford **33** as a white solid (23.4 mg, 41% yield).

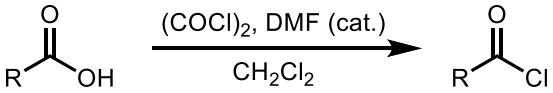
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.01 (t, *J* = 5.6 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 1H), 4.91 (dd, *J* = 10.1, 4.9 Hz, 1H), 4.59 (tt, *J* = 12.6, 6.8

Hz, 3H), 4.01 (d, *J* = 5.5 Hz, 2H), 3.73 (s, 3H), 3.72 (s, 3H), 3.24 – 3.07 (m, 2H), 2.66 (dtd, *J* = 14.7, 7.7, 4.9 Hz, 1H), 2.44 (ddt, *J* = 14.0, 10.1, 6.6 Hz, 1H), 2.37 (dt, *J* = 15.5, 6.6 Hz, 1H), 2.33 – 2.20 (m, 2H), 2.04 (dtd, *J* = 14.2, 8.6, 5.7 Hz, 1H), 1.40 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.94, 171.87, 171.18, 170.04, 169.41, 167.74, 134.44, 131.80, 123.79, 70.32, 53.00, 52.52, 52.26, 51.20, 41.31, 32.58, 31.76, 31.42, 24.78, 13.92.
HRMS (ES+) Exact mass calcd for $C_{24}H_{30}N_3O_9S_2$ $[M+H]^+$, 568.1427. Found 568.1424.

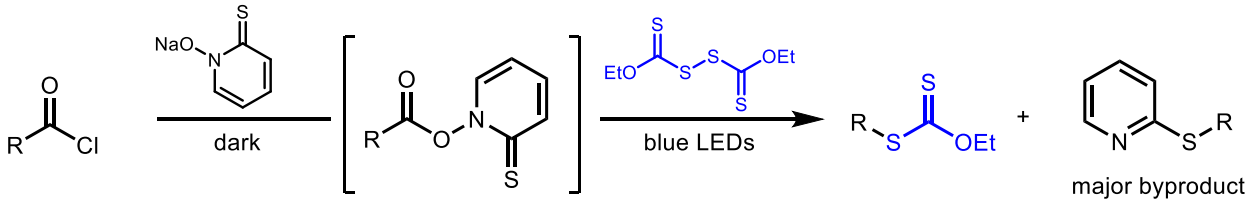
The basic aqueous layer was acidified using 3M HCl until pH = 2 and extracted with CH_2Cl_2 (20 mL x 3). The combined organic layer was washed with brine (30 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated to recover the starting tripeptide **S3** (23.2 mg, 47% recovery).

Comparison to a One-Pot Barton Approach

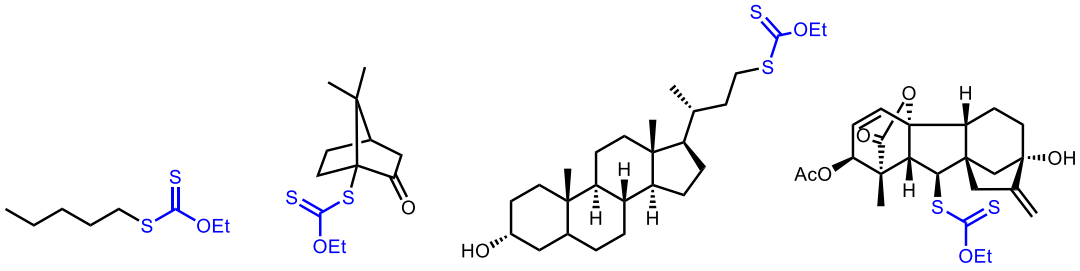
General Procedure C: *One-Pot Barton Decarboxylative Xanthylation*



The acid chloride was prepared as following: to a solution of the carboxylic acid (1.0 equiv) in CH_2Cl_2 (0.2 M) at 0 °C was added oxalyl chloride (1.2 equiv) dropwise followed by 1 to 2 drops of DMF. The resulting solution was stirred for 2-4 h and then concentrated to remove excess oxalyl chloride to give the acid chloride, which was used without further purification.



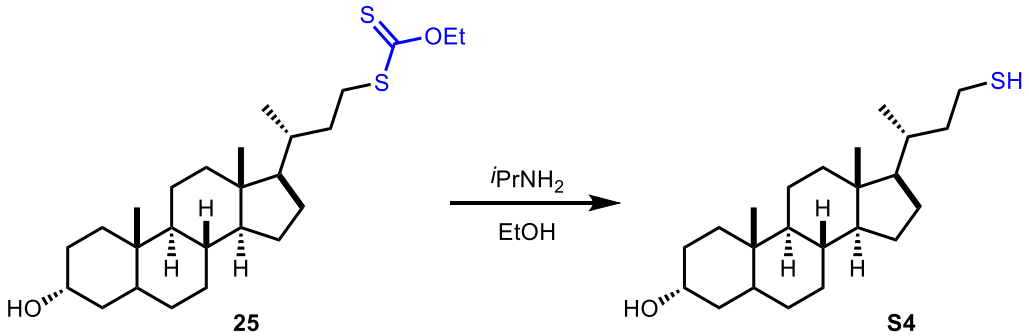
A solution of the acid chloride (0.10 mmol, 1 equiv) in benzene (0.1 M) was added dropwise to a suspension of *N*-hydroxypridin-2-thione sodium salt (17.9 mg, 1.2 mmol, 1.2 equiv) and xanthate dimer (97.0 mg, 0.200 mmol, 4 equiv). The solution was allowed to stir 2 h in the dark, then stirred an additional 2 h under blue light irradiation. The resulting mixture was filtered through a pad of celite and analyzed using ^{1}H & ^{13}C NMR.



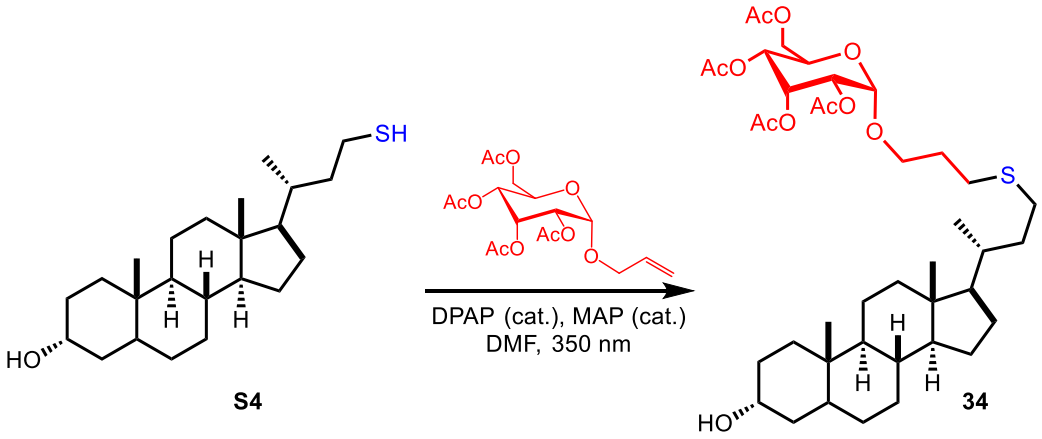
Barton approach	63% NMR yield	55% NMR yield	<5% NMR yield	<5% NMR yield
Our approach	70% GC yield	67% yield	77% yield	72% yield

Figure S2: Results for a handful of substrates using the Barton method to achieve a decarboxylative xanthylation (General Procedure C).

Further Derivatization



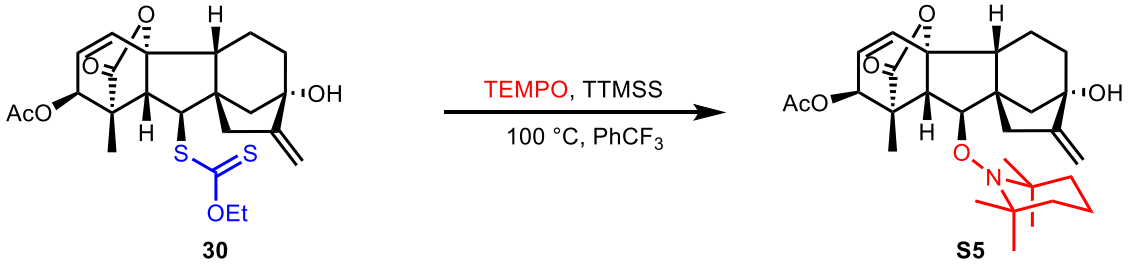
(3*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((*R*)-4-mercaptobutan-2-yl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-3-ol (S4): To a solution of xanthate **25** (29.7 mg, 65.0 µmol, 1 equiv) in EtOH (1 mL) was added isopropylamine (10.6 uL, 0.130 mmol, 2 equiv) and was then stirred for 4 h. The reaction mixture was concentrated *in vacuo*. Thiol **S4** was isolated by flash column chromatography as a yellow amorphous solid (21.5 mg, 90% yield) and used directly in the next step:



(2*R*,3*R*,4*R*,5*R*,6*S*)-2-(acetoxymethyl)-6-(2-(((3*R*)-3-((3*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)butyl)thio)ethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (34): In a vial in the glovebox, thiol **S3** (21.5 mg, 59.0 µmol, 1 equiv), allylglycoside (34.3 mg, 88.4 µmol, 1.5 equiv), 2,2-dimethoxy-2- phenylacetophenone (1.5 mg, 5.9 µmol, 0.1 equiv), and 4'-methoxyacetophenone (0.9 mg, 5.9 µmol) were dissolved in DMF (0.10 mL). The vial was sealed with a teflon-lined screw cap, sealed with Teflon tape, and placed in a UV-A box and irradiated for 14 h. The crude reaction mixture was diluted with EtOAc (2 mL), washed with H_2O (5 x 2 mL), brine (2 x 2 mL), dried over $MgSO_4$, and concentrated in vacuo. The yellow residue was purified by flash column chromatography on silica (30% EtOAc in hexanes) to afford thiol-ene adduct **34** as a white solid (26.6 mg, 60% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.46 (dd, *J* = 10.2, 9.4 Hz, 1H), 5.09 – 5.00 (m, 2H), 4.86 (dd, *J* = 10.2, 3.7 Hz, 1H), 4.26 (dd, *J* = 12.4, 4.4 Hz, 1H), 4.09 (dd, *J* = 12.4, 2.4 Hz, 1H), 4.02 (ddd, *J* = 10.3, 4.4, 2.3 Hz, 1H), 3.81 (dt, *J* = 9.9, 6.1 Hz, 1H), 3.62 (tt, *J* = 11.1, 4.6 Hz, 1H), 3.51 (dt, *J* = 9.9, 6.1 Hz, 1H), 2.60 (t, *J* = 7.0 Hz, 2H), 2.57 – 2.51 (m, 1H), 2.40 (ddd, *J* = 12.3, 10.0, 6.6 Hz, 1H), 2.10 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.96 (dd, *J* = 9.2, 6.1 Hz, 1H), 1.91 – 1.71 (m, 6H), 1.66 (ddt, *J* = 16.9, 10.3, 3.0 Hz, 3H), 1.56 (ddt, *J* = 7.9, 4.9, 3.0 Hz, 1H), 1.53 – 1.45 (m, 2H), 1.39 (tt, *J* = 10.0, 4.1 Hz, 5H), 1.34 – 1.27 (m, 2H), 1.24 (tdd, *J* = 11.5, 6.4, 4.5 Hz,

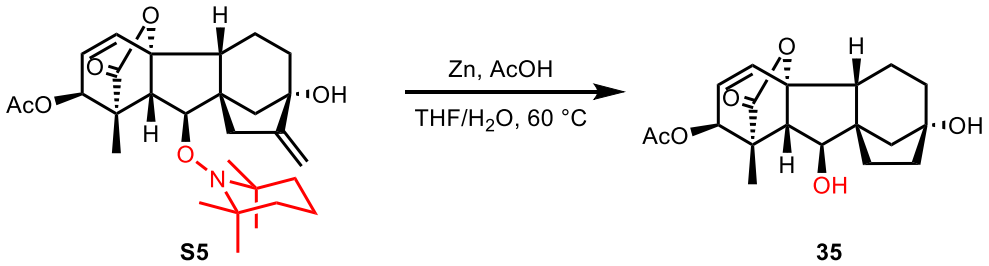
3H), 1.16 – 1.00 (m, 5H), 0.97 (dd, *J* = 14.2, 3.4 Hz, 1H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.91 (s, 3H), 0.64 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 170.85, 170.31, 170.30, 169.77, 95.88, 71.98, 70.93, 70.31, 68.62, 67.34, 66.93, 61.98, 56.60, 56.14, 42.89, 42.18, 40.52, 40.27, 36.54, 35.94, 35.90, 35.59, 35.44, 34.69, 30.64, 29.30, 29.08, 28.59, 28.46, 27.30, 26.54, 24.34, 23.50, 20.93, 20.92, 20.87, 20.79, 18.57, 12.17.
HRMS (ES+) Exact mass calcd for $C_{40}H_{64}NaO_{11}S$ $[M+Na]^+$, 775.4067. Found 775.4071.



30 **S5**

(1*S*,2*S*,4a*R*,4b*R*,7*S*,9a*S*,10*S*,10a*S*)-7-hydroxy-1-methyl-8-methylene-13-oxo-10-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-1,2,4b,5,6,7,8,9,10,10a-decahydro-4a,1-(epoxymethano)-7,9a-methanobenzo[a]azulen-2-yl acetate (S5): To a solution of xanthate **30** (44.1 mg, 94.9 µmol, 1 equiv) in PhCl (0.95 mL) stirring at 100 °C, TEMPO (89.1 mg, 0.569 mmol, 6 equiv) and tris(trimethylsilyl)silane (87.9 µL, 0.285 mmol, 3 equiv) were added in three portions over 48 h. The reaction mixture was stirred for an additional 24 h, then concentrated. The crude residue was resuspended in EtOAc (10 mL) and washed with saturated $Na_2S_2O_3$ (10 mL). The aqueous layer was further extracted with EtOAc (10 mL x 2). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated. TEMPO-trapped product **S5** was obtained after purification by column chromatography (40% EtOAc/hex) to give an amorphous yellow solid (29.9 mg, 63% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.41 (d, *J* = 9.2 Hz, 1H), 5.86 (dd, *J* = 9.2, 3.8 Hz, 1H), 5.36 (d, *J* = 3.8 Hz, 1H), 5.25 (dd, *J* = 3.3, 1.7 Hz, 1H), 5.06 (d, *J* = 2.1 Hz, 1H), 4.27 (d, *J* = 6.5 Hz, 1H), 3.27 (d, *J* = 6.5 Hz, 1H), 3.08 (dt, *J* = 16.6, 3.0 Hz, 1H), 2.27 (ddt, *J* = 16.5, 3.2, 1.7 Hz, 1H), 2.10 (s, 3H), 2.07 – 1.92 (m, 4H), 1.81 – 1.65 (m, 4H), 1.62 (dt, *J* = 13.2, 3.8 Hz, 1H), 1.58 (s, 3H), 1.52 – 1.34 (m, 5H), 1.27 (s, 2H), 1.23 (s, 3H), 1.20 (d, *J* = 1.7 Hz, 6H), 1.10 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 178.09, 169.97, 156.44, 134.88, 129.03, 106.59, 90.51, 85.05, 78.24, 72.17, 61.87, 59.28, 58.07, 52.66, 52.03, 47.87, 46.32, 41.26, 40.30, 40.23, 38.44, 34.87, 34.17, 21.65, 21.28, 20.88, 17.50, 17.42, 17.38.
HRMS (ES+) Exact mass calcd for $C_{29}H_{43}NNaO_6$ $[M+Na]^+$, 524.2988. Found 524.2993.



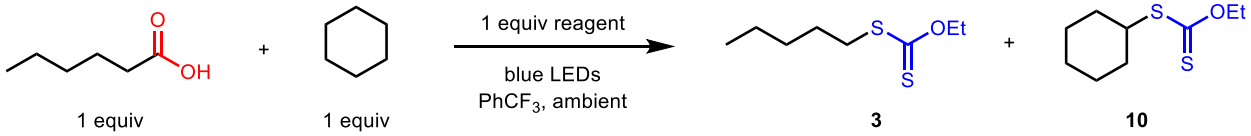
S5 **35**

(1*S*,2*S*,4a*R*,4b*R*,7*S*,9a*S*,10*S*,10a*S*)-7,10-dihydroxy-1-methyl-8-methylene-13-oxo-1,2,4b,5,6,7,8,9,10,10a-decahydro-4a,1-(epoxymethano)-7,9a-methanobenzo[a]azulen-2-yl

acetate (35): An oven-dried 1 dram vial equipped with a stir bar was charged with zinc nanopowder (31.4 mg, 480 μmol, 20 equiv) and a solution of alkoxyamine **S5** (12 mg, 24 μmol, 1 equiv) dissolved in a mixture of AcOH/THF/H_2O (3:1:1, 2 mL total). The reaction mixture was stirred at 60 °C under an Ar balloon. Additional zinc (20 equiv) was added every 3 h until full starting material conversion was observed by TLC (5 additions made). At 0 °C, a solution of NaOH (5 mL, 2.5 M) was added slowly to the reaction mixture and subsequently extracted with CH_2Cl_2 (10 mL x 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified by column chromatography (50% EtOAc/hex) to give **35** (6.8 mg, 79% yield) as a white solid:

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.36 (d, *J* = 9.2 Hz, 1H), 5.86 (dd, *J* = 9.3, 3.8 Hz, 1H), 5.35 (d, *J* = 3.9 Hz, 1H), 5.29 (dd, *J* = 3.2, 1.8 Hz, 1H), 5.00 (d, *J* = 2.1 Hz, 1H), 4.02 (d, *J* = 8.8 Hz, 1H), 2.75 – 2.66 (m, 2H), 2.15 – 2.05 (m, 4H), 2.04 –1.53 (m, 9H), 1.37 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 177.56, 170.12, 157.36, 134.59, 129.20, 107.34, 88.33, 78.57, 76.43, 70.64, 57.84, 52.01, 51.05, 49.93, 43.58, 40.51, 38.41, 21.01, 17.13, 14.51.
HRMS (ES+) Exact mass calcd for $C_{20}H_{25}O_6$ $[M+H]^+$, 361.1651. Found 361.1650.

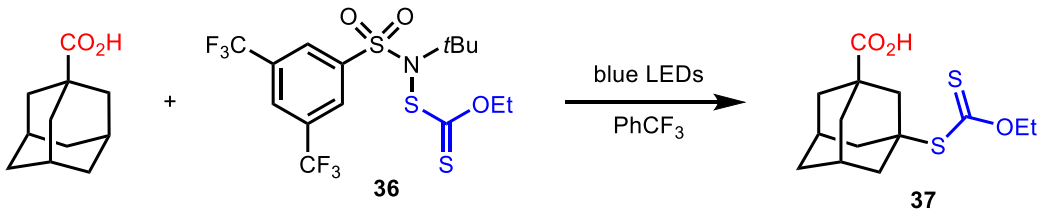
Selectivity Studies



A 1 dram vial was charged with hexanoic acid (1 equiv), cyclohexane (1 equiv), and reagent **1**, **2**, or **36** (1 equiv), fitted with a PTFE lined screw cap, and taken into the glovebox. The contents were dissolved in $PhCF_3$ (0.5 M), and the resulting solution was sealed with Teflon tape and removed from the glovebox. The vial was placed in a 3D-printed holder (see picture below). The holder was suspended above an Ecoxotic PAR38 23 W blue LED such that the bottom of each vial was directly aligned with and 2 cm above one of the five LEDs, and the apparatus was covered with aluminum foil. The reaction was irradiated until completion and then concentrated *in vacuo*. Product distribution was analyzed by ^{1}H NMR, with selectivity calculated by correcting for the number of reactive H's available (i.e. 1 H for hexanoic acid and 12 H's for cyclohexane).

Reagent	Product distribution (**3**:**10**)	Selectivity (**3**:**10**)
1	1:1.2	10:1
2	2.0:1	24:1
36	<1:25	<1:50

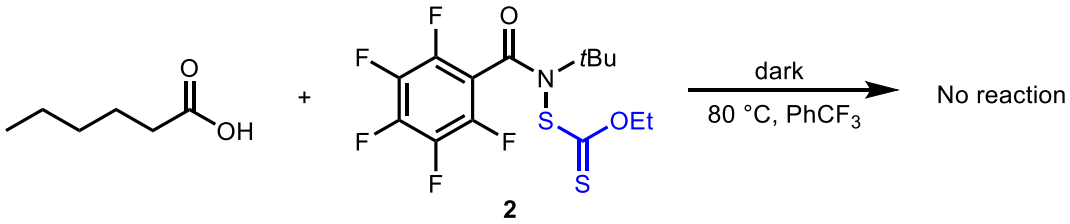
Figure S3. Light setup for small volume reactions.



(1*r*,3*s*,5*R*,7*S*)-3-((ethoxycarbonothioyl)thio)adamantane-1-carboxylic acid (37): A 1 dram vial was charged with 1-adamantanecarboxylic acid (18.0 mg, 0.100 mmol, 1 equiv) and xanthylsulfonamide **36** (46.9 mg, 0.100 mmol, 1 equiv), fitted with a PTFE lined screw cap, and taken into the glovebox. The contents were dissolved in $PhCF_3$ (0.10 mL), and the resulting solution was sealed with Teflon tape and removed from the glovebox. The vial was placed in a 3D-printed holder (see Figure S3). The holder was suspended above an Ecoxotic PAR38 23 W blue LED such that the bottom of each vial was directly aligned with and 1 cm above one of the five LEDs, and the apparatus was covered with aluminum foil. The reaction was irradiated until completion, and then concentrated *in vacuo*. The crude residue was purified by flash column chromatography (30/70/0.1 ethyl acetate/hexanes/acetic acid) to afford the functionalized product (20.0 mg, 67% yield) as a white solid:

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.66 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 2H), 2.24 – 2.19 (m, 2H), 2.14 – 2.08 (m, 2H), 2.07 – 2.01 (m, 2H), 1.93 – 1.87 (m, 4H), 1.75 – 1.65 (m, 2H), 1.48 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 213.39, 182.63, 69.61, 53.52, 42.57, 42.47, 40.87, 38.66, 37.54, 36.50, 35.22, 29.32, 27.90, 13.86.
HRMS (ES+) Exact mass calcd for $C_{14}H_{20}NaO_3S_2$ $[M+Na]^+$, 323.0752. Found 323.0751.

Mechanistic Experiments



Control: A 1 dram vial equipped with a stir bar was charged with xanthylamide **2** (38.7 mg, 0.100 mmol, 1 equiv), fitted with a PTFE lined screw cap, and taken into the glovebox. The content was dissolved in $PhCF_3$ (1.0 mL), and the resulting solution was sealed with Teflon tape and removed from the glovebox. Hexanoic acid (12.5 µL, 0.100 mmol, 1 equiv) was added through the septum using a Hamilton syringe. The vial was placed on a block plate at 80 °C, loosely covered in foil, and stirred for 15 h. The reaction was concentrated *in vacuo*, and the crude residue was dissolved in chloroform-*d* for NMR analysis.

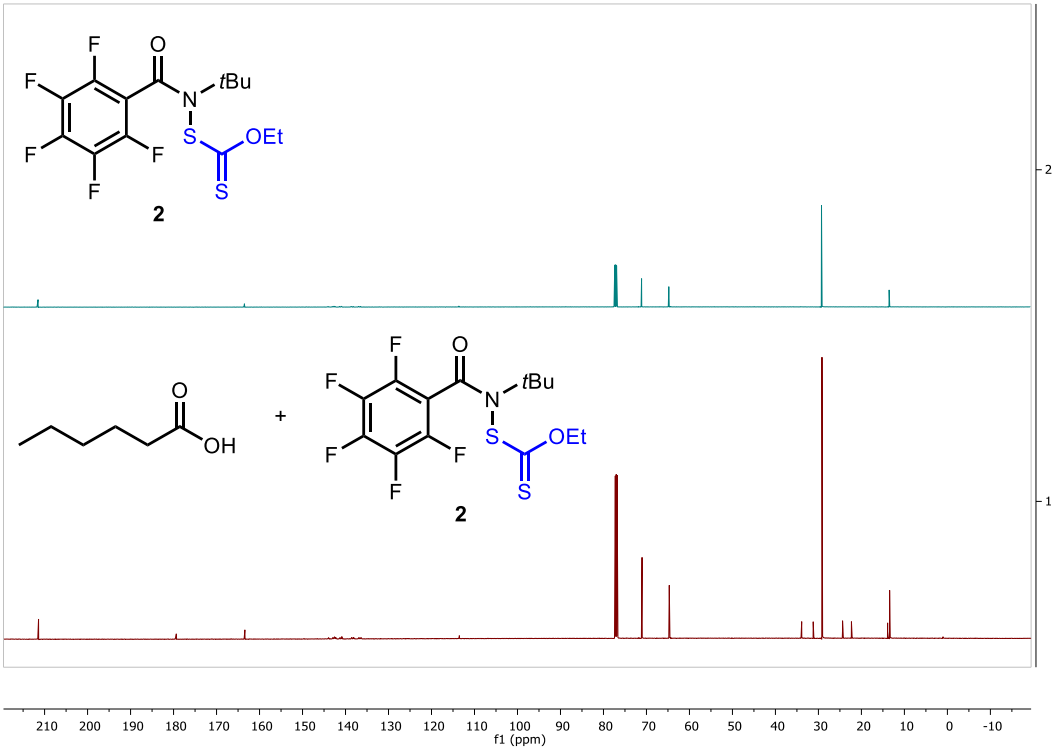
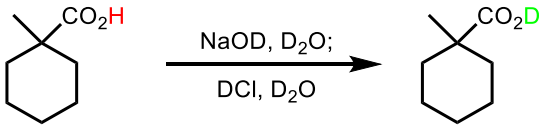
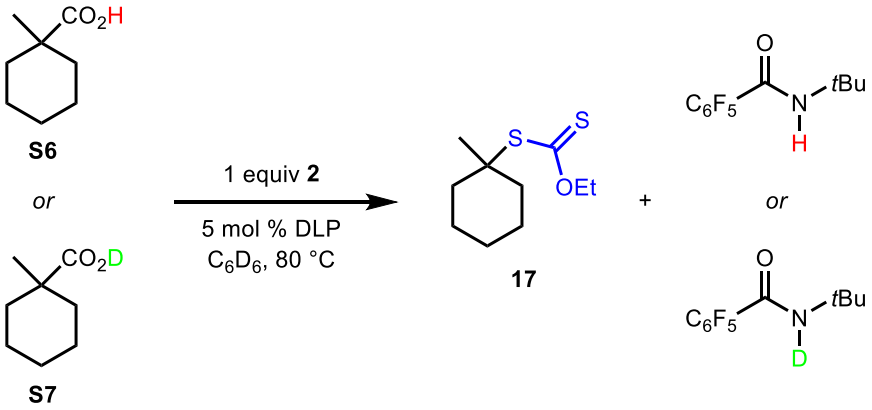


Figure S4: A stacked ^{13}C NMR (151 Hz, $CDCl_3$) plot of xanthylamide **2** (top) and the control experiment (bottom) indicating no reaction has taken place.



S6 **S7**

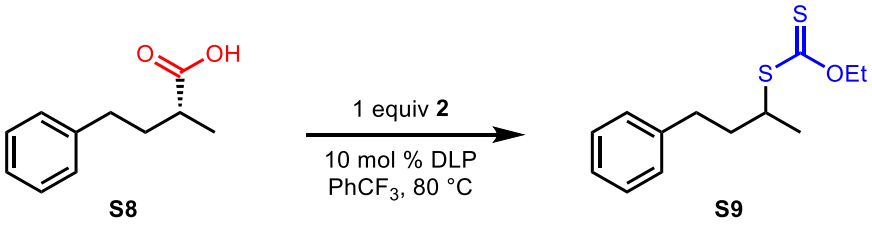
1-Methylcyclohexane-1-carboxylic acid-*d* (S7). Adapted from an analogous literature procedure.[13] An oven-dried 50 mL round-bottom flask was charged with 1-methylcyclohexane-1-carboxylic acid (**S5**) (0.43 g, 3.0 mmol, 1 equiv) and then sealed with septum and Teflon tape. Under positive nitrogen pressure, 20 mL D_2O and 3.0 g of a 30 wt. % in D_2O was added through the septum. After 30 minutes of stirring, concentrated DCl was added through the septum until the solution reached a pH of 1. The white solid that precipitated was filtered, washed with D_2O, dried under vacuum, and stored in a desiccator until use. Deuterium incorporation was confirmed by IR via the lack of an –OH stretch and by ^{1}H NMR via the reduction of the intensity of the carboxylic acid proton. A deuterium incorporation of 80% can be estimated comparing the ^{1}H NMR of the proteo and deutero acid. NMR samples were prepared using dry $CDCl_3$ in the glovebox and sealed with a Teflon coated cap.



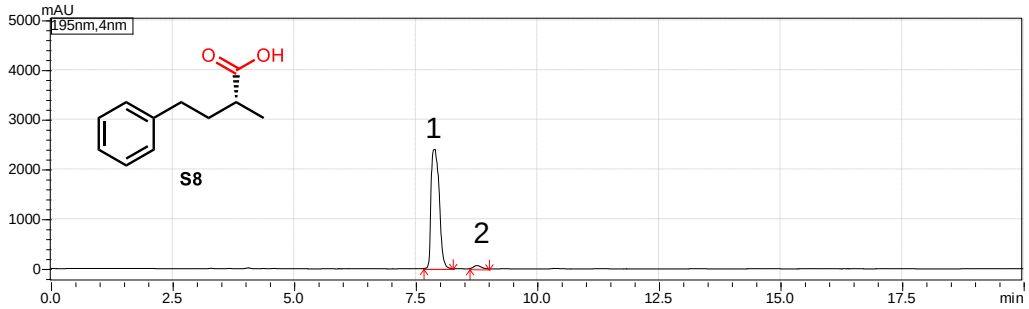
Determination of kinetic isotope effect (KIE) by initial rates: Stock solutions were prepared in oven-dried 1 dram vials charged with either **S6** (35.6 mg, 0.25 mmol, 1 equiv) or **S7** (35.8 mg, 0.25 mmol, 1 equiv), xanthylamide **2** (96.8 mg, 0.25 mmol, 1 equiv), and dilauroyl peroxide (5.0 mg, 12.5 µmol, 0.05 equiv). The contents were fully dissolved in benzene-d_6 (2.5 mL) and distributed evenly in four additional oven-dried 1 dram vials equipped with stir bars (0.5 mL each). The vials were fitted with a PTFE lined screw cap, sealed with Teflon tape, removed from the glovebox, and placed on a block plate at 80 °C. Reactions were stopped by immediately cooling the vials in an ice bath with simultaneous sparging with an O_2 balloon for 1 min. Initial rates were determined by calculating the instantaneous rate of the first five minutes of each reaction based from the conversion of **2** by ^{19}F NMR.

Table S1. KIE determination from initial rates

	Initial rate (M s^{-1})
k_H	9.36×10^{-6}
k_D	1.87×10^{-6}
k_H/k_D	5.4

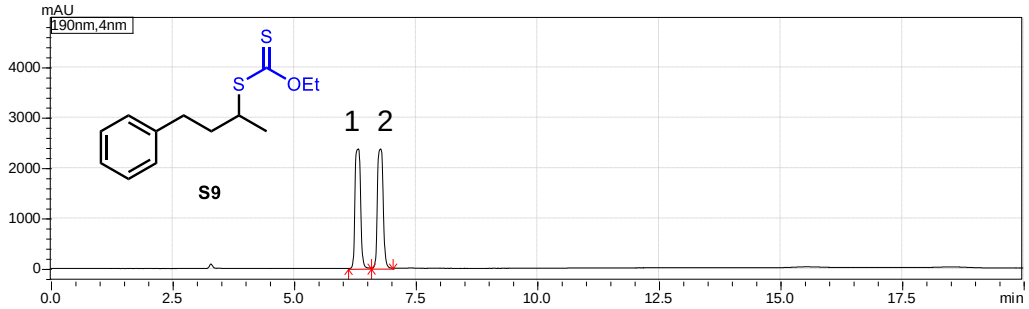


***O*-ethyl *S*-(4-phenylbutan-2-yl) carbonodithioate (S9):** Prepared according to General Procedure A using (*R*)-2-methyl-4-phenylbutanoic acid[14] (**S8**) (17.8 mg, 0.100 mmol, 1 equiv), xanthylamide **2** (38.7 mg, 0.100 mmol, 1 equiv) and dilauroyl peroxide (4.0 mg, 10 µmol, 0.1 equiv). The crude residue was purified by flash column chromatography (1–2.5% EtOAc/hex) to afford **S9** as a pale yellow oil (18.5 mg, 72% yield). Spectral data were in accordance with literature values.[1]



Peak #	Area (%)
1	97.6
2	2.4

Figure S5: HPLC trace of starting enantioriched carboxylic acid **S8**



Peak #	Area (%)
1	49.3
2	50.7

Figure S6: HPLC trace of racemate product xanthate **S9**

Computational Data

Methods. All calculations were carried out using the Gaussian16 program package (revision A.03) through the Longleaf cluster at the University of North Carolina at Chapel Hill.[15] In our investigation, all the stationary points have been initially optimized having recourse to density functional theory (DFT) by adopting the ωB97XD functional with an unrestricted (U) formalism when systems containing an unpaired number of electrons were considered, and the def2TZVP basis set in the gas phase.

To confirm the nature of stationary points, vibrational frequencies have been calculated for the optimized structures at the same level of theory as geometry optimizations, and it was verified that local minima had only real frequencies, while transition states (TS) were identified by the presence of a single imaginary frequency corresponding to the expected motion along the reaction coordinate.

The simulation has been focused on analyzing the feasibility of Hydrogen Atom Transfer from the COO–H bond in propanoic acid promoted by pentafluorophenyl-substituted amidyl radical **2'** (from reagent **2**) and the 3,5-bis(trifluoromethyl)phenyl-substituted sulfonamidyl radical **36'** (from reagent **36**) to give the carboxyl radical of propanoic acid and the corresponding amide/sulfonamide. For propanoic acid, the two reagents, the corresponding intermediates (carboxyl, amidyl and sulfonamidyl radicals) and the considered reacting situations, a systematic investigation on all of the possible conformations has been carried out. However, only the most stable conformation (in terms of Gibbs free energy value) has been reported and considered for further work, except where otherwise noted.

The solvent effect was included by single-point calculations on the optimized geometries obtained in the gas phase at the (U)ωB97XD/def2TZVP level of theory in dichloromethane bulk, by maintaining the default solvent options. The SMD model has been used, since this is the recommended choice for determining solvation energies. The choice of dichloromethane is justified as a convenient alternative from a computational standpoint to trifluorotoluene, the solvent used throughout this work.[16]

Spin density plots have been determined via the "cubegen" command and are shown in Figure S9.

For the two reacting situations reported in Figure 4A in the main text, the most stable TS describing the hydrogen transfer event has been located and fully analyzed. The detailed characterization of the TSs has been performed via the IRC method at the same level of theory as the optimizations (UωB97XD/def2TZVP) by describing 70 points in each direction (70 points in the forward and 70 points in the reverse direction).

The thermodynamic parameters reported in the text (see Figure 4A), *viz.* ΔG and $\Delta G^{\ddagger}$ values, have thus been determined according to the following equations:

$$\Delta G = \Sigma\ G\ (\text{products}) - \Sigma\ G\ (\text{reactants})$$

$$\Delta G^{\ddagger} = G\ (\text{TS}) - \Sigma\ G\ (\text{reactants}) - 1.90\ \text{kcal}\cdot\text{mol}^{-1}$$

Where the required Gibbs free energy (G) values were calculated via:

G = Electronic Energy at the SMD(CH_2Cl_2)-UωB97XD/def2TZVP level of theory + thermal correction to Gibbs Free Energy at the UωB97XD/def2TZVP level of theory

For the particular case of propanoic acid, two different conformations have been reported, namely the absolute minimum and one of the located relative minima, which is believed to be the reactive

conformation. This conformation lies +4.90 kcal·mol^{-1} above the absolute minimum in the gas phase (+2.07 kcal·mol^{-1} in the solvent phase). In any case, the data reported in the main text do refer to the absolute minimum.

Thermochemical data have been calculated adopting the default options, *viz.* temperature: 298.150 K and pressure: 1.00000 atm. The conversion factor between Hartree and kcal·mol^{-1} has been: 1 Hartree = 627.509 kcal·mol^{-1}. When summing the data for calculating the G values reported in the main text, all the digits available from the calculations were used; nevertheless, the energy values reported below in Hartree and kcal·mol^{-1} units have been rounded considering, respectively, 6 and 2 significant digits after the unit.

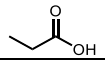
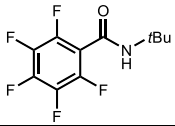
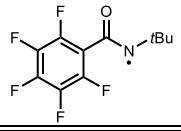
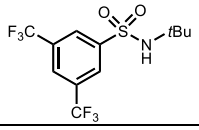
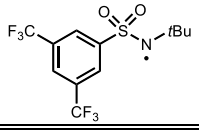
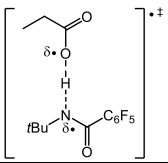
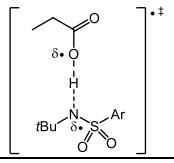
The 1.90 kcal·mol^{-1} correction value introduced into the expression for $\Delta G^{\ddagger}$ is related to the conversion of the computed Gibbs free energy values from the 1 atm standard state into the standard state of molar concentration (ideal mixture at 1 mol·L^{-1} and 1 atm) in order to allow a direct comparison with the experimental results in solution. Thus, the contribution RT ln R′T, where R′ is the value of R in L·atm·K^{-1}·mol^{-1} was added to the Gibbs free energy term. This contribution always cancels out unless a process where a molecularity change (Δn) between reagents and products occurs (as in the expression of $\Delta G^{\ddagger}$). Accordingly, this contribution should be written as ΔnRT ln R′T. As an example, in the reaction A + B → C, Δn = −1 and the contribution will be −RT ln R′T (−1.90 kcal·mol^{-1} at 298.150 K, as indicated in the expression of $\Delta G^{\ddagger}$).[17]

Table S2. Calculated parameters for the TSs describing the processes reported in Figure 4A in main text.

