

Electronic Supplementary Information

**A Diphenyl Ether Derived Bidentate Secondary Phosphine Oxide as a
Preligand for Nickel-Catalyzed C–S Cross-Coupling Reactions**

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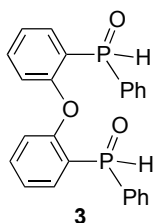
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General Experimental Methods. All reactions were carried out in oven-dried glassware under an argon atmosphere using standard Schlenk and glovebox techniques. Dry and oxygen free solvents (diethyl ether, THF and toluene) were collected from an Innovative Technology solvent purification system. DMF, DMSO, DMSO-*d*₆ and methanol were dried over 4 Å molecular sieves and then degassed by bubbling argon through them for 30 min to 1 h. CDCl₃ and DMSO-*d*₆ were purchased from Cambridge Isotope Laboratories. NaBH₄ was purchased from Acros Organics. Bromobenzene, chlorobenzene, KOH, NaOH, K₃PO₄, Na₂CO₃, NaOMe and concentrated HCl solution (37%) were purchased from Fisher Scientific. Ni(COD)₂ was purchased from Acros Organics, stored in a –30 °C freezer of a glove box, and used without further purification. All other reagents were purchased from Sigma Aldrich and used without further purification except *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and bis(diethylamino)phenylphosphine (PhP(NEt₂)₂). TMEDA was dried over calcium hydride and distilled under an argon atmosphere. PhP(NEt₂)₂ was purified by vacuum distillation prior to use. ¹H, ¹³C{¹H}, ³¹P, and ³¹P{¹H} NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer or a Bruker DMX 500 MHz spectrometer. Chemical shift values in ¹H and ¹³C{¹H} NMR spectra were referenced internally to the residual solvent resonances. ³¹P and ³¹P{¹H} NMR spectra were referenced externally to 85% H₃PO₄ (0 ppm). Infrared spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with smart orbit diamond attenuated total reflectance (ATR) accessory. High-resolution ESI-MS data for all the new compounds were obtained from either a Micromass Q-TOF-2TM or a ThermoFinnigan LTQ Linear Ion-Trap FTMS instrument. GC-MS data were collected on an Agilent 7890B GC & 5977A Series GC/MSD system.

Synthesis of PhP(Cl)NEt₂. This compound has been previously made from PhPCl₂ and PhP(NEt₂)₂.¹ In our hands, some modification of the procedures was necessary in order to obtain a pure product. In a glovebox, PhPCl₂ (407 μL, 3.0 mmol) and PhP(NEt₂)₂ (780 μL, 3.0 mmol) were dissolved in 4.5 mL of Et₂O in a separate oven-dried Schlenk flask. Both solutions were taken out of the glovebox and cooled by an ice bath (0 °C) for 5-10 min. At this temperature, the PhP(NEt₂)₂ solution was added via a cannula to the PhPCl₂ solution. The resulting mixture was warmed to room temperature and stirred for 1.5 h, during which time PhP(Cl)NEt₂ was formed as a white suspension. This material was used directly in the next step. ³¹P{¹H} NMR (162 MHz, Et₂O, δ): 138.62 (s).

Synthesis of Secondary Phosphine Oxide 3. Under an argon atmosphere, diphenyl ether (511 mg, 3.0 mmol) was dissolved in 8 mL of Et₂O. The resulting solution was cooled to –

78 °C, after which TMEDA (990 μ L, 6.6 mmol) was added, followed by slow addition of a 1.6 M solution of *n*-BuLi in hexanes (4.1 mL, 6.6 mmol). The reaction mixture was stirred at -78 °C for 30 min and then at room temperature for 16 h. The solution of PhP(Cl)NEt₂ in Et₂O prepared above was first diluted with Et₂O to 15 mL and then added slowly to the lithiated diphenyl ether at -78 °C over a period of 30 min using a syringe pump. After stirring at -78 °C for another 30 min, the reaction mixture was warmed to room temperature again and stirred for 5 h. The volatiles were removed under vacuum, resulting in a beige colored oil, which was dissolved in 12 mL of THF. To this solution chilled at 0 °C, a concentrated HCl solution (2.65 mL, 12 mmol) was added dropwise. After 10 min, the resulting mixture was warmed to room temperature and stirred for 4 h. Subsequently, 13 mL of water was added and the mixture was stirred for 40 min. The product was extracted with ethyl acetate (10 mL \times 3), and the combined organic layers were dried with anhydrous Na₂SO₄ and concentrated under vacuum, giving a yellow colored oil. The pure product was obtained via recrystallization from ethyl acetate at -5 °C and isolated as a white solid (583 mg, 46% overall yield). Both ¹H and ³¹P{¹H} NMR suggested that the isolated material was a 72 : 28 mixture of isomers. This ratio is independent of the solvent used (CDCl₃, THF and toluene).



¹H NMR (400 MHz, CDCl₃, δ): major isomer: 8.01 (dd, ³J_{P-H} = 13.2 Hz, ³J_{H-H} = 7.2 Hz, ArH, 2H), 7.88 (d, ¹J_{P-H} = 500 Hz, PH, 2H), 7.60-7.45 (m, ArH, 6H), 7.40-7.34 (m, ArH, 6H), 7.31-7.27 (m, ArH, 2H), 6.39 (t, ³J_{H-H} = 6.0 Hz, 2H); minor isomer: 8.02 (d, ¹J_{P-H} = 500 Hz, PH, 2H), 7.89 (dd, ³J_{P-H} = 13.8 Hz, ³J_{H-H} = 7.4 Hz, ArH, 2H), 7.60-7.45 (m, ArH, 6H), 7.40-7.34 (m, ArH, 6H), 7.31-7.27 (m, ArH, 2H), 6.45 (dd, ³J_{H-H} = 8.2 and 6.8 Hz, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): major isomer: 156.89 (d, J_{P-C} = 3.4 Hz), 134.48 (s), 133.31 (d, J_{P-C} = 6.0 Hz), 132.58 (s), 131.88 (d, J_{P-C} = 106.1 Hz), 130.49 (d, J_{P-C} = 12.3 Hz), 128.83 (d, J_{P-C} = 13.3 Hz), 124.75 (d, J_{P-C} = 11.1 Hz), 122.62 (d, J_{P-C} = 100.0 Hz), 118.02 (d, J_{P-C} = 5.6 Hz); minor isomer: 157.29 (d, J_{P-C} = 2.4 Hz), 134.52 (s), 133.19 (d, J_{P-C} = 7.0 Hz), 132.50 (s), 131.41 (d, J_{P-C} = 106.1 Hz), 130.49 (d, J_{P-C} = 12.3 Hz), 128.83 (d, J_{P-C} = 13.3 Hz), 124.68 (d, J_{P-C} = 10.9 Hz), 122.98 (d, J_{P-C} = 100.0 Hz), 118.34 (d, J_{P-C} = 5.6 Hz). ³¹P{¹H} NMR (162 MHz, CDCl₃, δ): 13.87 (s, major), 13.75 (s, minor). ³¹P{¹H} NMR (202 MHz, DMF, δ): 10.49 (s). ³¹P{¹H} NMR (202 MHz, THF, δ): 8.50 (s, major), 8.26 (s, minor). ³¹P{¹H} NMR (202 MHz, toluene, δ): 8.24 (s, major), 8.14 (s, minor). ³¹P NMR (162 MHz, CDCl₃, δ): 13.88 (dm, ¹J_{P-H} = 503 Hz, resonances for the two isomers were overlapped). ATR-IR (solid): ν_{P-H} = 2333 cm⁻¹. HRMS-ESI (m/z) [M+H]⁺ calcd for C₂₄H₂₁O₃P₂ 419.0966, found 419.0962.

Formation of Complex 10. In a glovebox, Ni(COD)₂ (1.4 mg, 5 μ mol) and **3** (2.1 mg, 5 μ mol) were mixed with 1.0 mL of solvent, and transferred to a J. Young NMR tube. The progress of the reaction was monitored by ³¹P{¹H} NMR spectroscopy. Figures S1-S3 shows the reaction as a function of time.

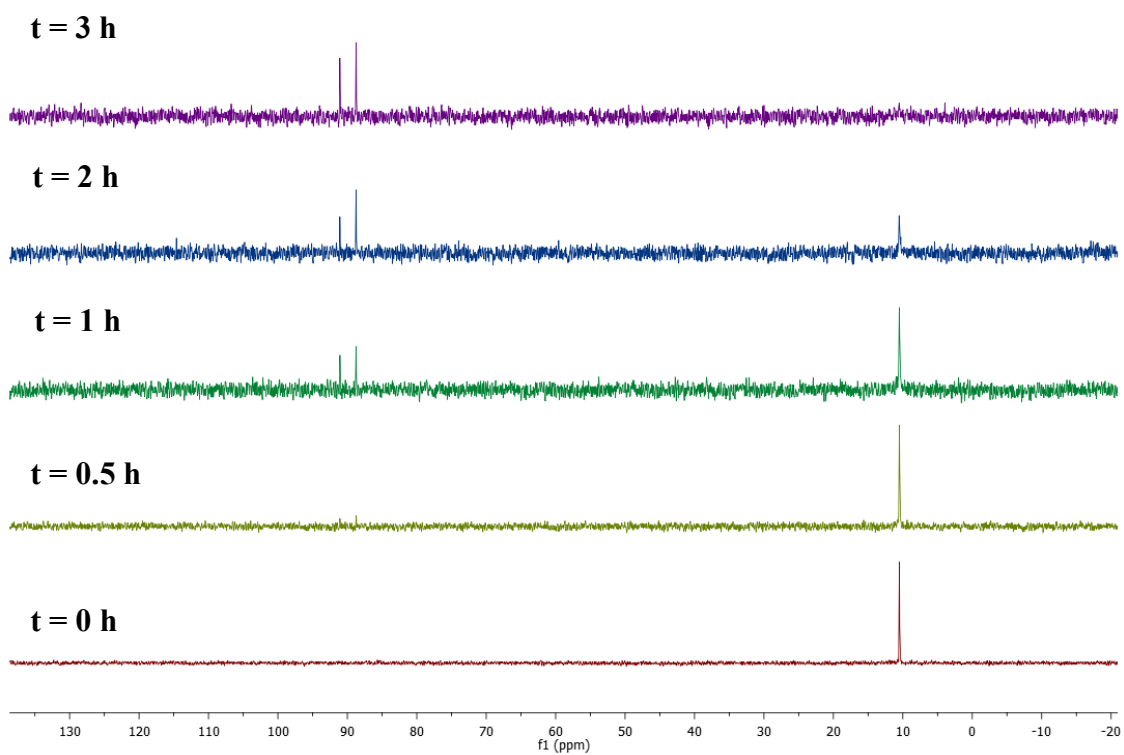


Figure S1. In-situ $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for the reaction of $\text{Ni}(\text{COD})_2$ with **3** in DMF

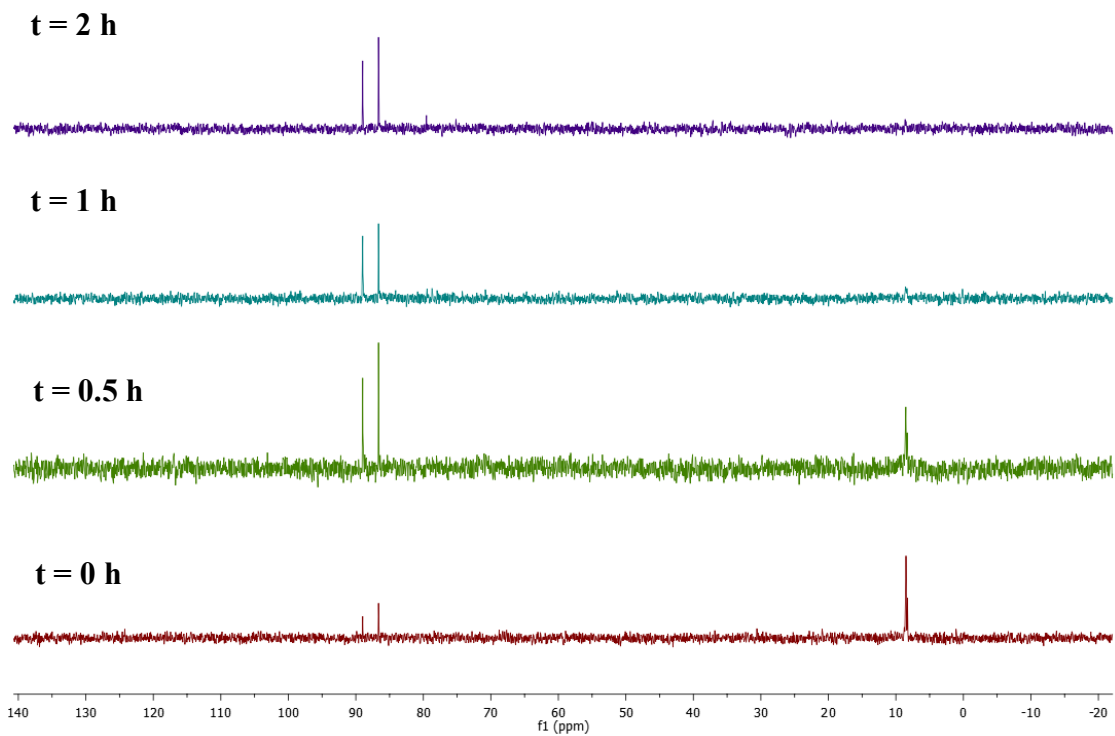


Figure S2. In-situ $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for the reaction of $\text{Ni}(\text{COD})_2$ with **3** in THF

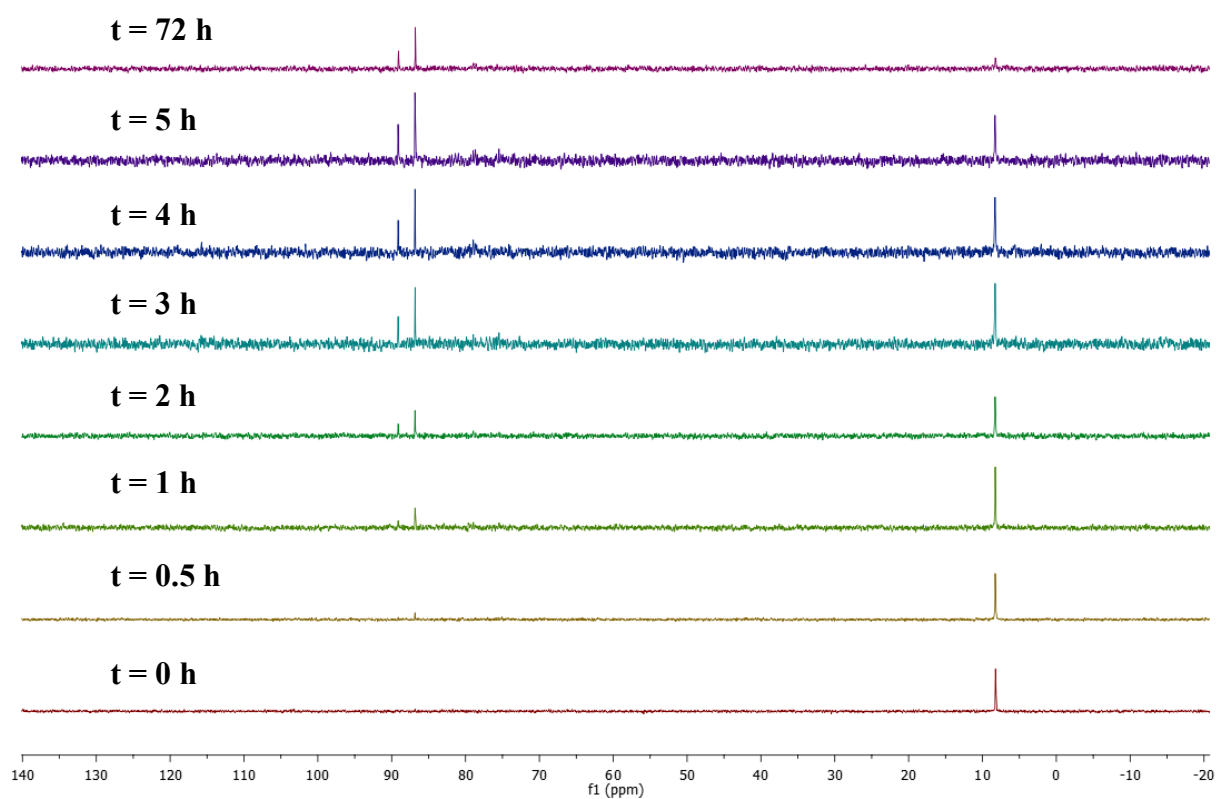
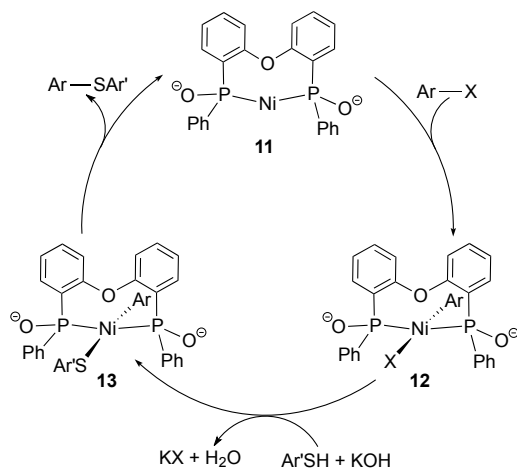


Figure S3. In-situ $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for the reaction of $\text{Ni}(\text{COD})_2$ with **3** in toluene

Proposed Reaction Mechanism. Oxidative addition of an aryl halide to **11** would generate a Ni(II) species **12** as shown in Scheme S1. Subsequent substitution of the halide by a thiolate would produce **13**, where the thiolate and aryl groups are *trans* to each other. Reductive elimination of the sulfides requires these two groups cis to each other, which is possible via isomerization or dissociation of one of the SPO arms. This proposed mechanism resembles the one proposed by others for palladium² and rhodium³ catalyzed C–S coupling of aryl halides with thiols.



