Electronic Supporting Information

for

Straightforward Chemoselective Access to Unsymmetrical Dithioacetals through a Thiosulfonates Homologation-Nucleophilic Substitution Sequence

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1. General Methods

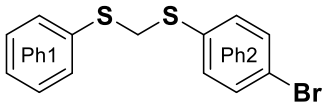
Melting points were determined on a Reichert–Kofler hot-stage microscope and are uncorrected. Mass spectra were obtained on a Shimadzu QP 1000 instrument (EI, 70 eV) and on a Bruker maXis 4G instrument (ESI-TOF, HRMS). ^{1}H, ^{13}C, ^{19}F and ^{15}N NMR spectra were recorded with a Bruker Avance III 400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 376 MHz for ^{19}F and 40 MHz for ^{15}N) at 298 K using a directly detecting broadband observe (BBFO) probe. The center of the (residual) solvent signal was used as an internal standard which was related to TMS with δ 7.26 ppm (^{1}H in $CDCl_3$) and δ 77.0 ppm (^{13}C in $CDCl_3$). ^{19}F NMR spectra were referenced via the Ξ ratio (absolute referencing). ^{15}N NMR spectra (gs-HMBC, gs-HSQC) were referenced against neat, external nitromethane. Spin-spin coupling constants (*J*) are given in Hz. In nearly all cases, full and unambiguous assignment of all resonances was performed by combined application of standard NMR techniques, such as APT, HSQC, HMBC, HSQCTOCSY, COSY and NOESY experiments. The starting thiosulfonates were commercially available ($PhSSO_2Ph$, $MeSSO_2Me$) or prepared according to literature (for compound **33** and **34**).[1] Chemicals were purchased from Fluorochem, Acros, Alfa Aesar or Sigma-Aldrich and used as received. MeLi-LiBr (1.5 M ethereal solution) was titrated immediately prior to use according to literature.[2]

2. General procedure for the homologation of *S*-thiosulfonate ester to asymmetric dithioacetals (General Procedure 1, GP1)

The *S*-thiosulfonate ester ($RSSO_2R$, 1.0 equiv) was dissolved in dry THF under Argon and cooled down to -78 °C. Chloroiodomethane (2.0 equiv) was added and, after 5 min, MeLi-LiBr (2.2 M solution in Et_2O, 1.8 equiv) was added *via* syringe pump (rate 0.2 mL/min) and then, the resulting mixture was stirred for 1 h. After increasing the temperature up to 0 °C, a solution of mercaptane (R^1SH, 1.3 equiv) and NaI (0.1 equiv) in dry DMF was added dropwise. Upon reaching room temperature, the reaction mixture was further stirred for 6 h and, subsequently was quenched with aqueous saturated NH_4Cl solution. The resulting organic phase was extracted 3 times with Et_2O, washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude compounds were purified as reported below through column chromatography.

3. Spectral and Characterization Data

1-[(Benzylsulfanyl)methyl]-4-bromobenzene (2)



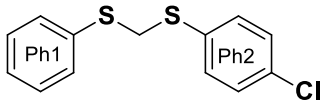
By following general procedure 1, starting from *S*-phenyl benzenesulfonothioate (250 mg, 0.20 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of 4-bromobenzene-1-thiol (246 mg, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **2** was obtained in 93% yield (289 mg) as colourless oil after chromatography on silica gel (90:10 v/v, *n*-hexane/dichloromethane).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (m, 2H, Ph2 H-2,6), 7.41 (m, 2H, Ph1 H-2,6), 7.32 (m, 2H, Ph1 H-3,5), 7.27 (m, 3H, Ph1 H-4, Ph2 H-3,5), 4.31 (s, 2H, SCH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.6 (Ph1 C-1), 134.0 (Ph2 C-4), 132.3 (Ph2 C-3,5), 132.1 (Ph2 C-2,6), 130.9 (Ph1 C-2,6), 129.1 (Ph1 C-3,5), 127.3 (Ph1 C-4), 121.3 (Ph2 C-1), 40.7 (SCH_2).

HRMS (ESI), *m/z*: calcd. for $C_{13}H_{12}BrS_2^+$: 292.9994 $[M+H]^+$; found: 292.9992.

1-Chloro-4-{[(phenylsulfanyl)methyl]sulfanyl}benzene (3)[3]



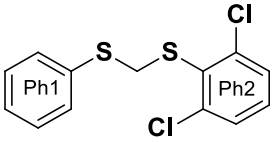
By following general procedure 1, starting from *S*-phenyl benzenesulfonothioate (250 mg, 0.20 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of 4-chlorobenzene-1-thiol (188 mg, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **3** was obtained in 93% yield (248 mg) as colourless oil after chromatography on silica gel (90:10 *v/v*, *n*-hexane/dichloromethane).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (m, 2H, Ph1 H-2,6), 7.35 (m, 2H, Ph2 H-3,5), 7.32 (m, 2H, Ph1 H-3,5), 7.28 (m, 2H, Ph2 H-2,6), 7.27 (m, 1H, Ph1 H-4), 4.31 (s, 2H, SCH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.6 (Ph1 C-1), 133.4 (Ph2 C-1), 133.3 (Ph2 C-4), 132.2 (Ph2 C-3,5), 130.9 (Ph1 C-2,6), 129.1 (Ph2 C-2,6), 129.0 (Ph1 C-3,5), 127.3 (Ph1 C-4), 40.9 (SCH_2).

HRMS (ESI), *m/z*: calcd. for $C_{13}H_{12}ClS_2^+$: 267.0063 $[M+H]^+$; found: 267.0065.

1,3-Dichloro-2-{[(phenylsulfanyl)methyl]sulfanyl}benzene (4)



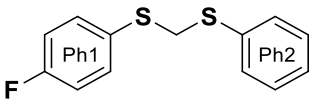
By following general procedure 1, starting from *S*-phenyl benzenesulfonothioate (250 mg, 0.20 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of 2,6-dichlorobenzene-1-thiol (233 mg, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **4** was obtained in 89% yield (268 mg) as orange solid (m.p.: 55-57 °C) after recrystallization with diethyl ether.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (m, 2H, Ph1 H-2,6), 7.36 (m, 2H, Ph2 H-4,6), 7.29 (m, 2H, Ph1 H-3,5), 7.22 (m, 1H, Ph1 H-4), 7.18 (m, 1H, Ph2 H-5), 4.40 (s, 2H, SCH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.5 (Ph2 C-1,3), 134.8 (Ph1 C-1), 131.7 (Ph2 C-2), 130.4 (Ph2 C-5), 130.2 (Ph1 C-2,6), 128.9 (Ph1 C-3,5), 128.6 (Ph2 C-4,6), 127.0 (Ph1 C-4), 40.3 (SCH_2).

HRMS (ESI), *m/z*: calcd. for $C_{13}H_{11}Cl_2S_2^+$: 300.9674 $[M+H]^+$; found: 300.9673.

1-Fluoro-4-{[(phenylsulfanyl)methyl]sulfanyl}benzene (5)



By following general procedure 1, starting from *S*-phenyl benzenesulfonothioate (250 mg, 0.20 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of 4-fluorobenzene-1-thiol (167 mg, 0.14 mL, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **5** was obtained in 91% yield (228 mg) as yellow oil after filtration on silica gel.

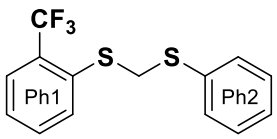
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (m, 2H, Ph1 H-3,5), 7.41 (m, 2H, Ph2 H-2,6), 7.32 (m, 2H, Ph2 H-3,5), 7.26 (m, 1H, Ph2 H-4), 7.01 (m, 2H, Ph1 H-2,6), 4.29 (s, 2H, SCH_2S).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.5 (d, *J* = 247.9 Hz, Ph1 C-1), 134.8 (Ph2 C-1), 134.2 (d, *J* = 8.2 Hz, Ph1 C-5), 134.1 (d, *J* = 8.2 Hz, Ph1 C-3), 130.7 (Ph2 C-2,6), 129.6 (d, *J* = 3.3 Hz, Ph1 C-4), 129.0 (Ph2 C-3,5), 127.1 (Ph2 C-4), 116.1 (d, *J* = 21.9 Hz, Ph1 C-2,6), 41.9 (d, *J* = 1.2 Hz, SCH_2S).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -113.7 (m, F).

HRMS (ESI), *m/z*: calcd. for $C_{13}H_{12}FS_2^+$: 251.0359 $[M+H]^+$; found: 251.0361.

1-{[(Phenylsulfanyl)methyl]sulfanyl}-2-(trifluoromethyl)benzene (6)



By following general procedure 1, starting from *S*-phenyl benzenesulfonothioate (250 mg, 0.20 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of 2-

(trifluoromethyl)benzene-1-thiol (232 mg, 0.18 mL, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **6** was obtained in 95% yield (285 mg) as yellow oil after filtration on silica gel.

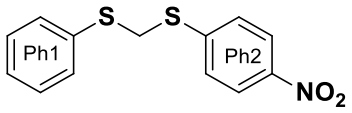
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (m, 1H, Ph1 H-3), 7.63 (m, 1H, Ph1 H-6), 7.50 (m, 1H, Ph1 H-5), 7.45 (m, 2H, Ph2 H-2,6), 7.35 (m, 1H, Ph1 H-4), 7.33 (m, 2H, Ph2 H-3,5), 7.27 (m, 1H, Ph2 H-4), 4.37 (s, 2H, SCH_2S).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.6 (Ph2 C-1), 134.3 (Ph1 C-1), 133.1 (Ph1 C-6), 132.0 (Ph1 C-5), 130.9 (q, *J* = 30.0 Hz, Ph1 C-2), 130.8 (Ph2 C-2,6), 129.1 (Ph2 C-3,5), 127.3 (Ph2 C-4), 127.1 (Ph1 C-4), 126.9 (q, *J* = 5.6 Hz, Ph1 C-3), 123.6 (q, *J* = 273.8 Hz, CF_3), 40.9 (SCH_2S).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -60.5 (s, CF_3).

HRMS (ESI), *m/z*: calcd. for $C_{14}H_{12}F_3S_2^+$: 301.0327 $[M+H]^+$; found: 301.0330.

1-Nitro-4{[(phenylsulfanyl)methyl]sulfanyl}benzene (7)



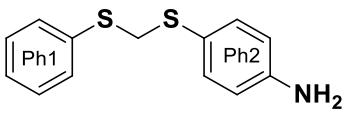
By following general procedure 1, starting from *S*-phenyl benzenesulfonothioate (250 mg, 0.20 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of 4-nitrobenzene-1-thiol (202 mg, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **7** was obtained in 85% yield (236 mg) as yellow oil after chromatography on silica gel (70:30 *v/v*, *n*-hexane/dichloromethane).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 (m, 2H, Ph2 H-2,6), 7.45 (m, 2H, Ph1 H-2,6), 7.41 (m, 2H, Ph2 H-3,5), 7.34 (m, 2H, Ph1 H-3,5), 7.30 (m, Ph1 H-4), 4.43 (s, 2H, SCH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.7 (Ph2 C-1), 145.4 (Ph2 C-4), 133.7 (Ph1 C-1), 131.5 (Ph1 C-2,6), 129.2 (Ph1 C-3,5), 127.9 (Ph1 C-4), 127.4 (Ph2 C-3,5), 123.9 (Ph2 C-2,6), 38.6 (SCH_2).

HRMS (ESI), *m/z*: calcd. for $C_{13}H_{12}NO_2S_2^+$: 278.0304 $[M+H]^+$; found: 278.0306.

4-{[(Phenylsulfanyl)methyl]sulfanyl}aniline (8)



By following general procedure 1, starting from *S*-phenyl benzenesulfonothioate (250 mg, 0.20 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of 4-aminobenzene-1-thiol (168 mg, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL),

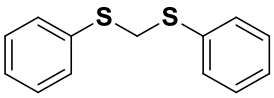
compound **8** was obtained in 88% yield (218 mg) as yellow solid (m.p.: 50 °C) after chromatography on silica gel (70:30 *v/v*, dichloromethane/*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (m, 2H, Ph1 H-2,6), 7.31 (m, 2H, Ph2 H-3,5), 7.30 (m, 2H, Ph1 H-3,5), 7.23 (m, 1H, Ph1 H-4); 6.64 (m, 2H, Ph2 H-2,6), 4.21 (s, 2H, SCH_2), 3.78 (brs, 2H, NH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.5 (Ph2 C-1), 135.4 (Ph1 C-1), 135.2 (Ph2 C-3,5), 130.2 (Ph1 C-2,6), 128.9 (Ph1 C-3,5), 126.7 (Ph1 C-4), 122.1 (Ph2 C-4), 115.6 (Ph2 C-2,6), 42.8 (SCH_2).

HRMS (ESI), *m/z*: calcd. for $C_{13}H_{14}NS_2^+$: 248.0562 $[M+H]^+$; found: 248.0562.

1,1´-(Methylenedisulfanyldiyl)dibenzene (9)[4]



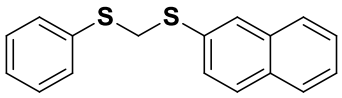
By following general procedure 1, starting from *S*-phenyl benzenesulfonothioate (250 mg, 0.20 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of benzenethiol (143 mg, 0.13 mL, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **9** was obtained in 93% yield (216 mg) as orange oil after filtration on silica gel.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (m, 4H, Ph H-2,6), 7.32 (m, 4H, Ph H-3,5), 7.25 (m, 2H, Ph H-4), 4.35 (s, 2H, SCH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.0 (Ph C-1), 130.7 (Ph C-2,6), 129.0 (Ph C-3,5), 127.1 (Ph C-4), 40.6 (SCH_2).

HRMS (ESI), *m/z*: calcd. for $C_{13}H_{12}NaS_2^+$: 255.0273 $[M+Na]^+$; found: 255.0272.

2-{[(Phenylsulfanyl)methyl]sulfanyl}naphthalene (10)



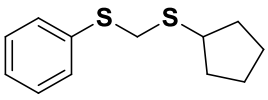
By following general procedure 1, starting from *S*-phenyl benzenesulfonothioate (250 mg, 0.20 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of naphthalene-2-thiol (208 mg, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **10** was obtained in 95% yield (268 mg) as orange solid (m.p.: 29 °C) after recrystallization with diethyl ether.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (m, 1H, Naph H-1), 7.81 (m, 1H, Naph H-5), 7.78 (m, 1H, Naph H-4), 7.77 (m, 1H, Naph H-8), 7.49 (m, 1H, Naph H-7), 7.48 (m, 1H, Naph H-3), 7.47 (m, 1H, Naph H-6), 7.45 (m, 2H, Ph H-2,6), 7.32 (m, 2H, Ph H-3,5), 7.26 (m, Ph H-4), 4.45 (s, 2H, SCH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.9 (Ph C-1), 133.6 (Naph C-8a), 132.4 (Naph C-2), 132.2 (Naph C-4a), 130.8 (Ph C-2,6), 129.1 (Naph C-1), 129.0 (Ph C-3,5), 128.6 (Naph C-4), 128.1 (Naph C-3), 127.7 (Naph C-5), 127.4 (Naph C-8), 127.2 (Ph C-4), 126.6 (Naph C-7), 126.1 (Naph C-6), 40.5 (SCH_2).

HRMS (ESI), *m/z*: calcd. for $C_{17}H_{14}NaS_2^+$: 305.0429 $[M+Na]^+$; found: 305.0429.

{[(Cyclopentylsulfanyl)methyl]sulfanyl}benzene (11)



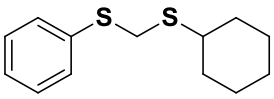
By following general procedure 1, starting from *S*-phenyl benzenesulfonothioate (250 mg, 0.20 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of cyclopentanethiol (133 mg, 0.14 mL, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **11** was obtained in 87% yield (213 mg) as colourless oil after chromatography on silica gel (*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (m, 2H, Ph H-2,6), 7.31 (m, 2H, Ph H-3,5), 7.23 (m, Ph H-4), 4.05 (s, 2H, SCH_2), 3.37 (m, 1H, Cyclopent H-1), 2.03 (m, 2H, Cyclopent H-2,5), 1.74 (m, 2H, Cyclopent H-3,4), 1.59 (m, 2H, Cyclopent H-3,4), 1.56 (m, 2H, Cyclopent H-2,5).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.7 (Ph C-1), 130.2 (Ph C-2,6), 128.9 (Ph C-3,5), 126.7 (Ph C-4), 43.7 (Cyclopent C-1), 37.8 (SCH_2), 33.4 (Cyclopent C-2,5), 24.8 (Cyclopent C-3,4).

HRMS (ESI), *m/z*: calcd. for $C_{12}H_{16}NaS_2^+$: 247.0586 $[M+Na]^+$; found: 247.0587.

{[(Cyclohexylsulfanyl)methyl]sulfanyl}benzene (12)[5]



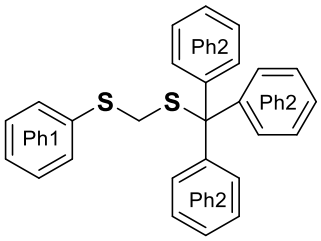
By following general procedure 1, starting from *S*-phenyl benzenesulfonothioate (250 mg, 0.20 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of cyclohexanethiol (151 mg, 0.16 mL, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **12** was obtained in 85% yield (203 mg) as colourless oil after chromatography on silica gel (95:05 *v*/*v*, *n*-hexane/dichloromethane).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (m, 2H, Ph H-2,6), 7.31 (m, 2H, Ph H-3,5), 7.23 (m, 1H, Ph H-4), 4.05 (s, 2H, SCH_2), 2.93 (m, 1H, Cyclohex H-1), 1.99 (m, 2H, Cyclohex H-2,6), 1.77 (m, 2H, Cyclohex H-3,5), 1.62 (m, 1H, Cyclohex H-4), 1.36 (m, 2H, Cyclohex H-2,6), 1.31 (m, 2H, Cyclohex H-3,5), 1.30 (m, H, Cyclohex H-4).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.8 (Ph C-1), 130.2 (Ph C-2,6), 128.9 (Ph C-3,5), 126.8 (Ph C-4), 43.3 (Cyclohex C-1), 36.1 (SCH_2), 33.2 (Cyclohex C-2,6), 26.0 (Cyclohex C-3,5), 25.8 (Cyclohex C-4).

HRMS (ESI), *m/z*: calcd. for $C_{13}H_{19}S_2^+$: 239.0923 $[M+H]^+$; found: 239.0925.

1,1´,1´´-({[(Phenylsulfanyl)methyl]sulfanyl}methanetriyl)tribenzene (13)



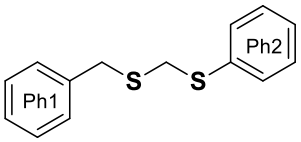
By following general procedure 1, starting from *S*-phenyl benzenesulfonothioate (250 mg, 0.20 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of triphenylmethanethiol (359 mg, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **13** was obtained in 96% yield (383 mg) as white solid (m.p.: 100 °C) after chromatography on silica gel (85:15 *v*/*v*, *n*-hexane/dichloromethane).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (m, 6H, Ph2 H-2,6), 7.33-7.22 (m, 5H, Ph1 H-2,3,4,5,6), 7.30 (m, 6H, Ph2 H-3,5), 7.24 (m, 3H, Ph H-4), 3.55 (s, 2H, SCH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.2 (Ph2 C-1), 134.9 (Ph1 C-1), 130.1 (Ph1 C-2,6), 129.5 (Ph2 C-2,6), 128.8 (Ph1 C-3,5), 128.0 (Ph2 C-3,5), 126.80 (Ph1 C-4), 126.76 (Ph2 C-4), 68.0 ($SC(Ph)_3$), 36.5 (SCH_2).

HRMS (ESI), *m/z*: calcd. for $C_{26}H_{22}NaS_2^+$: 421.1055 $[M+Na]^+$; found: 421.1057.

{[(Benzylsulfanyl)methyl]sulfanyl}benzene (14)[6]



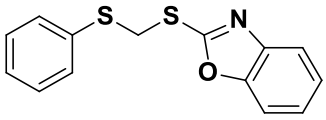
By following general procedure 1, starting from *S*-phenyl benzenesulfonothioate (250 mg, 0.20 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of phenylmethanethiol (180 mg, 0.17 mL,1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **14** was obtained in 91% (224 mg) as a colorless oil after chromatography on silica gel (95:05 *v*/*v*, *n*-hexane/dichloromethane).

^{1}H NMR (400 MHz, CDCl3) δ: 7.41 (m, 2H, Ph2 H-2,6), 7.32 (m, 6H, Ph2 H-3,5, Ph1 H-2,3,5,6), 7.25 (m, 2H, Ph2 H-4, Ph1 H-4), 3.88 (s, 2H, CH_2S), 3.85 (s, 2H, SCH_2S).

^{13}C NMR (100 MHz, CDCl3) δ: 137.4 (Ph1 C-1), 135.0 (Ph2 C-1), 130.6 (Ph2 C-2,6), 129.1 (Ph1 C-2,6), 129.0 (Ph2 C-3,5), 128.6 (Ph1 C-3,5), 127.2 (Ph2 C-4), 127.0 (Ph1 C-4), 36.8 (SCH_2S), 35.0 (CH_2S).

HRMS (ESI), *m/z*: calcd. for $C_{14}H_{15}S_2^+$: 247.0610 $[M+H]^+$; found: 247.0612.

2-{[(Phenylsulfanyl)methyl]sulfanyl}-1,3-benzoxazole (15)



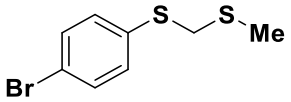
By following general procedure 1, starting from *S*-phenyl benzenesulfonothioate (250 mg, 0.20 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of 1,3-benzoxazole-2-thiol (197 mg, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **15** was obtained in 86% yield (235 mg) as white solid (m.p.: 54 °C) after chromatography on silica gel (80:20 *v*/*v*, *n*-hexane/dichloromethane).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (m, 1H, Benzox H-4), 7.51 (m, 2H, Ph H-2,6), 7.43 (m, 1H, Benzox H-7), 7.33 (m, 2H, Ph H-3,5), 7.29 (m, 1H, Benzox H-5), 7.27 (m, 1H, Ph H-4), 7.25 (m, 1H, Benzox H-6), 4.77 (s, 2H, SCH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.4 (Benzox C-2), 151.9 (Benzox C-7a), 141.8 (Benzox C-3a), 133.7 (Ph C-1), 131.5 (Ph C-2,6), 129.2 (Ph C-3,5), 127.9 (Ph C-4), 124.4 (Benzox C-5), 124.1 (Benzox C-6), 118.7 (Benzox C-4), 110.0 (Benzox C-7). 38.6 (SCH_2).

HRMS (ESI), *m/z*: calcd. for $C_{14}H_{11}NNaOS_2^+$: 296.0174 $[M+Na]^+$; found:296.0174

1-Bromo-4-{[(methylsulfanyl)methyl]sulfanyl}benzene (16)[7]



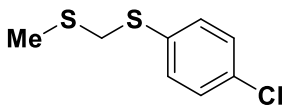
By following general procedure 1, starting from *S*-methyl methanesulfonothioate (126 mg, 0.11 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of 4-bromobenzene-1-thiol (246 mg, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **16** was obtained in 95% yield (237 mg) as yellow oil after filtration on silica gel.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (m, 2H, Ph H-2,6), 7.29 (m, 2H, Ph H-3,5), 3.97 (s, 2H, SCH_2S), 2.22 (s, 3H, SCH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.2 (Ph C-4), 132.2 (Ph C-3,5), 132.0 (Ph C-2,6), 121.0 (Ph C-1), 40.4 (SCH_2S), 15.1 (SCH_3).

HRMS (ESI), *m/z*: calcd. for $C_8H_{10}BrS_2^+$: 248.9402 $[M+H]^+$; found: 248.9405.

1-Chloro-4-{[(methylsulfanyl)methyl]sulfanyl}benzene (17)[8]



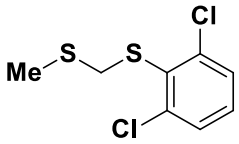
By following general procedure 1, starting from *S*-methyl methanesulfonothioate (126 mg, 0.11 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of 4-chlorobenzene-1-thiol (188 mg, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **17** was obtained in 93% yield (190 mg) as yellow oil after filtration on silica gel.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (m, 2H, Ph H-3,5), 7.29 (m, 2H, Ph H-2,6), 3.97 (s, 2H, SCH_2), 2.22 (s, 3H, CH_3S).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 133.5 (Ph C-4), 133.2 (Ph C-1), 132.1 (Ph C-3,5), 129.1 (Ph C-2,6), 40.7 (SCH_2), 15.1 (CH_3S).

HRMS (ESI), *m/z*: calcd. for $C_8H_{10}ClS_2^+$: 204.9907 $[M+H]^+$; found: 204.9905.

1,3-Dichloro-2-{[(methylsulfanyl)methyl]sulfanyl}benzene (18)



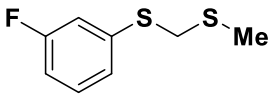
By following general procedure 1, starting from *S*-methyl methanesulfonothioate (126 mg, 0.11 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of 2,6-dichlorobenzene-1-thiol (233 mg, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **18** was obtained in 91% yield (218 mg) as yellow oil after filtration on silica gel.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (m, 2H, Ph H-4,6), 7.21 (m, 1H, Ph H-5), 4.04 (s, 2H, SCH_2), 2.30 (s, 3H, SCH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.6 (Ph C-1,3), 131.9 (Ph C-2), 130.3 (Ph C-5), 128.6 (Ph C-4,6), 41.1 (SCH_2), 15.6 (CH_3S).

HRMS (ESI), *m/z*: calcd. for $C_8H_9Cl_2S_2^+$: 238.9517 $[M+H]^+$; found: 238.9518.

1-Fluoro-3-{[(methylsulfanyl)methyl]sulfanyl}benzene (19)



By following general procedure 1, starting from *S*-methyl methanesulfonothioate (126 mg, 0.11 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of 3-fluorobenzene-1-thiol (167 mg, 0.14 mL, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **19** was obtained in 94% yield (177 mg) as brown oil after filtration on silica gel.

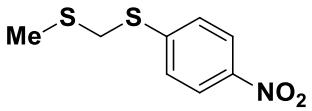
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (m, 1H, Ph H-5), 7.17 (m, 1H, Ph H-4), 7.13 (m, 1H, Ph H-2), 6.92 (m, 1H, Ph H-6), 4.01 (s, 2H, SCH_2S), 2.24 (s, 3H, SCH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.7 (d, *J* = 248.4 Hz, Ph C-1), 137.6 (d, *J* = 7.8 Hz, Ph C-3), 130.1 (d, *J* = 8.5 Hz, Ph C-5), 125.4 (d, *J* = 3.0 Hz, Ph C-4), 116.7 (d, *J* = 23.0 Hz, Ph C-2), 113.7 (d, *J* = 21.2 Hz, Ph C-6), 39.8 (SCH_2S), 15.2 (SCH_3).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -112.0 (m, F).

HRMS (ESI), *m/z*: calcd. for $C_8H_{10}FS_2^+$: 189.0202 $[M+H]^+$; found: 189.0201.

1-{[(Methylsulfanyl)methyl]sulfanyl}-4-nitrobenzene (20)



By following general procedure 1, starting from *S*-methyl methanesulfonothioate (126 mg, 0.11 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of 4-nitrobenzene-1-thiol (202 mg, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **20** was obtained in 85% yield (183 mg) as orange oil after filtration on silica gel.

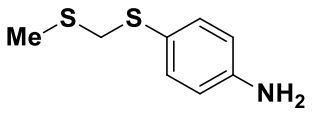
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16 (m, 2H, Ph H-3,5), 7.43 (m, 2H, Ph H-2,6), 4.11 (s, 2H, SCH_2), 2.26 (s, 3H, CH_3S).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.7 (Ph C-1), 127.5 (Ph C-2,6), 123.9 (Ph C-3,5), 38.0 (SCH_2), 15.4 (CH_3S).

^{15}N NMR (40MHz, $CDCl_3$) δ: -12.8 (NO_2).

HRMS (ESI), *m/z*: calcd. for $C_8H_{10}NO_2S_2^+$: 216.0147 $[M+H]^+$; found: 216.0149.

4-{[(Methylsulfanyl)methyl]sulfanyl}aniline (21)



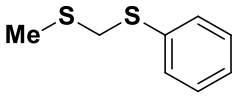
By following general procedure 1, starting from *S*-methyl methanesulfonothioate (126 mg, 0.11 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of 4-aminobenzene-1-thiol (168 mg, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **21** was obtained in 87% yield (161 mg) as brown oil after chromatography on silica gel (70:30 *v/v*, dichloromethane/*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (m, 2H, Ph H-3,5), 6.64 (m, 2H, Ph H-2,6), 4.20-3.20 (brs, 2H, NH_2), 3.84 (s, 2H, SCH_2), 2.20 (s, 3H, CH_3S).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.5 (Ph C-1), 135.1 (Ph C-3,5), 122.1 (Ph C-4), 115.5 (Ph C-2,6), 43.0 (SCH_2), 15.0 (CH_3S).

HRMS (ESI), *m/z*: calcd. for $C_8H_{12}NS_2^+$: 186.0406 $[M+H]^+$; found: 186.0408.

{[(Methylsulfanyl)methyl]sulfanyl}benzene (22)[9]



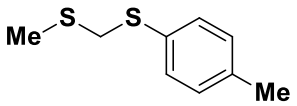
By following general procedure 1, starting from *S*-methyl methanesulfonothioate (126 mg, 0.11 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of benzenethiol (143 mg, 0.13 mL, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **22** was obtained in 96% yield (163 mg) as light yellow oil after filtration on silica gel.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (m, 2H, Ph H-2,6), 7.32 (m, 2H, Ph H-3,5), 7.25 (m, 1H, Ph H-4), 4.01 (s, 2H, SCH_2), 2.23 (s, 3H, SCH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.1 (Ph C-1), 130.6 (Ph C-2,6), 128.9 (Ph C-3,5), 127.0 (Ph C-4), 40.4 (SCH_2), 15.2 (CH_3S).

HRMS (ESI), *m/z*: calcd. for $C_8H_{10}NaS_2^+$: 193.0116 $[M+Na]^+$; found: 193.0117.

1-Methyl-4-{[(methylsulfanyl)methyl]sulfanyl}benzene (23)[8]



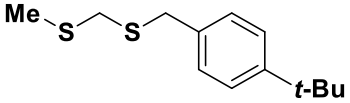
By following general procedure 1, starting from *S*-methyl methanesulfonothioate (126 mg, 0.11 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of 4-methylbenzene-1-thiol (162 mg, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **23** was obtained in 94% yield (173 mg) as yellow oil after filtration on silica gel.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (m, 2H, Ph H-3,5), 7.14 (m, 2H, Ph H-2,6), 3.96 (s, 2H, SCH_2), 2.34 (s, 3H, CH_3), 2.22 (s, 3H, CH_3S).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.3 (Ph C-1), 131.5 (Ph C-3,5), 131.2 (Ph C-4), 129.7 (Ph C-2,6), 41.2 (SCH_2), 21.1 (CH_3), 15.1 (CH_3S).

HRMS (ESI), *m/z*: calcd. for $C_9H_{13}S_2^+$: 185.0453 $[M+H]^+$; found: 185.0456.

1-(2-Methyl-2-propanyl)-4-({[(methylsulfanyl)methyl]sulfanyl}methyl)benzene (24)



By following general procedure 1, starting from *S*-methyl methanesulfonothioate (126 mg, 0.11 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of (4-*tert*-butylphenyl)methanethiol (234 mg, 0.24 mL, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1

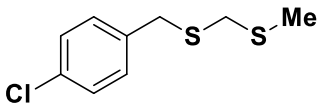
equiv) in dry DMF (3 mL), compound **24** was obtained in 89% yield (214 mg) as yellow oil after chromatography on silica gel (90:10 v/v, *n*-hexane/dichloromethane).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (m, 2H, Ph H-2,6), 7.26 (m, 2H, Ph H-3,5), 3.80 (s, 2H, CH_2S), 3.52 (s, 2H, SCH_2S), 2.18 (s, 3H, SCH_3), 1.32 (s, 9H, $C(CH_3)_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.9(Ph C-1), 134.5 (Ph C-4), 128.7 (Ph C-3,5), 125.4 (Ph C-2,6), 36.8 (SCH_2S), 34.5 ($\underline{C}(CH_3)_3$), 33.7 (CH_2S), 31.3 ($C(\underline{C}H_3)_3$) 14.4 (SCH_3).

HRMS (ESI), *m/z*: calcd. for $C_{13}H_{21}S_2^+$: 241.1079 $[M+H]^+$; found: 241.1078.

1-Chloro-4-({[(methylsulfanyl)methyl]sulfanyl}methyl)benzene (25)



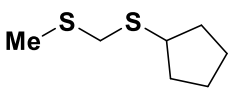
By following general procedure 1, starting from *S*-methyl methanesulfonothioate (126 mg, 0.11 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of (4-chlorophenyl)methanethiol (206 mg, 0.17 mL, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **25** was obtained in 87% yield (190 mg) as colourless oil after chromatography on silica gel (80:20 v/v, *n*-hexane/dichloromethane).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (m, 4H, Ph H-2,3,5,6), 3.78 (s, 2H, CH_2S), 3.47 (s, 2H, SCH_2S), 2.16 (s, 3H, SCH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.2 (Ph C-4), 132.8 (Ph C-1), 130.4 (Ph C-3,5), 128.6 (Ph C-2,6), 36.6 (SCH_2S), 33.4 (CH_2S), 14.3 (SCH_3).

