Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Construction of Diverse C–S/C-Se Bonds via Nickel Catalyzed Reductive Coupling Employing Thiosulfonates and A Selennofonate Under Mild Conditions

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I. General information

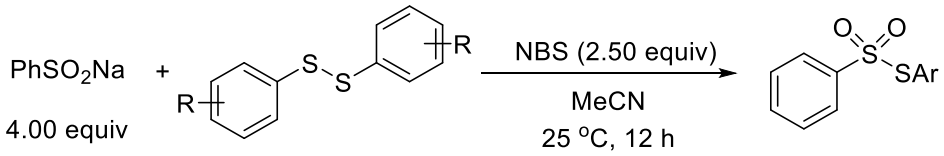
General procedures. General Information Unless specifically stated, all reagents were commercially obtained and where appropriate, purified prior to use. For example, dichloromethane (DCM) was freshly distilled from CaH_2; toluene, ether (Et_2O) was dried and distilled from metal sodium and benzophenone. 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 d_6-DMSO. Multiplicities were given as: s (singlet); d (doublet); dd (doublets of doublet); t (triplet); q (quartet); td (triplet of doublets); tt (triplet of triplets) ddd (doublet of doublet of doublets) or 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: 3-Aminoquinoline (Energy-Chemical), 6-aminoquinoline (Energy-Chemical), benzenesulfonyl hydrazid (Energy-Chemical), benzyl bromide (Energy-Chemical), bis(4-chlorophenyl)disulfide (Energy-Chemical), 1-bromo-4-iodobenzene (Energy-Chemical), 2-bromothiophenol (Energy-Chemical), 3-bromoquinoline (Energy-Chemical), 5-bromo-1*H*-indazole (Energy-Chemical), 5-bromo-2-iodopyridine (Adamas), 5-bromobenzofuran (Energy-Chemical), carbazole (Energy-Chemical), 4-chlorophenethyl bromide (Energy-Chemical), 1-chloro-4-iodobenzene (Energy-Chemical), 2-chloro-5-iodopyridine (bidepharm), 4-chlorobenzoyl chloride (Energy-Chemical), copper(ii) trifluoromethanesulfonate (Energy-Chemical), cyclopropylmethyl bromide (Energy-Chemical), cyclobutanemethanol (HEOWNS), dibenzothiophene (Energy-Chemical), 1,4-dibromobutane (Energy-Chemical), 2,2'-dithienyl disulfide (Energy-Chemical), 4,4'-dimethyl-2,2'-dipyridyl (Energy-Chemical), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (Energy-Chemical), 5,5'-dimethyl-2,2'-bipyridyl (Energy-Chemical), DL-menthol

(Energy-Chemical), ethyl bromodifluoroacetate (Energy-Chemical), 1-fluoro-2-[(2-fluorophenyl)disulfanyl]benzene (Energy-Chemical), 4-fluorophenethyl bromide (Energy-Chemical), 4-fluoroiodobenzene (Energy-Chemical), 4'-hydroxyacetophenone (leyan), 4-hydroxy benzaldehyde (Energy-Chemical), halquinol (Energy-Chemical), imidazole (Adamas), indole (Adamas), indomethacin (Energy-Chemical), 1-iodo-2-methoxybenzene (Energy-Chemical), 1-iodo-4-nitrobenzene (Energy-Chemical), 1-iodo-4-(trifluoromethoxy)benzene (Adamas), 3-iodothiophene (Energy-Chemical), 3-iodotoluene (Energy-Chemical), 4'-iodoacetophenone (Adamas), 4-iodoanisole (Energy-Chemical), 4-iodobenzyl bromide (Energy-Chemical), 4-iodobenzaldehyde (Adamas), 4-iodobenzoyl chloride (Energy-Chemical), 4-iodobenzoic acid (HEOWNS), 4-iodobenzonitrile (Energy-Chemical), 4-iodobenzyl alcohol (Energy-Chemical), iodomethane (Energy-Chemical), 4-iodo-m-xylene (Energy-Chemical), 4-iodophenol (Energy-Chemical), 4-iodopyridine (Energy-Chemical), 4-iodophenylboronic acid (Energy-Chemical), 5-iodo-1*H*-indazole (Energy-Chemical), 5-iodoindole (Adamas), 5-iodofuran-2-carboxaldehyde (Energy-Chemical), 6-iodoquinoline (Energy-Chemical), methyl 4-iodobenzoate (Energy-Chemical), N-bromosuccinimide (Energy-Chemical), N-iodosuccinimide (Energy-Chemical), 1,10-phenanthroline (Energy-Chemical), 3-phenylpropyl bromide (Energy-Chemical), 3-phenyl-1-propanol (Energy-Chemical), phenyl disulfide (Energy-Chemical), *p*-tolyl disulfide (Energy-Chemical), *p*-toluenesulfonyl hydrazide (Energy-Chemical), sodium benzenesulfinate dihydrate (Energy-Chemical), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (Energy-Chemical), triphenylphosphine (J&K), trifluoromethanesulfonic anhydride (Energy-Chemical).

II. Synthesis of starting materials

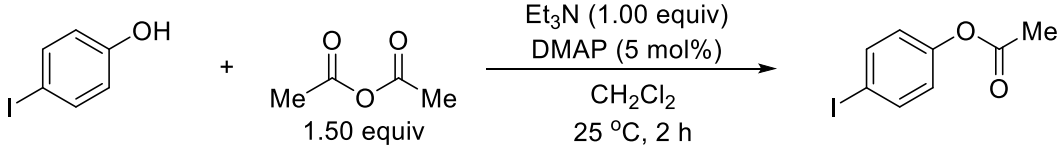
1. <u>General Method A:</u> Synthesis of *S*/*Se*-arylthiosulfonates 2a, 2c-h, 2p



An oven-dried 500-mL round-bottom flask, equipped with a stir bar, was charged with sodium sulfinate (20.0 mmol, 4.00 equiv), disulfide (5.00 mmol, 1.00 equiv) and *N*-bromosuccinimide (12.5 mmol, 2.50 equiv), MeCN (100 mL) was added under N_2. The mixture was stirred at room temperature for 12 h. Subsequently, the solvent was evaporated and the residue was re-disolved in EtOAc, washed with water and extracted with EtOAc (50.0 mL x 3). The combined organic layers were 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 product.

compound **2a**: white solid, 9.13 g, 9.13 mmol, 91.3% yield[1]; compound **2c**: white solid, 1.70 g, 6.00 mmol, 59.7% yield[1]; compound **2d**: light yellow solid, prepared on 0.74 mmol, 354 mg, 75.1% yield[2]; compound **2e**: white solid, 2.59 g, 9.80 mmol, 98.0%[1]; compound **2f**: white solid, prepared on 3.00 mmol, 1.25 g, 78.1% yield[1], compound **2g**: light yellow solid, prepared on 1.16 mmol, 625 mg, 84.5% yield[2]; compound **2h**: yellow solid, prepared on 7.00 mmol, 1.09 g, 30.4% yield[2]; compound **2p**: green solid, prepared on 7.00 mmol, 3.40 g, 81.7% yield[3]. Spectra were consistent with literature data[1-3].

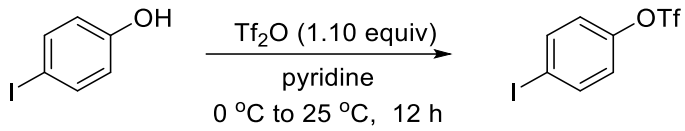
2. Synthesis of 4-iodophenyl acetate 1g:



An oven-dried 50-mL round-bottom flask, equipped with a stir bar, was charged with 4-iodophenol (1.00 g, 4.55 mmol, 1.00 equiv), DMAP (27.8 mg, 0.228 mmol,

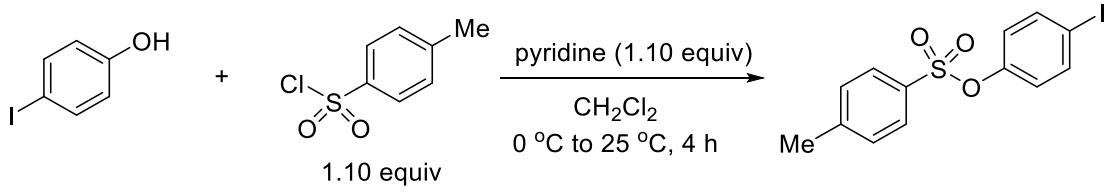
0.0500 equiv), DCM (9.00 mL), and Et_3N (0.650 mL, 4.55 mmol, 1.00 equiv) was added under N_2. Then acetic anhydride (1.03 mL, 1.50 equiv) in DCM (5.00 mL) was added dropwise to the mixture. The mixture was allowed to stir for 2 h at room temperature. H_2O (50.0 mL) were added to the reaction mixture, and the aqueous solution was then washed with DCM (50.0 mL x 3). The combined organic layers were 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 10:1 petroleum ether: ethyl acetate). The product was isolated as a white solid (1.01 g, 3.85 mmol, 84.6% yield) which is a known compound. The spectral data match those previously reported[4].

3. Synthesis of 4-iodophenyl trifluoromethanesulfonate 1h:



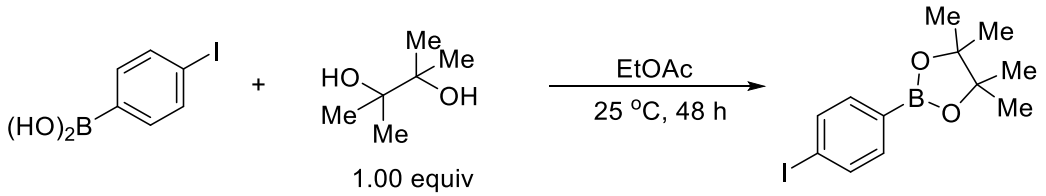
An oven-dried 50-mL round-bottom flask, equipped with a stir bar, was charged with 4-iodophenol (1.65 g, 7.50 mmol, 1.00 equiv) and dry pyridine (15.0 mL), trifluoromethanesulfonic anhydride (1.39 mL, 8.25 mmol, 1.10 equiv) was added dropwise under N_2 at 0 °C. Then the mixture was allowed to stir for 5 min at 0 °C then for overnight at room temperature. The mixture was poured into water and extracted with ethyl ether (50.0 mL). The organic layer was washed sequentially with water (50.0 mL), 10% HCl (20.0 mL x 2), and brine (50.0 mL) then 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: 50:1 to 2:1 petroleum ether: ethyl acetate). The product was isolated as a colorless oil (2.29 g, 6.50 mmol, 86.7% yield) and is a known compound. The spectral data match those previously reported[5].

4. Synthesis of 4-iodophenyl 4-methylbenzenesulfonate 1i:



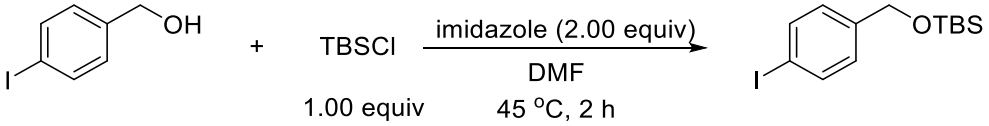
An oven-dried 25-mL round-bottom flask, equipped with a stir bar, was charged with 4-iodophenol (1.32 g, 6.00 mmol, 1.0 equiv), pyridine (0.52 g, 6.60 mmol, 1.10 equiv) and DCM (6.00 mL), TsCl (1.26 g, 6.60 mmol, 1.10 equiv) was added portion-wise at 0 °C under N_2. The reaction mixture was warmed to room temperature and stirred for 4 h. H_2O (20.0 mL) and saturated aqueous NH_4Cl (10.0 mL) were added to the reaction mixture, and the mixture was extracted with DCM (50.0 mL x 3). The combined organic layers were washed with brine (50.0 mL), 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 10:1 petroleum ether: ethyl acetate). The product was isolated as a white solid (1.28 g, 3.42 mmol, 57.0% yield) which is a known compound. The spectral data match those previously reported[5].

5. Synthesis of 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 1m：



An oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with 4-iodophenylboronic acid (1.24 g, 5.00 mmol, 1.00 equiv) and pinacol (0.590 g, 5.00 mmol, 1.00 equiv). Ethyl acetate (13.0 mL) was added under N_2 and the mixture was allowed to stir for 48 h at room temperature. 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 was isolated as a white solid (1.44 g, 4.36 mmol, 87.3% yield) which is a known compound. The spectral data match those previously reported[6].

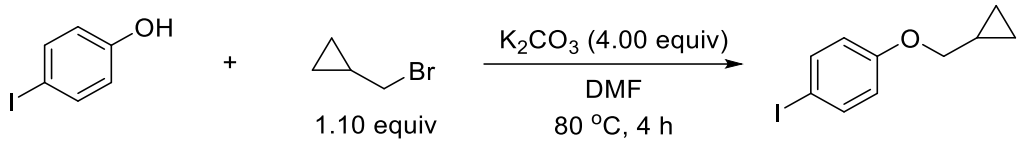
6. Synthesis of *tert*-butyl((4-iodobenzyl)oxy)dimethylsilane 1n:



An oven-dried 25-mL round-bottom flask, equipped with a stir bar, was charged with

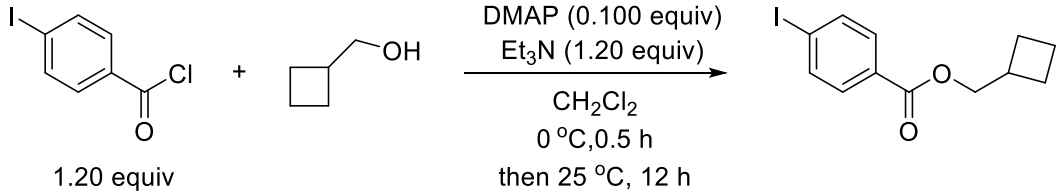
(4-iodophenyl)methanol (0.500 g, 2.14 mmol, 1.00 equiv), TBSCl (0.323 g, 2.14 mmol, 1.00 equiv), imidazole (0.291 g, 4.28 mmol, 2.00 equiv), and DMF (3.00 mL). The mixture was allowed to stir for 2 h at 45 °C. The mixture was then allowed to cool to room temperature and diluted with water (50.0 mL). The aqueous solution was then washed with ethyl acetate (50.0 mL x 3). The combined organic layers were 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 50:1 petroleum ether: ethyl acetate). The product was isolated as a white solid (0.544 g, 1.56 mmol, 72.9% yield) and is a known compound. The spectral data match those previously reported[7].

7. Synthesis of 1-(cyclopropylmethoxy)-4-iodobenzene 1o：



An oven-dried 50mL round-bottom flask, equipped with a stir bar, was charged with 4-iodophenol (2.20 g, 10.0 mmol, 1.00 equiv), potassium carbonate (5.50 g, 40.0 mmol, 4.00 equiv) and DMF (25.0 mL). (bromomethyl)Cyclopropane (1.49 g, 11.0 mol, 1.10 equiv) was added under N_2 and the mixture was stirred at 80 °C for 4 h. After cooling to room temperature, the resulting precipitates were filtered off and washed with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with water (50.0 mL) and brine (50.0 mL), 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: 50:1 to 5:1 petroleum ether: ethyl acetate). The product was isolated as a white solid (2.35 g, 8.57 mmol, 85.7% yield) which is a known compound. The spectral data match those previously reported[8].

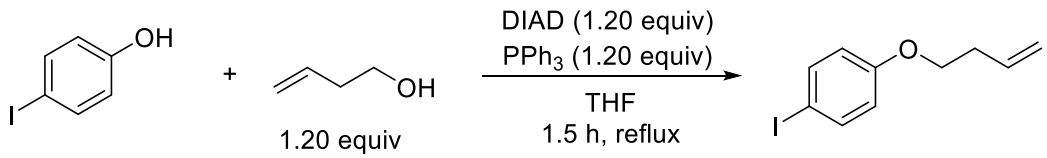
8. Synthesis of *tert*-butyl 5-iodo-1H-indole-1-carboxylate 1p:



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

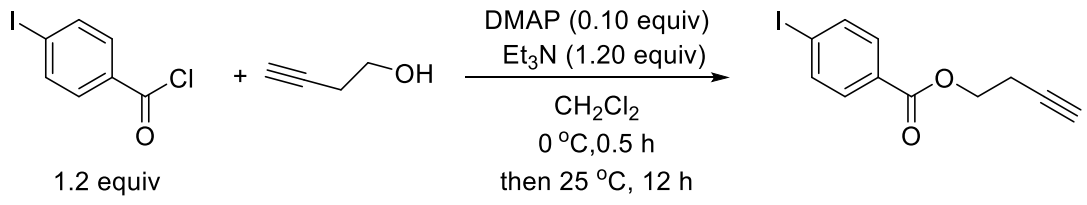
cyclobutylmethanol (860 mg, 10.0 mmol, 1.00 equiv), DMAP (12.2 mg, 0.100 mmol, 0.100 equiv), and DCM (20.0 mL). The mixture was cooled to 0 °C and 4-iodobenzoyl chloride (3.20 g, 12.0 mmol, 1.20 equiv) in DCM (20.0 mL) was added dropwise at 0 °C for 0.5 h under N_2. The reaction mixture was allowed to stir at room temperature for 12 h and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (Eluent: 50:1 to 20:1 petroleum ether: ethyl acetate) to obtain the product as a white solid (2.91 g, 9.20 mmol, 92.0% yield). **M.p.** = 35.2 – 36.1 °C; **IR** (thin film) 1703 (s), 1585 (m), 1391 (w), 1332 (w), 1265 (s), 1175 (w), 1119 (m), 1103 (m), 1007 (m), 970 (m), 848 (m), 754 (s), 681 (w) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (2H, d, J = 8.4 Hz), 7.72 (2H, d, J = 8.4 Hz), 4.26 (2H, d, J = 6.6 Hz), 2.78 – 2.66 (1H, m), 2.15 – 2.02 (2H, m), 1.98 – 1.77 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 137.8, 131.2, 130.1, 100.7, 69.0, 34.3, 24.9, 18.6; **MS** (EI): m/z (%) 316, 248, 231, 203, 104, 76. **HRMS** calc'd for $C_{12}H_{13}O_2I$: 315.9950, found: 315.9955.

9. Synthesis of 1-(cyclopropylmethoxy)-4-iodobenzene 1q:



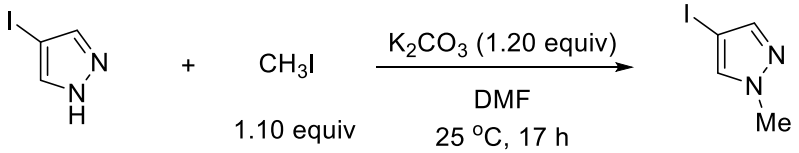
A solution of 4-iodophenol (0.660 g, 3.00 mmol, 1.00 equiv), 3-buten-1-ol (0.260 g, 3.60 mmol, 1.20 equiv), triphenylphosphine (0.940 g, 3.60 mmol, 1.20 equiv), diisopropyl azodicarboxylate (DIAD, 0.730 g, 3.60 mmol, 1.20 equiv) in THF (37.0 mL) was heated for 1.5 h at reflux, then the crude mixture was concentrated under reduced pressure. Purification by flash chromatography (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) afforded the desired product as a white solid (0.510 g, 1.86 mmol, 62.0% yield) as a white solid. Spectroscopic data agreed with the literature[9].

10. Synthesis of *tert*-butyl 5-iodo-1H-indole-1-carboxylate 1r:



An oven-dried 25-mL Schlenk tube, equipped with a stir bar, was charged with but-3-yn-ol (700 mg, 10.0 mmol, 1.00 equiv), DMAP (12.2 mg, 0.100 mmol, 0.100 equiv), and DCM (20.0 mL). The mixture was cooled to 0 °C and 4-iodobenzoyl chloride (3.20 g, 12.0 mmol, 1.20 equiv) in DCM (20.0 mL) was added dropwise at 0 °C for 0.5 h under N_2. The reaction mixture was allowed to stir at room temperature for 12 h and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (Eluent: 50:1 to 20:1 petroleum ether: ethyl acetate) to obtain the product as a white solid (2.60 g, 8.66 mmol, 86.6% yield). **M.p.** = 61.5 – 63.2 °C; **IR** (thin film) 3292 (w), 1722 (m), 1586 (w), 1391 (w), 1265 (s), 1174 (m), 1100 (s), 1005 (m), 979 (w), 840 (w), 802 (w), 748 (s), 681 (m), 637 (s) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (2H, d, J = 8.4 Hz), 7.76 (2H, d, J = 8.4 Hz), 4.42 (2H, t, J = 6.8 Hz), 2.66 (2H, td, J = 6.8, 2.6 Hz), 2.03 (2H, t, J = 2.6 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 137.9, 131.2, 129.5, 101.1, 80.0, 70.2, 62.9, 19.2; **MS** (EI): m/z (%) 300, 248, 231, 203, 104, 76. **HRMS** calc'd for $C_{11}H_9O_2I$: 299.9646, found: 299.9642.

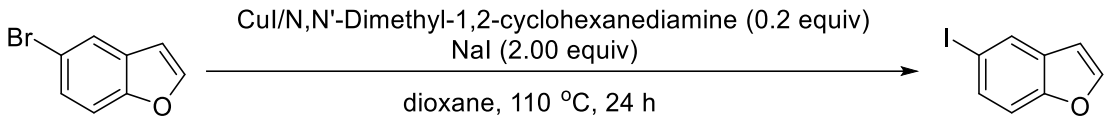
11. Synthesis of 4-iodo-1-methyl-1H-pyrazole 1v:



An oven-dried 50-mL round-bottom flask, equipped with a stir bar, was charged with 4-iodopyrazole (1.94 g, 10.0 mmol, 1.00 equiv) potassium carbonate (1.65 g, 12.0 mmol, 1.20 equiv), and DMF (20.0 mL). The mixture was allowed to stir for 2 mins at room temperature before iodomethane (1.56 g, 11.0 mmol, 1.10 equiv) was added under N_2. The mixture was allowed to stir for 17 h at room temperature and filtered through a celite pad. The filtrate was evaporated to approximative (10.0 mL) then water (10.0 mL) was added to the residue. The resultant mixture was extracted with EtOAc (10.0 mL x 3). The combined organics were washed with water and brine, 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: 50:1 to 5:1 petroleum ether: ethyl acetate). The product was isolated as a white solid (1.39 g, 6.68 mmol, 66.8% yield) which is a known compound. The spectral data match those

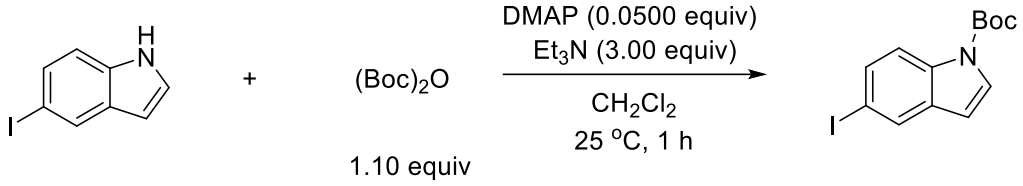
previously reported[10].

12. Synthesis of 5-iodobenzofuran 1aa:



An oven-dried 25-mL Schlenk tube, equipped with a stir bar, was charged with CuI (95.0 mg, 0.500 mmol, 0.100 equiv), NaI (1.50 g, 10.0 mmol, 2.00 equiv), briefly evacuated and backfilled with argon. Racemic *trans*-*N*,*N*'-dimethyl-1,2-cyclohexanediamine (0.300 g, 2.00 mmol, 0.200 equiv), 5-bromobenzofuran (0.980 g, 5.00 mmol, 1.00 equiv), and dioxane (5.00 mL) were added to the mixture under argon. The Schlenk tube was sealed with a Teflon valve and the reaction mixture was allowed to stirr for 24 h at 110 °C. The mixture was then allowed to cool to room temperature and diluted with 30% aqueous ammonia (25.0 mL), poured into water (100 mL), and extracted with DCM (15.0 mL x 3). The combined organic layers were 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: 100:0 to 500:1 petroleum ether: ethyl acetate) to provide the desired product as a colorless oil (1.07 g, 4.38 mmol, 87.7% yield) which is a known compound. The spectral data match those previously reported[11].

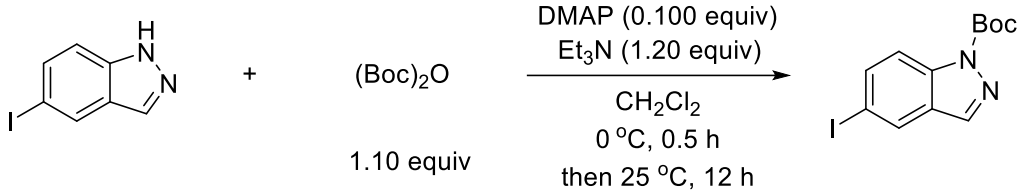
13. Synthesis of *tert*-butyl 5-iodo-1*H*-indole-1-carboxylate 1ac:



An oven-dried 25-mL round-bottom flask, equipped with a stir bar, was charged with 5-iodoindol (0.486 g, 2.00 mmol, 1.00 equiv), DMAP (12.2 mg, 0.100 mmol, 0.0500 equiv), Et_3N (0.606 g, 6.00 mmol, 3.00 equiv) and DCM (10.0 mL). di-*tert*-Butyl dicarbonate (480 mg, 2.20 mmol, 1.10 equiv) was added to the mixture under N_2. The reaction mixture was allowed to stir at room temperature for 1 h and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) to obtain the colorless oil (0.656 g, 1.91 mmol, 95.5% yield) which is a known compound. The spectral data

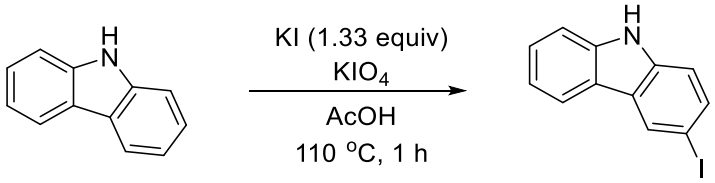
match those previously reported[12].

14. Synthesis of *tert*-butyl 5-iodo-1H-indole-1-carboxylate 1ad:



An oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with with 5-iodo-1*H*-indazole (2.44 g, 10.0 mmol, 1.00 equiv) in MeCN (30.0 mL) were added DMAP (122 mg, 1.00 mmol, 0.100 equiv), and Et_3N (1.23 g, 12.0 mmol, 1.20 equiv) The mixture was allowed to cool to 0 °C, and di-*tert*-butyl dicarbonate (328 mg, 15.0 mmol, 1.50 equiv) in MeCN (5.00 mL) was added dropwise under N_2. The reaction mixture was allowed to stir at room temperature for 12 h and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) to obtain the light green oil (2.90 g, 8.43 mmol, 84.3% yield) which is a known compound. The spectral data match those previously reported[11].

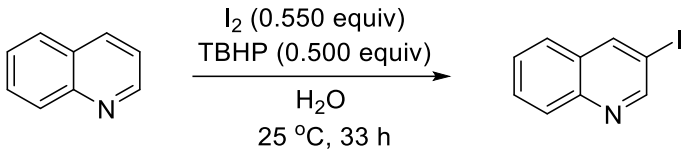
15. Synthesis of 3-iodo-9H-carbazole 1ae：



An oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with potassium iodide (1.24 g, 7.40 mmol, 1.33 equiv), 9*H*-carbazole (1.86 g, 11.1 mmol, 2.00 equiv) and acetic acid (34.0 mL) under N_2. The mixture was allowed to stir at 110 °C for 1 h. The reaction mixture was then cooled to 80 °C and potassium iodate (1.19 g, 5.56 mmol, 1.00 equiv) was slowly added, the temperature was increased to 100 °C, and the reaction was allowed to continue for 10 min. When the reaction was completed, the solution was cooled to room temperature, and water was added. The formed crystals were filtered under reduced pressure to obtain crystals. These crystals were recrystallized using DCM (50.0 mL), affording the final white solid (0.811 g,

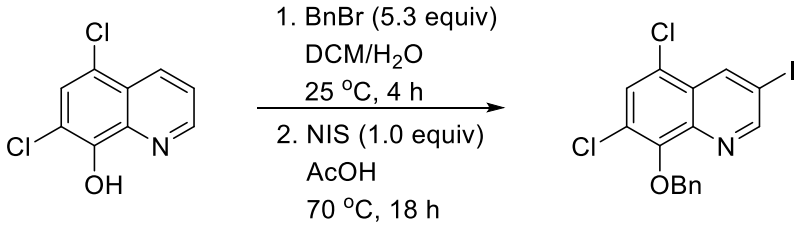
2.77 mmol, 49.8% yield) which is a known compound. The spectral data match those previously reported[13].

16. Synthesis of 3-iodoquinoline 1ag:



An oven-dried 10-mL Schlenk tube, equipped with a stir bar, was charged with quinoline (1.29 g, 10.0 mmol, 1.00 equiv), molecular iodine (1.40 g, 5.50 mmol, 0.550 equiv), and TBHP (0.450 g, 5.00 mmol, 0.500 equiv). H_2O (18.0 μL, 1.00 mmol, 0.100 equiv) was added into the reaction tube and the mixture was allowed to stir at room temperature for 33 h. After completion of the reaction, the reaction mixture was quenched with aqueous saturated $Na_2S_2O_3$ solution (10.0 mL). The reaction mixture was extracted with ethyl acetate (10.0 mL x 3). The combined organic layer was washed with water (10.0 mL x 2), dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure to produce the crude product which was purified by silica gel column chromatography (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) to give the colorless oil (0.976 g, 3.83 mmol, 38.3% yield) which is a known compound. The spectral data match those previously reported[14].

17. Synthesis of 8-(benzyloxy)-5,7-dichloro-3-iodoquinoline 1ah:

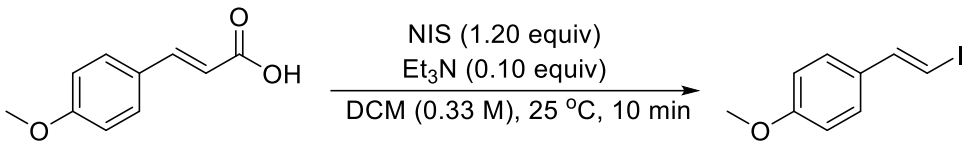


An oven-dried 100-mL Schlenk tube, equipped with a stir bar, was charged with 5,7-dichloroquinolin-8-ol (2.10 g, 3.70 mmol, 1.00 equiv), sodium hydroxide (0.600 g, 15.0 mmol, 4.00 equiv) and *tetra*-butylammonium bromide (83.0 mg, 0.240 mmol, 0.060 equiv), DCM (25.0 mL) and H_2O (25.0 mL). Benzyl bromide (3.40 g, 19.9 mmol, 5.30 equiv) was added dropwise to the solution. The mixture was allowed to stir at room temperature for 4 h. The organic layer was separated and the aqueous layer extracted

with DCM (50.0 mL x 3). The combined organic layers were dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure to produce the crude product which was purified by silica gel column chromatography (eluent: 100:1 to 10:1) to give the 8-(benzyloxy)-5,7-dichloroquinoline as a white solid (1.12 g, 3.68 mmol, 99.0% yield).

An oven-dried 200-mL Schlenk tube, equipped with a stir bar, was charged with 8-(benzyloxy)-5,7-dichloroquinoline (1.17 g, 3.85 mmol, 1.00 equiv) and acetic acid (5.00 mL), *N*-Iodo-succinimide (0.870 g, 3.85 mmol, 1.00 equiv) was added in portions to the stirred solution at 70 °C under argon. The mixture was allowed to stir to 70 °C for 18 h. After cooling to room temperature, the mixture was diluted with water (50.0 mL). The aqueous solution was then washed with ethyl acetate (50.0 mL x 3) and the combined organic layers were washed with 10% aqueous sodium thiosulfate solution (30.0 mL x 3) and 10% aqueous sodium hydrogen carbonate solution (30.0 mL x 3), and H_2O (50.0 mL x 5), 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 / EtOAc = 20:1) to give the 8-(benzyloxy)-5,7-dichloro-3-iodoquinoline as a white solid (0.514 g, 1.20 mmol, 31.2% yield) which is a known compound. The spectral data match those previously reported[11].

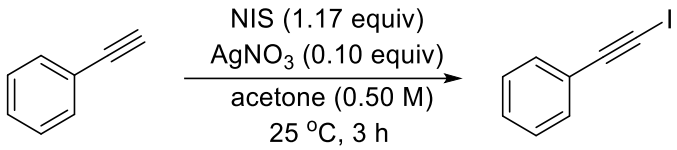
18. Synthesis of (E)-1-(2-iodovinyl)-4-methoxybenzene 1ai:



An oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with 2-Propenoic acid (1.78 g, 10.0 mmol, 1.00 equiv) in DCM (30.0 mL). Then triethylamine (102 mg, 1.00 mmol, 0.100 equiv) was added to the solution. The mixture was allowed to stir at room temperature for 5 minutes. Then NIS (2.70 g, 12.0 mmol, 1.20 equiv) was added. The mixture allowed to stir for 5 minutes and the solvent was removed by rotary evaporation. The residue was purified by flash silica gel chromatography (Eluent: 500:0 petroleum ether: ethyl acetate) and the product was isolated as a white solid (1.28 g, 4.92 mmol, 49.2% yield) which is a known compound.

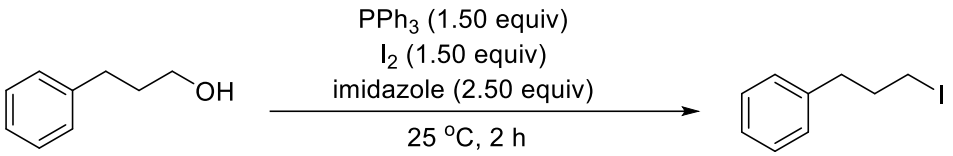
The spectral data match those previously reported.[15]

19. Synthesis of (iodoethynyl)benzene 1aj:



An oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with terminal alkyne (511 mg, 5.00 mmol, 1.00 equiv) in acetone (10.0 mL). NIS (1.32 g, 5.85 mmol, 1.17 equiv) and $AgNO_3$ (85.0 mg, 0.500 mmol, 0.100 equiv) was added to the solution. The reaction mixture was stirred at room temperature for 3 hours. On completion, the solvent was removed under reduced pressure and the residue was filtered through a pad of celite with petroleum ether. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: petroleum ether). The product was isolated as a colorless oil (905 mg, 3.97 mmol, 79.4% yield) and is a known compound. The spectral data match those previously reported.[16]

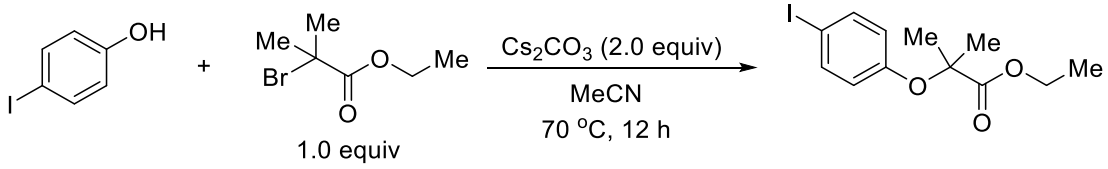
20. Synthesis of (3-Iodopropyl)benzene 1ak:



An oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with triphenylphosphine (2.62 g, 10.0 mmol, 1.50 equiv) and iodine (2.54 g, 10.0 mmol, 1.50 equiv) in DCM (45.0 mL). The reaction mixture was stirred at room temperature for 10 minutes. After addition of imidazole (1.14 g, 16.8 mmol, 2.50 equiv), the mixture was stirred for another 10 minutes, then 3-Phenyl-1-propanol (0.900 g, 6.70 mmol, 1.00 equiv) was added and stirring was continued for 2 hours. The reaction was quenched with a saturated aqueous $Na_2S_2O_3$ solution (30.0 mL). Separation of the layers and extraction of the aqueous layer with DCM (3 x 15.0 mL) followed by drying of the combined organic layers over $MgSO_4$ and removal of the solvent in the vacuum. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate). The product was isolated as a colorless oil (1.53 g, 6.22 mmol, 92.8% yield) and is a known

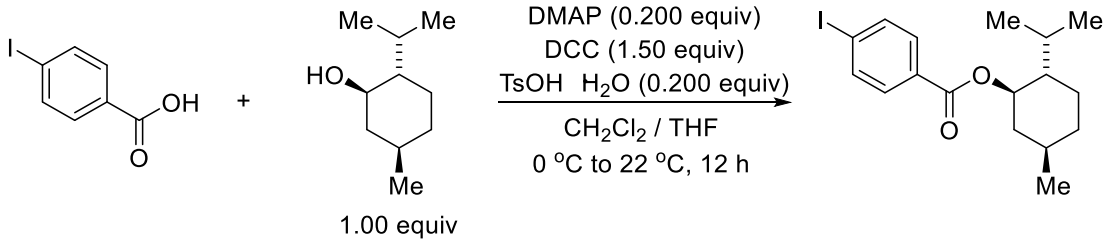
compound. The spectral data match those previously reported[17].

21. Synthesis of ethyl 2-(4-iodophenoxy)-2-methylpropanoate 6a:



An oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with 4-iodophenol (1.54 g, 7.00 mmol, 1.00 equiv), cesium carbonate (4.56 g, 14.0 mmol, 2.00 equiv), ethyl 2-bromoisobutyrate (1.37 g, 7.00 mmol, 1.00 equiv) and MeCN (16.0 mL). The mixture was allowed to stir for 12 h at 70 °C. The mixture was then allowed to cool to room temperature and diluted with water (50.0 mL). The aqueous solution was then washed with ethyl acetate (40.0 mL x 3). The combined organic layers were 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 10:1 petroleum ether: ethyl acetate). The product was isolated as a white solid (1.28 g, 3.83 mmol, 54.7% yield) which is a known compound. The spectral data match those previously reported.[7]

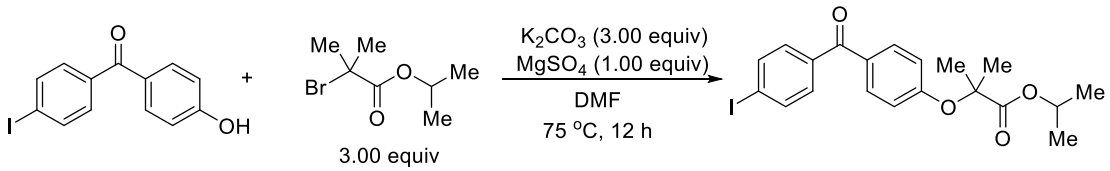
22. Synthesis of (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-iodobenzoate 6b:



An oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with 4-iodobenzoic acid (2.48 g, 10.0 mmol, 1.00 equiv), DCC (3.12 g, 15.0 mmol, 1.50 equiv), DMAP (0.244 g, 2.00 mmol, 0.200 equiv), TsOH·H_2O (0.355 g, 2.00 mmol, 0.200 equiv), and DCM/ THF (5:1 v/v, 50.0 mL). The mixture was allowed to cool to 0 °C with an ice bath. A solution of (L)-menthol (1.56 g, 10.0 mmol, 1.00 equiv) in DCM / THF (5:1 v/v, 24.0 mL) was added dropwise to the mixture. The mixture was allowed

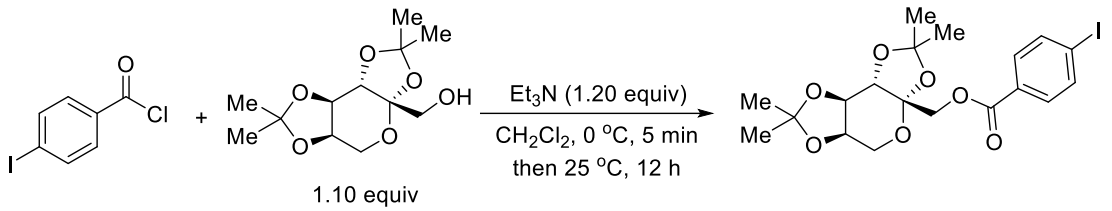
to warm to room temperature and stir for 12 h. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate). The product was isolated as a colorless oil (2.93 g, 7.59 mmol, 75.9% yield) and is a known compound. The spectral data match those previously reported.[7]

23. Synthesis of isopropyl 2-(4-(4-iodobenzoyl)phenoxy)-2-methylpropanoate 6c:



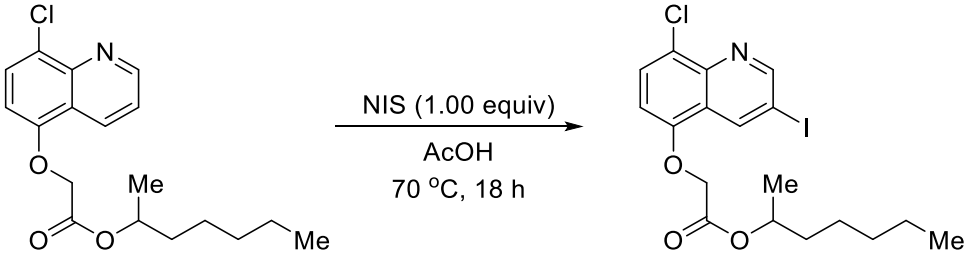
An oven-dried 50-mL round-bottom flask, equipped with a stir bar, was charged with (4-iodophenyl)(4-hydroxyphenyl)methanone (1.62 g, 5.00 mmol, 1.00 equiv), potassium carbonate (2.07 g, 15.0 mmol, 3.00 equiv), magnesium sulfate (0.602 g, 5.00 mmol, 1.00 equiv), isopropyl 2-bromo-2-methylpropanoate (3.21 g, 15.0 mmol, 3.00 equiv), and DMF (10.0 mL). The mixture was allowed to stir for 12 h at 75 °C. The mixture was then allowed to cool to room temperature and diluted with water (50.0 mL). The aqueous solution was then washed with ethyl acetate (50.0 mL x 3). The combined organic layers were 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 10:1 petroleum ether: ethyl acetate). The product was isolated as a white solid (1.34 g, 2.96 mmol, 59.2% yield) which is a known compound. The spectral data match those previously reported.[7]

24. Synthesis of ((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 4-iodobenzoate 6d:



An oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with with 4-iodobenzoyl chloride (1.07 g, 4.00 mmol, 1.00 equiv) in DCM (5.00 mL) were added diacetonefructose (1.15 g, 4.40 mmol, 1.10 equiv) and Et_3N (0.490 g, 4.80 mmol, 1.20 equiv). The mixture was allowed to cool to 0 °C, and di-*tert*-butyl decarbonate (328 mg, 15.0 mmol, 1.50 equiv) in DCM (5.00 mL) was added dropwise under N_2. The reaction mixture was allowed to stir at room temperature for 12 h and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) to obtain the yellow solid (1.45 g, 3.04 mmol, 74.1% yield) which is a known compound. The spectral data match those previously reported.[18]

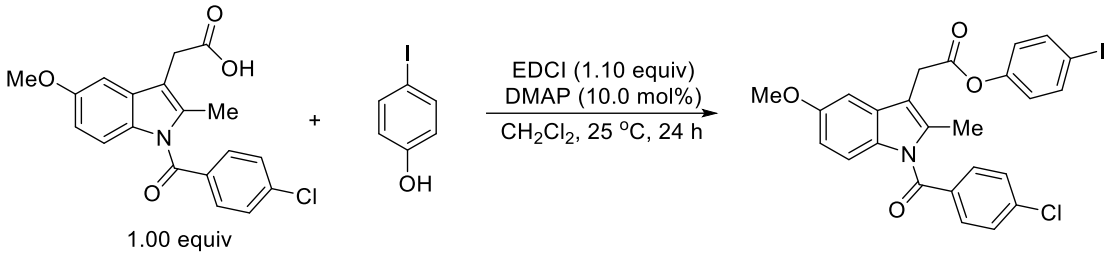
25. Synthesis of heptan-2-yl 2-((8-chloro-2-iodoquinolin-5-yl)oxy) acetate 6e:



An oven-dried 100-mL Schlenk tube, equipped with a stir bar, was charged with heptan-2-yl-2-((5-chloroquinolin-8-yl)oxy)acetate (3.36 g, 10.0 mmol, 1.00 equiv) and acetic acid (10.0 mL), *N*-Iodo-succinimide (2.25 g, 10.0 mmol, 1.00 equiv) was added in portions at 70 °C under argon under N_2. The mixture was heated to 70 °C for 18 h. After cooling to room temperature, the mixture was diluted with water (50.0 mL). The aqueous solution was then washed with ethyl acetate (50.0 mL x 3) and the combined organic layers were washed with 10 % aqueous sodium thiosulfate solution (30.0 mL x 3) and 10 % aqueous sodium hydrogen carbonate solution (30.0 mL x 3), and H_2O (50.0

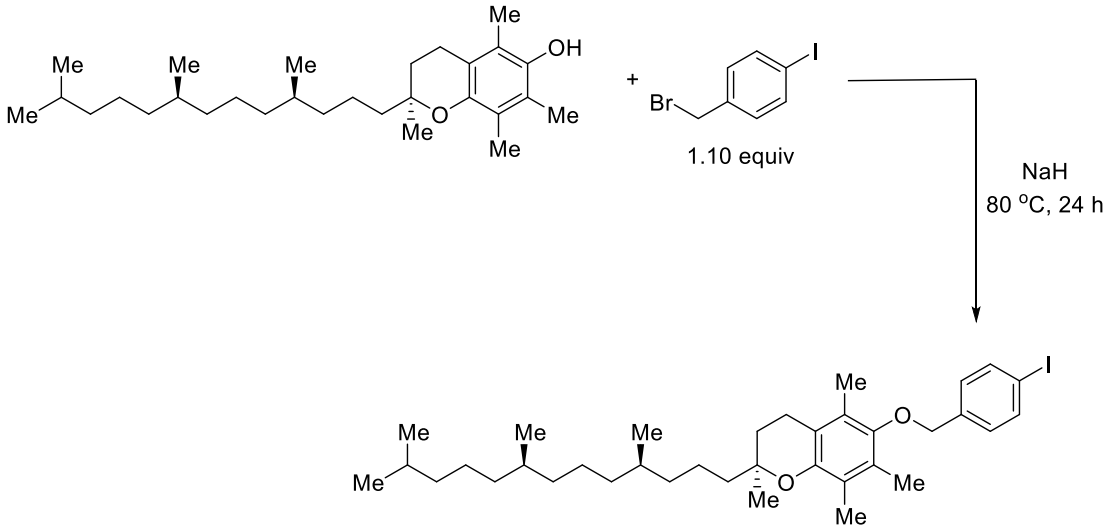
mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) to give the heptan-2-yl-2-((5-chloro-3-iodoquinolin-8-yl)oxy)acetate as a white solid (1.69 g, 3.67 mmol, 36.7% yield), The spectral data match those previously reported[11].

26. Synthesis of 4-iodophenyl 2-(1-(4-chlorobenzoyl)-5-methoxy- 2-methyl-1H-indol-3-yl)acetate 6f:



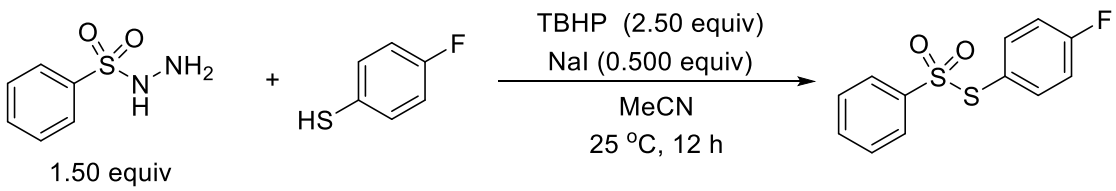
An oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with 4-iodophenol (0.880 g, 4.00 mmol, 1.00 equiv), indometacin (1.43 g, 4.00 mmol, 1.00 equiv), DMAP (48.9 mg, 0.0400 mmol, 0.0100 equiv), DCM (30.0 mL) was added under N_2. The mixture was allowed to stir for 24 h at room temperature. The aqueous solution was then washed with DCM (50.0 mL x 3). The combined organic layers were 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 5:1 petroleum ether: ethyl acetate). The product was isolated as a white solid (1.88 g, 3.36 mmol, 84.0% yield) which is a known compound. The spectral data match those previously reported[19].

27. Synthesis of (S)-6-((4-iodobenzyl)oxy)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chromane 6g：



A oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with sodium hydride (60% in paraffin liquid, 288 mg, 7.20 mmol, 1.20 equiv), (*S*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-ol (2.58 g, 6.00 mmol, 1.00 equiv) and DMF (10.0 mL). The mixture was allowed to cool to 0 °C with an ice bath. 1-(Bromomethyl)-4-iodobenzene (1.95 g, 6.60 mmol, 1.10 equiv) was added in one portion to the mixture. The mixture was allowed to stir for 24 h at 80 °C. The mixture was then allowed to cool to room temperature and diluted with water (50.0 mL). The aqueous solution was then washed with ethyl acetate (50.0 mL x 3). The combined organic layers were 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: 300:1 to 50:1 petroleum ether: ethyl acetate). The product was isolated as a yellow oil (2.20 g, 3.40 mmol, 56.7% yield) and is a known compound. The spectral data match those previously reported[20].

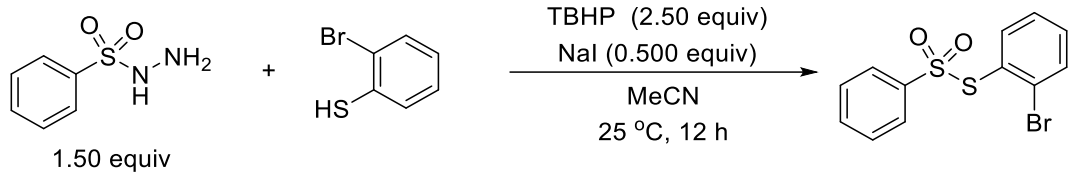
28. Synthesis of *S*-(4-fluorophenyl) benzenesulfonothioate 2b：



A oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with sulfonyl hydrazide (2.06 g, 12.0 mmol, 1.50 equiv), 4-fluorobenzenethiol (1.03 g, 8.00 mmol, 1.00 equiv), sodium iodide (0.600 g, 4.00 mmol, 0.500 equiv) and MeCN

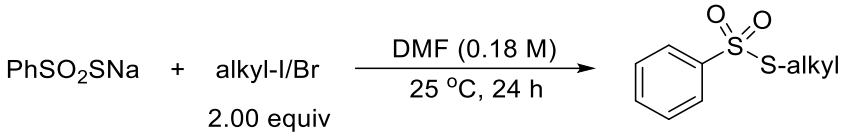
(50.0 mL), *tert*-butyl hydroperoxide (1.80 g, 20.0 mmol, 2.50 equiv) was added to the mixture under N_2. The mixture was allowed to stir for 12 h at 75 °C. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 300:1 to 50:1 petroleum ether: ethyl acetate). The product was isolated as a yellow oil (0.880 g, 3.28 mmol, 40.5% yield) and is a known compound. The spectral data match those previously reported[2].

29. Synthesis of *S*-(2-bromophenyl) benzenesulfonothioate 11：



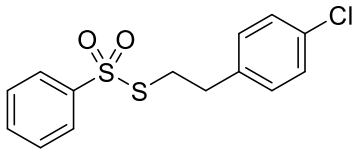
A oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with sulfonyl hydrazide (1.29 g, 7.50 mmol, 1.50 equiv), 2-bromobenzenethiol (0.940 g, 5.00 mmol, 1.00 equiv), sodium iodide (0.375 g, 2.5 mmol, 0.500 equiv) and MeCN (50.0 mL), *tert*-butyl hydroperoxide (1.13 g, 12.5 mmol, 2.50 equiv) was added to the mixture under N_2. The mixture was allowed to stir for 12 h at 25 °C. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 300:1 to 50:1 petroleum ether: ethyl acetate). The product was isolated as a yellow oil (0.950 g, 2.89 mmol, 57.9% yield) and is a known compound. The spectral data match those previously reported[2].

30. <u>General Method B:</u> Synthesis of *S*/*Se*-arylthiosulfonates 2i-o

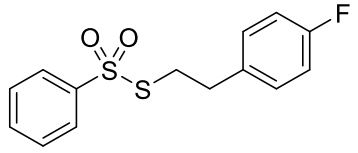


An oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with $PhSO_2SNa$ (0.979g, 5.00 mmol, 1.00 equiv) in DMF (10.0 ml), then alkyl-I/Br (14.0 mmol, 2.00 equiv) was added. The reaction mixture was stirred at room temperature for 24 hours. After the completion of the reaction, as monitored by TLC, the reaction mixture was diluted with ethyl acetate and washed with water. The organic phase was separated, dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated,

and the resulting residue was purified by column chromatography to provide the product. Compound **2i**: colorless liquid, 761.8 mg, 4.05 mmol (prepared on 7.00 mmol), 57.9% yield[21]; compound **2j**: white solid, 0.924 g, 3.50 mmol, 70.0% yield[22]; compound **2k**: colorless liquid, 1.17 g, 4.00 mmol, 80.0% yield[23]. Spectra were consistent with literature data.[19-22]

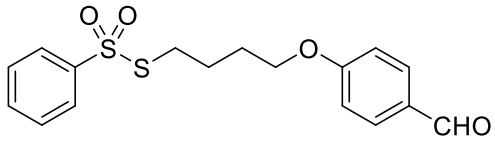


S-(4-chlorophenethyl) benzenesulfonothioate 2l： Prepared according to **General Method B** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (0.780 g, 2.50 mmol, 49.9% yield). **M.p.** = 49.8 – 51.3 °C; **IR** (thin film) 1492 (w), 1446 (w), 1318 (m), 1140 (s), 1091 (w), 1072 (m), 1017 (w), 810 (m), 756 (m), 714 (m), 684 (m) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (2H, d, J = 7.1 Hz), 7.65 (1H, t, J = 7.3 Hz), 7.56 (2H, t, J = 7.6 Hz), 7.25 (2H, d, J = 6.8 Hz), 7.02 (2H, d, J = 8.4 Hz), 3.21 (2H, t, J = 7.6 Hz), 2.90 (2H, t, J = 7.5 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.8, 137.0, 133.8, 132.8, 123.0, 129.4, 128.8, 127.0, 37.1, 34.5; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{14}H_{13}ClNaO_2S_2$: 334.9938, found: 334.9945.

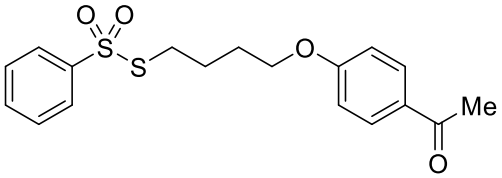


S-(4-fluorophenethyl) benzenesulfonothioate 2m: Prepared according to **General Method B** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (0.731 g, 2.47 mmol, 49.3% yield). **M.p.** = 48.7 – 49.6 °C; **IR** (thin film) 1509 (m), 1447 (w), 1317 (m), 1222 (m), 1139 (s), 1073 (m), 883 (w), 817 (m), 759 (m), 716 (m), 686 (s) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.92 (2H, m), 7.67 – 7.63 (1H, m), 7.58 – 7.54 (2H, m), 7.07 – 7.03 (2H, m), 6.97 – 6.93 (2H, m), 3.21 (2H, t, J = 7.6 Hz), 2.89 (2H, t, J = 7.6 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.9 (d, $J_{C\text{-}F}$ = 246.1 Hz), 144.9, 134.4 (d, $J_{C\text{-}F}$ = 3.5 Hz), 133.9, 130.2 (d, $J_{C\text{-}F}$ = 8.1 Hz), 129.5, 127.1, 115.6 (d, $J_{C\text{-}F}$ = 21.4 Hz), 37.4, 34.5; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –115.77; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{14}H_{13}NaO_2S_2F$: 319.0233, found:

319.0239.



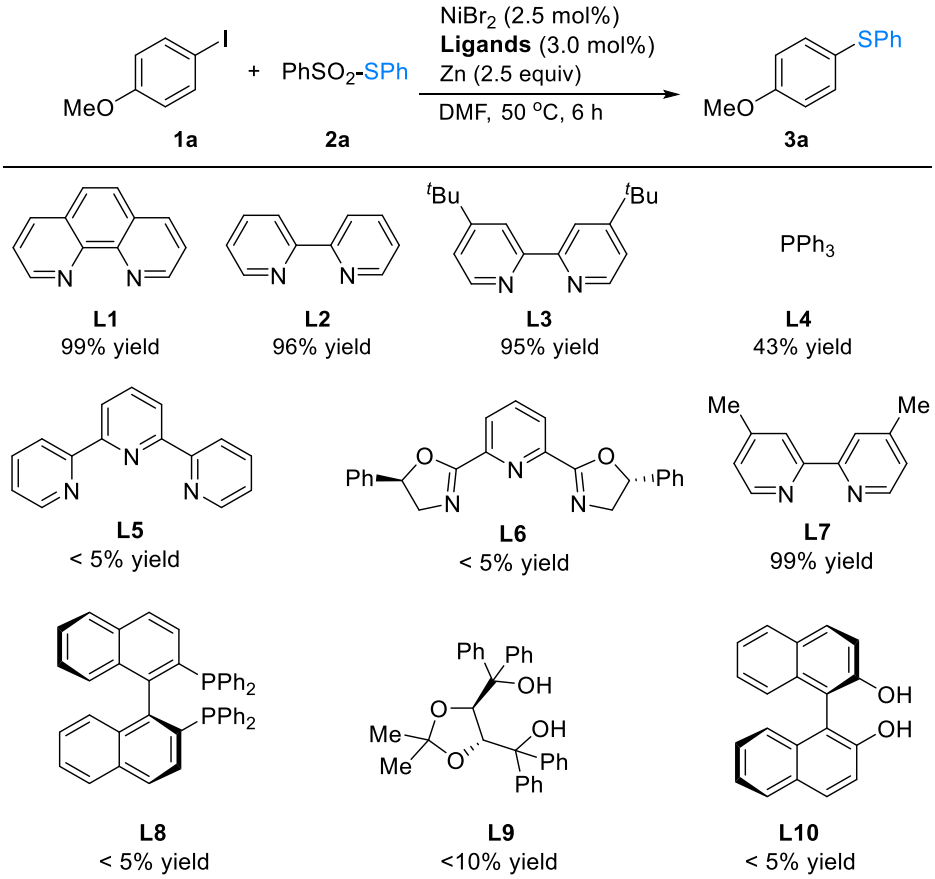
S-(4-(4-formylphenoxy)butyl) benzenesulfonothioate 2n： Prepared according to **General Method B** (Eluent: 20:1 to 1:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (1.31 g, 3.76 mmol, 75.1% yield). **IR** (thin film) 1686 (m), 1598 (s), 1576 (m), 1509 (w), 1447 (w), 1318 (m), 1253 (m), 1139 (s), 1076 (m), 831 (m), 755 (w), 714 (s), 685 (m) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.88 (1H, s), 7.94 (2H, d, J = 7.4 Hz), 7.83 (2H, d, J = 8.7 Hz), 7.66 – 7.64 (1H, m), 7.55 (2H, t, J = 7.7 Hz), 6.94 (2H, d, J = 8.7 Hz), 4.01 – 3.98 (2H, m), 3.11 – 3.08 (2H, m), 1.87 – 1.84 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.9, 163.9, 144.9, 133.8, 132.1, 130.1, 129.4, 127.1, 114.8, 67.4, 35.8, 27.9, 25.7; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{17}H_{19}NaO_4S_2$: 351.0719, found: 351.0725.



S-(4-(4-acetylphenoxy)butyl) benzenesulfonothioate 2o： Prepared according to **General Method B** (Eluent: 20:1 to 1:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (1.49 g, 4.11 mmol, 82.1% yield). **IR** (thin film) 1673 (m), 1599 (m), 1447 (w), 1321 (m), 1252 (m), 1172 (m), 1140 (s), 1076 (m), 835 (w), 755 (w), 715 (s), 685 (m) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.91 (4H, m), 7.66 – 7.62 (1H, m), 7.57 – 7.53 (2H, m), 6.87 (2H, d, J = 8.9 Hz), 3.98 – 3.96 (2H, m), 3.11 – 3.07 (2H, m), 2.56 (3H, s), 1.86 – 1.83 (4H, m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.9, 162.7, 144.8, 133.8, 130.7, 130.4, 129.4, 127.0, 114.2, 67.2, 35.8, 27.9, 26.5, 25.7. **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{18}H_{20}NaO_4S_2$: 387.0695, found: 387.0689.

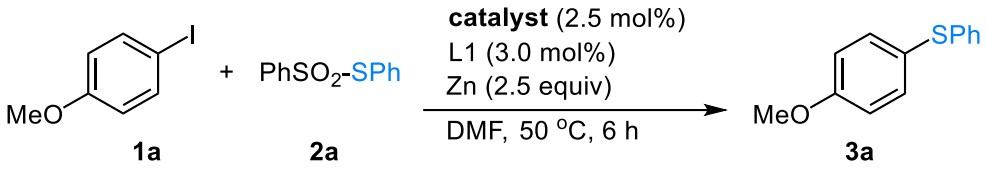
III. Optimization of reaction conditions

Table S1. Evaluation of different ligands



Reaction conditions: **1a** (0.500 mmol), *S*-arylthiosulfonates **2a** (1.00 mmol), $NiBr_2$ (2.50 mol%), Ligand (3.00 mol%), Zn (2.50 equiv), DMF (2.50 mL) at 50 °C for 6 h. Yield was determined by ^1H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table S2. Evaluation of different catalysts

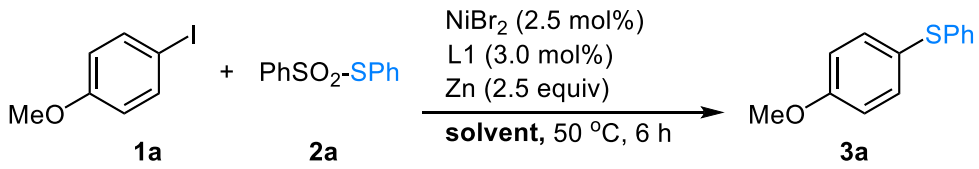


1a **2a** **3a**

Entry	Catalyst	yield of **3a** (%)
1	$NiBr_2$	99
2	$NiCl_2(PPh_3)_2$	97
3	$Ni(OAc)_2$	96
4	$Cu(OAc)_2$	<5
5	$CoBr_2$	<5
6	$Cu(OTf)_2$	<5
7	$PdCl_2(PPh_3)_2$	15
8	$FeCl_2$	<5
9	$PdCl_2$	<5
10	$PbCl_2$	<5
11	$CrCl_3$	<5

Reaction conditions: **1a** (0.500 mmol), *S*-arylthiosulfonates **2a** (1.00 mmol), catalyst (2.50 mol%), Ligand L1 (3.00 mol%), Zn (2.50 equiv), DMF (2.50 mL) at 50 °C for 6 h. Yield was determined by ^1H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table S3. Evaluation of different solvents

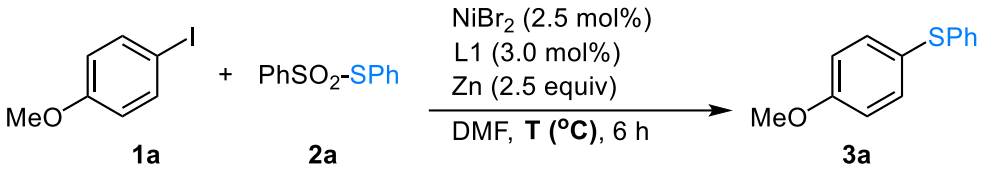


1a **2a** **3a**

Entry	solvent	yield of **3a** (%)
1	DMF	99
2	PhMe	<5
3	DCM	<5
4	MeCN	71
5	DMAc	96
6	NMP	97
7	DMSO	96
8	Ethyl acetate	<5
9	MeOH	98
10	Hexane	<5

Reaction conditions: **1a** (0.500 mmol), *S*-arylthiosulfonates **2a** (1.00 mmol), $NiBr_2$ (2.50 mol%), Ligand **L1** (3.00 mol%), Zn (2.50 equiv), solvent (2.50 mL) at 50 °C for 6 h. Yield was determined by ^1H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table S4. Evaluation of different temperature

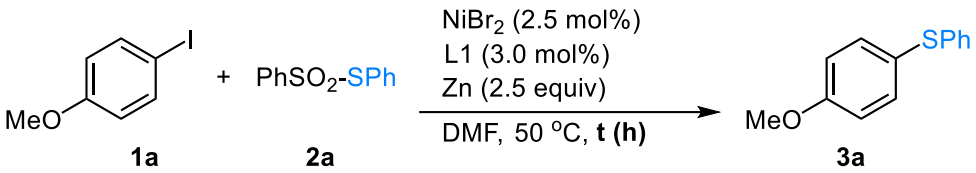


1a **2a** **3a**

Entry	T (°C)	yield of **3a** (%)
1	20	72
2	30	73
3	40	96
4	50	99

Reaction conditions: **1a** (0.500 mmol), *S*-arylthiosulfonates **2a** (1.00 mmol), $NiBr_2$ (2.50 mol%), Ligand **L1** (3.00 mol%), Zn (2.50 equiv), DMF (2.50 mL) at different temperature for 6 h. Yield was determined by ^1H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table S5. Evaluation of different reaction time



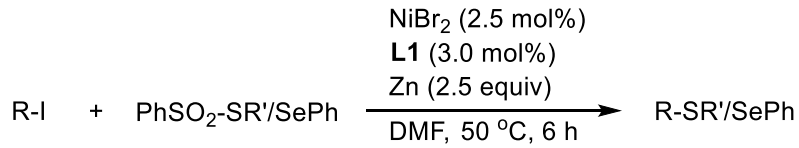
1a **2a** **3a**

Entry	t (h)	yield of **3a** (%)
1	2	86
2	3	91
3	4	89
4	5	97
5	6	99

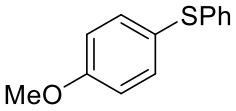
Reaction conditions: **1a** (0.500 mmol), *S*-arylthiosulfonates **2a** (1.00 mmol), $NiBr_2$ (2.50 mol%), Ligand **L1** (3.00 mol%), Zn (2.50 equiv), DMF (2.5 mL) at 50 °C for different time. Yield was determined by ^1H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

IV. Substrate scope

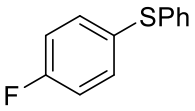
General Method C:



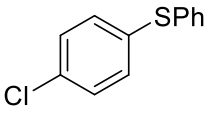
A 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with R-I (117 mg, 0.500 mmol, 1.00 equiv), *S*-phenyl benzenesulfonothioate (250 mg, 1.0 mmol, 2.00 equiv), Zn (82.0 mg, 1.25 mmol, 2.50 equiv), $NiBr_2$ (2.80 mg, 0.0125 mmol, 0.025 equiv), 1,10-phenanthroline (2.70 mg, 0.0150 mmol, 0.030 mmol). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for 6 h at 50 °C. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 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.



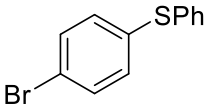
(4-Methoxyphenyl)(phenyl)sulfane 3a: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (98.1 mg, 0.454 mmol, 90.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (2H, d, J = 8.7 Hz), 7.22 – 7.20 (2H, m), 7.17 – 7.11 (3H, m), 6.88 (2H, d, J = 8.8 Hz), 3.79 (3H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.9, 138.7, 135.5, 129.0, 128.2, 125.8, 124.3, 115.1, 55.4. Spectra were consistent with literature data[24].



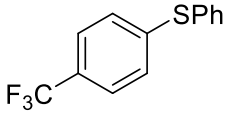
(4-Fluorophenyl)(phenyl)sulfane 3b: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (85.5 mg, 0.419 mmol, 83.8% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.35 (2H, m), 7.27 – 7.26 (4H, m), 7.22 – 7.19 (1H, m), 7.03 – 6.99 (2H, m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4 (d, J = 248.7 Hz), 136.8, 134.2 (d, J = 8.2 Hz), 130.3 (d, J = 3.4 Hz), 130.0, 129.3, 126.9, 116.5 (d, J = 22 Hz). Spectra were consistent with literature data[24].



(4-Chlorophenyl)(phenyl)sulfane 3c: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (103.0 mg, 0.467 mmol, 93.4% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.21 (9H, m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.2, 134.7, 133.1, 132.1, 131.4, 129.4, 129.4, 127.5. Spectra were consistent with literature data[24].

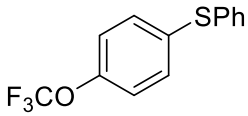


Bromophenyl)(phenyl)sulfane 3d: Prepared according to **General Method B** (Eluent: 100:0 to 500:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (132.5 mg, 0.499 mmol, 99% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.38 (2H, m), 7.35 – 7.26 (5H, m), 7.16 (2H, d, J = 8.1 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.6, 134.9, 132.3, 132.2, 131.7, 129.5, 127.7, 121.0. Spectra were consistent with literature data[24].

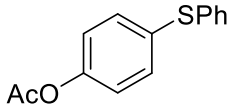


Phenyl(4-(trifluoromethyl)phenyl)sulfane 3e: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (113.0 mg, 0.444 mmol, 88.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.45 (4H, m), 7.38 – 7.36 (3H, m), 7.25 (2H, d, J = 8.2 Hz). **^{13}C**

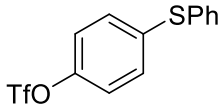
NMR (101 MHz, $CDCl_3$) δ 143.0 (q, J = 1.8 Hz), 133.7, 132.6, 129.8, 128.8, 128.4, 128.0 (q, J = 32.9 Hz), 125.9 (q, J = 3.8 Hz), 125.9 (q, J = 272.3 Hz). Spectra were consistent with literature data[24].



Phenyl(4-(trifluoromethoxy)phenyl)sulfane 3f: Prepared according to **General Method C** (Eluent: 500:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow oil (111.1 mg, 0.411 mmol, 82.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.35 (2H, m), 7.33 – 7.26 (5H, m), 7.12 – 7.10 (2H, d, J = 9.0 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.2 (q, J = 2.2 Hz), 135.2, 134.9, 131.8, 131.8, 129.6, 127.8, 121.8, 120.6 (q, J = 256.5 Hz). Spectra were consistent with literature data[25].

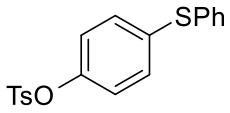


4-(Phenylthio)phenyl acetate 3g: Prepared according to **General Method C** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (107.3 mg, 0.439 mmol, 87.8% yield). **IR** (thin film) 1760 (s), 1487 (m), 1368 (m), 1191 (s), 1082 (w), 1013 (m), 907 (m), 842 (m), 740 (s), 689 (s) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.22 (7H, m), 7.04 – 7.01 (2H, m), 2.27 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.3, 149.9, 135.8, 132.9, 132.3, 130.9, 129.3, 127.2, 122.5, 21.2; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{14}H_{12}NaO_2S$: 267.0450, found: 267.0458.

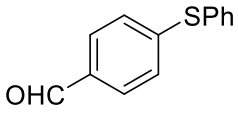


4-(Phenylthio)phenyl trifluoromethanesulfonate 3h: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (134.9 mg, 0.403 mmol, 80.6% yield). **IR** (thin film) 1583 (m), 1483 (s), 1422 (w), 1250 (w), 1206 (s), 1136 (s), 1082 (m), 1014 (w), 880 (s), 828 (m), 781 (w), 755 (m), 690 (w), 632 (m) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.41 (2H, m), 7.39 – 7.33 (3H, m), 7.28 – 7.24 (2H, m), 7.15 (2H, d, J = 8.8 Hz);

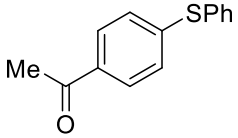
^{19}F NMR (471 MHz, $CDCl_3$) δ –72.8; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.0, 138.5, 133.3, 133.0, 130.7, 129.8, 128.5, 118.8 (q, $J_{C\text{-}F}$ = 322.3 Hz), 122.1, 29.8; **MS** (EI): m/z (%) 334, 201, 171, 129, 69, 45. **HRMS** calc'd for $C_{13}H_9F_3O_3S_2$: 333.9943, found:333.9940 .



4-(Phenylthio)phenyl 4-methylbenzenesulfonate 3i: Prepared according to **General Method C** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (164.2 mg, 0.461 mmol, 92.2% yield). **IR** (thin film) 1483 (m), 1372 (m), 1198 (m), 1175 (s), 1152 (s), 1092 (m), 1015 (w), 858 (s), 748 (s), 671 (s) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (2H, d, J = 8.3 Hz), 7.32 – 7.28 (7H, m), 7.17 (2H, d, J = 8.7 Hz), 6.88 (2H, d, J = 8.7 Hz), 2.42 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.3, 145.6, 135.7, 134.4, 132.2, 131.9, 131.2, 129.9, 129.5, 128.5, 127.8, 123.2, 21.8; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{19}H_{16}NaO_3S_2$: 379.0433, found: 379.0446.

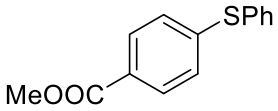


4-(Phenylthio)benzaldehyde 3j: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (83.3 mg, 0.389 mmol, 77.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.88 (1H, s), 7.70 (2H, d, J = 8.4 Hz), 7.52 – 7.50 (2H, m), 7.42 – 7.40 (3H, m), 7.22 (2H, d, J = 8.4 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.2, 147.3, 134.4, 133.7, 131.3, 130.2, 129.9, 129.2, 127.2; Spectra were consistent with literature data[24].

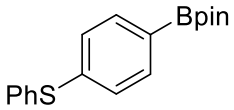


1-(4-(Phenylthio)phenyl)ethan-1-one 3k: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (86.2 mg, 0.378 mmol, 75.6% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (2H, d, J = 8.4 Hz), 7.51 – 7.49 (2H, m), 7.41 – 7.39 (3H, m), 7.21 (2H,

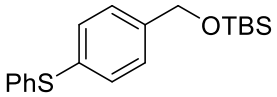
d, J = 8.5 Hz), 2.55 (3H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.1, 144.9, 134.4, 133.89, 132.0, 129.7, 128.9, 128.8, 127.4, 26.5. Spectra were consistent with literature data[24].



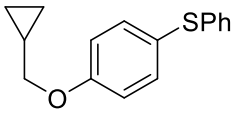
Methyl 4-(phenylthio)benzoate 3l: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (107.7 mg, 0.441 mmol, 88.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (2H, d, J = 8.5 Hz), 7.50 – 7.48 (2H, m), 7.40 – 7.37 (3H, m), 7.20 (2H, d, J = 8.5 Hz), 3.88 (3H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 144.4, 133.8, 132.3, 130.1, 129.7, 128.7, 127.5, 127.5, 52.1. Spectra were consistent with literature data[24].