Scheme S1 Proposed catalytic cycle.

General Procedures for Catalytic Cross-Coupling of Aryl Halides with Thiols.

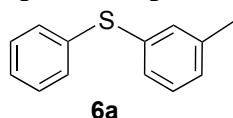
Under an argon atmosphere, Ni(COD)₂ (13.8 mg, 0.050 mmol) and **3** (20.9 mg, 0.050 mmol) were mixed in 10 mL of DMF at 23 °C. The resulting mixture was stirred at this temperature for 3 h to produce a stock solution of the catalyst (5.0 mM). A portion of the stock solution (1.0 mL, 0.5 mol% catalyst) was added to a 10 mL scintillation vial containing KOH (61.7 mg, 1.1 mmol). More DMF was added until the total volume was brought up to 6 mL, after which aryl halide (1.1 mmol) and thiol (1.0 mmol) were added. The reaction mixture was stirred at 80 °C for 1 h. Upon completion of the reaction, the volatiles were removed under vacuum to afford the crude product. The sulfide product was purified by column chromatography. For the reactions catalyzed by 1.0 mol% catalyst, 2.0 mL of the catalyst stock solution (5 mM) was used. For the coupling of iodobenzene with methyl thiosalicylate (entry 11, Table 2), Ni(COD)₂ (13.8 mg, 0.050 mmol) and **3** (20.9 mg, 0.050 mmol) were mixed with 6 mL of DMF at 23 °C for 2 h prior to the addition of substrates. The rest of the procedures were the same as described above.

All the diaryl sulfides (**6a-i**), diaryl disulfides resulted from 4-methoxythiophenol (entry 10) and methyl thiosalicylate (entry 11), and the by-product **8** were characterized by ¹H and ¹³C{¹H} NMR spectroscopy. The chemical shift values of the known compounds were compared to literature values. New compounds (**6c-f**, entries 5-8) were further characterized by high-resolution mass spectroscopy.

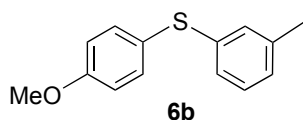
Procedures for Removing Disulfides from Sulfides. Without a polar functional group present in the molecule, separating the disulfide impurity from the desired sulfide was challenging (entries 8 and 9, Table 2). In that case, the following procedures were adopted prior to column chromatography. The crude product was first passed through a short pad of silica gel

and washed with hexanes. The resulting solution was concentrated under vacuum, and then dissolved in 20 ml of a 1: 1 THF-methanol mixture. Under an argon atmosphere, NaBH₄ (189 mg, 5.0 mmol) was added, and the resulting mixture was stirred at 55 °C for 16 h. The volatiles were removed under vacuum, and the product was extracted with ~ 10 mL of hexanes. The combined hexanes solutions were filtered through a short pad of Celite, and then evaporated to dryness. The residue was subjected to further purification by column chromatography.

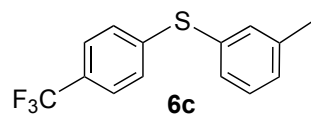
Spectroscopic Characterization Data for the Diary Sulfides and Isolated Byproducts



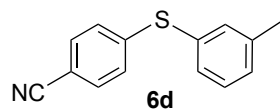
This compound was isolated as a colorless oil (172 mg, 86% yield) using hexanes as the eluent. ¹H NMR (400 MHz, CDCl₃, δ): 7.32-7.12 (m, ArH, 8H), 7.02 (d, ³J_{H-H} = 6.8 Hz, ArH, 1H), 2.27 (s, CH₃, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 139.08, 136.21, 135.34, 131.93, 130.81, 129.20, 129.12, 128.43, 128.10, 126.90, 21.36 (CH₃). The NMR data match those reported in the literature.⁴



This compound was isolated as a colorless oil (205 mg, 89% yield) using hexanes as the eluent, followed by a hexanes-diethyl ether mixture (9 : 1). ¹H NMR (400 MHz, CDCl₃, δ): 7.40 (d, ³J_{H-H} = 8.8 Hz, ArH, 2H), 7.11 (t, ³J_{H-H} = 7.8 Hz, ArH, 1H), 7.01 (s, ArH, 1H), 6.97-6.93 (m, ArH, 2H), 6.88 (d, ³J_{H-H} = 8.8 Hz, ArH, 2H), 3.80 (s, OCH₃, 3H), 2.26 (s, ArCH₃, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 159.83, 138.86, 138.30, 135.30, 129.06, 128.91, 126.86, 125.56, 124.65, 115.04, 55.46 (OCH₃), 21.45 (ArCH₃). The NMR data match those reported in the literature.⁵

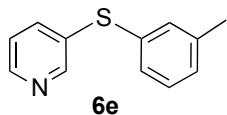


This compound was isolated as a white solid (240 mg, 90% yield) using hexanes as the eluent. ¹H NMR (400 MHz, CDCl₃, δ): 7.46 (d, ³J_{H-H} = 8.4 Hz, ArH, 2H), 7.31-7.23 (m, ArH, 5H), 7.18 (t, J_{H-H} = 4.0 Hz, ArH, 1H), 2.35 (s, CH₃, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 143.31, 139.79, 134.39, 132.07, 130.88, 129.73, 129.64, 128.15, 127.95 (q, ²J_{C-F} = 32.3 Hz), 125.89 (q, ³J_{C-F} = 4.0 Hz), 124.26 (q, ¹J_{C-F} = 272.8 Hz), 21.39 (CH₃). HRMS-ESI (m/z) [M]⁺ calcd for C₁₄H₁₁F₃S 268.05281, found 268.05287.

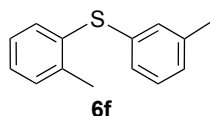


This compound was isolated as a white solid (194 mg, 86% yield) using hexanes as the eluent, followed by a hexanes-diethyl ether mixture (9 : 1). ¹H NMR (400 MHz, CDCl₃, δ): 7.47 (d, ³J_{H-H} = 8.8 Hz, ArH, 2H), 7.34-7.30 (m, ArH, 3H), 7.26-7.23 (m, ArH, 1H), 7.15 (d, ³J_{H-H} = 8.8 Hz,

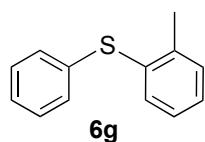
ArH, 2H), 2.37 (s, CH₃, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 146.13, 140.04, 135.21, 132.43, 131.71, 130.44, 130.38, 129.84, 127.26, 118.97, 108.60, 21.37 (CH₃). HRMS-ESI (m/z) [M+H]⁺ calcd for C₁₄H₁₂NS 226.06850, found 226.06854.



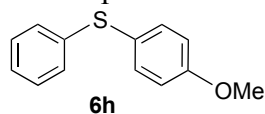
This compound was isolated as a yellow oil (189 mg, 94% yield) using hexanes as the eluent, followed by a hexanes-diethyl ether mixture (9 : 1). ¹H NMR (400 MHz, CDCl₃, δ): 8.54 (d, ⁴J_{H-H} = 2.0 Hz, ArH, 1H), 8.44 (dd, *J*_{H-H} = 4.8 and 1.2 Hz, ArH, 1H), 7.57 (dt, *J*_{H-H} = 8.0 and 1.8 Hz, ArH, 1H), 7.24-7.16 (m, ArH, 4H), 7.10 (d, ³J_{H-H} = 7.2 Hz, ArH, 1H), 2.31 (s, CH₃, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 150.90, 147.74, 139.50, 137.73, 133.94, 133.47, 132.52, 129.39, 129.01, 128.85, 123.90, 21.35 (CH₃). HRMS-ESI (m/z) [M+H]⁺ calcd for C₁₂H₁₂NS 202.06850, found 202.06847.



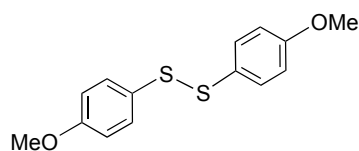
This compound was isolated as a colorless oil (125 mg, 58% yield) using hexanes as the eluent. ¹H NMR (400 MHz, CDCl₃, δ): 7.27-7.06 (m, ArH, 6H), 7.01-6.98 (m, ArH, 2H), 2.37 (s, CH₃, 3H), 2.27 (s, CH₃, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 139.74, 139.05, 135.73, 134.23, 132.69, 130.62 (two resonances overlapped here), 129.10, 127.75, 127.48, 127.09, 126.76, 21.43 (CH₃), 20.70 (CH₃). HRMS-ESI (m/z) [M+Ag]⁺ calcd for C₁₄H₁₄SAg 320.98617 (for ¹⁰⁷Ag) and 322.98565 (for ¹⁰⁹Ag), found 320.98618 and 322.98592; LRMS-EI (m/z) [M]⁺ found for C₁₄H₁₄S 214.1.



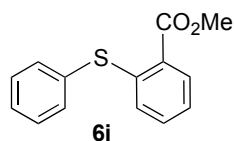
This compound was isolated as a colorless oil (73 mg, 37% yield) using hexanes as the eluent. The NMR yield (85%) was determined by adding 0.33 mmol of mesitylene to the crude product and then analyzed by ¹H NMR spectroscopy. ¹H NMR (400 MHz, CDCl₃, δ): 7.30-7.11 (m, ArH, 9H), 2.37 (s, CH₃, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 140.09, 136.27, 133.87, 133.12, 130.72, 129.75, 129.25, 128.03, 126.84, 126.46, 20.72 (CH₃). The NMR data match those reported in the literature.⁴



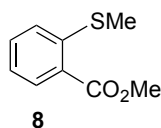
This compound was isolated as a colorless oil (87 mg with 0.5 mol% catalyst, 40% yield; 199 mg with 1 mol% catalyst, 91% yield) using a hexanes-diethyl ether mixture (8 : 2) as the eluent. ¹H NMR (400 MHz, CDCl₃, δ): 7.41 (d, ³J_{H-H} = 8.8 Hz, ArH, 2H), 7.24-7.10 (m, ArH, 5H), 6.88 (d, ³J_{H-H} = 8.8 Hz, ArH, 2H), 3.80 (s, OCH₃, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 159.93, 138.72, 135.49, 129.04, 128.28, 125.86, 124.37, 115.09, 55.45 (OCH₃). The NMR data match those reported in the literature.⁶



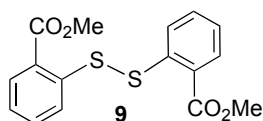
This compound was isolated as a yellow oil (24 mg with 0.5 mol% catalyst, 17% yield; 13 mg with 1 mol% catalyst, 9% yield) using a hexanes-diethyl ether mixture (8 : 2) as the eluent. ^1H NMR (400 MHz, CDCl_3 , δ): 7.39 (d, $^3J_{\text{H-H}} = 8.8$ Hz, ArH, 4H), 6.83 (d, $^3J_{\text{H-H}} = 9.2$ Hz, ArH, 4H), 3.79 (s, OCH_3 , 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , δ): 160.02, 132.80, 128.53, 114.73, 55.49 (OCH_3). The NMR data match those reported in the literature.⁷



This compound was isolated as a colorless oil (187 mg, 77% yield, entry 3, Table 3) using a hexanes-diethyl ether mixture (9 : 1) as the eluent. ^1H NMR (400 MHz, CDCl_3 , δ): 7.98 (dd, $^3J_{\text{H-H}} = 7.8$ Hz, $^4J_{\text{H-H}} = 1.4$ Hz, ArH, 1H), 7.57-7.55 (m, ArH, 2H), 7.43-7.42 (m, ArH, 3H), 7.23 (t, $^3J_{\text{H-H}} = 7.8$ Hz, ArH, 1H), 7.12 (t, $^3J_{\text{H-H}} = 7.6$ Hz, ArH, 1H), 6.81 (d, $^3J_{\text{H-H}} = 8.4$ Hz, ArH, 1H), 3.95 (s, OCH_3 , 3H). ^1H NMR (400 MHz, $\text{DMSO}-d_6$, δ): 7.91 (dd, $^3J_{\text{H-H}} = 7.6$ Hz, $^4J_{\text{H-H}} = 1.4$ Hz, ArH, 1H), 7.53-7.48 (m, ArH, 5H), 7.40 (t, $^3J_{\text{H-H}} = 7.6$ Hz, ArH, 1H), 7.24 (t, $^3J_{\text{H-H}} = 7.6$ Hz, ArH, 1H), 6.78 (d, $^3J_{\text{H-H}} = 8.4$ Hz, ArH, 1H), 3.86 (s, OCH_3 , 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , δ): 166.98, 143.30, 135.64, 132.61, 132.40, 131.11, 129.83, 129.19, 127.50, 126.82, 124.38, 52.28 (OCH_3). The NMR data match those reported in the literature.⁸



This compound was isolated as an off-white solid (46 mg, 25% yield, entry 2, Table 3) using a hexanes-diethyl ether mixture (9 : 1) as the eluent. ^1H NMR (400 MHz, CDCl_3 , δ): 8.00 (dd, $^3J_{\text{H-H}} = 7.8$ Hz, $^4J_{\text{H-H}} = 1.4$ Hz, ArH, 1H), 7.47 (td, $^3J_{\text{H-H}} = 7.7$ Hz, $^4J_{\text{H-H}} = 1.2$ Hz, ArH, 1H), 7.27 (d, $^3J_{\text{H-H}} = 8.0$ Hz, ArH, 1H), 7.15 (td, $^3J_{\text{H-H}} = 7.5$ Hz, $^4J_{\text{H-H}} = 1.0$ Hz, ArH, 1H), 3.91 (s, OCH_3 , 3H), 2.45 (s, SCH_3 , 3H). ^1H NMR (400 MHz, $\text{DMSO}-d_6$, δ): 7.90 (dd, $^3J_{\text{H-H}} = 7.6$ Hz, $^4J_{\text{H-H}} = 1.4$ Hz, ArH, 1H), 7.58 (td, $^3J_{\text{H-H}} = 7.8$ Hz, $^4J_{\text{H-H}} = 1.2$ Hz, ArH, 1H), 7.39 (d, $^3J_{\text{H-H}} = 8.0$ Hz, ArH, 1H), 7.22 (td, $^3J_{\text{H-H}} = 7.6$ Hz, $^4J_{\text{H-H}} = 1.0$ Hz, ArH, 1H), 3.82 (s, OCH_3 , 3H), 2.42 (s, SCH_3 , 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , δ): 166.90, 143.38, 132.58, 131.39, 126.76, 124.39, 123.49, 52.10 (OCH_3), 15.61 (SCH_3). The NMR data match those reported in the literature.⁹



This compound was isolated as a white solid (15 mg, 9% yield, entry 1, Table 3) using a hexanes-diethyl ether mixture (9 : 1) as the eluent. ^1H NMR (400 MHz, CDCl_3 , δ): 8.07 (dd, $^3J_{\text{H-H}} = 7.8$ Hz, $^4J_{\text{H-H}} = 1.4$ Hz, ArH, 2H), 7.76 (dd, $^3J_{\text{H-H}} = 8.2$ Hz, $^4J_{\text{H-H}} = 1.0$ Hz, ArH, 2H), 7.41

(td, $^3J_{\text{H-H}} = 7.8$ Hz, $^4J_{\text{H-H}} = 1.2$ Hz, ArH, 2H), 7.23 (td, $^3J_{\text{H-H}} = 7.4$ Hz, $^4J_{\text{H-H}} = 1.1$ Hz, ArH, 2H), 3.99 (s, OCH₃, 6H). ^1H NMR (400 MHz, DMSO-*d*₆, δ): 8.05 (dd, $^3J_{\text{H-H}} = 7.6$ Hz, $^4J_{\text{H-H}} = 1.4$ Hz, ArH, 2H), 7.65-7.60 (m, ArH, 4H), 7.38 (td, $^3J_{\text{H-H}} = 7.6$ Hz, $^4J_{\text{H-H}} = 1.4$ Hz, ArH, 2H), 3.92 (s, OCH₃, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl₃, δ): 167.06, 140.50, 133.23, 131.60, 127.41, 125.96, 125.62, 52.54 (OCH₃). The NMR data match those reported in the literature.¹⁰

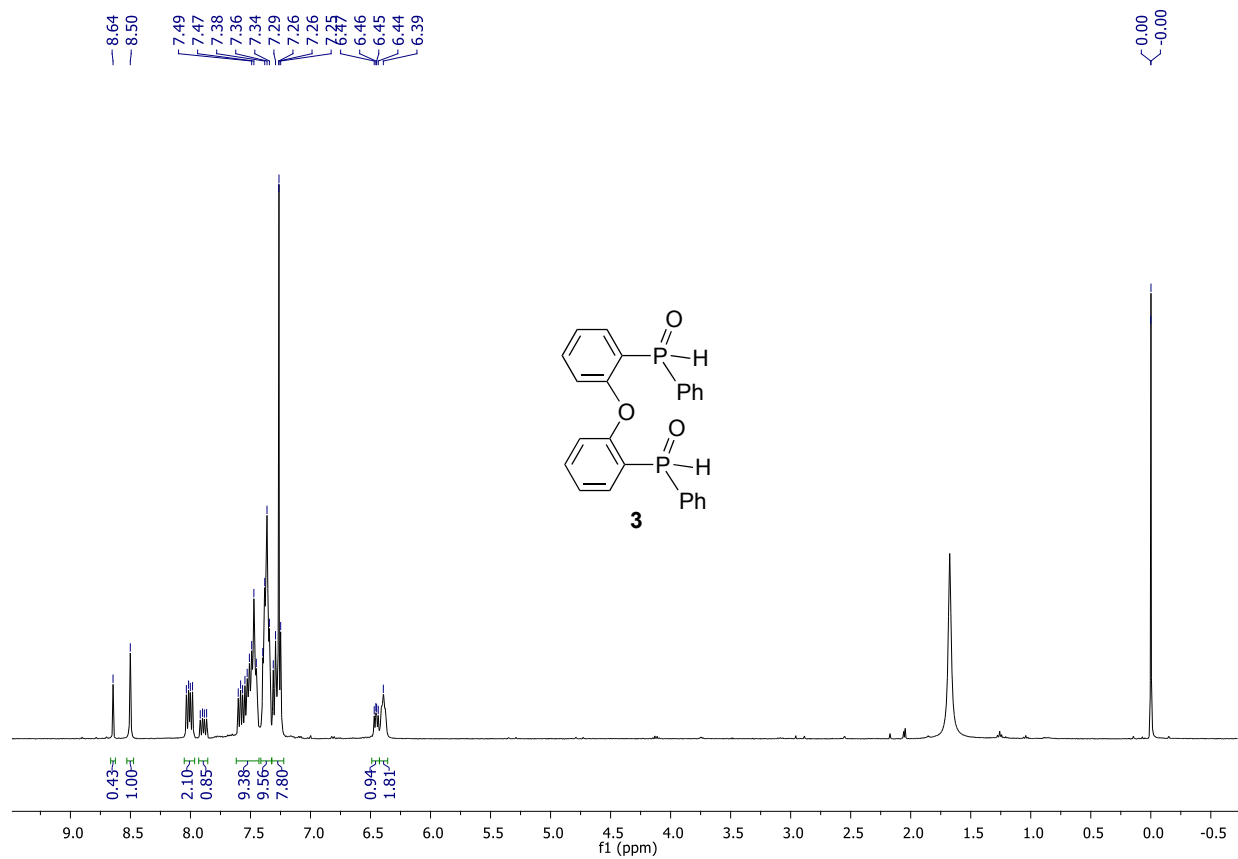


Figure S4. ¹H NMR of **3** in CDCl₃ (with TMS)

