Supporting Information

A General Approach to Site-Specific, Intramolecular C–H Functionalization using Dithiocarbamates

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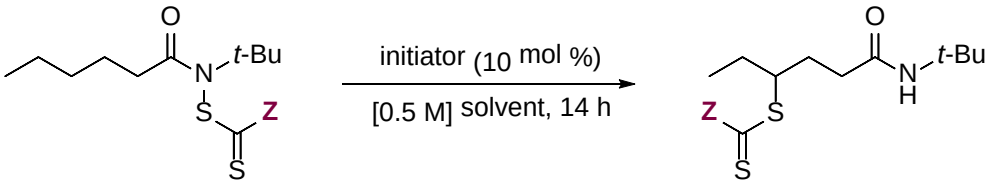
General Methods and Materials

Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Bruker model DRX 400, or a Bruker AVANCE III 600 CryoProbe (^{1}H NMR at 400 or 600 MHz and ^{13}C NMR at 100 or 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). ^{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 with electrospray introduction 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. Blue light irradiation of reactions was 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 KSH150B Blue 36W LED Grow Lights. Reaction temperatures reached 50 °C using the Ecoxotic lamp and 40–50 °C with the Kessil light. All other reagents were obtained from commercial sources and used without further purification unless otherwise noted.

Reaction Optimization

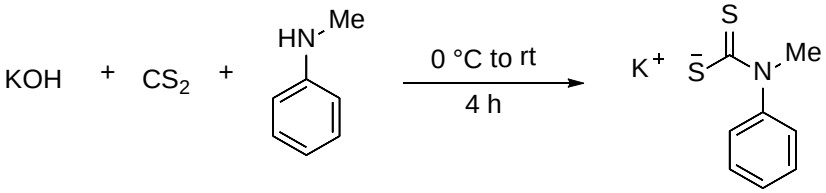
Table S1. Optimization of Intramolecular C–H Dithiocarbamylation[a]



Entry	Z	Initiator	T °C	Solvent	Conversion (%)	Yield (%)
1	NEt_2	DCP	130	PhCl	60	55
2	NMe_2	DCP	130	PhCl	95	66
3	NMe_2	450 nm LED	ambient	$PhCF_3$	100	54
4	NMePh	DLP	80	$PhCF_3$	56	41
5	NMePh	DCP	120	PhCl	100	81
6	NMePh	450 nm LED	ambient	$PhCF_3$	100	84

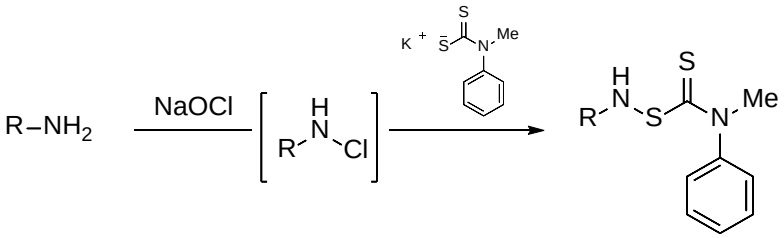
[a] NMR yield vs. hexamethyldisiloxane (HMDS) standard
DCP = dicumyl peroxide, DLP = dilauroyl peroxide

Reagent Synthesis



Potassium methyl(phenyl)carbamodithioate: KOH (1.0 equiv) was dissolved in a minimum volume of water and cooled to 0 °C in an ice bath. Carbon disulfide (1.0 equiv), then *N*-methylaniline (1.0 equiv) was added dropwise into the stirring solution. The resulting red-orange mixture was stirred for 4 h and used directly in the next step.

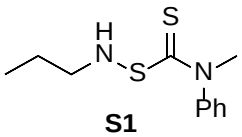
Thiocarbamylsulfenamide Synthesis – *General Procedure A*



Adapted from an analogous literature procedure by Smith et al.[1] A fresh solution of potassium methyl(phenyl)carbamodithioate (2.0 M in H_2O) was prepared and chilled in an ice bath. In a separate flask, the primary amine (1.2 equiv) was treated with sodium hypochlorite (~1.5 M in H_2O from Sigma Aldrich, 1.0 equiv) at 0 °C. After 5 to 10 minutes of stirring, the solution of potas-

sium methyl(phenyl)carbamodithioate salt (1.0 equiv) was added dropwise, and the reaction mixture was allowed to come to room temperature overnight. The mixture was diluted with water and Et_2O, and the layers were separated. The aqueous phase was extracted twice with Et_2O, and the combined organic phase was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The crude mixture was purified by column chromatography (2.5 to 5% EtOAc/hex) to give the corresponding thiocarbamylsulfenamide.

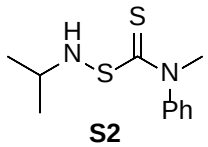
Warning: Rapid addition of the potassium methyl(phenyl)carbamodithioate solution, especially with low-boiling chloroamines, can cause an exotherm and gas evolution resulting from the decomposition of the reagents.



S1

***N*-methyl-*N*-(((propylamino)thio)carbonothioyl)aniline (S1):** Prepared from *N*-propylamine according to General Procedure A (100 mmol) as a yellow oil (13.4 g, 56% yield):

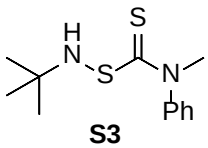
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 3H), 7.25 – 7.21 (m, 2H), 3.76 (s, 3H), 3.57 (t, *J* = 5.6 Hz, 1H), 2.82 (td, *J* = 7.2, 5.5 Hz, 2H), 1.50 (h, *J* = 7.3 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 205.86, 143.05, 129.81, 129.31, 126.73, 54.02, 54.00, 45.96, 23.43, 11.52.
HRMS (ES+) Exact mass calcd for $C_{11}H_{17}N_2S_2$ $[M+H]^+$ 241.0833. Found 241.0828.



S2

***N*-(((isopropylamino)thio)carbonothioyl)-*N*-methylaniline (S2):** Prepared from isopropylamine according to General Procedure A (100 mmol) as a light yellow solid (14.9 g, 62% yield):

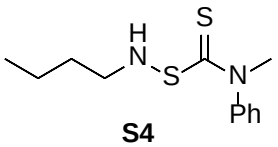
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 3H), 7.26 – 7.23 (m, 2H), 3.76 (s, 3H), 3.11 (heptd, *J* = 6.3, 1.2 Hz, 1H), 1.06 (d, *J* = 6.3 Hz, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 205.79, 143.04, 129.64, 129.11, 126.53, 50.69, 45.88, 22.37.
HRMS (ES+) Exact mass calcd for $C_{11}H_{17}N_2S_2$ $[M+H]^+$ 241.0833. Found 241.0828.



S3

***N*-(((*tert*-butylamino)thio)carbonothioyl)-*N*-methylaniline (S3):** Prepared from *tert*-butylamine according to General Procedure A (100 mmol) as a light yellow solid (15.3 g, 60% yield):

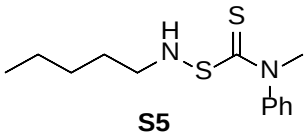
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 3H), 7.29 – 7.21 (m, 2H), 3.95 (s, 1H), 3.77 (s, 3H), 1.09 (s, 10H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 207.51, 143.54, 129.85, 129.26, 126.81, 55.76, 46.30, 29.12.
HRMS (ES+) Exact mass calcd for $C_{12}H_{19}N_2S_2$ $[M+H]^+$ 255.0990. Found 255.0984.



S4

***N*-(((butylamino)thio)carbonothioyl)-*N*-methylaniline (S4):** Prepared from *N*-butylamine according to General Procedure A (40 mmol) as an orange oil (4.58 g, 45% yield):

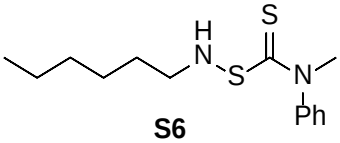
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 3H), 7.25 – 7.22 (m, 2H), 3.76 (s, 3H), 3.56 (t, *J* = 5.6 Hz, 1H), 2.85 (td, *J* = 7.2, 5.6 Hz, 2H), 1.50 – 1.43 (m, 2H), 1.37 – 1.27 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 205.90, 143.11, 129.85, 129.35, 126.76, 52.00, 46.01, 32.41, 20.17, 14.01.
HRMS (ES+) Exact mass calcd for $C_{12}H_{19}N_2S_2$ $[M+H]^+$ 255.0990. Found 255.0984.



S5

***N*-methyl-*N*-(((pentylamino)thio)carbonothioyl)aniline (S5):** Prepared from amylamine (10 mmol) according to General Procedure A (10 mmol) as a red-orange oil (1.15 g, 43% yield):

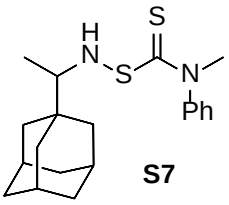
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 3H), 7.25 – 7.22 (m, 2H), 3.76 (s, 3H), 3.56 (t, *J* = 5.6 Hz, 1H), 2.84 (td, *J* = 7.2, 5.6 Hz, 2H), 1.53 – 1.45 (m, 2H), 1.32 – 1.26 (m, 4H), 0.87 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 205.89, 143.12, 129.85, 129.35, 126.76, 52.28, 46.01, 29.98, 29.17, 22.57, 14.10.
HRMS (ES+) Exact mass calcd for $C_{13}H_{21}N_2S_2$ $[M+H]^+$ 269.1146. Found 269.1142.



S6

***N*-(((hexylamino)thio)carbonothioyl)-*N*-methylaniline (S6):** Prepared from *N*-hexylamine according to General Procedure A (80 mmol) as a pale yellow oil (11.1 g, 49% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 3H), 7.25 – 7.21 (m, 2H), 3.76 (s, 3H), 3.56 (t, *J* = 5.6 Hz, 1H), 2.84 (td, *J* = 7.2, 5.6 Hz, 2H), 1.48 (p, *J* = 7.2 Hz, 2H), 1.34 – 1.20 (m, 6H), 0.86 (t, *J* = 6.9 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 205.85, 143.08, 129.81, 129.31, 126.73, 52.27, 45.97, 31.68, 30.23, 26.64, 22.63, 14.11.
HRMS (ES+) Exact mass calcd for $C_{14}H_{23}N_2S_2$ $[M+H]^+$ 283.1303. Found 283.1297.



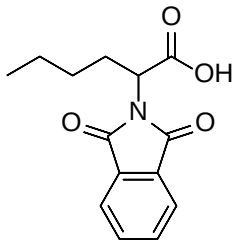
S7

***N*-((((1-((3*r*,5*r*,7*r*)-adamantan-1-yl)ethyl)amino)thio)carbonothioyl)-*N*-methylaniline (S7)**: Rimantadine hydrochloride (4.32 g, 20.0 mmol, 1.00 equiv) was charged to a 100-mL round-bottomed flask equipped with a stir bar and dissolved in methyl *tert*-butyl ether (20 mL) and *t*-BuOH (0.95 mL, 10 mmol, 0.50 equiv). With the laboratory lights off, an aqueous solution of sodium hypochlorite (14 mL, ~1.5 M in H_2O from Sigma-Aldrich) was added dropwise at 0 °C, and the mixture was stirred vigorously for 30 min. The contents of the flask were transferred to a separatory funnel, where the organic phase was dispensed directly into another 100-mL round-bottomed flask equipped with a stir bar. At 0 °C, solid sodium methyl(phenyl)carbamodithioate[2] (4.11 g, 20.0 mmol) was added slowly to the flask, and the mixture was left stirring overnight. The mixture was diluted with Et_2O (100 mL) and water (100 mL). The layers were separated, and the aqueous phase was extracted twice with Et_2O (2 x 100 mL). The combined organic phase was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The crude mixture was purified by column chromatography (5% EtOAc/hex) to give **S7** as a light yellow solid (3.75 g, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 3H), 7.25 – 7.22 (m, 2H), 3.74 (s, 3H), 2.68 (qd, *J* = 6.6, 2.6 Hz, 1H), 2.01 – 1.92 (m, 3H), 1.74 – 1.50 (m, 13H), 0.97 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 206.98, 143.41, 129.79, 129.21, 126.73, 63.44, 45.89, 38.60, 37.35, 36.65, 28.60, 13.36.
HRMS (ES+) Exact mass calcd for $C_{20}H_{29}N_2S_2$ $[M+H]^+$ 361.1772. Found 361.1766.

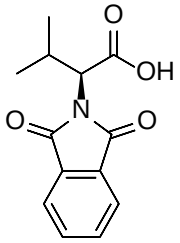
Substrates

Hexanoyl chloride, benzoyl chloride, butyric acid, pentanoic acid, 2-cyclohexylacetic acid, cyclohexanecarboxylic acid, nicotinic acid, gemfibrozil, and linoleic acid were obtained commercially and used without further purification.



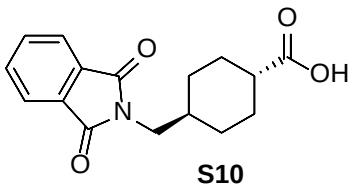
S8

***N*-phthalyl-(RS)-norleucine (S8)** was prepared from DL-norleucine according to a literature procedure, and spectral data were in accordance with the literature values.[3]



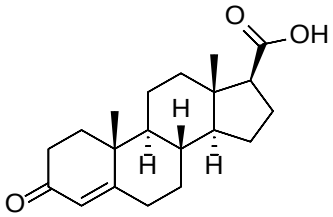
S9

***N*-phthaloyl L-valine (S9)** was prepared from L-valine according to a literature procedure, and spectral data were in accordance with the literature values.[4]



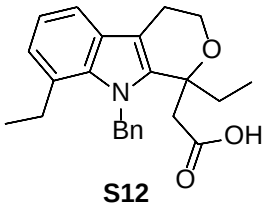
S10

(1*r*,4*r*)-4-((1,3-dioxoisoindolin-2-yl)methyl)cyclohexane-1-carboxylic acid (S10) was prepared from tranexamic acid according to a literature procedure, and spectral data were in accordance with the literature values.[5]



S11

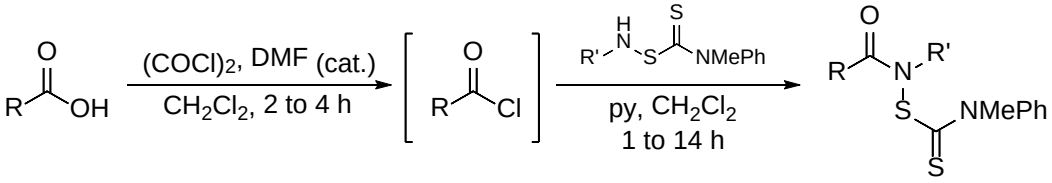
Androst-4-en-3-one-17β-carboxylic acid (S11) was prepared from progesterone according to a literature procedure, and spectral data were in accordance with the literature values.[6]



S12

2-(9-benzyl-1,8-diethyl-1,3,4,9-tetrahydropyrano[3,4-b]indol-1-yl)acetic acid (S12) was prepared from etodolac according to a literature procedure, and spectral data were in accordance with the literature values.[7]

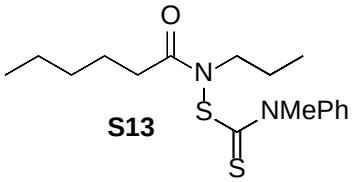
Substrate Synthesis – *General Procedure B*



The acid chloride was prepared as following: to a solution of the carboxylic acid (1.0 equiv) in CH_2Cl_2 (0.5 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.

The thiocarbamylsulfenamide (1.0 equiv) was charged to a separate round-bottomed flask with a stir bar and was dissolved in CH_2Cl_2 (0.5 M). Pyridine was added dropwise at 0 °C, followed by a solution of the acid chloride (2 M in CH_2Cl_2). The reaction mixture was allowed to warm to room temperature and was stirred until completion as determined by TLC and/or GC-MS (1 h to 14 h).

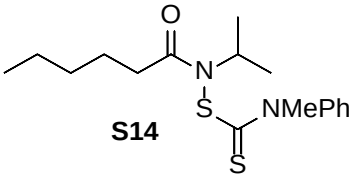
The reaction mixture was diluted with CH_2Cl_2 and washed with water. The aqueous layer was extracted with CH_2Cl_2 (x 2). The combined organic phase was then washed with 2 M NaOH solution and brine, then dried over anhydrous $MgSO_4$. The solid was filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica to afford the desired functionalized amides.



S13

***N*-((methyl(phenyl)carbamothioyl)thio)-*N*-propylhexanamide (S13)**: Prepared according to General Procedure B from hexanoyl chloride (1.00 mmol) and **S1** as a colorless oil (0.305 g, 90% yield):

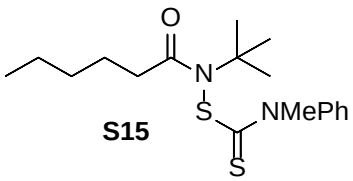
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 3H), 7.30 – 7.27 (m, 2H), 4.33 – 4.27 (m, 1H), 3.75 (s, 3H), 2.80 (ddd, *J* = 13.5, 7.9, 6.5 Hz, 1H), 2.48 (ddd, *J* = 16.0, 8.6, 6.4 Hz, 1H), 2.37 (ddd, *J* = 15.7, 8.7, 6.4 Hz, 1H), 1.61 – 1.51 (m, 2H), 1.51 – 1.43 (m, 2H), 1.32 – 1.23 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H), 0.79 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.88, 178.57, 142.78, 130.18, 129.96, 126.90, 53.36, 46.52, 33.58, 31.56, 25.09, 22.65, 21.61, 14.12, 11.34.
HRMS (ES+) Exact mass calcd for $C_{17}H_{26}N_2OS_2Na$ $[M+Na]^+$, 361.1384. Found 361.1376.



S14

***N*-isopropyl-*N*-((methyl(phenyl)carbamothioyl)thio)hexanamide (S14):** Prepared according to General Procedure B from hexanoyl chloride (1.00 mmol) and **S2** as a white solid (0.200 g, 59% yield):

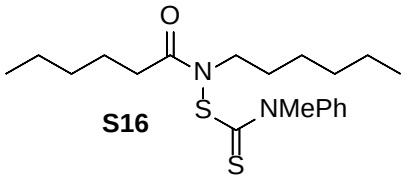
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 3H), 7.34 – 7.28 (m, 2H), 4.91 (hept, *J* = 6.7 Hz, 1H), 3.75 (s, 3H), 2.52 – 2.43 (m, 2H), 1.64 – 1.53 (m, 2H), 1.35 – 1.22 (m, 4H), 1.12 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.87 (t, *J* = 6.9 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 200.80, 178.75, 143.02, 130.18, 129.93, 126.91, 49.54, 46.76, 34.61, 31.56, 25.16, 22.68, 22.35, 19.45, 14.14.
HRMS (ES+) Exact mass calcd for $C_{17}H_{26}N_2OS_2Na$ $[M+Na]^+$, 361.1384. Found 361.1376.



S15

***N*-(*tert*-butyl)-*N*-((methyl(phenyl)carbamothioyl)thio)hexanamide (S15):** Prepared according to General Procedure B from hexanoyl chloride (2.00 mmol) and **S3** as a white solid (0.312 g, 44% yield):

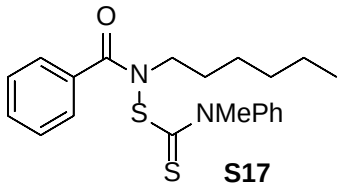
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 3H), 7.29 – 7.27 (m, 2H), 3.75 (s, 3H), 2.52 (ddd, *J* = 16.2, 8.6, 6.2 Hz, 1H), 2.43 (ddd, *J* = 16.2, 8.7, 6.5 Hz, 1H), 1.59 – 1.49 (m, 2H), 1.44 (s, 9H), 1.34 – 1.18 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 201.77, 179.01, 143.09, 130.14, 129.89, 126.81, 63.54, 46.67, 36.57, 31.52, 29.93, 25.34, 22.77, 14.18.
HRMS (ES+) Exact mass calcd for $C_{18}H_{28}N_2OS_2Na$ $[M+Na]^+$, 375.1541. Found 375.1534.



S16

***N*-hexyl-*N*-((methyl(phenyl)carbamothioyl)thio)hexanamide (S16):** Prepared according to General Procedure B from hexanoyl chloride (2.50 mmol) and **S6** to give a yellow oil (0.607 g, 64% yield):

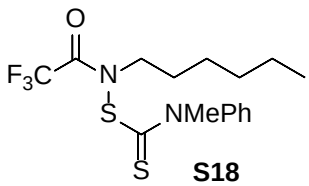
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 3H), 7.33 – 7.27 (m, 2H), 4.34 (ddd, *J* = 12.9, 8.6, 6.6 Hz, 1H), 3.75 (s, 3H), 2.80 (ddd, *J* = 14.0, 8.6, 5.8 Hz, 1H), 2.47 (ddd, *J* = 15.3, 8.5, 6.2 Hz, 1H), 2.36 (ddd, *J* = 15.7, 8.6, 6.2 Hz, 1H), 1.63 – 1.51 (m, 2H), 1.49 – 1.39 (m, *J* = 6.7 Hz, 2H), 1.36 – 1.14 (m, 10H), 0.87 (t, *J* = 6.8 Hz, 3H), 0.83 (t, *J* = 6.7 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.85, 178.56, 142.70, 130.18, 129.98, 126.89, 51.80, 46.56, 33.58, 31.59, 31.54, 28.31, 26.51, 25.07, 22.67, 22.65, 14.16, 14.14.
HRMS (ES+) Exact mass calcd for $C_{20}H_{32}N_2OS_2Na$ $[M+Na]^+$, 403.1854. Found 403.1846.



S17

***N*-hexyl-*N*-((methyl(phenyl)carbamothioyl)thio)benzamide (S17):** Prepared according to General Proceudre B from benzoyl chloride (2.00 mmol) and **S6** to give an amorphous yellow solid (0.619 g, 80% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.29 (m, 9H), 6.91 – 6.78 (m, 1H), 4.59 – 4.46 (m, 1H), 3.61 (s, 3H), 3.16 – 3.06 (m, 1H), 1.61 – 1.48 (m, 2H), 1.32 – 1.18 (m, 8H), 0.84 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.76, 176.28, 142.57, 136.31, 129.92, 129.72, 129.52, 127.51, 127.33, 126.75, 51.66, 46.14, 31.55, 28.11, 26.51, 22.62, 14.10.
HRMS (ES+) Exact mass calcd for $C_{21}H_{26}N_2OS_2Na$ $[M+Na]^+$, 409.1384. Found 409.1376.

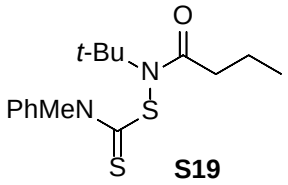


S18

2,2,2-trifluoro-*N*-hexyl-*N*-((methyl(phenyl)carbamothioyl)thio)acetamide (S18): To a solution of **S6** (2.0 mmol) dissolved in CH_2Cl_2 (0.5 M) was added DMAP (4.0 equiv) and trifluoroacetic anhydride (3.0 equiv) at 0 °C. The cooling bath was removed and the mixture was allowed to stir at room temperature until the reaction was complete as indicated by TLC. Upon complete conversion of the starting material, the reaction mixture was diluted with CH_2Cl_2, then washed with

sat. $NaHCO_3$ and brine. The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography to give an amorphous yellow solid (0.694 g, 92% yield).

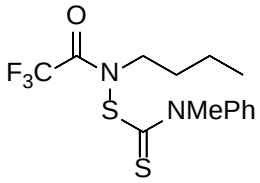
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 3H), 7.31 – 7.27 (m, 2H), 4.38 (dt, J = 13.6, 7.7 Hz, 1H), 3.74 (s, 3H), 3.03 (dt, J = 14.0, 7.3 Hz, 1H), 1.54 – 1.43 (m, 2H), 1.31 – 1.16 (m, 6H), 0.84 (t, J = 6.9 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 196.67, 161.41 (q, *J* = 35.9 Hz), 142.17, 130.37, 130.32, 126.97, 118.83, 115.96 (q, *J* = 288.6 Hz) 54.30, 46.46, 31.44, 27.19, 26.28, 22.55, 14.05.
^{19}F NMR (376 MHz, $CDCl_3$) δ -68.39.
HRMS (ES+) Exact mass calcd for $C_{16}H_{21}F_3N_2OS_2Na$ $[M+Na]^+$, 401.0945. Found 401.0938.



S19

***N*-(*tert*-butyl)-*N*-((methyl(phenyl)carbamothioyl)thio)butyramide (S19):** Prepared according to General Procedure B from butyric acid (2.50 mmol) and **S3** to give an egg-white solid (0.492 g, 61% yield):

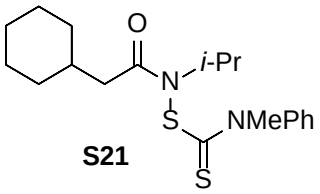
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 5.3, 2.0 Hz, 3H), 7.29 – 7.27 (m, 2H), 3.75 (s, 3H), 2.50 (ddd, *J* = 16.1, 8.0, 6.4 Hz, 1H), 2.42 (ddd, *J* = 16.2, 8.2, 6.8 Hz, 1H), 1.61 – 1.52 (m, 2H), 1.43 (s, 9H), 0.89 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 201.69, 178.74, 143.01, 130.12, 129.87, 126.76, 77.16, 63.50, 46.65, 38.36, 29.88, 18.87, 13.81.
HRMS (ES+) Exact mass calcd for $C_{16}H_{24}N_2OS_2Na$ $[M+Na]^+$, 347.1228. Found 347.1220.



S20

***N*-butyl-2,2,2-trifluoro-*N*-((methyl(phenyl)carbamothioyl)thio)acetamide (S20):**
To a solution of **S4** (2.0 mmol) dissolved in CH_2Cl_2 (0.5 M) was added DMAP (4.0 equiv) and trifluoroacetic anhydride (3.0 equiv) at 0 °C. The cooling bath was removed and the mixture was allowed to stir at room temperature until the reaction was complete as indicated by TLC. Upon complete conversion of the starting material, the reaction mixture was diluted with CH_2Cl_2, then washed with sat. $NaHCO_3$ and brine. The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography to give an amorphous yellow solid (0.700 g, 100% yield).

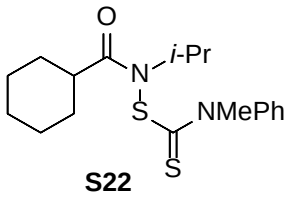
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 3H), 7.30 – 7.26 (m, 2H), 4.40 (dt, *J* = 13.6, 7.6 Hz, 1H), 3.74 (s, 3H), 3.03 (dt, *J* = 14.0, 6.9 Hz, 1H), 1.54 – 1.45 (m, 2H), 1.28 – 1.18 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 196.68, 161.43 (q, *J* = 35.9 Hz), 142.17, 130.38, 130.33, 126.97, 115.96 (q, *J* = 288.6 Hz), 54.06, 46.46, 29.34, 19.90, 13.80.
^{19}F NMR (376 MHz, $CDCl_3$) δ -68.39.
HRMS (ES+) Exact mass calcd for $C_{14}H_{17}F_3N_2OS_2Na$ $[M+Na]^+$, 373.0632. Found 373.0625.



S21

2-cyclohexyl-*N*-isopropyl-*N*-((methyl(phenyl)carbamothioyl)thio)acetamide (S21): Prepared according to General Procedure B from 2-cyclohexylacetic acid (1.00 mmol) and **S2** to give an amorphous colorless solid (0.299 g, 79% yield):

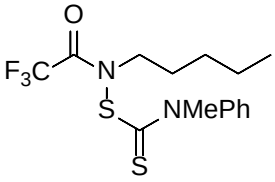
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.46 (m, 3H), 7.32 – 7.28 (m, 2H), 4.90 (hept, *J* = 6.6 Hz, 1H), 3.74 (s, 3H), 2.47 (dd, *J* = 15.5, 6.6 Hz, 1H), 2.27 (dd, *J* = 15.5, 6.9 Hz, 1H), 1.83 – 1.71 (m, 2H), 1.67 – 1.56 (m, 4H), 1.29 – 1.18 (m, 2H), 1.14 – 1.06 (m, 4H), 0.97 – 0.83 (m, 5H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 200.76, 177.90, 143.03, 130.14, 129.88, 126.85, 49.50, 46.70, 41.88, 35.14, 33.34, 33.26, 26.43, 26.32, 26.24, 22.39, 19.42.
HRMS (ES+) Exact mass calcd for $C_{19}H_{28}N_2OS_2Na$ $[M+Na]^+$, 387.1541. Found 387.1533.



S22

***N*-isopropyl-*N*-((methyl(phenyl)carbamothioyl)thio)cyclohexanecarboxamide (S22)**: Prepared according to General Procedure B from cyclohexanecarboxylic acid (1.00 mmol) and **S2** to give a white solid (0.281 g, 80% yield):

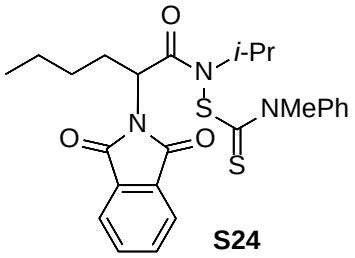
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 3H), 7.34 – 7.29 (m, 2H), 4.90 (hept, *J* = 6.7 Hz, 1H), 3.75 (s, 3H), 2.73 (tt, *J* = 11.5, 3.4 Hz, 1H), 1.83 – 1.74 (m, 2H), 1.71 – 1.57 (m, 4H), 1.28 – 1.13 (m, 4H), 1.09 (d, *J* = 6.7 Hz, 3H), 0.90 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 201.65, 181.87, 143.14, 130.18, 129.89, 126.84, 77.37, 77.16, 76.95, 49.13, 46.82, 41.98, 30.11, 29.17, 26.31, 26.05, 25.48, 22.38, 19.31.
HRMS (ES+) Exact mass calcd for $C_{18}H_{26}N_2OS_2Na$ $[M+Na]^+$, 373.1384. Found 373.1378.



S23

2,2,2-trifluoro-*N*-((methyl(phenyl)carbamothioyl)thio)-*N*-pentylacetamide (S23)
To a solution of **S5** (2.0 mmol) dissolved in CH_2Cl_2 (0.5 M) was added DMAP (4.0 equiv) and trifluoroacetic anhydride (3.0 equiv) at 0 °C. The cooling bath was removed and the mixture was allowed to stir at room temperature until the reaction was complete as indicated by TLC. Upon complete conversion of the starting material, the reaction mixture was diluted with CH_2Cl_2, then washed with sat. $NaHCO_3$ and brine. The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography to give an amorphous yellow solid (0.709 g, 97% yield).

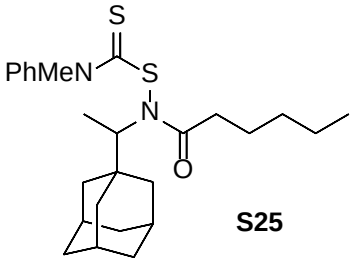
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 3H), 7.30 – 7.27 (m, 2H), 4.38 (dt, *J* = 13.6, 7.7 Hz, 1H), 3.73 (s, 3H), 3.02 (dt, *J* = 14.0, 7.2 Hz, 1H), 1.52 – 1.46 (m, 2H), 1.29 – 1.23 (m, 2H), 1.21 – 1.14 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 196.58, 161.39 (q, *J* = 35.8 Hz), 142.07, 130.37, 130.31, 126.93, 115.91 (q, *J* = 288.6 Hz), 54.23, 46.45, 28.70, 26.88, 22.33, 13.96.
^{19}F NMR (376 MHz, $CDCl_3$) δ -68.39.
HRMS (ES+) Exact mass calcd for $C_{15}H_{19}F_3N_2OS_2Na$ $[M+Na]^+$, 387.0789. Found 387.0784.



S24

2-(1,3-dioxoisoindolin-2-yl)-*N*-isopropyl-*N*-((methyl(phenyl)carbamothioyl)thio)hexanamide (S24): Prepared according to General Procedure B from **S8** (1.66 mmol) and **S2** to give a yellow solid (0.370 g, 46% yield):

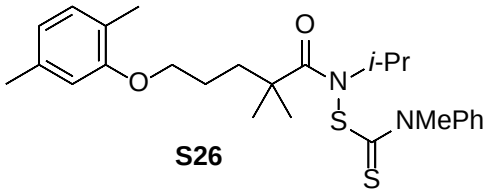
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.68 (ddd, *J* = 11.7, 5.5, 3.1 Hz, 2H), 7.34 (q, *J* = 8.6, 8.1 Hz, 5H), 4.96 (dd, *J* = 8.4, 6.3 Hz, 1H), 4.89 (p, *J* = 6.6 Hz, 1H), 3.73 (s, 3H), 2.17 (dp, *J* = 16.2, 5.6 Hz, 1H), 1.90 – 1.80 (m, 1H), 1.39 – 1.23 (m, 2H), 1.23 – 1.13 (m, 2H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.86 – 0.80 (m, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.83, 173.29, 167.08, 142.27, 134.07, 133.79, 131.65, 129.83, 129.75, 123.19, 52.12, 50.53, 46.78, 30.24, 28.06, 22.54, 22.11, 18.95, 13.95.
HRMS (ES+) Exact mass calcd for $C_{25}H_{29}N_3O_3S_2Na$ $[M+Na]^+$, 506.1548. Found 506.1542.



S25

***N*-(1-((3*r*,5*r*,7*r*)-adamantan-1-yl)ethyl)-*N*-((methyl(phenyl)carbamothioyl)thio)hexanamide (S25):** Prepared according to General Procedure B from hexanoyl chloride (0.750 mmol) and **S6** to give a pale yellow solid (0.335 g, 97% yield):

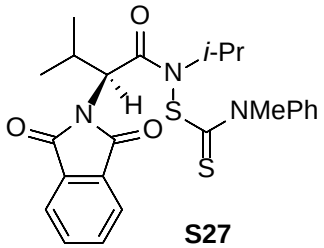
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 3H), 7.29 – 7.26 (m, 2H), 4.79 (q, *J* = 7.0 Hz, 1H), 3.71 (s, 3H), 2.58 (ddd, *J* = 15.3, 8.3, 6.7 Hz, 1H), 2.51 (ddd, *J* = 15.7, 8.4, 6.7 Hz, 1H), 1.82 (q, *J* = 3.2 Hz, 3H), 1.61 – 1.53 (m, 5H), 1.50 – 1.45 (m, 3H), 1.36 – 1.32 (m, 3H), 1.32 – 1.24 (m, 8H), 1.10 (d, *J* = 7.0 Hz, 3H), 0.87 – 0.84 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 201.58, 179.70, 142.98, 130.05, 129.84, 126.72, 59.58, 46.65, 38.82, 37.68, 37.00, 36.96, 34.93, 31.55, 28.56, 28.41, 25.46, 22.58, 14.06, 10.18.
HRMS (ES+) Exact mass calcd for $C_{26}H_{38}N_2OS_2Na$ $[M+Na]^+$, 481.2323. Found 481.2316.



S26

5-(2,5-dimethylphenoxy)-*N*-isopropyl-2,2-dimethyl-*N*-((methyl(phenyl)carbamothioyl)thio)pentanamide (S26): Prepared according to General Procedure B from gemfibrozil (1.50 mmol) and **S2** to give a pale yellow solid (0.481 g, 68% yield):

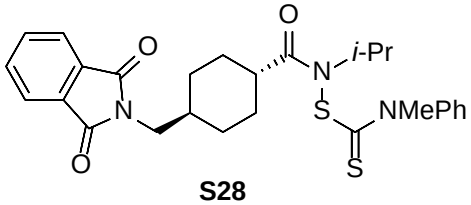
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.45 (m, 3H), 7.34 – 7.28 (m, 2H), 7.02 – 6.95 (m, 1H), 6.67 – 6.62 (m, 1H), 6.61 – 6.58 (m, 1H), 4.65 (hept, *J* = 6.5 Hz, 1H), 3.90 (dt, *J* = 9.1, 5.7 Hz, 1H), 3.85 (ddd, *J* = 9.1, 6.9, 5.4 Hz, 1H), 3.74 (s, 3H), 2.31 (s, 3H), 2.08 (s, 3H), 1.93 (td, *J* = 12.9, 12.4, 3.7 Hz, 1H), 1.79 (ddtd, *J* = 17.2, 11.1, 5.5, 3.7 Hz, 1H), 1.74 – 1.59 (m, 2H), 1.37 (s, 3H), 1.33 (s, 3H), 1.25 (d, *J* = 6.7 Hz, 3H), 1.08 (d, *J* = 6.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 201.61, 180.95, 157.03, 143.01, 136.44, 130.25, 130.10, 129.85, 126.81, 123.57, 120.60, 111.97, 68.15, 54.16, 46.47, 44.55, 37.84, 27.11, 26.75, 25.22, 22.54, 21.47, 19.66, 15.94.
HRMS (ES+) Exact mass calcd for $C_{26}H_{36}N_2O_2S_2Na$ $[M+Na]^+$, 495.2116. Found 495.2107.



S27

(*S*)-2-(1,3-dioxoisoindolin-2-yl)-*N*-isopropyl-3-methyl-*N*-((methyl(phenyl)carbamothioyl)thio)butanamide (S27): Prepared according to General Procedure B from **S9** (2.00 mmol) and **S2** to give a light yellow solid (0.514 g, 55% yield):

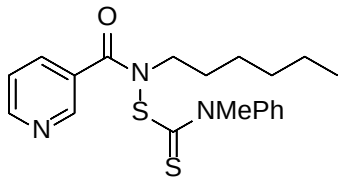
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.76 (m, 2H), 7.74 – 7.66 (m, 2H), 7.40 – 7.31 (m, 5H), 4.93 (hept, *J* = 6.6 Hz, 1H), 4.68 (d, *J* = 9.4 Hz, 1H), 3.76 (s, 3H), 2.74 (dhept, *J* = 9.3, 6.7 Hz, 1H), 1.14 (d, *J* = 6.5 Hz, 3H), 1.06 (d, *J* = 6.7 Hz, 3H), 0.84 (d, *J* = 8.4 Hz, 3H), 0.80 (d, *J* = 9.0 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.89, 172.53, 167.39, 142.39, 134.15, 133.86, 131.60, 129.89, 129.80, 123.31, 57.31, 50.37, 46.92, 28.96, 22.25, 21.04, 19.02, 18.89.
HRMS (ES+) Exact mass calcd for $C_{24}H_{27}N_3O_3S_2Na$ $[M+Na]^+$, 492.1392. Found 492.1383.



S28

(1*r*,4*r*)-4-((1,3-dioxoisoindolin-2-yl)methyl)-*N*-isopropyl-*N*-((methyl(phenyl)carbamothioyl)thio)cyclohexane-1-carboxamide (S28): Prepared according to General Procedure B from **S10** (1.50 mmol) and **S2** to give a yellow solid (0.710 g, 93% yield):

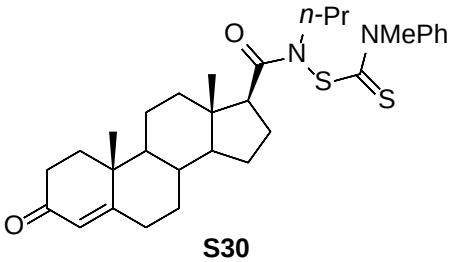
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 2H), 7.71 – 7.65 (m, 2H), 7.56 – 7.46 (m, 3H), 7.35 – 7.31 (m, 2H), 4.86 (hept, *J* = 6.6 Hz, 1H), 3.75 (s, 3H), 3.52 (d, *J* = 7.2 Hz, 2H), 2.71 (tt, *J* = 11.9, 3.4 Hz, 1H), 1.87 (dt, *J* = 13.3, 3.0 Hz, 1H), 1.84 – 1.72 (m, 2H), 1.72 – 1.59 (m, 3H), 1.15 (qd, *J* = 12.9, 3.4 Hz, 1H), 1.10 – 0.96 (m, 5H), 0.88 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 201.27, 181.39, 168.70, 143.06, 134.00, 132.07, 130.18, 129.87, 126.82, 123.28, 49.22, 46.81, 44.00, 41.68, 36.50, 30.39, 29.58, 29.18, 28.48, 22.31, 19.27.
HRMS (ES+) Exact mass calcd for $C_{27}H_{31}N_3O_3S_2Na$ [M+Na]$^+$, 532.1705. Found 532.1694.



S29

***N*-hexyl-*N*-((methyl(phenyl)carbamothioyl)thio)nicotinamide (S29):** Prepared according to General Procedure B from nicotinic acid (2.50 mmol) and **S6** to give a low-melting yellow-orange solid (0.708 g, 73% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 – 8.55 (m, 2H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.38 (dd, *J* = 16.2, 7.6 Hz, 3H), 7.29 – 7.23 (m, 2H), 6.89 (br s, 1H), 4.47 (dt, *J* = 14.9, 7.8 Hz, 1H), 3.58 (s, 3H), 3.02 (dt, *J* = 13.9, 7.1 Hz, 1H), 1.58 – 1.48 (m, 2H), 1.31 – 1.18 (m, 6H), 0.82 (t, *J* = 6.8 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 197.47, 173.90, 150.21, 148.05, 142.13, 135.18, 132.14, 129.98, 129.91, 129.86, 126.49, 122.38, 51.70, 46.15, 31.37, 27.85, 26.36, 22.47, 13.96.
HRMS (ES+) Exact mass calcd for $C_{20}H_{26}N_3OS_2$ [M+H]$^+$, 388.1517. Found 388.1510.

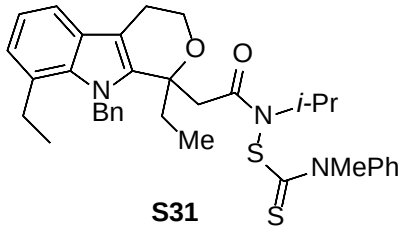


S30

(10*R*,13*S*,17*S*)-10,13-dimethyl-*N*-((methyl(phenyl)carbamothioyl)thio)-3-oxo-*N*-propyl-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthrene-17-carboxamide (S30): To a solution of **S11** (0.63 g, 2 mmol, 1.0 equiv) and pyridine (0.21 mL, 2.6 mmol, 1.3 equiv) dissolved in toluene (10 mL, 0.2 M) was added dropwise a solution of $COCl_2$ (0.19 mL, 2.3 mmol, 1.1 equiv) in toluene (4.5 mL) at 0 °C. The solution was stirred at rt for 1.5 h, then pyridine (0.18 mL, 2.2 mmol, 1.1 equiv) followed by a solution of **S1** (0.48 g, 2 mmol, 1.0 equiv) dissolved in 2.0 mL was added dropwise at 0 °C. The mixture was stirred at rt overnight. The reaction mixture was concentrated then resuspended in CH_2Cl_2 (50 mL) and washed with water (50 mL). The aqueous layer was extracted with CH_2Cl_2 (25 mL x 2). The combined organic phase was then washed with 2 M NaOH solution (100 mL) and brine (100 mL), then dried over anhydrous $MgSO_4$. The solid was filtered, and the filtrate was concentrated *in vacuo*. The crude mixture was purified by flash column chromatography to give a light yellow solid (0.312 g, 29% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 3H), 7.27 – 7.23 (m, 2H), 5.68 (s, 1H), 4.35 (dt, *J* = 13.5, 7.6 Hz, 1H), 3.69 (s, 3H), 3.09 (t, *J* = 9.1 Hz, 1H), 2.69 (dt, *J* = 13.6, 6.7 Hz, 1H), 2.41 – 2.19 (m, 6H), 1.95 (ddd, *J* = 13.3, 5.1, 3.1 Hz, 1H), 1.84 – 1.80 (m, 1H), 1.73 (dtd, *J* = 13.1, 9.2, 6.1

Hz, 1H), 1.69 – 1.62 (m, 2H), 1.55 – 1.46 (m, 2H), 1.46 – 1.37 (m, 2H), 1.32 – 1.25 (m, 2H), 1.17 – 1.08 (m, 2H), 1.11 (s, 3H), 1.06 – 0.99 (m, 1H), 0.88 (ddd, *J* = 12.4, 10.7, 4.3 Hz, 1H), 0.74 (t, *J* = 7.4 Hz, 3H), 0.63 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.38, 199.31, 178.49, 171.21, 142.64, 129.97, 129.84, 126.67, 123.75, 55.93, 53.82, 53.77, 50.59, 45.04, 38.59, 38.42, 35.70, 33.94, 32.81, 32.03, 26.58, 24.60, 21.78, 20.89, 17.27, 13.85, 11.26.
HRMS (ES+) Exact mass calcd for $C_{31}H_{43}N_2O_2S_2$ $[M+H]^+$, 539.2766. Found 539.2762.



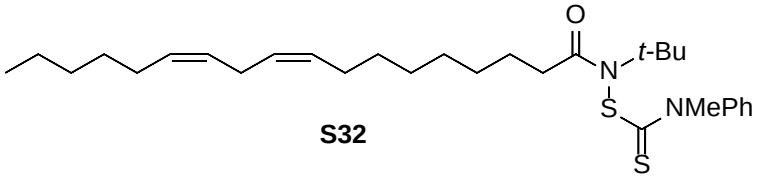
S31

2-(9-benzyl-1,8-diethyl-1,3,4,9-tetrahydropyrano[3,4-*b*]indol-1-yl)-*N*-isopropyl-*N*-((methyl(phenyl)carbamothioyl)thio)acetamide (S31): Prepared according to General Procedure B from **S12** (1.50 mmol) and **S2** to give a colorless amorphous solid (0.528 g, 59% yield):

Characterization data for the mixture of diastereomers:
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (tt, *J* = 7.5, 1.2 Hz, 0.5H), 7.35 (tt, *J* = 7.5, 1.2 Hz, 0.5H), 7.30 – 7.23 (m, 5H), 7.21 – 7.08 (m, 3H), 6.98 – 6.88 (m, 3H), 6.35 (dd, *J* = 7.4, 1.1 Hz, 1H), 6.23 (dd, *J* = 7.4, 1.1 Hz, 0.5H), 4.99 (tq, *J* = 13.0, 6.5 Hz, 0.5H), 4.32 (ddd, *J* = 12.0, 9.7, 6.8 Hz, 0.5H), 4.23 (td, *J* = 11.6, 4.4 Hz, 0.5H), 3.89 (ddd, *J* = 12.1, 7.9, 2.7 Hz, 0.5H), 3.85 (ddd, *J* = 12.1, 6.2, 2.2 Hz, 0.5H), 3.70 (s, 1.5H), 3.67 (s, 1.5H), 3.52 – 3.45 (m, 1H), 3.26 (d, *J* = 15.0 Hz, 0.5H), 3.13 (d, *J* = 14.7 Hz, 0.5H), 2.96 (ddtd, *J* = 56.5, 29.3, 14.5, 7.4 Hz, 2H), 2.67 (d, *J* = 13.5 Hz, 0.5H), 2.48 (dq, *J* = 14.0, 3.1 Hz, 2H), 2.26 (ddq, *J* = 28.5, 14.6, 7.3 Hz, 1H), 2.12 (dq, *J* = 14.4, 7.2 Hz, 0.5H), 2.01 (dt, *J* = 13.9, 6.9 Hz, 0.5H), 1.42 – 1.30 (m, 1H), 1.30 – 1.21 (m, 4H), 1.13 (t, *J* = 7.2 Hz, 3H), 1.05 (td, *J* = 7.3, 2.2 Hz, 3H), 1.00 (t, *J* = 6.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 200.52, 200.44, 186.32, 184.43, 174.63, 174.22, 152.94, 152.46, 142.73, 142.59, 137.05, 136.81, 136.79, 136.69, 131.23, 131.03, 130.09, 130.07, 129.85, 129.83, 127.85, 127.77, 127.27, 127.25, 126.76, 126.70, 126.64, 124.31, 124.18, 121.34, 121.24, 80.32, 80.19, 65.89, 58.04, 57.20, 56.74, 56.60, 49.50, 49.37, 46.71, 39.26, 38.95, 38.21, 37.78, 32.96, 31.18, 30.84, 29.40, 24.43, 24.15, 22.38, 22.34, 19.48, 15.36, 15.30, 8.59, 7.94.
HRMS (ES+) Exact mass calcd for $C_{35}H_{41}N_3O_2S_2Na$ $[M+Na]^+$, 622.2538. Found 622.2532.

The compound was stored in the cold and dark in a vial purged with N_2 due to its inherent instability.



S32

(9*Z*,12*Z*)-*N*-(*tert*-butyl)-*N*-((methyl(phenyl)carbamothioyl)thio)octadeca-9,12-dienamide (S32): Prepared according to General Procedure B from linoleic acid (3.0 mmol) and **S3** to give a golden oil (1.00 g, 65% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 3H), 7.29 – 7.27 (m, 2H), 5.41 – 5.30 (m, 4H), 3.76 (s, 3H), 2.79 – 2.75 (m, 2H), 2.52 (ddd, *J* = 16.2, 8.5, 6.2 Hz, 1H), 2.44 (ddd, *J* = 16.1, 8.6, 6.4

Hz, 1H), 2.08 – 2.00 (m, 4H), 1.54 – 1.50 (m, 1H), 1.45 (s, 9H), 1.38 – 1.24 (m, 15H), 0.89 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 201.83, 178.95, 130.35, 130.33, 130.15, 129.89, 128.09, 126.84, 63.58, 46.68, 36.61, 31.67, 29.96, 29.85, 29.66, 29.50, 29.37, 29.33, 27.41, 27.36, 25.79, 25.67, 22.73, 14.24.
HRMS (ES+) Exact mass calcd for $C_{30}H_{48}N_2OS_2Na$ $[M+Na]^+$, 539.3106. Found 539.3114.

Functionalized Products

General Procedure C – *Product functionalization from light initiation*
A 1 dram vial was charged with substrate (1.0 equiv), fitted with a PTFE lined screw cap, and taken into the glovebox. The contents were dissolved in $PhCF_3$ (0.5 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 in a 3D-printed holder (see below picture). 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. The temperature inside the reaction mixture reached 50 °C. The reaction was concentrated *in vacuo,* and the crude residue was purified by flash column chromatography to afford the functionalized product.

General Procedure D – *Product functionalization using heat and initiator*
A 1 dram vial equipped with a stir bar was charged with substrate (1.0 equiv) and dicumyl peroxide (10 mol %), fitted with a PTFE lined screw cap, and taken into the glovebox. The contents were dissolved in PhCl (0.5 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 120 °C to stir overnight. Upon completion, the reaction was concentrated *in vacuo*, and the crude residue was purified by flash column chromatography to afford the functionalized product.

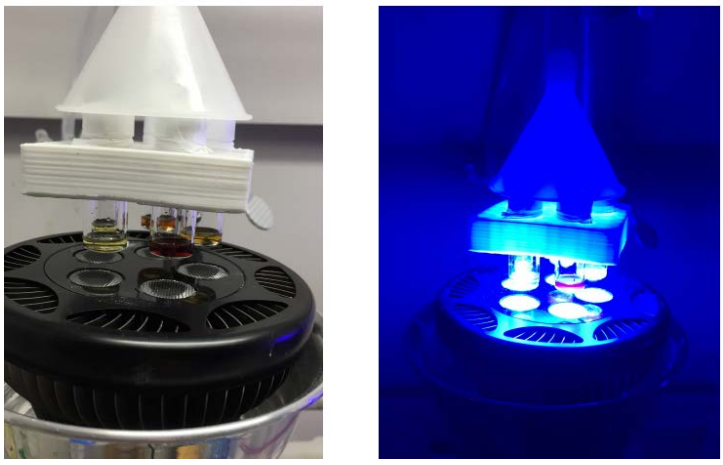
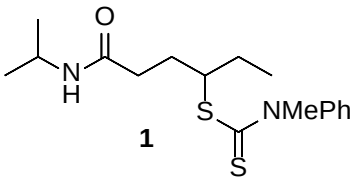


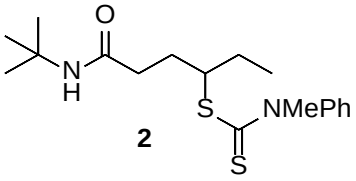
Figure S1. Pictures of the set up for General Procedure C with the blue LED turned off and on. The reaction vials are suspended in a 3D-printed vial holder such that the bottom of the vials is about 1 cm from the LED below.



1

6-(isopropylamino)-6-oxohexan-3-yl methyl(phenyl)carbamodithioate (1): Prepared according to General Procedures C and D from **S14** (51 mg, 0.15 mmol). The crude residue was purified by flash column chromatography (30 – 40% EtOAc in hexanes) to afford **1** as a white solid (C: 46.4 mg, 91% yield; D: 37.2 mg, 73% yield).

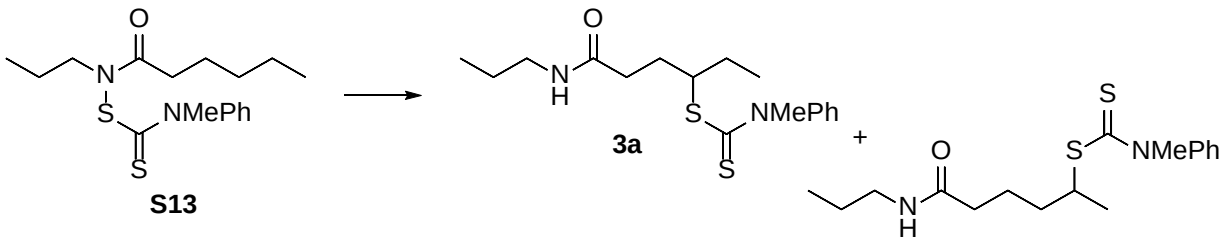
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 3H), 7.23 – 7.19 (m, 2H), 5.58 (d, *J* = 7.9 Hz, 1H), 4.05 (ddq, *J* = 13.0, 7.8, 6.4 Hz, 1H), 3.95 (ddd, *J* = 13.6, 8.6, 5.5 Hz, 1H), 3.74 (s, 3H), 2.22 (qdd, *J* = 14.8, 8.8, 6.4 Hz, 2H), 1.99 (ddt, *J* = 14.5, 9.0, 6.0 Hz, 1H), 1.85 (dq, *J* = 15.3, 8.2 Hz, 1H), 1.71 – 1.55 (m, 2H), 1.14 (dd, *J* = 13.9, 6.6 Hz, 6H), 0.92 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.58, 171.62, 129.82, 128.97, 126.94, 55.01, 41.45, 34.43, 30.23, 27.83, 22.89, 22.86, 11.45.
HRMS (ES+) Exact mass calcd for $C_{17}H_{27}N_2OS_2$ $[M+H]^+$, 339.1564. Found 339.1625.



2

6-(tert-butylamino)-6-oxohexan-3-yl methyl(phenyl)carbamodithioate (2): Prepared according to General Procedures C and D from **S15** (53 mg, 0.15 mmol). The crude residue was purified by flash column chromatography (15 – 30% EtOAc in hexanes) to afford **2** as a white solid (C: 32.2 mg, 61% yield; D: 29.6 mg, 56% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 3H), 7.24 – 7.20 (m, 2H), 5.44 (s, 1H), 3.97 – 3.91 (m, 1H), 3.74 (s, 3H), 2.18 (qdd, *J* = 14.8, 8.9, 6.3 Hz, 2H), 2.02 – 1.95 (m, 1H), 1.82 (tq, *J* = 14.8, 8.6, 7.4 Hz, 1H), 1.71 – 1.57 (m, 2H), 1.33 (s, 9H), 0.92 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.61, 171.93, 129.81, 128.95, 126.96, 55.07, 51.25, 46.26, 35.23, 30.14, 28.91, 28.02, 11.45.
HRMS (ES+) Exact mass calcd for $C_{18}H_{29}N_2OS_2$ $[M+H]^+$, 353.1783. Found 353.1783.



S13 **3a** **3b**

Reaction of S13: Prepared according to General Procedures C and D from **S13** (51 mg, 0.15 mmol). The crude residue was purified by flash column chromatography to afford **3** as a white solid (C: 40.5 mg, 79% yield, 3:1 *rr*; D: 44.0 mg, 85% yield, 3:1 *rr*).

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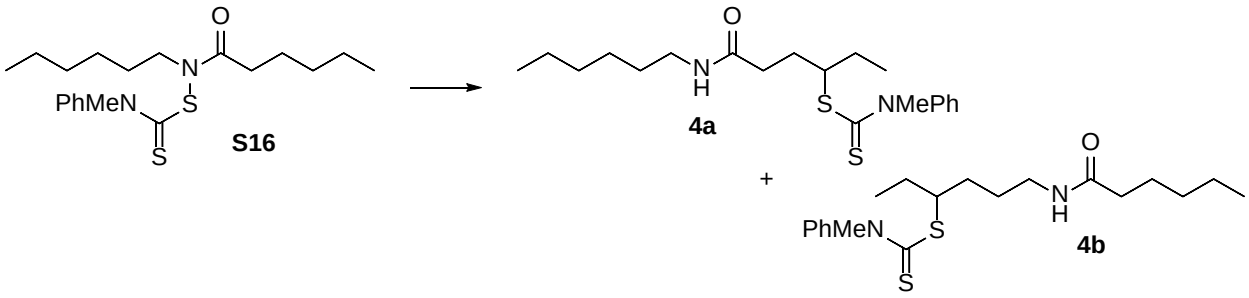
6-oxo-6-(propylamino)hexan-3-yl methyl(phenyl)carbamodithioate (3a):
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.37 (m, 3H), 7.24 – 7.17 (m, 2H), 5.83 (t, *J* = 5.8 Hz, 1H), 3.98 – 3.89 (m, 1H), 3.74 (s, 3H), 3.18 (tdd, *J* = 7.1, 5.8, 3.1 Hz, 2H), 2.25 (tdd, *J* = 14.7, 11.6, 7.4 Hz, 2H), 2.03 – 1.96 (m, 1H), 1.87 (p, *J* = 7.4, 6.8 Hz, 1H), 1.67 (dp, *J* = 14.4, 7.3 Hz, 1H), 1.59 (tt, *J* = 14.5, 7.4 Hz, 1H), 1.51 (h, *J* = 7.3 Hz, 2H), 0.91 (q, *J* = 7.1 Hz, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.57, 172.55, 129.82, 128.99, 126.91, 54.99, 41.36, 34.29, 30.30, 27.77, 22.92, 11.56, 11.44.
HRMS (ES+) Exact mass calcd for $C_{17}H_{27}N_2OS_2$ $[M+H]^+$, 339.1564. Found 339.1629.

6-oxo-6-(propylamino)hexan-2-yl methyl(phenyl)carbamodithioate (3b):
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 3H), 7.23 – 7.19 (m, 2H), 5.58 (s, 1H), 3.96 (p, *J* = 6.8 Hz, 1H), 3.74 (s, 3H), 3.19 (dt, *J* = 7.7, 6.3 Hz, 2H), 2.17 (ddt, *J* = 15.9, 14.4, 7.3 Hz, 2H), 1.70 (tt, *J* = 8.9, 5.3 Hz, 4H), 1.50 (p, *J* = 7.3 Hz, 2H), 1.30 (d, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.33, 172.78, 129.84, 128.98, 127.01, 47.63, 41.32, 36.37, 35.84, 23.30, 23.02, 20.66, 11.54.

HRMS (ES+) Exact mass calcd for $C_{17}H_{27}N_2OS_2$ $[M+H]^+$, 339.1564. Found 339.1629.

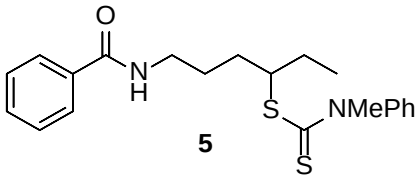
***The same ratio of products was obtained at lower concentrations (0.1 M), suggesting that the minor 1,6-product is not the result of background intermolecular functionalization.



Reaction of S16: Prepared according to General Procedures C and D from **S16** (57 mg, 0.15 mmol). The crude residue was purified by flash column chromatography (20 – 50% EtOAc in hexanes) to afford **4** as a colorless, amorphous solid (C: 49.6 mg, 87% yield, 2.5:1 *rr*; D: 49.6 mg, 87% yield, 1.6:1 *rr*).

6-(hexylamino)-6-oxohexan-3-yl methyl(phenyl)carbamodithioate (4a):
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.41 (m, 3H), 7.27 – 7.22 (m, 2H), 5.74 (s, 1H), 3.98 (tt, *J* = 8.3, 5.4 Hz, 1H), 3.78 (s, 3H), 3.30 – 3.19 (m, 3H), 2.35 – 2.22 (m, 2H), 2.21 – 2.13 (m, 1H), 2.09 – 1.98 (m, 1H), 1.89 (dq, *J* = 15.1, 8.1 Hz, 1H), 1.75 – 1.57 (m, 2H), 1.55 – 1.47 (m, 2H), 1.38 – 1.25 (m, 5H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.93 – 0.87 (m, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.67, 172.49, 129.86, 129.01, 126.97, 55.09, 39.74, 34.38, 31.63, 31.61, 30.39, 29.70, 27.87, 26.78, 22.71, 14.17, 11.48.

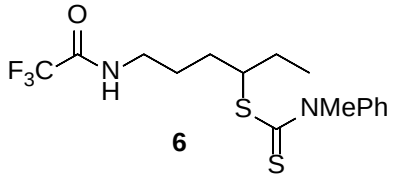
6-hexanamidohexan-3-yl methyl(phenyl)carbamodithioate (4b)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 3H), 7.27 – 7.21 (m, 2H), 5.80 (s, 1H), 4.00 – 3.88 (m, 1H), 3.77 (s, 3H), 3.33 (dq, *J* = 12.9, 6.4 Hz, 1H), 3.23 (dq, *J* = 13.3, 6.5 Hz, 1H), 2.22 – 2.13 (m, 2H), 1.76 – 1.53 (m, 7H), 1.38 – 1.25 (m, 5H), 0.99 – 0.87 (m, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.64, 173.12, 129.73, 128.84, 126.88, 54.49, 38.88, 36.91, 31.50, 31.43, 26.73, 26.69, 25.55, 22.44, 13.99, 11.40.
HRMS (ES+) Exact mass calcd for $C_{20}H_{33}N_2OS_2$ $[M+H]^+$, 381.2034. Found 381.2101.



5

6-benzamidohexan-3-yl methyl(phenyl)carbamodithioate (5): Prepared according to General Procedures C and D from **S17** (58 mg, 0.15 mmol). The crude residue was purified by flash column chromatography (20 – 50% EtOAc in hexanes) to afford **5** as a white solid (C: 47.4 mg, 82% yield; D: 47.5 mg, 82% yield):

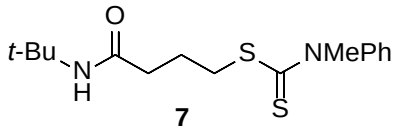
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 2H), 7.48 – 7.37 (m, 6H), 7.23 – 7.18 (m, 2H), 6.56 (t, *J* = 5.8 Hz, 1H), 3.99 – 3.93 (m, 1H), 3.73 (s, 3H), 3.52 (dq, *J* = 12.6, 6.3 Hz, 1H), 3.39 (dq, *J* = 12.7, 6.5 Hz, 1H), 1.76 – 1.65 (m, 5H), 1.57 (dt, *J* = 14.7, 7.5 Hz, 1H), 0.92 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.62, 167.50, 134.80, 131.32, 129.78, 129.75, 128.89, 128.55, 128.53, 127.04, 126.97, 126.92, 54.51, 39.52, 31.54, 26.76, 26.73, 11.50.
HRMS (ES+) Exact mass calcd for $C_{21}H_{27}N_2OS_2$ $[M+H]^+$, 387.1564. Found 387.1633.



6

6-(2,2,2-trifluoroacetamido)hexan-3-yl methyl(phenyl)carbamodithioate (6): Prepared according to General Procedures C and D from **S18** (57 mg, 0.15 mmol). The crude residue was purified by flash column chromatography (10 – 30% EtOAc in hexanes) to afford **6** as a white solid (C: 44.5 mg, 78% yield; D: 48.9 mg, 86% yield):

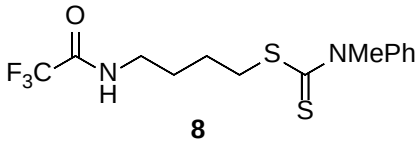
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 3H), 7.24 – 7.20 (m, 2H), 6.81 – 6.75 (m, 1H), 3.95 – 3.89 (m, 1H), 3.75 (s, 3H), 3.43 (dq, *J* = 12.6, 6.3 Hz, 1H), 3.33 (dq, *J* = 12.7, 6.3 Hz, 1H), 1.73 – 1.62 (m, 5H), 1.60 – 1.53 (m, 1H), 0.92 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.45, 157.28 (q, *J* = 36.9 Hz), 129.83, 129.00, 126.92, 120.08 – 112.19 (m), 54.17, 39.46, 31.36, 26.76, 26.02, 11.50.
HRMS (ES+) Exact mass calcd for $C_{16}H_{22}F_3N_2OS_2$ $[M+H]^+$, 379.1126. Found 379.1192.



7

4-(tert-butylamino)-4-oxobutyl methyl(phenyl)carbamodithioate (7): Prepared according to General Procedures C and D from **S19** (49 mg, 0.15 mmol). The crude residue was purified by flash column chromatography (20 – 30% EtOAc in hexanes) to afford **7** as a white solid (C: 31.9 mg, 65% yield; D: 37.2 mg, 76% yield):

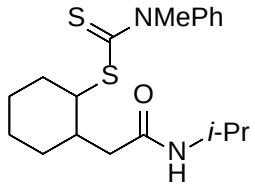
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.39 (m, 3H), 7.23 – 7.16 (m, 2H), 5.95 (s, 1H), 4.06 (ddd, *J* = 9.6, 7.0, 4.0 Hz, 1H), 3.75 (s, 3H), 2.76 (dd, *J* = 13.5, 4.1 Hz, 2H), 2.13 (dd, *J* = 13.4, 9.7 Hz, 2H), 1.34 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.77, 169.90, 129.83, 129.09, 126.81, 51.09, 45.76, 45.57, 28.78, 18.95.
HRMS (ES+) Exact mass calcd for $C_{16}H_{25}N_2OS_2$ $[M+H]^+$, 325.1408. Found 325.1466.