HRMS (ESI), *m/z*: calcd. for $C_9H_{12}ClS_2^+$: 219.0063 $[M+H]^+$; found: 219.0060.

{[(Methylsulfanyl)methyl]sulfanyl}cyclopentane (26)



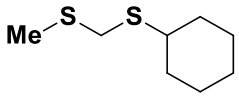
By following general procedure 1, starting from *S*-methyl methanesulfonothioate (126 mg, 0.11 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of cyclopentanethiol (133 mg, 0.14 mL, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **26** was obtained in 83% yield (135mg) as colourless oil after chromatography on silica gel (*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.66 (s, 2H, SCH_2), 3.30 (m, 1H, Cyclopent H-1), 2.19 (s, 3H, CH_3S), 2.02 (m, 2H, Cyclopent H-2,5), 1.74 (m, 2H, Cyclopent H-3,4), 1.59 (m, 2H, Cyclopent H-3,4).1.55 (m, 2H, Cyclopent H-2,5).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 42.9 (Cyclopent C-1), 37.7 (SCH_2), 33.4 (Cyclopent C-2,5), 24.8 (Cyclopent C-3,4), 14.8 (CH_3S).

HRMS (ESI), *m/z*: calcd. for $C_7H_{15}S_2^+$: 163.0610 $[M+H]^+$; found: 163.0608.

{[(Methylsulfanyl)methyl]sulfanyl}cyclohexane (27)



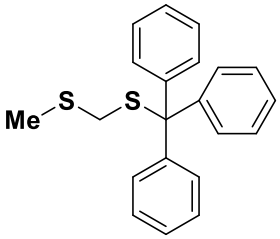
By following general procedure 1, starting from *S*-methyl methanesulfonothioate (126 mg, 0.11 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of cyclohexanethiol (151 mg, 0.16 mL, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **27** was obtained in 88% yield (155 mg) as colourless oil after chromatography on silica gel (95:05 *v*/*v*, *n*-hexane/dichloromethane).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.67 (s, 2H, SCH_2), 2.87 (m, 1H, Cyclohex H-1), 2.18 (s, 3H, CH_3S), 1.97 (m, 2H, Cyclohex H-2,6), 1.77 (m, 2H, Cyclohex H-3,5), 1.61 (m, 1H, Cyclohex H-4), 1.37 (m, 2H, Cyclohex H-2,6), 1.31 (m, 2H, Cyclohex H-3,5), 1.28 (m, 1H, Cyclohex H-4).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 42.4 (Cyclohex C-1), 36.0 (SCH_2), 33.2 (Cyclohex C-2,6), 26.0 (Cyclohex C-3,5), 25.8 (Cyclohex C-4), 14.7 (CH_3S).

HRMS (ESI), *m/z*: calcd. for $C_8H_{16}NaS_2^+$: 199.0586 $[M+Na]^+$; found:199.0587.

1,1´,1´´-({[(Methylsulfanyl)methyl]sulfanyl}methanetriyl)tribenzene (28)



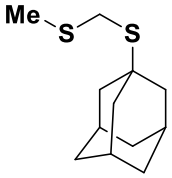
By following general procedure 1, starting from *S*-methyl methanesulfonothioate (126 mg, 0.11 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of triphenylmethanethiol (359 mg, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **28** was obtained in 91% yield (306 mg) as white solid (m.p.: 83 °C) after chromatography on silica gel (70:30 *v*/*v*, *n*-hexane/dichloromethane).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (m, 6H, Ph H-2,6), 7.29 (m, 6H, Ph H-3,5), 7.22 (m, 3H, Ph H-4), 3.17 (s, 2H, SCH_2), 2.10 (s, 3H, CH_3S).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.4 (Ph C-1), 129.5 (Ph C-2,6), 128.0 (Ph C-3,5), 126.8 (Ph C-4), 67.7 ($SC(Ph)_3$), 36.4 (SCH_2), 15.7 (CH_3S).

HRMS (ESI), *m/z*: calcd. for $C_{21}H_{20}NaS_2^+$: 359.0899 $[M+Na]^+$; found: 359.0898

1-{[(Methylsulfanyl)methyl]sulfanyl}adamantane (29)



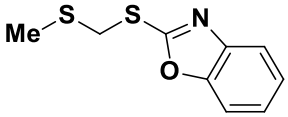
By following general procedure 1, starting from *S*-methyl methanesulfonothioate (126 mg, 0.11 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of adamantane-1-thiol (219 mg, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **29** was obtained in 87% yield (199 mg) as yellow oil after chromatography on silica gel (90:10 *v*/*v*, *n*-hexane/dichloromethane).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.61 (s, 2H, SCH_2), 2.14 (s, 3H, CH_3S), 1.99 (m, 3H, Adam H-3,5,7), 1.86 (m, 6H, Adam H-2,8,9), 1.63 (m, 6H, Adam H-4,6,10).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 45.4 (Adam C-1), 43.3 (Adam C-2,8,9), 36.1 (Adam C-4,6,10), 31.6 (SCH_2), 29.5 (Adam C-3,5,7), 15.2 (CH_3S).

HRMS (ESI), *m/z*: calcd. for $C_{12}H_{20}NaS_2^+$: 251.0899 $[M+Na]^+$; found:251.0901.

2-{[(Methylsulfanyl)methyl]sulfanyl}-1,3-benzoxazole (30)



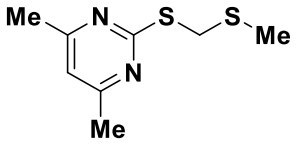
By following general procedure 1, starting from *S*-methyl methanesulfonothioate (126 mg, 0.11 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of 1,3-benzoxazole-2-thiol (197 mg, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **30** was obtained in 85% yield (180 mg) as colourless oil after chromatography on silica gel (94:06 *v*/*v*, *n*-hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (m, 1H, Benzox H-4), 7.45 (m, 1H, Benzox H-7), 7.29 (m, 1H, Benzox H-5), 7.26 (m, 1H, Benzox H-6), 4.47 (s, 2H, SCH_2), 2.30 (s, 3H, CH_3S).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.7 (Benzox C-2), 151.9 (Benzox C-7a), 141.8 (Benzox C-3a), 124.4 (Benzox C-5), 124.1 (Benzox C-6), 118.6 (Benzox C-4), 110.0 (Benzox C-7), 38.3 (SCH_2), 15.8 (CH_3S).

HRMS (ESI), *m/z*: calcd. for $C_9H_9NNaOS_2^+$: 234.0018 $[M+Na]^+$; found: 234.0021.

4,6-Dimethyl-2-{[(methylsulfanyl)methyl]sulfanyl}pyrimidine (31)



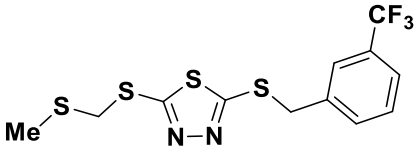
By following general procedure 1, starting from *S*-methyl methanesulfonothioate (126 mg, 0.11 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of 4,6-dimethylpyrimidine-2-thiol (182 mg, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **31** was obtained in 91% yield (182 mg) as colourless oil after filtration on silica gel.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.71 (s, 1H, Pyr H-5), 4.33 (s, 2H, SCH_2S), 2.40 (s, 6H, CH_3), 2.24 (s, 3H, SCH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.9 (Pyr C-2), 167.1 (Pyr C-4,6), 116.0 (Pyr C-5), 36.3 (SCH_2S), 23.8 (CH_3), 15.4 (SCH_3).

HRMS (ESI), *m/z*: calcd. for $C_8H_{13}N_2S_2^+$: 201.0515 $[M+H]^+$; found: 201.0517.

2-{[(Methylsulfanyl)methyl]sulfanyl}-5-{[3-(trifluoromethyl)benzyl]sulfanyl}-1,3,4-thiadiazole (32)



By following general procedure 1, starting from *S*-methyl methanesulfonothioate (126 mg, 0.11 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of 5-({[3-(trifluoromethyl)phenyl]methyl}sulfanyl)-1,3,4-thiadiazole-2-thiol (401 mg, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **32** was obtained in 95% yield (320 mg) as yellow oil after filtration on silica gel.

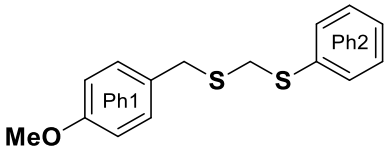
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (brs, 1H, Ph H-2), 7.63 (brd, *J* = 7.7 Hz, 1H, Ph H-6), 7.54 (brd, *J* = 7.7 Hz, 1H, Ph H-4), 7.45 (m, 1H, Ph H-5), 4.57 (s, 2H, SCH_2), 4.36 (s, 2H, SCH_2S), 2.27 (s, 3H, CH_3S).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.5 (Thiadiaz C-5), 164.3 (Thiadiaz C-2), 137.1 (Ph C-1), 132.6 (q, *J* = 1.3 Hz, Ph C-6), 131.1 (q, *J* = 32.4 Hz, Ph C-3), 129.2 (Ph C-5), 125.9 (q, *J* = 3.8 Hz, Ph C-2), 124.7 (q, *J* = 3.8 Hz, Ph C-4), 123.8 (q, *J* = 272.4, CF_3), 40.3 (SCH_2S), 37.5 (SCH_2), 15.7 (CH_3S).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.7 (s, CF_3).

HRMS (ESI), *m/z*: calcd. for $C_{12}H_{12}F_3N_2S_4^+$: 368.9830 $[M+H]^+$; found: 368.9834.

1-Methoxy-4-({[(phenylsulfanyl)methyl]sulfanyl}methyl)benzene (33)



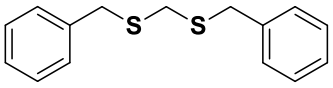
By following general procedure 1, starting from *S*-[(4-methoxyphenyl)methyl] 4-methylbenzene-1-sulfonothioate (308 mg, 0.20 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of benzenethiol (143 mg, 0.13 mL, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **33** was obtained in 92% yield (254 mg) as pink oil after chromatography on silica gel (70:30 v/v, *n*-hexane/dichloromethane).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (m, 2H, Ph2 H-2,6), 7.32 (m, 2H, Ph2 H-3,5), 7.25 (m, 1H, Ph2 H-4), 7.24 (m, 2H, Ph1 H-3,5),6.85 (m, 2H, Ph1 H-2,6), 3.86 (s, 2H, SCH_2S), 3.85 (s, 2H, CH_2S), 3.80 (s, 3H, OCH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.7 (Ph1 C-1), 135.2 (Ph2 C-1), 130.5 (Ph2 C-2,6), 130.2 (Ph1 C-3,5), 129.2 (Ph1 C-4, Ph2 C-3,5), 126.9 (Ph2 C-4), 113.9 (Ph1 C-2,6), 55.2 (OCH_3), 36.6 (SCH_2S), 34.4 (CH_2S).

HRMS (ESI), *m/z*: calcd. for $C_{15}H_{17}OS_2^+$: 277.0715 $[M+H]^+$; found: 277.0716.

1,1'-[Methylenebis(sulfanedimethylene)]dibenzene (34)[6]



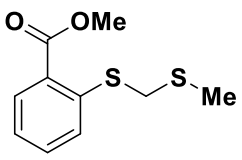
By following general procedure 1, starting from *S*-benzyl phenylmethanesulfonothioate (278 mg, 0.22 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of phenylmethanethiol (180 mg, 0.17 mL,1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **34** was obtained in 89% (232 mg) as a white solid (m.p.: 54 °C, lit. 55 °C) after chromatography on silica gel (95:05 v/v, *n*-hexane/dichloromethane).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (m, 8H, Ph H-2,3,5,6), 7.25 (m, 2H, Ph H-4), 3.84 (s, 4H, $PhCH_2S$), 3.38 (s, 2H, SCH_2S).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.7 (Ph C-1), 129.1 (Ph C-2,6), 128.5 (Ph C-3,5), 127.0 (Ph C-4), 34.4 ($PhCH_2S$), 33.4 (SCH_2S).

HRMS (ESI), *m/z*: calcd. for $C_{15}H_{17}S_2^+$: 261.0766 $[M+H]^+$; found: 261.0764.

Methyl 2-{[(methylsulfanyl)methyl]sulfanyl}benzoate (35)



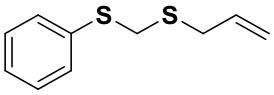
By following general procedure 1, starting from *S*-methyl methanesulfonothioate (126 mg, 0.11 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of methyl 2-sulfanylbenzoate (219 mg, 0.18 mL, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **35** was obtained in 95% yield (274 mg) as yellow oil after filtration on silica gel.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (m, 1H, Ph H-6), 7.47 (m, 1H, Ph H-4), 7.44 (m, 1H, Ph H-3), 7.20 (m, 1H, Ph H-5), 4.02 (s, 2H, SCH_2S), 3.91 (s, 3H, OCH_3), 2.26 (s, 3H, SCH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.8 (C=O), 140.3 (Ph C-2), 132.3 (Ph C-4), 131.2 (Ph C-6), 128.3 (Ph C-1), 126.6 (Ph C-3), 124.5 (Ph C-5), 52.1 (OCH_3), 37.6 (SCH_2S), 15.6 (SCH_3).

HRMS (ESI), *m/z*: calcd. for $C_{10}H_{13}O_2S_2^+$: 229.0351 $[M+H]^+$; found: 229.0348.

({[(Prop-2-en-1-yl)sulfanyl]methyl}sulfanyl)benzene (36)[10]



By following general procedure 1, starting from *S*-phenyl benzenesulfonothioate (250 mg, 0.20 mL, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (353 mg, 0.15 mL, 2.0 mmol, 2.0 equiv), MeLi-LiBr complex (0.8 mL of 2.2 M in Et_2O, 1.8 mmol, 1.8 equiv) in THF (5 mL), followed by the addition of prop-2-ene-1-thiol (96 mg, 0.11 mL, 1.3 mmol, 1.3 equiv) and NaI (15 mg, 0.1 mmol, 0.1 equiv) in dry DMF (3 mL), compound **36** was obtained in 87% yield (171 mg) as yellow oil after chromatography on silica gel (80:20 v/v, *n*-hexane/dichloromethane).

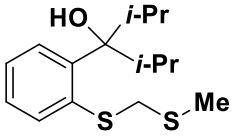
^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.45 (m, 2H, Ph H-2,6), 7.33 (m, 3H, Ph H-3,4,5), 5.79 (m, 1H, $CH_2C\underline{H}=CH_2$), 5.15 (m, 2H, $CH_2CH=C\underline{H}_2$), 3.99 (s, 2H, SCH_2S), 3.33 (m, 2H, $C\underline{H}_2CH=CH_2$).

^{13}C NMR (50 MHz, $CDCl_3$) δ: 135.1 (Ph C-1), 133.1 ($CH_2\underline{C}H=CH_2$), 130.6 (Ph C-2,6), 128.9 (Ph C-3,5), 126.9 (Ph C-4), 118.1 ($CH_2CH=\underline{C}H_2$), 36.3 (SCH_2S), 33.6 ($\underline{C}H_2CH=CH_2$).

HRMS (ESI), *m/z*: calcd. for $C_{10}H_{13}S_2^+$: 197.0453 $[M+H]^+$; found: 197.0457.

4. Applications

2,4-Dimethyl-3-(2-{[(methylsulfanyl)methyl]sulfanyl}phenyl)-3-pentanol (37)



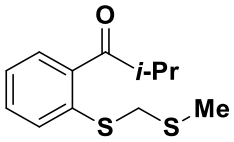
Methyl 2-{[(methylsulfanyl)methyl]sulfanyl}benzoate (228 mg, 1.0 mmol, 1.0 equiv)) was solubilized in dry 2-MeTHF (5 mL) under Argon atmosphere and *i*-PrMgCl (1.0 mL of 2.0 M in THF, 2.0 mmol, 2.0 equiv) wad added dropwise and the reaction was carried out at 0 °C for 1 hour. Subsequently it was quenched with aqueous saturated NH_4Cl solution. The resulting organic phase was extracted 3 times with Et_2O, washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Compound **37** was obtained in 87% yield (248 mg) as colourless oil after chromatography on silica gel (90:10 v/v, *n*-hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (m, 1H, Ph H-3), 7.25 (m, 2H, Ph H-5,6), 7.19 (m, 1H, Ph-4), 5.41 (brs, 1H, OH), 3.98 (s, 2H, SCH_2S), 2.36 (brs, 2H, C<u>H</u>$(CH_3)_2$), 2.24 (s, 3H, SCH_3), 0.91 (d, *J* = 6.7 Hz, 6H, CH(C<u>H</u>$_3)_2$), 0.80 (d, *J* = 6.8 Hz, 6H, CH(C<u>H</u>$_3)_2$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.4 (br, Ph C-1), 136.8 (br, Ph C-3), 133.1 (Ph C-2), 128.8 (Ph C-6), 127.2 (Ph C-5), 126.7 (Ph C-4), 85.0 (CHOH), 43.6 (br, SCH_2S), 35.6 (br, <u>C</u>H$(CH_3)_2$), 18.1 (CH(<u>C</u>H$_3)_2$), 16.8 (CH(<u>C</u>H$_3)_2$), 15.8 (SCH_3).

HRMS (ESI), *m/z*: calcd. for $C_{18}H_{25}OS_2^+$: 285.1341 $[M+H]^+$; found: 285.1338.

2-Methyl-1-(2-{[(methylsulfanyl)methyl]sulfanyl}phenyl)-1-propanone (38)



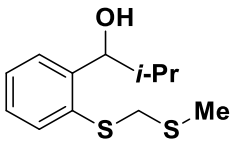
Methyl 2-{[(methylsulfanyl)methyl]sulfanyl}benzoate (228 mg, 1.0 mmol, 1.0 equiv)) was solubilized in dry CPME (5 mL) under Argon atmosphere and *N*-methoxymethanamine hydrogen chloride (195 mg, 2.0 mmol, 2.0 equiv)) was added at 0 °C. After that *i*-PrMgCl (0.9 mL of 2.0 M in THF, 1.8 mmol, 1.8 equiv) wad added dropwise and the reaction was carried out at 0 °C to room temperature for 2 hours. Subsequently, additional *i*-PrMgCl (0.65 mL of 2.0 M in THF, 1.3 mmol, 1.3 equiv) was added and, the resulting mixture was allowed to react for 1 h before it was quenched with aqueous saturated NH_4Cl solution. The resulting organic phase was extracted 3 times with Et_2O, washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Compound **38** was obtained in 85% yield (204 mg) as colourless oil after chromatography on silica gel (90:10 v/v, *n*-hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (m, 1H, Ph H-6), 7.52 (m, 1H, Ph H-3), 7.44 (m, 1H, Ph-4), 7.26 (m, 1H, Ph H-5), 3.98 (s, 2H, SCH_2S), 3.43 (sept, *J* = 6.9 Hz, 1H, C<u>H</u>$(CH_3)_2$), 2.22 (s, 3H, SCH_3), 1.20 (d, *J* = 6.9 Hz, 6H, CH(C<u>H</u>$_3)_2$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 207.0 (C=O), 138.4 (Ph C-1), 137.2 (Ph C-2), 131.2 (Ph C-4), 129.2 (Ph C-3), 128.8 (Ph C-6), 125.4 (Ph C-5), 39.2 (SCH_2S), 38.1 ($\underline{C}H(CH_3)_2$), 18.7 ($CH(\underline{C}H_3)_2$), 15.5 (SCH_3).

HRMS (ESI), *m/z*: calcd. for $C_{12}H_{17}OS_2^+$: 241.0715 $[M+H]^+$; found: 241.07119.

2-Methyl-1-(2-{[(methylsulfanyl)methyl]sulfanyl}phenyl)-1-propanol (39)



2-Methyl-1-(2-{[(methylsulfanyl)methyl]sulfanyl}phenyl)-1-propanone (240 mg, 1.0 mmol, 1.0 equiv)) was solubilized in AcOEt (5 mL) and $NaBH_4$ (76 mg, 2.0 mmol, 2.0 equiv) wad added and the reaction was carried out at 0 °C for 2 hours. Subsequently it was quenched with aqueous saturated NH_4Cl solution. The resulting organic phase was extracted 3 times with Et_2O, washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. C

ompound **39** was obtained in 93% yield (225 mg) as colourless oil after chromatography on silica gel (90:10 v/v, *n*-hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (m, 2H, Ph H-3,6), 7.29 (m, 1H, Ph H), 7.24 (m, 1H, Ph H), 4.96 (d, J = 6.9 Hz, 1H, C$\underline{H}$OH), 3.95 (A-part of an AB-system, $^2J_{AB}$ = 13.3 Hz, 1H, SCH_2S), 3.92 (B-part of an AB-system, $^2J_{AB}$ = 13.3 Hz, 1H, SCH_2S), 2.22 (s, 3H, SCH_3), 2.22 (brs, 1H, OH), 2.02 (m, 1H, C$\underline{H}(CH_3)_2$), 1.02 (d, J = 6.6 Hz, 3H, $CH(C\underline{H}_3)_2$), 0.83 (d, J = 6.9 Hz, 3H, $CH(C\underline{H}_3)_2$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.5 (Ph C-1), 133.0 (Ph C-2), 131.9 (Ph C-3), 127.7 (Ph C-4), 127.6 (Ph C-5), 127.0 (Ph C-6), 76.0 (CHOH), 41.7 (SCH_2S), 34.5 ($\underline{C}H(CH_3)_2$), 19.4 ($CH(\underline{C}H_3)_2$), 15.4 (SCH_3).

HRMS (ESI), *m/z*: calcd. for $C_{12}H_{19}OS_2^+$: 243.0872 $[M+H]^+$; found: 243.0875.

5. X-Ray Analysis of Compound 10, 15 and 28

The X-ray intensity data were measured on Bruker D8 Venture diffractometer equipped with multilayer monochromator, Mo K/α INCOATEC micro focus sealed tube and Oxford cooling system. The structures were solved by *Direct Methods*. Non-hydrogen atoms were refined with *anisotropic displacement parameters*. Hydrogen atoms were inserted at calculated positions and refined with riding model. The following software was used: *Bruker SAINT software package*[11] using a narrow-frame algorithm for frame integration, *SADABS*[12] for absorption correction, *OLEX2*[13] for structure solution, refinement, molecular diagrams and graphical user-interface, *ShelxIe*[14] for refinement and graphical user-interface *SHELXS-2015*[15] for structure solution, *SHELXL-2015*[15] for refinement, *Platon*[16] for symmetry check. Experimental data and CCDC-Codes Experimental data (Available online: http://www.ccdc.cam.ac.uk/conts/retrieving.html) can be found in Table 1. Crystal data, data collection parameters, and structure refinement details are given in Tables 2 to 9. Asymmetric Unit visualized in Figures 1 to 4. Samples for X-ray analysis were recrystallized from ethanol.

Table 1 Experimental parameter and CCDC-Code.

Sample	Machine	Source	Temp.	Detector Distance	Time/ Frame	#Frames	Frame width	CCDC
	Bruker		[K]	[mm]	[s]		[°]	
10	D8	Mo	100	30	8	1050	0.300	2016505
15	D8	Mo	100	30	60	1853	0.300	2016506
28	D8	Mo	100	30	15	1864	0.300	2016507

2-{[(Phenylsulfanyl)methyl]sulfanyl}naphthalene

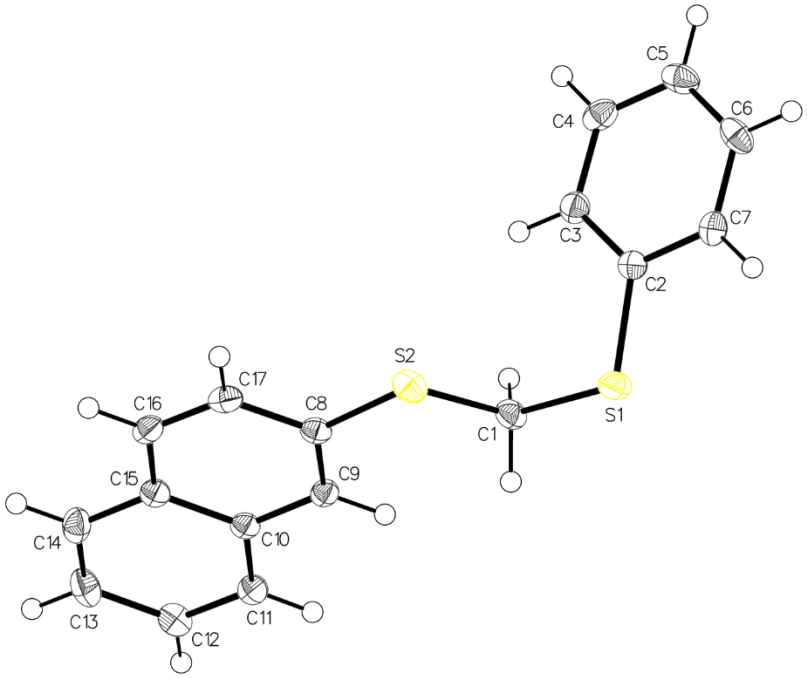


Figure 1 Crystal structure, drawn with 50% displacement ellipsoid. The bond precision for C-C single bonds is 0.0030Å.

Table 2 Sample and crystal data. **[10]**

Radiation [Å]	MoKα (λ = 0.71073)	Z	4	Measurement method	\f and \w scans
Crystal habit	clear colourless stick	a [Å]	14.9903(9)		
Crystal size [mm³]	0.1 × 0.05 × 0.02	b [Å]	5.9477(4)	Abs. correction type	multiscan
Empirical formula	C17H14S2	c [Å]	16.5251(15)	Abs. correction Tmin	0.6474
Formula weight [g/mol]	282.40	α [°]	90	Abs. correction Tmax	0.7460
Temperature [K]	100.0	β [°]	110.467(4)	Density (calculated) [g/cm³]	1.359
Crystal system	monoclinic	γ [°]	90	Absorption coefficient [mm^{-1}]	0.368
Space group	P21/c	Volume [Å³]	1380.33(18)	F (000) [e$^-$]	592.0

Table 3 Data collection and structure refinement. **[10]**

2Θ range for data collection [°]	5.042 to 50.696	Index ranges		Goodness-of-fit on F^2	1.052
Reflections collected	12148	h	-18 ≤ h ≤ 17	Diff. peak and hole [e$^-$Å^{-3}]	0.24/-0.26
Data / restraints / parameters	2513/0/0172	k	-6 ≤ k ≤ 7		
Refinement method	Direct Methods	l	-19 ≤ l ≤ 19	Function minimized	$\Sigma w (F_o^2 - F_c^2)^2$
		all data	R1 = 0.0414, wR2 = 0.0776	Weighting scheme	where
		I>2σ(I)	R1 = 0.0324, wR2 = 0.0722	$w=1/[\sigma^2(Fo^2) + (0.0257P)^2 + 0.8649P]$	$P=(F_o^2+2F_c^2)/3$

2-{[(Phenylsulfanyl)methyl]sulfanyl}-1,3-benzoxazole

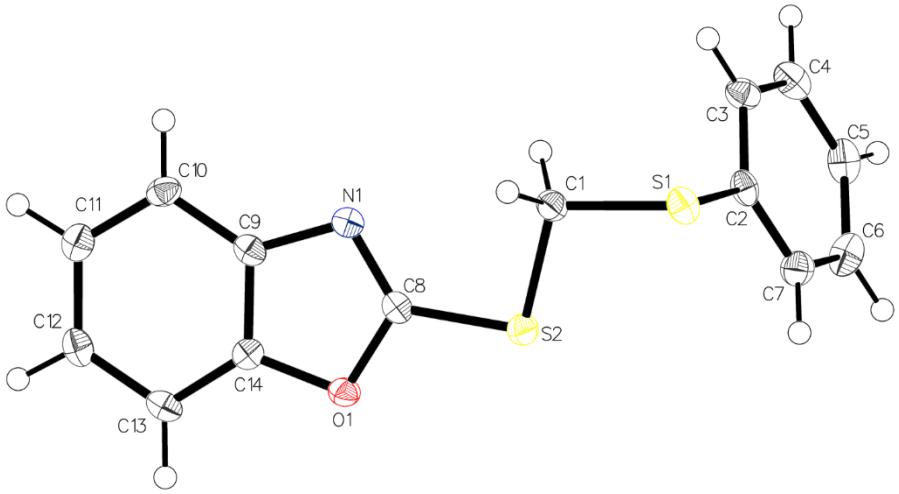


Figure 2 Crystal structure, drawn with 50% displacement ellipsoid. The bond precision for C-C single bonds is 0.0038Å.

Table 4 Sample and crystal data. **[15]**

Radiation [Å]	MoKα (λ = 0.71073)	Z	2	Measurement method	\f and \w scans
Crystal habit	clear colourless block	a [Å]	9.5155(11)		
Crystal size [mm³]	0.045 × 0.04 × 0.03	b [Å]	4.8412(4)	Abs. correction type	multiscan
Empirical formula	C14H11NOS2	c [Å]	13.9736(18)	Abs. correction Tmin	0.7062
Formula weight [g/mol]	273.36	α [°]	90	Abs. correction Tmax	0.7460
Temperature [K]	100.0	β [°]	96.436(5)	Density (calculated) [g/cm³]	1.419
Crystal system	monoclinic	γ [°]	90	Absorption coefficient [mm^{-1}]	0.401
Space group	P21	Volume [Å³]	639.66(12)	F (000) [e$^-$]	284.0

Table 5 Data collection and structure refinement. **[15]**

2Θ range for data collection [°]	4.932 to 60.168	Index ranges		Goodness-of-fit on F^2	1.148
Reflections collected	15673	h	-13 ≤ h ≤ 13	Diff. peak and hole [e$^-$Å^{-3}]	0.30/-0.28
Data / restraints / parameters	3715/1/163	k	-6 ≤ k ≤ 6		
Refinement method	Direct Methods	l	-19 ≤ l ≤ 19	Function minimized	$\Sigma w (F_o^2 - F_c^2)^2$
		all data	R1 = 0.0423, wR2 = 0.0680	Weighting scheme	where
		I>2σ(I)	R1 = 0.0303, wR2 = 0.0555	$w=1/[\sigma^2(Fo^2) + (0.0109P)^2 + 0.3131P]$	$P=(F_o^2+2F_c^2)/3$

1,1´,1´´-({[(Methylsulfanyl)methyl]sulfanyl}methanetriyl)tribenzene

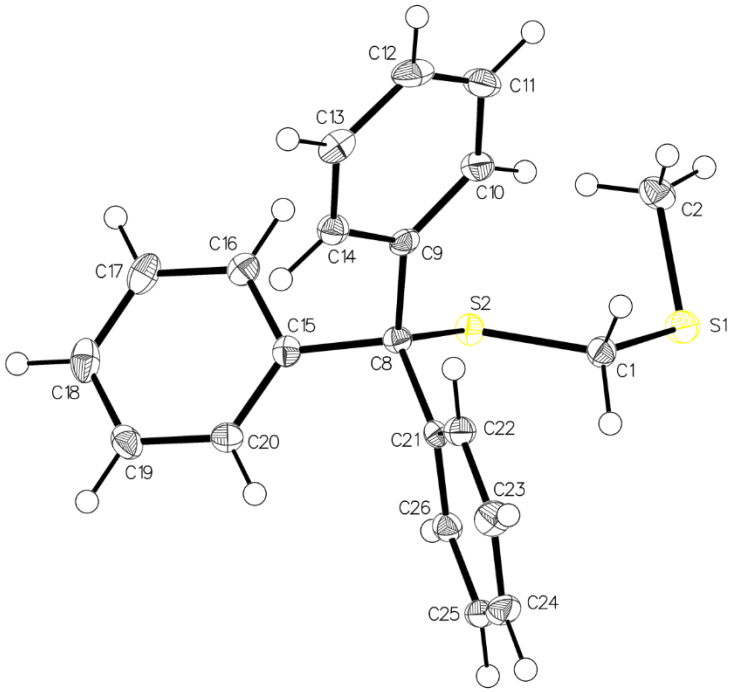


Figure 3 Crystal structure, drawn with 50% displacement ellipsoid. The bond precision for C-C single bonds is 0.0022Å.

Table 6 Sample and crystal data. **[28]**

Radiation [Å]	MoKα (λ = 0.71073)	Z	4	Measurement method	\f and \w scans
Crystal habit	clear colourless block	a [Å]	16.4219(5)		
Crystal size [mm³]	0.1 × 0.05 × 0.03	b [Å]	7.1899(2)	Abs. correction type	multiscan
Empirical formula	C21H20S2	c [Å]	16.4782(7)	Abs. correction Tmin	0.6709
Formula weight [g/mol]	336.49	α [°]	90	Abs. correction Tmax	0.7460
Temperature [K]	100.0	β [°]	118.3742(10)	Density (calculated) [g/cm³]	1.306
Crystal system	monoclinic	γ [°]	90	Absorption coefficient [mm^{-1}]	0.308
Space group	P21/n	Volume [Å³]	1711.87(10)	F (000) [e$^-$]	712.0

Table 7 Data collection and structure refinement. **[28]**

2Θ range for data collection [°]	4.834 to 50.7	Index ranges		Goodness-of-fit on F^2	1.069
Reflections collected	32414	h	-19 ≤ h ≤ 19	Diff. peak and hole [e$^-$Å^{-3}]	0.29/-0.25
Data / restraints / parameters	3136/0/209	k	-8 ≤ k ≤ 8		
Refinement method	Direct Methods	l	-19 ≤ l ≤ 19	Function minimized	$\Sigma\, w\,(F_o^2 - F_c^2)^2$
		all data	R1 = 0.0335, wR2 = 0.0732	Weighting scheme	where
		I>2σ(I)	R1 = 0.0287, wR2 = 0.0702	$w=1/[\sigma^2(Fo^2) + (0.0270P)^2 + 1.2512P]$	$P=(F_o^2+2F_c^2)/3$

Table 8 The main characteristic of the common backbone (C2-S1-C1-S2-C8) is the difference in the two C-S bonds. All three compounds show smaller values on C1-S1.

