Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Selective Nickel-Catalyzed Disulfuration of Alkyl Halides *via* Di/Trithiosulfonates

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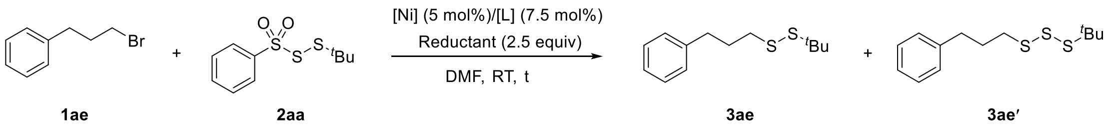
I. General information

General procedures. All reactions were carried out under an argon atmosphere using standard Schlenk-Lines. ^{1}H, ^{13}C and ^{19}F NMR spectra were acquired on 400 MHz, 100 MHz, 376 MHz on JOEL-ZETA 400 MHz or Bruker-AVANCE III-400 MHz spectrometer (400 MHz for ^{1}H; 100 MHz for ^{13}C; 376 MHz for ^{19}F). ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 ppm and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as inter standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. All reactions were monitored by TLC with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F_{254}). Flash column chromatograph was carried out using 300-400 mesh silica gel at medium pressure. Mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer or Agilent 7890B-5977A mass spectrometer. Cyclic Voltammetry experiments were acquired on an electrochemical station (CHI660E). Raman frequency was carried out at the 532nm-2mw-50slit-50X level by Thermo DXR2 Raman Microscope.

Materials. All reagents were received from commercial sources unless otherwise noted. Solvents were freshly dried and degassed according to the purification handbook *Purification of Laboratory Chemicals* before using.

II. Optimization of the reaction conditions

Optimization the reaction of $PhSO_2SS^tBu$ and alkyl bromides. [a,b]



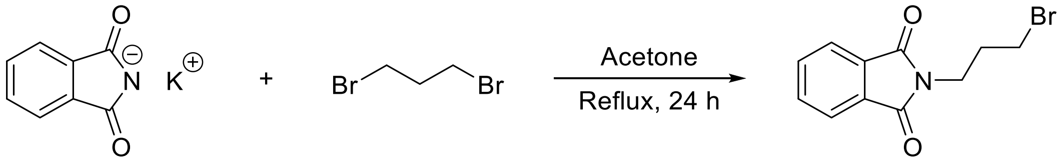
Entry	[Ni]	[L]	Reductant	t (h)	Yield (**3ae**, %)	Yield (**3ae′**, %)
1	$NiCl_2(PPh_3)_2$	L3	Mn	12	87	11
2	$NiBr_2$	L3	Mn	12	34	60
3	NiI_2	L3	Mn	12	46	50
4	$NiBr_2$•diglyme	L3	Mn	12	50	41
5	$NiBr_2$•DME	L3	Mn	12	48	46
6	$NiCl_2$•$6H_2O$	L3	Mn	12	47	48
7	$NiCl_2$	L3	Mn	12	38	58
8	$NiCl_2$•DME	L3	Mn	12	27	69
9	$Ni(acac)_2$	L3	Mn	12	69	31
10	$Ni(OAc)_2$•$4H_2O$	L3	Mn	12	39	13
11	$NiCl_2(PPh_3)_2$	L1	Mn	12	Trace	Trace
12	$NiCl_2(PPh_3)_2$	L2	Mn	12	26	31
13	$NiCl_2(PPh_3)_2$	L4	Mn	12	85	13
14	$NiCl_2(PPh_3)_2$	L5	Mn	12	53	45
15	$NiCl_2(PPh_3)_2$	L6	Mn	12	39	40
16	$NiCl_2(PPh_3)_2$	L4	Zn	12	ND	ND
17	$NiCl_2(PPh_3)_2$	L4	Sn	12	ND	ND
18	$NiCl_2(PPh_3)_2$	L4	PPh_3	12	ND	ND
19	$NiCl_2(PPh_3)_2$	L4	Mn	24	99	0

[a] Reaction conditions: **1ae** (0.2 mmol, 1.0 equiv), **2aa** (0.3 mmol, 1.5 equiv), [Ni] (5 mol%), [L] (7.5 mol%) and reductant (0.5 mmol, 2.5 equiv) were added in DMF (2.0 mL) in argon atmosphere and reacted at RT. [b] Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. ND = no detection of product.

III. Synthesis of the starting materials

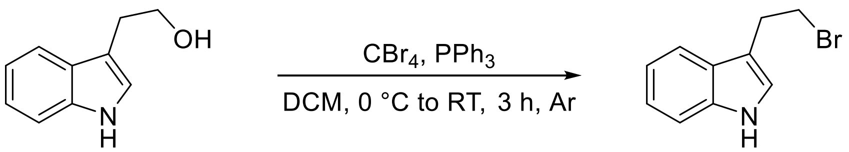
A. Preparation of substrates

Synthesis of 2-(3-bromopropyl)isoindoline-1,3-dione 1aj



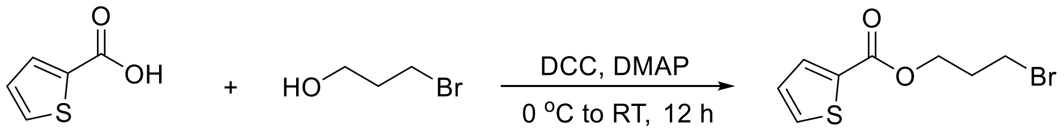
An oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with 1,3-dioxoisoindolin-2-ide (834 mg, 4.50 mmol, 1.00 equiv) in Acetong (30.0 mL). Then 1,3-dibromopropane (1.21 g, 6.00 mmol, 1.33 equiv) was added to the solution. The mixture was stirred at 40 °C for 24 hours. After filtering off the precipitated potassium bromide, the solvent and excess dibromopentane were distilled off and the phthalimido bromide was distilled at reduced pressure to obtain a yellow oil (808.4 mg, 67% yield). Spectra were consistent with literature data. [1]

Synthesis of 3-(2-bromoethyl)-1*H*-indole 1ap



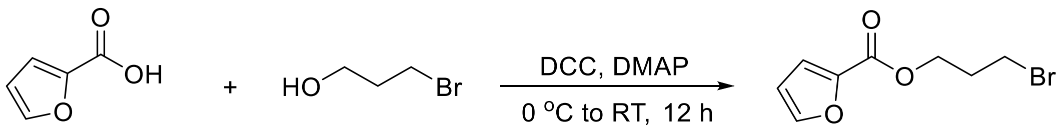
An oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with tryptophol (1.61 g, 10.00 mmol, 1.00 equiv) and triphenyl phosphine (3.41 g, 13.00 mmol, 1.30 equiv) in dry CH_2Cl_2 (15.0 ml). In an addition funnel, carbon tetrabromide (4.31 g, 13.00 mmol, 1.30 equiv) dissolved in dry CH_2Cl_2 (5.0 ml) was added drop-wise, under inert atmosphere at 0 °C, until the addition was complete. The reaction was allowed to stir at room temperature for an additional 3 h, or until complete disappearance of starting materials by TLC. Solvent was removed under reduced pressure and the residue was purified by column chromatography using hexane and ethyl acetate to obtain an off-white solid. (3.67 g, 60.8% yield). Spectra were consistent with literature data. [2]

Synthesis of 3-bromopropyl thiophene-2-carboxylate 1aq



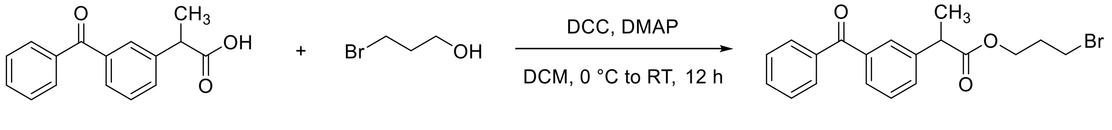
To a 250 mL round-bottom flask were added thiophene-2-carboxylic acid (2.563 g, 20.0 mmol, 1.00 equiv), DMAP (0.244 g, 2.00 mmol, 0.100 equiv), anhydrous DCM (50 mL), and 3-bromopropan-1-ol (3.058 g, 22.0 mmol, 1.10 equiv). A solution of DCC (4.539 g, 22.0 mmol, 1.10 equiv) in DCM (10.0 mL) was added dropwise at 0 °C. After stirring for 12 h at room temperature, the reaction mixture was filtered with a pad of celite and washed with ethyl acetate. The filtrate was concentrated, and the residue was purified with silica gel chromatography (eluent: 200:1 petroleum ether: ethyl acetate) to obtain a yellow oil (4.12g, 83% yield). Spectra were consistent with literature data. [3]

Synthesis of 3-bromopropyl furan-2-carboxylate 1ar



To a 250 mL round-bottom flask were added furan-2-carboxylic acid (2.241 g, 20.0 mmol, 1.00 equiv), DMAP (0.244 g, 2.00 mmol, 0.100 equiv), anhydrous DCM (50 mL), and 3-bromopropan-1-ol (3.058 g, 22.0 mmol, 1.10 equiv). A solution of DCC (4.539 g, 22.0 mmol, 1.10 equiv) in DCM (10.0 mL) was added dropwise at 0 °C. After stirring for 12 h at room temperature, the reaction mixture was filtered with a pad of celite and washed with ethyl acetate. The filtrate was concentrated, and the residue was purified with silica gel chromatography (eluent: 200:1 petroleum ether: ethyl acetate) to obtain a colorless oil (3.45g, 74% yield). Spectra were consistent with literature data. [4]

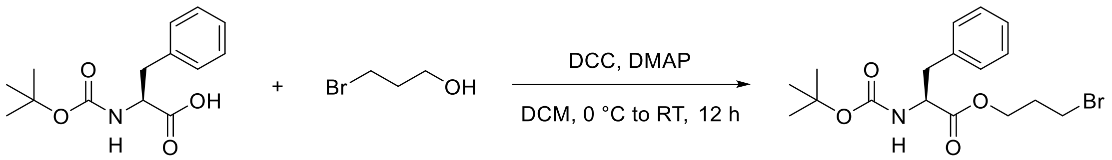
Synthesis of 3-bromopropyl 2-(3-benzoylphenyl)propanoate 1as



To a 250 mL round-bottom flask were added Ketoprofen (5.085 g, 20.0 mmol, 1.0 equiv), DMAP (0.244 g, 2.00 mmol, 0.100 equiv), anhydrous DCM (50 mL), and 3-

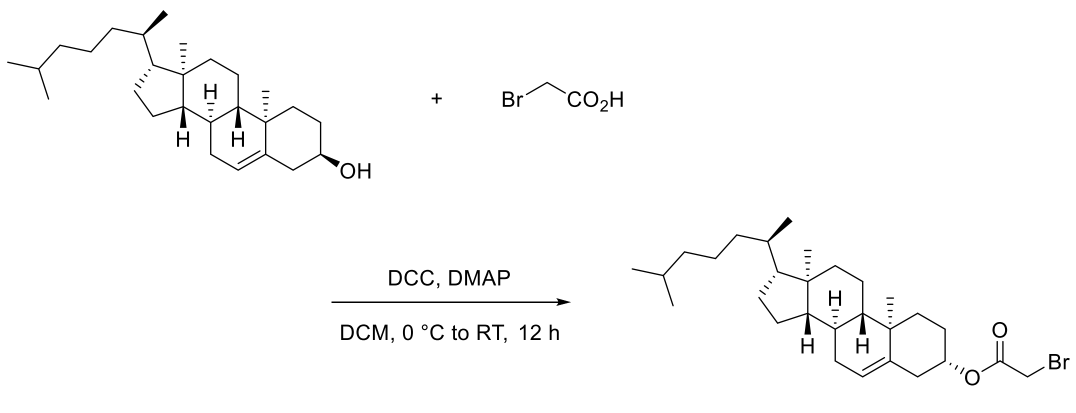
bromopropan-1-ol (2.779 g, 20.0 mmol, 1.0 equiv). A solution of DCC (4.539 g, 22.0 mmol, 1.10 equiv) in DCM (10.0 mL) was added dropwise at 0 °C. After stirring for 12 h at room temperature, the reaction mixture was filtered with a pad of celite and washed with ethyl acetate. The filtrate was concentrated, and the residue was purified with silica gel chromatography (eluent: 30:1 petroleum ether: ethyl acetate) to obtain a colorless oil (3.90g, 52% yield). HRMS (ESI): m/z for $C_{19}H_{19}BrO_3$ $[M+Na]^+$ calcd 397.0410, found 397.0406.

Synthesis of 3-bromopropyl (*tert*-butoxycarbonyl)-*L*-phenylalaninate 1at



To a 250 mL round-bottom flask were added Boc-L-phenylalanine (5.306 g, 20.0 mmol, 1.0 equiv), DMAP (0.244 g, 2.00 mmol, 0.100 equiv), anhydrous DCM (50 mL), and 3-bromopropan-1-ol (2.779 g, 20.0 mmol, 1.0 equiv). A solution of DCC (4.539 g, 22.0 mmol, 1.10 equiv) in DCM (10.0 mL) was added dropwise at 0 °C. After stirring for 12 h at room temperature, the reaction mixture was filtered with a pad of celite and washed with ethyl acetate. The filtrate was concentrated, and the residue was purified with silica gel chromatography (eluent: 30:1 petroleum ether: ethyl acetate) to obtain a white solid (4.25g, 55% yield). HRMS (ESI): m/z for $C_{17}H_{24}BrNO_4$ $[M+Na]^+$ calcd 408.0781, found 408.0789.

Synthesis of (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 2-bromoacetate 1au



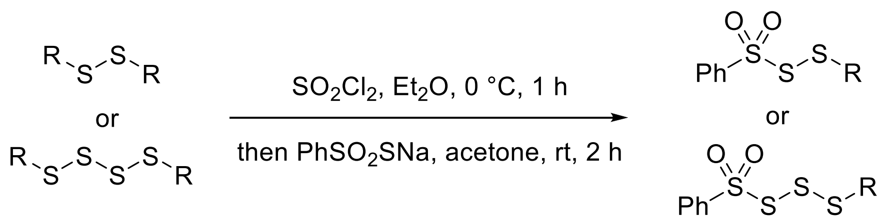
To a 250 mL round-bottom flask were added Cholesterol (7.733 g, 20.0 mmol, 1.0 equiv), DMAP (0.244 g, 2.00 mmol, 0.100 equiv), anhydrous DCM (50 mL), and 2-bromoacetic acid (2.779 g, 20.0 mmol, 1.0 equiv). A solution of DCC (4.539 g, 22.0 mmol, 1.10 equiv) in DCM (10.0 mL) was added dropwise at 0 ℃. After stirring for 12 h at room temperature, the reaction mixture was filtered with a pad of celite and washed with ethyl acetate. The filtrate was concentrated, and the residue was purified with silica gel chromatography (eluent: 30:1 petroleum ether: ethyl acetate) to obtain a white solid (5.48g, 54% yield). [5]

B. <u>General procedure for the preparation of di/trithiosulfonates</u>

General procedure for the synthesis of tetrasulfide.

A solution of S_2Cl_2 (0.80 mL, 10.00 mmol, 0.50 equiv) in dry ether (50.0 mL) is cooled to -78 °C in a dry ice/acetone bath. A solution of thiol (20.00 mmol, 1.00 equiv) and Et_3N (1.62 mL, 20.00 mmol, 1.00 equiv) in dry ether (50.0 mL) is added dropwise over 1 hour. After the addition is complete, the solution is stirred at -78 °C for an additional 30 minutes after which is warmed to room temperature and quenched with water. The organic layer was separated and washed with water, Na_2CO_3 (sat.) and brine, dried over $NaSO_4$, filtered and concentrated in vacuo. The crude residue was purified by column chromatography to give the desired product. [6]

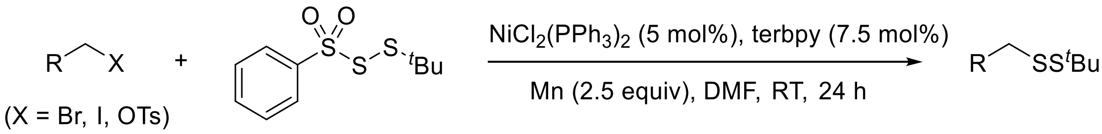
General procedure for the preparation of di/trithiosulfonates



A flame-dried Schlenk-tube equipped witzzh a magnetic stir bar was sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before a solution of RSSR or RSSSSR (10.00 mmol, 1.00 equiv) in Et_2O (40.0 mL) was added. SO_2Cl_2 (1.35 g, 10.00 mmol, 1.00 equiv) was slowly added to the result solution at 0 ºC and the mixture was stirred at the same temperature for 1 h. Then a solution of $PhSO_2SNa$ (3.92 g, 20.00 mmol, 2.00 equiv) in acetone (50.0 mL) was added slowly at 0 ºC and then the mixture was allowed to warm to room temperature stirred for 2 h. The precipitate was filtered and the filtrate was evaporated under reduced pressure with the aid of a rotary evaporator the crude residue was purified by column chromatography to give the desired product. [7]

IV. General procedure for cross coupling and substrate scope

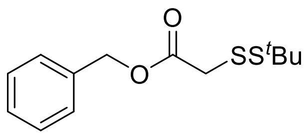
General procedure for reaction of alkyl halides and $PhSO_2SS^tBu$.



An oven-dried 25 mL Schlenk tube, equipped with a stirring bar, was charged with $PhSO_2SS^tBu$ (0.75 mmol, 1.5 equiv), alkyl halides (0.5 mmol, 1.0 equiv), $Ni(PPh_3)_2Cl_2$ (5 mol%), terpyridine (7.5 mol%), Mn (1.5 mmol, 3.0 equiv) and DMF (4.0 mL) in argon atmosphere. The reaction mixture was stirred at RT for 24 h. After completion of the reaction, the solution was filtered and washed with ethyl acetate for 3 times. The combined solvents were removed under vacuum, and the residue was purified by flash column chromatography to obtain the desired thioether.

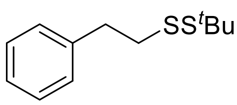
1. Substrate scope of alkyl bromides

Benzyl 2-(*tert*-butylsulfinothioyl)acetate 3aa



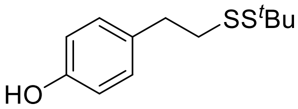
Colorless oil (50 °C, 66.2 mg, 49%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.70). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.30 (m, 5H), 5.18 (s, 2H), 3.53 (s, 2H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.2, 135.4, 128.6, 128.3, 67.1, 48.3, 43.1, 29.8 ppm. HRMS (ESI): m/z for $C_{13}H_{18}O_2S_2$ $[M+Na]^+$ calcd 293.0640, found 293.0637.

(2-(*Tert*-butylsulfinothioyl)ethyl)benzene 3ab



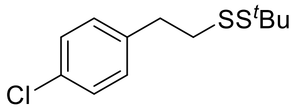
Pale yellow oil (74.7 mg, 66%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.84). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 2H), 7.26 – 7.18 (m, 3H), 3.01 – 2.94 (m, 4H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.2, 128.5, 128. 5, 126.3, 47.8, 41.8, 35.7, 30.0 ppm. Spectra were consistent with literature data. [6]

1-(2-(*Tert*-butylsulfinothioyl)ethyl)-4-hydroxybenzene 3ac



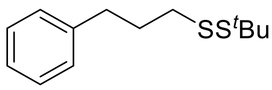
Colorless oil (50 °C, 66.7 mg, 55%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.45). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.07 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 5.00 (s, 1H), 2.90 (s, 4H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.0, 132.4, 129.7, 115.3, 47.9, 42.1, 34.8, 29.9 ppm. HRMS (ESI): m/z for $C_{12}H_{18}OS_2$ $[M+Na]^+$ calcd 265.0691, found 265.0695.

1-(2-(*Tert*-butylsulfinothioyl)ethyl)-4-chlorobenzene 3ad



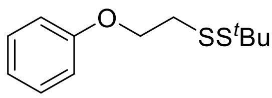
Colorless oil (50 °C, 73.0 mg, 56%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.85). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 2.95 – 2.86 (m, 4H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.6, 132.1, 130.0, 128.6, 48.0, 41.6, 34.9, 29.9 ppm. HRMS (ESI): m/z for $C_{12}H_{17}ClS_2$ $[M+Na]^+$ calcd 283.0352, found 283.0344.

(3-(*Tert*-butylsulfinothioyl)propyl)benzene 3ae



Pale yellow oil (119.0 mg, 99%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.86). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 2H), 7.24 – 7.18 (m, 3H), 2.76 – 2.70 (m, 4H), 2.02 (p, *J* = 7.4 Hz, 2H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.4, 128.5, 128.3, 125.9, 47.7, 39.8, 34.4, 30.6, 29.9 ppm. Spectra were consistent with literature data. [6]

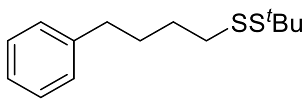
(2-(*Tert*-butylsulfinothioyl)ethoxy)benzene 3af



Pale yellow oil (78.8 mg, 65%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.81). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 2H), 7.00 – 6.89 (m, 3H), 4.23 (t, *J* = 7.0 Hz, 2H), 3.06 (t, *J* = 7.0 Hz, 2H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-

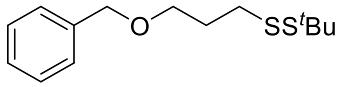
d) δ 158.4, 129.5, 121.0, 114.6, 66.5, 48.0, 38.9, 29.8 ppm. Spectra were consistent with literature data. [6]

(4-(*Tert*-butylsulfinothioyl)butyl)benzene 3ag



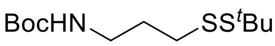
Pale yellow oil (67.4 mg, 53%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.70). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 2H), 7.20 – 7.15 (m, 3H), 2.72 (t, *J* = 6.9 Hz, 2H), 2.62 (t, *J* = 7.1 Hz, 2H), 1.71 (t, *J* = 3.7 Hz, 4H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.2, 128.4, 128.3, 125.8, 47.7, 40.7, 35.5, 30.3, 29.9, 28.9 ppm. Spectra were consistent with literature data. [6]

((3-(*Tert*-butylsulfinothioyl)propoxy)methyl)benzene 3ah



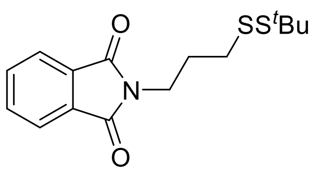
Colorless oil (50 °C, 90.6 mg, 67%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.72). ^{1}HNMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 1.3 Hz, 5H), 4.50 (s, 2H), 3.56 (t, *J* = 6.1 Hz, 2H), 2.86 – 2.75 (m, 2H), 2.04 – 1.92 (m, 2H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.4, 128.3, 127.6, 127.5, 72.9, 68.4, 47.7, 37.3, 29.9, 29.4 ppm. HRMS (ESI): m/z for $C_{14}H_{22}OS_2$ $[M+Na]^+$ calcd 293.1004, found 293.0989.

***Tert*-butyl (3-(*tert*-butylsulfinothioyl)propyl)carbamate 3ai**



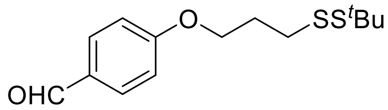
Pale yellow oil (99.2 mg, 71%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.47). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.62 (s, 1H), 3.25 – 3.12 (m, 2H), 2.69 (td, *J* = 7.3, 3.1 Hz, 2H), 1.83 (dd, *J* = 8.6, 5.5 Hz, 2H), 1.41 (s, 9H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.9, 79.2, 47.9, 39.2, 37.7, 29.9, 29.6, 28.4 ppm. Spectra were consistent with literature data. [6]

2-(3-(*Tert*-butylsulfinothioyl)propyl)isoindoline-1,3-dione 3aj



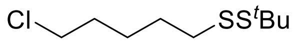
Pale yellow oil (50 °C, 112.9 mg, 73%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.49). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.67 (dd, *J* = 5.5, 3.0 Hz, 2H), 3.73 (t, *J* = 7.0 Hz, 2H), 2.72 – 2.63 (m, 2H), 2.02 (p, *J* = 7.1 Hz, 2H), 1.25 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 133.9, 131.9, 123.1, 47.7, 37.6, 36.8, 29.8, 28.2 ppm. Spectra were consistent with literature data. [6]

4-(3-(*Tert*-butylsulfinothioyl)propoxy)benzaldehyde 3ak



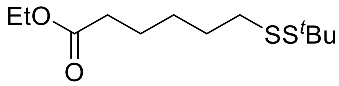
Colorless oil (79.6 mg, 56%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.51). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.87 (s, 1H), 7.82 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 4.15 (t, *J* = 6.1 Hz, 2H), 2.87 (t, *J* = 7.0 Hz, 2H), 2.24 – 2.15 (m, 2H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.8, 163.9, 132.0, 129.9, 114.8, 66.1, 49.1, 35.2, 29.9, 28.1 ppm. HRMS (ESI): m/z for $C_{14}H_{20}O_2S_2$ $[M+Na]^+$ calcd 307.0797, found 307.0790.

1-(*Tert*-butylsulfinothioyl)-6-chlorohexane 3al



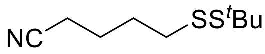
Colorless oil (60.2 mg, 50%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.80). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.54 (t, *J* = 6.7 Hz, 2H), 2.70 (t, *J* = 7.3 Hz, 2H), 1.84 – 1.75 (m, 2H), 1.69 (p, *J* = 7.4 Hz, 2H), 1.57 – 1.51 (m, 2H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 47.8, 44.8, 40.5, 32.2, 29.9, 28.5, 25.8 ppm. HRMS (ESI): m/z for $C_9H_{19}ClS_2$ $[M+Na]^+$ calcd 249.0509, found 249.0517.

Ethyl 6-(*tert*-butylsulfinothioyl)hexanoate 3am



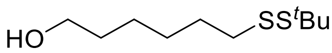
Pale yellow oil (50 °C，82.0 mg, 62%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.70). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.06 (q, *J* = 7.1 Hz, 2H), 2.64 (t, *J* = 7.4 Hz, 2H), 2.24 (t, *J* = 7.5 Hz, 2H), 1.66 – 1.55 (m, 4H), 1.36 (dd, *J* = 8.8, 6.6 Hz, 2H), 1.26 (d, *J* = 1.2 Hz, 9H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.4, 60.0, 47.5, 40.4, 34.0, 29.8, 28.8, 27.8, 24.4, 14.1 ppm. Spectra were consistent with literature data. [6]

6-(*Tert*-butylsulfinothioyl)hexanenitrile 3an



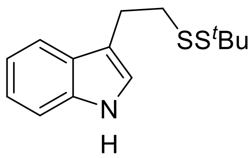
Pale yellow oil (87.0 mg, 80%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.56). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.71 (t, *J* = 6.7 Hz, 2H), 2.38 (t, *J* = 6.7 Hz, 2H), 1.81 (m, 4H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 119.4, 53.4, 47.9, 39.3, 29.9, 28.0, 24.0, 16.8 ppm. HRMS (ESI): m/z for $C_9H_{17}NS_2$ $[M+Na]^+$ calcd 226.0695, found 226.0690.

1-(*Tert*-butylsulfinothioyl)-6-hydroxyhexane 3ao



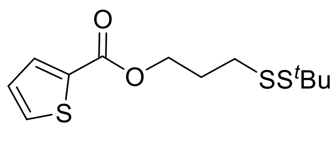
Pale yellow oil (38.9 mg, 35%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.20). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.62 (t, *J* = 6.6 Hz, 2H), 2.74 – 2.64 (m, 2H), 1.72 – 1.62 (m, 2H), 1.61 – 1.51 (m, 3H), 1.42 – 1.34 (m, 4H), 1.31 (d, *J* = 0.8 Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 62.8, 47.6, 40.7, 32.5, 29.9, 29.2, 28.2, 25.3 ppm. Spectra were consistent with literature data. [6]

3-(2-(*Tert*-butylsulfinothioyl)ethyl)-1*H*-indole 3ap



Pale yellow oil (65.0 mg, 49%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.34). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.12 (m, 2H), 7.05 (s, 1H), 3.20 – 3.12 (m, 2H), 3.05 (dd, *J* = 8.5, 6.4 Hz, 2H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.2, 127.2, 122.0, 121.8, 119.3, 118.7, 114.6, 111.2, 47.8, 41.0, 30.0, 25.4 ppm. Spectra were consistent with literature data. [6]

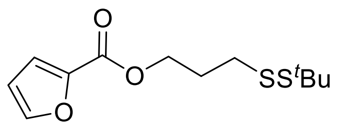
3-(*Tert*-butylsulfinothioyl)propyl thiophene-2-carboxylate 3aq



Pale yellow oil (74.1 mg, 51%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.75).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 3.7 Hz, 1H), 7.55 (d, *J* = 4.9 Hz, 1H), 7.13 – 7.05 (m, 1H), 4.42 (t, *J* = 6.1 Hz, 2H), 3.01 (t, *J* = 7.1 Hz, 2H), 2.26 – 2.18 (m, 2H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.1, 133.6, 133.4, 132.4, 127.7, 63.2, 49.0, 35.3, 29.8, 27.9 ppm. HRMS (ESI): m/z for $C_{12}H_{18}O_2S_3$ $[M+Na]^+$ calcd 313.0361, found 313.0348.

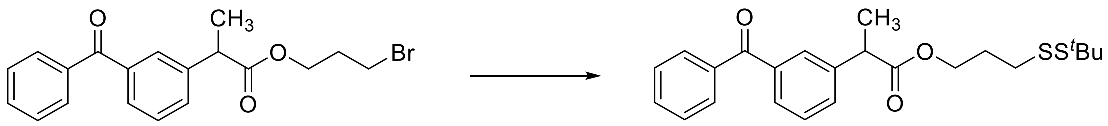
3-(*Tert*-butylsulfinothioyl)propyl furan-2-carboxylate 3ar



Colorless oil (76.8 mg, 56%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.64). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (s, 1H), 7.15 (d, *J* = 3.5 Hz, 1H), 6.49 (s, 1H), 4.38 (t, *J* = 6.2 Hz, 2H), 2.79 (t, *J* = 7.2 Hz, 2H), 2.12 (p, *J* = 6.8 Hz, 2H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.6, 146.3, 144.5, 117.9, 111.8, 63.2, 47.8, 36.5, 29.9, 28.3 ppm. HRMS (ESI): m/z for $C_{12}H_{18}O_3S_2$ $[M+Na]^+$ calcd 297.0590, found 297.0591.

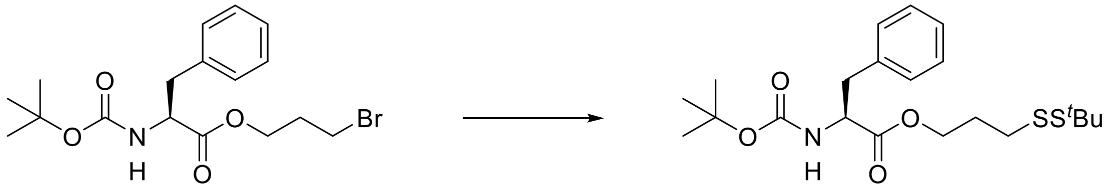
2. Late-stage modification of natural products or bioactive molecules

Synthesis 3-(*tert*-butylsulfinothioyl)propyl 2-(3-benzoylphenyl)propanoate 3as



An oven-dried 25 mL Schlenk tube, equipped with a stirring bar, was charged with $PhSO_2SS^tBu$ (0.75 mmol, 1.5 equiv), **1as** (0.5 mmol, 1.0 equiv), $Ni(PPh_3)_2Cl_2$ (5 mol%), terpyridine (7.5 mol%), Mn (1.5 mmol, 3.0 equiv) and DMF (4.0 mL) in argon atmosphere. The reaction mixture was stirred at RT for 24 h. After completion of the reaction, the solution was filtered and washed with ethyl acetate for 3 times. The combined solvents were removed under vacuum, and the residue was purified by flash column chromatography to obtain a colorless oil (114.6 mg, 55% yield). Eluent: petroleum ether/ethyl acetate (5:1, R_f = 0.50). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.78 (m, 2H), 7.75 (t, *J* = 1.8 Hz, 1H), 7.68 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.54 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.51 – 7.44 (m, 3H), 4.20 (t, *J* = 6.2 Hz, 2H), 3.80 (d, J = 7.2 Hz, 1H), 2.80 (t, J = 6.9 Hz, 2H), 2.10 – 2.01 (m, 2H), 1.54 (d, J = 7.2 Hz, 3H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.5, 174.0, 140.8, 137.8, 137.4, 132.5, 131.5, 130.1, 129.2, 129.1, 128.6, 128.3, 63.0, 49.0, 45.3, 35.1, 29.8, 27.6, 18.4 ppm. HRMS (ESI): m/z for $C_{23}H_{28}O_3S_2$ $[M+Na]^+$ calcd 439.1372, found 439.1370.

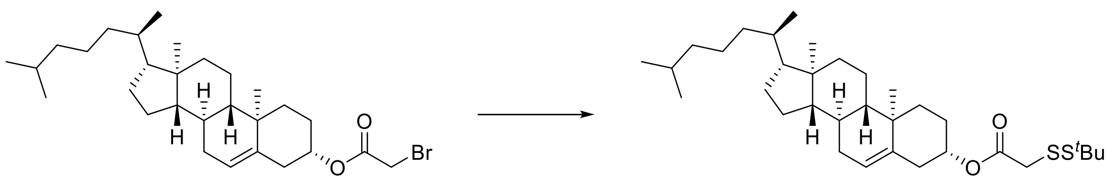
Synthesis 3-(*tert*-butylsulfinothioyl)propyl (*tert*-butoxycarbonyl)-*L*-phenylalaninate 3at



1at **3at**

An oven-dried 25 mL Schlenk tube, equipped with a stirring bar, was charged with $PhSO_2SS^tBu$ (0.75 mmol, 1.5 equiv), **1at** (0.5 mmol, 1.0 equiv), $Ni(PPh_3)_2Cl_2$ (5 mol%), terpyridine (7.5 mol%), Mn (1.5 mmol, 3.0 equiv) and DMF (4.0 mL) in argon atmosphere. The reaction mixture was stirred at RT for 24 h. After completion of the reaction, the solution was filtered and washed with ethyl acetate for 3 times. The combined solvents were removed under vacuum, and the residue was purified by flash column chromatography to obtain a colorless oil (111.2 mg, 52% yield). Eluent: petroleum ether/ethyl acetate (5:1, R_f = 0.42). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.25 (m, 3H), 7.16 – 7.11 (m, 2H), 4.99 (d, J = 8.3 Hz, 1H), 4.65 – 4.49 (m, 1H), 4.20 (t, J = 6.1 Hz, 2H), 3.07 (d, J = 6.3 Hz, 2H), 2.80 – 2.74 (m, 2H), 2.08 – 2.00 (m, 2H), 1.42 (s, 9H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.0, 135.9, 129.3, 128.6, 127.1, 79.9, 63.4, 54.5, 49.0, 38.5, 35.0, 29.8, 28.3, 27.5 ppm. HRMS (ESI): m/z for $C_{21}H_{44}NO_4S_2$ $[M+Na]^+$ calcd 450.1743, found 450.1765.

Synthesis of (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 2-bromoacetate 3au

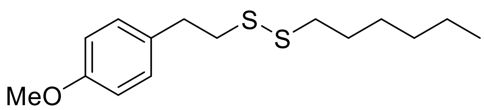


1au **3au**

An oven-dried 25 mL Schlenk tube, equipped with a stirring bar, was charged with $PhSO_2SS^tBu$ (0.75 mmol, 1.5 equiv), **1au** (0.5 mmol, 1.0 equiv), $Ni(PPh_3)_2Cl_2$ (5 mol%), terpyridine (7.5 mol%), Mn (1.5 mmol, 3.0 equiv) and DMF (4.0 mL) in argon atmosphere. The reaction mixture was stirred at RT for 24 h. After completion of the reaction, the solution was filtered and washed with ethyl acetate for 3 times. The combined solvents were removed under vacuum, and the residue was purified by flash column chromatography to obtain a white solid (115.3 mg, 42% yield). MP: 95-96 °C. Eluent: petroleum ether/ethyl acetate (5:1, R_f = 0.78). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.38 (dd, *J* = 5.0, 2.0 Hz, 1H), 4.73 – 4.59 (m, 1H), 3.46 (s, 2H), 2.35 (d, *J* = 7.4 Hz, 2H), 2.08 – 1.75 (m, 6H), 1.69 – 1.37 (m, 10H), 1.34 (s, 9H), 1.30 – 1.21 (m, 2H), 1.21 – 1.04 (m, 8H), 1.02 (s, 5H), 0.99 – 0.93 (m, 2H), 0.91 (d, *J* = 6.5 Hz, 4H), 0.86 (dd, *J* = 6.7, 1.8 Hz, 7H), 0.67 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 139.4, 122.8, 75.2, 56.6, 56.1, 49.9, 48.3, 43.4, 42.3, 39.7, 39.5, 38.0, 36.9, 36.5, 36.1, 35.8, 31.9, 31.8, 29.8, 28.2, 28.0, 27.7, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8 ppm. HRMS (ESI): m/z for $C_{33}H_{56}O_2S_2$ $[M+Na]^+$ calcd 571.3614, found 571.3606.

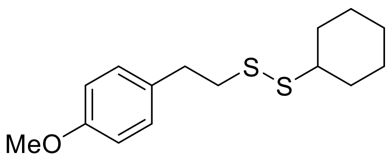
3. Substrate scope of di/trithiosulfonate reagents

1-Hexyl-2-(4-methoxyphenethyl)disulfane 4aa



Pale yellow oil (80 °C, 85.3 mg, 60%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.65). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.95 – 2.87 (m, 4H), 2.72 – 2.66 (m, 2H), 1.67 (p, *J* = 7.4 Hz, 2H), 1.38 (dt, *J* = 2.9, 1.6 Hz, 2H), 1.30 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.1, 132.2, 129.5, 113.8, 55.2, 40.5, 39.2, 34.8, 31.4, 29.2, 28.2, 22.5, 14.0 ppm. Spectra were consistent with literature data. [6]

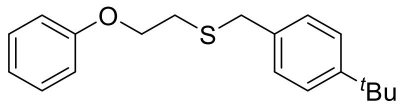
1-Cyclohexyl-2-(4-methoxyphenethyl)disulfane 4ab



Pale yellow oil (97.4 mg, 69%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.64).

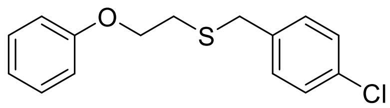
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.91 (s, 4H), 2.73 (tq, *J* = 6.7, 3.4 Hz, 1H), 2.03 (d, *J* = 12.2 Hz, 2H), 1.87 – 1.75 (m, 2H), 1.63 (d, *J* = 10.4 Hz, 1H), 1.41 – 1.25 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.1, 132.3, 129.5, 113.8, 55.2, 49.6, 41.6, 34.8, 32.9, 26.1, 25.6 ppm. Spectra were consistent with literature data. [6]

(4-(*Tert*-butyl)benzyl)(2-phenoxyethyl)sulfane 4ac



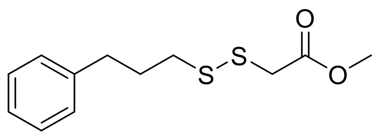
Colorless oil (105.2 mg, 70%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.81). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.26 (m, 4H), 6.98 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.93 – 6.89 (m, 2H), 4.13 (t, *J* = 6.6 Hz, 2H), 3.93 (s, 2H), 2.81 (t, *J* = 6.7 Hz, 2H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.3, 150.6, 134.0, 129.6, 128.9, 125.5, 121.0, 114.5, 66.0, 43.4, 37.1, 34.5, 31.3 ppm. HRMS (ESI): m/z for $C_{19}H_{24}OS$ $[M+Na]^+$ calcd 355.1161, found 355.1158.

(4-Chlorobenzyl)(2-phenoxyethyl)sulfane 4ad



Colorless oil (90.6 mg, 65%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.76). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.21 (m, 6H), 6.99 – 6.94 (m, 1H), 6.92 – 6.83 (m, 2H), 4.09 (t, *J* = 6.5 Hz, 2H), 3.85 (s, 2H), 2.81 (t, *J* = 6.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.3, 135.8, 133.4, 130.6, 129.5, 128.7, 121.1, 114.6, 66.0, 42.8, 37.5 ppm. HRMS (ESI): m/z for $C_{15}H_{15}ClOS$ $[M+Na]^+$ calcd 333.0145, found 333.0139.