	Gibbs Free Energy (G) at the SMD(CH_2Cl_2)-UωB97XD/def2TZVP//UωB97XD/def2TZVP level of theory, [Hartree]			**$\Delta G^{\ddagger}$ [kcal·mol^{-1}] (Figure 4A)**	**ΔG [kcal·mol^{-1}] (Figure 4A)**
Reacting situation	**Reactants**	**TS**	**Products**		
propanoic acid + radical **2'**	-1322.035861	-1322.000897	-1322.038536	**+ 20.04** [a]	**- 1.68**
propanoic acid + radical **36'**	-1935.273307	-1935.229825	-1935.263908	**+ 25.39** [a]	**+ 5.90**

[a] These values already include the conversion factor from 1 atm standard state to 1 mol·L^{-1} standard state.

Table S3. Terms adopted to calculate the Gibbs Free Energy (G) values reported in Table S2.

	Electronic Energy, gas phase	**Thermal correction to Gibbs Free Energy**	**Electronic Energy, solvent (SMD-CH_2Cl_2)**
propanoic acid (absolute minimum) (relative minimum) 	-268.428720 -268.420698	0.062037 0.061823	-268.438299 -268.434792
carboxyl radical 	-267.744103	0.046723	-267.753089
amide **S10** 	-1054.472444	0.154631	-1054.486802
radical **2'** 	-1053.787000	0.139074	-1053.798673
sulfonamide **S11** 	-1667.736890	0.197628	-1667.755171
radical **36'** 	-1667.063127	0.181385	-1667.078430
TS **38** 	-1322.201434	0.220542	-1322.221439
TS **39** 	-1935.468302	0.261892	-1935.491717

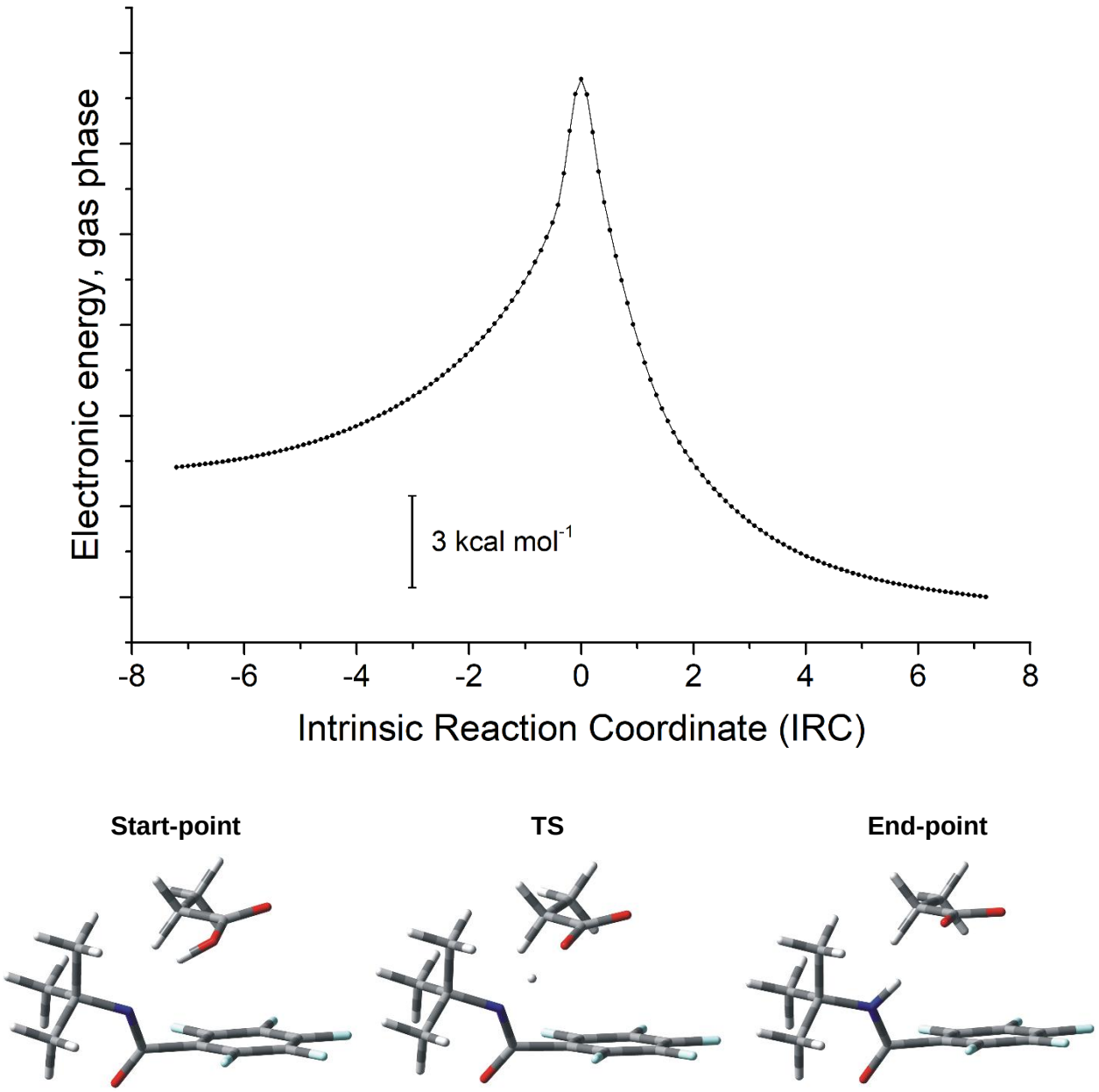


Figure S7. Intrinsic Reaction Coordinate (IRC) plot at the UwB97XD/def2TZVP level of theory (gas phase) obtained for TS **38**, along with the structures of the starting, TS and end-points (see Table S4).

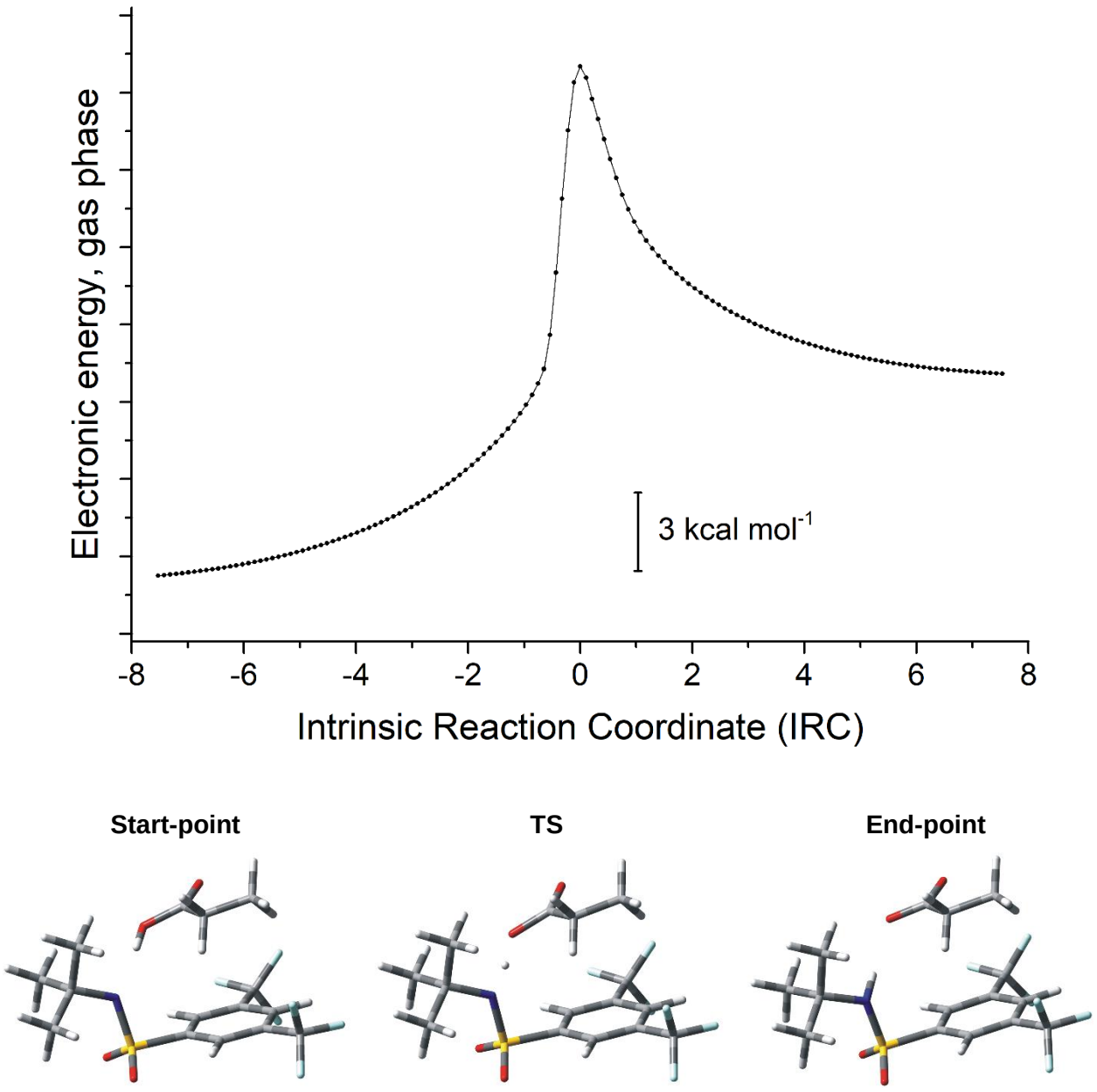


Figure S8. Intrinsic Reaction Coordinate (IRC) plot at the UwB97XD/def2TZVP level of theory (gas phase) obtained for TS **39**, along with the structures of the starting, TS and end points (see Table S5).

Table S4. Data adopted to construct the IRC plot for TS **38** (see Figure S7).

Step #	IRC (forward)	Electronic energy, gas phase	IRC (reverse)	Electronic energy, gas phase
0 (TS)	0.000000	-1322.201434	0.000000	-1322.201434
1	0.103100	-1322.202289	-0.103120	-1322.202265
2	0.206020	-1322.204363	-0.206210	-1322.204302
3	0.308480	-1322.206533	-0.309220	-1322.206636
4	0.410230	-1322.208235	-0.411430	-1322.208374
5	0.513250	-1322.209769	-0.511280	-1322.209361
6	0.616330	-1322.211201	-0.614180	-1322.210171
7	0.719410	-1322.212540	-0.717160	-1322.210888
8	0.822490	-1322.213790	-0.820170	-1322.211530
9	0.925580	-1322.214962	-0.923220	-1322.212120
10	1.028660	-1322.216060	-1.026260	-1322.212666
11	1.131740	-1322.217079	-1.129270	-1322.213173
12	1.234750	-1322.218015	-1.232230	-1322.213651
13	1.337680	-1322.218859	-1.335100	-1322.214093
14	1.440460	-1322.219613	-1.438020	-1322.214523
15	1.543320	-1322.220296	-1.540970	-1322.214923
16	1.646250	-1322.220916	-1.644020	-1322.215310
17	1.749270	-1322.221473	-1.747100	-1322.215672
18	1.852320	-1322.221982	-1.850210	-1322.216016
19	1.955400	-1322.222451	-1.953320	-1322.216343
20	2.058490	-1322.222887	-2.056450	-1322.216655
21	2.161590	-1322.223295	-2.159570	-1322.216953
22	2.264700	-1322.223678	-2.262700	-1322.217238
23	2.367820	-1322.224038	-2.365830	-1322.217510
24	2.470940	-1322.224378	-2.468960	-1322.217770
25	2.574070	-1322.224700	-2.572090	-1322.218019
26	2.677190	-1322.225004	-2.675230	-1322.218257
27	2.780320	-1322.225292	-2.778360	-1322.218486
28	2.883450	-1322.225564	-2.881490	-1322.218705
29	2.986570	-1322.225823	-2.984620	-1322.218914
30	3.089700	-1322.226067	-3.087750	-1322.219115
31	3.192820	-1322.226299	-3.190890	-1322.219307
32	3.295930	-1322.226518	-3.294020	-1322.219491
33	3.399030	-1322.226726	-3.397150	-1322.219668
34	3.502090	-1322.226922	-3.500280	-1322.219839
35	3.605110	-1322.227107	-3.603410	-1322.220002
36	3.708040	-1322.227282	-3.706530	-1322.220159
37	3.810850	-1322.227445	-3.809650	-1322.220310
38	3.913750	-1322.227604	-3.912760	-1322.220455
39	4.016750	-1322.227750	-4.015850	-1322.220593
40	4.119810	-1322.227889	-4.118920	-1322.220727
41	4.222830	-1322.228020	-4.221940	-1322.220854
42	4.325840	-1322.228144	-4.324910	-1322.220977
43	4.428820	-1322.228262	-4.427840	-1322.221092
44	4.531770	-1322.228374	-4.530770	-1322.221205
45	4.634690	-1322.228480	-4.633720	-1322.221312
46	4.737590	-1322.228581	-4.736740	-1322.221416

47	4.840450	-1322.228677	-4.839780	-1322.221514
48	4.943280	-1322.228769	-4.942840	-1322.221609
49	5.046200	-1322.228858	-5.045860	-1322.221698
50	5.149220	-1322.228940	-5.148770	-1322.221783
51	5.252290	-1322.229020	-5.251700	-1322.221866
52	5.355280	-1322.229094	-5.354670	-1322.221943
53	5.458160	-1322.229165	-5.457660	-1322.222018
54	5.561130	-1322.229233	-5.560460	-1322.222087
55	5.664090	-1322.229296	-5.663360	-1322.222156
56	5.767120	-1322.229357	-5.766310	-1322.222219
57	5.870010	-1322.229413	-5.869310	-1322.222281
58	5.973010	-1322.229469	-5.972160	-1322.222338
59	6.075980	-1322.229521	-6.075110	-1322.222394
60	6.179020	-1322.229572	-6.178110	-1322.222445
61	6.281960	-1322.229621	-6.281140	-1322.222495
62	6.384780	-1322.229668	-6.384070	-1322.222541
63	6.487680	-1322.229715	-6.486900	-1322.222584
64	6.590650	-1322.229758	-6.589820	-1322.222627
65	6.693690	-1322.229801	-6.692800	-1322.222667
66	6.796650	-1322.229842	-6.795840	-1322.222706
67	6.899530	-1322.229881	-6.898780	-1322.222742
68	7.002520	-1322.229919	-7.001610	-1322.222776
69	7.105490	-1322.229955	-7.104560	-1322.222810
70	7.208560	-1322.229991	-7.207520	-1322.222842

Table S5. Data adopted to construct the IRC plot for TS **39** (see Figure S8).

Step #	IRC (forward)	Electronic energy, gas phase	IRC (reverse)	Electronic energy, gas phase
0 (TS)	0.000000	-1935.468302	0.000000	-1935.468302
1	0.107340	-1935.469029	-0.107740	-1935.469341
2	0.214130	-1935.470409	-0.215500	-1935.472441
3	0.320360	-1935.471708	-0.323270	-1935.476863
4	0.428050	-1935.473009	-0.431050	-1935.481641
5	0.535770	-1935.474294	-0.538750	-1935.485679
6	0.643500	-1935.475510	-0.644400	-1935.487874
7	0.751220	-1935.476608	-0.748790	-1935.488819
8	0.858890	-1935.477555	-0.855830	-1935.489550
9	0.966450	-1935.478346	-0.963290	-1935.490187
10	1.073960	-1935.479010	-1.070840	-1935.490750
11	1.181520	-1935.479581	-1.178490	-1935.491263
12	1.289170	-1935.480087	-1.286200	-1935.491739
13	1.396860	-1935.480544	-1.393930	-1935.492184
14	1.504570	-1935.480961	-1.501690	-1935.492605
15	1.612310	-1935.481346	-1.609460	-1935.493003
16	1.720070	-1935.481706	-1.717230	-1935.493382
17	1.827830	-1935.482045	-1.825000	-1935.493743
18	1.935600	-1935.482364	-1.932770	-1935.494088
19	2.043370	-1935.482667	-2.040540	-1935.494417
20	2.151120	-1935.482953	-2.148300	-1935.494732

21	2.258730	-1935.483223	-2.256030	-1935.495032
22	2.366390	-1935.483482	-2.363700	-1935.495320
23	2.474010	-1935.483725	-2.471250	-1935.495594
24	2.581750	-1935.483960	-2.578840	-1935.495860
25	2.689410	-1935.484179	-2.686490	-1935.496112
26	2.797010	-1935.484388	-2.794230	-1935.496356
27	2.904530	-1935.484585	-2.901920	-1935.496588
28	3.012020	-1935.484774	-3.009590	-1935.496811
29	3.119510	-1935.484955	-3.117220	-1935.497024
30	3.227070	-1935.485129	-3.224820	-1935.497230
31	3.334680	-1935.485296	-3.332390	-1935.497426
32	3.442340	-1935.485455	-3.439970	-1935.497615
33	3.550040	-1935.485607	-3.547580	-1935.497797
34	3.657750	-1935.485752	-3.655210	-1935.497972
35	3.765450	-1935.485891	-3.762880	-1935.498140
36	3.873120	-1935.486023	-3.870580	-1935.498302
37	3.980710	-1935.486150	-3.978290	-1935.498457
38	4.088350	-1935.486272	-4.086010	-1935.498607
39	4.196030	-1935.486388	-4.193730	-1935.498751
40	4.303770	-1935.486500	-4.301420	-1935.498890
41	4.411470	-1935.486607	-4.409110	-1935.499023
42	4.519160	-1935.486709	-4.516780	-1935.499153
43	4.626810	-1935.486806	-4.624440	-1935.499277
44	4.734420	-1935.486899	-4.732120	-1935.499397
45	4.842010	-1935.486988	-4.839810	-1935.499512
46	4.949580	-1935.487072	-4.947510	-1935.499624
47	5.057160	-1935.487153	-5.055230	-1935.499730
48	5.164740	-1935.487230	-5.162960	-1935.499833
49	5.272370	-1935.487304	-5.270680	-1935.499932
50	5.380010	-1935.487373	-5.378410	-1935.500027
51	5.487680	-1935.487439	-5.486120	-1935.500119
52	5.595360	-1935.487502	-5.593820	-1935.500207
53	5.703050	-1935.487562	-5.701500	-1935.500291
54	5.810720	-1935.487618	-5.809150	-1935.500371
55	5.918350	-1935.487670	-5.916760	-1935.500448
56	6.025880	-1935.487720	-6.024320	-1935.500521
57	6.133500	-1935.487768	-6.131850	-1935.500592
58	6.241130	-1935.487812	-6.239350	-1935.500658
59	6.348830	-1935.487854	-6.346830	-1935.500722
60	6.456430	-1935.487893	-6.454300	-1935.500783
61	6.563890	-1935.487929	-6.561770	-1935.500840
62	6.671430	-1935.487965	-6.669250	-1935.500896
63	6.779020	-1935.487997	-6.776740	-1935.500948
64	6.886690	-1935.488029	-6.884290	-1935.500999
65	6.994230	-1935.488058	-6.991880	-1935.501047
66	7.101860	-1935.488086	-7.099520	-1935.501093
67	7.209490	-1935.488112	-7.207210	-1935.501138
68	7.317170	-1935.488137	-7.314910	-1935.501180
69	7.424710	-1935.488161	-7.422590	-1935.501221
70	7.532340	-1935.488184	-7.530220	-1935.501260

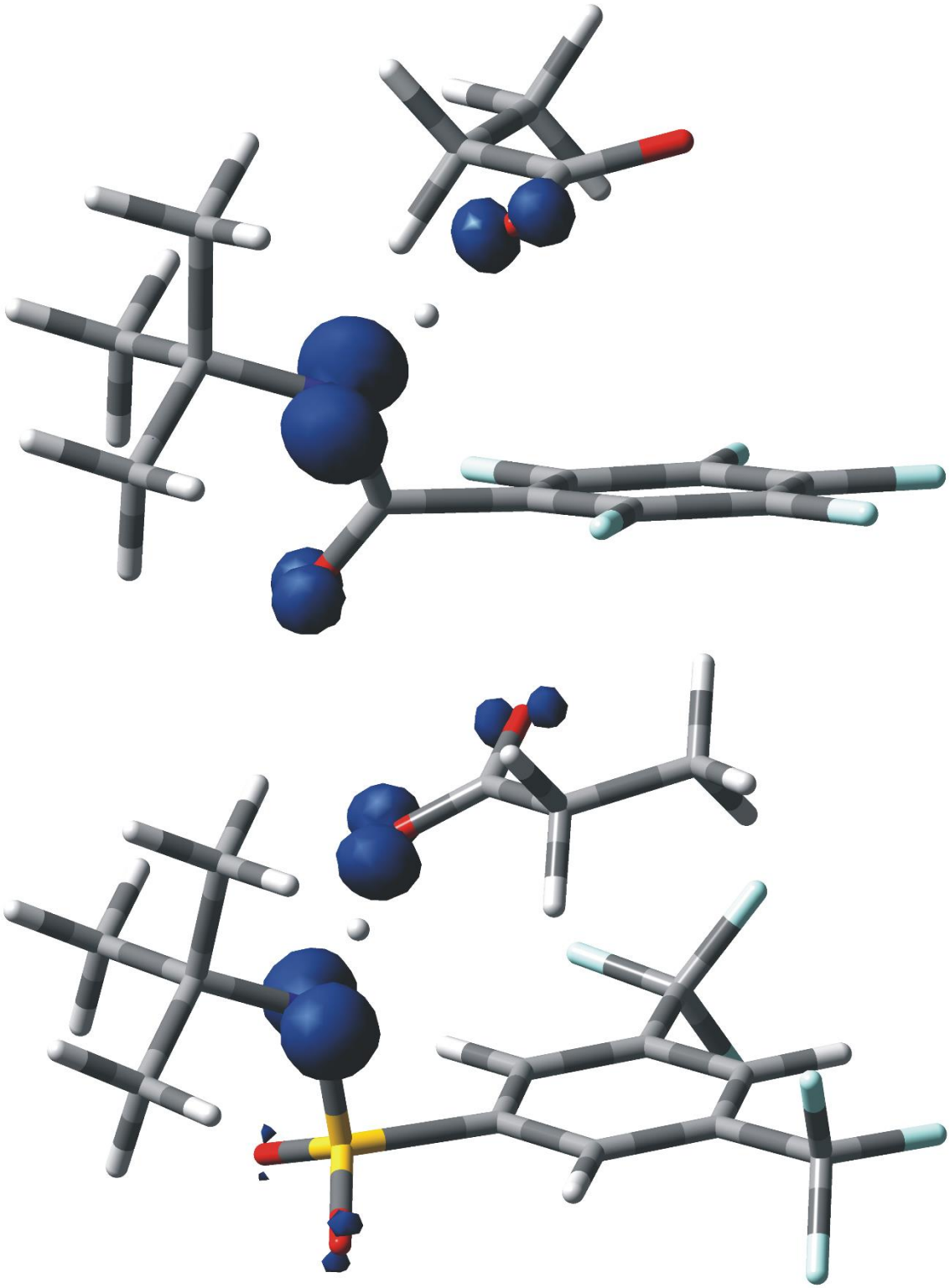
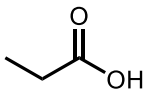


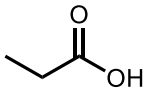
Figure S9. Spin density plots for TS structures **38** (top) and **39** (bottom) as from the calculations at the SMD(CH_2Cl_2)-UωB97XD/def2TZVP//UωB97XD/def2TZVP level of theory.

Optimized Structures



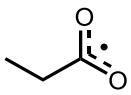
propanoic acid (absolute minimum)

C	0.56205700	0.10314200	0.00006800
O	0.61148400	1.30194100	0.00006900
C	-0.68997200	-0.73228900	0.00017200
H	-0.64048900	-1.39163600	-0.87015400
H	-0.64061700	-1.39112000	0.87090200
O	1.66958600	-0.66228800	-0.00013100
H	2.42522400	-0.06232800	-0.00018100
C	-1.96168400	0.09659900	-0.00014100
H	-2.00949000	0.73858700	-0.87928700
H	-2.83603900	-0.55457600	0.00001600
H	-2.00956400	0.73912600	0.87860500



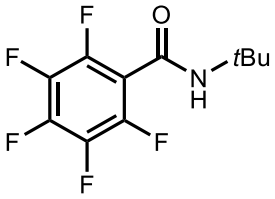
propanoic acid (relative minimum)

C	0.57837700	0.15095000	0.00011900
O	0.55942600	1.34378800	-0.00003400
C	-0.65136500	-0.73576700	-0.00001400
H	-0.59283200	-1.38993600	-0.87552600
H	-0.59291000	-1.39010100	0.87537600
O	1.75859500	-0.50604800	-0.00002000
H	1.61687700	-1.45617100	-0.00003700
C	-1.95049100	0.04899700	-0.00000200
H	-2.01546000	0.68936000	-0.87817400
H	-2.80339300	-0.62930300	-0.00013300
H	-2.01557000	0.68915400	0.87831400



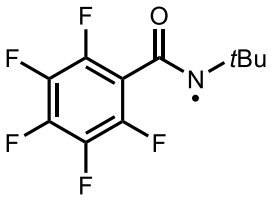
carboxyl radical

C	0.61396200	-0.01946700	0.00000200
O	1.73070500	-0.59082700	0.00005200
C	-0.69279200	-0.74252900	-0.00006500
H	-0.68954800	-1.39993300	0.87318600
H	-0.68955500	-1.39969800	-0.87349500
O	0.75442200	1.21783700	-0.00003500
C	-1.90002700	0.18447500	0.00004900
H	-2.81778400	-0.40269200	0.00069900
H	-1.90511900	0.82606400	0.88082800
H	-1.90586900	0.82530400	-0.88127500



amide **S10**

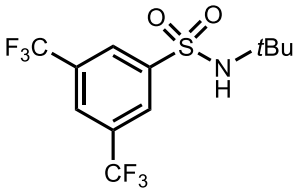
C	-2.28268200	1.27322300	0.00436900
C	-3.06451400	0.14439800	0.18541500
C	-2.48658800	-1.11494400	0.14820600
C	-1.12578700	-1.23289000	-0.07662800
C	-0.32384800	-0.11893400	-0.26118300
C	-0.92279500	1.12763600	-0.21254800
C	1.14708200	-0.27717900	-0.59695100
O	1.48397700	-0.68784700	-1.68456600
C	3.44622900	0.07570200	0.34824300
C	3.92432100	0.57184500	1.71063800
C	3.95897000	-1.34346000	0.09938400
H	5.01353600	0.59404600	1.73539200
H	3.58285500	-0.08868900	2.51114900
H	3.56283900	1.58360800	1.90960300
H	5.05026800	-1.34515300	0.09530500
H	3.61609900	-2.01799700	0.88589100
H	3.60656700	-1.71827200	-0.85983600
N	1.97421200	0.07421300	0.40604600
C	3.92340700	1.02616800	-0.75112400
H	3.57526400	0.69281100	-1.72720100
H	3.55043200	2.03620500	-0.57255100
H	5.01416100	1.05810600	-0.76283900
F	-0.19027500	2.22457200	-0.38707500
F	-0.59109800	-2.44601100	-0.09723500
F	-3.23711200	-2.19013200	0.33326300
F	-4.36324700	0.26819600	0.39789400
F	-2.83750000	2.47560800	0.03987600
H	1.54700300	0.40914000	1.25186400



radical **2'**

C	2.30168600	-1.19135200	0.06799800
C	2.91734500	0.03125500	0.28284000
C	2.20433600	1.20836700	0.11974700
C	0.87634500	1.14929200	-0.26364700
C	0.23732900	-0.06246800	-0.48007500
C	0.96871800	-1.22780500	-0.30436700
C	-1.20830800	-0.07873500	-0.91282900
O	-1.56573900	0.36012300	-1.97951200
C	-3.21304500	-0.07054900	0.52627300
C	-3.55312400	-0.78465500	1.83415000
C	-3.03150800	1.43164100	0.75845300

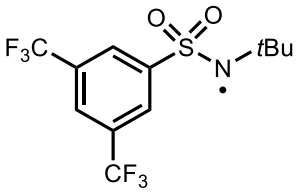
H	-4.48690900	-0.39267700	2.24018600
H	-2.76581800	-0.63132700	2.57355800
H	-3.66392600	-1.85593600	1.66663400
H	-3.94469000	1.85102700	1.18244900
H	-2.21735100	1.61768100	1.46157600
H	-2.81596200	1.95450800	-0.17306900
N	-2.01822500	-0.70190900	-0.00459400
C	-4.32908000	-0.32318500	-0.50990500
H	-4.10592400	0.17839100	-1.44937300
H	-4.44450100	-1.39069000	-0.69637200
H	-5.26477500	0.06668200	-0.10461400
F	0.41112700	-2.40899800	-0.52237800
F	0.20838900	2.28755500	-0.39830700
F	2.79470100	2.37373100	0.33510800
F	4.18716900	0.07523000	0.64324300
F	2.99185600	-2.31153100	0.21516200



sulfonamide **S11**

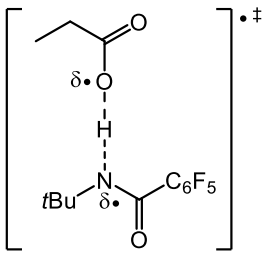
C	-2.31159800	0.05597100	-0.17264500
C	-1.69831700	-1.16232600	0.02992600
C	-0.38578400	-1.22411300	0.48742500
C	0.29593500	-0.05258500	0.73249700
C	-0.30931800	1.18330000	0.54131300
C	-1.61032600	1.23008900	0.08771800
O	2.32701900	-1.49678400	1.37948900
C	3.40076200	0.10128800	-1.05376100
C	2.35812700	-0.72837300	-1.79950400
H	2.06886500	-1.61301900	-1.23266100
H	2.78135700	-1.06502900	-2.74625400
N	2.81203200	0.67528000	0.17761100
H	3.31571800	1.44844700	0.58636700
H	-3.33071700	0.10111600	-0.53133900
H	1.46653300	-0.13732800	-2.01445400
C	4.63153600	-0.74687100	-0.72838700
H	5.37692700	-0.15219700	-0.19630200
H	4.36113900	-1.59799500	-0.10542100
H	5.08635000	-1.11672400	-1.64916600
C	3.80124800	1.30352000	-1.90773800
H	4.25707600	0.96329700	-2.83798100
H	2.93120100	1.91559100	-2.14912800
H	4.53283900	1.92772100	-1.38853000
H	0.23824800	2.09266400	0.74596800
H	0.10585800	-2.17438100	0.64852800
S	1.97348100	-0.11323700	1.32359900
O	2.04935000	0.71742500	2.48364400
C	-2.42195700	-2.45554400	-0.24975500
C	-2.30604600	2.54720100	-0.14668400
F	-3.67683500	-2.25553000	-0.66044200
F	-1.79577100	-3.16112900	-1.20251600
F	-2.47311200	-3.22999400	0.84051400

F	-1.52784600	3.59111000	0.14731200
F	-3.41630100	2.65003000	0.59493500
F	-2.67989500	2.67420100	-1.42846700



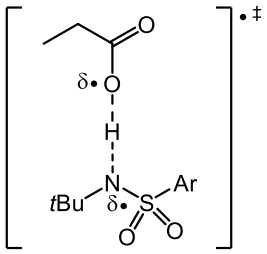
radical **36'**

C	-2.50819200	0.07815500	0.17831500
C	-1.76797300	1.23837400	-0.01647700
C	-0.43163200	1.16959200	-0.35696700
C	0.16093900	-0.07736100	-0.49595700
C	-0.55873100	-1.24024400	-0.31253900
C	-1.90265000	-1.15383600	0.02757000
O	2.21137600	1.01767600	-1.64526600
C	3.99111900	0.00456600	0.73370500
C	4.20073900	1.52132500	0.94076000
H	3.96219500	2.07081500	0.03154000
H	5.24846400	1.68878000	1.19540400
N	2.55324900	-0.15999200	0.56069200
H	-3.55478400	0.14109200	0.44294200
H	3.57911200	1.89030100	1.75646000
C	4.86304300	-0.49440300	-0.42177300
H	4.69613000	-1.55471700	-0.60817900
H	4.66927800	0.05451000	-1.34266800
H	5.91098500	-0.35135400	-0.15489100
C	4.34052100	-0.74164700	2.02446300
H	5.39052300	-0.57762900	2.27149900
H	3.72401000	-0.38911200	2.85116000
H	4.17798700	-1.81304100	1.90273100
H	-0.07780900	-2.20086600	-0.44262300
H	0.14862700	2.06601400	-0.52424200
S	1.87640400	-0.17669800	-0.92970000
O	2.11056500	-1.46333500	-1.51104900
C	-2.46304600	2.56820100	0.13812300
C	-2.67923100	-2.43251000	0.22332400
F	-3.95130600	-2.20460000	0.55956600
F	-2.13626500	-3.18450300	1.18985600
F	-2.68368700	-3.17189600	-0.89271800
F	-3.04610200	2.67250400	1.34015600
F	-1.62239900	3.59635800	0.00896600
F	-3.42856300	2.71950500	-0.77844300



TS **38**

C	-0.01954400	1.37536500	-1.68960500
O	-1.07757900	1.49767500	-2.25873500
C	-2.26200200	-1.48342100	-0.49632600
C	-3.01848100	-0.52358100	0.15721500
C	-2.42911100	0.31316200	1.09139400
C	-1.08026000	0.18136500	1.36456200
C	-0.29977200	-0.76036000	0.71121300
C	-0.91226400	-1.58886000	-0.21675500
C	1.17192000	-0.83599100	1.00007400
O	1.59744600	-1.14097100	2.08947600
C	3.39914300	-0.25195900	0.01581900
C	3.85733500	0.20091700	-1.36960300
C	3.67625500	0.83858200	1.05294900
H	4.93141000	0.38396000	-1.35255700
H	3.35387100	1.12194000	-1.66567500
H	3.64443900	-0.55906400	-2.12183100
H	4.74567800	1.05131000	1.06623800
H	3.15415300	1.75945200	0.78884200
H	3.37300300	0.53127600	2.05115900
N	1.98015800	-0.58066100	-0.08563700
C	4.13480900	-1.55831600	0.39023800
H	3.85293300	-1.88722800	1.38760500
H	3.90687200	-2.34632800	-0.32746600
H	5.20739400	-1.36162500	0.36377600
H	1.40894000	-0.22569300	-1.06259700
C	0.52596000	2.40925800	-0.72259700
H	0.90560300	1.90239300	0.16672700
H	1.40198400	2.85440400	-1.20490600
O	0.74594600	0.33264700	-1.94214600
F	-0.20184800	-2.51167700	-0.84880700
F	-0.52574900	1.01120600	2.24044800
F	-3.15290500	1.23529400	1.70535900
F	-4.30407900	-0.40787200	-0.10755200
F	-2.83180900	-2.28548500	-1.37727800
C	-0.48990700	3.47207400	-0.34759100
H	-1.34885700	3.03075100	0.15852400
H	-0.04171900	4.20719100	0.32156900
H	-0.86027400	3.98447100	-1.23415000



TS **39**

C	0.47428300	-1.66475000	1.85789000
O	-0.12922900	-2.68209200	2.11183700
C	-1.87325500	1.41766600	-0.24853000
C	-2.53547400	0.20789100	-0.33613200
C	-1.86576500	-0.91692700	-0.80136800
C	-0.53698200	-0.83982500	-1.17115400
C	0.11290500	0.38130100	-1.06410100
C	-0.53935800	1.51424600	-0.61820600

O	2.13146500	1.83633500	-1.82861700
C	3.91927300	0.17715300	0.32455500
C	4.06754000	0.24929300	1.84422100
C	4.47276800	-1.16106100	-0.19446600
H	5.12203000	0.18415000	2.11358900
H	3.54586800	-0.58004700	2.32493800
H	3.66781000	1.18891100	2.22713800
H	5.52332200	-1.23393100	0.09027000
H	3.93181300	-1.99820200	0.24570400
H	4.39652300	-1.22668800	-1.27786600
N	2.46480500	0.27985800	0.07743000
C	4.66606800	1.34211000	-0.33308900
H	4.64278600	1.28002800	-1.41955000
H	4.24468000	2.30072100	-0.03318400
H	5.70627300	1.29736300	-0.00886500
H	1.92213900	-0.57608100	0.60830400
C	0.19807400	-0.33156800	2.50466500
H	1.01403300	-0.15363100	3.21247600
H	0.28680400	0.45325300	1.75050000
O	1.44845900	-1.75346100	0.98087100
S	1.83538500	0.49069400	-1.45321000
O	2.17620400	-0.58888000	-2.32202100
H	-0.00880800	2.45542500	-0.55467600
H	-0.00072000	-1.71168200	-1.51757700
H	-3.57328300	0.13462100	-0.04082800
C	-2.62741100	-2.21723000	-0.90385600
C	-2.56312600	2.64739300	0.28668100
F	-3.26467600	-2.49266100	0.23883800
F	-1.83415100	-3.24481400	-1.19175100
F	-3.56111700	-2.14333000	-1.86553100
F	-2.01010100	3.03640000	1.44618600
F	-2.45639100	3.67543300	-0.56167800
F	-3.86133400	2.44087400	0.51306900
C	-1.15045800	-0.27191800	3.20374300
H	-1.21617800	-1.01903300	3.99299300
H	-1.30346200	0.71433900	3.64149700
H	-1.96118200	-0.46460900	2.50060200

