Supporting Information

Discovery of Zinc-bound Dithiolates for C(sp^3)-S Couplings of Alkyllodides: A Radical Solution to Nucleophilic Substitution

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1. General information

General procedures. Unless specifically stated, all reagents were commercially obtained and where appropriate, purified prior to use. For example, dichloromethane (DCM), acetonitrile (MeCN) was freshly distilled from CaH_2; toluene, dibutyl ether was dried and distilled from metal sodium and benzophenone. Other commercially available reagents and solvents were used directly without purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica (200 – 300 mesh). ^{1}H, ^{13}C, ^{19}F NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer in $CDCl_3$ or CD_3COCD_3. Multiplicities were given as: s (singlet); d (doublet); dd (doublets of doublet); t (triplet); q (quartet); td (triplet of doublets); m (multiplets). High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOF-spectrometer.

Reagents. The following chemicals were used as received: Acetic acid (Leybold), 2-Adamantone-5-carboxylic acid (Adamas), 4-Aminoveratrole (Energy-Chemical), Anisole (Energy-Chemical), Boron trifluoride etherate (Energy-Chemical), 1-Bromo-4-chlorobutane (Energy-Chemical), 3-Bromopropionate (leyan), 1,3-Butanediol (Energy-Chemical), 1-Bromobutane (Energy-Chemical), 1-Bromohexane (Energy-Chemical), 1-Bromopentane (Energy-Chemical), 4-Biphenylcarboxaldehyde (Energy-Chemical), Copper(II) trifluoromethanesulfonate (Adamas), Diphenyl diselenide (Adamas), Dibenzothiophene (Energy-Chemical), 4,4'-DichlorodIiphenyl disulfide (leyan), 4-Dimethylaminopyridine (Energy-Chemical), 3,5-Dimethyl-1-adamantanol (Energy-Chemical), Ethyl Fluoroboric acid (Energy-Chemical), Ferric nitrate nonahydrate (Energy-Chemical), 3-Hydroxyadamantane-1-carboxylic acid (Adamas), Imidazole (Adamas), Imidazole (Adamas), Iodine (Energy-Chemical), Lithium iodide (Energy-Chemical), *m*-Anisidine (Energy-Chemical), 4-Methylpentan-1-ol (Energy-Chemical), Methanesulfonic acid (Adamas), 4-Methoxybenzenethiol (Energy-Chemical), Sodium

nitrite (Hushi), *N*-bromosuccinimide (Adamas), *N*,*N*'-dicyclohexylcarbodiimide (Energy-Chemical), *N*-hydroxyphthalimide (Energy-Chemical), *N*,*N*,*N*',*N*'-Tetramethylethylenediamine (Energy-Chemical), *N*-(tert-Butoxycarbonyl)-L-cysteine methyl ester (leyan), *o*-Anisidine (Energy-Chemical), Phenyl disulfide (leyan), Propyl disulfide (Adamas), *p*-Toluenesulfonyl chloride (Energy-Chemical), *p*-Tolyl disulfide (leyan), Sodium bromide (leyan), Sodium hydroxide (Hushi), Sodium iodide (leyan), Silver trifluoromethanesulfonate (Energy-Chemical), *tert*-Butyl nitrite (Energy-Chemical), Thianthrene (Energy-Chemical), 2-Thiophenecarbonyl chloride (Energy-Chemical), Triphenylphosphin (Energy-Chemical), 2,4,6-Trimethylaniline (Energy-Chemical), Trifluoroacetic anhydride (Energy-Chemical), Triethylamine (HUSHI), Triphenylphosphine (Energy-Chemical).

2. Synthesis of the starting materials

2.1. Synthesis of diazodium salts 4a, 4b, 4c, 4d:

The diazodium salts **4a**, **4b**, **4**c, **4d** were synthesized according to our previous report[1].

2.2. Synthesis of diaryliodonium salt 4k:

The diaryliodonium salt **4k** was synthesized according to our previous report[2].

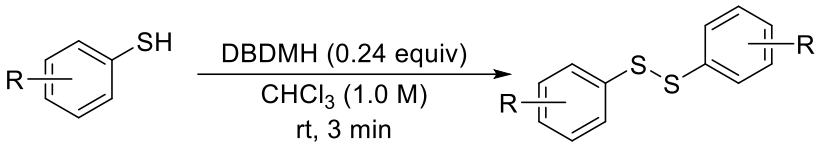
2.3. Synthesis of alkyl iodides 3a-3c, 3e, 3g-3m, 3o-3t, 3v-3z, 3af-3ai, 3ap-3at:

The alkyl iodides **3a-3c**, **3e**, **3g-3m**, **3o-3t**, **3v-3z**, **3af-3ai**, **3ap-3at** were synthesized according to our previous report[1].

2.4. Synthesis of alkyl iodides 3aa-3ae:

The alkyl iodides **3aa-3ae** were synthesized according to our previous report[3].

2.5. Synthesis of disulfides 1c, 1e-1h, 1j-1l:



General Method A: A oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with benzenethiol (20.0 mmol, 1.0 equiv) and DBDMH (1.37 g, 4.8 mmol, 0.24 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then $CHCl_3$ (20.0 mL) was added under N_2 and the mixture was allowed to stir for 3 min at room temperature. The mixture was diluted with saturated NaCl aqueous solution (50.0 mL) and ethyl acetate (30.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (30.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (50.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 500:1 to 250:1 petroleum ether: ethyl acetate) to provide the desired product.

Compound **1c**: a yellow oil (2.30 g, 9.1 mmol, 91% yield), Spectra were consistent with the literature data[4].

Compound **1e**: a white solid (3.18 g, 8.5 mmol, 85% yield), Spectra were consistent with the literature data[4].

Compound **1f**: a white solid (2.44 g, 7.4 mmol, 69% yield, 17.7 mmol was used), Spectra were consistent with the literature data[4].

Compound **1g**: a orange solid (0.965 g, 3.9 mmol, 39% yield), Spectra were consistent with the literature data[4].

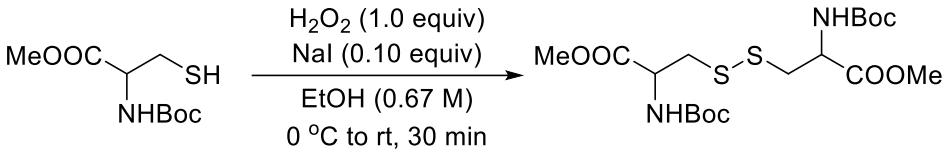
Compound **1h**: a yellow oil (1.62 g, 5.8 mmol, 58% yield), Spectra were consistent with the literature data[4].

Compound **1j**: a yellow oil (2.38 g, 8.7 mmol, 87% yield), Spectra were consistent with the literature data[4].

Compound **1k**: a yellow solid (2.24 g, 9.1 mmol, 91% yield), Spectra were consistent with the literature data[4].

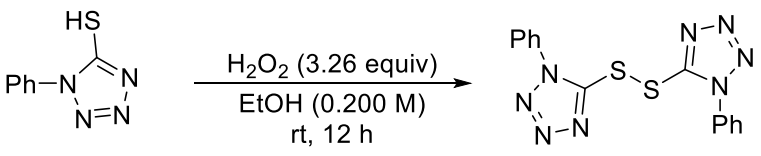
Compound **1l**: a yellow solid (1.22 g, 5.3 mmol, 53% yield), Spectra were consistent with the literature data[4].

2.6. Synthesis of disulfides 1o:



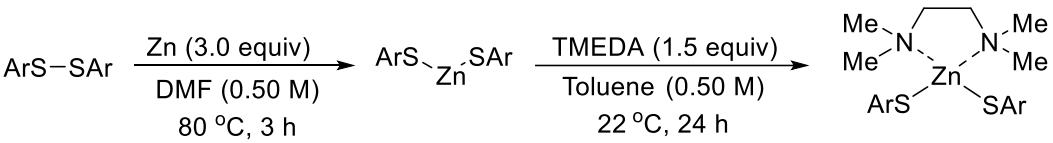
A oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with methyl (*tert*-butoxycarbonyl)cysteinate (4.69 g, 20.0 mmol, 1.0 equiv) and EtOH (30.0 mL), The mixture was cooled at 0 °C and NaI (299.8 mg, 2.0 mmol, 0.100 equiv), 30% H_2O_2 (299.8 mg, 2.3 mL, 1.0 equiv) were added to the mixture. Then, saturated aqueous $Na_2S_2O_3$ (60.0 mL) was added, and the resulting mixture was extracted with EtOAc (15 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (50.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation. The product **1o** was isolated as a white solid (4.68 g, 10.0 mmol, 100% yield). The spectral data match those previously reported[5].

2.7. Synthesis of disulfides 1m:

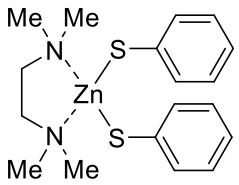


A oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with methyl 1-phenyl-1*H*-tetrazole-5-thiol (3.56 g, 20.0 mmol, 1.0 equiv) and EtOH (100.0 mL), The mixture was evacuated and backfilled with N_2 for three times. 30% H_2O_2 (299.8 mg, 2.3 mL, 1.00 equiv) was added to the mixture. The reaction was cooled to 0 °C, and the white precipitate was collected via filtration with washing by cold diethyl ether. The disulfide was purified via recrystallization form a $CHCl_3$/EtOH mixture. The pure product **1m** was filtered and obtained as a crystalline white-yellow solid (1.73 g, 4.9 mmol, 49% yield). The spectral data match those previously reported[6].

2.8. Synthesis of zinc thiolates 2a-2o:

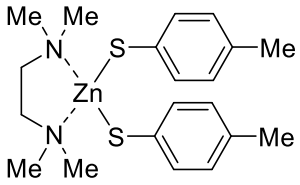


General Method B: A oven-dried 50-mL glass schlenck, equipped with a stirring bar, was charged with disulfides (5.0 mmol, 1.0 equiv) and Zn (0.98 g, 15.0 mmol, 3.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (10.0 mL) was added under N_2 and the mixture was allowed to stir for 3 h at 80 °C. The mixture was filtered through a celite pad and the organic layers were separated. The solvent was removed by vacuum. The mixture was evacuated and backfilled with nitrogen for three times. Then dry toluene (10.0 mL) and TMEDA (0.87 g, 7.5 mmol, 1.5 equiv) was added under N_2 and the mixture was allowed to stir for 24 h at room temperature. The solvent was removed by rotary evaporation to provide the desired product.

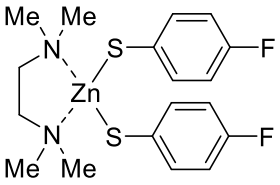


***N*^{1},*N*^{1},*N*^{2},*N*^{2}-tetramethylethane-1,2diamine • bis(phenylthio)zinc 2a**: Prepared according to **General Method B** and the title compound was isolated as a white solid

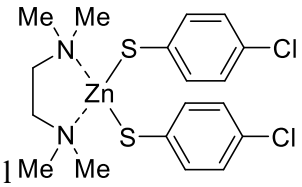
(3.09 g, 8.8 mmol, 88% yield). **M.p.** = 142.1 °C – 142.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (4H, d, J =7.3 Hz), 6.92 (2H, dd, J = 7.6, 7.6 Hz), 6.92 (2H, dd, J = 7.4, 7.4 Hz), 2.68 (4H, s), 2.50 (12H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.5, 132.7, 128.3, 123.0, 57.2, 47.6; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{18}H_{26}N_2NaS_2Zn$: 421.0721, found: 421.0712.



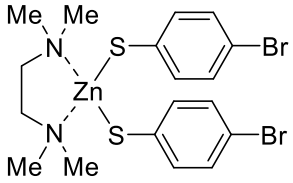
***N*^{1},*N*^{1},*N*^{2},*N*^{2}-tetramethylethane-1,2diamine • bis(*p*-tolylthio)zinc 2b**: Prepared according to **General Method H** and the title compound was isolated as a white solid (1.46 g, 3.4 mmol, 68% yield). **M.p.** = 146.3 °C – 147.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (4H, d, J = 8.1 Hz), 6.83 (4H, d, J = 7.9 Hz), 2.65 (4H, s), 2.48 (12H, s), 2.20 (6H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.4, 132.6, 132.3, 129.1, 57.2, 47.6, 20.9; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{20}H_{30}N_2NaS_2Zn$: 449.1034, found: 449.1030.



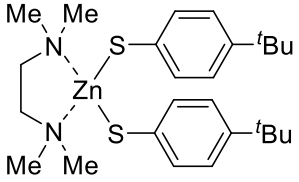
***N*^{1},*N*^{1},*N*^{2},*N*^{2}-tetramethylethane-1,2diamine • bis((4-fluorophenyl)thio)zinc 2c**: Prepared according to **General Method B** and the title compound was isolated as a white solid (1.81 g, 4.2 mmol, 83% yield). **M.p.** = 130.1 °C – 131.1 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (4H, dd, J = 8.6, 5.5 Hz), 6.71 (4H, dd, J = 8.8, 8.8 Hz), 2.68 (4H, s), 2.50 (12H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.2 (d, $J_{C\text{-}F}$ = 242.2 Hz), 135.0 (d, $J_{C\text{-}F}$ = 3.1 Hz), 133.8 (d, $J_{C\text{-}F}$ = 7.4 Hz), 115.1 (d, $J_{C\text{-}F}$ = 21.4 Hz), 57.2, 47.7; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –121.4 – –121.5 (2F, m). **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{18}H_{24}F_2N_2NaS_2Zn$: 457.0533, found: 457.0522.



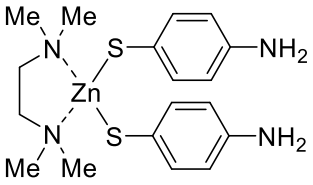
***N*^{1},*N*^{1},*N*^{2},*N*^{2}-tetramethylethane-1,2diamine • bis((4-chlorophenyl)thio)zinc 2d**: Prepared according to **General Method B** and the title compound was isolated as a white solid (2.12 g, 4.5 mmol, 90% yield). **M.p.** = 120.1 °C – 120.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (4H, d, *J* = 8.5 Hz), 6.95 (4H, d, *J* = 8.5 Hz), 2.65 (4H, s), 2.48 (12H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.1, 133.8, 128.8, 128.2, 57.2, 47.6; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{18}H_{24}Cl_2N_2NaS_2Zn$: 488.9942, found: 488.9936.



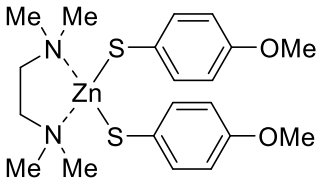
***N*^{1},*N*^{1},*N*^{2},*N*^{2}-tetramethylethane-1,2diamine • bis((4-bromophenyl)thio)zinc 2e**: Prepared according to **General Method B** and the title compound was isolated as a white solid (2.55 g, 4.6 mmol, 91% yield). **M.p.** = 81.5 °C – 82.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (4H, d, *J* = 8.0 Hz), 7.09 (4H, d, *J* = 8.2 Hz), 2.66 (4H, s), 2.48 (12H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.8, 134.3, 131.1, 116.6, 57.2, 47.7; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{18}H_{24}Br_2N_2NaS_2Zn$: 576.8931, found: 576.8929.



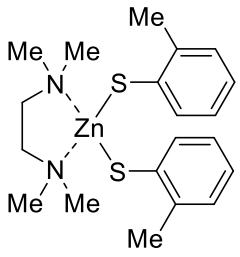
***N*^{1},*N*^{1},*N*^{2},*N*^{2}-tetramethylethane-1,2diamine • bis((4-(*tert*-butyl)phenyl)thio)zinc 2f**: Prepared according to **General Method B** and the title compound was isolated as a white solid (2.03 g, 4.0 mmol, 79% yield). **M.p.** = 155.9 °C – 156.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (4H, d, *J* = 8.4 Hz), 7.04 (4H, d, *J* = 8.4 Hz), 2.67 (4H, s), 2.50 (12H, s), 1.23 (18H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.7, 136.5, 132.3, 125.3, 57.3, 47.6, 34.2, 31.5; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{26}H_{42}N_2NaS_2Zn$: 533.1973, found: 533.1961.



***N*^{1},*N*^{1},*N*^{2},*N*^{2}-tetramethylethane-1,2diamine • bis((4-aminophenyl)thio)zinc 2g**: Prepared according to **General Method B** and the title compound was isolated as a yellow solid (0.893 g, 2.1 mmol, 57% yield, 3.67 mmol was used). **M.p.** = 210.8 °C – 211.4 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (4H, d, J = 8.4 Hz), 6.46 (4H, d, J = 8.5 Hz), 3.41 (4H, s), 2.66 (4H, s), 2.48 (12H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.3, 129.2, 127.5, 123.0, 57.2, 47.6; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{18}H_{28}N_4NaS_2Zn$: 451.0939, found: 451.0932.

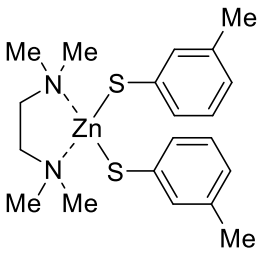


***N*^{1},*N*^{1},*N*^{2},*N*^{2}-tetramethylethane-1,2diamine • bis((4-methoxyphenyl)thio)zinc 2h**: Prepared according to **General Method B** and the title compound was isolated as a white solid (1.52 g, 3.3 mmol, 66% yield). **M.p.** = 118.2 °C – 118.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (4H, d, J = 8.7 Hz), 6.59 (4H, d, J = 8.7 Hz), 3.68 (6H, s), 2.62 (4H, s), 2.45 (12H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.2, 133.6, 130.6, 114.0, 57.1, 55.3, 47.5; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{20}H_{30}N_2NaO_2S_2Zn$: 481.0932, found: 481.0913.

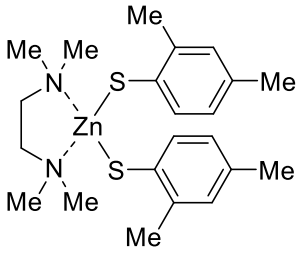


***N*^{1},*N*^{1},*N*^{2},*N*^{2}-tetramethylethane-1,2diamine • bis(*o*-tolylthio)zinc 2i**: Prepared according to **General Method B** and the title compound was isolated as a white solid (1.66 g, 3.9 mmol, 78% yield). **M.p.** = 166.3 °C – 166.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (2H, dd, J = 7.3, 1.7 Hz), 7.03 (2H, dd, J = 7.1, 1.9 Hz), 6.86 – 6.79

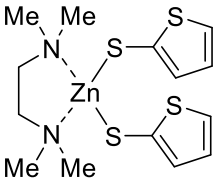
(4H, m), 2.66 (4H, s), 2.49 (12H, s), 2.43 (6H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.3, 139.2, 133.9, 129.5, 125.8, 123.2, 57.3, 47.6, 22.6; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{20}H_{30}N_2NaS_2Zn$: 449.1034, found: 449.1022.



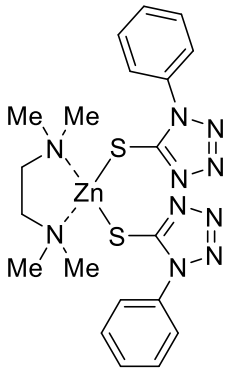
***N*^{1},*N*^{1},*N*^{2},*N*^{2}-tetramethylethane-1,2diamine • bis(*m*-tolylthio)zinc 2j**: Prepared according to **General Method B** and the title compound was isolated as a white solid (1.72 g, 4. mmol, 81% yield). **M.p.** = 154.9 ^{o}C – 155.6 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (4H, d, J = 8.9 Hz), 6.91 (2H, dd, J = 7.5, 7.5 Hz), 6.72 (2H, d, J = 7.5 Hz), 2.68 (4H, s), 2.51 (12H, s), 2.14 (6H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.0, 137.7, 133.6, 129.7, 128.1, 123.9, 57.3, 47.7, 21.3; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{20}H_{30}N_2NaS_2Zn$: 449.1034, found: 449.1020.



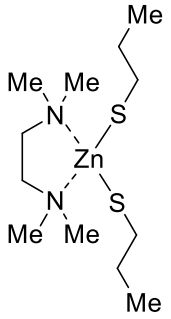
***N*^{1},*N*^{1},*N*^{2},*N*^{2}-tetramethylethane-1,2diamine • bis((2,4-dimethylphenyl)thio)zinc 2k**: Prepared according to **General Method B** and the title compound was isolated as a white solid (1.70 g, 3.7 mmol, 74% yield). **M.p.** = 178.6 ^{o}C – 178.9 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (2H, d, J = 7.8 Hz), 6.85 (2H, s), 6.62 (2H, d, J = 7.8 Hz), 2.64 (4H, s), 2.48 (12H, s), 2.39 (6H, s), 2.18 (6H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.9, 136.3, 133.8, 132.5, 130.5, 126.5, 57.3, 47.6, 22.6, 20.8; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{22}H_{34}N_2NaS_2Zn$: 477.1347, found: 477.1337.



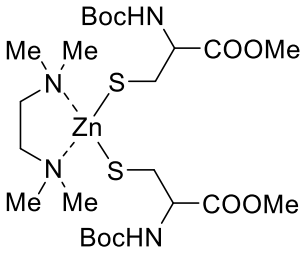
***N*^{1},*N*^{1},*N*^{2},*N*^{2}-tetramethylethane-1,2diamine • bis(thiophen-2-ylthio)zinc 2l:** Prepared according to **General Method B** and the title compound was isolated as a white solid (1.56 g, 3.8 mmol, 76% yield). **M.p.** = 102.9 °C – 103.4 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.89 – 6.85 (4H, m), 6.75 (2H, dd, J = 5.4, 3.4 Hz), 2.67 (4H, s), 2.51 (12H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.1, 132.5, 126.9, 114.9, 56.1, 46.5; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{14}H_{22}N_2NaS_4Zn$: 432.9849, found: 432.9835.



***N*^{1},*N*^{1},*N*^{2},*N*^{2}-tetramethylethane-1,2diamine • bis((1-phenyl-1*H*-tetrazol-5-yl)thio)zinc 2m**: Prepared according to **General Method B** and the title compound was isolated as a white solid (5.04 g, 7.8 mmol, 78% yield, 10.0 mmol was used). **M.p.** = 145.9 °C – 146.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (4H, d, J = 7.9 Hz), 7.52 – 7.48 (4H, m), 7.45 – 7.41 (2H, m), 3.05 (4H, s), 2.80 (12H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.4, 135.3, 129.2, 129.0, 124.1, 57.4, 47.6; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{20}H_{27}N_{10}S_2Zn$: 535.1148, found: 535.1135.

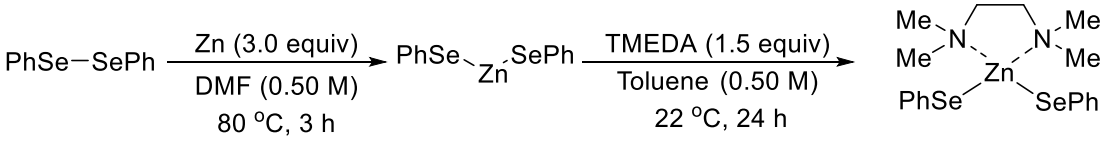


***N*^{1},*N*^{1},*N*^{2},*N*^{2}-tetramethylethane-1,2diamine • bis(propylthio)zinc 2n:** Prepared according to **General Method B** and the title compound was isolated as a white solid (1.46 g, 4.2 mmol, 84% yield). **M.p.** = 280.6 °C – 280.8 °C; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{12}H_{31}N_2S_2Zn$: 331.1215, found: 331.1224.



• ***N*^{1},*N*^{1},*N*^{2},*N*^{2}-tetramethylethane-1,2diamine bis((2-((*tert*-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)thio)zinc 2o**: Prepared according to **General Method B** and the title compound was isolated as a colorless oil (5.04 g, 7.8 mmol, 78% yield, 10.0 mmol was used). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.74 (2H, d, J = 8.3 Hz), 4.45 (2H, dt, J = 8.8, 4.6 Hz), 3.74 (6H, s), 3.07 (2H, dd, J = 12.8, 4.6 Hz), 3.07 (2H, dd, J = 12.8, 4.6 Hz), 2.60 (4H, s), 2.51 (12H, s), 1.42 (18H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.4, 155.7, 79.6, 57.0, 55.7, 52.3, 47.6, 28.5, 28.2; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{24}H_{49}N_4O_8S_2Zn$: 649.2278, found: 649.2278.

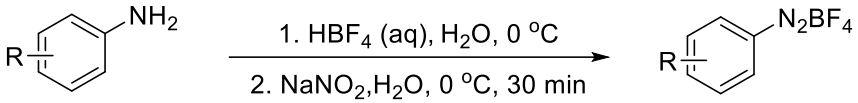
2.9. Synthesis of zinc selenole 2p:



A oven-dried 50-mL glass schlenck, equipped with a stirring bar, was charged with 1,2-diphenyldiselane (1.56 g, 5.0 mmol, 1.0 equiv) and Zn (0.98 g, 15.0 mmol, 3.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (10.0 mL) was added under N_2 and the mixture was allowed to stir for 3 h at 80 °C. The mixture was filtered through a celite pad and the organic layers were separated. The solvent was removed by vacuum. The mixture was evacuated and backfilled with nitrogen for three times. Then dry toluene (10.0 mL) and TMEDA (0.87 g, 7.5 mmol, 1.5 equiv) was added under N_2 and the mixture was allowed to stir for 24 h at room temperature. The solvent was removed by rotary evaporation to provide the desired product **3k** as a white solid (1.92 g, 3.9 mmol, 78% yield).

***N*^{1},*N*^{1},*N*^{2},*N*^{2}-tetramethylethane-1,2diamine • bis(phenylselanyl)zinc 3k: M.p.** = 107.6 °C – 108.4 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (4H, dd, J = 7.3, 2.2 Hz), 7.01 – 6.99 (4H, m), 2.67 (4H, s), 2.48 (12H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.5, 130.9, 128.4, 124.1, 57.2, 48.0; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{19}H_{30}N_2Se_2Zn$: 498.0144, found: 498.0128.

2.10. Synthesis of diazodium salts 4e, 4g:

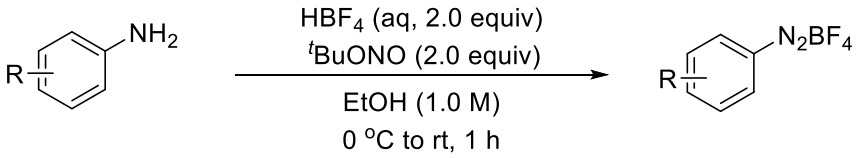


General Method C: A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, the aniline (20.0 mmol, 1.0 equiv) was dissolved of H_2O (7.5 mL) and an aqueous solution of HBF_4 (11.0 g, 48.0 wt%, 3.0 equiv). The mixture was cooled at 0 °C with an ice bath and a solution of $NaNO_2$ (1.52 g, 1.1 equiv, in 3.0 mL H_2O) was added dropwise. The reaction was stirred at 0 °C for 30 min. The diazodium salt was precipitated by the addition of the ice-cooled Et_2O (40.0 mL), and washed with small amounts of cooled the Et_2O wascrude product, and dissolved in the minimal amount of acetone. The arene diazonium tetrafluoroborate was the precipitated by the slow addition of Et_2O.

Compound **4e**: a white solid (3.39 g, 15.3 mmol, 76% yield). The spectral data match those previously reported[7].

Compound **4g**: a white solid (3.76 g, 14.9 mmol, 75% yield). The spectral data match those previously reported[8].

2.11. Synthesis of diazodium salts 4f, 4h:



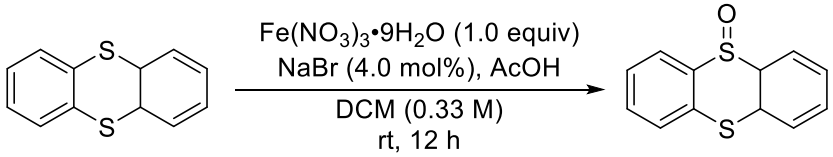
General Method D: A 120 °C oven-dried 100-mL glass, equipped with a stir bar, the

aniline (20.0 mmol, 1.0 equiv) was dissolved in a mixture of absolute EtOH (6.0 mL) and an aqueous solution of HBF_4 (7.32 g, 48.0 wt%, 2.0 equiv). The mixture was cooled at 0 °C with an ice bath and ^{t}BuONO (4.12 g, 2.0 equiv) was added dropwise. Was allowed to warm to room temperature and mixture was stirred at room temperature for 1 h, the arene diazonium tetrafluoroborate was precipitated by the addition of the ice-cooled Et_2O (40.0 mL), and washed with small amounts of cooled the Et_2O wascrude product, and dissolved in the minimal amount of acetone. The diazodium salt was the precipitated by the slow addition of Et_2O.

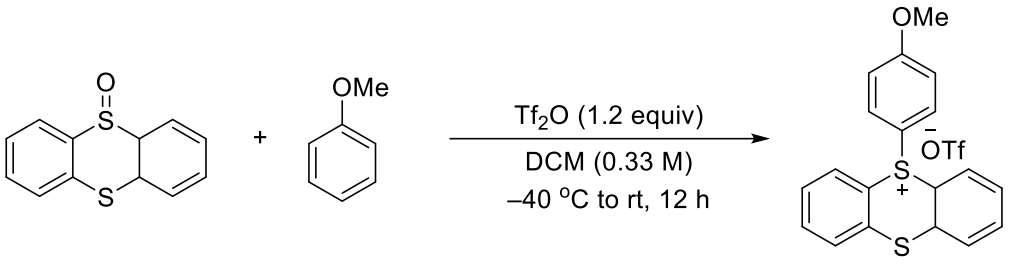
Compound **4f**: a white solid (2.52 g, 11.4 mmol, 57% yield). The spectral data match those previously reported[9].

Compound **4h**: a white solid (3.47 g, 14.8 mmol, 71% yield). The spectral data match those previously reported[8].

2.12. Synthesis of sulfonium salt 4i:

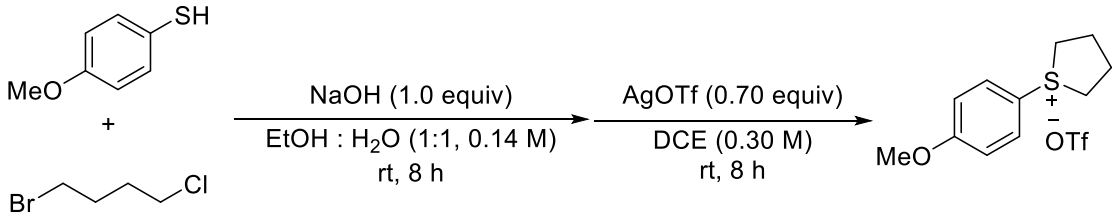


A 120 °C oven-dried 100-mL glass, equipped with a stir bar, was charged with thianthrene (2.16 g, 10.0 mmol, 1.0 equiv), $Fe(NO_3)_3 \cdot 9H_2O$ (4.04 g, 10.0 mmol, 1.0 equiv) and NaBr (41.2 mg, 0.40 mmol, 4.0 mol%). The mixture was evacuated and backfilled with N_2 for three times. Then dry DCM (30.0 mL) and AcOH (0.50 mL) were added under N_2. Stirring was continued at room temperature for 12 h. After that, the reaction was dilute with DCM, and then washed with water. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum, the product was isolated as a white solid (2.25g, 9.7 mmol, 97% yield). The spectral data match those previously reported[10].



A 120 °C oven-dried 100-mL glass, equipped with a stir bar, was charged with thianthrenium-S-oxide (TTO) (0.77 g, 3.3 mmol, 1.1 equiv), anisole (0.32 g, 3.0 mmol, 1.0 equiv), The mixture was evacuated and backfilled with N_2 for three times. Then dry DCM (30.0 mL) were added under N_2. The mixture was cooled at –40 °C and Tf_2O (1.01 g, 3.6 mmol, 1.2 equiv) was added dropwise. The mixture was allowed to warm to room temperature and Stir at room temperature for 12 h, After the completion of the reaction, the reaction mixture was added into $NaHCO_3$ aqueous solution (25.0 mL) and extracted with DCM (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (25.0 mL x 3), dried over Na_2SO_4 and filtered, then filtered and concentrated under reduced pressure and purified by precipitation with Et_2O/DCM, the product **4i** was isolated as a white solid (1.06 g, 2.20 mmol, 75% yield). The spectral data match those previously reported[11].

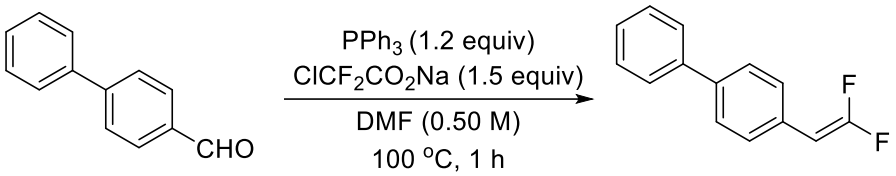
2.13. Synthesis of sulfonium salt 4j:



A 120 °C oven-dried 100-mL glass, equipped with a stir bar, was charged with 4-methoxybenzenethiol (1.28 g, 9.1 mmol, 1.0 equiv), 1-bromo-4-chlorobutane (1.71 g, 10.0 mmol, 1.1 equiv) and NaOH (0.36 g, 9.1 mmol, 1.0 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then EtOH (32.5 mL) and H_2O (32.5 mL) were added under N_2. The mixture was allowed to stir at room temperature for 8 h. The solvent was removed by rotary evaporation, The mixture was poured into

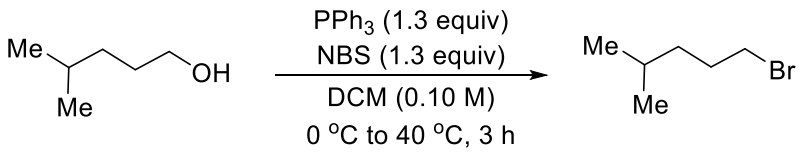
H_2O (20.0 mL) and extracted with Et_2O (10.0 mL x 3). The combined organic layers extracts were washed with water (25.0 mL x 3), dried over Na_2SO_4 and filtered. Was charged with AgOTf (1.80 g, 7.0 mmol, 0.70 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then DCE (30.0 mL) were added under N_2. The mixture was allowed to stir at room temperature for 8 h, then filtered and concentrated under reduced pressure, the product **4j** was isolated as a black solid (0.30 g, 0.87 mmol, 9.6% yield). The spectral data match those previously reported[12].

2.14. Synthesis of 4-(2,2-difluorovinyl)-1,1'-biphenyl:



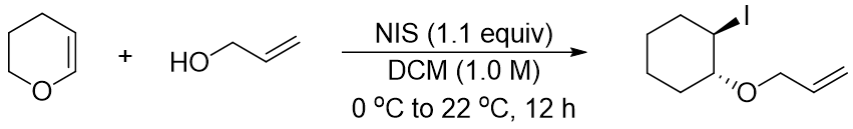
A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with [1,1'-biphenyl]-4-carbaldehyde (1.82 g, 10.0 mmol, 1.0 equiv), PPh_3 (3.14 g, 12.0 mmol, 1.2 equiv), The mixture was evacuated and backfilled with N_2 for three times. Then DMF (20.0 mL) were added under N_2. The mixture allowed to warm to 100 °C and $ClCF_2CO_2Na$ (2.29 g, 15.0 mmol, 1.0 equiv, in 7.5 ml DCM) was added dropwise. The reaction was stirred at 100 °C for 1 h, The mixture was poured into water (50.0 mL) and extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated $Na_2S_2O_3$ aqueous solution (25.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired products. The product 4-(2,2-difluorovinyl)-1,1'-biphenyl was isolated as a white solid (1.80 g, 8.34 mmol, 83% yield). The spectral data match those previously reported[13].

2.15. Synthesis of 1-bromo-4-methylpentane:



A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with 4-methylpentan-1-ol (1.40 g, 13.7 mmol, 1.0 equiv), PPh_3 (5.11 g, 19.5 mmol, 1.3 equiv), The mixture was evacuated and backfilled with N_2 for three times. Then DCM (50.0 mL) were added under N_2. The mixture was cooled at 0 °C and NBS (3.47 g, 19.5 mmol, 1.3 equiv, in 42.2 mL DCM) was added dropwise. The mixture was allowed to warm to 40 °C and stir at 40 °C for 3 h, The mixture was poured into water (50.0 mL) and extracted with DCM (20.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (20.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: petroleum ether). The product 1-bromo-4-methylpentane was isolated as a colorless oil (1.56 g, 9.4 mmol, 69% yield). The spectral data match those previously reported[14].

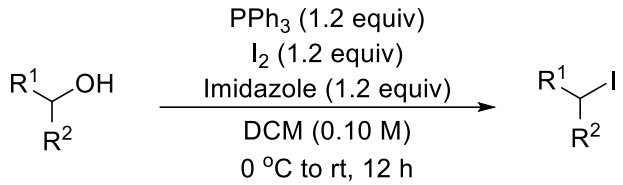
2.16. Synthesis of alkyl iodide 92:



A 120 °C oven-dried 100-mL round-bottom flask equipped with a stir bar, was charged with prop-2-en-1-ol (0.58 g, 10.0 mmol, 1.0 equiv), NIS (2.47 g, 11.0 mmol, 1.1 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then DCM (10.0 mL) were added under N_2. The mixture was cooled at 0 °C and 3,4-dihydro-2*H*-pyran (0.84g, 10.0 mmol, 1.0 equiv) was added dropwise. The mixture was allowed to stir at 22 °C for 5 h, The mixture was poured into water (50.0 mL) and extracted with DCM (20.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (20.0 mL x 3), dried over Na_2SO_4 and

filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate). The product **92** was isolated as a colorless oil (2.01 g, 7.5 mmol, 75% yield). The spectra were consistent with the literature data[15].

2.17. Synthesis of alkyl iodide 3f, 3u, 3av-3ax, 90:



General Method E: A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with alcohol (4.0 mmol, 1.0 equiv), PPh_3 (1.26 g, 4.8 mmol, 1.2 equiv), imidazole (0.33 g, 4.8 mmol, 1.2 equiv), The mixture was evacuated and backfilled with N_2 for three times. Then DCM (40.0 mL) were added under N_2. I_2 (1.22 g, 4.8 mmol, 1.2 equiv) was added to the mixture. The mixture was allowed to stir at room temperature for 12 h. The mixture was poured into water (50.0 mL) and extracted with DCM (20.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (20.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired products.

Compound **3f**: a colorless oil (0.89 g, 3.2 mmol, 81% yield). The spectral data match those previously reported[16].

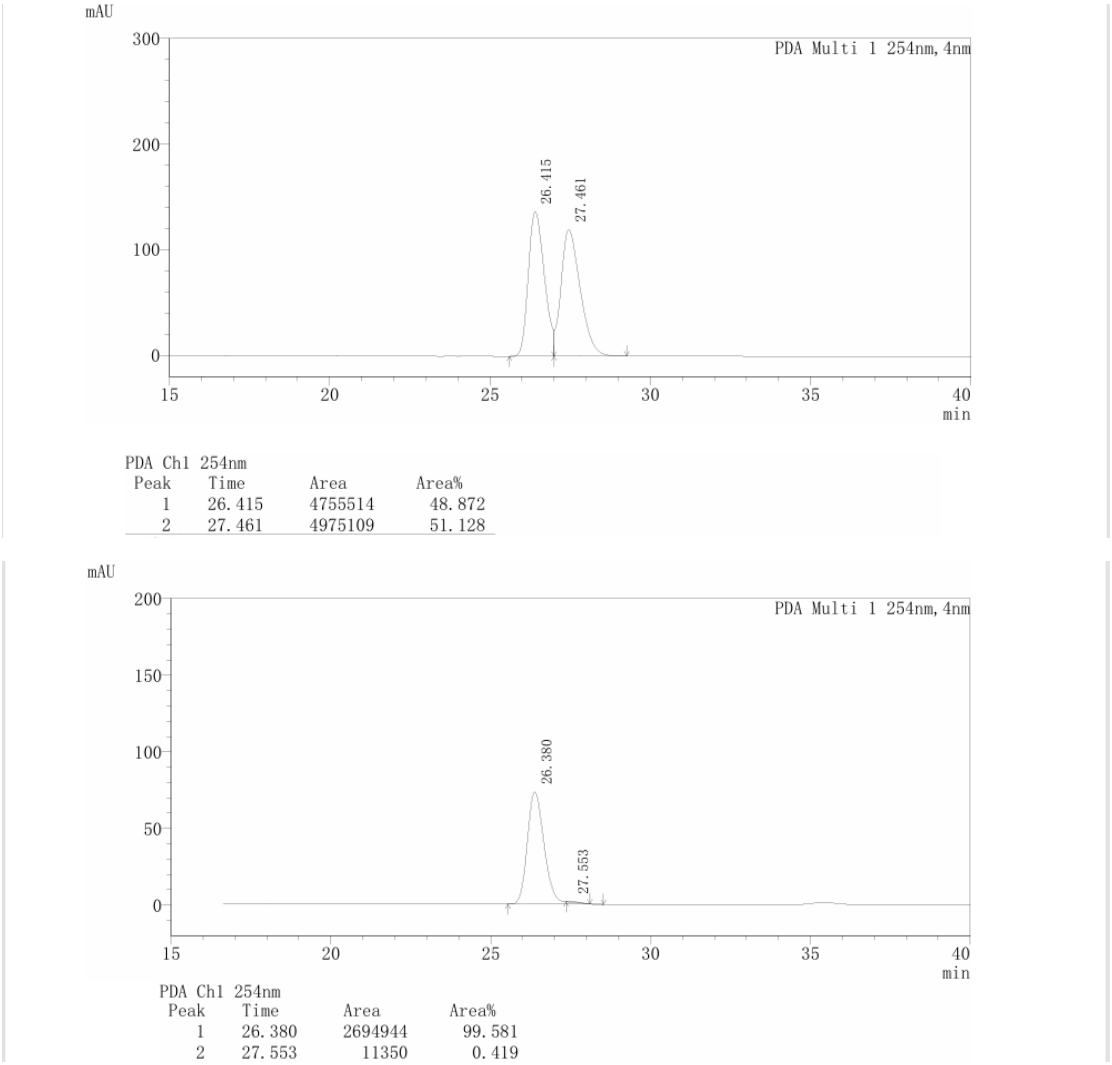
Compound **3u**: a colorless oil (2.92 g, 9.4 mmol, 94% yield, 10.0 mmol was used). The spectral data match those previously reported[17].

Compound **3av**: a colorless oil (0.92 g, 2.9 mmol, 97% yield, 3.0 mmol was used). The spectral data match those previously reported[18].

Compound **3aw**: a white solid (0.95 g, 2.8 mmol, 94% yield, 3.0 mmol was used). The spectral data match those previously reported[19].

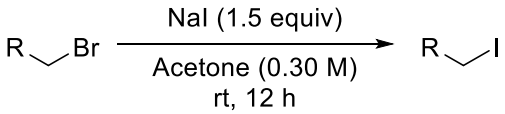
Compound **3ax**: a white solid (1.0 g, 2.8 mmol, 92% yield, 3.0 mmol was used). The spectral data match those previously reported[19].

Compound **90**: a white solid (0.22 g, 0.84 mmol, 84% yield, 1.0 mmol was used). The spectral data match those previously reported[20], **HPLC**: Column: CHIRALPAK-AD-H, 90:10 hexanes, 0.2 mL/min, 254 nm, in comparison with racemic material, >99:1 ee,; $[\alpha]^{22}$= –163.4 (*c*= 1.0, $CHCl_3$).



Supplementary Fig. 1 HPLC traces for compound 90

2.18. Synthesis of alkyl iodides 3aj-3al:



General Method F: A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with alkyl bromide (5.0 mmol, 1.0 equiv), sodium iodide

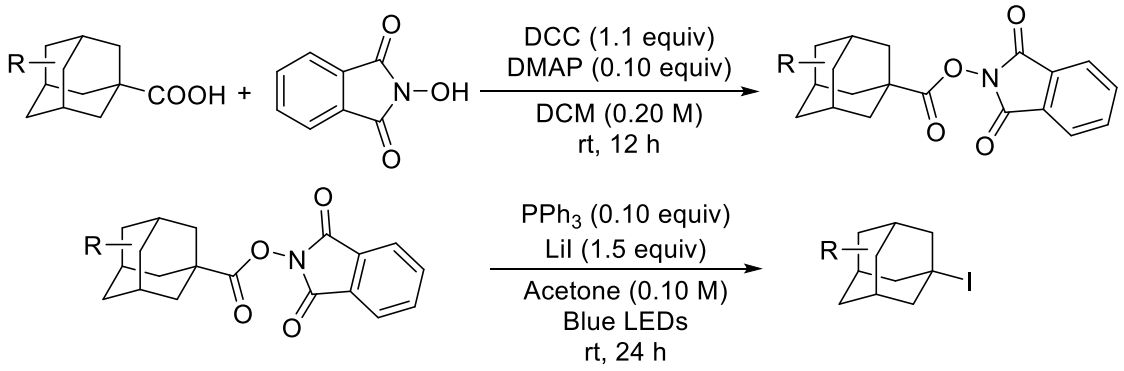
(1.10 g, 7.5 mmol, 1.5 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then acetone (16.7 mL) were added under N_2 and was stirred in the dark for 16 h. The mixture was poured into water (50.0 mL) and extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated $Na_2S_2O_3$ aqueous solution (25.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired products.

Compound **3aj**: a white solid (1.41 g, 4.7 mmol, 94% yield). The spectral data match those previously reported[17].

Compound **3ak**: a colorless oil (0.44 g, 1.4 mmol, 72% yield, 2.0 mmol was used). The spectral data match those previously reported[21].

Compound **3al**: a colorless oil (1.52 g, 4.6 mmol, 93% yield). The spectral data match those previously reported[22].

2.19. Synthesis of alkyl iodides 3am, 3an:



General Method G: A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with carboxylic acid (10.0 mmol, 1.0 equiv), DMAP (0.12 g, 1.0 mmol, 0.10 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then acetone (40.0 mL) were added under N_2 and DCC (2.27 g, 11.0 mmol, 1.1 equiv, in 10.0 mL acetone) was added dropwise. The mixture was allowed to stir at room temperature for 12 h. The mixture was poured into water (50.0 mL) and extracted with DCM (20.0 mL x 3). The combined organic layers were

washed with saturated NaCl aqueous solution (20.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired products.

A 120 ºC oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with Redox-active esters (1.5 mmol, 1.0 equiv), LiI (0.30 g, 2.3 mmol, 1.5 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then acetone (15.0 mL) were added under N_2. The mixture was allowed to stir at room temperature for 24 h with blue LEDs. The mixture was transferred to a round bottom flask and solvent was removed by rotary evaporation, the residue was purified by flash silica gel chromatography to provide the desired products.

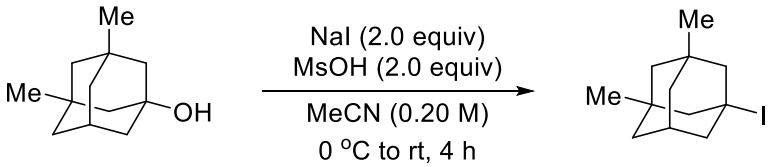
Compound **3am'**: a white solid (2.60 g, 7.7 mmol, 77% yield). The spectral data match those previously reported[23].

Compound **3an'**: a white solid (2.53 g, 7.4 mmol, 74% yield). The spectral data match those previously reported[23].

Compound **3am**: a white solid (0.17 g, 0.62 mmol, 41% yield). The spectral data match those previously reported[23].

Compound **3an**: a white solid (0.26 g, 0.94 mmol, 62% yield). The spectral data match those previously reported[23].

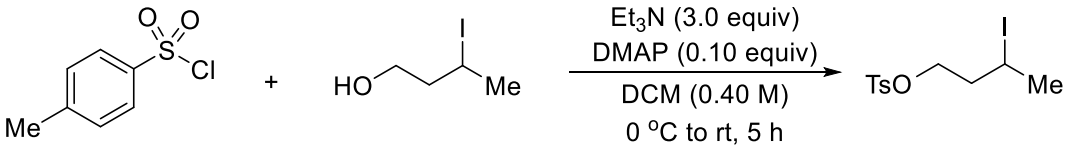
2.20. Synthesis of alkyl iodides 1ao:



A 120 ºC oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with (1*r*,3*R*,5*S*,7*r*)-3,5-dimethyladamantan-1-ol (0.90 g, 5.0 mmol, 5.0 equiv), NaI (1.5 g, 10.0 mmol, 2.0 equiv), The mixture was evacuated and backfilled with N_2 for three times. Then MeCN (25.0 mL) were added under N_2. The mixture was cooled at 0 ºC and MsOH (0.96 g, 10.0 mmol, 2.0 equiv) was added dropwise. Was allowed to warm to room temperature. The mixture was allowed stirr at room temperature

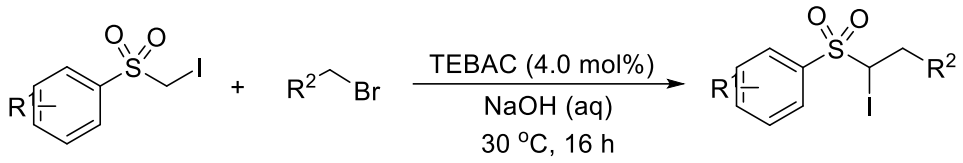
for 4 h, The mixture was poured into water (50.0 mL) and extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (20.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: petroleum ether). The product **1ao** was isolated as a colorless oil (0.27 g, 0.93 mmol, 18% yield). The spectral data match those previously reported[24].

2.21. Synthesis of alkyl iodides 3au:



A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with (3-iodobutan-1-ol (0.60 g, 3.0 mmol, 1.0 equiv), Et_3N (0.91 g, 9.0 mmol, 3.0 equiv) and DMAP (35.7 mg, 0.30 mmol, 0.10 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then DCM (7.50 mL) were added under N_2. The mixture was cooled at 0 °C and 4-methylbenzenesulfonyl chloride (0.74 g, 0.74 mmol, 1.30 equiv) was added dropwise. The mixture was allowed to stir at room temperature for 5 h, The mixture was poured into water (50.0 mL) and extracted with DCM (20.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (20.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 3:1 petroleum ether : ethyl acetate). The product **3au** was isolated as a colorless oil (1.03 g, 2.9 mmol, 97% yield). The spectral data match those previously reported[25].

2.22. Synthesis of alkyl iodides 67a-67j:

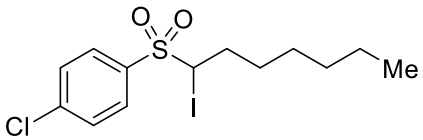


General Method H: A 120 °C oven-dried 50-mL round-bottom flask, equipped with a stir bar, was charged with iodomethyl aryl sulfone (3.0 mmol, 1.0 equiv). 50% aqueous sodium hydroxide (4.50 mL), benzyltriethylammonium chloride (27.3 mg, 0.12 mmol, 0.04 equiv) and the alkyl halide (4.5 mmol, 1.5 equiv). The reaction was stirred at 30 °C for 16 h, The mixture was poured into water (50.0 mL) and extracted with DCM (20.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (20.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography provide the desired products.

Compound **67a**: a colorless oil (0.87 g, 2.3 mmol, 76% yield). The spectral data match those previously reported[26].

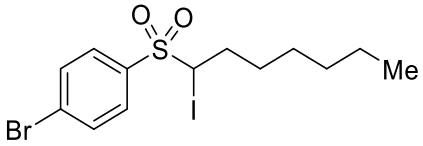
Compound **67e**: a colorless oil (0.14 g, 0.37 mmol, 37% yield, 1.0 mmol was used). The spectral data match those previously reported[27].

Compound **99f**: a colorless oil (0.30 g, 0.76 mmol, 76% yield, 1.0 mmol was used). The spectral data match those previously reported[27].

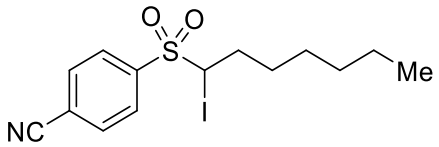


1-Chloro-4-((1-iodoheptyl)sulfonyl)benzene 67b: Prepared according to **General Method H** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (0.91 g, 2.3 mmol, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (2H, d, J = 8.6 Hz), 7.56 (2H, d, J = 8.7 Hz), 4.85 (1H, dd, J = 11.3, 3.0 Hz), 2.20 – 1.98 (1H, m), 1.91 – 1.81 (1H, m), 1.62 – 1.56 (1H, m), 1.35 – 1.22 (7H, m), 0.87 (3H, t, J = 6.7 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.4,

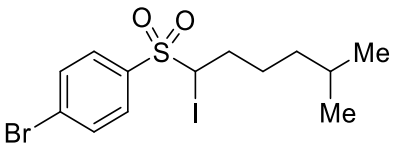
133.7, 131.5, 129.6, 45.0, 32.9, 31.5, 29.2, 28.1, 22.6, 14.1; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{13}H_{19}ClIO_2S$: 400.9833, found: 400.9834.



1-Bromo-4-((1-iodoheptyl)sulfonyl)benzene 67c: Prepared according to **General Method H** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (0.26 g, 0.57 mmol, 29% yield, 2.00 mmol was used). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (2H, d, J = 8.7 Hz), 7.73 (2H, d, J = 8.6 Hz), 4.84 (1H, dd, J = 11.3, 3.0 Hz), 2.11 – 2.00 (1H, m), 1.90 – 1.80 (1H, m), 1.63 – 1.55 (1H, m), 1.37 – 1.24 (7H, m), 0.87 (3H, t, J = 6.7 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.1, 132.5, 131.5, 130.0, 45.0, 32.9, 31.4, 29.2, 28.1, 22.6, 14.1; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{13}H_{19}BrIO_2S$: 444.9328, found: 444.9307.

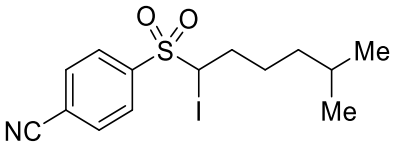


4-((1-Iodoheptyl)sulfonyl)benzonitrile 67d: Prepared according to **General Method H** (Eluent: 100:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (0.934 g, 2.4 mmol, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (2H, d, J = 8.2 Hz), 7.89 (2H, d, J = 8.2 Hz), 4.87 (1H, dd, J = 11.3, 3.0 Hz), 2.12 – 2.03 (1H, m), 1.92 – 1.80 (1H, m), 1.65 – 1.56 (1H, m), 1.40 – 1.30 (2H, m), 1.29 – 1.18 (5H, m), 0.86 (3H, t, J = 6.7 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.6, 132.8, 130.7, 118.1, 117.1, 44.1, 32.6, 31.4, 29.1, 28.0, 22.5, 14.1; **HRMS** (ESI^+) $[M+K]^+$ calc'd for $C_{14}H_{18}NKIO_2S$: 429.9735, found: 429.9724.

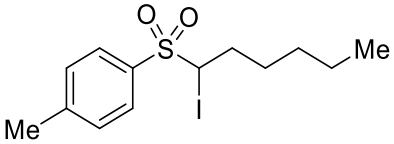


1-Bromo-4-((1-iodo-5-methylhexyl)sulfonyl)benzene 67g: Prepared according to **General Method H** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (0.37 g, 0.82 mmol, 41% yield, 2.00 mmol was used). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (2H, d, J = 8.1 Hz), 7.90 (2H, d, J =

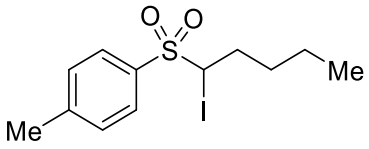
8.1 Hz), 4.86 (1H, dd, *J* = 11.3, 3.0 Hz), 2.12 – 2.03 (1H, m), 1.93 – 1.83 (1H, m), 1.66 – 1.60 (1H, m), 1.56 – 1.49 (1H, m), 1.40 – 1.29 (1H, m), 1.26 – 1.18 (2H, m), 0.87 (6H, dd, *J* = 6.7, 2.2 Hz; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.1, 132.5, 131.5, 130.0, 45.1, 37.5, 33.1, 27.7, 27.1, 22.7, 22.4; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{13}H_{19}BrIO_2S$: 444.9328, found: 444.9339.



4-((1-Iodo-5-methylhexyl)sulfonyl)benzonitrile 67h: Prepared according to **General Method H** (Eluent: 100:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (0.21 g, 0.55 mmol, 55% yield, 1.00 mmol was used). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (2H, d, *J* = 8.5 Hz), 7.89 (2H, d, *J* = 8.5 Hz), 4.88 (1H, dd, *J* = 11.3, 3.0 Hz), 2.06 – 2.00 (1H, m), 1.91 – 1.83 (1H, m), 1.64 – 1.58 (1H, m), 1.54 – 1.47 (1H, m), 1.36 – 1.30 (1H, m), 1.20 – 1.14 (2H, m), 0.85 (6H, dd, *J* = 6.6, 2.2 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.5, 132.9, 130.7, 118.1, 117.1, 44.1, 37.5, 32.8, 27.7, 27.0, 22.7, 22.3; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{14}H_{18}NIO_2SNa$: 413.9995, found: 413.9999.



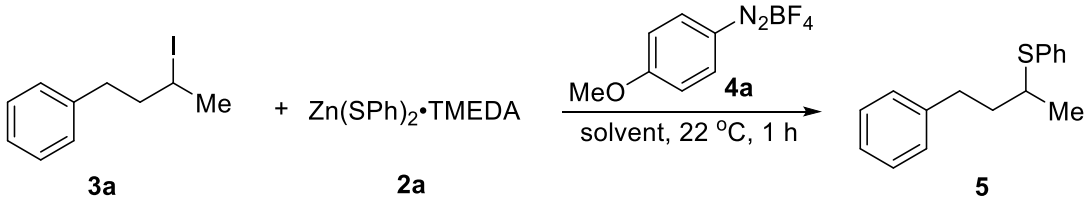
1-((1-Iodohexyl)sulfonyl)-4-methylbenzene 67i: Prepared according to **General Method H** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (0.94 g, 2.6 mmol, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (2H, d, *J* = 8.2 Hz), 7.36 (2H, d, *J* = 8.0 Hz), 4.85 (1H, dd, *J* = 11.2, 3.0 Hz), 2.46 (3H, s), 2.08 – 1.95 (1H, m), 1.89 – 1.79 (1H, m), 1.64 – 1.54 (1H, m), 1.35 – 1.17 (5H, m), 0.85 (3H, t, *J* = 6.8 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 132.0, 130.0, 129.8, 45.8, 33.0, 30.5, 28.9, 22.3, 21.8, 14.0; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{13}H_{19}IO_2SNa$: 389.0043, found: 389.0029.



1-((1-Iodopentyl)sulfonyl)-4-methylbenzene 67j: Prepared according to **General Method H** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (0.88 g, 2.5 mmol, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (2H, d, J = 8.4 Hz), 7.38 (2H, d, J = 8.4 Hz), 4.86 (1H, dd, J = 11.2, 3.0 Hz), 2.48 (3H, s), 2.11 – 1.98 (1H, m), 1.94 – 1.80 (1H, m), 1.64 – 1.49 (1H, m), 1.41 – 1.21 (3H, m), 0.88 (3H, t, J = 7.0 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 132.0, 130.0, 129.9, 45.8, 32.8, 31.3, 21.9, 21.6, 13.8; **HRMS** (ESI^+) $[M+K]^+$ calc'd for $C_{12}H_{17}IO_2SK$: 390.9626, found: 390.9622.

3. Optimization of the reaction conditions

Table 3.1 Evaluation of different solvents

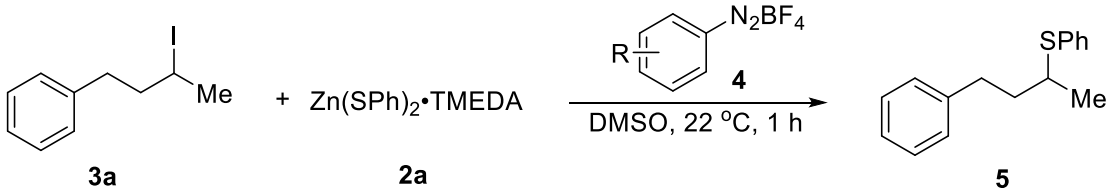


3a **2a** **5**

Entry	solvent	^{1}H NMR yield (%)[a]
1	DMSO	78
2	NMP	44
3	DMF	20
4	THF	<5
5	1,4-Dioxane	56
6	MeOH	24
7	DCM	24
8	MeCN	8
9	^{n}Bu$_2$O	<5
10	2-MeTHF	44
11	DMAC	40
12	EtOAc	24
13	Acetone	<5

Reaction conditions: **3a** (0.10 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), **4a** (0.25 mmol, 2.5 equiv) in solvent (0.60 mL) at 22 °C for 1 h; [a]Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table 3.2 Evaluation of different diazodium salts

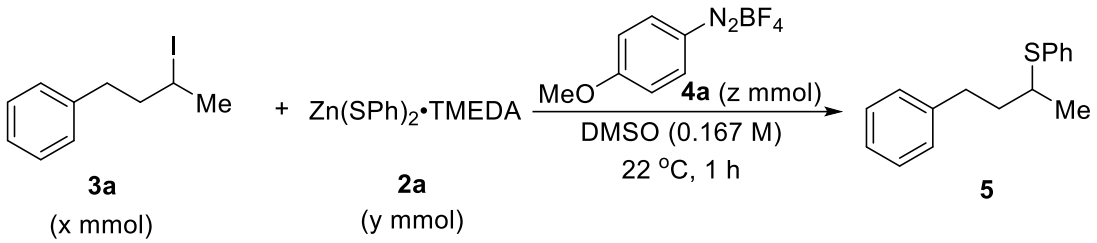


3a **2a** **5**

Entry	R =	^{1}H NMR yield (%)[a]
1	4-OMe (**4a**)	78
2	4-NO_2 (**4b**)	24
3	4-CF_3 (**4c**)	44
4	4-Br (**4d**)	48
5	2-OMe (**4e**)	56
6	3-OMe (**4f**)	68
7	3,4-OMe (**4g**)	76
8	2,4,6-Me (**4h**)	56
9	4-OCF_3	40
10	-	24

Reaction conditions: **3a** (0.10 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), **4** (0.25 mmol, 2.5 equiv) in DMSO (0.60 mL) at 22 °C for 1 h; [a]Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table 3.3 Evaluation of different of the starting materials

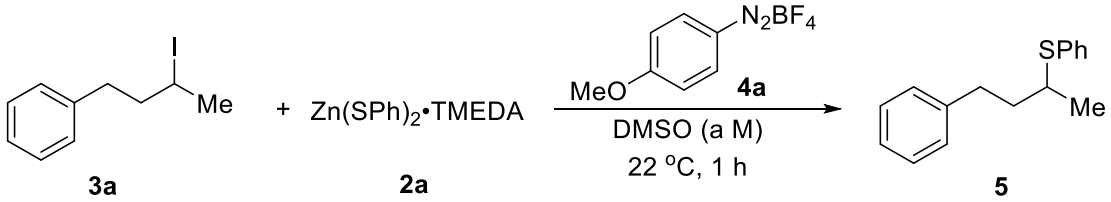


3a (x mmol) **2a** (y mmol) **5**

Entry	x/y/z	^{1}H NMR yield (%)[a]
1	0.10/0.15/0.15	48
2	0.10/0.15/0.20	56
3	0.10/0.15/0.30	56
4	0.10/0.20/0.20	76
5	0.15/0.10/0.15	48
6	0.15/0.15/0.10	36

Reaction conditions: **2a** , **3a** , **4a** in DMSO (0.60 mL) at 22 °C for 1 h; [a]Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table 3.4 Evaluation of different concentrations

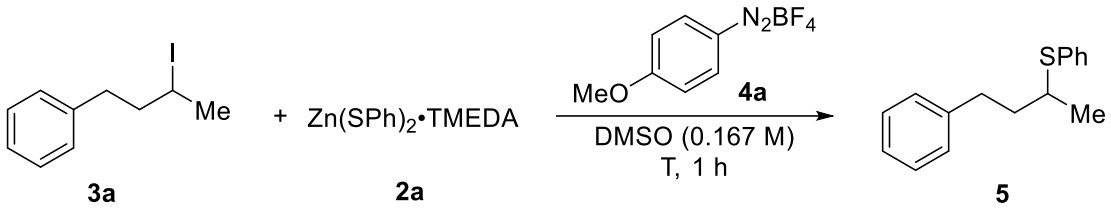


3a **2a** **5**

Entry	a	^{1}H NMR yield (%)[a]
1	0.10	56
2	0.20	72

Reaction conditions: **3a** (0.10 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), **4a** (0.25 mmol, 2.5 equiv) in DMSO at 22 °C for 1 h; [a]Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table 3.5 Evaluation of different temperature

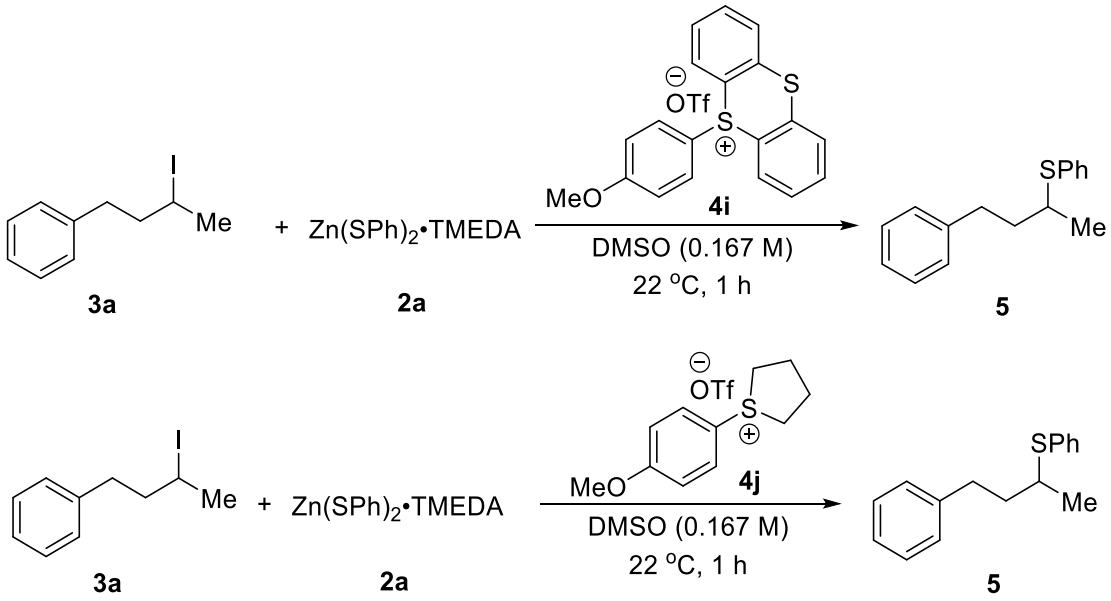


3a **2a** **5**

Entry	T (^{o}C)	^{1}H NMR yield (%)[a]
1	0	64
2	10	64

Reaction conditions: **3a** (0.10 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), **4a** (0.25 mmol, 2.5 equiv) in DMSO (0.60 mL) at T for 1 h; [a]Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table 3.6 Evaluation of different sulfonium salts



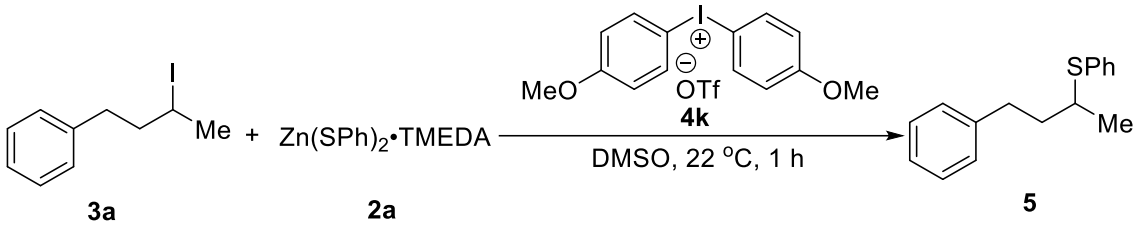
3a **2a** **5**

3a **2a** **5**

Entry	sulfonium salt	^{1}H NMR yield (%)[a]
1	**4i**	24
2	**4j**	56

Reaction conditions: **3a** (0.10 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), sulfonium salt **4i** or **4j** (0.25 mmol, 2.5 equiv) in DMSO (0.60 mL) at 22 ^{o}C for 1 h; [a]Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table 3.7 Evaluation of different diaryliodonium salt



3a **2a** **5**

Entry	diaryliodonium salt	^{1}H NMR yield (%)[a]
1	**4k**	12

Reaction conditions: **3a** (0.10 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), diaryliodonium salt **4k** (0.25 mmol, 2.5 equiv) in DMSO (0.60 mL) at 22 °C for 1 h; [a]Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

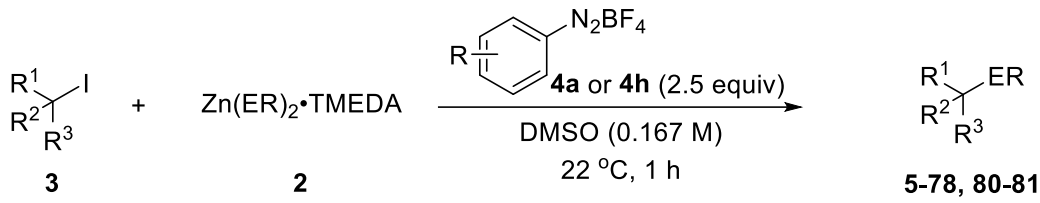
Table 3.8 Background S_N2 pathway

3a **2a** **5**

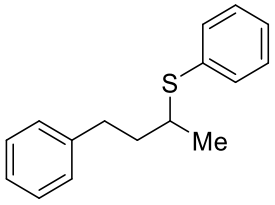
Entry	T	^{1}H NMR yield (%)[a]
1	22	<5
2	60	40
3	80	56
4	100	60

Reaction conditions: **3a** (0.10 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), in DMSO (0.60 mL) at T °C for 1 h; [a]Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

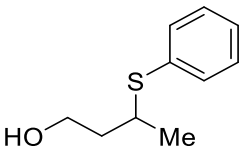
4. Substrate scope



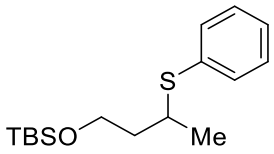
General Method I: A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with alkyl iodide (0.30 mmol, 1.0 equiv), zinc thiolate (0.45 mmol, 1.5 equiv) and arene diazodium salt (0.75 mmol, 2.5 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then DMSO (1.8 mL) were added under N_2 and was stirred for 1 h. The mixture was poured into water (20.0 mL) and extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired products.



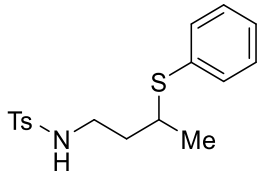
Phenyl(4-phenylbutan-2-yl)sulfane 5: Prepared according to **General Method I** (Eluent: petroleum ether) and the title compound was isolated as a colorless oil (51.0 mg, 0.21 mmol, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.34 (2H, m), 7.29 – 7.24 (4H, m), 7.22 – 7.20 (1H, m), 7.18 – 7.15 (3H, m), 3.22 – 3.17 (1H, m), 2.83 – 2.72 (2H, m), 1.97 – 1.88 (1H, m), 1.86 – 1.76 (1H, m), 1.31 (3H, d, J = 6.7 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.8, 135.2, 132.1, 128.9, 128.6, 128.5, 126.8, 126.0, 42.6, 38.3, 33.3, 21.3. The spectral data match those previously reported[28].



3-(Phenylthio)butan-1-ol 6: Prepared according to **General Method J** (Eluent: 100:1 to 3:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (54.6 mg, 0.30 mmol, >99% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.41 (2H, m), 7.32 – 7.28 (2H, m), 7.27 – 7.19 (1H, m), 3.93 – 3.69 (2H, m), 3.44 – 3.35 (1H, m), 1.89 (1H, s), 1.84 – 1.78 (2H, m), 1.32 (3H, d, J = 6.8 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.7, 132.3, 129.0, 127.1, 60.7, 40.5, 39.2, 21.6. The spectral data match those previously reported[29].

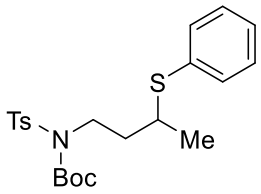


***tert*-Butyldimethyl(3-(phenylthio)butoxy)silane 7:** Prepared according to **General Method I** (Eluent: 100:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (84.9 mg, 0.29 mmol, 95% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (2H, m), 7.31 – 7.25 (2H, m), 7.23 – 7.17 (1H, m), 3.83 – 3.66 (2H, m), 3.46 – 3.48 (1H, m), 1.88 – 1.82 (1H, m), 1.72 – 1.66 (1H, m), 1.30 (3H, d, J = 6.8 Hz), 0.89 (9H, s), 0.05 (6H, d, J = 1.8 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.5, 131.7, 128.9, 126.6, 60.6, 39.6 (d, J = 7.4 Hz), 26.1, 21.4, 18.4, –5.3 (d, J = 4.56 Hz); **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{16}H_{28}NaSSiO$: 319.1522, found: 319.1513.

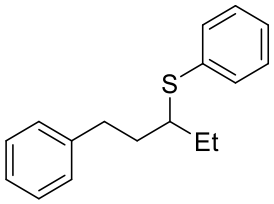


4-Methyl-*N*-(3-(phenylthio)butyl)benzenesulfonamide 8: Prepared according to **General Method I** (Eluent: 100:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a brown oil (51.1 mg, 0.15 mmol, 51% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (2H, d, J = 8.3 Hz), 7.27 – 7.24 (2H, m), 7.22 – 7.18 (3H, m), 7.17 – 7.14 (2H, m), 4.95 (1H, t, J = 6.3 Hz), 3.13 (1H, q, J = 6.8 Hz), 3.02 (2H, q, J = 6.7 Hz), 2.33 (3H, s), 1.61 (2H, q, J = 6.9 Hz), 1.13 (3H, q, J = 6.7 Hz); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.5, 136.9, 134.2, 132.5, 129.8, 129.0, 127.2, 127.2, 41.0, 40.8,

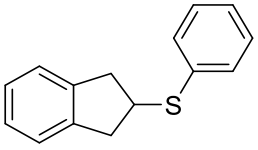
36.2, 21.6, 21.4; **HRMS** (ESI$^+$) $[M+H]^+$ calc'd for $C_{17}H_{22}NO_2S_2$: 336.1086, found: 336.1080.



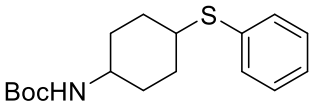
***tert*-Butyl (3-(phenylthio)butyl)(tosyl)carbamate 9:** Prepared according to **General Method I** (Eluent: 100:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (100.3 mg, 0.23 mmol, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (2H, d, J = 8.4 Hz), 7.37 (2H, d, J = 6.9 Hz), 7.25 – 7.21 (3H, m), 7.20 – 7.14 (2H, m), 4.03 – 3.81 (2H, m), 3.18 (1H, q, J = 6.7 Hz), 2.35 (3H, s), 2.00 – 1.87 (2H, m), 1.27 (3H, d, J = 6.8 Hz), 1.25 (9H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.9, 144.3, 137.4, 134.5, 132.6, 129.4, 129.0, 127.9, 127.1, 84.4, 45.4, 41.1, 36.8, 28.0, 21.7, 21.3; **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{22}H_{29}NaNO_4S$: 458.1430, found: 458.1441.



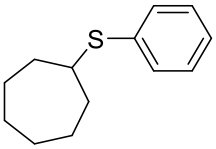
Phenyl(1-phenylpentan-3-yl)sulfane 10: Prepared according to **General Method I** (Eluent: petroleum ether) and the title compound was isolated as a colorless oil (67.7 mg, 0.26 mmol, 88% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.38 (2H, m), 7.31 – 7.27 (4H, m), 7.25 – 7.19 (2H, m), 7.18 (2H, d, J = 7.0 Hz), 3.07 – 3.05 (1H, m), 2.88 – 2.77 (2H, m), 1.96 – 1.85 (2H, m), 1.74 – 1.63 (2H, m), 1.04 (3H, t, J = 7.4 Hz); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.0, 135.6, 132.1, 128.9, 128.6, 128.5, 126.7, 126.0, 50.1, 35.8, 33.1, 27.5, 11.3; **HRMS** (ESI$^+$) $[M+K]^+$ calc'd for $C_{17}H_{20}KS$: 295.0917, found: 295.0923.



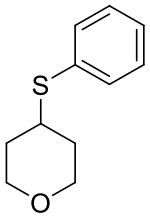
(2,3-Dihydro-1*H*-inden-2-yl)(phenyl)sulfane 11: Prepared according to **General Method I** (Eluent: petroleum ether) and the title compound was isolated as a colorless oil (52.6 mg, 0.23 mmol, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (2H, d, J = 7.4 Hz), 7.24 – 7.20 (2H, m), 7.16 – 7.07 (5H, m), 4.03 (1H, tt, J = 7.5, 5.9 Hz), 3.29 (2H, dd, J = 16.2, 7.5 Hz), 2.92 (2H, dd, J = 16.2, 5.9 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 136.2, 130.7, 129.1, 126.8, 126.5, 124.6, 45.4, 40.3. The spectral data match those previously reported[28].



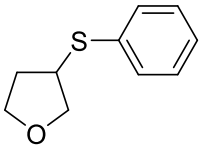
***tert*-Butyl (4-(phenylthio)cyclohexyl)carbamate 12:** Prepared according to **General Method I** (Eluent: 100:1 to 15:1 petroleum ether: ethyl acetate) and the title compound was isolated as a grey solid (68.4 mg, 0.22 mmol, 74% yield). **M.p.** = 67.4 ^{o}C – 68.3 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (2H, d, J = 7.3 Hz), 7.20 – 7.13 (2H, m), 7.10 (1H, d, J = 6.6 Hz), 4.53 (1H, s), 3.48 (1H, s), 3.29 (1H, s), 1.77 – 1.67 (3H, m), 1.65 – 1.64 (1H, m), 1.62 – 1.56 (4H, m), 1.34 (9H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.3, 135.2, 131.8, 129.0, 126.9, 79.2, 47.8, 44.8, 35.4, 29.0, 28.5; **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{17}H_{25}NNaO_2S$: 330.1498, found: 330.1491.



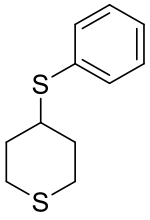
Cycloheptyl(phenyl)sulfane 13: Prepared according to **General Method I** (Eluent: petroleum ether) and the title compound was isolated as a colorless oil (61.5 mg, 0.30 mmol, >99% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.28 (2H, m), 7.23 – 7.19 (2H, m), 7.15 – 7.11 (1H, m), 3.30 – 3.24 (1H, m), 1.98 – 1.91 (2H, m), 1.68 – 1.63 (2H, m), 1.56 – 1.55 (1H, m), 1.51 – 1.47 (5H, m), 1.43 – 1.35 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.2, 131.2, 128.8, 126.3, 48.0, 34.6, 28.3, 26.0. The spectral data match those previously reported[30].



4-(Phenylthio)tetrahydro-2*H*-pyran 14: Prepared according to **General Method I** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (53.6 mg, 0.28 mmol, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.34 (2H, m), 7.25 – 7.21 (2H, m), 7.20 – 7.15 (1H, m), 3.89 (2H, dt, J = 11.7, 3.8 Hz), 3.35 (2H, ddd, J = 11.7, 10.7, 2.4 Hz), 3.19 (1H, tt, J = 10.7, 4.0 Hz), 1.86 – 1.79 (2H, m), 1.64 – 1.54 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.8, 132.8, 129.0, 127.4, 67.4, 43.5, 33.2. The spectral data match those previously reported[31].

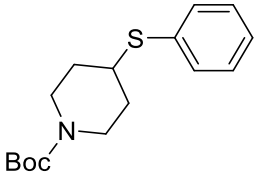


3-(Phenylthio)tetrahydrofuran 15: Prepared according to **General Method I** (Eluent: 100:1 to 70:1 petroleum ether: ethyl acetate) and the title compound was isolated as a brown oil (41.6 mg, 0.23 mmol, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.29 (2H, m), 7.25 – 7.21 (2H, m), 7.17 – 7.13 (1H, m), 4.03 (1H, dd, J = 9.2, 6.5 Hz), 3.91 – 3.85 (1H, m), 3.82 – 3.70 (2H, m), 3.61 (1H, dd, J = 9.2, 5.4 Hz), 2.30 – 2.21 (1H, m), 1.89 – 1.81 (1H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.7, 130.7, 129.1, 126.8, 73.7, 67.7, 44.9, 33.2. The spectral data match those previously reported[32].

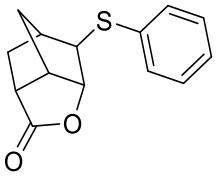


4-(Phenylthio)tetrahydro-2*H*-thiopyran 16: Prepared according to **General Method I** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (57.2 mg, 0.27 mmol, 91% yield). **^{1}H NMR**

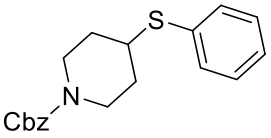
(400 MHz, $CDCl_3$) δ 7.35 – 7.30 (2H, m), 7.25 – 7.23 (1H, m), 7.22 – 7.16 (2H, m), 3.06 (1H, tt, J = 10.2, 3.4 Hz), 2.71 – 2.65 (2H, m), 2.55 (2H, ddd, J = 13.7, 10.5, 2.7 Hz), 2.22 – 2.16 (2H, m), 1.77 – 1.68 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.8, 132.8, 129.1, 127.4, 46.1, 34.0, 28.0. The spectral data match those previously reported[31].



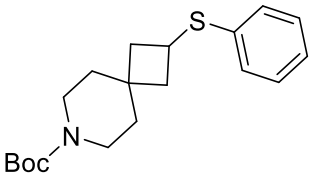
***tert*-Butyl 4-(phenylthio)piperidine-1-carboxylate 17:** Prepared according to **General Method I** (Eluent: 100:1 to 15:1 petroleum ether: ethyl acetate) and the title compound was isolated as a brown solid (58.6 mg, 0.20 mmol, 67% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (2H, m), 7.26 – 7.20 (2H, m), 7.20 – 7.15 (1H, m), 3.89 (2H, dt, J = 14.0, 4.3 Hz), 3.17 – 3.10 (1H, m), 2.84 (2H, dt, J = 13.6, 10.7 Hz, 3.0 Hz), 1.86 – 1.82 (2H, m), 1.49 – 1.40 (2H, m), 1.37 (1H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.8, 133.8, 132.8, 129.0, 127.4, 79.7, 44.6, 43.3, 32.2, 28.5. The spectral data match those previously reported[32].



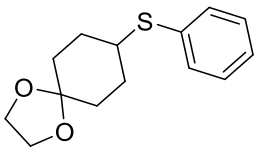
6-(Phenylthio)hexahydro-2*H*-3,5-methanocyclopenta[*b*]furan-2-one 18: Prepared according to **General Method I** (Eluent: 100:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (60.8 mg, 0.25 mmol, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (4H, m), 7.25 – 7.20 (1H, m), 4.60 (1H, d, J = 5.0 Hz), 3.30 – 3.19 (2H, m), 2.61 (1H, ddt, J = 11.4, 4.7, 1.5 Hz), 2.50 (1H, s), 2.25 (1H, dd, J = 11.4, 1.9 Hz), 2.13 (1H, ddd, J = 13.4, 11.3Hz, 3.9 Hz), 1.83 (1H, d, J = 13.4 Hz), 1.66 (1H, dd, J = 11.4, 1.9 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.2, 134.1, 129.7, 129.4, 126.8, 85.8, 54.0, 46.4, 41.2, 38.9, 36.1, 35.1. The spectral data match those previously reported[34].



Benzyl 4-(phenylthio)piperidine-1-carboxylate 19: Prepared according to **General Method I** (Eluent: 100:1 to 15:1 petroleum ether: ethyl acetate) and the title compound was isolated as a brown oil (75.6 mg, 0.23 mmol, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.39 (2H, m), 7.37 – 7.33 (4H, m), 7.31 – 7.30 (1H, m), 7.30 – 7.27 (2H, m), 7.27 – 7.22 (1H, m), 5.11 (2H, s), 4.03 (2H, s), 3.21 (1H, tt, J = 10.1, 3.8 Hz), 3.00 (2H, t, J = 10.9 Hz), 2.01 – 1.83 (2H, m), 1.56 – 1.53 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.2, 136.8, 133.7, 132.8, 129.0, 128.5, 128.1, 127.9, 127.5, 67.2, 44.3, 43.4, 32.0; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{19}H_{22}NO_2S$: 328.1366, found: 328.1359.

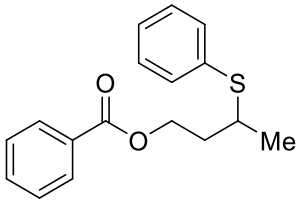


***tert*-Butyl 2-(phenylthio)-7-azaspiro[3.5]nonane-7-carboxylate 20:** Prepared according to **General Method I** (Eluent: 100:1 to 40:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow oil (64.9 mg, 0.20 mmol, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.22 (4H, m), 7.19 – 7.14 (1H, m), 3.88 – 3.80 (1H, m), 3.34 (2H, t, J = 5.6 Hz), 3.26 (2H, t, J = 5.6 Hz), 2.40 – 2.34 (2H, m), 1.90 – 1.85 (2H, m), 1.59 (2H, t, J = 5.6 Hz), 1.55 (2H, t, J = 5.6 Hz), 1.44 (9H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.0, 136.8, 129.0, 128.9, 125.9, 79.5, 40.2, 39.1, 36.4, 35.1, 34.1, 28.5; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{19}H_{27}NNaO_2S$: 356.1655, found: 356.1642.

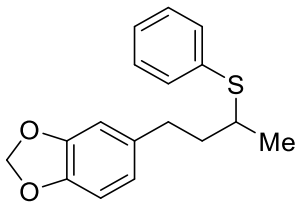


8-(Phenylthio)-1,4-dioxaspiro[4.5]decane 21: Prepared according to **General Method I** (Eluent: 100:1 to 15:1 petroleum ether: ethyl acetate) and the title compound was isolated as a brown oil (45.0 mg, 0.18 mmol, 60% yield). **^{1}H NMR**

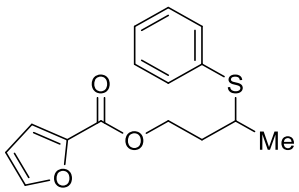
(400 MHz, $CDCl_3$) δ 7.41 (2H, d, J = 7.4 Hz), 7.30 – 7.27 (2H, m), 7.24 – 7.20 (1H, m), 3.93 (4H, s), 3.19 (1H, tt, J = 9.6, 3.8 Hz), 2.02 – 1.96 (2H, m), 1.87 – 1.81 (2H, m), 1.71 (2H, dtd, J = 13.3, 9.9, 3.5 Hz), 1.60 – 1.53 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.1, 132.1, 128.9, 126.9, 108.2, 64.4, 44.9, 33.8, 30.2. The spectral data match those previously reported[34].



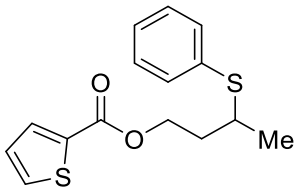
3-(Phenylthio)butyl benzoate 22: Prepared according to **General Method I** (Eluent: 100:1 to 30:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (80.3 mg, 0.28 mmol, 93% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (2H, d, J = 7.0 Hz), 7.60 – 7.54 (1H, m), 7.46 – 7.42 (4H, m), 7.30 – 7.25 (2H, m), 7.24 – 7.20 (1H, m), 4.48 (2H, t, J = 6.4 Hz), 3.44 – 3.36 (1H, m), 2.13 – 1.94 (2H, m), 1.38 (3H, d, J = 6.8 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 134.6, 133.1, 132.5, 130.3, 129.7, 129.0, 128.5, 127.2, 62.7, 40.5, 35.8, 21.4; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{17}H_{18}NaO_2S$: 309.0920, found: 309.0929.



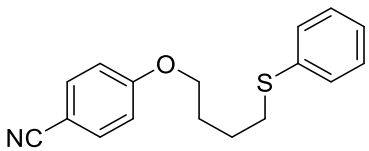
5-(3-(Phenylthio)butyl)benzo[*d*][1,3]dioxole 23: Prepared according to **General Method I** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (53.3 mg, 0.19 mmol, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.27 (2H, m), 7.20 – 7.18 (2H, m), 7.16 – 7.11 (1H, m), 6.64 (1H, d, J = 7.8 Hz), 6.60 – 6.52 (2H, m), 5.83 (2H, s), 3.10 (1H, q, J = 6.7 Hz), 2.67 – 2.58 (2H, m), 1.82 – 1.65 (2H, m), 1.22 (3H, d, J = 6.7 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.7, 145.8, 135.6, 135.1, 132.2, 128.9, 126.9, 121.3, 109.0, 108.3, 100.9, 42.5, 38.5, 33.0, 21.3; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{17}H_{18}NaO_2S$: 309.0920, found: 309.0918.



3-(Phenylthio)butyl furan-2-carboxylate 24: Prepared according to **General Method I** (Eluent: 100:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (65.6 mg, 0.24 mmol, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (1H, s), 7.42 (2H, d, J = 7.2 Hz), 7.30 – 7.26 (2H, m), 7.25 – 7.20 (1H, m), 7.16 (1H, d, J = 3.4 Hz), 6.51 (1H, dd, J = 3.6, 1.7 Hz), 4.46 (2H, t, J = 6.5 Hz), 3.37 (1H, q, J = 6.8 Hz), 2.07 – 1.94 (2H, m), 1.36 (3H, d, J = 6.8 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.7, 146.4, 144.7, 134.5, 132.5, 129.0, 127.2, 118.0, 111.9, 62.7, 40.3, 35.6, 21.4; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{15}H_{16}NaO_3S$: 299.0712, found: 299.0719.

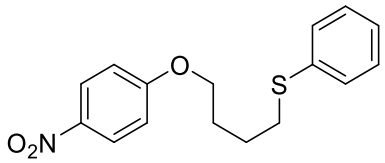


3-(Phenylthio)butyl thiophene-2-carboxylate 25: Prepared according to **General Method I** (Eluent: 100:1 to 80:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (73.8 mg, 0.25 mmol, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (1H, dd, J = 3.7, 1.3 Hz), 7.56 (1H, dd, J = 5.0, 1.3 Hz), 7.44 – 7.41 (2H, m), 7.31 – 7.26 (2H, m), 7.25 – 7.21 (1H, m), 7.10 (1H, dd, J = 5.0, 3.6 Hz), 4.45 (2H, td, J = 6.3, 1.2 Hz), 3.39 (1H, q, J = 6.8 Hz), 2.08 – 1.92 (2H, m), 1.37 (3H, d, J = 6.8 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2, 134.6, 133.8, 133.6, 132.5, 132.4, 129.0, 127.9, 127.2, 62.9, 40.4, 35.7, 21.3; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{15}H_{16}NaO_2S_2$: 315.0484, found: 315.0481.