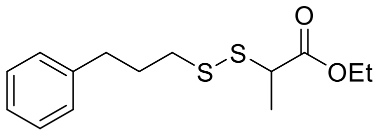
Methyl 2-((3-phenylpropyl)disulfaneyl)acetate 4ae



Pale yellow oil (92.3 mg, 72%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.59). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.26 (m, 2H), 7.24 – 7.14 (m, 3H), 3.71 (s, 3H), 3.45 (s, 2H), 2.74 (dt, *J* = 12.3, 7.4 Hz, 4H), 2.07 – 1.98 (m, 2H). ^{13}C NMR

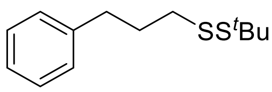
(101 MHz, Chloroform-*d*) δ 170.0, 141.0, 128.4, 128.3, 125.9, 52.4, 41.1, 37.7, 34.2, 30.3 ppm. HRMS (ESI): m/z for $C_{12}H_{16}O_2S_2$ $[M+Na]^+$ calcd 279.0484, found 279.0497.

Ethyl 2-((3-phenylpropyl)disulfaneyl)propanoate 4af



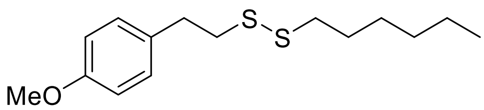
Pale yellow oil (128.0 mg, 90%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.68). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 2H), 7.19 (td, *J* = 6.6, 1.7 Hz, 3H), 4.20 – 4.11 (m, 2H), 3.49 (q, *J* = 7.1 Hz, 1H), 2.70 (td, *J* = 7.4, 1.9 Hz, 4H), 2.00 (q, *J* = 7.6 Hz, 2H), 1.48 (d, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.4, 141.2, 128.4, 128.4, 125.9, 61.3, 47.1, 38.2, 34.3, 30.4, 16.7, 14.1 ppm. HRMS (ESI): m/z for $C_{14}H_{20}O_2S_2$ $[M+Na]^+$ calcd 307.0797, found 307.0816.

(3-(*Tert*-butylsulfinothioyl)propyl)benzene 4ag



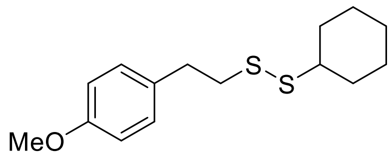
Pale yellow oil (69.7 mg, 58%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.86). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 2H), 7.24 – 7.18 (m, 3H), 2.76 – 2.70 (m, 4H), 2.02 (p, *J* = 7.4 Hz, 2H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.4, 128.5, 128.3, 125.9, 47.7, 39.8, 34.4, 30.6, 29.9 ppm. Spectra were consistent with literature data. [6]

1-Hexyl-2-(4-methoxyphenethyl)disulfane 4ah



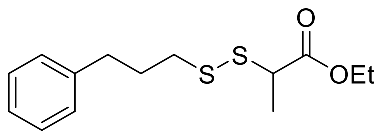
Pale yellow oil (85.3 mg, 60%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.65). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.95 – 2.87 (m, 4H), 2.72 – 2.66 (m, 2H), 1.67 (p, *J* = 7.4 Hz, 2H), 1.38 (dt, *J* = 2.9, 1.6 Hz, 2H), 1.30 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.1, 132.2, 129.5, 113.8, 55.2, 40.5, 39.2, 34.8, 31.4, 29.2, 28.2, 22.5, 14.0 ppm. Spectra were consistent with literature data. [6]

1-Cyclohexyl-2-(4-methoxyphenethyl)disulfane 4ai



Pale yellow oil (83.3 mg, 59%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.64). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.91 (s, 4H), 2.73 (tq, *J* = 6.7, 3.4 Hz, 1H), 2.03 (d, *J* = 12.2 Hz, 2H), 1.87 – 1.75 (m, 2H), 1.63 (d, *J* = 10.4 Hz, 1H), 1.41 – 1.25 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.1, 132.3, 129.5, 113.8, 55.2, 49.6, 41.6, 34.8, 32.9, 26.1, 25.6 ppm. Spectra were consistent with literature data. [6]

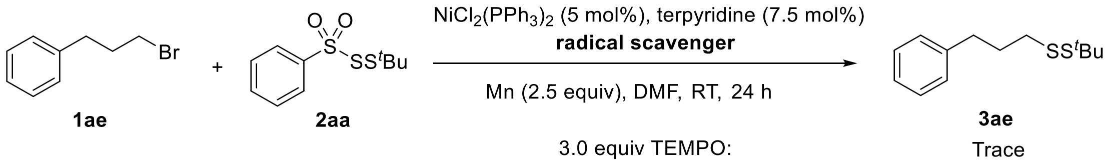
Ethyl 2-((3-phenylpropyl)disulfaneyl)propanoate 4aj



Pale yellow oil (96.7 mg, 68%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.68). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 2H), 7.19 (td, *J* = 6.6, 1.7 Hz, 3H), 4.20 – 4.11 (m, 2H), 3.49 (q, *J* = 7.1 Hz, 1H), 2.70 (td, *J* = 7.4, 1.9 Hz, 4H), 2.00 (q, *J* = 7.6 Hz, 2H), 1.48 (d, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.4, 141.2, 128.4, 128.4, 125.9, 61.3, 47.1, 38.2, 34.3, 30.4, 16.7, 14.1 ppm. HRMS (ESI): m/z for $C_{14}H_{20}O_2S_2$ [M+Na]$^+$ calcd 307.0797, found 307.0816.

V. Mechanistic studies

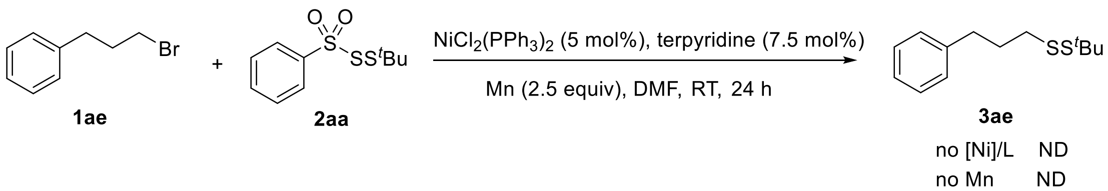
1. Radical inhibition experiment



An oven-dried 25 mL Schlenck tube, equipped with a stirring bar, was charged with **2aa** (0.75 mmol, 1.5 equiv), **1ae** (0.5 mmol, 1.0 equiv), $Ni(PPh_3)_2Cl_2$ (5 mol%), terpyridine (7.5 mol%), Mn (1.25 mmol, 2.5 equiv) and DMF (4.0 mL) in argon atmosphere, the reaction mixture was stirred at RT for 24 h. The reaction mixture was stirred at RT for 24 h. After simple filtration and removal of solvent, the crude products were subjected to ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. However, only a trace amount of desired cross-coupling product **3ae** was observed, indicating that a radical pathway may be involved in the current C-S reductive coupling.

2. Control experiment

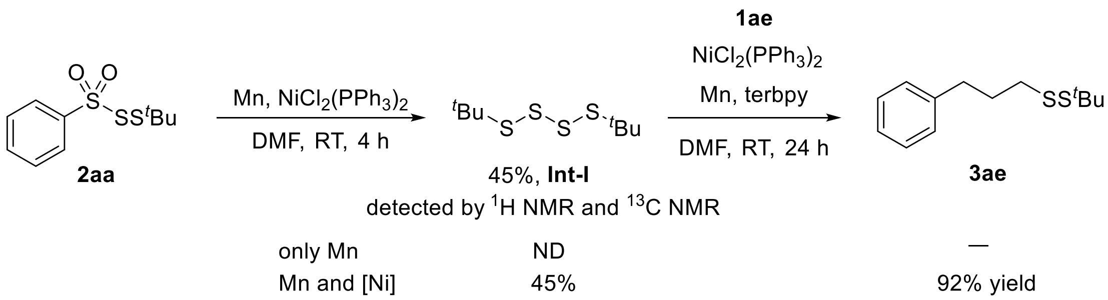
<u>Catalytic system and Mn</u>



An oven-dried 25 mL Schlenk tube, equipped with a stirring bar, was charged with **2aa** (0.75 mmol, 1.5 equiv), **1ae** (0.5 mmol, 1.0 equiv), Mn (1.25 mmol, 2.5 equiv) and DMF (4.0 mL) in argon atmosphere. The reaction mixture was stirred at RT for 24 h. After completion of the reaction, the solution was filtered and washed with ethyl acetate for 3 times. After removal of solvent, no desired product was observed by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

Another oven-dried 25 mL Schlenk tube, equipped with a stirring bar, was charged with **2aa** (0.75 mmol, 1.5 equiv), **1ae** (0.5 mmol, 1.0 equiv), $Ni(PPh_3)_2Cl_2$ (5 mol%), terpyridine (7.5 mol%) and DMF (4.0 mL) in argon atmosphere. The reaction mixture was stirred at RT for 24 h. After completion of the reaction, the solution was filtered and washed with ethyl acetate for 3 times. After removal of solvent, no desired product was observed by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

3. Isolation of reactive intermediates



General procedure for the capture of reductive intermediate Int-I

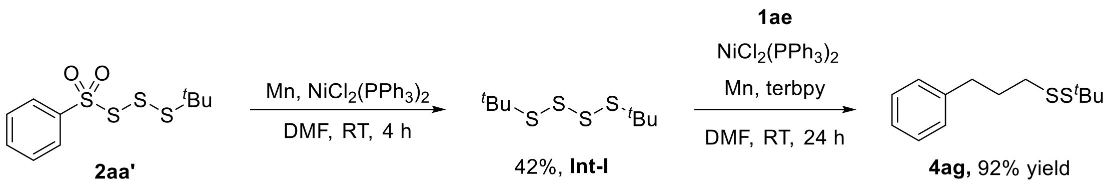
An oven-dried 25 mL Schlenk tube, equipped with a stirring bar, was charged with **2aa** (0.75 mmol, 1.0 equiv), Mn (1.5 mmol, 2.0 equiv) and DMF (4.0 mL) in argon atmosphere. The reaction mixture was stirred at RT for 4 h. After completion of the reaction, the solution was filtered and washed with ethyl acetate for 3 times. After removal of solvent, no desired product was observed by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

Another oven-dried 25 mL Schlenk tube, equipped with a stirring bar, was charged with **2aa** (0.75 mmol, 1.0 equiv), Mn (1.5 mmol, 2.0 equiv), Ni $(PPh_3)_2Cl_2$ (5 mol%) and DMF (4.0 mL) in argon atmosphere. The reaction mixture was stirred at RT for 4 h. After completion of the reaction, the solution was filtered and washed with ethyl acetate for 3 times. The combined solvents were removed under vacuum, and the residue was purified by flash column chromatography to obtain **Int-I** as a yellow oil (54.5 mg, 45% yield). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.91). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 49.1, 30.2 ppm. Spectra were consistent with literature data. [8]

General procedure for the conversion of Int-I under standard condition

An oven-dried 25 mL Schlenk tube, equipped with a stirring bar, was charged with

Int-I (0.75 mmol, 1.5 equiv), **1ae** (0.5 mmol, 1.0 equiv), $Ni(PPh_3)_2Cl_2$ (5 mol%), terpyridine (7.5 mol%), Mn (1.25 mmol, 2.5 equiv) and DMF (4.0 mL) in argon atmosphere. The reaction mixture was stirred at RT for 24 h. After completion of the reaction, the solution was filtered and washed with ethyl acetate for 3 times. The combined solvents were removed under vacuum, and the residue was purified by flash column chromatography to obtain the desired product **3ae** (110.6 mg, 92% yield)，indicating that 1,4-di-*tert*-butyltetrasulfane intermediate may be involved in the current C-S coupling.



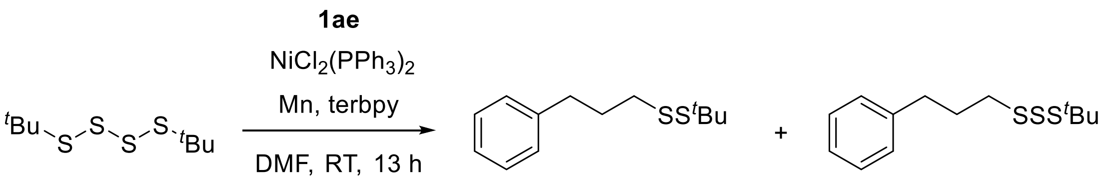
General procedure for the capture of reductive intermediate Int-I

An oven-dried 25 mL Schlenk tube, equipped with a stirring bar, was charged with $PhSO_2SSS^tBu$ (**2aa'**, 0.75 mmol, 1.5 equiv), Mn (1.5 mmol, 3.0 equiv), Ni $(PPh_3)_2Cl_2$ (5 mol%) and DMF (4.0 mL) in argon atmosphere. The reaction mixture was stirred at RT for 4 h. After completion of the reaction, the solution was filtered and washed with ethyl acetate for 3 times. The combined solvents were removed under vacuum, and the residue was purified by flash column chromatography to obtain **Int-I** as a yellow oil (50.9 mg, 42% yield). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.91). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 49.1, 30.2 ppm. Spectra were consistent with literature data. [6]

General procedure for the conversion of Int-I under standard condition

An oven-dried 25 mL Schlenk tube, equipped with a stirring bar, was charged with **Int-I** (0.75 mmol, 1.5 equiv), **1ae** (0.5 mmol, 1.0 equiv), $Ni(PPh_3)_2Cl_2$ (5 mol%), terpyridine (7.5 mol%), Mn (1.25 mmol, 2.5 equiv) and DMF (4.0 mL) in argon atmosphere. The reaction mixture was stirred at RT for 24 h. After completion of the reaction, the solution was filtered and washed with ethyl acetate for 3 times. The combined solvents were removed under vacuum, and the residue was purified by flash column chromatography to obtain the desired product **4ag** (110.6 mg, 92% yield) indicating that 1,4-di-*tert*-butyltetrasulfane intermediate may be involved in the current C-S coupling.

4. Capture and conversion of trisulfide intermediates

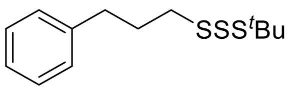


64%, **3ae** 27%, **3ae'**

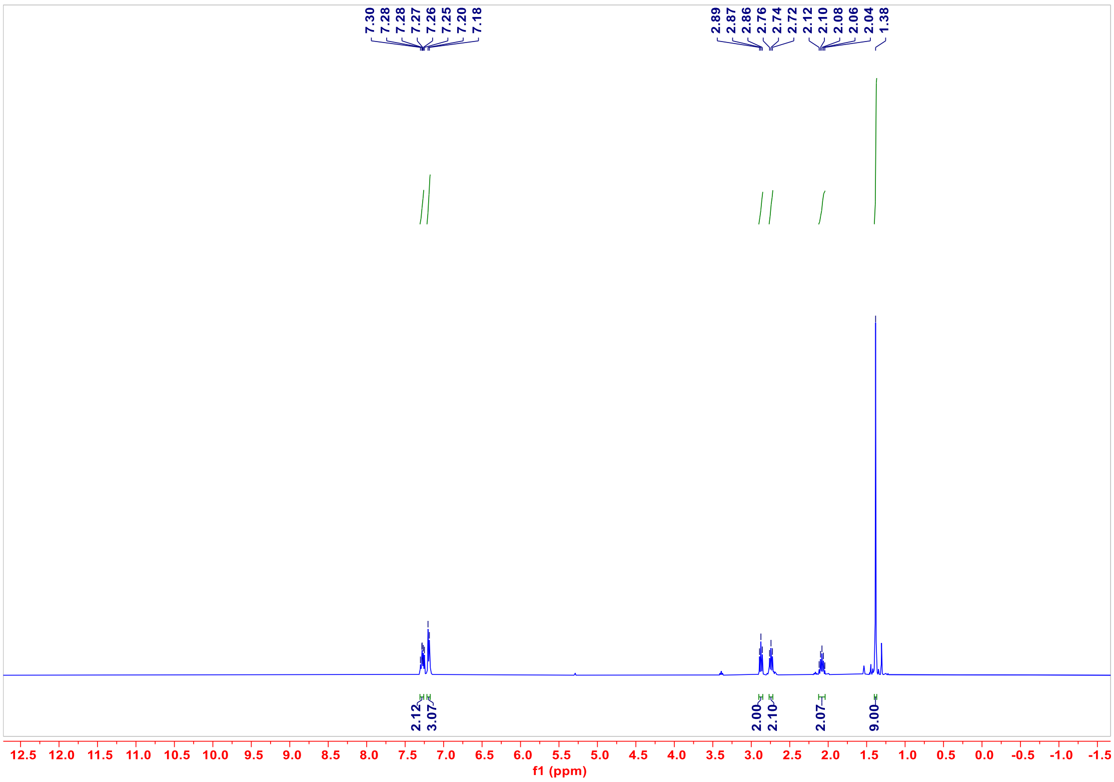
3ae : **3ae'** = 2.2 : 1

An oven-dried 25 mL Schlenk tube, equipped with a stirring bar, was charged with **Int-I** (0.75 mmol, 1.5 equiv), **1ae** (0.5 mmol, 1.0 equiv), $Ni(PPh_3)_2Cl_2$ (5 mol%), terpyridine (7.5 mol%), Mn (1.25 mmol, 2.5 equiv) and DMF (4.0 mL) in argon atmosphere. The reaction mixture was stirred at RT for 13 h. After simple filtration and removal of solvent, the crude products were subjected to ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. In addition to the expected product **3ae**, there is also a trace amount of trisulfide product **3ae'** was observed.

(3-(*Tert*-butylsulfonodithioyl)propyl)benzene 3ae'



Pale yellow oil (36.8 mg, 27%). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.86). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H), 7.19 (d, *J* = 7.2 Hz, 3H), 2.87 (t, *J* = 7.2 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 2.08 (p, *J* = 7.3 Hz, 2H), 1.38 (s, 9H) ppm. ^{1}H NMR spectra was consistent with literature data. [6]

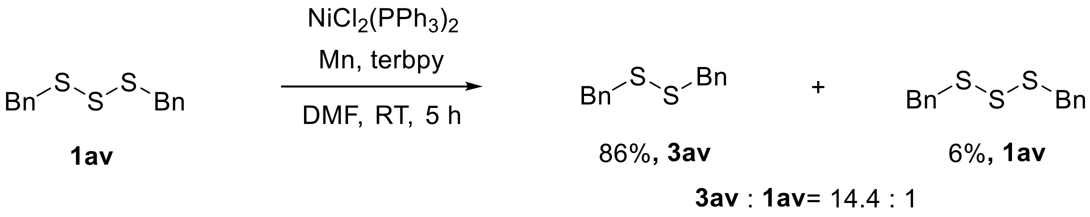


General procedure for the synthesis of BnSSSBn

To a stirred solution of sodium thiosulfate pentahydrate ($Na_2S_2O_3$, 3.54 mmol, 1.3 equiv) in 30% of ethanol-water mixture (10.0 ml), was added the corresponding Benzyl mercaptan (2.72 mmol, 1.0 equiv) and stirred at room temperature for 4-5 h. Progress of the reaction was monitored by TLC study. Upon completion of the reaction, ethanol component was removed under reduced pressure and the residue was used for the next step in general without any further purification.

To a stirred solution of the crude Bunte salt (2.72 mmol, 1.0 equiv) in water (30.0 ml), was added an aqueous solution (40.0 ml) of sodium sulfide nonahydrate (1.36 mmol, 0.5 equiv) at 0 °C in a drop-wise manner and the mixture was stirred at that temperature for the required duration. A white colored suspension appeared upon completion of the addition of sodium sulfide. The progress of the reaction was monitored by TLC study. Upon the completion of the reaction, the mixture was diluted with ethyl acetate and washed with brine solution. The combined organic layer was dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure to afford a white solid (246.1 mg, 65% yield). Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.76). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.26 (m, 5H), 4.04 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.5, 129.4, 128.6, 127.5, 43.1 ppm. Spectra were consistent with literature data. [9]

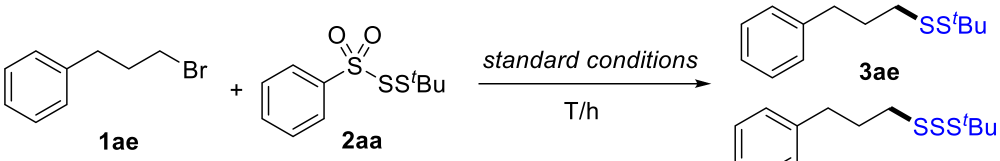
General procedure for the conversion of BnSSSBn under standard condition

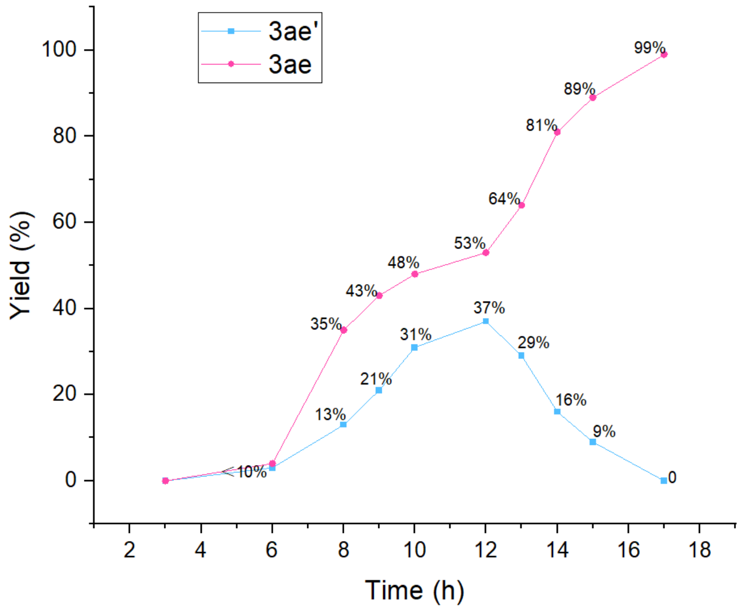


An oven-dried 25 mL Schlenk tube, equipped with a stirring bar, was charged with **1av** (0.75 mmol, 1.0 equiv), $Ni(PPh_3)_2Cl_2$ (5 mol%), terpyridine (7.5 mol%), Mn (1.25 mmol, 1.67 equiv) and DMF (4.0 mL) in argon atmosphere. The reaction mixture was stirred at RT for 5 h. After completion of the reaction, the solution was filtered and washed with ethyl acetate for 3 times. The combined solvents were removed under vacuum, and the residue was purified by flash column chromatography to obtain the product **3av** (158.9 mg, 86% yield) and recycle the starting material **1av**. Eluent: petroleum ether/ethyl acetate (10:1, R_f = 0.69). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.26 (m, 5H), 3.62 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.3, 129.4, 128.5, 127.4, 43.2 ppm. Spectra were consistent with literature data. [6]

5. Investigation of the reaction process

I. The reaction process of (3-bromopropyl)benzene with $PhSO_2SS^t$Bu (**2aa**)

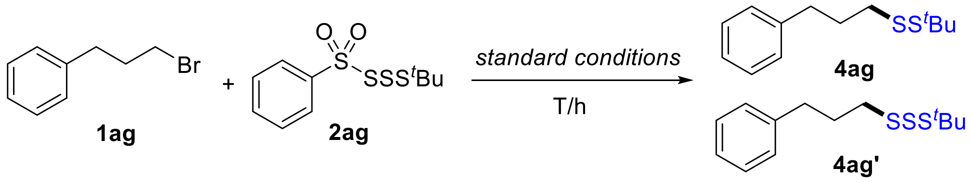


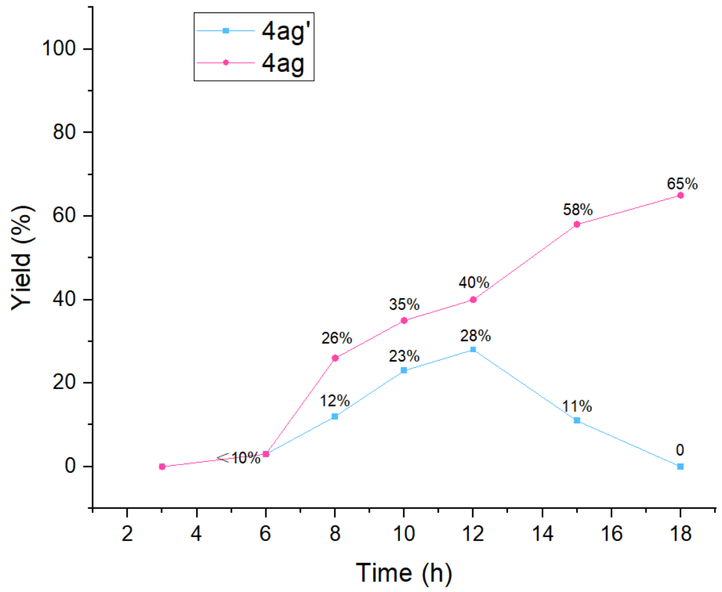


An oven-dried 25 mL Schlenk tube, equipped with a stirring bar, was charged with $PhSO_2SS^tBu$ (**2aa**, 0.75 mmol, 1.5 equiv), **1ae** (0.5 mmol, 1.0 equiv), $Ni(PPh_3)_2Cl_2$ (5 mol%), terpyridine (7.5 mol%), Mn (1.25 mmol, 2.5 equiv) and DMF (4.0 mL) in argon atmosphere. The reaction mixture was stirred at RT for T h. After simple filtration and removal of solvent, the crude products were subjected to ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. The results show that the reaction has different proportions for the products **3ae** and **3ae'** at different time periods.

T/h	Yield of **3ae**	Yield of **3ae'**
3	0	0
6	4%	3%
8	35%	13%
9	43%	21%
10	48%	31%
12	53%	37%
13	64%	29%
14	81%	16%
15	89%	9%
17	99%	0

II. The reaction process of (3-bromopropyl)benzene with $PhSO_2SSS^tBu$ (**2ag**)

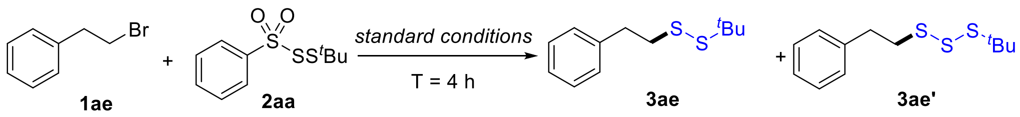


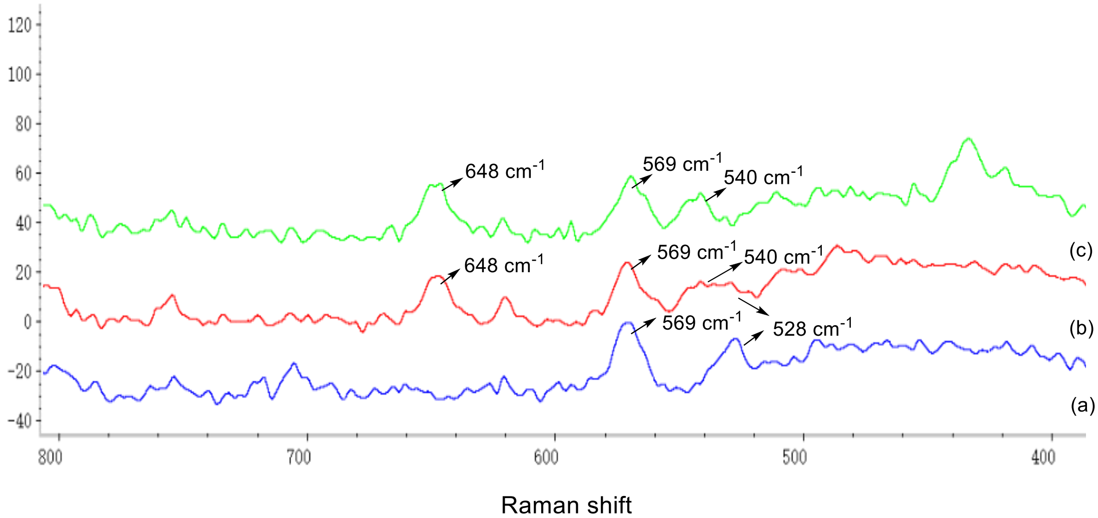


An oven-dried 25 mL Schlenk tube, equipped with a stirring bar, was charged with $PhSO_2SSS^tBu$ (**2ag**, 0.75 mmol, 1.5 equiv), **1ae** (0.5 mmol, 1.0 equiv), $Ni(PPh_3)_2Cl_2$ (5 mol%), terpyridine (7.5 mol%), Mn (1.25 mmol, 2.5 equiv) and DMF (4.0 mL) in argon atmosphere. The reaction mixture was stirred at RT for T h. After simple filtration and removal of solvent, the crude products were subjected to ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. The results show that the reaction has different proportions for the products **4ag** and **4ag'** at different time periods.

T/h	Yield of **4ag**	Yield of **4ag'**
3	0	0
6	3%	3%
8	26%	12%
10	35%	23%
12	40%	28%
15	58%	11%
18	65%	0%

6. Raman study





Raman frequency of the samples was carried out at the 532nm-2mw-50slit-50X level by Thermo DXR2 Raman Microscope. Raman spectra of (a) **3ae**. (b) **1ae** with $PhSO_2SS^t$Bu under optimized reaction conditions, T = 4 h. (c) **3ae'**.

General procedure for the preparation of 3ae

An oven-dried 25 mL Schlenk tube, equipped with a stirring bar, was charged with $PhSO_2SS^t$Bu (0.75 mmol, 1.5 equiv), **1ae** (0.5 mmol, 1.0 equiv), $Ni(PPh_3)_2Cl_2$ (5 mol%), terpyridine (7.5 mol%), Mn (1.25 mmol, 2.5 equiv) and DMF (4.0 mL) in argon atmosphere. The reaction mixture was stirred at RT for 24 h. After completion of the reaction, the solution was filtered and washed with ethyl acetate for 3 times. The combined solvents were removed under vacuum, and the residue was purified by flash column chromatography to obtain the product **3ae.**

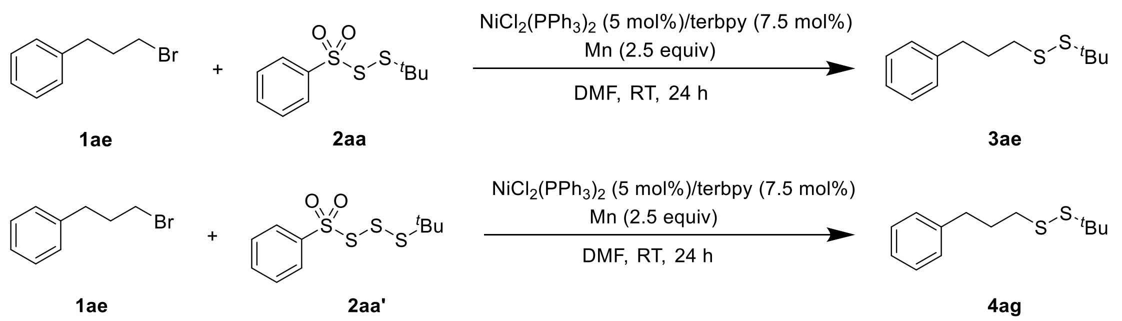
General procedure for the preparation of the mixed products 3ae and 3ae'

An oven-dried 25 mL Schlenk tube, equipped with a stirring bar, was charged with $PhSO_2SS^t$Bu (0.75 mmol, 1.5 equiv), **1ae** (0.5 mmol, 1.0 equiv), $Ni(PPh_3)_2Cl_2$ (5 mol%), terpyridine (7.5 mol%), Mn (1.25 mmol, 2.5 equiv) and DMF (4.0 mL) in argon atmosphere. The reaction mixture was stirred at RT for 4 h. After completion of the reaction, the solution was filtered and washed with ethyl acetate for 3 times. The combined solvents were removed under vacuum, and the residue was purified by flash column chromatography to obtain the mixed products **3ae** and **3ae'.**

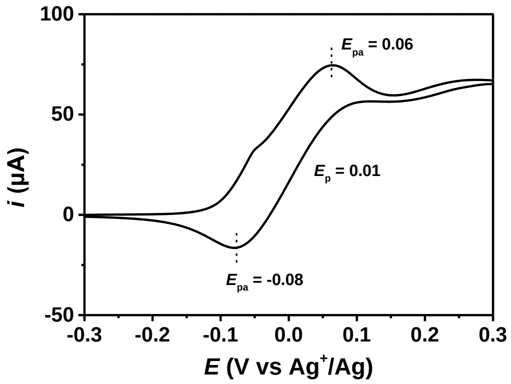
General procedure for the preparation of 3ae'

An oven-dried 25 mL Schlenk tube, equipped with a stirring bar, was charged with *t*BuSSSS*t*Bu (0.75 mmol, 1.5 equiv), **1ae** (0.5 mmol, 1.0 equiv), $Ni(acac)_2$ (5 mol%), dtbbpy (7.5 mol%), Mn (1.25 mmol, 2.5 equiv) and DMF (4.0 mL) in argon atmosphere. The reaction mixture was stirred at 40 °C for 12 h. After completion of the reaction, the solution was filtered and washed with ethyl acetate for 3 times. The combined solvents were removed under vacuum, and the residue was purified by thin layer chromatography to obtain the product **3ae'**. [6]

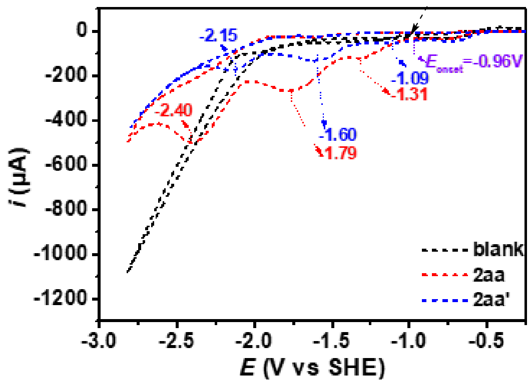
7. CV test of di/trithiosulfonates



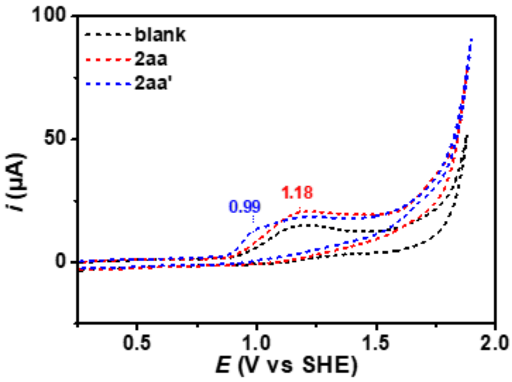
The Cyclic Voltammetry (CV) measurements were performed under N_2 atmosphere at room temperature over an electrochemical station (CHI660E) using a standard three electrode system. Glassy carbon (GC) and platinum mesh were employed as working electrode and counter electrode, respectively. Then, Ag^+/Ag was used as reference electrode and the redox potential (V vs SHE) was calibrated by Fc^+/Fc pair. The CV test was performed at scan rate of 100 $mV{\cdot}s^{-1}$ in 0.05 M tetrabutylammonium perchlorate and N, N-dimethylformamide (DMF) solution.



reference potential: Fc^+/Fc = 0.69 V vs. SHE
test potantial: Fc^+/Fc=0.01 V vs. Ag^+/Ag



reduction potantials



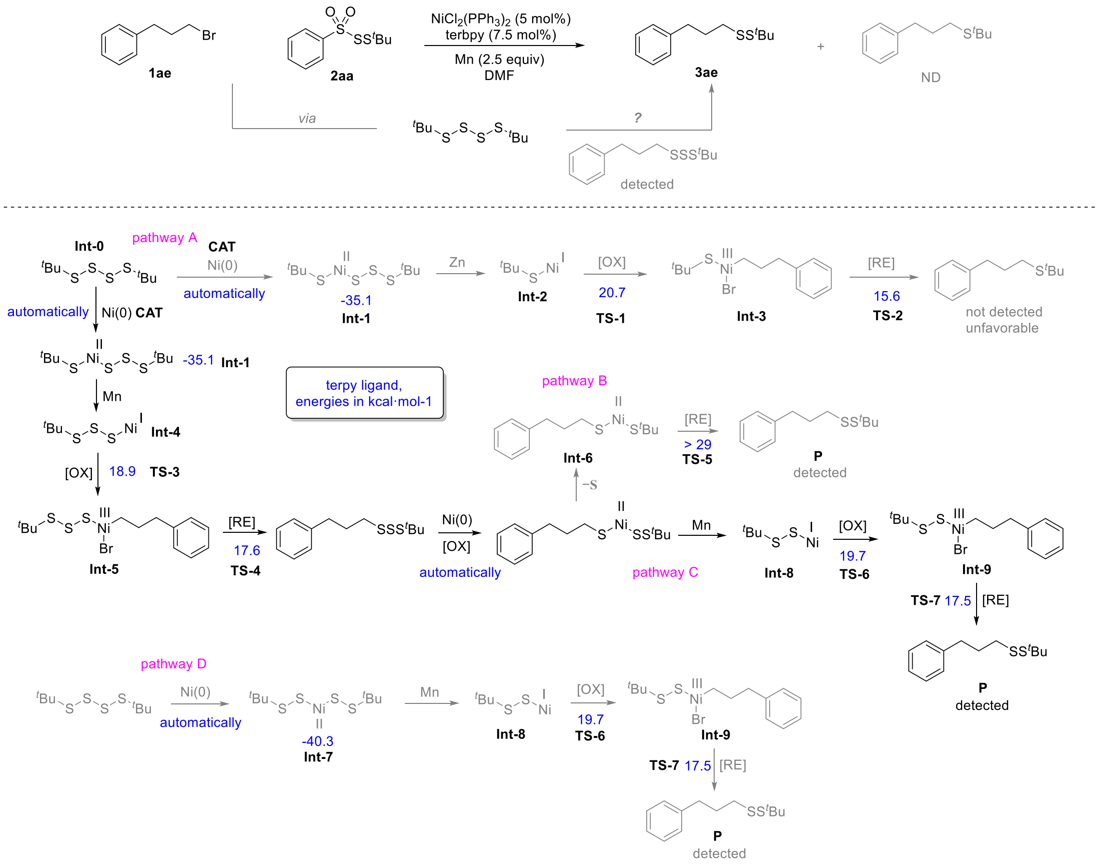
oxidation potantials

According to the CV tests, these reagents (**2aa**, **2aa'**) can be reduced under electrochemical conditions, and their onset reduction potential is -0.96 V vs SHE. Considering the reduction potential of Mn (-1.185 V vs SHE), it is reasonable to expect that the four reagents can be reduced by Mn in our system. In addition, as a comparison, reagent **2aa'** possesses relatively low reduction potential when comparing with **2aa**. Three reduction peaks of **2aa** are located at -1.31, -1.79 and -2.40 V vs SHE. For reagent **2aa'**, its reduction potentials are -1.09, -1.60 and -2.15 V vs SHE. This phenomenon may also indicate that reagents **2aa** and **2aa'** may have different activation modes (a different pattern of breaking S-S bond).

8. DFT calculations

Computational Details

All species involved in the catalytic process were optimized at the B3LYP-D3(BJ)/Def2-SVP/SDD(Ni) level.[1−6] The harmonic vibrational modes were computed to verify the characters of local minima and obtain free energy corrections as well. Electronic energies were further improved by single point calculations at the aforementioned optimized geometries with larger Def2-TZVP basis sets and the SMD solvation model [7] to account the solvation effects in dimethyl sulfoxide (DMSO). All calculations were performed employing the Gaussian 16 program (version b.01). [8]



DFT calculations were conducted for the reaction of (3-bromopropyl)benzene and $PhSO_2SS^tBu$ (**2aa**) in the presence of $NiCl_2(PPh_3)_2$ (5 mol%), terpy (7.5 mol%) and Mn in the solvent DMF. Through detailed mechanistic studies (please see Scheme 2 in the manuscript), we found that tetrasulfide reagent ($^tBuSSSS^tBu$) is a key intermediate, which is responsible for nickel-catalyzed reductive thiolation.

