Supporting Information

Photochemical Organocatalytic Synthesis of Thioethers from Aryl Chlorides and Alcohols

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A. General Information

The NMR spectra were recorded at 400 MHz and 500 MHz for ^{1}H, 101 or 126 MHz for ^{13}C and 376 MHz for $^{19}F\{^{1}H\}$. The chemical shift (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvents ($CHCl_3$ @ 7.26 ppm ^{1}H NMR and 77.16 ppm ^{13}C NMR). Coupling constants are given in Hertz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; q, quartet; m, multiplet; br, broad signal

High resolution mass spectra (HRMS) were obtained from the ICIQ HRMS unit on MicroTOF Focus and Maxis Impact (Bruker Daltonics) with electrospray ionization (ESI) and Atmospheric-pressure chemical ionization (APCI). Optical rotations were measured on a Polarimeter Jasco P-1030 and are reported as follows: $[\alpha]_D$ ambient temperature (c in g per 100 mL, solvent). Cyclic voltammetry studies were carried out on a Princeton Applied Research PARSTAT 2273 potentiostat, offering compliance voltage up to ± 100 V (available at the counter electrode), ± 10 V scan range and ±2 A current range.

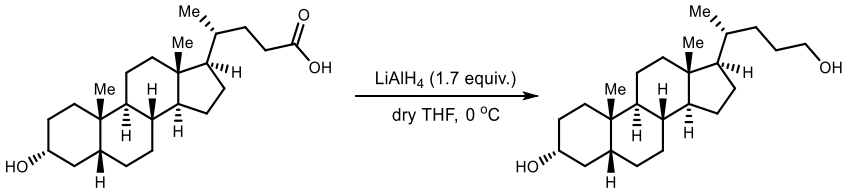
Yields refer to isolated materials of >95% purity as determined by ^{1}H NMR analysis.

General Procedures. All reactions were set up under an argon atmosphere in oven-dried glassware. Synthesis grade solvents were used as purchased, anhydrous solvents were taken from a commercial SPS solvent dispenser. Chromatographic purification of products was accomplished using forced-flow chromatography (FC) on silica gel (230-400 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were employed, using UV light as the visualizing agent and an acidic mixture of vanillin or basic aqueous potassium permanganate ($KMnO_4$) stain solutions, and heat as developing agents. Organic solutions were concentrated under reduced pressure on a Büchi rotatory evaporator.

Materials. Commercial grade reagents and solvents were purchased at the highest quality from commercial suppliers and used as received, unless otherwise stated.

B. Synthesis of Substrates and Catalysts

B1. Substrate Synthesis



An oven-dried 25 mL round-bottom flask equipped with magnetic stirring bar was charged with lithocholic acid (5 mmol, 1.0 equiv.). The flask was sealed, evacuated and refilled with nitrogen (3 times). Anhydrous THF (15 mL) was added and the resulting clear solution was cooled to 0 °C and stirred for 5 min at the same temperature. $LiAlH_4$ (8.5 mmol, 1.7 equiv.) was then added in small portions at 0 °C. After stirring at 0 °C for 1 hour, the mixture was allowed to stir at room temperature for additional 16 hours. The reaction was quenched by adding H_2O (1.4 mL) dropwise over 10 min. Then 15% w/w NaOH (1.4 mL) was added and the reaction was allowed to stirred at room temperature for 20 minutes. Then the resulting suspension was diluted with H_2O (15 mL) followed by extraction with ethyl acetate (3 ×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated to dryness under reduced pressure. The crude residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10: 1) to afford product as white solid (1.1g, 65% yield).

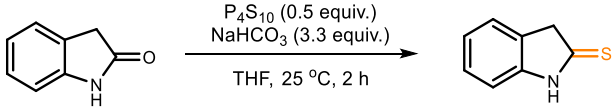
^{1}H NMR (400 MHz, CD_3OD) δ 3.68 – 3.47 (m, 3H), 2.15 – 2.06 (m, 1H), 2.05 – 1.80 (m, 4H), 1.76 – 1.63 (m, 3H), 1.60 – 1.31 (m, 14H), 1.29 – 1.12 (m, 6H), 1.06 – 0.98 (m, 6H), 0.78 (s, 3H).

^{13}C NMR (101 MHz, CD_3OD) δ 71.1, 62.2, 56.6, 56.4, 42.5, 42.2, 40.6, 40.2, 35.9, 35.9, 35.6, 35.2, 34.4, 31.9, 29.9, 29.0, 28.0, 27.0, 26.3, 24.0, 22.6, 20.6, 17.9, 11.2.

HRMS: calculated for $C_{24}H_{42}NaO_2$ ($M+Na^+$): 385.3077, found 385.3086.