	C1-S1	C1-S2	S1-S2	S2-C1-S1	C2-S1	C8-S2
10	**1.795 Å**	**1.814 Å**	**2.943 Å**	**109.249**	**1.774 Å**	**1.766 Å**
15	**1.801 Å**	**1.819 Å**	**2.932 Å**	**108.179**	**1.782 Å**	**1.735 Å**
28	**1.804 Å**	**1.816 Å**	**2.945 Å**	**105.846**	**1.803 Å**	**1.863 Å**

6. References

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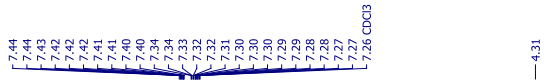
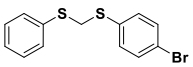
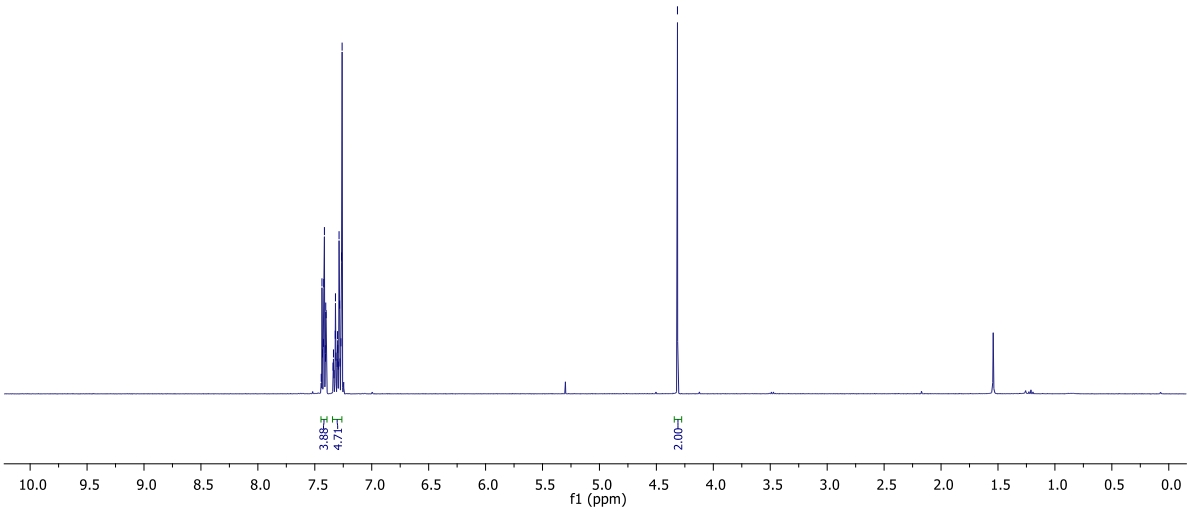
7. Copies of ^{1}H- and ^{13}C-NMR Spectra for all the compounds

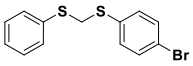
1-[(Benzylsulfanyl)methyl]-4-bromobenzene (2)



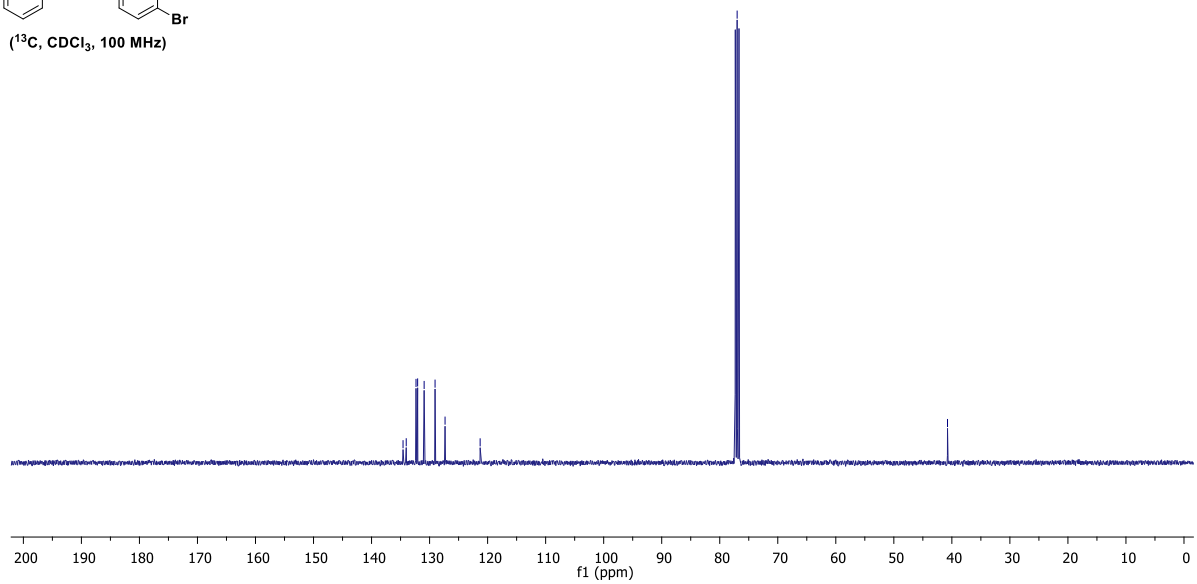


(^{1}H, $CDCl_3$, 400 MHz)

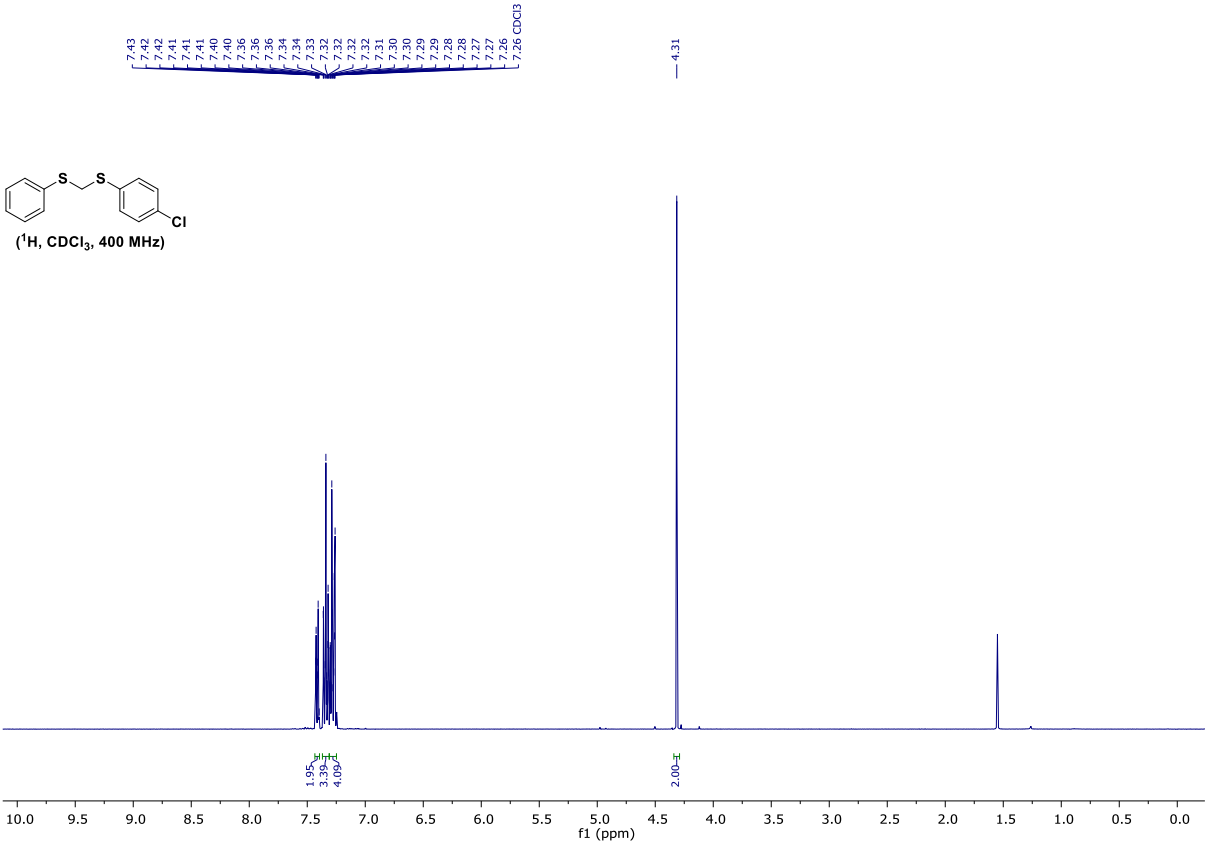


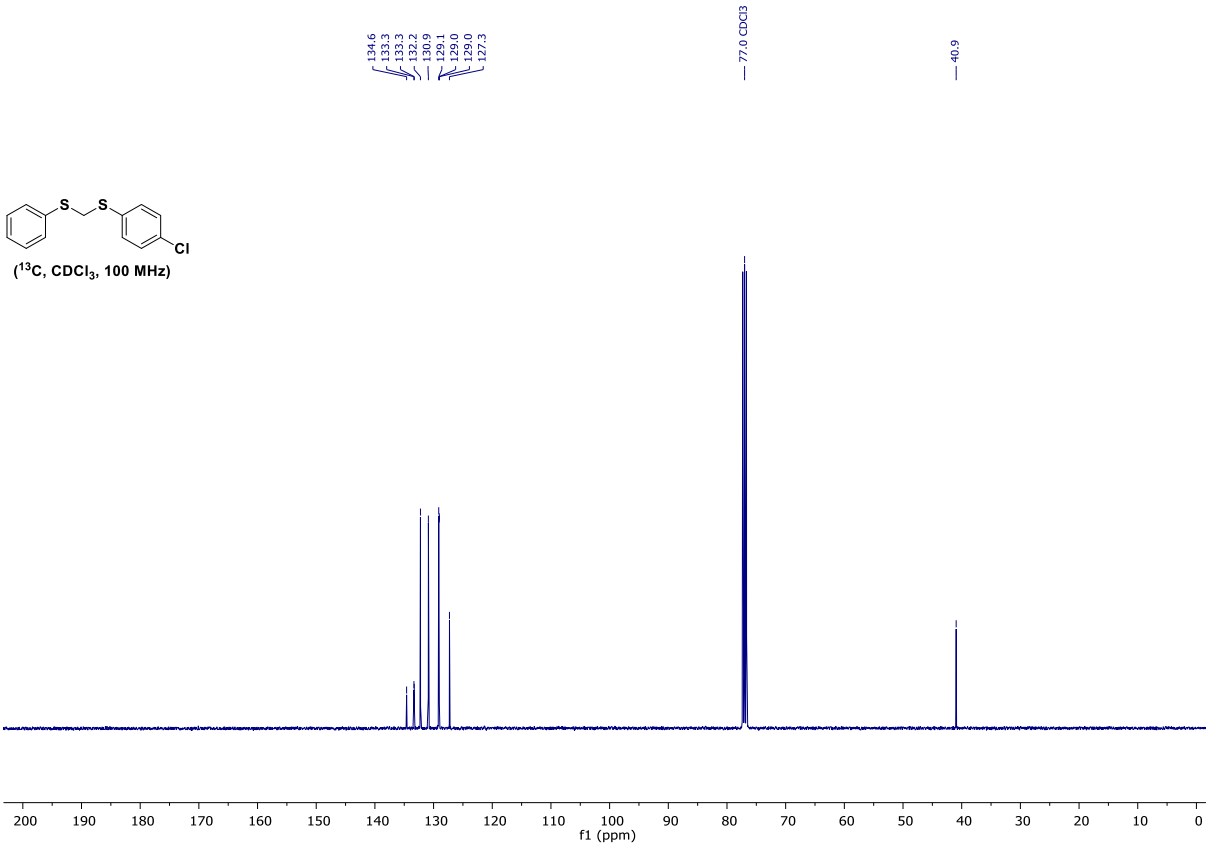


(^{13}C, $CDCl_3$, 100 MHz)

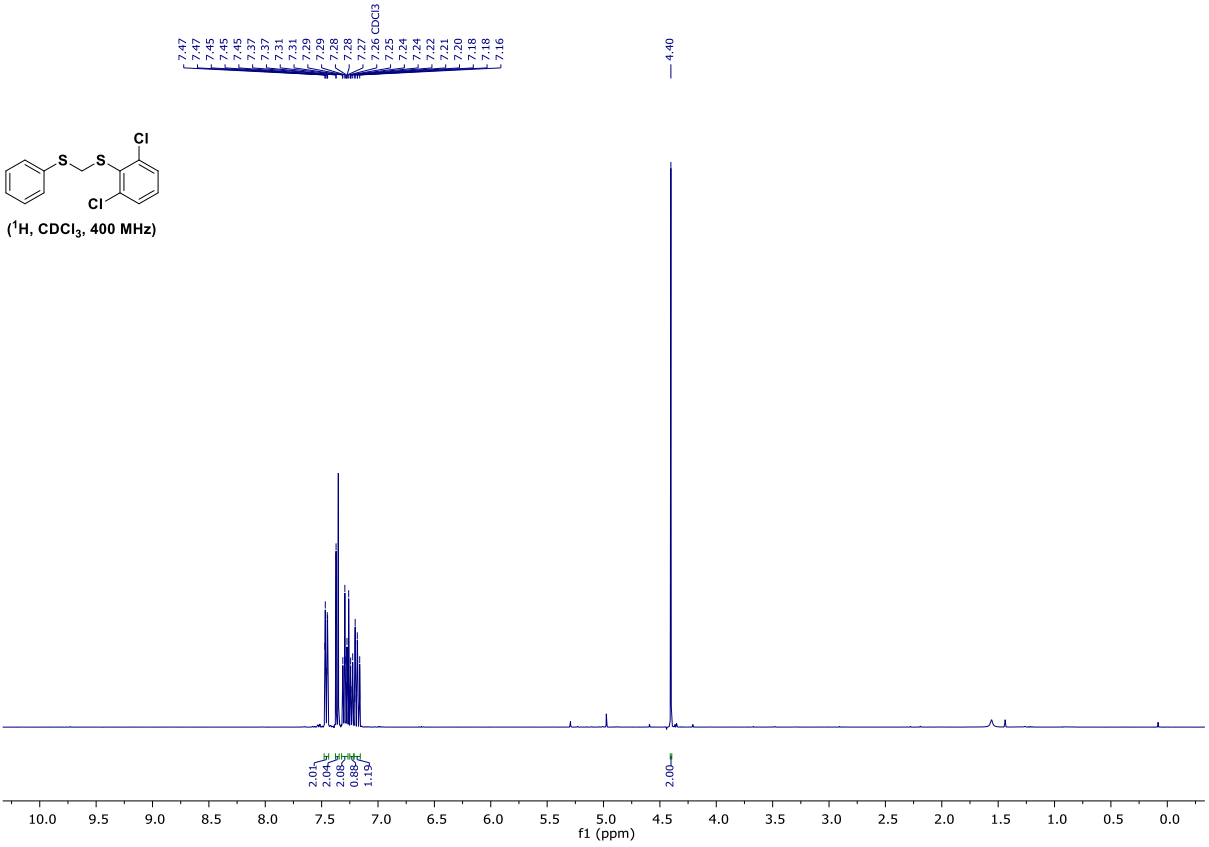


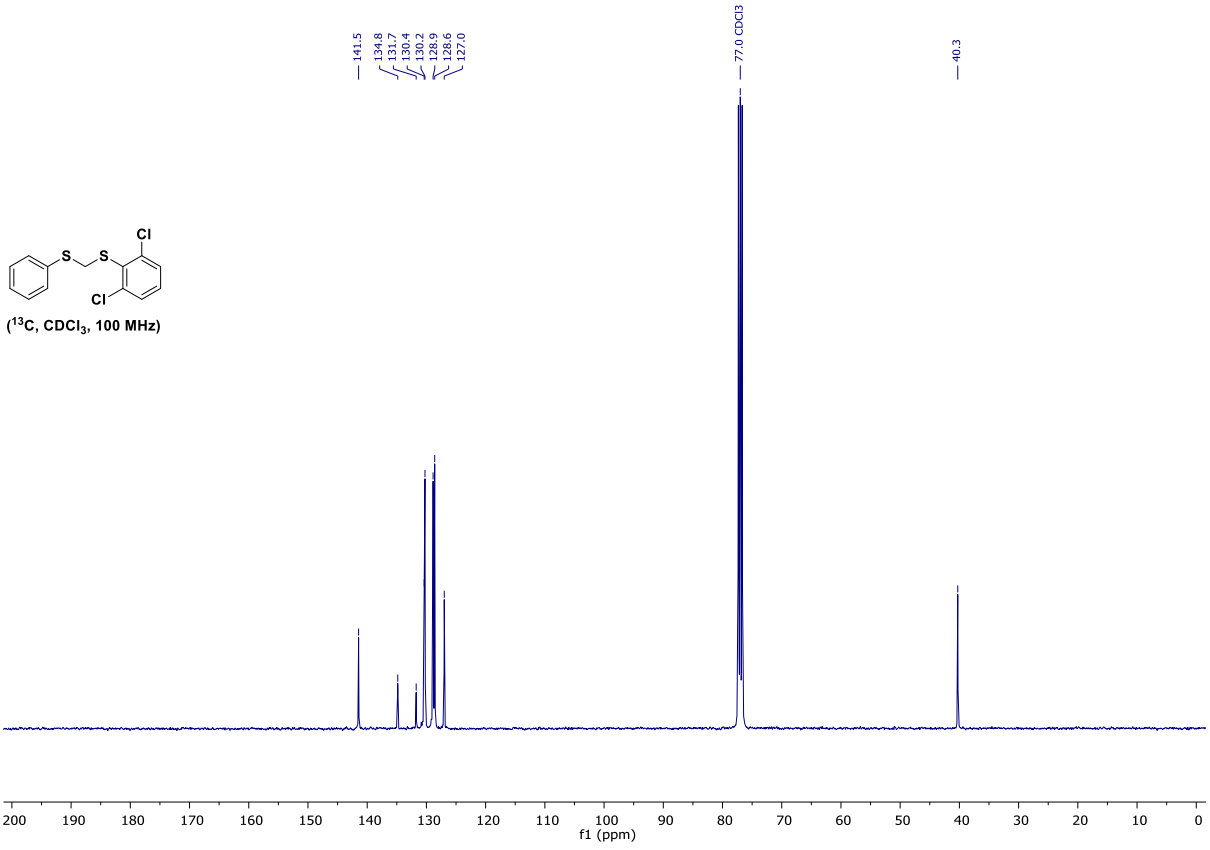
1-Chloro-4-{[(phenylsulfanyl)methyl]sulfanyl}benzene (3)



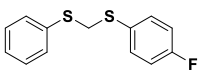


1,3-Dichloro-2-{[(phenylsulfanyl)methyl]sulfanyl}benzene (4)





1-Fluoro-4-{[(phenylsulfanyl)methyl]sulfanyl}benzene (5)



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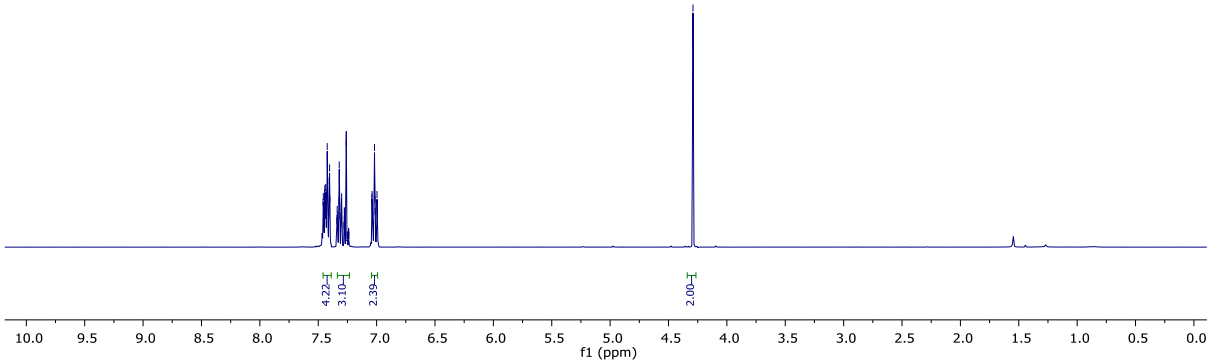
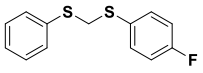
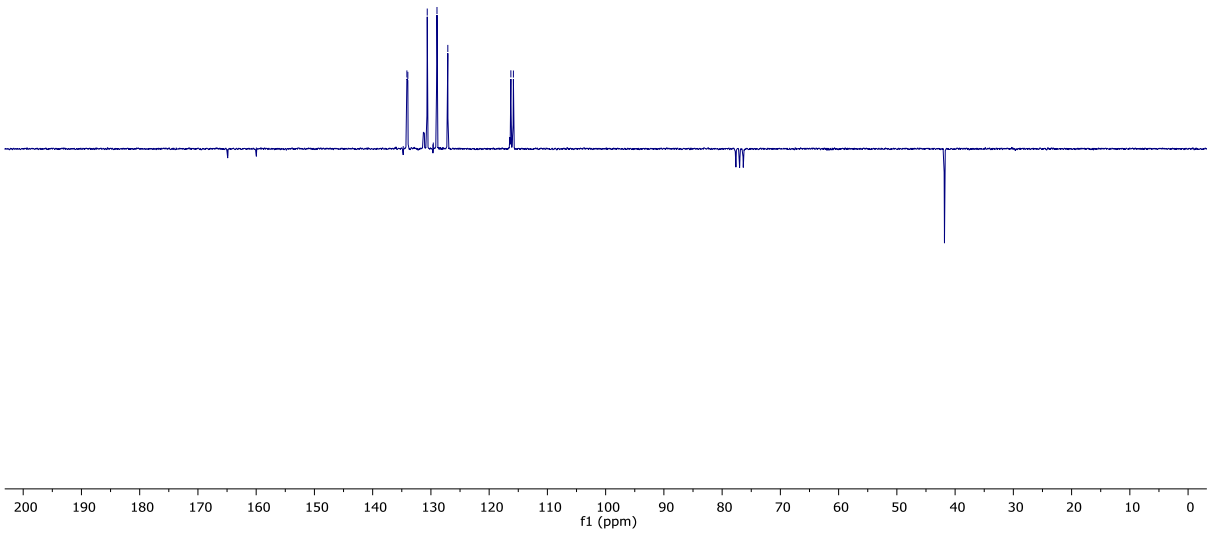
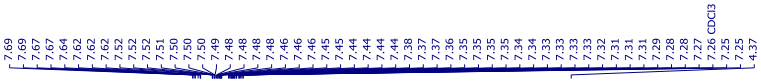


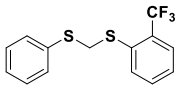


(^{13}C, $CDCl_3$, 50 MHz)

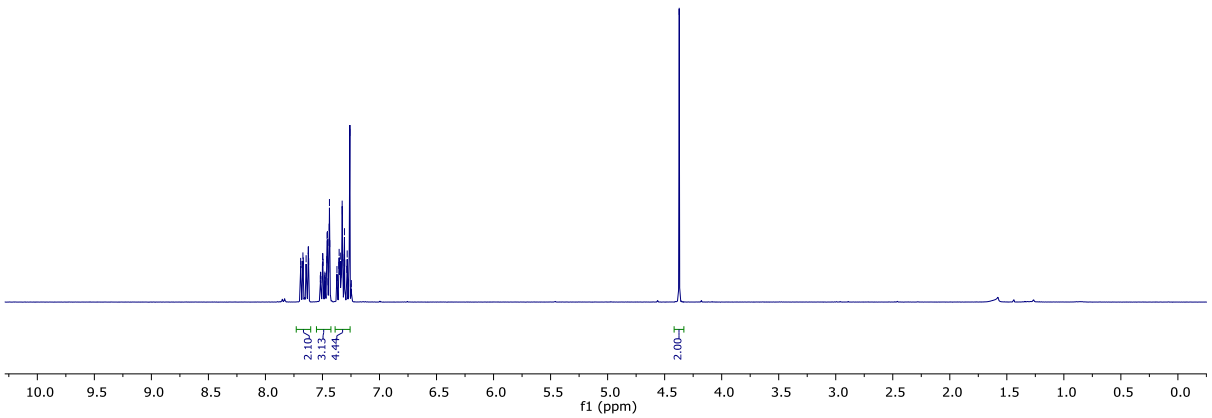


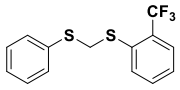
1-{[(Phenylsulfanyl)methyl]sulfanyl}-2-(trifluoromethyl)benzene (6)



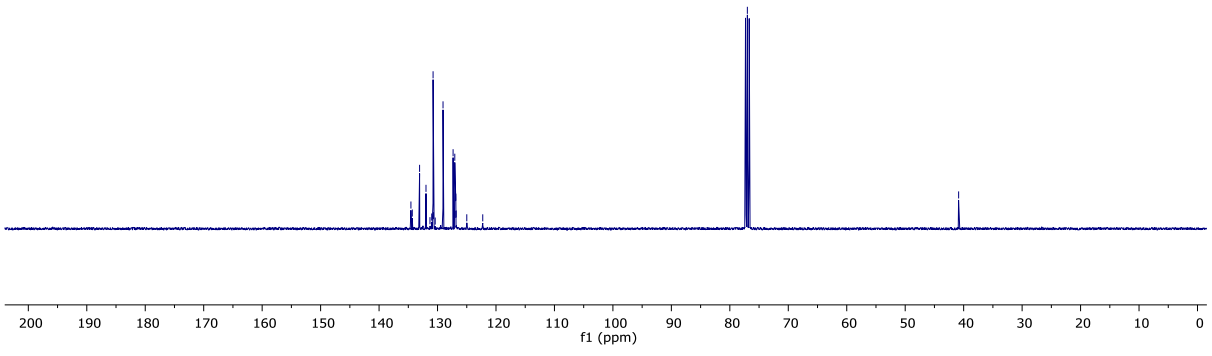


(^{1}H, $CDCl_3$, 400 MHz)

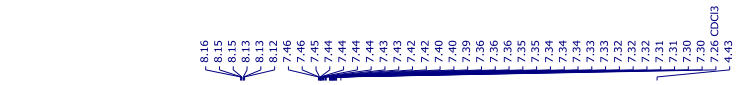


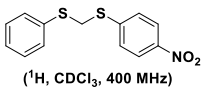


(^{13}C, $CDCl_3$, 100 MHz)

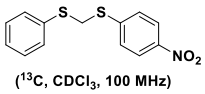


1-Nitro-4-{[(phenylsulfanyl)methyl]sulfanyl}benzene (7)

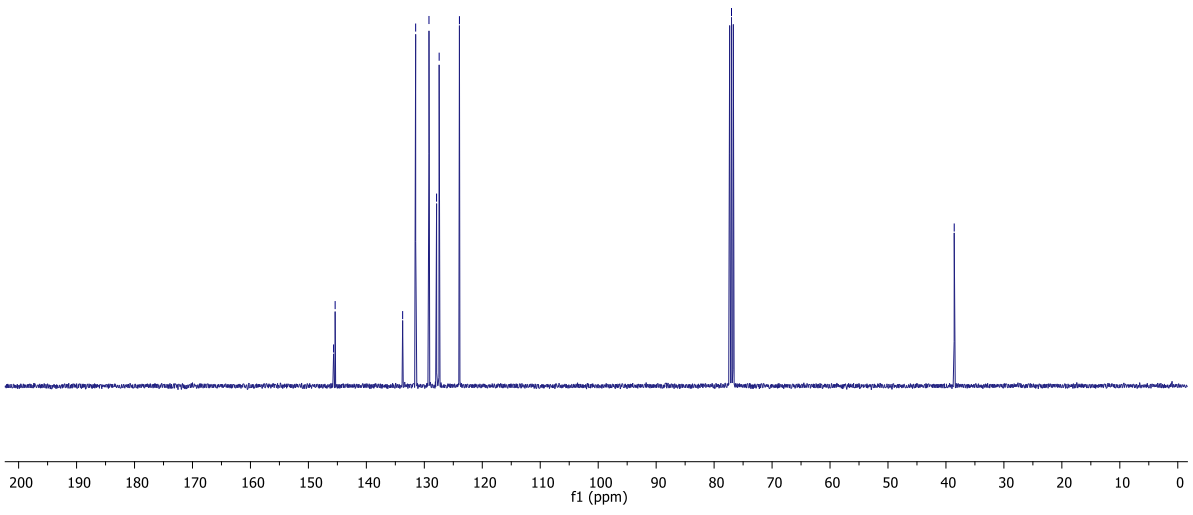




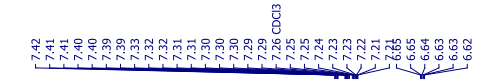
(^{1}H, $CDCl_3$, 400 MHz)

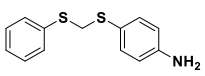


(^{13}C, $CDCl_3$, 100 MHz)

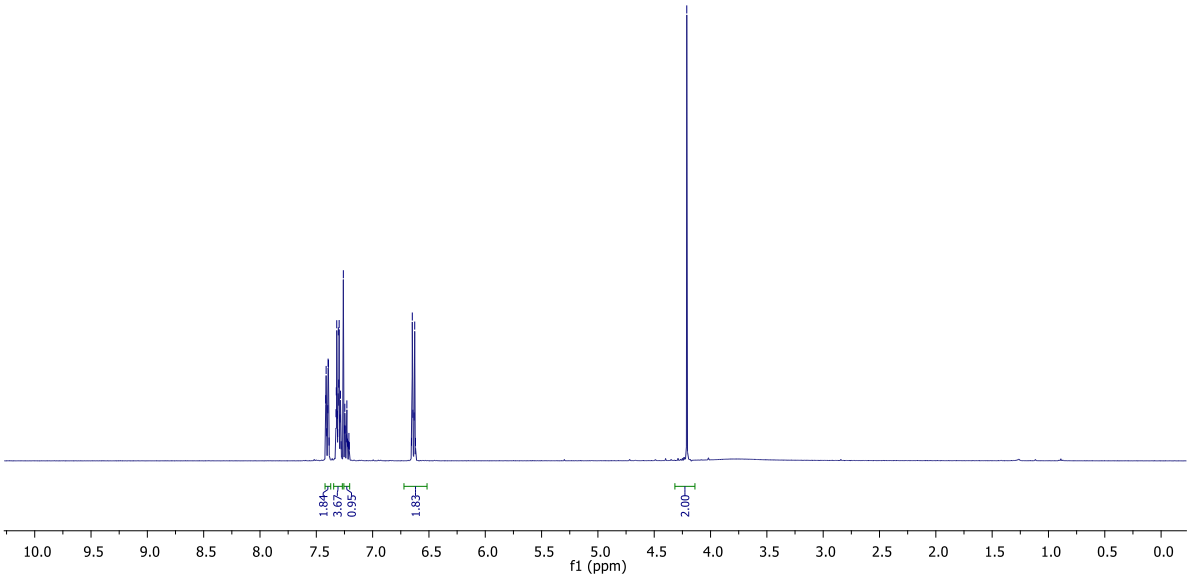


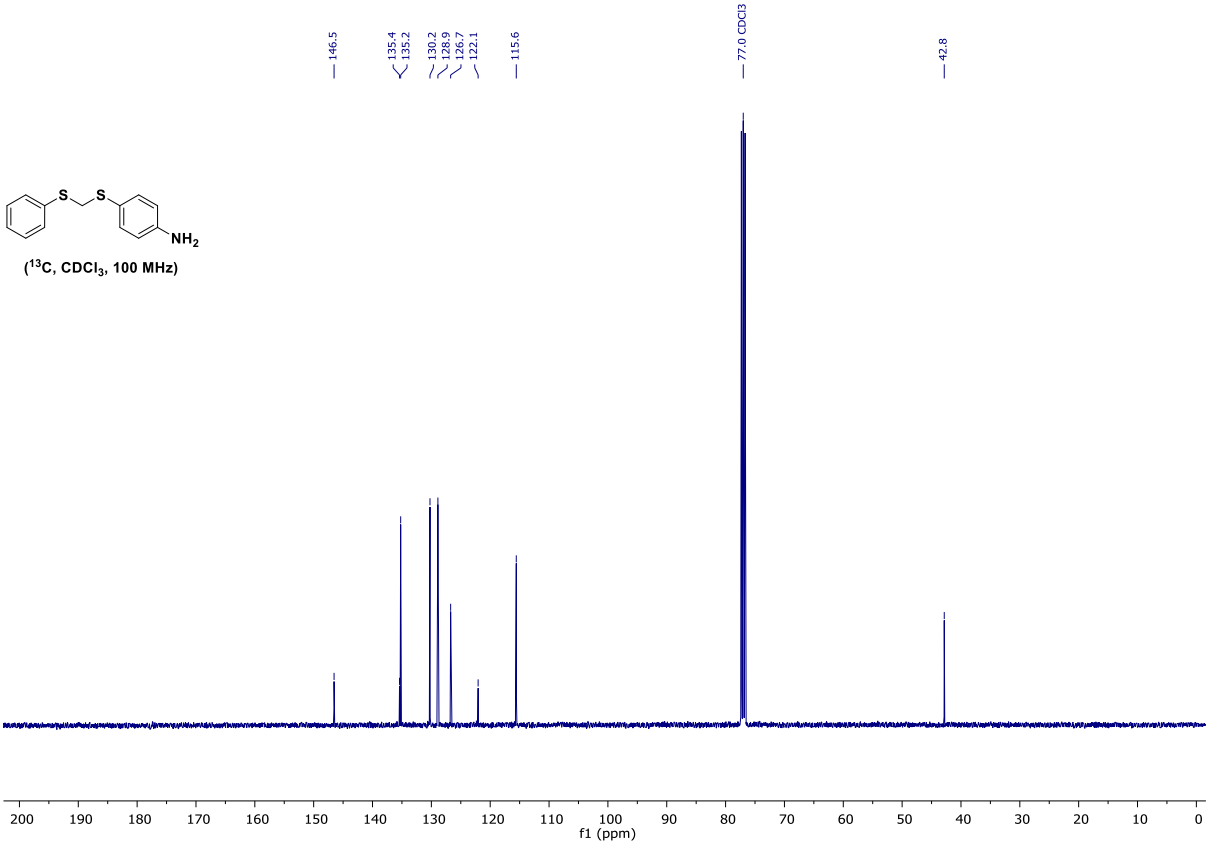
4-{[(Phenylsulfanyl)methyl]sulfanyl}aniline (8)