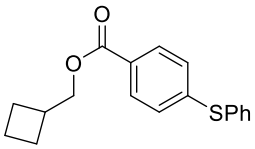
4,4,5,5-Tetramethyl-2-(4-(phenylthio)phenyl)-1,3,2-Dioxaborolane 3m: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (123.8 mg, 0.396 mmol, 79.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (2H, m, J = 8.1 Hz), 7.39 – 7.38 (2H, m), 7.33 – 7.26 (5H, m), 1.32 (12H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.5, 135.5, 134.6, 132.2, 129.4, 129.0, 127.7, 83.9, 25.0 (the signal of one carbon connected to B atom was not observed); Spectra were consistent with literature data[26].



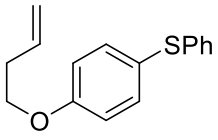
***tert*-Butyldimethyl((4-(phenylthio)benzyl)oxy)silane 3n:** Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (130.4 mg, 0.394 mmol, 78.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.37 (2H, m), 7.35 – 7.28 (6H, m), 7.25 – 7.23 (1H, m), 4.77 (2H, s), 0.99 (9H, s), 0.15 (6H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.9, 136.6, 133.6, 131.7, 130.5, 129.2, 127.0, 126.8, 64.6, 26.1, 18.5, – 5.1; Spectra were consistent with literature data[26].



(4-(Cyclopropylmethoxy)phenyl)(phenyl)sulfane 3o: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (114.4 mg, 0.446 mmol, 89.2% yield). **IR** (thin film) 1592 (w), 1492 (s), 1283 (w), 1239 (s), 1170 (m), 1006 (s), 827 (m), 738 (s), 689 (m) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (2H, d, J = 8.4 Hz), 7.25 – 7.13 (5H, m), 6.89 (2H, d, J = 8.4 Hz), 3.80 (2H, d, J = 7.0 Hz), 1.29 – 1.25 (1H, m), 0.68 – 0.63 (2H, m), 0.36 – 0.35 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4, 138.8, 135.5, 129.0, 128.2, 125.8, 124.2, 115.7, 73.0, 10.3, 3.4; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{16}H_{17}OS$: 257.1000, found: 257.1022.

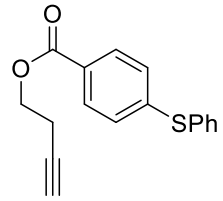


Cyclobutylmethyl 4-(phenylthio)benzoate 3p: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (145.6 mg, 0.488 mmol, 97.6% yield). **IR** (thin film) 1714 (s), 1594 (m), 1475 (w), 1399 (w), 1266 (s), 1177 (m), 1106 (s), 1014 (m), 845 (w), 747 (m), 689 (s) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (2H, d, J = 8.5 Hz), 7.49 – 7.47 (2H, m), 7.39 – 7.35 (3H, m), 7.21 (2H, d, J = 8.5 Hz), 4.27 (2H, d, J = 6.6 Hz), 2.75 – 2.71 (1H, m), 2.13 – 2.06 (2H, m), 1.96 – 1.82 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.3, 144.2, 133.6, 132.5, 130.1, 129.6, 128.6, 127.9, 127.6, 68.6, 34.2, 24.8, 18.5; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{18}H_{18}NaO_2S$: 321.0920, found: 321.0930.

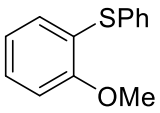


(4-(But-3-en-1-yloxy)phenyl)(phenyl)sulfane 3q: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (110.3 mg, 0.430 mmol, 86.0% yield). **M.p.** = 32.6 – 33.7 ^{o}C; **IR** (thin film) 1583 (m), 1492 (m), 1477 (w), 1282 (w), 1241 (s), 1174 (m), 1082

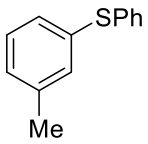
(w), 1023 (s), 923 (m), 829 (m), 738 (s), 690 (s) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (2H, d, J = 8.8 Hz), 7.23 – 7.18 (2H, m), 7.16 – 7.09 (3H, m), 6.87 (2H, d, J = 8.8 Hz), 5.89 (1H, ddt, J = 17.0, 10.2, 6.7 Hz), 5.19 – 5.09 (2H, m), 3.99 (2H, t, J = 6.7 Hz), 2.56 – 2.51 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 138.7, 135.5, 134.3, 129.0, 128.2, 125.8, 124.3, 117.3, 115.6, 67.4, 3 3.6; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{16}H_{16}NaOS$: 279.0814, found: 279.0808.



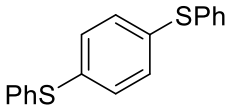
But-3-yn-1-yl 4-(phenylthio)benzoate 3r: Prepared according to **General Method C** (Eluent: 200:1 to 30:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (88.8 mg, 0.314 mmol, 62.8% yield). **M.p.** = 42.2 – 43.4 ^oC; **IR** (thin film) 1714 (s), 1593 (m), 1475 (w), 1400 (w), 1266 (s), 1178 (m), 1106 (s), 1014 (m), 845 (w), 748 (m), 689 (m) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (2H, d, J = 8.5 Hz), 7.51 – 7.47 (2H, m), 7.42 – 7.37 (3H, m), 7.20 (2H, d, J = 8.6 Hz), 4.40 (2H, t, J = 6.8 Hz), 2.64 (2H, td, J = 6.8, 2.7 Hz), 2.02 (1H, t, J = 2.7 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 144.8, 133.9, 132.3, 130.3, 129.8, 128.8, 127.6, 127.3, 80.1, 70.1, 62.6, 19.2. **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{17}H_{14}NaO_2S$: 305.0607, found: 305.0618.



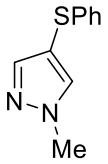
(2-Methoxyphenyl)(phenyl)sulfane 3s: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (94.0 mg, 0.435 mmol, 87.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.32 (2H, m), 7.29 – 7.25 (2H, m), 7.23 – 7.18 (2H, m), 7.07 (1H, dd, J = 7.7, 1.7 Hz), 6.87 – 6.82 (2H, m), 3.81 (3H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.3, 134.5, 131.6, 131.5, 129.2, 128.4, 127.1, 124.1, 121.3, 110.9, 55.9. Spectra were consistent with literature data[24].



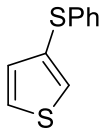
Phenyl(*m*-tolyl)sulfane 3t: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (81.2 mg, 0.405 mmol, 81.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (4H, m), 7.23 – 7.14 (4H, m), 7.05 (1H, d, J = 7.1 Hz), 2.29 (3H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.2, 136.2, 135.3, 132.0, 130.9, 129.3, 129.2, 128.5, 128.2, 127.0, 21.4. Spectra were consistent with literature data[24].



1,4-Bis(phenylthio)benzene 3u: Prepared according to **General Method C** (5.0 equiv Zn, 4.0 equiv $PhSO_2SPh$, 5.0 mol% $NiBr_2$， 6.0 mol% ligand were used.) (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (111.6 mg, 0.379 mmol, 75.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.34 (4H, m), 7.32 – 7.28 (4H, m), 7.27 – 7.21 (6H, m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.1, 135.0, 131.6, 131.3, 129.4, 127.5. Spectra were consistent with literature data[24].

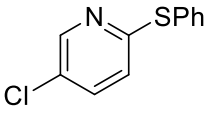


1-Methyl-4-(phenylthio)-1H-pyrazole 3v: Prepared according to **General Method C** (time = 12 h) (Eluent: 100:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (66.5 mg, 0.350 mmol, 70.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (1H, s), 7.50 (1H, s), 7.22 – 7.18 (2H, m), 7.12 – 7.07 (3H, m), 3.92 (3H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.8, 139.0, 135.3, 128.9, 126.2, 125.3, 107.4, 39.4; Spectra were consistent with literature data[26].

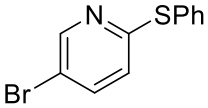


3-(Phenylthio)thiophene 3w: Prepared according to **General Method C** (time:12 h) (Eluent: 100:0 to 500:1 petroleum ether: ethyl acetate) and the title compound was

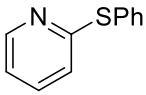
isolated as a colorless oil (86.7 mg, 0.451 mmol, 90.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (2H, m), 7.25 – 7.18 (4H, m), 7.16 – 7.12 (1H, m), 7.02 (1H, dd, J = 4.9, 1.4 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.4, 131.3, 129.4, 129.1, 128.5, 128.3, 126.9, 126.2. Spectra were consistent with literature data[24].



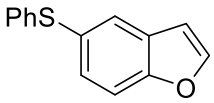
5-Chloro-2-(phenylthio)pyridine 3x: Prepared according to **General Method C** (Eluent: 100:0 to 500:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (58.7 mg, 0.265 mmol, 53.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (1H, d, J = 2.6 Hz), 7.59 – 7.57 (2H, m), 7.44 – 7.40 (4H, m), 6.83 (1H, d, J = 8.6 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.8, 148.3, 136.6, 135.1, 130.7, 129.9, 129.5, 128.4, 122.2; Spectra were consistent with literature data[27].



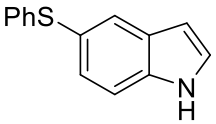
5-Bromo-2-(phenylthio)pyridine 3y: Prepared according to **General Method C** (Eluent: 500:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (66.5 mg, 0.250 mmol, 50.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (1H, d, J = 2.4 Hz), 7.59 – 7.53 (3H, m), 7.44 – 7.42 (3H, m), 6.77 (1H, d, J = 8.6 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.9, 151.8, 139.9, 135.2, 130.8, 129.9, 129.5, 127.5, 121.6; Spectra were consistent with literature data[28].



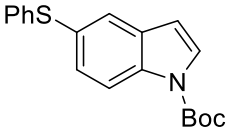
2-(Phenylthio)pyridine 3z: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (53.6 mg, 0.286 mmol, 57.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (1H, d, J = 4.0 Hz), 7.60 – 7.58 (2H, m), 7.46 – 7.39 (4H, m), 7.00 – 6.97 (1H, m), 6.87 (1H, d, J = 8.1 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.7, 149.7, 136.8, 135.1, 131.1, 129.8, 129.2, 121.4, 120.0. Spectra were consistent with literature data[27].



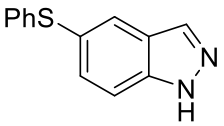
5-(Phenylthio)benzofuran 3aa: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (105.5 mg, 0.466 mmol, 93.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (1H, d, J = 1.8 Hz), 7.62 (1H, d, J = 2.3 Hz), 7.47 (1H, d, J = 8.5 Hz), 7.39 (1H, dd, J = 8.5, 1.9 Hz), 7.25 – 7.20 (4H, m), 7.17 – 7.13 (1H, m), 6.71 (1H, d, J = 2.1 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.8, 146.0, 138.3, 129.8, 129.1, 129.0, 128.7, 127.9, 126.5, 126.2, 112.5, 106.6. Spectra were consistent with literature data[29].



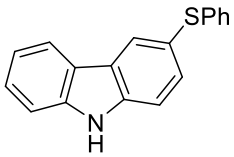
6-(Phenylthio)-1H-indole 3ab: Prepared according to **General Method C** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a light yellow solid (97.1 mg, 0.431 mmol, 86.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (1H, s), 7.84 – 7.83 (1H, m), 7.32 – 7.27 (2H, m), 7.20 – 7.13 (5H, m), 7.10 – 7.05 (1H, m), 6.51 – 6.49 (1H, m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.7, 135.7, 128.9, 128.9, 128.2, 127.7, 127.4, 125.4, 125.3, 122.9, 112.3, 102.8. Spectra were consistent with literature data[30].



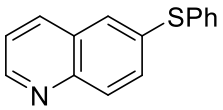
***tert*-Butyl 6-(phenylthio)-1H-indole-1-carboxylate 3ac:** Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (136.4 mg, 0.419 mmol, 83.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (1H, d, J = 8.5 Hz), 7.69 (1H, d, J = 1.7 Hz), 7.62 (1H, d, J = 3.7 Hz), 7.41 (1H, dd, J = 8.6, 1.8 Hz), 7.26 – 7.20 (4H, m), 7.17 – 7.13 (1H, m), 6.53 (1H, d, J = 3.7 Hz), 1.67 (9H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.7, 138.4, 134.9, 131.7, 129.5, 129.1, 128.9, 127.6, 126.9, 126.2, 126.1, 116.2, 107.1, 84.2, 28.3. Spectra were consistent with literature data[26].



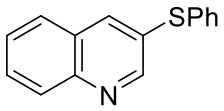
5-(Phenylthio)-1H-indazole 3ad: Prepared according to **General Method C** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a light yellow solid (85.7 mg, 0.379 mmol, 75.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.30 (1H, s), 8.09 (1H, s), 7.92 (1H, s), 7.50 – 7.44 (1H, m), 7.27 – 7.14 (5H, m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.7, 138.1, 134.6, 132.3, 129.2, 128.9, 126.4, 126.2, 126.0, 124.2, 111.1. Spectra were consistent with literature data[31].



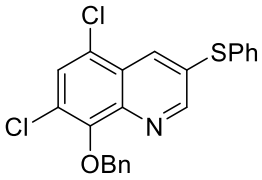
3-(Phenylthio)-9H-carbazole 3ae: Prepared according to **General Method C** (Eluent: 50:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (86.3 mg, 0.313 mmol, 62.6% yield). **M.p.** = 186.7 – 187.4 ^{o}C; **IR** (thin film) 3396 (m), 1579 (w), 1451 (m), 1333 (w), 1268 (w), 1239 (w), 885 (w), 805 (s), 752 (s), 728 (s), 688 (s) cm^{-1}; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.52 (1H, s), 8.38 (1H, d, J = 1.8 Hz), 8.18 (1H, d, J = 7.8 Hz), 7.58 – 7.50 (3H, m), 7.44 – 7.40 (1H, m), 7.28 – 7.24 (2H, m), 7.20 – 7.09 (4H, m); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 140.1, 139.9, 139.4, 132.0, 129.0, 127.1, 126.8, 126.2, 125.4, 123.7, 121.9, 120.6, 120.1, 119.1, 112.3, 111.2; **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{18}H_{14}NS$: 276.0847, found: 276.0847.



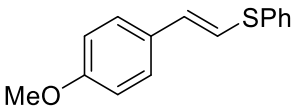
6-(Phenylthio)quinoline 3af: Prepared according to **General Method C** (Eluent: 50:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (101.4 mg, 0.427 mmol, 85.4% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.85 (1H, dd, J = 4.2, 1.8 Hz), 8.01 – 7.96 (2H, m), 7.67 (1H, d, J = 2.1 Hz), 7.58 (1H, dd, J = 8.8, 2.1 Hz), 7.44 – 7.42 (2H, m), 7.36 – 7.30 (4H, m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.4, 147.2, 135.3, 135.4, 134.4, 132.1, 131.5, 130.3, 129.5, 128.7, 128.0, 127.9, 121.7. Spectra were consistent with literature data[32].



3-(Phenylthio)quinoline 3ag: Prepared according to **General Method C** (Eluent: 50:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow oil (68.3 mg, 0.288 mmol, 57.6% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.81 (1H, d, J = 2.3 Hz), 8.09 – 8.05 (2H, m), 7.70 – 7.66 (2H, m), 7.54 – 7.50 (1H, m), 7.40 – 7.38 (2H, m), 7.35 – 7.28 (3H, m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.3, 146.8, 137.2, 134.4, 131.5, 130.1, 129.7, 129.6, 129.3, 128.3, 127.9, 127.4, 127.3. Spectra were consistent with literature data[33].

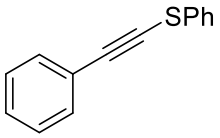


8-(Benzyloxy)-5,7-dichloro-3-(phenylthio)quinoline 3ah: Prepared according to **General Method C** (time = 12 h) (Eluent: 500:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (127.4 mg, 0.309 mmol, 61.8% yield). **M.p.** = 81.2 – 82.4 ^{o}C; **IR** (thin film) 1572 (w), 1439 (m), 1344 (s), 1242 (w), 1203 (w), 1174 (w), 1109 (m), 1065 (m), 957 (m), 904 (s), 890 (m), 858 (m), 762 (w), 746 (m), 731 (s), 698 (s), 626 (m) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.82 (1H, d, J = 2.2 Hz), 8.32 (1H, d, J = 2.2 Hz), 7.60 – 7.58 (3H, m), 7.51 – 7.49 (2H, m), 7.41 – 7.33 (6H, m), 5.43 (2H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.5, 150.5, 141.9, 137.0, 133.2, 132.8, 132.6, 132.4, 129.9, 128.8, 128.7, 128.5, 128.3, 126.8, 126.4, 125.5, 29.8. **HRMS** (ESI$^+$) $[M+H]^+$ calc'd for $C_{22}H_{16}Cl_2NOS$: 412.0330, found: 412.0331.

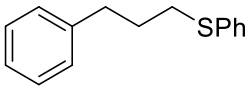


(*E*)-(4-methoxystyryl)(phenyl)sulfane 3ai： Prepared according to **General Method C** (Eluent: 500:0 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (103.0 mg, 0.425 mmol, 85.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (2H, d, J = 7.0 Hz), 7.36 – 7.27 (4H, m), 7.24 (1H, d, J = 8.0 Hz), 6.86 (2H, d, J = 8.7 Hz), 6.79 – 6.66 (2H, m), 3.81 (3H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4, 136.0,

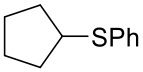
132.8, 129.4, 129.3, 129.2, 127.5, 126.7, 120.1, 114.2, 55.4. Spectra were consistent with literature data.[34]



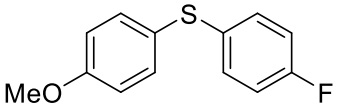
(Phenyl(phenylethynyl)sulfane 3aj： Prepared according to **General Method C** (Eluent: 500:0 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (58.0 mg, 0.276 mmol, 55.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (4H, m), 7.40 – 7.20 (6H, m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.0, 131.9, 129.4, 128.8, 128.5, 126.6, 126.3, 123.0, 98.0, 75.5. Spectra were consistent with literature data.[35]



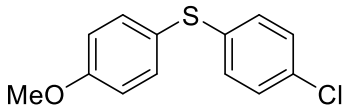
Phenyl(3-phenylpropyl)sulfane 3ak： Prepared according to **General Method C** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (81.9 mg, 0.359 mmol, 71.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.13 (9H, m), 2.90 (2H, t, J = 7.3 Hz), 2.74 (2H, t, J = 7.5 Hz), 1.99 – 1.91 (2H, m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.4, 136.6, 129.1, 128.9, 128.6, 128.5, 126.1, 125.9, 34.8, 32.9, 30.7. Spectra were consistent with literature data[36].



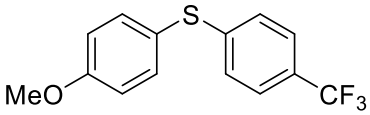
Cyclopentyl(phenyl)sulfane 3al： Prepared according to **General Method C** (Eluent: 500:0 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (72.2 mg, 0.276 mmol, 81.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (2H, d, J = 7.7 Hz), 7.29 (2H, d, J = 7.4 Hz), 7.19 – 7.16 (1H, m), 3.62 – 3.57 (1H, m), 2.08 – 2.02 (2H, m), 1.88 – 1.71 (2H, m), 1.66 – 1.59 (4H, m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.4, 130.0, 128.9, 126.0, 45.9, 33.7, 24.9. Spectra were consistent with literature data[37].



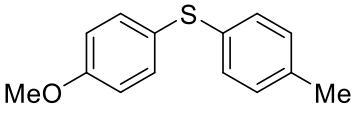
(4-Fluorophenyl)(4-methoxyphenyl)sulfane 4a: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (90.1 mg, 0.385 mmol, 77.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (2H, d, J = 8.8 Hz), 7.19 – 7.16 (2H, m), 6.95 – 6.90 (2H, m), 6.86 (2H, d, J = 8.8 Hz), 3.77 (3H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.7 (d, $J_{C\text{-}F}$ = 246.4 Hz), 159.8, 134.6, 133.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 131.1 (d, $J_{C\text{-}F}$ = 8.0 Hz), 125.28, 116.2 (d, $J_{C\text{-}F}$ = 22.0 Hz), 115.1, 55.4. Spectra were consistent with literature data[38].



(4-Chlorophenyl)(4-methoxyphenyl)sulfane 4b: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (117.6 mg, 0.469 mmol, 93.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (2H, d, J = 8.8 Hz), 7.16 (2H, d, J = 8.6 Hz), 7.05 (2H, d, J = 8.6 Hz), 6.87 (2H, d, J = 8.8 Hz), 3.78 (3H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.1, 137.5, 135.6, 131.6, 129.3, 129.1, 123.8, 115.2, 55.5; Spectra were consistent with literature data[38].

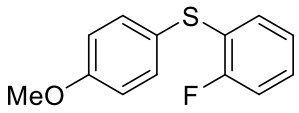


(4-Methoxyphenyl)(4-(trifluoromethyl)phenyl)sulfane 4c: Prepared according to **General Method A** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (117.3 mg, 0.413 mmol, 82.6% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (4H, m), 7.12 (2H, d, J = 8.2 Hz), 6.93 (2H, d, J = 8.6 Hz), 3.81 (3H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.7, 145.0, 136.9, 127.2 (q, $J_{C\text{-}F}$ = 32.7 Hz), 126.5, 125.7 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.4 (q, $J_{C\text{-}F}$ = 272.7 Hz), 121.7, 115.5, 55.5. Spectra were consistent with literature data[38].

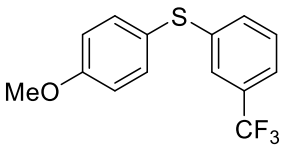


(4-Methoxyphenyl)(*p*-Tolyl)sulfane 4d: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (110.7 mg, 0.481 mmol, 96.2% yield). **^{1}H NMR** (400 MHz,

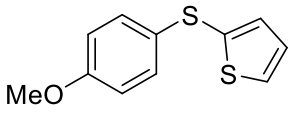
$CDCl_3$) δ 7.37 (2H, d, J = 8.7 Hz), 7.14 (2H, d, J = 8.2 Hz), 7.07 (2H, d, J = 8.0 Hz), 6.88 (2H, d, J = 8.7 Hz), 3.81 (3H, s), 2.31 (3H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.6, 136.2, 134.5, 134.5, 129.9, 129.5, 125.7, 114.9, 55.5, 21.1. Spectra were consistent with literature data[38].



(2-Fluorophenyl)(4-methoxyphenyl)sulfane 4e: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (108.9 mg, 0.465 mmol, 93.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (2H, d, J = 8.7 Hz), 7.17 – 7.13 (1H, m), 7.07 – 6.99 (3H, m), 6.92 (2H, d, J = 8.7 Hz), 3.83 (3H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.7 (d, J = 246.0 Hz), 158.7, 135.6, 130.5 (d, J = 1.9 Hz), 127.8 (d, J = 7.6 Hz), 125.8 (d, J = 17.2 Hz), 124.6 (d, J = 3.7 Hz), 122.7, 115.6 (d, J = 21.2 Hz), 115.1, 55.4. Spectra were consistent with literature data[39].

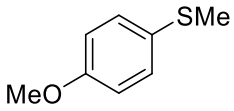


(4-Methoxyphenyl)(3-(trifluoromethyl)phenyl)sulfane 4f: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (89.7 mg, 0.316 mmol, 63.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (2H, d, J = 8.8 Hz), 7.28 – 7.23 (2H, m), 7.21 – 7.14 (2H, m), 6.84 (2H, d, J = 8.8 Hz), 3.74 (3H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.6, 141.0, 136.4, 131.4 (q, J = 32.3 Hz), 130.4, 129.3, 123.9 (q, $J_{C\text{-}F}$ = 273.7 Hz), 123.8 (q, $J_{C\text{-}F}$ = 3.9 Hz), 122.4, 122.3 (q, $J_{C\text{-}F}$ = 3.8 Hz), 115.4, 55.5. Spectra were consistent with literature data[38].

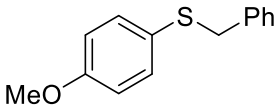


2-((4-Methoxyphenyl)thio)thiophene 4g: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (76.6 mg, 0.345 mmol, 69.0% yield). **^{1}H NMR** (400 MHz,

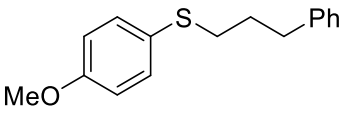
$CDCl_3$) δ 7.38 (1H, dd, J = 5.3, 1.3 Hz), 7.28 (2H, d, J = 8.8 Hz), 7.21 (1H, dd, J = 3.6, 1.3 Hz), 7.00 (1H, dd, J = 5.4, 3.6 Hz), 6.83 (2H, d, J = 8.8 Hz), 3.78 (3H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.0, 134.3, 134.0, 131.2, 130.1, 128.4, 127.7, 114.8, 55.4; Spectra were consistent with literature data[38].



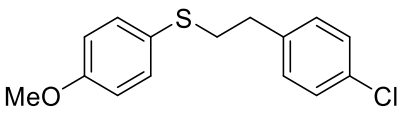
(4-Methoxyphenyl)(methyl)sulfane 4h： Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (62.5 mg, 0.405 mmol, 81.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (1H, d, J = 8.9 Hz), 6.85 (1H, d, J = 8.8 Hz), 3.79 (3H, s). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.3, 130.3, 128.9, 114.7, 55.5, 18.2. Spectra were consistent with literature data.[40]



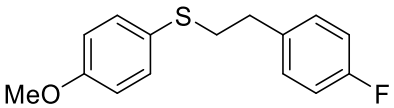
Benzyl(4-methoxyphenyl)sulfane 4i： Prepared according to **General Method C** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (105.2 mg, 0.457 mmol, 91.4% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.16 (7H, m), 6.79 (2H, d, J = 8.8 Hz), 3.98 (2H, s), 3.78 (3H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 138.2, 134.2, 129.0, 128.4, 127.1, 126.1, 114.5, 55.4, 41.3. Spectra were consistent with literature data.[41]



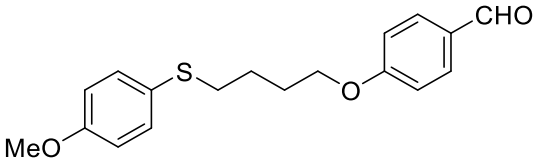
Phenyl(3-phenylpropyl)sulfane 4j： Prepared according to **General Method C** (Eluent: 500:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (108.0 mg, 0.420 mmol, 84.1% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (2H, d, J = 8.7 Hz), 7.27 – 7.25 (2H, m), 7.20 – 7.14 (3H, m), 6.83 (2H, d, J = 8.7 Hz), 3.79 (3H, s), 2.82 (2H, t, J = 7.2 Hz), 2.72 (2H, t, J = 7.4 Hz), 1.93 – 1.85 (2H, m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 141.6, 133.3, 128.6, 128.5, 126.5, 126.0, 114.6, 55.6, 35.3, 34.7, 30.9. Spectra were consistent with literature data.[36]



(4-Chlorophenethyl)(4-methoxyphenyl)sulfane 4k： Prepared according to **General Method C** (Eluent: 500:0 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (107.6 mg, 0.386 mmol, 77.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (2H, d, J = 8.6 Hz), 7.24 (2H, d, J = 8.2 Hz), 7.08 (2H, d, J = 8.1 Hz), 6.85 (2H, d, J = 8.7 Hz), 3.80 (3H, s), 3.02 (2H, t, J = 7.7 Hz), 2.82 (2H, t, J = 7.7 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.1, 138.8, 133.5, 132.2, 130.0, 128.6, 126.0, 114.7, 55.4, 37.3, 35.2. Spectra were consistent with literature data.[42]

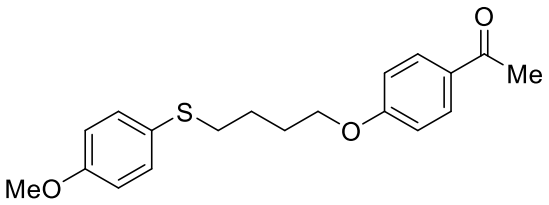


(4-Fluorophenethyl)(4-methoxyphenyl)sulfane 4l： Prepared according to **General Method C** (Eluent: 500:0 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (101.5 mg, 0.387 mmol, 77.4% yield). **IR** (thin film) 1529 (w), 1509 (s), 1493 (s), 1284 (m), 1243 (s), 1220 (s), 1173 (m), 1157 (m), 1030 (w), 821 (s), 638 (w) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (2H, d, J = 8.7 Hz), 7.13 – 7.09 (2H, m), 6.98 – 6.94 (2H, m), 6.86 (2H, d, J = 8.8 Hz), 3.80 (3H, s), 3.03 (2H, t, J = 7.8 Hz), 2.82 (2H, t, J = 7.6 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.6 (d, $J_{C\text{-}F}$ = 244.8 Hz), 159.1, 136.1 (d, $J_{C\text{-}F}$ = 3.1 Hz), 133.5, 130.1 (d, $J_{C\text{-}F}$ = 8.0 Hz), 126.2, 115.3 (d, $J_{C\text{-}F}$ = 21.3 Hz), 114.7, 55.4, 37.5, 35.1; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –116.82; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{15}H_{16}FOS$: 263.0900, found: 263.0912.

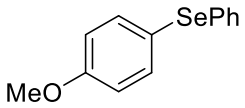


4-(4-((4-Methoxyphenyl)thio)butoxy)benzaldehyde 4m： Prepared according to **General Method C** (Eluent: 500:0 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (83.6 mg, 0.264 mmol, 52.8% yield). **M.p.** = 33.0 – 34.1 ^{o}C; **IR** (thin film) 1677 (m), 1601 (m), 1574 (m), 1511 (s), 1493 (w), 1394 (w), 1256 (s), 1215 (m), 1163 (s), 1022 (s), 813 (s), 743 (w), 649 (m), 625 (w) cm^{-1}; **^{1}H**

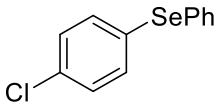
NMR (400 MHz, $CDCl_3$) δ 9.87 (1H, s), 7.82 (2H, d, J = 8.7 Hz), 7.35 (2H, d, J = 8.6 Hz), 6.96 (2H, d, J = 8.5 Hz), 6.84 (2H, d, J = 8.7 Hz), 4.03 (2H, t, J = 6.2 Hz), 3.79 (3H, s), 2.89 (2H, t, J = 7.2 Hz), 1.97 – 1.91 (2H, m), 1.80 – 1.73 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.9, 164.1, 159.0, 133.4, 132.1, 129.9, 126.3, 114.8, 114.7, 67.8, 55.4, 35.6, 28.0, 25.8; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{18}H_{20}NaO_3S$: 339.1025, found: 339.1040.



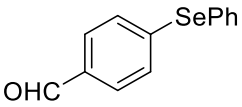
4-(4-((4-Methoxyphenyl)thio)butoxy)benzaldehyde 4： Prepared according to **General Method C** (Eluent: 500:0 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (80.2 mg, 0.243 mmol, 48.6% yield). **M.p.** = 74.8 – 75.9 ^oC; **IR** (thin film) 1673 (m), 1598 (m), 1572 (w), 1494 (m), 1358 (w), 1242 (m), 1176 (m), 1113 (w), 1025 (m), 1000 (w), 955 (w), 842 (m), 808 (s), 668 (w), 638 (w), 609 (w) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.87 (1H, s), 7.82 (2H, d, J = 8.7 Hz), 7.35 (2H, d, J = 8.6 Hz), 6.96 (2H, d, J = 8.5 Hz), 6.84 (2H, d, J = 8.7 Hz), 4.03 (2H, t, J = 6.2 Hz), 3.79 (3H, s), 2.89 (2H, t, J = 7.2 Hz), 1.97 – 1.91 (2H, m), 1.80 – 1.73 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.0, 163.0, 159.0, 133.4, 130.7, 130.3, 126.3, 114.7, 114.2, 67.7, 55.5, 35.7, 28.1, 26.5, 25.9; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{19}H_{22}NaO_3S$: 353.1182, found: 353.1190.



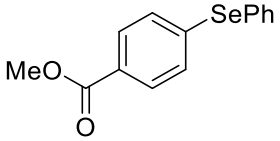
(4-Methoxyphenyl)(phenyl)selane 5a: Prepared according to **General Method C** (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (125.1 mg, 0.474 mmol, 94.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (2H, d, J = 8.7 Hz), 7.33 – 7.30 (2H, m), 7.20 – 7.15 (3H, m), 6.83 (2H, d, J = 8.7 Hz), 3.76 (3H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.8, 136.6, 133.3, 130.9, 129.2, 126.5, 119.9, 115.2, 55.3. Spectra were consistent with literature data[43].



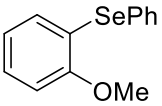
(4-Chlorophenyl)(phenyl)selane 5b: Prepared according to **General Method C using** (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a light yellow oil (120.3 mg, 0.449 mmol, 89.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (2H, m), 7.35 (2H, d, J = 8.4 Hz), 7.29 – 7.23 (3H, m), 7.20 (2H, d, J = 8.4 Hz), 2.42 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.2, 133.6, 133.3, 130.7, 129.6, 129.6, 129.5, 127.8. Spectra were consistent with literature data[44].



4-(Phenylselanyl)benzaldehyde 5c: Prepared according to **General Method C** (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a light yellow oil (105.1 mg, 0.401 mmol, 80.2% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.81 (1H, s), 7.58 (2H, d, J = 8.4 Hz), 7.53 – 7.49 (2H, m), 7.33 – 7.25 (5H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.5, 142.8, 135.6, 134.5, 130.2, 129.9, 129.0, 128.0 (one carbon was missing due to the overlap). Spectra were consistent with literature data[45].

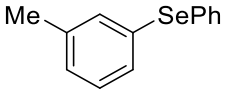


Methyl 4-(phenylselanyl)benzoate 5d: Prepared according to **General Method C** (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (110.8 mg, 0.379 mmol, 75.8% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (2H, d, J = 8.4 Hz), 7.60 – 7.56 (2H, m), 7.49 – 7.31 (5H, m), 3.89 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.9, 139.8, 135.1, 130.4, 130.2, 129.8, 128.7, 128.6, 128.3, 52.2. Spectra were consistent with literature data[46].

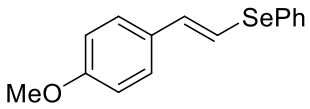


(2-Methoxyphenyl)(phenyl)selane 5e: Prepared according to **General Method C** (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was

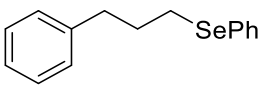
isolated as a light yellow oil (117.3 mg, 0.445 mmol, 88.9% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (2H, m), 7.34 – 7.26 (3H, m), 7.18 – 7.14 (1H, m), 6.94 (1H, dd, J = 7.7, 1.6 Hz), 6.82 (1H, dd, J = 8.2, 1.3 Hz), 6.79 – 6.74 (1H, m), 3.84 (3H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.6, 135.5, 130.7, 129.5, 128.2, 128.2, 127.7, 121.9, 121.6, 110.4, 55.9. Spectra were consistent with literature data[47].



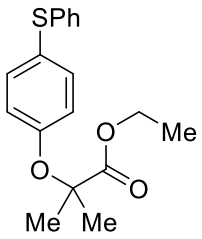
Phenyl(m-tolyl)selane 5f: Prepared according to **General Method C** (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a light yellow oil (99.3 mg, 0.400 mmol, 80.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (4H, m), 7.32 (1H, s), 7.29 – 7.22 (4H, m), 7.16 (1H, dd, J = 7.6, 7.6 Hz), 7.08 (d, J = 7.6 Hz), 2.30 (3H, s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.3, 133.9, 132.9, 131.5, 130.8, 130.3, 129.4, 129.3, 128.4, 127.3, 21.4. Spectra were consistent with literature data[45].



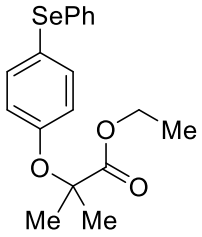
(*E*)-(4-methoxystyryl)(phenyl)selane 5h: Prepared according to **General Method C using** (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a light yellow oil (119.2 mg, 0.411 mmol, 82.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (2H, m), 7.31 – 7.25 (5H, m), 7.03 – 6.81 (4H, m), 3.79 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.5, 136.0, 132.1, 130.9, 123.0, 129.4, 127.5, 127.2, 116.0, 114.2, 55.4. Spectra were consistent with literature data[45].



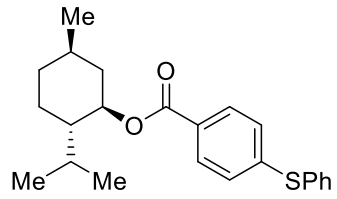
Phenyl(3-phenylpropyl)selane 5i： Prepared according to **General Method C** (Eluent: 300:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (103.2 mg, 0.374 mmol, 74.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (2H, m), 7.28 – 7.10 (8H, m), 2.87 (2H, d, J = 7.2 Hz), 2.71 (2H, d, J = 7.4 Hz), 2.03 – 1.96 (2H, m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.3, 132.6, 130.4, 129.1, 128.6, 128.5, 126.8, 126.0, 35.8, 31.7, 27.2. Spectra were consistent with literature data[48].



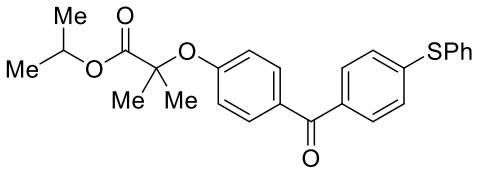
Ethyl 2-methyl-2-(4-(phenylthio)phenoxy)propanoate 7a: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (142.8 mg, 0.452 mmol, 90.4% yield). **IR** (thin film) 1732 (m), 1590 (w), 1489 (m), 1383 (w), 1282 (m), 1237 (m), 1175 (m), 1135 (s), 1023 (m), 969 (w), 830 (m), 739 (m), 690 (m) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (2H, d, J = 8.7 Hz), 7.24 – 7.18 (4H, m), 7.15 – 7.13 (1H, m), 6.81 (2H, d, J = 8.7 Hz), 4.22 (2H, q, J = 7.1 Hz), 1.61 (6H, s), 1.22 (3H, t, J = 7.1 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 155.5, 137.7, 134.2, 129.0, 128.9, 126.4, 126.1, 119.6, 79.2, 61.5, 25.4, 14.1; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{18}H_{20}NaO_3S$: 339.1025, found: 339.1022.



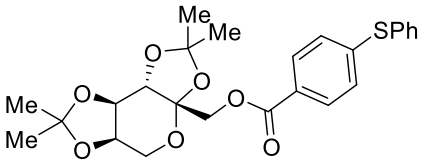
Ethyl 2-methyl-2-(4-(phenylselanyl)phenoxy)propanoate 7b: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (158.3 mg, 0.435 mmol, 87.0% yield). **IR** (thin film) 1731 (m), 1585 (w), 1488 (m), 1383 (w), 1283 (m), 1235 (m), 1175 (m), 1135 (s), 1021 (m), 969 (w), 827 (m), 735 (m), 690 (m) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (2H, d, J = 8.4 Hz), 7.36– 7.31 (2H, m), 7.23 – 7.17 (3H, m), 6.77 (2H, d, J = 8.4 Hz), 4.20 (2H, q, J = 7.0 Hz), 1.60 (6H, s), 1.22 (3H, t, J = 7.0 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.0, 155.6, 135.6, 132.6, 131.5, 129.2, 126.7, 121.9, 119.8, 79.2, 61.6, 25.4, 14.1. **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{18}H_{20}NaO_3Se$: 387.0471, found: 387.0482.



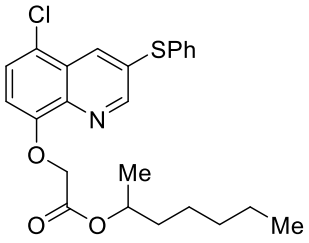
(2S,5R)-2-Isopropyl-5-methylcyclohexyl 4-(phenylthio)benzoate 7c: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (133.9 mg, 0.363 mmol, 72.6% yield). **M.p.** = 44.5 – 45.7 °C; **IR** (thin film) 2953 (w), 1706 (s), 1593 (m), 1462 (w), 1401 (w), 1288 (s), 1270 (s), 1180 (m), 1110 (s), 1012 (m), 961 (m), 845 (m), 759 (s), 747 (s), 689 (s) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (2H, d, J = 8.3 Hz), 7.48 – 7.46 (2H, m), 7.39 – 7.34 (3H, m), 7.21 (2H, d, J = 8.3 Hz), 4.91 (1H, td, J = 10.9, 4.4 Hz), 2.17 – 2.05 (1H, m), 1.93 (1H, m), 1.71 (2H, m), 1.64 – 1.47 (2H, m), 1.10 – 1.06 (2H, m), 0.91 (7H, m), 0.78 (3H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 144.1, 133.6, 132.7, 130.1, 129.7, 128.6, 128.3, 127.8, 74.9, 47.3, 41.0, 34.4, 31.5, 26.6, 23.7, 22.1, 20.8, 16.6; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{23}H_{28}NaO_2S$: 391.1702, found: 391.1708.



Isopropyl 2-methyl-2-(4-(4-(phenylthio)benzoyl)phenoxy)propanoate 7d: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (190.1 mg, 0.437 mmol, 87.4% yield). **M.p.** = 53.2 – 54.8 °C; **IR** (thin film) 1737 (m), 1647 (m), 1598 (m), 1504 (w), 1478 (w), 1312 (w), 1243 (m), 1139 (s), 1104 (s), 929 (m), 846 (m), 759 (m), 746 (s), 691 (w), 674 (m), 652 (m) cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (2H, d, J = 8.8 Hz), 7.65 (2H, d, J = 8.4 Hz), 7.50 – 7.48 (2H, m), 7.40 – 7.35 (3H, m), 7.24 (2H, d, J = 8.4 Hz), 6.86 (2H, d, J = 8.9 Hz), 5.11 – 5.06 (1H, m), 1.65 (6H, s), 1.20 (3H, s), 1.19 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.5, 173.1, 159.5, 143.4, 135.4, 133.6, 132.5, 131.9, 130.6, 130.5, 129.7, 128.6, 127.6, 117.2, 79.4, 69.3, 25.4, 21.5; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{26}H_{27}O_4S$: 435.1630, found: 435.1629.

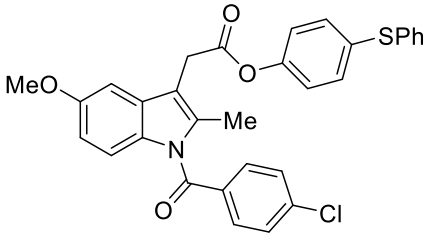


((3aS,5aR,8aR,8bS)-2,2,7,7-*tetra*methyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 4-(phenylthio)benzoate 7e: Prepared according to **General Method C** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (208.3 mg, 0.441 mmol, 88.2% yield). **M.p.** = 94.2 – 95.0 ^{o}C; **IR** (thin film) 1718 (m), 1593 (m), 1443 (w), 1376 (w), 1274 (s), 1248 (m), 1204 (m), 1163 (m), 1106 (s), 1067 (s), 1038 (m), 1015 (m), 883 (m), 845 (w), 757 (s), 690 (w) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (2H, d, J = 4.7 Hz), 7.48 – 7.45 (2H, m), 7.39 – 7.36 (3H, m), 7.17 (2H, d, J = 4.7 Hz), 4.65 (1H, d, J_{AB} = 11.8 Hz), 4.61 (1H, dd, J = 7.9, 2.6 Hz), 4.43 (1H, d, J = 2.7 Hz), 4.29 (1H, d, J_{AB} = 11.8 Hz), 4.23 (1H, dd, J = 7.8, 1.6 Hz), 3.93 (1H, dd, J = 13.0, 1.9 Hz), 3.77 (1H, d, J = 13.0 Hz), 1.52 (s, 3H), 1.44 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 144.8, 133.8, 132.1, 130.3, 129.7, 128.8, 127.3, 127.1, 109.1, 108.8, 101.6, 70.8, 70.5, 70.1, 65.3, 61.3, 26.5, 25.9, 25.6, 24.0; **HRMS** (ESI^{+}) $[M+Na]^{+}$ calc'd for $C_{25}H_{28}NaO_7S$: 495.1448, found: 495.1460.

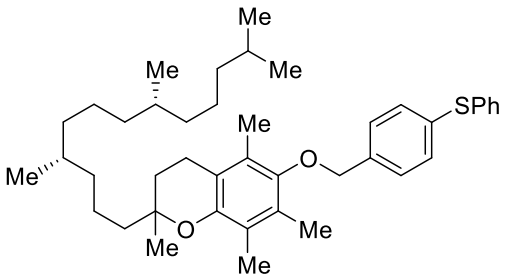


Heptan-2-yl 2-((5-chloro-3-(phenylthio)quinolin-8-yl)oxy)acetate 7f: Prepared according to **General Method C** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (125.3 mg, 0.282 mmol, 56.4% yield). **M.p.** = 45.1 – 46.2 ^{o}C; **IR** (thin film) 2927 (w), 1748 (s), 1601 (w), 1487 (m), 1365 (m), 1312 (w), 1222 (s), 1157 (m), 1117 (s), 972 (m), 816 (m), 789 (m), 744 (s), 688 (m), 640 (m) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (1H, d, J = 2.2 Hz), 8.32 (1H, d, J = 2.1 Hz), 7.44 – 7.42 (3H, m), 7.37 – 7.31 (3H, m), 6.82 (1H, d, J = 2.2 Hz), 5.02 – 4.97 (1H, m), 4.88 (2H, s), 1.56 – 1.49 (1H, m), 1.44 – 1.42 (1H, m), 1.20 – 1.18

(9H, m), 0.83 – 0.80 (3H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.1, 153.0, 150.8, 138.7, 133.4, 132.8, 132.4, 132.3, 129.7, 128.4, 127.2, 126.9, 122.8, 109.5, 72.8, 66.5, 35.7, 31.5, 24.9, 22.5, 19.9, 14.0; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{19}H_{16}NaO_3S_2$: 466.1219, found: 466.1220.



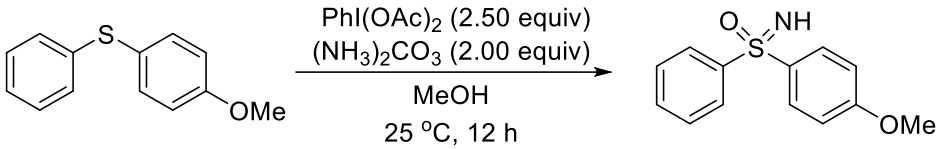
4-(Phenylthio)phenyl-2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate 7g: Prepared according to **General Method C** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow solid (213 mg, 0.393 mmol, 78.6% yield). **M.p.** = 103.1 – 104.2 ^oC; **IR** (thin film) 1758 (w), 1675 (m), 1607 (w), 1477 (m), 1437 (m), 1355 (m), 1325 (m), 1235(m), 1197 (m), 1167 (m), 1121 (s), 1082 (s), 1038 (m), 1012 (m), 910 (m), 841 (m), 808 (m), 738 (m), 690 (m), cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (2H, d, J = 8.2 Hz), 7.44 (2H, d, J = 8.3 Hz), 7.32 – 7.20 (7H, m), 7.04 – 6.99 (3H, m), 6.88 (1H, d, J = 9.0 Hz), 6.68 (1H, dd, J = 9.0, 2.5 Hz), 3.88 (2H, s), 3.81 (3H, s), 2.43 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.2, 168.3, 156.2, 149.9, 139.4, 136.3, 135.7, 133.8, 133.2, 132.3, 131.2, 130.9, 130.9, 130.5, 129.3, 129.2, 127.2, 122.3, 115.1, 111.9, 111.8, 101.3, 55.7, 30.6, 13.5; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{31}H_{24}ClNNaO_4S$: 564.1007, found: 564.1020.



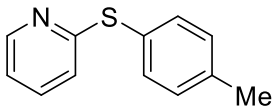
(S)-2,5,7,8-Tetramethyl-6-((4-(phenylthio)benzyl)oxy)-2-((4R,8R)-4,8,12-trimethyltridecyl)chromane 7h: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (242 mg, 0.385 mmol, 77.0% yield). **IR** (thin film) 2924 (m), 1458 (m), 1369 (w), 1255 (m), 1084 (s), 1015 (m), 808 (m), 736 (m), 690 (m) cm^{-1}; **^{1}H NMR** (400

MHz, $CDCl_3$) δ 7.42 (2H, d, J = 8.3 Hz), 7.38 – 7.32 (4H, m), 7.30 – 7.25 (2H, m), 7.22 – 7.19 (1H, m), 4.65 (2H, s), 2.57 (2H, t, J = 6.8 Hz), 2.20 (3H, s), 2.15 (3H, s), 2.10 (3H, s), 1.80 – 1.73 (2H, m), 1.54 – 1.05 (24H, m), 0.87 – 0.84 (12H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.1, 137.2, 136.1, 135.2, 131.4, 130.9, 129.3, 128.6, 127.9, 127.0, 126.0, 123.1, 117.7, 74.9, 74.2, 40.1, 39.5, 37.6, 37.5, 37.4, 32.9, 32.8, 31.4, 28.1, 24.9, 24.6, 24.0, 22.9, 22.8, 21.1, 20.8, 19.9, 19.8, 13.0, 12.1, 12.0; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{42}H_{60}NaO_2S$: 651.4206, found: 651.4230.

Synthesis of Imino(4-methoxyphenyl)(phenyl)-l6-sulfanone 8:

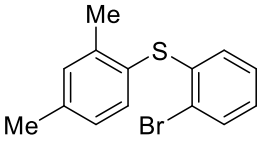


An oven-dried 25-mL Schlenk tube, equipped with a stir bar, was charged with (4-methoxyphenyl)(phenyl)sulfane (216 mg, 1.00 mmol, 1.00 equiv), $PhI(OAc)_2$ (805 mg, 2.50 mmol. 2.50 equiv) and ammonium carbamate (156 mg, 2.00 mmol, 2.00 equiv) and methanol (2.50 mL). The mixture was stirred at room temperature for 12 h. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 30:1 to 1:1 petroleum ether: ethyl acetate) to provide the desired product as a white solid (232 mg, 0.940 mmol, 94.0% yield) which is a known compound. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.91 (4H, m), 7.43 (2H, d, J = 8.0 Hz), 6.89 (2H, d, J = 8.0 Hz), 3.77 (3H, s), 2.91 (1H, brs). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0, 144.0, 134.6, 132.3, 130.1, 129.1, 127.6, 114.4, 55.6; The spectral data match those previously reported[49].



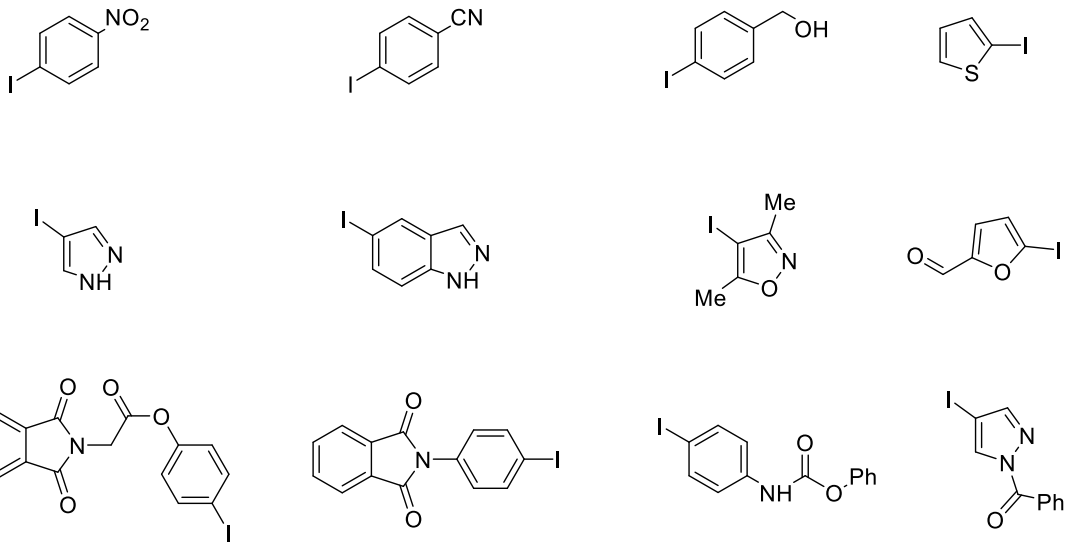
2-(*p*-Tolylthio)pyridine 9: Prepared according to **General Method B** (1.0 mmol 2-Iodopyridine) (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (100 mg, 0.497 mmol, 49.7% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 – 8.37 (1H, m), 7.46 (2H, d, J = 8.1 Hz), 7.41 – 7.36 (1H, m), 7.21 (2H, d, J = 7.8 Hz), 6.95 – 6.91 (1H, m), 6.81 (1H, d, J = 8.6 Hz), 2.37 (3H,

s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.3, 149.6, 139.6, 136.7, 135.4, 130.6, 127.2, 120.9, 119.7, 21.4. Spectra were consistent with literature data[50].

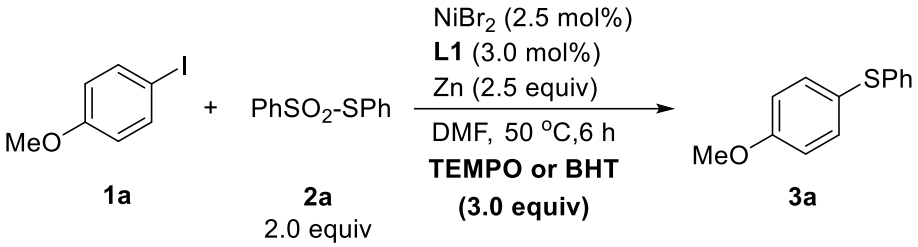


(2-Bromophenyl)(2,4-dimethylphenyl)sulfane 12: Prepared according to **General Method B** (Eluent: 100:0 to 500:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (92.6 mg, 0.316 mmol, 63.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.50 (1H, m), 7.40 (1H, d, J = 7.8 Hz), 7.16 (1H, s), 7.08 – 7.03 (2H, m), 6.96 – 6.92 (1H, m), 6.56 (1H, d, J = 8.0 Hz), 2.36 (3H, s), 2.33 (3H, s). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.5, 140.0, 139.6, 136.3, 132.9, 132.1, 128.2, 127.8, 127.5, 127.2, 126.2, 121.3, 21.4, 20.7. Spectra were consistent with literature data[51].

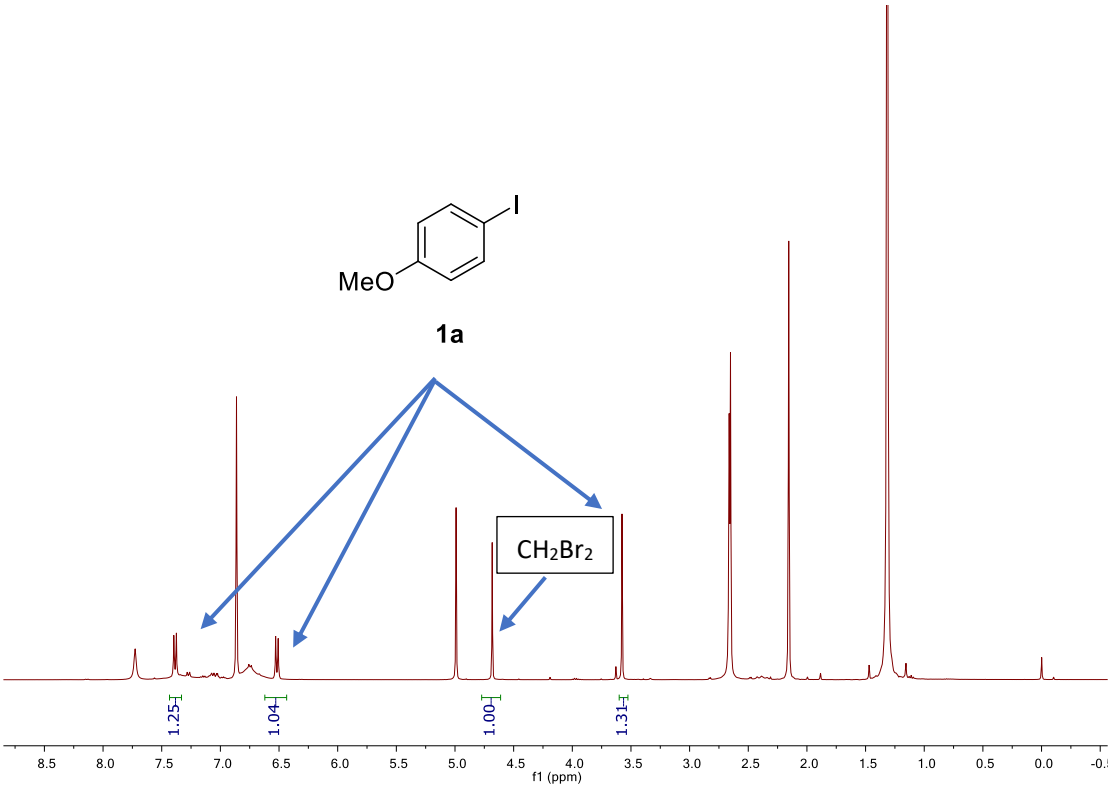
Failed substrate:



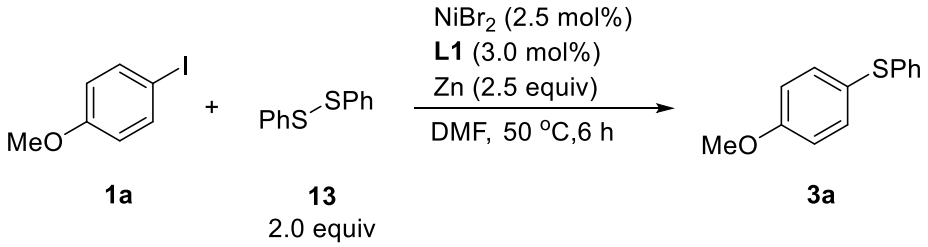
V. Mechanistic studies



A 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with 4-iodoanisole (117 mg, 0.500 mmol, 1.00 equiv), *S*-phenyl benzenesulfonothioate **2a** (250 mg, 1.00 mmol, 2.00 equiv), Zn (82.0 mg, 1.25 mmol, 2.50 equiv), $NiBr_2$ (2.80 mg, 0.0125 mmol, 0.0250 equiv), 1,10-phenanthroline (2.70 mg, 0.0150 mmol, 0.0300 equiv), 2,2,6,6-tetramethyl-1-piperidinyloxy (Tempo) (234 mg, 1.50 mmol, 3.00 equiv) or BHT (330 mg, 1.50 mmol, 3.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for 6 h at 50 °C. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^1H NMR spectroscopy in the presence of CH_2Br_2 (86.9 mg, 0.500 mmol).

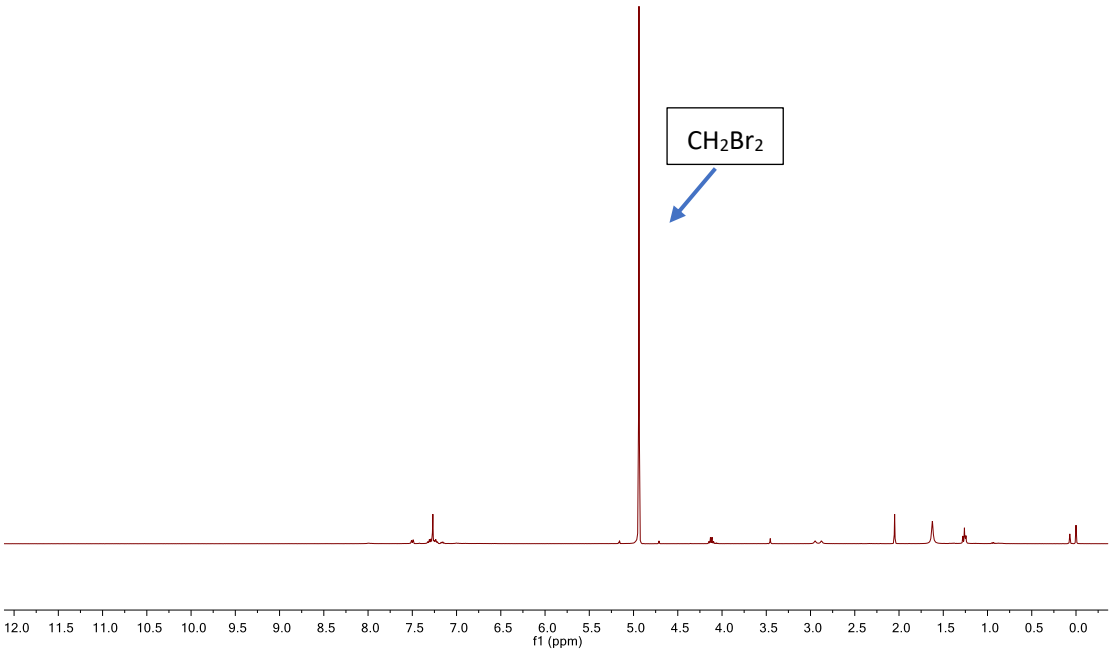


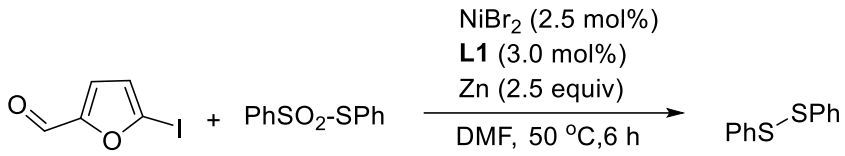
BHT as the additive in the reductive coupling



A 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with 4-iodoanisole (117 mg, 0.500 mmol, 1.00 equiv), diphenyl disulfide (218 mg, 1.00 mmol, 2.00 equiv), Zn (82.0 mg, 1.25 mmol, 2.50 equiv), $NiBr_2$ (2.80 mg, 0.0125 mmol, 0.0250 equiv), 1,10-phenanthroline (2.70 mg, 0.0150 mmol, 0.0300 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for 6 h at 50 °C. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 mL x 3), dried over Na_2SO_4 and filtered.

The solvent was removed by rotary evaporation, the crude mixture was subjected to ^{1}H NMR spectroscopy in the presence of CH_2Br_2 (86.9 mg, 0.500 mmol, 1.00 equiv). No disulfide **13** was obtained.

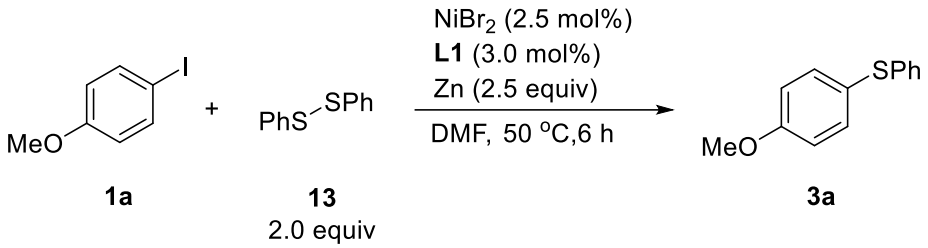




14 **2a** 2.0 equiv **13**

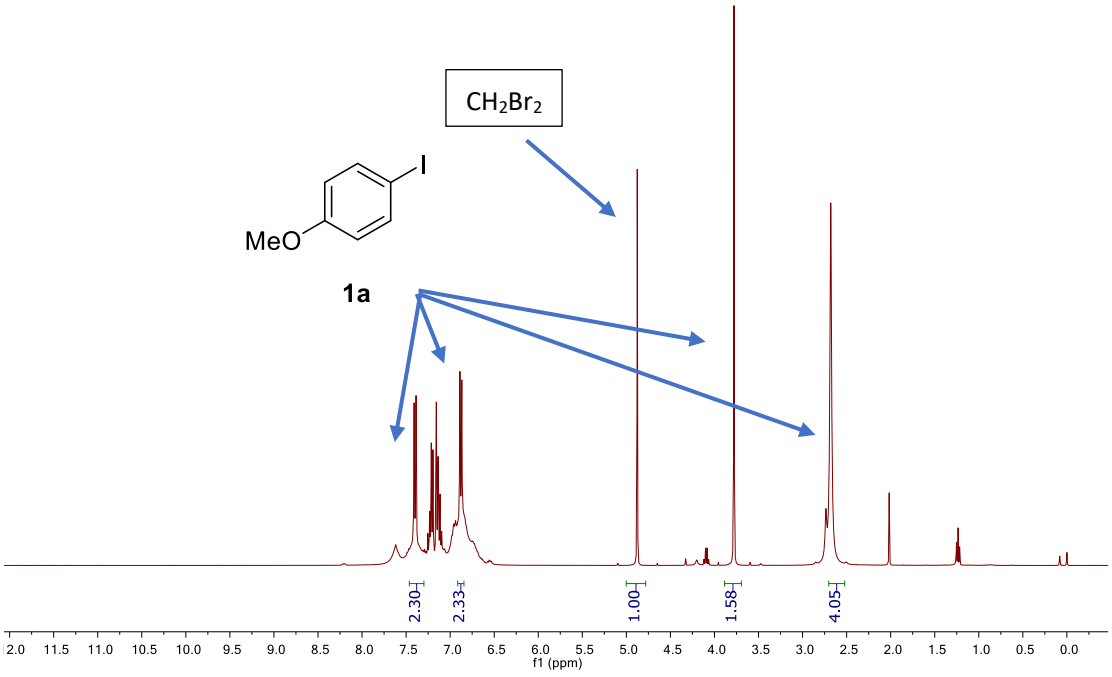
A 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with 5-iodofuran-2-carbaldehyde **14** (111 mg, 0.500 mmol, 1.00 equiv), *S*-phenyl benzenesulfonothioate (250 mg, 1.00 mmol, 2.00 equiv), Zn (82.0 mg, 1.25 mmol, 2.50 equiv), $NiBr_2$ (2.80 mg, 0.0125 mmol, 0.025 equiv), 1,10-phenanthroline (2.70 mg, 0.0150 mmol, 0.0300 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for 6 h at 50 °C. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 3). The combined

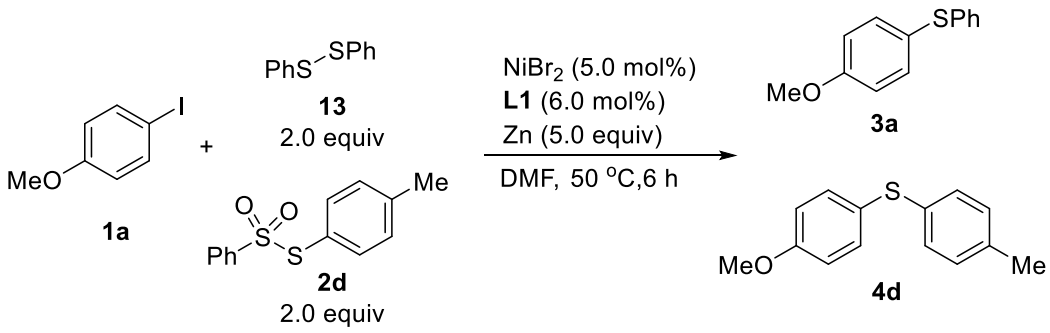
organic layers were washed with saturated NaCl aqueous solution (15.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 500:0 petroleum ether: ethyl acetate). The diphenyl disulfide was isolated as a white solid (52.4 mg, 0.240 mmol, 48.0% yield) which is a known compound.[52] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (4H, d, J = 8.0 Hz), 7.35 (4H, dd, J = 8.0, 7.4 Hz), 7.26 – 7.24 (2H, m).



1a **13** 2.0 equiv **3a**

A 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with 4-iodoanisole (117 mg, 0.500 mmol, 1.00 equiv), diphenyl disulfide (218 mg, 1.00 mmol, 2.00 equiv), Zn (82.0 mg, 1.25 mmol, 2.50 equiv), $NiBr_2$ (2.80 mg, 0.0125 mmol, 0.0250 equiv), 1,10-phenanthroline (2.70 mg, 0.0150 mmol, 0.0300 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for 6 h at 50 °C. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^{1}H NMR spectroscopy in the presence of CH_2Br_2 (86.9 mg, 0.500 mmol, 1.00 equiv). Crude yield of **3a** is >99%.

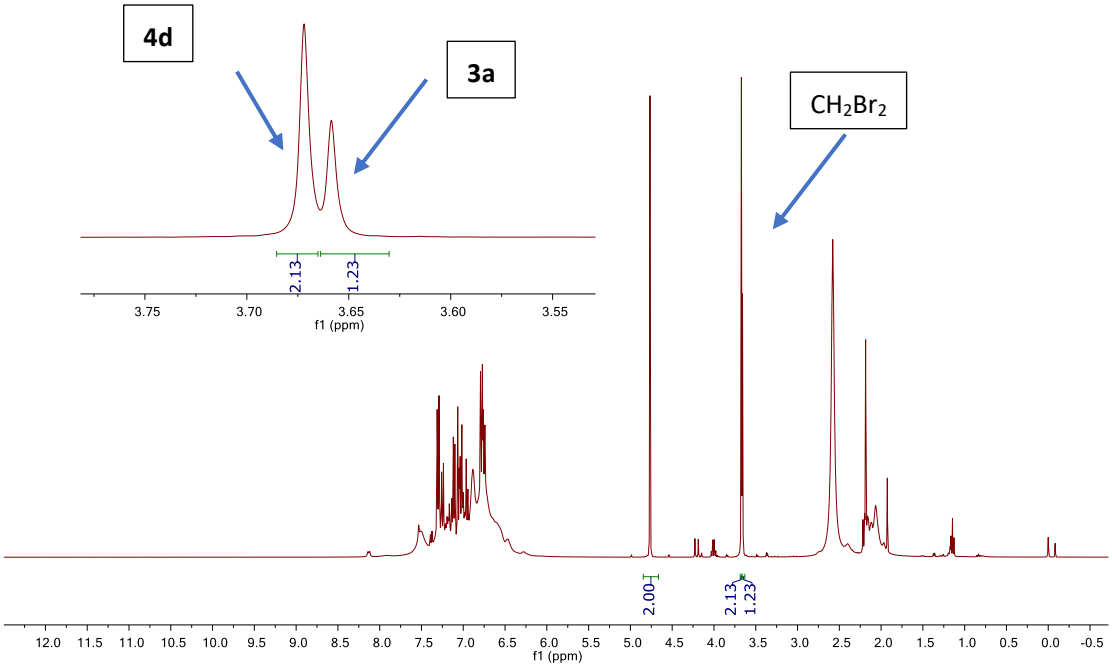


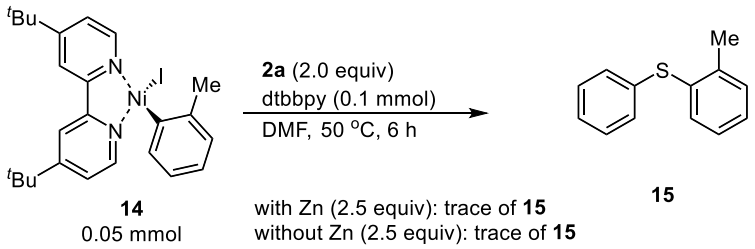


A

120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with 4-iodoanisole (117 mg, 0.500 mmol, 1.00 equiv), diphenyl disulfide (218 mg, 1.00 mmol, 2.00 equiv), *S*-(*p*-tolyl) benzenesulfonothioate (264 mg, 1.00 mmol, 2.00 equiv), Zn (163 mg, 2.50 mmol, 5.00 equiv), $NiBr_2$ (5.50 mg, 0.0250 mmol, 0.0500 equiv), 1,10-phenanthroline (5.41 mg, 0.0300 mmol, 0.0600 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for 6 h at 50 °C. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was

extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^1H NMR spectroscopy in the presence of CH_2Br_2 (86.9 mg, 0.500 mmol, 1.00 equiv). The ratio of **4d** and **3a** is about 2:1.





14
0.05 mmol

with Zn (2.5 equiv): trace of **15**
without Zn (2.5 equiv): trace of **15**

15

A 120 °C oven-dried 5-mL vial, equipped with a stirring bar, was charged with **14**[53] (13.9 mg, 0.0250 mmol, 1.00 equiv), dtbbpy (6.70 mg, 0.0250 mmo, 1.00 equiv), with or without Zn (4.00 mg, 0.0626 mmol, 2.50 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (0.500 mL) was added under N_2 and the mixture was allowed to stir for room temperature at 50 °C. The mixture was diluted with saturated NaCl aqueous solution (10.0 mL) and ethyl acetate (10.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated.

The aqueous layer was extracted with ethyl acetate (5.00 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^1H NMR spectroscopy in the presence of CH_2Br_2 (86.9 mg, 0.500 mmol, 1.00 equiv). No cross-coupling product was observed.

