Supporting Information

C–H Xanthylation: A Synthetic Platform for Alkane Functionalization

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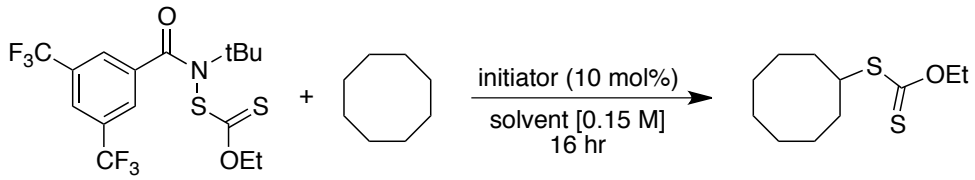
General Methods and Materials

Infrared (IR) spectra were obtained using a Jasco 260 Plus Fourier transform infrared spectrometer. GC spectra were obtained using a Shimadzu GC-2010 gas chromatograph with a Shimadzu AOC-20s Autosampler, and Shimadzu SHRXI-5MS GC column. The results of the kinetic isotope study were analyzed using an Agilent Gas Chromatograph-Mass Spectrometer with a 6850 series GC system and a 5973 Network Mass Selective Detector. 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, br. s. = broad singlet, app = apparent), coupling constants (Hz), and integration. Mass spectra were obtained using a Thermo LTqFT 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. Irradiation of xanthylation reactions was performed using either 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. UV light experiments were performed in a Luzchem LZC-ORG photoreactor containing UVA lamps. All other reagents were obtained from commercial sources and used without further purification unless otherwise noted.

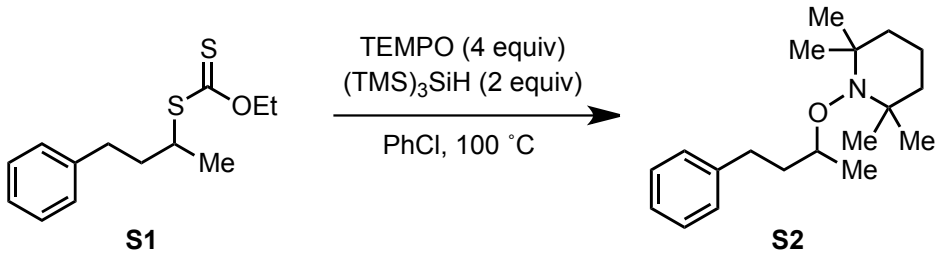
Reaction Optimization

Table S1. Optimization of Aliphatic Xanthylation



Entry	Initiator	Temperature	Solvent	N–S Cleaved	Yield (Based on Cleaved N–S)
1	AIBN	80 ˚C	PhH	24%	22% (92%)
2	DLP	80 ˚C	PhH	36%	25% (69%)
3	BPO	80 ˚C	PhH	26%	17% (65%)
4	BPO	100 ˚C	PhCl	63%	39% (62%)
5	*t*BuOO*t*Bu	130 ˚C	PhCl	37%	23% (62%)
6	23 W CFL (1M)	ambient	PhH	26%	17% (65%)
7	450 nm LED (1M)	ambient	PhH	22%	13% (59%)
8	450 nm LED (1M)	ambient	PhCF3	100%	81% (81%)

[a] NMR yield vs. hexamethyldisiloxane (HMDS) standard
AIBN = azobisisobutyronitrile, DLP = dilauroyl peroxide, BPO = benzoyl peroxide



2,2,6,6-tetramethyl-1-((4-phenylbutan-2-yl)oxy)piperidine (S2). Adapted from an analogous literature procedure using alkyl iodides.[1] Xanthate **S1** (51 mg, 0.20 mmol) was dissolved in PhCl (2.0 mL) and stirred at 100 °C, after which 2,2,6,6-tetramethylpiperidine-1-oxoammonium tetrafluoroborate (TEMPO; 125 mg, 0.80 mmol) and tris(trimethylsilyl)silane (TTMSS; 123 µL, 0.40 mmol) were added in two portions over 24 h. The reaction mixture was stirred for an additional 24 h. Next, Et_2O and saturated $Na_2S_2O_3$ were added. The organic layer was extracted, washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated. An analytical sample of

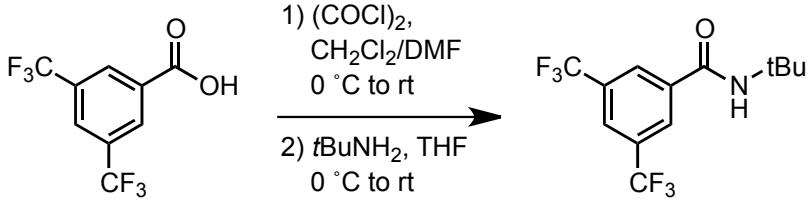
TEMPO-trapped product **S2** was obtained after purification by column chromatography (100:1 pentane/Et_2O). Spectral data were in accordance with literature values.[2]

Table S2. TEMPO-Trapping Condition Optimization

Entry	Deviations from standard conditions	% conversion	% yield (brsm)[a]
1	None	84	83 (98)
2	TEMPO and TTMSS added over 24 h by syringe pump	84	81 (96)
3	TEMPO and TTMSS added in one portion	85	51 (64)
4	2 equiv TEMPO and 1 equiv TTMSS added in one portion	50	46 (92)
5	2 equiv TEMPO and 1.5 equiv TTMSS added in one portion	70	41 (59)
6	1 equiv TEMPO and 1 equiv TTMSS added in one portion	48	28 (57)
7	[0.5 M] PhCl	89	57 (64)
8	120 °C	88	71 (81)
9	No silane added	0	-

[a] ^1H NMR yields based on trimethoxybenzene internal standard

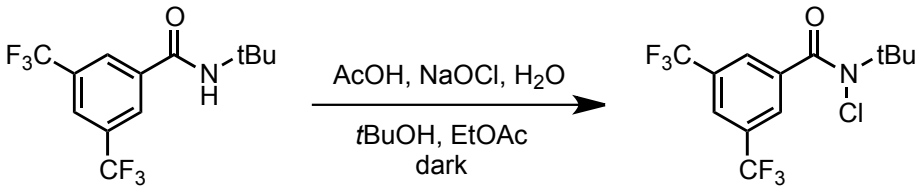
Xanthylamide Synthesis



S3

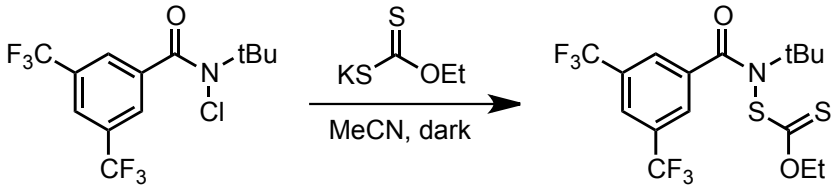
***N*-(*tert*-butyl)-3,5-bis(trifluoromethyl)benzamide (S3):** Prepared similarly to previous reports from our lab.[3, 4] To a solution of 3,5-bis(trifluoromethyl)benzoic acid (15 g, 58.11 mmol) in CH_2Cl_2/DMF (232 mL/1 mL) at 0 ˚C was added oxalyl chloride (9.85 mL, 116.23 mmol) dropwise, and the resulting solution was allowed to warm to rt overnight. The mixture was concentrated *in vacuo* and resuspended in THF (200 mL) and chilled to 0 ˚C. *t*-Butylamine (12.21 mL, 116.23 mmol) was added, and the mixture was warmed to rt and stirred overnight. The ammonium salts were filtered and the mixture was concentrated *in vacuo* and the residue suspended in Et_2O (250 mL) and washed with

3M NaOH (1 x 200 mL), 1M HCl (1 x 200 mL), brine (1 x 200 mL), dried with $MgSO_4$ and concentrated to afford **S3** as a pale yellow solid (16.12 g, 89% yield), which was used without purification.



S3 **S4**

***N*-(*tert*-butyl)-*N*-chloro-3,5-bis(trifluoromethyl)benzamide (S4):** Prepared similarly to a previous report from our lab.[4] With the laboratory lights off, to a solution of amide **S3** in EtOAc (296 mL) was added *t*BuOH (7.8 mL). To this solution was added a solution of AcOH (68 mL), NaOCl (172 mL), and H_2O (103 mL) dropwise over 2 h via addition funnel. The mixture was stirred vigorously for 2 days, then diluted with CH_2Cl_2 (200 mL) and quenched with sat. aq. $NaHCO_3$ (200 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 300 mL), and the combined organic phase was washed with brine (1 x 500 mL), dried with $MgSO_4$, and concentrated *in vacuo* followed by 1 day under high vacuum to afford chloroamide **S4** as a yellow oil (14.2 g, 97% yield), which was used without any additional purification.



S4 **1**

***N*-(*tert*-butyl)-*N*-((ethoxycarbonothioyl)thio)-3,5-bis(trifluoromethyl)benzamide (1):** Adapted from an analogous literature procedure using *N*-chlorophthalimide.[5] With the laboratory and hood lights off, in a 2-neck, 5L round-bottom flask, potassium ethyl xanthate (6.55 g, 40.84 mmol) was suspended in MeCN (1.7 L). To this suspension was added a solution of chloroamide **S4** (14.2 g, 40.84 mmol) in MeCN (350 mL) via cannula wire over 20 min. The round-bottom was foil wrapped and stirred for 16 h, at which point the suspension was concentrated *in vacuo* and left under high-vacuum for 20 h. The residue was taken up in CH_2Cl_2/H_2O (1:1, 2L total volume) and the layers were separated. The organic layer was washed with brine, dried with $MgSO_4$, and concentrated *in vacuo*. The resultant orange solid was purified by careful flash column chromatography on a short, wide silica column (hexanes flush until the first yellow band

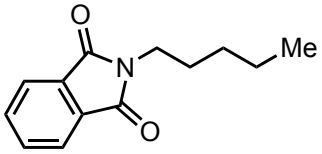
had fully eluted, then 0–5% Et_2O in hexanes) to afford xanthylamide **1** as a yellow solid (8.47 g, 48% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.86 (s, 2H), 4.71 – 4.61 (m, 2H), 1.58 (s, 9H), 1.49 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 212.00, 172.59, 139.98, 131.60 (q, *J* = 33.8 Hz), 127.11 (d, *J* = 3.9 Hz), 123.69 (q, *J* = 3.7 Hz), 123.05 (q, *J* = 272.8 Hz), 70.84, 64.15, 28.94, 13.77.
IR (film) 2981.41, 2938.02, 2360.44, 1680.66, 1368.25, 1279.59, 1183.11, 1136.83 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{16}H_{18}F_6NO_2S_2$ $[M+H]^+$, 434.0677. Found 434.0686.

The xanthylamide shows no degradation to the parent amide after being stored foil-wrapped at 0 ˚C for four months. At room temperature in $CDCl_3$ solution in ambient laboratory light, less than 5% degradation to the parent amide is observed after two months.

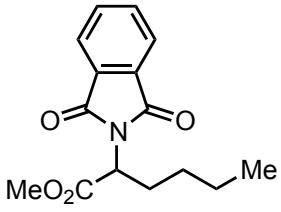
Substrates for C-H Xanthylation

Cyclopentane, cyclohexane, cycloheptane, cyclooctane, adamantane, *trans*-decalin, norbornane, *n*-hexane, 2-methylanisole, 15-crown-5, amyl acetate, methyl hexanoate, 2-heptanone, (3aR)-(+)-sclareolide, (–)-ambroxide, 2-(1-adamantyl)-4-bromoanisole, and (+)-longifolene were obtained commercially and used without further purification. Tetrahydrofuran and 1,4-dioxane were degassed with argon over 3Å molecular sieves prior to use.



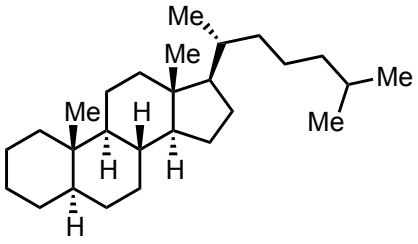
S5

2-Pentylisoindoline-1,3-dione (S5) was prepared according to a literature procedure, and spectral data were in accordance with the literature values.[3]



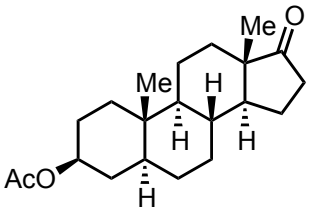
S6

Methyl 2-(1,3-dioxoisoindolin-2-yl)hexanoate (S6) was prepared according to a literature procedure, and spectral data were in accordance with the literature values.[4]



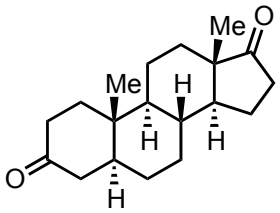
S7

Cholestane (S7) was prepared according to a literature procedure, and spectral data were in accordance with the literature values.[6]



S8

***Trans*-androsterone acetate (S8)** was prepared according to a literature procedure, and spectral data were in accordance with the literature values.[7]



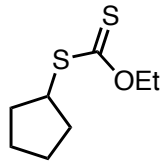
S9

5α-Androstanedione (S9): Pyridinium chlorochromate (PCC, 0.89 g, 4.2 mmol) was added to a solution of *trans*-androsterone (0.61 g, 2.1 mmol) in CH_2Cl_2 (15 mL). After stirring for 12 h at rt, the mixture was filtered, and the filtrate was washed with saturated $NaHSO_3$ and brine, dried over anhydrous Na_2SO_4, and concentrated. The resulting green residue was purified by column chromatography (20 – 50% EtOAc in hexanes) to yield the product (0.56 g, 93% yield) as a white solid. Physical and spectral data were in accordance with literature data.[8]

Independent Synthesis of Xanthate Standards

General Procedure A: To a suspension of potassium ethyl xanthate (1.5 equiv) in acetone (0.75 M wrt xanthate) was added alkyl bromide (1 equiv). The mixture was

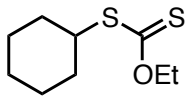
stirred at rt until consumption of the alkyl bromide as determined by GC-MS. The salts were removed by filtration and the filtrate concentrated. The residue was taken up in CH_2Cl_2 and washed with H_2O, brine, dried with $MgSO_4$, and concentrated to afford the alkyl xanthate.



2

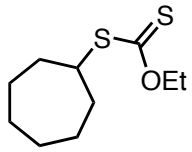
***S*-cyclopentyl *O*-ethyl carbonodithioate (2):** Prepared from cyclopentyl bromide according to General Procedure A (1 mmol scale) as a yellow oil (154 mg, 81% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.62 (q, *J* = 7.2 Hz, 2H), 3.95 – 3.83 (m, 1H), 2.20 – 2.11 (m, 2H), 1.73 – 1.67 (m, 2H), 1.63 – 1.58 (m, 4H), 1.41 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 215.26, 69.52, 48.28, 32.65, 24.95, 13.91.
IR (film) 2958.27, 2867.63, 2265.95, 1445.39, 1363.43, 1212.04, 1111.76, 1052.94 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_8H_{15}OS_2$ $[M+H]^+$, 191.0559. Found 191.0563.



3

***S*-cyclohexyl *O*-ethyl carbonodithioate (3)** was prepared according to a literature procedure, and spectral data were in accordance with the literature values.[9, 10]

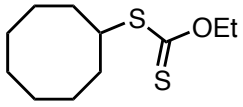


4

***S*-cycloheptyl *O*-ethyl carbonodithioate (4):** Prepared from cycloheptyl bromide according to General Procedure A (1 mmol scale) as a yellow oil (170.3 mg, 80% yield):

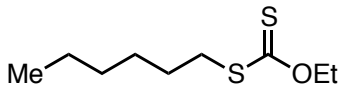
^{1}H NMR (600 MHz, CDCl3) δ 4.62 (q, *J* = 7.1 Hz, 2H), 3.79 (dt, *J* = 9.3, 4.8 Hz, 1H), 2.10 – 2.04 (m, 2H), 1.73 – 1.65 (m, 4H), 1.62 – 1.50 (m, 6H), 1.40 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, CDCl3) δ 214.86, 69.50, 50.56, 34.22, 28.27, 26.27, 13.91.
IR (film) 2981.41, 2927.41, 2853.17, 2359.48, 1457.92, 1210.11, 1110.80, 1051.98 cm^{-1}.

HRMS (ES+) Exact mass calcd for $C_{10}H_{19}OS_2$ $[M+H]^+$, 219.0872. Found 219.0877.



5

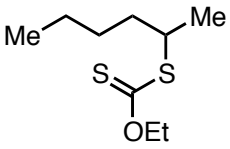
***S*-cyclooctyl *O*-ethyl carbonodithioate (5)** was prepared according to a literature procedure, and spectral data were in accordance with the literature values.[11]



6-1

***O*-ethyl *S*-hexyl carbonodithioate (6-1):** Prepared from 1-bromohexane according to General Procedure A (1 mmol scale) as a yellow oil (164.2 mg, 80% yield):

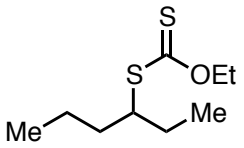
^{1}H NMR (600 MHz, CDCl3) δ 4.63 (q, *J* = 7.1 Hz, 2H), 3.10 (t, *J* = 7.5 Hz, 2H), 1.67 (q, *J* = 7.5 Hz, 2H), 1.43 – 1.37 (m, 5H), 1.32 – 1.26 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 215.29, 69.79, 36.01, 31.40, 28.67, 28.43, 22.60, 14.10, 13.90.
IR (film) 2956.34, 2928.38, 2856.06, 1457.92, 1363.43, 1218.79, 1111.76, 1051.01 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_9H_{19}OS_2$ $[M+H]^+$, 207.0872. Found 207.0872.



6-2

***O*-ethyl *S*-hexan-2-yl carbonodithioate (6-2):** Prepared from 2-bromohexane according to General Procedure A (1 mmol scale) as a yellow oil (388 mg, 84% yield):

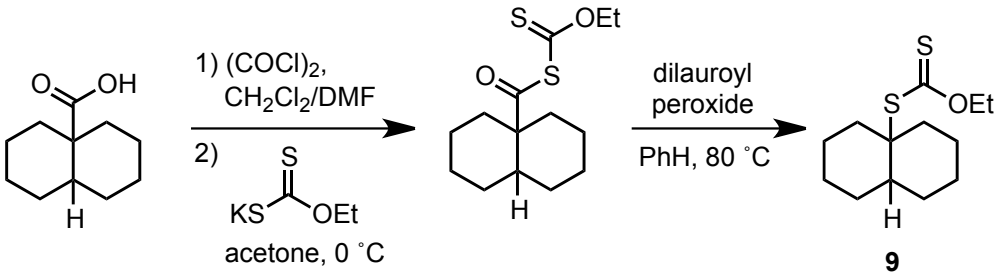
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.66 (q, *J* = 7.3 Hz, 2H), 3.77 – 3.68 (m, 1H), 1.75 – 1.66 (m, 1H), 1.66 – 1.55 (m, 1H), 1.47 – 1.30 (m, 10H), 0.96 – 0.90 (m, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.89, 69.62, 46.00, 35.68, 29.29, 22.62, 20.63, 14.12, 13.93.
IR (film) 2962.13, 2932.23, 2872.45, 2360.44, 2342.12, 1213.01, 1111.76, 1049.09 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_9H_{19}OS_2$ $[M+H]^+$, 207.0872. Found 207.0885.



6-3

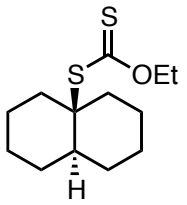
***O*-ethyl *S*-hexan-3-yl carbonodithioate (6-3):** Prepared from 3-bromohexane according to General Procedure A (1 mmol scale) as a yellow oil (190 mg, 85% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.64 (q, *J* = 7.1 Hz, 2H), 3.72 – 3.65 (m, 1H), 1.79 – 1.71 (m, 1H), 1.70 – 1.56 (m, 3H), 1.48 – 1.38 (m, 5H), 1.02 – 0.97 (m, 3H), 0.94 – 0.88 (m, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 215.37, 69.75, 52.69, 35.80, 27.25, 20.20, 14.12, 13.95, 11.34.
IR (film) 2958.27, 2929.34, 2859.72, 1456.96, 1211.08, 1111.76, 1051.98 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_9H_{19}OS_2$ $[M+H]^+$, 207.0872. Found 207.0880.



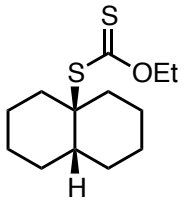
9

***S*-(decahydronaphthalen-4a-yl) *O*-ethyl carbonodithioate (9):** A solution of decahydronaphthalene-4a-carboxylic acid[12] (182 mg, 1 mmol) in CH_2Cl_2 (5 mL) was treated with oxalyl chloride (2 mmol, 0.17 mL) and DMF (1 drop) in in a 25 mL round-bottom flask. After stirring at rt for 2 h, the reaction mixture was concentrated *in vacuo*, yielding the crude acid chloride which was used directly without further purification. To a solution of acid chloride in acetone (5 mL) at 0 °C was added potassium ethyl xanthate (152 mg, 0.95 mmol). After stirring for 2 h, the solution was concentrated, redissolved in CH_2Cl_2, and washed with H_2O. The aqueous layer was extracted with CH_2Cl_2 (x 2), and the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting product was purified by flash column chromatography on silica (5% EtOAc in hexanes) to give a yellow oil (60.1 mg, 0.21 mmol, 21% yield), which was dissolved in benzene (0.42 mL) and heated at 80 ˚C with dilauroyl peroxide (4 mg, 5 mol %) overnight. The solution was concentrated *in vacuo* and the residue purified by flash column chromatography on silica (hexanes) to give the *trans*- (16.1 mg, 30% yield) and *cis*- (7.4 mg, 14% yield) isomers as off-white solids:



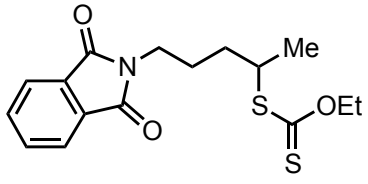
9-trans

***S*-((4a*s*,8a*s*)-decahydronaphthalen-4a-yl) *O*-ethyl carbonodithioate (9-trans):**
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.65 (q, *J* = 7.1 Hz, 2H), 2.58 (dt, *J* = 13.9, 3.9 Hz, 2H), 1.89 (qt, *J* = 13.2, 4.0 Hz, 2H), 1.81 – 1.71 (m, 2H), 1.60 – 1.49 (m, 3H), 1.50 – 1.38 (m, 4H), 1.38 – 1.15 (m, 7H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.03, 69.55, 64.32, 48.19, 37.58, 28.98, 26.55, 22.43, 13.86.
IR (film) 2924.52, 2846.42, 1445.39, 1243.86, 1213.97, 1114.65, 1035.59, 933.34 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{13}H_{23}OS_2$ $[M+H]^+$, 259.1185. Found 259.1192.



9-cis

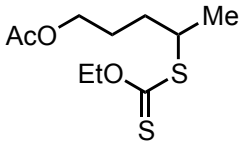
***S*-((4a*r*,8a*r*)-decahydronaphthalen-4a-yl) *O*-ethyl carbonodithioate (9-cis):**
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (q, *J* = 7.1 Hz, 2H), 2.16 – 1.97 (m, 5H), 2.16 – 1.37 (m, 15H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.87, 69.42, 63.16, 38.77, 28.18, 22.87, 13.88.
IR (film) 2928.38, 2859.92, 1456.96, 1215.90, 1111.76, 1040.41, 970.02 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{13}H_{23}OS_2$ $[M+H]^+$, 259.1185. Found 259.1198.



15

***S*-(5-(1,3-dioxoisoindolin-2-yl)pentan-2-yl) *O*-ethyl carbonodithioate (15):** Prepared from 2-(4-bromopentyl)isoindoline-1,3-dione[3] according to General Procedure A (1 mmol scale) as a yellow oil (137.6 mg, 41% yield):

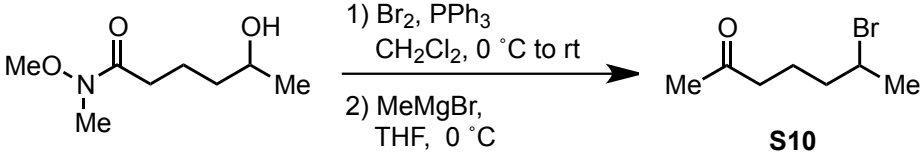
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.82 (m, 2H), 7.73 – 7.70 (m, 2H), 4.61 (q, *J* = 7.2 Hz, 2H), 3.76 (q, *J* = 6.9 Hz, 1H), 3.72 – 3.66 (m, 2H), 1.85 – 1.71 (m, 3H), 1.69 – 1.62 (m, 1H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.37 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.33, 168.49, 134.09, 132.17, 123.37, 69.78, 45.52, 37.75, 33.24, 26.29, 20.61, 13.92.
IR (film) 2934.16, 1772.26, 1714.41, 1615.09, 1466.60, 1396.21, 1213.01, 1048.12 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{16}H_{20}NO_3S_2$ $[M+H]^+$, 338.0879. Found 338.0897.



17

4-((ethoxycarbonothioyl)thio)pentyl acetate (17): Prepared from 4-chloropentyl acetate[4] according to General Procedure A (1 mmol scale) as a yellow oil (38.2 mg, 40% yield):

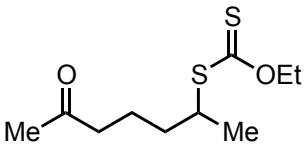
^{1}H NMR (600 MHz, CDCl3) δ 4.63 (q, *J* = 7.1 Hz, 2H), 4.08 – 4.04 (m, 2H), 3.76 – 3.72 (m, 1H), 2.04 (s, 3H), 1.78 – 1.71 (m, 3H), 1.71 – 1.63 (m, 1H), 1.43 – 1.37 (m, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.36, 171.21, 69.77, 64.14, 45.56, 32.50, 26.24, 21.10, 20.57, 13.91.
IR (film) 2959.23, 2868.59, 2360.44, 1739.48, 1365.35, 1237.11, 1111.76, 1048.12 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{10}H_{19}O_3S_2$ $[M+H]^+$, 251.0770. Found 251.0769.



S10

6-bromoheptan-2-one (S10): To a solution of triphenylphosphine (1.15 g, 4.4 mmol) in CH_2Cl_2 (15 mL) at 0 ˚C was added bromine (225 uL, 4.4 mmol) followed by a solution of 5-hydroxy-*N*-methoxy-*N*-methylhexanamide[13] (701 mg, 4 mmol) in CH_2Cl_2 (5 mL). The mixture was warmed to room temperature and stirred overnight, after which it was quenched by the addition of H_2O (20 mL). The layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were dried with $MgSO_4$ and concentrated *in vacuo* to afford a yellow solid that was purified by flash column chromatography (30 – 40% EtOAc in hexanes) to afford 5-bromo-*N*-methoxy-*N*-methylhexanamide as a yellow oil (822 mg, 86% yield).

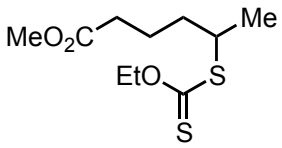
To a solution of 4-bromo-*N*-methoxy-*N*-methylpentanamide (200 mg, 0.84 mmol) in THF (3.5 mL) at 0 ˚C was added MeMgBr (0.56 mL, 1.68, 3M in Et_2O) dropwise over 10 min. The mixture was maintained at 0 ˚C for 2 h and then quenched with 8 mL saturated aqueous NH_4Cl. The aqueous phase was extracted with Et_2O (3 x 10 mL), and the combined organic phase was washed with brine (20 mL), dried with $MgSO_4$, and concentrated *in vacuo* to afford 5-bromohexan-2-one (**S10**) (84 mg, 52% yield) in accordance with literature data.



18

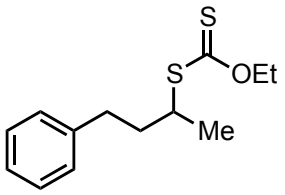
O-ethyl S-(6-oxoheptan-2-yl) carbonodithioate (18): Prepared from 5-bromohexan-2-one[3] according to General Procedure A (1 mmol scale) to afford xanthate **18** as a yellow oil (47.3 mg, 86% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.63 (q, *J* = 6.8 Hz, 2H), 3.76 – 3.65 (m, 1H), 2.51 – 2.40 (m, 2H), 2.13 (s, 3H), 1.73 – 1.55 (m, 4H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.37 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.57, 208.56, 69.74, 45.68, 43.24, 35.36, 30.08, 21.18, 20.40, 13.91.
IR (film) 2926.45, 1716.34, 1540.85, 1455.99, 1361.50, 1213.01, 1111.76, 1048.12 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{10}H_{19}O_2S_2$ $[M+H]^+$, 235.0821. Found 235.0838.



19

Methyl 5-((ethoxycarbonothioyl)thio)hexanoate (19): Prepared from methyl 5-bromohexanoate[3] according to General Procedure A (1 mmol scale) as a yellow oil (128 mg, 51% yield):
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.63 (q, *J* = 7.1 Hz, 2H), 3.72 (m, 1H), 3.66 (s, 3H), 2.33 (t, *J* = 7.2 Hz, 2H), 1.79 – 1.69 (m, 3H), 1.66 – 1.60 (m, 1H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.37 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.49, 173.78, 69.73, 51.69, 45.57, 35.44, 33.78, 22.48, 20.44, 13.91.
IR (film) 2952.48, 2868.59, 1738.51, 1436.71, 1364.39, 1213.01, 1111.76, 1048.12 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{10}H_{19}O_3S_2$ $[M+H]^+$, 251.0770. Found 251.0770.



S1

O-ethyl S-(4-phenylbutan-2-yl) carbonodithioate (S1): Prepared from (3-bromobutyl)benzene (3 mmol) according to General Procedure A (3 mmol scale) as a yellow oil (526 mg, 69%):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.22 – 7.17 (m, 3H), 4.64 (q, *J* = 7.1 Hz, 2H), 3.76 (h, *J* = 6.9 Hz, 1H), 2.83 – 2.67 (m, 2H), 2.02 (ddt, *J* = 13.7, 9.7, 6.8 Hz, 1H), 1.91 (ddt, *J* = 13.8, 9.5, 6.6 Hz, 1H), 1.45 – 1.41 (m, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.41, 141.47, 128.56, 128.53, 126.14, 69.75, 45.50, 37.87, 33.46, 20.71, 13.94.
IR (film) 3437.49, 3084.58, 3025.76, 2977.55, 2924.52, 2860.88, 1213.01, 1055.84 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{13}H_{19}OS_2$ $[M+H]^+$, 255.0872. Found 255.0885.

Synthesis of Alkyl Xanthates via C–H Xanthylation

General Procedure B: A 1 dram vial was charged with xanthylamide **1** (1 equiv) in the dark (overhead laboratory lights turned off), fitted with a PTFE lined screw cap, and taken into the glovebox. The xanthylamide was dissolved in $PhCF_3$ (1M wrt substrate), and the resulting solution was sealed with Teflon tape and removed from the glovebox. Liquid substrate (1 equiv) was added by syringe, and the vial was placed in a 3D-printed holder (see below pictures). 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. A steady stream of nitrogen was blown over the top of the vials to keep the reaction temperature as close to room temperature as possible, and the apparatus was covered with aluminum foil. The reaction was irradiated until completion and then either diluted with CH_2Cl_2 and added dodecane (1 equiv) for GC analysis or concentrated *in vacuo* and added hexamethyldisiloxane (0.17 equiv) for NMR analysis. When a standard could not be easily prepared, the crude residue was purified by flash column chromatography to afford the alkyl xanthate products.

General Procedure C: A 1 dram vial was charged with xanthylamide **1** (1–3 equiv) in the dark (overhead laboratory lights turned off), fitted with a PTFE lined screw cap, and taken into the glovebox. The xanthylamide was dissolved in $PhCF_3$ (0.15 mL), and the

resulting solution was sealed with Teflon tape and removed from the glovebox. Liquid substrate (0.15 mmol, 1 equiv) was added by syringe (note: solid substrate is added at the same time as xanthylamide outside the glovebox), and the vial was placed in a 3D-printed holder. The holder was suspended above an Ecoxotic PAR38 23 W blue LED such that the bottom of each vial was directly aligned with and 1 cm above one of the five LEDs, and the apparatus was covered with aluminum foil. The reaction was irradiated until completion and then either diluted with CH_2Cl_2 and added dodecane (1 equiv) for GC analysis or concentrated *in vacuo* and added hexamethyldisiloxane (0.17 equiv) for NMR analysis. When a standard could not be easily prepared or for complex substrates, the crude residue was purified by flash column chromatography to afford the alkyl xanthate products.

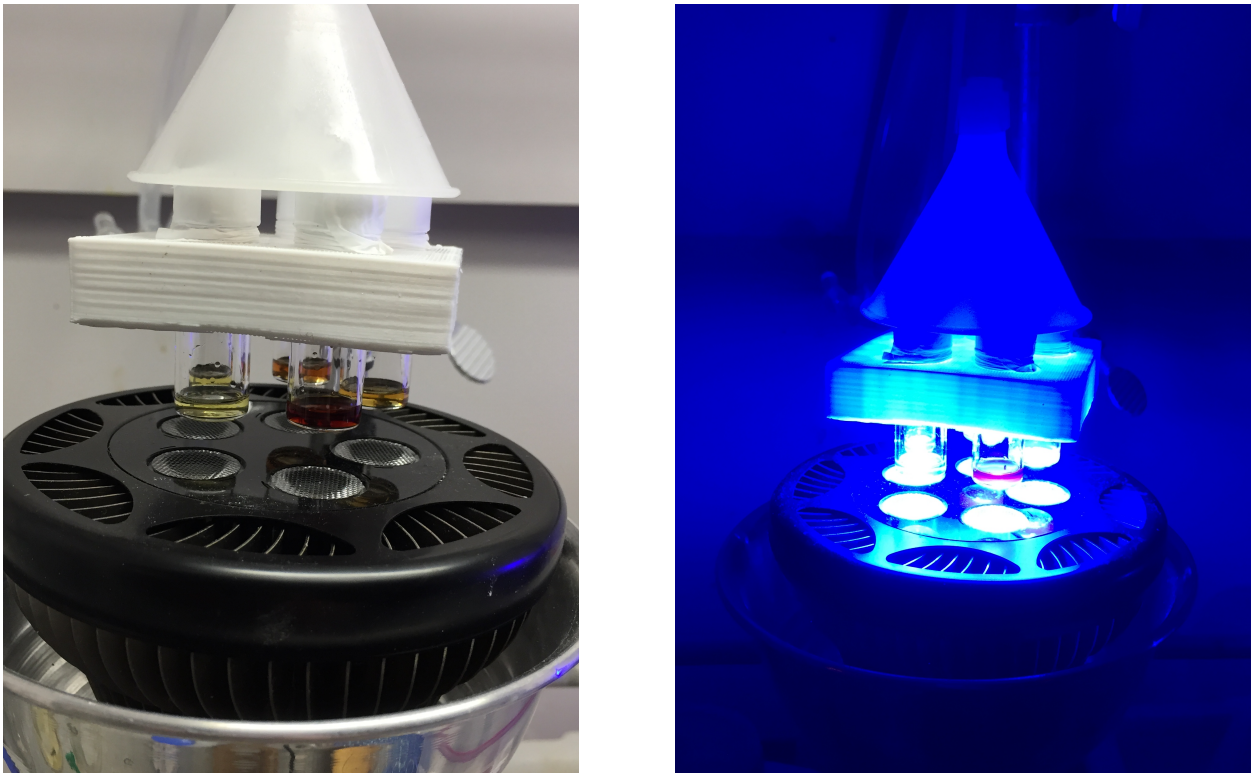


Figure S1. Pictures of C–H xanthylation reactions with the blue LED turned off or on for General Procedures B and C. The reaction vials are suspended in a 3D-printed vial holder such that the bottom of the vials is about 1 cm from the LED below. The inverted funnel above the reactions is used to pass N_2 gas over the reactions in General Procedure B to keep them as close to room temperature as possible for volatile substrates. For other substrates using General Procedure C, the inverted funnel is simply omitted.

General Procedure D: A 1 dram vial with a stir bar was charged with xanthylamide **1** (1–3 equiv) and solid substrate (1 equiv) in the dark (overhead laboratory lights turned off), fitted with a PTFE lined screw cap, and taken into the glovebox. The xanthylamide was dissolved in $PhCF_3$ or C_6F_6 (1 M), 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 34W LED Grow Light from the side (2 cm away) with the apparatus covered by aluminum foil until completion. The reaction was then concentrated *in vacuo* or by passing a stream of nitrogen over the solution. The crude residue was purified by flash column chromatography to afford the alkyl xanthate products.

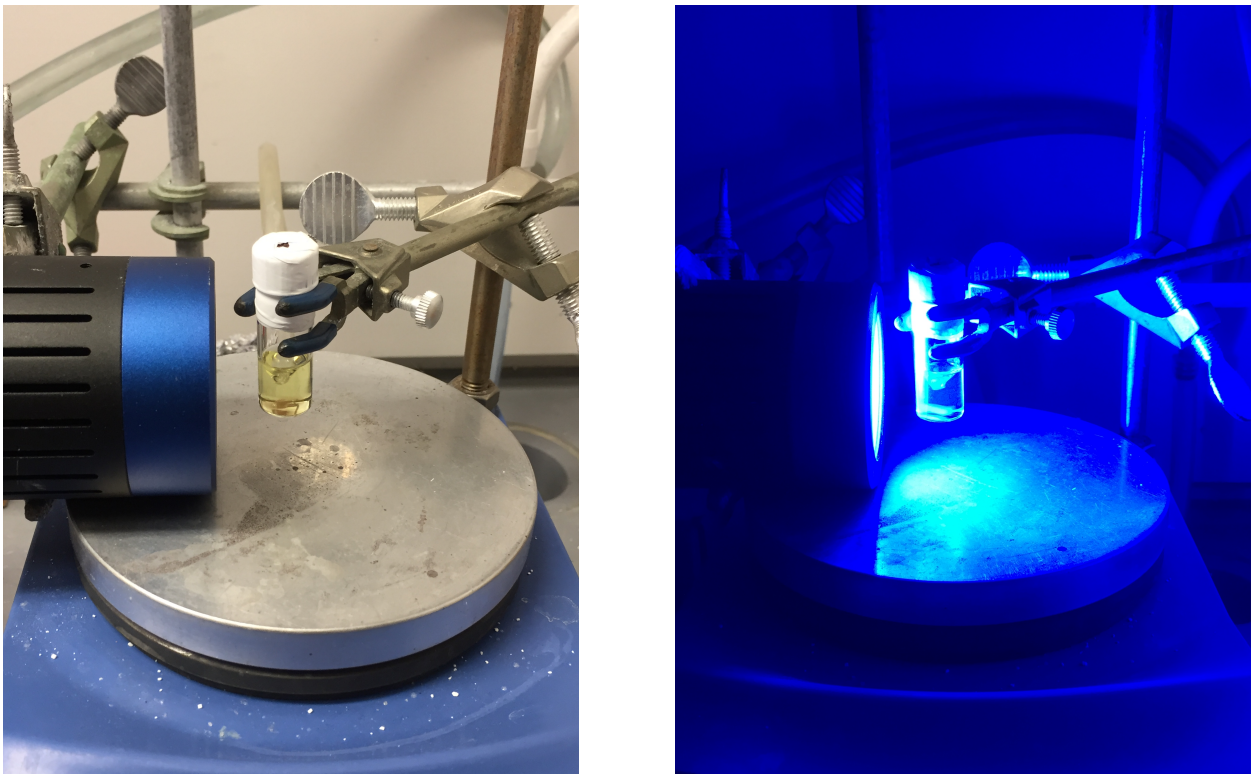


Figure S2. Pictures of C–H xanthylation reactions with the blue LED turned off or on for General Procedure D. The reaction vial is suspended such that it is approximately 1–2 cm away from the Kessil blue LED.

General Procedure E: A 1 dram vial with a stir bar was charged with xanthylamide **1** (3 equiv) and solid substrate (1 equiv) in the dark (overhead laboratory lights turned off), fitted with a PTFE lined screw cap, and taken into the glovebox. The xanthylamide was dissolved in MeCN or C_6F_6 (1 M), and the resulting solution was sealed with Teflon tape and removed from the glovebox. The vial was placed directly on a stir plate maintained at 80 °C and irradiated with a Kessil Blue KSH150B 34W LED Grow Light from the side

(2 cm away) with the apparatus covered by aluminum foil until completion. The reaction was then concentrated *in vacuo* or by passing a stream of nitrogen over the solution. The crude residue was purified by flash column chromatography to afford the alkyl xanthate products.

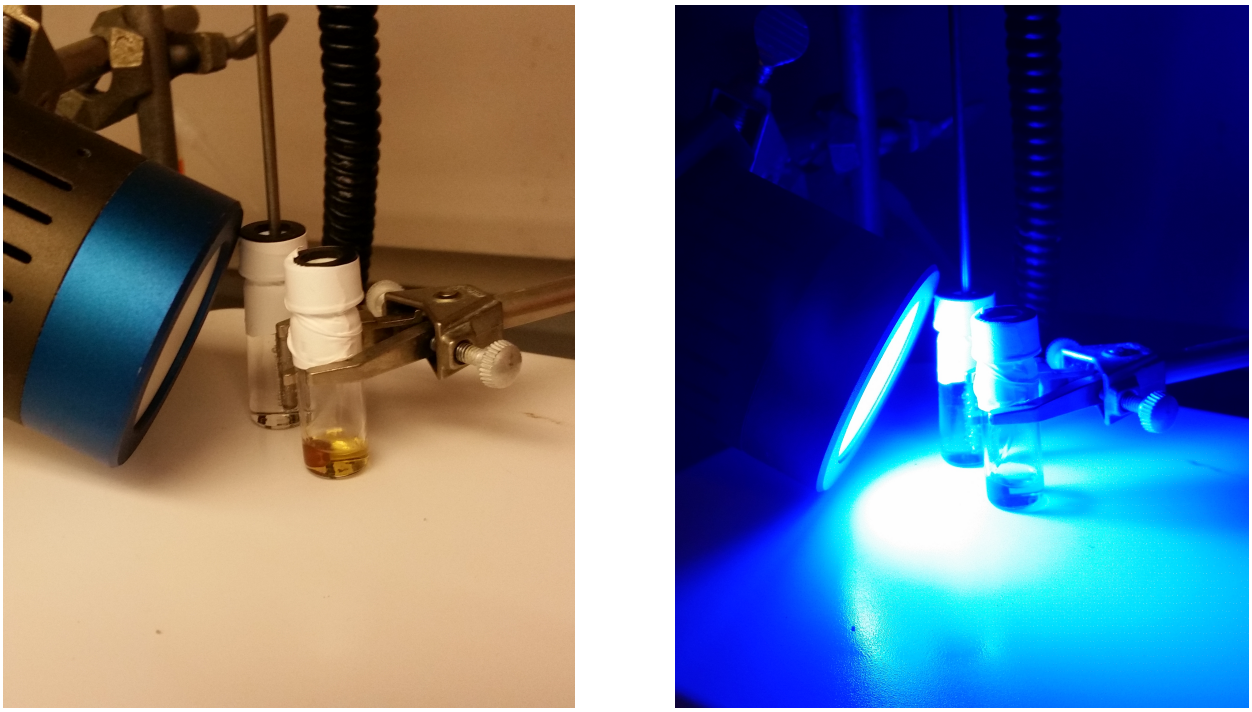
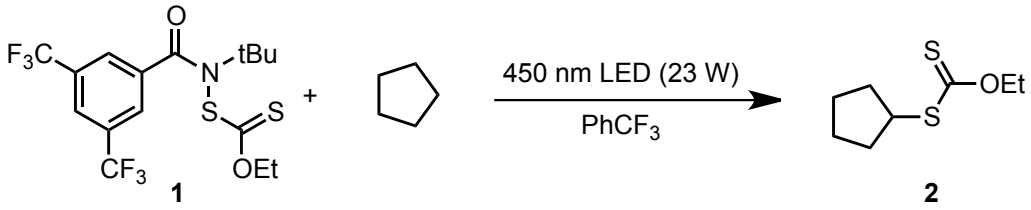
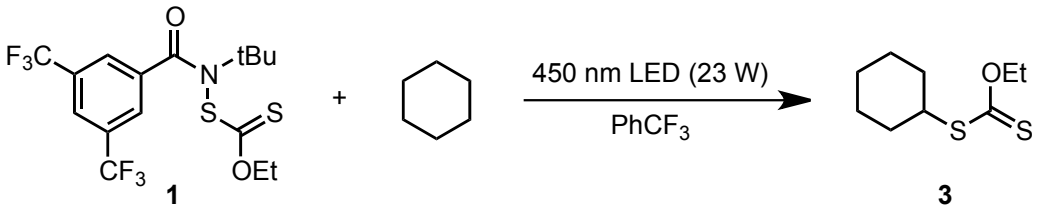


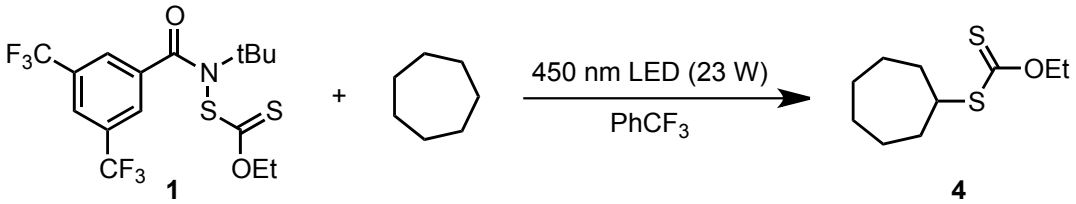
Figure S3. Pictures of C–H xanthylation reactions with the blue LED turned off or on for General Procedure E. The reaction vial is placed directly on the hot plate such that it is approximately 1–2 cm away from the Kessil blue LED. The temperature probe of the IKA is placed in a vial of $PhCF_3$ and set at 80 ˚C as means of temperature regulation.



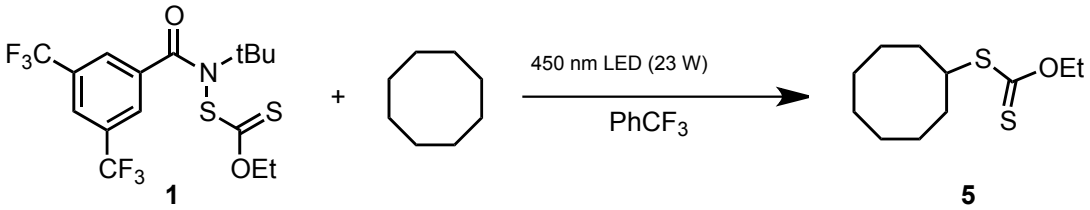
***S*-cyclopentyl *O*-ethyl carbonodithioate (2):** Prepared according to General Procedure B (0.15 mmol scale) using cyclopentane and xanthylamide **1** (1 equiv), giving 59% NMR yield.



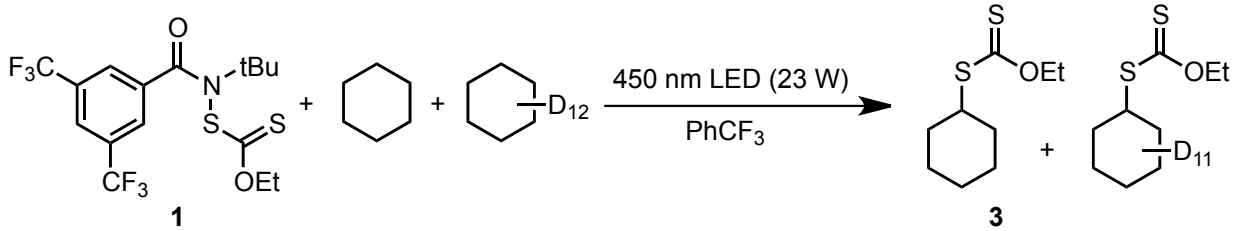
***S*-cyclohexyl *O*-ethyl carbonodithioate (3):** Prepared according to General Procedure B (0.15 mmol scale) using cyclohexane and xanthylamide **1** (1 equiv), giving 77% NMR yield.



***S*-cycloheptyl *O*-ethyl carbonodithioate (4):** Prepared according to General Procedure B (0.15 mmol scale) using cycloheptane and xanthylamide **1** (1 equiv), giving 73% NMR yield.

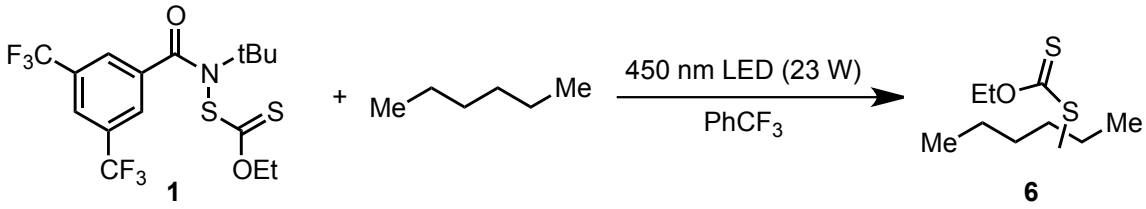


***S*-cyclooctyl *O*-ethyl carbonodithioate (5):** Prepared according to General Procedure B (0.15 mmol scale) using cyclooctane and xanthylamide **1** (1 equiv), giving 85% NMR yield.



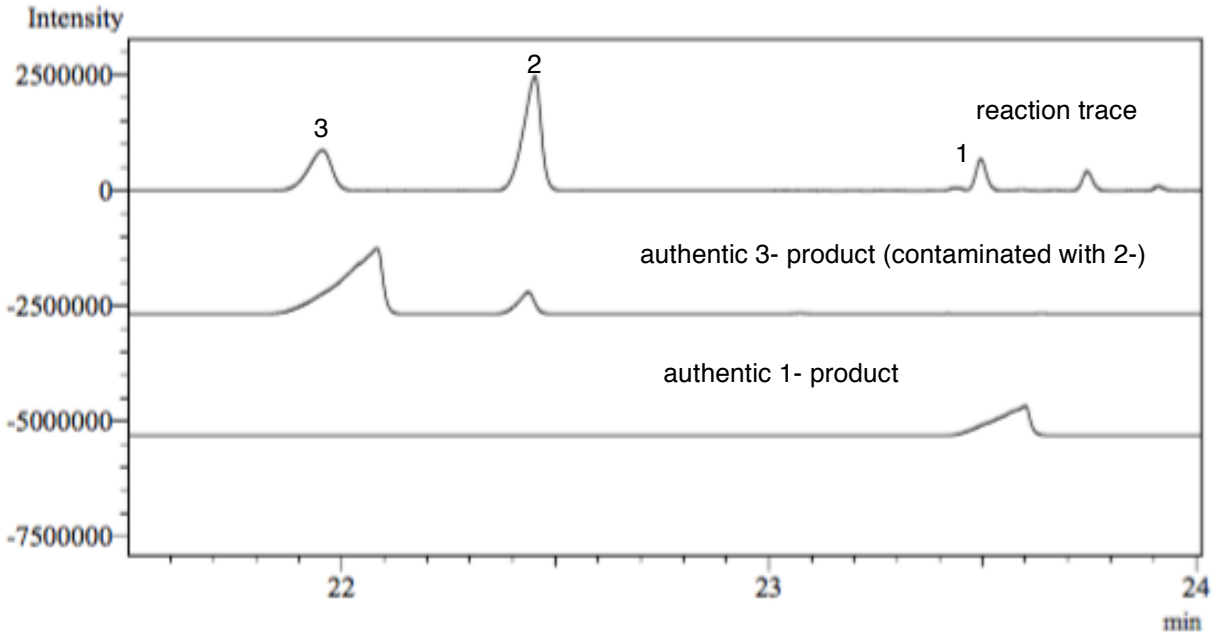
Competition Experiment: A 1 dram vial was charged with xanthylamide **1** (65 mg, 0.15 mmol) in the dark (overhead laboratory lights turned off), fitted with a PTFE lined screw cap, and was taken into the glovebox. The xanthylamide was dissolved in $PhCF_3$ (0.15 mL), and cyclohexane (81 uL, 0.75 mmol) and cyclohexane-d12 (80.8 uL, 0.75 mmol) were added. The reaction mixture was sealed with Teflon tape, removed from the glovebox, and irradiated from below according to General Procedure B for 5 min. The

reaction mixture was diluted with CH_2Cl_2, passed over a short silica plug, and analyzed using an Agilent Gas Chromatograph-Mass Spectrometer with a 6850 series GC system and a 5973 Network Mass Selective Detector to determine the ratio of non-deuterated to deuterated product (K_H/K_D = 6.3).