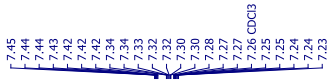
(^{1}H, $CDCl_3$, 400 MHz)

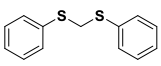




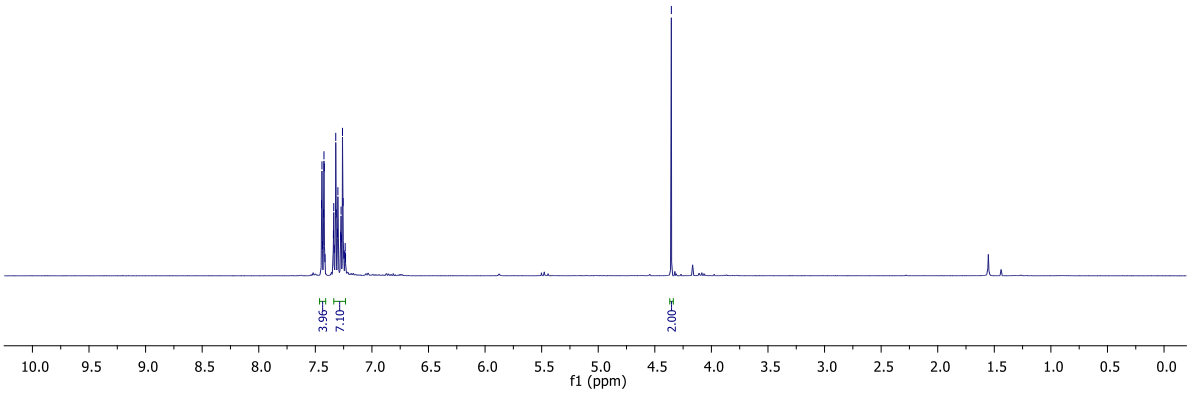
(^{13}C, $CDCl_3$, 100 MHz)

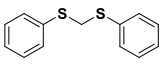
1,1´(Methylenedisulfanyldiyl)dibenzene (9)



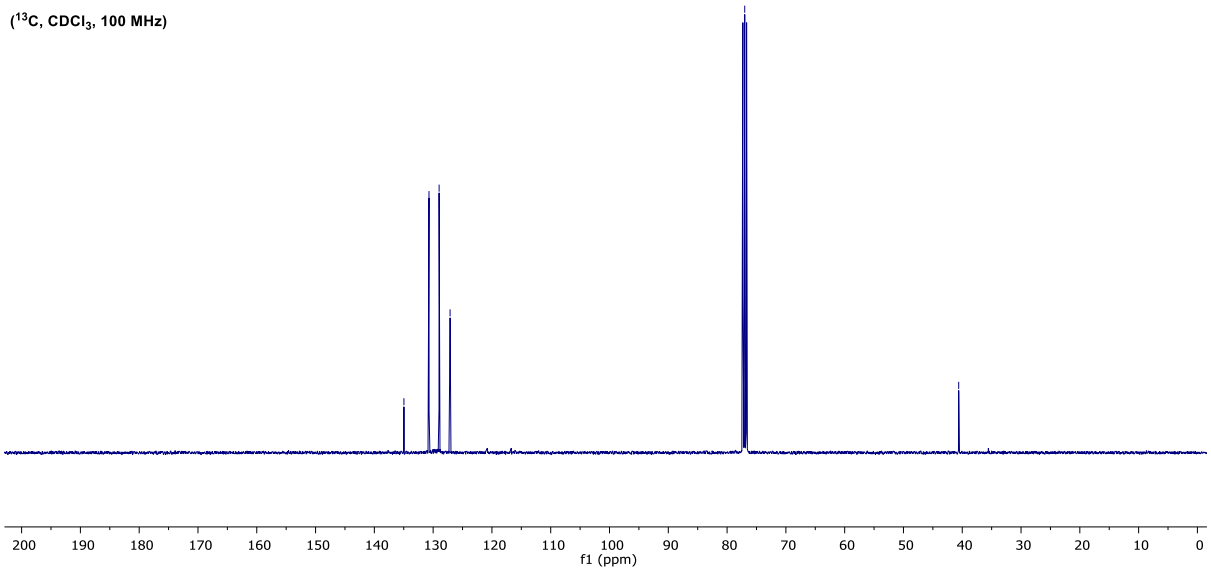


(^{1}H, $CDCl_3$, 400 MHz)

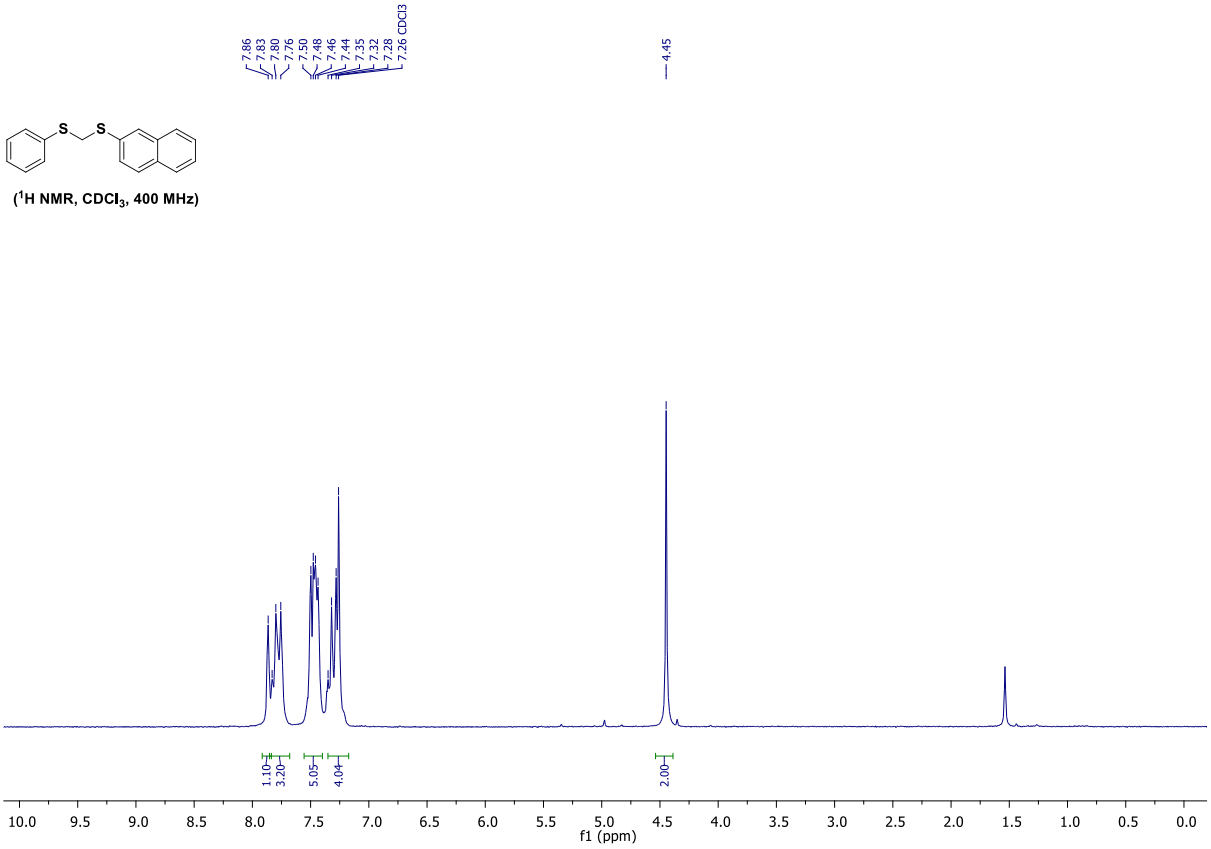




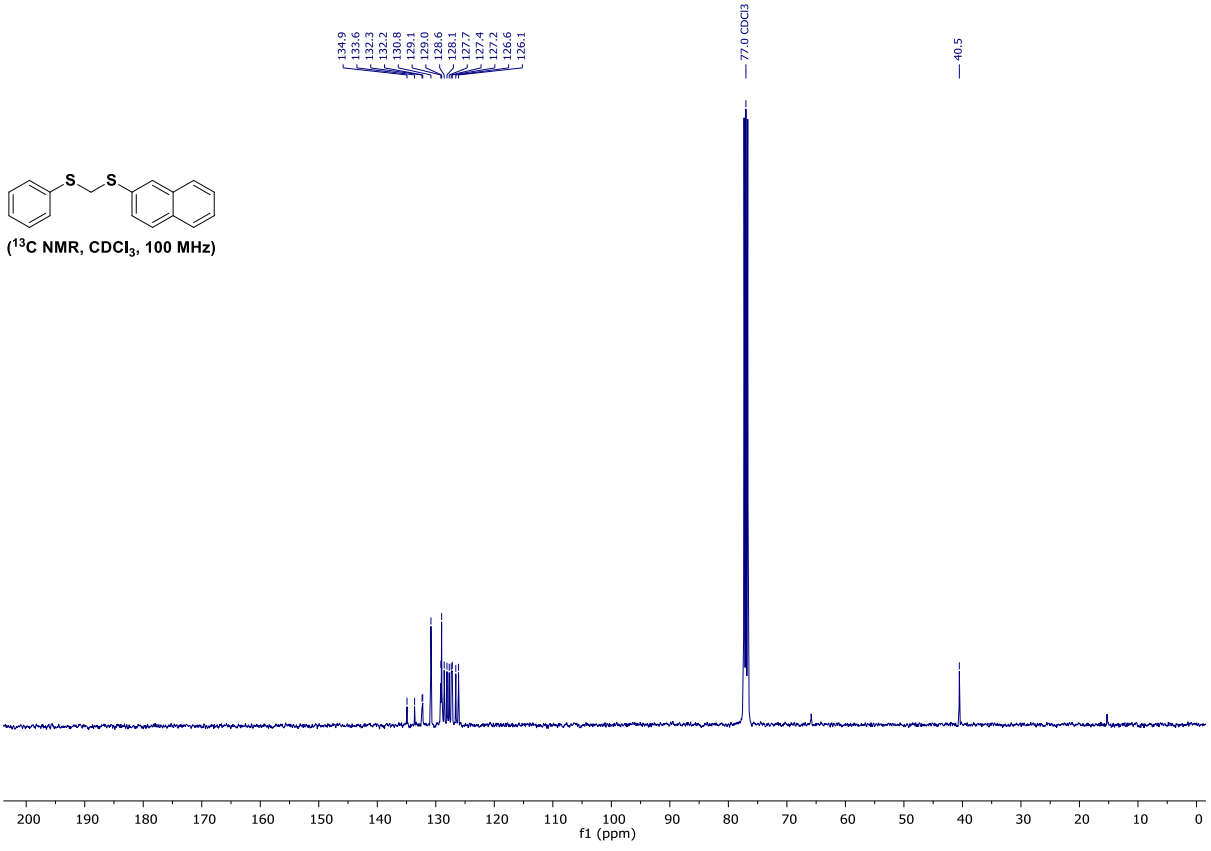
(^{13}C, $CDCl_3$, 100 MHz)



2-{[(Phenylsulfanyl)methyl]sulfanyl}naphthalene (10)

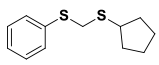


(^{1}H NMR, $CDCl_3$, 400 MHz)

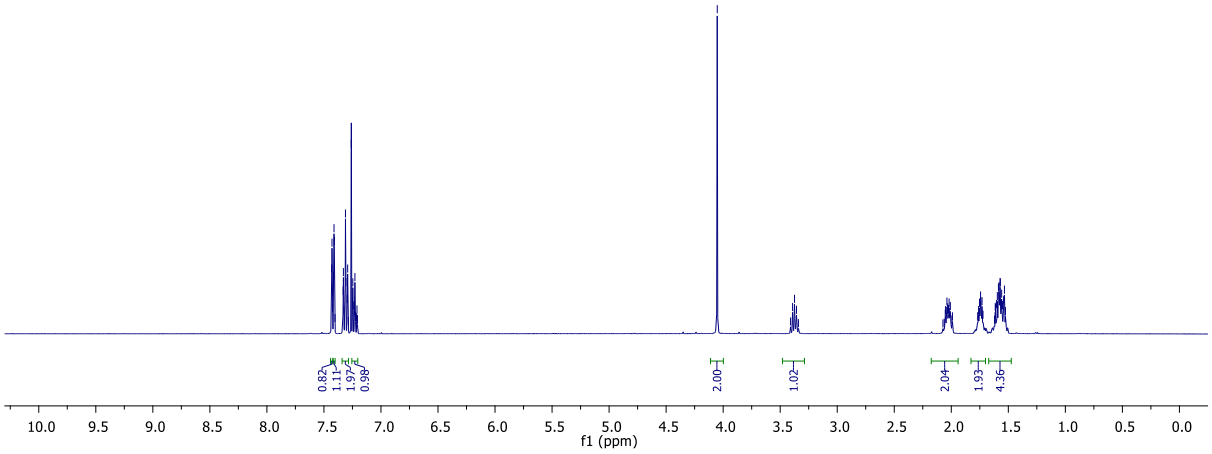


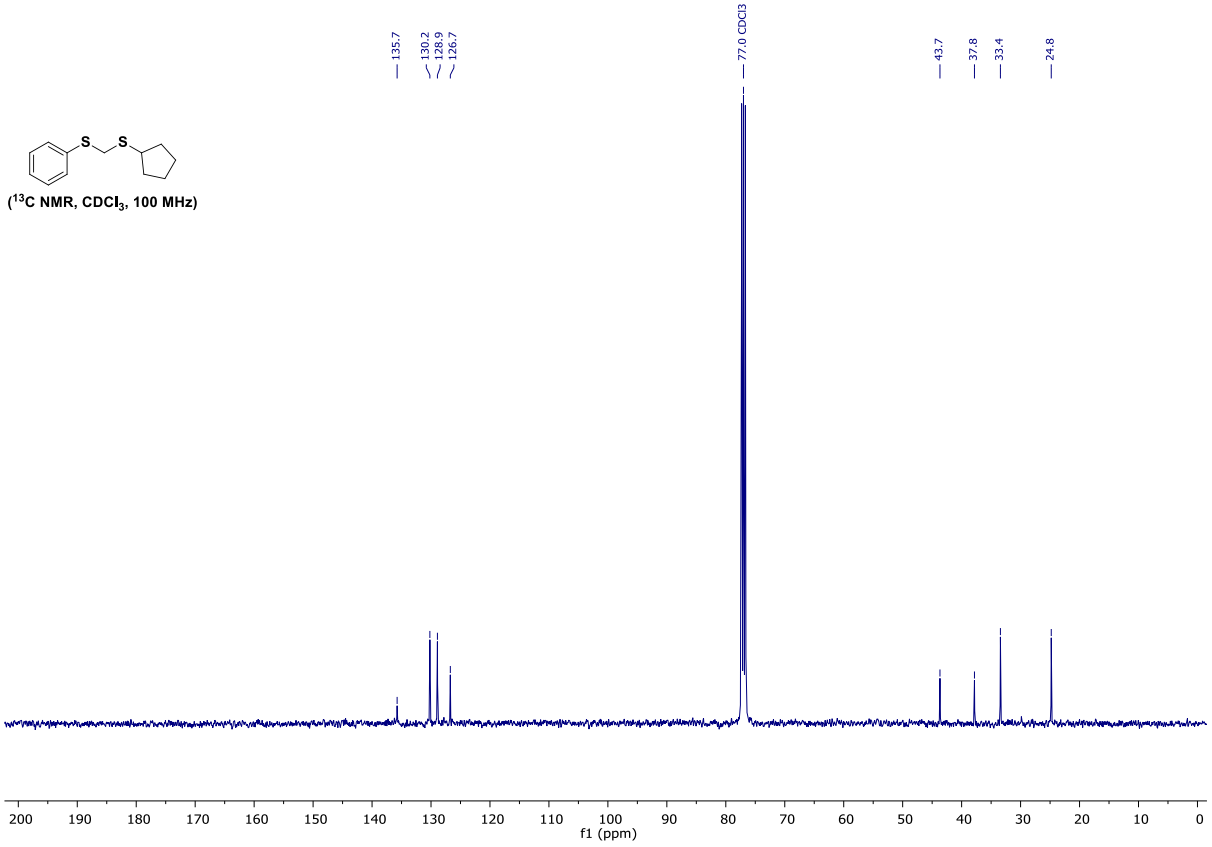
(^{13}C NMR, $CDCl_3$, 100 MHz)

{[(Cyclopentylsulfanyl)methyl]sulfanyl}benzene (11)



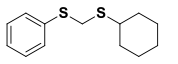
(^{1}H NMR, $CDCl_3$, 400 MHz)



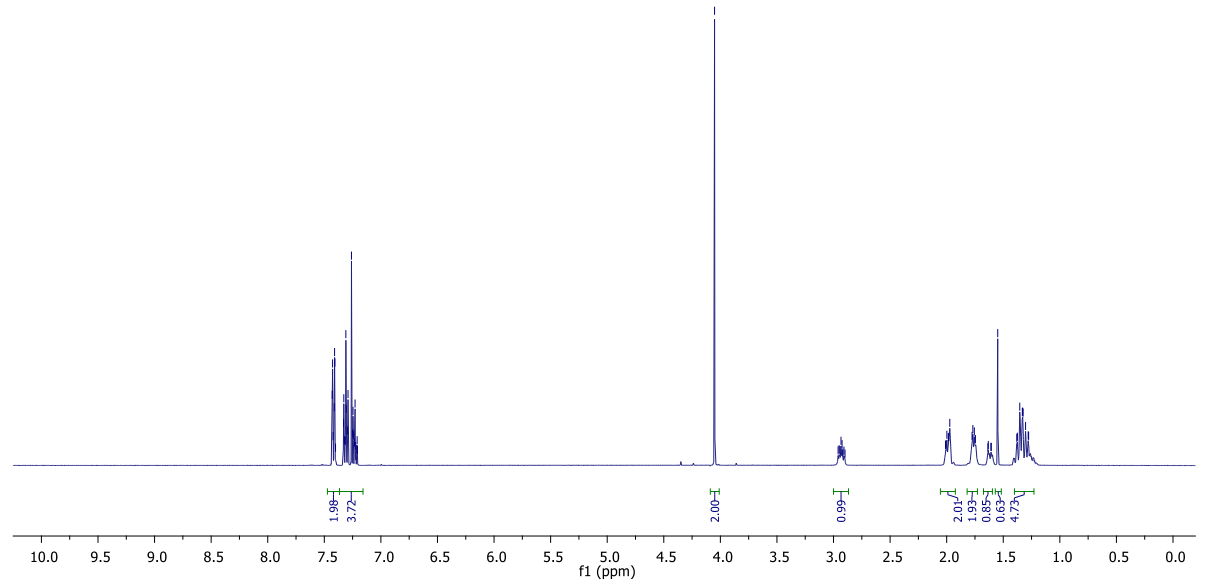


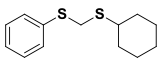
(^{13}C NMR, $CDCl_3$, 100 MHz)

{[(Cyclohexylsulfanyl)methyl]sulfanyl}benzene (12)



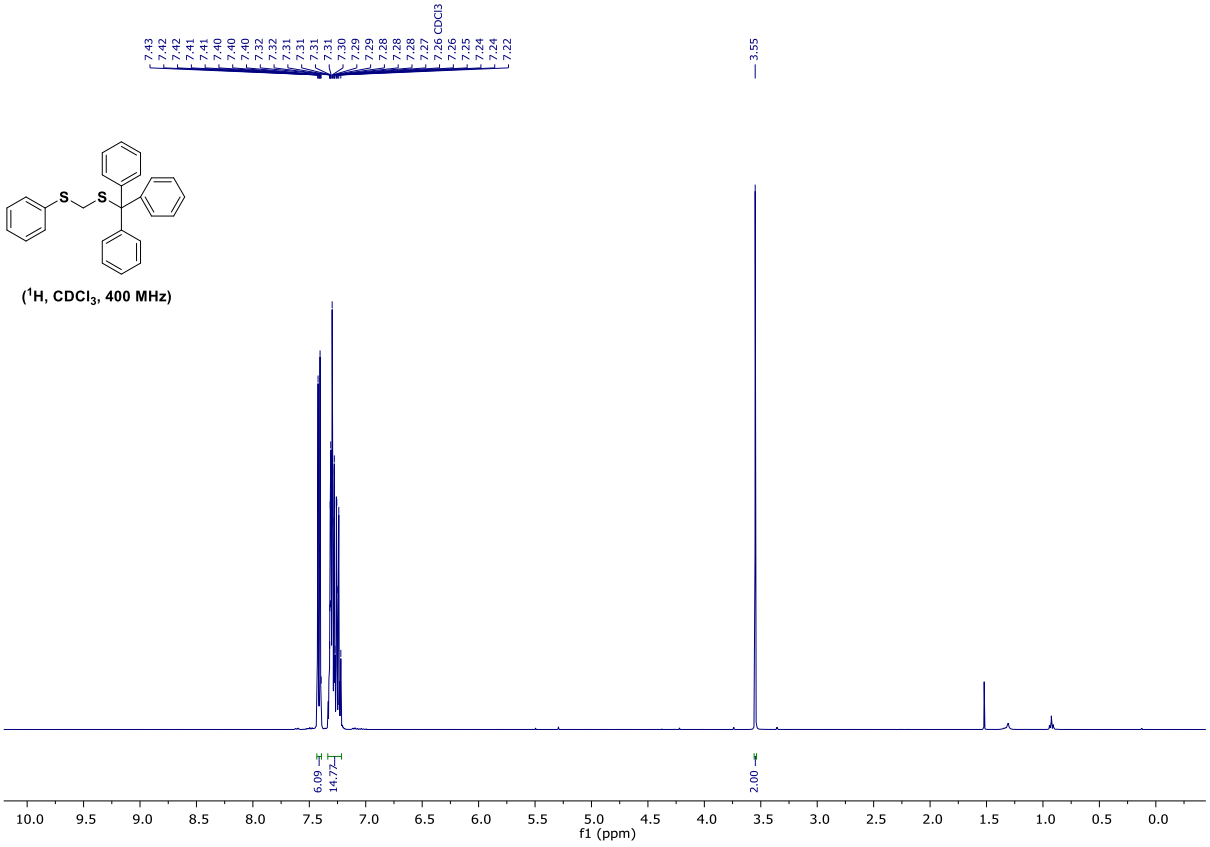
(^{1}H NMR, $CDCl_3$, 400 MHz)

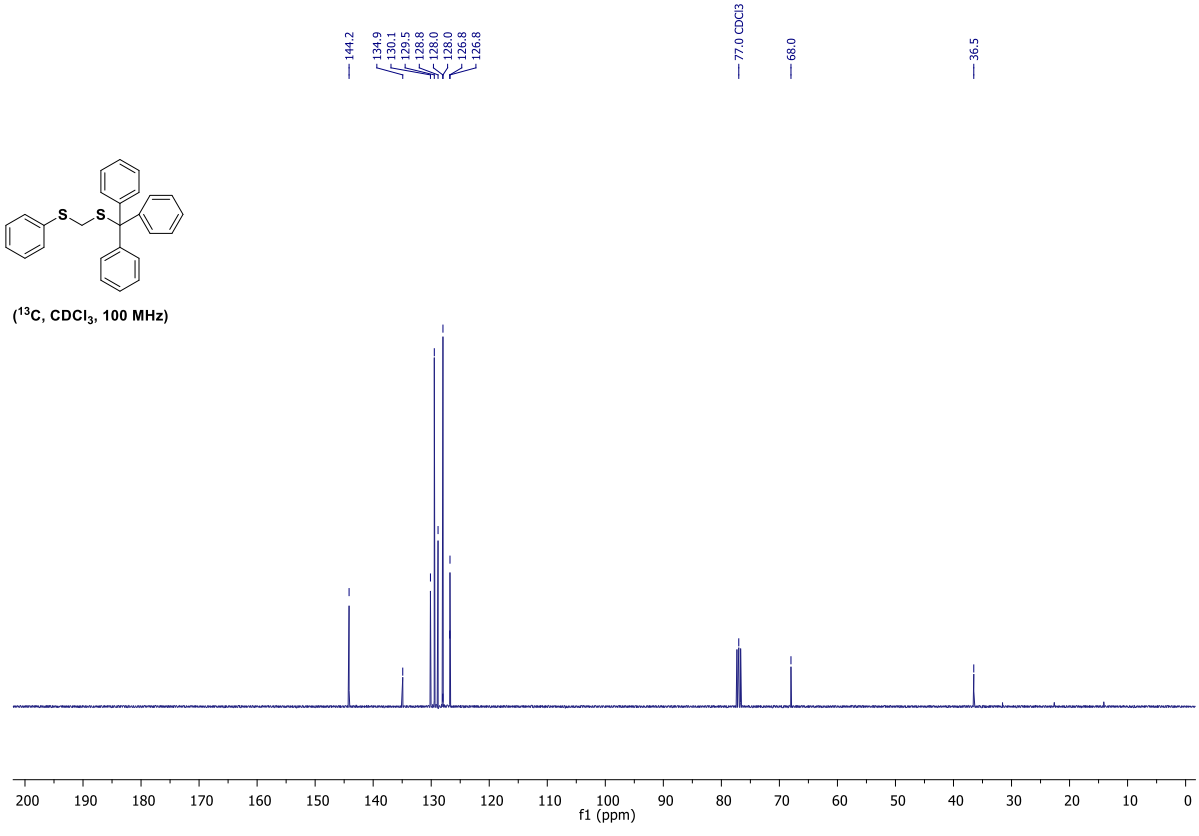




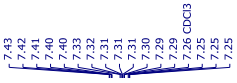
(^{13}C NMR, $CDCl_3$, 100 MHz)

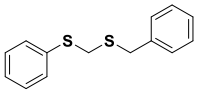
1,1´,1´´-({[(Phenylsulfanyl)methyl]sulfanyl}methanetriyl)tribenzene (13)



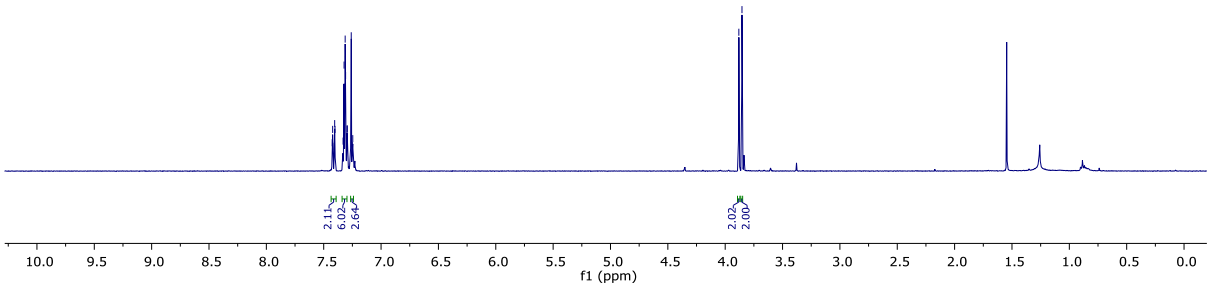


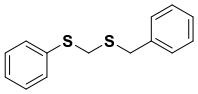
{[(Benzylsulfanyl)methyl]sulfanyl}benzene (14)



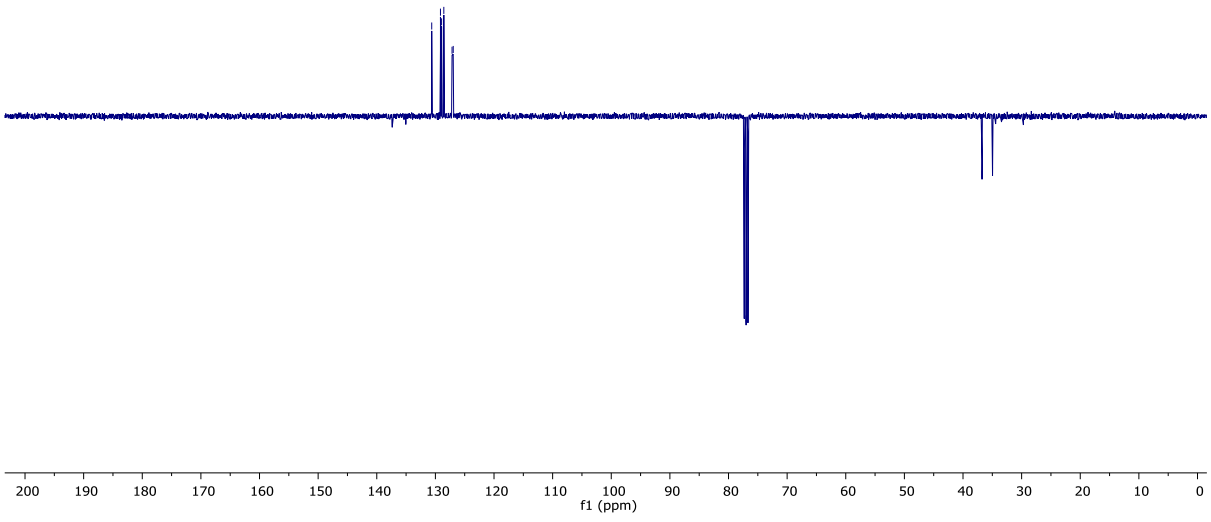


(^{1}H, $CDCl_3$, 400 MHz)