8

4-(2,2,2-trifluoroacetamido)butyl methyl(phenyl)carbamodithioate (8): Prepared according to General Procedure D from **S20** (52.5 mg, 0.15 mmol). The crude residue was purified by flash column chromatography (5 – 10% EtOAc in hexanes) to afford **8** as a white solid (27.4 mg, 52% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 3H), 7.24 – 7.22 (m, 2H), 6.69 (s, 1H), 3.76 (s, 3H), 3.39 (q, *J* = 6.5 Hz, 2H), 3.18 (t, *J* = 7.3 Hz, 2H), 1.73 – 1.60 (m, 4H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.22, 157.22 (q, *J* = 36.8 Hz), 144.70, 129.80, 129.07, 126.87, 115.85 (q, *J* = 287.8 Hz), 46.17, 39.08, 36.46, 27.85, 26.00.
HRMS (ES+) Exact mass calcd for $C_{14}H_{18}F_3N_2OS_2$ $[M+H]^+$, 351.0813. Found 351.0876.



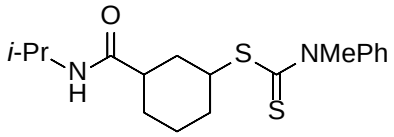
9

2-(2-(isopropylamino)-2-oxoethyl)cyclohexyl methyl(phenyl)carbamodithioate (9): Prepared according to General Procedures C and D from **S21** (57 mg, 0.15 mmol). The crude residue was purified by flash column chromatography (20 – 50% EtOAc in hexanes) to afford **9** as a white solid (C: 50.6 mg, 89% yield, 2:1 *dr*; D: 44.8 mg, 79% yield, 2:1 *dr*).

Major diastereomer (*trans*):
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 3H), 7.20 – 7.18 (m, 2H), 5.37 (d, *J* = 7.9 Hz, 1H), 4.08 – 4.00 (m, 1H), 3.81 (td, *J* = 10.9, 4.2 Hz, 1H), 3.74 (s, 3H), 2.62 (dd, *J* = 12.4, 3.0 Hz, 1H), 2.15 – 2.11 (m, 1H), 1.94 – 1.86 (m, 2H), 1.76 – 1.61 (m, 3H), 1.43 – 1.34 (m, 2H), 1.29 – 1.19 (m, 2H), 1.16 – 1.08 (m, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.33, 171.35, 129.87, 129.00, 126.94, 56.95, 41.88, 41.38, 39.18, 34.39, 33.26, 32.65, 26.88, 25.41, 23.10, 22.84.

Minor diastereomer (*cis*):
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 3H), 7.27 – 7.20 (m, 2H), 5.37 (d, *J* = 7.7 Hz, 1H), 4.50 – 4.44 (m, 1H), 4.11 – 4.04 (m, 1H), 3.78 (s, 3H), 2.38 – 2.30 (m, 1H), 2.27 (dd, *J* = 14.2, 5.3 Hz, 1H), 2.01 – 1.89 (m, 2H), 1.81 – 1.53 (m, 5H), 1.43 – 1.22 (m, 2H), 1.15 (d, *J* = 7.6 Hz, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.96, 171.23, 129.88, 128.92, 127.02, 56.11, 41.50, 41.44, 38.75, 32.31, 30.42, 23.02, 22.93.

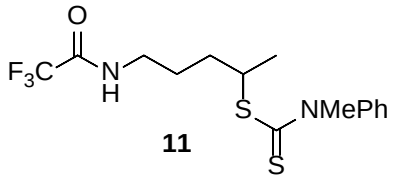
HRMS (ES+) Exact mass calcd for $C_{19}H_{29}N_2OS_2$ $[M+H]^+$, 365.1721. Found 365.1786.



10

3-(isopropylcarbamoyl)cyclohexyl methyl(phenyl)carbamodithioate (10): Prepared according to General Procedures C and D from **S22** (52.6 mg, 0.15 mmol). The crude residue was purified by flash column chromatography (30% EtOAc in hexanes) to afford **10** as a white solid (C: 42.5 mg, 81% yield, 2:1 *dr*; D: 45.7 mg, 87% yield, 2:1 *dr*).

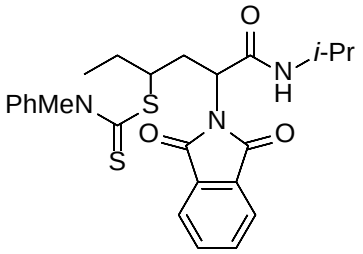
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 3H), 7.21 – 7.17 (m, 2H), 6.36 (s, 0.33H), 5.43 (s, 0.67H), 4.10 (hept, *J* = 6.9 Hz, 0.33H), 4.05 – 3.96 (m, 1H), 3.78 – 3.72 (m, 0.67H), 3.72 (s, 1H), 3.71 (s, 2H), 2.32 (d, *J* = 8.4 Hz, 0.67H), 2.24 (d, *J* = 12.7 Hz, 0.67H), 2.16 (tt, *J* = 11.9, 3.5 Hz, 0.67H), 2.02 (t, *J* = 7.3 Hz, 0.33H), 1.92 (t, *J* = 9.0 Hz, 0.33H), 1.85 – 1.73 (m, 2.67H), 1.61 (m, 0.33H), 1.53 – 1.31 (m, 2.67H), 1.23 (m, .67H), 1.17 (dd, *J* = 17.0, 6.6 Hz, 3H), 1.09 (dd, *J* = 6.6, 2.2 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.78, 198.47, 173.82, 173.19, 144.82, 129.85, 129.74, 128.94, 126.89, 126.83, 49.94, 48.34, 45.69, 45.66, 41.49, 41.42, 41.12, 40.94, 35.75, 33.99, 31.59, 30.74, 29.73, 28.60, 28.50, 25.85, 25.81, 22.99, 22.94, 22.89, 22.83, 22.81, 22.74.
HRMS (ES+) Exact mass calcd for $C_{18}H_{27}N_2OS_2$ $[M+H]^+$, 351.1565. Found 351.1627.



11

5-(2,2,2-trifluoroacetamido)pentan-2-yl methyl(phenyl)carbamodithioate (11): Prepared according to General Procedures C and D from **S23** (55 mg, 0.15 mmol). The crude residue was purified by flash column chromatography (10 – 30% EtOAc in hexanes) to afford **11** as a white solid (C: 47.2 mg, 86% yield; D: 47.2 mg, 86% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.38 (m, 3H), 7.25 – 7.20 (m, 2H), 6.83 (s, 1H), 3.92 (h, *J* = 7.0 Hz, 1H), 3.75 (d, *J* = 6.4 Hz, 3H), 3.45 (dq, *J* = 13.2, 6.5 Hz, 1H), 3.32 (dq, *J* = 13.4, 6.8 Hz, 1H), 1.79 (dq, *J* = 14.1, 7.2 Hz, 1H), 1.71 – 1.61 (m, *J* = 7.2 Hz, 2H), 1.55 (dq, *J* = 15.9, 8.6, 7.0 Hz, 1H), 1.28 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.90, 157.31 (q, *J* = 36.7 Hz), 144.78, 129.86, 129.09, 126.92, 115.95 (q, *J* = 287.9 Hz), 46.83, 39.22, 33.53, 26.21, 19.86.
HRMS (ES+) Exact mass calcd for $C_{15}H_{19}F_3N_2OS_2$ $[M+H]^+$, 364.0891. Found 364.0923.



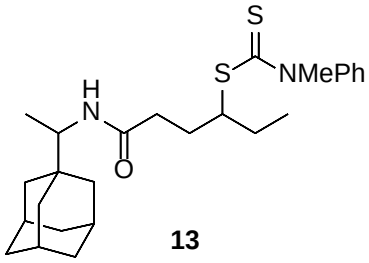
12

5-(1,3-dioxoisoindolin-2-yl)-6-(isopropylamino)-6-oxohexan-3-yl methyl(phenyl)carbamodithioate (12): Prepared according to General Procedures C and D from **S24** (72 mg, 0.15 mmol). The crude residue was purified by flash column chromatography (20 – 50% EtOAc in hexanes) to afford **12** as an off-white solid (C: 59.8 mg, 82% yield; D: 53.5 mg, 74% yield) in a 1:1 diastereomeric mixture:

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 2H), 7.78 – 7.70 (m, 2H), 7.48 – 7.27 (m, 5H), 6.03 (d, *J* = 7.4 Hz, 1H), 4.94 (dd, *J* = 11.1, 4.8 Hz, 1H), 4.08 – 4.01 (m, 1H), 4.01 – 3.94 (m, 1H), 3.64 (s, 3H), 2.84 (ddd, *J* = 15.5, 11.1, 4.8 Hz, 1H), 2.27 (ddd, *J* = 18.4, 12.3, 6.2 Hz, 1H), 1.73 (dp, *J* = 13.5, 7.3, 6.8 Hz, 1H), 1.59 (dp, *J* = 14.6, 7.4 Hz, 1H), 1.13 (d, *J* = 6.5 Hz, 3H), 1.12 (d, *J* = 6.5 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.39, 168.35, 168.12, 134.15, 132.21, 129.84, 127.14, 123.57, 52.77, 52.53, 42.10, 33.43, 28.50, 22.72, 22.70, 11.25.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 2H), 7.79 – 7.69 (m, 2H), 7.46 – 7.37 (m, 3H), 7.21 – 7.14 (m, 2H), 6.27 (d, *J* = 7.8 Hz, 1H), 4.84 (dd, *J* = 8.3, 5.4 Hz, 1H), 4.05 (hept, *J* = 6.8 Hz, 1H), 3.89 (qd, *J* = 7.8, 4.4 Hz, 1H), 3.67 (s, 3H), 2.58 (dt, *J* = 14.0, 6.5 Hz, 1H), 2.39 (dt, *J* = 14.8, 7.5 Hz, 1H), 1.88 – 1.80 (m, 1H), 1.58 (dq, *J* = 15.8, 8.0 Hz, 1H), 1.16 (d, *J* = 6.6 Hz, 3H), 1.14 (d, *J* = 6.6 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.74, 168.28, 167.73, 134.27, 132.08, 129.83, 127.01, 123.66, 52.87, 52.70, 42.18, 35.60, 26.54, 22.69, 22.66, 11.58.

HRMS (ES+) Exact mass calcd for $C_{25}H_{31}N_3O_3S_2$ $[M+H]^+$, 485.1807. Found 485.1815.

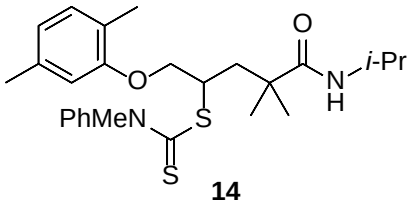


13

6-((1-((3r,5r,7r)-adamantan-1-yl)ethyl)amino)-6-oxohexan-3-yl methyl(phenyl)carbamodithioate (13): Prepared according to General Procedures C and D from **S25** (46 mg, 0.15 mmol). The crude residue was purified by flash column chromatography (15 – 30% EtOAc in hexanes) to afford **13** as a light yellow solid (C: 36.3 mg, 79% yield; D: 22.1 mg, 48% yield and 17.5 mg **S25** recovered) in a 1:1 diastereomeric mixture:

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 3H), 7.24 – 7.21 (m, 2H), 5.54 (t, *J* = 9.2 Hz, 1H), 4.03 – 3.92 (m, 1H), 3.75 (s, 3H), 3.71 (dq, *J* = 9.8, 6.9 Hz, 1H), 2.35 – 2.20 (m, 2H), 2.06 – 1.94 (m, 3H), 1.88 (dq, *J* = 14.5, 7.7 Hz, 1H), 1.72 – 1.66 (m, 4H), 1.65 – 1.57 (m, 4H), 1.57 – 1.49 (m, 4H), 1.49 – 1.44 (m, 2H), 1.03 (d, *J* = 6.9 Hz, 2H), 1.00 (dd, *J* = 6.9, 2.1 Hz, 2H), 0.93 (td, *J* = 7.4, 4.7 Hz, 3H).

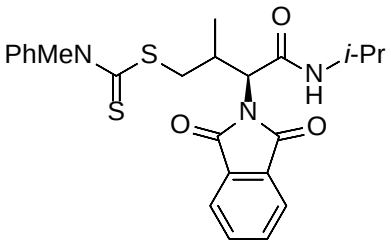
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.71, 199.60, 172.03, 171.94, 129.85, 128.99, 126.97, 55.46, 55.15, 53.02, 38.54, 38.52, 37.19, 35.94, 35.90, 34.72, 34.65, 30.57, 30.49, 28.45, 28.44, 28.42, 28.22, 27.96, 14.72, 14.69, 11.52, 11.48.
HRMS (ES+) Exact mass calcd for $C_{26}H_{39}N_2OS_2$ $[M+H]^+$, 459.2504. Found 459.2586.



14

1-(2,5-dimethylphenoxy)-5-(isopropylamino)-4,4-dimethyl-5-oxopentan-2-yl methyl(phenyl)carbamodithioate (14): Prepared according to General Procedure C from **S26** (71 mg, 0.15 mmol). The crude residue was purified by flash column chromatography (10 – 50% EtOAc in hexanes) to afford **14** as a light yellow solid (40.5 mg, 57% yield).

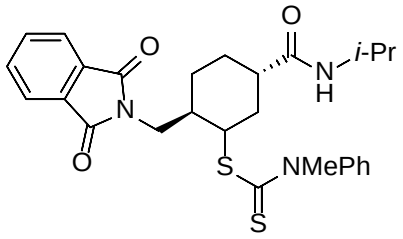
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.34 (m, 3H), 7.23 – 7.15 (m, 2H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.70 – 6.62 (m, 2H), 5.60 (d, *J* = 7.6 Hz, 1H), 4.44 (ddt, *J* = 8.3, 6.4, 4.1 Hz, 1H), 4.17 – 4.08 (m, 1H), 4.00 (dq, *J* = 7.4, 6.4 Hz, 1H), 3.87 (dd, *J* = 9.3, 6.5 Hz, 1H), 3.74 (s, 3H), 2.29 (s, 3H), 2.19 (dd, *J* = 15.0, 4.0 Hz, 1H), 2.13 (s, 3H), 1.98 – 1.88 (m, 1H), 1.24 (s, 3H), 1.20 (s, 3H), 1.12 (d, *J* = 6.4 Hz, 3H), 1.11 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.49, 176.14, 156.59, 144.65, 136.65, 130.32, 129.86, 129.09, 126.96, 123.71, 121.14, 112.61, 70.84, 49.25, 42.09, 41.59, 40.42, 26.12, 22.80, 22.67, 21.44, 16.02.
HRMS (ES+) Exact mass calcd for $C_{26}H_{37}N_2O_2S_2$ $[M+H]^+$, 473.2296. Found 473.2383.



15

(3*S*)-3-(1,3-dioxoisoindolin-2-yl)-4-(isopropylamino)-2-methyl-4-oxobutyl methyl(phenyl)carbamodithioate (15): Prepared according to General Procedures C and D from **S27** (70 mg, 0.15 mmol). The crude residue was purified by flash column chromatography (30% EtOAc in hexanes) to afford **15** as a white solid (C: 59.5 mg, 85% yield; D: 38.4 mg, 55% yield and 25.6 mg **S27** recovered):

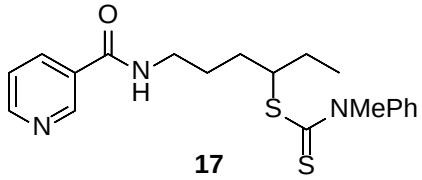
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.79 (m, 2H), 7.77 – 7.69 (m, 2H), 7.47 – 7.39 (m, 3H), 7.25 – 7.21 (m, 2H), 7.03 (d, *J* = 7.6 Hz, 1H), 4.50 (d, *J* = 10.5 Hz, 1H), 4.10 – 4.02 (m, 1H), 3.75 (s, 3H), 3.76 – 3.72 (m, 1H), 3.08 (tqd, *J* = 10.2, 6.7, 3.7 Hz, 1H), 2.91 (dd, *J* = 13.8, 9.8 Hz, 1H), 1.23 (d, *J* = 6.6 Hz, 3H), 1.16 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.79, 168.19, 166.66, 134.42, 131.52, 129.87, 129.11, 126.90, 123.70, 60.54, 42.14, 41.67, 32.17, 22.69, 22.59, 16.37.
HRMS (ES+) Exact mass calcd for $C_{24}H_{28}N_3O_3S_2$ $[M+H]^+$, 470.1572. Found 470.1657.



16

(2R,5S)-2-((1,3-dioxoisoindolin-2-yl)methyl)-5-(isopropylcarbamoyl)cyclohexyl methyl(phenyl)carbamodithioate (16): Prepared according to General Procedures C and D from **S28** (77 mg, 0.15 mmol). The crude residue was purified by flash column chromatography (40 – 50% EtOAc in hexanes) to afford **16** as an off-white solid (C: 65.3 mg, 85% yield; D: 61.6 mg, 81% yield) in a 2:1 diastereomeric mixture. The reaction can be performed without any special treatment under air to provide the title compound in slightly lowered yield (C: 43.7 mg, 57% yield):

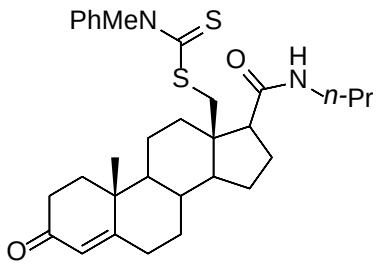
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.76 (m, 2H), 7.74 – 7.66 (m, 2H), 7.52 – 7.30 (m, 4H), 7.20 (d, *J* = 7.4 Hz, 1H), 5.33 (d, *J* = 7.9 Hz, 0.66H), 5.23 (d, *J* = 7.9 Hz, 0.33H), 4.65 (d, *J* = 3.8 Hz, 0.33H), 4.06 – 3.91 (m, 2H), 3.73 (d, *J* = 13.4 Hz, 3H), 3.58 (dd, *J* = 13.8, 10.5 Hz, 0.66H), 3.52 (d, *J* = 6.8 Hz, 0.33H), 3.46 (dd, *J* = 13.9, 8.0 Hz, 0.33H), 2.45 (qt, *J* = 8.7, 4.1 Hz, 0.33H), 2.28 (d, *J* = 13.2 Hz, 0.66H), 2.16 (tt, *J* = 12.2, 3.3 Hz, 0.66H), 2.07 (d, *J* = 13.0 Hz, 0.66H), 1.99 – 1.83 (m, 1.33H), 1.82 – 1.75 (m, 1.66H), 1.64 – 1.55 (m, 1H), 1.50 – 1.31 (m, 1H), 1.31 – 1.18 (m, 1H), 1.14 – 1.05 (m, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.29, 197.82, 173.95, 173.40, 168.53, 168.49, 134.04, 134.02, 133.93, 132.19, 132.07, 129.87, 126.94, 123.33, 123.31, 123.23, 54.34, 52.70, 45.59, 41.99, 41.67, 41.56, 41.25, 41.21, 39.70, 39.23, 37.22, 35.69, 30.11, 30.06, 28.98, 28.19, 22.88, 22.85.
HRMS (ES+) Exact mass calcd for $C_{27}H_{32}N_3O_3S_2$ $[M+H]^+$, 510.1885. Found 510.1976.



17

6-(nicotinamido)hexan-3-yl methyl(phenyl)carbamodithioate (17): Prepared according to General Procedures C and D from **S29** (58 mg, 0.15 mmol). The crude residue was purified by flash column chromatography (75 – 100% EtOAc in hexanes) to afford **17** as a pale yellow amorphous solid (C: 47.1 mg, 81% yield; D: 47.4 mg, 82% yield):

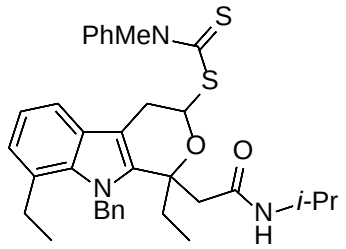
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.01 – 8.95 (m, 1H), 8.69 – 8.63 (m, 1H), 8.15 – 8.06 (m, 1H), 7.45 – 7.36 (m, 3H), 7.34 (dd, *J* = 8.0, 4.7 Hz, 1H), 7.21 – 7.17 (m, 2H), 6.91 (t, *J* = 6.0 Hz, 1H), 3.96 – 3.88 (m, 1H), 3.72 (s, 3H), 3.58 – 3.52 (m, 1H), 3.45 – 3.36 (m, 1H), 1.77 – 1.64 (m, 4H), 1.61 – 1.51 (m, 1H), 1.30 – 1.25 (m, 1H), 0.90 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.73, 165.67, 152.26, 148.18, 147.81, 135.25, 130.52, 129.90, 129.05, 126.98, 123.57, 54.35, 39.44, 31.77, 26.56, 11.65.
HRMS (ES+) Exact mass calcd for $C_{20}H_{26}N_3OS_2$ $[M+H]^+$, 388.1517. Found 388.1586.



18

((10R,13R)-10-methyl-3-oxo-17-(propylcarbamoyl)-1,2,3,6,7,8,9,10,11,12,14,15,16,17-tetradecahydro-13H-cyclopenta[a]phenanthren-13-yl)methyl methyl(phenyl)carbamodithioate (18): Prepared according to General Procedure C from **S30** (54 mg, 0.10 mmol). The crude residue was purified by flash column chromatography (10 – 30% EtOAc in hexanes) to afford **18** as a white solid (24.7 mg, 46% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.40 – 7.35 (m, 1H), 7.24 – 7.20 (m, 2H), 5.72 (s, 1H), 5.15 (s, 1H), 3.99 (d, *J* = 13.9 Hz, 1H), 3.74 (s, 3H), 3.31 – 3.28 (m, 1H), 3.05 (d, *J* = 13.8 Hz, 1H), 2.52 – 2.38 (m, 2H), 2.33 – 2.20 (m, 4H), 2.06 – 1.87 (m, 4H), 1.79 – 1.70 (m, 2H), 1.69 – 1.61 (m, 2H), 1.53 – 1.34 (m, 4H), 1.26 (s, 3H), 1.25 – 1.19 (m, 2H), 1.09 – 1.01 (m, 2H), 0.95 – 0.86 (m, 2H), 0.78 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 200.67, 199.65, 171.63, 171.38, 129.74, 129.39, 127.22, 123.98, 57.61, 56.36, 54.24, 48.21, 41.39, 38.81, 37.79, 35.84, 35.41, 35.34, 34.07, 32.82, 32.03, 24.09, 23.69, 22.45, 21.07, 18.18, 13.80, 11.64.
HRMS (ES+) Exact mass calcd for $C_{31}H_{43}N_2O_2S_2$ $[M+H]^+$, 539.2766. Found 539.2865.

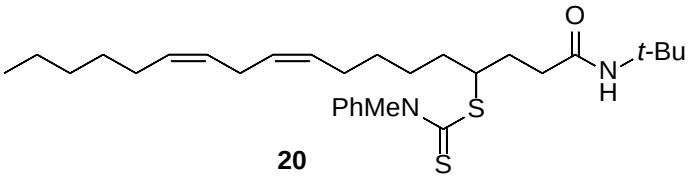


19

9-benzyl-1,8-diethyl-1-(2-(isopropylamino)-2-oxoethyl)-1,3,4,9-tetrahydropyrano[3,4-b]indol-3-yl methyl(phenyl)carbamodithioate (19): Prepared according to General Procedure D from **S31** (60 mg, 0.10 mmol). The crude residue was purified by flash column chromatography to afford **19** as a pale yellow amorphous solid (49.7 mg, 83% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.44 – 7.23 (m, 7H), 7.17 – 7.01 (m, 4H), 5.61 (s, 1H), 4.98 – 4.91 (m, 1H), 4.26 – 4.22 (m, 1H), 4.00 – 3.87 (m, 2H), 3.66 (s, 3H), 3.25 (t, *J* = 7.6 Hz, 2H), 2.79 (q, *J* = 8.0 Hz, 2H), 2.70 (q, *J* = 7.4 Hz, 2H), 1.33 (t, *J* = 8.0 Hz, 3H), 1.21 (d, *J* = 6.6 Hz, 3H), 1.16 (t, *J* = 7.5 Hz, 3H), 1.00 (d, *J* = 6.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 200.81, 174.34, 143.09, 138.73, 134.49, 134.05, 129.02, 128.83, 128.74, 128.58, 128.26, 126.73, 126.26, 120.36, 116.18, 115.98, 109.20, 92.30, 67.93, 32.47, 25.66, 24.29, 24.14, 24.00, 22.56, 19.98, 19.87, 14.02, 13.87, 12.20, 12.12.
HRMS (ES+) Exact mass calcd for $C_{35}H_{42}N_3O_2S_2$ $[M+H]^+$, 600.2718. Found 600.2807.

The compound was stored in the cold and dark in a vial purged with N_2 due to its inherent instability.

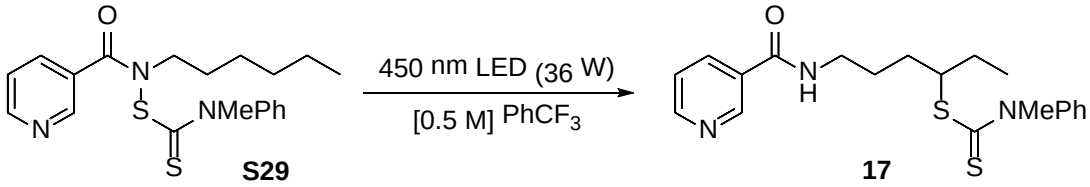


20

(9Z,12Z)-1-(*tert*-butylamino)-1-oxooctadeca-9,12-dien-4-yl methyl(phenyl)carbamodithioate (20): Prepared according to General Procedure C from **S32** (207 mg, 0.40 mmol). The crude residue was purified by flash column chromatography (10% EtOAc in hexanes) to afford **20** as a clear oil (110 mg, 53% yield):

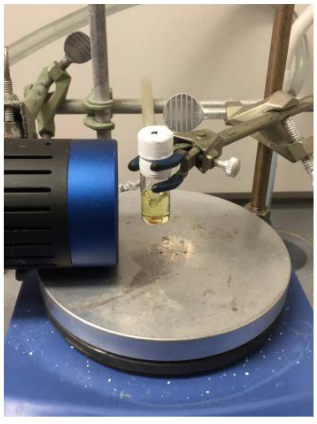
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.38 (m, 3H), 7.24 – 7.20 (m, 2H), 5.47 – 5.26 (m, 5H), 4.00 (dtd, *J* = 10.7, 5.8, 5.0, 2.9 Hz, 1H), 3.75 (s, 3H), 2.79 – 2.64 (m, 2H), 2.18 (dt, *J* = 8.7, 6.5 Hz, 2H), 2.07 – 1.91 (m, 5H), 1.82 (dq, *J* = 15.0, 8.0 Hz, 1H), 1.63 – 1.55 (m, 2H), 1.41 – 1.21 (m, 19H), 0.91 – 0.84 (m, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.47, 171.91, 130.32, 129.92, 129.79, 128.92, 128.22, 127.98, 126.96, 53.56, 51.22, 46.20, 35.18, 34.92, 31.59, 30.66, 29.55, 29.42, 28.89, 27.28, 27.14, 26.59, 25.72, 22.66, 14.18.
HRMS (ES+) Exact mass calcd for $C_{30}H_{49}N_2OS_2$ $[M+H]^+$, 517.3286. Found 517.3377.

Reaction Scale-Up



S29 2 mmol **17**

6-(nicotinamido)hexan-3-yl methyl(phenyl)carbamodithioate (17) was prepared from substrate **S29** (0.775 g, 2.00 mmol) charged to a 2 dram vial equipped with a stir bar. The vial was fitted with a PTFE lined screw cap and taken into the glovebox. The contents were dissolved in $PhCF_3$ (4.0 mL), and the resulting solution was sealed with Teflon tape and removed from the glovebox. The vial was suspended on a stir plate and irradiated with a Kessil Blue KSH150B 36W LED Grow Light from the side (2 cm away) until completion. Reaction temperatures ranged between 40 and 50 °C. The reaction was then concentrated *in vacuo*, and the crude residue was purified by flash column chromatography (75 – 100% EtOAc in hexanes) to afford **17** as a pale yellow amorphous solid (0.604 g, 78% yield).



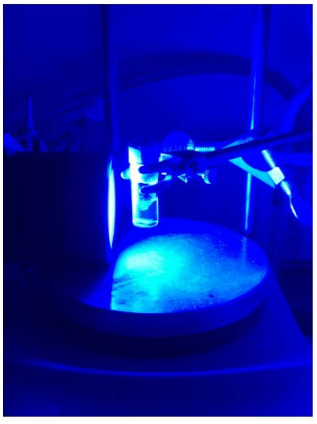
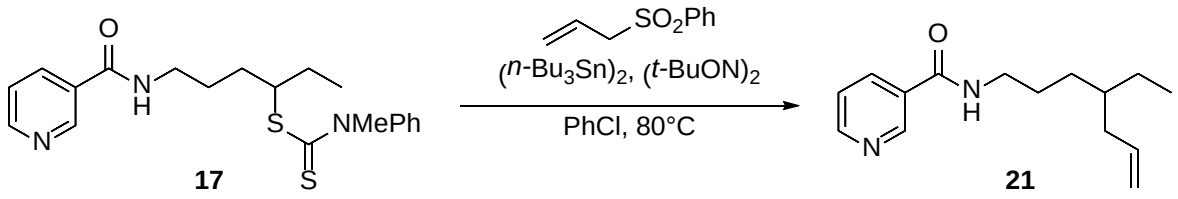


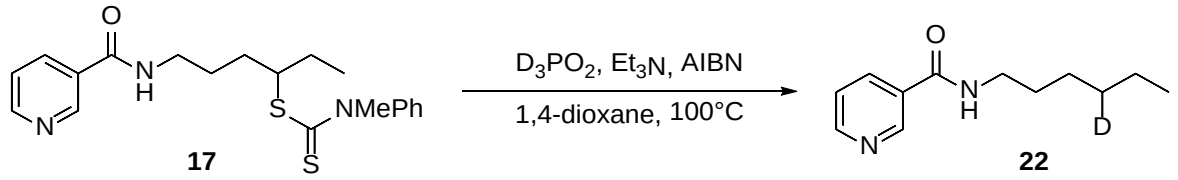
Figure S2. Pictures of the set up used for scaled-up reactions with the blue LED turned off and on. The reaction vial is suspended such that it is approximately 1-2 cm away from the Kessil blue LED.

Further Derivatization



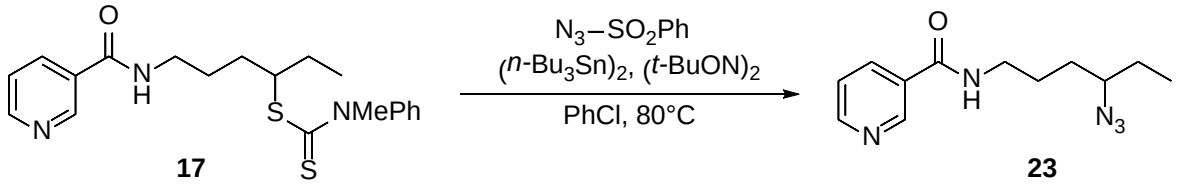
***N*-(4-ethylhept-6-en-1-yl)nicotinamide (21):** In a 1 dram vial, dithiocarbamate **17** (42 mg, 0.11 mmol. 1.0 equiv), allyl phenyl sulfone (50 µL, 0.33 mmol, 3.0 equiv), bis(tributyltin) (82 µL, 0.17 mmol, 1.5 equiv), and di-*tert*-butylhyponitrite (DTBHN; 2.3 mg, 0.013 mmol) were dissolved in chlorobenzene (0.22 mL, 0.50 M). The vial was heated at 80 °C under an argon atmosphere, and additional DTBHN (2.3 mg, 0.013 mmol) was added every 2 h until full consumption of **17** as indicated by TLC (4.6 mg additional DTBHN). The crude mixture was then filtered through silica gel (hexane, then hexane/EtOAc), and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography (85 – 100% EtOAc in hexanes) to give **21** as a pale yellow amorphous solid (23.9 mg, 90% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.94 (d, *J* = 2.3 Hz, 1H), 8.71 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.10 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.38 (ddd, *J* = 8.0, 4.9, 1.0 Hz, 1H), 6.25 (s, 1H), 5.75 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.05 – 4.95 (m, 2H), 3.47 – 3.42 (m, 2H), 2.10 – 1.98 (m, 2H), 1.65 – 1.58 (m, 2H), 1.41 – 1.28 (m, 5H), 0.86 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.69, 152.28, 147.83, 137.32, 135.22, 130.63, 123.65, 116.04, 40.64, 38.68, 37.64, 30.14, 26.87, 25.86, 11.09.
HRMS (ES+) Exact mass calcd for $C_{15}H_{23}N_2O$ $[M+H]^+$, 247.1810. Found 247.1805.



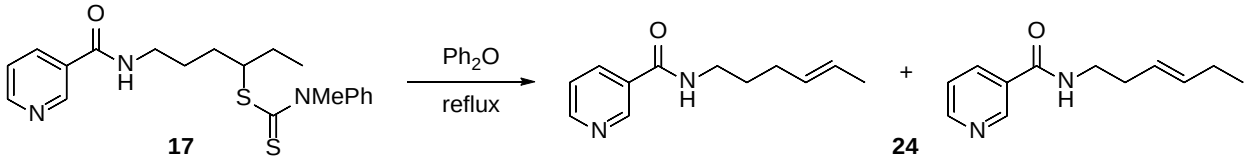
***N*-(hexyl-4-d)nicotinamide (22)**: Adapted from a literature procedure.[8] In a 1 dram vial, dithiocarbamate **17** (39 mg, 0.10 mmol), hypophosphorous acid (50% solution in water, 50 µL, 0.50 mmol, 5.0 equiv), triethylamine (60 µL, 0.55 mmol, 5.5 equiv), and AIBN (2.3 mg, 0.010 mmol) was dissolved in dioxane (1.24 mL, 0.08 M). The vial was heated to 100 °C under an argon atmosphere, and additional AIBN was added every 1 h until full consumption of **17** as indicated by TLC. The reaction mixture was then cooled and poured into water. Extraction with EtOAc and subsequent flash chromatography (90 – 100% EtOAc in hexanes) afforded deuterated product **22** as a pale yellow amorphous solid (16.4 mg, 79% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.95 (d, *J* = 7.9 Hz, 1H), 8.69 (s, 1H), 8.10 (t, *J* = 7.0 Hz, 1H), 7.37 (d, *J* = 8.9 Hz, 1H), 6.48 (s, 1H), 3.44 (q, *J* = 8.4, 7.5 Hz, 2H), 1.64 – 1.55 (m, 2H), 1.39 – 1.21 (m, 5H), 0.87 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.60, 152.00, 147.72, 135.18, 130.58, 123.54, 40.26, 31.05 (t, *J* = 17.7 Hz), 29.52, 26.55, 22.45, 13.99.
HRMS (ES+) Exact mass calcd for $C_{12}H_{18}DN_2O$ $[M+H]^+$, 208.1560. Found 208.1553.



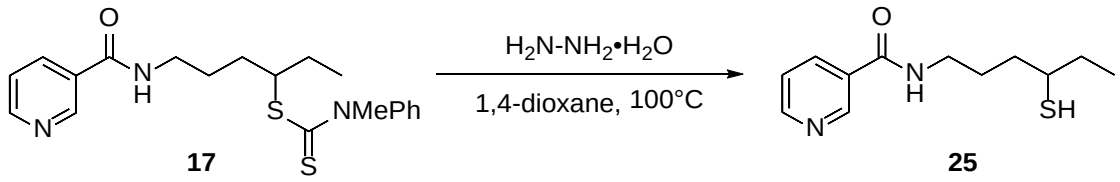
***N*-(4-azidohexyl)nicotinamide (23):** Adapted from a literature procedure.[9] In a 1 dram vial, dithiocarbamate **17** (51 mg, 0.13 mmol), benzenesulfonyl azide (73 mg, 0.39 mmol, 3.0 equiv), bis(tributyltin) (100 µL, 0.20 mmol, 1.5 equiv), and di-*tert*-butylhyponitrite (DTBHN; 2.3 mg, 0.013 mmol) was dissolved in chlorobenzene (0.26 mL, 0.50 M). The vial was heated to 80 °C under an argon atmosphere, and additional DTBHN was added every 2 h. Another addition of benzenesulfonyl azide (73 mg, 0.39 mmol, 3.0 equiv) and bis(tributyltin) (100 µL, 0.20 mmol, 1.5 equiv) was used after the first three additions of DTBHN for full conversion of **17**. Upon completion, the crude mixture was then filtered through silica gel (hexane, then hexane/EtOAc), and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography (85 – 100% EtOAc in hexanes) to give **23** as a pale yellow amorphous solid (24.8 mg, 77% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.99 (d, *J* = 2.3 Hz, 1H), 8.74 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.14 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.41 (dd, *J* = 8.0, 4.6 Hz, 1H), 6.43 (s, 1H), 3.53 (td, *J* = 6.5, 5.7, 2.1 Hz, 2H), 3.31 – 3.25 (m, 1H), 1.81 (dddd, *J* = 16.2, 11.9, 7.4, 1.8 Hz, 1H), 1.74 (dtd, *J* = 13.2, 6.5, 3.4 Hz, 1H), 1.69 – 1.53 (m, 4H), 1.01 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.81, 152.36, 147.87, 135.25, 130.41, 123.69, 64.22, 39.96, 31.38, 27.57, 26.46, 10.63.
HRMS (ES+) Exact mass calcd for $C_{12}H_{18}N_5O$ $[M+H]^+$, 248.1511. Found 248.1506.



***N*-(hex-4-en-1-yl)nicotinamide, *N*-(hex-3-en-1-yl)nicotinamide (24):** Adapted from a literature procedure.[10] A solution of **17** (40 mg, 0.10 mmol) in diphenyl ether (1.0 mL) was heated under reflux for 1 h using alumina beads. Upon cooling, the reaction mixture was directly subjected to flash column chromatography (50 – 100% EtOAc in hexanes) to give **24** (20.5 mg, 99% yield) as a pale yellow oil in a 1:1 regioisomeric mixture.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.00 – 8.89 (m, 1H), 8.71 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.16 – 8.05 (m, 1H), 7.38 (ddd, *J* = 8.0, 4.8, 0.9 Hz, 1H), 6.22 (d, *J* = 28.2 Hz, 1H), 5.66 – 5.33 (m, 2H), 3.55 – 3.44 (m, 2H), 2.33 (qd, *J* = 6.8, 1.3 Hz, 1H), 2.13 – 2.08 (m, 1H), 2.08 – 2.00 (m, 1H), 1.74 – 1.60 (m, 3H), 0.98 (t, *J* = 7.5 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.72, 165.67, 165.60, 152.20, 152.17, 152.15, 147.90, 147.88, 147.82, 135.72, 135.21, 135.18, 130.27, 126.12, 125.31, 123.62, 123.59, 40.35, 39.96, 39.56, 32.55, 31.57, 30.19, 29.65, 29.29, 26.76, 25.73, 22.65, 18.04, 14.12, 13.96.
HRMS (ES+) Exact mass calcd for $C_{12}H_{17}N_2O$ $[M+H]^+$, 205.1341. Found 205.1337.



***N*-(4-mercaptohexyl)nicotinamide (25)**: Adapted from a literature procedure.[11] Hydrazine hydrate (50 µL) was added to a solution of **17** (22 mg, 0.057 mmol) dissolved in 1,4-dioxane (50 µL) and was left stirring overnight at 100 °C. The reaction mixture was then concentrated, and **25** was isolated by flash column chromatography (90 – 100% EtOAc in hexanes) as a yellow amorphous solid (11.4 mg, 84% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.97 (d, *J* = 2.3 Hz, 1H), 8.71 – 8.70 (m, 1H), 8.12 (dt, *J* = 5.8, 1.9 Hz, 1H), 7.40 – 7.37 (m, 1H), 6.48 (s, 1H), 3.50 – 3.43 (m, 2H), 2.77 – 2.70 (m, 1H), 1.84 (ddt, *J* = 12.4, 9.7, 7.1 Hz, 1H), 1.79 – 1.65 (m, 2H), 1.62 (p, *J* = 7.4 Hz, 1H), 1.56 – 1.48 (m, 2H), 1.35 (d, *J* = 7.0 Hz, 1H), 0.99 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.73, 152.22, 147.84, 135.33, 130.51, 123.69, 42.66, 40.04, 35.82, 32.16, 27.38, 11.67.
HRMS (ES+) Exact mass calcd for $C_{12}H_{19}N_2OS$ $[M+H]^+$, 239.1218. Found 239.1213.

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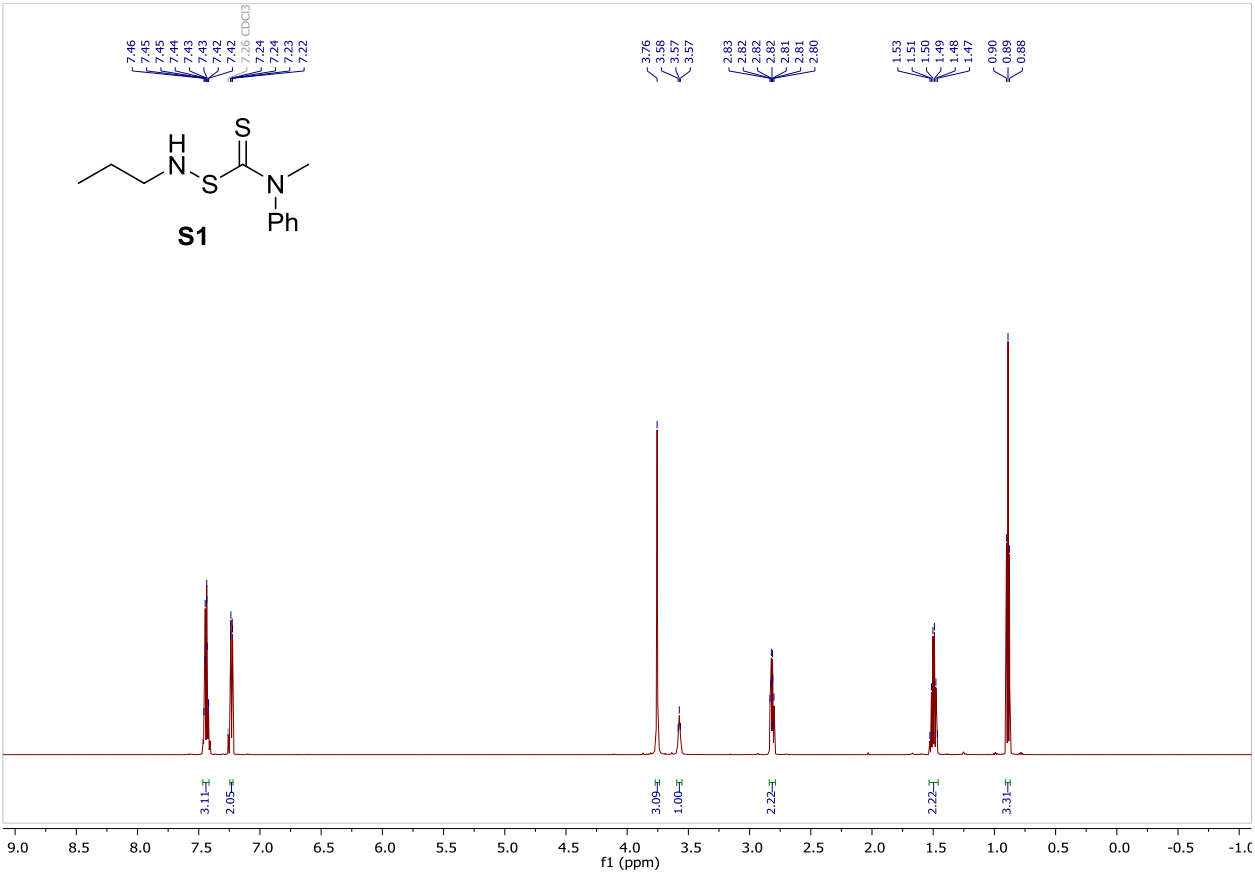
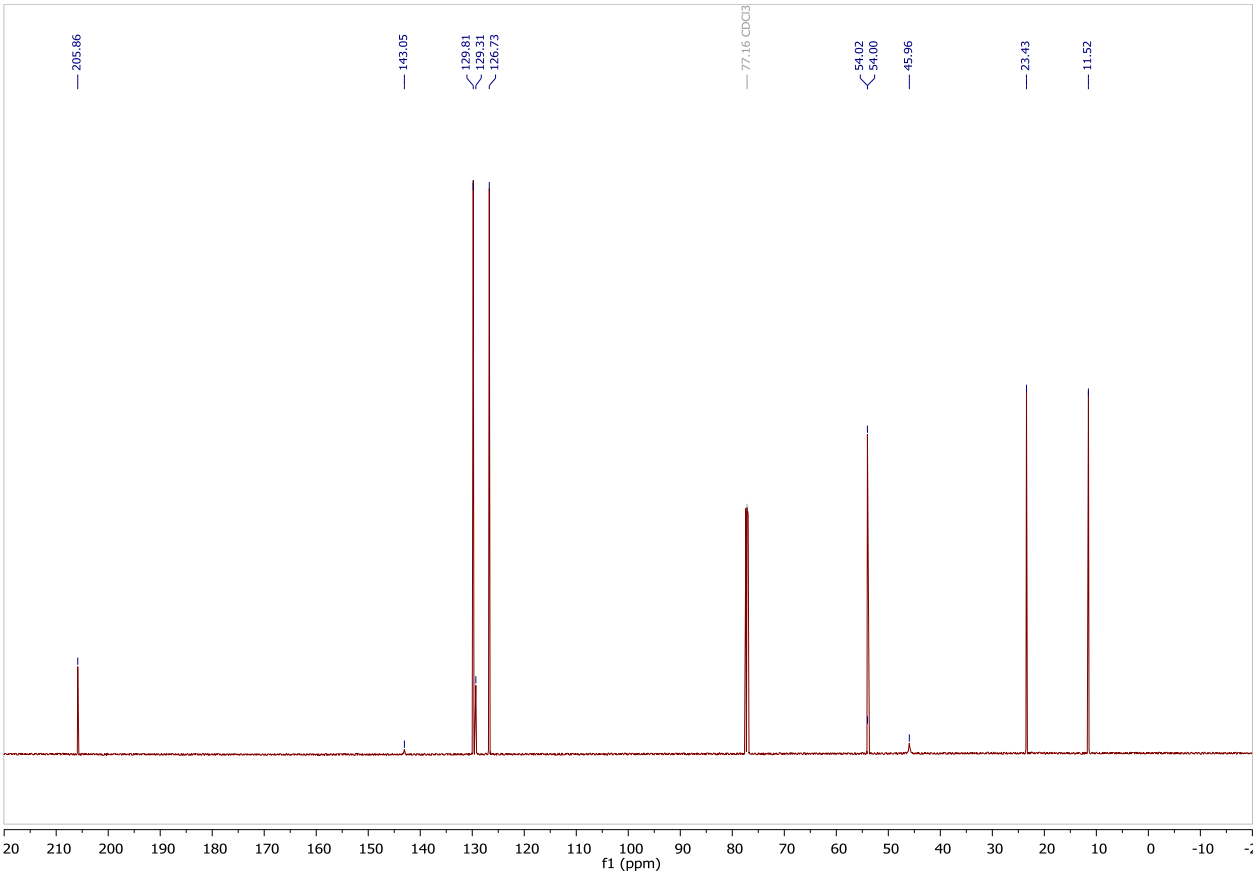
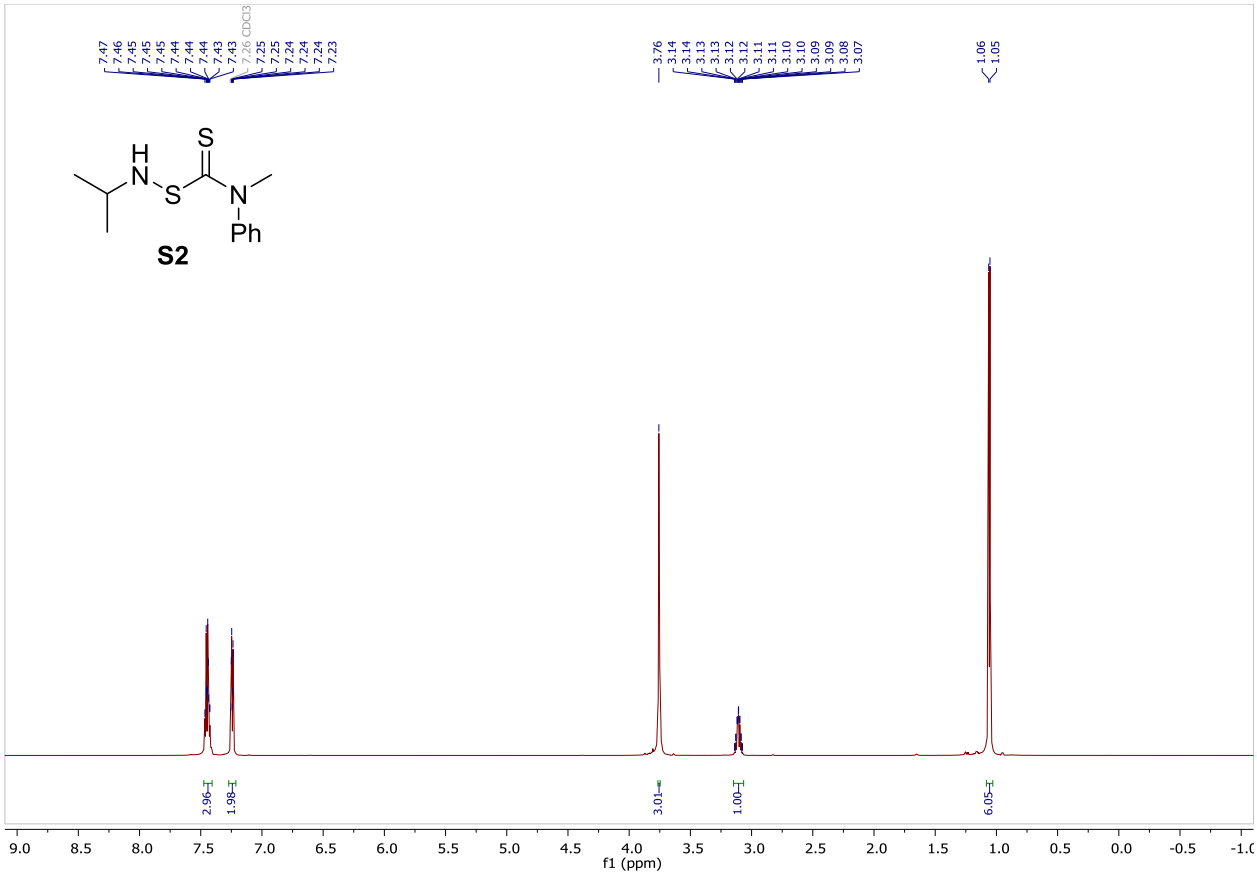
NMR Spectra of New Compounds