B2. Catalysts Synthesis

Indoline-2-thione (catalyst **C1):**



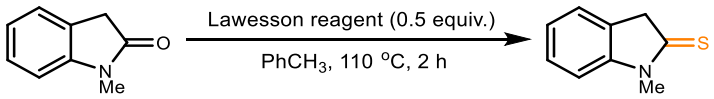
To a solution of 2-oxindole (5 mmol, 1.0 equiv.) in 15 mL of anhydrous THF, $NaHCO_3$ (10 mmol, 2.0 equiv.) was added and the reaction was stirred at room temperature for 10 minutes. P_4S_{10} (3 mmol, 0.6 equiv.) was then added portion wise and the resulting mixture was stirred at room temperature for 3 hours. On completion of the reaction, as indicated by TLC, the mixture was concentrated in vacuo to one fourth of its volume. Ice-cold water (10 mL) was then added in small portions to the oily residue with vigorous stirring, which resulted in precipitate formation. The mixture was left to stand in the ice-cold water for 15 minutes before vacuum filtration. The precipitates collected were washed with water followed by hexanes and air dried to yield product (597 mg, 80% yield). The purity was confirmed by ^{1}HNMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 7.15 – 7.09 (m, 1H), 7.06 – 6.99 (m, 1H), 4.08 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.5, 144.4, 130.5, 128.1, 124.2, 124.2, 110.2, 49.3.

Matching reported literature data.[1]

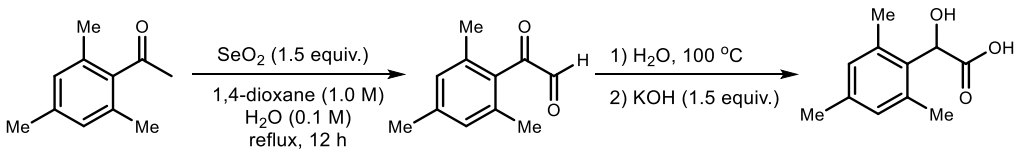
1-Methylindoline-2-thione (catalyst **C2):**



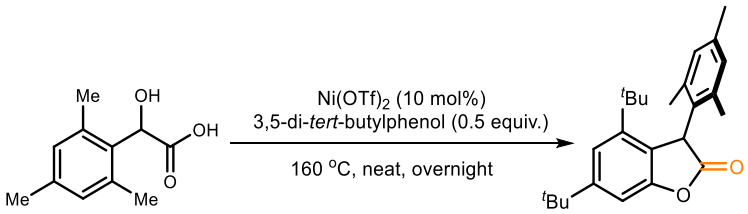
An oven dried flask was charged with 1-methylindolin-2-one (736.0 mg, 5.0 mmol, 1.0 equiv.), the Lawesson reagent (2.5 mmol, 0.5 equiv.) and toluene (20 mL). The flask was placed in an oil-bath preheated to 110 °C. After 2 hours stirring, the solution was concentrated in vacuo and the crude mixture was purified by flash column chromatography on silica gel (1% ethyl acetate in hexanes as eluent) to afford the catalyst as light yellow solid (620.5 mg, 76% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 2H), 7.19 – 7.14 (m, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 4.11 (s, 2H), 3.63 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.2, 146.6, 129.2, 128.0, 124.4, 124.0, 109.6, 49.1, 31.3.
Matching reported literature data.[2]

1-Methyl-3,4-dihydroquinoline-2(1H)-thione (catalyst **C3):**



Based on a procedure reported in the literature[3]: a solution containing 2,4,6-trimethylacetophenone (10.0 mmol), SeO_2 (15.0 mol) and water (1 mL) in 1,4-dioxane (10 mL) was heated at reflux for 12 h. During the reaction, black selenium precipitated and was broken up to aid stirring. The solution was carefully decanted to separate free selenium. Removal of the solvent in vacuo gave a yellow oil which was used for the next step without further purification. Glyoxal was then added to water (20 mL) and heated until the yellow colour disappeared. White needle-like crystals of 2,4,6-trimethylphenylgloxal hydrate precipitated from water and were collected by filtration. Crude gloxal hydrate was heated with aqueous potassium hydroxide (10 mL, 1.5 M) at 100°C for 1 h and then cooled down to ambient temperature. The solution was filtered and acidified with conc. HC1 to reach pH 1-3, when precipitation occurred. The solid was collected, carefully washed with water, air dried and recrystallised from ethanol to afford white crystalline 2,4,6-trimethylmandelic acid (1.77g, 91% yield).