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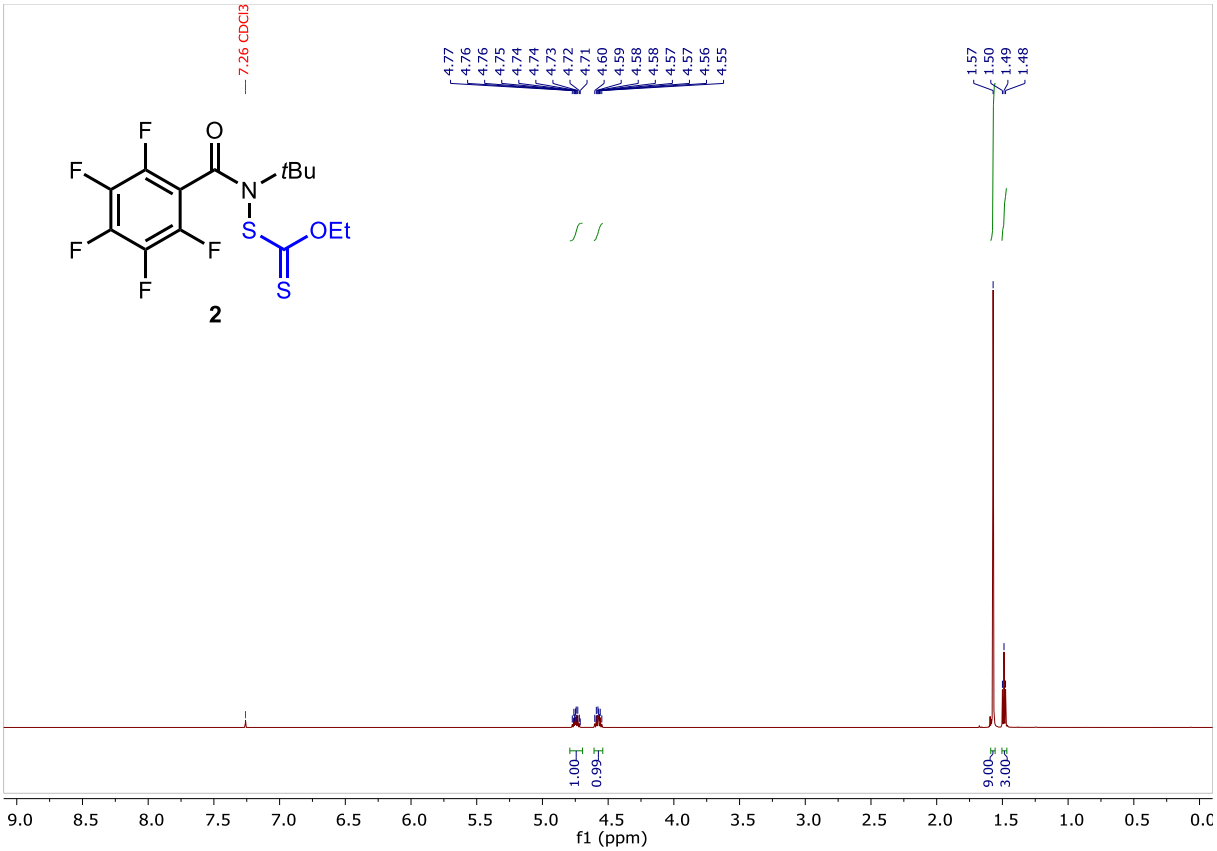
^{1}H NMR ($CDCl_3$, 600 MHz)



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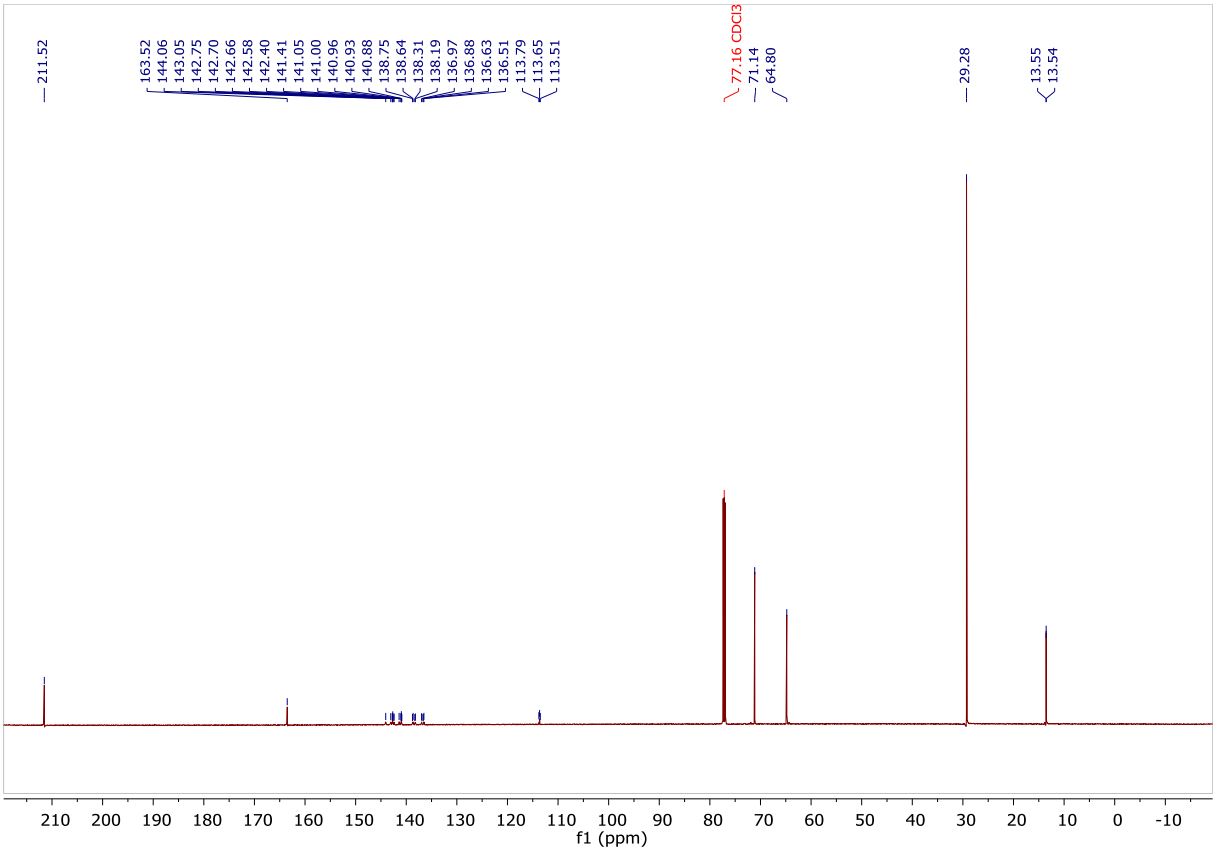

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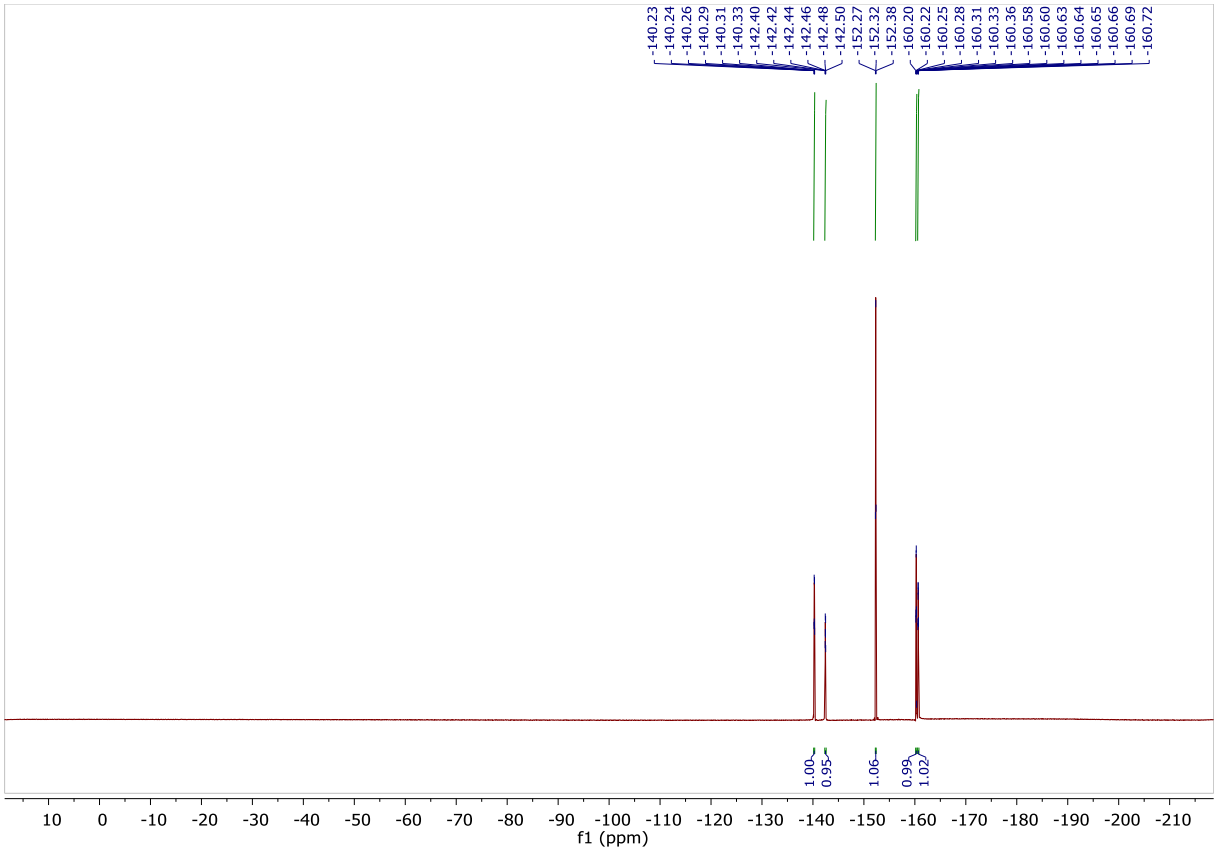

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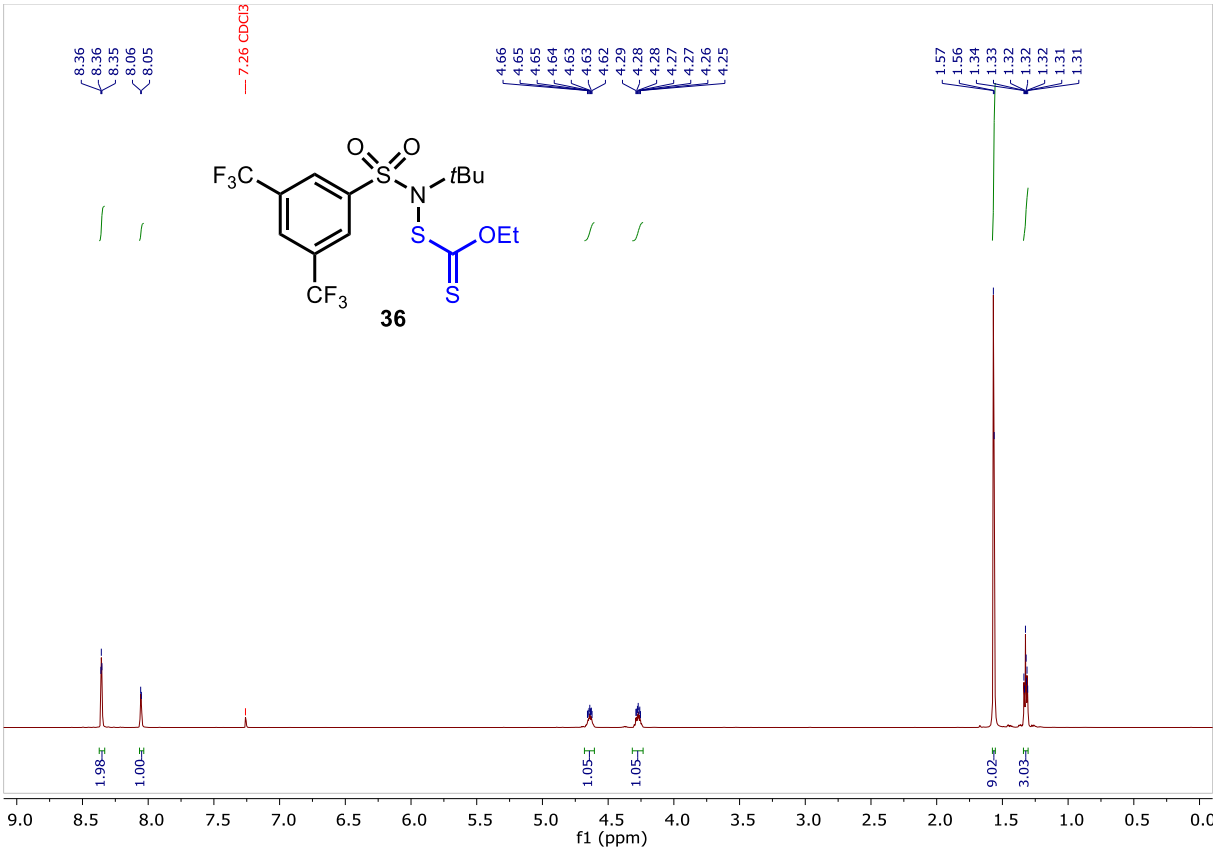

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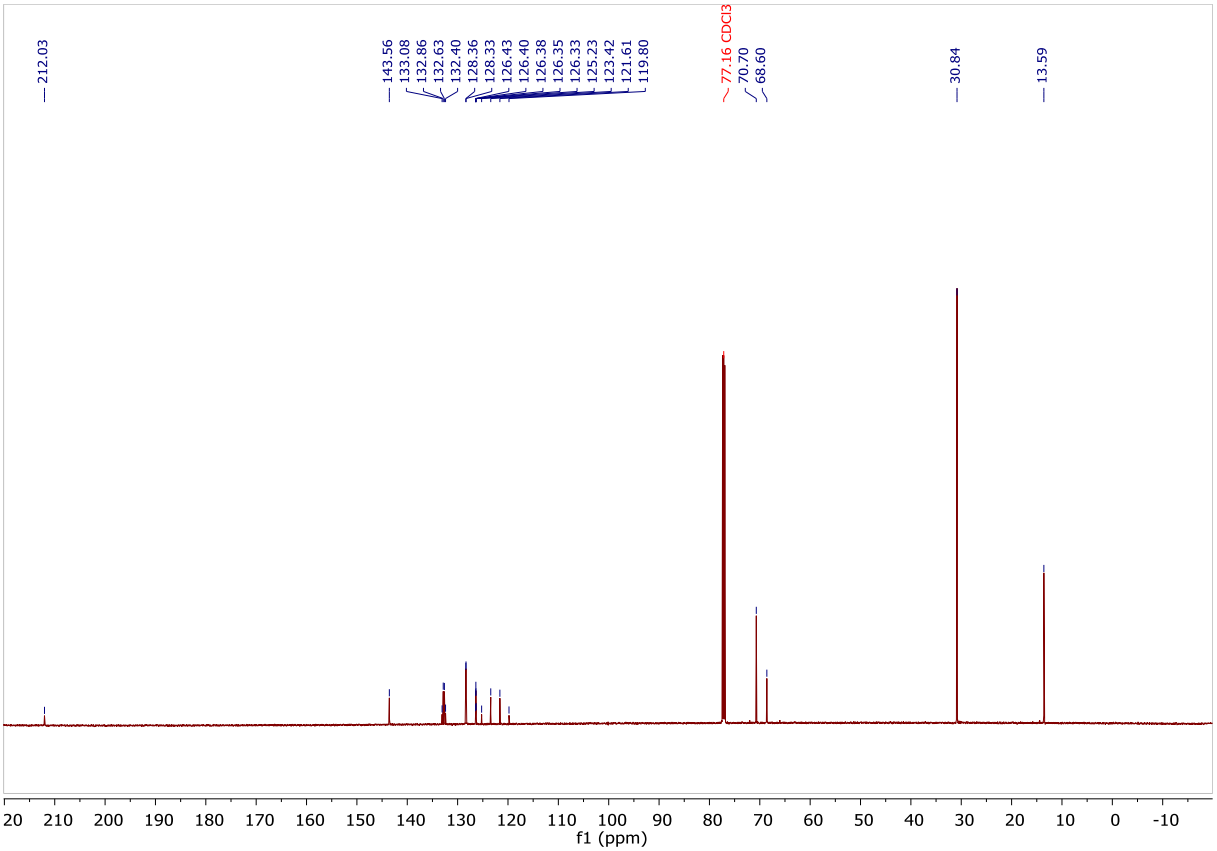

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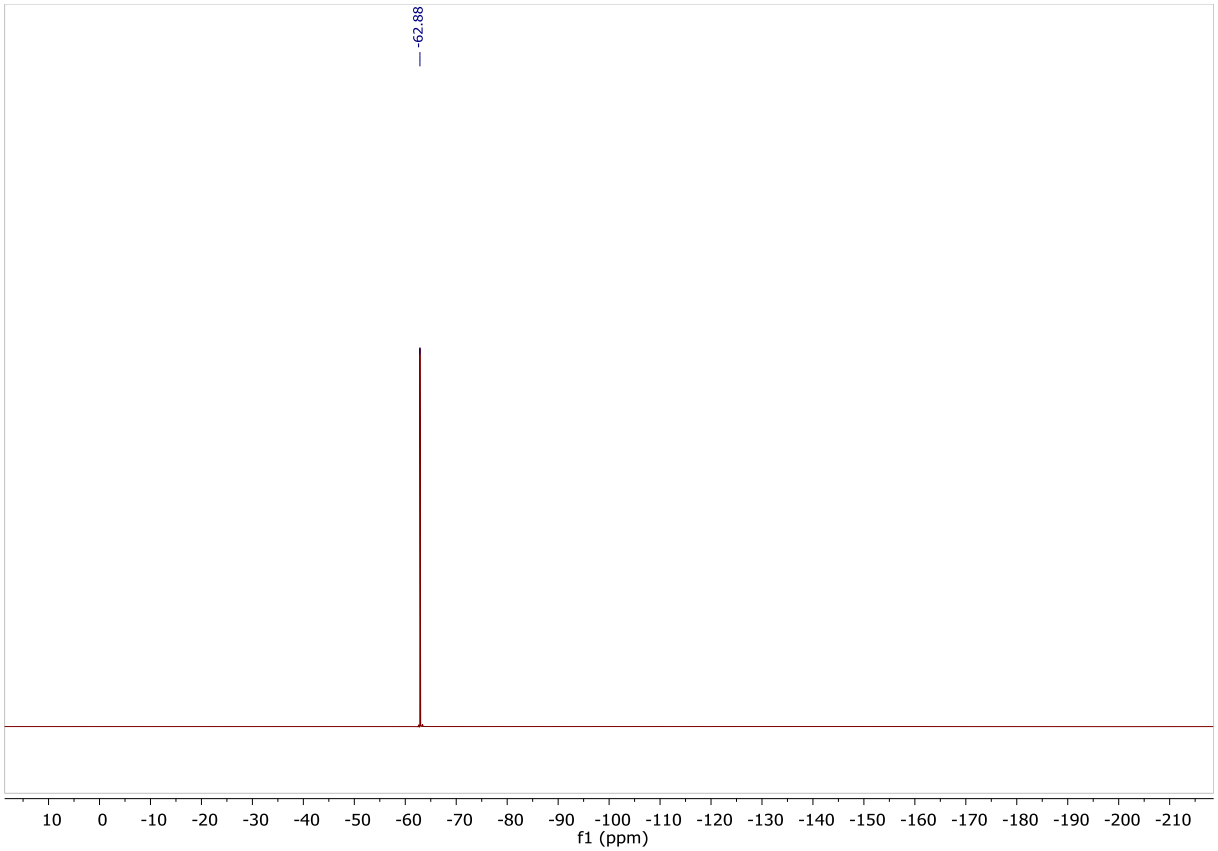

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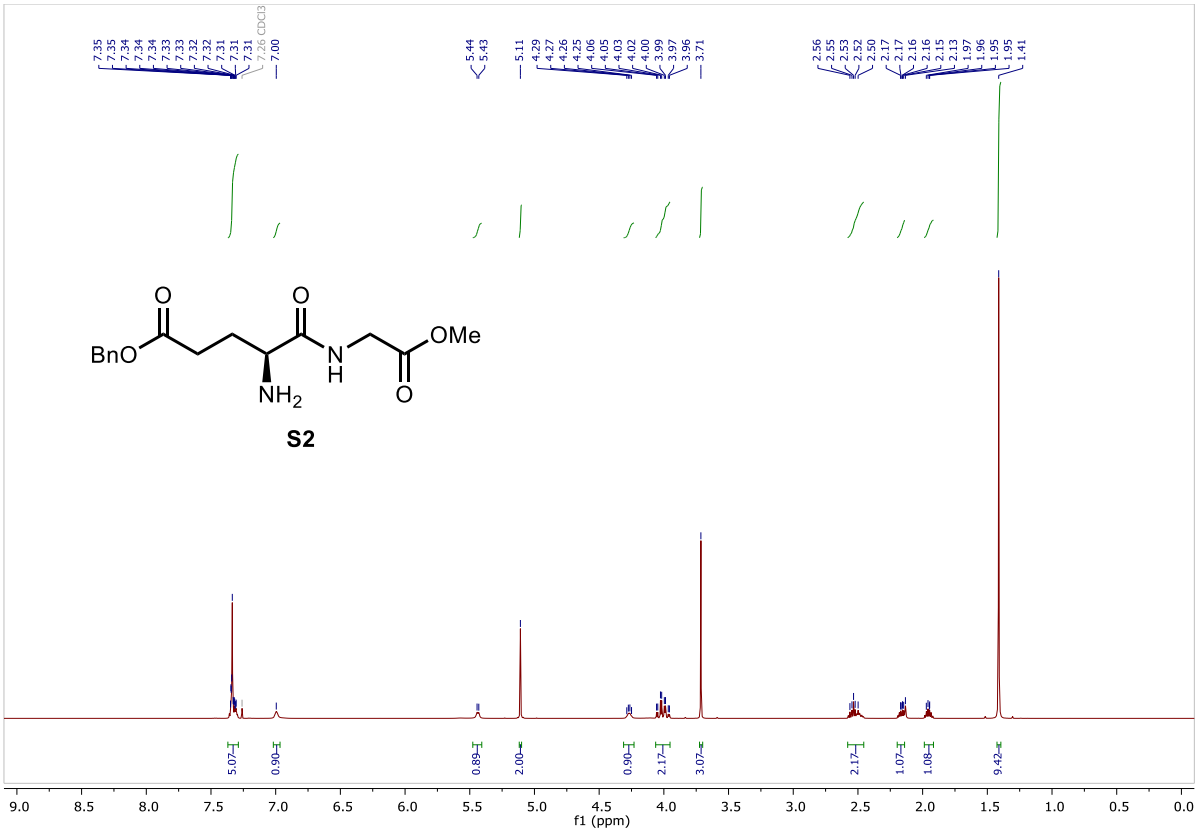

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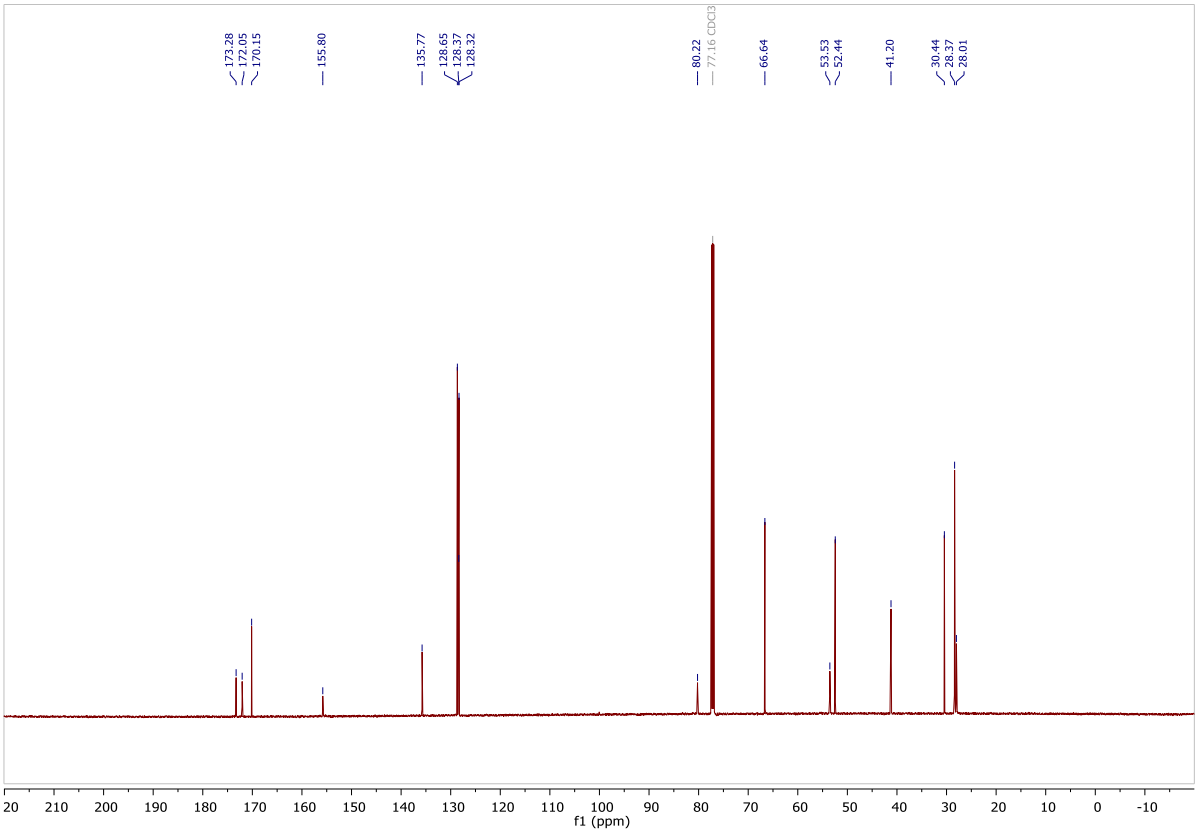

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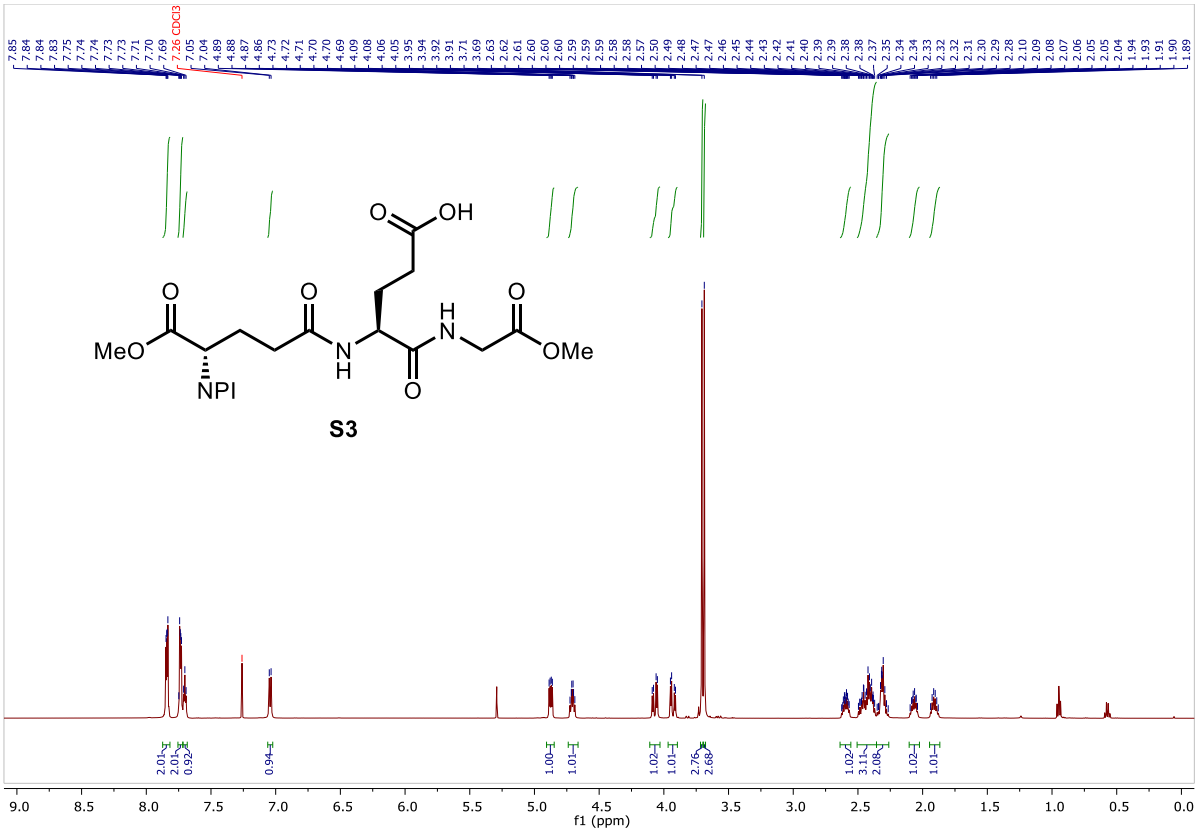

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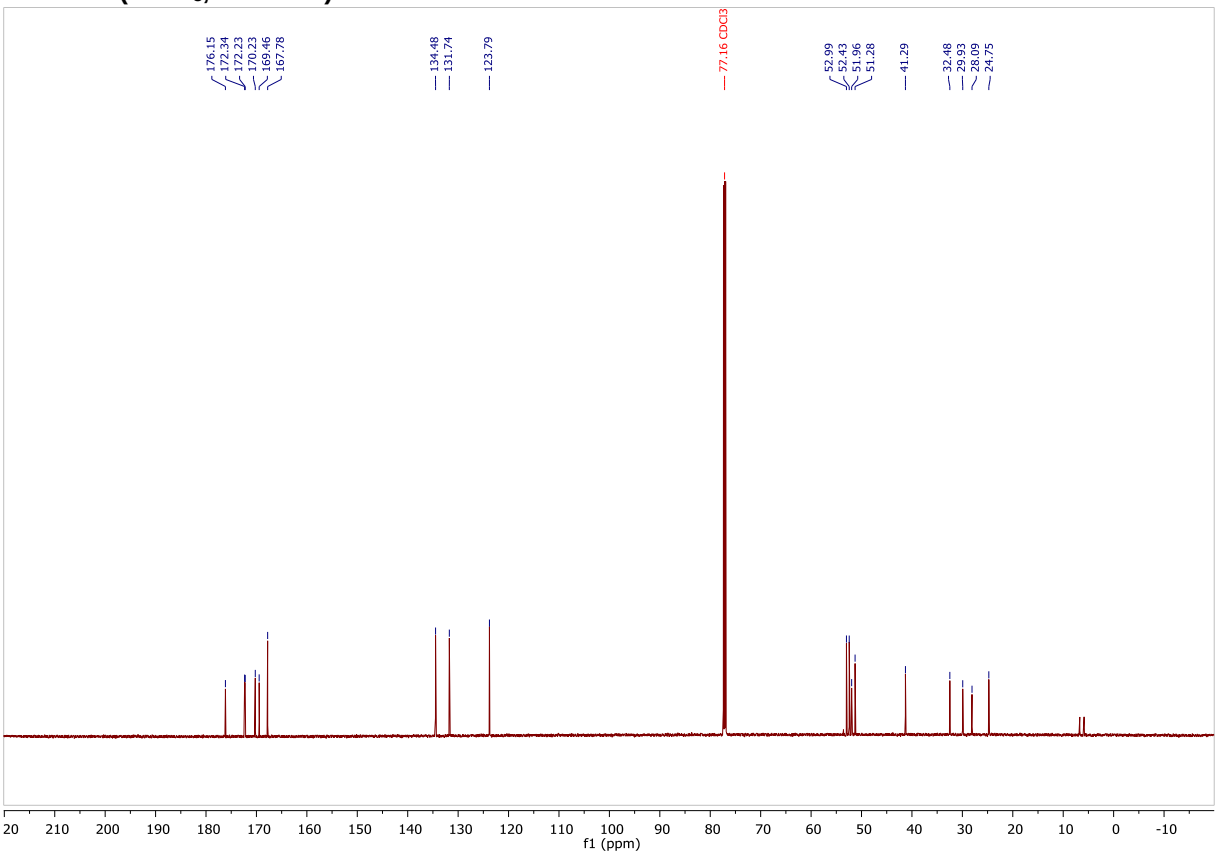

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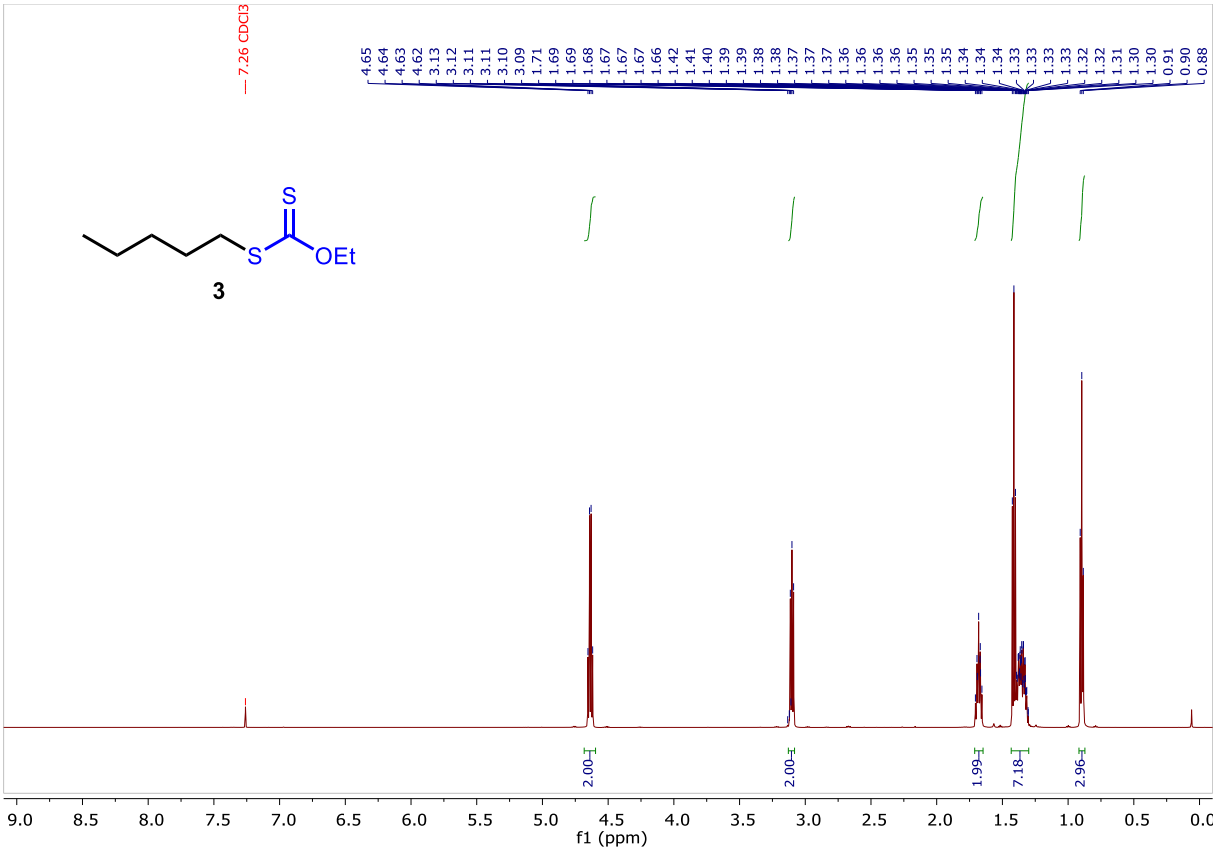

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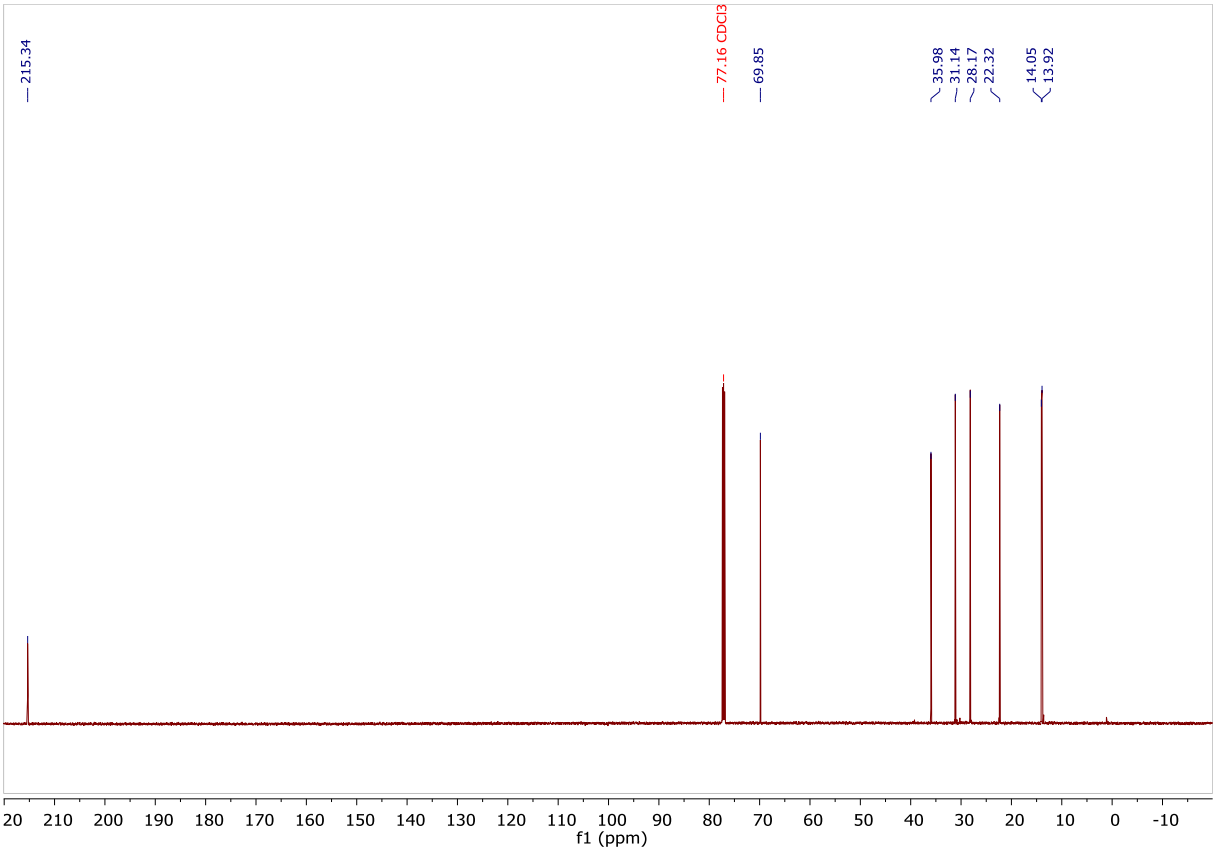