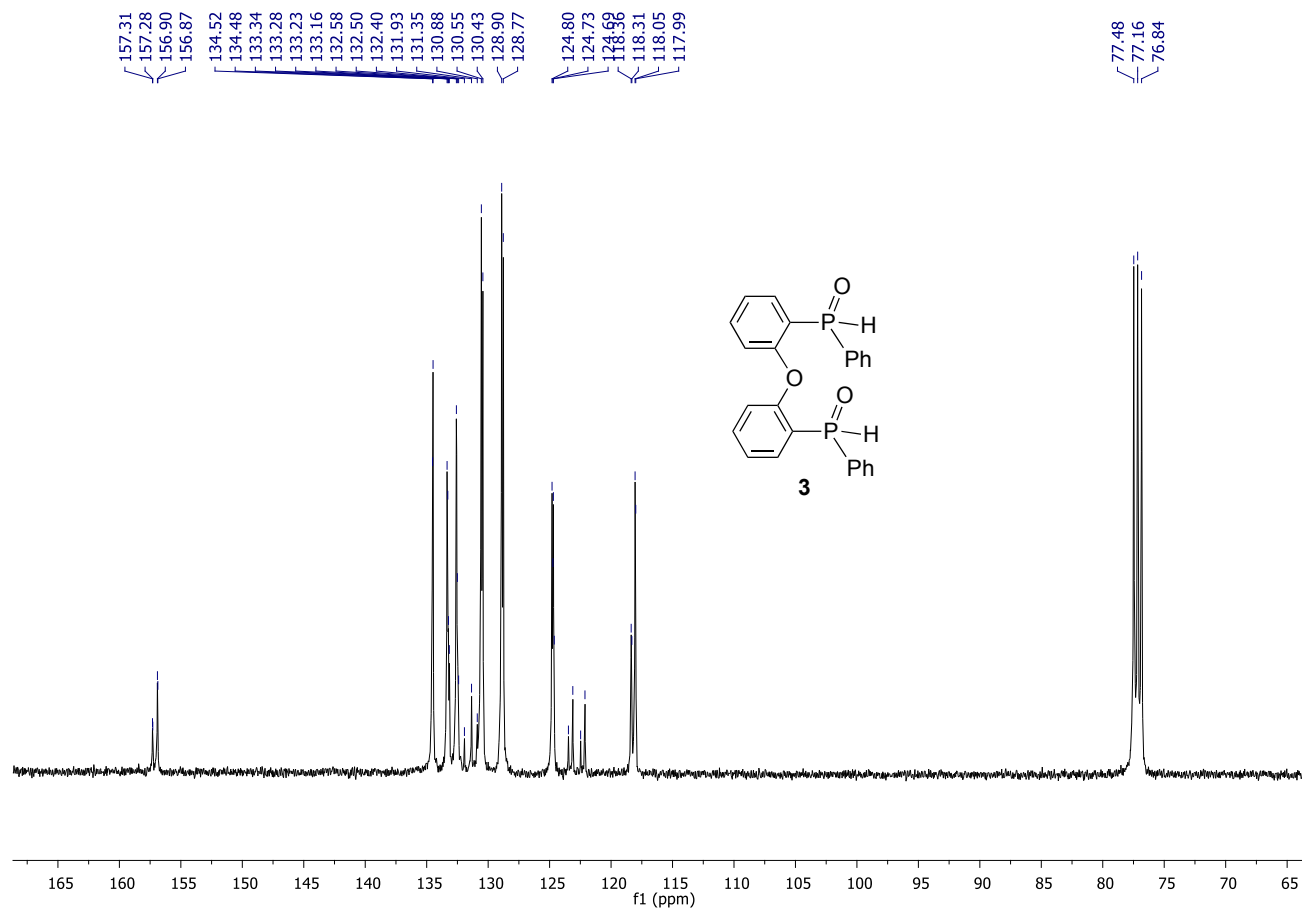


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR of **3** in CDCl_3 (with TMS)

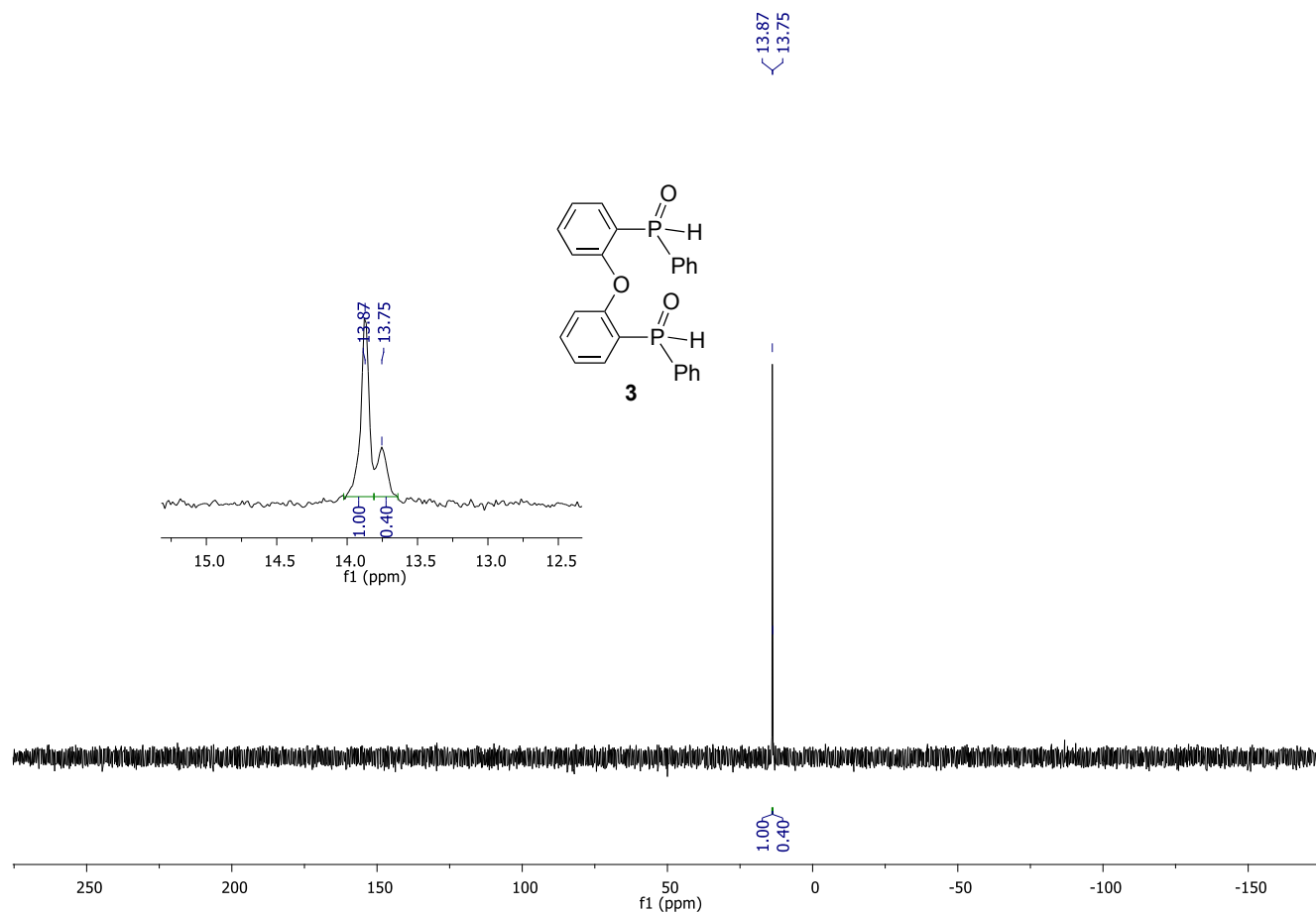


Figure S6. $^{31}\text{P}\{^1\text{H}\}$ NMR of **3** in CDCl_3 (with TMS)

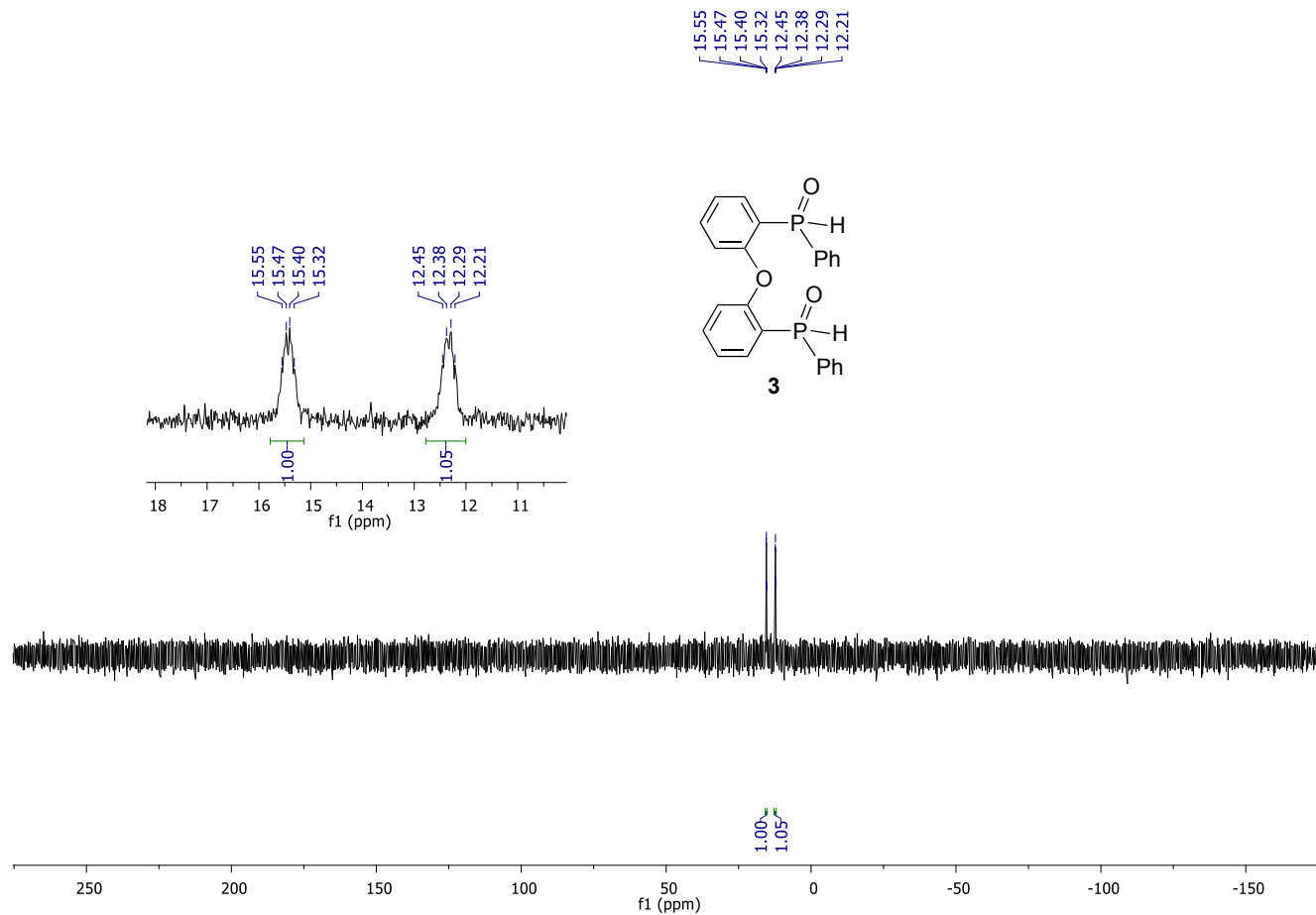


Figure S7. ^{31}P NMR of **3** in CDCl_3 (with TMS)

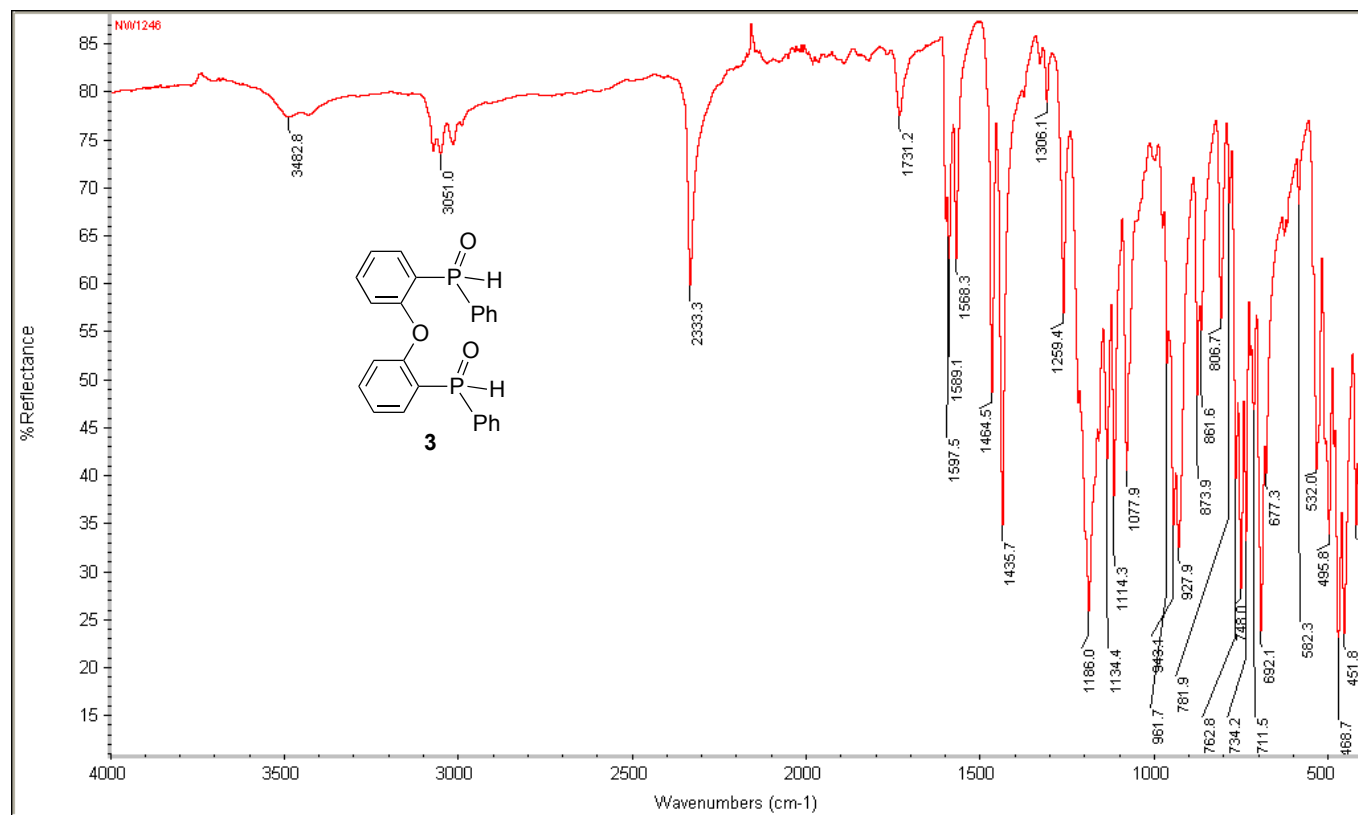


Figure S8. IR spectrum of **3** (solid)