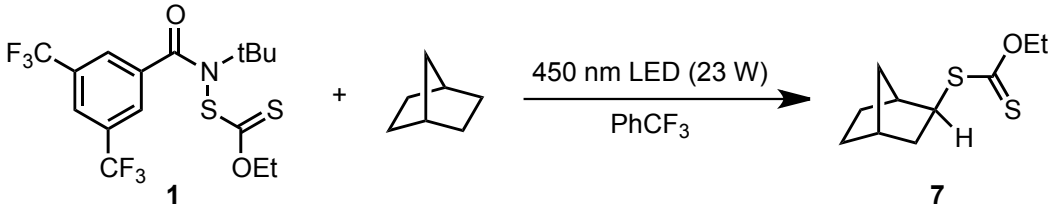


Reaction with *n*-Hexane: Prepared according to General Procedure B (0.15 mmol scale) using *n*-hexane and xanthylamide **1** (1 equiv), giving 64% combined NMR yield. The product distribution was determined by GC analysis and comparison to independently synthesized standards.

Figure S4. Distribution of *n*-Hexane Xanthates

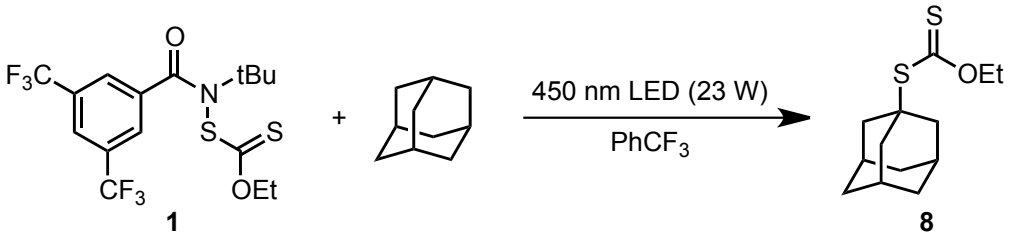


Product	% area
1	6.6
2	63.7
3	29.7



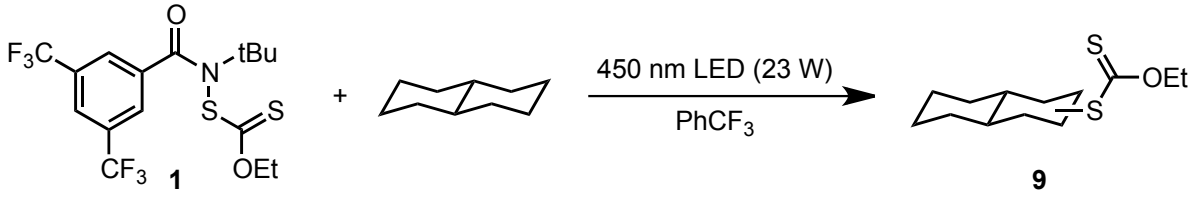
***S*-(1*S*,2*S*,4*R*)-bicyclo[2.2.1]heptan-2-yl *O*-ethyl carbonodithioate (7):** Prepared according to General Procedure B (0.15 mmol scale) using norbornane (note: the norbornane was added in the glovebox to prevent sublimation upon entering the glovebox) and xanthylamide **1** (1 equiv), giving 49% NMR yield. The residue was purified by flash column chromatography on silica (pentanes) to afford pure norbornyl xanthate as a yellow oil (4.9 mg, 15% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.62 (q, *J* = 7.1 Hz, 2H), 3.57 – 3.50 (m, 1H), 2.41 (s, 1H), 2.31 (s, 1H), 1.83 (ddd, *J* = 13.3, 8.6, 2.4 Hz, 1H), 1.64 (tt, *J* = 12.3, 4.5 Hz, 1H), 1.56 – 1.51 (m, 1H), 1.46 – 1.34 (m, 6H), 1.26 – 1.20 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 215.20, 69.55, 50.94, 43.00, 37.23, 36.53, 36.33, 29.03, 28.53, 13.96.
IR (film) 2955.38, 2870.52, 2359.48, 1453.10, 1213.97, 1138.76, 1110.80, 1056.80 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{10}H_{16}OS_2Na$ $[M+Na]^+$, 239.0540. Found 239.1271.

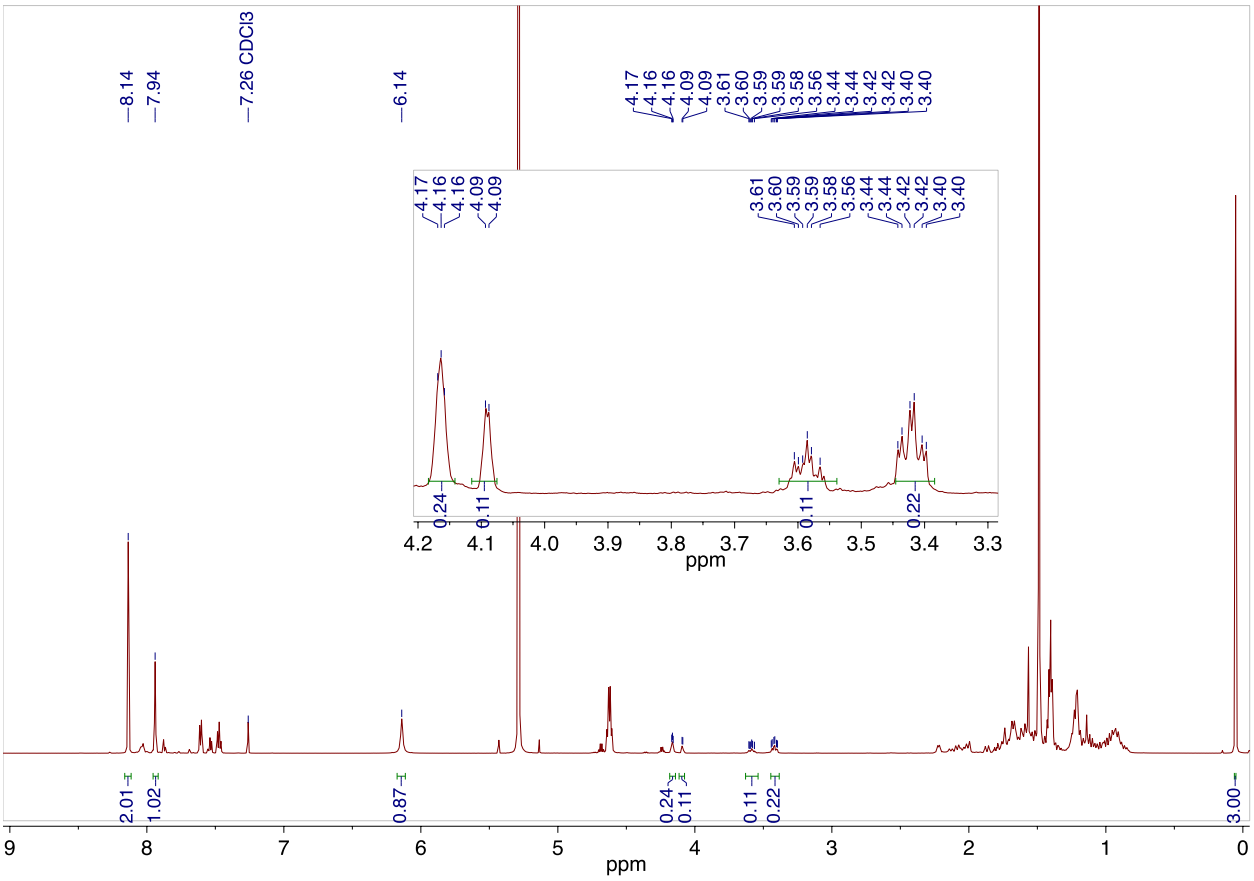


***S*-adamantan-1-yl *O*-ethyl carbonodithioate (8):** Prepared according to General Procedure C (0.15 mmol scale) using adamantane and xanthylamide **1** (1 equiv), giving 70% NMR yield. The residue was purified by flash column chromatography on silica (pentanes) to afford an inseparable mixture of adamantyl xanthate and bisxanthate as a yellow oil (23.1 mg, 60% yield):

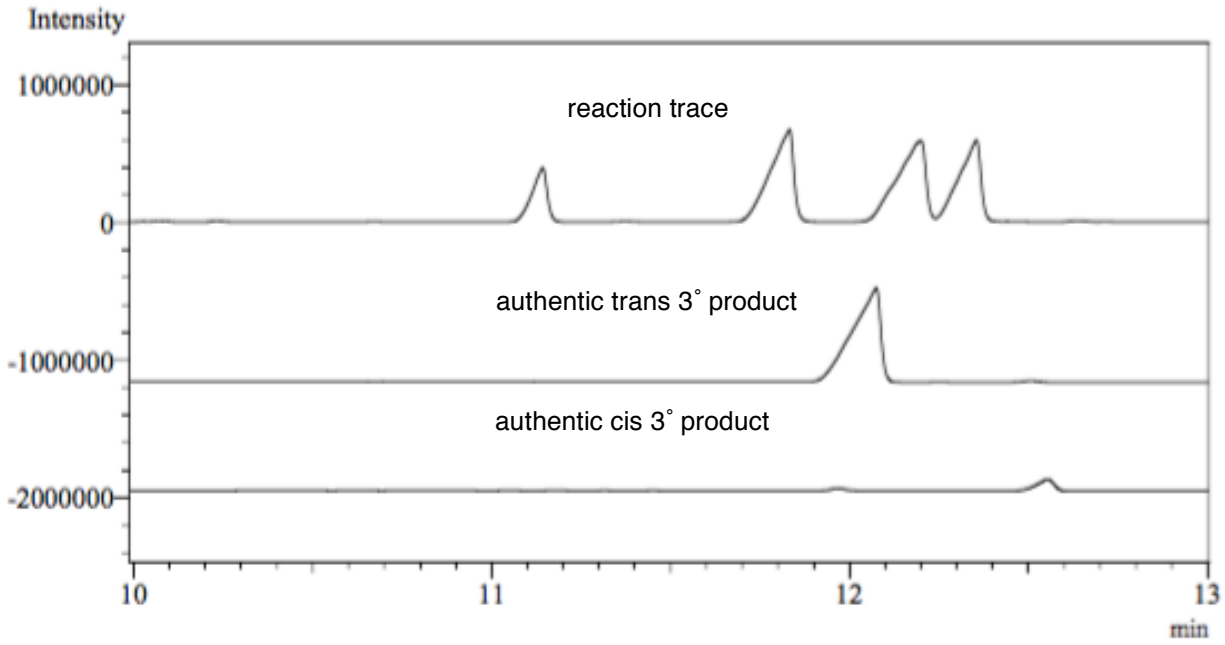
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.66 (q, *J* = 7.1 Hz, 2H), 2.17 – 2.11 (m, 6H), 2.11 – 2.04 (m, 3H), 1.72 (d, *J* = 3.0 Hz, 6H), 1.48 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.45, 69.40, 54.65, 42.00, 36.32, 29.93, 13.87.
IR (film) 2908.13, 2850.27, 2360.44, 1453.10, 1366.32, 1219.76, 1112.73, 1027.87 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{13}H_{21}OS_2$ $[M+H]^+$, 257.1028. Found 257.1036.

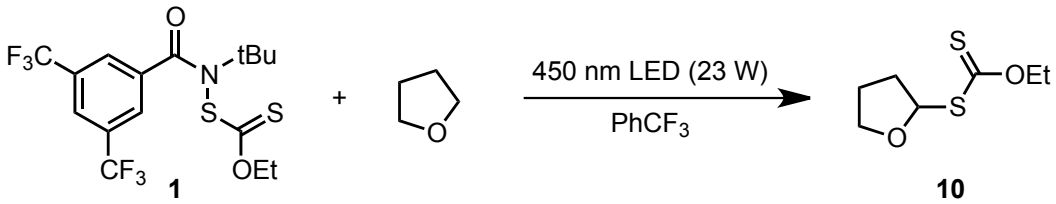


Reaction with *trans*-decalin: Prepared according to General Procedure C (0.15 mmol scale) using trans-decalin and xanthylamide **1** (1 equiv), giving 69% combined NMR yield of secondary xanthate products (as determined by analogy with our previous halogenation chemistry).[3]

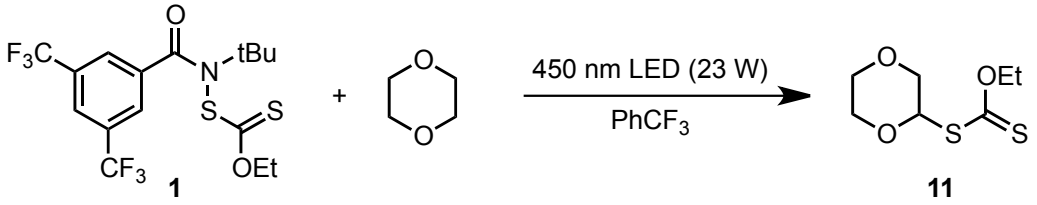


GC analysis was used to verify that no tertiary product was formed in the reaction.

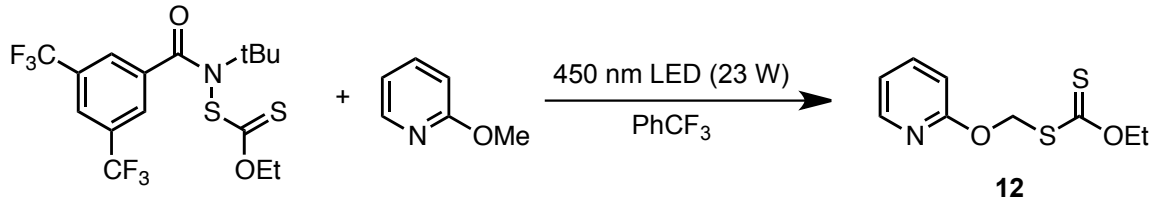




O-ethyl S-(tetrahydrofuran-2-yl) carbonodithioate (10): Prepared according to General Procedure B (0.15 mmol scale) using tetrahydrofuran and xanthylamide **1** (1 equiv), giving 54% NMR yield. Spectral data was in accordance with literature values.[11]



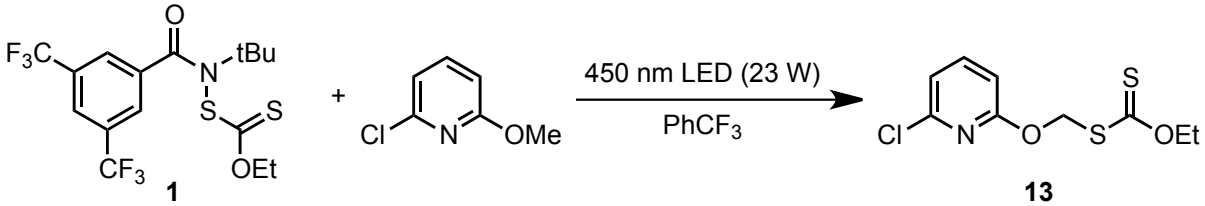
S-(1,4-dioxan-2-yl) O-ethyl carbonodithioate (11): Prepared according to General Procedure B (0.15 mmol scale) using dioxane and xanthylamide **1** (1 equiv), giving 50% NMR yield. Spectral data was in accordance with literature values.[11]



12

O-ethyl S-((pyridin-2-yloxy)methyl) carbonodithioate (12): Prepared according to General Procedure C (0.30 mmol scale) using 2-methoxypyridine and xanthylamide **1** (1 equiv), giving 55% NMR yield. The crude residue was purified by flash column chromatography to afford pure **12** as a yellow oil (35.1 mg, 51% yield):

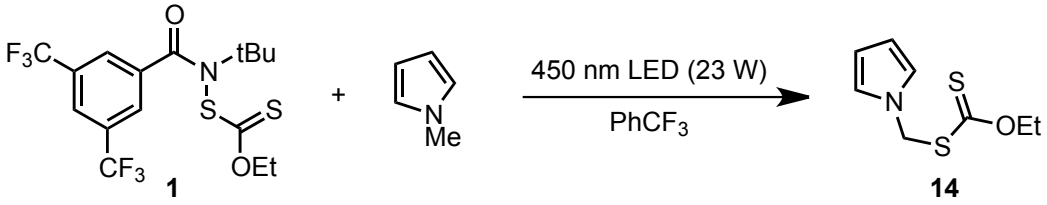
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 5.0, 1.9 Hz, 1H) 7.60 (ddd, *J* = 8.7, 7.2, 2.1 Hz, 1H), 6.93 (ddd, *J* = 7.1, 5.1, 1.0 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.05 (s, 2H), 4.68 (q, *J* = 7.0 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 213.24, 161.97, 146.62, 139.12, 117.96, 111.83, 70.48, 69.08, 13.87.
IR (film) 2980.45, 1471.42, 1434.78, 1279.54, 1230.36, 1141.65, 1054.87, 1008.59, 778.13 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_9H_{12}NO_2S_2$ $[M+H]^+$, 230.0304. Found 230.0304.



1 **13**

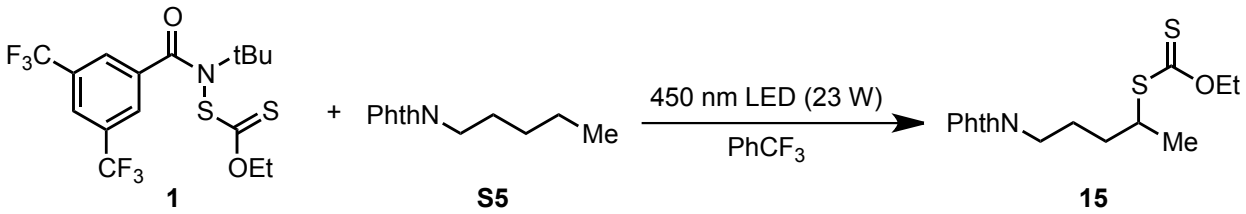
S-(((6-chloropyridin-2-yl)oxy)methyl) O-ethyl carbonodithioate (13): Prepared according to General Procedure C (0.15 mmol scale) using 2-chloro-6-methoxypyridine and xanthylamide **1** (1 equiv), giving 53% NMR yield. The crude residue was purified by flash column chromatography to afford pure **13** as a yellow oil (13.2 mg, 33% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.03 (s, 2H), 4.68 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 212.61, 161.72, 148.20, 141.24, 117.72, 109.99, 70.67, 69.56, 13.87.
IR (film) 2983.34, 1646.91, 1471.42, 1434.78, 1277.61, 1230.36, 1110.8, 1055.84, 1001.55 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_9H_{11}ClNO_2S_2$ $[M+H]^+$, 263.9920. Found 264.2329.



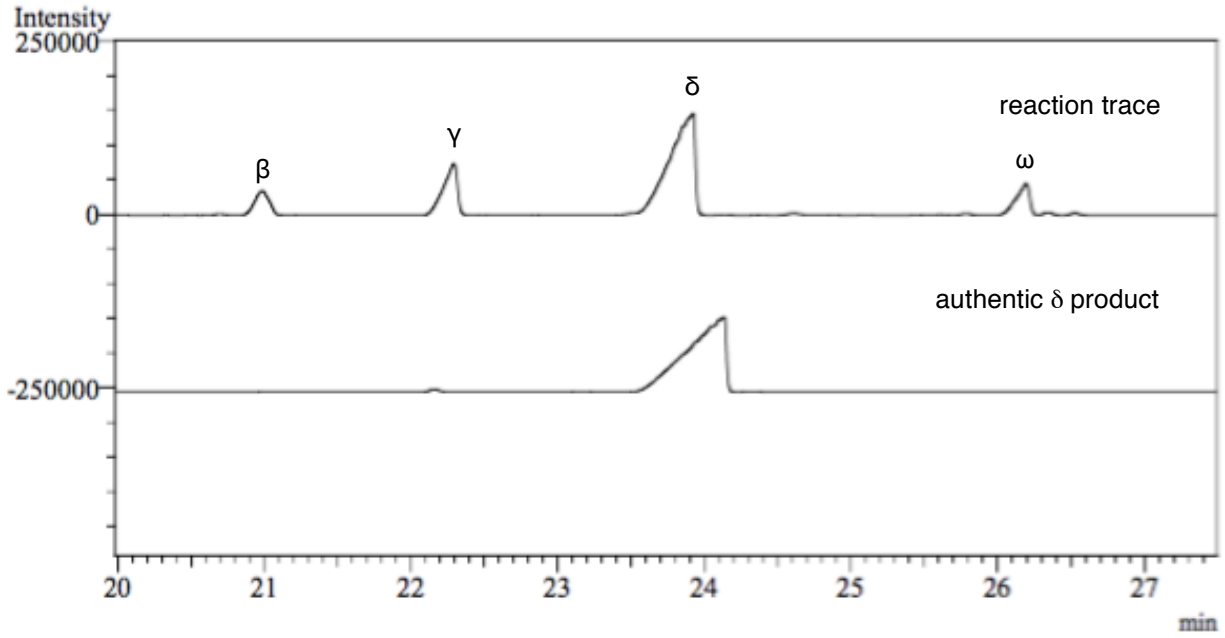
Prepared according to General Procedure C (0.15 mmol scale) using *N*-methylpyrrole and xanthylamide **1** (1 equiv). The crude residue was purified by flash column chromatography to afford pure **14** as a yellow oil (12.1 mg, 40% yield):

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (d, *J* = 2.2 Hz, 2H), 6.18 (d, *J* = 2.2 Hz, 2H), 5.65 (s, 2H), 4.69 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 212.23, 121.34, 109.68, 70.78, 53.65, 13.88.
IR (film) 2922.41, 2856.06, 1682.59, 1489.74, 1278.57, 1225.54, 1045.23, 725.10 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_8H_{12}NOS_2$ $[M+H]^+$, 202.0355. Found 202.0363.

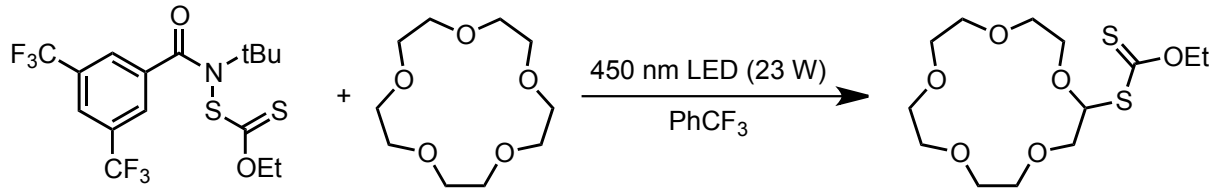


Reaction with *N*-Pentylphthalimide: Prepared according to General Procedure C (0.15 mmol scale) using *N*-pentylphthalimide (**S5)** and xanthylamide **1** (2 equiv), giving 68% combined GC yield of xanthate products (64% selectivity for major δ product):

Figure S5. Distribution of *N*-Pentylphthalimide Xanthates



Product	% area
β	8.4
γ	17.8
δ	63.7
ω	10.1



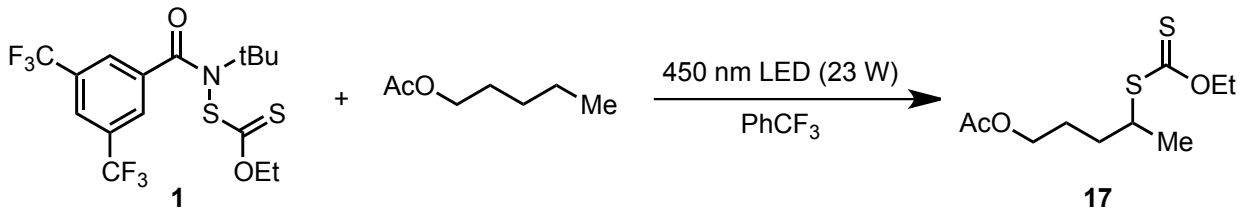
1 **16**

***O*-ethyl *S*-1,4,7,10,13-pentaoxacyclopentadecan-2-yl carbonodithioate (16).** Prepared according to General Procedure C (0.30 mmol scale) using 15-crown-5 and xanthylamide **1** (1 equiv), giving 67% NMR yield. The residue was purified by flash column chromatography on silica to afford pure crown ether xanthate **16** as a yellow oil (48.6 mg, 48% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.83 – 5.76 (m, 1H), 4.69 – 4.58 (m, 2H), 3.94 – 3.60 (m, 18H), 1.46 – 1.35 (m, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 213.09, 90.60, 73.05, 70.94, 70.79, 70.76, 70.72, 70.70, 70.65, 70.03, 69.93, 69.76, 13.87.

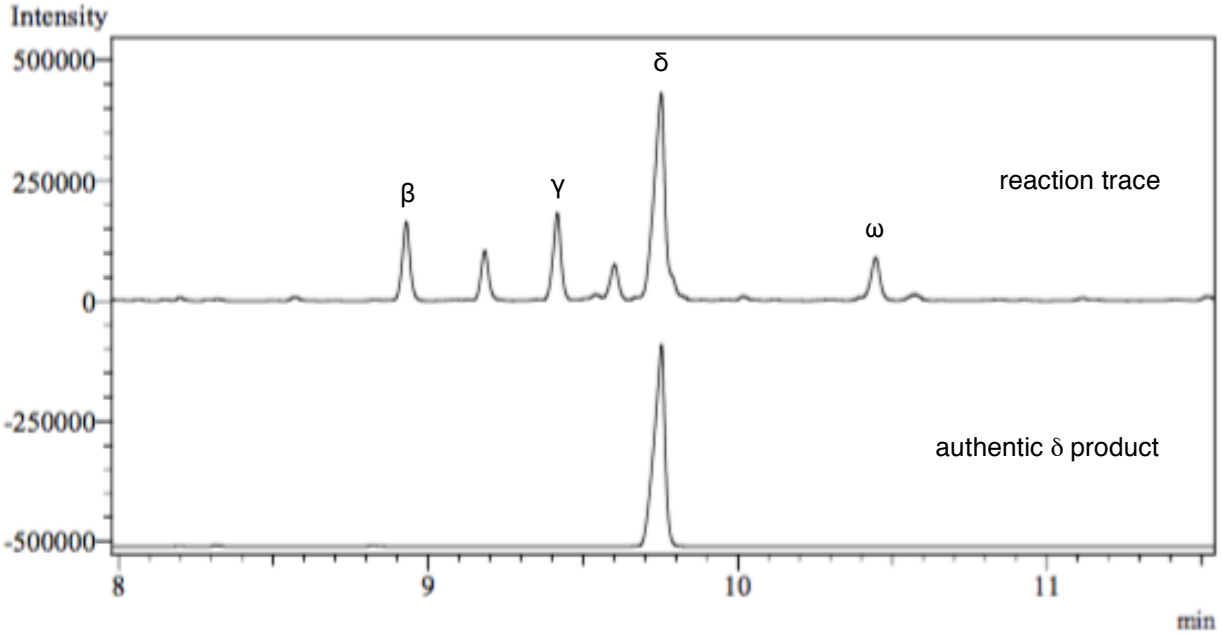
IR (film) 2924.52, 2856.06, 1716.34, 1652.70, 1558.20, 1540.85, 1225.54, 1113.69, 1044.26 cm^{-1}.

HRMS (ES+) Exact mass calcd for $C_{13}H_{24}O_6S_2Na$ $[M+Na]^+$, 363.0907. Found 363.0904.

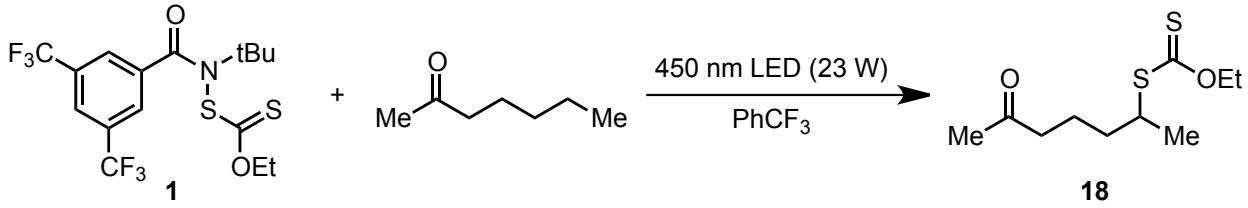


Reaction with Amyl Acetate: Prepared according to General Procedure C (0.15 mmol scale) using amyl acetate and xanthylamide **1** (2 equiv) with the addition of 2-chloropyridine (2.8 uL, 0.2 equiv) to minimize byproduct formation, giving 48% combined GC yield of xanthate products (58% selectivity for major δ product):

Figure S6. Distribution of Amyl Acetate Xanthates

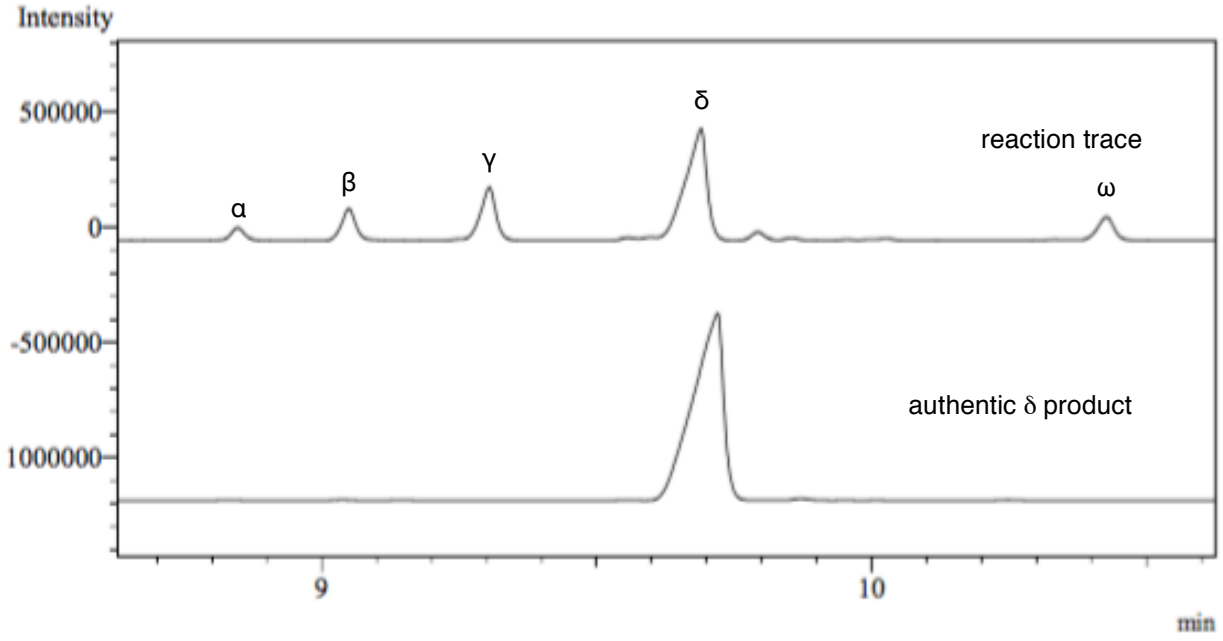


Product	% area
β	14.5
γ	17.2
δ	58.3
ω	10.0

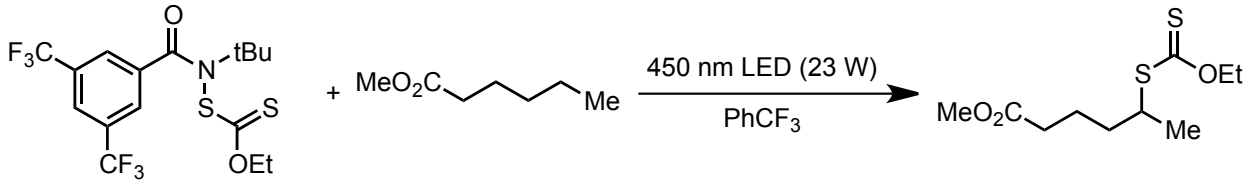


Reaction with 2-Heptanone: Prepared according to General Procedure C (0.15 mmol scale) using 2-heptanone and xanthylamide **1** (2 equiv) with the addition of 2-chloropyridine (2.8 uL, 0.2 equiv) to minimize byproduct formation, giving 47% combined GC yield of xanthate products (55% selectivity for major δ product):

Figure S7. Distribution of 2-Heptanone Xanthates



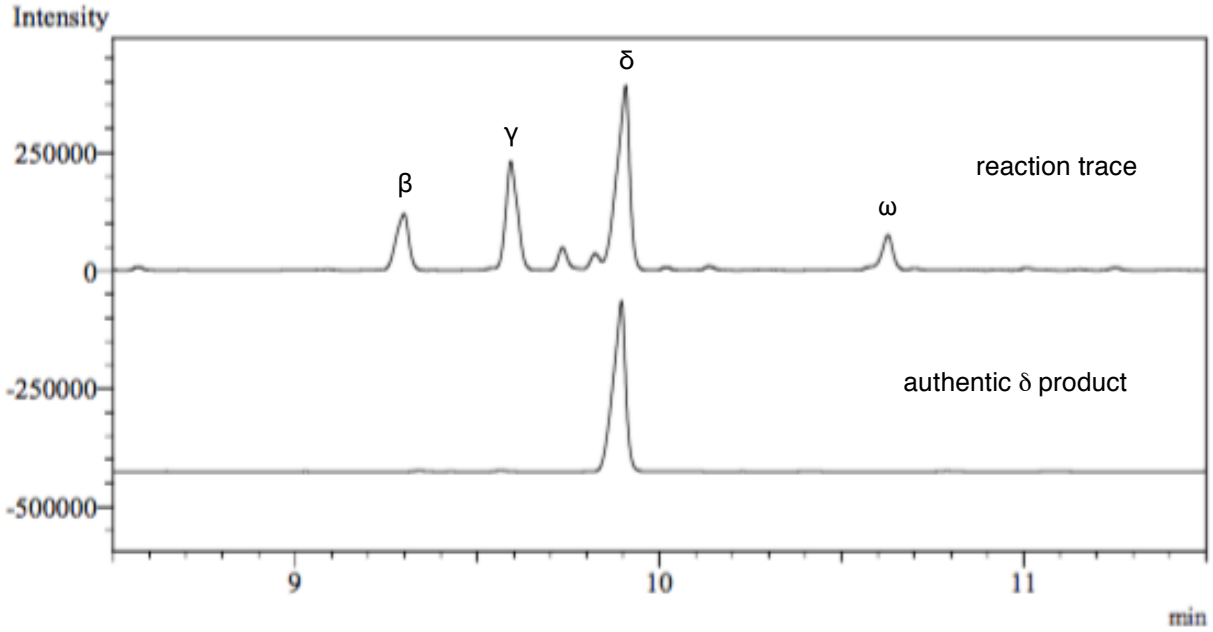
Product	% area
α	4.1
β	10.2
γ	18.8
δ	54.7
ω	12.2



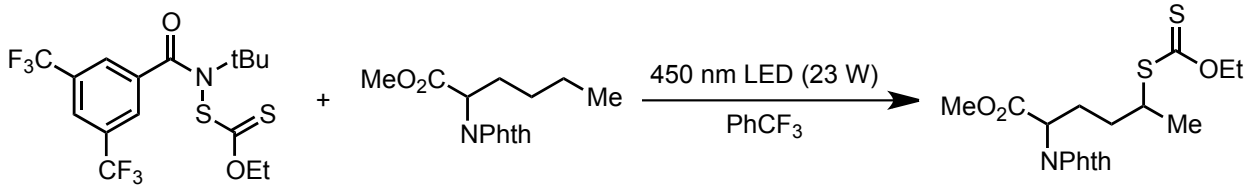
1 **19**

Reaction with Methyl Hexanoate: Prepared according to General Procedure C (0.15 mmol scale) using methyl hexanoate and xanthylamide **1** (2 equiv) with the addition of 2-chloropyridine (2.8 uL, 0.2 equiv) to minimize byproduct formation, giving 52% combined GC yield of xanthate products (53% selectivity for major δ product):

Figure S8. Distribution of Methyl Hexanoate Xanthates



Product	% area
β	11.6
γ	26.9
δ	53.2
ω	8.3



1 **S6** **20**

Reaction with *N*-Phthalimide Norleucine Methyl Ester (S6): Prepared according to General Procedure C (0.15 mmol scale) using *N*-phthalimide norleucine methyl ester (**S6)** and xanthylamide **1** (3 equiv). The crude residue was purified by flash column chromatography on silica (20% – 50% Et_2O in hexanes) to afford the xanthate products as an amorphous solid (39 mg, 68% yield).

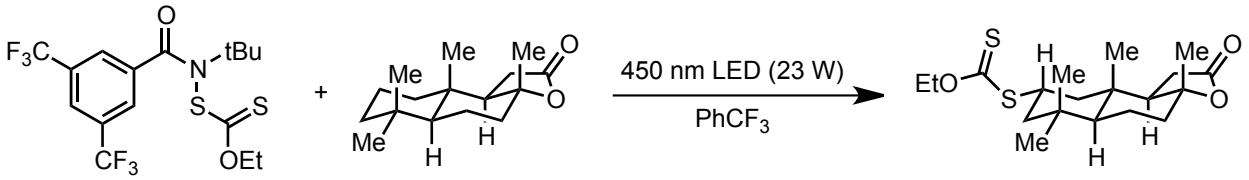
NMR Data listed for major products (mixture of diastereomers). NMR contains other regioisomers of xanthylation products, which exist both as diastereomers and rotamers and complicate the NMR spectrum.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 4.9 Hz, 2H), 7.76 (d, *J* = 3.0 Hz, 2H), 4.87 – 4.79 (m, 1H), 4.73 – 4.47 (m, 2H), 3.76 – 3.70 (m, 4H), 2.41 – 2.21 (m, 2H), 1.74 – 1.64 (m, 1H), 1.42 (s, 3H), 1.39 – 1.23 (m, 4H, overlap with other products).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.05, 169.58, 167.79, 167.75, 167.71, 135.82, 134.41, 134.37, 131.82, 125.63, 123.74, 69.79, 69.75, 52.98, 52.96, 51.99, 51.88, 45.24, 45.20, 35.47, 34.33, 32.81, 32.70, 30.41, 29.81, 28.35, 27.89, 26.59, 26.50, 20.55, 20.25, 14.37, 13.87, 13.85.

IR (film) 2926.45, 1772.26, 1748.16, 1716.34, 1652.70, 1540.85, 1387.53, 1219.76, 1047.16 cm^{-1}.

HRMS (ES+) Exact mass calcd for $C_{18}H_{22}NO_5S_2$ $[M+H]^+$, 396.0934. Found 396.0954.



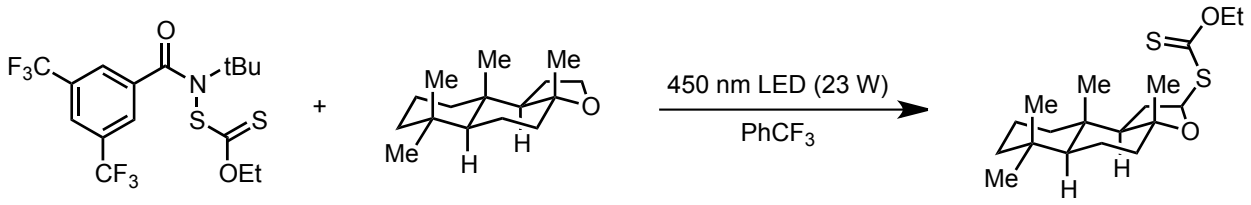
1 **21**

***O*-ethyl *S*-((3a*R*,5a*S*,8*S*,9a*S*,9b*R*)-3a,6,6,9a-tetramethyl-2-oxododecahydronaphtho[2,1-*b*]furan-8-yl) carbonodithioate:** Prepared according to General Procedure C using sclareolide (1 mmol, 1 equiv) and xanthylamide **1** (1 mmol, 1 equiv) in $PhCF_3$ (1 mL) giving 55% NMR yield. The crude residue was purified by flash column chromatography (10 – 20% EtOAc in hexanes) to afford pure **21** as an off-white solid (0.205 g, 55% yield, 91% yield brsm):

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.63 (q, *J* = 7.1, 2H), 4.01 (tt, *J* = 12.9, 3.6 Hz, 1H), 2.43 (t, *J* = 14.9 Hz, 1H), 2.24 (dd, *J* = 16.3, 6.6 Hz, 1H), 2.09 (dt, *J* = 12.0, 3.2 Hz, 1H), 1.99 (dd, *J* = 14.7, 6.6 Hz, 1H), 1.90 (td, *J* = 13.0, 3.1 Hz, 3H), 1.69 (td, *J* = 12.6, 4.1 Hz, 1H), 1.41 (td, *J* = 7.2, 2.3 Hz, 3H), 1.36 – 1.31 (m, 4H), 1.26 – 1.23 (m, 1H), 1.17 (t, *J* = 12.4 Hz, 1H), 1.11 (dd, *J* = 12.7, 2.5 Hz, 1H), 1.05 (s, 3H), 0.96 (s, *3*H), 0.94 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.06, 176.37, 86.12, 69.89, 58.75, 56.22, 47.24, 45.23, 42.37, 38.57, 37.68, 35.16, 32.93, 28.74, 21.75, 21.27, 20.38, 15.59, 13.93.
IR (film) 2950.55, 2360.44, 2342.12, 1777.08, 1385.60, 1220.72, 1113.69, 1049.09 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{19}H_{31}O_3S_2$ $[M+H]^+$, 371.1709. Found 371.1704.

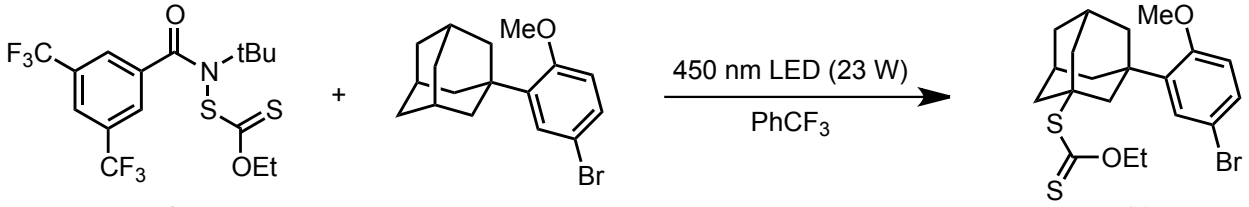
A gram-scale reaction was run with sclareolide (4 mmol, 1 equiv) and xanthylamide **1** (4 mmol, 1 equiv) using General Procedure D on 4 mmol scale (0.804 g, 54% yield).



1 **22**

***O*-ethyl *S*-((2*R*,3a*R*,5a*S*,9a*S*,9b*R*)-3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-*b*]furan-2-yl) carbonodithioate (22):** The reaction was run according to General Procedure C for 4 hr on a 0.3 mmol scale (note: product decomposition occurs under reaction conditions after 4 hr). The mixture was concentrated *in vacuo* and extensively dried via high-vacuum. ^{1}H NMR of the crude reaction with an HMDS internal standard reveals an NMR yield of 80% with 1.2:1 dr. The solid residue was triturated with pentanes, and the solution was passed over a cotton plug and concentrated *in vacuo* to remove amide **S3**. The resultant residue was heated at 115 ˚C in a sand bath under high vacuum overnight to remove unreacted ambroxide, which is chromatographically inseparable from the xanthate products. Finally, the resultant residue was purified through rapid flash column chromatography on silica (5% EtOAc in hexanes, less than five minutes spent on the column) to afford pure ambroxide xanthates **22** as an inseparable mixture of diastereomers (34 mg, 32% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.10 (t, *J* = 7.8 Hz, 0.32H), 5.96 (dd, *J* = 7.5 Hz, 1.1 Hz, 0.56H), 4.72 – 4.59 (m, 2H), 2.41 (td, *J* = 13.4, 7.6 Hz, 0.61H), 2.33 (dd, *J* = 12.8, 6.5 Hz, 0.37H), 2.01 – 1.94 (m, 1.53H), 1.88 (td, *J* = 13.1, 8.1 Hz, 0.48H), 1.81 – 1.74 (m, 1H), 1.69 – 1.56 (m, 3H), 1.48 – 1.40 (m, 6H), 1.30 – 1.15 (m, 5H), 1.10 – 1.03 (m, 1 H), 1.02 – 0.94 (m, 1H), 0.88 – 0.81 (m, 9H)
^{13}C NMR (151 MHz, $CDCl_3$) δ 213.85, 213.43, 86.06, 84.24, 83.29, 69.88, 69.44, 60.35, 58.51, 57.12, 57.07, 42.43, 40.02, 39.99, 39.96, 39.61, 36.40, 36.29, 33.65, 33.63, 33.21, 31.90, 29.90, 22.63, 22.40, 21.20, 21.18, 20.88, 20.57, 18.43, 15.58, 15.32, 13.94, 13.91.
IR (film) 2978.52, 2941.88, 1518.67, 1378.85, 1267.00, 1230.36, 1130.08, 992.20 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{19}H_{32}O_2S_2Na$ $[M+Na]^+$, 379.1736. Found 379.1784.



1 **23**

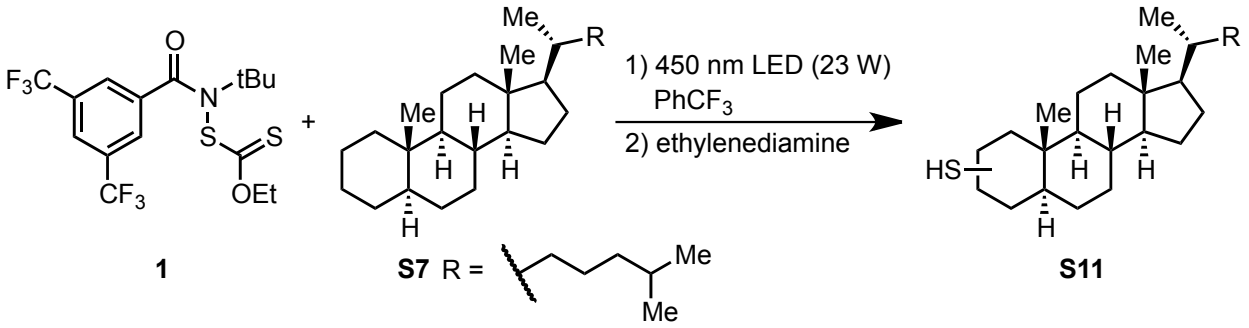
***S*-((1*s*,3*r*,5*R*,7*S*)-3-(5-bromo-2-methoxyphenyl)adamantan-1-yl) *O*-ethyl carbonodithioate (23).** Prepared according to General Procedure D (0.15 mmol scale) using 2-(1-adamantyl)-4-bromoanisole and xanthylamide **1** (1 equiv). The crude residue was purified by flash column chromatography to afford **23** as an off-white solid (33.8 mg, 51% yield) containing 5% of a minor regioisomer arising from functionalization on the methoxy group. Due to the nonpolar nature of the product, a minor amount of an inseparable impurity was isolated alongside the xanthylated products (annotated on ^{1}H NMR spectrum):

^{1}H NMR (600 MHz, $CDCl_3$) 7.29 (d, *J* = 8.7 Hz, 1H), 7.26 (br. s, 1H, underneath residual $CHCl_3$), 6.75 (d, *J* = 8.6 Hz, 1H), 4.67 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 2.45 (s, 1H), 2.27 – 2.23 (m, 2H), 2.19 – 2.13 (m, 7H), 1.91 (d, *J* = 12.4 Hz, 2H), 1.74 – 1.69 (m, 2H), 1.46 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.15, 157.73, 138.80, 129.99, 129.67, 113.43, 113.38, 69.37, 55.41, 55.09, 43.89, 41.26, 39.31, 39.23, 35.76, 30.36, 13.94 (overlap of adamantyl carbons).

IR (film) IR 2915.84, 2853.17, 1744.30, 1483.46, 1455.03, 1234.22, 1133.94, 1112.73, 1046.19, 1027.87 cm^{-1}.

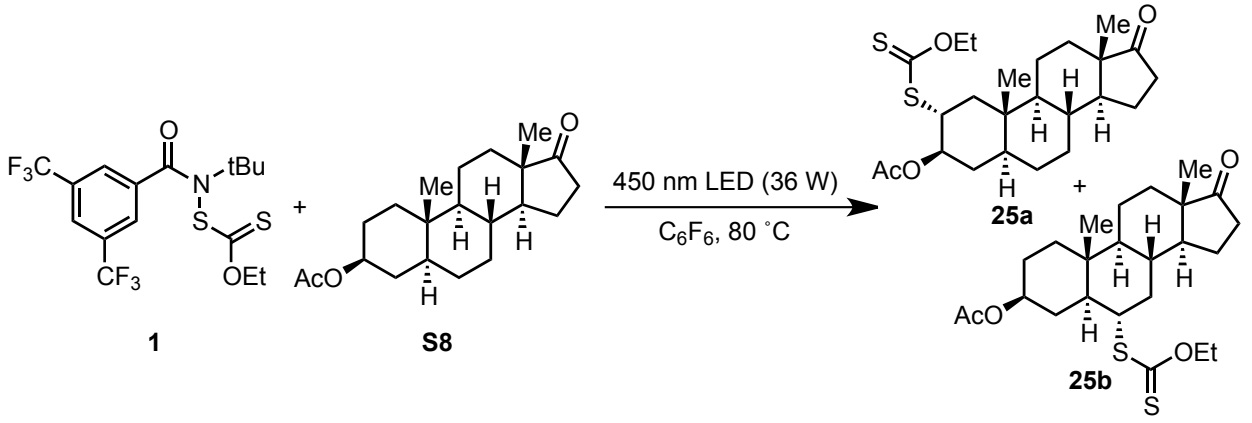
HRMS (ES+) Exact mass calcd for $C_{20}H_{26}BrO_2S_2$ $[M+H]^+$, 441.0552. Found 441.0568.



1 **S7** R = **S11**

Reaction with 5α-cholestane (S7): The xanthate was prepared according to General Procedure D (0.15 mmol scale) using cholestane (**S7**) and xanthylamide **1** (1 equiv), giving 60% NMR yield. The resulting crude residue was dissolved in EtOH (1 mL) and

treated with ethylene diamine (4 equiv). After 4 h the mixture was concentrated *in vacuo*, redissolved in Et_2O (2 mL), and washed with 2M H_2SO_4 (2 mL), brine (2 mL), dried over $MgSO_4$, and concentrated *in vacuo* to afford **S11** in 60% NMR yield.



Reaction with *trans*-androsterone acetate (S8): Prepared according to General Procedure E (0.064 mmol scale) using *trans*-androsterone acetate (**S8**) and xanthylamide **1** (3 equiv) in C_6F_6 for 24 h giving 63% NMR yield. The crude residue was purified by flash column chromatography to afford pure **25** as an off-white solid (16.1 mg, 56% yield):

(3R,5S,8R,9S,10S,13S,14S)-2-((ethoxycarbonothioyl)thio)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (25a):

^{1}H NMR (600 MHz $CDCl_3$) δ 4.76 (td, *J* = 11.3, 5.1 Hz, 1H), 4.67 – 4.59 (m, 2H), 3.96 (td, *J* = 12.2, 4.3 Hz, 1H), 2.43 (dd, *J* = 19.3, 8.8 Hz, 1H), 2.33 (dd, *J* = 13.1, 4.3 Hz, 1H), 2.11 – 2.00 (m, 1H), 2.03 (s, 3H), 1.93 (ddd, *J* = 14.3, 8.5, 5.9 Hz, 1H), 1.84 – 1.77 (m, 3H), 1.66 – 1.61 (m, 1H), 1.56 – 1.46 (m, 2H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.39 – 1.19 (m, 7H), 1.02 – 0.94 (m, 1H), 0.99 (s, 3H), 0.89 – 0.83 (m, 1H), 0.86 (s, 3H), 0.76 (td, *J* = 12.7, 4.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 221.27, 213.80, 170.61, 72.74, 70.01, 54.15, 51.32, 50.32, 47.88, 44.61, 44.54, 37.54, 35.95, 34.83, 34.59, 31.49, 30.71, 27.73, 21.89, 21.28, 20.63, 13.95, 12.42.

(3S,5S,8R,9S,10R,13S,14S)-6-((ethoxycarbonothioyl)thio)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (25b):

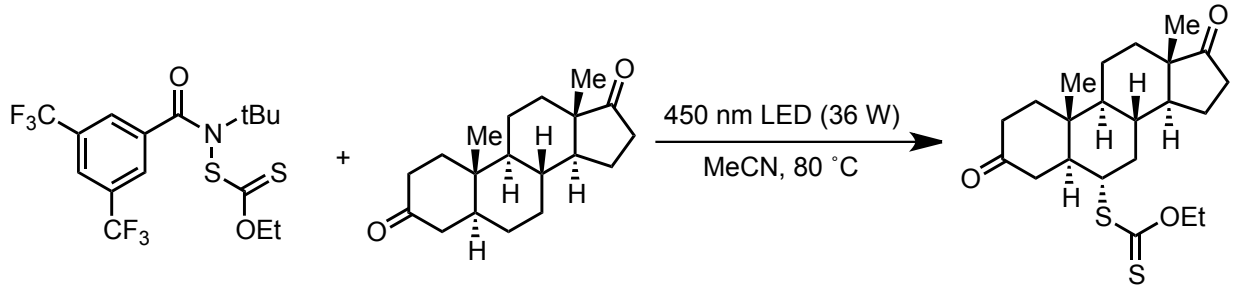
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.67 – 4.60 (m, 3H), 3.81 (td, *J* = 12.3, 4.1 Hz, 1H), 2.47 (dd, *J* = 19.4, 7.9 Hz, 1H), 2.31 (dt, *J* = 12.8, 4.0 Hz, 1H), 2.17 (ddt, *J* = 12.4, 4.6, 2.6 Hz, 1H), 2.13 – 2.03 (m, 2H), 2.04 (s, 3H), 1.97 – 1.92 (m, 1H), 1.90 – 1.79 (m, 2H), 1.78 – 1.69 (m, 2H), 1.56 – 1.50 (m, 2H), 1.45 (t, *J* = 7.0 Hz, 3H), 1.37 – 1.25 (m, 5H), 1.10 (td, *J* = 13.7, 4.0 Hz, 1H), 1.02 (s, 3H), 0.90 (s, 3H), 0.89 – 0.87 (m, 1H), 0.82 (td, *J* = 11.3, 3.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 220.77, 214.68, 170.67, 73.16, 70.15, 53.78, 51.13, 50.75, 48.72, 47.88, 38.58, 37.80, 36.75, 35.95, 35.64, 31.47, 30.44, 27.34, 21.76, 21.57, 20.58, 13.96, 12.95.
IR (film) 2943.8, 1771.30, 1734.66, 1652.70, 1540.85, 1239.04, 1047.16 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{24}H_{37}O_4S_2$ $[M+H]^+$, 453.2128. Found 453.2159.