Preliminary DFT calculations revealed that 1) the generation of trisulfides ((3-(*tert*-butylsulfonodithioyl)propyl)benzene) in the initial stage may be more favorable than direct generation of disulfides (pathway D, (3-(tert-butylsulfinothioyl)propyl)benzene) or monosulfides (pathway A, *tert*-butyl(3-phenylpropyl)sulfane); 2) the desulfurization process of trisulfides ((3-(tert-butylsulfonodithioyl)propyl)benzene) to disulfides is unfavorable at this stage. The oxidative addition of trisulfide R'-$(S)_3{}^t$Bu in the presence of Ni(0) with releasing the corresponding sulfur intermediates might furnish the target disulfide product **P** (R'-SS^{t}Bu). The energy barrier for reductive elimination of this step (pathway B, **TS-5**) is 29.0 kcal/mol. By contrast, R'S-L_nNi^{II}-SS^{t}Bu tends to be reduced to $L_nNi(I)(S)_2{}^t$Bu (**Int-8**) in the presence of reducing agents and reacts with alkyl bromide (R'-Br) to yield the final product **P** (R'-SS^{t}Bu). The energy barrier for oxidative addition (pathway C, **TS-6**) and reductive elimination (pathway C, **TS-7**) of this step is 19.7 and 17.5 kcal/mol, respectively. Compared to the desulfurization reaction (pathway B), this process (pathway C) may be more reasonable.

30
CAT E = -2251.26193513 G = -2251.077682

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N	1.924492	-0.956654	-0.000001
C	2.897313	-1.892525	0.000000
C	4.250450	-1.595776	0.000002
C	4.646184	-0.241496	0.000005
C	3.663636	0.737474	0.000005
C	2.305878	0.380112	0.000002
H	2.556601	-2.931218	-0.000002
H	4.983957	-2.403529	0.000003
H	5.703092	0.032164	0.000008
H	3.934529	1.794644	0.000009
C	1.196351	1.328976	0.000004
C	1.222990	2.724922	-0.000004
H	2.166799	3.272952	-0.000011
N	0.000000	0.694294	0.000012
C	0.000000	3.419936	-0.000007
N	-1.924493	-0.956653	-0.000001
C	-2.897313	-1.892525	0.000000
C	-4.250451	-1.595776	0.000002
C	-4.646185	-0.241496	0.000005
C	-3.663636	0.737474	0.000005
C	-2.305878	0.380112	0.000002
H	-2.556601	-2.931218	-0.000002
H	-4.983957	-2.403528	0.000003
H	-5.703092	0.032164	0.000007
H	-3.934529	1.794644	0.000008
C	-1.196351	1.328976	0.000004
C	-1.222990	2.724922	-0.000004

H	-2.166799	3.272952	-0.000011
H	0.000000	4.511536	-0.000014

30

Int-0 E = -1908.82114665 G = -1908.619502

S	0.582565	0.898342	0.679272
S	-0.582299	-0.896678	0.680589
S	-1.964663	-0.717612	-0.843514
C	-3.438354	0.151445	-0.061813
C	-4.436386	0.250799	-1.221923
H	-4.031309	0.850486	-2.051585
H	-4.706315	-0.744223	-1.608829
H	-5.359286	0.738750	-0.867868
C	-3.031295	1.538354	0.432055
H	-2.293981	1.468934	1.244744
H	-2.591588	2.140227	-0.376442
H	-3.917116	2.066984	0.823216
C	-3.998205	-0.700389	1.076280
H	-4.878729	-0.203473	1.517724
H	-4.303642	-1.694453	0.717203
H	-3.249482	-0.833203	1.871514
S	1.965001	0.716935	-0.844466
C	3.438190	-0.151921	-0.061603
C	3.997781	0.700460	1.076203
C	4.436689	-0.252251	-1.221231
C	3.030496	-1.538411	0.432933
H	4.303686	1.694205	0.716640
H	3.248724	0.834001	1.870997
H	4.877949	0.203551	1.518363
H	4.031786	-0.852264	-2.050743
H	4.707107	0.742470	-1.608572
H	5.359272	-0.740308	-0.866503
H	3.915999	-2.067098	0.824740
H	2.292857	-1.468289	1.245268
H	2.590907	-2.140614	-0.375386

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Int-1 E = -4160.16452657 G = -4159.753095

Ni	-0.446325	0.073365	-0.279308
S	-2.533083	0.928985	0.313203
S	-0.000410	-0.137342	-2.591878
S	1.346696	-1.751922	-2.331615
N	-0.054968	0.003884	1.703378
C	0.399692	1.107150	2.306973

C	-0.406449	-1.098186	2.374995
C	0.684725	2.230673	1.379839
C	0.557941	1.131575	3.698112
C	-0.938380	-2.187593	1.518768
C	-0.272723	-1.141855	3.768164
N	0.482506	1.956369	0.075623
C	1.123460	3.492859	1.794543
H	0.931377	2.019665	4.207372
C	0.220649	-0.012312	4.424994
N	-0.971579	-1.909554	0.200559
C	-1.393215	-3.415154	2.011127
H	-0.549508	-2.032021	4.332388
C	0.693238	2.893103	-0.847180
C	1.335954	4.481366	0.832988
H	1.289147	3.705550	2.850809
H	0.335099	-0.020676	5.510797
C	-1.447893	-2.803038	-0.664537
C	-1.895830	-4.355406	1.110869
H	-1.361972	-3.633887	3.078571
C	1.115828	4.180594	-0.512398
H	0.531454	2.577896	-1.881964
H	1.670793	5.476452	1.133838
C	-1.927872	-4.046765	-0.249711
H	-1.435718	-2.496193	-1.713179
H	-2.260451	-5.319662	1.471627
H	1.272879	4.925051	-1.294497
H	-2.313876	-4.755209	-0.984234
C	-3.494470	1.278565	-1.237760
C	-3.755630	-0.020658	-2.008087
H	-4.381676	0.171712	-2.898835
H	-2.808171	-0.464087	-2.346855
H	-4.275186	-0.750458	-1.368326
C	-2.736305	2.275087	-2.121638
H	-2.511365	3.196954	-1.563547
H	-1.786562	1.845200	-2.472036
H	-3.331671	2.541346	-3.013933
C	-4.825217	1.896292	-0.786318
H	-4.655114	2.826252	-0.221916
H	-5.458188	2.130427	-1.661061
H	-5.377966	1.201239	-0.135601
S	2.226434	-1.496127	-0.450267
C	3.820668	-0.553761	-0.771764
C	3.518715	0.798635	-1.412530
H	4.463085	1.315590	-1.655537

H	2.936199	0.679329	-2.337302
H	2.942688	1.435444	-0.729348
C	4.723784	-1.399558	-1.668269
H	5.676750	-0.873172	-1.848883
H	4.944512	-2.373707	-1.206405
H	4.240498	-1.577731	-2.640528
C	4.428114	-0.377948	0.624220
H	4.628190	-1.349196	1.103323
H	5.384011	0.166645	0.545930
H	3.759236	0.202610	1.279551

65

Int-2 E = -5731.44770191 G = -5730.990036

Ni	-1.042902	0.081014	-0.346177
S	0.549231	-0.278021	1.226137
C	1.698161	-2.249786	-1.384718
H	1.973473	-3.207362	-1.845094
H	1.130574	-2.391475	-0.456785
C	2.867871	-1.320807	-1.146227
H	2.469822	-0.346072	-0.835547
H	3.449205	-1.167622	-2.069961
C	3.773378	-1.830565	-0.012086
H	4.275134	-2.765621	-0.311352
H	3.130120	-2.057180	0.853391
C	4.794889	-0.791221	0.385657
C	4.388635	0.340528	1.114011
C	6.139651	-0.901573	0.008579
C	5.310481	1.331431	1.455521
H	3.338990	0.435830	1.409318
C	7.064229	0.090441	0.350857
H	6.468098	-1.777751	-0.558144
C	6.651753	1.210986	1.075348
H	4.979849	2.203120	2.026398
H	8.110180	-0.014388	0.051049
H	7.372733	1.986612	1.345764
Br	0.377693	-1.429338	-2.617772
N	-2.557212	1.251674	-0.088685
C	-3.757372	0.699478	0.230708
C	-2.355702	2.591641	-0.057145
C	-3.772919	-0.752526	0.077392
C	-4.818152	1.516960	0.634329
C	-1.001264	2.978995	-0.479451
C	-3.381378	3.448813	0.334217
N	-2.592920	-1.287442	-0.366770

C	-4.884318	-1.573399	0.339807
H	-5.784947	1.085043	0.895989
C	-4.626033	2.900363	0.689591
N	-0.228060	1.950559	-0.921240
C	-0.506046	4.291912	-0.441445
H	-3.229781	4.528447	0.356887
C	-2.522212	-2.611506	-0.583701
C	-4.795084	-2.939887	0.119464
H	-5.809901	-1.131864	0.711176
H	-5.443149	3.554722	0.998013
C	1.021208	2.201728	-1.331336
C	0.792250	4.544421	-0.869614
H	-1.134019	5.102448	-0.070226
C	-3.586632	-3.473556	-0.366145
H	-1.562391	-2.979397	-0.953704
H	-5.650906	-3.588663	0.317198
C	1.575658	3.476765	-1.330310
H	1.593267	1.338405	-1.677228
H	1.194245	5.559524	-0.842519
H	-3.474890	-4.540577	-0.564365
H	2.599479	3.627033	-1.676088
C	-0.190639	-1.130983	2.708050
C	-0.430417	-2.614745	2.411439
H	0.510276	-3.115945	2.135894
H	-0.846526	-3.129457	3.296662
H	-1.140523	-2.739497	1.583431
C	-1.507182	-0.447009	3.090426
H	-1.928507	-0.896671	4.007714
H	-1.349984	0.627318	3.267627
H	-2.250522	-0.549987	2.288861
C	0.824517	-0.986127	3.848659
H	1.010181	0.074828	4.073904
H	0.450669	-1.477574	4.764564
H	1.787405	-1.447575	3.579571

65

Int-3 E = -5731.45299772 G = -5730.991459

Ni	-0.664271	-0.390500	-0.142140
S	-1.283435	-0.800388	2.054123
C	0.371498	-2.095816	-0.248409
H	0.104214	-2.416760	-1.264960
H	-0.104696	-2.742016	0.496262
C	1.876086	-2.040543	-0.066062
H	2.230659	-3.050759	0.218515

H	2.134156	-1.414458	0.803197
C	2.646883	-1.563373	-1.306531
H	2.070187	-0.771838	-1.807283
H	2.683418	-2.390101	-2.039128
C	4.048006	-1.063137	-1.037629
C	4.889240	-1.668346	-0.090009
C	4.533752	0.061341	-1.726339
C	6.171163	-1.170337	0.158804
H	4.537510	-2.540735	0.465418
C	5.814436	0.562945	-1.481700
H	3.884655	0.552413	-2.456596
C	6.639854	-0.051457	-0.535059
H	6.807267	-1.658673	0.901684
H	6.168324	1.439409	-2.031089
H	7.641265	0.339529	-0.338820
Br	-0.332330	0.108149	-2.550152
N	-1.963841	1.195101	-0.060859
C	-3.268243	0.961499	-0.254231
C	-1.506384	2.413337	0.246150
C	-3.616060	-0.436541	-0.606525
C	-4.205568	1.993817	-0.125548
C	-0.034504	2.525319	0.374898
C	-2.391842	3.488950	0.399939
N	-2.584588	-1.298193	-0.640212
C	-4.921640	-0.854409	-0.895416
H	-5.267595	1.808833	-0.280391
C	-3.754686	3.268401	0.213234
N	0.656370	1.375902	0.255996
C	0.614778	3.752735	0.566880
H	-2.027605	4.481034	0.662539
C	-2.797827	-2.575309	-0.946388
C	-5.147628	-2.190522	-1.221004
H	-5.751469	-0.148865	-0.869958
H	-4.464856	4.089484	0.329154
C	1.987314	1.415014	0.292906
C	2.007432	3.787379	0.612987
H	0.042535	4.674801	0.662749
C	-4.066785	-3.072083	-1.247363
H	-1.920096	-3.224042	-0.950687
H	-6.157269	-2.537455	-1.451153
C	2.712579	2.594395	0.463073
H	2.509862	0.469848	0.178620
H	2.530593	4.735644	0.754044
H	-4.197109	-4.126504	-1.495966

H	3.802958	2.558295	0.470089
C	0.001396	-1.020384	3.383382
C	-0.770147	-0.797566	4.693915
H	-0.098533	-0.942076	5.558828
H	-1.183095	0.221463	4.737393
H	-1.606304	-1.507831	4.784785
C	1.126905	0.009476	3.275688
H	0.724960	1.032598	3.240078
H	1.805368	-0.070582	4.143699
H	1.725969	-0.151183	2.371386
C	0.575705	-2.442551	3.369499
H	1.148578	-2.637446	2.453984
H	1.254364	-2.593318	4.228600
H	-0.231980	-3.186790	3.430962

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Int-4 E = -6527.93621554 G = -6527.477562

Ni	0.836964	-0.970267	0.596947
S	-0.252901	-0.329066	-1.335127
C	-1.720997	-3.258546	-0.539557
H	-2.129987	-4.270714	-0.651730
H	-1.113151	-2.979666	-1.408872
C	-2.756655	-2.200293	-0.224985
H	-2.230615	-1.287621	0.085879
H	-3.390490	-2.515257	0.620113
C	-3.628892	-1.842886	-1.440944
H	-4.259118	-2.700210	-1.728961
H	-2.961184	-1.620379	-2.289112
C	-4.487204	-0.633335	-1.147667
C	-3.890014	0.636114	-1.063032
C	-5.861849	-0.747911	-0.904702
C	-4.652815	1.759720	-0.743832
H	-2.815924	0.731183	-1.245548
C	-6.628649	0.378174	-0.586893
H	-6.339520	-1.730095	-0.967436
C	-6.025842	1.635447	-0.504230
H	-4.169804	2.738272	-0.683495
H	-7.700995	0.271204	-0.404083
H	-6.623725	2.516082	-0.256385
Br	-0.392587	-3.396627	0.937767
S	1.226297	0.732647	-2.372663
S	1.657638	2.494632	-1.328612
C	0.106827	3.557554	-1.412582
C	-0.810287	3.152552	-0.252531

H	-1.737693	3.752395	-0.273488
H	-1.070906	2.087678	-0.317577
H	-0.316454	3.319337	0.715938
C	-0.601668	3.403033	-2.754343
H	-1.470846	4.081962	-2.789146
H	0.068505	3.650207	-3.591323
H	-0.961125	2.374450	-2.896507
C	0.623378	4.987634	-1.221080
H	-0.229245	5.683289	-1.139052
H	1.217939	5.077049	-0.297153
H	1.251459	5.304058	-2.067481
N	2.191373	0.263777	1.195161
C	3.383535	0.265977	0.552208
C	1.829527	1.275361	2.019723
C	3.547824	-0.872063	-0.359793
C	4.297232	1.298320	0.763537
C	0.474176	1.125390	2.550972
C	2.706319	2.333280	2.266783
N	2.509866	-1.751021	-0.363017
C	4.661621	-1.062171	-1.194338
H	5.259222	1.305205	0.250600
C	3.954677	2.339088	1.635767
N	-0.185079	0.004289	2.135603
C	-0.140981	2.051326	3.410710
H	2.422445	3.150283	2.930796
C	2.541602	-2.793123	-1.202927
C	4.695288	-2.156464	-2.047041
H	5.481354	-0.343590	-1.182330
H	4.653744	3.158519	1.811054
C	-1.433143	-0.209982	2.580943
C	-1.437375	1.825133	3.851333
H	0.400009	2.945391	3.721770
C	3.607692	-3.043803	-2.057453
H	1.668993	-3.450303	-1.178423
H	5.550192	-2.315636	-2.707763
C	-2.100865	0.661246	3.430662
H	-1.911397	-1.127645	2.235551
H	-1.929774	2.540548	4.513283
H	3.587853	-3.911985	-2.718108
H	-3.118645	0.436079	3.752592

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Int-5 E = -6527.95407289 G = -6527.49658

Ni	0.012421	-0.981254	-0.028053

S	0.377395	0.311715	-1.888560
C	-1.640427	-1.528658	-0.999758
H	-1.751471	-2.567654	-0.661907
H	-1.432846	-1.500447	-2.080351
C	-2.848377	-0.698976	-0.643914
H	-2.722216	0.331583	-1.016567
H	-2.954850	-0.649074	0.451256
C	-4.164751	-1.254412	-1.230927
H	-4.317545	-2.277809	-0.850402
H	-4.073012	-1.329446	-2.327089
C	-5.343579	-0.386079	-0.868998
C	-5.791298	0.623829	-1.733707
C	-5.974196	-0.522074	0.377964
C	-6.842006	1.469974	-1.368945
H	-5.309194	0.744808	-2.708112
C	-7.024385	0.321075	0.747367
H	-5.634147	-1.301665	1.065658
C	-7.462798	1.321441	-0.125787
H	-7.179085	2.246915	-2.060079
H	-7.505299	0.195075	1.720854
H	-8.286663	1.979866	0.160494
Br	-0.737013	-2.252280	1.919547
S	2.413460	0.704346	-1.987200
S	2.968626	2.174443	-0.586384
C	2.383465	3.813171	-1.290724
C	0.856615	3.885664	-1.215752
H	0.510041	4.861493	-1.598750
H	0.389040	3.088253	-1.809163
H	0.507762	3.777485	-0.178409
C	2.880730	3.982302	-2.724020
H	2.550615	4.957023	-3.121836
H	3.979461	3.940310	-2.770717
H	2.477970	3.191403	-3.373326
C	3.020442	4.850568	-0.358343
H	2.706630	5.862322	-0.665542
H	2.698232	4.700277	0.684521
H	4.119869	4.805777	-0.394302
N	1.758969	-0.638645	0.950553
C	2.760550	-1.503730	0.737626
C	1.858405	0.332888	1.864398
C	2.508906	-2.511883	-0.316803
C	3.939628	-1.435586	1.487650
C	0.707191	1.262703	1.940828
C	3.006603	0.449040	2.658350

N	1.252599	-2.541767	-0.796300
C	3.492505	-3.384045	-0.801210
H	4.747434	-2.147580	1.324858
C	4.052703	-0.448248	2.464417
N	-0.357278	0.949240	1.183012
C	0.734678	2.424476	2.724560
H	3.086238	1.230109	3.412203
C	0.925920	-3.415801	-1.747363
C	3.153099	-4.301364	-1.792874
H	4.511892	-3.338410	-0.419320
H	4.956438	-0.378242	3.072869
C	-1.412524	1.762522	1.177748
C	-0.370942	3.271578	2.721301
H	1.613370	2.674622	3.317424
C	1.843515	-4.323130	-2.275999
H	-0.107191	-3.384279	-2.097739
H	3.904700	-4.988487	-2.187347
C	-1.470647	2.935639	1.932674
H	-2.249129	1.468500	0.545270
H	-0.368925	4.183794	3.321817
H	1.533949	-5.024862	-3.052016
H	-2.360278	3.566079	1.892015

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Int-6 E = -3555.49821429 G = -3555.04158

Ni	-0.968789	-0.000765	0.162405
S	-2.988475	0.001484	1.318797
S	1.025250	-0.001838	1.366655
N	-2.177945	-0.000167	-1.474350
C	-2.674556	-1.175033	-1.882062
C	-2.672309	1.175311	-1.883010
C	-2.026890	-2.353909	-1.253058
C	-3.723984	-1.210369	-2.808007
C	-2.022361	2.353461	-1.255003
C	-3.721654	1.211910	-2.808988
N	-1.074636	-2.057028	-0.345356
C	-2.353058	-3.681239	-1.548324
H	-4.140052	-2.157294	-3.151294
C	-4.240820	0.001076	-3.273691
N	-1.070662	2.055537	-0.347079
C	-2.345951	3.681170	-1.551415
H	-4.135918	2.159347	-3.153041
C	-0.422654	-3.026632	0.294225
C	-1.680375	-4.703843	-0.876551

H	-3.120507	-3.916302	-2.286180
H	-5.062454	0.001576	-3.992728
C	-0.416747	3.024404	0.291605
C	-1.671207	4.703047	-0.880600
H	-3.112985	3.917098	-2.289428
C	-0.698718	-4.376030	0.060200
H	0.333061	-2.679358	1.008704
H	-1.923218	-5.748084	-1.085464
C	-0.690129	4.374149	0.056374
H	0.338231	2.676316	1.006472
H	-1.912013	5.747575	-1.090437
H	-0.152974	-5.148513	0.604541
H	-0.142824	5.146039	0.599985
C	-2.581039	0.003757	3.131664
C	-1.783952	1.262453	3.492633
H	-1.590590	1.302204	4.580235
H	-0.813353	1.273926	2.975865
H	-2.340556	2.167841	3.205055
C	-1.785971	-1.255178	3.496257
H	-2.344211	-2.160502	3.211671
H	-0.815550	-1.269985	2.979236
H	-1.592315	-1.291907	4.583914
C	-3.925294	0.005887	3.872568
H	-4.518632	-0.884576	3.612875
H	-3.761491	0.007203	4.965043
H	-4.517105	0.896671	3.610498
C	2.084182	-0.000667	-0.143892
H	1.855766	0.885197	-0.764347
H	1.855460	-0.885307	-0.765953
C	3.569532	-0.001272	0.207529
H	3.794697	-0.882113	0.832044
H	3.795035	0.878342	0.833651
C	4.480804	-0.000332	-1.031467
H	4.249432	0.884323	-1.649282
H	4.249039	-0.883746	-1.650903
C	5.947464	-0.000995	-0.677397
C	6.640615	-1.205234	-0.482039
C	6.641056	1.202546	-0.479333
C	7.985259	-1.209139	-0.103723
H	6.115708	-2.153315	-0.630984
C	7.985703	1.205107	-0.101012
H	6.116500	2.151153	-0.626148
C	8.663690	-0.002354	0.088480
H	8.506767	-2.158988	0.040014

H	8.507557	2.154440	0.044856
H	9.716072	-0.002878	0.382701

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Int-7 E = -4160.17342818 G = -4159.761359

Ni	-0.000702	0.003692	0.535410
S	-1.363365	1.702857	1.341894
S	1.362459	-1.690350	1.353130
S	3.118196	-0.789146	2.043413
C	4.402220	-1.281879	0.765935
C	5.698222	-0.634671	1.263376
H	5.601621	0.461769	1.311867
H	5.968745	-1.002487	2.265497
H	6.526872	-0.875039	0.575988
C	4.013128	-0.740298	-0.609290
H	2.997214	-1.071043	-0.873419
H	4.039450	0.358294	-0.621826
H	4.713324	-1.109272	-1.378864
C	4.522488	-2.805515	0.734997
H	5.277838	-3.115501	-0.008392
H	4.818743	-3.196396	1.720008
H	3.557361	-3.258162	0.462312
N	0.000000	-0.006375	-1.537652
C	-0.817010	-0.852364	-2.188634
C	0.818233	0.833316	-2.195268
C	-1.671156	-1.706796	-1.325109
C	-0.836590	-0.883214	-3.588478
C	1.671548	1.695180	-1.338392
C	0.839980	0.851119	-3.595303
N	-1.500533	-1.548166	-0.000831
C	-2.618173	-2.608141	-1.826379
H	-1.493578	-1.568119	-4.122845
C	0.002187	-0.019272	-4.292365
N	1.499287	1.548246	-0.012925
C	2.619583	2.591626	-1.846410
H	1.497940	1.530877	-4.135022
C	-2.243389	-2.234241	0.866208
C	-3.399336	-3.333793	-0.925671
H	-2.755612	-2.738242	-2.899389
H	0.003002	-0.024357	-5.384042
C	2.241767	2.241275	0.848947
C	3.400242	3.324578	-0.951190
H	2.758196	2.712344	-2.920365
C	-3.215297	-3.145000	0.444199

H	-2.047673	-2.048355	1.922931
H	-4.148030	-4.038242	-1.294410
C	3.214723	3.147673	0.420063
H	2.044695	2.064847	1.907033
H	4.149722	4.025393	-1.325216
H	-3.810125	-3.689629	1.178989
H	3.809178	3.698204	1.150741
S	-3.119503	0.806034	2.037153
C	-4.402131	1.288205	0.754244
C	-5.698569	0.644660	1.255291
H	-5.970490	1.020578	2.254020
H	-6.526403	0.879135	0.564892
H	-5.601704	-0.451317	1.312860
C	-4.011228	0.735664	-0.616121
H	-2.994782	1.063832	-0.881437
H	-4.037943	-0.362987	-0.620041
H	-4.710166	1.098801	-1.389603
C	-4.522822	2.811507	0.711007
H	-4.820340	3.210101	1.692542
H	-3.557542	3.262325	0.435851
H	-5.277429	3.115303	-0.035684

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Int-8 E = -6129.69612105 G = -6129.238197

Ni	0.987029	0.544994	0.420939
S	-0.554109	-0.407146	-0.970701
C	-1.808066	-0.997591	2.357016
H	-2.116541	-1.495077	3.285427
H	-1.273572	-1.702723	1.710156
C	-2.939590	-0.314417	1.620638
H	-2.501840	0.314273	0.834321
H	-3.515242	0.333161	2.301866
C	-3.862255	-1.338727	0.935240
H	-4.380334	-1.953630	1.689850
H	-3.236111	-2.016701	0.331998
C	-4.868015	-0.660239	0.035821
C	-4.446528	-0.105621	-1.184814
C	-6.213981	-0.533155	0.403309
C	-5.354202	0.555146	-2.014007
H	-3.394913	-0.193356	-1.474661
C	-7.124771	0.128002	-0.426926
H	-6.554442	-0.961292	1.350701
C	-6.696949	0.674601	-1.638882
H	-5.011590	0.977295	-2.962377

H	-8.172005	0.214098	-0.125601
H	-7.407068	1.189757	-2.290702
Br	-0.411479	0.302282	2.907318
N	2.617499	1.343365	-0.223872
C	3.749869	0.594709	-0.249225
C	2.569096	2.582098	-0.778261
C	3.582965	-0.706731	0.403518
C	4.906517	1.088819	-0.852971
C	1.253654	3.214775	-0.642365
C	3.699484	3.122246	-1.393008
N	2.351637	-0.908190	0.956614
C	4.576405	-1.695608	0.466555
H	5.821175	0.495155	-0.874325
C	4.879792	2.366735	-1.429247
N	0.345107	2.483351	0.065070
C	0.908378	4.463421	-1.185292
H	3.670717	4.118661	-1.835668
C	2.090391	-2.079995	1.553767
C	4.299756	-2.902868	1.097683
H	5.552705	-1.517414	0.014816
H	5.775386	2.772725	-1.902445
C	-0.895456	2.964182	0.232033
C	-0.375900	4.958824	-0.997907
H	1.643592	5.032073	-1.755753
C	3.027468	-3.101879	1.653941
H	1.089986	-2.192695	1.970762
H	5.060728	-3.684196	1.152541
C	-1.302261	4.193309	-0.271897
H	-1.580515	2.328670	0.797432
H	-0.659922	5.926929	-1.415990
H	2.764275	-4.035037	2.154174
H	-2.322573	4.541275	-0.104073
S	-0.479934	-2.482446	-0.698343
C	0.536305	-3.095163	-2.153405
C	1.928876	-2.467709	-2.117257
H	2.496495	-2.751470	-3.020236
H	1.854588	-1.370695	-2.083057
H	2.491777	-2.806427	-1.237133
C	-0.190449	-2.739225	-3.449868
H	0.387606	-3.094397	-4.320742
H	-1.190060	-3.198387	-3.481065
H	-0.309180	-1.648495	-3.532446
C	0.608131	-4.611562	-1.953113
H	-0.396601	-5.062732	-1.947364

H	1.183269	-5.070423	-2.774858
H	1.108186	-4.863093	-1.004443

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Int-9 E = -6129.70944369 G = -6129.248041

Ni	0.628459	-0.736730	-0.248831
S	0.917800	0.855751	-1.926447
C	-0.403189	-1.695918	-1.671631
H	-0.213329	-2.748799	-1.419348
H	0.125503	-1.433842	-2.601065
C	-1.887054	-1.405699	-1.782977
H	-2.218545	-1.636577	-2.813710
H	-2.066218	-0.322677	-1.674714
C	-2.738408	-2.205705	-0.785070
H	-2.198746	-2.279010	0.171734
H	-2.811977	-3.248720	-1.143818
C	-4.127883	-1.664823	-0.531917
C	-4.884982	-1.045707	-1.539175
C	-4.688729	-1.752468	0.753728
C	-6.159007	-0.536041	-1.273129
H	-4.473048	-0.955916	-2.546654
C	-5.961437	-1.244812	1.024832
H	-4.105319	-2.217926	1.553050
C	-6.703314	-0.632153	0.010171
H	-6.728882	-0.057817	-2.074059
H	-6.374529	-1.325391	2.033815
H	-7.698203	-0.231106	0.218837
Br	0.260224	-2.521824	1.394882
S	1.342214	2.691827	-1.058678
N	1.935128	0.225894	0.963022
C	3.244108	-0.022134	0.813549
C	1.490251	1.162254	1.808663
C	3.577008	-1.091231	-0.156613
C	4.194643	0.699422	1.544040
C	0.017760	1.305767	1.873014
C	2.389073	1.911028	2.580738
N	2.527973	-1.636181	-0.798736
C	4.884928	-1.532030	-0.396099
H	5.259599	0.509663	1.418379
C	3.752823	1.675496	2.437519
N	-0.681138	0.546748	1.009105
C	-0.623686	2.139326	2.799591
H	2.031662	2.674428	3.269947
C	2.726755	-2.618851	-1.674163

C	5.096216	-2.556036	-1.317526
H	5.727749	-1.087696	0.132384
H	4.474182	2.253723	3.018251
C	-2.011860	0.580061	1.046194
C	-2.016525	2.166855	2.839297
H	-0.044395	2.748872	3.492152
C	3.997313	-3.114506	-1.970524
H	1.835379	-3.025286	-2.155440
H	6.107736	-2.915115	-1.518874
C	-2.729448	1.365753	1.948200
H	-2.538898	-0.042878	0.331036
H	-2.534249	2.803274	3.560227
H	4.114424	-3.921198	-2.695864
H	-3.819943	1.336527	1.936395
C	-0.112250	3.791997	-1.514789
C	-1.415419	3.221333	-0.966611
H	-2.269089	3.837528	-1.297036
H	-1.567719	2.195966	-1.332948
H	-1.409605	3.204629	0.131379
C	-0.174487	3.924120	-3.036881
H	-1.004950	4.590856	-3.327389
H	0.763337	4.337679	-3.437314
H	-0.342451	2.940209	-3.499724
C	0.223167	5.133791	-0.856144
H	-0.562317	5.871557	-1.090596
H	0.282747	5.035169	0.239390
H	1.183237	5.531156	-1.221495

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TS-1 E = -5731.41278424 G = -5730.957017

Ni	-0.813050	-0.004204	-0.517189
S	0.374195	0.013848	1.445663
C	1.180345	-2.340051	-1.113659
H	1.172324	-3.231541	-1.744600
H	0.493417	-2.343018	-0.265229
C	2.439054	-1.569556	-0.945750
H	2.184043	-0.537512	-0.669816
H	3.015312	-1.539612	-1.883731
C	3.332907	-2.099887	0.207108
H	3.695550	-3.114135	-0.024844
H	2.707259	-2.163779	1.110407
C	4.490509	-1.164815	0.458565
C	4.267219	0.059459	1.113168
C	5.782675	-1.455836	0.001054

C	5.314372	0.962052	1.306271
H	3.259410	0.295852	1.467456
C	6.832859	-0.553021	0.195136
H	5.968928	-2.403796	-0.512081
C	6.601574	0.660003	0.848130
H	5.125173	1.907289	1.822046
H	7.835212	-0.799493	-0.164719
H	7.421323	1.366258	1.002433
Br	-0.137758	-1.009272	-2.847024
N	-2.236886	1.306696	-0.107427
C	-3.439372	0.832218	0.284209
C	-1.881758	2.592373	0.069187
C	-3.609750	-0.605758	0.057281
C	-4.373926	1.695552	0.872727
C	-0.516459	2.903566	-0.407302
C	-2.770814	3.498502	0.646133
N	-2.496433	-1.251700	-0.390419
C	-4.811064	-1.302638	0.271896
H	-5.345661	1.325303	1.200111
C	-4.034268	3.036068	1.049326
N	0.153577	1.854474	-0.936578
C	0.064557	4.175529	-0.345359
H	-2.495601	4.543496	0.786594
C	-2.565440	-2.558593	-0.669912
C	-4.867997	-2.663642	0.002224
H	-5.692832	-0.773838	0.634920
H	-4.746016	3.724676	1.508287
C	1.382260	2.030641	-1.426839
C	1.357031	4.355073	-0.835701
H	-0.485106	5.013779	0.083010
C	-3.721920	-3.309130	-0.490284
H	-1.652592	-3.009110	-1.065031
H	-5.795067	-3.218603	0.160605
C	2.031221	3.264305	-1.391359
H	1.851584	1.149570	-1.868467
H	1.830822	5.337996	-0.789046
H	-3.726529	-4.372567	-0.732979
H	3.041622	3.360474	-1.791426
C	-0.354575	-1.017985	2.814081
C	-0.460451	-2.491033	2.408375
H	0.525620	-2.898711	2.140873
H	-0.866197	-3.095649	3.239359
H	-1.129369	-2.615154	1.546289
C	-1.736843	-0.474147	3.191092

H	-2.145657	-1.018477	4.061628
H	-1.680407	0.595287	3.442662
H	-2.444636	-0.590044	2.360524
C	0.601913	-0.877789	4.005808
H	0.697706	0.175799	4.308733
H	0.228765	-1.456393	4.869520
H	1.606456	-1.248747	3.750368

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TS-2 E = -5731.42598812 G = -5730.966559

Ni	-0.638095	-0.381647	-0.194520
S	-1.201873	0.172001	2.010094
C	0.677427	-1.233661	1.632491
H	0.415108	-2.085699	0.998582
H	0.555271	-1.500952	2.684100
C	2.031397	-0.658955	1.298727
H	2.368372	0.052913	2.067581
H	1.985342	-0.102348	0.359193
C	3.113211	-1.747899	1.111297
H	2.714269	-2.501594	0.416113
H	3.319752	-2.246289	2.072845
C	4.371959	-1.146649	0.537553
C	5.439312	-0.749638	1.354538
C	4.454998	-0.899483	-0.844418
C	6.565577	-0.123689	0.811030
H	5.387396	-0.935735	2.431410
C	5.578265	-0.273180	-1.388655
H	3.624108	-1.208787	-1.486232
C	6.637951	0.118581	-0.563000
H	7.390340	0.174203	1.463857
H	5.630327	-0.096155	-2.466367
H	7.518559	0.605275	-0.989932
Br	0.687972	-1.784779	-1.800944
N	-2.323321	0.657315	-0.807730
C	-3.510095	0.119268	-0.500649
C	-2.184806	1.963141	-1.058297
C	-3.453907	-1.336433	-0.221142
C	-4.663250	0.911311	-0.452264
C	-0.794669	2.368804	-1.372534
C	-3.289805	2.823010	-1.004408
N	-2.211857	-1.839735	-0.071262
C	-4.586231	-2.157592	-0.155260
H	-5.632240	0.479381	-0.201549
C	-4.540404	2.280296	-0.701690

N	0.150784	1.448861	-1.086372
C	-0.470609	3.597371	-1.961996
H	-3.178443	3.893399	-1.178986
C	-2.046905	-3.149912	0.109765
C	-4.416360	-3.524282	0.061797
H	-5.583326	-1.738167	-0.291805
H	-5.418721	2.926744	-0.648216
C	1.418140	1.692837	-1.426386
C	0.860921	3.867516	-2.273949
H	-1.252221	4.320868	-2.195401
C	-3.123268	-4.034751	0.190428
H	-1.012191	-3.497622	0.165580
H	-5.284352	-4.185235	0.114211
C	1.824459	2.892535	-2.012060
H	2.133953	0.891650	-1.235399
H	1.137788	4.818490	-2.734394
H	-2.944603	-5.100361	0.342736
H	2.876303	3.045908	-2.258312
C	-0.397602	1.563535	2.957858
C	-1.588619	2.369029	3.501167
H	-1.223284	3.220416	4.101731
H	-2.205459	2.761232	2.678404
H	-2.230687	1.746481	4.142927
C	0.453838	2.459560	2.057476
H	-0.154921	2.904475	1.258626
H	0.890317	3.281227	2.651997
H	1.276635	1.907038	1.588980
C	0.423489	1.017576	4.131465
H	1.300838	0.452309	3.790742
H	0.786828	1.849773	4.759364
H	-0.189145	0.353941	4.759933

67

TS-3 E = -6527.90200601 G = -6527.447428

Ni	0.177553	-1.314343	0.284189
S	-0.172419	0.721023	-0.803018
C	-1.914896	-2.103763	-1.450423
H	-2.231817	-2.999553	-1.988450
H	-1.032894	-1.612395	-1.869192
C	-2.985324	-1.188180	-0.955823
H	-2.577761	-0.517120	-0.187970
H	-3.804281	-1.756444	-0.487470
C	-3.549516	-0.281742	-2.080462
H	-4.078441	-0.893457	-2.828894

H	-2.698262	0.202305	-2.583470
C	-4.467704	0.771541	-1.509583
C	-3.923308	1.881397	-0.840728
C	-5.861718	0.644823	-1.575186
C	-4.755225	2.839505	-0.259358
H	-2.836021	1.986418	-0.780587
C	-6.696968	1.604363	-0.994647
H	-6.298369	-0.215248	-2.091095
C	-6.145860	2.704946	-0.334091
H	-4.315270	3.699491	0.252321
H	-7.782227	1.491563	-1.060374
H	-6.796930	3.457021	0.118558
Br	-1.208924	-3.522065	0.420774
S	1.590728	1.147003	-1.828687
S	2.805587	2.317108	-0.589863
C	2.220938	4.077748	-0.872528
C	0.767814	4.223244	-0.419745
H	0.447068	5.274234	-0.526989
H	0.099363	3.592699	-1.022099
H	0.647233	3.923047	0.631619
C	2.379821	4.450201	-2.345601
H	2.044460	5.488404	-2.512011
H	3.429734	4.367515	-2.665145
H	1.771703	3.787800	-2.979372
C	3.155310	4.912365	0.011294
H	2.894010	5.979991	-0.079304
H	3.061968	4.628270	1.071379
H	4.208036	4.792853	-0.289628
N	1.798006	-0.737672	1.259764
C	2.981430	-0.863741	0.628629
C	1.643326	0.063163	2.330265
C	2.919824	-1.695616	-0.584101
C	4.118038	-0.220937	1.130710
C	0.252268	0.138679	2.815608
C	2.740541	0.731929	2.876222
N	1.683082	-2.157957	-0.901194
C	4.036220	-2.010023	-1.372868
H	5.080825	-0.315738	0.629555
C	3.992688	0.571252	2.273003
N	-0.648471	-0.573299	2.092915
C	-0.142304	0.873912	3.941303
H	2.627851	1.375994	3.748159
C	1.533334	-2.937252	-1.977792
C	3.871877	-2.808396	-2.498080

H	5.021075	-1.627360	-1.105310
H	4.864793	1.087670	2.677551
C	-1.927208	-0.601060	2.482036
C	-1.480056	0.864997	4.327288
H	0.592598	1.443347	4.510517
C	2.592152	-3.287856	-2.808982
H	0.521595	-3.301943	-2.167246
H	4.729120	-3.059595	-3.126266
C	-2.393554	0.106500	3.587500
H	-2.593761	-1.226671	1.885846
H	-1.805553	1.435416	5.199839
H	2.417822	-3.925774	-3.676725
H	-3.449097	0.059501	3.859404

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TS-4 E = -6527.92613476 G = -6527.468476

Ni	0.286890	-0.964885	-0.129865
S	0.281275	0.036679	-2.179674
C	-0.953461	-1.793506	-2.027624
H	-0.798750	-2.532437	-1.224300
H	-0.530557	-2.179379	-2.958516
C	-2.401452	-1.336179	-2.129129
H	-2.832395	-1.703623	-3.076872
H	-2.438064	-0.235930	-2.220558
C	-3.251304	-1.800880	-0.935326
H	-2.626341	-1.815329	-0.028704
H	-3.531388	-2.859157	-1.086665
C	-4.492122	-0.987960	-0.646099
C	-5.210115	-0.319939	-1.649435
C	-4.936556	-0.862732	0.681510
C	-6.336952	0.447895	-1.337923
H	-4.885893	-0.393994	-2.689786
C	-6.062009	-0.099646	0.996613
H	-4.372226	-1.361358	1.474470
C	-6.767626	0.562308	-0.013921
H	-6.880067	0.960707	-2.136009
H	-6.386401	-0.015160	2.037121
H	-7.647136	1.163453	0.229659
Br	-0.534030	-2.604183	1.547983
S	2.337887	1.107613	-2.003664
S	2.388478	2.479127	-0.465481
C	1.424375	3.978061	-1.063945
C	-0.058423	3.621922	-1.172476
H	-0.627342	4.494712	-1.537376