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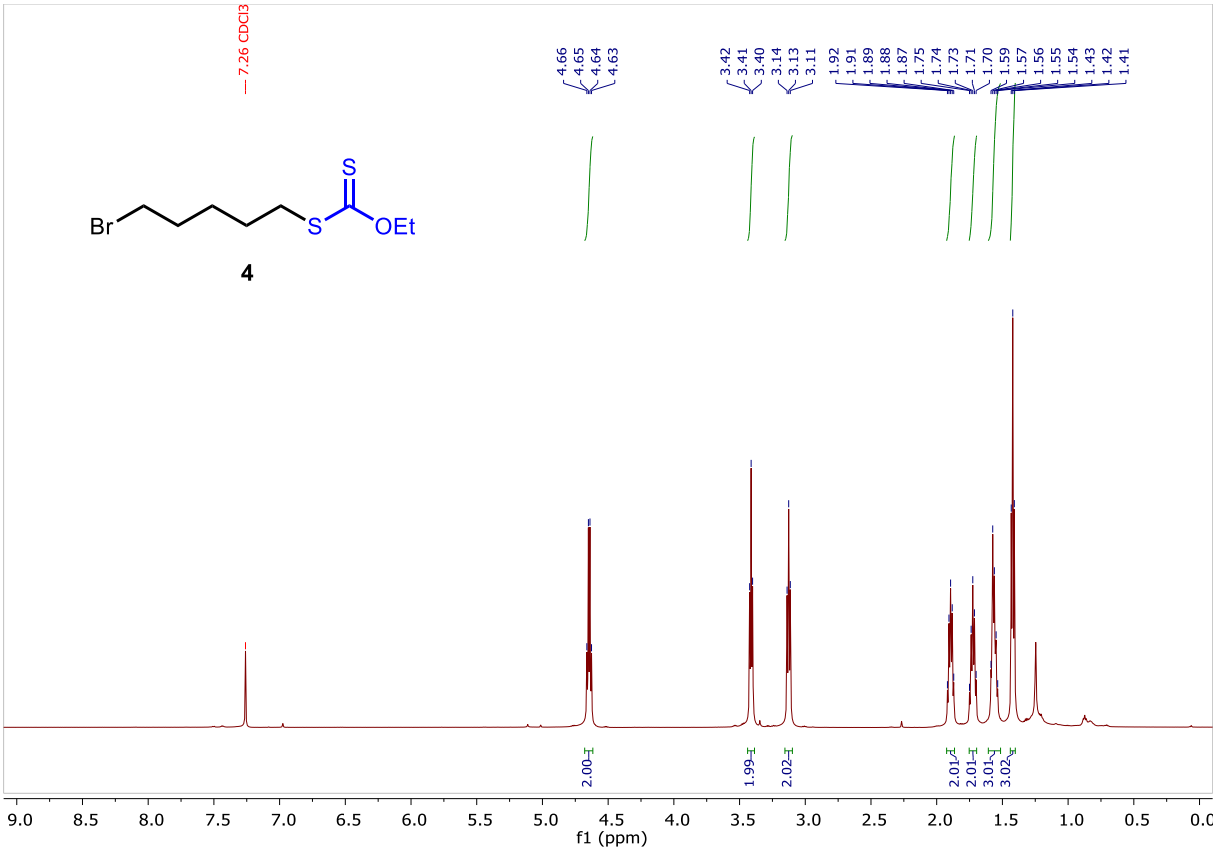

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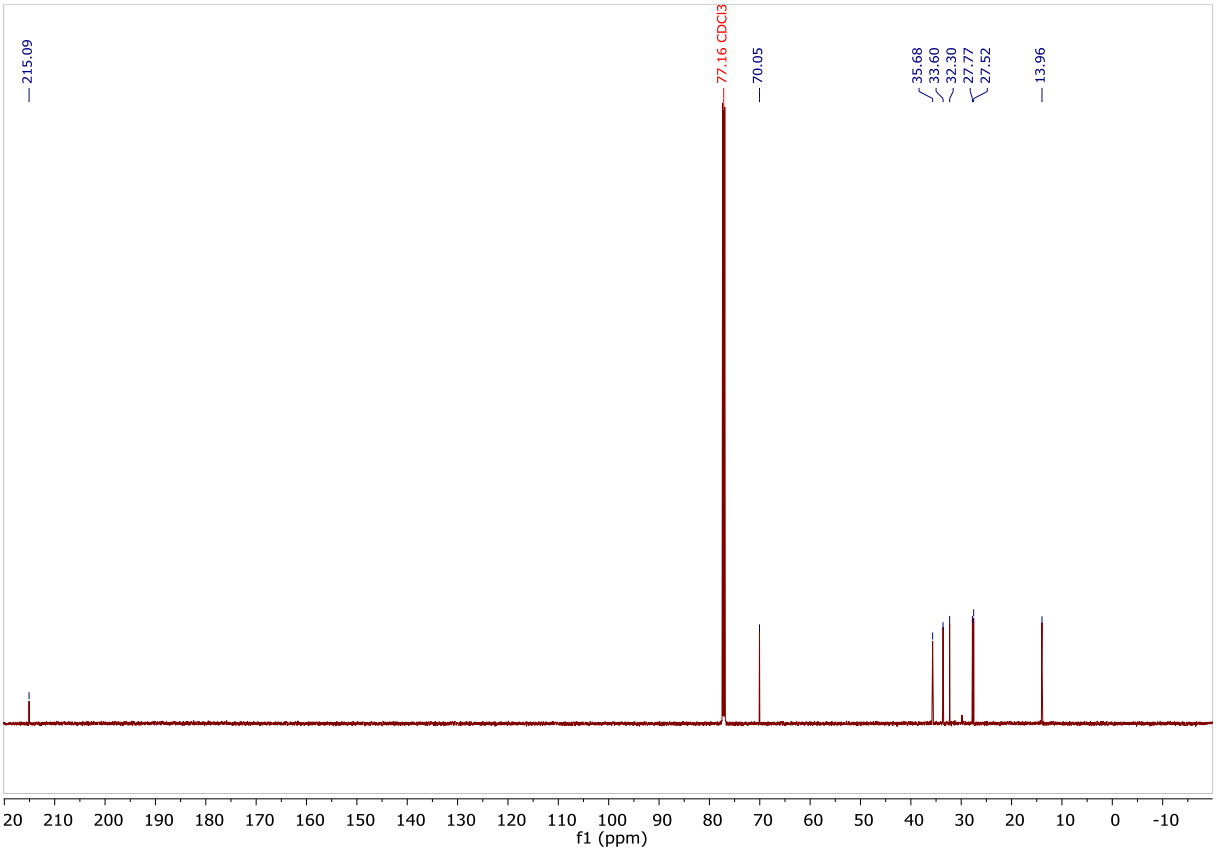

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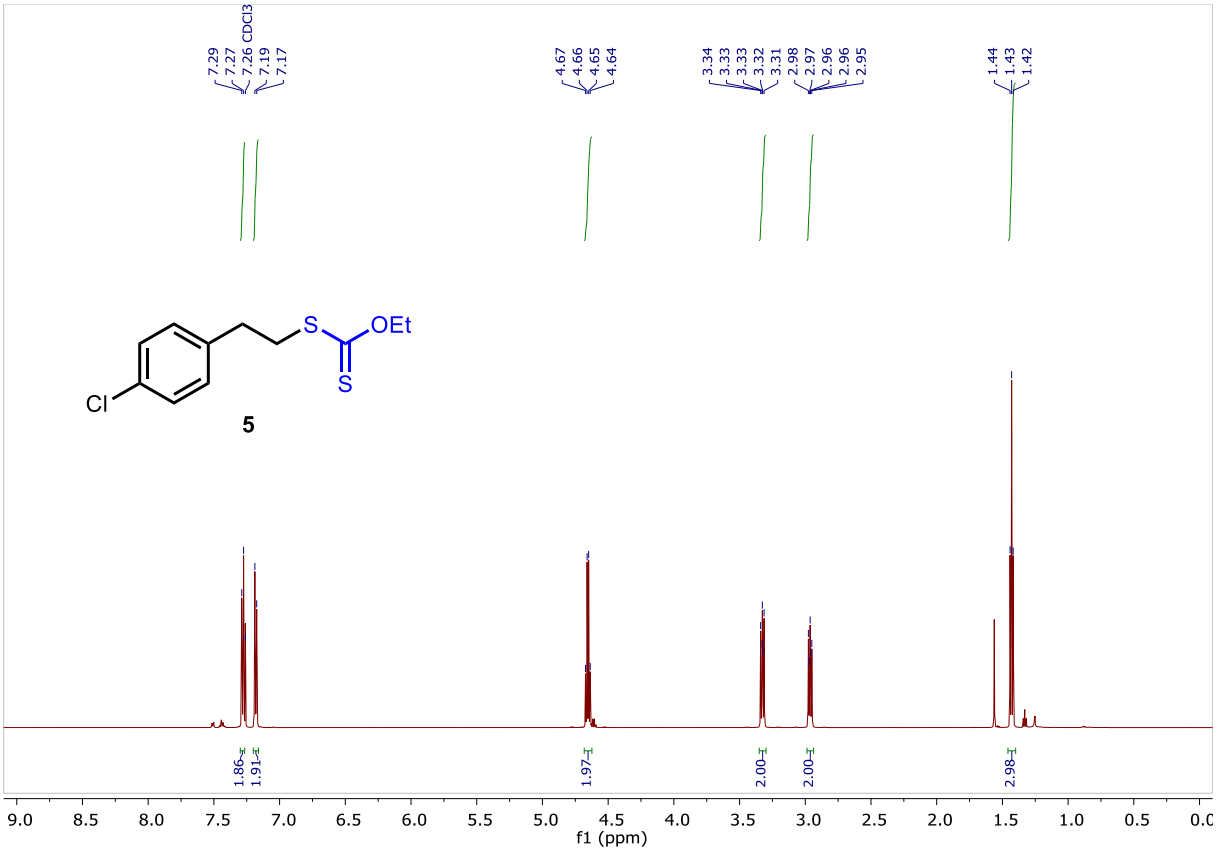

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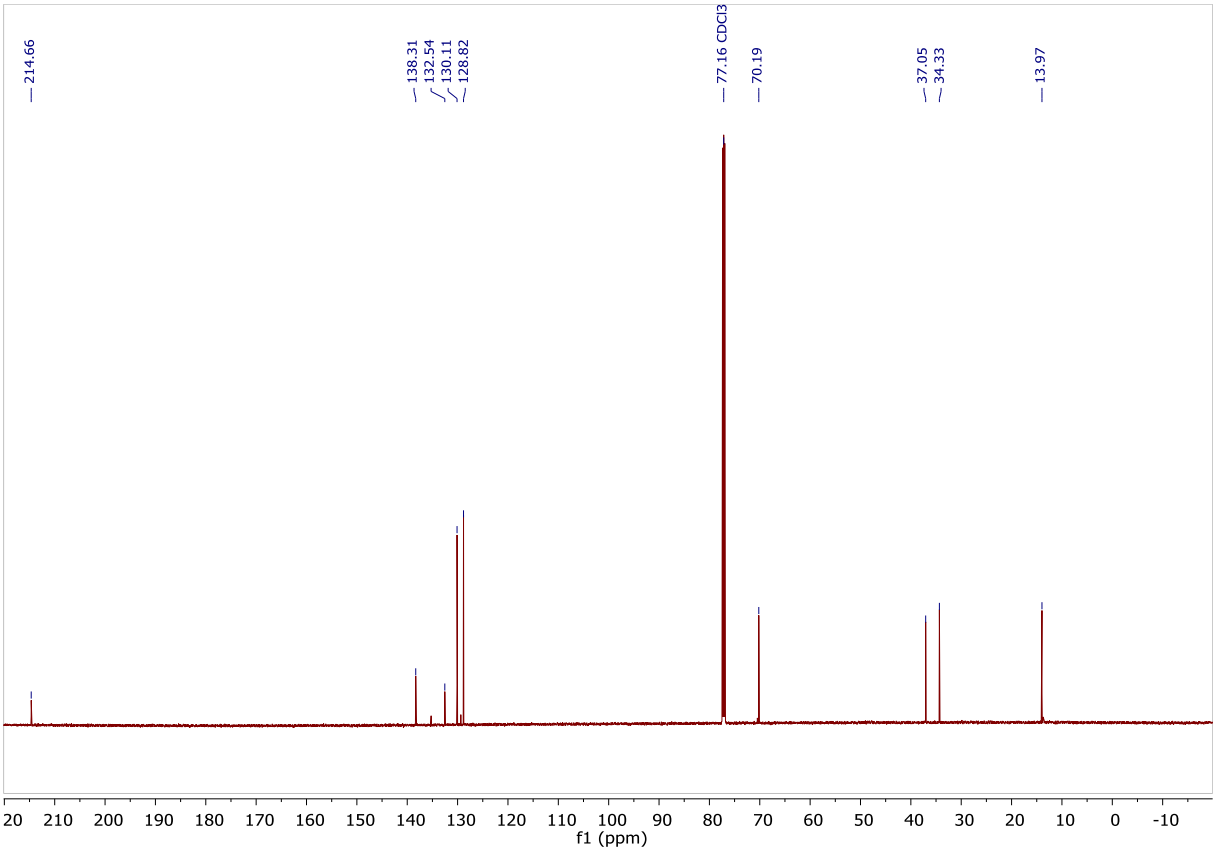

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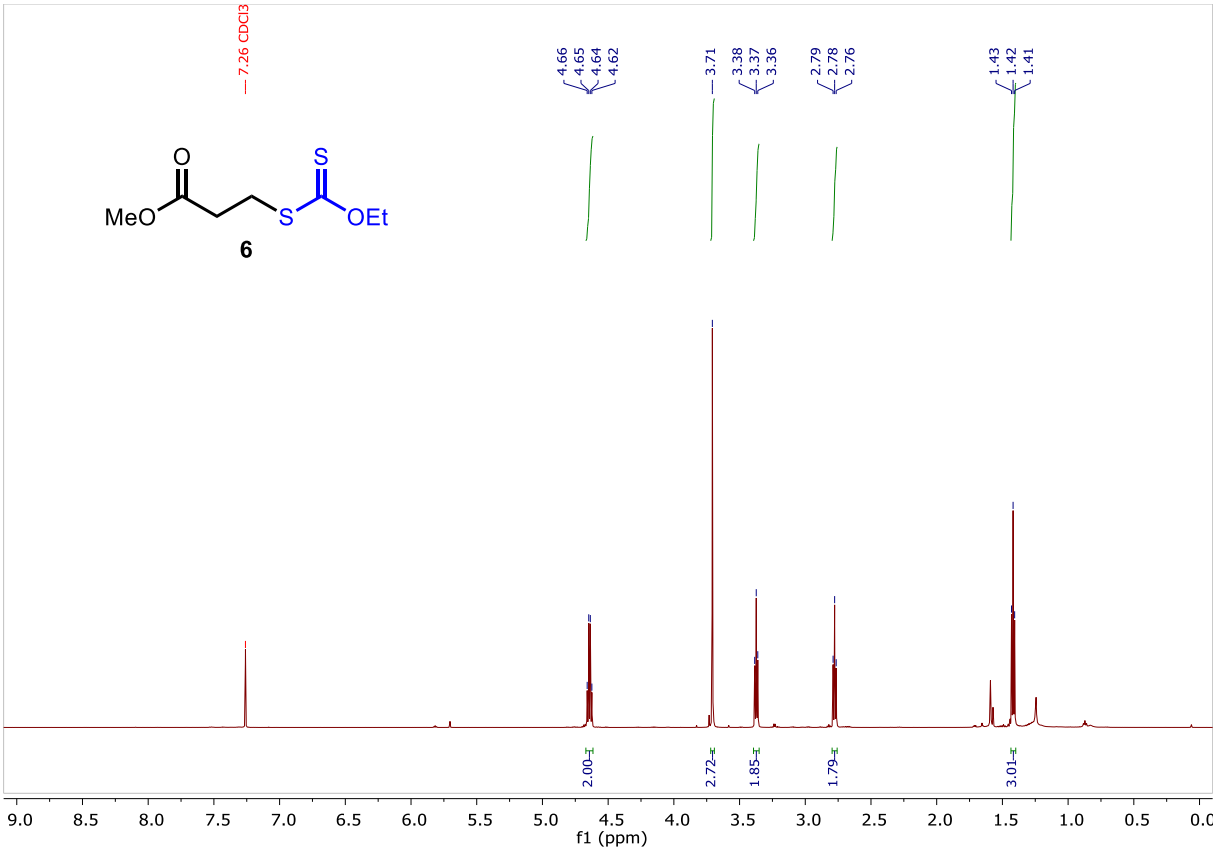

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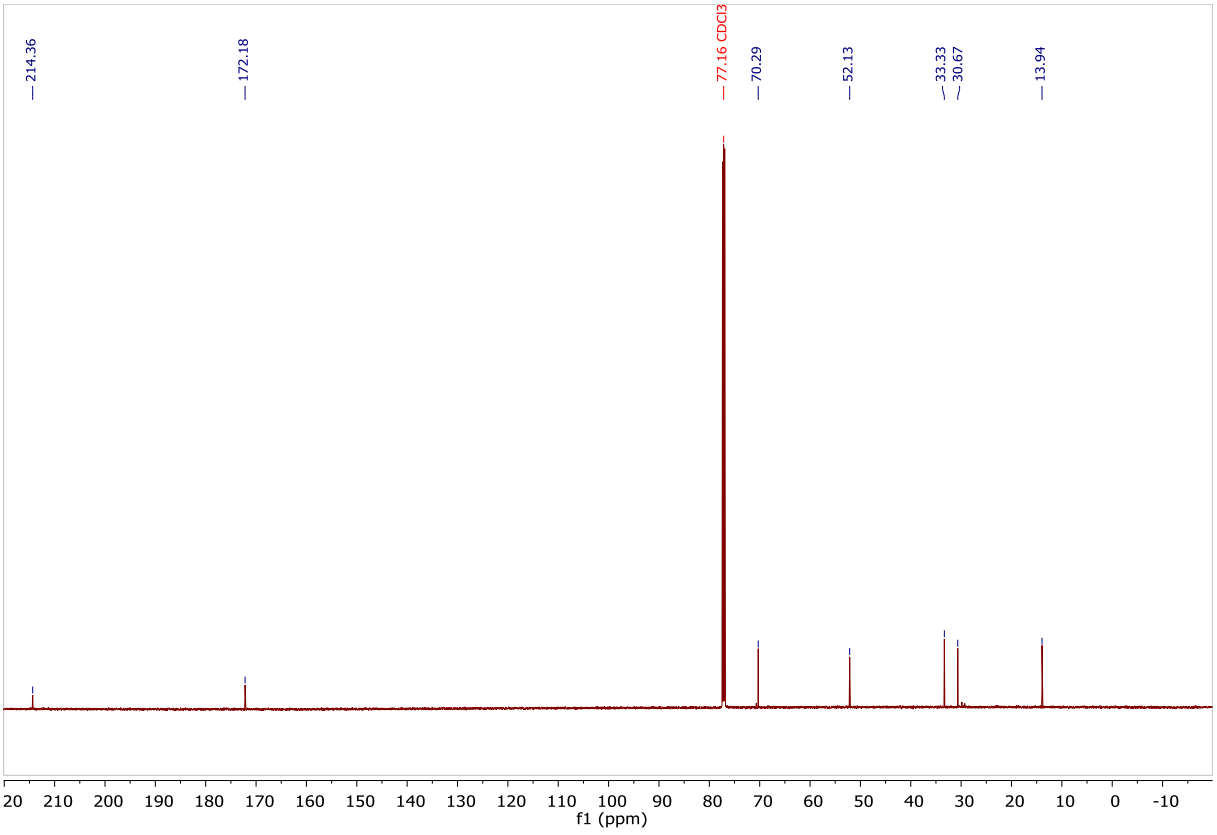

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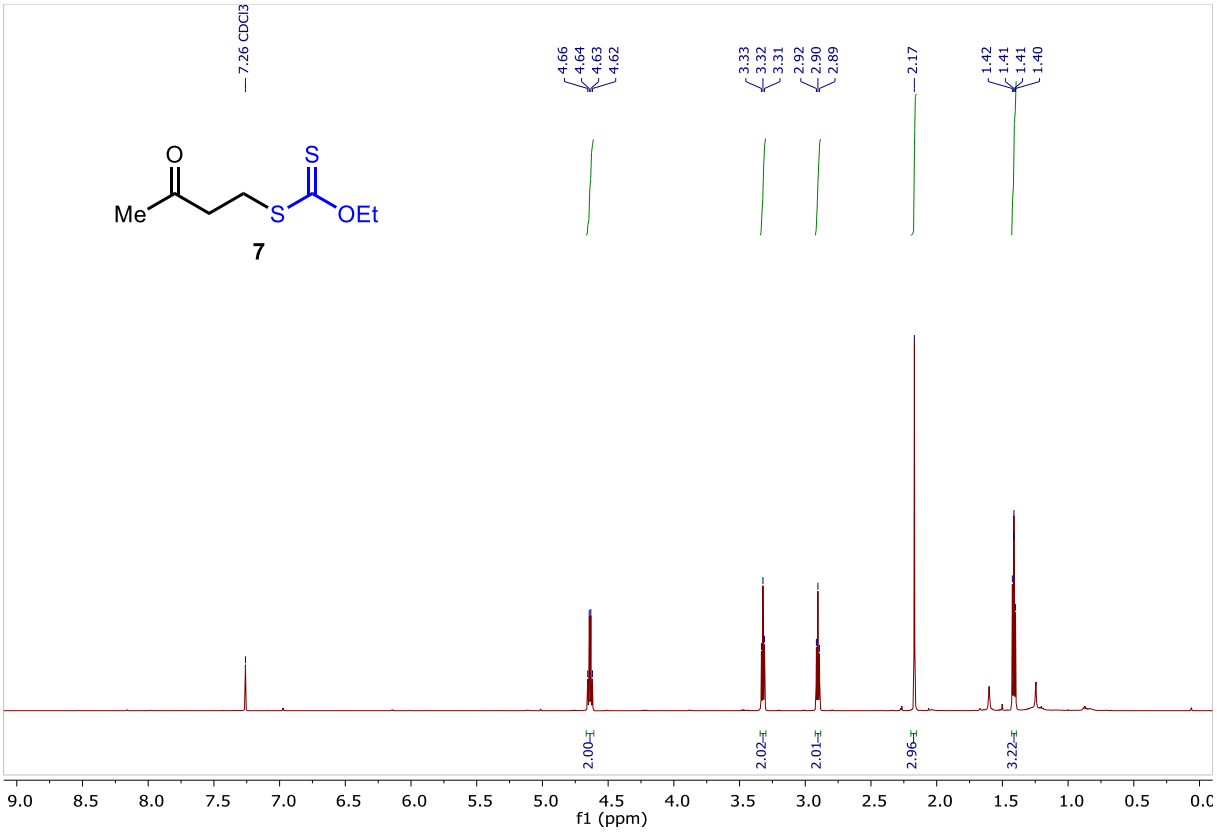

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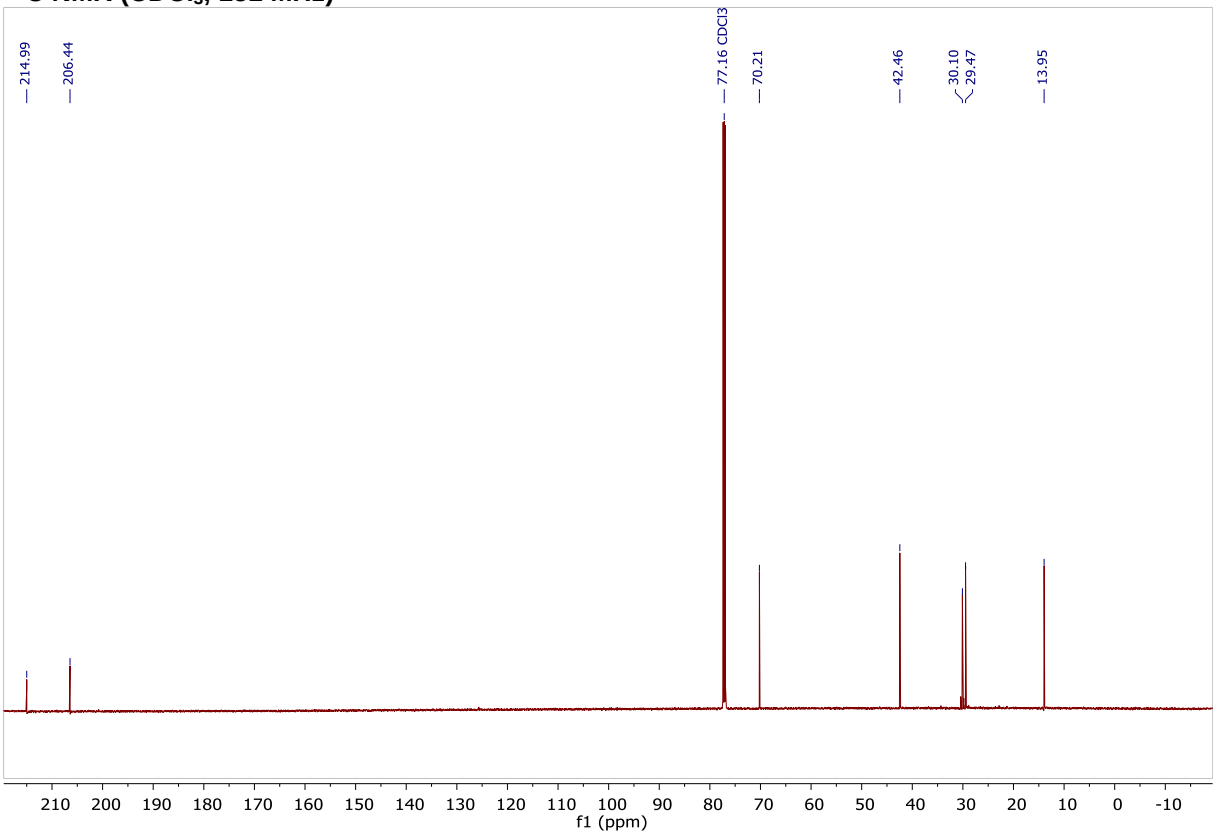

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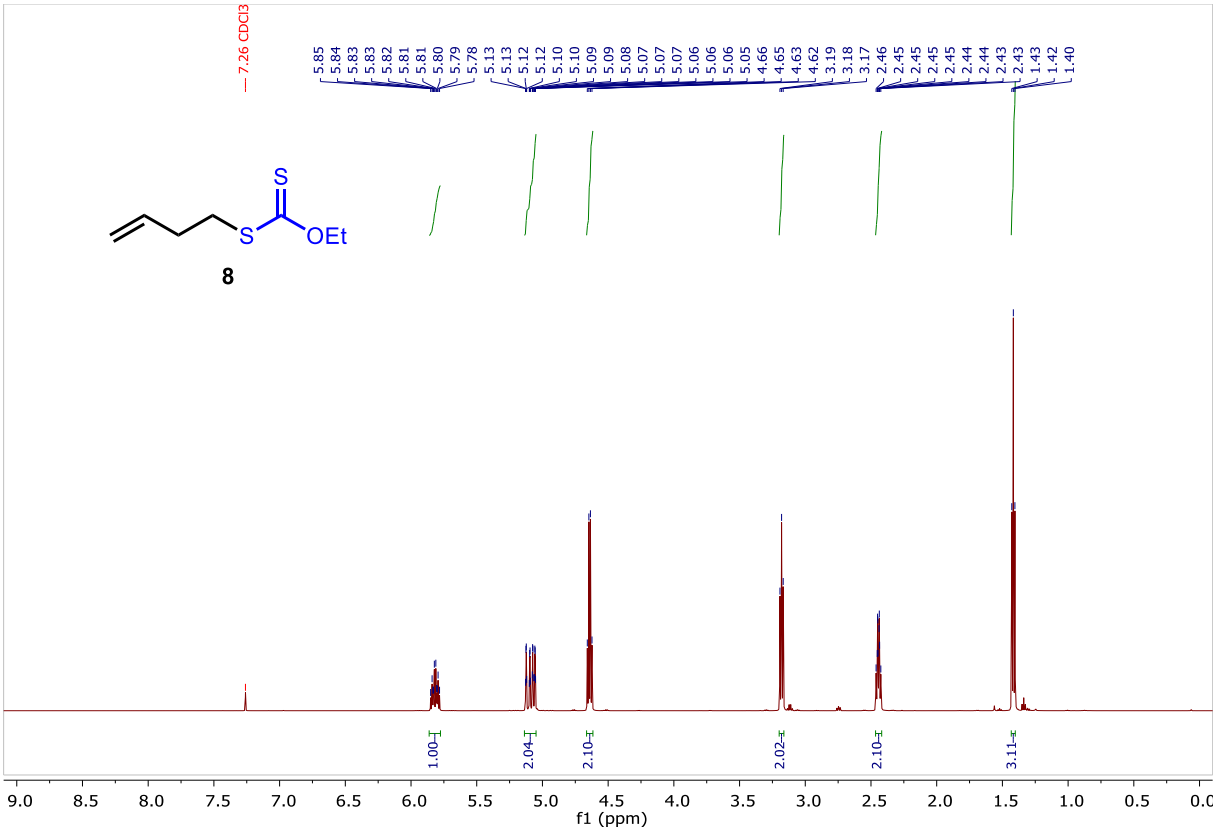

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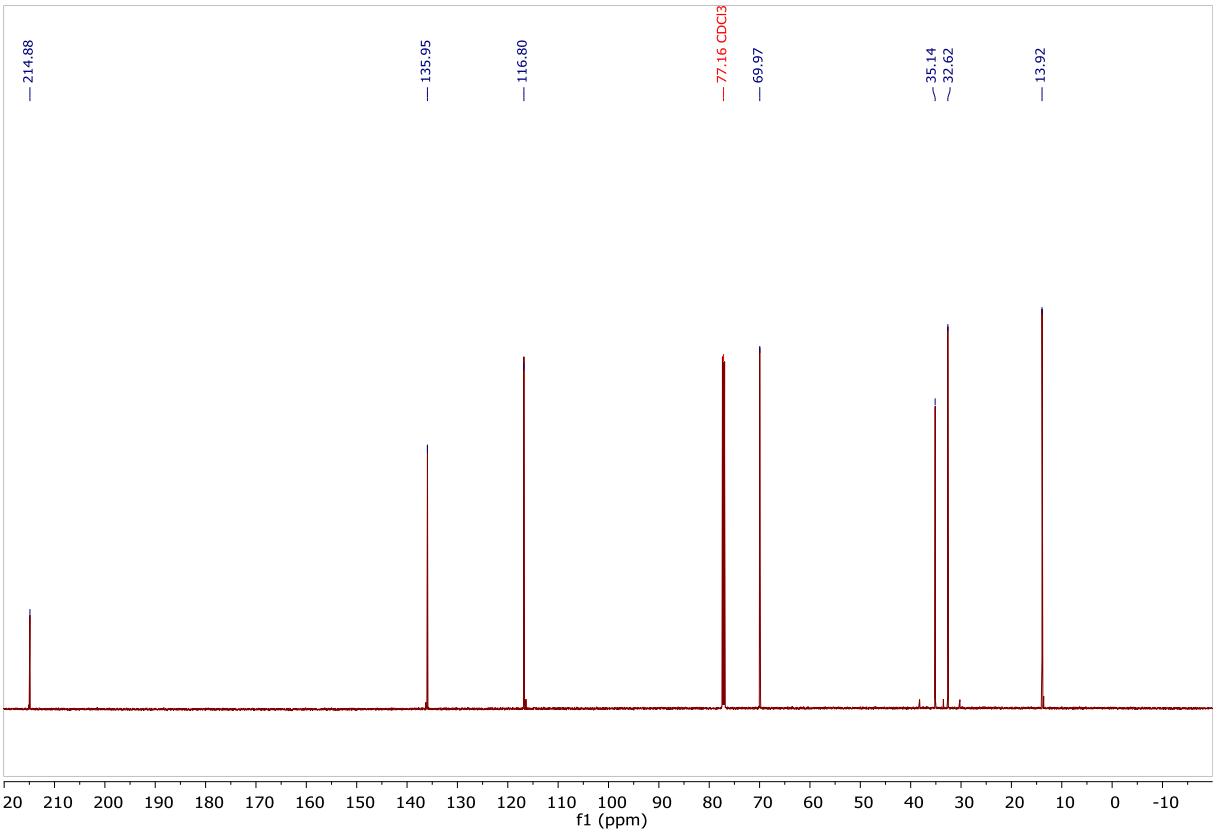
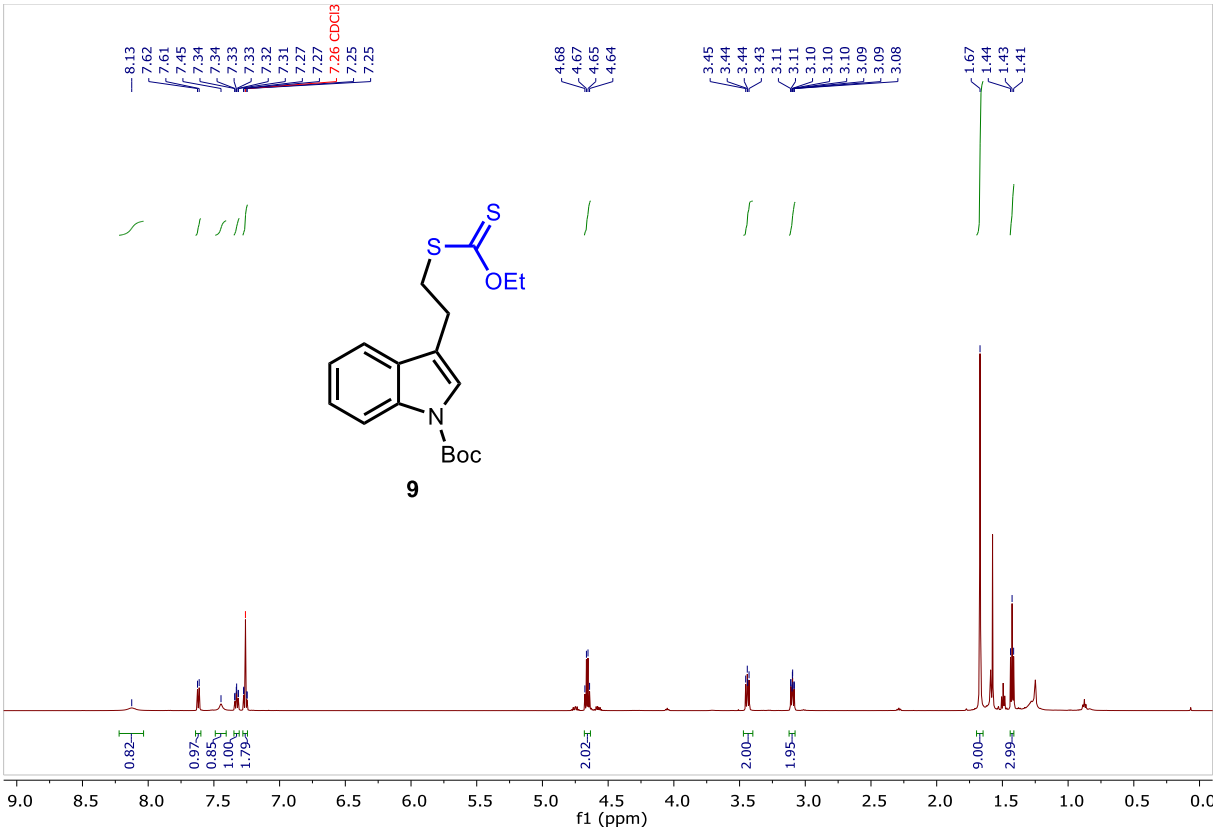
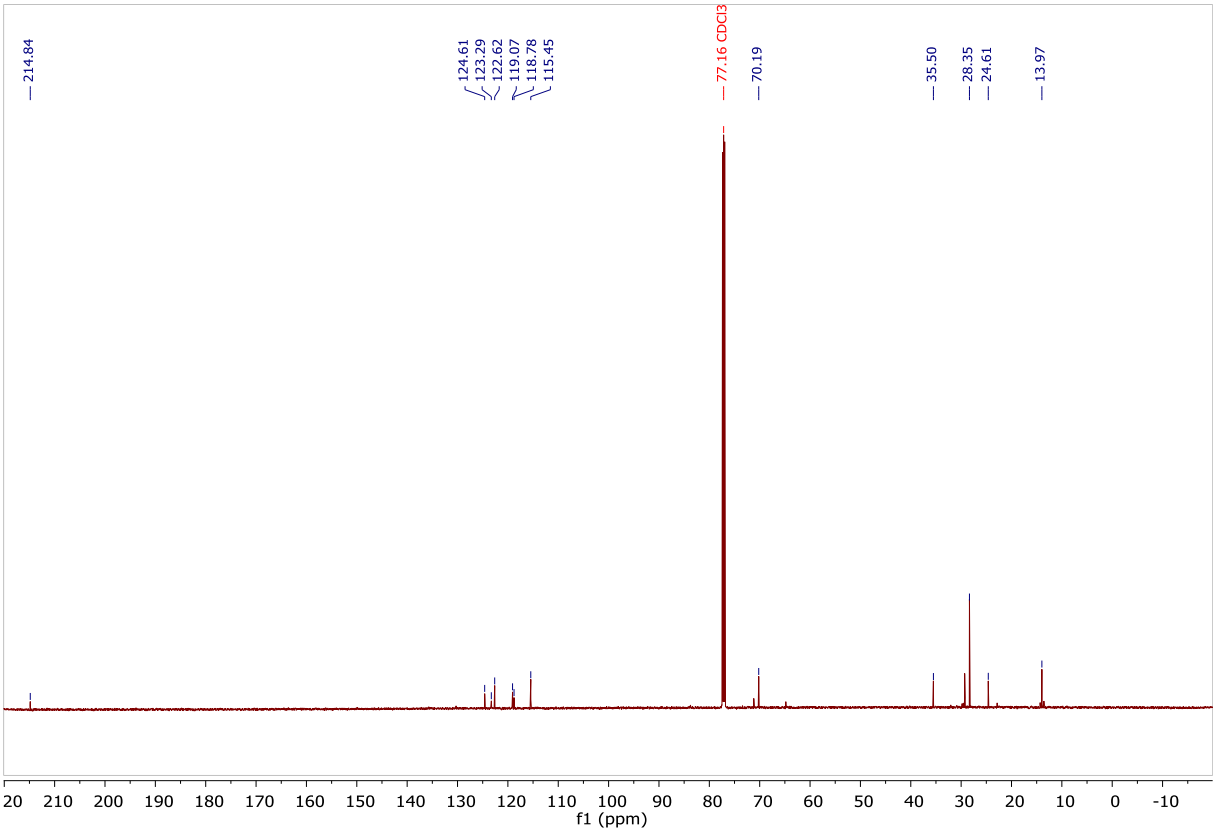