Steroid regiochemistry assignments were made by converting the xanthate to the TEMPO adduct (optimization discussed in **Table S2)** and oxidation to the corresponding ketone via the following procedure:

The starting xanthate was dissolved in PhCl (0.1 M) and stirred at 100 °C. TEMPO (6 equiv) and tris(trimethylsilyl)silane (3 equiv) were added in three portions over 48 h. The reaction mixture was stirred for an additional 24 hr, then was concentrated. The crude mixture was redissolved in CH_2Cl_2 (0.1 M) and cooled to 0 °C, into which a solution of 3-chloroperbenzoic acid (2 equiv) dissolved in CH_2Cl_2 was added dropwise. After the addition, the reaction mixture was stirred for 2 h, then quenched with saturated $Na_2S_2O_3$ and saturated $NaHCO_3$. After stirring for 5 min at rt, EtOAc and 10% NaOH was added to the mixture. The organic layer was extracted and washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated.

The spectroscopic data was then compared to the literature values to identify the regioisomer of xanthate functionalization.[14]

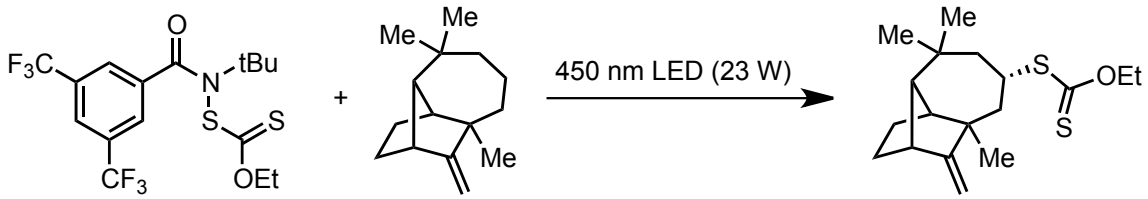


1 **S9** **26**

S-((5S,6S,8R,9S,10R,13S,14S)-10,13-dimethyl-3,17-dioxohexadecahydro-1H-cyclopenta[a]phenanthren-6-yl) O-ethyl carbonodithioate (26): Prepared according to General Procedure E (0.10 mmol scale) using 5α-androstanedione (**S9**) and xanthylamide **1** (3 equiv) in MeCN for 3 days giving 38% NMR yield. A mix of the starting material and product was recovered by flash chromatography and resubjected to the reaction conditions. The resulting crude residue was purified by flash column chromatography to afford pure **26** as an off-white solid (18.0 mg, 44% yield):

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.63 (q, *J* = 7.1 Hz, 2H), 3.89 (td, *J* = 12.4, 4.2 Hz, 1H), 2.71 (ddd, *J* = 15.5, 4.1, 2.0 Hz, 1H), 2.51 – 2.29 (m, 5H), 2.13 – 2.04 (m, 2H), 1.98 – 1.91 (m, 1H), 1.89 – 1.80 (m, 2H), 1.78 – 1.68 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.36 – 1.22 (m, 4H), 1.19 (s, 3H), 1.10 – 1.03 (m, 2H), 0.91 (s, 3H), 0.90 – 0.84 (m, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 220.49, 214.47, 210.66, 70.39, 53.40, 51.08, 50.83, 50.42, 47.84, 41.23, 38.12, 37.86, 37.82, 35.90, 35.65, 31.44, 21.80, 20.78, 13.98, 12.30.
IR (film) 2945.73, 2856.06, 1735.62, 1715.37, 1670.05, 1540.85, 1218.79, 1047.16 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{22}H_{33}O_3S_2$ $[M+H]^+$, 409.1866. Found 409.1885.

The site selectivity of xanthate functionalization was determined through a similar procedure as described above for *trans*-androsterone acetate.

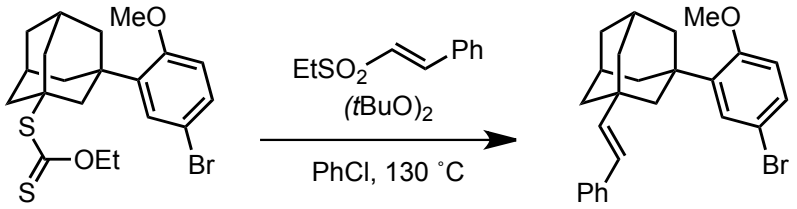


1 **27**

***O*-ethyl *S*-((6*S*)-4,8,8-trimethyl-9-methylenedecahydro-1,4-methanoazulen-6-yl) carbonodithioate (27):** Prepared according to General Procedure C using (+)-longifolene (0.50 mmol, 1 equiv) and xanthylamide **1** (0.50 mmol, 1 equiv) with the exception that no solvent was used. The crude residue was purified by flash column chromatography to afford pure **27** as an off-white solid (87.6 mg, 54% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.81 (s, 1H), 4.64 (qdd, *J* = 10.3, 7.2, 3.5 Hz, 2H), 4.55 (d, *J* = 2.1 Hz, 1H), 3.93 (td, *J* = 12.2, 6.2 Hz, 1H), 2.65 (d, *J* = 4.8 Hz, 1H), 2.19 (d, *J* = 3.7 Hz, 1H), 2.17 – 2.11 (m, 2H), 1.78 – 1.67 (m, 4H), 1.42 (tdd, *J* = 12.3, 5.8, 1.6 Hz, 6H), 1.12 (s, 3H), 1.03 (s, 3H), 0.93 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.43, 166.47, 100.29, 69.66, 61.70, 48.39, 47.69, 44.92, 44.61, 43.96, 43.09, 34.06, 30.80, 30.36, 29.92, 29.60, 25.56, 14.04.
IR (film) 3063.37, 2955.38, 2867.63, 1655.59, 1364.39, 1213.01, 1111.76, 1051.98 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{18}H_{28}OS_2Na$ $[M+Na]^+$, 347.1474. Found 347.1474.

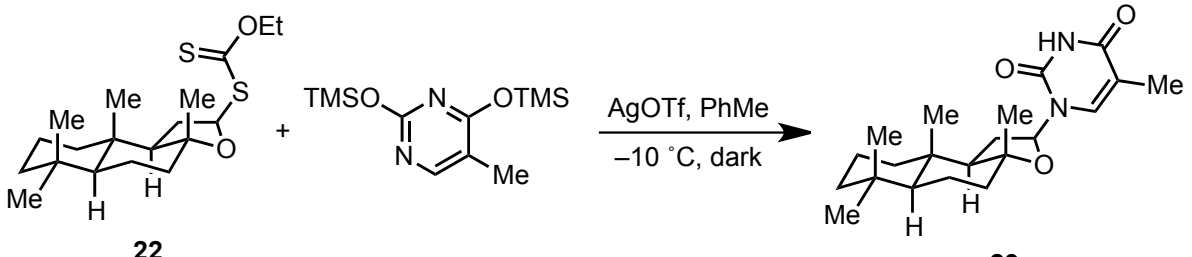
Further Derivatization of Xanthate Products



23 **28**

(1*s*,3*r*,5*R*,7*S*)-1-(5-bromo-2-methoxyphenyl)-3-((*E*)-styryl)adamantane (28): Adapted from the literature procedure.[15] To a solution of adamantyl bromoanisole xanthate **23** (30 mg, 0.068 mmol) and styryl ethyl sulfone (40 mg, 0.20 mmol) dissolved in PhCl (1.5 mL) and stirring at 130 °C, tert-butyl peroxide (10 µL, 0.068 mmol) was added. Four more tert-butyl peroxide (5 µL, 0.034 mmol) additions were added in the following 12 hours. After the last addition, the reaction was left stirring overnight. The resulting dark brown mixture was concentrated, and the product was isolated by flash column chromatography (pentanes) to yield styrene **28** as a white solid (15.8 mg, 55% yield). Due to the nonpolar nature of the product, it is contaminated with an inseparable grease impurity (annotated on the ^{1}H spectrum).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 2H), 7.32 – 7.26 (m, 4H, overlap with residual $CHCl_3$), 7.21 – 7.17 (m, 1H), 6.74 (d, *J* = 8.6 Hz, 1H), 6.29 (d, *J* = 16.2 Hz, 1H), 6.16 (d, *J* = 16.3 Hz, 1H), 3.81 (s, 3H), 2.25 – 2.19 (m, 2H), 2.07 – 2.00 (m, 4H), 1.99 – 1.94 (m, 2H), 1.75 – 1.68 (m, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 157.97, 141.72, 140.13, 138.17, 129.86, 129.62, 128.62, 126.92, 126.12, 124.91, 113.40, 113.36, 55.37, 44.85, 41.62, 39.75, 37.89, 36.33, 36.21, 29.27 (peak overlap of adamantyl carbons).
IR (film) 2908.13, 2856.06, 1698.98, 1483.96, 1439.60, 1234.22, 1032.69, 805.14 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{25}H_{28}BrO$ $[M+H]^+$, 424.3932. Found 424.3903.

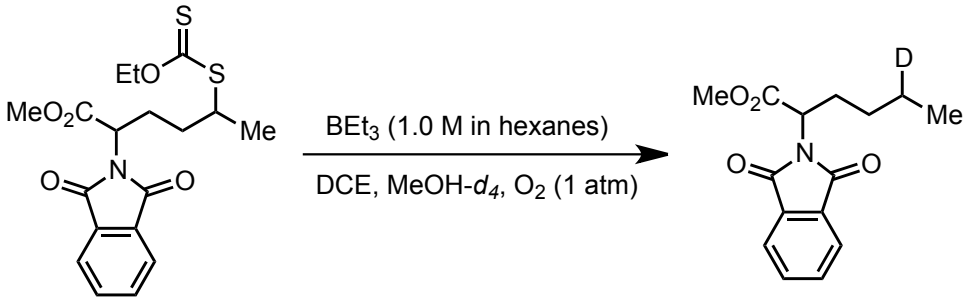


22 **29**

5-methyl-1-((2*S*,3a*R*,5a*S*,9a*S*,9b*R*)-3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-*b*]furan-2-yl)pyrimidine-2,4(1*H*,3*H*)-dione (29): Adapted from the literature

procedure.[16] To a solution of ambroxide xanthate **22** (50 mg, 0.14 mmol) in PhMe (2.2 mL) at –10 ˚C was added 5-methyl-2,4-bis((trimethylsilyl)oxy)pyrimidine (57 mg, 0.21 mmol)[17] followed by silver (I) triflate (54 mg, 0.21 mmol). The suspension was stirred at –10 ˚C for 2 h then rt for 2 h. Some of the salts were filtered, and the suspension was diluted with EtOAc (5 mL), washed with $NaHCO_3$ (2 x 5 mL), brine (5 mL), dried with $MgSO_4$, and concentrated *in vacuo.* The residue was purified by flash column chromatography on silica (40 – 50% EtOAc in hexanes) to afford thymine adduct **29** as a white solid (44.1 mg, 4:1 dr, 87% yield):

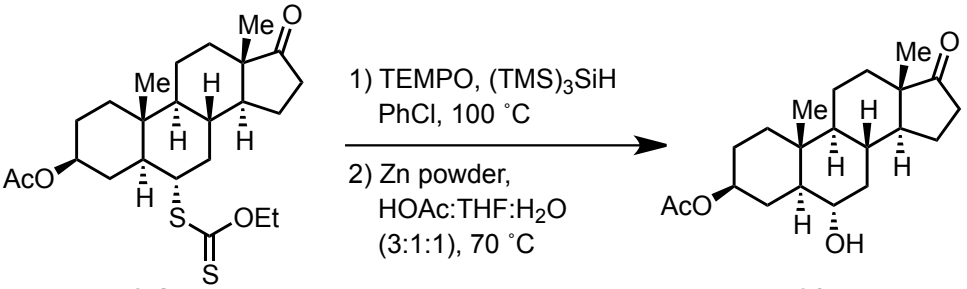
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.95 – 8.75 (br. m, 1H), 7.51 (s, 0.2H), 7.30 (s, 0.8H), 6.06 – 6.03 (m, 0.8H), 5.80 – 5.77 (m, 0.2H), 2.51 (dt, *J* = 9.6, 4.2 Hz, 0.2H), 2.31 (td, *J* = 13.6, 7.4 Hz, 0.8H), 2.10 – 2.02 (m, 1H), 1.96 – 1.90 (m, 3H), 1.87 – 1.82 (m, 1H), 1.78 – 1.54 (m, 4H), 1.49 – 1.37 (m, 4H), 1.37 – 1.27 (m, 1H), 1.26 – 1.20 (m, 3H), 1.05 – 0.97 (m, 2H), 0.90 (s, 3H), 0.86 – 0.81 (m, 6H).
^{13}C NMR (major diastereomer, 151 MHz, $CDCl_3$) δ 164.02, 150.39, 135.65, 110.22, 87.26, 84.19, 58.70, 57.41, 42.36, 39.93, 39.65, 36.40, 33.58, 33.25, 31.26, 22.31, 21.20, 20.73, 18.35, 15.14, 12.97.
IR (film) 3170.40, 2927.41, 2867.63, 1697.05, 1682.59, 1472.38, 1380.78, 1271.82 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{21}H_{33}N_2O_3$ $[M+H]^+$, 361.2486. Found 361.2598.



20 **30**

Methyl 5-deutero-2-(1,3-dioxoisoindolin-2-yl)hexanoate (30): Adapted from the literature procedure.[18] In a 1 dram vial in the glovebox, to a solution of norleucine xanthate **20** (20 mg, 0.051 mmol) in DCE/MeOH-d_4 (0.2 mL/0.08 mL) was added triethylborane (0.25 mL, 0.25 mmol, 1M in hexanes). The vial was fitted with a Teflon-lined screw cap and sealed with Teflon tape. The vial headspace was purged with a dry O_2 balloon for 2 min and then stirred under an O_2 atmosphere for 48 h. The reaction mixture was diluted with DCM (1 mL), passed over a short silica plug, and concentrated. The residue was purified by flash column chromatography on silica (10% EtOAc in hexanes) to afford **30** as a pale yellow amorphous solid (10 mg, 71% yield). GC-MS analysis according to the literature revealed 85% D incorporation:

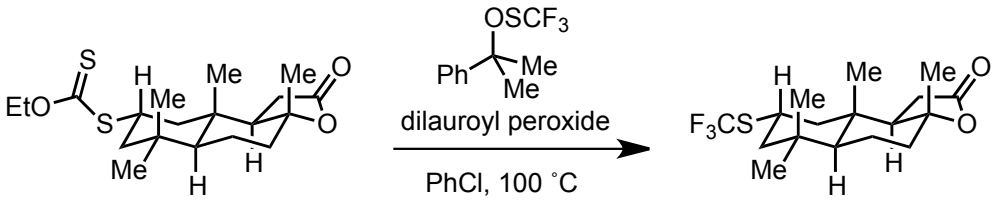
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (dt, *J* = 7.3, 3.9 Hz, 2H), 7.75 (dq, *J* = 7.8, 4.5, 4.0 Hz, 2H), 4.88 – 4.80 (m, 1H), 3.73 (s, 3H), 2.40 – 2.30 (m, 1H), 2.29 – 2.17 (m, 1H), 1.70 – 1.53 (m, 3H), 1.37 – 1.28 (m, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 170.14, 167.87, 167.75, 134.40, 134.32, 131.92, 123.78, 123.76, 123.69, 77.16, 63.49, 63.42, 52.86, 52.28, 33.32, 29.85, 28.48, 26.40, 14.40, 13.90.
IR (film) 2957.3, 2924.52, 2853.17, 1747.19, 1717.3, 1456.96, 1388.50, 1253.50 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{15}H_{17}DNO_4$ $[M+H]^+$, 277.1292. Found 277.1315.



25b **31**

(3*S*,5*S*,6*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-6-hydroxy-10,13-dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl acetate (31): To a solution of steroidal xanthate **25b** (35 mg, 0.077 mmol) in PhCl (0.77 mL) stirring at 100 °C, TEMPO (72 mg, 0.23 mmol) and tris(trimethylsilyl)silane (72 µL, 0.15 mmol) were added in three portions over 48 h. The reaction mixture was stirred for an additional 24 h, then concentrated. Zinc powder (0.203 g, 3.08 mmol), then a mixture of HOAc/THF/H_2O (3:1:1, 1.9 mL) was added and heated at 70 °C overnight. The reaction mixture was filtered through a cotton plug and washed with EtOAc. The resulting filtrate was washed with saturated $NaHCO_3$, water, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude material was purified by column chromatography (20 – 50% EtOAc in hexanes) to yield **31** (14.9 mg, 56% yield) as a white solid in accordance with the literature data.[14]

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.67 (ddt, *J* = 16.4, 11.2, 4.9 Hz, 1H), 3.44 (td, *J* = 10.8, 4.5 Hz, 1H), 2.45 (dd, *J* = 19.4, 8.8 Hz, 1H), 2.22 (app d, *J* = 12.1, 1H), 2.15 – 2.04 (m, 2H), 2.02 (s, 3H), 1.95 (ddd, *J* = 14.1, 8.7, 5.8 Hz, 1H), 1.87 – 1.76 (m, 2H), 1.76 – 1.60 (m, 3H), 1.57 – 1.45 (m, 2H), 1.38 – 1.20 (m, 4H), 1.14 – 1.04 (m, 2H), 0.99 – 0.91 (m, 1H), 0.89 – 0.83 (m, 1H), 0.85 (s, 6H), 0.75 (td, *J* = 11.4, 4.0 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 221.00, 170.76, 73.48, 69.29, 53.85, 51.74, 51.18, 47.89, 40.54, 37.08, 36.54, 35.93, 34.01, 31.46, 28.39, 27.25, 21.89, 21.56, 20.48, 13.93, 13.46.



21 **32**

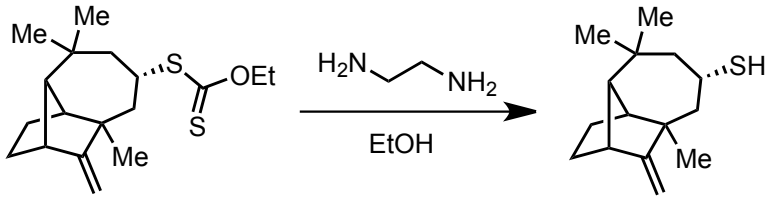
(3a*R*,5a*S*,8*S*,9a*S*,9b*R*)-3a,6,6,9a-tetramethyl-8-((trifluoromethyl)thio)decahydronaphtho[2,1-*b*]furan-2(3a*H*)-one (32): Sclareolide xanthate **21** (10 mg, 0.027 mmol) and ((2-phenylpropan-2-yl)oxy)(trifluoromethyl)sulfane[19] (19 mg, 0.081 mmol) were dissolved in PhCl (1.35 mL) and heated to 100 °C. DLP (5 mg, 0.014 mmol) was added every half-hour for a total of eight additions under an argon atmosphere. After the last addition, the reaction was stirred for another 30 minutes. The mixture was then concentrated, and the product was isolated by flash chromatography (10% EtOAc in hexanes) to yield **32** as a white solid in accordance with the literature data (6.7 mg, 71% yield):[20]

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.52 (tt, *J* = 12.8, 3.8 Hz, 1H), 2.44 (dd, *J* = 16.2, 14.7 Hz, 1H), 2.27 (dd, *J* = 16.2, 6.5 Hz, 1H), 2.10 (dt, *J* = 12.0, 3.3 Hz, 1H), 1.99 (dd, *J* = 14.7, 6.5 Hz, 1H), 1.93 – 1.89 (m, 2H), 1.86 (ddd, *J* = 12.5, 3.7, 2.1 Hz, 1H), 1.70 (td, *J* = 12.6, 4.3 Hz, 1H), 1.42 – 1.31 (m, 1H), 1.34 (s, 3H), 1.21 (app t, *J* = 12.6 Hz, 1H), 1.10 (dd, *J* = 12.6, 2.9 Hz, 1H), 0.98 (s, 3H), 0.97 (s, 3H), 0.92 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 176.19, 131.08 (q, *J* = 306.5 Hz), 86.00, 55.85, 49.14, 46.75, 38.53, 37.60, 37.23, 35.13, 32.98, 28.69, 21.76, 21.30, 20.38, 15.73.
^{19}F NMR (565 MHz, $CDCl_3$) δ -38.78.

Table S3. Trifluoromethylthiolation Optimization[a]

Entry	Deviations from standard conditions	% conversion	% yield
1	None	full	86
2	DLP (10 mol% x 3)	0	-
3	DLP (50 mol % x 3)	50	45
4	DLP (10 mol % x 10), [0.5 M] PhCl	full	40
5[b]	DLP (30 mol % x 3), [0.5 M] DCE, 80 °C	full	28

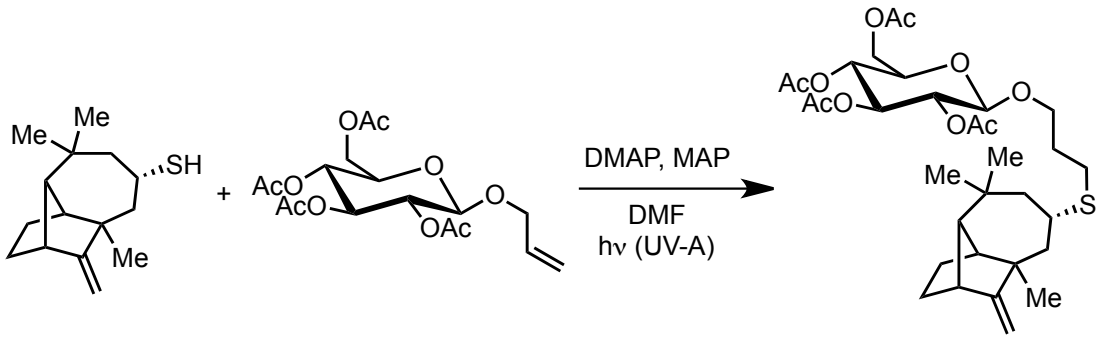
[a] ^{1}H NMR yields based on 2,5-dimethyl furan internal standard; [b]DLP additions made every 4 h.



27 **S12**

(6*S*)-4,8,8-trimethyl-9-methylenedecahydro-1,4-methanoazulene-6-thiol (S12): To a solution of xanthate **27** (57 mg, 0.18 mmol) in EtOH (0.9 mL) was added ethylene diamine (47 uL, 0.70 mmol), leading to persistence of a deep yellow color. After 4 h the mixture was concentrated *in vacuo*, redissolved in Et_2O (2 mL), and washed with 2M H_2SO_4 (2 mL), brine (2 mL), dried over $MgSO_4$, and concentrated *in vacuo* to afford thiol **S12** as a yellow oil (42 mg, 99% yield), which was used directly without further purification:

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.81 (s, 1H), 4.56 (s, 1H), 3.22 – 3.09 (m, 1H), 2.63 (d, *J* = 5.0 Hz, 1H), 2.14 (dd, *J* = 13.9, 11.6 Hz, 1H), 2.10 – 2.06 (m, 2H), 1.77 (dd, *J* = 13.6, 11.8 Hz, 1H), 1.74 – 1.69 (m, 1H), 1.67 (ddd, *J* = 12.4, 9.0, 3.2 Hz, 1H), 1.58 (d, *J* = 6.3 Hz, 1H), 1.44 – 1.37 (m, 2H), 1.28 (dq, *J* = 14.0, 1.5 Hz, 1H), 1.14 (ddd, *J* = 11.9, 9.0, 5.8 Hz, 1H), 1.01 (s, 3H), 1.01 (s, 3H), 0.90 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.67, 100.20, 61.58, 55.13, 47.65, 47.51, 44.97, 44.31, 34.08, 33.79, 30.73, 30.13, 29.87, 29.60, 25.53.

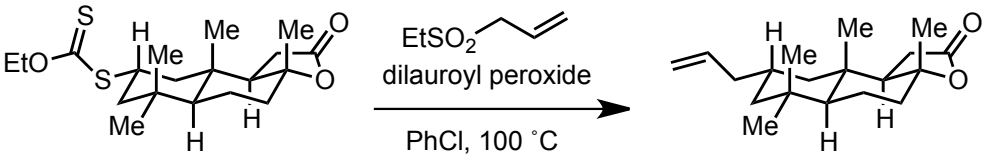


S12 **33**

(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(3-(((6*S*)-4,8,8-trimethyl-9-methylenedecahydro-1,4-methanoazulen-6-yl)thio)propoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (33): Adapted from the literature.[21] In a vial in the glovebox, thiol **S12** (27 mg, 0.11 mmol), allylglycoside (160 mg, 0.41 mmol), 2,2-dimethoxy-2-phenylacetophenone (3 mg, 0.011 mmol), and 4'-methoxyacetophenone (2 mg, 0.011 mmol) were dissolved in DMF (0.22 mL). The vial was sealed with a teflon-lined screw cap, sealed with Teflon tape, and placed in a UV-A box and irradiated for 22 h. The crude reaction mixture was diluted with EtOAc (2 mL), washed with H_2O (5 x 2 mL),

brine (2 x 2 mL), dried with $MgSO_4$, and concentrated *in vacuo*. The yellow residue was purified by flash column chromatography on silica (20% EtOAc in hexanes) to afford thiol-ene adduct **33** as a white solid (36.5 mg, 62% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.46 (td, *J* = 9.8, 2.2 Hz, 1H), 5.07 – 5.04 (m, 2H), 4.87 (dd, *J* = 10.4, 3.7 Hz, 1H), 4.80 (s, 1H), 4.55 (s, 1H), 4.26 (dd, *J* = 12.4, 4.3 Hz, 1H), 4.09 (dd, *J* = 12.4, 2.2 Hz, 1H), 4.05 – 4.00 (m, 1H), 3.85 – 3.78 (m, 1H), 3.54 – 3.47 (m, 1H), 2.90 (td, *J* = 12.0, 6.1 Hz, 1H), 2.64 (d, *J* = 4.6 Hz, 1H), 2.62 – 2.55 (m, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.63 – 1.57 (m, 4H), 1.29 – 1.22 (m, 7H), 1.02 (s, 3H), 1.00 (s, 3H), 0.93 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 170.86, 170.31, 170.26, 169.77, 166.68, 100.18, 95.84, 70.94, 70.32, 68.60, 67.34, 67.02, 61.96, 61.55, 50.19, 47.75, 45.04, 43.97, 43.58, 38.27, 33.70, 31.71, 30.84, 30.17, 30.05, 29.63, 29.27, 26.90, 25.54, 20.94, 20.89, 20.80.
IR (film) 2926.45, 1750.08, 1455.99, 1367.28, 1225.54, 1168.65, 1036.55, 2351.77 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{32}H_{49}O_{10}S$ $[M+H]^+$, 625.3041. Found 625.3156.



21 **S13**

(3a*R*,5a*S*,8*S*,9a*S*,9b*R*)-8-allyl-3a,6,6,9a-tetramethyldecahydronaphtho[2,1-*b*]furan 2(3a*H*)-one (S13): Adapted from the literature procedure.[22] In a 2 dram vial in a glovebox, sclareolide xanthate **21** (50 mg, 0.13 mmol), allyl ethyl sulfone (54 mg, 0.40 mmol), and dilauroyl peroxide (5.4 mg, 0.013 mmol) were dissolved in chlorobenzene (0.5 mL). The vial was fitted with a rubber septum, wrapped with Teflon tape, and placed under a balloon of argon once removed from the glovebox. The vial was heated at 100 ˚C, and additional dilauroyl peroxide was added every 30 minutes until the sclareolide xanthate had been consumed as determined by TLC (48.6 mg additional DLP). The crude reaction mixture was concentrated by passing a stream of nitrogen over the heated vial. The residue was purified via flash column chromatography on silica (10 – 20% EtOAc in hexanes) to afford allylated sclareolide **S13** as a clear oil (18 mg, 49% yield):

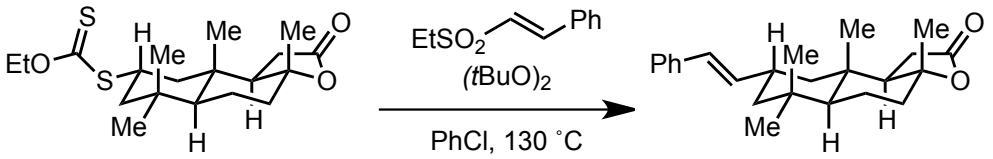
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.79 – 5.71 (m, 1H), 5.00 – 4.97 (m, 2H), 2.75 – 2.70 (m, 1H), 2.40 (d, *J* = 17.9 Hz, 1H), 2.27 – 2.22 (m, 1H), 1.93 (t, *J* = 6.6 Hz, 2H), 1.78 – 1.72

(m, 1H), 1.66 – 1.57 (m, 4H), 1.54 – 1.41 (m, 4H), 1.32 (s, 3H), 1.22 – 1.18 (m, 1H), 0.91 (s, 6H), 0.87 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 177.91, 137.09, 116.02, 85.83, 54.84, 51.65, 48.54, 47.47, 41.75, 36.80, 35.29, 33.76, 33.73, 32.59, 30.13, 28.61, 22.94, 18.41, 15.42.

IR (film) 3446.17, 2925.48, 1867.72, 1772.26, 1670.05, 1540.85, 1521.56, 1456.96 cm^{-1}.

HRMS (ES+) Exact mass calcd for $C_{19}H_{31}O_2$ $[M+H]^+$, 291.2319. Found 291.2339.



21 **S14**

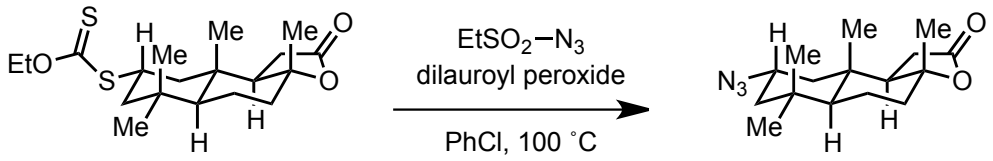
(3a*R*,5a*S*,8*S*,9a*S*,9b*R*)-3a,6,6,9a-tetramethyl-8-((*E*)-styryl)decahydronaphtho[2,1-*b*]furan-2(3a*H*)-one (S14): Adapted from the literature procedure.[15] To a solution of sclareolide xanthate **21** (32 mg, 0.086 mmol) and styryl ethyl sulfone (51 mg, 0.26 mmol) dissolved in PhCl (1.35 mL) and stirring at 130 °C, tert-butyl peroxide (10 µL, 0.068 mmol) was added. Four more tert-butyl peroxide (5 µL, 0.034 mmol) additions were added in the following 24 hours. After the last addition, the reaction was left stirring overnight. The resulting dark brown mixture was concentrated, and the product was isolated by flash column chromatography (10% EtOAc in hexanes) to yield styrene **S14** as a yellow oil (22.2 mg, 73% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.32 – 7.27 (t, *J* = 7.7 Hz, 2H), 7.22 – 7.17 (m, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.09 (dd, *J* = 15.9, 7.0 Hz, 1H), 2.75 (dd, *J* = 17.9, 7.9 Hz, 1H), 2.49 – 2.39 (m, 2H), 2.35 (ddd, *J* = 14.8, 5.0, 2.0 Hz, 1H), 1.80 (d, *J* = 7.9 Hz, 1H), 1.72 (dt, *J* = 12.6, 2.7 Hz, 1H), 1.67 – 1.55 (m, 2H), 1.50 (td, *J* = 13.6, 12.7, 4.8 Hz, 1H), 1.34 (s, 3H), 1.11 (app t, *J* = 12.8 Hz, 1H), 0.99 (s, 3H), 0.96 (s, 3H), 0.95 (s, 3H), 0.93 – 0.79 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 177.78, 137.75, 135.70, 128.64, 128.09, 127.11, 126.04, 85.75, 54.80, 51.26, 48.09, 47.18, 36.71, 35.25, 33.73, 33.63, 32.56, 32.54, 30.14, 22.93, 18.38, 15.39.

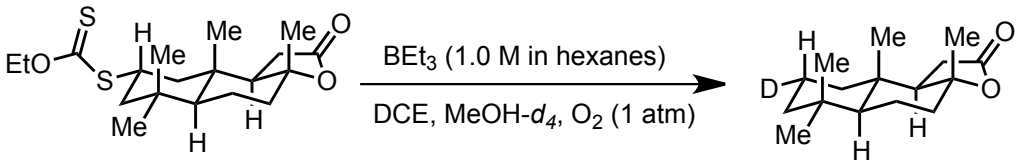
IR (film) 2951.52, 1772.26, 1646.91, 1576.52, 1540.85, 1507.10, 1473.35, 1456.96 cm^{-1}.

HRMS (ES+) Exact mass calcd for $C_{24}H_{33}O_2$ $[M+H]^+$, 353.2475. Found 353.2507.



(3a*R*,5a*S*,8*S*,9a*S*,9b*R*)-8-azido-3a,6,6,9a-tetramethyldecahydronaphtho[2,1-*b*]furan-2(3a*H*)-one (S15): Adapted from the literature procedure.[23] In a 2 dram vial in a glovebox, sclareolide xanthate **21** (50 mg, 0.13 mmol), azide ethyl sulfone (55 mg, 0.40 mmol), and dilauroyl peroxide (5.4 mg, 0.013 mmol) were dissolved in chlorobenzene (0.5 mL). The vial was fitted with a rubber septum, wrapped with Teflon tape, and placed under a balloon of argon once removed from the glovebox. The vial was heated at 100 ˚C, and additional dilauroyl peroxide was added every 30 minutes until the sclareolide xanthate had been consumed as determined by TLC (48.6 mg additional DLP). The crude reaction mixture was concentrated by passing a stream of nitrogen over the heated vial. The residue was purified via flash column chromatography on silica (10 – 20% EtOAc in hexanes) to afford the azide **S15** as a yellow oil in a 5:1 diastereomeric mixture (28.2 mg, 74% yield) in accordance with the literature (NMR shifts are reported for the major diastereomer only):[24]

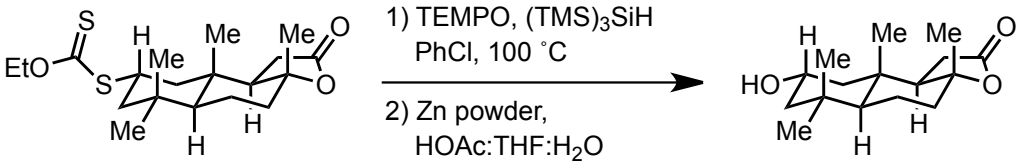
^{1}H NMR (major diastereomer, 600 MHz, $CDCl_3$) δ 3.61 (tt, *J* = 12.1, 4.2 Hz, 1H), 2.47 – 2.38 (m, 1H), 2.28 (dd, *J* = 16.1, 6.4 Hz, 1H), 2.12 – 2.07 (m, 1H), 2.01 (dd, *J* = 14.7, 6.4 Hz, 1H), 1.93 – 1.88 (m, 1H), 1.86 – 1.75 (m, 2H), 1.73 – 1.67 (m, 1H), 1.64 – 1.54 (m, 2H), 1.33 (s, 3H), 1.10 – 1.04 (m, 2H), 0.98 (s, 3H), 0.96 (s, 3H), 0.90 (s, 3H).
^{13}C NMR (major diastereomer, 151 MHz, $CDCl_3$) δ 176.30, 86.03, 58.76, 56.05, 54.02, 47.06, 44.61, 38.48, 37.09, 34.54, 33.11, 32.01, 28.73, 21.75, 20.30, 16.03.



(3a*R*,5a*S*,8*S*,9a*S*,9b*R*)-8-deutero-3a,6,6,9a-tetramethyldecahydronaphtho[2,1-*b*]furan-2(3a*H*)-one (S16): Adapted from the literature procedure.[18] In a 1 dram vial in the glovebox, to a solution of sclareolide xanthate **21** (40 mg, 0.11 mmol) in DCE/MeOH-d_4 (0.4 mL/0.2 mL) was added triethylborane (0.54 mL, 0.54 mmol, 1M in hexanes). The vial was fitted with a Teflon-lined screw cap and sealed with Teflon tape. The vial headspace was purged with a dry O_2 balloon for 2 min and then stirred under an O_2 atmosphere for 72 h. The reaction mixture was diluted with DCM (1 mL), passed

over a short silica plug, and concentrated to afford **S16** as a pale yellow amorphous solid (16 mg, 62% yield). GC-MS analysis according to the literature revealed 72% D incorporation:

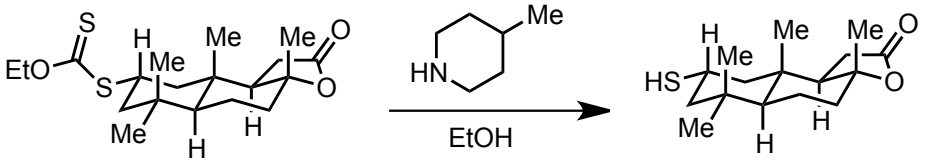
^{1}H NMR (600 MHz, $CDCl_3$) δ 2.44 – 2.37 (m, 1H), 2.23 (dd, *J* = 16.3, 6.5 Hz, 1H), 2.07 (dt, *J* = 12.0, 3.3 Hz, 1H), 1.96 (dd, *J* = 14.9, 6.5 Hz, 1H), 1.89 – 1.85 (m, 1H), 1.73 – 1.60 (m, 2H), 1.44 – 1.36 (m, 2H), 1.33 (s, 3H), 1.22 – 1.14 (m, 2H), 1.08 – 1.02 (m, 1H), 0.99 – 0.93 (m, 1H), 0.91 (s, 3H), 0.88 (s, 3H), 0.83 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 177.10, 86.58, 59.23, 56.75, 42.18, 39.51, 38.81, 36.15, 33.43, 33.31, 28.86, 21.71, 21.06, 20.68, 17.83 (t, *J* = 19.6 Hz), 15.21.
IR (film) 2926.45, 2869.56, 1844.58, 1773.23, 1716.34, 1540.85, 1497.45, 1456.96 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{16}H_{26}O_2D$ $[M+H]^+$, 252.2067. Found 252.2083.



21 **S17**

(3a*R*,5a*S*,8*S*,9a*S*,9b*R*)-8-hydroxy-3a,6,6,9a-tetramethyldecahydronaphtho[2,1-*b*]furan-2(3a*H*)-one (S17): To a solution of sclareolide xanthate **21** (37 mg, 0.1 mmol) in PhCl (1 mL) stirring at 100 °C, TEMPO (94 mg, 0.6 mmol) and tris(trimethylsilyl)silane (93 µL, 0.3 mmol) were added in three portions over 48 h. The reaction mixture was stirred for an additional 24 h, then concentrated. Zinc powder (262 mg, 4.0 mmol), then a mixture of HOAc/THF/H_2O (3:1:1, 2.5 mL) was added and heated at 70 °C overnight. The reaction mixture was filtered through a cotton plug and washed with EtOAc. The resulting filtrate was washed with saturated $NaHCO_3$ and water, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude material was purified by flash column chromatography (20 – 50% EtOAc in hexanes) to yield **S17** as a white solid in accordance with the literature data (16.2 mg, 61% yield):[25]

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.98 (tt, *J* = 11.3, 4.3 Hz, 1H), 2.43 (dd, *J* = 16.2, 14.7 Hz, 1H), 2.26 (dd, *J* = 16.2, 6.4 Hz, 1H), 2.08 (dt, *J* = 11.9, 3.3 Hz, 1H), 2.00 (dd, *J* = 14.7, 6.4 Hz, 1H), 1.90 (dd, *J* = 14.2, 3.6 Hz, 1H), 1.86 – 1.79 (m, 2H), 1.69 (td, *J* = 12.6, 4.3 Hz, 1H), 1.52 (br. s, 1H), 1.41 – 1.31 (m, 1H), 1.32 (s, 3H), 1.15 (t, *J* = 12.1 Hz, 1H), 1.07 (dd, *J* = 12.7, 2.9 Hz, 1H), 0.99 – 0.94 (m, 7H), 0.88 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 176.66, 86.27, 64.42, 58.98, 56.23, 51.47, 48.39, 38.56, 37.44, 34.86, 33.35, 28.84, 21.90, 21.76, 20.32, 16.29.



21 **S18**

(3a*R*,5a*S*,8*S*,9a*S*,9b*R*)-8-mercapto-3a,6,6,9a-tetramethyldecahydronaphtho[2,1-*b*]furan-2(3a*H*)-one (S18): 4-Methyl piperidine (49 μL, 0.40 mmol) was added to a solution of sclareolide xanthate **21** (37 mg, 0.10 mmol) dissolved in EtOH (0.5 mL) and was left stirring overnight at room temperature. The reaction mixture was then concentrated, and **S18** was isolated by flash column chromatography (30% EtOAc in hexanes) as a white solid (20.2 mg, 71% yield):

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.97 (td, *J* = 10.7, 8.8, 6.3 Hz, 1H), 2.44 (app t, *J* = 15.4 Hz, 1H), 2.24 (dd, *J* = 16.2, 6.4 Hz, 1H), 2.09 (app d, *J* = 11.9 Hz, 1H), 2.00 (dd, *J* = 14.8, 6.5 Hz, 1H), 1.90 (dd, *J* = 14.5, 3.7 Hz, 1H), 1.86 – 1.77 (m, 2H), 1.70 (td, *J* = 12.6, 4.1 Hz, 1H), 1.65 (br. s, 1H), 1.40 – 1.31 (m, 1H), 1.33 (s, 3H), 1.25 (app t, *J* = 13.0 Hz, 1H), 1.10 (app t, *J* = 12.8 Hz, 2H), 0.95 (s, 3H) ,0.94 (s, 3H), 0.87 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 176.38, 86.21, 58.83, 56.08, 48.66, 46.01, 43.41, 38.54, 37.59, 35.04, 33.09, 28.77, 21.75, 21.55, 20.44, 16.04.
IR (film) 3445.21, 2947.66, 1772.26, 1646.91, 1540.85, 1473.35, 1033.66, 916.99 cm^{-1}.
HRMS (ES+) Exact mass calcd for $C_{32}H_{53}O_4S_2$ $[2M+H]^+$, 565.3380. Found 565.3271.

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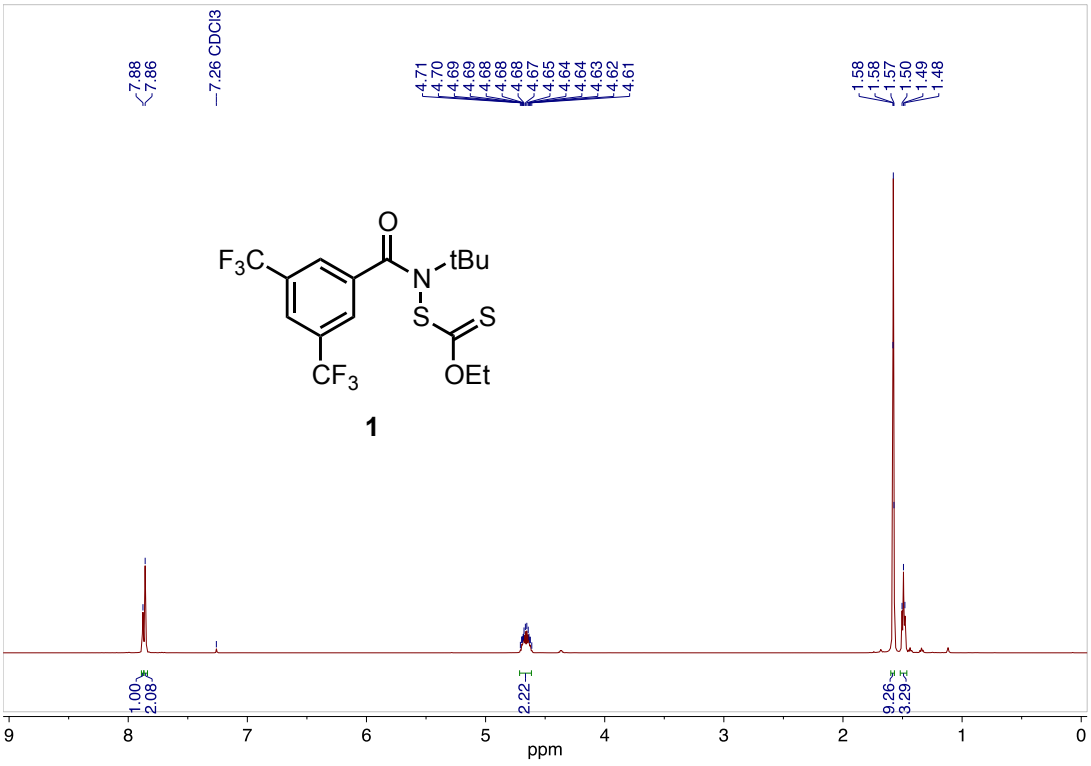
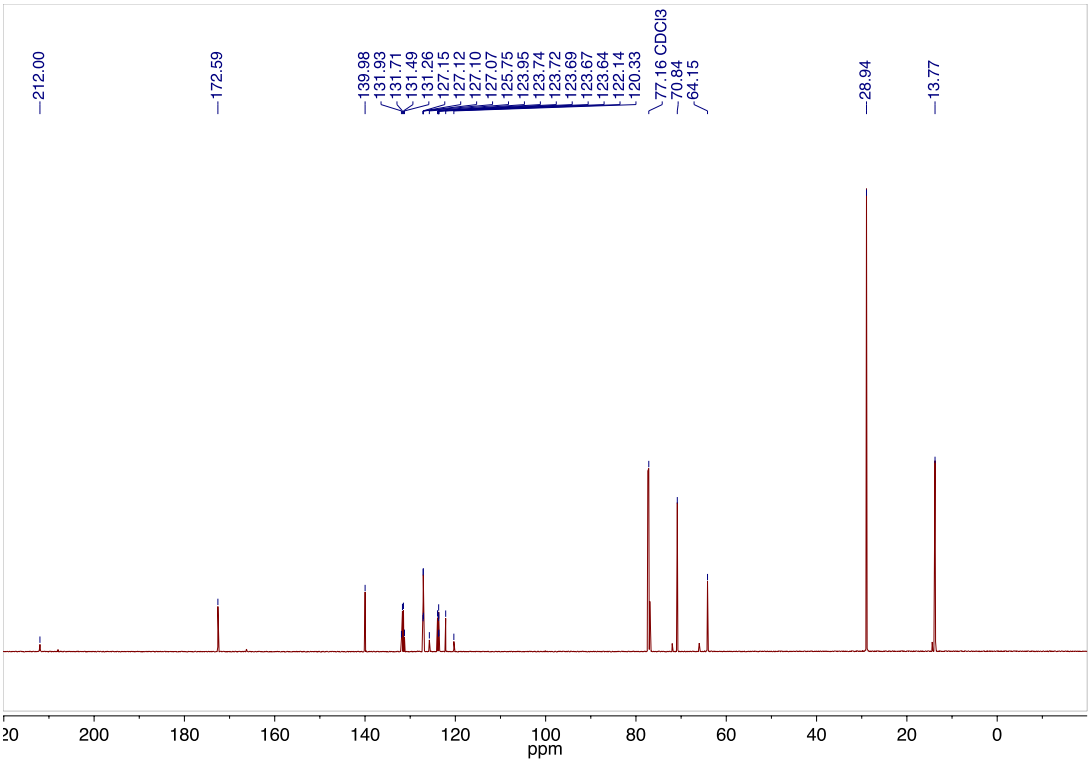
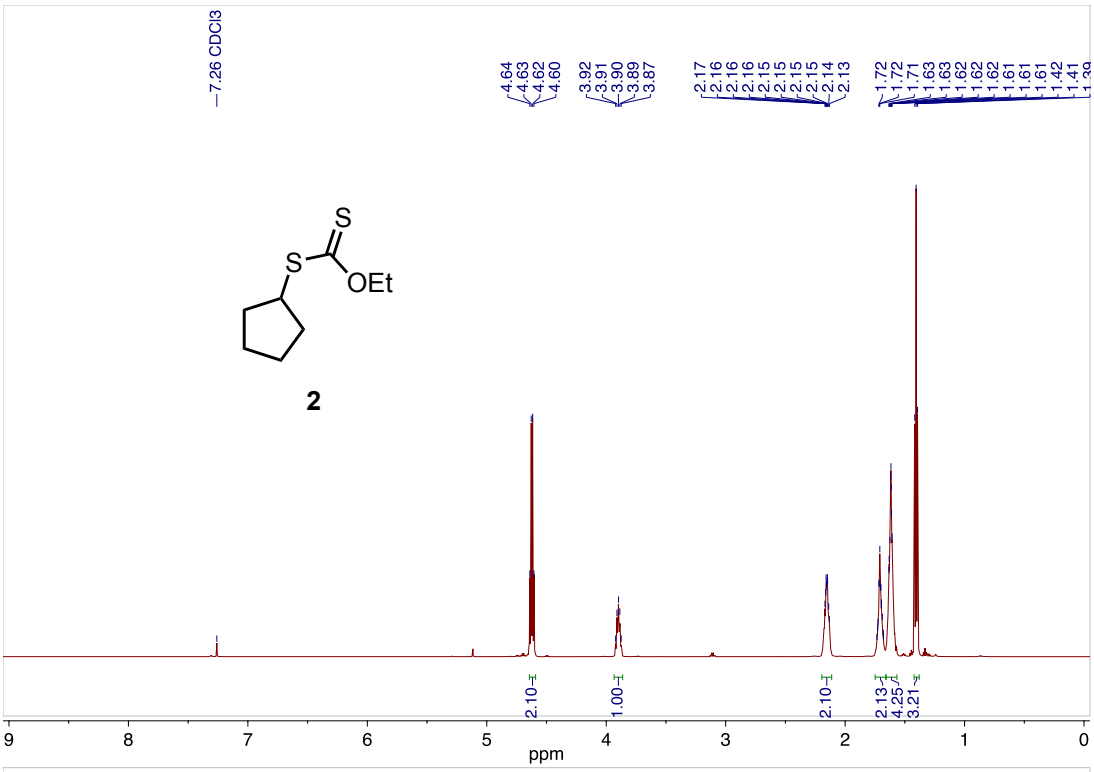
NMR Spectra for New Compounds