VI. References

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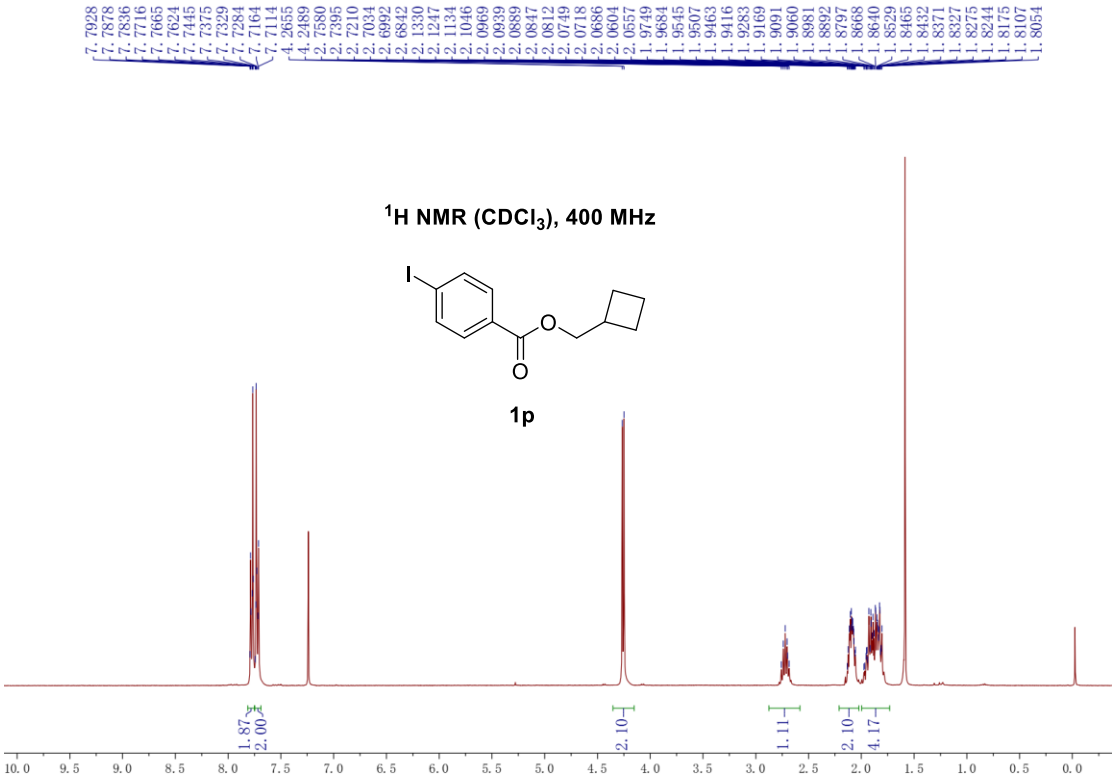
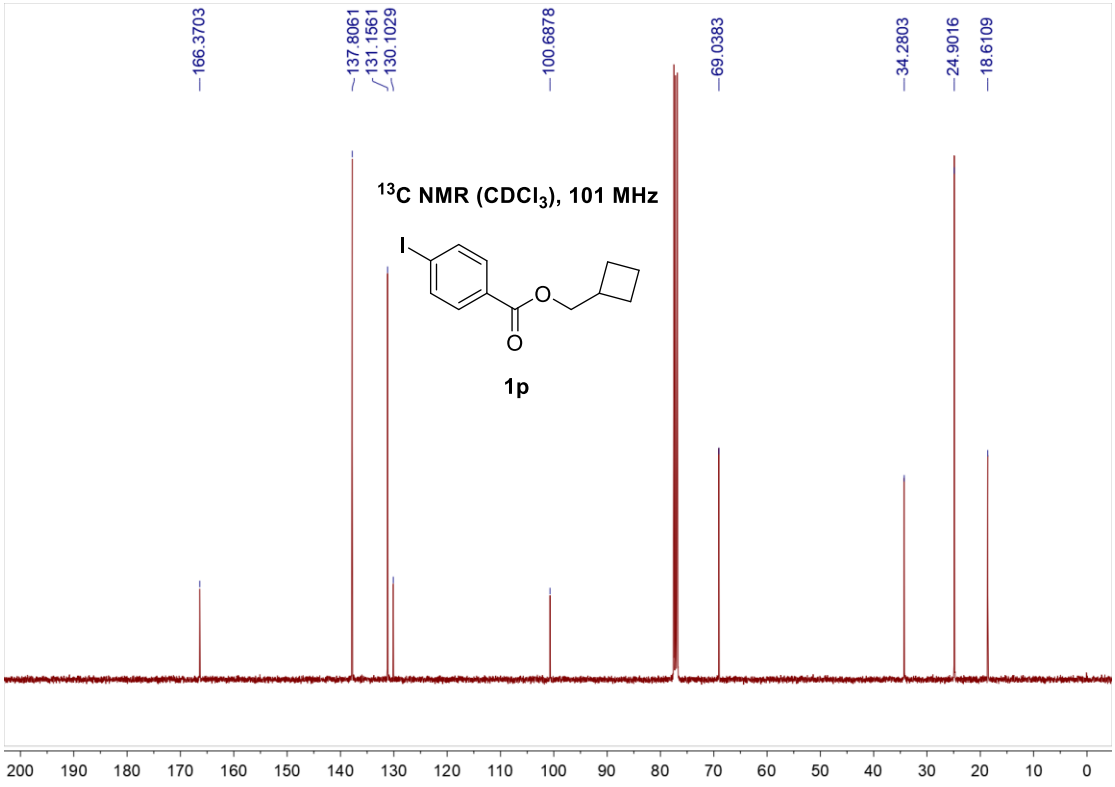
VI. NMR spectra

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O
1p
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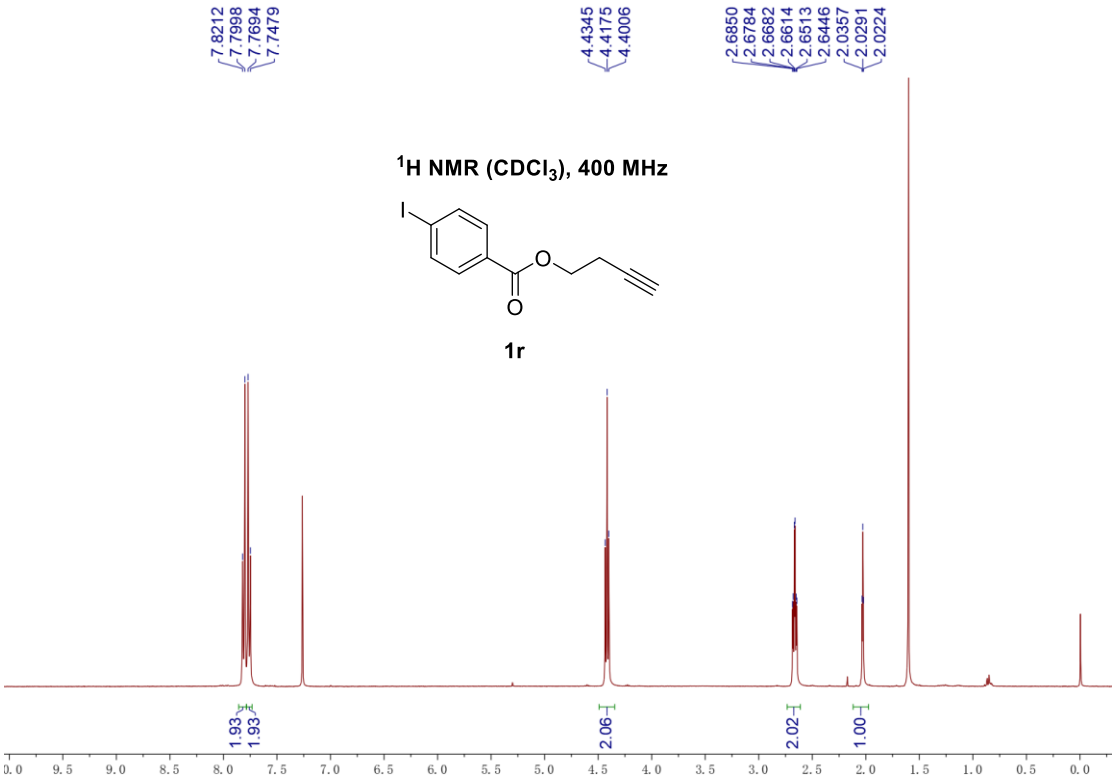
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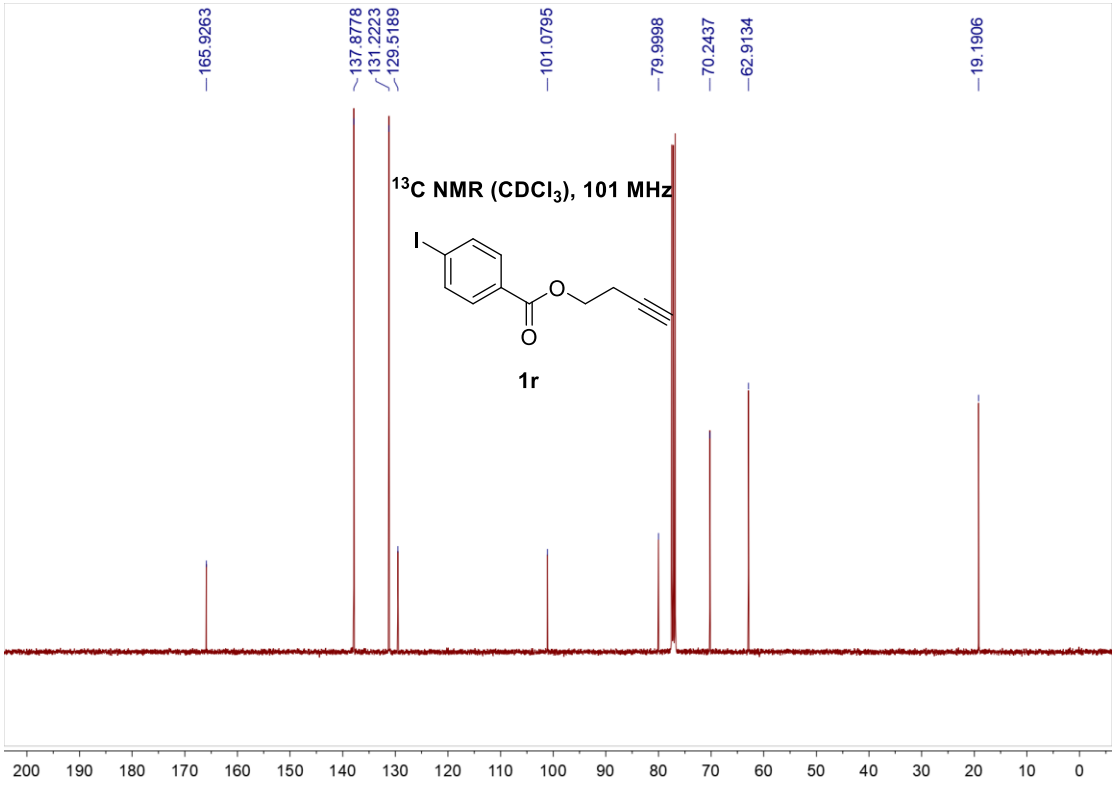
2.6513
2.6446
2.0357
2.0291
2.0224
1H NMR (CDCl3), 400 MHz
I
O
O
1r
1.93
1.93
2.06
2.02
1.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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I
O
O
1r
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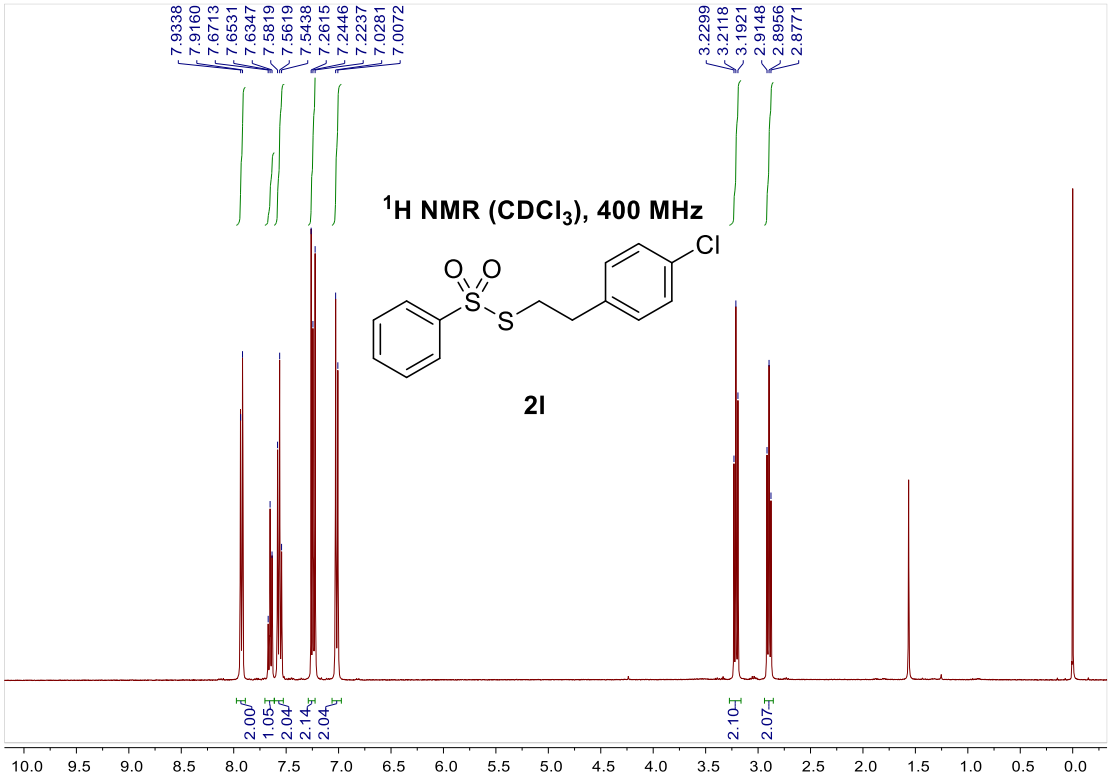
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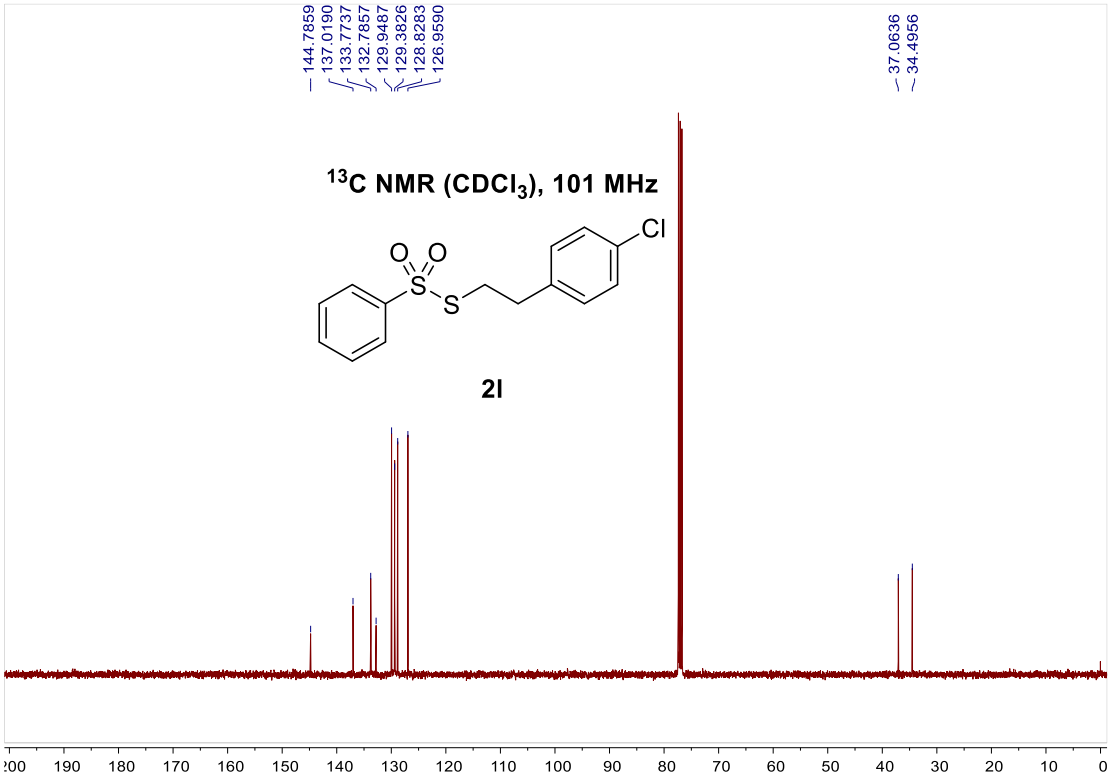
7.0281
7.0072
3.2299
3.2118
3.1921
2.9148
2.8956
2.8771
1H NMR (CDCl3), 400 MHz
Cl
O
O
S
S
2l
2.00
1.05
2.04
2.14
2.04
2.10
2.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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Cl
O
O
S
S
2l
200
190
180
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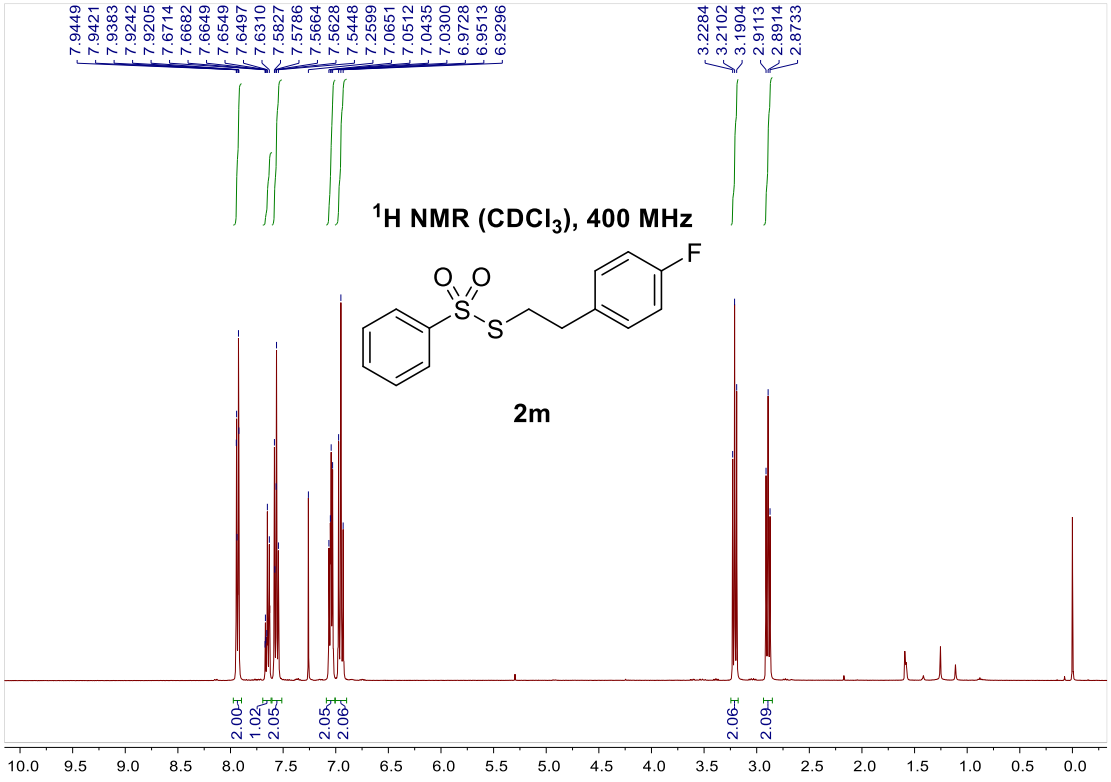
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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6.9296
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3.1904
2.9113
2.8914
2.8733
1H NMR (CDCl3), 400 MHz
F
O
O
S
S
2m
2.00
1.02
2.05
2.05
2.06
2.06
2.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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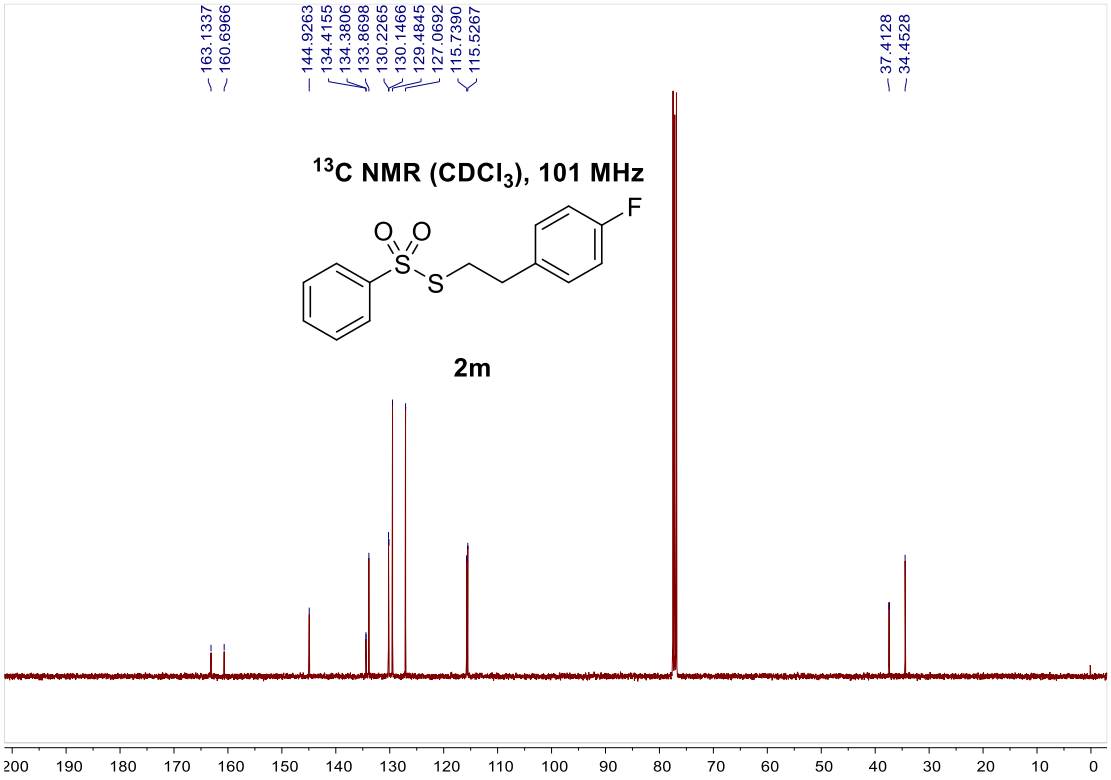
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115.5267
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34.4528
13C NMR (CDCl3), 101 MHz
F
O
O
S
S
2m
200
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160
150
140
130
120
110
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70
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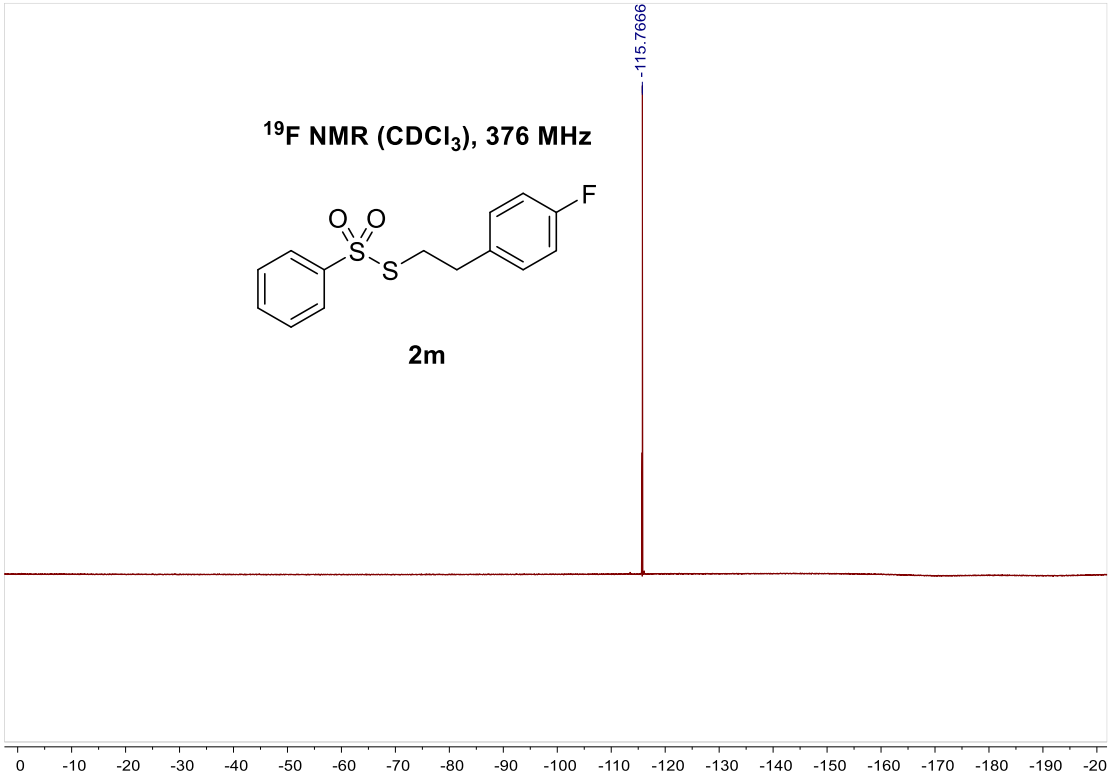
30
20
10
0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O
S
S
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-150
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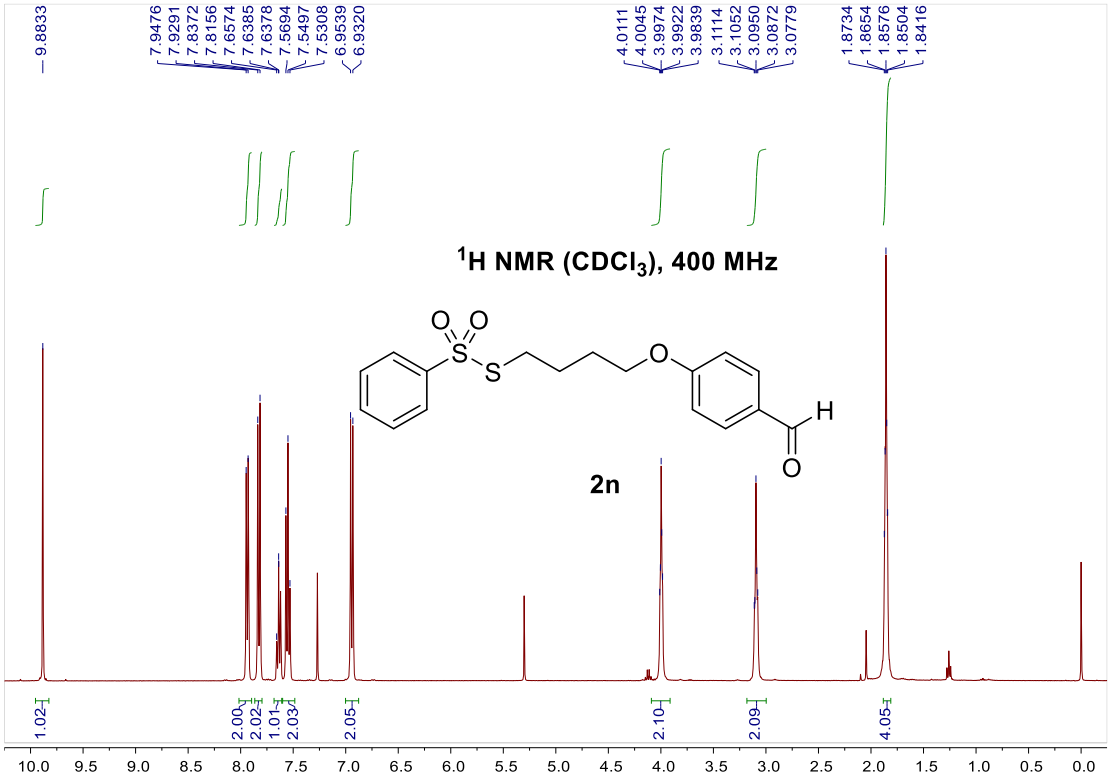
-180
-190
-20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3.1114
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1H NMR (CDCl3), 400 MHz
2n
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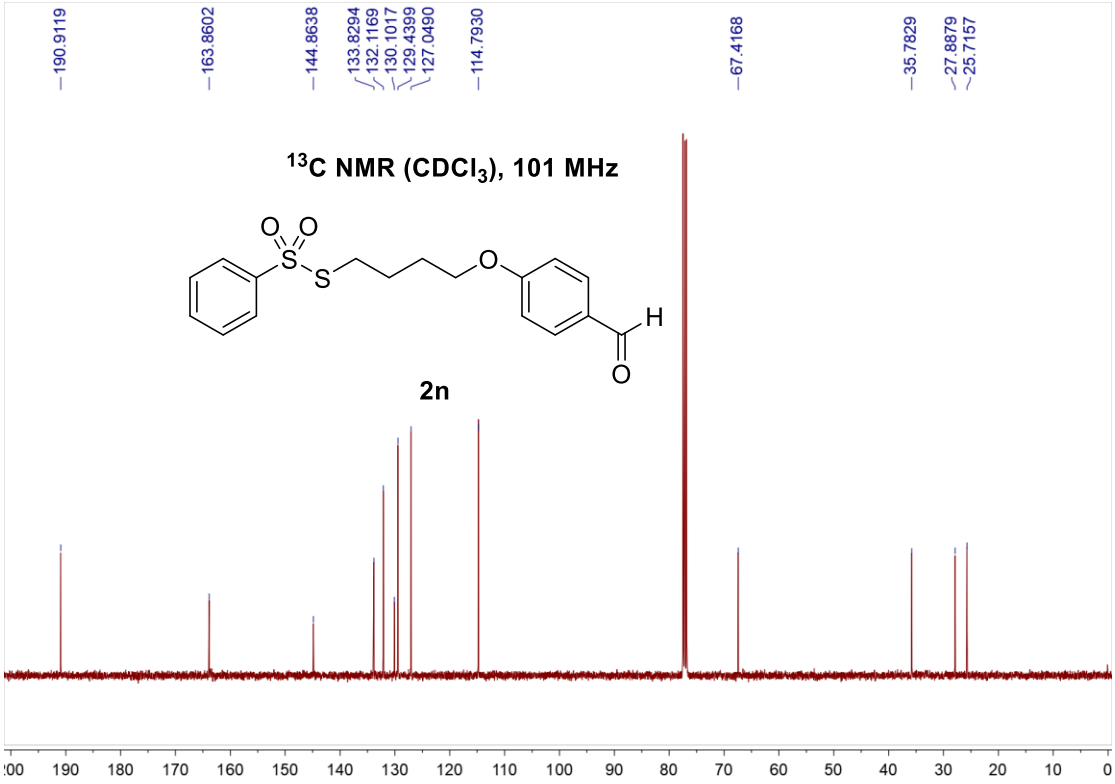
2.00
2.02
1.01
2.03
2.05
2.10
2.09
4.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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2n
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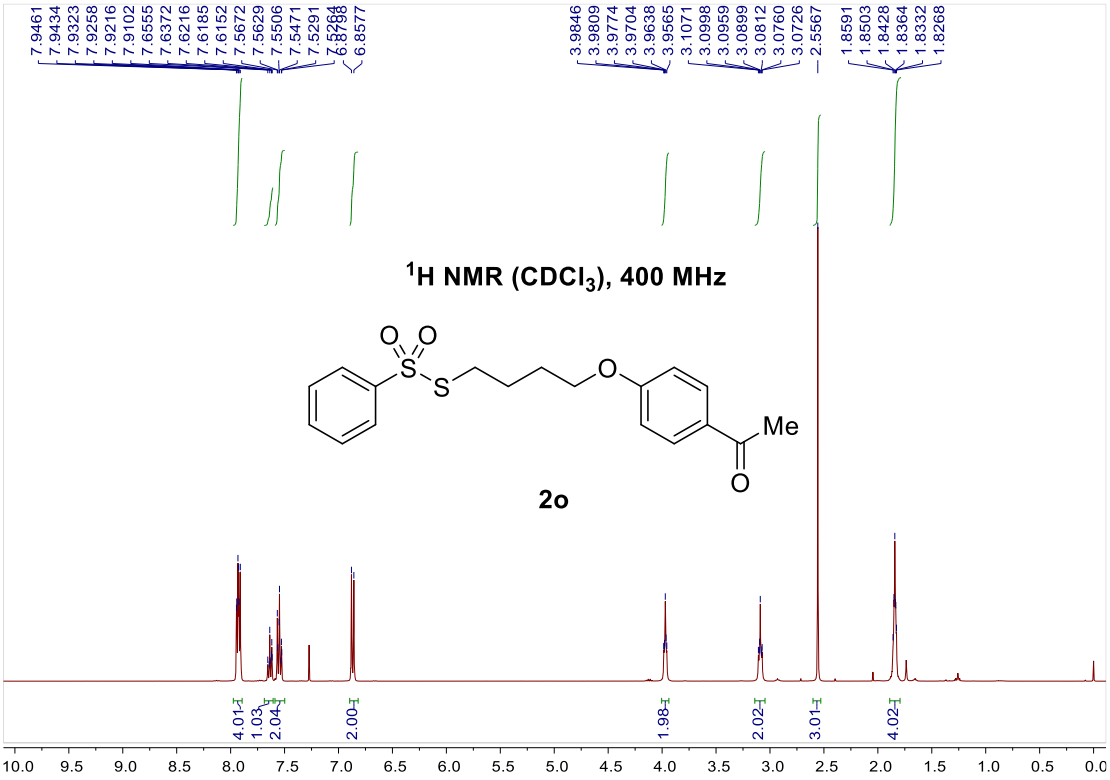
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2o
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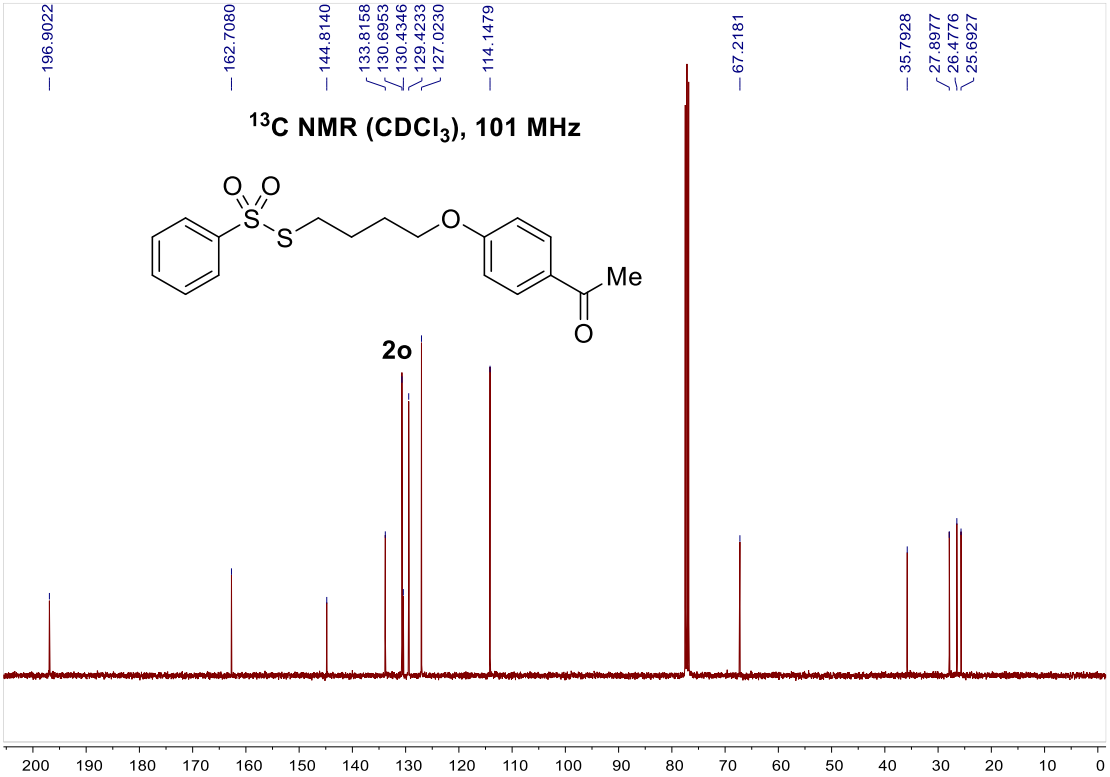
2.04
2.00
1.98
2.02
3.01
4.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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2o
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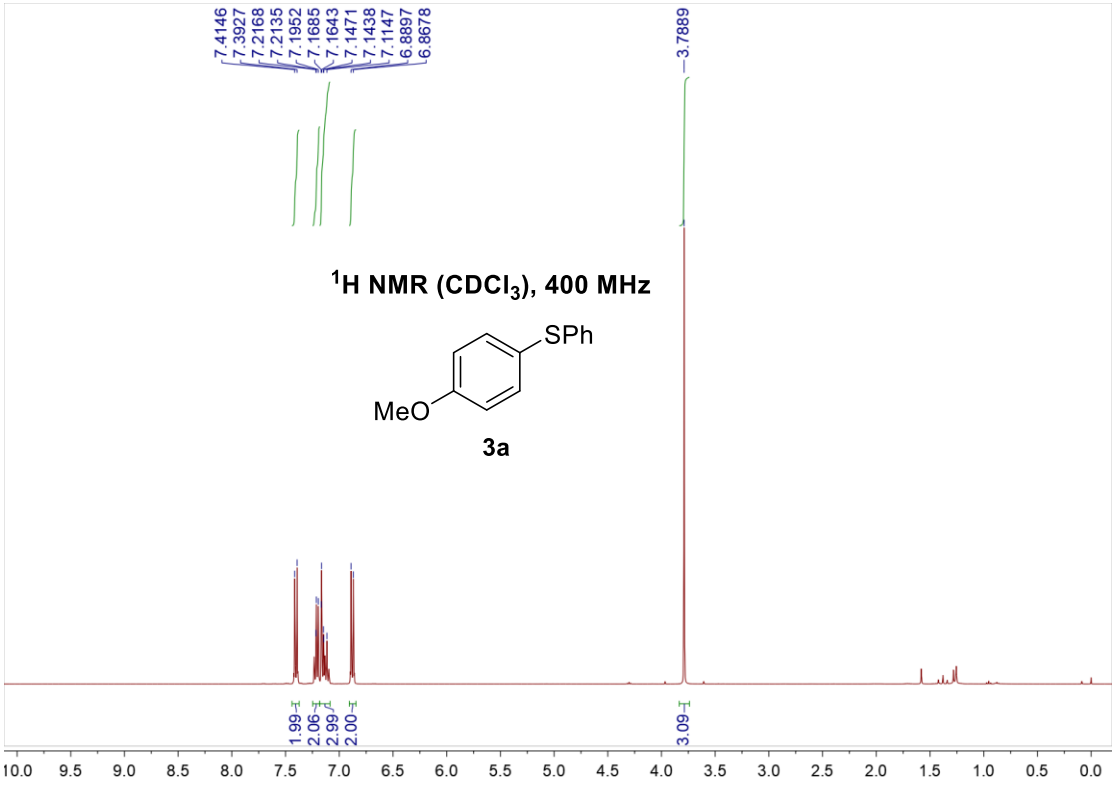
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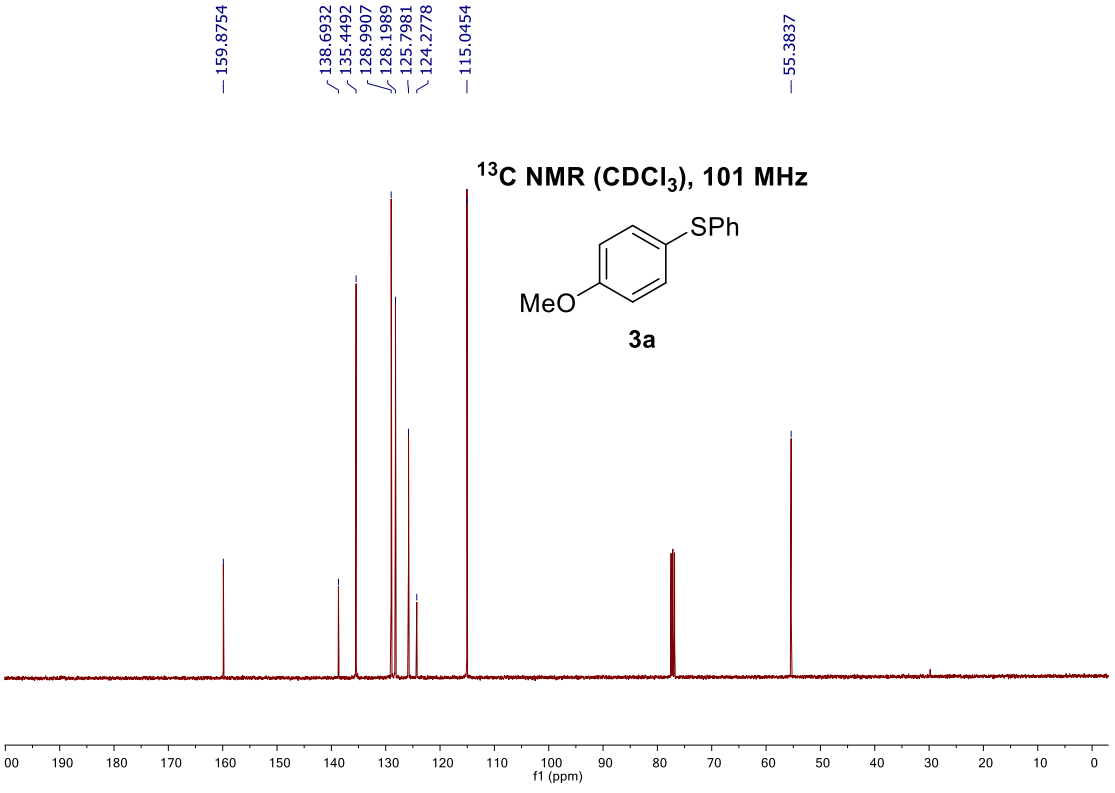
SPh
MeO
3a
1.99
2.06
2.99
2.00
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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SPh
MeO
3a
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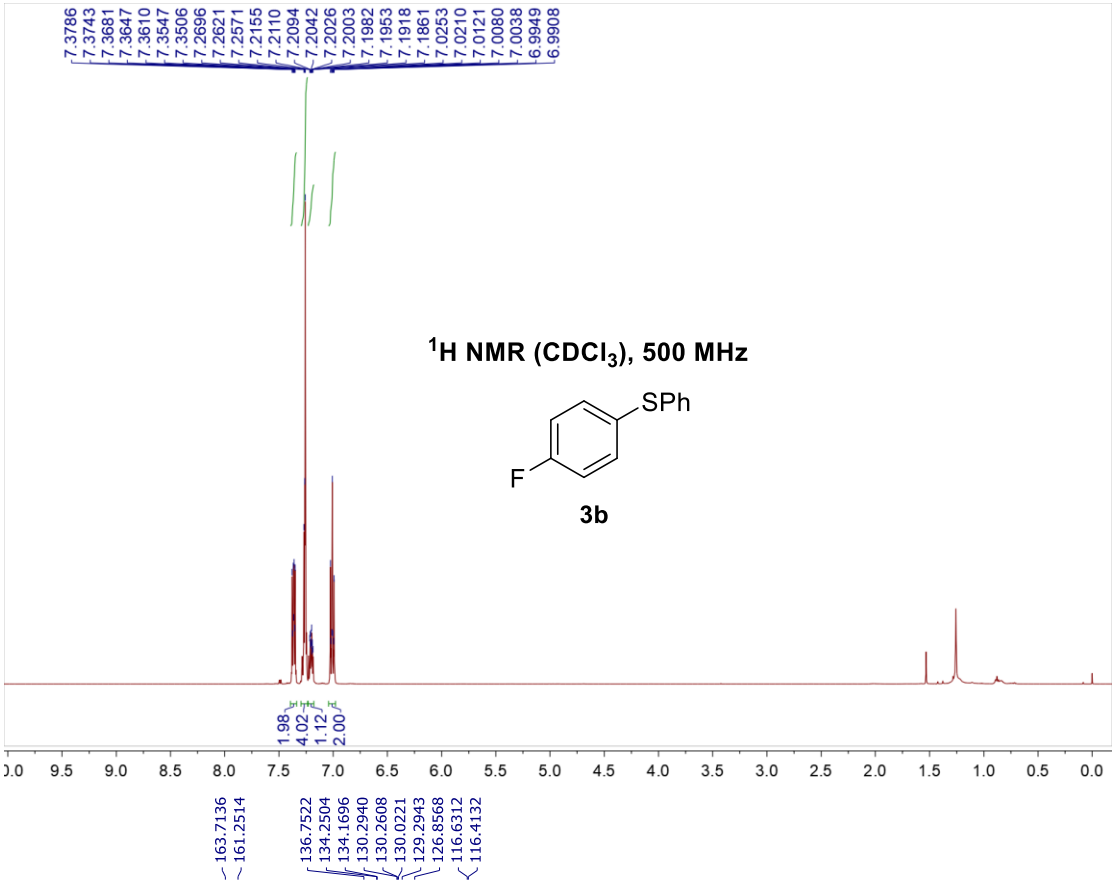
f1 (ppm)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7.1982
7.1953
7.1918
7.1861
7.0253
7.0210
7.0121
7.0080
7.0038
6.9949
6.9908
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3b
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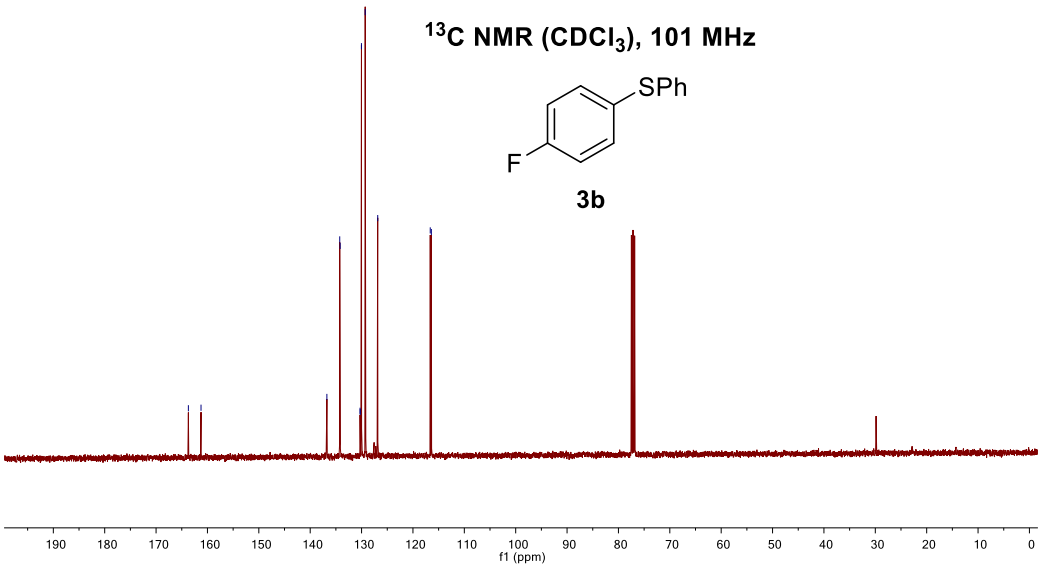
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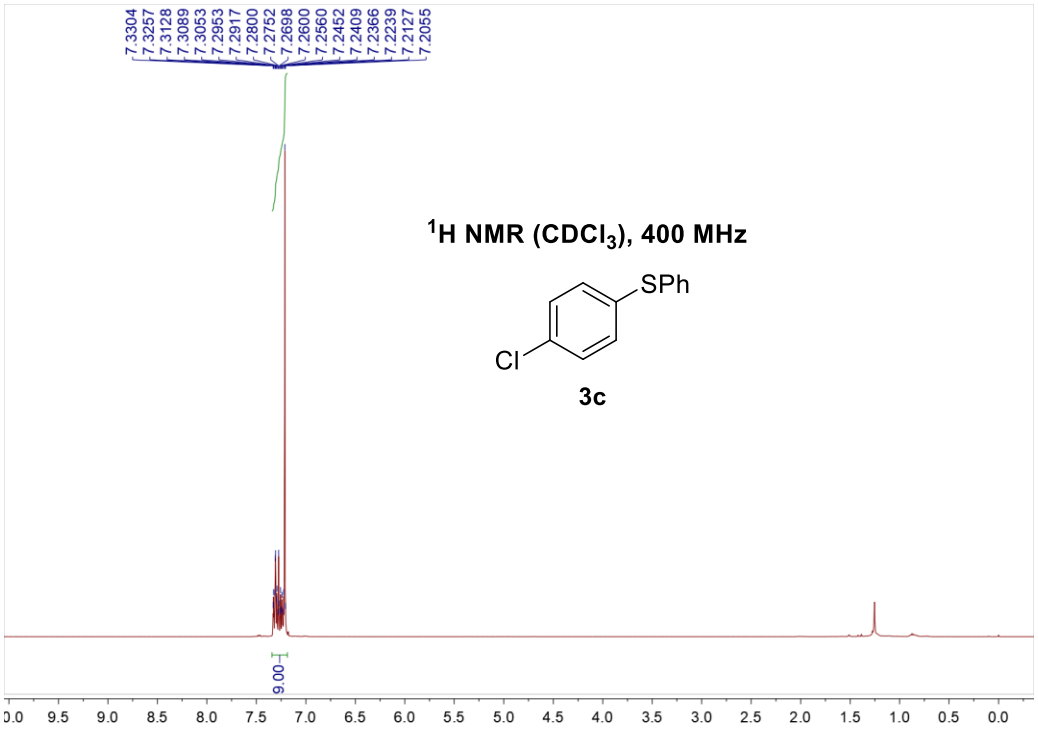

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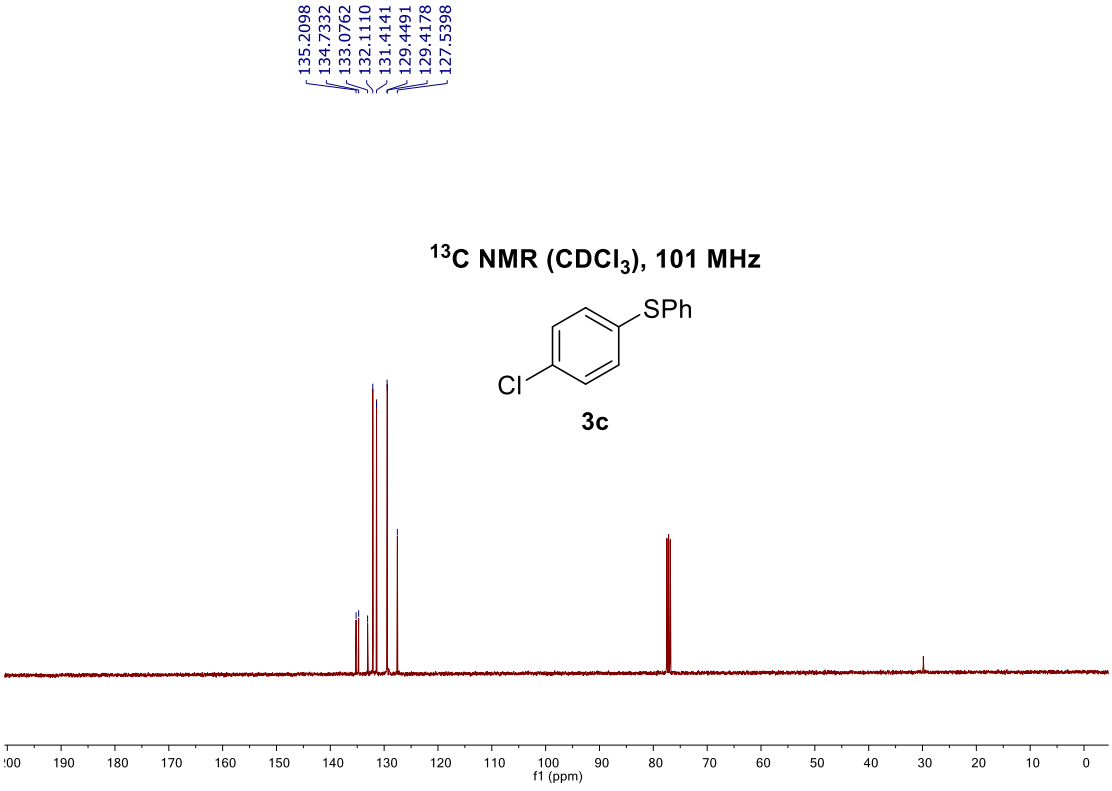

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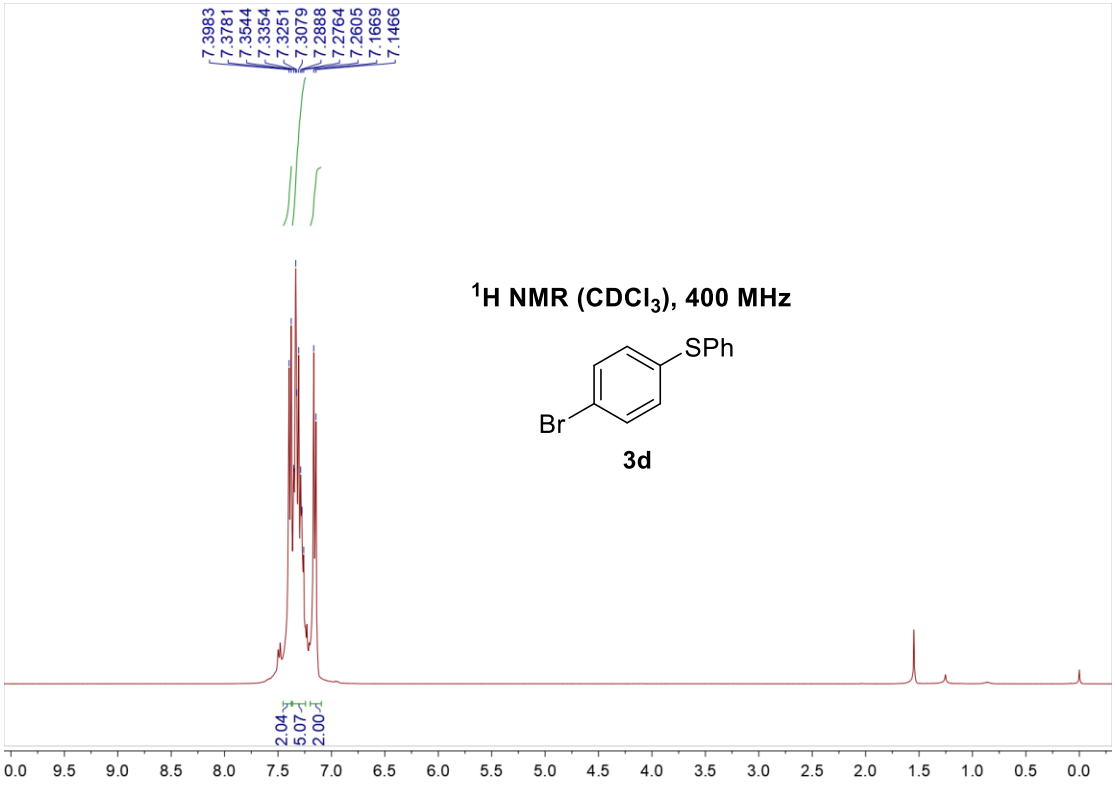
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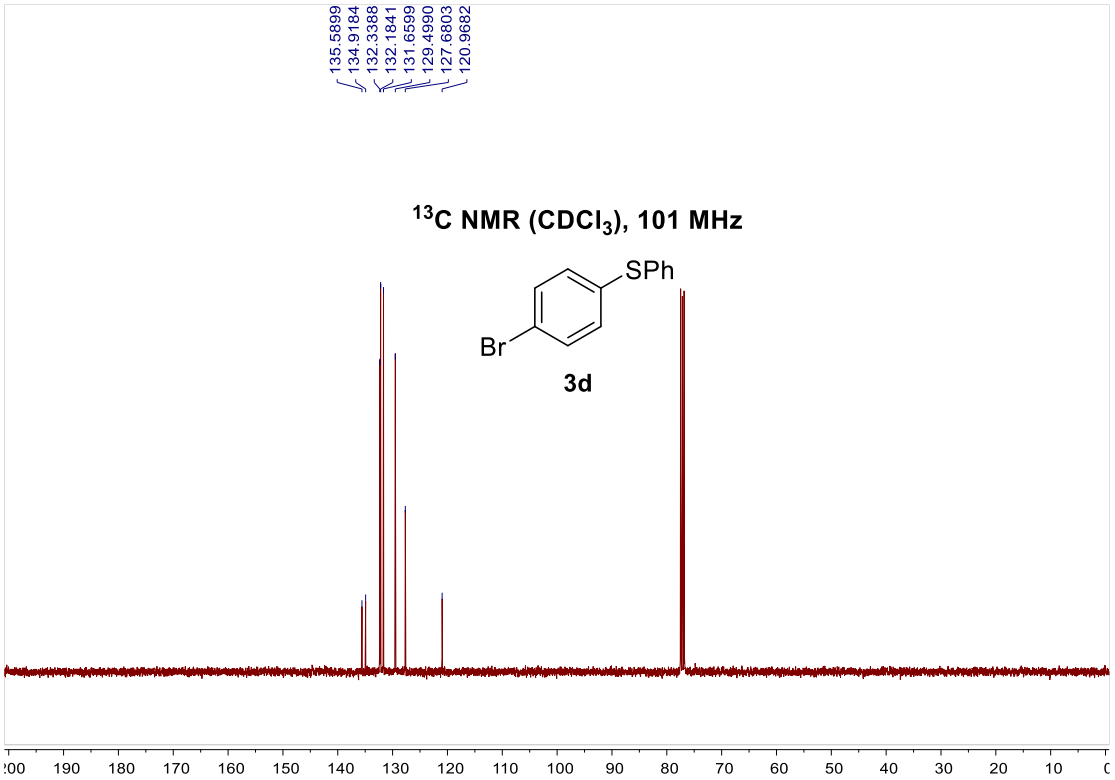
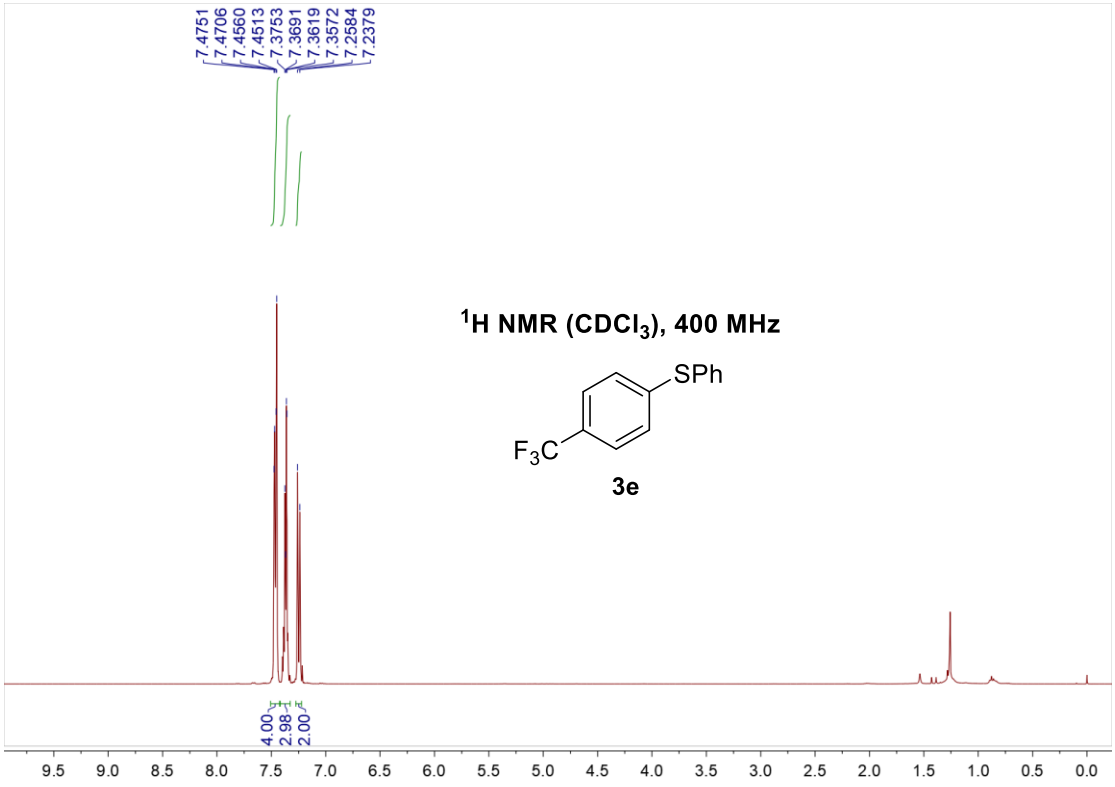
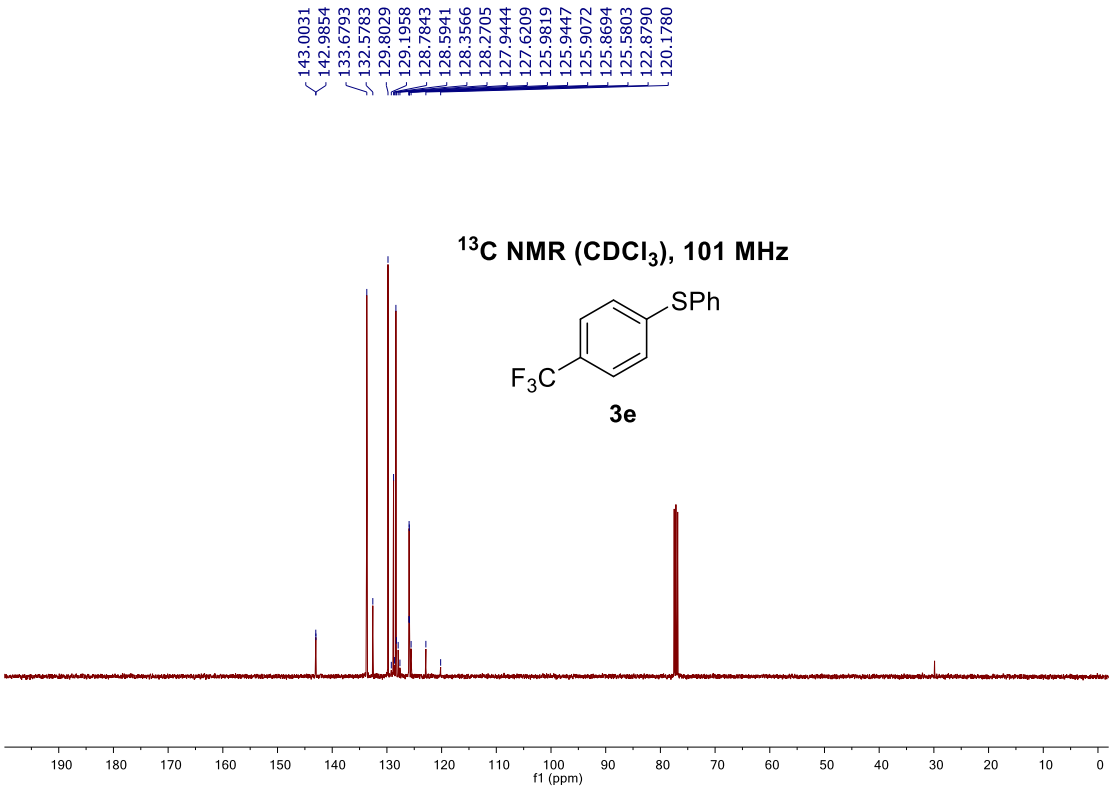
7.1466
^{1}H NMR (CDCl$_3$), 400 MHz
SPh
Br
3d
2.04
5.07
2.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


135.5899
134.9184
132.3388
132.1841
131.6599
129.4990
127.6803
120.9682
^{13}C NMR (CDCl$_3$), 101 MHz
SPh
Br
3d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10



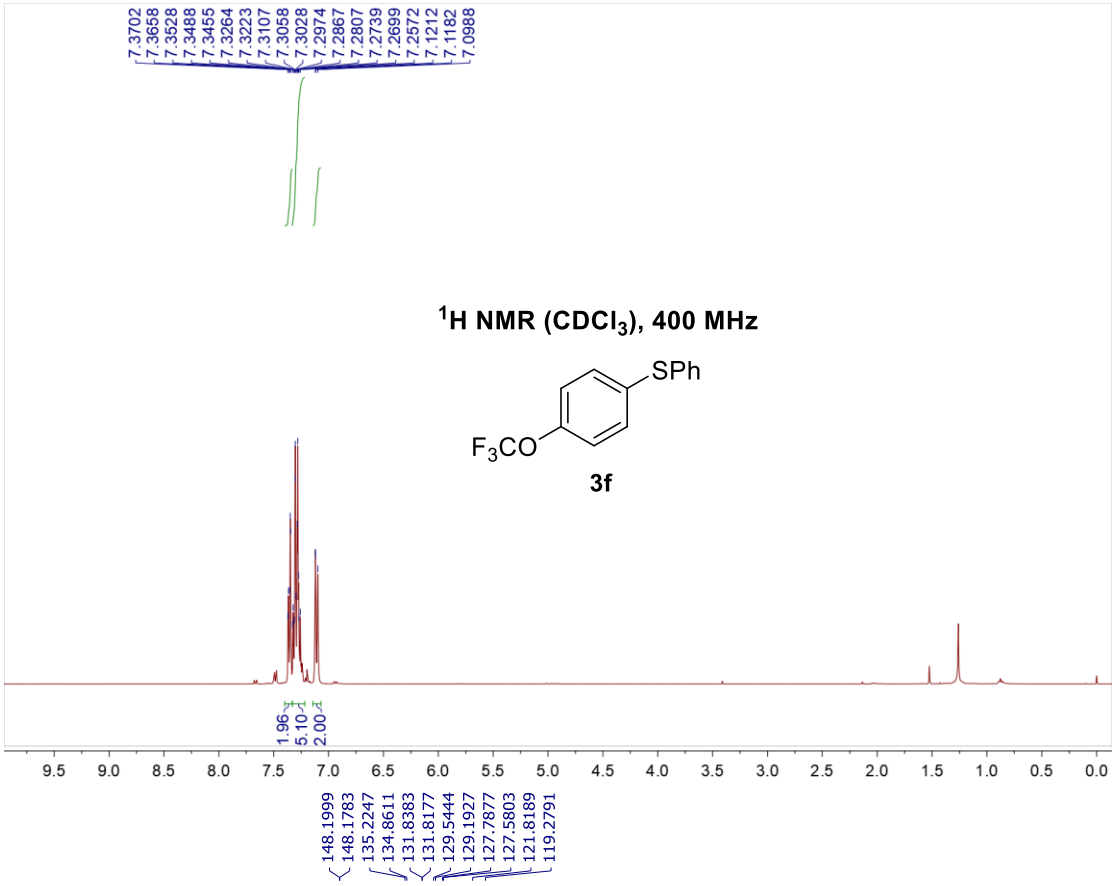
^{1}H NMR ($CDCl_3$), 400 MHz

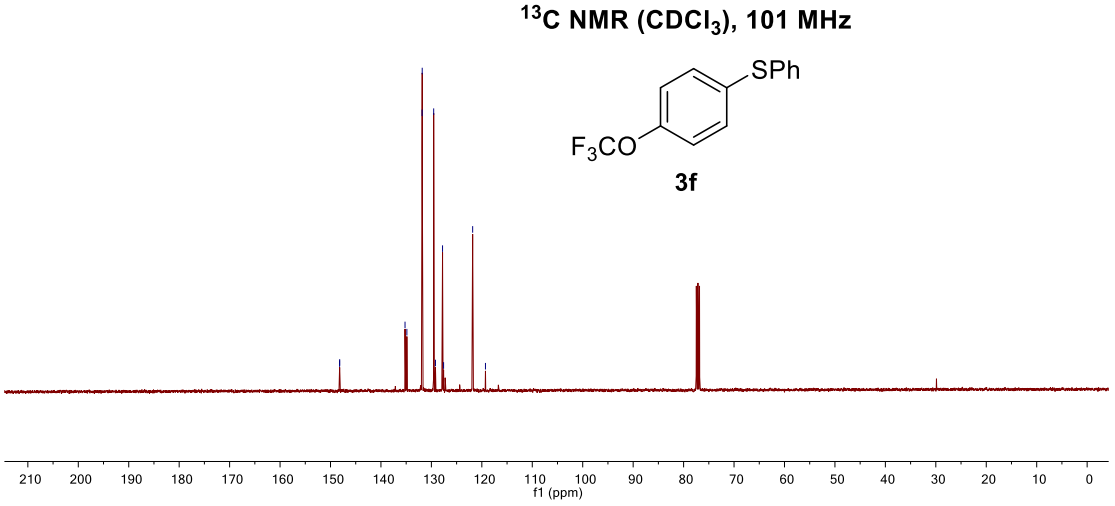
3e

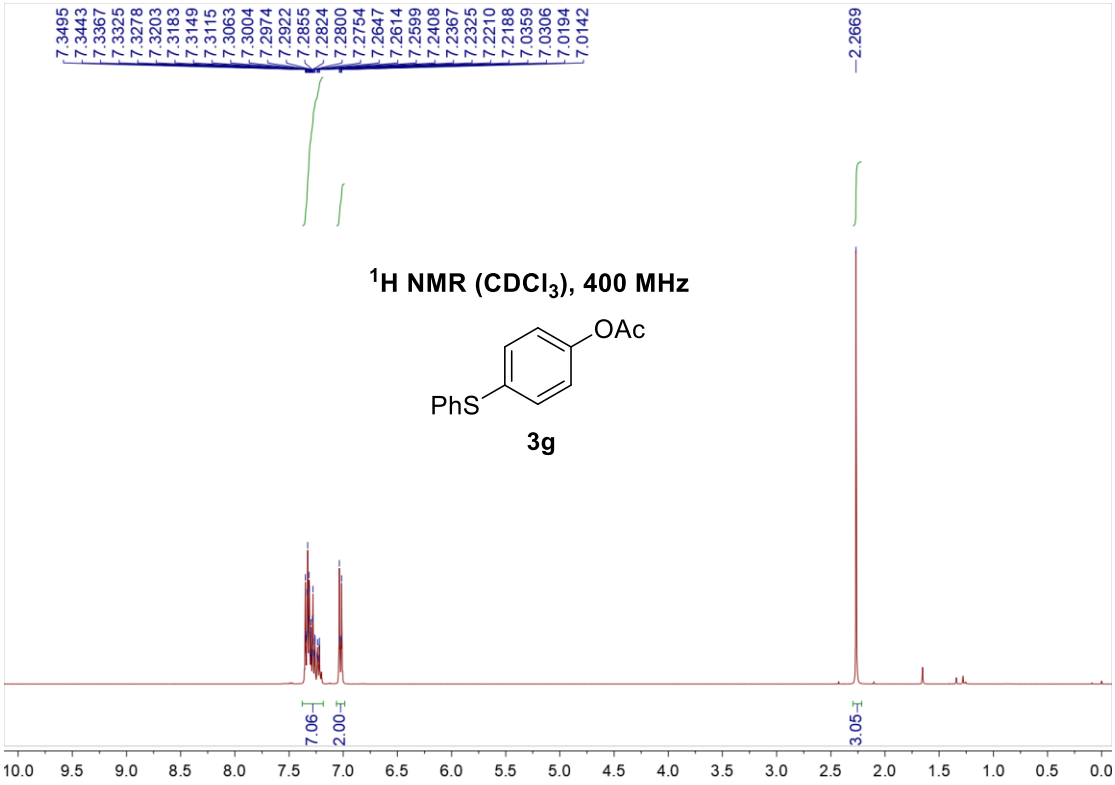


^{13}C NMR ($CDCl_3$), 101 MHz

3e

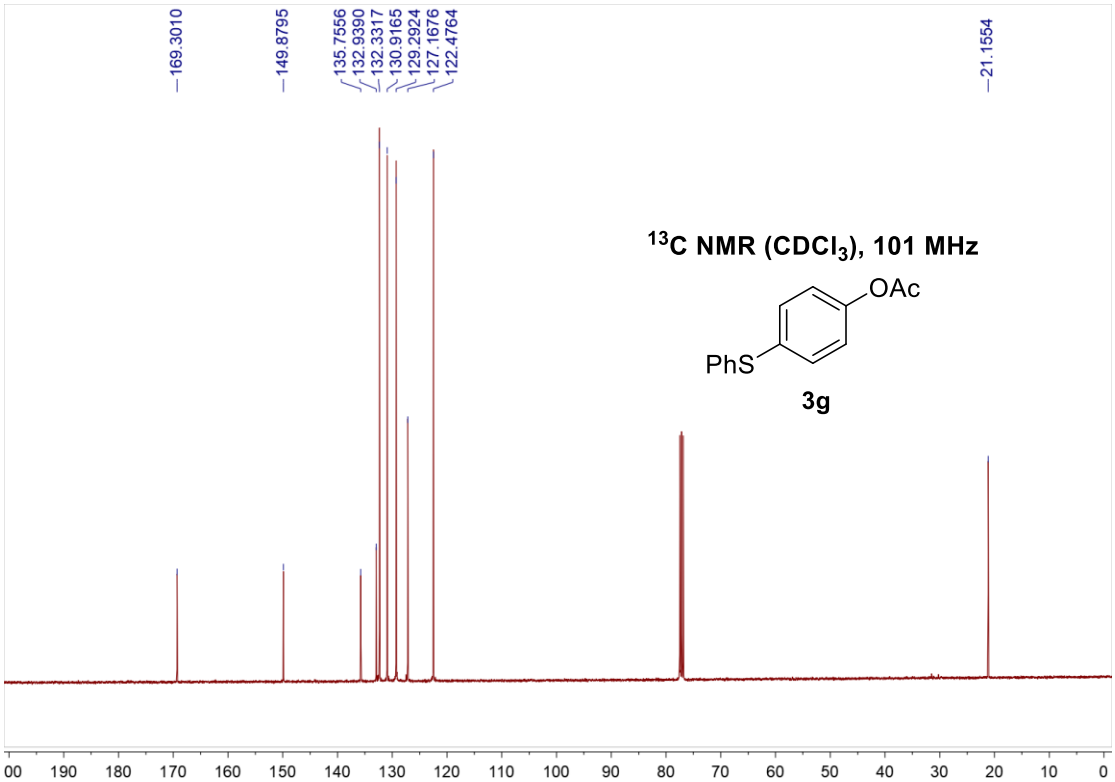

7.3702
7.3658
7.3528
7.3488
7.3455
7.3264
7.3223
7.3107
7.3058
7.3028
7.2974
7.2867
7.2807
7.2739
7.2699
7.2572
7.1212
7.1182
7.0988
1H NMR (CDCl3), 400 MHz
SPh
F3CO
3f
1.96
5.10
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
148.1999
148.1783
135.2247
134.8611
131.8383
131.8177
129.5444
129.1927
127.7877
127.5803
121.8189
119.2791


13C NMR (CDCl3), 101 MHz
SPh
F3CO
3f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