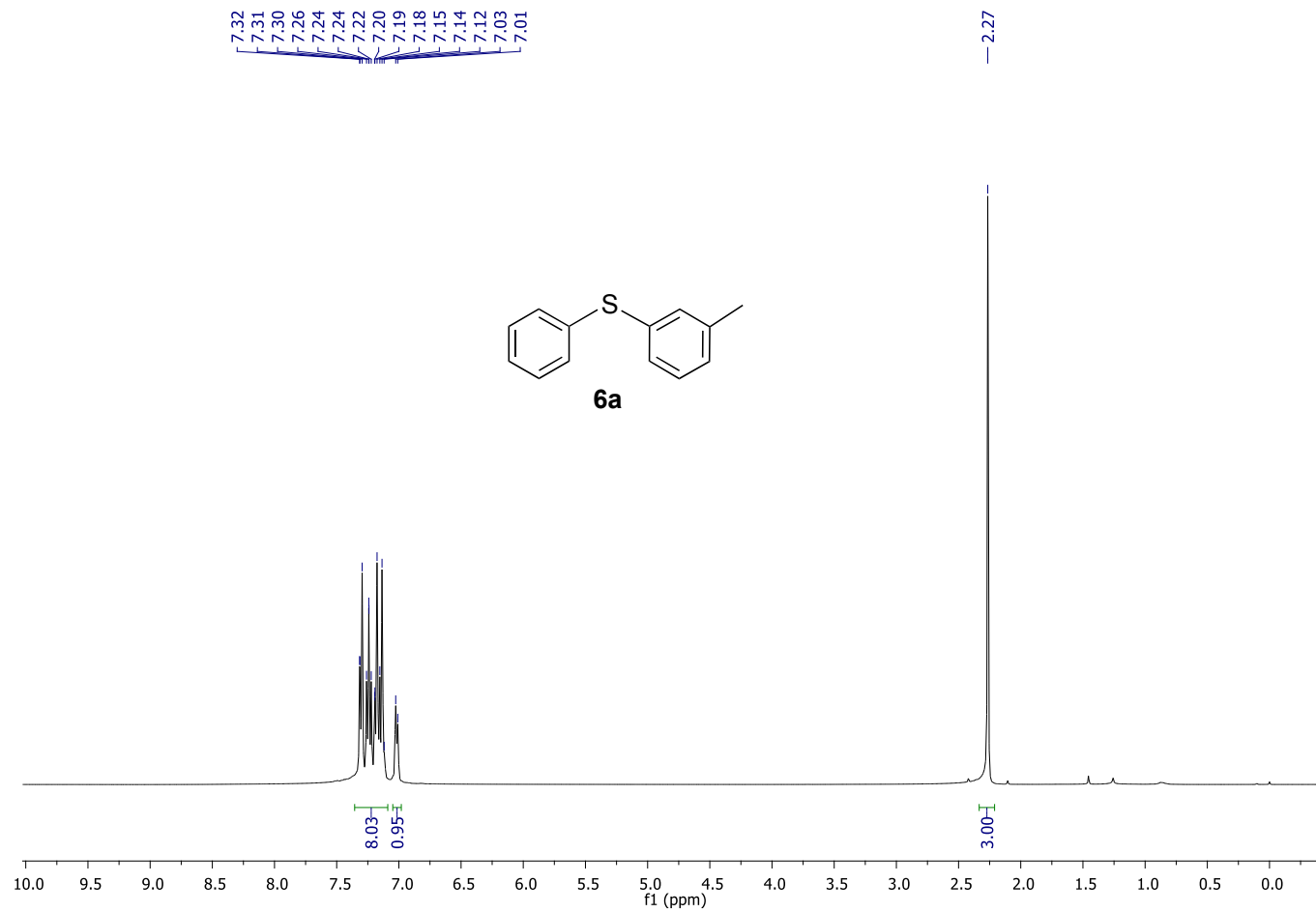


Figure S9. ^1H NMR of **6a** in CDCl_3 (with TMS)

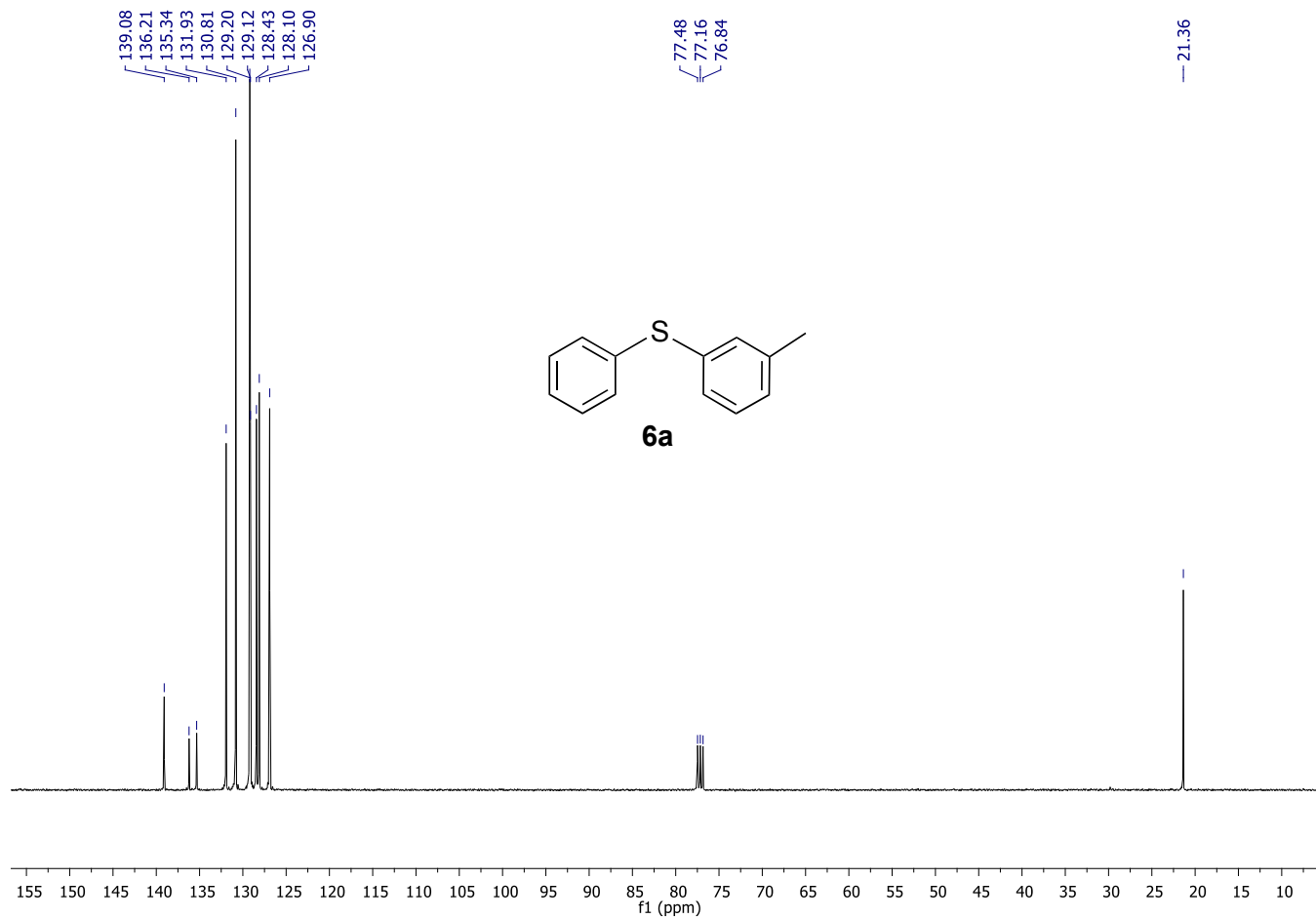


Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR of **6a** in CDCl_3 (with TMS)

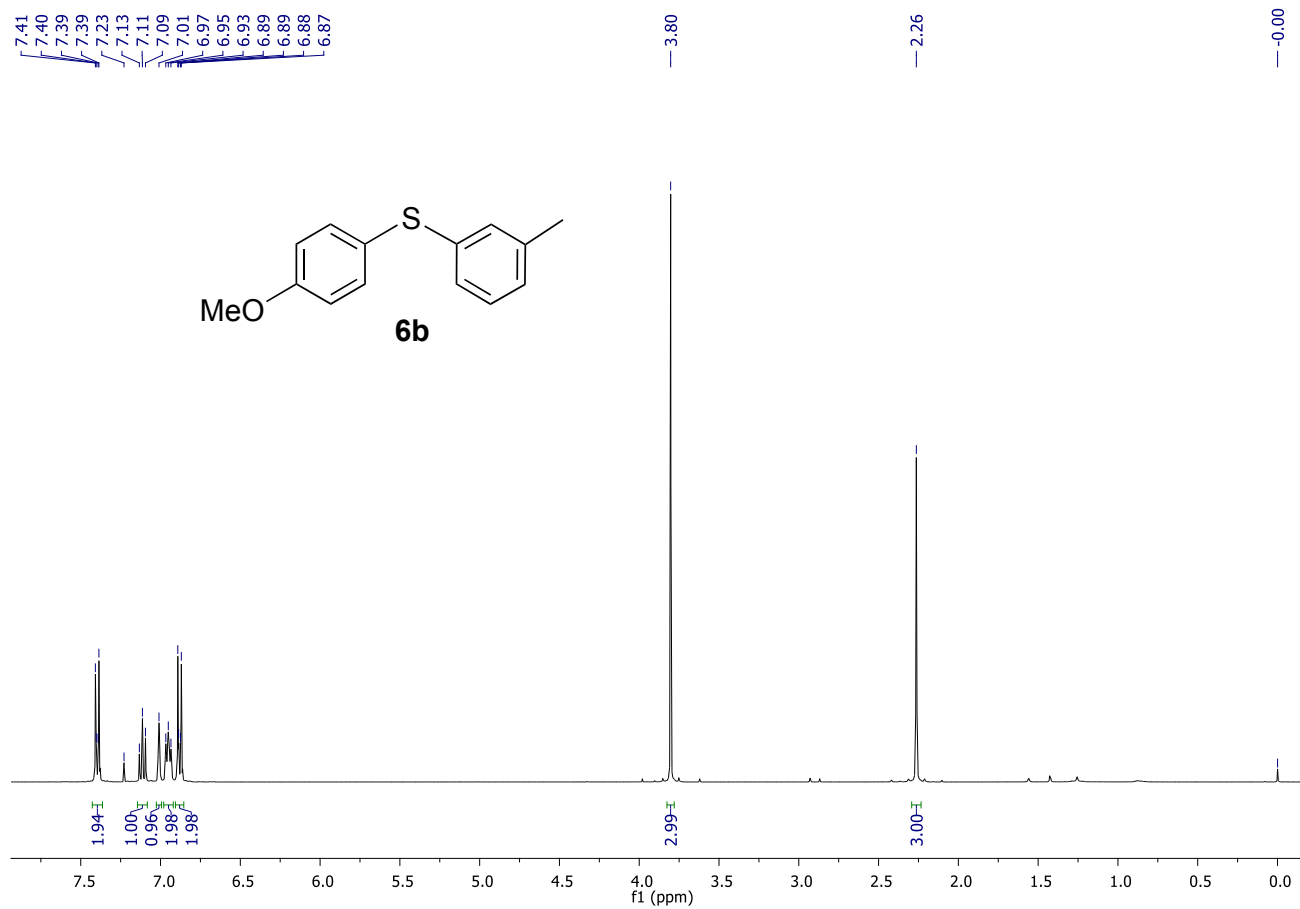


Figure S11. ¹H NMR of **6b** in CDCl₃ (with TMS)

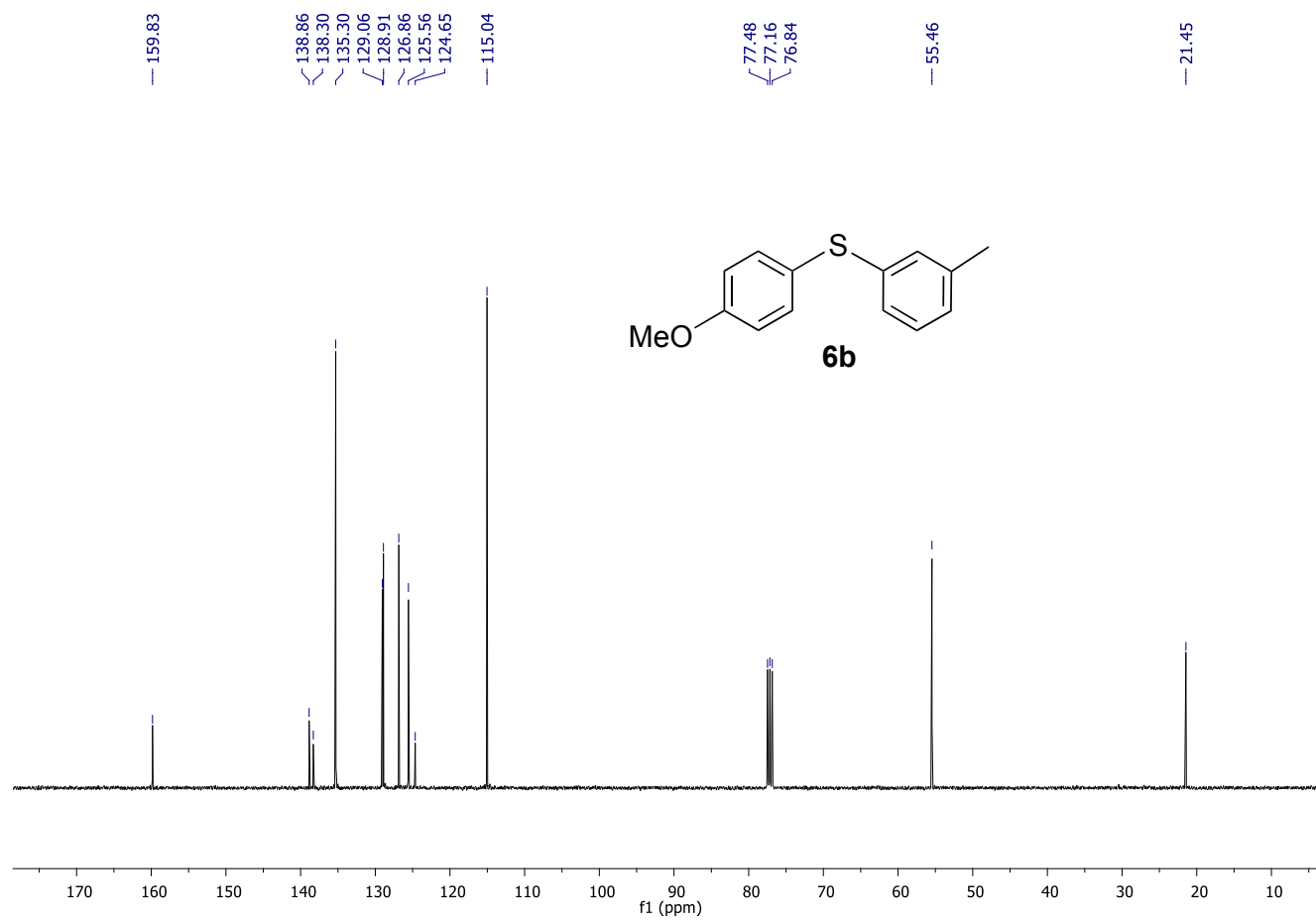


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR of **6b** in CDCl_3 (with TMS)

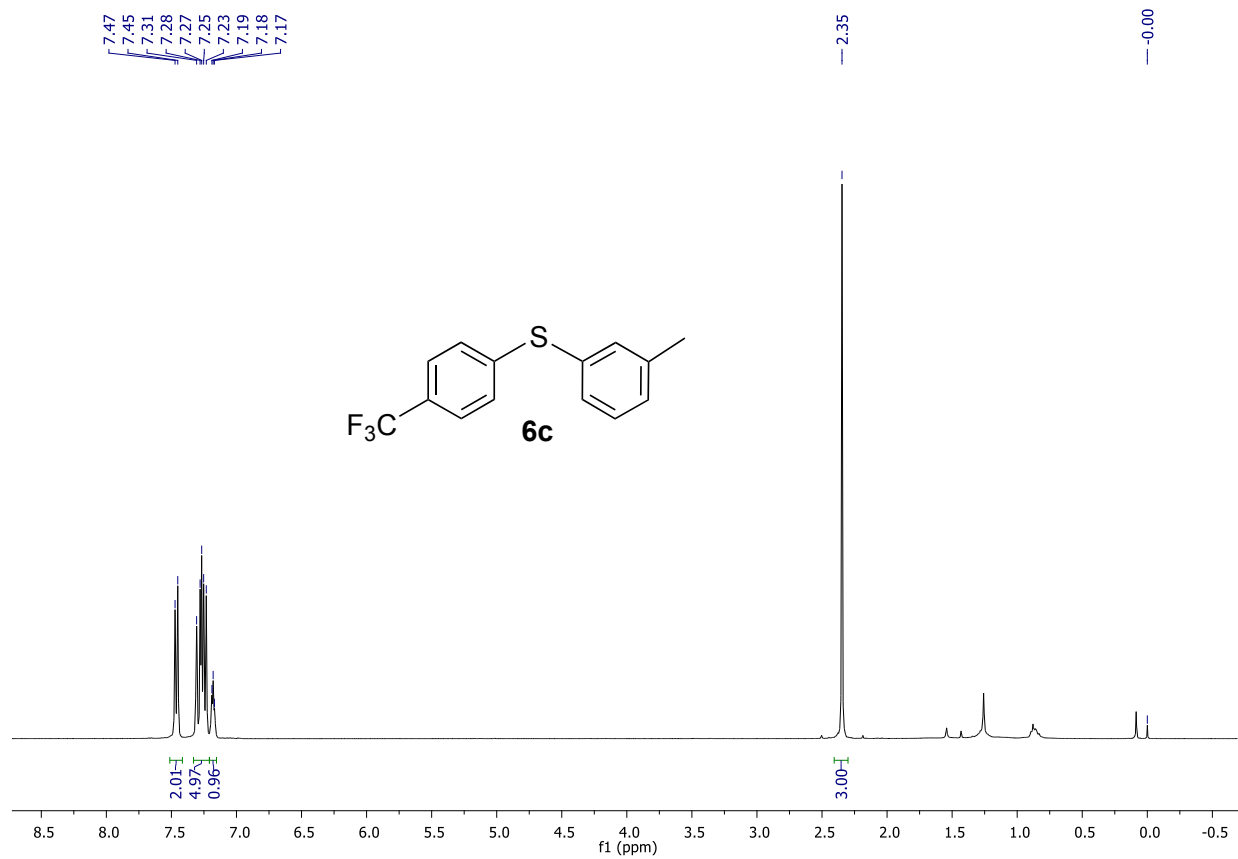


Figure S13. ^1H NMR of **6c** in CDCl_3 (with TMS)