7.47
7.46
7.45
7.45
7.45
7.44
7.44
7.44
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7.43
7.26 CDCl3
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7.24
7.24
7.24
7.23
3.76
3.14
3.14
3.13
3.13
3.12
3.12
3.11
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3.09
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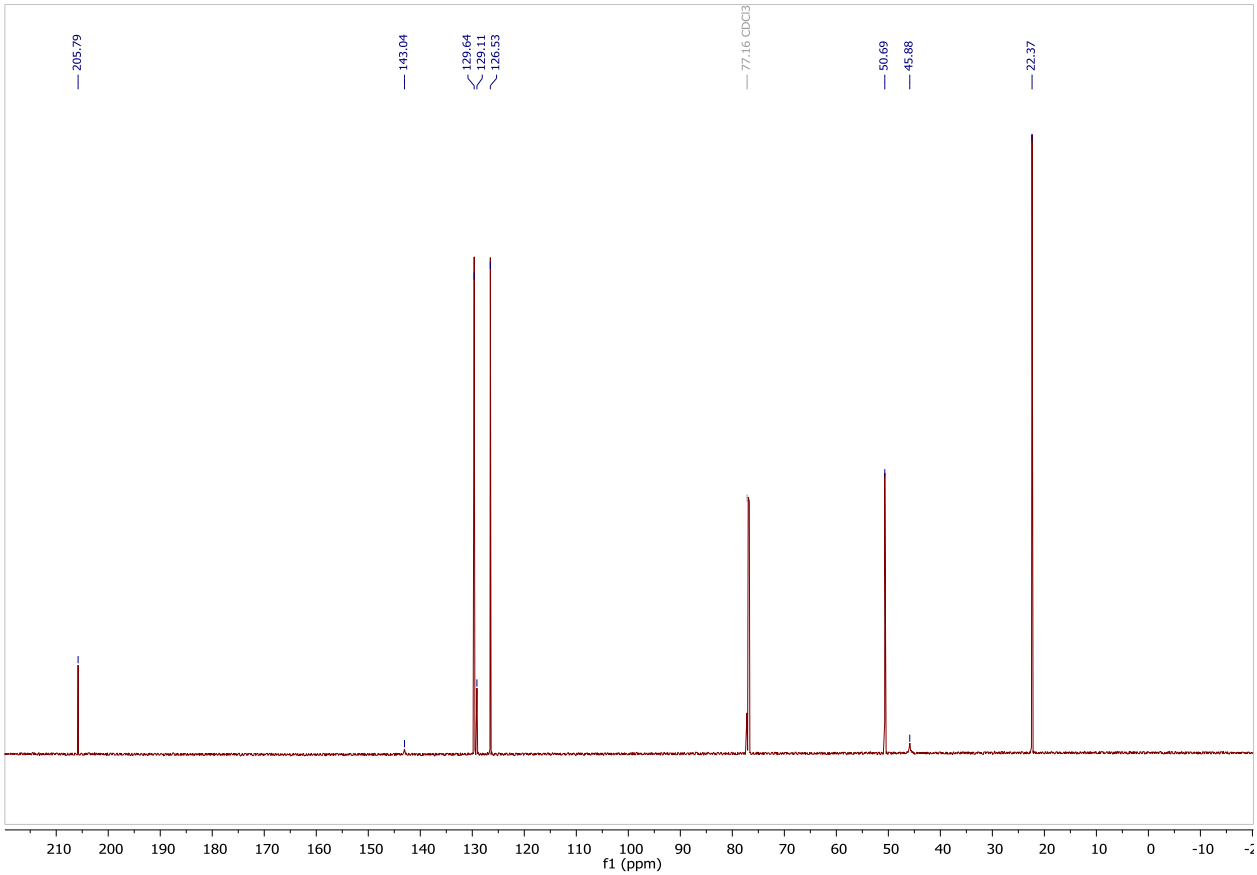
1.98
3.01
1.00
6.05
f1 (ppm)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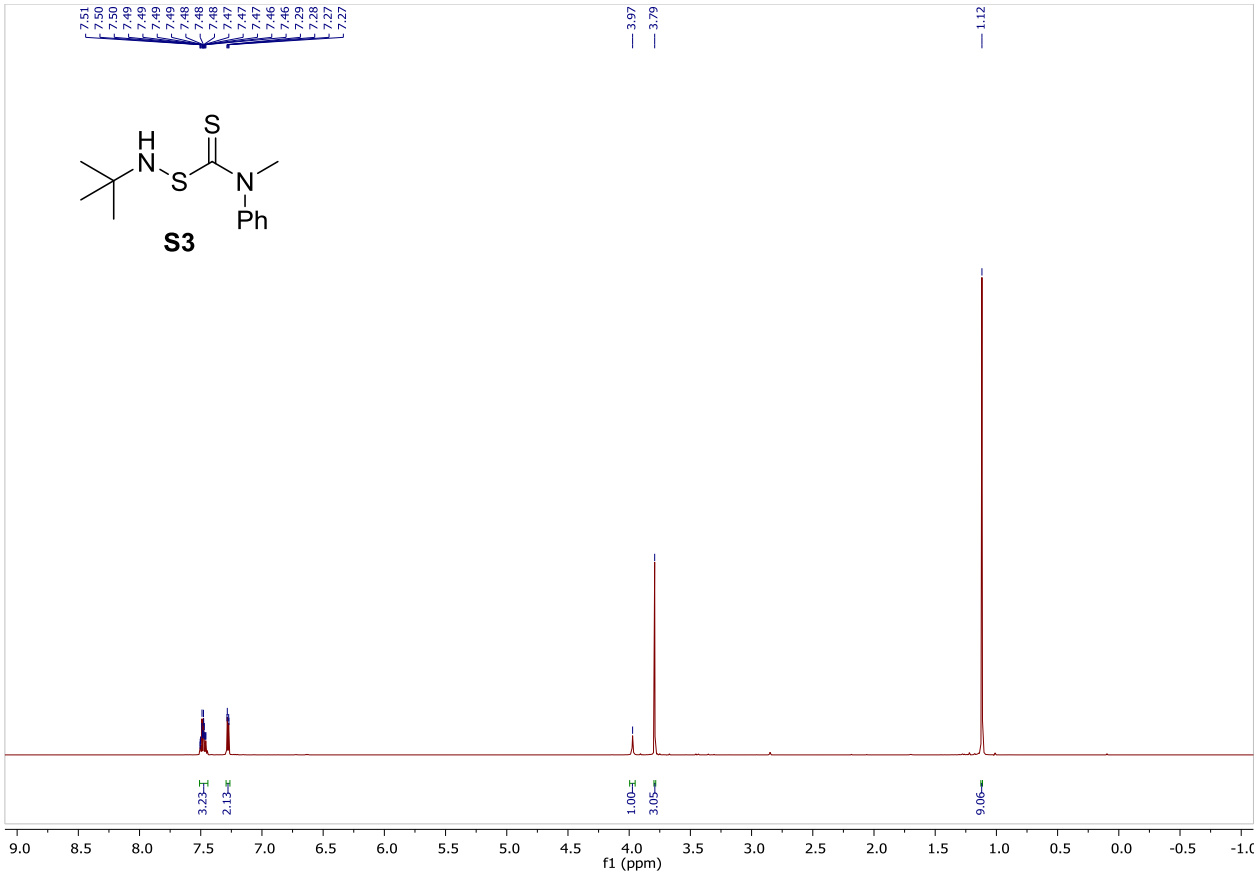
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3.97
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S
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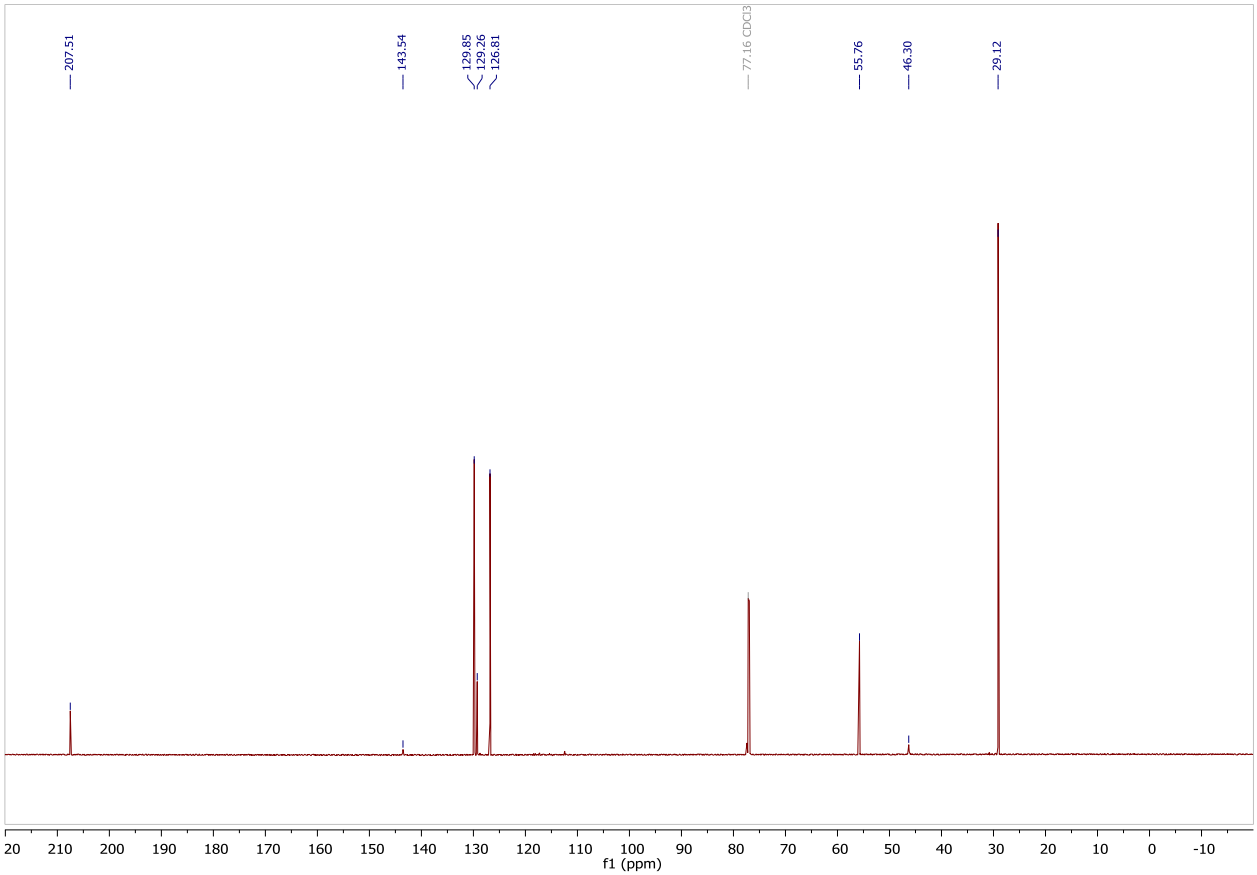
9.06
f1 (ppm)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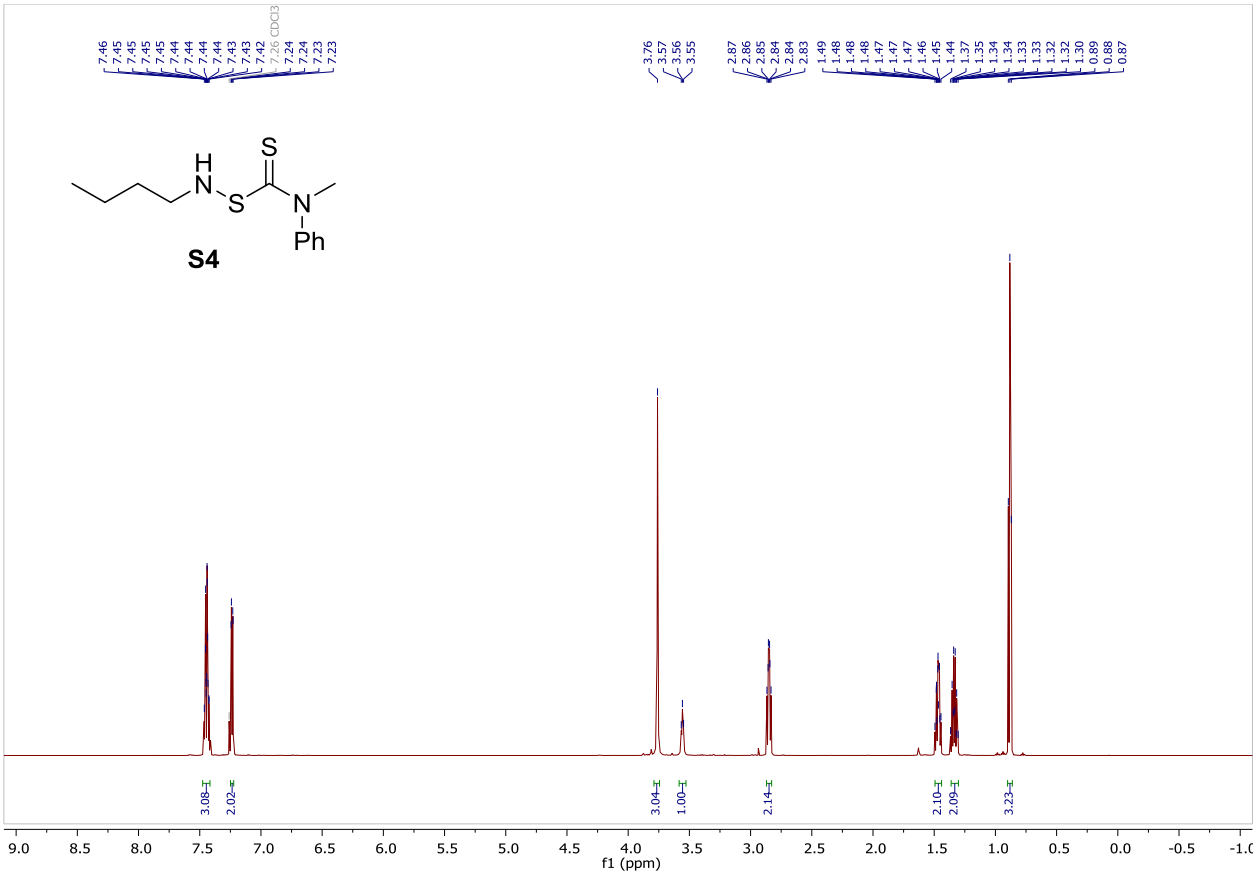
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1.32
1.32
1.30
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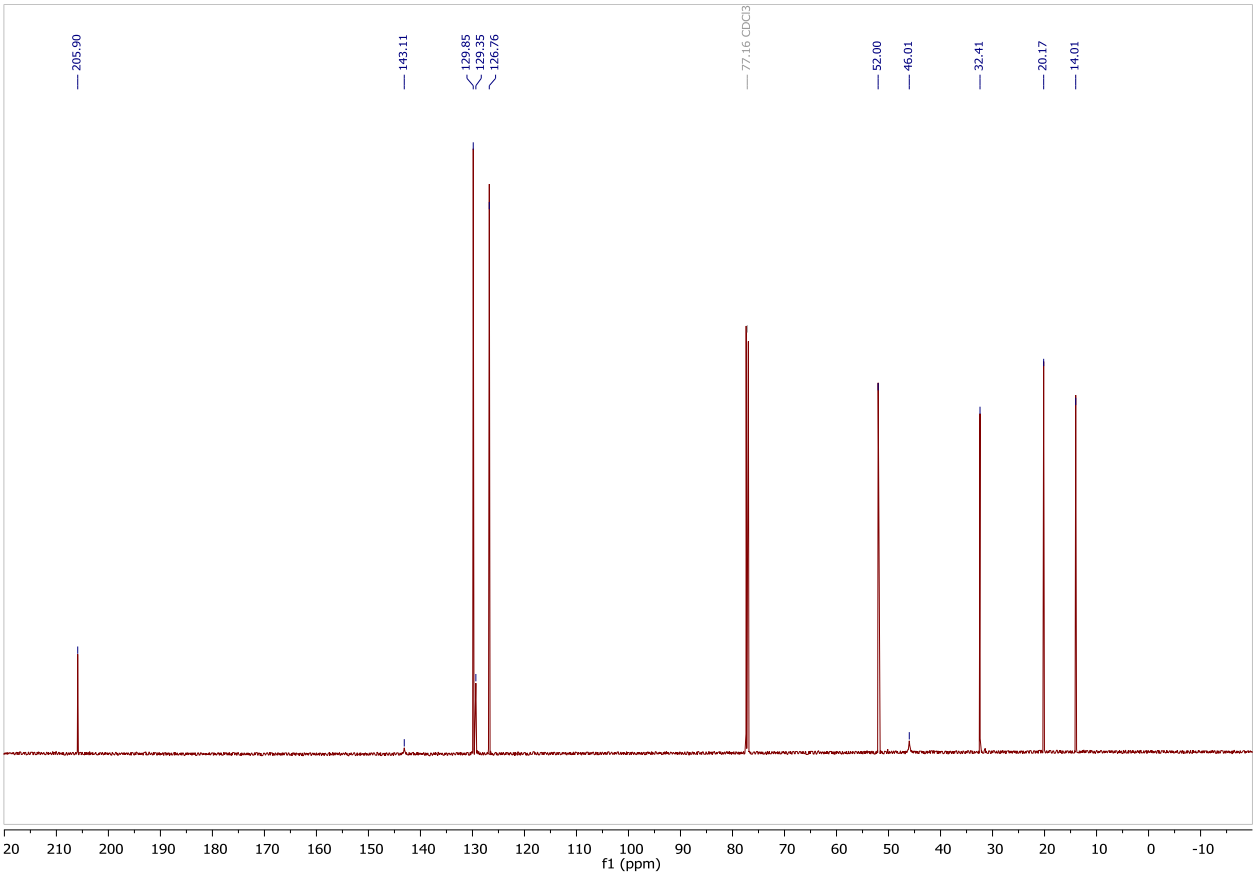
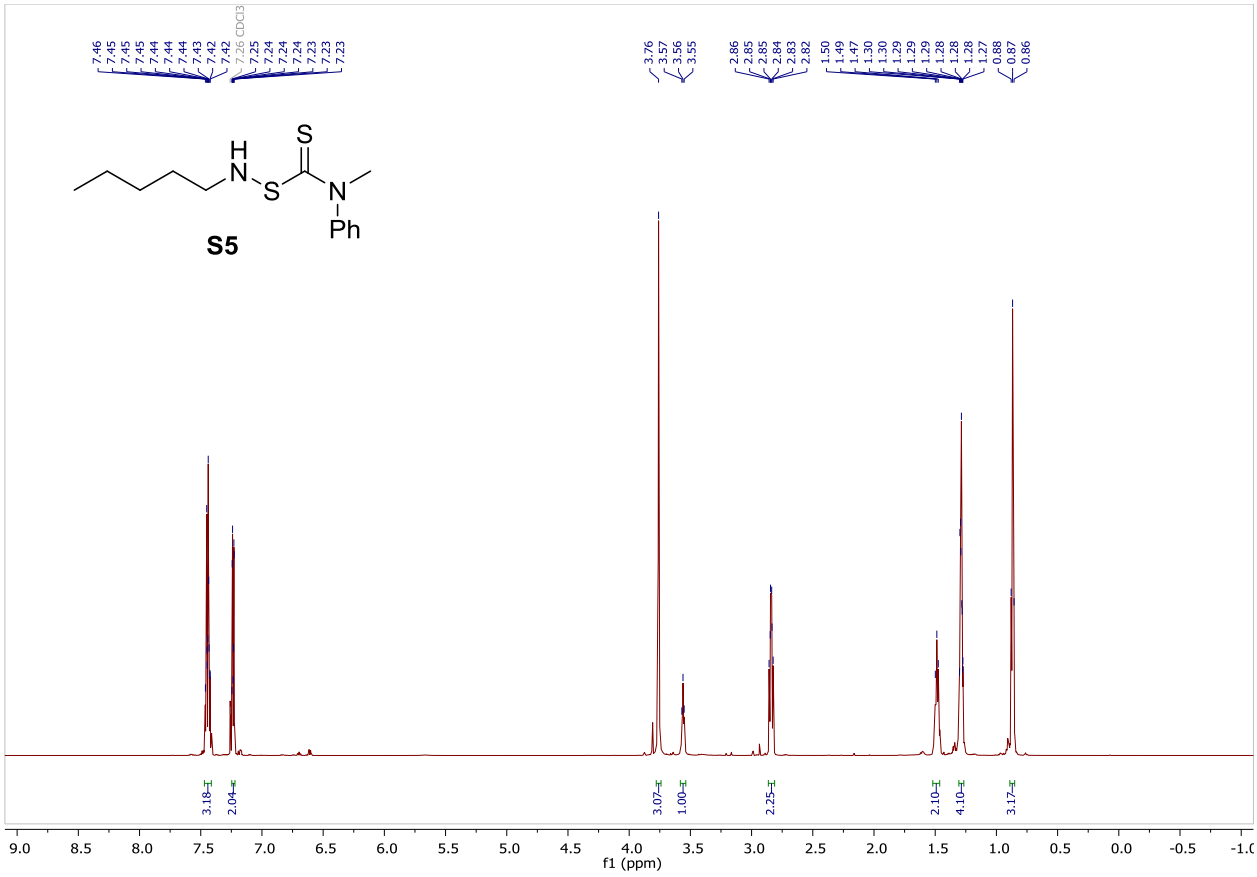
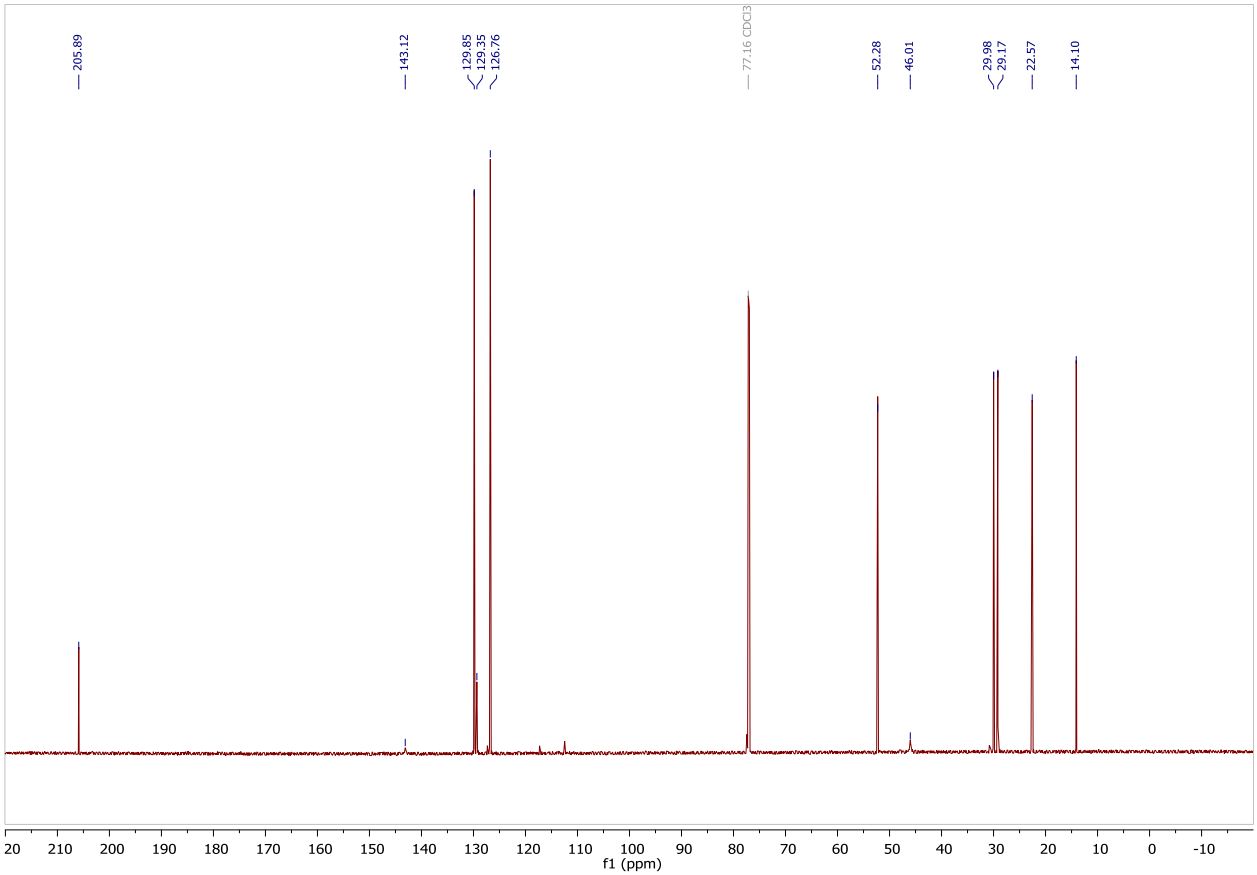
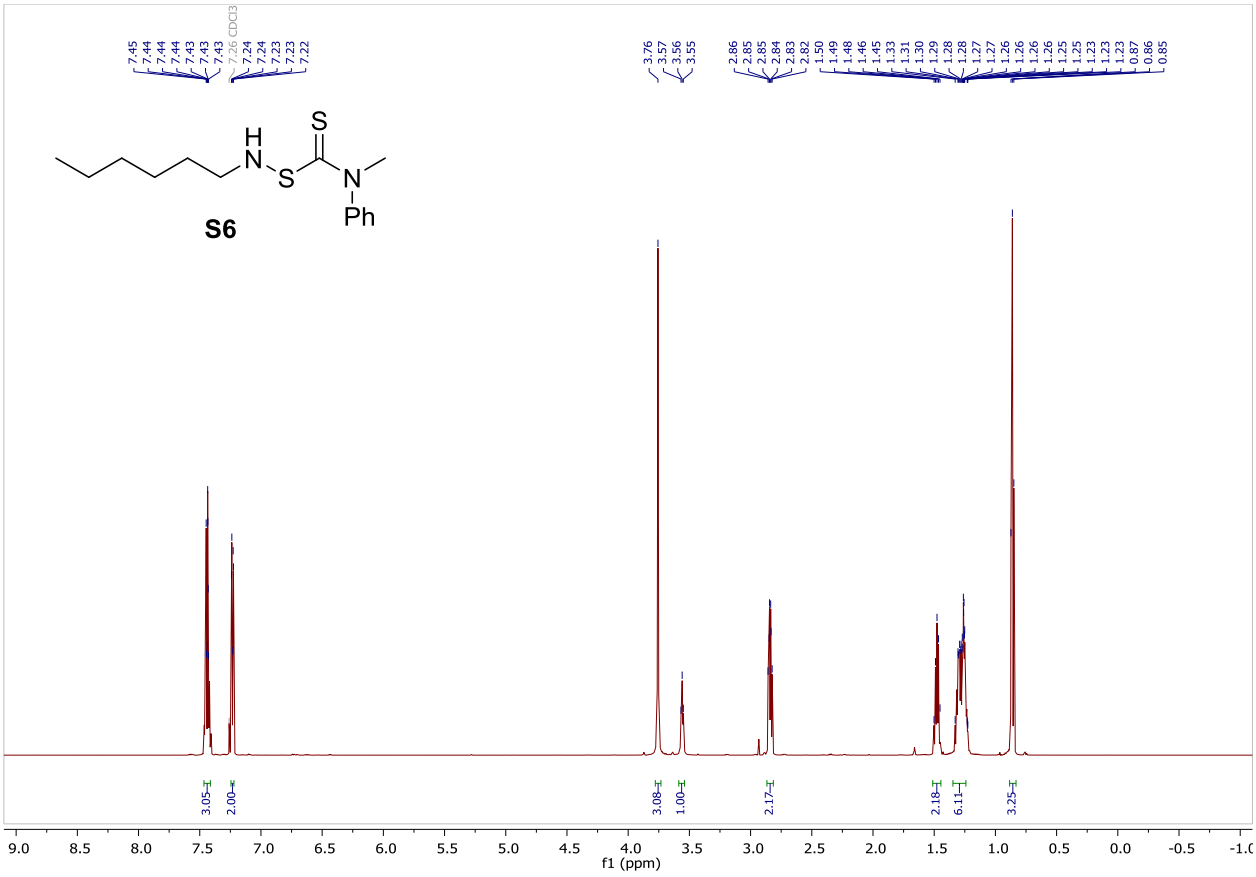
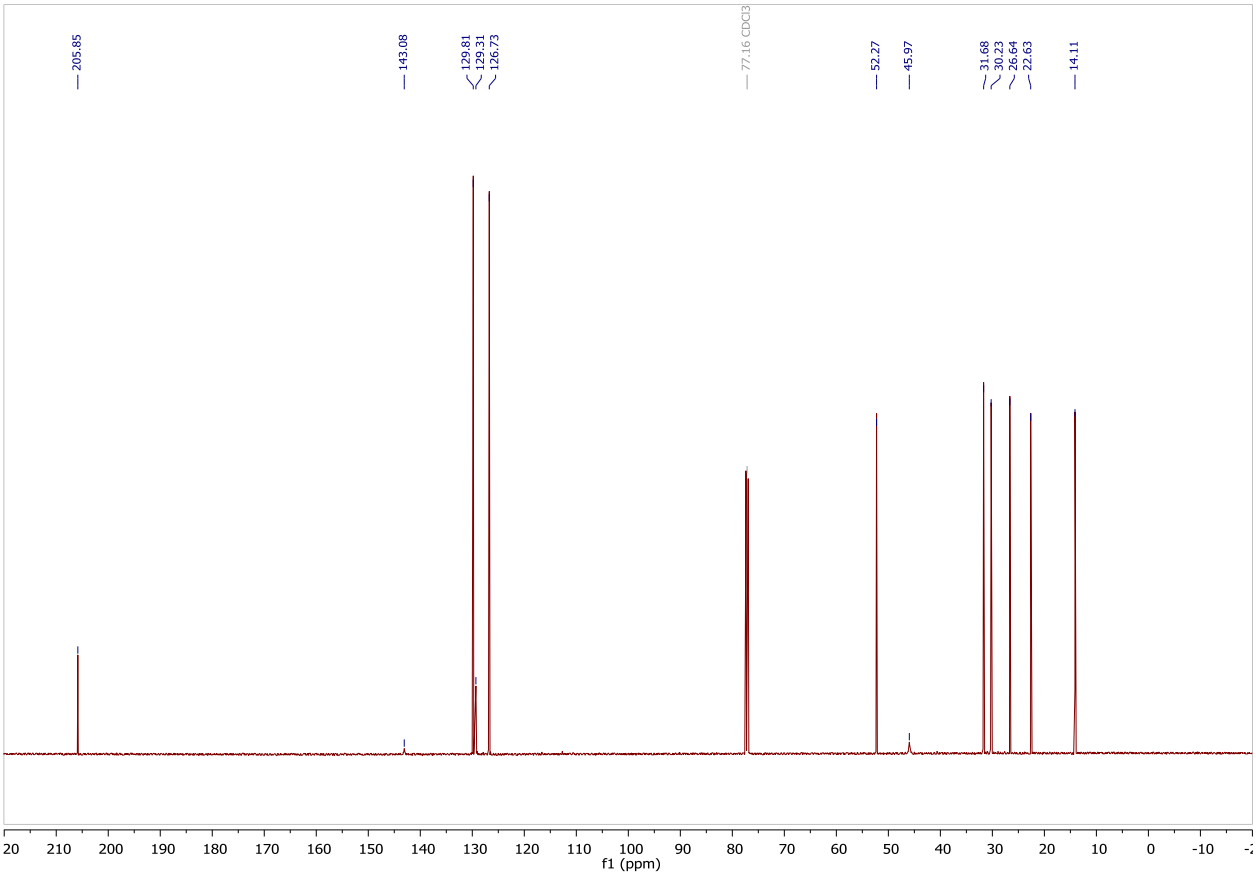
0.88
0.87
H
N
S
S
N
Ph
S4
3.08
2.02
3.04
1.00
2.14
2.10
2.09
3.23
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

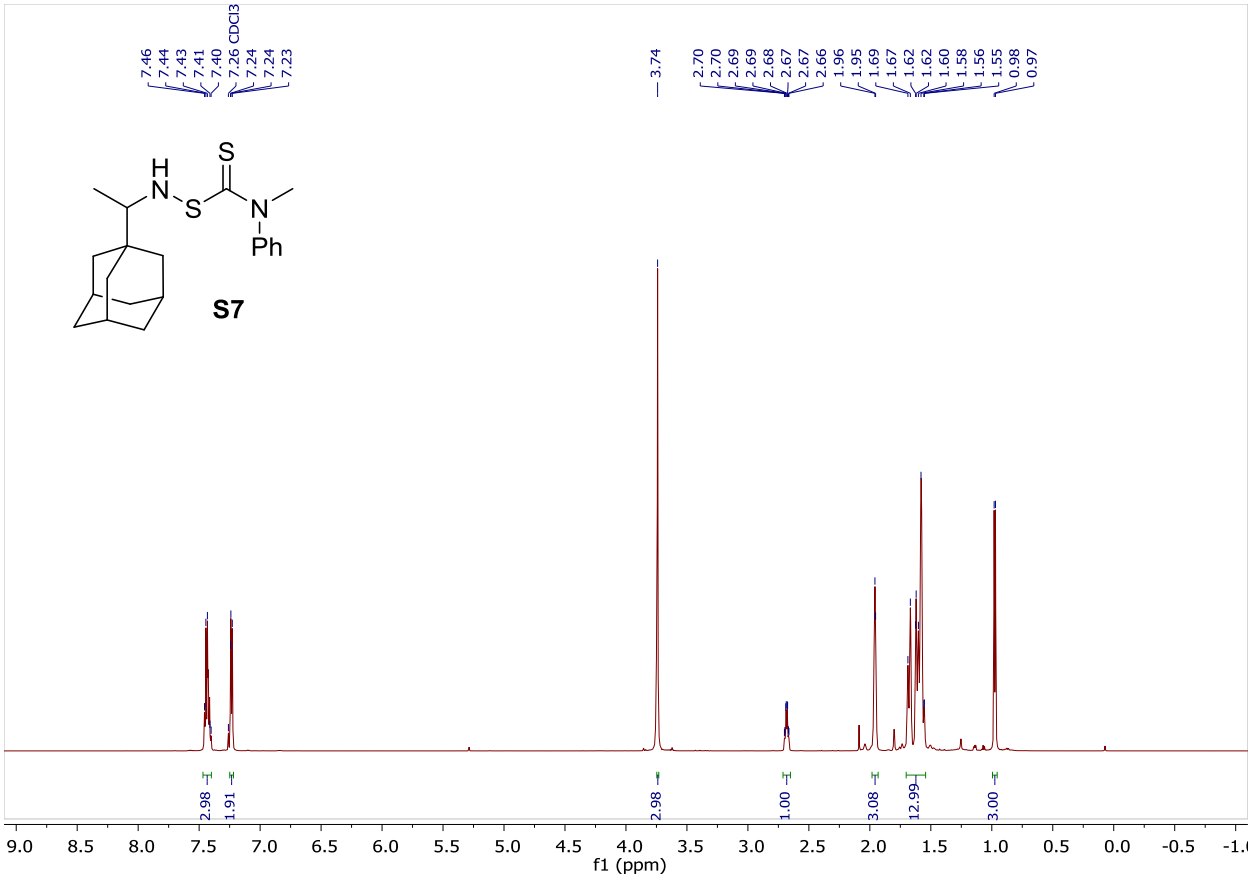

205.90
143.11
129.85
129.35
126.76
77.16 CDCl3
52.00
46.01
32.41
20.17
14.01
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

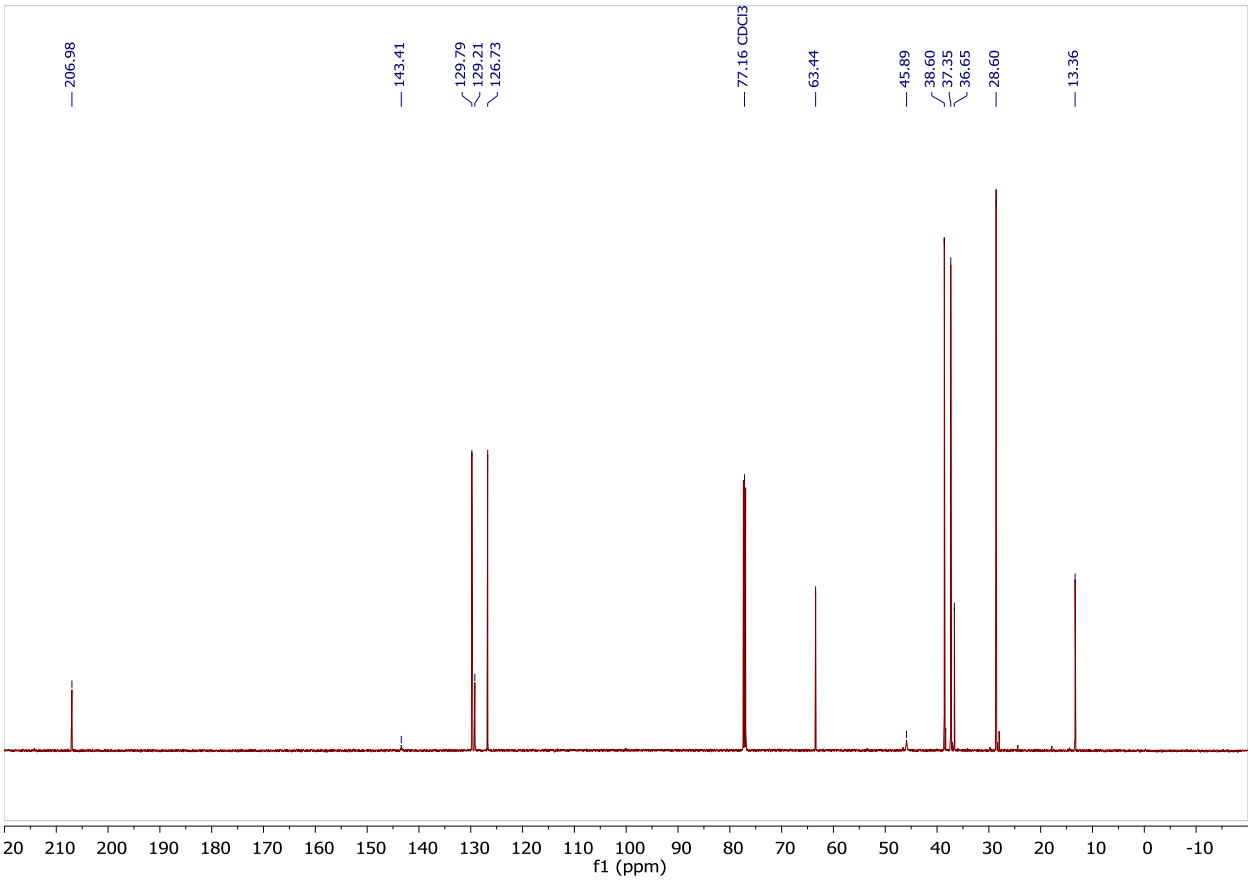

S5
f1 (ppm)

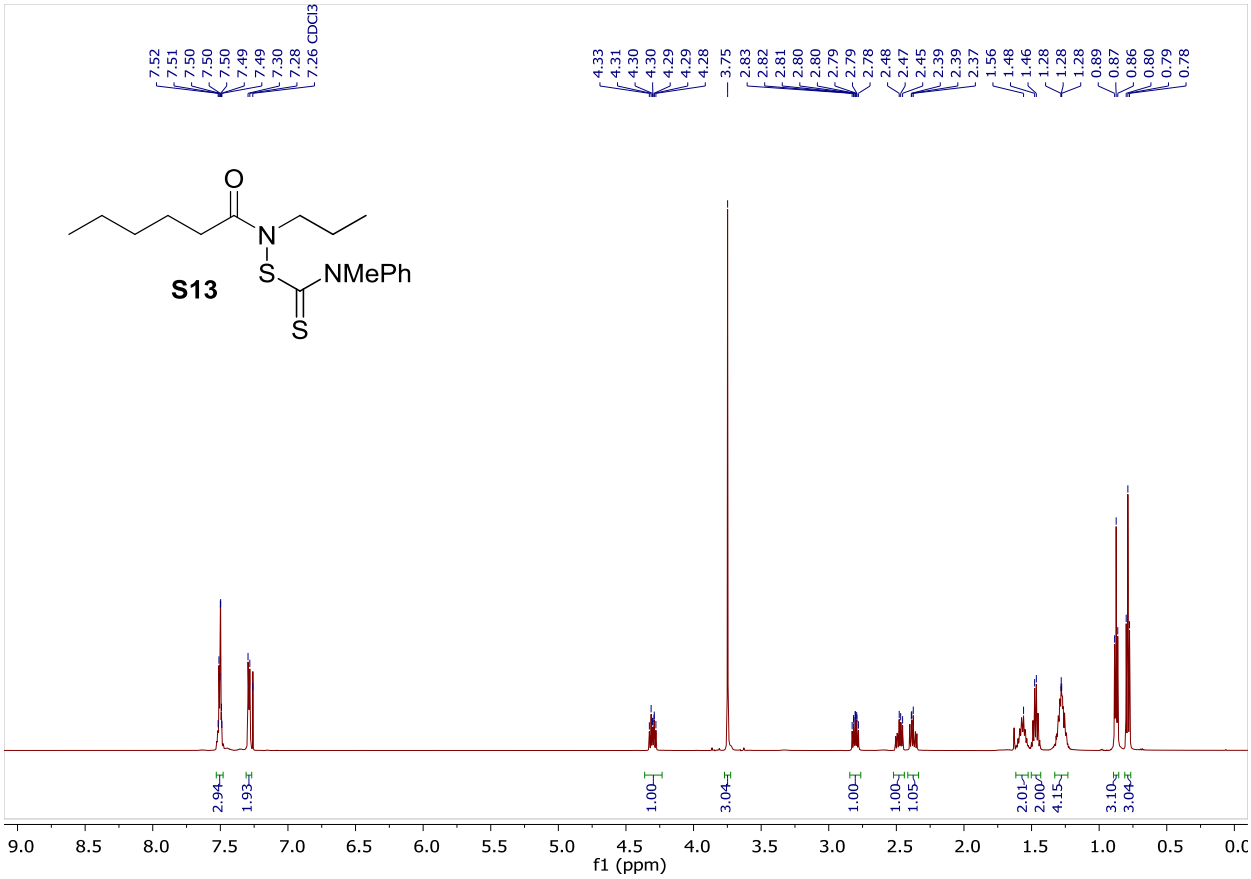

f1 (ppm)

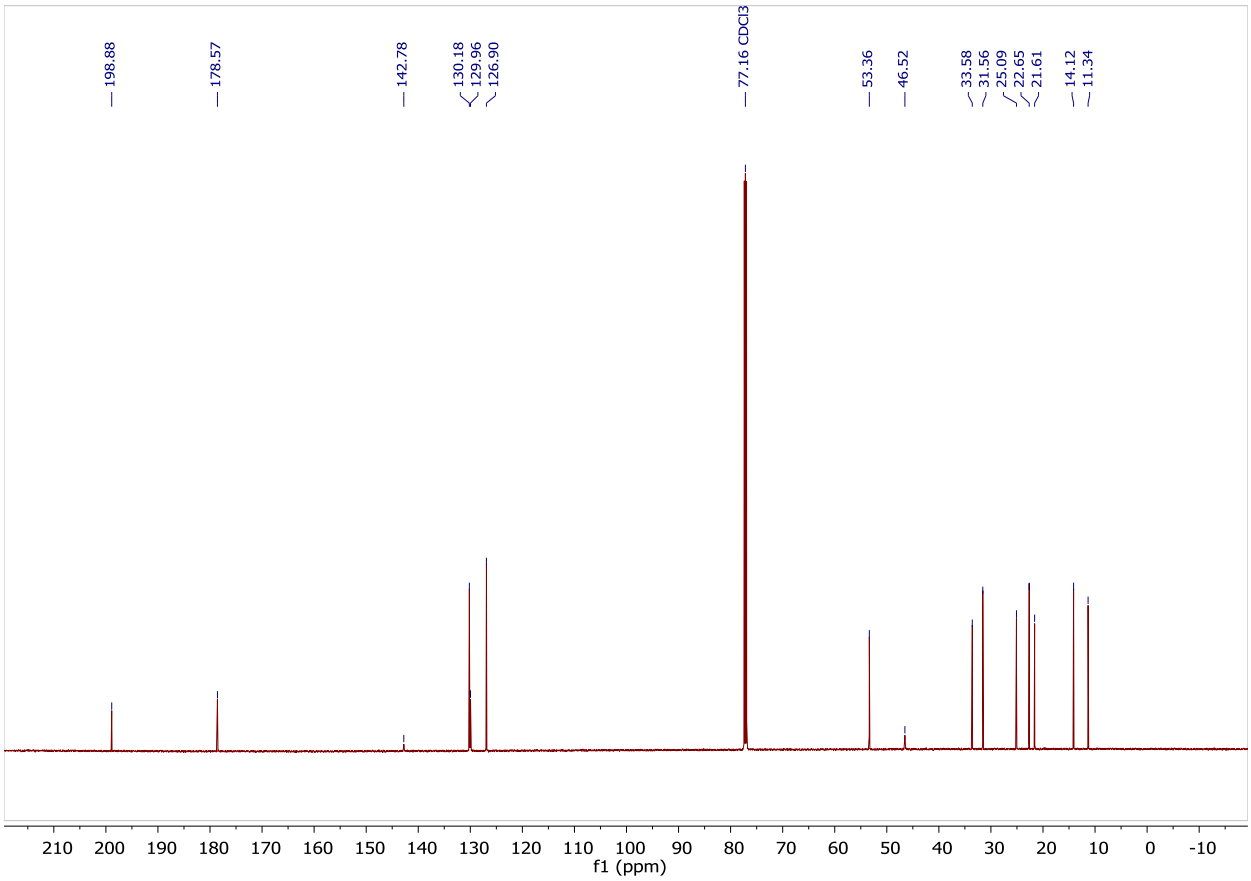

S6
f1 (ppm)

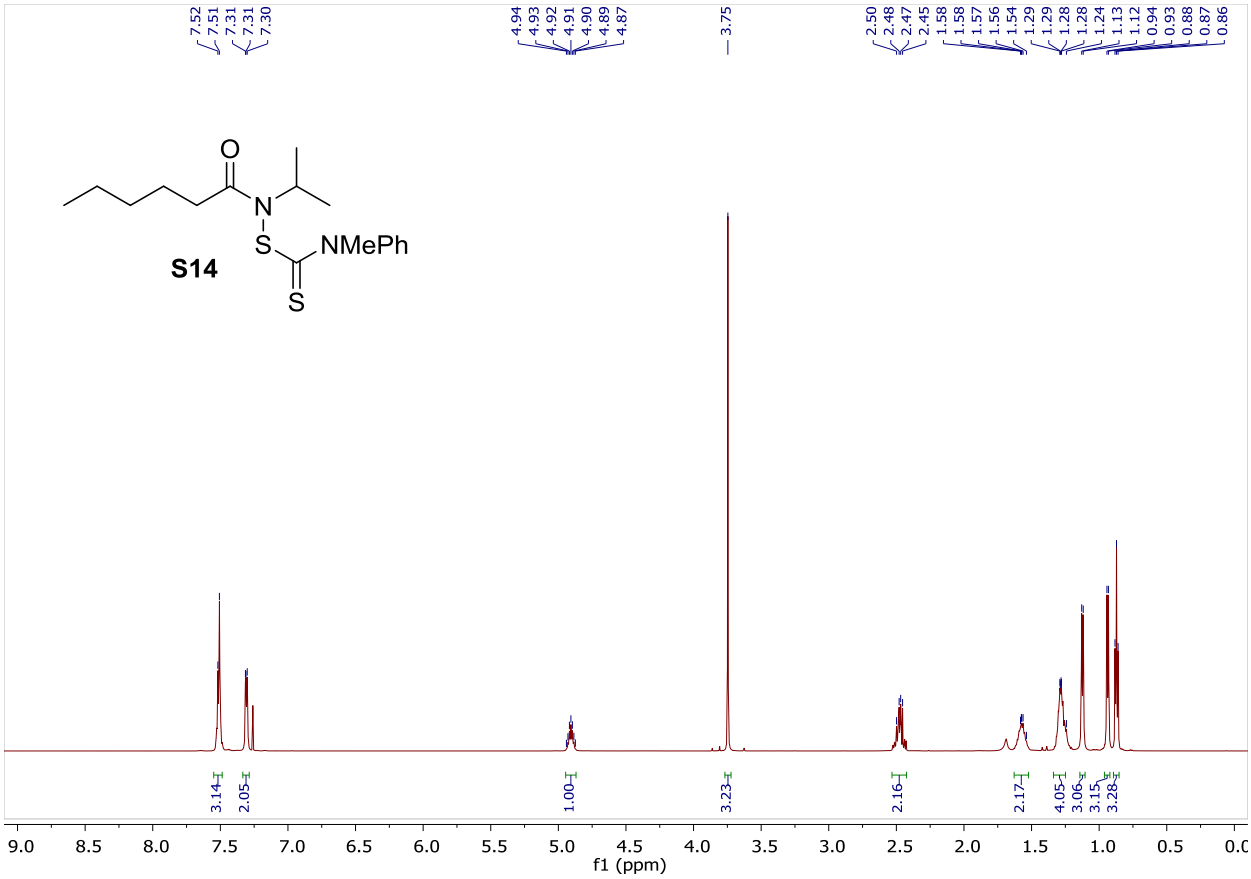

f1 (ppm)

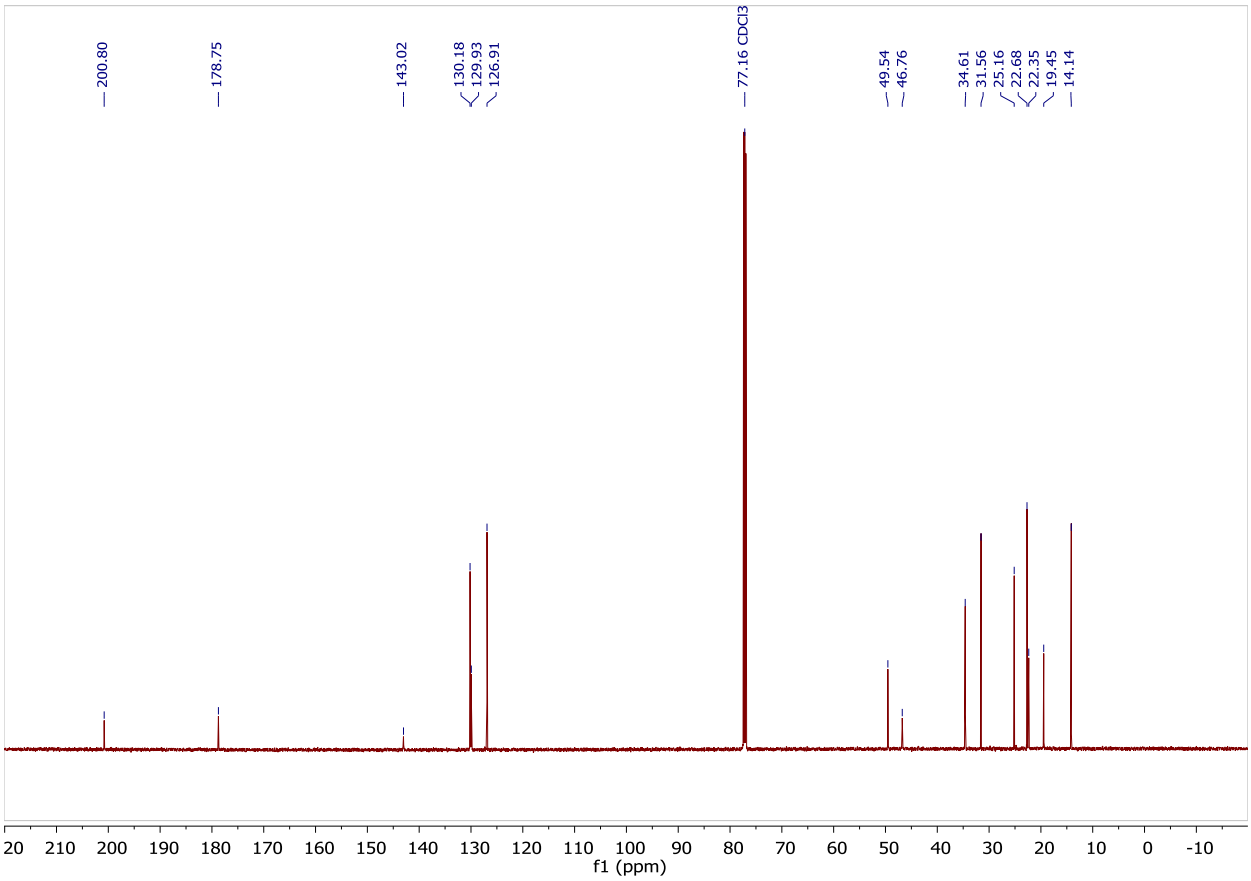

7.46
7.44
7.43
7.41
7.40
7.26 CDCl3
7.24
7.24
7.23
3.74
2.70
2.70
2.69
2.69
2.68
2.67
2.67
2.66
1.96
1.95
1.69
1.67
1.62
1.62
1.60
1.58
1.56
1.55
0.98
0.97
H
N
S
S
N
Ph
S7
2.98
1.91
2.98
1.00
3.08
12.99
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

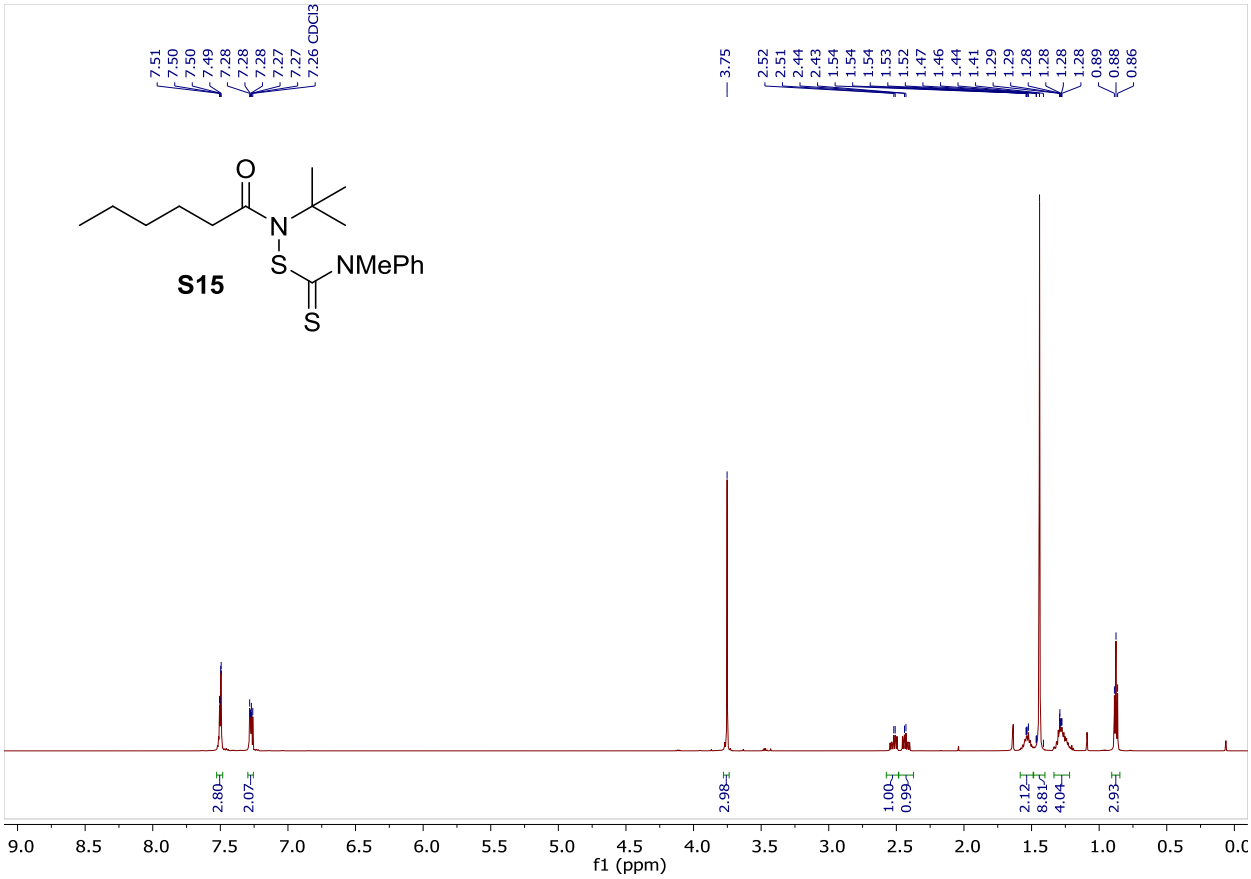

206.98
143.41
129.79
129.21
126.73
77.16 CDCl3
63.44
45.89
38.60
37.35
36.65
28.60
13.36
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

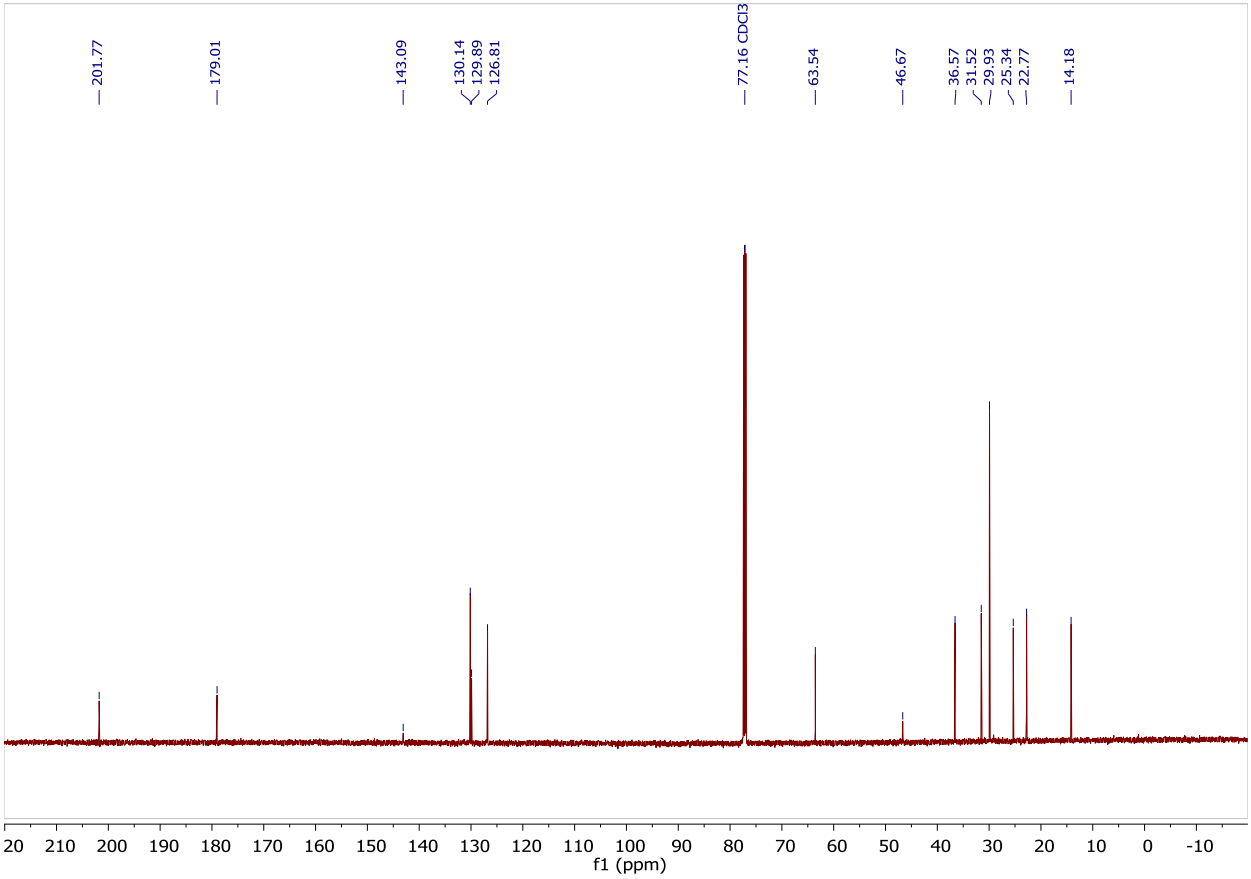

7.52
7.51
7.50
7.50
7.50
7.49
7.49
7.30
7.28
7.26 CDCl3
4.33
4.31
4.30
4.30
4.29
4.29
4.28
3.75
2.83
2.82
2.81
2.80
2.80
2.79
2.79
2.78
2.48
2.47
2.45
2.39
2.39
2.37
1.56
1.48
1.46
1.28
1.28
1.28
0.89
0.87
0.86
0.80
0.79
0.78
O
N
S
NMePh
S
S13
2.94
1.93
1.00
3.04
1.00
1.00
1.05
2.01
2.00
4.15
3.10
3.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

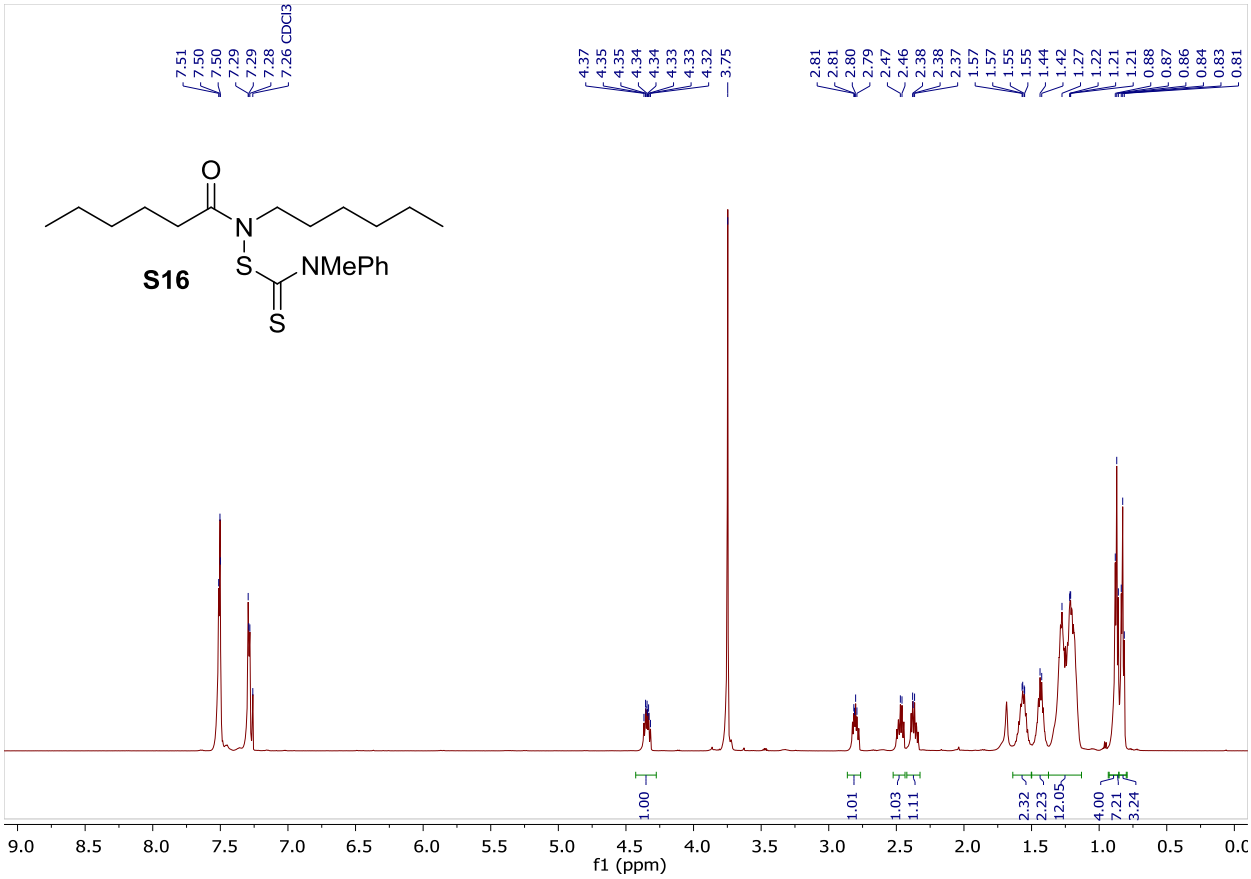

198.88
178.57
142.78
130.18
129.96
126.90
77.16 CDCl3
53.36
46.52
33.58
31.56
25.09
22.65
21.61
14.12
11.34
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

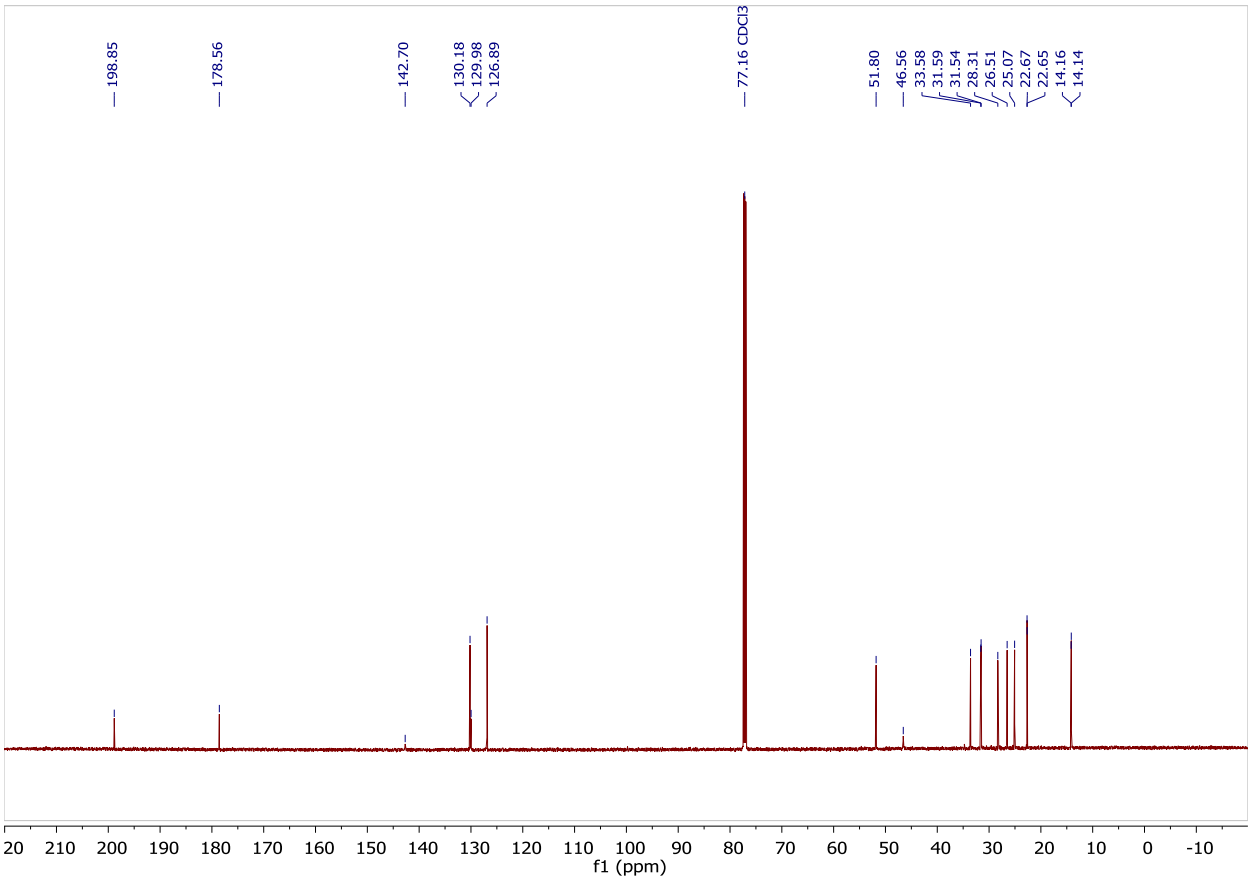

7.52
7.51
7.31
7.31
7.30
4.94
4.93
4.92
4.91
4.90
4.89
4.87
3.75
2.50
2.48
2.47
2.45
1.58
1.58
1.57
1.56
1.54
1.29
1.29
1.28
1.28
1.24
1.13
1.12
0.94
0.93
0.88
0.87
0.86
O
N
S
NMePh
S
S14
3.14
2.05
1.00
3.23
2.16
2.17
4.05
3.06
3.15
3.28
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

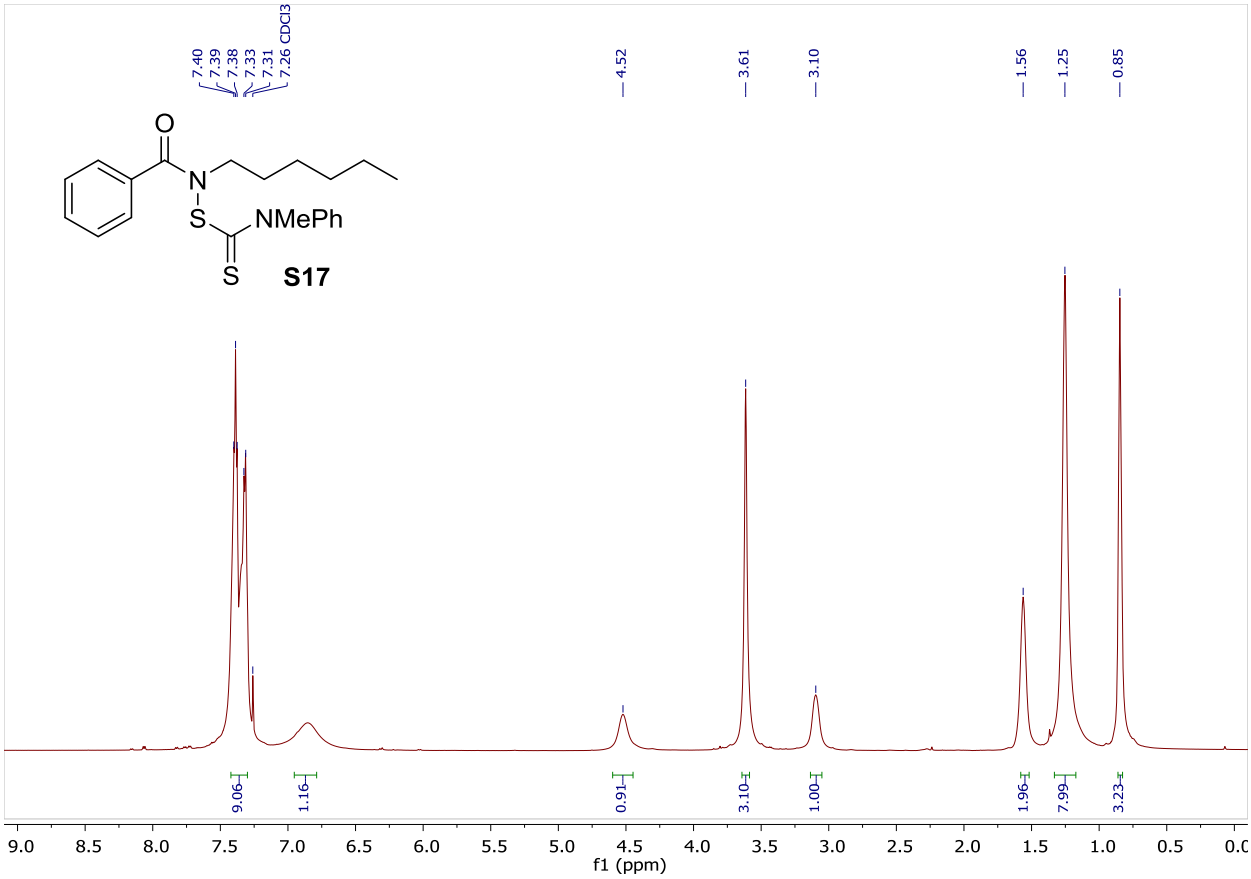

200.80
178.75
143.02
130.18
129.93
126.91
77.16 CDCl3
49.54
46.76
34.61
31.56
25.16
22.68
22.35
19.45
14.14
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

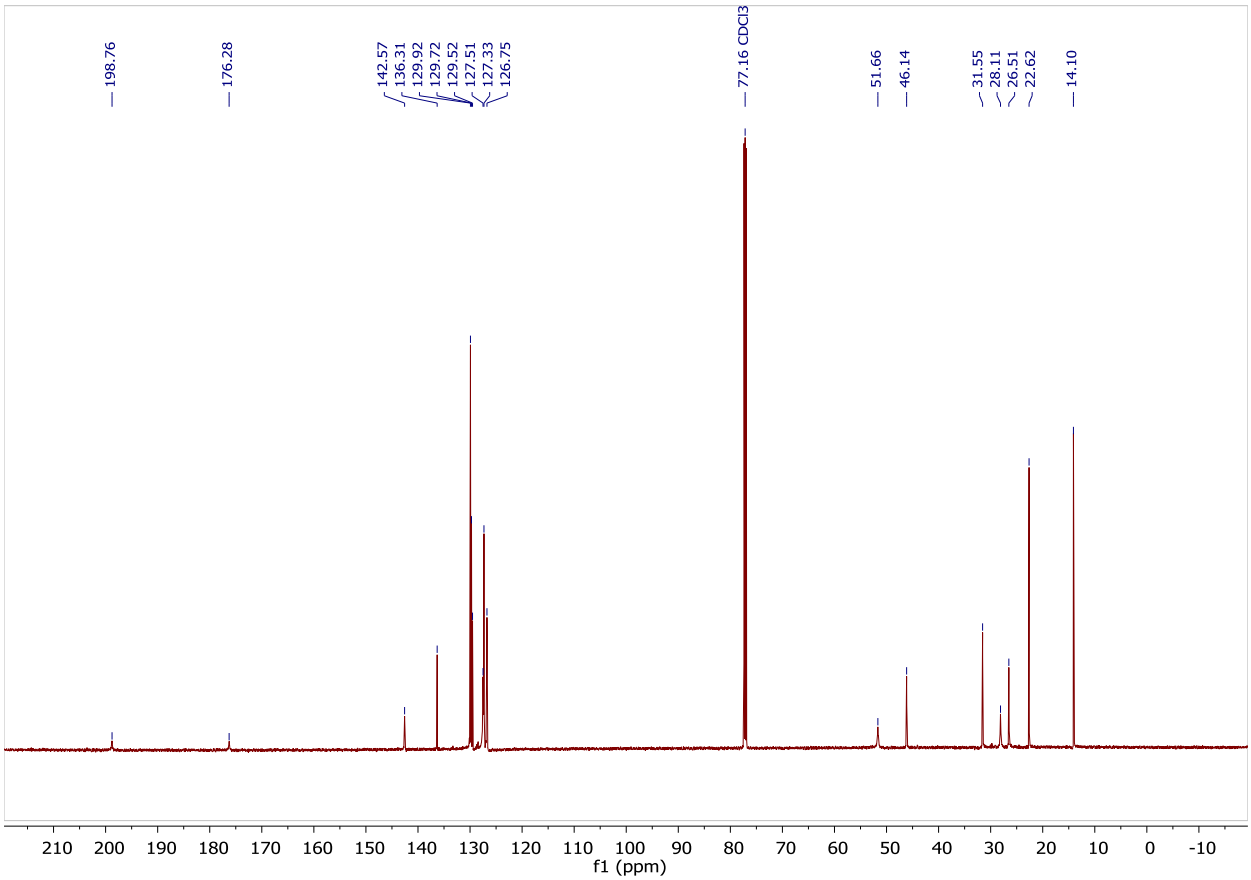

7.51
7.50
7.50
7.49
7.28
7.28
7.28
7.27
7.27
7.26 CDCl3
3.75
2.52
2.51
2.44
2.43
1.54
1.54
1.54
1.53
1.52
1.47
1.46
1.44
1.41
1.29
1.29
1.28
1.28
1.28
1.28
0.89
0.88
0.86
O
N
S
NMePh
S
S15
2.80
2.07
2.98
1.00
0.99
2.12
8.81
4.04
2.93
f1 (ppm)

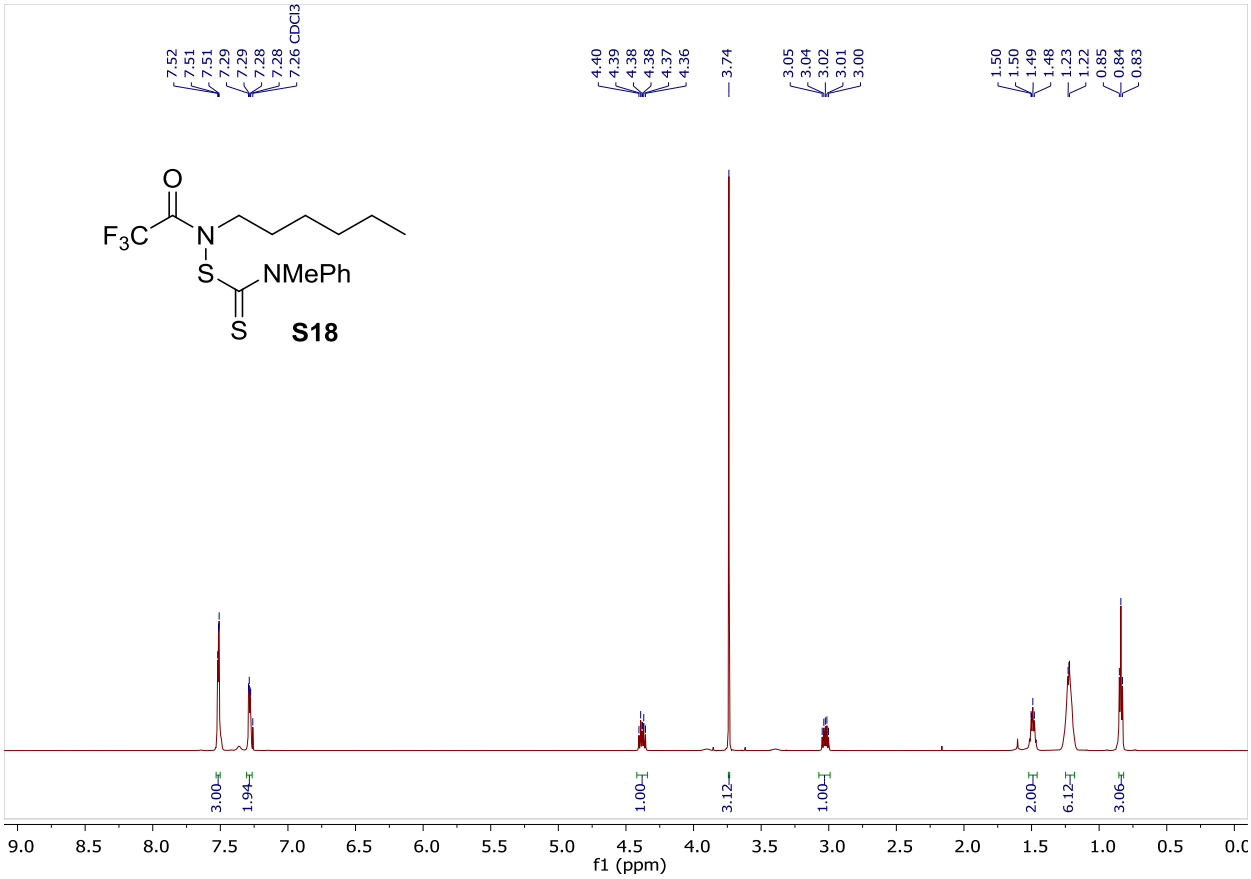

201.77
179.01
143.09
130.14
129.89
126.81
77.16 CDCl3
63.54
46.67
36.57
31.52
29.93
25.34
22.77
14.18
f1 (ppm)