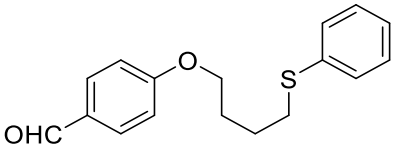


4-(4-(Phenylthio)butoxy)benzonitrile 26: Prepared according to **General Method I** (Eluent: 100:1 to 30:1 petroleum ether: ethyl acetate) and the title compound was

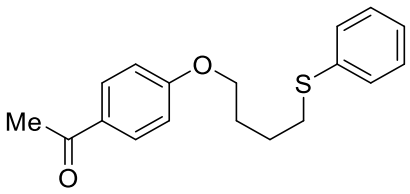
isolated as a colorless oil (73.2 mg, 0.26 mmol, 86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (2H, d, J = 8.8 Hz), 7.33 (2H, dd, J = 8.3, 1.4 Hz), 7.29 – 7.26 (2H, m), 7.20 – 7.16 (1H, m), 6.90 (2H, d, J = 8.8 Hz), 4.00 (2H, t, J = 6.2 Hz), 2.99 (2H, t, J = 7.1 Hz), 1.97 – 1.91 (2H, m), 1.86 – 1.80 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4, 136.3, 134.0, 129.3, 129.0, 126.1, 119.3, 115.2, 103.8, 67.7, 33.4, 28.0, 25.6; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{17}H_{17}NNaOS$: 306.0923, found: 306.0917.



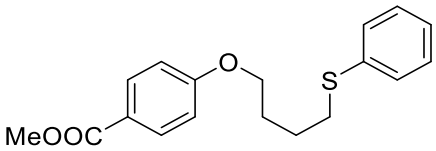
(4-(4-Nitrophenoxy)butyl)(phenyl)sulfane 27: Prepared according to **General Method I** (Eluent: 100:1 to 30:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow solid (53.7 mg, 0.18 mmol, 59% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (2H, d, J = 9.2 Hz), 7.35 – 7.30 (2H, m), 7.28 (2H, dd, J = 8.5, 6.8 Hz), 7.19 – 7.16 (1H, m), 6.91 (2H, d, J = 9.2 Hz), 4.05 (2H, t, J = 6.2 Hz), 3.00 (2H, t, J = 7.1 Hz), 1.99 – 1.94 (2H, m), 1.88 – 1.82 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.1, 141.5, 136.3, 129.4, 129.0, 126.1, 126.0, 114.5, 68.2, 33.4, 28.0, 25.6. The spectral data match those previously reported[35].



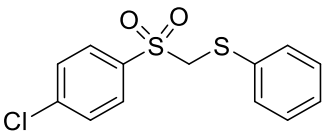
4-(4-(Phenylthio)butoxy)benzaldehyde 28: Prepared according to **General Method I** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (58.4 mg, 0.20 mmol, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.87 (1H, s), 7.81 (2H, d, J = 8.6 Hz), 7.35 – 7.32 (2H, m), 7.29 – 7.26 (2H, m), 7.20 – 7.15 (1H, m), 6.96 (2H, d, J = 8.4 Hz), 4.04 (2H, t, J = 6.2 Hz), 3.00 (2H, t, J = 7.1 Hz), 2.00 – 1.93 (2H, m), 1.88 – 1.80 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.9, 164.1, 136.4, 132.1, 130.0, 129.3, 129.0, 126.1, 114.8, 67.8, 33.4, 28.1, 25.7. The spectral data match those previously reported[28].



1-(4-(4-(Phenylthio)butoxy)phenyl)ethan-1-one 29: Prepared according to **General Method I** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (67.4 mg, 0.22 mmol, 75% yield). **M.p.** = 93.9 °C – 94.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (2H, d, J = 8.8 Hz), 7.35 – 7.32 (2H, m), 7.30 – 7.26 (2H, m), 7.20 – 7.15 (1H, m), 6.96 (2H, d, J = 8.9 Hz), 4.02 (2H, t, J = 6.2 Hz), 2.99 (2H, t, J = 7.1 Hz), 2.55 (3H, s), 1.99 – 1.90 (2H, m), 1.85 – 1.82 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.9, 162.9, 136.4, 130.7, 130.4, 129.3, 129.0, 126.1, 114.2, 67.6, 33.4, 28.2, 26.4, 25.7; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{18}H_{20}NaO_2S$: 323.1076, found: 323.1073.

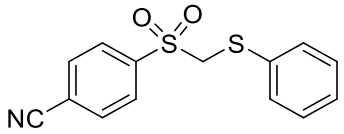


Methyl 4-(4-(phenylthio)butoxy)benzoate 30: Prepared according to **General Method I** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (66.5 mg, 0.20 mmol, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (2H, d, J = 8.9 Hz), 7.35 – 7.32 (2H, m), 7.29 – 7.26 (2H, m), 7.19 – 7.15 (1H, m), 6.88 (2H, d, J = 8.8 Hz), 4.01 (2H, t, J = 6.1 Hz), 3.88 (3H, s), 2.99 (2H, t, J = 7.1 Hz), 1.97 – 1.91 (2H, m), 1.87 – 1.80 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 162.8, 136.5, 131.7, 129.3, 129.0, 126.1, 122.6, 114.1, 67.6, 52.0, 33.5, 28.2, 25.8. The spectral data match those previously reported[28].

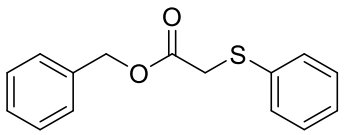


Methyl 4-(4-(phenylthio)butyl)benzoate 31: Prepared according to **General Method I** (Eluent: 100:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (51.9 mg, 0.17 mmol, 58% yield). **M.p.** = 63.9 °C – 64.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (2H, d, J = 8.6 Hz), 7.44 (2H, d, J =

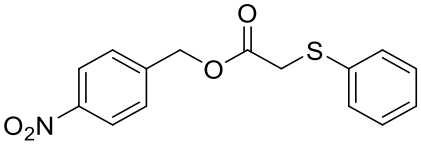
8.6 Hz), 7.34 – 7.31 (2H, m), 7.26 – 7.22 (3H, m), 4.36 (2H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.0, 136.0, 132.6, 131.6, 130.6, 129.5, 129.4, 128.3, 59.8; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{13}H_{11}ClNaO_2S_2$: 320.9781, found: 320.9773.



4-(((Phenylthio)methyl)sulfonyl)benzonitrile 32: Prepared according to **General Method I** (Eluent: 100:1 to 4:1 petroleum ether: ethyl acetate) and the title compound was isolated as a brown solid (55.7 mg, 0.19 mmol, 64% yield). **M.p.** = 80.1 °C – 80.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (2H, d, J = 8.5 Hz), 7.77 (2H, d, J = 8.5 Hz), 7.32 – 7.30 (2H, m), 7.28 – 7.22 (3H, m), 4.41 (2H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.8, 132.8, 132.2, 131.6, 129.9, 129.5, 128.6, 117.8, 117.1, 59.5; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{14}H_{11}NNaO_2S_2$: 312.0123, found: 312.0127.

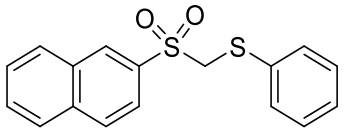


Benzyl 2-(phenylthio)acetate 33: Prepared according to **General Method I** (Eluent: 100:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow oil (48.0 mg, 0.19 mmol, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (2H, m), 7.34 – 7.32 (2H, m), 7.31 – 7.30 (1H, m), 7.29 – 7.25 (3H, m), 7.25 – 7.23 (1H, m), 7.23 – 7.19 (1H, m), 5.13 (2H, s), 3.67 (2H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.7, 135.4, 134.9, 130.2, 129.2, 128.7, 128.5, 128.4, 127.1, 67.3, 36.8. The spectral data match those previously reported[36].

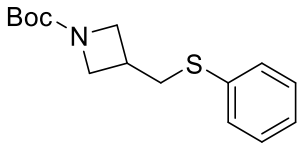


4-Nitrobenzyl 2-(phenylthio)acetate 34: Prepared according to **General Method I** (Eluent: 100:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow oil (58.4 mg, 0.19 mmol, 64% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (2H, d, J = 8.7 Hz), 7.40 – 7.38 (2H, m), 7.38 – 7.37 (2H, m), 7.31 – 7.26 (2H, m), 7.26 – 7.22 (1H, m), 5.21 (2H, s), 3.72 (2H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ

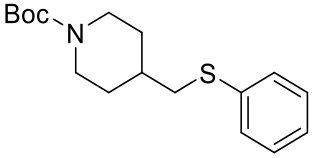
169.4, 147.8, 142.7, 134.5, 130.3, 129.3, 128.4, 127.4, 123.8, 65.6, 36.6; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{15}H_{13}NNaO_4S$: 326.0457, found: 326.0459.



((Naphthalen-2-ylsulfonyl)methyl)(phenyl)sulfane 35: Prepared according to **General Method I** (Eluent: 100:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow solid (51.0 mg, 0.16 mmol, 54% yield). **M.p.** = 58.3 ºC – 59.1 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (1H, s), 7.94 (1H, d, J = 8.1 Hz), 7.89 (1H, d, J = 4.1 Hz), 7.87 (1H, d, J = 3.5 Hz), 7.82 (1H, dd, J = 8.6, 1.9 Hz), 7.68 – 7.59 (2H, m), 7.29 (2H, dd, J = 7.6, 2.1 Hz), 7.11 – 7.05 (3H, m), 4.43 (2H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.6, 134.6, 132.8, 132.1, 131.6, 131.3, 129.6, 129.5, 129.2, 128.1, 128.0, 127.8, 123.3, 59.9 (one carbon was missing due to overlap); **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{17}H_{14}NaO_2S_2$: 337.0327, found: 337.0319.

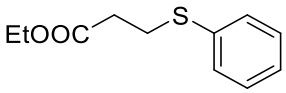


***tert*-Butyl 3-((phenylthio)methyl)azetidine-1-carboxylate 36:** Prepared according to **General Method I** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow oil (54.5 mg, 0.20 mmol, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (2H, d, J = 7.5 Hz), 7.31 – 7.27 (2H, m), 7.24 – 7.19 (1H, m), 4.00 (2H, t, J = 8.4 Hz), 3.63 (2H, dd, J = 8.8, 5.3 Hz), 3.11 (2H, d, J = 7.8 Hz), 2.68 (1H, tt, J = 8.0, 5.3 Hz), 1.43 (9H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.4, 135.2, 130.4, 129.1, 126.8, 79.5, 54.3, 38.5, 28.5, 28.4; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{15}H_{21}NNaO_2S$: 302.1185, found: 302.1182.

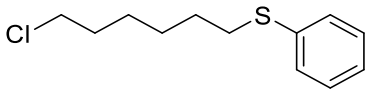


***tert*-Butyl 4-((phenylthio)methyl)piperidine-1-carboxylate 37:** Prepared according to **General Method I** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the

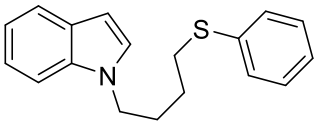
title compound was isolated as a yellow oil (67.4 mg, 0.22 mmol, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.23 (2H, m), 7.23 – 7.18 (2H, m), 7.12 – 7.08 (1H, m), 4.02 (2H, s), 2.77 (2H, d, J = 7.2 Hz), 2.59 (2H, t, J = 12.9 Hz), 1.78 (2H, d, J = 13.8 Hz), 1.65 – 1.55 (1H, m), 1.38 (9H, s), 1.15 – 1.05 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.9, 136.9, 129.1, 129.0, 125.9, 79.5, 43.8, 40.2, 36.1, 31.7, 28.5; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{17}H_{25}NNaO_2S$: 330.1498, found: 330.1507.



Methyl 3-(phenylthio)propanoate 38: Prepared according to **General Method I** (Eluent: 100:1 to 30:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (49.9 mg, 0.24 mmol, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.36 (2H, m), 7.32 – 7.30 (2H, m), 7.29 – 7.19 (1H, m), 4.14 (2H, q, J = 7.1 Hz), 3.17 (2H, t, J = 7.4 Hz), 2.62 (2H, t, J = 7.4 Hz), 1.25 (3H, t, J = 7.1 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 135.4, 130.2, 129.2, 126.7, 60.9, 34.6, 29.2, 14.3. The spectral data match those previously reported[37].

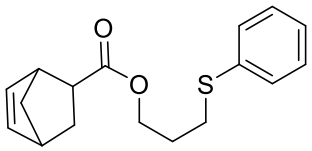


(6-Chlorohexyl)(phenyl)sulfane 39: Prepared according to **General Method I** (Eluent: petroleum ether) and the title compound was isolated as a colorless oil (45.2 mg, 0.20 mmol, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (4H, m), 7.19 – 7.14 (1H, m), 3.52 (2H, t, J = 6.7 Hz), 2.92 (2H, t, J = 7.3 Hz), 1.80 – 1.73 (2H, m), 1.70 – 1.63 (2H, m), 1.47 – 1.43 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.9, 129.1, 129.0, 125.9, 45.1, 33.6, 32.6, 29.1 28.1, 26.5.The spectral data match those previously reported[38].

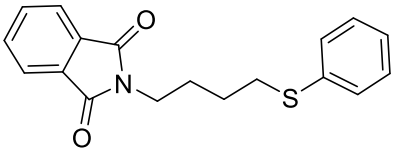


1-(4-(Phenylthio)butyl)-1H-indole 40: Prepared according to **General Method I** (Eluent: 100:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a brown oil (61.2 mg, 0.22 mmol, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$)

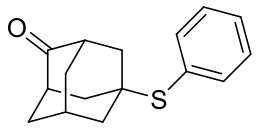
δ 7.61 (1H, d, J = 8.0 Hz), 7.29 (1H, d, J = 8.2 Hz), 7.26 – 7.22 (3H, m), 7.21 – 7.16 (2H, m), 7.15 – 7.11 (1H, m), 7.10 – 7.06 (1H, m), 7.00 (1H, d, J = 3.1 Hz), 6.45 (1H, d, J = 3.1 Hz), 4.05 (2H, t, J = 7.0 Hz), 2.84 (2H, t, J = 7.1 Hz), 1.95 – 1.89 (2H, m), 1.63 – 1.58 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.3, 135.9, 129.5, 129.0, 128.7, 127.7, 126.1, 121.5, 121.1, 119.4, 109.4, 101.2, 45.9, 33.4, 29.2, 26.5. The spectral data match those previously reported[28].



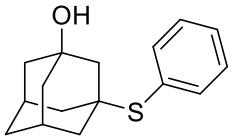
3-(Phenylthio)propyl bicyclo[2.2.1]hept-5-ene-2-carboxylate 41: Prepared according to **General Method I** (Eluent: 100:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (48.4 mg, 0.17 mmol, 56% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (2H, d, J = 7.3 Hz), 7.31 – 7.27 (2H, m), 7.21 – 7.19 (1H, m), 6.20 – 6.18 (1H, m), 5.92 – 5.89 (1H, m), 4.13 (2H, td, J = 6.3, 1.5 Hz), 3.20 (1H, s), 3.00 – 2.94 (3H, m), 2.91 – 2.90 (1H, m), 1.95 – 1.89 (3H, m), 1.44 – 1.40 (2H, m), 1.27 (1H, d, J = 8.5 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.8, 138.0, 136.1, 132.4, 129.5, 129.1, 126.2, 62.7, 49.7, 45.8, 43.4, 42.6, 30.4, 29.3, 28.5. The spectral data match those previously reported[28].



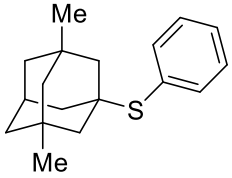
3-(Phenylthio)propyl bicyclo[2.2.1]hept-5-ene-2-carboxylate 42: Prepared according to **General Method I** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (72.6 mg, 0.23 mmol, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.81 (2H, m), 7.71 – 7.69 (2H, m), 7.30 (2H, d, J = 7.8 Hz), 7.25 – 7.22 (2H, m), 7.15 – 7.11 (1H, m), 3.69 (2H, t, J = 7.1 Hz), 2.95 (2H, t, J = 7.2 Hz), 1.87 – 1.79 (2H, m), 1.71 – 1.63 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 136.3, 134.0, 132.1, 129.4, 128.9, 126.0, 123.3, 37.5, 33.2, 27.7, 26.3. The spectral data match those previously reported[28].



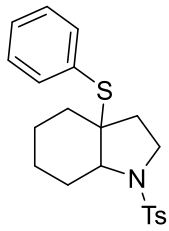
(1*R*,3*S*,5*s*,7*s*)-5-(phenylthio)adamantan-2-one 43: Prepared according to **General Method I** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (69.9 mg, 0.27 mmol, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (2H, d, J = 6.9 Hz), 7.41 – 7.36 (1H, m), 7.35 – 7.31 (2H, m), 2.54 (2H, s), 2.18 (1H, s), 2.14 – 2.07 (2H, m), 2.06 – 2.03 (4H, m), 1.97– 1.89 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 216.6, 137.8, 129.7, 129.3, 128.7, 47.3, 45.9, 44.4, 42.3, 38.1, 29.0. The spectral data match those previously reported[39].



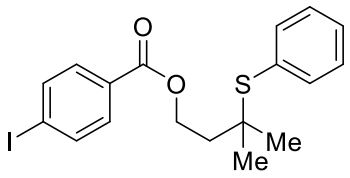
(1*r*,3*s*,5*R*,7*S*)-3-(phenylthio)adamantan-1-ol 44: Prepared according to **General Method I** (Eluent: 100:1 to 3:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (70.9 mg, 0.27 mmol, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (2H, d, J = 6.5 Hz), 7.38 – 7.29 (3H, m), 2.21 (2H, s), 1.75 (3H, d, J = 8.6 Hz), 1.76 – 1.68 (4H, m), 1.64 – 1.55 (4H, m), 1.49 (2H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.8, 130.0, 128.9, 128.5, 69.6, 51.1, 49.0, 44.0, 42.2, 34.7, 31.5. The spectral data match those previously reported[40].



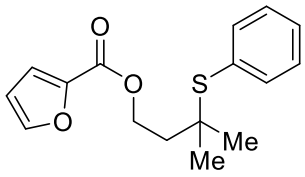
((1*r*,3*R*,5*S*,7*r*)-3,5-dimethyladamantan-1-yl)(phenyl)sulfane 45: Prepared according to **General Method I** (Eluent: 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (63.4 mg, 0.23 mmol, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (2H, d, J = 6.5 Hz), 7.39 – 7.30 (3H, m), 2.10 – 2.07 (1H, m), 1.63 (1H, s), 1.49 – 1.39 (4H, m), 1.31 – 1.22 (4H, m), 1.12 – 1.04 (2H, m), 0.80 (6H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.8, 130.6, 128.7, 128.5, 50.5, 49.7, 48.9, 42.5, 42.2, 32.9, 30.8, 30.4. The spectral data match those previously reported[40].



3a-(Phenylthio)-1-tosyloctahydro-1H-indole 46: Prepared according to **General Method I** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow solid (102.3 mg, 0.26 mmol, 88% yield). **M.p.** = 62.5 ºC – 63.1 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (2H, d, J = 8.3 Hz), 7.36 – 7.31 (2H, m), 7.31 – 7.28 (2H, m), 7.27 – 7.25 (3H, m), 3.53 – 3.44 (2H, m), 3.31 (1H, dd, J = 7.4, 5.0 Hz), 2.40 (3H, s), 2.15 – 2.08 (1H, m), 1.96 – 1.91 (1H, m), 1.89 – 1.80 (1H, m), 1.76 – 1.70 (2H, m), 1.63 – 1.54 (3H, m), 1.36 – 1.28 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.2, 137.3, 135.0, 130.6, 129.6, 129.2, 128.8, 127.6, 63.2, 56.9, 46.0, 34.0, 33.8, 29.7, 21.9, 21.7, 21.6; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{21}H_{25}NNaO_2S_2$: 410.1219, found: 410.1221.

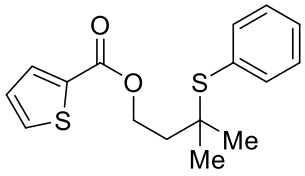


3-Methyl-3-(phenylthio)butyl 4-iodobenzoate 47: Prepared according to **General Method I** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (99.1 mg, 0.24 mmol, 78% yield). **M.p.** = 69.1 ºC – 69.7 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (2H, d, J = 8.6 Hz), 7.66 (2H, d, J = 8.5 Hz), 7.47 (2H, d, J = 6.4 Hz), 7.29 – 7.24 (3H, m), 4.49 (2H, t, J = 7.0 Hz), 1.87 (2H, t, J = 7.0 Hz), 1.25 (6H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 137.8, 137.7, 131.7, 131.1, 129.9, 129.1, 128.8, 100.9, 62.7, 47.7, 40.3, 29.3; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{18}H_{19}INaO_2S$: 449.0043, found: 449.0053.

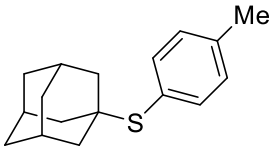


3-Methyl-3-(phenylthio)butyl furan-2-carboxylate 48: Prepared according to

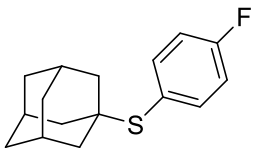
General Method I (Eluent: 100:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (56.5 mg, 0.19 mmol, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (1H, s), 7.47 (2H, dd, J = 7.8, 1.7 Hz), 7.32 – 7.29 (1H, m), 7.28 – 7.24 (2H, m), 7.09 (1H, dd, J = 3.5, 0.7 Hz), 6.43 (1H, dd, J = 3.5, 1.7 Hz), 4.49 (2H, t, J = 7.1 Hz) 1.86 (2H, t, J = 7.1 Hz), 1.24 (6H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 146.4, 144.9, 137.7, 131.7, 129.1, 128.8, 118.0, 111.9, 62.4, 47.7, 40.3, 29.2; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{16}H_{18}NaO_3S$: 313.0869, found: 313.0866.



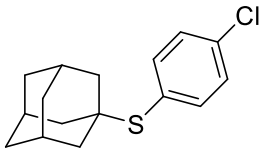
3-Methyl-3-(phenylthio)butyl thiophene-2-carboxylate 49: Prepared according to **General Method I** (Eluent: 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (78.4 mg, 0.26 mmol, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (1H, dd, J = 3.8, 1.2 Hz), 7.56 – 7.54 (3H, m), 7.39 – 7.32 (3H, m), 7.10 (1H, dd, J = 5.0, 3.8 Hz), 4.56 (2H, t, J = 6.9 Hz), 1.94 (2H, t, J = 6.9 Hz), 1.33 (6H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2, 137.6, 133.9, 133.4, 132.4, 131.7, 129.0, 128.7, 127.8, 62.5, 47.7, 40.2, 29.1; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{15}H_{16}NaO_2S_2$: 315.0484, found: 315.0481.



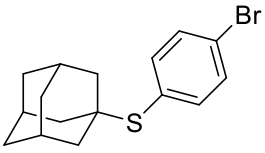
((3*s*,5*s*,7*s*)-Adamantan-1-yl)(*p*-tolyl)sulfane 50: Prepared according to **General Method I** (Eluent: petroleum ether) and the title compound was isolated as a white solid (64.7 mg, 0.25 mmol, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (2H, d, J = 8.0 Hz), 7.13 (2H, d, J = 7.8 Hz), 2.36 (3H, s), 2.01 (3H, s), 1.80 (6H, d, J = 2.8 Hz), 1.67 – 1.57 (6H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.7, 137.7, 129.2, 127.1, 47.7, 43.7, 36.3, 30.1, 21.4. The spectral data match those previously reported[41].



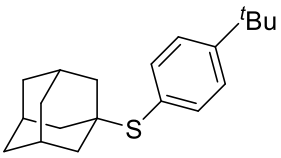
((3*s*,5*s*,7*s*)-Adamantan-1-yl)(*p*-tolyl)sulfane 51: Prepared according to **General Method I** (Eluent: petroleum ether) and the title compound was isolated as a white solid (69.5 mg, 0.26 mmol, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.44 (2H, m), 7.03 – 6.99 (2H, m), 2.01 (3H, s), 1.78 (6H, s), 1.67 – 1.57 (6H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.4 (d, J = 249.5 Hz), 139.5 (d, J = 83.1 Hz), 125.9 (d, J = 34.3 Hz), 115.5 (d, J = 21.6 Hz), 47.9, 43.6, 36.2, 30.0; **^{19}F NMR** (471 MHz, CD_3COCD_3) δ –113.0 – –113.1 (1F, m). The spectral data match those previously reported[41].



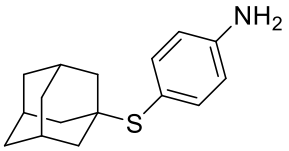
((3s,5s,7s)-Adamantan-1-yl)(4-chlorophenyl)sulfane 52: Prepared according to **General Method I** (Eluent: petroleum ether) and the title compound was isolated as a white solid (80.6 mg, 0.29 mmol, 96% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (2H, d, J = 8.5 Hz), 7.28 (2H, d, J = 8.5 Hz), 2.01 (3H, s), 1.78 (6H, d, J = 2.9 Hz) 1.62 – 1.57 (6H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.9, 135.2, 129.2, 128.6, 48.3, 43.6, 36.2, 30.1. The spectral data match those previously reported[42].



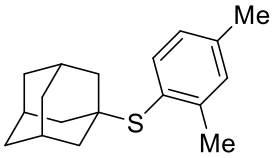
((3s,5s,7s)-Adamantan-1-yl)(4-bromophenyl)sulfane 53: Prepared according to **General Method I** (Eluent: petroleum ether) and the title compound was isolated as a white solid (81.9 mg, 0.25 mmol, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (2H, d, J = 8.3 Hz), 7.35 (2H, d, J = 8.3 Hz), 2.01 (3H, s), 1.79 (2H, d, J = 2.3 Hz), 1.67 – 1.58 (6H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.2, 131.6, 129.8, 123.5, 48.3, 43.7, 36.2, 30.1. The spectral data match those previously reported[42].



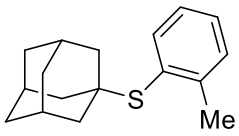
((3s,5s,7s)-Adamantan-1-yl)(4-(*tert*-butyl)phenyl)sulfane 54: Prepared according to **General Method I** (Eluent: petroleum ether) and the title compound was isolated as a white solid (60.2 mg, 0.20 mmol, 67% yield). **M.p.** = 85.4 ºC – 85.9 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (2H, d, J = 8.3 Hz), 7.33 (2H, d, J = 8.4 Hz), 2.02 (3H, s), 1.83 – 1.82 (6H, m) 1.68 – 1.58 (6H, m), 1.33 (9H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.7, 137.3, 127.0, 125.4, 47.6, 43.6, 36.2, 34.6, 31.3, 30.0; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{20}H_{28}NaS$: 323.1804, found: 323.1813.



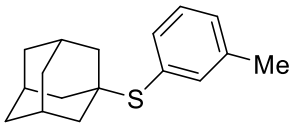
4-(((3*s*,5*s*,7*s*)-Adamantan-1-yl)thio)aniline 55: Prepared according to **General Method I** (Eluent: 100:1 to 2:1 petroleum ether: ethyl acetate) and the title compound was isolated as a grey solid (42.2 mg, 0.16 mmol, 54% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (2H, d, J = 8.4 Hz), 6.64 (2H, d, J = 8.4 Hz), 3.77 (2H, brs), 2.02 (2H, s), 1.80 – 1.79 (6H, m) 1.67 – 1.59 (6H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.1, 139.1, 118.6, 115.0, 47.4, 43.5, 36.4, 30.1. The spectral data match those previously reported[44].



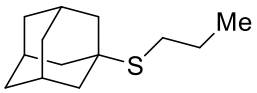
((3*s*,5*s*,7*s*)-Adamantan-1-yl)(2,4-dimethylphenyl)sulfane 56: Prepared according to **General Method I** (Eluent: petroleum ether) and the title compound was isolated as a white solid (64.4 mg, 0.24 mmol, 79% yield). **M.p.** = 51.3 ºC – 52.1 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (1H, d, J = 7.8 Hz), 7.10 (1H, s), 6.95 (1H, d, J = 7.6 Hz), 2.48 (3H, s), 2.32 (3H, s), 2.00 (3H, s), 1.84 (6H, d, J = 2.8 Hz) 1.62 – 1.58 (6H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.9, 139.4, 138.9, 131.3, 126.8, 126.5, 49.2, 43.8, 36.3, 30.1, 22.1, 21.3; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{18}H_{24}NaS$: 295.1491, found: 295.1499.



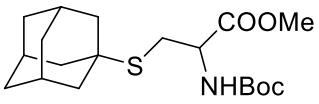
((3*s*,5*s*,7*s*)-Adamantan-1-yl)(*o*-tolyl)sulfane 57: Prepared according to **General Method I** (Eluent: petroleum ether) and the title compound was isolated as a white solid (66.8 mg, 0.26 mmol, 86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (1H, d, J = 7.5 Hz), 7.29 – 7.22 (2H, m), 7.15 – 7.11 (1H, m), 2.52 (3H, s), 2.00 (3H, s), 1.86 – 1.85 (6H, m), 1.67 – 1.57 (6H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.2, 139.4, 130.4, 130.3, 128.9, 125.6, 49.5, 43.9, 36.3, 30.1, 22.2. The spectral data match those previously reported[40].



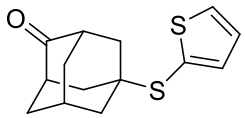
((3*s*,5*s*,7*s*)-Adamantan-1-yl)(*m*-tolyl)sulfane 58: Prepared according to **General Method I** (Eluent: petroleum ether) and the title compound was isolated as a white solid (57.2 mg, 0.22 mmol, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.30 (2H, m), 7.23 – 7.16 (2H, m), 2.36 (3H, s), 2.01 (3H, s), 1.81 (6H, d, J = 2.8 Hz) 1.67 – 1.57 (6H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.4, 138.1, 134.8, 130.3, 129.5, 128.2, 47.8, 43.8, 36.3, 30.1, 21.4. The spectral data match those previously reported[44].



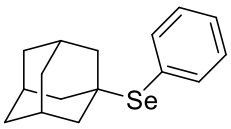
2-(((3*s*,5*s*,7*s*)-Adamantan-1-yl)thio)thiophene 59: Prepared according to **General Method I** (Eluent: petroleum ether) and the title compound was isolated as a colorelss oil (37.0 mg, 0.18 mmol, 59% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.48 (2H, t, J = 7.5 Hz), 2.03 (3H, s), 1.86 (6H, d, J = 3.0 Hz), 1.72 – 1.63 (6H, m), 1.60 – 1.52 (2H, m), 0.98 (3H, t, J = 7.3 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 44.1, 43.8, 36.5, 29.8, 27.8, 23.8, 14.0; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{13}H_{22}NaS$: 233.1334, found: 233.1336.



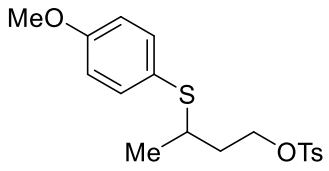
Methyl *S*-((3*s*,5*s*,7*s*)-adamantan-1-yl)-*N*-(*tert*-butoxycarbonyl)cysteinate 60: Prepared according to **General Method I** (Eluent: 100:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (58.3 mg, 0.16 mmol, 53% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.32 (1H, d, J = 8.1 Hz), 4.52 (1H, dt, J = 8.6, 5.0 Hz), 3.73 (3H, s), 2.94 (2H, d, J = 5.0 Hz), 2.01 (3H, s), 1.80 (6H, s), 1.69 – 1.60 (6H, m), 1.42 (9H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.6, 155.2, 80.0, 53.4, 52.6, 44.8, 43.4, 36.2, 29.7, 28.4, 28.2; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{19}H_{31}NNaO_4S$: 392.1866, found: 392.1864.



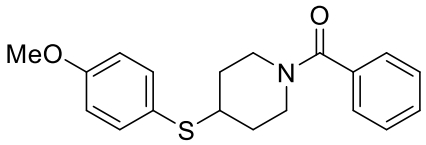
2-(((3*s*,5*s*,7*s*)-Adamantan-1-yl)thio)thiophene 61: Prepared according to **General Method I** (Eluent: petroleum ether) and the title compound was isolated as a grey solid (74.0 mg, 0.28 mmol, 93% yield). **M.p.** = 88.8 ºC – 89.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (1H, dd, J = 5.4, 1.2 Hz), 7.13 (1H, dd, J = 3.5, 1.2 Hz), 7.04 (1H, dd, J = 5.4, 3.5 Hz), 2.58 (2H, s), 2.22 (1H, s), 2.19 – 2.11 (2H, m), 2.11 – 2.04 (4H, m), 2.01 – 1.91 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 216.5, 137.7, 131.6, 128.6, 127.9, 47.3, 46.7, 44.0, 42.0, 38.1, 29.8, 29.2; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{14}H_{17}OS_2$: 265.0715, found: 265.0713.



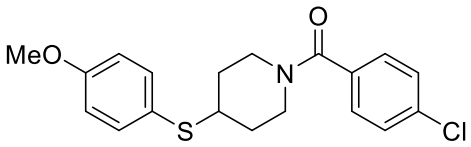
((3*s*,5*s*,7*s*)-Adamantan-1-yl)(phenyl)selane 62: Prepared according to **General Method I** (Eluent: petroleum ether) and the title compound was isolated as a colorless oil (35.5 mg, 0.12 mmol, 41% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (2H, d, J = 6.5 Hz), 7.38 – 7.28 (1H, m), 7.32 – 7.27 (2H, m), 1.97 (9H, s), 1.69 – 1.60 (6H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.5, 128.6, 128.5, 126.4, 47.1, 44.8, 36.3, 30.8. The spectral data match those previously reported[45].



3-((4-methoxyphenyl)thio)butyl 4-methylbenzenesulfonate 63: Prepared according to **General Method I** (Eluent: 100:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a brown oil (78.3 mg, 0.21 mmol, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (2H, d, J = 8.4 Hz), 7.34 (2H, d, J = 8.0 Hz), 7.29 (2H, d, J = 8.7 Hz), 6.82 (2H, d, J = 8.7 Hz), 4.25 – 4.14 (2H, m), 3.80 (3H, s), 3.04 (1H, q, J = 6.9 Hz), 2.45 (3H, s), 1.83 – 1.75 (2H, m), 1.18 (3H, d, J = 6.8 Hz); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 144.9, 136.3, 133.1, 130.0, 128.0, 123.6, 114.6, 68.3, 55.4, 40.7, 35.4, 21.8, 21.3; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{18}H_{22}NaO_4S_2$: 389.0852, found: 389.0845.

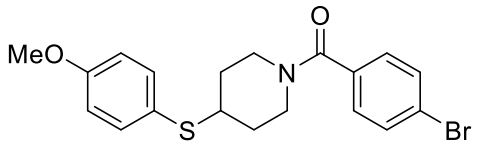


(4-((4-Methoxyphenyl)thio)piperidin-1-yl)(phenyl)methanone 64: Prepared according to **General Method I** (Eluent: 100:1 to 3:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow oil (69.5 mg, 0.21 mmol, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (7H, m), 6.85 (2H, d, J = 8.4 Hz), 4.46 (1H, s), 3.80 (3H, s), 3.72 (1H, s), 3.15 – 3.11 (1H, m), 3.10 – 3.03 (2H, m), 1.92 (2H, d, J = 64.2 Hz), 1.55 (2H, d, J = 48.9 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.4, 159.9, 136.3, 136.1, 129.7, 128.6, 126.9, 123.5, 114.6, 55.4, 47.2, 45.6, 41.7, 32.8, 32.0; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{19}H_{21}NNaO_2S$: 350.1185, found: 350.1188.



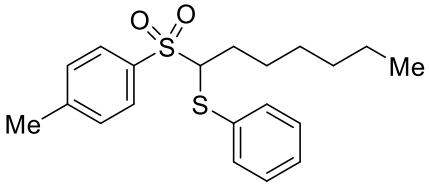
(4-Chlorophenyl)(4-((4-methoxyphenyl)thio)piperidin-1-yl)methanone 65: Prepared according to **General Method I** (Eluent: 100:1 to 4:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow solid (71.3 mg, 0.20 mmol, 66% yield). **M.p.** = 76.4 ºC – 76.9 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (2H, d, J =

8.8 Hz), 7.36 (2H, d, *J* = 8.5 Hz), 7.30 (2H, d, *J* = 8.5 Hz), 6.84 (2H, d, *J* = 8.7 Hz), 4.42 (1H, s), 3.79 (3H, s), 3.68 (1H, s), 3.14 – 3.02 (3H, m), 1.92 (2H, d, *J* = 54.8 Hz), 1.53 (2H, d, *J* = 38.7 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 169.3, 159.9, 136.3, 135.7, 134.4, 128.8, 128.5, 123.3, 114.6, 55.4, 47.2, 45.4, 41.7, 32.7, 31.9; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{19}H_{20}ClNNaO_2S$: 384.0795, found: 384.0799.



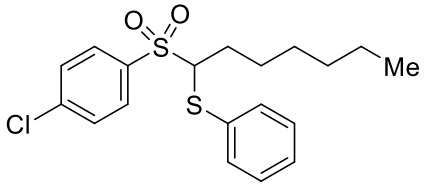
(4-Chlorophenyl)(4-((4-methoxyphenyl)thio)piperidin-1-yl)methanone 66: Prepared according to **General Method I** (Eluent: 100:1 to 4:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow solid (78.0 mg, 0.19 mmol, 64% yield). **M.p.** = 80.1 °C – 80.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.52 (2H, d, *J* = 8.3 Hz), 7.39 (2H, d, *J* = 8.7 Hz), 7.24 (2H, d, *J* = 8.4 Hz), 6.84 (2H, d, *J* = 8.8 Hz), 4.42 (1H, s), 3.79 (3H, s), 3.68 (1H, s), 3.15 – 3.02 (3H, m), 1.99 – 1.85 (2H, m), 1.60 – 1.48 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 169.3, 159.9, 136.3, 134.8, 131.8, 128.7, 124.0, 123.3, 114.6, 55.4, 47.2, 45.4, 41.7, 32.8, 31.9; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{19}H_{20}BrNNaO_2S$: 428.0290, found: 428.0296.

5. Synethetic application of current method

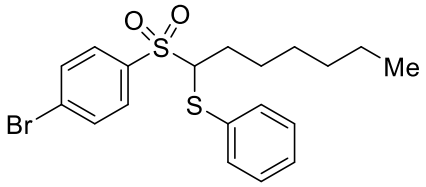


Phenyl(1-tosylheptyl)sulfane 68: Prepared according to **General Method I** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (63.4 mg, 0.17 mmol, 58% yield). **M.p.** = 38.0 °C – 38.1 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.77 (2H, d, *J* = 8.3 Hz), 7.30 – 7.28 (2H, m), 7.27 – 7.26 (2H, m), 7.24 – 7.21 (2H, m), 7.20 – 7.18 (1H, m), 4.06 (1H, dd, *J* = 11.3, 2.9 Hz), 2.43 (3H, s), 2.31 – 2.23 (1H, m), 1.86 – 1.76 (1H, m), 1.68 – 1.58 (1H, m), 1.54 – 1.45 (1H, m), 1.36 – 1.21 (6H, m), 0.88 – 0.85 (3H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ*

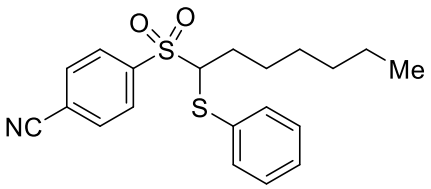
144.9, 133.9, 133.4, 132.8, 129.8, 129.6, 129.1, 128.2, 74.1, 31.5, 28.7, 28.7, 26.8, 22.6, 21.8, 14.2; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{20}H_{26}NaO_2S_2$: 385.1266, found: 385.1260.



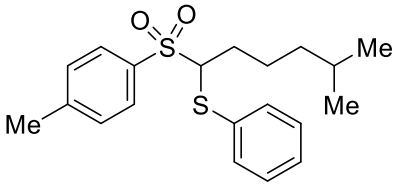
(1-((4-Chlorophenyl)sulfonyl)heptyl)(phenyl)sulfane 69: Prepared according to **General Method I** (Eluent: 100:1 to 30:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow solid (88.7 mg, 0.23 mmol, 77% yield). **M.p.** = 48.1 ºC – 49.1 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (2H, d, J = 8.7 Hz), 7.41 (2H, d, J = 8.6 Hz), 7.25 – 7.23 (3H, m), 7.21 – 7.18 (2H, m), 4.10 (1H, dd, J = 11.2, 2.9 Hz), 2.33 – 2.26 (1H, m), 1.86 – 1.79 (1H, m), 1.70 – 1.61 (1H, m), 1.57 – 1.49 (1H, m), 1.38 – 1.24 (6H, m), 0.89 – 0.86 (3H, m); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.7, 135.5, 133.1, 132.6, 131.2, 129.2, 128.4, 74.1, 31.5, 28.7, 28.4, 26.7, 22.6, 14.1 (one carbon was missing due to overlap); **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{19}H_{23}ClNaO_2S_2$: 405.0720, found: 405.0727.



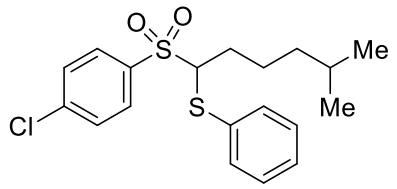
(1-((4-Bromophenyl)sulfonyl)heptyl)(phenyl)sulfane 70: Prepared according to **General Method I** (Eluent: 100:1 to 30:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow solid (84.7 mg, 0.20 mmol, 66% yield). **M.p.** = 53.3 ºC – 54.1 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (2H, d, J = 8.7 Hz), 7.58 (2H, d, J = 8.6 Hz), 7.27 – 7.19 (5H, m), 4.10 (1H, dd, J = 11.2, 3.0 Hz), 2.34 – 2.26 (1H, m), 1.89 – 1.79 (1H, m), 1.72 – 1.60 (1H, m), 1.59 – 1.48 (1H, m), 1.38 – 1.24 (6H, m), 0.90 – 0.86 (3H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.0, 133.1, 132.6, 132.2, 131.2, 129.4, 129.2, 128.4, 74.1, 31.5, 28.7, 28.3, 26.8, 22.6, 14.2; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{19}H_{23}BrNaO_2S_2$: 449.0215, found: 449.0215.



4-((1-(Phenylthio)heptyl)sulfonyl)benzonitrile 71: Prepared according to **General Method I** (Eluent: 100:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow solid (54.3 mg, 0.15 mmol, 48% yield). **M.p.** = 56.4 °C – 56.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (2H, d, J = 8.4 Hz), 7.73 (2H, d, J = 8.4 Hz), 7.29 – 7.23 (1H, m), 7.22 – 7.19 (3H, m), 7.17 – 7.16 (1H, m), 4.17 (1H, dd, J = 11.2, 3.0 Hz), 2.37 – 2.28 (1H, m), 1.91 – 1.81 (1H, m), 1.73 – 1.63 (1H, m), 1.60 – 1.51 (1H, m), 1.42 – 1.25 (6H, m), 0.90 – 0.85 (3H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.5, 132.7, 132.5, 132.3, 130.4, 129.3, 128.5, 117.5, 117.2, 73.7, 31.5, 28.7, 28.0, 26.7, 22.6, 14.1; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{20}H_{23}NNaO_2S_2$: 396.1062, found: 396.1055.

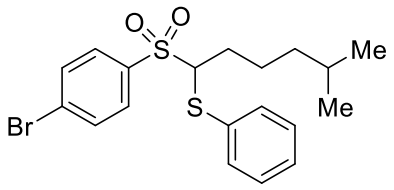


(5-Methyl-1-tosylhexyl)(phenyl)sulfane 72: Prepared according to **General Method I** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (61.2 mg, 0.17 mmol, 56% yield). **M.p.** = 48.1 °C – 48.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (2H, d, J = 8.2 Hz), 7.30 – 7.27 (4H, m), 7.24 – 7.18 (3H, m), 4.07 (1H, dd, J = 11.3, 2.9 Hz), 2.43 (3H, s), 2.29 – 2.21 (1H, m), 1.84 – 1.77 (1H, m), 1.66 – 1.58 (1H, m), 1.55 – 1.43 (2H, m), 1.21 – 1.14 (2H, m), 0.86 (6H, d, J = 6.6 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.9, 133.9, 133.4, 132.9, 129.9, 129.6, 129.1, 128.3, 74.1, 38.3, 29.0, 27.8, 24.7, 22.8, 22.5, 21.8; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{20}H_{26}NaO_2S_2$: 385.1266, found: 385.1268.

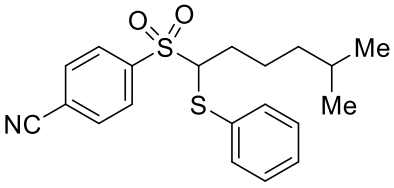


(1-((4-Chlorophenyl)sulfonyl)-5-methylhexyl)(phenyl)sulfane 73: Prepared

according to **General Method I** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow oil (60.5 mg, 0.16 mmol, 53% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (2H, d, J = 8.6 Hz), 7.43 (2H, d, J = 8.6 Hz), 7.26 – 7.19 (5H, m), 4.10 (1H, dd, J = 11.1, 2.9 Hz), 2.32– 2.24 (1H, m), 1.89 – 1.79 (1H, m), 1.63 – 1.59 (1H, m), 1.57 – 1.51 (2H, m), 1.23 – 1.18 (2H, m), 0.88 (6H, d, J = 6.6 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.8, 135.5, 133.1, 132.6, 131.2, 129.3, 129.2, 128.4, 74.1, 38.3, 28.7, 27.8, 24.7, 22.8, 22.5; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{19}H_{23}ClNaO_2S_2$: 405.0720, found: 405.0712.

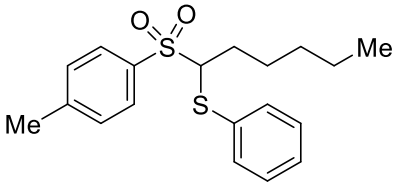


(1-((4-Bromophenyl)sulfonyl)-5-methylhexyl)(phenyl)sulfane 74: Prepared according to **General Method I** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow oil (61.8 mg, 0.14 mmol, 48% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (2H, d, J = 8.6 Hz), 7.59 (2H, d, J = 8.6 Hz), 7.26 – 7.24 (2H, m), 7.23 – 7.21 (3H, m), 4.10 (1H, dd, J = 11.1, 3.0 Hz), 2.32 – 2.24 (1H, m), 1.89 – 1.79 (1H, m), 1.69 – 1.62 (1H, m), 1.61 – 1.52 (2H, m), 1.26 – 1.18 (2H, m), 0.88 (6H, d, J = 6.6 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.0, 133.1, 132.6, 132.2, 131.3, 129.4, 129.3, 128.4, 74.1, 38.3, 28.6, 27.8, 24.7, 22.8, 22.5; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{19}H_{23}BrNaO_2S_2$: 449.0215, found: 449.0222.

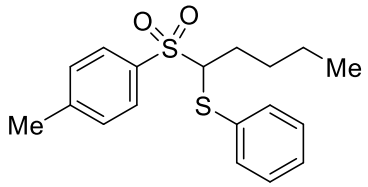


4-((5-Methyl-1-(phenylthio)hexyl)sulfonyl)benzonitrile 75: Prepared according to **General Method I** (Eluent: 100:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow oil (41.3 mg, 0.11 mmol, 37% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (2H, d, J = 8.4 Hz), 7.73 (2H, d, J = 8.4 Hz), 7.28 – 7.22 (2H, m), 7.21 – 7.17 (3H, m), 4.17 (1H, dd, J = 11.1, 3.0 Hz), 2.34 – 2.26 (1H, m), 1.91 – 1.81 (1H, m), 1.70 – 1.62 (1H, m), 1.60 – 1.52 (2H, m), 1.26 – 1.19 (2H, m),

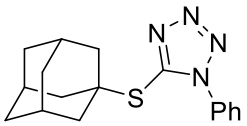
0.89 (6H, d, J = 6.7 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.5, 132.7, 132.5, 132.4, 130.4, 129.3, 128.6, 117.5, 117.2, 73.7, 38.2, 28.3, 27.8, 24.6, 22.7, 22.5; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{20}H_{23}NNaO_2S_2$: 396.1062, found: 396.1071.



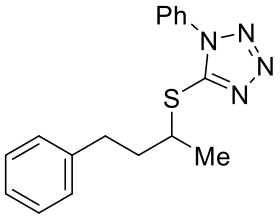
Phenyl(1-tosylhexyl)sulfane 76: Prepared according to **General Method I** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (47.5 mg, 0.14 mmol, 45% yield). **M.p.** = 41.1 ºC – 41.6 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (2H, d, J = 8.3 Hz), 7.30 – 7.28 (2H, m), 7.27 – 7.26 (2H, m), 7.24 – 7.17 (3H, m), 4.06 (1H, dd, J = 11.2, 2.9 Hz), 2.42 (3H, s), 2.31 – 2.23 (1H, m), 1.85 – 1.78 (1H, m), 1.68 – 1.61 (1H, m), 1.56 – 1.46 (1H, m), 1.34 – 1.22 (4H, m), 0.89 – 0.86 (3H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.9, 134.0, 133.4, 132.8, 129.8, 129.6, 129.1, 128.2, 74.1, 31.2, 28.7, 26.5, 22.4, 21.8, 14.1; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{19}H_{24}NaO_2S_2$: 371.1110, found: 371.1111.



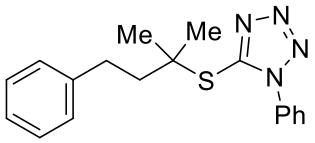
Phenyl(1-tosylpentyl)sulfane 77: Prepared according to **General Method I** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (67.2 mg, 0.20 mmol, 67% yield). **M.p.** = 38.3 ºC – 38.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (2H, d, J = 8.3 Hz), 7.29 – 7.26 (4H, m), 7.23 – 7.17 (3H, m), 4.06 (1H, dd, J = 11.3, 3.0 Hz), 2.42 (3H, s), 2.36 – 2.22 (1H, m), 1.82 – 1.77 (1H, m), 1.66 – 1.59 (1H, m), 1.54 – 1.49 (1H, m), 1.38 – 1.26 (2H, m), 0.90 (3H, t, J = 7.4 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.9, 133.9, 133.4, 132.8, 129.8, 129.6, 129.1, 128.2, 74.1, 28.9, 28.4, 22.2, 21.8, 13.9; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{18}H_{22}NaO_2S_2$: 357.0953, found: 357.0949.



5-(((3*s*,5*s*,7*s*)-Adamantan-1-yl)thio)-1-phenyl-1*H*-tetrazole 78: Prepared according to **General Method I** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (40.2 mg, 0.13 mmol, 43% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (5H, m), 2.18 (6H, d, J = 3.0 Hz), 2.10 (2H, s), 1.76 – 1.68 (6H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.0, 134.0, 130.2, 129.7, 125.0, 54.2, 43.1, 36.0, 30.3. The spectral data match those previously reported[46].

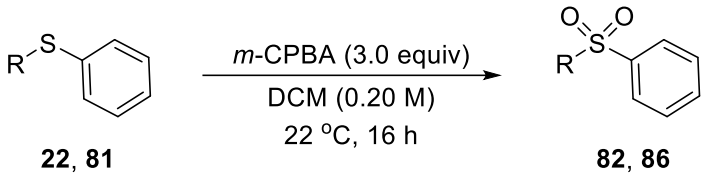


1-Phenyl-5-((4-phenylbutan-2-yl)thio)-1*H*-tetrazole 80: Prepared according to **General Method I** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (49.9 mg, 0.16 mmol, 54% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (5H, m), 7.29 – 7.20 (2H, m), 7.19 – 7.16 (3H, m), 4.06 (1H, q, J = 6.8 Hz), 2.80 – 2.75 (2H, m), 2.17 – 2.01 (2H, m), 1.56 (1H, d, J = 6.8 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.0, 140.9, 133.8, 130.2, 129.8, 128.6, 128.4, 126.2, 124.1. 44.4, 38.3, 33.2, 21.6. The spectral data match those previously reported[47].



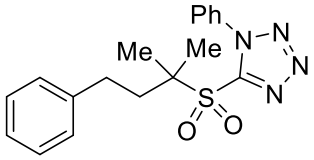
5-((2-Methyl-4-phenylbutan-2-yl)thio)-1-phenyl-1*H*-tetrazole 81: Prepared according to **General Method I** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (51.4 mg, 0.16 mmol, 53% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (5H, m), 7.27 – 7.24 (2H, m), 7.20 – 7.14 (3H, m), 2.73 – 2.69 (2H, m), 2.25 – 2.21 (2H, m), 1.63 (6H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.7, 141.5, 133.9, 130.3, 129.7, 128.6, 128.5, 126.1, 124.9.

55.2, 43.8, 31.6, 28.7; **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{18}H_{20}NaN_4S$: 347.1301, found: 347.1309.

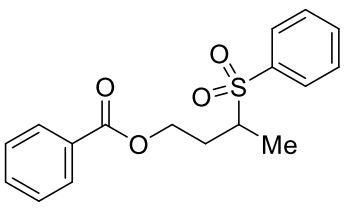


22, **81** **82**, **86**

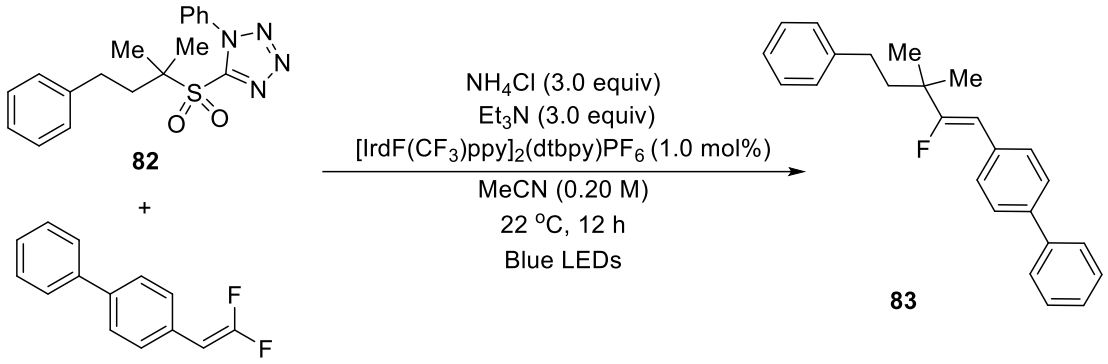
General Method J: A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with compound **22** or compound **81** (0.30 mmol, 1.0 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then DCM (1.5 mL) were added under N_2. The mixture was cooled at 0 °C and *m*-CPBA (155.3 mg, 0.90 mmol, 3.0 equiv) was added. Was allowed to warm to room temperature. The reaction was stirred at 22 °C for 16 h. The mixture was poured into $NaHCO_3$ aqueous solution (20.0 mL) and extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography.



5-((2-Methyl-4-phenylbutan-2-yl)sulfonyl)-1-phenyl-1*H*-tetrazole 82: Prepared according to **General Method J** (Eluent: 100:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (58.3 mg, 0.16 mmol, 55% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (5H, m), 7.57 – 7.52 (4H, m), 7.31 – 7.29 (1H, m), 7.27 – 7.26 (1H, m), 7.23 – 7.19 (1H, m), 7.14 (2H, d, J = 6.8 Hz), 2.72 – 2.68 (2H, m), 2.17 – 2.13 (2H, m), 1.59 (6H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.0, 140.4, 133.4, 131.6, 129.4, 128.8, 128.4, 126.6, 126.3, 67.8, 36.9, 30.1, 20.5; The spectral data match those previously reported[51].



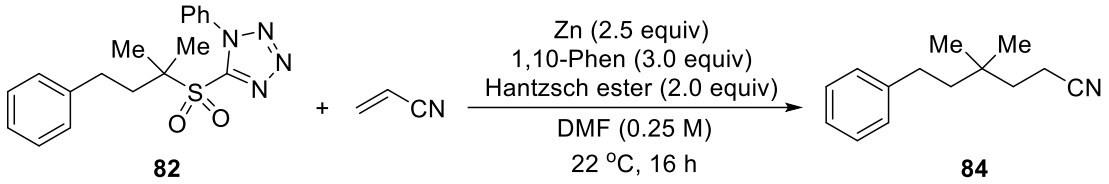
3-(Phenylsulfonyl)butyl benzoate 86: Prepared according to **General Method J** (Eluent: 100:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (83.3 mg, 0.22 mmol, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (2H, d, J = 6.9 Hz), 7.89 (2H, d, J = 7.0 Hz), 7.67 – 7.62 (1H, m), 7.57 – 7.53 (3H, m), 7.44 – 7.40 (2H, m), 4.46 – 4.33 (2H, m), 3.32 – 3.19 (1H, m), 2.52 – 2.44 (1H, m), 1.88 – 1.77 (1H, m), 1.35 (3H, d, J = 6.9 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 136.9, 133.9, 133.3, 129.7, 129.6, 129.3, 129.1, 128.5, 61.6, 57.3, 28.9, 13.5; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{17}H_{18}NaO_4S$: 341.0818, found: 341.0819.



A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with compound **82** (142.6 mg, 0.40 mmol, 2.0 equiv), 4-(2,2-difluorovinyl)-1,1'-biphenyl (43.2 mg, 0.20 mmol, 1.00 equiv), NH_4Cl (32.1 mg, 0.60 mmol, 3.0 equiv), Et_3N (121.4 mg, 1.2 mmol, 6.0 equiv) and $[IrF(CF_3)ppy](dtbpy)PF_6$ (2.2 mg, 0.02 mmol, 0.01 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then MeCN (1.0 mL) were added under N_2. The mixture was allowed to stir at 22 °C for 16 h with blue LEDs. The mixture was transferred to a round bottom flask and solvent was removed by rotary evaporation, the residue was purified by flash silica gel chromatography (Eluent: petroleum ether). The product **83** was isolated a colorless oil (60.9 mg, 0.18 mmol, 88% yield).

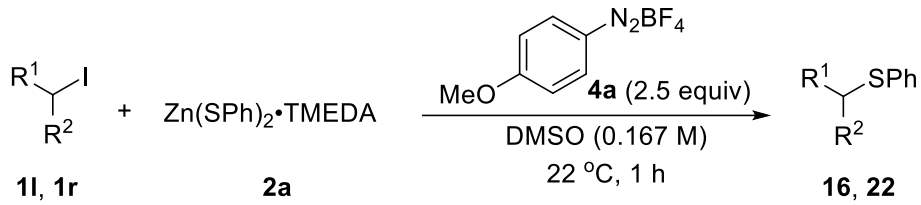
4-(2-fluoro-3,3-dimethyl-5-phenylpent-1-en-1-yl)-1,1'-biphenyl 83: E/Z = 93:7, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (2H, d, J = 7.6 Hz), 7.45 (2H, d, J = 8.0 Hz), 7.38 – 7.34 (2H, m), 7.28 – 7.24 (1H, m), 7.20 (2H, d, J = 8.1 Hz), 7.16 – 7.13 (2H, m), 7.09 – 7.06 (1H, m), 7.02 (2H, d, J = 7.0 Hz), 6.34 (1H, d, J = 27.4 Hz), 2.56 – 2.52 (2H,

m), 1.68 – 1.63 (2H, m), 1.01 (6H, s);**^{13}C NMR** (101 MHJz, $CDCl_3$) δ 166.5, 164.0, 142.7, 140.8, 139.8, 133.5 (d, $J_{C\text{-}F}$ = 15.3 Hz), 130.4 (d, $J_{C\text{-}F}$ = 2.3 Hz), 128.9, 128.5, 127.5, 127.1, 126.6, 125.8, 108.1 (d, $J_{C\text{-}F}$ = 33.5 Hz), 43.3 (d, $J_{C\text{-}F}$ = 2.1 Hz), 40.1, 39.8, 31.7, 27.2 (d, $J_{C\text{-}F}$ = 4.4 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ –101.4 (d, J = 27.4 Hz), –109.4 (d, J = 27.4 Hz). The spectral data match those previously reported[49].



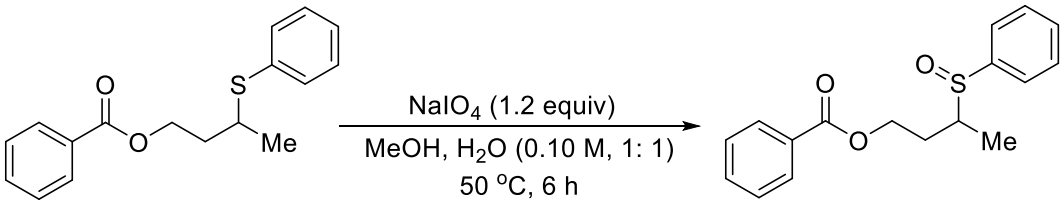
A 120 ºC oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with compound **82** (71.3 mg, 0.20 mmol, 1.0 equiv), acrylonitrile (21.2 mg, 0.40 mmol, 2.0 equiv), zinc powder (32.7 mg, 0.50 mmol, 2.5 equiv), 1,10-Phen (108.1 mg, 0.60 mmol, 3.0 equiv) and Hantzsch ester (101.3 mg, 0.40 mmol, 2.0 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then DMF (1.00 mL) were added under N_2. The mixture was allowed to stir at 22 ºC for 16 h with blue LEDs. The mixture was poured into water (20.0 mL) and extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: petroleum ether). The product **84** was isolated a colorless oil (33.2 mg, 0.16 mmol, 82% yield).

4,4-Dimethyl-6-phenylhexanenitrile 84: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (2H, m), 7.21 – 7.16 (3H, m), 2.57 – 2.53 (2H, m), 2.32 – 2.27 (2H, m), 1.72 – 1.68 (2H, m), 1.53 – 1.48 (2H, m), 0.98 (6H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.6, 128.6, 128.4, 126.0, 120.6, 43.8, 37.1, 33.4, 30.6, 26.4, 12.5. The spectral data match those previously reported[48].



1l, **1r** **2a** **16**, **22**

A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with compound **1l** or **1r** (5.0 mmol, 1.0 equiv), zinc thiolate **2a** (3.0 g, 7.5 mmol, 1.5 equiv) and diazodium salt **4a** (2.77 g, 12.5 mmol, 2.5 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then DMSO (30.0 mL) were added under N_2. The mixture was allowed to stir at 22 °C for 16 h. he mixture was poured into water (30.0 mL) and extracted with ethyl acetate (30.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (30.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 30:1 petroleum ether: ethyl acetate). The product **16** was isolated as a colorless oil (0.76 g, 3.6 mmol, 73% yield) and product **22** was isolated as a colorless oil (1.13 g, 3.95 mmol, 79% yield).

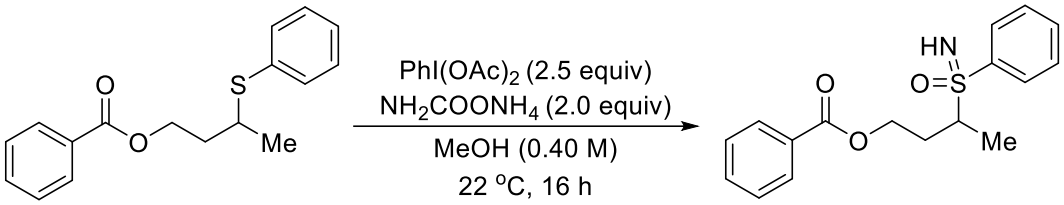


22 **85**

A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with compound **22** (86.0 mg, 0.30 mmol, 1.0 equiv), $NaIO_4$ (77.0 mg, 0.36 mmol, 1.2 equiv), H_2O (1.5 mL) and MeOH (1.5 mL). The mixture was allowed to stir at 50 °C for 6 h. The mixture was poured into $NaHCO_3$ aqueous solution (20.0 mL) and extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 1:1 petroleum ether: ethyl acetate). The product **85** was isolated a colorless oil (69.5 mg, 0.23 mmol, 77% yield).

3-(Phenylsulfinyl)butyl benzoate 85: dr = 3:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 –

7.94 (2H, m), 7.63 – 7.60 (2H, m), 7.58 – 7.54 (1H, m), 7.51 – 7.50 (3H, m), 7.46 – 7.40 (2H, m), 4.38 – 4.35 (2H, m), 2.99 – 2.84 (1H, m), 2.25 – 2.17 (1H, m), 1.87 – 1.77 (1H, m), 1.37 – 1.29 (3H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 141.4, 133.2, 131.0, 129.9, 129.7, 129.1, 128.5, 124.8, 62.1, 56.3, 29.8, 10.8; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{17}H_{18}NaO_3S$: 325.0869, found: 325.0878.

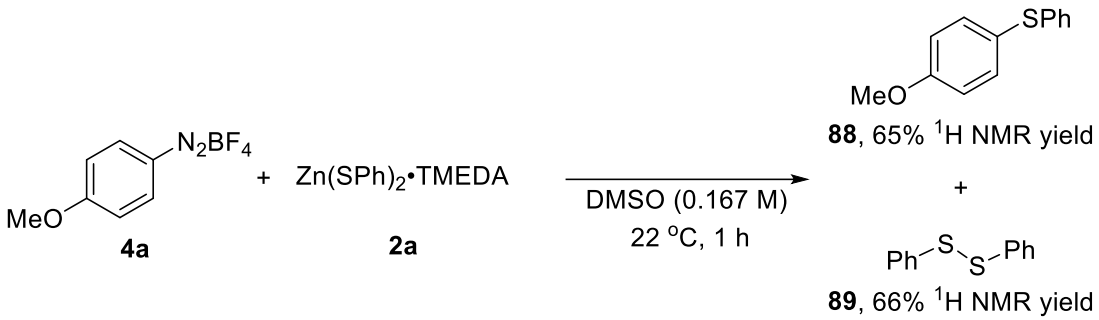


22 **87**

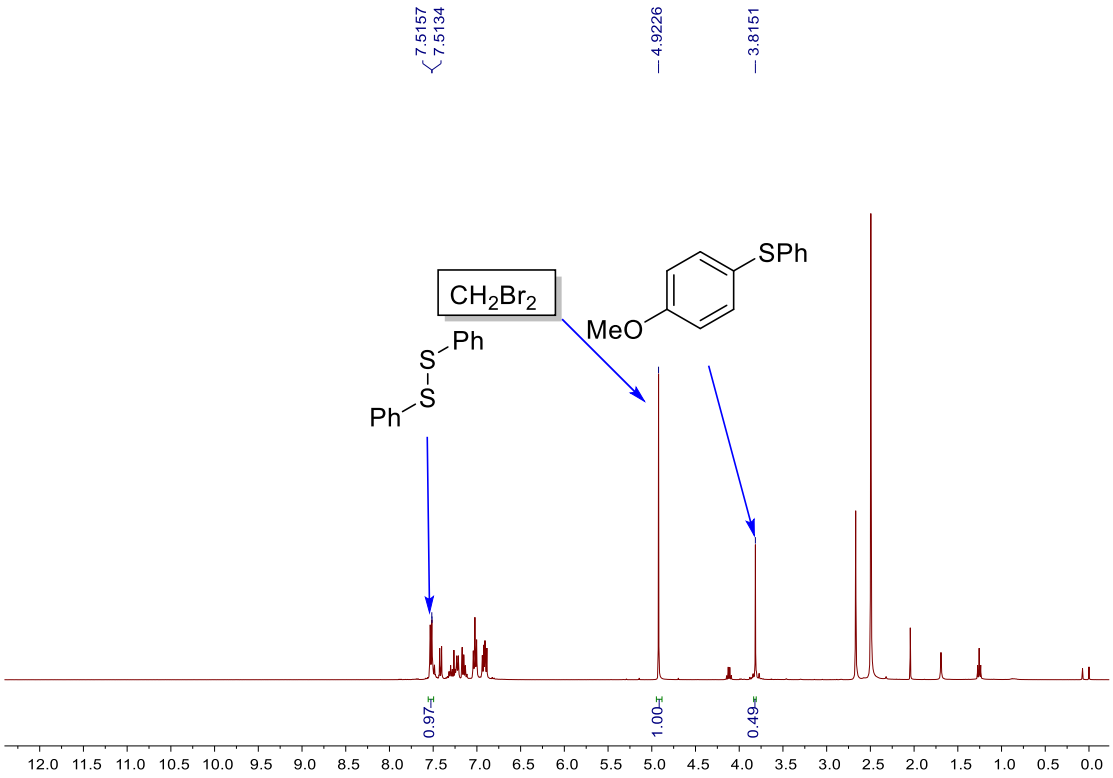
A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with compound **22** (86.0 mg, 0.30 mmol, 1.0 equiv), $PhI(OAc)_2$ (241.6 mg, 0.75 mmol, 2.5 equiv) and NH_2COONH_4 (46.8 mg, 0.60 mmol, 2.0 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then MeOH (1.00 mL) were added under N_2. The reaction was stirred at room temperature for 16 h. The mixture was poured into H_2O (20.0 mL) and extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 1:2 petroleum ether: ethyl acetate). The product **87** was isolated a colorless oil (78.2 mg, 0.25 mmol, 82% yield).

3-(Phenylsulfonimidoyl)butyl benzoate 87: dr = 1:1; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.85 (4H, m), 7.61 – 7.55 (1H, m), 7.53 – 7.49 (3H, m), 7.42 – 7.37 (2H, m), 4.43 – 4.29 (2H, m), 3.31 – 3.24 (1H, m), 2.64 (1H, s), 2.51 – 2.46 (1H, m), 1.83 – 1.75 (1H, m), 1.37 – 1.33 (3H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.3, 166.3, 139.7, 139.7, 133.3, 133.2, 129.8, 129.6, 129.4, 129.2, 128.5, 61.9, 58.4, 58.3, 29.4, 29.2, 13.8, 13.7; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{17}H_{19}NNaO_3S$: 340.0978, found: 340.0982.

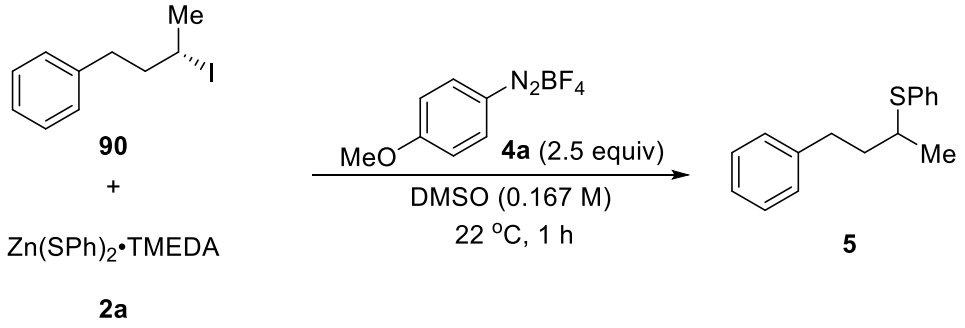
6. Mechanistic study



A 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with diazodium salt **4a** (22.2 mg, 0.10 mmol, 1.0 equiv) and zinc thiolate **2a** (60.0 mg, 0.15 mmol, 1.5 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then DMSO (0.60 mL) were added under N_2 and was stirred for 1 h. The mixture was poured into water (20.0 mL) and extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was added 0.20 mmol CH_2Br_2. The yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 (35.1 mg, 0.20 mmol) as an internal standard.

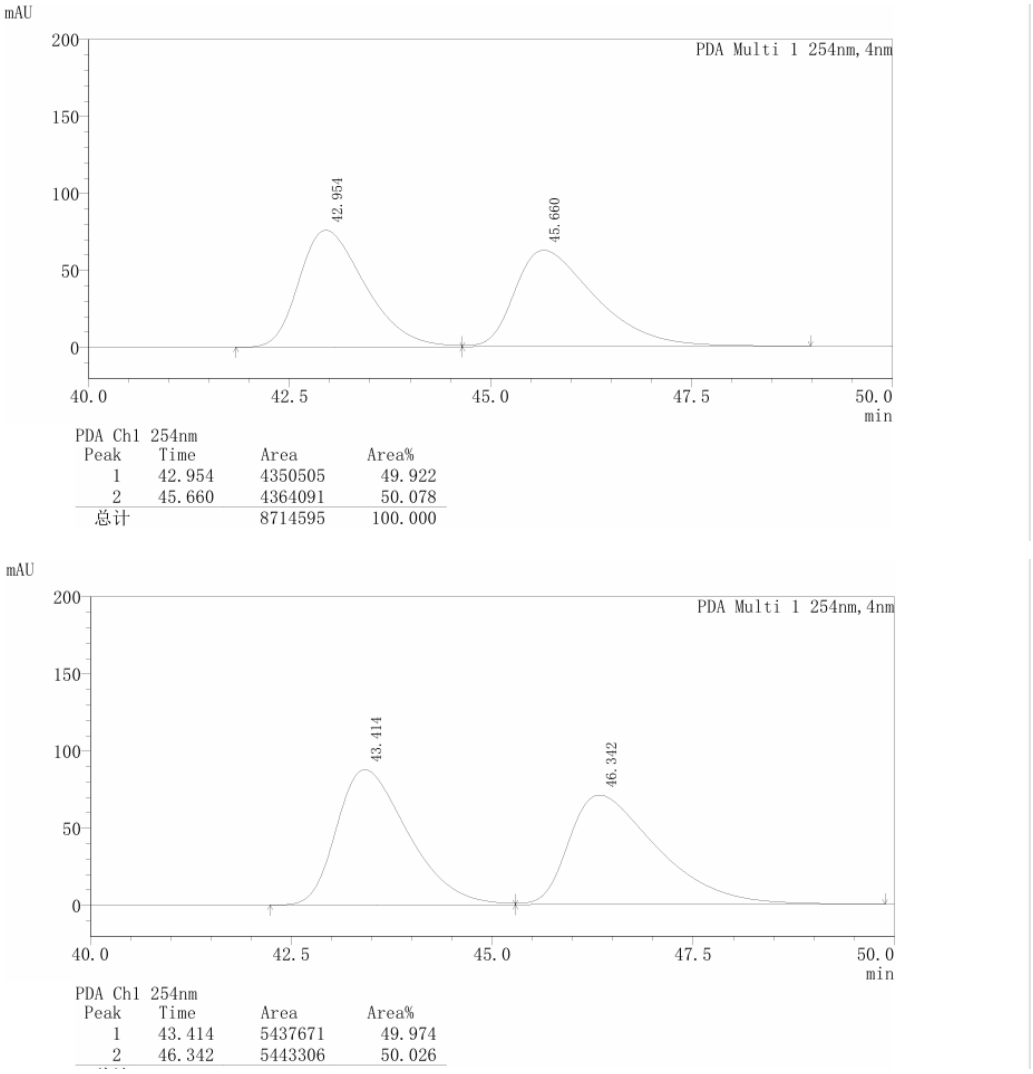


Supplementary Fig. 2 ^{1}H NMR of controlled experiment

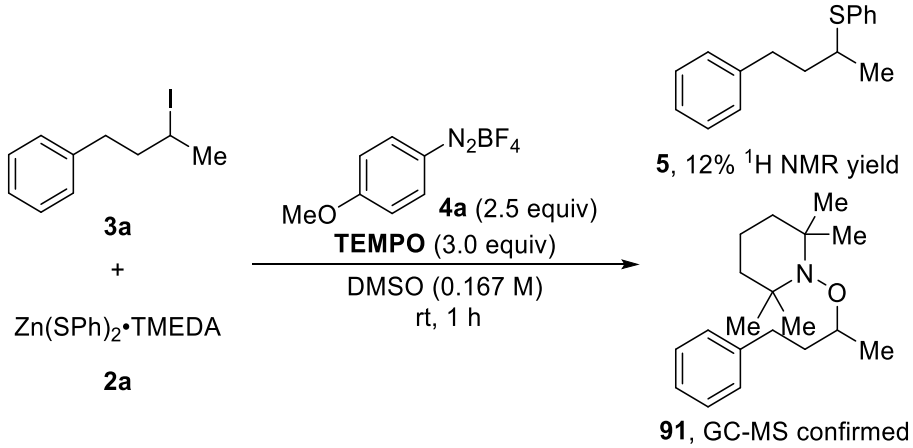


A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with alkyl iodide **90** (78.0 mg, 0.30 mmol, 1.0 equiv), zinc thiolate **2a** (299.9 mg, 0.45 mmol, 1.5 equiv) and diazodium salt **4a** (166.5 mg, 0.75 mmol, 2.5 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then DMSO (1.80 mL) were added under N_2 and was stirred for 1 h. The mixture was poured into water (20.0 mL) and extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 petroleum ether: ethyl acetate). The product **5** was isolated a colorless oil (60.8 mg, 0.25 mmol, 84% yield),

HPLC: Column: CHIRALPAK-AD-H, 100% hexanes, 0.2 mL/min, 254 nm, in comparison with racemic material, ee = 0%; $[\alpha]^{22}$= +5.05 (*c* = 0.7125, $CHCl_3$).

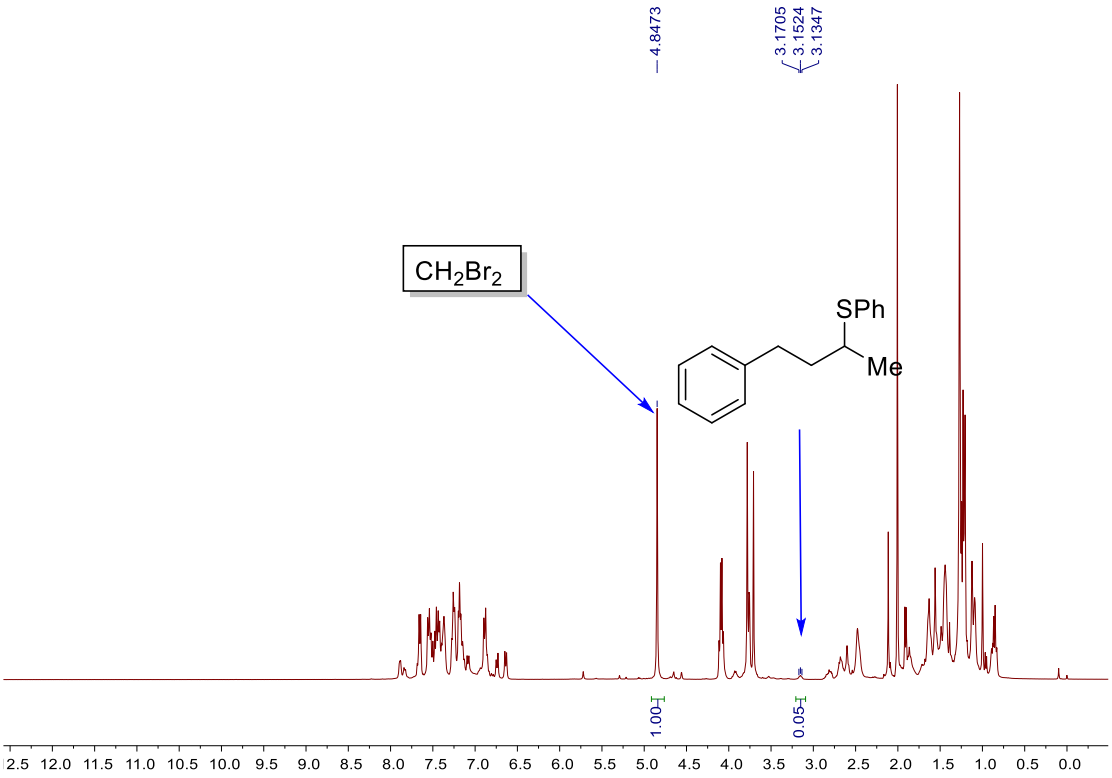


Supplementary Fig. 3. HPLC traces for compound 5

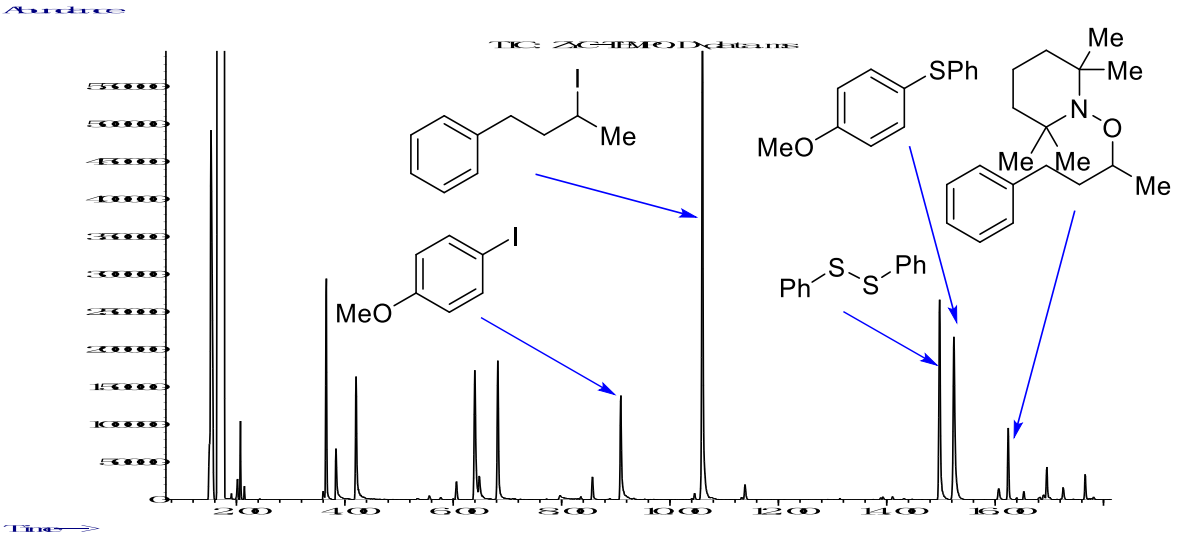


A 120 ºC oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with (3-iodobutyl)benzene **3a** (26.0 mg, 0.10 mmol, 1.0 equiv), zinc thiolate

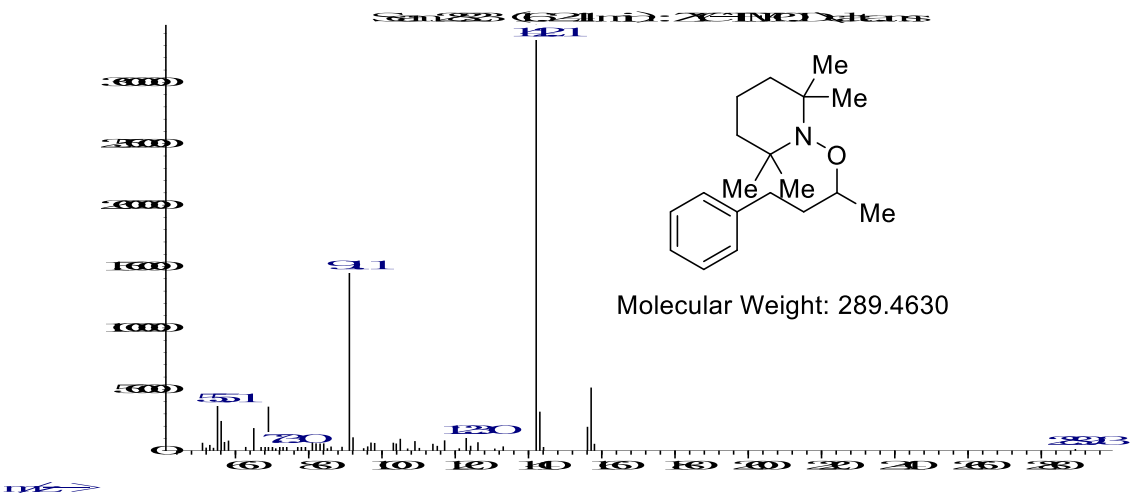
2a (60.0 mg, 0.15 mmol, 1.5 equiv), diazodium salt **4a** (60.0 mg, 0.25 mmol, 2.5 equiv) and TEMPO (46.9 mg, 0.30 mmol, 3.0 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then DMSO (0.60 mL) were added under N_2 and was stirred for 1 h. The mixture was poured into water (20.0 mL) and extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was added CH_2Br_2 (35.1 mg, 0.20 mmol) as an internal standard. The yield was determined by ^1H NMR spectroscopy. .



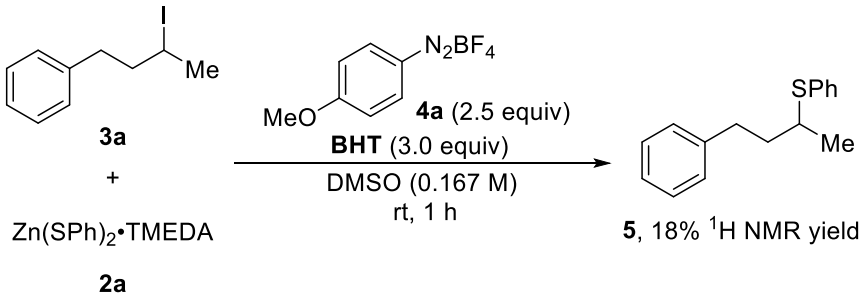
Supplementary Fig. 4. ^1H NMR of radical inhibition studie



Supplementary Fig. 5. GC-MS of radical inhibition studie

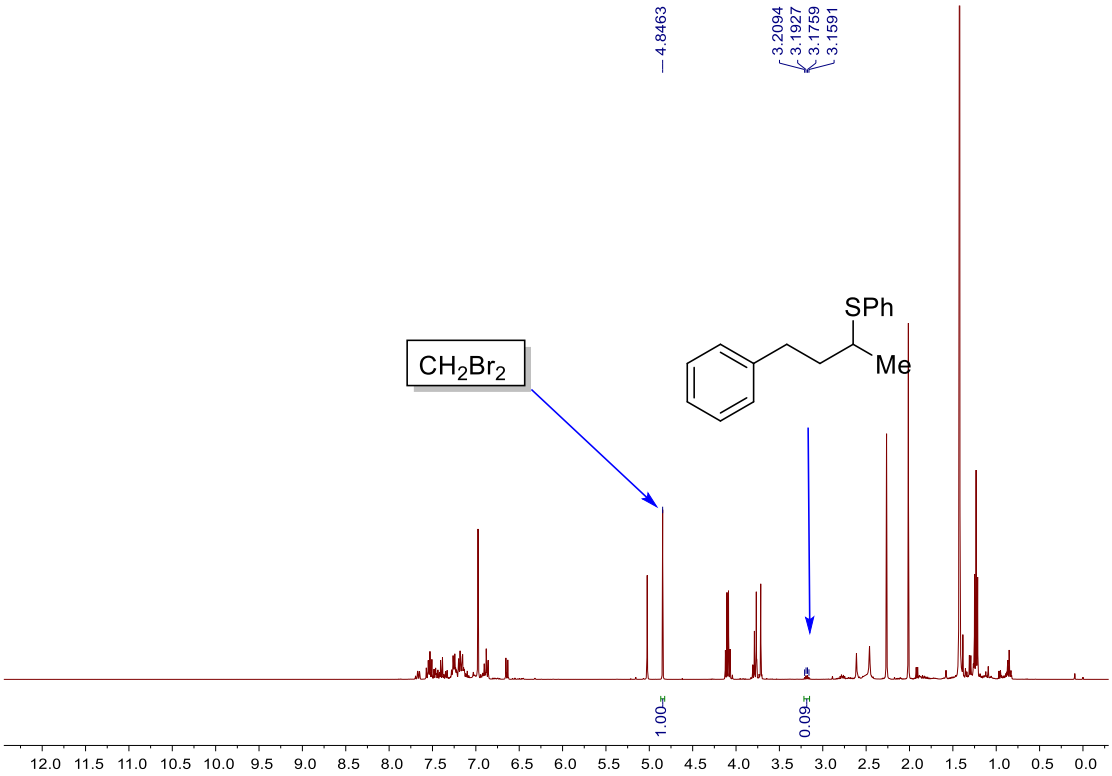


Supplementary Fig. 6. Compound 91 was detected by GC-MS in the reaction

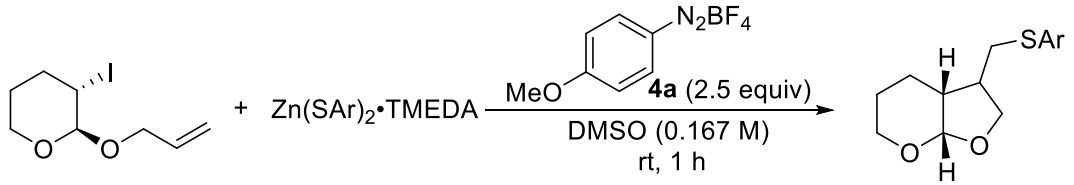


A 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with (3-iodobutyl)benzene **3a** (26.0 mg, 0.10 mmol, 1.0 equiv), zinc thiolate **2a** (60.0 mg, 0.15 mmol, 1.5 equiv), diazodium salt **4a** (60.0 mg, 0.25 mmol, 2.5 equiv) and **BHT** (66.1 mg, 0.30 mmol, 3.0 equiv). The mixture was evacuated and

backfilled with N_2 for three times. Then DMSO (0.60 mL) were added under N_2 and was stirred for 1 h. The mixture was poured into water (20.0 mL) and extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was added CH_2Br_2 (17.4 mg, 0.10 mmol) as an internal standard.



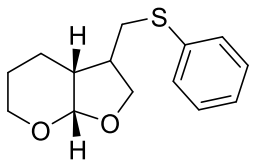
Supplementary Fig. 7. Addition of BHT in the reaction mixture



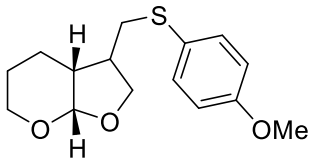
92 **2** **93**, **94**

A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with zinc thiolate **2a** or **2h** (0.45 mmol, 1.5 equiv) and diazodium salt **4a** (166.5 mg, 0.75 mmol, 2.5 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then (2*R*,3*S*)-2-(allyloxy)-3-iodotetrahydro-2*H*-pyran **92** (80.4 mg, 0.30 mmol, 1.0 equiv) and DMSO (1.8 mL) were added under N_2 and was stirred in the dark for 1 h. The mixture was poured into water (20.0 mL) and extracted with ethyl acetate

(10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography.