H	-0.217884	2.783504	-1.864780
H	-0.465831	3.332319	-0.193678
C	1.981875	4.453569	-2.403092
H	1.424152	5.340801	-2.748263
H	3.046031	4.721396	-2.318059
H	1.884514	3.665767	-3.164363
C	1.655578	5.018852	0.037150
H	1.102754	5.941903	-0.204846
H	1.293021	4.654242	1.011737
H	2.722205	5.273870	0.135124
N	1.619771	-0.209489	1.179517
C	2.855240	-0.716353	1.189060
C	1.211548	0.693546	2.075622
C	3.117267	-1.723000	0.134189
C	3.781791	-0.305095	2.155646
C	-0.172122	1.179690	1.870297
C	2.078901	1.136036	3.079841
N	2.044652	-2.089557	-0.593817
C	4.381005	-2.277683	-0.101001
H	4.791800	-0.712489	2.175015
C	3.377874	0.628900	3.108872
N	-0.828733	0.626084	0.832266
C	-0.763842	2.172432	2.659323
H	1.756101	1.869091	3.817849
C	2.181695	-3.001832	-1.554799
C	4.525664	-3.229346	-1.107921
H	5.242492	-1.961690	0.486577
H	4.077598	0.961733	3.878014
C	-2.055721	1.045740	0.533640
C	-2.063069	2.588151	2.365716
H	-0.218684	2.617639	3.491215
C	3.404540	-3.604763	-1.849177
H	1.278914	-3.259594	-2.110500
H	5.503375	-3.670899	-1.312121
C	-2.724953	2.017111	1.279930
H	-2.526881	0.597256	-0.336582
H	-2.545815	3.355138	2.975136
H	3.469771	-4.348015	-2.645180
H	-3.740779	2.302927	1.004142

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TS-6 E = -6129.66327297 G = -6129.206782

Ni	0.626423	0.601612	0.542627
S	-0.313577	-0.615622	-1.197206

C	-1.189631	-0.769765	2.194630
H	-1.200558	-1.100888	3.234955
H	-0.510904	-1.341414	1.556215
C	-2.490151	-0.389428	1.574286
H	-2.297690	0.173194	0.651898
H	-3.083453	0.245193	2.251184
C	-3.319220	-1.633228	1.155097
H	-3.656554	-2.181544	2.049322
H	-2.666732	-2.309254	0.580479
C	-4.496496	-1.232321	0.300845
C	-4.284812	-0.850008	-1.035340
C	-5.798037	-1.180891	0.817103
C	-5.352977	-0.433739	-1.831402
H	-3.268969	-0.876692	-1.440918
C	-6.869441	-0.765406	0.020042
H	-5.974899	-1.474085	1.856041
C	-6.649823	-0.390332	-1.307435
H	-5.172981	-0.144449	-2.870172
H	-7.879067	-0.736559	0.438141
H	-7.485976	-0.067621	-1.932963
Br	-0.034000	1.280983	2.945641
N	2.131873	1.477096	-0.413423
C	3.323645	0.844794	-0.416666
C	1.853857	2.465485	-1.287430
C	3.411087	-0.268075	0.541408
C	4.328688	1.231996	-1.308722
C	0.481474	2.994896	-1.172246
C	2.817501	2.896385	-2.201868
N	2.246988	-0.585354	1.163368
C	4.589894	-0.984487	0.794401
H	5.291799	0.721821	-1.320015
C	4.071363	2.273616	-2.204086
N	-0.302760	2.356025	-0.271929
C	-0.004182	4.079595	-1.916578
H	2.599261	3.696367	-2.909205
C	2.225901	-1.611276	2.020757
C	4.561908	-2.049569	1.687837
H	5.518178	-0.706556	0.295300
H	4.838805	2.589587	-2.912874
C	-1.553805	2.779158	-0.071729
C	-1.313612	4.507661	-1.717713
H	0.638368	4.585626	-2.637283
C	3.351984	-2.375856	2.312559
H	1.268813	-1.824643	2.496886

H	5.469749	-2.619414	1.896499
C	-2.107187	3.848231	-0.772767
H	-2.126295	2.242826	0.686332
H	-1.709911	5.350488	-2.288091
H	3.279909	-3.204232	3.018721
H	-3.136387	4.153587	-0.578581
S	-0.143999	-2.637790	-0.684972
C	1.124187	-3.322795	-1.884871
C	2.456364	-2.598331	-1.711124
H	3.188445	-2.961070	-2.453500
H	2.322045	-1.516502	-1.856110
H	2.869168	-2.768774	-0.707364
C	0.598507	-3.163719	-3.311443
H	1.327976	-3.568667	-4.034535
H	-0.355965	-3.695589	-3.441489
H	0.433812	-2.100358	-3.541279
C	1.245247	-4.800259	-1.499222
H	0.277480	-5.317792	-1.590371
H	1.965428	-5.303413	-2.166123
H	1.602385	-4.912439	-0.463293

66

TS-7 E = -6129.67863623 G = -6129.220185

Ni	0.723646	-0.726843	0.022530
S	0.728867	0.526037	-1.960565
C	-0.586362	-1.218215	-1.956219
H	-0.360608	-2.069362	-1.295277
H	-0.236215	-1.452132	-2.969491
C	-2.028140	-0.790040	-1.825054
H	-2.341587	-0.203462	-2.703393
H	-2.111815	-0.098206	-0.976996
C	-2.999780	-1.970564	-1.572103
H	-2.472556	-2.732736	-0.979023
H	-3.281668	-2.438880	-2.529985
C	-4.223490	-1.526066	-0.809518
C	-5.254722	-0.806382	-1.431965
C	-4.305129	-1.749209	0.575003
C	-6.334850	-0.316630	-0.693725
H	-5.207738	-0.625868	-2.509817
C	-5.384064	-1.258963	1.316953
H	-3.505325	-2.308322	1.069646
C	-6.401967	-0.538121	0.685484
H	-7.129528	0.240260	-1.197053
H	-5.431385	-1.447321	2.392861

H	-7.247876	-0.156932	1.262998
Br	-0.183605	-2.681139	1.280794
S	1.225330	2.580415	-1.117907
N	2.169728	0.288465	0.985221
C	3.443531	0.020885	0.668628
C	1.818745	1.371281	1.686635
C	3.621362	-1.201429	-0.152704
C	4.470899	0.865281	1.100483
C	0.359213	1.502956	1.909219
C	2.799424	2.250090	2.166585
N	2.477766	-1.790264	-0.553864
C	4.869908	-1.739374	-0.486667
H	5.510214	0.664924	0.842095
C	4.133255	1.986434	1.864475
N	-0.401223	0.588845	1.274531
C	-0.208459	2.453246	2.766209
H	2.525794	3.134496	2.740539
C	2.521284	-2.918219	-1.260356
C	4.919561	-2.908494	-1.244799
H	5.789079	-1.259112	-0.151199
H	4.915867	2.663458	2.212649
C	-1.714303	0.553509	1.500118
C	-1.587852	2.442288	2.969467
H	0.419293	3.183586	3.276282
C	3.725172	-3.514965	-1.637448
H	1.556670	-3.361794	-1.518164
H	5.882302	-3.346338	-1.517110
C	-2.358183	1.467780	2.333775
H	-2.270989	-0.245038	1.012573
H	-2.051565	3.178072	3.630168
H	3.719806	-4.437400	-2.220142
H	-3.438178	1.400853	2.473114
C	-0.220437	3.614004	-1.680624
C	-1.511335	3.113252	-1.030268
H	-2.368030	3.725228	-1.362378
H	-1.705349	2.069167	-1.309946
H	-1.451257	3.172460	0.065608
C	-0.329577	3.571889	-3.206412
H	-1.171401	4.200609	-3.545879
H	0.594227	3.941028	-3.676776
H	-0.501853	2.542183	-3.551499
C	0.102086	5.035214	-1.199928
H	-0.707827	5.723192	-1.497942
H	0.195336	5.071168	-0.103101

H	1.042456	5.402493	-1.639124

35

P E = -1304.16941973 G = -1303.917428

S	1.502866	0.858701	0.860215
S	3.312402	1.124972	-0.122598
C	0.337663	0.503067	-0.523143
H	0.396752	1.335906	-1.239948
H	0.659847	-0.413925	-1.037479
C	-1.074990	0.352281	0.032114
H	-1.103001	-0.468710	0.768604
H	-1.362799	1.266538	0.578131
C	-2.108332	0.075355	-1.073294
H	-1.818011	-0.838589	-1.618142
H	-2.082502	0.900074	-1.805069
C	-3.507172	-0.079264	-0.526984
C	-3.987292	-1.335057	-0.126756
C	-4.338685	1.037668	-0.356518
C	-5.262446	-1.473233	0.426653
H	-3.352764	-2.216875	-0.254693
C	-5.614509	0.905020	0.196430
H	-3.980844	2.024178	-0.665189
C	-6.080784	-0.352232	0.590631
H	-5.619887	-2.460941	0.728416
H	-6.248739	1.786779	0.317340
H	-7.079419	-0.458392	1.021041
C	4.159248	-0.550830	-0.021874
C	4.439180	-0.893427	1.441157
H	3.499776	-0.968133	2.009318
H	4.958748	-1.864556	1.509733
H	5.070158	-0.126621	1.914413
C	3.301107	-1.629068	-0.680742
H	2.351271	-1.753977	-0.139790
H	3.081630	-1.380446	-1.729854
H	3.830497	-2.596707	-0.656477
C	5.463272	-0.333464	-0.798184
H	6.068177	0.470552	-0.350604
H	6.061976	-1.258946	-0.777768
H	5.267275	-0.076870	-1.850804

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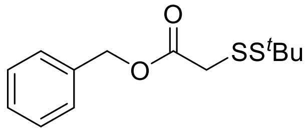
VII. NMR spectrum of the products



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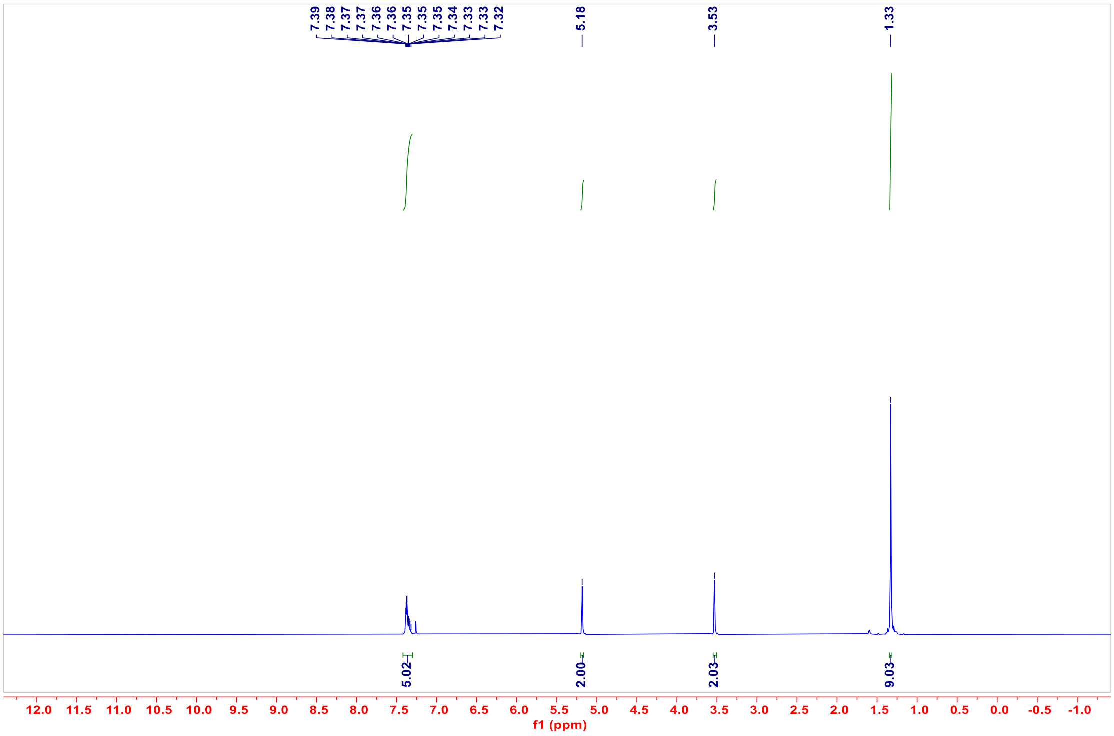

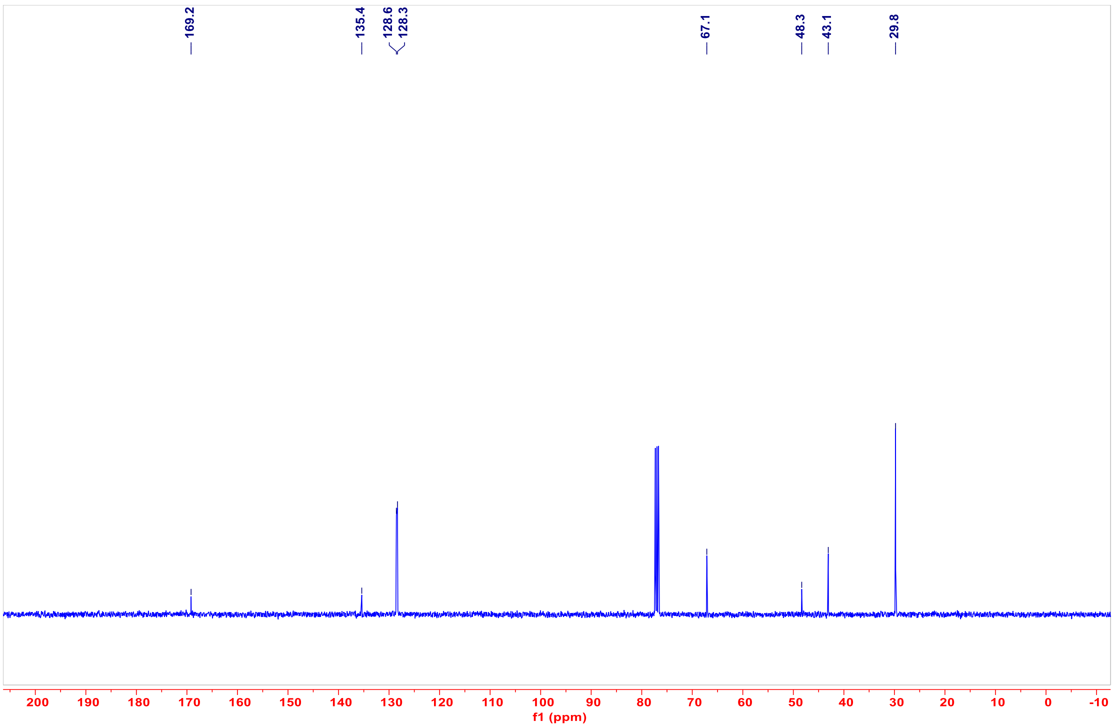

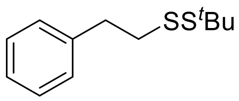

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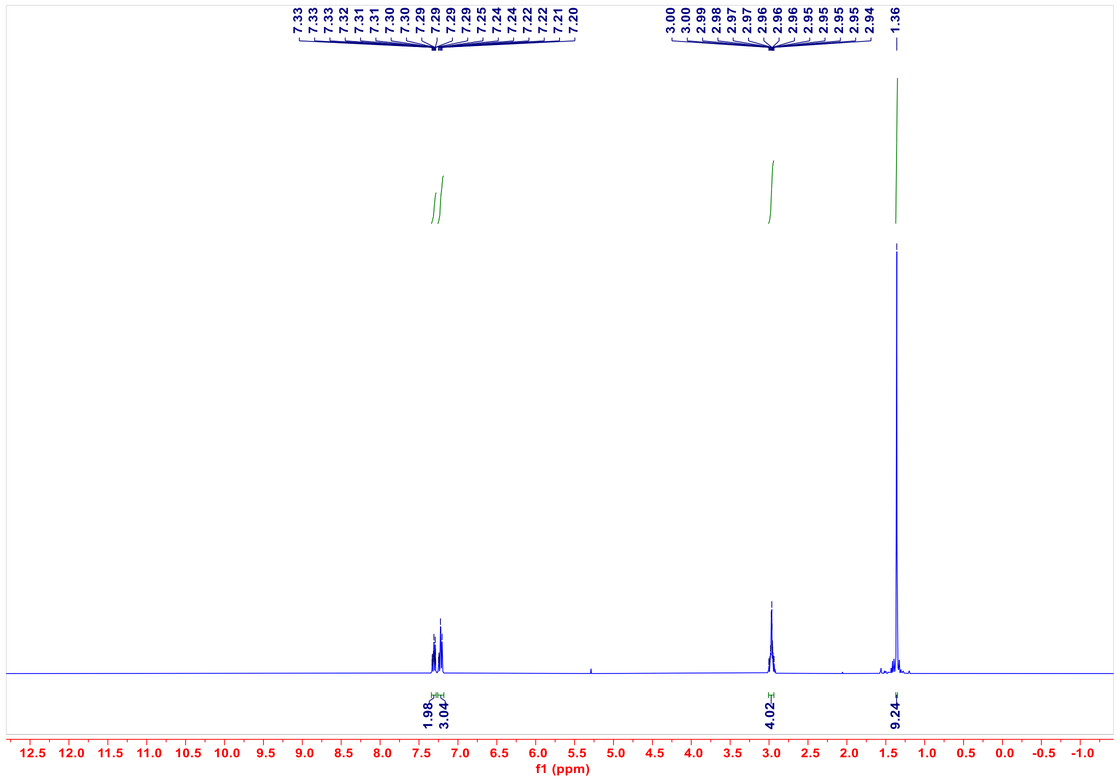
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7.31
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7.30
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7.29
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7.24
7.24
7.22
7.22
7.21
7.20
3.00
3.00
2.99
2.98
2.97
2.97
2.96
2.96
2.96
2.96
2.95
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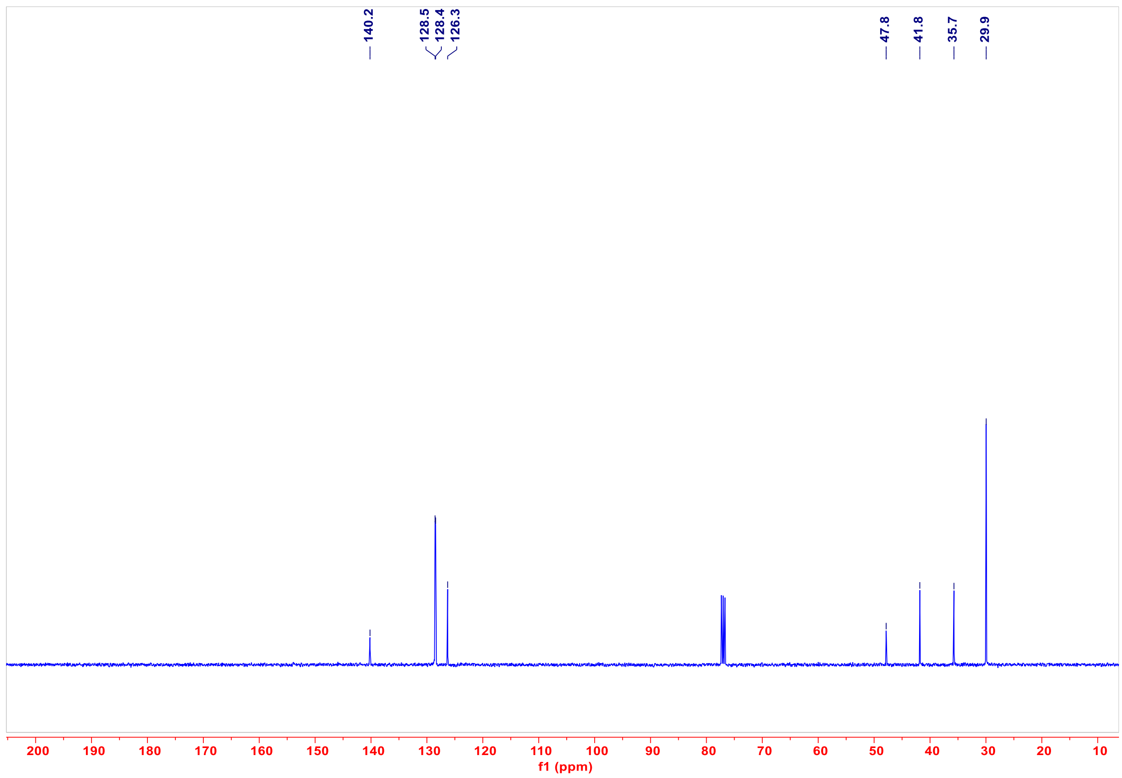
2.95
2.95
2.94
1.36
1.98
3.04
4.02
9.24
f1 (ppm)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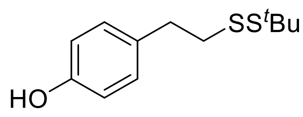
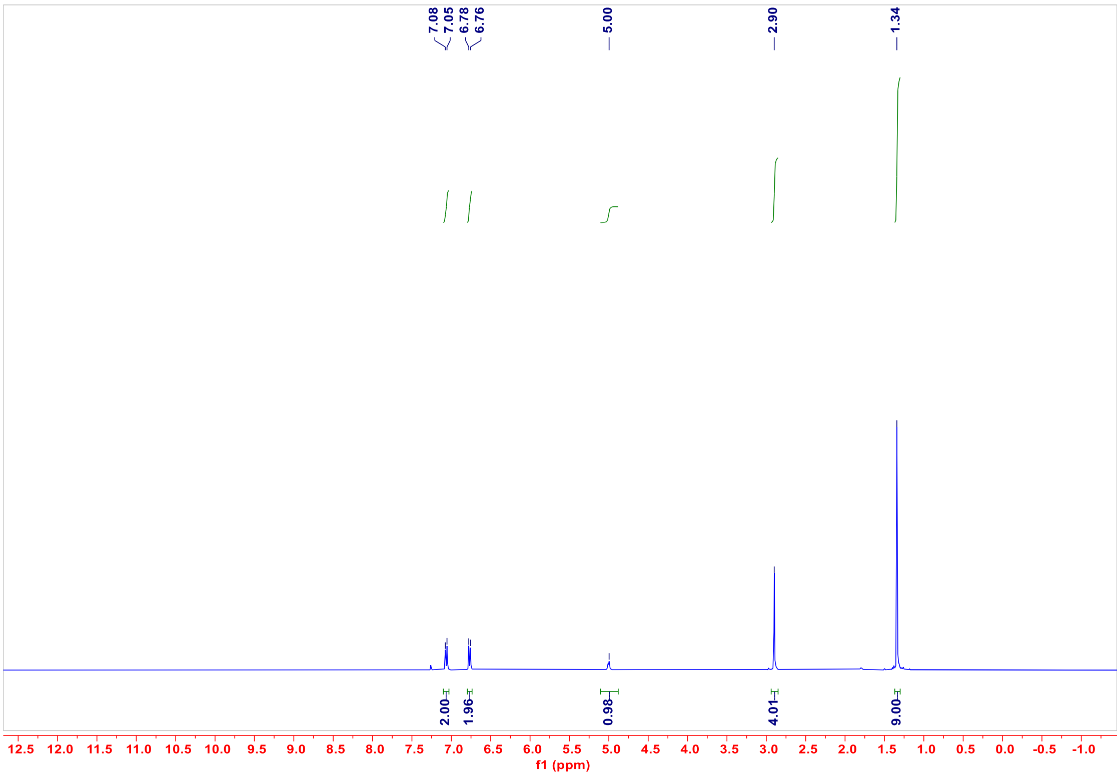

SS^tBu
HO

3ac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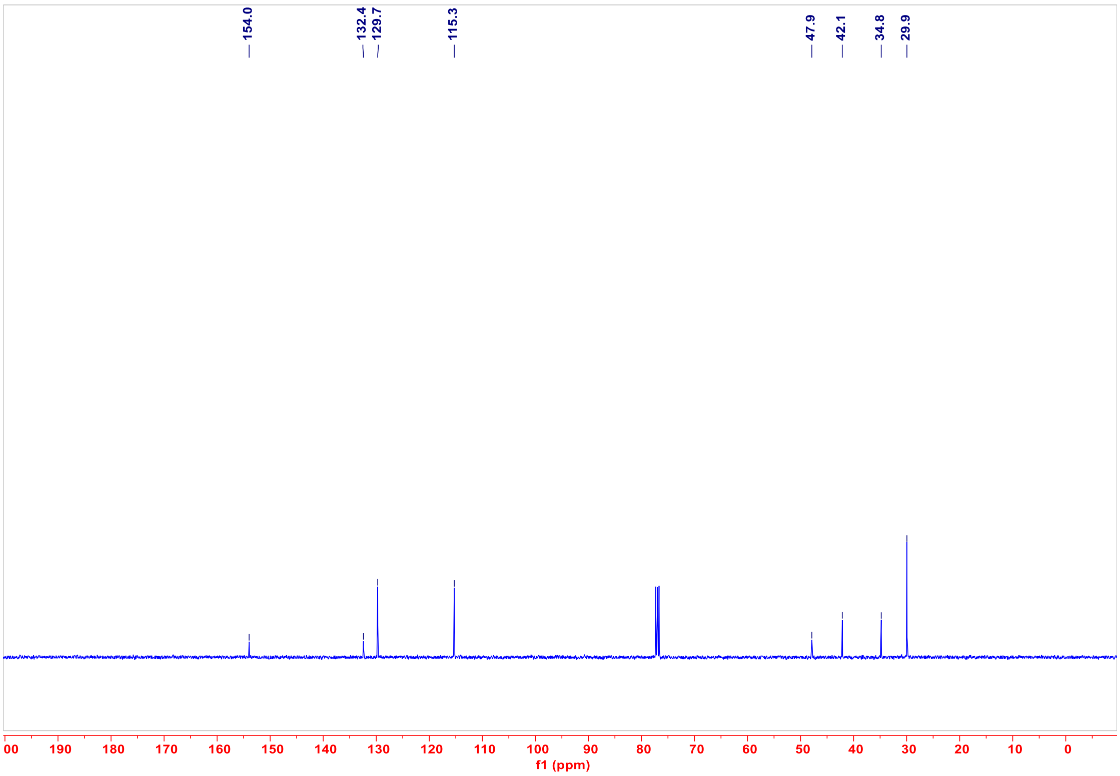
6.76
5.00
2.90
1.34
2.00
1.96
0.98
4.01
9.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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132.4
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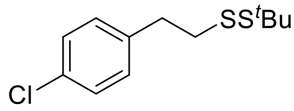
f1 (ppm)



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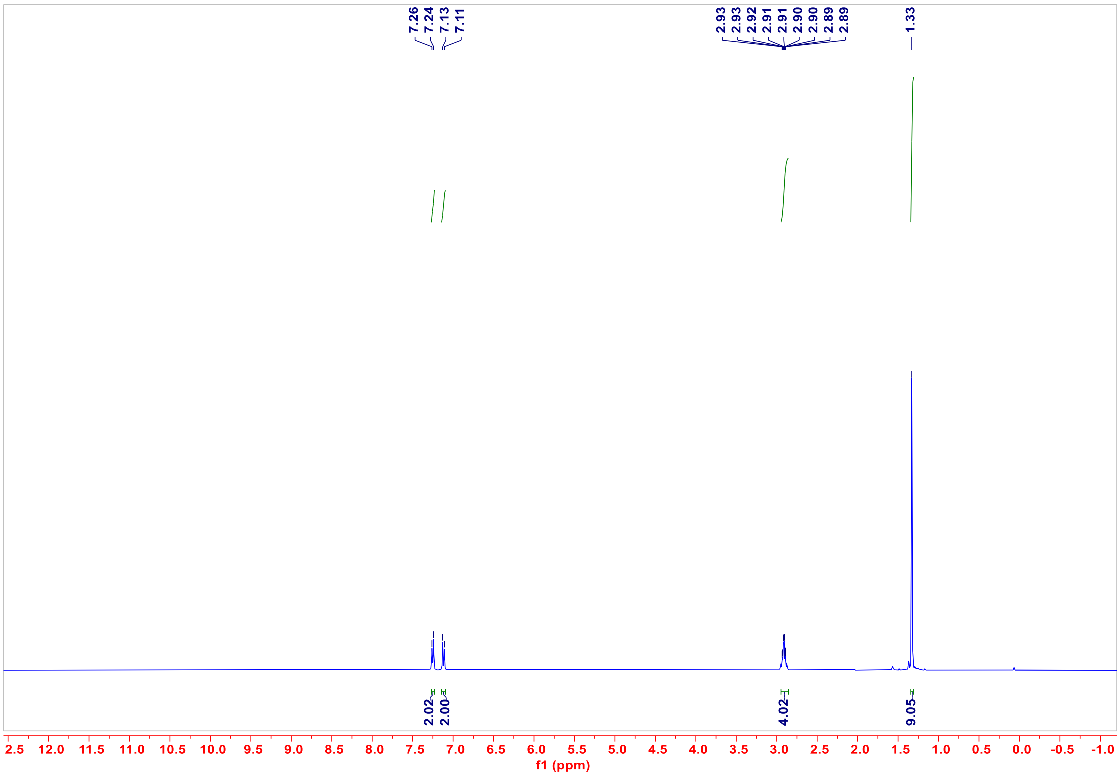

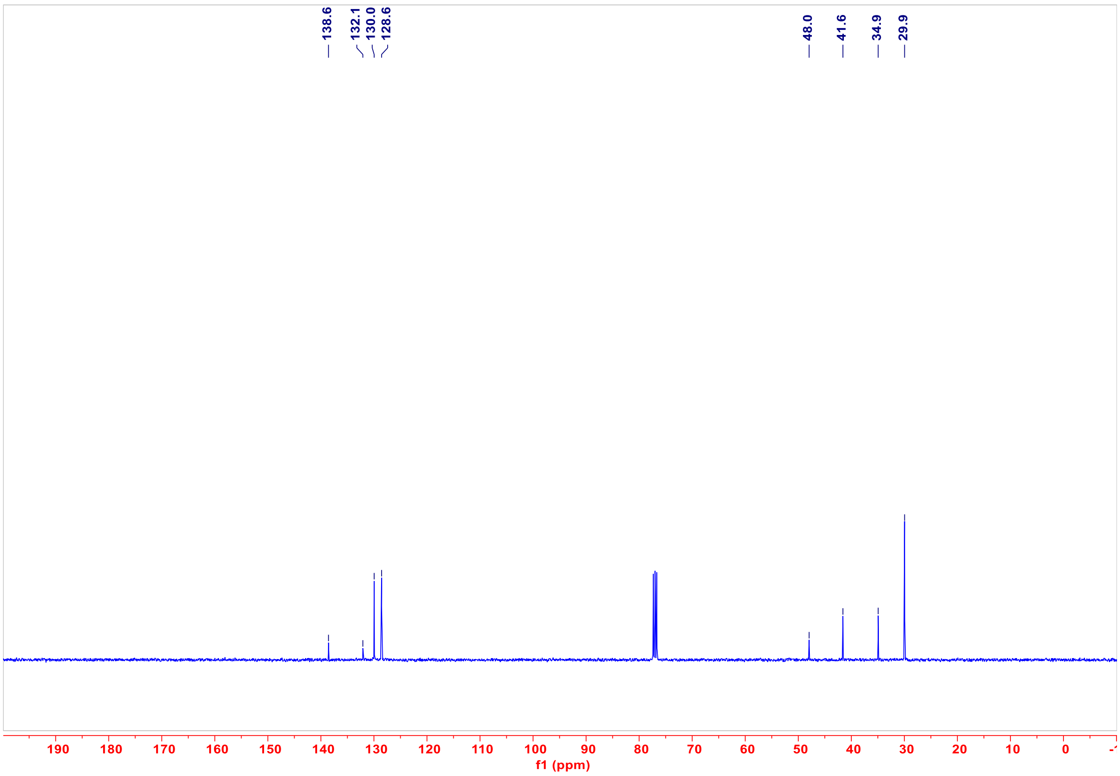

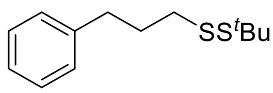
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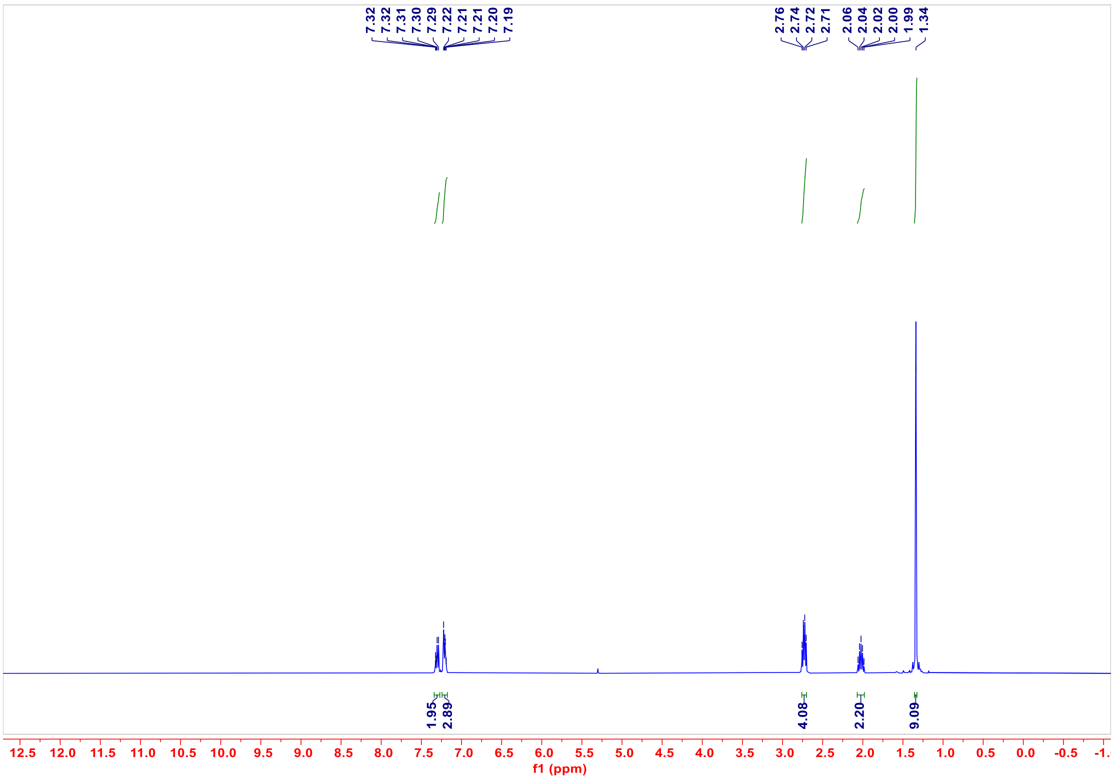
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7.19
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2.72
2.71
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1.95
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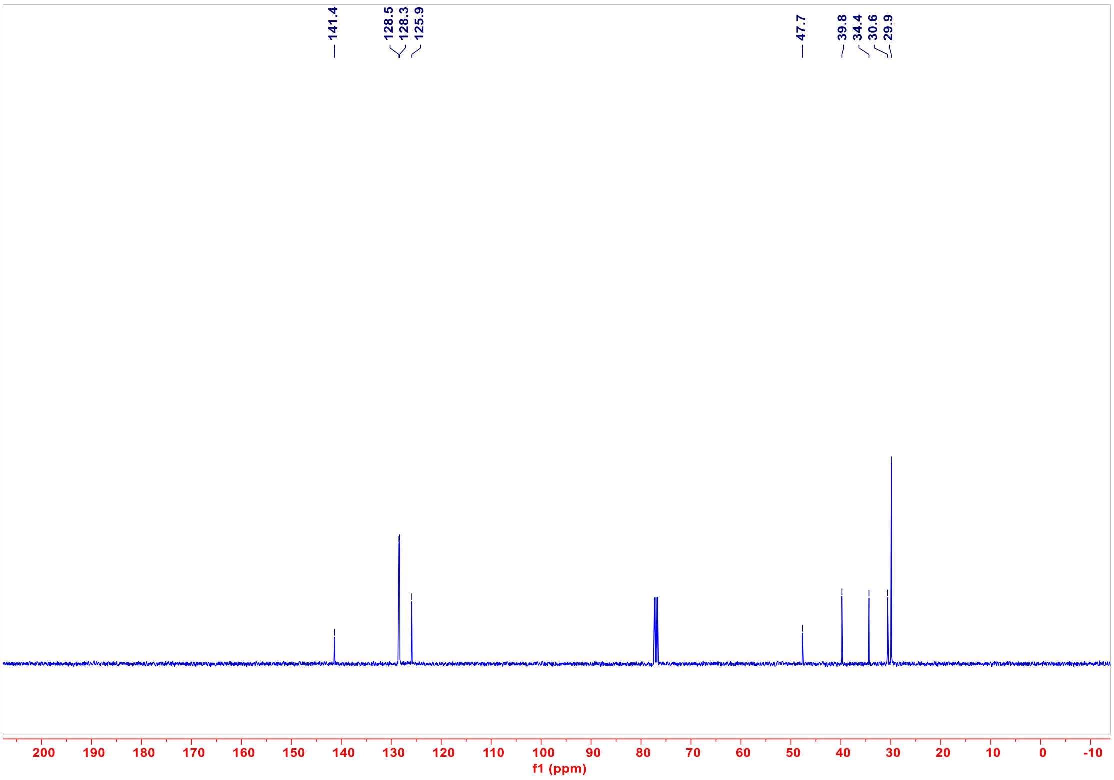
4.08
2.20
9.09
f1 (ppm)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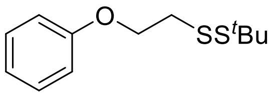
O
SS^{t}Bu

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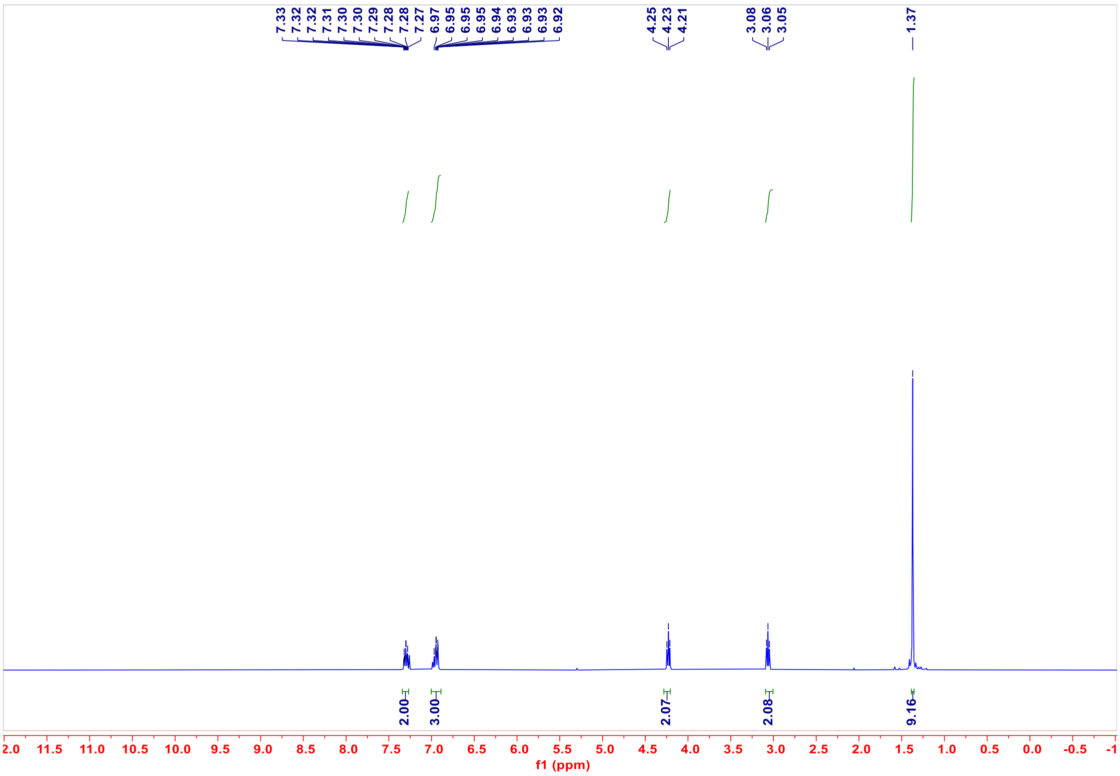
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6.94
6.93
6.93
6.93
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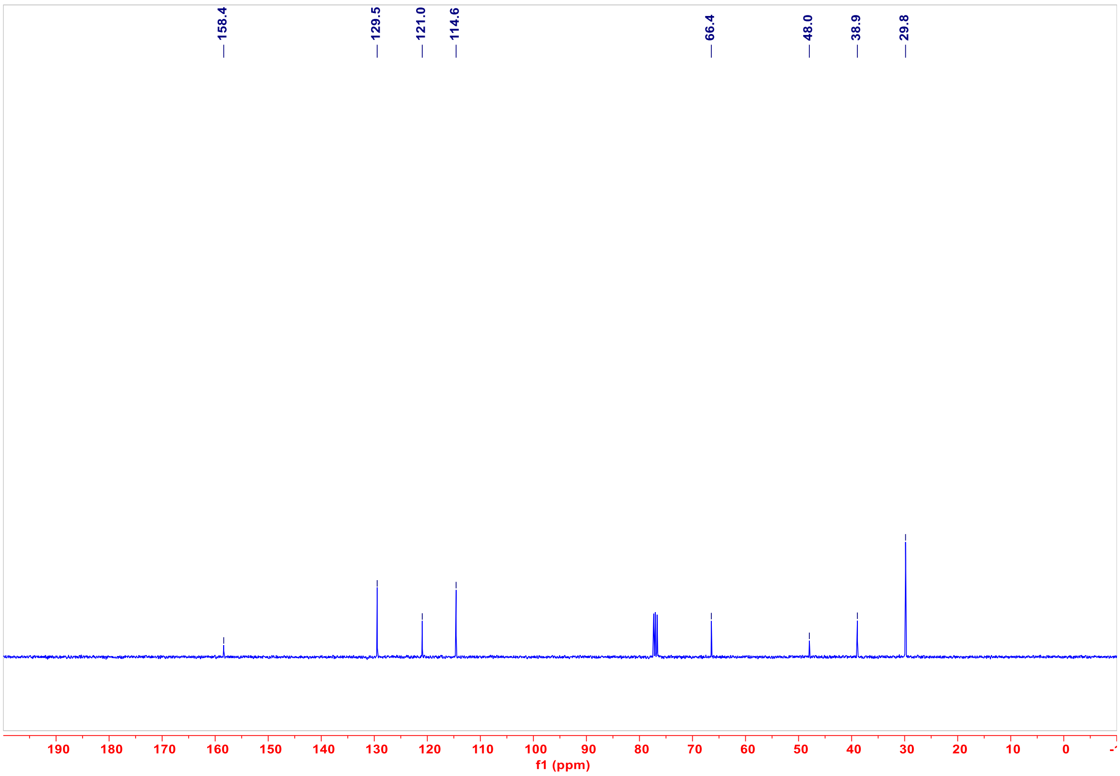
2.08
9.16
f1 (ppm)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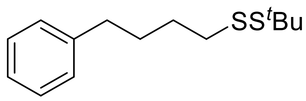
SS^{t}Bu