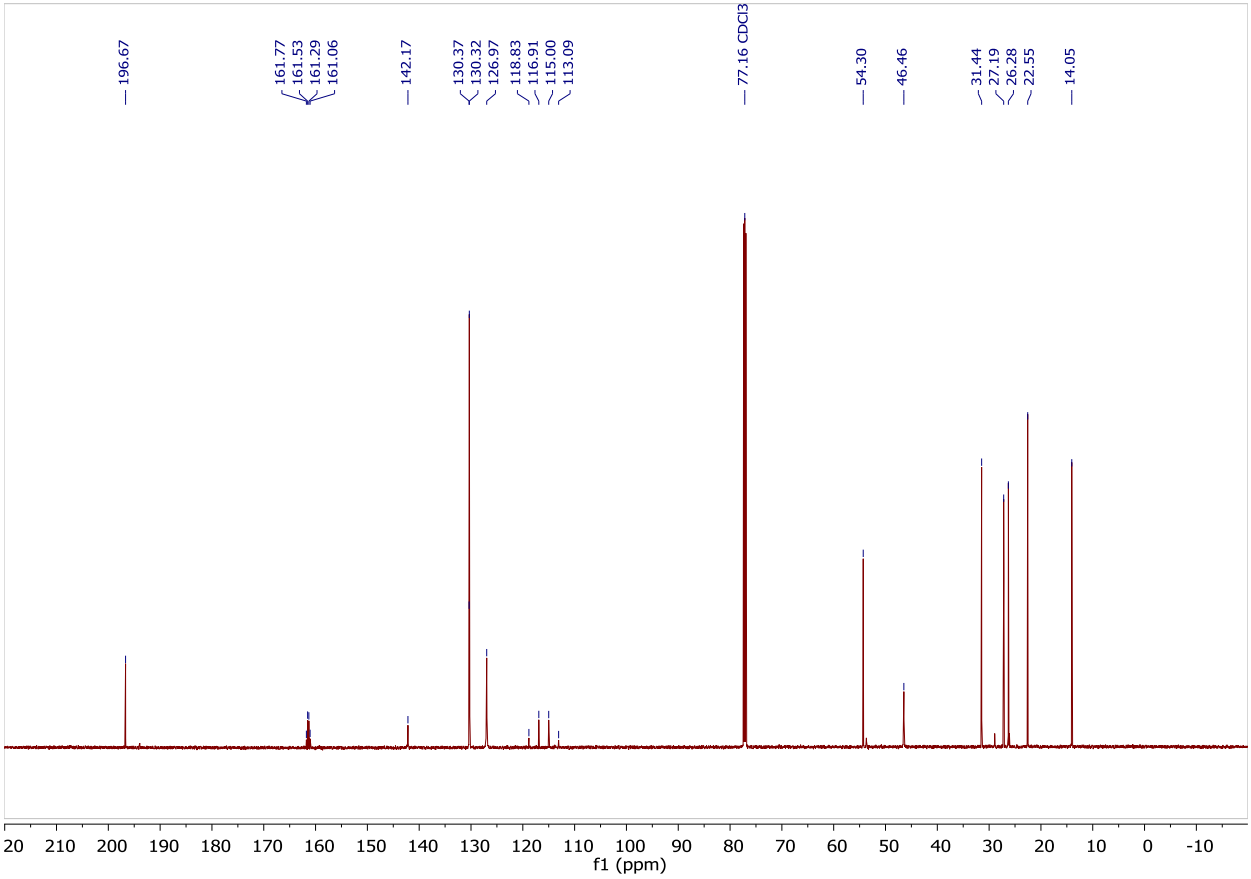

7.51
7.50
7.50
7.29
7.29
7.28
7.26 CDCl3
4.37
4.35
4.35
4.34
4.34
4.33
4.33
4.32
3.75
2.81
2.81
2.80
2.79
2.47
2.46
2.38
2.38
2.37
1.57
1.57
1.55
1.55
1.44
1.42
1.27
1.22
1.21
1.21
0.88
0.87
0.86
0.84
0.83
0.81
O
N
S
NMePh
S
S16
1.00
1.01
1.03
1.11
2.32
2.23
12.05
4.00
7.21
3.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

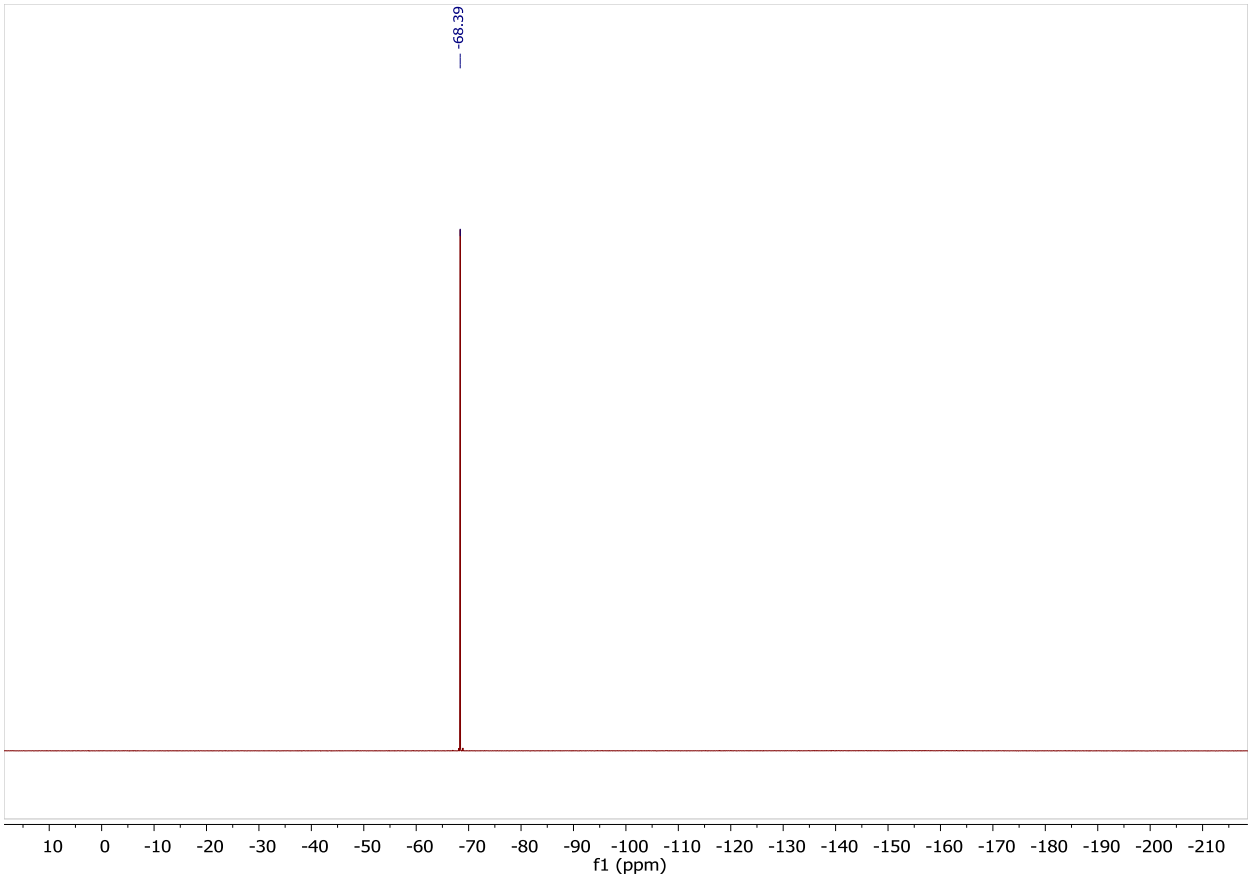

198.85
178.56
142.70
130.18
129.98
126.89
77.16 CDCl3
51.80
46.56
33.58
31.59
31.54
28.31
26.51
25.07
22.67
22.65
14.16
14.14
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

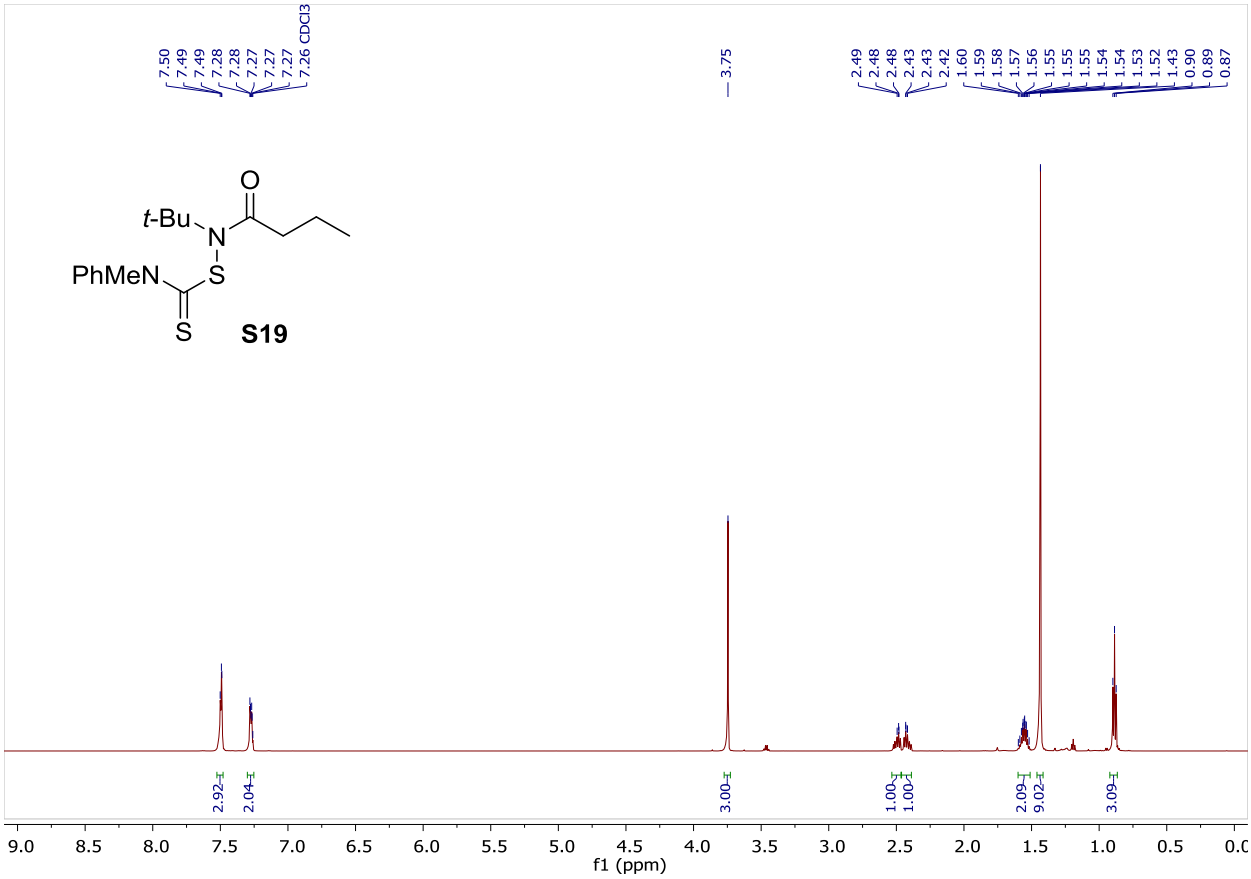

7.40
7.39
7.38
7.33
7.31
7.26 CDCl3
4.52
3.61
3.10
1.56
1.25
0.85
O
N
S
NMePh
S
S17
9.06
1.16
0.91
3.10
1.00
1.96
7.99
3.23
f1 (ppm)

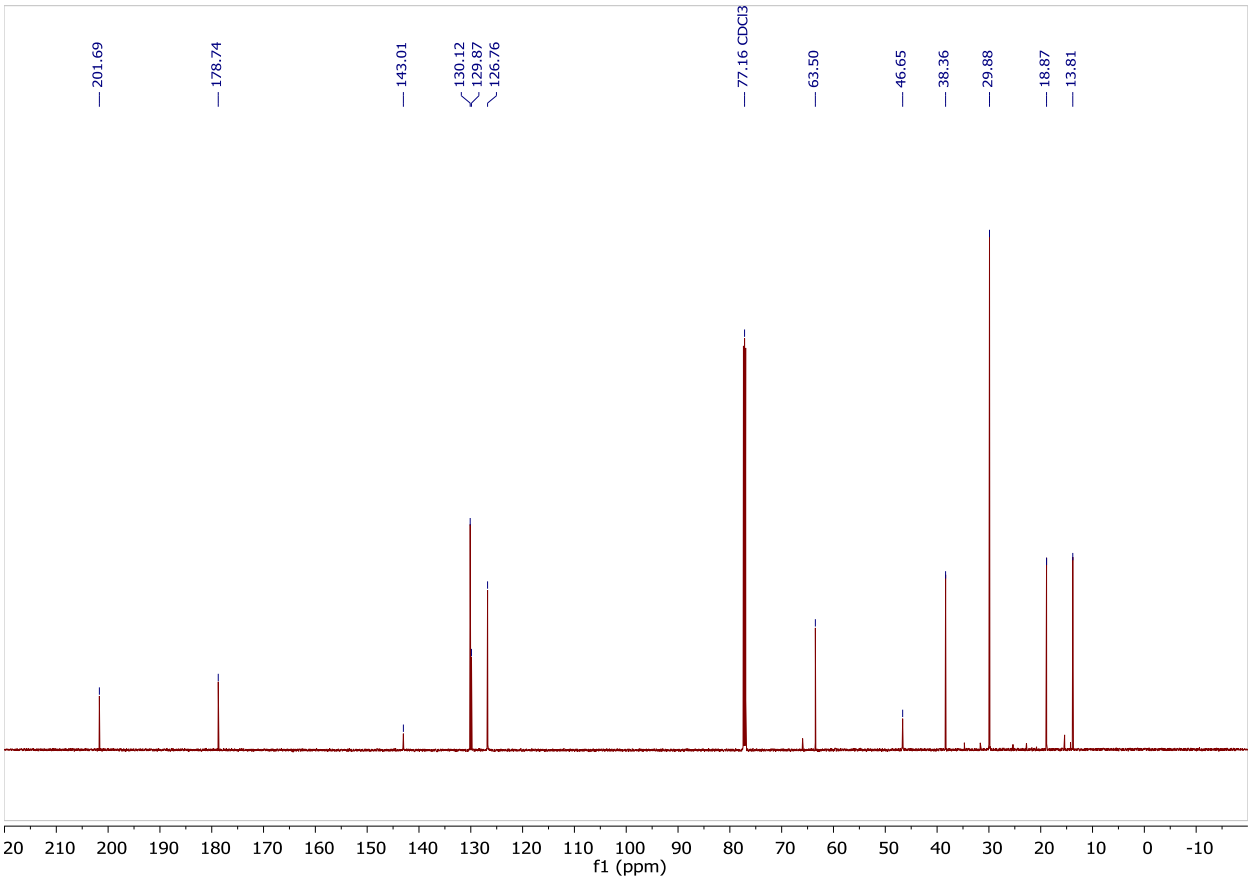

198.76
176.28
142.57
136.31
129.92
129.72
129.52
127.51
127.33
126.75
77.16 CDCl3
51.66
46.14
31.55
28.11
26.51
22.62
14.10
f1 (ppm)


7.52
7.51
7.51
7.29
7.29
7.28
7.28
7.26 CDCl3
4.40
4.39
4.38
4.38
4.37
4.36
3.74
3.05
3.04
3.02
3.01
3.00
1.50
1.50
1.49
1.48
1.23
1.22
0.85
0.84
0.83
O
F3C
N
S
NMePh
S
S18
3.00
1.94
1.00
3.12
1.00
2.00
6.12
3.06
f1 (ppm)


196.67
161.77
161.53
161.29
161.06
142.17
130.37
130.32
126.97
118.83
116.91
115.00
113.09
77.16 CDCl3
54.30
46.46
31.44
27.19
26.28
22.55
14.05
f1 (ppm)


-68.39
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.50
7.49
7.49
7.28
7.28
7.27
7.27
7.27
7.26 CDCl3
3.75
2.49
2.48
2.48
2.43
2.43
2.42
1.60
1.59
1.58
1.57
1.56
1.55
1.55
1.55
1.54
1.54
1.53
1.52
1.43
0.90
0.89
0.87
O
t-Bu
N
S
PhMeN
S
S
S19
2.92
2.04
3.00
1.00
1.00
2.09
9.02
3.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


201.69
178.74
143.01
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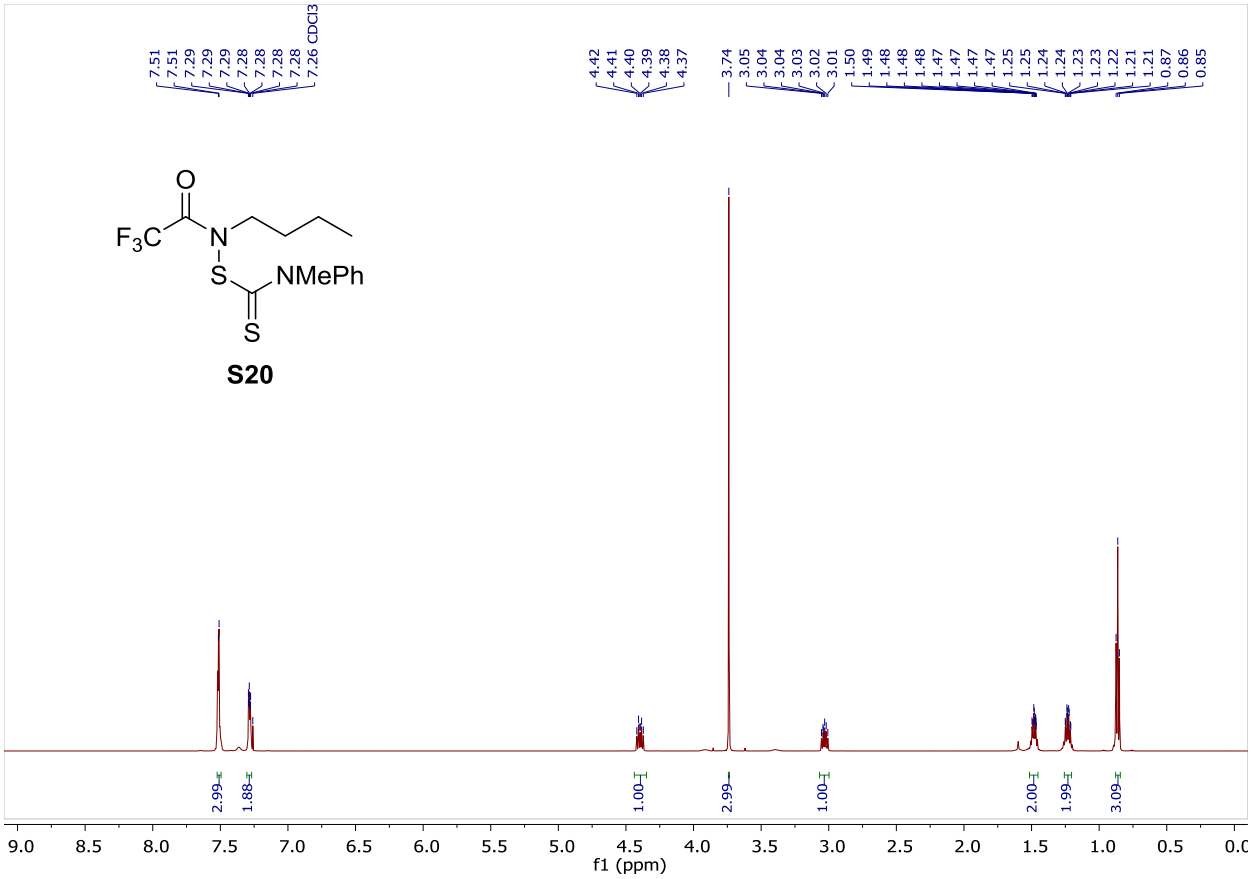
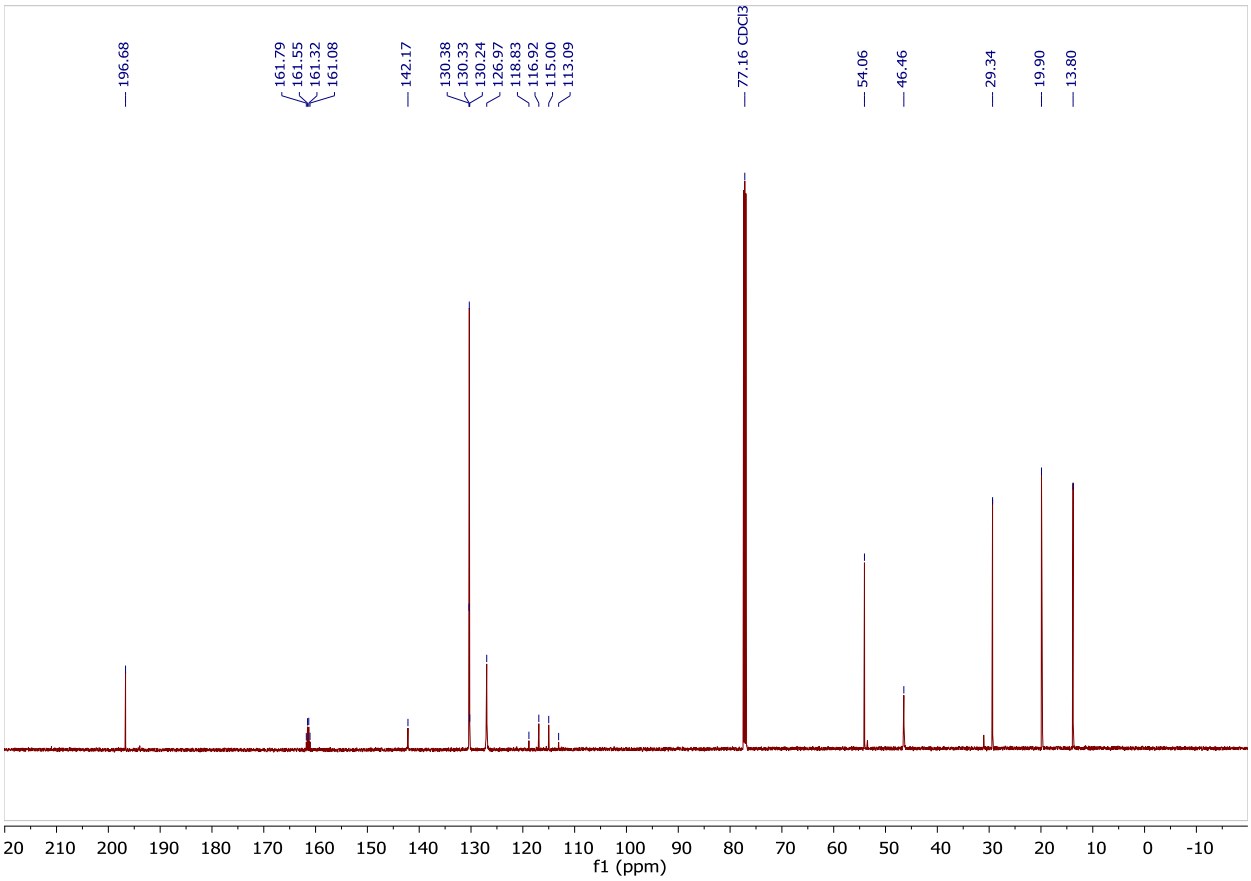
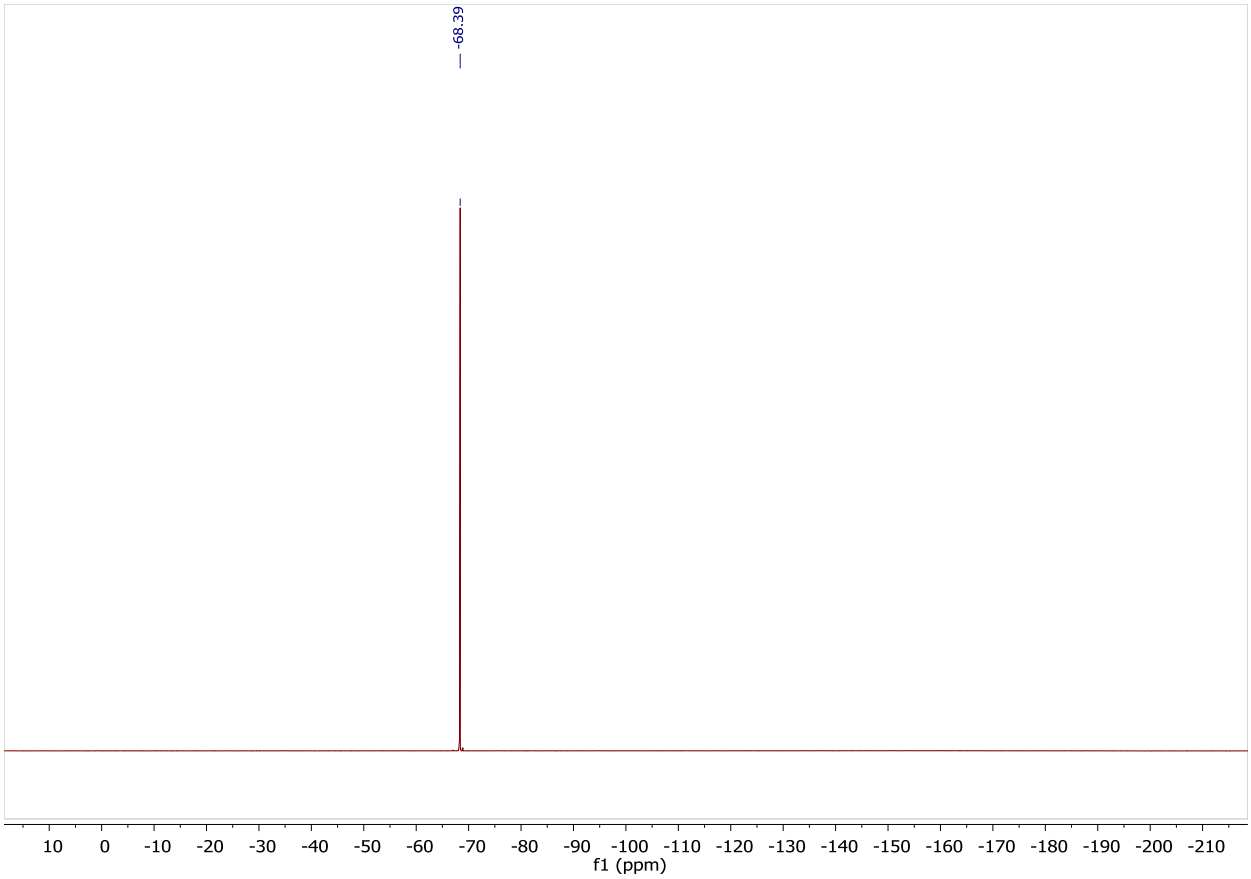
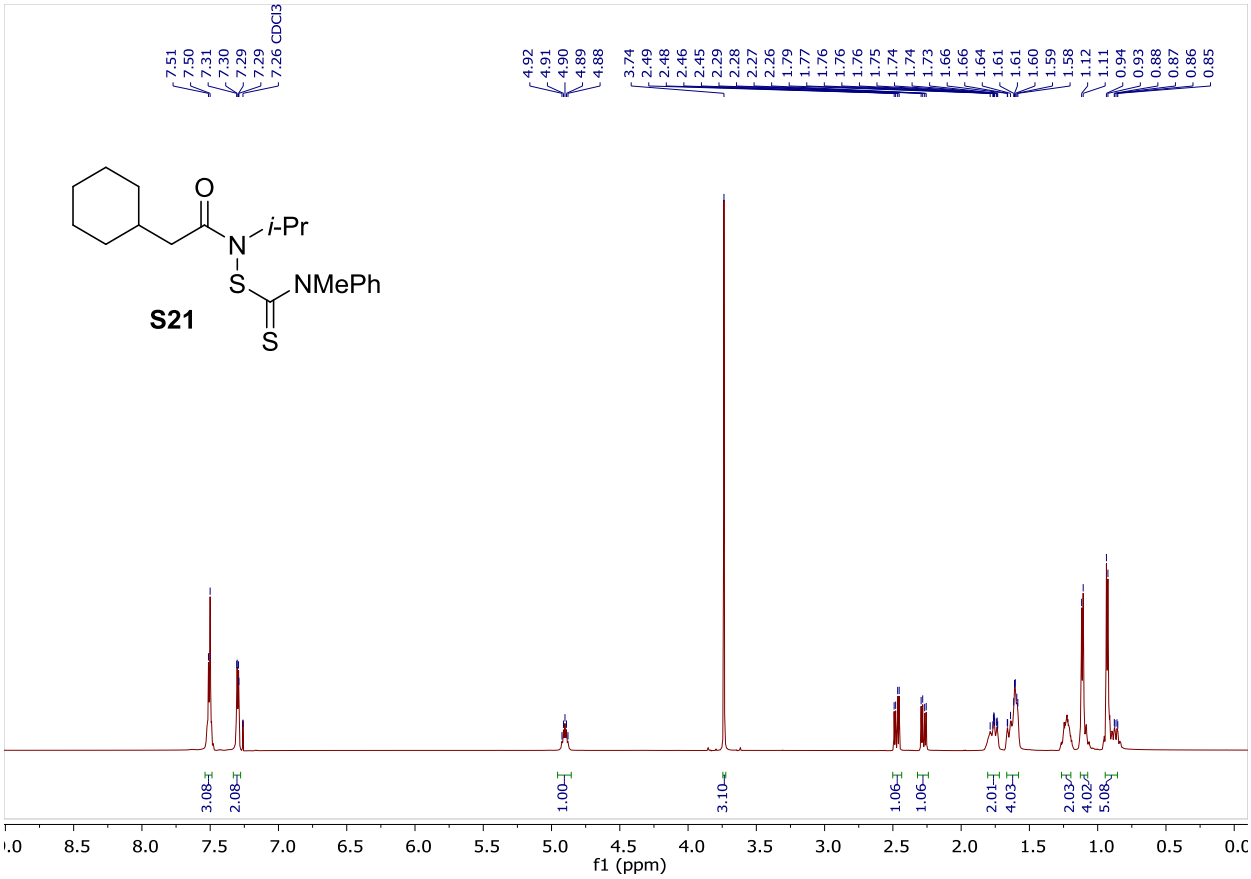
129.87
126.76
77.16 CDCl3
63.50
46.65
38.36
29.88
18.87
13.81
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

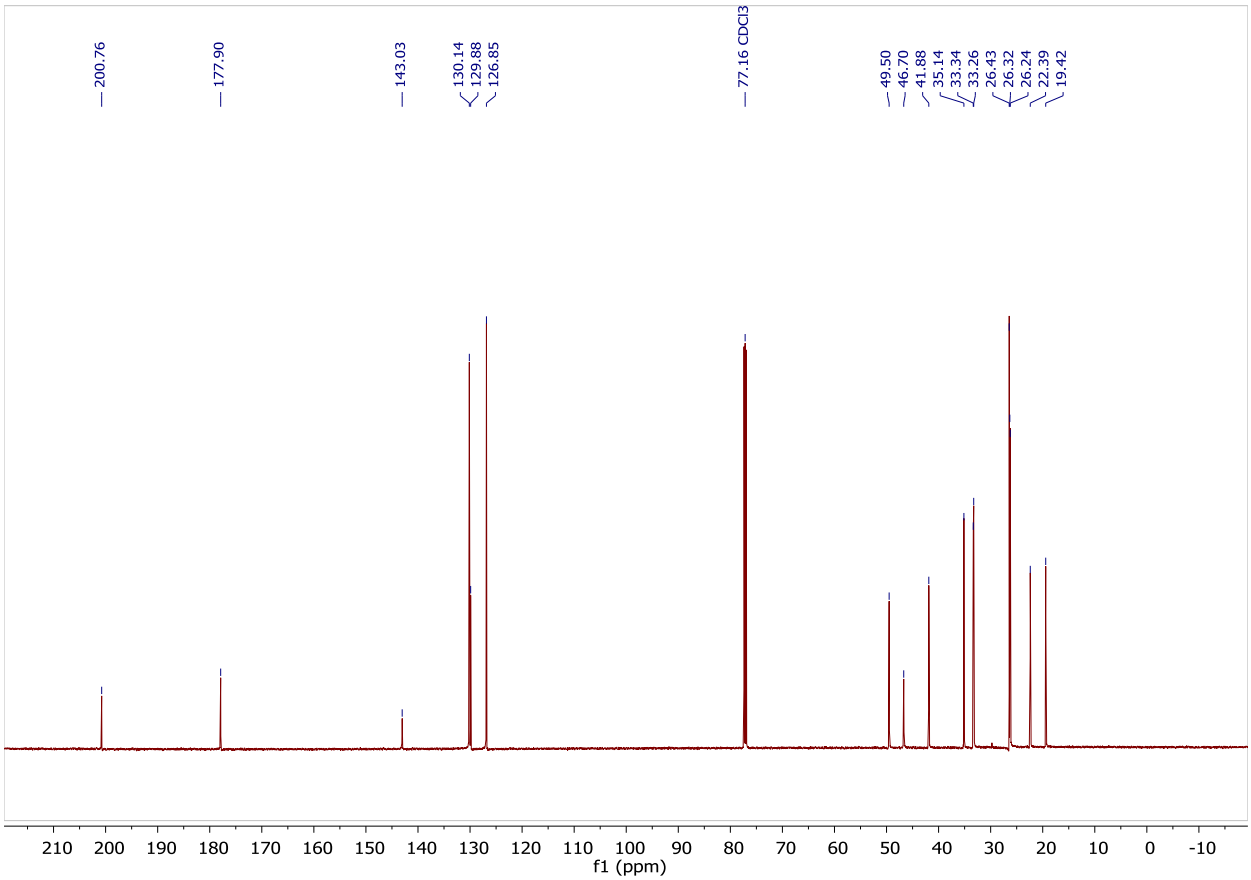

7.51
7.51
7.29
7.29
7.29
7.28
7.28
7.28
7.28
7.26 CDCl3
4.42
4.41
4.40
4.39
4.38
4.37
3.74
3.05
3.04
3.04
3.03
3.02
3.01
1.50
1.49
1.48
1.48
1.48
1.47
1.47
1.47
1.47
1.25
1.25
1.24
1.24
1.23
1.23
1.22
1.21
1.21
0.87
0.86
0.85
O
F3C
N
S
NMePh
S
2.99
1.88
1.00
2.99
1.00
2.00
1.99
3.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

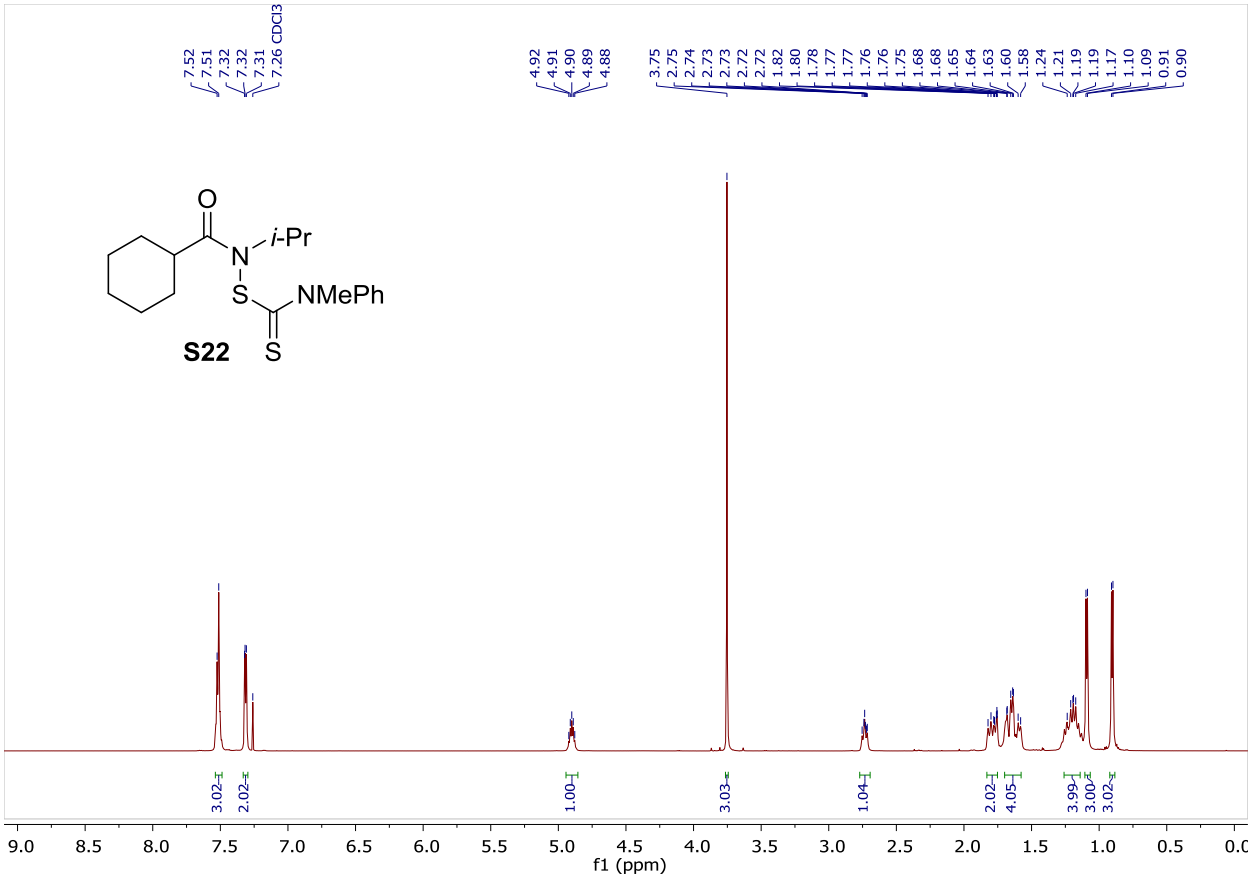
S20

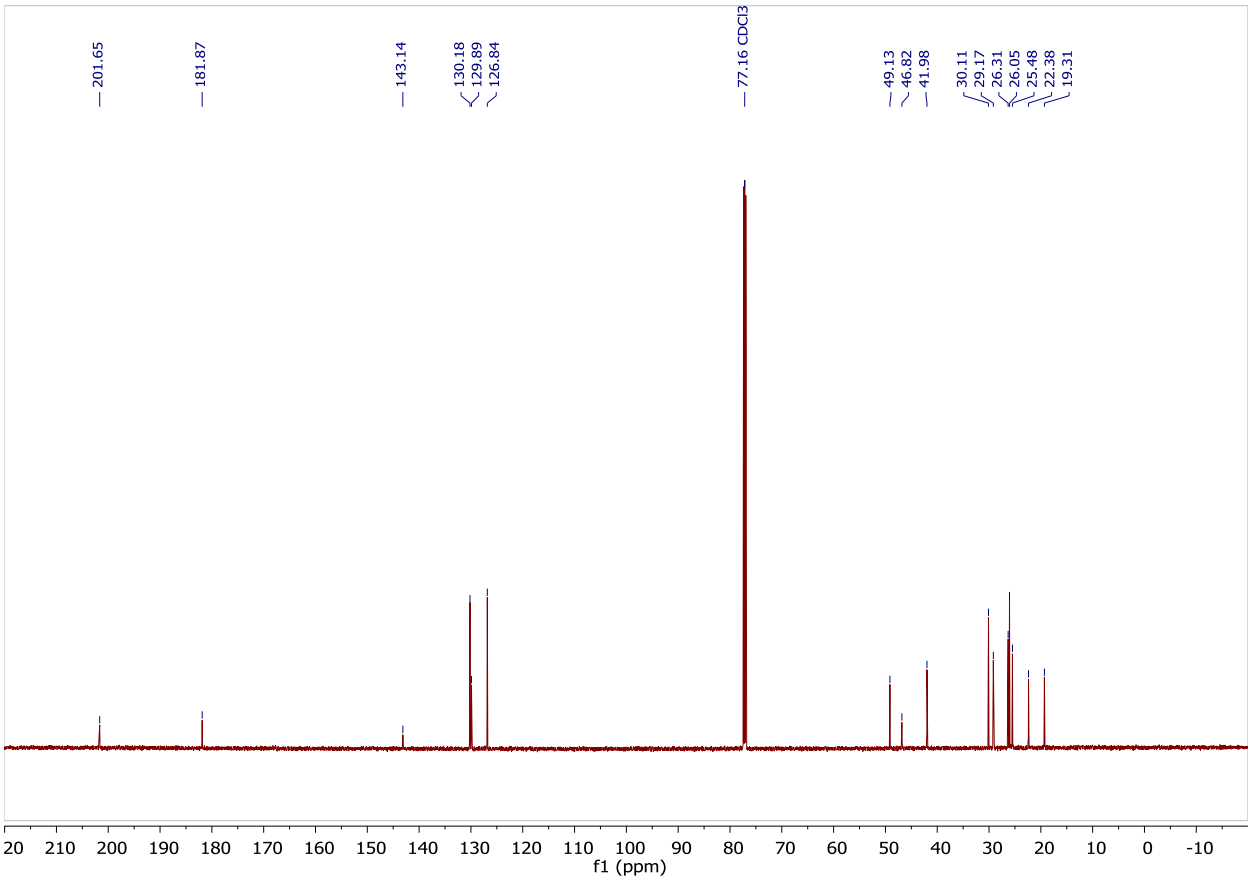

196.68
161.79
161.55
161.32
161.08
142.17
130.38
130.33
130.24
126.97
118.83
116.92
115.00
113.09
77.16 CDCl3
54.06
46.46
29.34
19.90
13.80
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

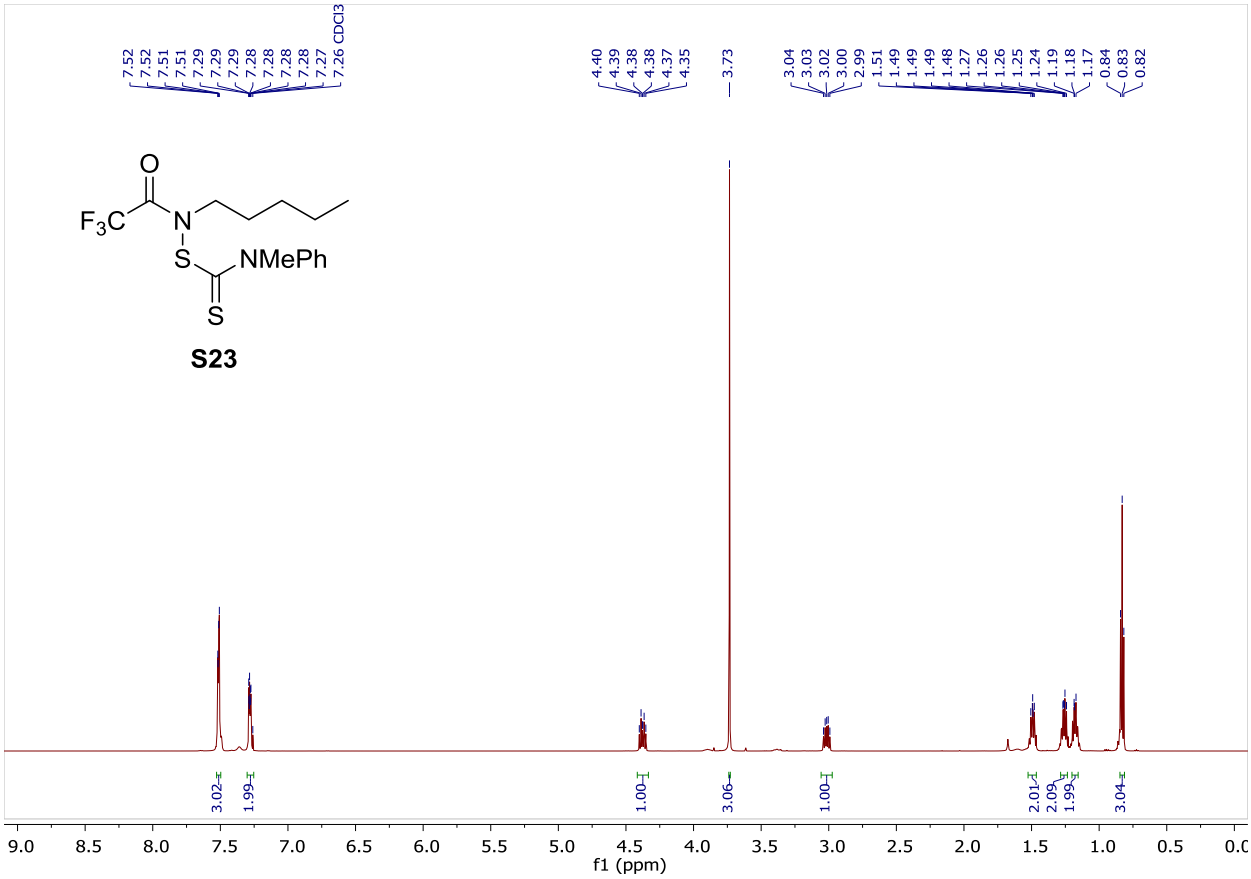

-68.39
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.51
7.50
7.31
7.30
7.29
7.29
7.26 CDCl3
4.92
4.91
4.90
4.89
4.88
3.74
2.49
2.48
2.46
2.45
2.29
2.28
2.27
2.26
1.79
1.77
1.76
1.76
1.76
1.75
1.74
1.74
1.73
1.66
1.66
1.64
1.61
1.61
1.60
1.59
1.58
1.12
1.11
0.94
0.93
0.88
0.87
0.86
0.85
O
N
i-Pr
S
NMePh
S
S21
3.08
2.08
1.00
3.10
1.06
1.06
2.01
4.03
2.03
4.02
5.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

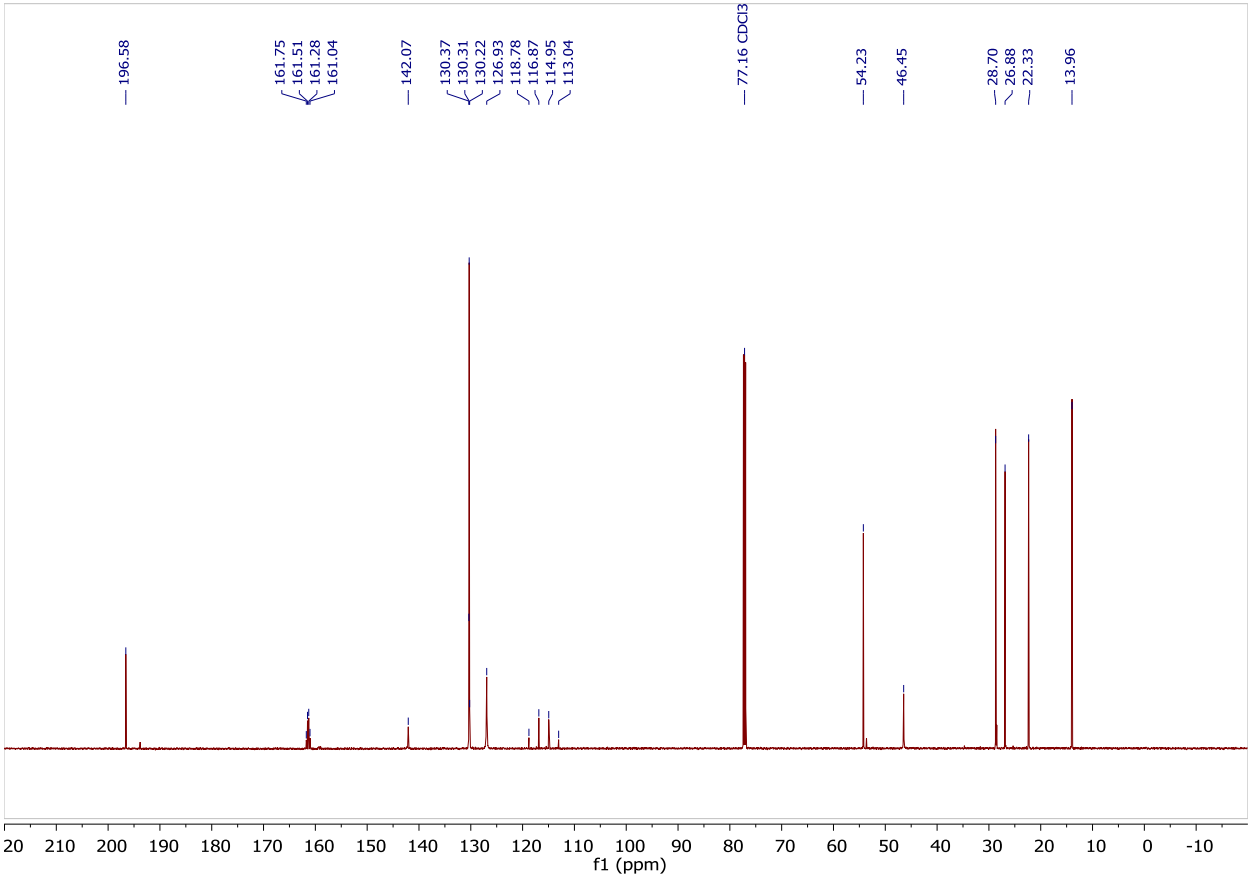

200.76
177.90
143.03
130.14
129.88
126.85
77.16 CDCl3
49.50
46.70
41.88
35.14
33.34
33.26
26.43
26.32
26.24
22.39
19.42
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

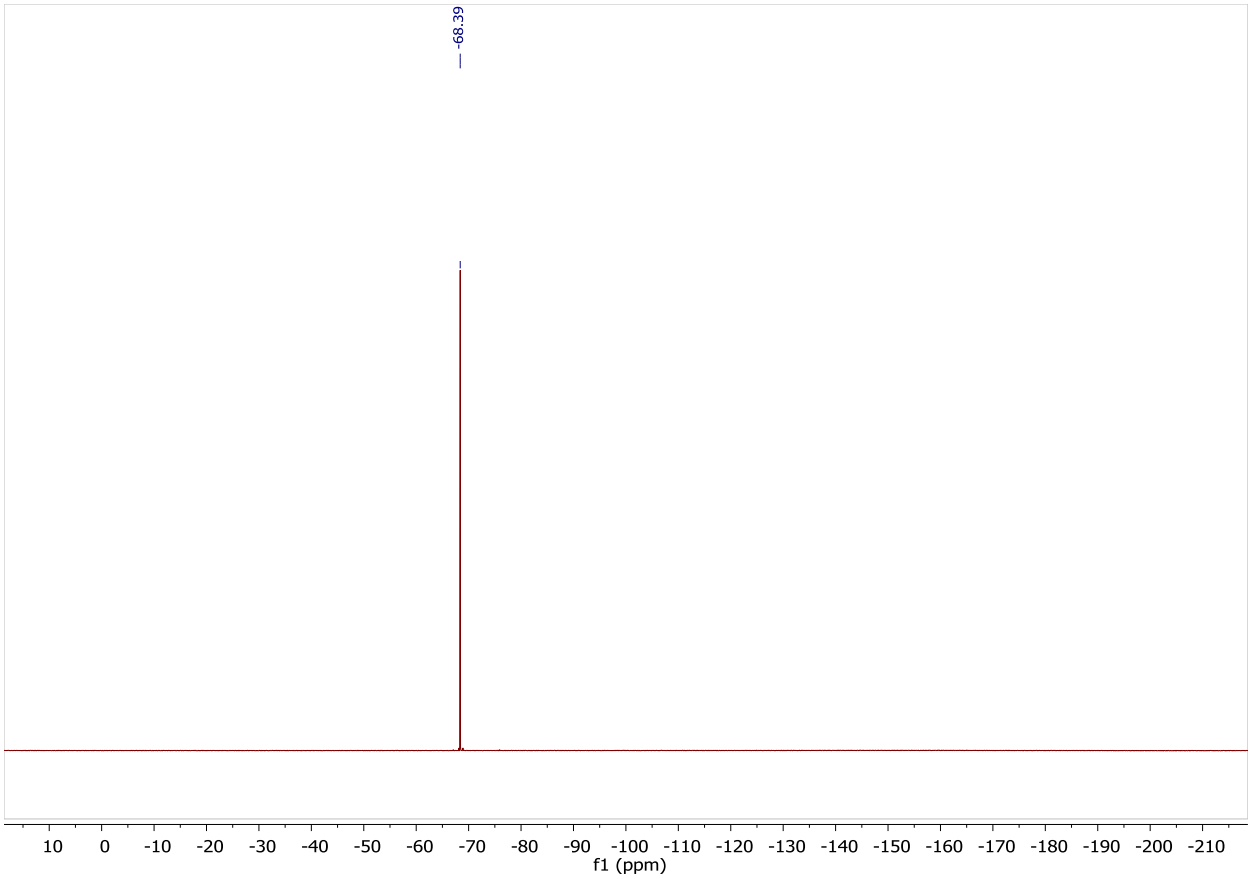

7.52
7.51
7.32
7.32
7.31
7.26 CDCl3
4.92
4.91
4.90
4.89
4.88
3.75
2.75
2.74
2.73
2.73
2.72
2.72
1.82
1.80
1.78
1.77
1.77
1.76
1.76
1.75
1.68
1.68
1.65
1.64
1.63
1.60
1.58
1.24
1.21
1.19
1.19
1.17
1.10
1.09
0.91
0.90
O
N
i-Pr
S
NMePh
S
S22
3.02
2.02
1.00
3.03
1.04
2.02
4.05
3.99
3.00
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

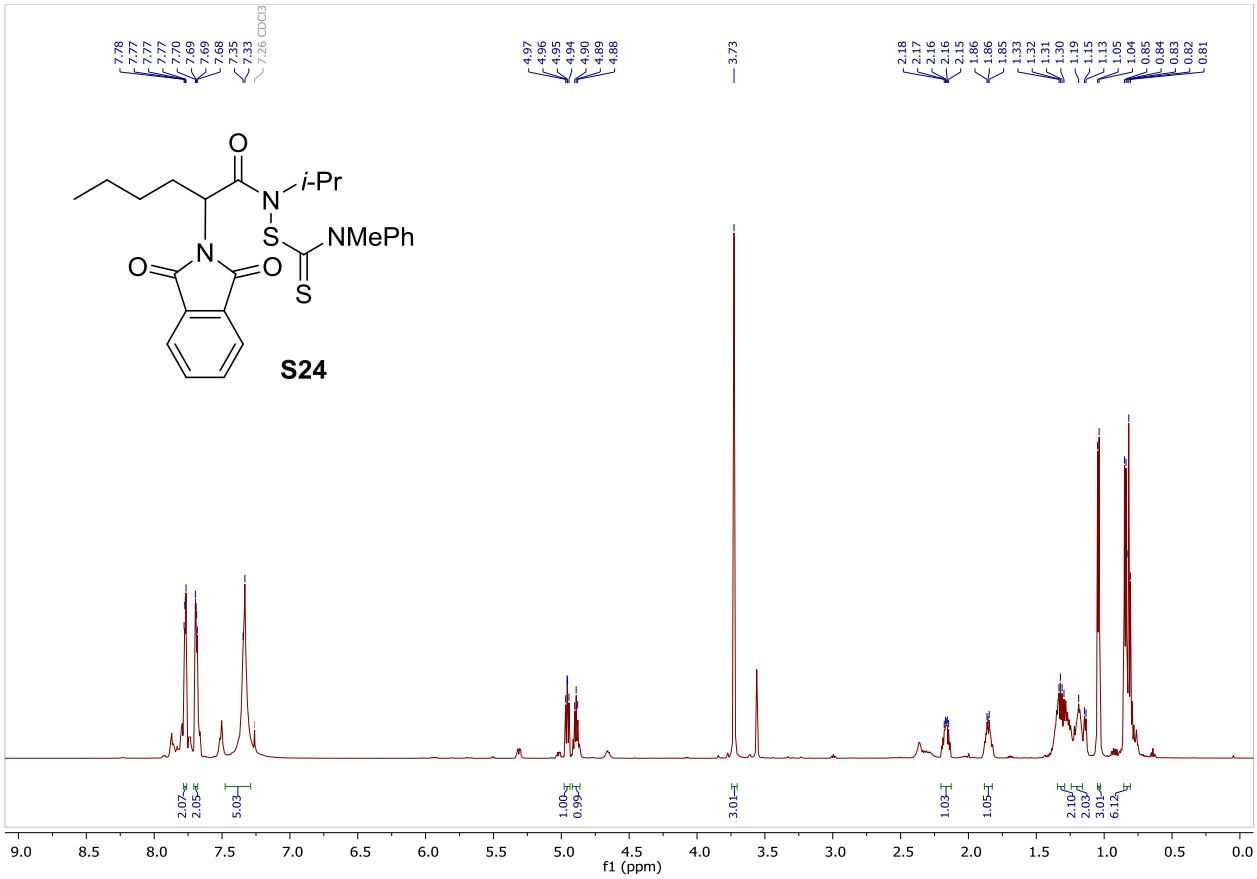

201.65
181.87
143.14
130.18
129.89
126.84
77.16 CDCl3
49.13
46.82
41.98
30.11
29.17
26.31
26.05
25.48
22.38
19.31
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

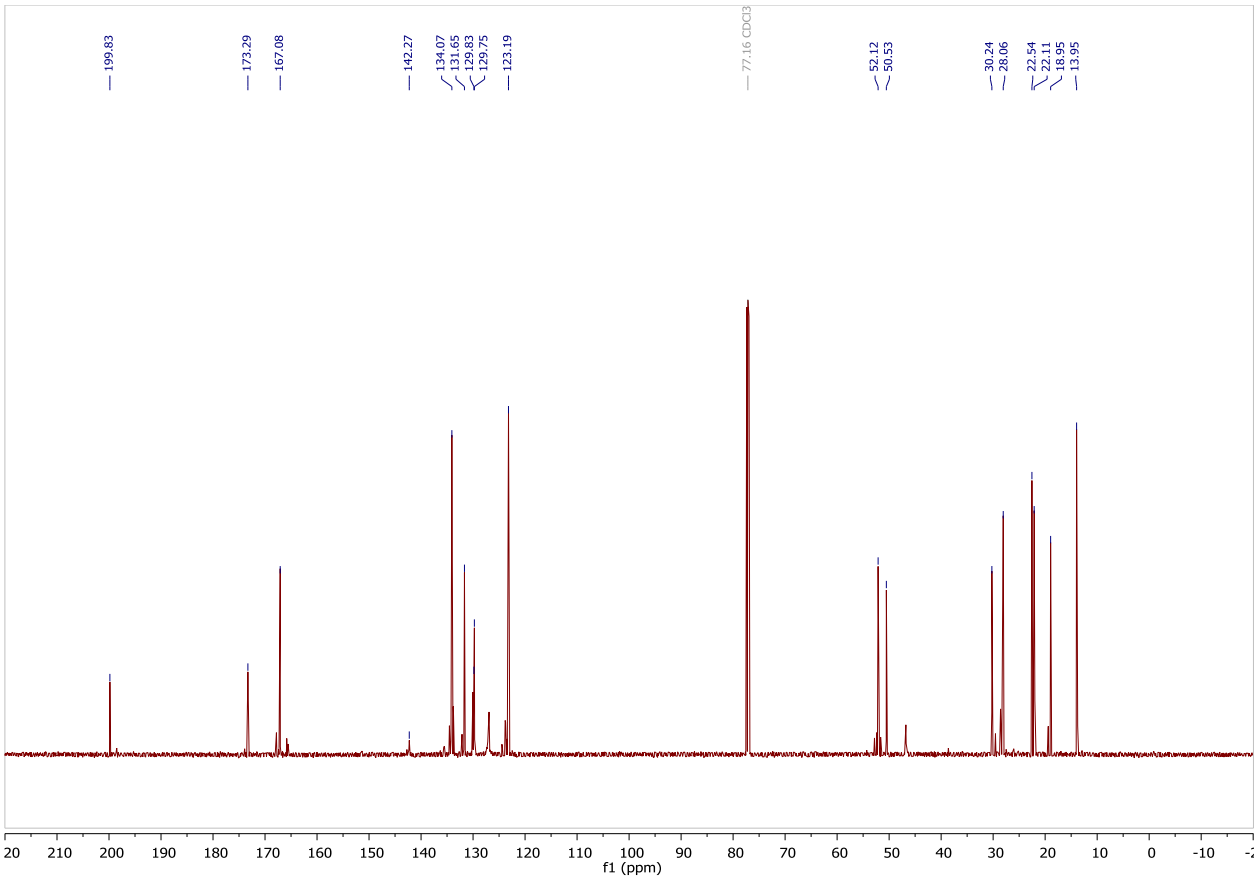

7.52
7.52
7.51
7.51
7.29
7.29
7.28
7.28
7.28
7.28
7.27
7.26 CDCl3
4.40
4.39
4.38
4.38
4.37
4.35
3.73
3.04
3.03
3.02
3.00
2.99
1.51
1.49
1.49
1.49
1.48
1.27
1.26
1.26
1.25
1.24
1.19
1.18
1.17
0.84
0.83
0.82
O
F3C
N
S
NMePh
S
3.02
1.99
1.00
3.06
1.00
2.01
2.09
1.99
3.04
f1 (ppm)

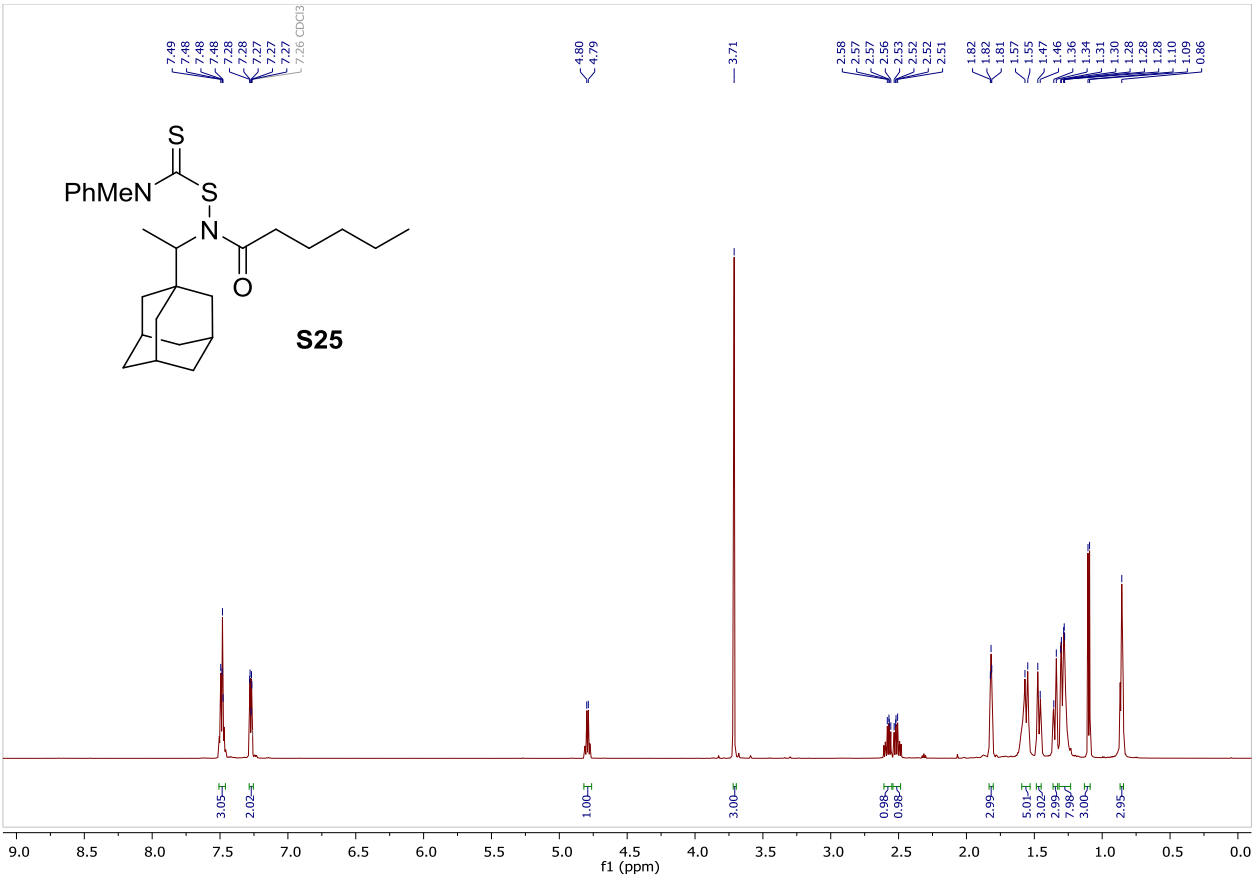
S23

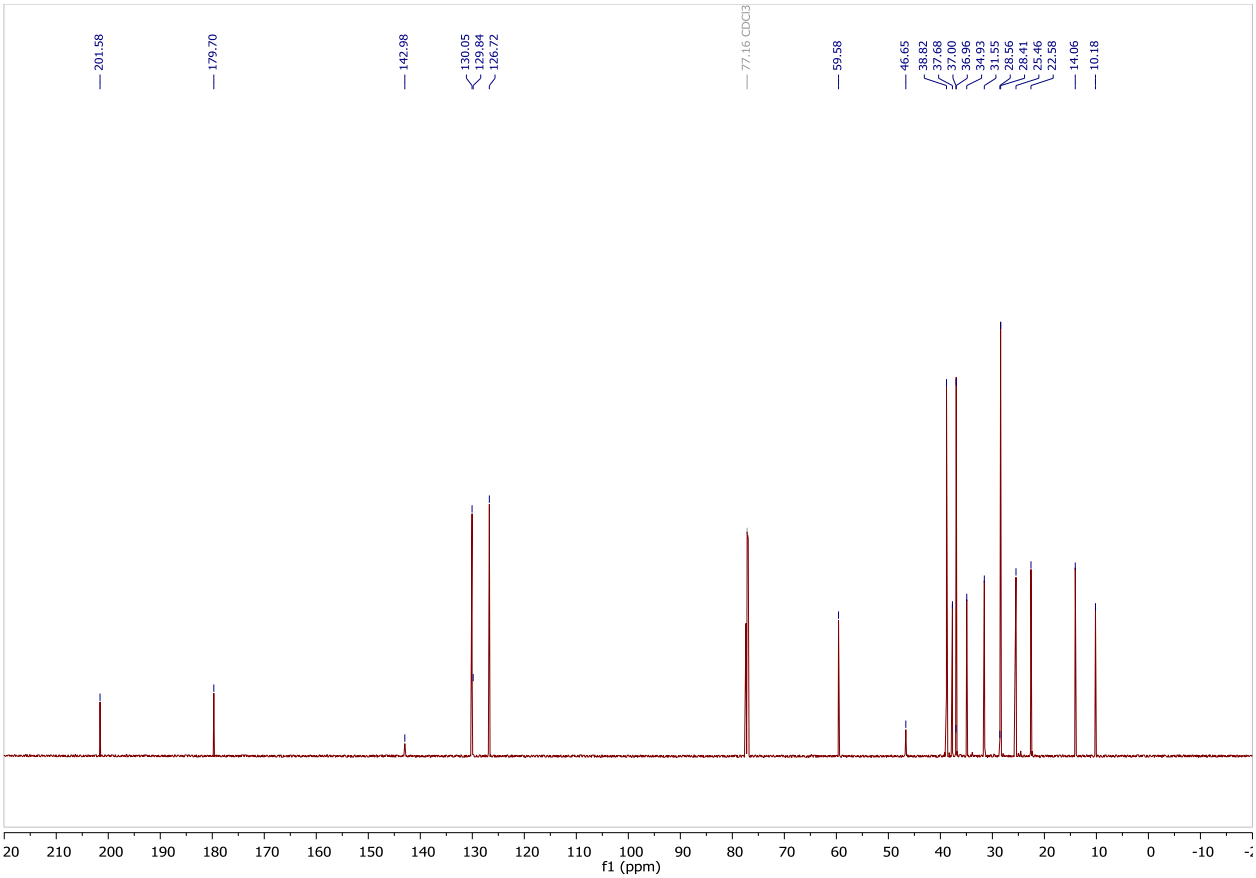

196.58
161.75
161.51
161.28
161.04
142.07
130.37
130.31
130.22
126.93
118.78
116.87
114.95
113.04
77.16 CDCl3
54.23
46.45
28.70
26.88
22.33
13.96
f1 (ppm)