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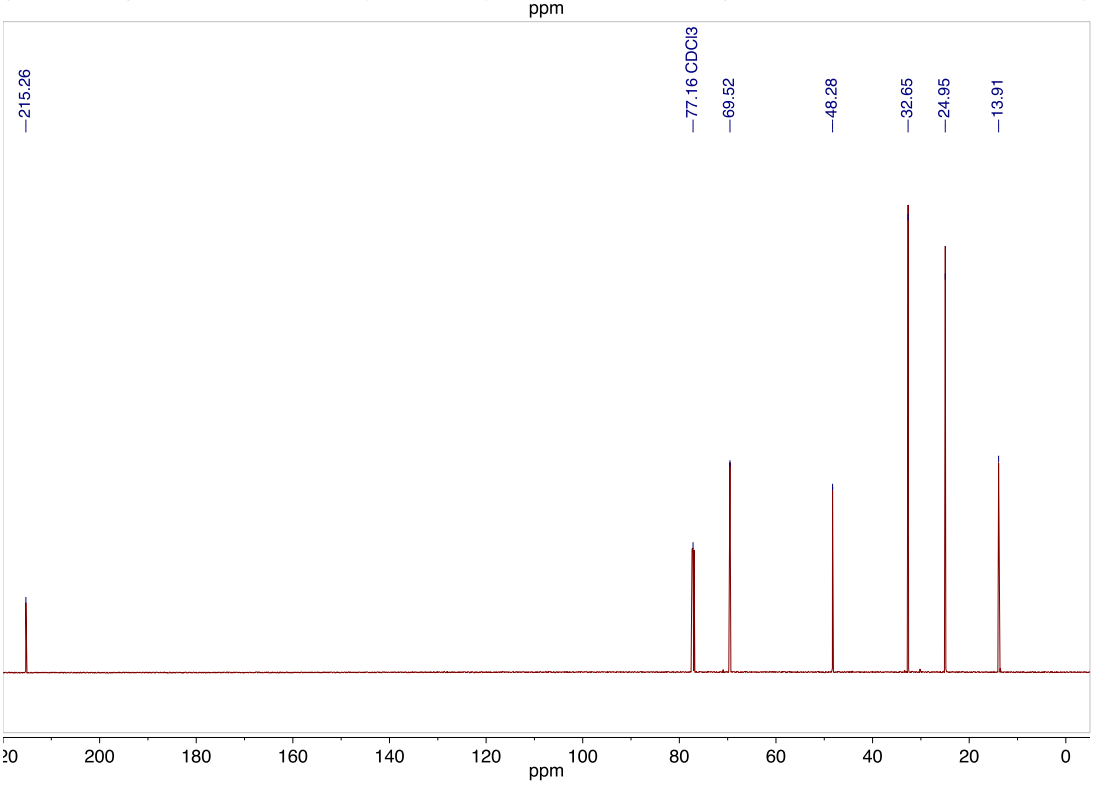
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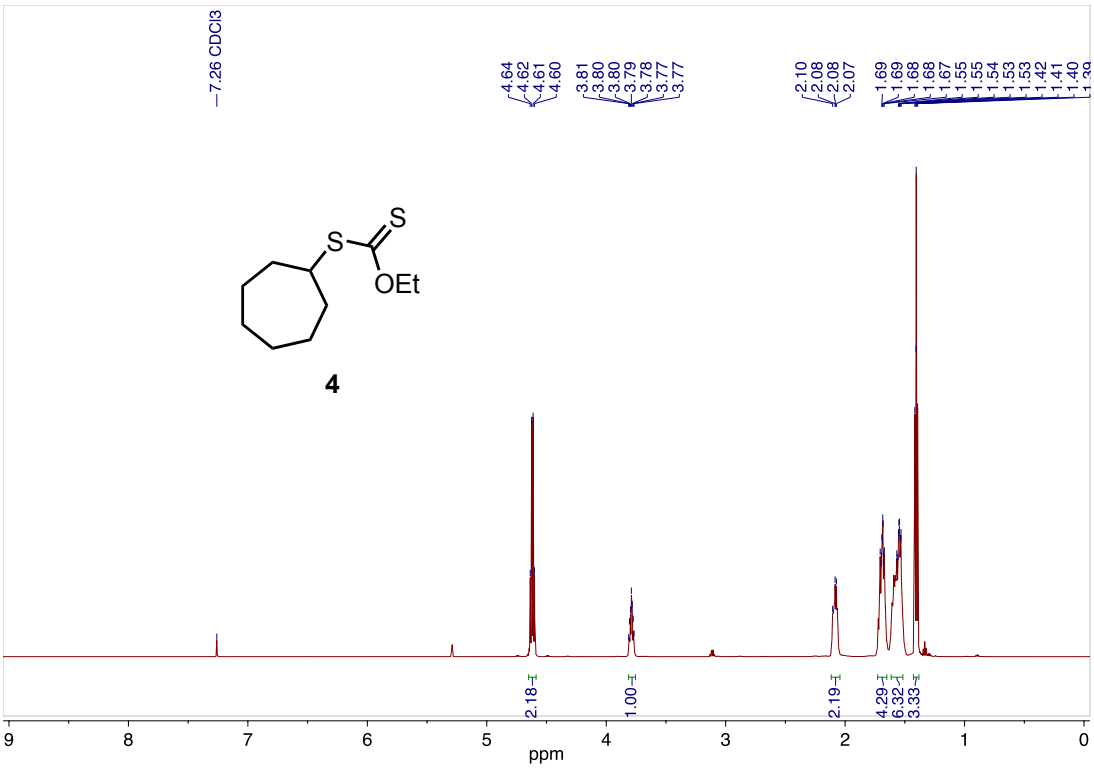
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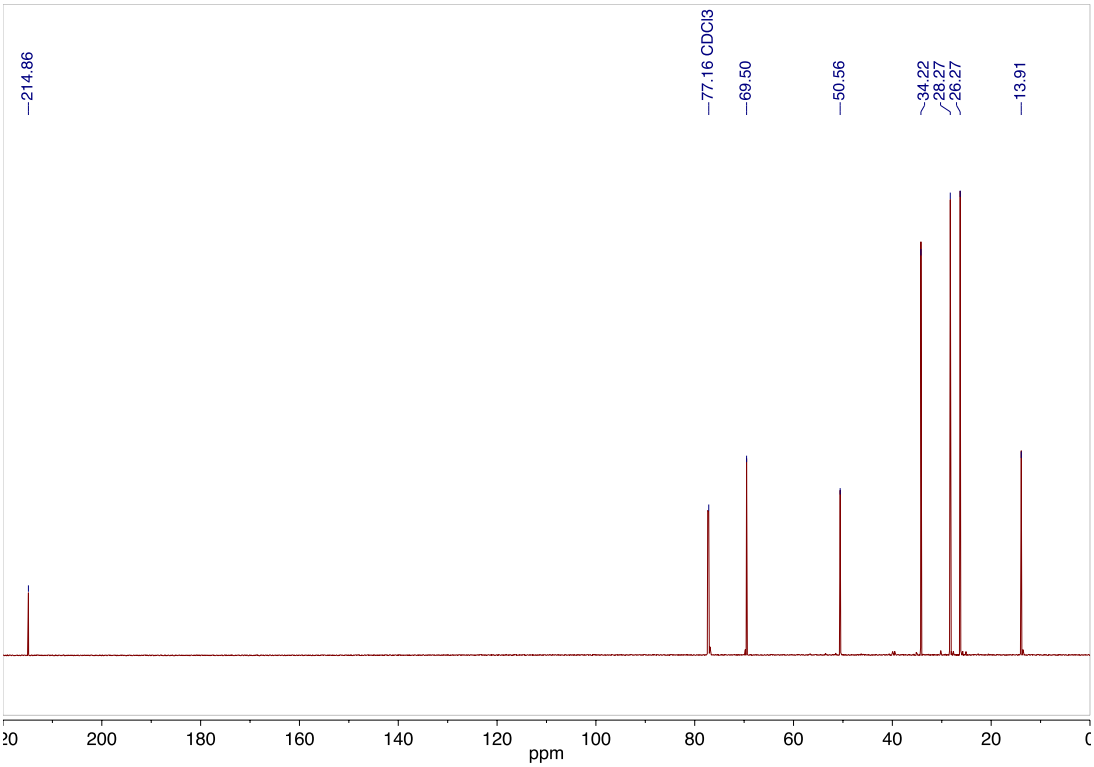
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20
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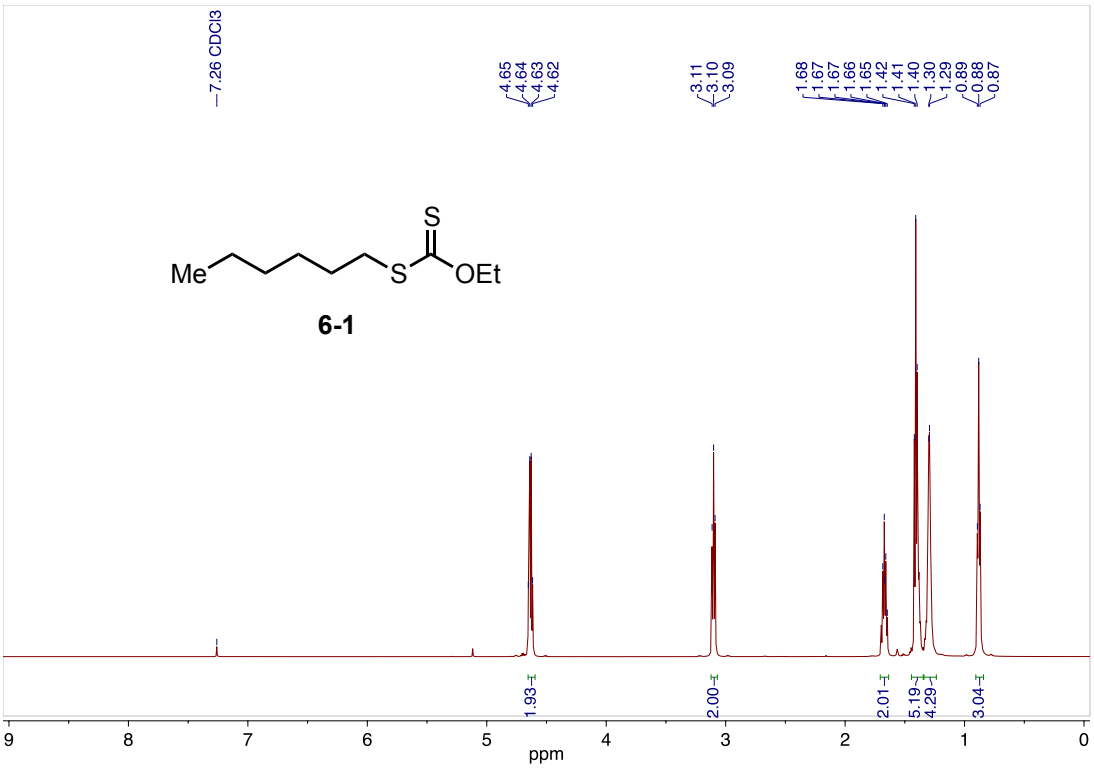
7.26 CDCl3
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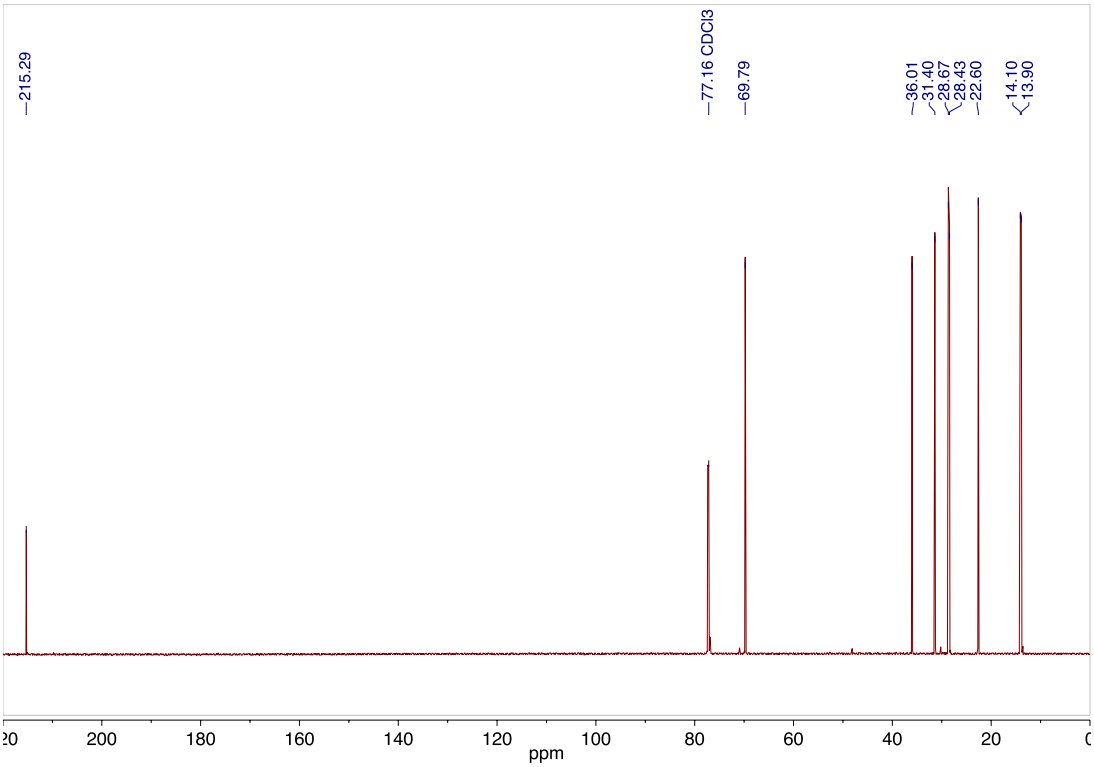
4.63
4.62
3.11
3.10
3.09
1.68
1.67
1.67
1.66
1.65
1.42
1.41
1.40
1.30
1.29
0.89
0.88
0.87
S
Me
S
OEt
1.93
2.00
2.01
5.19
4.29
3.04
9
8
7
6
5
4
3
2
1
0
ppm

6-1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77.16 CDCl3
69.79
36.01
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22.60
14.10
13.90
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140
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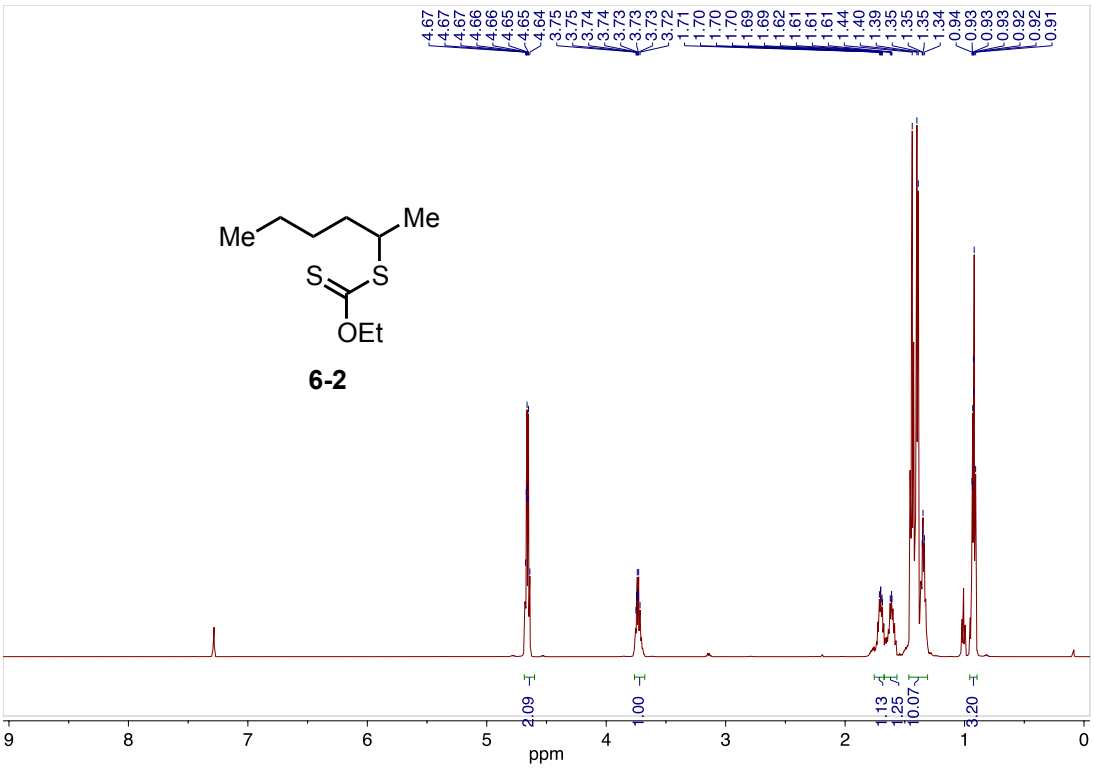
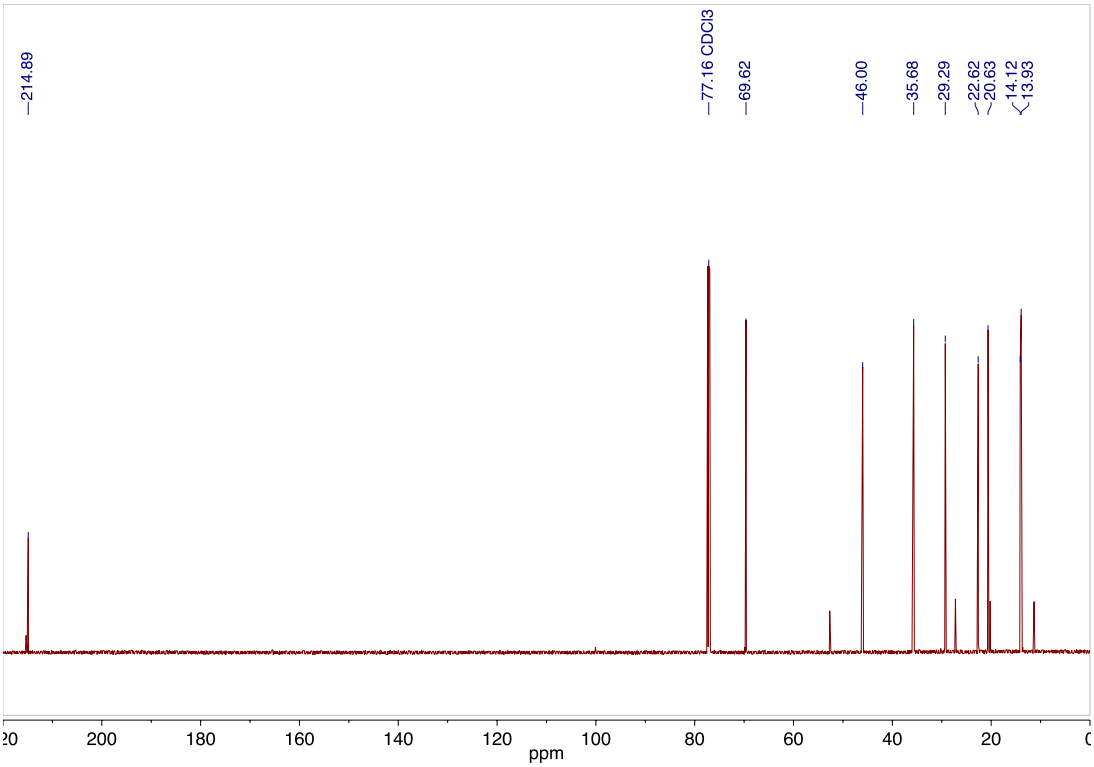
100
80
60
40
20
ppm


Me
Me
S
S
OEt
6-2
ppm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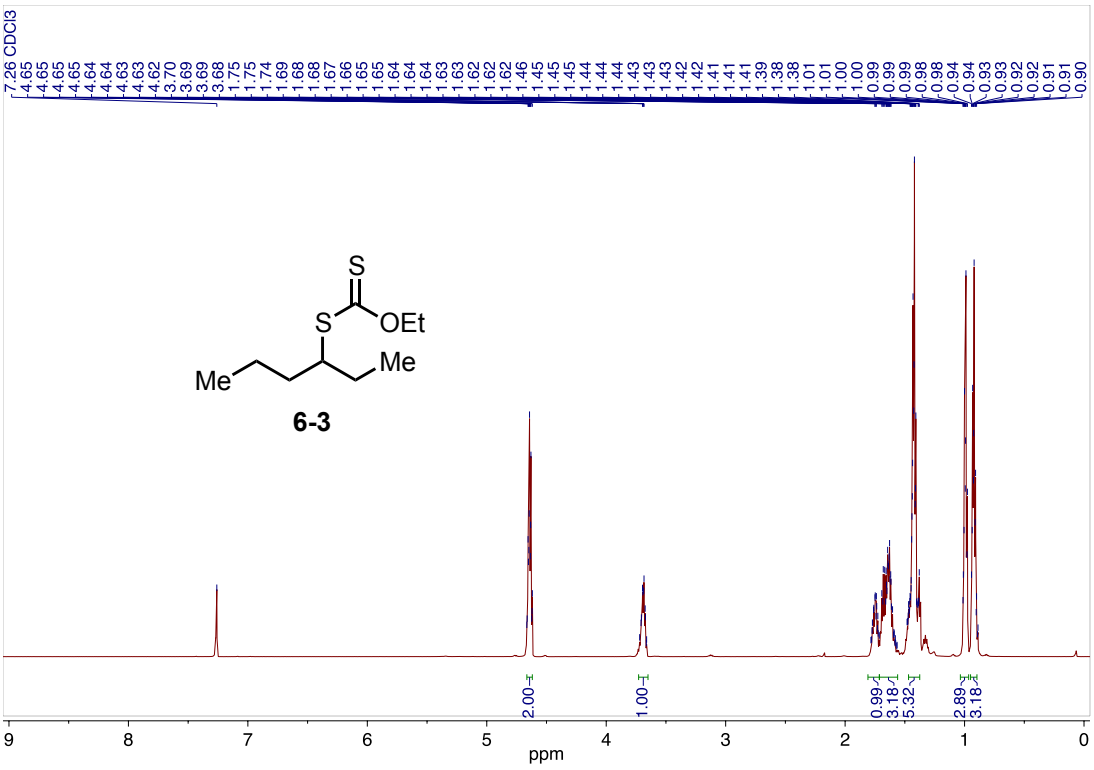
20.63
14.12
13.93
ppm


7.26 CDCl3
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S
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Me
Me
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1.00
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2.89
3.18
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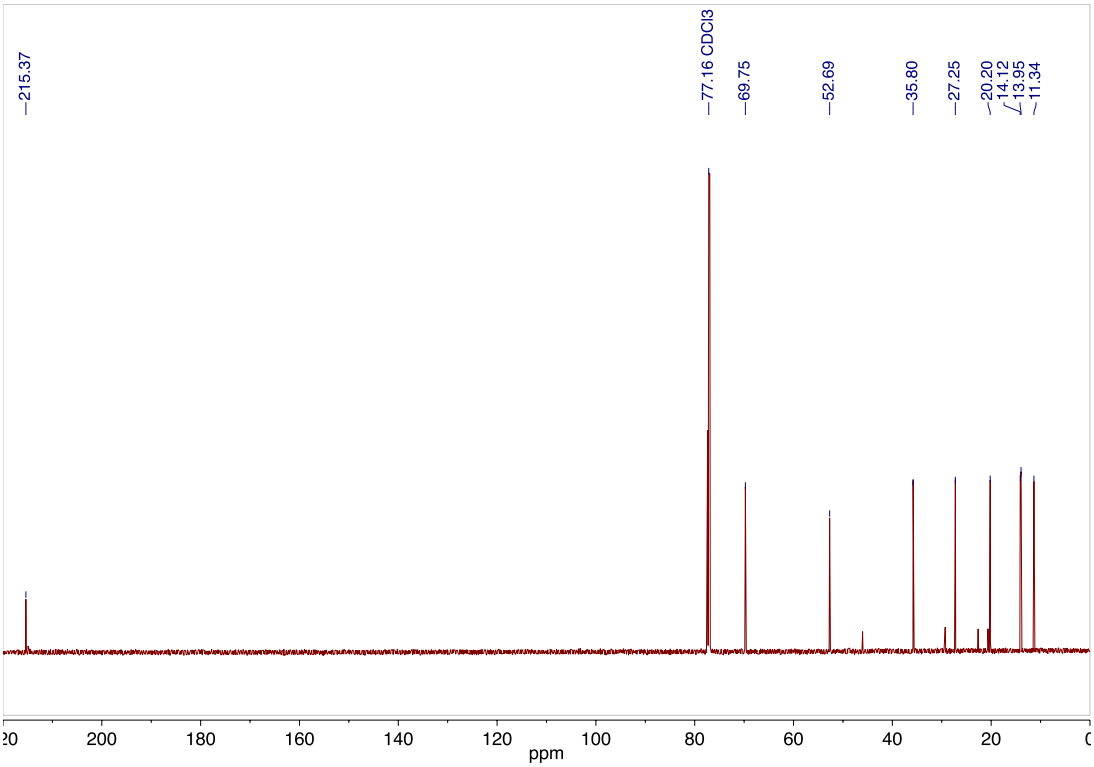
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20.20
14.12
13.95
11.34
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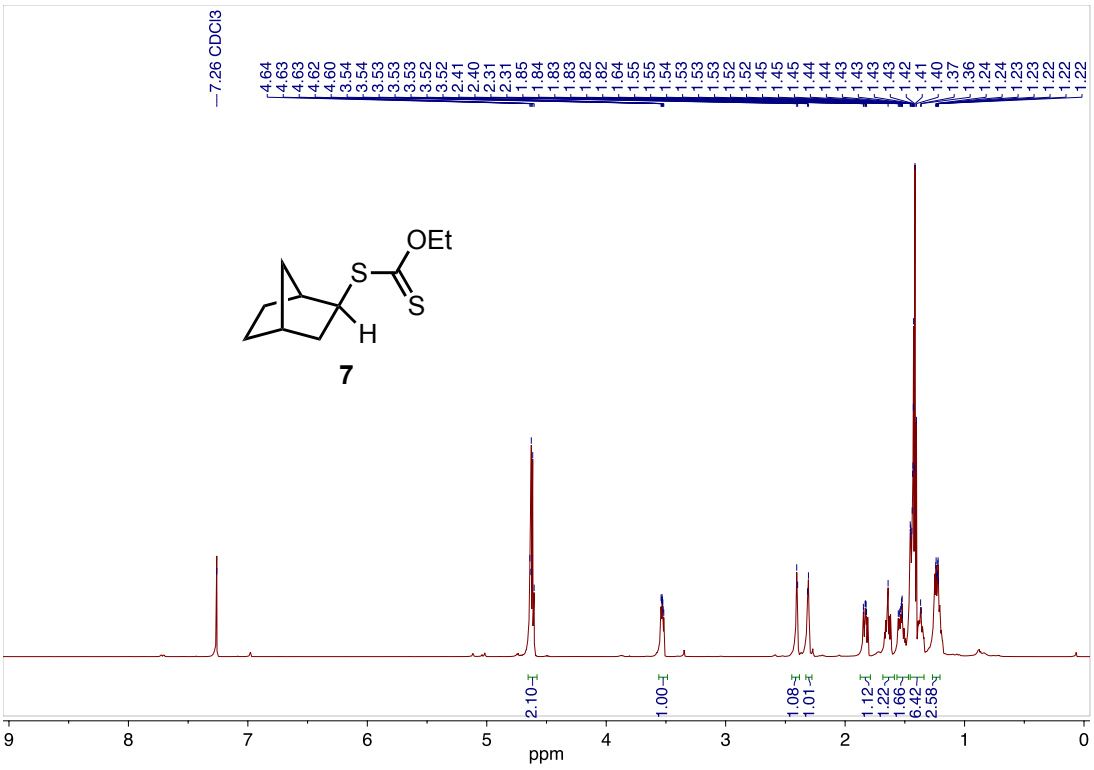
7.26 CDCl3
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4.63
4.63
4.62
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3.54
3.54
3.53
3.53
3.53
3.52
3.52
2.41
2.40
2.31
2.31
1.85
1.84
1.83
1.83
1.82
1.82
1.64
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1.43
1.42
1.41
1.40
1.37
1.36
1.24
1.24
1.23
1.23
1.22
1.22
1.22
OEt
S
S
H
7
2.10
1.00
1.08
1.01
1.12
1.22
1.66
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6
5
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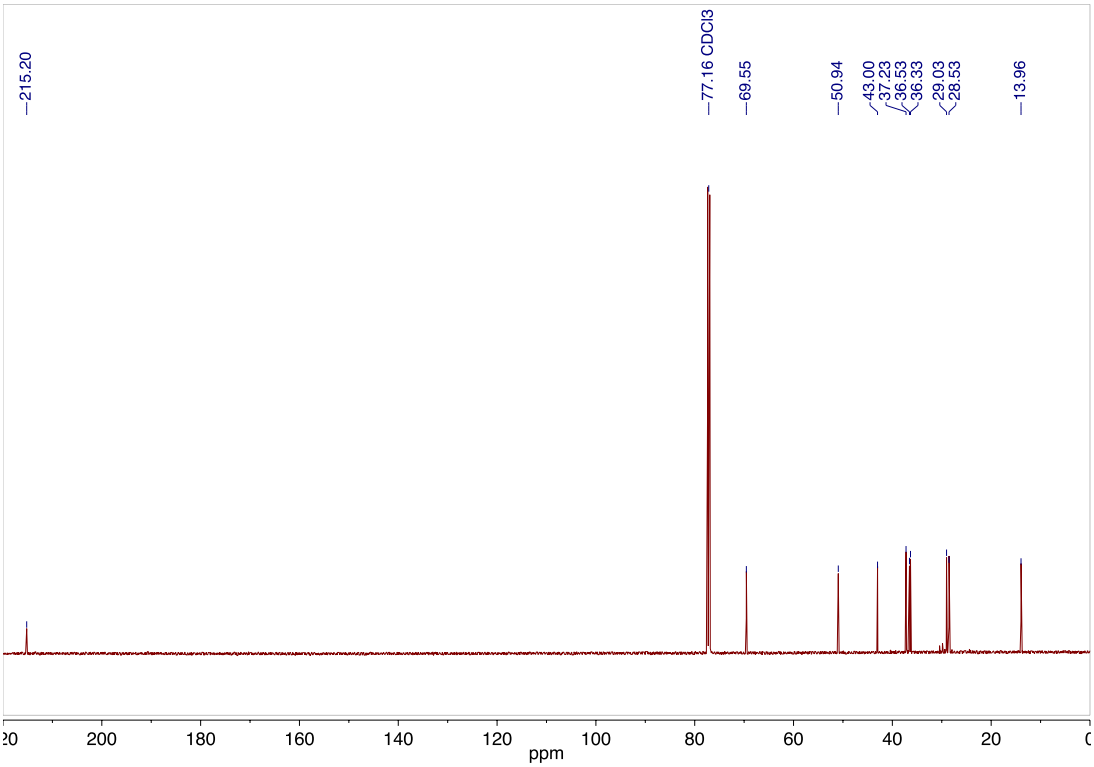
0
ppm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77.16 CDCl3
69.55
50.94
43.00
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36.33
29.03
28.53
13.96
200
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140
120
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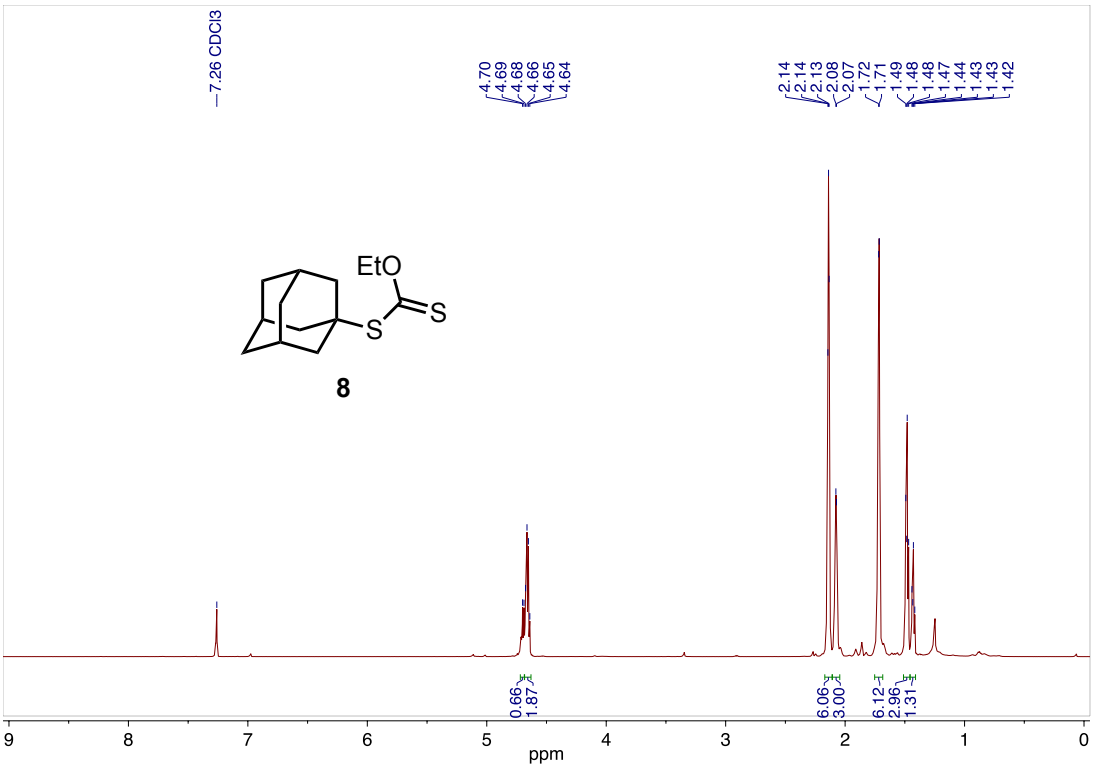
80
60
40
20
ppm


7.26 CDCl3
4.70
4.69
4.68
4.66
4.65
4.64
2.14
2.14
2.13
2.08
2.07
1.72
1.71
1.49
1.48
1.48
1.47
1.44
1.43
1.43
1.42
EtO
S
S
0.66
1.87
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2.96
1.31
9
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5
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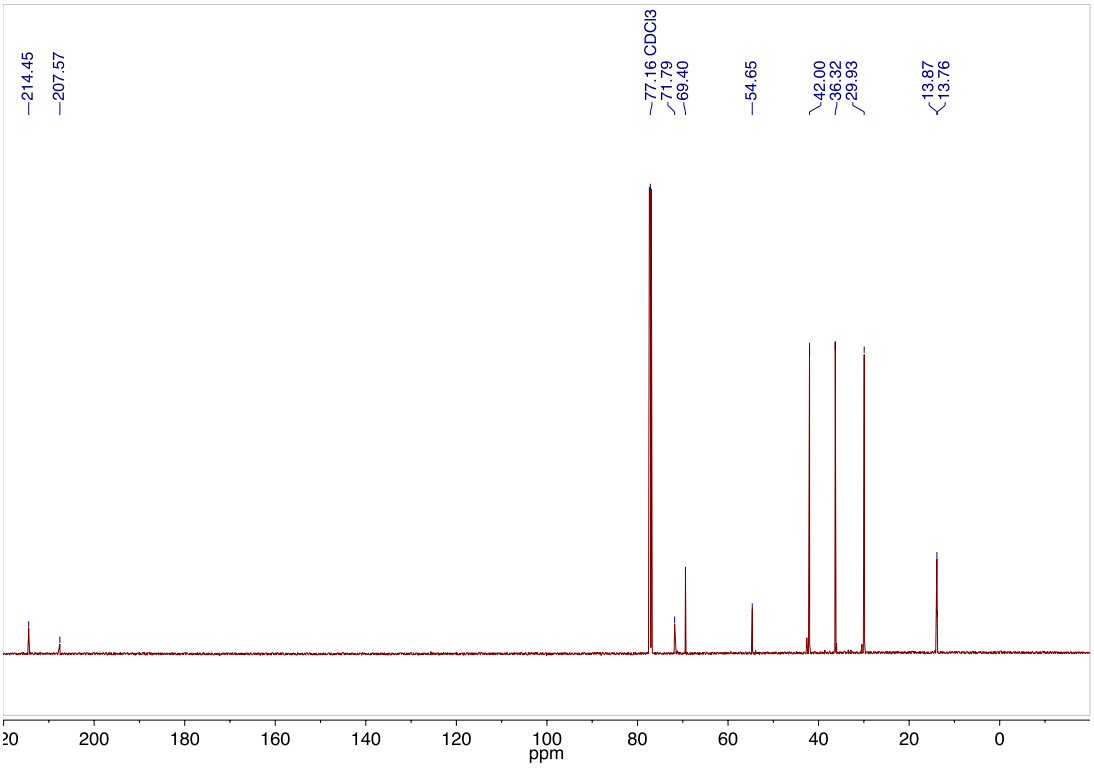
1
0
ppm

8


214.45
207.57
77.16 CDCl3
71.79
69.40
54.65
42.00
36.32
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13.87
13.76
200
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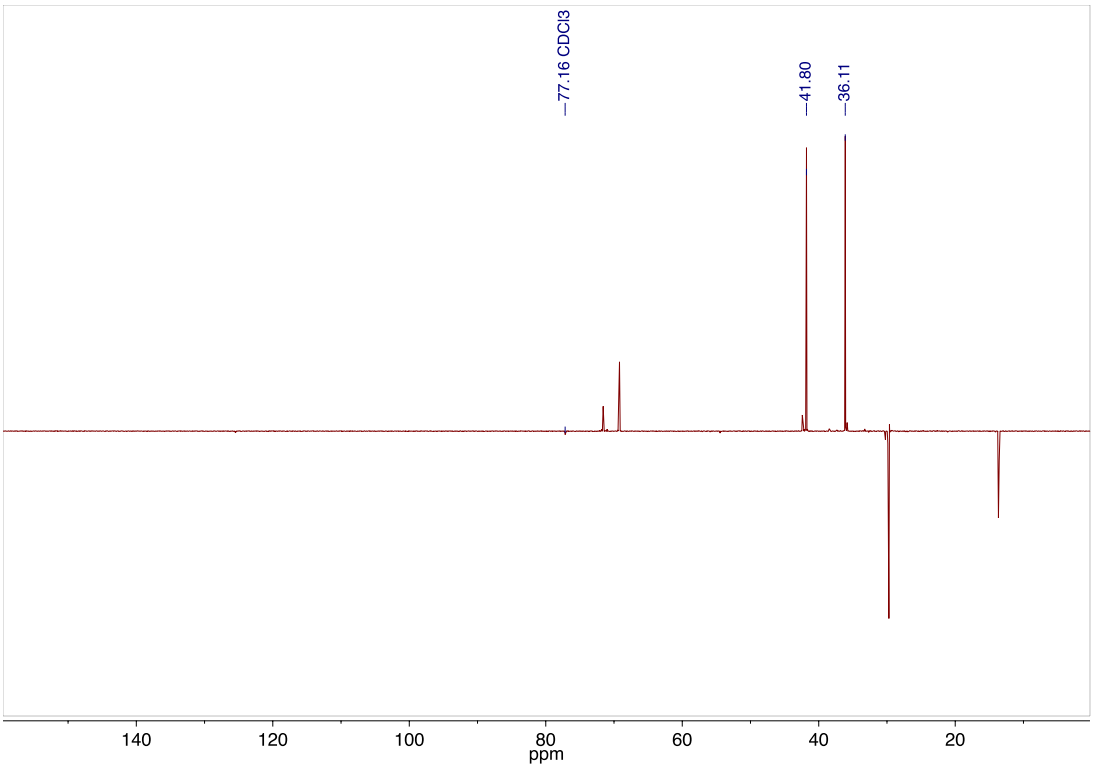
120
100
80
60
40
20
0
ppm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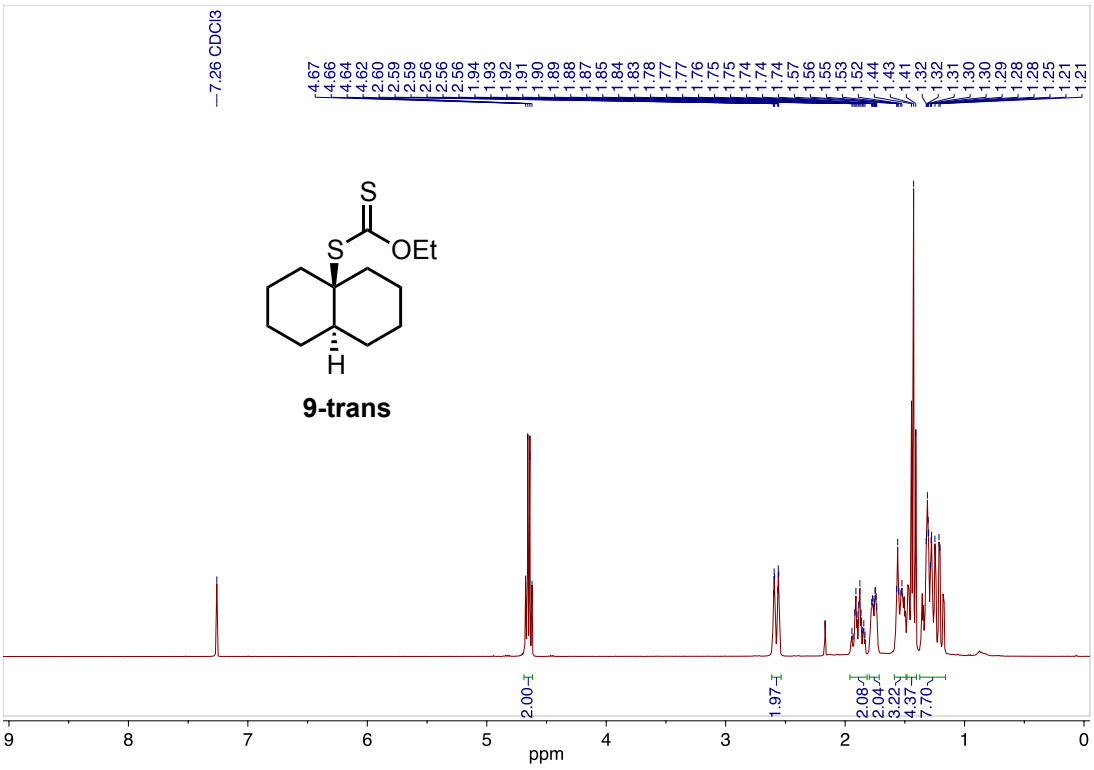
36.11
140
120
100
80
60
40
20
ppm


7.26 CDCl3
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4.66
4.64
4.62
2.60
2.59
2.59
2.56
2.56
2.56
1.94
1.93
1.92
1.91
1.90
1.89
1.88
1.87
1.85
1.84
1.83
1.78
1.77
1.77
1.76
1.75
1.75
1.74
1.74
1.74
1.57
1.56
1.55
1.53
1.52
1.44
1.43
1.41
1.32
1.32
1.31
1.30
1.30
1.29
1.28
1.28
1.25
1.21
1.21
S
S
OEt
H
9-trans
2.00
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3.22
4.37
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9
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6
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2
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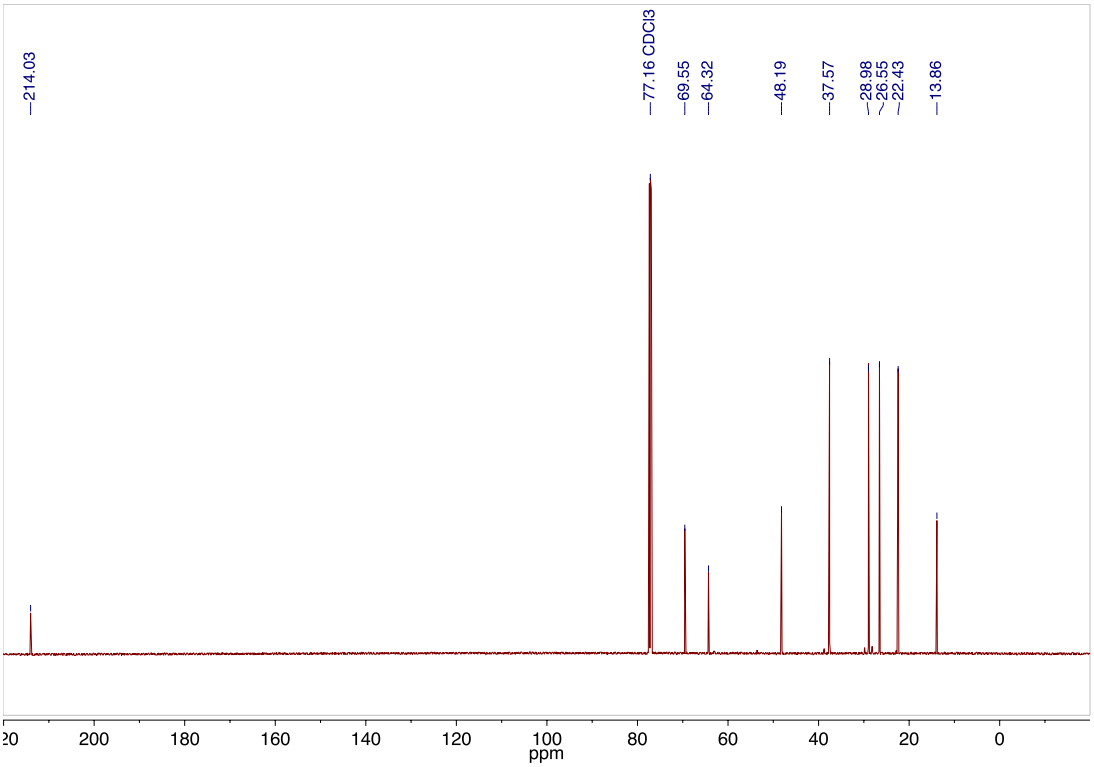
0
ppm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77.16 CDCl3
69.55
64.32
48.19
37.57
28.98
26.55
22.43
13.86
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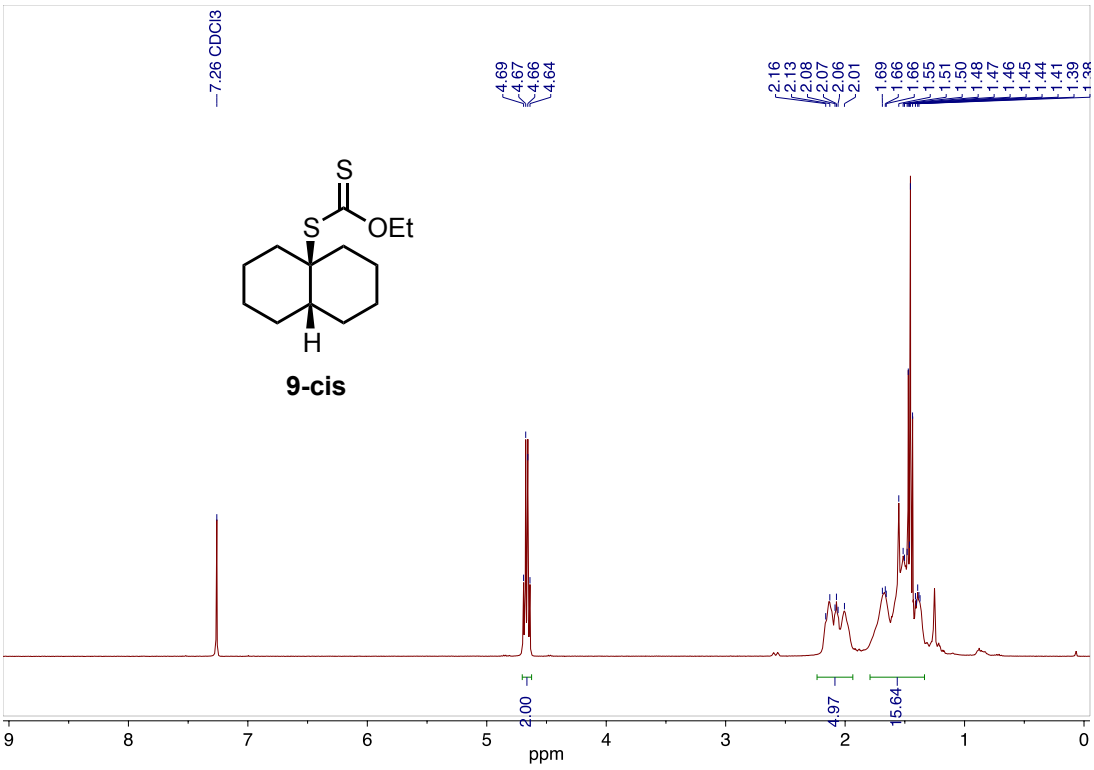
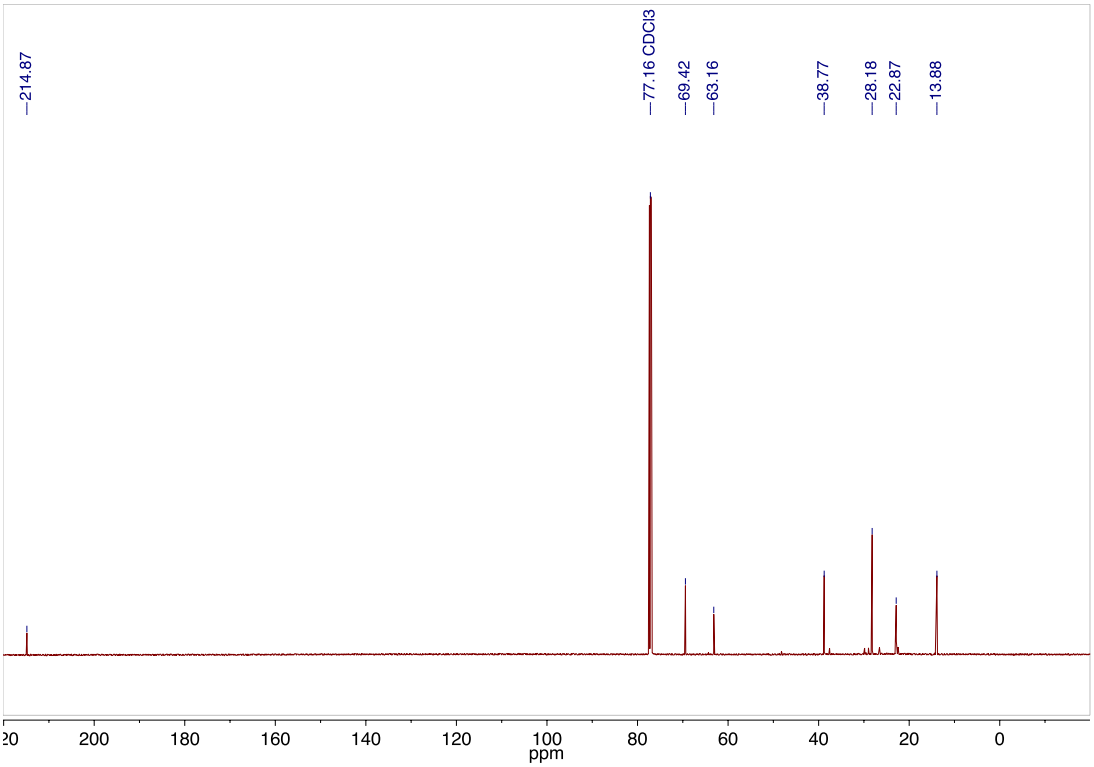
160
140
120
100
80
60
40
20
0
ppm


7.26 CDCl3
4.69
4.67
4.66
4.64
2.16
2.13
2.08
2.07
2.06
2.01
1.69
1.66
1.66
1.55
1.51
1.50
1.48
1.47
1.46
1.45
1.44
1.41
1.39
S
S
OEt
H
2.00
4.97
15.64
9
8
7
6
5
4
3
2
1
0
ppm