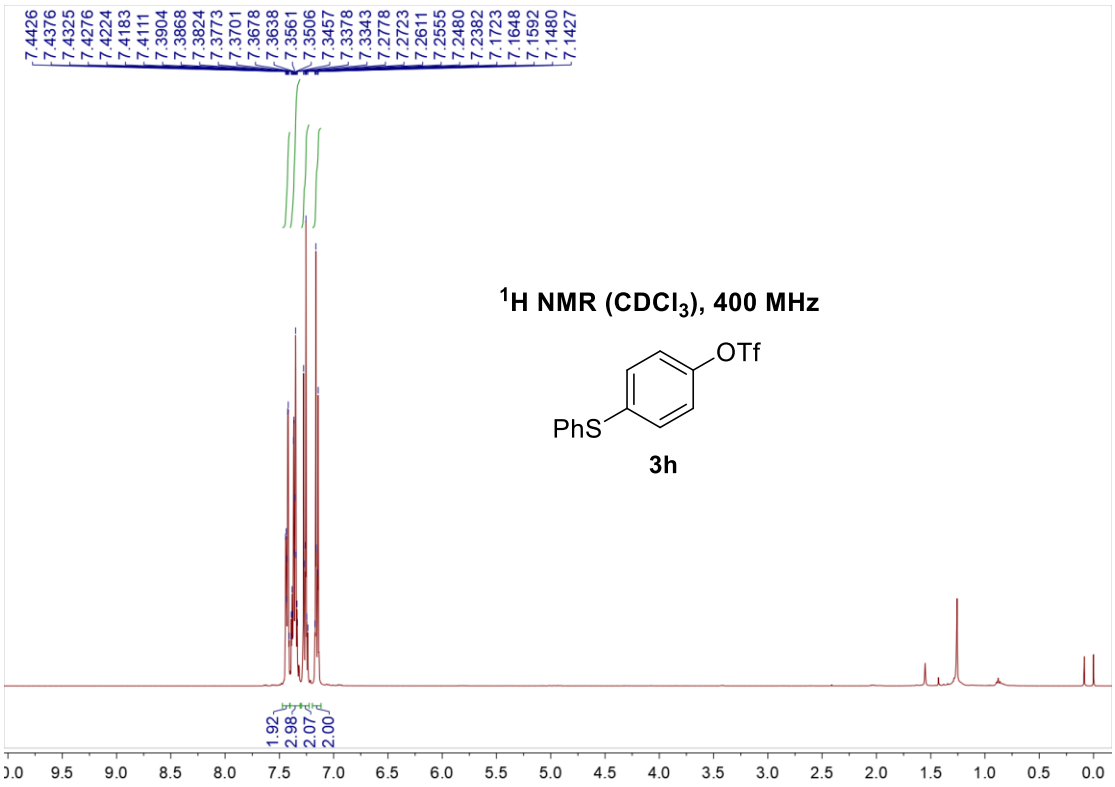
^{1}H NMR ($CDCl_3$), 400 MHz

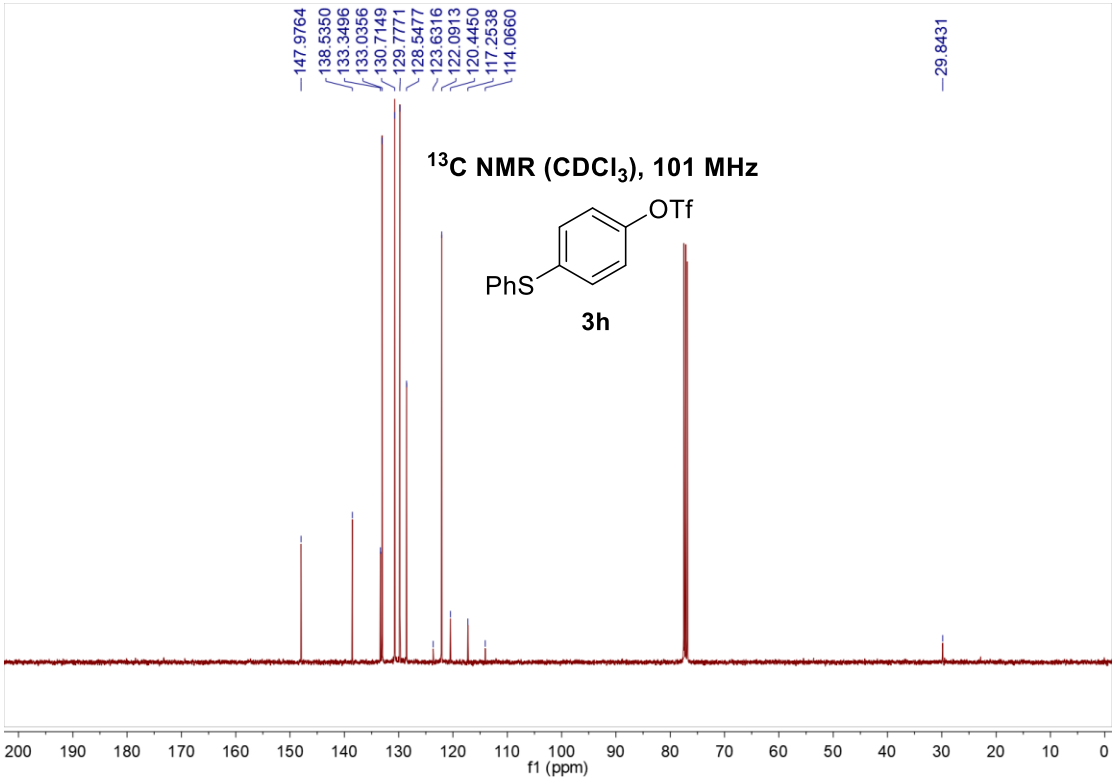
3g

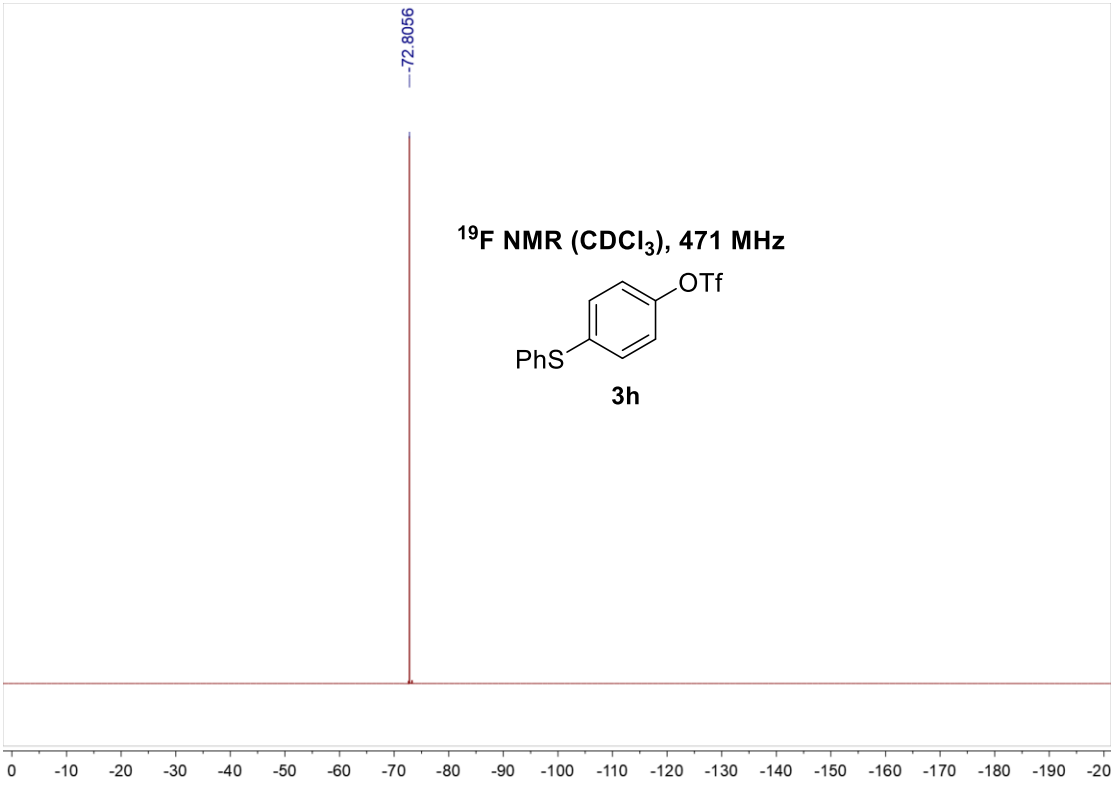


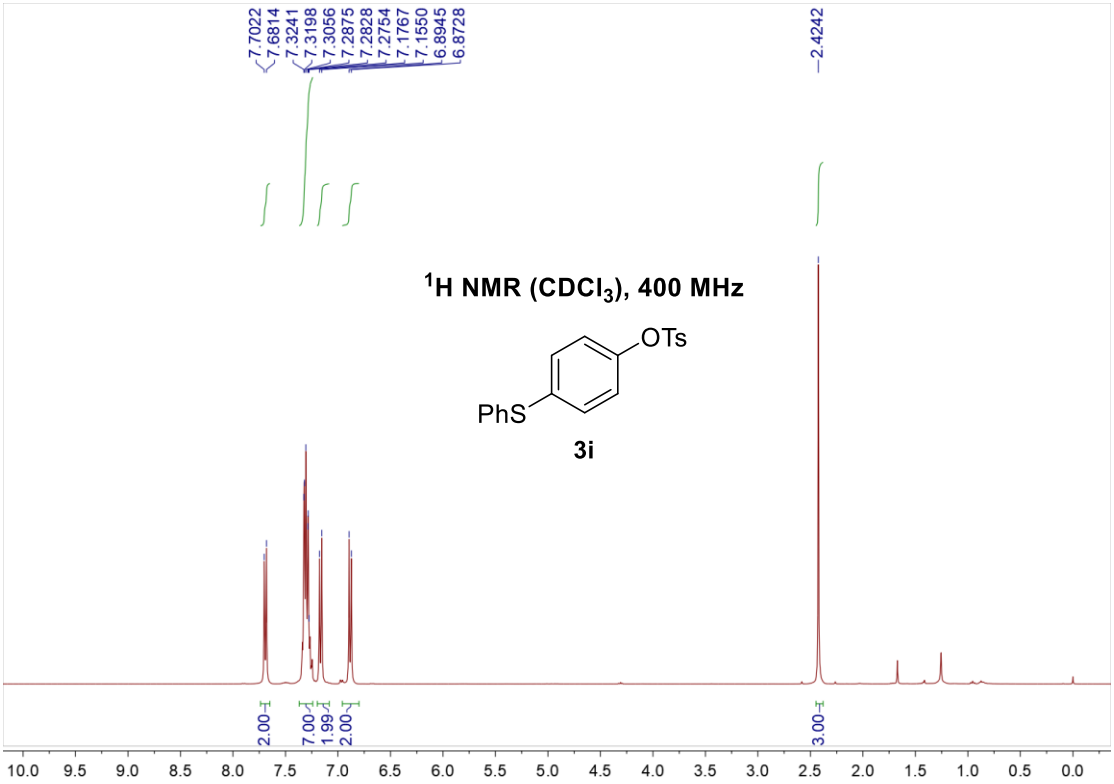
^{13}C NMR ($CDCl_3$), 101 MHz

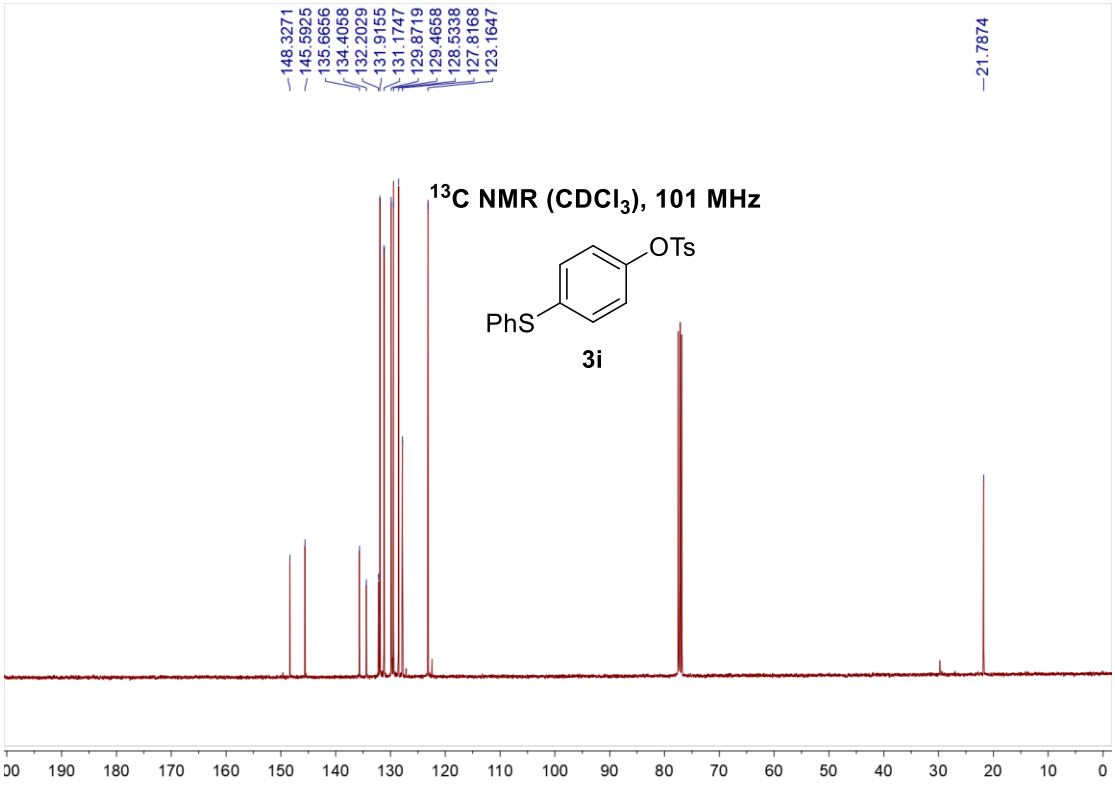
3g

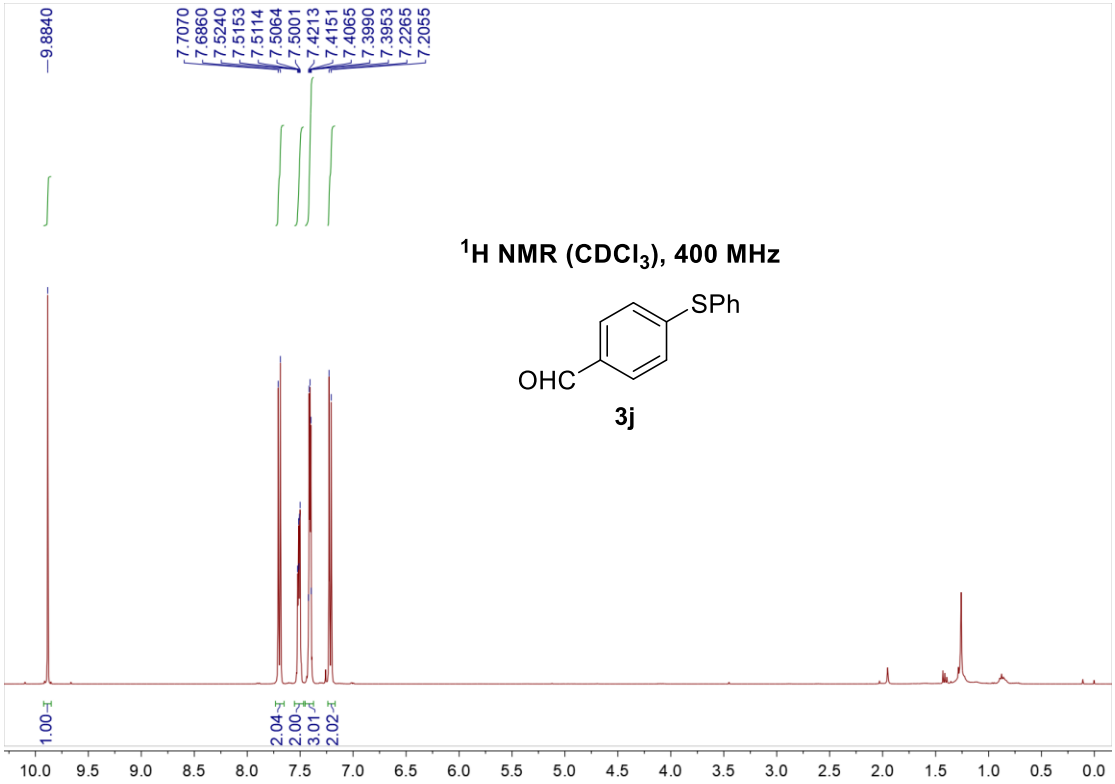

7.4426
7.4376
7.4325
7.4276
7.4224
7.4183
7.4111
7.3904
7.3868
7.3824
7.3773
7.3701
7.3678
7.3638
7.3561
7.3506
7.3457
7.3378
7.3343
7.2778
7.2723
7.2611
7.2555
7.2480
7.2382
7.1723
7.1648
7.1592
7.1480
7.1427
1.92
2.98
2.07
2.00
^{1}H NMR (CDCl$_3$), 400 MHz
OTf
PhS
3h

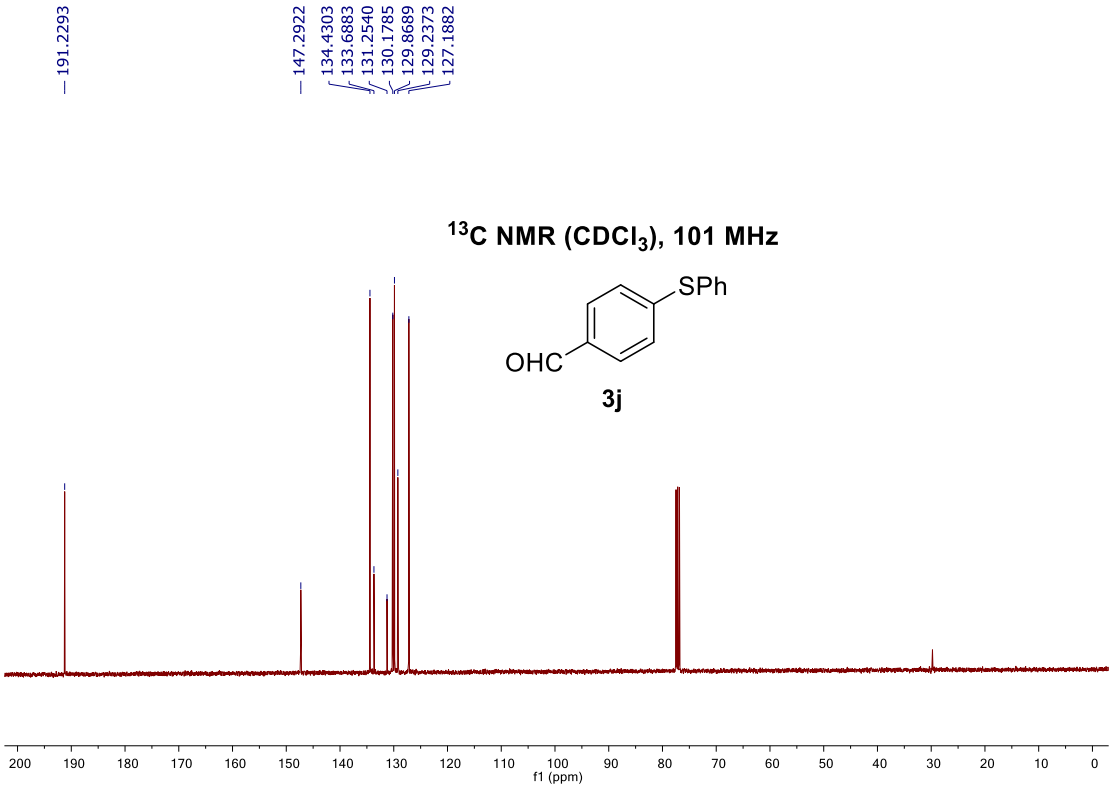

147.9764
138.5350
133.3496
133.0356
130.7149
129.7771
128.5477
123.6316
122.0913
120.4450
117.2538
114.0660
29.8431
^{13}C NMR (CDCl$_3$), 101 MHz
OTf
PhS
3h
f1 (ppm)

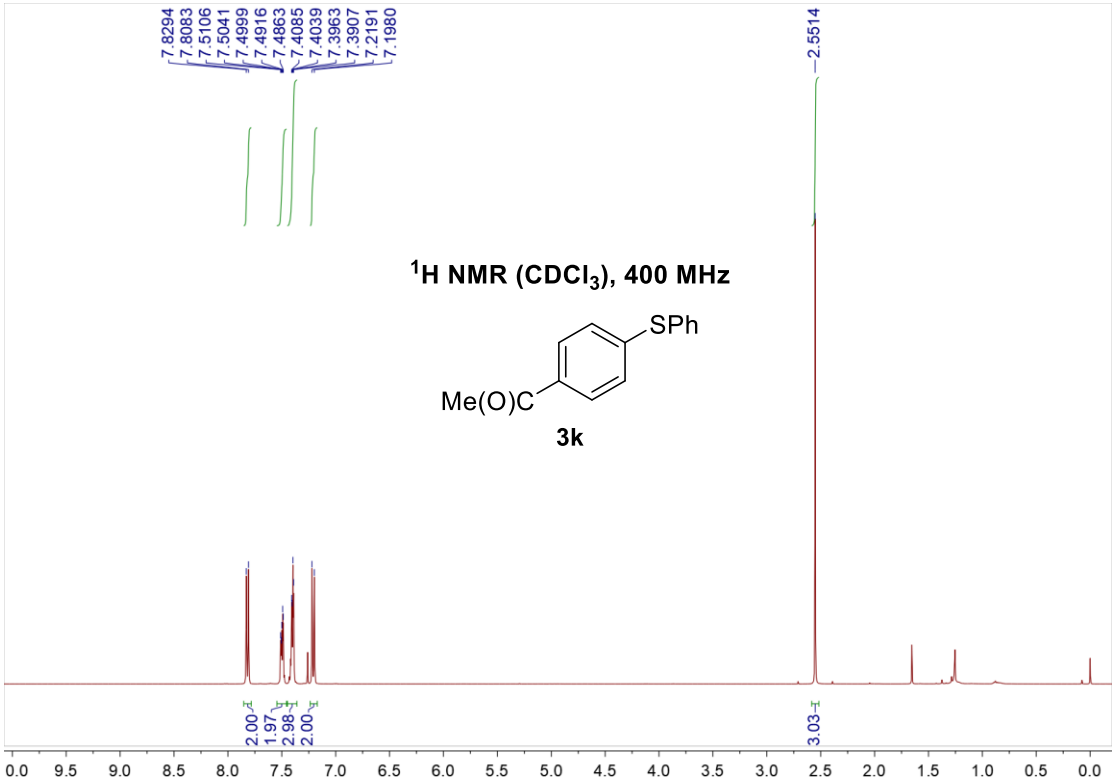

-72.8056
^{19}F NMR (CDCl$_3$), 471 MHz
OTf
PhS
3h
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20

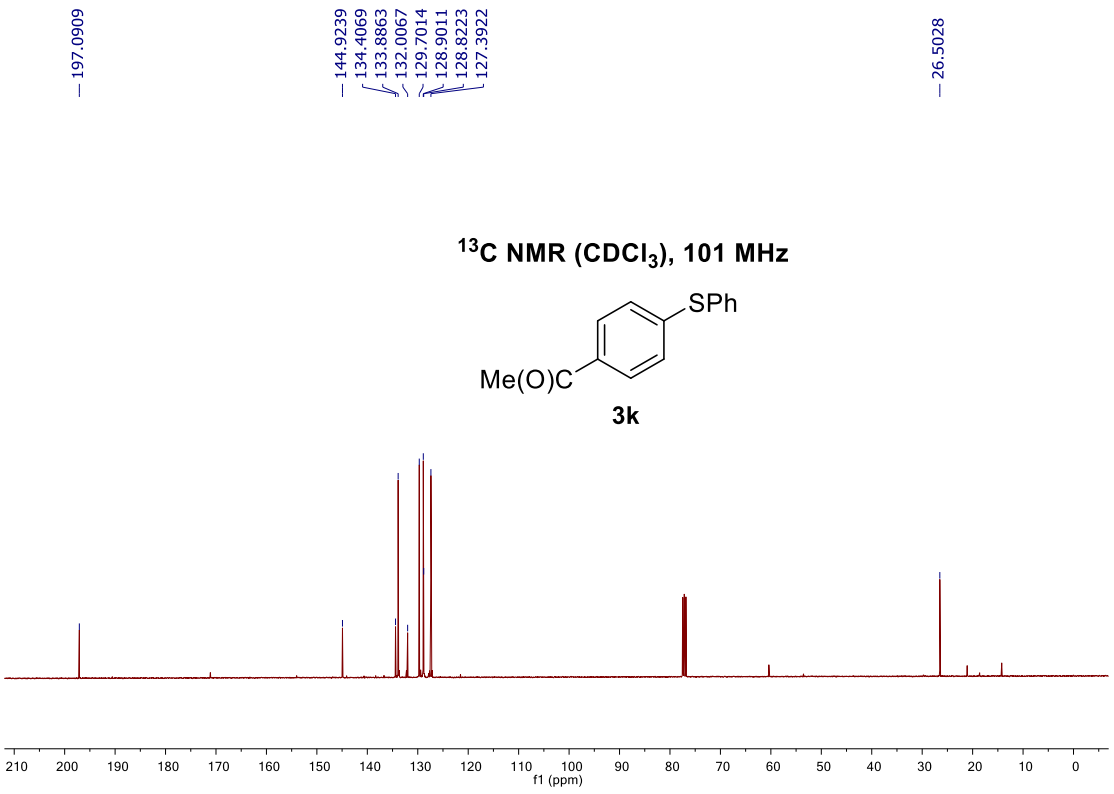

7.7022
7.6814
7.3241
7.3198
7.3056
7.2875
7.2828
7.2754
7.1767
7.1550
6.8945
6.8728
2.4242
^{1}H NMR (CDCl$_3$), 400 MHz
OTs
PhS
3i
2.00
7.00
1.99
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

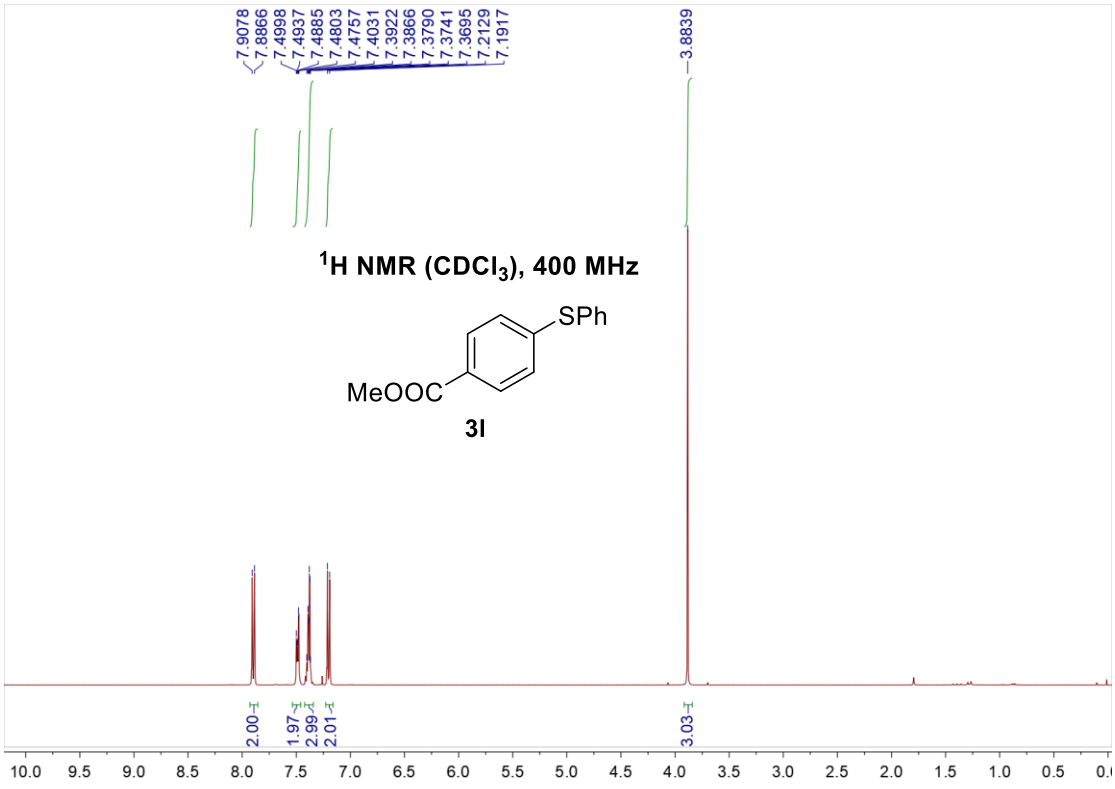

148.3271
145.5925
135.6656
134.4058
132.2029
131.9155
131.1747
129.8719
129.4658
128.5338
127.8168
123.1647
21.7874
13C NMR (CDCl3), 101 MHz
OTs
PhS
3i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

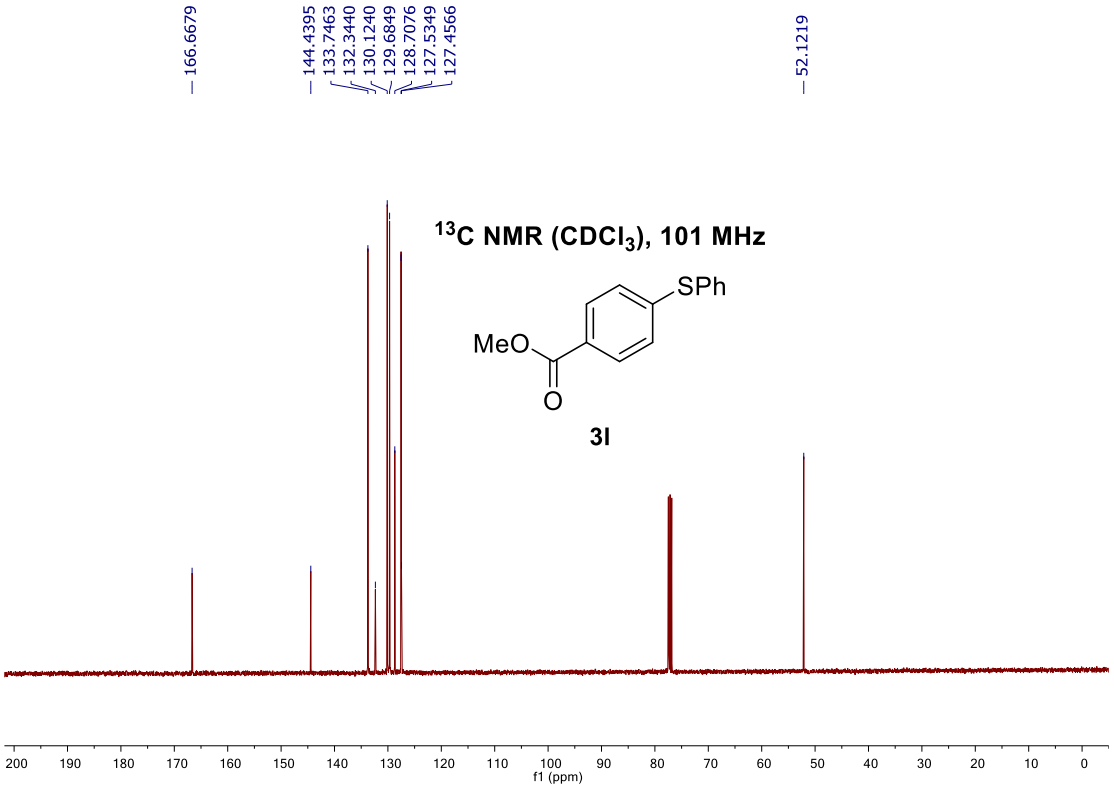

9.8840
7.7070
7.6860
7.5240
7.5153
7.5114
7.5064
7.5001
7.4213
7.4151
7.4065
7.3990
7.3953
7.2265
7.2055
1H NMR (CDCl3), 400 MHz
SPh
OHC
3j
1.00
2.04
2.00
3.01
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

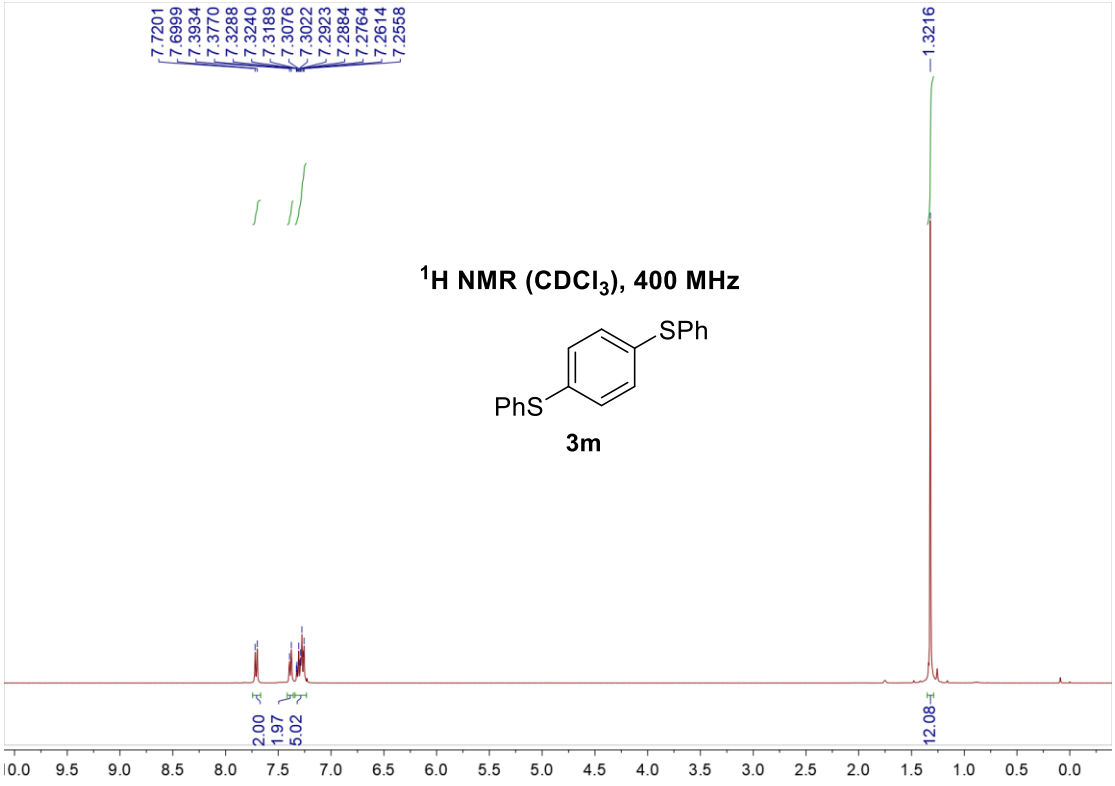

191.2293
147.2922
134.4303
133.6883
131.2540
130.1785
129.8689
129.2373
127.1882
13C NMR (CDCl3), 101 MHz
SPh
OHC
3j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

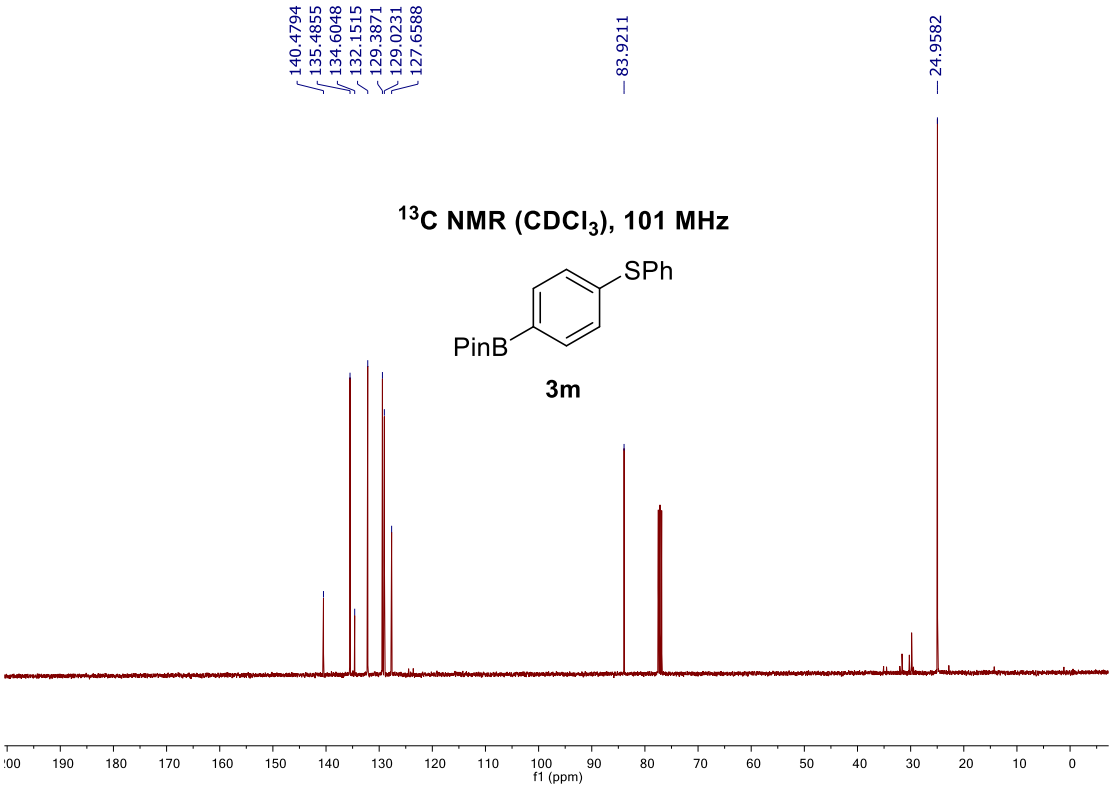

7.8294
7.8083
7.5106
7.5041
7.4999
7.4916
7.4863
7.4085
7.4039
7.3963
7.3907
7.2191
7.1980
2.5514
1H NMR (CDCl3), 400 MHz
SPh
Me(O)C
3k
2.00
1.97
2.98
2.00
3.03
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

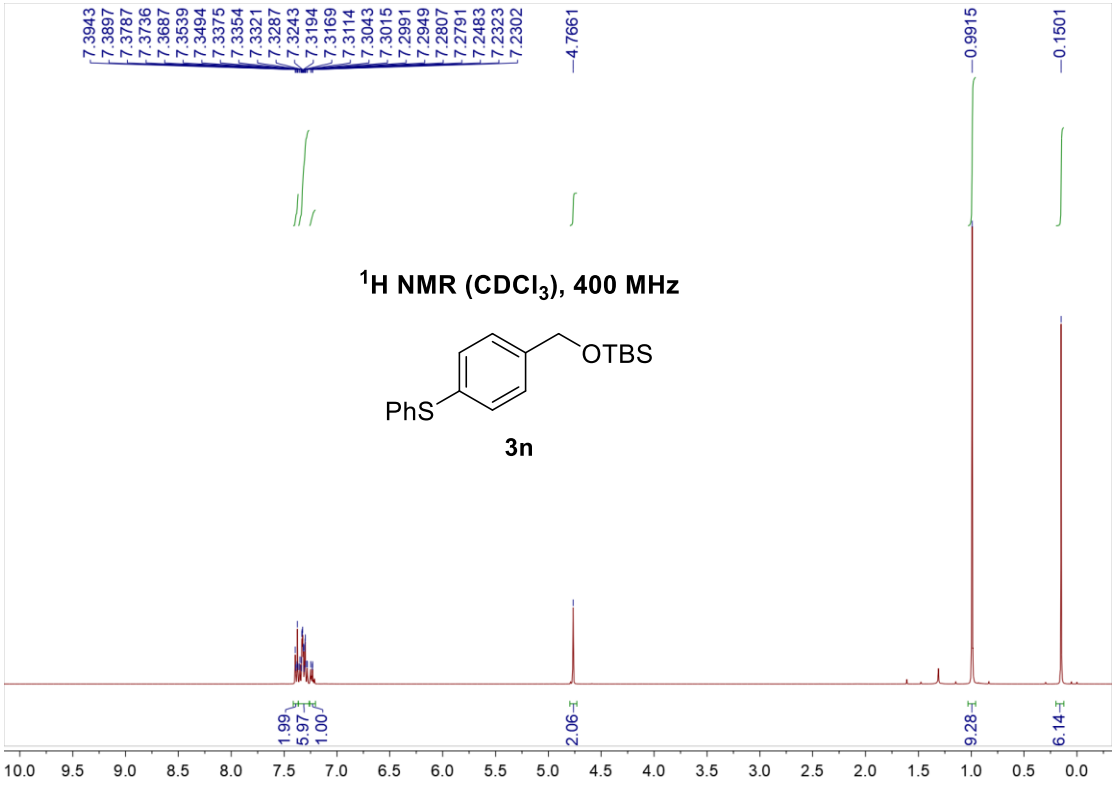

197.0909
144.9239
134.4069
133.8863
132.0067
129.7014
128.9011
128.8223
127.3922
26.5028
^{13}C NMR (CDCl$_3$), 101 MHz
SPh
Me(O)C
3k
f1 (ppm)


7.9078
7.8866
7.4998
7.4937
7.4885
7.4803
7.4757
7.4031
7.3922
7.3866
7.3790
7.3741
7.3695
7.2129
7.1917
3.8839
^{1}H NMR (CDCl$_3$), 400 MHz
SPh
MeOOC
3l
2.00
1.97
2.99
2.01
3.03


166.6679
144.4395
133.7463
132.3440
130.1240
129.6849
128.7076
127.5349
127.4566
52.1219
13C NMR (CDCl3), 101 MHz
SPh
MeO
O
3l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.7201
7.6999
7.3934
7.3770
7.3288
7.3240
7.3189
7.3076
7.3022
7.2923
7.2884
7.2764
7.2614
7.2558
1.3216
1H NMR (CDCl3), 400 MHz
SPh
PhS
3m
2.00
1.97
5.02
12.08
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


140.4794
135.4855
134.6048
132.1515
129.3871
129.0231
127.6588
83.9211
24.9582
13C NMR (CDCl3), 101 MHz
SPh
PinB
3m
f1 (ppm)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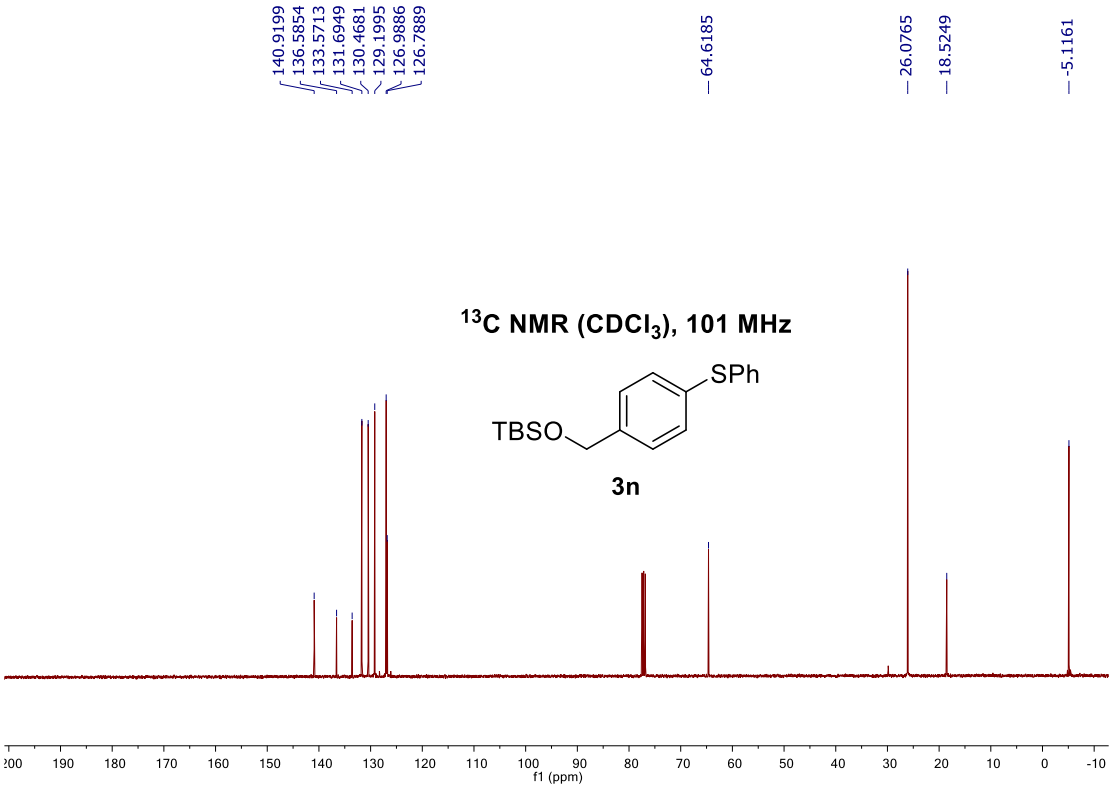
7.3897
7.3787
7.3736
7.3687
7.3539
7.3494
7.3375
7.3354
7.3321
7.3287
7.3243
7.3194
7.3169
7.3114
7.3043
7.3015
7.2991
7.2949
7.2807
7.2791
7.2483
7.2323
7.2302
4.7661
0.9915
0.1501
1H NMR (CDCl3), 400 MHz
OTBS
PhS
3n
1.99
5.97
1.00
2.06
9.28
6.14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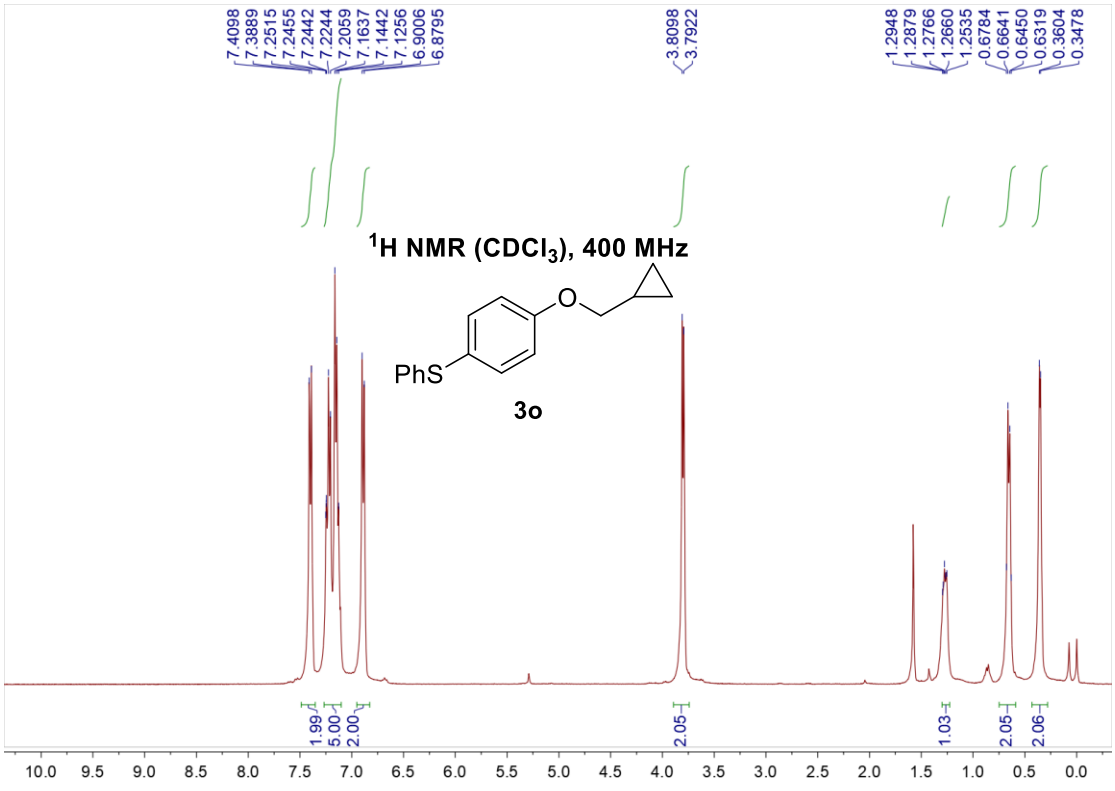
136.5854
133.5713
131.6949
130.4681
129.1995
126.9886
126.7889
64.6185
26.0765
18.5249
-5.1161
13C NMR (CDCl3), 101 MHz
SPh
TBSO
3n
f1 (ppm)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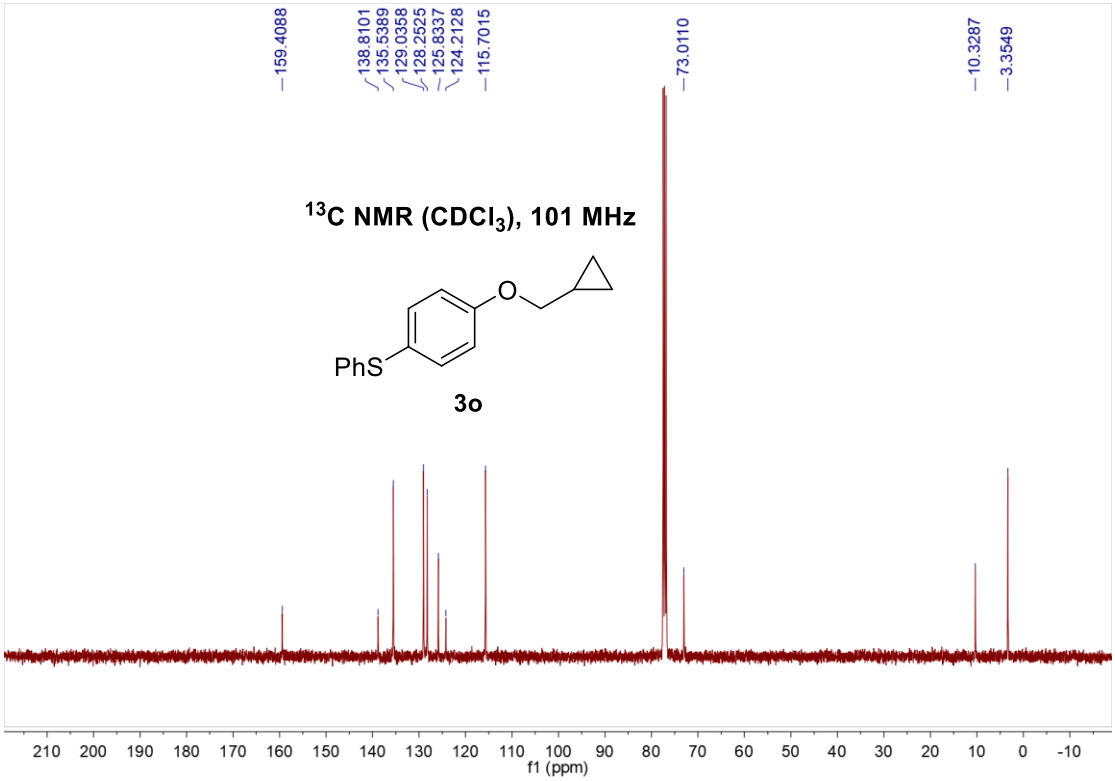
7.2515
7.2455
7.2442
7.2244
7.2059
7.1637
7.1442
7.1256
6.9006
6.8795
3.8098
3.7922
1.2948
1.2879
1.2766
1.2660
1.2535
0.6784
0.6641
0.6450
0.6319
0.3604
0.3478
1H NMR (CDCl3), 400 MHz
O
PhS
3o
1.99
5.00
2.00
2.05
1.03
2.05
2.06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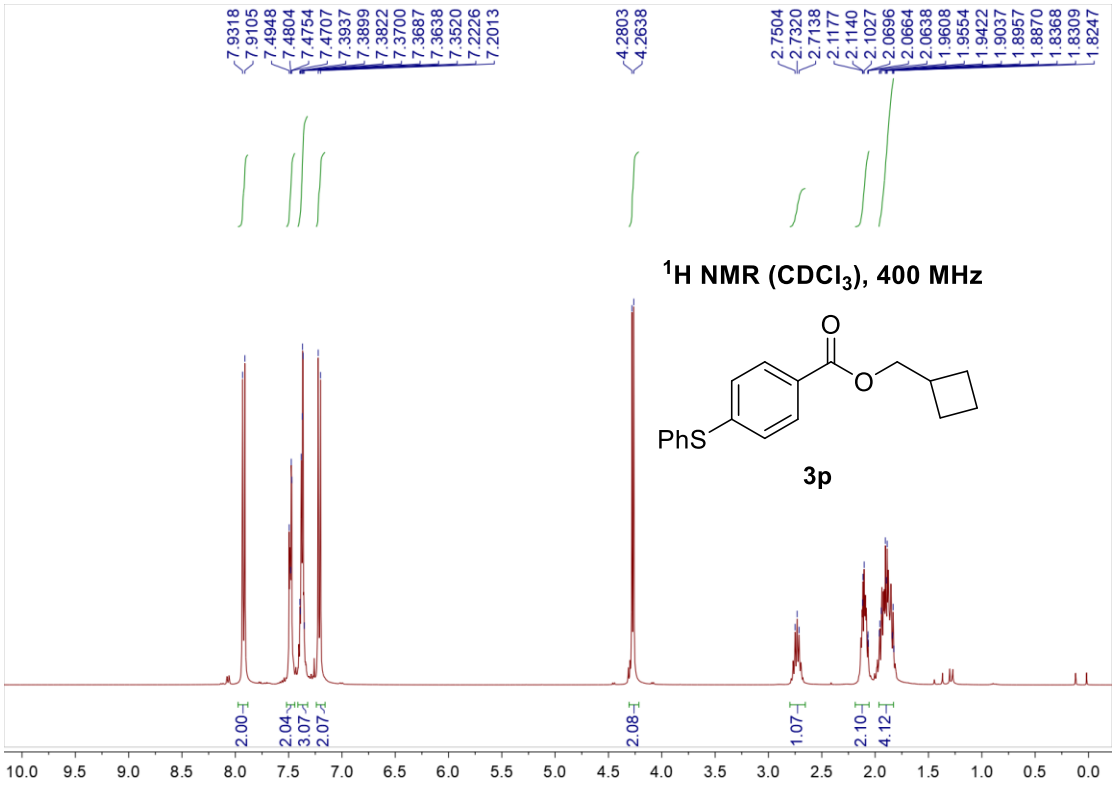
138.8101
135.5389
129.0358
128.2525
125.8337
124.2128
115.7015
73.0110
10.3287
3.3549
13C NMR (CDCl3), 101 MHz
O
PhS
3o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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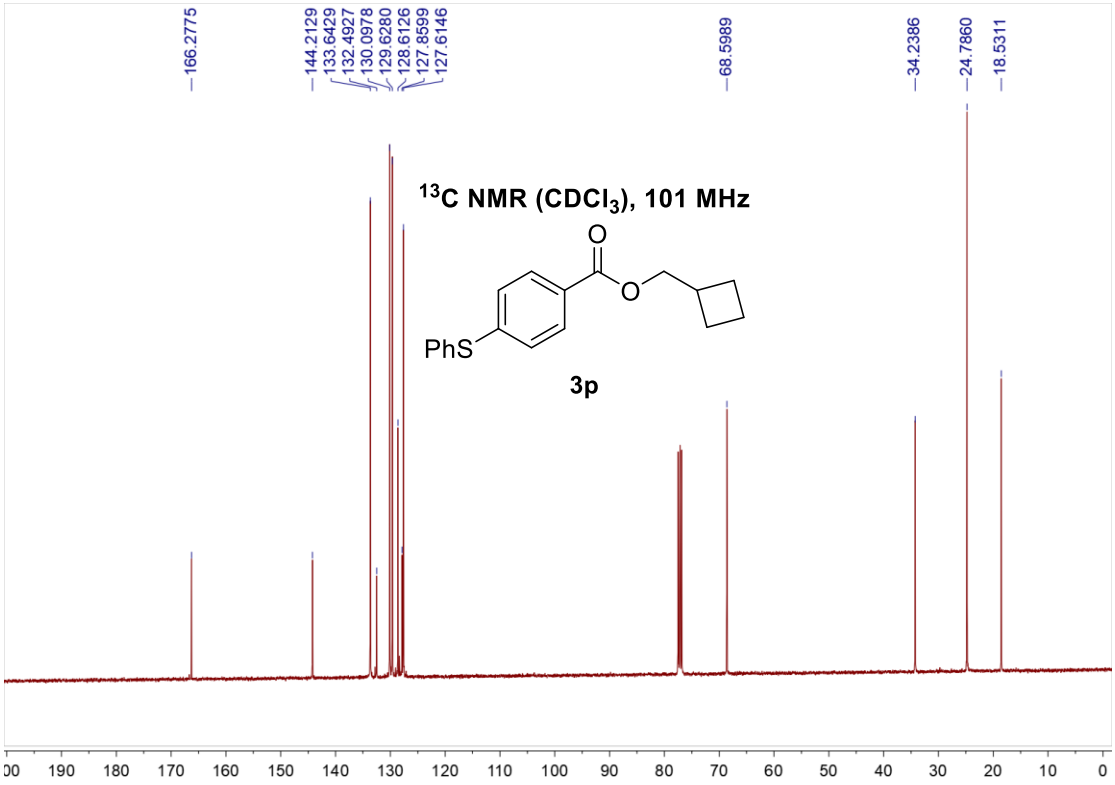
7.4948
7.4804
7.4754
7.4707
7.3937
7.3899
7.3822
7.3700
7.3687
7.3638
7.3520
7.2226
7.2013
4.2803
4.2638
2.7504
2.7320
2.7138
2.1177
2.1140
2.1027
2.0696
2.0664
2.0638
1.9608
1.9554
1.9422
1.9037
1.8957
1.8870
1.8368
1.8309
1.8247
1H NMR (CDCl3), 400 MHz
O
O
PhS
3p
2.00
2.04
3.07
2.07
2.08
1.07
2.10
4.12
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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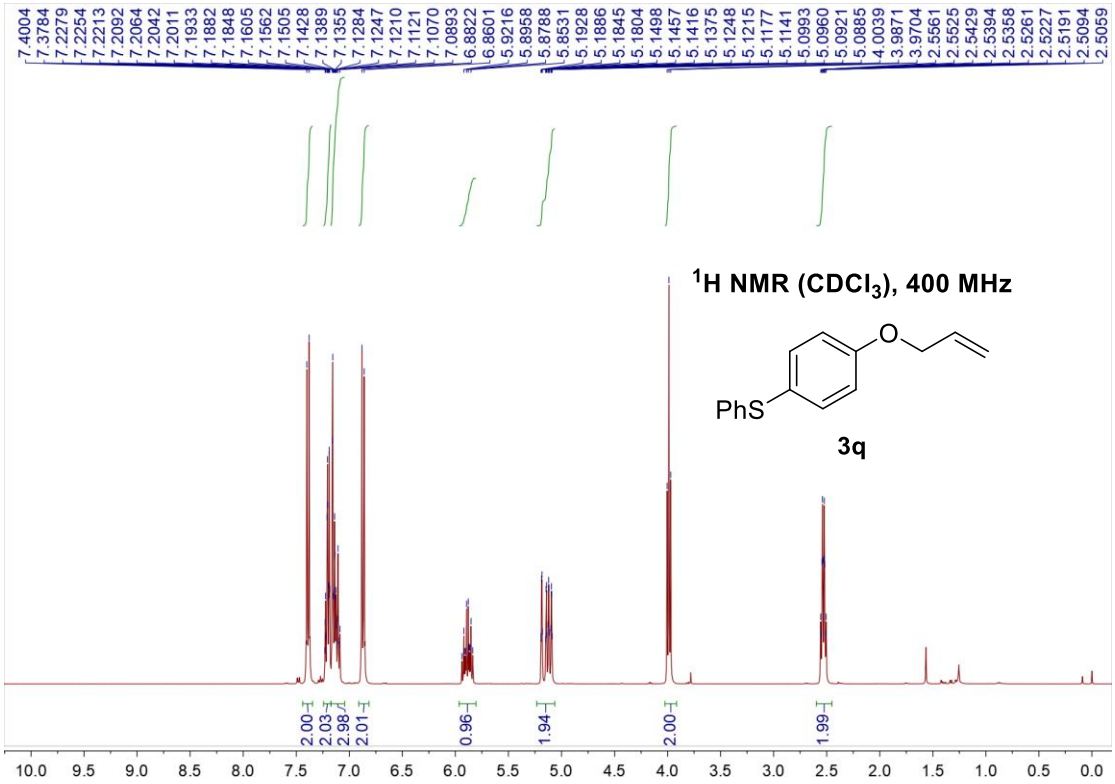
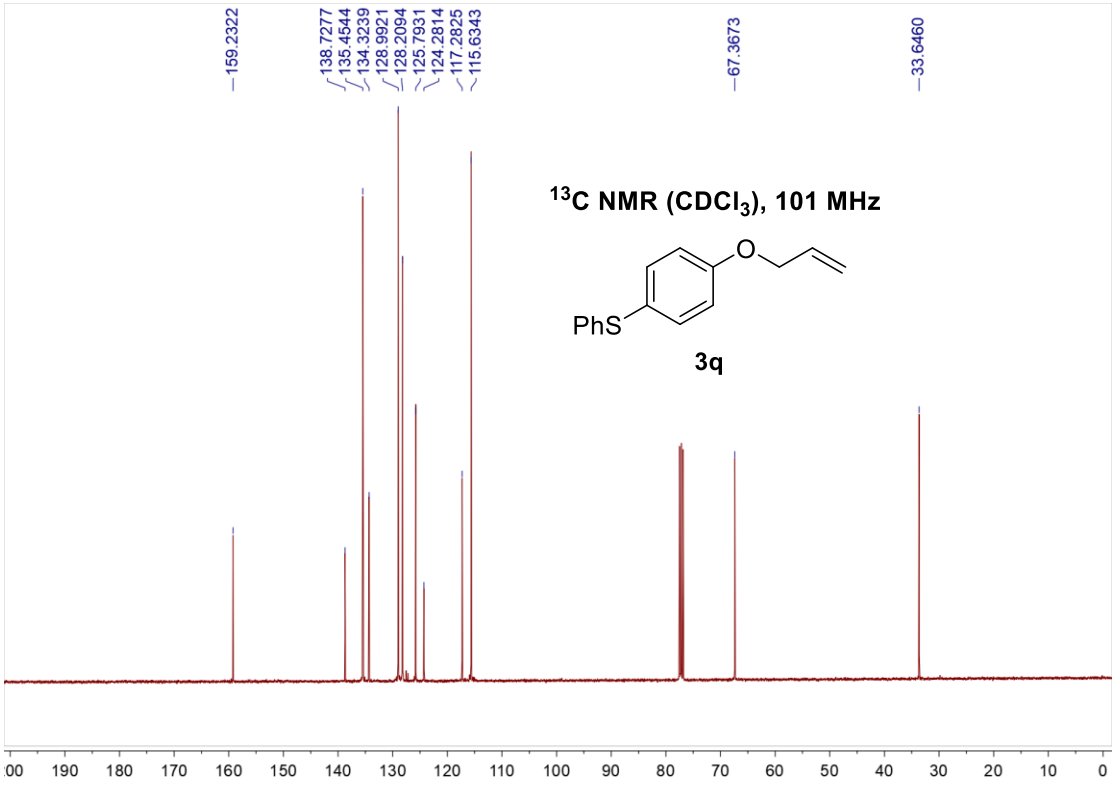
144.2129
133.6429
132.4927
130.0978
129.6280
128.6126
127.8599
127.6146
68.5989
34.2386
24.7860
18.5311
13C NMR (CDCl3), 101 MHz
O
O
PhS
3p


1H NMR (CDCl3), 400 MHz
O
PhS
3q
2.00
2.03
2.98
2.01
0.96
1.94
2.00
1.99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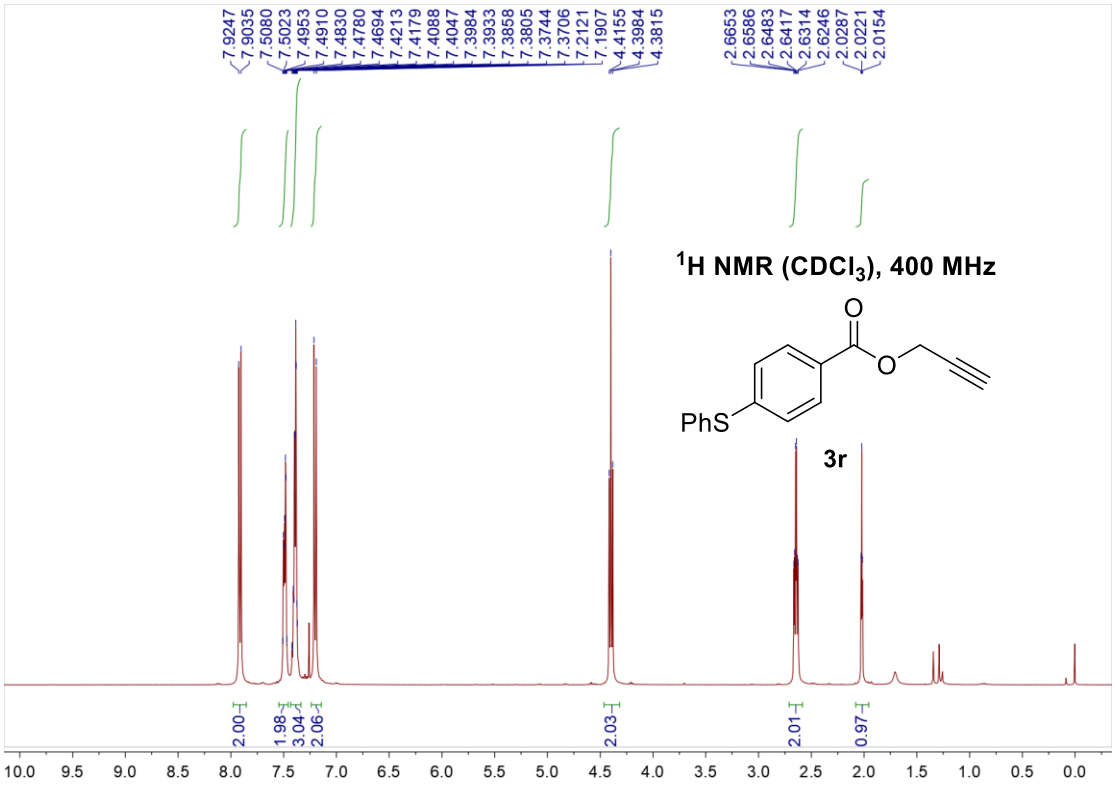
138.7277
135.4544
134.3239
128.9921
128.2094
125.7931
124.2814
117.2825
115.6343
67.3673
33.6460
13C NMR (CDCl3), 101 MHz
O
PhS
3q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7.5080
7.5023
7.4953
7.4910
7.4830
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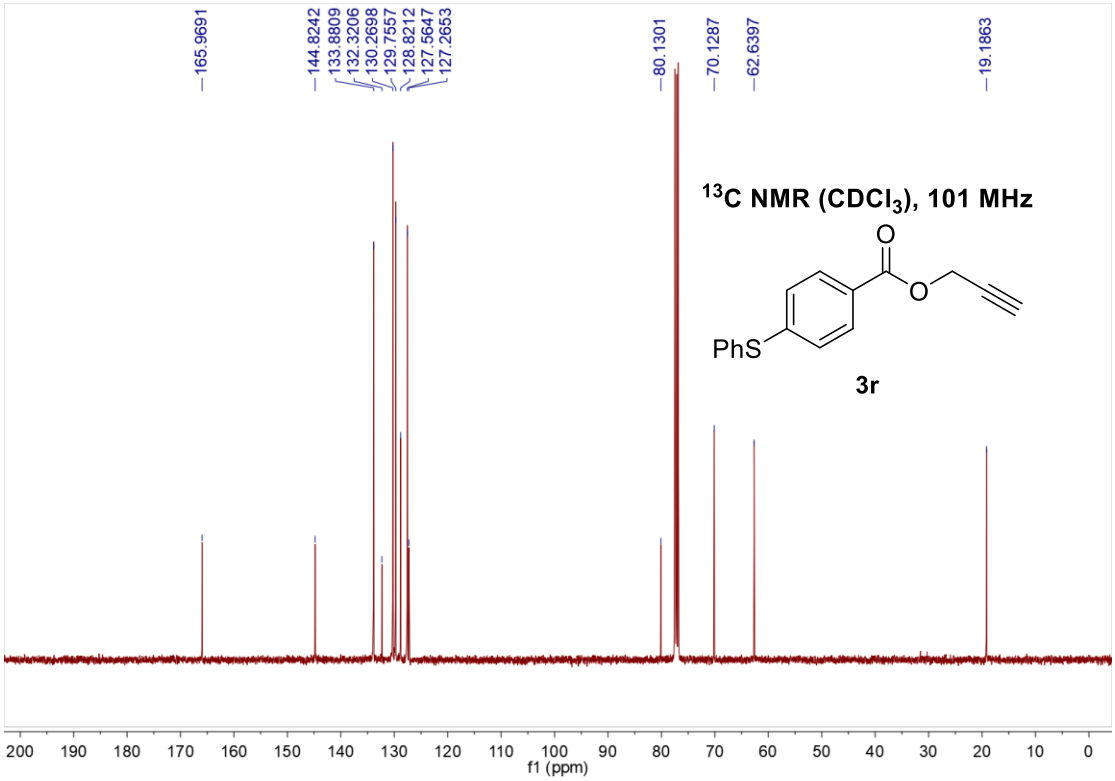
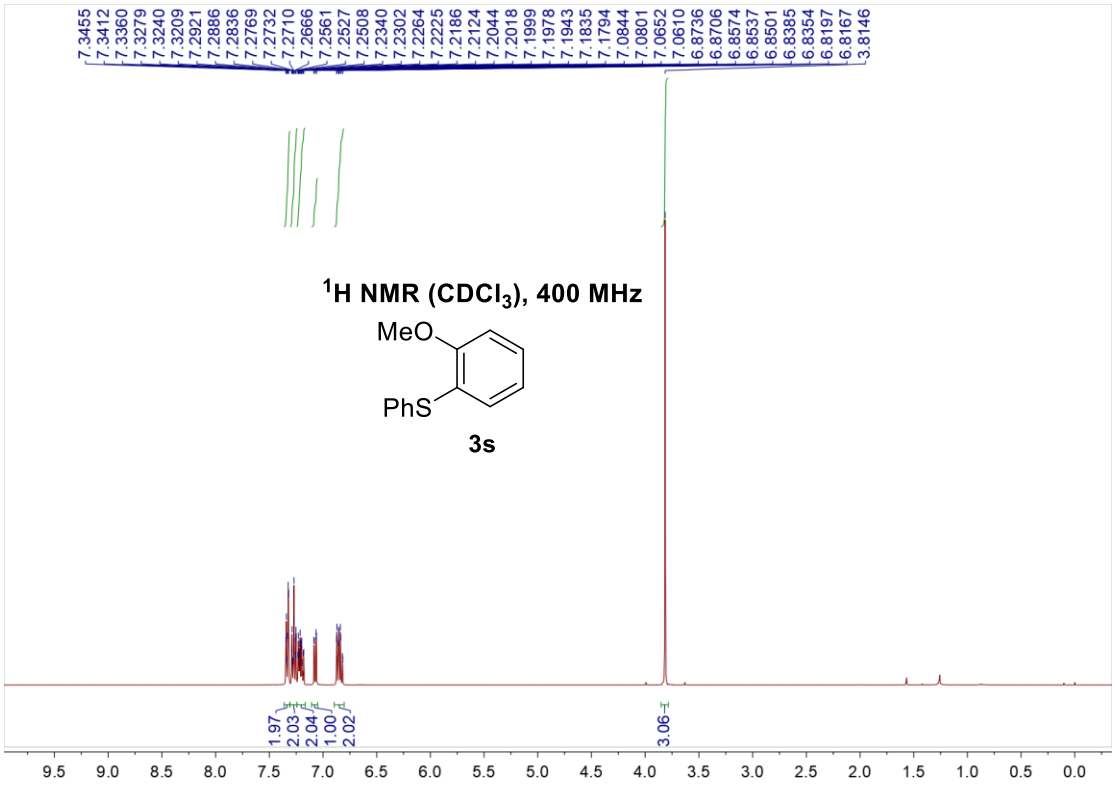
7.4694
7.4213
7.4179
7.4088
7.4047
7.3984
7.3933
7.3858
7.3805
7.3744
7.3706
7.2121
7.1907
4.4155
4.3984
4.3815
2.6653
2.6586
2.6483
2.6417
2.6314
2.6246
2.0287
2.0221
2.0154
1H NMR (CDCl3), 400 MHz
O
O
PhS
3r
2.00
1.98
3.04
2.06
2.03
2.01
0.97