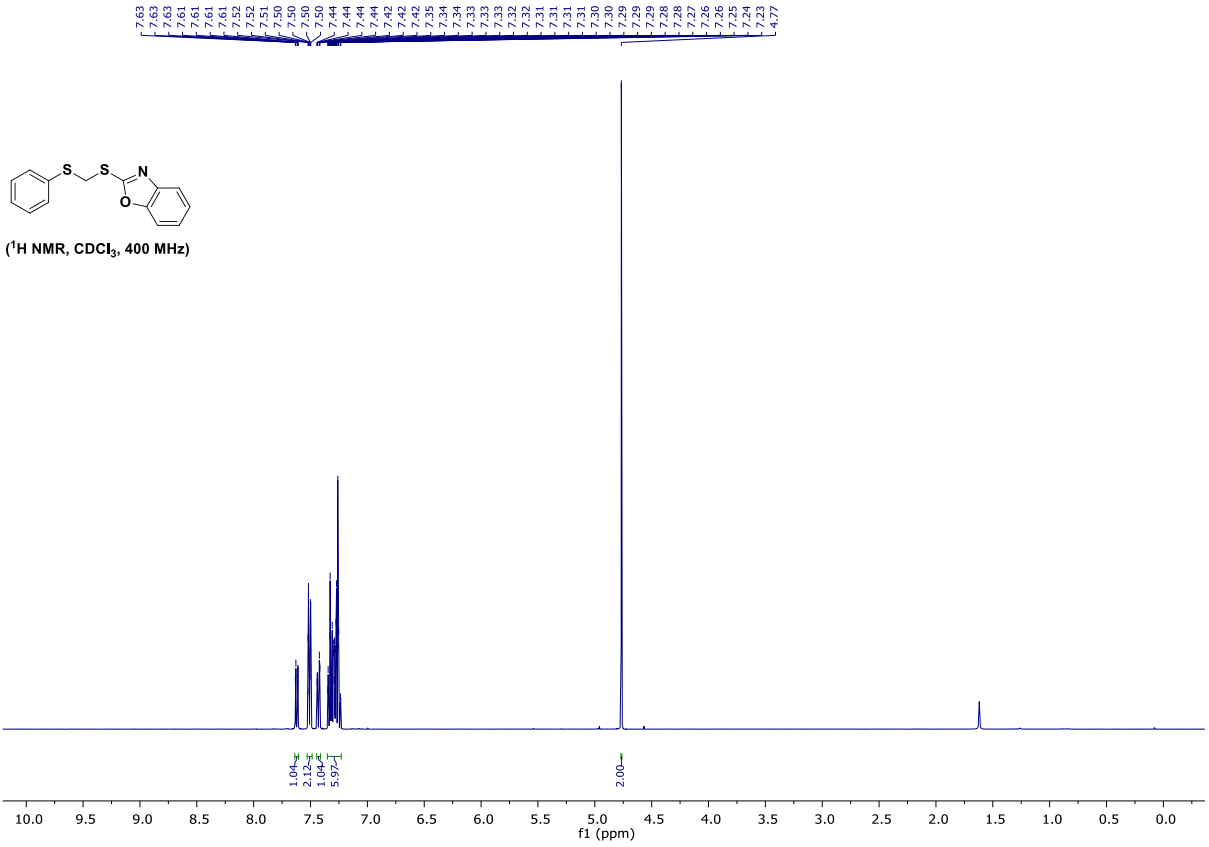


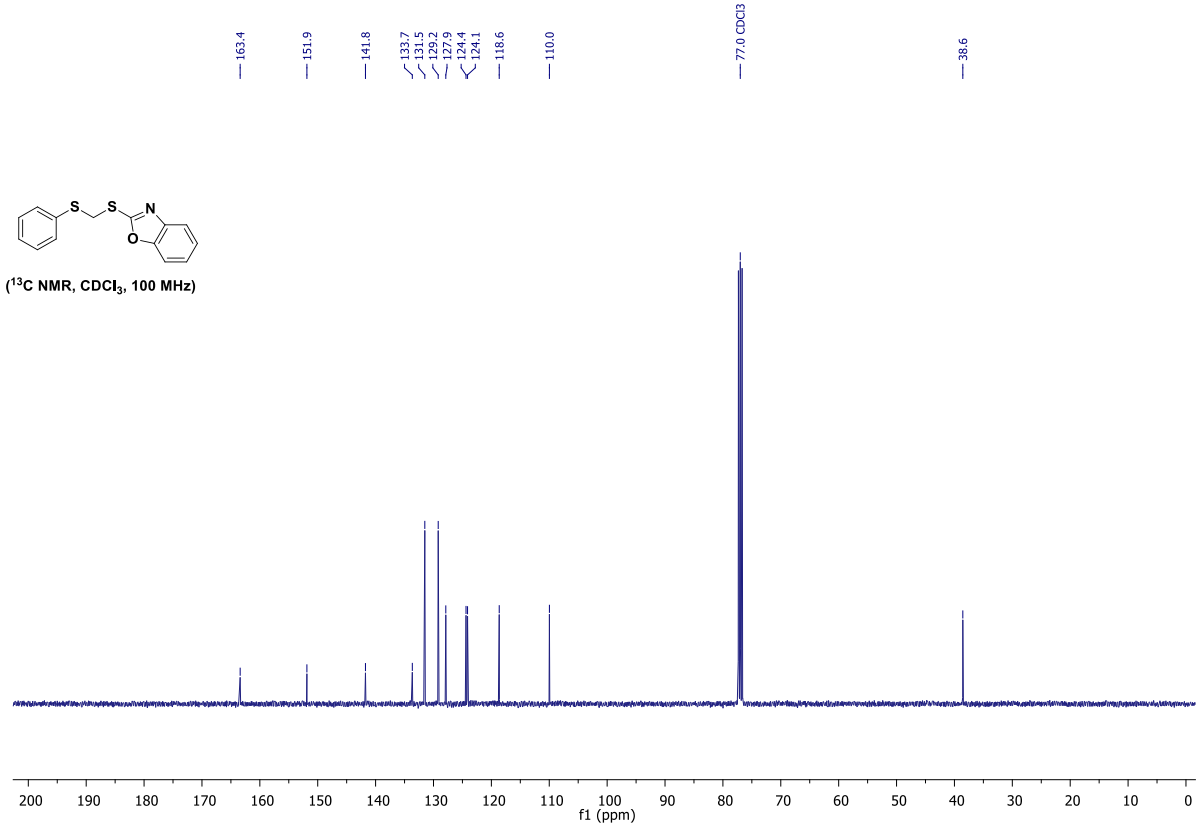


(^{13}C, $CDCl_3$, 100 MHz)

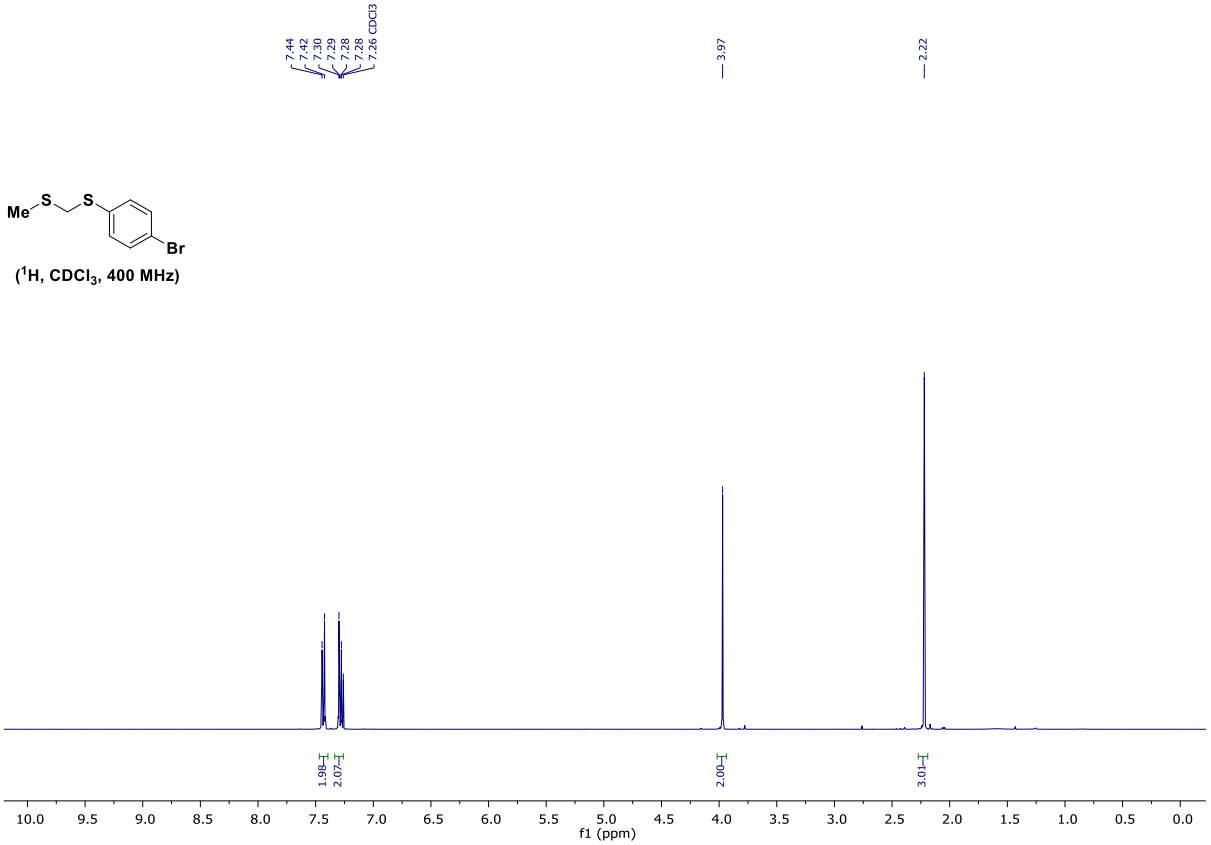


2-{[(Phenylsulfanyl)methyl]sulfanyl}-1,3-benzoxazole (15)

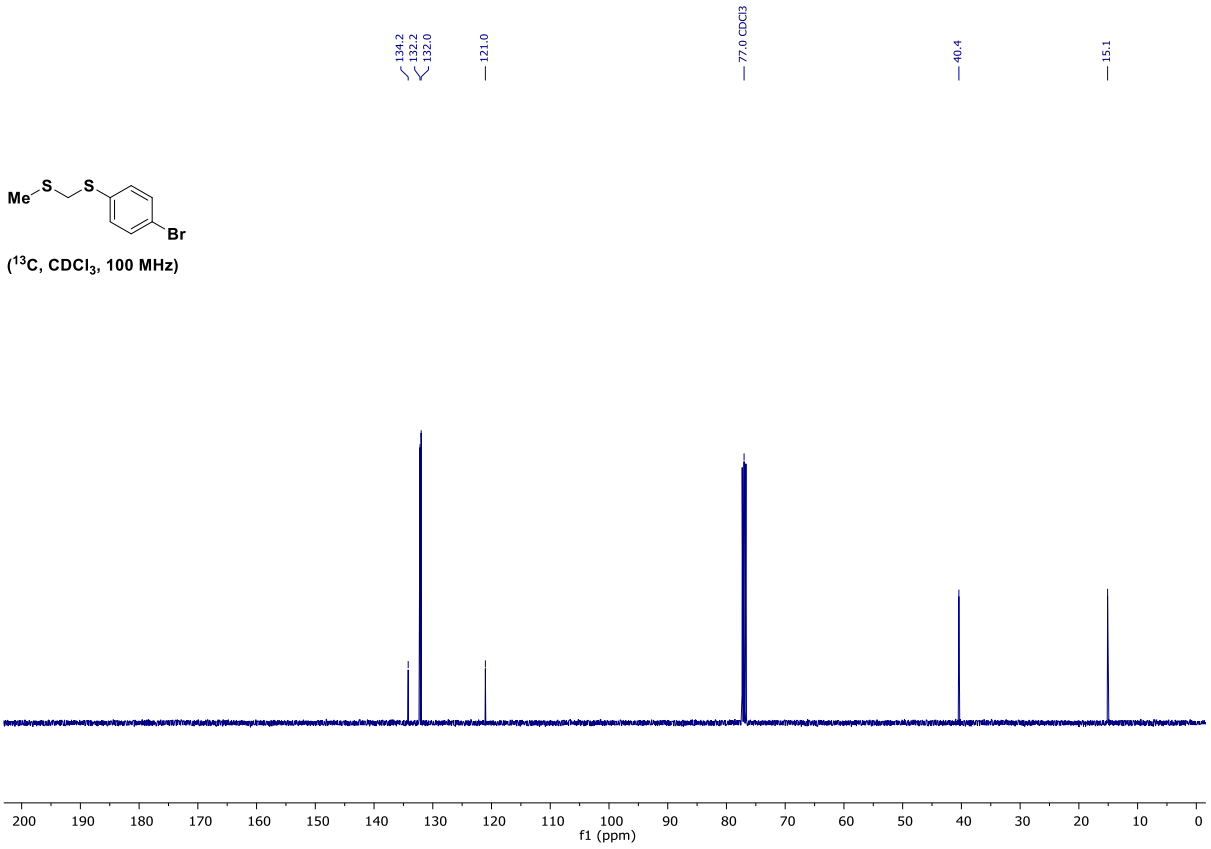




1-Bromo-4-{[(methylsulfanyl)methyl]sulfanyl}benzene (16)

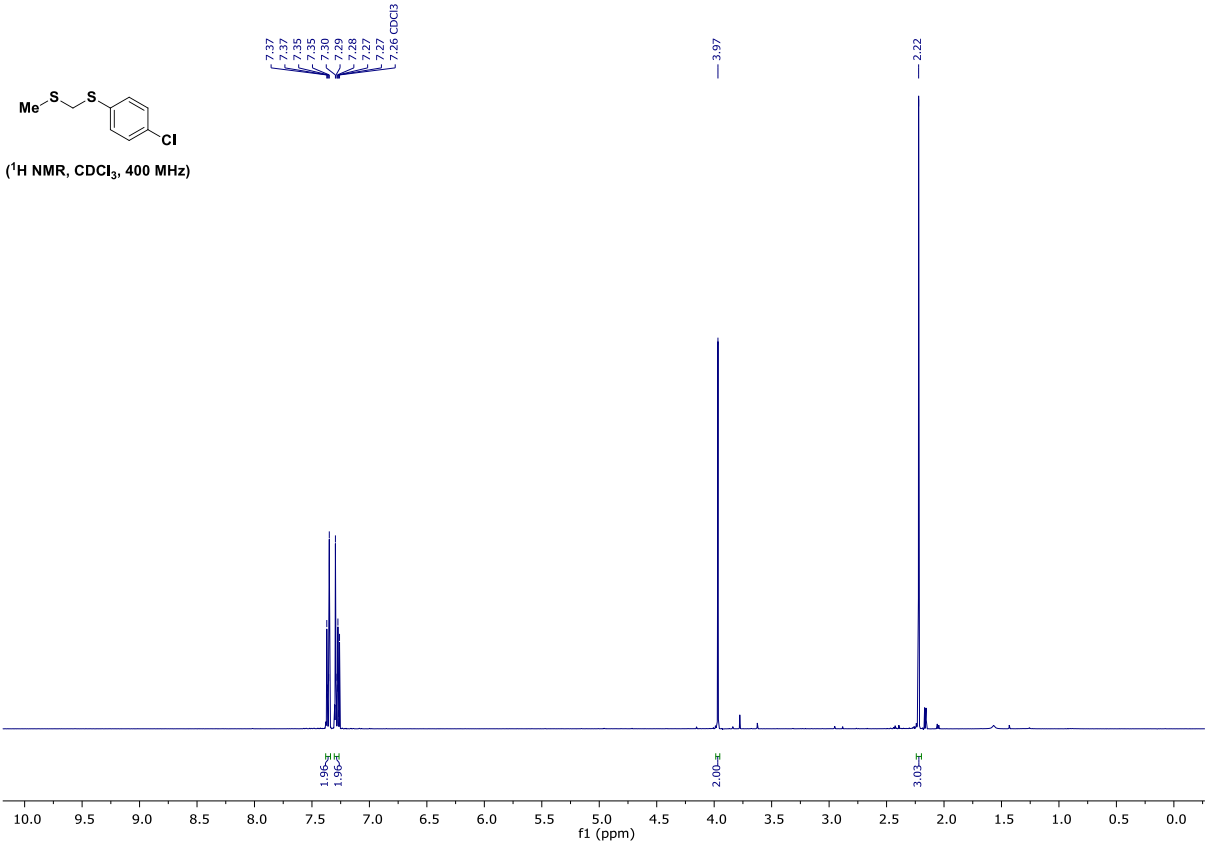


(^{1}H, $CDCl_3$, 400 MHz)

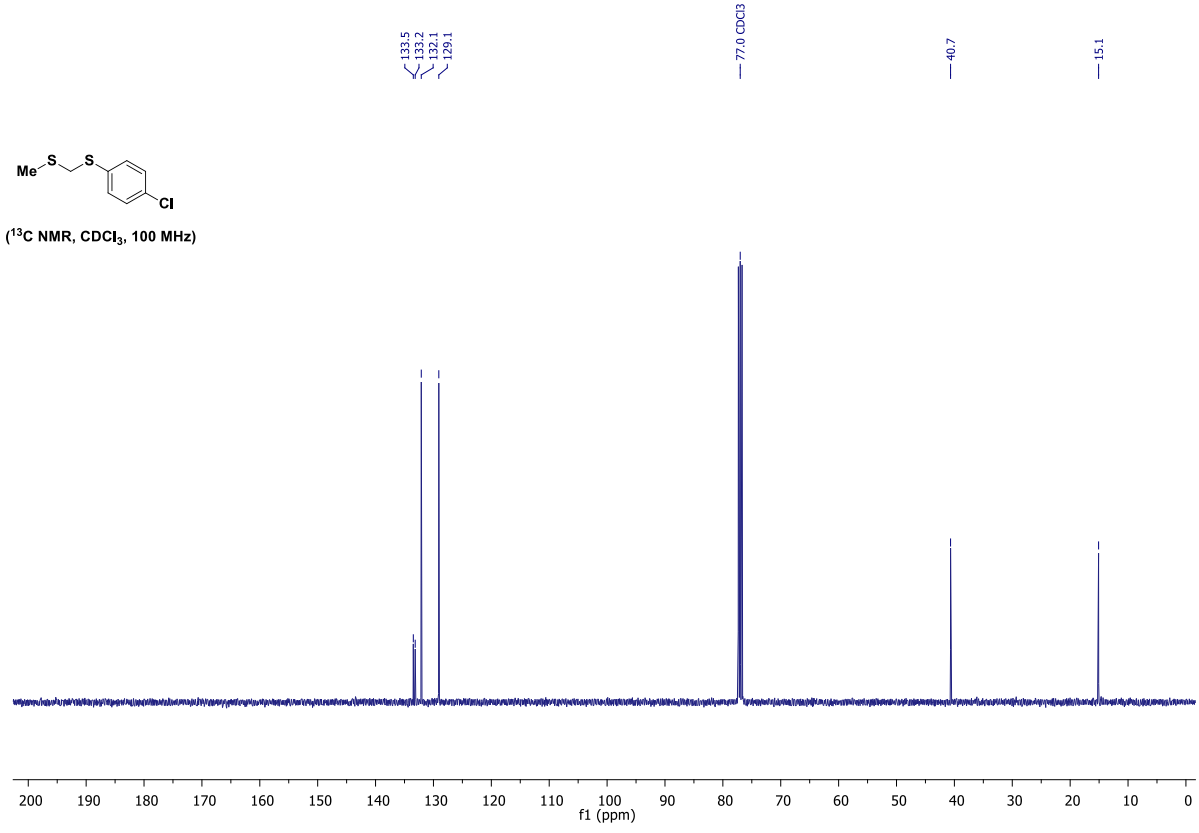


(^{13}C, $CDCl_3$, 100 MHz)

1-Chloro-4-{[(methylsulfanyl)methyl]sulfanyl}benzene (17)

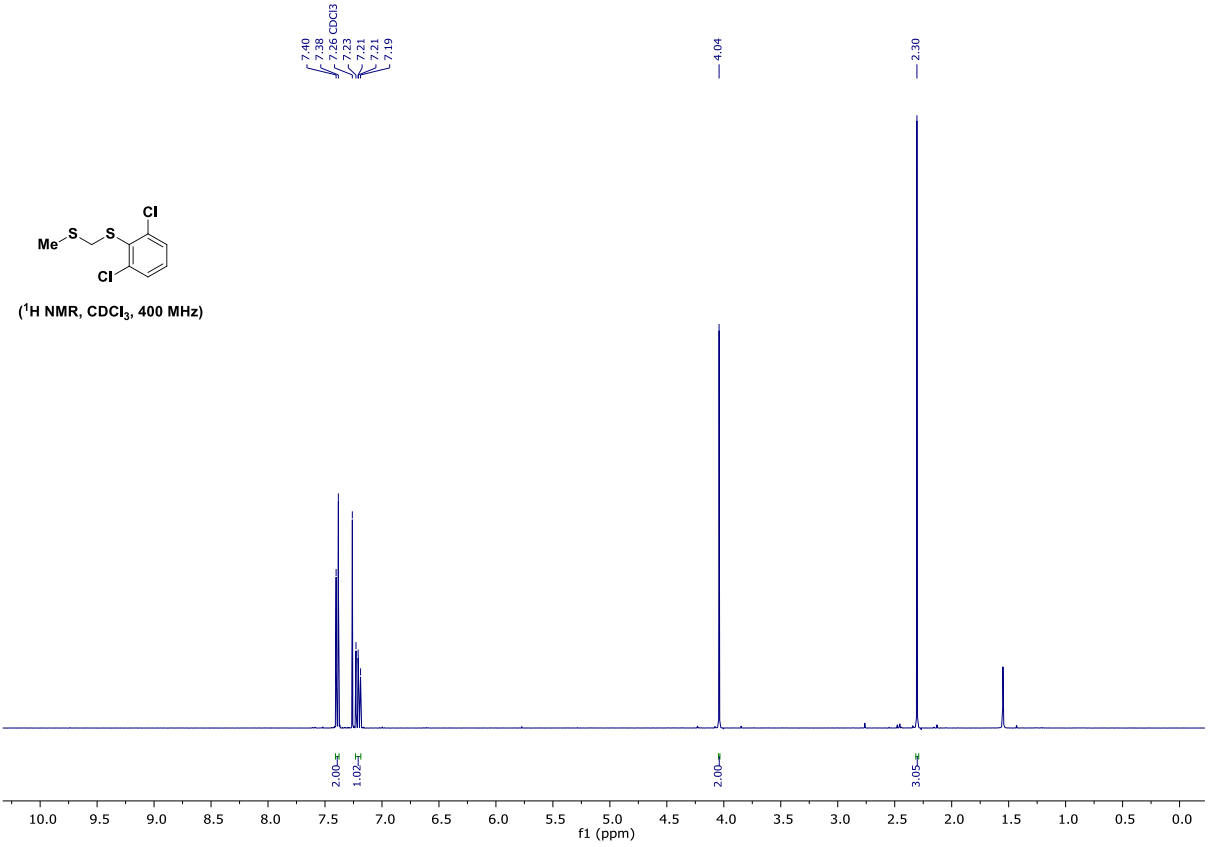


(^{1}H NMR, $CDCl_3$, 400 MHz)

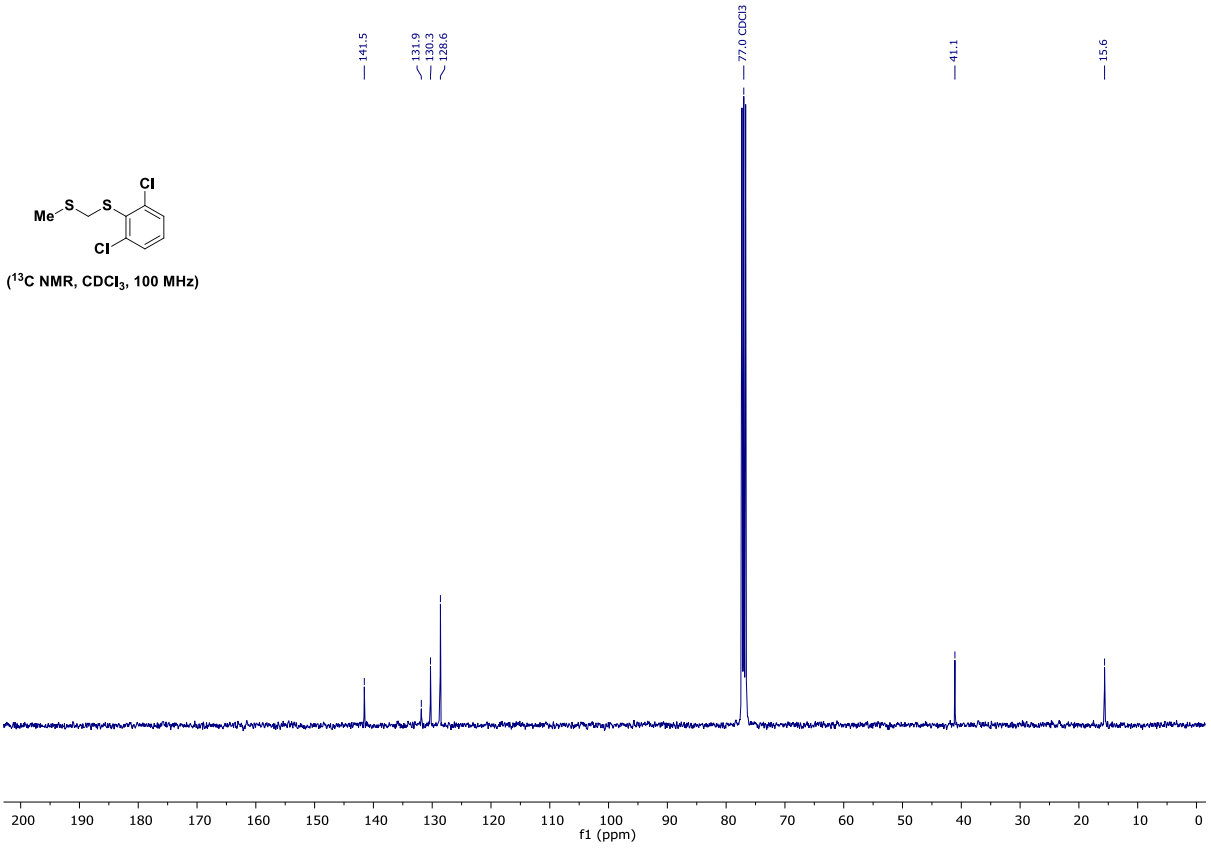


(^{13}C NMR, $CDCl_3$, 100 MHz)

1,3-Dichloro-2-{[(methylsulfanyl)methyl]sulfanyl}benzene (18)

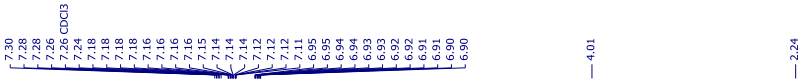


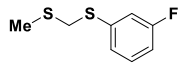
(^{1}H NMR, $CDCl_3$, 400 MHz)



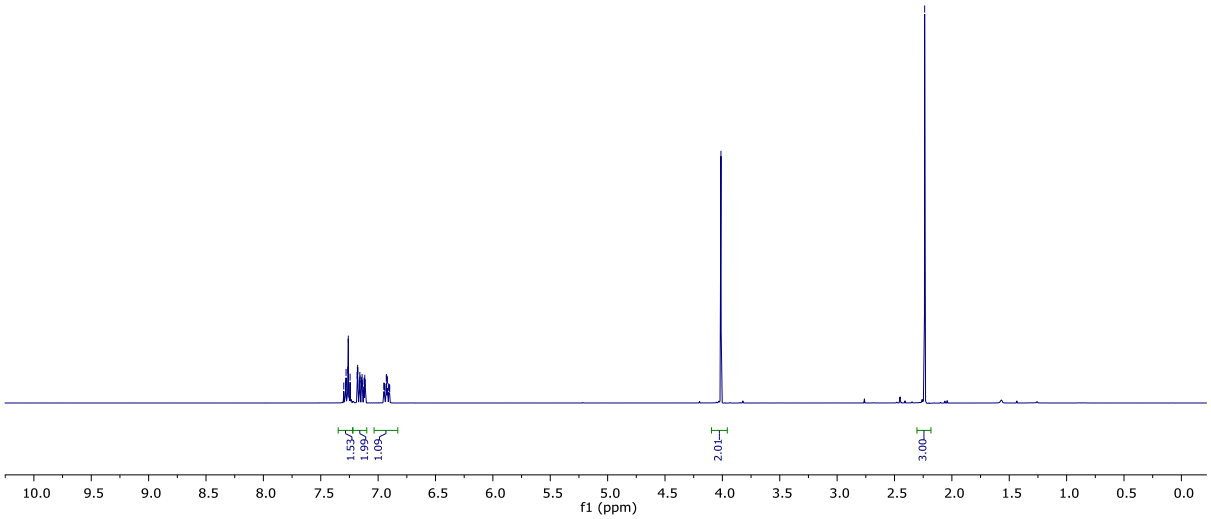
(^{13}C NMR, $CDCl_3$, 100 MHz)

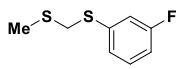
1-Fluoro-3-{[(methylsulfanyl)methyl]sulfanyl}benzene (19)



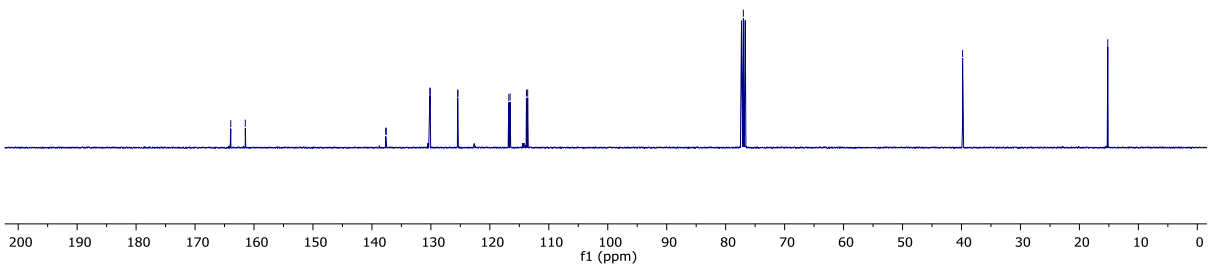


(^{1}H, $CDCl_3$, 400 MHz)

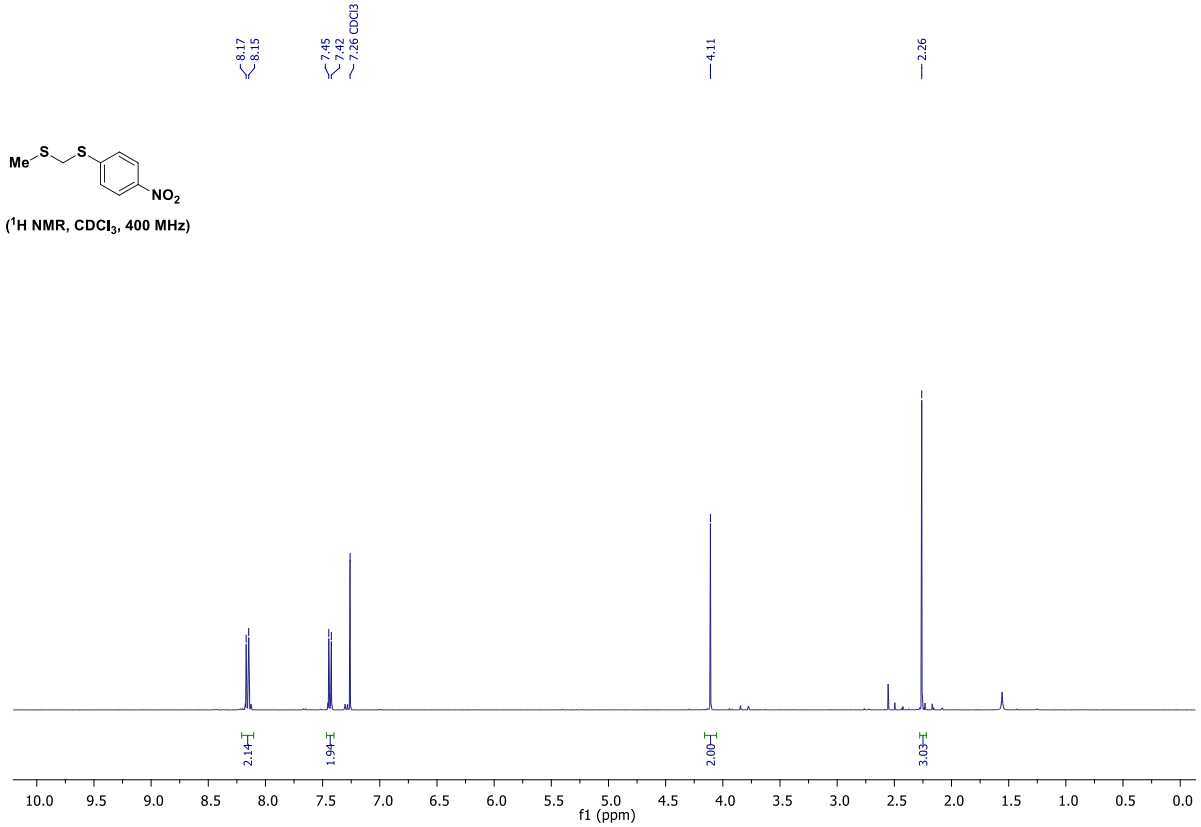




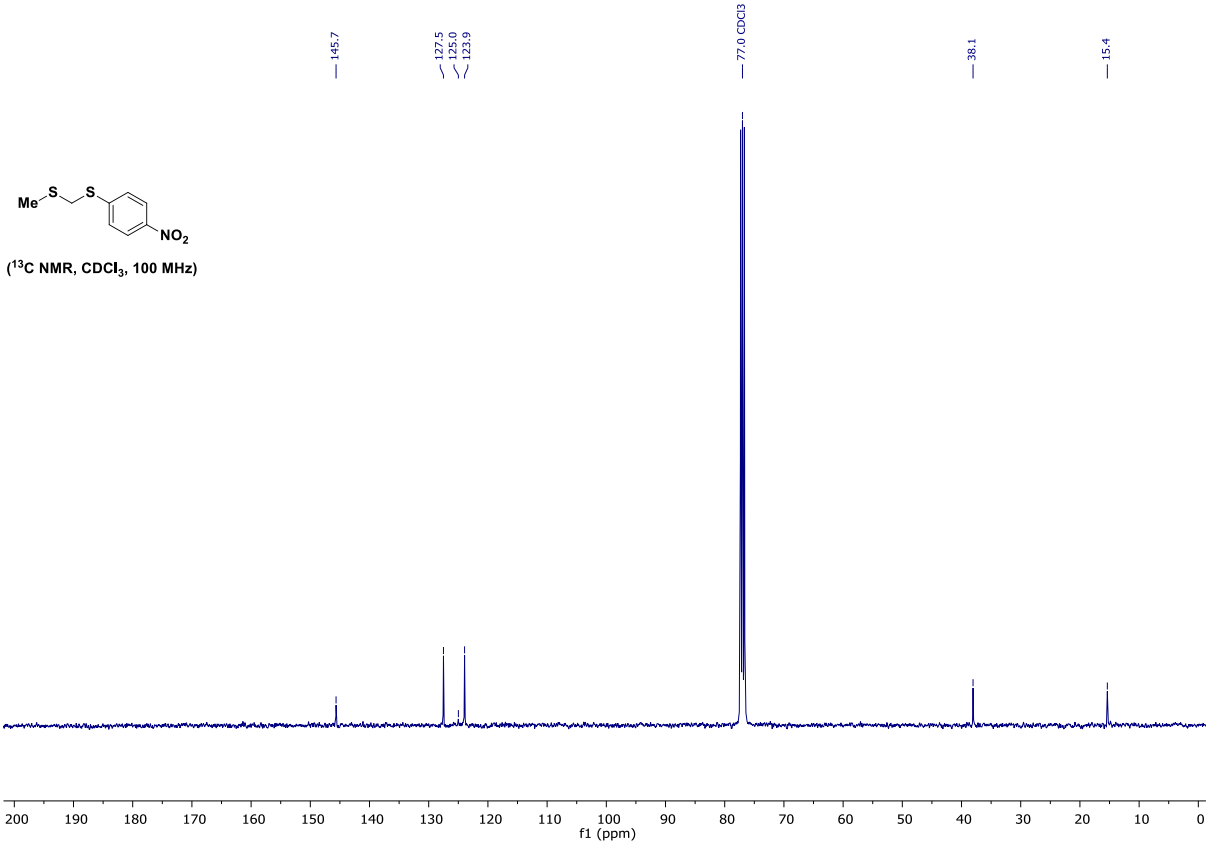
(^{13}C, $CDCl_3$, 100 MHz)