^{1}H NMR ($CDCl_3$, 600 MHz)

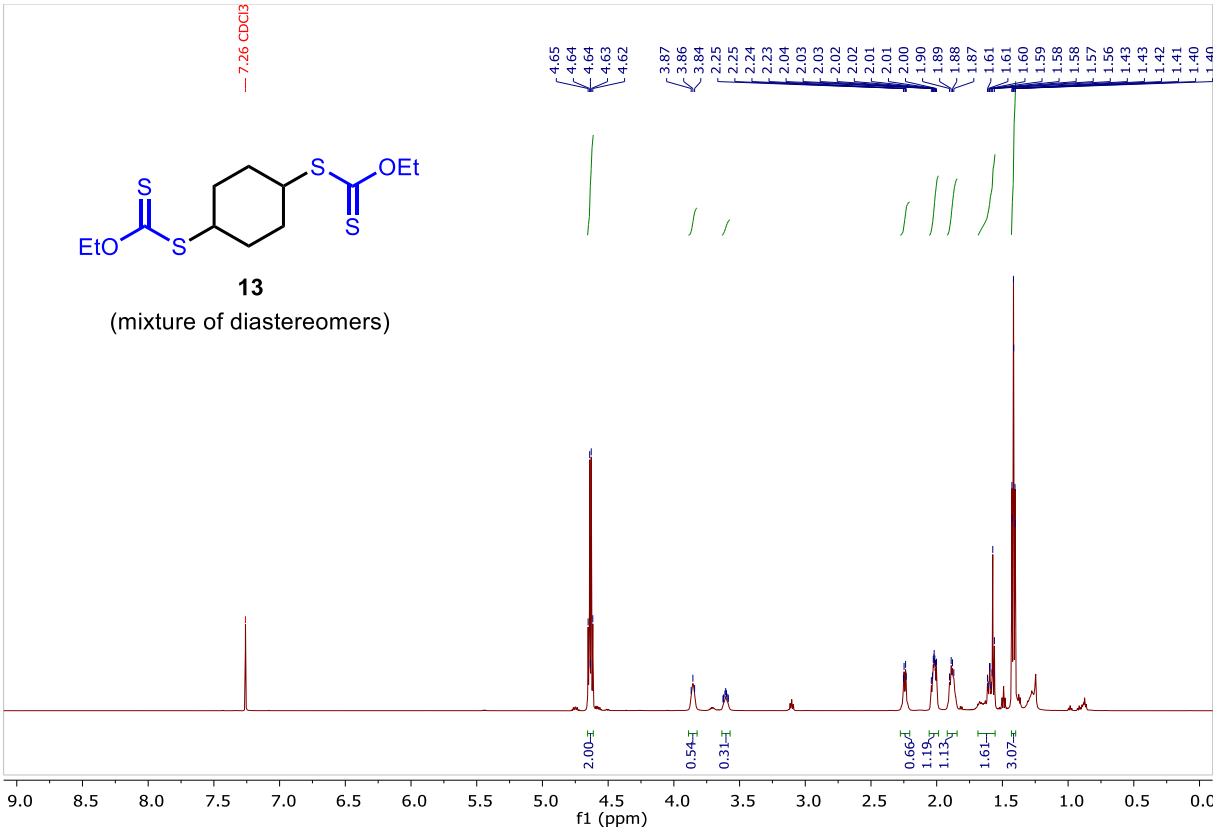


9

^{13}C NMR ($CDCl_3$, 151 MHz)



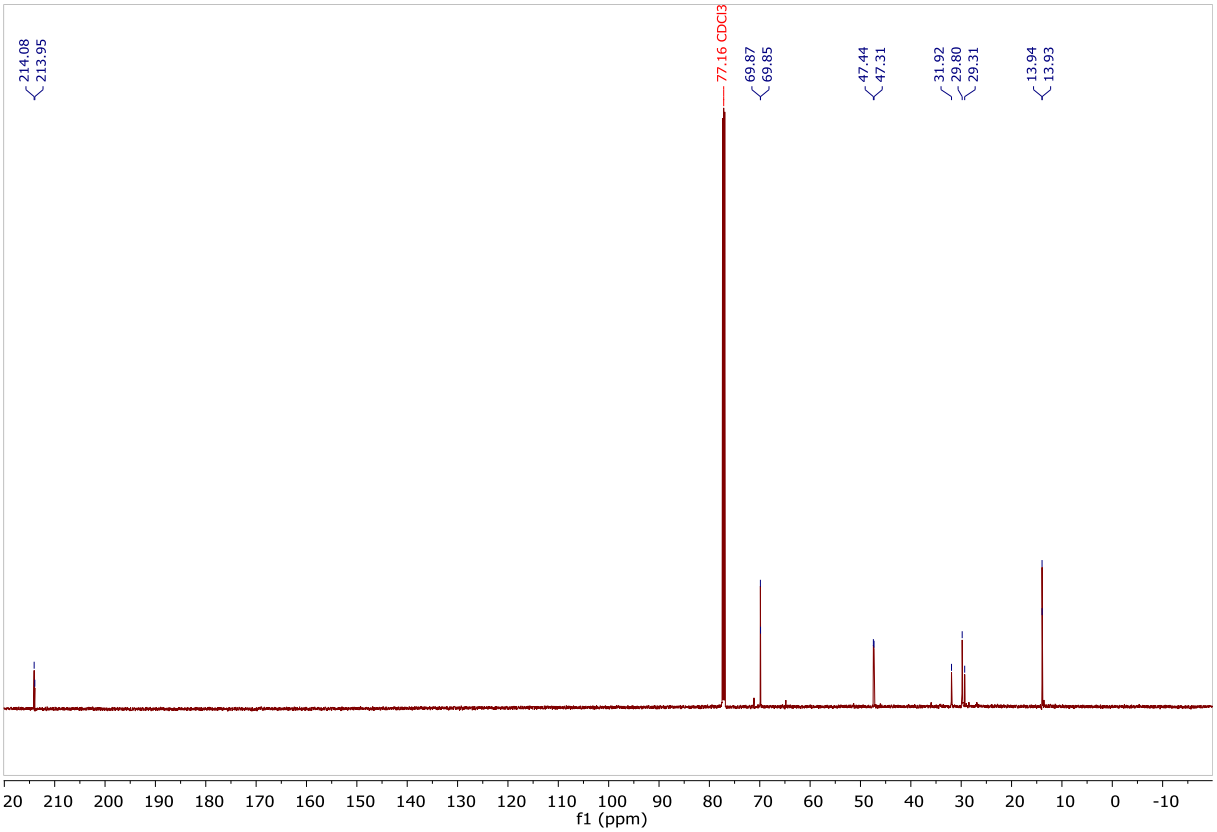
^{1}H NMR ($CDCl_3$, 600 MHz)



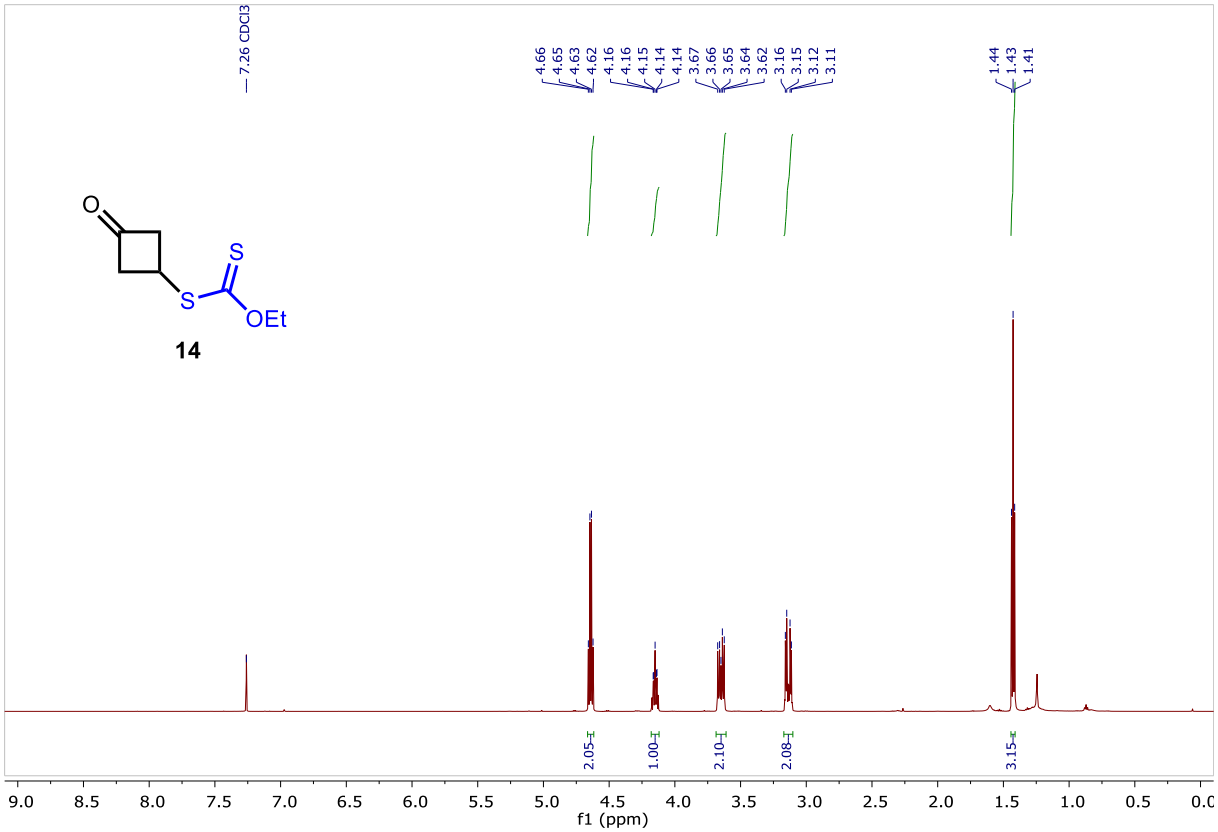
13

(mixture of diastereomers)

^{13}C NMR ($CDCl_3$, 151 MHz)



^{1}H NMR ($CDCl_3$, 600 MHz)



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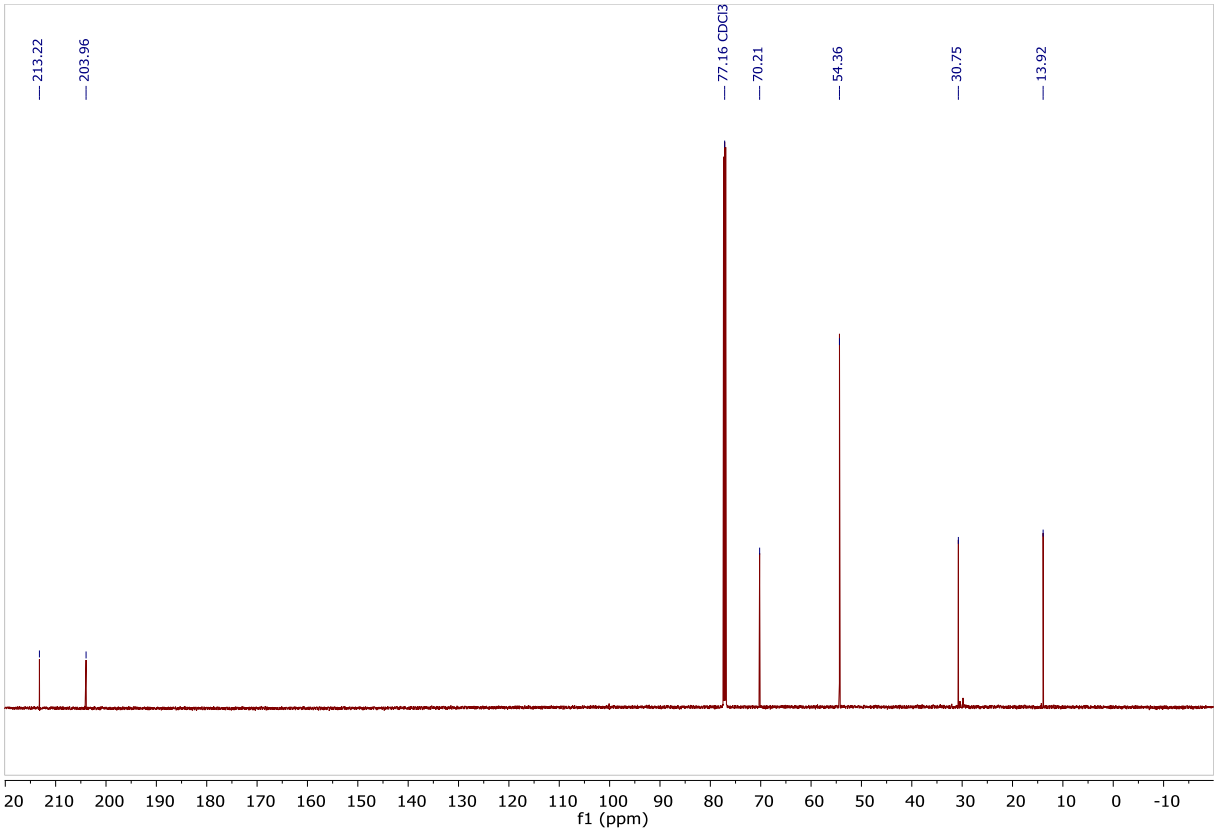
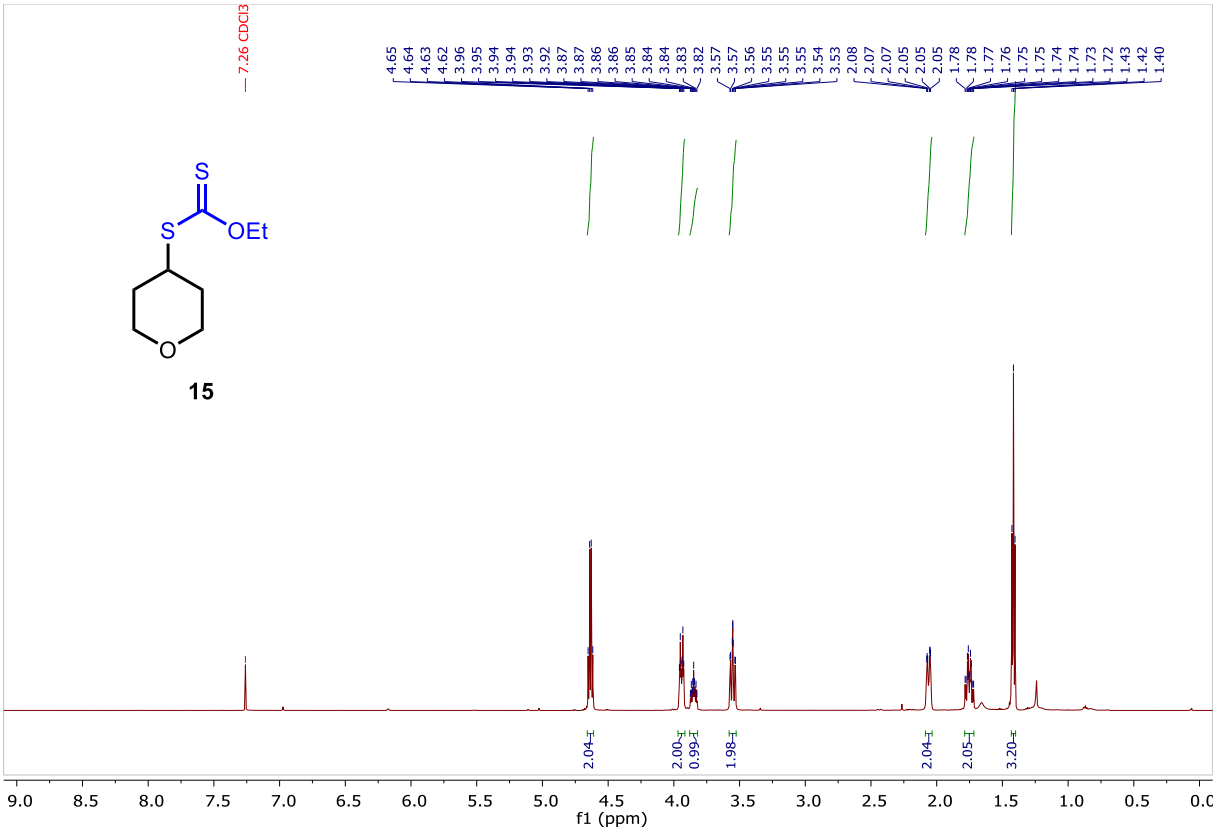


^{1}H NMR ($CDCl_3$, 600 MHz)



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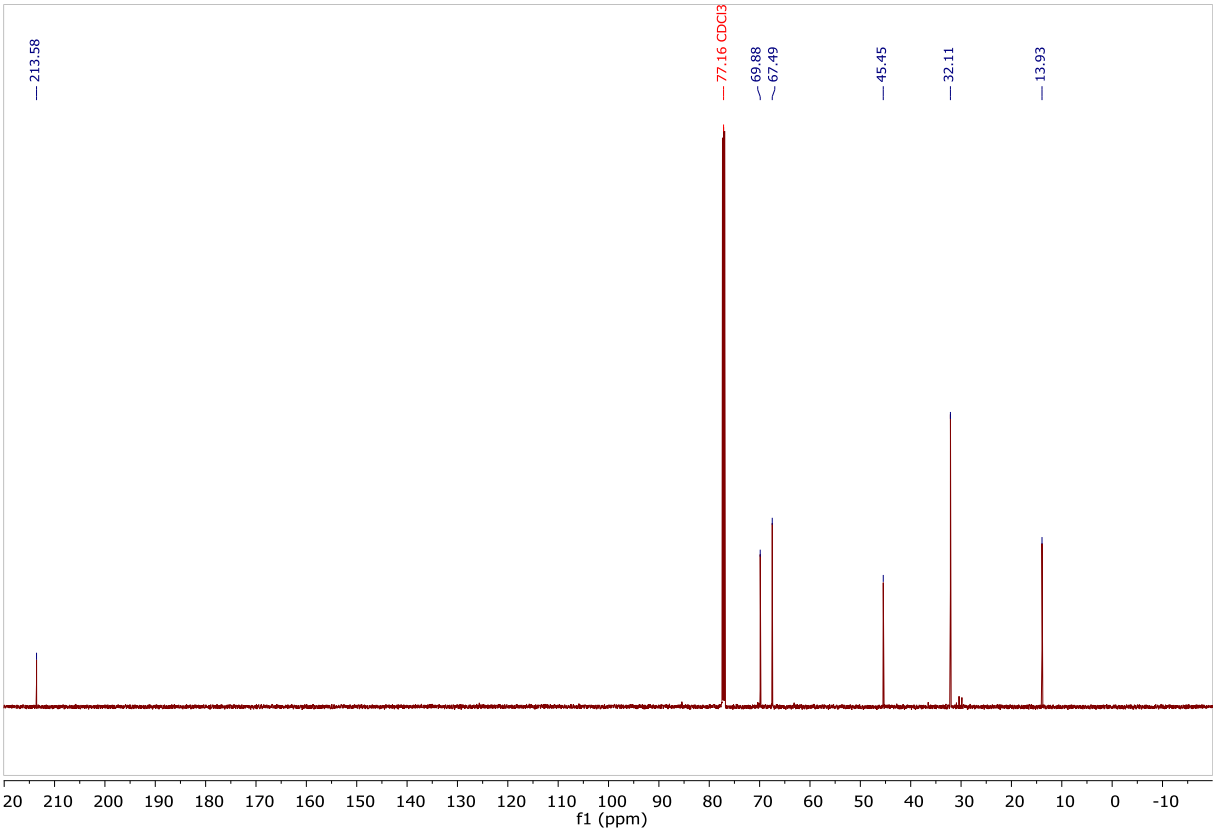

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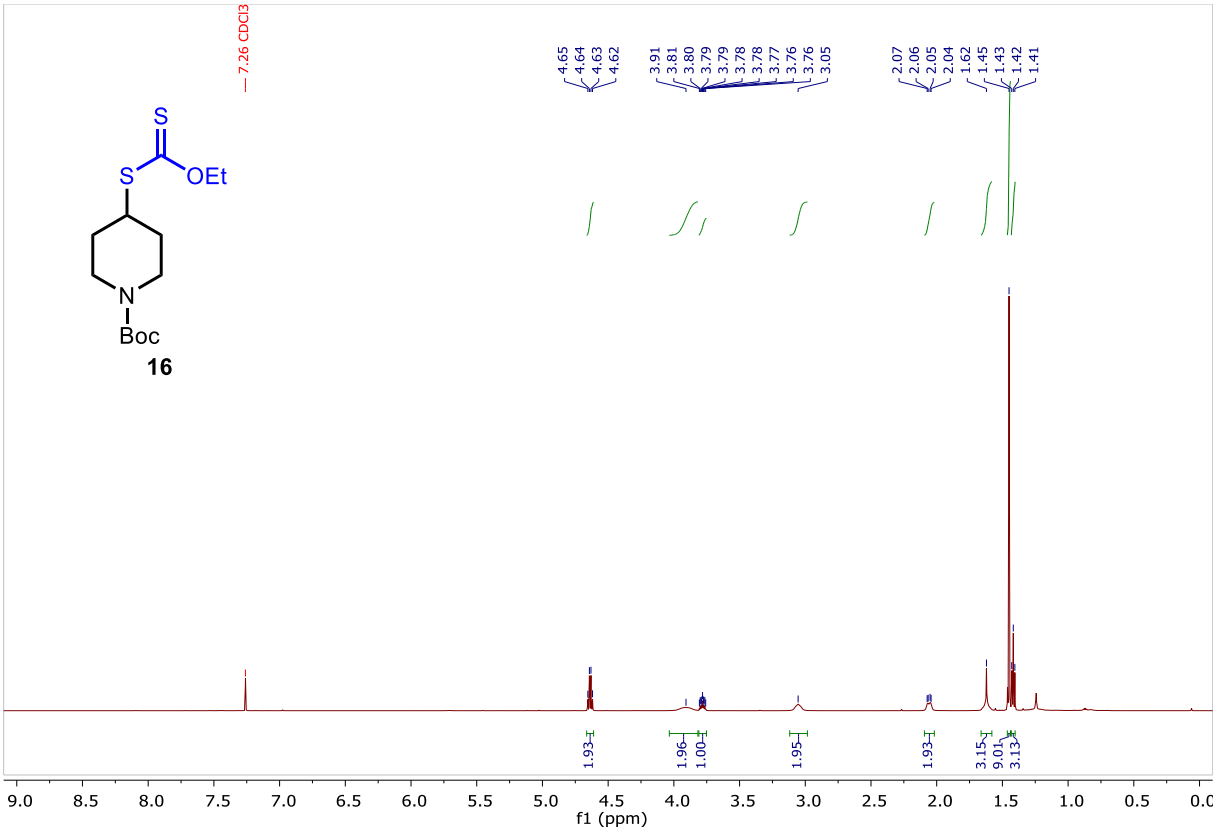

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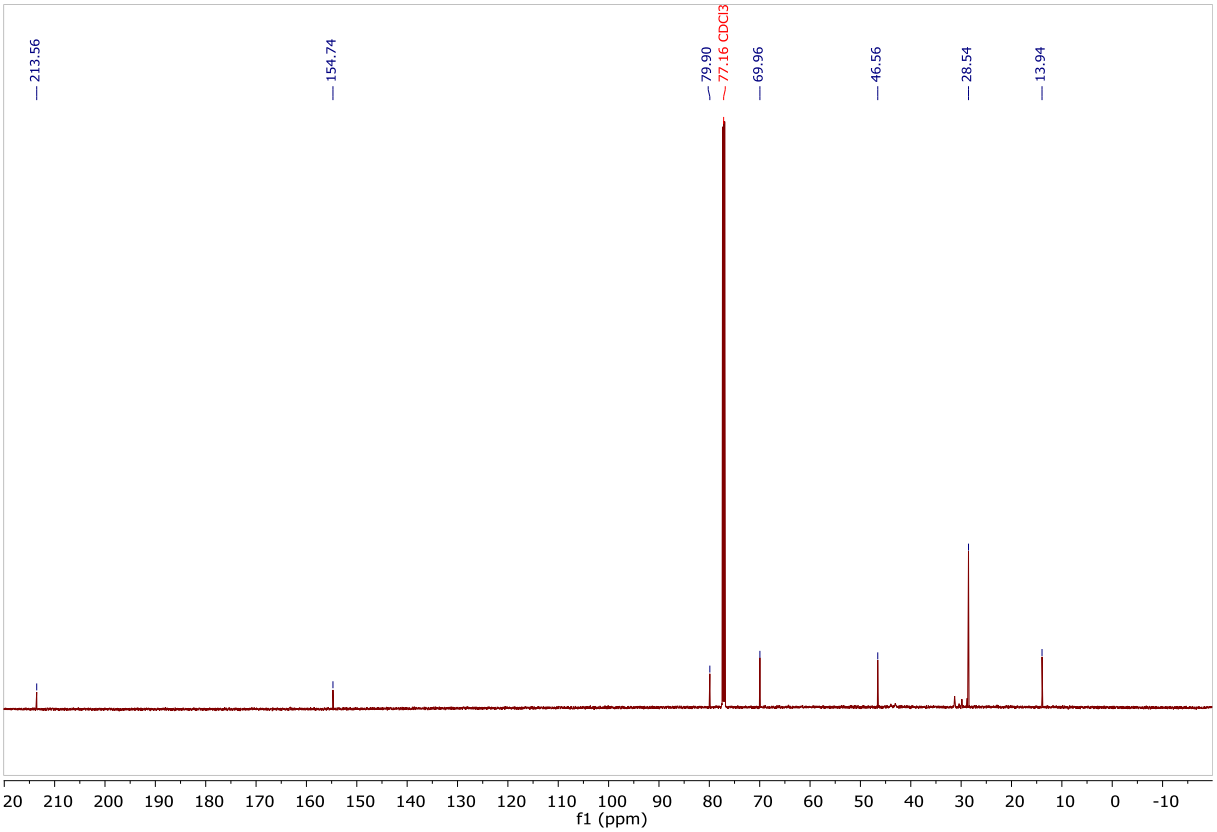
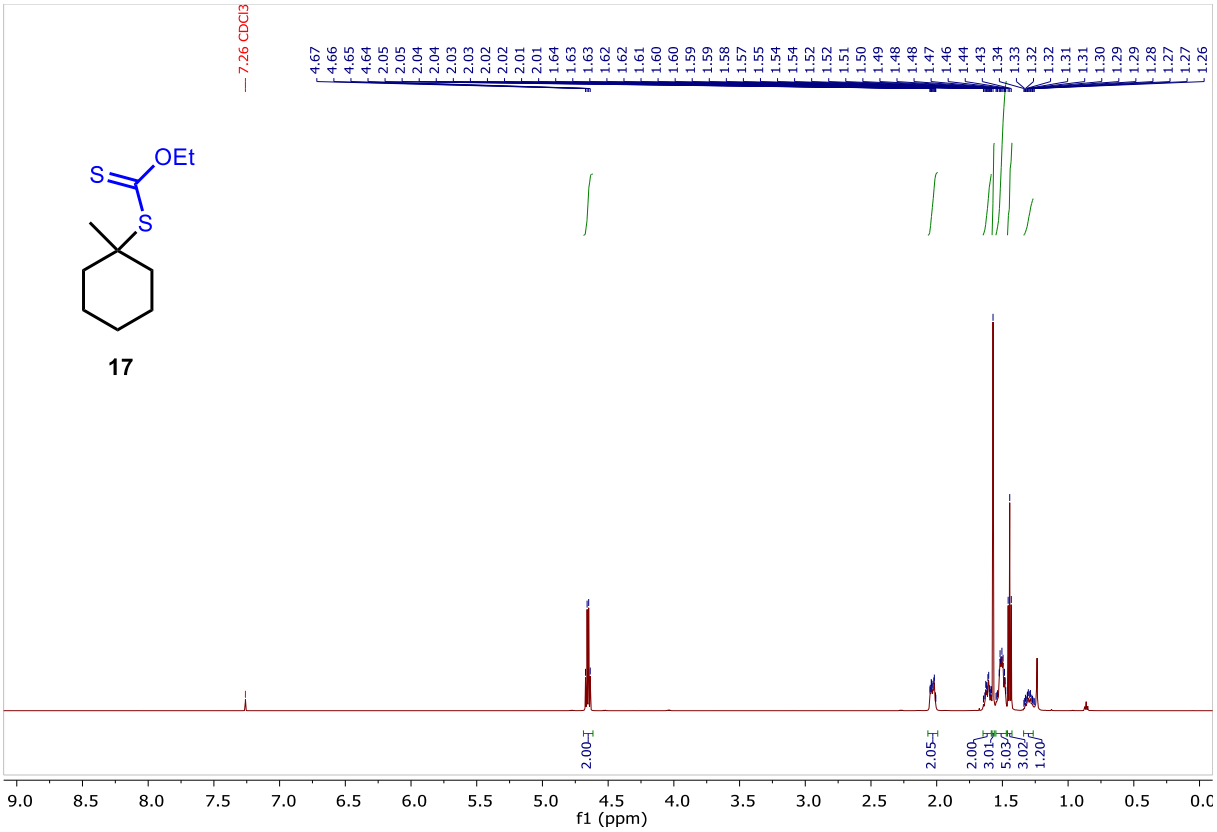


^{1}H NMR ($CDCl_3$, 600 MHz)



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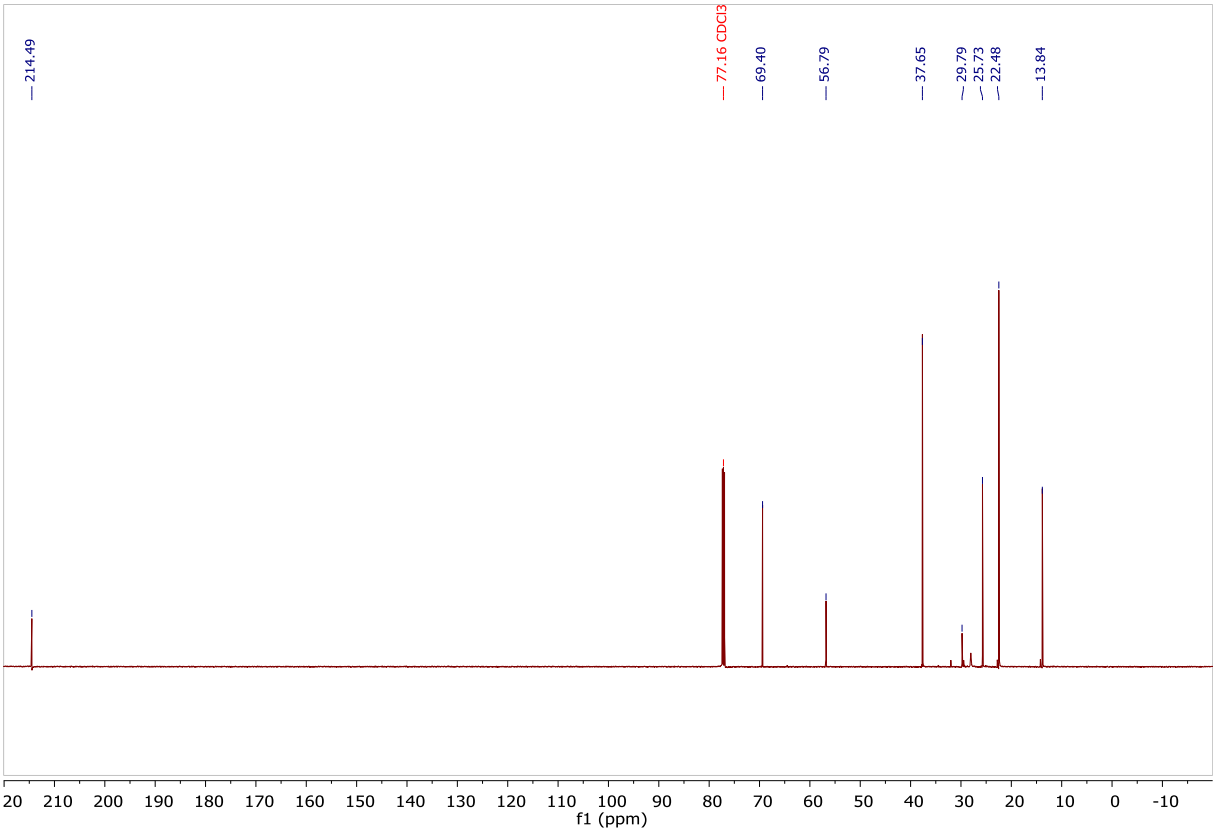

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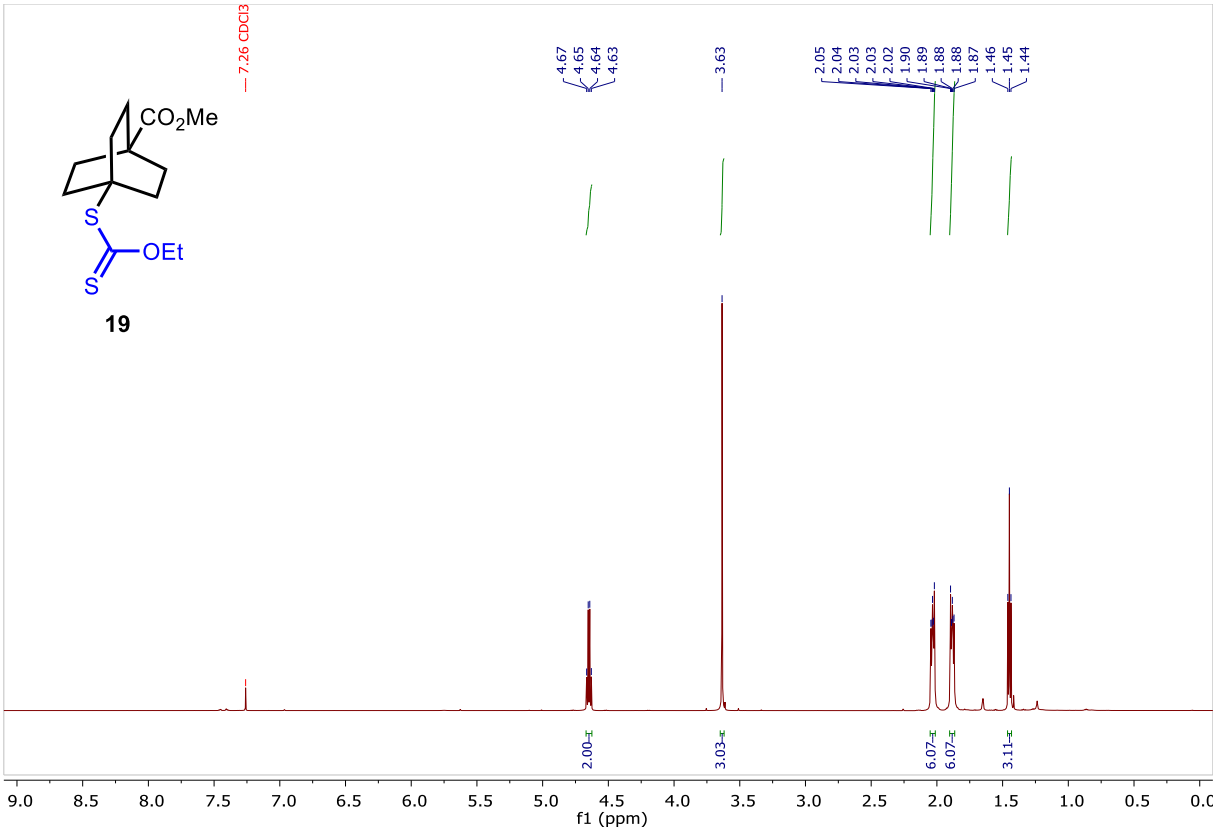

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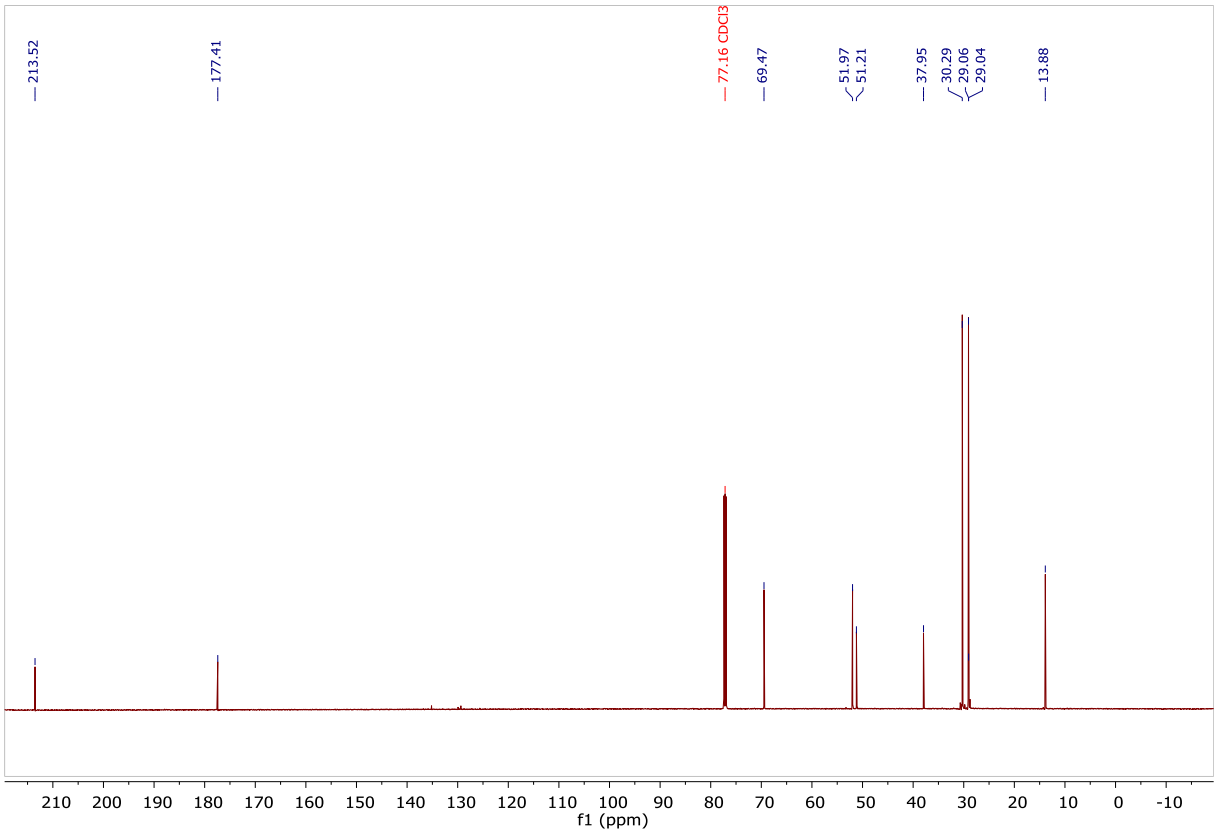