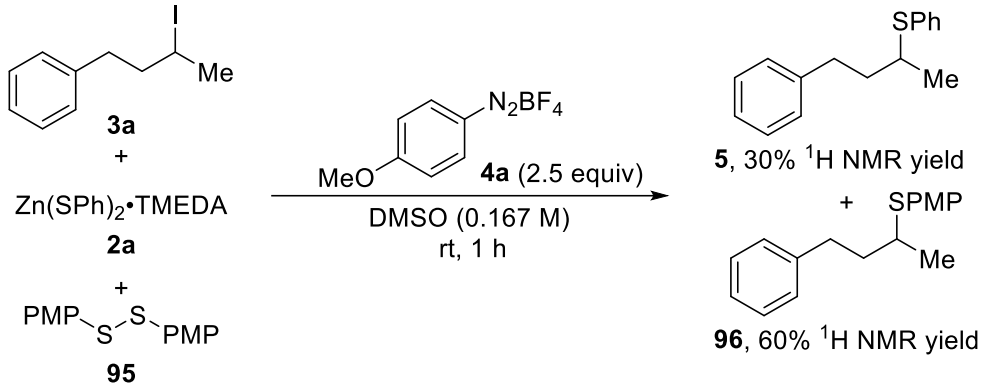


(3a*R*,7a*S*)-3-((phenylthio)methyl)hexahydro-4*H*-furo[2,3-*b*]pyran 93: (Eluent: 100:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (62.4 mg, 0.25 mmol, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.24 (2H, m), 7.31 – 7.26 (2H, m), 7.23 – 7.18 (1H, m), 5.23 (1H, d, J = 3.7 Hz), 4.01 (1H, t, J = 8.2 Hz), 3.80 – 3.74 (2H, m), 3.63 (1H, dtd, J = 11.1, 3.7, 1.6 Hz), 3.01 (1H, dd, J = 12.6, 7.7 Hz), 2.90 (1H, dd, J = 12.6, 8.0 Hz), 2.62 – 2.55 (1H, m), 2.11 – 2.05 (1H, m), 1.79 – 1.73 (1H, m), 1.62 – 1.55 (2H, m), 1.51 – 1.41 (1H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.7, 129.8, 129.1, 126.5, 101.9, 69.9, 61.3, 40.2, 36.8, 32.5, 23.1, 19.4; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{14}H_{18}NaO_2S$: 273.0920, found: 273.0926.

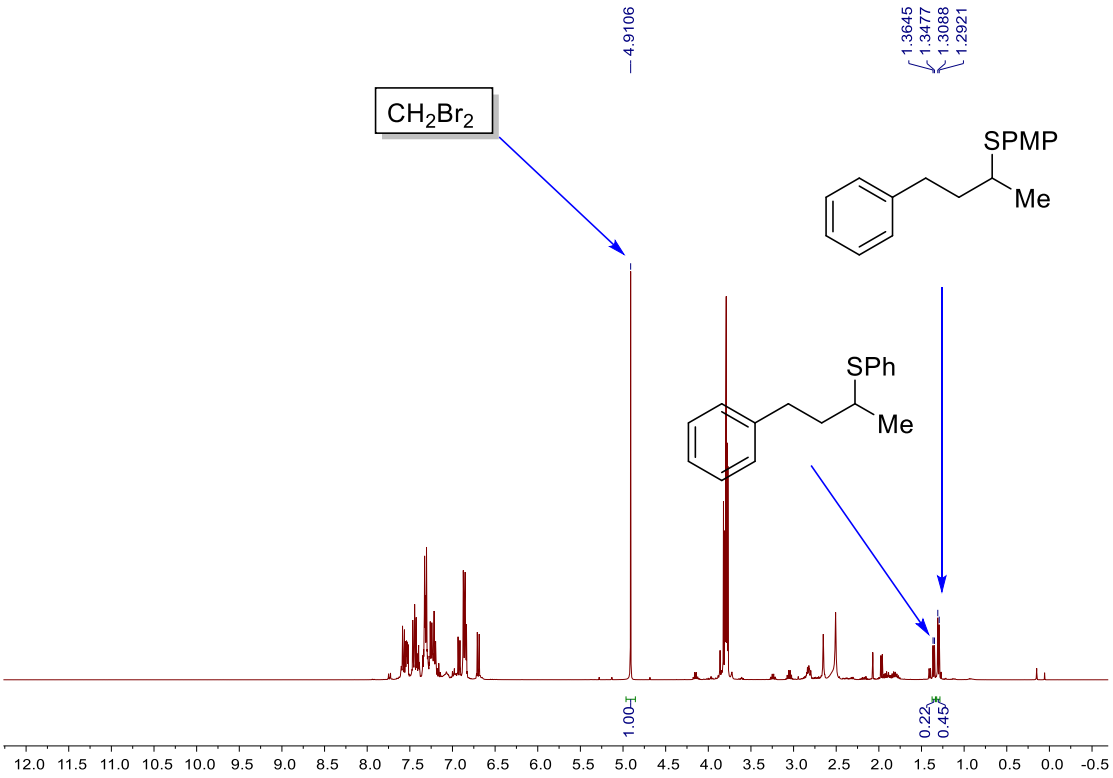


(3a*R*,7a*S*)-3-(((4-methoxyphenyl)thio)methyl)hexahydro-4*H*-furo[2,3-*b*]pyran 94: (Eluent: 100:1 to 30:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (58.8 mg, 0.21 mmol, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (2H, d, J = 8.8 Hz), 6.84 (2H, d, J = 8.7 Hz), 5.22 (1H, d, J = 3.6 Hz), 3.99 (1H, t, J = 8.2 Hz), 3.79 (3H, s), 3.77 – 3.70 (2H, m), 3.62 (1H, dtd, J = 11.1, 3.7, 1.6 Hz), 2.90 (1H, dd, J = 12.8, 7.4 Hz), 2.78 (1H, dd, J = 12.8, 8.1 Hz), 2.54 – 2.49 (1H, m), 2.06 – 2.03 (1H, m), 1.72 – 1.61 (1H, m), 1.60 – 1.54 (2H, m), 1.47 – 1.37 (1H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.3, 133.8, 125.6, 114.8, 101.9, 69.6, 61.2, 55.4, 40.4, 36.8, 34.6, 23.1, 19.4; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{15}H_{21}O_3S$:

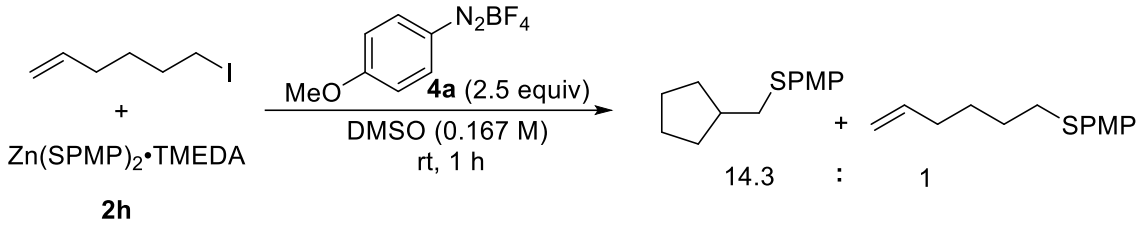
281.1206, found: 281.1215.



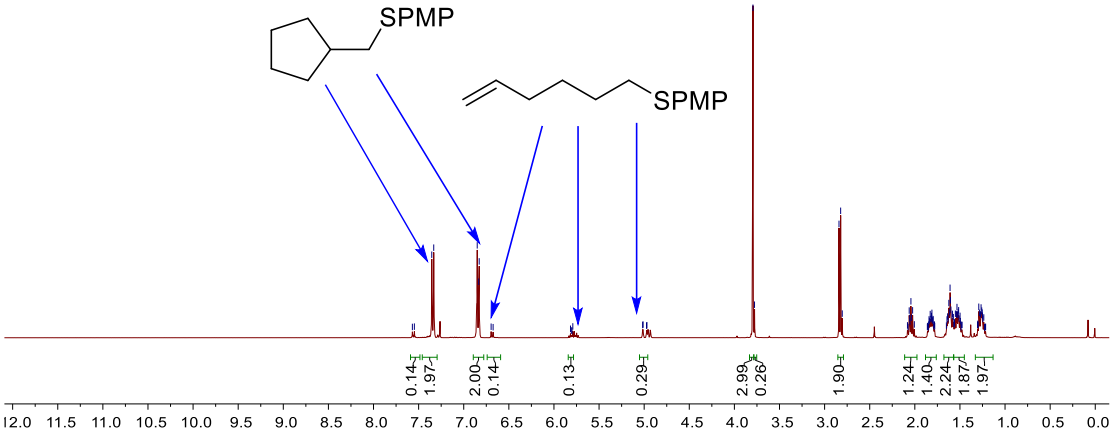
A 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with (3-iodobutyl)benzene (26.0 mg, 0.10 mmol, 1.0 equiv), zinc thiolate **2a** (60.0 mg, 0.15 mmol, 1.5 equiv), diazodium salt **4a** (55.5 mg, 0.25 mmol, 2.5 equiv) and compound **95** (41.7 mg, 0.15 mmol, 1.5 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then DMSO (0.60 mL) were added under N_2 and was stirred for 1 h. The mixture was poured into water (20.0 mL) and extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was added 0.20 mmol CH_2Br_2. The yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 (35.1 mg, 0.20 mmol) as an internal standard.



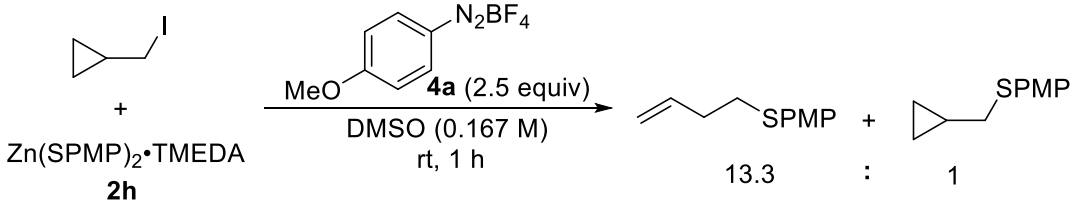
Supplementary Fig. 8. Evidence of generation on alkyl radicals



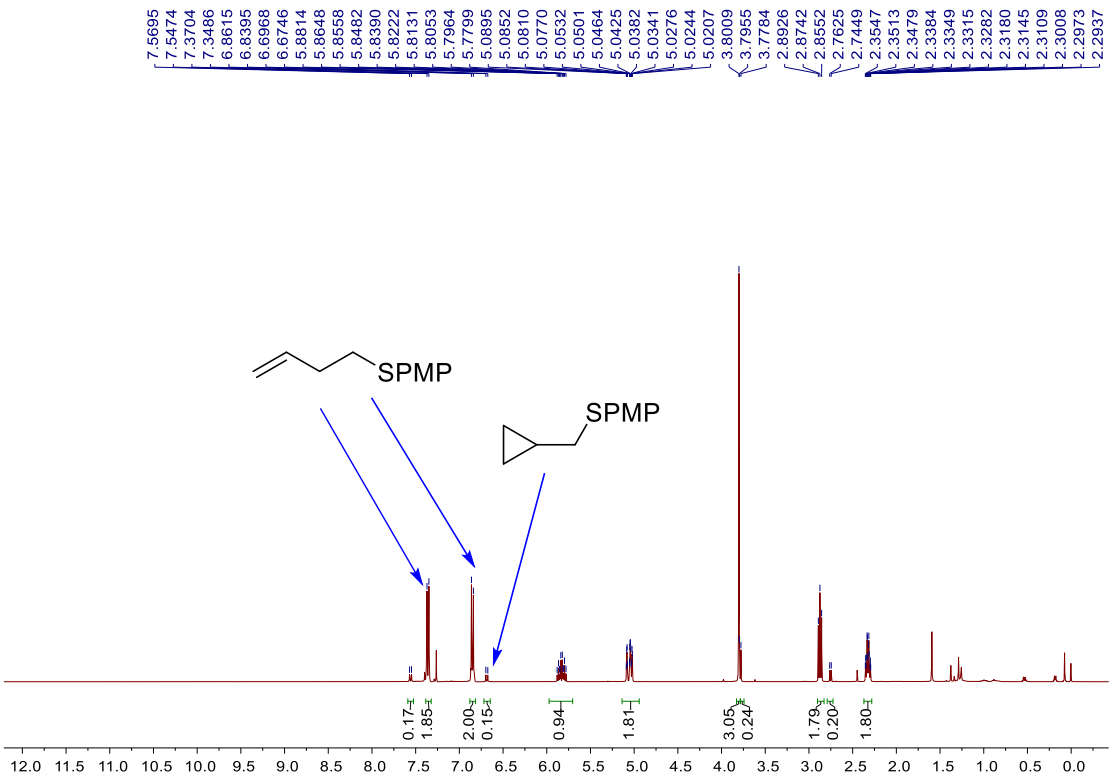
A 120 ºC oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with zinc thiolate **2h** (207.9 mg, 0.45 mmol, 1.5 equiv) and diazodium salt **4a** (166.5 mg, 0.75 mmol, 2.5 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then 6-iodohex-1-ene (63.0 mg, 0.30 mmol, 1.0 equiv) and DMSO (1.8 mL) were added under N_2 and was stirred in the dark for 1 h. The mixture was poured into water (20.0 mL) and extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography. The product **4** was isolated a colorless oil (59.0 mg, 0.27 mmol, 88% yield).



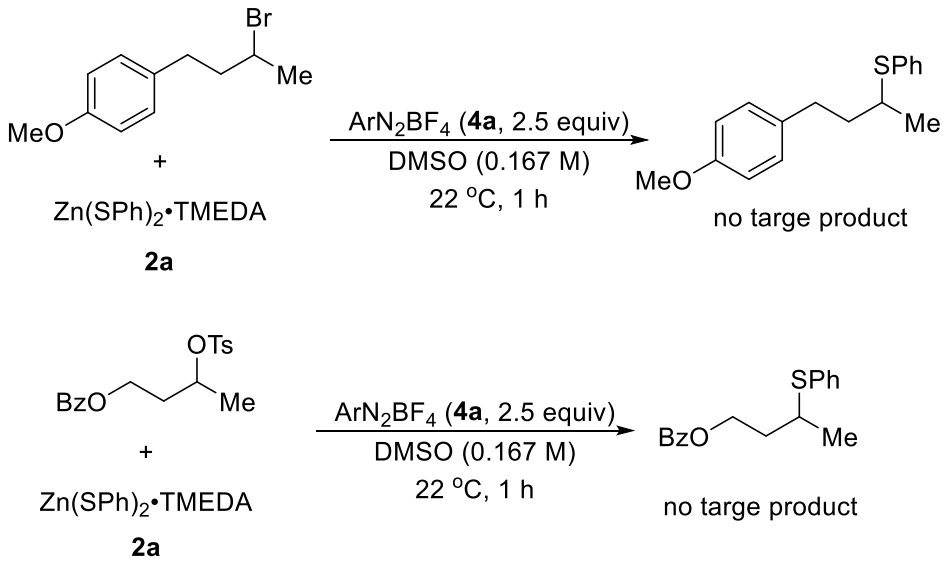
Supplementary Fig. 9. Radical clock of primary alkyl iodie



A 120 ºC oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with zinc thiolate **2h** (207.9 mg, 0.45 mmol, 1.5 equiv) and diazodium salt **4a** (166.5 mg, 0.75 mmol, 2.5 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then (iodomethyl)cyclopropane (54.6 mg, 0.30 mmol, 1.0 equiv) and DMSO (1.8 mL) were added under N_2 and was stirred in the dark for 1 h. The mixture was poured into water (20.0 mL) and extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography. The product **4** was isolated a colorless oil (66.0 mg, 0.30 mmol, >99% yield).



Supplementary Fig. 9. Radical clock of primary alkyl iodie



A 120 ºC oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 1-(3-bromobutyl)-4-methoxybenzene or 3-(tosyloxy)butyl benzoate (0.10 mmol, 1.0 equiv), zinc thiolate **2a** (0.15 mmol, 1.5 equiv) and arene diazodium salt **4a** (0.25 mmol, 2.5 equiv). The mixture was evacuated and backfilled with N_2 for three times. Then DMSO (0.60 mL) were added under N_2 and was stirred for 1 h. The mixture was poured into water (10.0 mL) and extracted with ethyl acetate (10.0 mL x 3). The

combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was added 0.20 mmol CH_2Br_2. The yield was determined by ^1H NMR spectroscopy in the presence of CH_2Br_2 (35.1 mg, 0.20 mmol) as an internal standard.

7. DFT calculation

Computational Methods:

All calculations were performed using Gaussian 16 package.[1] All the reactants, intermediates, transition states, and products were optimized with the ωB97X-D functional.[2] For H, C, O, S, and N, we employed 6-31G(d) basis sets for geometry optimizations and frequency calculations and the Stuttgart-Dresden basis set (SDD) used for the Iodine atom. All the stationary structures were characterized with no imaginary frequency and the transition state structures (TSs) were characterized with a single imaginary frequency. Intrinsic reaction coordinate (IRC) calculations were performed on the TSs. The solvent effect of Dimethyl sulfoxide was evaluated through the SMD method, [3] The basis set 6-311++G (d, p) was employed for H, C, O, S, N, and SDD for heavy atoms. All reported energies are free energies at a concentration of 1 M and a temperature of 298.15 K.

[1] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[2] S. Grimme, J. Comput. Chem., 2006, 27, 1787.

[3] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378.

Coordinates for each structures examined in this study

Int1

E = -970.704405681 a.u.

0 1

C	-0.34417800	0.10881800	-0.16596500
C	1.03478000	0.09331900	-0.32536800
C	1.74177600	1.29947500	-0.30056600
C	1.06858300	2.50617800	-0.11717700
C	-0.31372200	2.51436800	0.04165500
C	-1.02120500	1.31586500	0.01743800
H	-0.89760100	-0.82539600	-0.18432600
H	1.57337100	-0.83695300	-0.46862300
H	1.64838500	3.42359500	-0.10274400
H	-0.83680200	3.45503000	0.18419700
H	-2.10006000	1.31856200	0.14134300
N	3.15603800	1.41522100	-0.45202700
N	3.74246100	0.33643700	-0.62157900
S	5.45876400	0.41087200	-0.81073400
C	5.86706900	2.13900400	-0.69229300
C	5.89549400	2.92903100	-1.84319400
C	6.15499300	2.70362000	0.55185800
C	6.22018100	4.27861500	-1.74883100
H	5.66337200	2.48400400	-2.80571900
C	6.47875100	4.05367800	0.64137300
H	6.12387300	2.08406900	1.44267600
C	6.51208300	4.84007700	-0.50794200

H	6.24477800	4.89201300	-2.64439700
H	6.70487200	4.49182700	1.60873600
H	6.76699900	5.89333400	-0.43642600

TS1

E = -970.640871697 a.u.

0 3

C	1.81052600	0.63889400	-0.82357100
C	1.95463900	0.89186500	0.54160000
C	2.14319800	2.20314500	0.91410300
C	2.20972000	3.27481800	0.05696000
C	2.07049400	3.00033600	-1.30594900
C	1.87070100	1.69013400	-1.73918000
H	1.65504500	-0.37856800	-1.17136900
H	1.93662900	0.09458900	1.27994400
H	2.37777700	4.28152800	0.42594000
H	2.12111900	3.81049300	-2.02790700
H	1.76080000	1.48563900	-2.79993300
N	2.47310200	2.58164900	2.75319500
N	2.81728800	1.70841100	3.38890300
C	5.45023700	1.82482500	1.68560900
C	5.31521300	1.11593200	0.47305800
C	5.45636300	1.76599500	-0.74349600
C	5.72676100	3.13432800	-0.77579100
C	5.86200000	3.85250800	0.41345000
C	5.72625900	3.20730400	1.63389100
H	5.08626400	0.05601500	0.50986100

H	5.33785400	1.21242500	-1.66946600
H	5.82737600	3.64327800	-1.72989000
H	6.07217300	4.91747700	0.38462800
H	5.82430300	3.75609200	2.56509600
S	5.21230000	1.03220100	3.20402600

Int2

E = -231.471515710 a.u.

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C	2.37971000	-2.00183200	0.00214800
C	3.08327200	-0.79806300	0.00161900
C	2.39443800	0.42084600	0.00073600
C	1.02023200	0.35326100	0.00035800
C	0.27443900	-0.80299700	0.00080100
H	0.44500100	-2.95199900	0.00215900
H	2.92258800	-2.94216600	0.00286300
H	4.17005100	-0.80164000	0.00192900
H	2.92895900	1.36619100	0.00032500
H	-0.81150500	-0.79298100	0.00048900

TS2

E = -475.888942276 a.u.

0 2

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C	0.06660966	-0.52608083	0.68759454
H	1.35659307	0.72859839	-0.53869361
H	-0.08787451	0.12708553	-1.37731948
H	-0.23772000	1.41562949	-0.16591951

C	-1.40483919	-0.86096336	0.88254273
H	0.50857915	-0.17880880	1.62424138
C	-1.72103861	-1.76083678	2.06734721
H	-1.92565709	0.09273208	1.04858820
H	-1.82399411	-1.29594249	-0.03161536
H	-1.33013439	-2.77212071	1.88793349
H	-1.22477479	-1.36835980	2.97102965
O	-3.12645315	-1.76830491	2.21584957
H	-3.35351913	-2.41740343	2.89045645
I	1.40786896	-2.57729597	0.19257937
C	2.58592548	-6.93751625	0.22906343
C	3.44207115	-7.23091515	-0.83162101
C	3.90988599	-6.21765430	-1.66739006
C	3.52343595	-4.88971946	-1.44949647
C	2.67780610	-4.65902577	-0.38897745
C	2.18544855	-5.61721889	0.46693771
H	2.22604022	-7.73350066	0.87559685
H	3.74726677	-8.25782565	-1.00841023
H	4.57692573	-6.45528229	-2.49182598
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Int3

E = -232.917750639 a.u.

0 2

C	0.02902400	1.14340200	0.05129400

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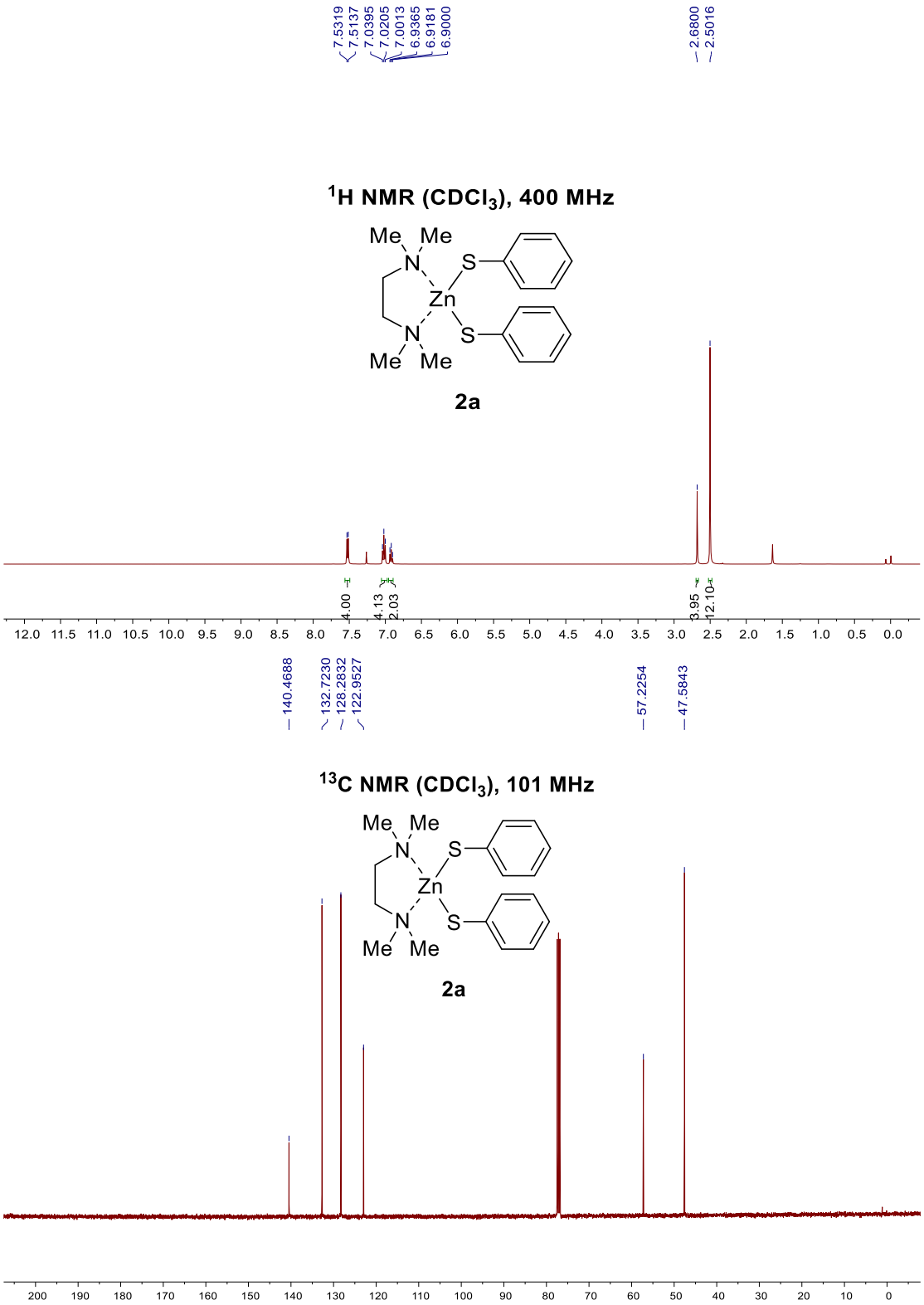
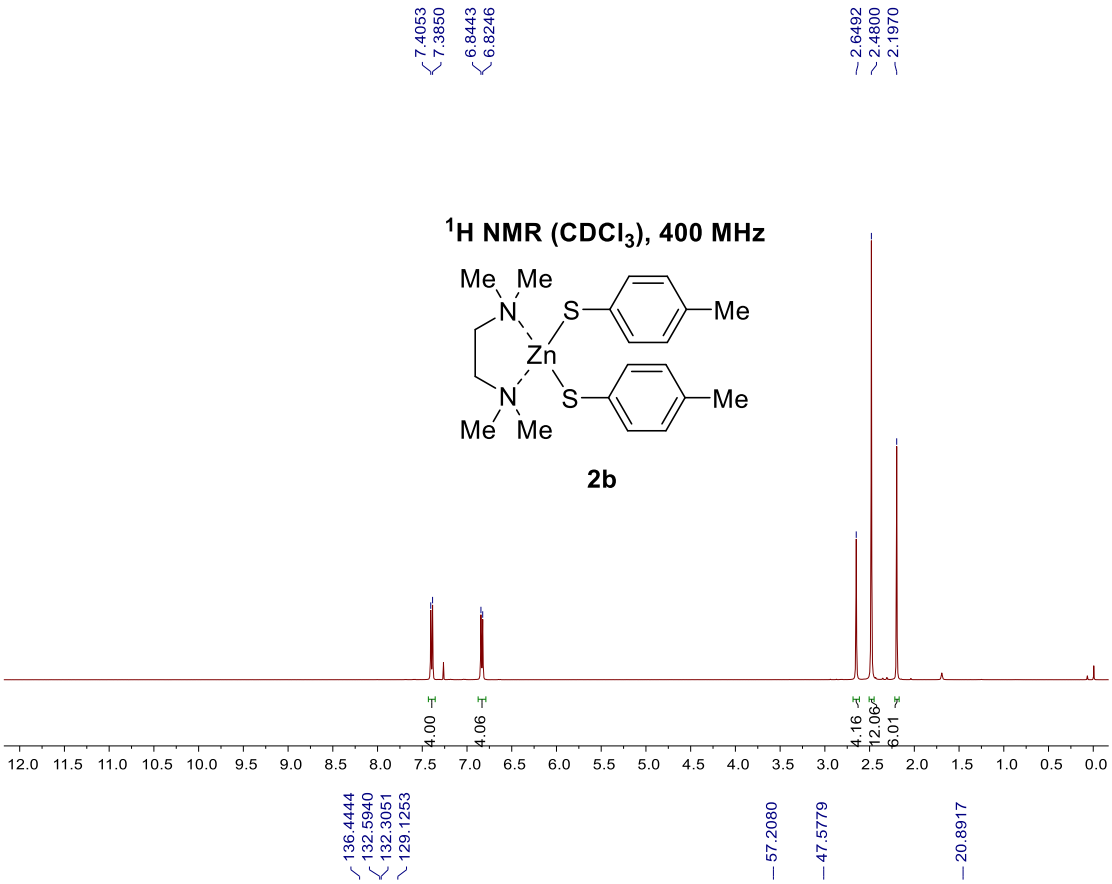
9. NMR spectra





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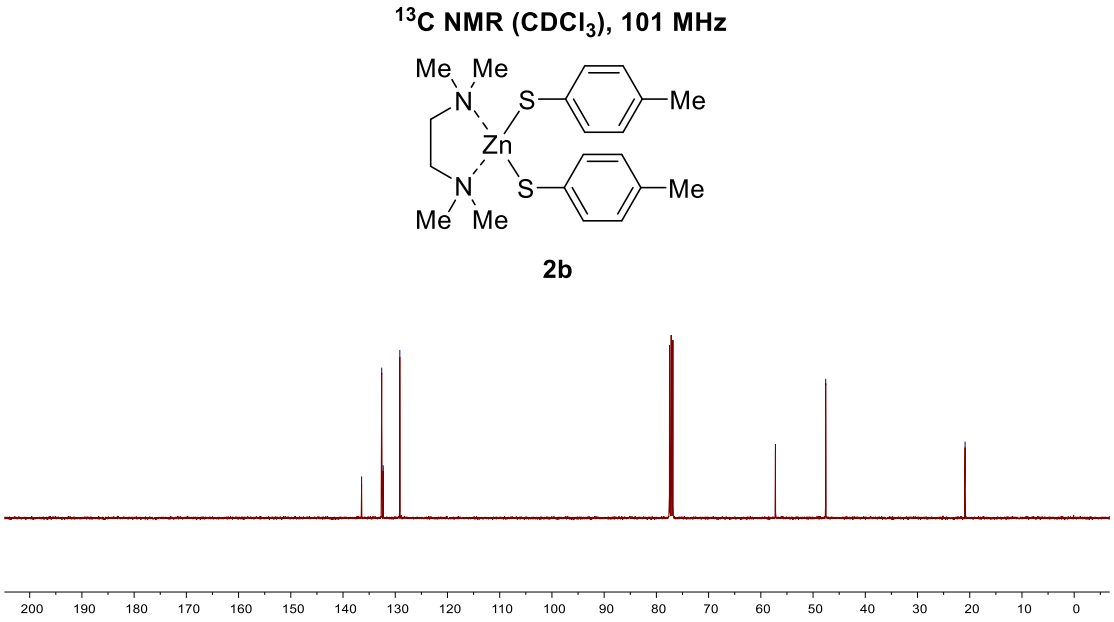
2b



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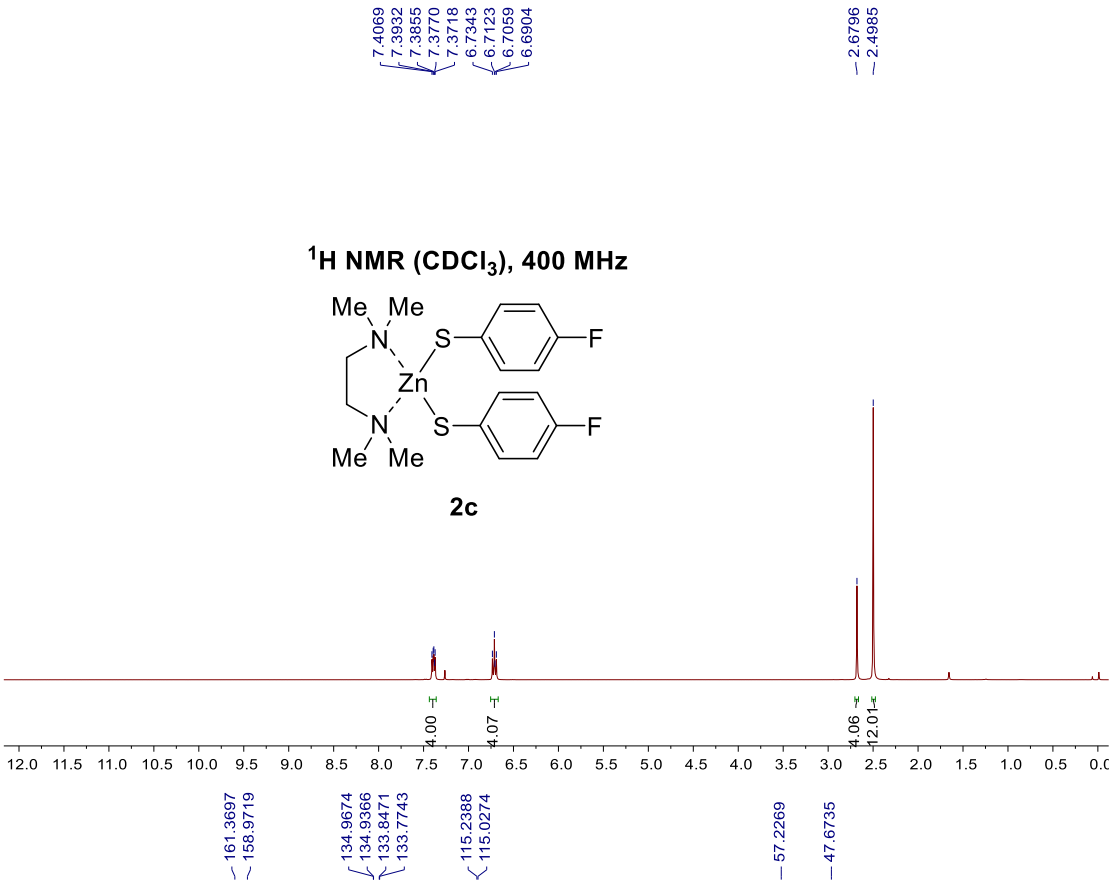
2b



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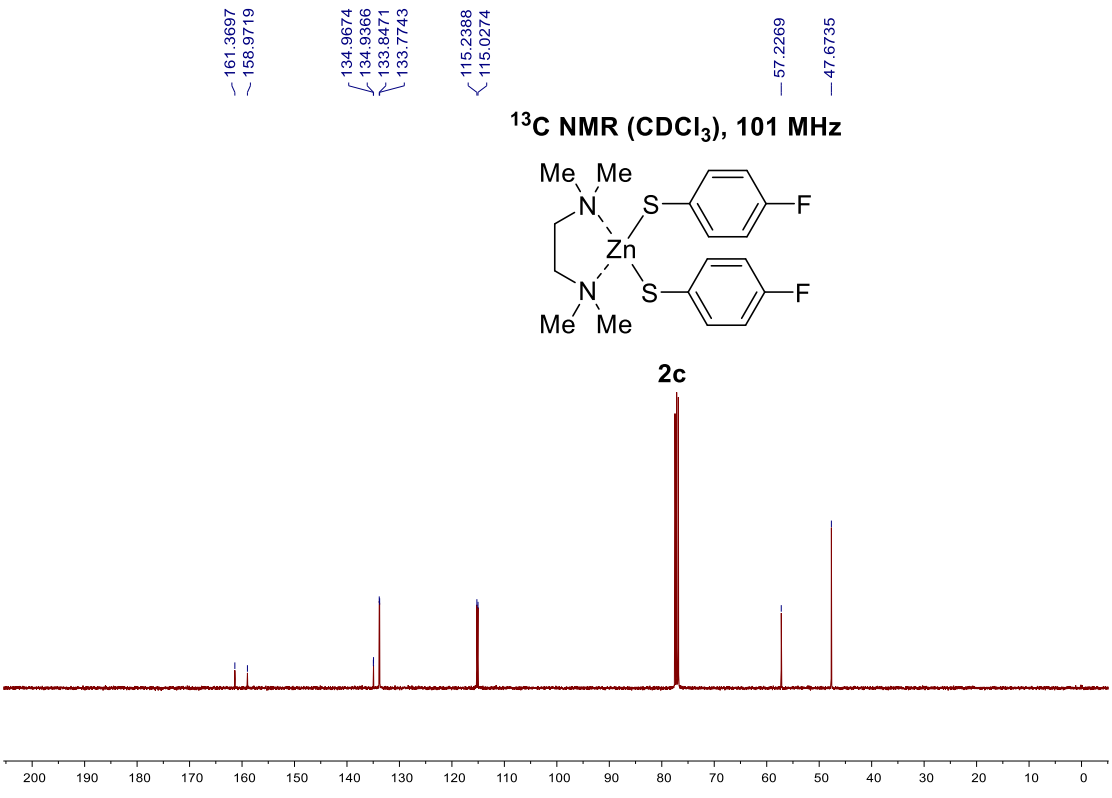

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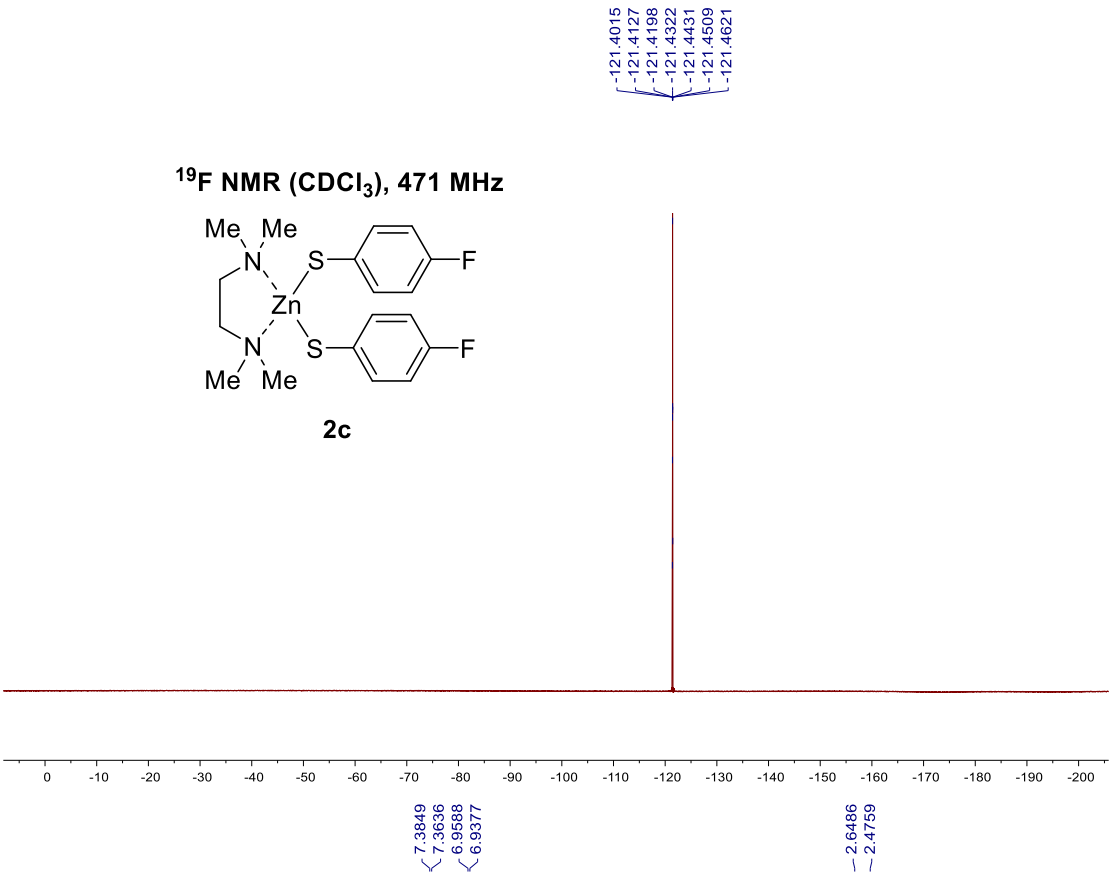
2c



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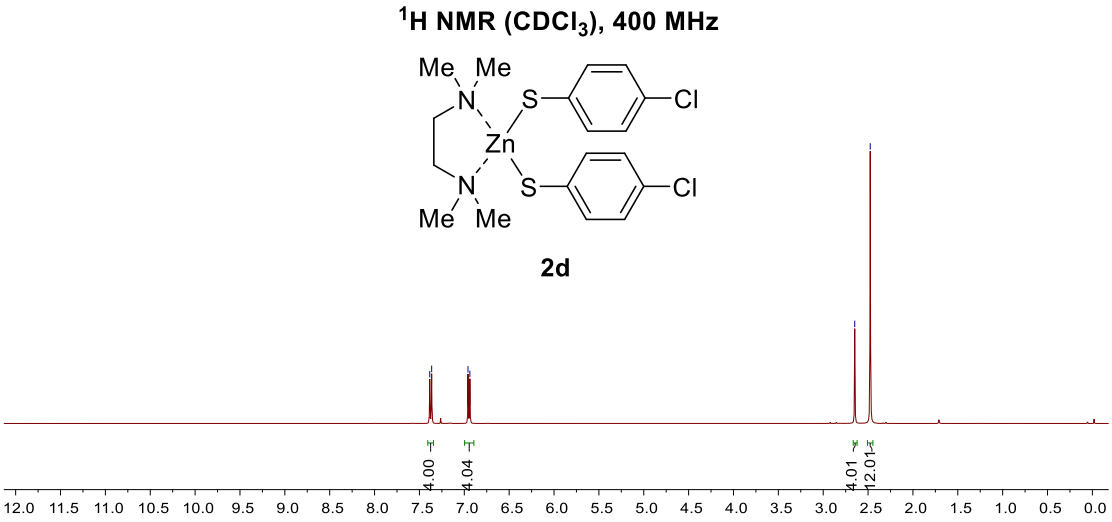

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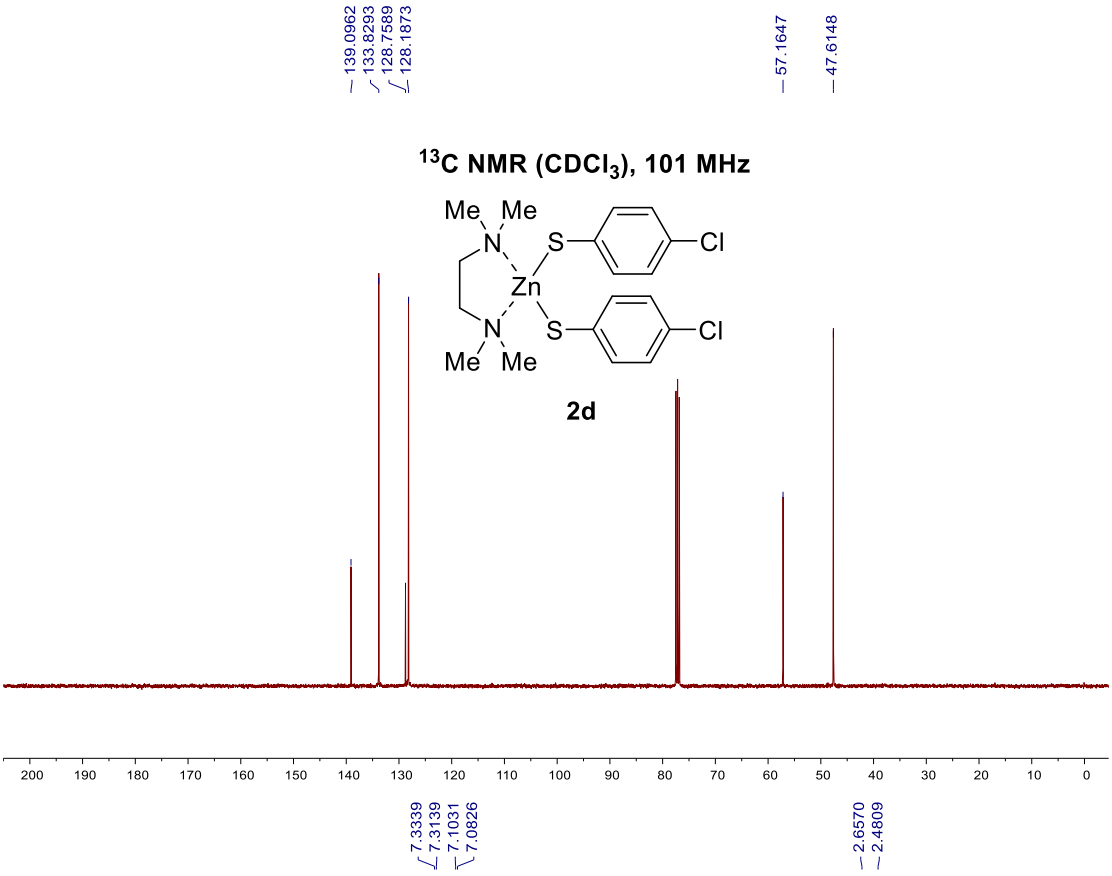
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133.8293
128.7589
128.1873
57.1647
47.6148
13C NMR (CDCl3), 101 MHz
Me Me
N
S
Cl
Zn
N
S
Cl
Me Me
2d
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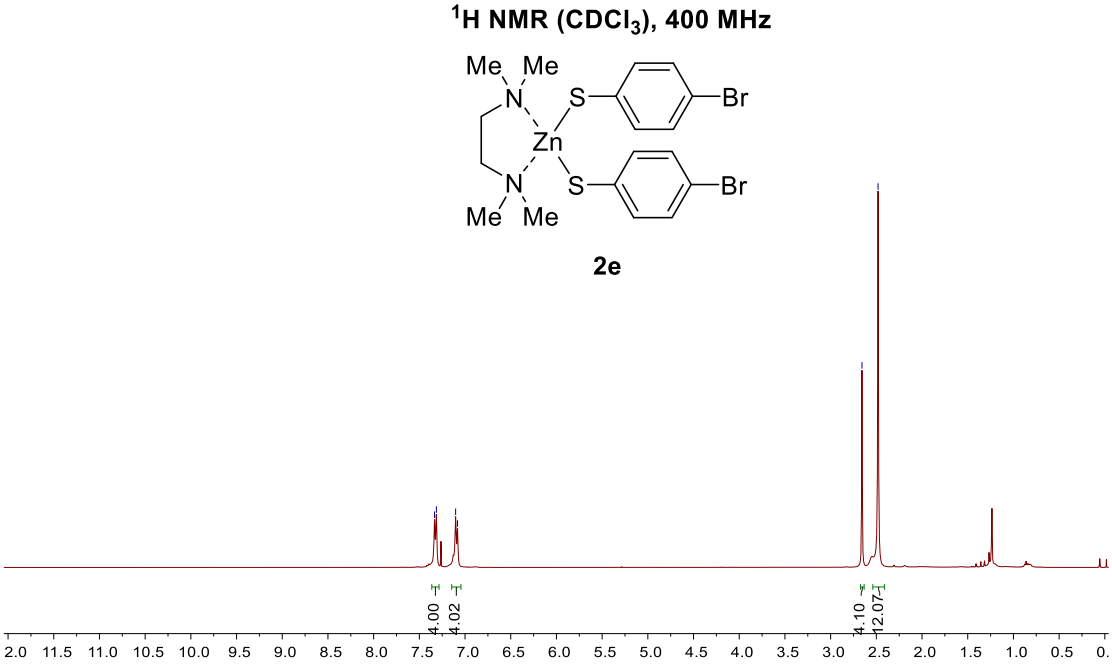
7.3139
7.1031
7.0826
2.6570
2.4809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N
S
Br
Zn
N
S
Br
Me Me
2e
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4.10
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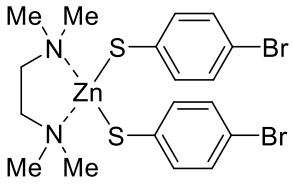
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.

^{13}C NMR ($CDCl_3$), 101 MHz



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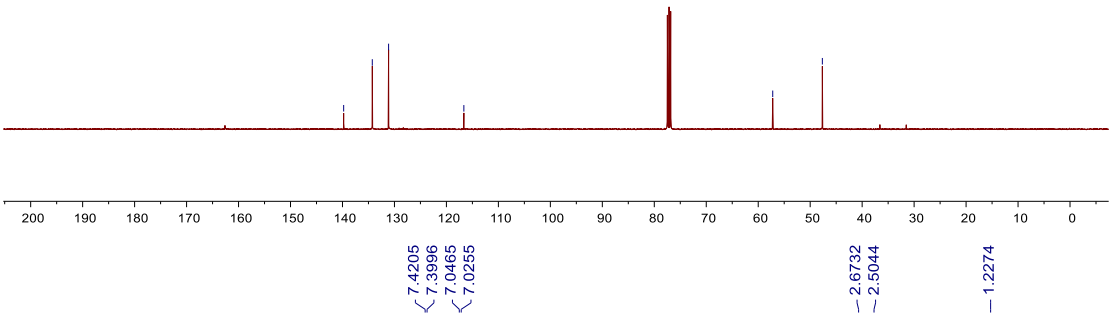

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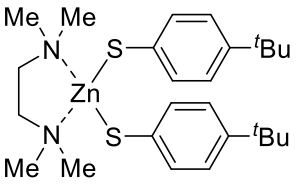

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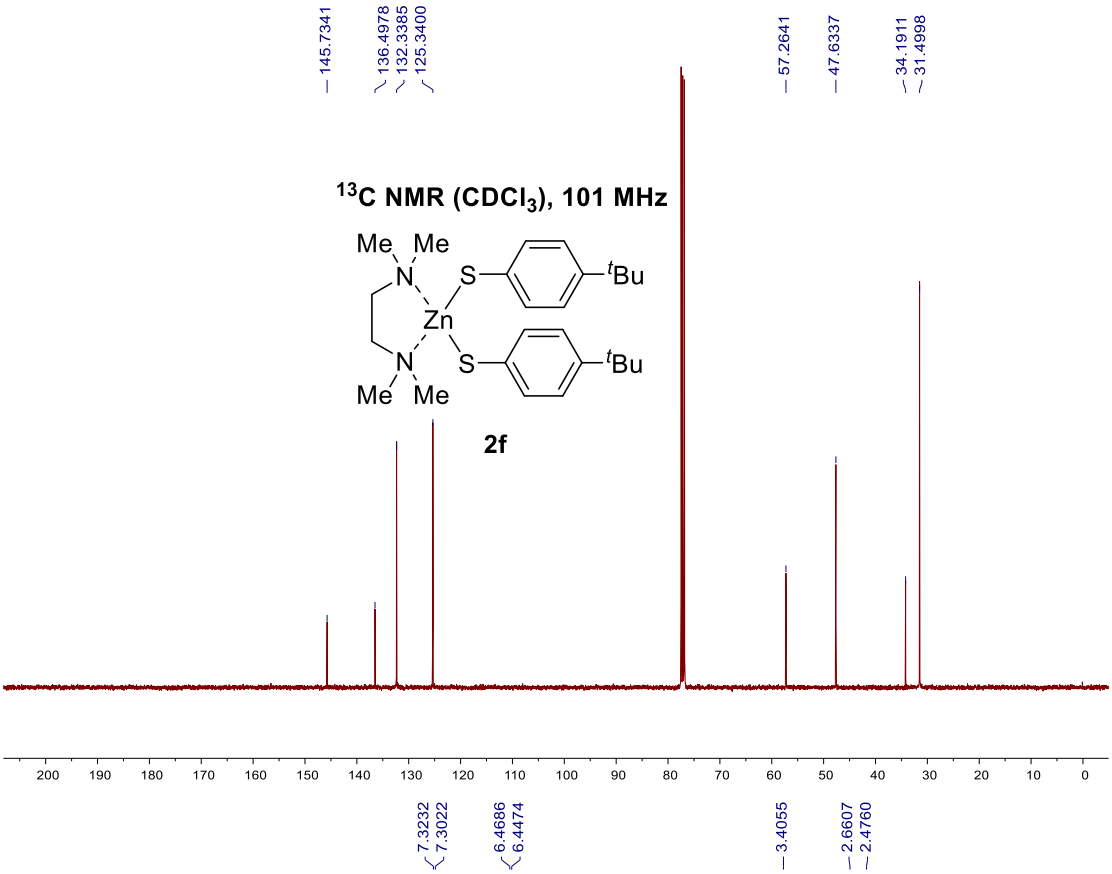
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132.3385
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34.1911
31.4998
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Me Me
N
S
tBu
Zn
N
S
tBu
Me Me
2f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
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6.4474
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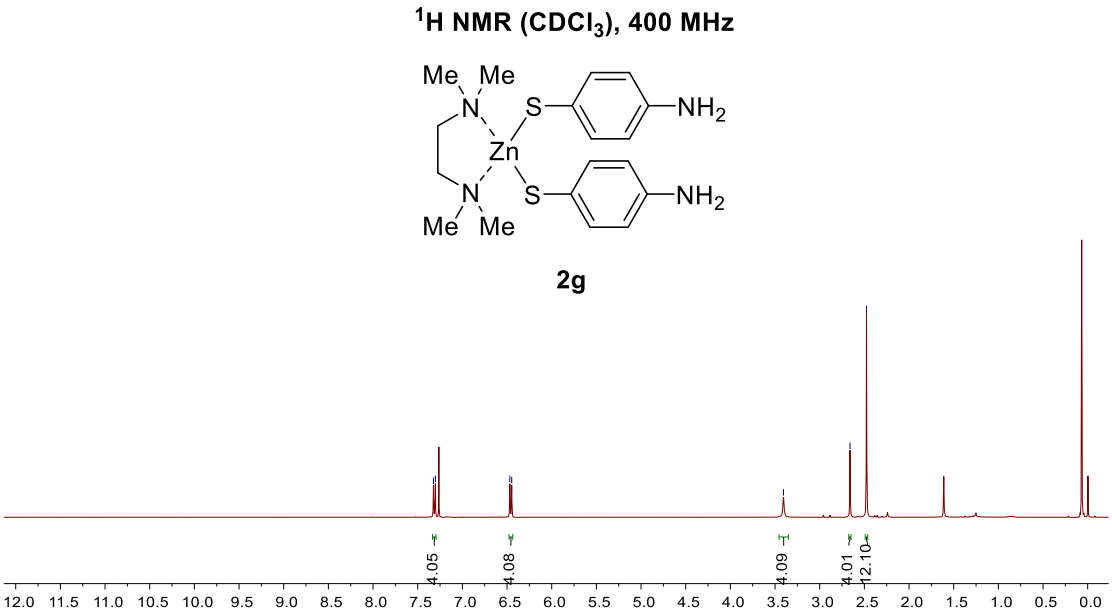
2.6607
2.4760


1H NMR (CDCl3), 400 MHz
Me Me
N
S
NH2
Zn
N
S
NH2
Me Me
2g
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4.08
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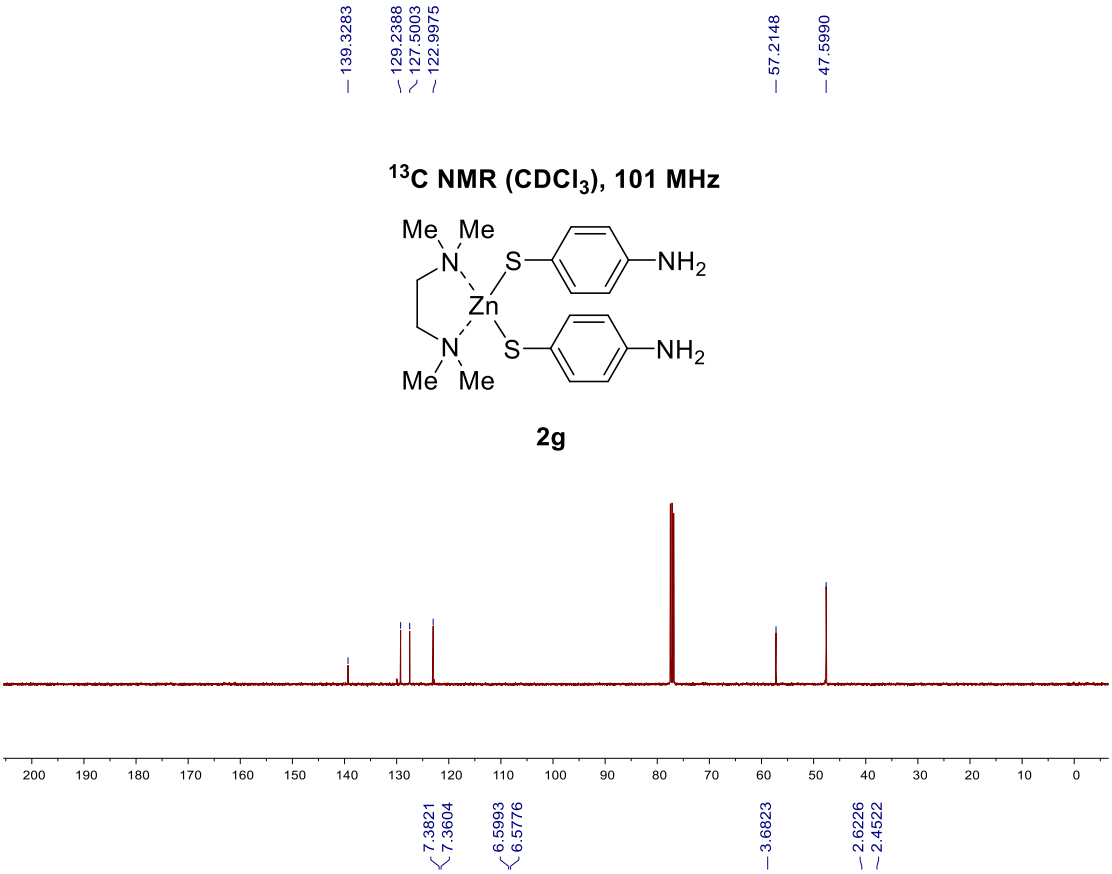
12.10
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0



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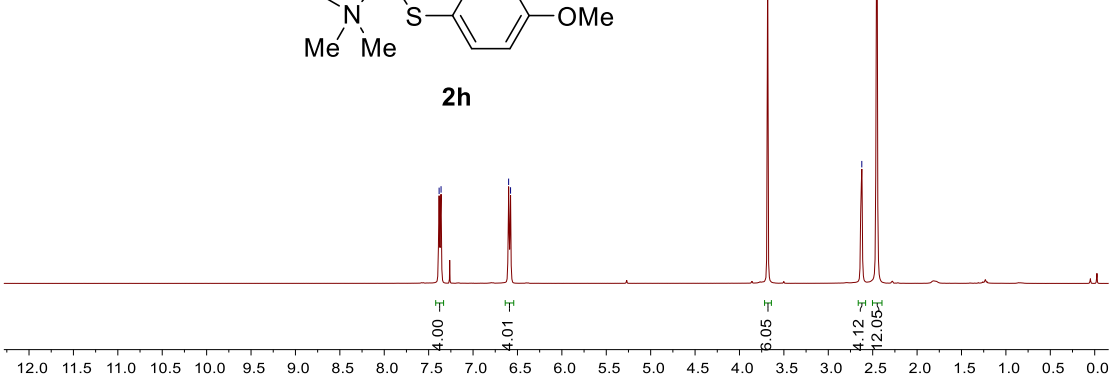
2g



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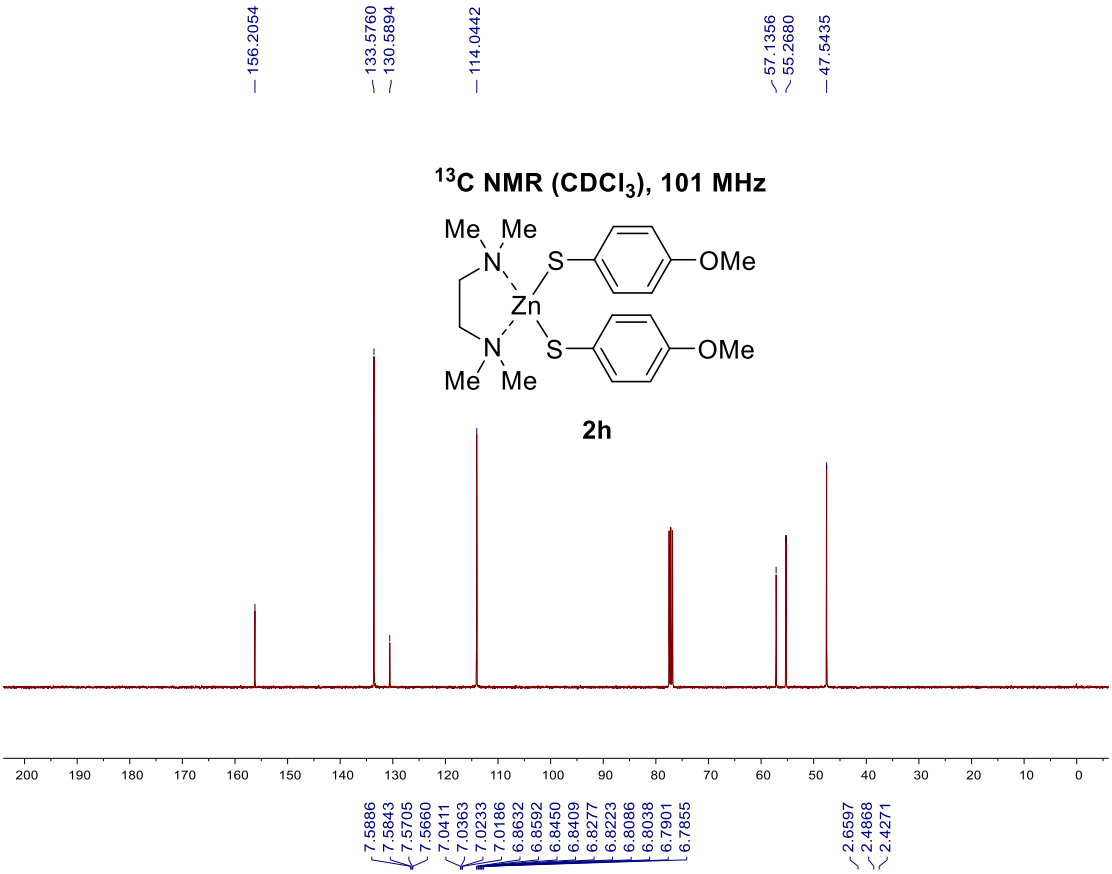
2h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13C NMR (CDCl3), 101 MHz
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N
S
OMe
Zn
N
S
OMe
Me Me
2h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.5886
7.5843
7.5705
7.5660
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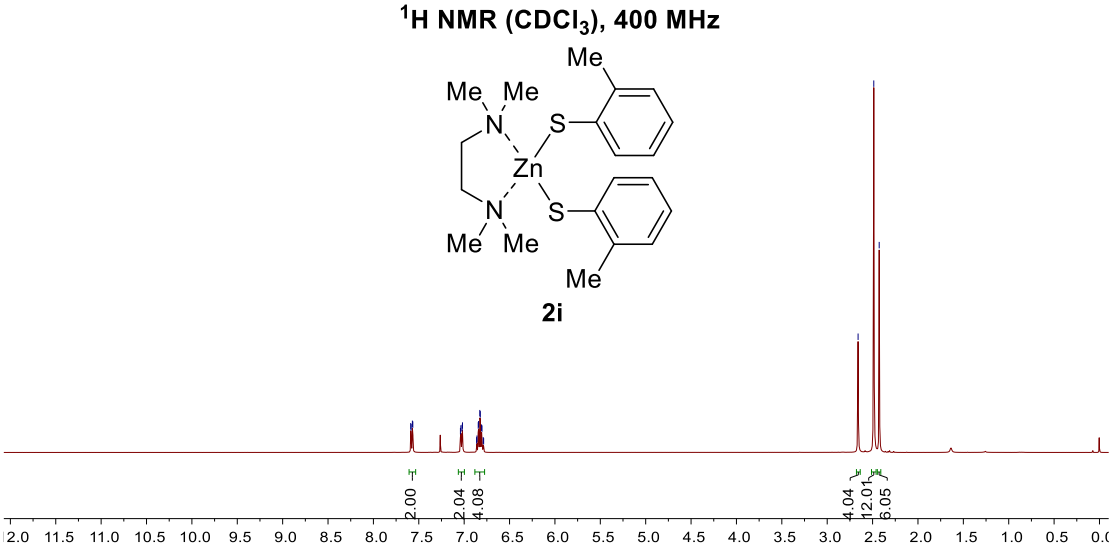
2.4868
2.4271


1H NMR (CDCl3), 400 MHz
Me
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N
S
Zn
N
S
Me Me
Me
2i
2.00
2.04
4.08
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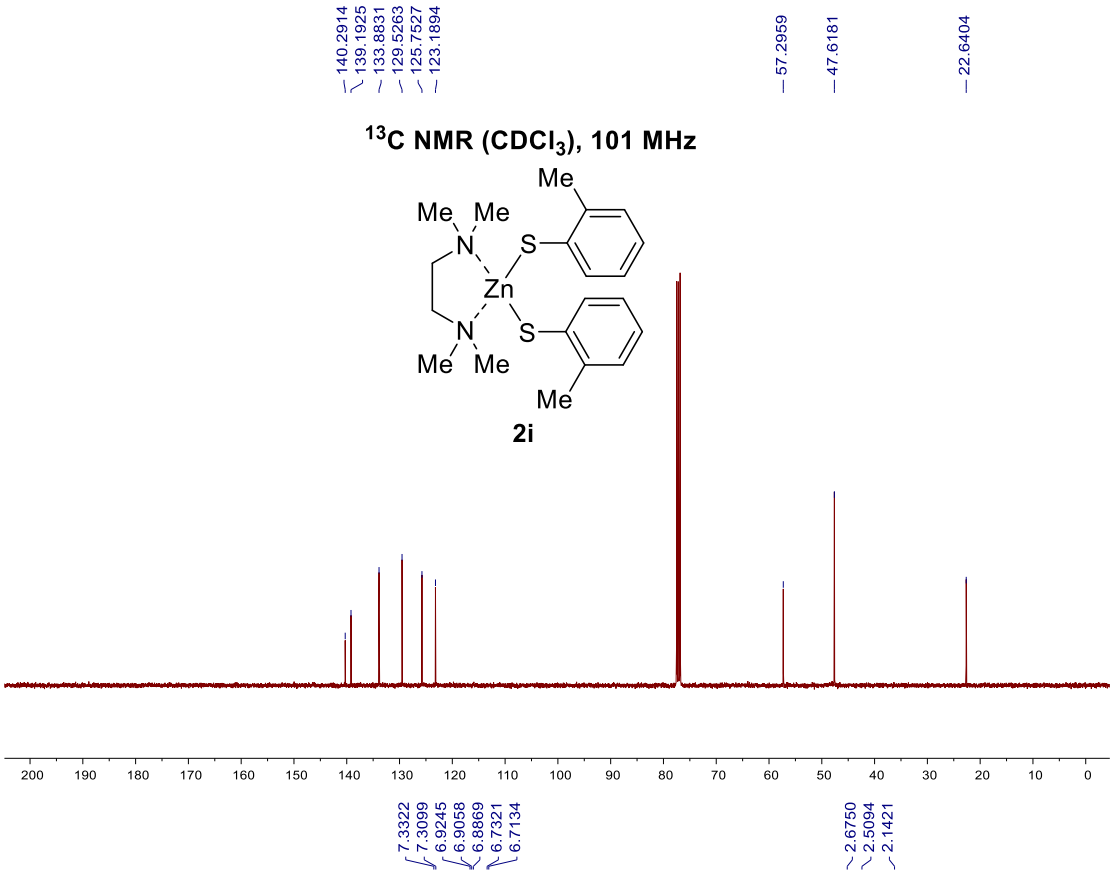
12.01
6.05
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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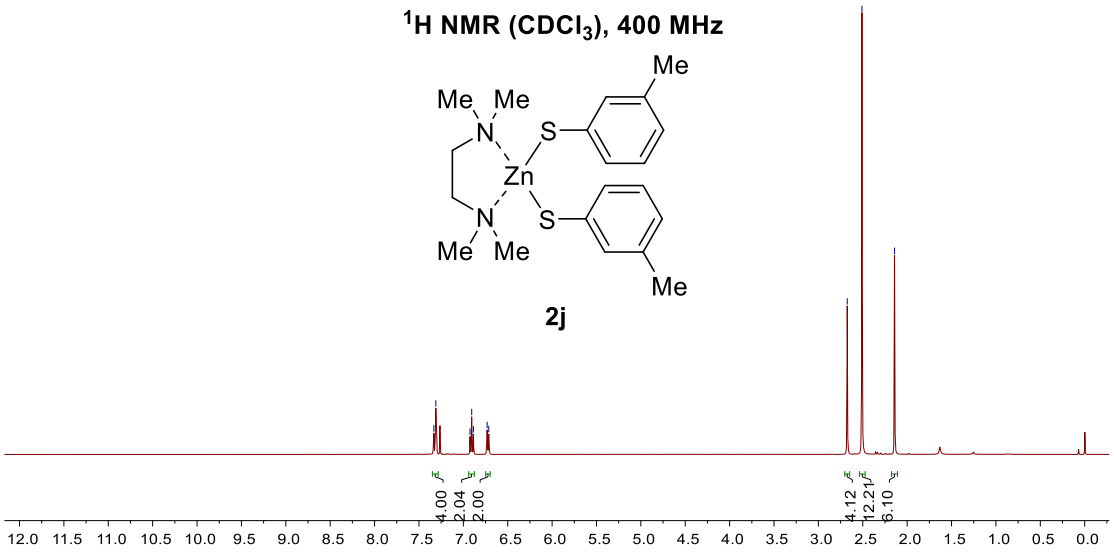
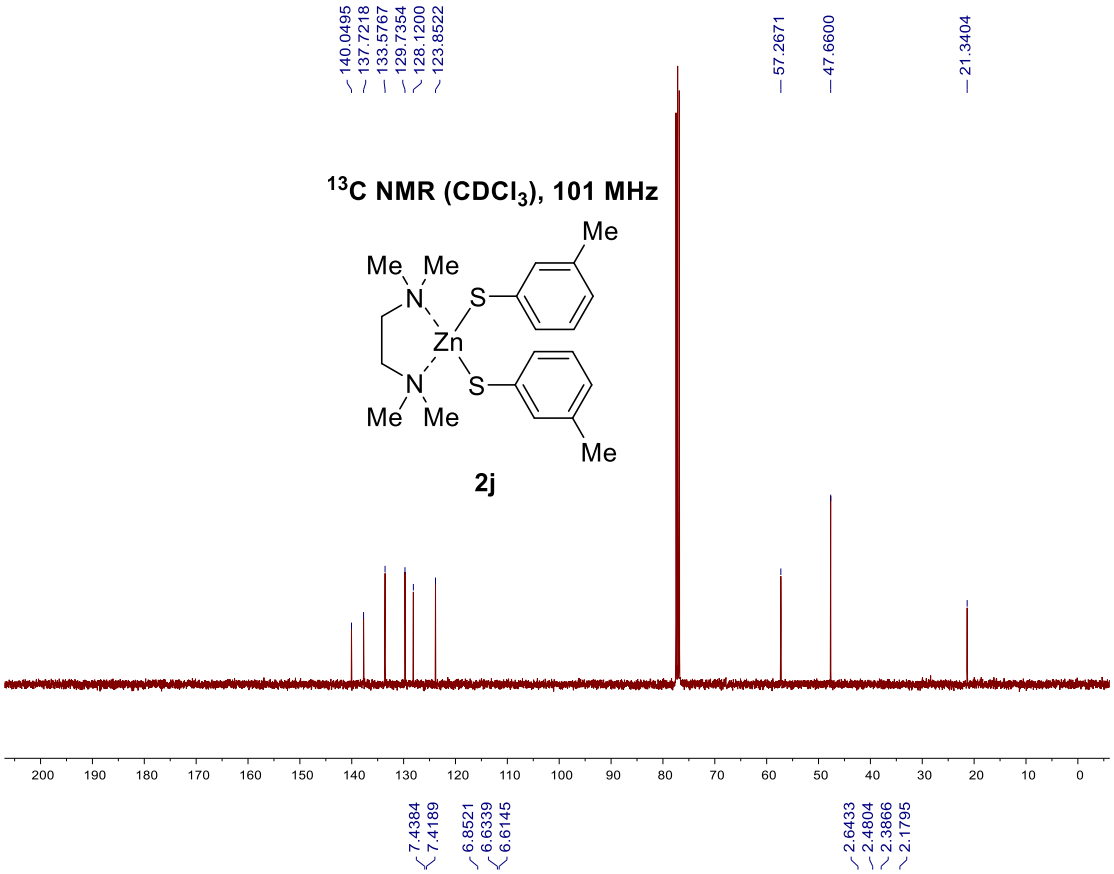
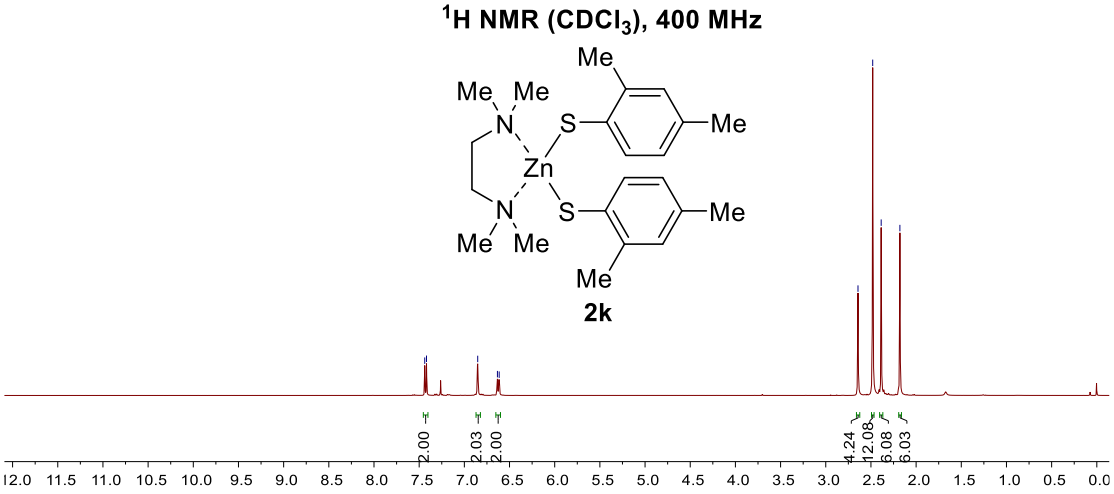
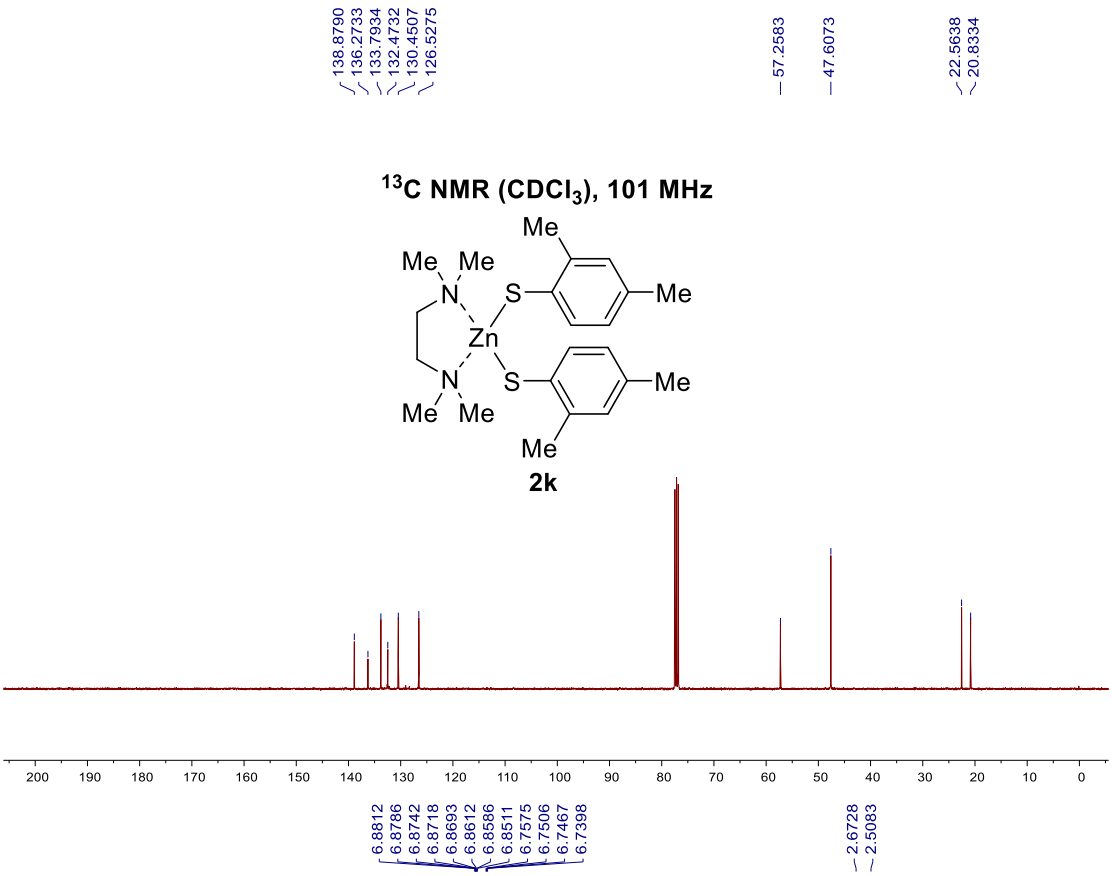
13C NMR (CDCl3), 101 MHz
Me
Me Me
N
S
Zn
N
S
Me Me
Me
2i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.3322
7.3099
6.9245
6.9058
6.8869
6.7321
6.7134
2.6750
2.5094
2.1421


1H NMR (CDCl3), 400 MHz
Me
Me Me
N
S
Zn
N
S
Me Me
Me
2j
4.00
2.04
2.00
4.12
12.21
6.10
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


140.0495
137.7218
133.5767
129.7354
128.1200
123.8522
57.2671
47.6600
21.3404
13C NMR (CDCl3), 101 MHz
Me
Me Me
N
S
Zn
N
S
Me Me
Me
2j
7.4384
7.4189
6.8521
6.6339
6.6145
2.6433
2.4804
2.3866
2.1795


1H NMR (CDCl3), 400 MHz
Me
Me Me
N
S
Me
Zn
N
S
Me
Me Me
Me
2k
2.00
2.03
2.00
4.24
12.08
6.08
6.03

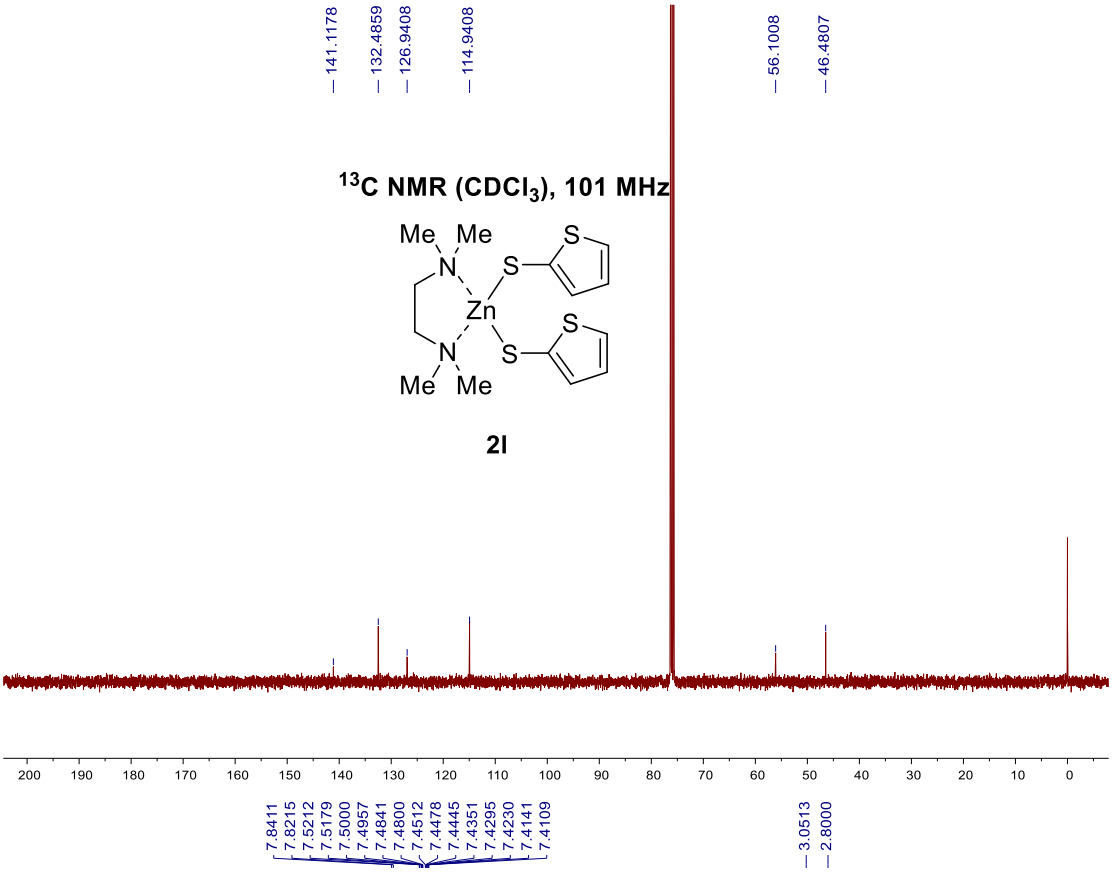


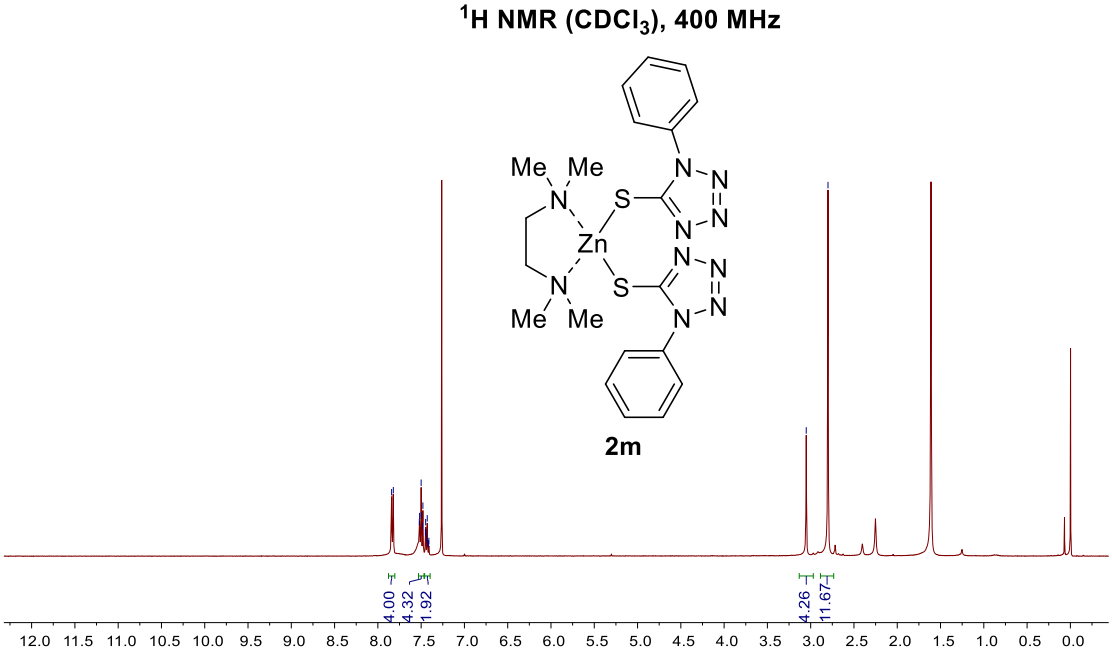
^{13}C NMR ($CDCl_3$), 101 MHz

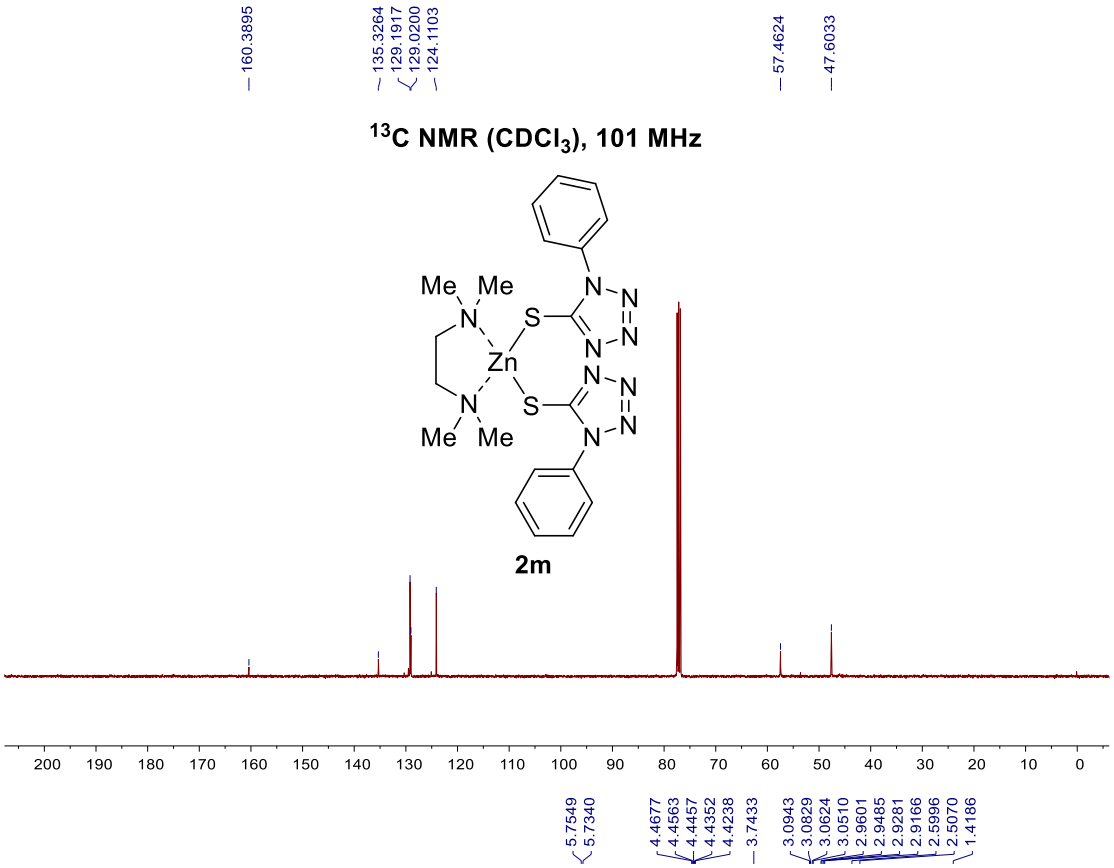
2k

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

2l

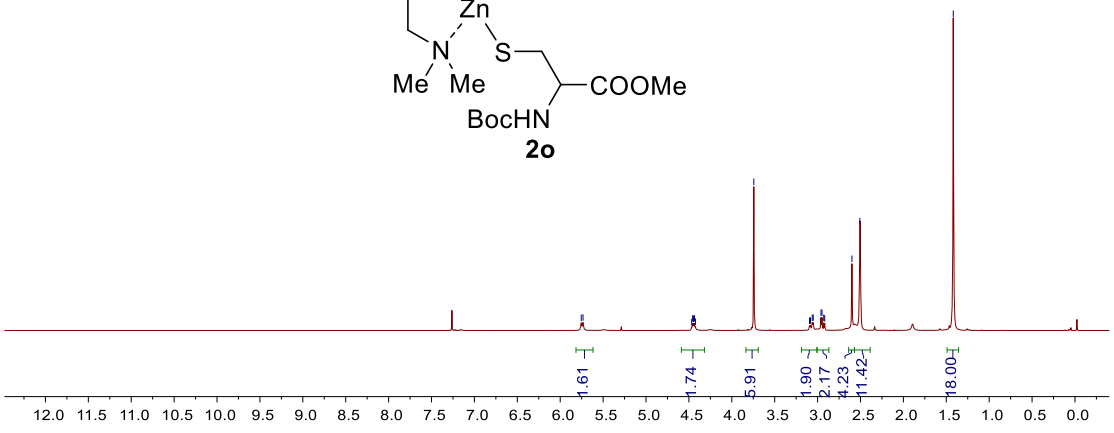

141.1178
132.4859
126.9408
114.9408
56.1008
46.4807
13C NMR (CDCl3), 101 MHz
Me Me
N
S
Zn
S
N
S
Me Me
2l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.8411
7.8215
7.5212
7.5179
7.5000
7.4957
7.4841
7.4800
7.4512
7.4478
7.4445
7.4351
7.4295
7.4230
7.4141
7.4109
3.0513
2.8000


1H NMR (CDCl3), 400 MHz
Me Me
N
S
Zn
S
N
Me Me
N
N
N
N
N
N
2m
4.00
4.32
1.92
4.26
11.67
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