1-{[(Methylsulfanyl)methyl]sulfanyl}-4-nitrobenene (20)

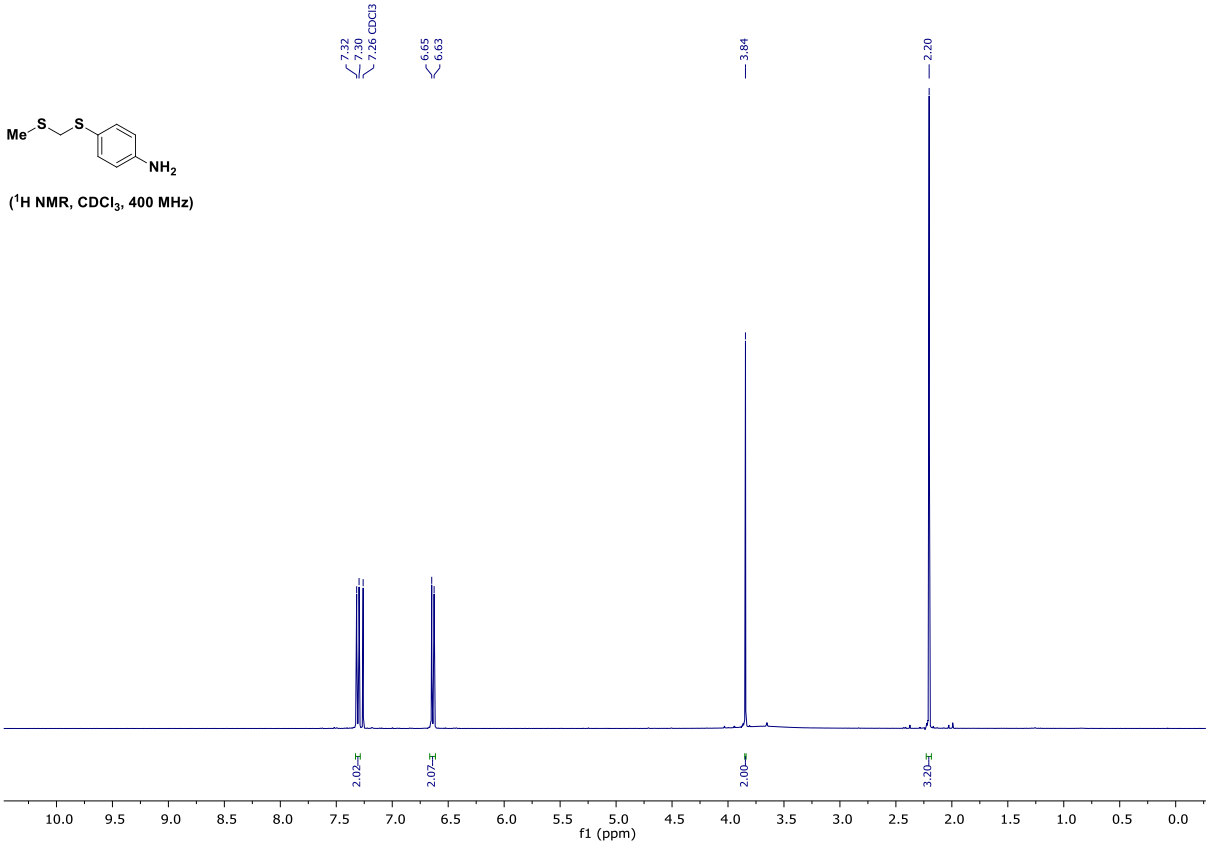


(^{1}H NMR, $CDCl_3$, 400 MHz)

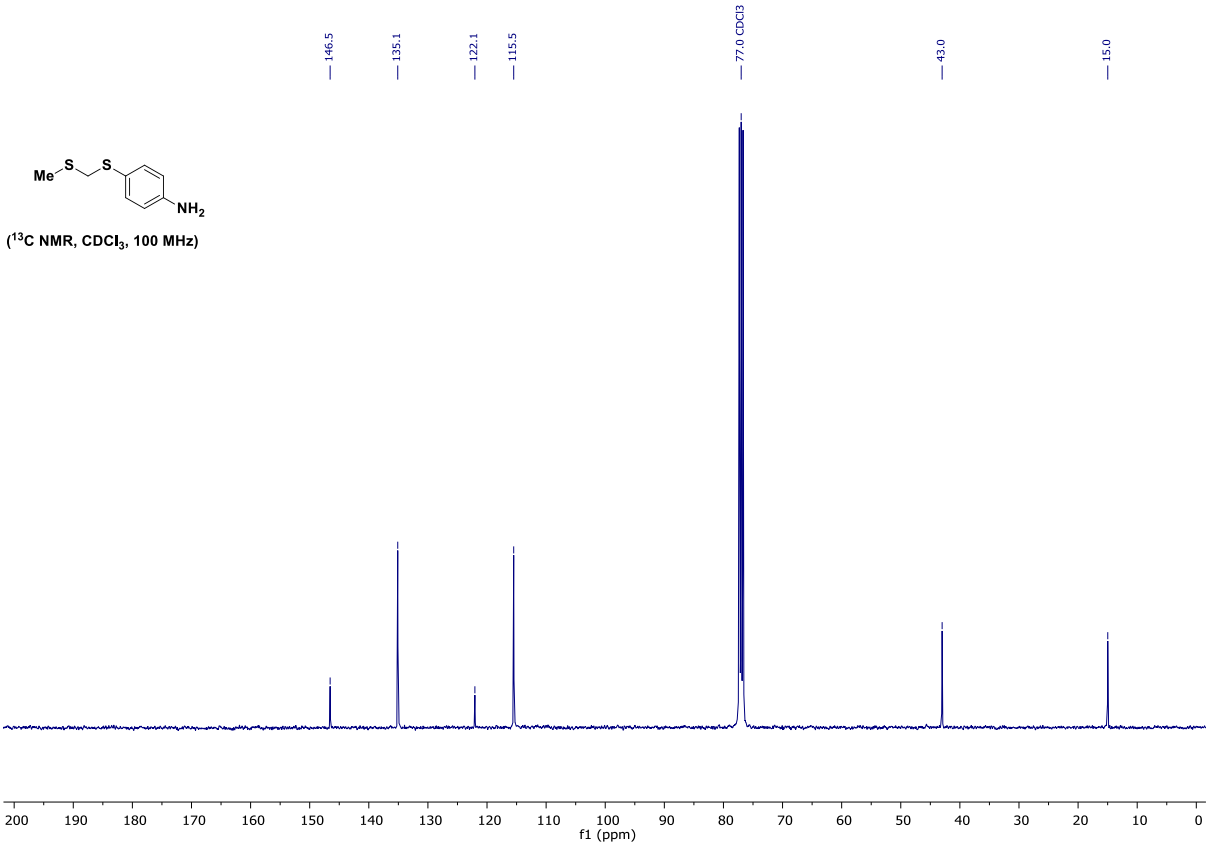


(^{13}C NMR, $CDCl_3$, 100 MHz)

4-{[(Methylsulfanyl)methyl]sulfanyl}aniline (21)

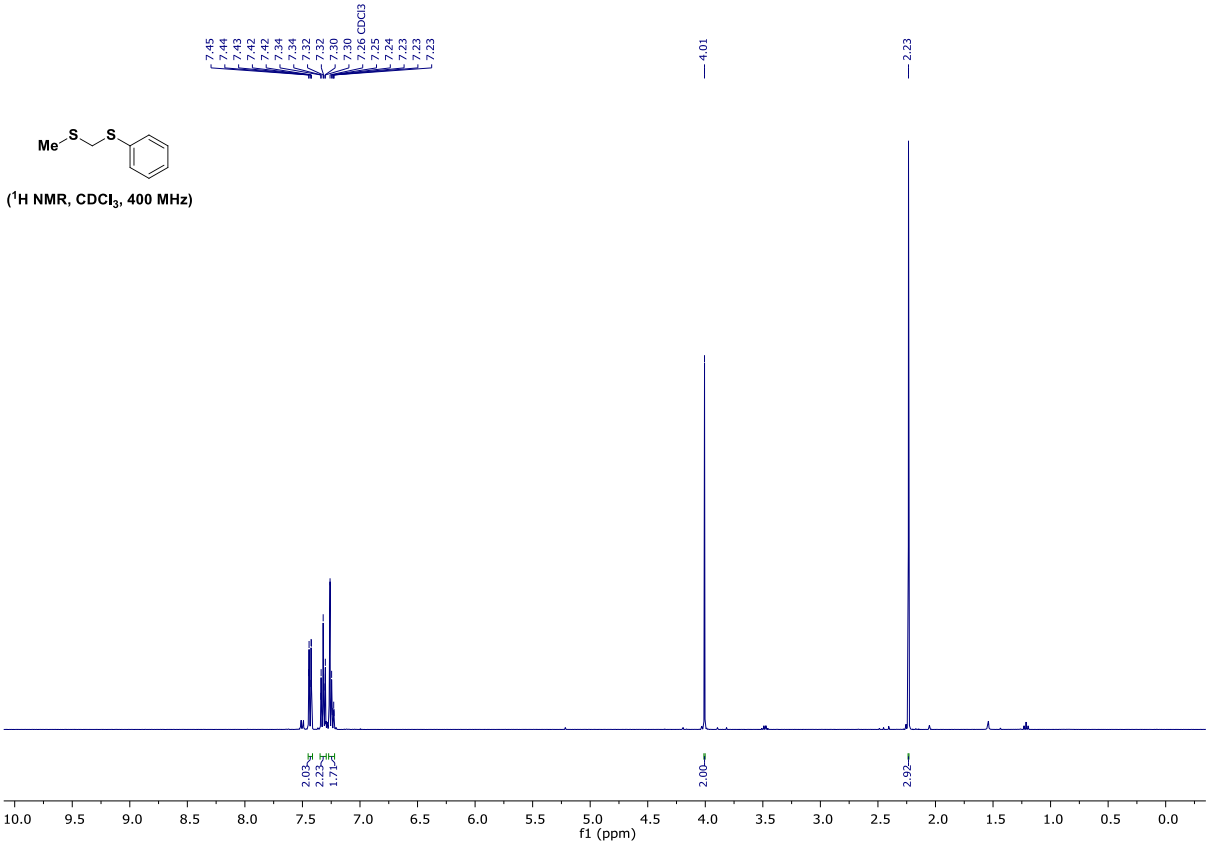


(^{1}H NMR, $CDCl_3$, 400 MHz)

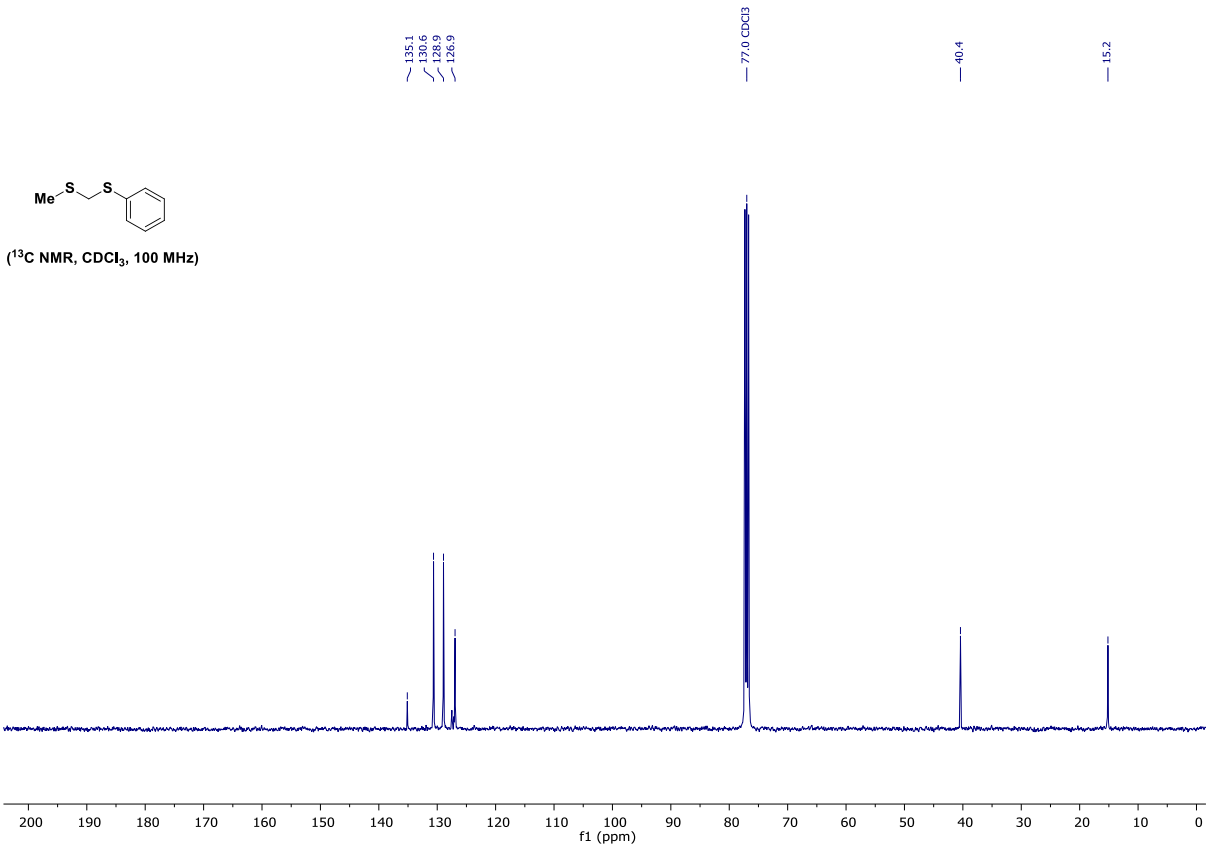


(^{13}C NMR, $CDCl_3$, 100 MHz)

{[(Methylsulfanyl)methyl]sulfanyl}benzene (22)

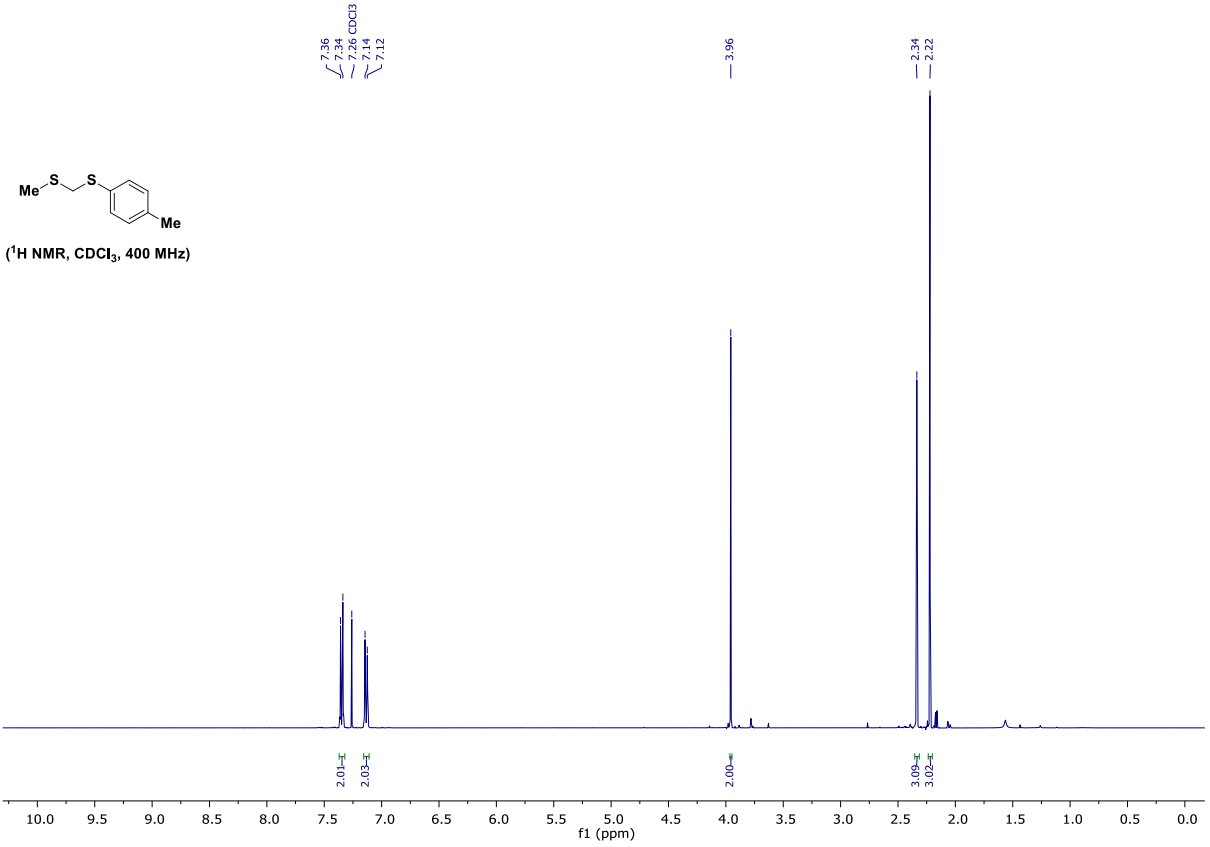


(^{1}H NMR, $CDCl_3$, 400 MHz)

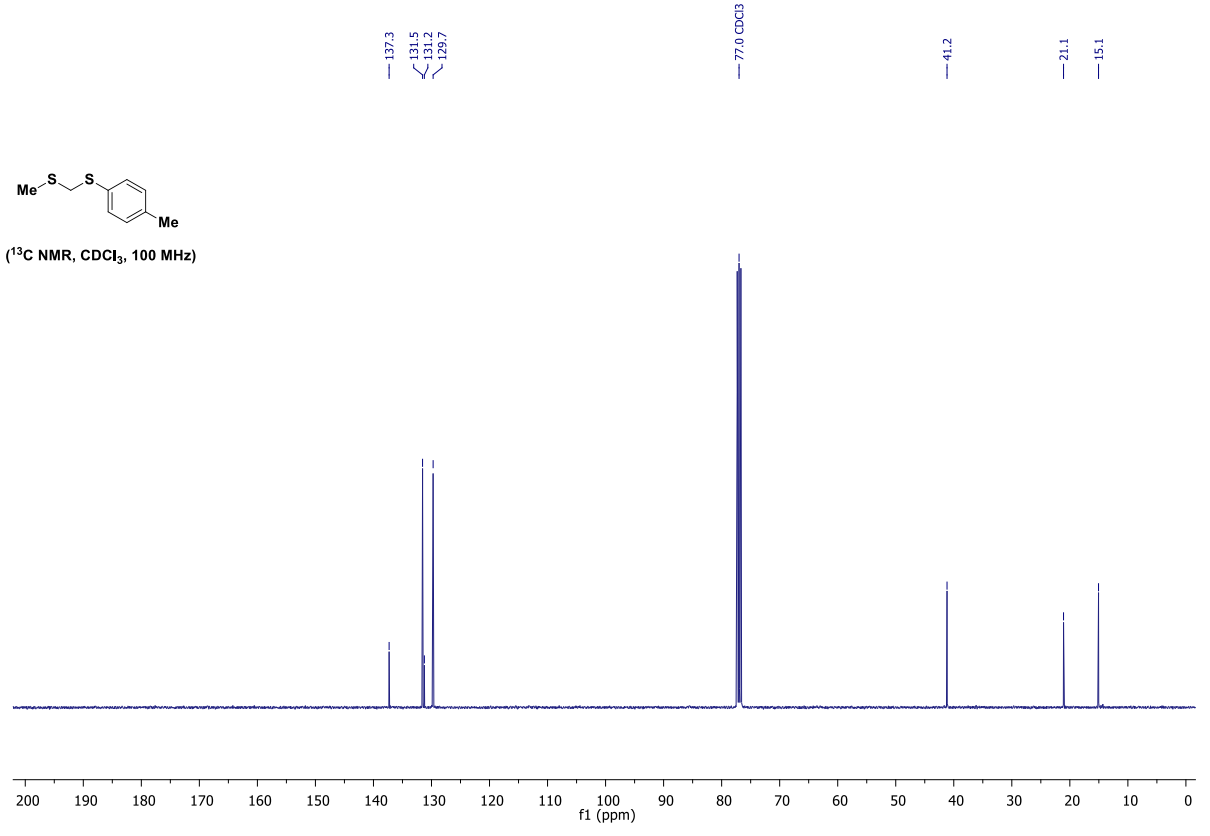


(^{13}C NMR, $CDCl_3$, 100 MHz)

1-Methyl-4-{[(methylsulfanyl)methyl]sulfanyl}benzene (23)

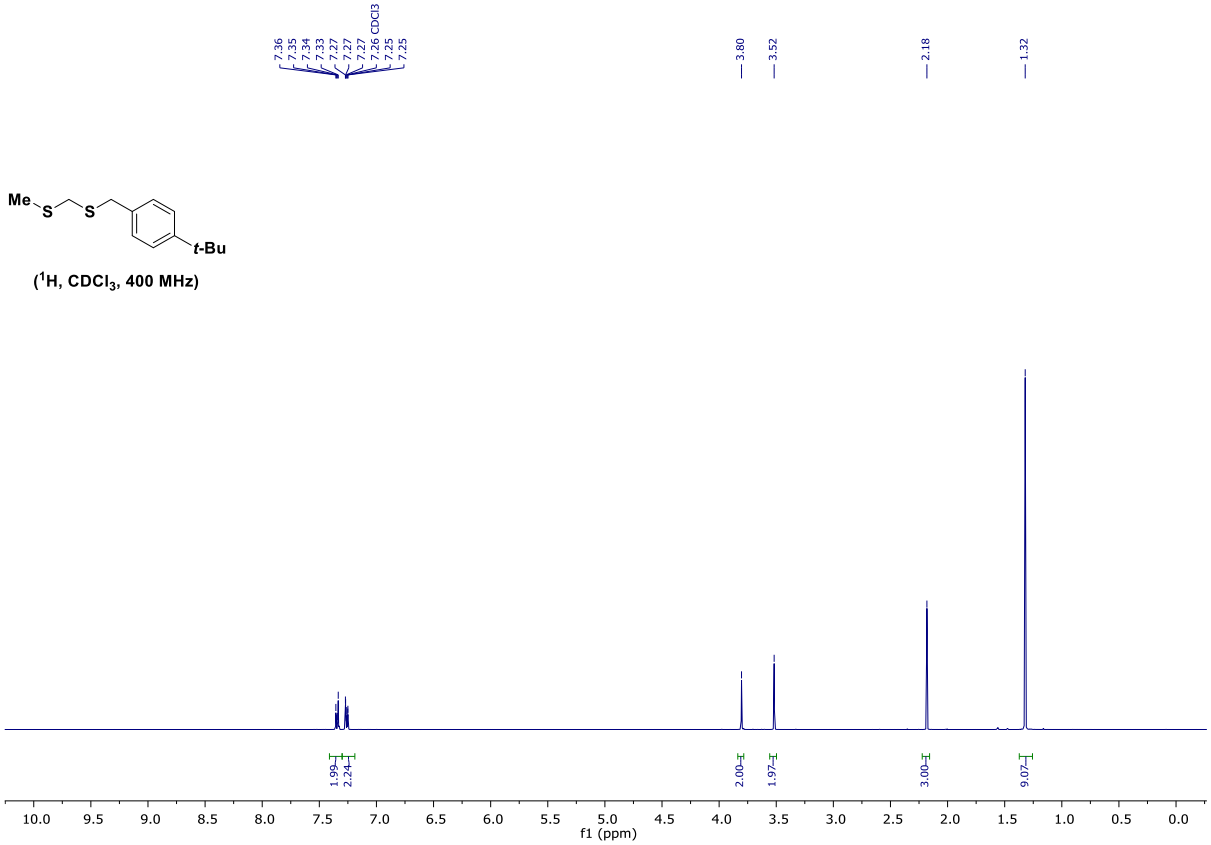


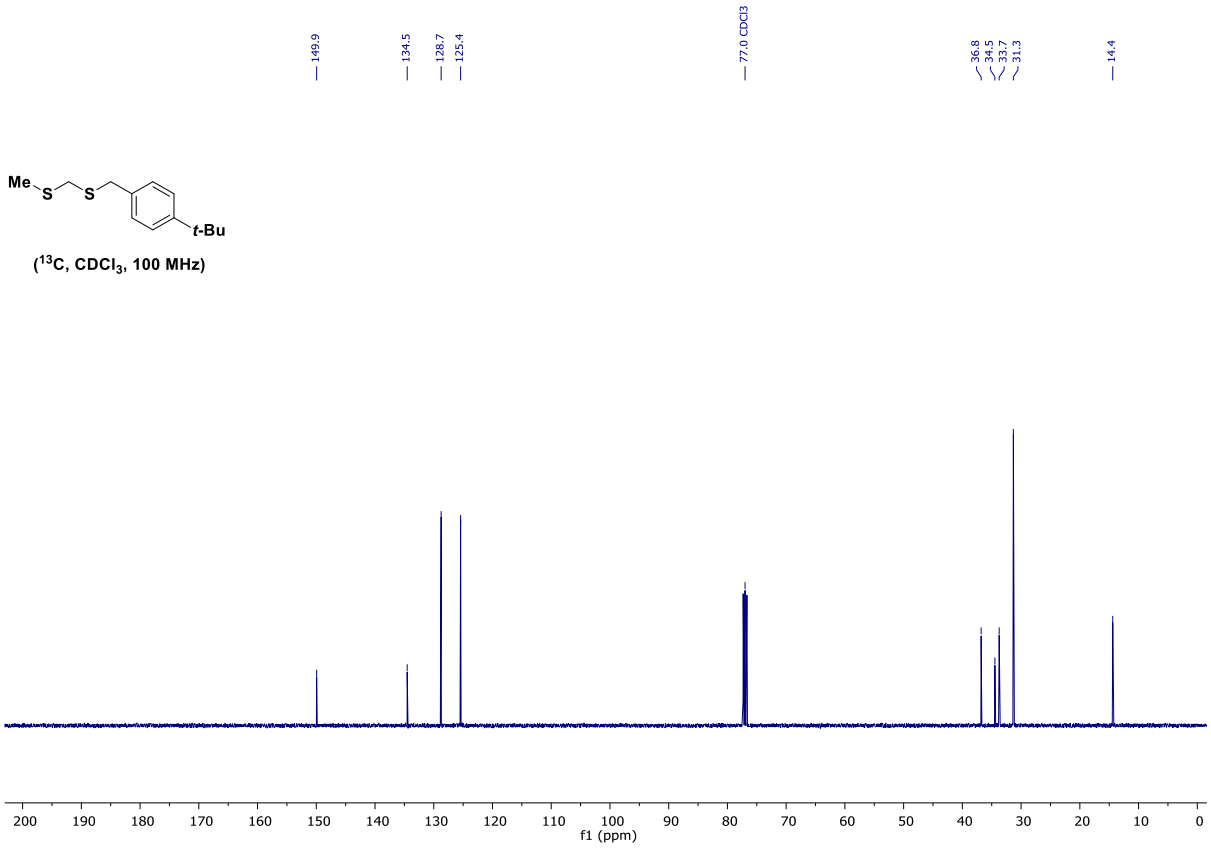
(^{1}H NMR, $CDCl_3$, 400 MHz)



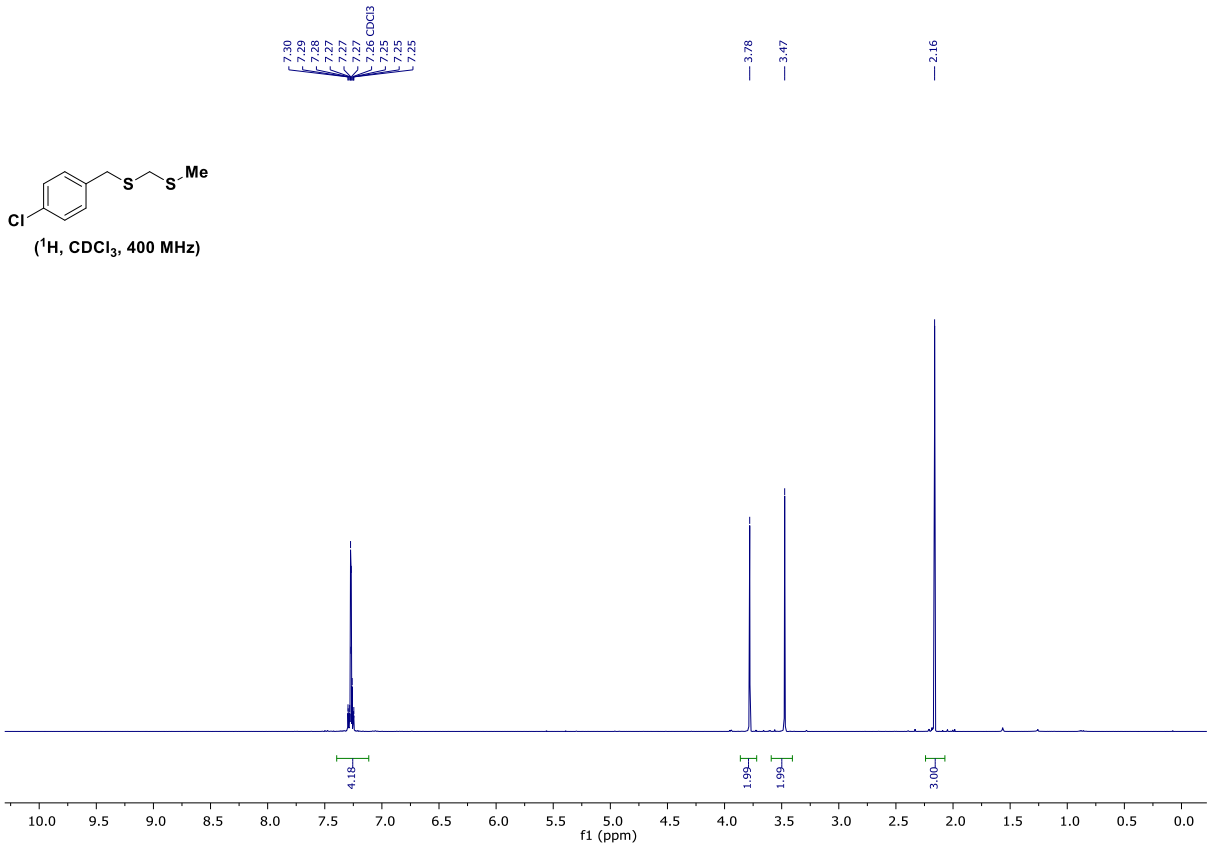
(^{13}C NMR, $CDCl_3$, 100 MHz)