165.9691
144.8242
133.8809
132.3206
130.2698
129.7557
128.8212
127.5647
127.2653
80.1301
70.1287
62.6397
19.1863
13C NMR (CDCl3), 101 MHz
O
O
PhS
3r
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.3412
7.3360
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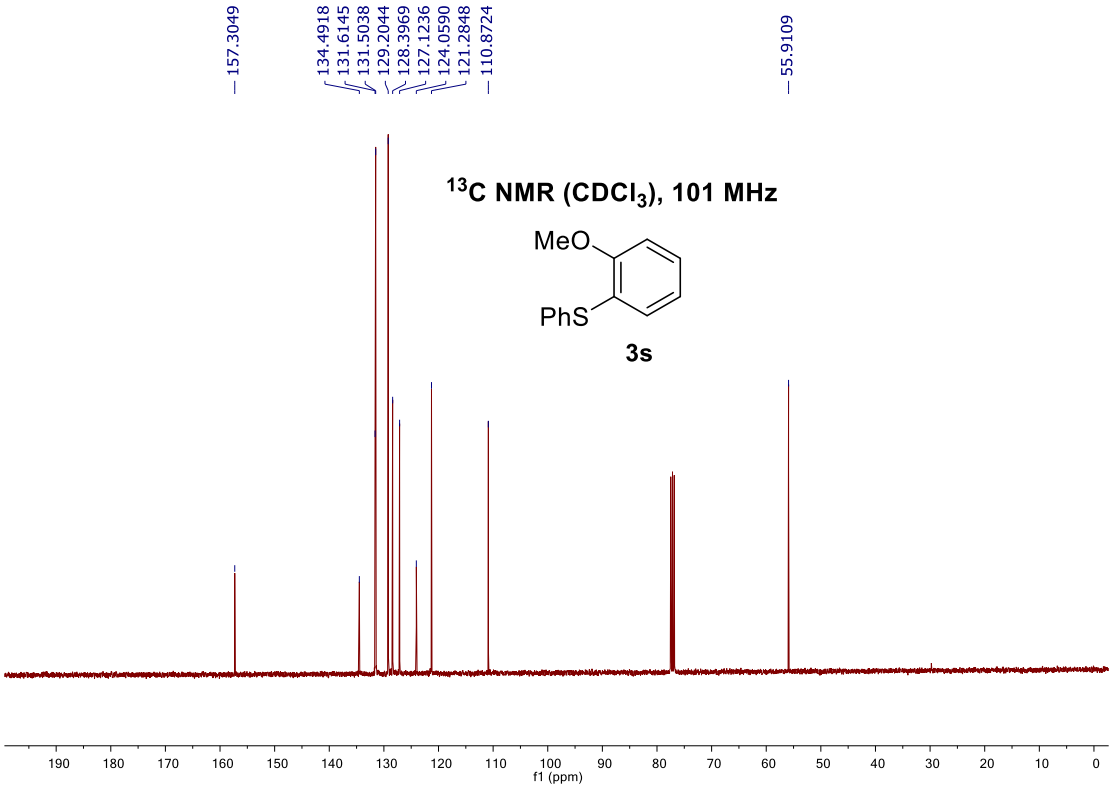
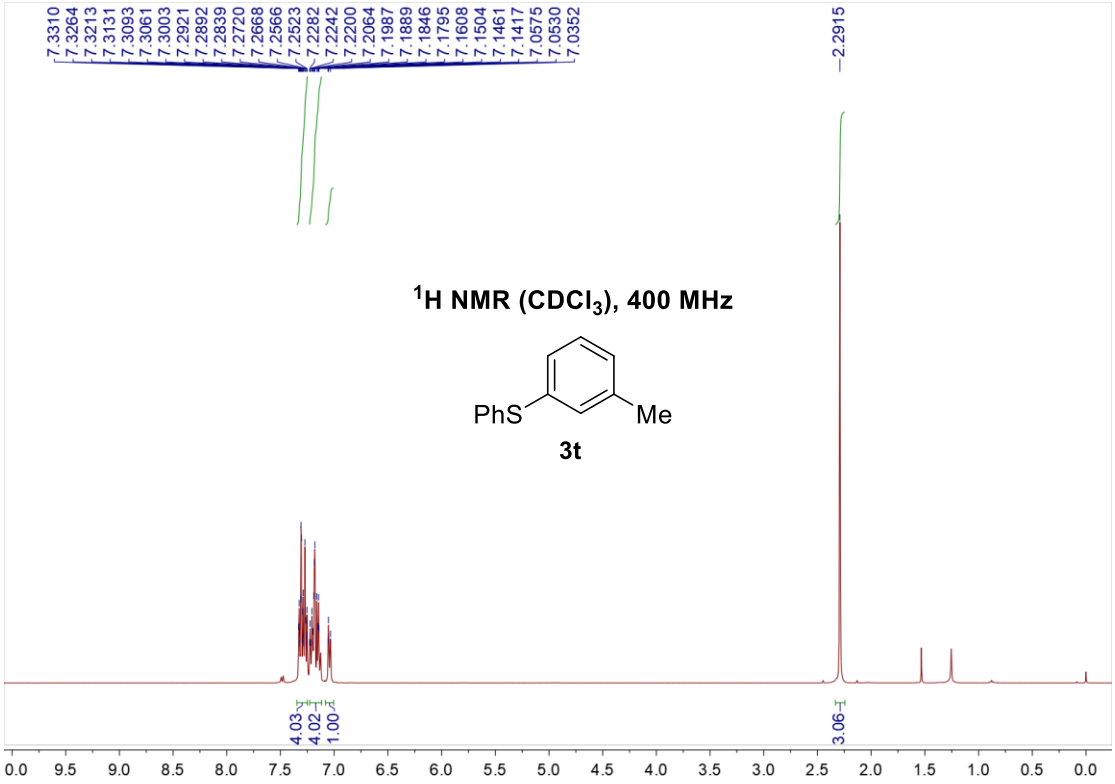
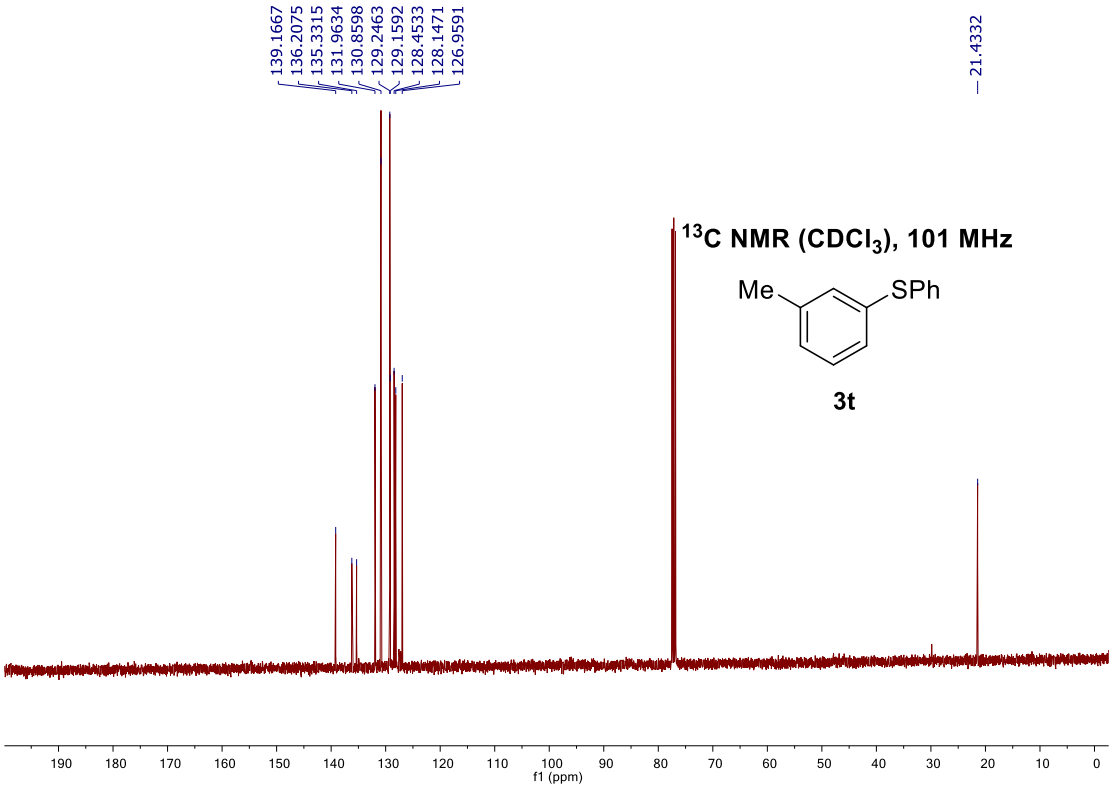
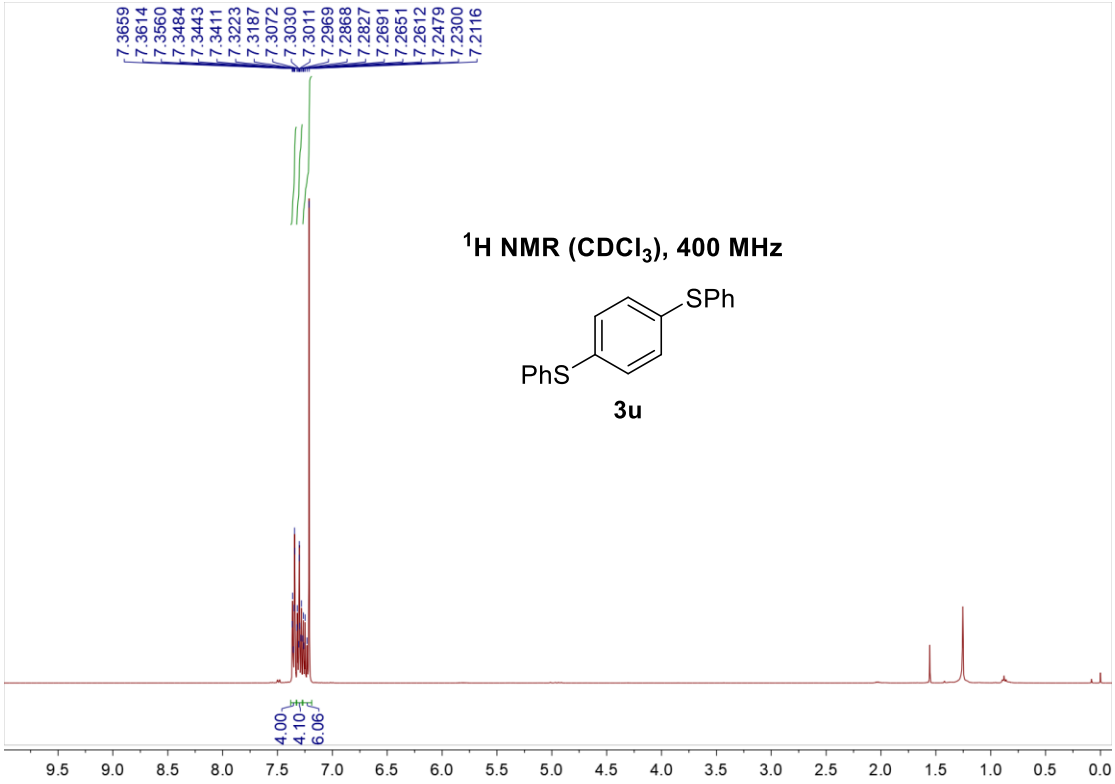
7.3240
7.3209
7.2921
7.2886
7.2836
7.2769
7.2732
7.2710
7.2666
7.2561
7.2527
7.2508
7.2340
7.2302
7.2264
7.2225
7.2186
7.2124
7.2044
7.2018
7.1999
7.1978
7.1943
7.1835
7.1794
7.0844
7.0801
7.0652
7.0610
6.8736
6.8706
6.8574
6.8537
6.8501
6.8385
6.8354
6.8197
6.8167
3.8146
1H NMR (CDCl3), 400 MHz
MeO
PhS
3s
1.97
2.03
2.04
1.00
2.02
3.06
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


157.3049
134.4918
131.6145
131.5038
129.2044
128.3969
127.1236
124.0590
121.2848
110.8724
55.9109
13C NMR (CDCl3), 101 MHz
MeO
PhS
3s
f1 (ppm)

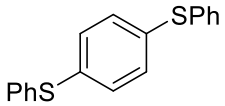

7.3310
7.3264
7.3213
7.3131
7.3093
7.3061
7.3003
7.2921
7.2892
7.2839
7.2720
7.2668
7.2566
7.2523
7.2282
7.2242
7.2200
7.2064
7.1987
7.1889
7.1846
7.1795
7.1608
7.1504
7.1461
7.1417
7.0575
7.0530
7.0352
2.2915
1H NMR (CDCl3), 400 MHz
PhS
Me
3t
4.03
4.02
1.00
3.06


139.1667
136.2075
135.3315
131.9634
130.8598
129.2463
129.1592
128.4533
128.1471
126.9591
21.4332
^{13}C NMR (CDCl$_3$), 101 MHz
Me
SPh
3t
f1 (ppm)

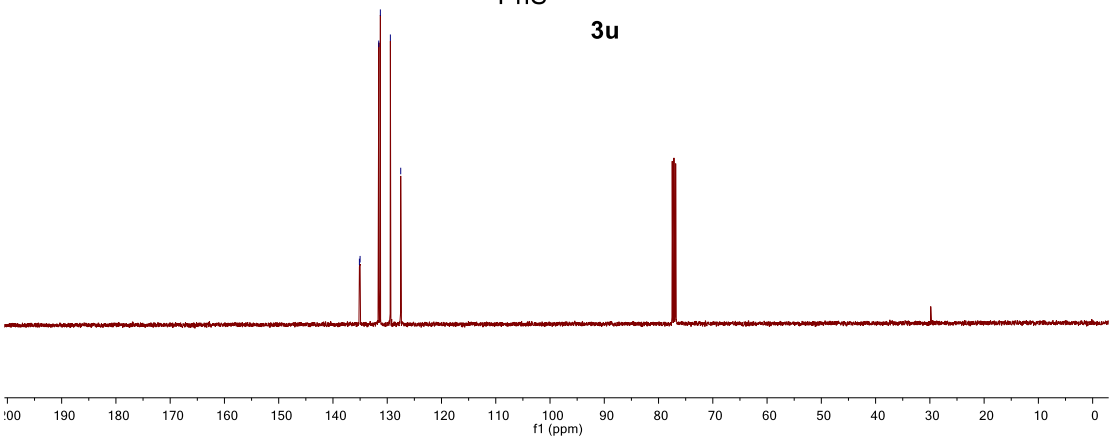

7.3659
7.3614
7.3560
7.3484
7.3443
7.3411
7.3223
7.3187
7.3072
7.3030
7.3011
7.2969
7.2868
7.2827
7.2691
7.2651
7.2612
7.2479
7.2300
7.2116
^{1}H NMR (CDCl$_3$), 400 MHz
SPh
PhS
3u
4.00
4.10
6.06

135.1274
135.0011
131.5617
131.2651
129.4215
127.5161

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

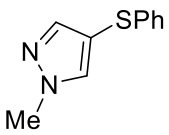


3u

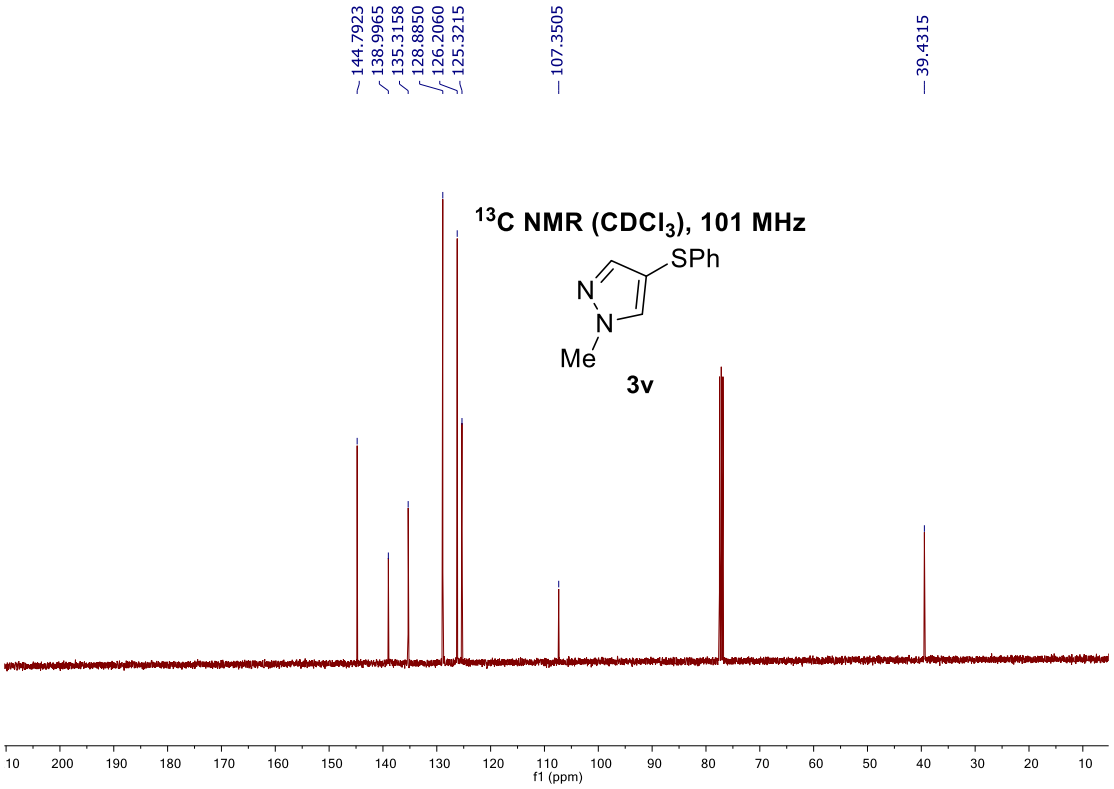


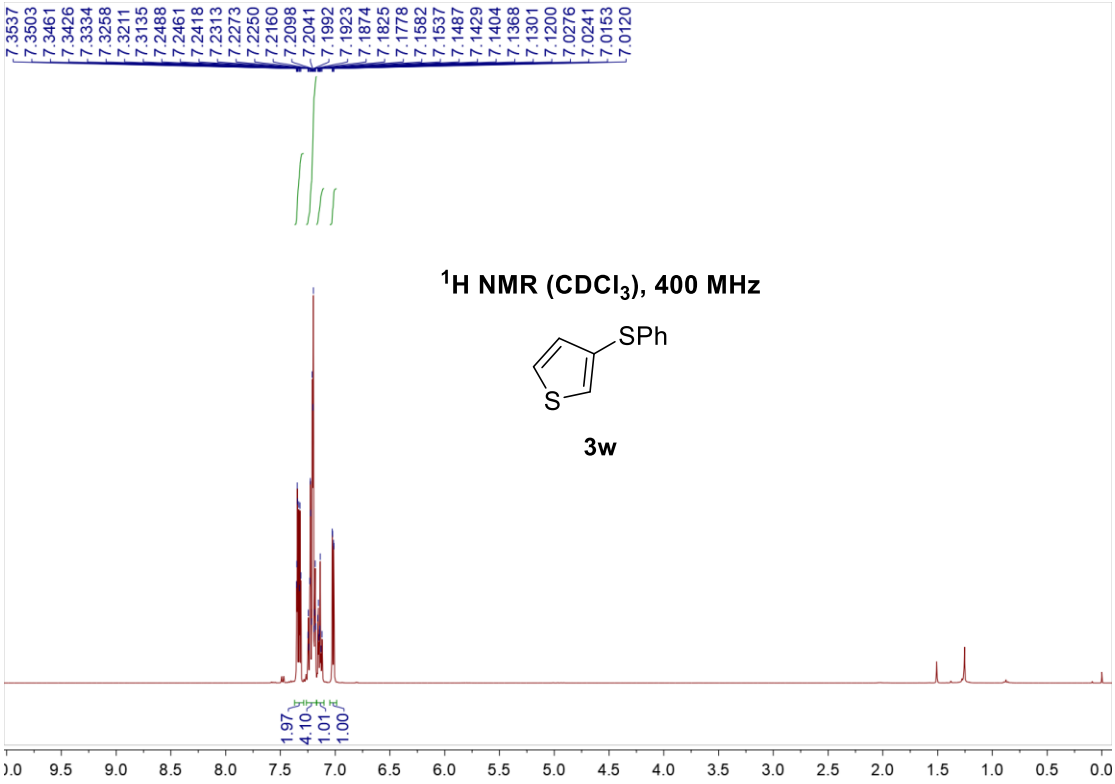
7.5814
7.5047
7.2224
7.2177
7.2054
7.2015
7.1895
7.1837
7.1165
7.1122
7.1070
7.1030
7.0966
7.0931
7.0911
7.0874
7.0826
7.0699
3.9159

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



3v


144.7923
138.9965
135.3158
128.8850
126.2060
125.3215
107.3505
39.4315
13C NMR (CDCl3), 101 MHz
SPh
N
N
Me
3v
f1 (ppm)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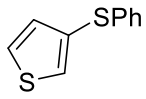
7.3503
7.3461
7.3426
7.3334
7.3258
7.3211
7.3135
7.2488
7.2461
7.2418
7.2313
7.2273
7.2250
7.2160
7.2098
7.2041
7.1992
7.1923
7.1874
7.1825
7.1778
7.1582
7.1537
7.1487
7.1429
7.1404
7.1368
7.1301
7.1200
7.0276
7.0241
7.0153
7.0120
1H NMR (CDCl3), 400 MHz
SPh
S
3w
1.97
4.10
1.01
1.00

137.4433
131.3402
129.3673
129.1005
128.4628
128.3442
126.8605
126.2137

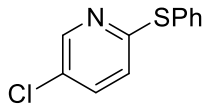
^{13}C NMR ($CDCl_3$), 101 MHz



3w

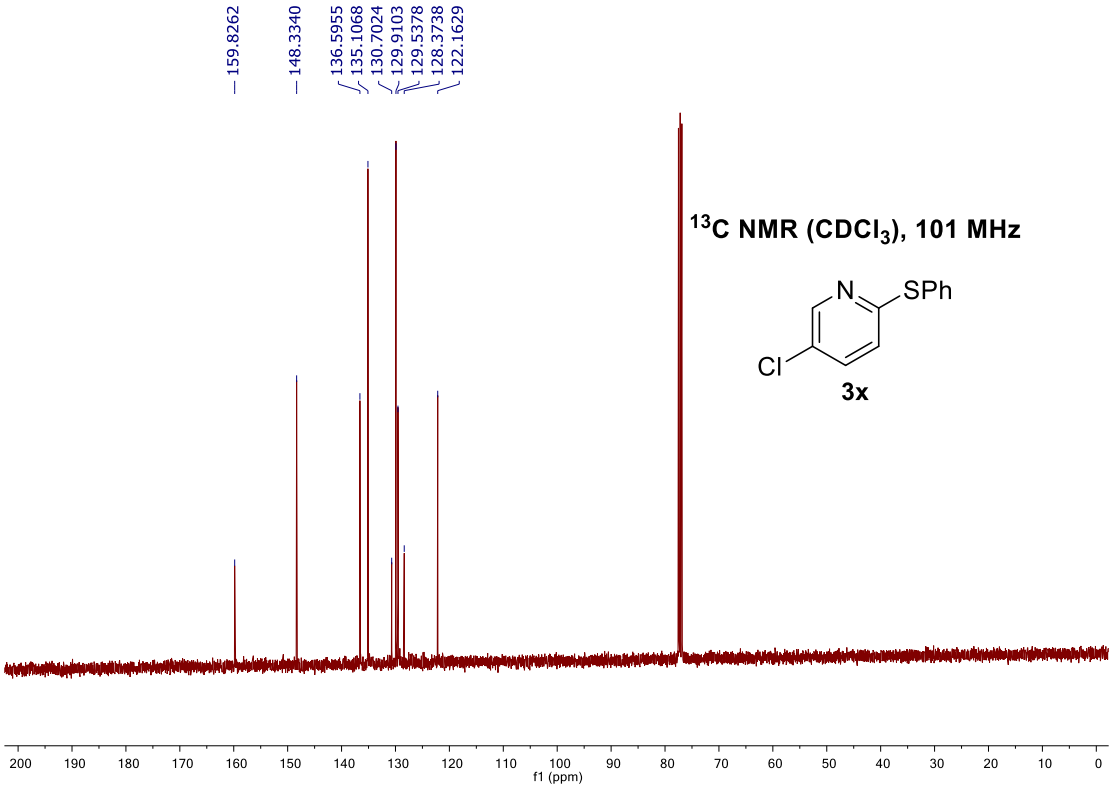
8.3768
8.3704
7.5903
7.5862
7.5812
7.5771
7.5726
7.5661
7.4410
7.4358
7.4272
7.4199
7.4157
7.4100
7.4051
7.3986
6.8385
6.8171

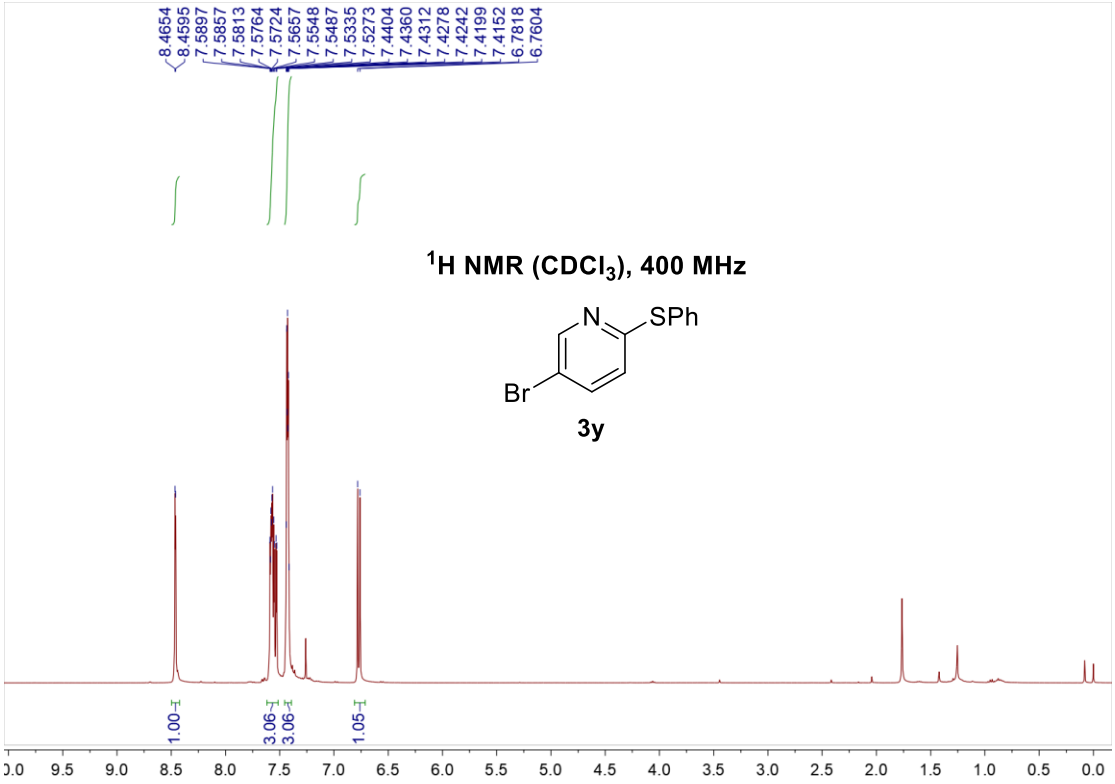
^{1}H NMR ($CDCl_3$), 400 MHz



3x

1.00
2.03
4.06
1.07


159.8262
148.3340
136.5955
135.1068
130.7024
129.9103
129.5378
128.3738
122.1629
13C NMR (CDCl3), 101 MHz
N
SPh
Cl
3x
f1 (ppm)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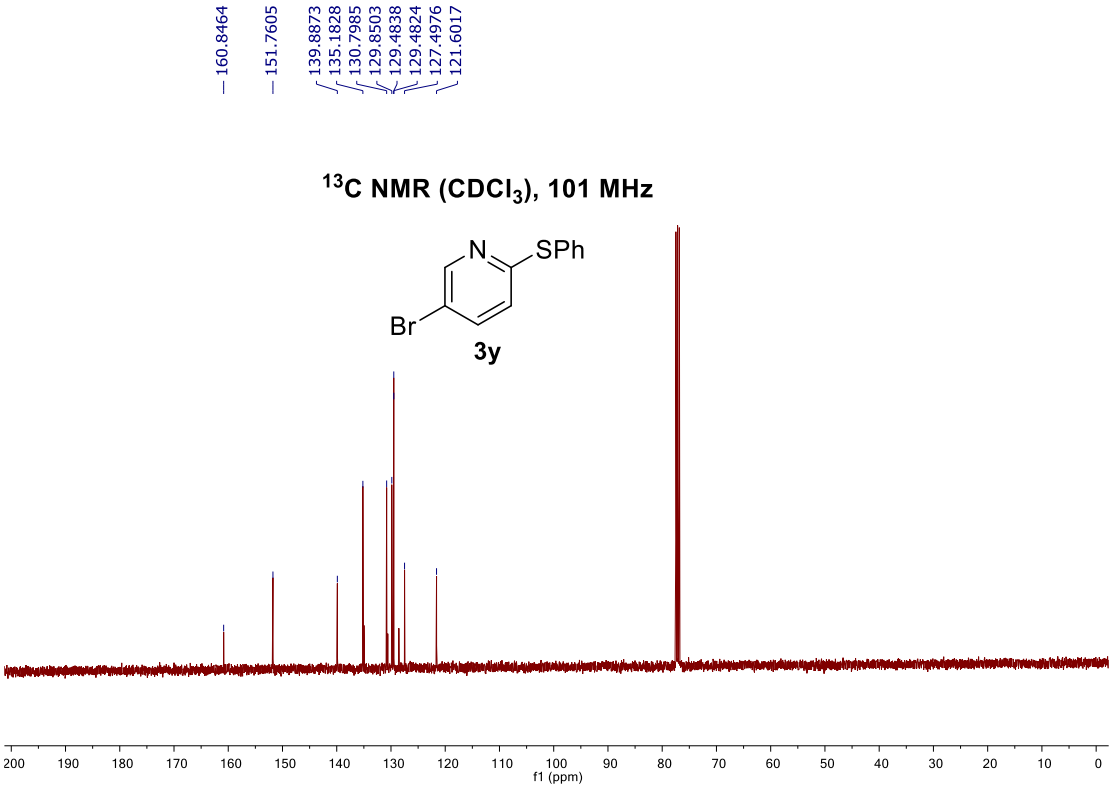
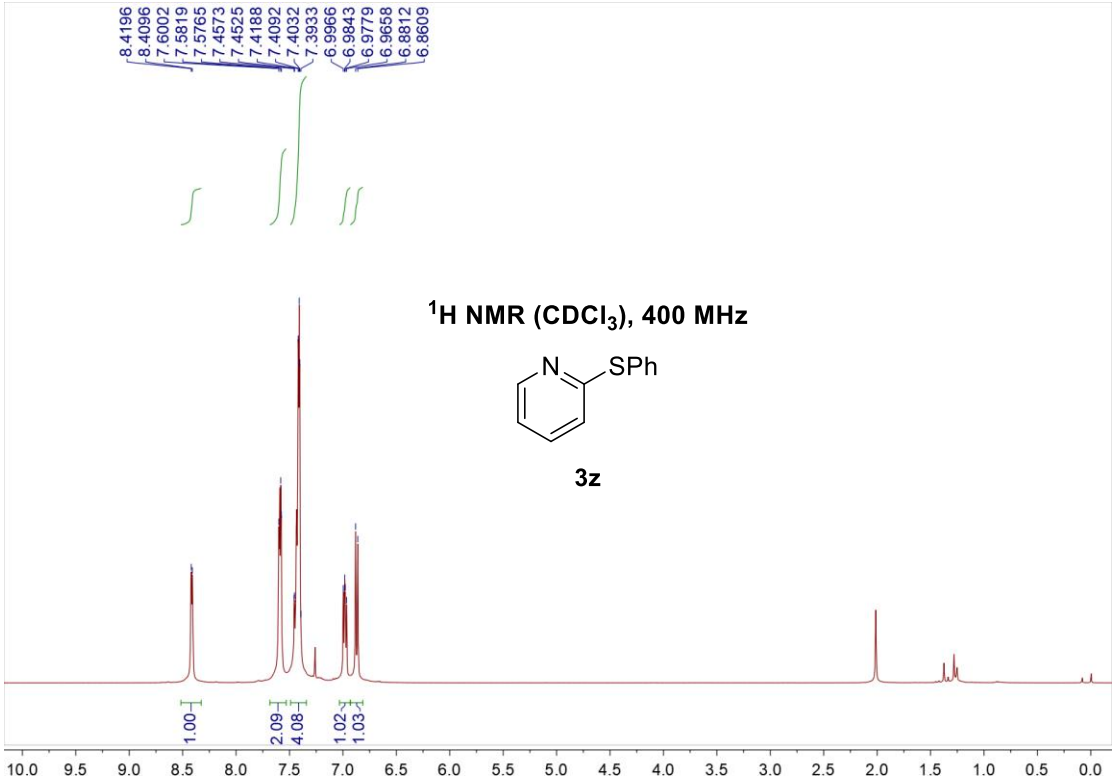
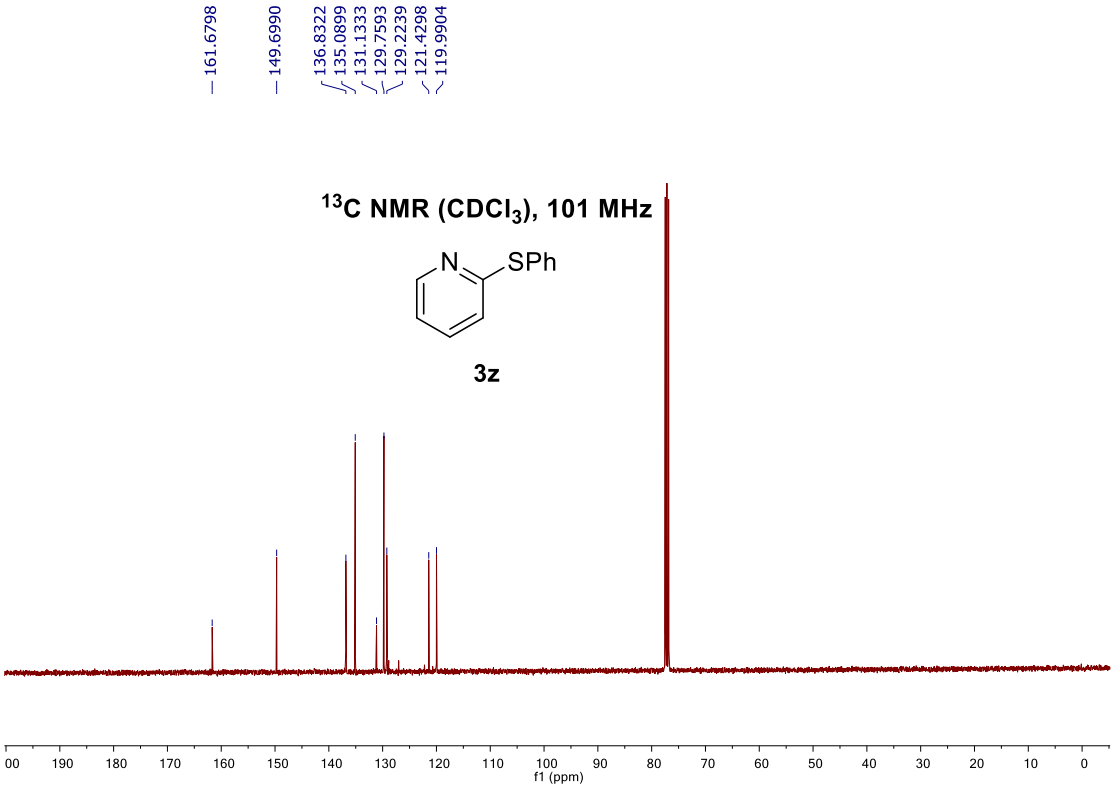
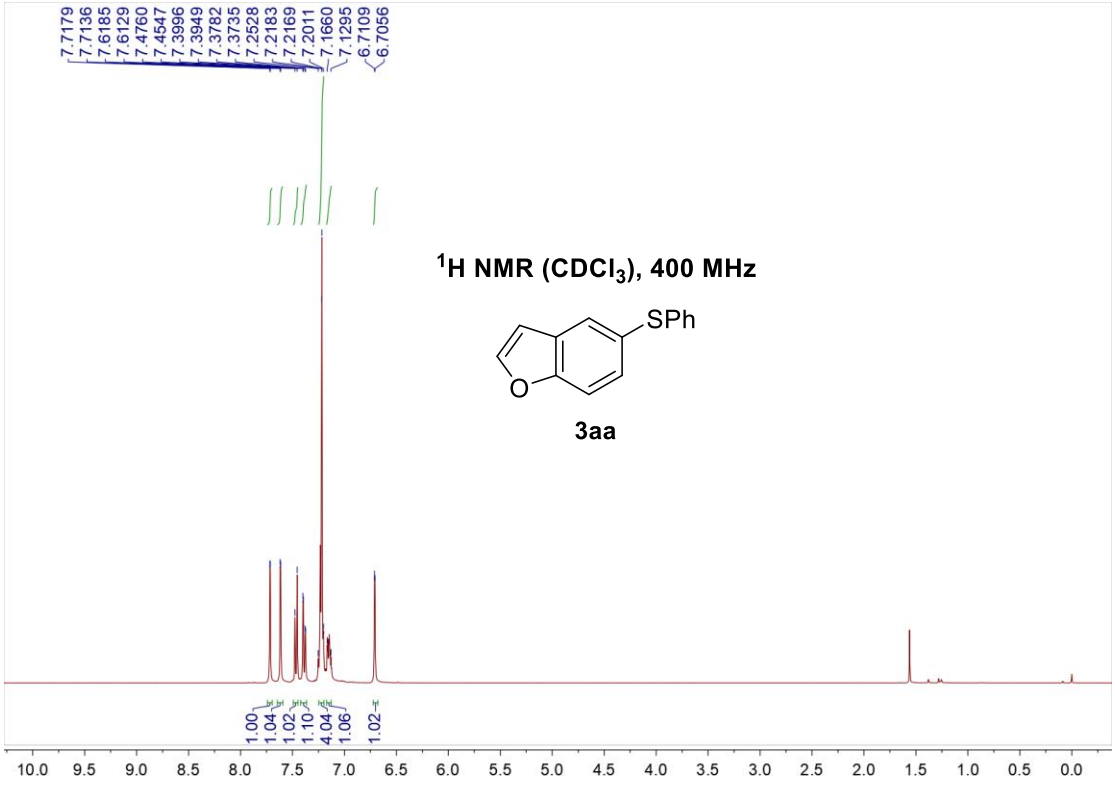
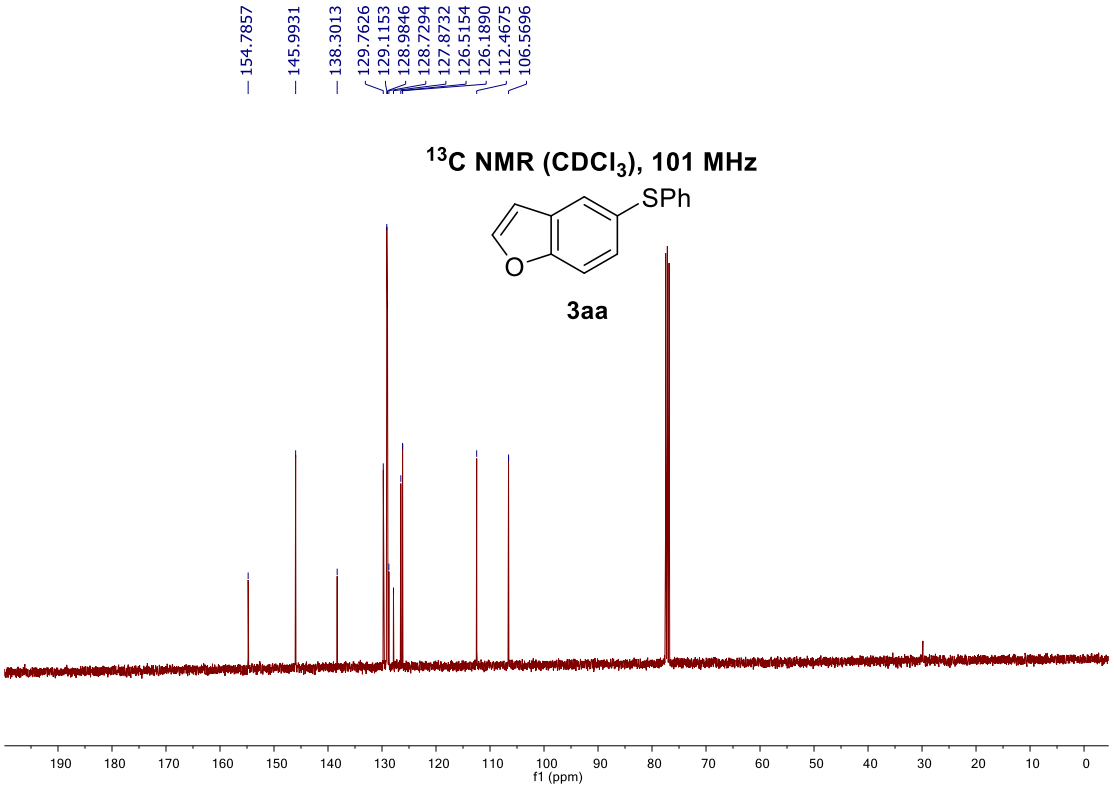
8.4595
7.5897
7.5857
7.5813
7.5764
7.5724
7.5667
7.5548
7.5487
7.5335
7.5273
7.4404
7.4360
7.4312
7.4278
7.4242
7.4199
7.4152
6.7818
6.7604
1H NMR (CDCl3), 400 MHz
N
SPh
Br
3y
1.00
3.06
3.06
1.05

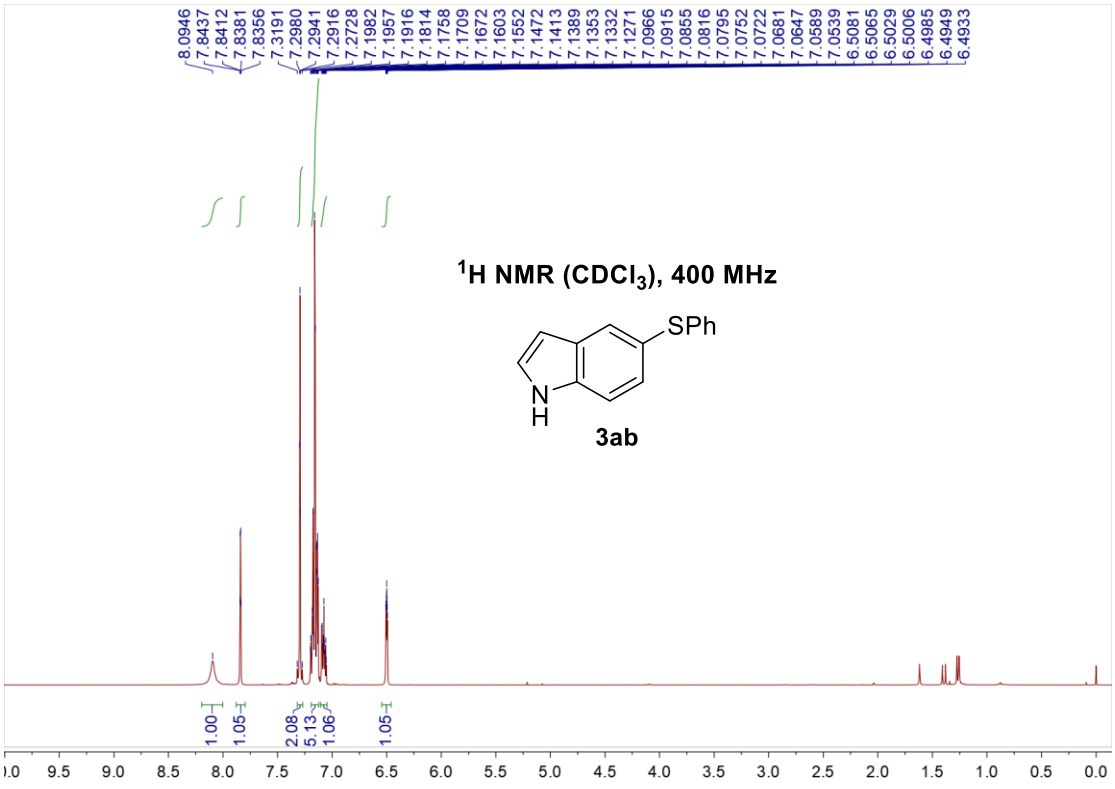

160.8464
151.7605
139.8873
135.1828
130.7985
129.8503
129.4838
129.4824
127.4976
121.6017
13C NMR (CDCl3), 101 MHz
N
SPh
Br
3y
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.4196
8.4096
7.6002
7.5819
7.5765
7.4573
7.4525
7.4188
7.4092
7.4032
7.3933
6.9966
6.9843
6.9779
6.9658
6.8812
6.8609
1H NMR (CDCl3), 400 MHz
N
SPh
3z
1.00
2.09
4.08
1.02
1.03
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


161.6798
149.6990
136.8322
135.0899
131.1333
129.7593
129.2239
121.4298
119.9904
13C NMR (CDCl3), 101 MHz
N
SPh
3z
f1 (ppm)


7.7179
7.7136
7.6185
7.6129
7.4760
7.4547
7.3996
7.3949
7.3782
7.3735
7.2528
7.2183
7.2169
7.2011
7.1660
7.1295
6.7109
6.7056
1H NMR (CDCl3), 400 MHz
SPh
O
3aa
1.00
1.04
1.02
1.10
4.04
1.06
1.02


154.7857
145.9931
138.3013
129.7626
129.1153
128.9846
128.7294
127.8732
126.5154
126.1890
112.4675
106.5696
13C NMR (CDCl3), 101 MHz
SPh
O
3aa
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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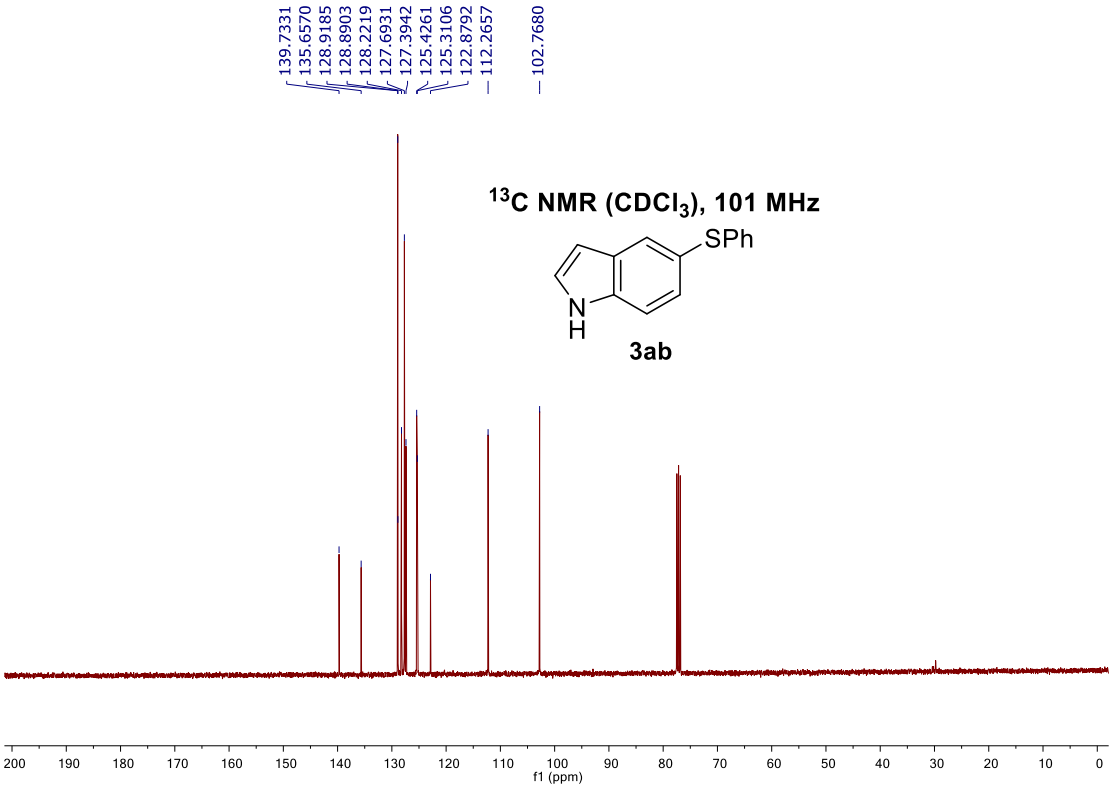
7.8412
7.8381
7.8356
7.3191
7.2980
7.2941
7.2916
7.2728
7.1982
7.1957
7.1916
7.1814
7.1758
7.1709
7.1672
7.1603
7.1552
7.1472
7.1413
7.1389
7.1353
7.1332
7.1271
7.0966
7.0915
7.0855
7.0816
7.0795
7.0752
7.0722
7.0681
7.0647
7.0589
7.0539
6.5081
6.5065
6.5029
6.5006
6.4985
6.4949
6.4933
1H NMR (CDCl3), 400 MHz
SPh
N
H
3ab
1.00
1.05
2.08
5.13
1.06
1.05
0.0 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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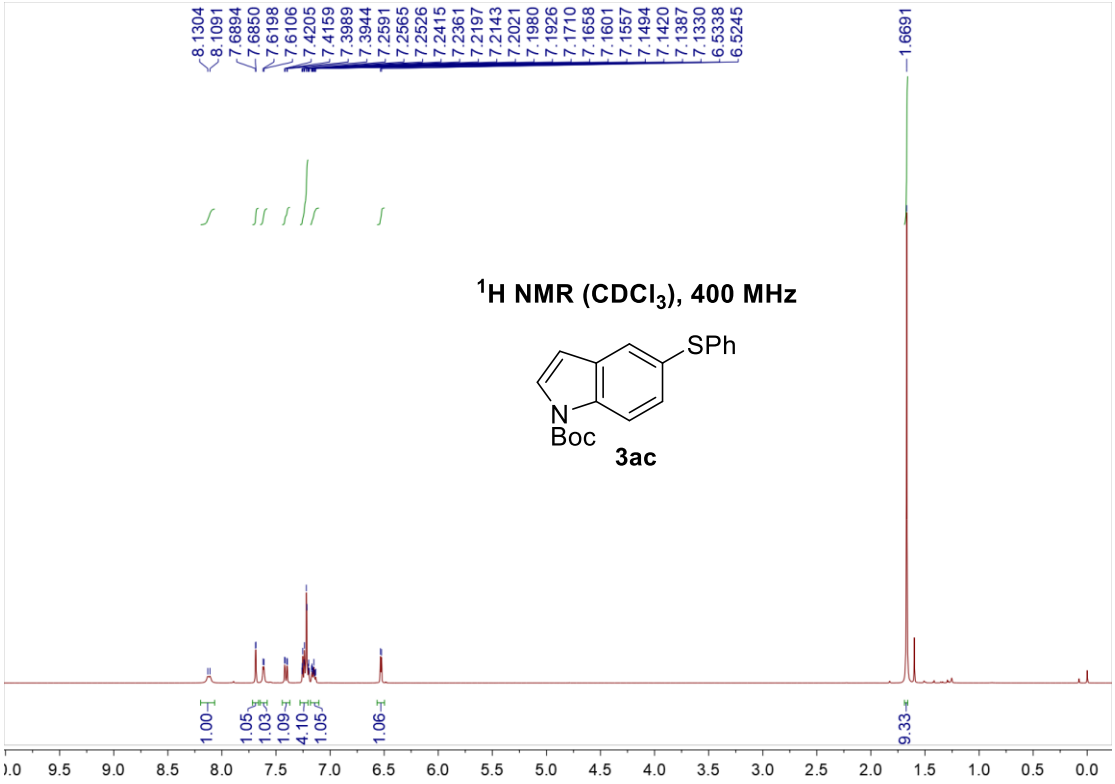
135.6570
128.9185
128.8903
128.2219
127.6931
127.3942
125.4261
125.3106
122.8792
112.2657
102.7680
13C NMR (CDCl3), 101 MHz
SPh
N
H
3ab
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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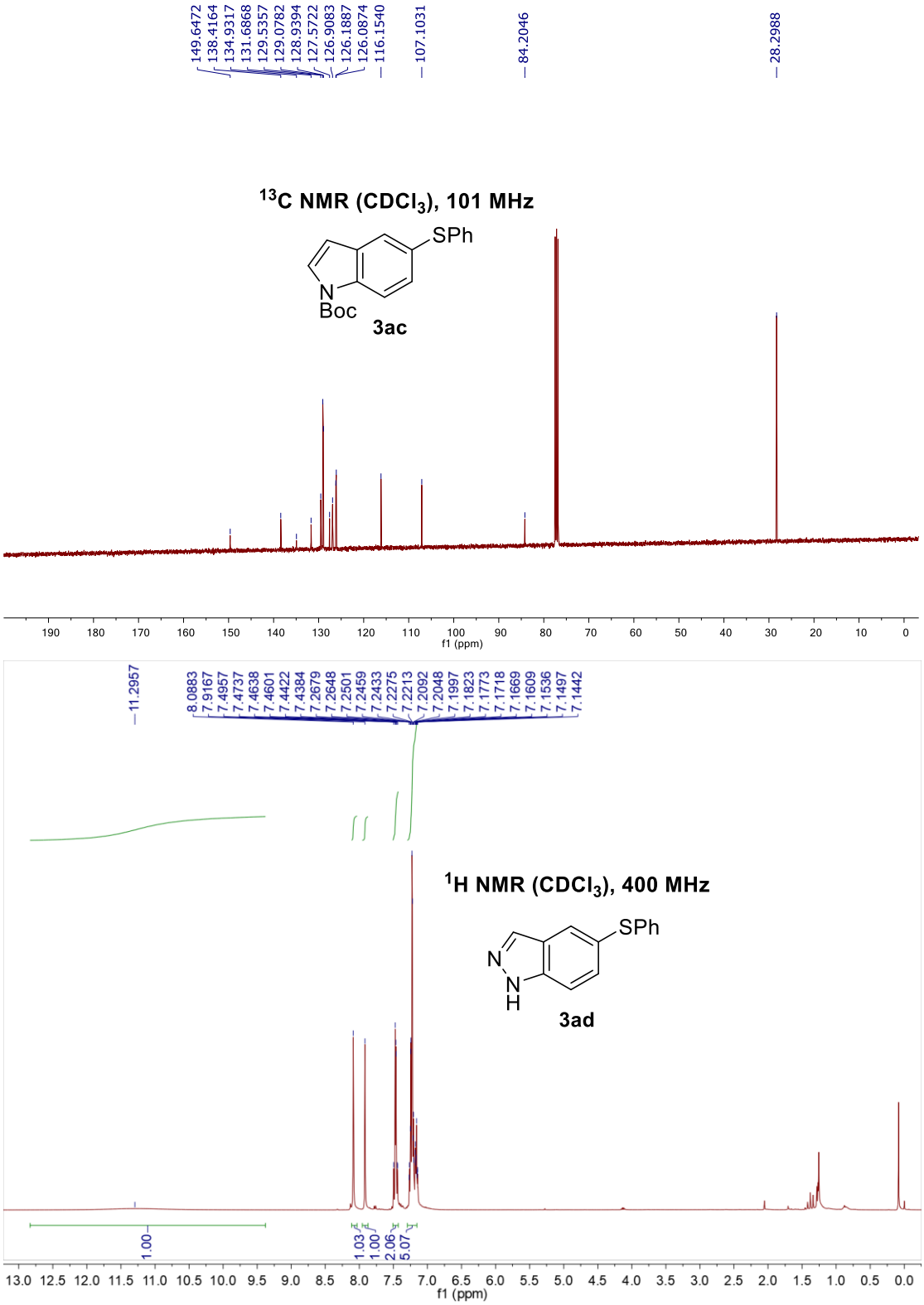
7.6850
7.6198
7.6106
7.4205
7.4159
7.3989
7.3944
7.2591
7.2565
7.2526
7.2415
7.2361
7.2197
7.2143
7.2021
7.1980
7.1926
7.1710
7.1658
7.1601
7.1557
7.1494
7.1420
7.1387
7.1330
6.5338
6.5245
1.6691
1H NMR (CDCl3), 400 MHz
SPh
N
Boc
3ac
1.00
1.05
1.03
1.09
4.10
1.05
1.06
9.33
0.0 9.5 9.0 8.5 8.0 7.5 7.0 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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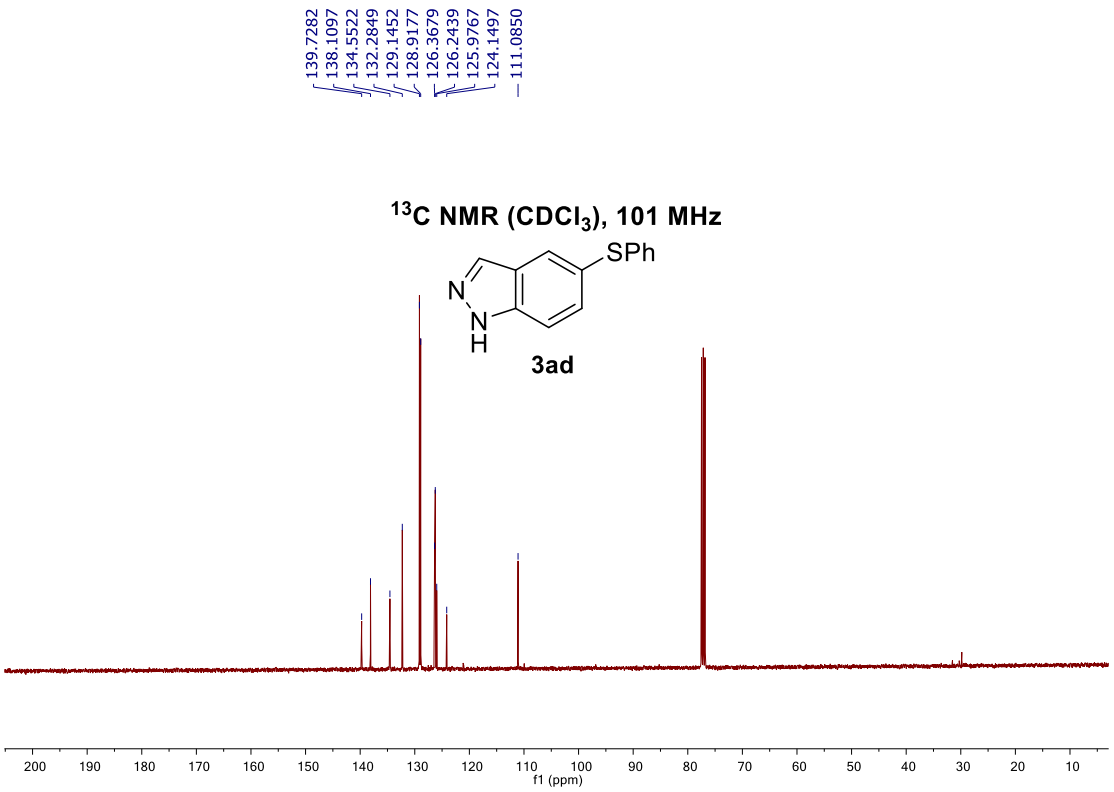
134.9317
131.6868
129.5357
129.0782
128.9394
127.5722
126.9083
126.1887
126.0874
116.1540
107.1031
84.2046
28.2988
13C NMR (CDCl3), 101 MHz
SPh
N
Boc
3ac
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
11.2957
8.0883
7.9167
7.4957
7.4737
7.4638
7.4601
7.4422
7.4384
7.2679
7.2648
7.2501
7.2459
7.2433
7.2275
7.2213
7.2092
7.2048
7.1997
7.1823
7.1773
7.1718
7.1669
7.1609
7.1536
7.1497
7.1442
1H NMR (CDCl3), 400 MHz
SPh
N
N
H
3ad
1.00
1.03
1.00
2.06
5.07
13.0 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
f1 (ppm)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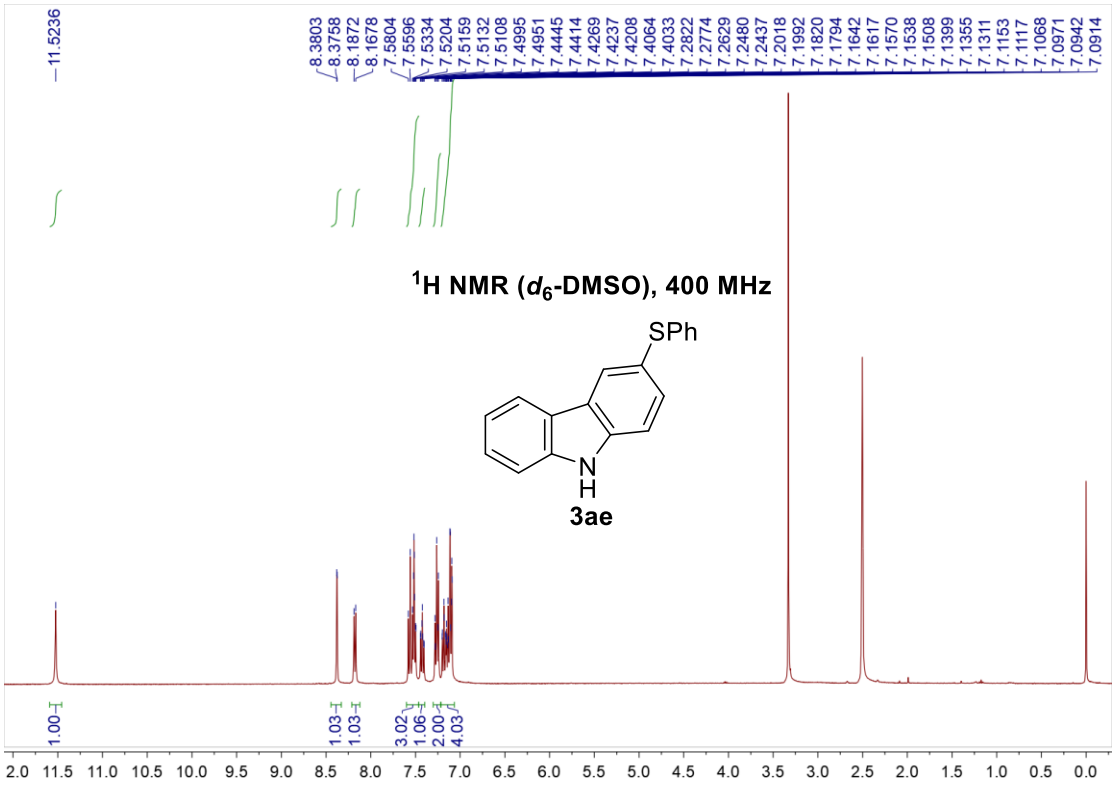
138.1097
134.5522
132.2849
129.1452
128.9177
126.3679
126.2439
125.9767
124.1497
111.0850
13C NMR (CDCl3), 101 MHz
SPh
N
N
H
3ad
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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8.1678
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7.5204
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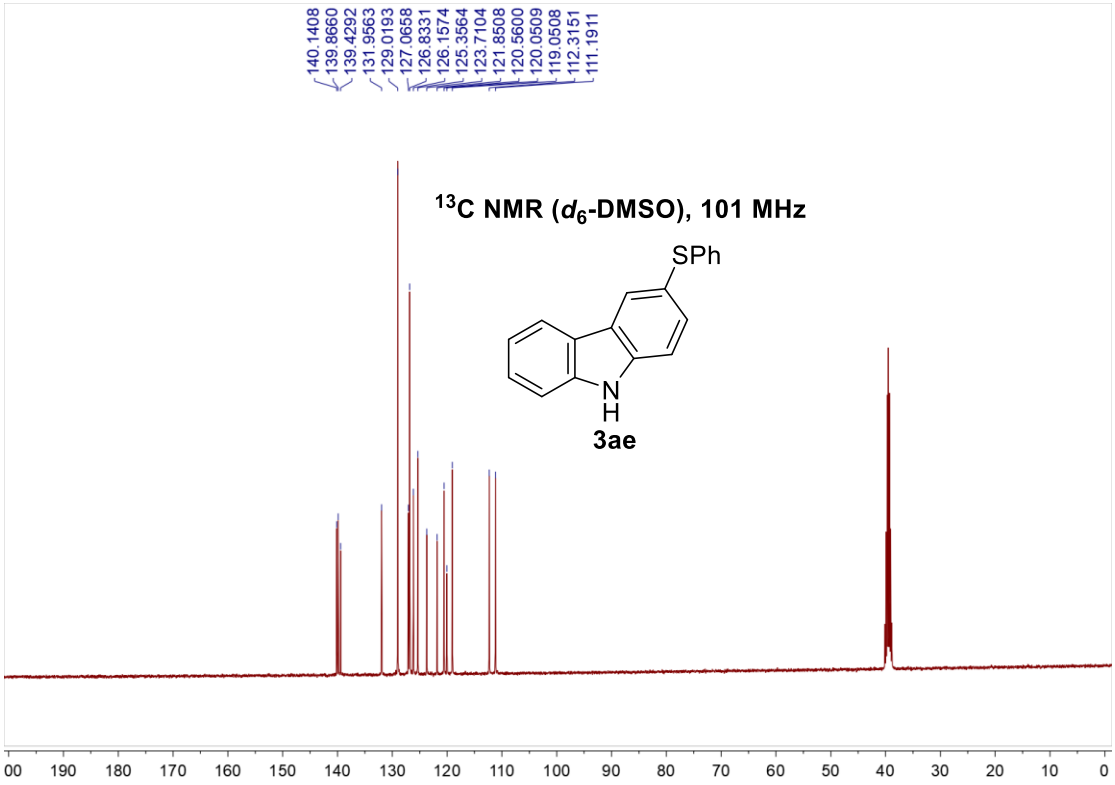
7.5132
7.5108
7.4995
7.4951
7.4445
7.4414
7.4269
7.4237
7.4208
7.4064
7.4033
7.2822
7.2774
7.2629
7.2480
7.2437
7.2018
7.1992
7.1820
7.1794
7.1642
7.1617
7.1570
7.1538
7.1508
7.1399
7.1355
7.1311
7.1153
7.1117
7.1068
7.0971
7.0942
7.0914
1H NMR (d6-DMSO), 400 MHz
SPh
N
H
3ae
1.00
1.03
1.03
3.02
1.06
2.00
4.03
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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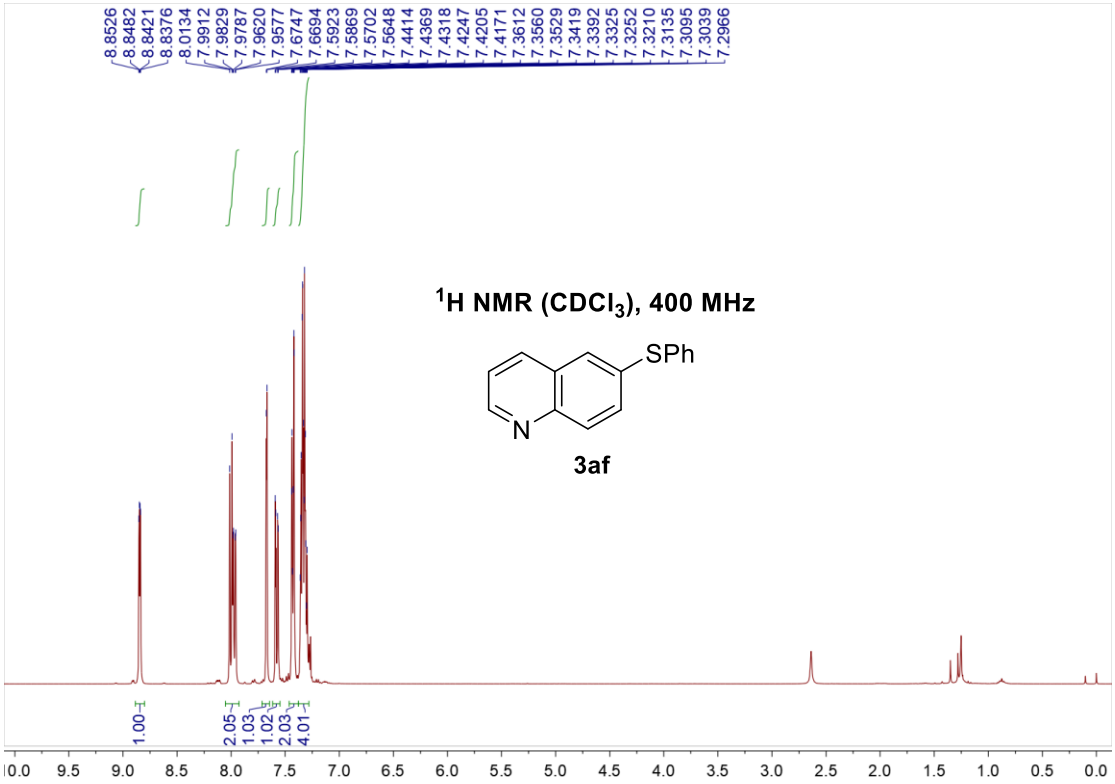
139.4292
131.9563
129.0193
127.0658
126.8331
126.1574
125.3564
123.7104
121.8508
120.5600
120.0509
119.0508
112.3151
111.1911
^{13}C NMR (d_6-DMSO), 101 MHz
SPh
N
H
3ae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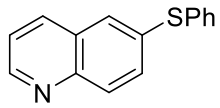
8.8482
8.8421
8.8376
8.0134
7.9912
7.9829
7.9787
7.9620
7.9577
7.6747
7.6694
7.5923
7.5869
7.5702
7.5648
7.4414
7.4369
7.4318
7.4247
7.4205
7.4171
7.3612
7.3560
7.3529
7.3419
7.3392
7.3325
7.3252
7.3210
7.3135
7.3095
7.3039
7.2966
^{1}H NMR ($CDCl_3$), 400 MHz
SPh
N
3af
1.00
2.05
1.03
1.02
2.03
4.01

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



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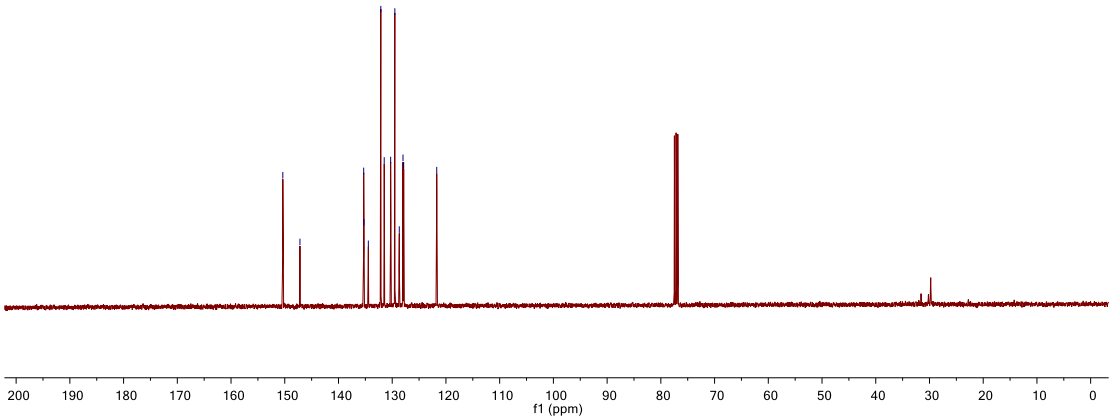
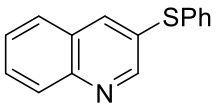