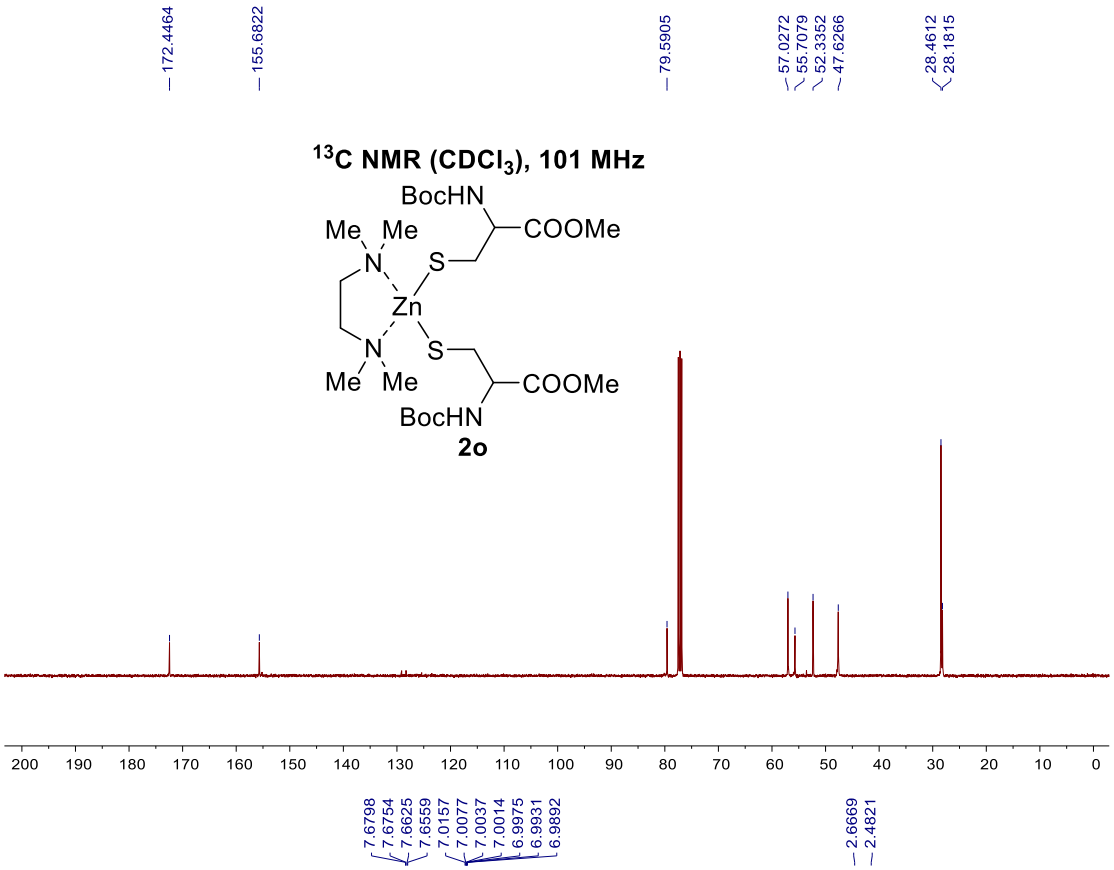
^{13}C NMR ($CDCl_3$), 101 MHz

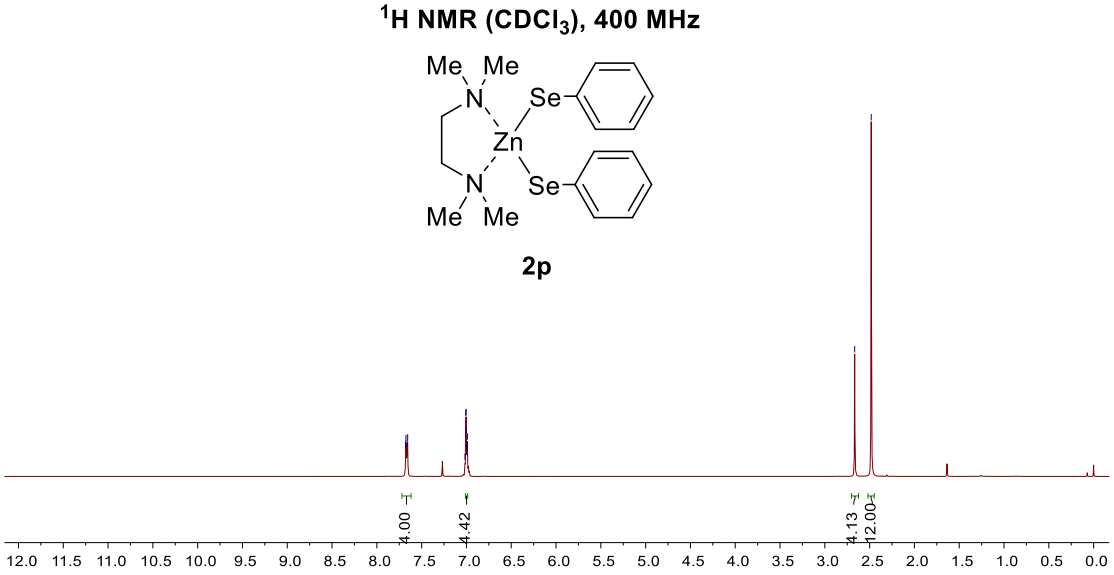
2m

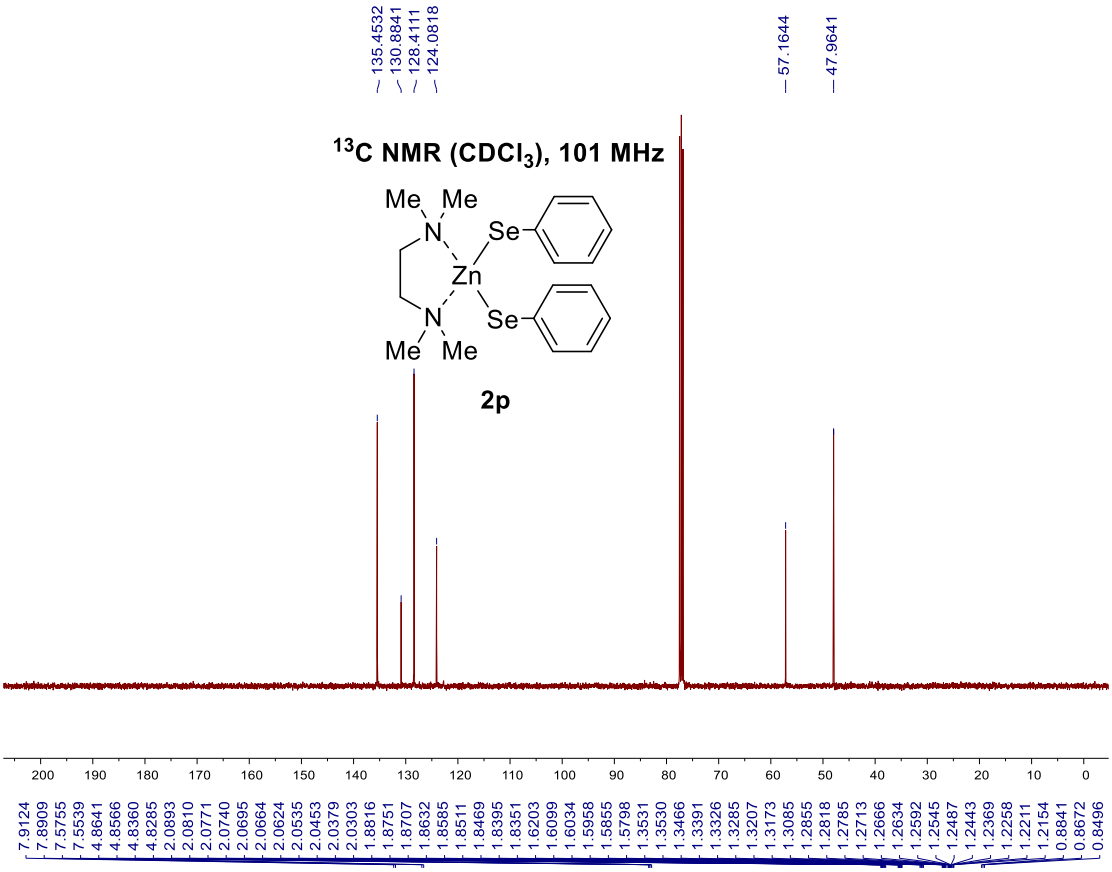


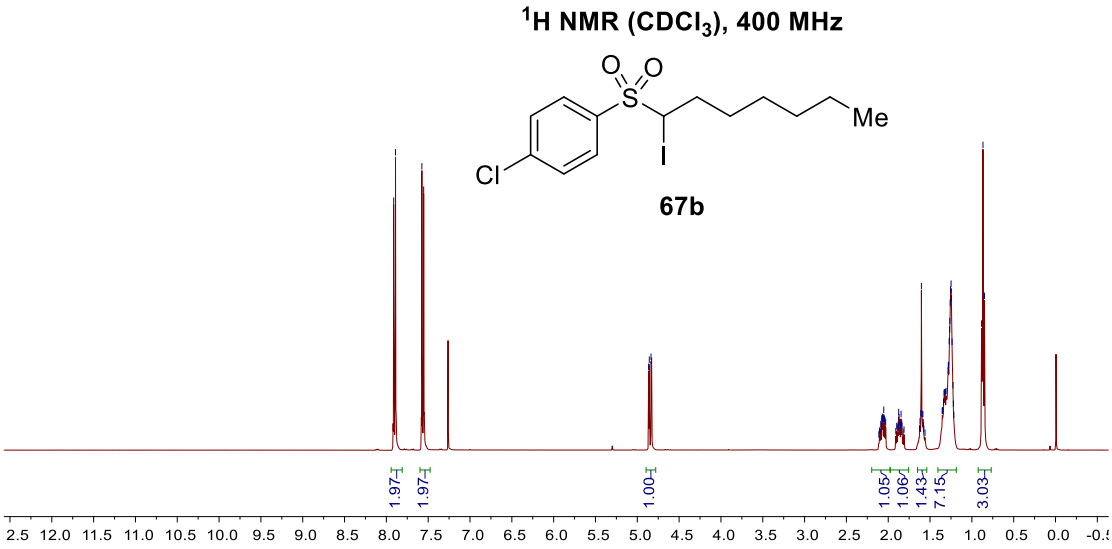
^{1}H NMR ($CDCl_3$), 400 MHz

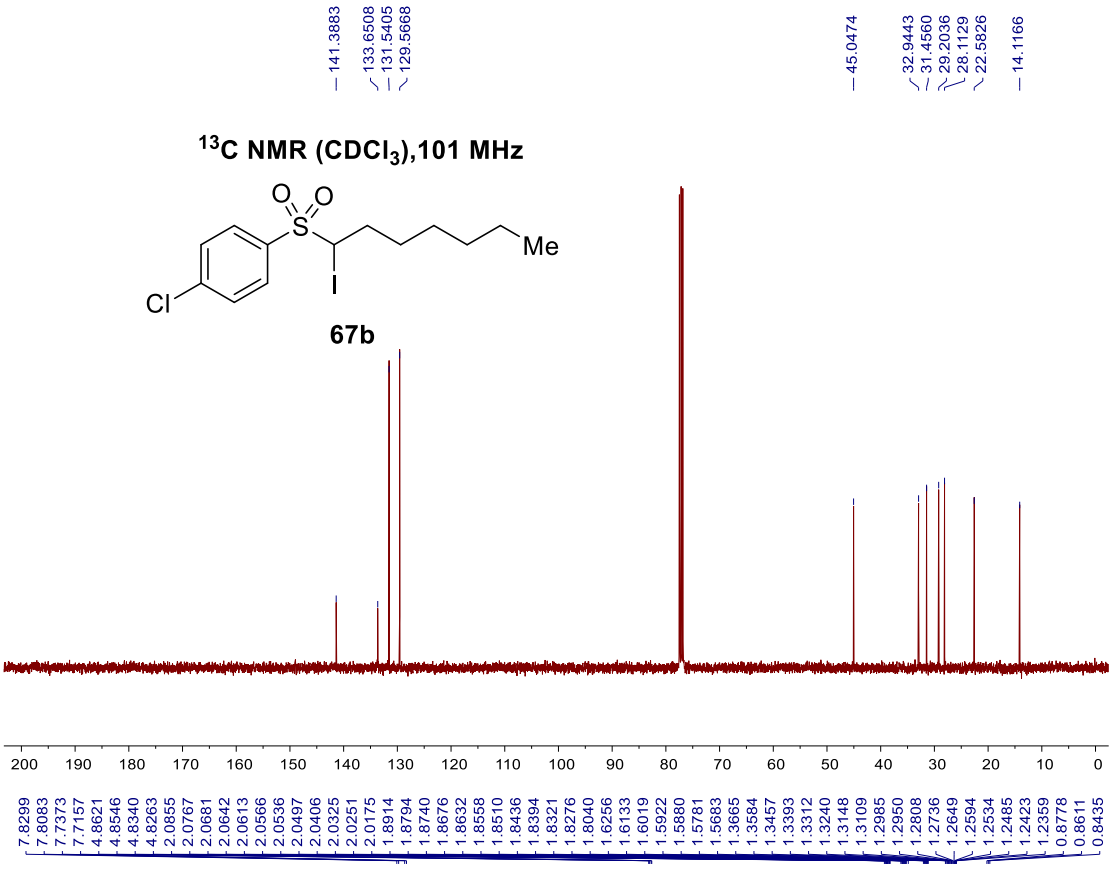
2o

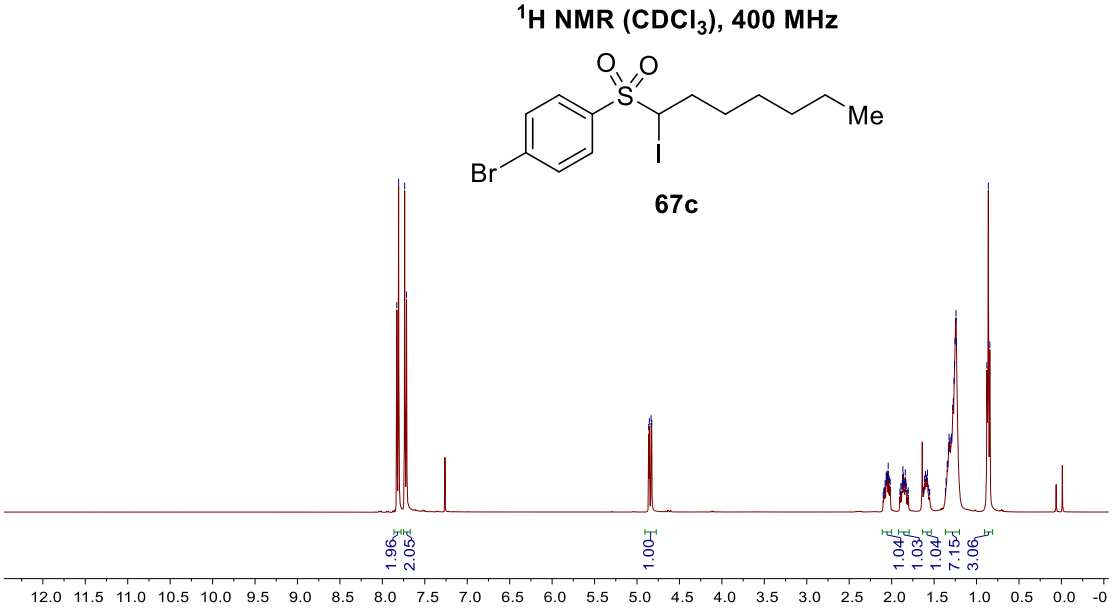

172.4464
155.6822
79.5905
57.0272
55.7079
52.3352
47.6266
28.4612
28.1815
13C NMR (CDCl3), 101 MHz
BocHN
Me Me
COOMe
N
S
Zn
N
S
Me Me
COOMe
BocHN
2o
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.6798
7.6754
7.6625
7.6559
7.0157
7.0077
7.0037
7.0014
6.9975
6.9931
6.9892
2.6669
2.4821

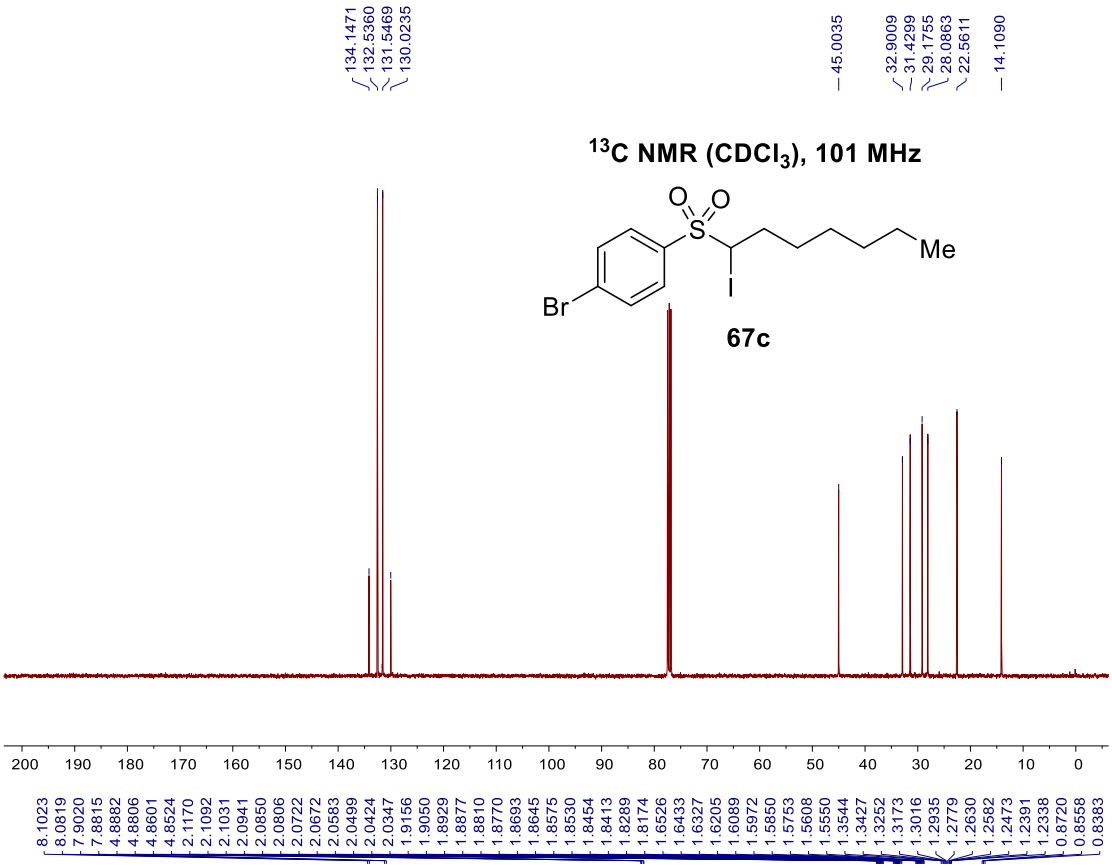

1H NMR (CDCl3), 400 MHz
Me Me
N
Se
Zn
N
Se
Me Me
2p
4.00
4.42
4.13
12.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

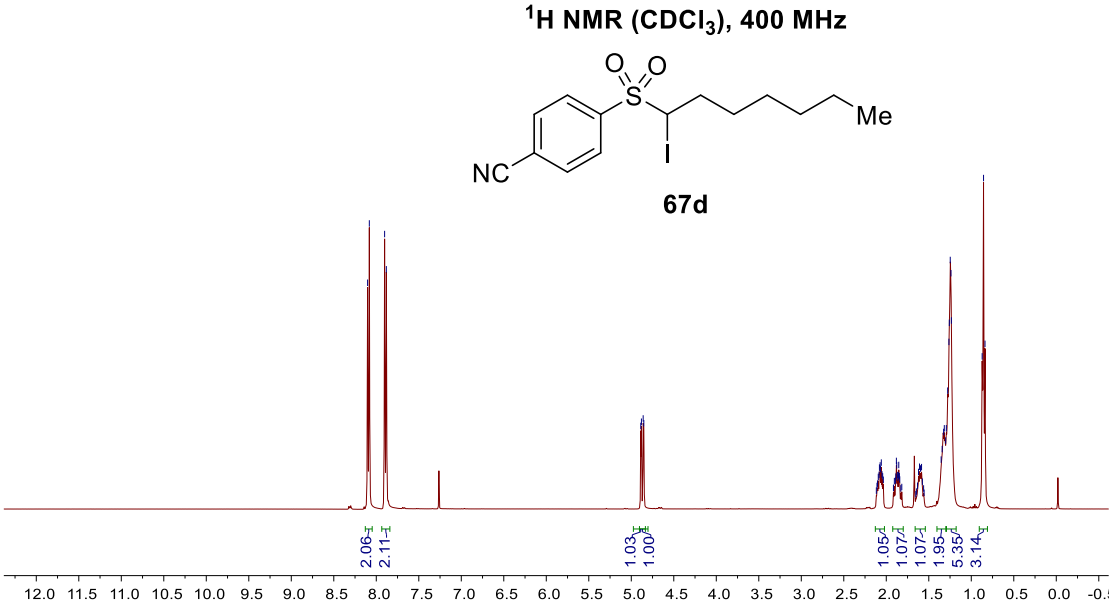

135.4532
130.8841
128.4111
124.0818
57.1644
47.9641
13C NMR (CDCl3), 101 MHz
Me
Me
N
Se
Zn
N
Se
Me
Me
2p

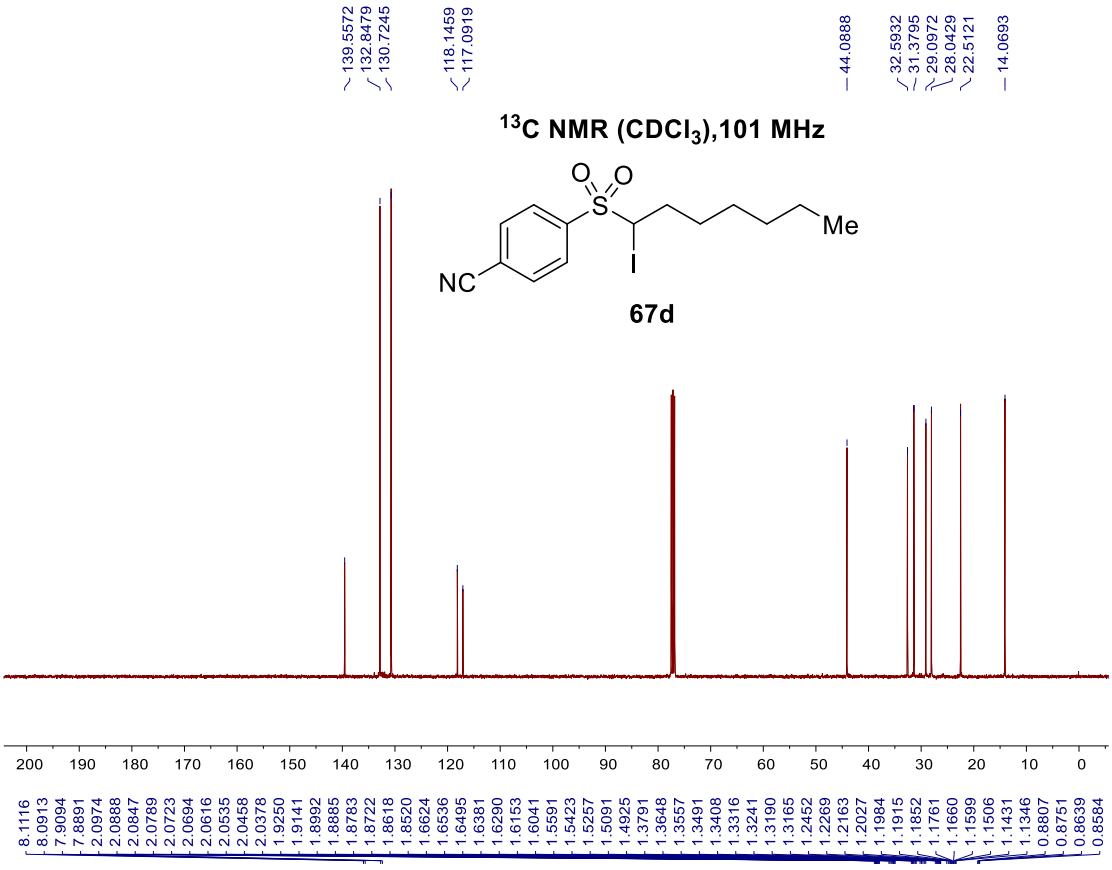

1H NMR (CDCl3), 400 MHz
O
O
S
Me
I
Cl
67b
1.97
1.97
1.00
1.05
1.06
1.43
7.15
3.03

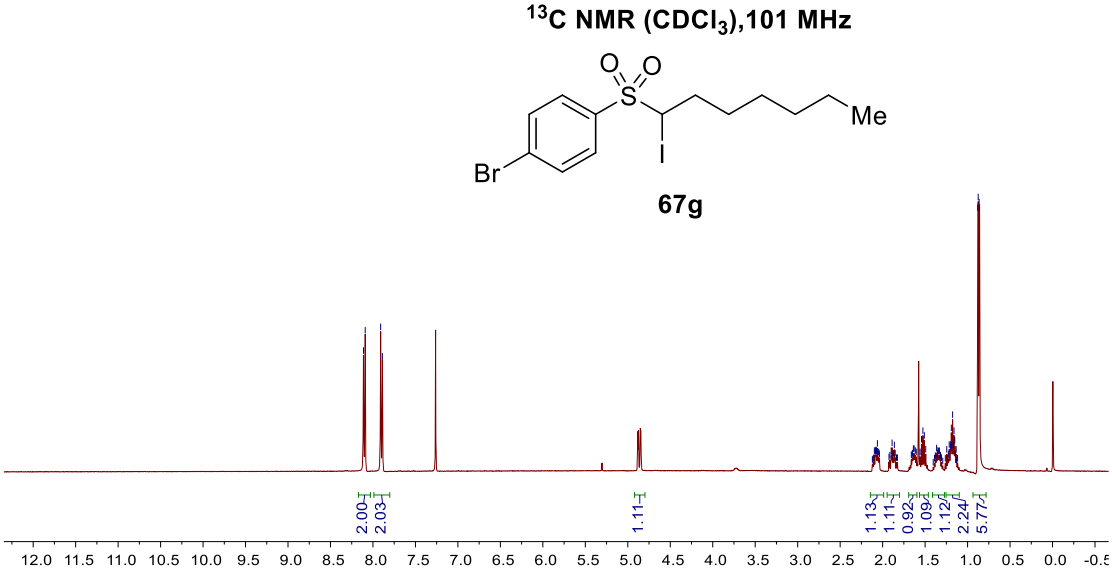

141.3883
133.6508
131.5405
129.5668
45.0474
32.9443
31.4560
29.2036
28.1129
22.5826
14.1166
13C NMR (CDCl3),101 MHz
O
O
S
Me
Cl
I
67b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.8299
7.8083
7.7373
7.7157
4.8621
4.8546
4.8340
4.8263
2.0855
2.0767
2.0681
2.0642
2.0613
2.0566
2.0536
2.0497
2.0406
2.0325
2.0251
2.0175
1.8914
1.8794
1.8740
1.8676
1.8632
1.8558
1.8510
1.8436
1.8394
1.8321
1.8276
1.8040
1.6256
1.6133
1.6019
1.5922
1.5880
1.5781
1.5683
1.3665
1.3584
1.3457
1.3393
1.3312
1.3240
1.3148
1.3109
1.2985
1.2950
1.2808
1.2736
1.2649
1.2594
1.2534
1.2485
1.2423
1.2359
0.8778
0.8611
0.8435

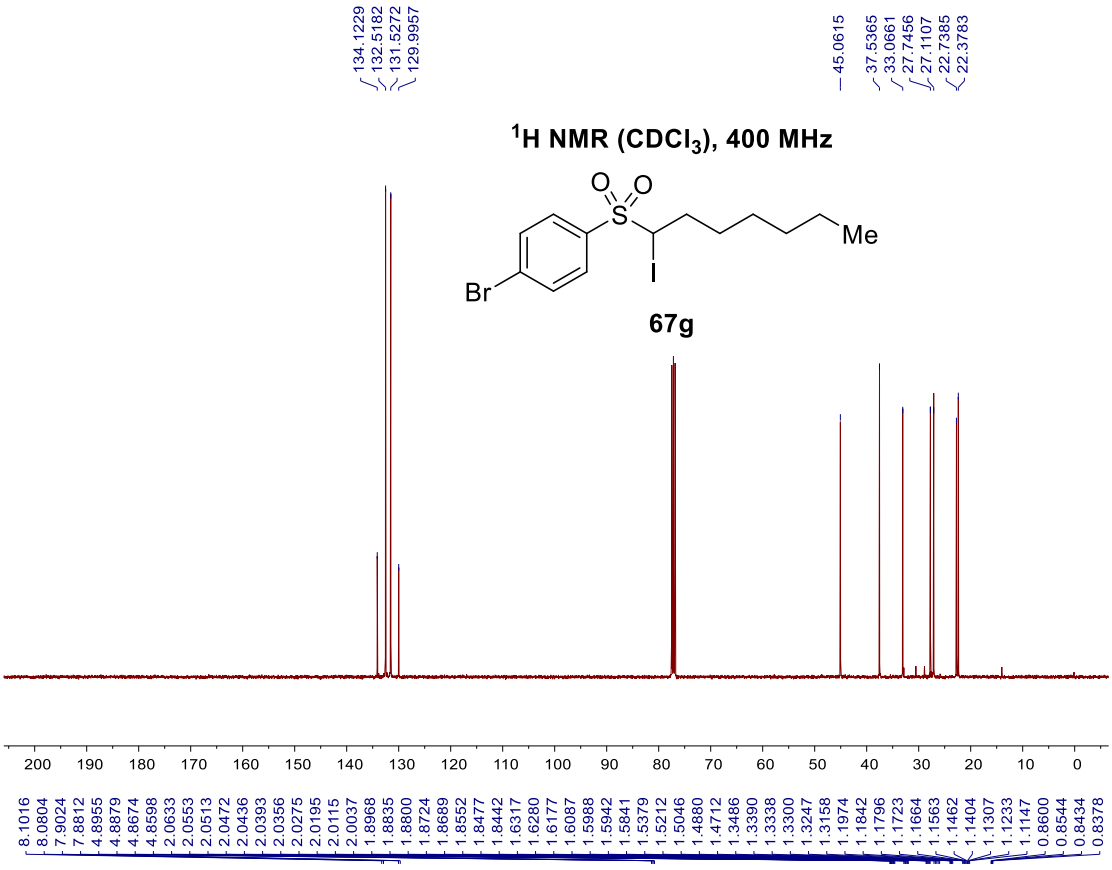

1H NMR (CDCl3), 400 MHz
O
O
S
Me
Br
I
67c
1.96
2.05
1.00
1.04
1.03
1.04
7.15
3.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

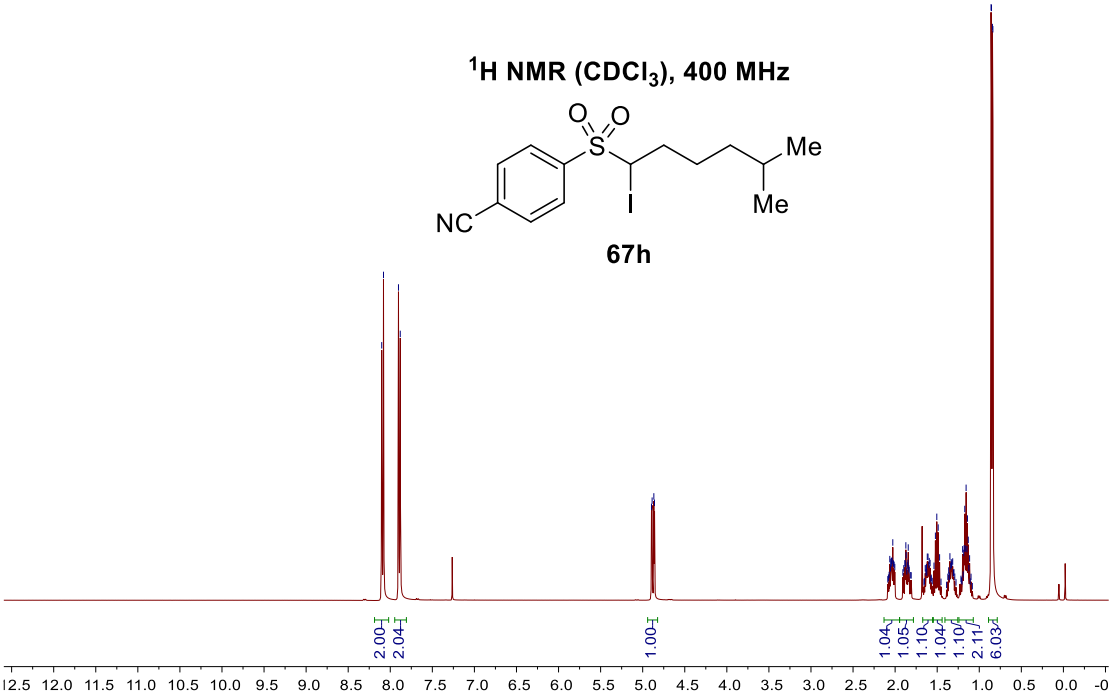

134.1471
132.5360
131.5469
130.0235
45.0035
32.9009
31.4299
29.1755
28.0863
22.5611
14.1090
13C NMR (CDCl3), 101 MHz
O
O
S
Me
Br
I
67c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
8.1023
8.0819
7.9020
7.8815
4.8882
4.8806
4.8601
4.8524
2.1170
2.1092
2.1031
2.0941
2.0850
2.0806
2.0722
2.0672
2.0583
2.0499
2.0424
2.0347
1.9156
1.9050
1.8929
1.8877
1.8810
1.8770
1.8693
1.8645
1.8575
1.8530
1.8454
1.8413
1.8289
1.8174
1.6526
1.6433
1.6327
1.6205
1.6089
1.5972
1.5850
1.5753
1.5608
1.5550
1.3544
1.3427
1.3252
1.3173
1.3016
1.2935
1.2779
1.2630
1.2582
1.2473
1.2391
1.2338
0.8720
0.8558
0.8383

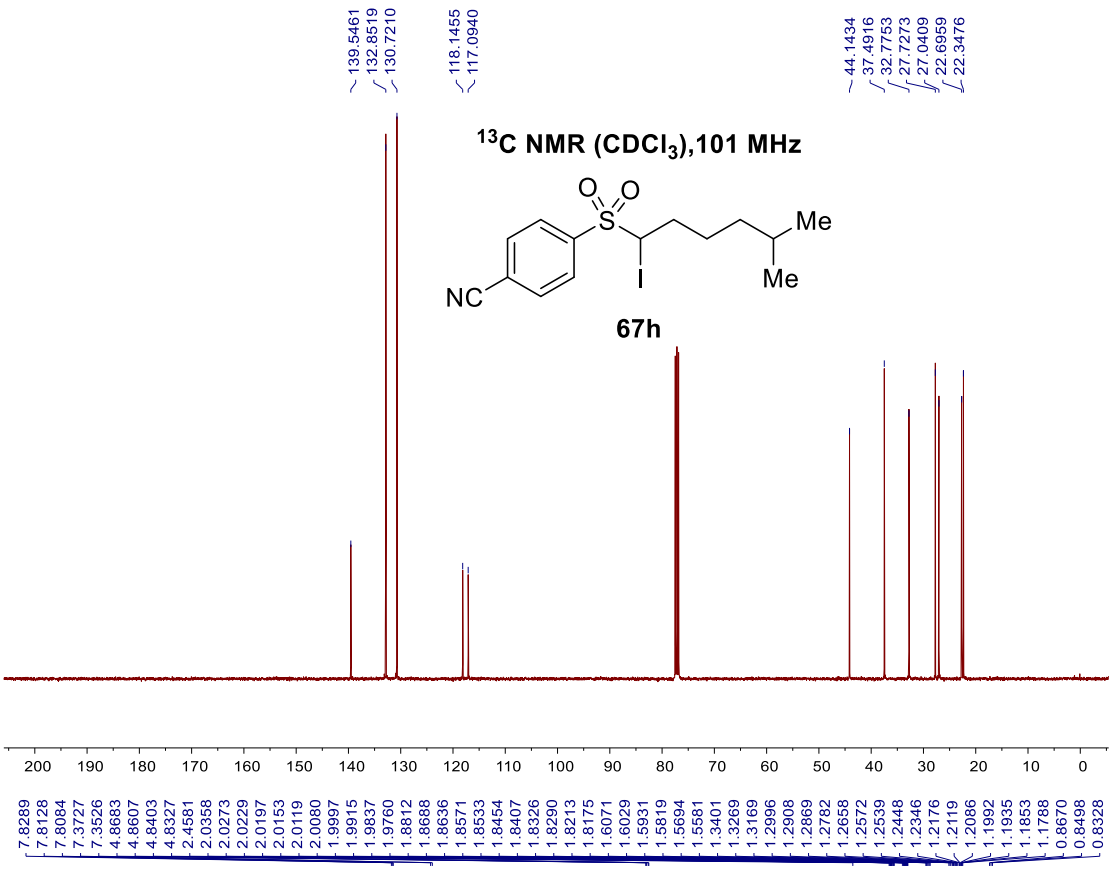

1H NMR (CDCl3), 400 MHz
O
O
S
Me
NC
I
67d
2.06
2.11
1.03
1.00
1.05
1.07
1.07
1.95
5.35
3.14
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

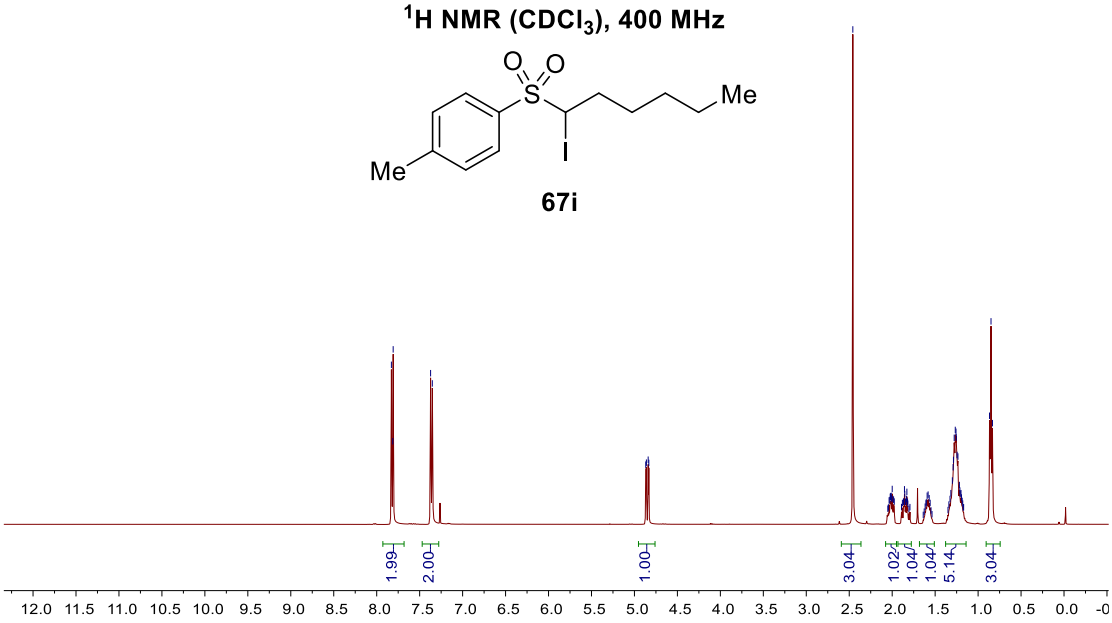

139.5572
132.8479
130.7245
118.1459
117.0919
44.0888
32.5932
31.3795
29.0972
28.0429
22.5121
14.0693
13C NMR (CDCl3),101 MHz
O
O
S
Me
I
NC
67d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
8.1116
8.0913
7.9094
7.8891
2.0974
2.0888
2.0847
2.0789
2.0723
2.0694
2.0616
2.0535
2.0458
2.0378
1.9250
1.9141
1.8992
1.8885
1.8783
1.8722
1.8618
1.8520
1.6624
1.6536
1.6495
1.6381
1.6290
1.6153
1.6041
1.5591
1.5423
1.5257
1.5091
1.4925
1.3791
1.3648
1.3557
1.3491
1.3408
1.3316
1.3241
1.3190
1.3165
1.2452
1.2269
1.2163
1.2027
1.1984
1.1915
1.1852
1.1761
1.1660
1.1599
1.1506
1.1431
1.1346
0.8807
0.8751
0.8639
0.8584

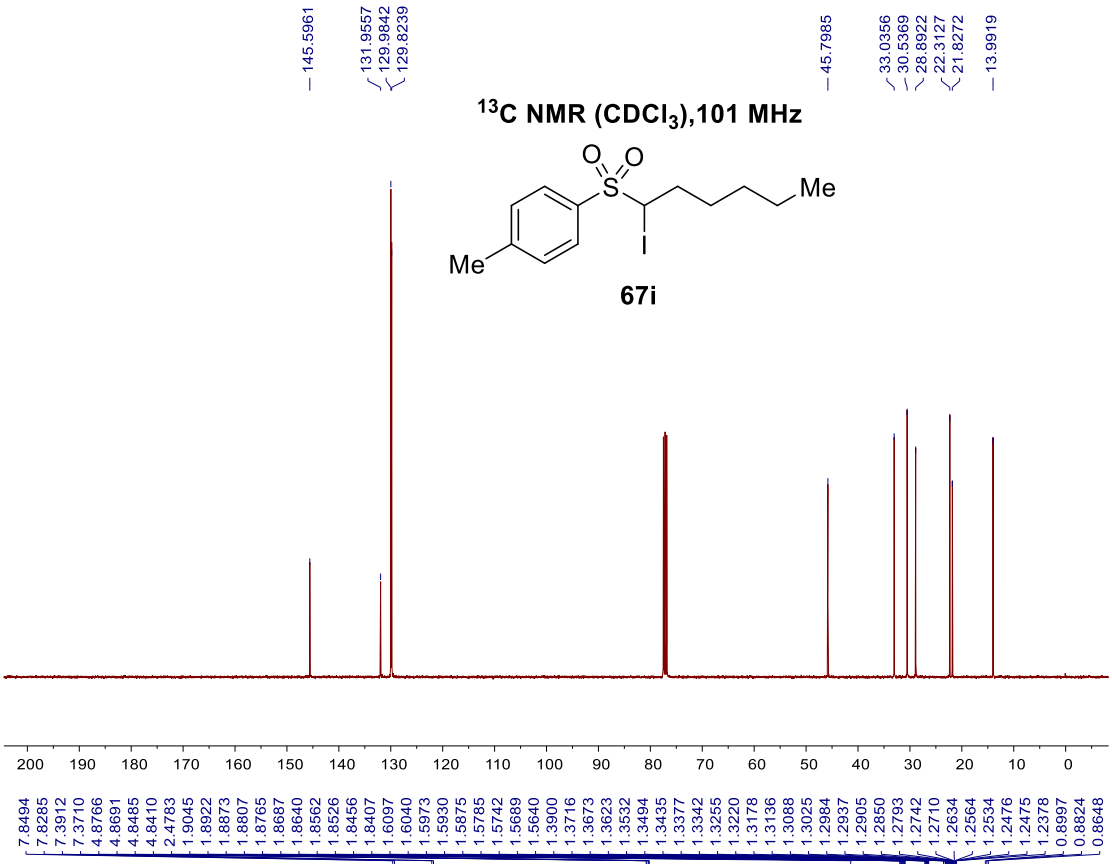

13C NMR (CDCl3),101 MHz
O
O
S
Me
I
Br
67g
2.00
2.03
1.11
1.13
1.11
0.92
1.09
1.12
2.24
5.77
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

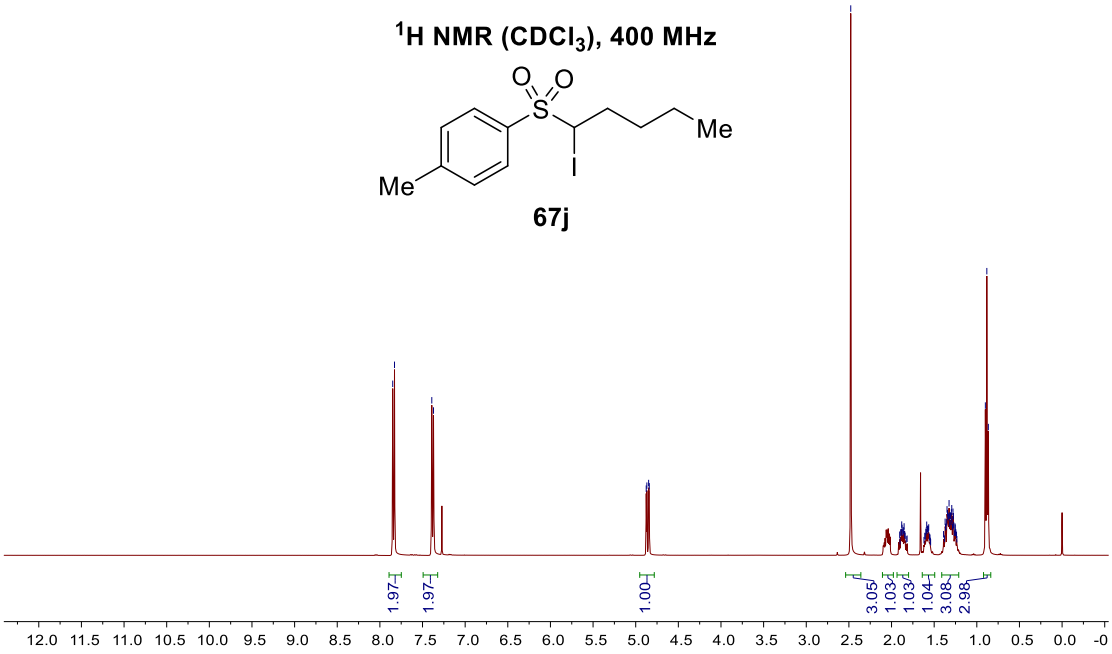

134.1229
132.5182
131.5272
129.9957
45.0615
37.5365
33.0661
27.7456
27.1107
22.7385
22.3783
^{1}H NMR ($CDCl_3$), 400 MHz
O
O
S
Me
I
Br
67g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
8.1016
8.0804
7.9024
7.8812
4.8955
4.8879
4.8674
4.8598
2.0633
2.0553
2.0513
2.0472
2.0436
2.0393
2.0356
2.0275
2.0195
2.0115
2.0037
1.8968
1.8835
1.8800
1.8724
1.8689
1.8552
1.8477
1.8442
1.6317
1.6280
1.6177
1.6087
1.5988
1.5942
1.5841
1.5379
1.5212
1.5046
1.4880
1.4712
1.3486
1.3390
1.3338
1.3300
1.3247
1.3158
1.1974
1.1842
1.1796
1.1723
1.1664
1.1563
1.1462
1.1404
1.1307
1.1233
1.1147
0.8600
0.8544
0.8434
0.8378

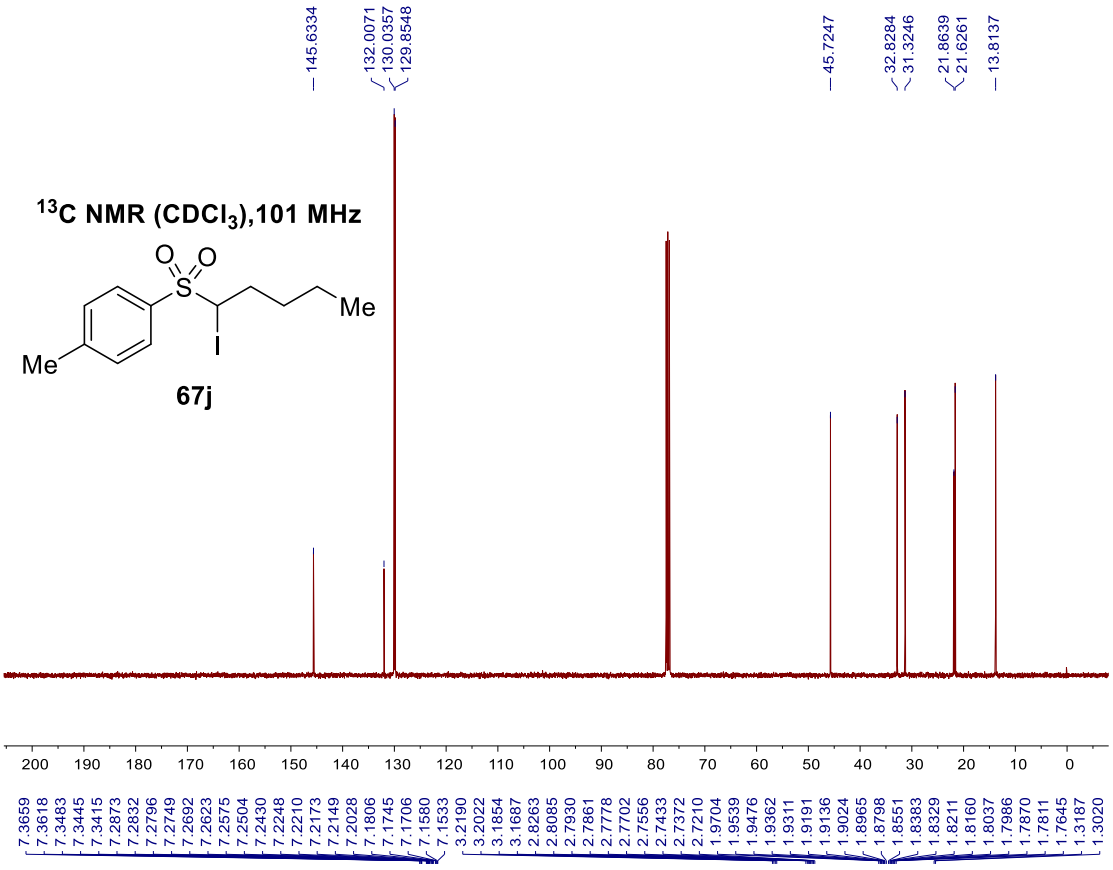

^{1}H NMR ($CDCl_3$), 400 MHz
O
O
S
Me
Me
I
NC
67h
2.00
2.04
1.00
1.04
1.05
1.10
1.04
1.10
2.11
6.03
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

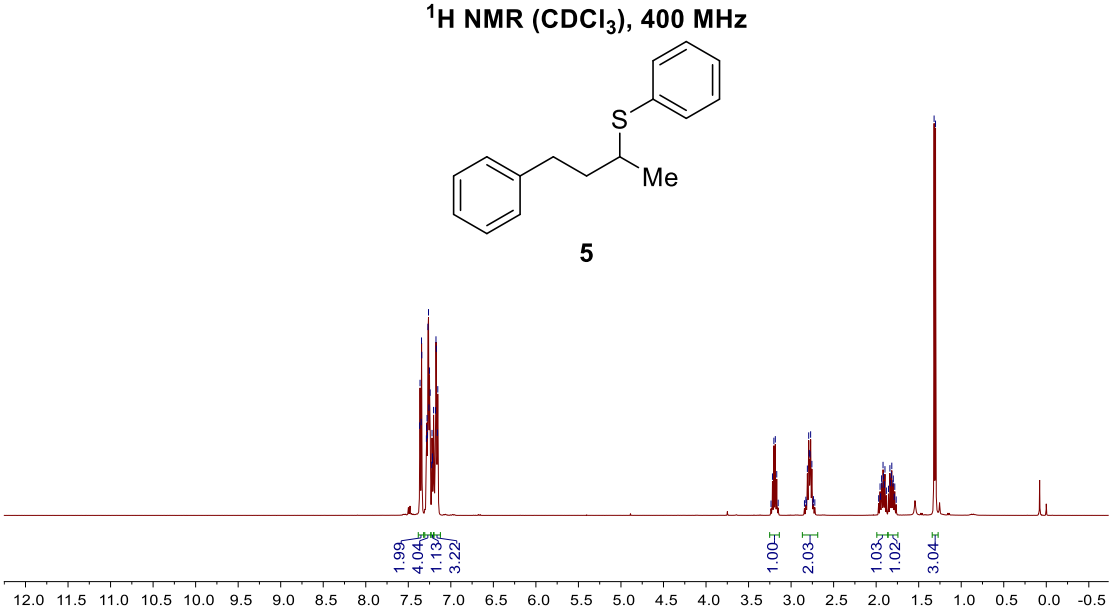

139.5461
132.8519
130.7210
118.1455
117.0940
44.1434
37.4916
32.7753
27.7273
27.0409
22.6959
22.3476
13C NMR (CDCl3),101 MHz
O
O
S
Me
I
Me
NC
67h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.8289
7.8128
7.8084
7.3727
7.3526
4.8683
4.8607
4.8403
4.8327
2.4581
2.0358
2.0273
2.0229
2.0197
2.0153
2.0119
2.0080
1.9997
1.9915
1.9837
1.9760
1.8812
1.8688
1.8636
1.8571
1.8533
1.8454
1.8407
1.8326
1.8290
1.8213
1.8175
1.6071
1.6029
1.5931
1.5819
1.5694
1.5581
1.3401
1.3269
1.3169
1.2996
1.2908
1.2869
1.2782
1.2658
1.2572
1.2539
1.2448
1.2346
1.2176
1.2119
1.2086
1.1992
1.1935
1.1853
1.1788
0.8670
0.8498
0.8328


1H NMR (CDCl3), 400 MHz
O
O
S
Me
I
Me
67i
1.99
2.00
1.00
3.04
1.02
1.04
1.04
5.14
3.04
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


145.5961
131.9557
129.9842
129.8239
45.7985
33.0356
30.5369
28.8922
22.3127
21.8272
13.9919
13C NMR (CDCl3),101 MHz
Me
Me
67i


1H NMR (CDCl3), 400 MHz
Me
Me
67j


145.6334
132.0071
130.0357
129.8548
45.7247
32.8284
31.3246
21.8639
21.6261
13.8137
13C NMR (CDCl3),101 MHz
O
O
S
Me
I
Me
67j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.3659 7.3618 7.3483 7.3445 7.3415 7.2873 7.2832 7.2796 7.2749 7.2692 7.2623 7.2575 7.2504 7.2430 7.2248 7.2210 7.2173 7.2149 7.2028 7.1806 7.1745 7.1706 7.1580 7.1533
3.2190 3.2022 3.1854 3.1687 2.8263 2.8085 2.7930 2.7861 2.7778 2.7702 2.7556 2.7433 2.7372 2.7210 1.9704 1.9539 1.9476 1.9362 1.9311 1.9191 1.9136 1.9024 1.8965 1.8798 1.8551 1.8383 1.8329 1.8211 1.8160 1.8037 1.7986 1.7870 1.7811 1.7645 1.3187 1.3020


1H NMR (CDCl3), 400 MHz
S
Me
5
1.99
4.04
1.13
3.22
1.00
2.03
1.03
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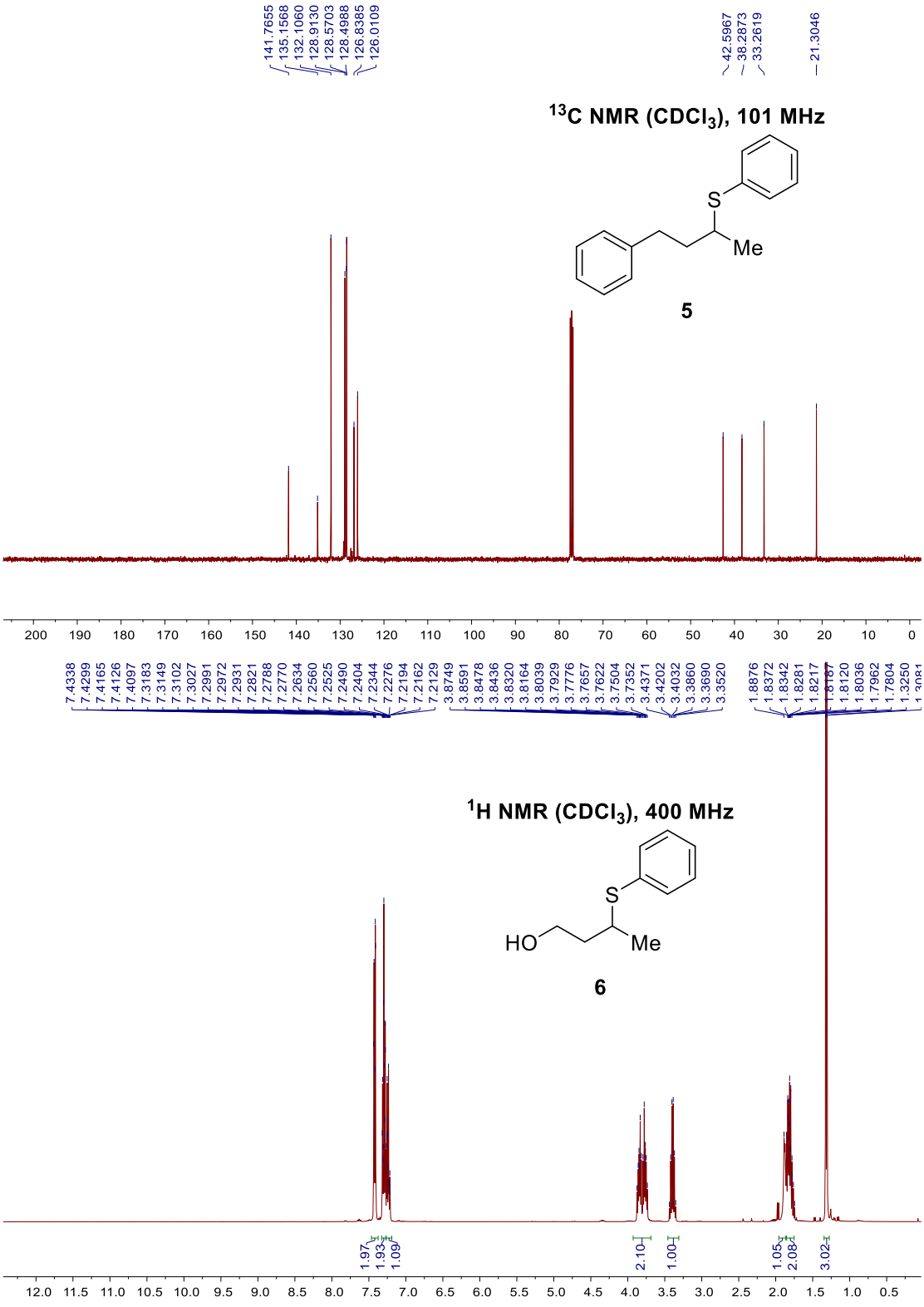
3.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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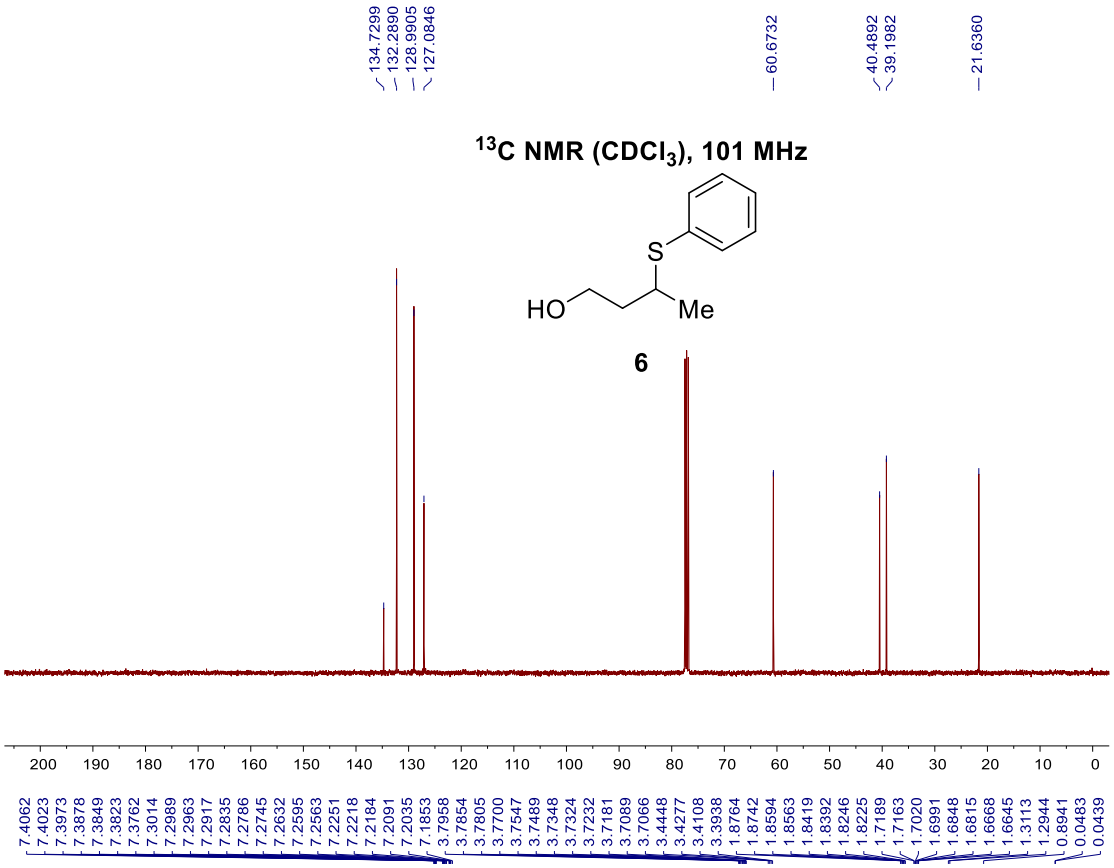
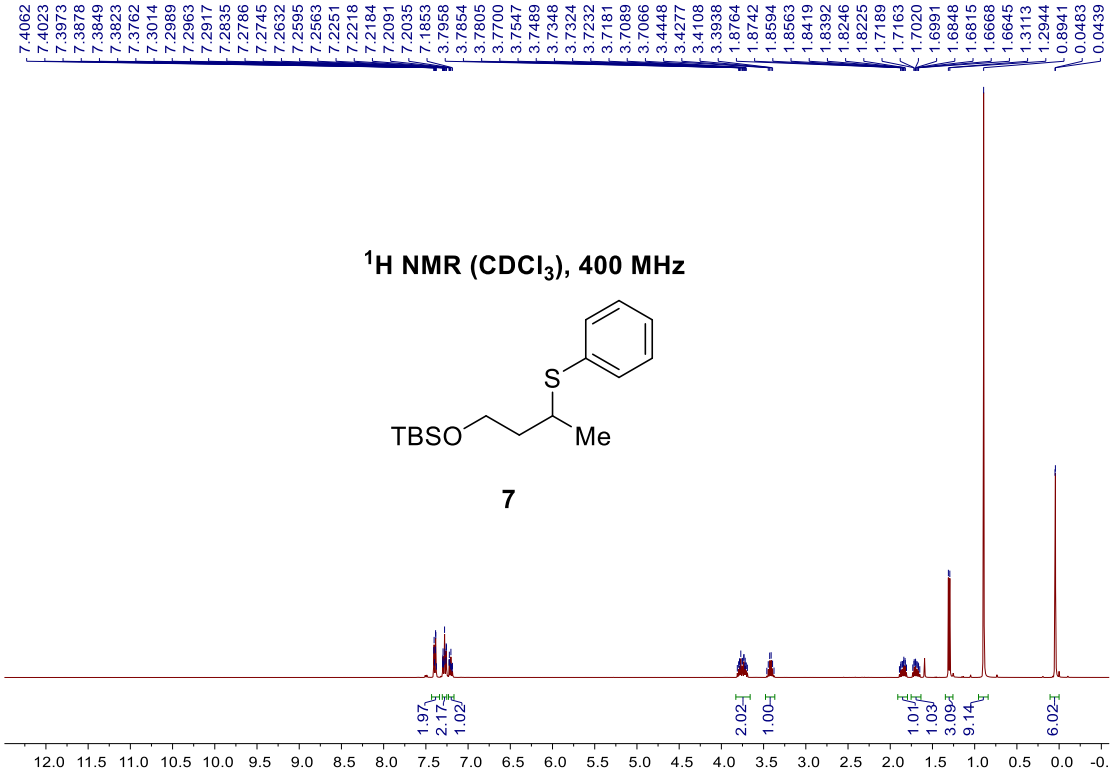
132.1060
128.9130
128.5703
128.4988
126.8385
126.0109
42.5967
38.2873
33.2619
21.3046
13C NMR (CDCl3), 101 MHz
S
Me
5
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.4338
7.4299
7.4165
7.4126
7.4097
7.3183
7.3149
7.3102
7.3027
7.2991
7.2972
7.2931
7.2821
7.2788
7.2770
7.2634
7.2560
7.2525
7.2490
7.2404
7.2344
7.2276
7.2194
7.2162
7.2129
3.8749
3.8591
3.8478
3.8436
3.8320
3.8164
3.8039
3.7929
3.7776
3.7657
3.7622
3.7504
3.7352
3.4371
3.4202
3.4032
3.3860
3.3690
3.3520
1.8876
1.8372
1.8342
1.8281
1.8217
1.8187
1.8120
1.8036
1.7962
1.7804
1.3250
1H NMR (CDCl3), 400 MHz
S
HO
Me
6
1.97
1.93
1.09
2.10
1.00
1.05
2.08
3.02
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


134.7299
132.2890
128.9905
127.0846
60.6732
40.4892
39.1982
21.6360
13C NMR (CDCl3), 101 MHz
S
HO
Me
6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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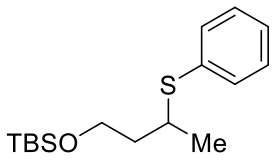
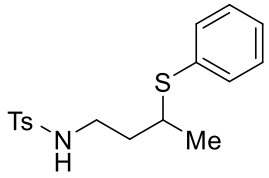
7.4023
7.3973
7.3878
7.3849
7.3823
7.3762
7.3014
7.2989
7.2963
7.2917
7.2835
7.2786
7.2745
7.2632
7.2595
7.2563
7.2251
7.2218
7.2184
7.2091
7.2035
7.1853
3.7958
3.7854
3.7805
3.7700
3.7547
3.7489
3.7348
3.7324
3.7232
3.7181
3.7089
3.7066
3.4448
3.4277
3.4108
3.3938
1.8764
1.8742
1.8594
1.8563
1.8419
1.8392
1.8246
1.8225
1.7189
1.7163
1.7020
1.6991
1.6848
1.6815
1.6668
1.6645
1.3113
1.2944
0.8941
0.0483
0.0439
1H NMR (CDCl3), 400 MHz
S
TBSO
Me
7
1.97
2.17
1.02
2.02
1.00
1.01
1.03
3.09
9.14
6.02
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.

^{13}C NMR ($CDCl_3$), 101 MHz



7

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



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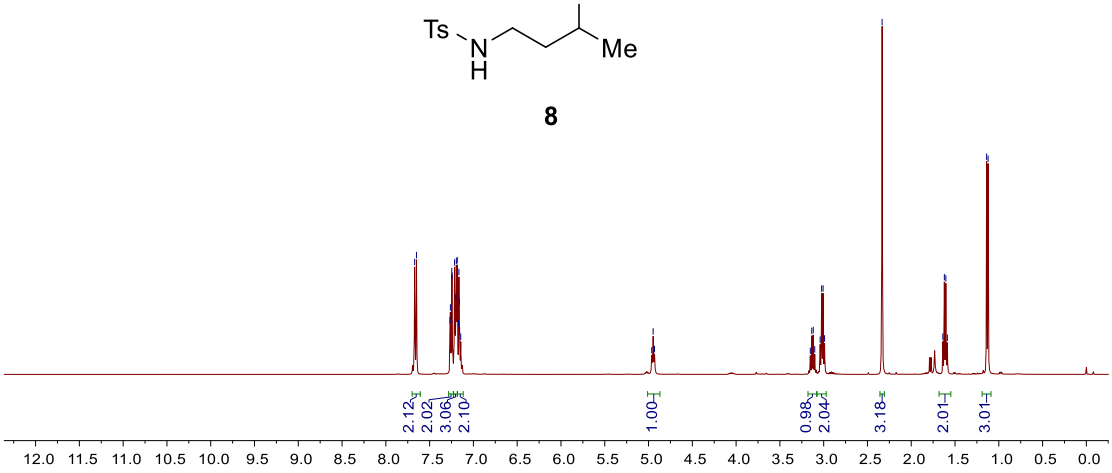
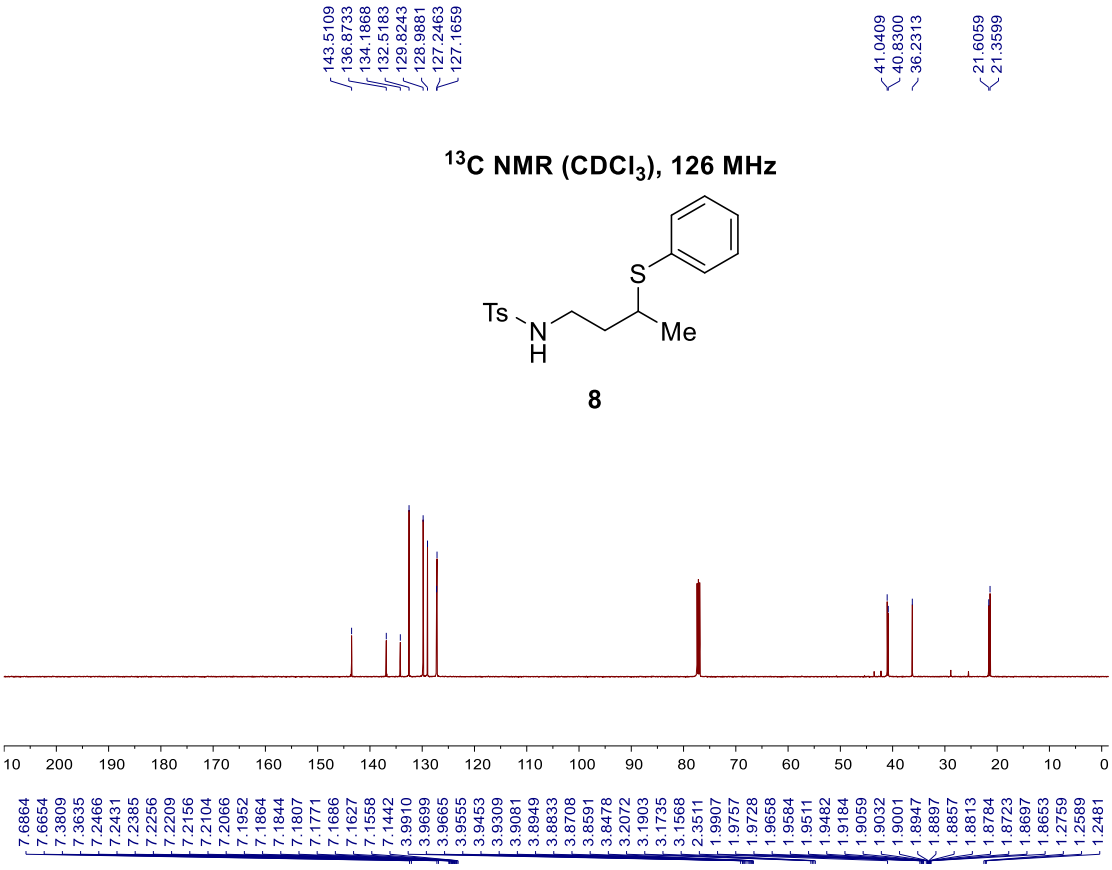
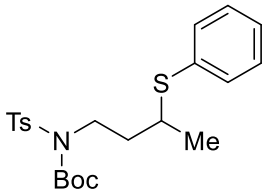




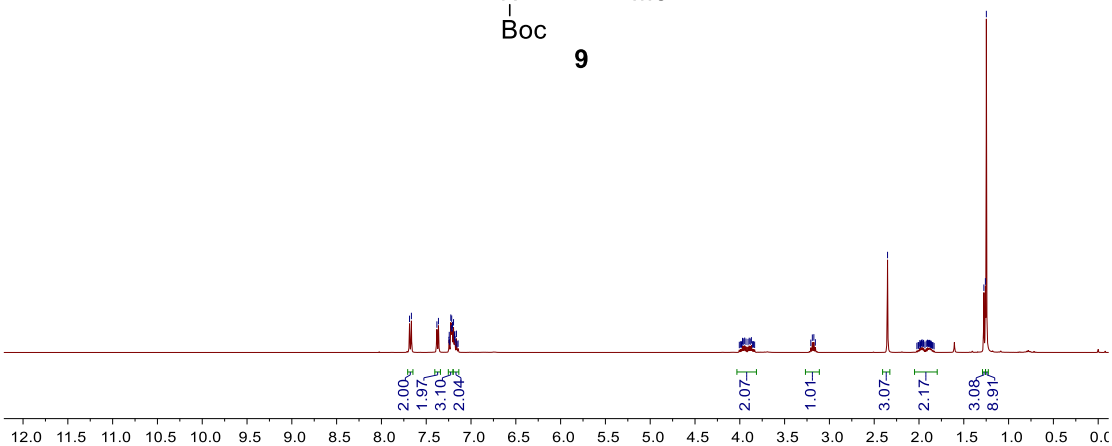
^{13}C NMR ($CDCl_3$), 126 MHz

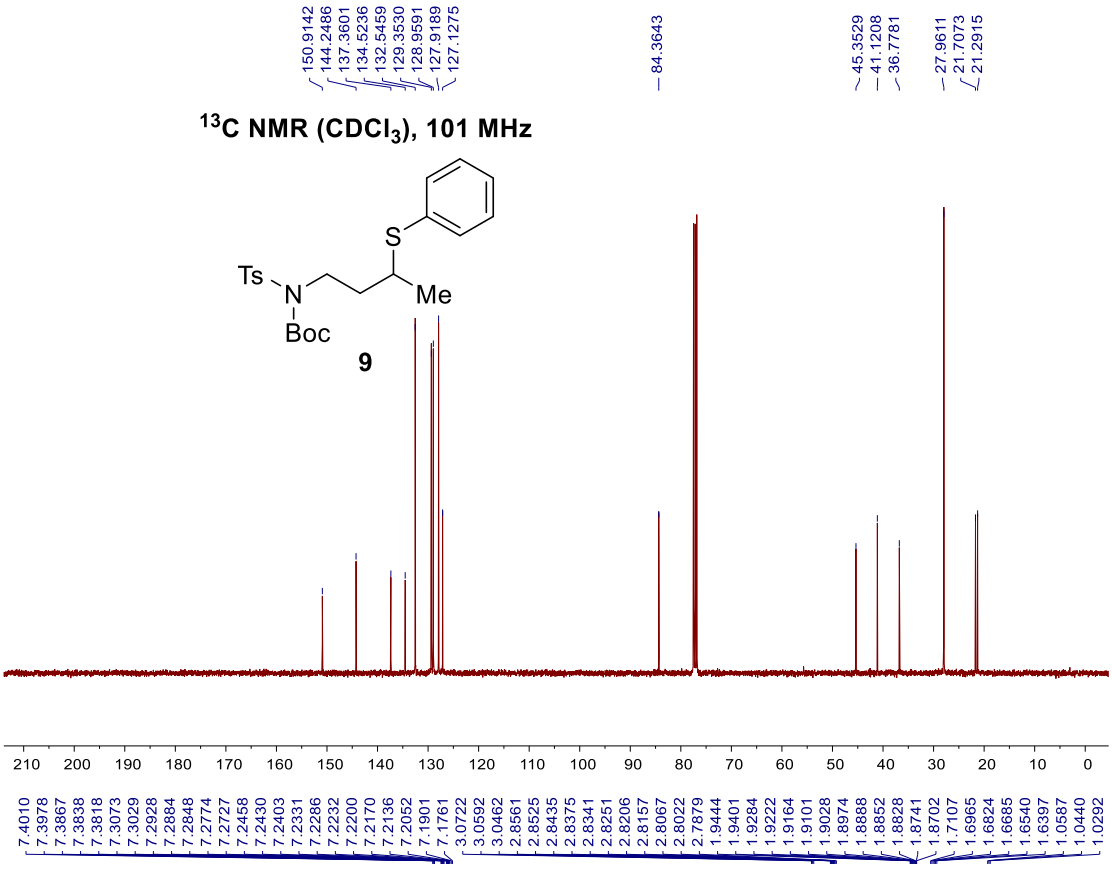
8

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



9

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134.5236
132.5459
129.3530
128.9591
127.9189
127.1275
84.3643
45.3529
41.1208
36.7781
27.9611
21.7073
21.2915
13C NMR (CDCl3), 101 MHz
S
Ts
N
Me
Boc
9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.4010
7.3978
7.3867
7.3838
7.3818
7.3073
7.3029
7.2928
7.2884
7.2848
7.2774
7.2727
7.2458
7.2430
7.2403
7.2331
7.2286
7.2232
7.2200
7.2170
7.2136
7.2052
7.1901
7.1761
3.0722
3.0592
3.0462
2.8561
2.8525
2.8435
2.8375
2.8341
2.8251
2.8206
2.8157
2.8067
2.8022
2.7879
1.9444
1.9401
1.9284
1.9222
1.9164
1.9101
1.9028
1.8974
1.8888
1.8852
1.8828
1.8741
1.8702
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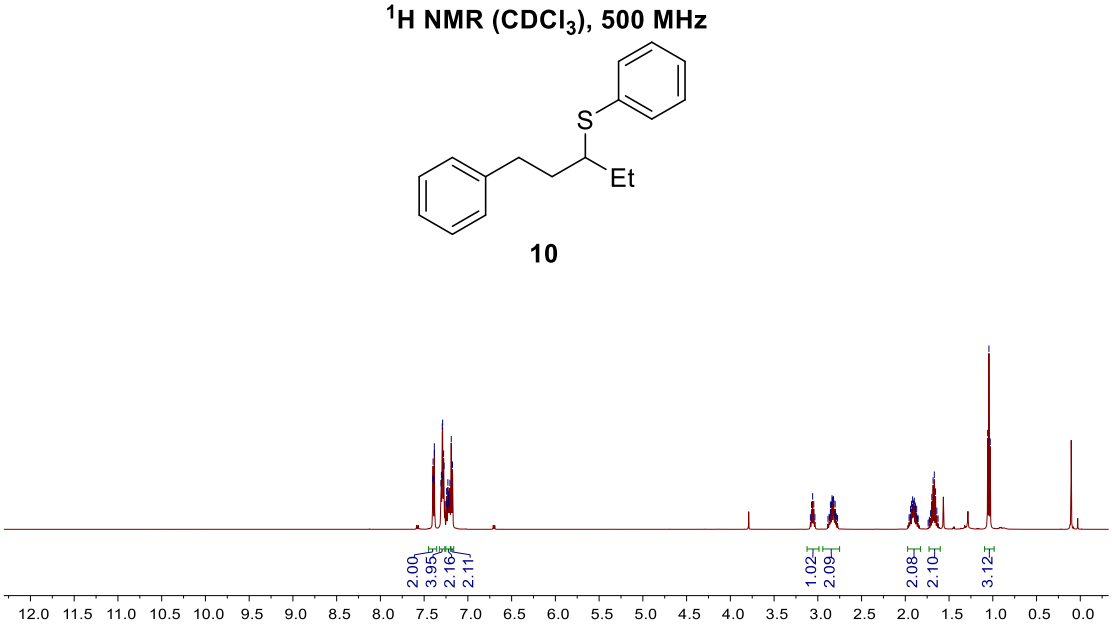
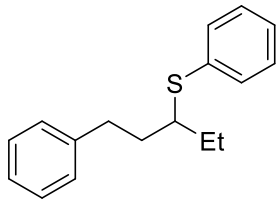
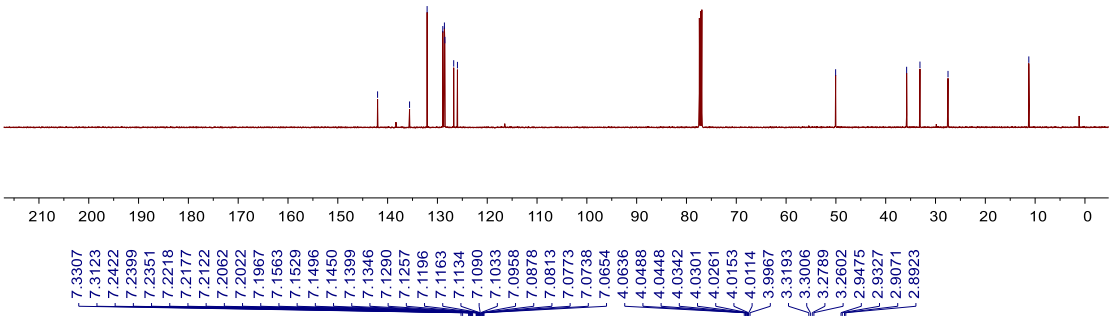
1.6685
1.6540
1.6397
1.0587
1.0440
1.0292


1H NMR (CDCl3), 500 MHz
S
Et
10
2.00
3.95
2.16
2.11
1.02
2.09
2.08
2.10
3.12
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

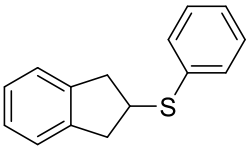
^{13}C NMR ($CDCl_3$), 126 MHz



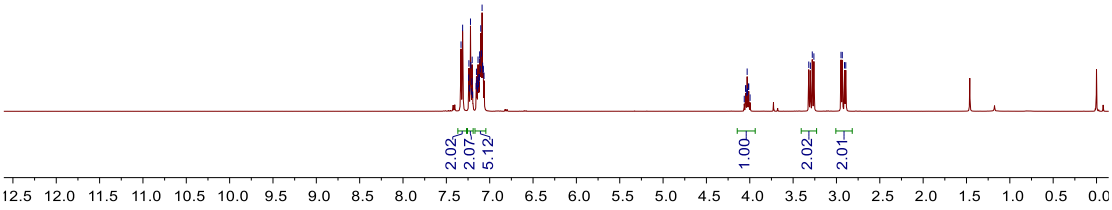
10

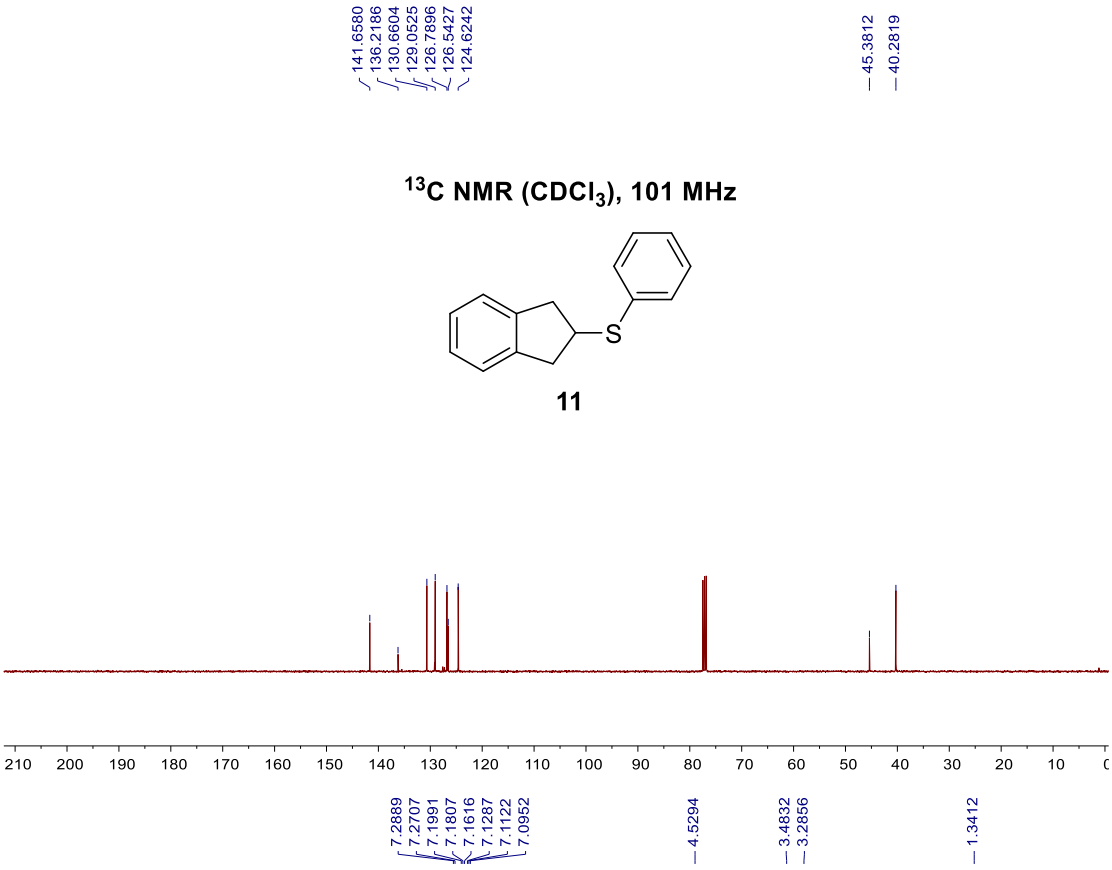


^{1}H NMR ($CDCl_3$), 400 MHz



11

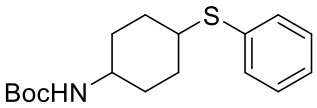




^{13}C NMR ($CDCl_3$), 101 MHz

11

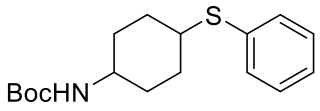
^{1}H NMR ($CDCl_3$), 400 MHz



12

155.2780
135.2220
131.7871
129.0045
126.8785
79.2424
47.7649
44.7579
35.4453
29.0027
28.5158

^{13}C NMR ($CDCl_3$), 101 MHz



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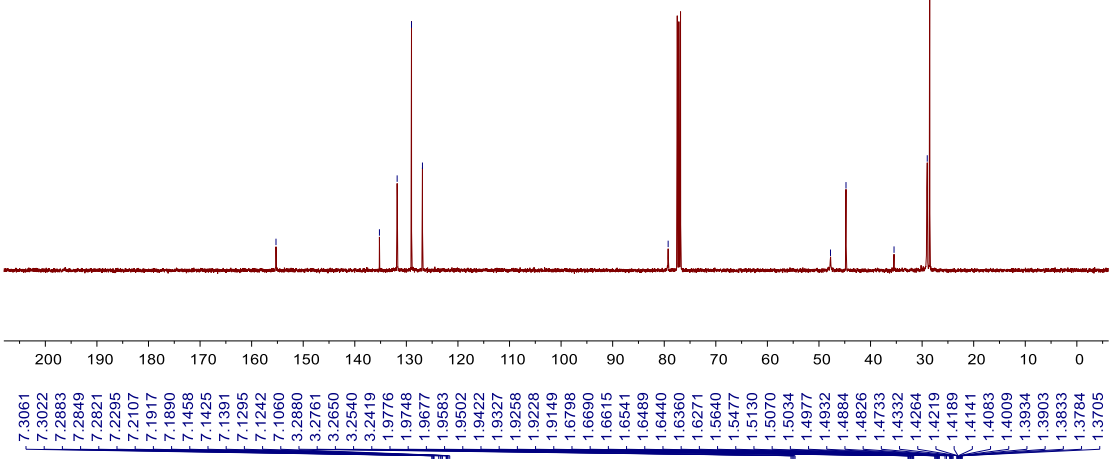
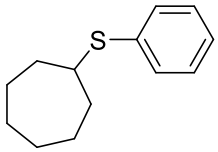


^{1}H NMR ($CDCl_3$), 400 MHz



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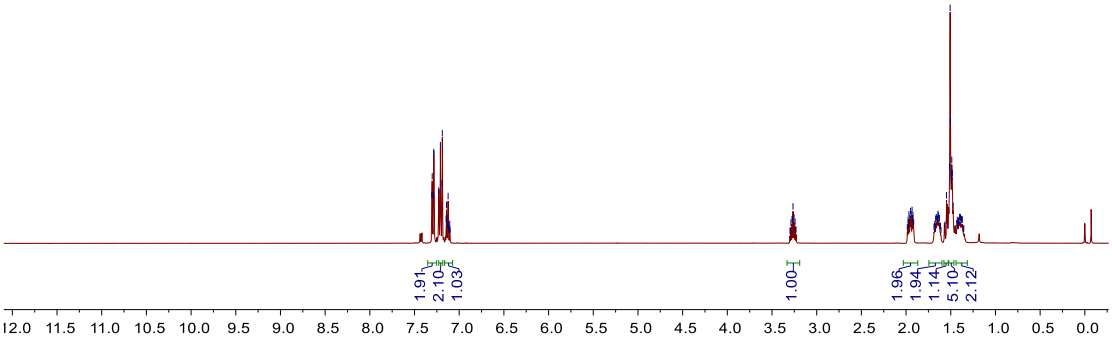
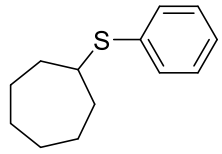


^{13}C NMR ($CDCl_3$), 101 MHz



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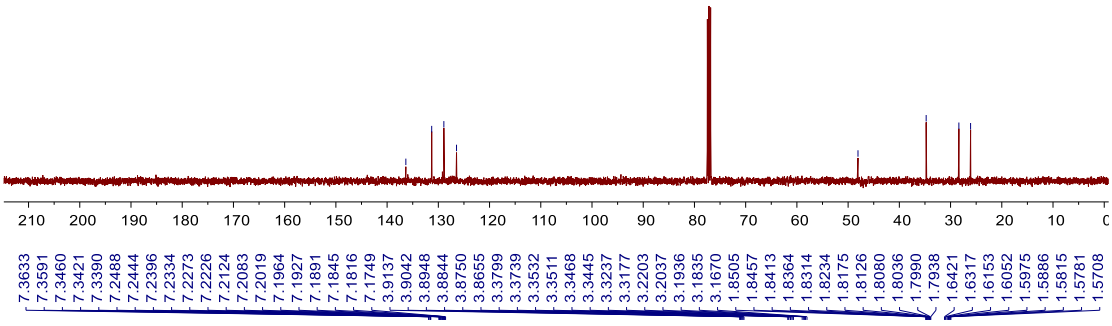
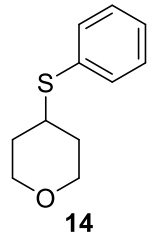