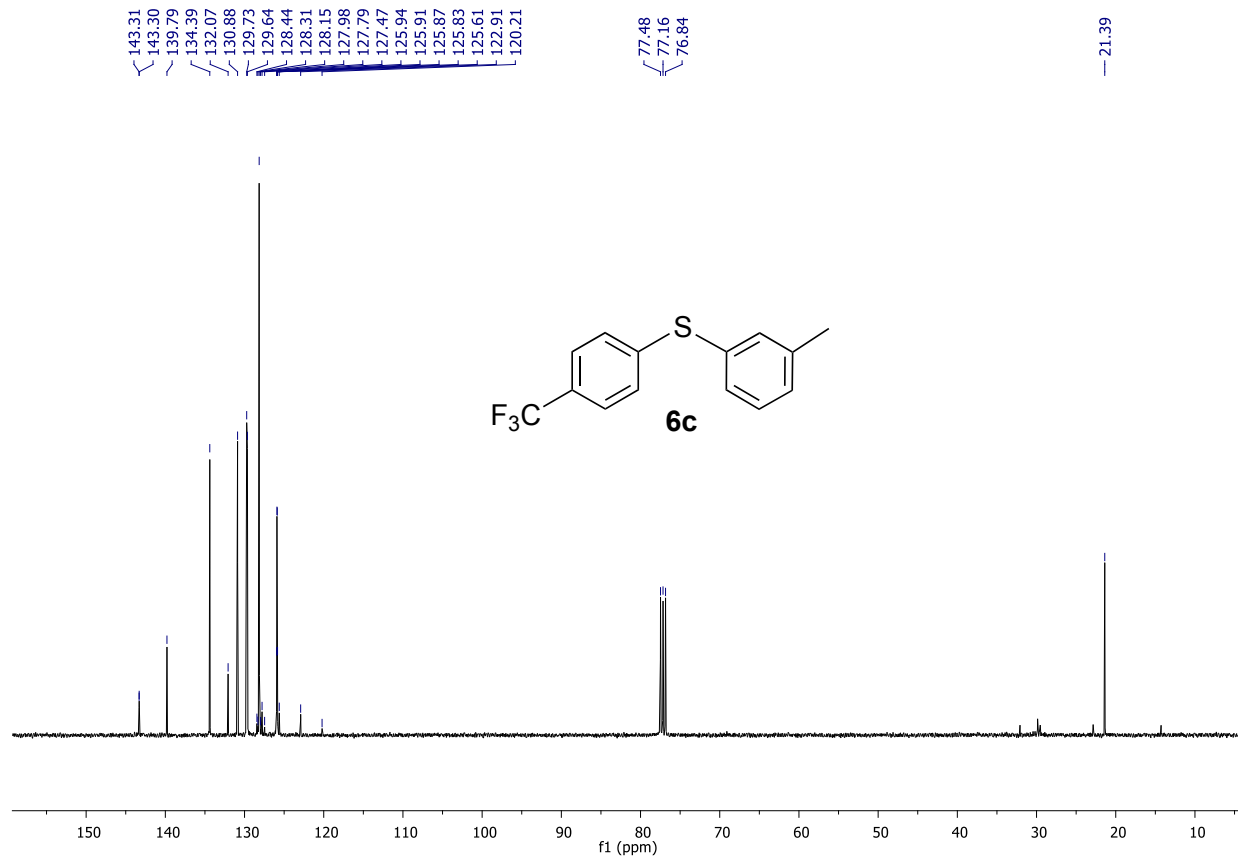


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR of **6c** in CDCl_3 (with TMS)

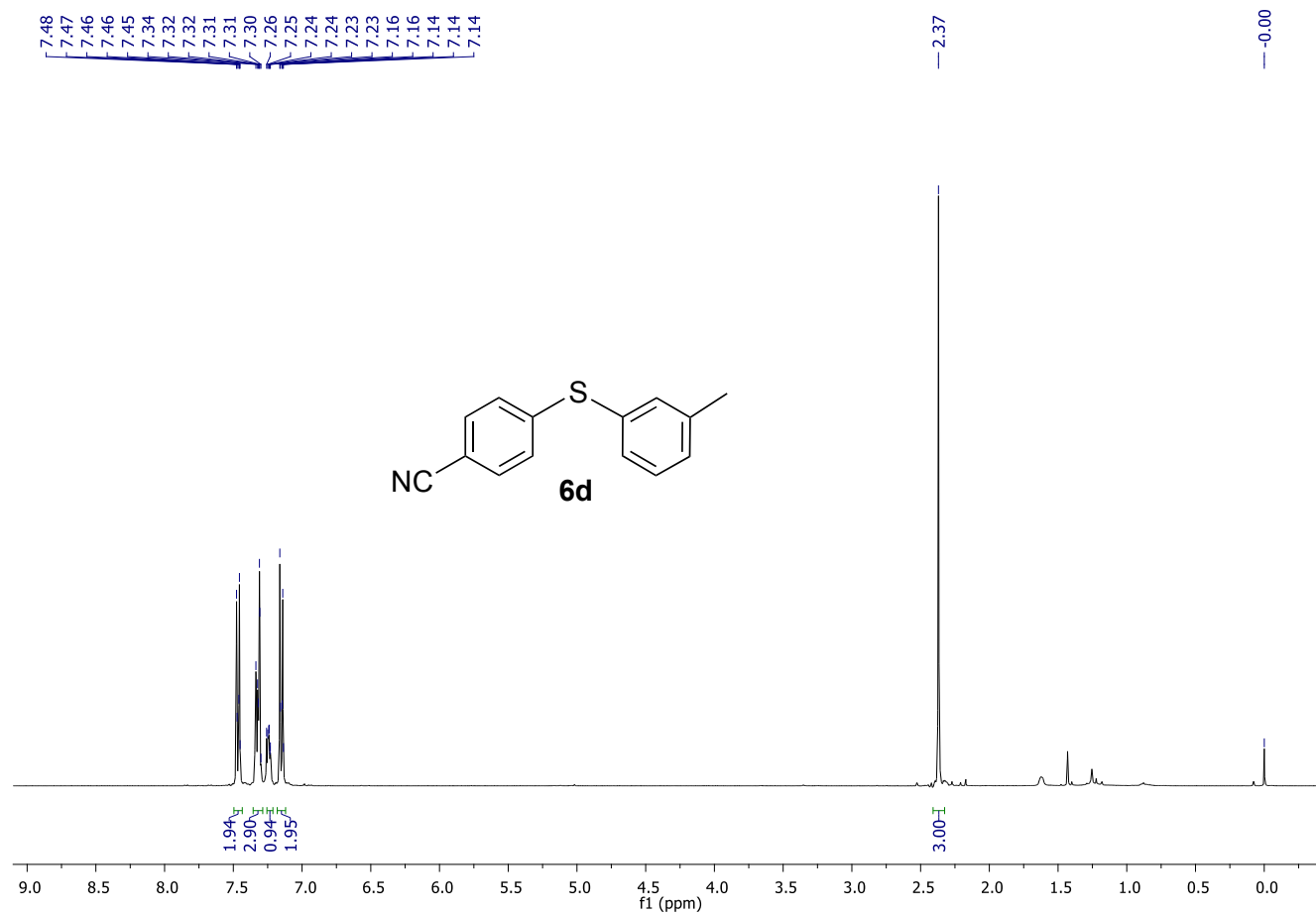


Figure S15. ¹H NMR of **6d** in CDCl₃ (with TMS)

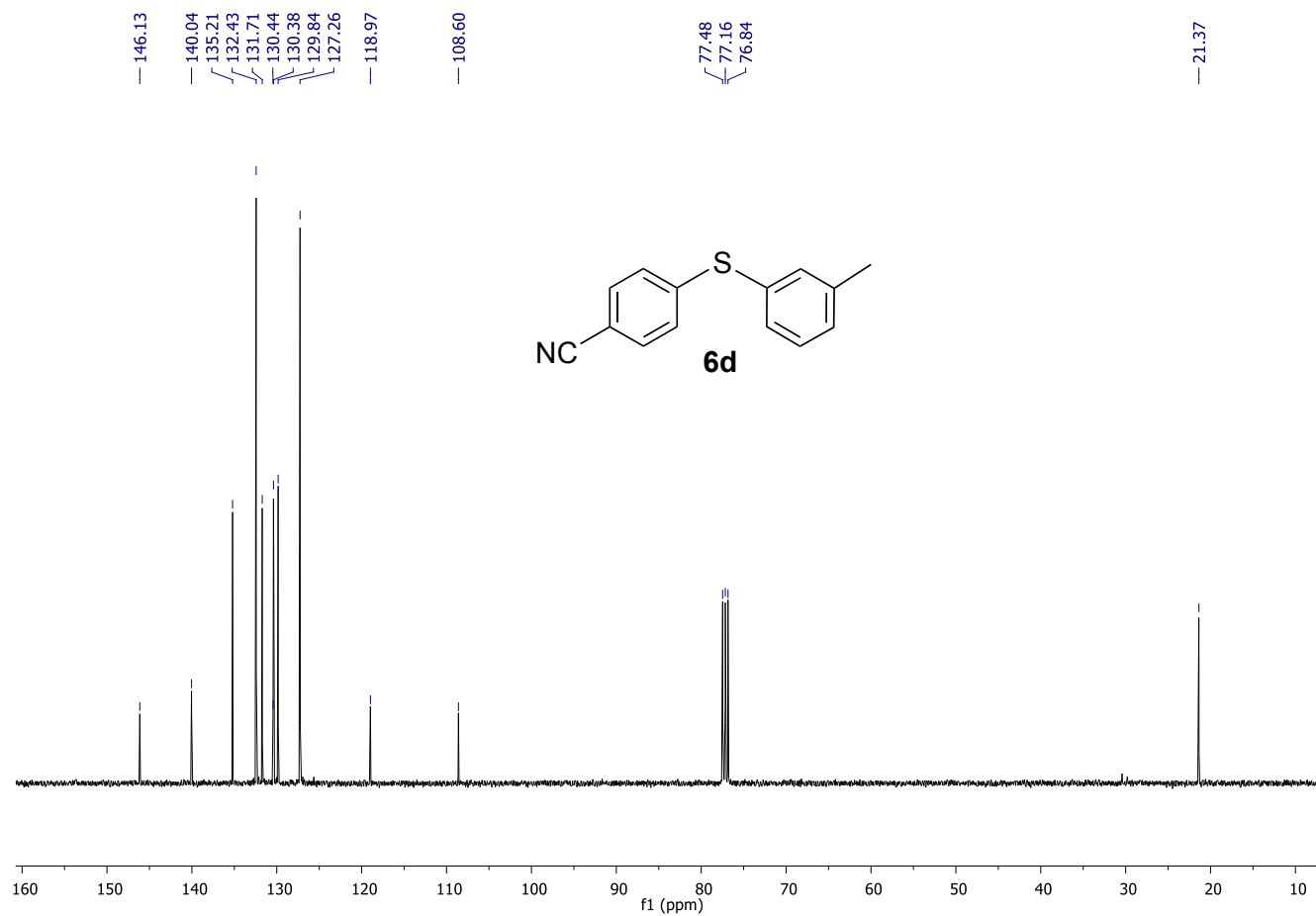


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR of **6d** in CDCl_3 (with TMS)

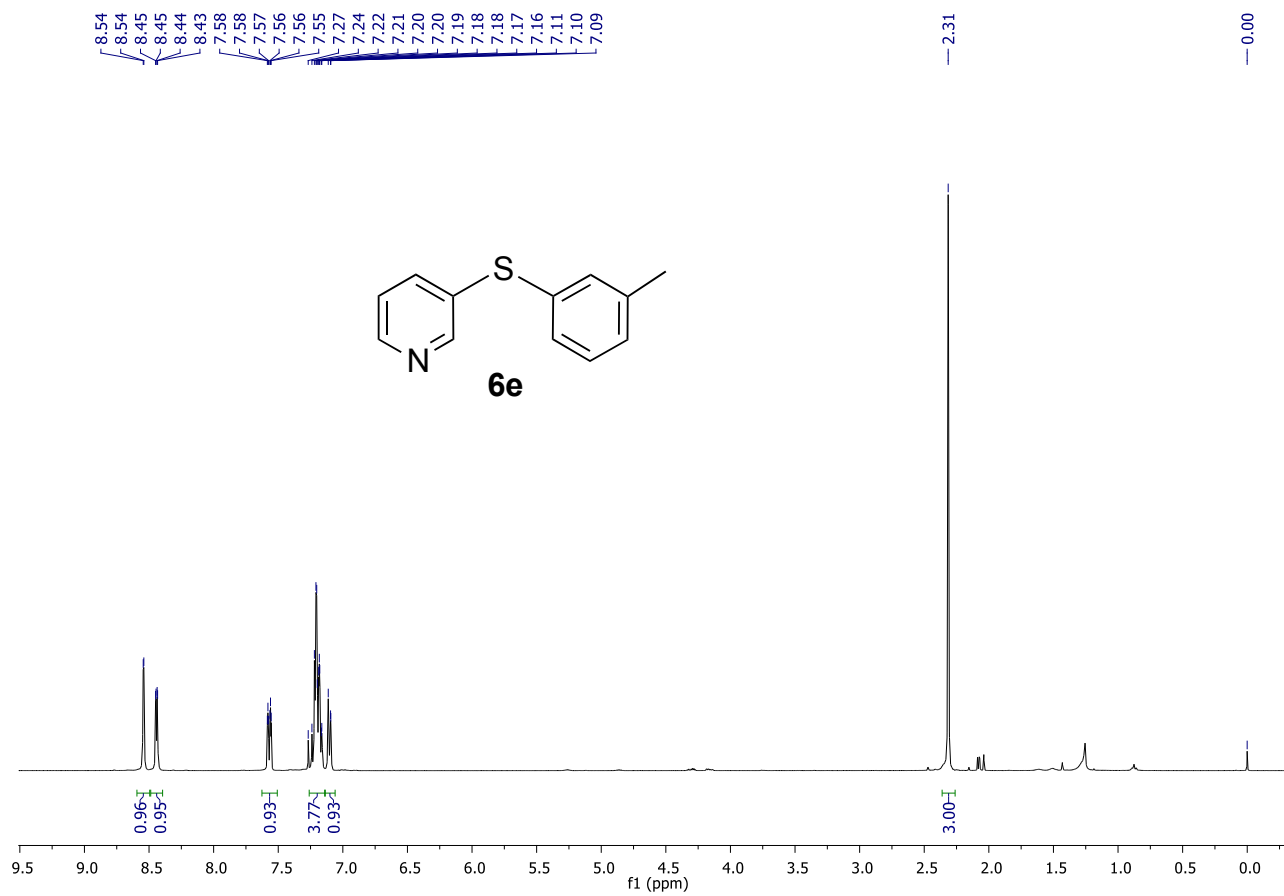


Figure S17. ¹H NMR of **6e** in CDCl₃ (with TMS)

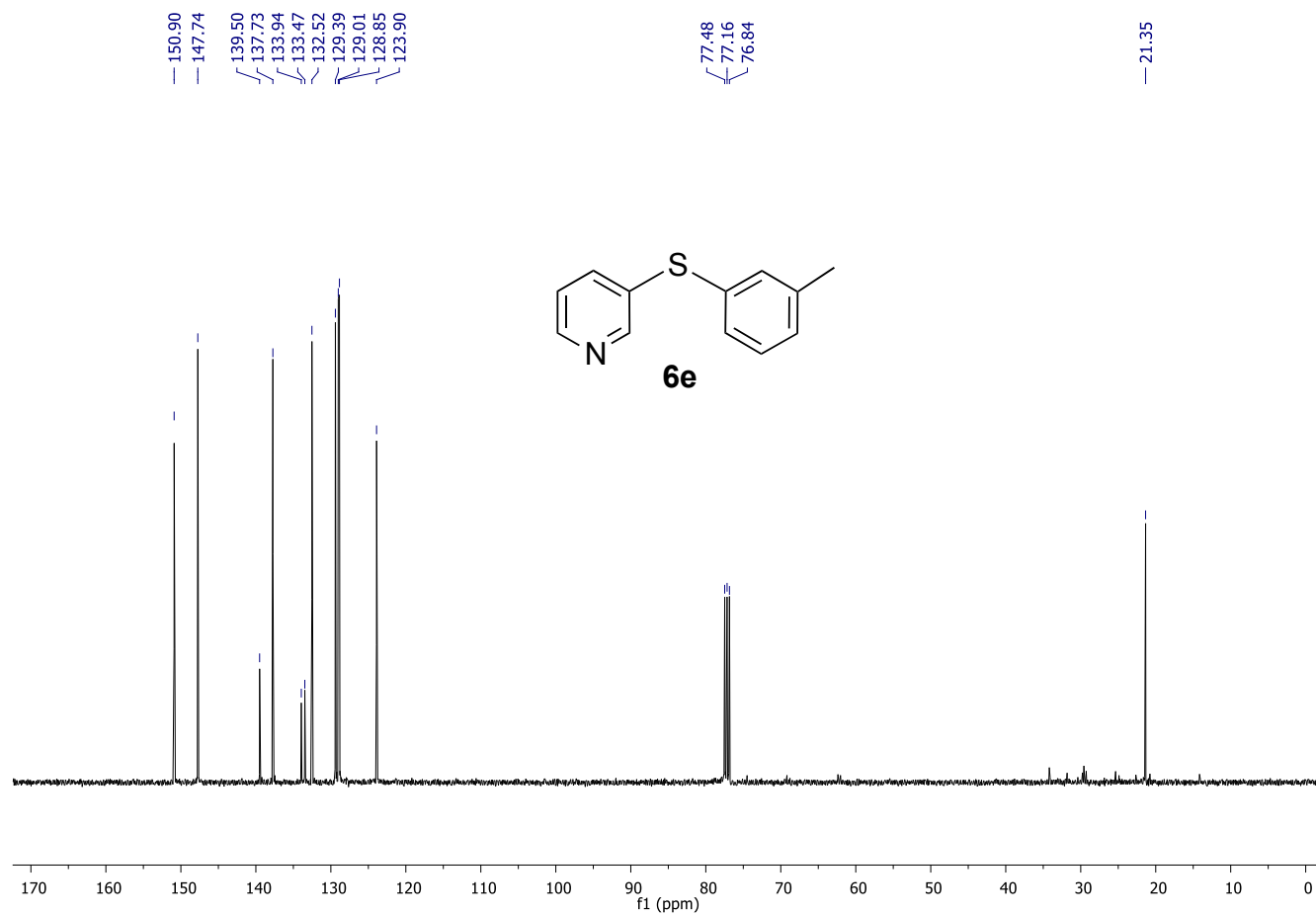


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR of **6e** in CDCl_3 (with TMS)