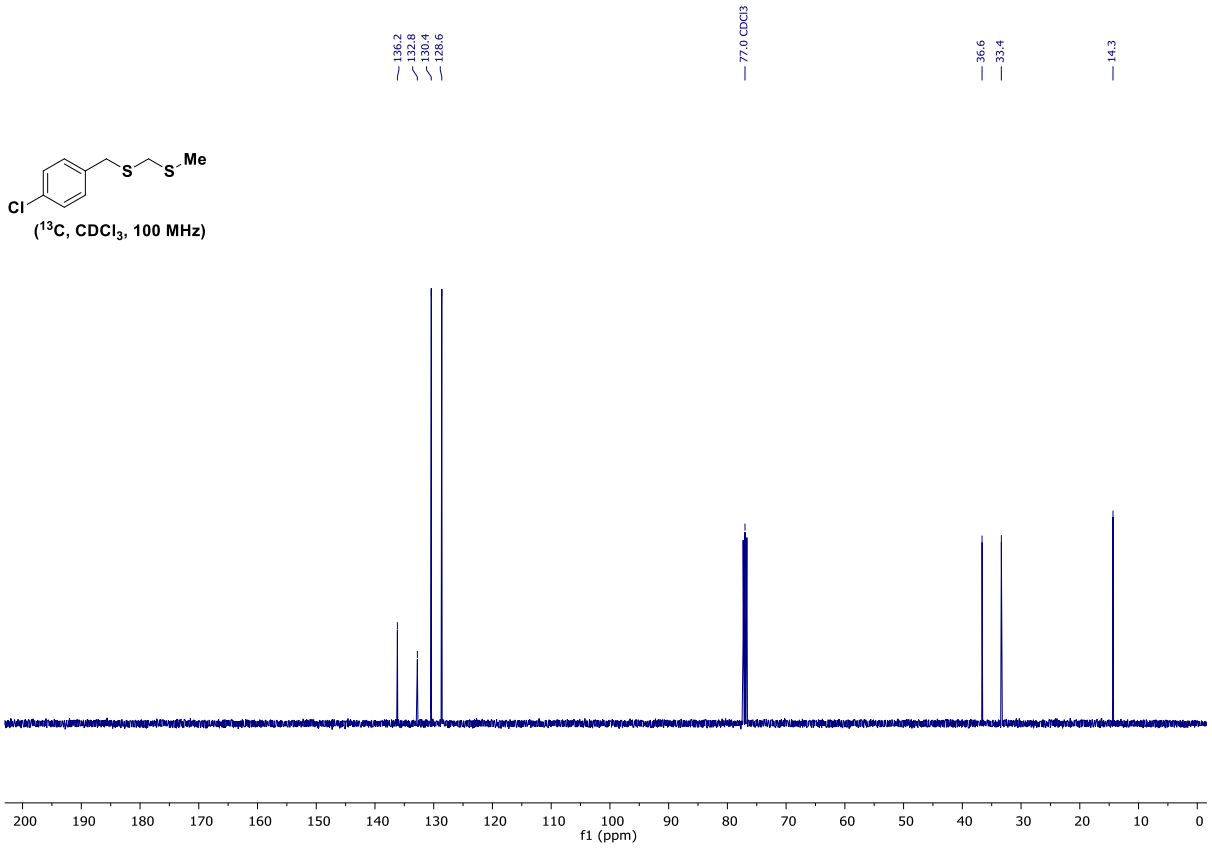
1-(2-Methyl-2-propanyl)-4-({[(methylsulfanyl)methyl]sulfanyl}methyl)benzene (24)



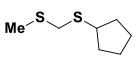


1-Chloro-4-({[(methylsulfanyl)methyl]sulfanyl}methyl)benzene (25)

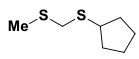




{[(Methylsulfanyl)methyl]sulfanyl}cyclopentane (26)

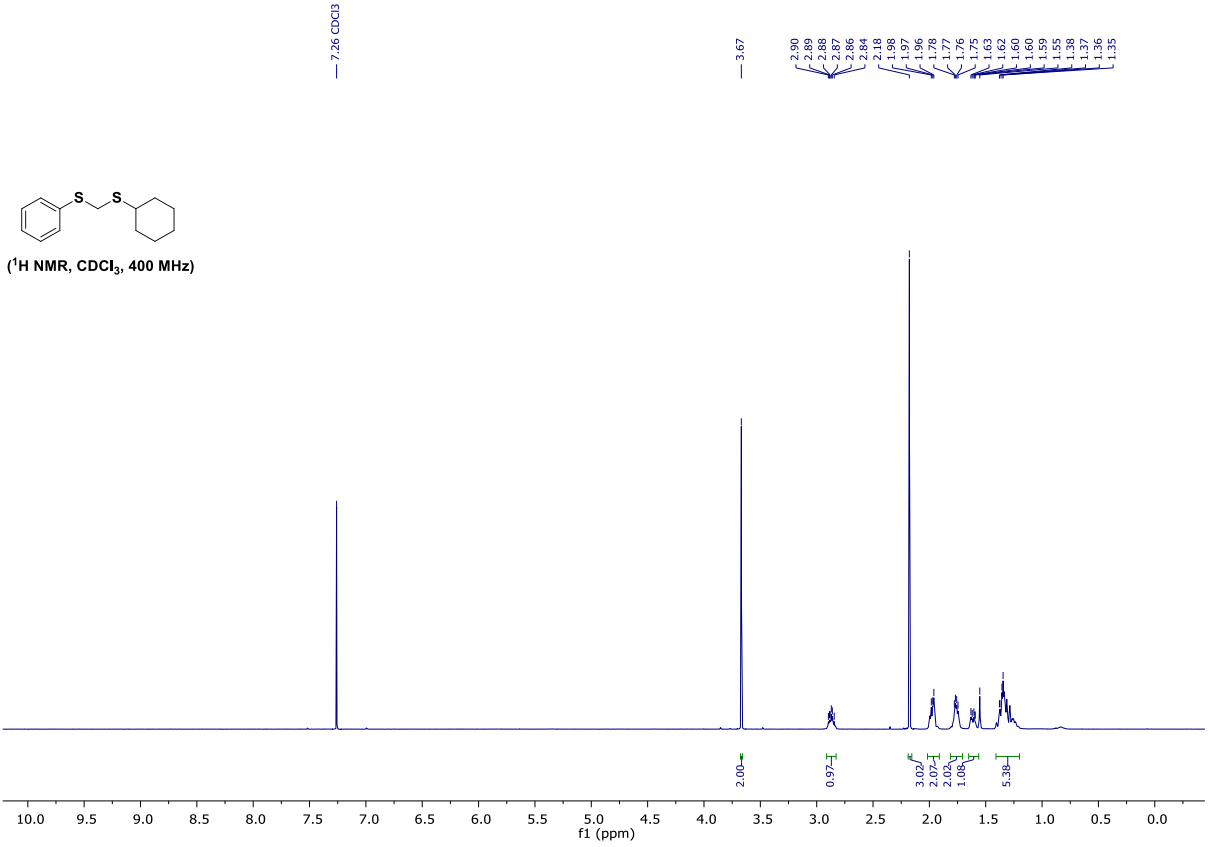


(^{1}H NMR, $CDCl_3$, 400 MHz)

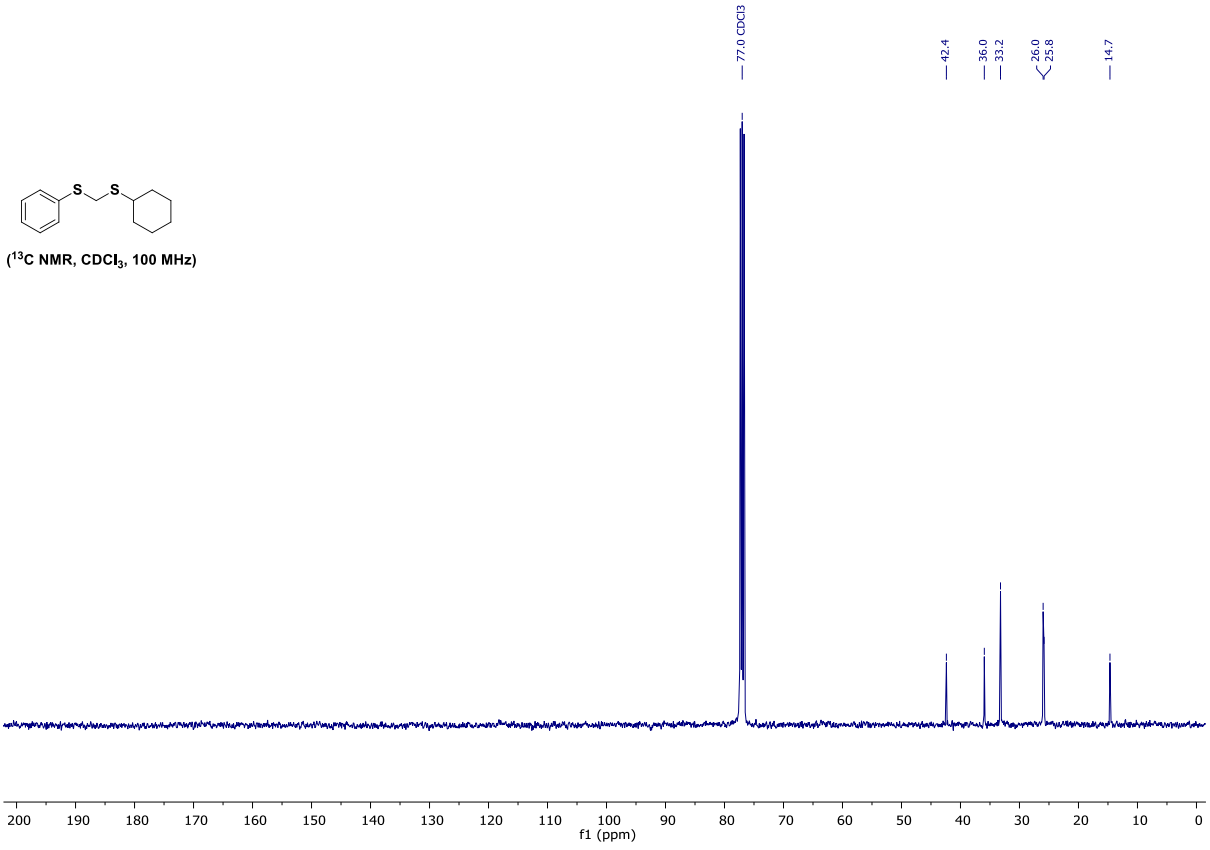


(^{13}C NMR, $CDCl_3$, 100 MHz)

{[(Methylsulfanyl)methyl]sulfanyl}cyclohexane (27)

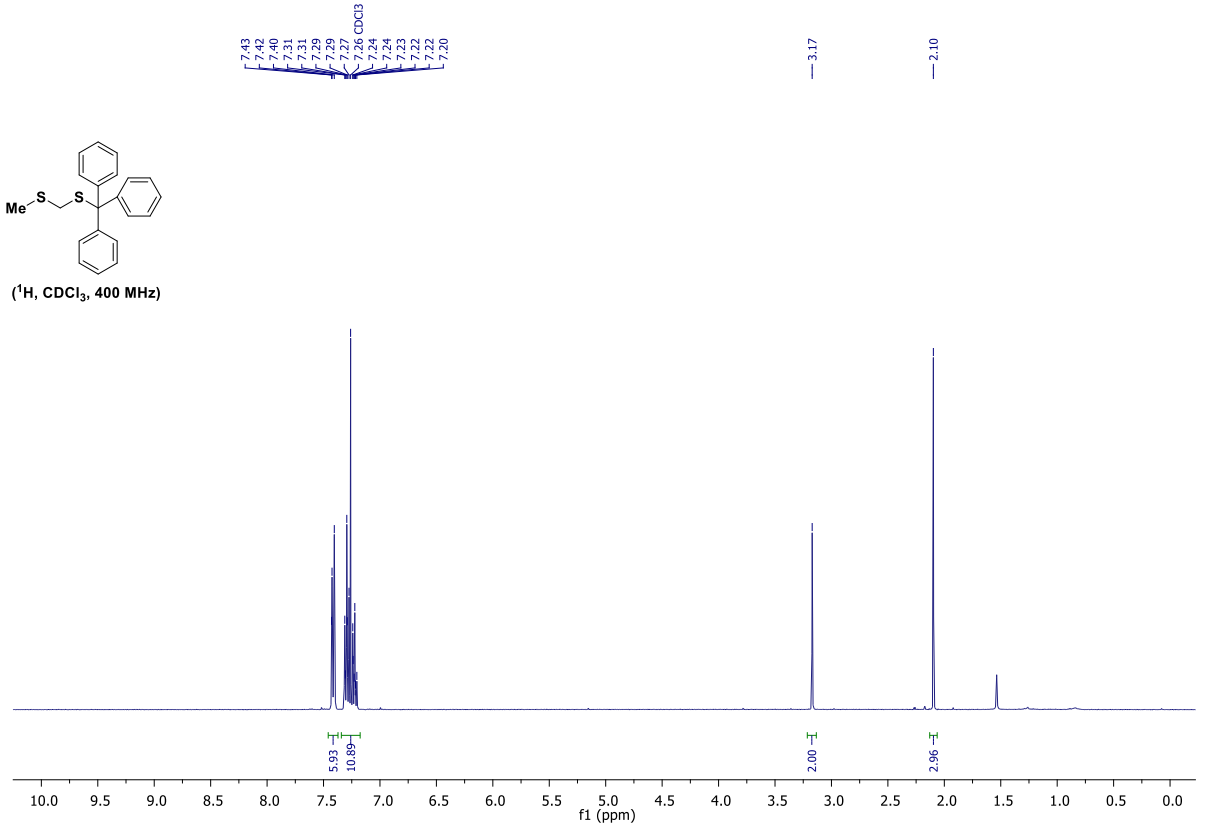


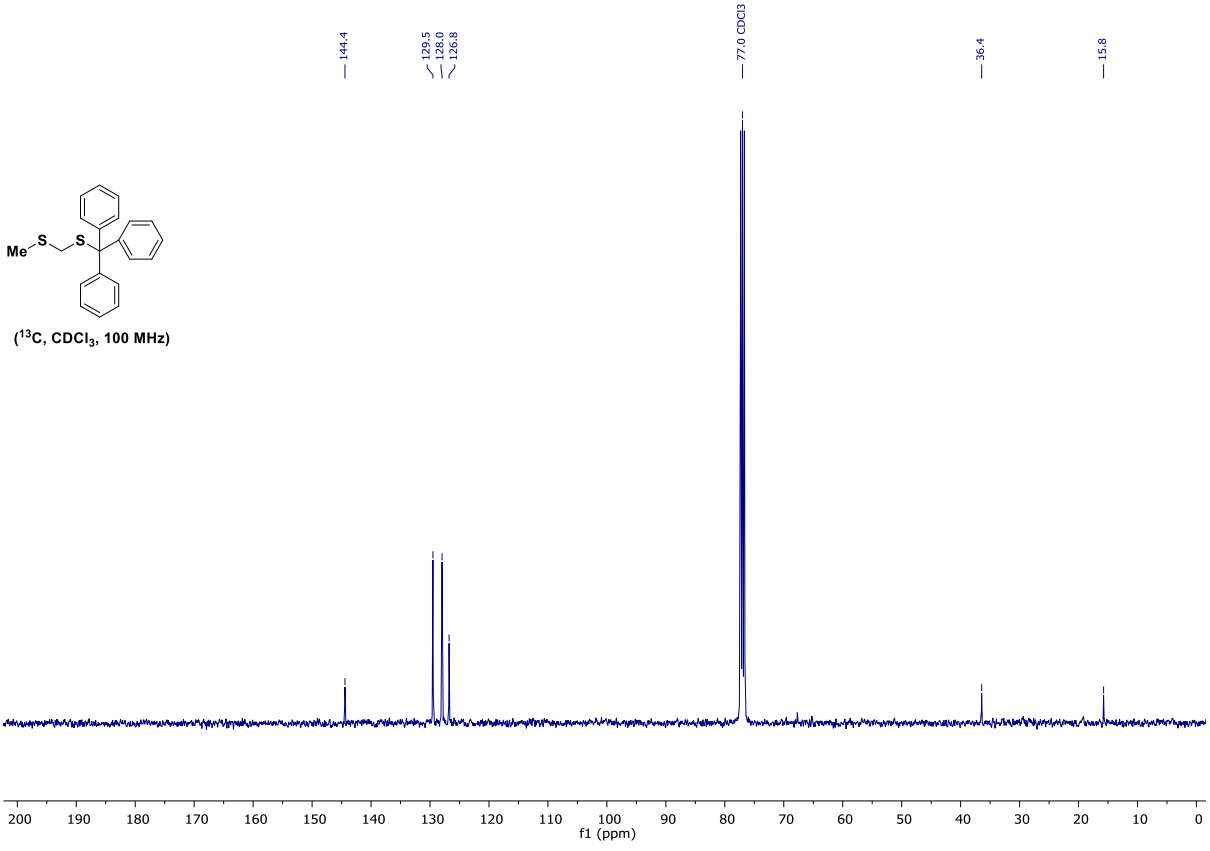
(^{1}H NMR, $CDCl_3$, 400 MHz)



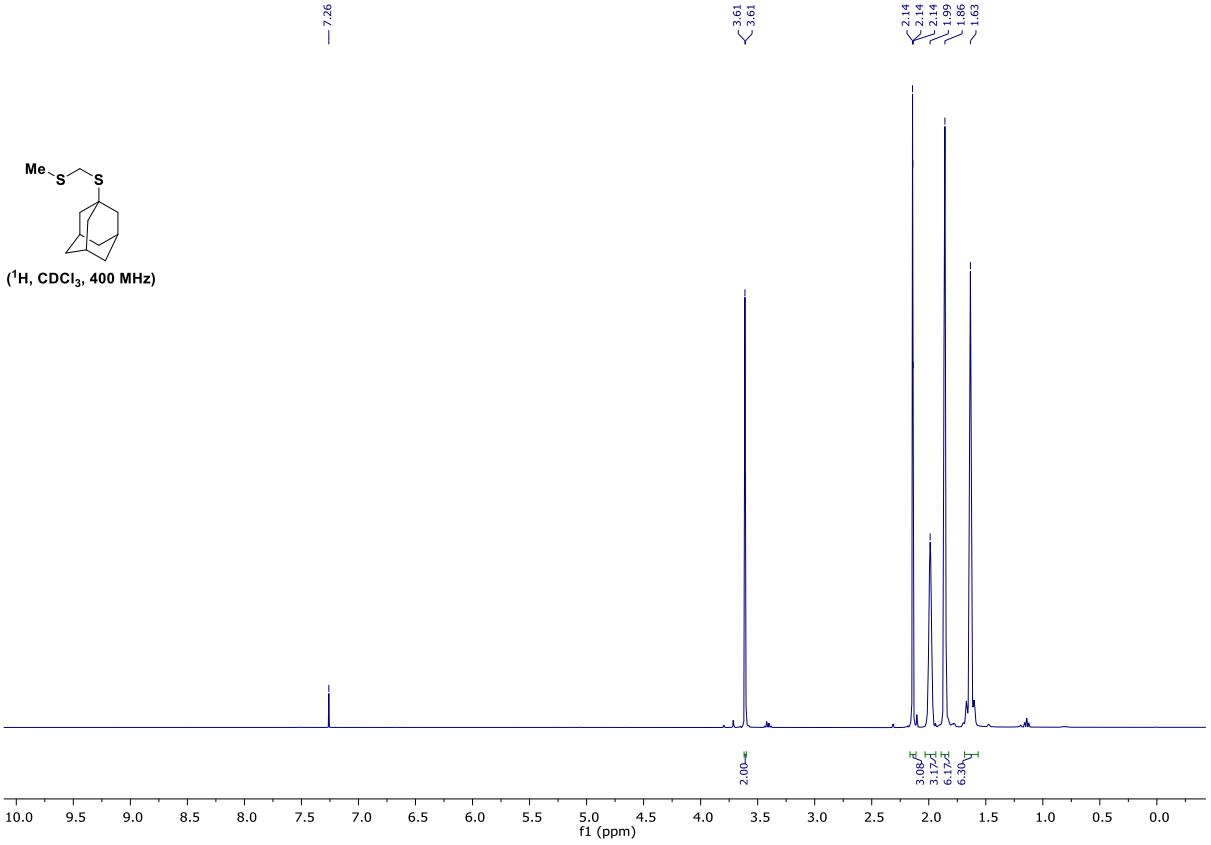
(^{13}C NMR, $CDCl_3$, 100 MHz)

1,1´,1´´-({[(Methylsulfanyl)methyl]sulfanyl}methanetriyl)tribenzene (28)

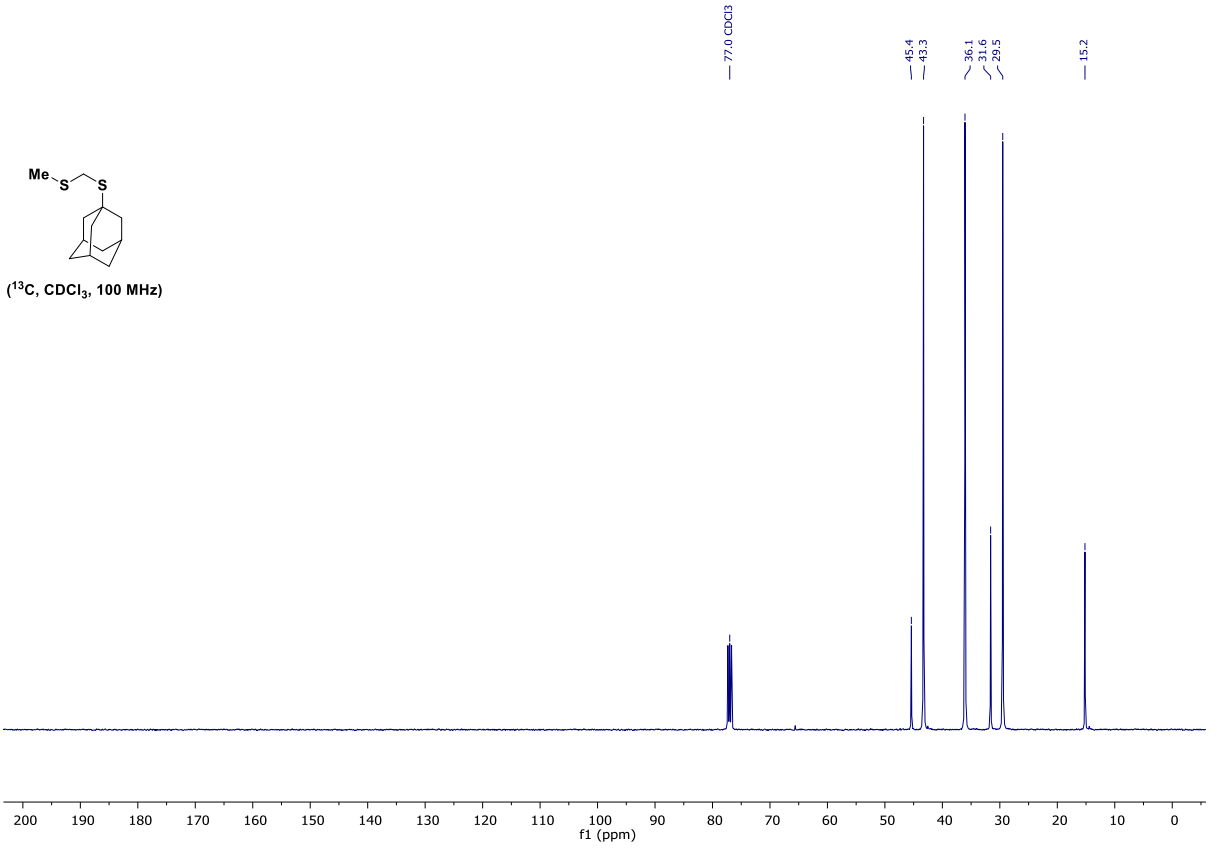




1-{[(Methylsulfanyl)methyl]sulfanyl}adamantine (29)

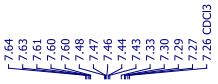


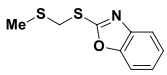
(^{1}H, $CDCl_3$, 400 MHz)



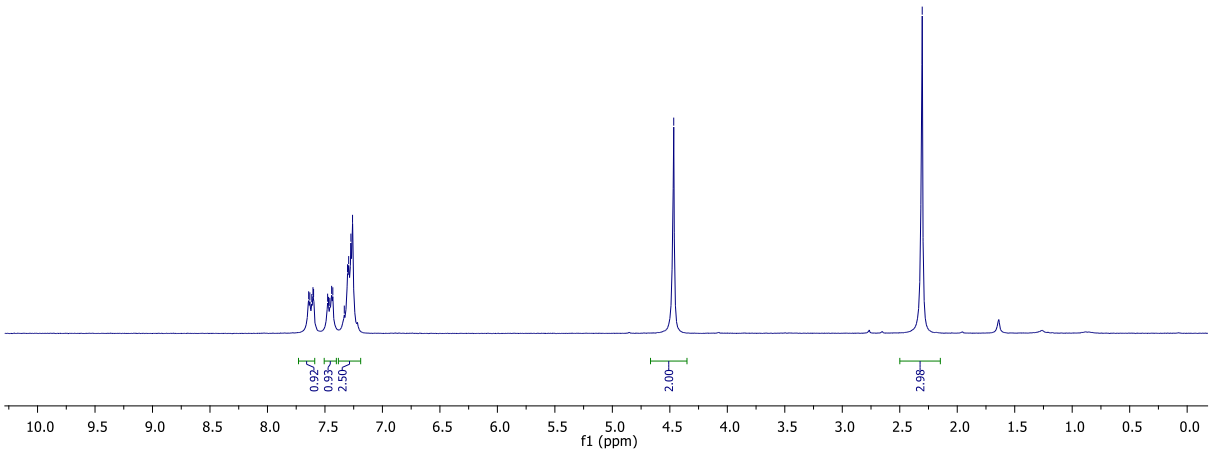
(^{13}C, $CDCl_3$, 100 MHz)

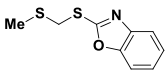
2-{[(Methylsulfanyl)methyl]sulfanyl}-1,3-benzoxazole (30)



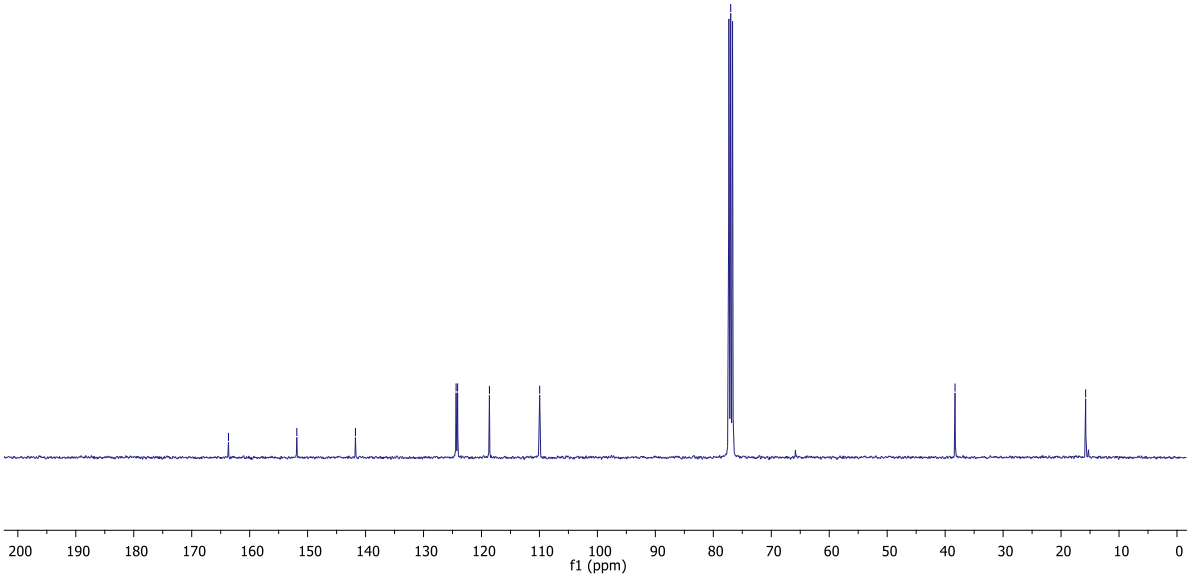


(^{1}H NMR, $CDCl_3$, 400 MHz)

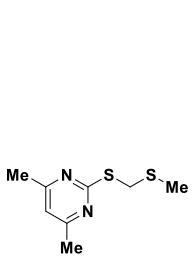




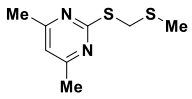
(^{13}C NMR, $CDCl_3$, 100 MHz)



4,6-Dimethyl-2-{[(methylsulfanyl)methyl]sulfanyl}pyrimidine (31)

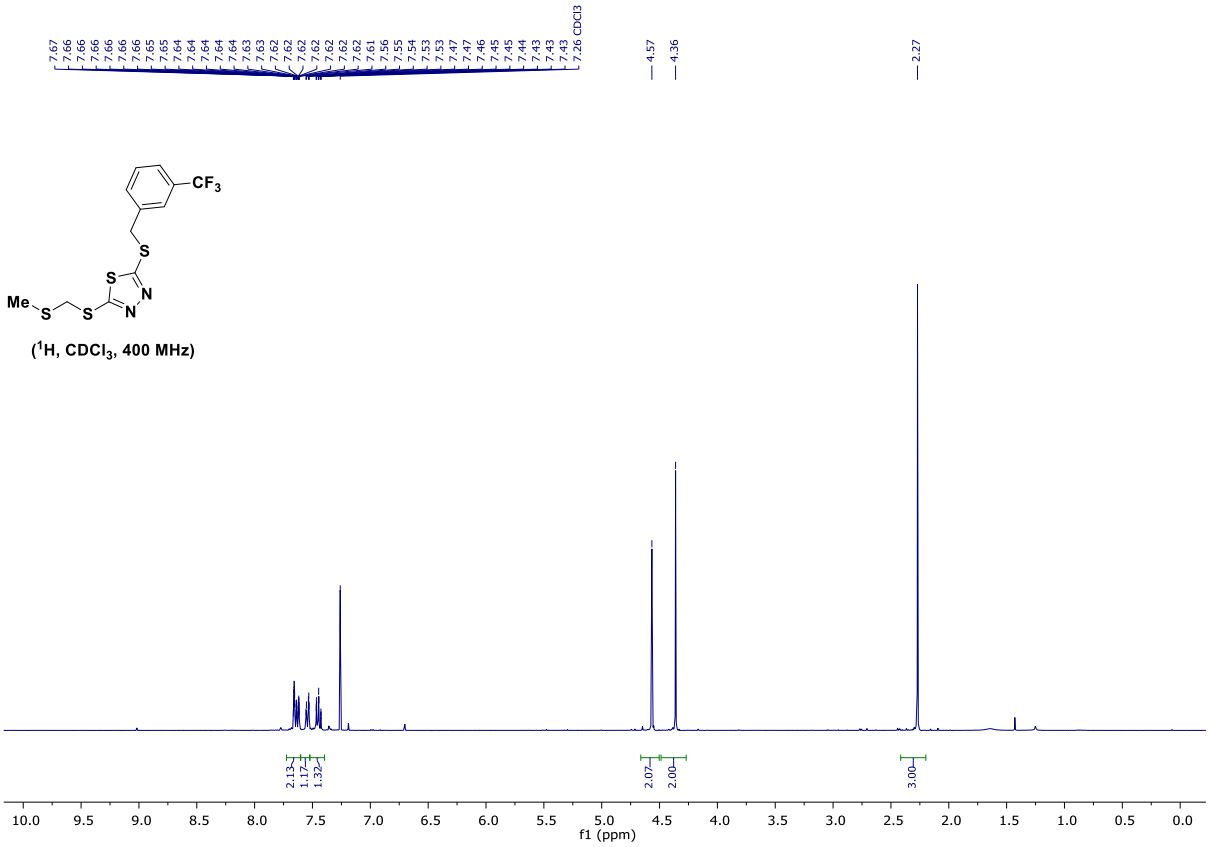


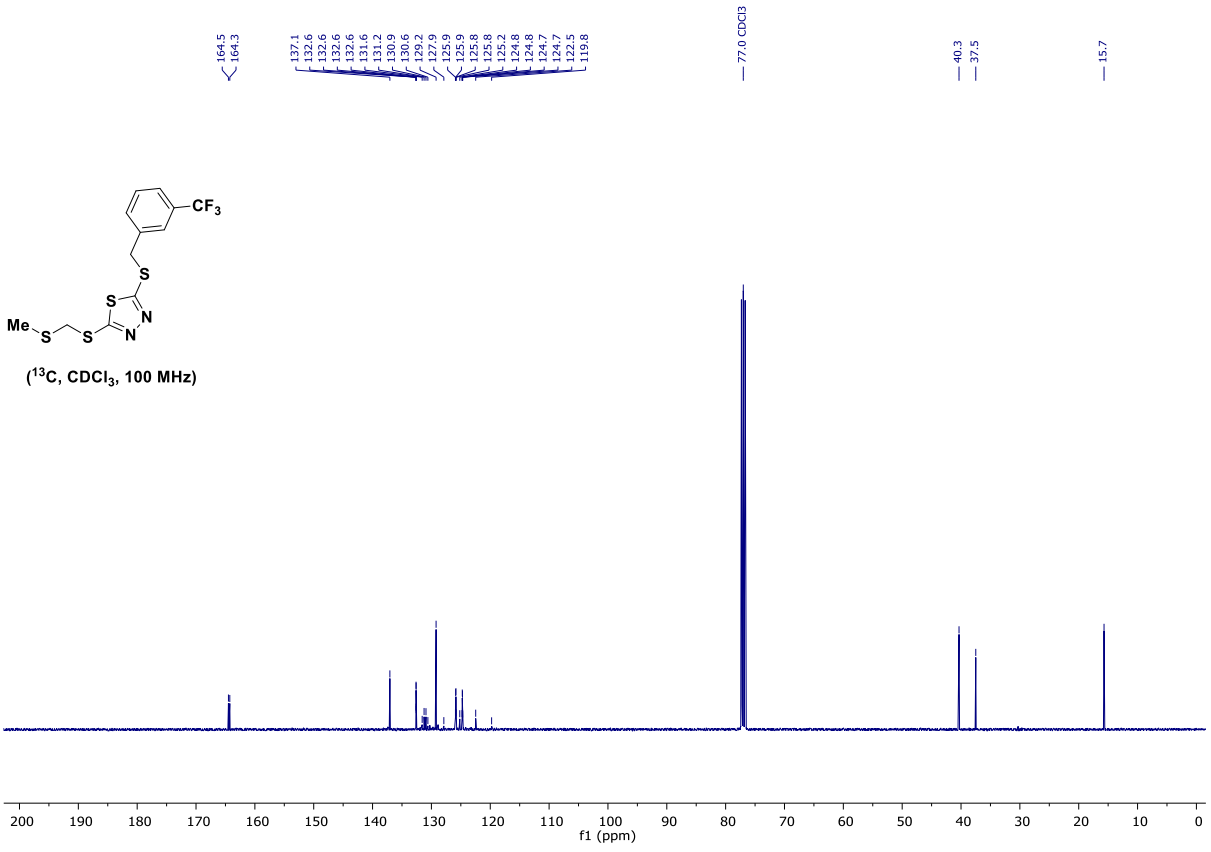
(^{1}H, $CDCl_3$, 400 MHz)