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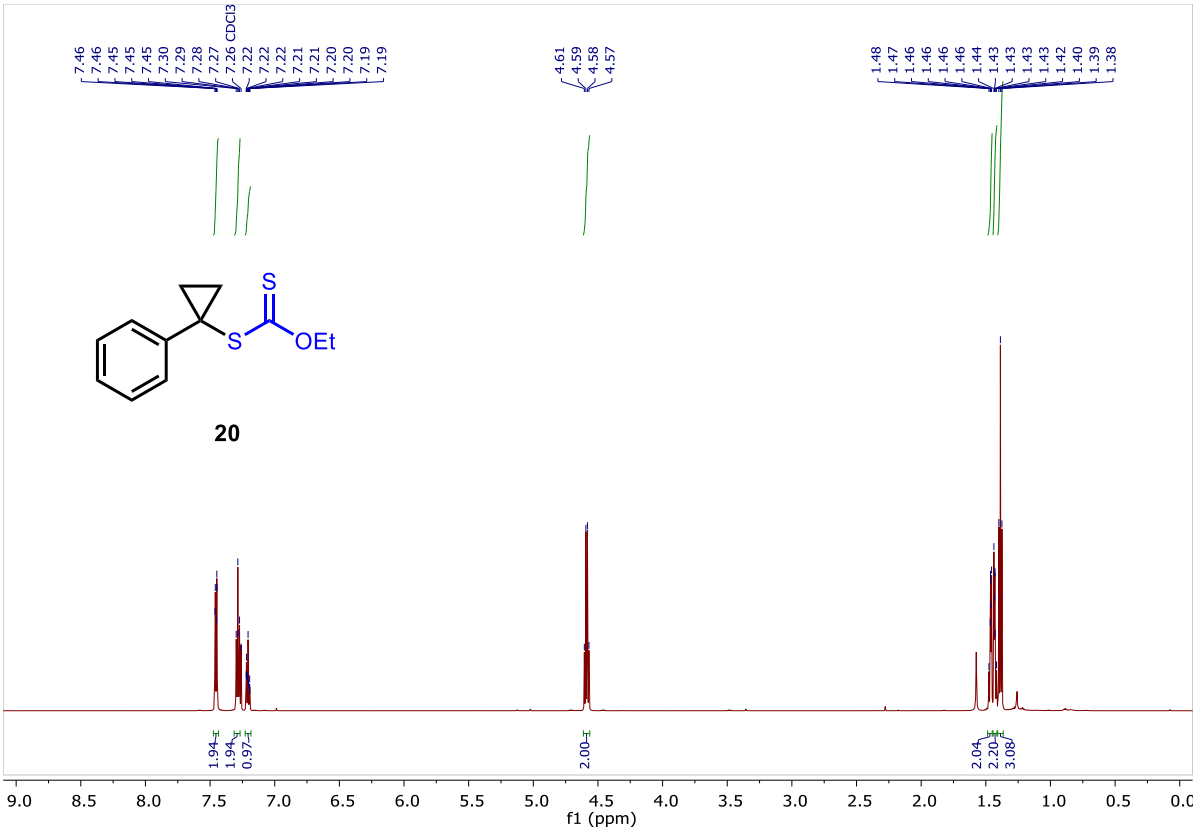

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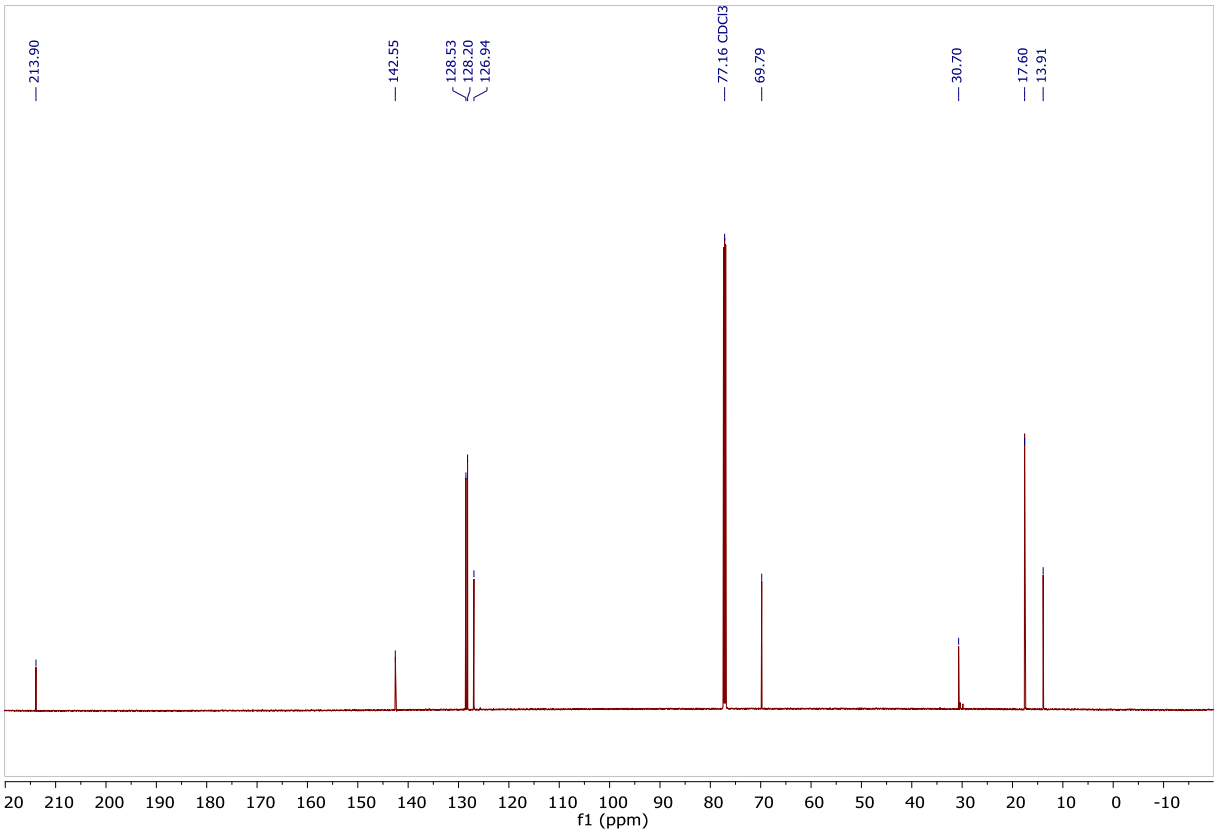
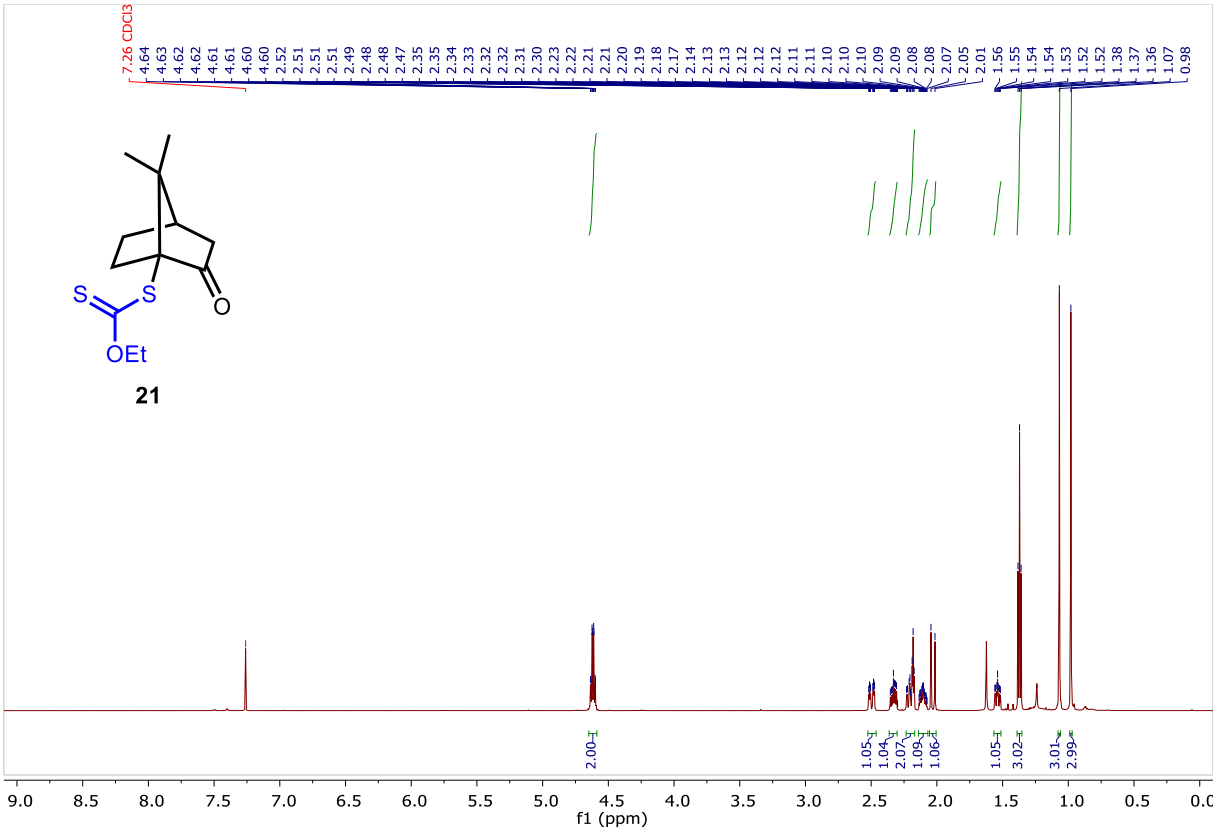


c

^{1}H NMR ($CDCl_3$, 600 MHz)



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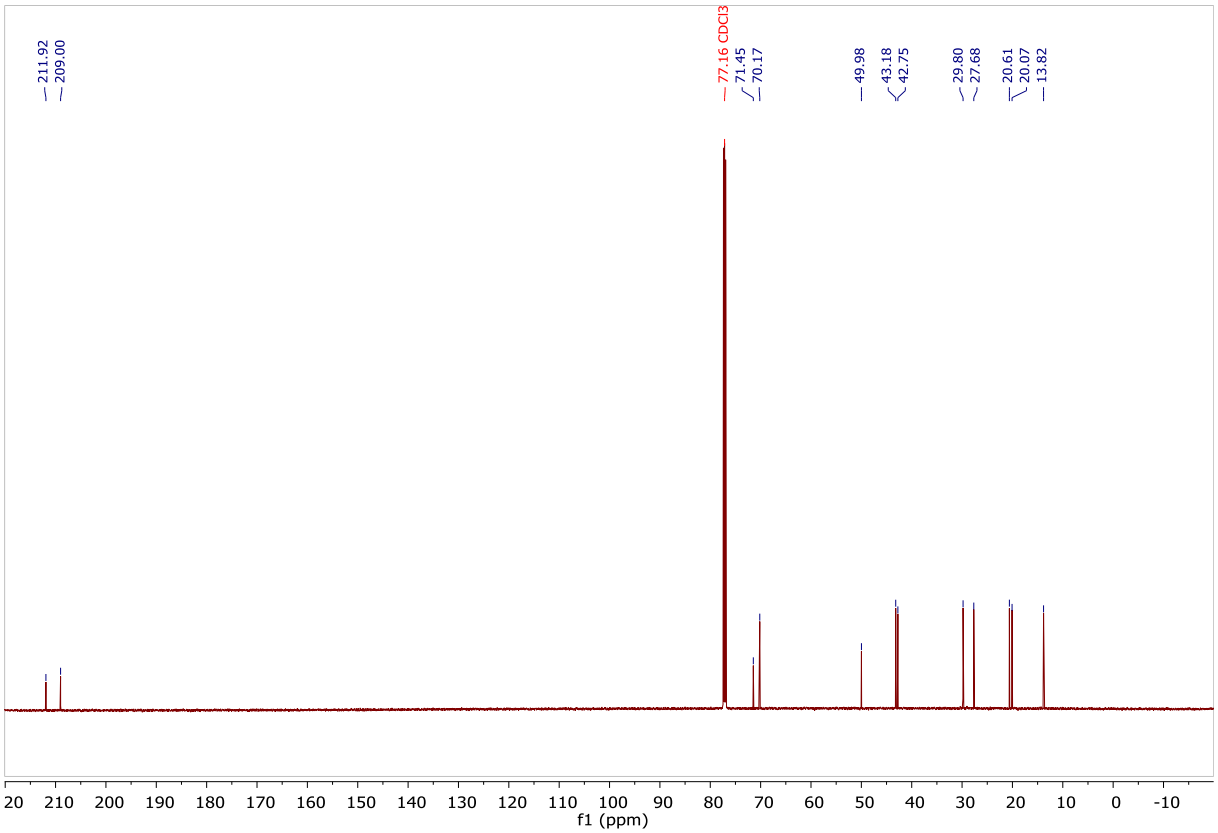

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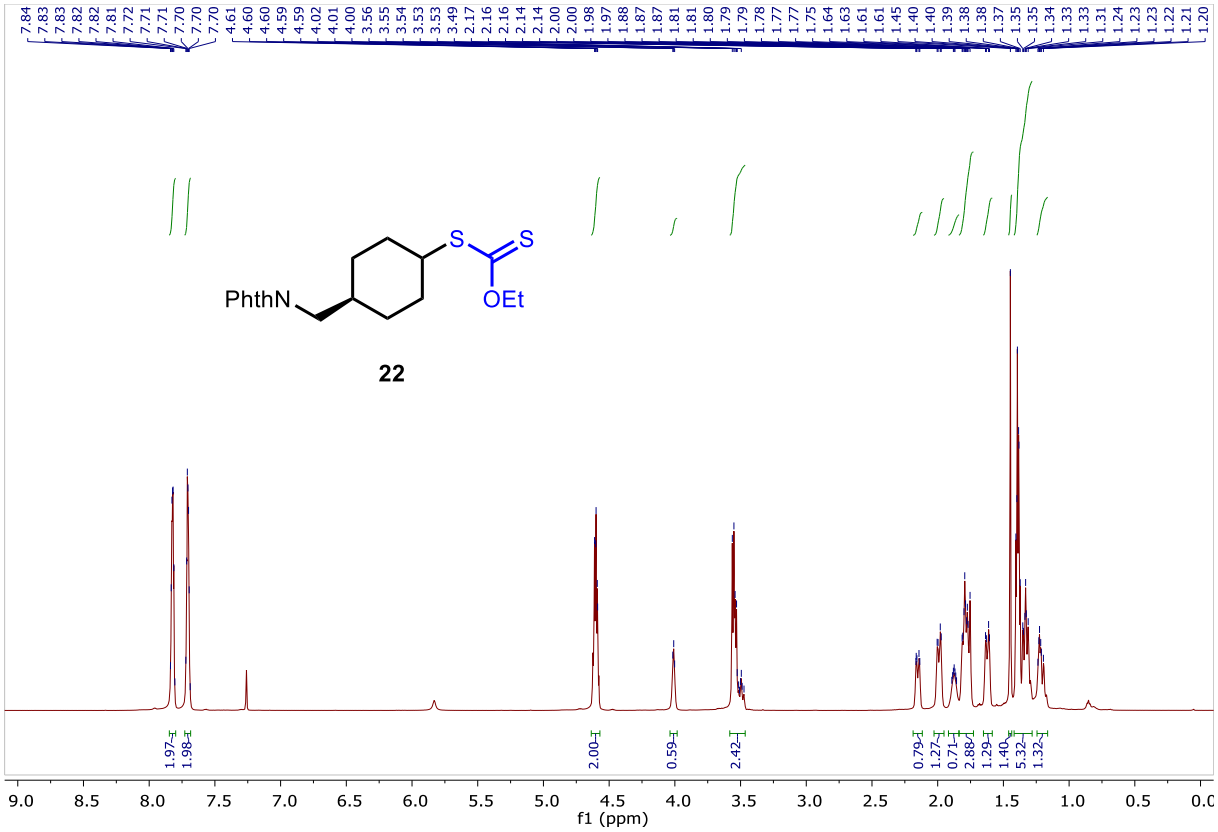

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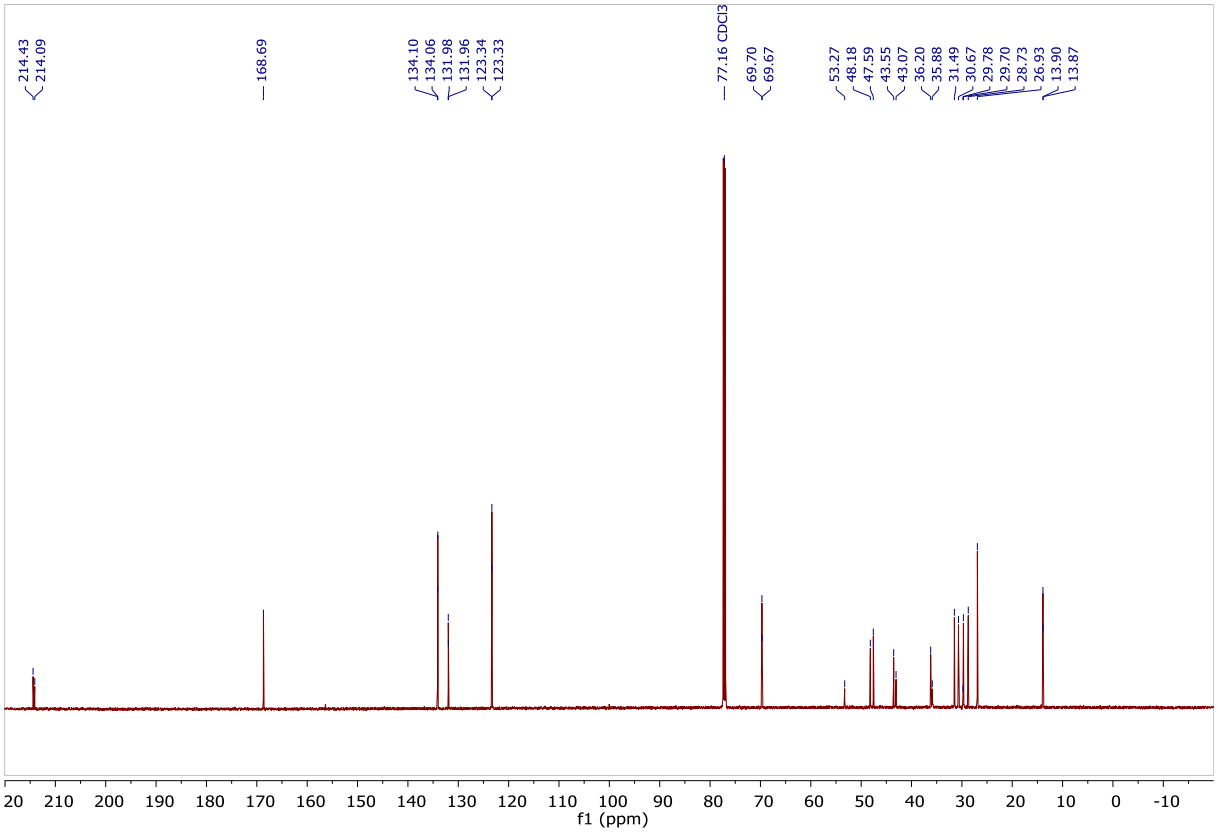

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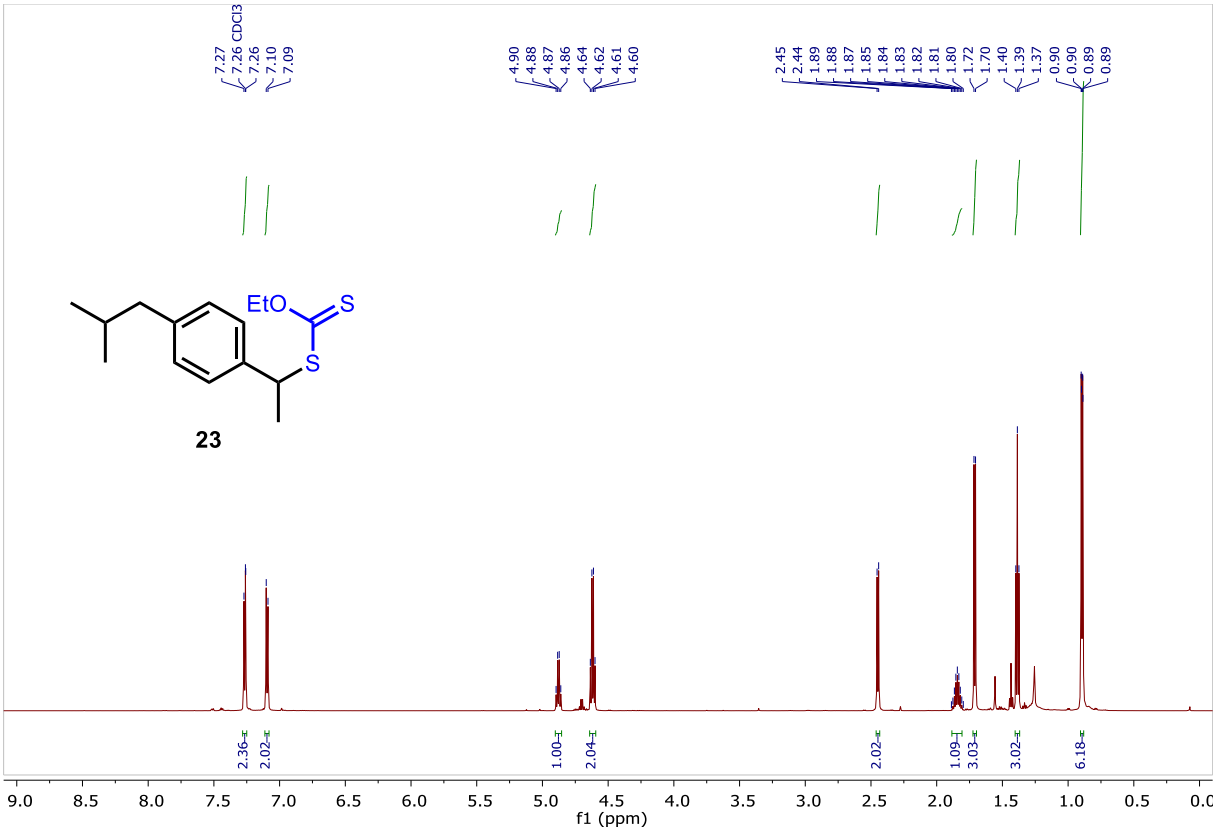

23

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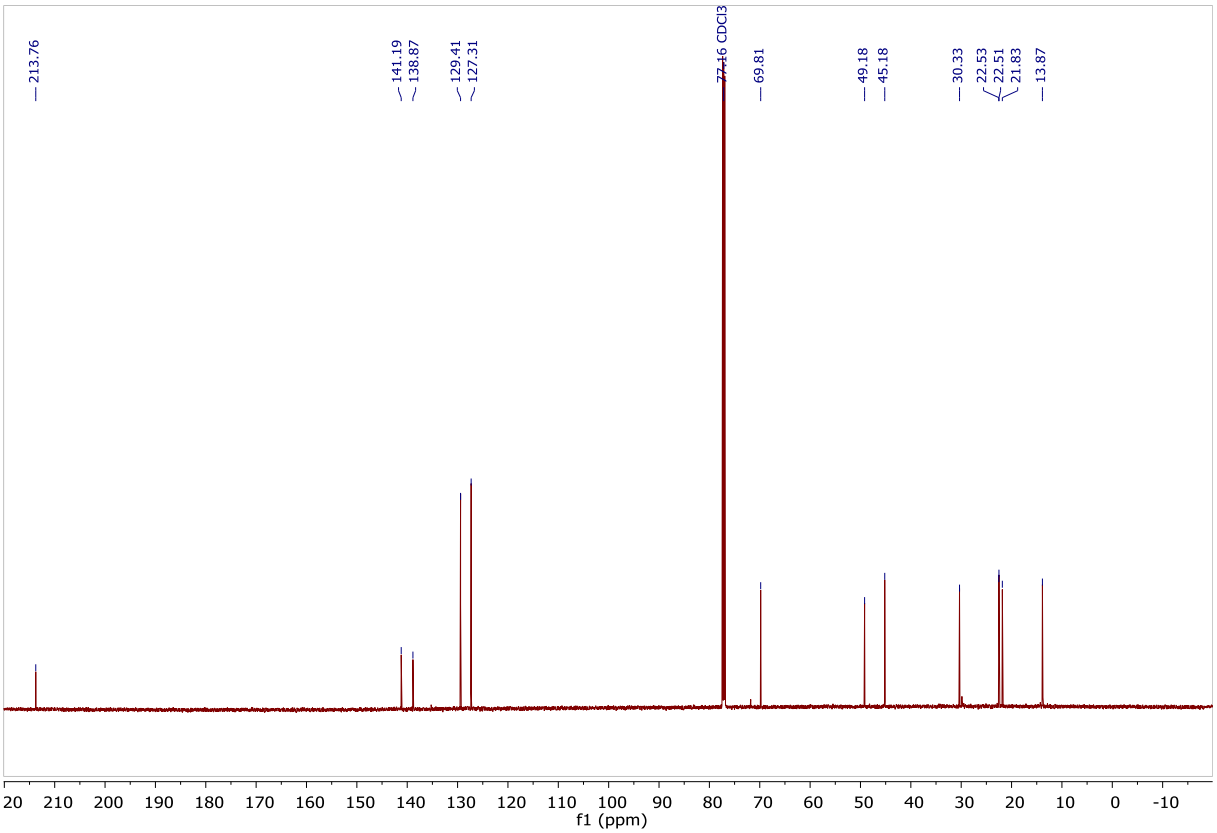
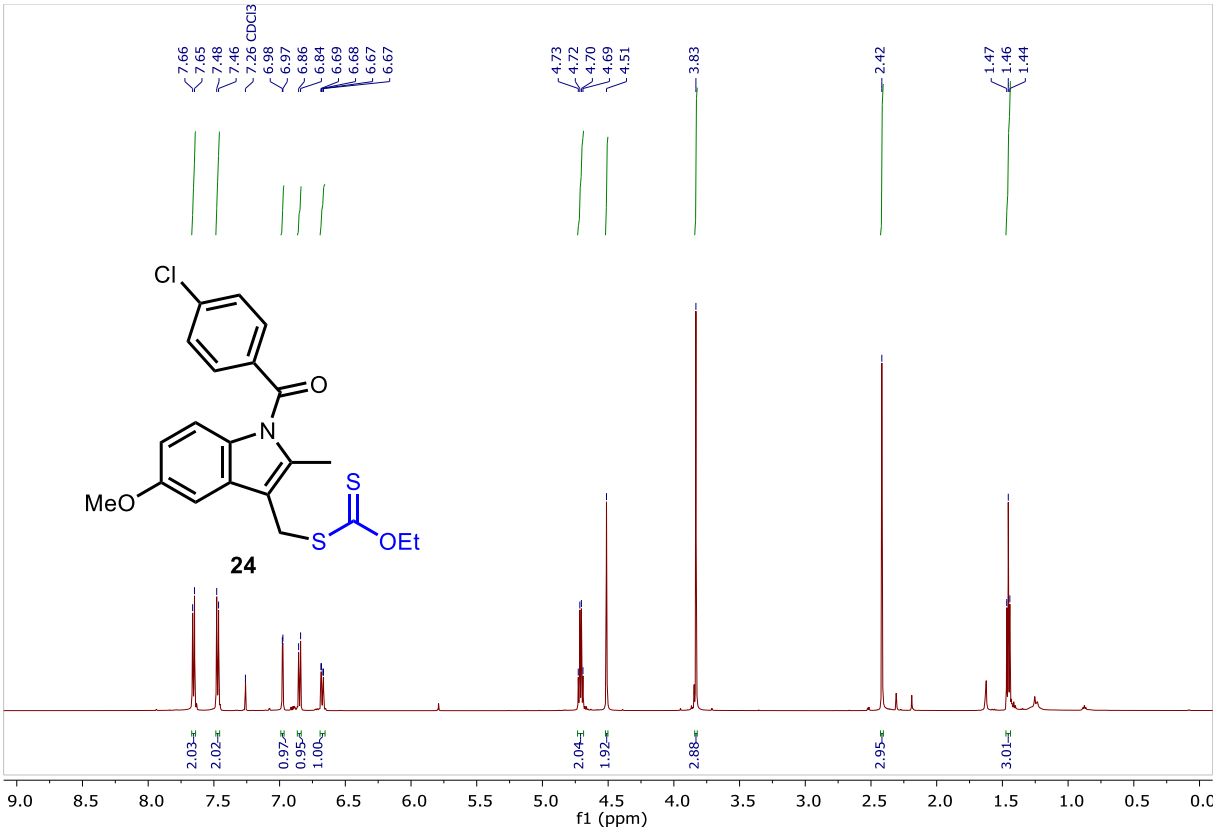
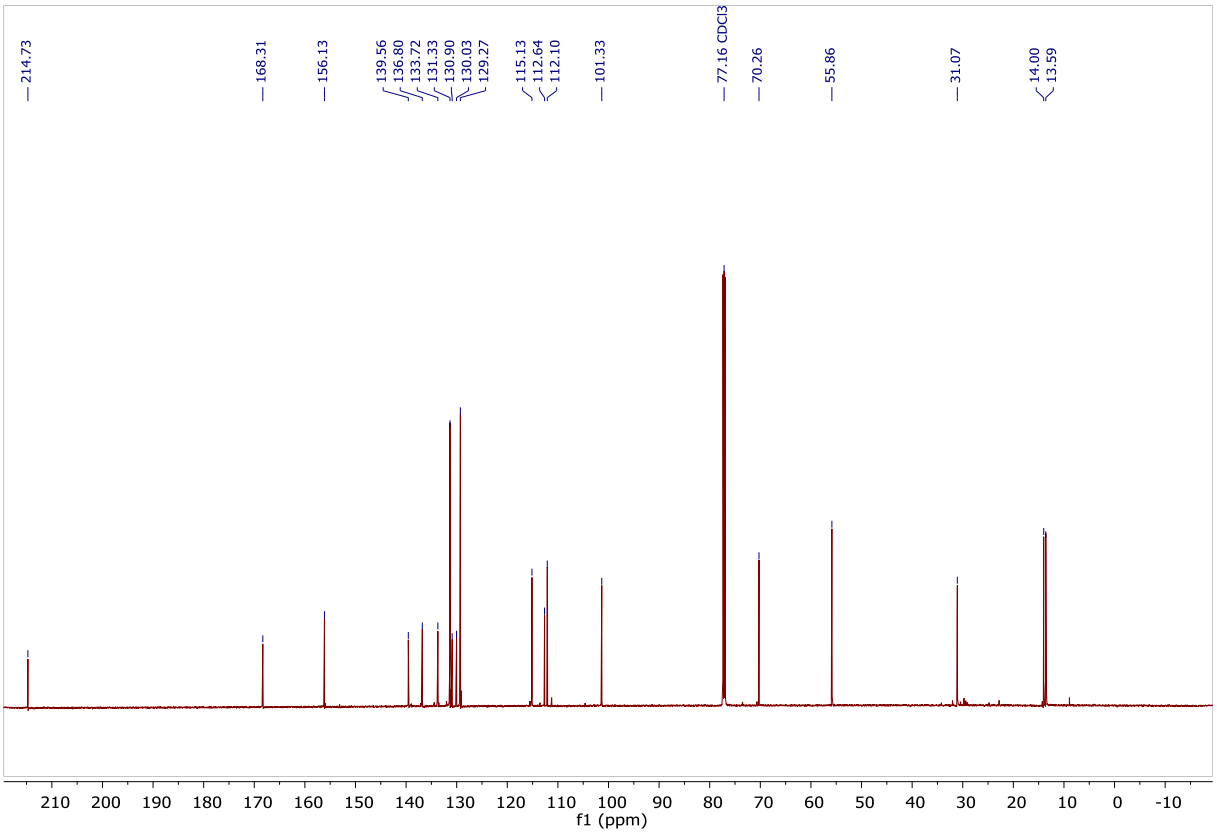


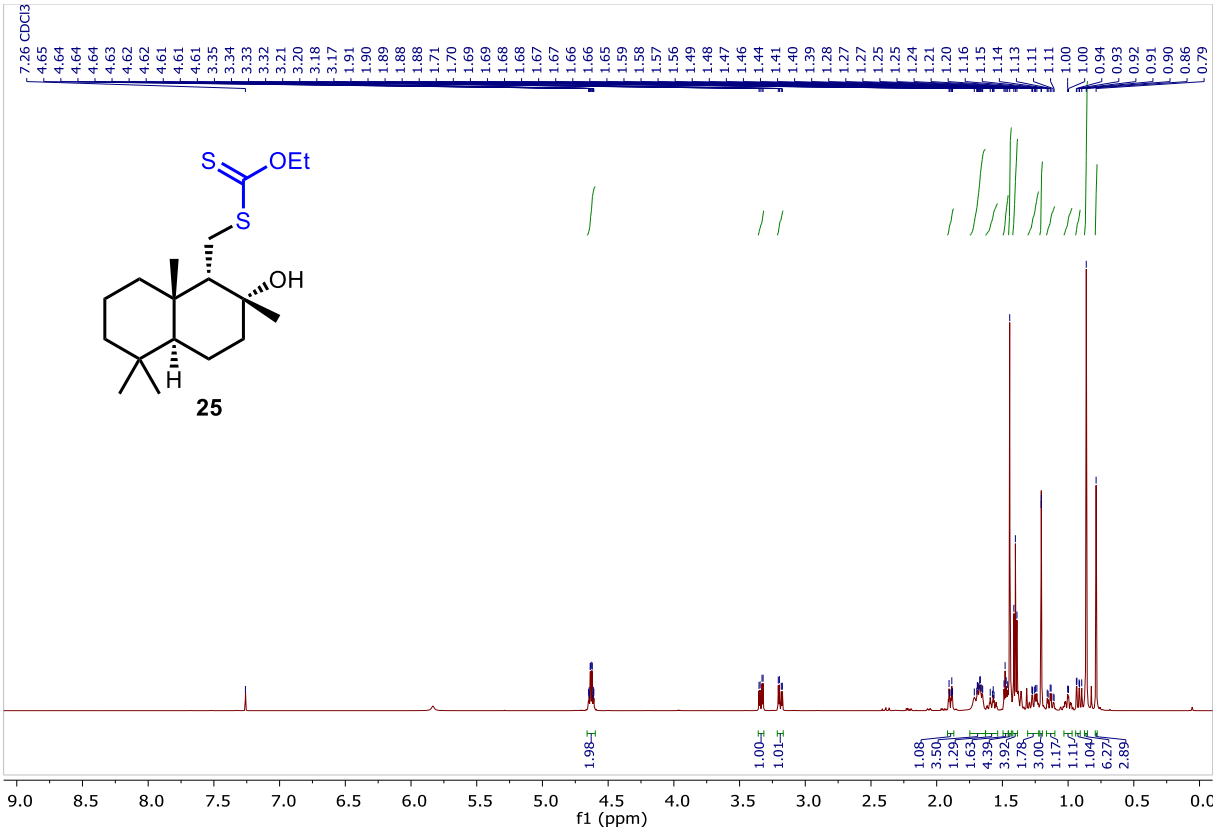
^{1}H NMR ($CDCl_3$, 600 MHz)



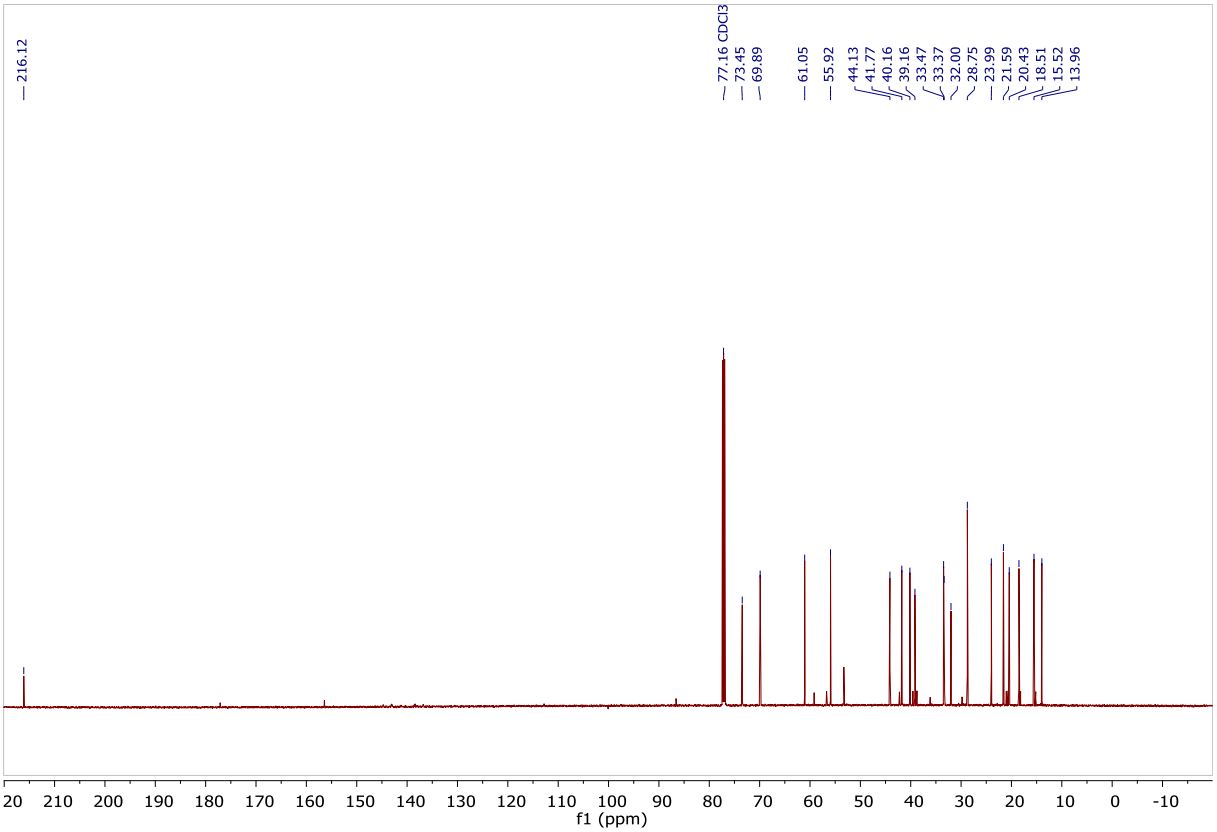
^{13}C NMR ($CDCl_3$, 151 MHz)