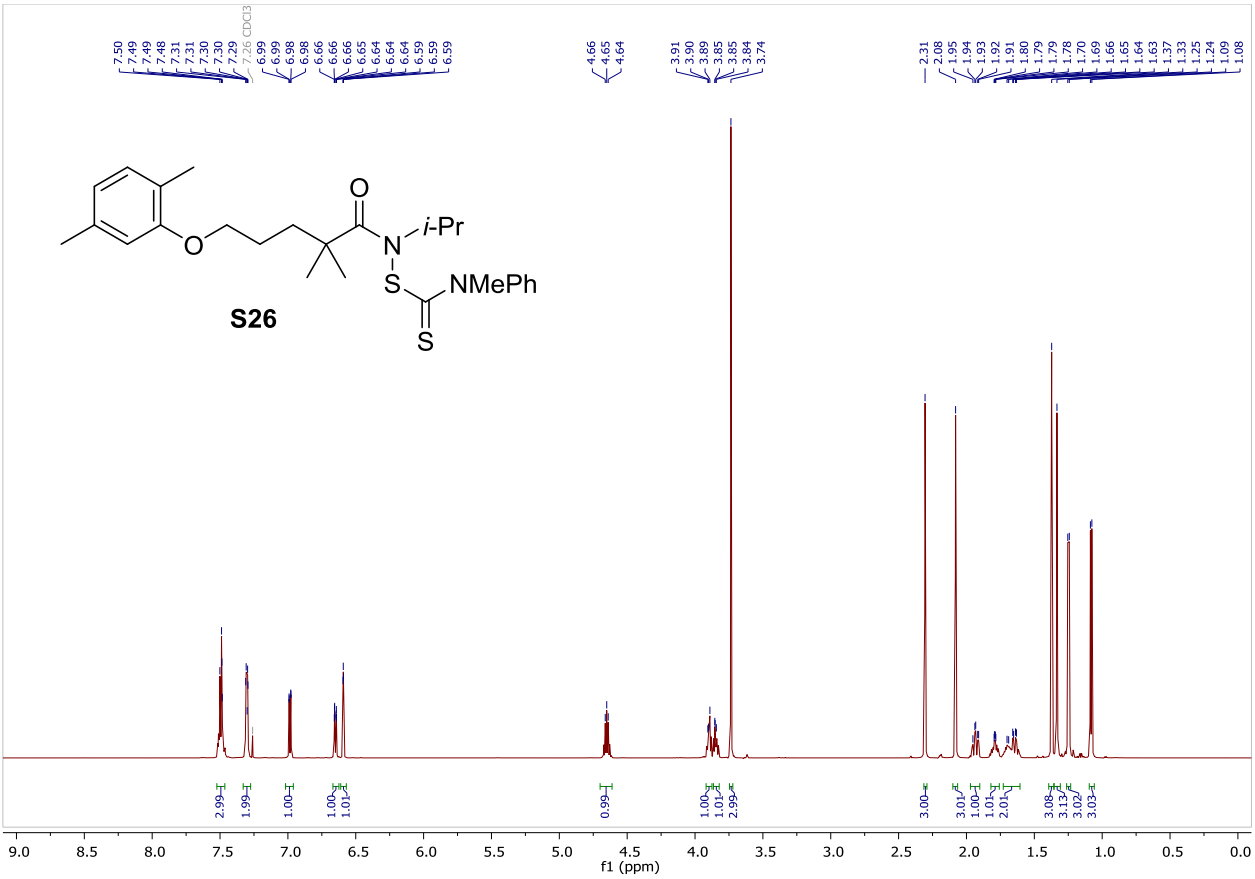

-68.39
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

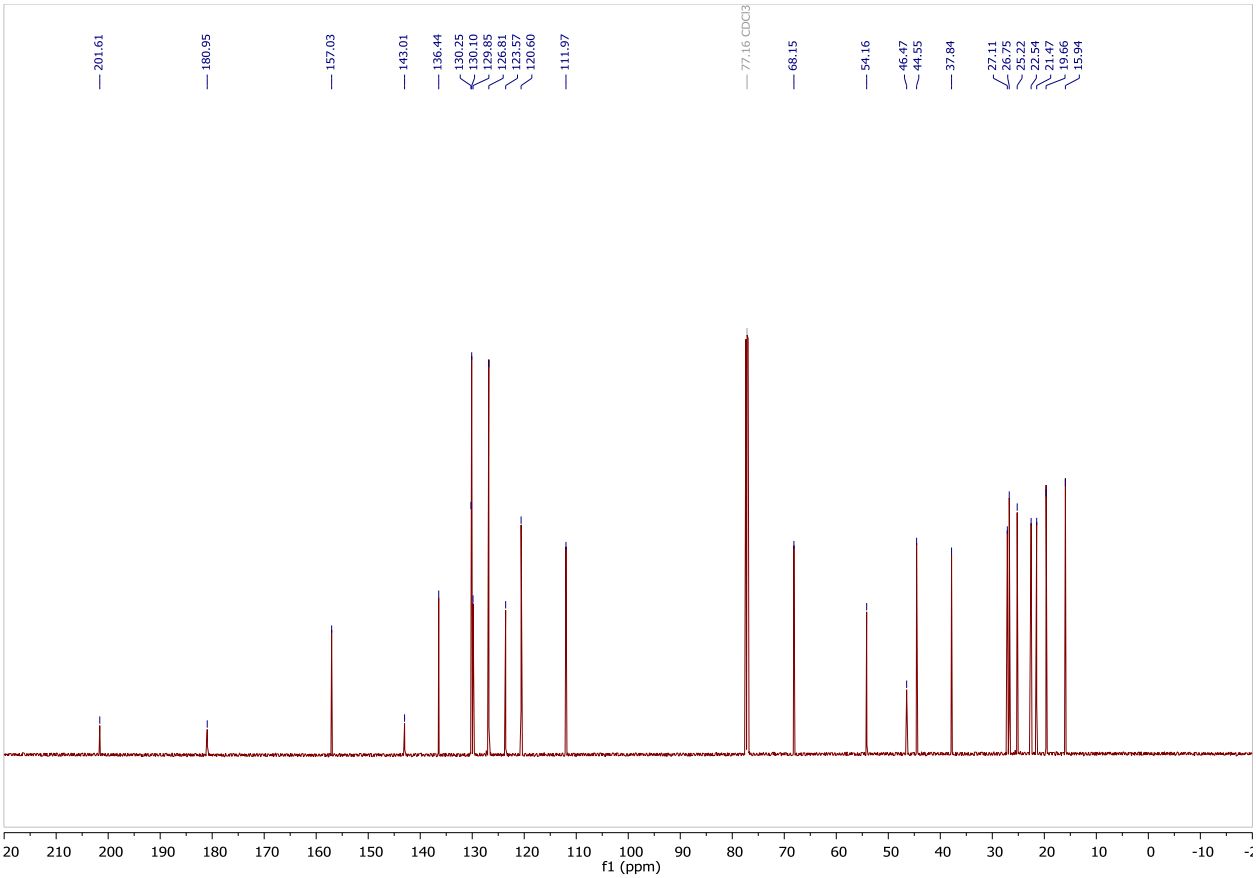

7.78
7.77
7.77
7.77
7.70
7.69
7.69
7.68
7.35
7.33
7.26 CDCl3
4.97
4.96
4.95
4.94
4.90
4.89
4.88
3.73
2.18
2.17
2.16
2.16
2.15
1.86
1.86
1.85
1.33
1.32
1.31
1.30
1.19
1.15
1.13
1.05
1.04
0.85
0.84
0.83
0.82
0.81
O
N
i-Pr
S
NMePh
O
N
O
S
S24
2.07
2.05
5.03
1.00
0.99
3.01
1.03
1.05
2.10
2.03
3.01
6.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

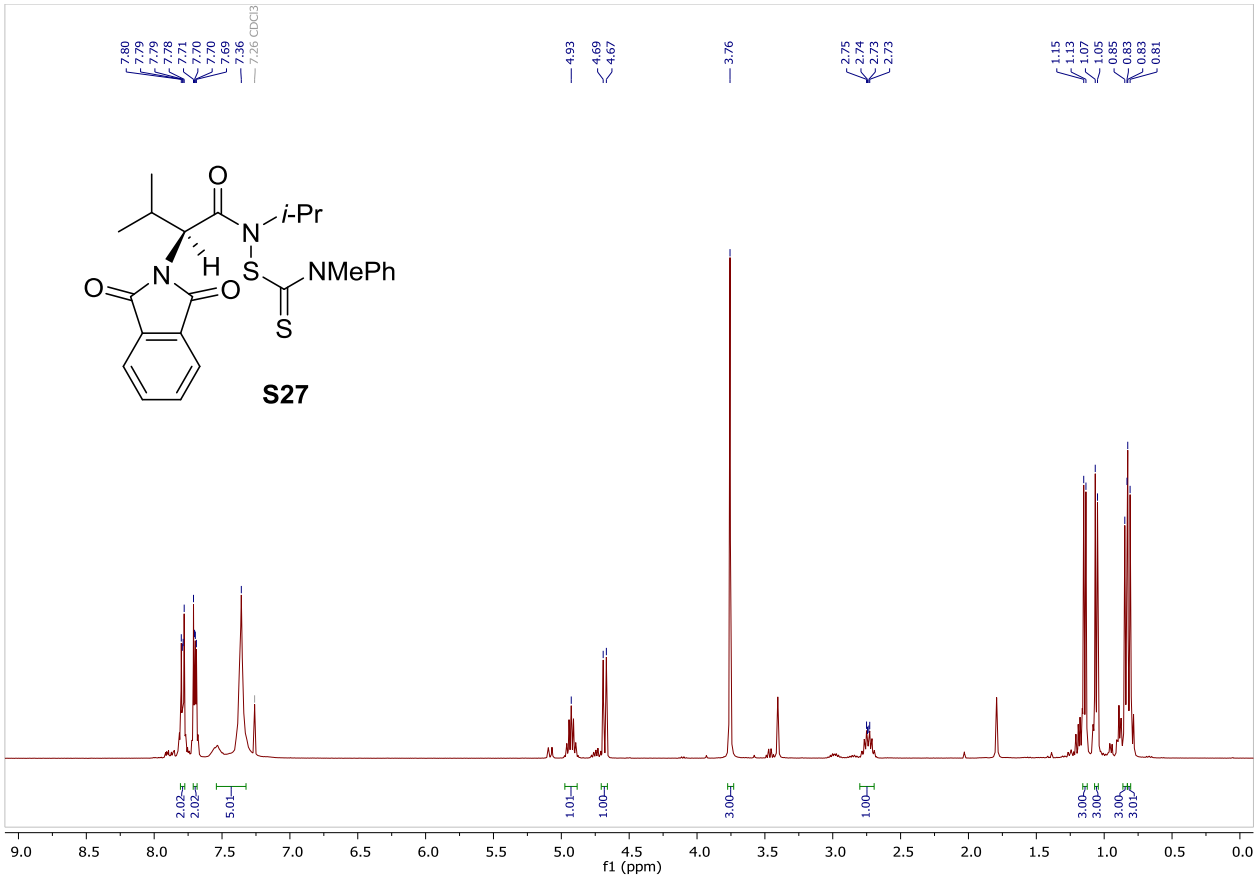

199.83
173.29
167.08
142.27
134.07
131.65
129.83
129.75
123.19
77.16 CDCl3
52.12
50.53
30.24
28.06
22.54
22.11
18.95
13.95
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

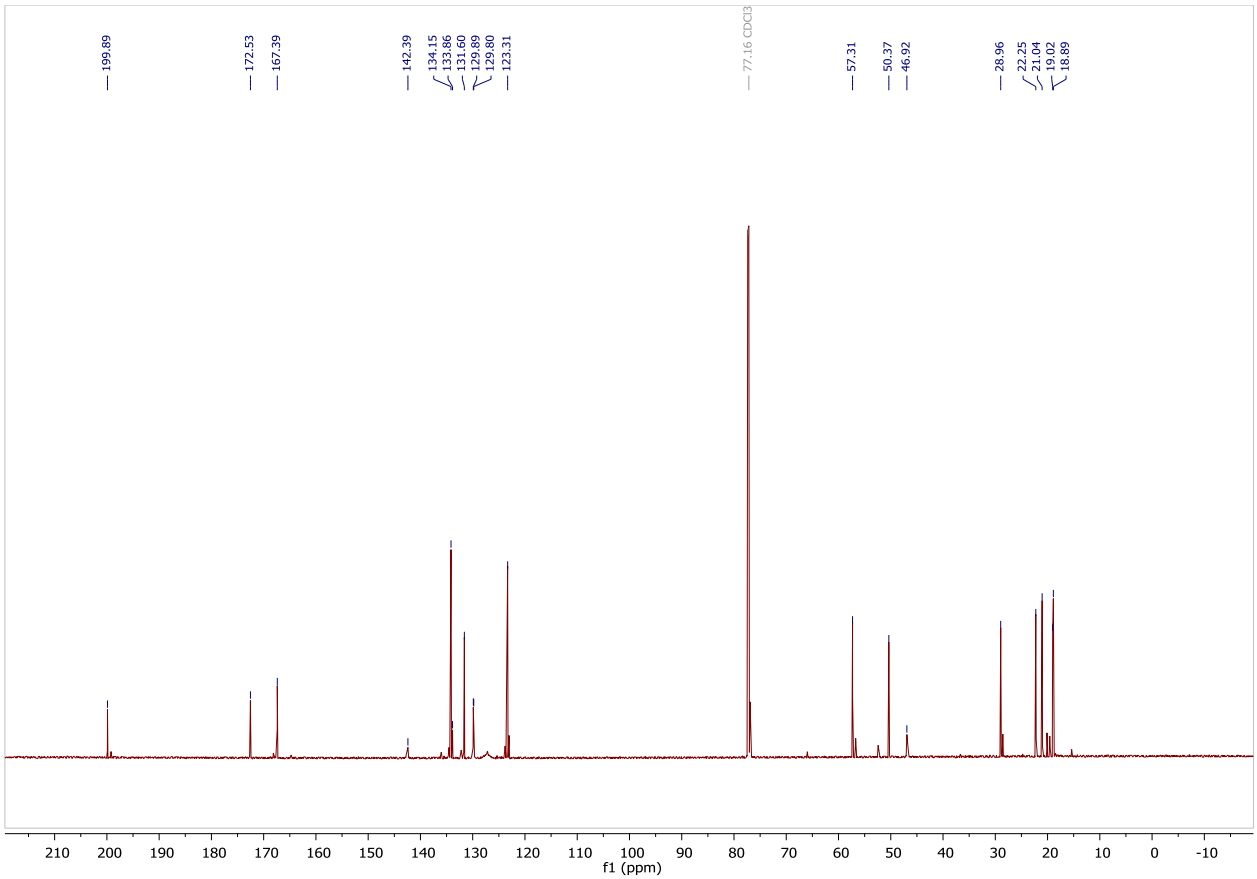

PhMeN
S
N
O
S25
f1 (ppm)

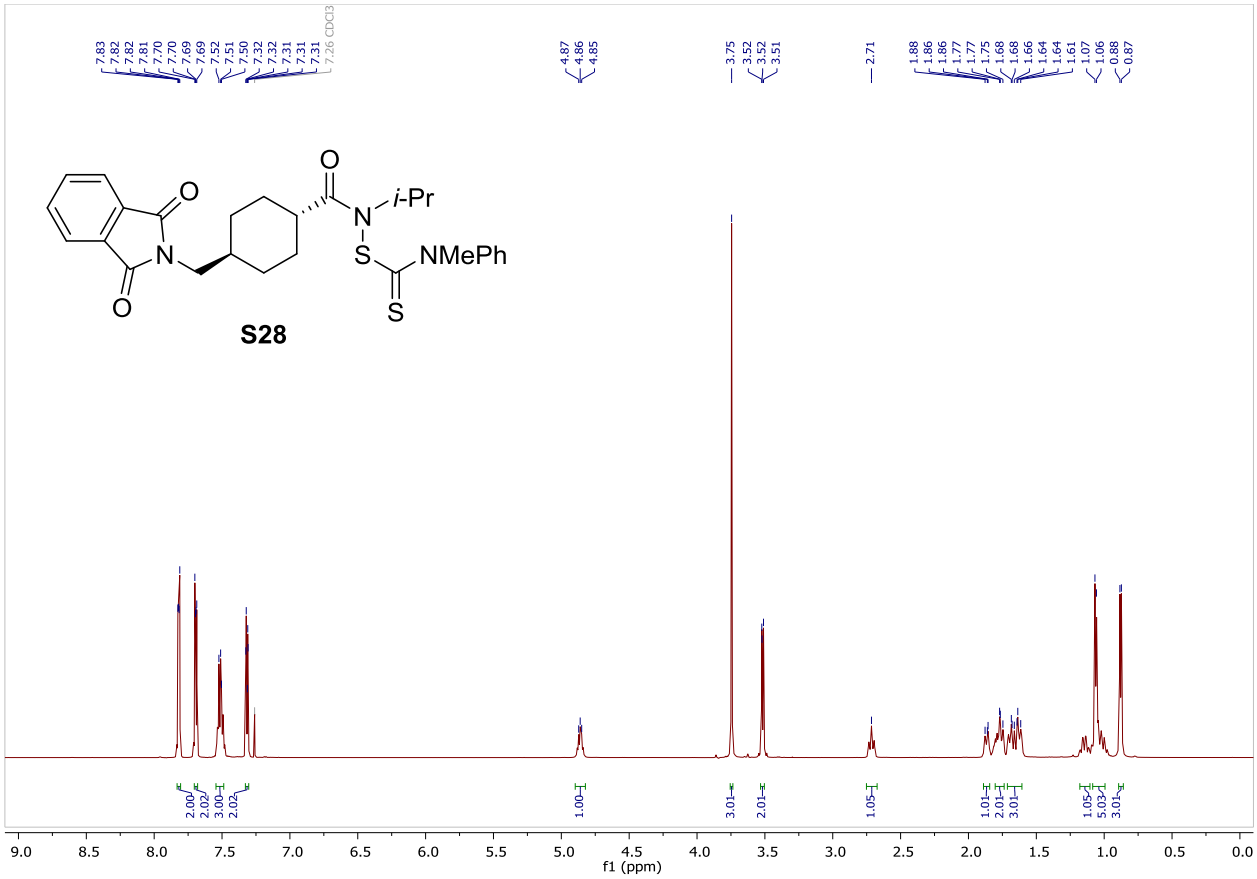

f1 (ppm)


S26
O
N
i-Pr
S
NMePh
S
O
f1 (ppm)

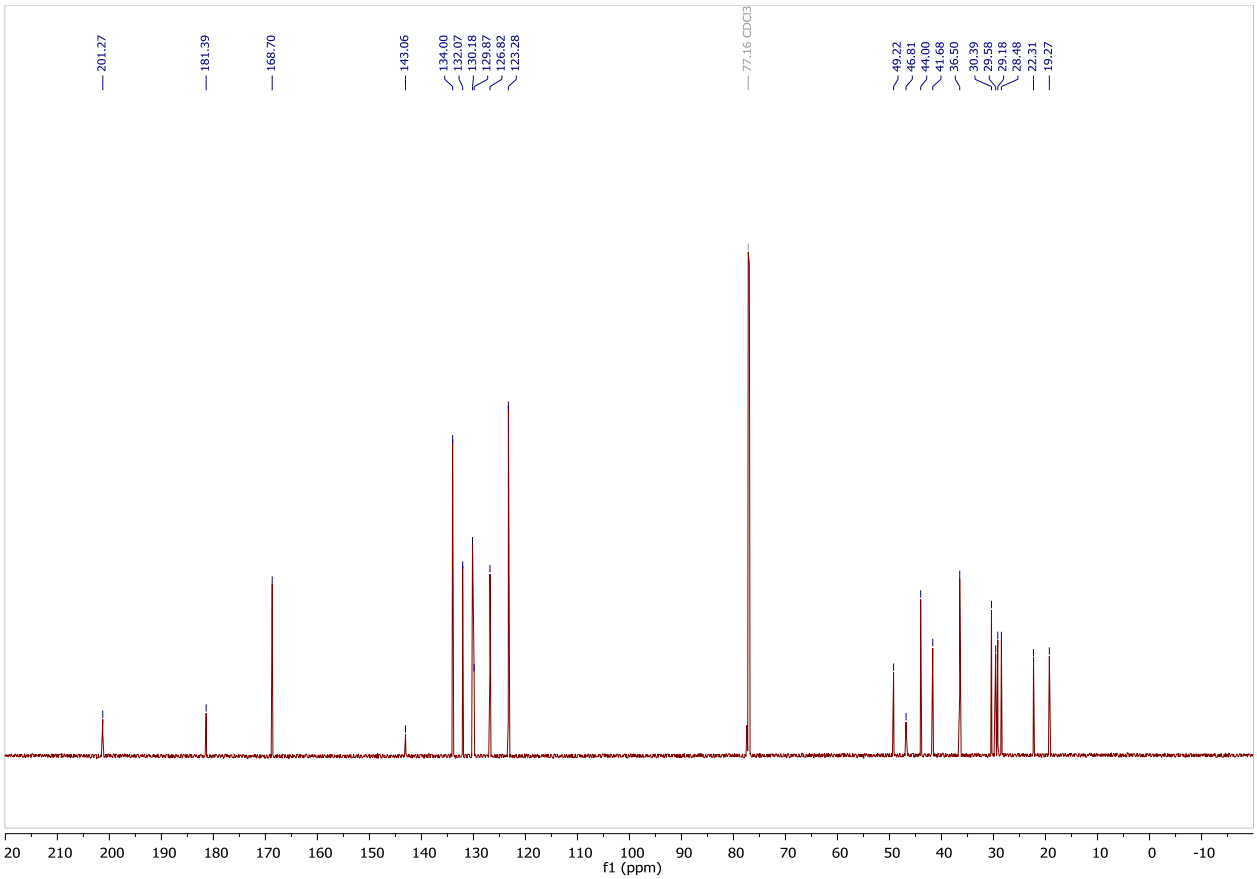

f1 (ppm)

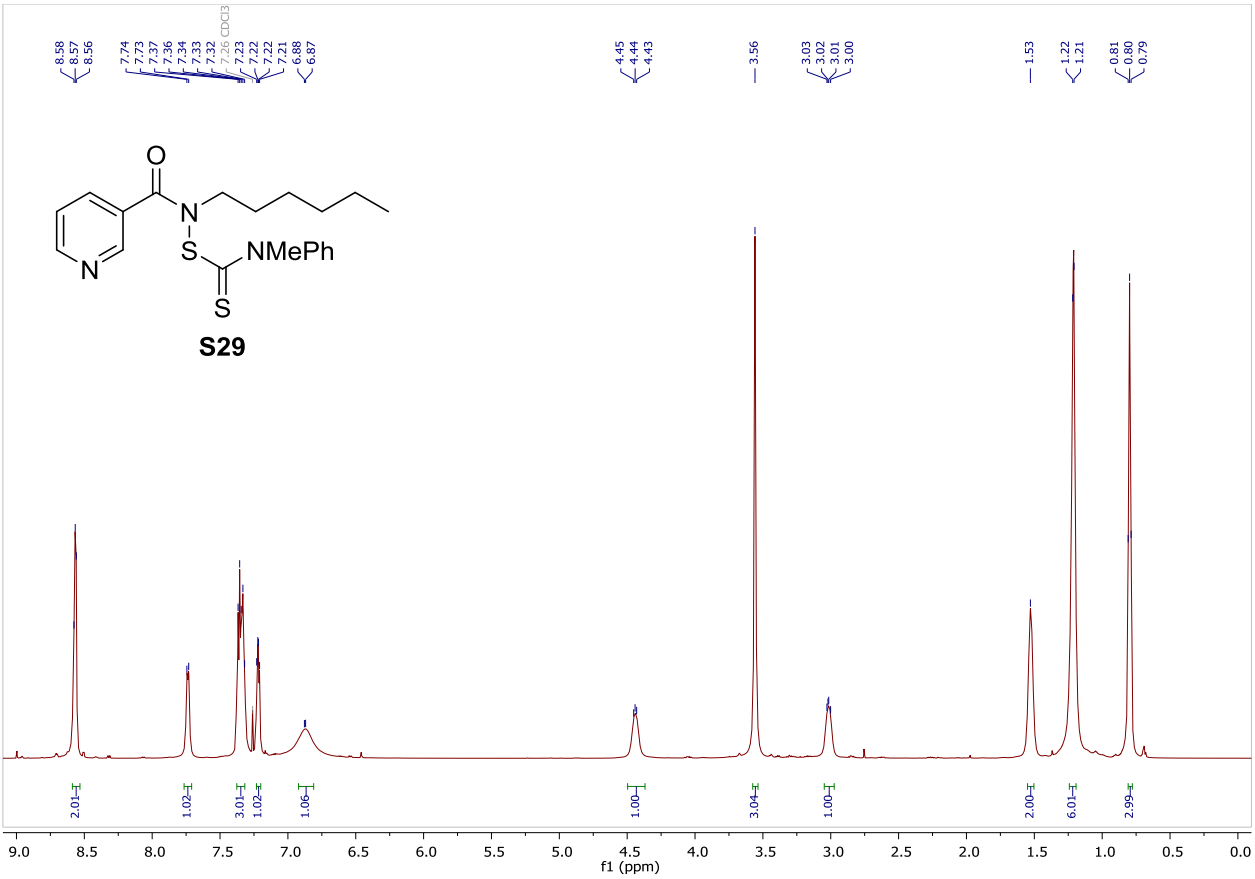

7.80
7.79
7.79
7.78
7.71
7.70
7.70
7.69
7.36
7.26 CDCl3
4.93
4.69
4.67
3.76
2.75
2.74
2.73
2.73
1.15
1.13
1.07
1.05
0.85
0.83
0.83
0.81
O
N
i-Pr
H
S
NMePh
O
N
O
S
S27
2.02
2.02
5.01
1.01
1.00
3.00
1.00
3.00
3.00
3.00
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


199.89
172.53
167.39
142.39
134.15
133.86
131.60
129.89
129.80
123.31
77.16 CDCl3
57.31
50.37
46.92
28.96
22.25
21.04
19.02
18.89
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

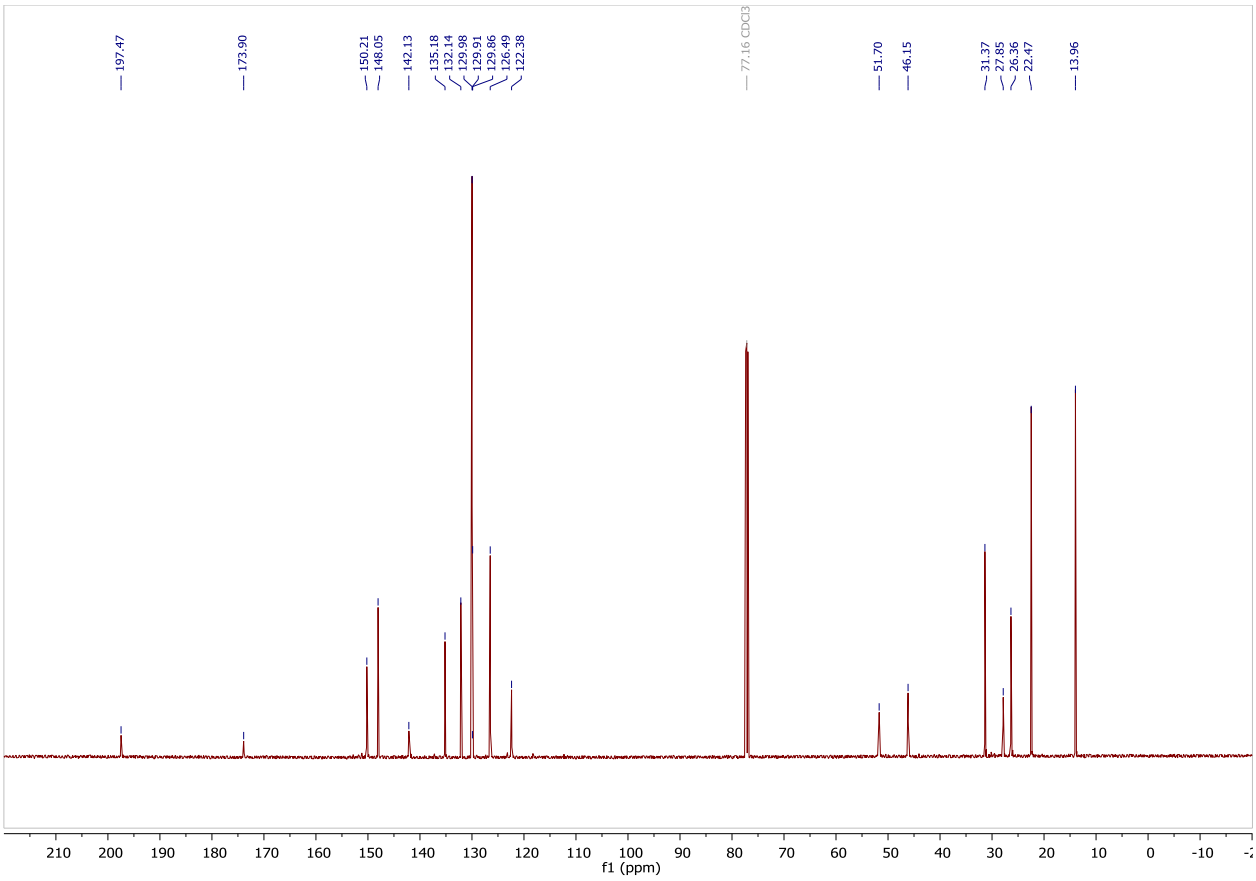

7.83
7.82
7.82
7.81
7.70
7.70
7.69
7.69
7.52
7.51
7.50
7.32
7.31
7.31
7.31
7.26 CDCl3
4.87
4.86
4.85
3.75
3.52
3.52
3.51
2.71
1.88
1.86
1.86
1.77
1.77
1.75
1.68
1.68
1.66
1.64
1.64
1.61
1.07
1.06
0.88
0.87
O
O
N
O
O
N
S
i-Pr
NMePh
S
2.00
2.02
3.00
2.02
1.00
3.01
2.01
1.05
1.01
2.01
3.01
1.05
5.03
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

S28


201.27
181.39
168.70
143.06
134.00
132.07
130.18
129.87
126.82
123.28
77.16 CDCl3
49.22
46.81
44.00
41.68
36.50
30.39
29.58
29.18
28.48
22.31
19.27
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.58
8.57
8.56
7.74
7.73
7.37
7.36
7.34
7.33
7.32
7.26 CDCl3
7.23
7.22
7.22
7.21
6.88
6.87
4.45
4.44
4.43
3.56
3.03
3.02
3.01
3.00
1.53
1.22
1.21
0.81
0.80
0.79
O
N
S
NMePh
S
N
2.01
1.02
3.01
1.02
1.06
1.00
3.04
1.00
2.00
6.01
2.99
f1 (ppm)

S29


197.47
173.90
150.21
148.05
142.13
135.18
132.14
129.98
129.91
129.86
126.49
122.38
77.16 CDCl3
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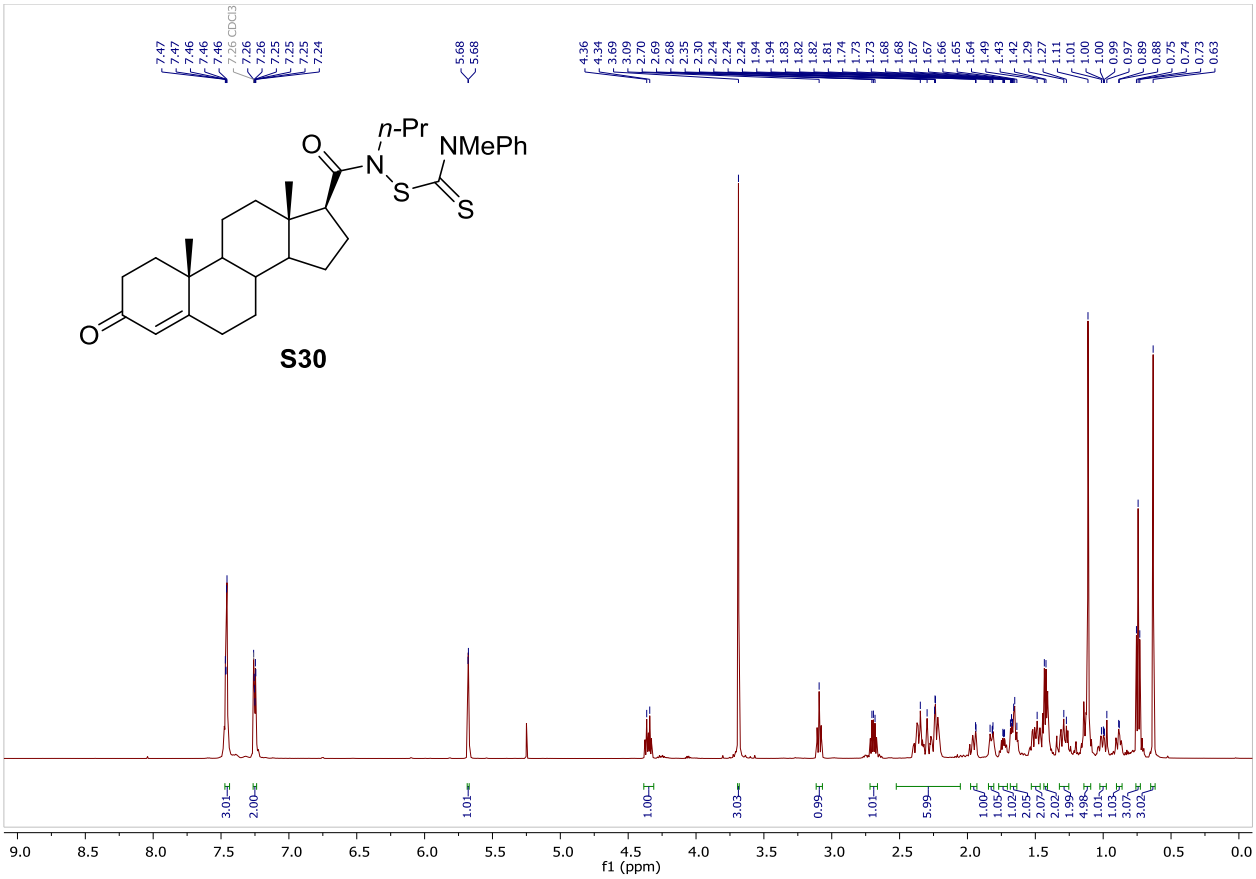
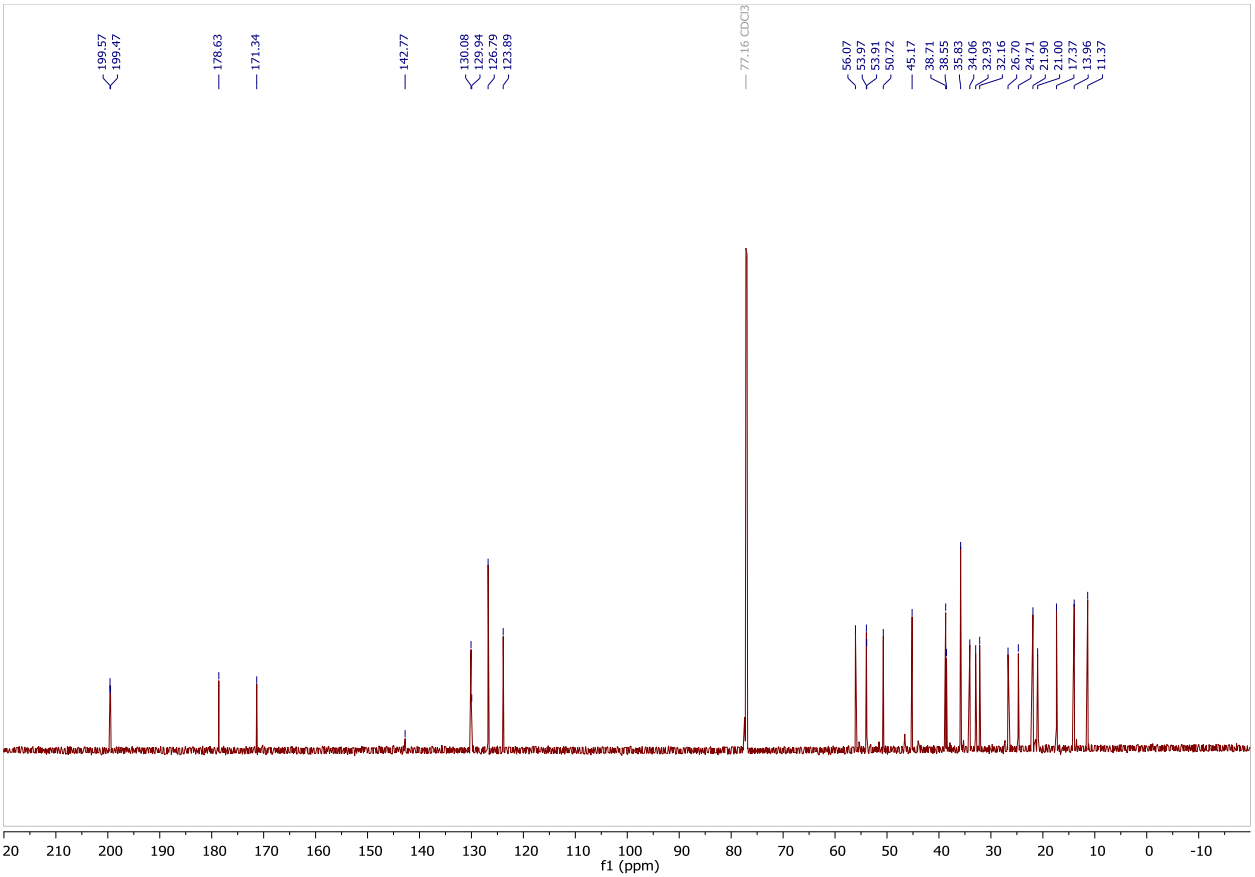
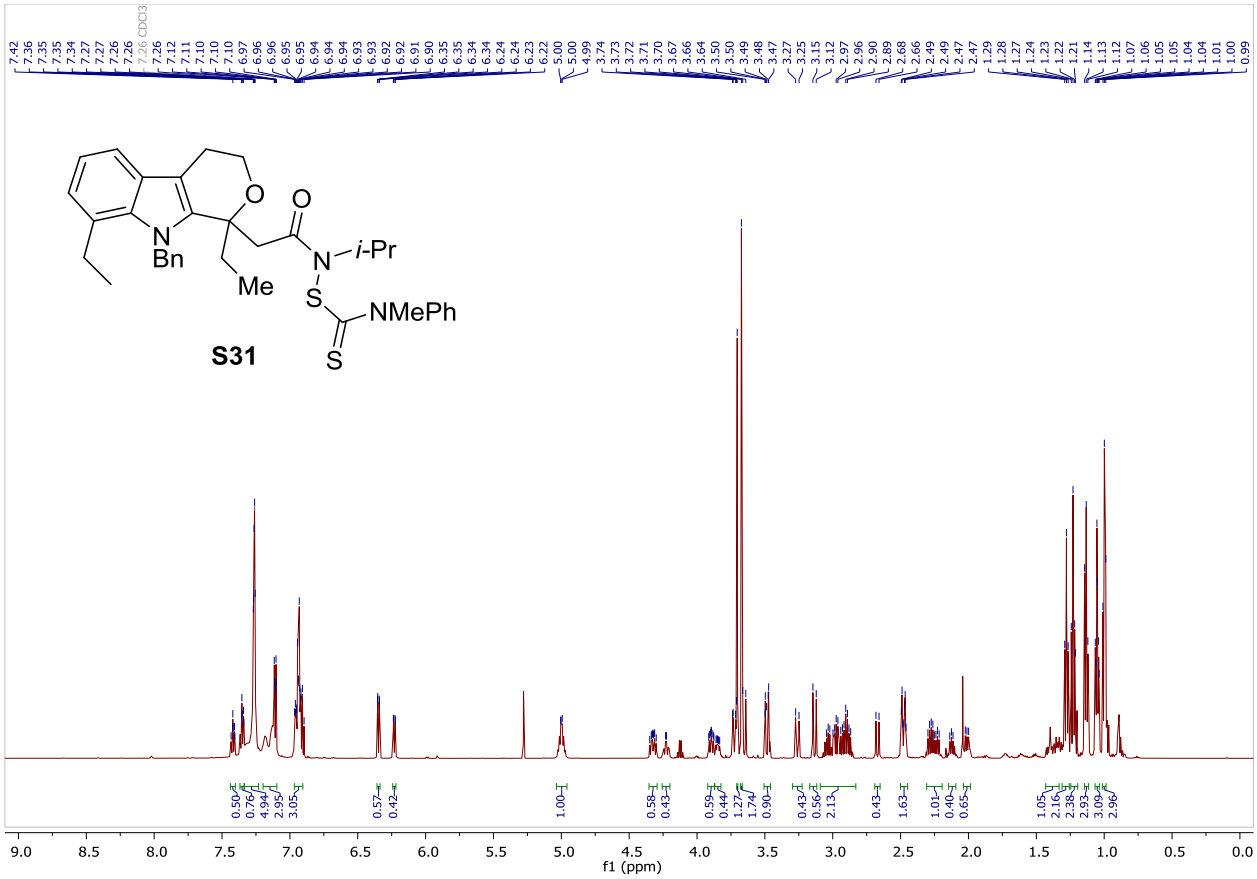
31.37
27.85
26.36
22.47
13.96
f1 (ppm)

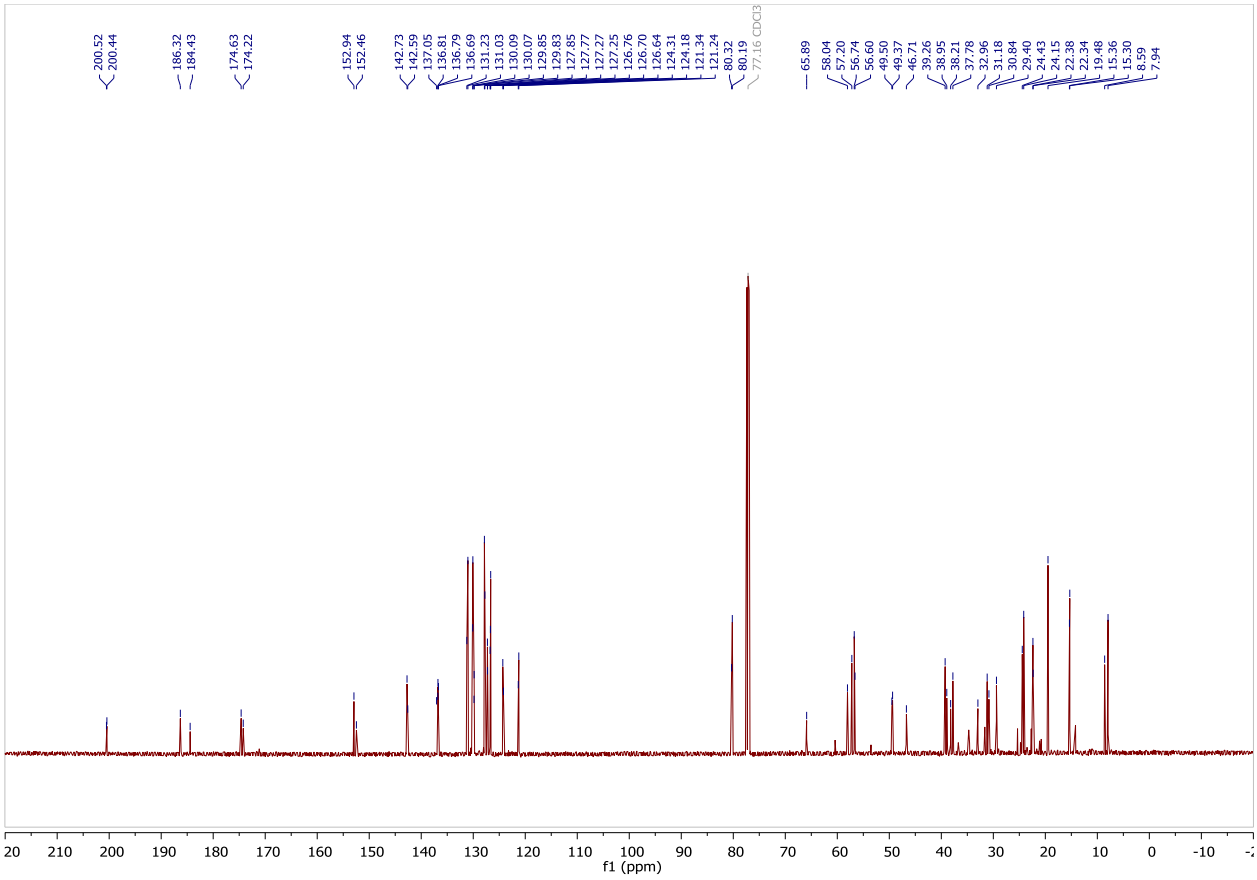


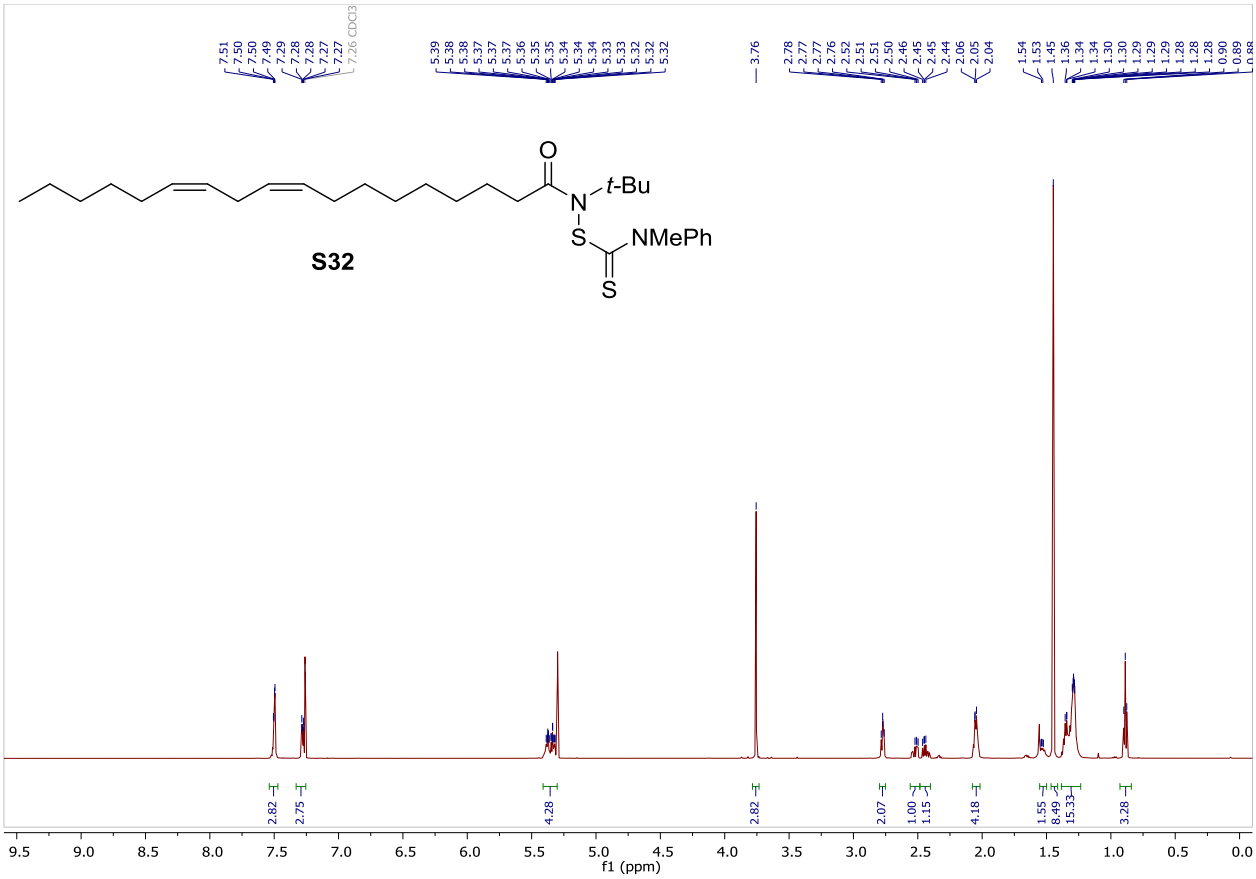
S30

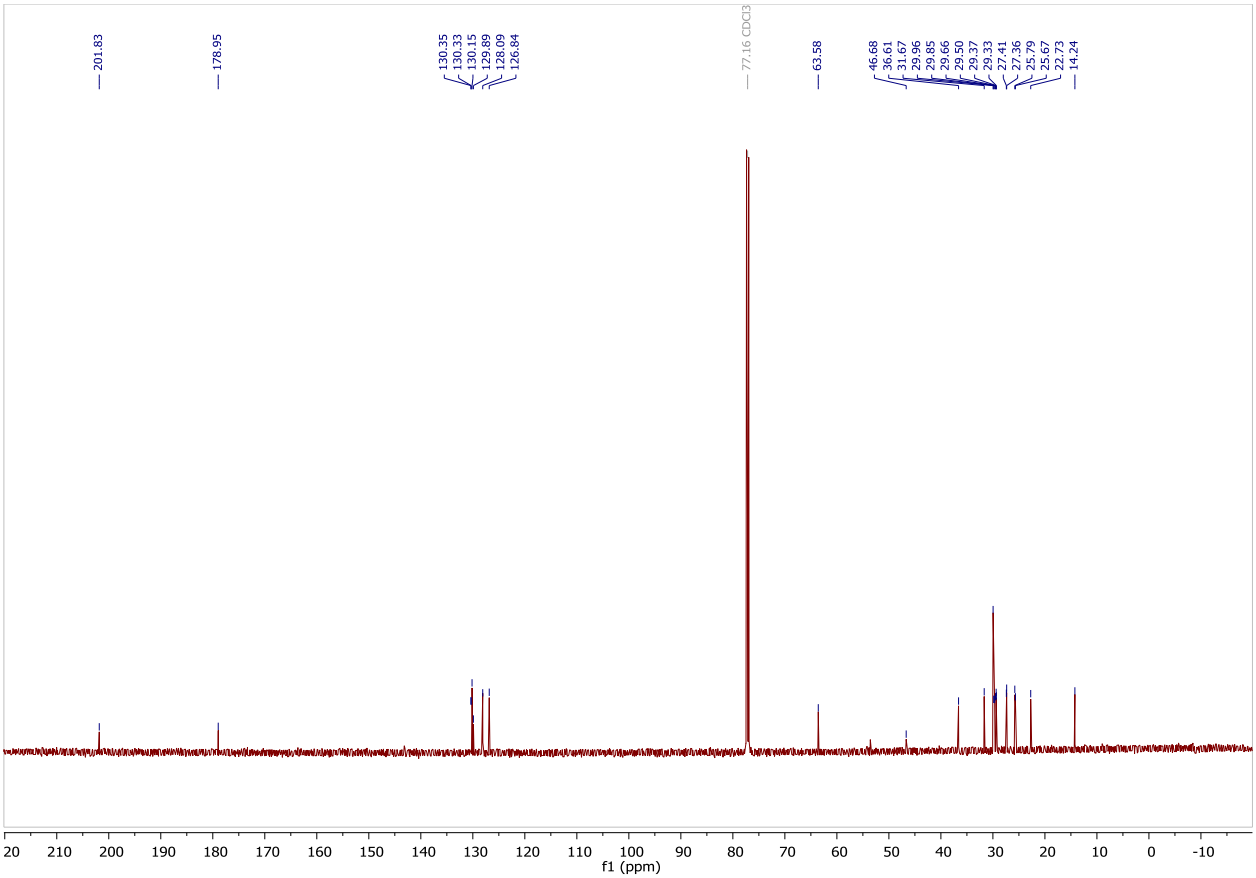


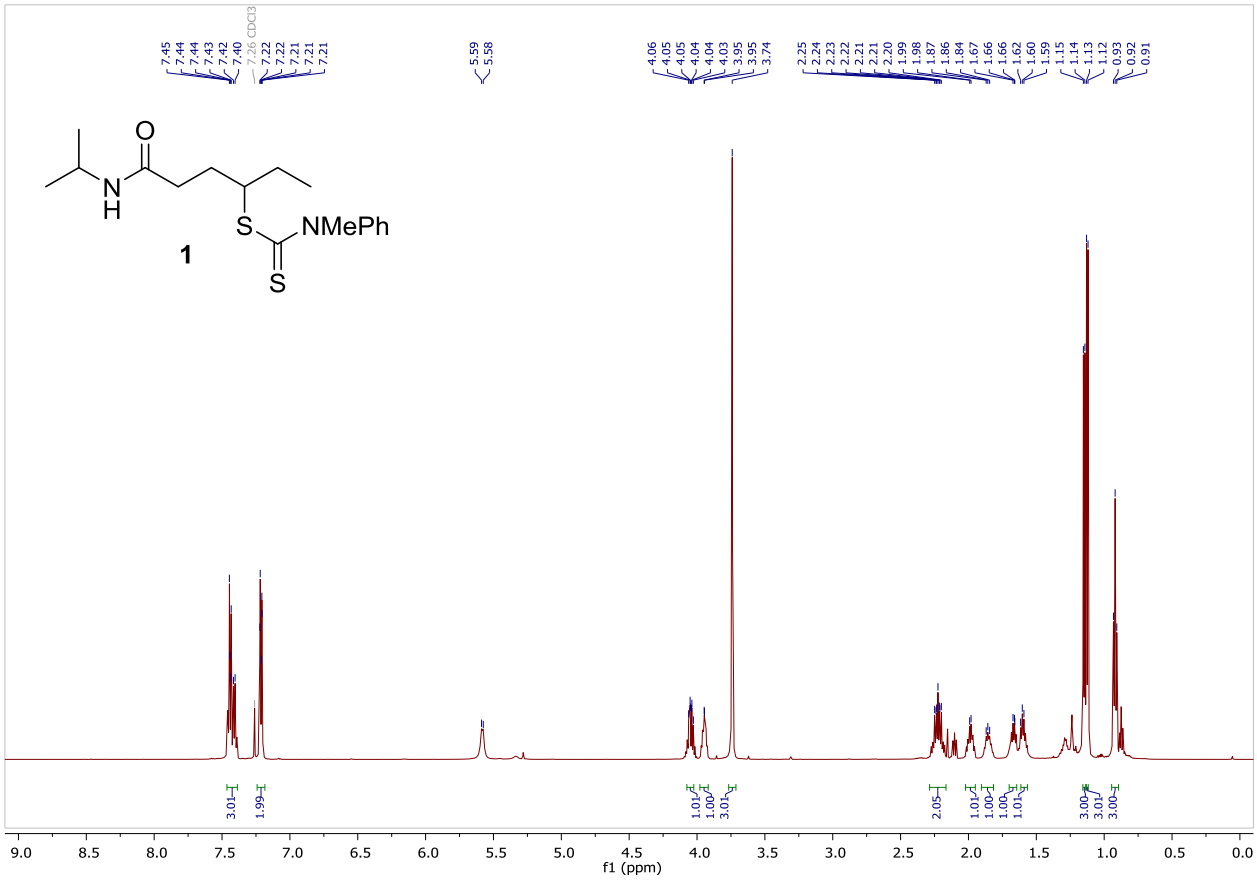


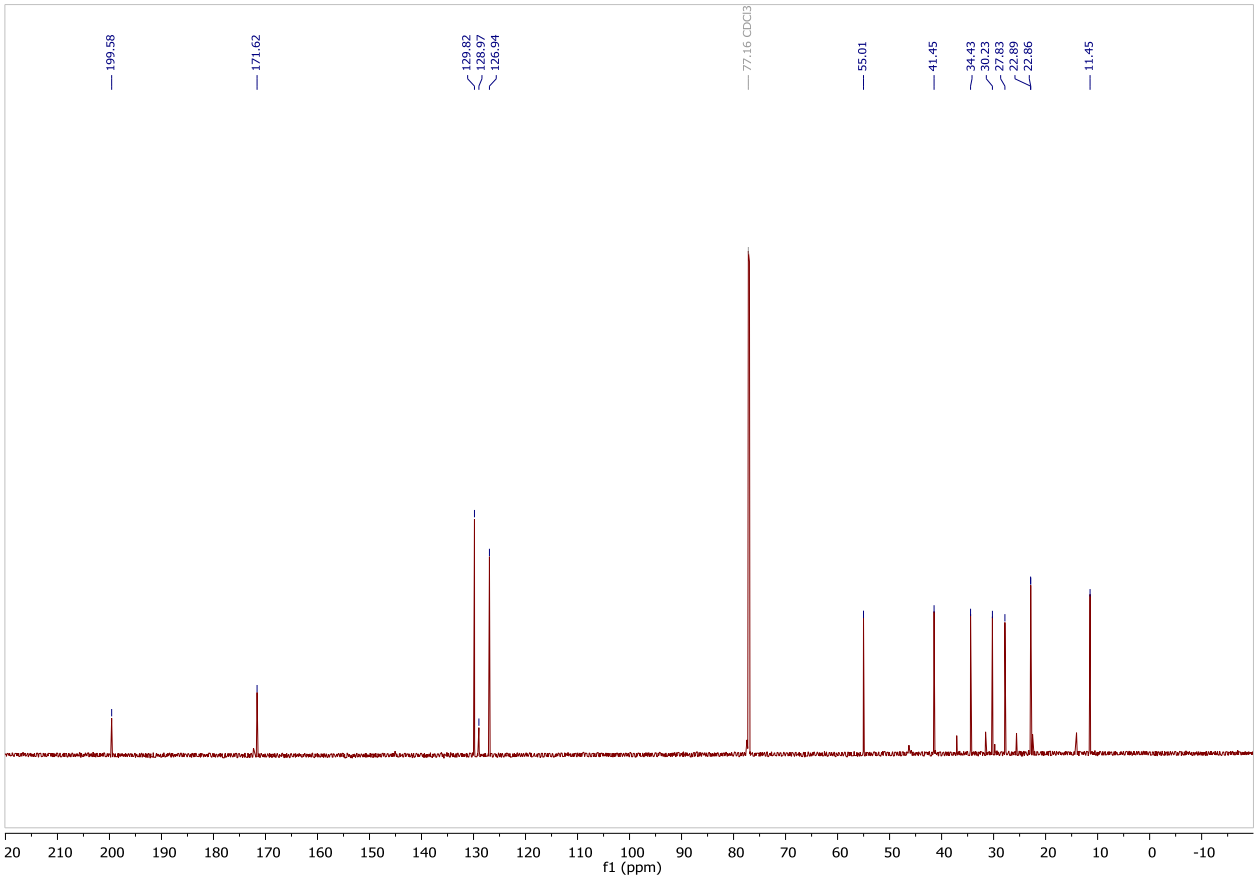
S31

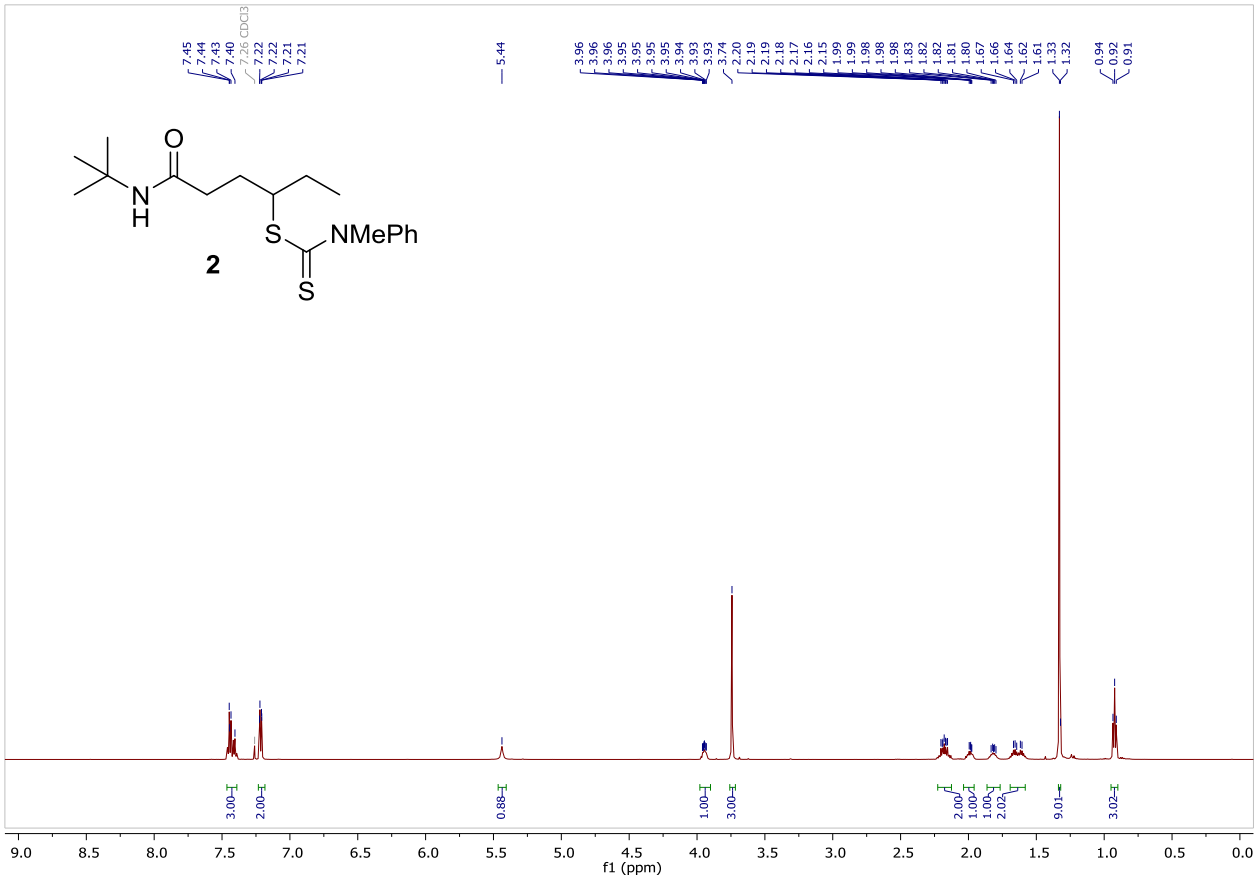



7.51
7.50
7.50
7.49
7.29
7.28
7.28
7.27
7.27
7.26 CDCl3
5.39
5.38
5.38
5.37
5.37
5.37
5.36
5.35
5.35
5.34
5.34
5.34
5.33
5.33
5.32
5.32
5.32
3.76
2.78
2.77
2.77
2.76
2.52
2.51
2.51
2.50
2.46
2.45
2.45
2.44
2.06
2.05
2.04
1.54
1.53
1.45
1.36
1.34
1.34
1.30
1.30
1.29
1.29
1.29
1.28
1.28
1.28
0.90
0.89
O
N
t-Bu
S
NMePh
S
S32
2.82
2.75
4.28
2.82
2.07
1.00
1.15
4.18
1.55
8.49
15.33
3.28
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


201.83
178.95
130.35
130.33
130.15
129.89
128.09
126.84
77.16 CDCl3
63.58
46.68
36.61
31.67
29.96
29.85
29.66
29.50
29.37
29.33
27.41
27.36
25.79
25.67
22.73
14.24
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.45
7.44
7.44
7.43
7.42
7.40
7.26 CDCl3
7.22
7.22
7.21
7.21
7.21
5.59
5.58
4.06
4.05
4.05
4.04
4.04
4.03
3.95
3.95
3.74
2.25
2.24
2.23
2.22
2.21
2.21
2.20
1.99
1.98
1.87
1.86
1.84
1.67
1.66
1.66
1.62
1.60
1.59
1.15
1.14
1.13
1.12
0.93
0.92
0.91
O
N
H
S
NMePh
S
1
3.01
1.99
1.01
1.00
3.01
2.05
1.01
1.00
1.00
1.01
3.00
3.01
3.00
f1 (ppm)


199.58
171.62
129.82
128.97
126.94
77.16 CDCl3
55.01
41.45
34.43
30.23
27.83
22.89
22.86
11.45
f1 (ppm)