^{1}H NMR ($CDCl_3$), 400 MHz



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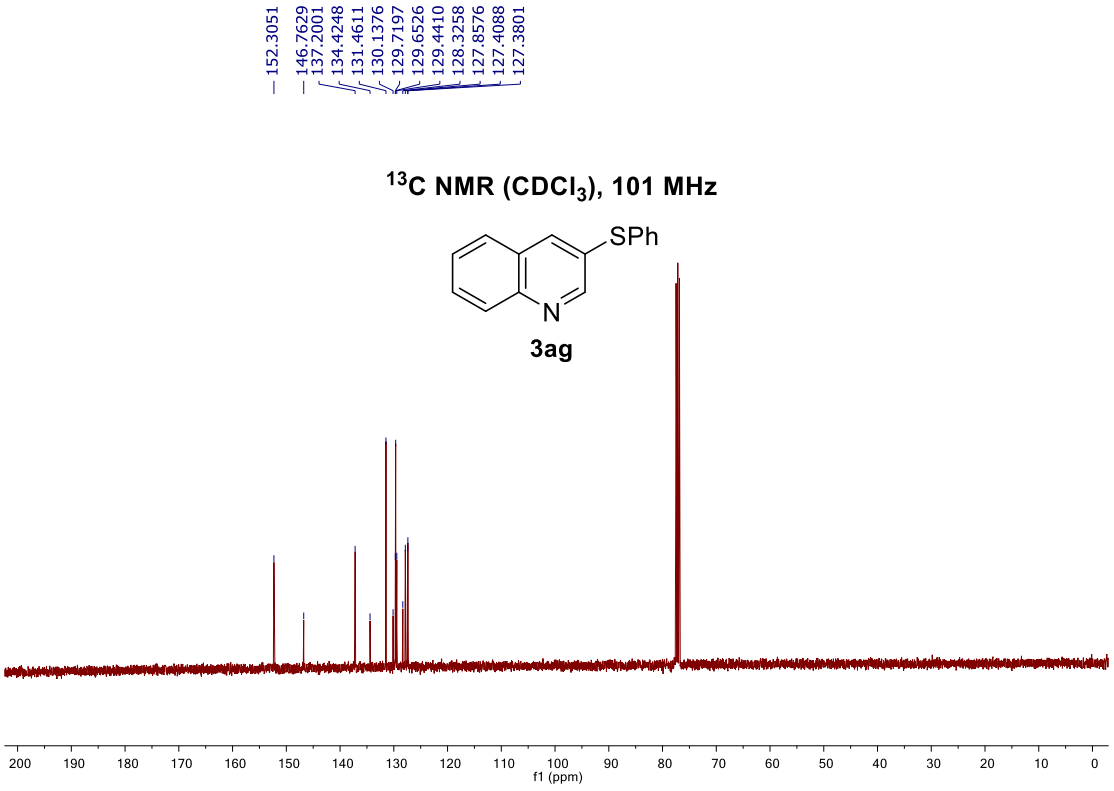
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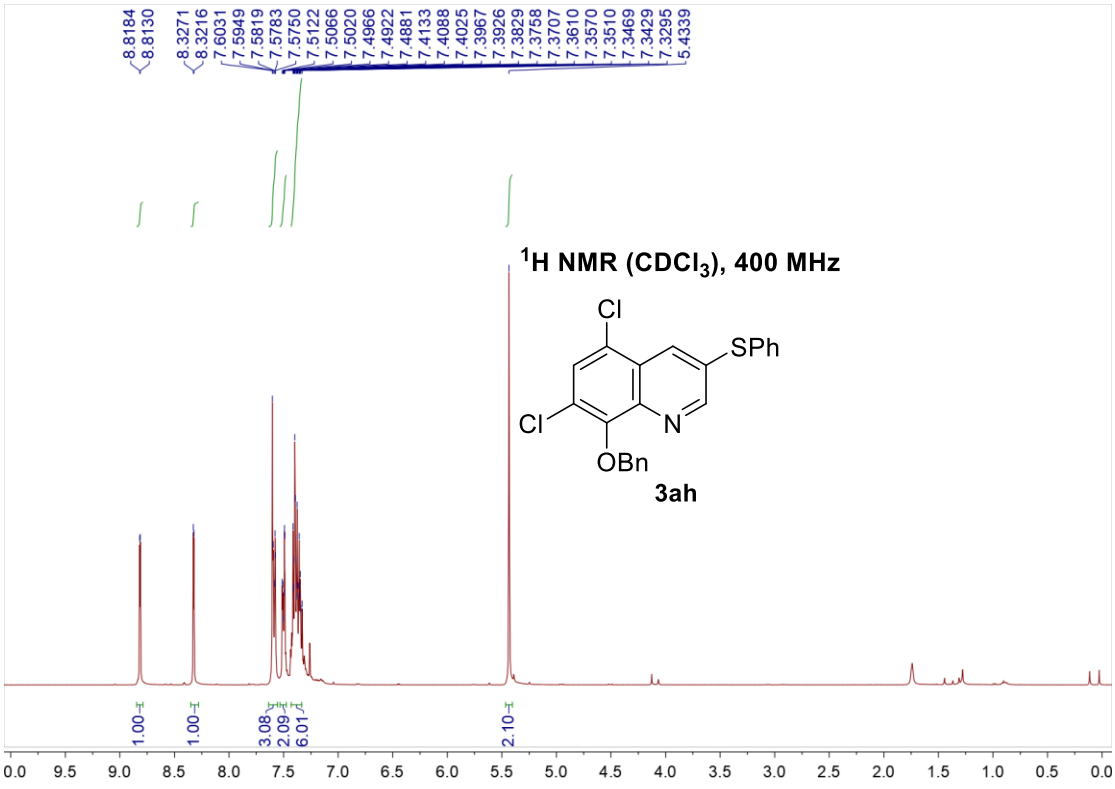
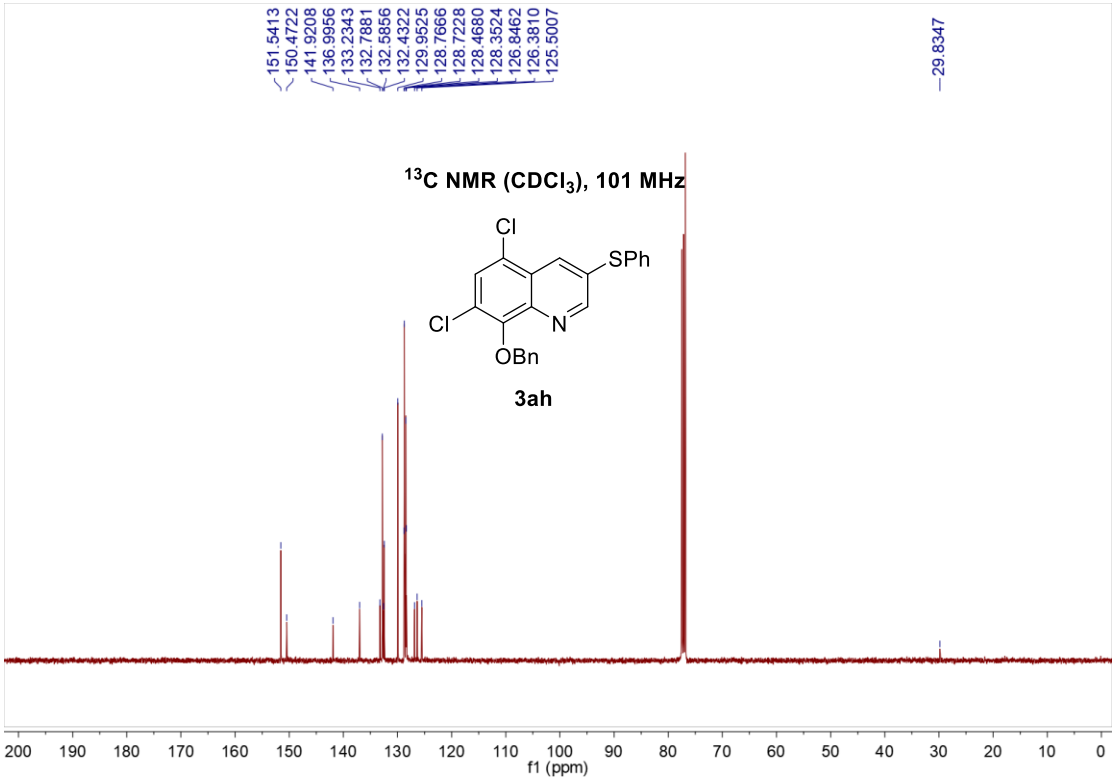
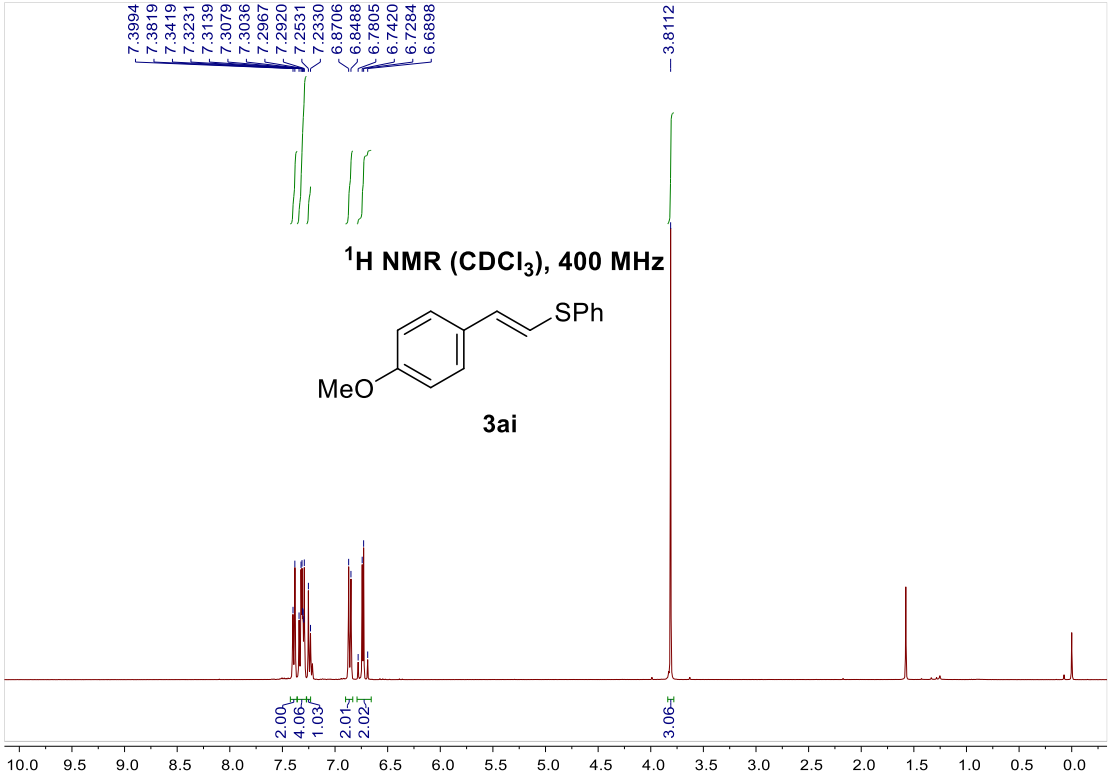
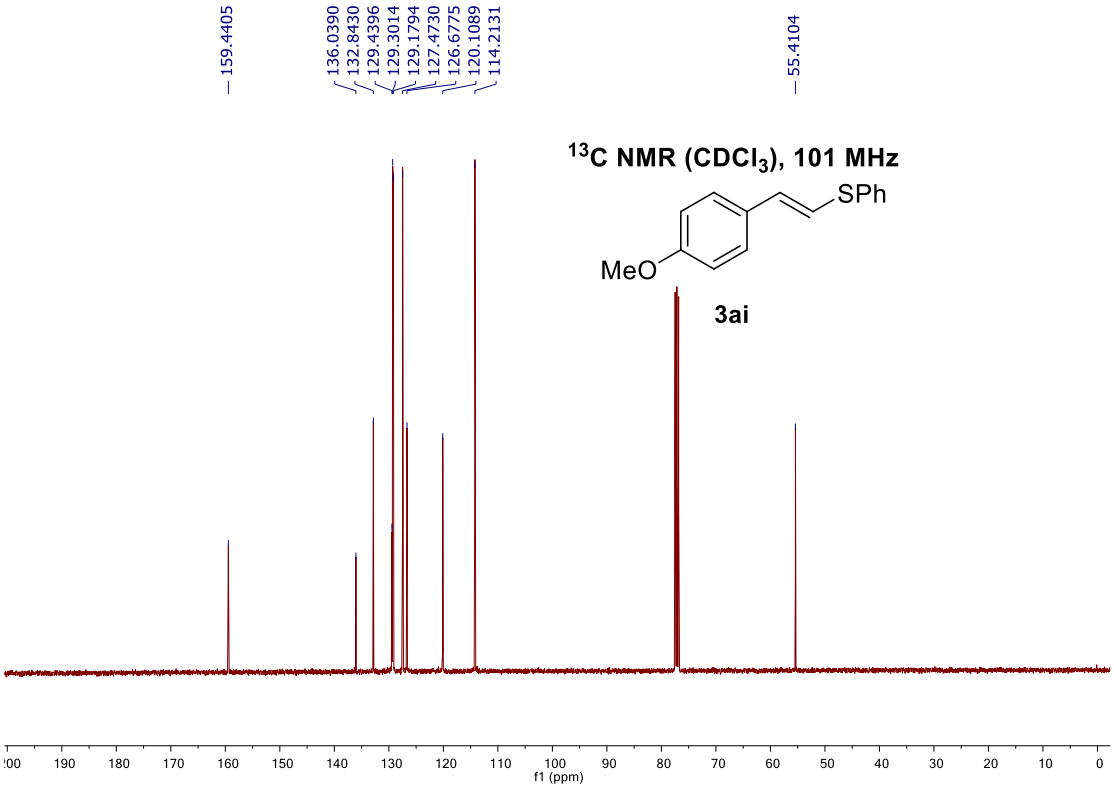
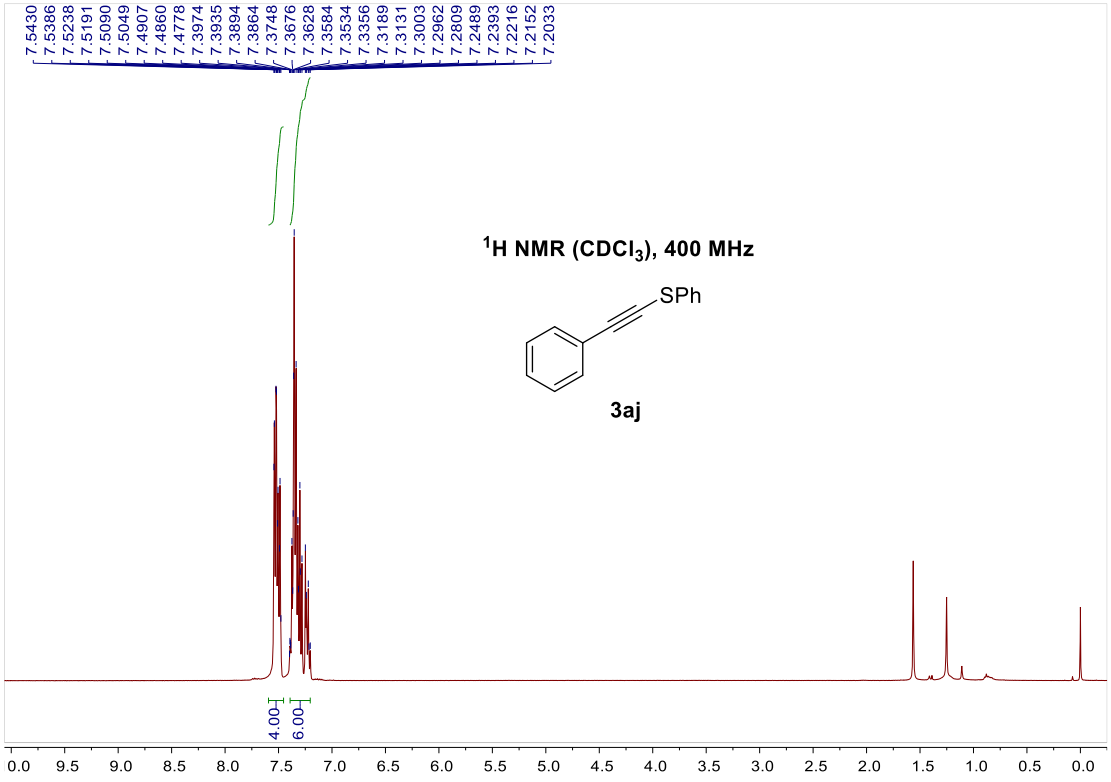
146.7629
137.2001
134.4248
131.4611
130.1376
129.7197
129.6526
129.4410
128.3258
127.8576
127.4088
127.3801
13C NMR (CDCl3), 101 MHz
SPh
N
3ag
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.8184
8.8130
8.3271
8.3216
7.6031
7.5949
7.5819
7.5783
7.5750
7.5122
7.5066
7.5020
7.4966
7.4922
7.4881
7.4133
7.4088
7.4025
7.3967
7.3926
7.3829
7.3758
7.3707
7.3610
7.3570
7.3510
7.3469
7.3429
7.3295
5.4339
1H NMR (CDCl3), 400 MHz
Cl
SPh
Cl
N
OBn
3ah
1.00
1.00
3.08
2.09
6.01
2.10
0.0 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


151.5413
150.4722
141.9208
136.9956
133.2343
132.7881
132.5856
132.4322
129.9525
128.7666
128.7228
128.4680
128.3524
126.8462
126.3810
125.5007
29.8347
13C NMR (CDCl3), 101 MHz
Cl
SPh
Cl
N
OBn
3ah
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.3994
7.3819
7.3419
7.3231
7.3139
7.3079
7.3036
7.2967
7.2920
7.2531
7.2330
6.8706
6.8488
6.7805
6.7420
6.7284
6.6898
3.8112
1H NMR (CDCl3), 400 MHz
SPh
MeO
3ai
2.00
4.06
1.03
2.01
2.02
3.06
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


159.4405
136.0390
132.8430
129.4396
129.3014
129.1794
127.4730
126.6775
120.1089
114.2131
55.4104
^{13}C NMR ($CDCl_3$), 101 MHz
SPh
MeO
3ai
f1 (ppm)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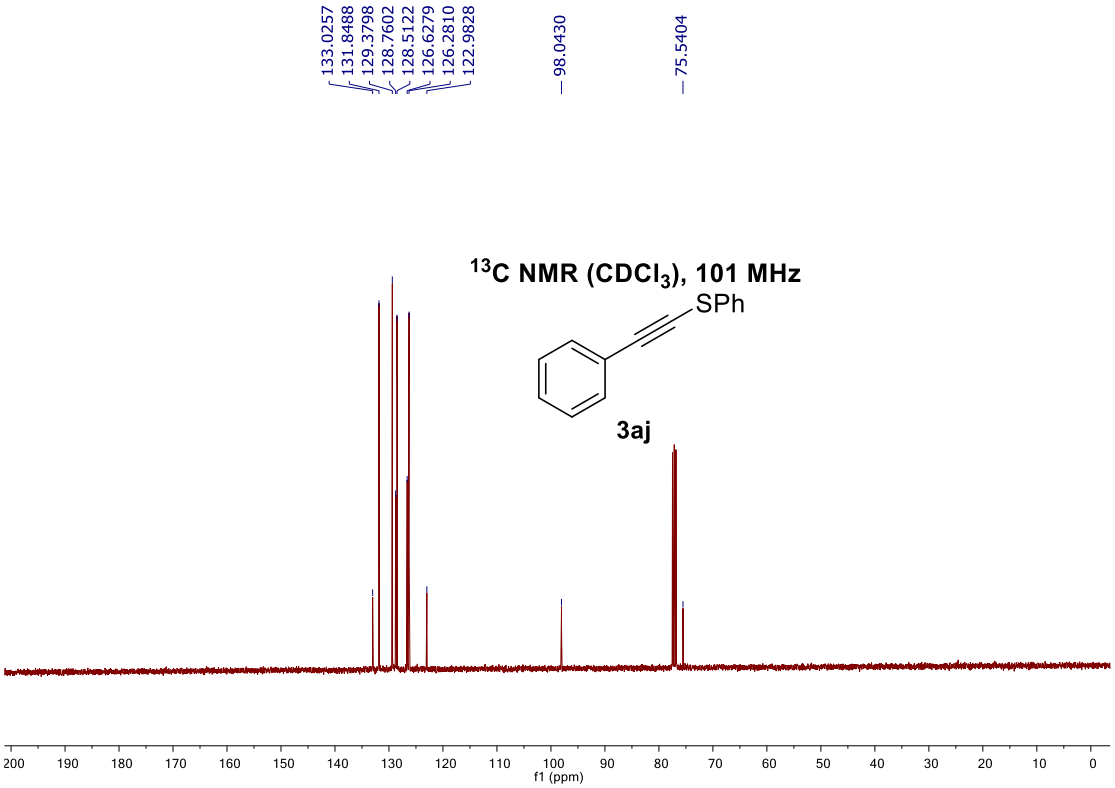
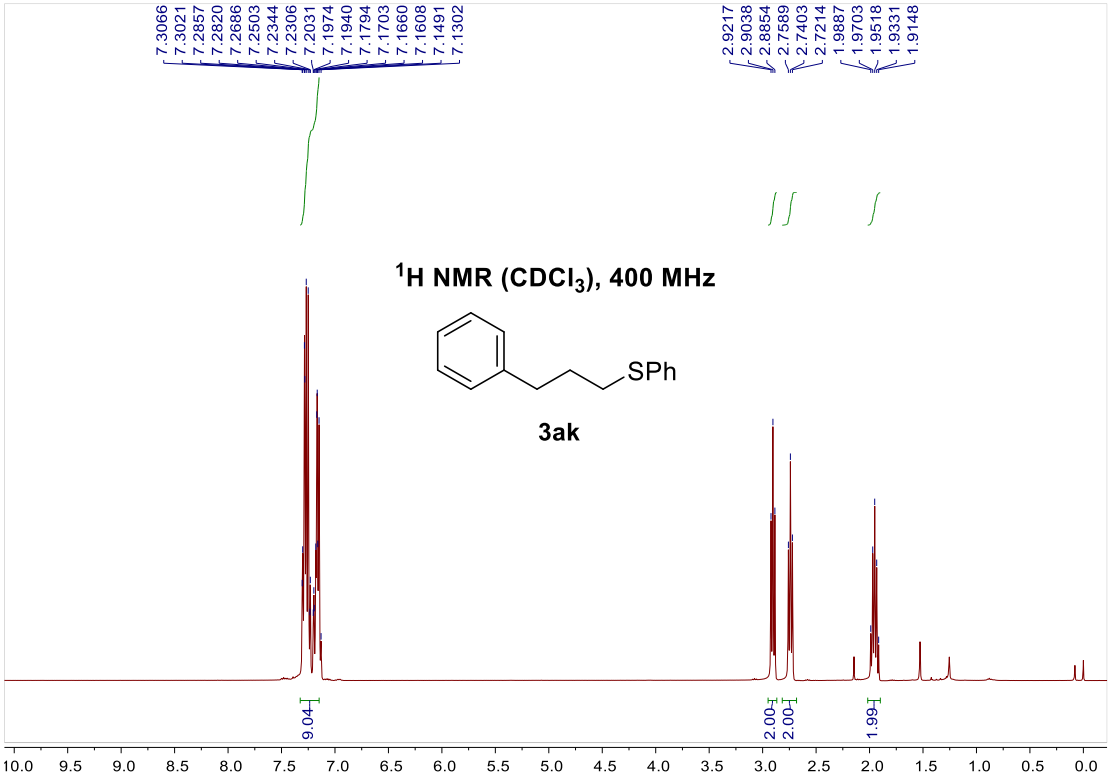
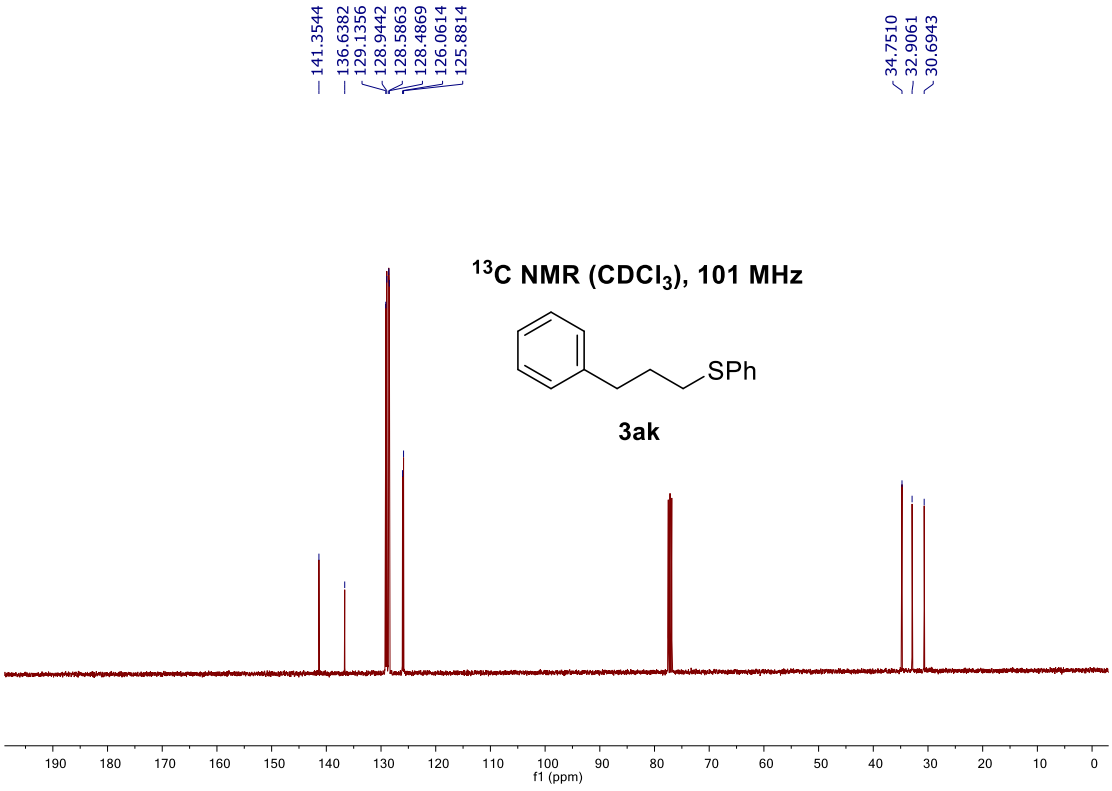
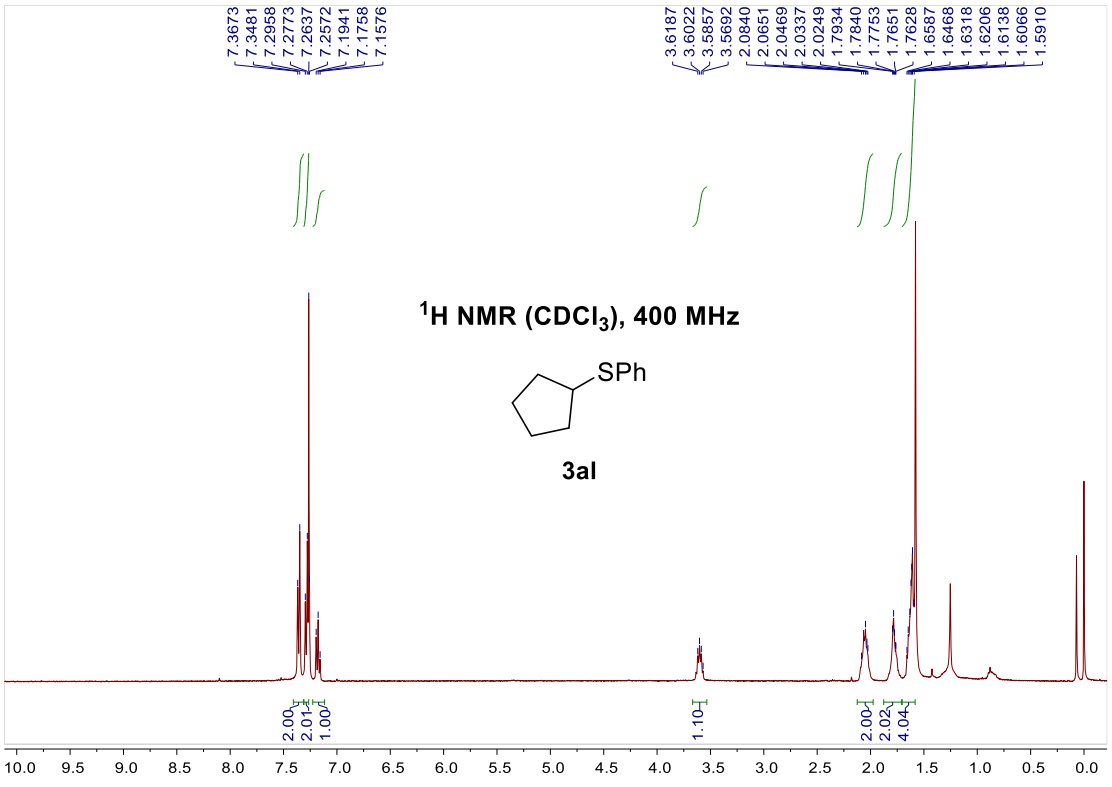
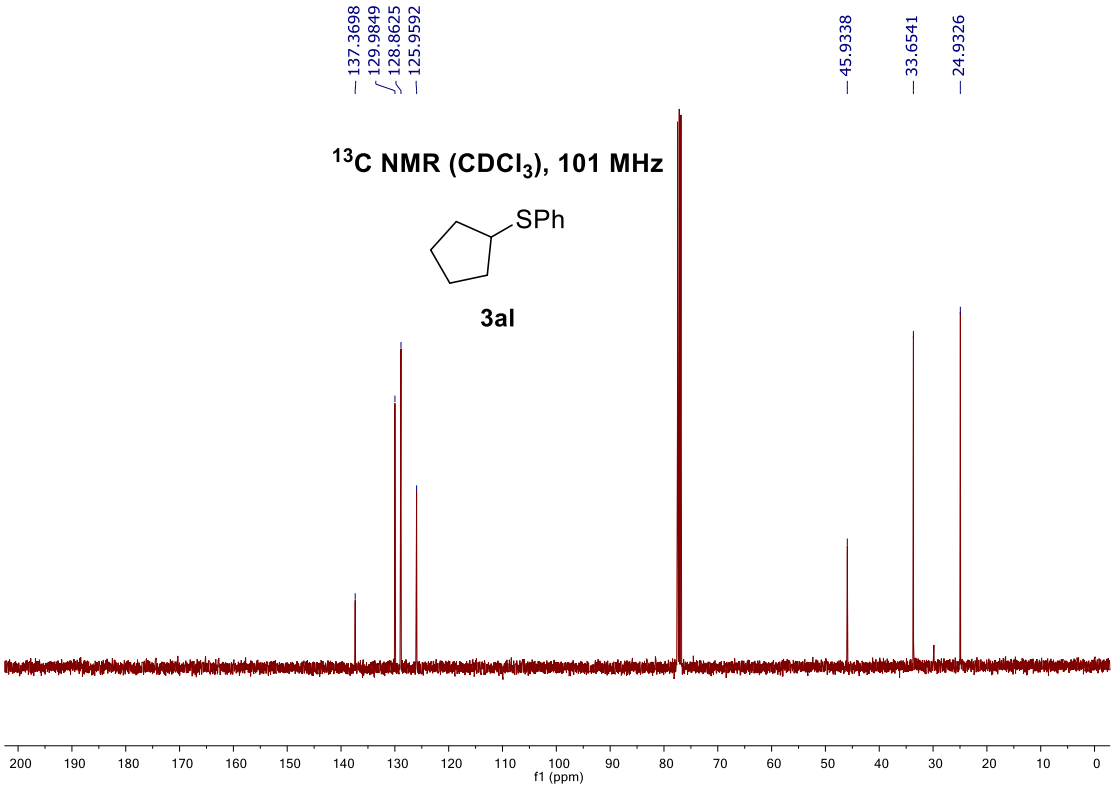
7.5386
7.5238
7.5191
7.5090
7.5049
7.4907
7.4860
7.4778
7.3974
7.3935
7.3894
7.3864
7.3748
7.3676
7.3628
7.3584
7.3534
7.3356
7.3189
7.3131
7.3003
7.2962
7.2809
7.2489
7.2393
7.2216
7.2152
7.2033
^{1}H NMR ($CDCl_3$), 400 MHz
SPh
3aj
4.00
6.00

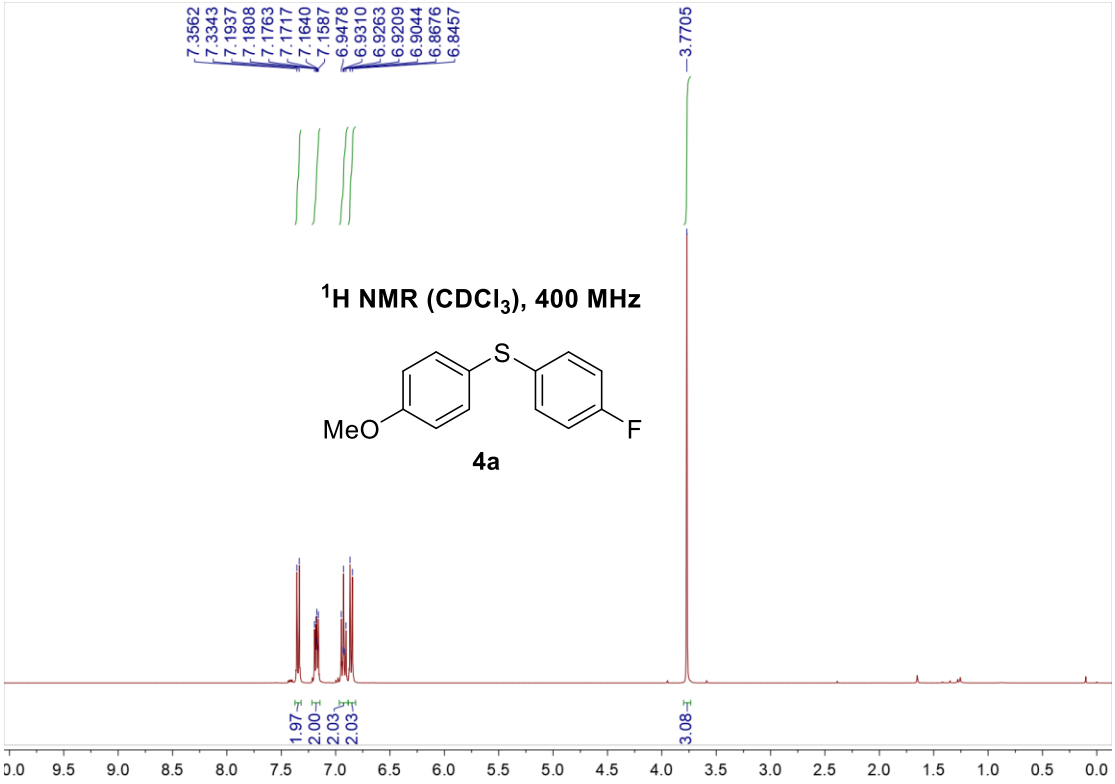

133.0257
131.8488
129.3798
128.7602
128.5122
126.6279
126.2810
122.9828
98.0430
75.5404
13C NMR (CDCl3), 101 MHz
SPh
3aj
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.3066
7.3021
7.2857
7.2820
7.2686
7.2503
7.2344
7.2306
7.2031
7.1974
7.1940
7.1794
7.1703
7.1660
7.1608
7.1491
7.1302
2.9217
2.9038
2.8854
2.7589
2.7403
2.7214
1.9887
1.9703
1.9518
1.9331
1.9148
1H NMR (CDCl3), 400 MHz
SPh
3ak
9.04
2.00
2.00
1.99
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


141.3544
136.6382
129.1356
128.9442
128.5863
128.4869
126.0614
125.8814
34.7510
32.9061
30.6943
13C NMR (CDCl3), 101 MHz
SPh
3ak
f1 (ppm)


7.3673
7.3481
7.2958
7.2773
7.2637
7.2572
7.1941
7.1758
7.1576
3.6187
3.6022
3.5857
3.5692
2.0840
2.0651
2.0469
2.0337
2.0249
1.7934
1.7840
1.7753
1.7651
1.7628
1.6587
1.6468
1.6318
1.6206
1.6138
1.6066
1.5910
1H NMR (CDCl3), 400 MHz
SPh
3al
2.00
2.01
1.00
1.10
2.00
2.02
4.04


137.3698
129.9849
128.8625
125.9592
45.9338
33.6541
24.9326
13C NMR (CDCl3), 101 MHz
SPh
3al
f1 (ppm)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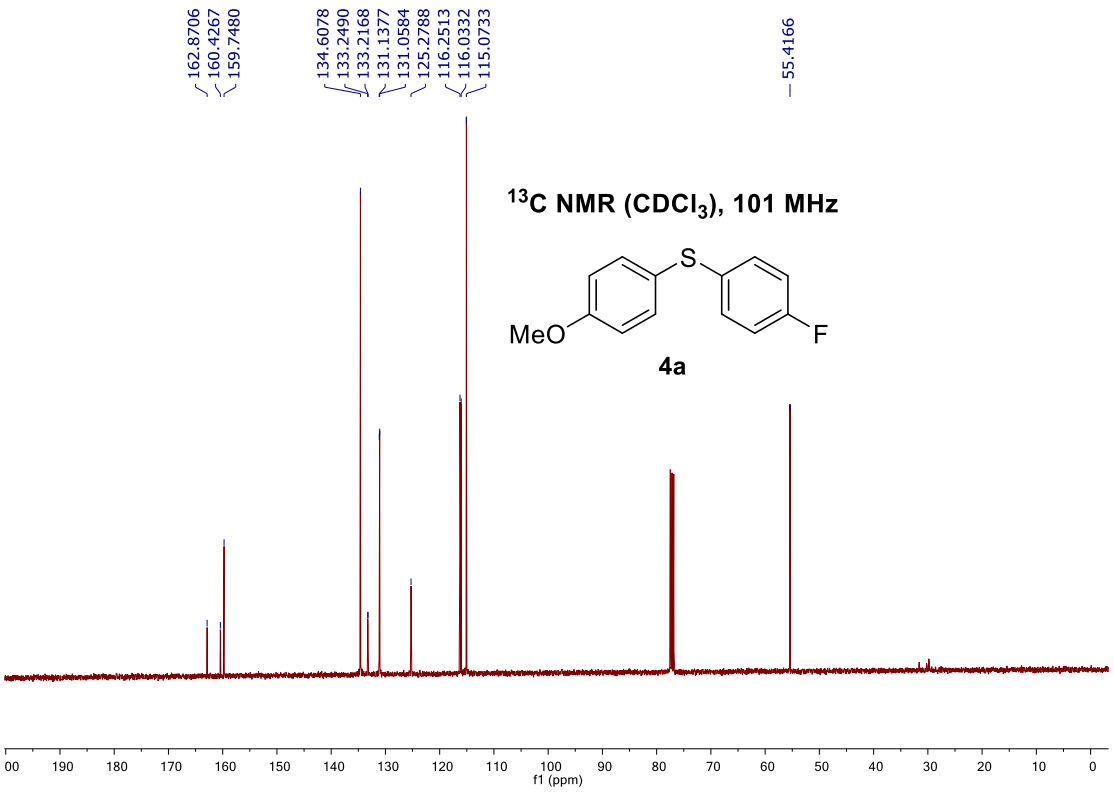
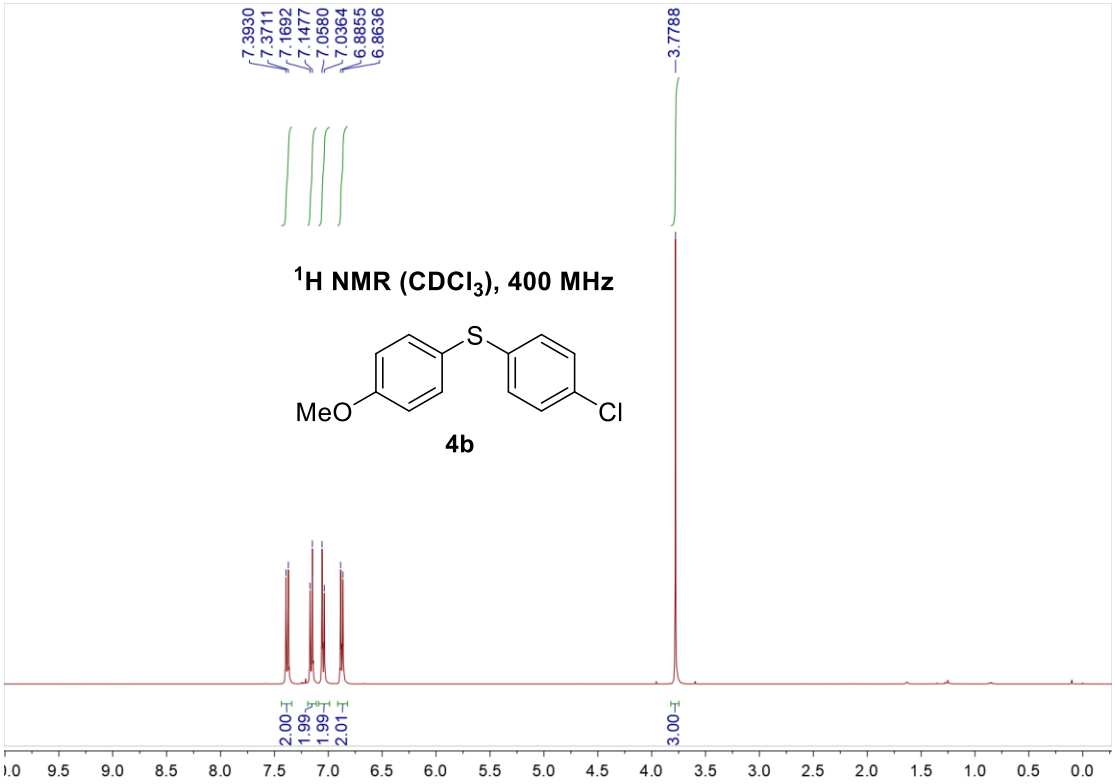
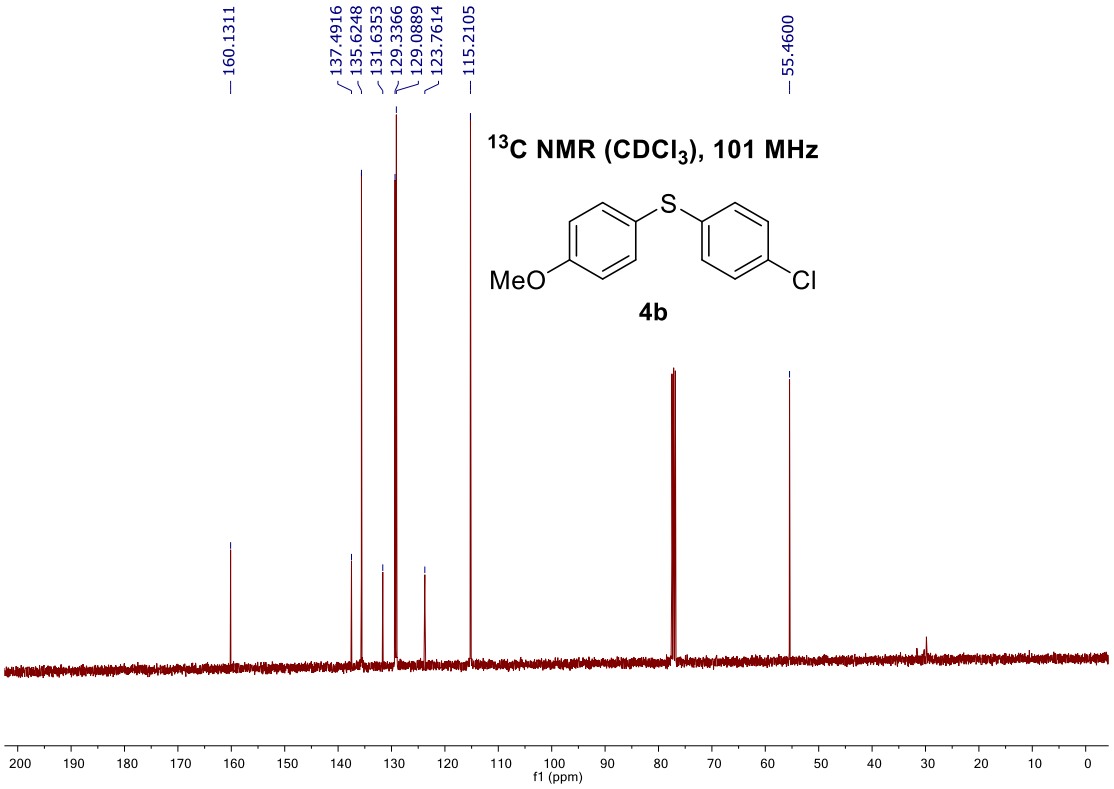
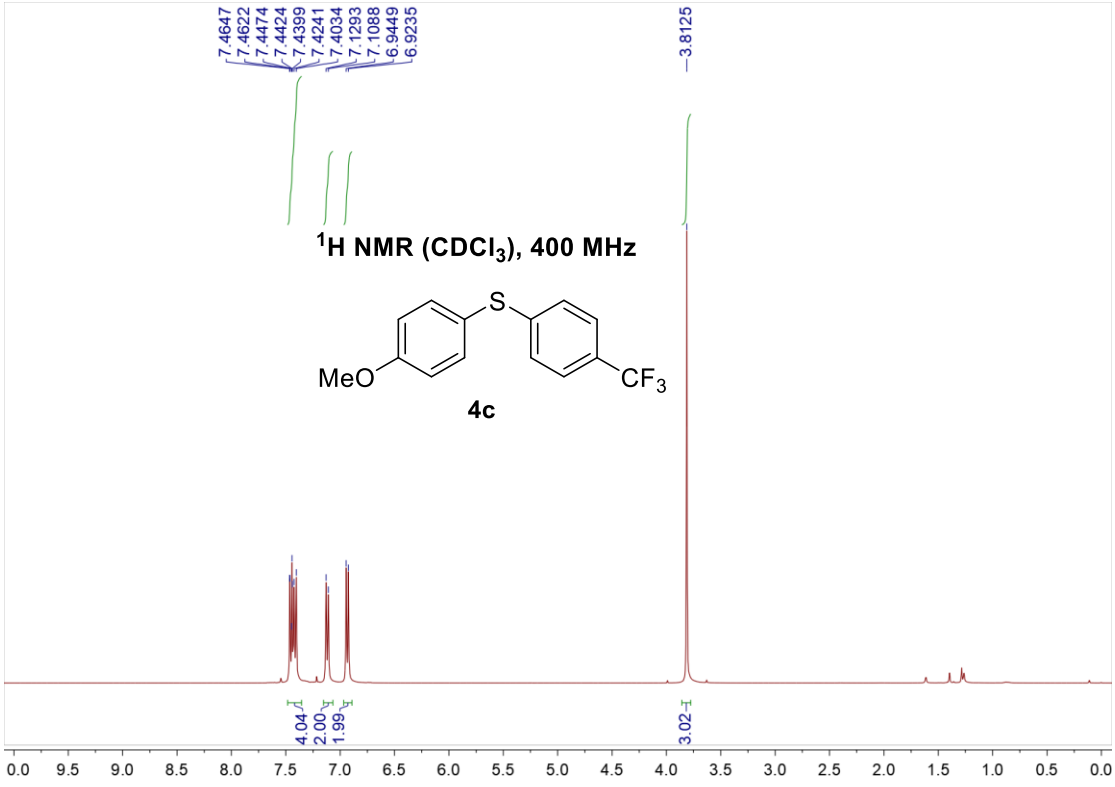
7.3343
7.1937
7.1808
7.1763
7.1717
7.1640
7.1587
6.9478
6.9310
6.9263
6.9209
6.9044
6.8676
6.8457
3.7705
1H NMR (CDCl3), 400 MHz
S
MeO
F
4a
1.97
2.00
2.03
2.03
3.08


162.8706
160.4267
159.7480
134.6078
133.2490
133.2168
131.1377
131.0584
125.2788
116.2513
116.0332
115.0733
55.4166
13C NMR (CDCl3), 101 MHz
S
MeO
F
4a
f1 (ppm)


7.3930
7.3711
7.1692
7.1477
7.0580
7.0364
6.8855
6.8636
3.7788
1H NMR (CDCl3), 400 MHz
S
MeO
Cl
4b
2.00
1.99
1.99
2.01
3.00


160.1311
137.4916
135.6248
131.6353
129.3366
129.0889
123.7614
115.2105
55.4600
^{13}C NMR (CDCl$_3$), 101 MHz
S
MeO
Cl
4b
f1 (ppm)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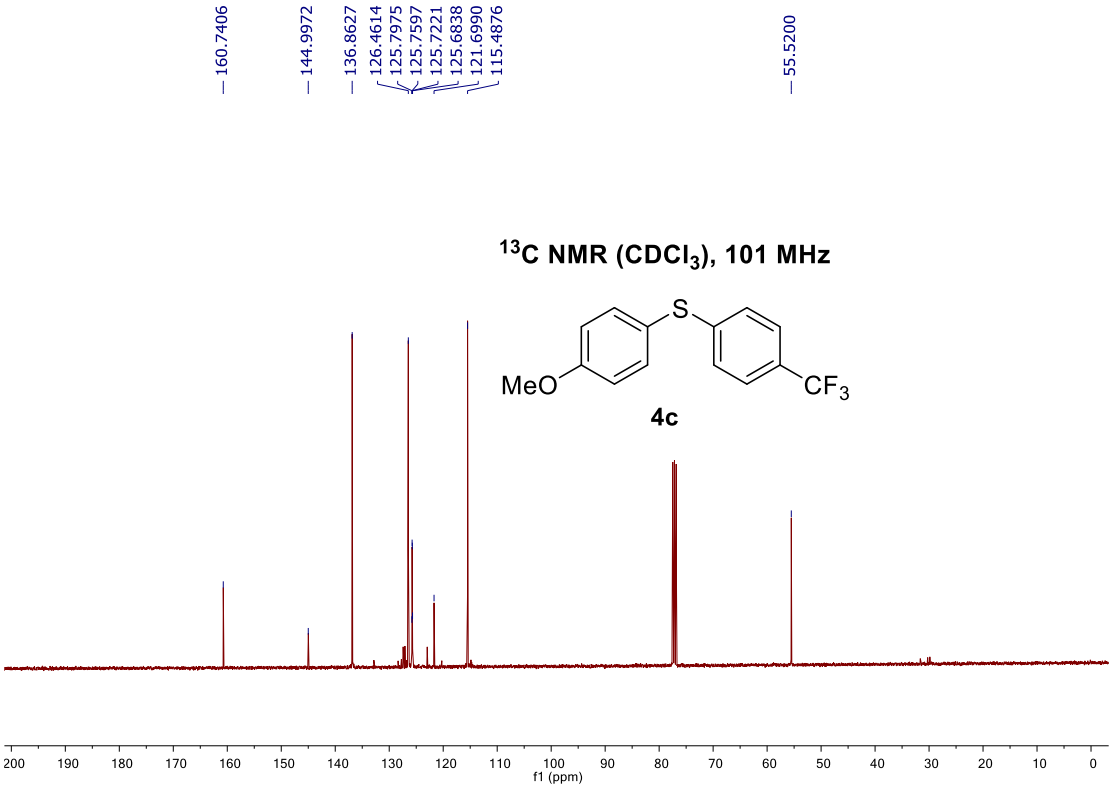
7.4474
7.4424
7.4399
7.4241
7.4034
7.1293
7.1088
6.9449
6.9235
3.8125
^{1}H NMR (CDCl$_3$), 400 MHz
S
MeO
CF$_3$
4c
4.04
2.00
1.99
3.02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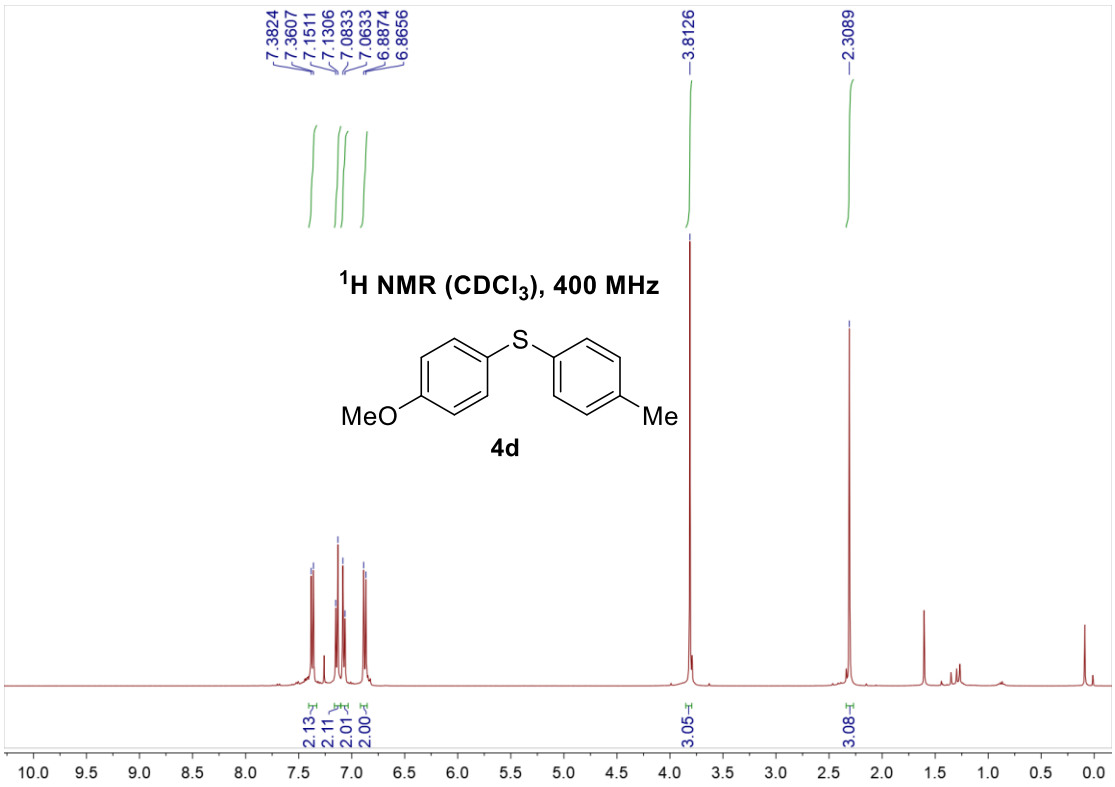
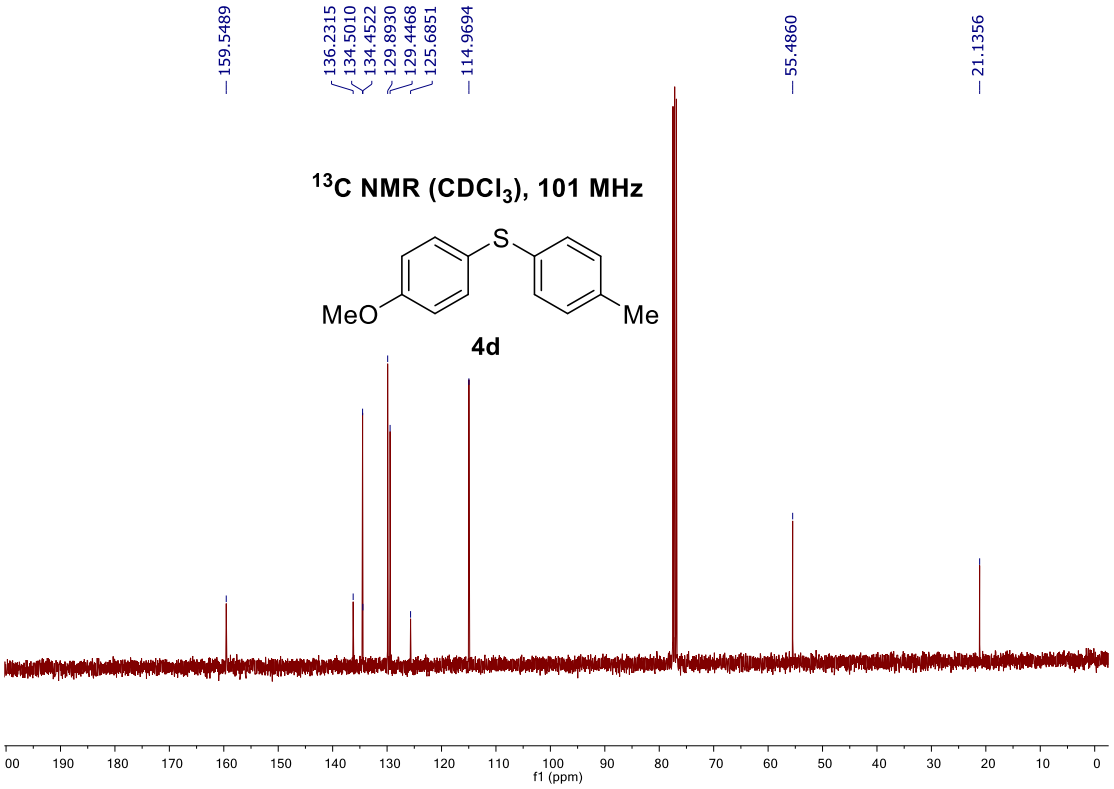
144.9972
136.8627
126.4614
125.7975
125.7597
125.7221
125.6838
121.6990
115.4876
55.5200
13C NMR (CDCl3), 101 MHz
S
MeO
CF3
4c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.3824
7.3607
7.1511
7.1306
7.0833
7.0633
6.8874
6.8656
3.8126
2.3089
1H NMR (CDCl3), 400 MHz
S
MeO
Me
4d
2.13
2.11
2.01
2.00
3.05
3.08
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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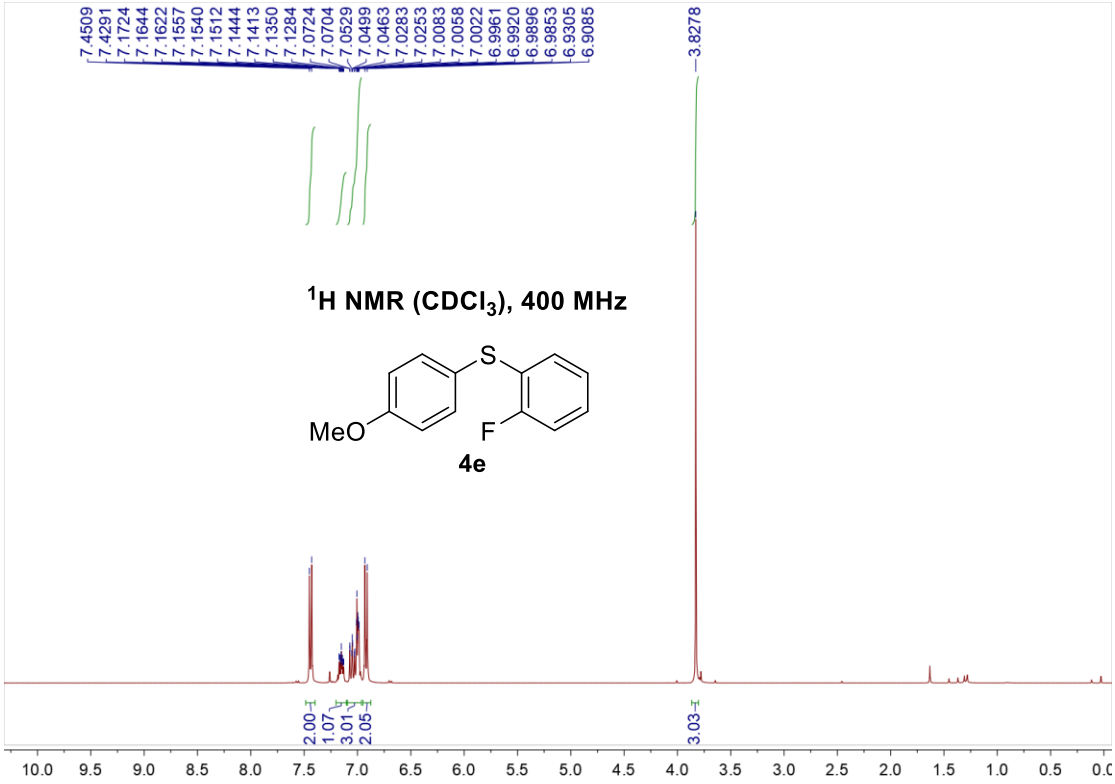
136.2315
134.5010
134.4522
129.8930
129.4468
125.6851
114.9694
55.4860
21.1356
13C NMR (CDCl3), 101 MHz
S
MeO
Me
4d
f1 (ppm)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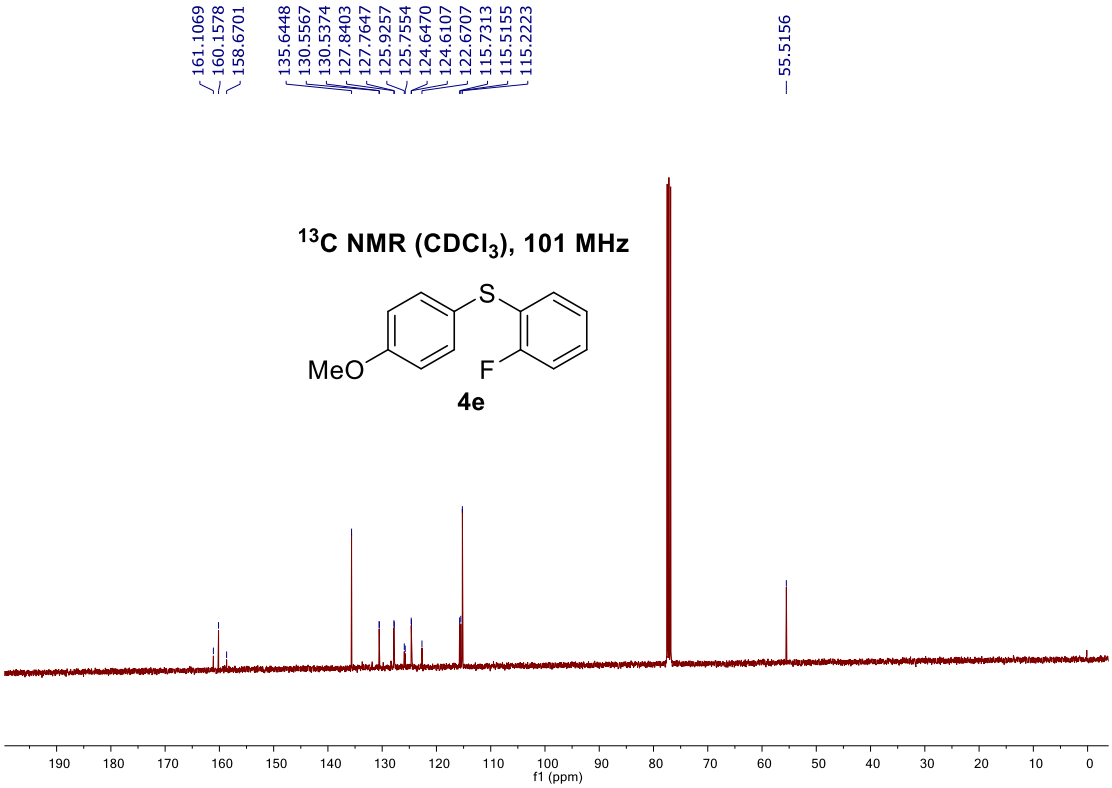
7.1644
7.1622
7.1557
7.1540
7.1512
7.1444
7.1413
7.1350
7.1284
7.0724
7.0704
7.0529
7.0499
7.0463
7.0283
7.0253
7.0083
7.0058
7.0022
6.9961
6.9920
6.9896
6.9853
6.9305
6.9085
3.8278
1H NMR (CDCl3), 400 MHz
S
MeO
F
4e
2.00
1.07
3.01
2.05
3.03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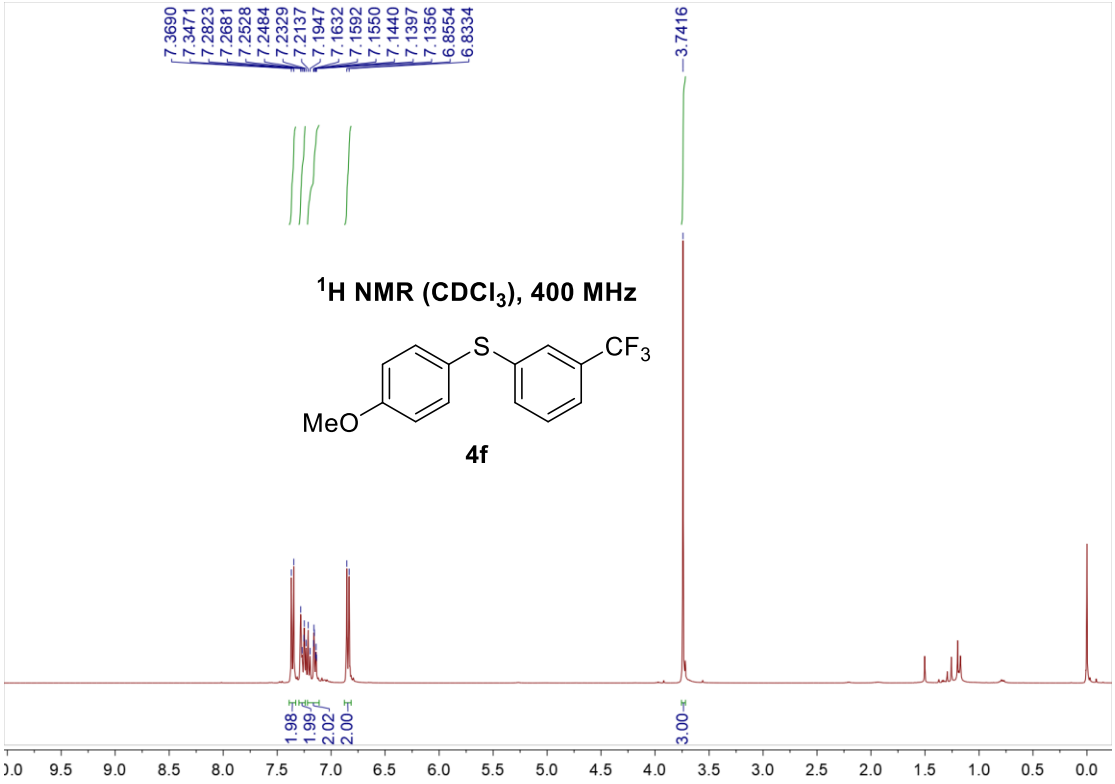
135.6448
130.5567
130.5374
127.8403
127.7647
125.9257
125.7554
124.6470
124.6107
122.6707
115.7313
115.5155
115.2223
55.5156
13C NMR (CDCl3), 101 MHz
S
MeO
F
4e
f1 (ppm)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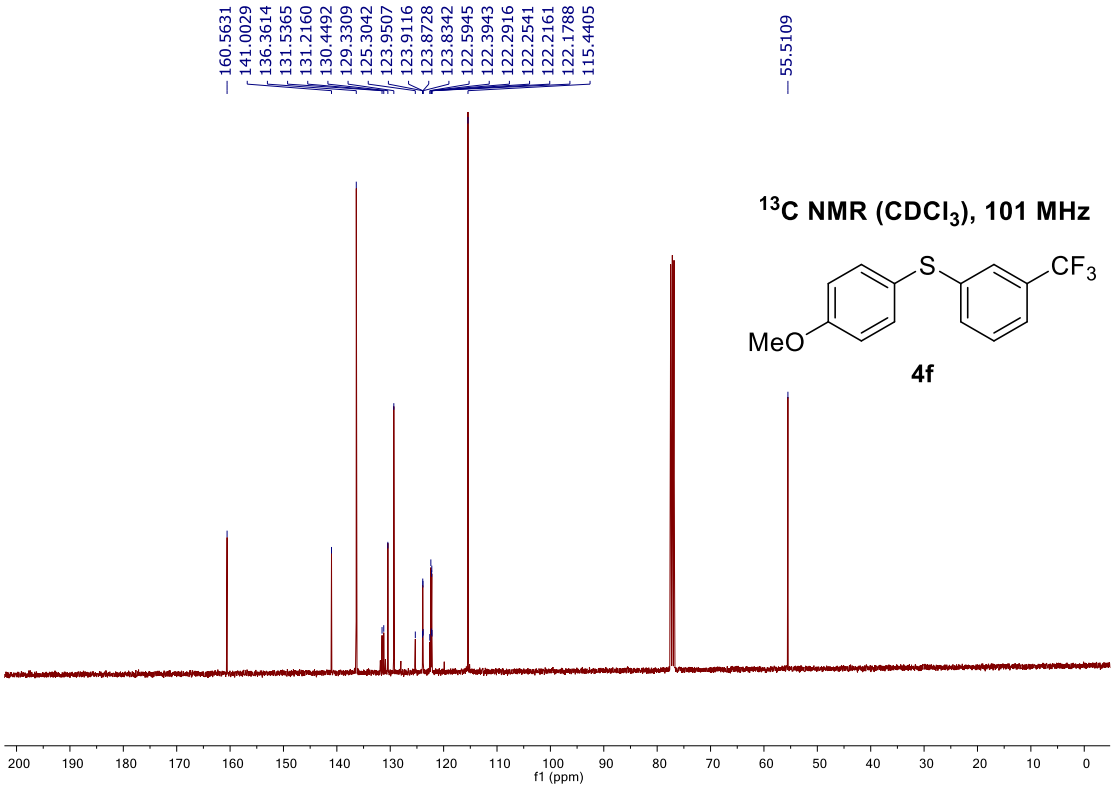
7.2681
7.2528
7.2484
7.2329
7.2137
7.1947
7.1632
7.1592
7.1550
7.1440
7.1397
7.1356
6.8554
6.8334
3.7416
1H NMR (CDCl3), 400 MHz
S
CF3
MeO
4f
1.98
1.99
2.02
2.00
3.00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136.3614
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131.2160
130.4492
129.3309
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123.9507
123.9116
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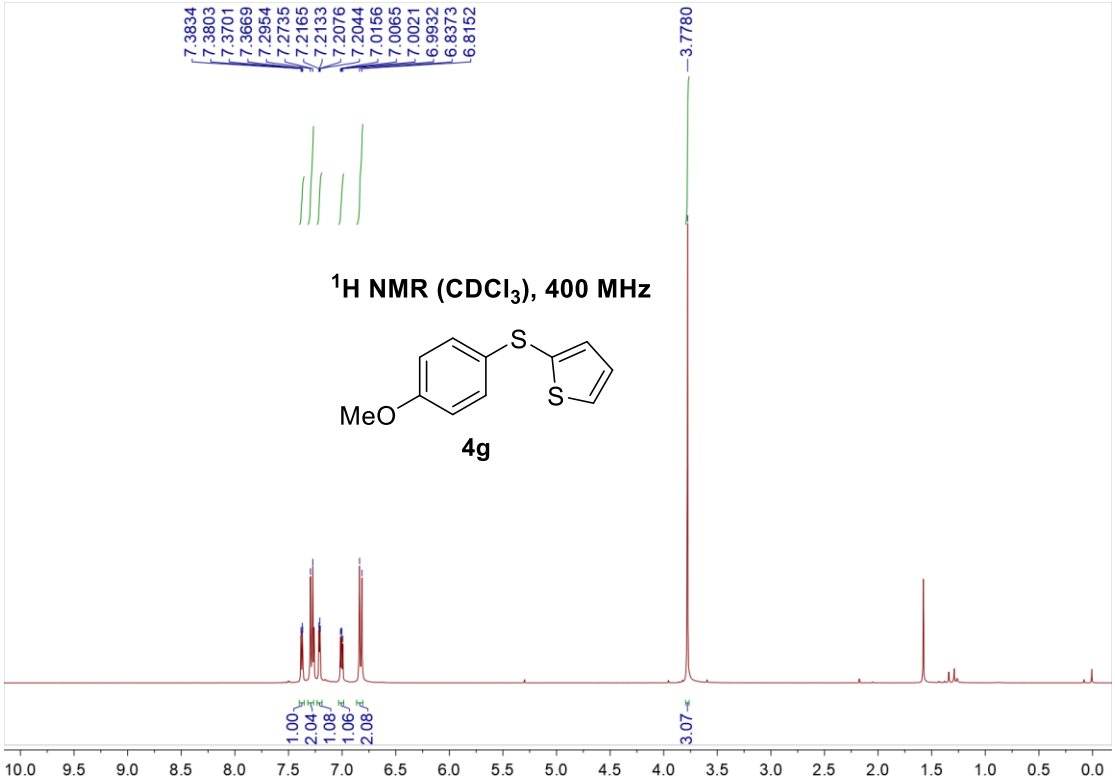
123.8342
122.5945
122.3943
122.2916
122.2541
122.2161
122.1788
115.4405
55.5109
^{13}C NMR ($CDCl_3$), 101 MHz
S
CF_3
MeO
4f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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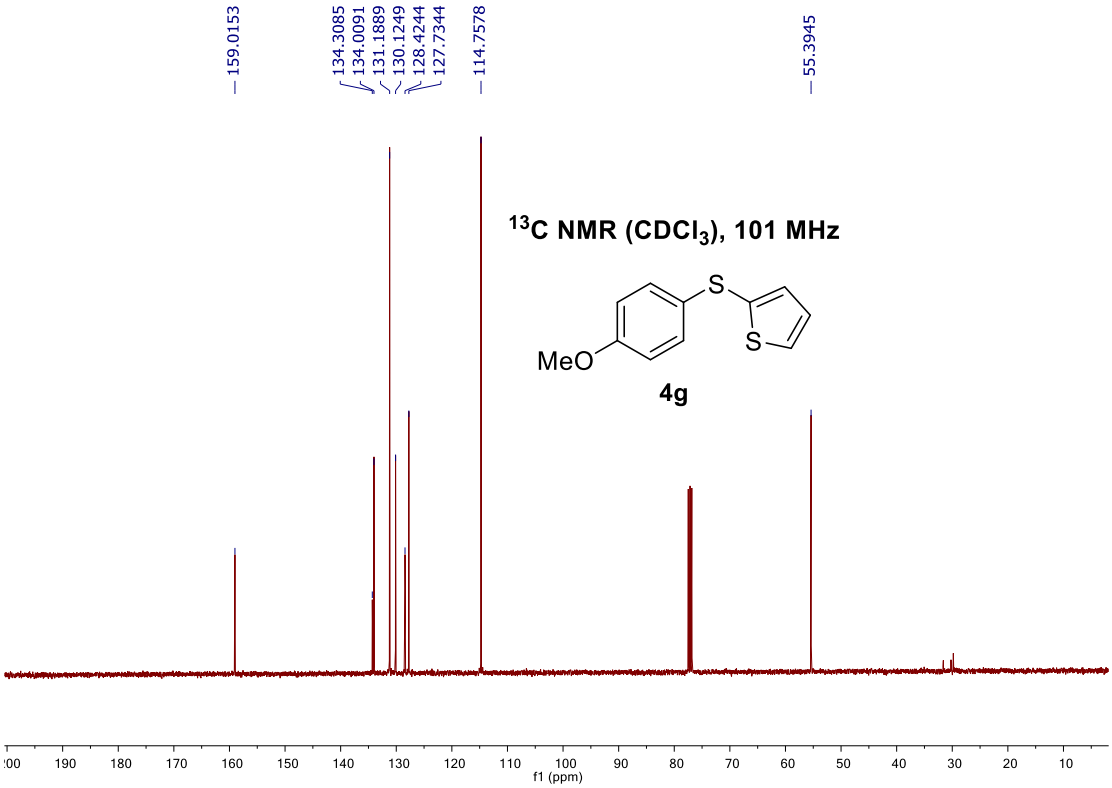
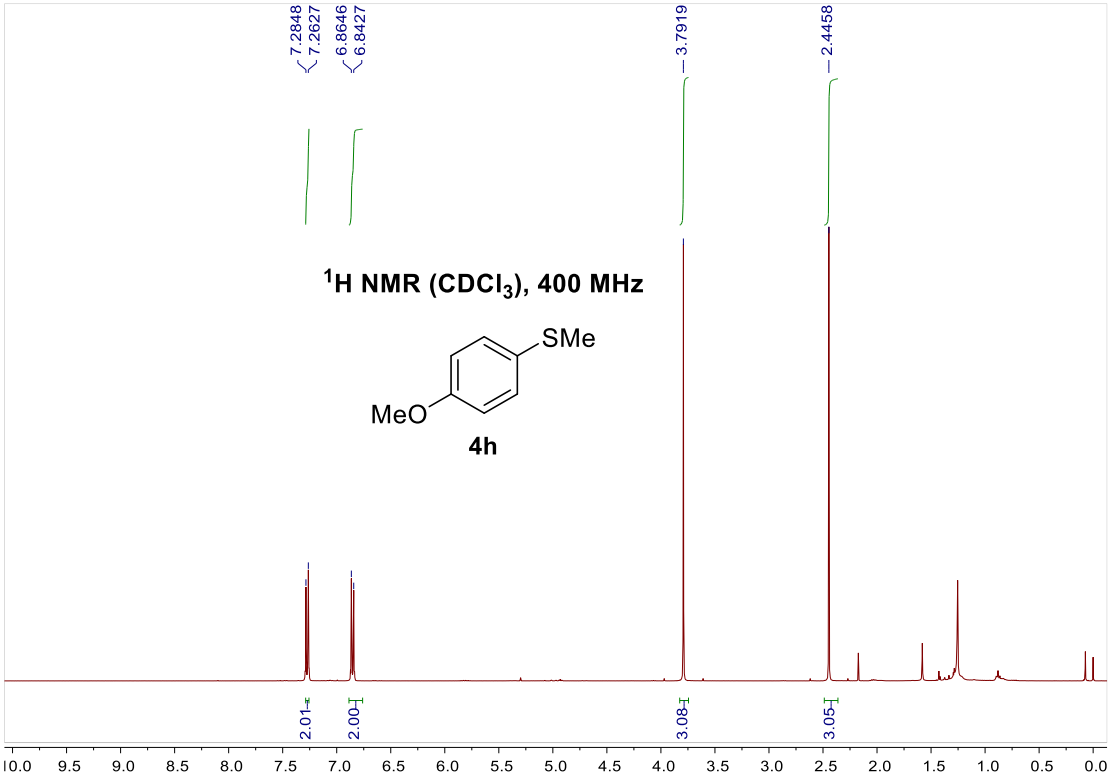
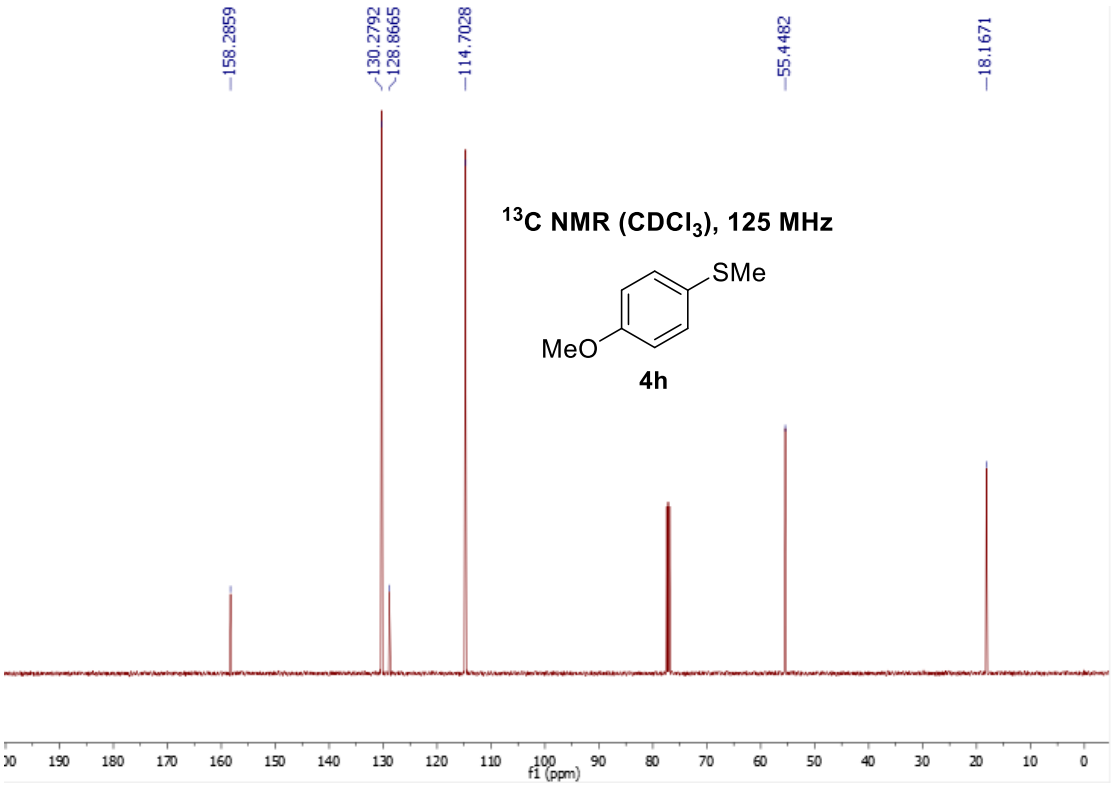
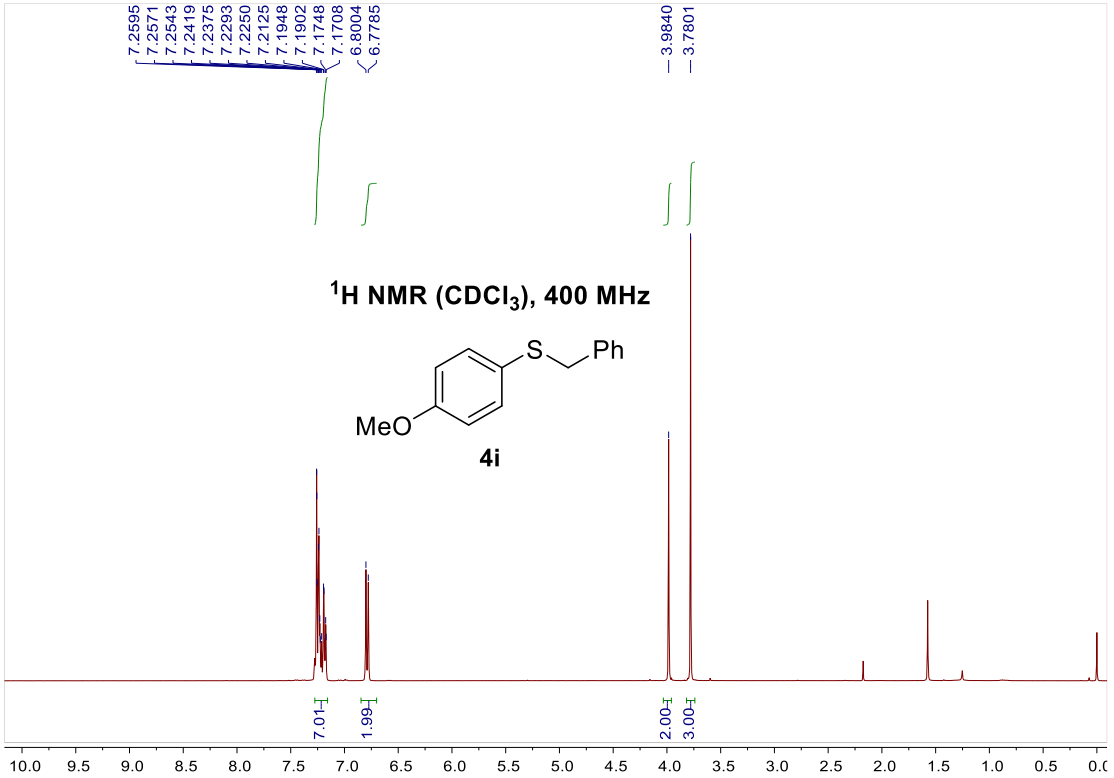
7.3803
7.3701
7.3669
7.2954
7.2735
7.2165
7.2133
7.2076
7.2044
7.0156
7.0065
7.0021
6.9932
6.8373
6.8152
3.7780
^{1}H NMR ($CDCl_3$), 400 MHz
S
S
MeO
4g
1.00
2.04
1.08
1.06
2.08
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