^{1}H NMR ($CDCl_3$), 400 MHz



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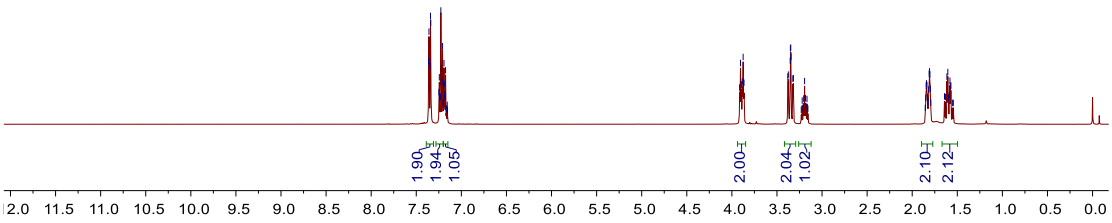
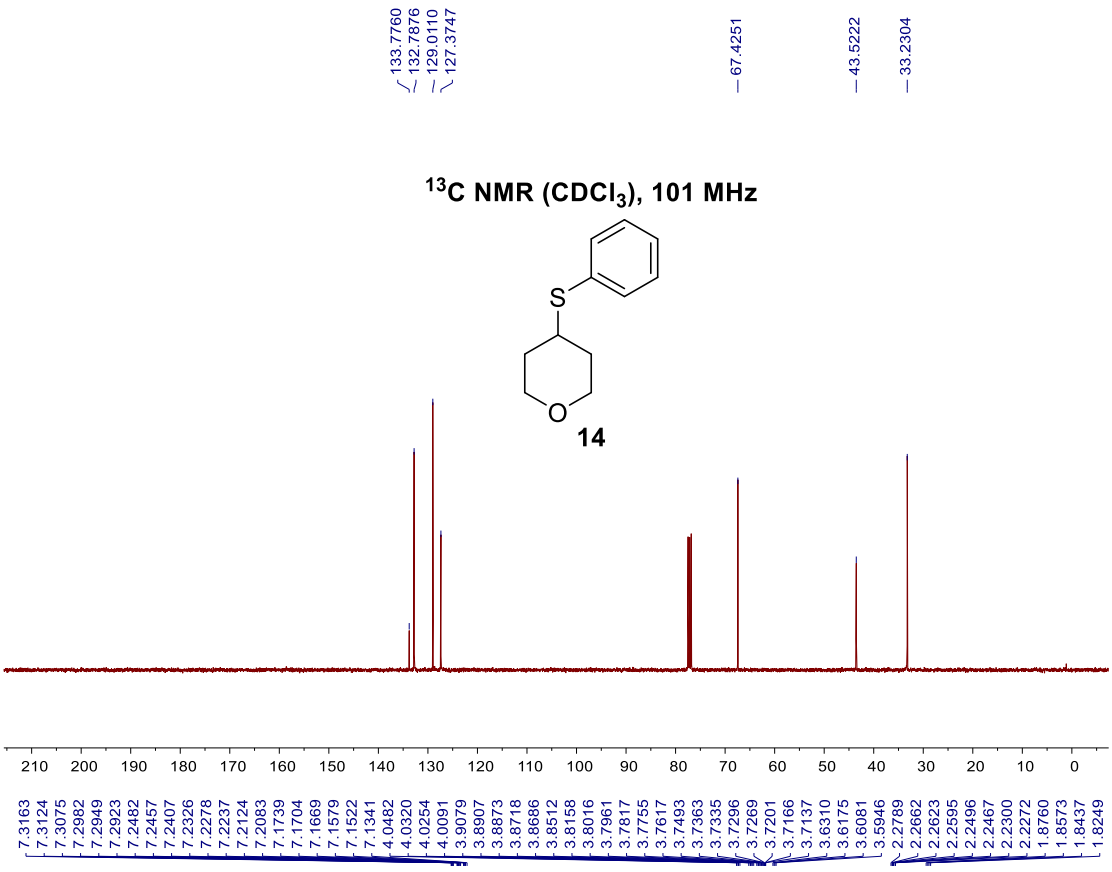
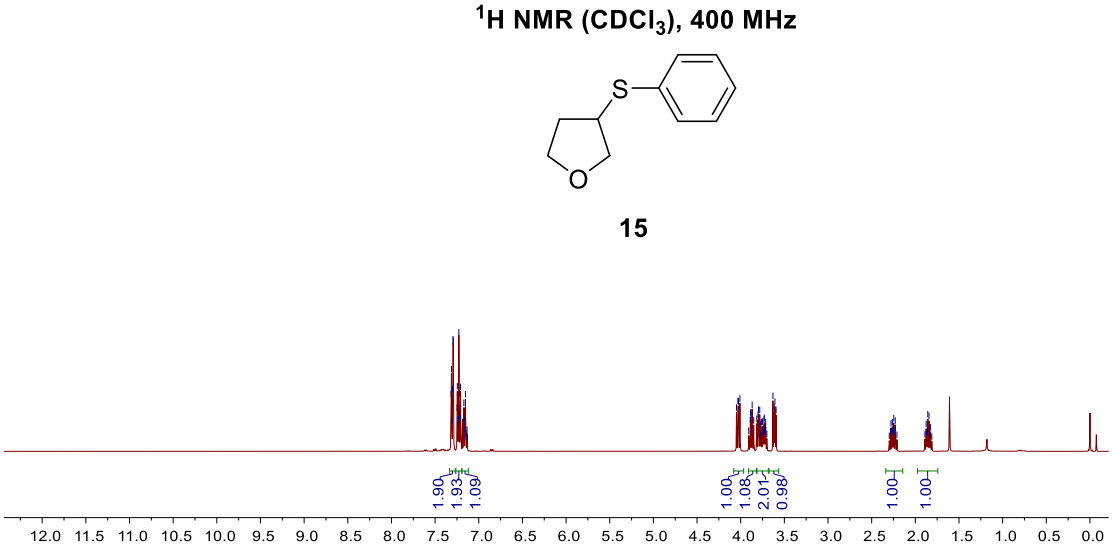
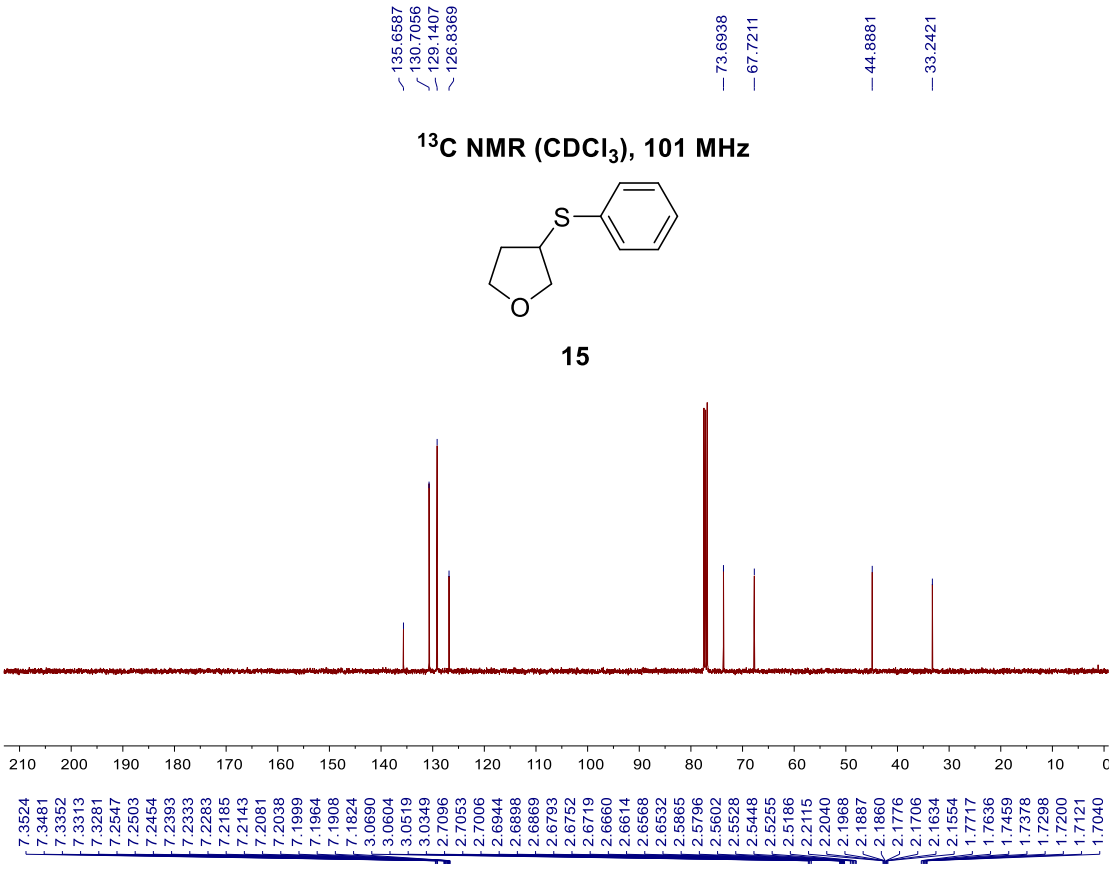



133.7760
132.7876
129.0110
127.3747
67.4251
43.5222
33.2304
13C NMR (CDCl3), 101 MHz
S
O
14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.3163 7.3124 7.3075 7.2982 7.2949 7.2923 7.2482 7.2457 7.2407 7.2326 7.2278 7.2237 7.2124 7.2083 7.1739 7.1704 7.1669 7.1579 7.1522 7.1341 4.0482 4.0320 4.0254 4.0091 3.9079 3.8907 3.8873 3.8718 3.8686 3.8512 3.8158 3.8016 3.7961 3.7817 3.7755 3.7617 3.7493 3.7363 3.7335 3.7296 3.7269 3.7201 3.7166 3.7137 3.6310 3.6175 3.6081 3.5946 2.2789 2.2662 2.2623 2.2595 2.2496 2.2467 2.2300 2.2272 1.8760 1.8573 1.8437 1.8249


1H NMR (CDCl3), 400 MHz
S
O
15
1.90 1.93 1.09 1.00 1.08 2.01 0.98 1.00 1.00
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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130.7056
129.1407
126.8369
73.6938
67.7211
44.8881
33.2421
13C NMR (CDCl3), 101 MHz
S
O
15
7.3524
7.3481
7.3352
7.3313
7.3281
7.2547
7.2503
7.2454
7.2393
7.2333
7.2283
7.2185
7.2143
7.2081
7.2038
7.1999
7.1964
7.1908
7.1824
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3.0604
3.0519
3.0349
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2.6869
2.6793
2.6752
2.6719
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2.6614
2.6568
2.6532
2.5865
2.5796
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2.5448
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2.1860
2.1776
2.1706
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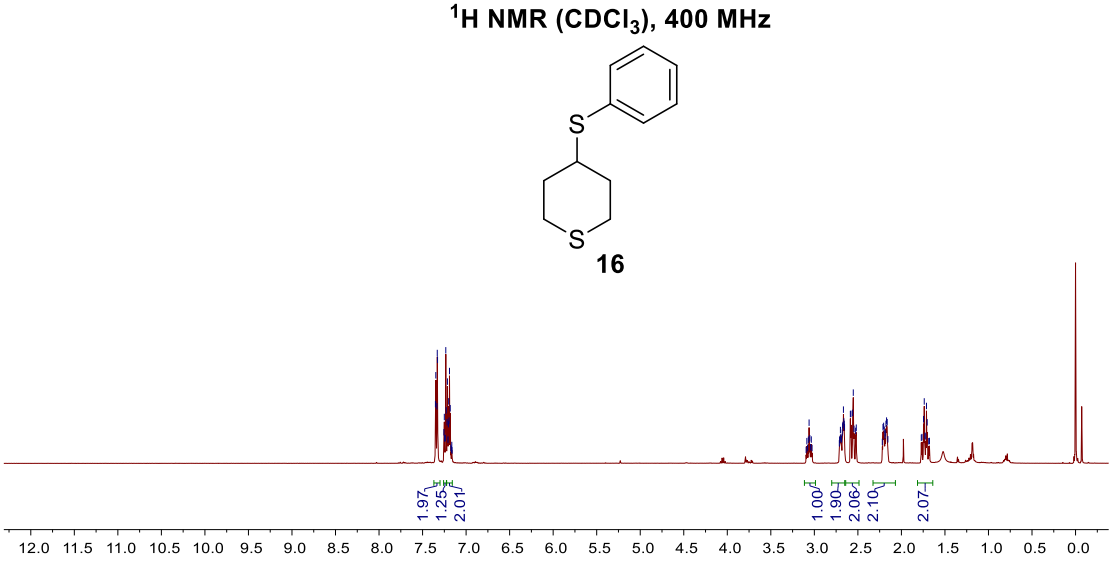
1H NMR (CDCl3), 400 MHz
S
S
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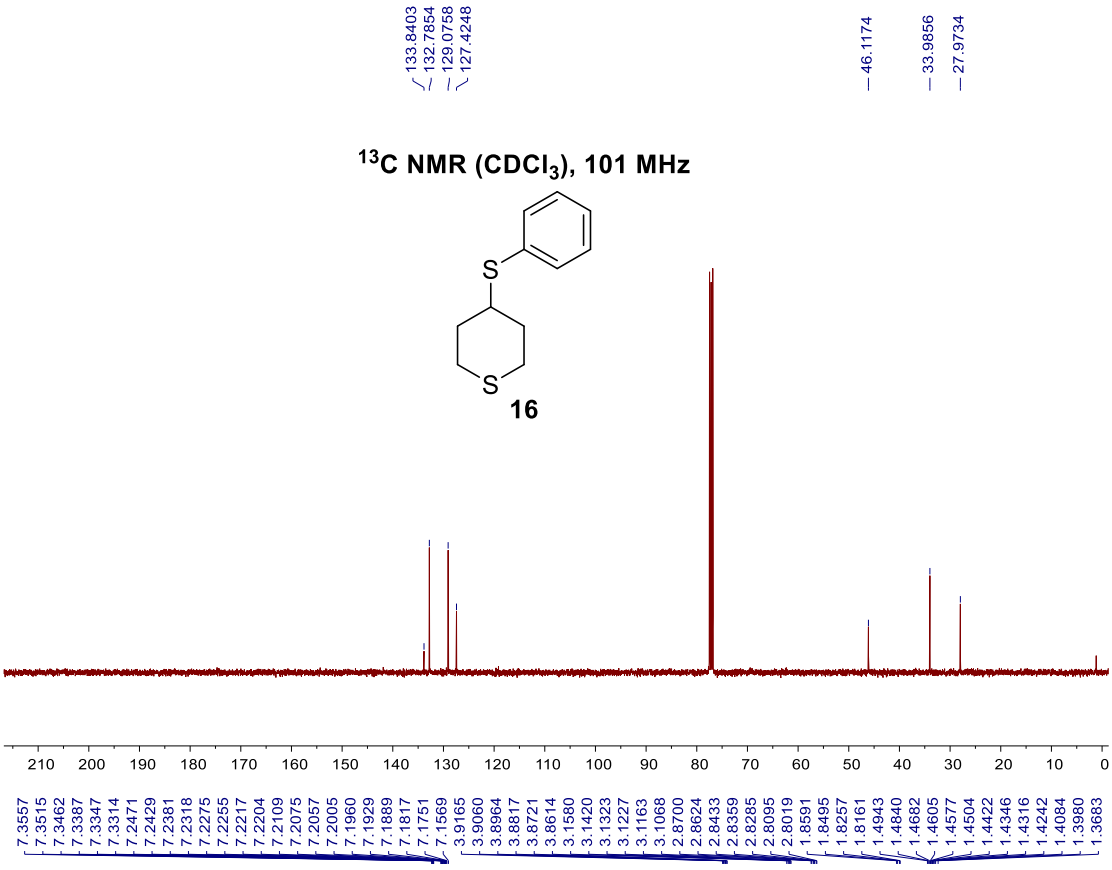
2.01
1.00
1.90
2.06
2.10
2.07


133.8403
132.7854
129.0758
127.4248
46.1174
33.9856
27.9734
13C NMR (CDCl3), 101 MHz
S
S
16
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.3557
7.3515
7.3462
7.3387
7.3347
7.3314
7.2471
7.2429
7.2381
7.2318
7.2275
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7.1929
7.1889
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3.8964
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3.8614
3.1580
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3.1323
3.1227
3.1163
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2.8700
2.8624
2.8433
2.8359
2.8285
2.8095
2.8019
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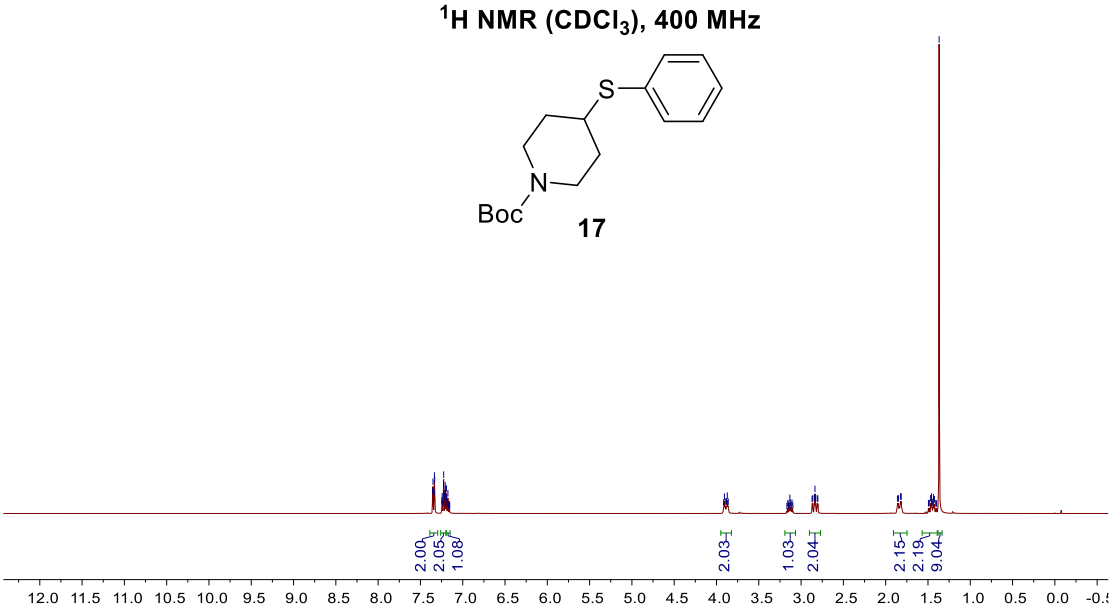
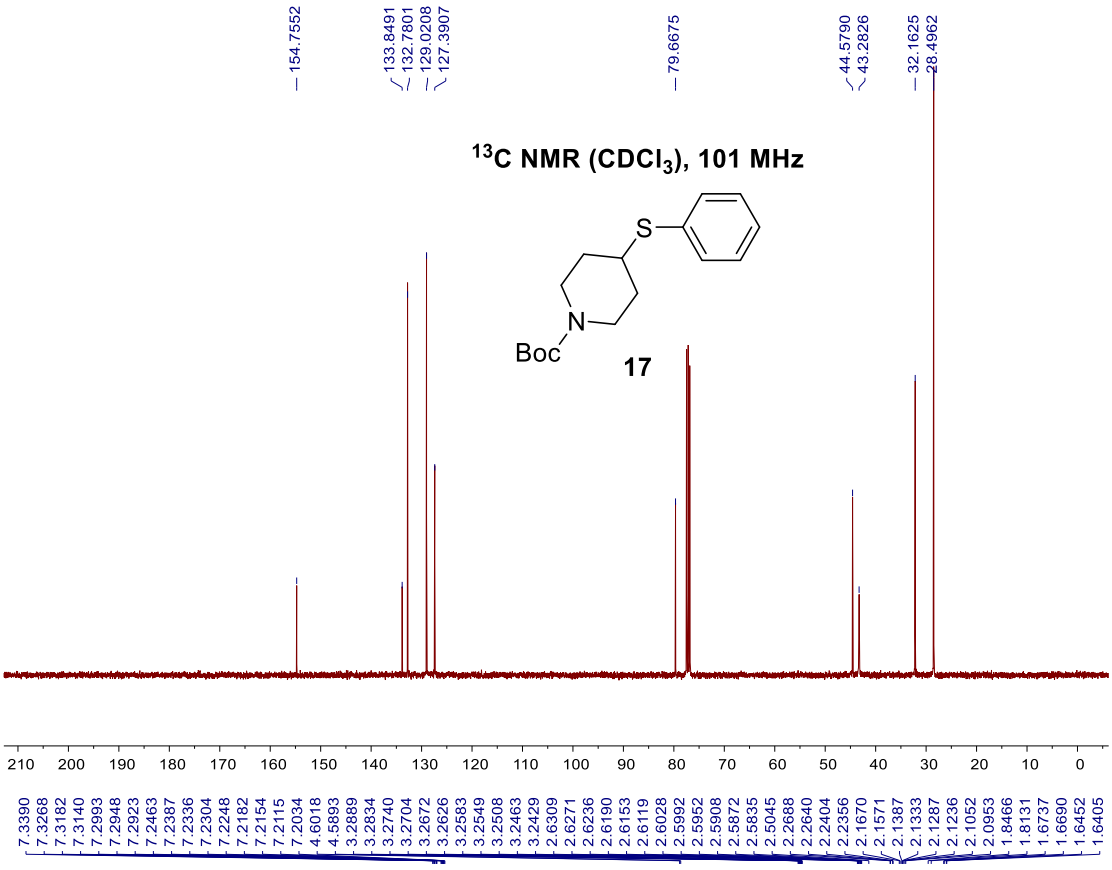
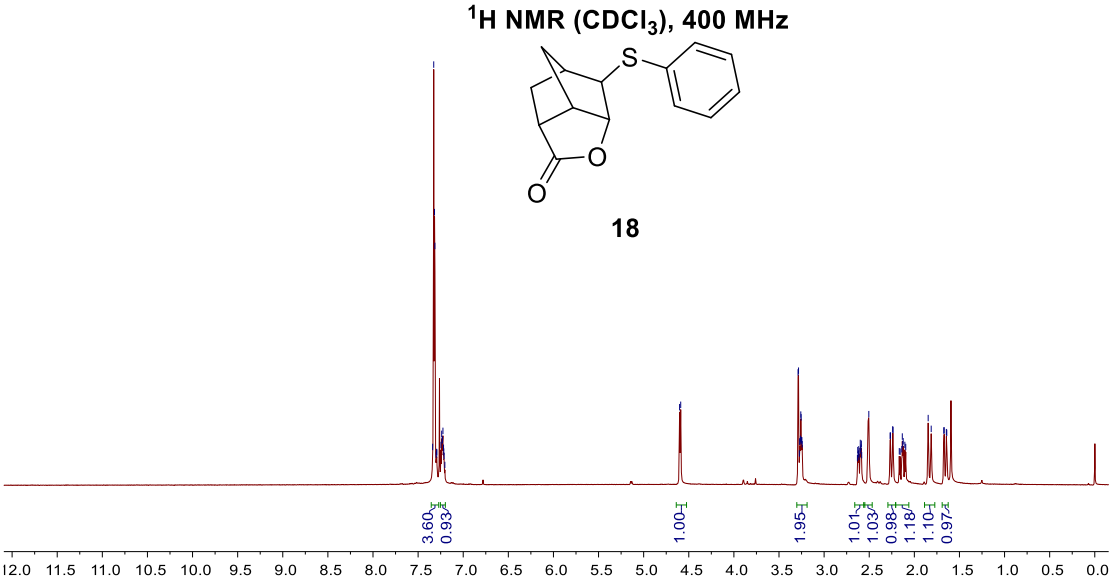
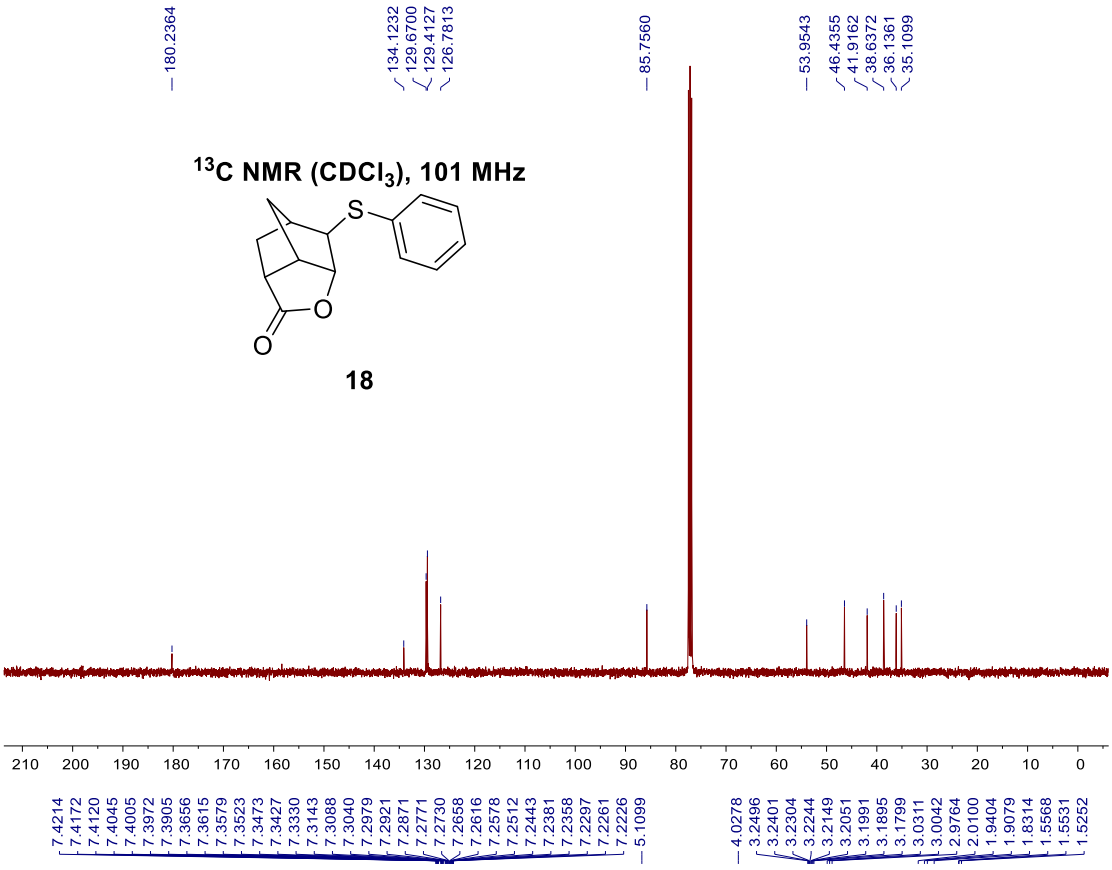
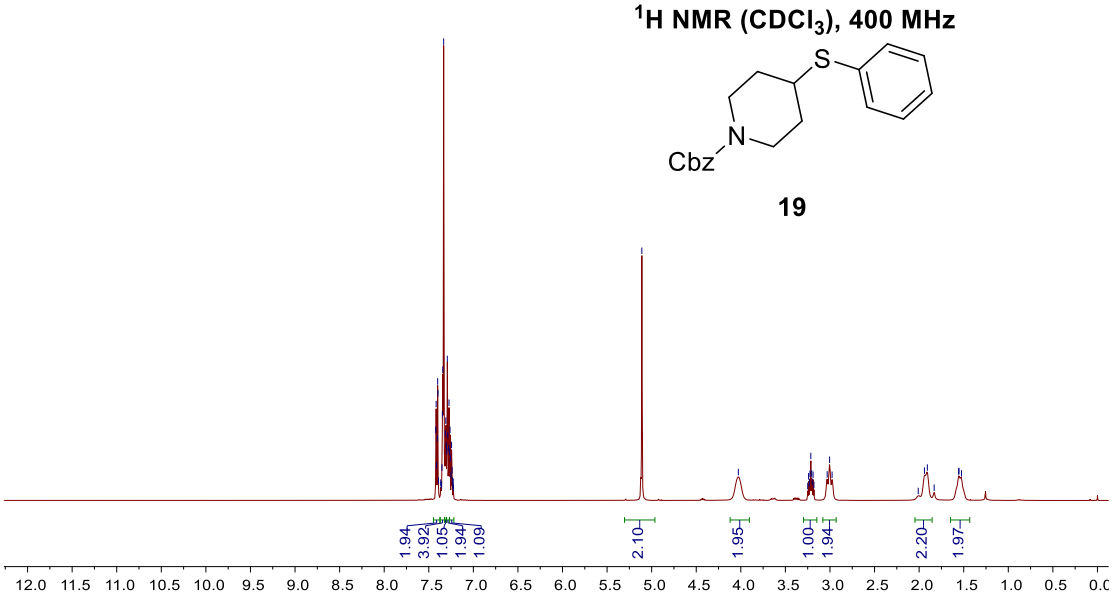
1.3683

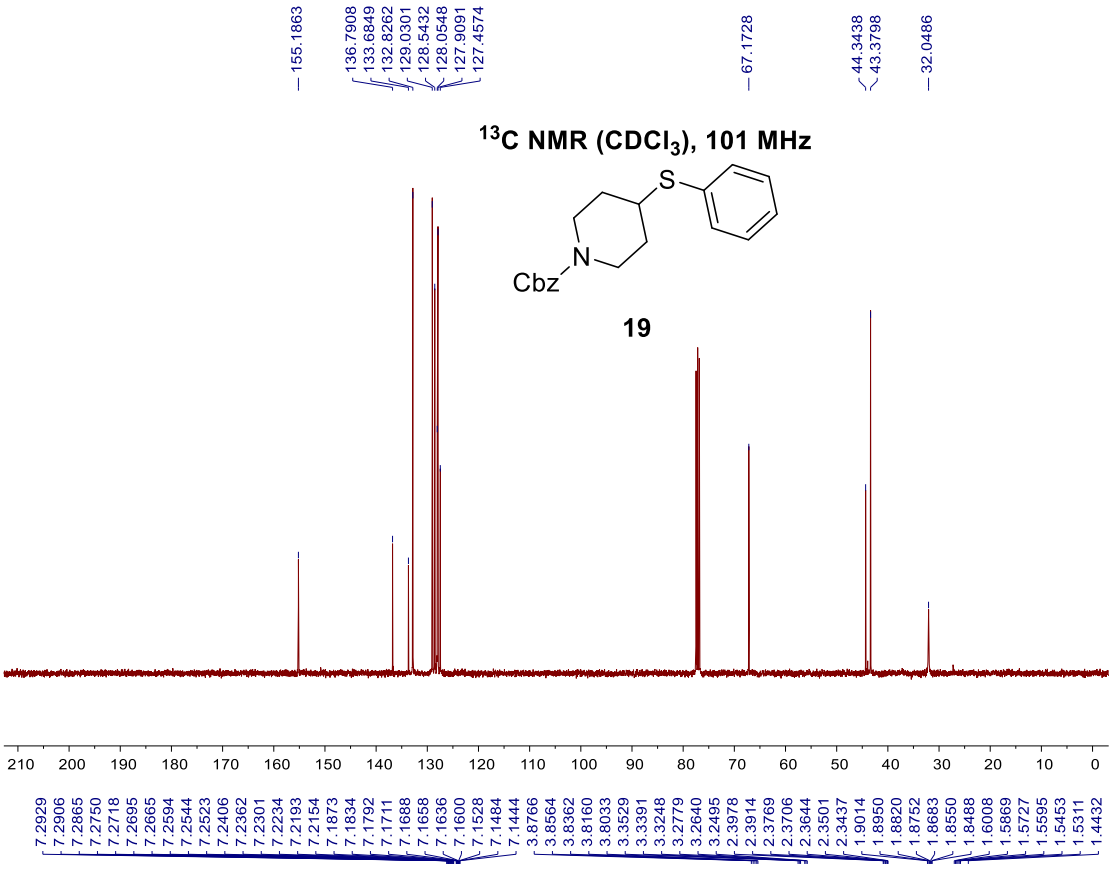

1H NMR (CDCl3), 400 MHz
S
N
Boc
17
2.00
2.05
1.08
2.03
1.03
2.04
2.15
2.19
9.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


154.7552
133.8491
132.7801
129.0208
127.3907
79.6675
44.5790
43.2826
32.1625
28.4962
13C NMR (CDCl3), 101 MHz
S
N
Boc
17
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.3390 7.3268 7.3182 7.3140 7.2993 7.2948 7.2923 7.2463 7.2387 7.2336 7.2304 7.2248 7.2182 7.2154 7.2115 7.2034 4.6018 4.5893 3.2889 3.2834 3.2740 3.2704 3.2672 3.2626 3.2583 3.2549 3.2508 3.2463 3.2429 2.6309 2.6271 2.6236 2.6190 2.6153 2.6119 2.6028 2.5992 2.5952 2.5908 2.5872 2.5835 2.5045 2.2688 2.2640 2.2404 2.2356 2.1670 2.1571 2.1387 2.1333 2.1287 2.1236 2.1052 2.0953 1.8466 1.8131 1.6737 1.6690 1.6452 1.6405


1H NMR (CDCl3), 400 MHz
S
O
O
18
3.60 0.93 1.00 1.95 1.01 1.03 0.98 1.18 1.10 0.97
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


180.2364
134.1232
129.6700
129.4127
126.7813
85.7560
53.9543
46.4355
41.9162
38.6372
36.1361
35.1099
13C NMR (CDCl3), 101 MHz
S
O
O
18
7.4214
7.4172
7.4120
7.4045
7.4005
7.3972
7.3905
7.3656
7.3615
7.3579
7.3523
7.3473
7.3427
7.3330
7.3143
7.3088
7.3040
7.2979
7.2921
7.2871
7.2771
7.2730
7.2658
7.2616
7.2578
7.2512
7.2443
7.2381
7.2358
7.2297
7.2261
7.2226
5.1099
4.0278
3.2496
3.2401
3.2304
3.2244
3.2149
3.2051
3.1991
3.1895
3.1799
3.0311
3.0042
2.9764
2.0100
1.9404
1.9079
1.8314
1.5568
1.5531
1.5252
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


1H NMR (CDCl3), 400 MHz
S
N
Cbz
19
1.94
3.92
1.05
1.94
1.09
2.10
1.95
1.00
1.94
2.20
1.97
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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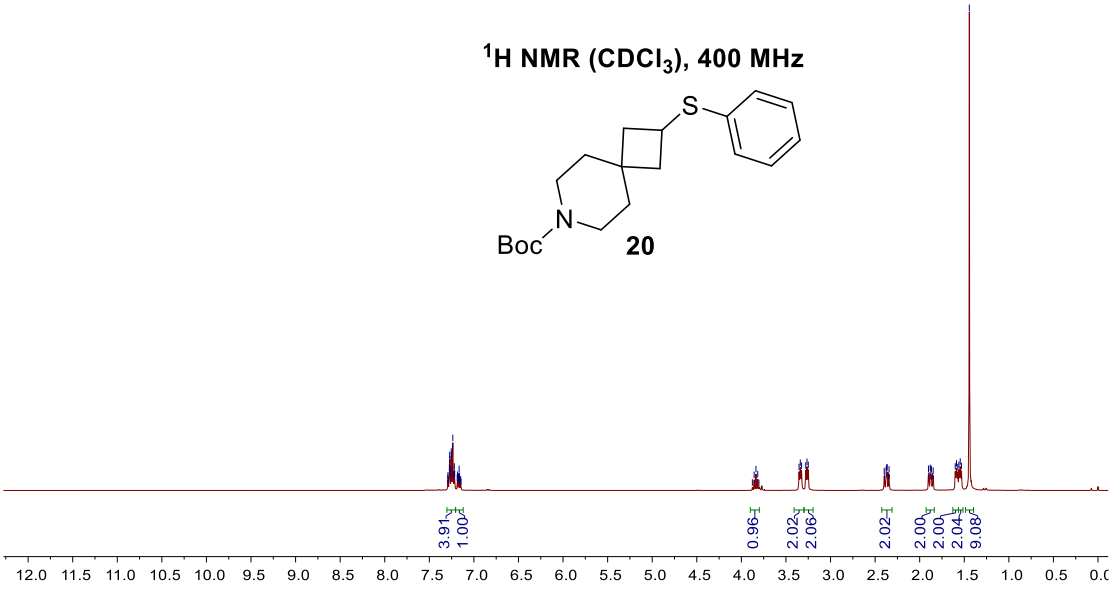
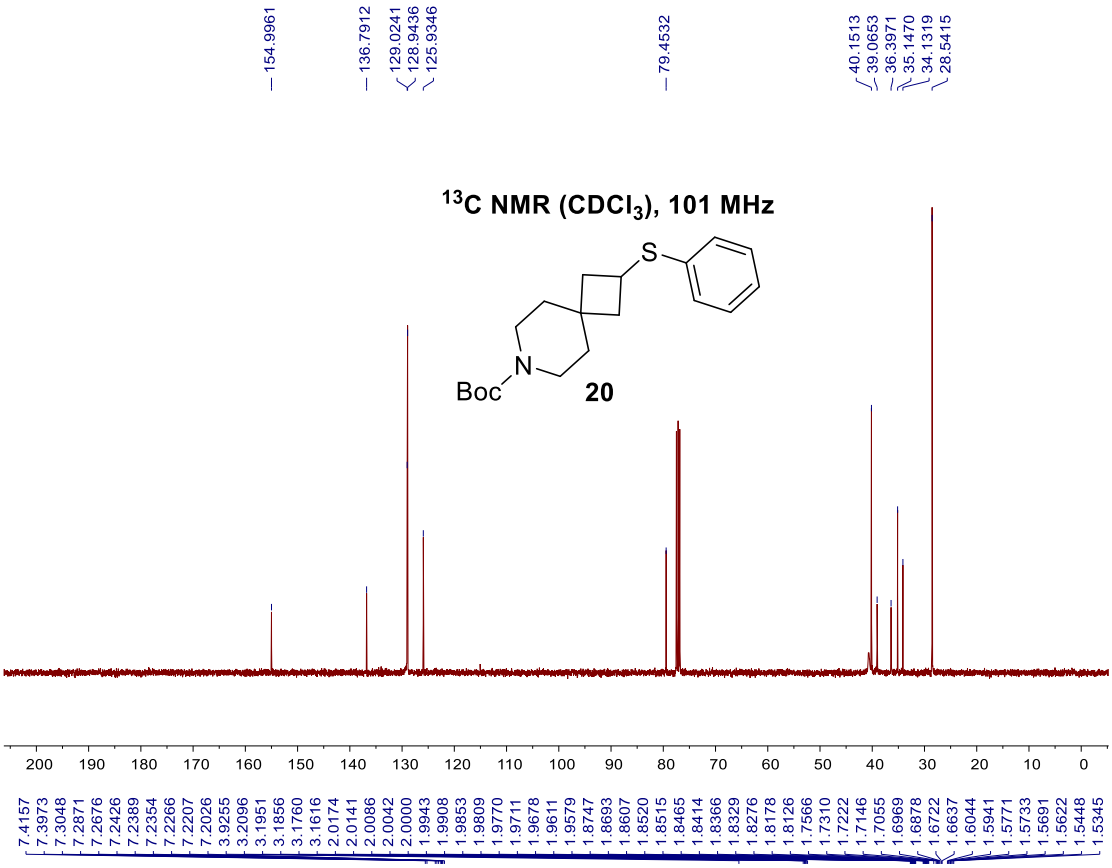
136.7908
133.6849
132.8262
129.0301
128.5432
128.0548
127.9091
127.4574
67.1728
44.3438
43.3798
32.0486
13C NMR (CDCl3), 101 MHz
S
N
Cbz
19
7.2929
7.2906
7.2865
7.2750
7.2718
7.2695
7.2665
7.2594
7.2544
7.2523
7.2406
7.2362
7.2301
7.2234
7.2193
7.2154
7.1873
7.1834
7.1792
7.1711
7.1688
7.1658
7.1636
7.1600
7.1528
7.1484
7.1444
3.8766
3.8564
3.8362
3.8160
3.8033
3.3529
3.3391
3.3248
3.2779
3.2640
3.2495
2.3978
2.3914
2.3769
2.3706
2.3644
2.3501
2.3437
1.9014
1.8950
1.8820
1.8752
1.8683
1.8550
1.8488
1.6008
1.5869
1.5727
1.5595
1.5453
1.5311
1.4432


1H NMR (CDCl3), 400 MHz
S
N
Boc
20
3.91
1.00
0.96
2.02
2.06
2.02
2.00
2.00
2.04
9.08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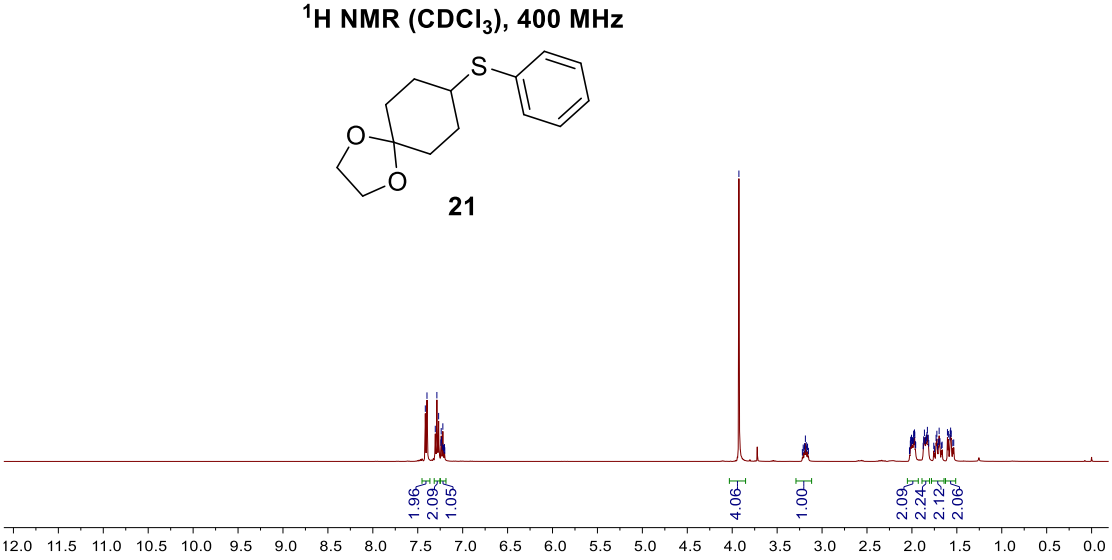
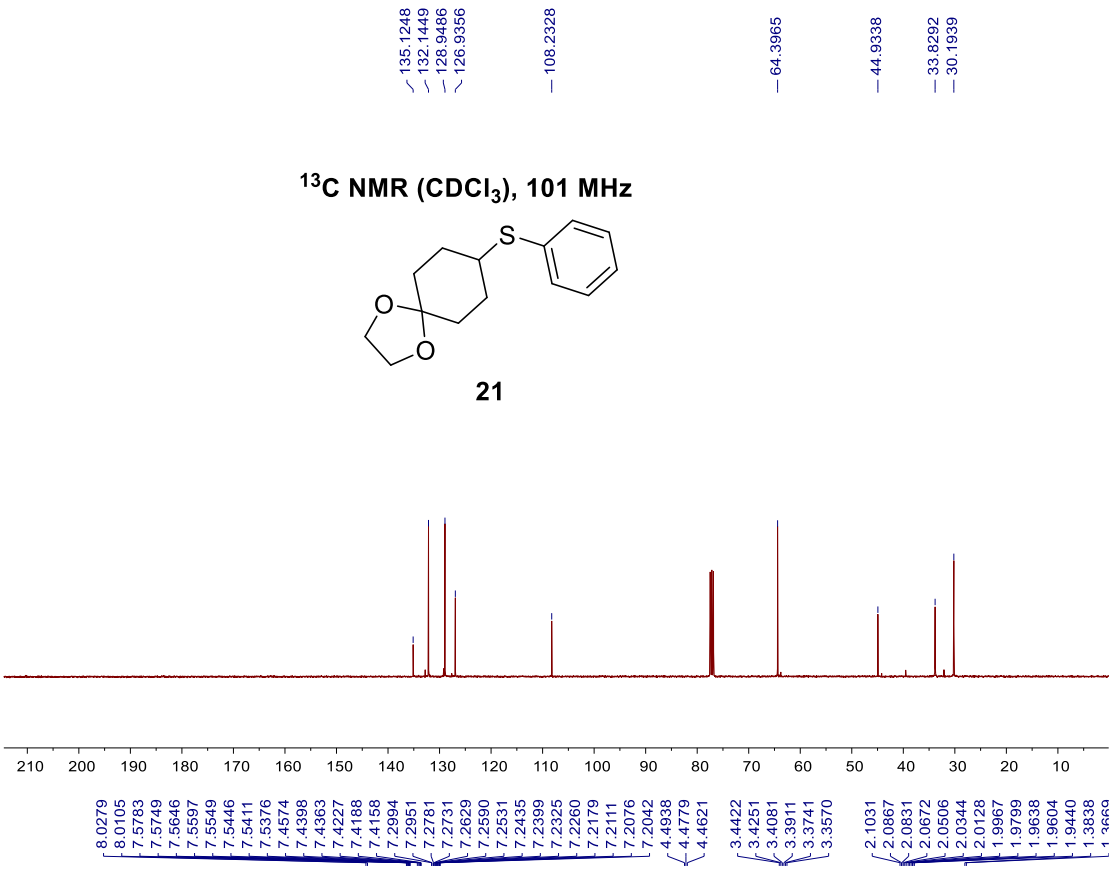
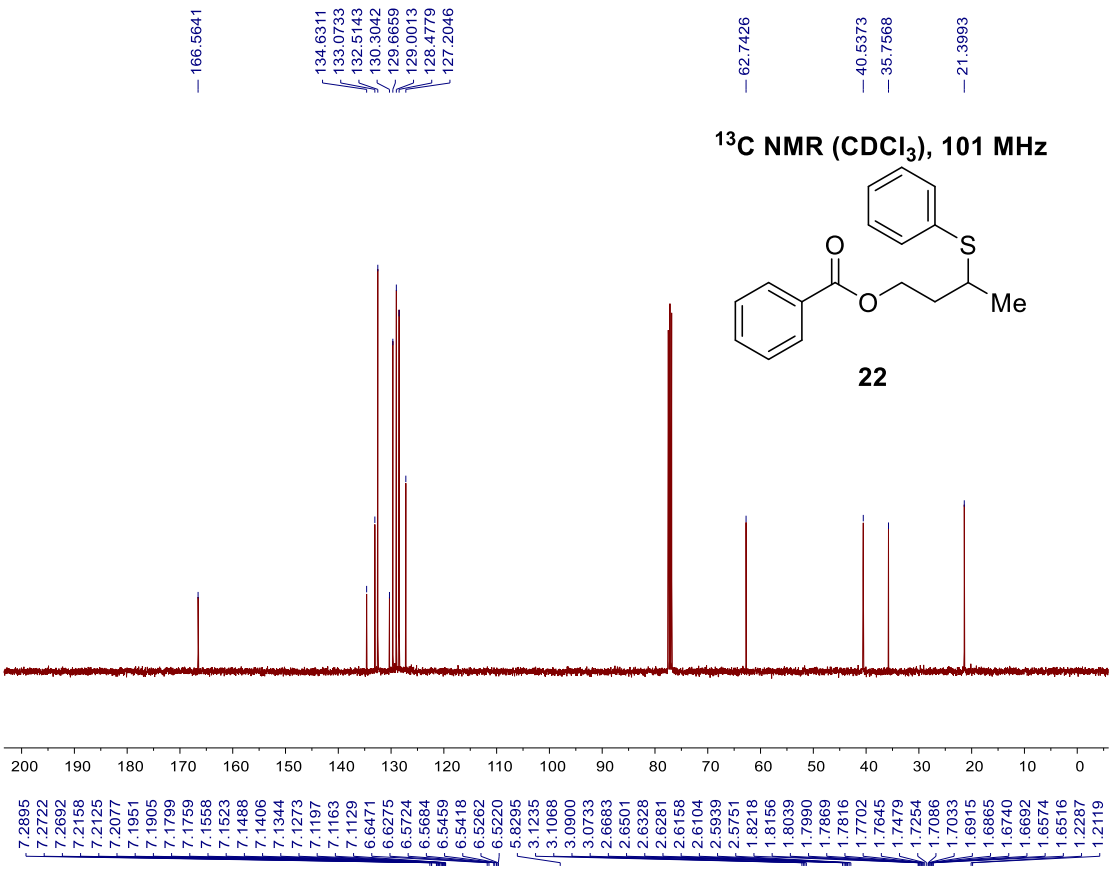
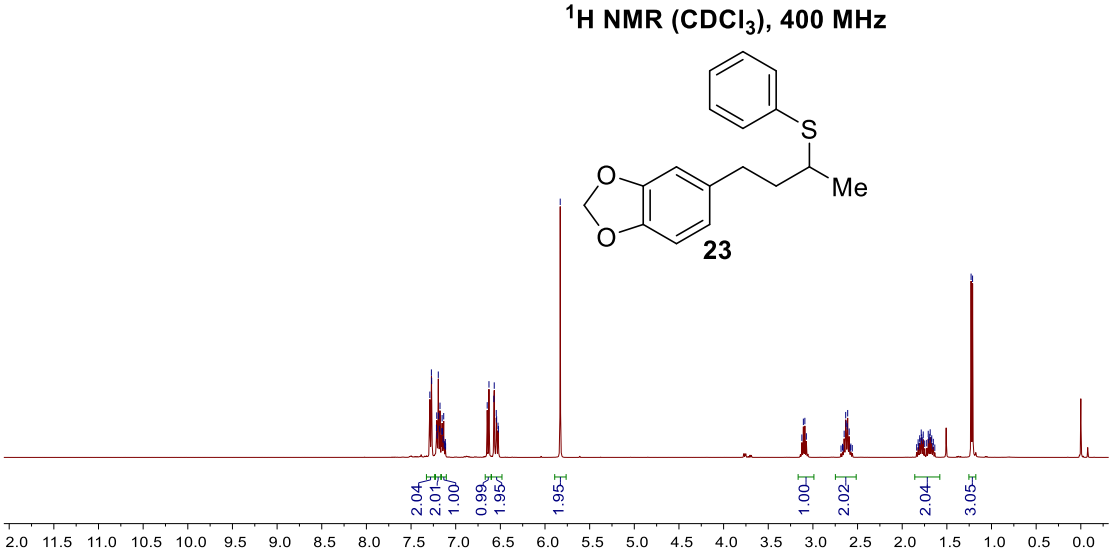
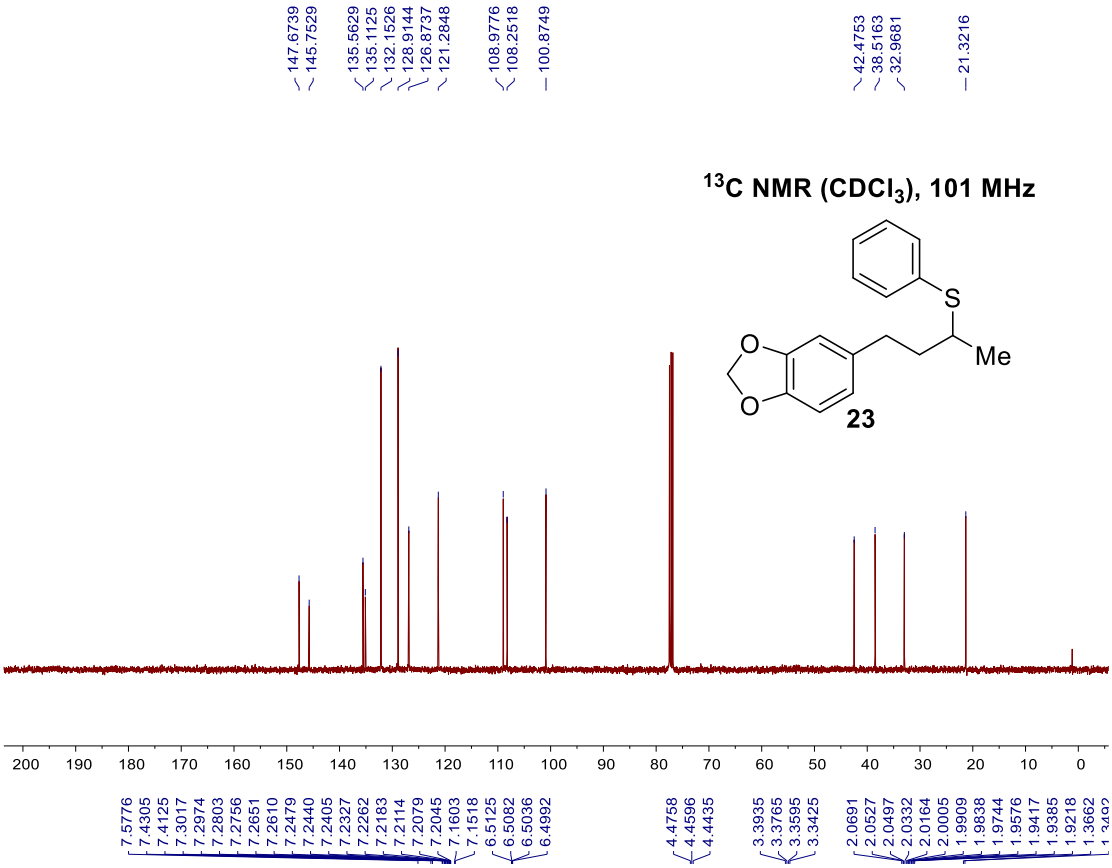
136.7912
129.0241
128.9436
125.9346
79.4532
40.1513
39.0653
36.3971
35.1470
34.1319
28.5415
13C NMR (CDCl3), 101 MHz
S
N
Boc
20
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.4157
7.3973
7.3048
7.2871
7.2676
7.2426
7.2389
7.2354
7.2266
7.2207
7.2026
3.9255
3.2096
3.1951
3.1856
3.1760
3.1616
2.0174
2.0141
2.0086
2.0042
2.0000
1.9943
1.9908
1.9853
1.9809
1.9770
1.9711
1.9678
1.9611
1.9579
1.8747
1.8693
1.8607
1.8520
1.8515
1.8465
1.8414
1.8366
1.8329
1.8276
1.8178
1.8126
1.7566
1.7310
1.7222
1.7146
1.7055
1.6969
1.6878
1.6722
1.6637
1.6044
1.5941
1.5771
1.5733
1.5691
1.5622
1.5448
1.5345


1H NMR (CDCl3), 400 MHz
S
O
O
21
1.96
2.09
1.05
4.06
1.00
2.09
2.24
2.12
2.06
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


135.1248
132.1449
128.9486
126.9356
108.2328
64.3965
44.9338
33.8292
30.1939
13C NMR (CDCl3), 101 MHz
S
O
O
21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
8.0279
8.0105
7.5783
7.5749
7.5646
7.5597
7.5549
7.5446
7.5411
7.5376
7.4574
7.4398
7.4363
7.4227
7.4188
7.4158
7.2994
7.2951
7.2781
7.2731
7.2629
7.2590
7.2531
7.2435
7.2399
7.2325
7.2260
7.2179
7.2111
7.2076
7.2042
4.4938
4.4779
4.4621
3.4422
3.4251
3.4081
3.3911
3.3741
3.3570
2.1031
2.0867
2.0831
2.0672
2.0506
2.0344
2.0128
1.9967
1.9799
1.9638
1.9604
1.9440
1.3838
1H NMR (CDCl3), 400 MHz
O
S
O
Me
22
2.00
1.04
3.97
2.11
1.01
2.00
0.98
2.14
3.04
2.0 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


166.5641
134.6311
133.0733
132.5143
130.3042
129.6659
129.0013
128.4779
127.2046
62.7426
40.5373
35.7568
21.3993
13C NMR (CDCl3), 101 MHz
O
S
O
Me
22
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.2895 7.2722 7.2692 7.2158 7.2125 7.2077 7.1951 7.1905 7.1799 7.1759 7.1558 7.1523 7.1488 7.1406 7.1344 7.1273 7.1197 7.1163 7.1129 6.6471 6.6275 6.5724 6.5684 6.5459 6.5418 6.5262 6.5220 5.8295 3.1235 3.1068 3.0900 3.0733 2.6683 2.6501 2.6328 2.6281 2.6158 2.6104 2.5939 2.5751 1.8218 1.8156 1.8039 1.7990 1.7869 1.7816 1.7702 1.7645 1.7479 1.7254 1.7086 1.7033 1.6915 1.6865 1.6740 1.6692 1.6574 1.6516 1.2287 1.2119


1H NMR (CDCl3), 400 MHz
S
Me
O
O
23
2.04 2.01 1.00 0.99 1.95 1.95 1.00 2.02 2.04 3.05
2.0 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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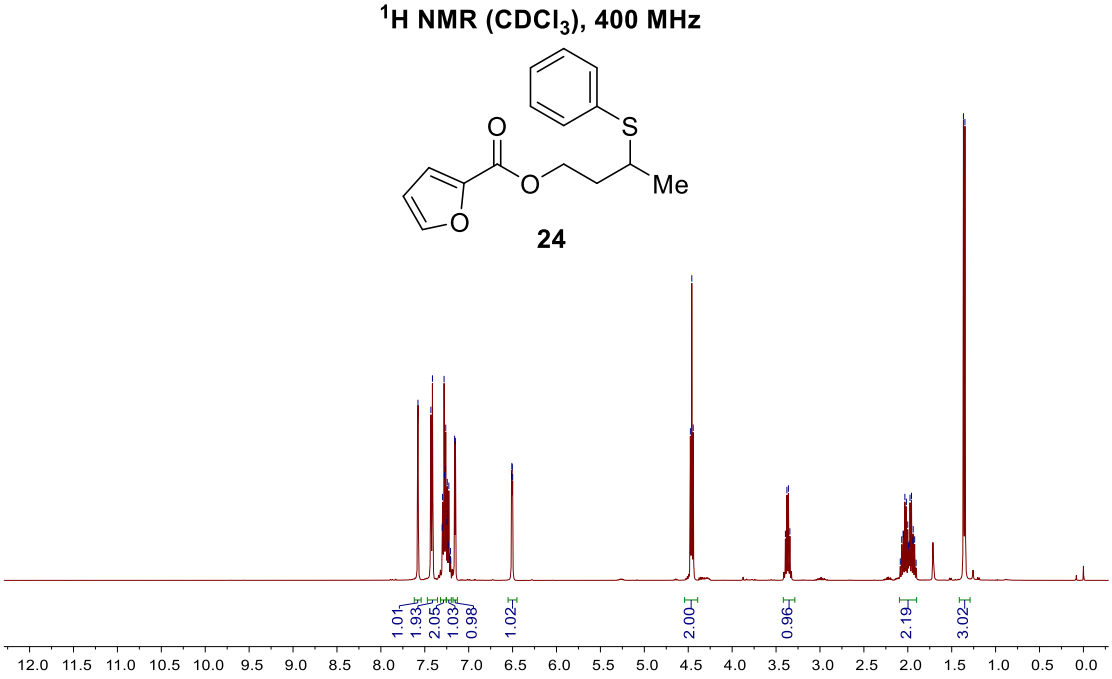
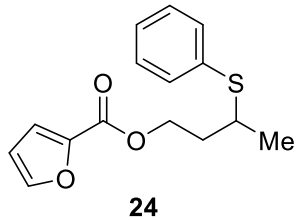
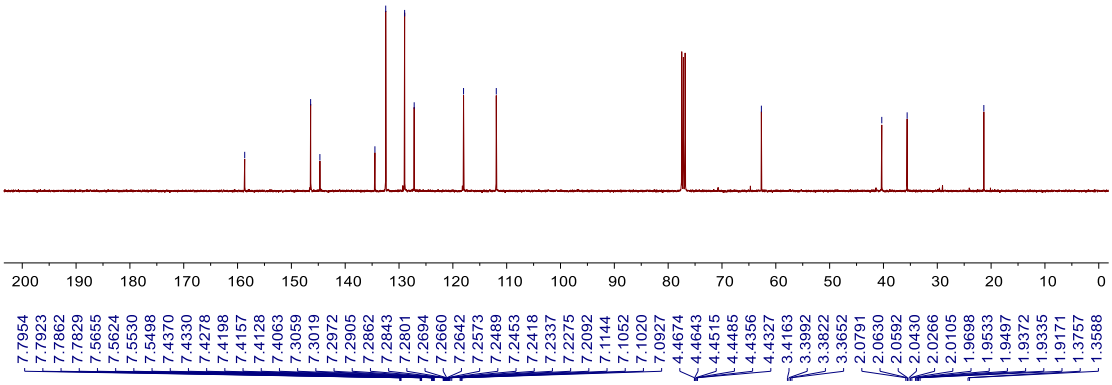
145.7529
135.5629
135.1125
132.1526
128.9144
126.8737
121.2848
108.9776
108.2518
100.8749
42.4753
38.5163
32.9681
21.3216
13C NMR (CDCl3), 101 MHz
S
Me
O
O
23
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.5776 7.4305 7.4125 7.3017 7.2974 7.2803 7.2756 7.2651 7.2610 7.2479 7.2440 7.2405 7.2327 7.2262 7.2183 7.2114 7.2079 7.2045 7.1603 7.1518 6.5125 6.5082 6.5036 6.4992
4.4758 4.4596 4.4435
3.3935 3.3765 3.3595 3.3425
2.0691 2.0527 2.0497 2.0332 2.0164 2.0005 1.9909 1.9838 1.9744 1.9576 1.9417 1.9385 1.9218 1.3662


1H NMR (CDCl3), 400 MHz
O
S
O
Me
O
24
1.01 1.93 2.05 1.03 0.98 1.02 2.00 0.96 2.19 3.02
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

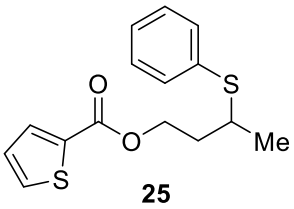
^{13}C NMR ($CDCl_3$), 101 MHz



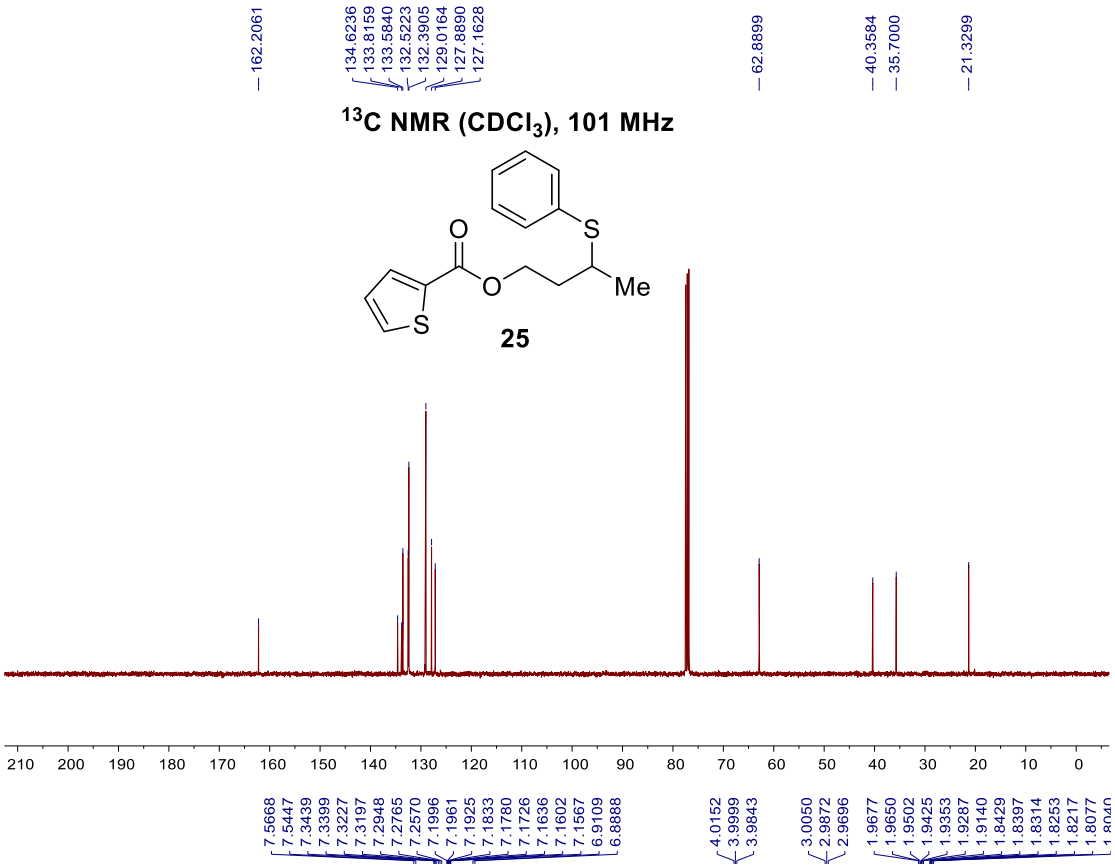
24



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



25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134.6236
133.8159
133.5840
132.5223
132.3905
129.0164
127.8890
127.1628
62.8899
40.3584
35.7000
21.3299
13C NMR (CDCl3), 101 MHz
O
S
O
Me
S
25
7.5668
7.5447
7.3439
7.3399
7.3227
7.3197
7.2948
7.2765
7.2570
7.1996
7.1961
7.1925
7.1833
7.1780
7.1726
7.1636
7.1602
7.1567
6.9109
6.8888
4.0152
3.9999
3.9843
3.0050
2.9872
2.9696
1.9677
1.9650
1.9502
1.9425
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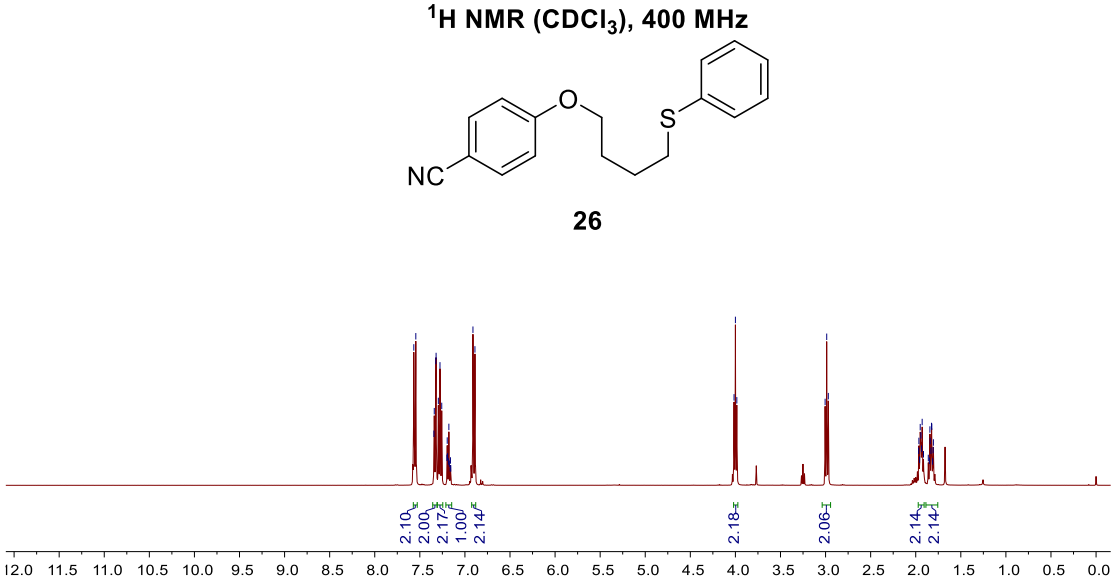
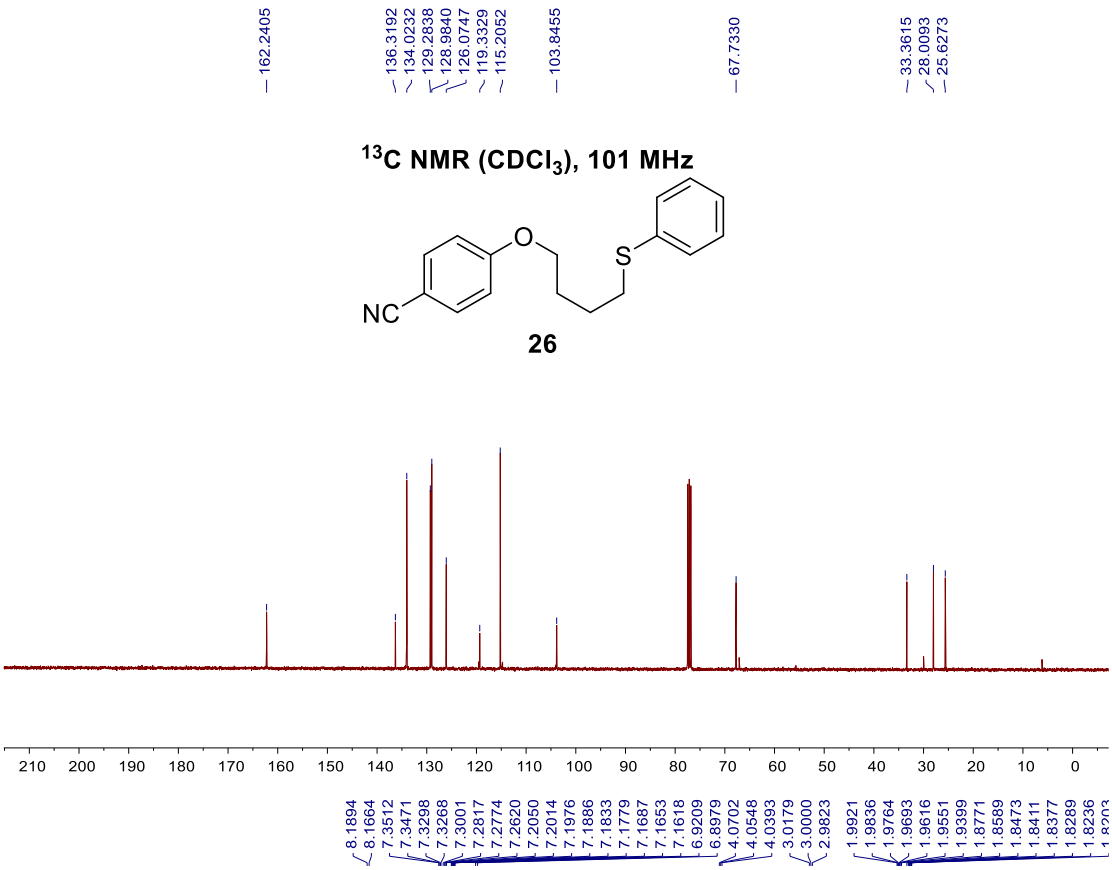
1.9287
1.9140
1.8429
1.8397
1.8314
1.8253
1.8217
1.8077


1H NMR (CDCl3), 400 MHz
O
S
NC
26
2.10
2.00
2.17
1.00
2.14
2.18
2.06
2.14
2.14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134.0232
129.2838
128.9840
126.0747
119.3329
115.2052
103.8455
67.7330
33.3615
28.0093
25.6273
13C NMR (CDCl3), 101 MHz
O
S
NC
26
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
8.1894
8.1664
7.3512
7.3471
7.3298
7.3268
7.3001
7.2817
7.2774
7.2620
7.2050
7.2014
7.1976
7.1886
7.1833
7.1779
7.1687
7.1653
7.1618
6.9209
6.8979
4.0702
4.0548
4.0393
3.0179
3.0000
2.9823
1.9921
1.9836
1.9764
1.9693
1.9616
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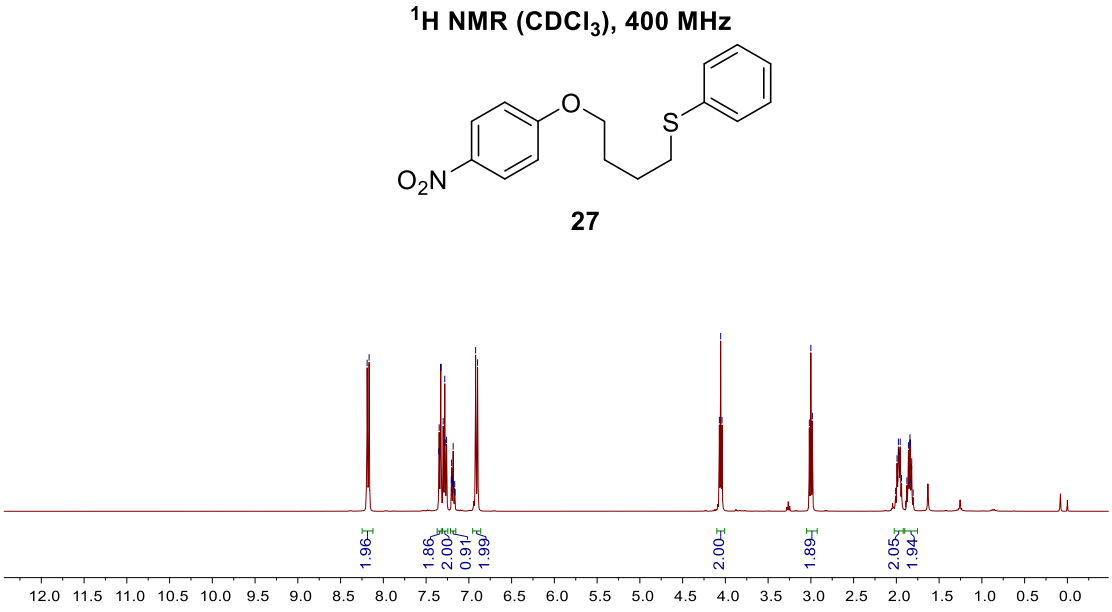
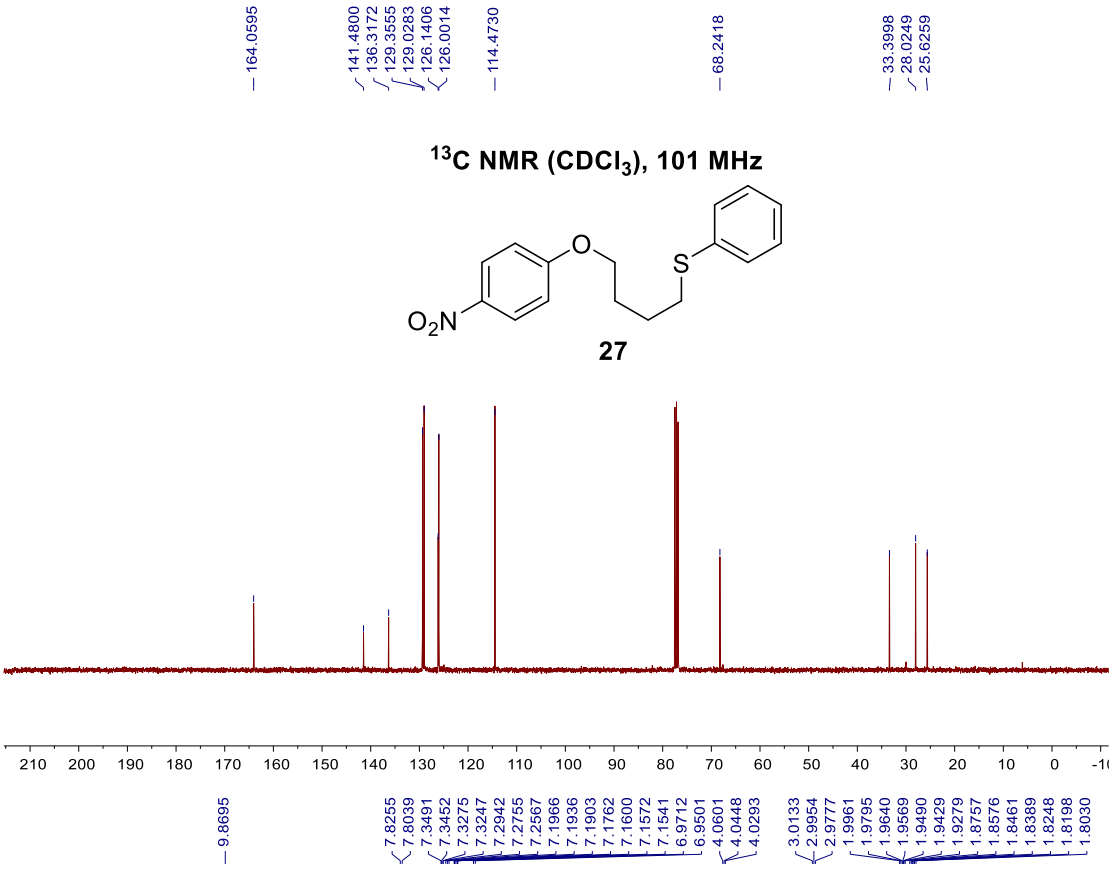
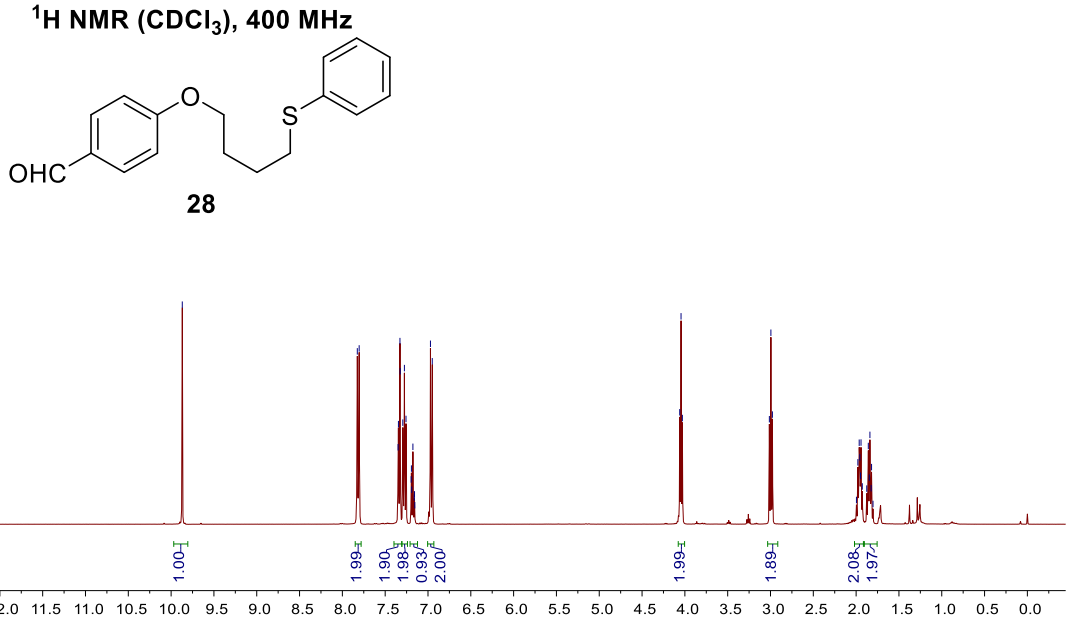
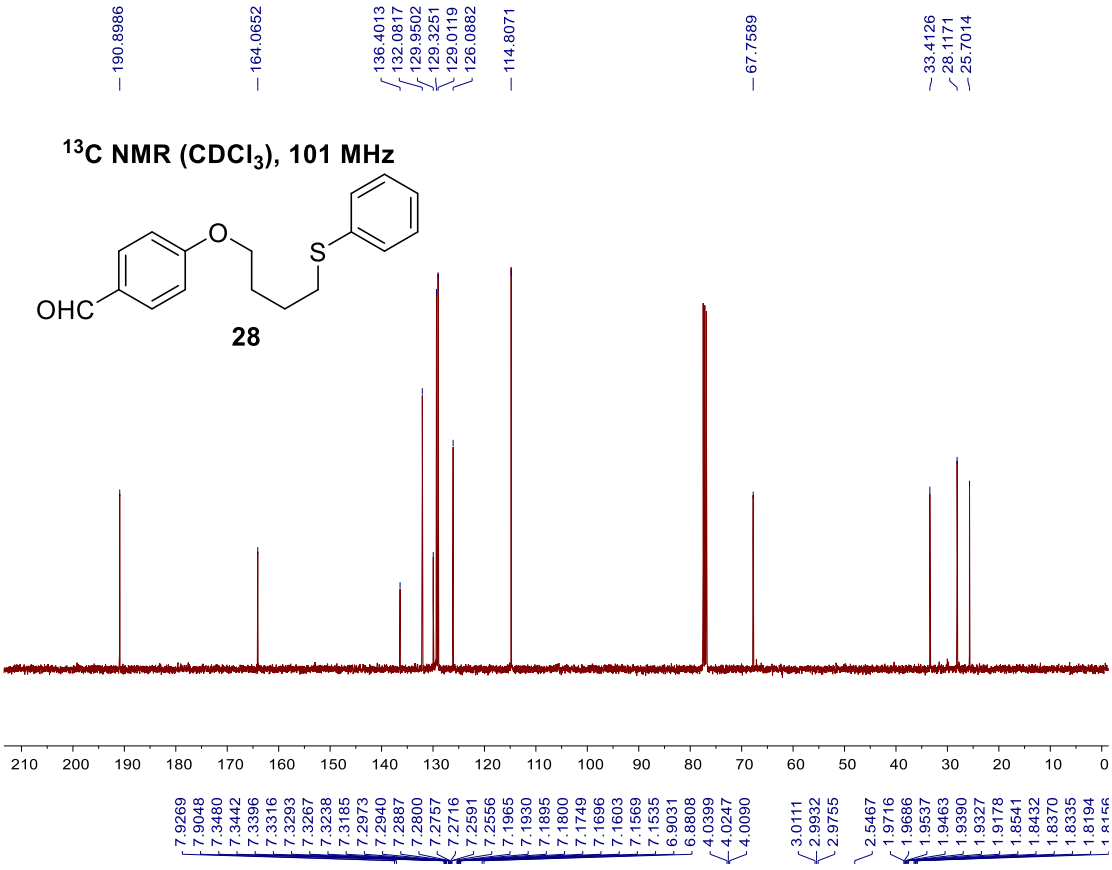
1.9399
1.8771
1.8589
1.8473
1.8411
1.8377
1.8289
1.8236


1H NMR (CDCl3), 400 MHz
O
S
O2N
27
1.96
1.86
2.00
0.91
1.99
2.00
1.89
2.05
1.94
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


164.0595
141.4800
136.3172
129.3555
129.0283
126.1406
126.0014
114.4730
68.2418
33.3998
28.0249
25.6259
13C NMR (CDCl3), 101 MHz
O
S
O2N
27
9.8695
7.8255
7.8039
7.3491
7.3452
7.3275
7.3247
7.2942
7.2755
7.2567
7.1966
7.1936
7.1903
7.1762
7.1600
7.1572
7.1541
6.9712
6.9501
4.0601
4.0448
4.0293
3.0133
2.9954
2.9777
1.9961
1.9795
1.9640
1.9569
1.9490
1.9429
1.9279
1.8757
1.8576
1.8461
1.8389
1.8248
1.8198
1.8030


1H NMR (CDCl3), 400 MHz
O
S
OHC
28
1.00
1.99
1.90
1.98
0.93
2.00
1.99
1.89
2.08
1.97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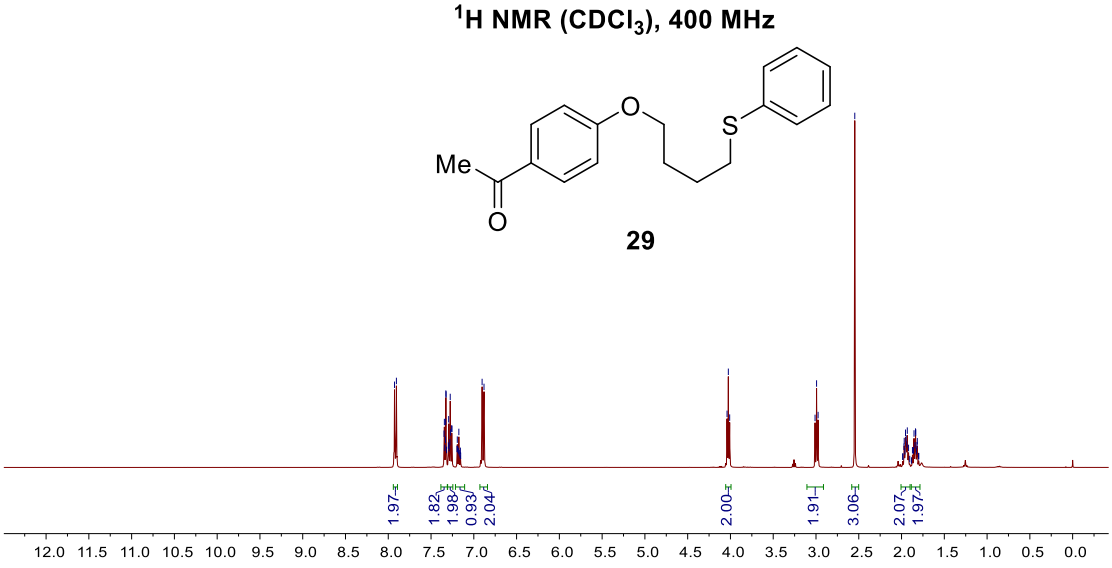
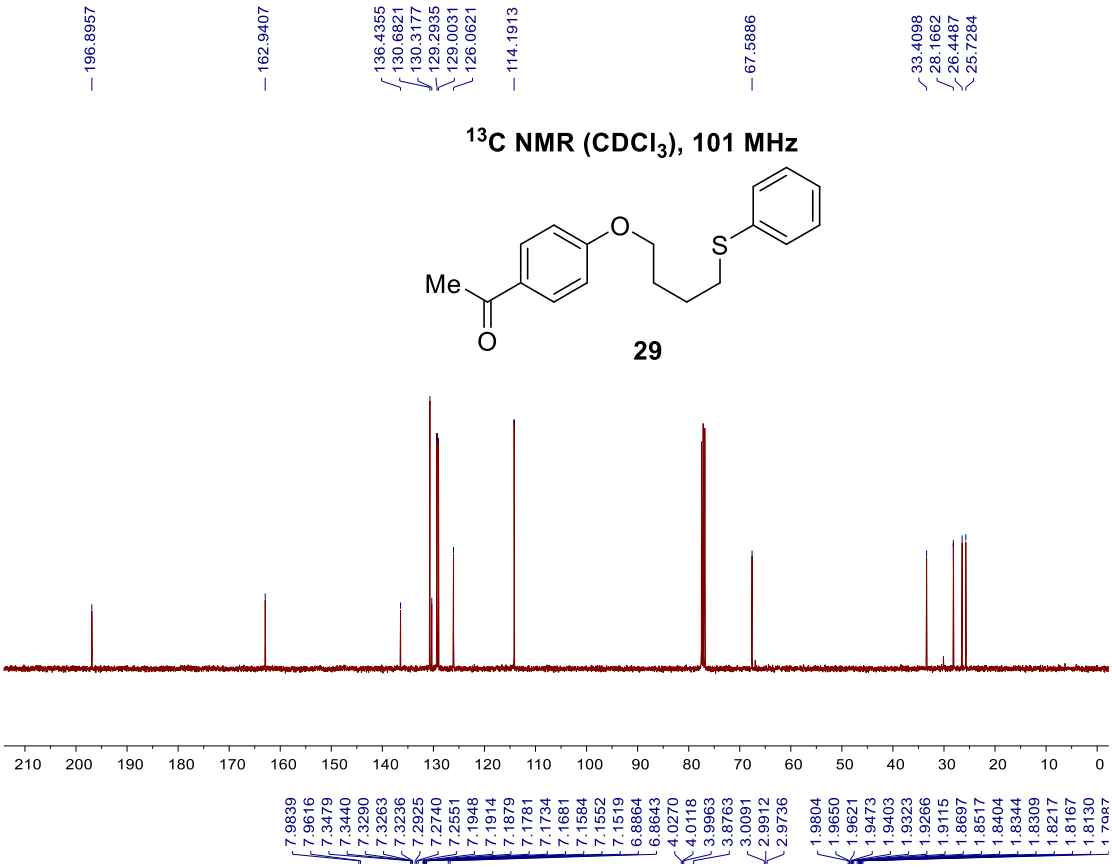
164.0652
136.4013
132.0817
129.9502
129.3251
129.0119
126.0882
114.8071
67.7589
33.4126
28.1171
25.7014
13C NMR (CDCl3), 101 MHz
O
S
OHC
28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.9269
7.9048
7.3480
7.3442
7.3396
7.3316
7.3293
7.3267
7.3238
7.3185
7.2973
7.2940
7.2887
7.2800
7.2757
7.2716
7.2591
7.2556
7.1965
7.1930
7.1895
7.1800
7.1749
7.1696
7.1603
7.1569
7.1535
6.9031
6.8808
4.0399
4.0247
4.0090
3.0111
2.9932
2.9755
2.5467
1.9716
1.9686
1.9537
1.9463
1.9390
1.9327
1.9178
1.8541
1.8432
1.8370
1.8335
1.8194


1H NMR (CDCl3), 400 MHz
O
S
Me
O
29
1.97
1.82
1.98
0.93
2.04
2.00
1.91
3.06
2.07
1.97
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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162.9407
136.4355
130.6821
130.3177
129.2935
129.0031
126.0621
114.1913
67.5886
33.4098
28.1662
26.4487
25.7284
13C NMR (CDCl3), 101 MHz
O
S
Me
O
29
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.9839
7.9616
7.3479
7.3440
7.3290
7.3263
7.3236
7.2925
7.2740
7.2551
7.1948
7.1914
7.1879
7.1781
7.1734
7.1681
7.1584
7.1552
7.1519
6.8864
6.8643
4.0270
4.0118
3.9963
3.8763
3.0091
2.9912
2.9736
1.9804
1.9650
1.9621
1.9473
1.9403
1.9323
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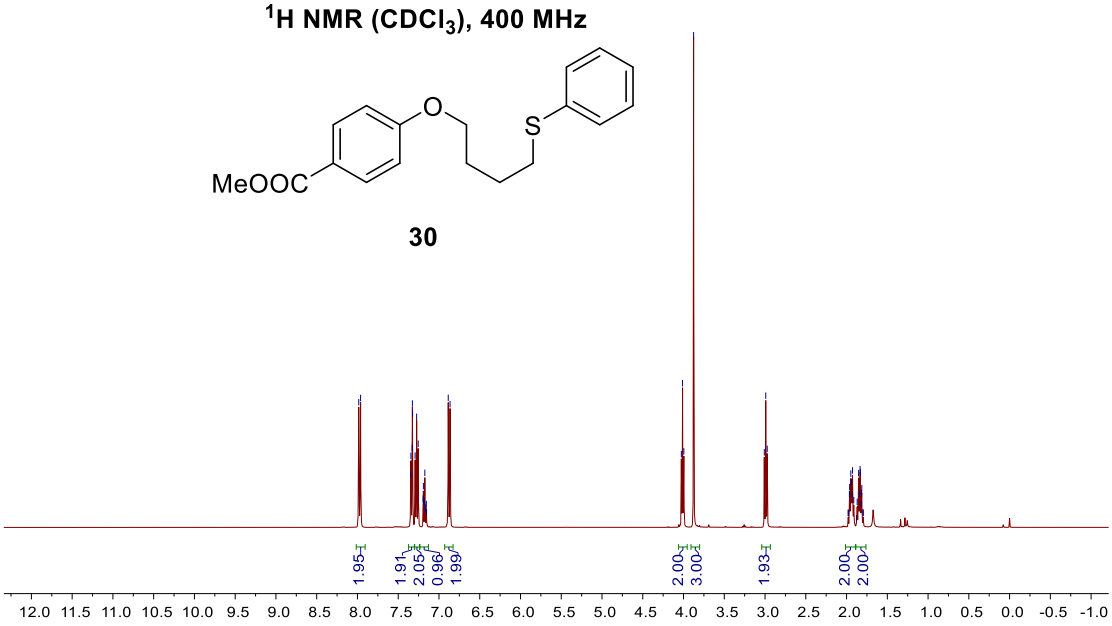
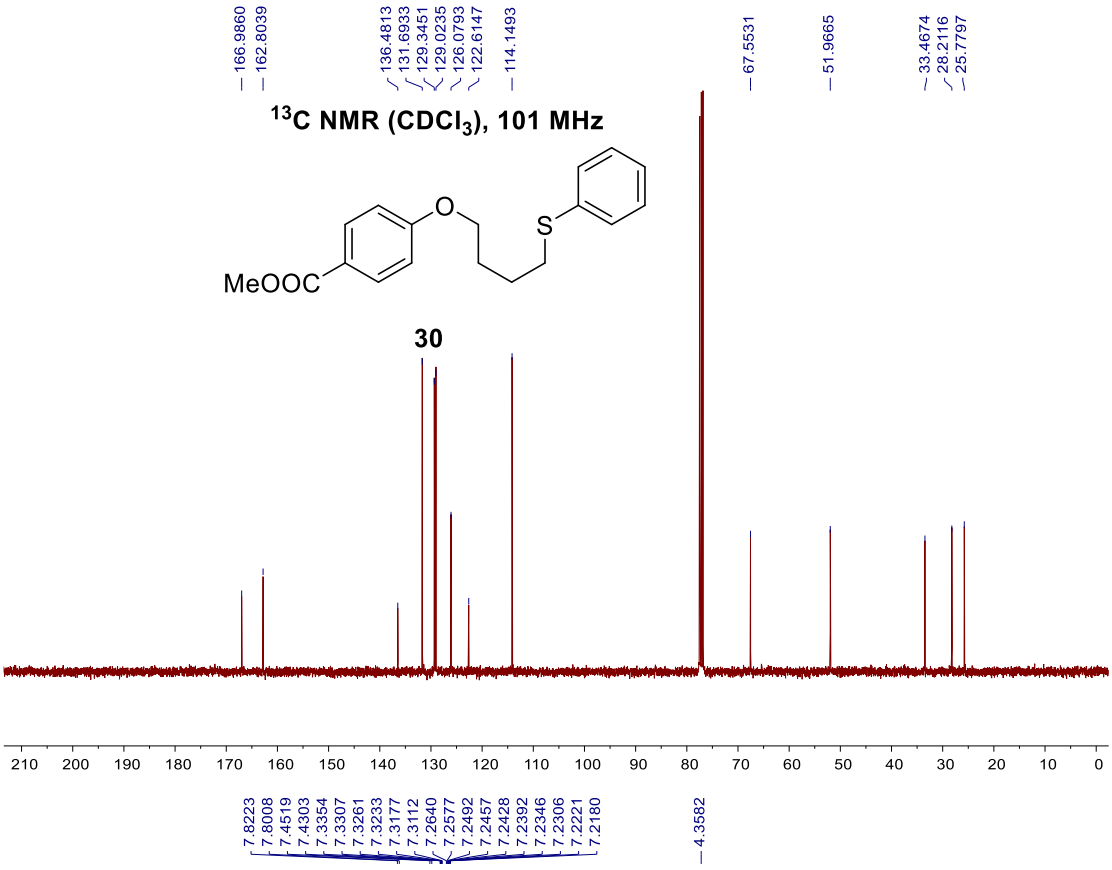
1.8344
1.8309
1.8217
1.8167
1.8130