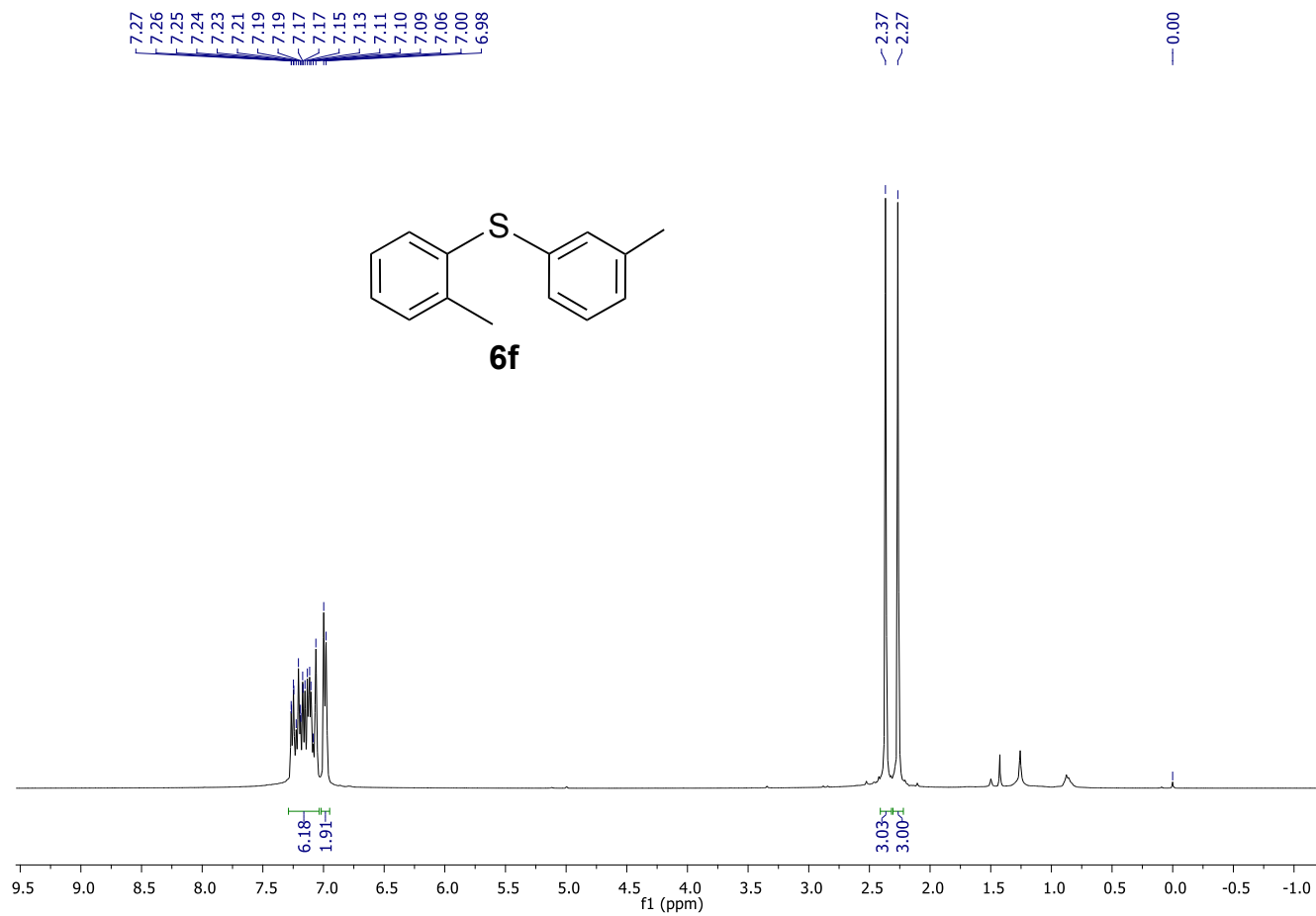


Figure S19. ¹H NMR of **6f** in CDCl₃ (with TMS)

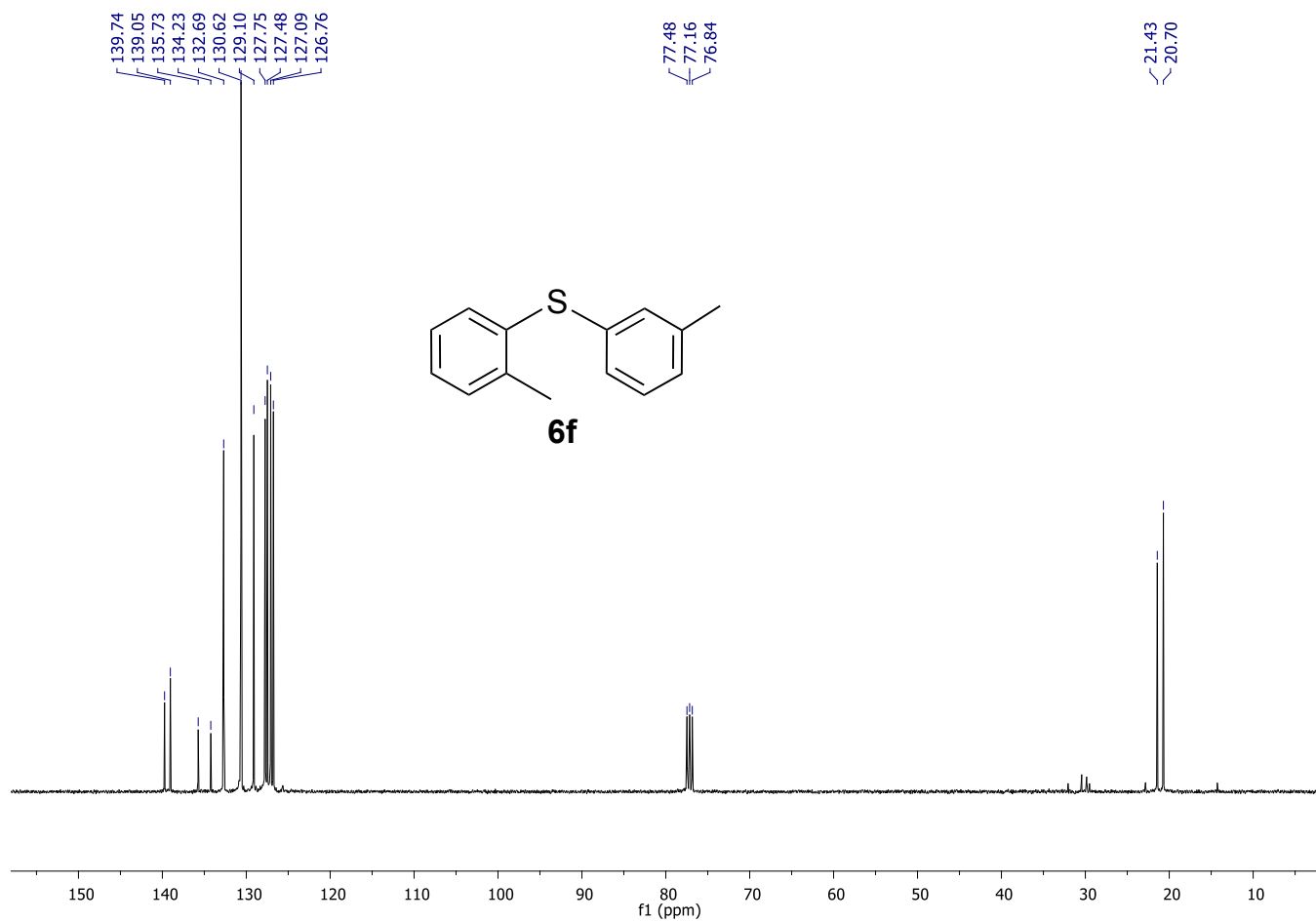


Figure S20. $^{13}\text{C}\{^1\text{H}\}$ NMR of **6f** in CDCl_3 (with TMS)

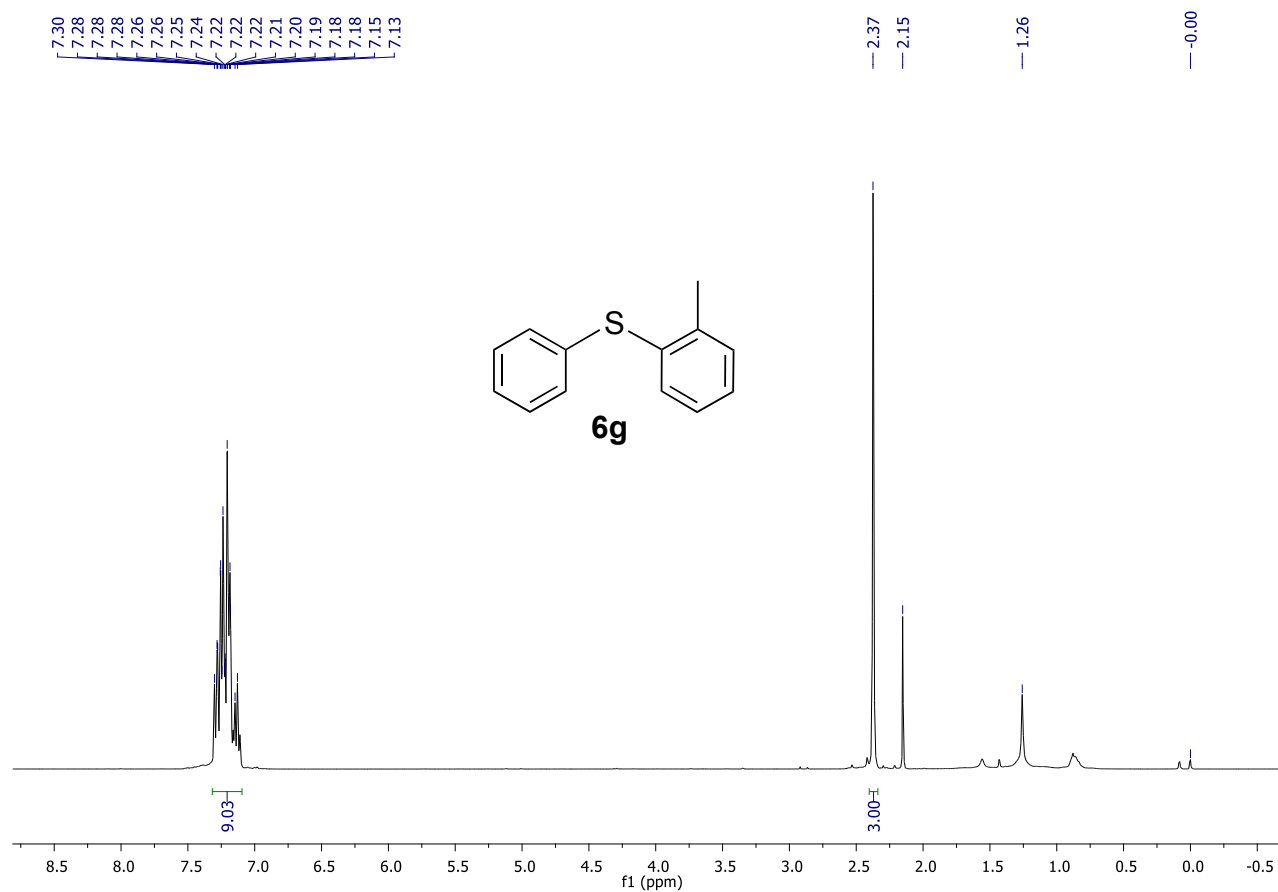


Figure S21. ^1H NMR of **6g** in CDCl_3 (with TMS)

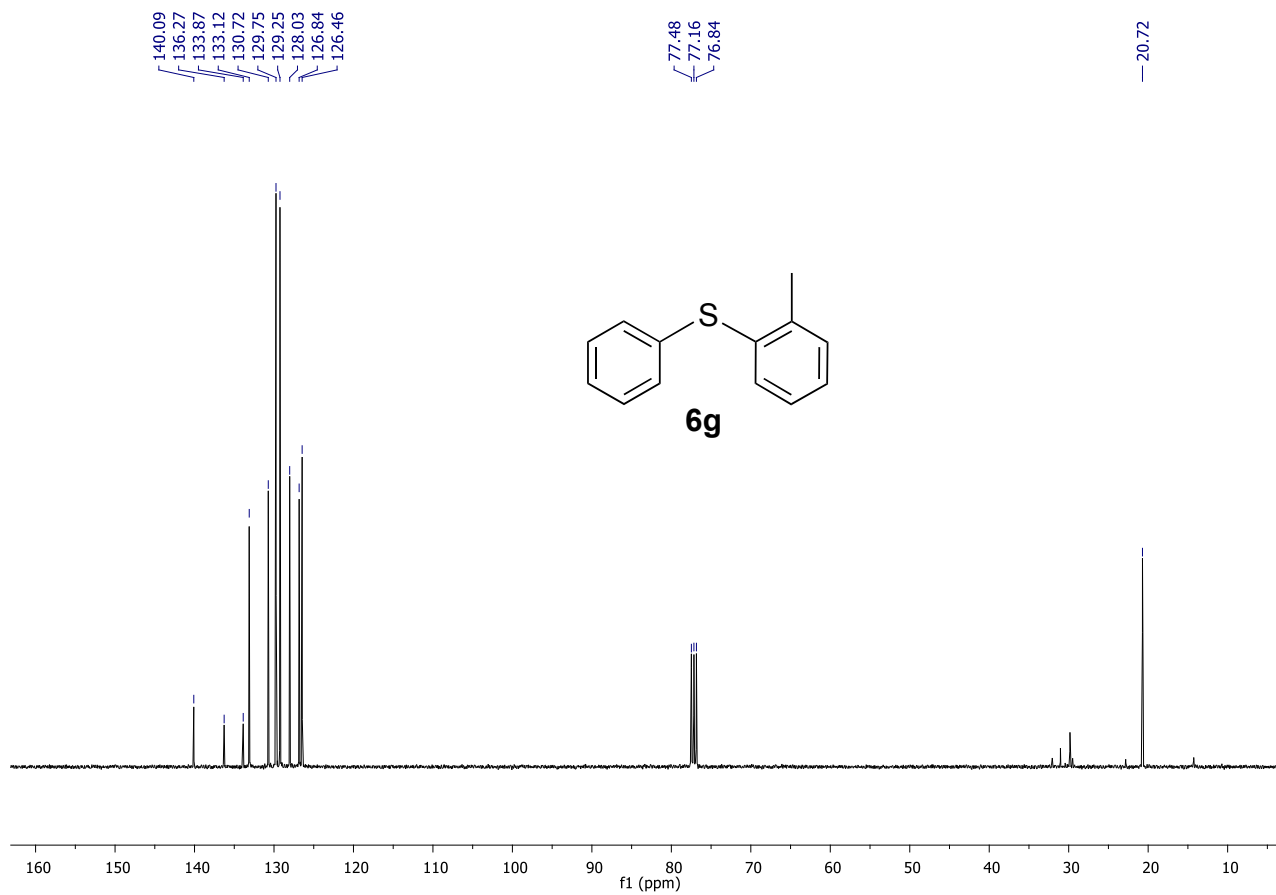


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR of **6g** in CDCl_3 (with TMS)

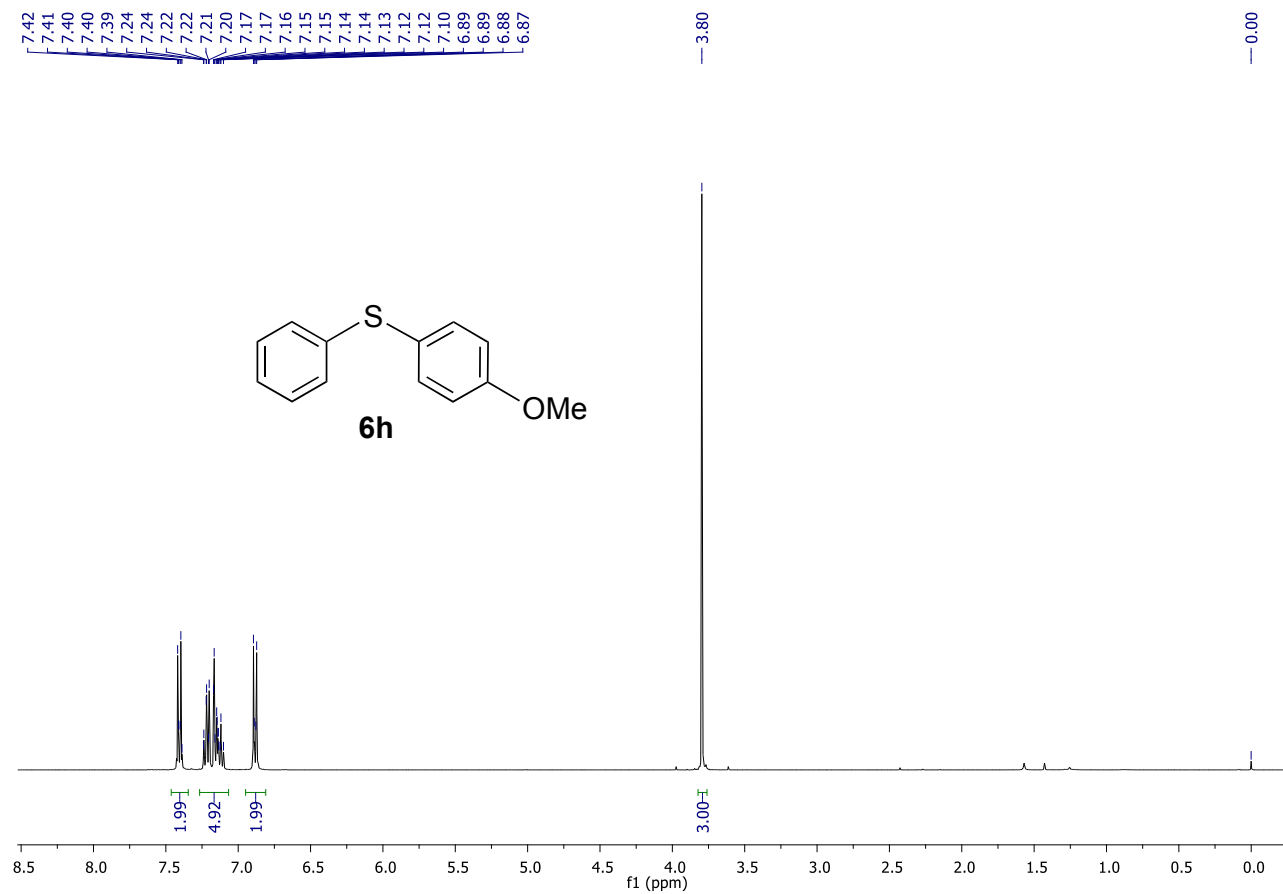


Figure S23. ¹H NMR of **6h** in CDCl₃ (with TMS)