9-cis


214.87
77.16 CDCl3
69.42
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38.77
28.18
22.87
13.88
200
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120
100
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60
40
20
0
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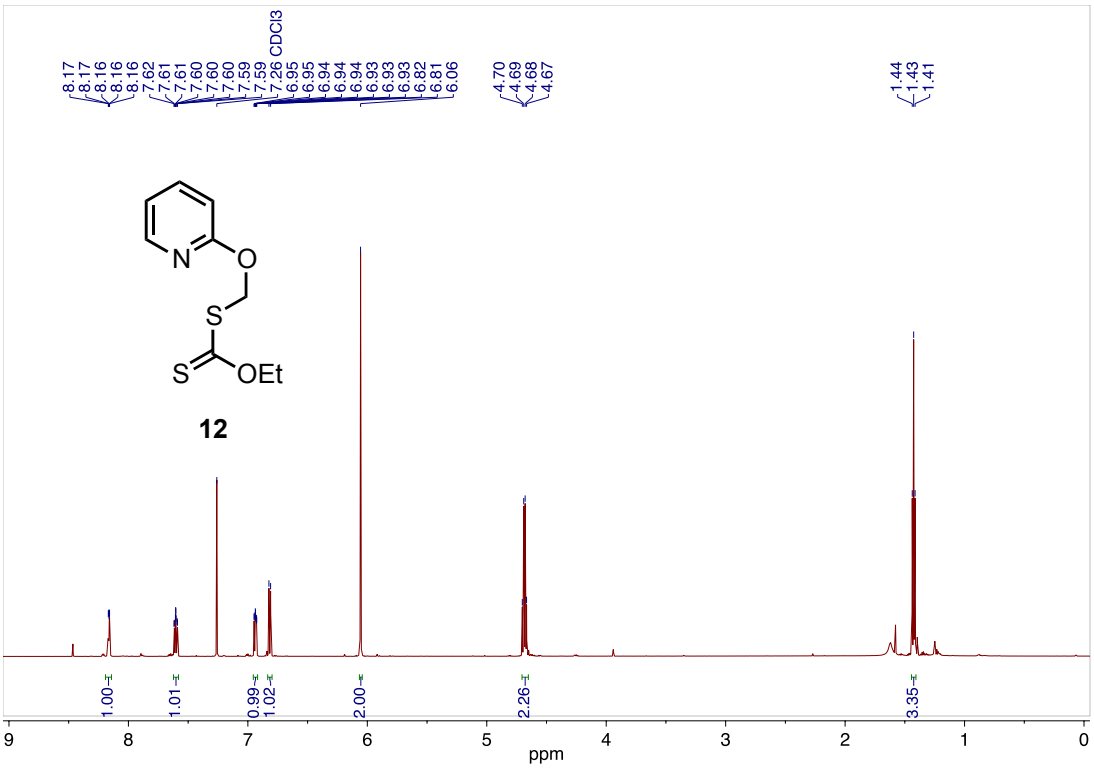
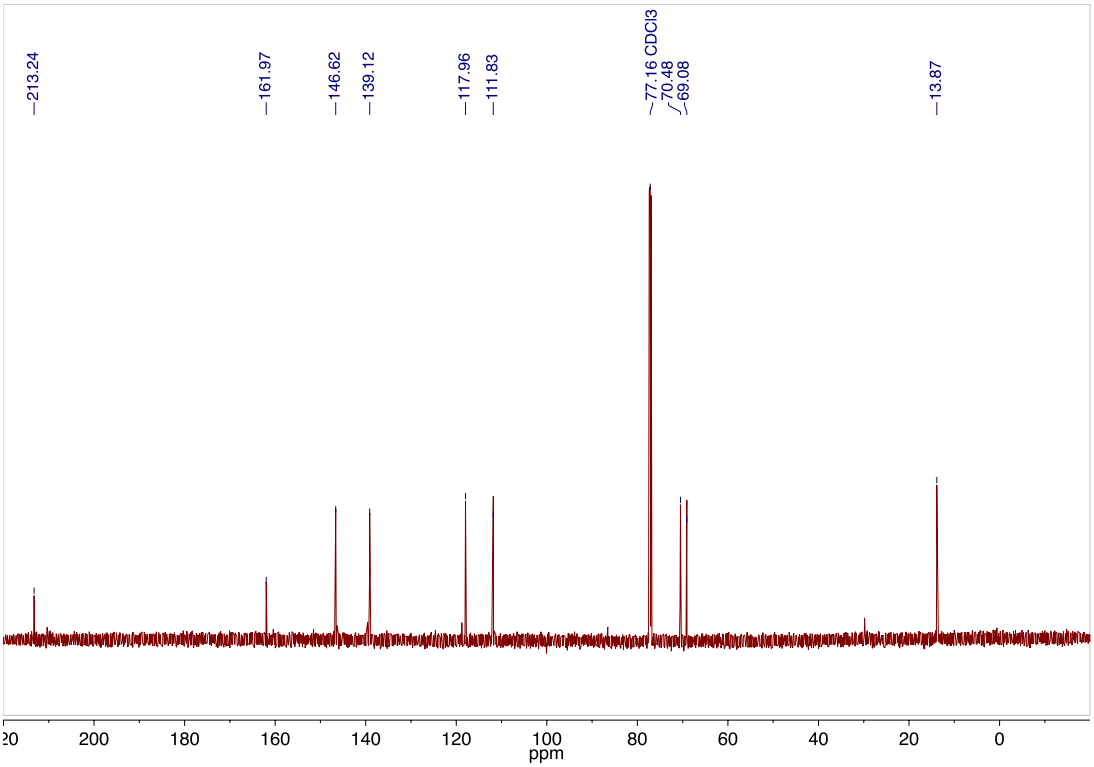
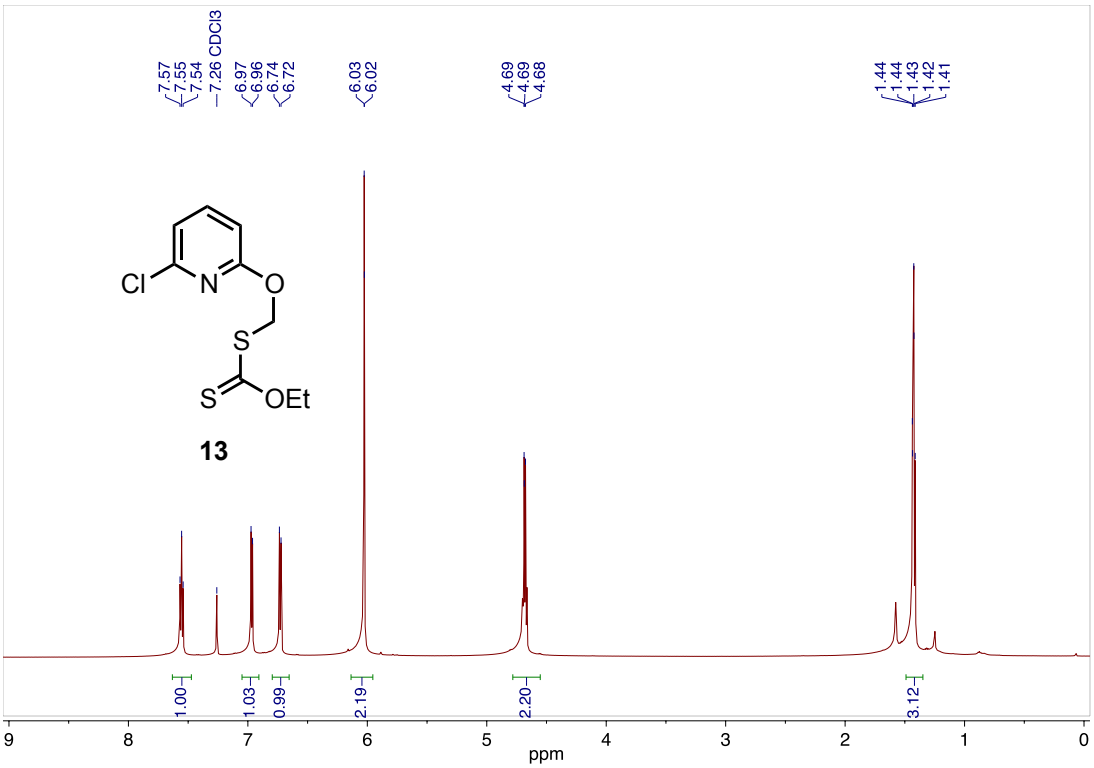
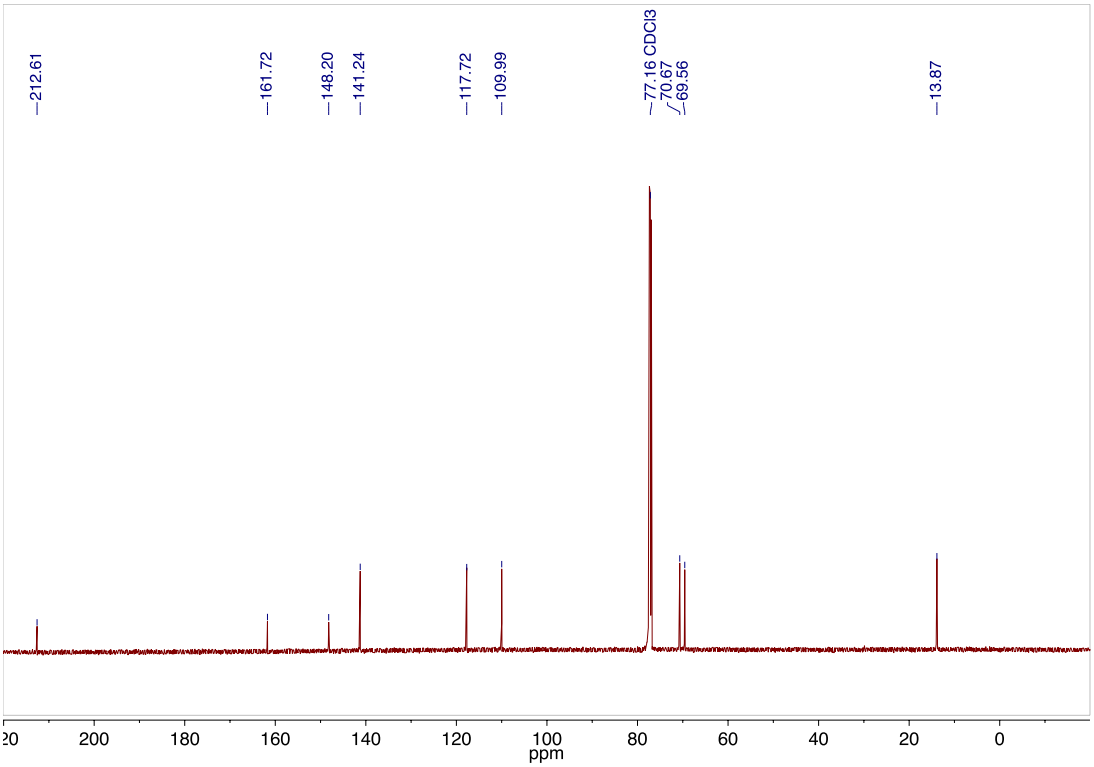
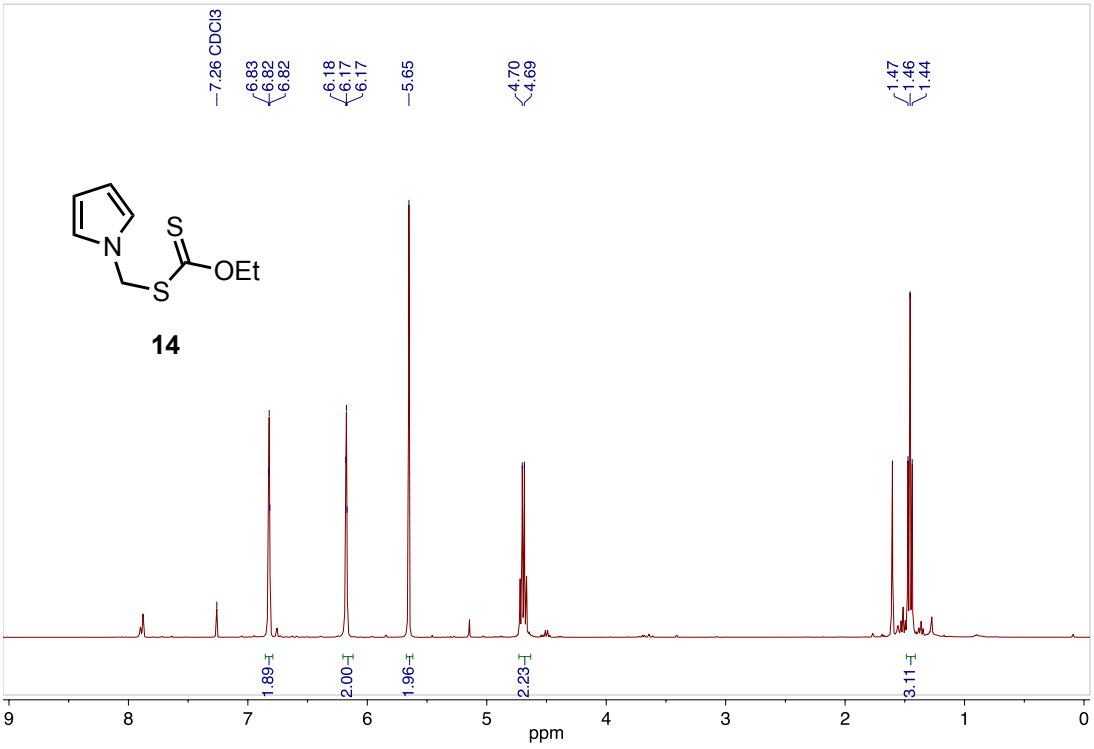

8.17
8.17
8.16
8.16
8.16
7.62
7.61
7.61
7.60
7.60
7.60
7.59
7.59
7.26 CDCl3
6.95
6.95
6.94
6.94
6.94
6.94
6.93
6.93
6.93
6.82
6.81
6.06
4.70
4.69
4.68
4.67
1.44
1.43
1.41
N
O
S
S
OEt
12
1.00
1.01
0.99
1.02
2.00
2.26
3.35
9
8
7
6
5
4
3
2
1
0
ppm


213.24
161.97
146.62
139.12
117.96
111.83
77.16 CDCl3
70.48
69.08
13.87
200
180
160
140
120
100
80
60
40
20
0
ppm

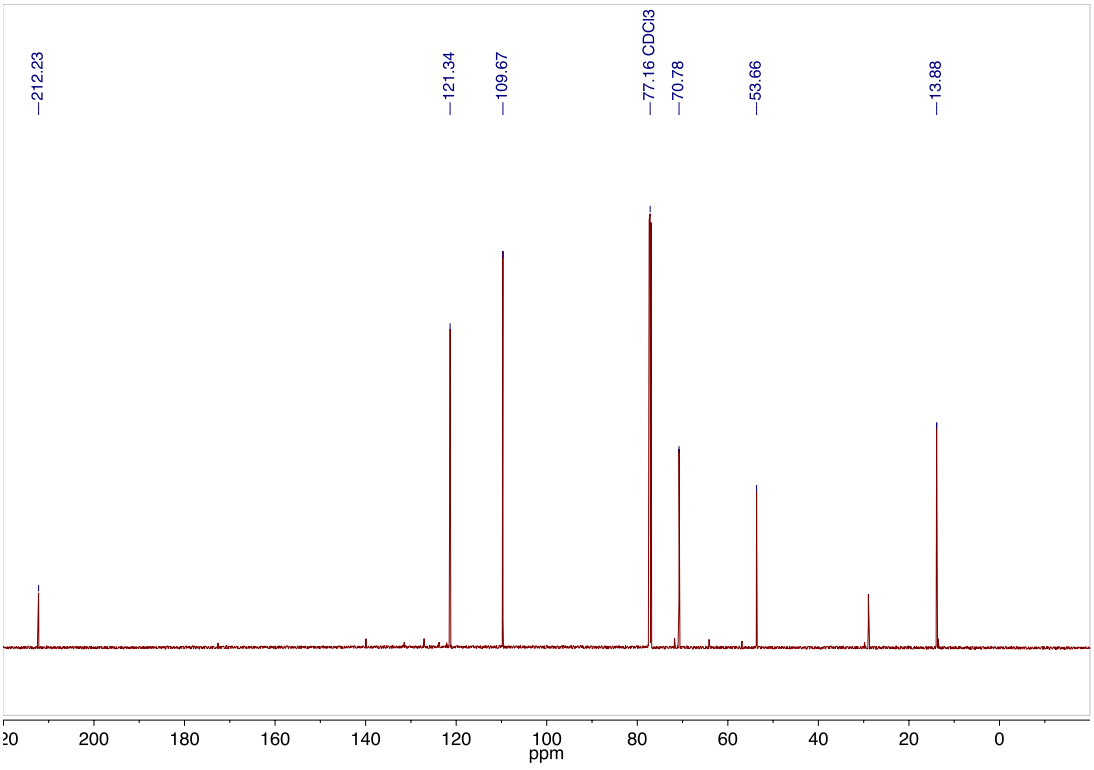

7.57
7.55
7.54
7.26 CDCl3
6.97
6.96
6.74
6.72
6.03
6.02
4.69
4.69
4.68
1.44
1.44
1.43
1.42
1.41
Cl
N
O
S
S
OEt
13
1.00
1.03
0.99
2.19
2.20
3.12
9
8
7
6
5
4
3
2
1
0
ppm


212.61
161.72
148.20
141.24
117.72
109.99
77.16 CDCl3
70.67
69.56
13.87
200
180
160
140
120
100
80
60
40
20
0
ppm

CGN 175


7.26 CDCl3
6.83
6.82
6.82
6.18
6.17
6.17
5.65
4.70
4.69
1.47
1.46
1.44
S
N
S
OEt
1.89
2.00
1.96
2.23
3.11
9
8
7
6
5
4
3
2
1
0
ppm

14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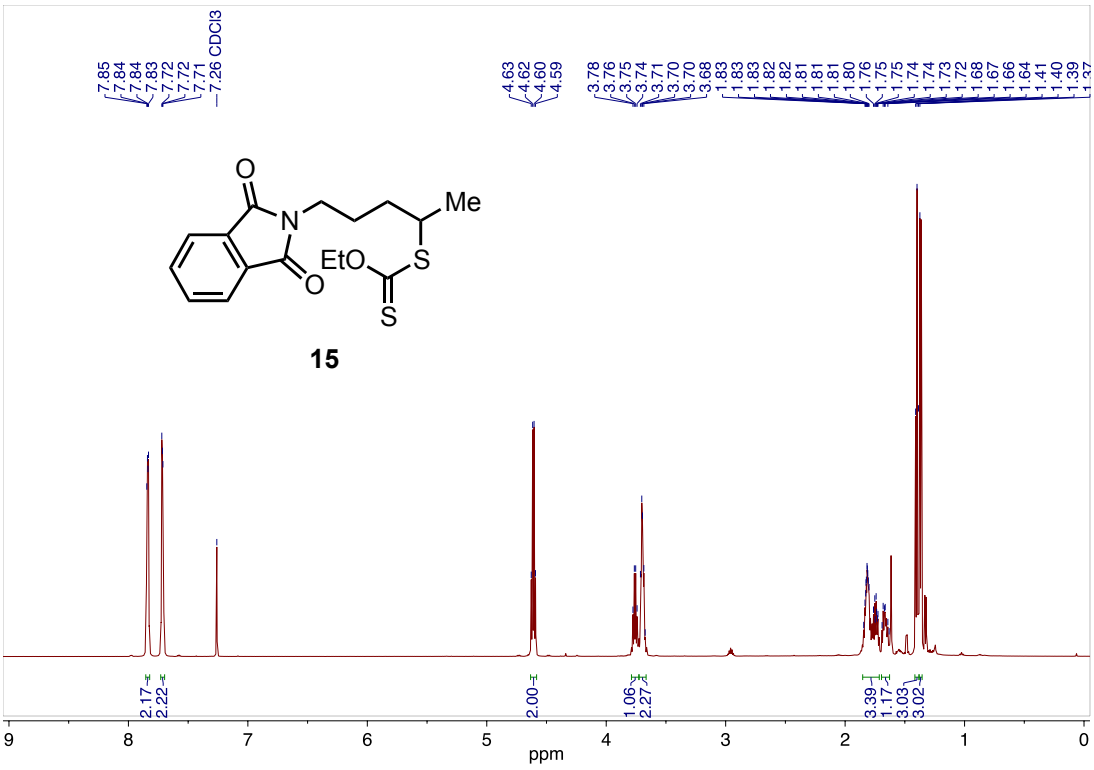
121.34
109.67
77.16 CDCl3
70.78
53.66
13.88
200
180
160
140
120
100
80
60
40
20
0
ppm


7.85
7.84
7.84
7.83
7.72
7.72
7.71
7.26 CDCl3
4.63
4.62
4.60
4.59
3.78
3.76
3.75
3.74
3.71
3.70
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3.68
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1.81
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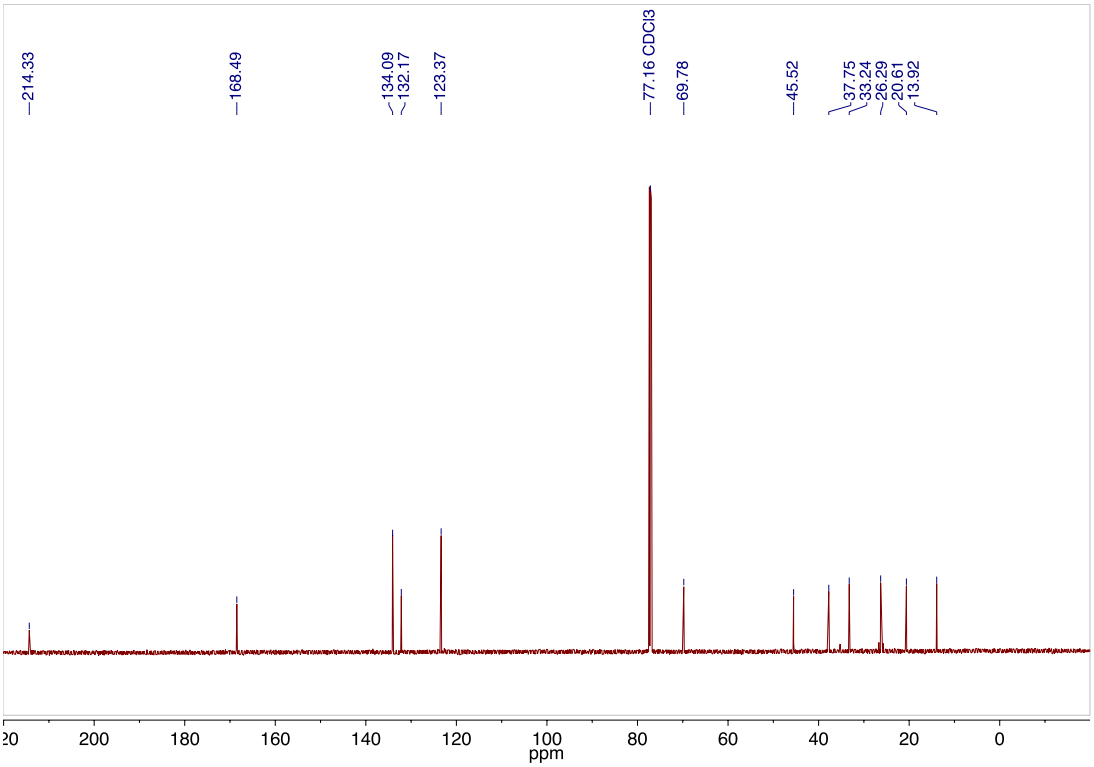
1.74
1.74
1.73
1.72
1.68
1.67
1.66
1.64
1.41
1.40
1.39
O
N
Me
EtO
S
O
S
15
2.17
2.22
2.00
1.06
2.27
3.39
1.17
3.03
3.02
9
8
7
6
5
4
3
2
1
0
ppm


214.33
168.49
134.09
132.17
123.37
77.16 CDCl3
69.78
45.52
37.75
33.24
26.29
20.61
13.92
200
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160
140
120
100
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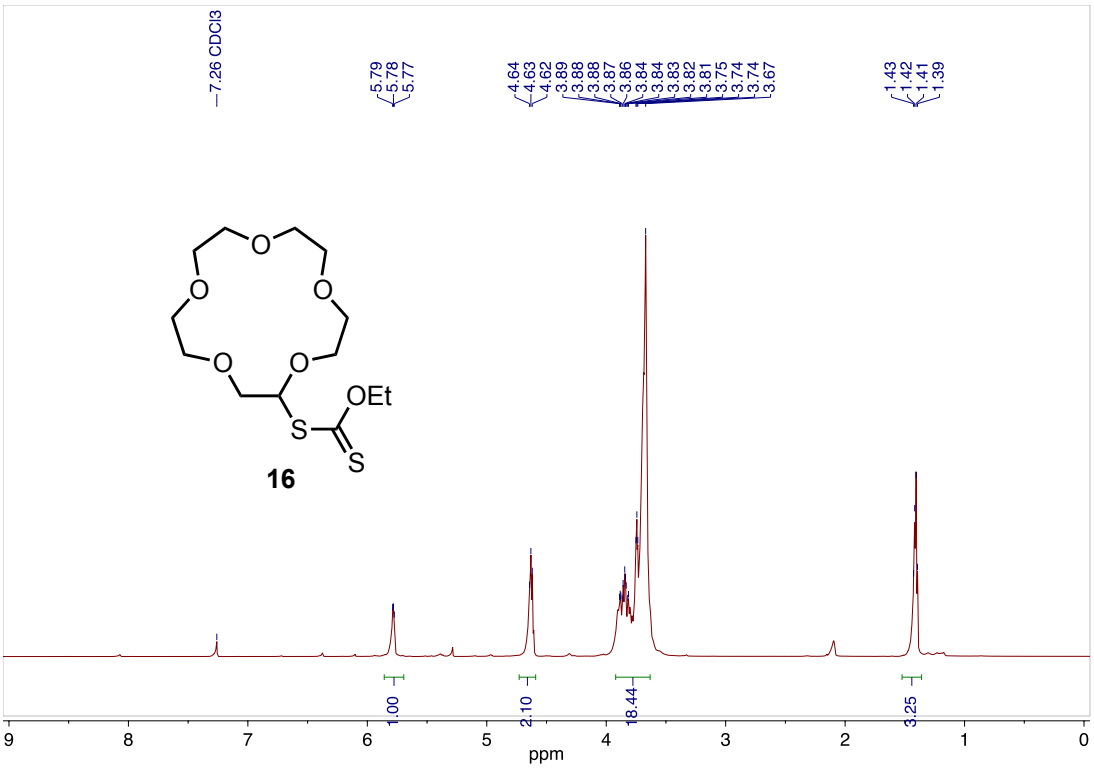
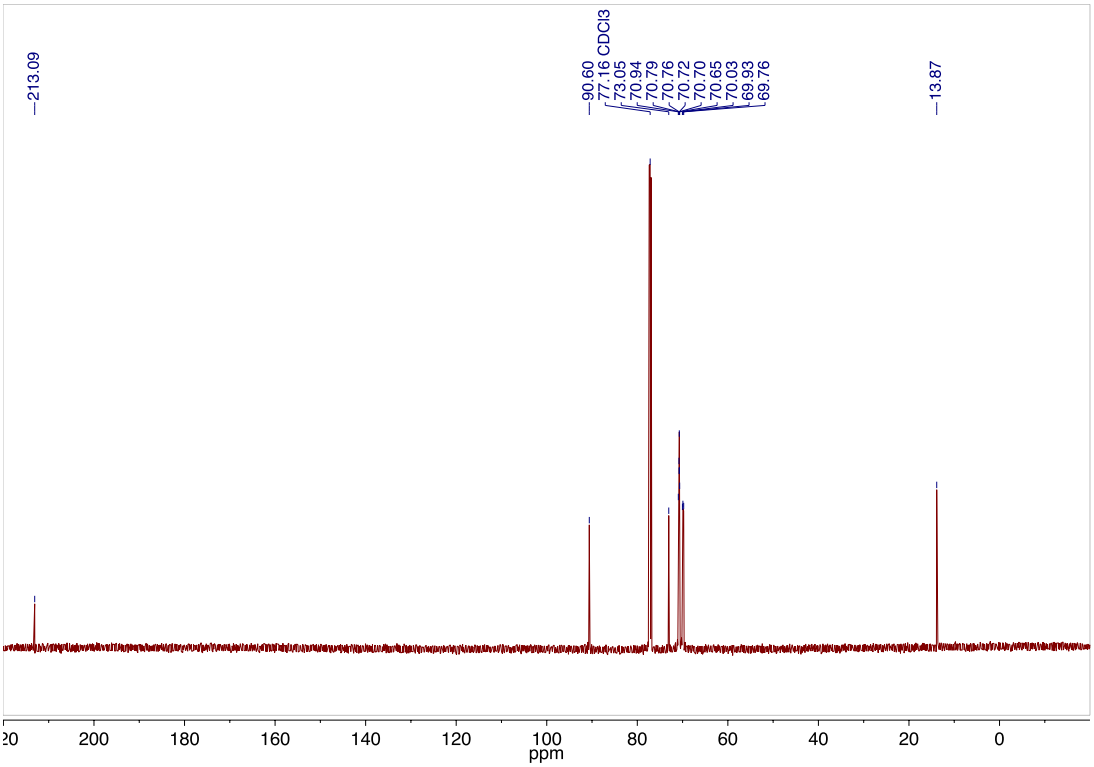
40
20
0
ppm


7.26 CDCl3
5.79
5.78
5.77
4.64
4.63
4.62
3.89
3.88
3.88
3.87
3.86
3.84
3.84
3.83
3.82
3.81
3.75
3.74
3.74
3.67
1.43
1.42
1.41
1.39
OEt
S
S
16
1.00
2.10
18.44
3.25
ppm


213.09
90.60
77.16 CDCl3
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70.76
70.72
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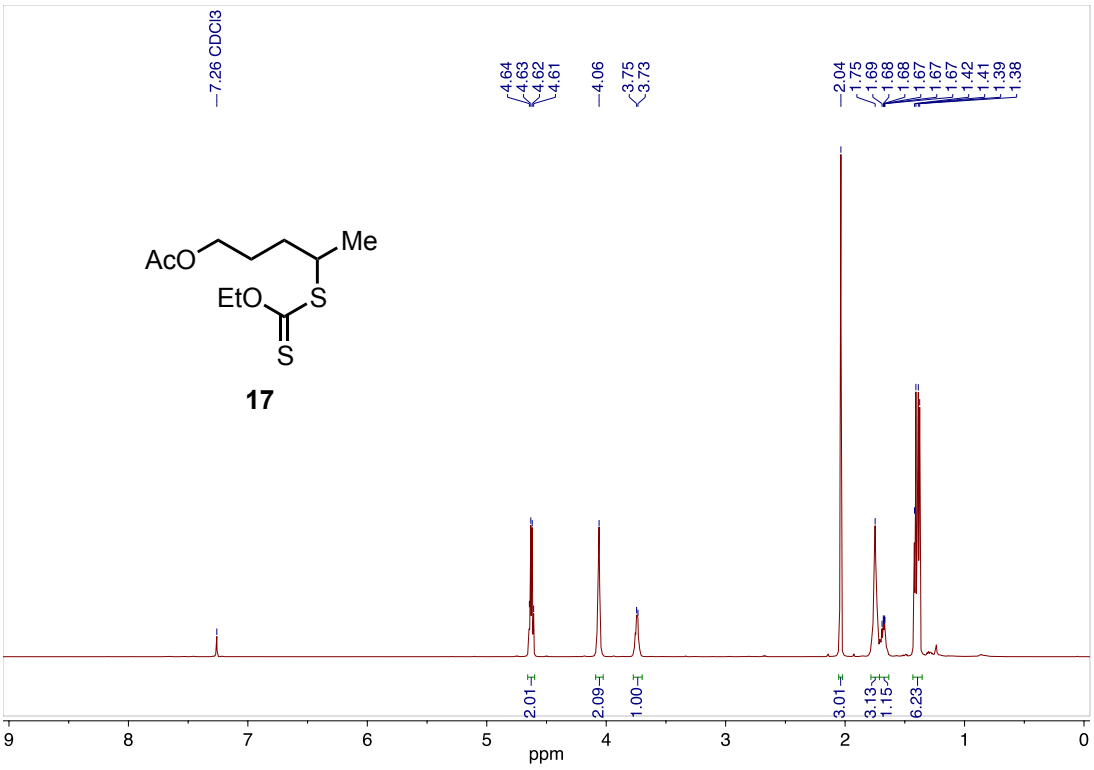
70.65
70.03
69.93
69.76
13.87
ppm


7.26 CDCl3
4.64
4.63
4.62
4.61
4.06
3.75
3.73
2.04
1.75
1.69
1.68
1.68
1.67
1.67
1.67
1.42
1.41
1.39
1.38
AcO
Me
EtO
S
S
2.01
2.09
1.00
3.01
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1.15
6.23
9
8
7
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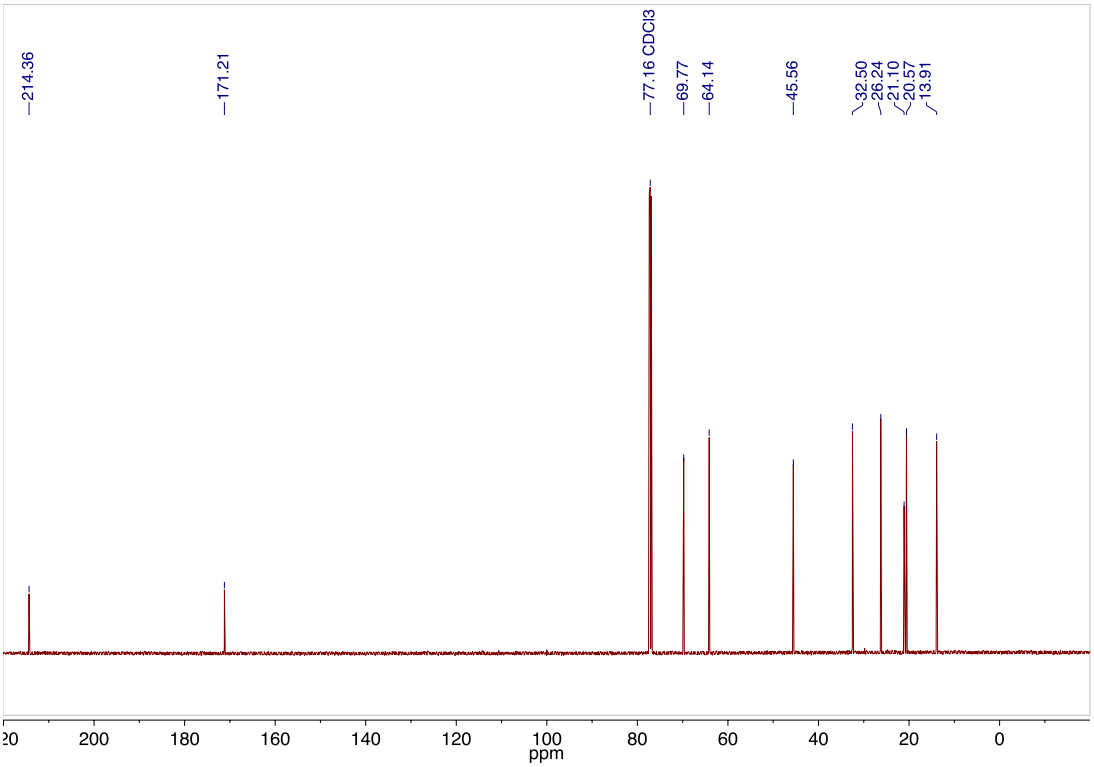
5
4
3
2
1
0
ppm

17


214.36
171.21
77.16 CDCl3
69.77
64.14
45.56
32.50
26.24
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20.57
13.91
200
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120
100
80
60
40
20
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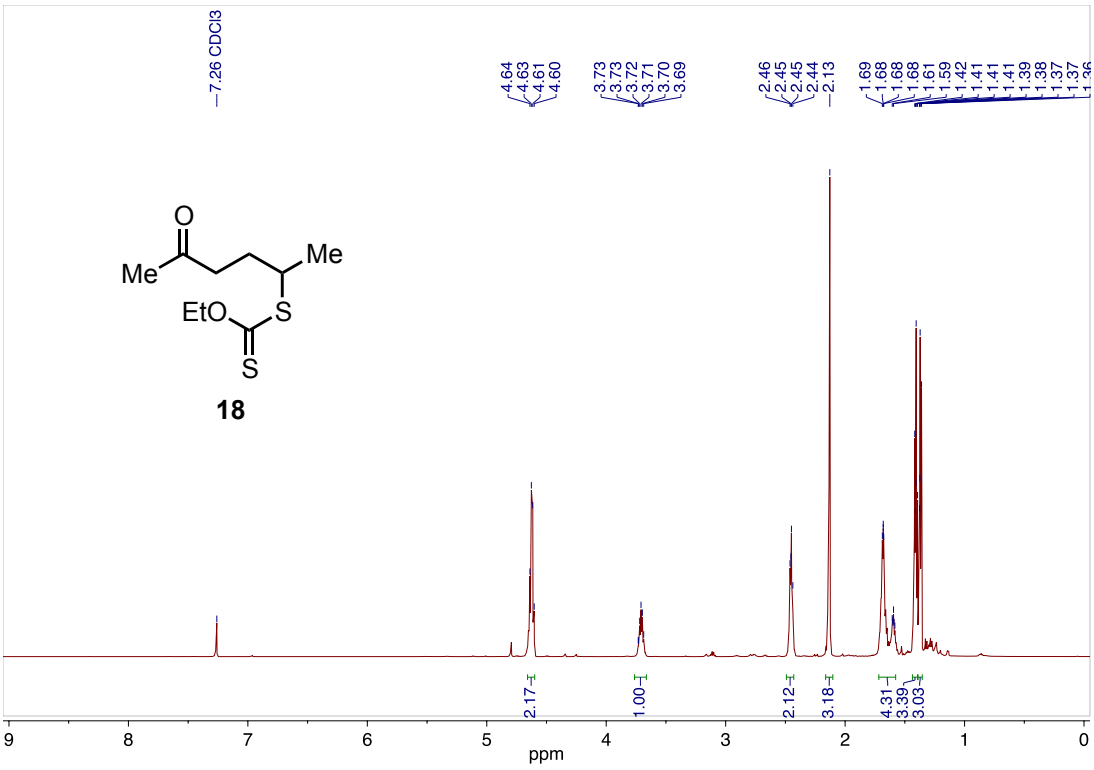
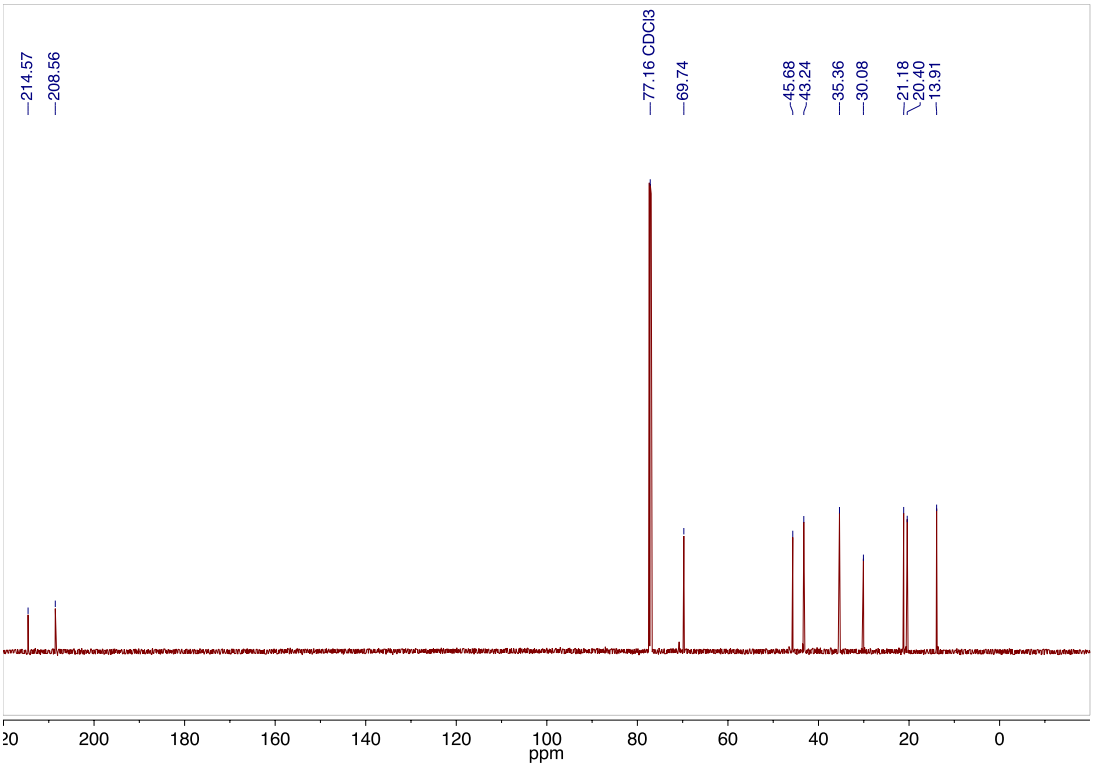
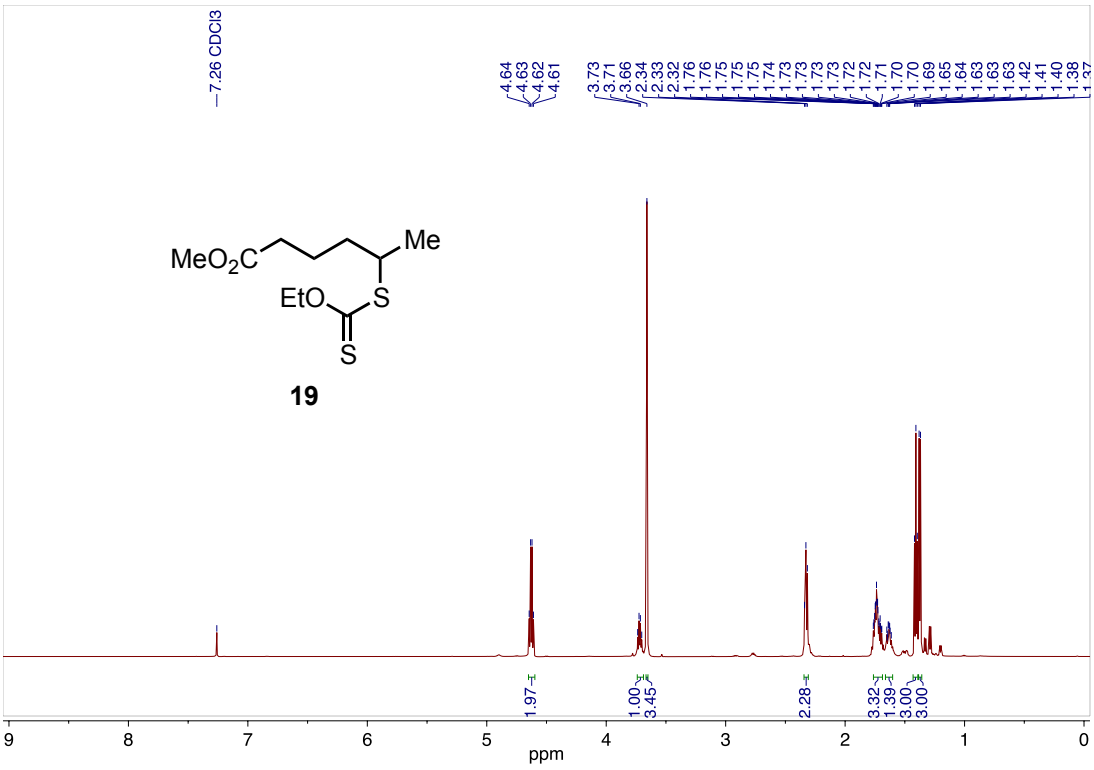
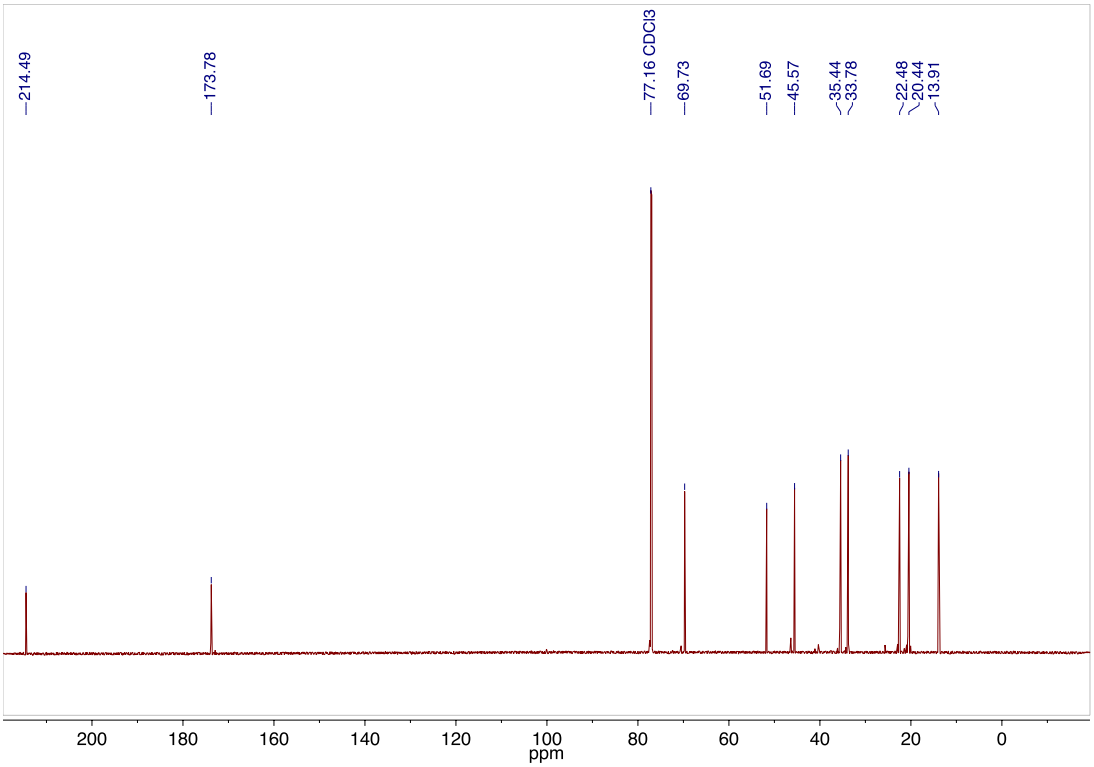
ppm

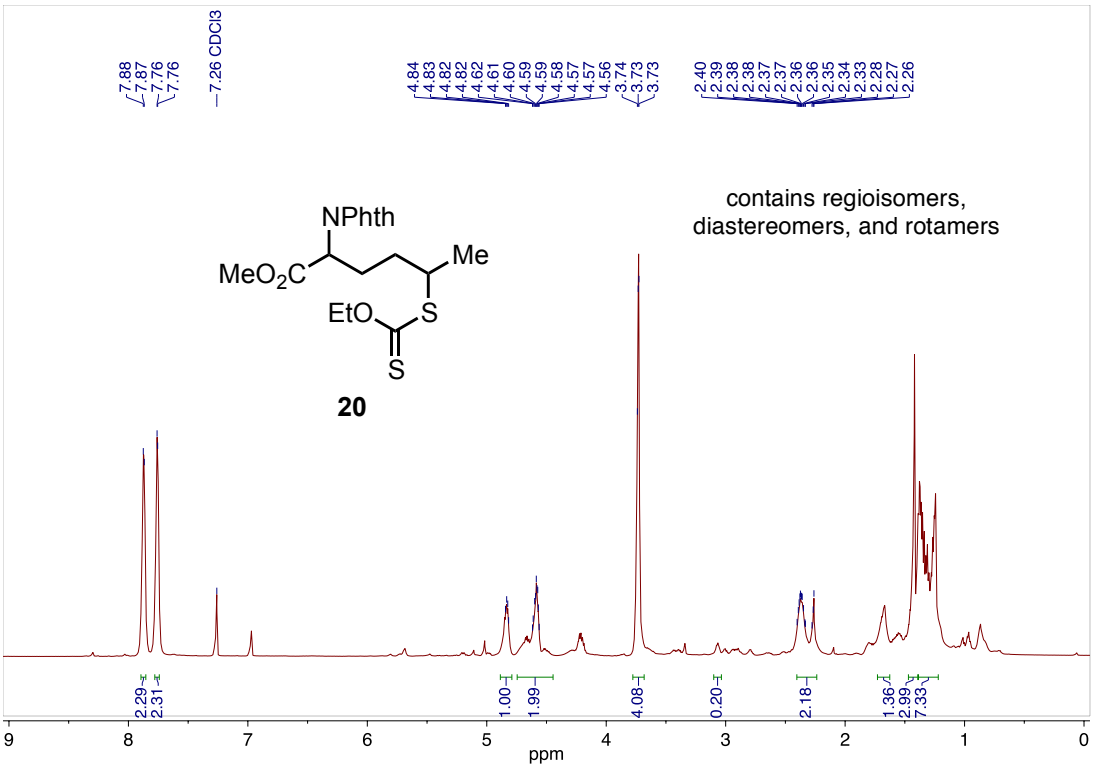

7.26 CDCl3
4.64
4.63
4.61
4.60
3.73
3.73
3.72
3.71
3.70
3.69
2.46
2.45
2.45
2.44
2.13
1.69
1.68
1.68
1.68
1.61
1.59
1.42
1.41
1.41
1.41
1.39
1.38
1.37
1.37
O
Me
Me
EtO
S
S
2.17
1.00
2.12
3.18
4.31
3.39
3.03
9
8
7
6
5
4
3
2
1
0
ppm

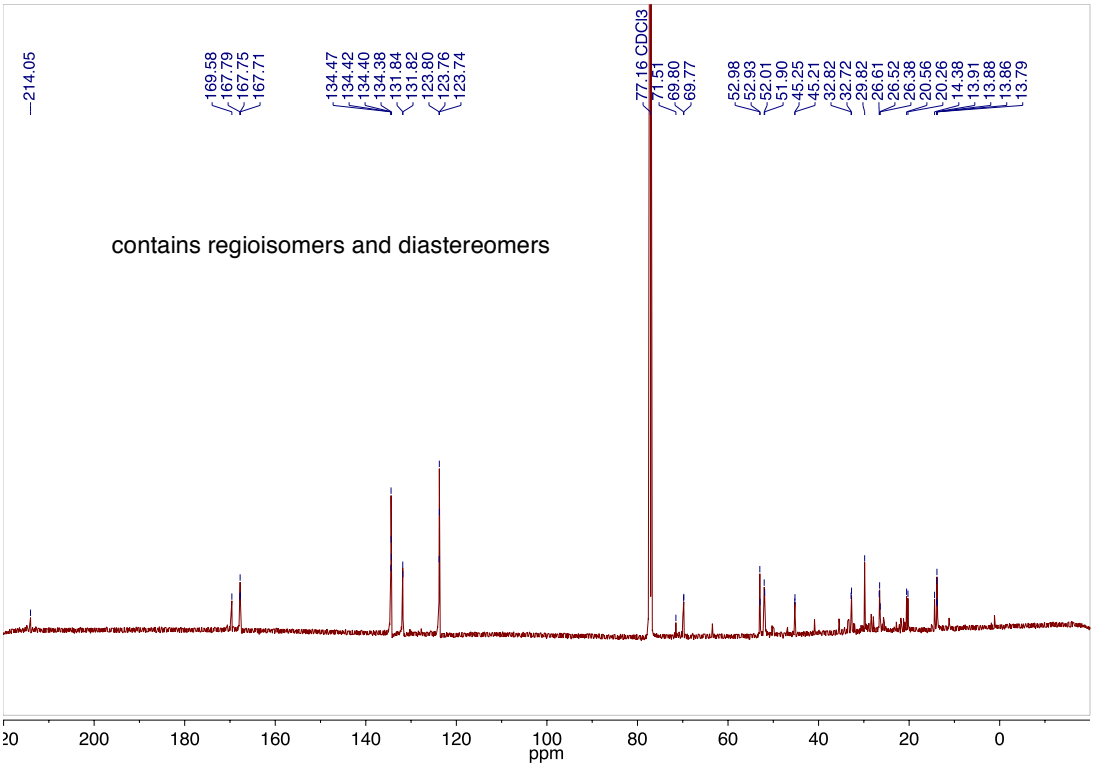
18

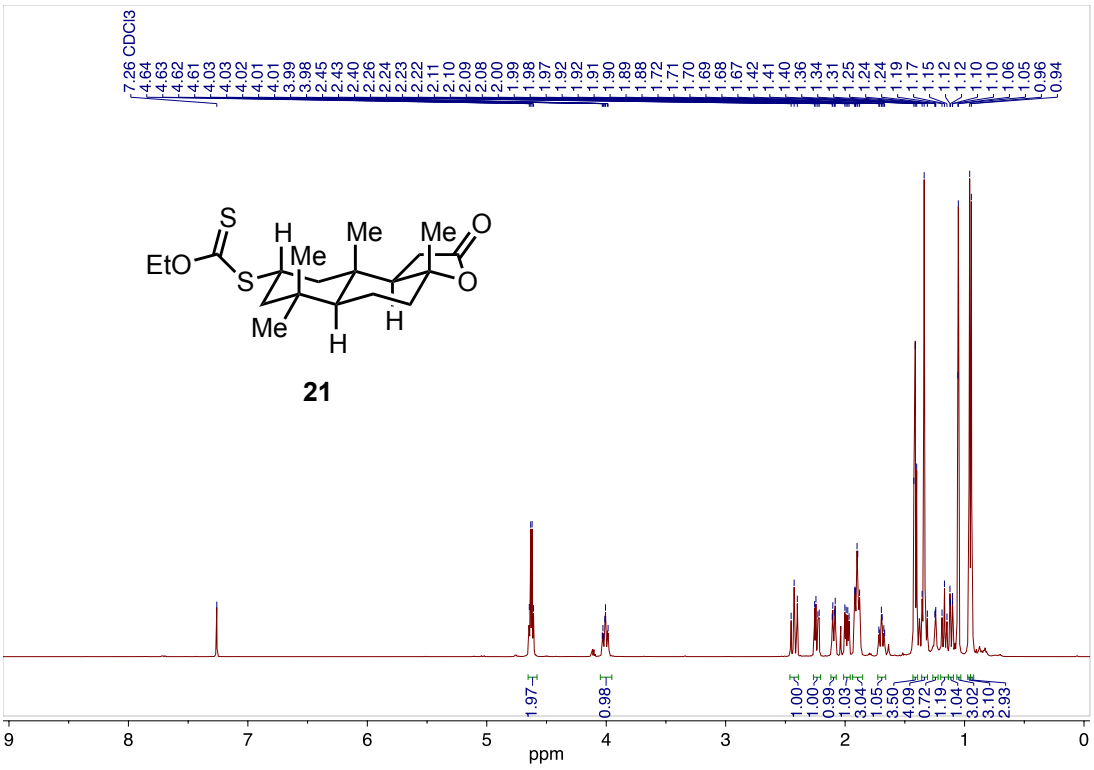

214.57
208.56
77.16 CDCl3
69.74
45.68
43.24
35.36
30.08
21.18
20.40
13.91
200
180
160
140
120
100
80
60
40
20
0
ppm