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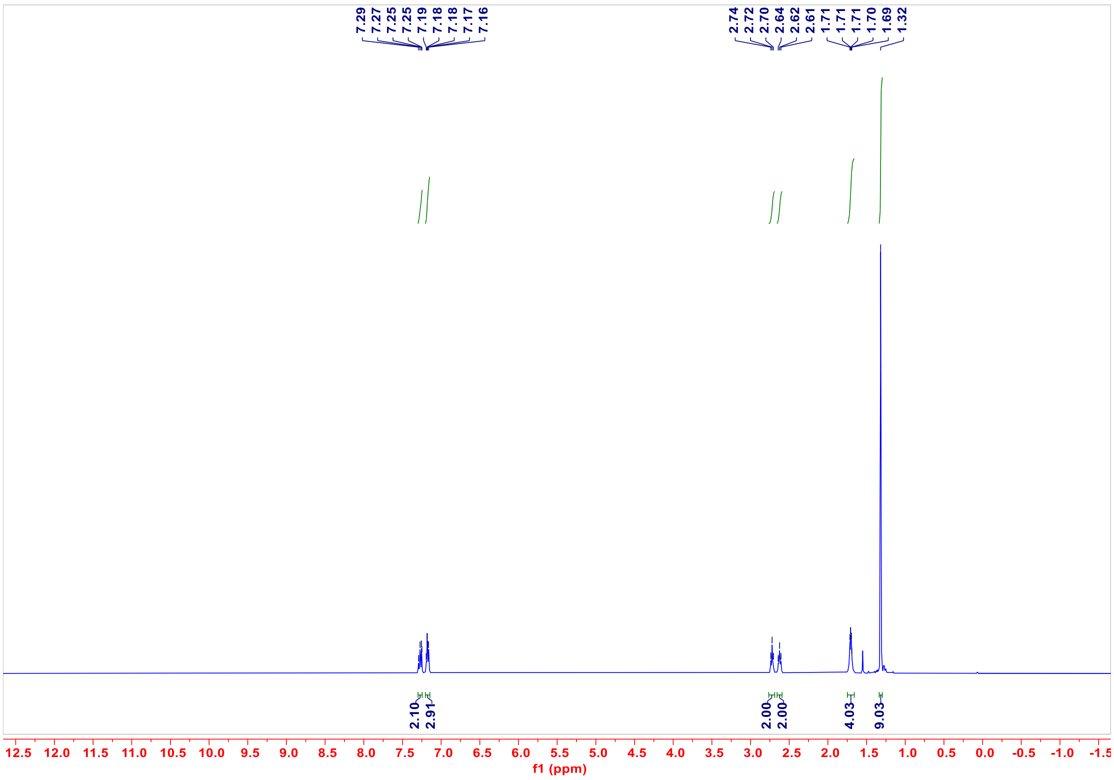
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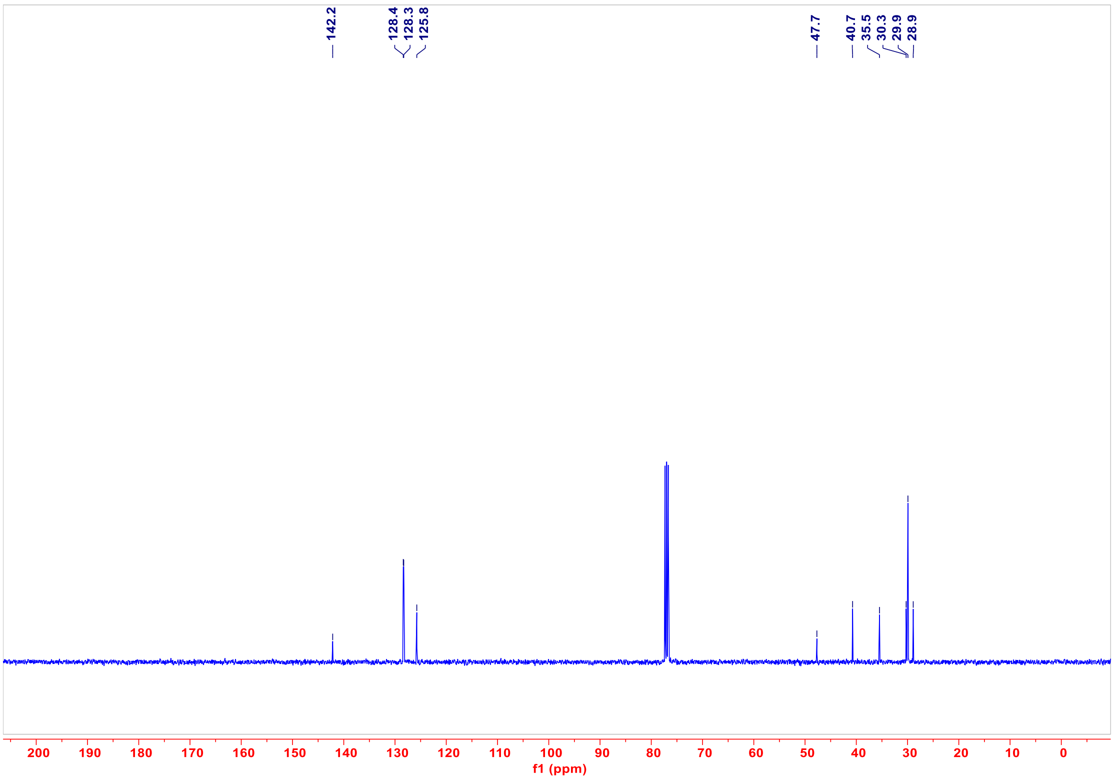
2.62
2.61
1.71
1.71
1.71
1.70
1.69
1.32
2.10
2.91
2.00
2.00
4.03
9.03
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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35.5
30.3
29.9
28.9
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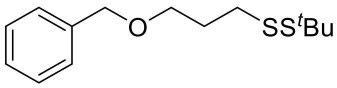
f1 (ppm)



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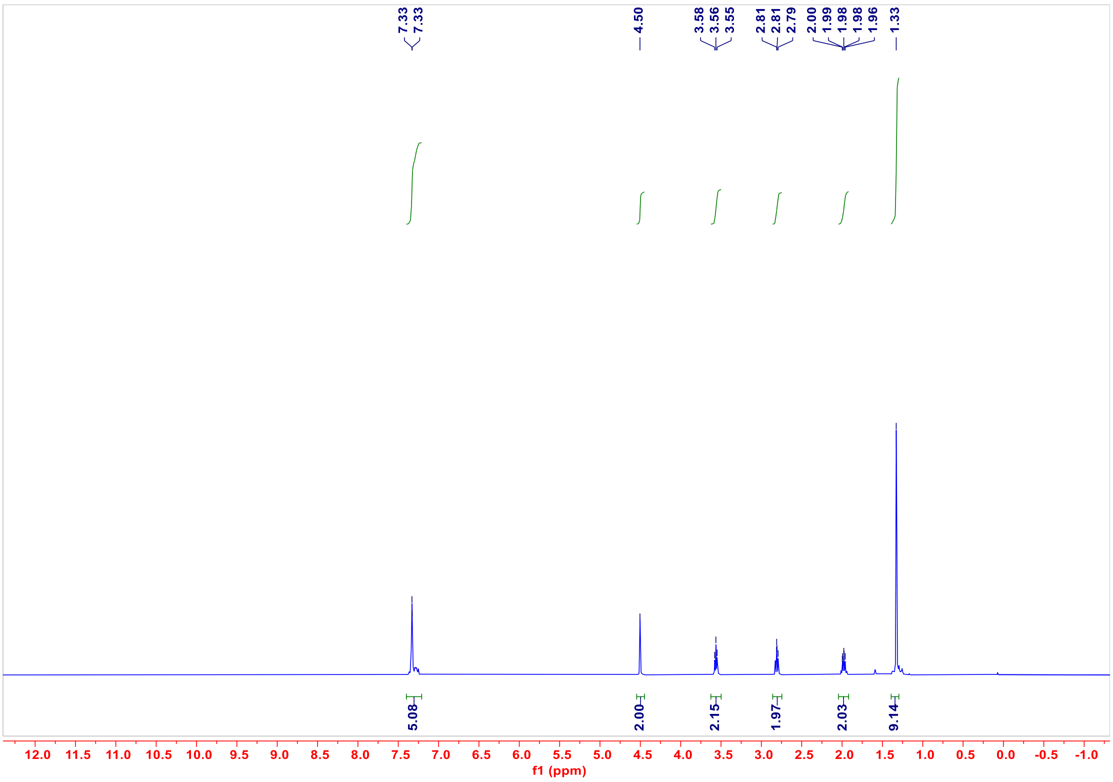

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2.81
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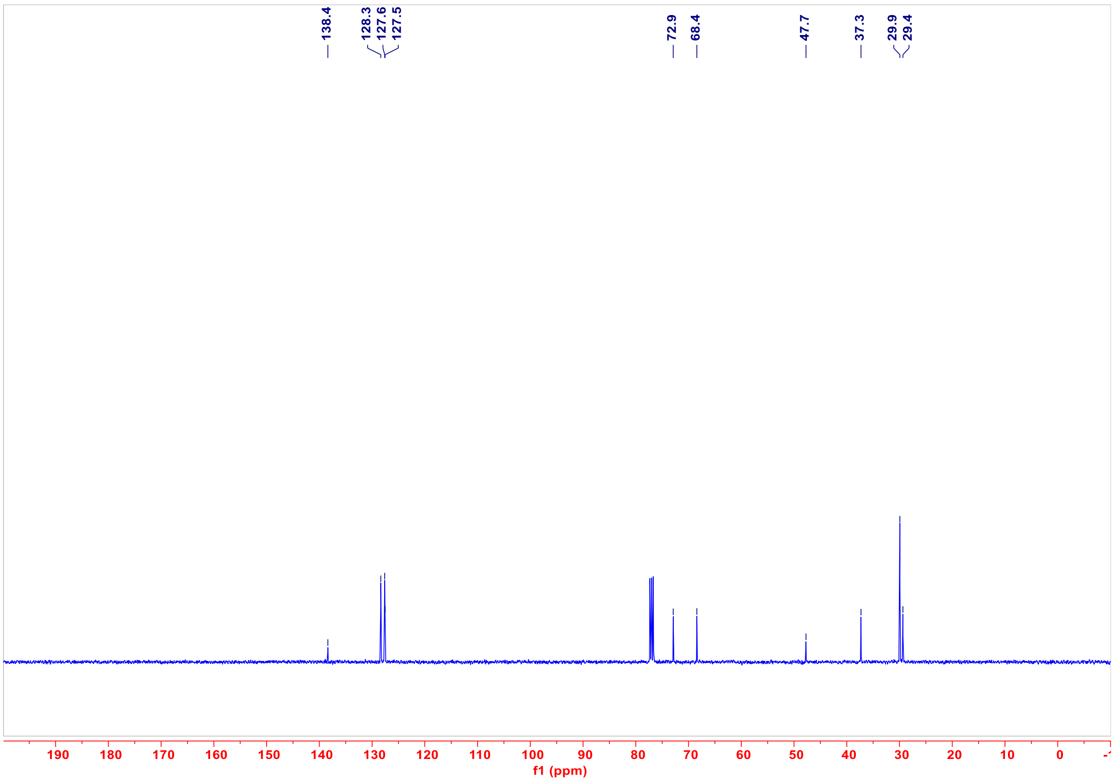
1.97
2.03
9.14
f1 (ppm)



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29.4
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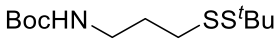

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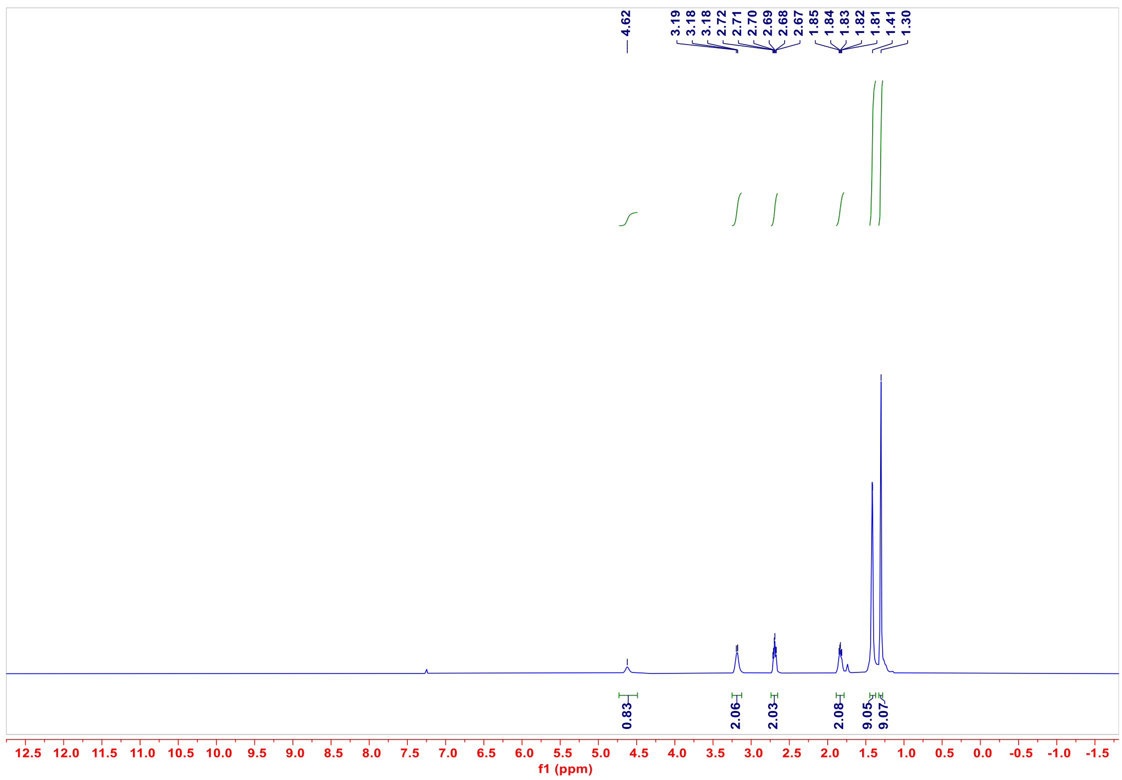
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2.03
2.08
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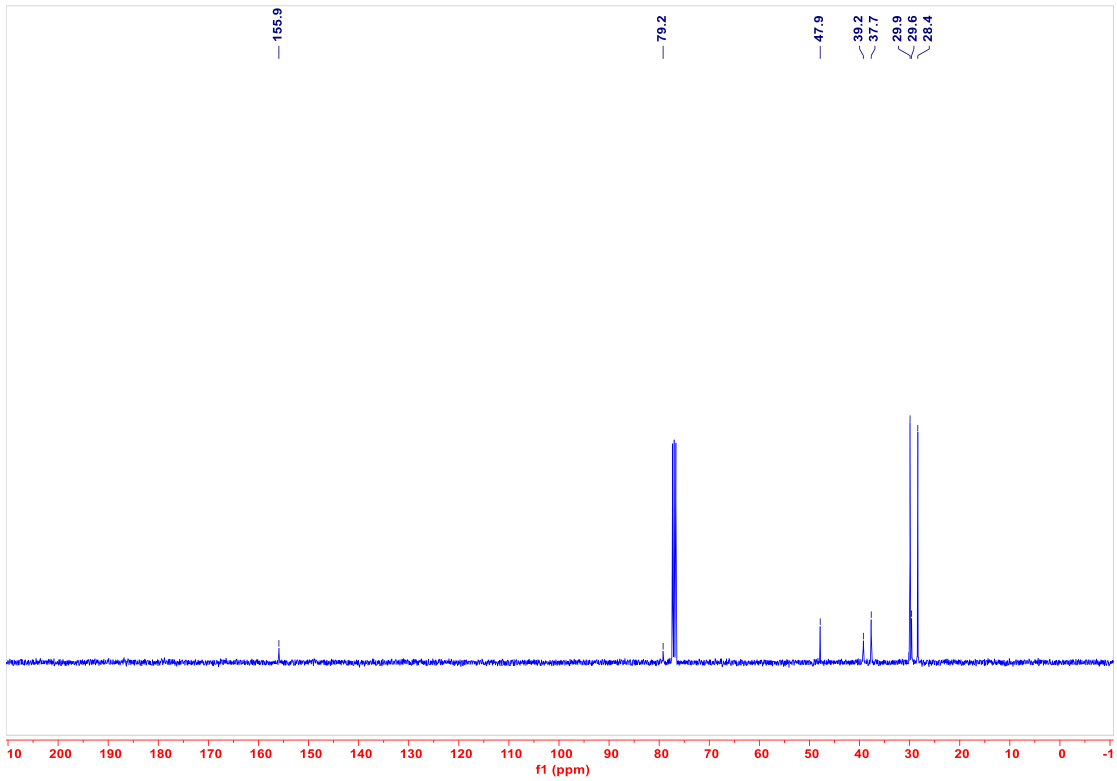
9.07
f1 (ppm)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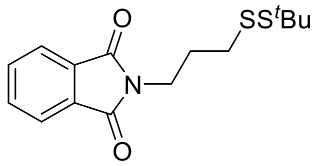
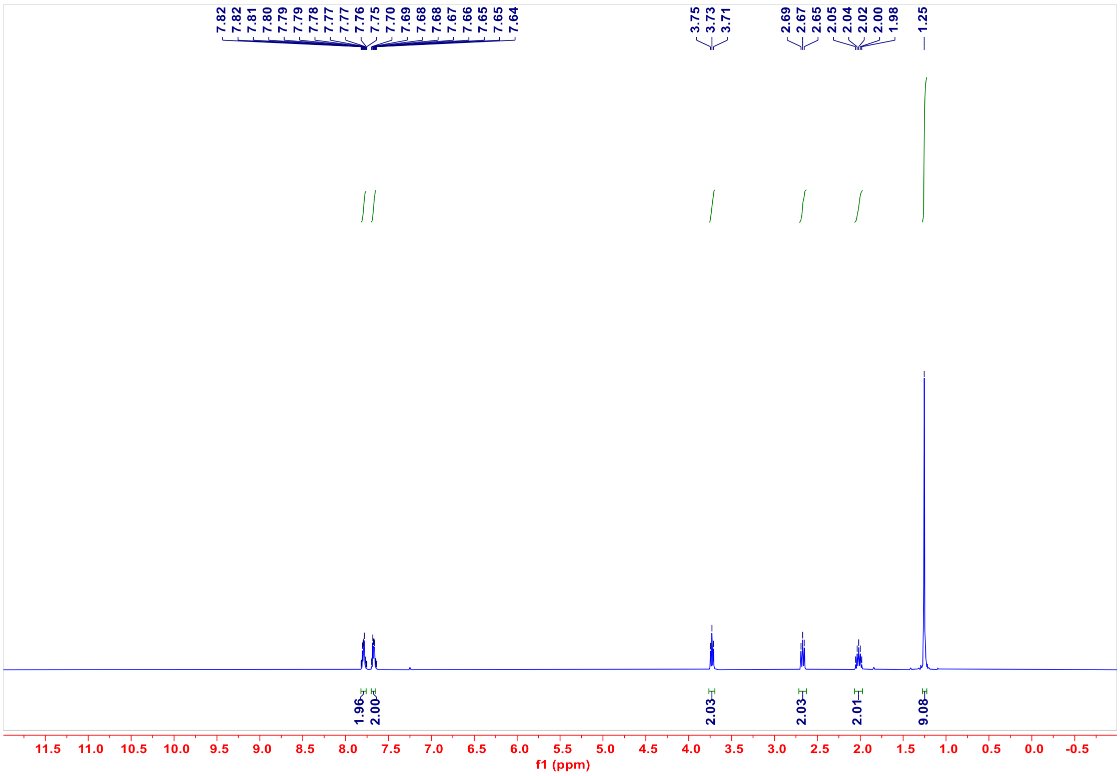

O
SS^{t}Bu
N
O

3aj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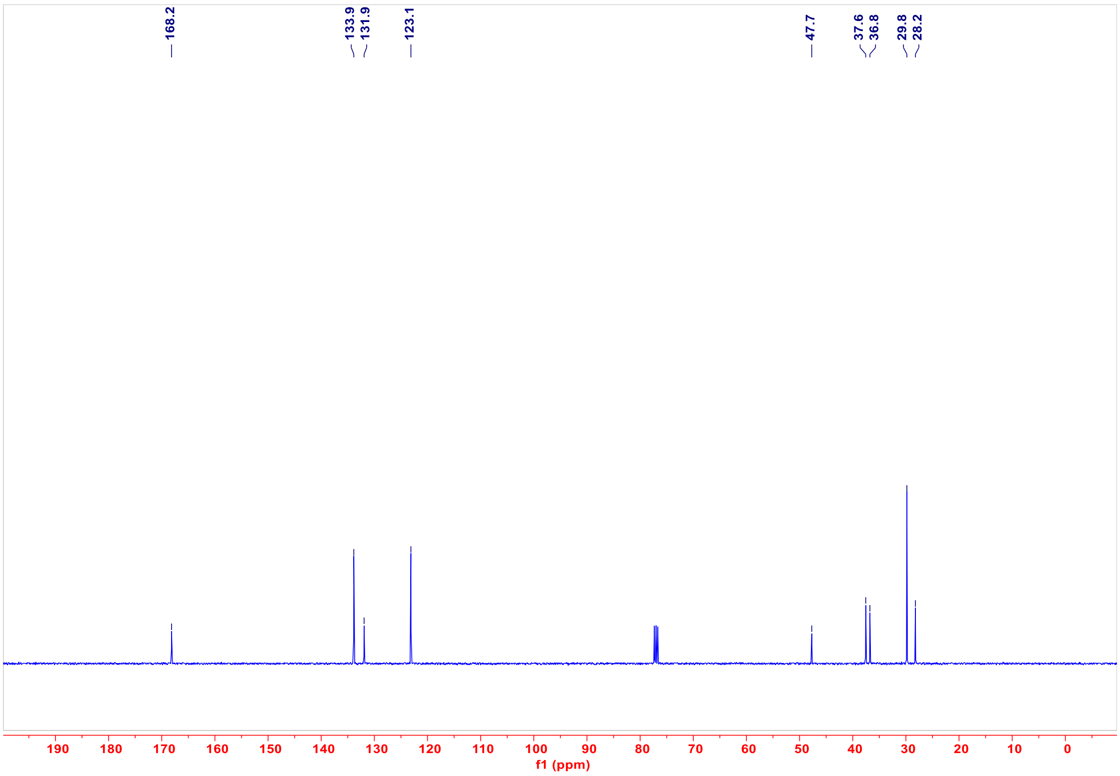
7.69
7.68
7.68
7.67
7.66
7.65
7.65
7.64
3.75
3.73
3.71
2.69
2.67
2.65
2.05
2.04
2.02
2.00
1.98
1.25
1.96
2.00
2.03
2.03
2.01
9.08
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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131.9
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37.6
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29.8
28.2
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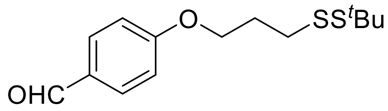
f1 (ppm)



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O
SS^{t}Bu

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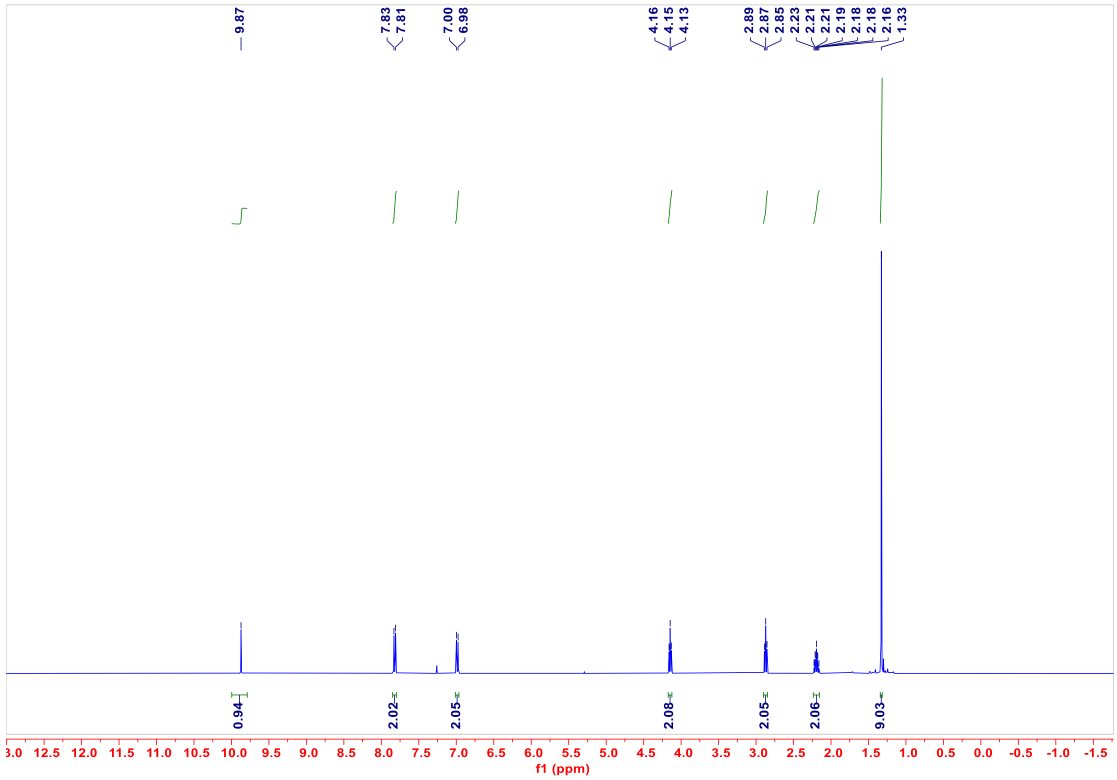

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2.87
2.85
2.23
2.21
2.21
2.19
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2.05
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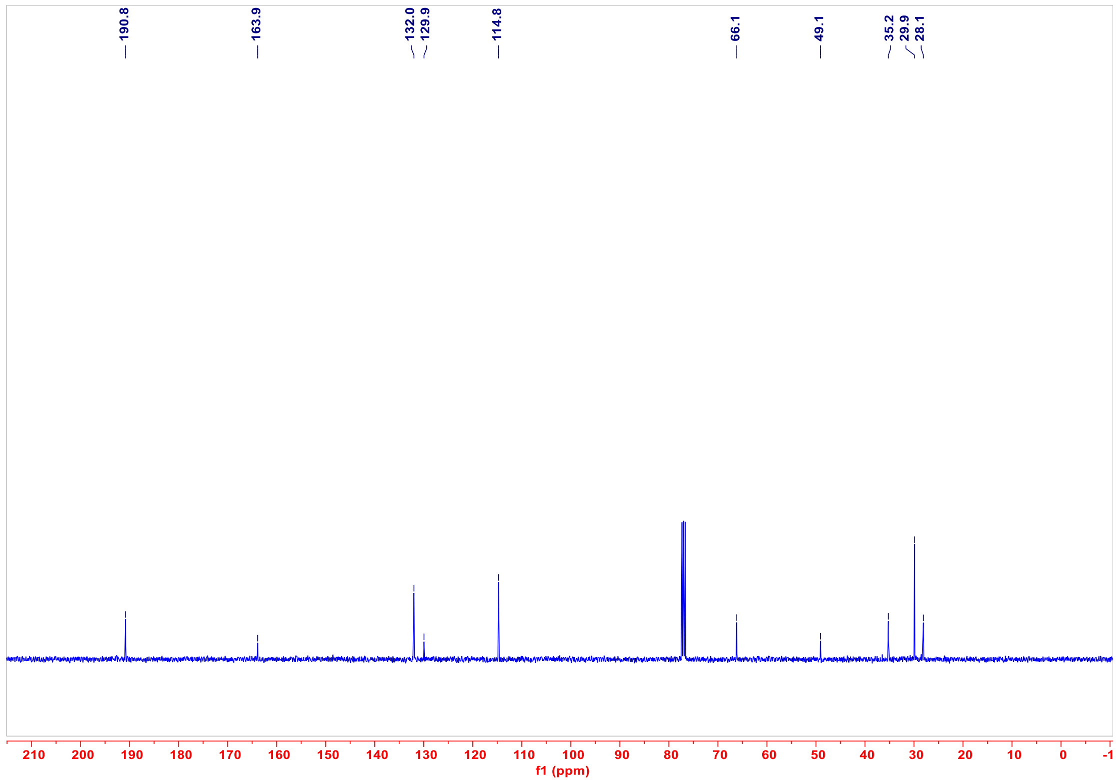
f1 (ppm)



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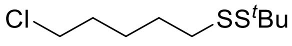
28.1
f1 (ppm)


Cl
SS^{t}Bu

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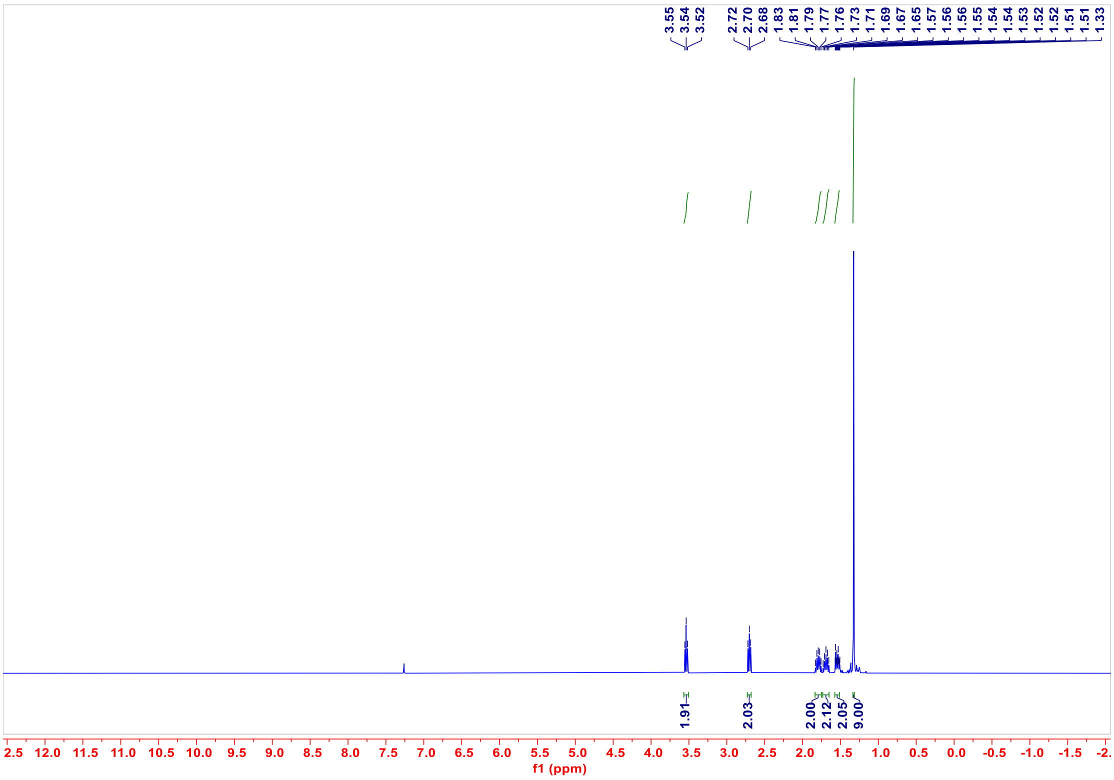
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1.67
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1.54
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1.53
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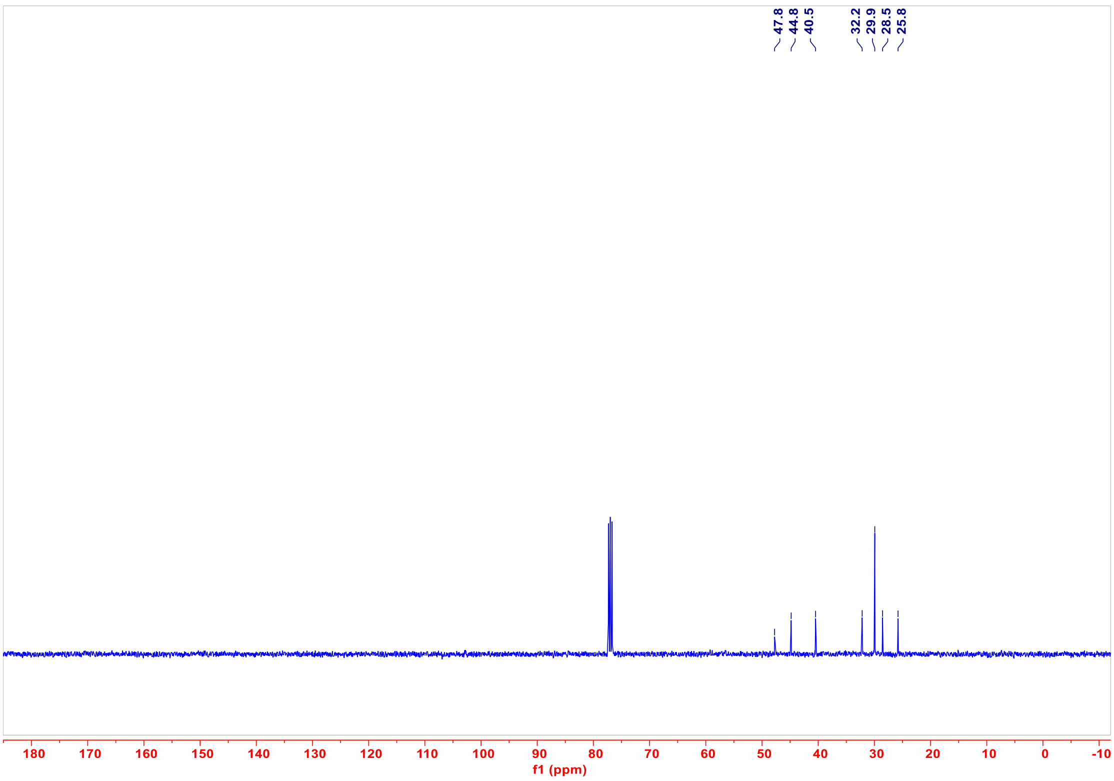
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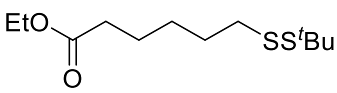

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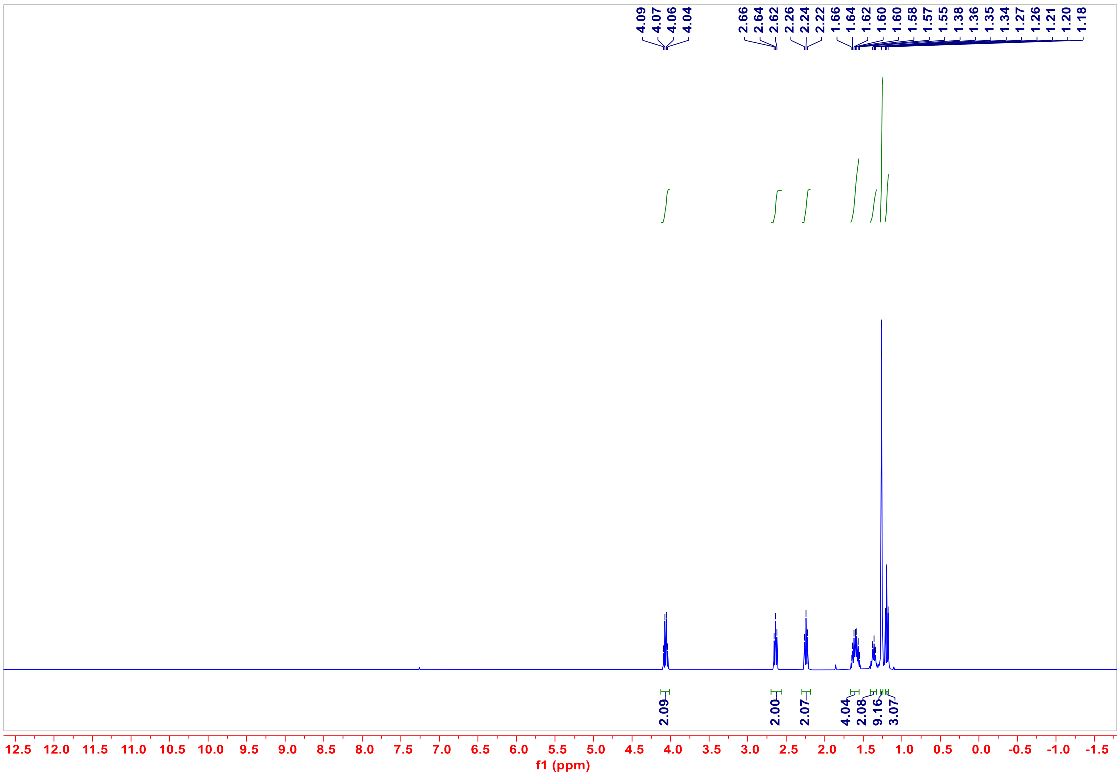