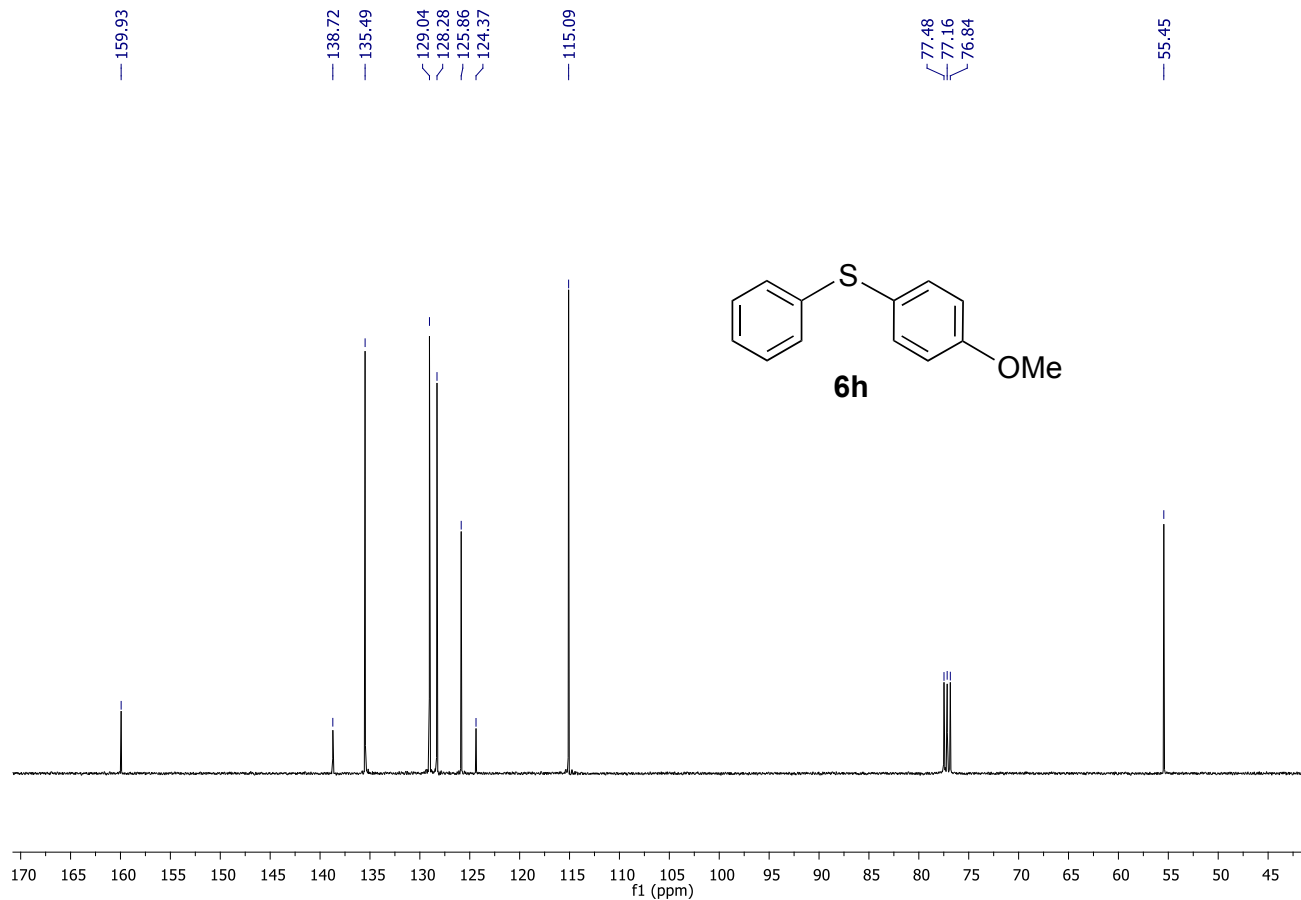


Figure S24. $^{13}\text{C}\{^1\text{H}\}$ NMR of **6h** in CDCl_3 (with TMS)

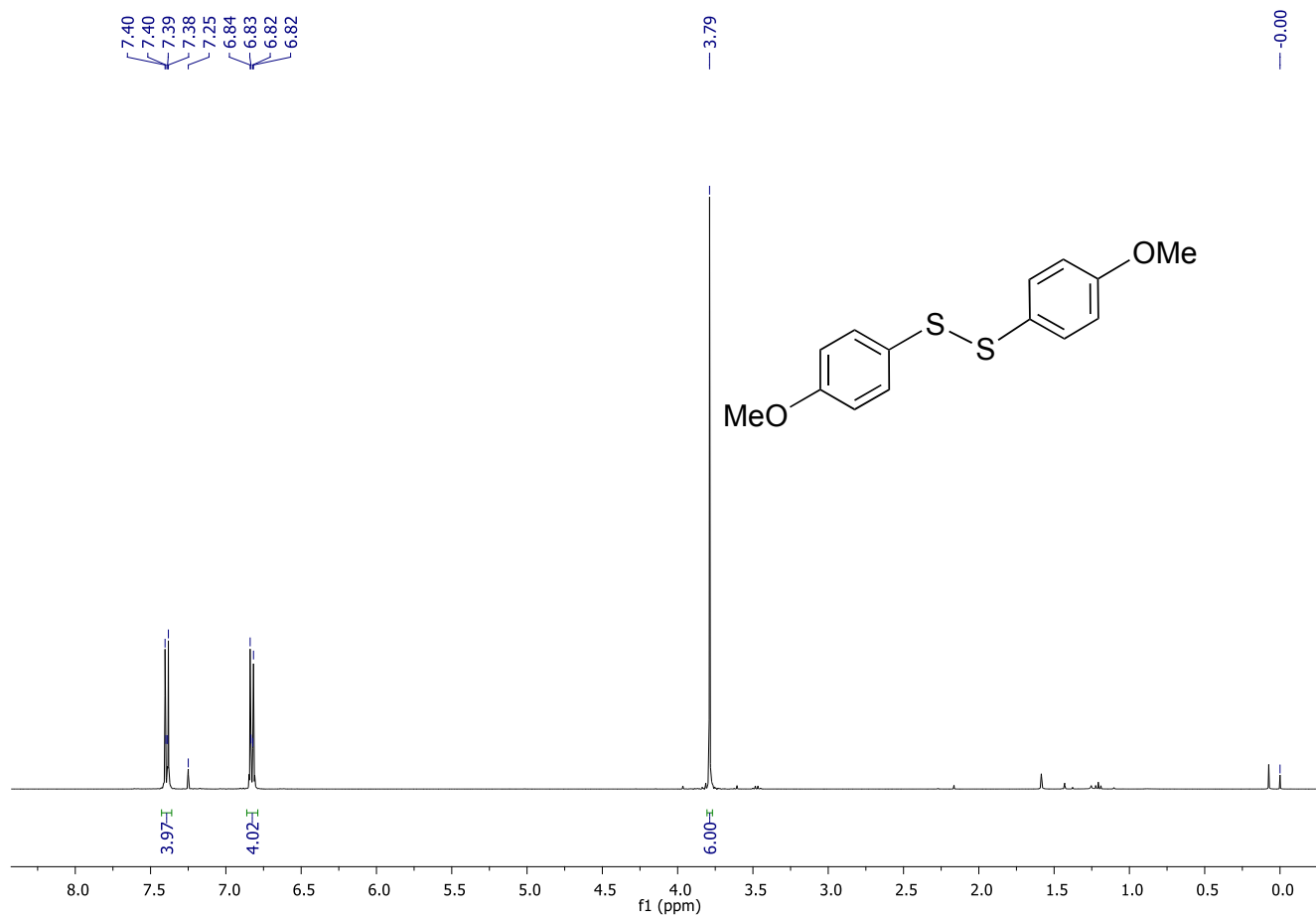


Figure S25. ¹H NMR of (p-MeOC₆H₄S)₂ in CDCl₃ (with TMS)

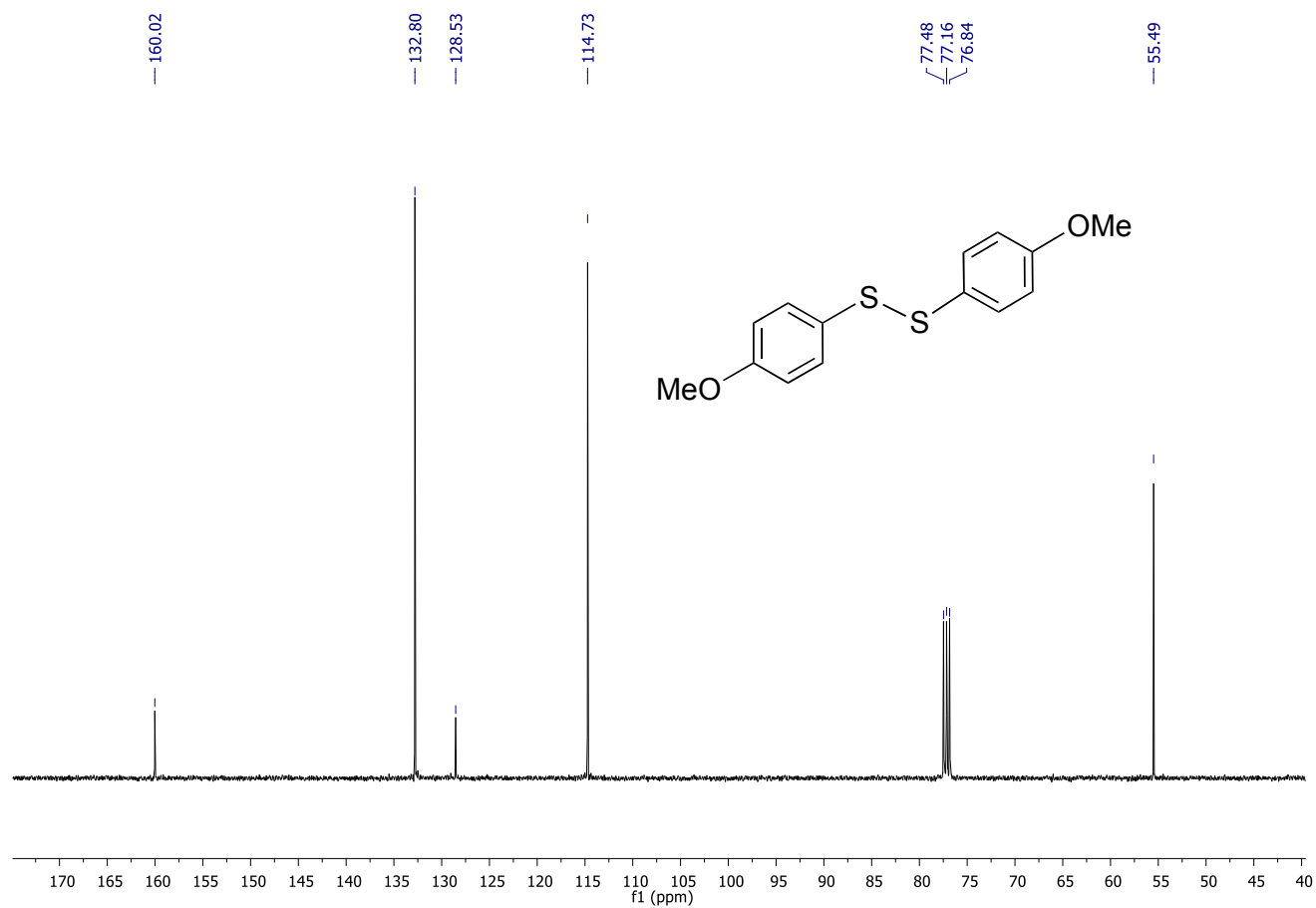


Figure S26. $^{13}\text{C}\{^1\text{H}\}$ NMR of (*p*-MeOC₆H₄S)₂ in CDCl₃ (with TMS)

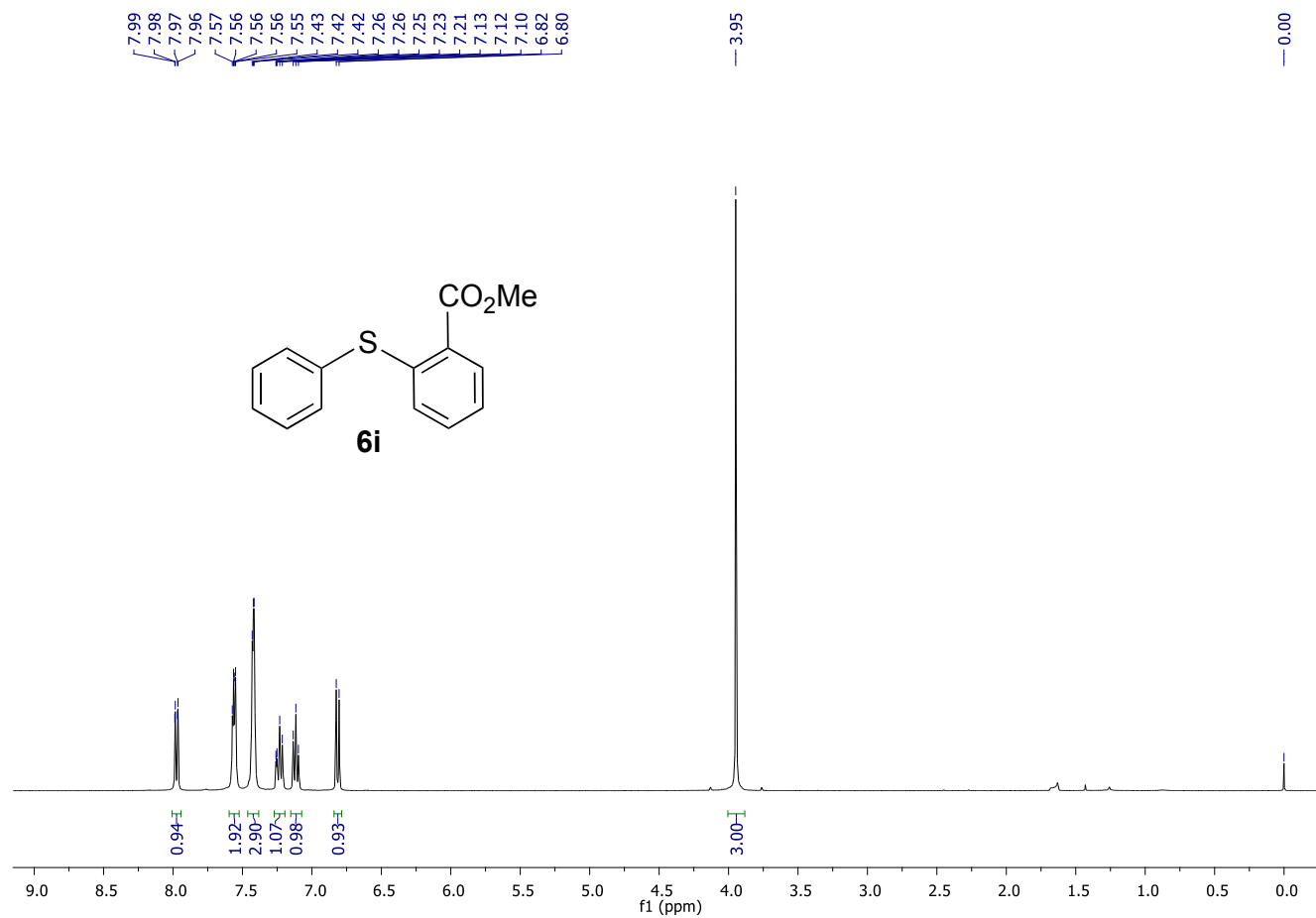


Figure S27. ¹H NMR of **6i** in CDCl₃ (with TMS)