7.26 CDCl3
4.64
4.63
4.62
4.61
3.73
3.71
3.66
2.34
2.33
2.32
1.76
1.75
1.75
1.75
1.74
1.73
1.73
1.73
1.72
1.72
1.71
1.70
1.70
1.69
1.65
1.64
1.63
1.63
1.63
1.42
1.41
1.40
1.38
MeO2C
Me
EtO
S
S
19
1.97
1.00
3.45
2.28
3.32
1.39
3.00
3.00
9
8
7
6
5
4
3
2
1
0
ppm

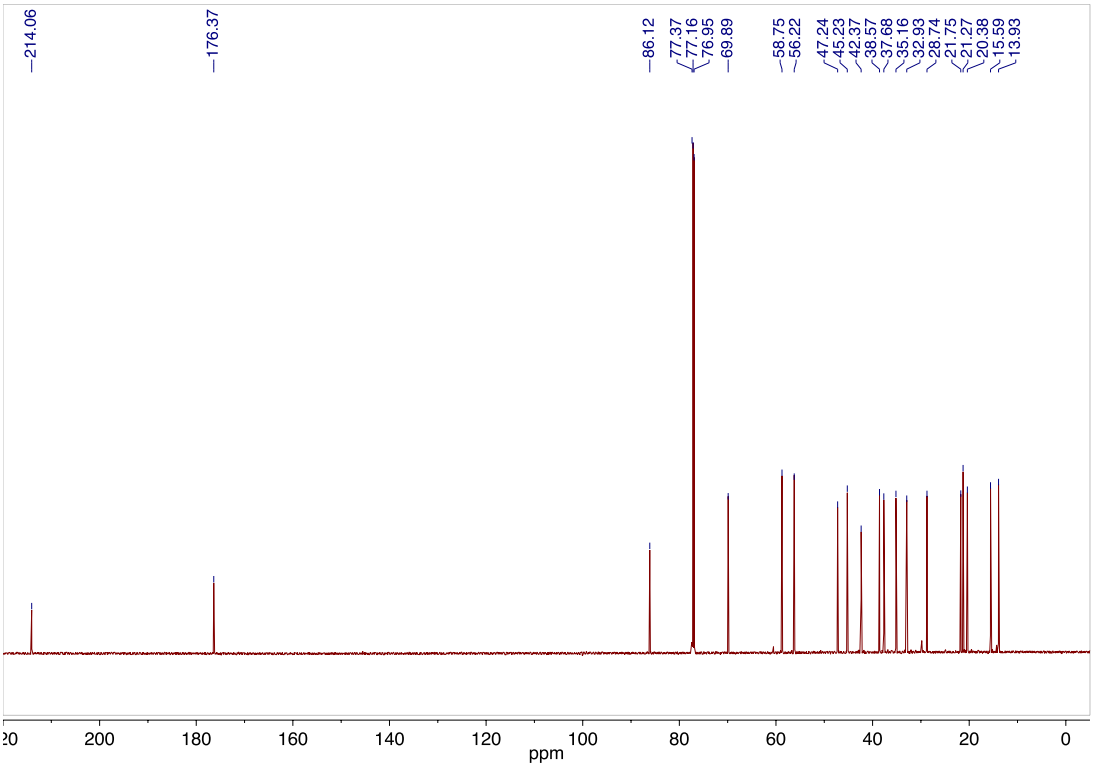

214.49
173.78
77.16 CDCl3
69.73
51.69
45.57
35.44
33.78
22.48
20.44
13.91
200
180
160
140
120
100
80
60
40
20
0
ppm


7.88
7.87
7.76
7.76
7.26 CDCl3
4.84
4.83
4.82
4.82
4.62
4.61
4.60
4.59
4.59
4.58
4.57
4.57
4.56
3.74
3.73
3.73
2.40
2.39
2.38
2.38
2.37
2.37
2.36
2.36
2.35
2.34
2.33
2.28
2.27
2.26
NPhth
MeO2C
Me
EtO
S
S
20
contains regioisomers,
diastereomers, and rotamers
2.29
2.31
1.00
1.99
4.08
0.20
2.18
1.36
2.99
7.33
9
8
7
6
5
4
3
2
1
0
ppm

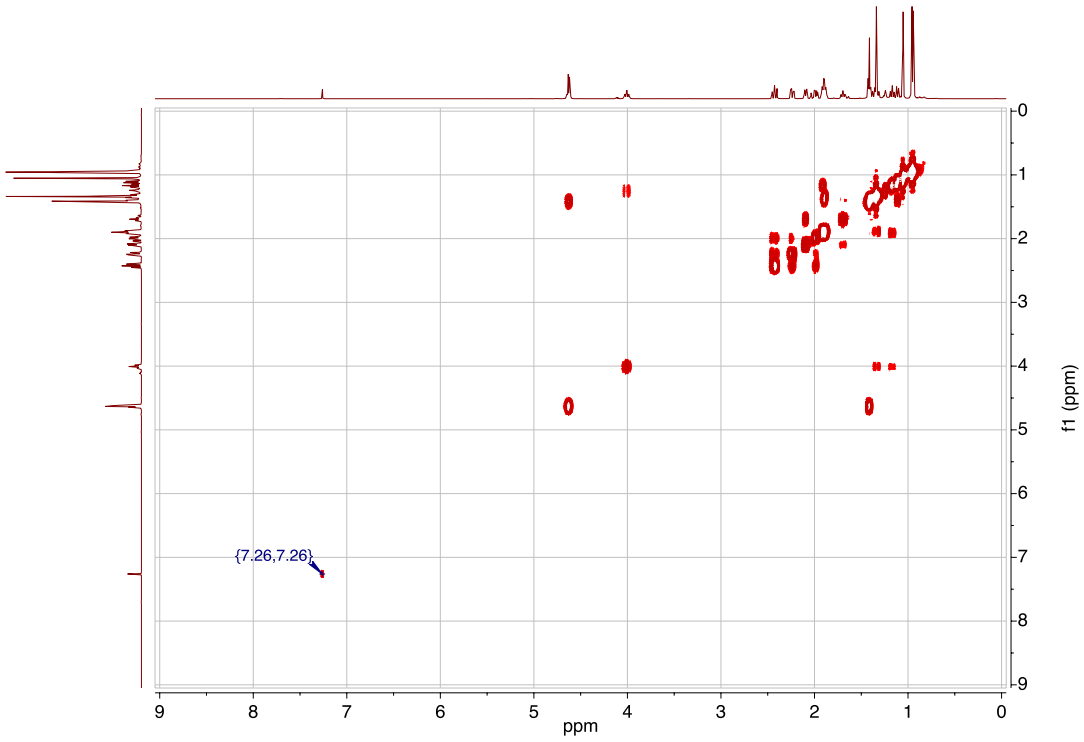

214.05
169.58
167.79
167.75
167.71
134.47
134.42
134.40
134.38
131.84
131.82
123.80
123.76
123.74
77.16 CDCl3
71.51
69.80
69.77
52.98
52.93
52.01
51.90
45.25
45.21
32.82
32.72
29.82
26.61
26.52
26.38
20.56
20.26
14.38
13.91
13.88
13.86
13.79
contains regioisomers and diastereomers
200
180
160
140
120
100
80
60
40
20
0
ppm


7.26 CDCl3
4.64
4.63
4.62
4.61
4.03
4.02
4.01
4.01
3.99
3.98
2.45
2.43
2.40
2.26
2.24
2.23
2.22
2.11
2.10
2.09
2.08
2.00
1.99
1.98
1.97
1.92
1.92
1.91
1.90
1.89
1.88
1.72
1.71
1.70
1.69
1.68
1.67
1.42
1.41
1.40
1.36
1.34
1.31
1.25
1.24
1.24
1.19
1.17
1.15
1.12
1.12
1.10
1.10
1.06
1.05
0.96
0.94
S
H
Me
Me
O
EtO
S
Me
O
Me
H
H
1.97
0.98
1.00
1.00
0.99
1.03
3.04
1.05
3.50
4.09
0.72
1.19
1.04
3.02
3.10
2.93
9
8
7
6
5
4
3
2
1
0
ppm

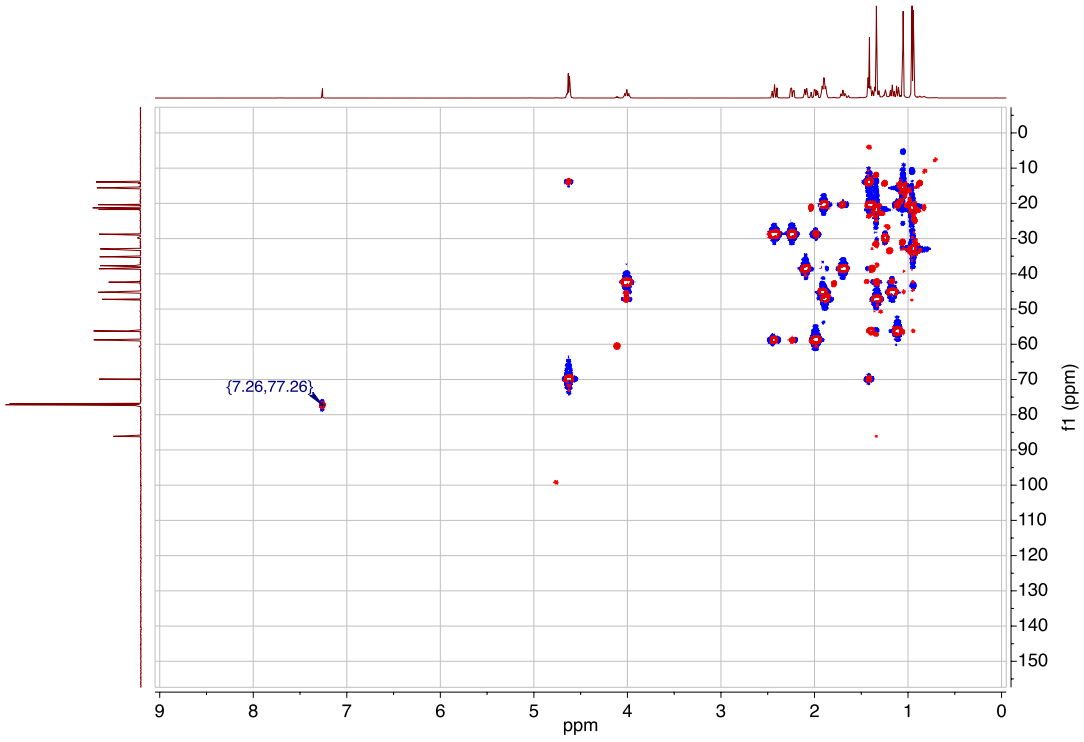
21

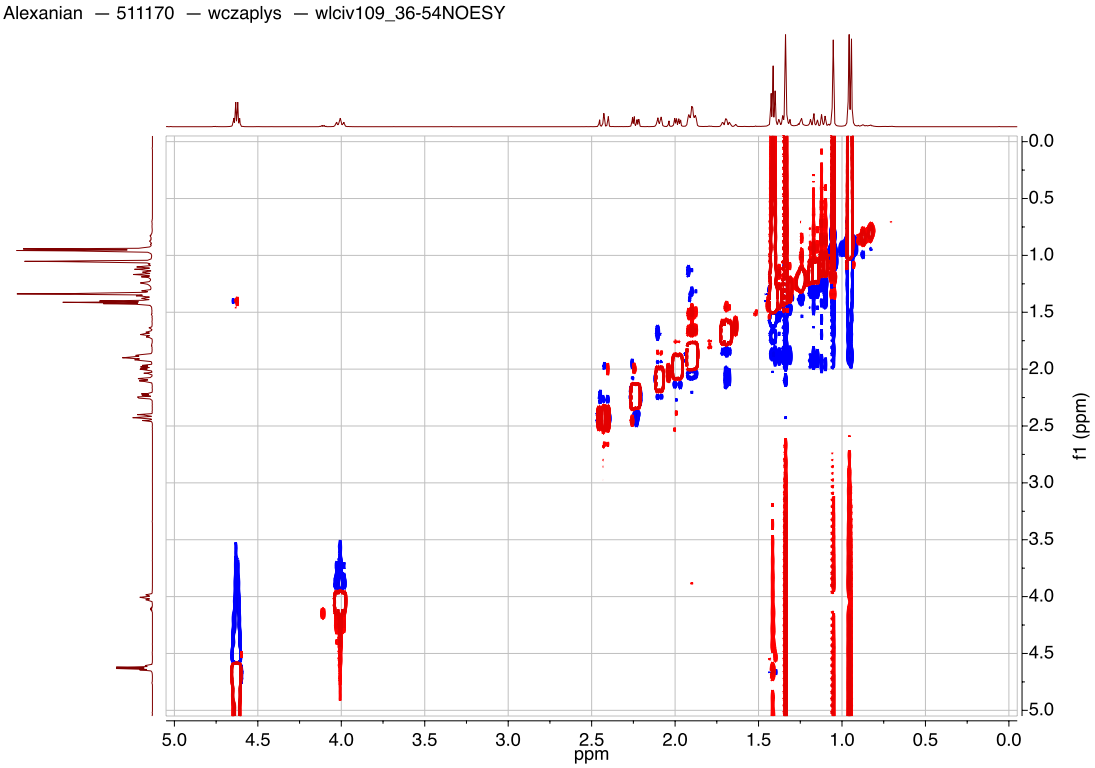

214.06
176.37
86.12
77.37
77.16
76.95
69.89
58.75
56.22
47.24
45.23
42.37
38.57
37.68
35.16
32.93
28.74
21.75
21.27
20.38
15.59
13.93
200
180
160
140
120
100
80
60
40
20
0
ppm

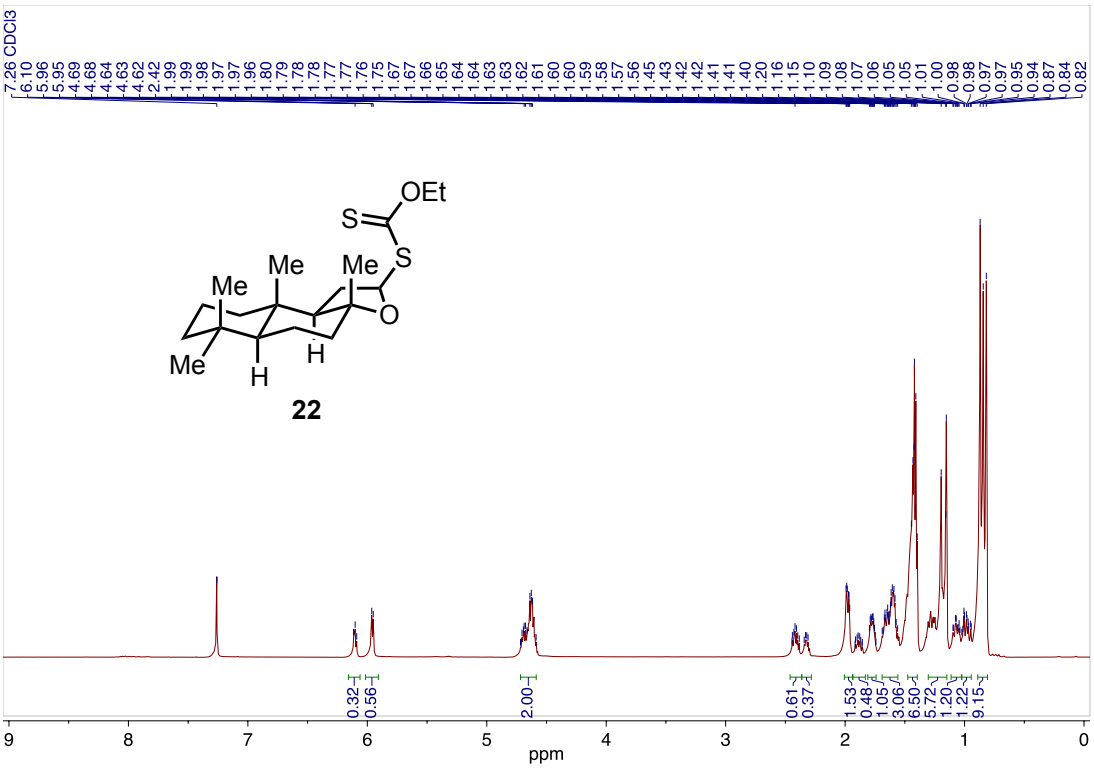
wlciv109_36-54COSY



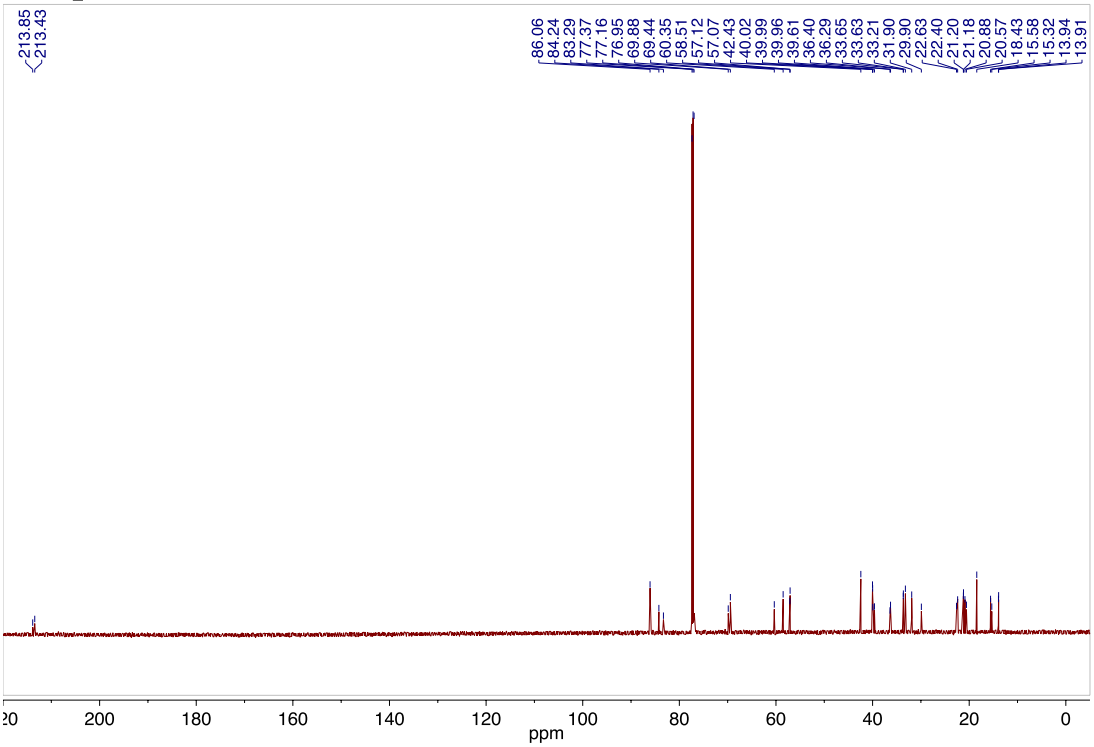
wlciv109_36-54HSQC

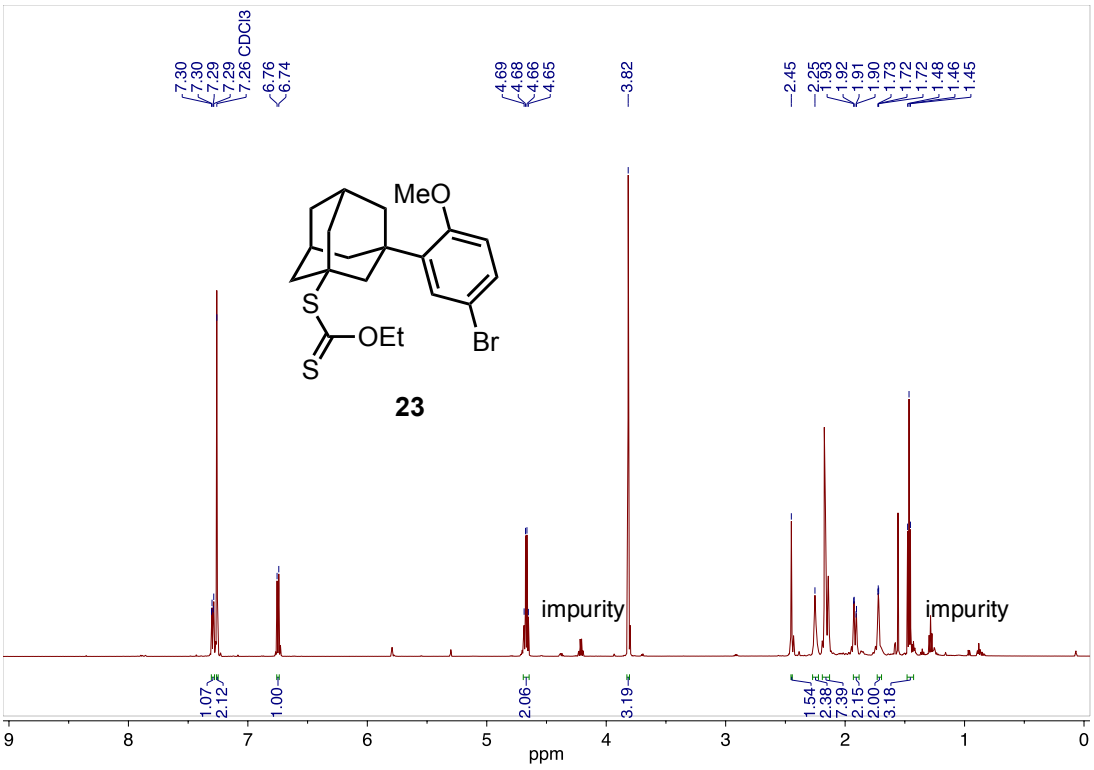


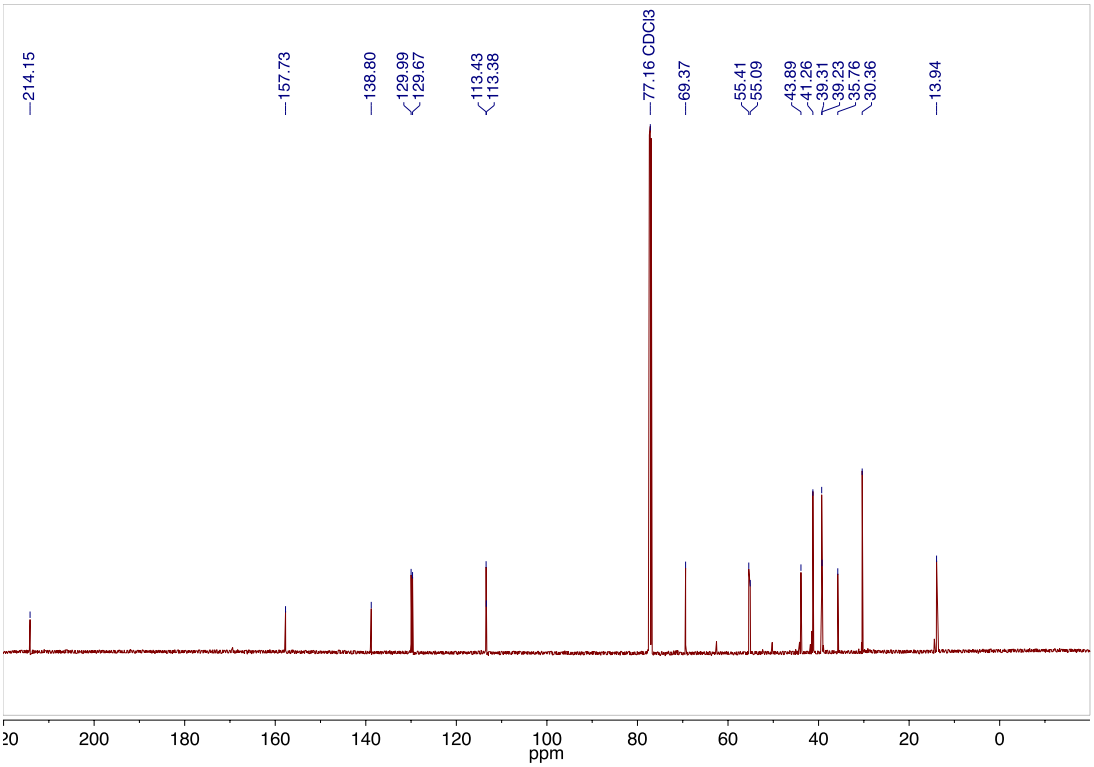

Alexanian — 511170 — wczaplys — wlciv109_36-54NOESY
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
f1 (ppm)



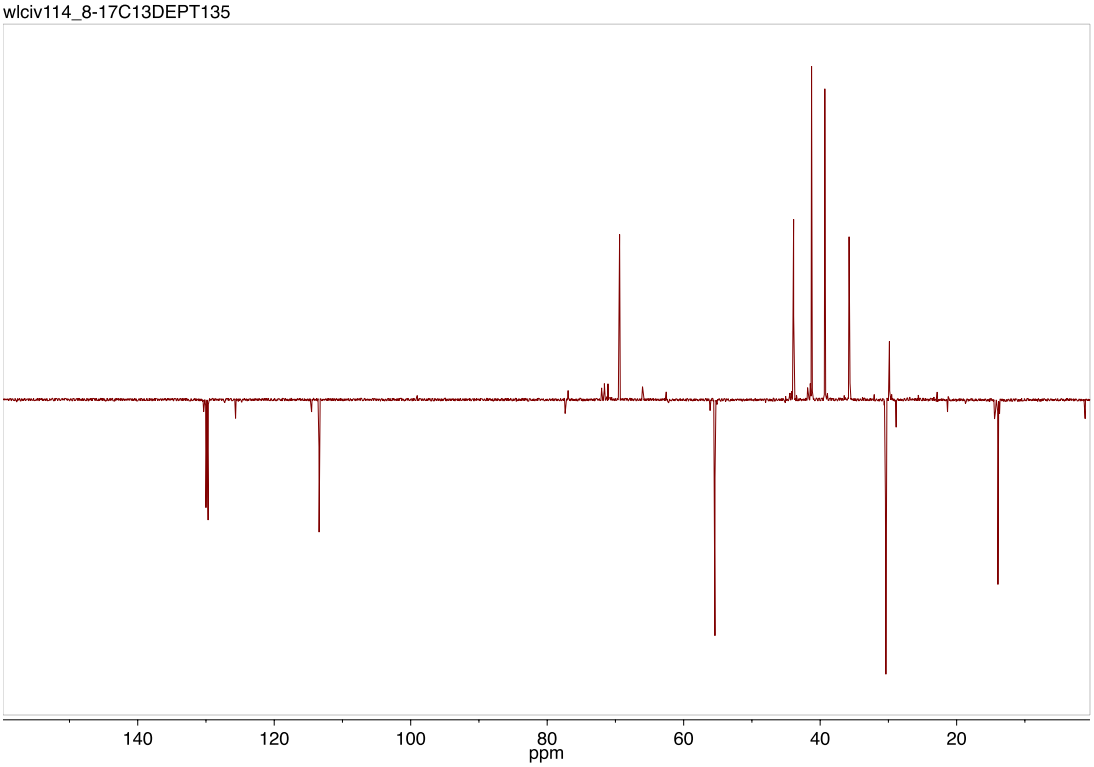
wlciv208_1-2C

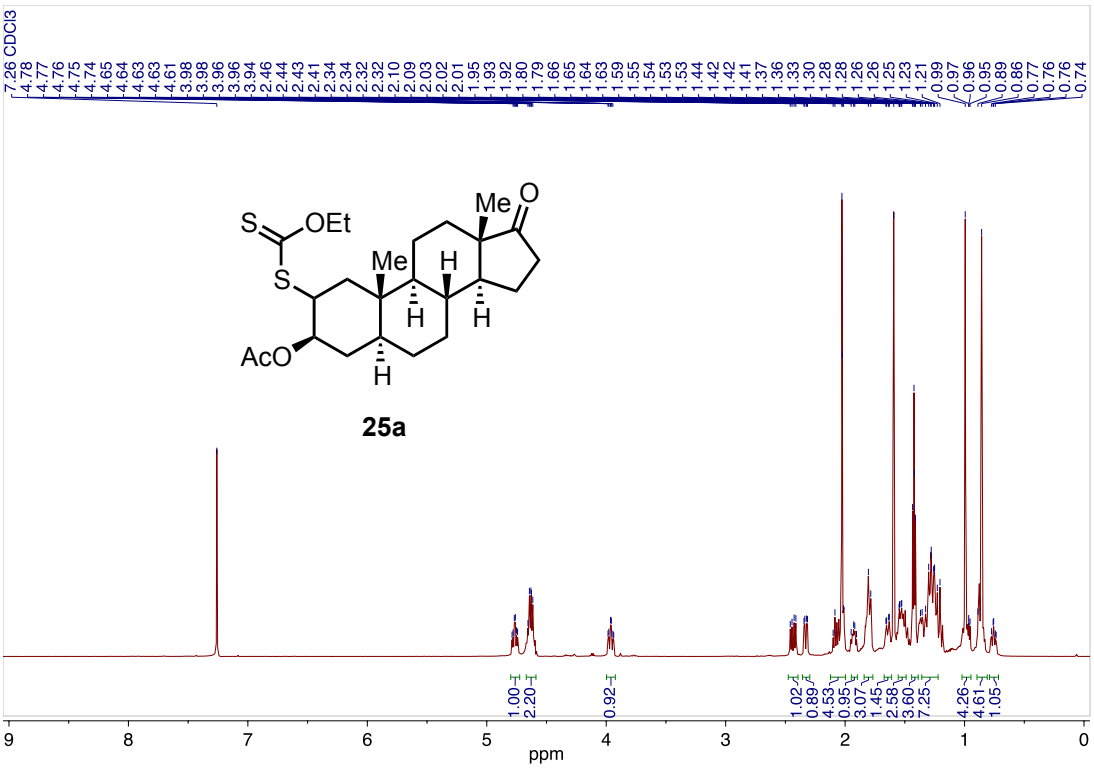


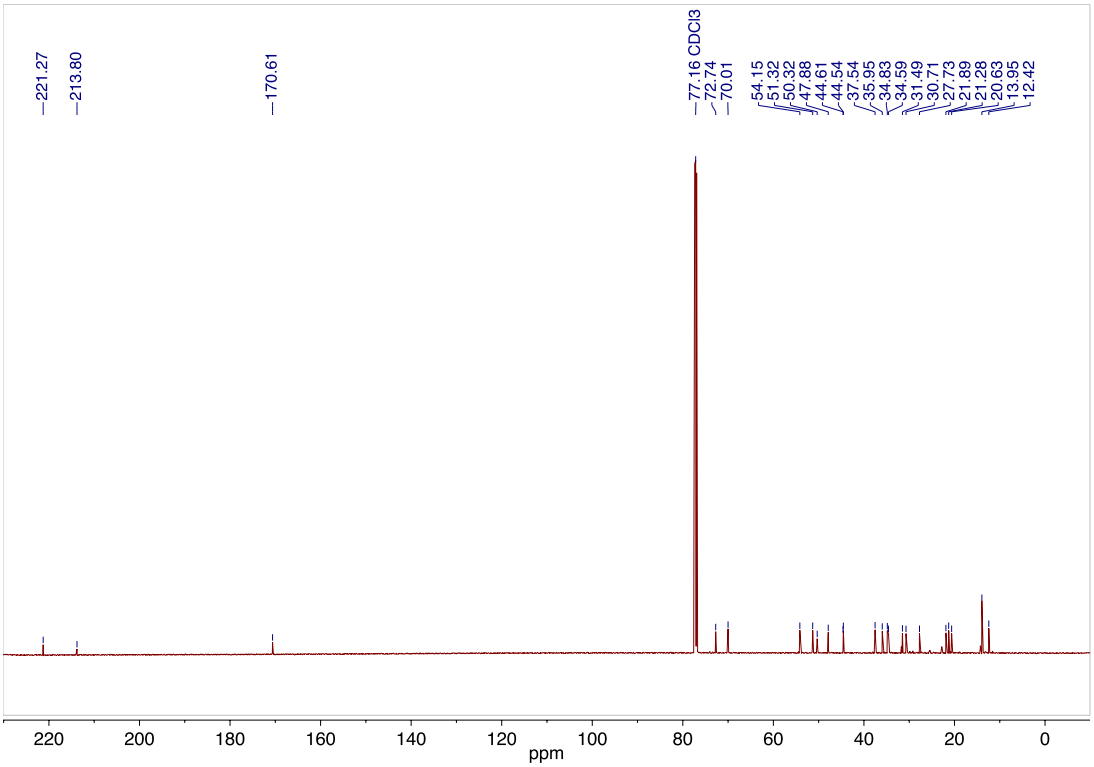

7.30
7.30
7.29
7.29
7.26 CDCl3
6.76
6.74
4.69
4.68
4.66
4.65
3.82
2.45
2.25
1.93
1.92
1.91
1.90
1.73
1.72
1.72
1.48
1.46
1.45
MeO
S
OEt
S
Br
23
impurity
impurity
1.07
2.12
1.00
2.06
3.19
1.54
2.38
7.39
2.15
2.00
3.18
9
8
7
6
5
4
3
2
1
0
ppm


214.15
157.73
138.80
129.99
129.67
113.43
113.38
77.16 CDCl3
69.37
55.41
55.09
43.89
41.26
39.31
39.23
35.76
30.36
13.94
200
180
160
140
120
100
80
60
40
20
0
ppm

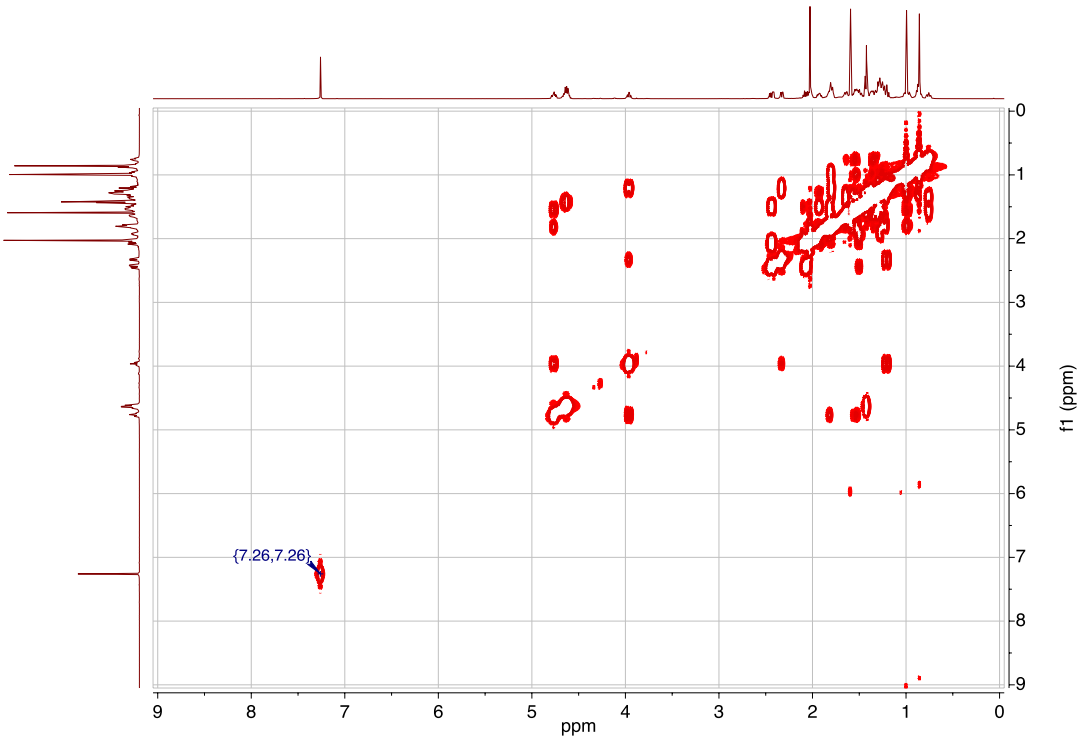
wlciv114_8-17C13DEPT135



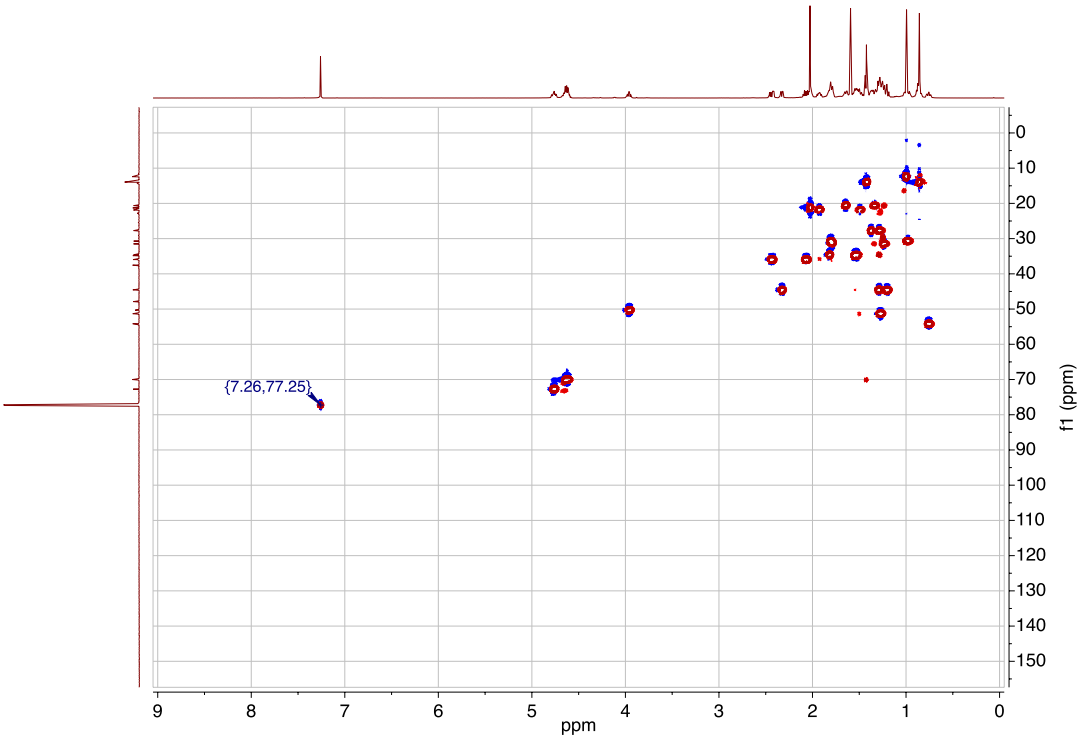

7.26 CDCl3
4.78 4.77 4.76 4.75 4.74 4.65 4.64 4.63 4.63 4.61 3.98 3.98 3.96 3.96 3.94 2.46 2.44 2.43 2.41 2.34 2.34 2.32 2.32 2.10 2.09 2.03 2.02 2.01 1.95 1.93 1.92 1.80 1.79 1.66 1.65 1.64 1.63 1.59 1.55 1.54 1.53 1.53 1.44 1.42 1.42 1.41 1.37 1.36 1.33 1.30 1.28 1.28 1.26 1.26 1.25 1.23 1.21 0.99 0.97 0.96 0.95 0.89 0.86 0.77 0.76 0.76 0.74
Me
O
S
OEt
S
Me
H
H
H
AcO
H
25a
1.00 2.20 0.92 1.02 0.89 4.53 0.95 3.07 1.45 2.58 3.60 7.25 4.26 4.61 1.05
9 8 7 6 5 4 3 2 1 0
ppm


221.27
213.80
170.61
77.16 CDCl3
72.74
70.01
54.15
51.32
50.32
47.88
44.61
44.54
37.54
35.95
34.83
34.59
31.49
30.71
27.73
21.89
21.28
20.63
13.95
12.42
220 200 180 160 140 120 100 80 60 40 20 0
ppm

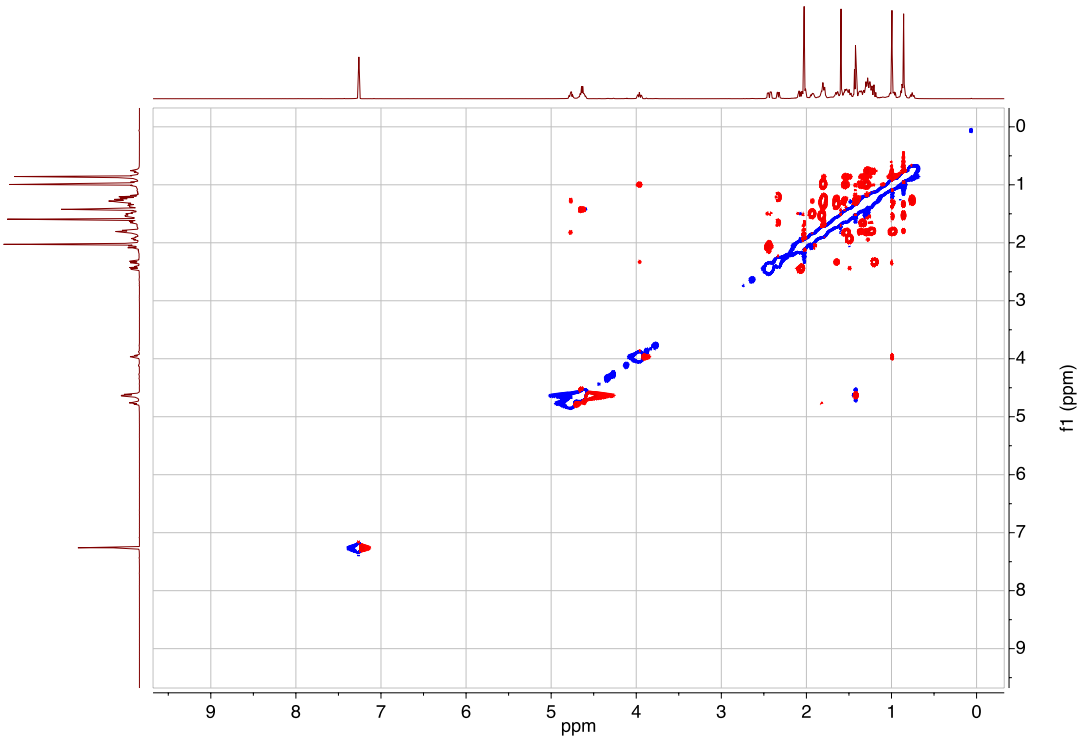
CGN 128A COSY

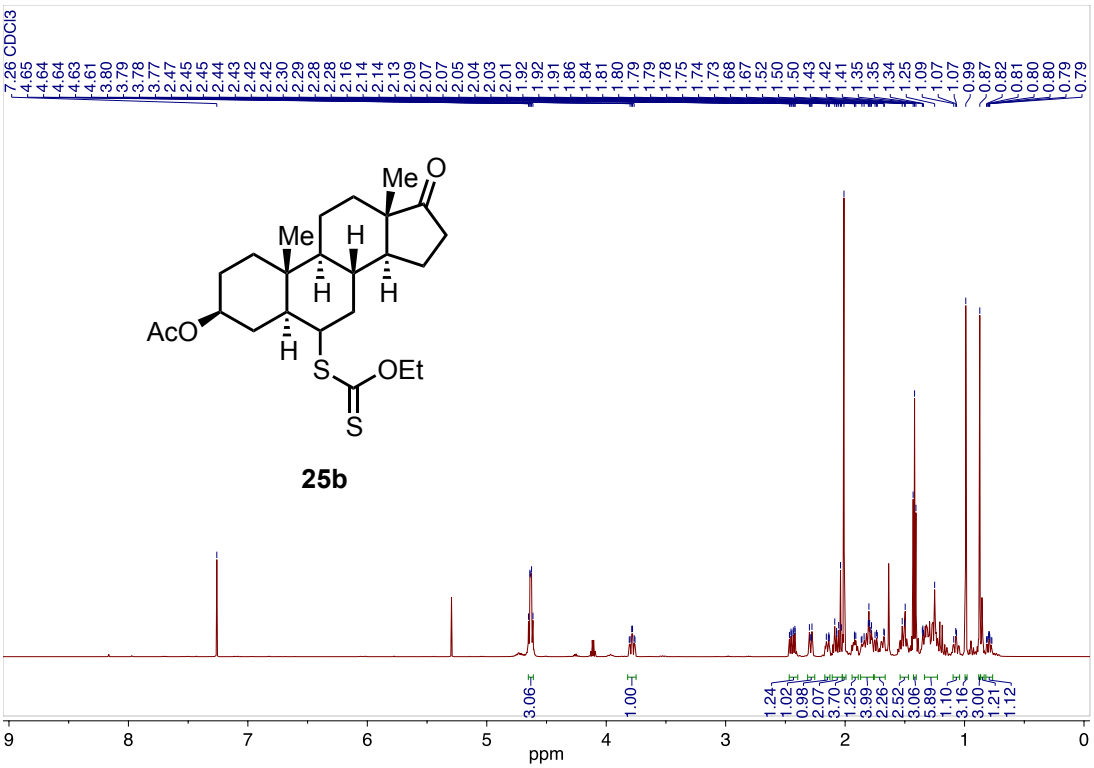


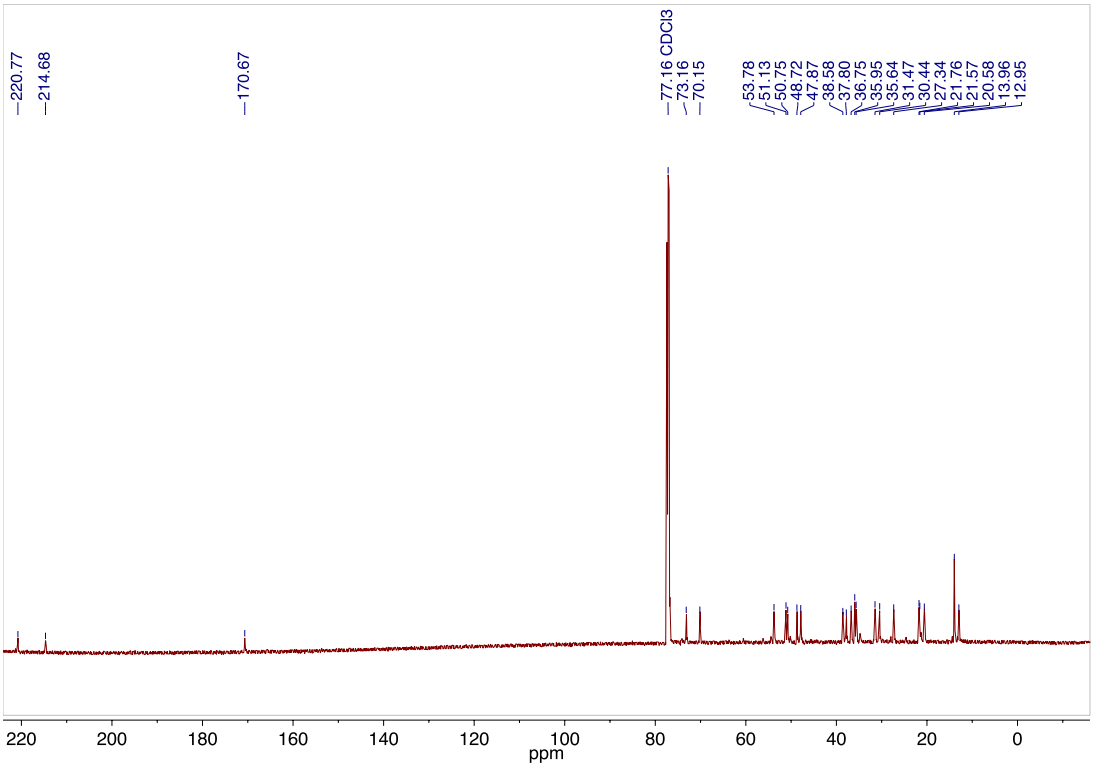
CGN 128A HSQC



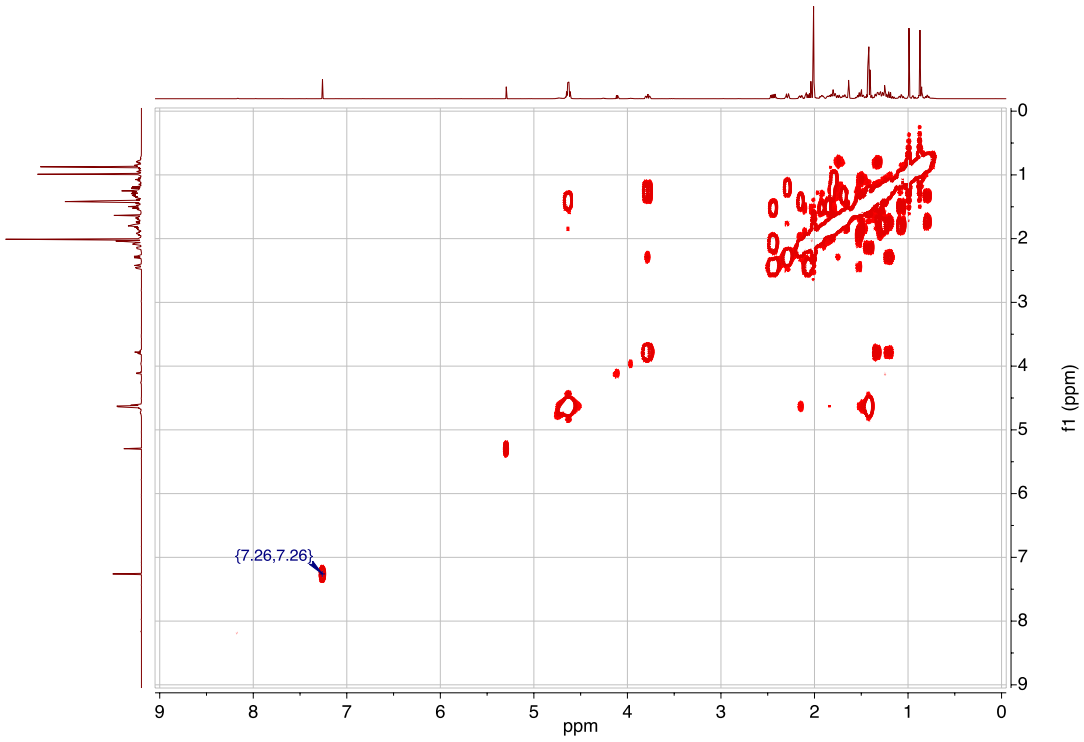
CGN 128A NOESY



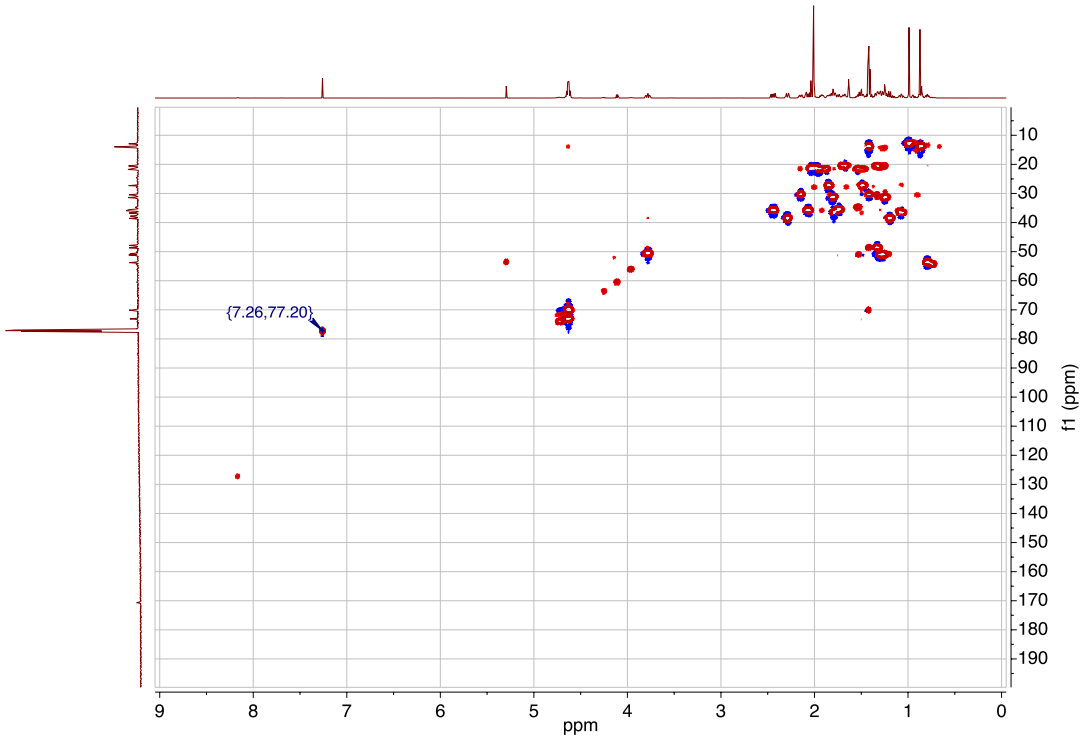

7.26 CDCl3
Me
O
Me
H
H
H
AcO
H
S
OEt
S
25b
3.06
1.00
1.24
1.02
0.98
2.07
3.70
1.25
3.99
2.26
2.52
3.06
5.89
1.10
3.16
3.00
1.21
1.12
9
8
7
6
5
4
3
2
1
0
ppm