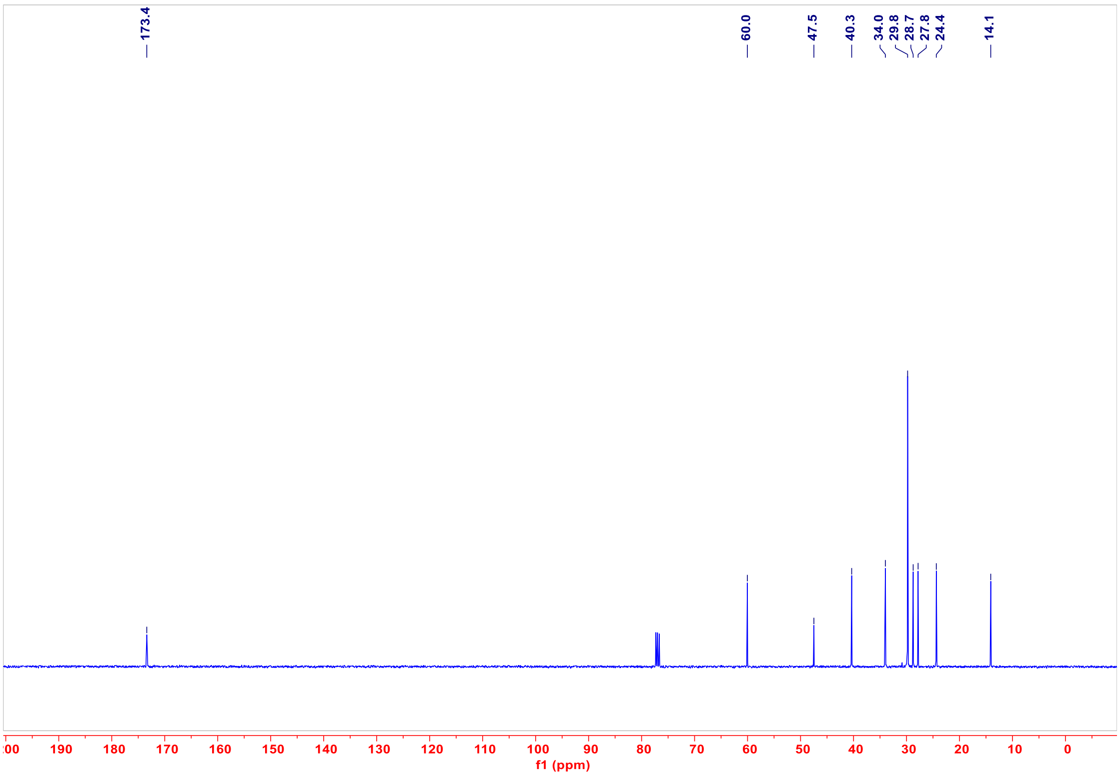

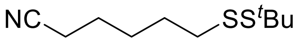
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SS^{t}Bu

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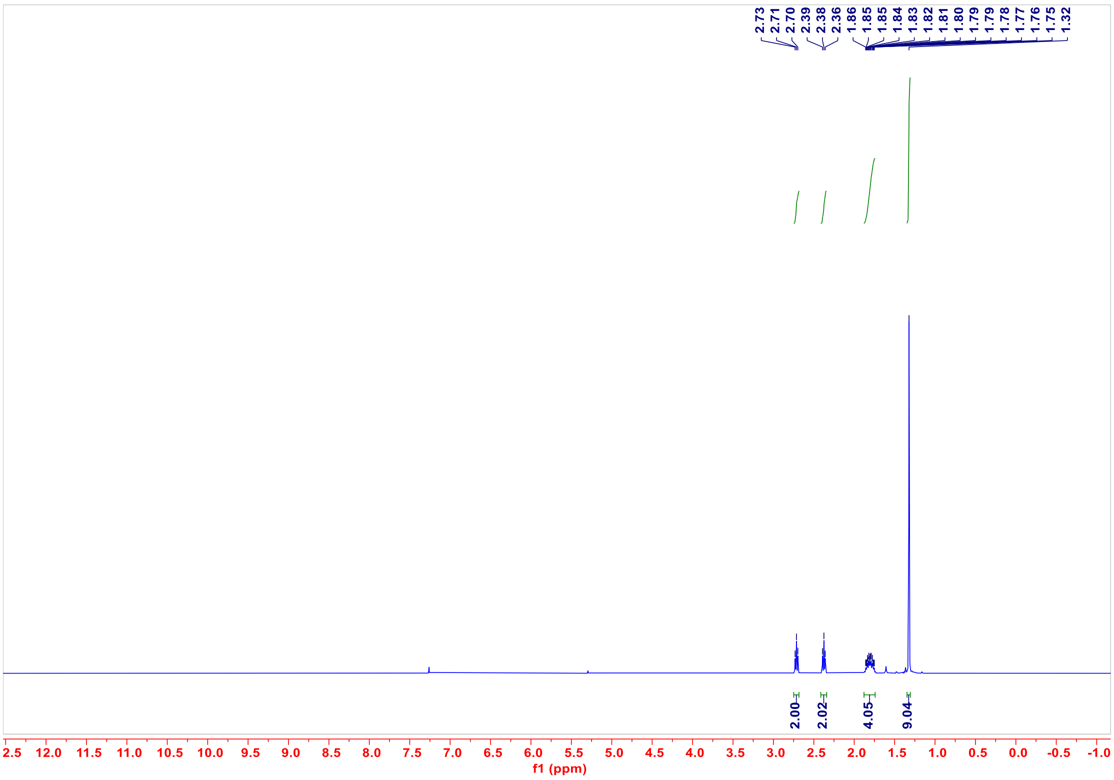
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1.80
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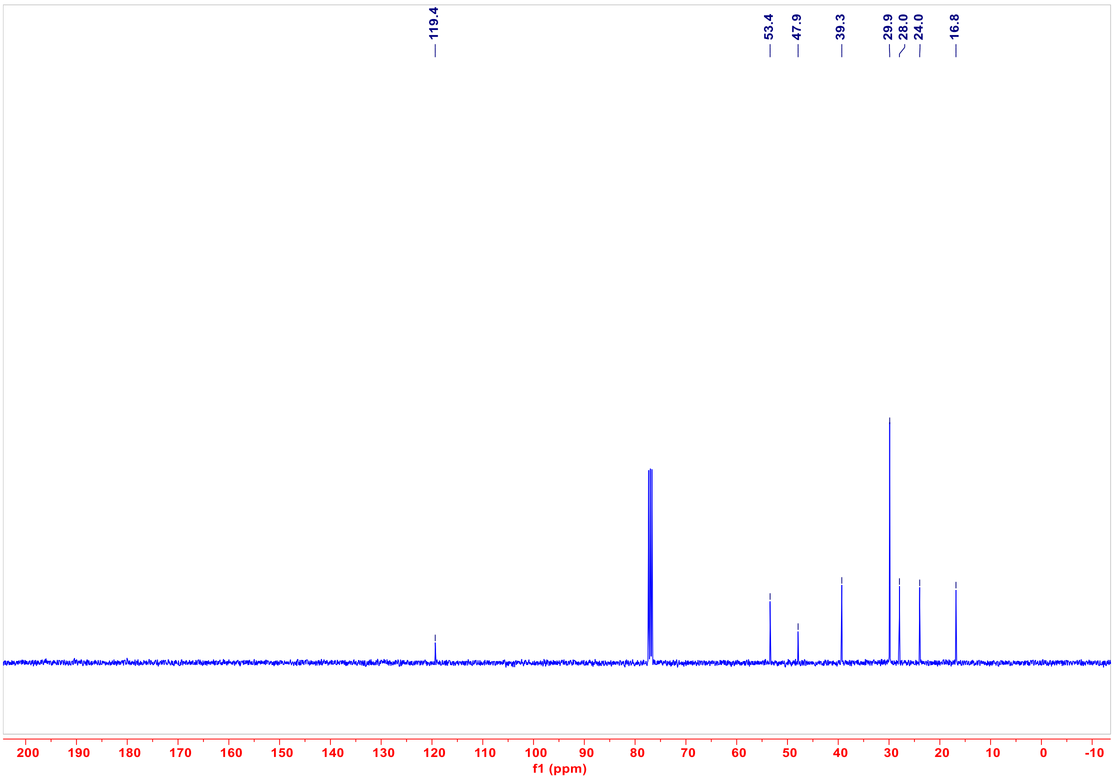
9.04
f1 (ppm)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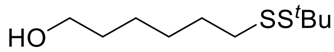
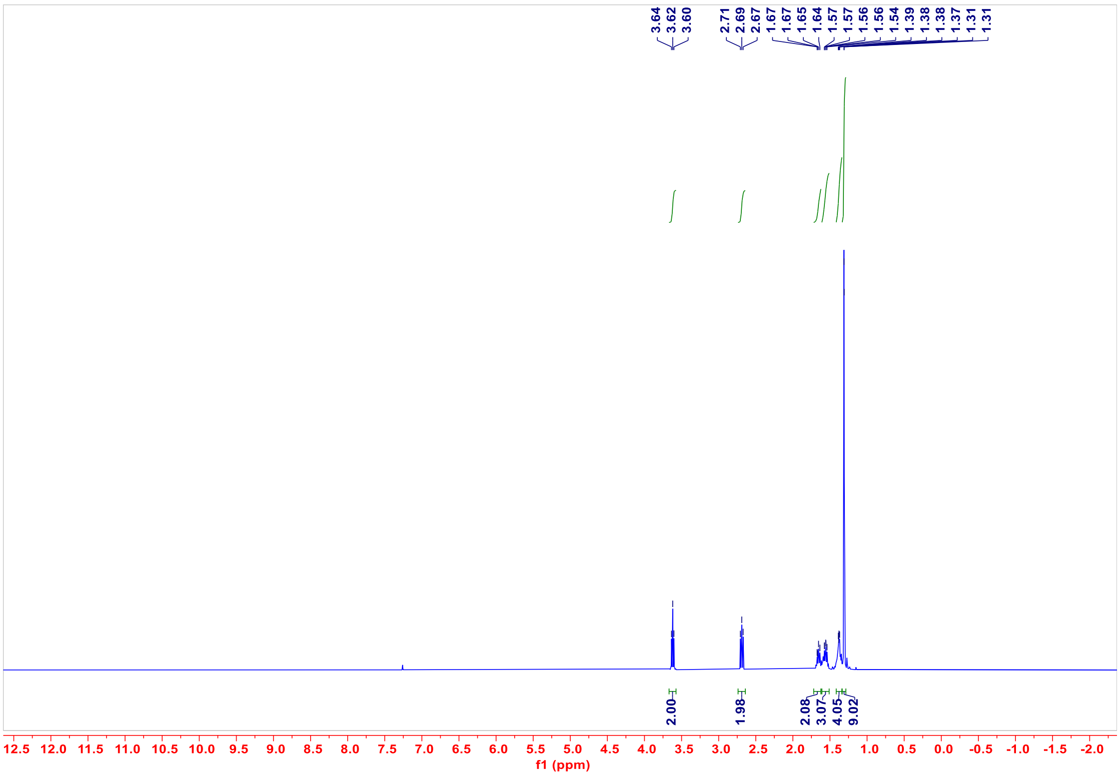

HO
SS^{t}Bu

3ao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4.05
9.02
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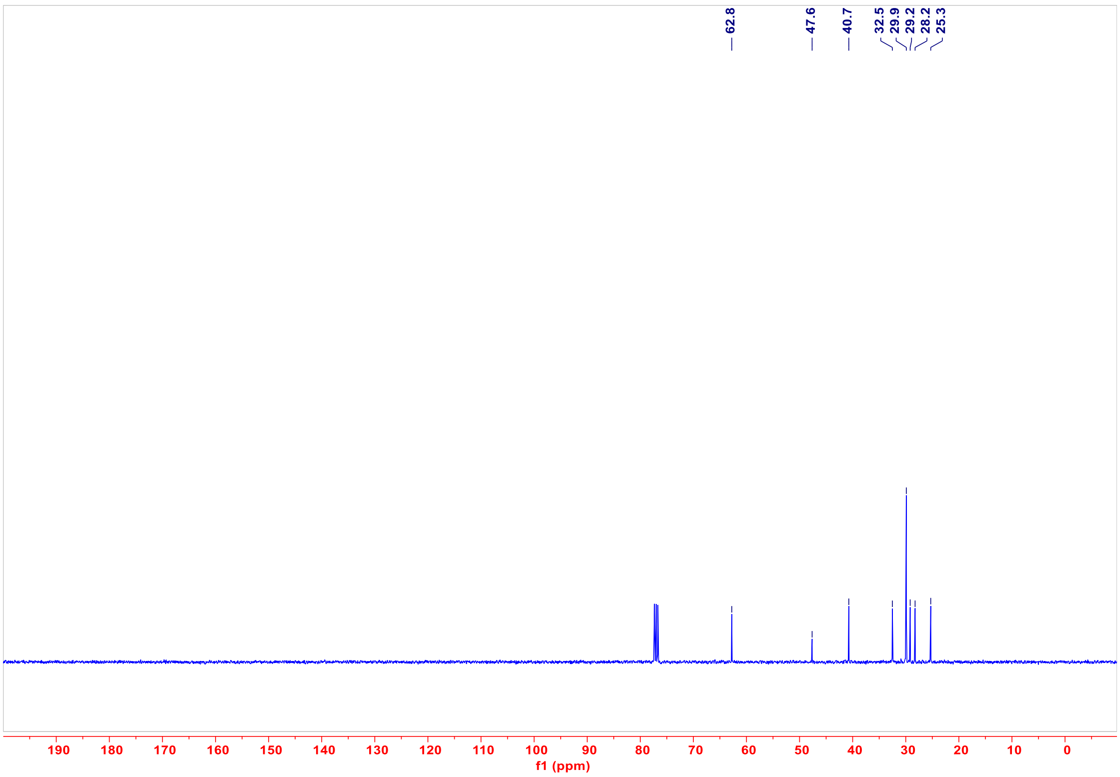
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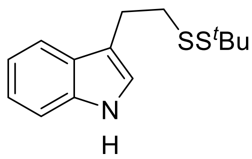
29.2
28.2
25.3
f1 (ppm)



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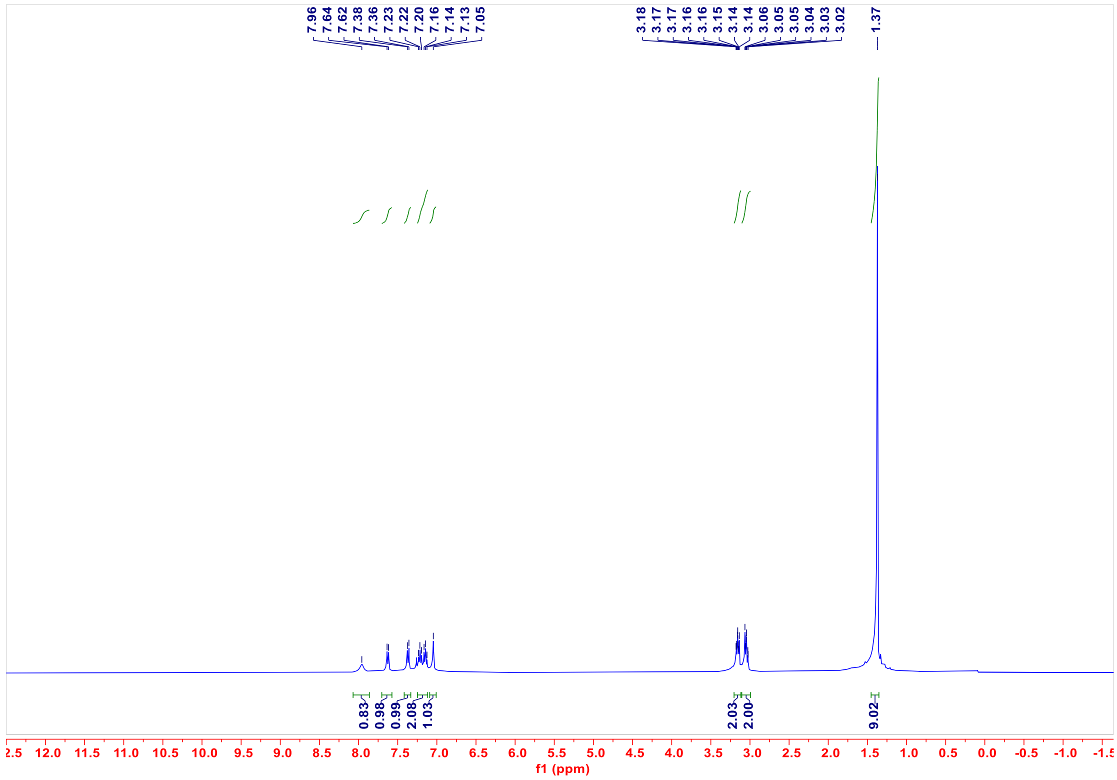

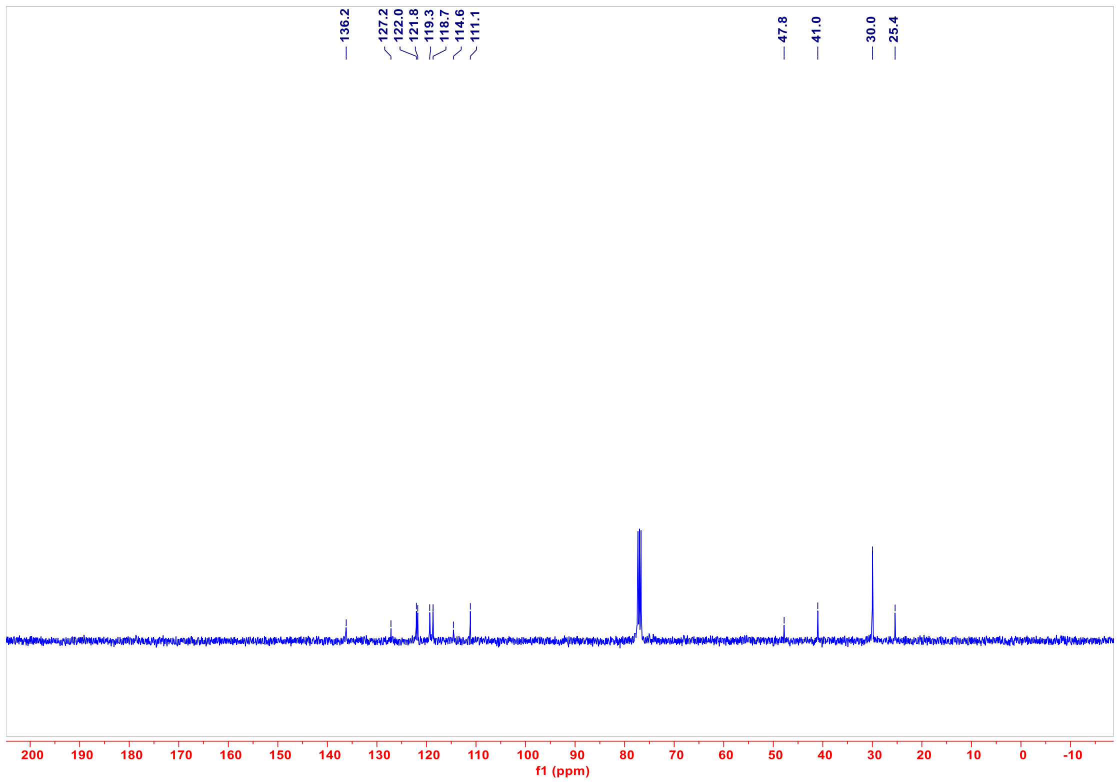

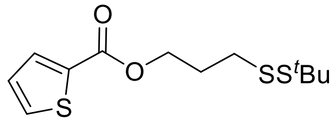

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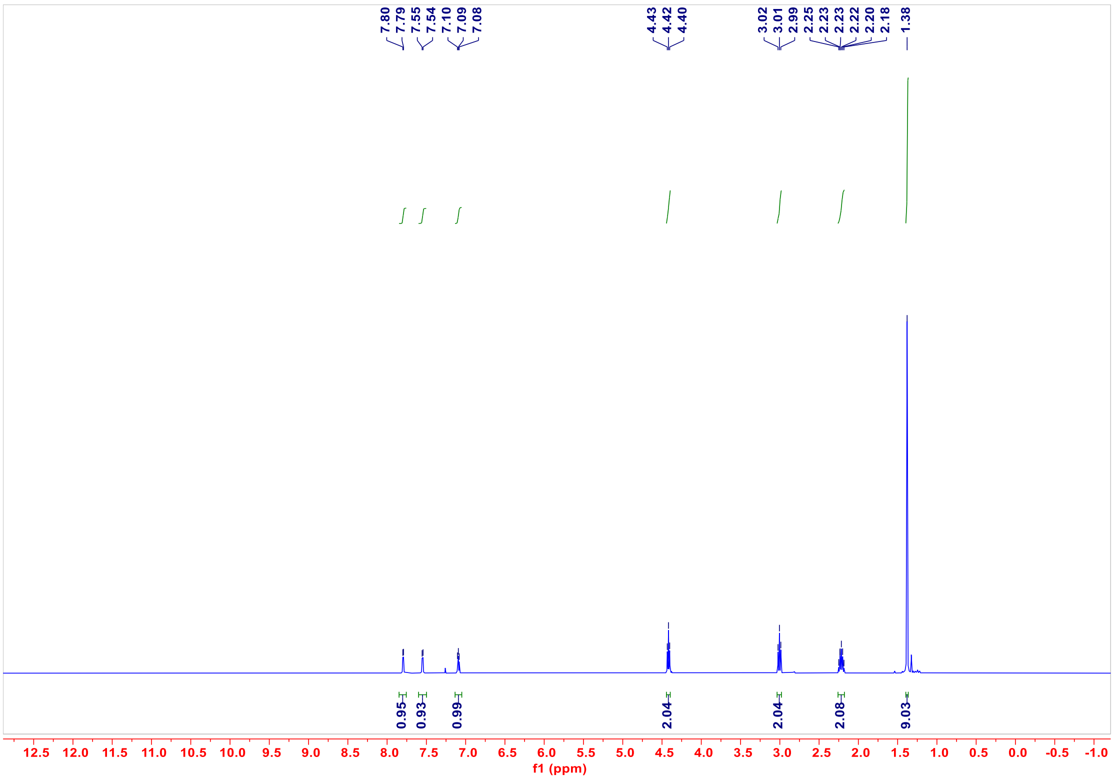
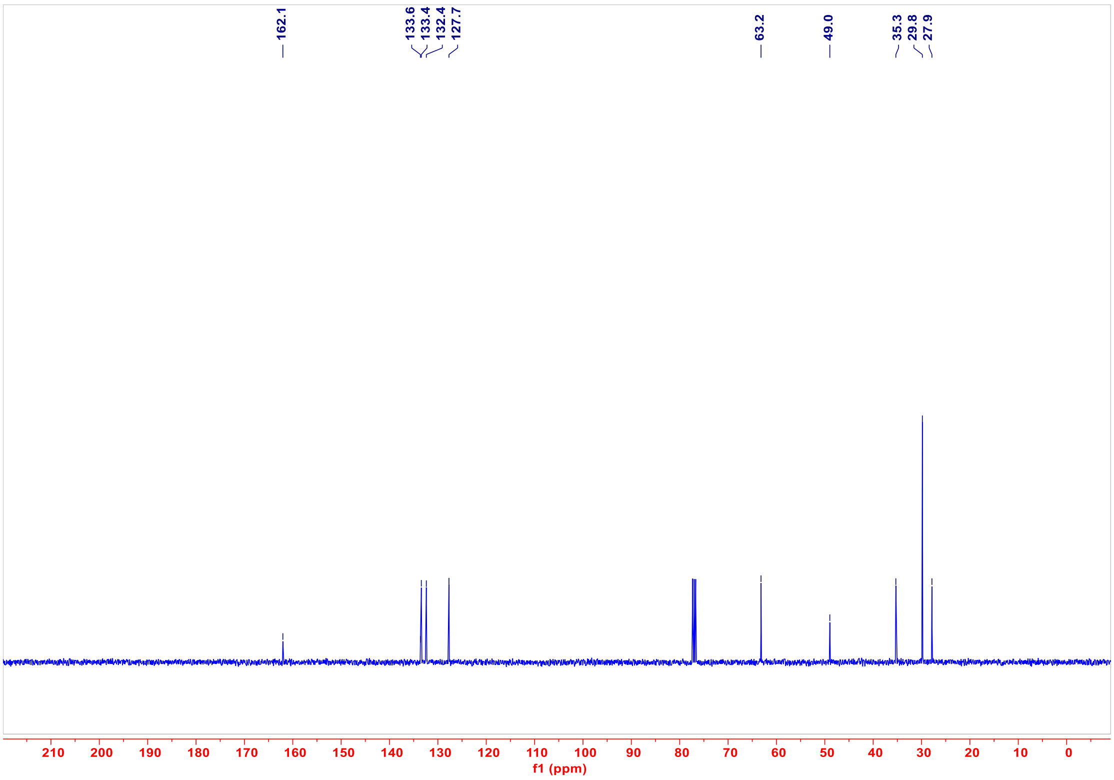
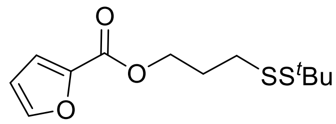
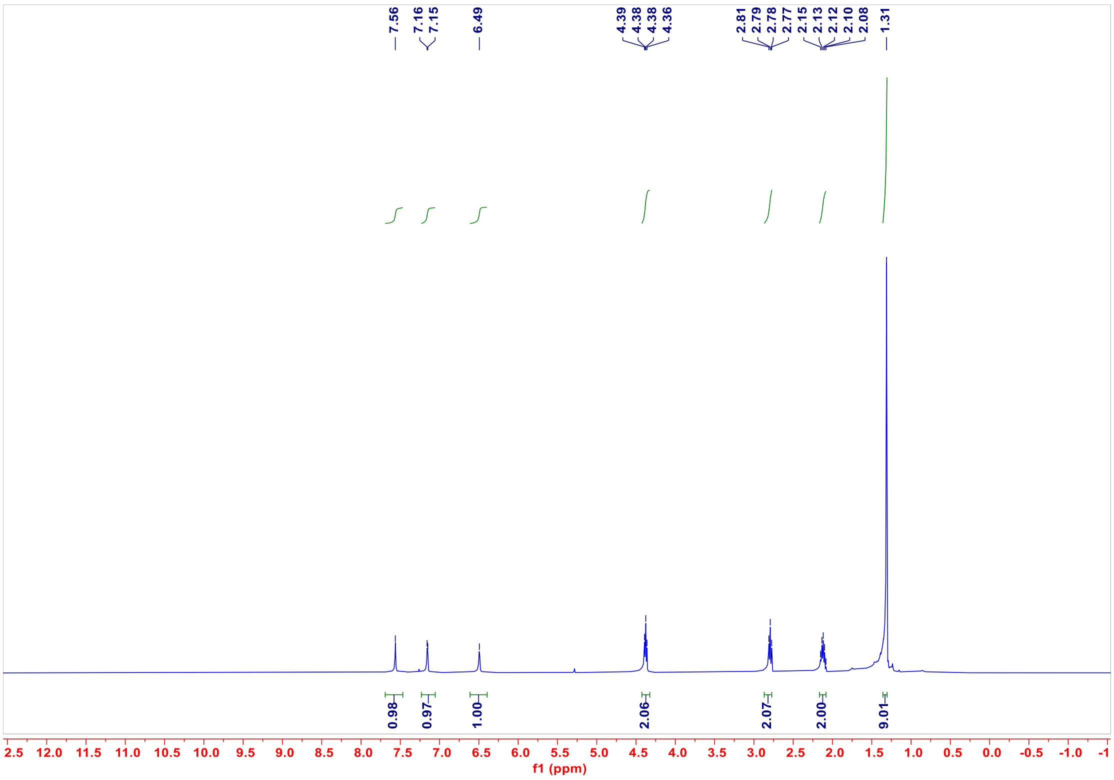





O
O
O
SS^{t}Bu

3ar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4.38
4.36
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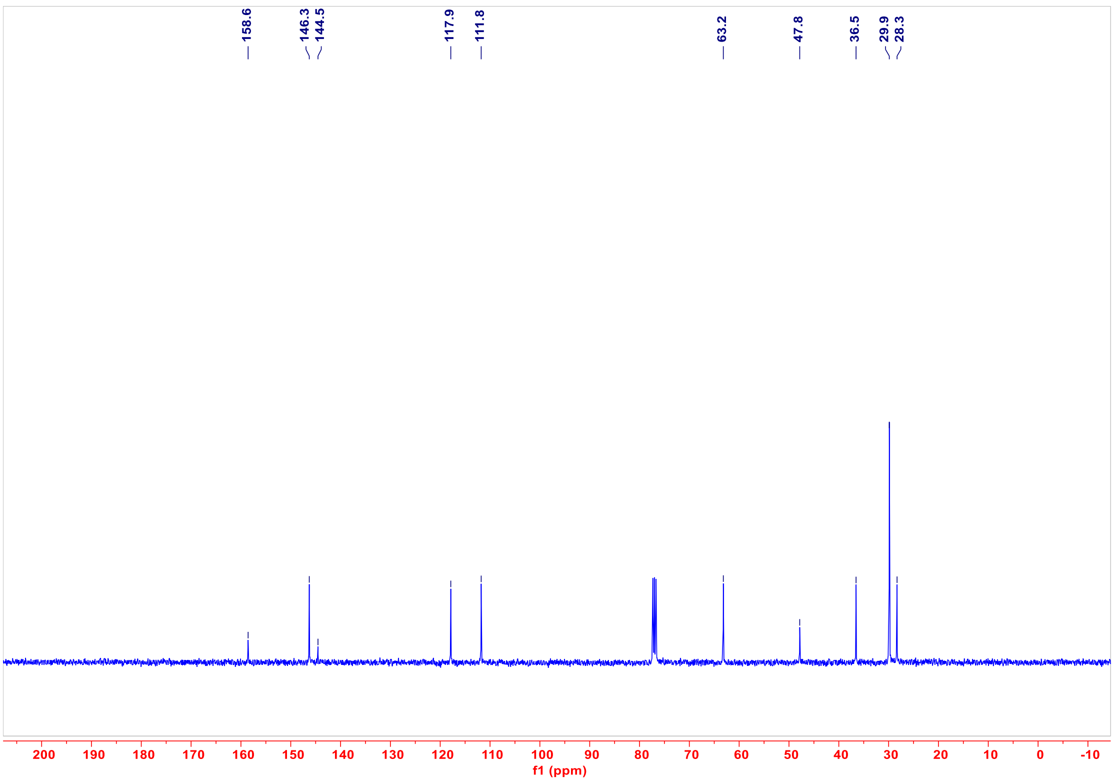
2.79
2.78
2.77
2.15
2.13
2.12
2.10
2.08
1.31
0.98
0.97
1.00
2.06
2.07
2.00
9.01
f1 (ppm)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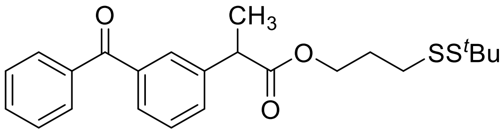
144.5
117.9
111.8
63.2
47.8
36.5
29.9
28.3
f1 (ppm)



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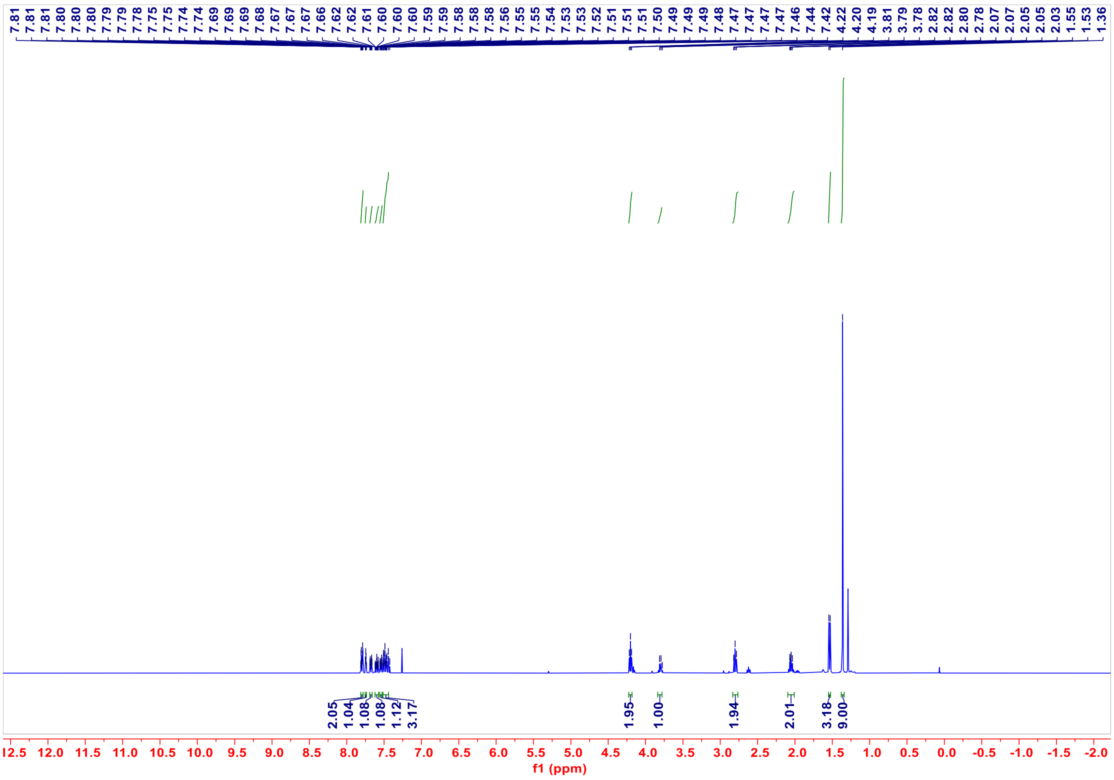
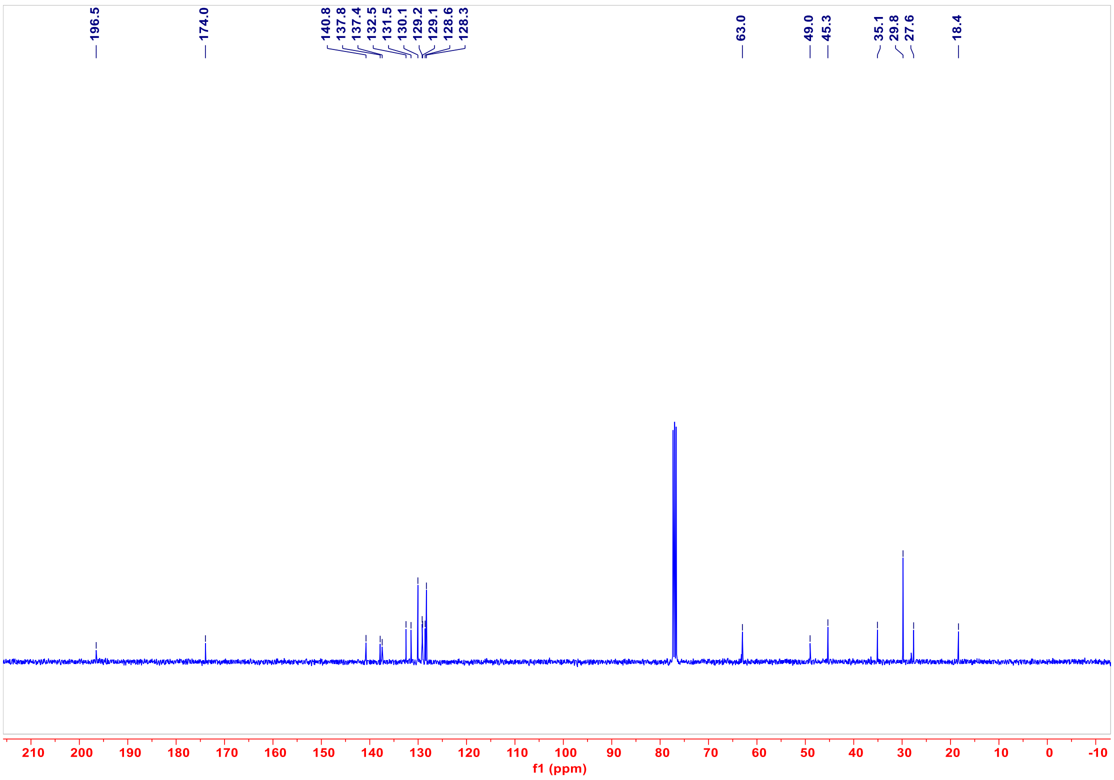
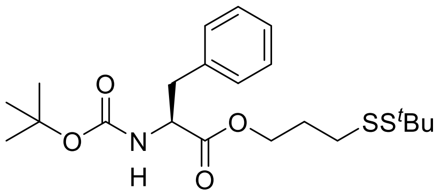
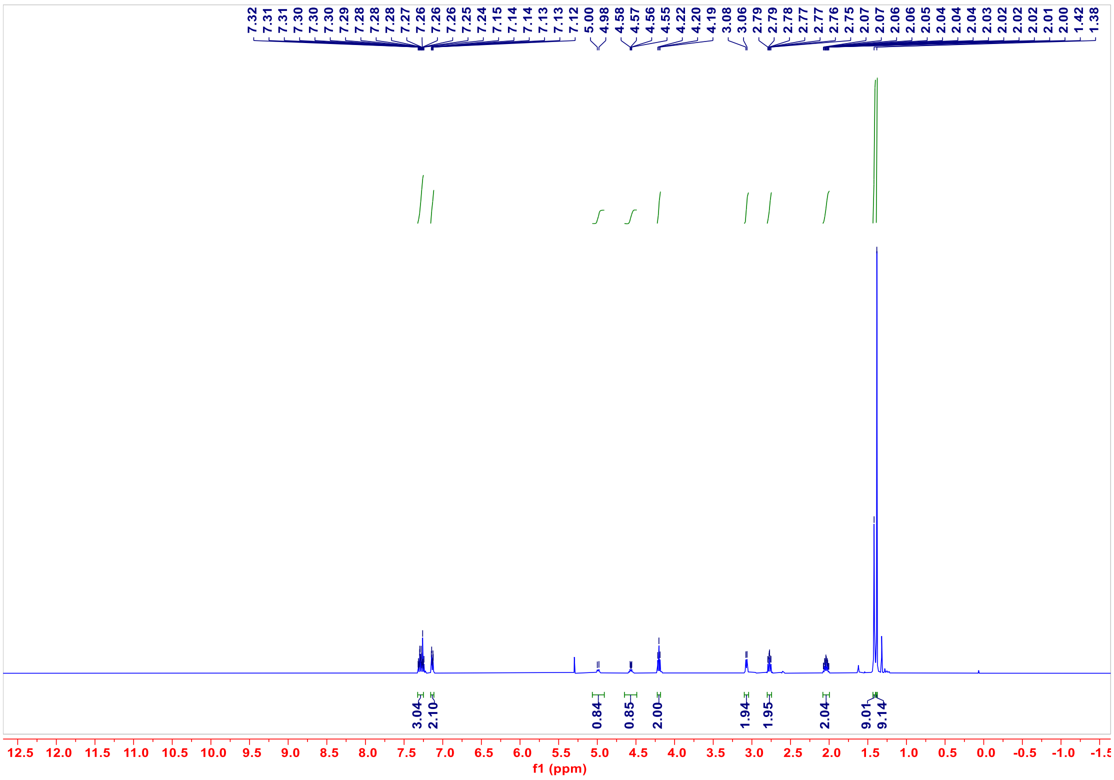