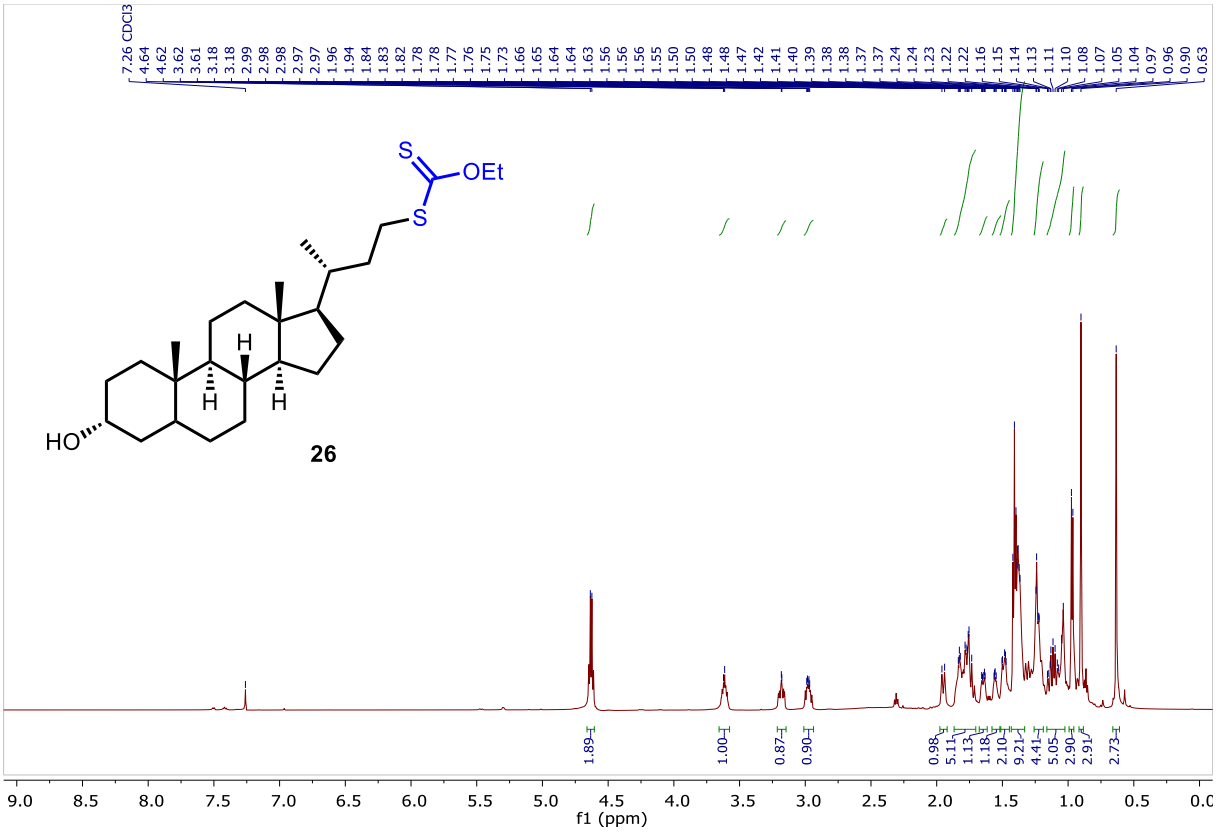
^{1}H NMR ($CDCl_3$, 600 MHz)



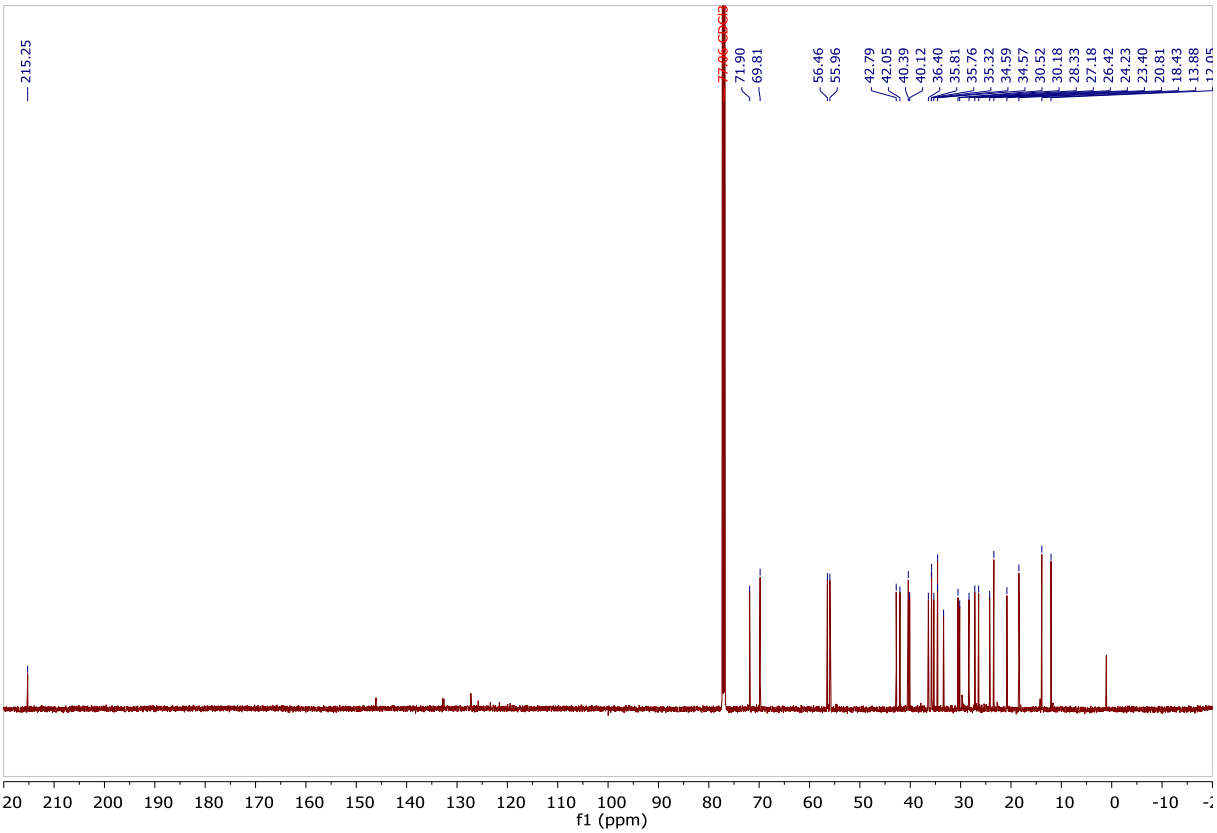
^{13}C NMR ($CDCl_3$, 151 MHz)



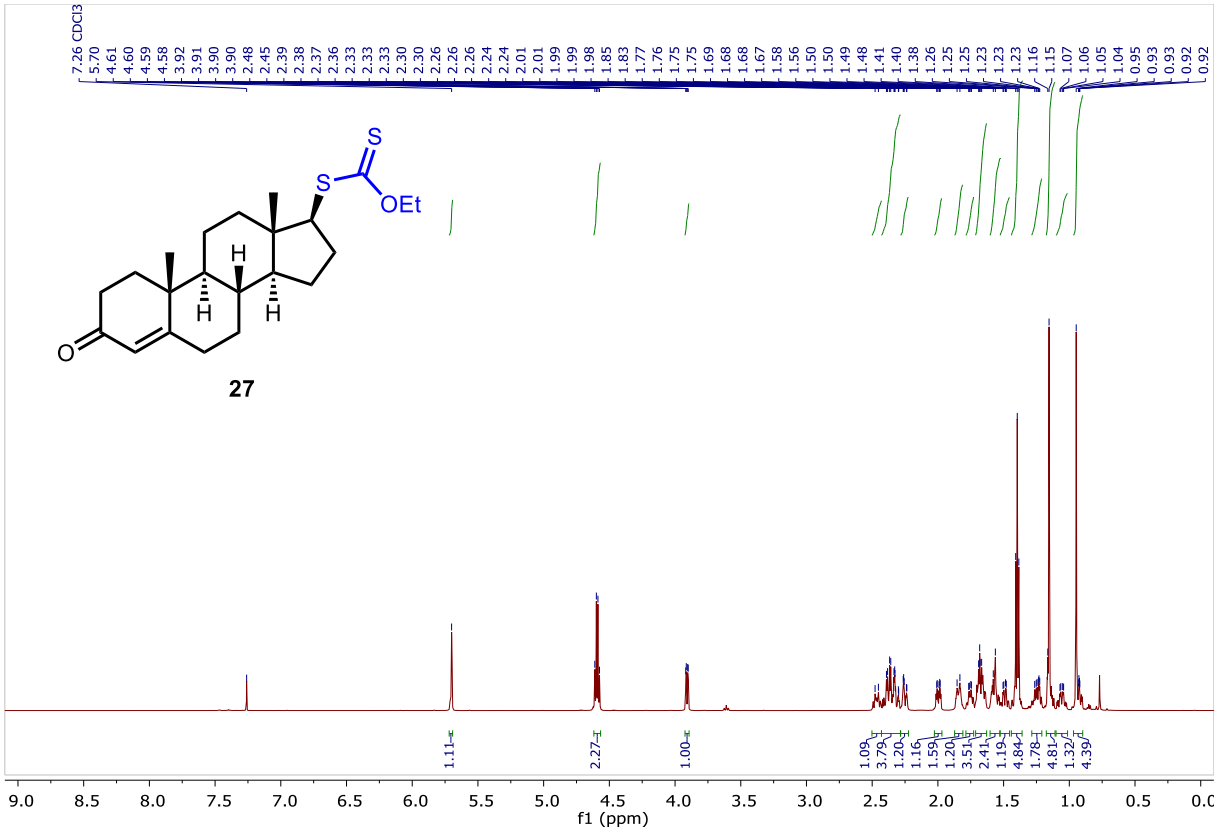
^{1}H NMR ($CDCl_3$, 600 MHz)



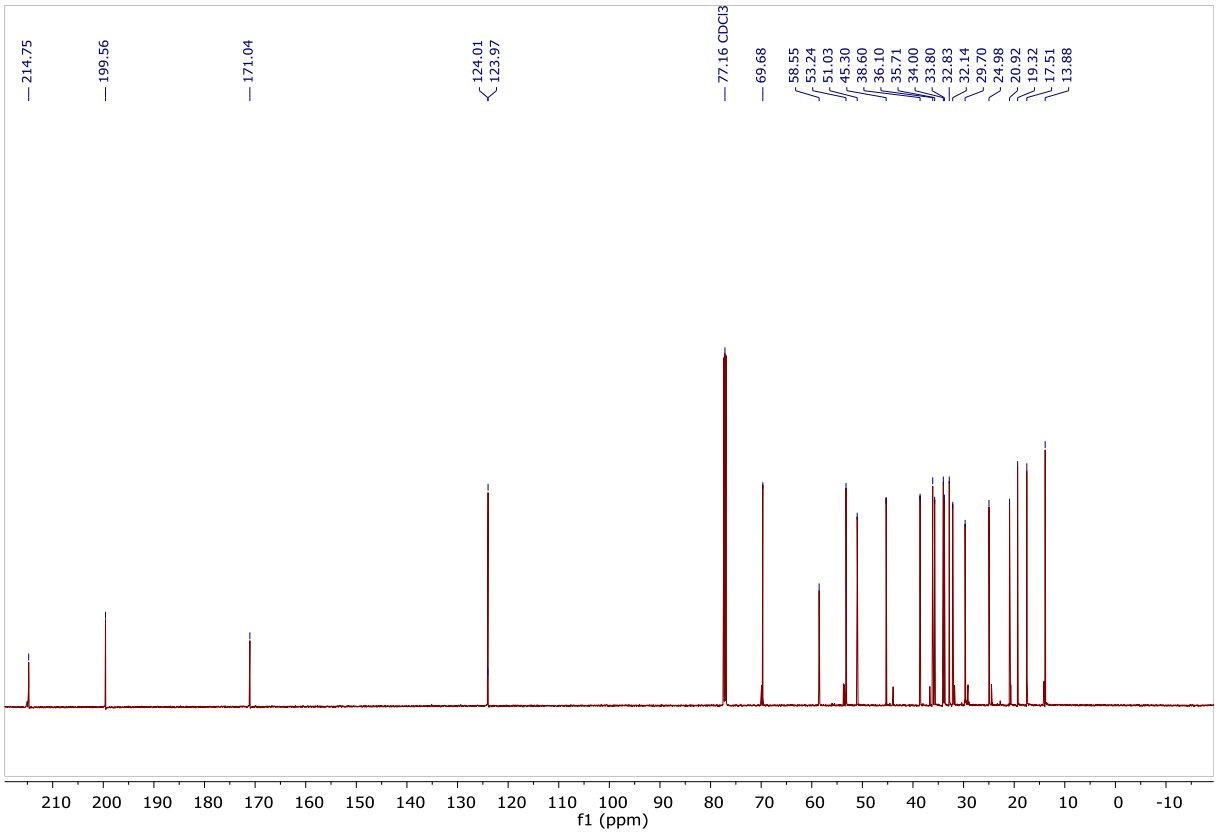
^{13}C NMR ($CDCl_3$, 151 MHz)



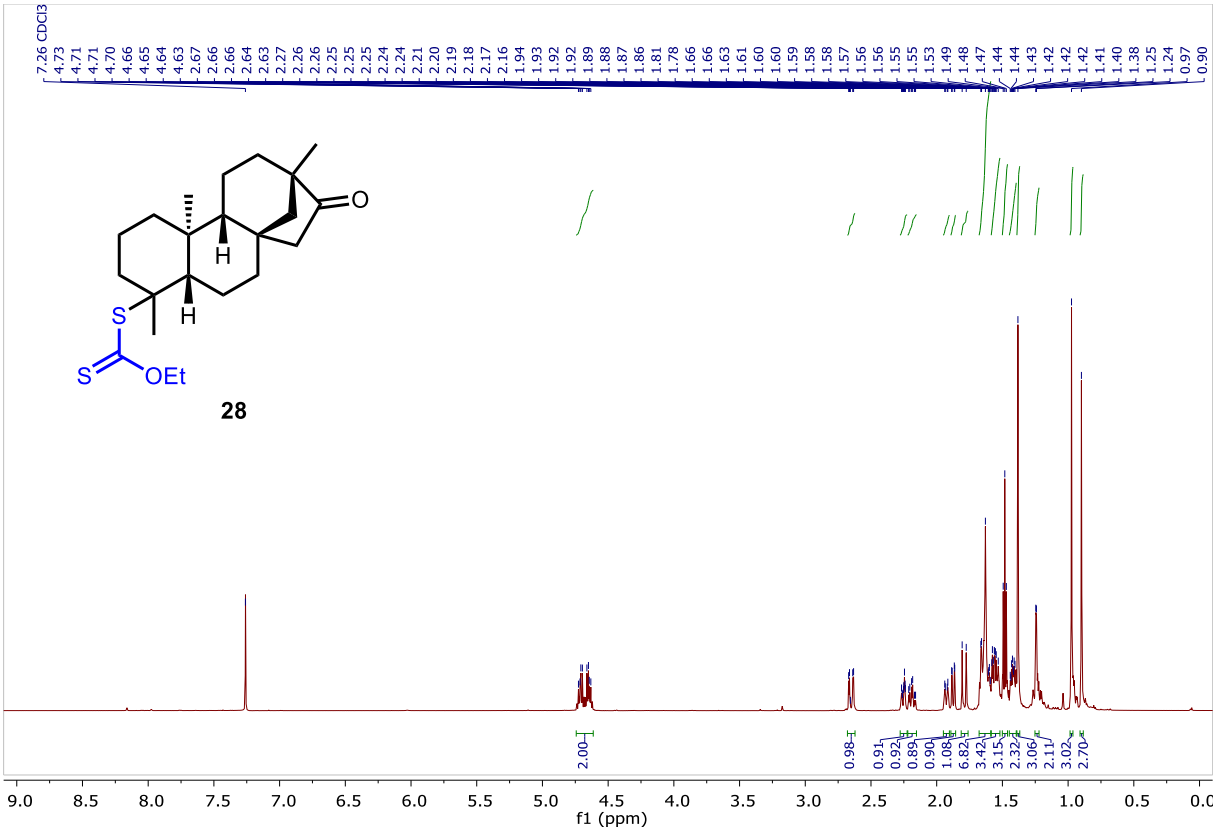
^{1}H NMR ($CDCl_3$, 600 MHz)



^{13}C NMR ($CDCl_3$, 151 MHz)



^{1}H NMR ($CDCl_3$, 600 MHz)



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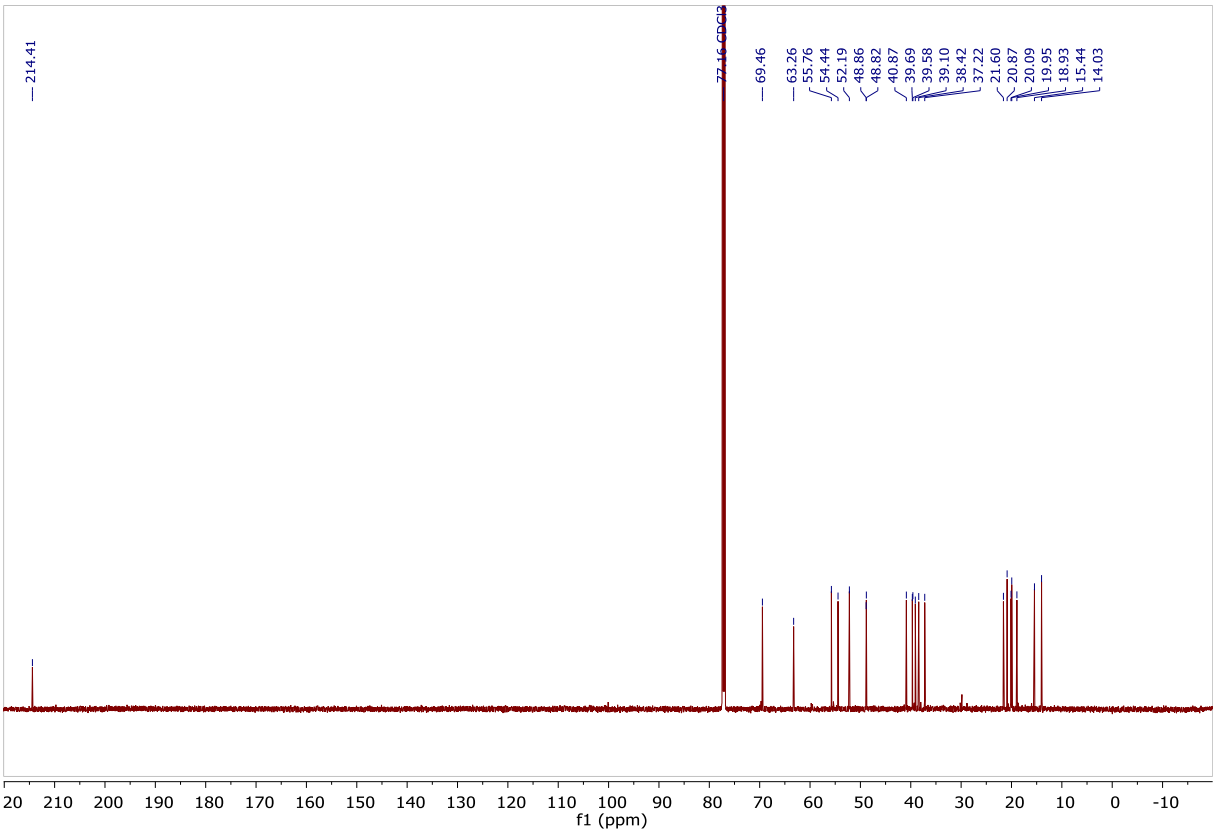
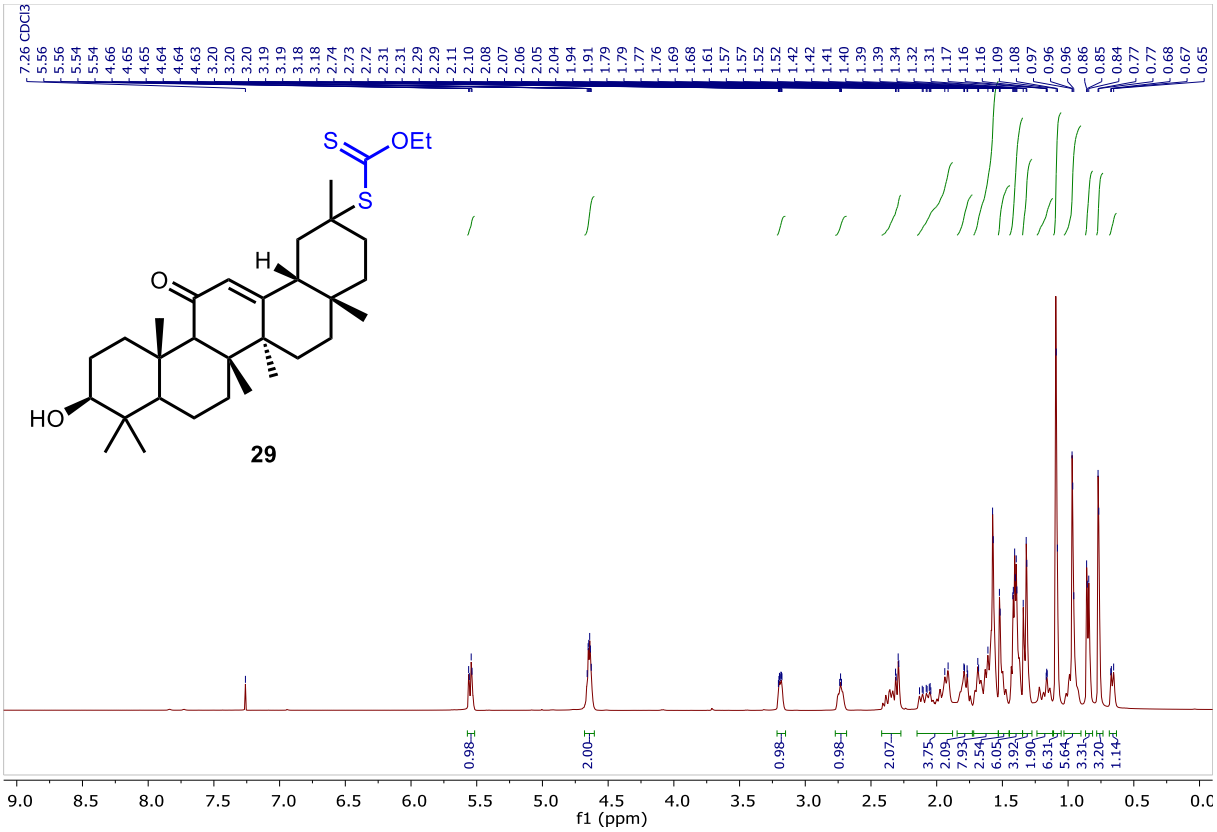
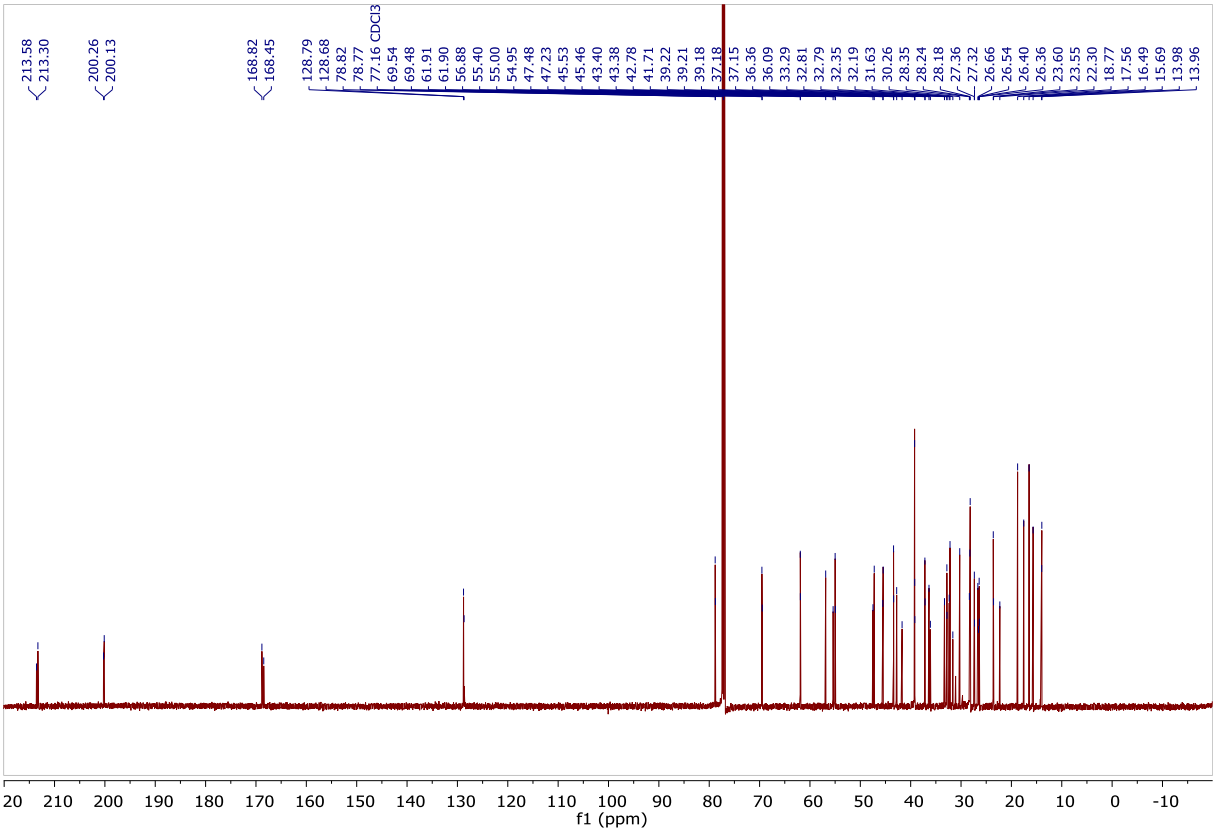
^{13}C NMR ($CDCl_3$, 151 MHz)



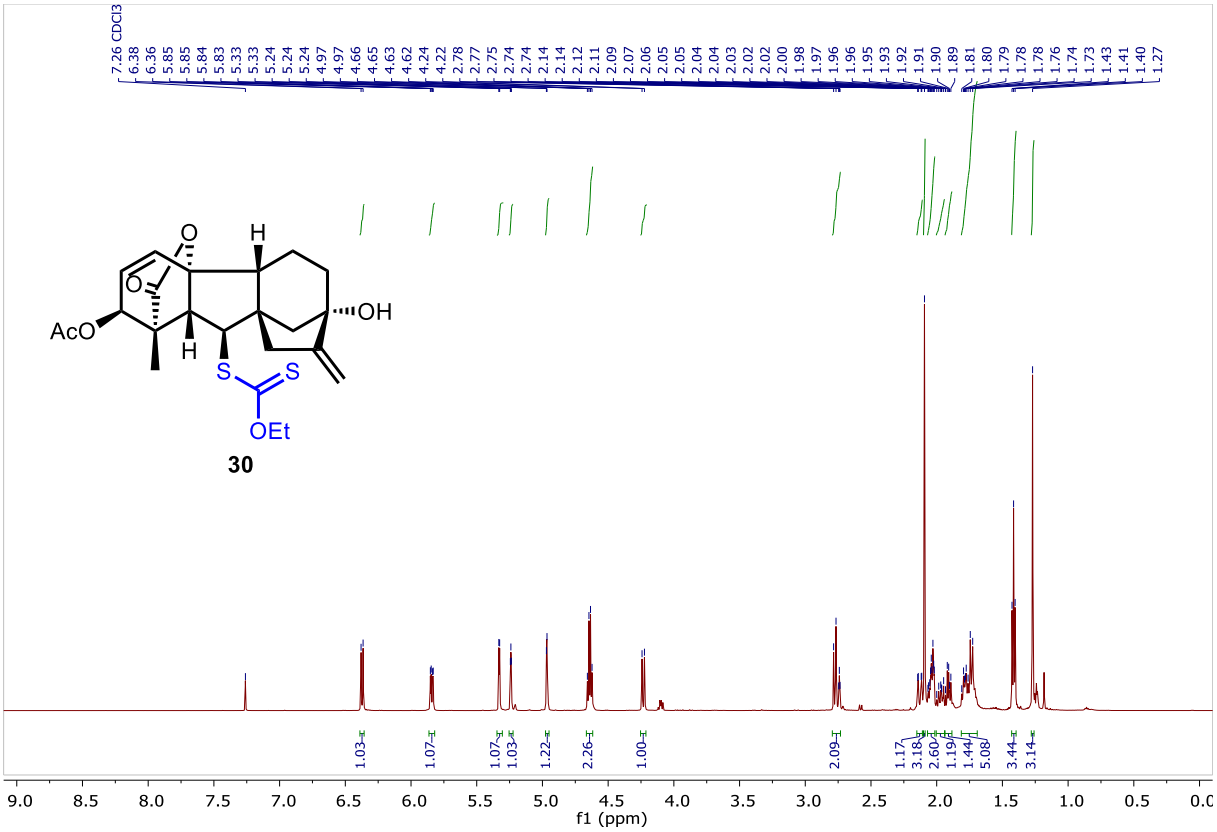
^{1}H NMR ($CDCl_3$, 600 MHz)



^{13}C NMR ($CDCl_3$, 151 MHz)

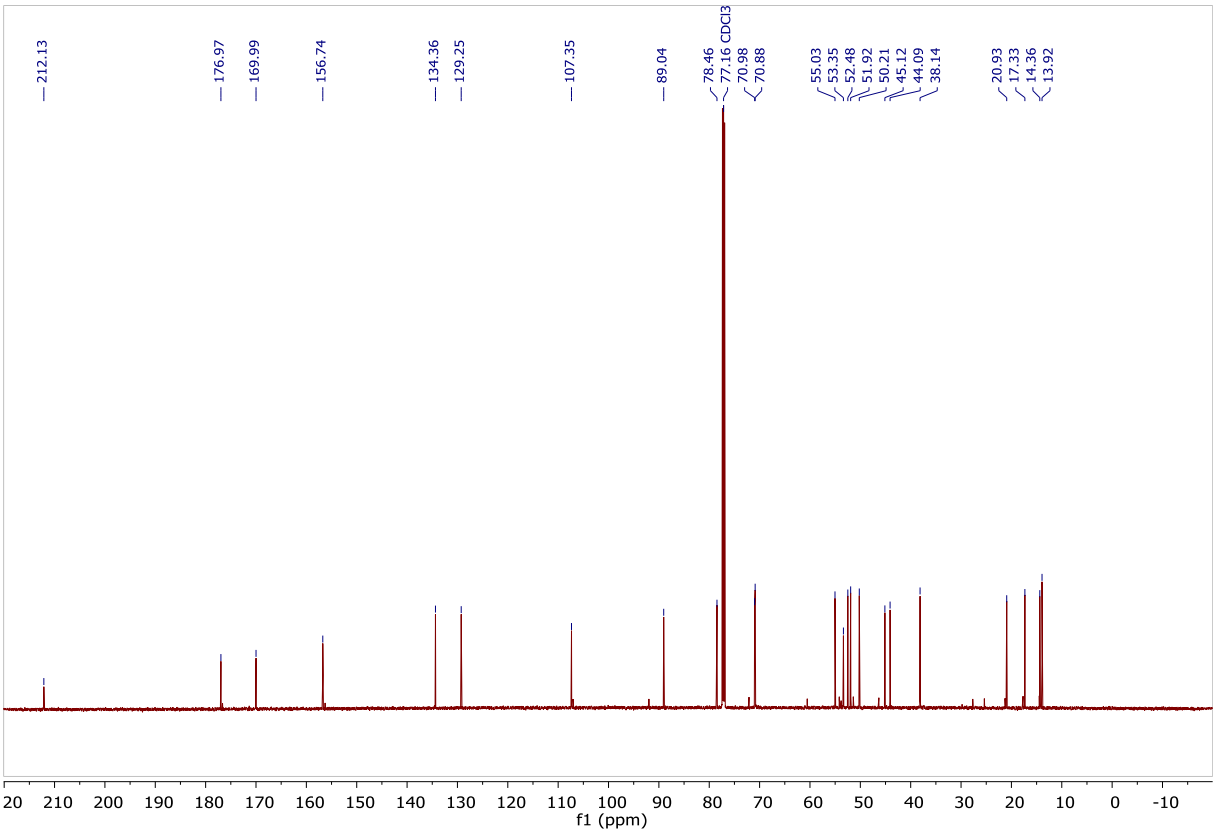


^{1}H NMR ($CDCl_3$, 600 MHz)

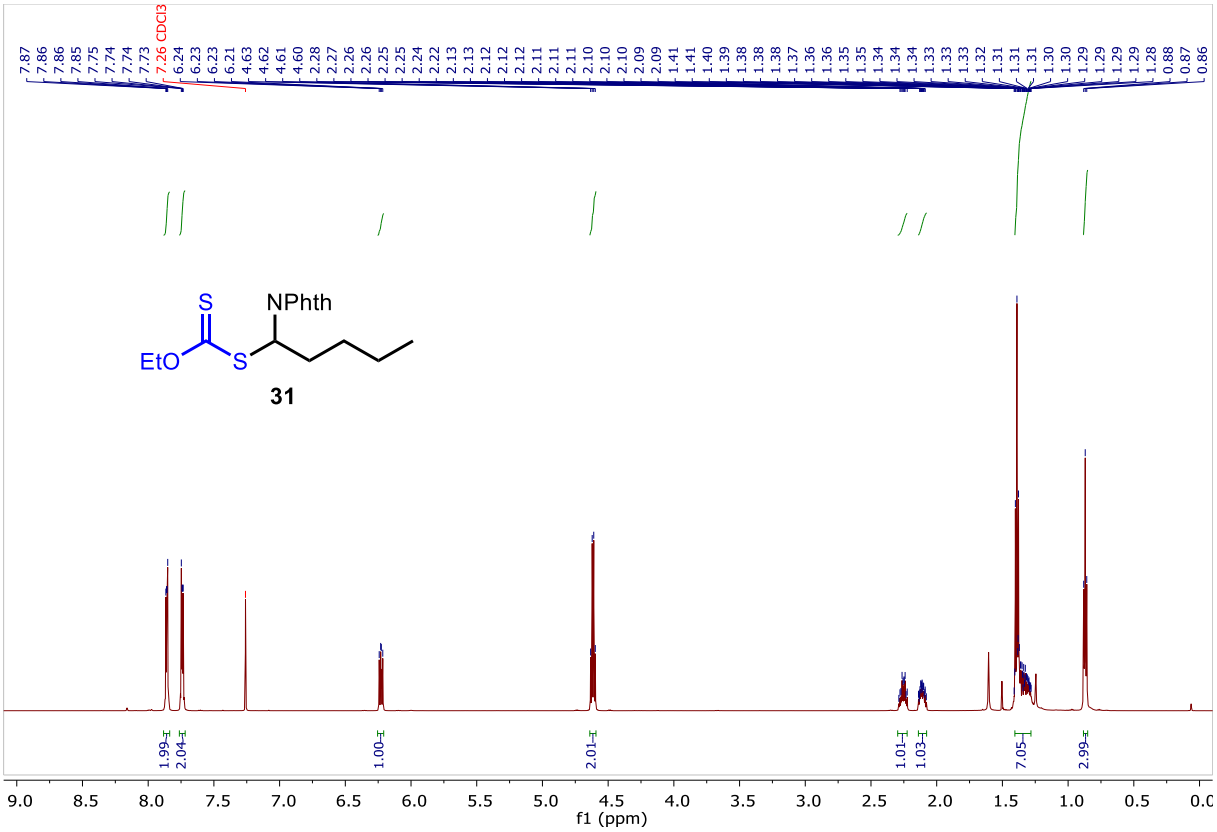


30

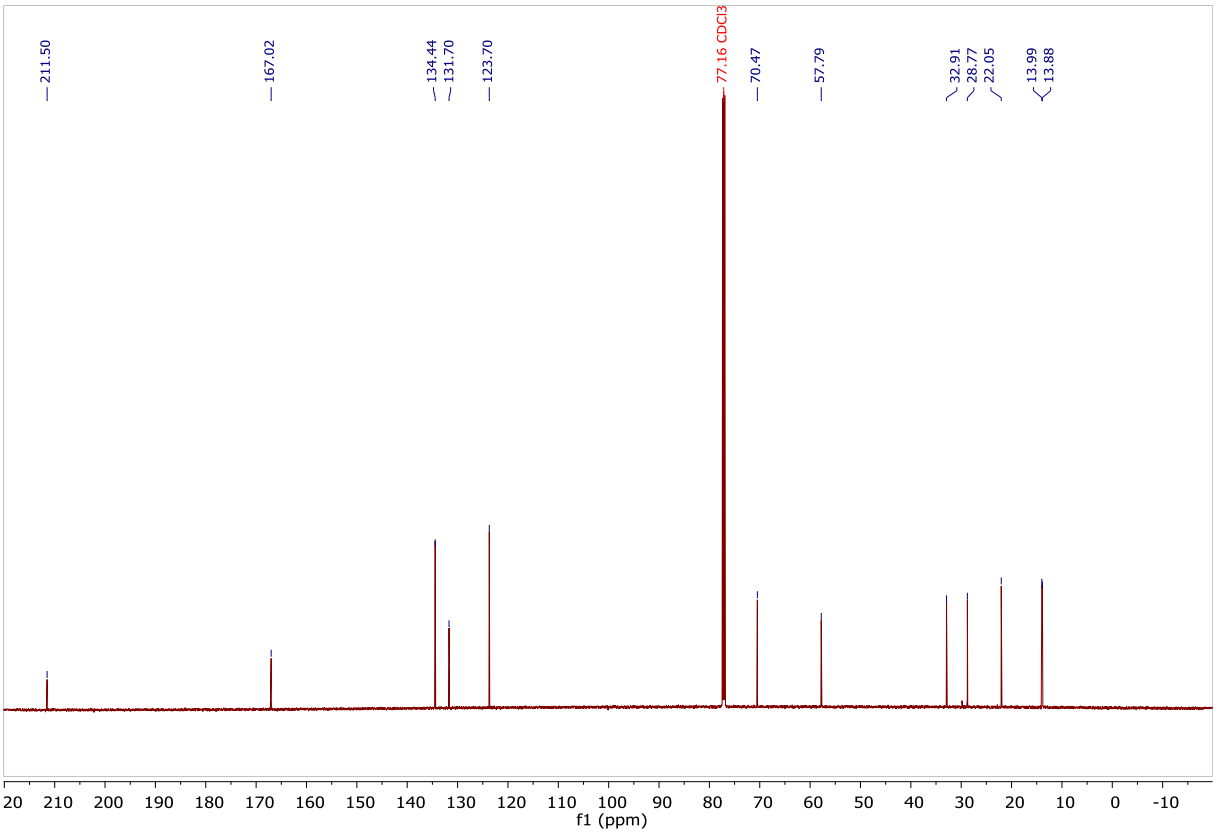
^{13}C NMR ($CDCl_3$, 151 MHz)