7.45
7.44
7.43
7.40
7.26 CDCl3
7.22
7.22
7.21
7.21
5.44
3.96
3.96
3.96
3.95
3.95
3.95
3.95
3.94
3.93
3.93
3.74
2.20
2.19
2.19
2.18
2.17
2.16
2.15
1.99
1.99
1.98
1.98
1.98
1.83
1.82
1.82
1.81
1.80
1.67
1.66
1.64
1.62
1.61
1.33
1.32
0.94
0.92
0.91
O
N
H
S
NMePh
S
2
3.00
2.00
0.88
1.00
3.00
2.00
1.00
1.00
2.02
9.01
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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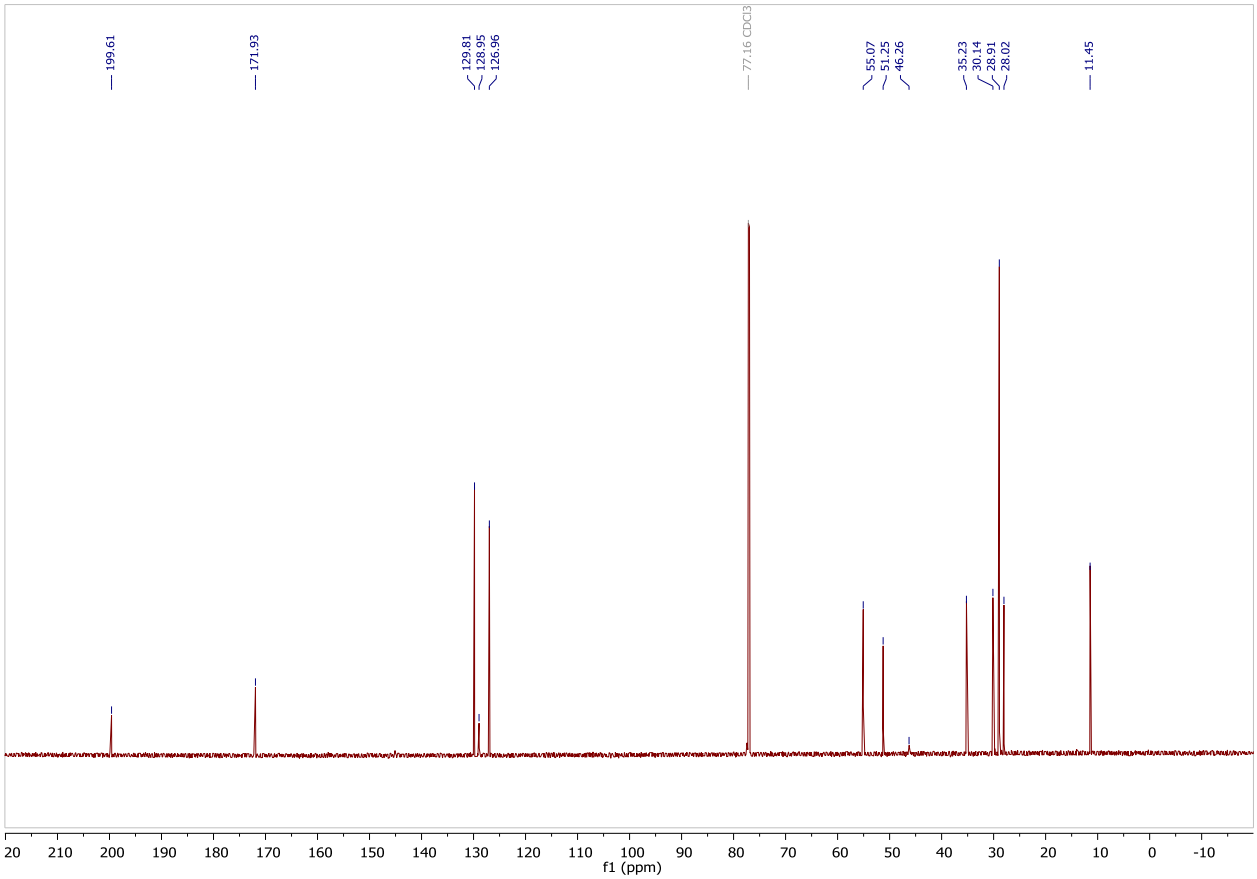
f1 (ppm)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126.96
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46.26
35.23
30.14
28.91
28.02
11.45
20
210
200
190
180
170
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30
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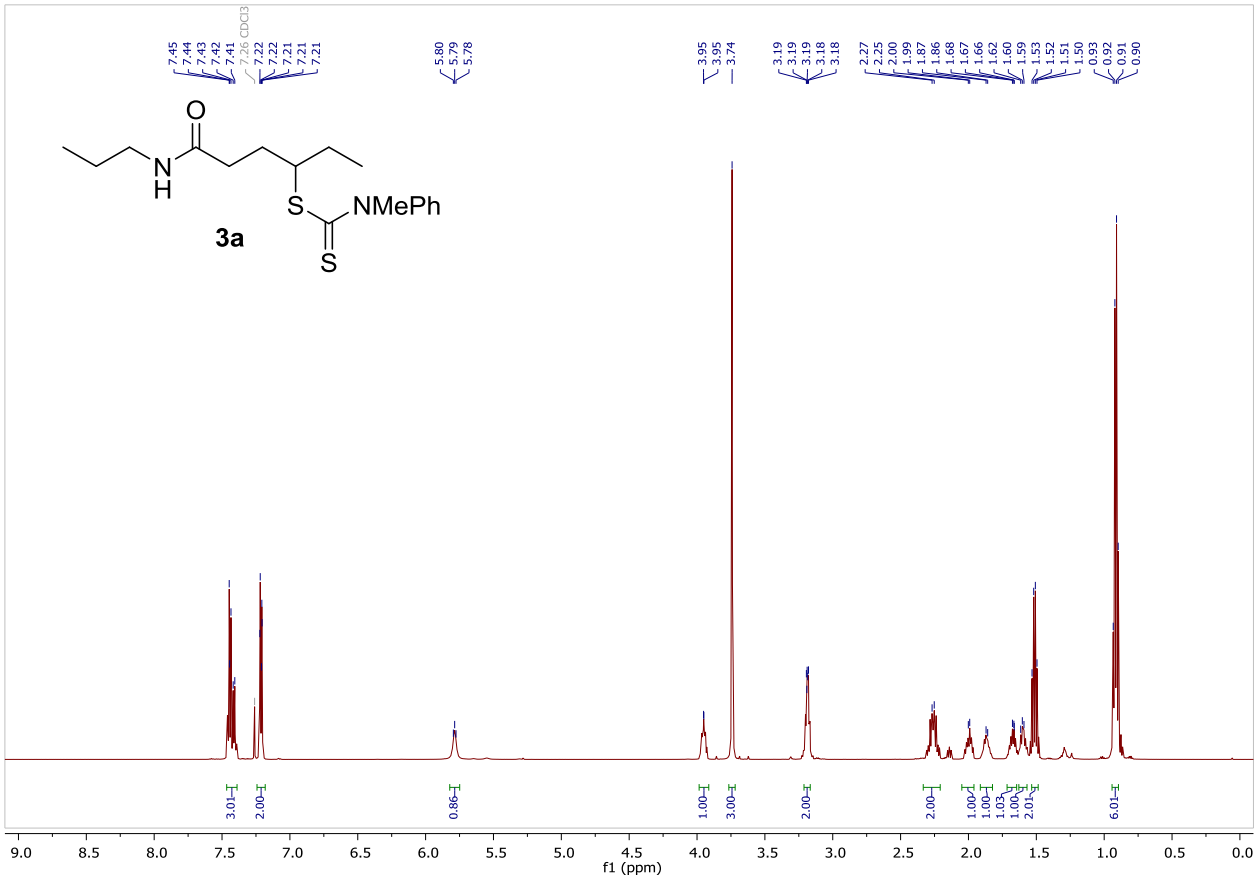
-10
f1 (ppm)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5.79
5.78
3.95
3.95
3.74
3.19
3.19
3.19
3.18
3.18
2.27
2.25
2.00
1.99
1.87
1.86
1.68
1.67
1.66
1.62
1.60
1.59
1.53
1.52
1.51
1.50
0.93
0.92
0.91
0.90
O
N
H
S
NMePh
S
3a
3.01
2.00
0.86
1.00
3.00
2.00
2.00
1.00
1.00
1.03
1.00
2.01
6.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
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1.0
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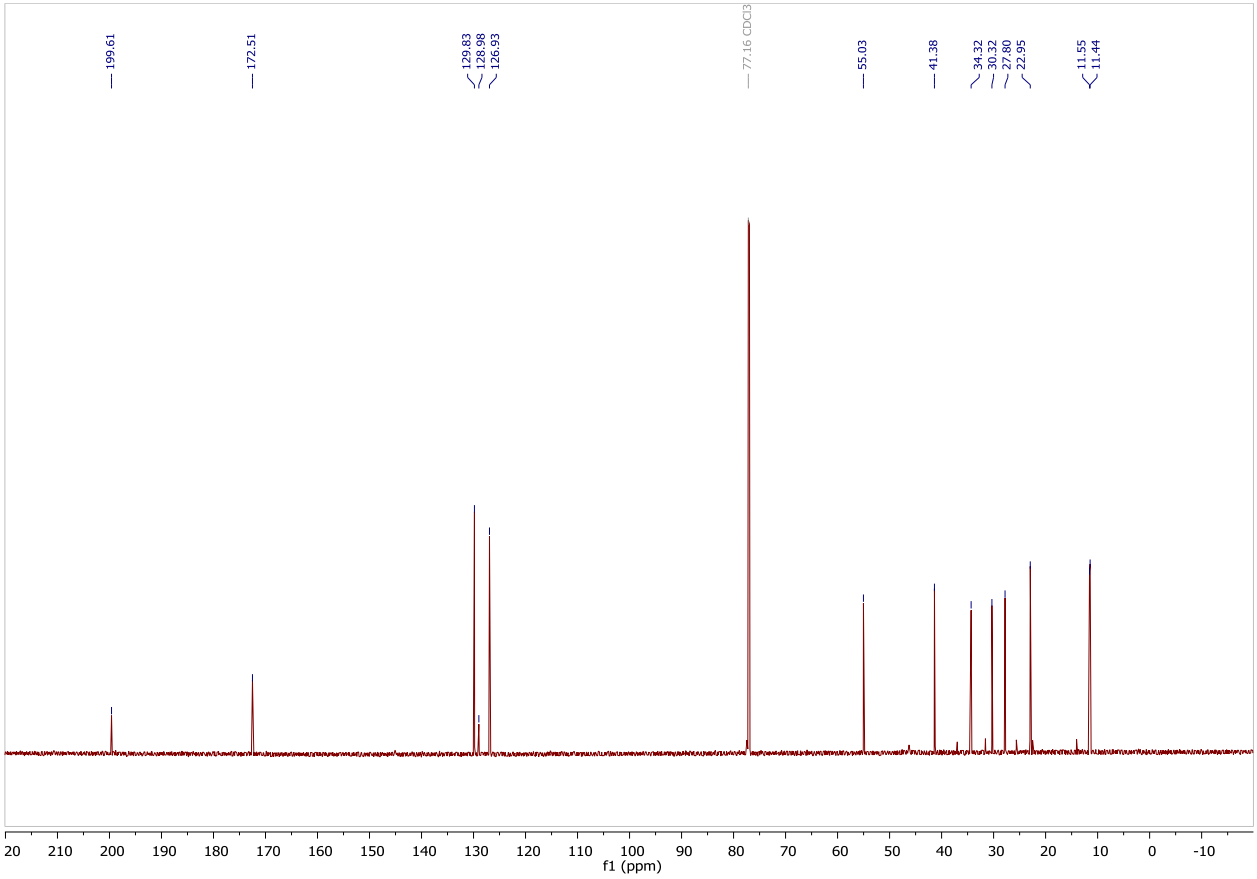
0.0
f1 (ppm)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30.32
27.80
22.95
11.55
11.44
20
210
200
190
180
170
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140
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120
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100
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80
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30
20
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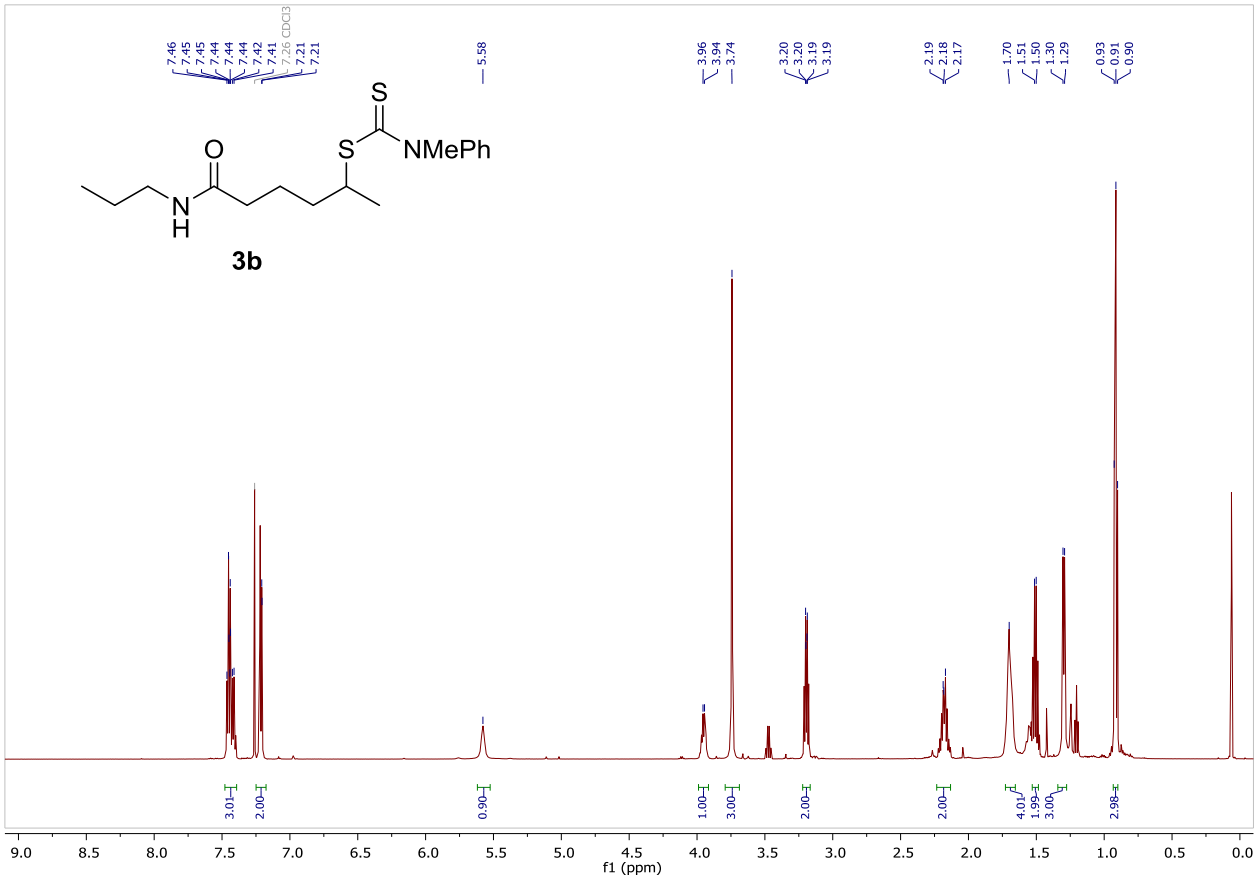
-10
f1 (ppm)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7.44
7.42
7.41
7.26 CDCl3
7.21
7.21
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3.96
3.94
3.74
3.20
3.20
3.19
3.19
2.19
2.18
2.17
1.70
1.51
1.50
1.30
1.29
0.93
0.91
0.90
S
S
NMePh
O
N
H
3b
3.01
2.00
0.90
1.00
3.00
2.00
2.00
4.01
1.99
3.00
2.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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1.0
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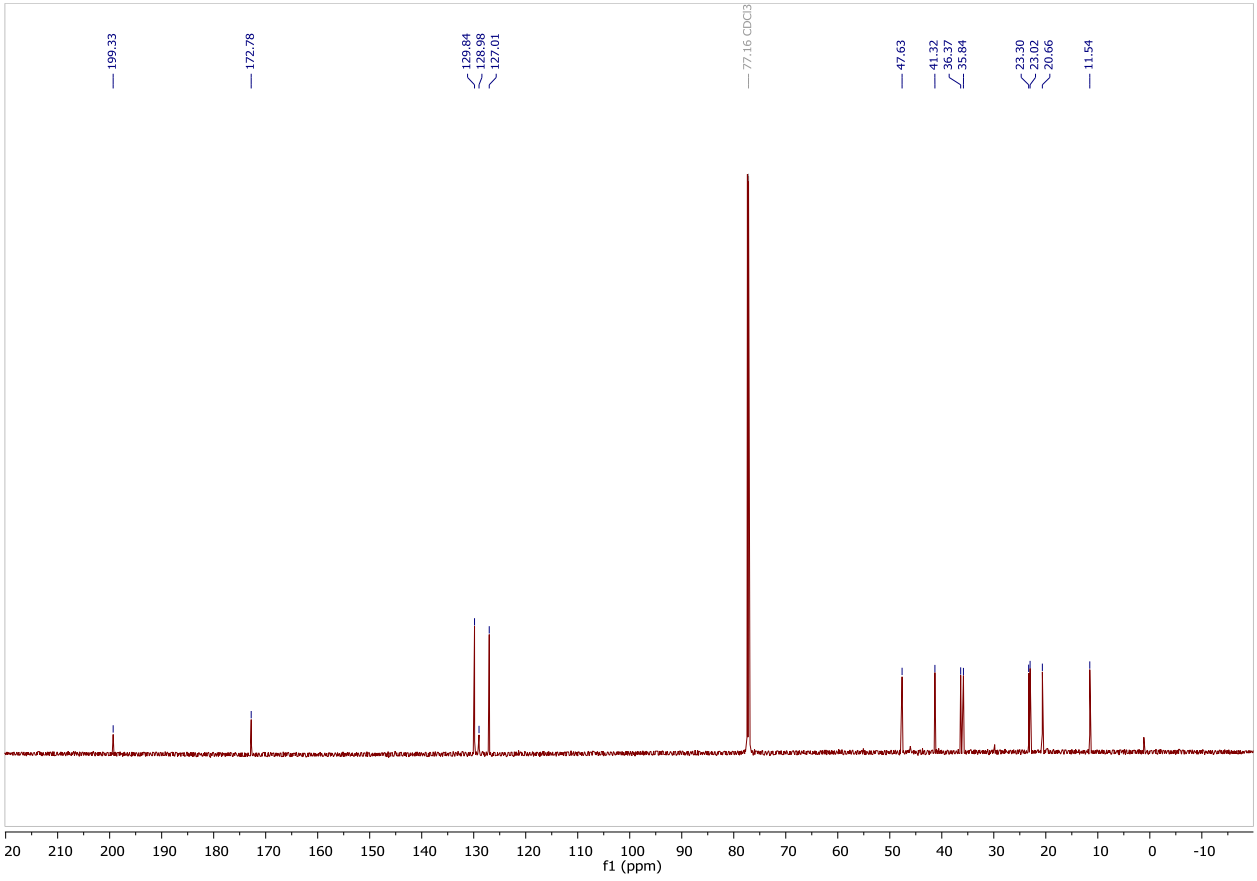
0.0
f1 (ppm)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127.01
77.16 CDCl3
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35.84
23.30
23.02
20.66
11.54
20
210
200
190
180
170
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120
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100
90
80
70
60
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40
30
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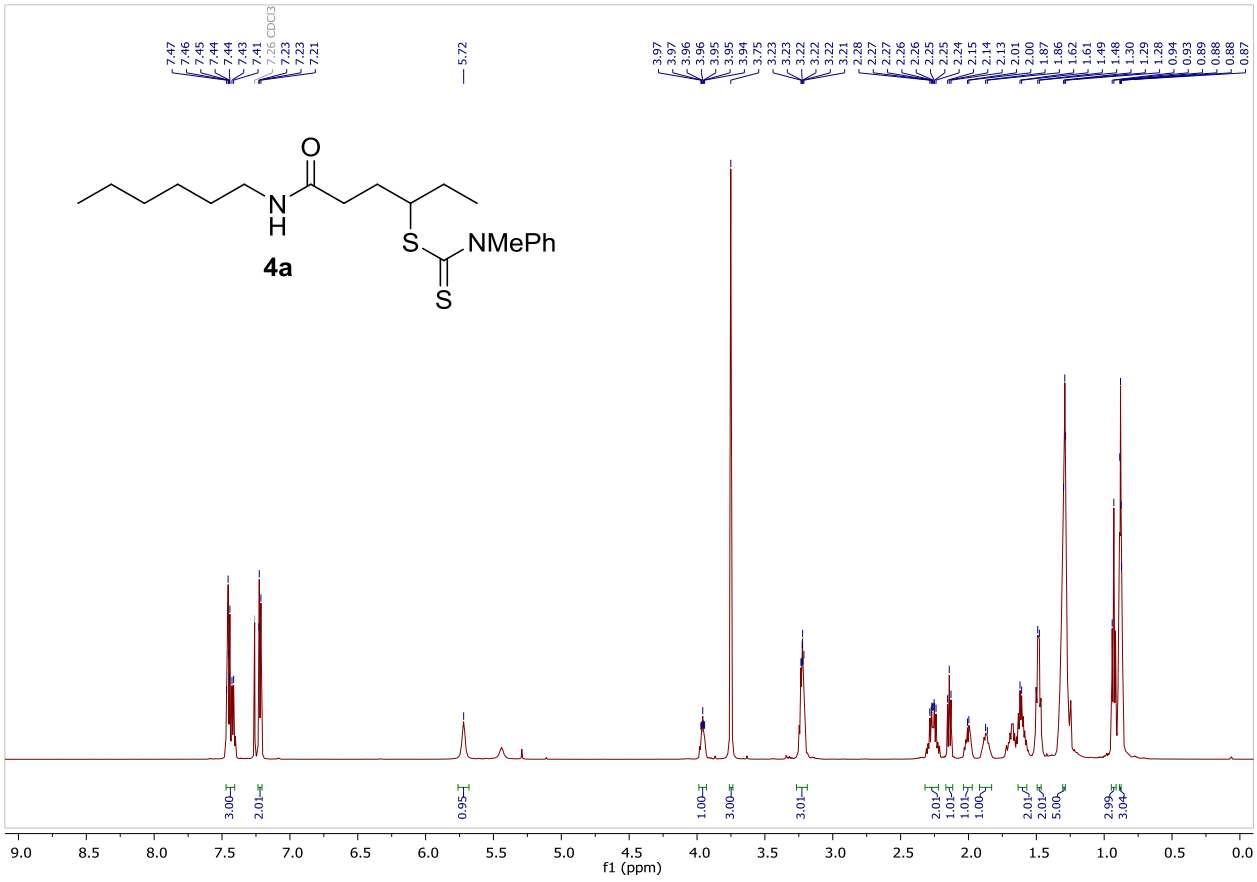
-10
f1 (ppm)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7.23
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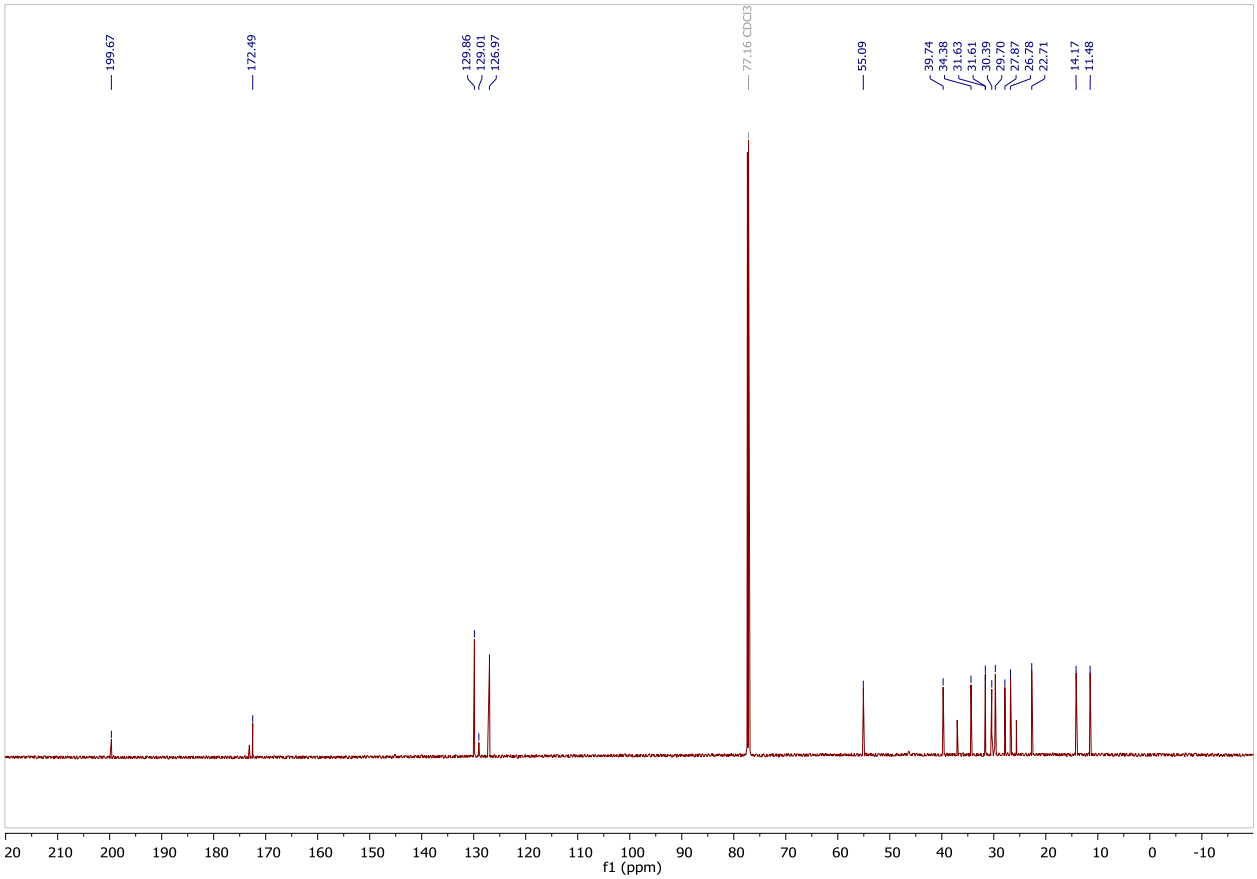
3.97
3.96
3.96
3.95
3.95
3.94
3.75
3.23
3.23
3.22
3.22
3.22
3.21
2.28
2.27
2.27
2.26
2.26
2.25
2.25
2.24
2.15
2.14
2.13
2.01
2.00
1.87
1.86
1.62
1.61
1.49
1.48
1.30
1.29
1.28
0.94
0.93
0.89
0.88
0.88
0.87
O
N
H
S
NMePh
S
4a
3.00
2.01
0.95
1.00
3.00
3.01
2.01
1.01
1.01
1.00
2.01
2.01
5.00
2.99
3.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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77.16 CDCl3
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34.38
31.63
31.61
30.39
29.70
27.87
26.78
22.71
14.17
11.48
20
210
200
190
180
170
160
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140
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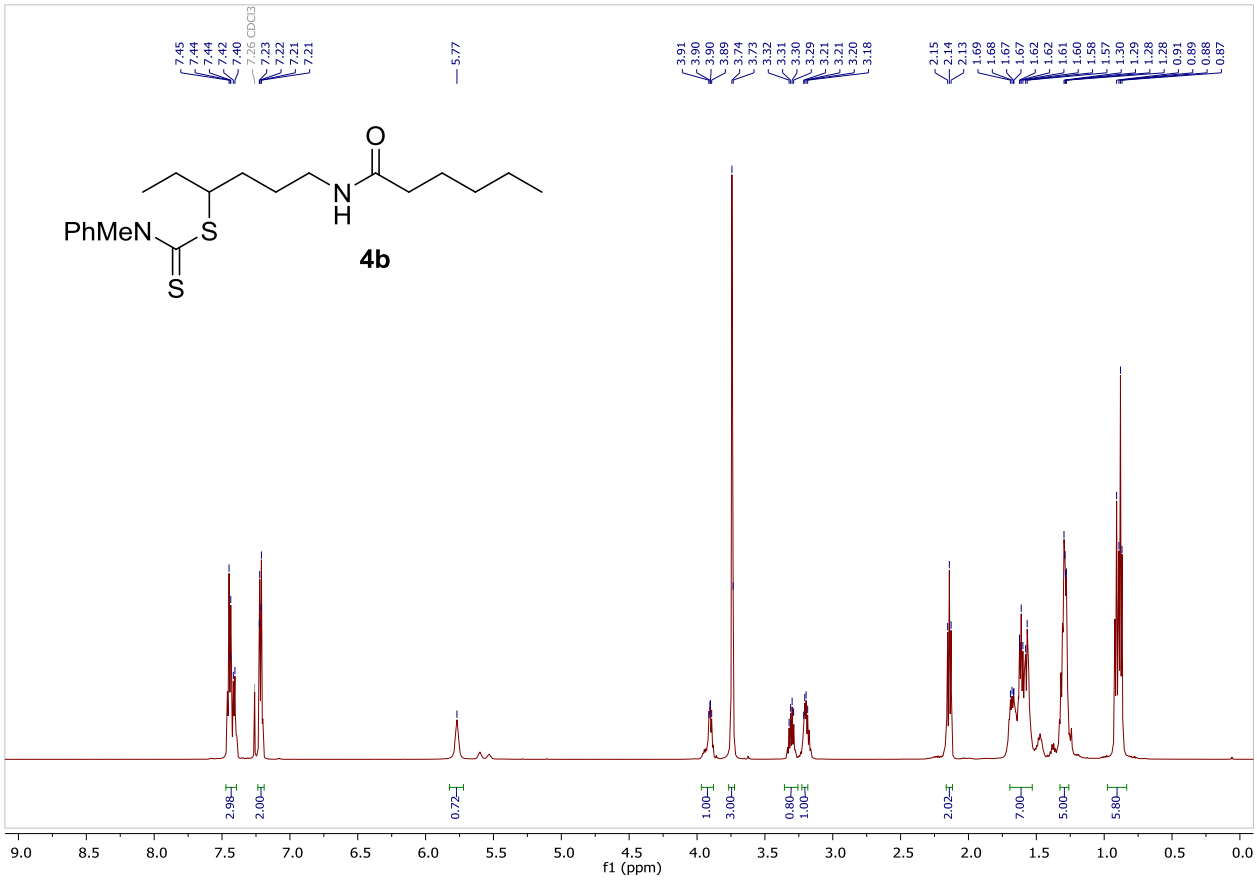
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.44
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7.40
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7.23
7.22
7.21
7.21
5.77
3.91
3.90
3.90
3.89
3.74
3.73
3.32
3.31
3.30
3.29
3.21
3.21
3.20
3.18
2.15
2.14
2.13
1.69
1.68
1.67
1.67
1.62
1.62
1.61
1.60
1.58
1.57
1.30
1.29
1.28
1.28
0.91
0.89
0.88
0.87
O
N
H
S
PhMeN
S
4b
2.98
2.00
0.72
1.00
3.00
0.80
1.00
2.02
7.00
5.00
5.80
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.0
1.5
1.0
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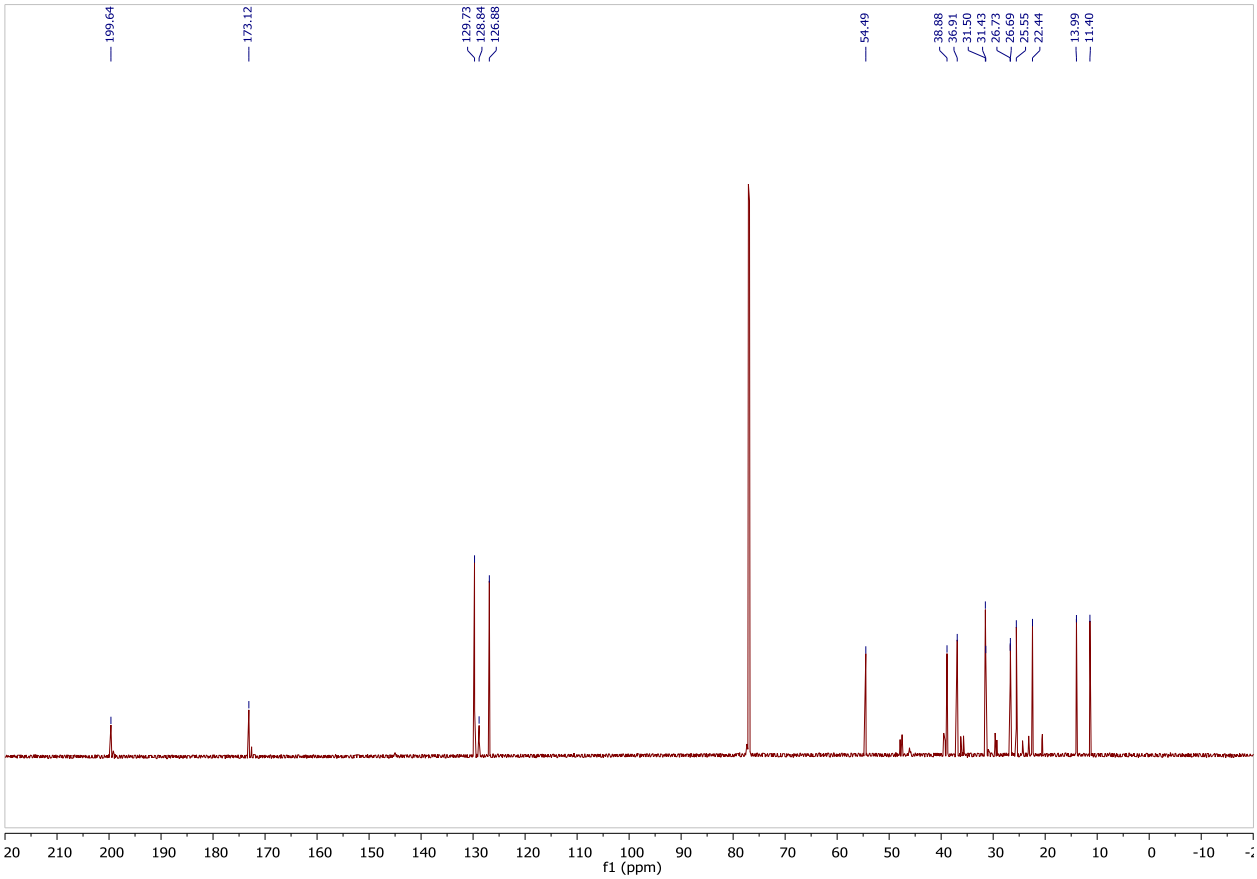
0.0
f1 (ppm)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126.88
54.49
38.88
36.91
31.50
31.43
26.73
26.69
25.55
22.44
13.99
11.40
20
210
200
190
180
170
160
150
140
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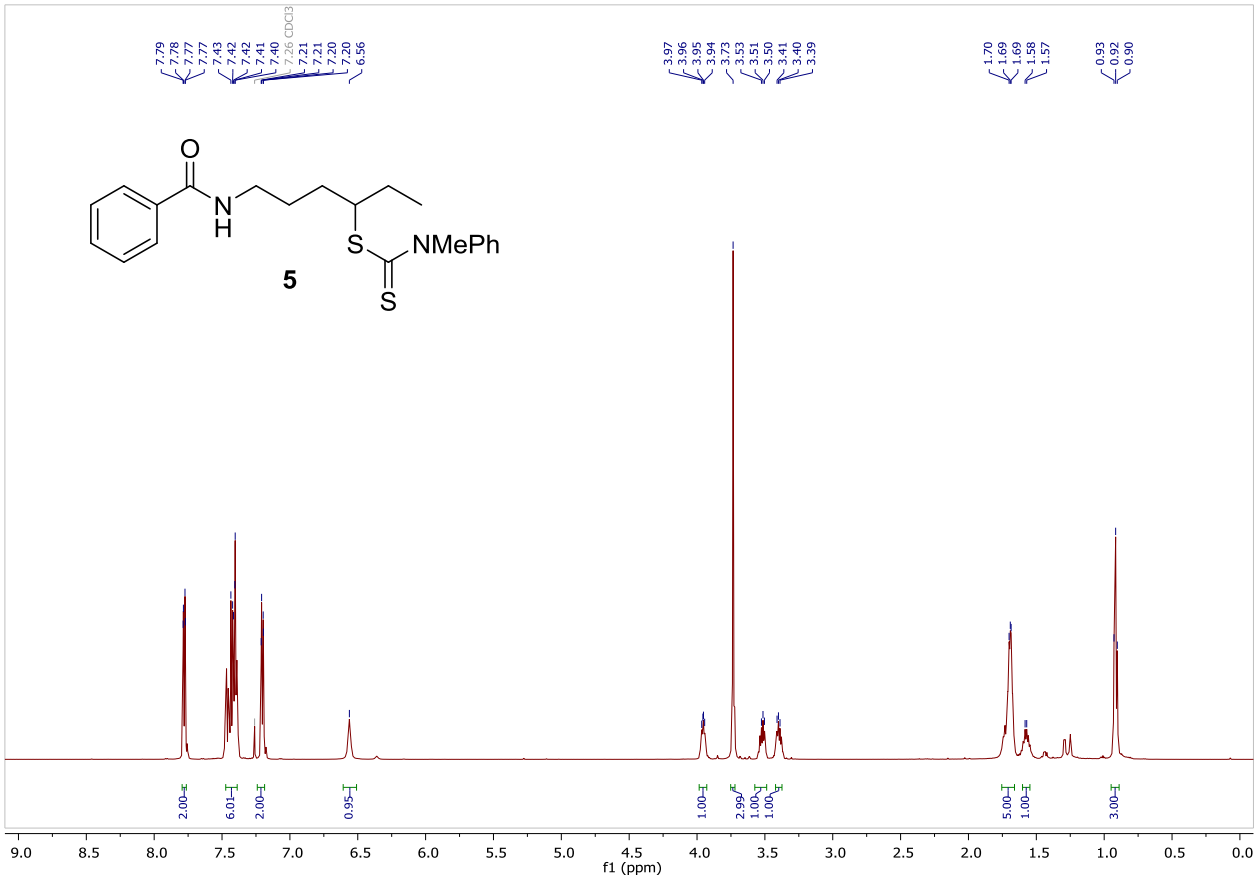
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.77
7.77
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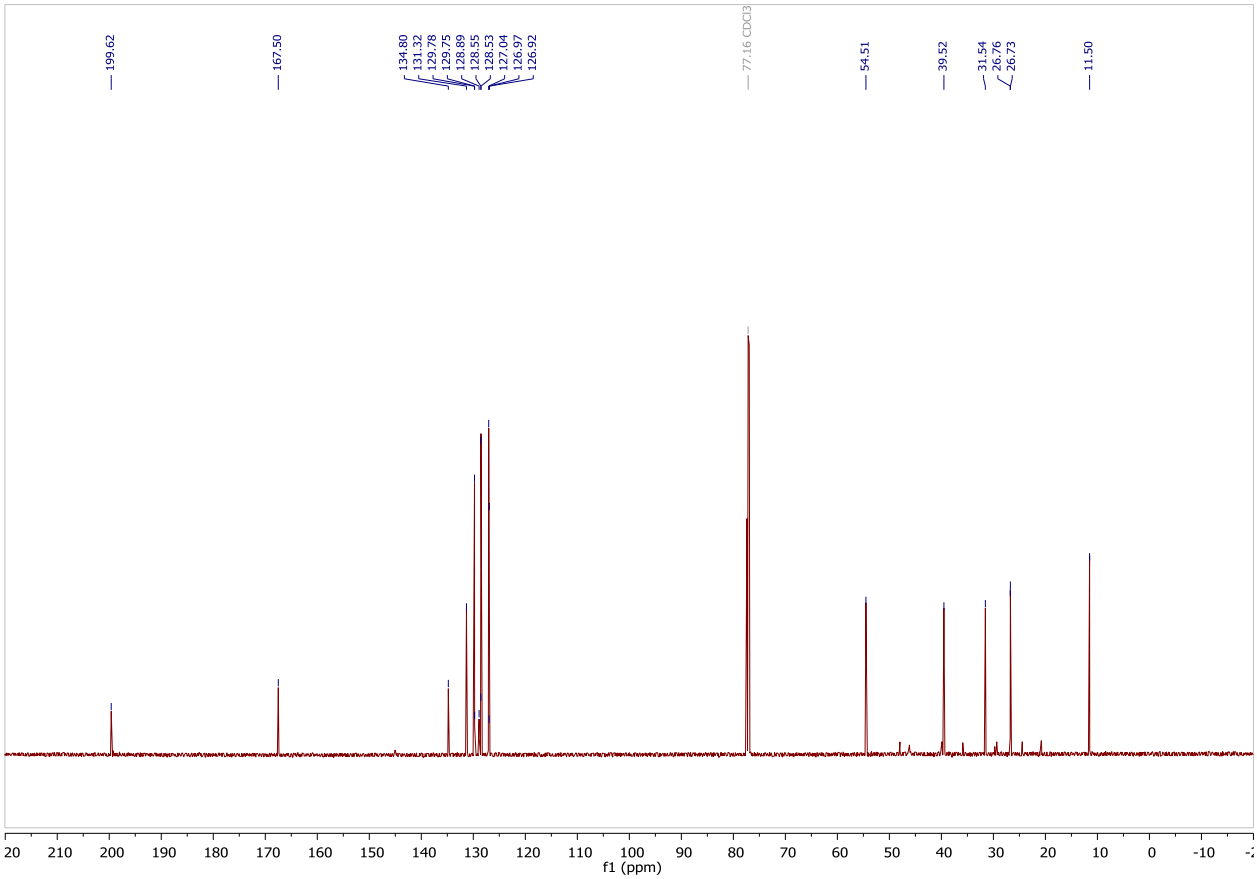
7.42
7.42
7.41
7.40
7.26 CDCl3
7.21
7.21
7.20
7.20
6.56
3.97
3.96
3.95
3.94
3.73
3.53
3.51
3.50
3.41
3.40
3.39
1.70
1.69
1.69
1.58
1.57
0.93
0.92
0.90
O
N
H
S
NMePh
S
5
2.00
6.01
2.00
0.95
1.00
2.99
1.00
1.00
5.00
1.00
3.00
f1 (ppm)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129.75
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128.55
128.53
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54.51
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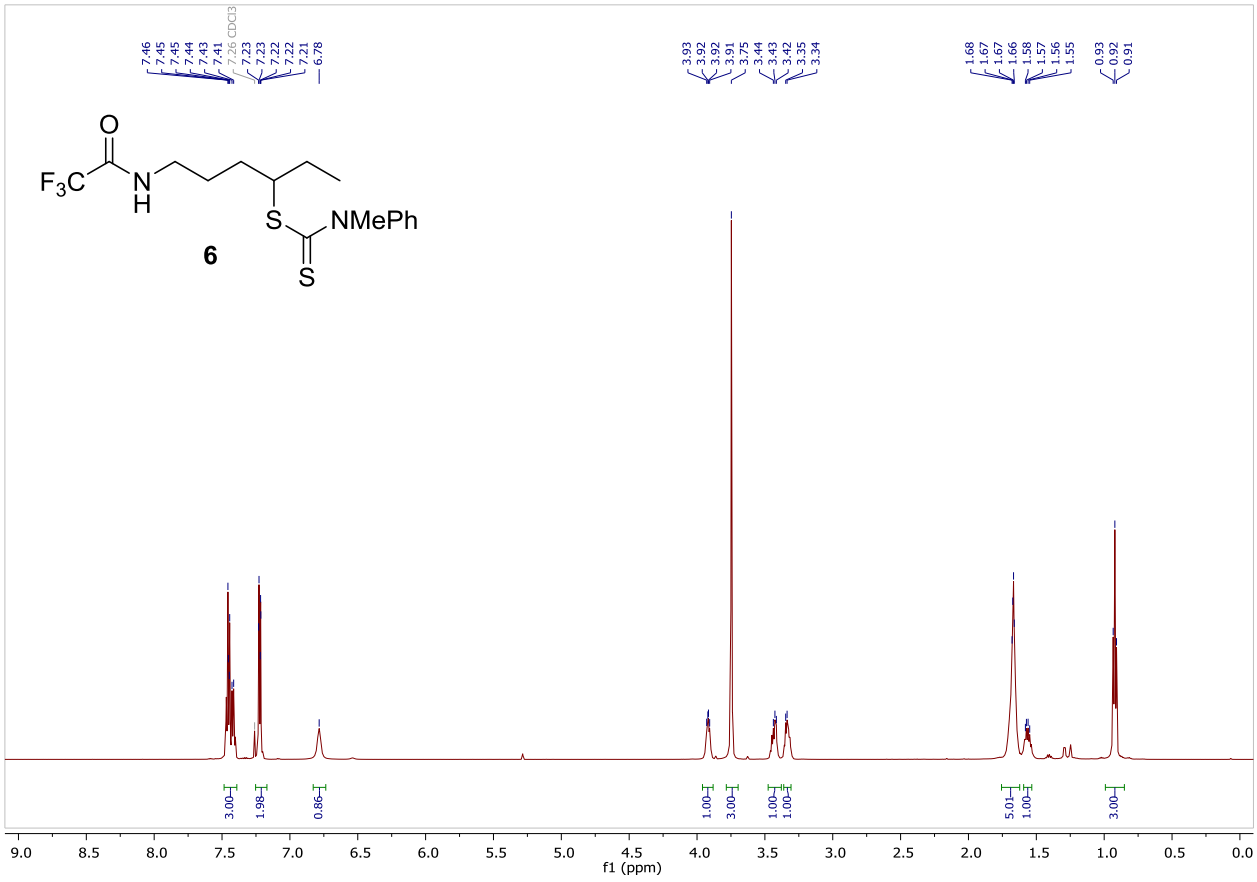
31.54
26.76
26.73
11.50
f1 (ppm)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7.45
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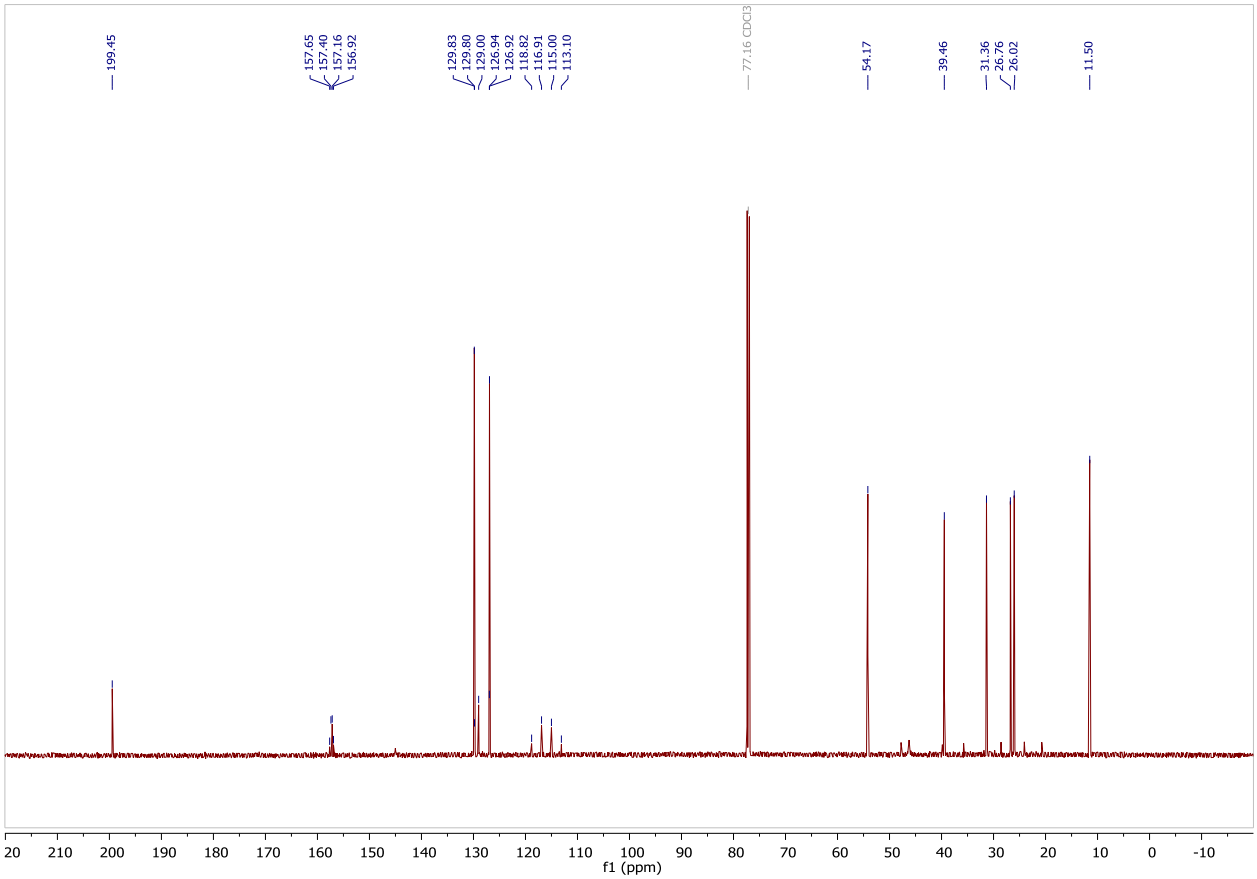
7.43
7.41
7.26 CDCl3
7.23
7.23
7.22
7.22
7.21
6.78
3.93
3.92
3.92
3.91
3.75
3.44
3.43
3.42
3.35
3.34
1.68
1.67
1.67
1.66
1.58
1.57
1.56
1.55
0.93
0.92
0.91
O
F3C
N
H
S
NMePh
S
6
3.00
1.98
0.86
1.00
3.00
1.00
1.00
5.01
1.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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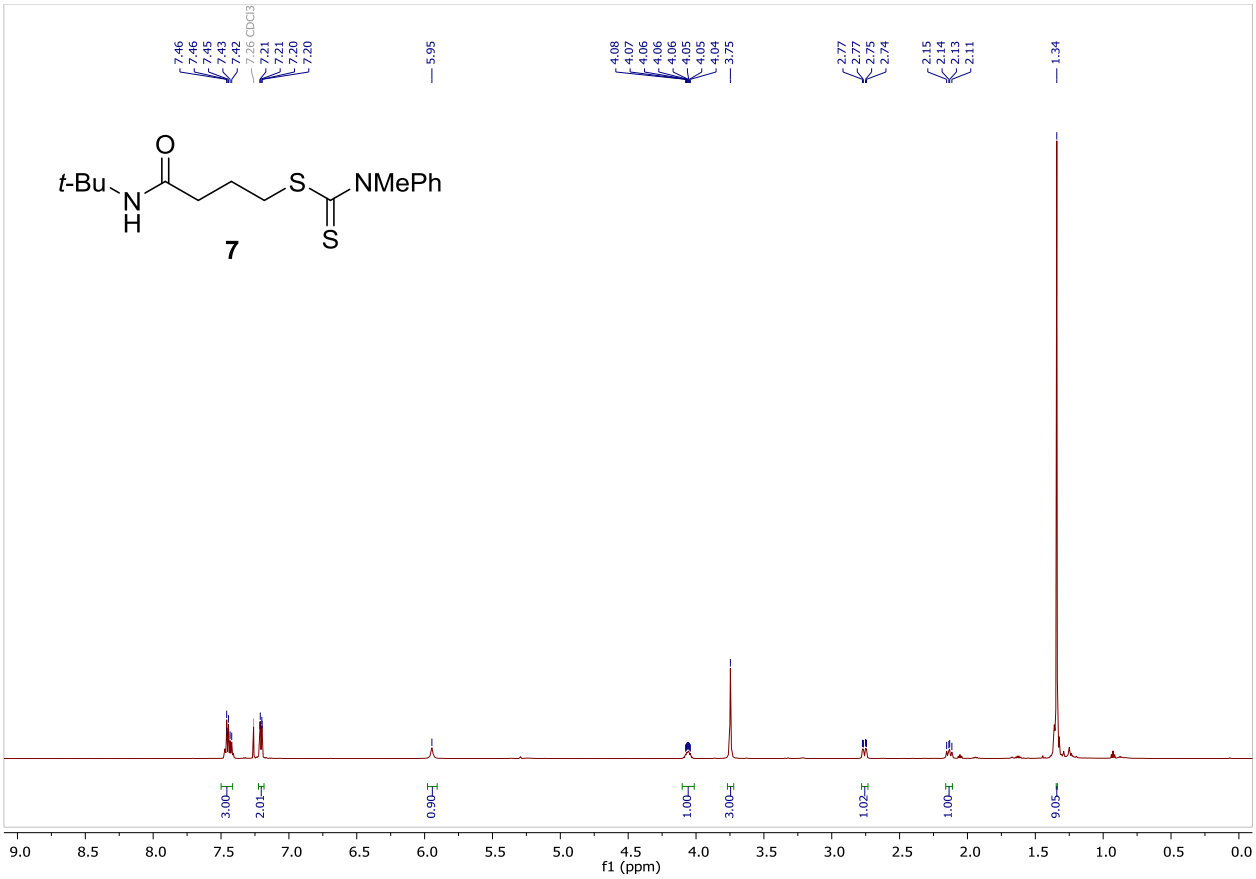
129.80
129.00
126.94
126.92
118.82
116.91
115.00
113.10
77.16 CDCl3
54.17
39.46
31.36
26.76
26.02
11.50
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.43
7.42
7.26 CDCl3
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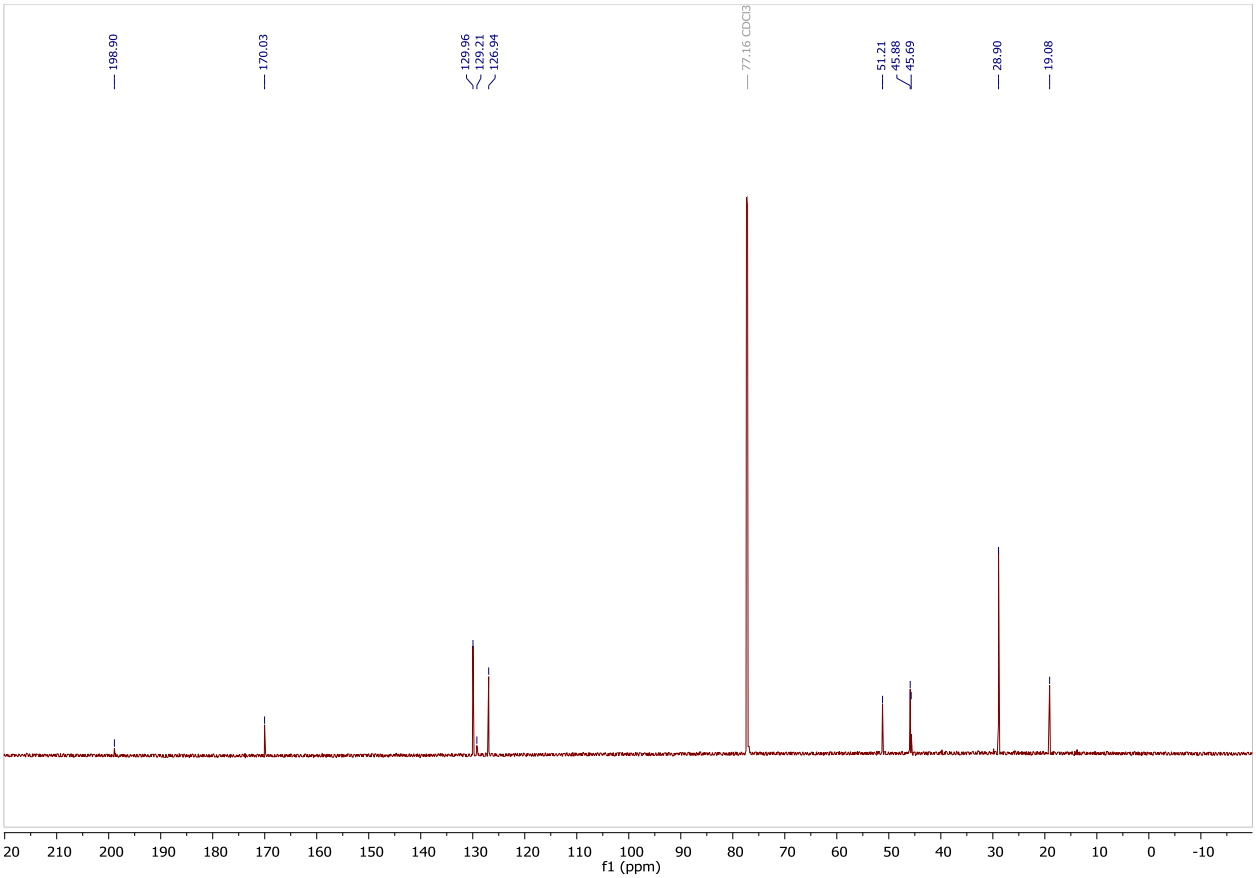
7.21
7.20
7.20
5.95
4.08
4.07
4.06
4.06
4.06
4.05
4.05
4.04
3.75
2.77
2.77
2.75
2.74
2.15
2.14
2.13
2.11
1.34
t-Bu
N
H
O
S
S
NMePh
7
3.00
2.01
0.90
1.00
3.00
1.02
1.00
9.05
f1 (ppm)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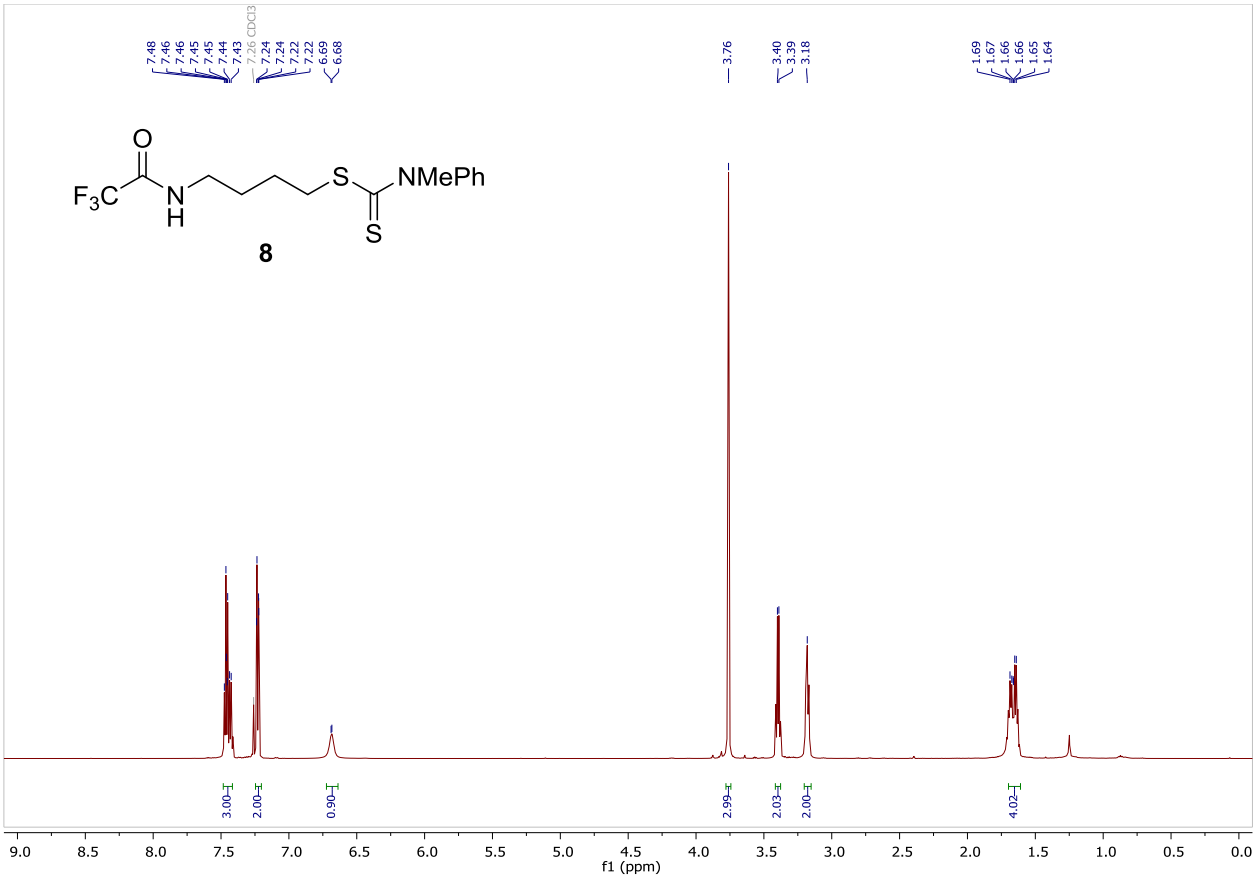
45.69
28.90
19.08
f1 (ppm)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7.45
7.44
7.43
7.26 CDCl3
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7.24
7.22
7.22
6.69
6.68
3.76
3.40
3.39
3.18
1.69
1.67
1.66
1.66
1.65
1.64
O
F3C
N
H
S
NMePh
S
8
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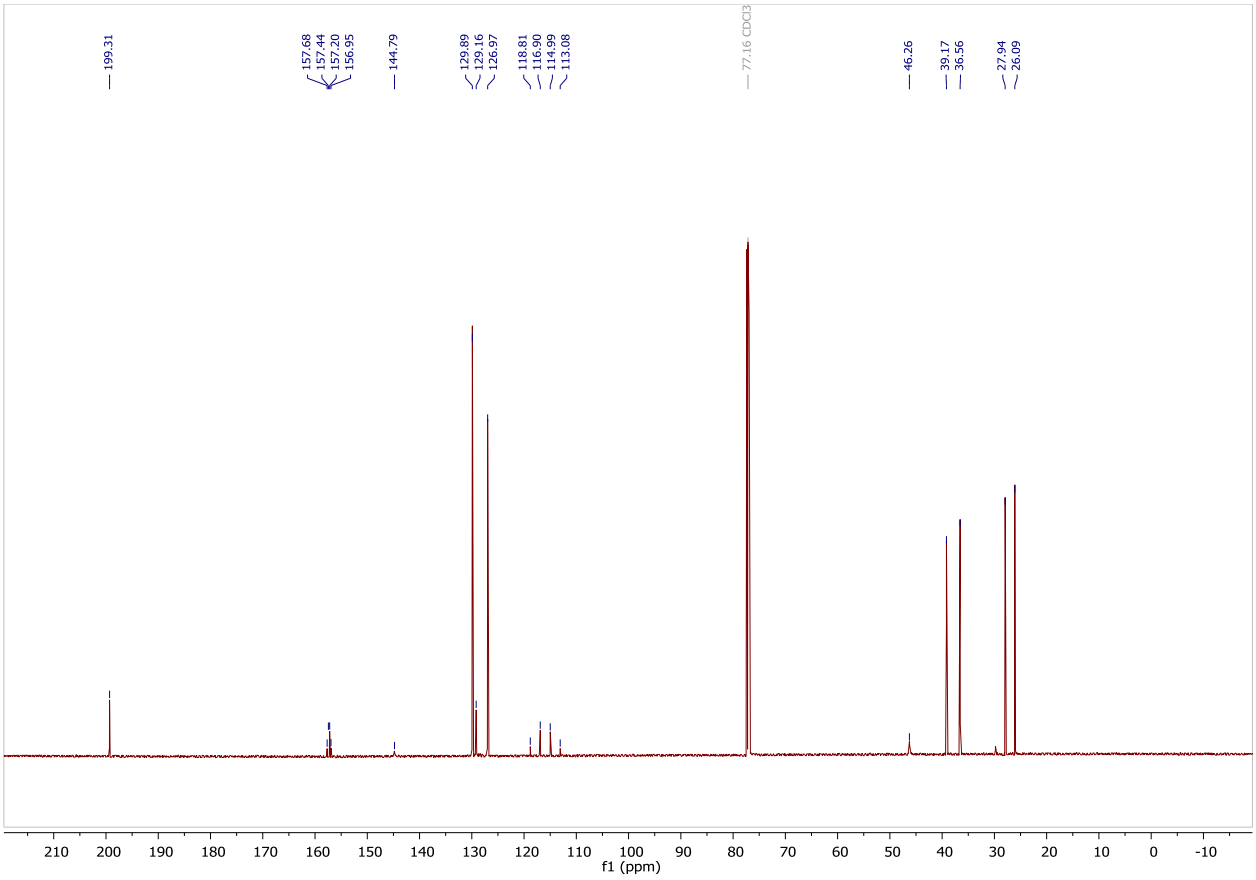
2.00
0.90
2.99
2.03
2.00
4.02
f1 (ppm)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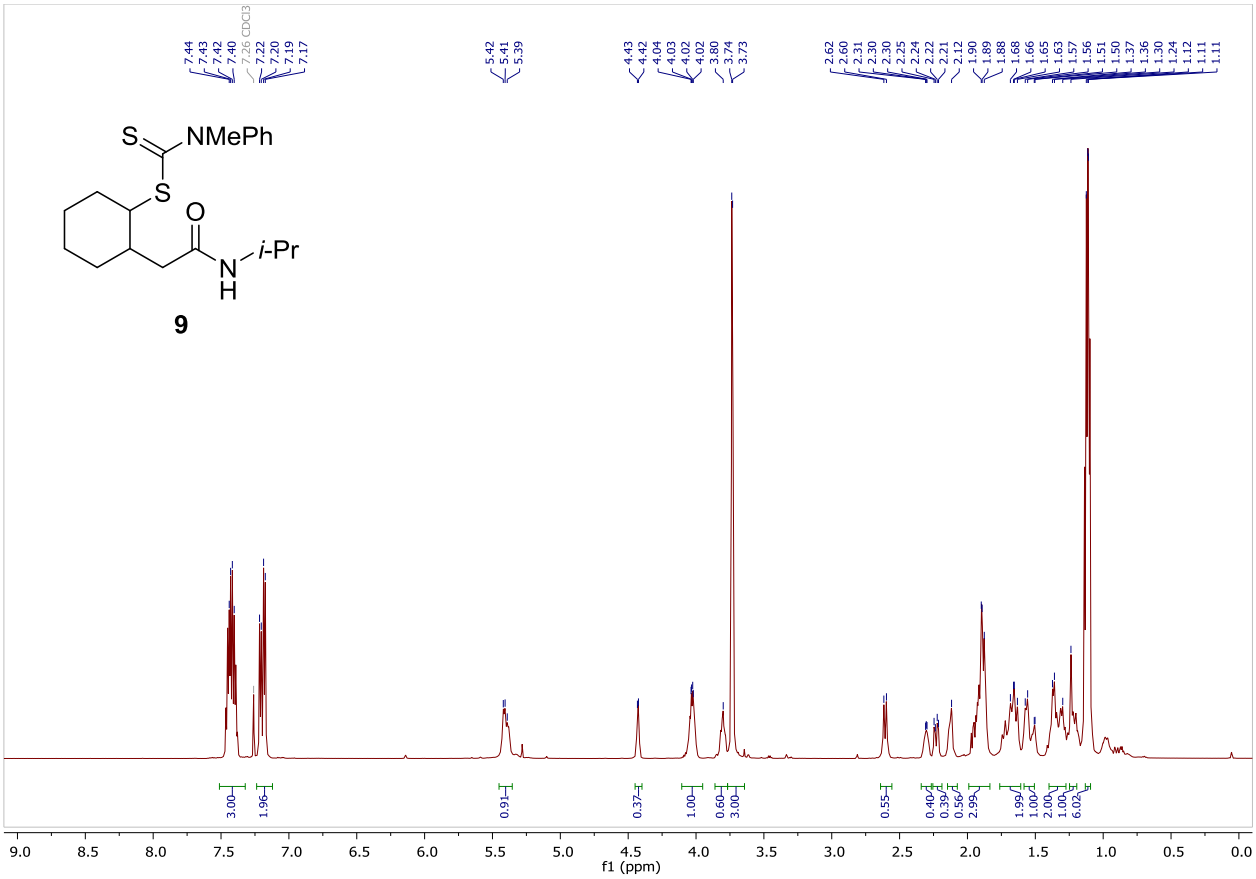
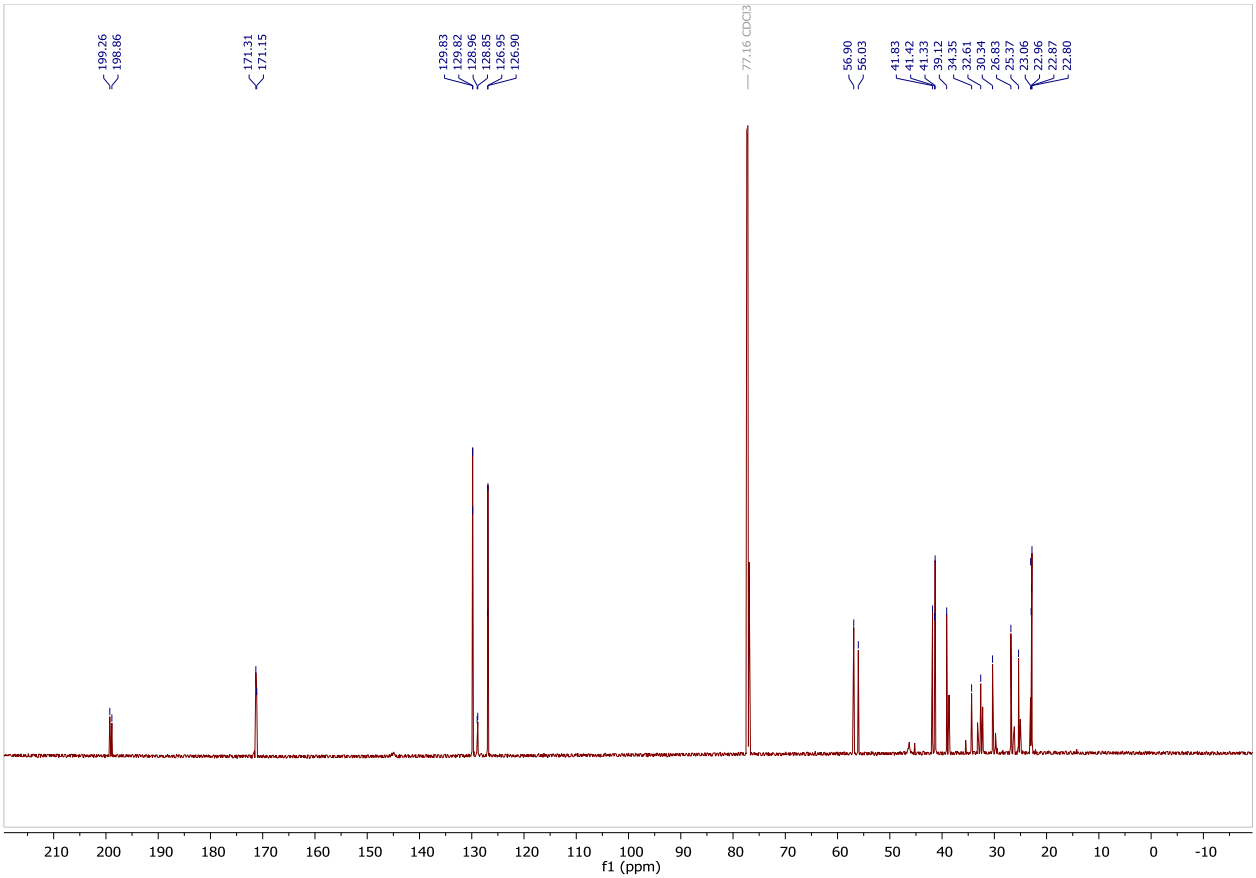
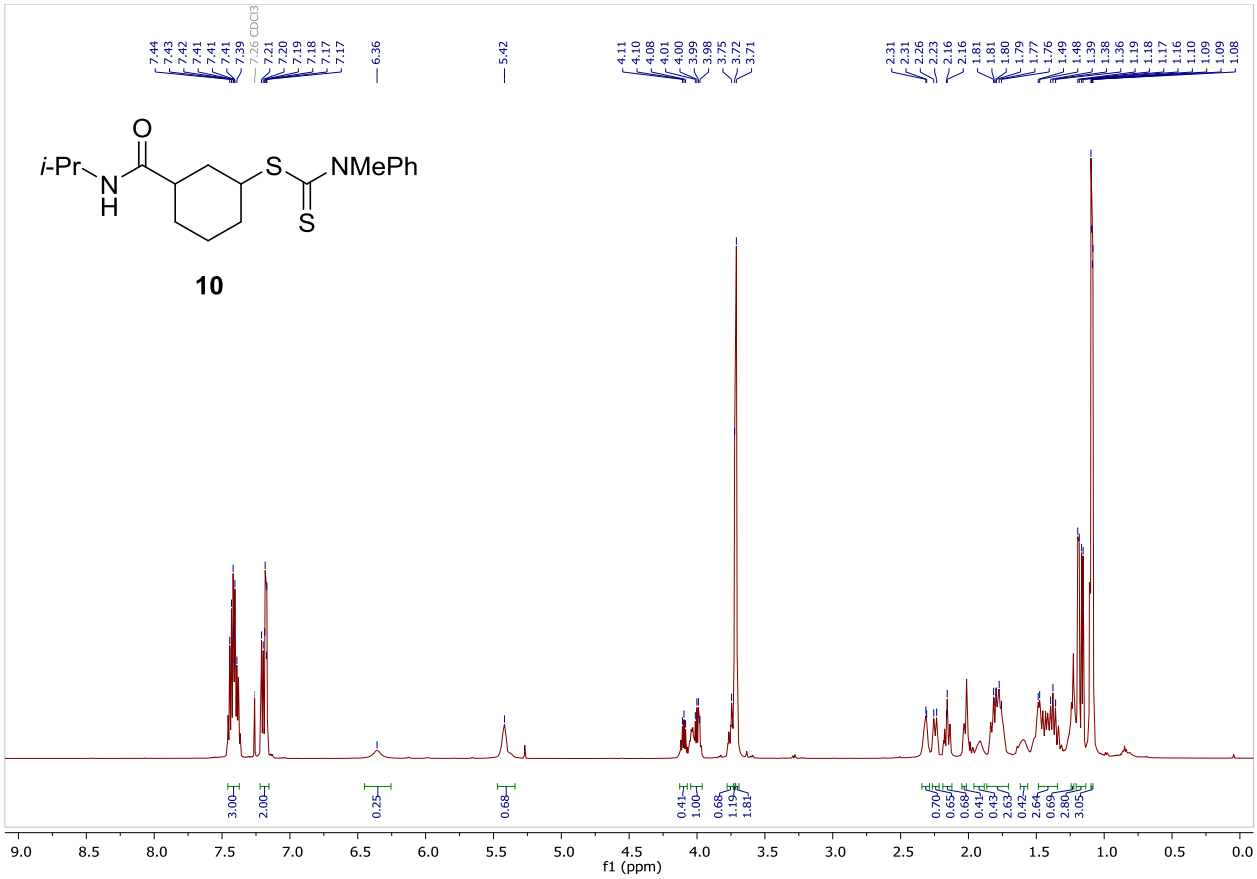
129.89
129.16
126.97
118.81
116.90
114.99
113.08
77.16 CDCl3
46.26
39.17
36.56
27.94
26.09
f1 (ppm)