O
O
N
H
O
O
SStBu

3at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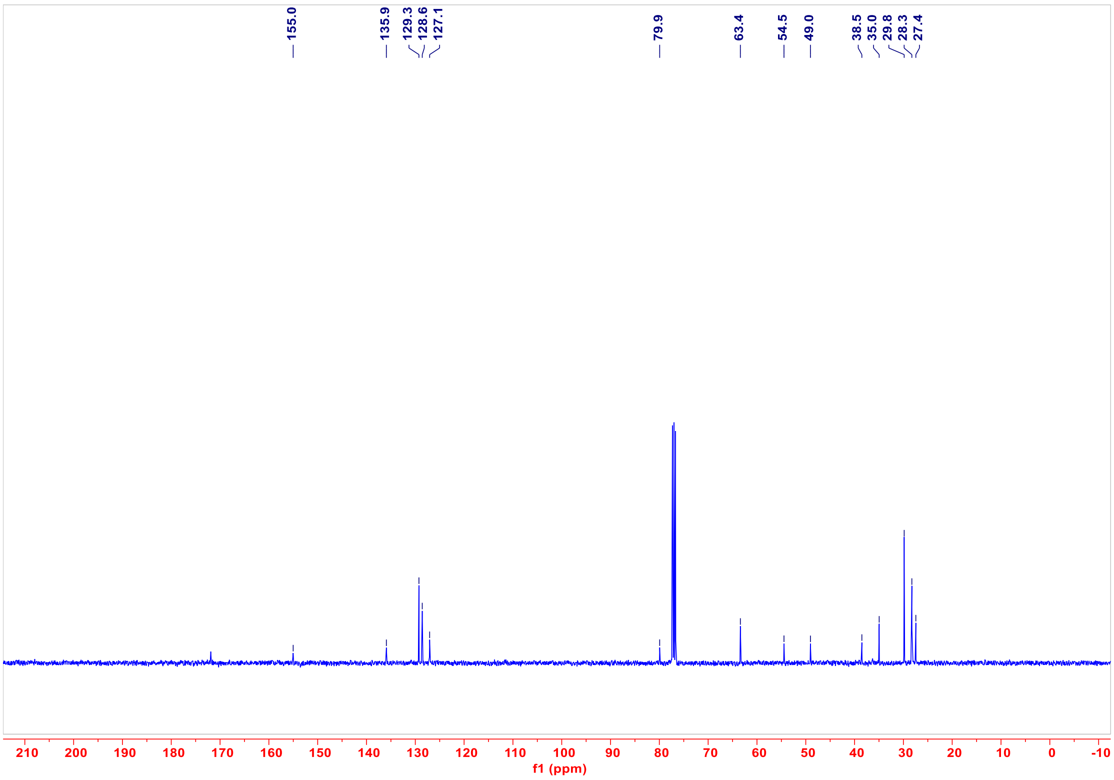
3.04 2.10 0.84 0.85 2.00 1.94 1.95 2.04 9.01 9.14
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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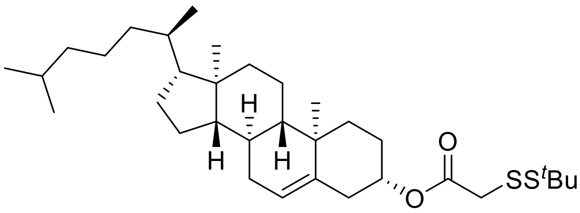
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



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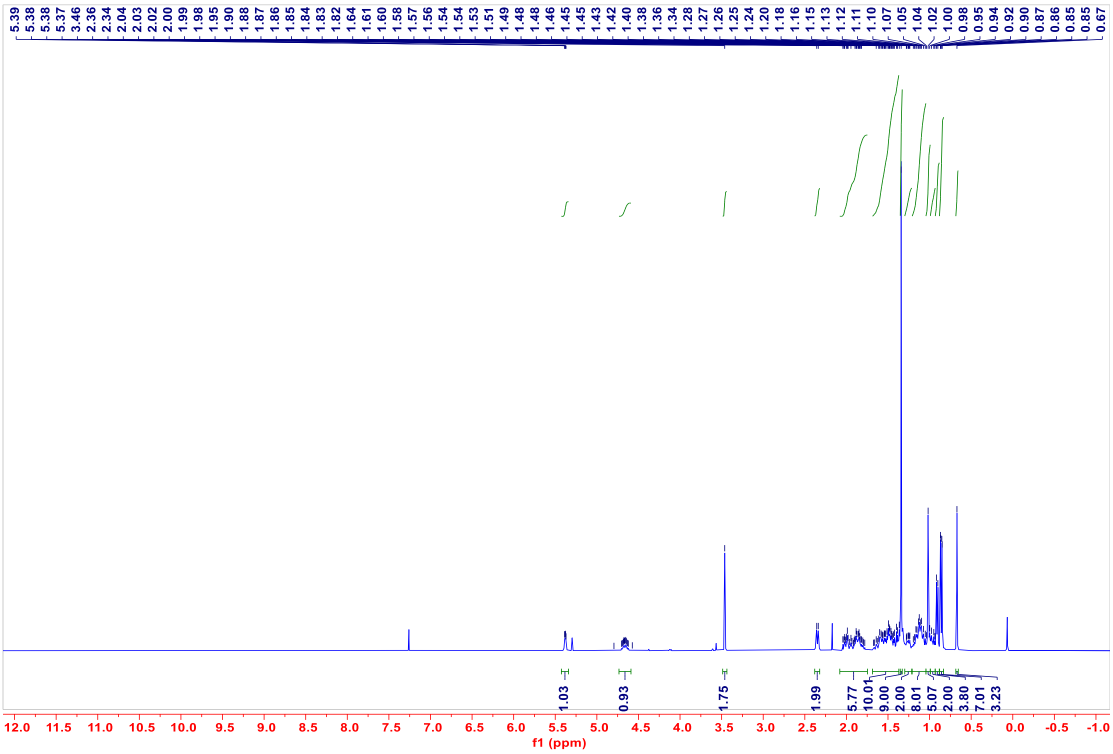

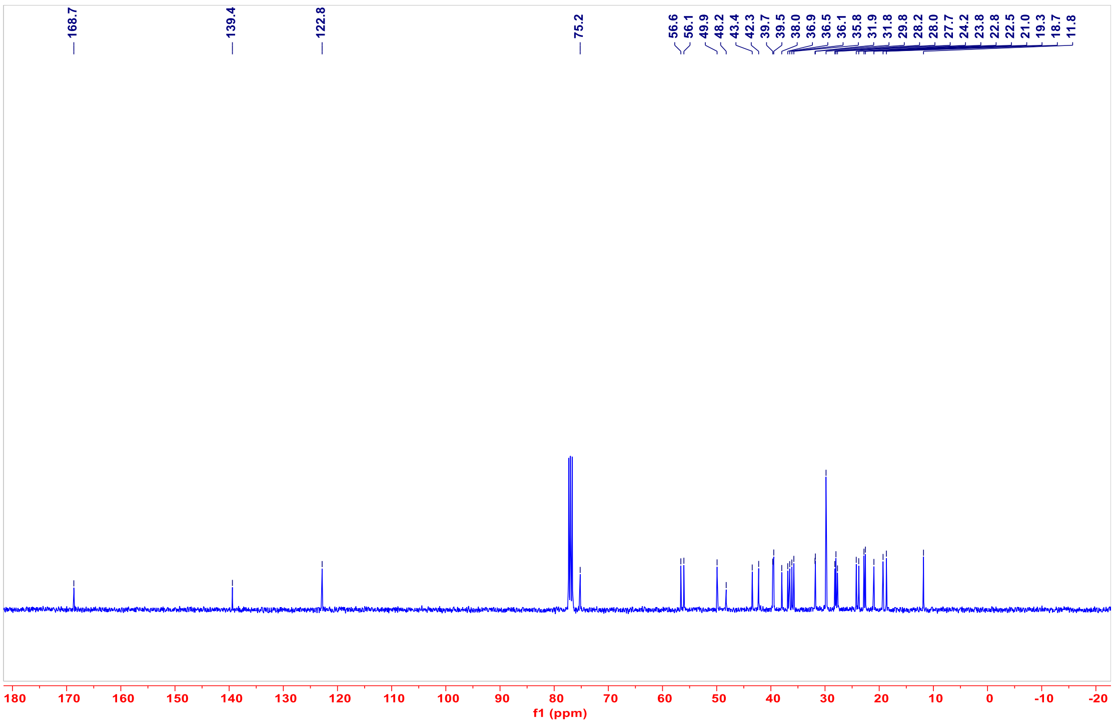

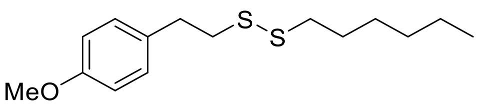

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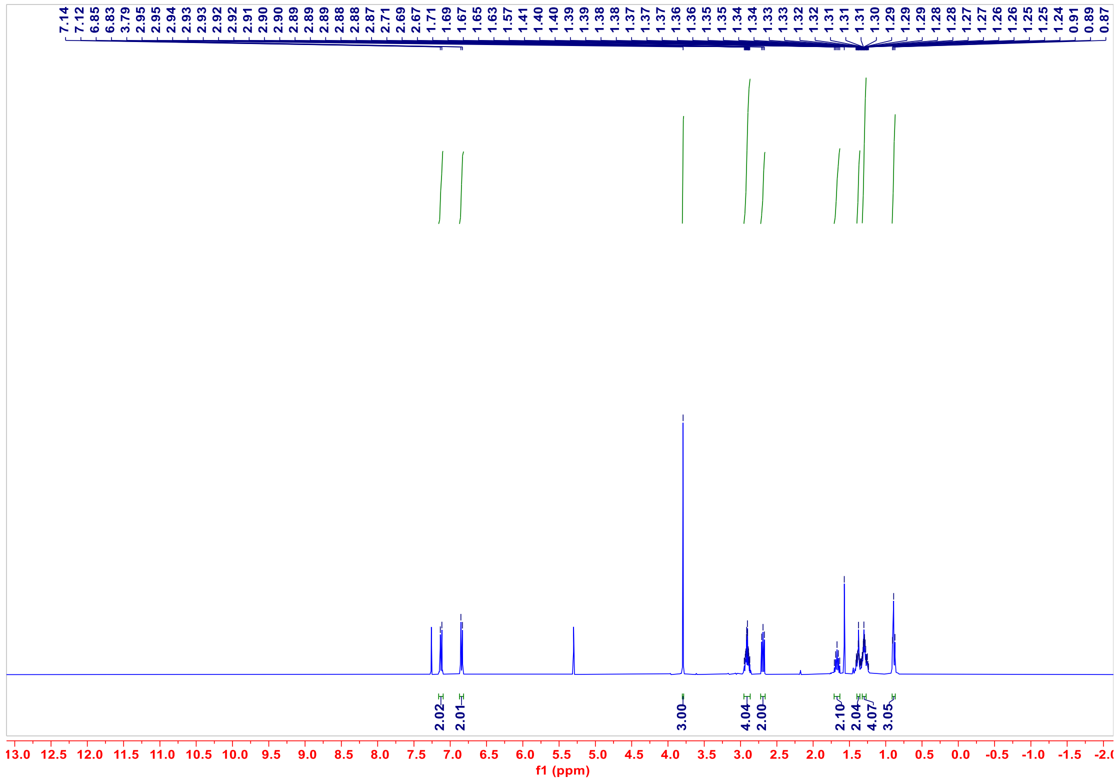

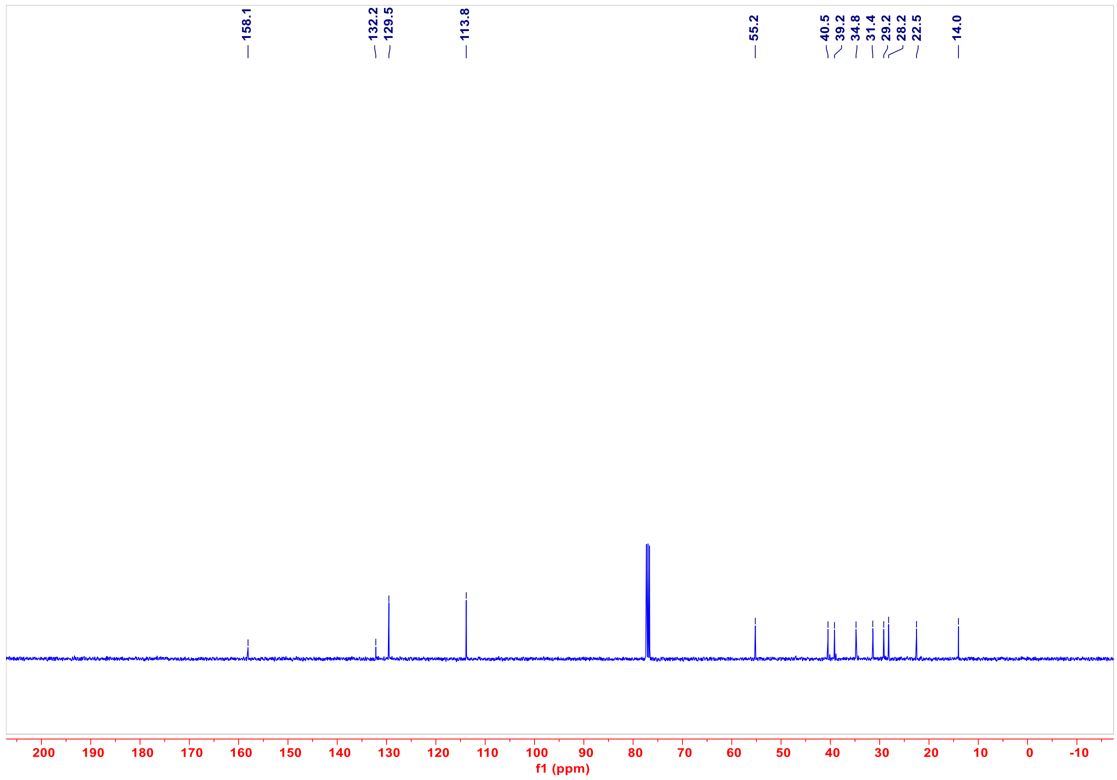

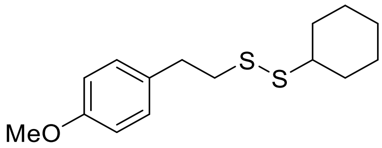

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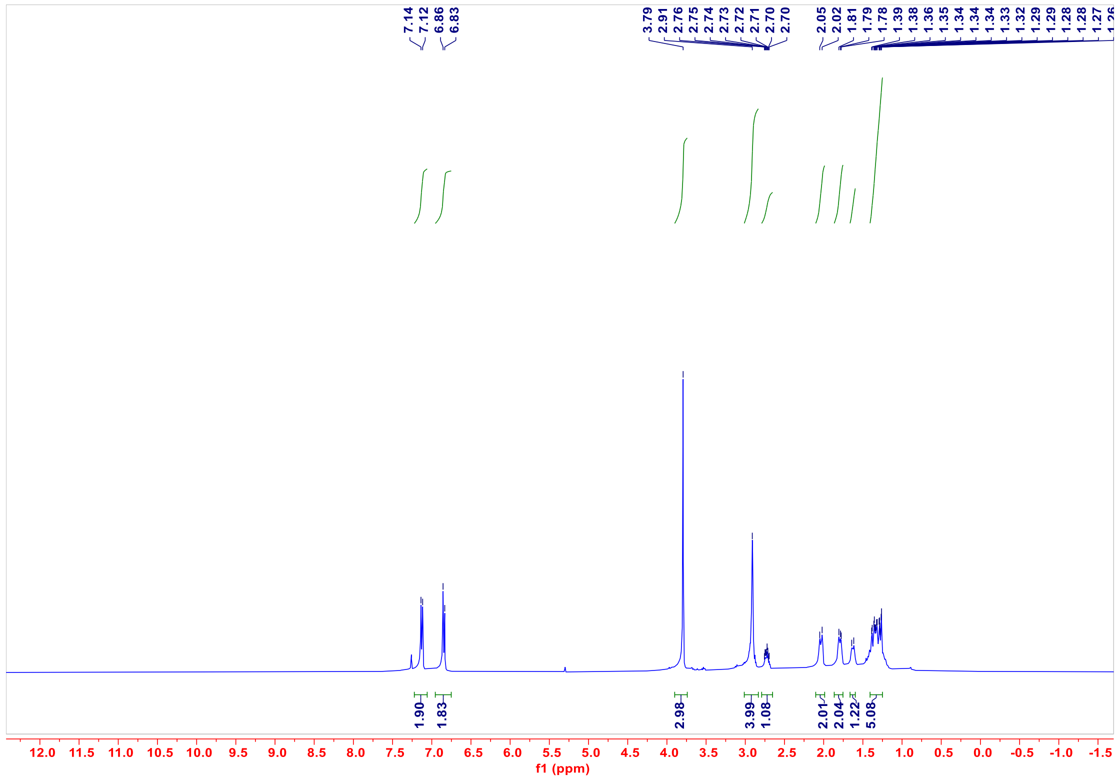
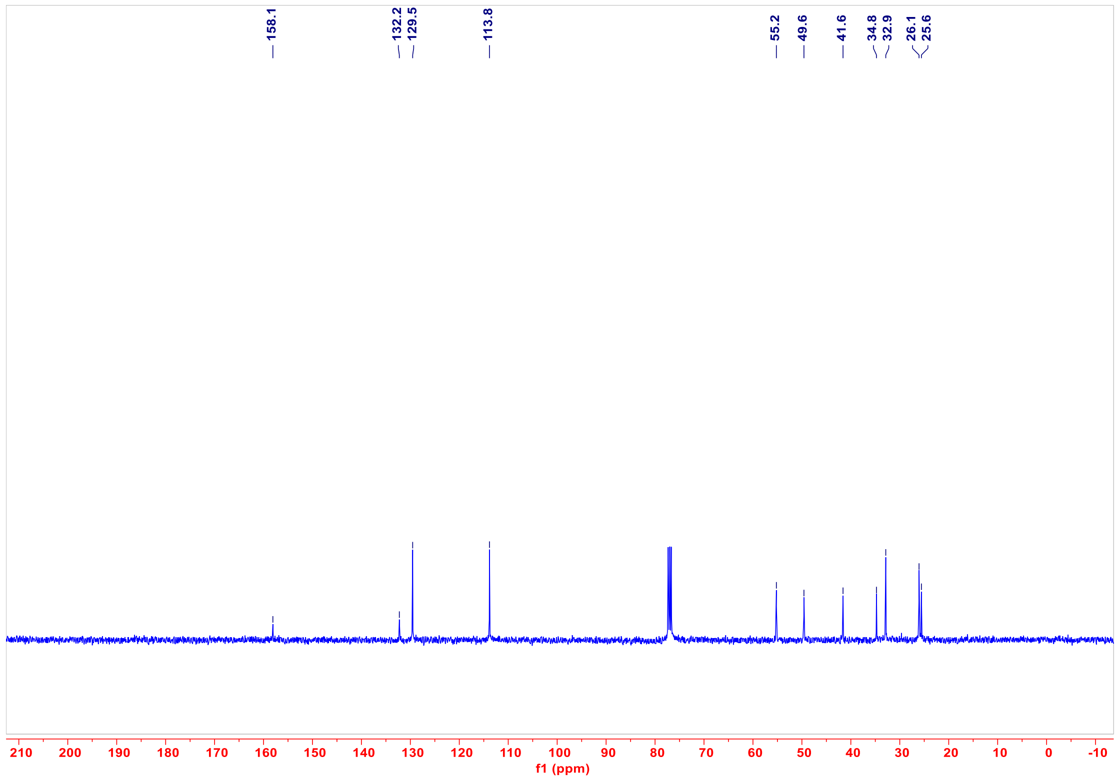
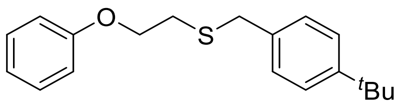
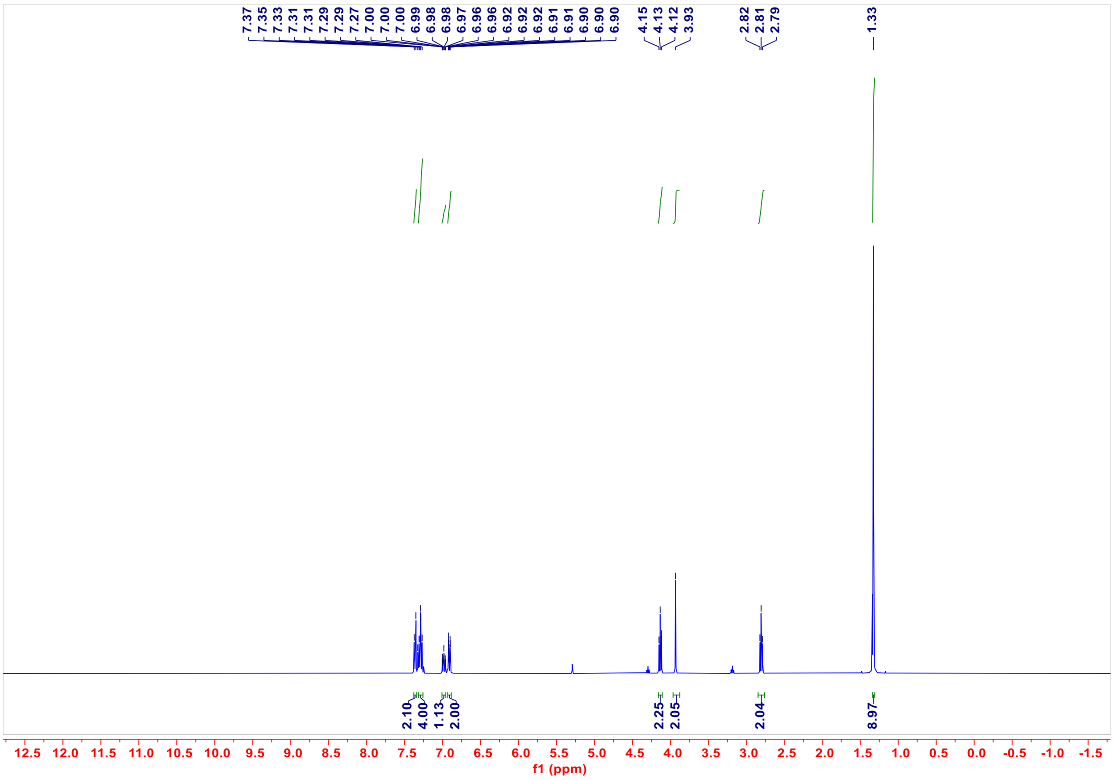





O
S
tBu

4ac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7.29
7.29
7.27
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7.00
6.99
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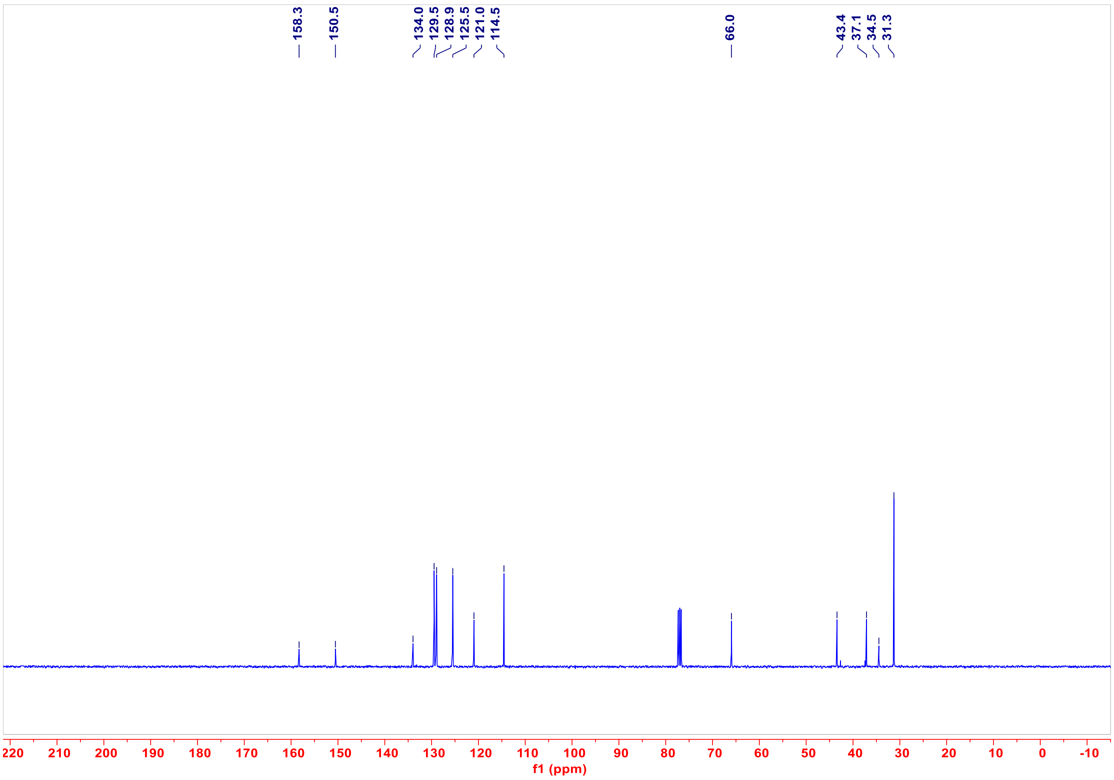
6.97
6.96
6.96
6.92
6.92
6.92
6.91
6.91
6.90
6.90
6.90
4.15
4.13
4.12
3.93
2.82
2.81
2.79
1.33
2.10
4.00
1.13
2.00
2.25
2.05
2.04
8.97
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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128.9
125.5
121.0
114.5
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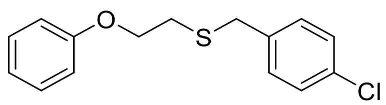
37.1
34.5
31.3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



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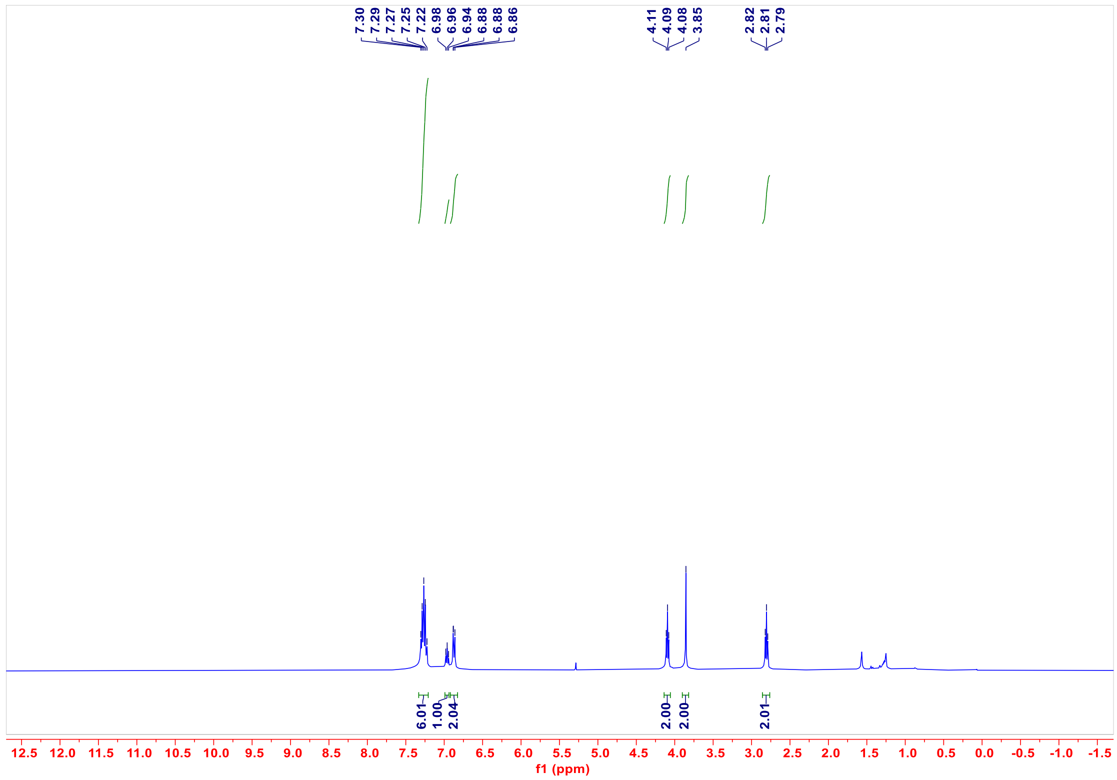
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6.88
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4.09
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3.85
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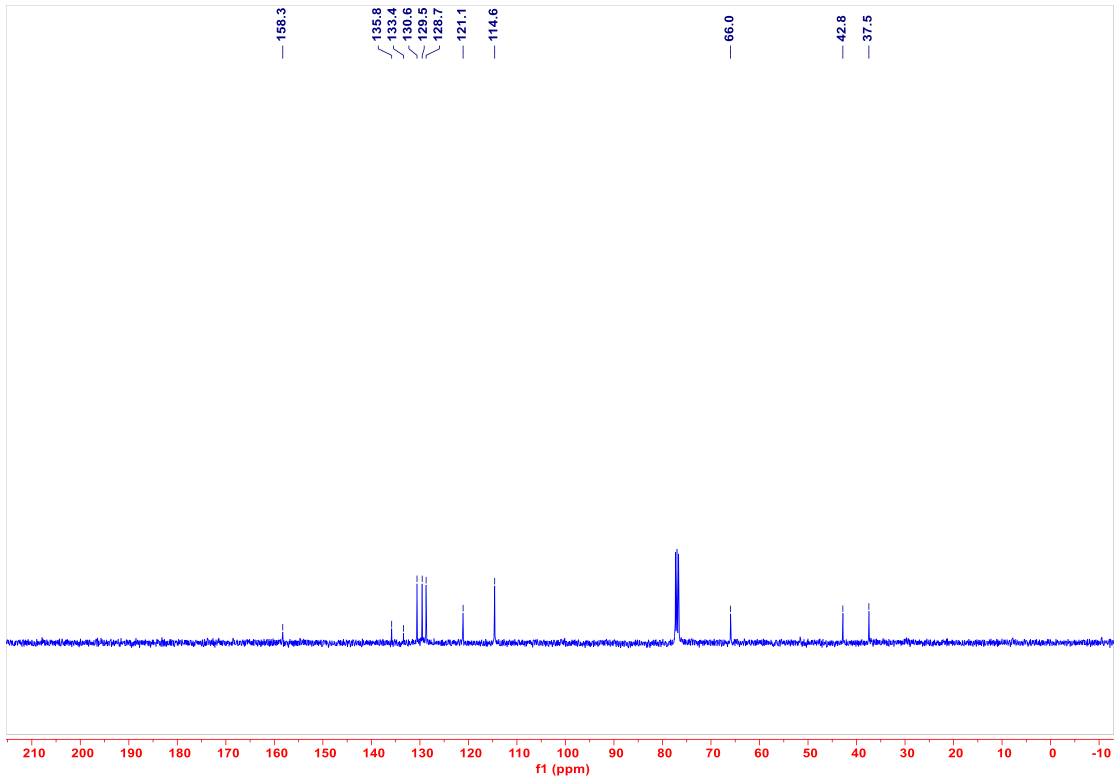
2.81
2.79
6.01
1.00
2.04
2.00
2.00
2.01
f1 (ppm)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66.0
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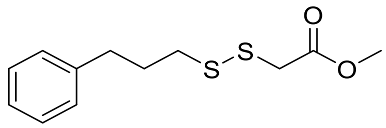
37.5
f1 (ppm)



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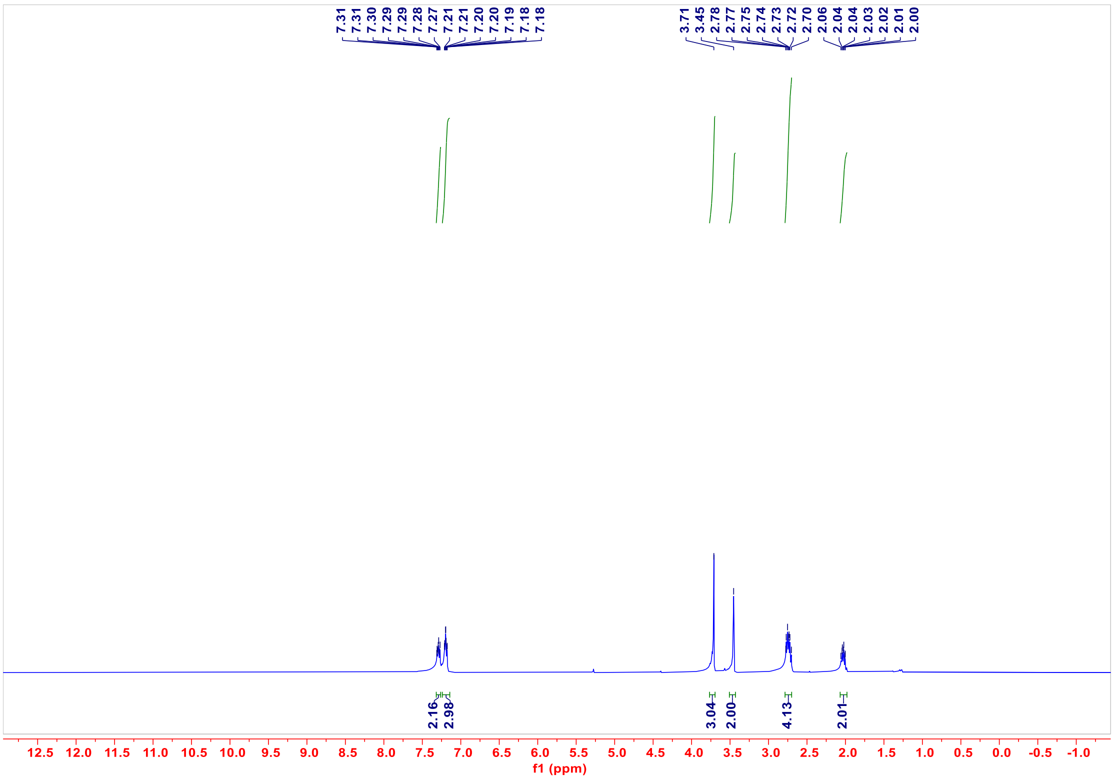
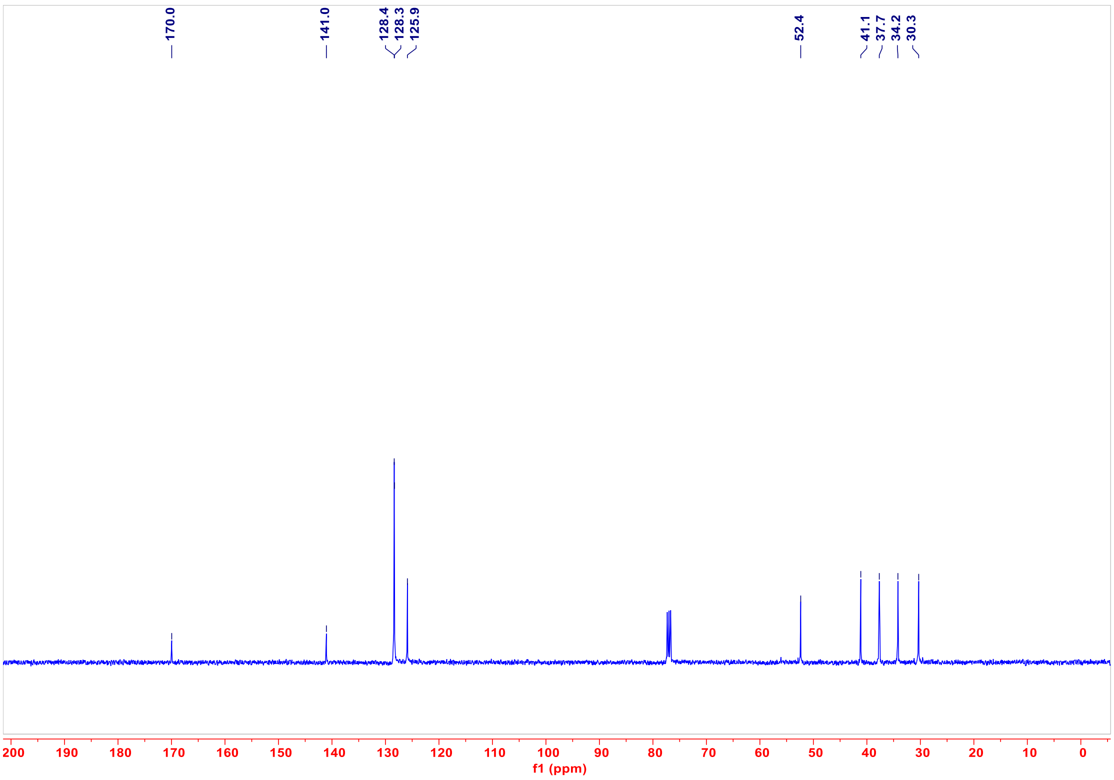
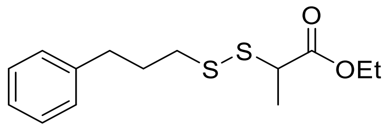
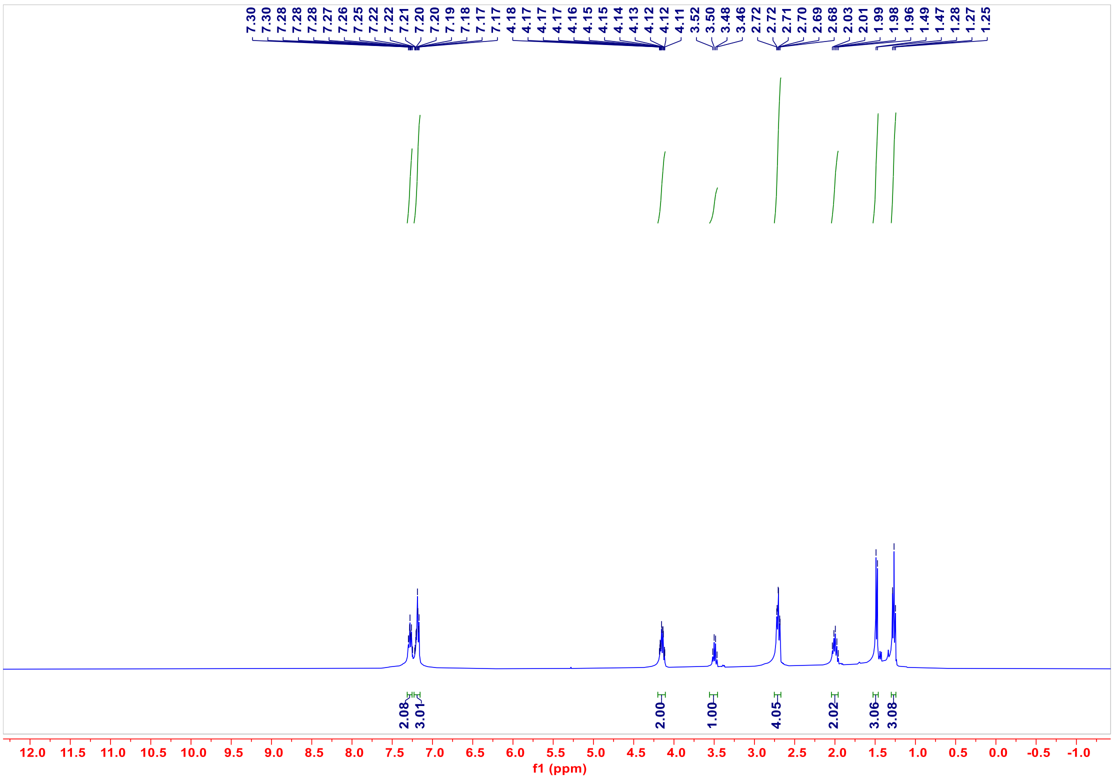





S
S
O
OEt

4af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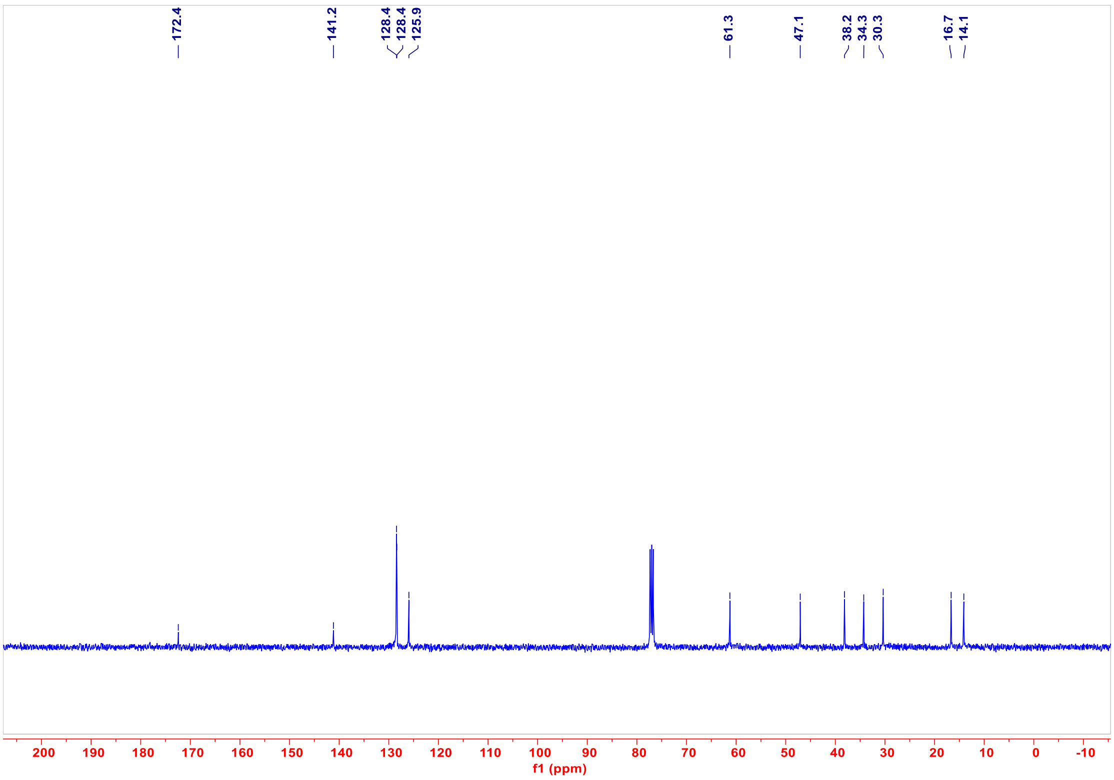
2.08 3.01 2.00 1.00 4.05 2.02 3.06 3.08
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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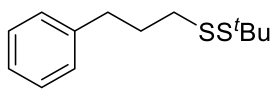
f1 (ppm)