159.0153
134.3085
134.0091
131.1889
130.1249
128.4244
127.7344
114.7578
55.3945
13C NMR (CDCl3), 101 MHz
S
S
MeO
4g
f1 (ppm)


7.2848
7.2627
6.8646
6.8427
3.7919
2.4458
1H NMR (CDCl3), 400 MHz
SMe
MeO
4h
2.01
2.00
3.08
3.05


158.2859
130.2792
128.8665
114.7028
55.4482
18.1671
13C NMR (CDCl3), 125 MHz
SMe
MeO
4h
f1 (ppm)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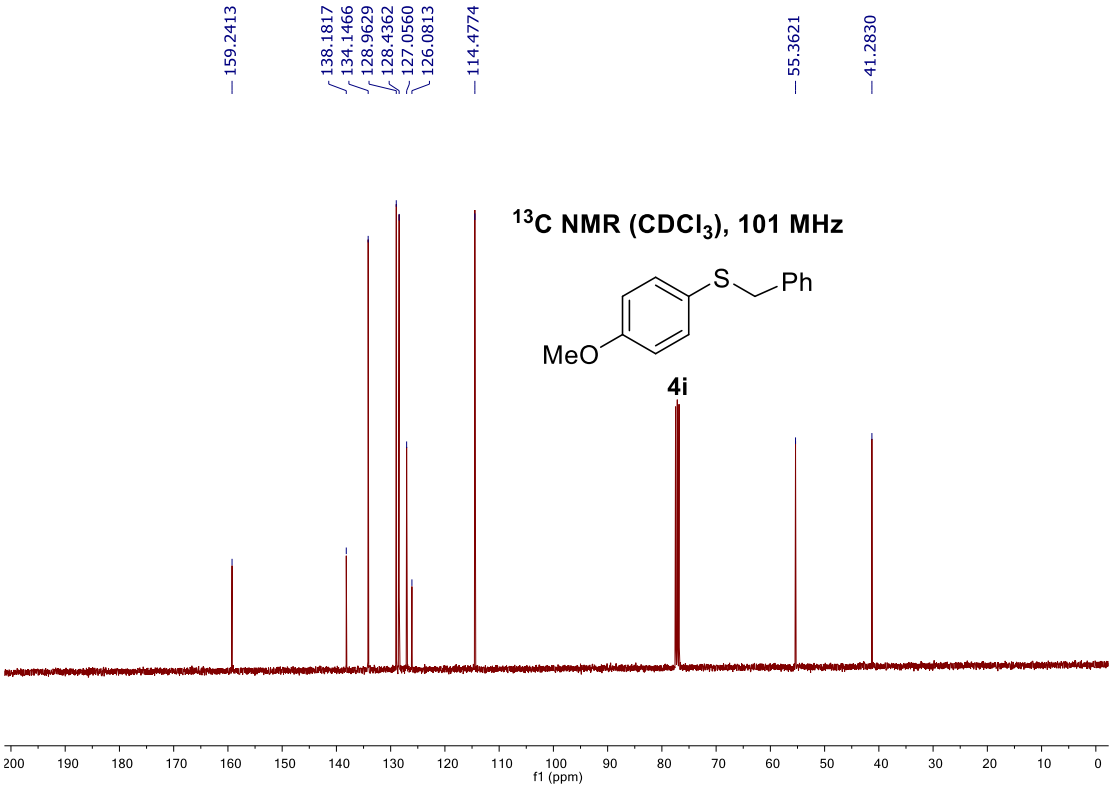
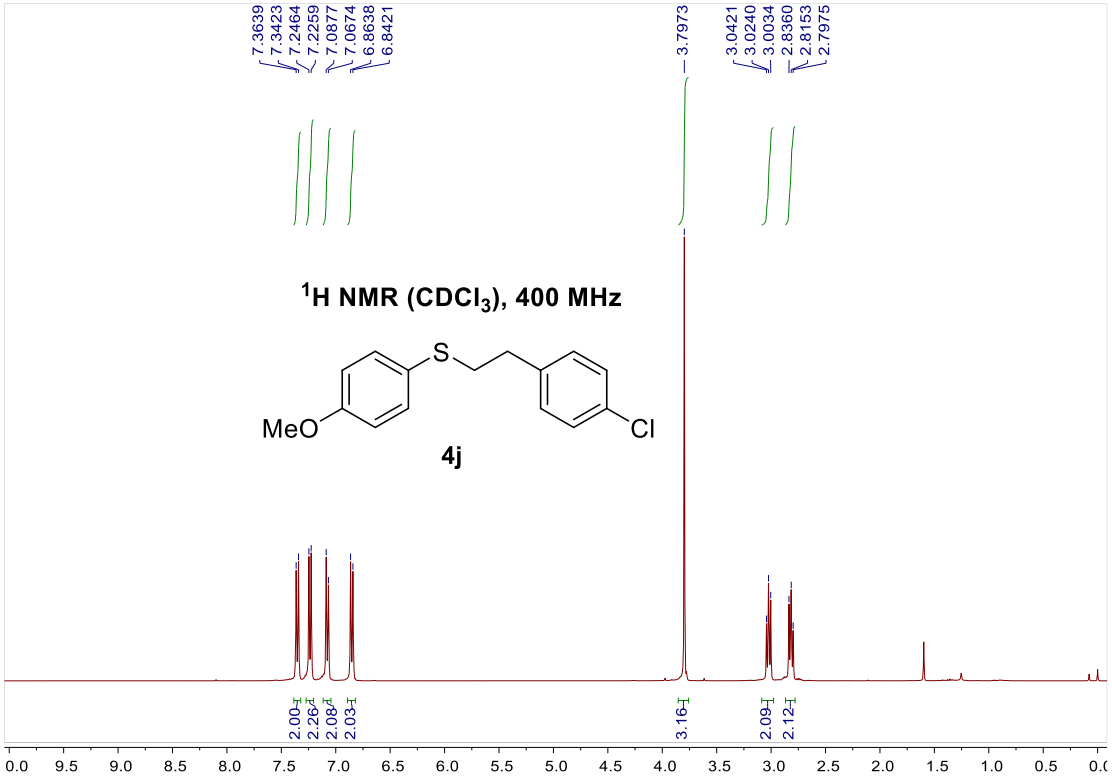
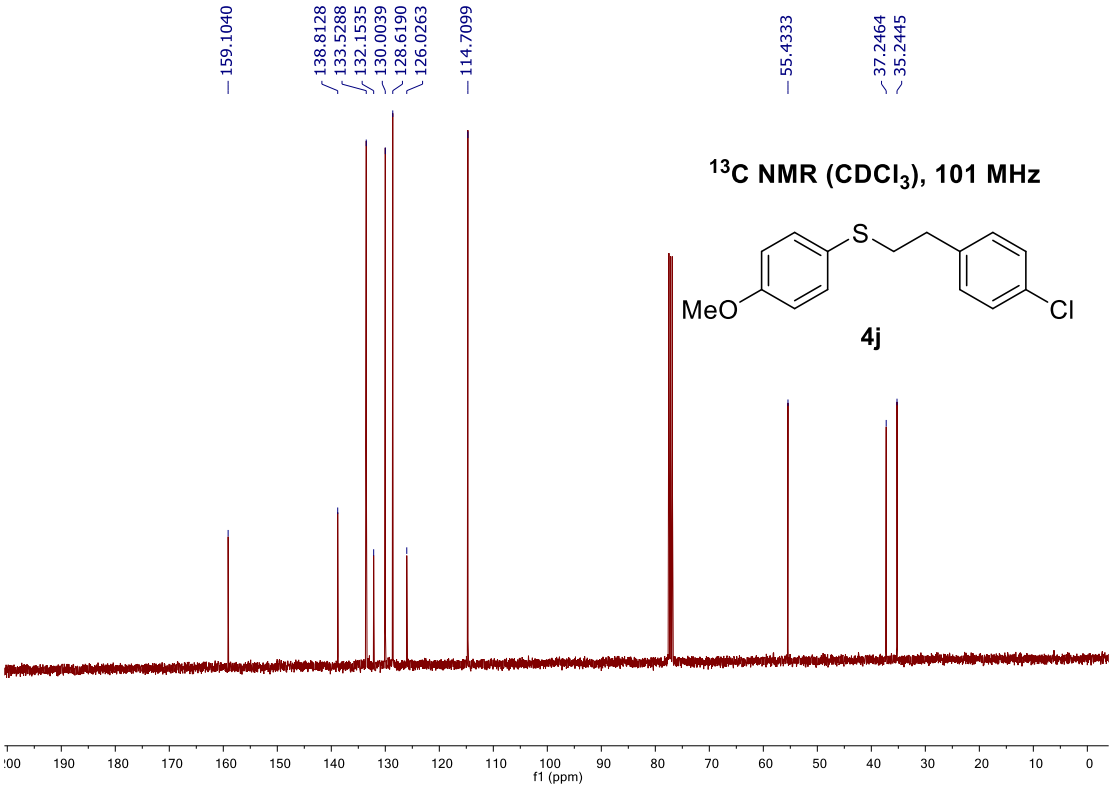
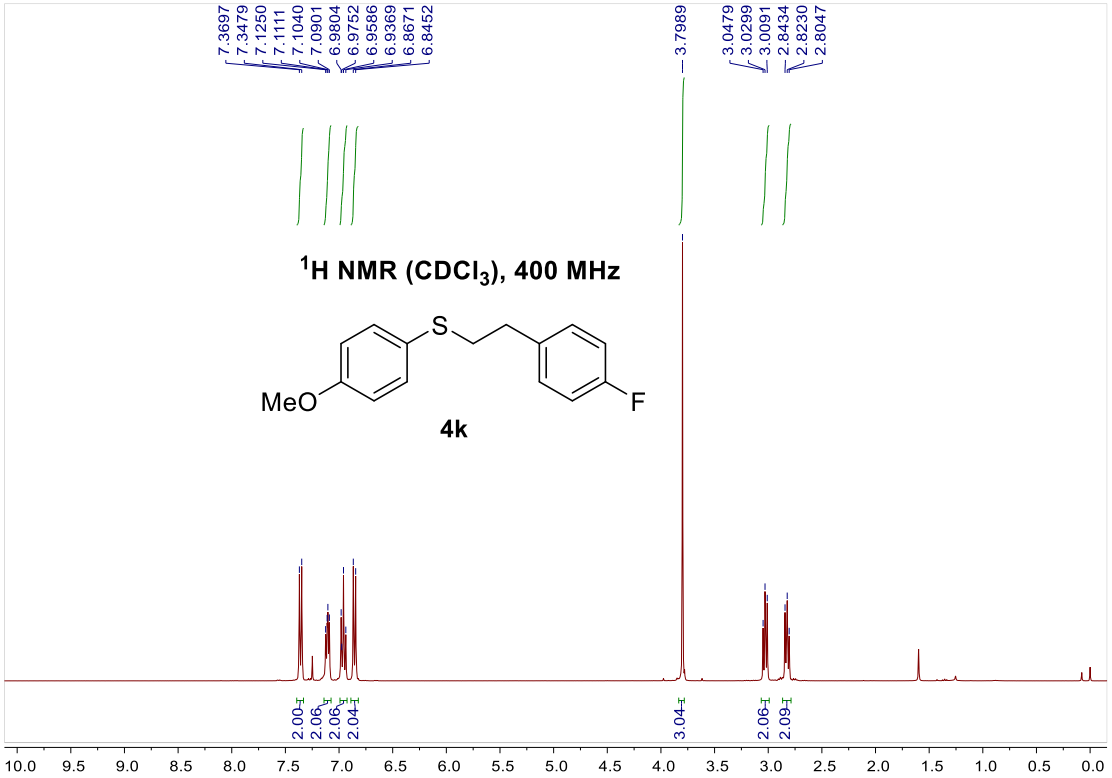
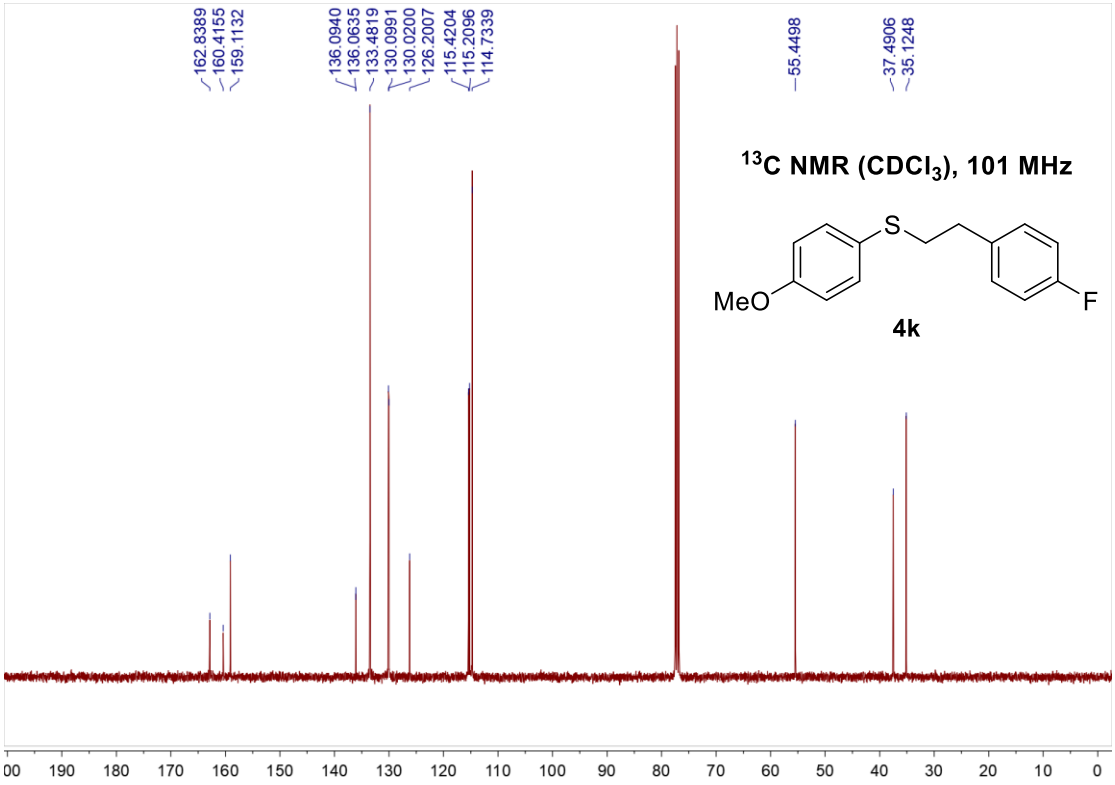
7.2571
7.2543
7.2419
7.2375
7.2293
7.2250
7.2125
7.1948
7.1902
7.1748
7.1708
6.8004
6.7785
3.9840
3.7801
1H NMR (CDCl3), 400 MHz
S
Ph
MeO
4i
7.01
1.99
2.00
3.00


159.2413
138.1817
134.1466
128.9629
128.4362
127.0560
126.0813
114.4774
55.3621
41.2830
13C NMR (CDCl3), 101 MHz
S
Ph
MeO
4i
f1 (ppm)


7.3639
7.3423
7.2464
7.2259
7.0877
7.0674
6.8638
6.8421
3.7973
3.0421
3.0240
3.0034
2.8360
2.8153
2.7975
1H NMR (CDCl3), 400 MHz
S
MeO
Cl
4j
2.00
2.26
2.08
2.03
3.16
2.09
2.12


159.1040
138.8128
133.5288
132.1535
130.0039
128.6190
126.0263
114.7099
55.4333
37.2464
35.2445
13C NMR (CDCl3), 101 MHz
S
MeO
Cl
4j
f1 (ppm)


7.3697
7.3479
7.1250
7.1111
7.1040
7.0901
6.9804
6.9752
6.9586
6.9369
6.8671
6.8452
3.7989
3.0479
3.0299
3.0091
2.8434
2.8230
2.8047
1H NMR (CDCl3), 400 MHz
S
MeO
F
4k
2.00
2.06
2.06
2.04
3.04
2.06
2.09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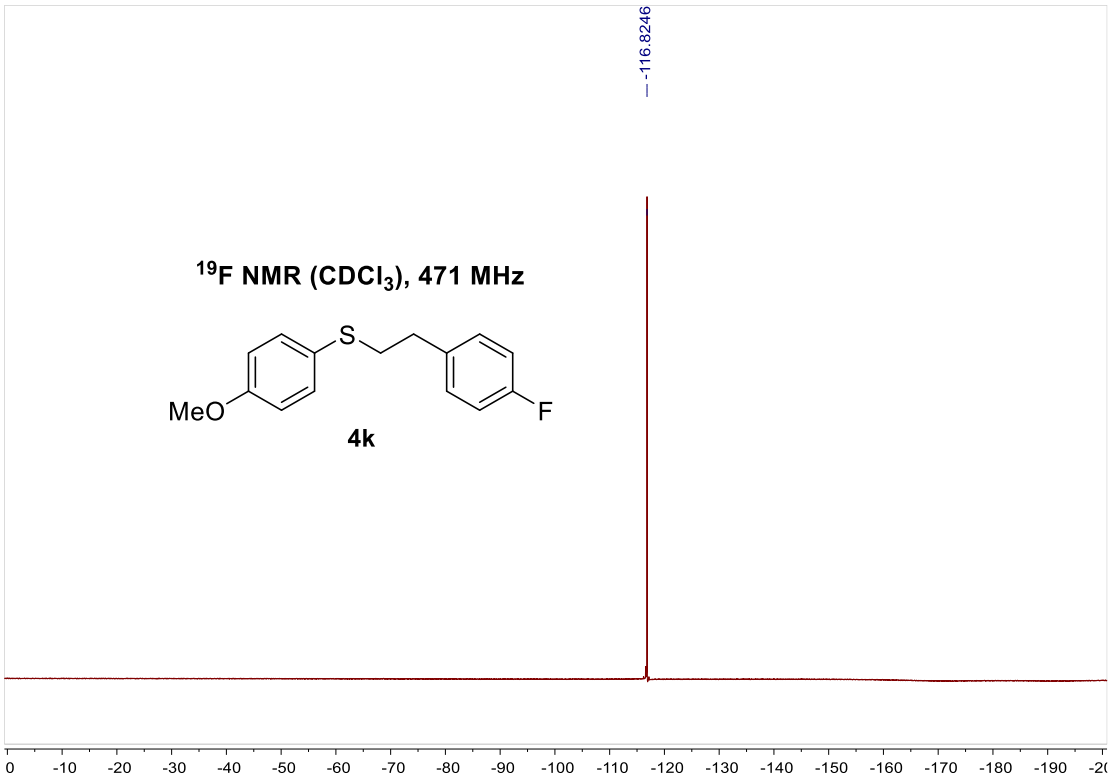
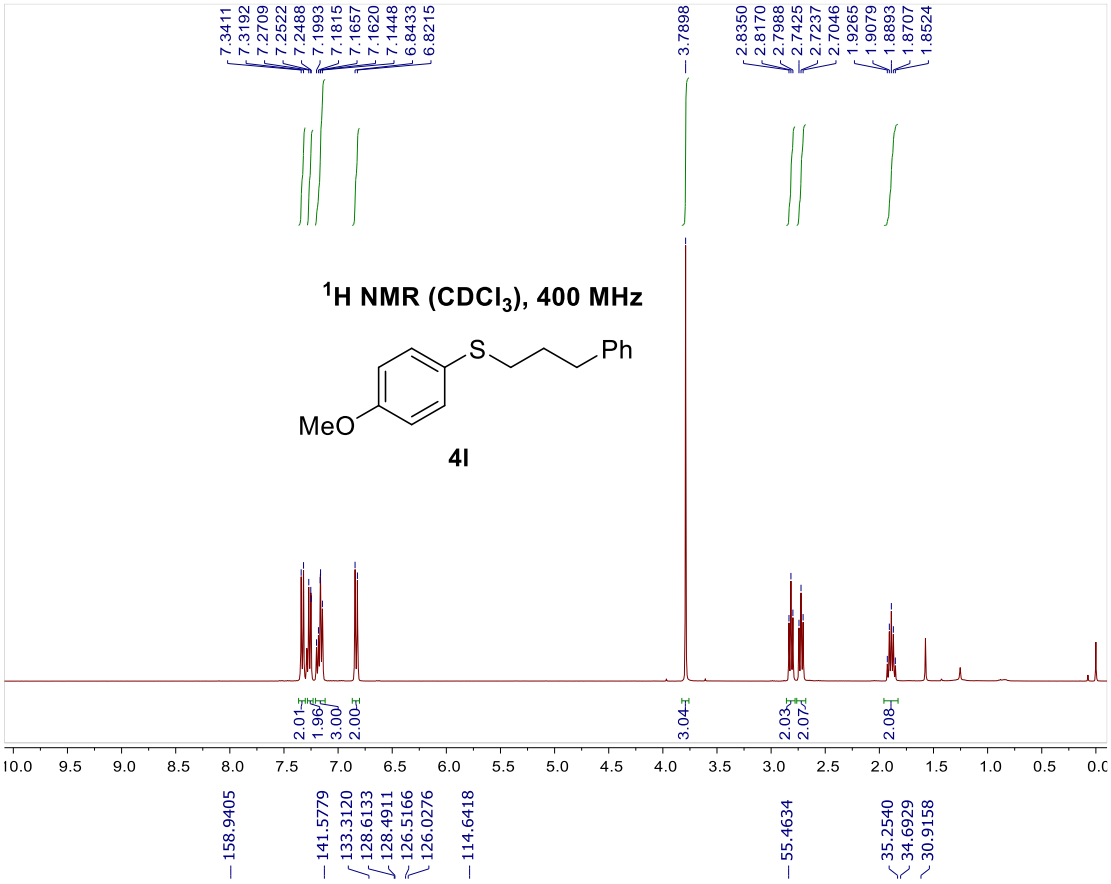
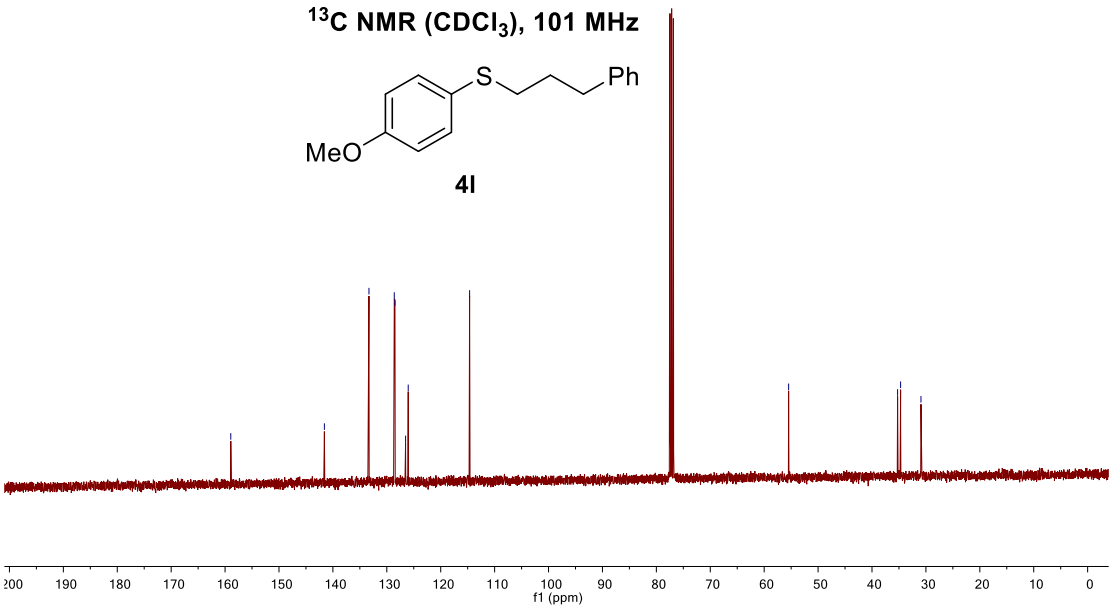
160.4155
159.1132
136.0940
136.0635
133.4819
130.0991
130.0200
126.2007
115.4204
115.2096
114.7339
55.4498
37.4906
35.1248
13C NMR (CDCl3), 101 MHz
S
MeO
F
4k


-116.8246
19F NMR (CDCl3), 471 MHz
S
MeO
F
4k



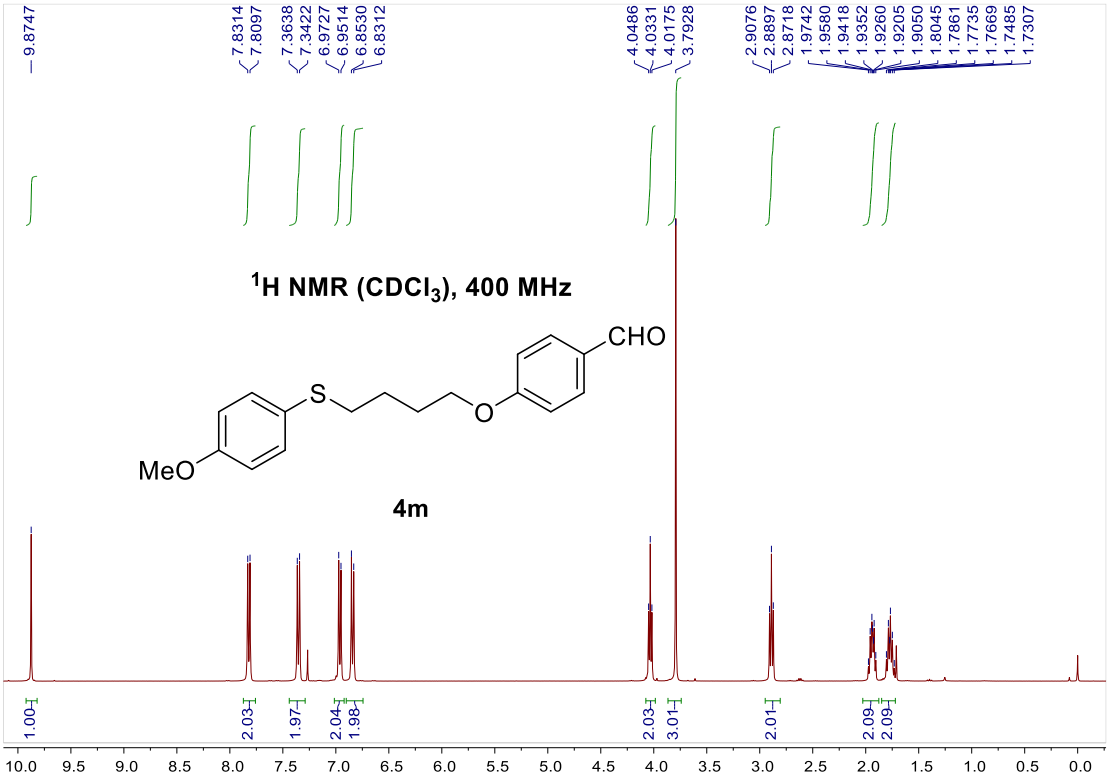
^{1}H NMR ($CDCl_3$), 400 MHz

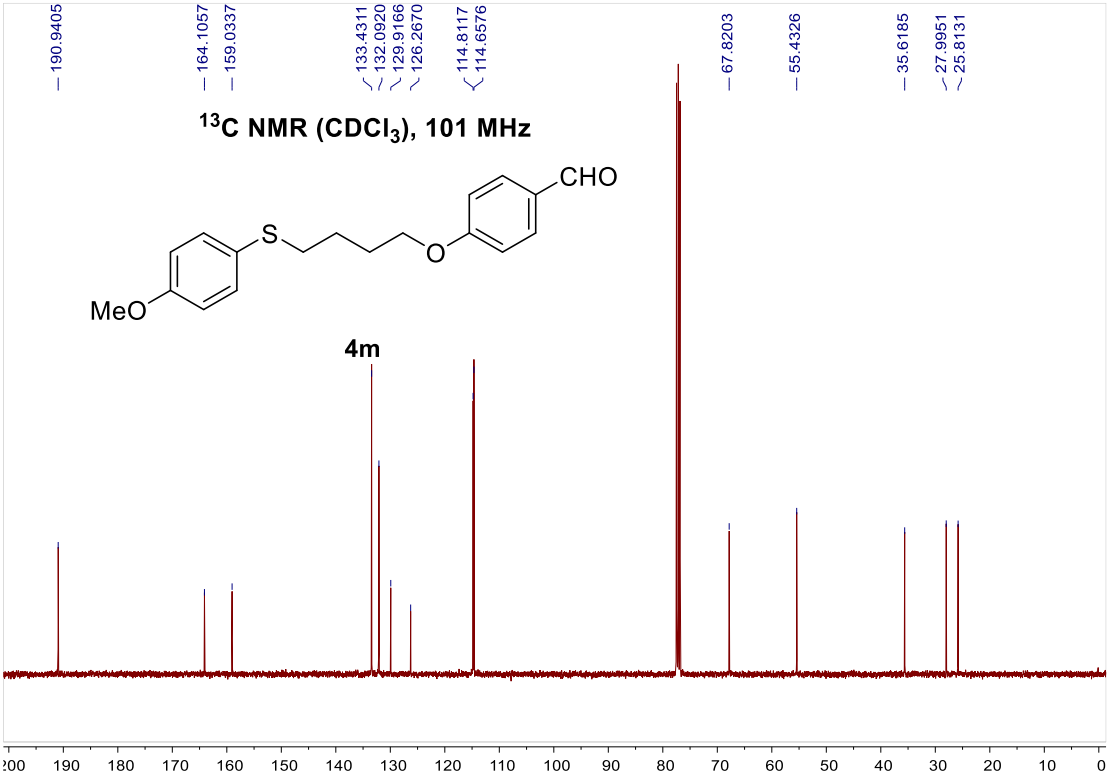
4l



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

4l


9.8747
7.8314
7.8097
7.3638
7.3422
6.9727
6.9514
6.8530
6.8312
4.0486
4.0331
4.0175
3.7928
2.9076
2.8897
2.8718
1.9742
1.9580
1.9418
1.9352
1.9260
1.9205
1.9050
1.8045
1.7861
1.7735
1.7669
1.7485
1.7307
1H NMR (CDCl3), 400 MHz
CHO
S
O
MeO
4m
1.00
2.03
1.97
2.04
1.98
2.03
3.01
2.01
2.09
2.09
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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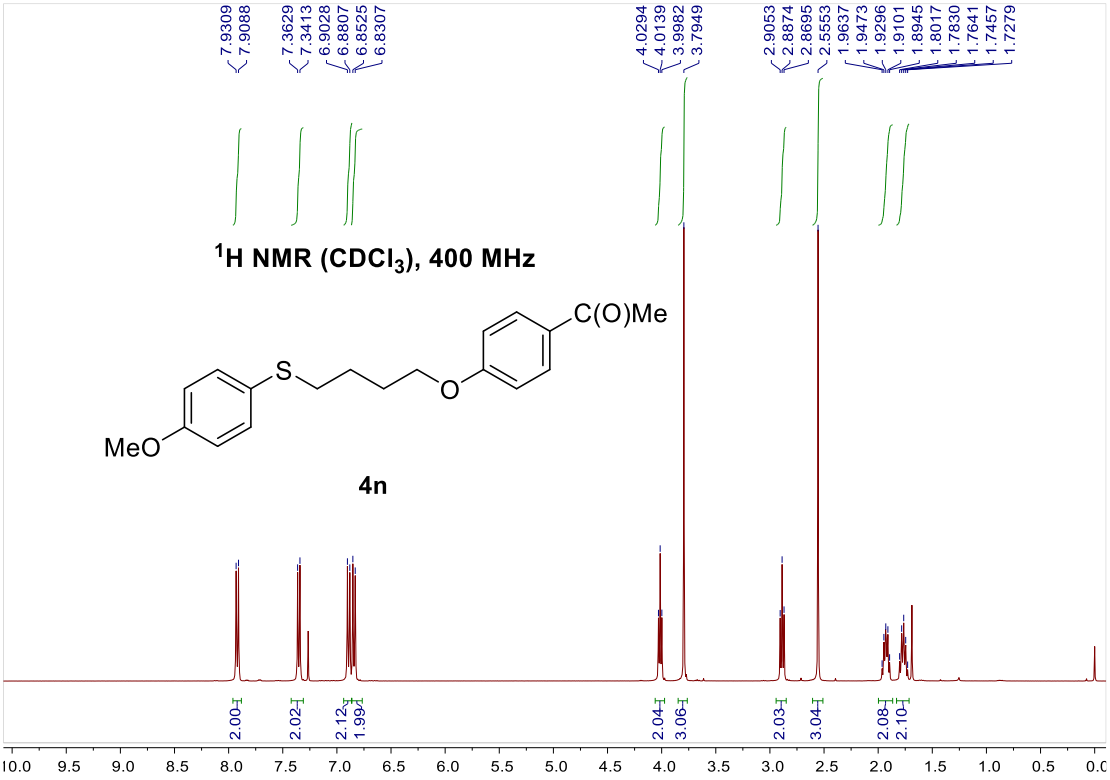
164.1057
159.0337
133.4311
132.0920
129.9166
126.2670
114.8117
114.6576
67.8203
55.4326
35.6185
27.9951
25.8131
13C NMR (CDCl3), 101 MHz
CHO
S
O
MeO
4m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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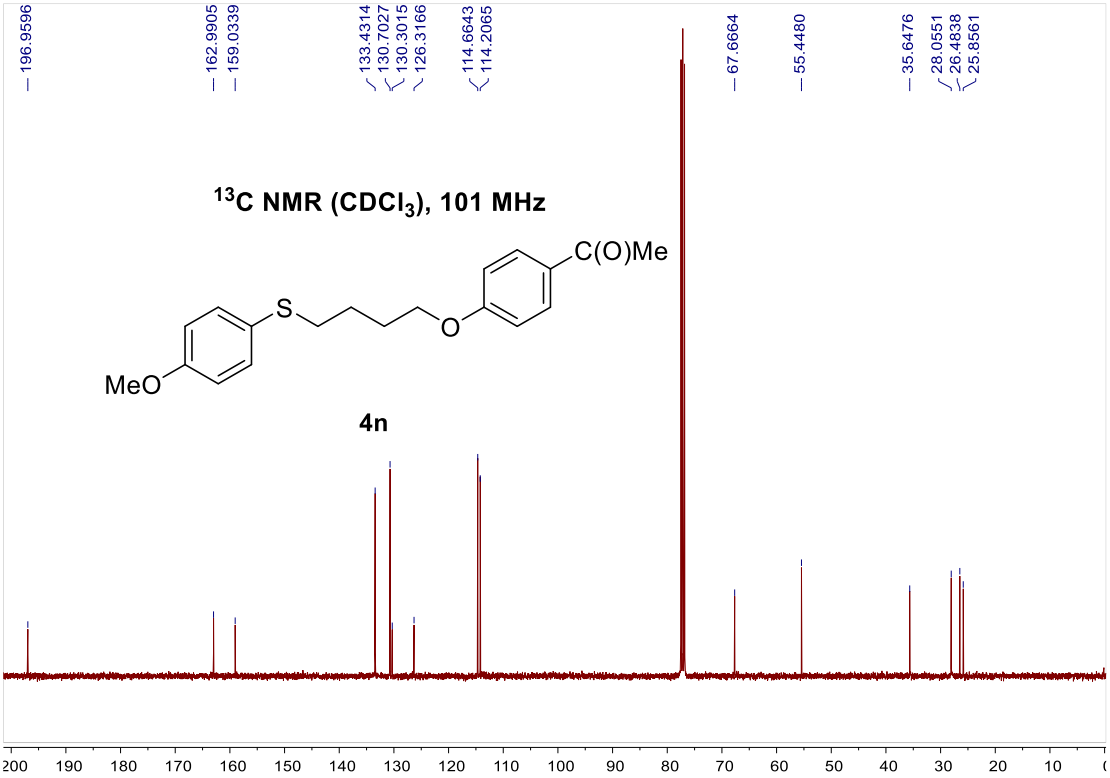
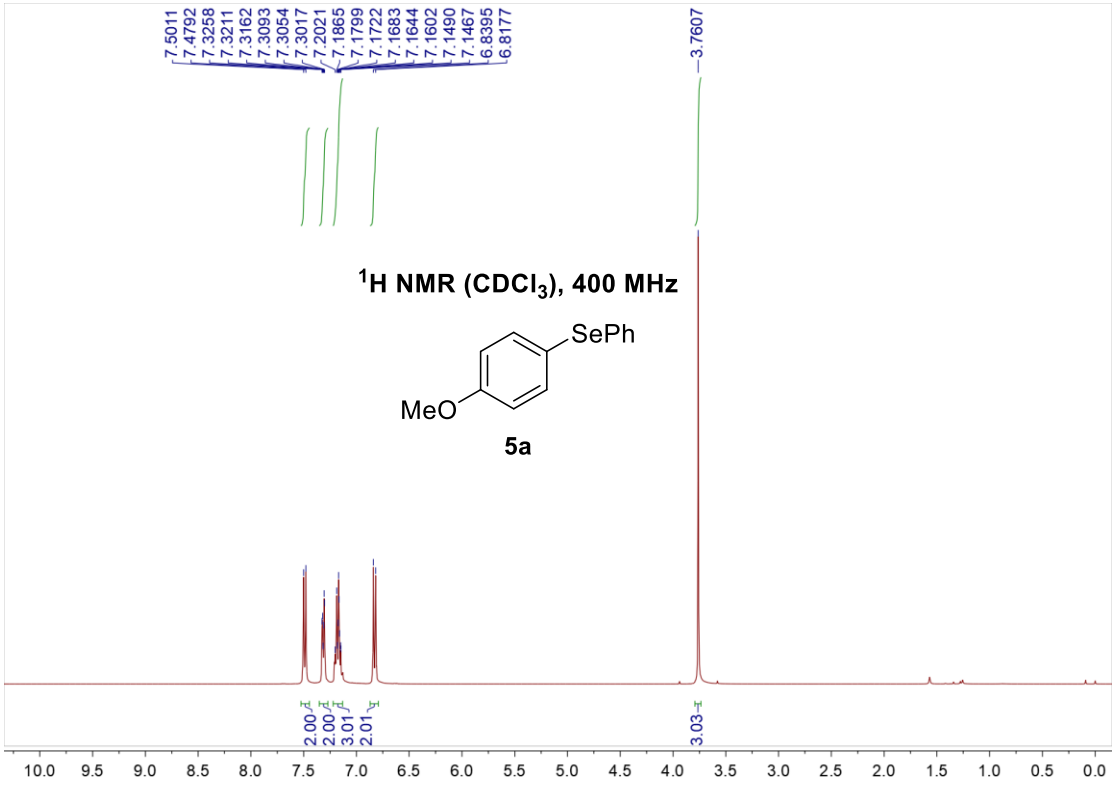
7.9088
7.3629
7.3413
6.9028
6.8807
6.8525
6.8307
4.0294
4.0139
3.9982
3.7949
2.9053
2.8874
2.8695
2.5553
1.9637
1.9473
1.9296
1.9101
1.8945
1.8017
1.7830
1.7641
1.7457
1.7279
^{1}H NMR ($CDCl_3$), 400 MHz
C(O)Me
S
O
MeO
4n
2.00
2.02
2.12
1.99
2.04
3.06
2.03
3.04
2.08
2.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 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


196.9596
162.9905
159.0339
133.4314
130.7027
130.3015
126.3166
114.6643
114.2065
67.6664
55.4480
35.6476
28.0551
26.4838
25.8561
^{13}C NMR ($CDCl_3$), 101 MHz
C(O)Me
S
O
MeO
4n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10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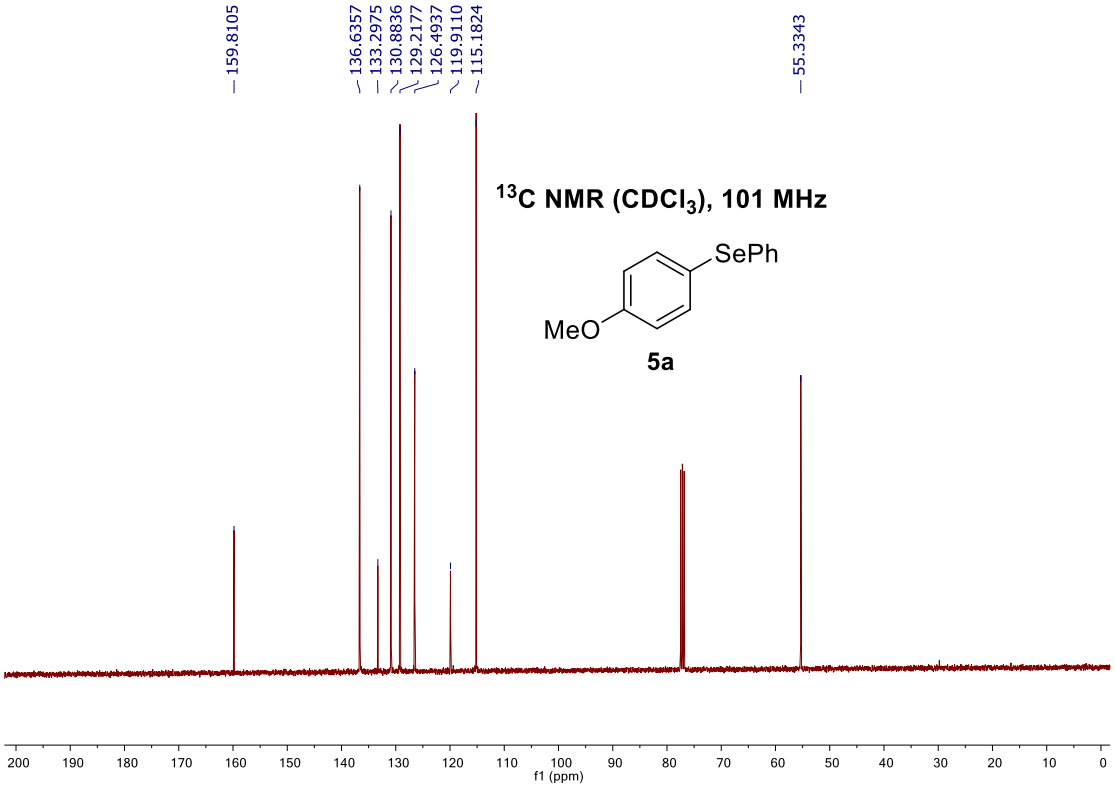
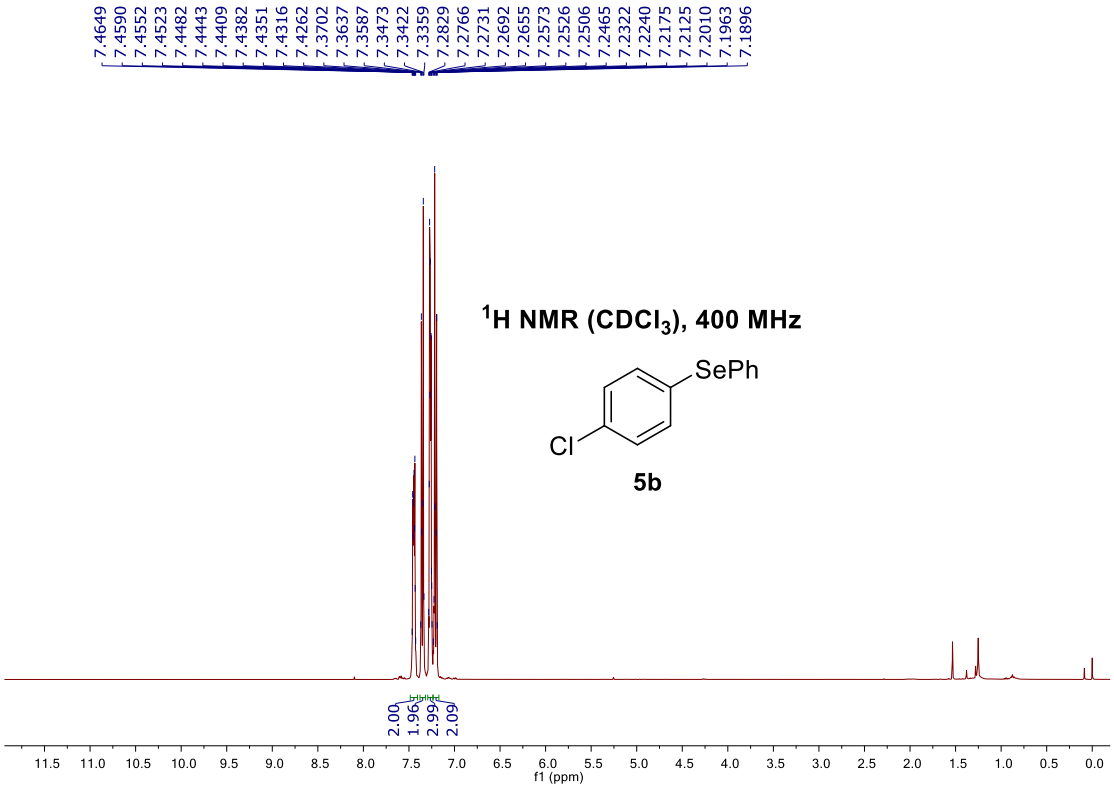
7.4792
7.3258
7.3211
7.3162
7.3093
7.3054
7.3017
7.2021
7.1865
7.1799
7.1722
7.1683
7.1644
7.1602
7.1490
7.1467
6.8395
6.8177
3.7607
^{1}H NMR (CDCl$_3$), 400 MHz
SePh
MeO
5a
2.00
2.00
3.01
2.01
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


159.8105
136.6357
133.2975
130.8836
129.2177
126.4937
119.9110
115.1824
55.3343
^{13}C NMR (CDCl$_3$), 101 MHz
SePh
MeO
5a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.4523
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7.4443
7.4409
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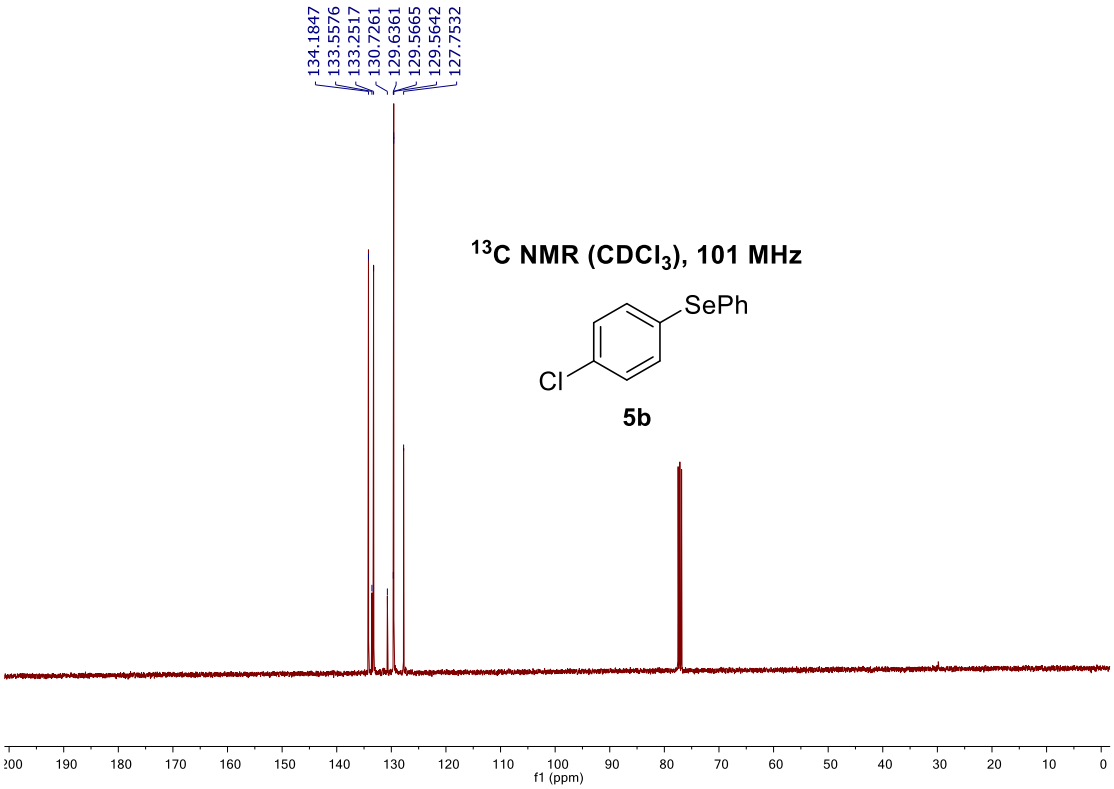
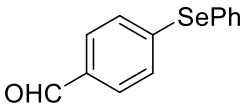
7.4351
7.4316
7.4262
7.3702
7.3637
7.3587
7.3473
7.3422
7.3359
7.2829
7.2766
7.2731
7.2692
7.2655
7.2573
7.2526
7.2506
7.2465
7.2322
7.2240
7.2175
7.2125
7.2010
7.1963
7.1896
^{1}H NMR ($CDCl_3$), 400 MHz
SePh
Cl
5b
2.00
1.96
2.99
2.09
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

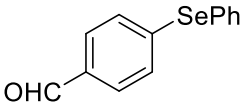

134.1847
133.5576
133.2517
130.7261
129.6361
129.5665
129.5642
127.7532
^{13}C NMR ($CDCl_3$), 101 MHz
SePh
Cl
5b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

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

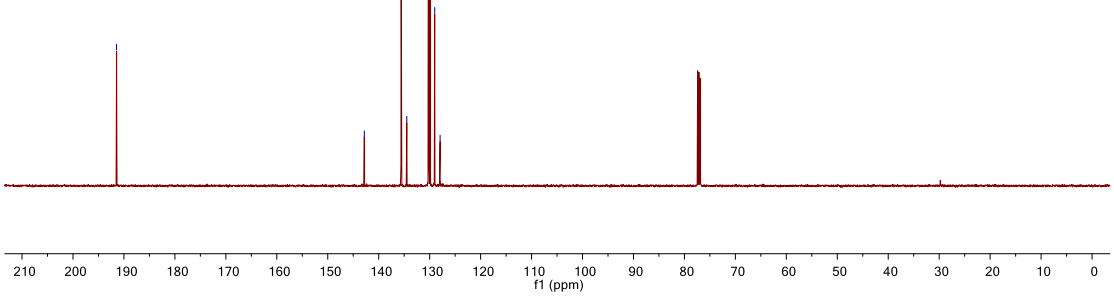


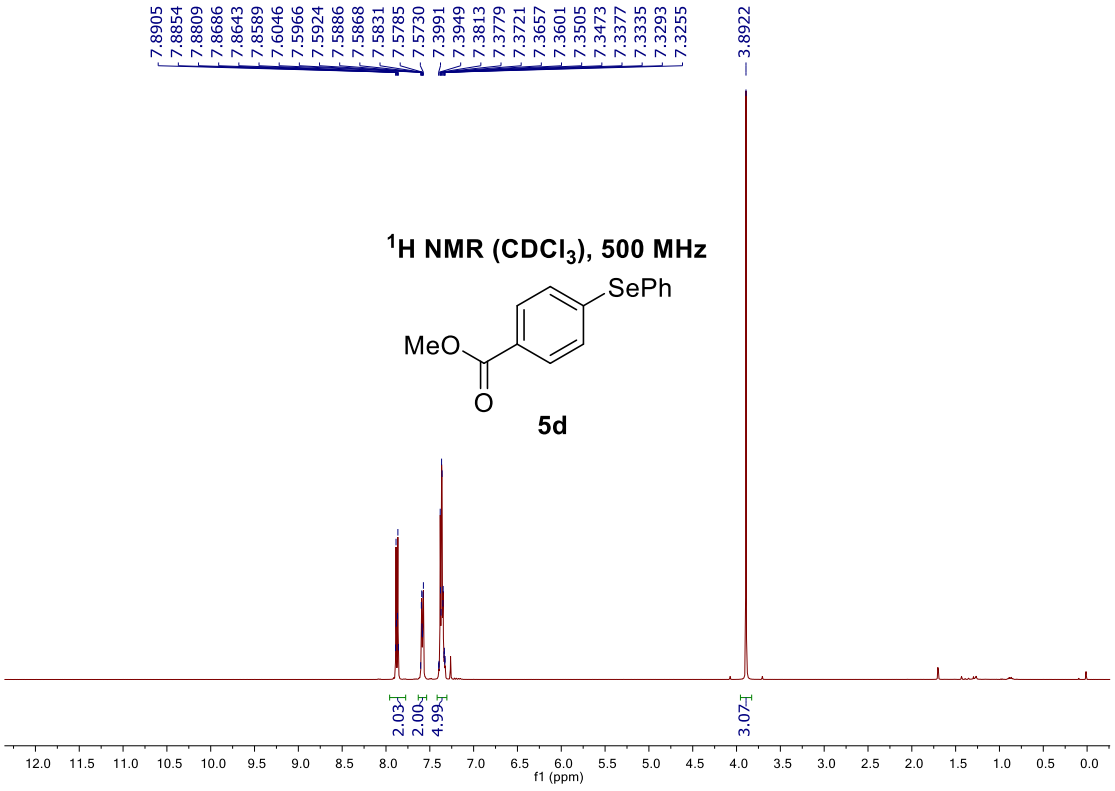
5c

^{13}C NMR ($CDCl_3$), 125 MHz



5c

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7.8686
7.8643
7.8589
7.6046
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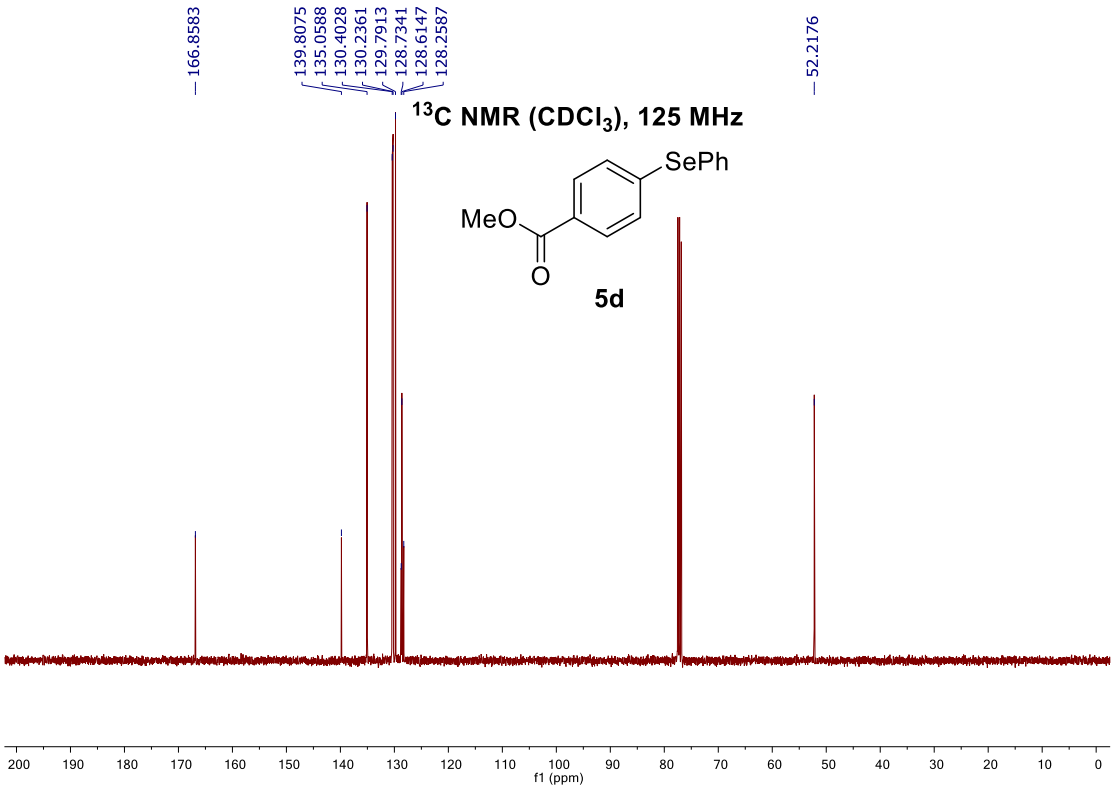
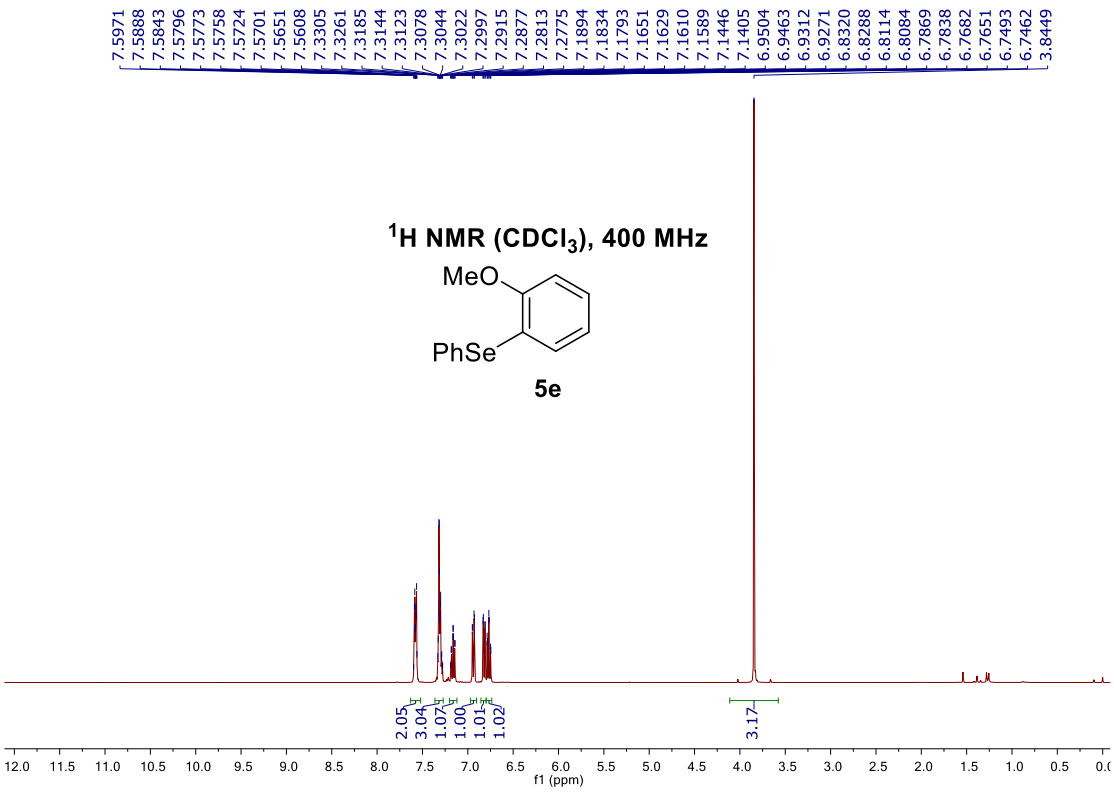
7.5924
7.5886
7.5868
7.5831
7.5785
7.5730
7.3991
7.3949
7.3813
7.3779
7.3721
7.3657
7.3601
7.3505
7.3473
7.3377
7.3335
7.3293
7.3255
3.8922
1H NMR (CDCl3), 500 MHz
SePh
MeO
O
5d
2.03
2.00
4.99
3.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.8583
139.8075
135.0588
130.4028
130.2361
129.7913
128.7341
128.6147
128.2587
52.2176
13C NMR (CDCl3), 125 MHz
SePh
MeO
O
5d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.5773
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7.5651
7.5608
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7.3144
7.3123
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7.3044
7.3022
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7.2813
7.2775
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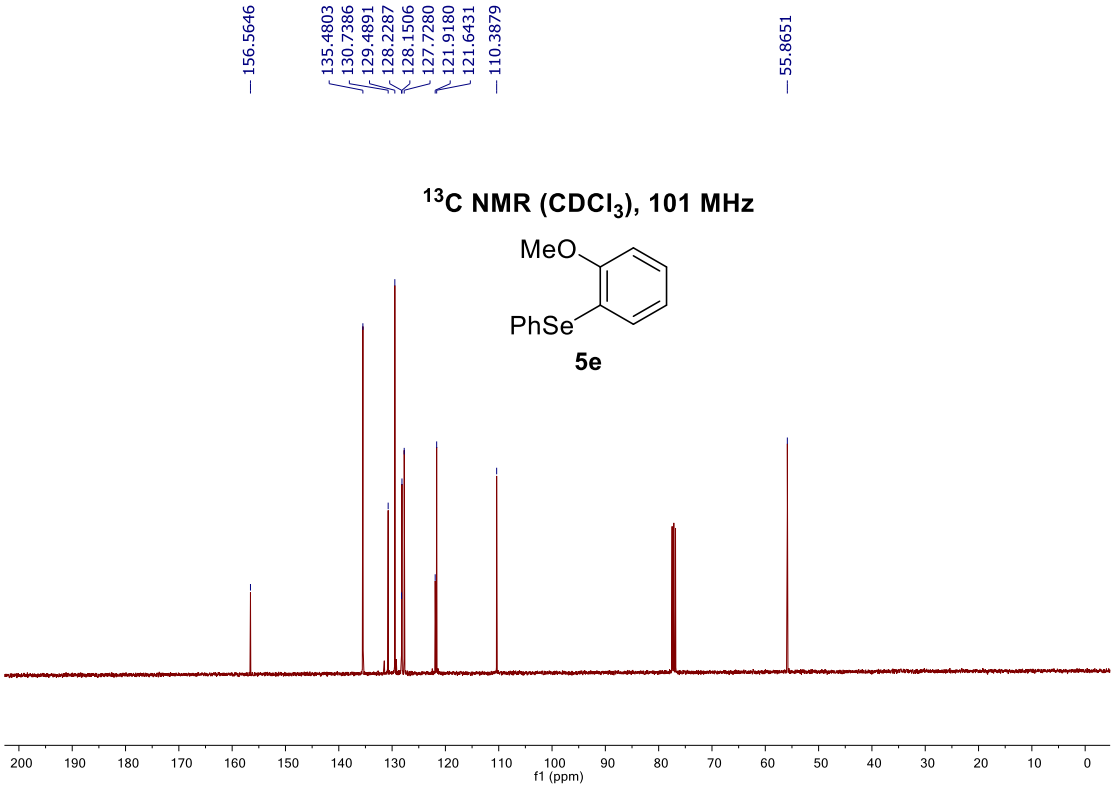
7.1834
7.1793
7.1651
7.1629
7.1610
7.1589
7.1446
7.1405
6.9504
6.9463
6.9312
6.9271
6.8320
6.8288
6.8114
6.8084
6.7869
6.7838
6.7682
6.7651
6.7493
6.7462
3.8449
1H NMR (CDCl3), 400 MHz
MeO
PhSe
5e
2.05
3.04
1.07
1.00
1.01
1.02
3.17
f1 (ppm)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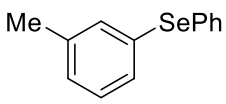
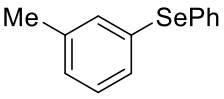
135.4803
130.7386
129.4891
128.2287
128.1506
127.7280
121.9180
121.6431
110.3879
55.8651
13C NMR (CDCl3), 101 MHz
MeO
PhSe
5e
f1 (ppm)

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



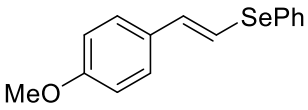
5f

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



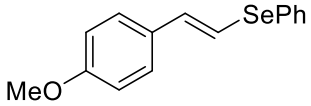
5f

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

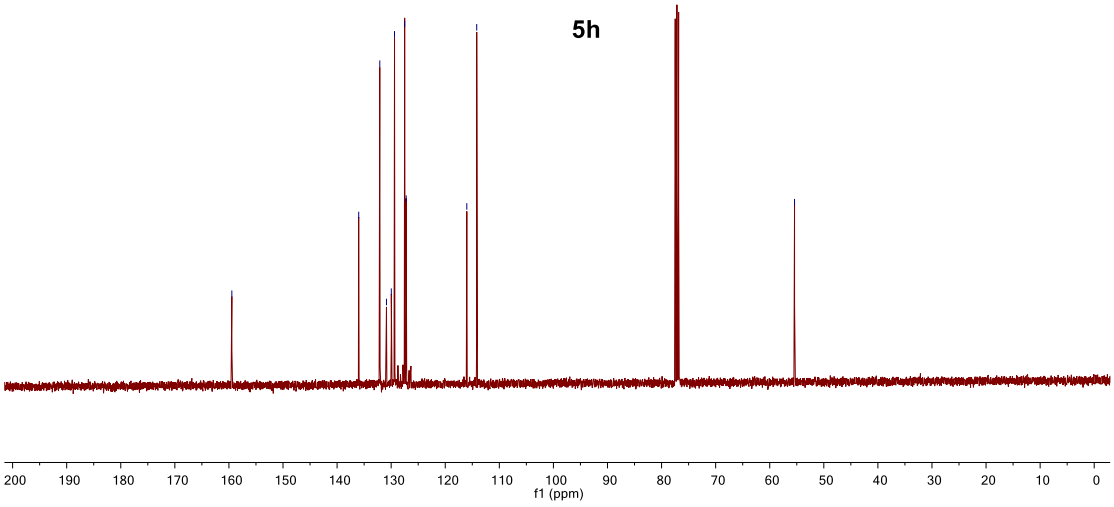


5h

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



5h

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7.4534
7.4514
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7.4435
7.4391
7.4347
7.2717
7.2687
7.2646
7.2557
7.2512
7.2477
7.2422
7.2361
7.2322
7.2201
7.2162
7.2111
7.2054
7.2013
7.1935
7.1887
7.1854
7.1818
7.1781
7.1632
7.1575
7.1432
7.1391
7.1334
7.1258
7.1220
2.8787
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2.0131
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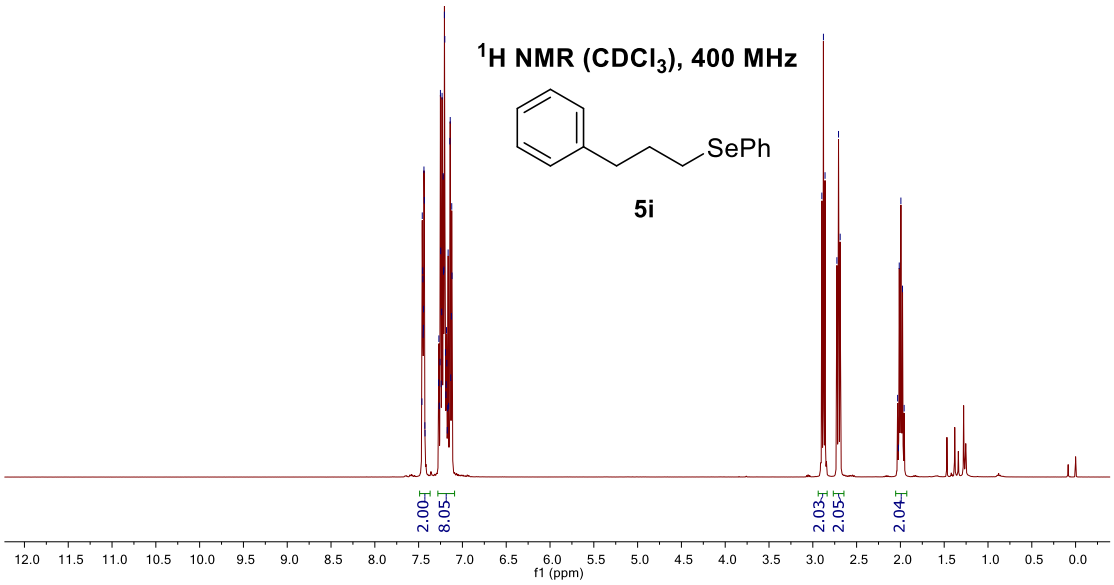
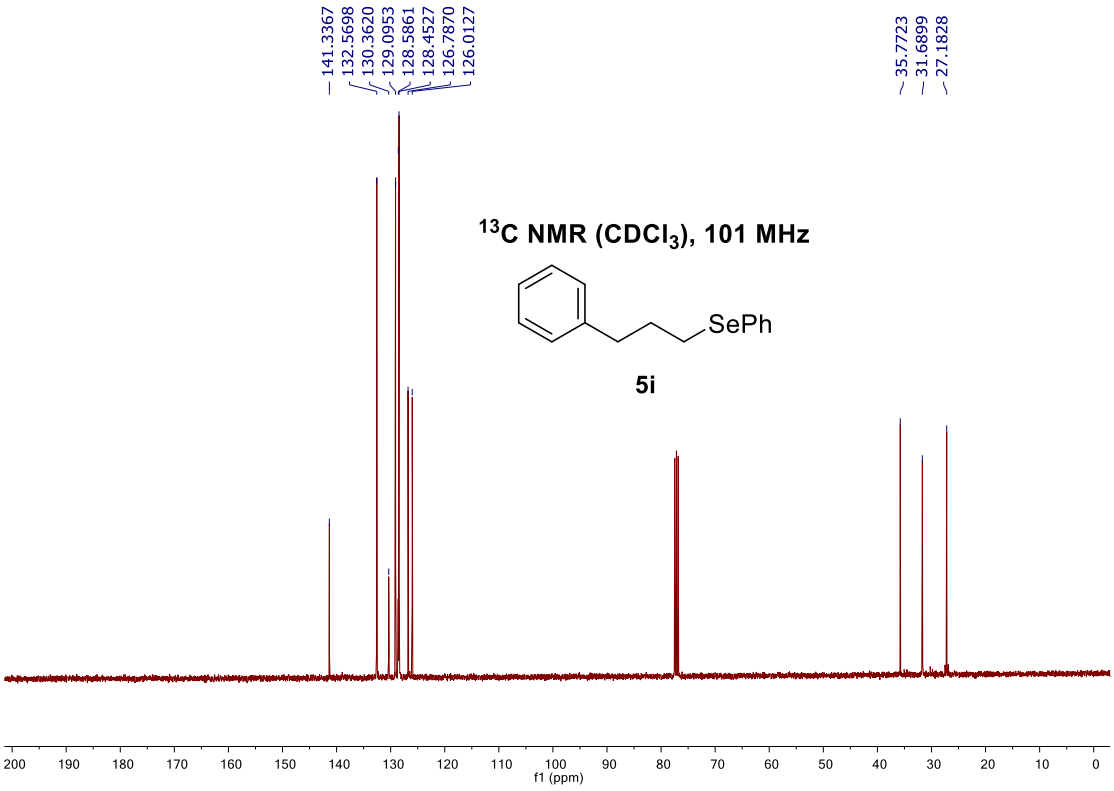
1.9760
1.9574