Based on a literature procedure[4]: 2-hydroxy-2-mesitylacetic acid (2.0 mmol), 3,5-di-*tert*-butylphenol (1.0 mmol, 0.5 equiv.), and $Ni(OTf)_2$ (0.1 mmol, 10 mol%) were added to an oven-dried 25 mL Schlenk tube equipped with a magnetic stirring bar. The mixture was vigorously stirred at 160 °C for 12 hours under argon conditions before being cooled to ambient temperature. Then 15 mL of water was added, and the resulting mixture was extracted with EtOAc (15 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 150: 1) provided catalyst **C3** as a white solid (310 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 1.9 Hz, 1H), 7.05 (d, *J* = 1.9 Hz, 1H), 6.97 (s, 1H), 6.69 (s, 1H), 5.38 (s, 1H), 2.55 (s, 3H), 2.25 (s, 3H), 1.59 (s, 3H), 1.34 (s, 9H), 1.08 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 154.7, 152.6, 147.9, 137.5, 137.2, 137.2, 131.3, 130.9, 130.0, 121.6, 119.5, 106.3, 46.5, 35.8, 35.2, 31.4, 30.5, 21.1, 20.9, 19.6.
HRMS: calculated for $C_{24}H_{42}NaO_2$ ($M+Na^+$): 387.2295, found 387.2302.

C. Experimental Procedures

C1. Experimental Setup

- ***Set-up 1*** *405 nm EvoluChem setup* (**Figure S1**)

The reactions were performed using an *EvoluChem* P303-30-1 lamp (18 W, λ_{max}= 405 nm, 2-3 cm away), and a fan to cool down the vials (under these conditions, the reaction temperature within the reaction vessel was measured to be between 40-42 ºC).

Figure S1. Reaction setup using *EvoluChem* lamps emitting at 405 nm

- ***Set-up 2*** Gram scale experiment (**Figure S2**)

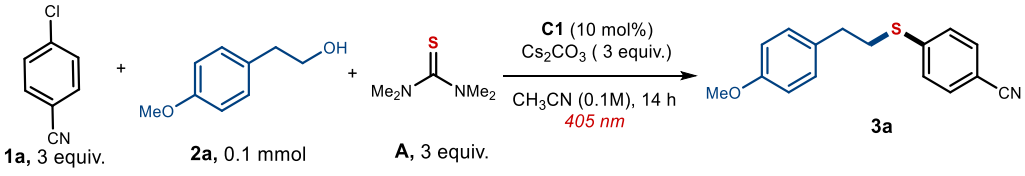
The gram scale reaction was performed under illumination by two EvoluChem P303-30-1 lamps (18 W, λ_{max}= 405 nm, 2-3 cm away from the reaction vessel) and using a fan to cool the flask.

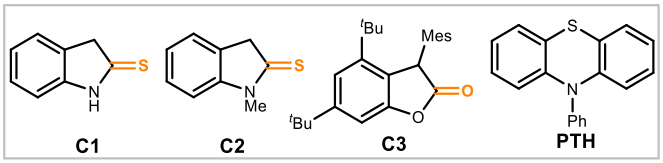
Figure S2. Setup for the gram-scale experiment using two *EvoluChem* lamps emitting at 405 nm.

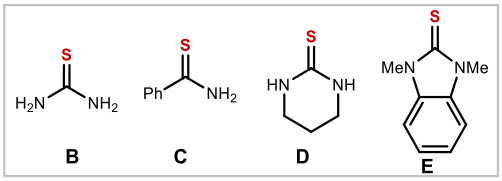
C2. Preparation of Thioethers from Alcohols and Aryl Halides Using C1 as Photocatalyst

C2.1. Optimization Studies

Table S1. Optimization of the model reaction using **C1** as catalyst



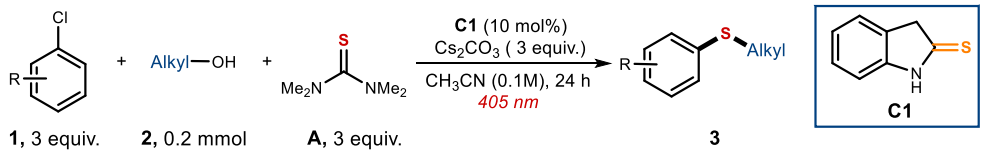




Entry	Deviations	NMRy **3a**
1	none	80%
2	No light	0%
3	No base	0%
4	No **C1**	20%
5	No **C1** and light, 50 or 70 °C	0%
6	2 equiv. **1a**, **A** and Cs_2CO_3	60%
7	5 mol% **C1**	44%
8	**C2** (10 mol%)	50%
9	**C3** (10 mol%)	30%
10	PTH (10 mol%), 456 nm	57%
11	Ir-$(ppy)_3$ (3 mol%), 456 nm	45%
12	**B-D** or elemental S_8	0%
13	**E**	60%
14	DMSO, DMF, THF, DCM as solvent	0
15	Acetone as solvent	59%
16	$KHCO_3$, K_2CO_3, K_3PO_4, TMG, *t*-BuOK as base	20-60%
17	PhCl as radical precursor	5%
18	With TEMPO	0%
19	0.2 mmol scale, 14 h	63% [a]
20	0.2 mmol scale, 24 h	85% (83%) [a]