9

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7.41
7.41
7.39
7.26 CDCl3
7.21
7.20
7.19
7.18
7.17
7.17
6.36
5.42
4.11
4.10
4.08
4.01
4.00
3.99
3.98
3.75
3.72
3.71
2.31
2.31
2.26
2.23
2.16
2.16
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1.81
1.80
1.79
1.77
1.76
1.49
1.48
1.39
1.38
1.36
1.19
1.18
1.17
1.16
1.10
1.09
1.09
1.08
O
i-Pr
N
H
S
NMePh
S
10
3.00
2.00
0.25
0.68
0.41
1.00
0.68
1.19
1.81
0.70
0.65
0.68
0.41
0.43
2.63
0.42
2.64
0.69
2.80
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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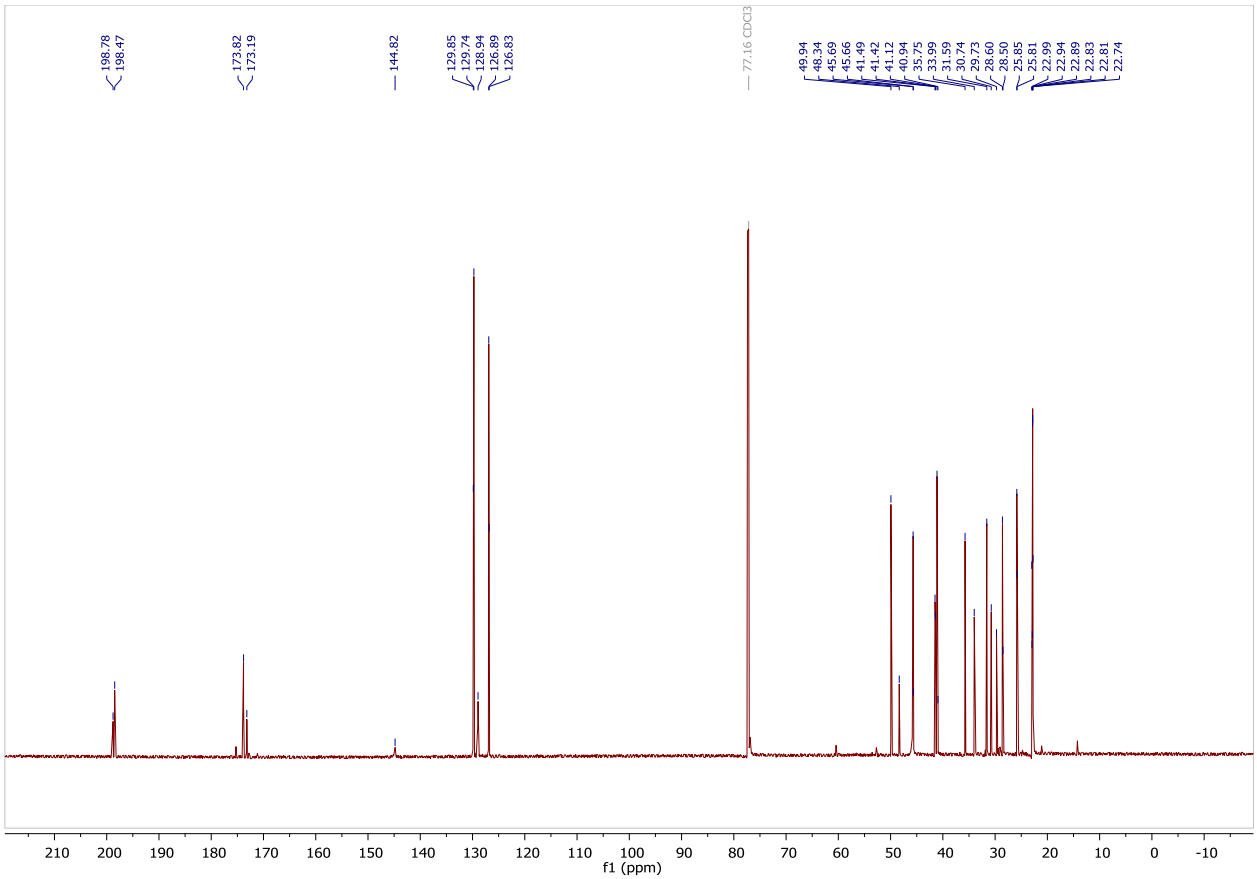
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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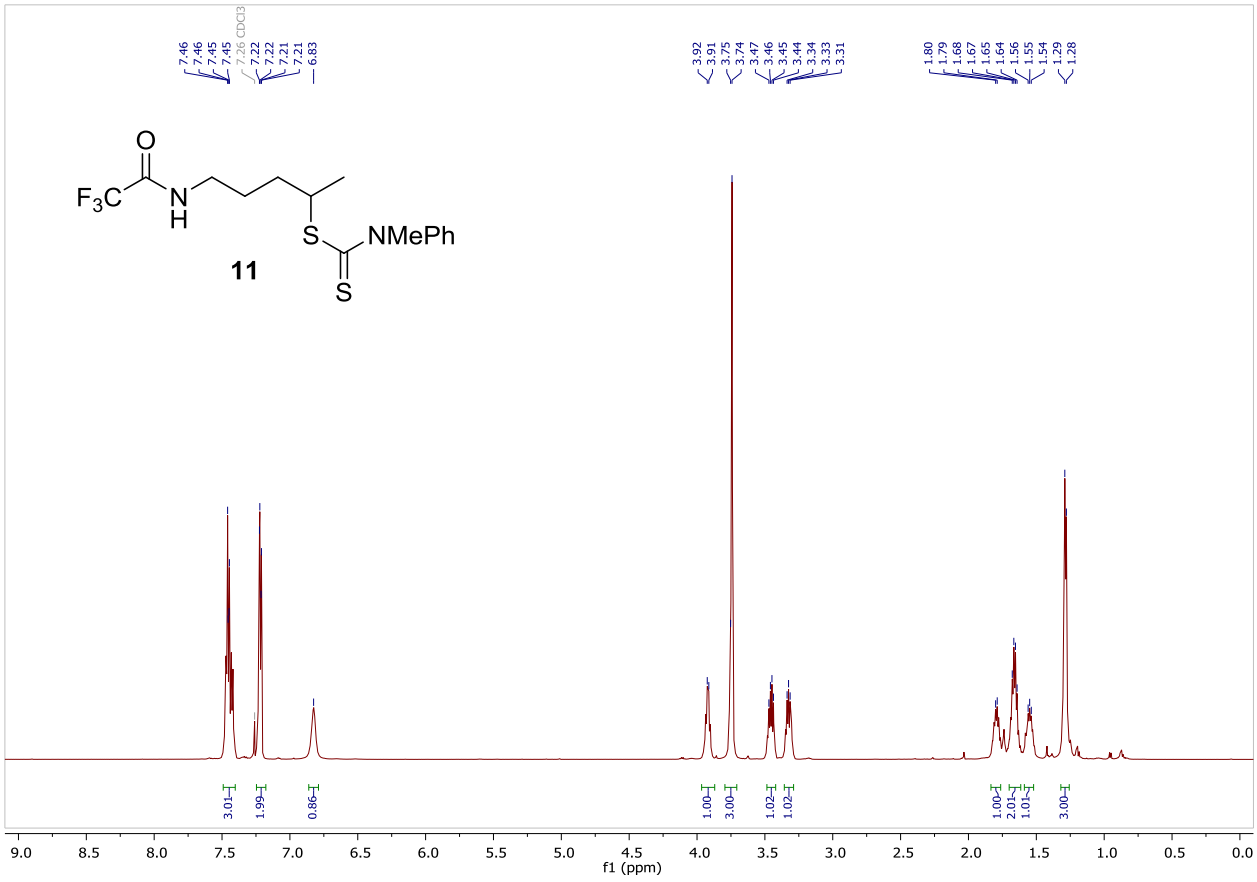
128.94
126.89
126.83
77.16 CDCl3
49.94
48.34
45.69
45.66
41.49
41.42
41.12
40.94
35.75
33.99
31.59
30.74
29.73
28.60
28.50
25.85
25.81
22.99
22.94
22.89
22.83
22.81
22.74
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.46
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7.45
7.45
7.26 CDCl3
7.22
7.22
7.21
7.21
6.83
3.92
3.91
3.75
3.74
3.47
3.46
3.45
3.44
3.34
3.33
3.31
1.80
1.79
1.68
1.67
1.65
1.64
1.56
1.55
1.54
1.29
1.28
O
F3C
N
H
S
NMePh
S
11
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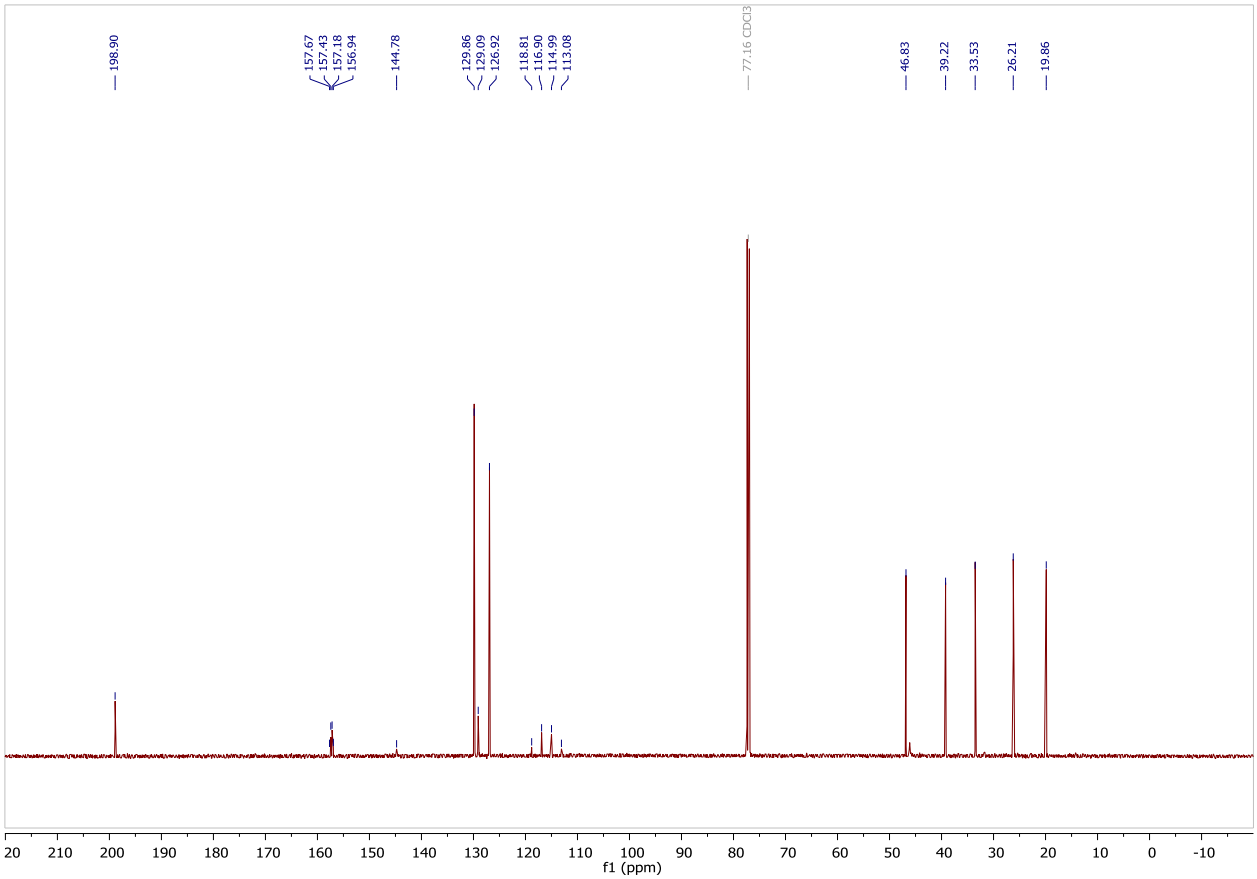
1.00
3.00
1.02
1.02
1.00
2.01
1.01
3.00
f1 (ppm)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157.18
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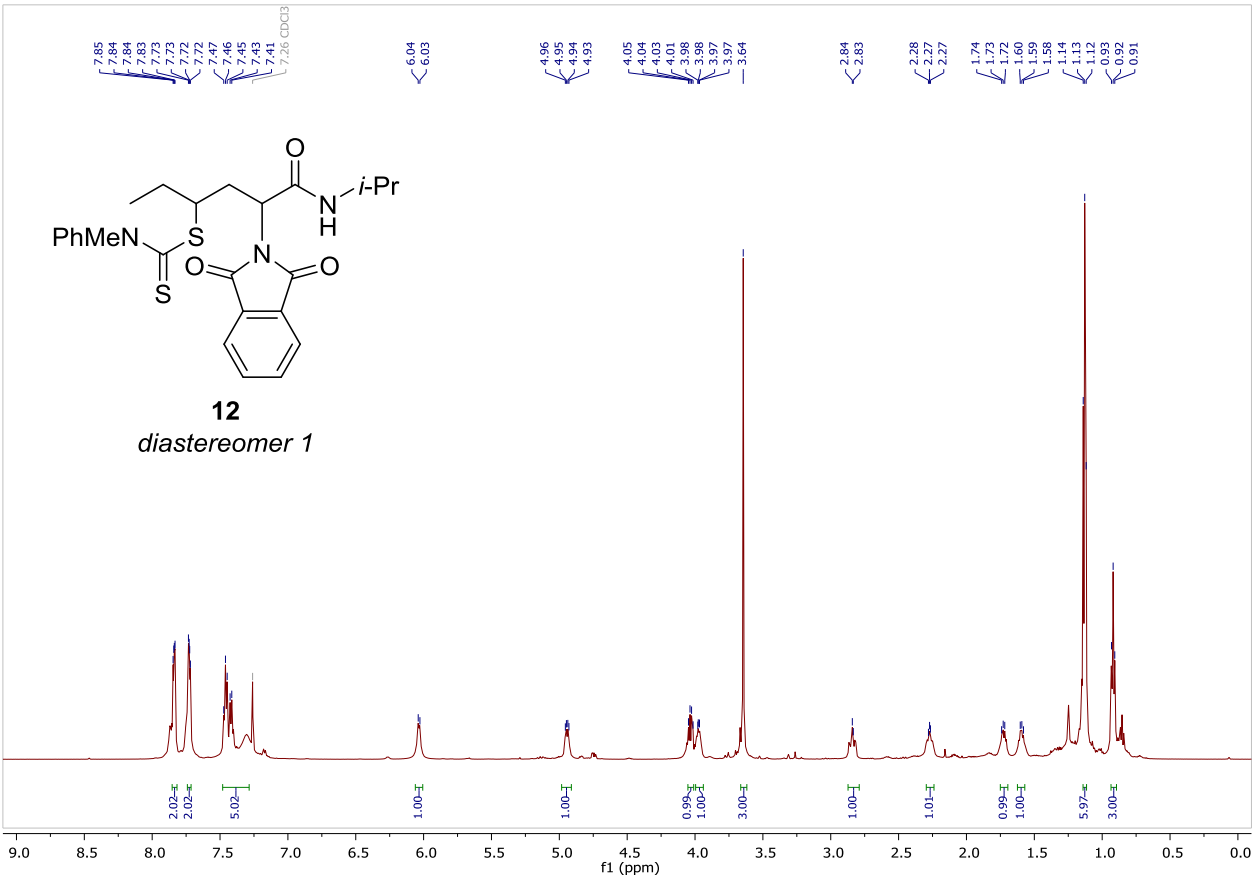
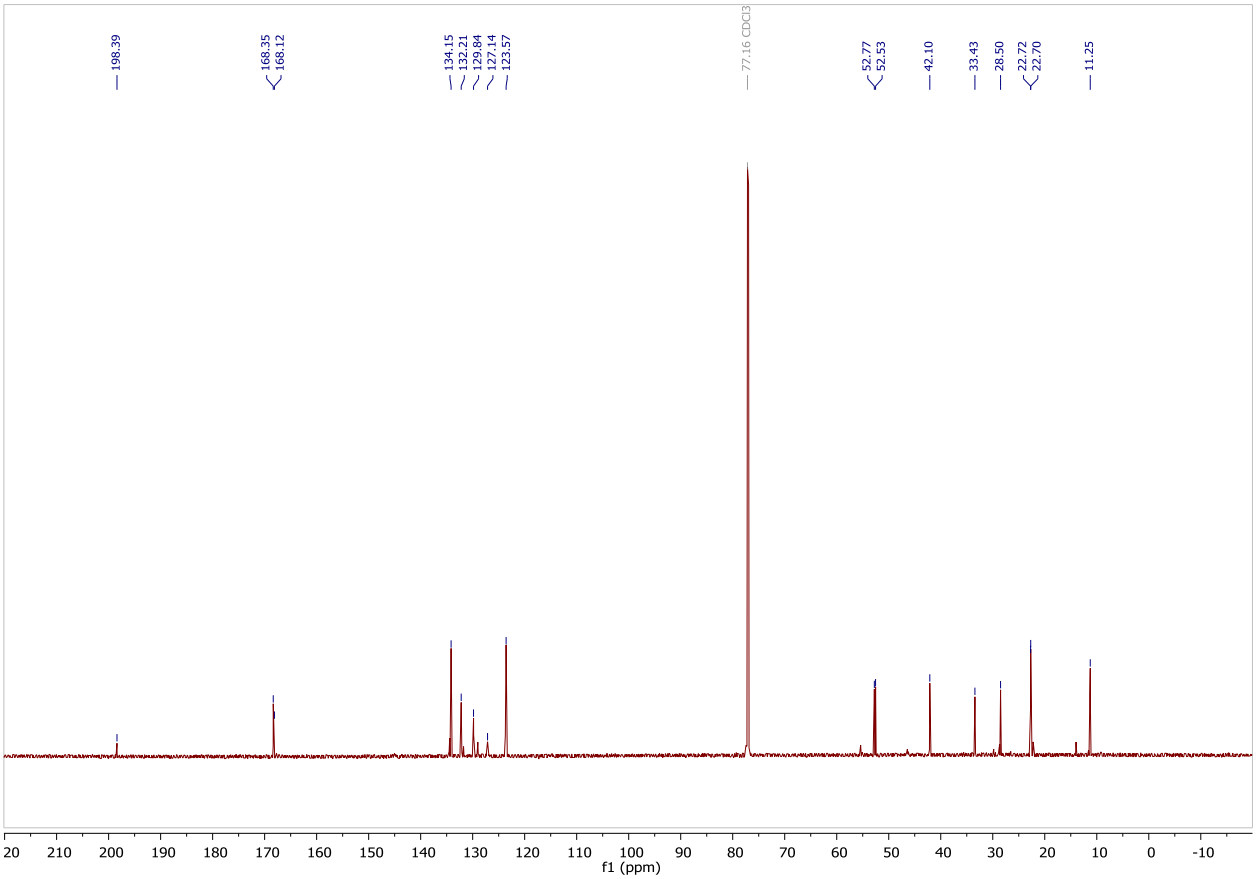
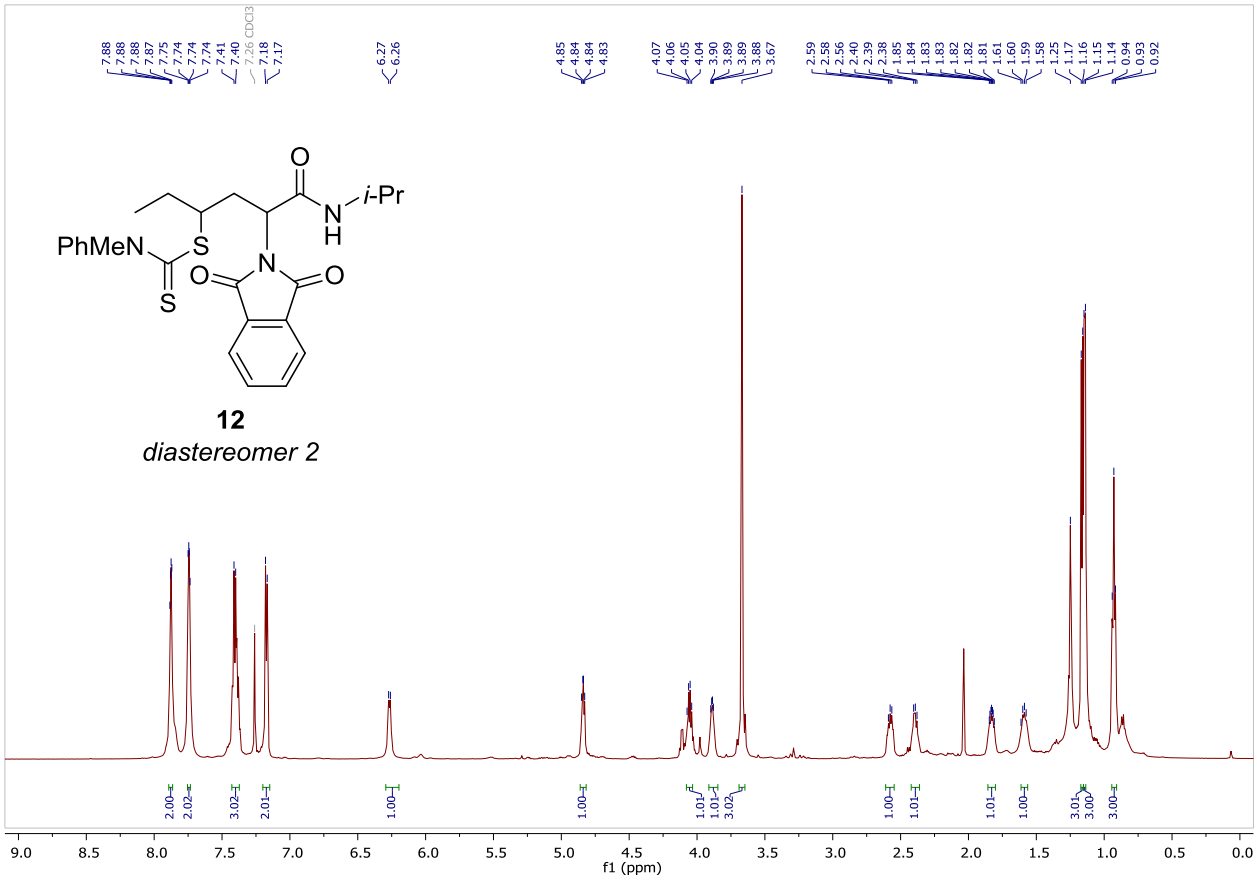
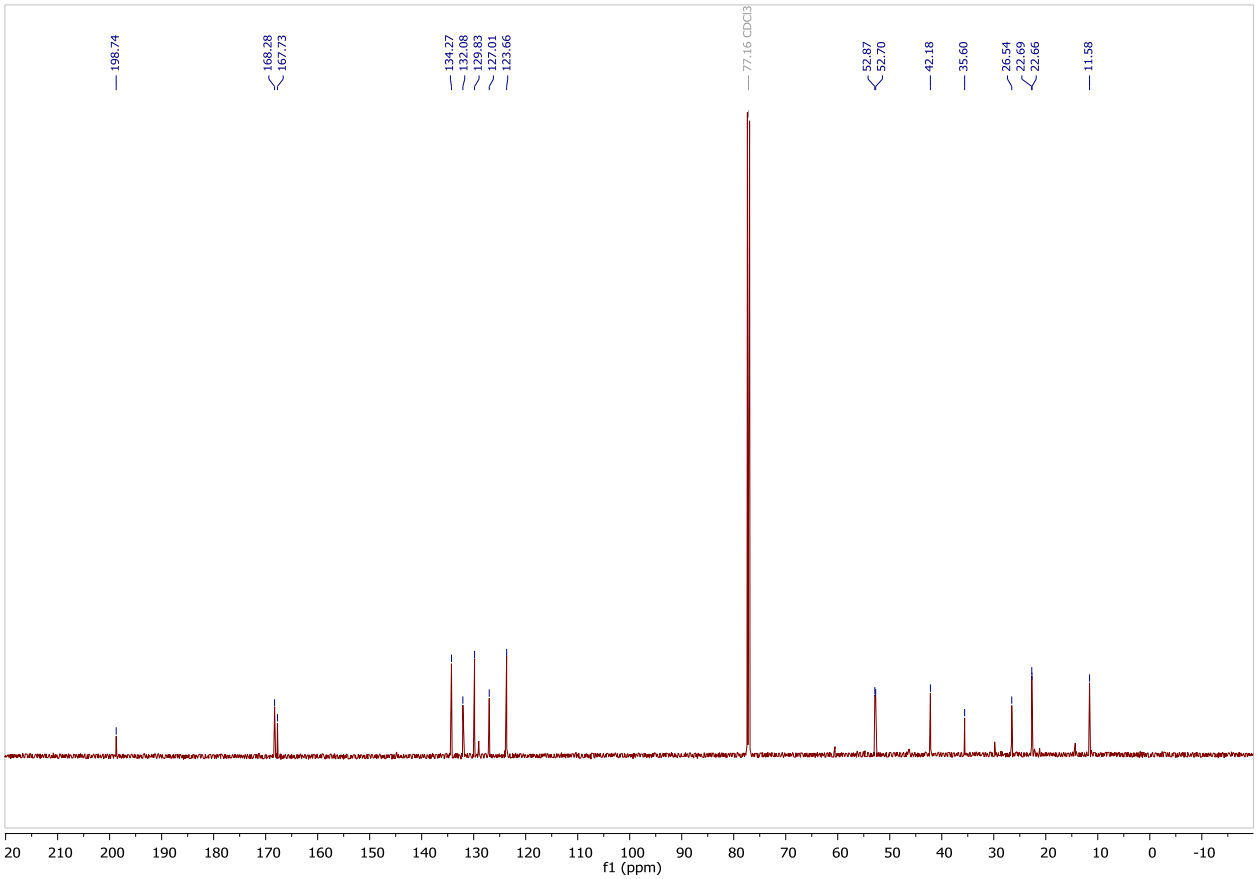
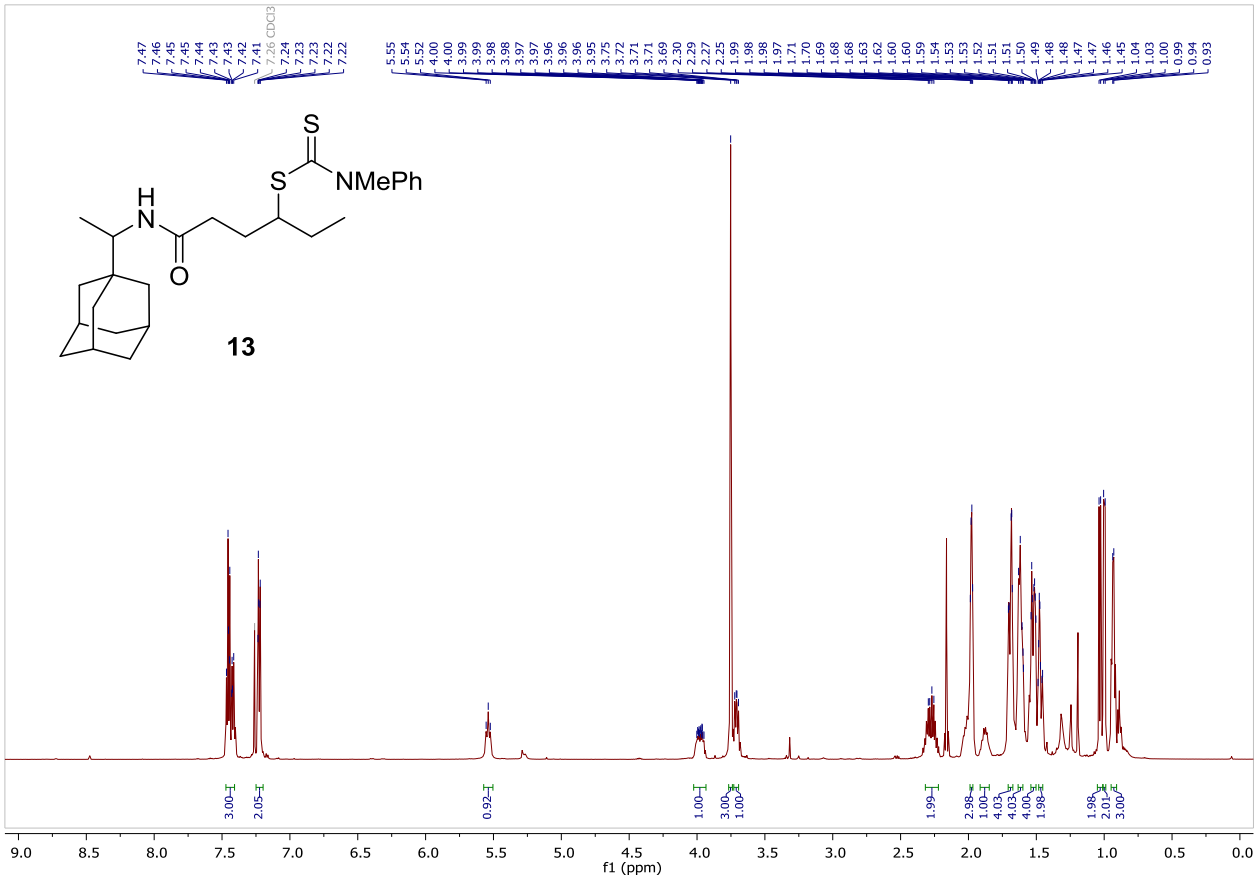
129.09
126.92
118.81
116.90
114.99
113.08
77.16 CDCl3
46.83
39.22
33.53
26.21
19.86
f1 (ppm)

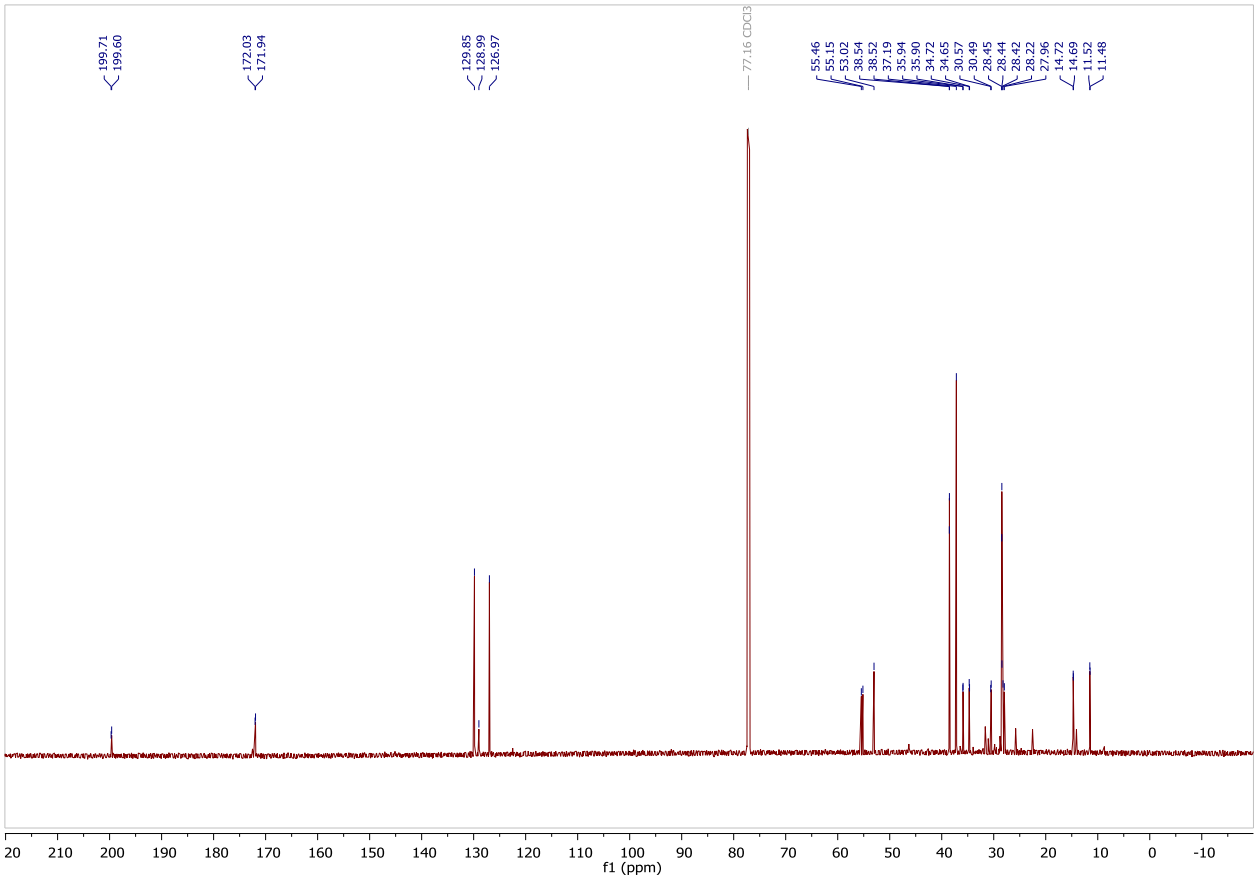

7.85 7.84 7.84 7.83 7.73 7.73 7.72 7.72 7.47 7.46 7.45 7.43 7.41 7.26 CDCl3
6.04 6.03
4.96 4.95 4.94 4.93
4.05 4.04 4.03 4.01 3.98 3.98 3.97 3.97 3.64
2.84 2.83
2.28 2.27 2.27
1.74 1.73 1.72 1.60 1.59 1.58
1.14 1.13 1.12 0.93 0.92 0.91
O
N
H
i-Pr
PhMeN
S
S
O
N
O
O
12
diastereomer 1
2.02 2.02 5.02 1.00 1.00 0.99 1.00 3.00 1.00 1.01 0.99 1.00 5.97 3.00
f1 (ppm)

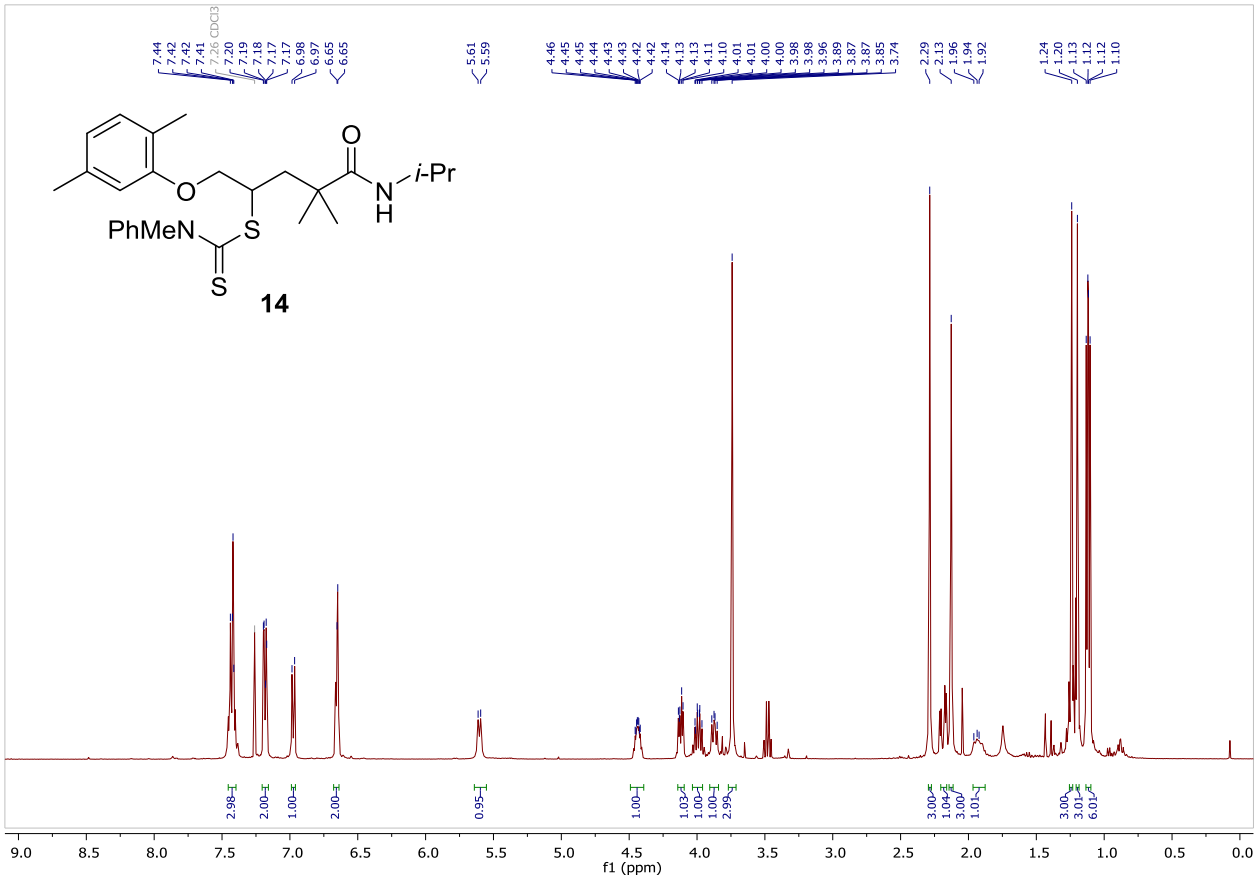

198.39
168.35 168.12
134.15 132.21 129.84 127.14 123.57
77.16 CDCl3
52.77 52.53
42.10
33.43
28.50
22.72 22.70
11.25
f1 (ppm)

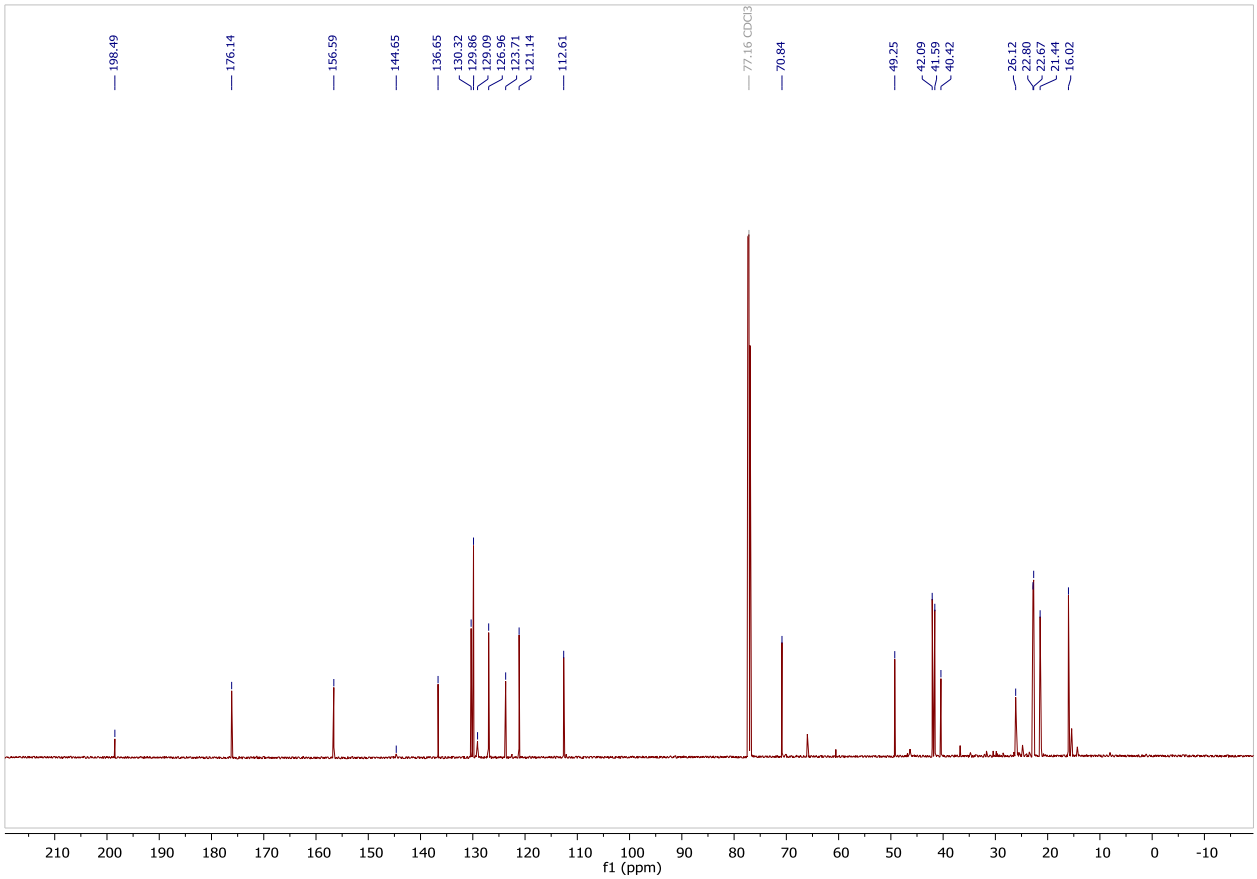

PhMeN
S
S
O
N
O
O
N
H
i-Pr
12
diastereomer 2
f1 (ppm)

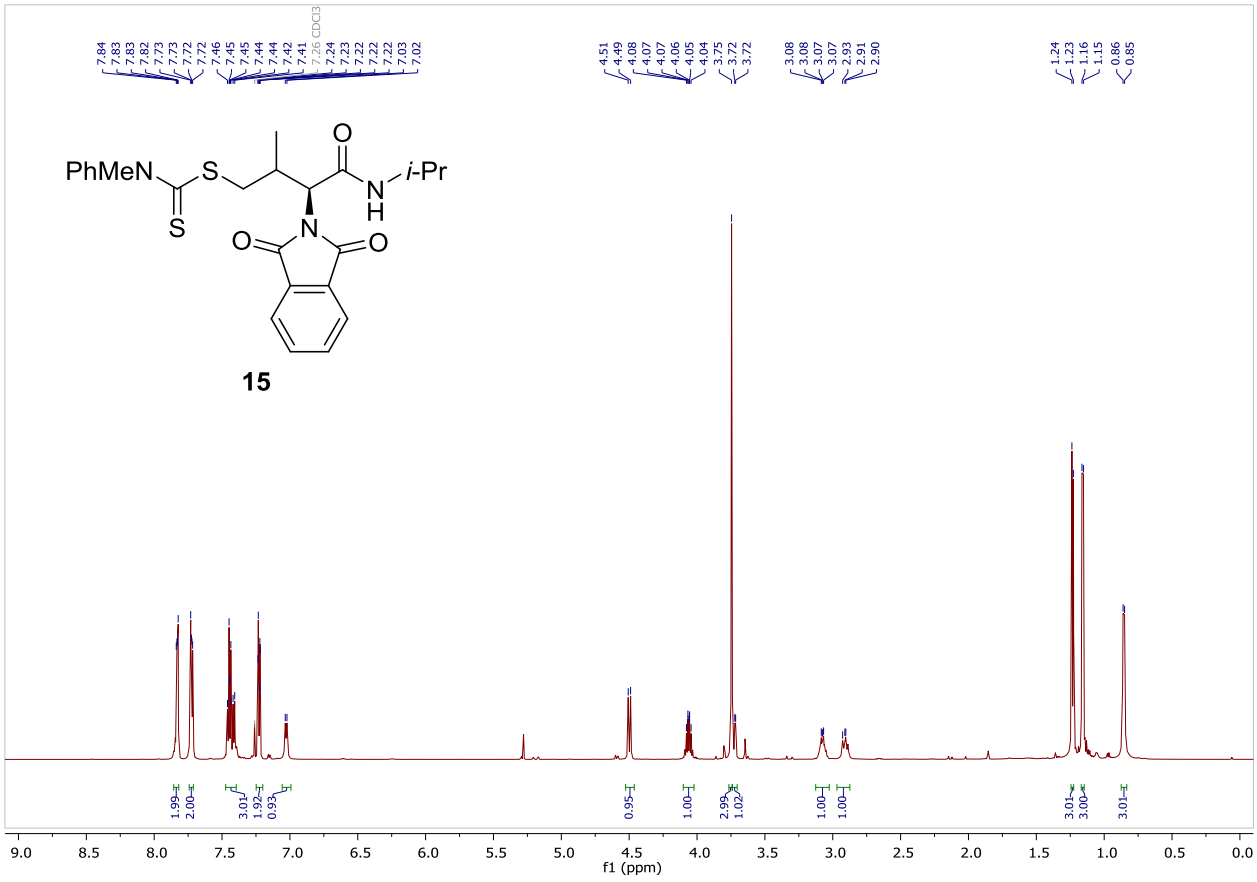

f1 (ppm)

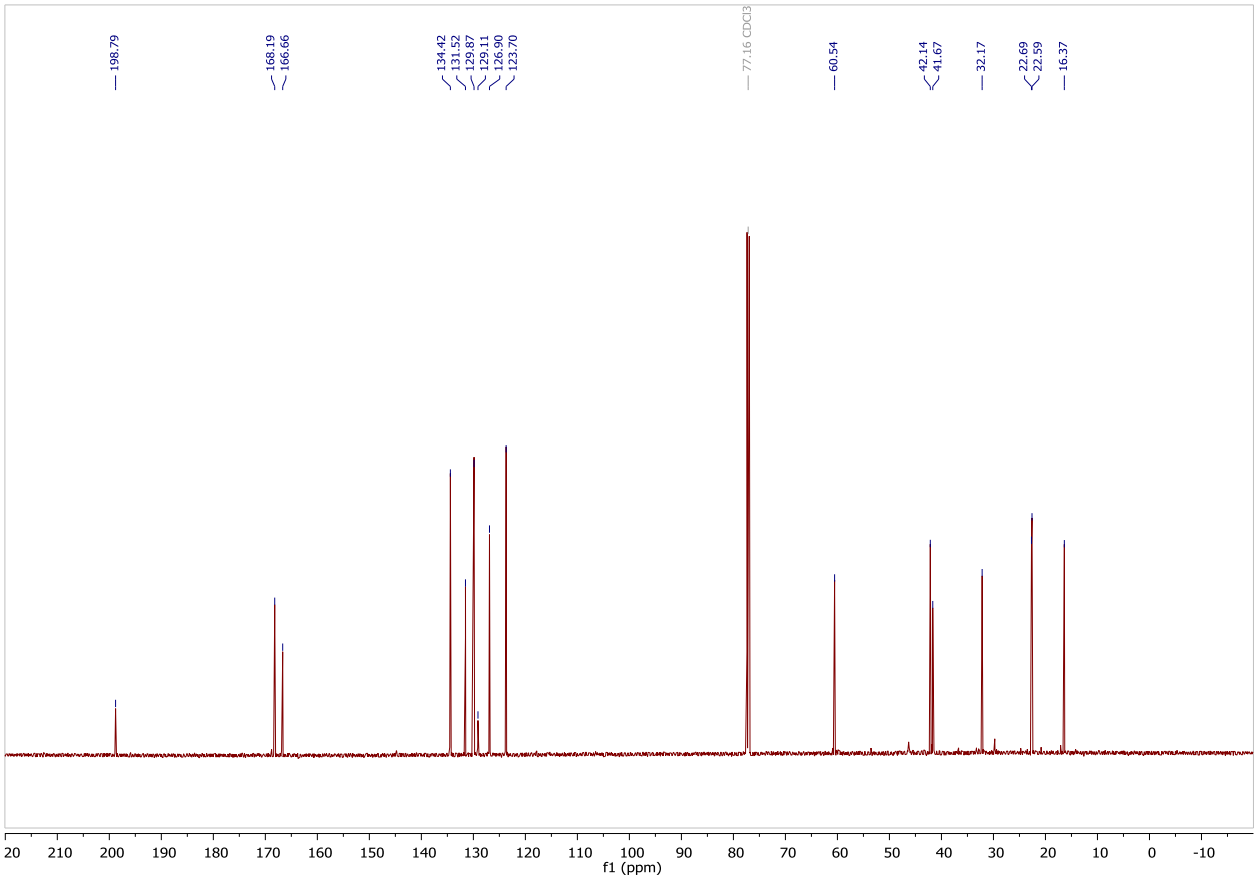

S
S
NMePh
H
N
O
13
f1 (ppm)

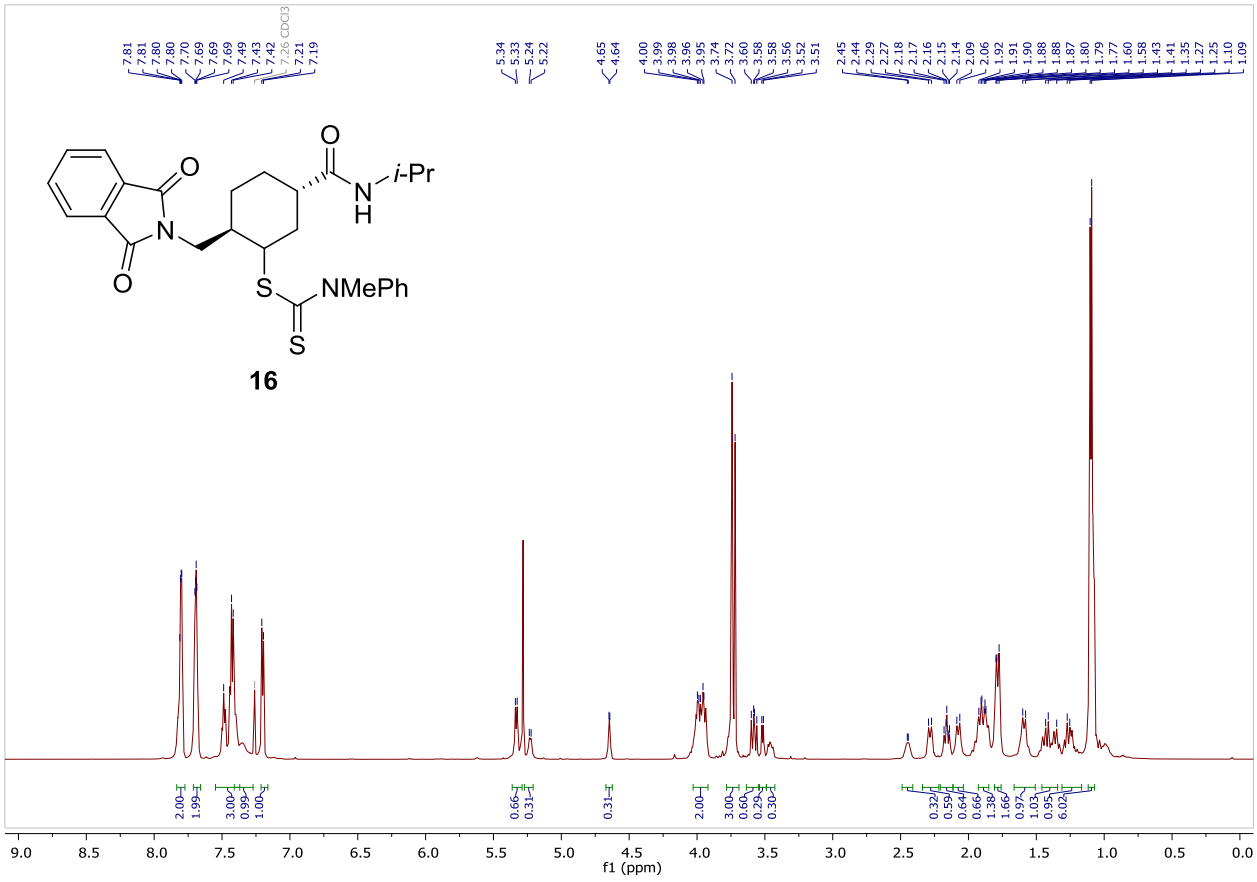

f1 (ppm)

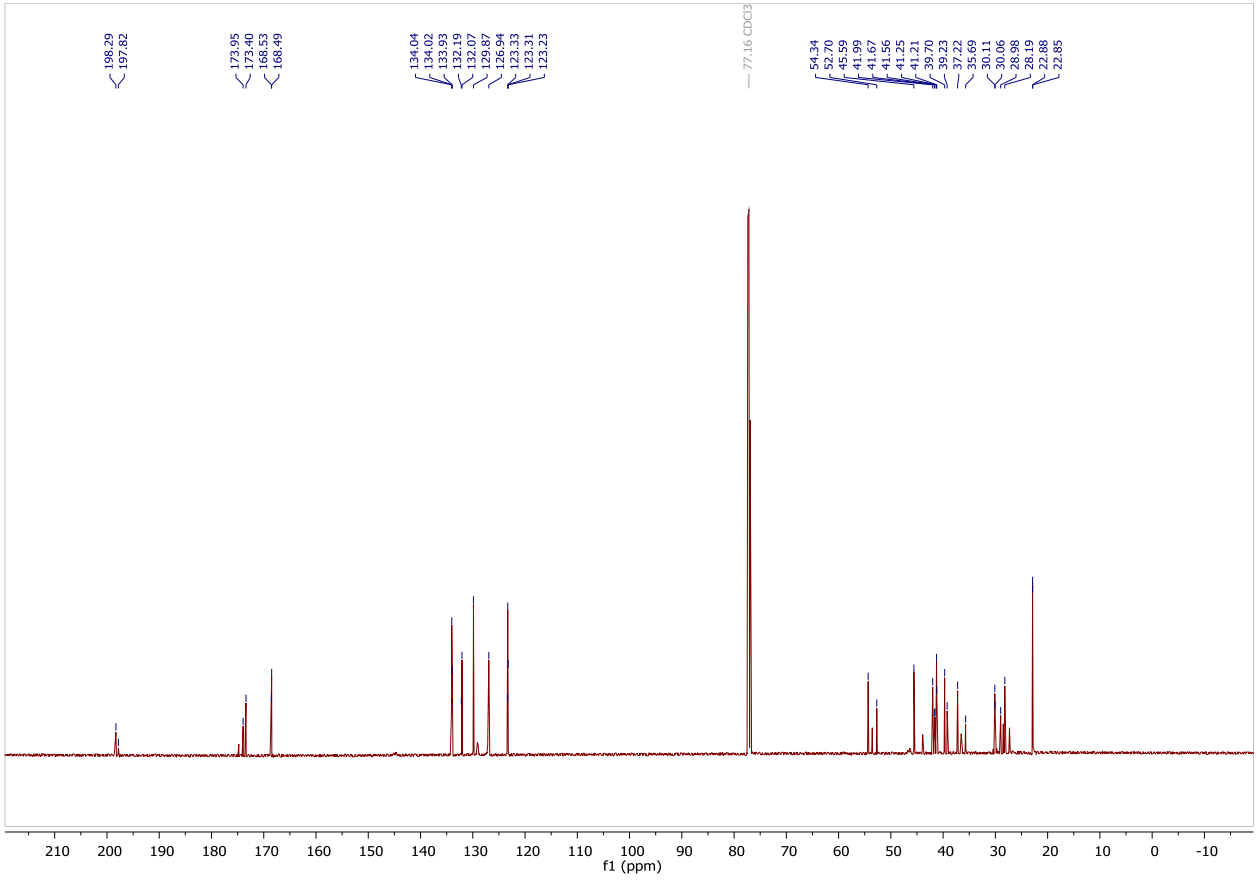

7.44 7.42 7.42 7.41 7.26 CDCl3 7.20 7.19 7.18 7.17 7.17 6.98 6.97 6.65 6.65
5.61 5.59
4.46 4.45 4.45 4.44 4.43 4.43 4.42 4.42 4.14 4.13 4.13 4.11 4.10 4.01 4.01 4.00 4.00 3.98 3.98 3.96 3.89 3.87 3.87 3.85 3.74
2.29 2.13 1.96 1.94 1.92
1.24 1.20 1.13 1.12 1.12 1.10
O
N
H
i-Pr
O
PhMeN
S
S
14
2.98 2.00 1.00 2.00 0.95 1.00 1.03 1.00 1.00 2.99 3.00 1.04 3.00 1.01 3.00 3.01 6.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