SS^{t}Bu

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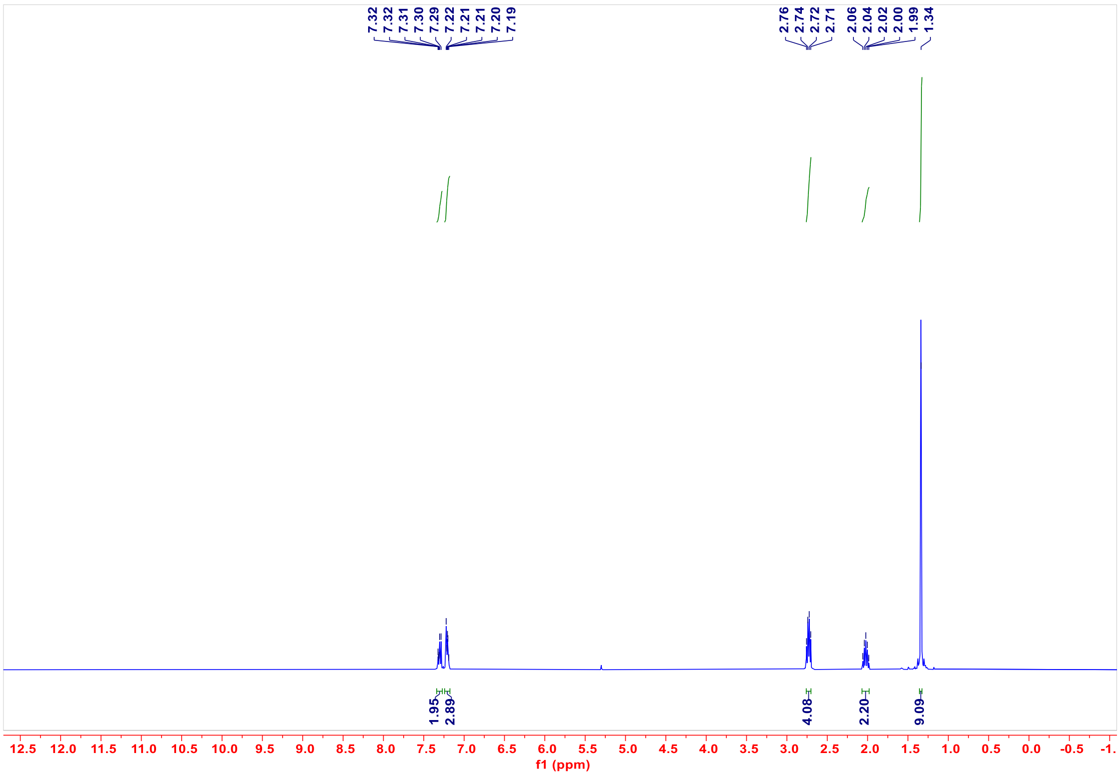
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7.19
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2.72
2.71
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2.04
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1.34
1.95
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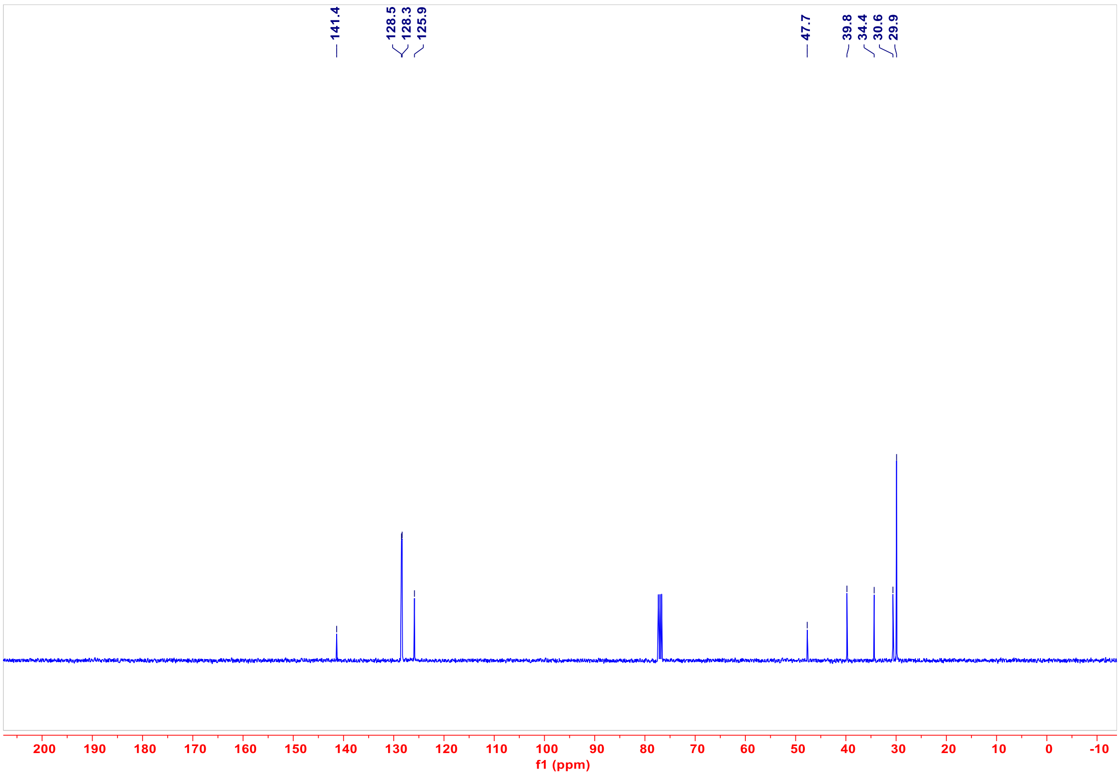
4.08
2.20
9.09
f1 (ppm)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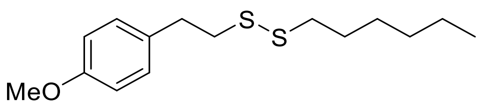
29.9
f1 (ppm)



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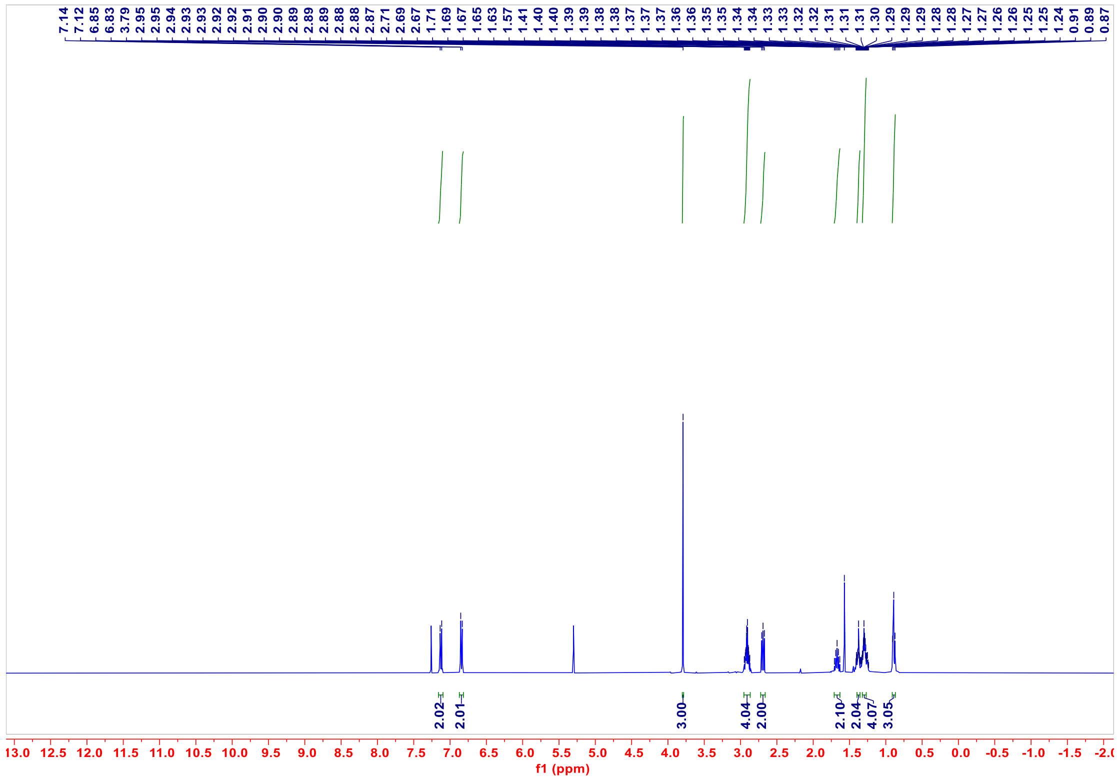
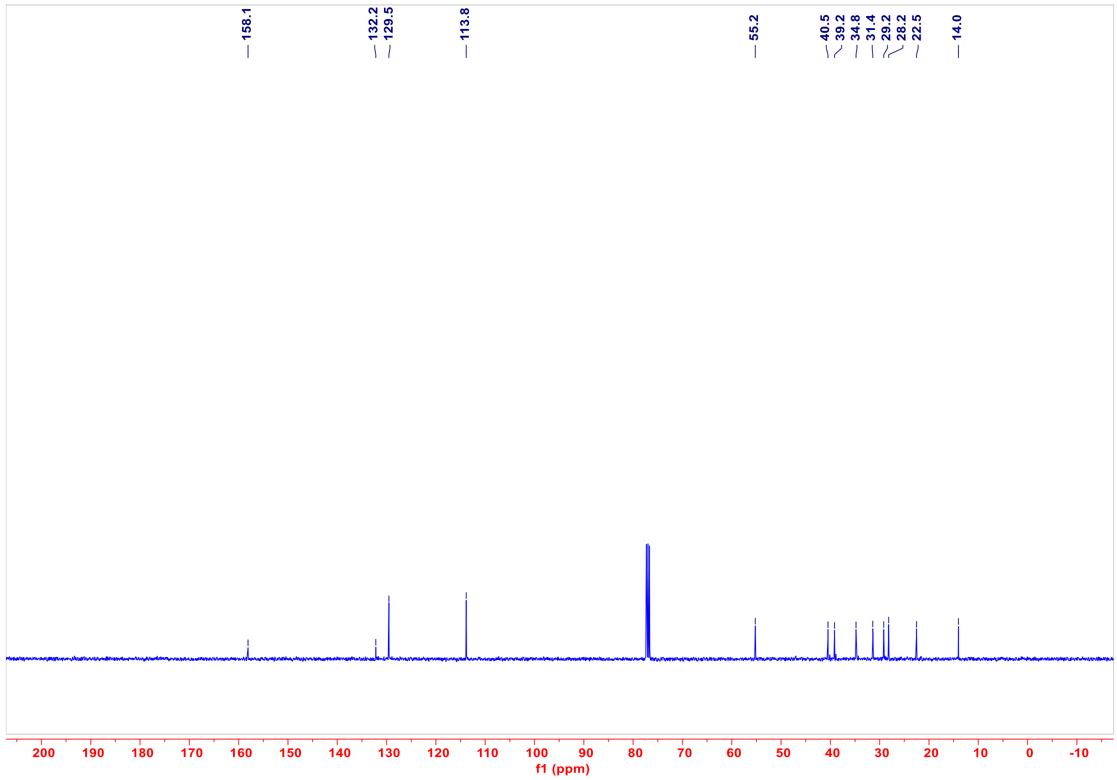
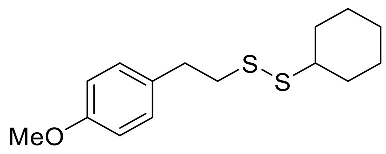
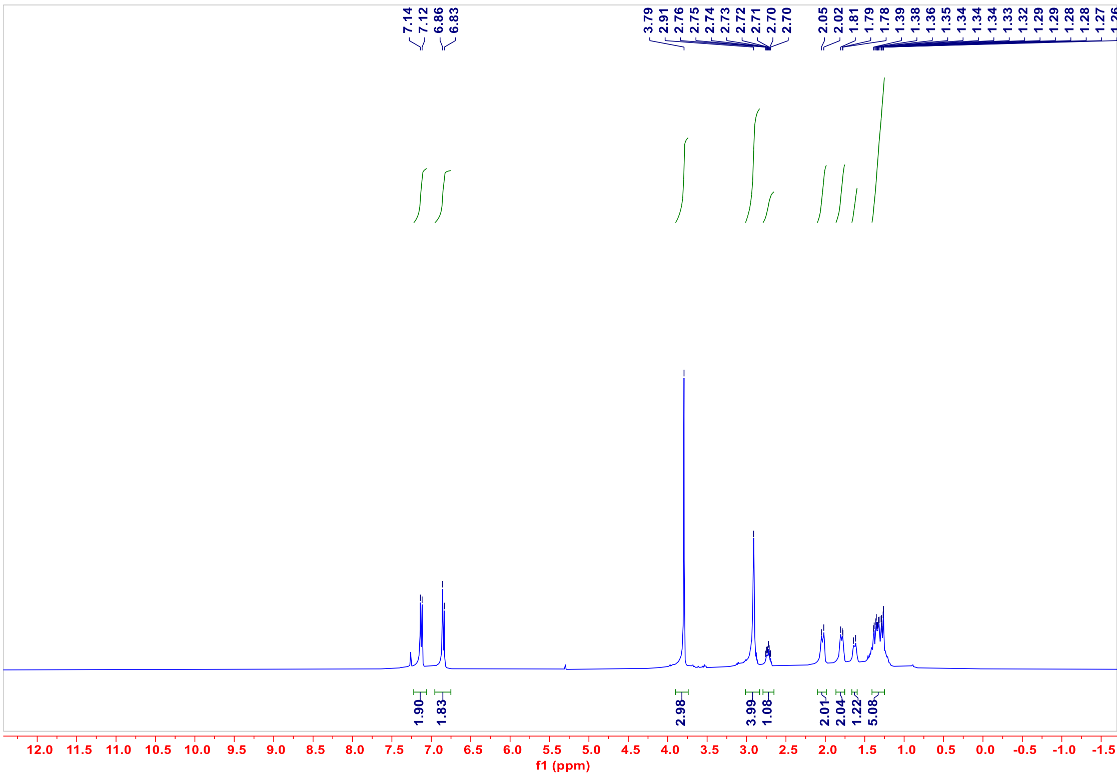





MeO
S
S

4ai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2.02
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1.79
1.78
1.39
1.38
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1.34
1.33
1.32
1.29
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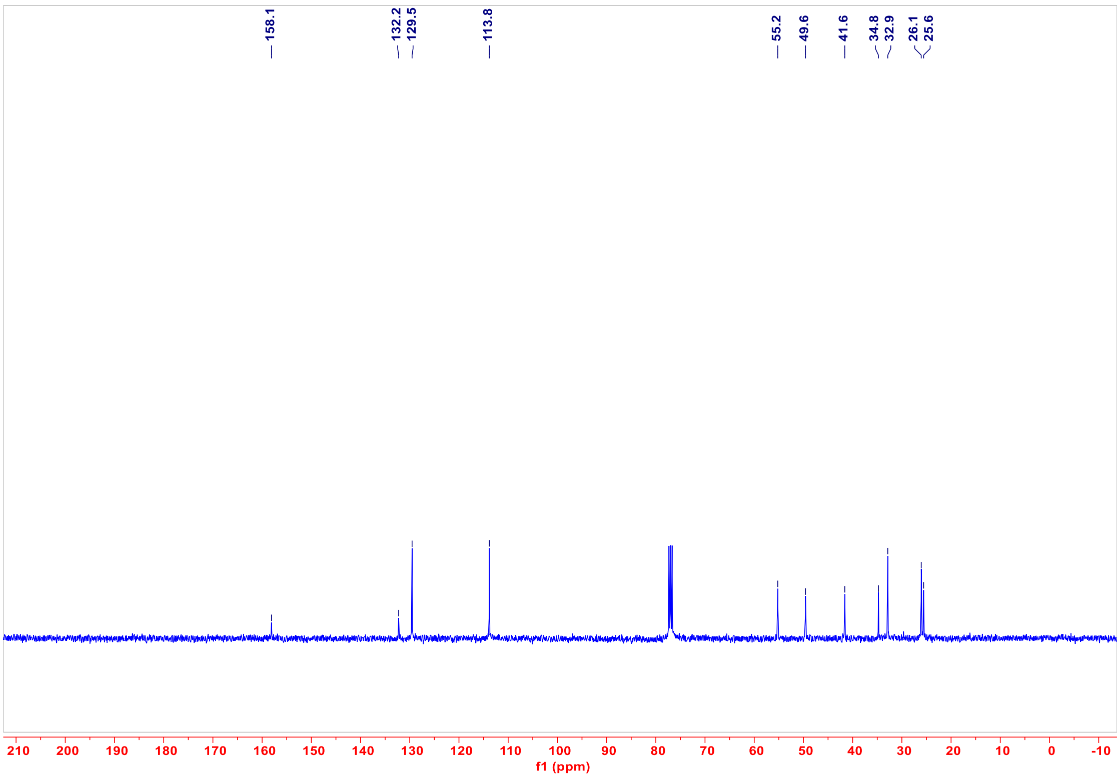
1.28
1.28
1.27
1.90
1.83
2.98
3.99
1.08
2.01
2.04
1.22
5.08
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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129.5
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55.2
49.6
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32.9
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25.6
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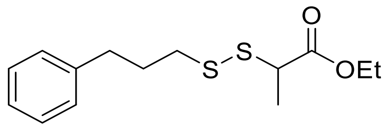
f1 (ppm)



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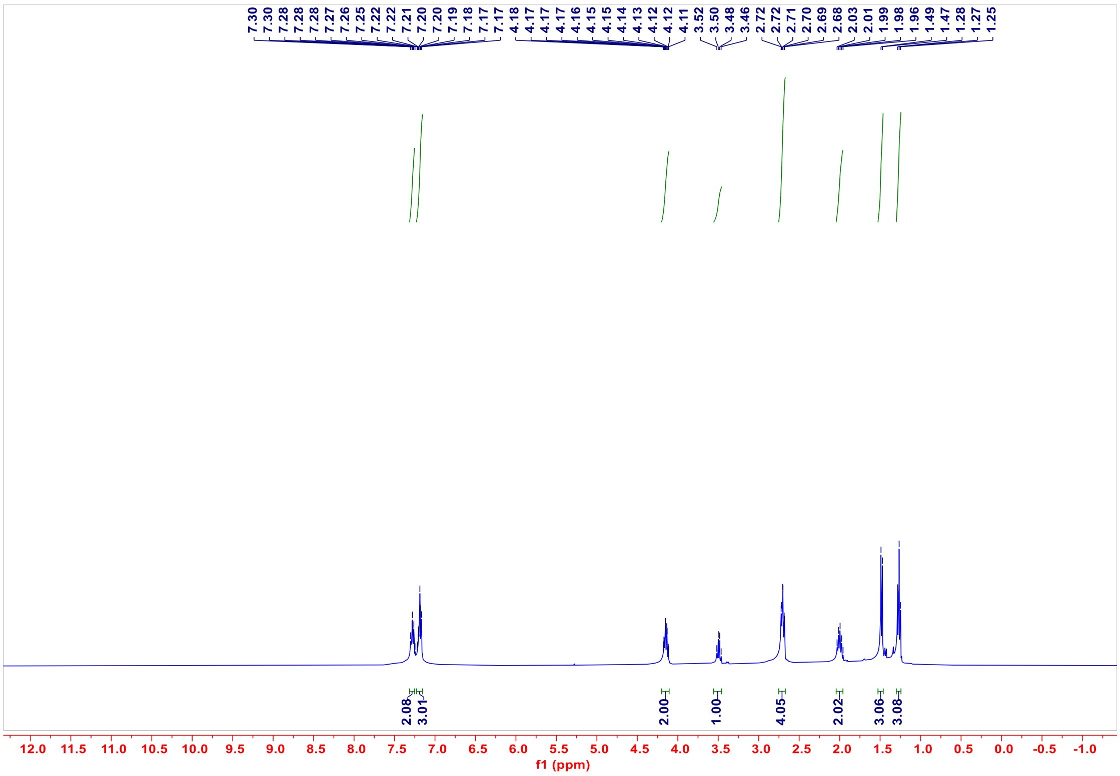

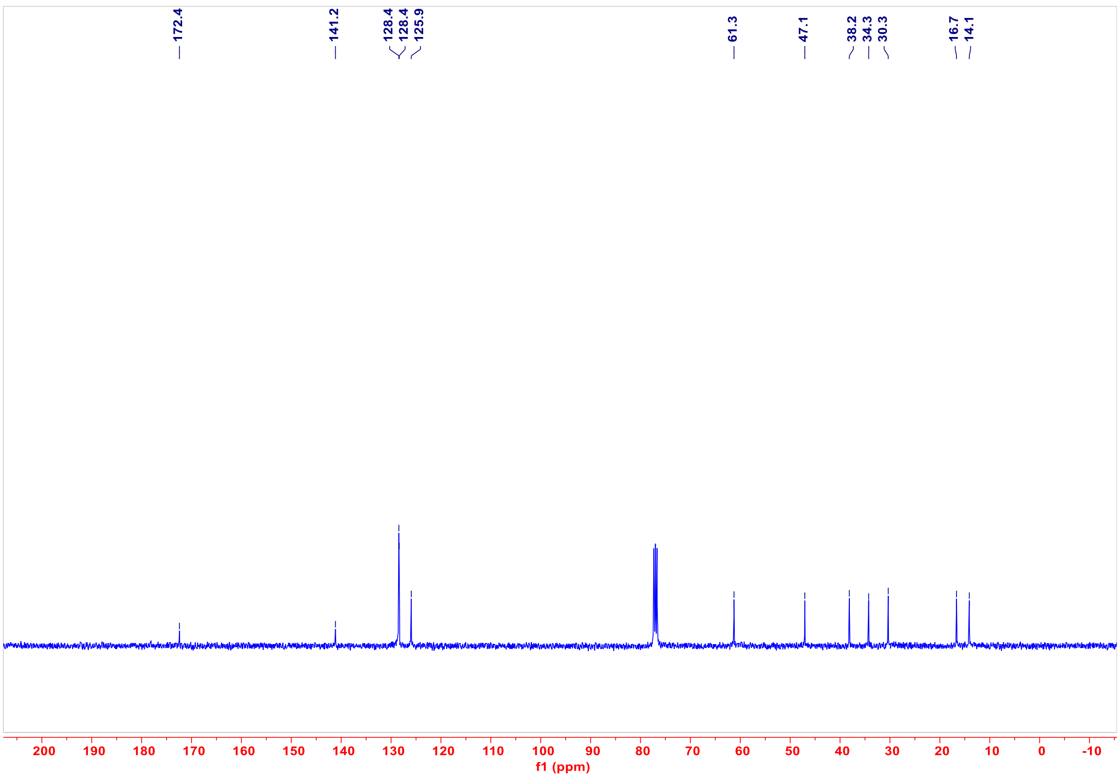

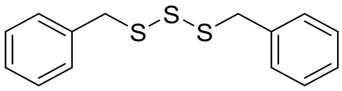

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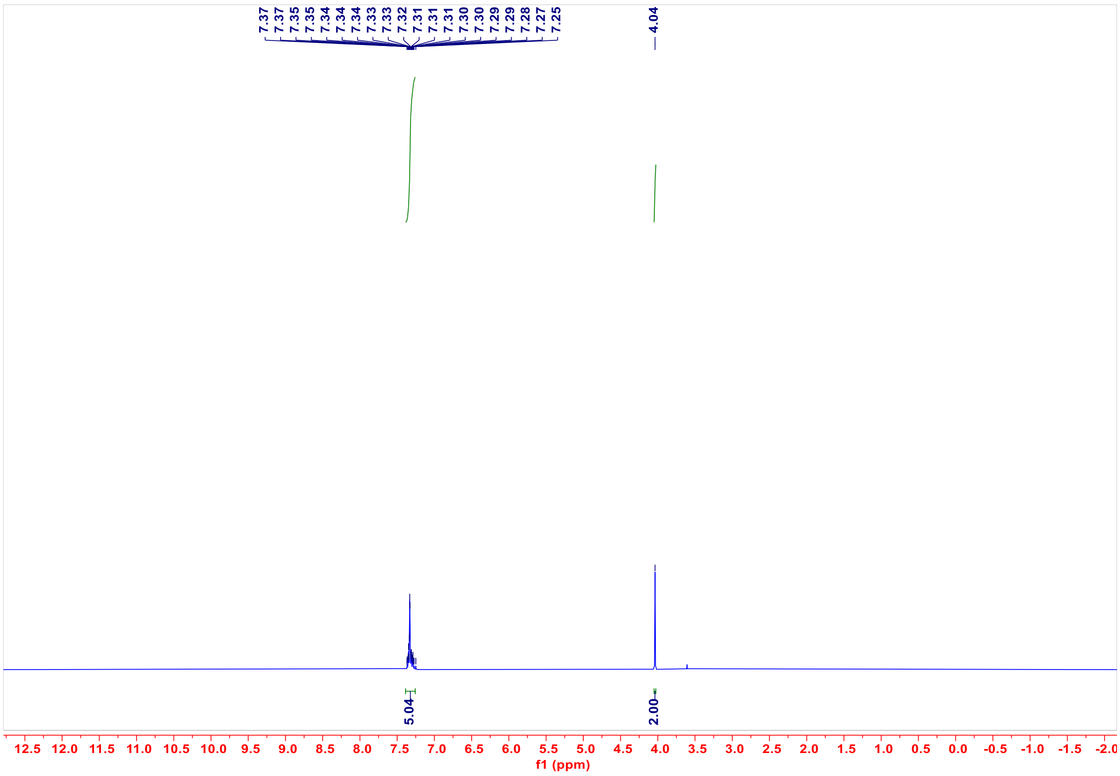
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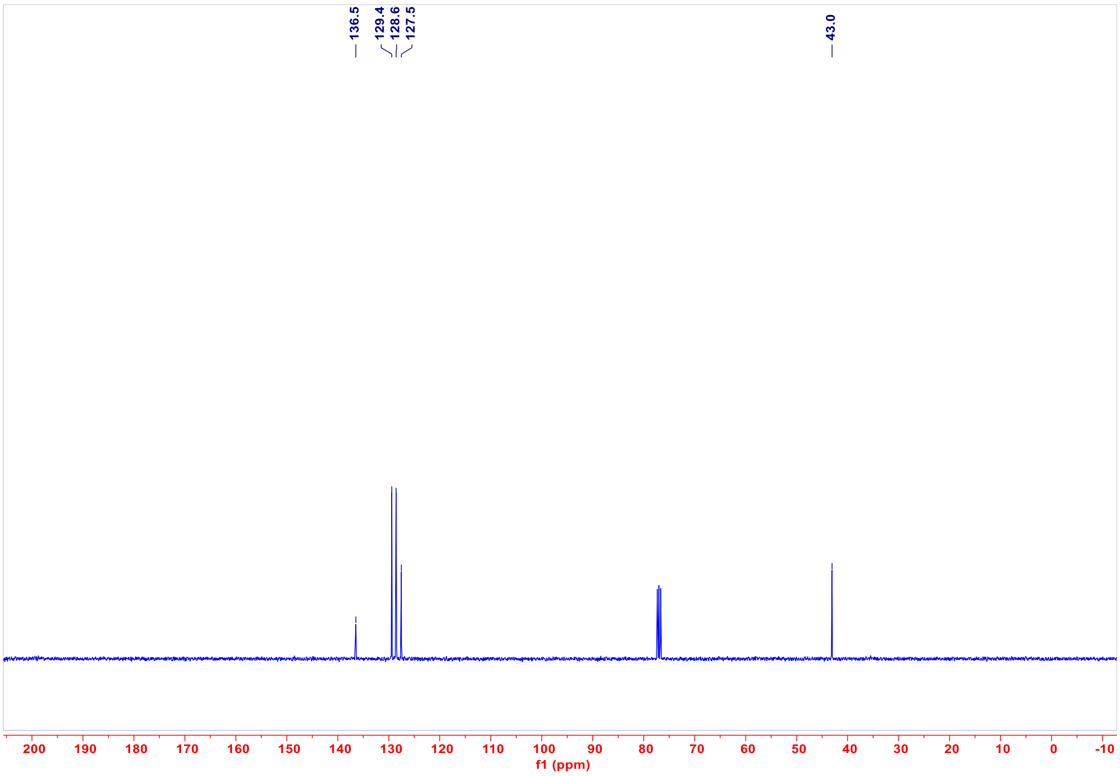
5.04
2.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)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127.5
43.0
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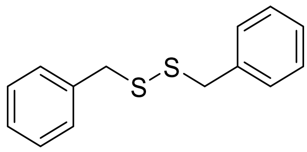
f1 (ppm)



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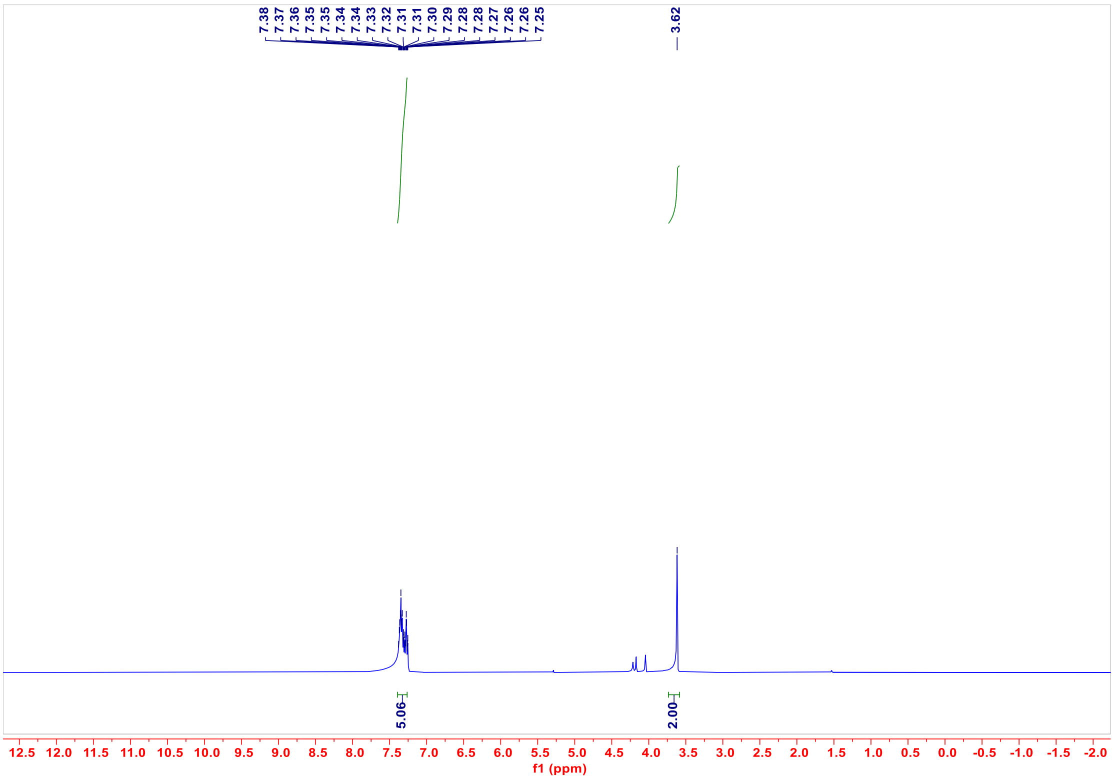
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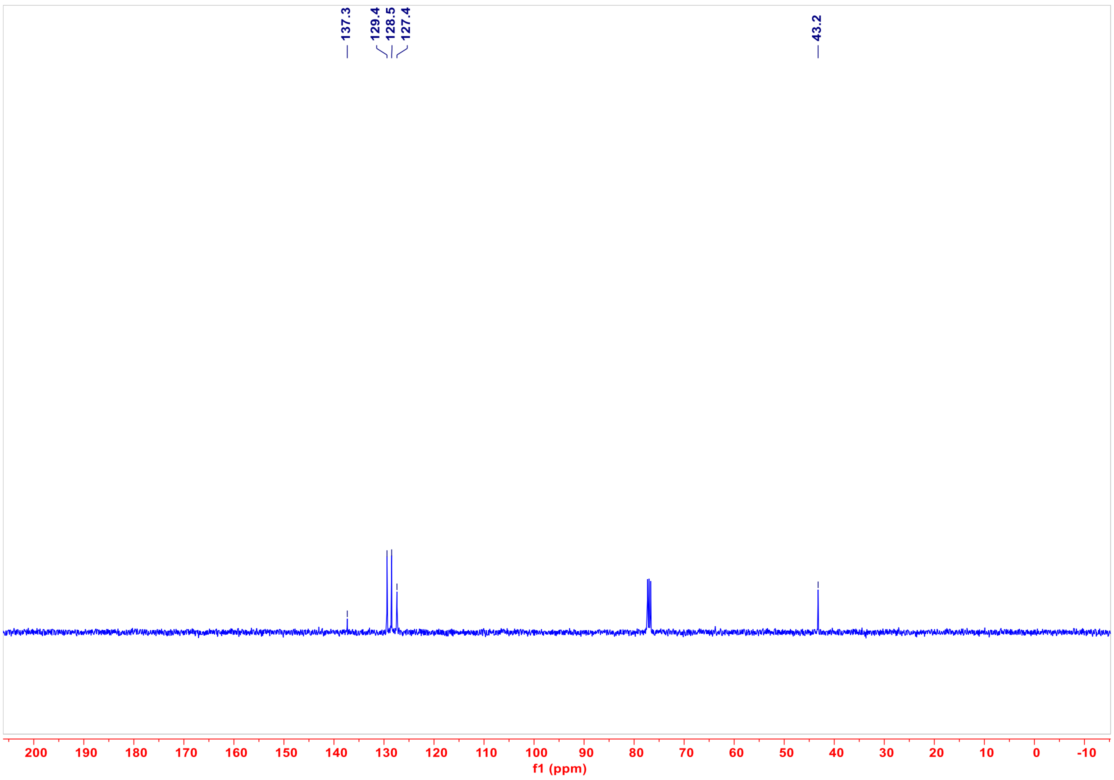
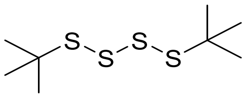
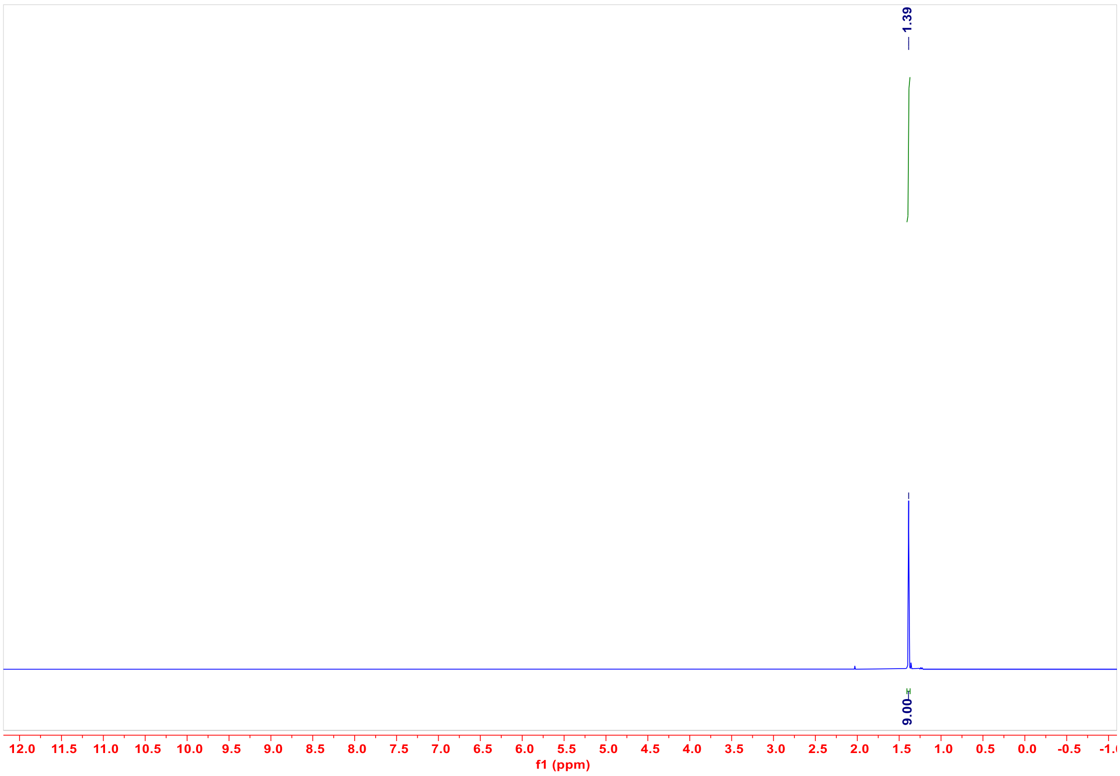
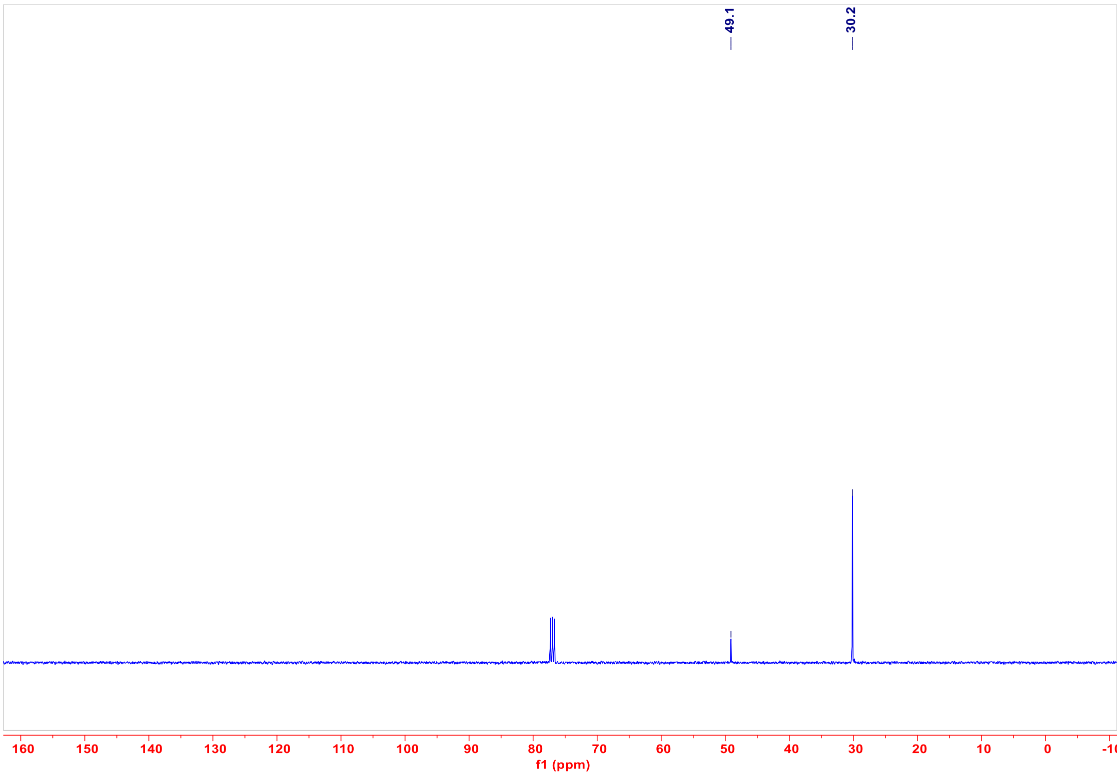
7.29
7.28
7.28
7.27
7.26
7.26
7.25
3.62
5.06
2.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)


137.3
129.4
128.5
127.4
43.2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


S
S
S
S

Int-I


1.39
9.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


49.1
30.2
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)