All reactions were performed on a 0.1 mmol scale; yield of **3a** determined by ^{1}H NMR analysis of the crude reaction mixture by comparison with 1,3,5-trimethoxybenzene as internal standard. [a] Yield of isolated **3a**. Mes: mesityl.

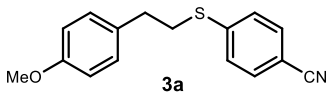
C2.2. General Procedure A for electron-deficient aryl halides



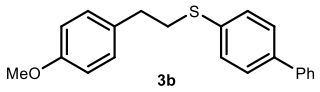
To a 7 mL glass vial, catalyst **C1** (3 mg, 0.02 mmol, 0.1 equiv.), cesium carbonate (196 mg, 0.6 mmol, 3.0 equiv.), 1,1,3,3-tetramethylthiourea (79.3 mg, 0.6 mmol, 3.0 equiv.), alcohols **2** (if solid, 0.2 mmol, 1 equiv.) and aryl chlorides **1** (if solid, 0.6 mmol, 3 equiv.) were sequentially added. The vial was sealed with a screw-top cap with septum and then vacuumed and backfilled with argon for 3 times. Afterwards, aryl chlorides **1** (if liquid, 0.6 mmol, 3.0 equiv.) and alcohols (if liquid, 0.2 mmol, 1 equiv.) followed by argon-sparged acetonitrile (0.1 M, 2.0 mL) were added *via* syringe. The vial was sealed with Parafilm and then stirred under 405 nm for 24 hours using ***Set-up 1*** detailed in **Figure S1**. After reaction was completed, the crude mixture was concentrated

and purified by column chromatography to afford the corresponding products with the reported yields (>95% purity according to ^{1}H NMR analysis).

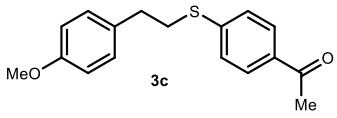
C2.3. Characterization of Products



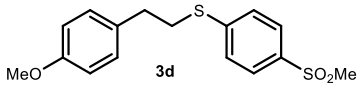
4-(4-Methoxyphenethyl)thio)benzonitrile (3a): Synthesized according to the General Procedure A using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-fluorobenzonitrile (72.5 mg, 0.6 mmol, 3.0 equiv.) or 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.) or 4-bromobenzonitrile (109.0 mg, 0.6 mmol, 3.0 equiv.) or 4-iodobenzonitrile (137.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 30: 1 as eluent) to afford **3a** (40.5 mg, 75% yield with 4-fluorobenzonitrile; 44.7 mg, 83% yield with 4-chlorobenzonitrile; 42.5 mg, 79% yield with 4-bromobenzonitrile; 35.5 mg, 66% yield with 4-iodobenzonitrile and 1.0g, 75% yield was obtained from 5 mmol scale) as a pale yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.33 – 7.27 (m, 2H), 7.16 – 7.10 (m, 2H), 6.89 – 6.82 (m, 2H), 3.80 (s, 3H), 3.24 – 3.17 (m, 2H), 2.92 (t, *J* = 7.7 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 144.8, 132.3, 131.5, 129.5, 126.90, 118.9, 114.1, 108.2, 55.3, 34.1, 33.7. HRMS: calculated for $C_{16}H_{15}NNaOS$ ($M+Na^+$): 292.0767, found 292.0763.



[1,1'-Biphenyl]-4-yl(4-methoxyphenethyl)sulfane (3b): Synthesized according to the General Procedure A using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chloro-1,1'-biphenyl (113.0 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (hexane:EtOAc = 500: 1 as eluent) to afford **3b** (47.0 mg, 73% yield) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.55 – 7.51 (m, 2H), 7.47 – 7.39 (m, 4H), 7.37 – 7.31 (m, 1H), 7.17 – 7.11 (m, 2H), 6.89 – 6.82 (m, 2H), 3.80 (s, 3H), 3.22 – 3.15 (m, 2H), 2.95 – 2.88 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 140.5, 138.9, 135.6, 132.3, 129.5, 129.4, 128.8, 127.6, 127.3, 126.9, 114.0, 55.3, 35.4, 34.8.
HRMS: calculated for $C_{21}H_{21}OS$ ($M+H^+$): 321.1308, found 321.1293.