^{1}H NMR ($CDCl_3$), 400 MHz
SePh
5i
2.00
8.05
2.03
2.05
2.04
f1 (ppm)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129.0953
128.5861
128.4527
126.7870
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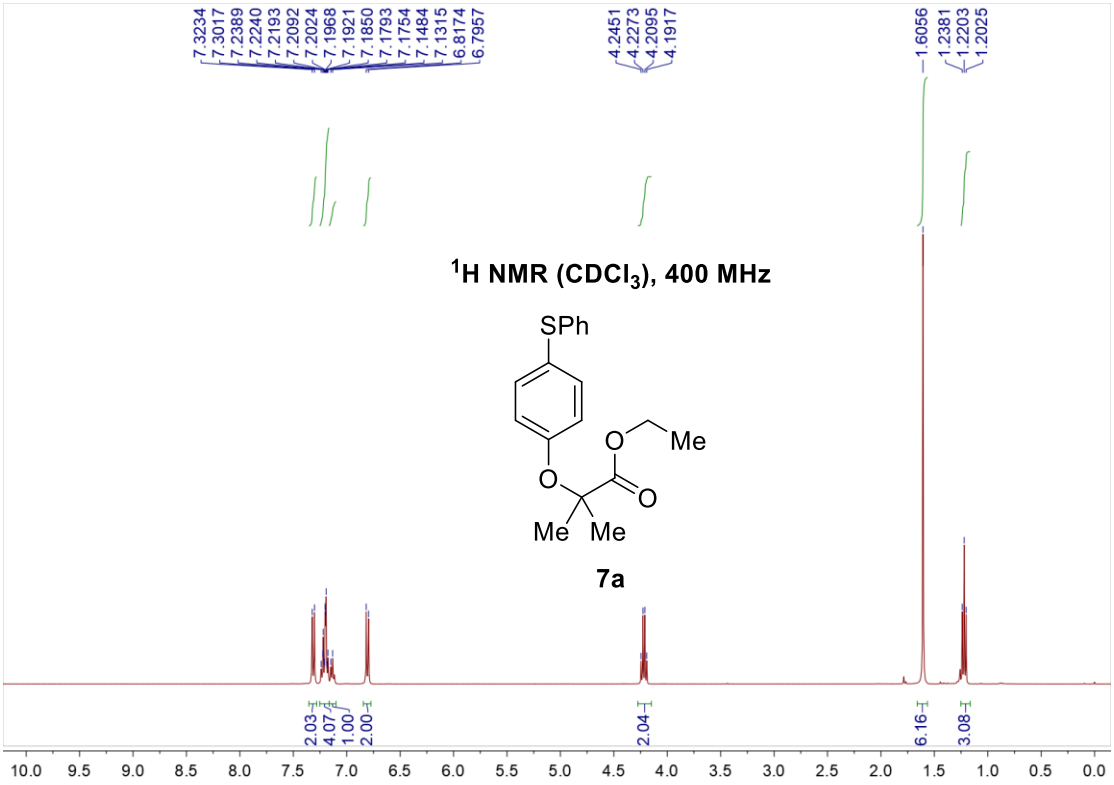
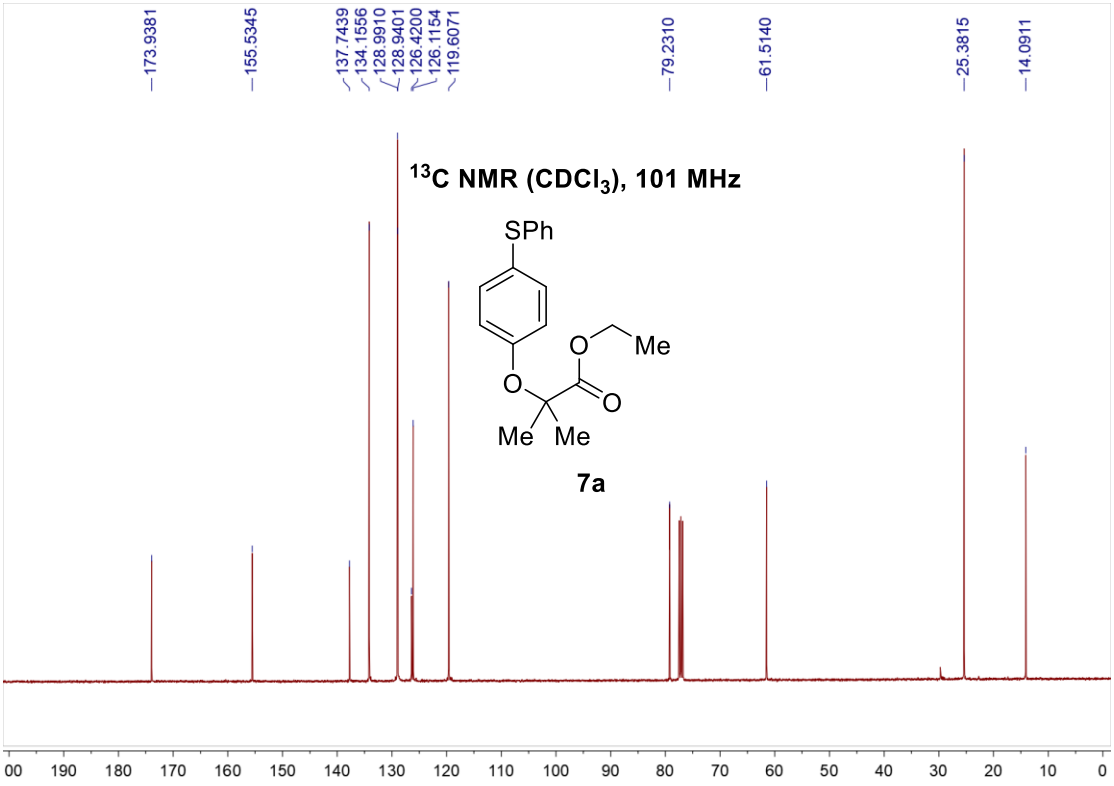
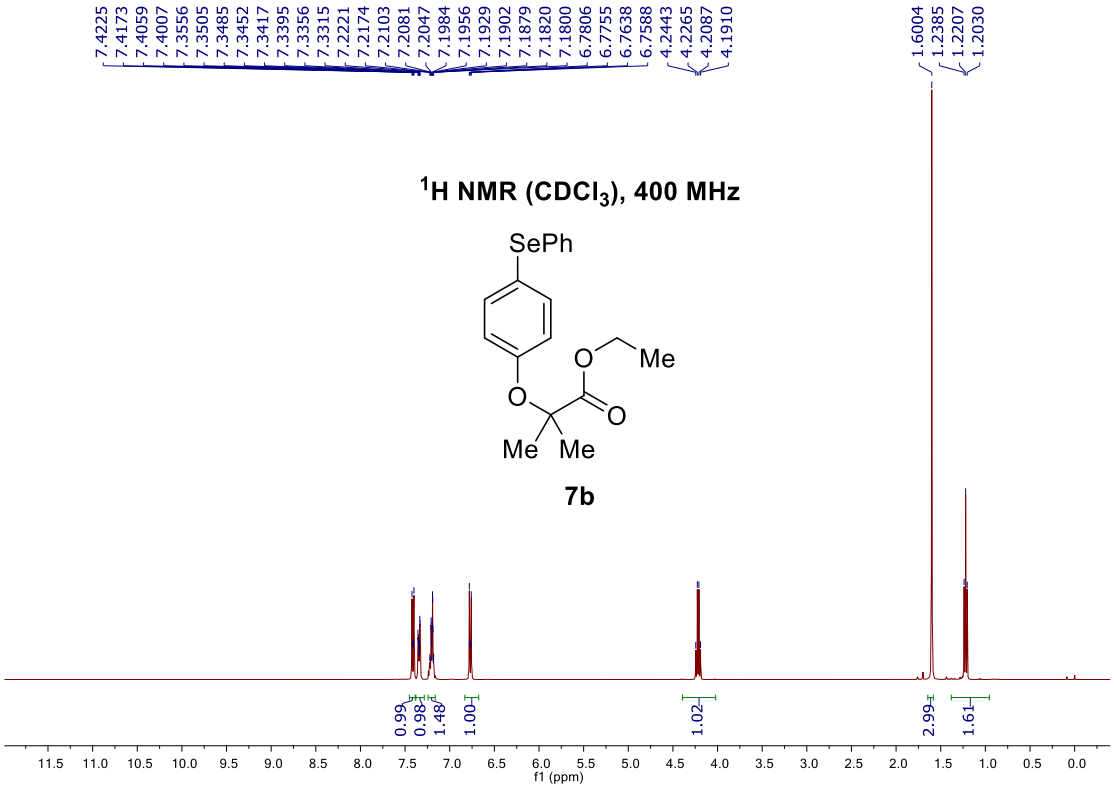
35.7723
31.6899
27.1828
^{13}C NMR ($CDCl_3$), 101 MHz
SePh
5i
f1 (ppm)

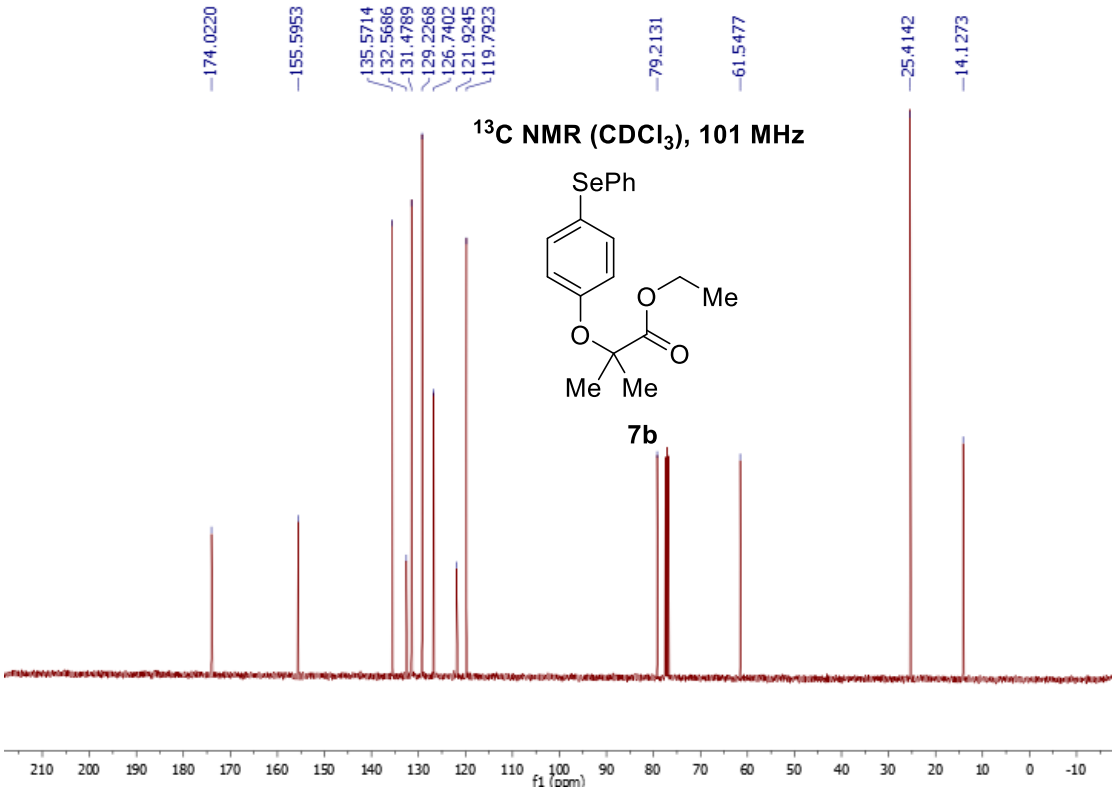

7.3234
7.3017
7.2389
7.2240
7.2193
7.2092
7.2024
7.1968
7.1921
7.1850
7.1793
7.1754
7.1484
7.1315
6.8174
6.7957
4.2451
4.2273
4.2095
4.1917
1.6056
1.2381
1.2203
1.2025
^{1}H NMR ($CDCl_3$), 400 MHz
SPh
O
Me
O
O
Me
Me
7a
2.03
4.07
1.00
2.00
2.04
6.16
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


173.9381
155.5345
137.7439
134.1556
128.9910
128.9401
126.4200
126.1154
119.6071
79.2310
61.5140
25.3815
14.0911
^{13}C NMR ($CDCl_3$), 101 MHz
SPh
O
Me
O
O
Me
Me
7a
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



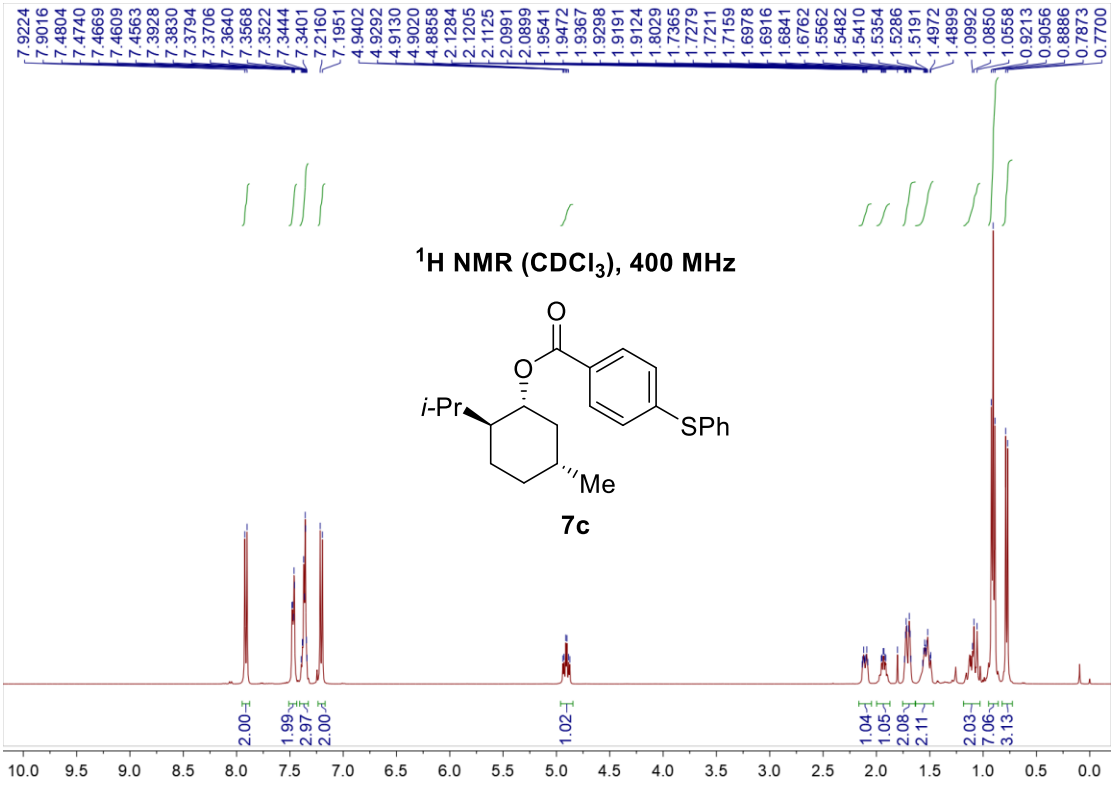
^{1}H NMR ($CDCl_3$), 400 MHz

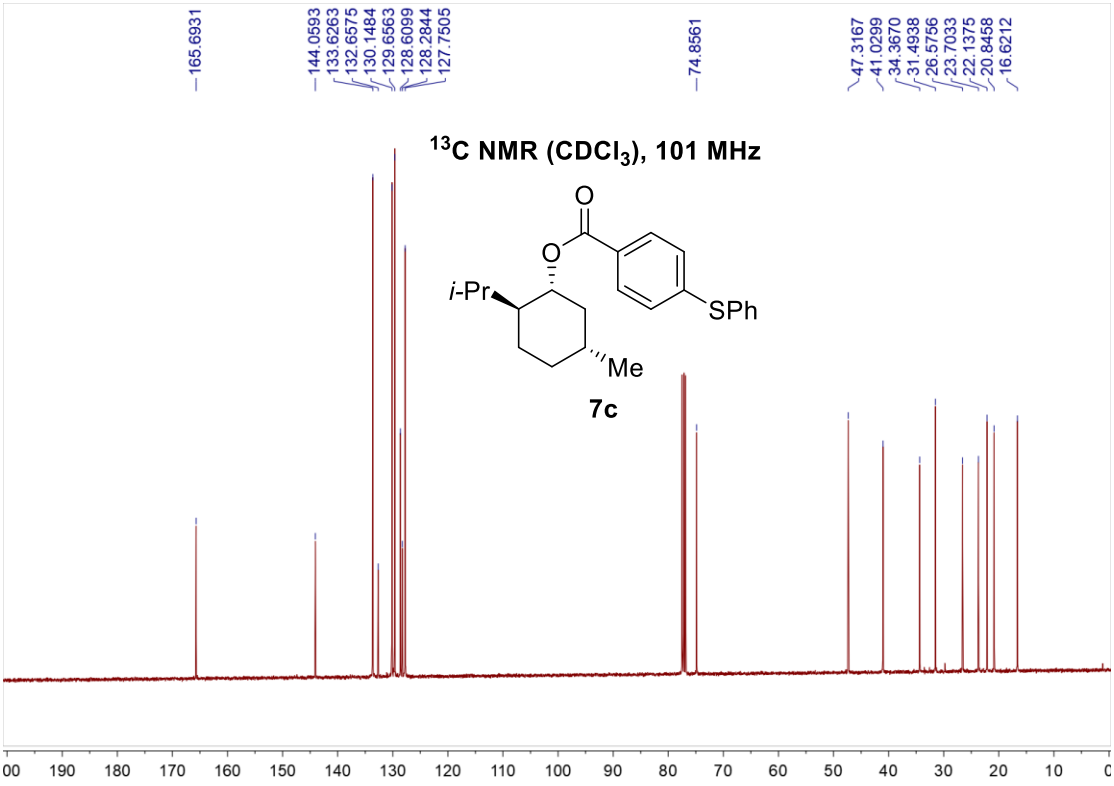
7b

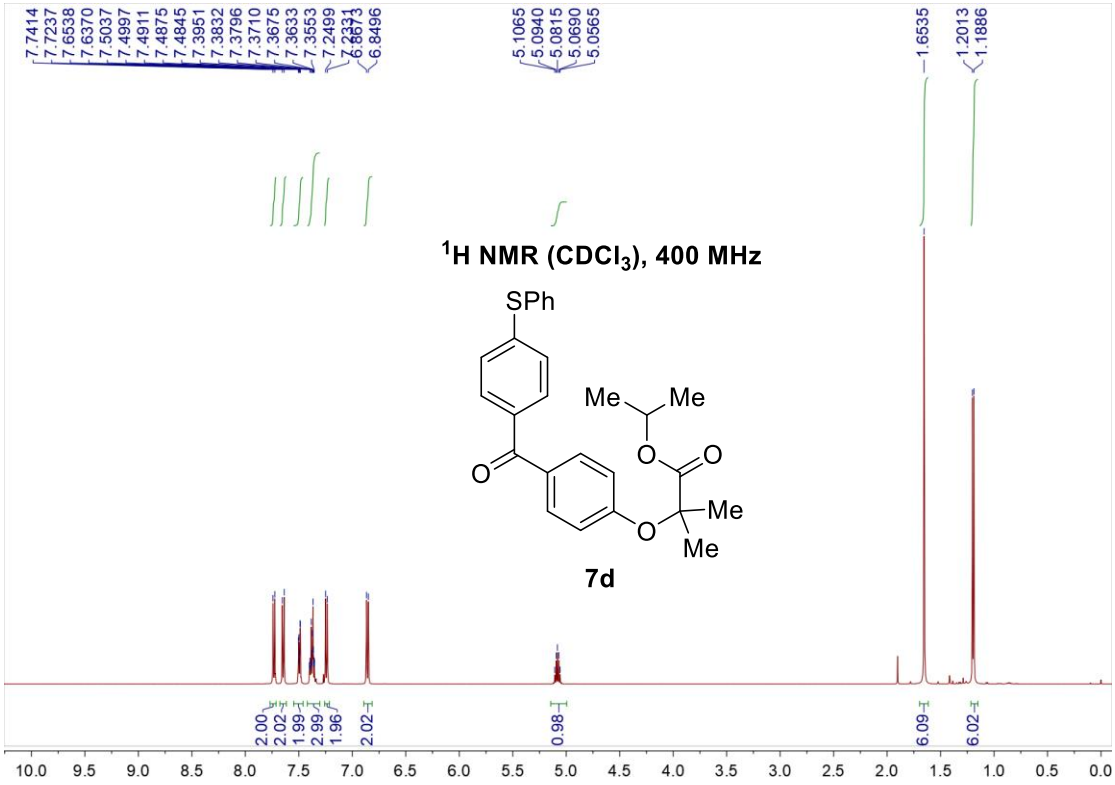


^{13}C NMR ($CDCl_3$), 101 MHz

7b

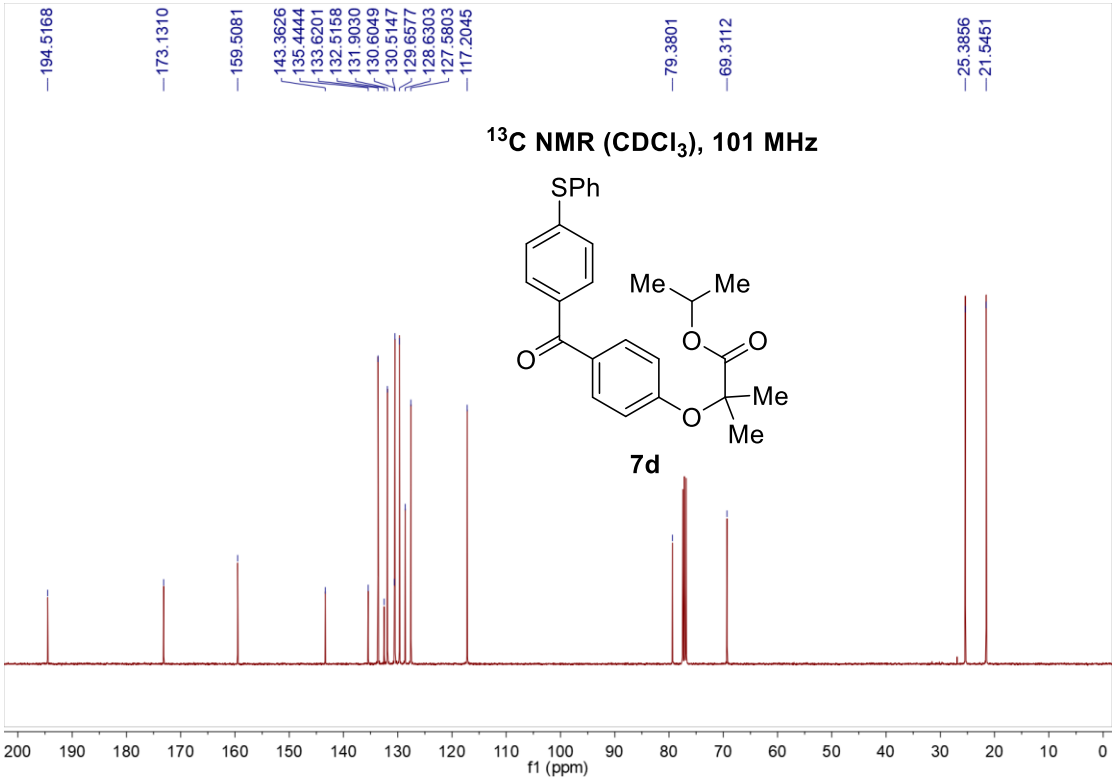

7.9224
7.9016
7.4804
7.4740
7.4669
7.4609
7.4563
7.3928
7.3830
7.3794
7.3706
7.3640
7.3568
7.3522
7.3444
7.3401
7.2160
7.1951
4.9402
4.9292
4.9130
4.9020
4.8858
2.1284
2.1205
2.1125
2.0991
2.0899
1.9541
1.9472
1.9367
1.9298
1.9191
1.9124
1.8029
1.7365
1.7279
1.7211
1.7159
1.6978
1.6916
1.6841
1.6762
1.5562
1.5482
1.5410
1.5354
1.5286
1.5191
1.4972
1.4899
1.0992
1.0850
1.0558
0.9213
0.9056
0.8886
0.7873
0.7700
^{1}H NMR (CDCl$_3$), 400 MHz
O
O
i-Pr
SPh
Me
7c
2.00
1.99
2.97
2.00
1.02
1.04
1.05
2.08
2.11
2.03
7.06
3.13
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


165.6931
144.0593
133.6263
132.6575
130.1484
129.6563
128.6099
128.2844
127.7505
74.8561
47.3167
41.0299
34.3670
31.4938
26.5756
23.7033
22.1375
20.8458
16.6212
^{13}C NMR (CDCl$_3$), 101 MHz
O
O
i-Pr
SPh
Me
7c
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



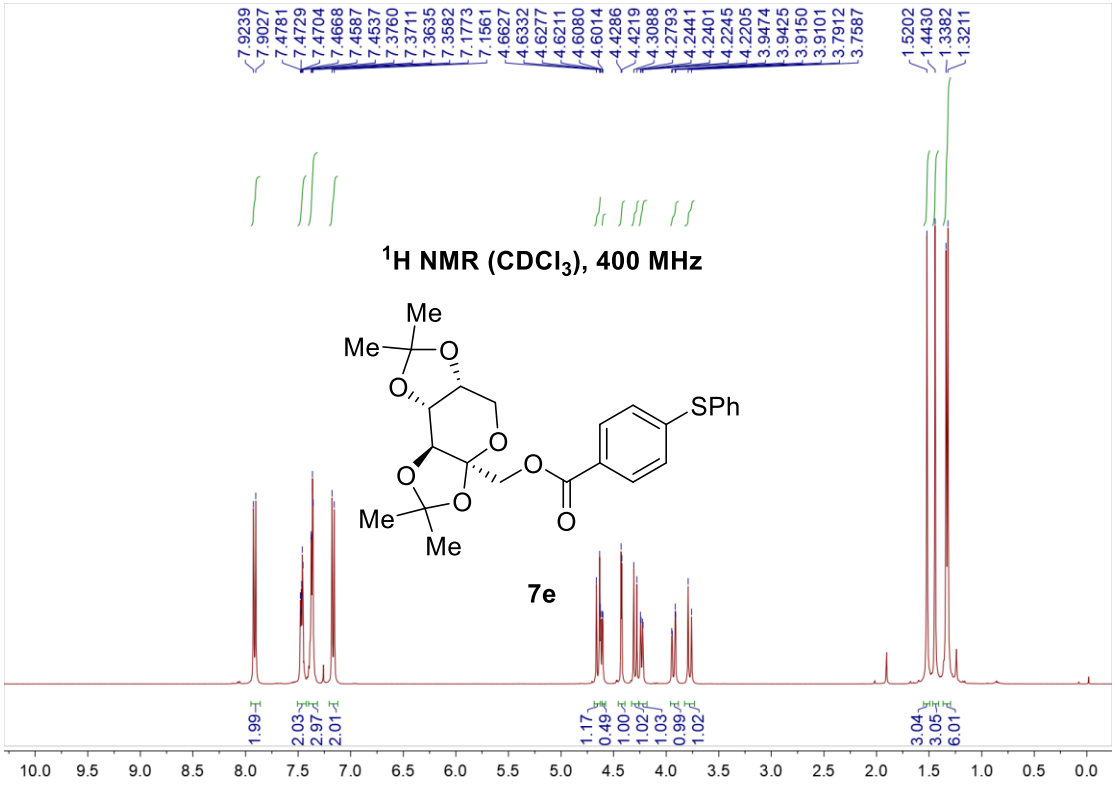
^{1}H NMR ($CDCl_3$), 400 MHz

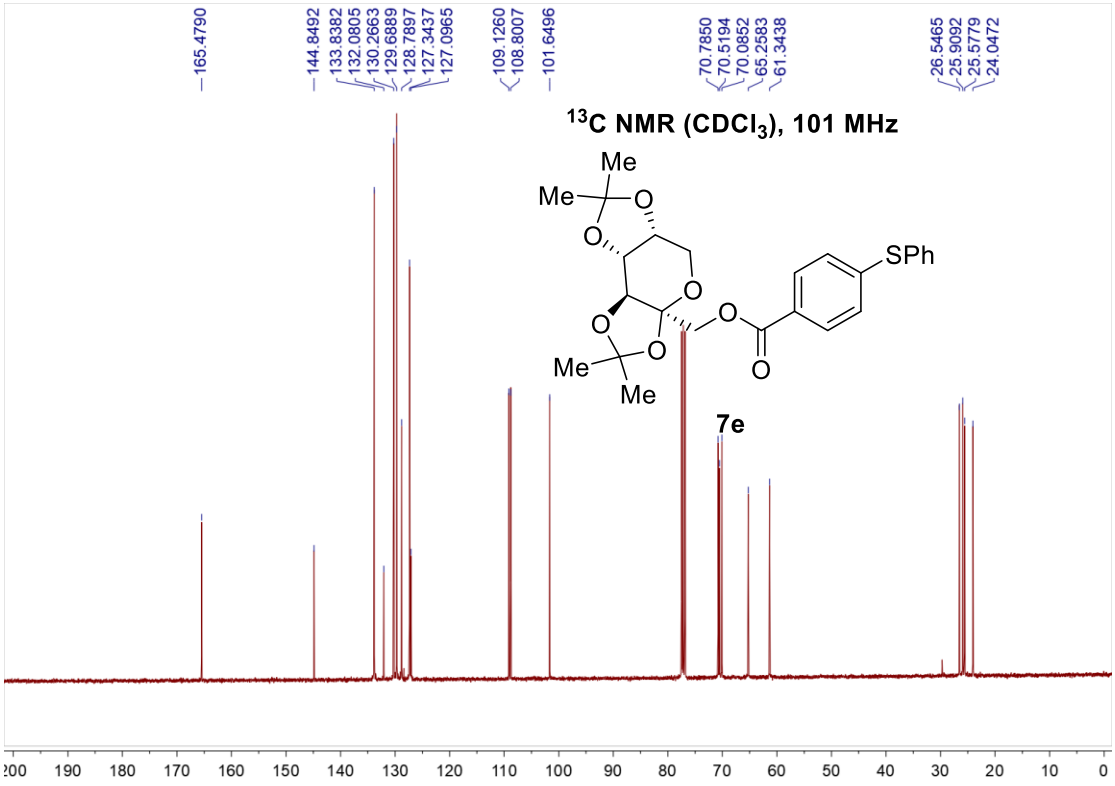
7d

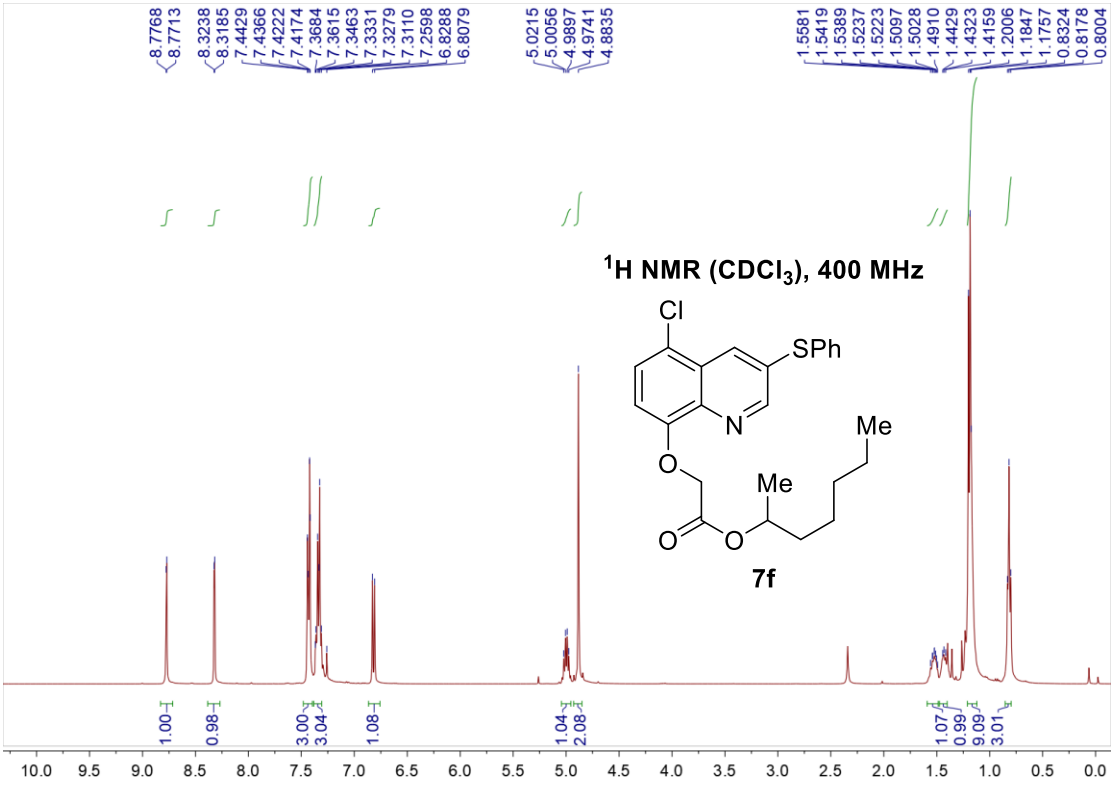


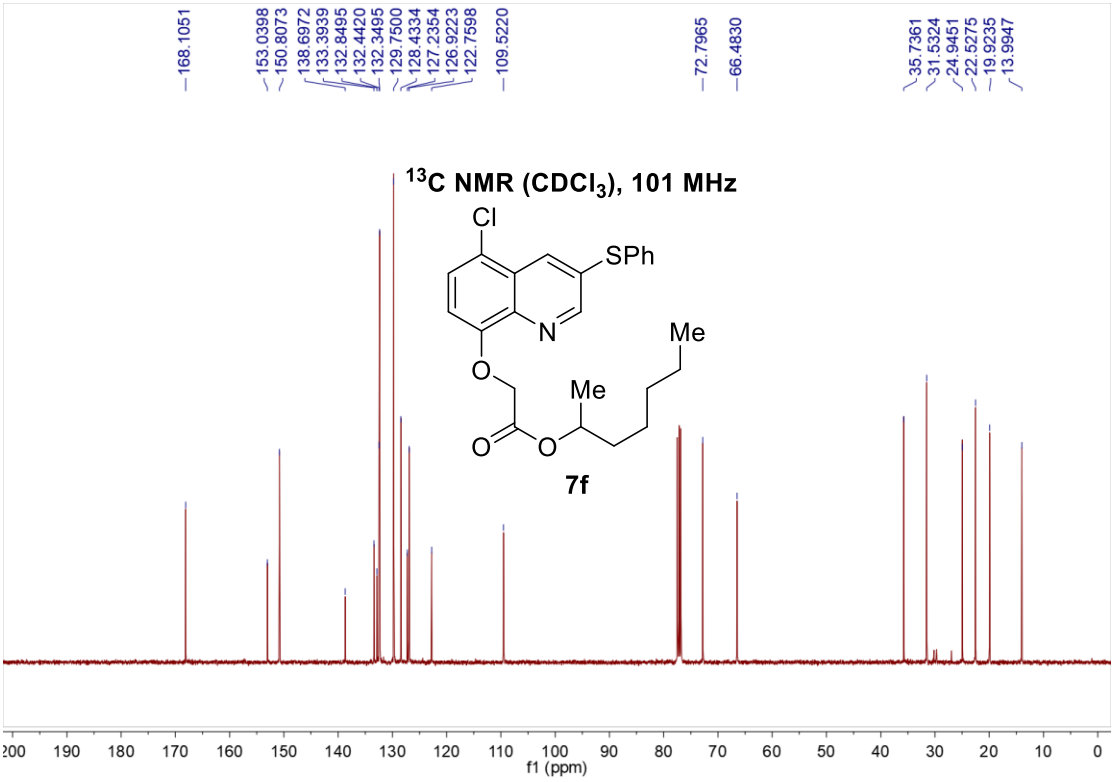
^{13}C NMR ($CDCl_3$), 101 MHz

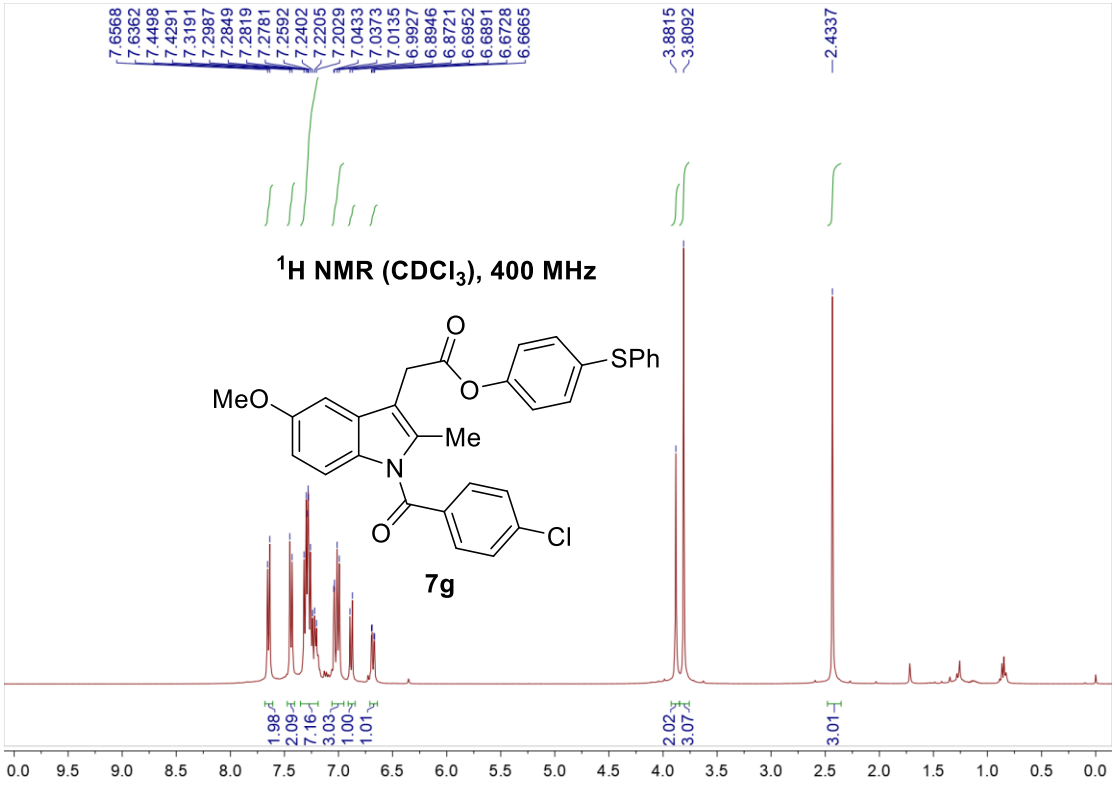
7d

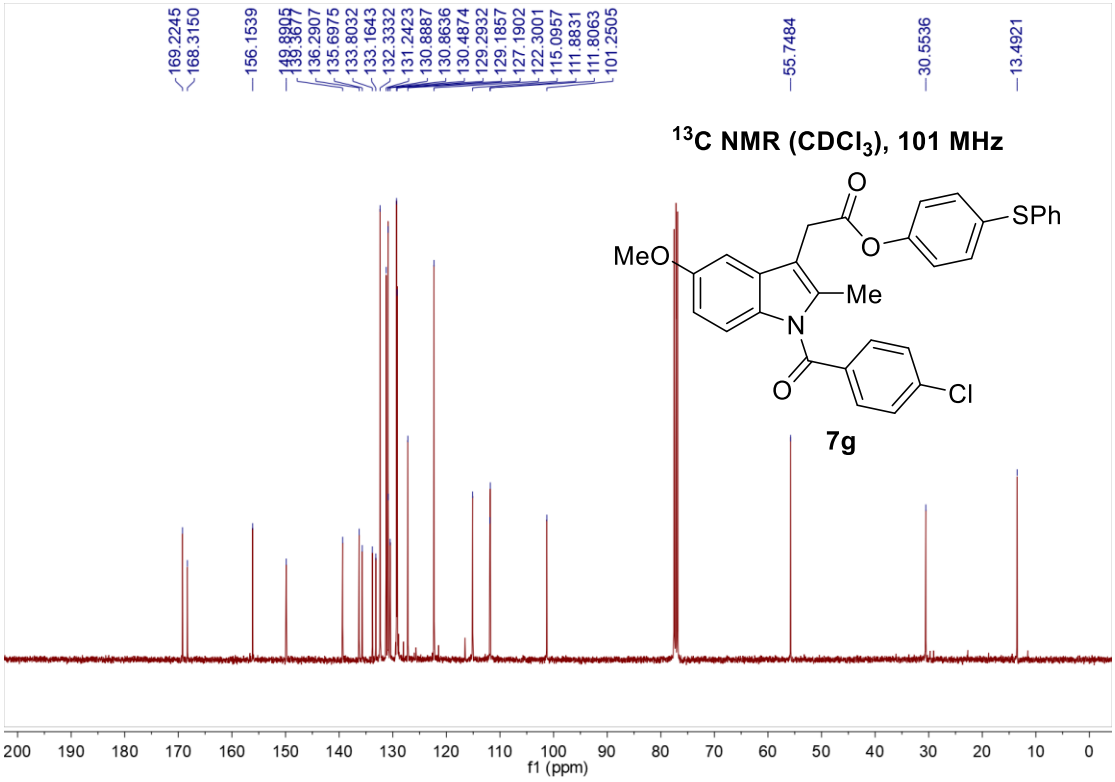

7.9239
7.9027
7.4781
7.4729
7.4704
7.4668
7.4587
7.4537
7.3760
7.3711
7.3635
7.3582
7.1773
7.1561
4.6627
4.6332
4.6277
4.6211
4.6080
4.6014
4.4286
4.4219
4.3088
4.2793
4.2441
4.2401
4.2245
4.2205
3.9474
3.9425
3.9150
3.9101
3.7912
3.7587
1.5202
1.4430
1.3382
1.3211
1H NMR (CDCl3), 400 MHz
Me
Me
O
O
O
O
O
O
O
SPh
Me
Me
7e
1.99
2.03
2.97
2.01
1.17
0.49
1.00
1.02
1.03
0.99
1.02
3.04
3.05
6.01
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

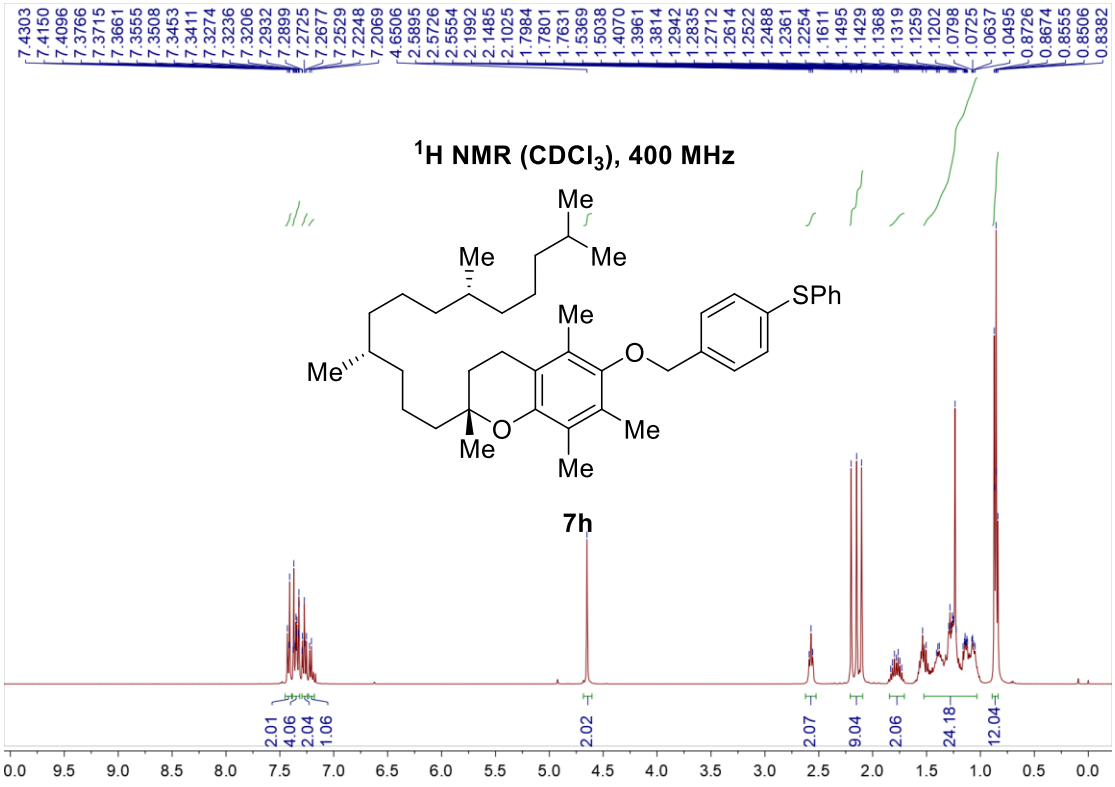

165.4790
144.8492
133.8382
132.0805
130.2663
129.6889
128.7897
127.3437
127.0965
109.1260
108.8007
101.6496
70.7850
70.5194
70.0852
65.2583
61.3438
26.5465
25.9092
25.5779
24.0472
13C NMR (CDCl3), 101 MHz
Me
Me
O
O
O
O
O
O
O
SPh
Me
Me
7e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

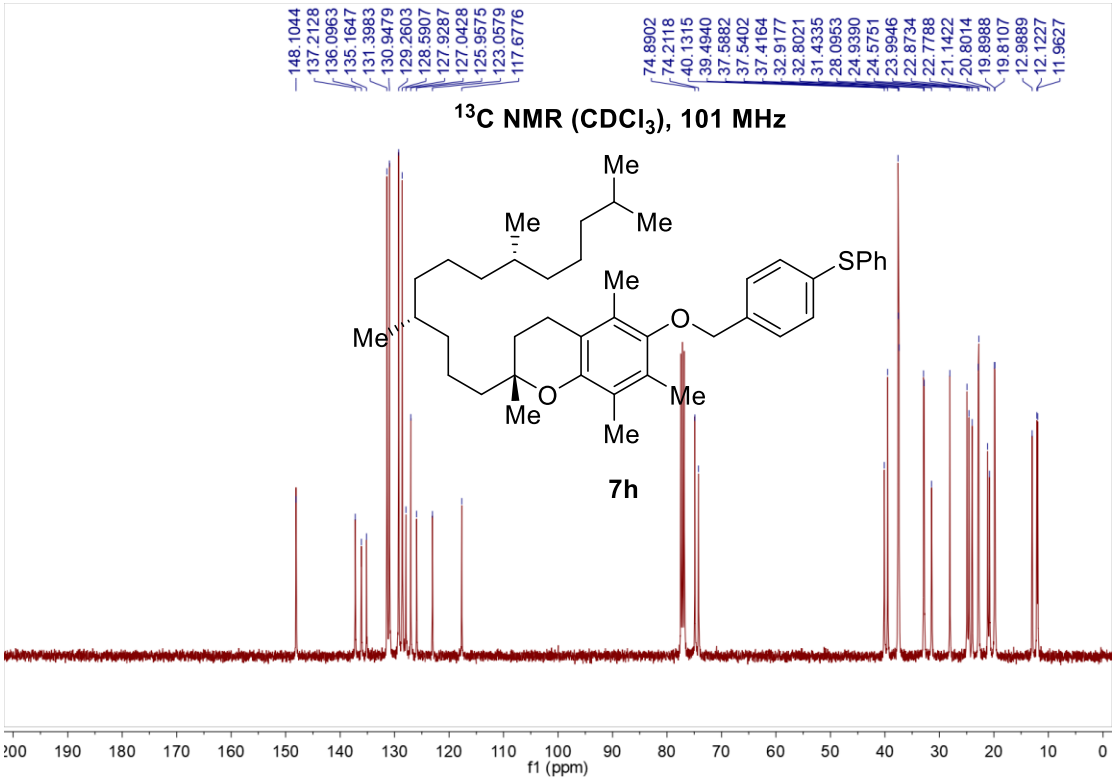

8.7768
8.7713
8.3238
8.3185
7.4429
7.4366
7.4222
7.4174
7.3684
7.3615
7.3463
7.3331
7.3279
7.3110
7.2598
6.8288
6.8079
5.0215
5.0056
4.9897
4.9741
4.8835
1.5581
1.5419
1.5389
1.5237
1.5223
1.5097
1.5028
1.4910
1.4429
1.4323
1.4159
1.2006
1.1847
1.1757
0.8324
0.8178
0.8004
1H NMR (CDCl3), 400 MHz
Cl
SPh
N
Me
O
Me
O
O
7f
1.00
0.98
3.00
3.04
1.08
1.04
2.08
1.07
0.99
9.09
3.01
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

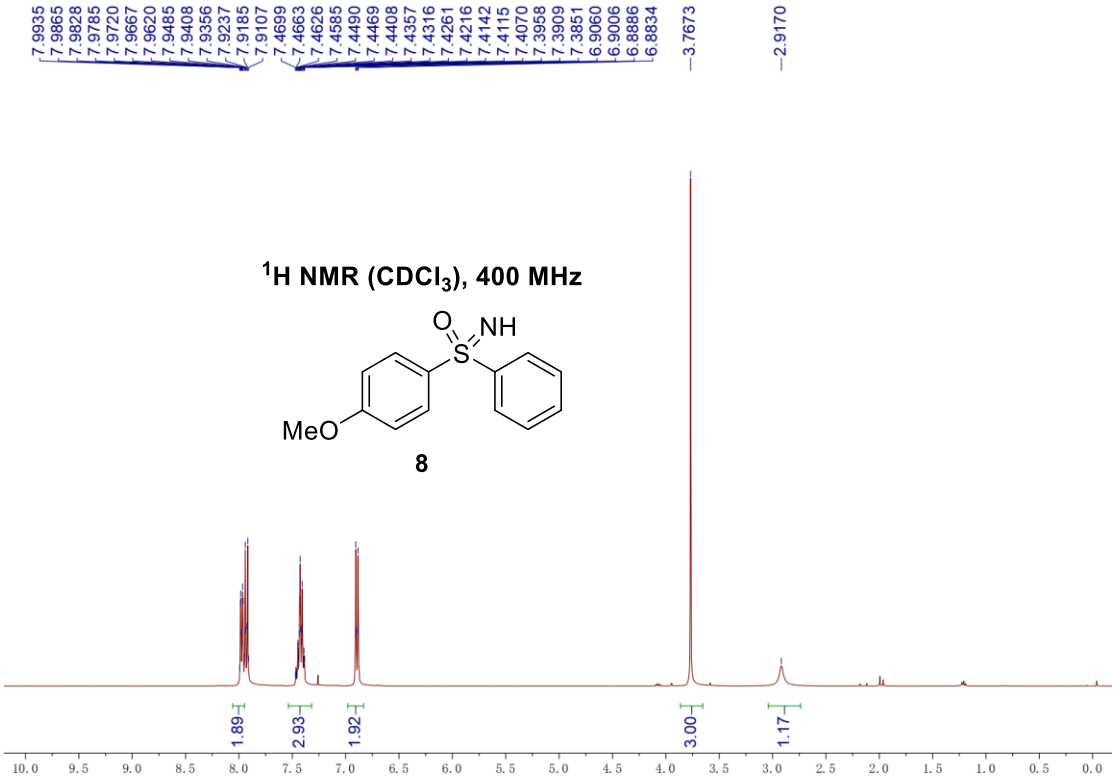

168.1051
153.0398
150.8073
138.6972
133.3939
132.8495
132.4420
132.3495
129.7500
128.4334
127.2354
126.9223
122.7598
109.5220
72.7965
66.4830
35.7361
31.5324
24.9451
22.5275
19.9235
13.9947
13C NMR (CDCl3), 101 MHz
Cl
SPh
N
Me
O
Me
O
O
7f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

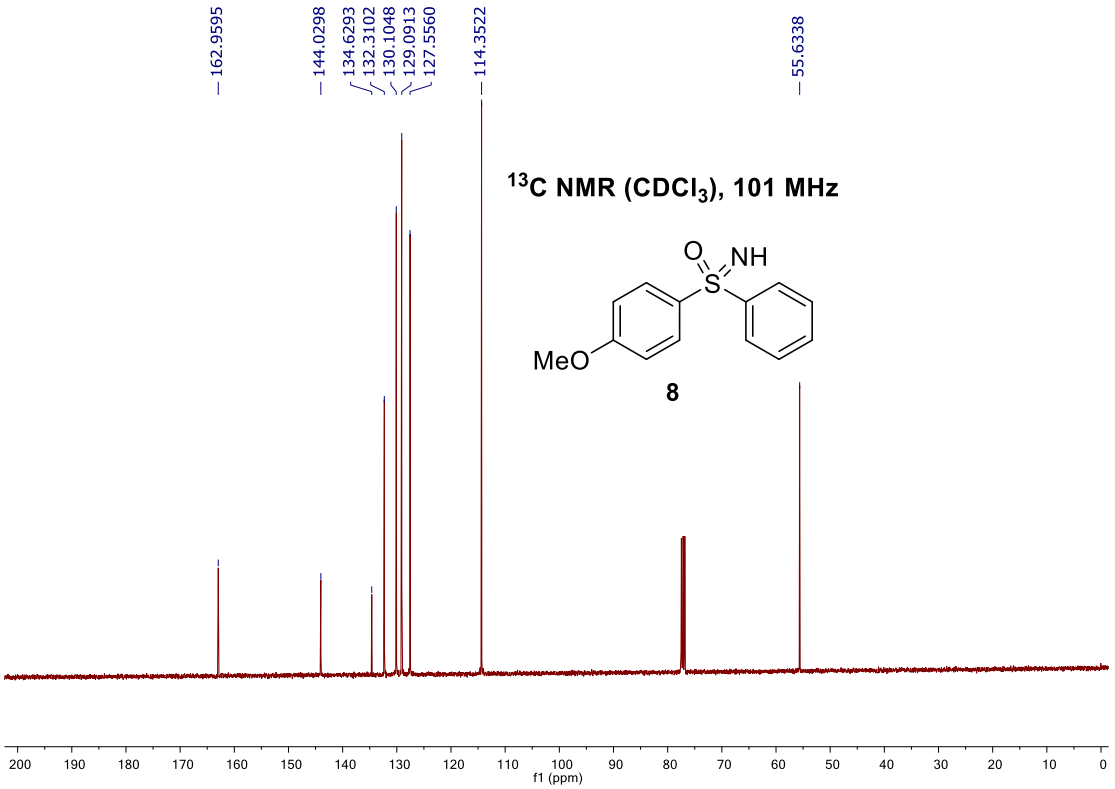

7.6568
7.6362
7.4498
7.4291
7.3191
7.2987
7.2849
7.2819
7.2781
7.2592
7.2402
7.2205
7.2029
7.0433
7.0373
7.0135
6.9927
6.8946
6.8721
6.6952
6.6891
6.6728
6.6665
3.8815
3.8092
2.4337
1H NMR (CDCl3), 400 MHz
O
SPh
O
MeO
Me
N
O
Cl
7g
1.98
2.09
7.16
3.03
1.00
1.01
2.02
3.07
3.01
0.0 9.5 9.0 8.5 8.0 7.5 7.0 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

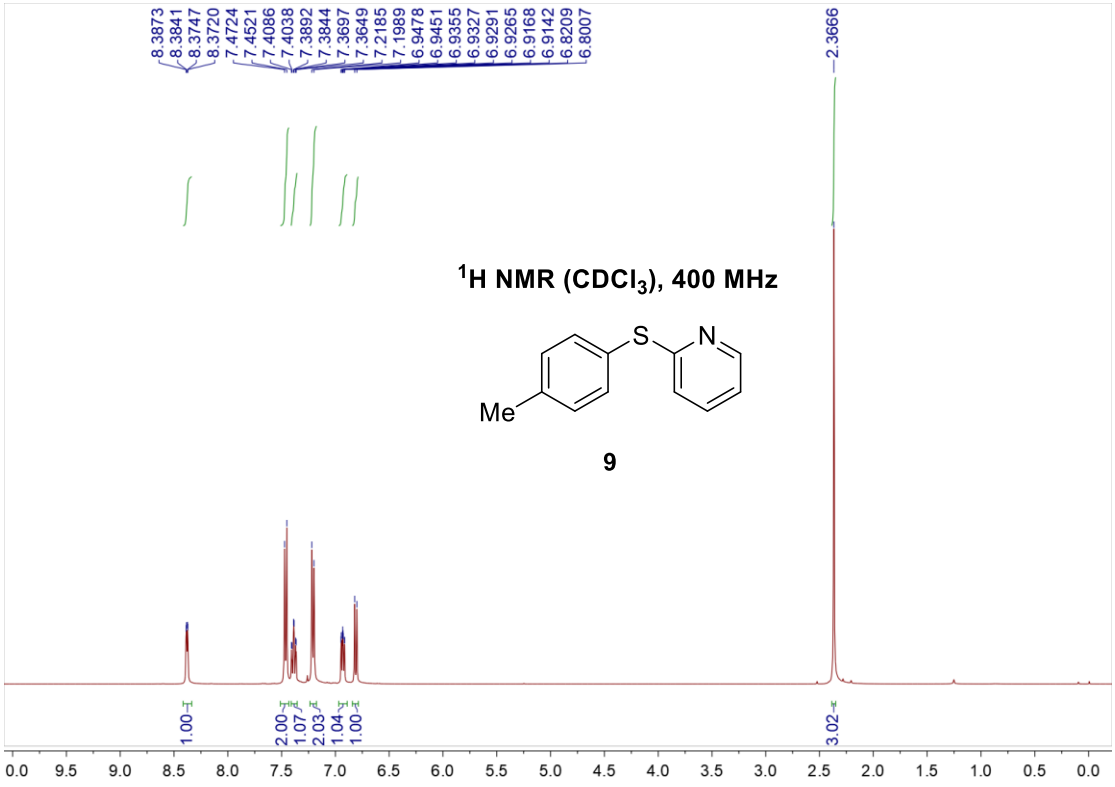

169.2245
168.3150
156.1539
136.2907
135.6975
133.8032
133.1643
132.3332
131.2423
130.8887
130.8636
130.4874
129.2932
129.1857
127.1902
122.3001
115.0957
111.8831
111.8063
101.2505
55.7484
30.5536
13.4921
13C NMR (CDCl3), 101 MHz
O
SPh
O
MeO
Me
N
O
Cl
7g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


^{1}H NMR ($CDCl_3$), 400 MHz
Me
Me
Me
SPh
Me
O
Me
O
Me
Me
Me
7h


^{13}C NMR ($CDCl_3$), 101 MHz
Me
Me
Me
SPh
Me
O
Me
O
Me
Me
Me
7h
f1 (ppm)

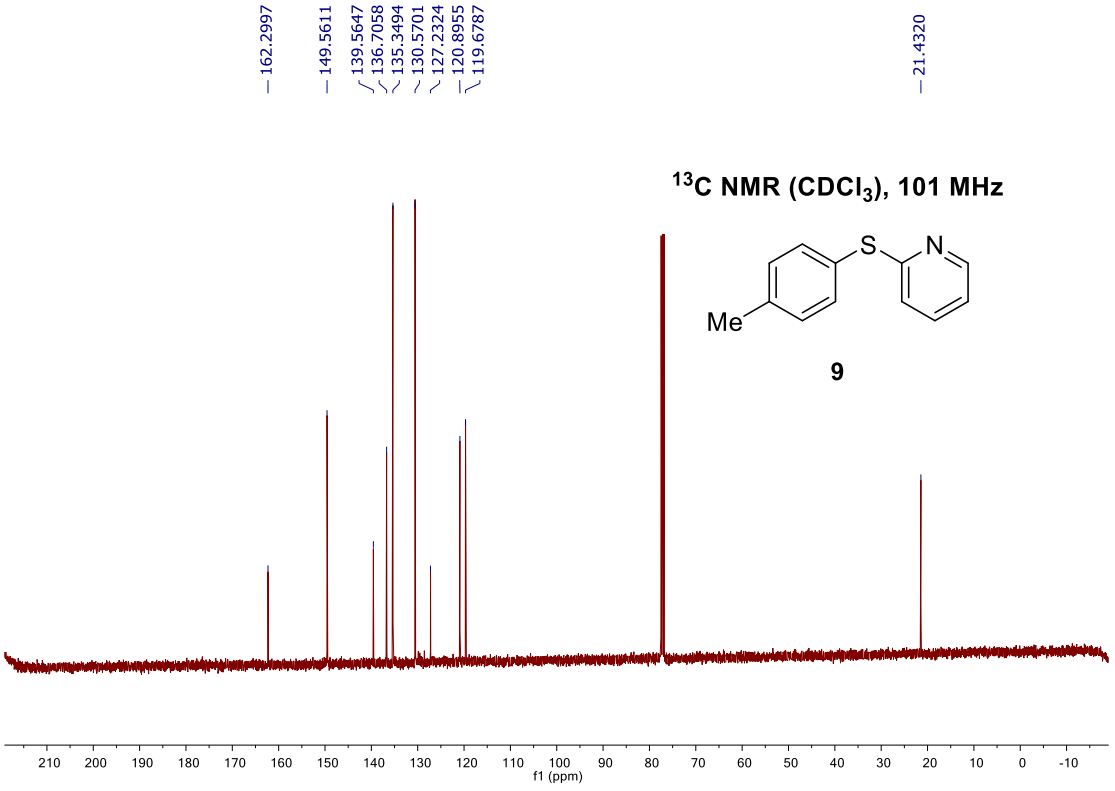

7.9935
7.9865
7.9828
7.9785
7.9720
7.9667
7.9620
7.9485
7.9408
7.9356
7.9237
7.9185
7.9107
7.4699
7.4663
7.4626
7.4585
7.4490
7.4469
7.4408
7.4357
7.4316
7.4261
7.4216
7.4142
7.4115
7.4070
7.3958
7.3909
7.3851
6.9060
6.9006
6.8886
6.8834
3.7673
2.9170
1H NMR (CDCl3), 400 MHz
O
NH
S
MeO
8
1.89
2.93
1.92
3.00
1.17
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


162.9595
144.0298
134.6293
132.3102
130.1048
129.0913
127.5560
114.3522
55.6338
13C NMR (CDCl3), 101 MHz
O
NH
S
MeO
8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



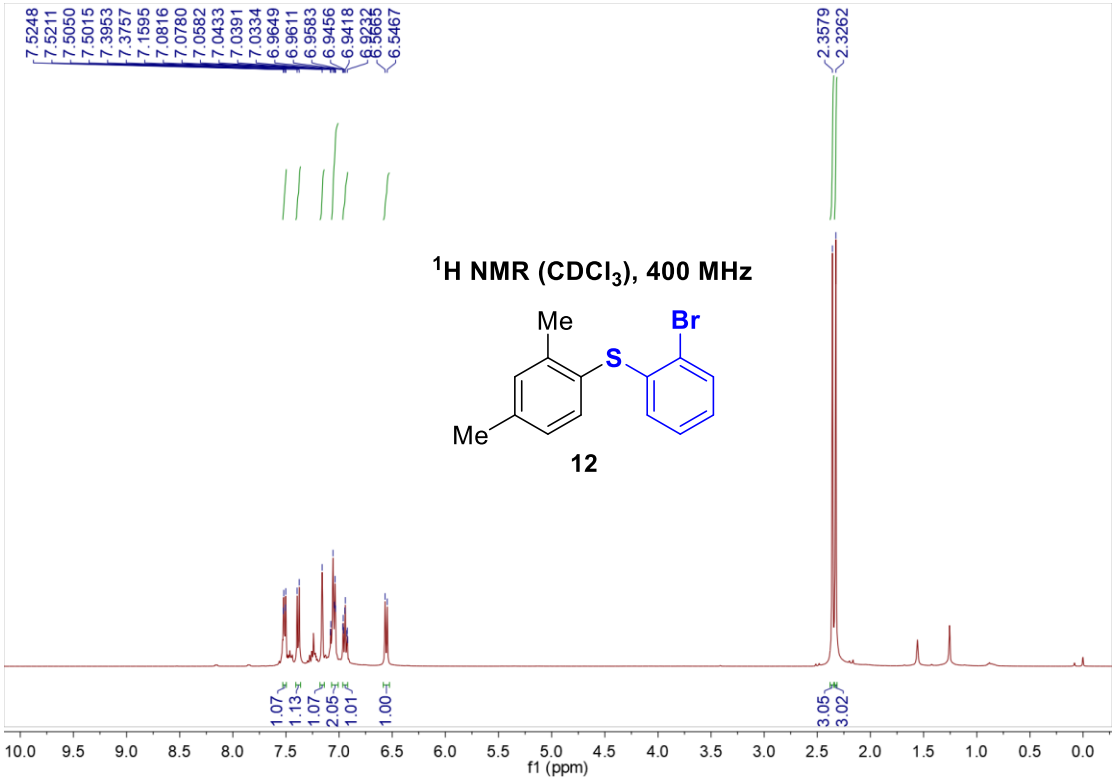
^{1}H NMR ($CDCl_3$), 400 MHz

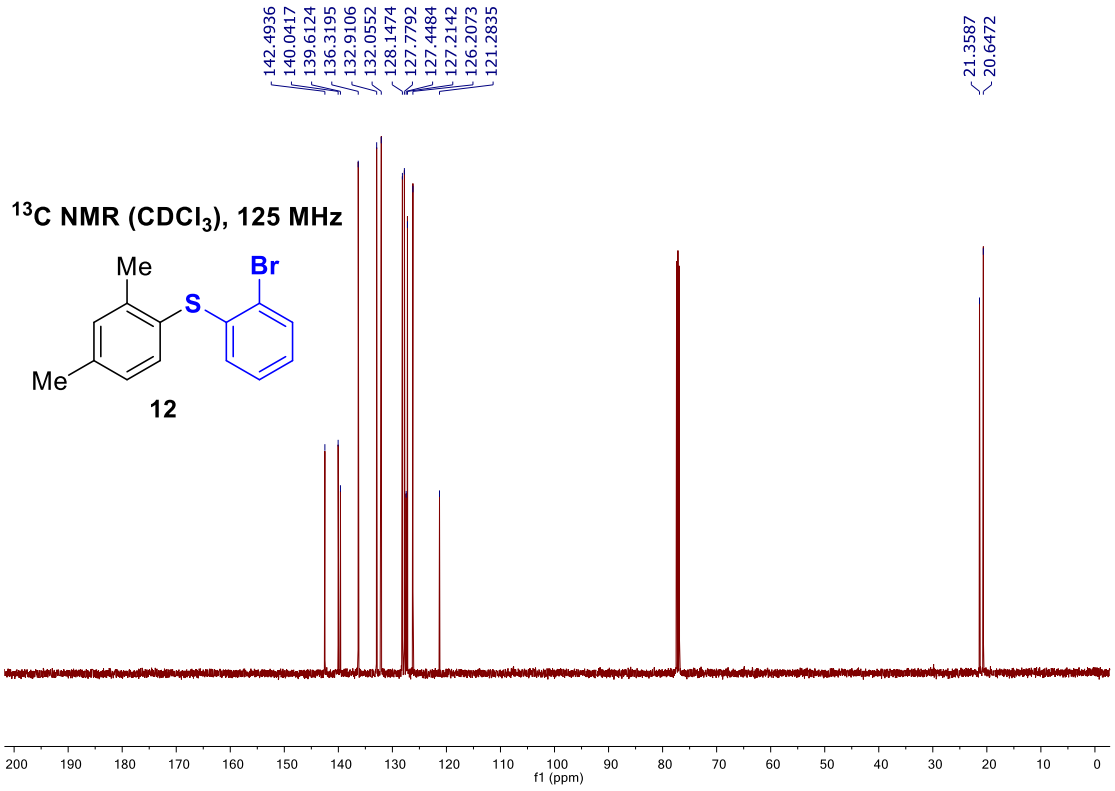
9

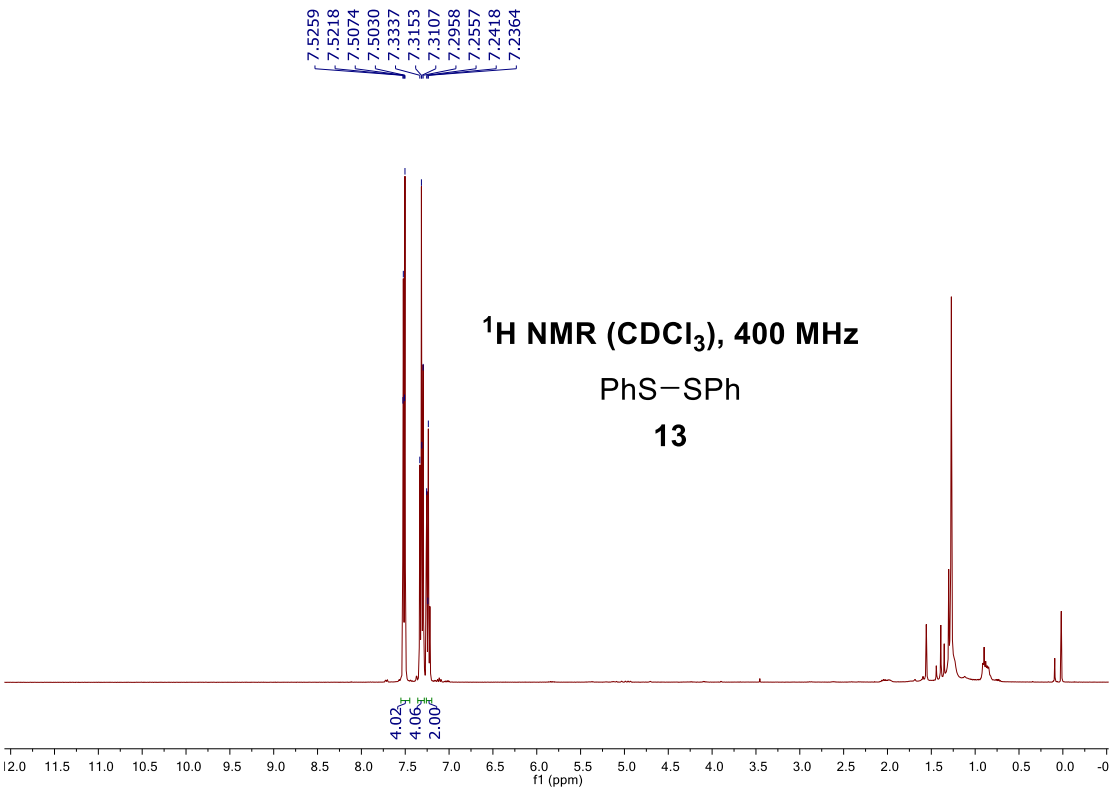


^{13}C NMR ($CDCl_3$), 101 MHz

9


7.5248
7.5211
7.5050
7.5015
7.3953
7.3757
7.1595
7.0816
7.0780
7.0582
7.0433
7.0391
7.0334
6.9649
6.9611
6.9583
6.9456
6.9418
6.5467
2.3579
2.3262
1H NMR (CDCl3), 400 MHz
Me
Br
S
Me
12
1.07
1.13
1.07
2.05
1.01
1.00
3.05
3.02
f1 (ppm)


142.4936
140.0417
139.6124
136.3195
132.9106
132.0552
128.1474
127.7792
127.4484
127.2142
126.2073
121.2835
21.3587
20.6472
13C NMR (CDCl3), 125 MHz
Me
Br
S
Me
12
f1 (ppm)


7.5259
7.5218
7.5074
7.5030
7.3337
7.3153
7.3107
7.2958
7.2557
7.2418
7.2364
^{1}H NMR ($CDCl_3$), 400 MHz
PhS−SPh
13
4.02
4.06
2.00
f1 (ppm)