1H NMR (CDCl3), 400 MHz
O
S
MeOOC
30
1.95
1.91
2.05
0.96
1.99
2.00
3.00
1.93
2.00
2.00
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 -1.0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162.8039
136.4813
131.6933
129.3451
129.0235
126.0793
122.6147
114.1493
67.5531
51.9665
33.4674
28.2116
25.7797
13C NMR (CDCl3), 101 MHz
O
S
MeOOC
30
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.8223
7.8008
7.4519
7.4303
7.3354
7.3307
7.3261
7.3233
7.3177
7.3112
7.2640
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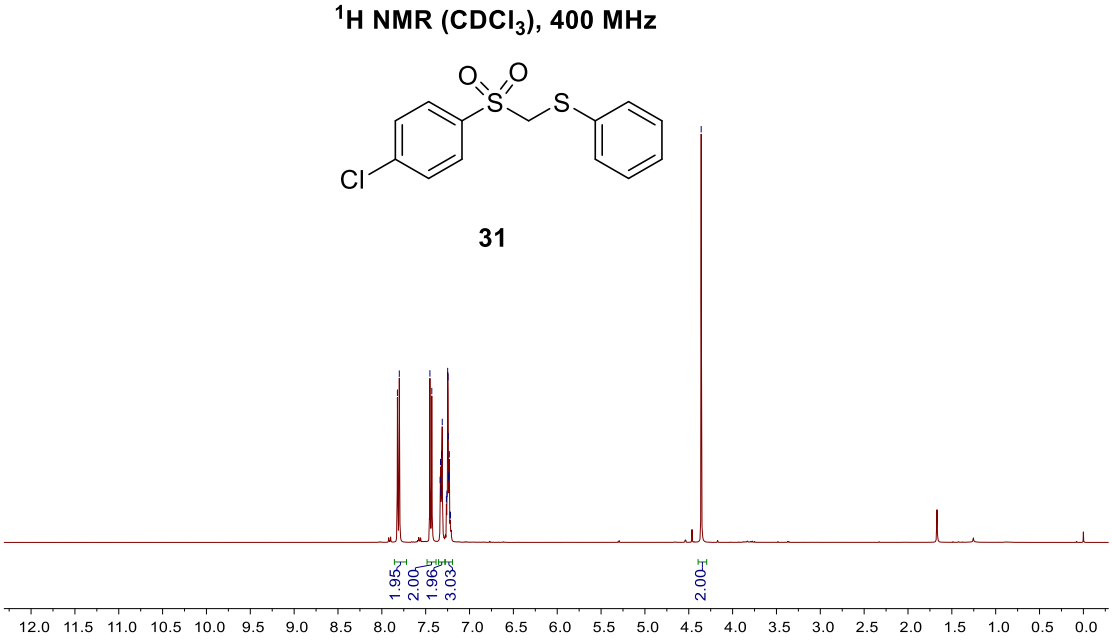
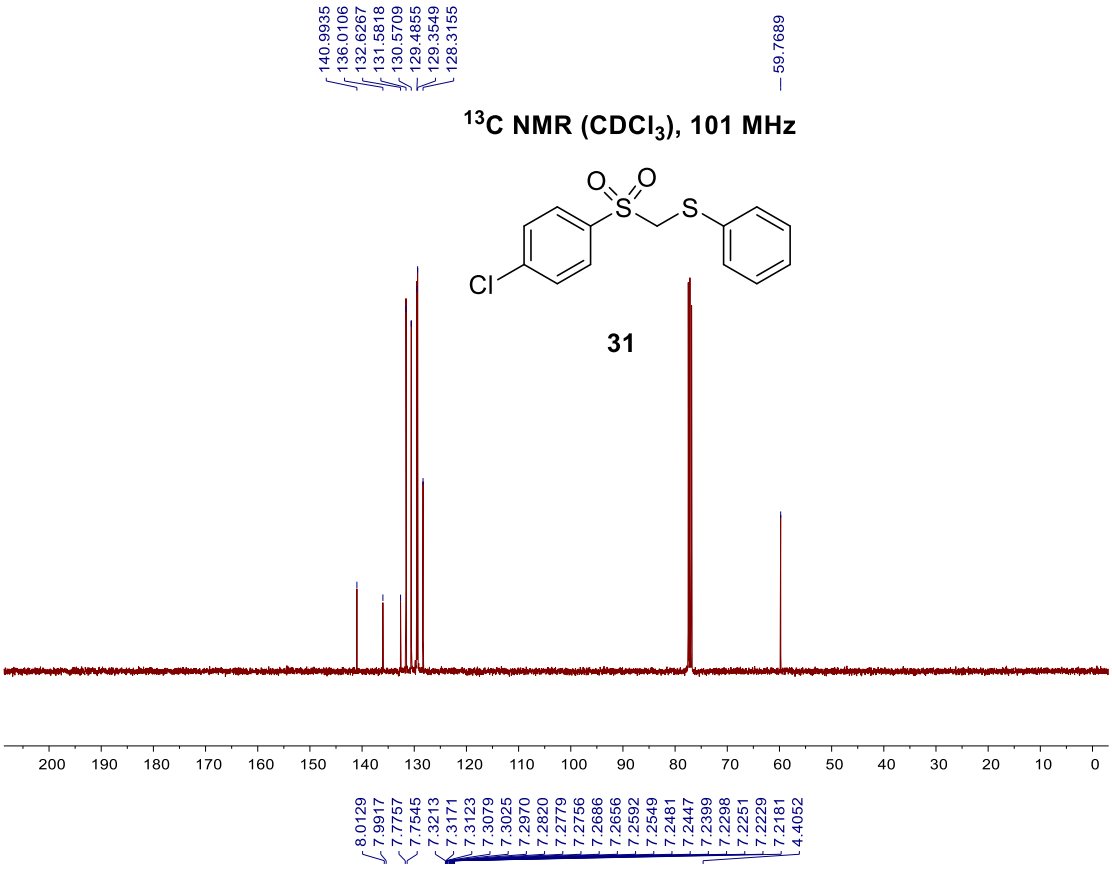
7.2346
7.2306
7.2221
7.2180
4.3582

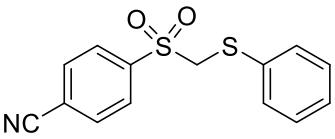

1H NMR (CDCl3), 400 MHz
O
O
S
S
Cl
31
1.95
2.00
1.96
3.03
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0



^{13}C NMR ($CDCl_3$), 101 MHz

31

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



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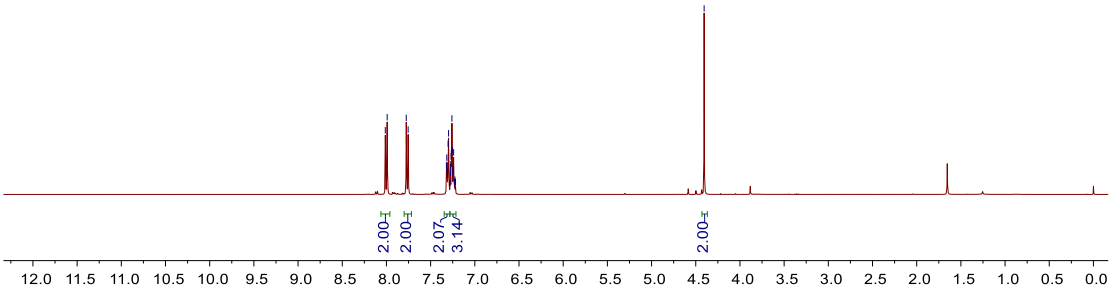

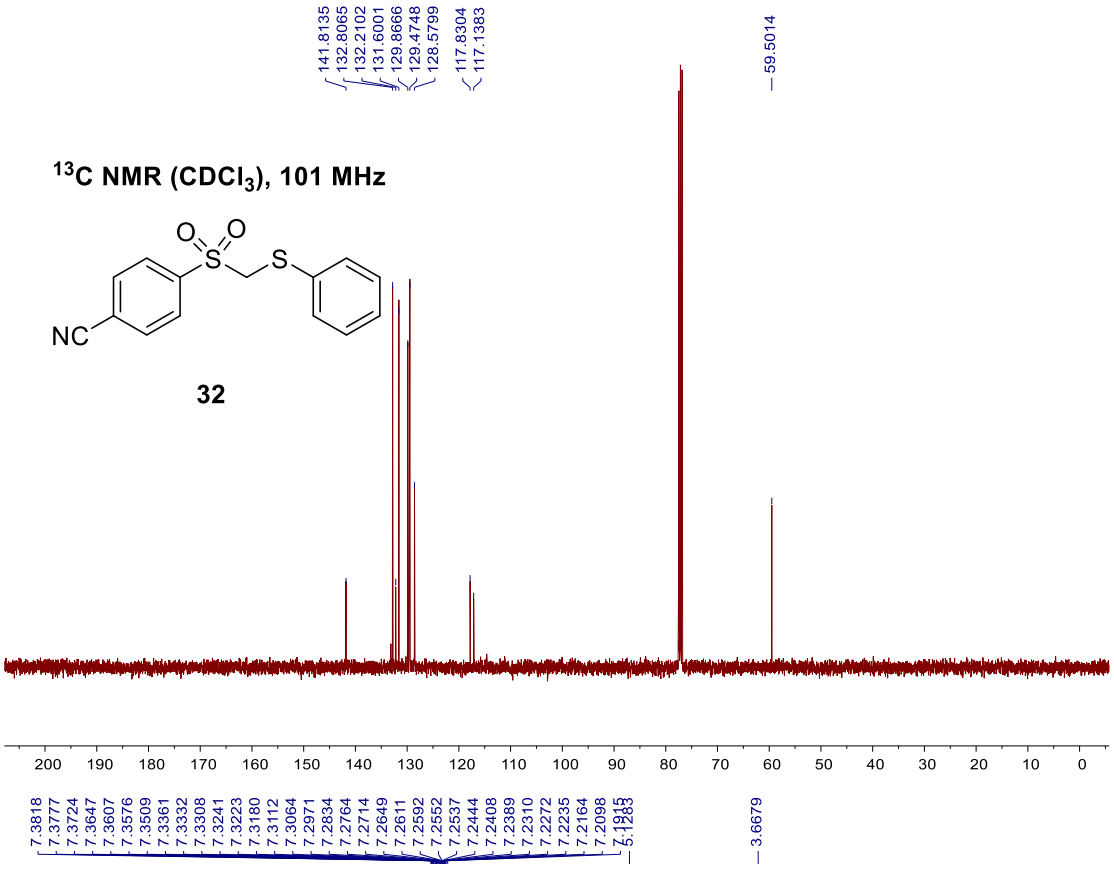
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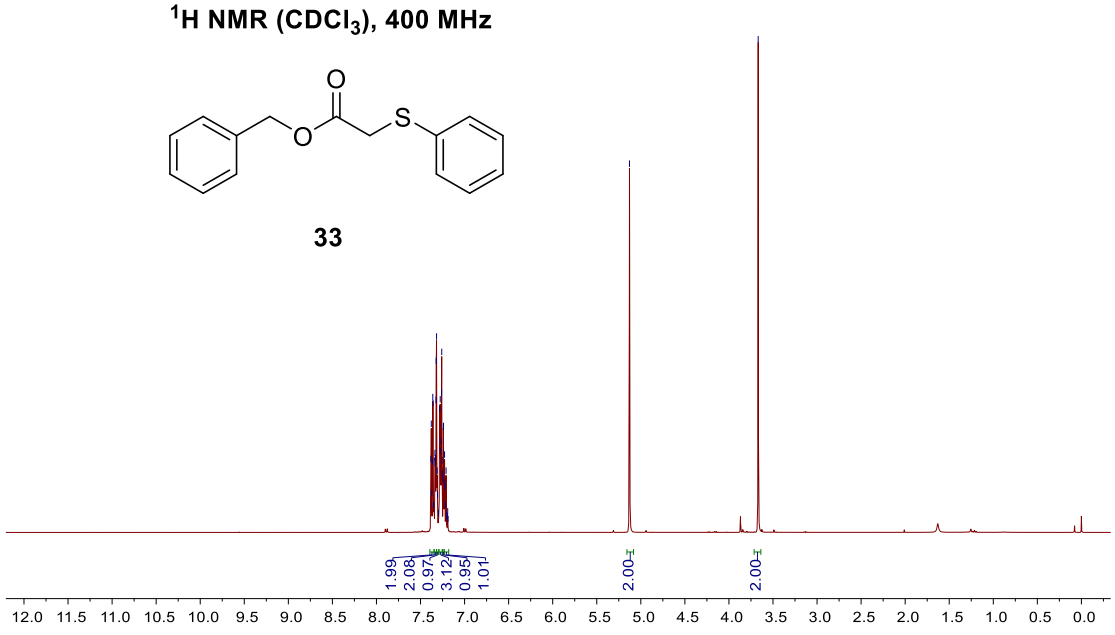
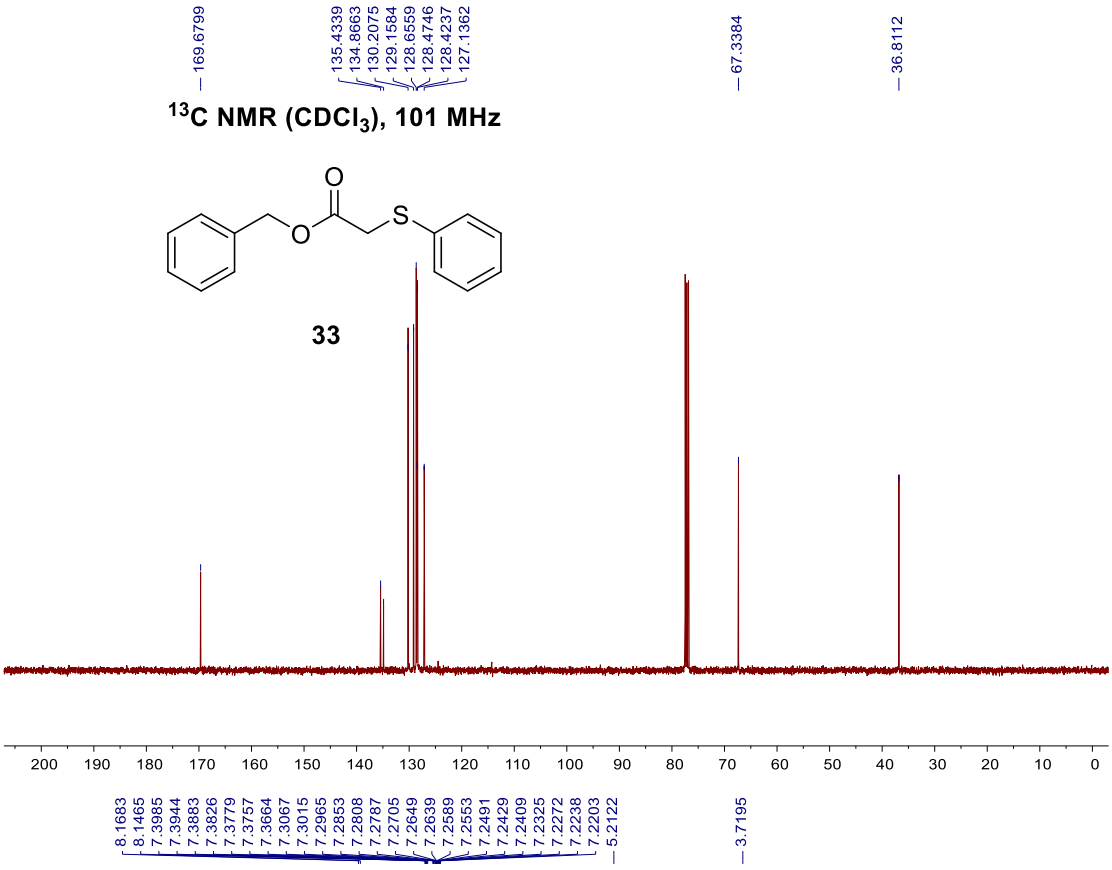
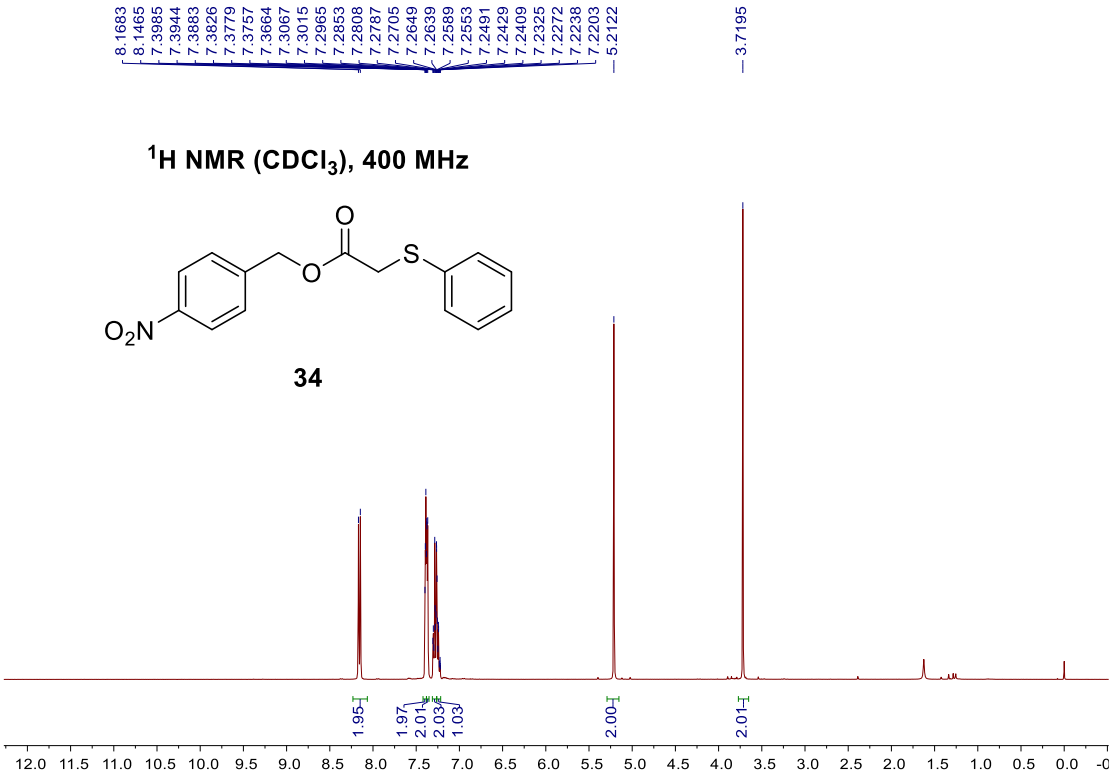
132.8065
132.2102
131.6001
129.8666
129.4748
128.5799
117.8304
117.1383
59.5014
13C NMR (CDCl3), 101 MHz
O
O
S
S
NC
32
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.3818
7.3777
7.3724
7.3647
7.3607
7.3576
7.3509
7.3361
7.3332
7.3308
7.3241
7.3223
7.3180
7.3112
7.3064
7.2971
7.2834
7.2764
7.2714
7.2649
7.2611
7.2592
7.2552
7.2537
7.2444
7.2408
7.2389
7.2310
7.2272
7.2235
7.2164
7.2098
3.6679


1H NMR (CDCl3), 400 MHz
O
O
S
33
1.99
2.08
0.97
3.12
0.95
1.01
2.00
2.00
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



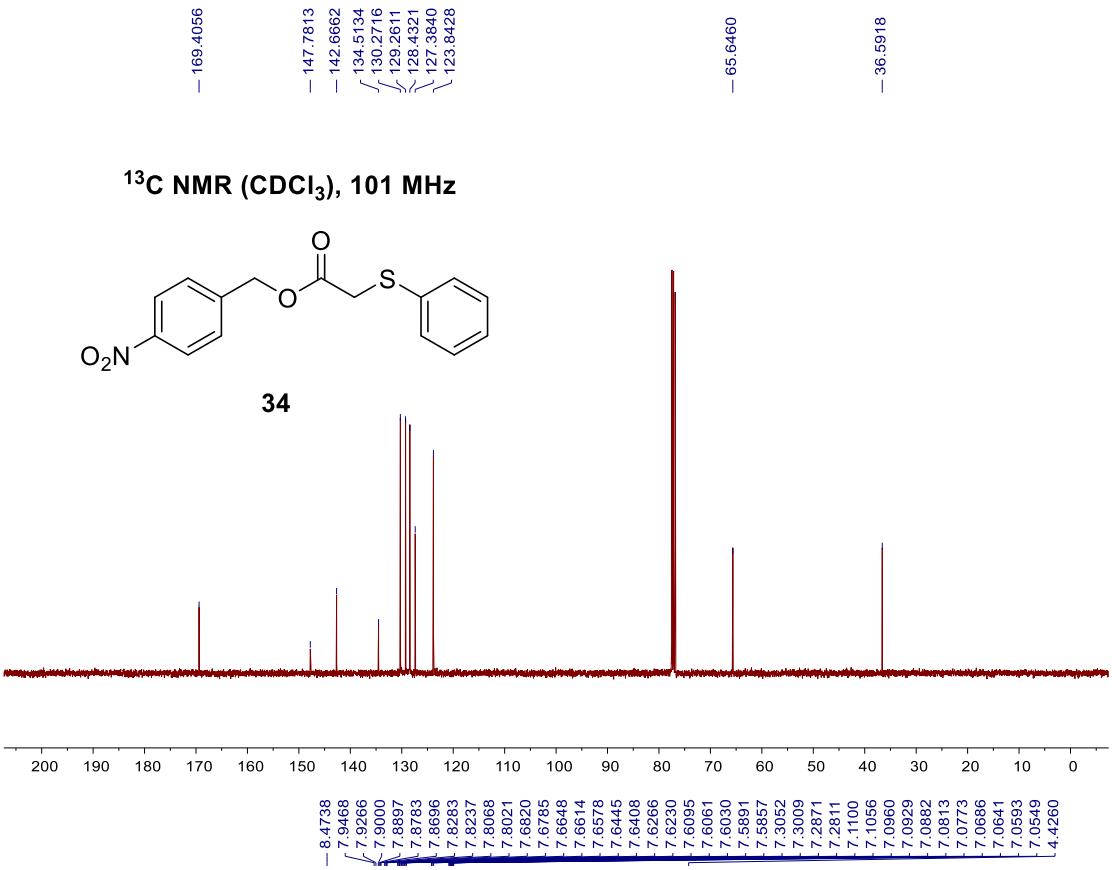
^{13}C NMR ($CDCl_3$), 101 MHz

33



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

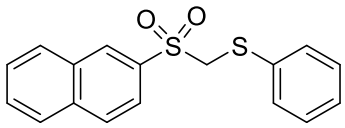
34



^{13}C NMR ($CDCl_3$), 101 MHz

34

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



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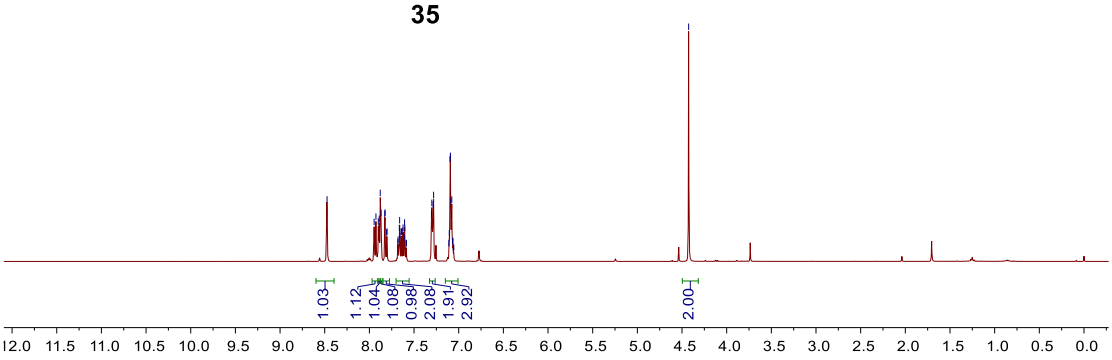
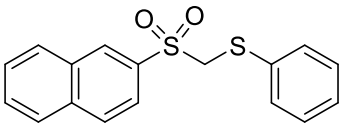
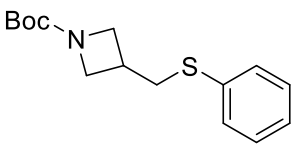


^{13}C NMR ($CDCl_3$), 101 MHz

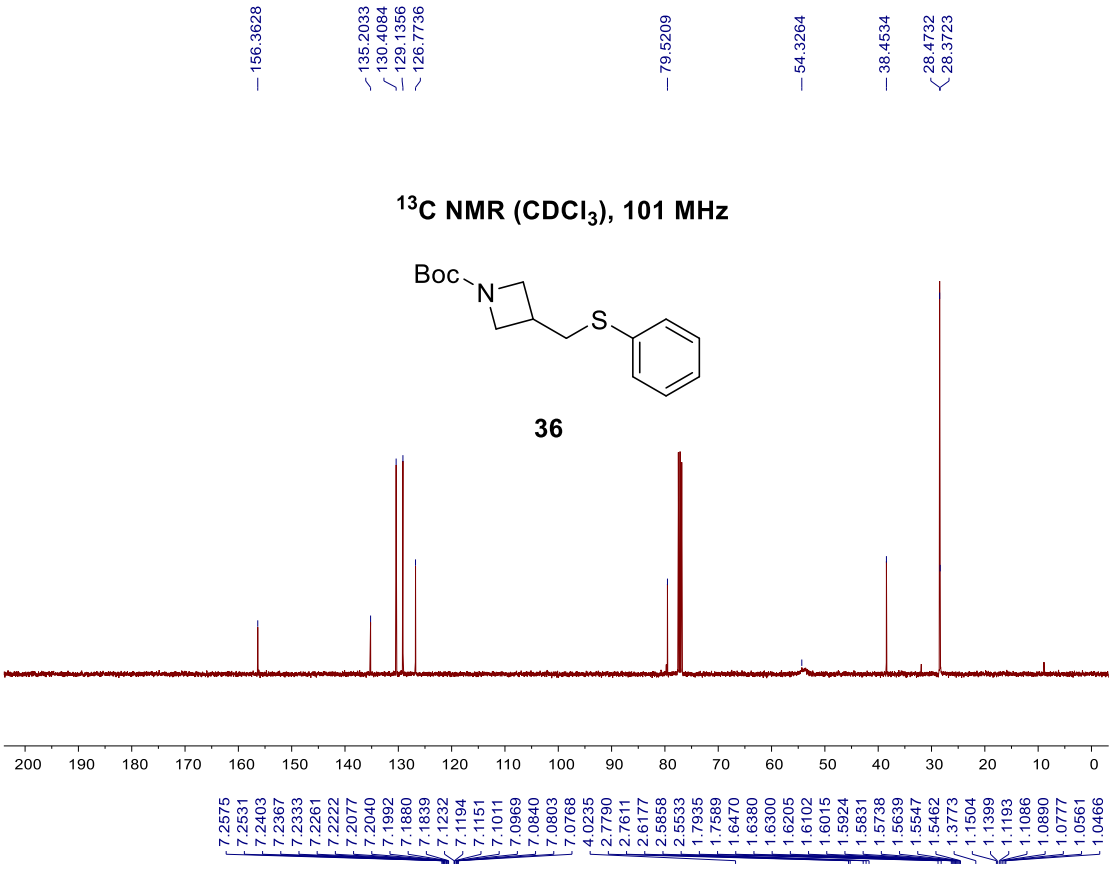


35

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

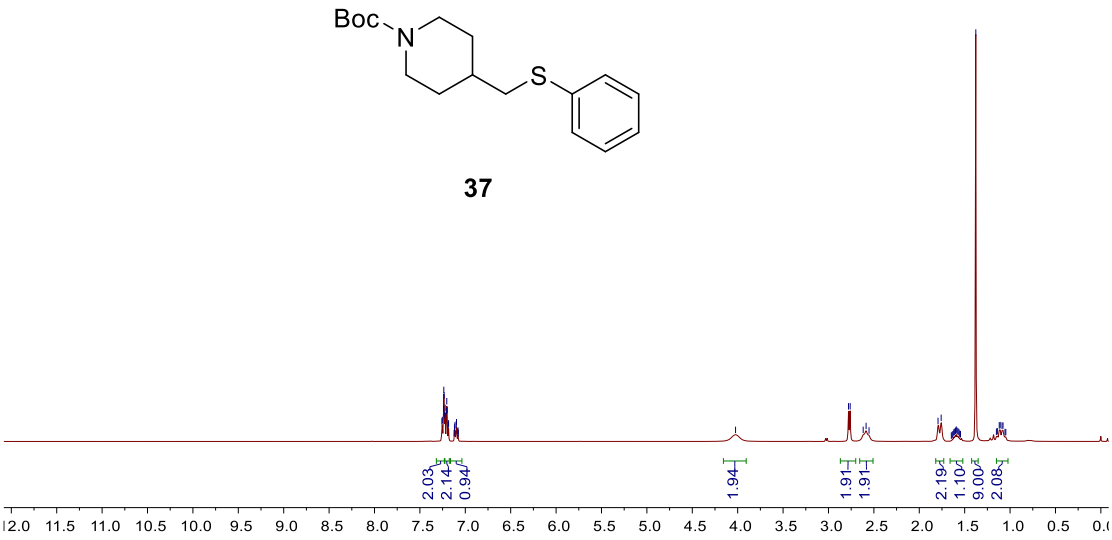


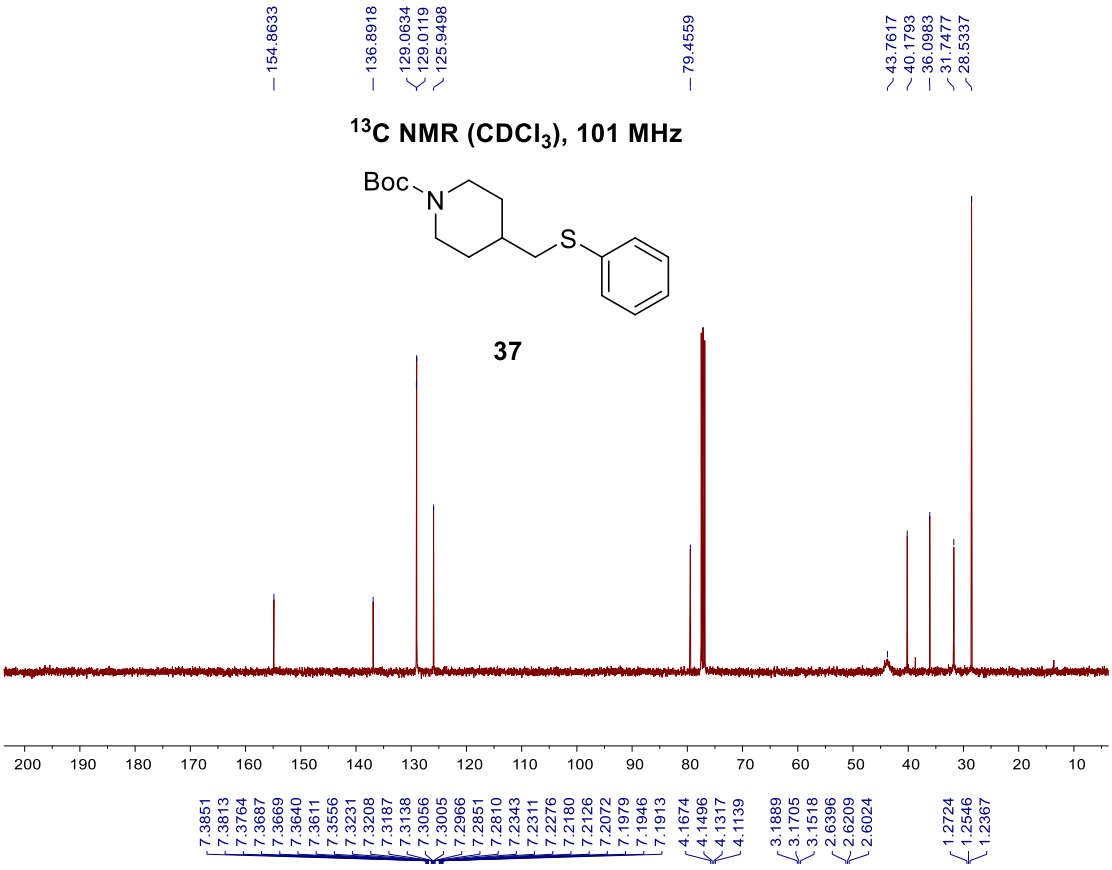
36



^{13}C NMR ($CDCl_3$), 101 MHz

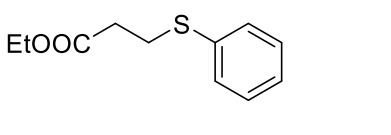
^{1}H NMR ($CDCl_3$), 400 MHz



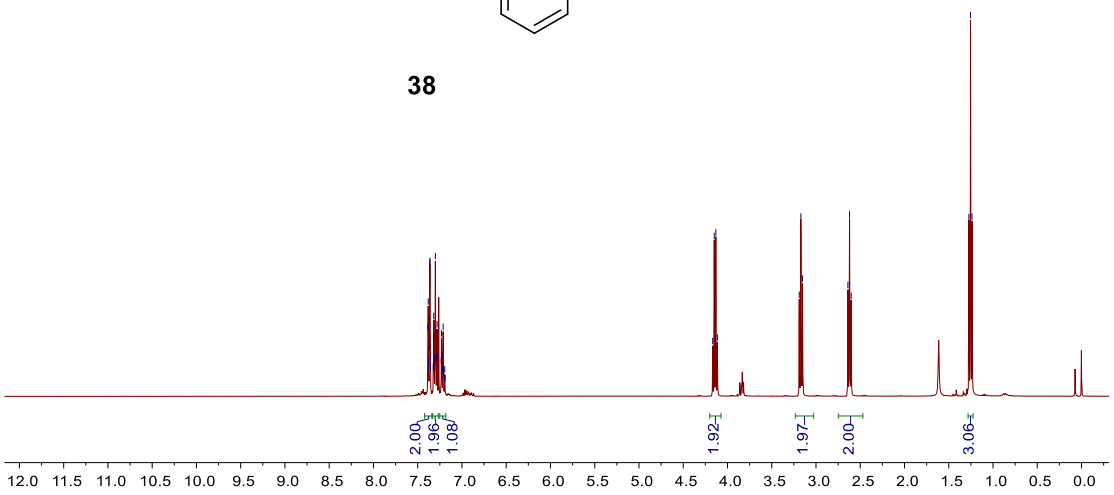


^{13}C NMR ($CDCl_3$), 101 MHz

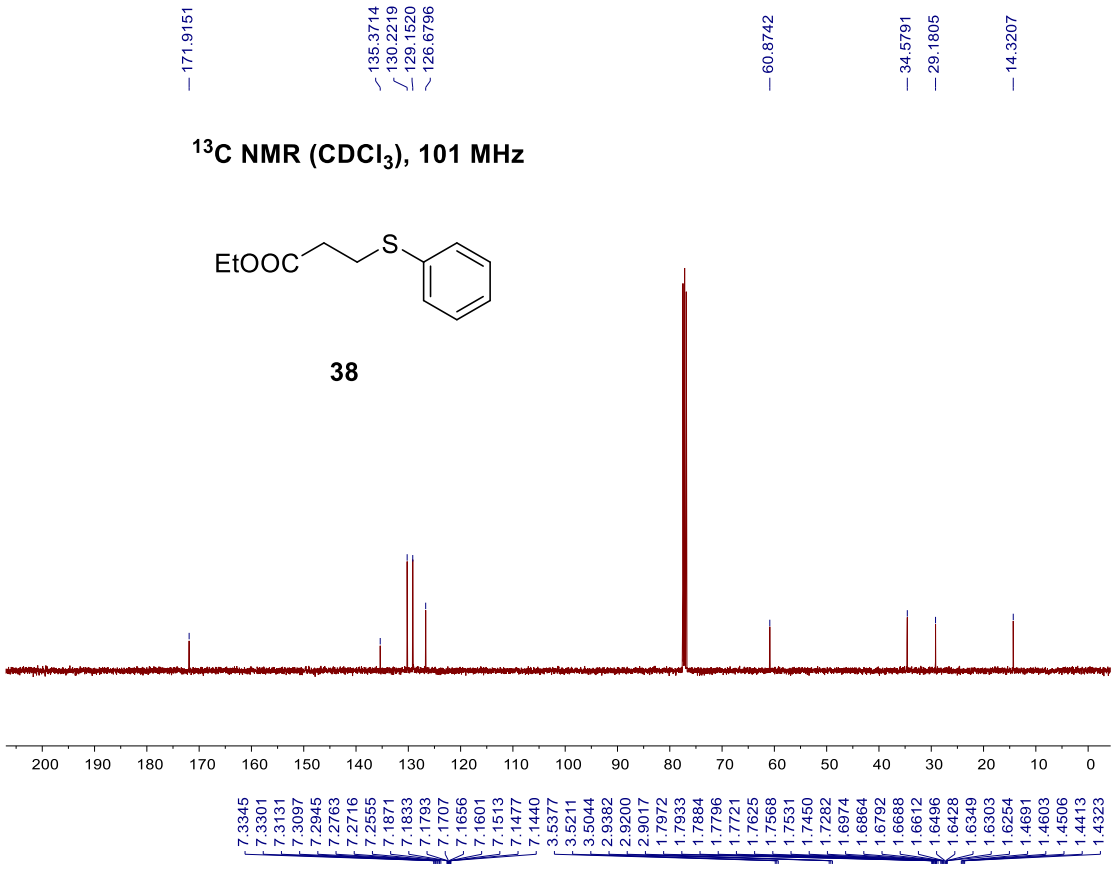
37



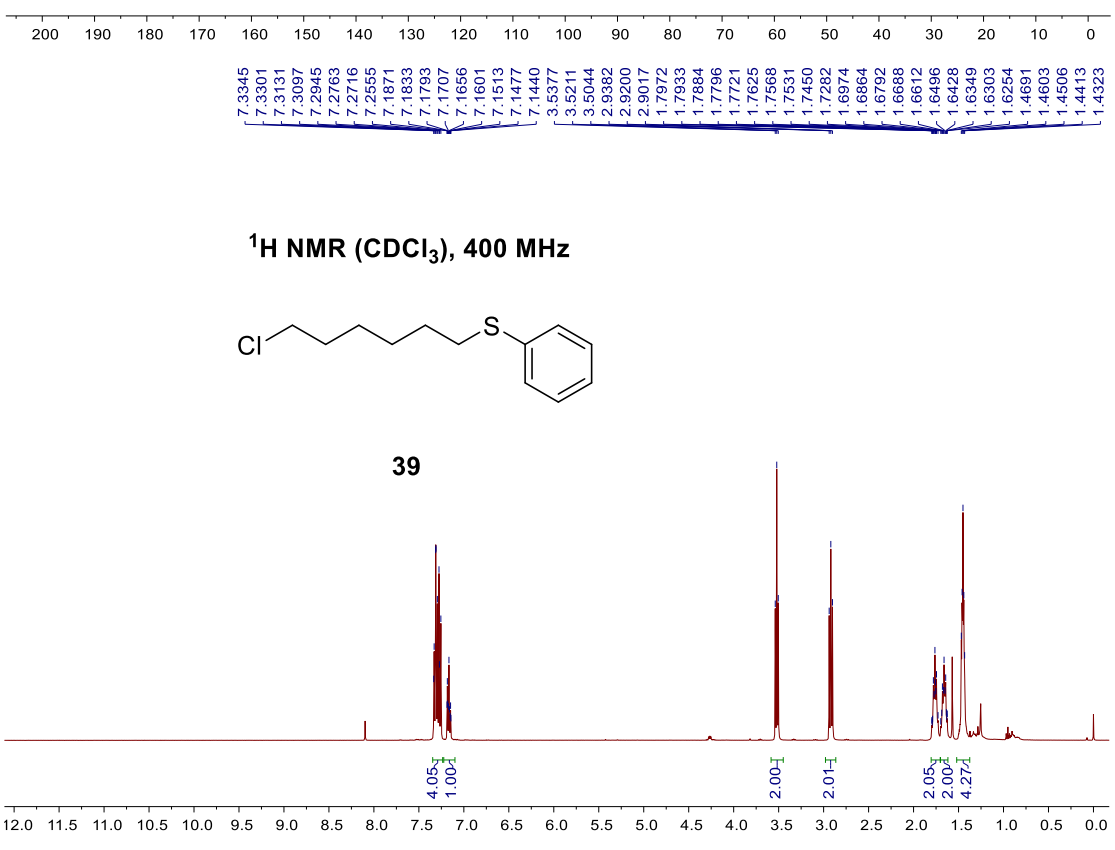
38



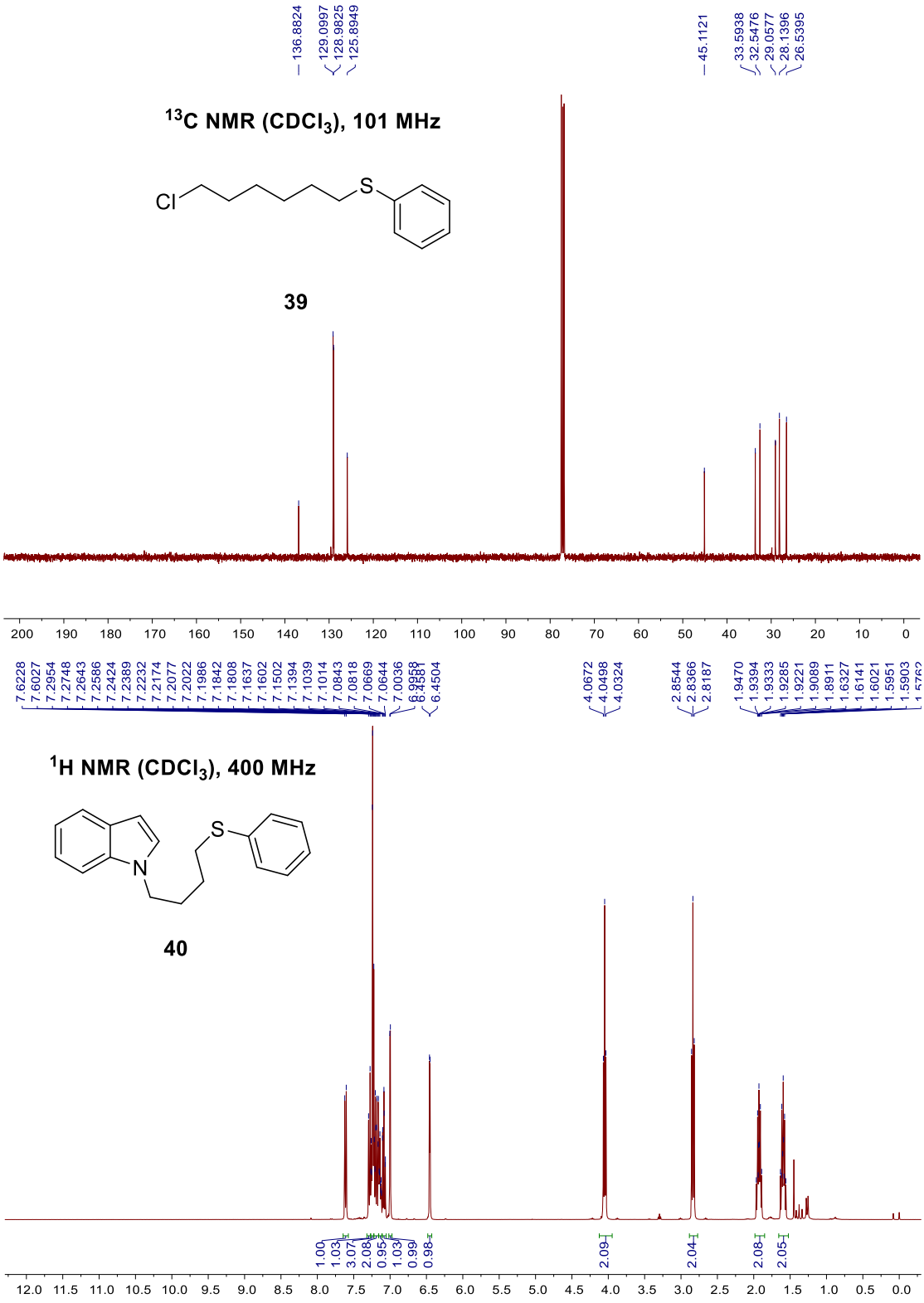
^{1}H NMR ($CDCl_3$), 400 MHz

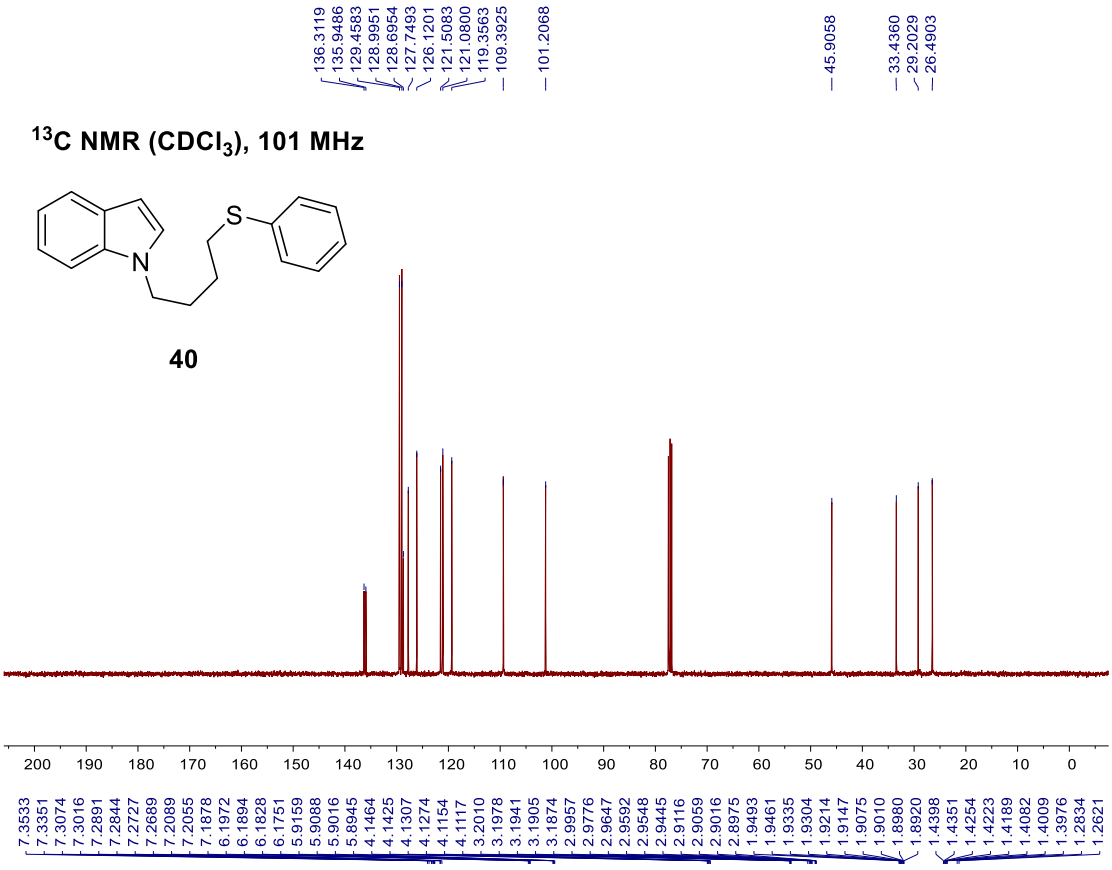


^{13}C NMR ($CDCl_3$), 101 MHz



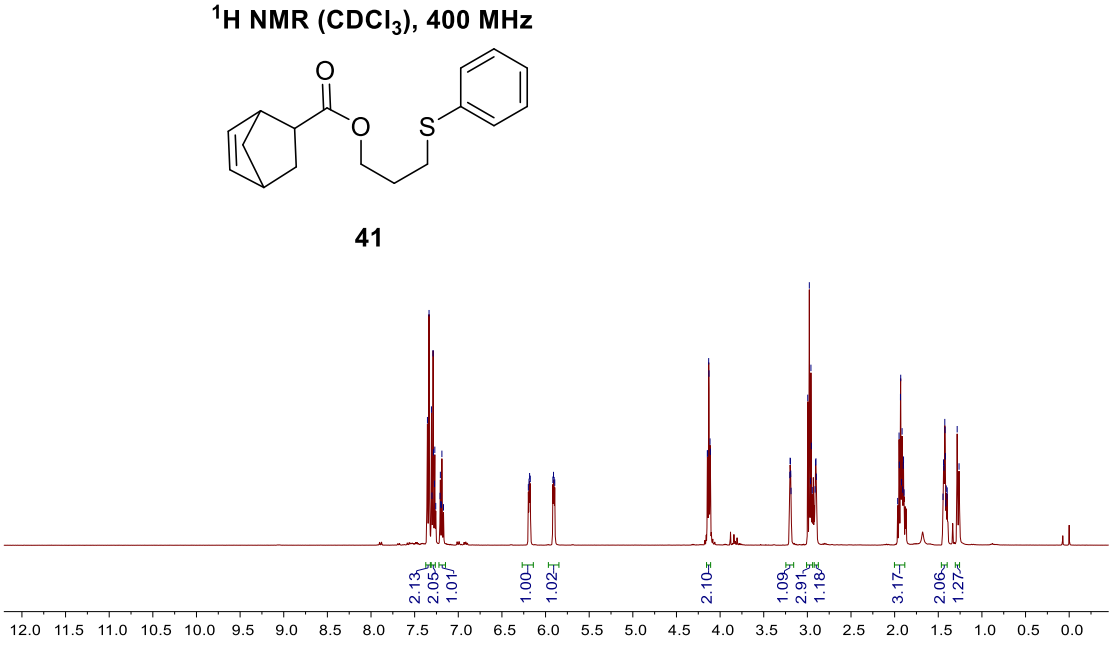
^{1}H NMR ($CDCl_3$), 400 MHz


136.8824
129.0997
128.9825
125.8949
45.1121
33.5938
32.5476
29.0577
28.1396
26.5395
13C NMR (CDCl3), 101 MHz
Cl
S
39
1H NMR (CDCl3), 400 MHz
N
S
40



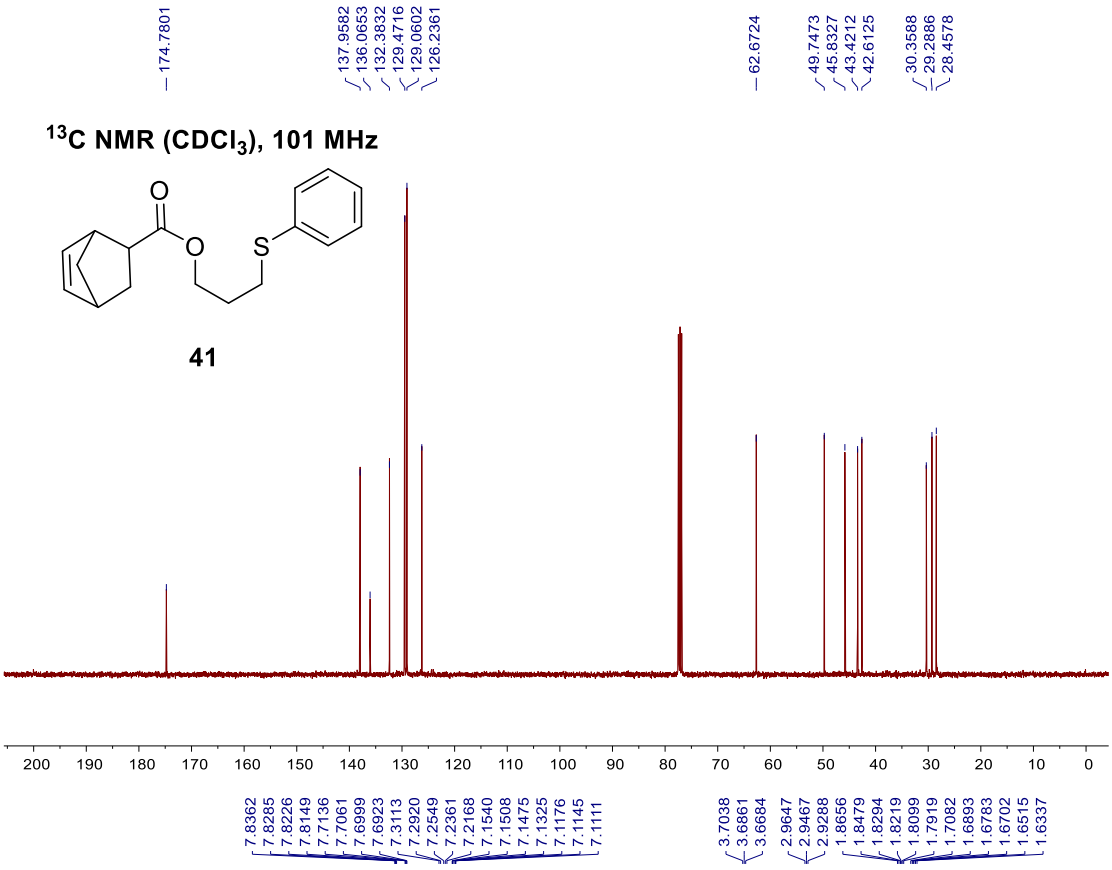
^{13}C NMR ($CDCl_3$), 101 MHz

40



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

41


174.7801
137.9582
136.0653
132.3832
129.4716
129.0602
126.2361
62.6724
49.7473
45.8327
43.4212
42.6125
30.3588
29.2886
28.4578
13C NMR (CDCl3), 101 MHz
O
O
S
41
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.8362
7.8285
7.8226
7.8149
7.7136
7.7061
7.6999
7.6923
7.3313
7.2920
7.2549
7.2361
7.2168
7.1540
7.1508
7.1475
7.1325
7.1176
7.1145
7.1111
3.7038
3.6861
3.6684
2.9647
2.9467
2.9288
1.8656
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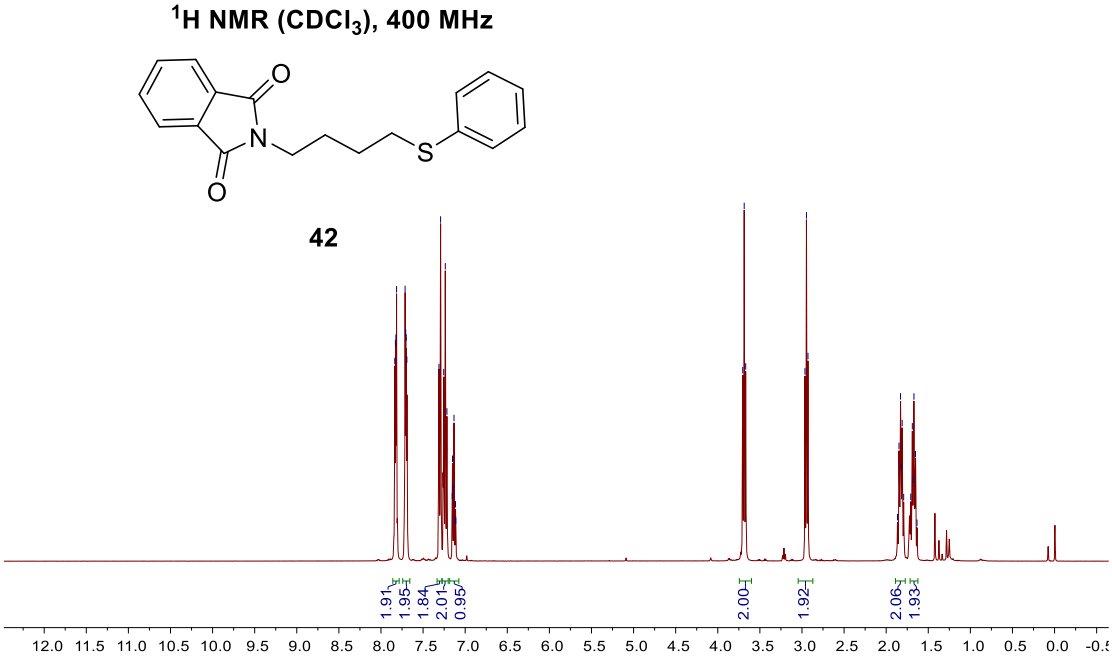
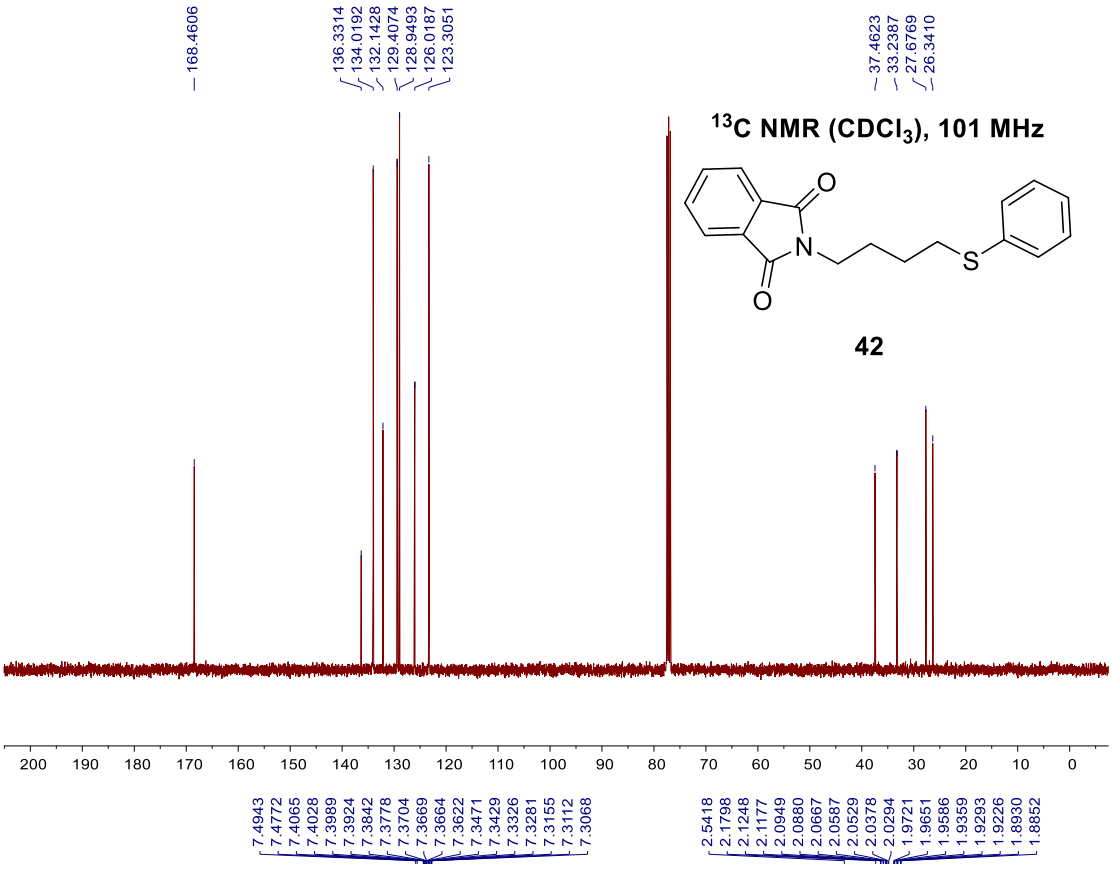
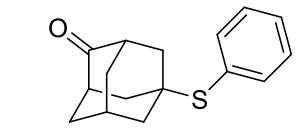
1.6515
1.6337


1H NMR (CDCl3), 400 MHz
O
N
O
S
42
1.91
1.95
1.84
2.01
0.95
2.00
1.92
2.06
1.93
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

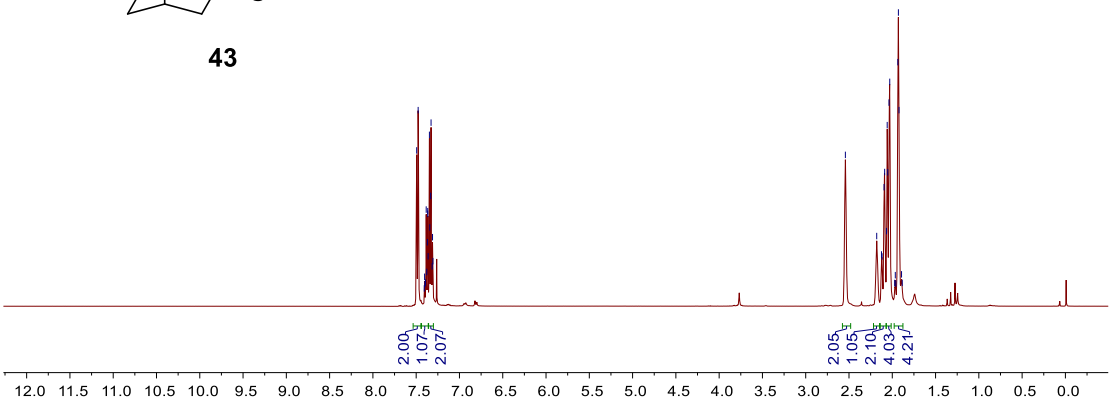


^{13}C NMR ($CDCl_3$), 101 MHz

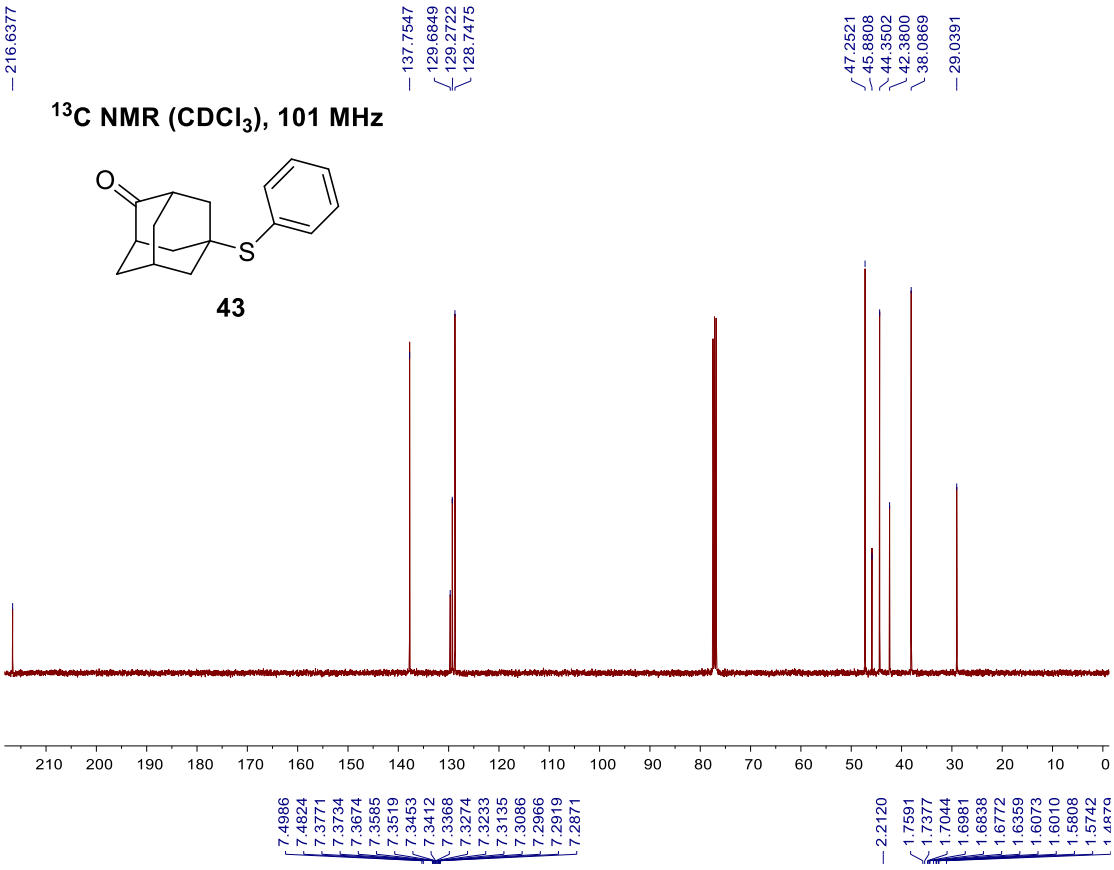
42



43



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


216.6377
137.7547
129.6849
129.2722
128.7475
47.2521
45.8808
44.3502
42.3800
38.0869
29.0391
13C NMR (CDCl3), 101 MHz
O
S
43
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.4986
7.4824
7.3771
7.3734
7.3674
7.3585
7.3519
7.3453
7.3412
7.3368
7.3274
7.3233
7.3135
7.3086
7.2966
7.2919
7.2871
2.2120
1.7591
1.7377
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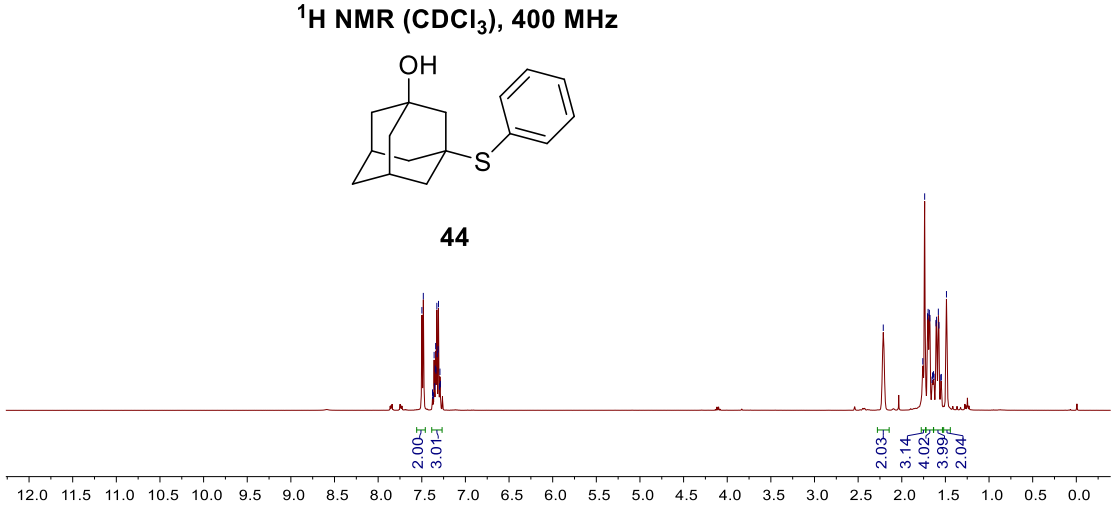
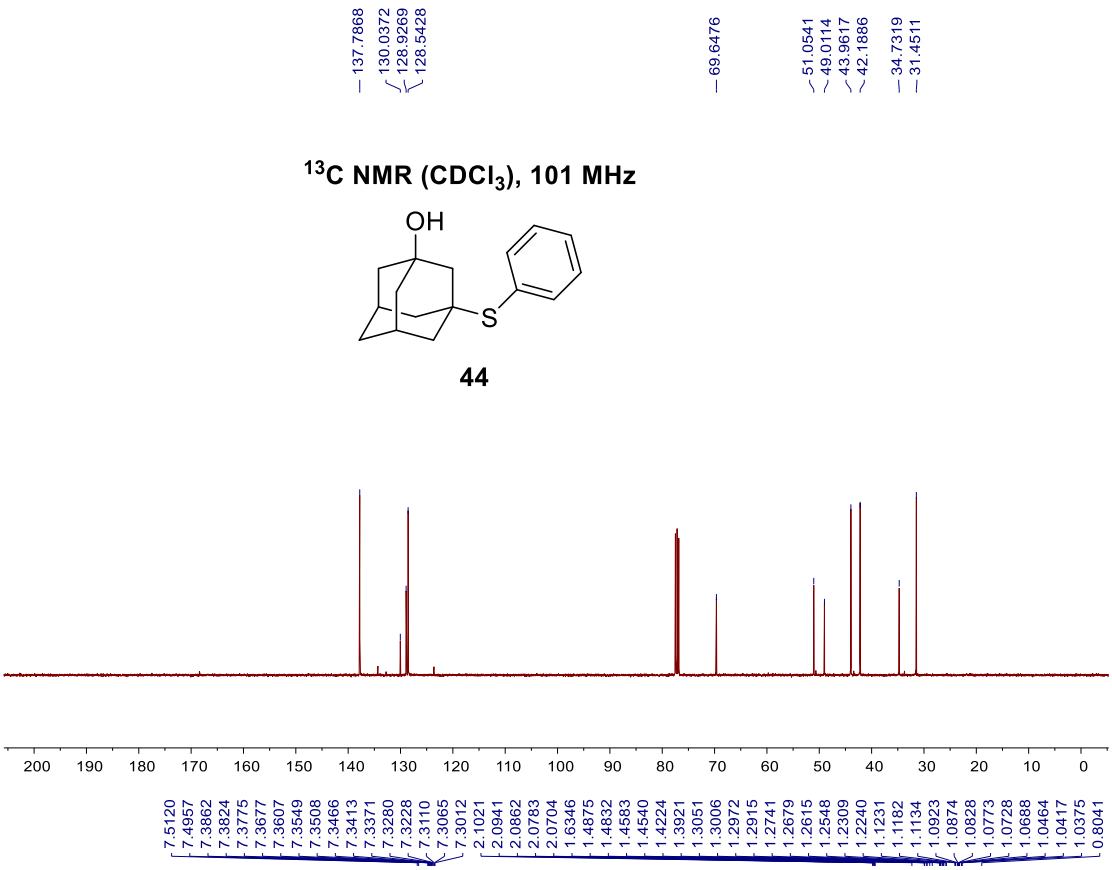
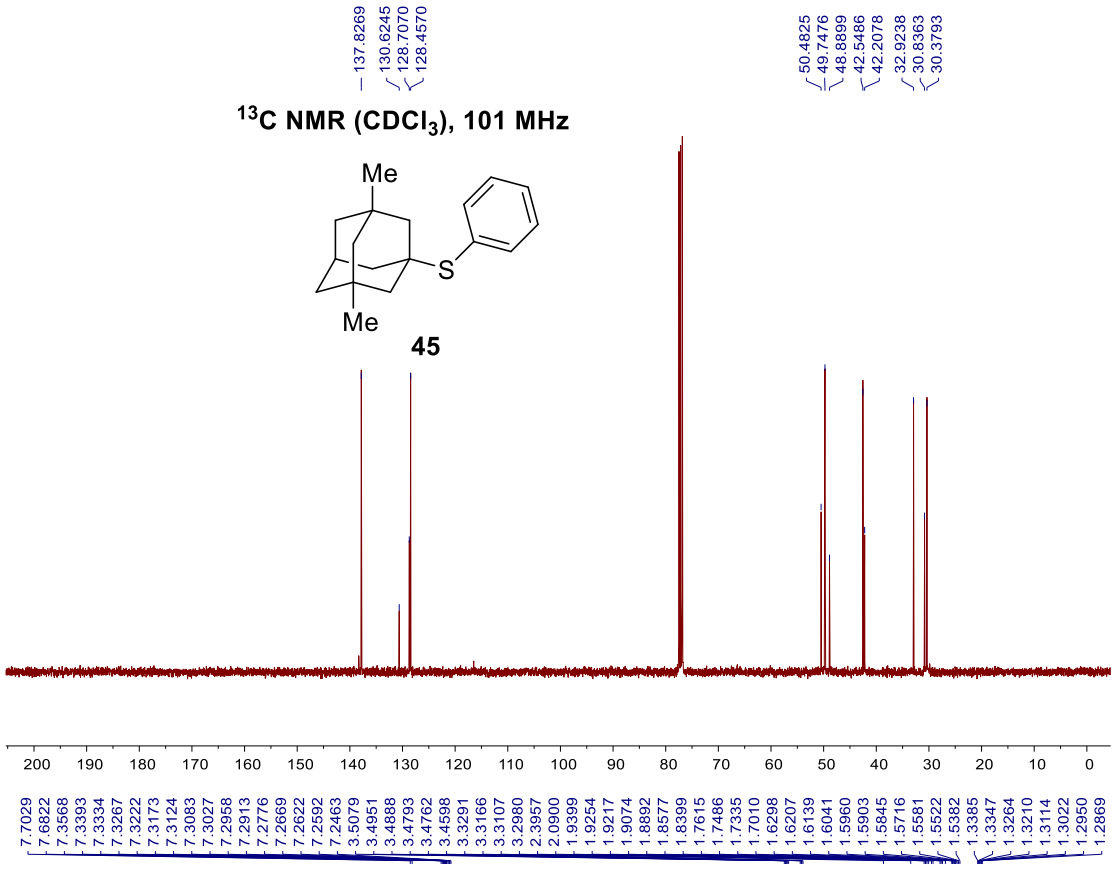
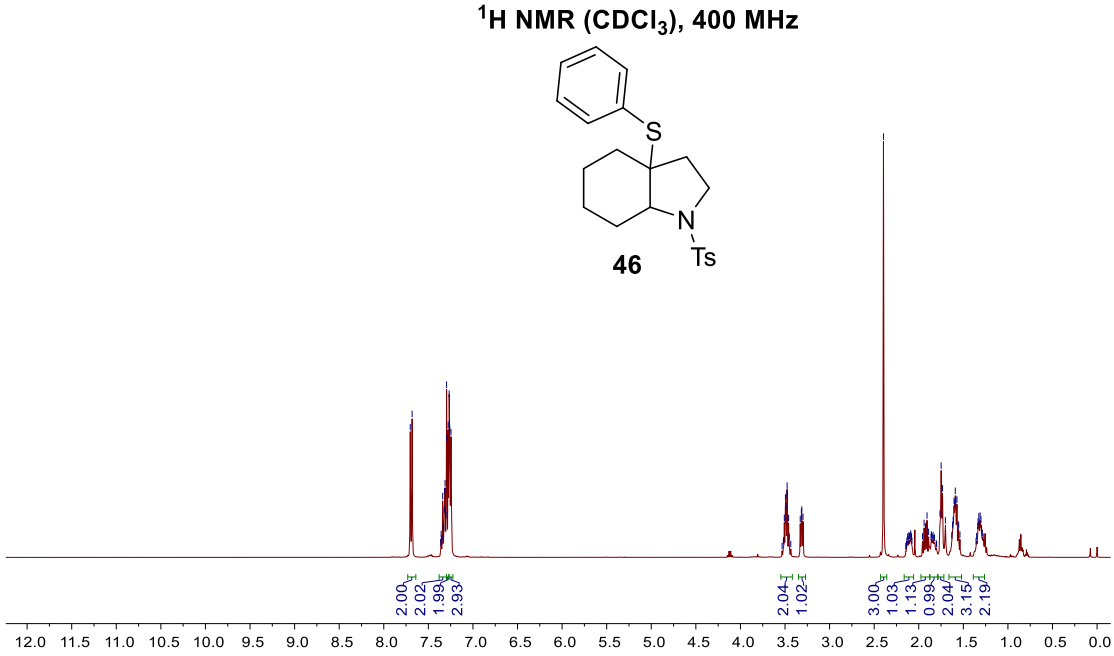
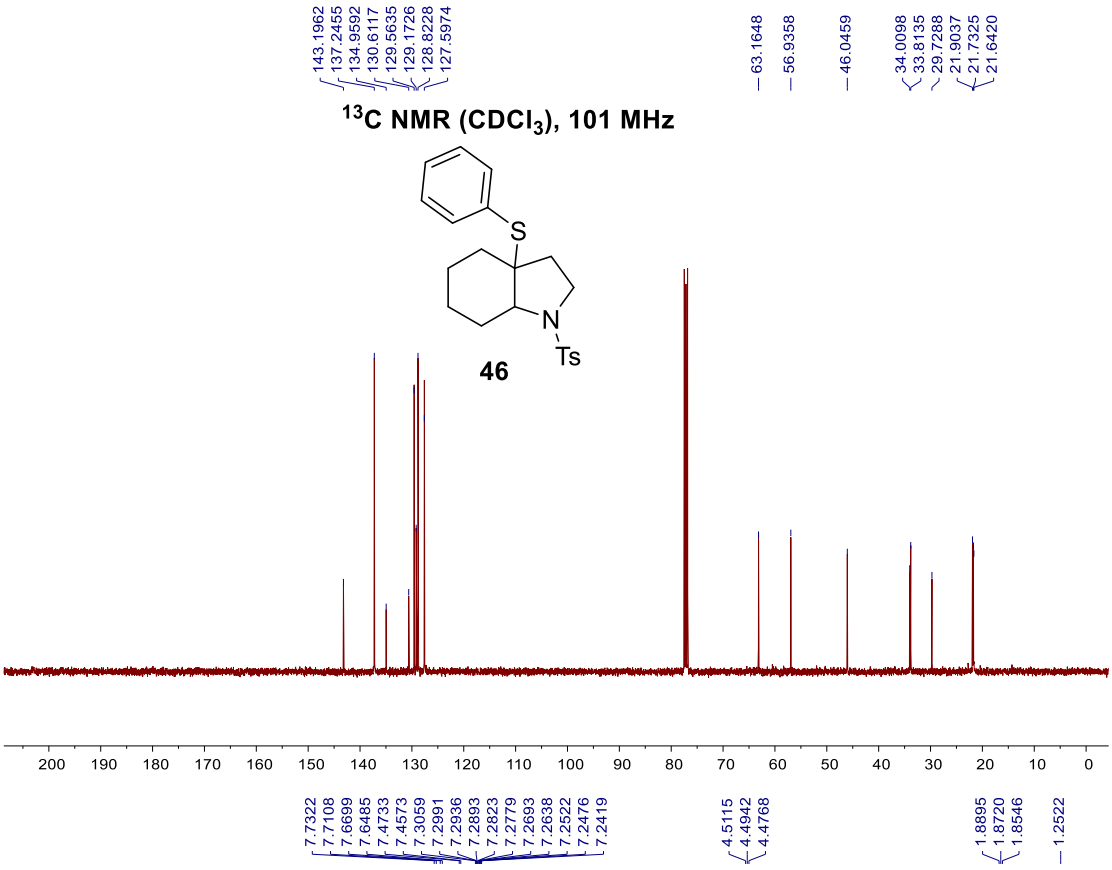
1.6981
1.6838
1.6772
1.6359
1.6073
1.6010
1.5808
1.5742


1H NMR (CDCl3), 400 MHz
OH
S
44
2.00
3.01
2.03
3.14
4.02
3.99
2.04
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


137.7868
130.0372
128.9269
128.5428
69.6476
51.0541
49.0114
43.9617
42.1886
34.7319
31.4511
13C NMR (CDCl3), 101 MHz
OH
S
44
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.5120
7.4957
7.3862
7.3824
7.3775
7.3677
7.3607
7.3549
7.3508
7.3466
7.3413
7.3371
7.3280
7.3228
7.3110
7.3065
7.3012
2.1021
2.0941
2.0862
2.0783
2.0704
1.6346
1.4875
1.4832
1.4583
1.4540
1.4224
1.3921
1.3051
1.3006
1.2972
1.2915
1.2741
1.2679
1.2615
1.2548
1.2309
1.2240
1.1231
1.1182
1.1134
1.0923
1.0874
1.0828
1.0773
1.0728
1.0688
1.0464
1.0417
1.0375
0.8041
1H NMR (CDCl3), 400 MHz
Me
S
Me
45
1.90
2.90
1.00
1.98
4.12
4.34
2.10
6.02
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


137.8269
130.6245
128.7070
128.4570
50.4825
49.7476
48.8899
42.5486
42.2078
32.9238
30.8363
30.3793
13C NMR (CDCl3), 101 MHz
Me
S
Me
45


1H NMR (CDCl3), 400 MHz
S
N
Ts
46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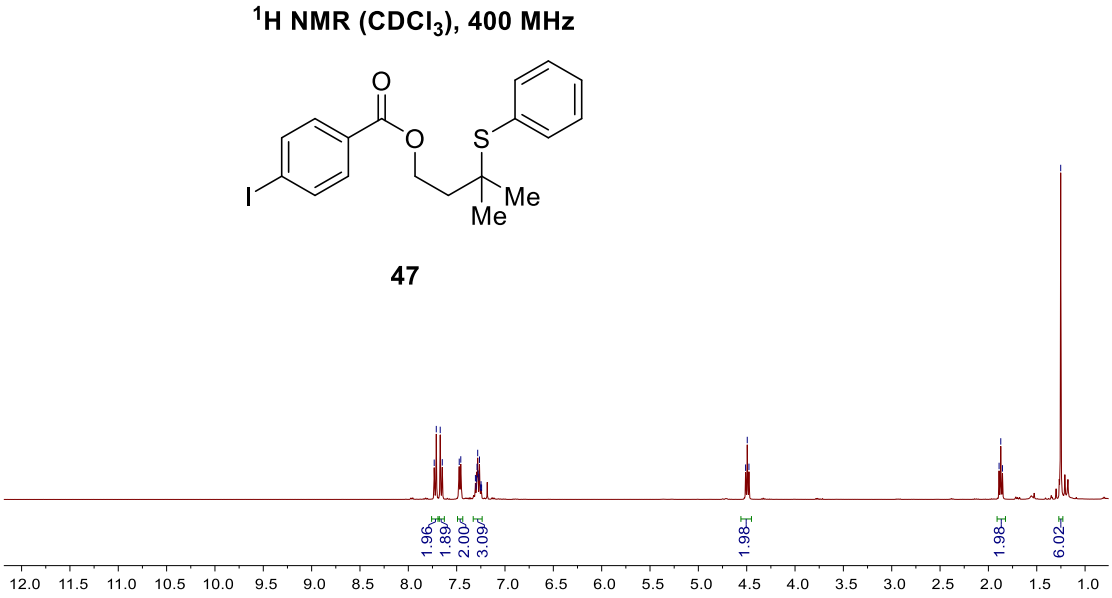
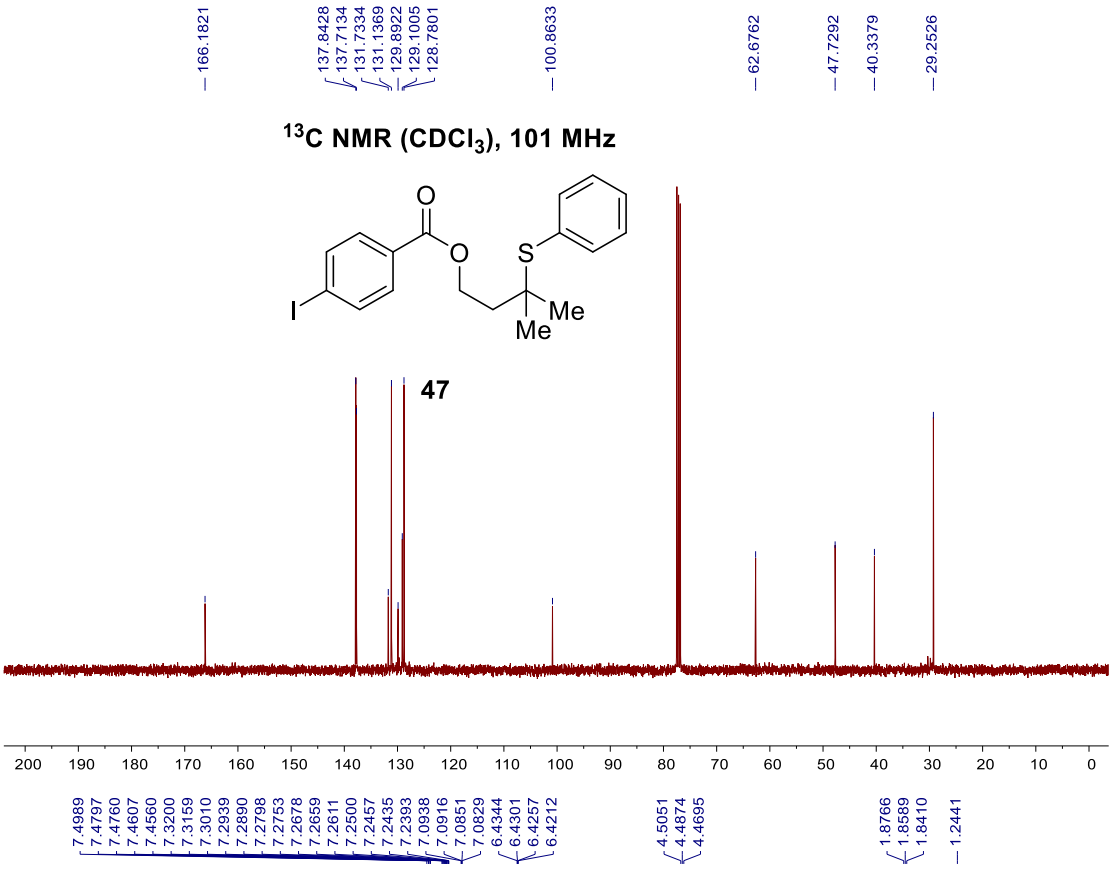
137.2455
134.9592
130.6117
129.5635
129.1726
128.8228
127.5974
63.1648
56.9358
46.0459
34.0098
33.8135
29.7288
21.9037
21.7325
21.6420
13C NMR (CDCl3), 101 MHz
S
N
Ts
46
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.7322
7.7108
7.6699
7.6485
7.4733
7.4573
7.3059
7.2991
7.2936
7.2893
7.2823
7.2779
7.2693
7.2638
7.2522
7.2476
7.2419
4.5115
4.4942
4.4768
1.8895
1.8720
1.8546
1.2522


1H NMR (CDCl3), 400 MHz
O
O
S
I
Me
Me
47
1.96
1.89
2.00
3.09
1.98
1.98
6.02
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


166.1821
137.8428
137.7134
131.7334
131.1369
129.8922
129.1005
128.7801
100.8633
62.6762
47.7292
40.3379
29.2526
13C NMR (CDCl3), 101 MHz
O
O
S
I
Me
Me
47
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.4989
7.4797
7.4760
7.4607
7.4560
7.3200
7.3159
7.3010
7.2939
7.2890
7.2798
7.2753
7.2678
7.2659
7.2611
7.2500
7.2457
7.2435
7.2393
7.0938
7.0916
7.0851
7.0829
6.4344
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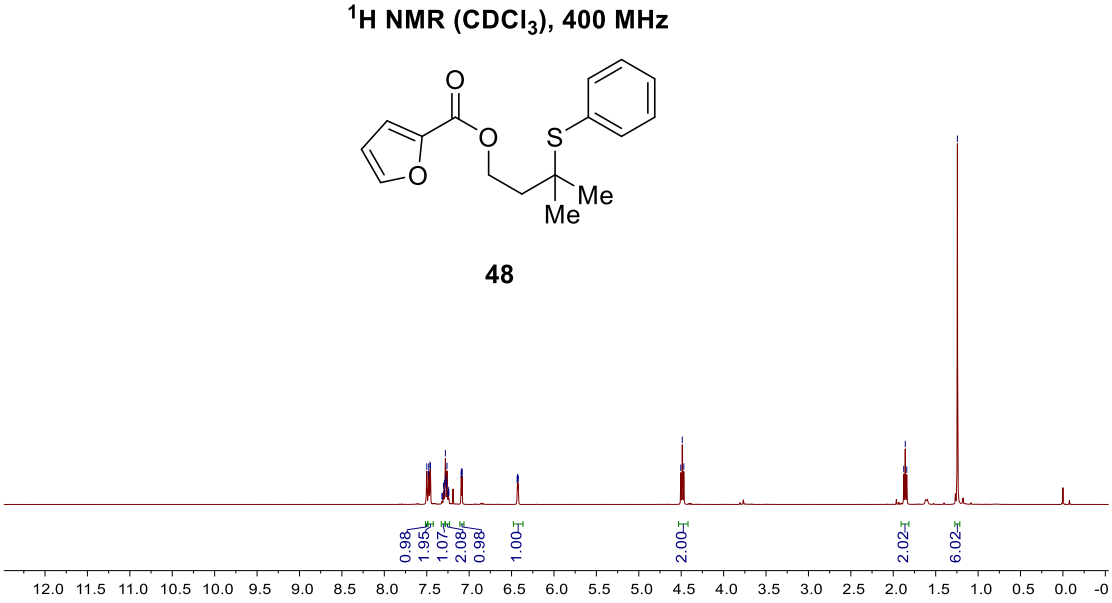
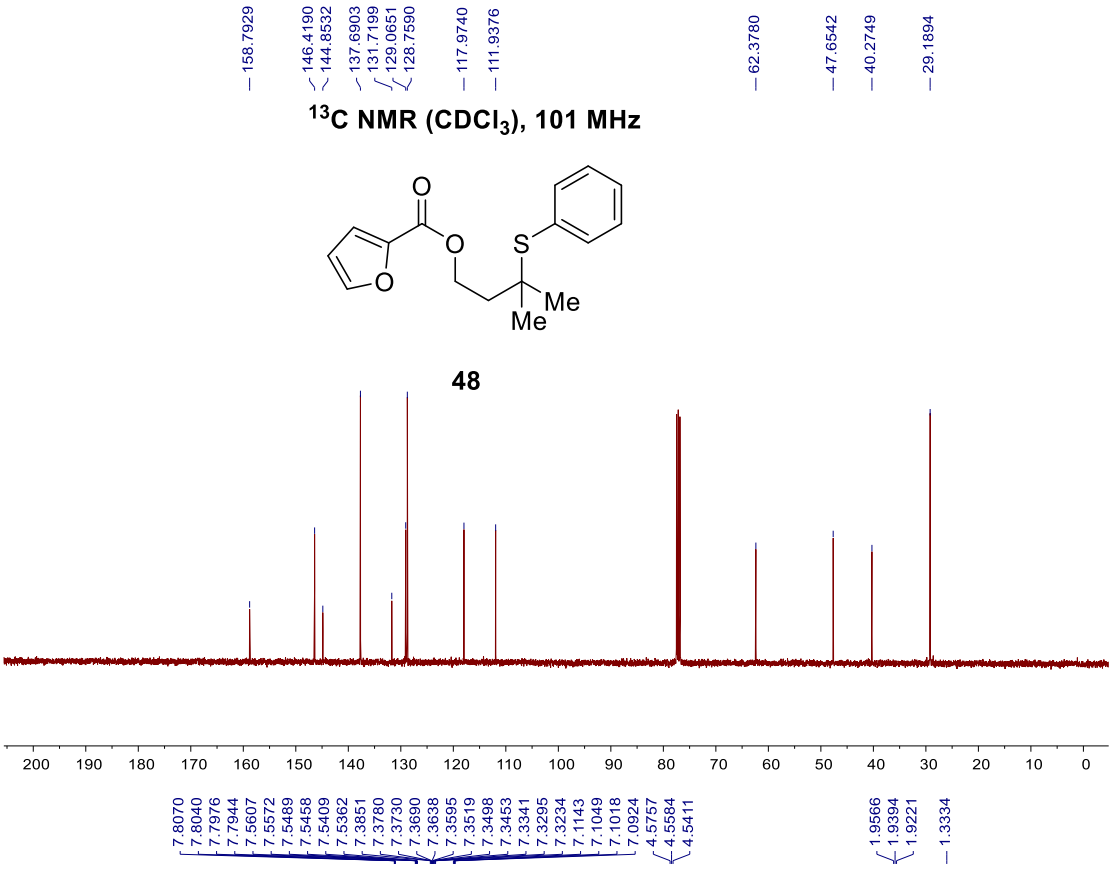
4.4695
1.8766
1.8589
1.8410
1.2441