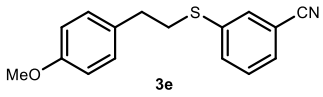


1-(4-((4-Methoxyphenethyl)thio)phenyl)ethan-1-one (3c): Synthesized according to the General Procedure A using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 1-(4-chlorophenyl)ethan-1-one (93.0 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 30: 1 as eluent) to afford **3c** (23.0 mg, 40% yield) as a pale yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 2H), 7.35 – 7.29 (m, 2H), 7.17 – 7.11 (m, 2H), 6.89 – 6.82 (m, 2H), 3.80 (s, 3H), 3.24 – 3.18 (m, 2H), 2.96 – 2.89 (m, 2H), 2.57 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 158.4, 144.4, 134.0, 131.8, 129.5, 128.8, 126.5, 114.0, 55.3, 34.3, 33.8, 26.4. HRMS: calculated for $C_{17}H_{18}NaO_2S$ ($M+Na^+$): 309.0920, found 309.0930.



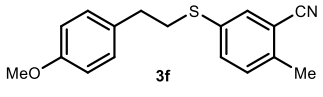
(4-Methoxyphenethyl)(4-(methylsulfonyl)phenyl)sulfane (3d): Synthesized according to the General Procedure A using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 1-chloro-4-(methylsulfonyl)benzene (114.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by

flash column chromatography on silica gel (Hexane: DCM = 1:1 as eluent) to afford **3d** (46.5 mg, 72% yield) as a yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 2H), 7.41 – 7.34 (m, 2H), 7.16 – 7.10 (m, 2H), 6.88 – 6.82 (m, 2H), 3.79 (s, 3H), 3.25 – 3.19 (m, 2H), 2.96 – 2.90 (m, 2H), 3.03 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 145.8, 136.7, 131.5, 129.5, 127.7, 126.9, 114.1, 55.3, 44.7, 34.2, 33.8.
HRMS: calculated for $C_{16}H_{18}NaO_3S_2$ ($M+Na^+$): 345.0590, found 345.0592.



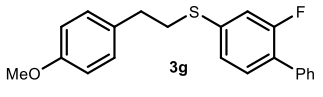
3e

3-((4-Methoxyphenethyl)thio)benzonitrile (3e): Synthesized according to the General Procedure A using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 3-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 30: 1 as eluent) to afford **3e** (34.5 mg, 64% yield) as a pale yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.45 – 7.40 (m, 1H), 7.39 – 7.32 (m, 1H), 7.15 – 7.09 (m, 2H), 6.88 – 6.81 (m, 2H), 3.80 (s, 3H), 3.21 – 3.14 (m, 2H), 2.93 – 2.86 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 139.3, 132.5, 131.5, 131.1, 129.5, 129.4, 129.0, 118.4, 114.1, 113.2, 55.3, 34.9, 34.4.
HRMS: calculated for $C_{16}H_{16}NOS$ ($M+H^+$): 270.0947, found 270.0943.



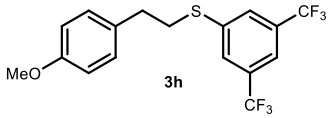
3f

5-((4-Methoxyphenethyl)thio)-2-methylbenzonitrile (3f): Synthesized according to the General Procedure A using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 5-chloro-2-methylbenzonitrile (91.0 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 30: 1 as eluent) to afford **3f** (23.5 mg, 41% yield) as a pale yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 2.1 Hz, 1H), 7.42 (dd, *J* = 8.1, 2.1 Hz, 1H). 7.24 – 7.19 (m, 1H), 7.12 – 7.07 (m, 2H), 6.87 – 6.81 (m, 2H), 3.79 (s, 3H), 3.16 – 3.10 (m, 2H), 2.89 – 2.83 (m, 2H), 2.51 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 139.4, 135.3, 133.5, 132.4, 131.7, 130.7, 129.5, 117.7, 114.0, 113.6, 55.3, 35.5, 34.6, 20.0.
HRMS: calculated for $C_{17}H_{17}NNaOS$ ($M+Na^+$): 306.0923, found 306.0928.