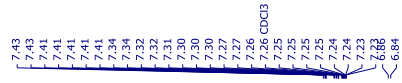
(^{13}C, $CDCl_3$, 100 MHz)

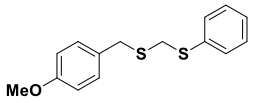
2-{[(Methylsulfanyl)methyl]sulfanyl}-5-{[3-(trifluoromethyl)benzyl]sulfanyl}-1,3,4-thiadiazole (32)



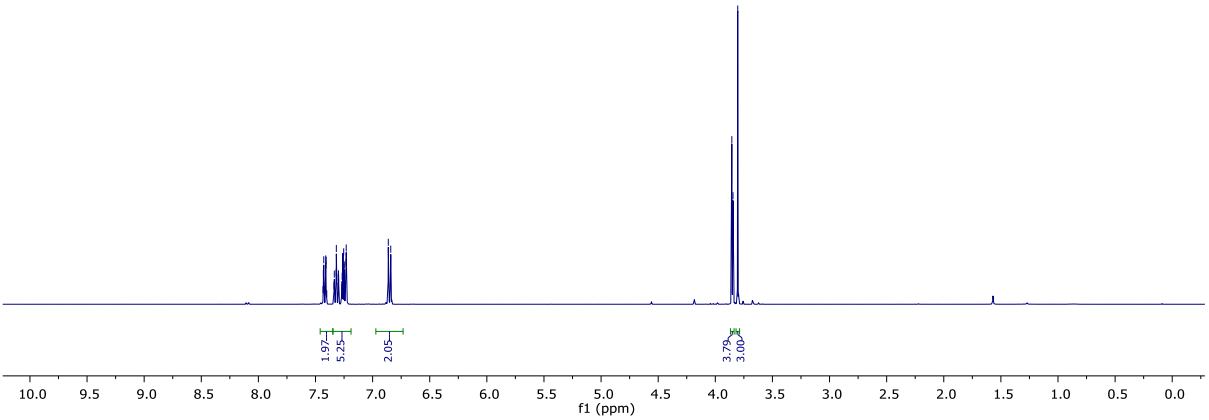


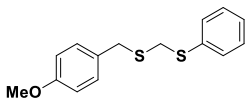
1-Methoxy-4-({[(phenylsulfanyl)methyl]sulfanyl}methyl)benzene (33)



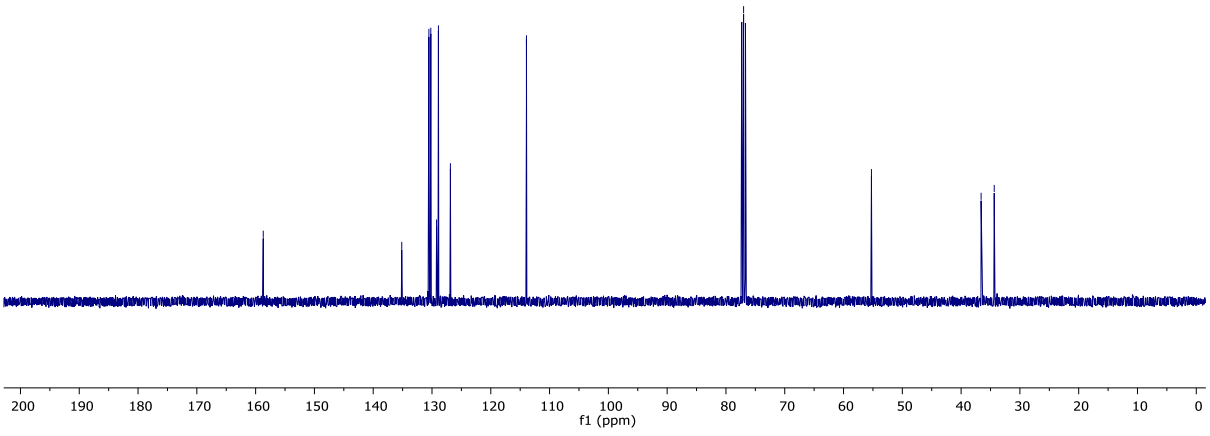


(^{1}H, $CDCl_3$, 400 MHz)

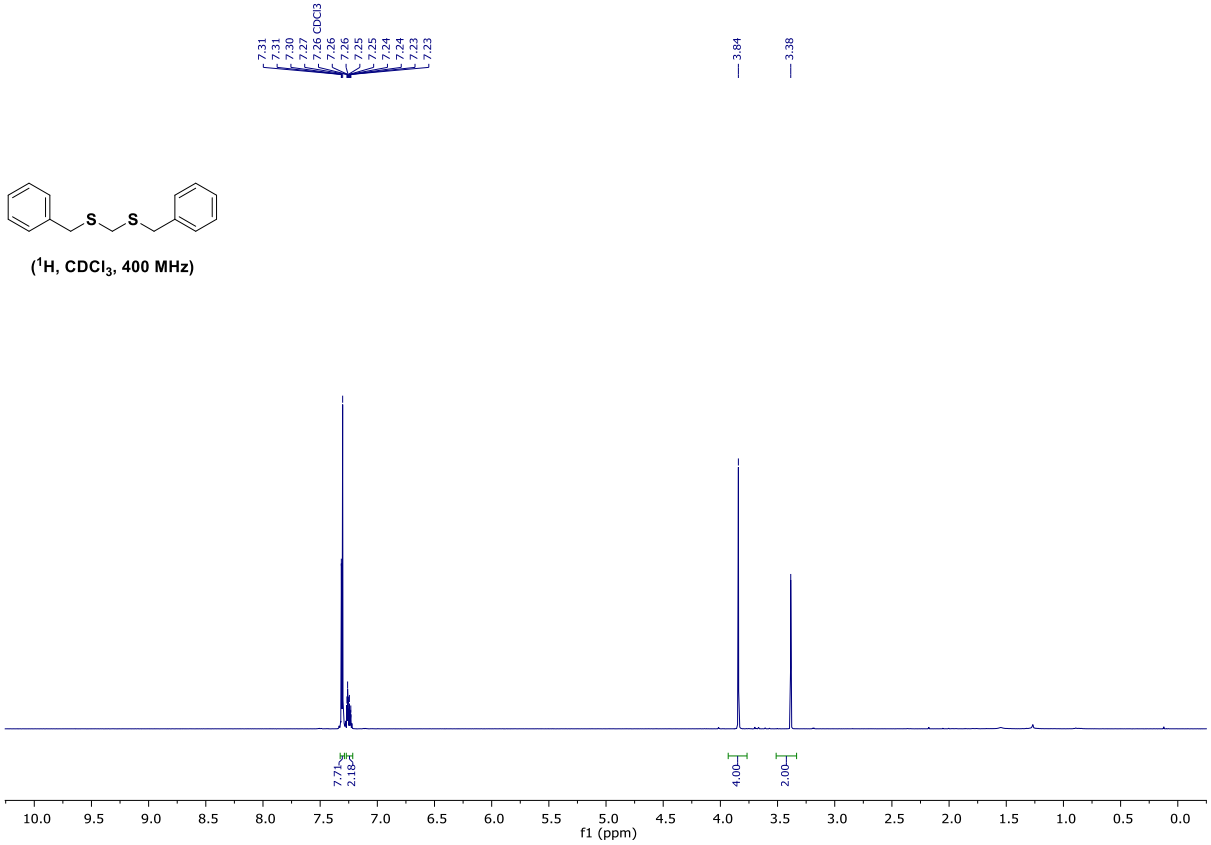




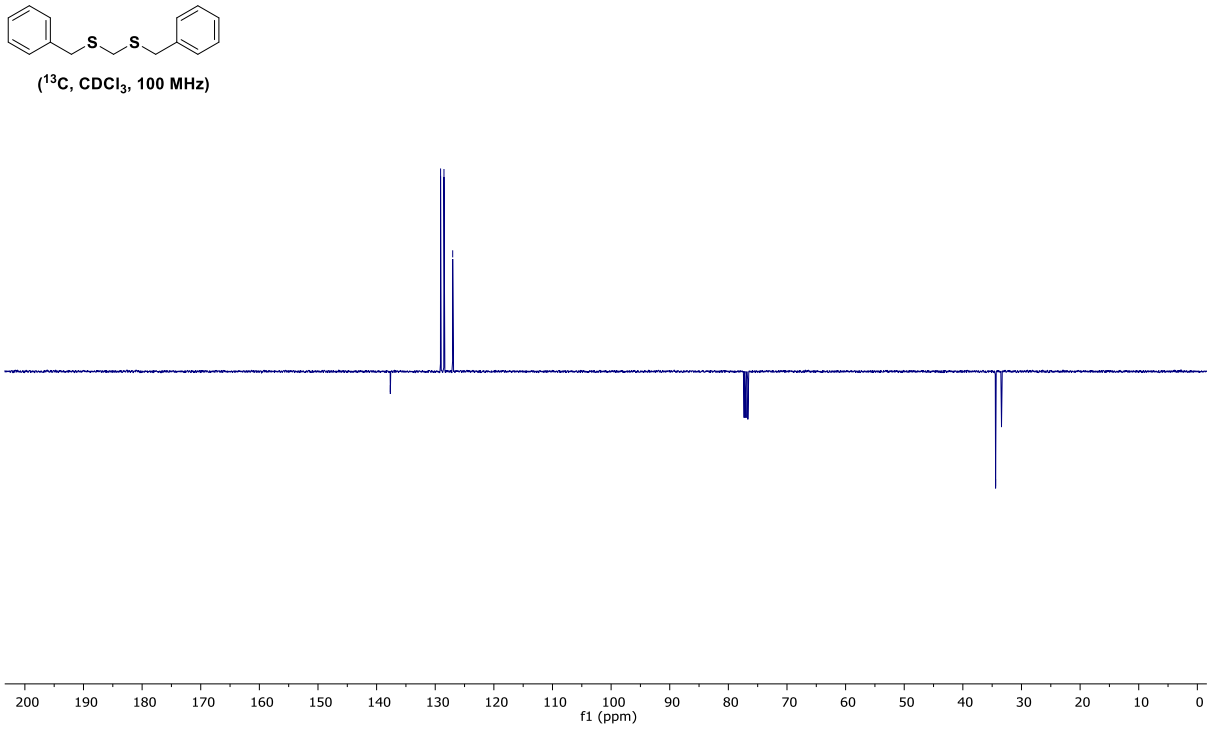
(^{13}C, $CDCl_3$, 100 MHz)



1,1’-[Methylenebis(sulfanedimethylene)]dibenzene (34)

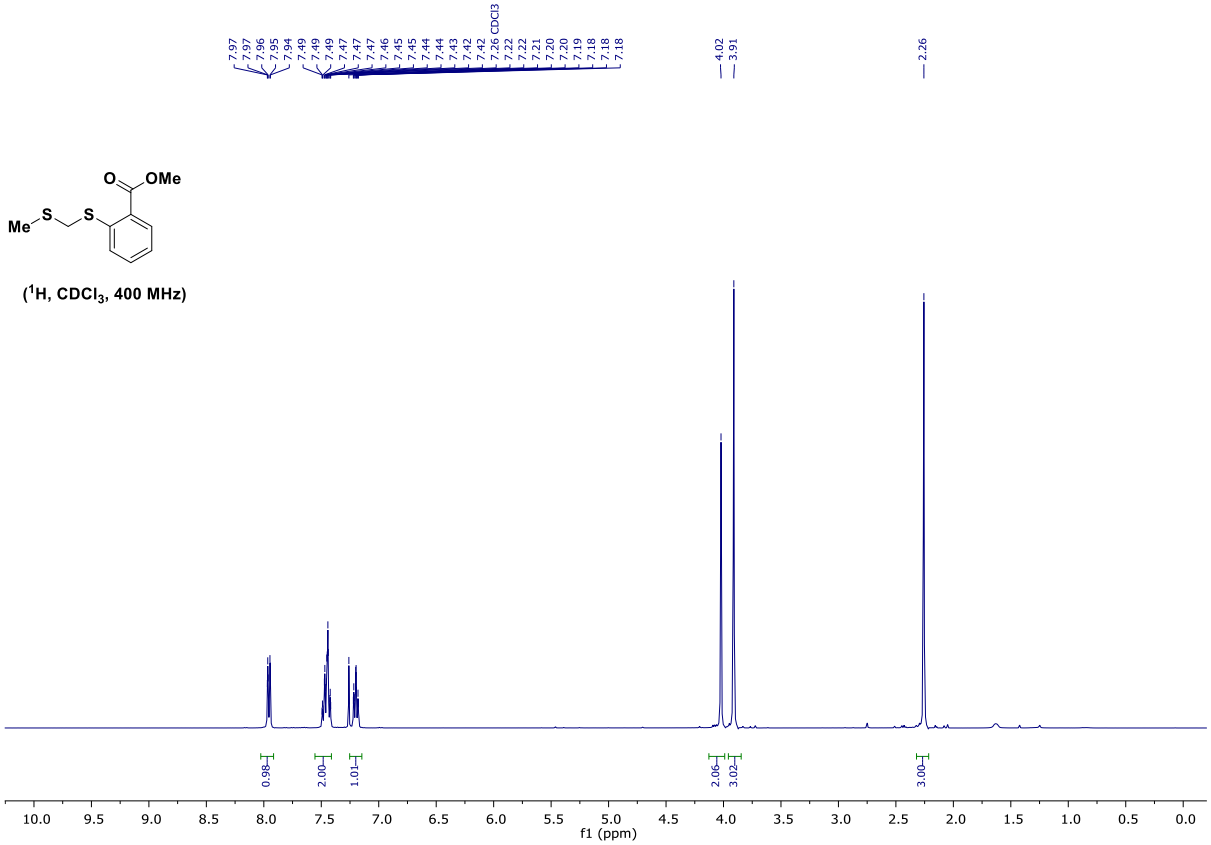


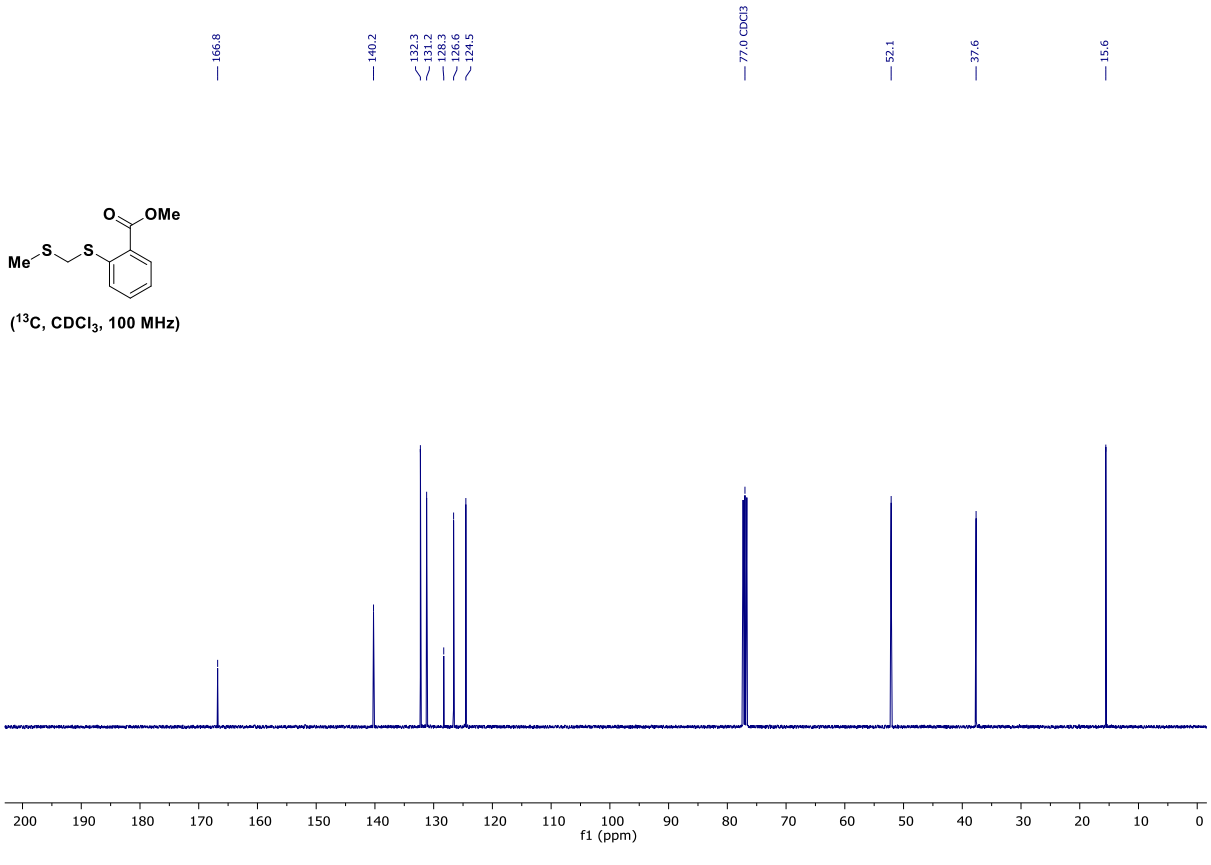
(^{1}H, $CDCl_3$, 400 MHz)



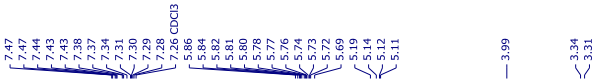
(^{13}C, $CDCl_3$, 100 MHz)

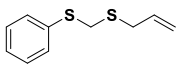
Methyl 2-{[(methylsulfanyl)methyl]sulfanyl}benzoate (35)



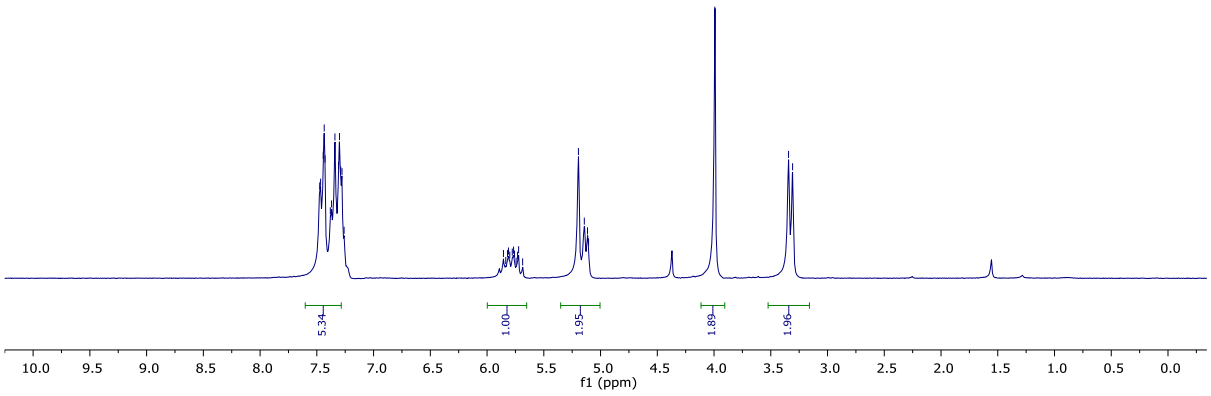


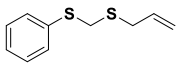
({[(Prop-2-en-1-yl)sulfanyl]methyl}sulfanyl)benzene (36)



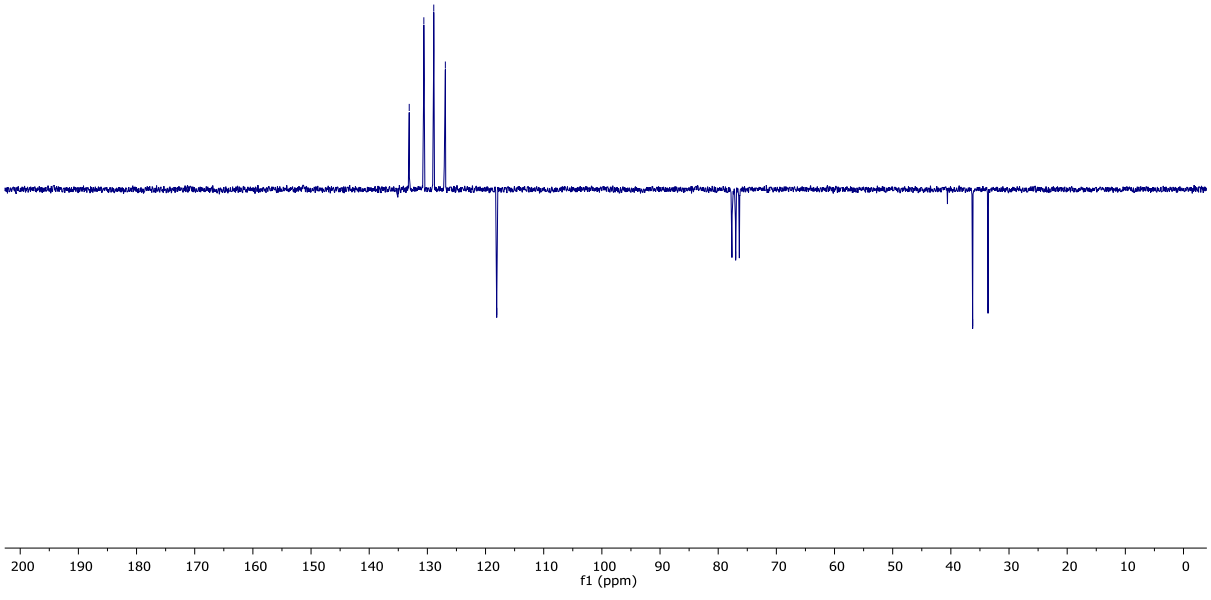


(^{1}H, $CDCl_3$, 200 MHz)

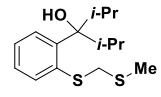




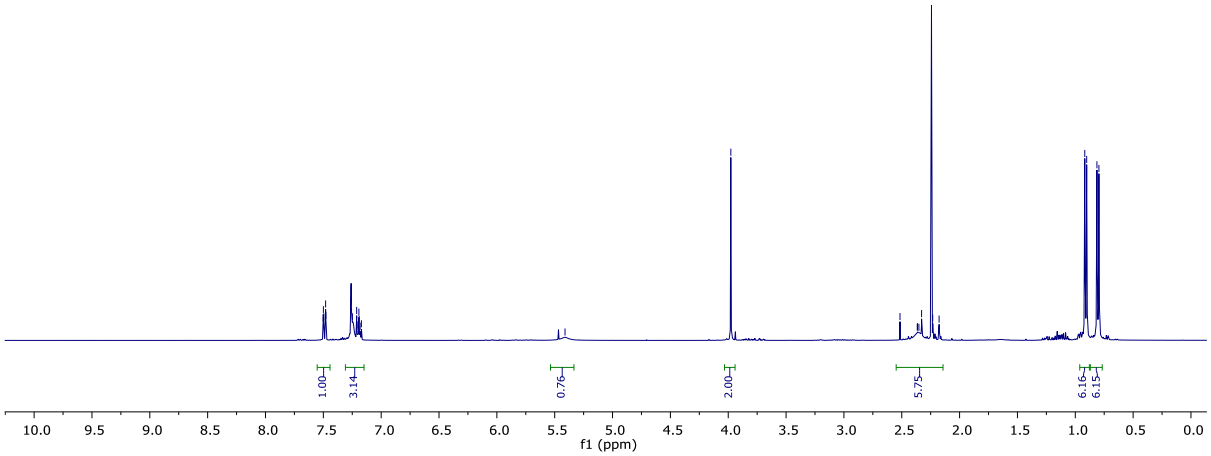
(^{13}C, $CDCl_3$, 50 MHz)

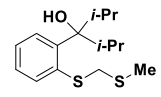


2,4-Dimethyl-3-(2-{[(methylsulfanyl)methyl]sulfanyl}phenyl)-3-pentanol (37)

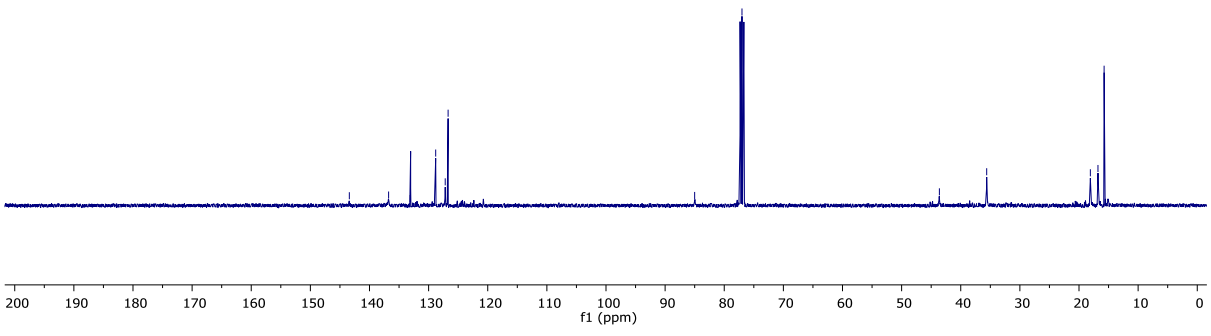


(^{1}H, $CDCl_3$, 400 MHz)

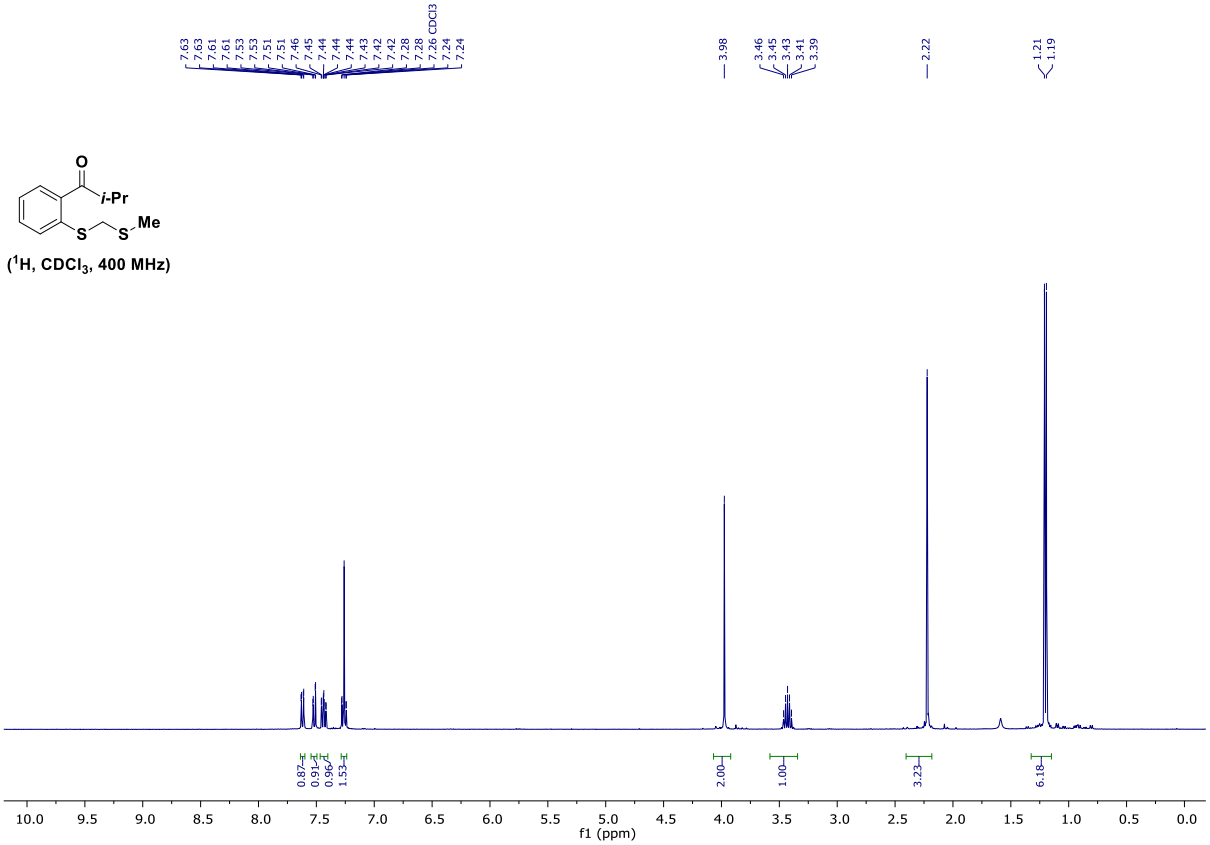


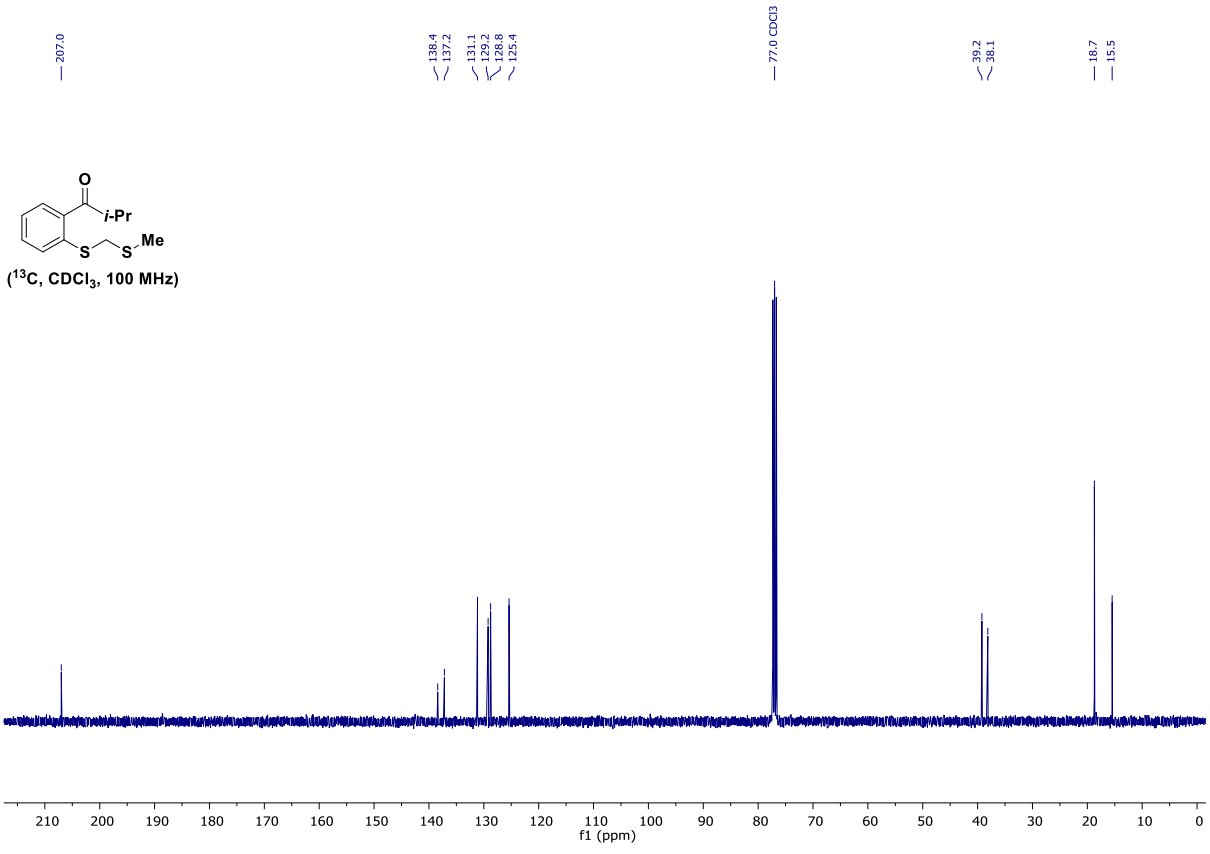


(^{13}C, $CDCl_3$, 100 MHz)



2-Methyl-1-(2-{[(methylsulfanyl)methyl]sulfanyl}phenyl)-1-propanone (38)





2-Methyl-1-(2-{[(methylsulfanyl)methyl]sulfanyl}phenyl)-1-propanol (39)