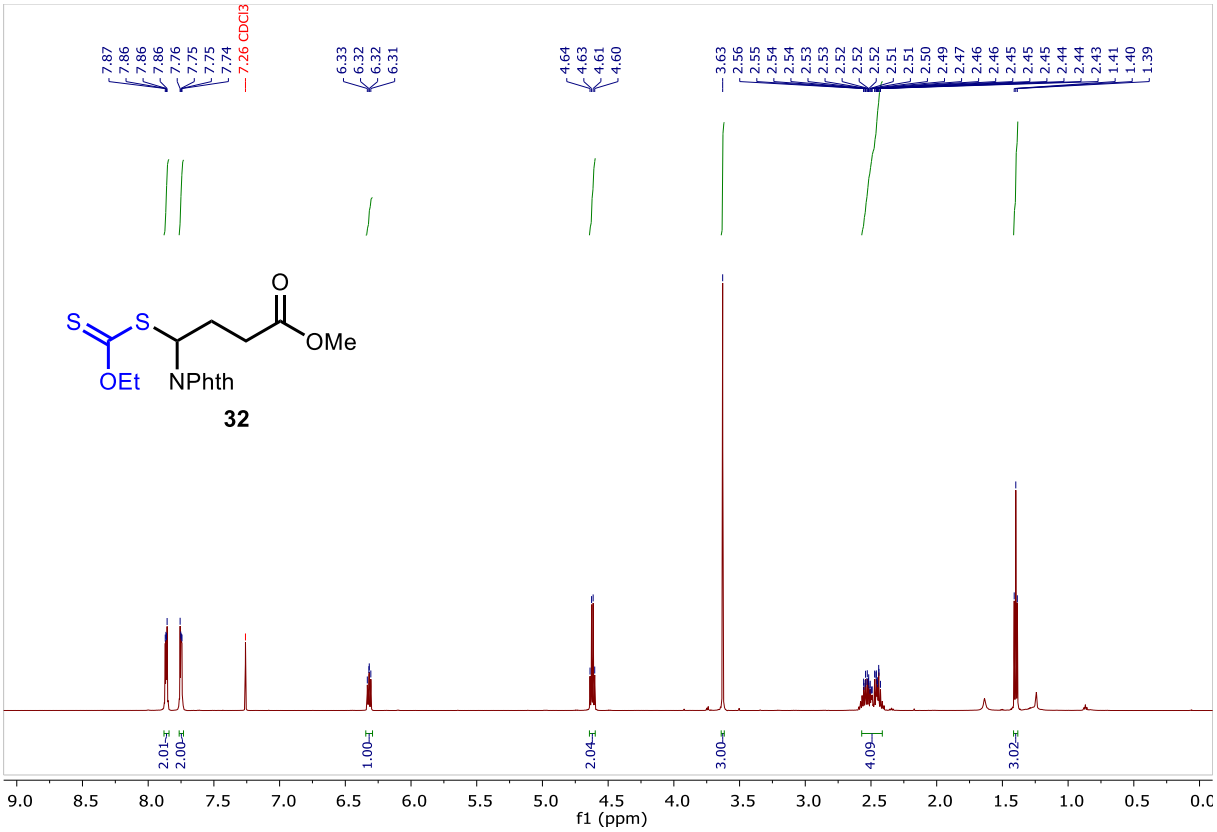
^{1}H NMR ($CDCl_3$, 600 MHz)



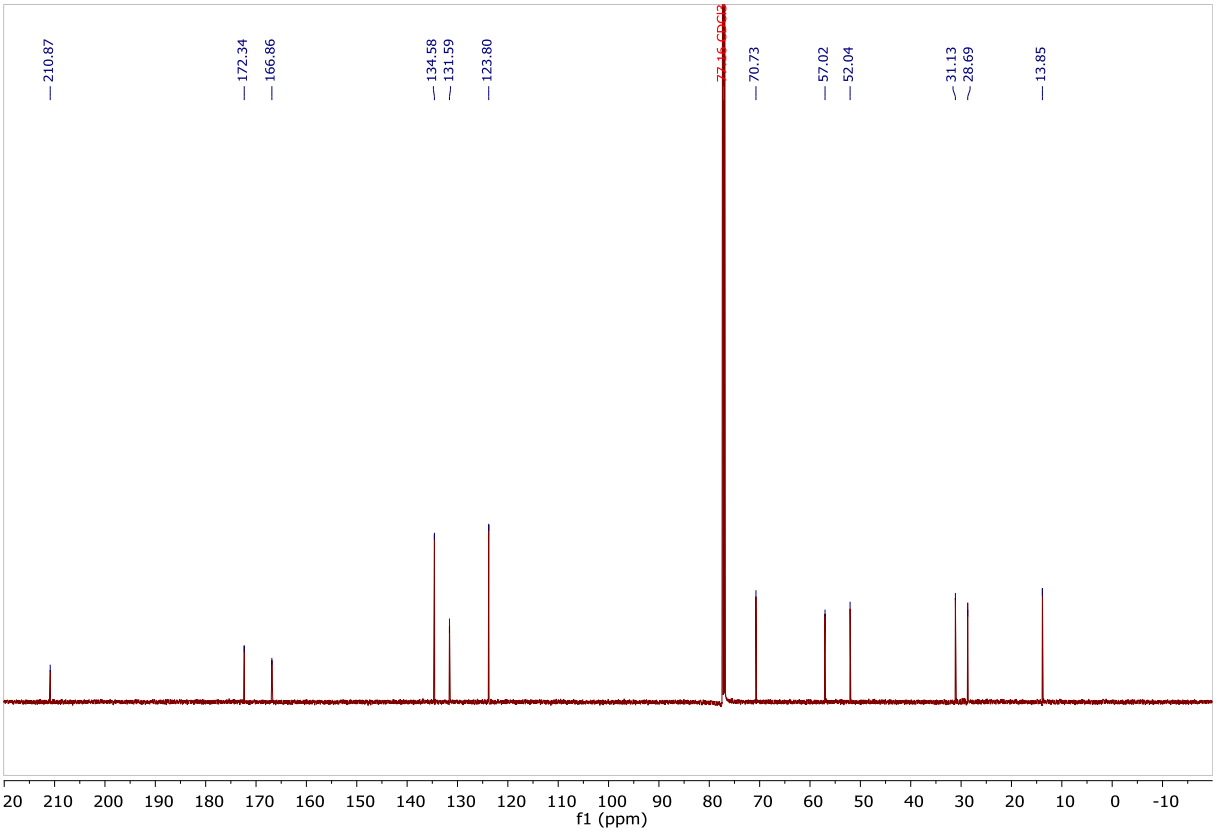
^{13}C NMR ($CDCl_3$, 151 MHz)



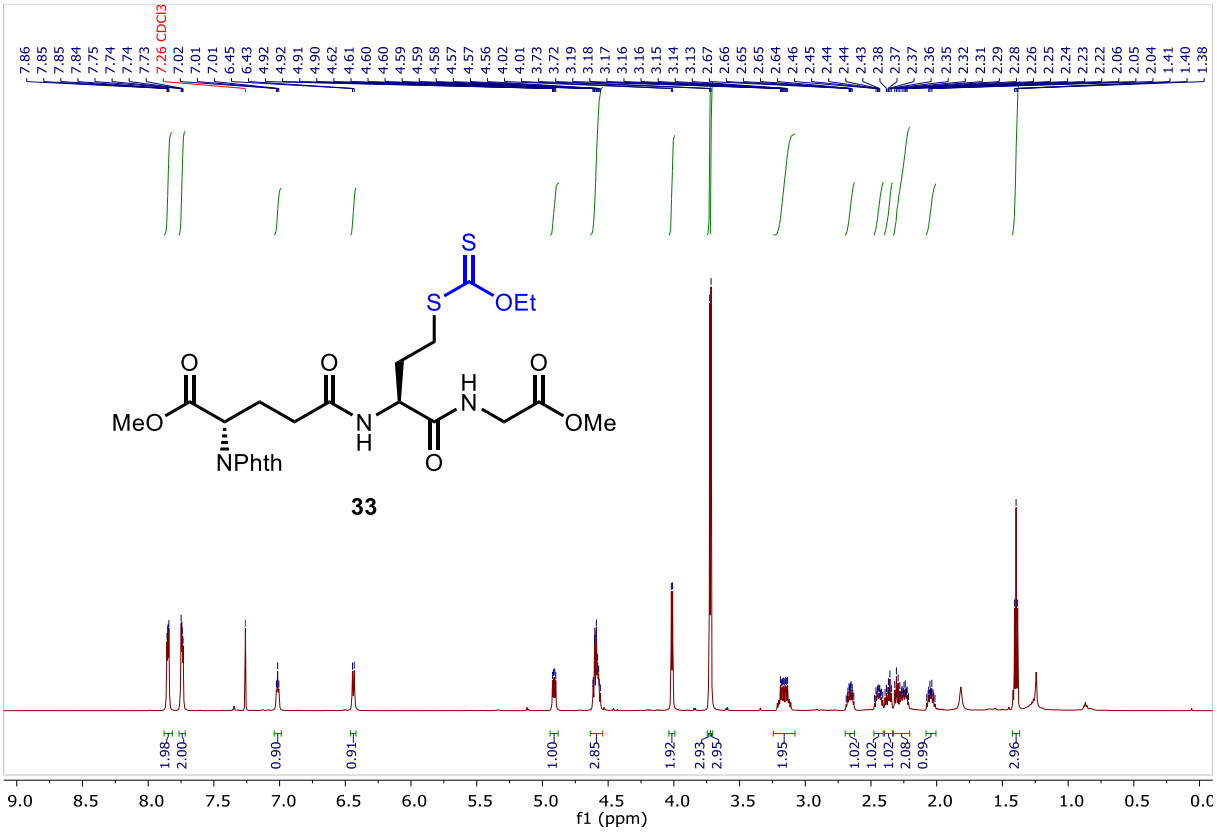
^{1}H NMR ($CDCl_3$, 600 MHz)



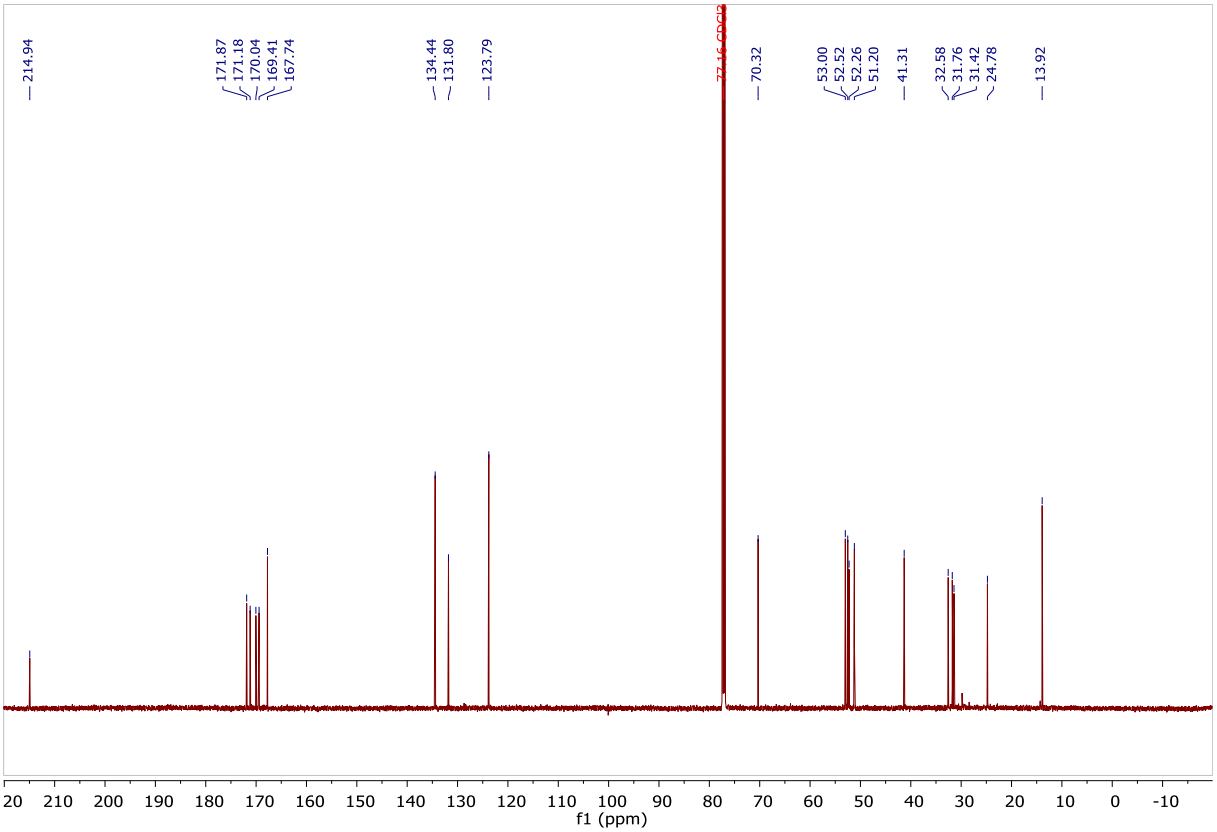
^{13}C NMR ($CDCl_3$, 151 MHz)



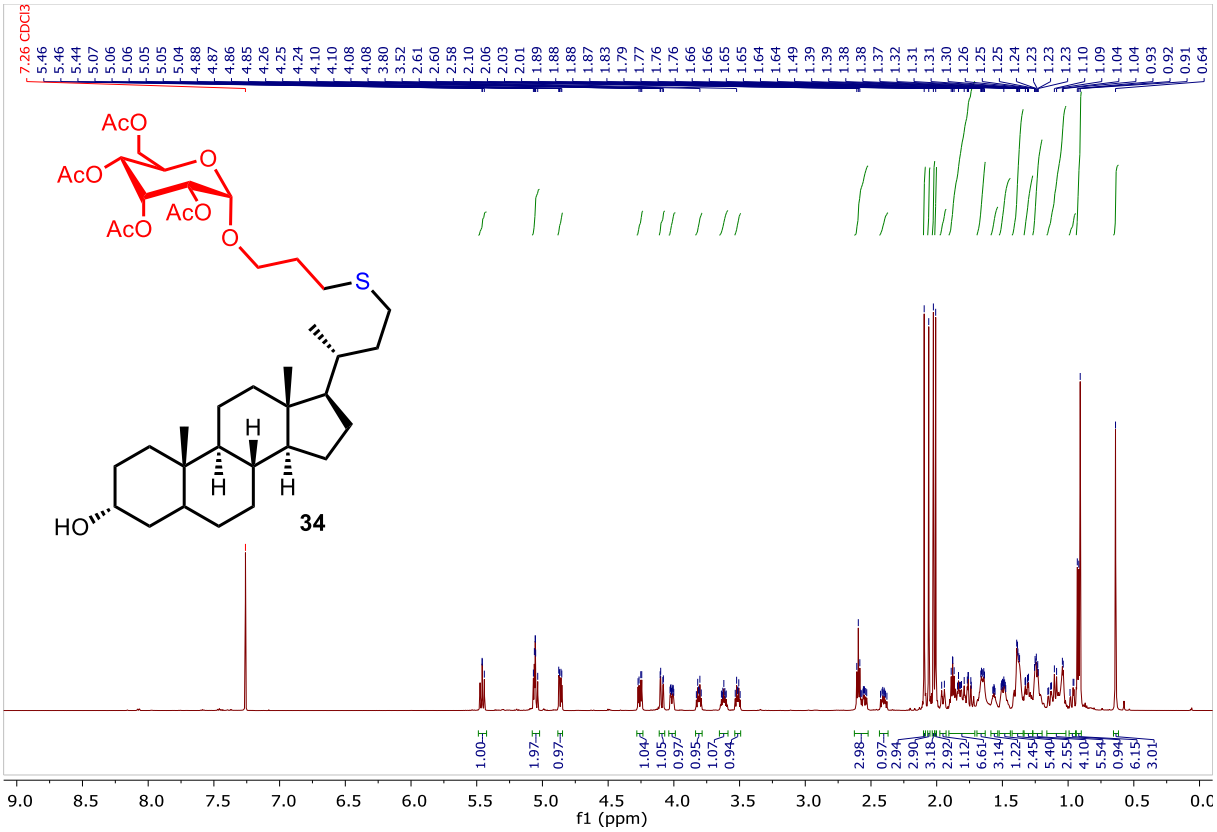
^{1}H NMR ($CDCl_3$, 600 MHz)



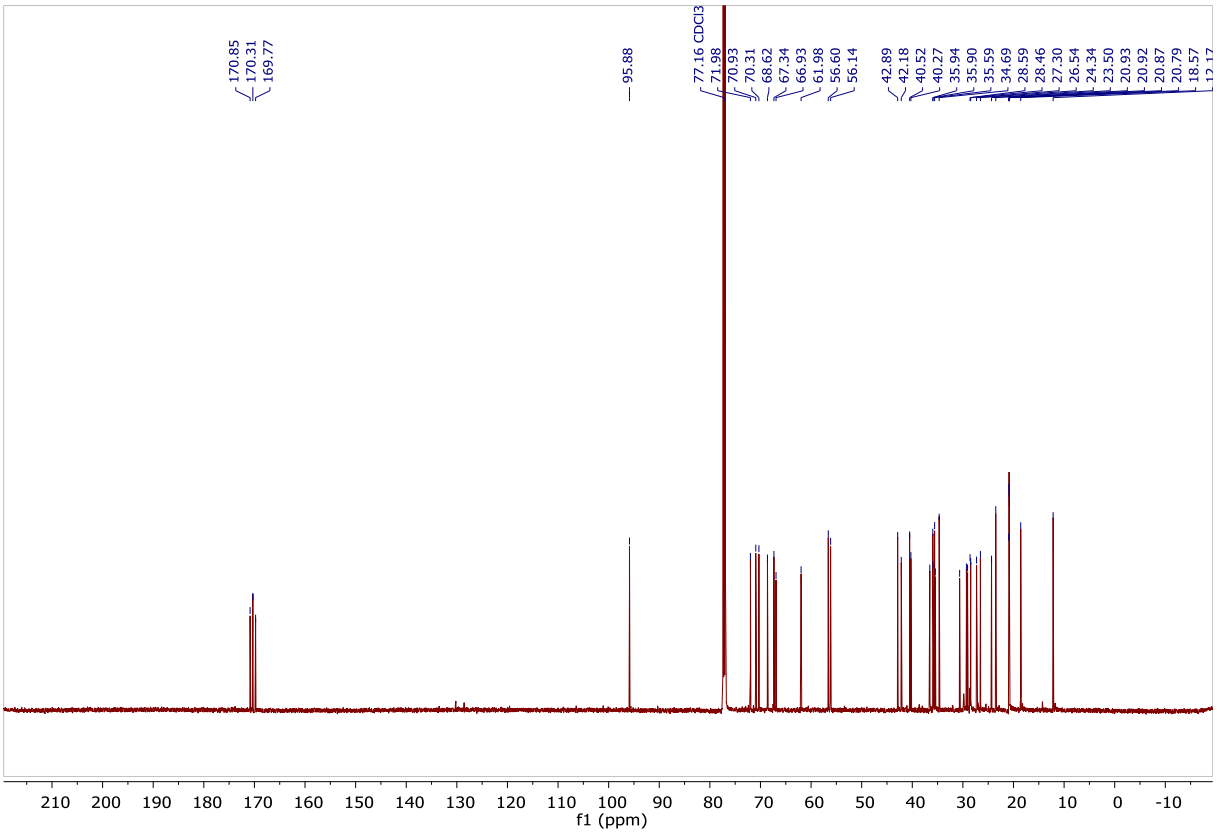
^{13}C NMR ($CDCl_3$, 151 MHz)



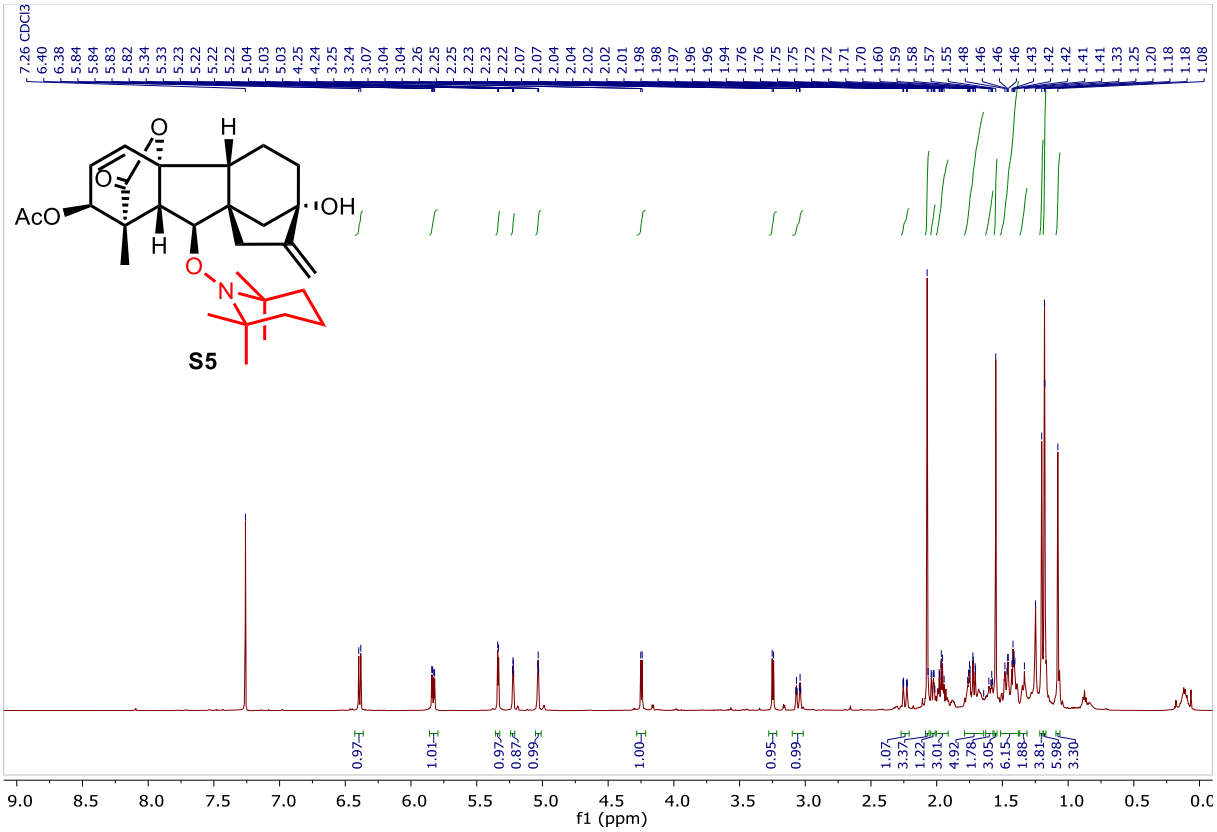
^{1}H NMR ($CDCl_3$, 600 MHz)



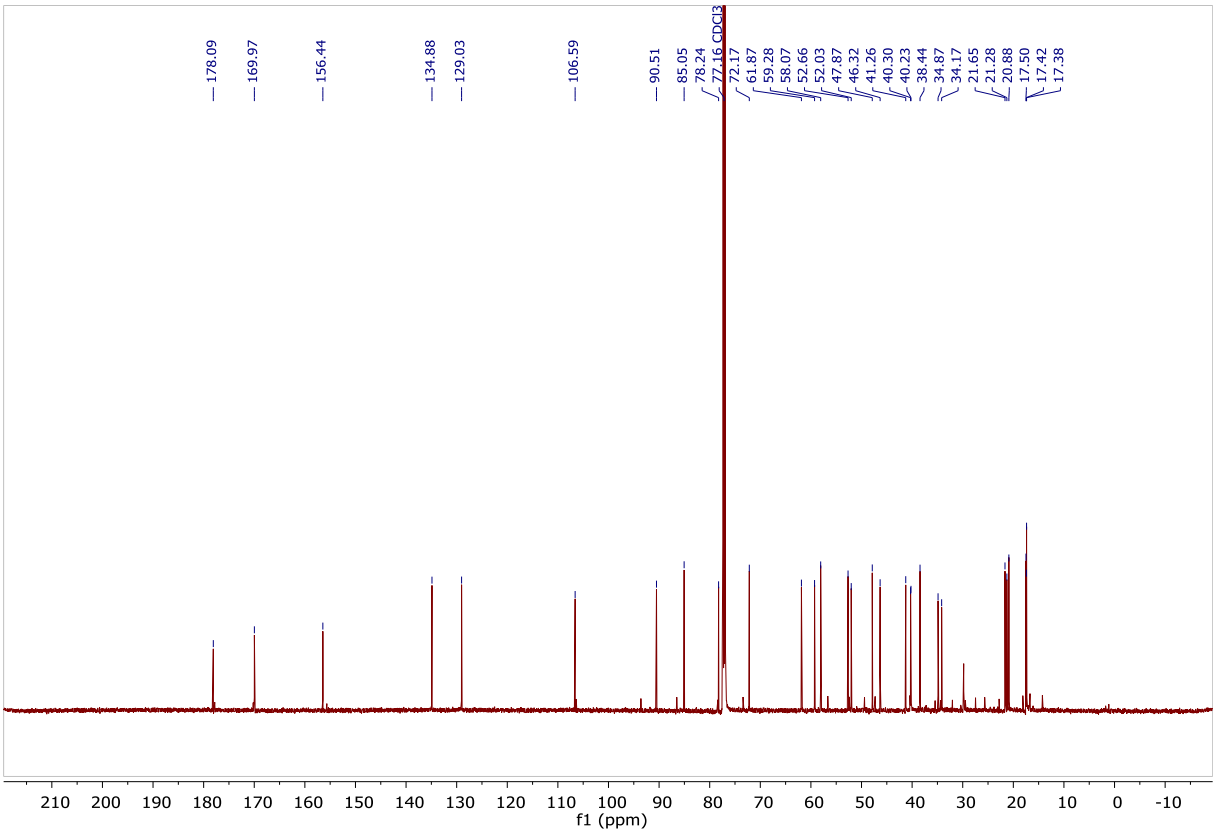
^{13}C NMR ($CDCl_3$, 151 MHz)



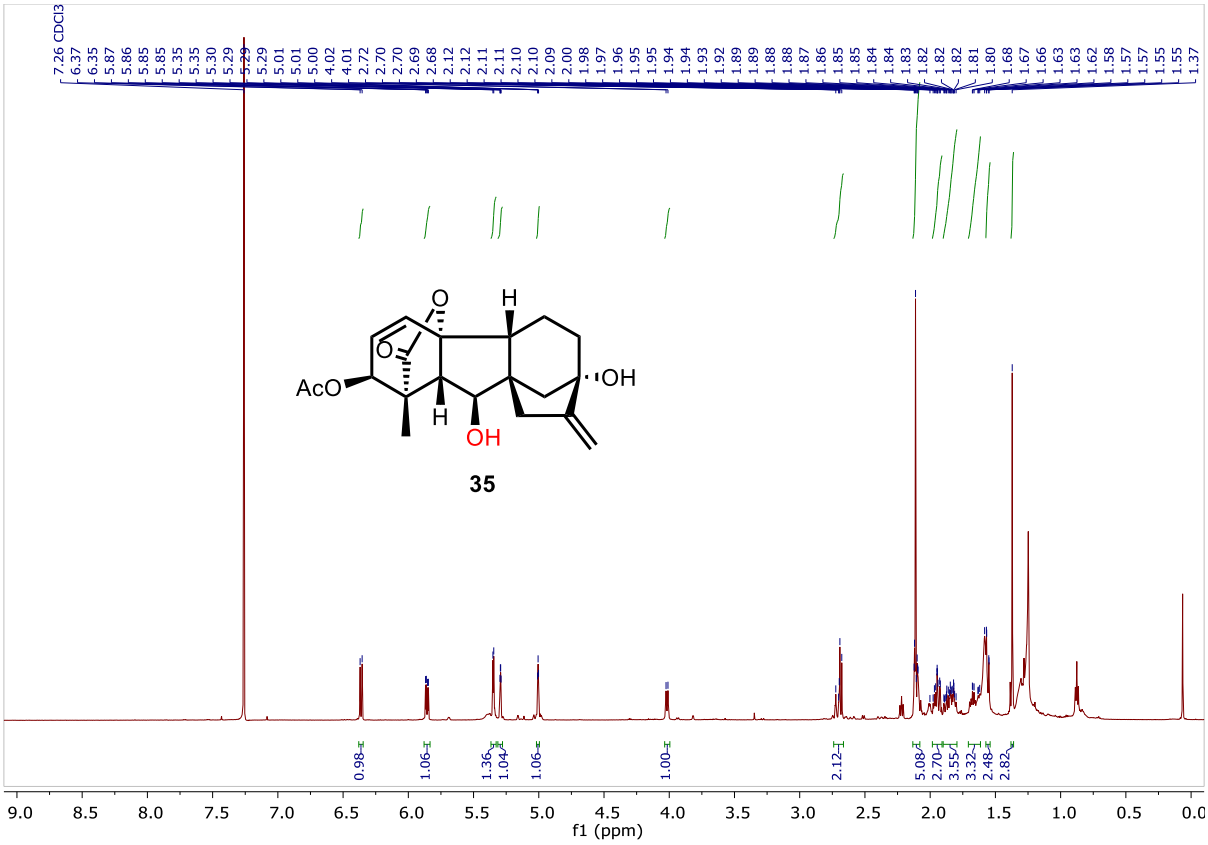
^{1}H NMR ($CDCl_3$, 600 MHz)



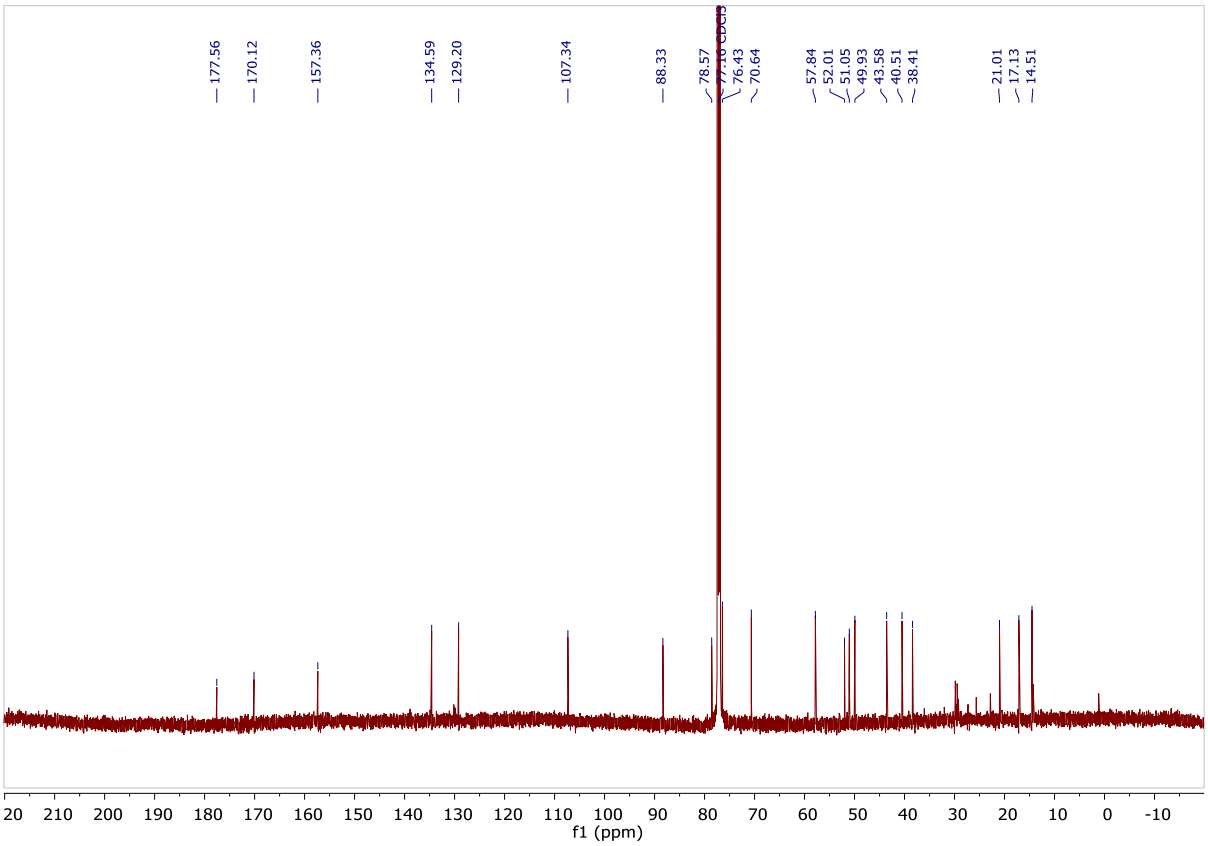
^{13}C NMR ($CDCl_3$, 151 MHz)



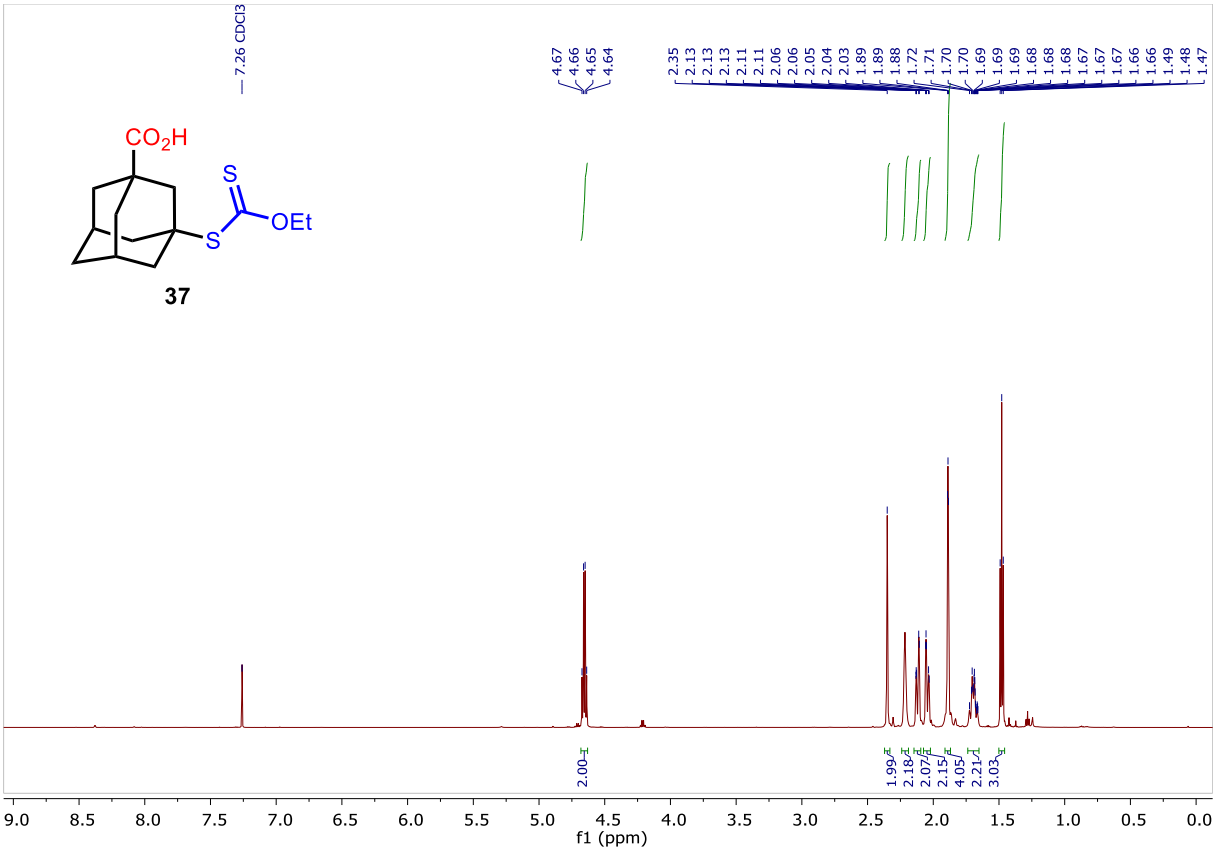
^{1}H NMR ($CDCl_3$, 600 MHz)



^{13}C NMR ($CDCl_3$, 151 MHz)



^{1}H NMR ($CDCl_3$, 600 MHz)



^{13}C NMR ($CDCl_3$, 151 MHz)