3g

(2-Fluoro-[1,1'-biphenyl]-4-yl)(4-methoxyphenethyl)sulfane (3g): Synthesized according to the General Procedure A using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-bromo-2-fluoro-1,1'-biphenyl (151.0 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane:EtOAc = 200: 1 as eluent) to afford **3g** (27.0 mg, 40% yield) as a pale yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 2H), 7.49 – 7.42 (m, 3H), 7.39 – 7.34 (m, 2H), 7.17 – 7.13 (m, 3H), 6.89 – 6.84 (m, 2H), 3.80 (s, 3H), 3.22 – 3.16 (m, 2H), 2.97 – 2.90 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 158.4, 138.1 (d, *J* = 8.3 Hz), 135.4 (d, *J* = 8.3 Hz), 132.0, 130.9 (d, *J* = 4.3 Hz), 129.5, 128.9 (d, *J* = 3.1 Hz), 128.5, 127.7, 126.4 (d, *J* = 13.9 Hz), 124.4 (d, *J* = 3.4 Hz), 115.8 (d, *J* = 25.1 Hz), 114.0, 55.3, 35.0, 34.6.
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -117.3.
HRMS: calculated for $C_{21}H_{19}FNaOS$ ($M+Na^+$): 361.1033, found 361.1033.



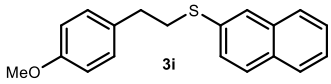
(3,5-Bis(trifluoromethyl)phenyl)(4-methoxyphenethyl)sulfane (3h): Synthesized according to the General Procedure A using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 1-bromo-3,5-bis(trifluoromethyl)benzene (175.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 500: 1 as eluent) to afford **3h** (49.5 mg, 65% yield) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.64 – 7.60 (m, 1H), 7.17 – 7.10 (m, 2H), 6.89 – 6.83 (m, 2H), 3.80 (s, 3H), 3.28 – 3.22 (m, 2H), 2.97 – 2.90 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 140.9, 132.1 (q, J = 33.3 Hz), 131.2 129.5, 127.6 – 127.3 (m, 1C), 124.5(q, J = 273.7 Hz), 119.1 – 118.8 (m, 1C), 114.1, 55.2, 34.8, 34.3.

^{19}F{^{1}H} NMR (376 MHz, CDCl3) δ -63.2.

HRMS: calculated for $C_{17}H_{13}F_6OS$ (M^+): 379.0586, found 379.0588.

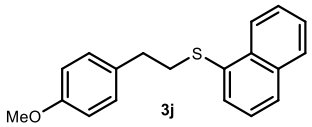


(4-Methoxyphenethyl)(naphthalen-2-yl)sulfane (3i): Synthesized according to the General Procedure A using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 2-chloronaphthalene (97.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford **3i** (44.5 mg, 75% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.73 (m, 4H), 7.52 – 7.42 (m, 3H), 7.18 – 7.13 (m, 2H), 6.90 – 6.83 (m, 2H), 3.80 (s, 3H), 3.29 – 3.23 (m, 2H), 2.97 – 2.91 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 134.1, 133.8, 132.3, 131.8, 129.5, 128.4, 127.6, 127.4, 127.1, 126.8, 126.6, 125.6, 114.0, 55.3, 35.3, 34.7.

HRMS: calculated for $C_{19}H_{19}OS$ ($M+H^+$): 295.1151, found 295.1138.

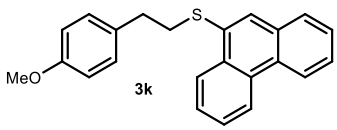


(4-Methoxyphenethyl)(naphthalen-1-yl)sulfane (3j): Synthesized according to the General Procedure A using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 1-chloronaphthalene (97.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford **3j** (47.0 mg, 80% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.40 (m, 1H), 7.89 – 7.85 (m, 1H), 7.77 – 7.74 (m, 1H), 7.63 – 7.60 (m, 1H), 7.59 – 7.51 (m, 2H), 7.45 – 7.41 (m, 1H), 7.14 – 7.10 (m, 2H), 6.86 – 6.82 (m, 2H), 3.80 (s, 3H), 3.24 – 3.19 (m, 2H), 2.94 – 2.89 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 134.0, 133.7, 133.1, 132.4, 129.5, 128.6, 128.1, 127.2, 126.4, 126.2, 125.6, 125.1, 113.9, 55.3, 36.0, 34.8.

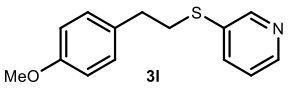
HRMS: calculated for $C_{19}H_{19}OS$ ($M+H^+$): 295.1151, found 295.1137.



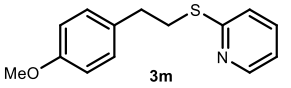
(4-Methoxyphenethyl)(phenanthren-9-yl)sulfane (3k): Synthesized according to the General Procedure A using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 9-bromophenanthrene (154.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford **3k** (34.5 mg, 50% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.70 (m, 1H), 8.67 – 8.63 (m, 1H), 8.51 – 8.47 (m, 1H), 7.84 – 7.80 (m, 2H), 7.72 – 7.67 (m, 2H), 7.65 – 7.58 (m, 2H), 7.17 – 7.12 (m, 2H), 6.87 – 6.82 (m, 2H), 3.79 (s, 3H), 3.31 – 3.26 (m, 2H), 3.00 – 2.94 (m, 2H).