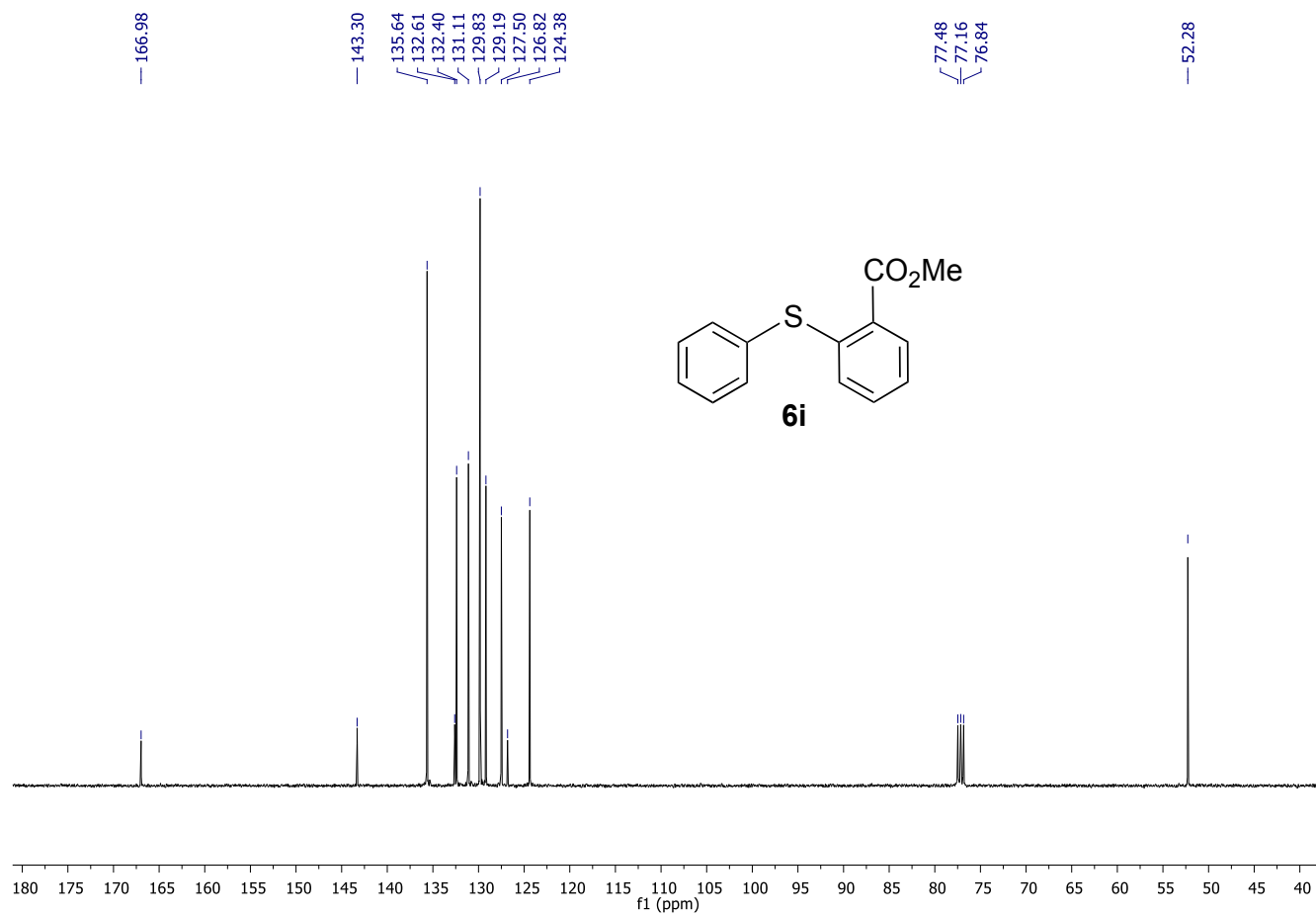


Figure S28. $^{13}\text{C}\{^1\text{H}\}$ NMR of **6i** in CDCl_3 (with TMS)

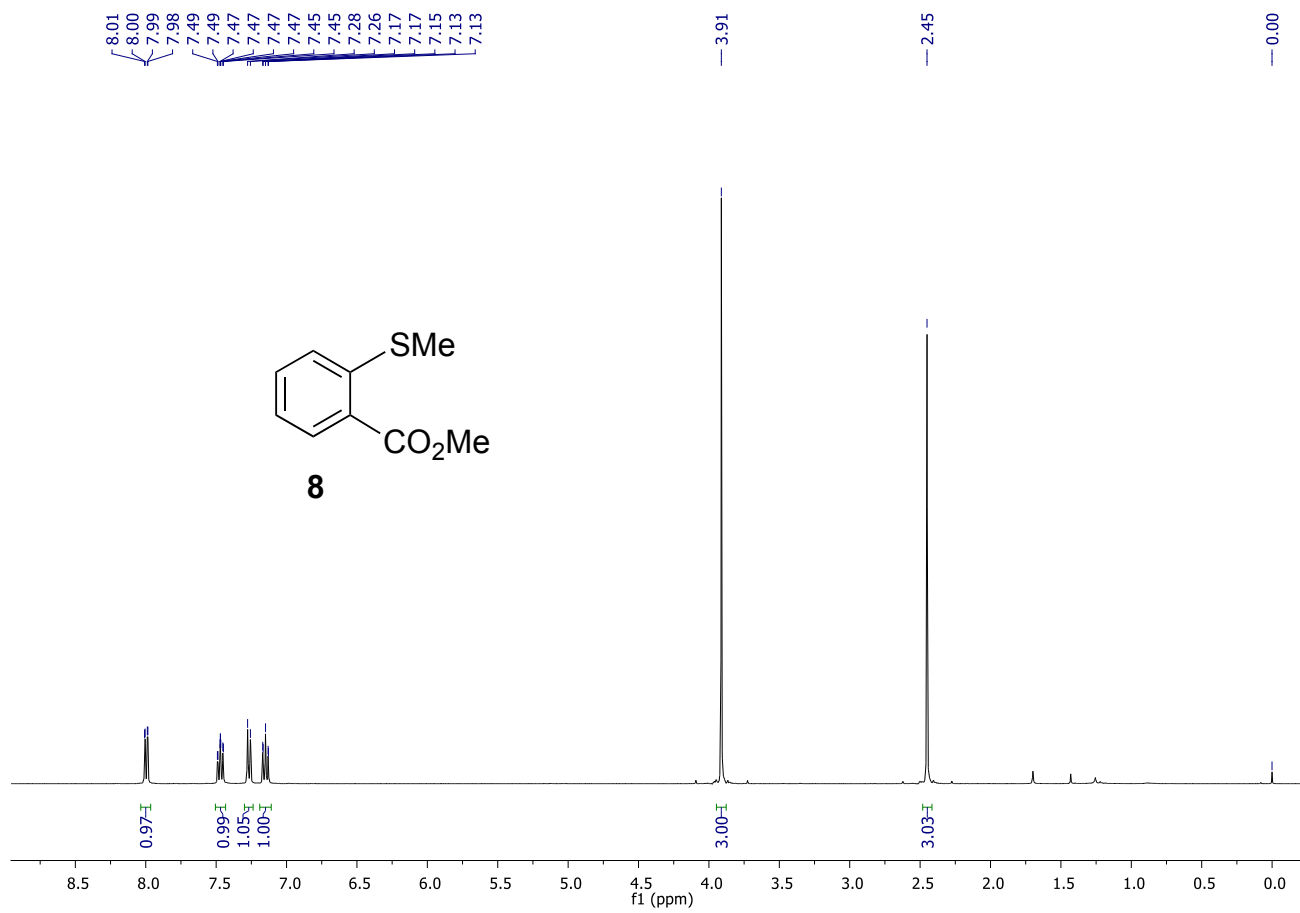


Figure S29. ¹H NMR of **8** in CDCl₃ (with TMS)

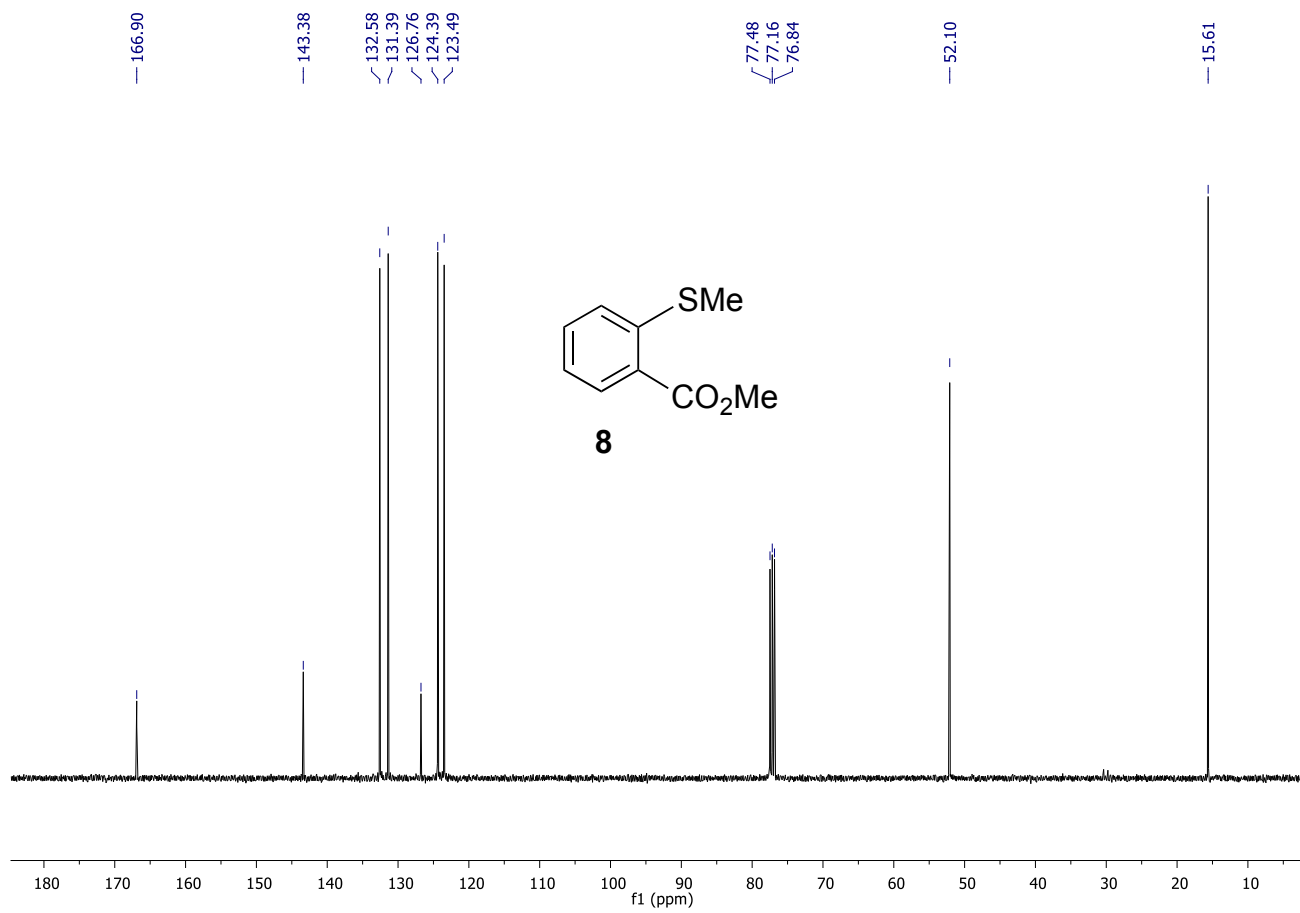


Figure S30. $^{13}\text{C}\{^1\text{H}\}$ NMR of **8** in CDCl_3 (with TMS)

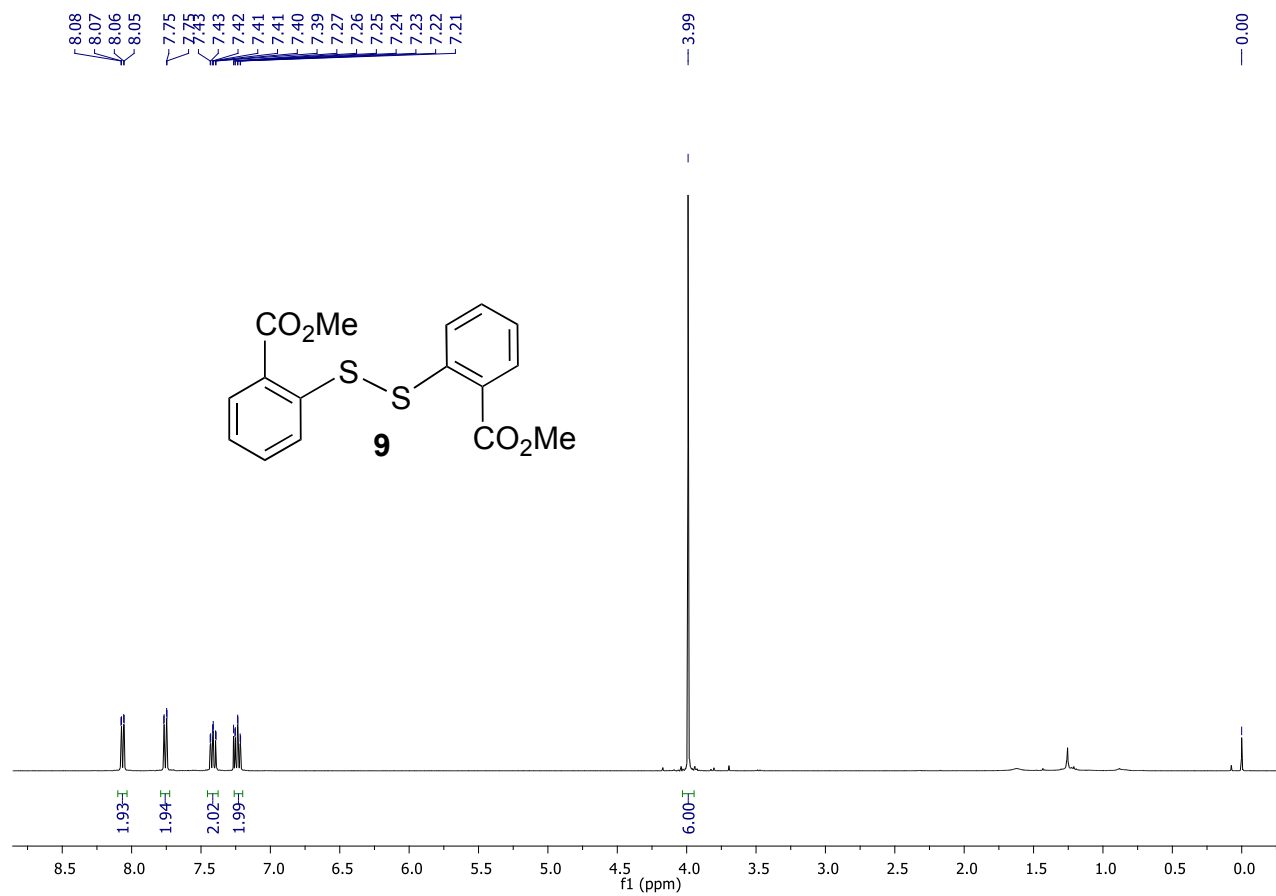


Figure S31. ¹H NMR of **9** in CDCl₃ (with TMS)

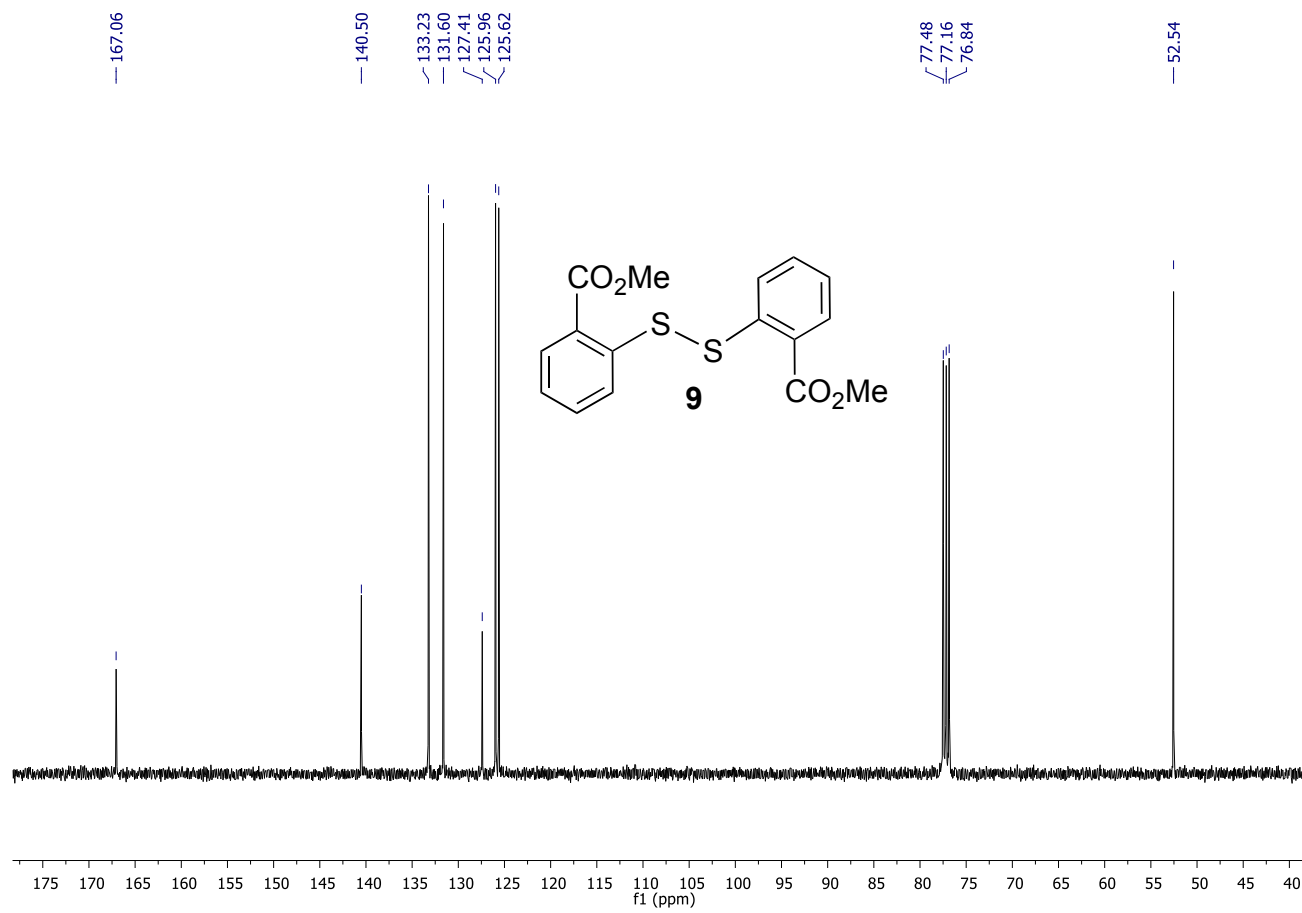


Figure S32. $^{13}\text{C}\{^1\text{H}\}$ NMR of **9** in CDCl_3 (with TMS)

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