220.77
214.68
170.67
77.16 CDCl3
73.16
70.15
53.78
51.13
50.75
48.72
47.87
38.58
37.80
36.75
35.95
35.64
31.47
30.44
27.34
21.76
21.57
20.58
13.96
12.95
220
200
180
160
140
120
100
80
60
40
20
0
ppm

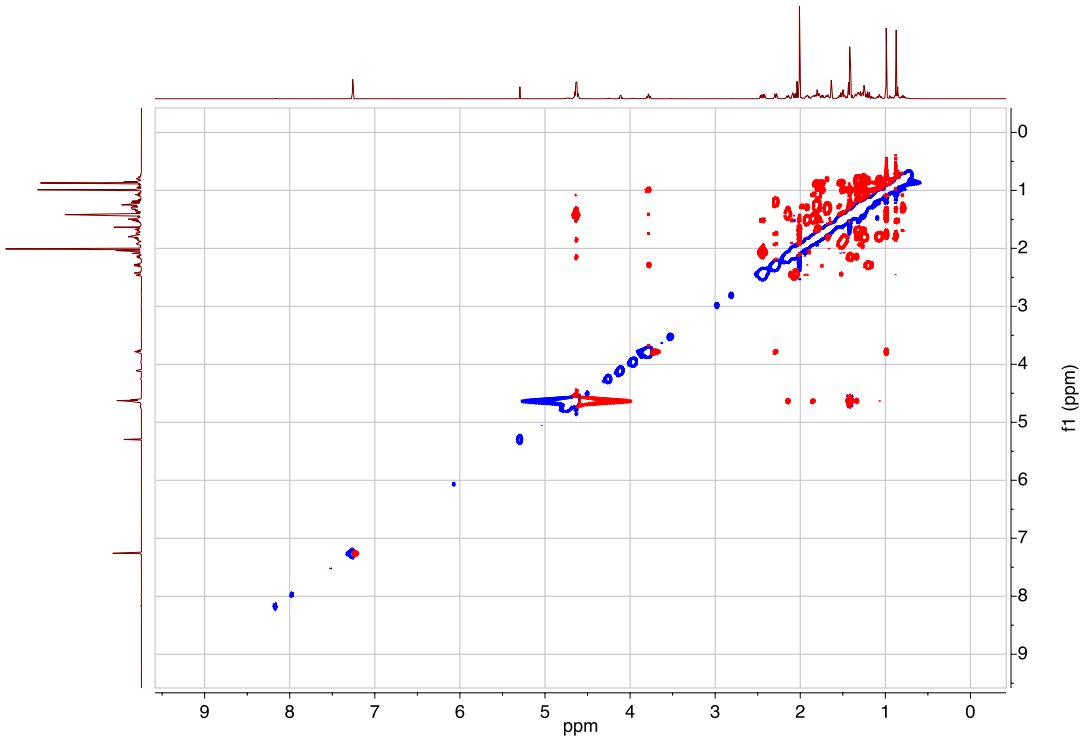
CGN 128B - COSY

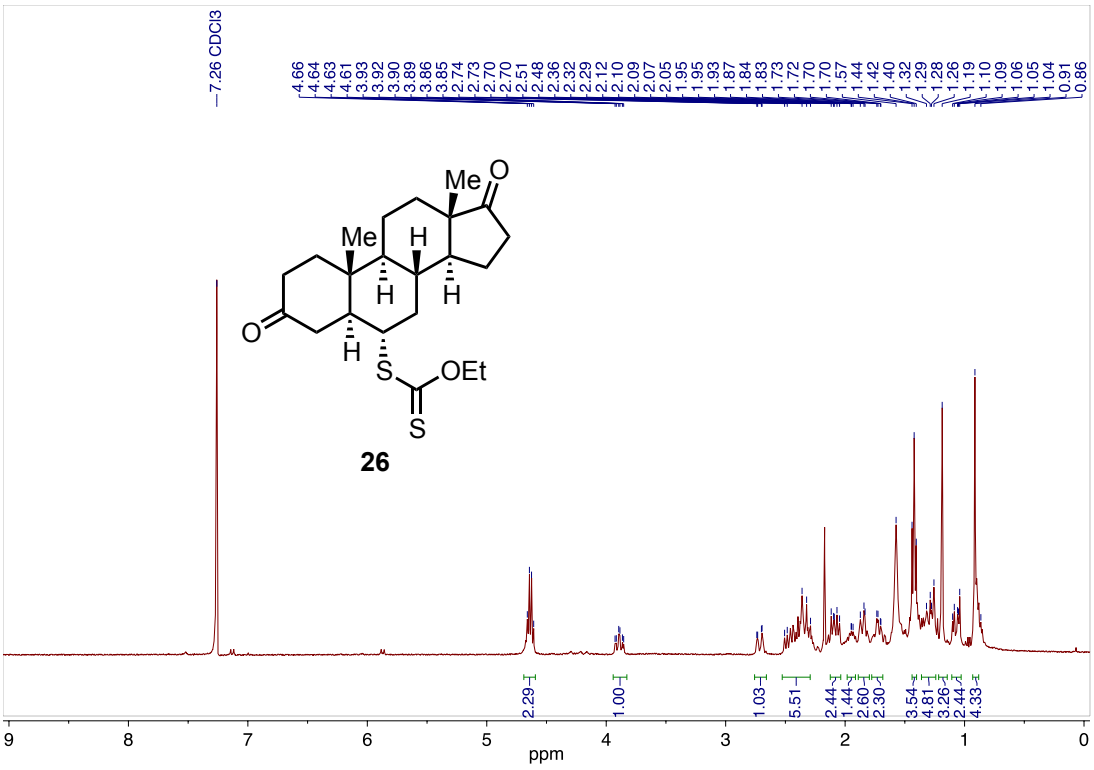


CGN 128B - HSQC

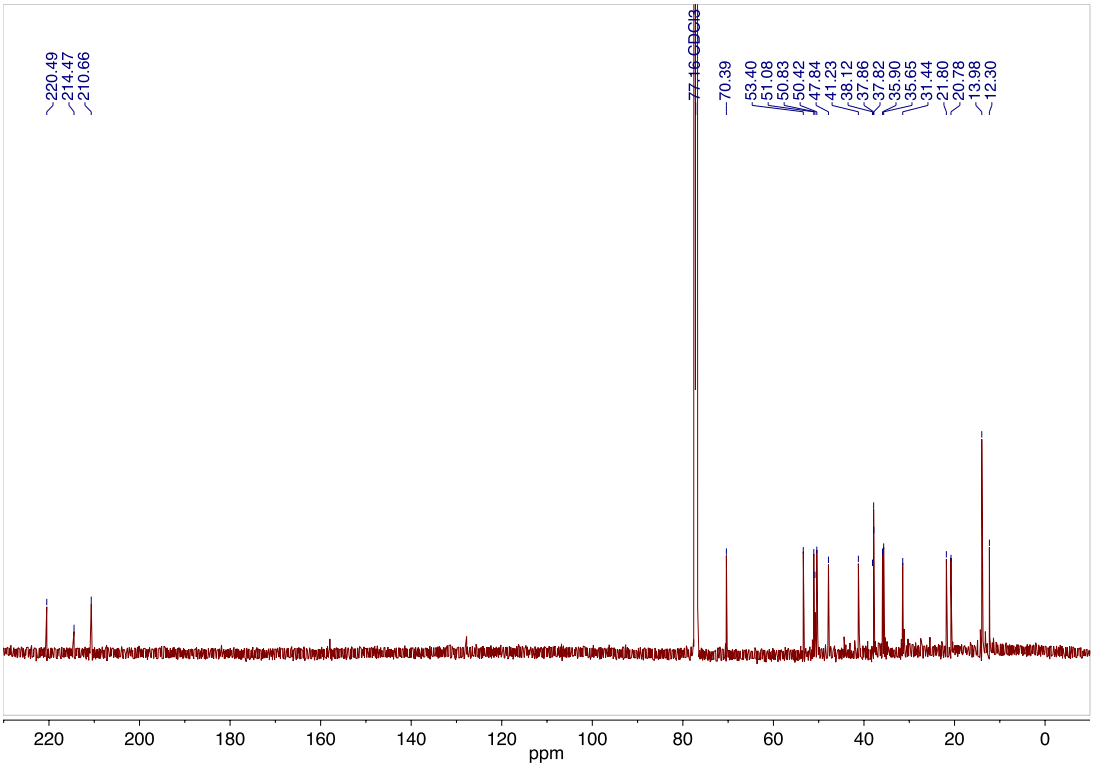


CGN 128B - NOESY

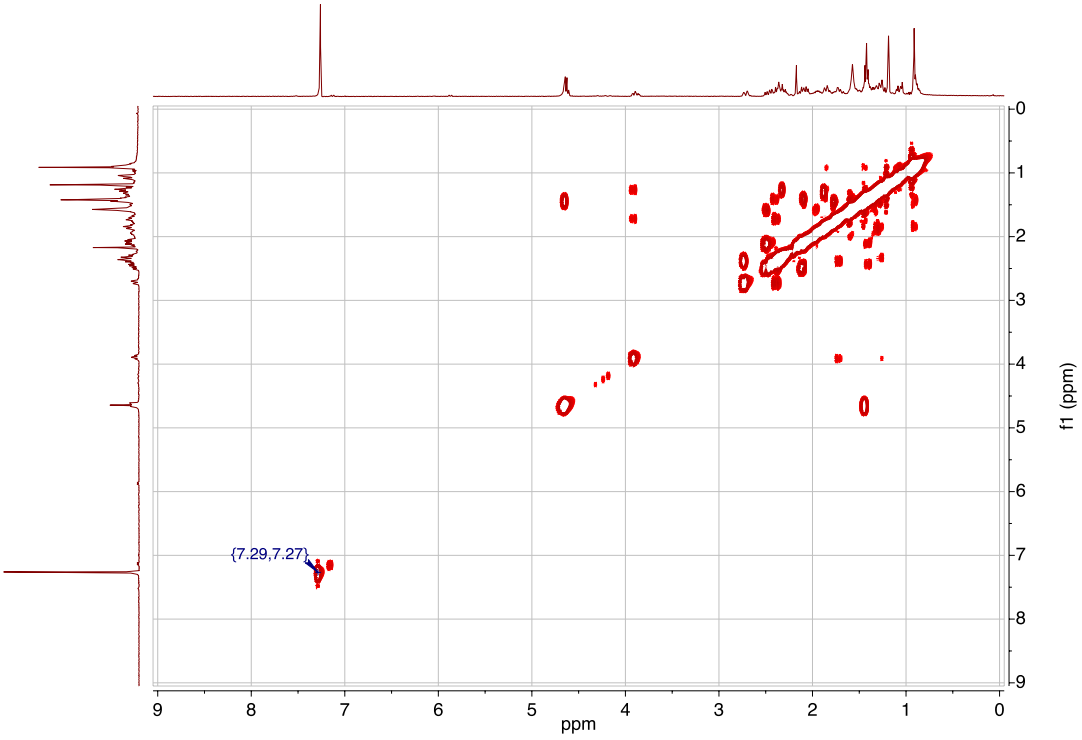



7.26 CDCl3
4.66
4.64
4.63
4.61
3.93
3.92
3.90
3.89
3.86
3.85
2.74
2.73
2.70
2.70
2.51
2.48
2.36
2.32
2.29
2.12
2.10
2.09
2.07
2.05
1.95
1.95
1.93
1.87
1.84
1.83
1.73
1.72
1.70
1.70
1.57
1.44
1.42
1.40
1.32
1.29
1.28
1.26
1.19
1.10
1.09
1.06
1.05
1.04
0.91
0.86
Me
O
Me
H
H
H
O
H
S
OEt
S
2.29
1.00
1.03
5.51
2.44
1.44
2.60
2.30
3.54
4.81
3.26
2.44
4.33
9
8
7
6
5
4
3
2
1
0
ppm

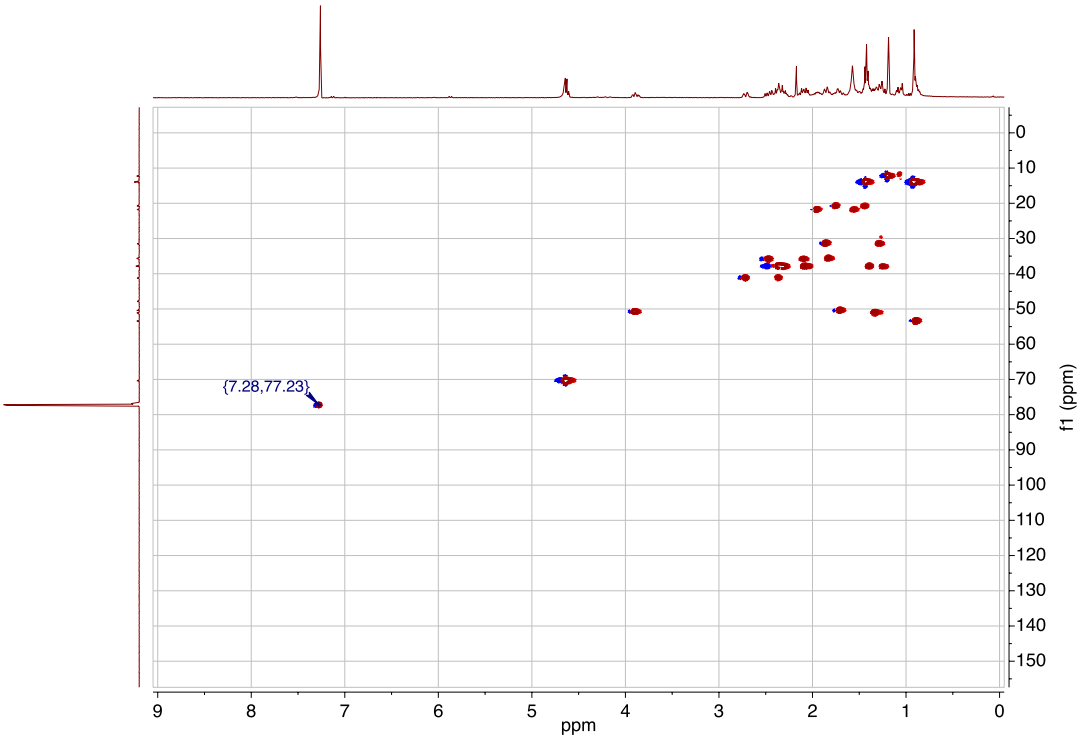
26


220.49
214.47
210.66
77.16 CDCl3
70.39
53.40
51.08
50.83
50.42
47.84
41.23
38.12
37.86
37.82
35.90
35.65
31.44
21.80
20.78
13.98
12.30
220
200
180
160
140
120
100
80
60
40
20
0
ppm

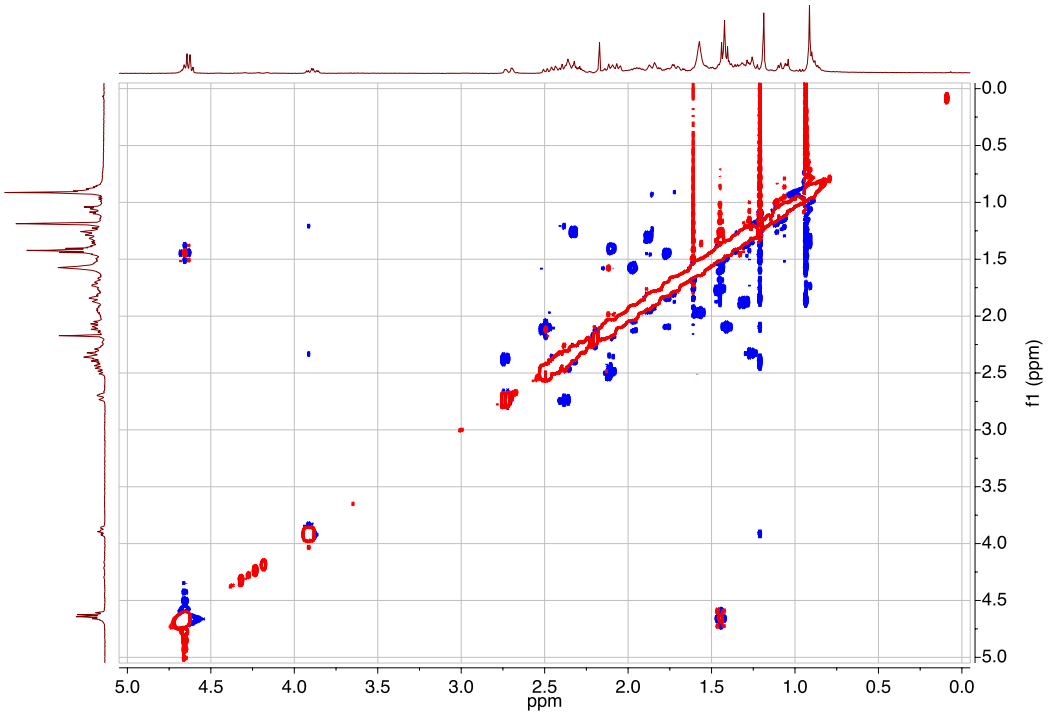
CGN diketone xanthate2 COSY

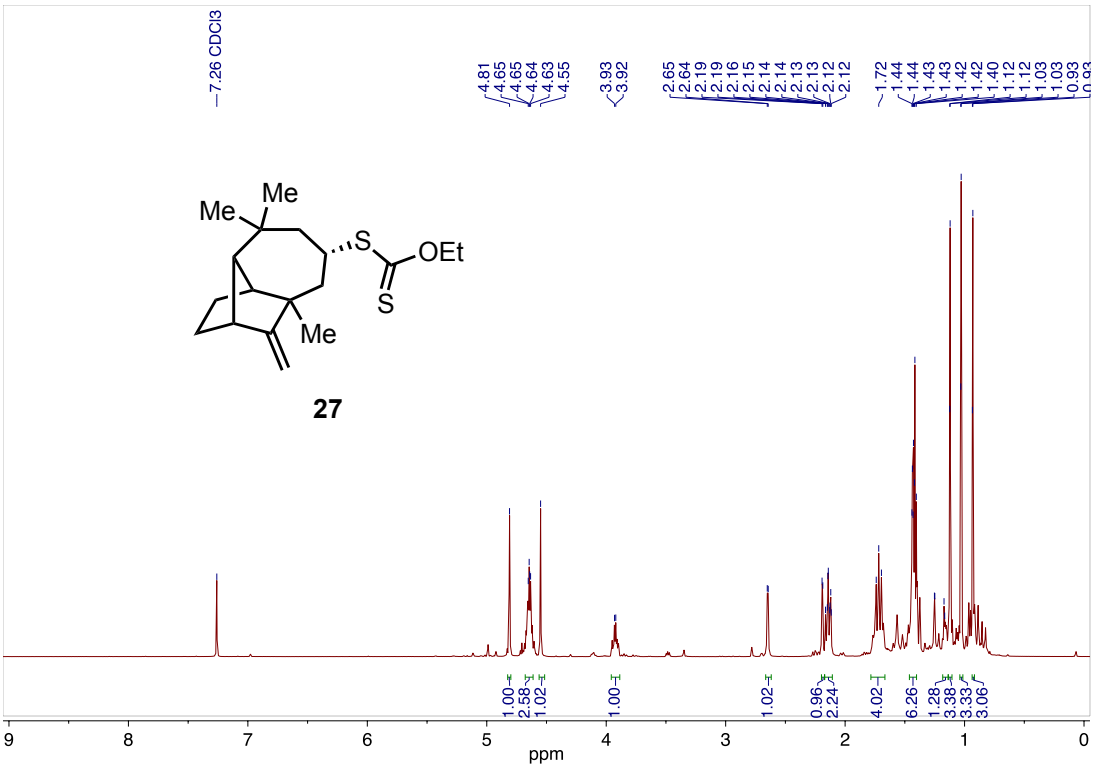


CGN diketone xanthate2 HSQC

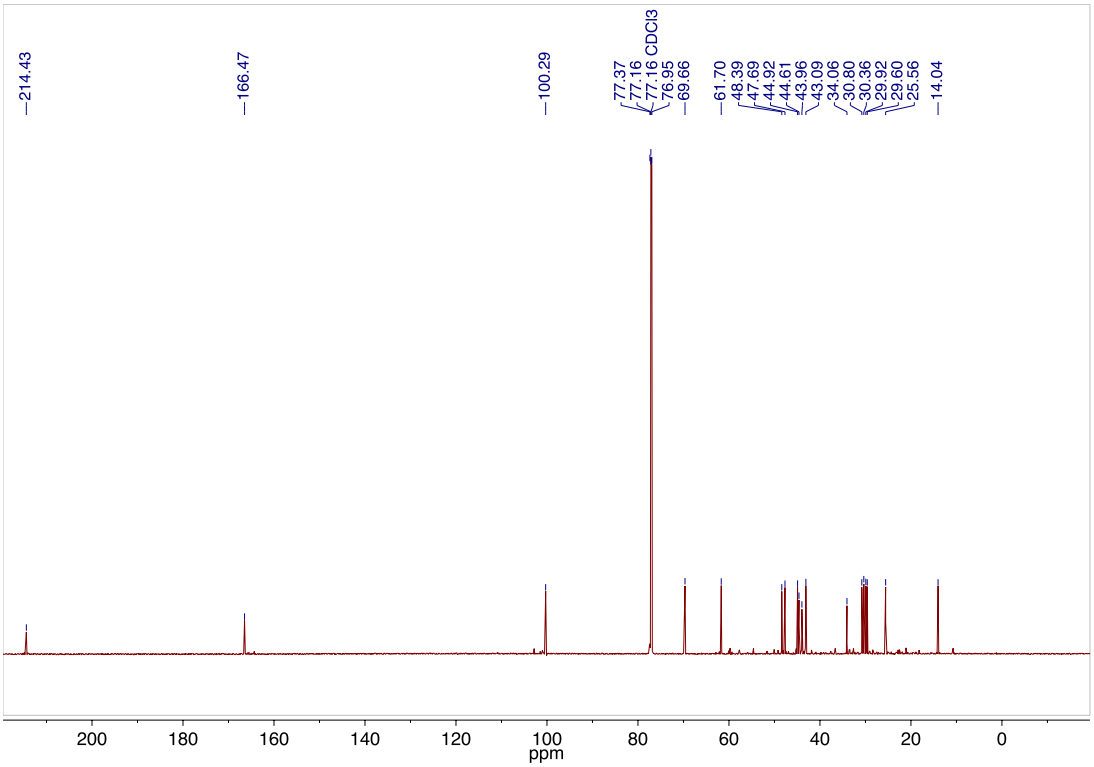


Alexanian — 534474 — cgna — CGN_diketx_NOESY

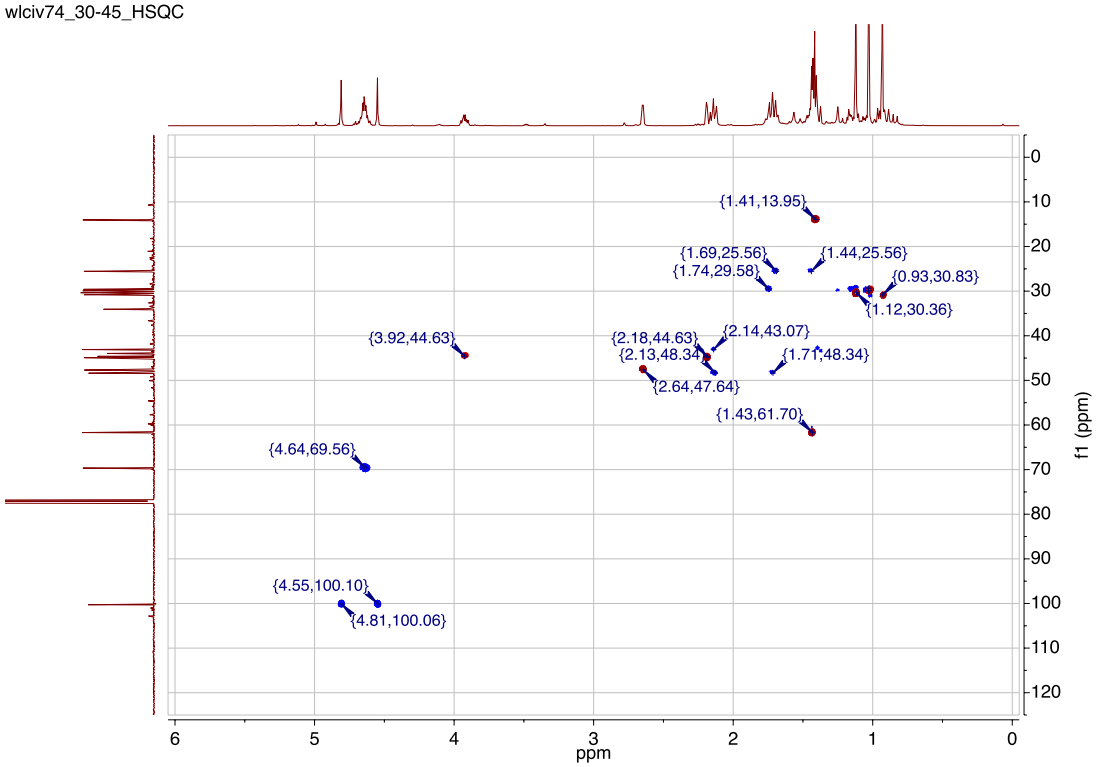



7.26 CDCl3
4.81
4.65
4.65
4.64
4.63
4.55
3.93
3.92
2.65
2.64
2.19
2.19
2.16
2.15
2.14
2.14
2.13
2.13
2.12
2.12
1.72
1.44
1.44
1.43
1.43
1.42
1.42
1.40
1.12
1.12
1.03
1.03
0.93
Me
Me
S
OEt
S
Me
1.00
2.58
1.02
1.00
1.02
0.96
2.24
4.02
6.26
1.28
3.38
3.33
3.06
9
8
7
6
5
4
3
2
1
0
ppm

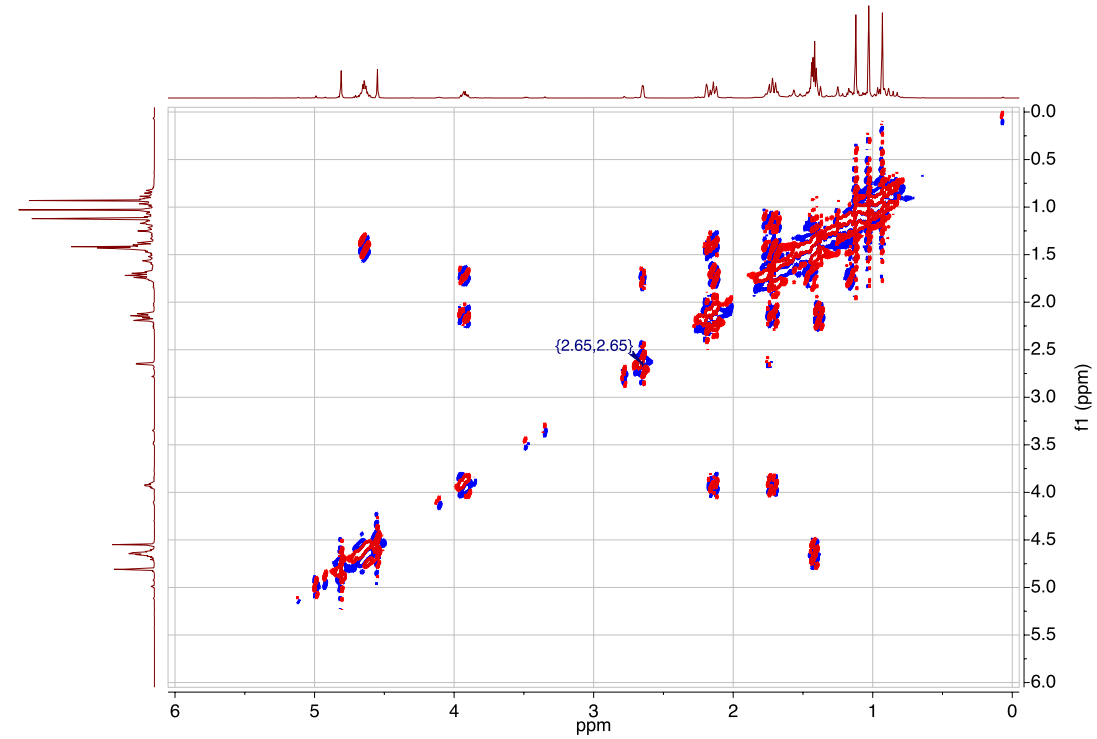
27


214.43
166.47
100.29
77.37
77.16
77.16 CDCl3
76.95
69.66
61.70
48.39
47.69
44.92
44.61
43.96
43.09
34.06
30.80
30.36
29.92
29.60
25.56
14.04
200
180
160
140
120
100
80
60
40
20
0
ppm

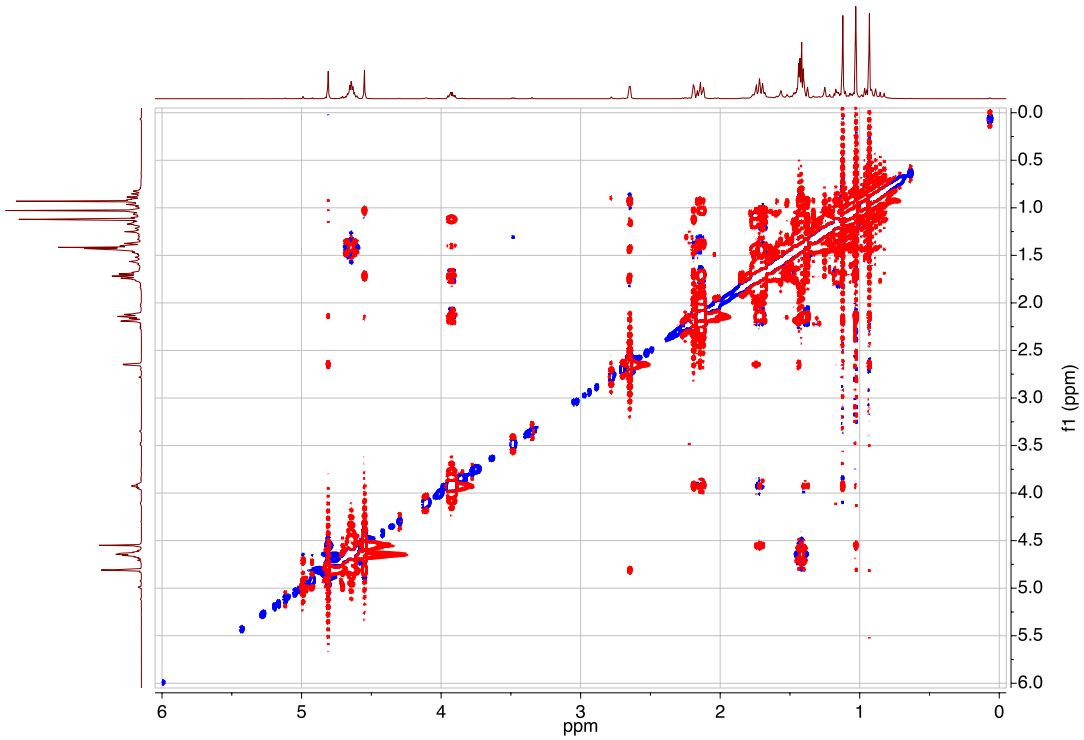
wlciv74_30-45_HSQC

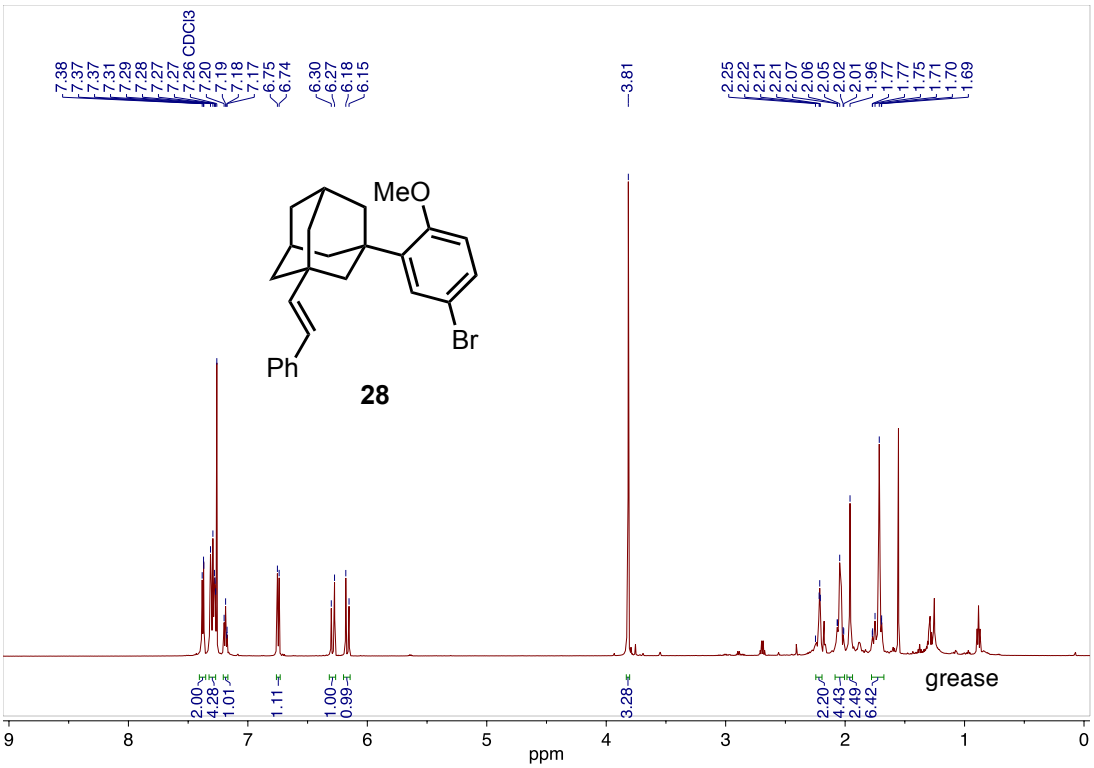


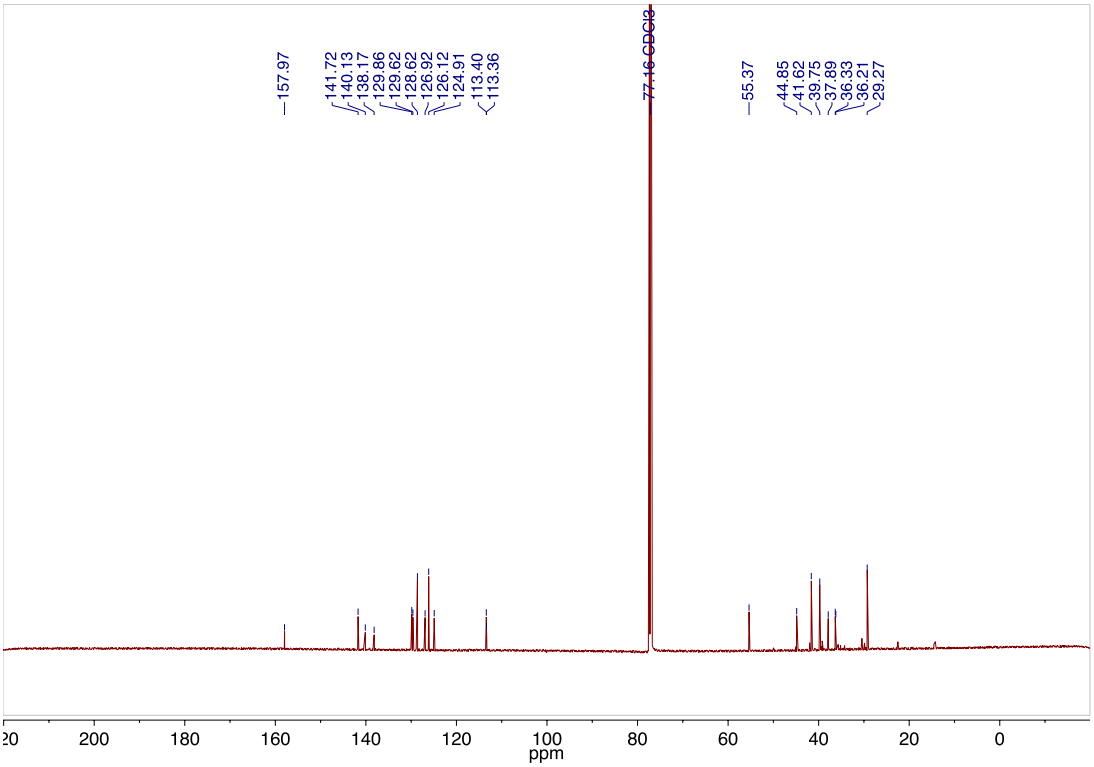
wlciv74_30-45_COSY

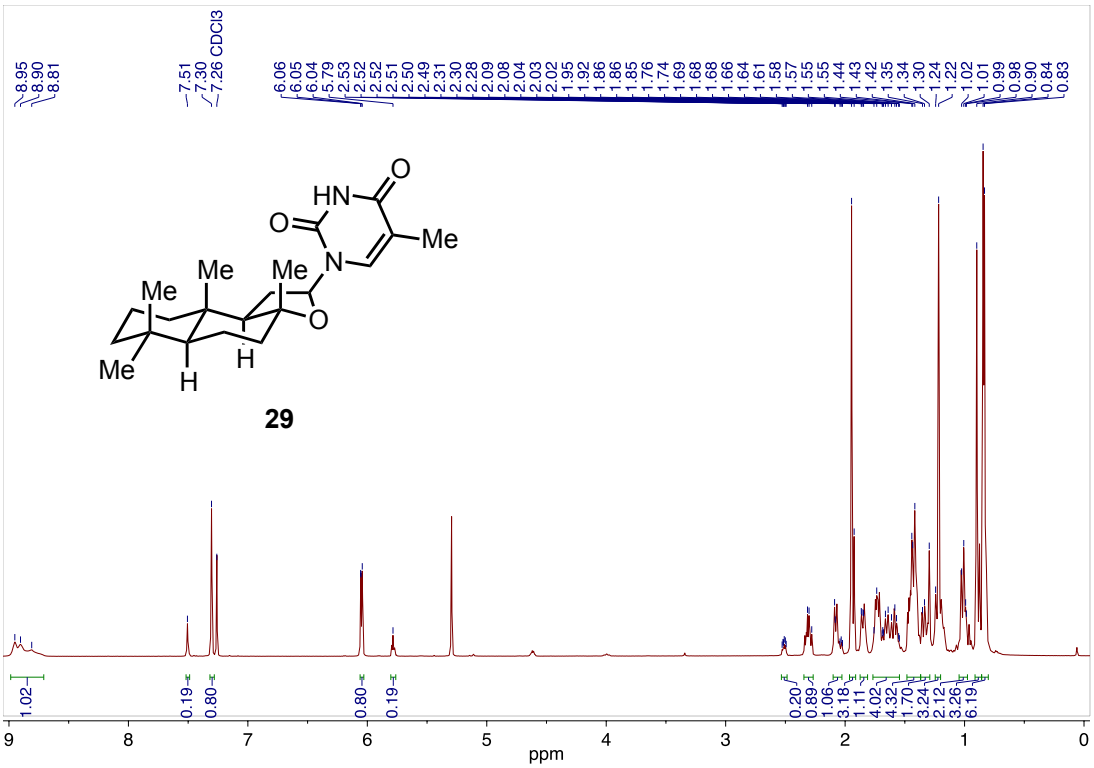


wlciv74_30-45_NOESY

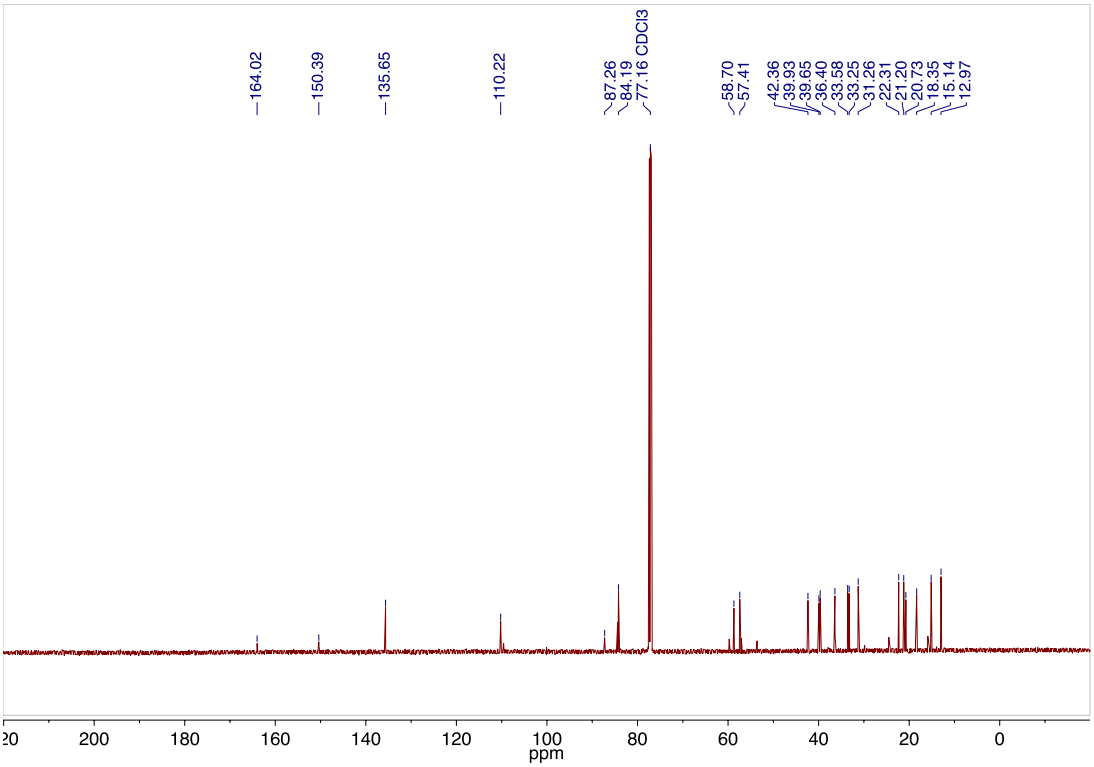


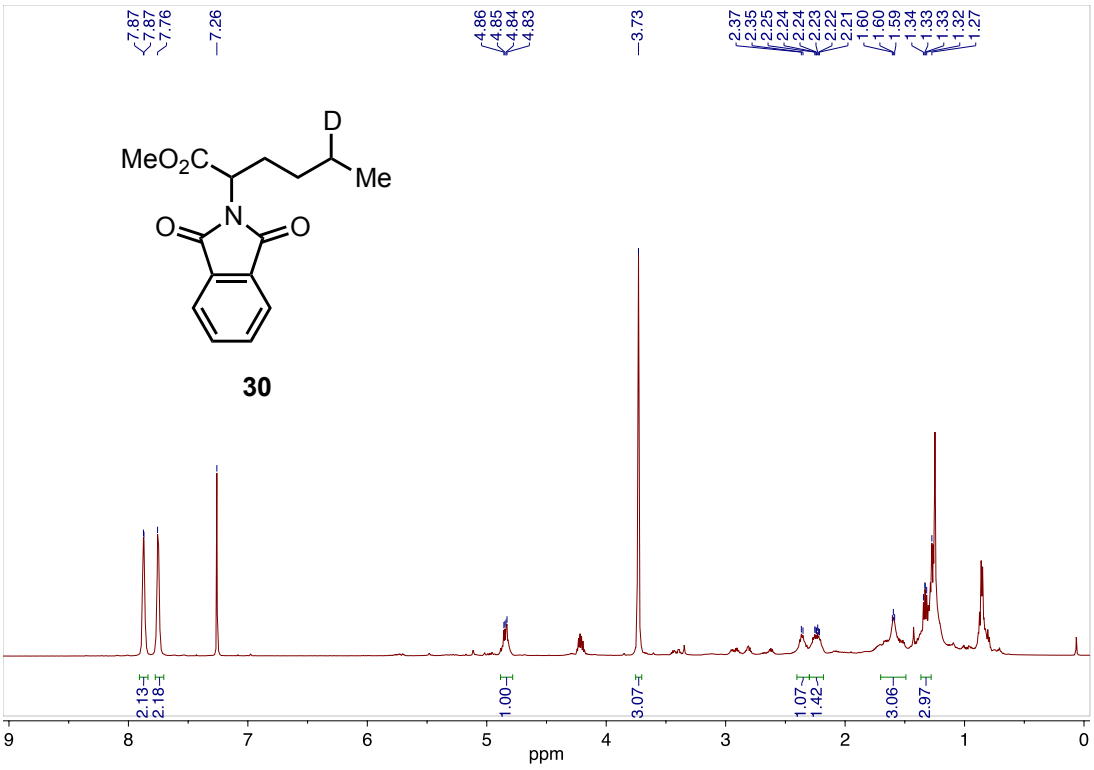

7.38
7.37
7.37
7.31
7.29
7.28
7.27
7.27
7.26 CDCl3
7.20
7.19
7.18
7.17
6.75
6.74
6.30
6.27
6.18
6.15
3.81
2.25
2.22
2.21
2.21
2.07
2.06
2.05
2.02
2.01
1.96
1.77
1.77
1.75
1.71
1.70
1.69
MeO
Br
Ph
28
2.00
4.28
1.01
1.11
1.00
0.99
3.28
2.20
4.43
2.49
6.42
grease
9
8
7
6
5
4
3
2
1
0
ppm


157.97
141.72
140.13
138.17
129.86
129.62
128.62
126.92
126.12
124.91
113.40
113.36
77.16 CDCl3
55.37
44.85
41.62
39.75
37.89
36.33
36.21
29.27
200
180
160
140
120
100
80
60
40
20
0
ppm

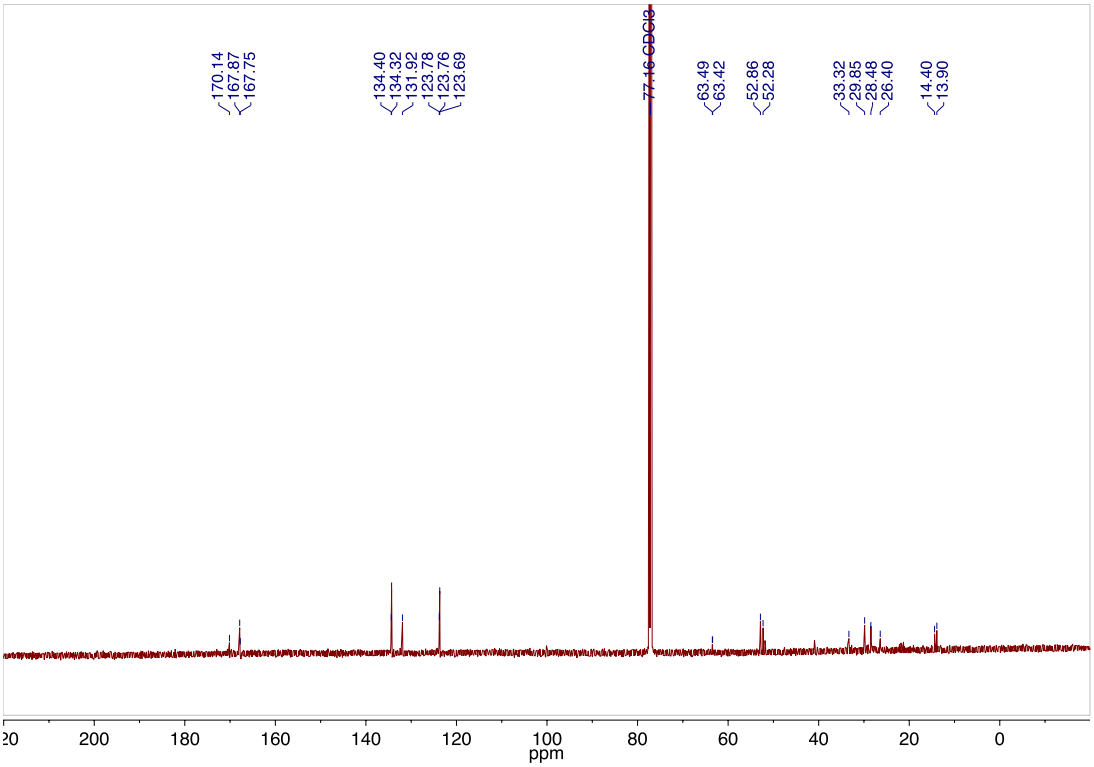

8.95
8.90
8.81
7.51
7.30
7.26 CDCl3
6.06
6.05
6.04
5.79
2.53
2.52
2.51
2.50
2.49
2.31
2.30
2.28
2.09
2.08
2.04
2.03
2.02
1.95
1.92
1.86
1.86
1.85
1.76
1.74
1.69
1.68
1.66
1.64
1.61
1.58
1.57
1.55
1.55
1.44
1.43
1.42
1.35
1.34
1.30
1.24
1.22
1.02
1.01
0.99
0.98
0.90
0.84
0.83
HN
O
O
N
Me
Me
Me
Me
O
H
Me
H
1.02
0.19
0.80
0.80
0.19
0.20
0.89
1.06
3.18
1.11
4.02
4.32
1.70
3.24
2.12
3.26
6.19
9
8
7
6
5
4
3
2
1
0
ppm

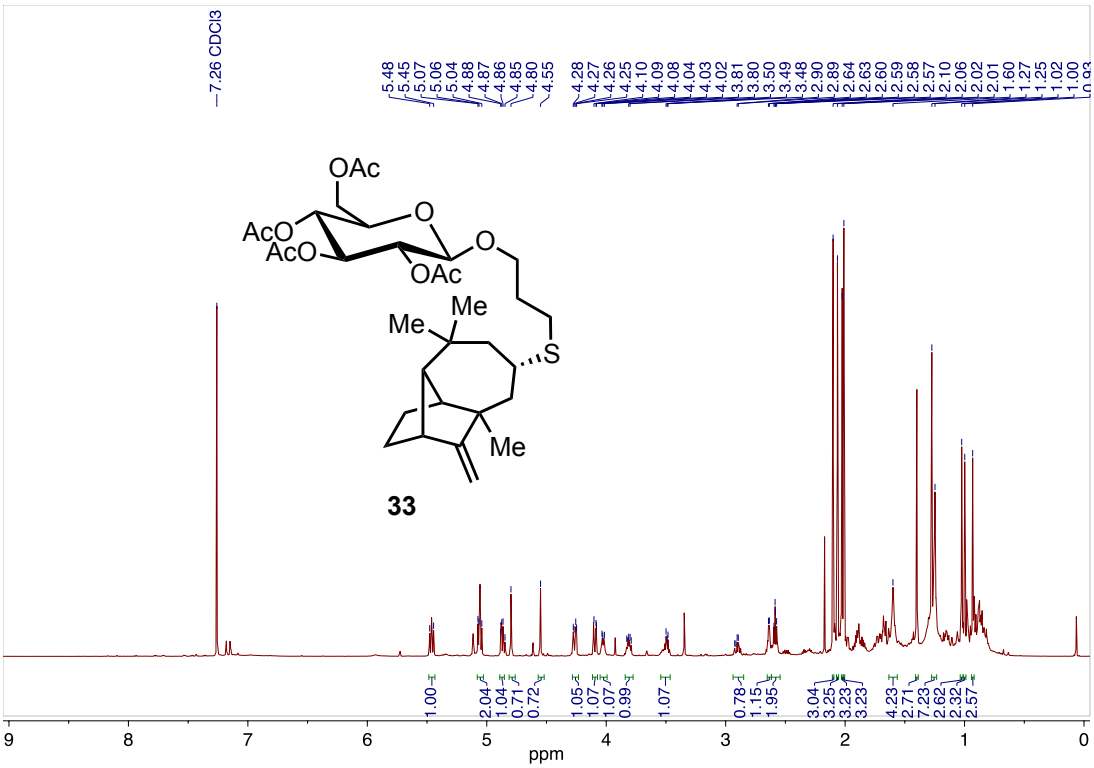
29

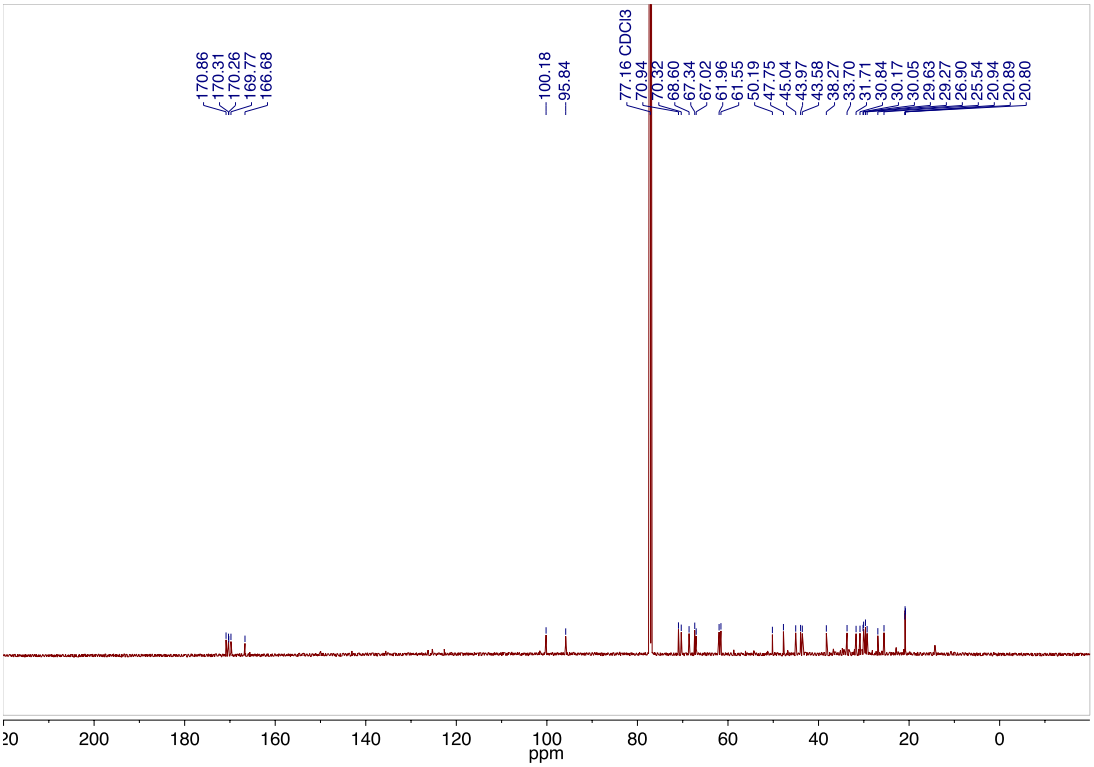

164.02
150.39
135.65
110.22
87.26
84.19
77.16 CDCl3
58.70
57.41
42.36
39.93
39.65
39.40
36.40
33.58
33.25
31.26
22.31
21.20
20.73
18.35
15.14
12.97
200
180
160
140
120
100
80
60
40
20
0
ppm