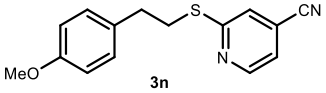
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 134.1, 133.8, 132.3, 131.6, 129.5, 128.4, 127.8, 127.4, 127.1, 126.8, 126.6, 125.6, 114.0, 55.3, 35.3, 34.7.
HRMS: calculated for $C_{23}H_{21}OS$ ($M+H^+$): 345.1308, found 345.1294.



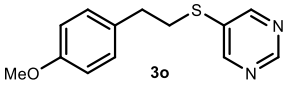
3-((4-Methoxyphenethyl)thio)pyridine (3l): Synthesized according to the General Procedure A using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 3-chloropyridine (68.0 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (DCM as eluent) to afford **3l** (37.5 mg, 76% yield) as a yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 1.6 Hz, 1H), 8.42 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.63 (ddd, *J* = 8.0, 2.4, 1.5 Hz, 1H), 7.20 (ddd, *J* = 8.0, 4.8, 0.8 Hz, 1H). 7.12 – 7.07 (m, 2H), 6.86 – 6.82 (m, 2H), 3.78 (s, 3H), 3.17 – 3.12 (m, 2H), 2.89 – 2.85 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 150.3, 147.2, 136.9, 133.6, 131.7, 129.5, 123.6, 114.0, 55.3, 35.5, 34.7.
HRMS: calculated for $C_{14}H_{16}NOS$ ($M+H^+$): 246.0947, found 246.0956.



2-((4-Methoxyphenethyl)thio)pyridine (3m): Synthesized according to the General Procedure A using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 2-chloropyridine (80.0 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 100: 1 as eluent) to afford **3m** (24.5 mg, 50% yield) as a yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 – 8.42 (m, 1H), 7.50 – 7.43 (m, 1H), 7.22 – 7.14 (m, 3H), 7.01 – 6.94 (m, 1H), 6.88 – 6.82 (m, 2H), 3.80 (s, 3H), 3.43 – 3.36 (m, 2H), 3.00 – 2.92 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 158.2, 149.5, 135.8, 132.7, 129.6, 122.4, 119.3, 113.9, 55.3, 34.9, 31.7.
HRMS: calculated for $C_{14}H_{16}NOS$ ($M+H^+$): 246.0947, found 246.0957.

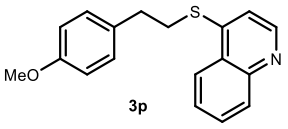


2-((4-Methoxyphenethyl)thio)isonicotinonitrile (3n): Synthesized according to the General Procedure A using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 2-chloroisonicotinonitrile (83.0 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 50: 1 as eluent) to afford **3n** (22.0 mg, 41% yield) as a yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.19 – 7.13 (m, 3H), 6.87 – 6.83 (m, 2H), 3.80 (s, 3H), 3.43 – 3.38 (m, 2H), 2.97 – 2.93 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 158.3, 150.2, 132.1, 129.6, 124.0, 120.2, 119. 9, 116.3, 113.9, 55.3, 34.7, 31.8.
HRMS: calculated for $C_{15}H_{15}N_2OS$ ($M+H^+$): 271.0900, found 271.0897.



5-((4-Methoxyphenethyl)thio)pyrimidine (3o): Synthesized according to the General Procedure A using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 5-bromopyrimidine (95.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (DCM: EtOAc = 50: 1 as eluent) to afford **3o** (20.5 mg, 42% yield) as a yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.66 (s, 2H), 7.13 – 7.07 (m, 2H), 6.87 – 6.81 (m, 2H), 3.79 (s, 3H), 3.22 – 3.15 (m, 2H), 2.93 – 2.87 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 156.9, 155.9, 133.1, 131.1, 129.5, 114.1, 55.3, 35.3, 34.7.

HRMS: calculated for $C_{13}H_{15}N_2OS$ ($M+H^+$): 247.0900, found 247.0896.