1H NMR (CDCl3), 400 MHz
O
O
O
S
Me
Me
48
0.98
1.95
1.07
2.08
0.98
1.00
2.00
2.02
6.02
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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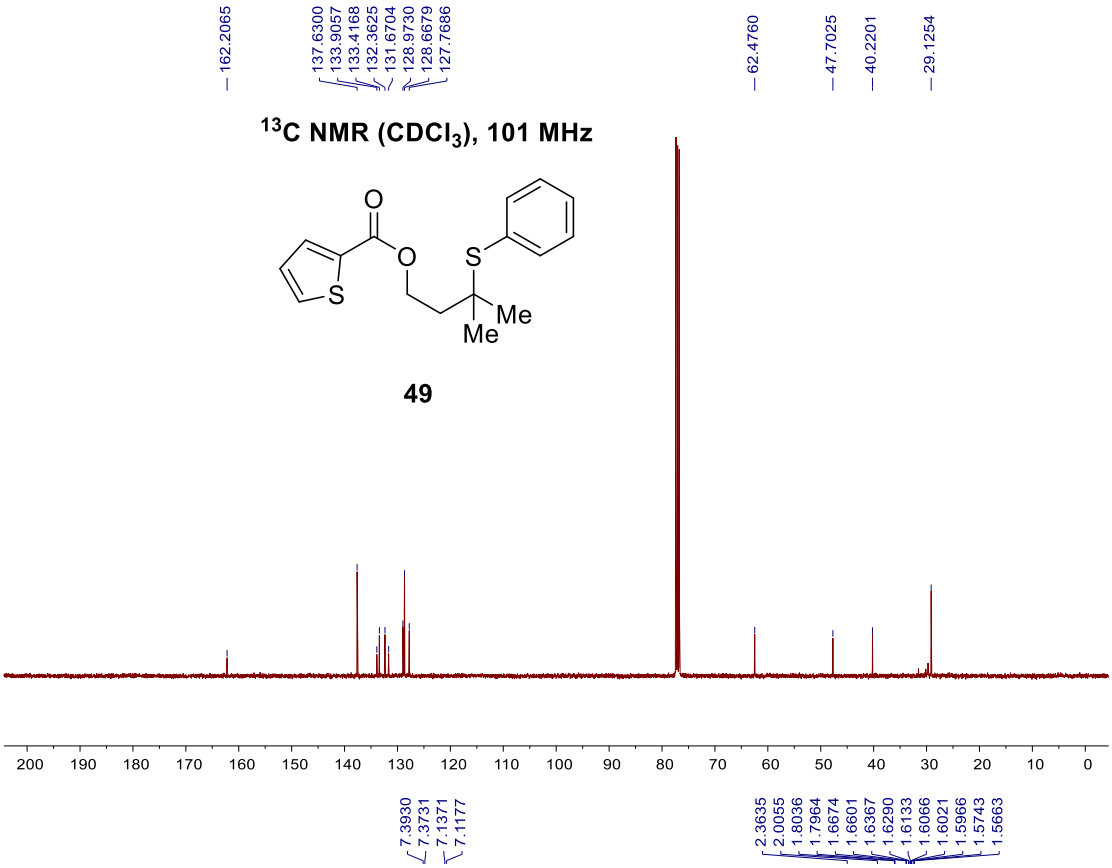
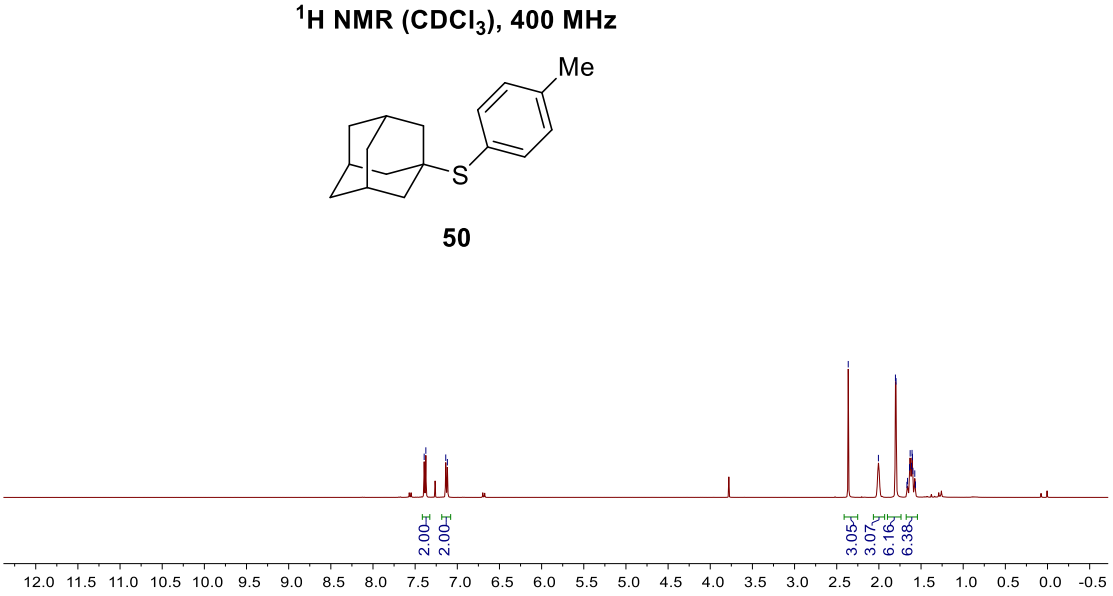
146.4190
144.8532
137.6903
131.7199
129.0651
128.7590
117.9740
111.9376
62.3780
47.6542
40.2749
29.1894
13C NMR (CDCl3), 101 MHz
O
O
O
S
Me
Me
48
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.8070
7.8040
7.7976
7.7944
7.5607
7.5572
7.5489
7.5458
7.5409
7.5362
7.3851
7.3780
7.3730
7.3690
7.3638
7.3595
7.3519
7.3498
7.3453
7.3341
7.3295
7.3234
7.1143
7.1049
7.1018
7.0924
4.5757
4.5584
4.5411
1.9566
1.9394
1.9221
1.3334
1H NMR (CDCl3), 400 MHz
O
O
S
S
Me
Me
49
1.01
2.91
3.05
1.08
1.99
2.04
6.00
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



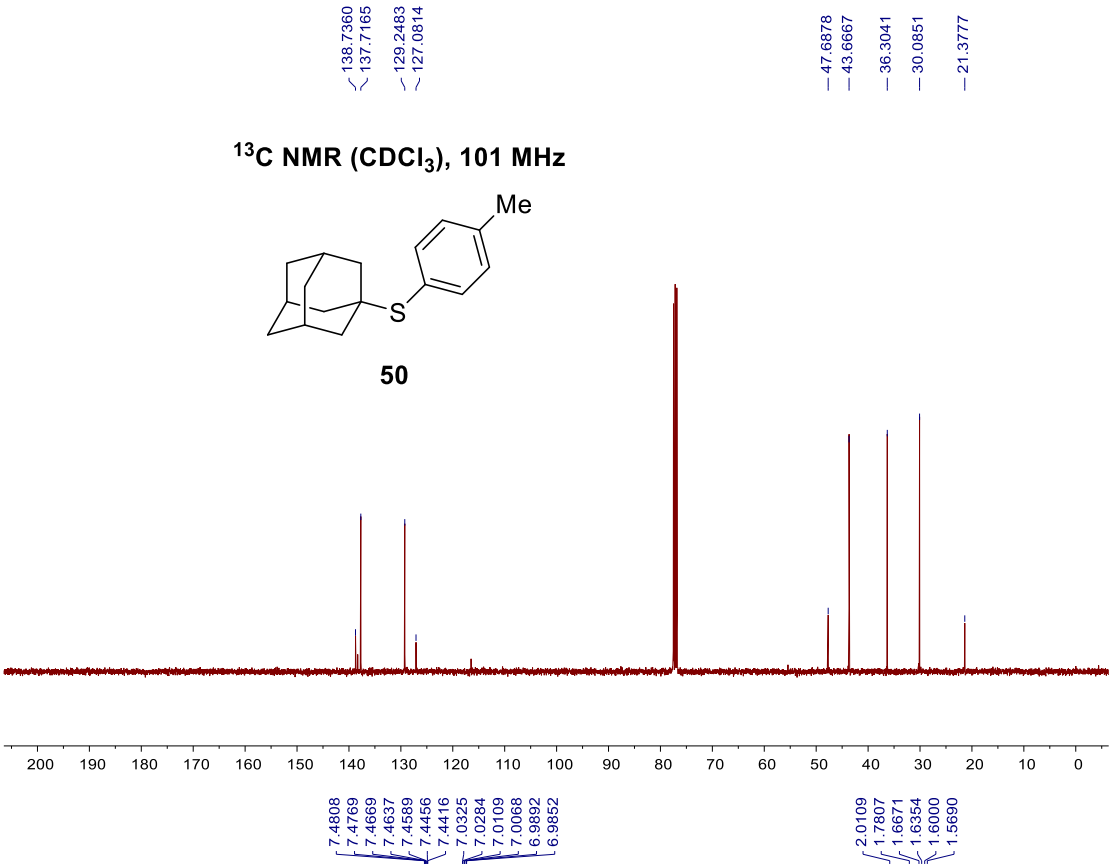
^{13}C NMR ($CDCl_3$), 101 MHz

49



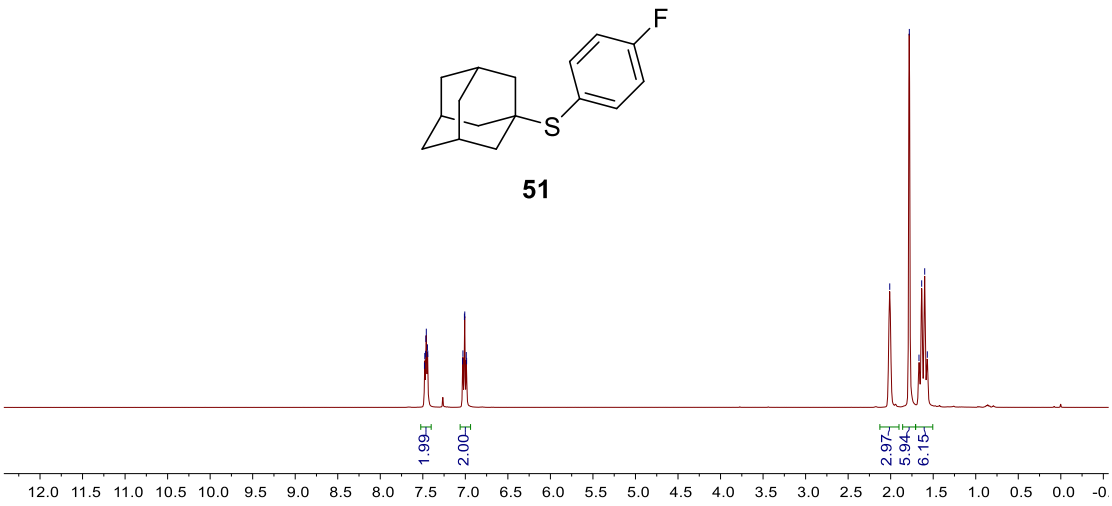
^{1}H NMR ($CDCl_3$), 400 MHz

50



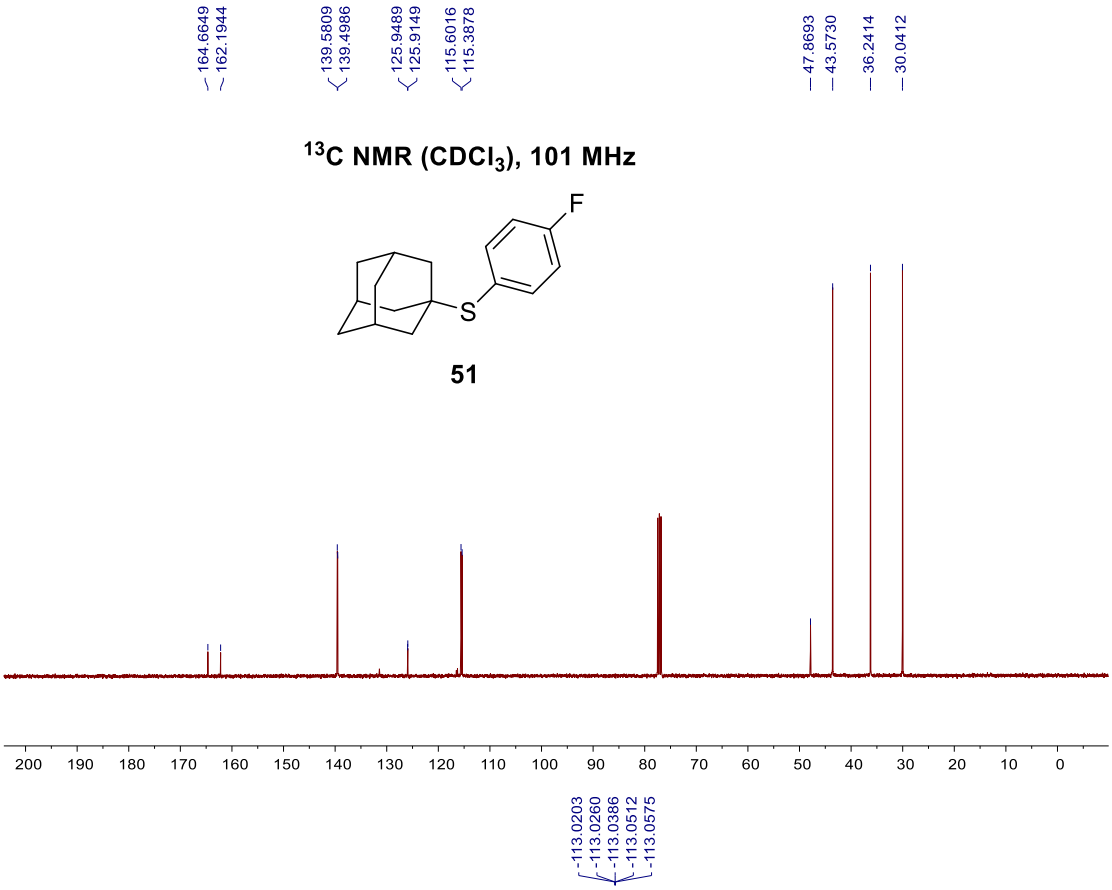
^{13}C NMR ($CDCl_3$), 101 MHz

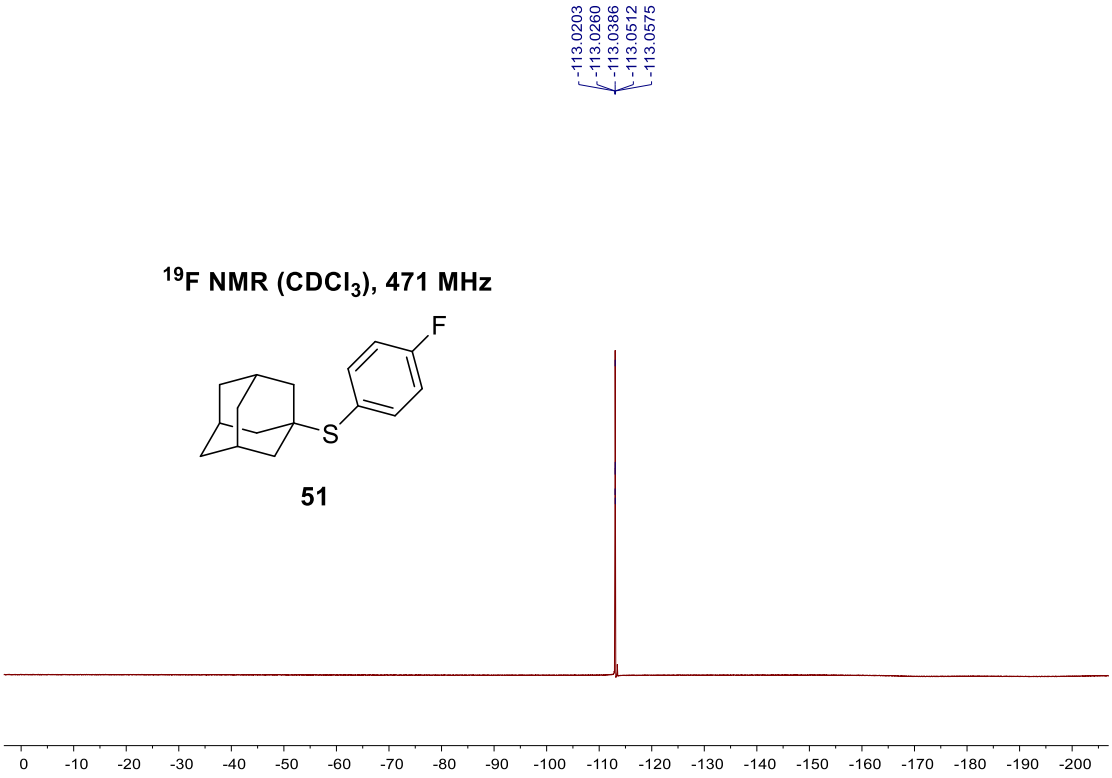
50

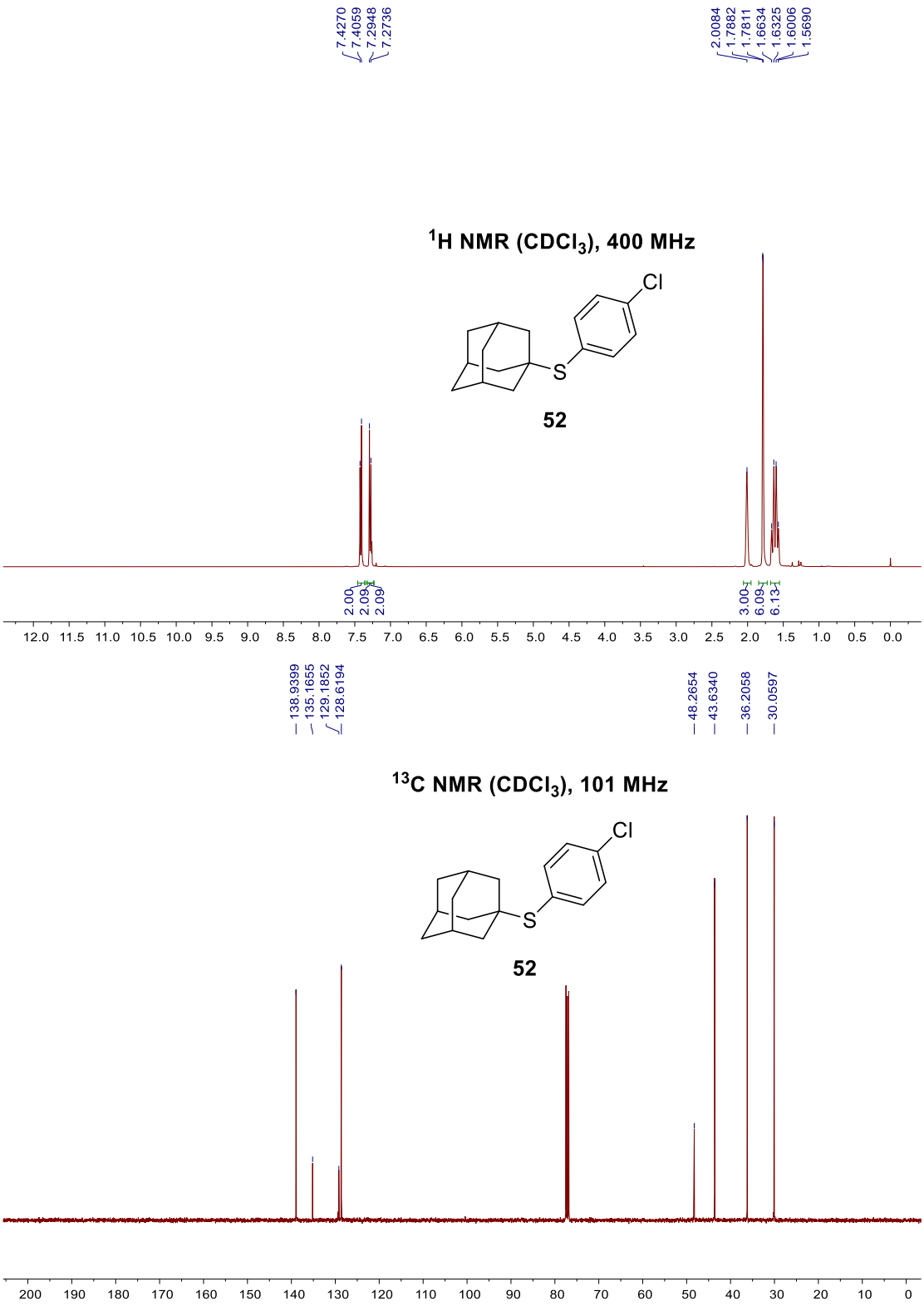


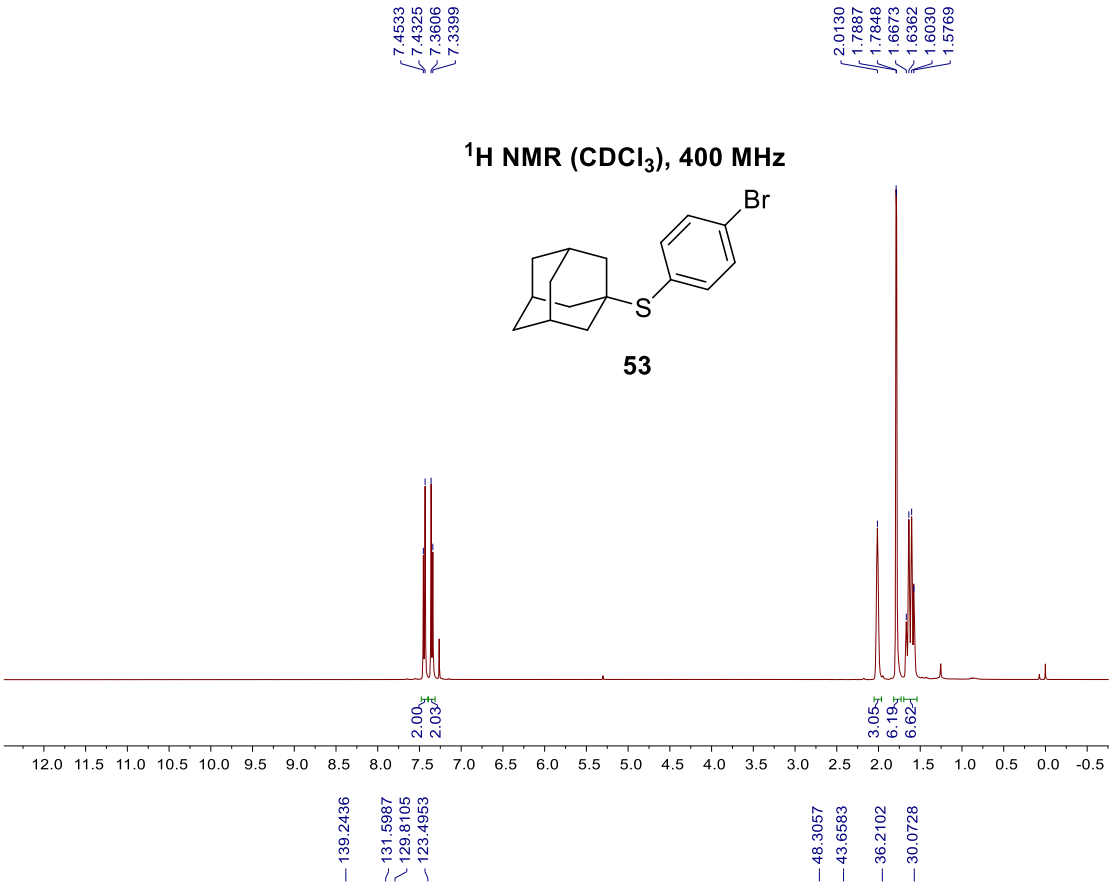
^{1}H NMR ($CDCl_3$), 400 MHz

51


164.6649
162.1944
139.5809
139.4986
125.9489
125.9149
115.6016
115.3878
47.8693
43.5730
36.2414
30.0412
^{13}C NMR ($CDCl_3$), 101 MHz
F
S
51
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

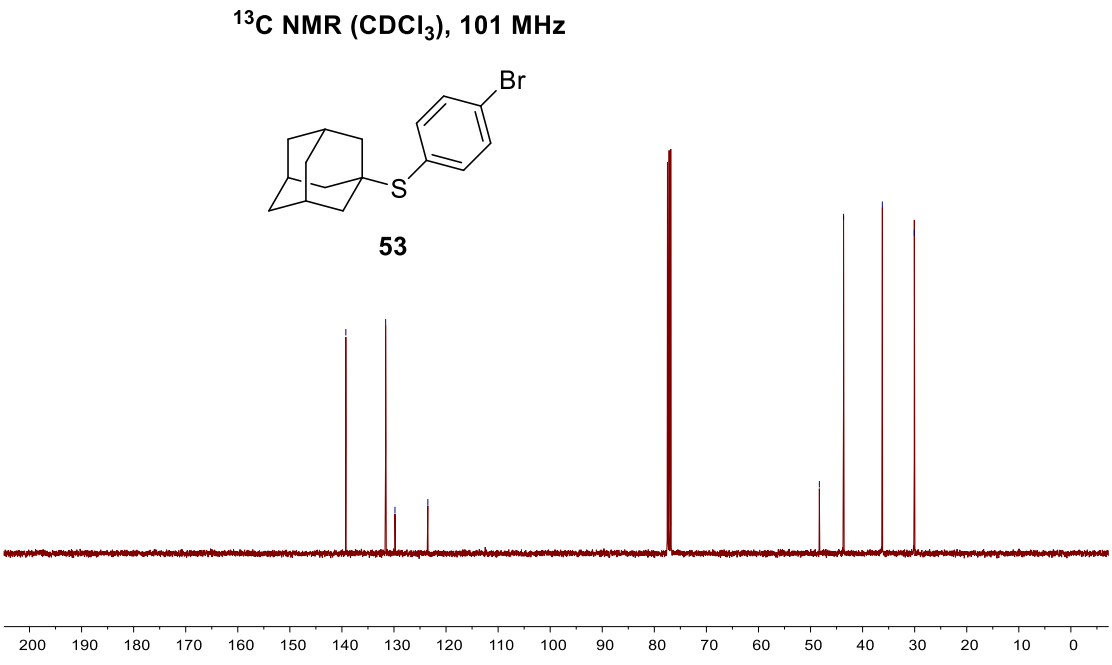

-113.0203
-113.0260
-113.0386
-113.0512
-113.0575
^{19}F NMR ($CDCl_3$), 471 MHz
F
S
51
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200


7.4270
7.4059
7.2948
7.2736
2.0084
1.7882
1.7811
1.6634
1.6325
1.6006
1.5690
^{1}H NMR ($CDCl_3$), 400 MHz
Cl
S
52
2.00
2.09
2.09
3.00
6.09
6.13
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
138.9399
135.1655
129.1852
128.6194
48.2654
43.6340
36.2058
30.0597
^{13}C NMR ($CDCl_3$), 101 MHz
Cl
S
52
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



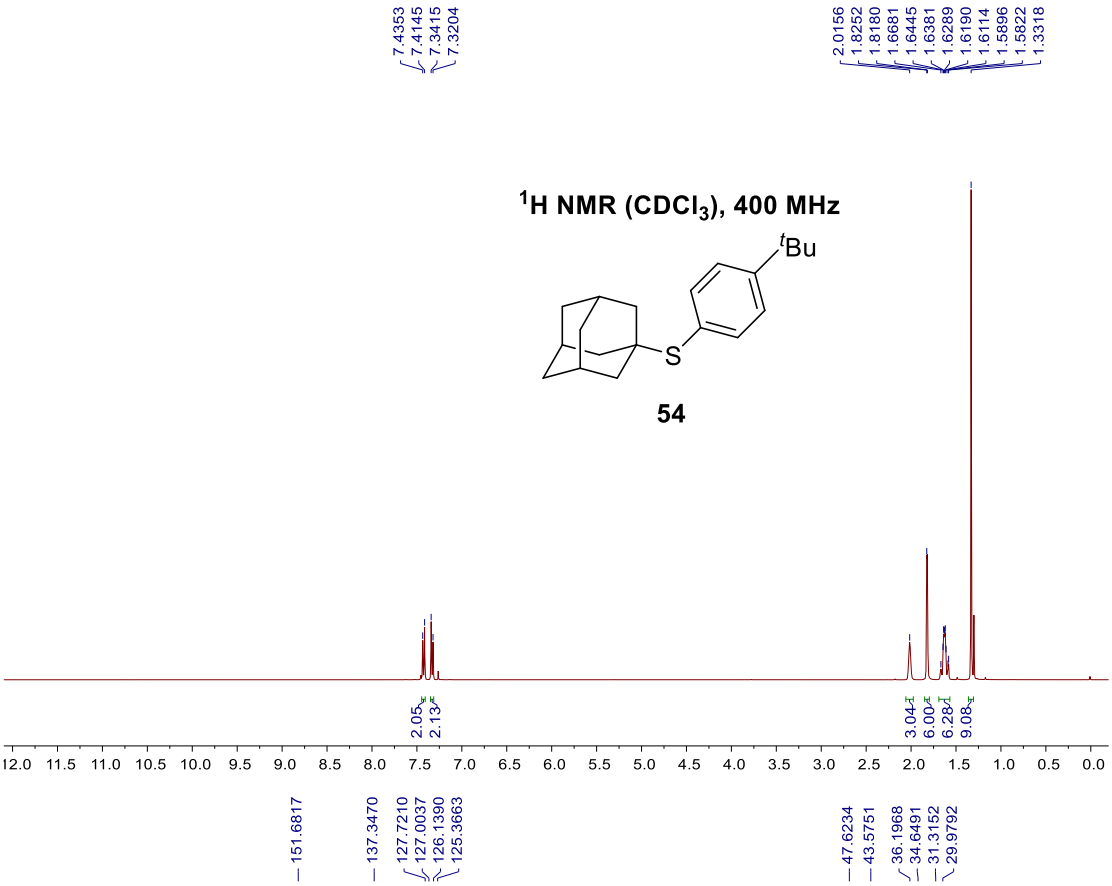
^{1}H NMR ($CDCl_3$), 400 MHz

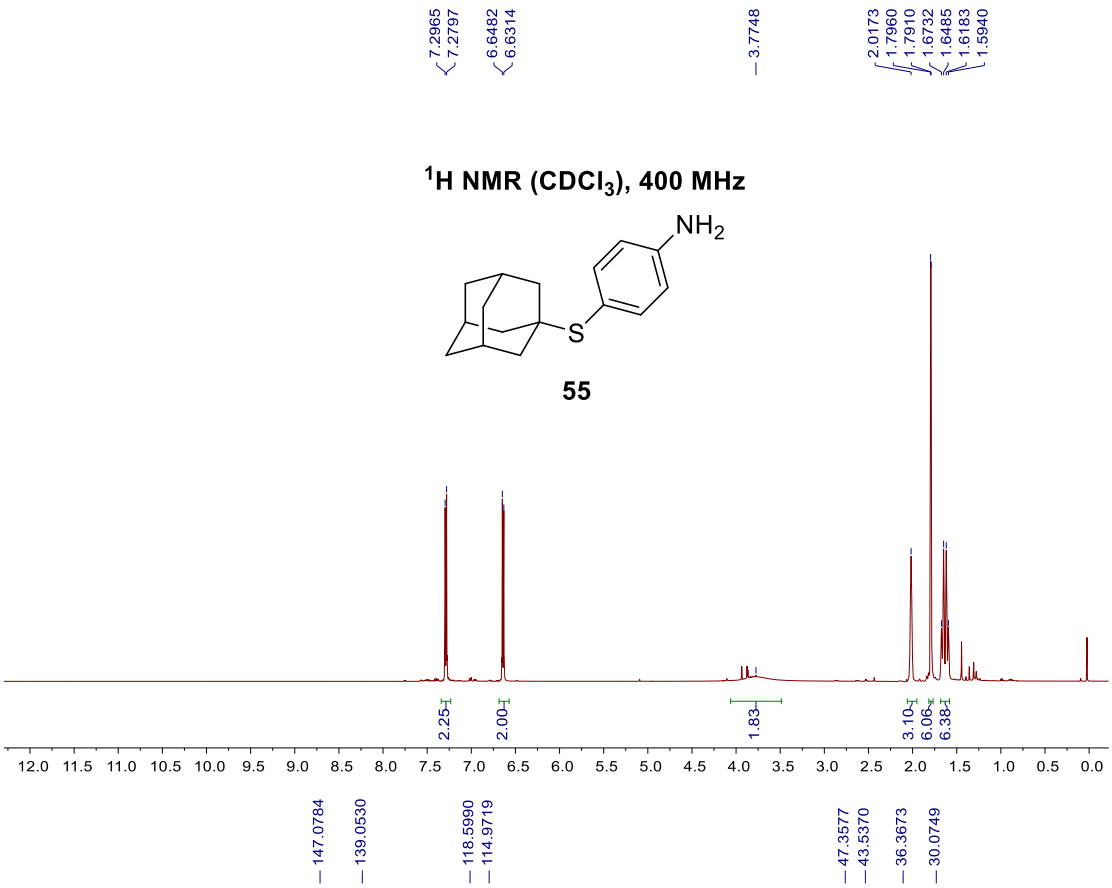
53



^{13}C NMR ($CDCl_3$), 101 MHz

53


7.4353
7.4145
7.3415
7.3204
2.0156
1.8252
1.8180
1.6681
1.6445
1.6381
1.6289
1.6190
1.6114
1.5896
1.5822
1.3318
^{1}H NMR ($CDCl_3$), 400 MHz
^{t}Bu
S
54
2.05
2.13
3.04
6.00
6.28
9.08
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
151.6817
137.3470
127.7210
127.0037
126.1390
125.3663
47.6234
43.5751
36.1968
34.6491
31.3152
29.9792
^{13}C NMR ($CDCl_3$), 101 MHz
^{t}Bu
S
54
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

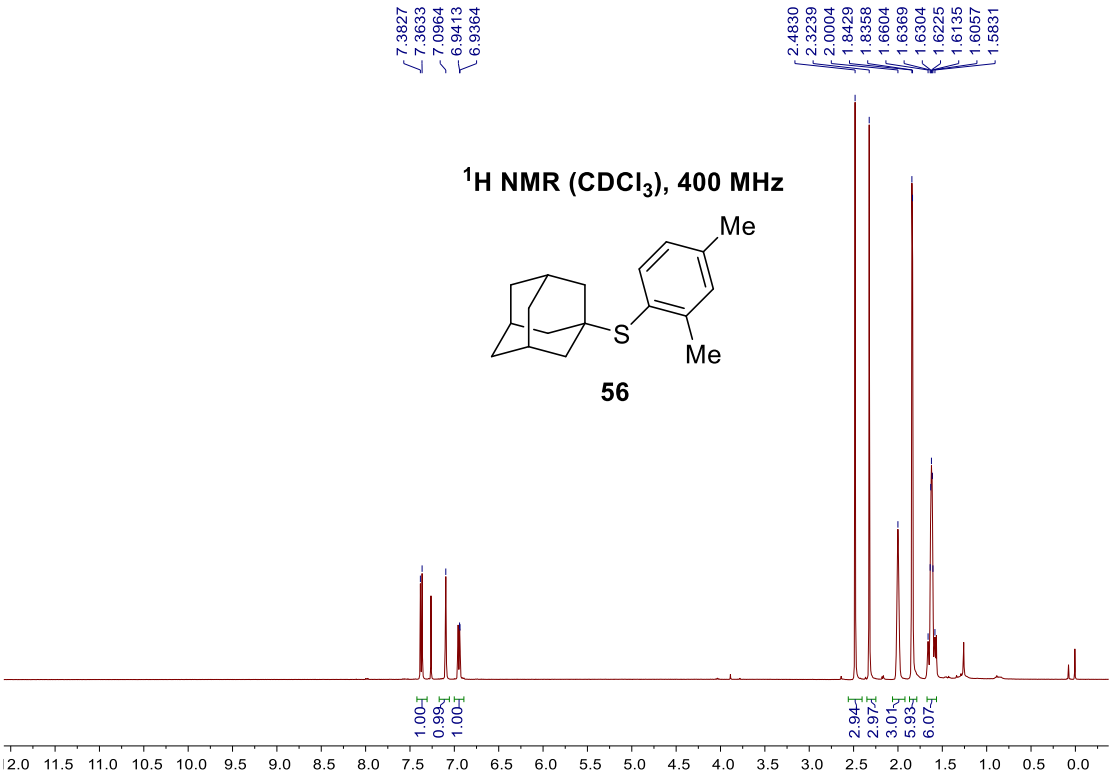


^{1}H NMR ($CDCl_3$), 400 MHz

55

^{13}C NMR ($CDCl_3$), 101 MHz

55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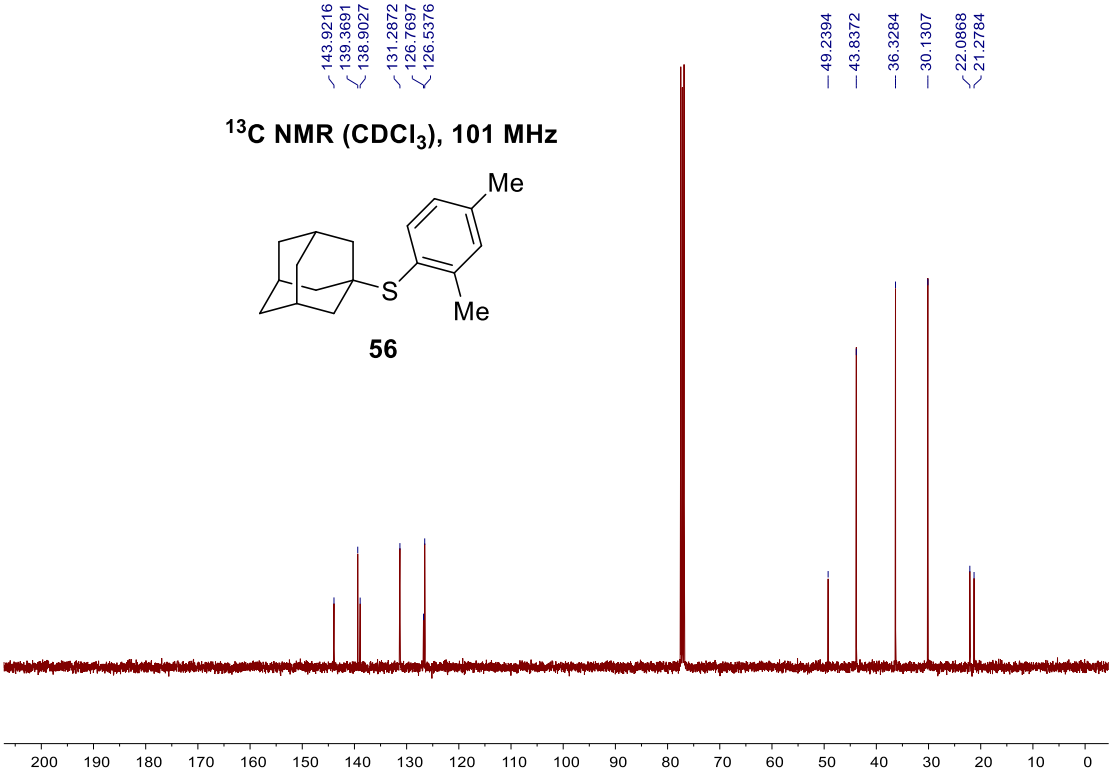
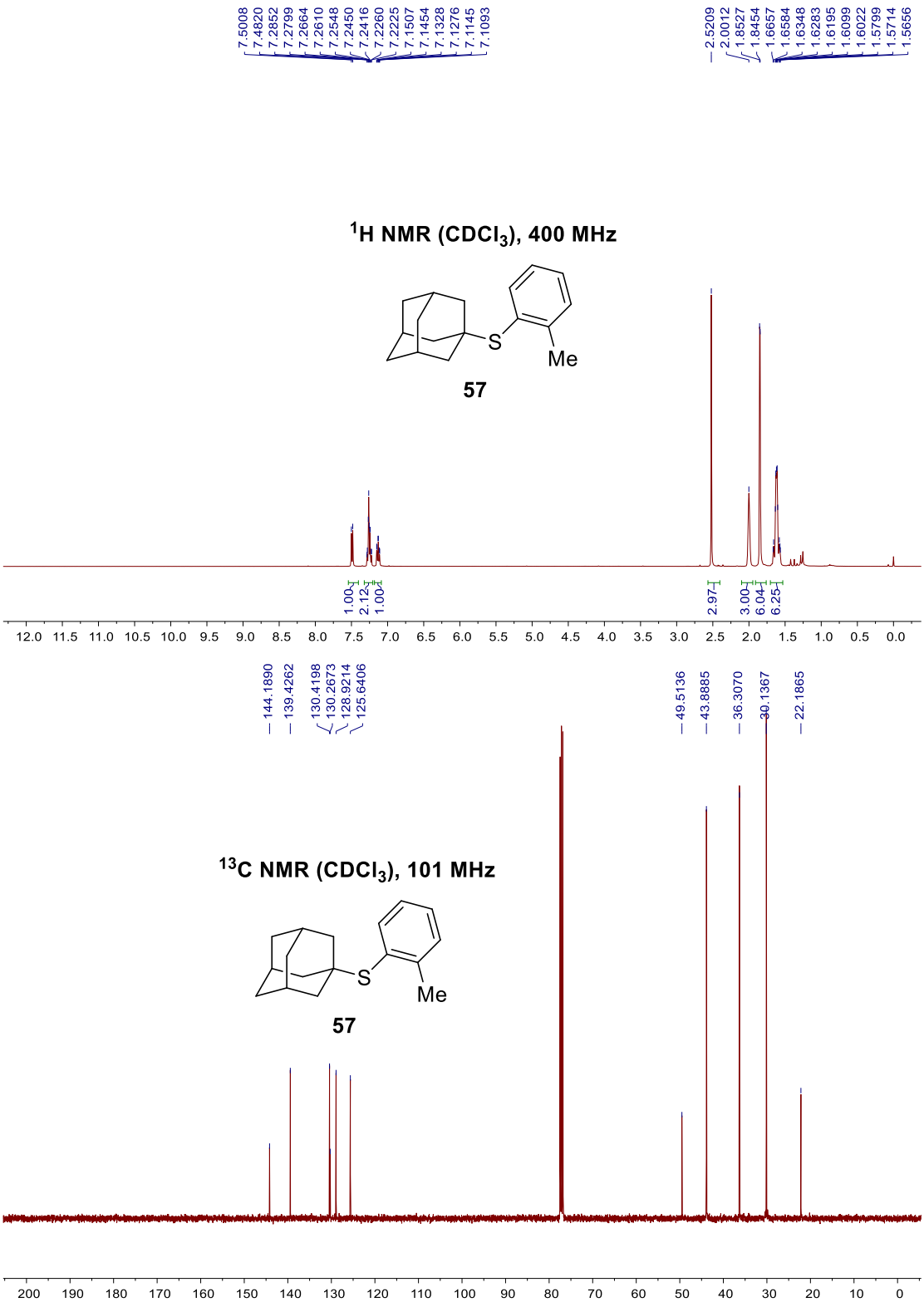
7.3633
7.0964
6.9413
6.9364
2.4830
2.3239
2.0004
1.8429
1.8358
1.6604
1.6369
1.6304
1.6225
1.6135
1.6057
1.5831
1H NMR (CDCl3), 400 MHz
Me
S
Me
56
1.00
0.99
1.00
2.94
2.97
3.01
5.93
6.07
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


143.9216
139.3691
138.9027
131.2872
126.7697
126.5376
49.2394
43.8372
36.3284
30.1307
22.0868
21.2784
13C NMR (CDCl3), 101 MHz
Me
S
Me
56
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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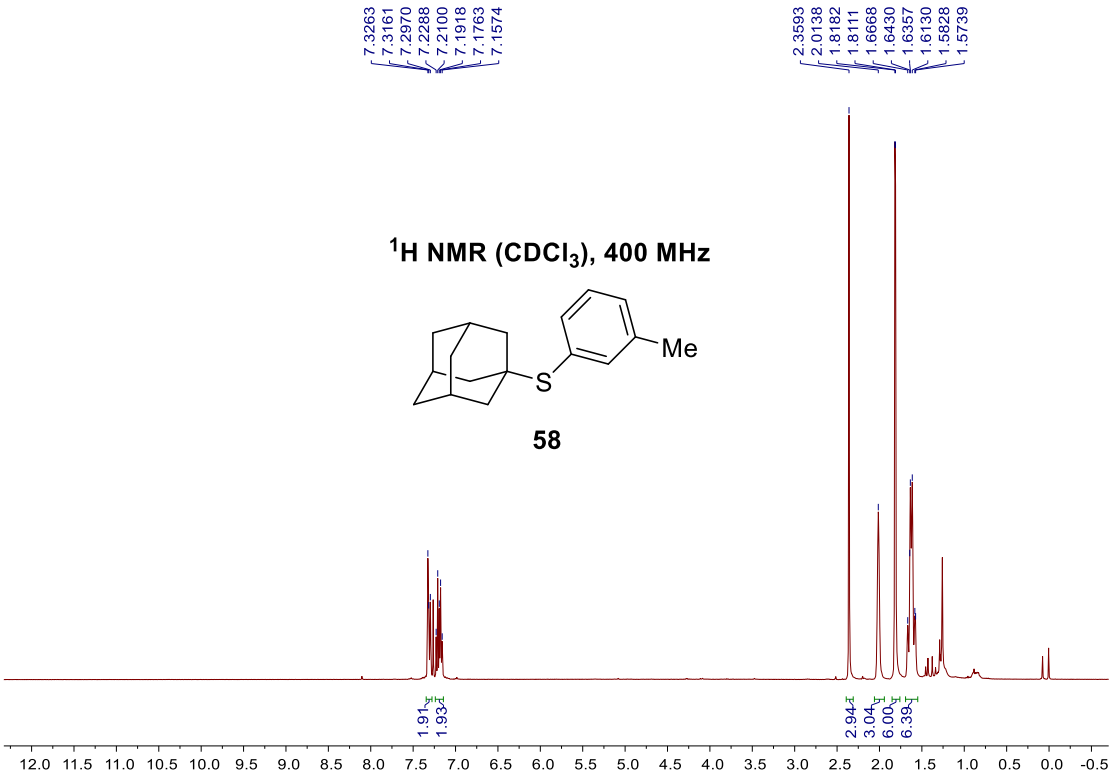
7.4820
7.2852
7.2799
7.2664
7.2610
7.2548
7.2450
7.2416
7.2260
7.2225
7.1507
7.1454
7.1328
7.1276
7.1145
7.1093
2.5209
2.0012
1.8527
1.8454
1.6657
1.6584
1.6348
1.6283
1.6195
1.6099
1.6022
1.5799
1.5714
1.5656
1H NMR (CDCl3), 400 MHz
S
Me
57
1.00
2.12
1.00
2.97
3.00
6.04
6.25
12.0 11.5 11.0 10.5 10.0 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
144.1890
139.4262
130.4198
130.2673
128.9214
125.6406
49.5136
43.8885
36.3070
30.1367
22.1865
13C NMR (CDCl3), 101 MHz
S
Me
57
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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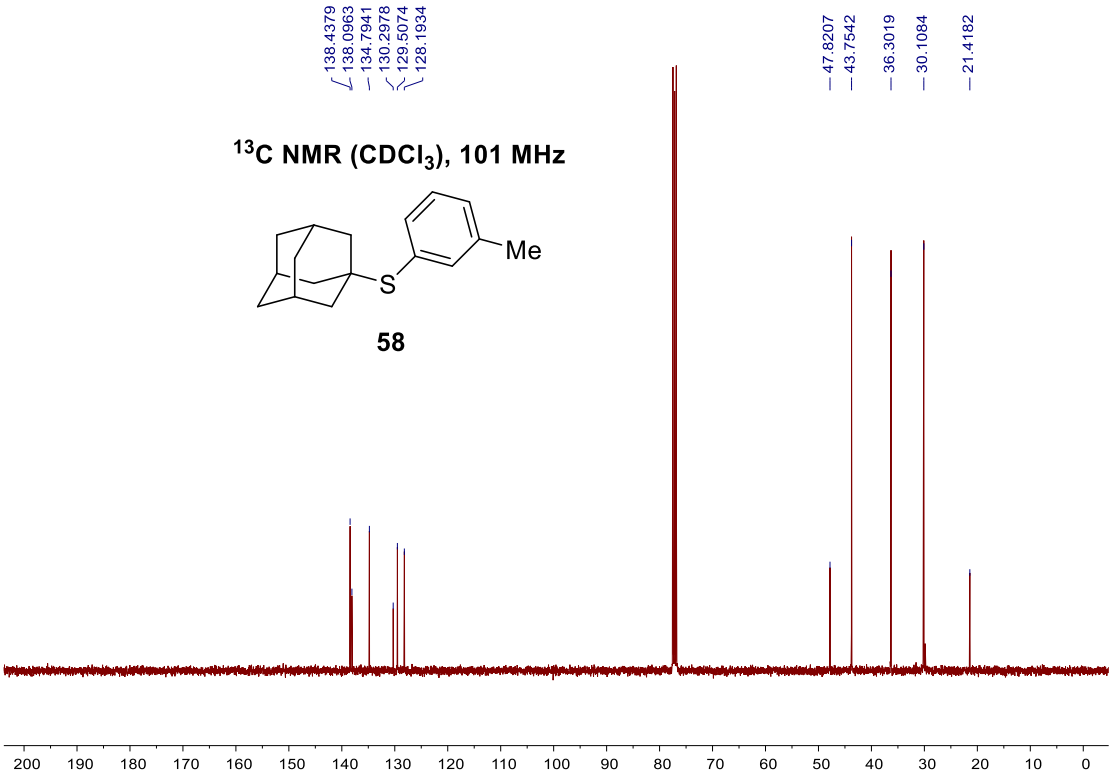
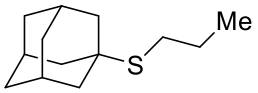
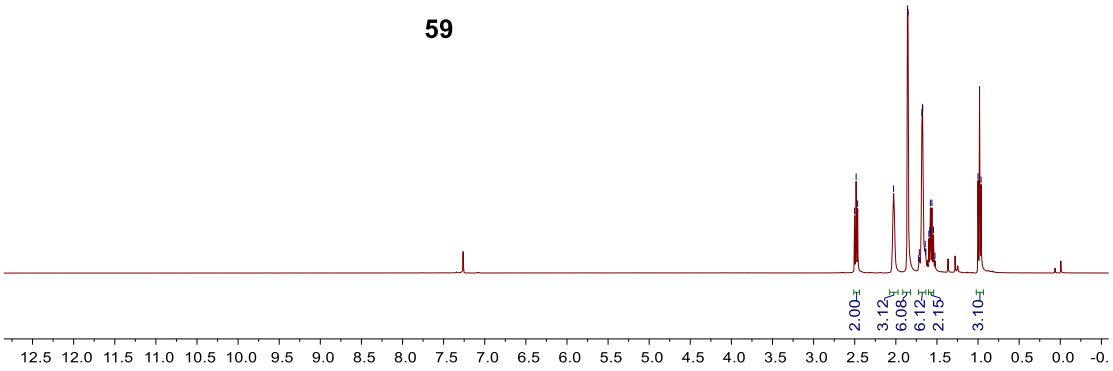
7.3161
7.2970
7.2288
7.2100
7.1918
7.1763
7.1574
2.3593
2.0138
1.8182
1.8111
1.6668
1.6430
1.6357
1.6130
1.5828
1.5739
1H NMR (CDCl3), 400 MHz
Me
S
58
1.91
1.93
2.94
3.04
6.00
6.39
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


138.4379
138.0963
134.7941
130.2978
129.5074
128.1934
47.8207
43.7542
36.3019
30.1084
21.4182
13C NMR (CDCl3), 101 MHz
Me
S
58
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

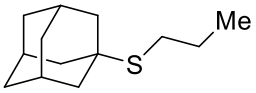
^{1}H NMR ($CDCl_3$), 400 MHz



59



^{13}C NMR ($CDCl_3$), 101 MHz



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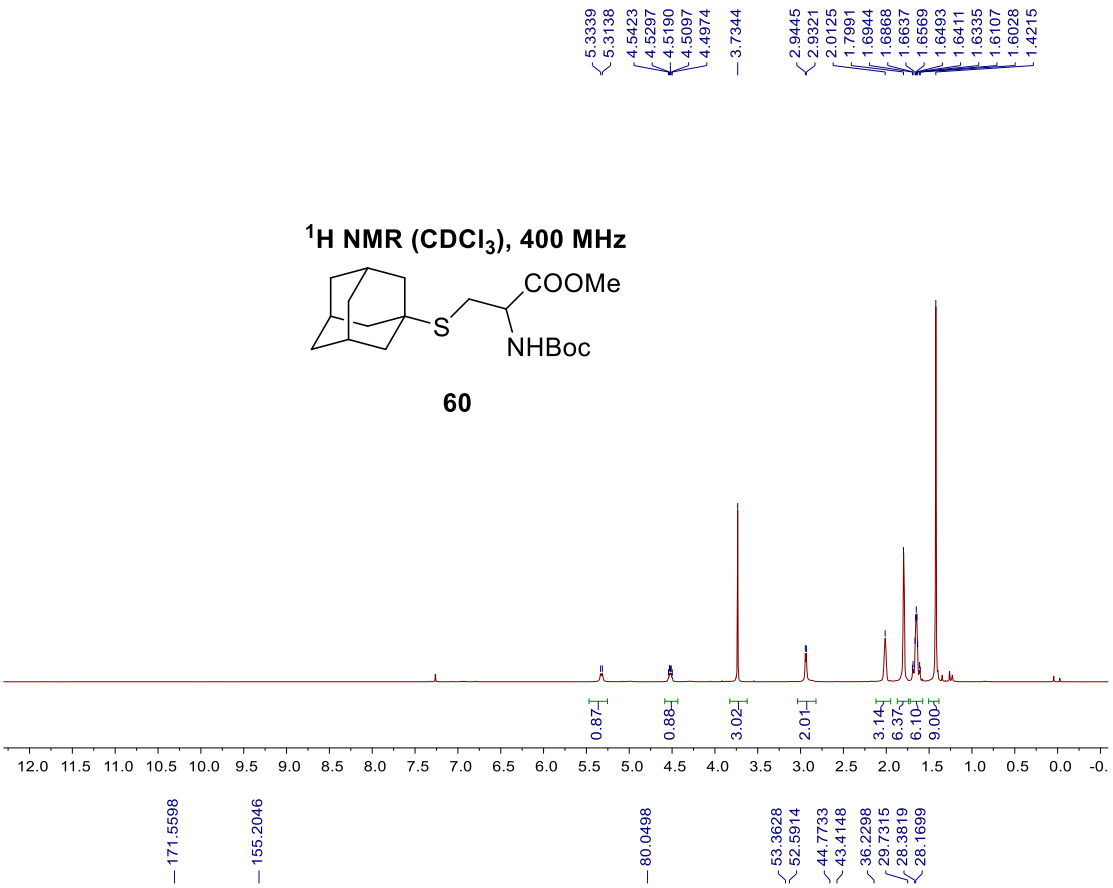
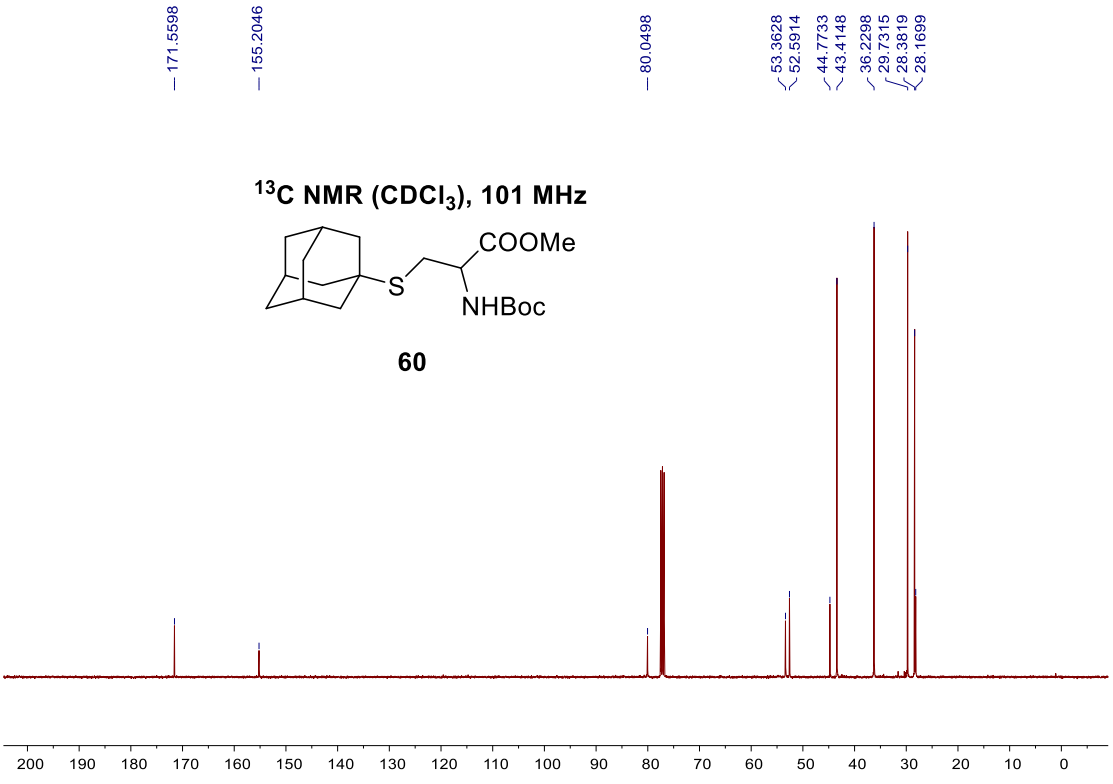


^{1}H NMR ($CDCl_3$), 400 MHz

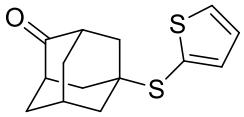
60



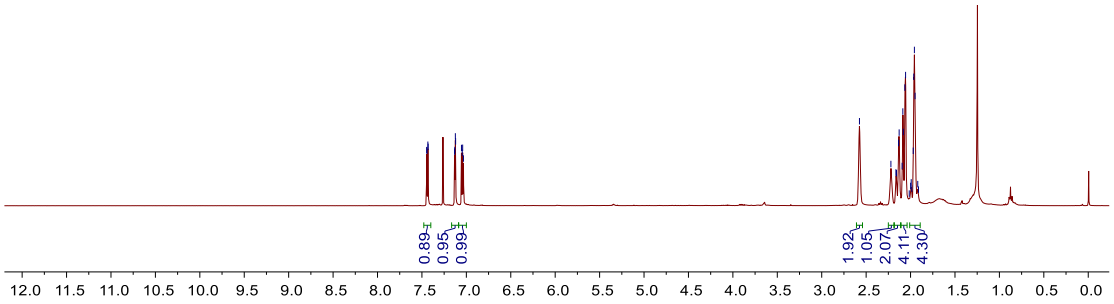
^{13}C NMR ($CDCl_3$), 101 MHz

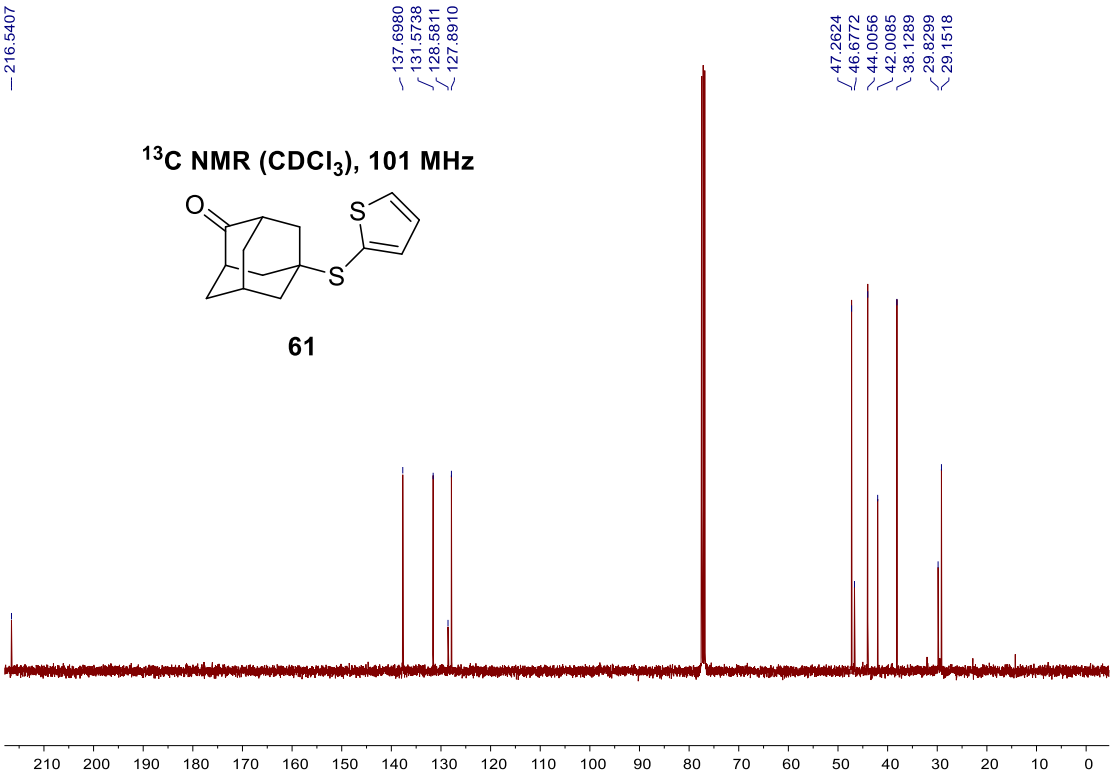
60

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



61

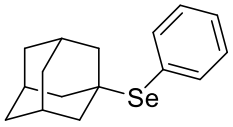




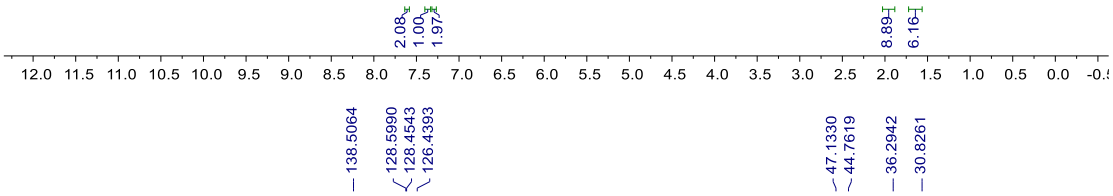
^{13}C NMR ($CDCl_3$), 101 MHz

61

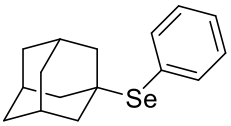
^{1}H NMR ($CDCl_3$), 400 MHz



62

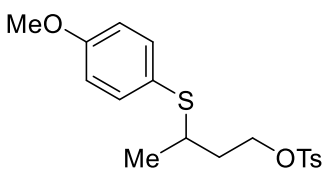


^{13}C NMR ($CDCl_3$), 101 MHz



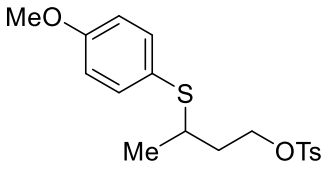
62

^{1}H NMR ($CDCl_3$), 500 MHz

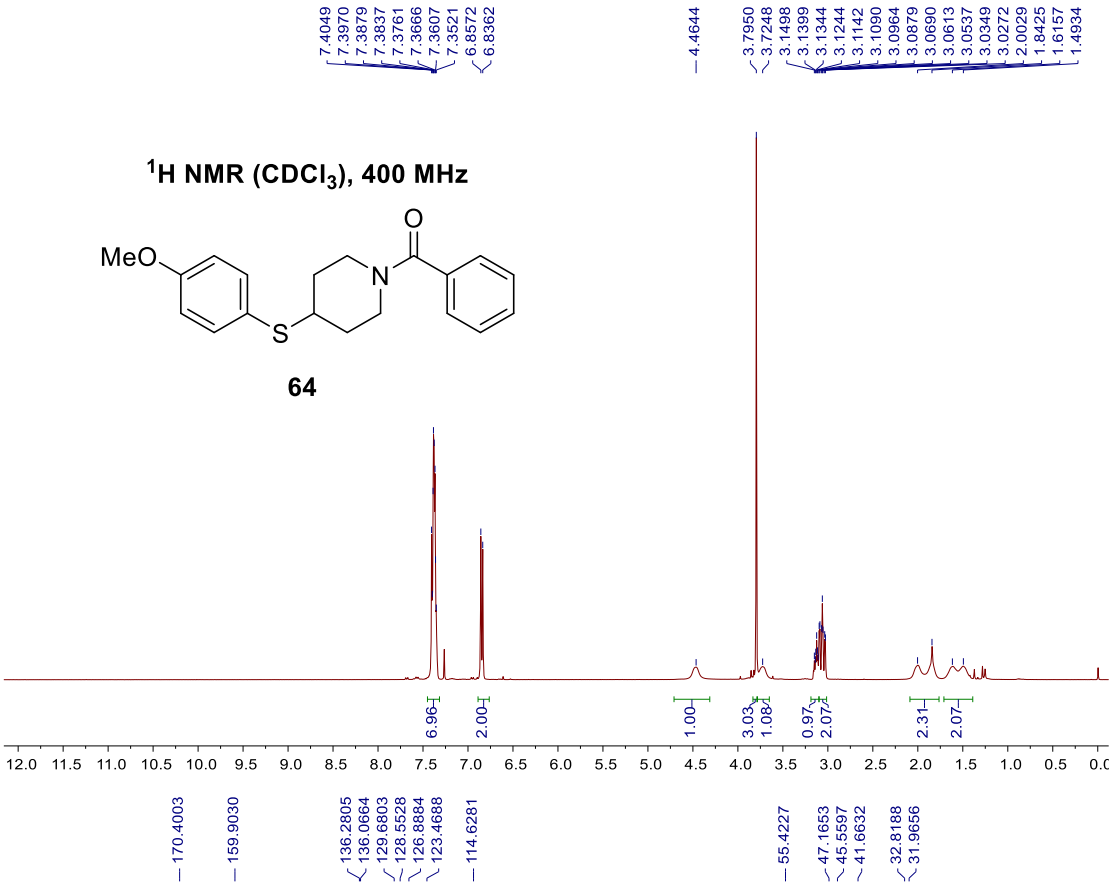


63

^{13}C NMR ($CDCl_3$), 126 MHz

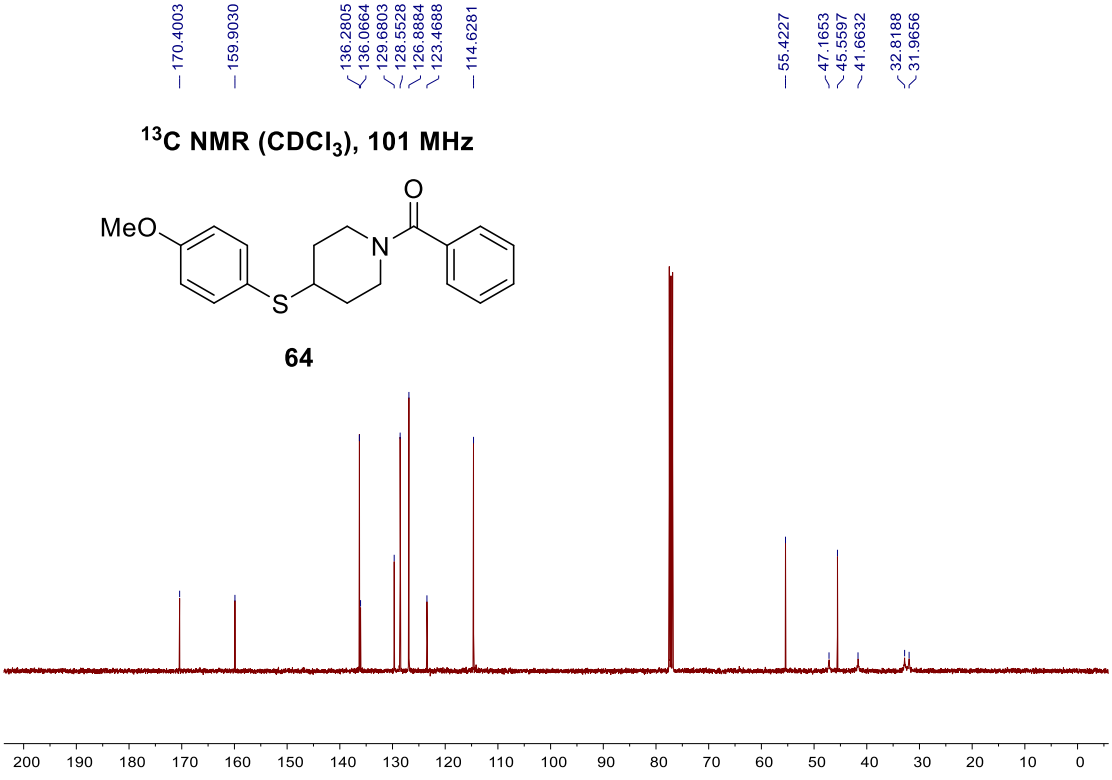


63



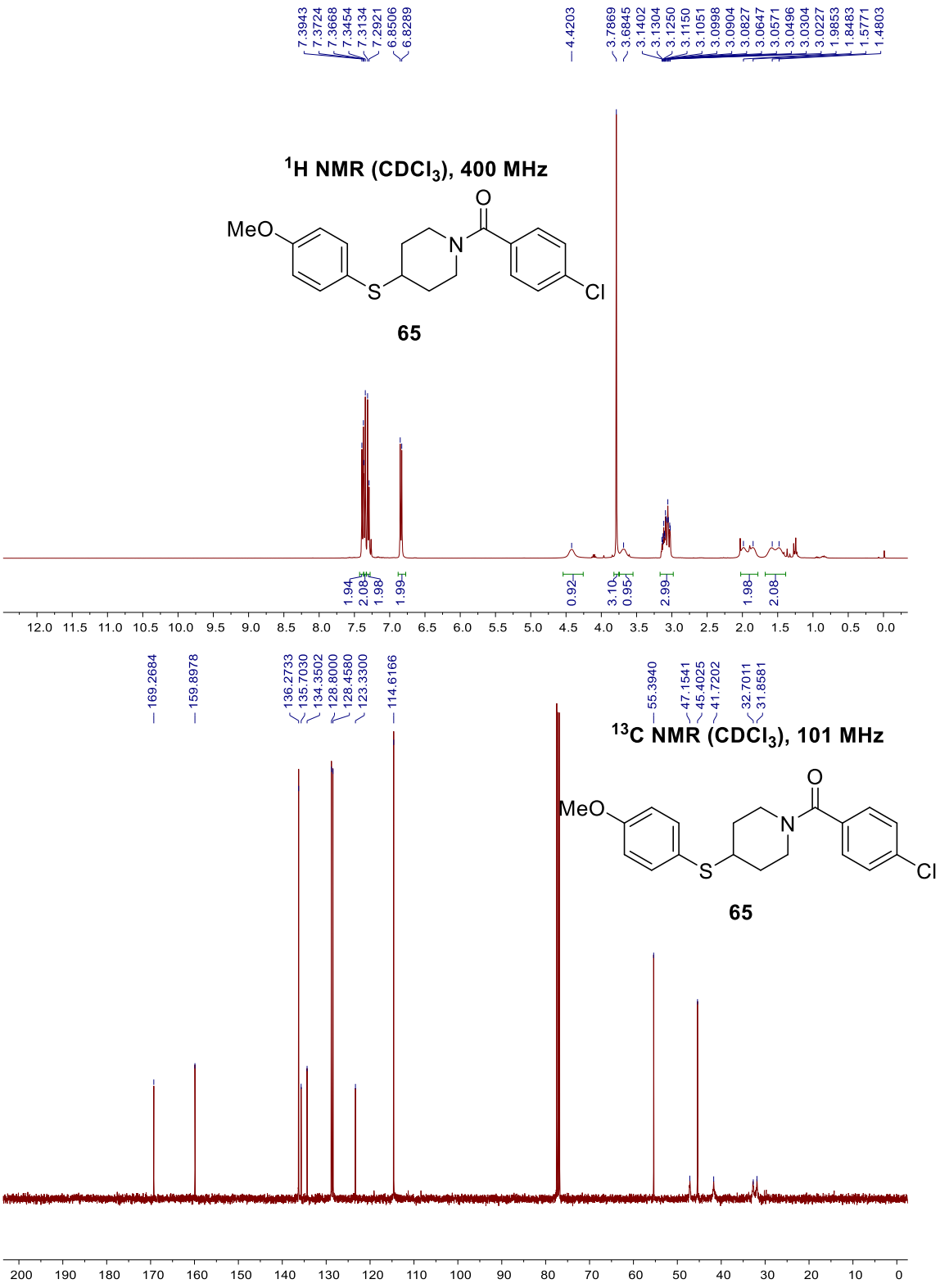
^{1}H NMR ($CDCl_3$), 400 MHz

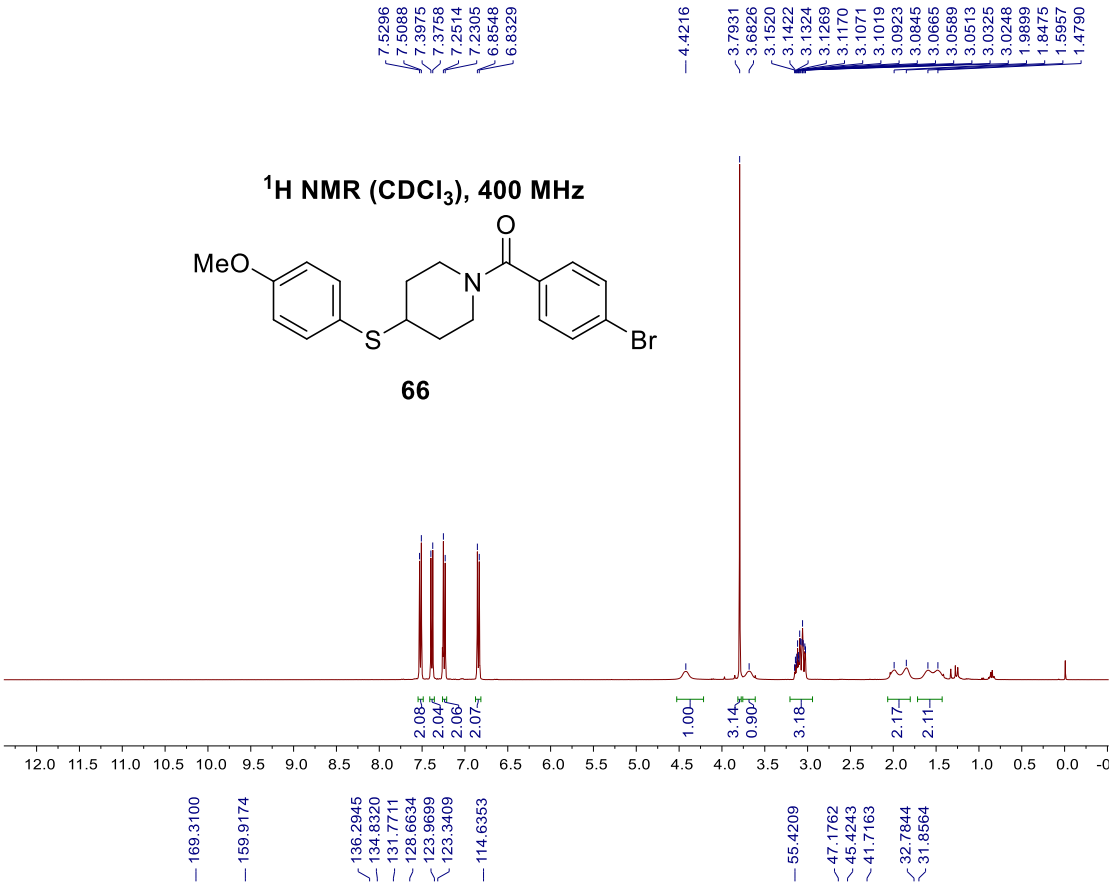
64

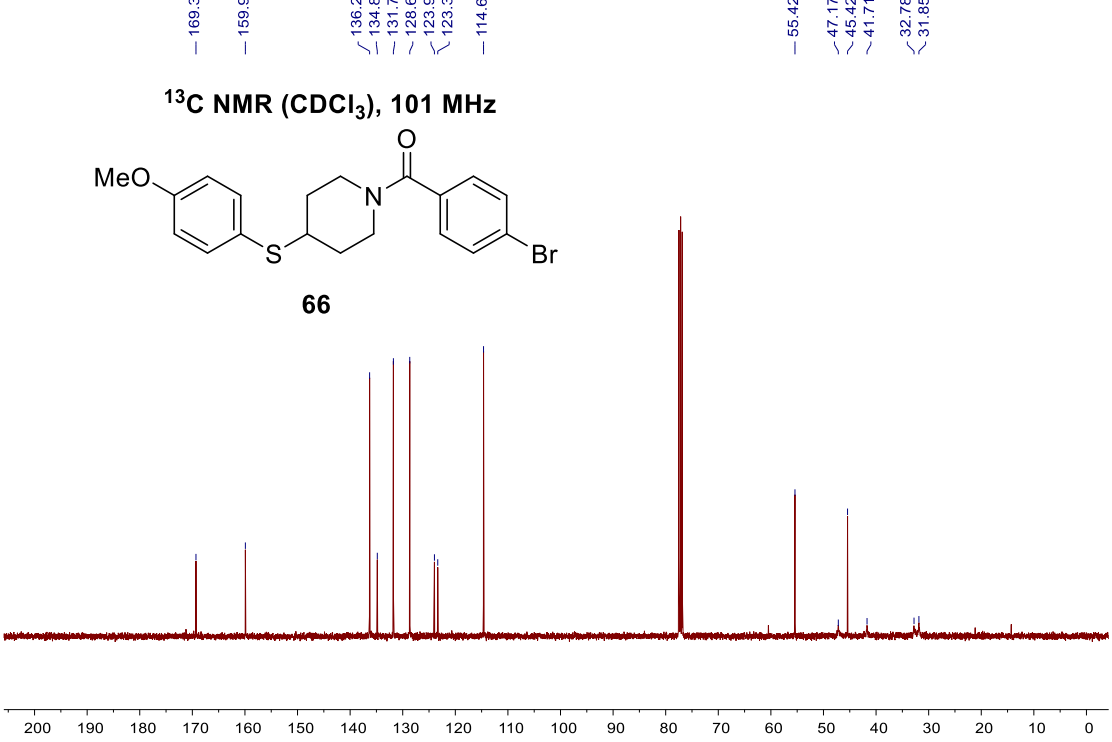


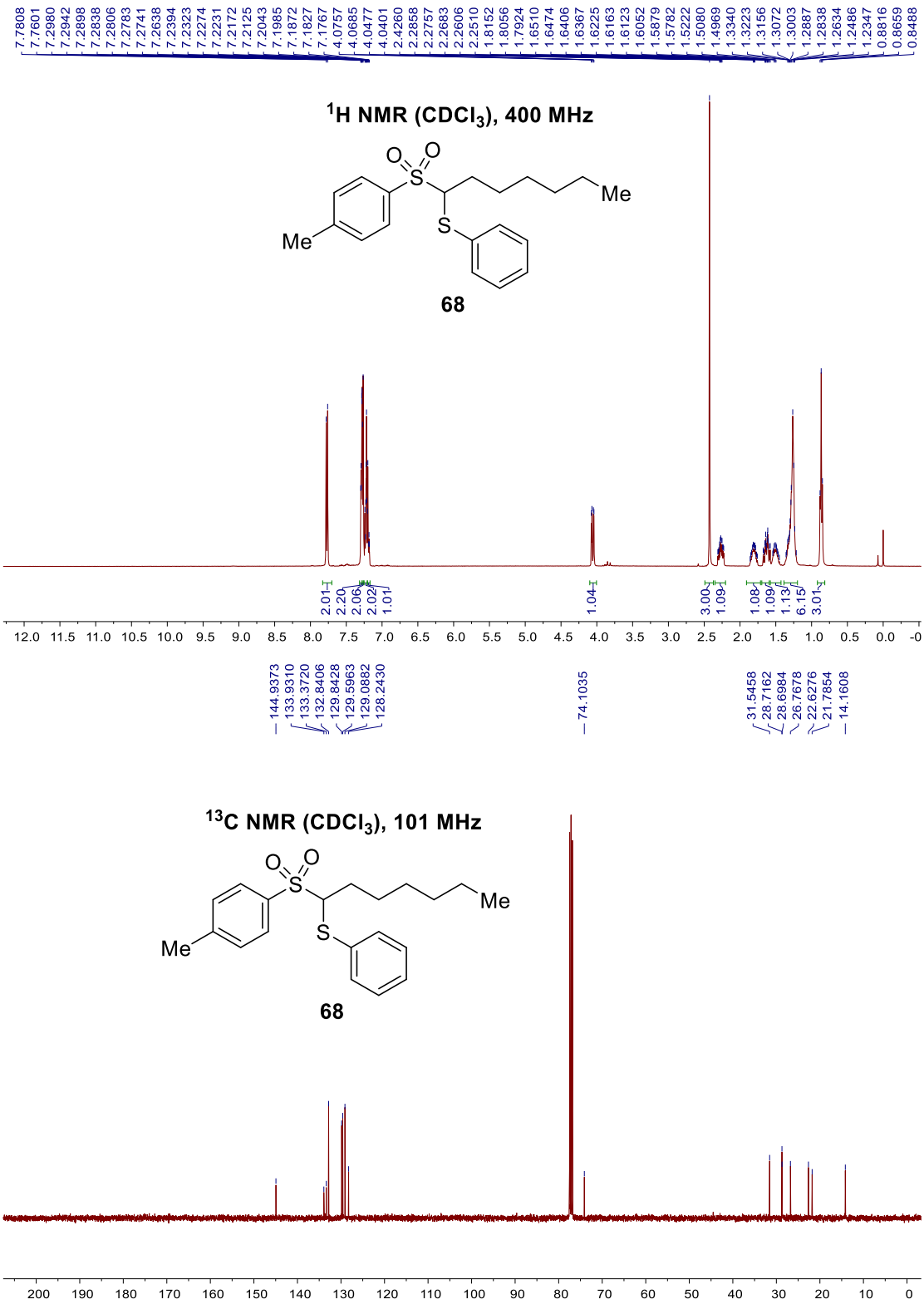
^{13}C NMR ($CDCl_3$), 101 MHz

64

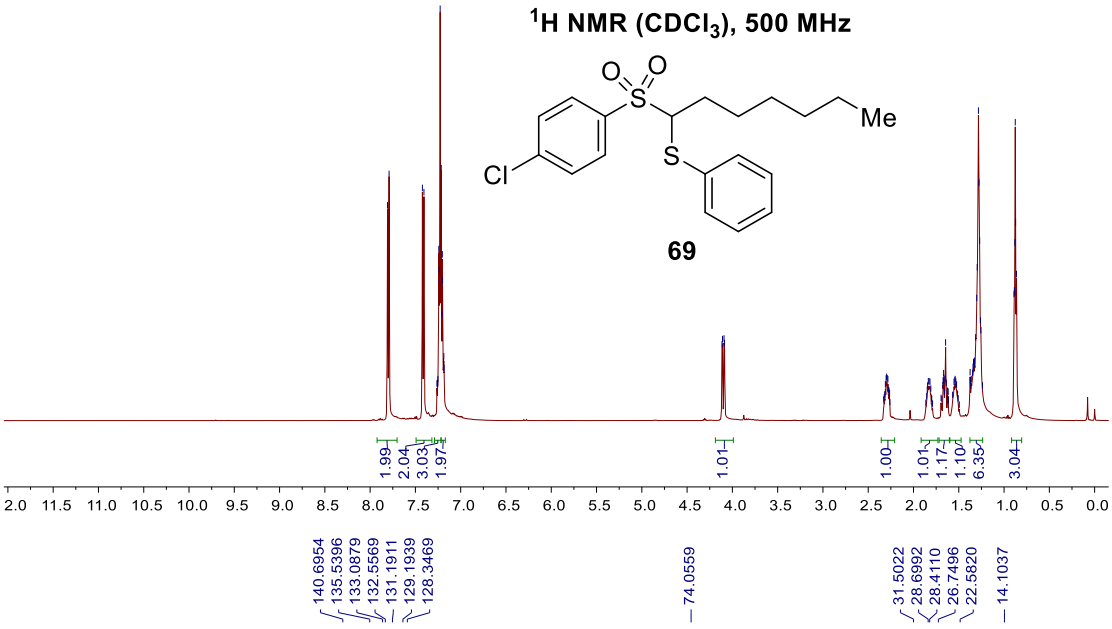

7.3943
7.3724
7.3668
7.3454
7.3134
7.2921
6.8506
6.8289
4.4203
3.7869
3.6845
3.1402
3.1304
3.1250
3.1150
3.1051
3.0998
3.0904
3.0827
3.0647
3.0571
3.0496
3.0304
3.0227
1.9853
1.8483
1.5771
1.4803
1H NMR (CDCl3), 400 MHz
MeO
O
N
S
Cl
65
1.94
2.08
1.98
1.99
0.92
3.10
0.95
2.99
1.98
2.08
12.0 11.5 11.0 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
169.2684
159.8978
136.2733
135.7030
134.3502
128.8000
128.4580
123.3300
114.6166
55.3940
47.1541
45.4025
41.7202
32.7011
31.8581
13C NMR (CDCl3), 101 MHz
MeO
O
N
S
Cl
65
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

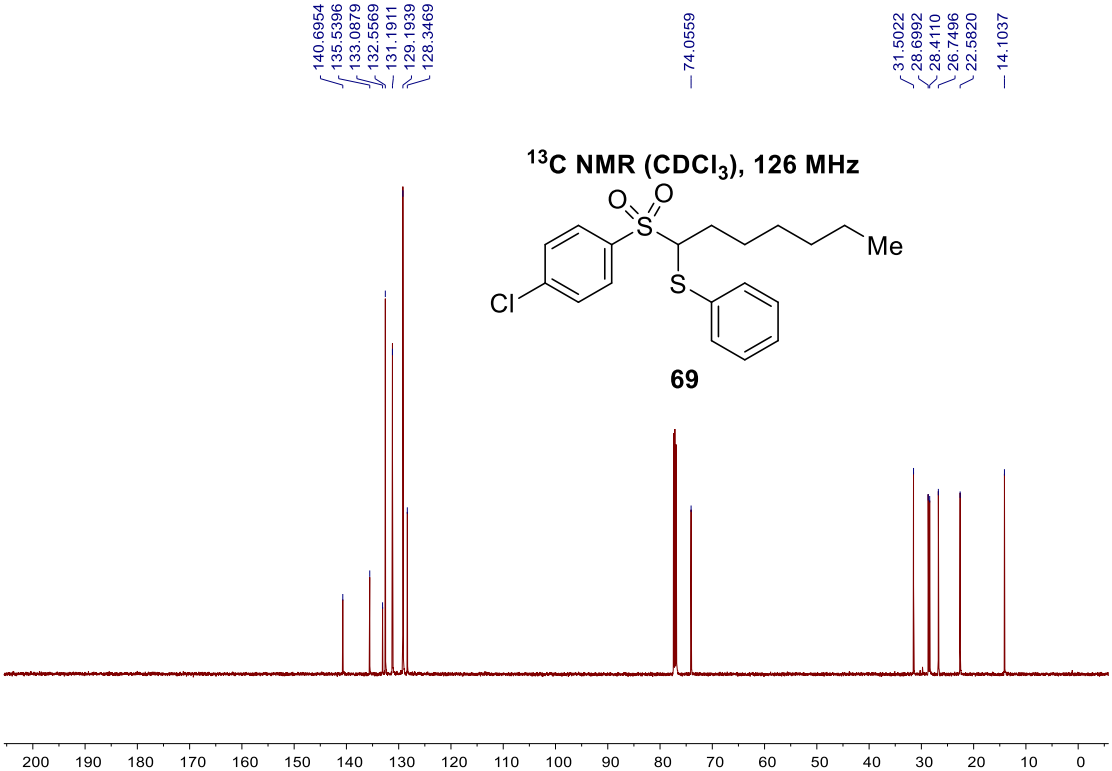

7.5296
7.5088
7.3975
7.3758
7.2514
7.2305
6.8548
6.8329
4.4216
3.7931
3.6826
3.1520
3.1422
3.1324
3.1269
3.1170
3.1071
3.1019
3.0923
3.0845
3.0665
3.0589
3.0513
3.0325
3.0248
1.9899
1.8475
1.5957
1.4790
1H NMR (CDCl3), 400 MHz
MeO
O
N
S
Br
66
2.08
2.04
2.06
2.07
1.00
3.14
0.90
3.18
2.17
2.11
12.0 11.5 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