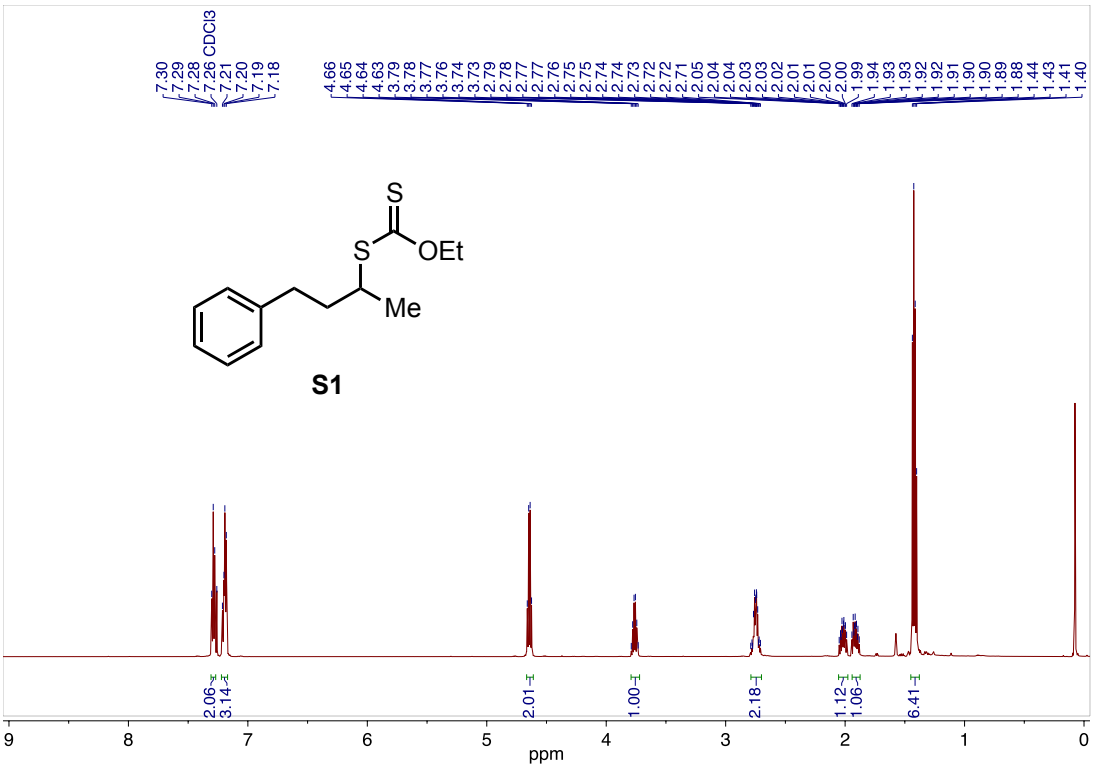

7.87
7.87
7.76
7.26
4.86
4.85
4.84
4.83
3.73
2.37
2.35
2.25
2.24
2.24
2.23
2.22
2.21
1.60
1.60
1.59
1.34
1.33
1.33
1.32
1.27
D
MeO2C
Me
O
N
O
2.13
2.18
1.00
3.07
1.07
1.42
3.06
2.97
9
8
7
6
5
4
3
2
1
0
ppm

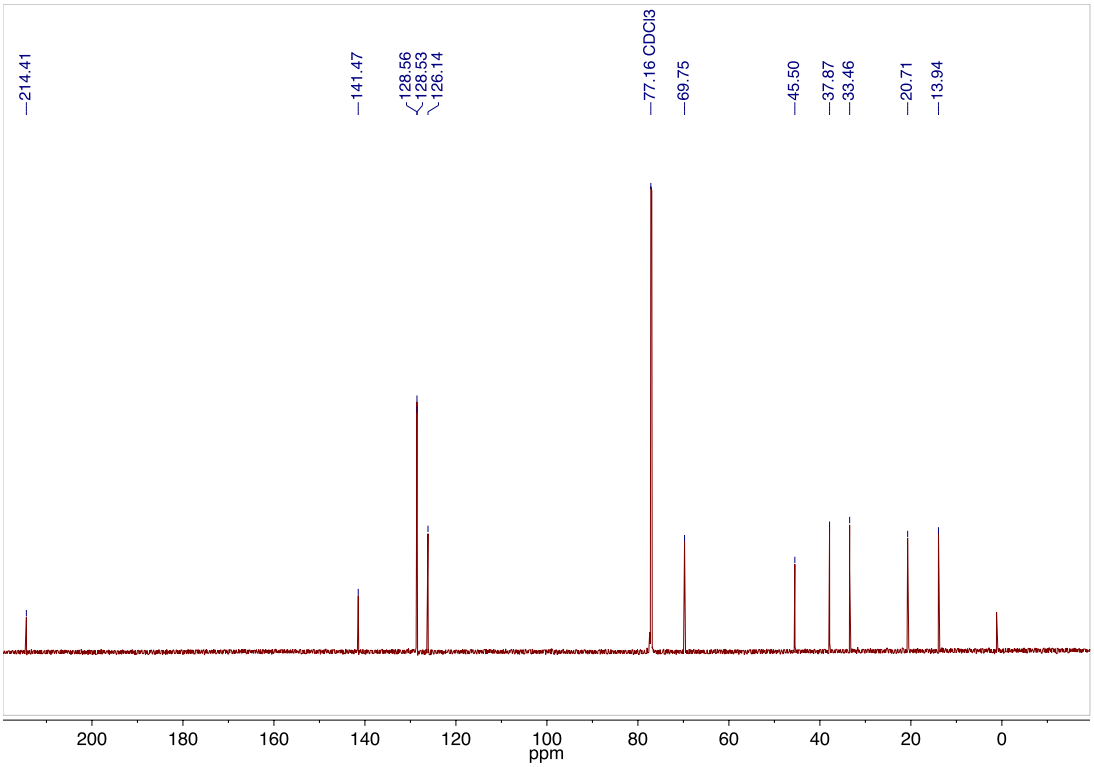
30

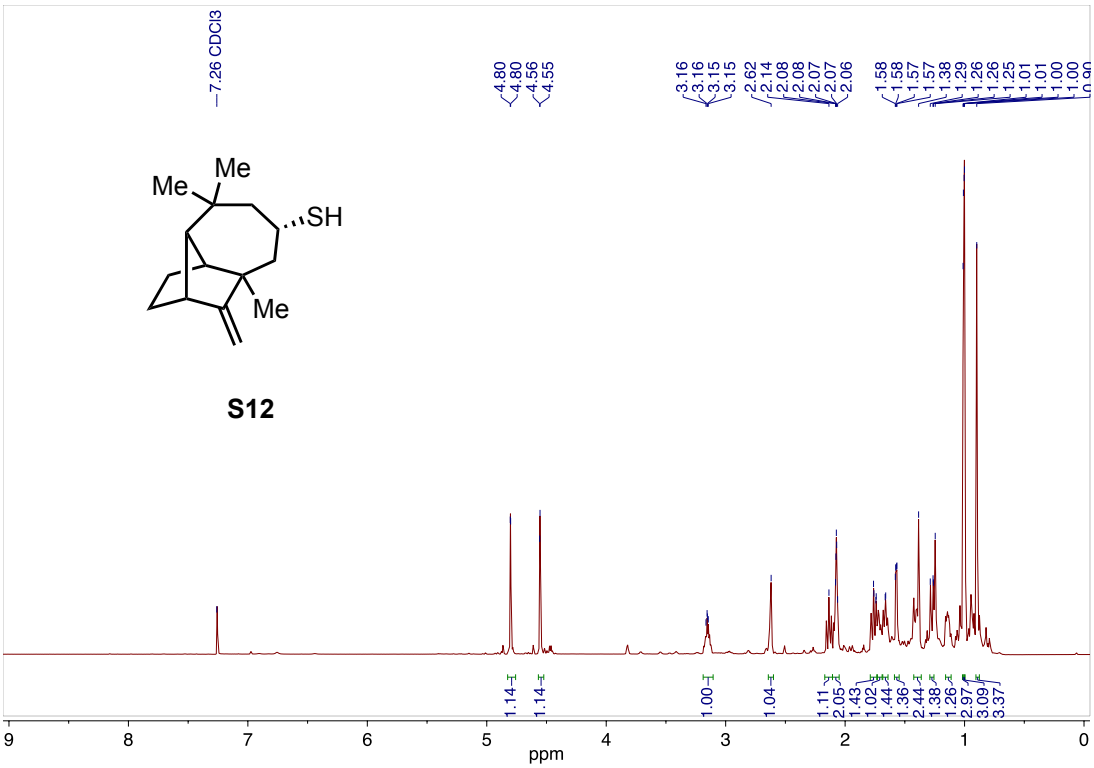

170.14
167.87
167.75
134.40
134.32
131.92
123.78
123.76
123.69
77.16 CDCl3
63.49
63.42
52.86
52.28
33.32
29.85
28.48
26.40
14.40
13.90
200
180
160
140
120
100
80
60
40
20
0
ppm


7.26 CDCl3
OAc
AcO
AcO
O
O
OAc
Me
Me
S
Me
33
ppm

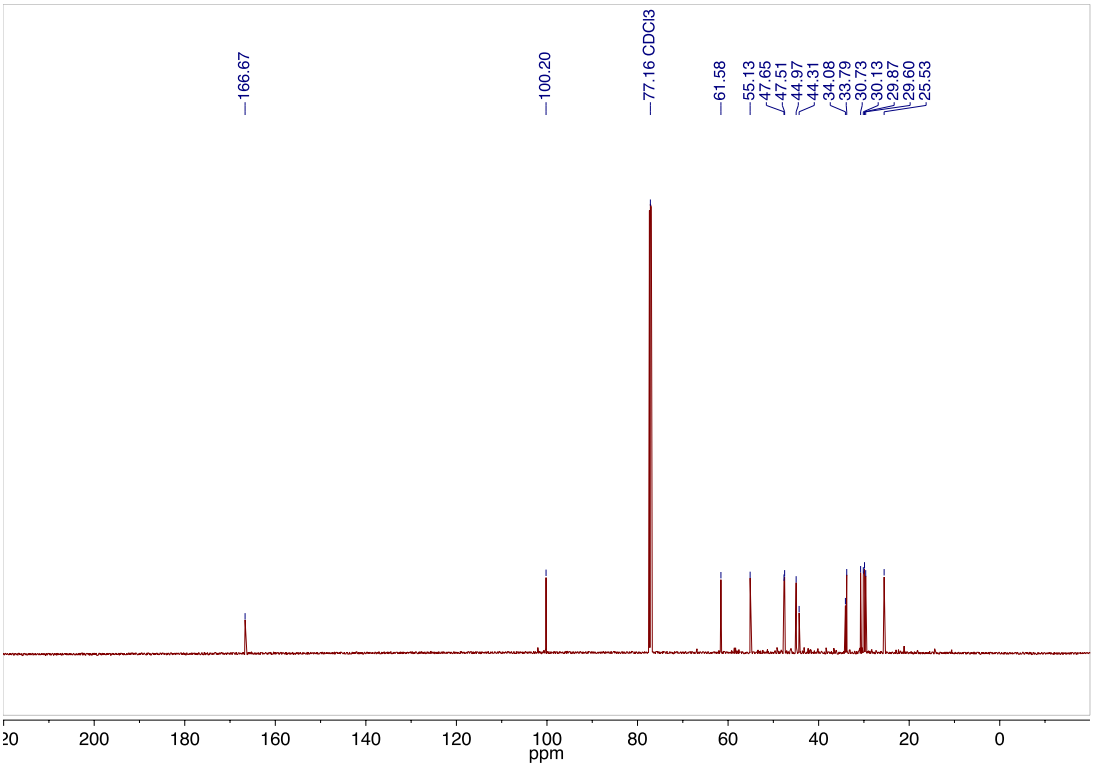

170.86
170.31
170.26
169.77
166.68
100.18
95.84
77.16 CDCl3
70.94
70.32
68.60
67.34
67.02
61.96
61.55
50.19
47.75
45.04
43.97
43.58
38.27
33.70
31.71
30.84
30.17
30.05
29.63
29.27
26.90
25.54
20.94
20.89
20.80
ppm

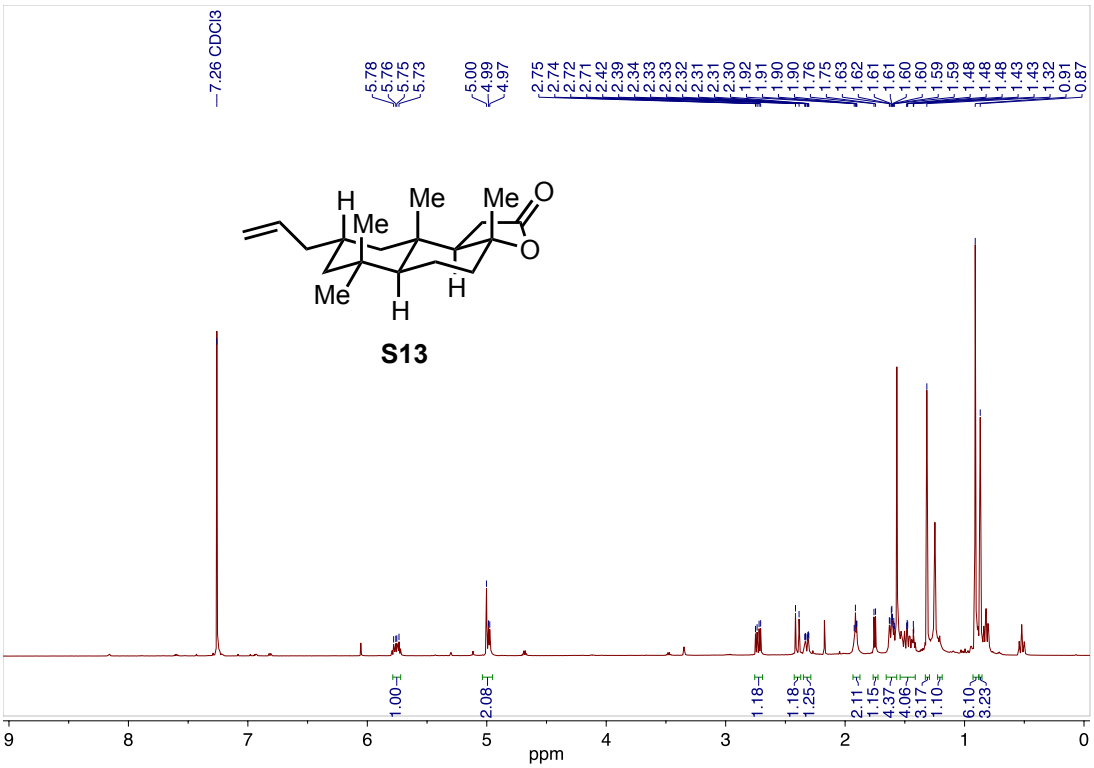

7.30
7.29
7.28
7.26 CDCl3
7.21
7.20
7.19
7.18
4.66
4.65
4.64
4.63
3.79
3.78
3.77
3.76
3.74
3.73
2.79
2.78
2.77
2.76
2.75
2.75
2.74
2.74
2.73
2.72
2.72
2.71
2.05
2.04
2.04
2.03
2.03
2.02
2.01
2.01
2.00
2.00
1.99
1.94
1.93
1.93
1.92
1.92
1.91
1.90
1.90
1.89
1.88
1.44
1.43
1.41
1.40
S
S
OEt
Me
S1
2.06
3.14
2.01
1.00
2.18
1.12
1.06
6.41
9
8
7
6
5
4
3
2
1
0
ppm


214.41
141.47
128.56
128.53
126.14
77.16 CDCl3
69.75
45.50
37.87
33.46
20.71
13.94
200
180
160
140
120
100
80
60
40
20
0
ppm

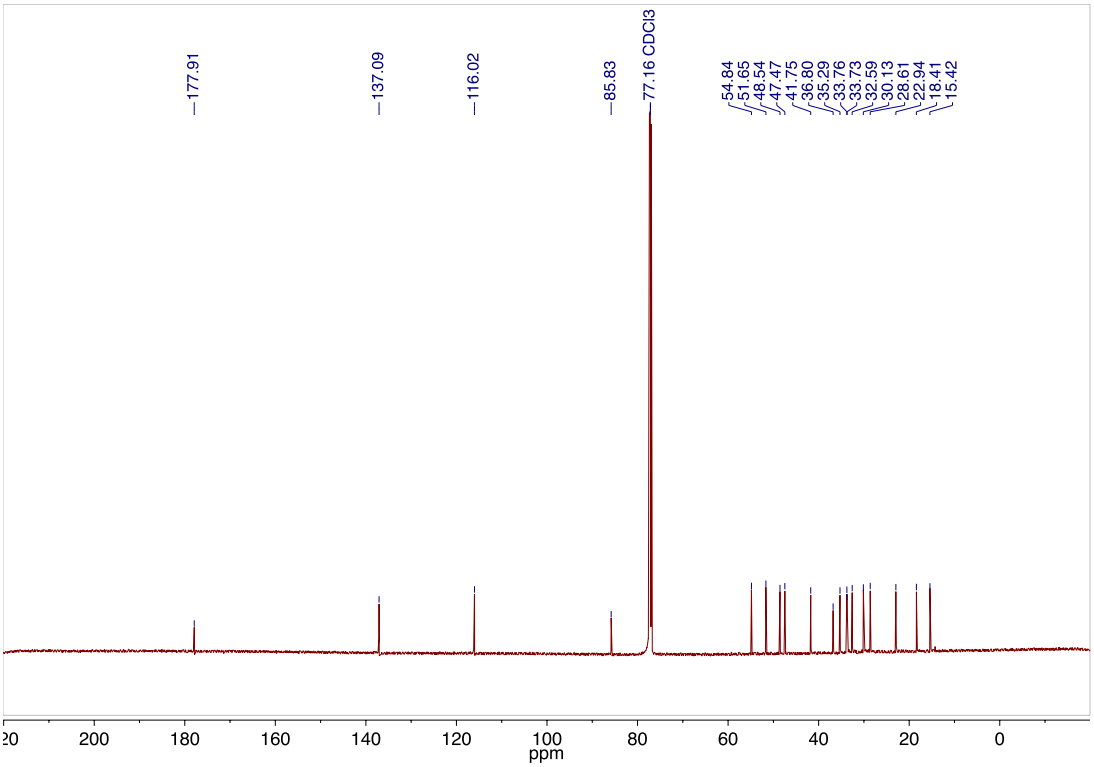

7.26 CDCl3
4.80
4.80
4.56
4.55
3.16
3.16
3.15
3.15
2.62
2.14
2.08
2.08
2.07
2.07
2.06
1.58
1.58
1.57
1.57
1.38
1.29
1.26
1.26
1.25
1.01
1.01
1.00
1.00
1.00
Me
Me
SH
Me
1.14
1.14
1.00
1.04
1.11
2.05
1.43
1.02
1.44
1.36
2.44
1.38
1.26
2.97
3.09
3.37
9
8
7
6
5
4
3
2
1
0
ppm

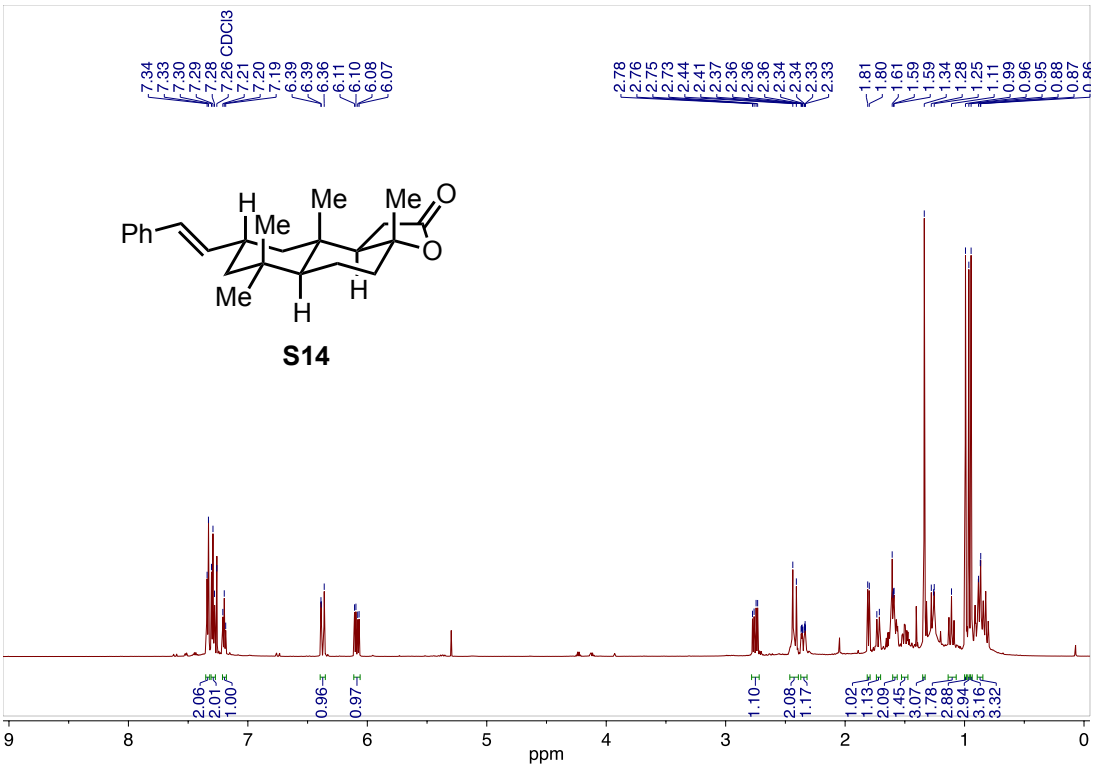
S12


166.67
100.20
77.16 CDCl3
61.58
55.13
47.65
47.51
44.97
44.31
34.08
33.79
30.73
30.13
29.87
29.60
25.53
200
180
160
140
120
100
80
60
40
20
0
ppm

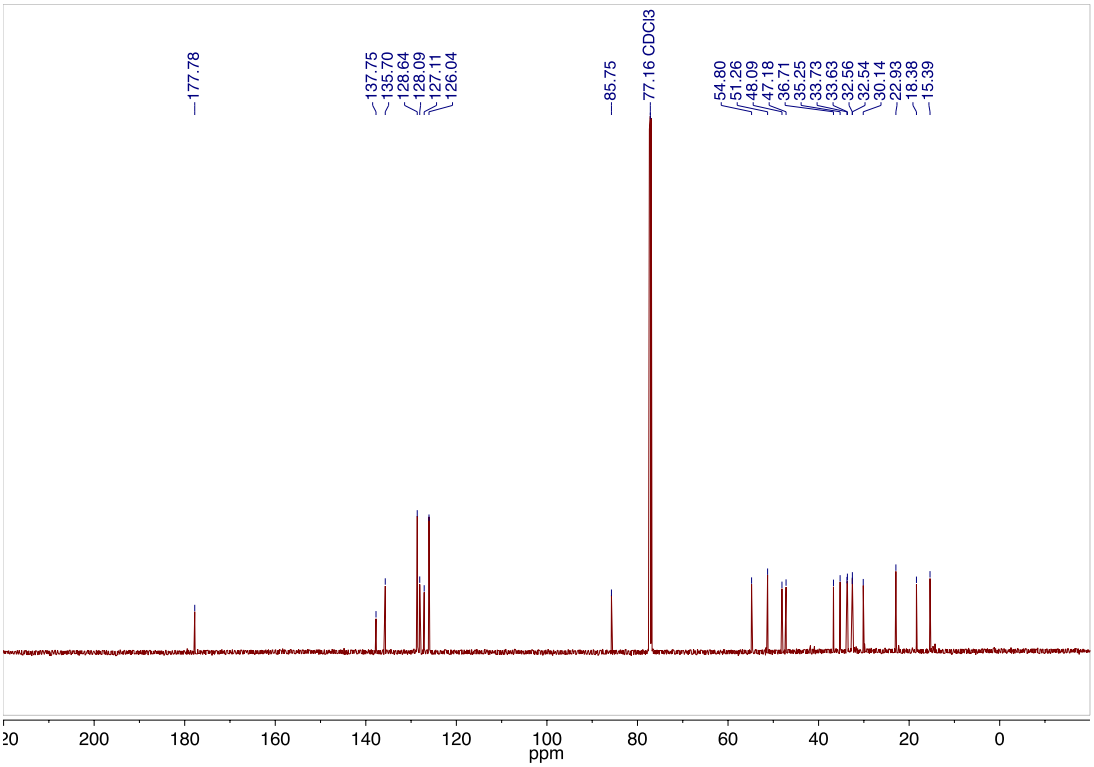

7.26 CDCl3
5.78
5.76
5.75
5.73
5.00
4.99
4.97
2.75
2.74
2.72
2.71
2.42
2.39
2.34
2.33
2.33
2.32
2.31
2.31
2.30
1.92
1.91
1.90
1.90
1.76
1.75
1.63
1.62
1.61
1.61
1.60
1.60
1.59
1.59
1.48
1.48
1.48
1.43
1.43
1.32
0.91
0.87
H
Me
Me
Me
O
O
Me
H
H
1.00
2.08
1.18
1.18
1.25
2.11
1.15
4.37
4.06
3.17
1.10
6.10
3.23
9
8
7
6
5
4
3
2
1
0
ppm

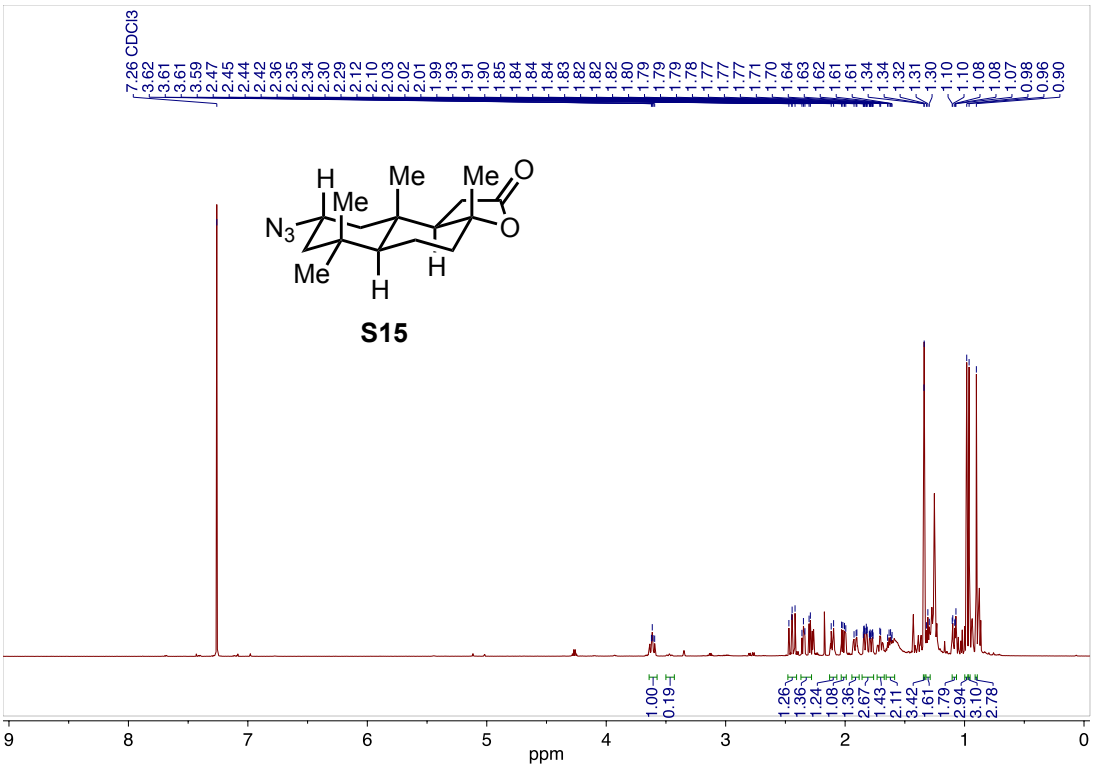
S13


177.91
137.09
116.02
85.83
77.16 CDCl3
54.84
51.65
48.54
47.47
41.75
36.80
35.29
33.76
33.73
32.59
30.13
28.61
22.94
18.41
15.42
200
180
160
140
120
100
80
60
40
20
0
ppm

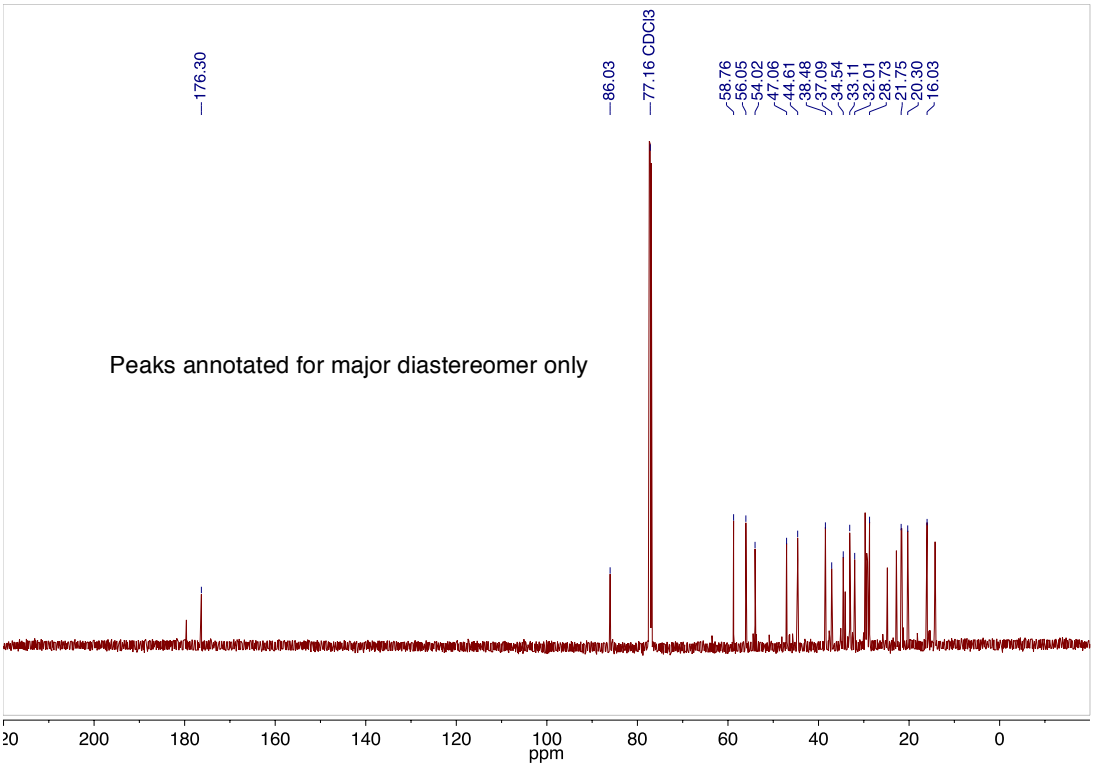

7.34
7.33
7.30
7.29
7.28
7.26 CDCl3
7.21
7.20
7.19
6.39
6.39
6.36
6.11
6.10
6.08
6.07
2.78
2.76
2.75
2.73
2.44
2.41
2.37
2.36
2.36
2.34
2.34
2.33
2.33
1.81
1.80
1.61
1.59
1.59
1.34
1.28
1.25
1.11
0.99
0.96
0.95
0.88
0.87
Ph
H
Me
Me
Me
O
O
Me
H
H
2.06
2.01
1.00
0.96
0.97
1.10
2.08
1.17
1.02
1.13
2.09
1.45
3.07
1.78
2.88
2.94
3.16
3.32
9
8
7
6
5
4
3
2
1
0
ppm

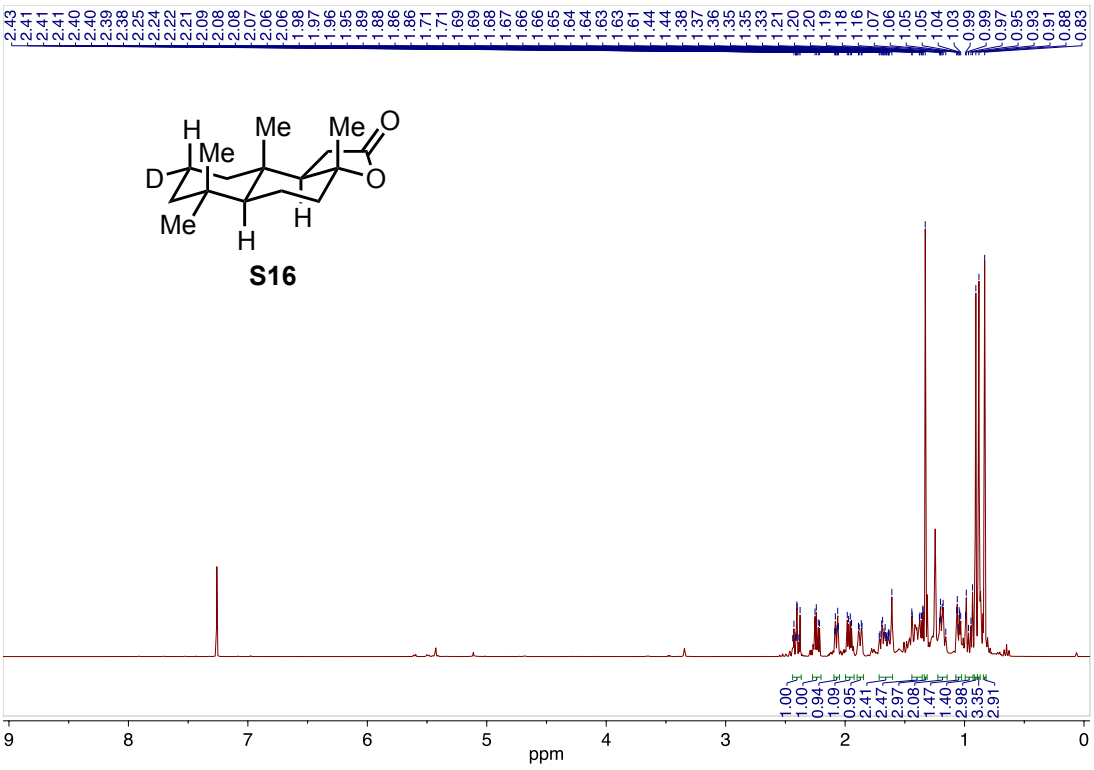
S14


177.78
137.75
135.70
128.64
128.09
127.11
126.04
85.75
77.16 CDCl3
54.80
51.26
48.09
47.18
36.71
35.25
33.73
33.63
32.56
32.54
30.14
22.93
18.38
15.39
200
180
160
140
120
100
80
60
40
20
0
ppm

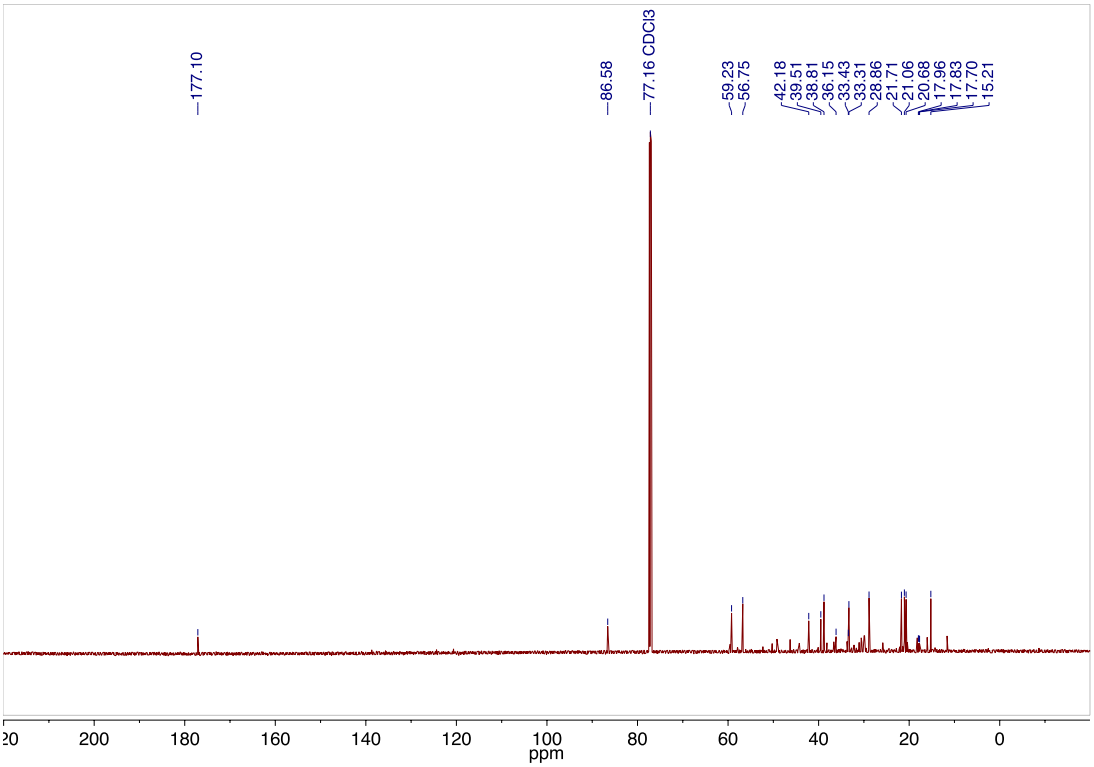

7.26 CDCl3
3.62
3.61
3.61
3.59
2.47
2.45
2.44
2.42
2.36
2.35
2.34
2.30
2.29
2.12
2.10
2.03
2.02
2.01
1.99
1.93
1.91
1.90
1.85
1.84
1.84
1.84
1.83
1.82
1.82
1.82
1.80
1.79
1.79
1.79
1.78
1.77
1.77
1.77
1.71
1.70
1.64
1.63
1.62
1.61
1.61
1.34
1.34
1.32
1.31
1.30
1.10
1.10
1.08
1.08
1.07
0.98
0.96
0.90
H
Me
Me
O
Me
N3
O
Me
H
H
1.00
0.19
1.26
1.36
1.24
1.08
1.36
2.67
1.43
2.11
3.42
1.61
1.79
2.94
3.10
2.78
9
8
7
6
5
4
3
2
1
0
ppm

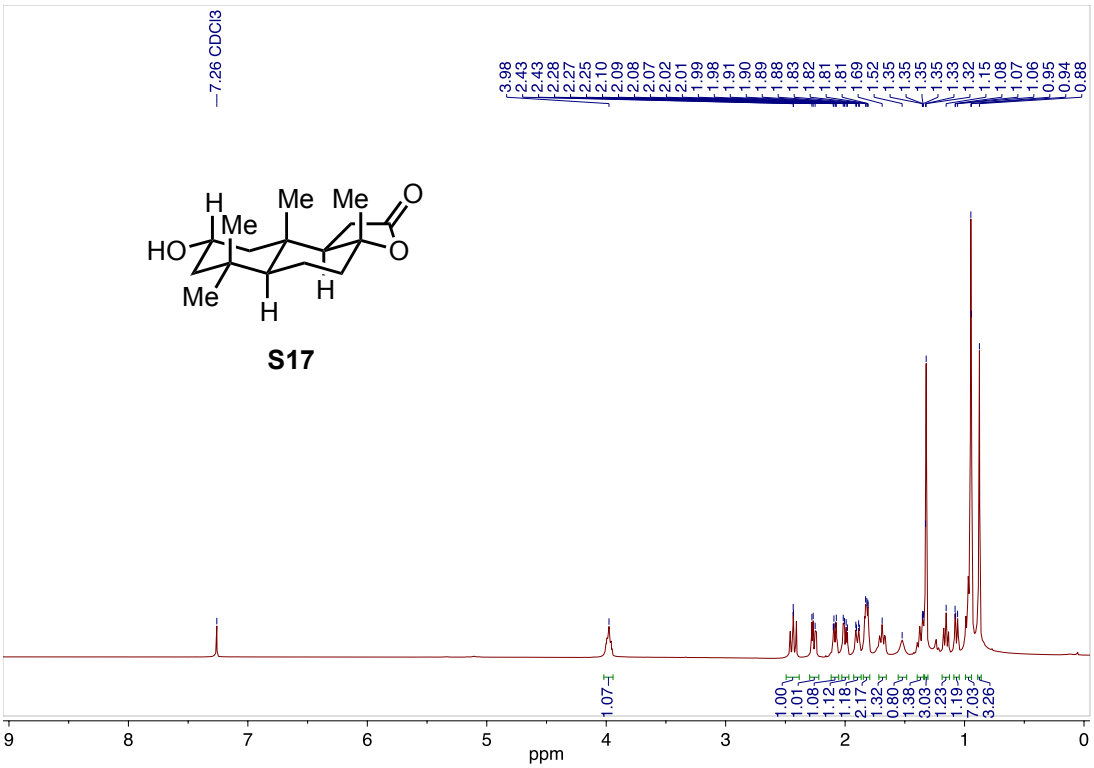
S15


176.30
86.03
77.16 CDCl3
58.76
56.05
54.02
47.06
44.61
38.48
37.09
34.54
33.11
32.01
28.73
21.75
20.30
16.03
Peaks annotated for major diastereomer only
200
180
160
140
120
100
80
60
40
20
0
ppm

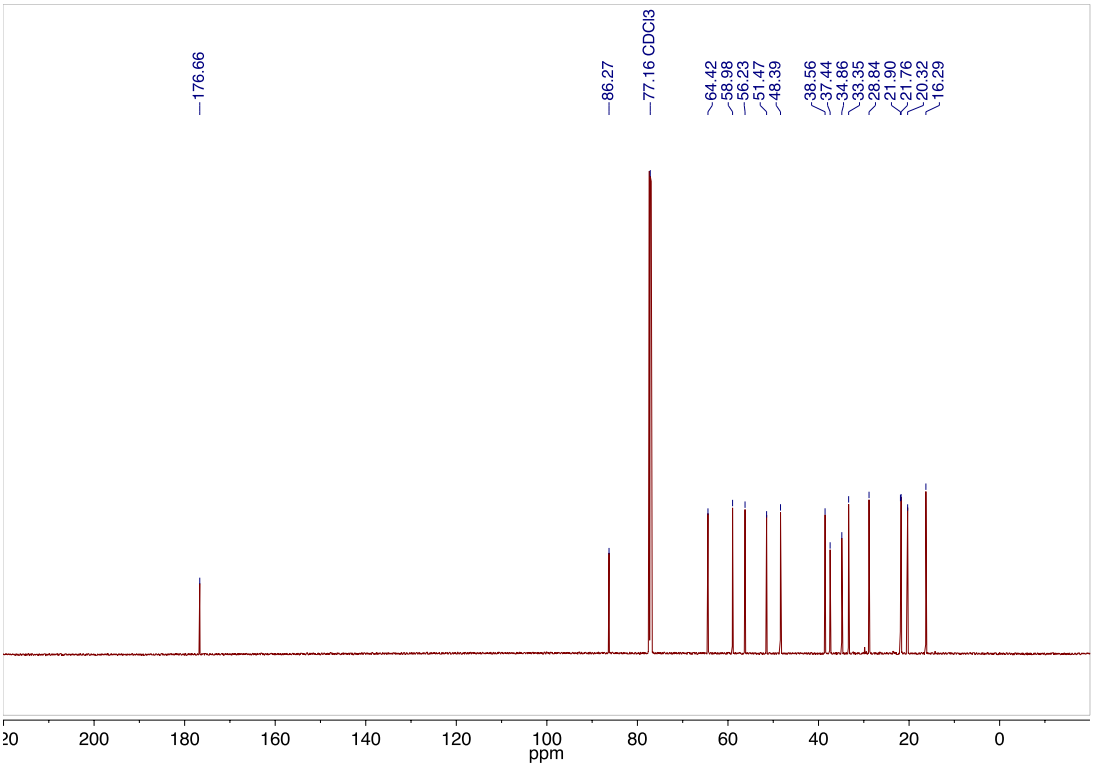

H
Me
Me
Me
O
D
Me
O
Me
H
H

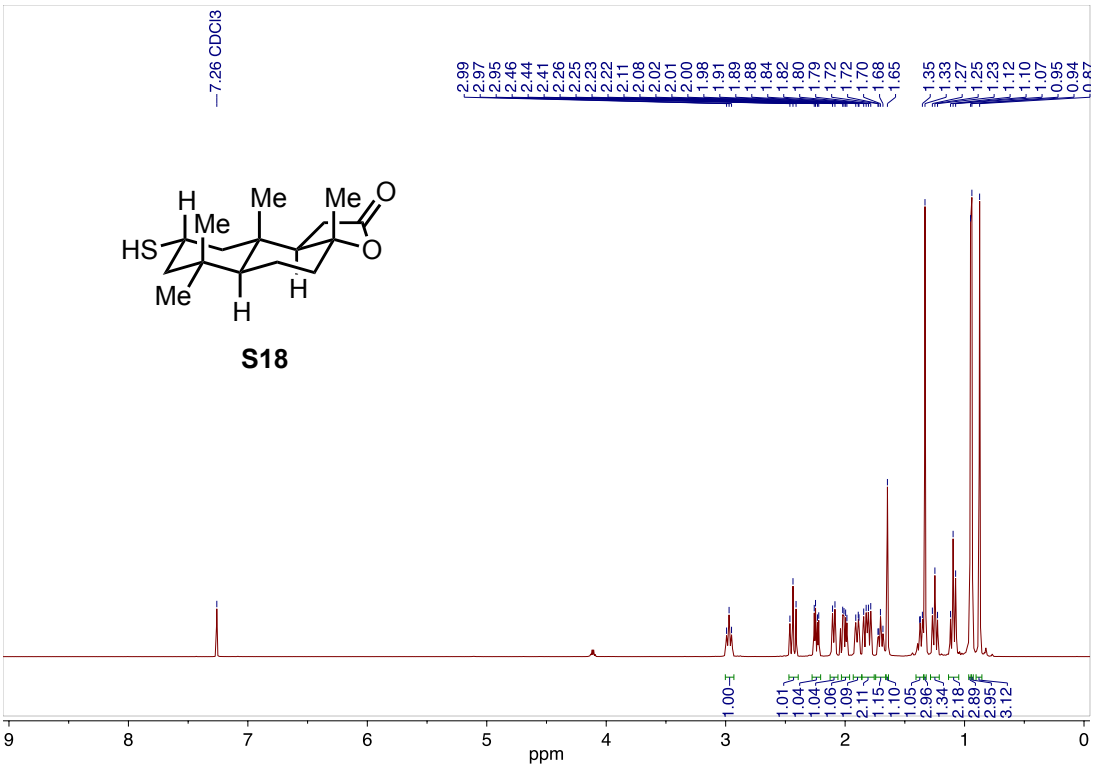
S16


177.10
86.58
77.16 CDCl3
59.23
56.75
42.18
39.51
38.81
36.15
33.43
33.31
28.86
21.71
21.06
20.68
17.96
17.83
17.70
15.21
ppm


7.26 CDCl3
3.98
2.43
2.43
2.28
2.27
2.25
2.10
2.09
2.08
2.07
2.02
2.01
1.99
1.98
1.91
1.90
1.89
1.88
1.83
1.82
1.81
1.81
1.69
1.52
1.35
1.35
1.35
1.33
1.32
1.15
1.08
1.07
1.06
0.95
0.94
0.88
H
Me
Me
O
HO
Me
O
Me
H
H
1.07
1.00
1.01
1.08
1.12
1.18
2.17
1.32
0.80
1.38
3.03
1.23
1.19
7.03
3.26
9
8
7
6
5
4
3
2
1
0
ppm

S17


176.66
86.27
77.16 CDCl3
64.42
58.98
56.23
51.47
48.39
38.56
37.44
34.86
33.35
28.84
21.90
21.76
20.32
16.29
220
200
180
160
140
120
100
80
60
40
20
0
ppm


7.26 CDCl3
2.99
2.97
2.95
2.46
2.44
2.41
2.26
2.25
2.23
2.22
2.11
2.08
2.02
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1.07
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0.94
H
Me
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1.00
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1.04
1.04
1.06
1.09
2.11
1.15
1.10
1.05
2.96
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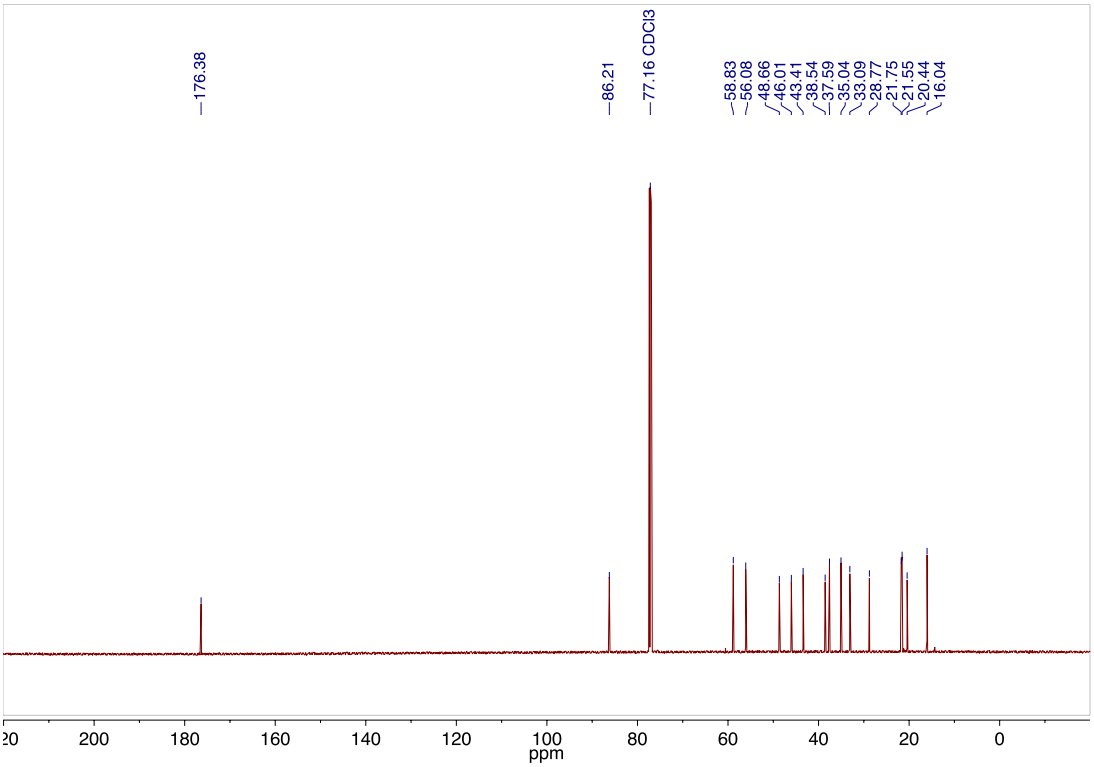
S18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16.04
200
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20
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ppm