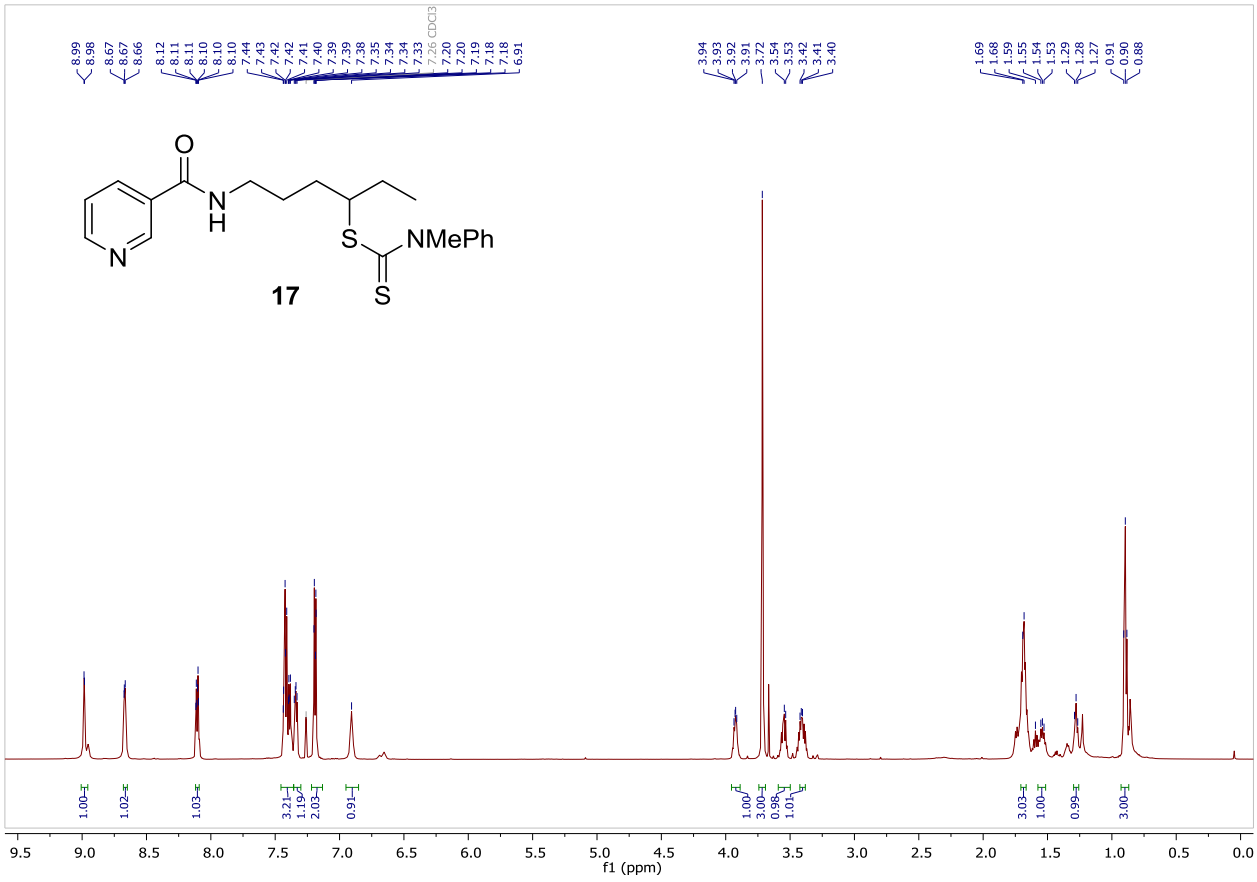

198.49
176.14
156.59
144.65
136.65
130.32
129.86
129.09
126.96
123.71
121.14
112.61
77.16 CDCl3
70.84
49.25
42.09
41.59
40.42
26.12
22.80
22.67
21.44
16.02
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

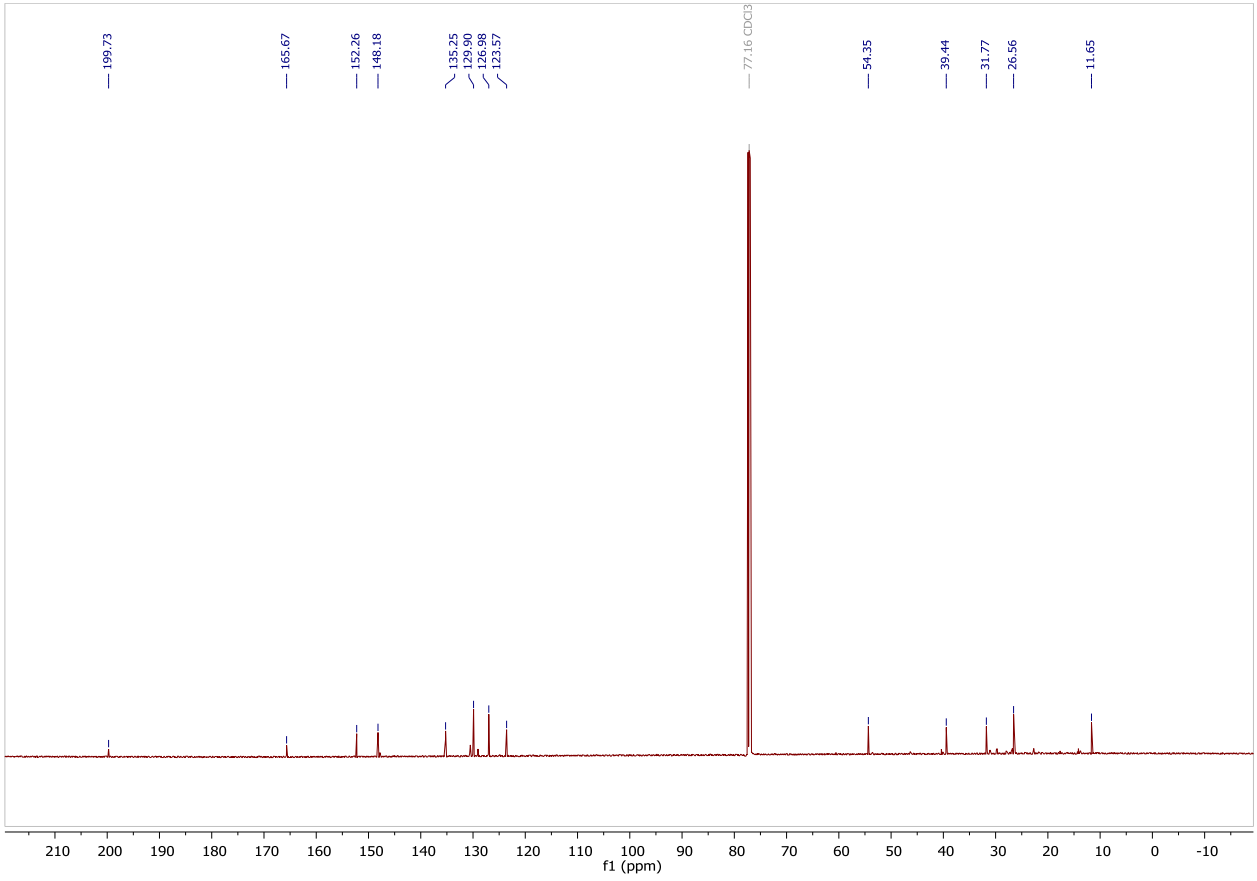

7.84 7.83 7.83 7.82 7.73 7.73 7.72 7.72 7.46 7.45 7.45 7.44 7.44 7.42 7.41 7.26 CDCl3 7.24 7.23 7.22 7.22 7.22 7.03 7.02
4.51 4.49 4.08 4.07 4.07 4.06 4.05 4.04 3.75 3.72 3.72
3.08 3.08 3.07 3.07 2.93 2.91 2.90
1.24 1.23 1.16 1.15 0.86 0.85
PhMeN
S
S
O
N
H
i-Pr
O
N
O
15
1.99 2.00 3.01 1.92 0.93 0.95 1.00 2.99 1.02 1.00 1.00 3.01 3.00 3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

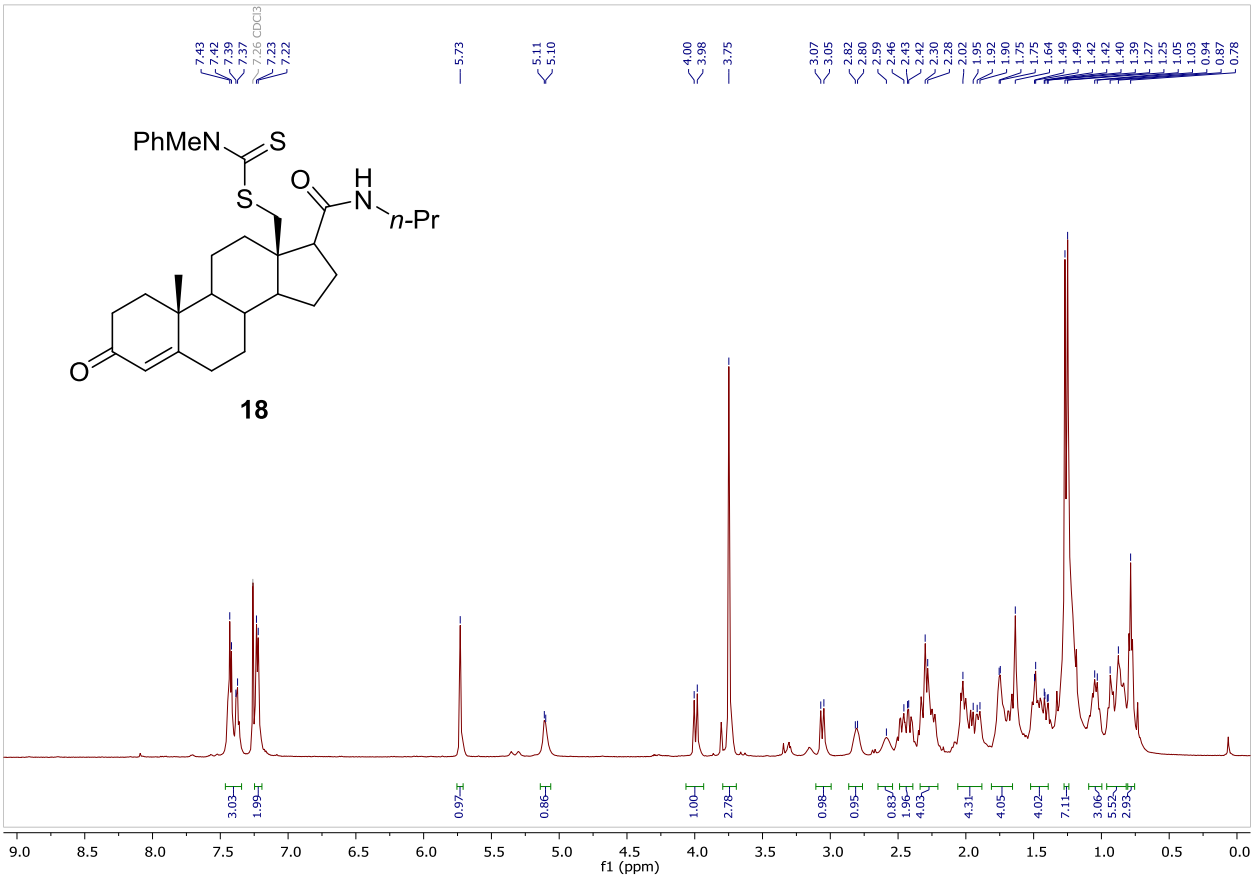

198.79
168.19 166.66
134.42 131.52 129.87 129.11 126.90 123.70
77.16 CDCl3
60.54
42.14 41.67
32.17
22.69 22.59
16.37
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

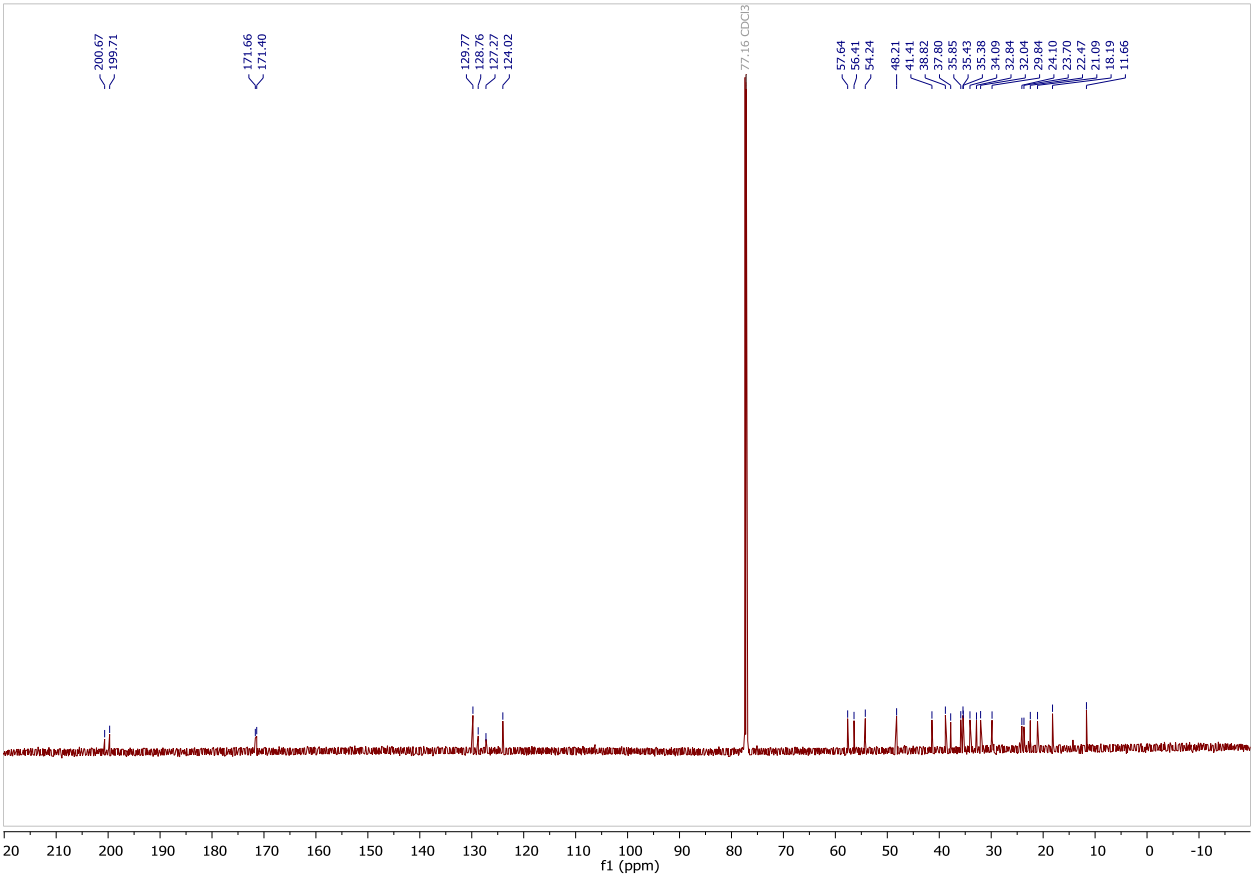

7.81 7.81 7.80 7.80 7.70 7.69 7.69 7.69 7.49 7.43 7.42 7.26 CDCl3 7.21 7.19
5.34 5.33 5.24 5.22
4.65 4.64
4.00 3.99 3.98 3.96 3.95 3.74 3.72 3.60 3.58 3.58 3.56 3.52 3.51
2.45 2.44 2.29 2.27 2.18 2.17 2.16 2.15 2.14 2.09 2.06 1.92 1.91 1.90 1.88 1.88 1.87 1.80 1.79 1.77 1.60 1.58 1.43 1.41 1.35 1.27 1.25 1.10 1.09
O
O
N
O
N
H
i-Pr
S
NMePh
S
16
2.00 1.99 3.00 0.99 1.00 0.66 0.31 0.31 2.00 3.00 0.60 0.29 0.30 0.32 0.59 0.64 0.66 1.38 1.66 0.97 1.03 0.95 6.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

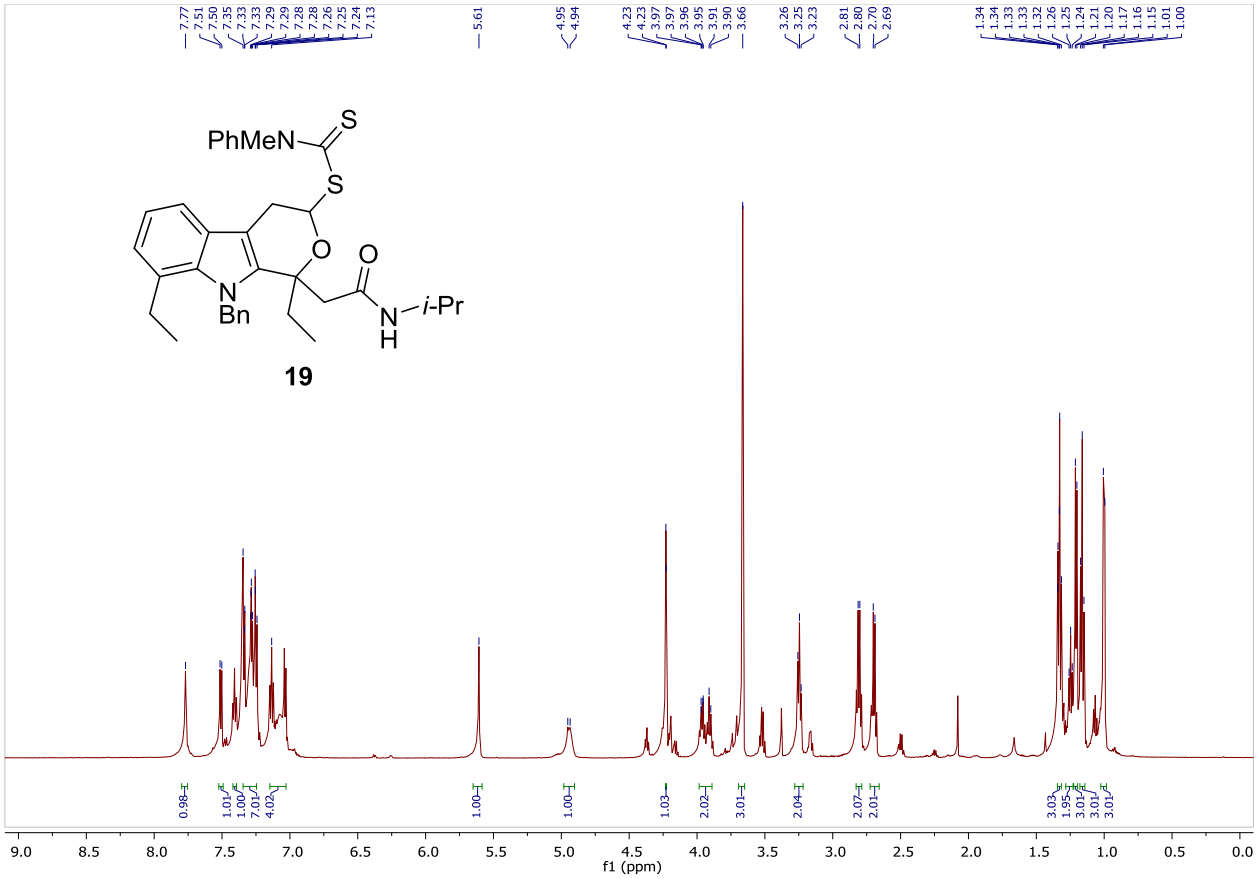

198.29 197.82
173.95 173.40 168.53 168.49
134.04 134.02 133.93 132.19 132.07 129.87 126.94 123.33 123.31 123.23
77.16 CDCl3
54.34 52.70 45.59 41.99 41.67 41.56 41.25 41.21 39.70 39.23 37.22 35.69 30.11 30.06 28.98 28.19 22.88 22.85
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

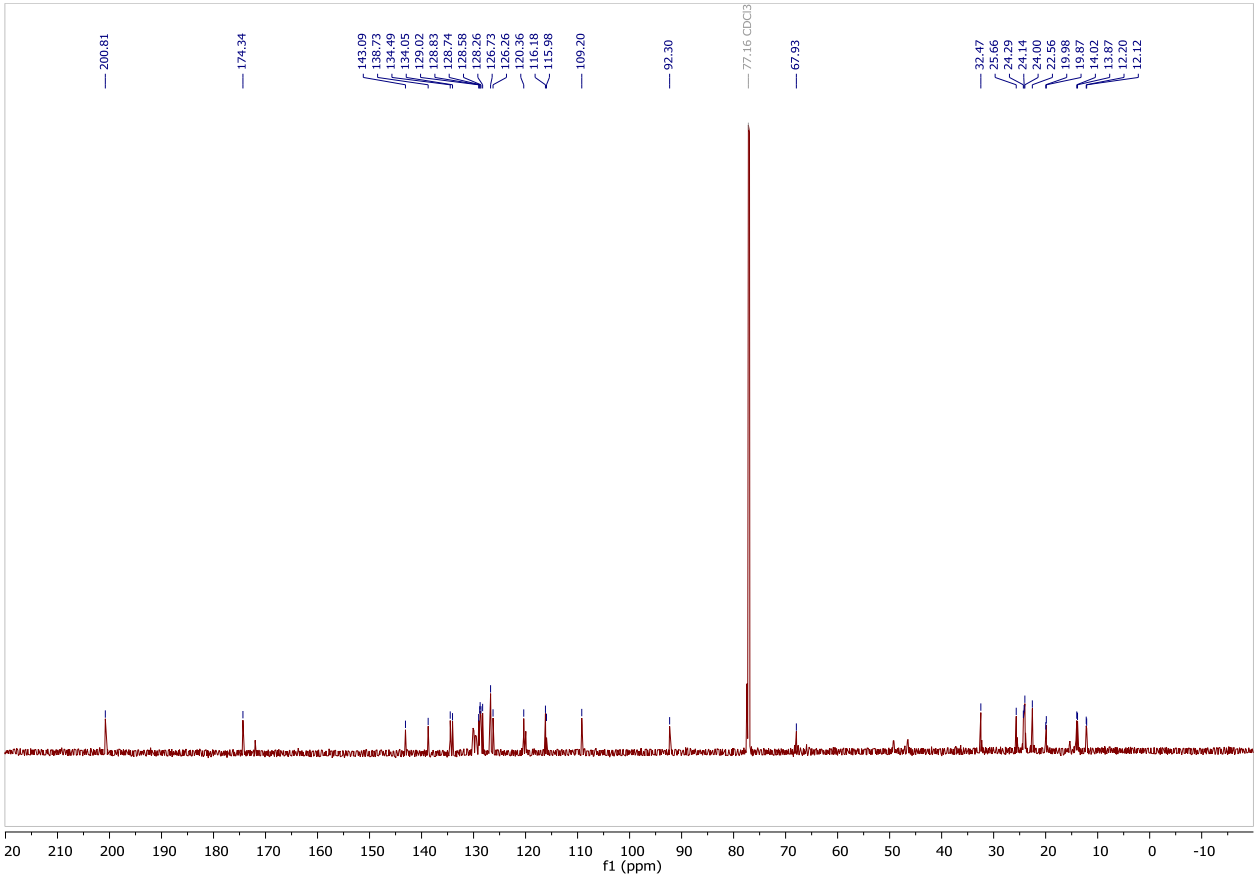

8.99
8.98
8.67
8.67
8.66
8.12
8.11
8.11
8.10
8.10
8.10
7.44
7.43
7.42
7.42
7.41
7.40
7.39
7.39
7.38
7.35
7.34
7.34
7.33
7.26 CDCl3
7.20
7.20
7.19
7.18
7.18
6.91
3.94
3.93
3.92
3.91
3.72
3.54
3.53
3.42
3.41
3.40
1.69
1.68
1.59
1.55
1.54
1.53
1.29
1.28
1.27
0.91
0.90
0.88
O
N
H
N
S
NMePh
S
17
1.00
1.02
1.03
3.21
1.19
2.03
0.91
1.00
3.00
0.98
1.01
3.03
1.00
0.99
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

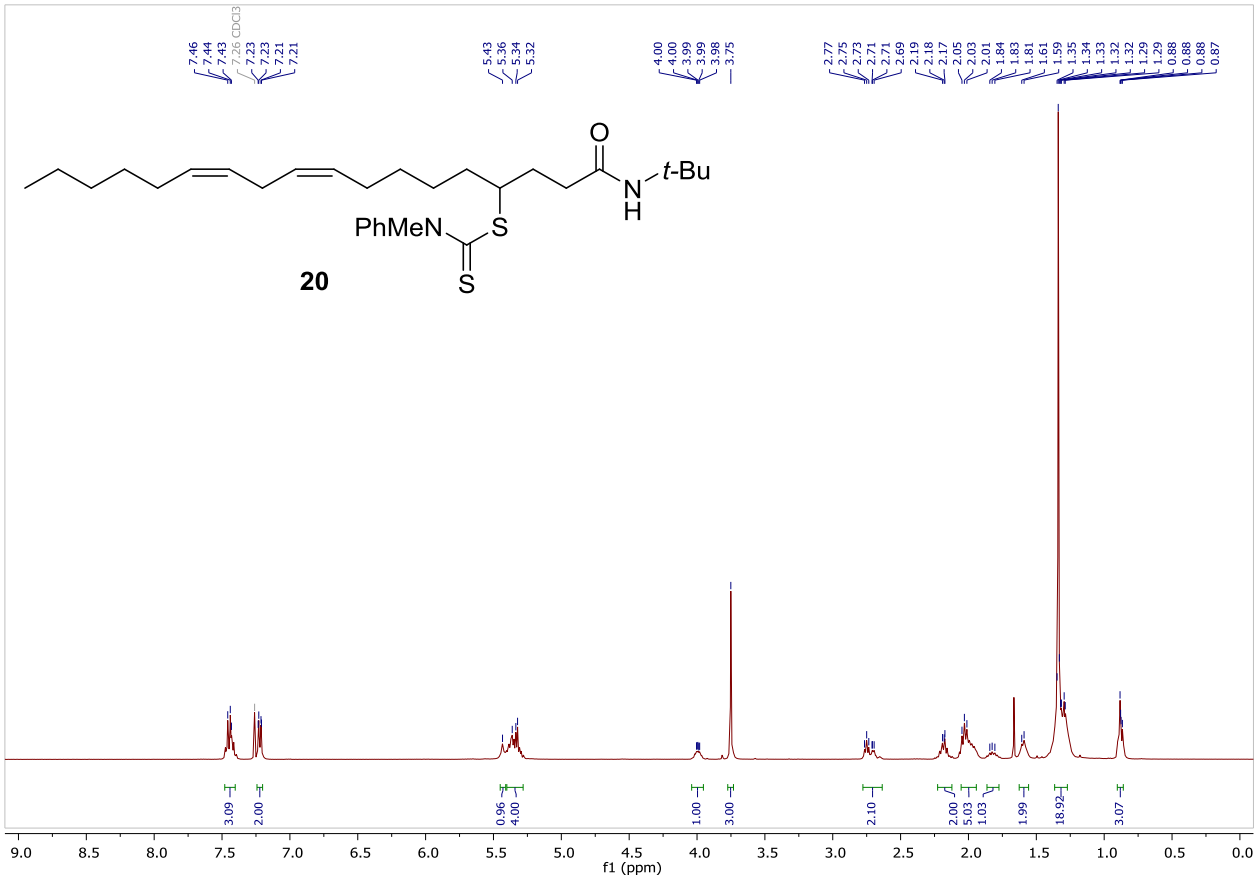

199.73
165.67
152.26
148.18
135.25
129.90
126.98
123.57
77.16 CDCl3
54.35
39.44
31.77
26.56
11.65
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

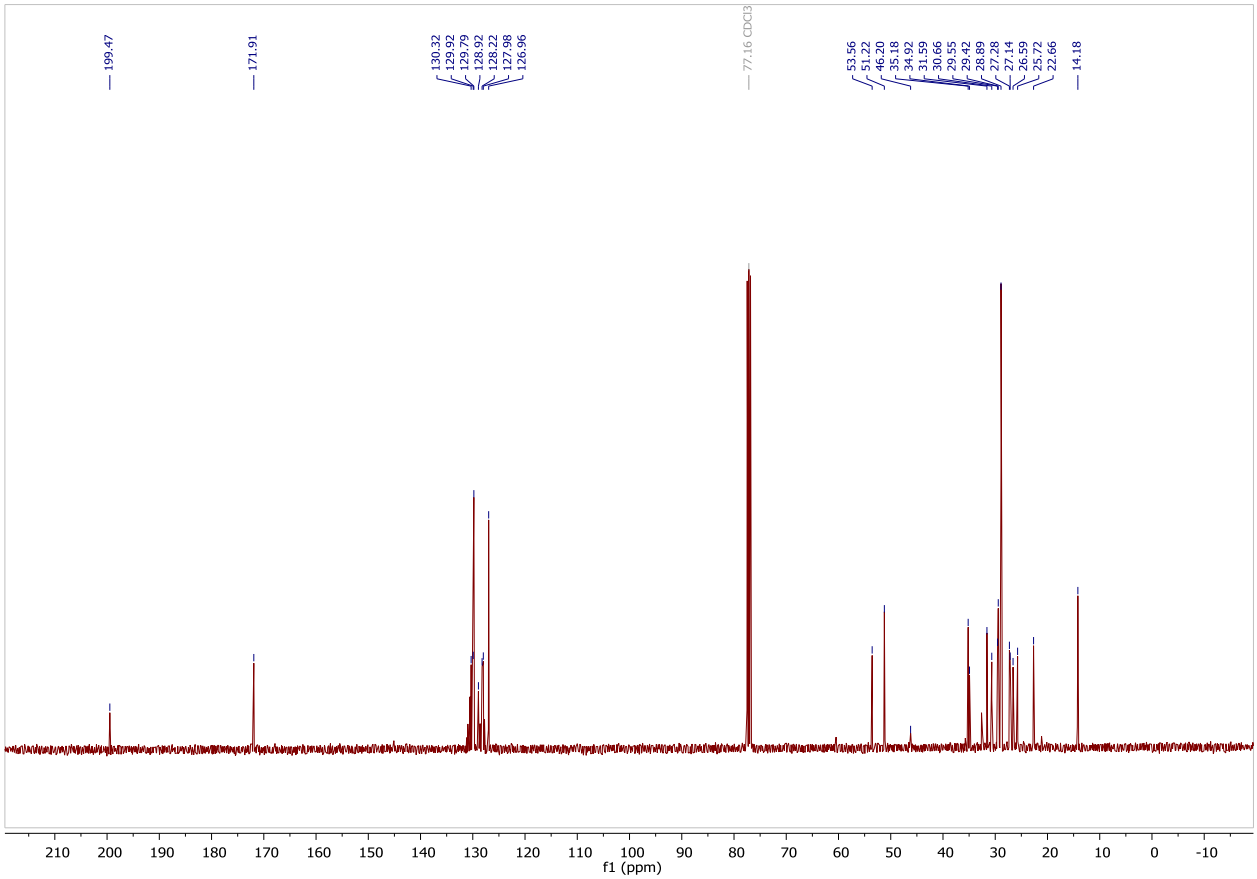

PhMeN
S
S
O
H
N
n-Pr
O
18
f1 (ppm)

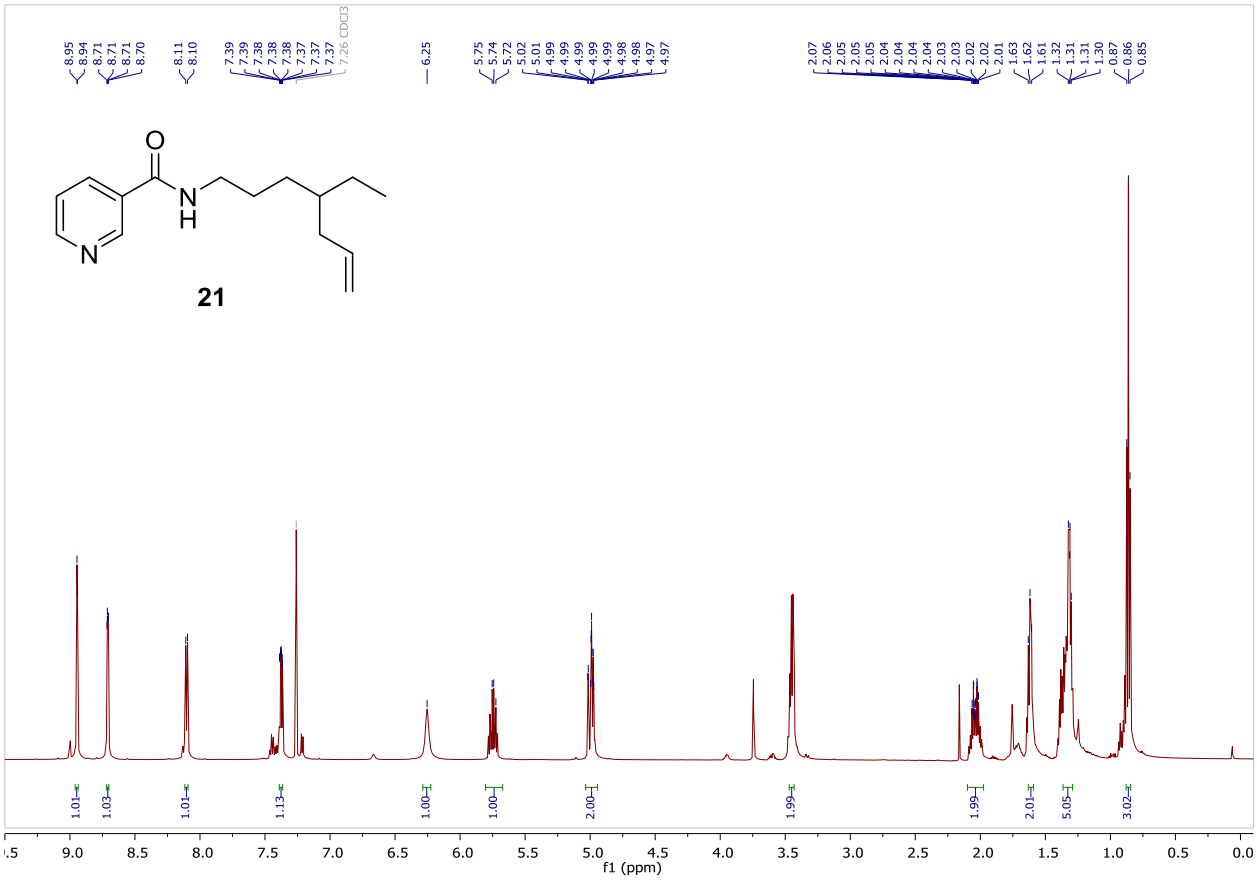

f1 (ppm)

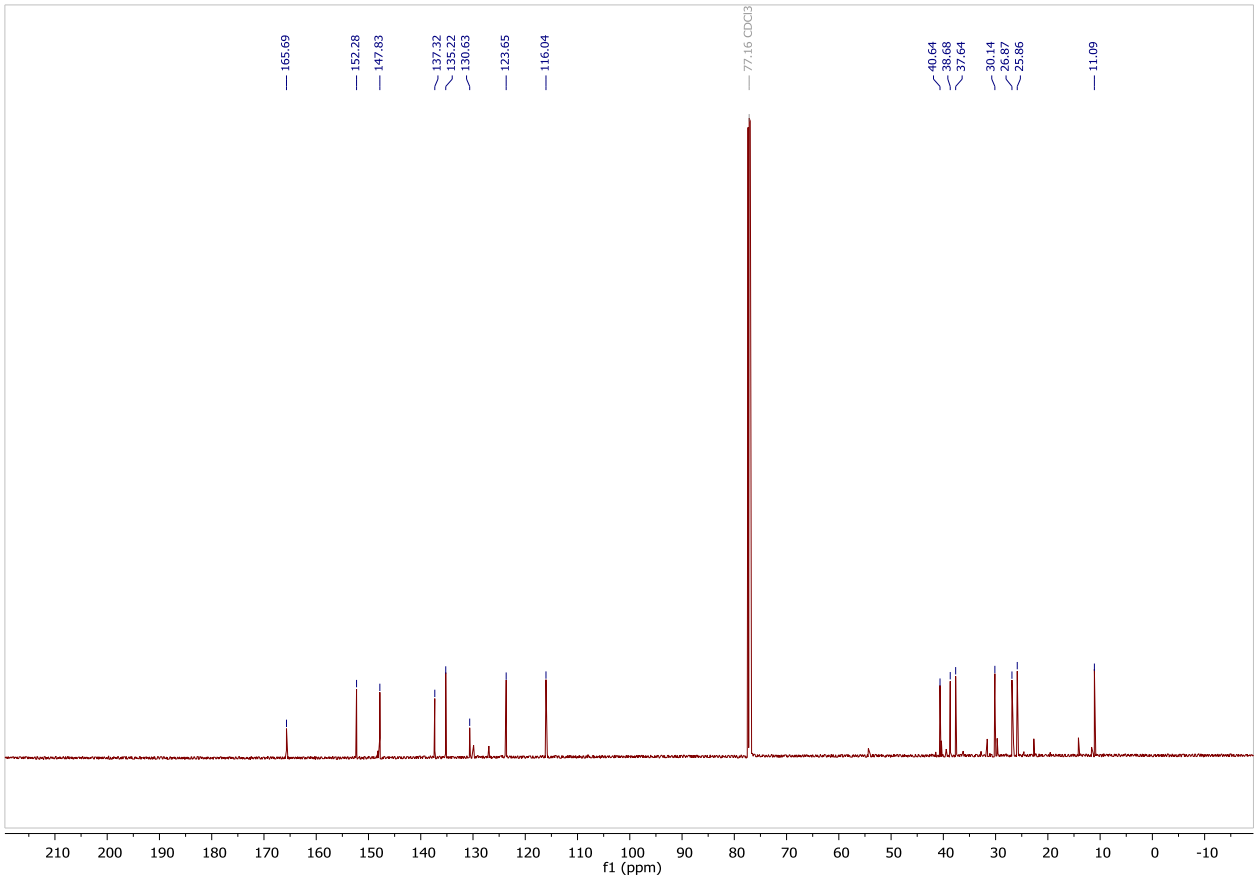

PhMeN
S
S
O
O
N
Bn
N
H
i-Pr
19
f1 (ppm)

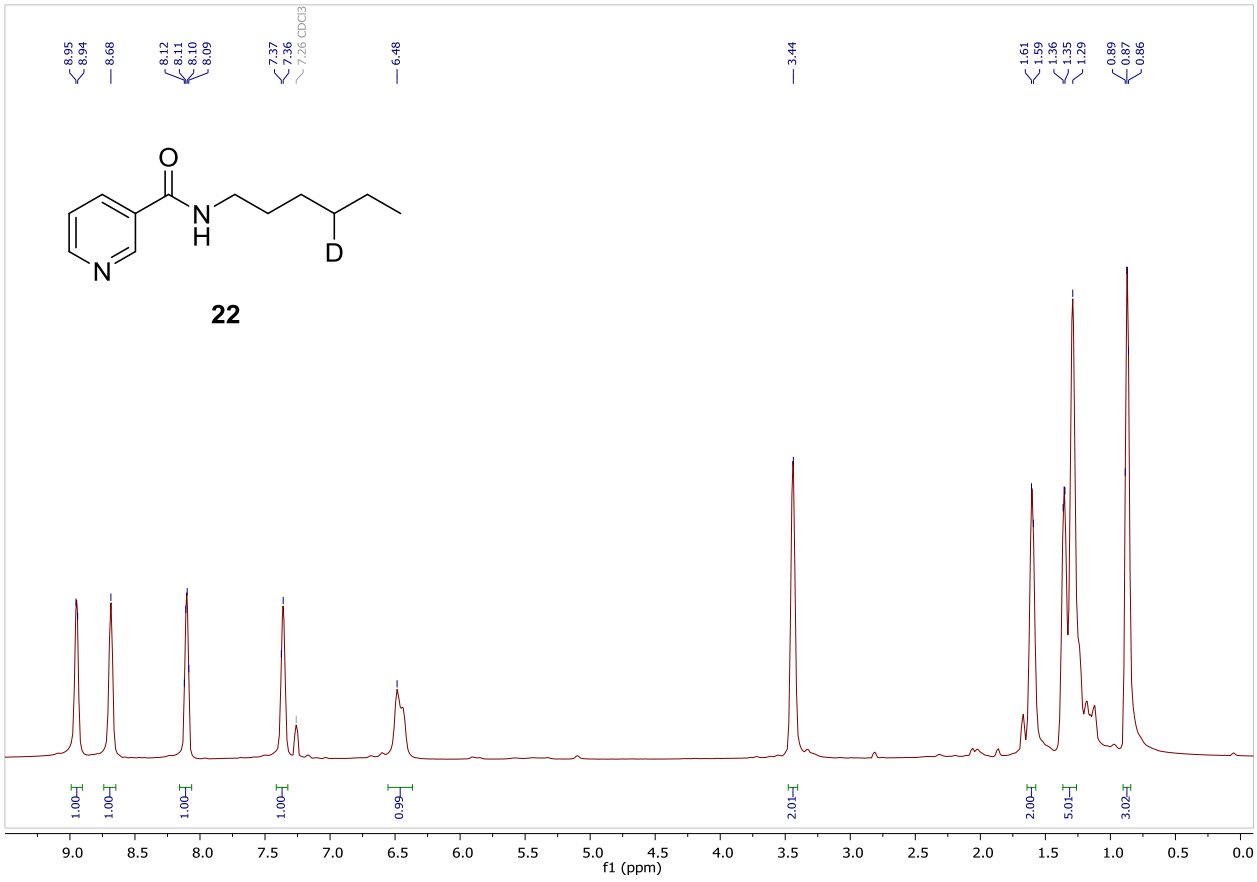

f1 (ppm)


7.46
7.44
7.43
7.26 CDCl3
7.23
7.23
7.21
7.21
5.43
5.36
5.34
5.32
4.00
4.00
3.99
3.99
3.98
3.75
2.77
2.75
2.73
2.71
2.71
2.69
2.19
2.18
2.17
2.05
2.03
2.01
1.84
1.83
1.81
1.61
1.59
1.35
1.34
1.33
1.32
1.32
1.29
1.29
0.88
0.88
0.88
0.87
O
N
H
t-Bu
PhMeN
S
S
20
3.09
2.00
0.96
4.00
1.00
3.00
2.10
2.00
5.03
1.03
1.99
18.92
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

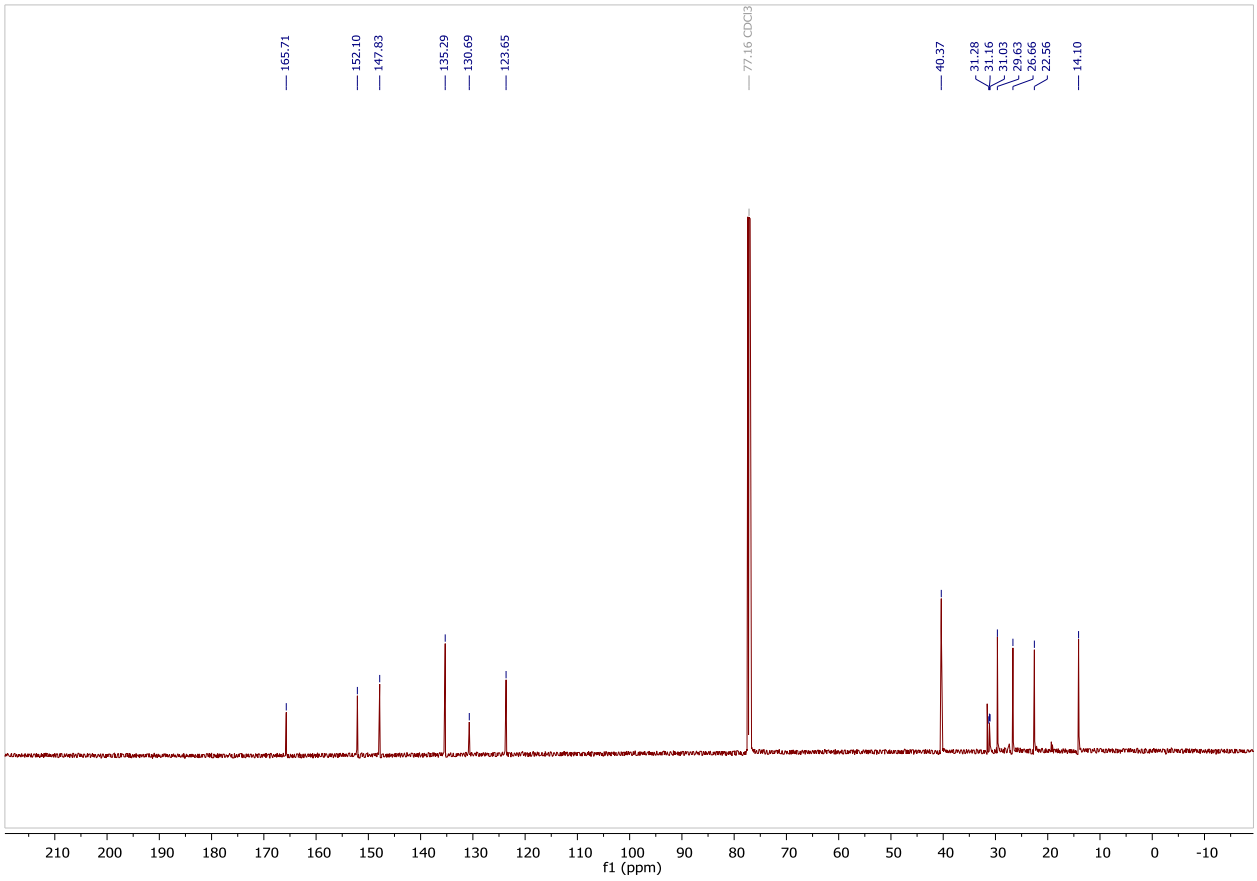

199.47
171.91
130.32
129.92
129.79
128.92
128.22
127.98
126.96
77.16 CDCl3
53.56
51.22
46.20
35.18
34.92
31.59
30.66
29.55
29.42
28.89
27.28
27.14
26.59
25.72
22.66
14.18
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

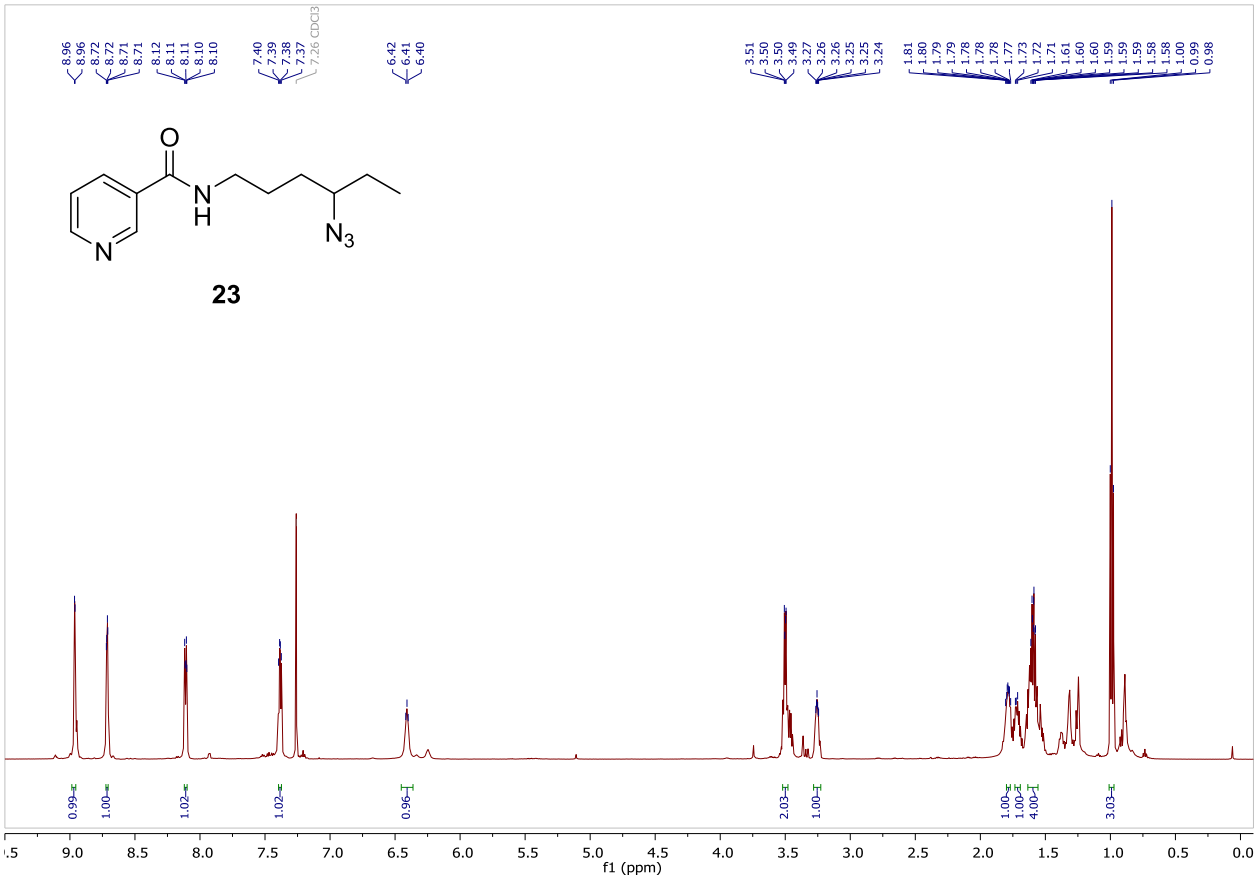

8.95
8.94
8.71
8.71
8.71
8.70
8.11
8.10
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.37
7.26 CDCl3
6.25
5.75
5.74
5.72
5.02
5.01
4.99
4.99
4.99
4.99
4.99
4.98
4.98
4.97
4.97
2.07
2.06
2.05
2.05
2.05
2.04
2.04
2.04
2.04
2.03
2.03
2.02
2.02
2.01
1.63
1.62
1.61
1.32
1.31
1.31
1.30
0.87
0.86
0.85
O
N
H
N
21
1.01
1.03
1.01
1.13
1.00
1.00
2.00
1.99
1.99
2.01
5.05
3.02
f1 (ppm)


165.69
152.28
147.83
137.32
135.22
130.63
123.65
116.04
77.16 CDCl3
40.64
38.68
37.64
30.14
26.87
25.86
11.09
f1 (ppm)

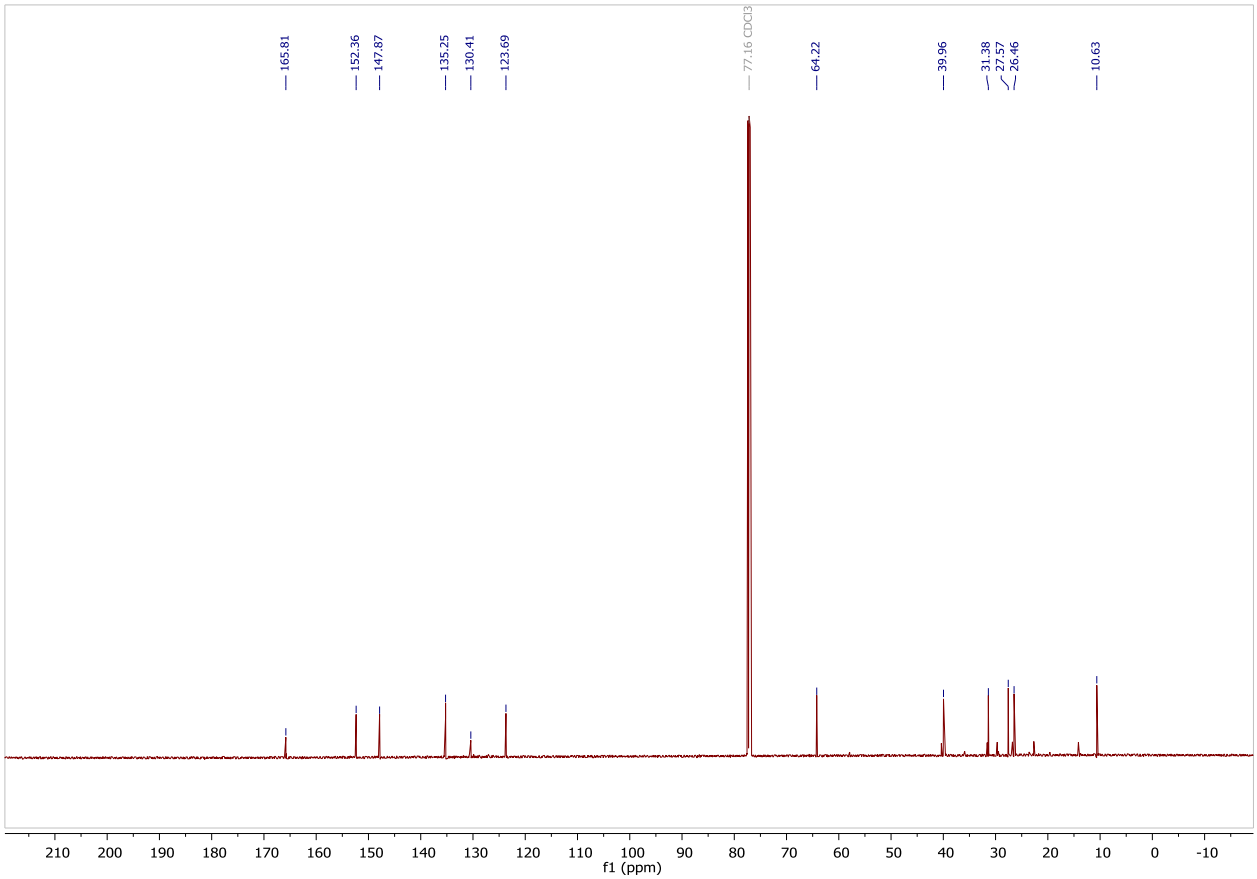

8.95
8.94
8.68
8.12
8.11
8.10
8.09
7.37
7.36
7.26 CDCl3
6.48
3.44
1.61
1.59
1.36
1.35
1.29
0.89
0.87
0.86
O
N
H
N
D
1.00
1.00
1.00
1.00
0.99
2.01
2.00
5.01
3.02
f1 (ppm)

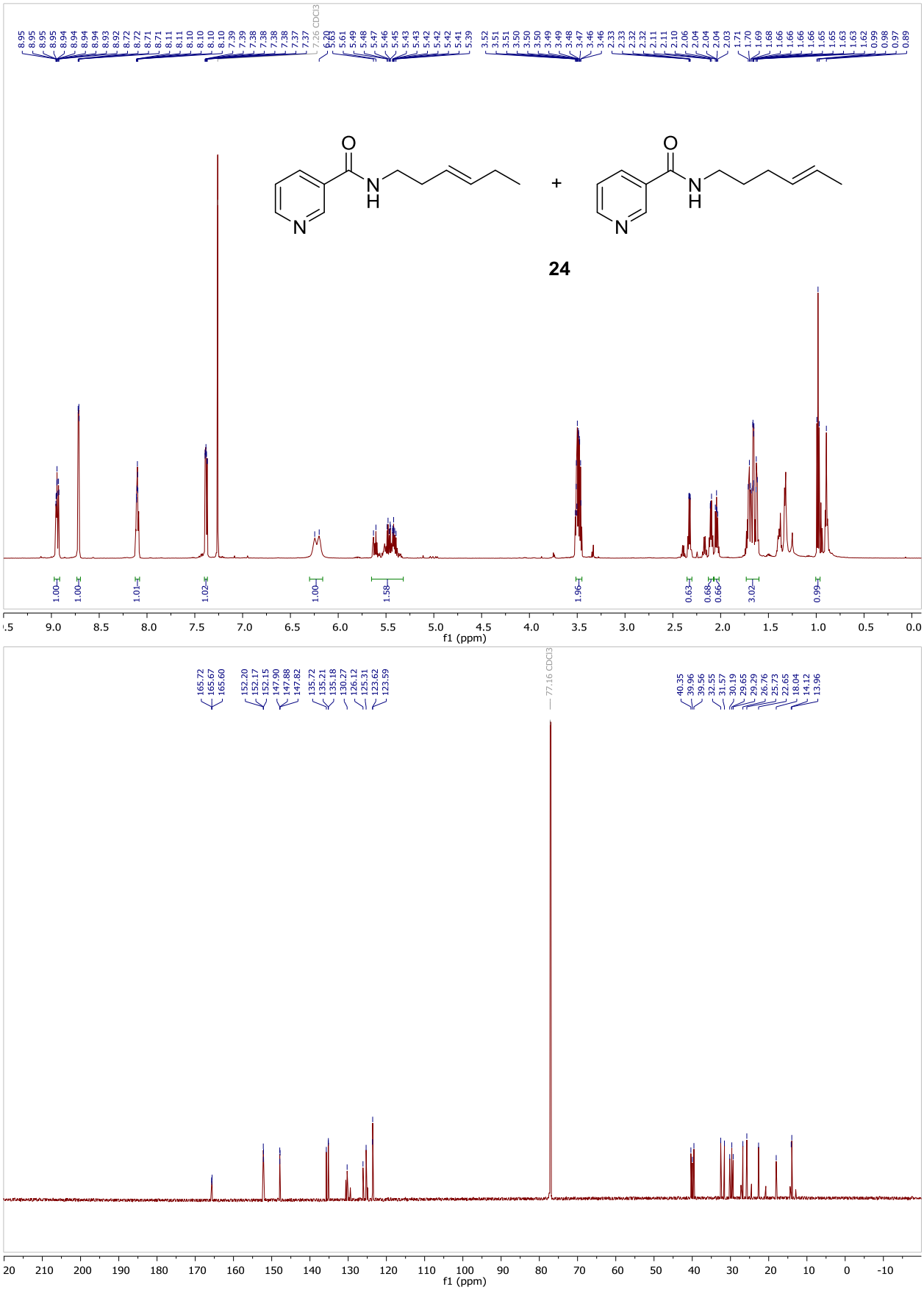
22

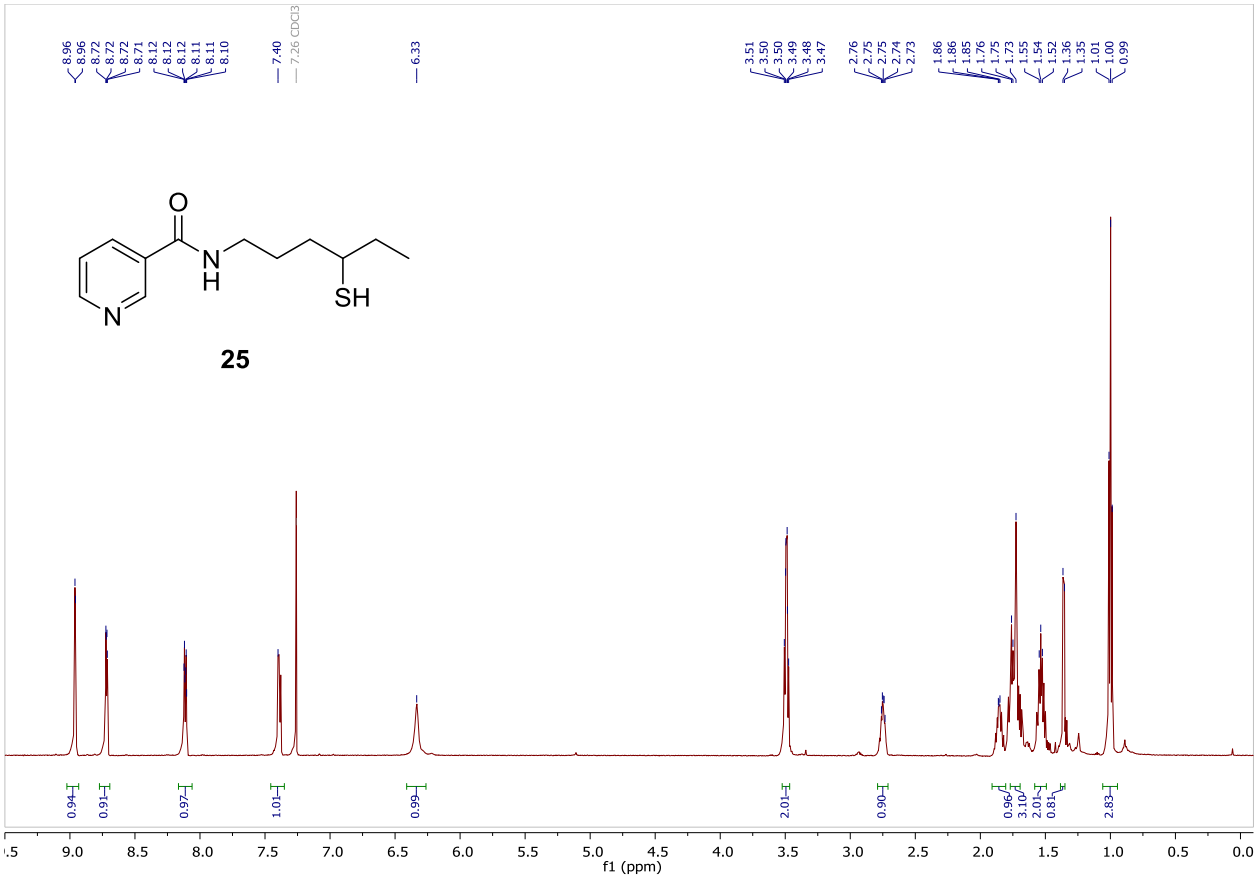

165.71
152.10
147.83
135.29
130.69
123.65
77.16 CDCl3
40.37
31.28
31.16
31.03
29.63
26.66
22.56
14.10
f1 (ppm)


8.96
8.96
8.72
8.72
8.71
8.71
8.12
8.11
8.11
8.10
8.10
7.40
7.39
7.38
7.37
7.26 CDCl3
6.42
6.41
6.40
3.51
3.50
3.50
3.49
3.27
3.26
3.26
3.25
3.25
3.24
1.81
1.80
1.79
1.79
1.78
1.78
1.78
1.77
1.73
1.72
1.71
1.61
1.60
1.60
1.59
1.59
1.59
1.59
1.58
1.58
1.00
0.99
0.98
O
N
H
N
N3
0.99
1.00
1.02
1.02
0.96
2.03
1.00
1.00
1.00
4.00
3.03
f1 (ppm)

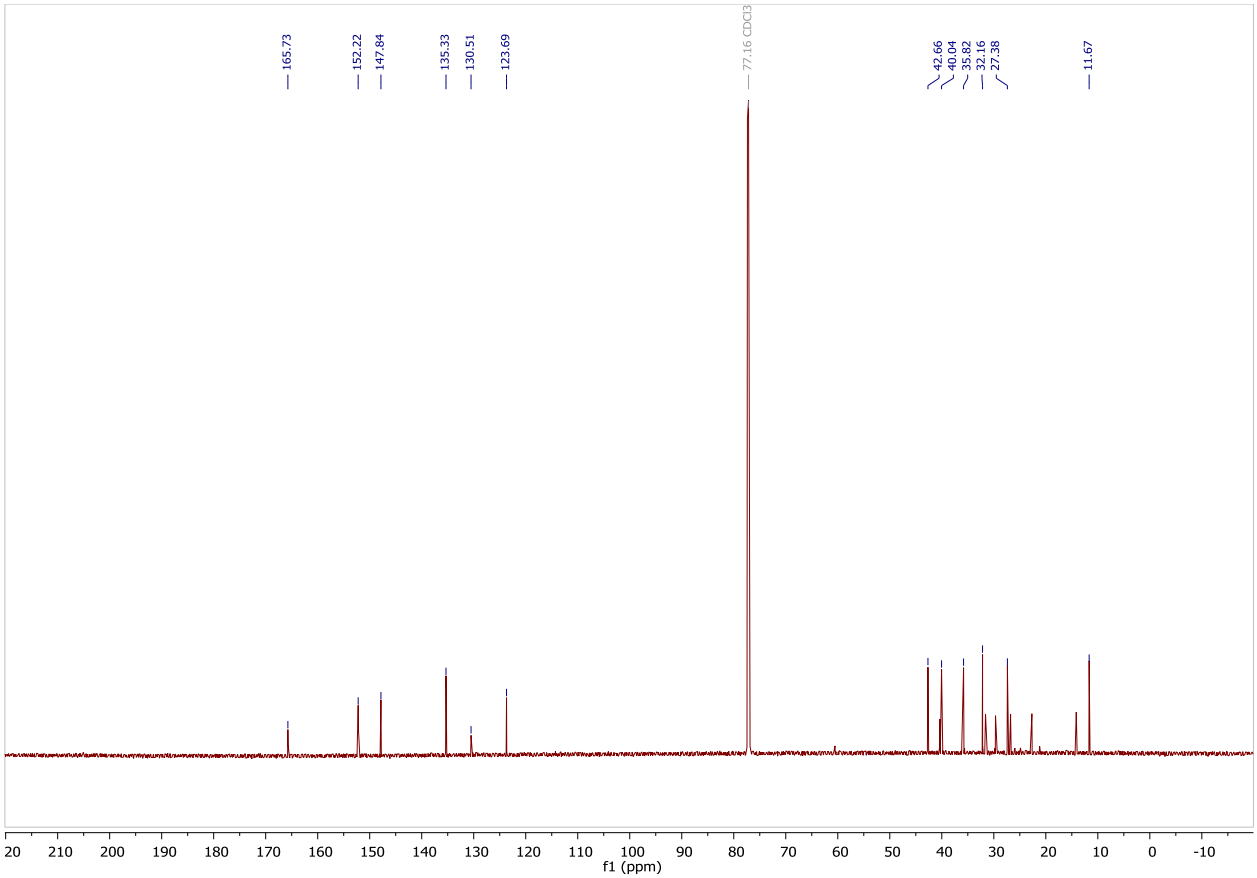
23


165.81
152.36
147.87
135.25
130.41
123.69
77.16 CDCl3
64.22
39.96
31.38
27.57
26.46
10.63
f1 (ppm)


24
f1 (ppm)
f1 (ppm)


8.96
8.96
8.72
8.72
8.72
8.71
8.12
8.12
8.12
8.11
8.11
8.10
7.40
7.26 CDCl3
6.33
3.51
3.50
3.50
3.49
3.48
3.47
2.76
2.75
2.75
2.74
2.73
1.86
1.86
1.85
1.76
1.75
1.73
1.55
1.54
1.52
1.36
1.35
1.01
1.00
0.99
O
N
H
N
SH
0.94
0.91
0.97
1.01
0.99
2.01
0.90
0.96
3.10
2.01
0.81
2.83
f1 (ppm)

25


165.73
152.22
147.84
135.33
130.51
123.69
77.16 CDCl3
42.66
40.04
35.82
32.16
27.38
11.67
f1 (ppm)