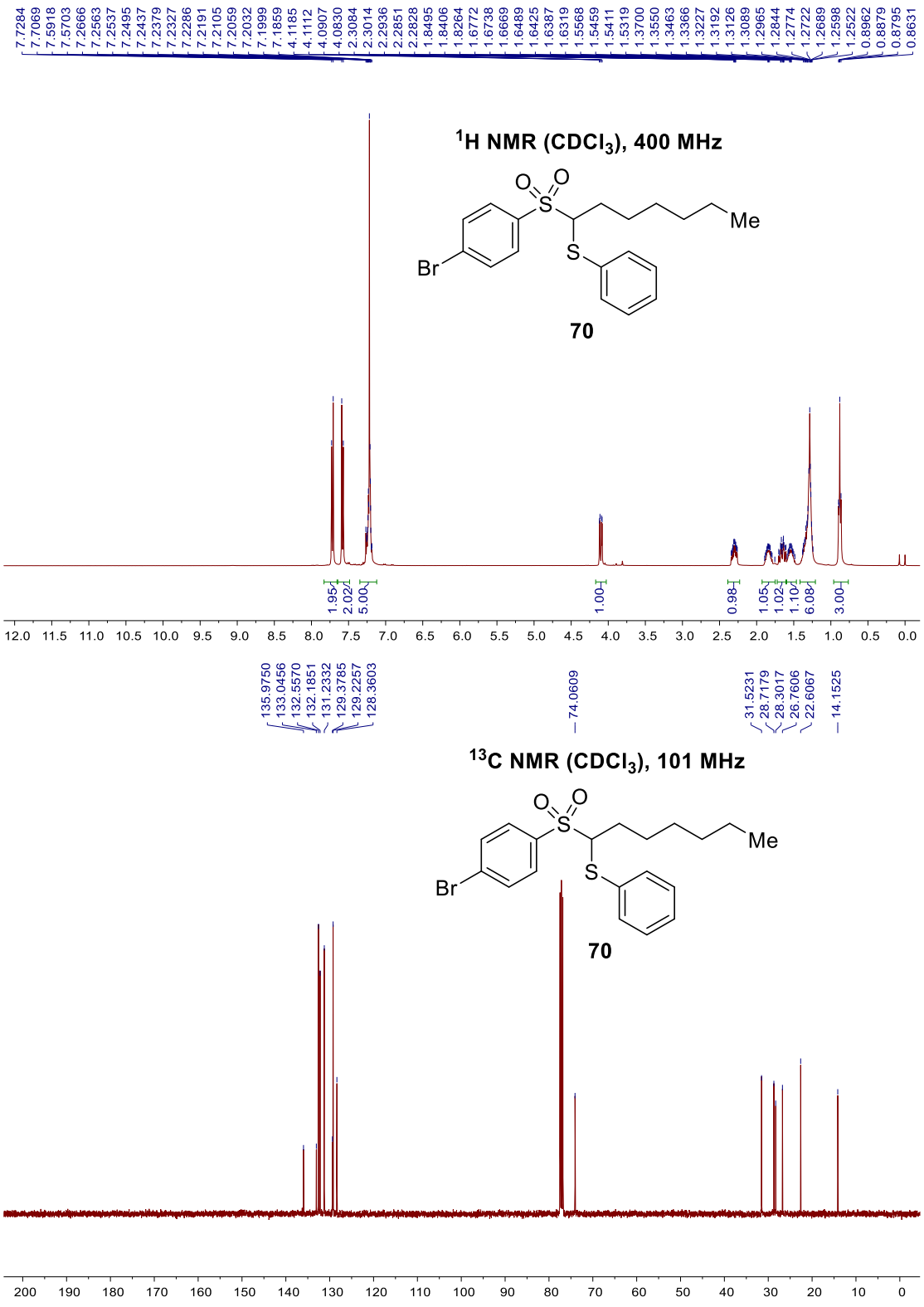

169.3100
159.9174
136.2945
134.8320
131.7711
128.6634
123.9699
123.3409
114.6353
55.4209
47.1762
45.4243
41.7163
32.7844
31.8564
13C NMR (CDCl3), 101 MHz
MeO
O
N
S
Br
66
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.7808
7.7601
7.2980
7.2942
7.2898
7.2838
7.2806
7.2783
7.2741
7.2638
7.2394
7.2323
7.2274
7.2231
7.2172
7.2125
7.2043
7.1985
7.1872
7.1827
7.1767
4.0757
4.0685
4.0477
4.0401
2.4260
2.2858
2.2757
2.2683
2.2606
2.2510
1.8152
1.8056
1.7924
1.6510
1.6474
1.6406
1.6367
1.6225
1.6163
1.6123
1.6052
1.5879
1.5782
1.5222
1.5080
1.4969
1.3340
1.3223
1.3156
1.3072
1.3003
1.2887
1.2838
1.2634
1.2486
1.2347
0.8816
0.8659
0.8488
^{1}H NMR (CDCl$_3$), 400 MHz
O
O
S
Me
Me
S
68
2.01
2.20
2.06
2.02
1.01
1.04
3.00
1.09
1.08
1.09
1.13
6.15
3.01
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
144.9373
133.9310
133.3720
132.8406
129.8428
129.5963
129.0882
128.2430
74.1035
31.5458
28.7162
28.6984
26.7678
22.6276
21.7854
14.1608
^{13}C NMR (CDCl$_3$), 101 MHz
O
O
S
Me
Me
S
68
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

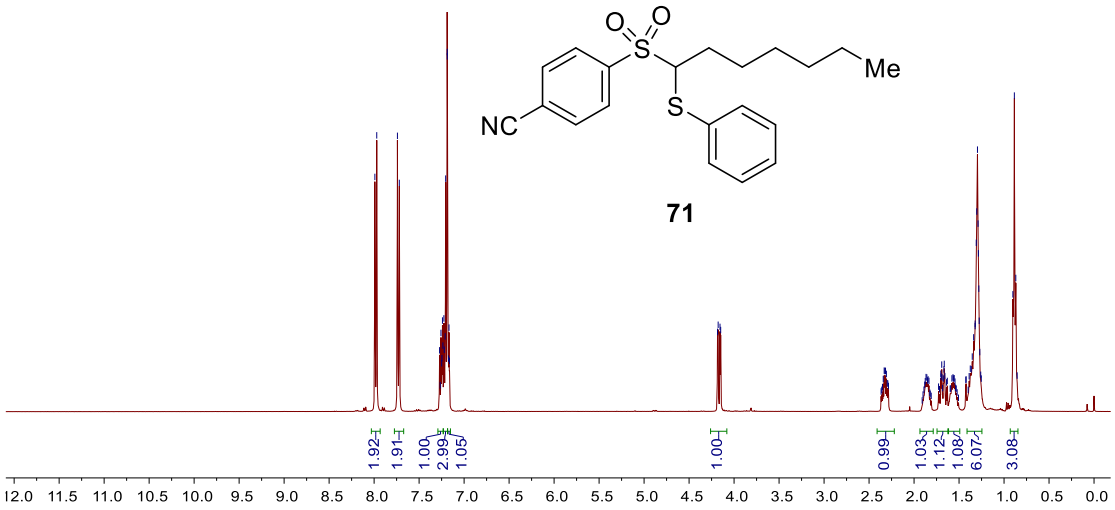

7.8082
7.7907
7.4231
7.4059
7.2549
7.2512
7.2417
7.2380
7.2268
7.2147
7.2062
7.2028
7.1996
7.1904
7.1863
7.1830
4.1146
4.1089
4.0922
4.0863
2.3026
2.2967
2.2902
2.2826
1.8367
1.8279
1.8182
1.6730
1.6676
1.6646
1.6530
1.6456
1.6376
1.5526
1.5437
1.5402
1.5328
1.3750
1.3717
1.3618
1.3480
1.3426
1.3371
1.3338
1.3286
1.3253
1.3138
1.3018
1.2963
1.2831
1.2766
1.2696
1.2597
1.2553
0.8898
0.8864
0.8806
0.8762
0.8729
0.8628


^{1}H NMR ($CDCl_3$), 500 MHz
O
O
S
Me
Cl
S
69
1.99
2.04
3.03
1.97
1.01
1.00
1.01
1.17
1.10
6.35
3.04
2.0 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

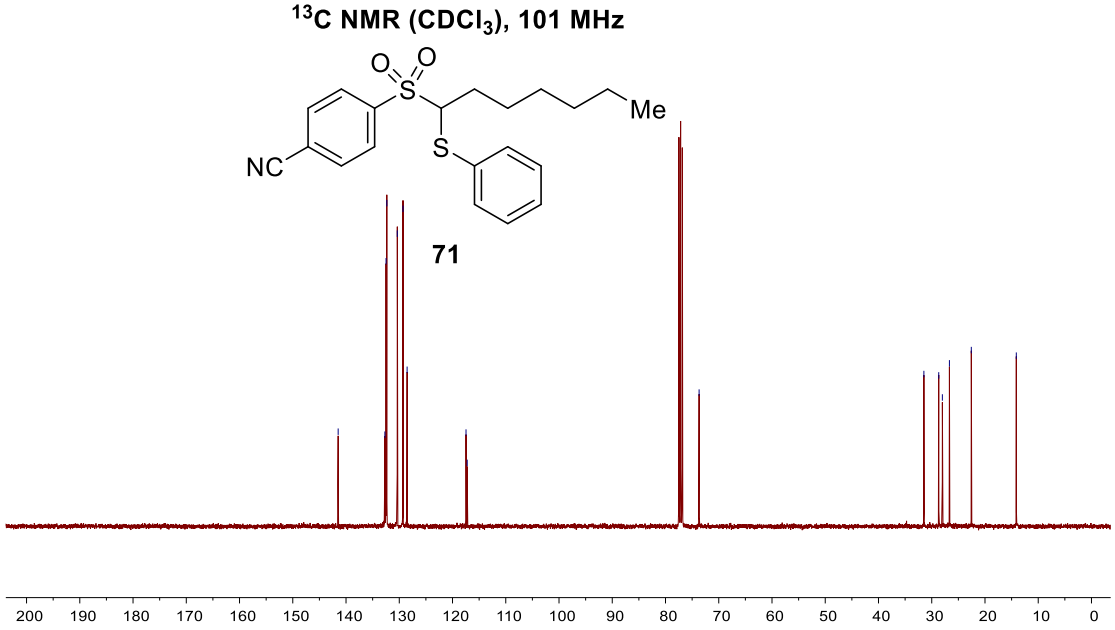

140.6954
135.5396
133.0879
132.5569
131.1911
129.1939
128.3469
74.0559
31.5022
28.6992
28.4110
26.7496
22.5820
14.1037
^{13}C NMR ($CDCl_3$), 126 MHz
O
O
S
Me
Cl
S
69
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.7284
7.7069
7.5918
7.5703
7.2666
7.2563
7.2537
7.2495
7.2437
7.2379
7.2327
7.2286
7.2191
7.2105
7.2059
7.2032
7.1999
7.1859
4.1185
4.1112
4.0907
4.0830
2.3084
2.3014
2.2936
2.2851
2.2828
1.8495
1.8406
1.8264
1.6772
1.6738
1.6669
1.6489
1.6425
1.6387
1.6319
1.5568
1.5459
1.5411
1.5319
1.3700
1.3550
1.3463
1.3366
1.3227
1.3192
1.3126
1.3089
1.2965
1.2844
1.2774
1.2722
1.2689
1.2598
1.2522
0.8962
0.8879
0.8795
0.8631
1H NMR (CDCl3), 400 MHz
O
O
S
Me
Br
S
70
1.95
2.02
5.00
1.00
0.98
1.05
1.02
1.10
6.08
3.00
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
135.9750
133.0456
132.5570
132.1851
131.2332
129.3785
129.2257
128.3603
74.0609
31.5231
28.7179
28.3017
26.7606
22.6067
14.1525
13C NMR (CDCl3), 101 MHz
O
O
S
Me
Br
S
70
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

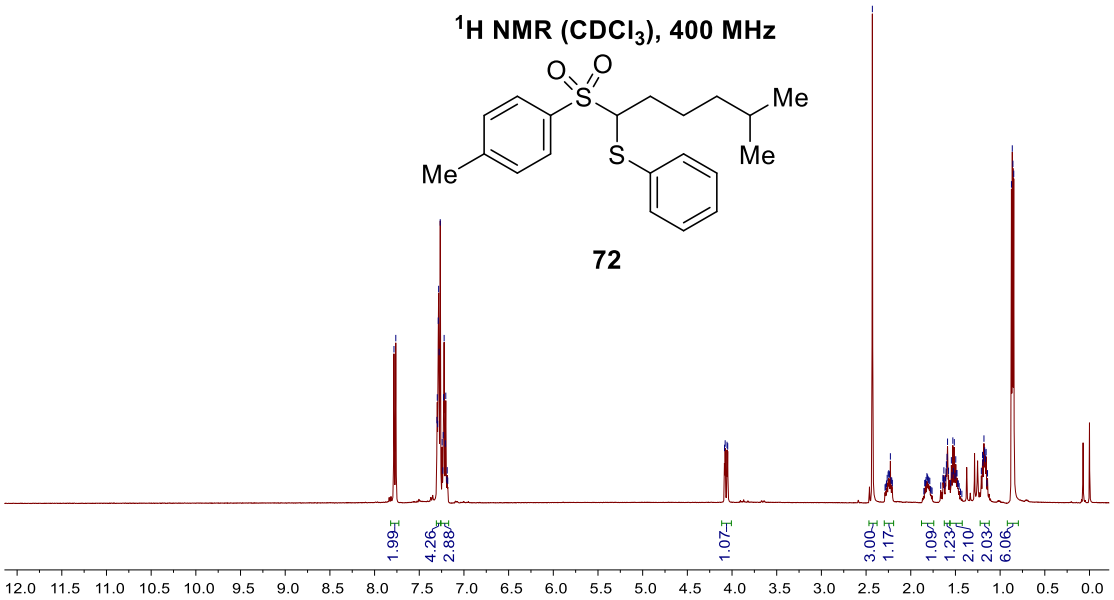
^{1}H NMR ($CDCl_3$), 400 MHz

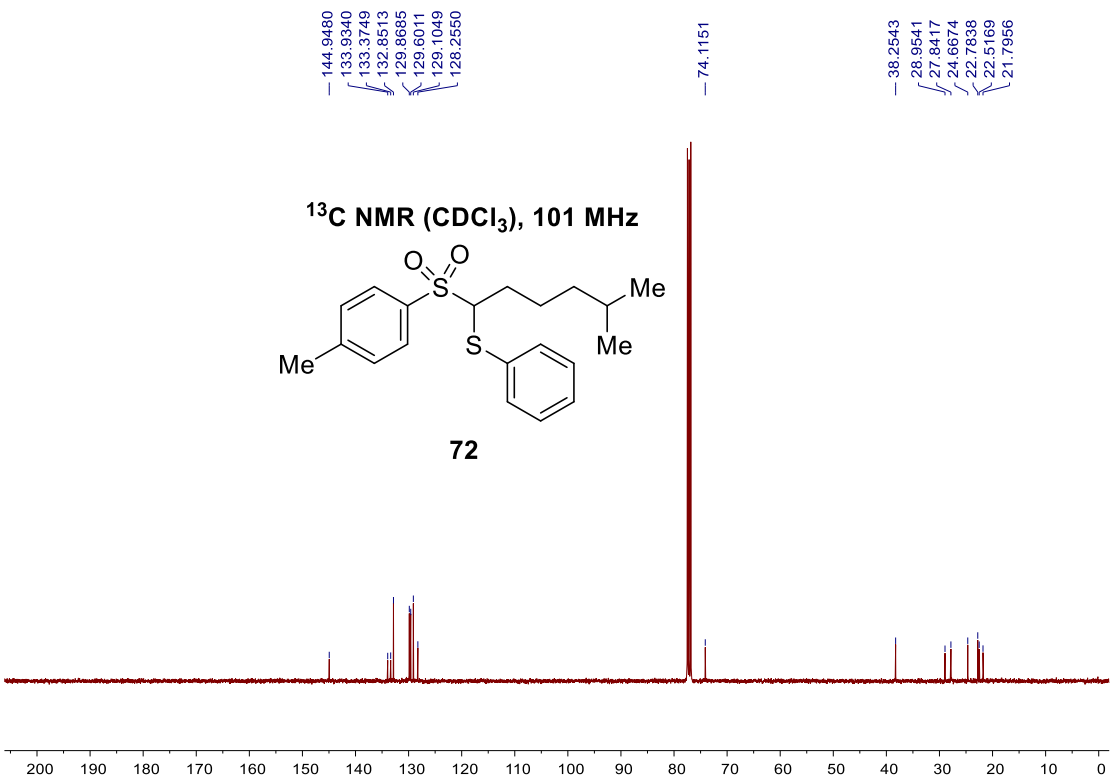


^{13}C NMR ($CDCl_3$), 101 MHz

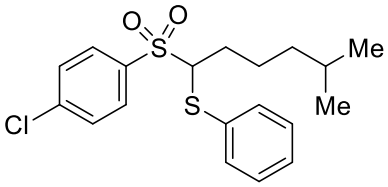



7.7830
7.7626
7.3021
7.2983
7.2939
7.2874
7.2832
7.2780
7.2653
7.2437
7.2364
7.2317
7.2275
7.2216
7.2090
7.2032
7.1871
4.0839
4.0768
4.0560
4.0484
2.4295
2.2639
2.2534
2.2465
2.2385
2.2280
1.8194
1.8116
1.6397
1.6293
1.6112
1.6049
1.6012
1.5939
1.5883
1.5769
1.5456
1.5390
1.5291
1.5235
1.5129
1.5050
1.4964
1.4911
1.4825
1.2101
1.1968
1.1927
1.1861
1.1809
1.1727
1.1693
1.1643
1.1566
1.1410
0.8733
0.8639
0.8567
0.8474

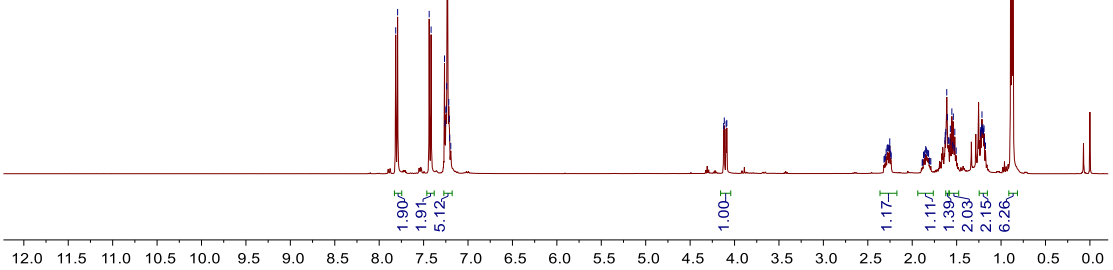

1H NMR (CDCl3), 400 MHz
O
O
S
Me
Me
S
Me
72
1.99
4.26
2.88
1.07
3.00
1.17
1.09
1.23
2.10
2.03
6.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


144.9480
133.9340
133.3749
132.8513
129.8685
129.6011
129.1049
128.2550
74.1151
38.2543
28.9541
27.8417
24.6674
22.7838
22.5169
21.7956
13C NMR (CDCl3), 101 MHz
O
O
S
Me
Me
S
Me
72
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

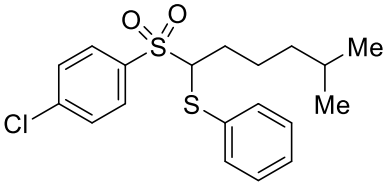
^{1}H NMR ($CDCl_3$), 400 MHz



73

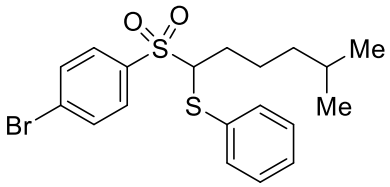


^{13}C NMR ($CDCl_3$), 101 MHz

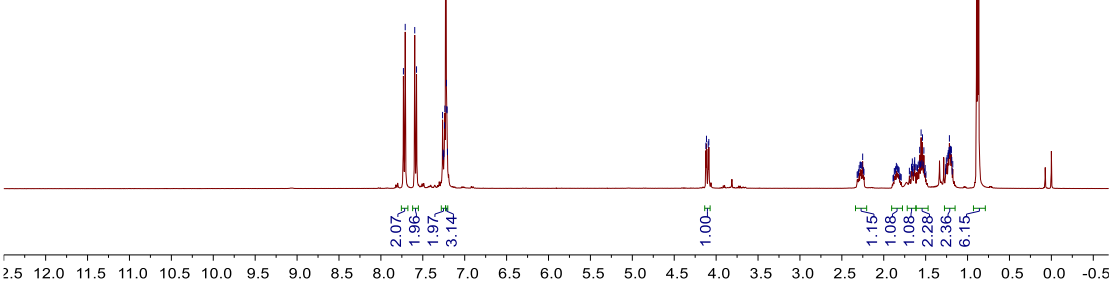


73

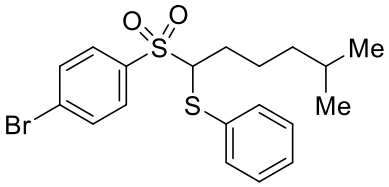
^{1}H NMR ($CDCl_3$), 400 MHz



74

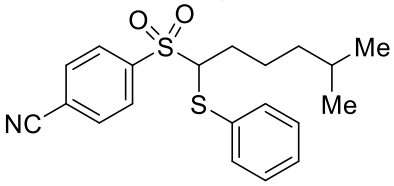


^{13}C NMR ($CDCl_3$), 101 MHz

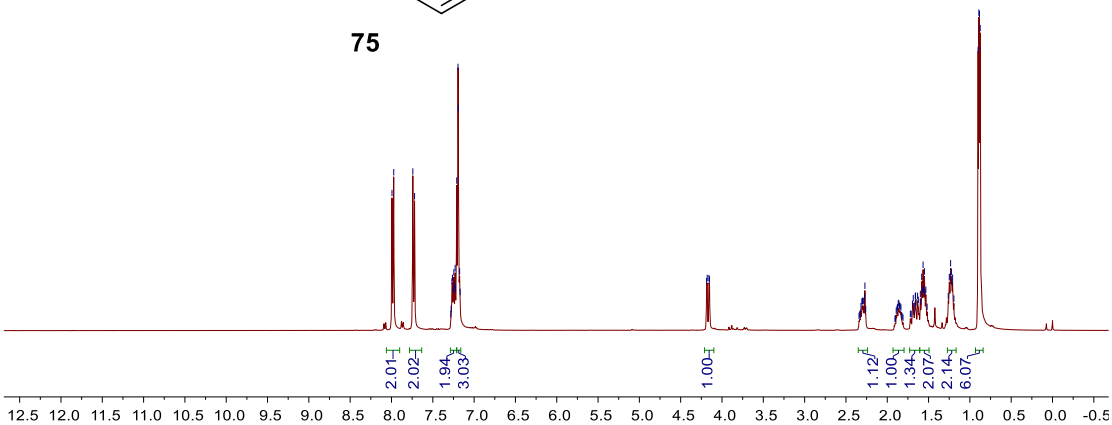


74

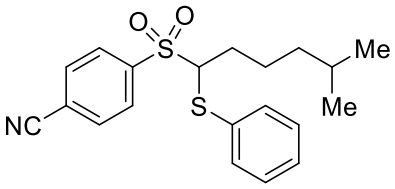
^{1}H NMR ($CDCl_3$), 400 MHz



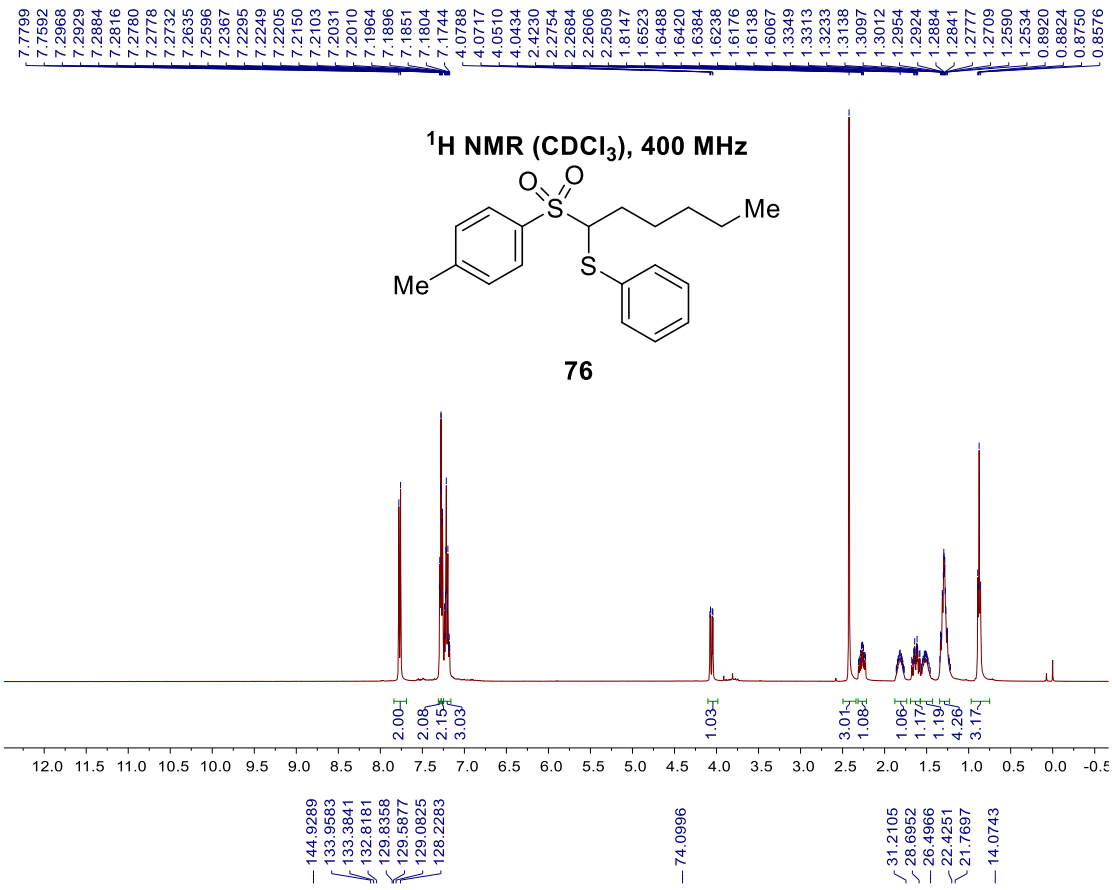
75



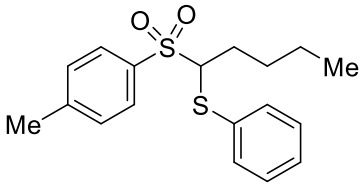
^{13}C NMR ($CDCl_3$), 101 MHz



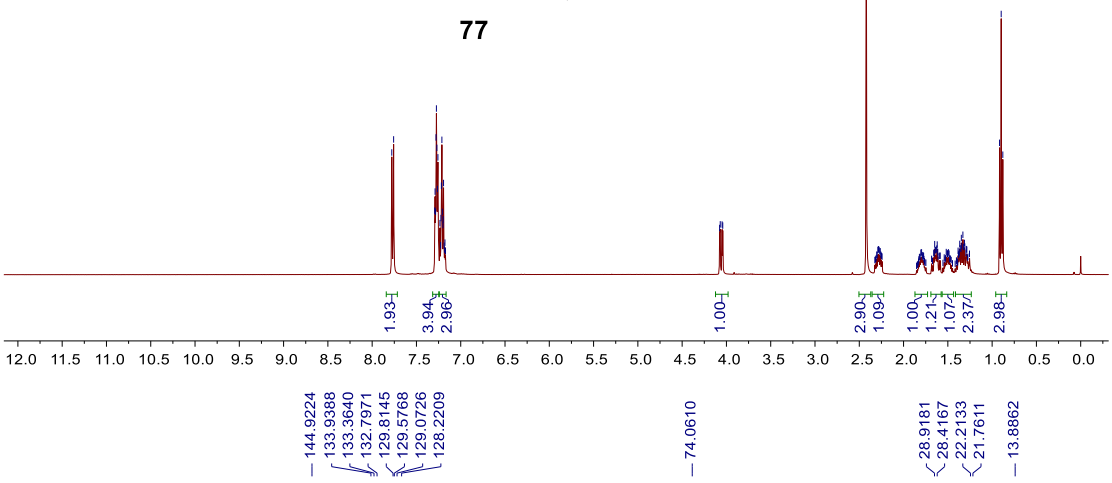
75


7.7799
7.7592
7.2968
7.2929
7.2884
7.2816
7.2780
7.2778
7.2732
7.2635
7.2596
7.2367
7.2295
7.2249
7.2205
7.2150
7.2103
7.2031
7.2010
7.1964
7.1896
7.1851
7.1804
7.1744
4.0788
4.0717
4.0510
4.0434
4.0230
2.2754
2.2684
2.2606
2.2509
1.8147
1.6523
1.6488
1.6420
1.6384
1.6238
1.6176
1.6138
1.6067
1.3349
1.3313
1.3233
1.3138
1.3097
1.3012
1.2954
1.2924
1.2884
1.2841
1.2777
1.2709
1.2590
1.2534
0.8920
0.8824
0.8750
0.8576
1H NMR (CDCl3), 400 MHz
O
O
S
Me
Me
S
76
2.00
2.08
2.15
3.03
1.03
3.01
1.08
1.06
1.17
1.19
4.26
3.17
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
144.9289
133.9583
133.3841
132.8181
129.8358
129.5877
129.0825
128.2283
74.0996
31.2105
28.6952
26.4966
22.4251
21.7697
14.0743
13C NMR (CDCl3), 101 MHz
O
O
S
Me
Me
S
76
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

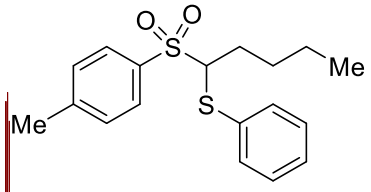
^{1}H NMR ($CDCl_3$), 400 MHz



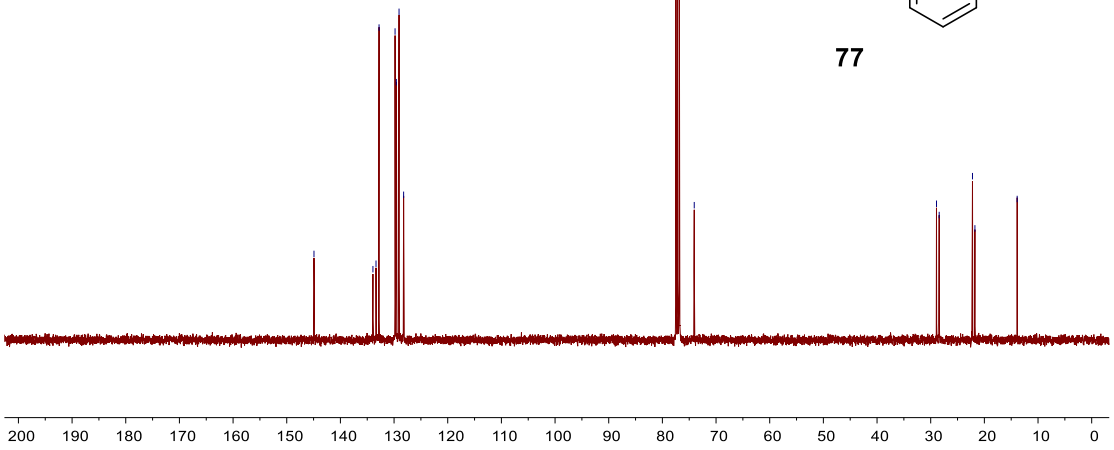
77

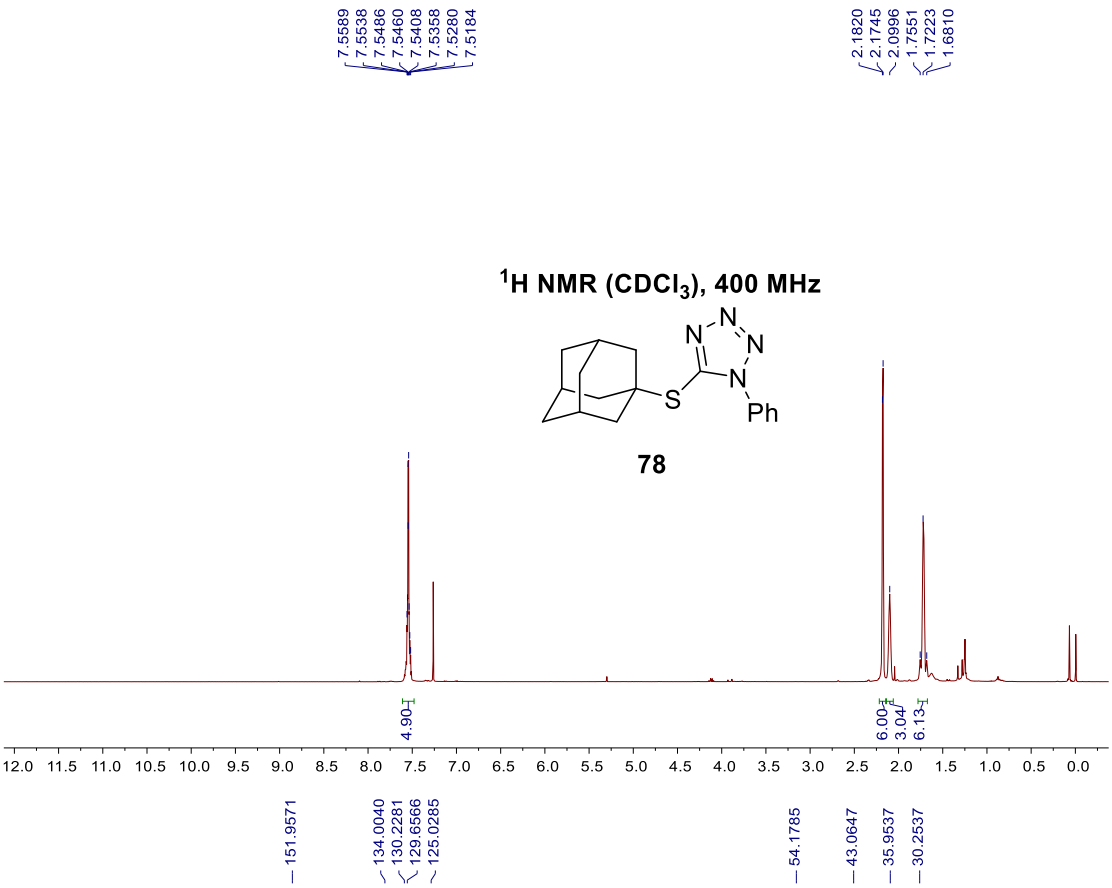


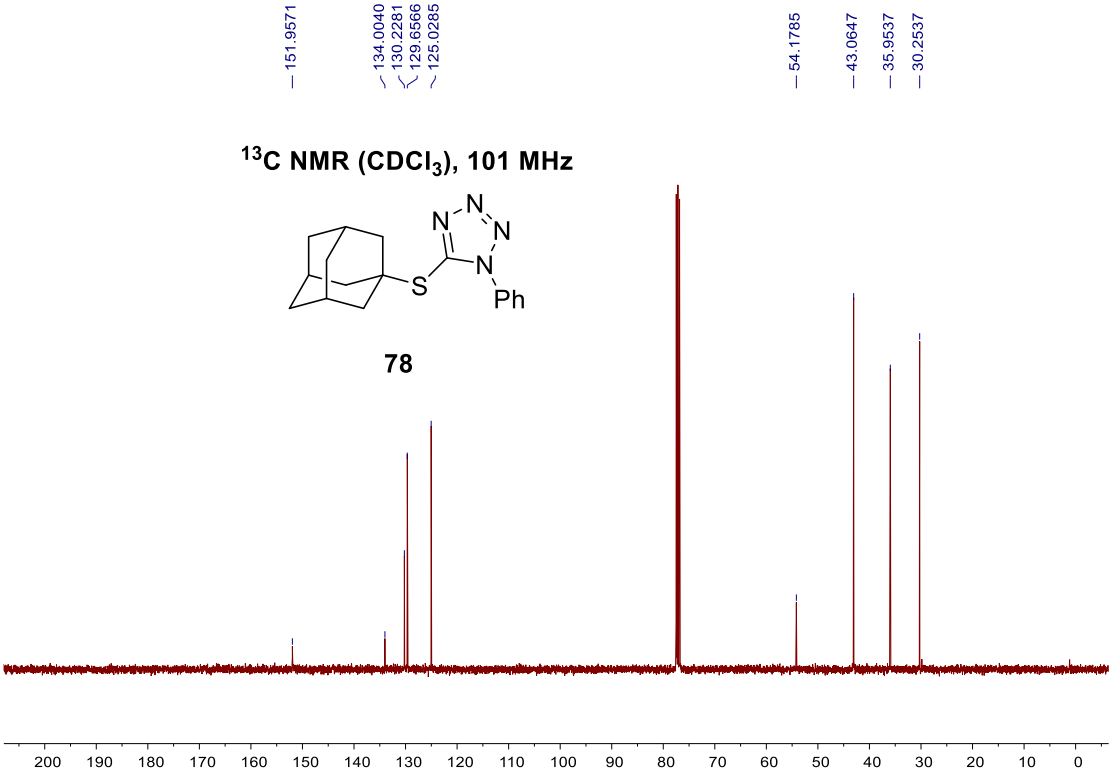
^{13}C NMR ($CDCl_3$), 101 MHz

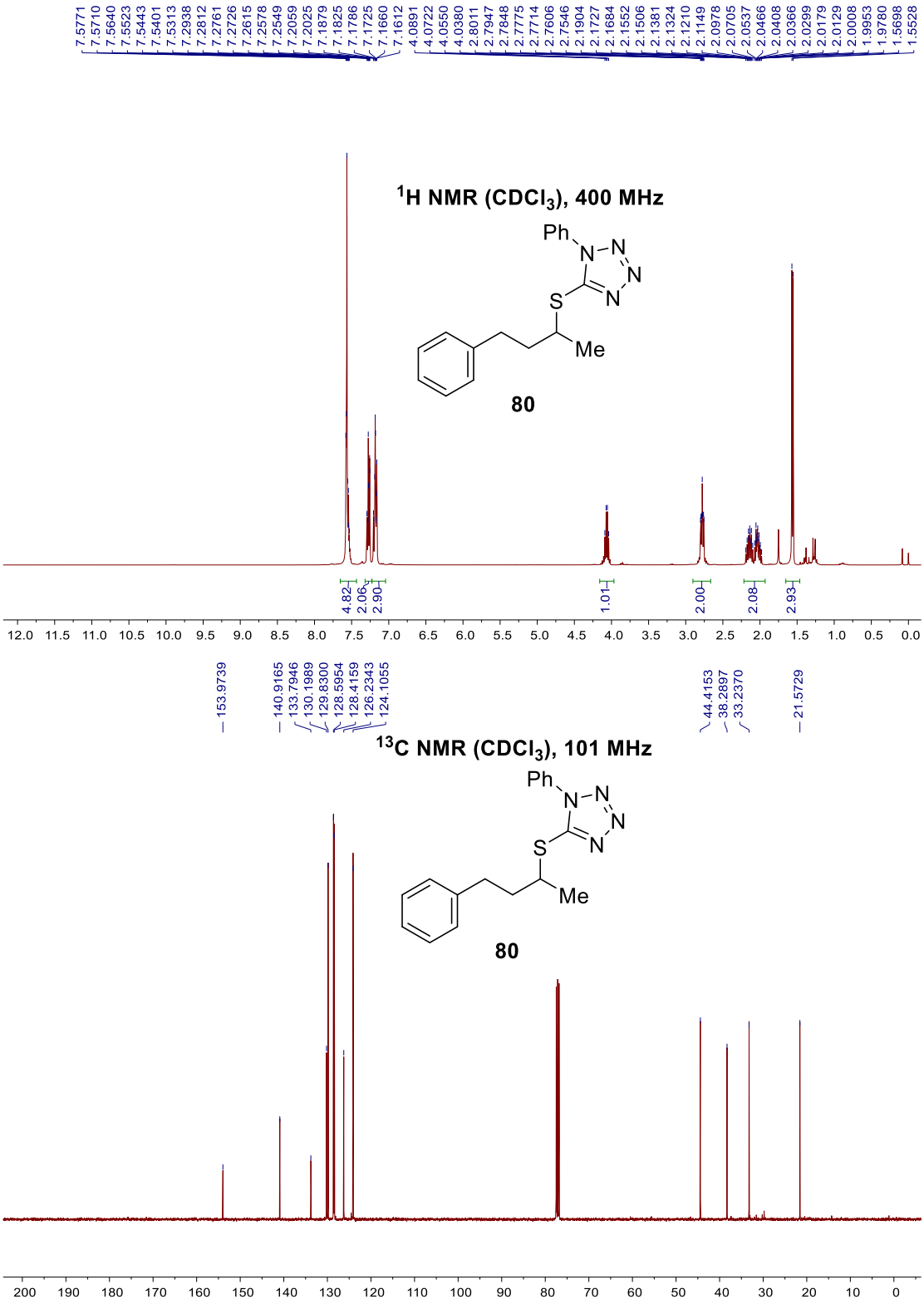


77

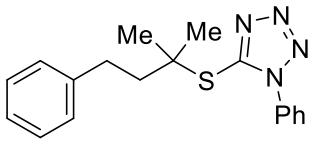



7.5589
7.5538
7.5486
7.5460
7.5408
7.5358
7.5280
7.5184
2.1820
2.1745
2.0996
1.7551
1.7223
1.6810
^{1}H NMR (CDCl$_3$), 400 MHz
N
N
N
N
S
Ph
78
4.90
6.00
3.04
6.13
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

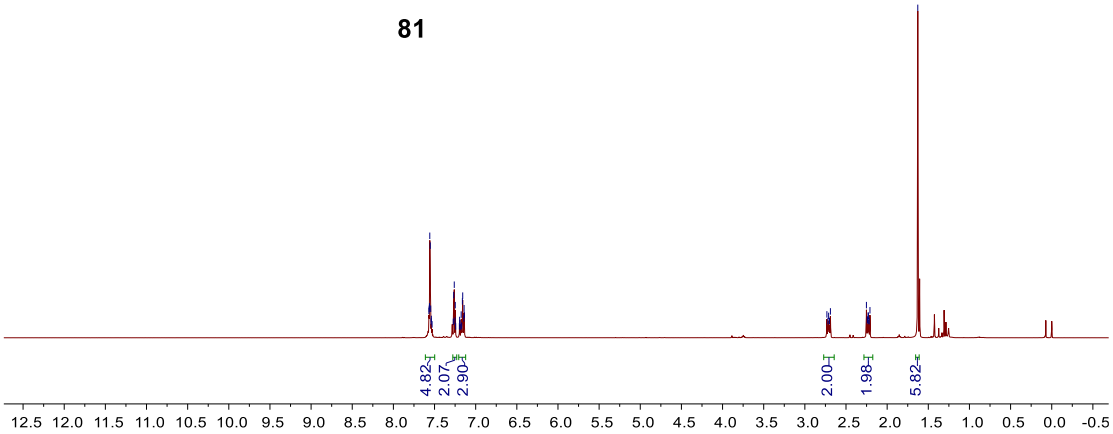

151.9571
134.0040
130.2281
129.6566
125.0285
54.1785
43.0647
35.9537
30.2537
^{13}C NMR (CDCl$_3$), 101 MHz
N
N
N
N
S
Ph
78
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.5771
7.5710
7.5640
7.5523
7.5443
7.5401
7.5313
7.2938
7.2812
7.2761
7.2726
7.2615
7.2578
7.2549
7.2059
7.2025
7.1879
7.1825
7.1786
7.1725
7.1660
7.1612
4.0891
4.0722
4.0550
4.0380
2.8011
2.7947
2.7848
2.7775
2.7714
2.7606
2.7546
2.1904
2.1727
2.1684
2.1552
2.1506
2.1381
2.1324
2.1210
2.1149
2.0978
2.0705
2.0537
2.0466
2.0408
2.0366
2.0299
2.0179
2.0129
2.0008
1.9953
1.9780
1.5698
1.5528
1H NMR (CDCl3), 400 MHz
Ph
N
N
N
N
S
Me
80
4.82
2.06
2.90
1.01
2.00
2.08
2.93
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
153.9739
140.9165
133.7946
130.1989
129.8300
128.5954
128.4159
126.2343
124.1055
44.4153
38.2897
33.2370
21.5729
13C NMR (CDCl3), 101 MHz
Ph
N
N
N
N
S
Me
80
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

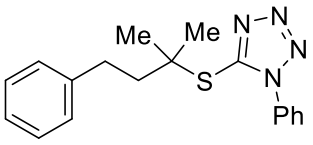
^{1}H NMR ($CDCl_3$), 400 MHz



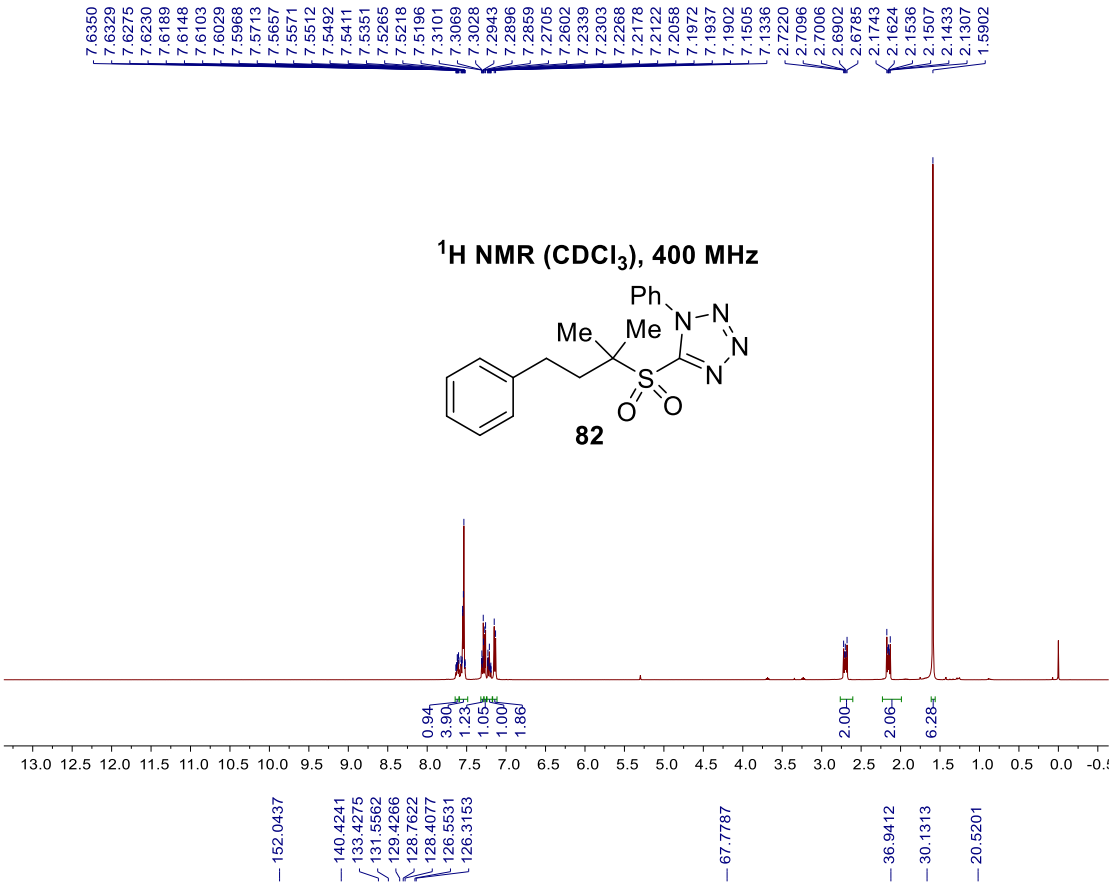
81



^{13}C NMR ($CDCl_3$), 101 MHz

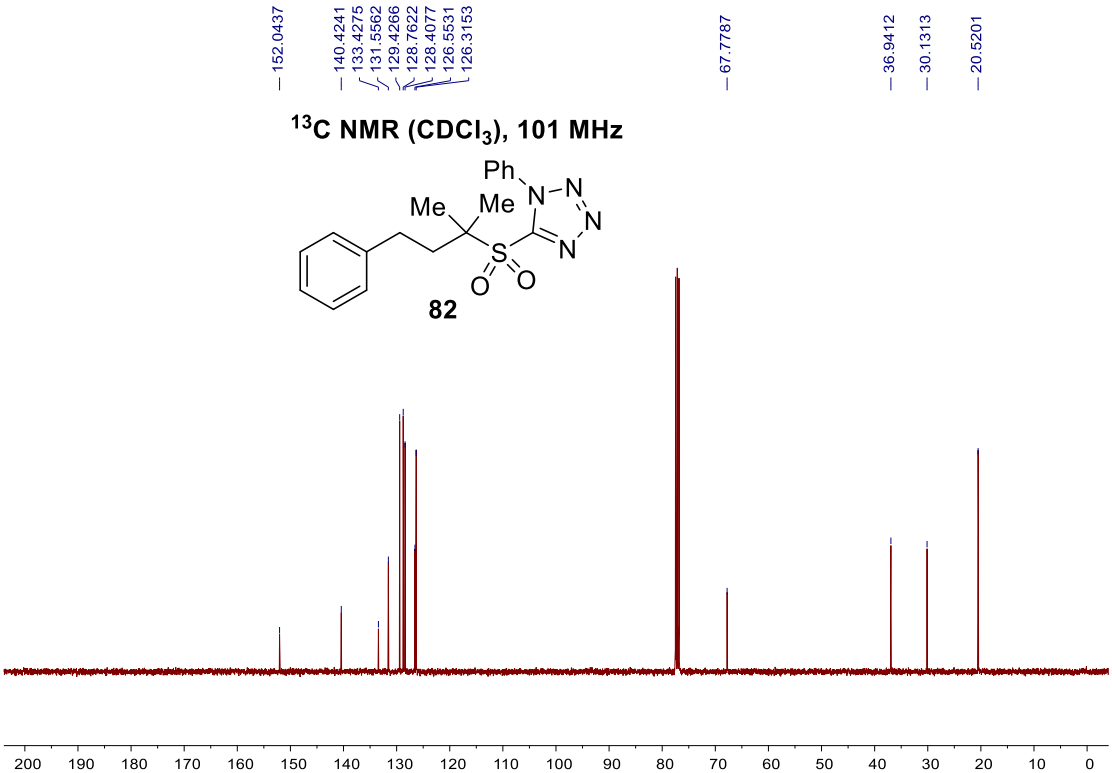


81



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

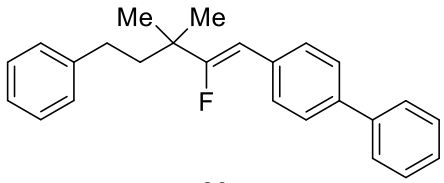
82



^{13}C NMR ($CDCl_3$), 101 MHz

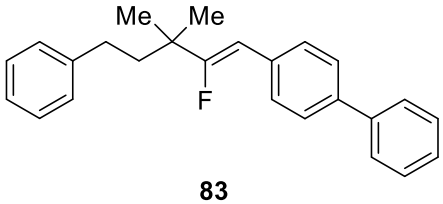
82

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

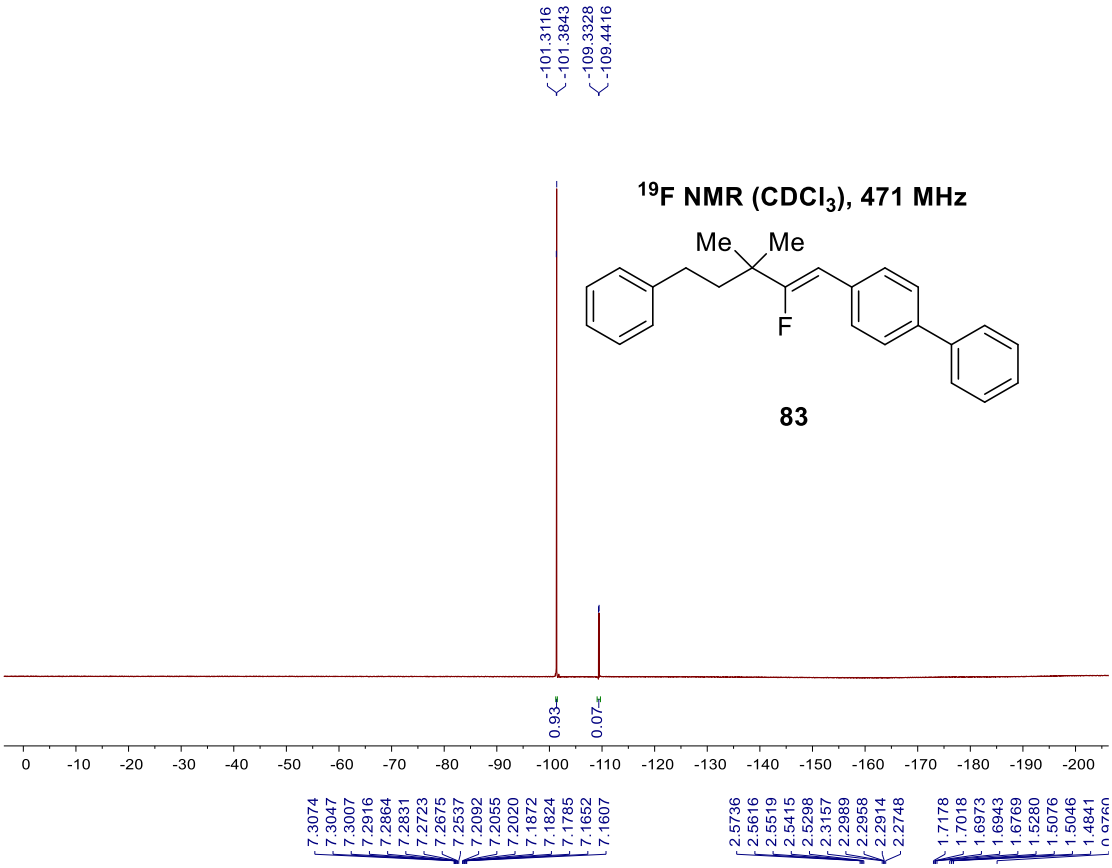


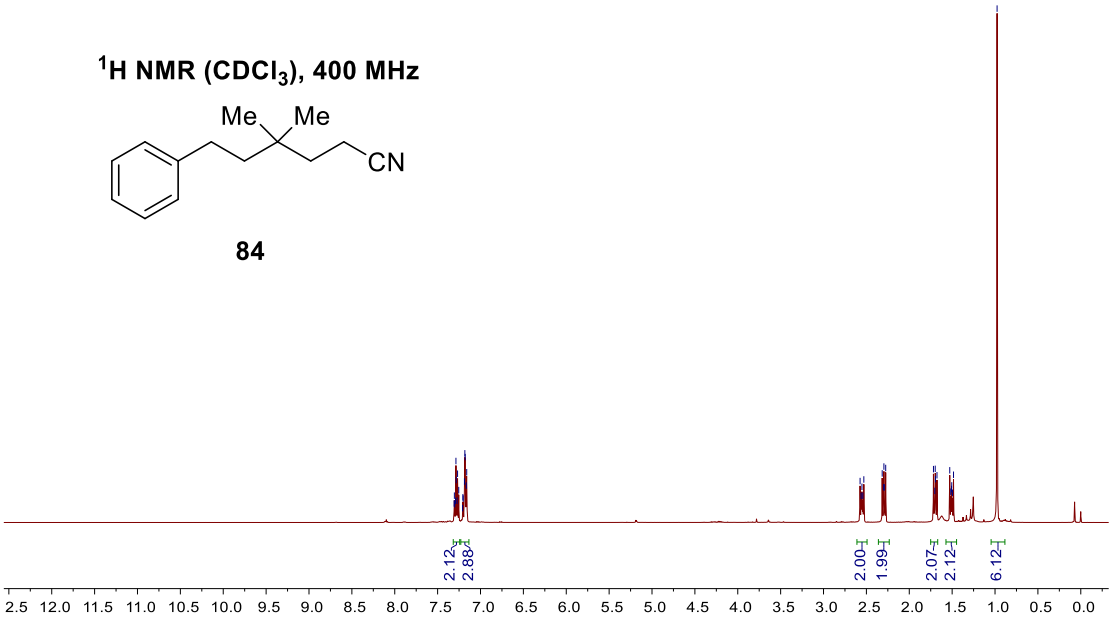
83

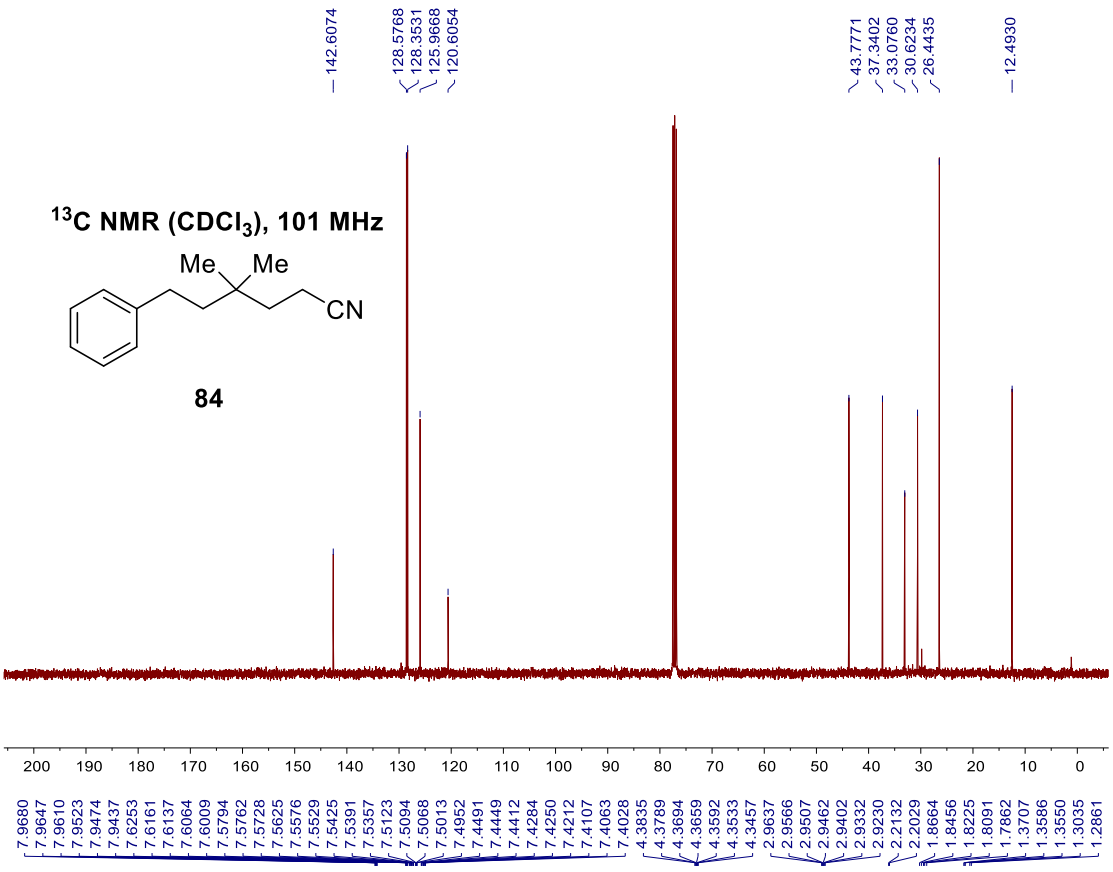
^{13}C NMR ($CDCl_3$), 101 MHz

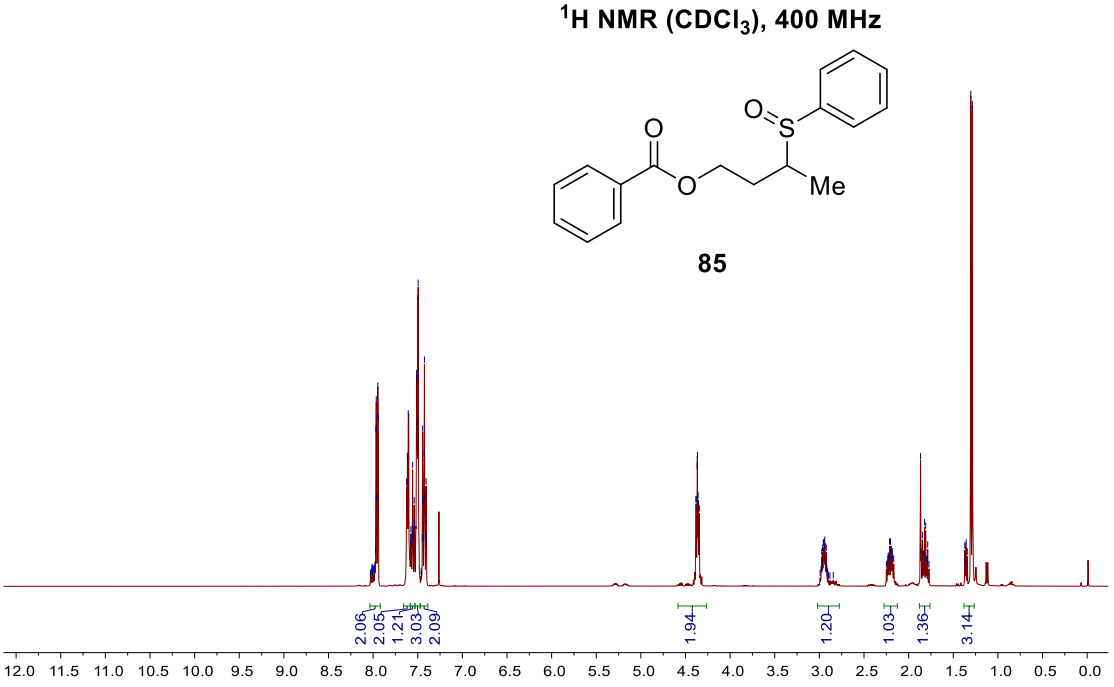


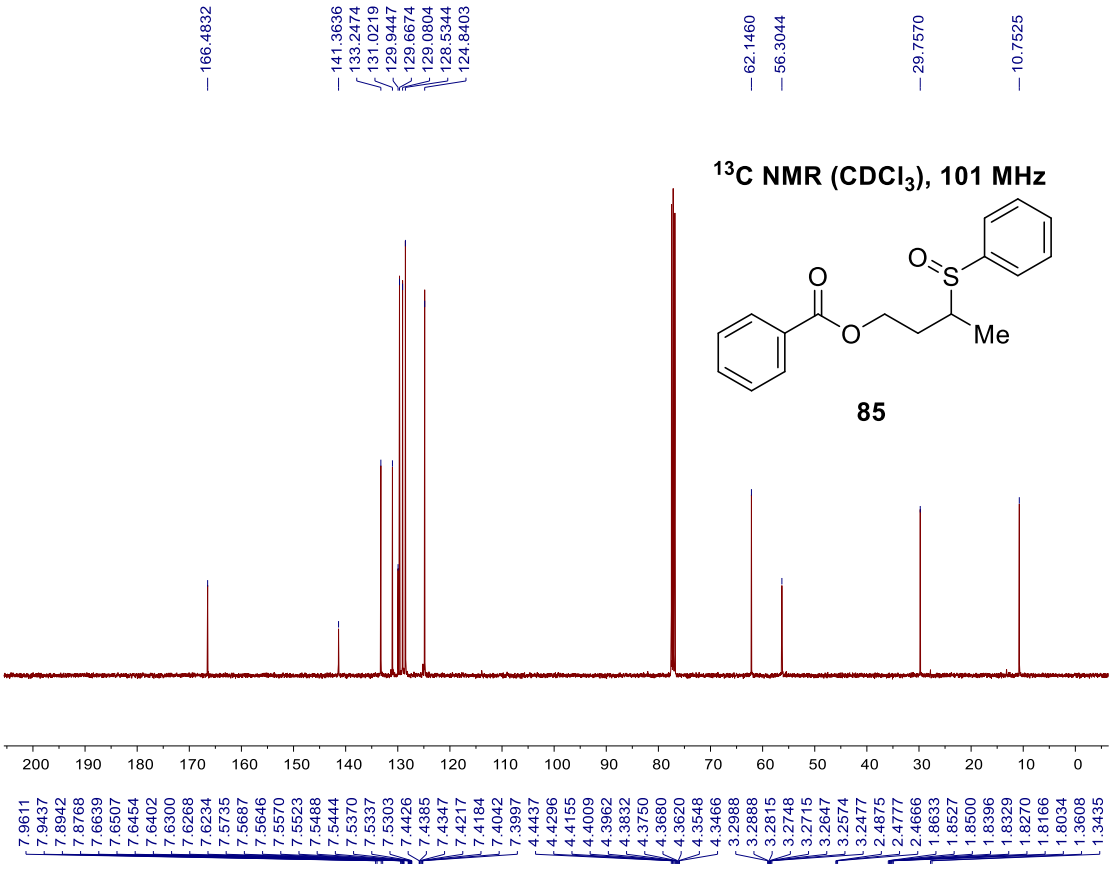
83

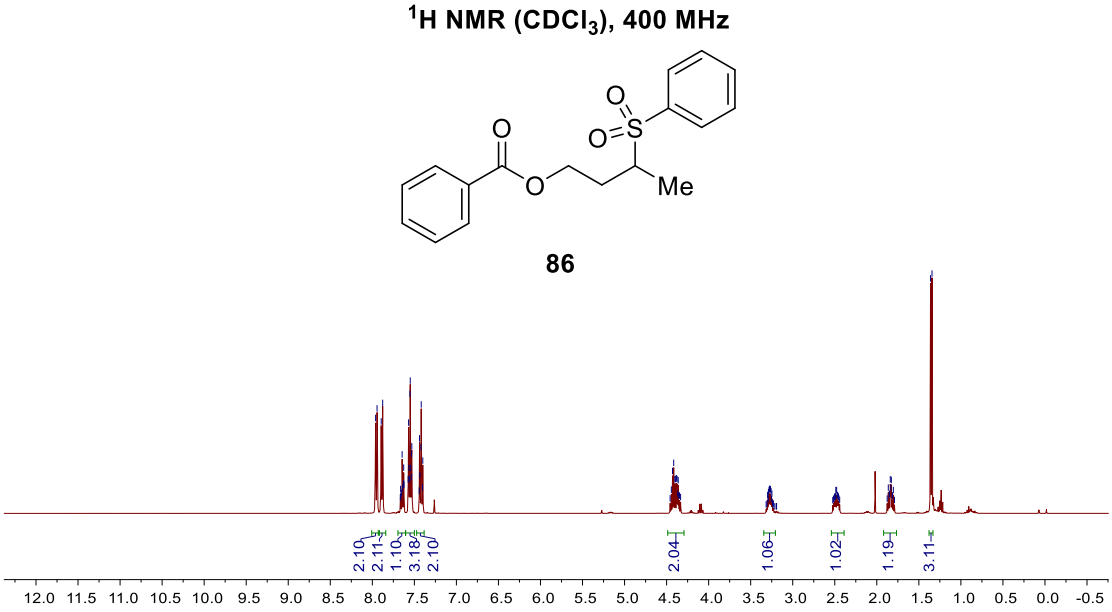

-101.3116
-101.3843
-109.3328
-109.4416
19F NMR (CDCl3), 471 MHz
Me
Me
F
83
0.93
0.07
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
7.3074
7.3047
7.3007
7.2916
7.2864
7.2831
7.2723
7.2675
7.2537
7.2092
7.2055
7.2020
7.1872
7.1824
7.1785
7.1652
7.1607
2.5736
2.5616
2.5519
2.5415
2.5298
2.3157
2.2989
2.2958
2.2914
2.2748
1.7178
1.7018
1.6973
1.6943
1.6769
1.5280
1.5076
1.5046
1.4841

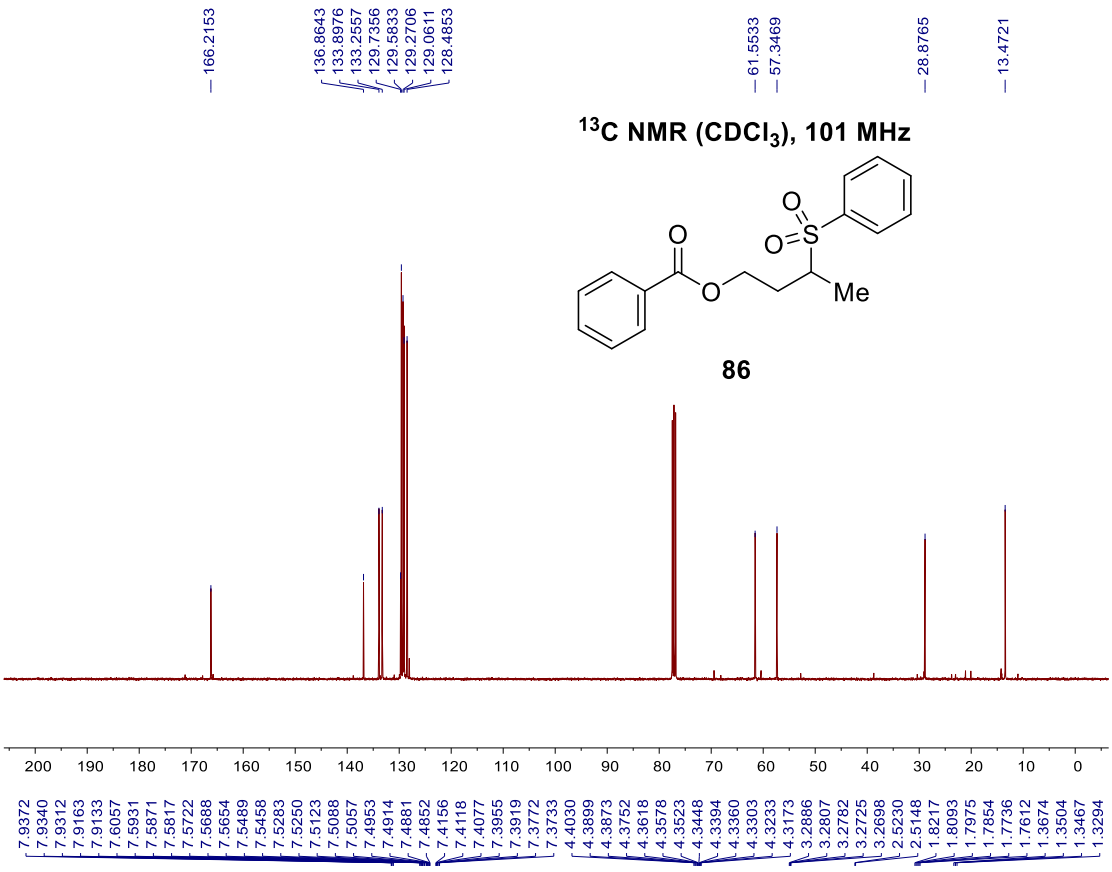

1H NMR (CDCl3), 400 MHz
Me
Me
CN
84
2.12
2.88
2.00
1.99
2.07
2.12
6.12
2.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

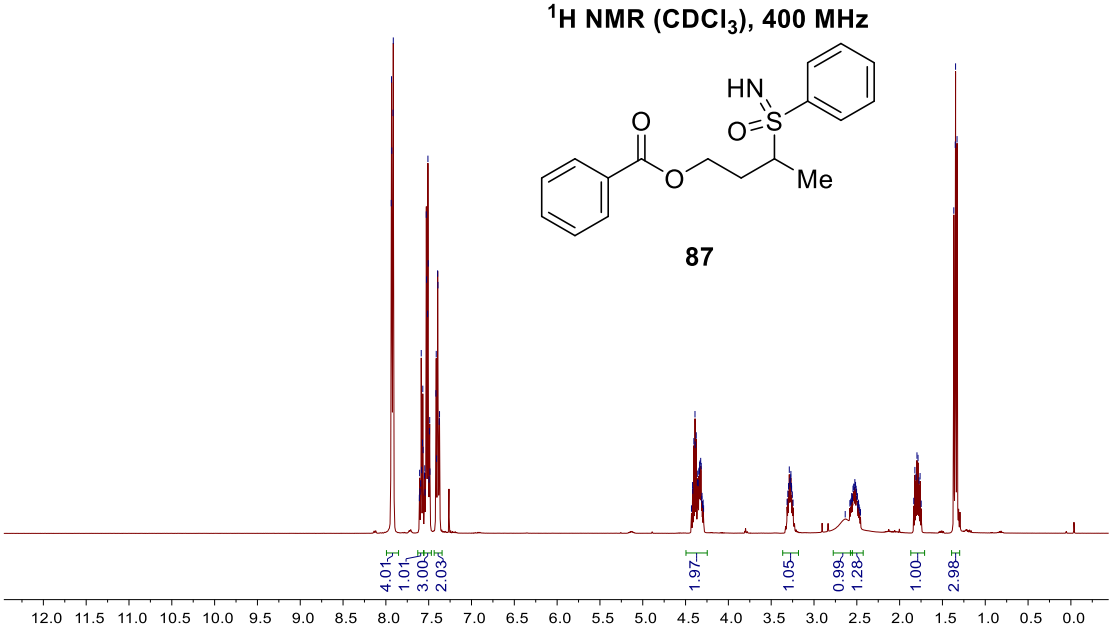

142.6074
128.5768
128.3531
125.9668
120.6054
43.7771
37.3402
33.0760
30.6234
26.4435
12.4930
13C NMR (CDCl3), 101 MHz
Me
Me
CN
84

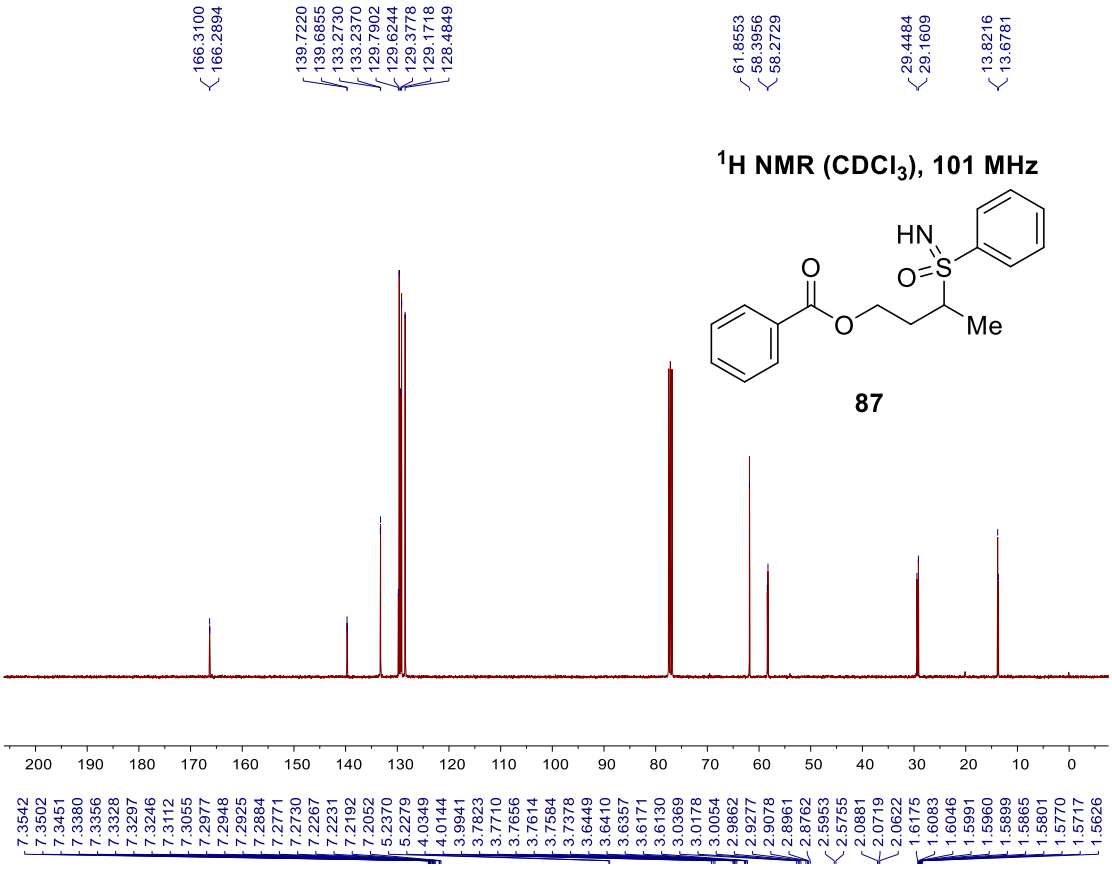

1H NMR (CDCl3), 400 MHz
O
S
O
O
Me
85


166.4832
141.3636
133.2474
131.0219
129.9447
129.6674
129.0804
128.5344
124.8403
62.1460
56.3044
29.7570
10.7525
13C NMR (CDCl3), 101 MHz
O
O
S
O
Me
85
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.9611
7.9437
7.8942
7.8768
7.6639
7.6507
7.6454
7.6402
7.6300
7.6268
7.6234
7.5735
7.5687
7.5646
7.5570
7.5523
7.5488
7.5444
7.5370
7.5337
7.5303
7.4426
7.4385
7.4347
7.4217
7.4184
7.4042
7.3997
4.4437
4.4296
4.4155
4.4009
4.3962
4.3832
4.3750
4.3680
4.3620
4.3548
4.3466
3.2988
3.2888
3.2815
3.2748
3.2715
3.2647
3.2574
3.2477
2.4875
2.4777
2.4666
1.8633
1.8527
1.8500
1.8396
1.8329
1.8270
1.8166
1.8034
1.3608
1.3435


1H NMR (CDCl3), 400 MHz
O
O
O
S
O
Me
86
2.10
2.11
1.10
3.18
2.10
2.04
1.06
1.02
1.19
3.11
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


166.2153
136.8643
133.8976
133.2557
129.7356
129.5833
129.2706
129.0611
128.4853
61.5533
57.3469
28.8765
13.4721
13C NMR (CDCl3), 101 MHz
O
O
O=S
O
Me
86
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.9372
7.9340
7.9312
7.9163
7.9133
7.6057
7.5931
7.5871
7.5817
7.5722
7.5688
7.5654
7.5489
7.5458
7.5283
7.5250
7.5123
7.5088
7.5057
7.4953
7.4914
7.4881
7.4852
7.4156
7.4118
7.4077
7.3955
7.3919
7.3772
7.3733
4.4030
4.3899
4.3873
4.3752
4.3618
4.3578
4.3523
4.3448
4.3394
4.3360
4.3303
4.3233
4.3173
3.2886
3.2807
3.2782
3.2725
3.2698
2.5230
2.5148
1.8217
1.8093
1.7975
1.7854
1.7736
1.7612
1.3674
1.3504
1.3467
1.3294

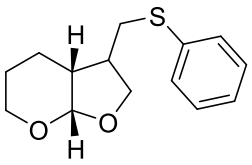

1H NMR (CDCl3), 400 MHz
HN
O=S
O
O
Me
87
4.01
1.01
3.00
2.03
1.97
1.05
0.99
1.28
1.00
2.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0



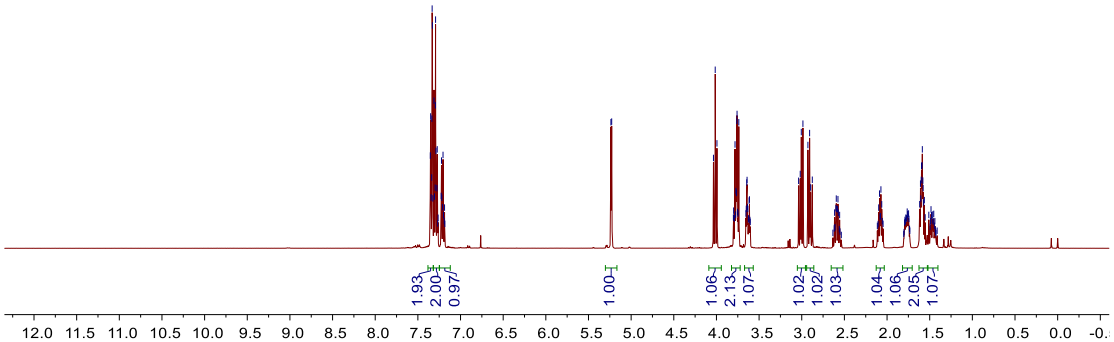
^{1}H NMR ($CDCl_3$), 101 MHz

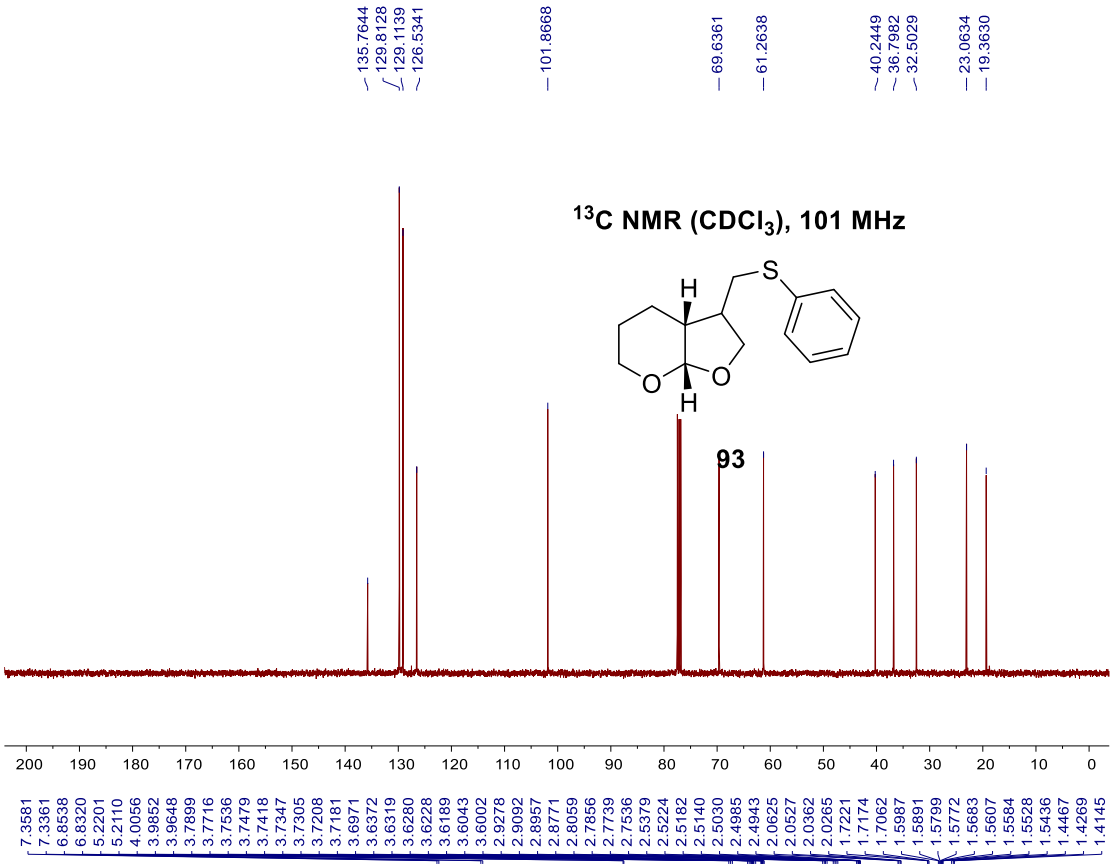
87

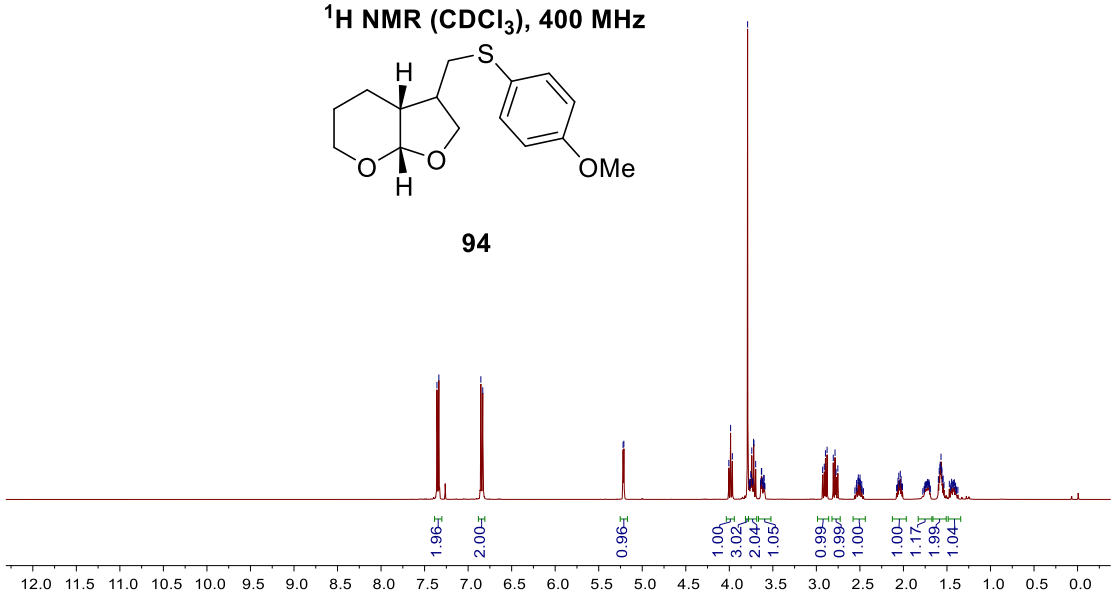
^{1}H NMR ($CDCl_3$), 400 MHz

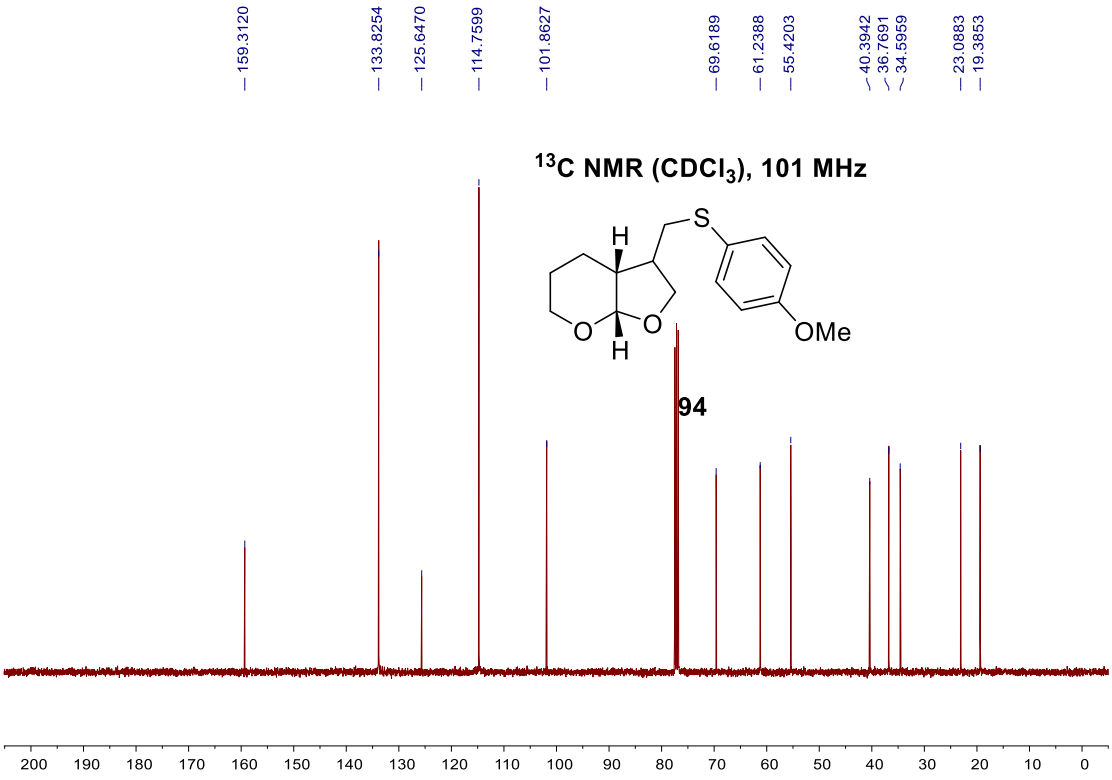


93




135.7644
129.8128
129.1139
126.5341
101.8668
69.6361
61.2638
40.2449
36.7982
32.5029
23.0634
19.3630
13C NMR (CDCl3), 101 MHz
H
S
O
O
H
93
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.3581
7.3361
6.8538
6.8320
5.2201
5.2110
4.0056
3.9852
3.9648
3.7899
3.7716
3.7536
3.7479
3.7418
3.7347
3.7305
3.7208
3.7181
3.6971
3.6372
3.6319
3.6280
3.6228
3.6189
3.6043
3.6002
2.9278
2.9092
2.8957
2.8771
2.8059
2.7856
2.7739
2.7536
2.5379
2.5224
2.5182
2.5140
2.5030
2.4985
2.4943
2.0625
2.0527
2.0362
2.0265
1.7221
1.7174
1.7062
1.5987
1.5891
1.5799
1.5772
1.5683
1.5607
1.5584
1.5528
1.5436
1.4467
1.4269
1.4145


1H NMR (CDCl3), 400 MHz
H
S
O
O
H
OMe
94
1.96
2.00
0.96
1.00
3.02
2.04
1.05
0.99
0.99
1.00
1.00
1.17
1.99
1.04
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


159.3120
133.8254
125.6470
114.7599
101.8627
69.6189
61.2388
55.4203
40.3942
36.7691
34.5959
23.0883
19.3853
13C NMR (CDCl3), 101 MHz
S
H
O
O
H
OMe
94
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0