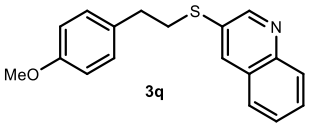


4-((4-Methoxyphenethyl)thio)quinoline (3p): Synthesized according to the General Procedure A using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chloroquinoline (98.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 3: 1 as eluent) to afford **3p** (38.5 mg, 65% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.8 Hz, 1H), 8.15 – 8.10 (m, 1H), 8.10 – 8.05 (m, 1H), 7.74 – 7.68 (m, 1H), 7.57 – 7.50 (m, 1H), 7.21 – 7.14 (m, 3H), 6.90 – 6.84 (m, 2H), 3.80 (s, 3H), 3.35 – 3.28 (m, 2H), 3.06 – 3.00 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 149.2, 147.6, 147.4, 131.6, 130.0, 129. 8, 129.5, 126.6, 126.3, 123.7, 115.9, 114.1, 55.3, 33. 8, 32.9.

HRMS: calculated for $C_{18}H_{18}NOS$ ($M+H^+$): 296.1104, found 296.1115.

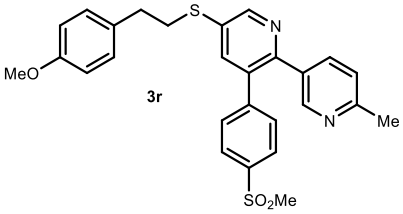


3-((4-Methoxyphenethyl)thio)quinoline (3q): Synthesized according to the General Procedure A using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 3-bromoquinoline (124.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 20: 1 as eluent) to afford **3q** (35.5 mg, 60% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 2.3 Hz, 1H), 8.09 – 8.05 (m, 1H), 8.03 – 8.00 (m, 1H), 7.74 – 7.69 (m, 1H), 7.69 – 7.64 (m, 1H), 7.56 – 7.51 (m, 1H), 7.14 – 7.10 (m, 2H), 6.85 – 6.81 (m, 2H), 3.77 (s, 3H), 3.27 – 3.22 (m, 2H), 2.96 – 2.90 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 151.6, 146.3, 135.1, 131.7, 130.6, 129.6, 129.3, 129.1, 128.2, 127.2, 127.0, 114.0, 55.3, 35.7, 34.8.

HRMS: calculated for $C_{18}H_{18}NOS$ ($M+H^+$): 296.1104, found 296.1115.

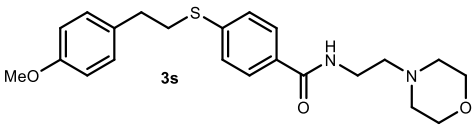


5-((4-Methoxyphenethyl)thio)-6'-methyl-3-(4-(methylsulfonyl)phenyl)-2,3'-bipyridine (3r): Synthesized according to the General Procedure A using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 5-chloro-6'-methyl-3-(4-(methylsulfonyl)phenyl)-2,3'-bipyridine (215.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: Acetone= 3: 1 as eluent) to afford **3r** (34.5 mg, 35% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 2.2 Hz, 1H), 8.37 (s, 1H), 7.92 – 7.85 (m, 2H), 7.60 – 7.53 (m, 2H), 7.39 – 7.33 (m, 2H), 7.15 – 7.04 (m, 3H), 6.84 – 6.78 (m, 2H), 3.76 (s, 3H), 3.26 – 3.20 (m, 2H), 3.08 (s, 3H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.52 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 158.1, 151.2, 149.8, 149.2, 144.7, 139.9, 138.4, 137.4, 134.3, 133.4, 131.8, 131.4, 130.5 , 129.6, 127.8, 122.8, 114.0, 55.3, 44.5, 35.3, 34.9, 24.2.

HRMS: calculated for $C_{27}H_{27}N_2O_3S_2$ ($M+H^+$): 491.1458, found 491.1472.



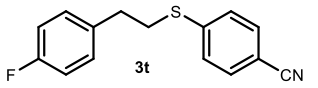
4-((4-Methoxyphenethyl)thio)-N-(2-morpholinoethyl)benzamide (3s): Synthesized according to the General Procedure A using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0

equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chloro-N-(2-morpholinoethyl)benzamide (161.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (EtOAc: MeOH= 50: 1 as eluent) to afford **3s** (36.0 mg, 45% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.06 (m, 2H), 7.77 – 7.70 (m, 2H), 7.55 – 7.50 (m, 2H), 7.28 – 7.23 (m, 2H), 7.18 (br, 1H), 4.19 (s, 3H), 4.14 (t, *J* = 4.7 Hz, 4H), 3.99 – 3.93 (m, 2H), 3.63 – 3.55 (m, 2H), 3.34 – 3.27 (m, 2H), 3.03 (t, *J* = 6.0 Hz, 2H), 2.94 (t, *J* = 4.0 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 158.4, 141.7, 131.9, 131.4, 129.5, 127.4, 127.4, 114.0, 66.9, 56.96, 56.0, 53.3, 36.0, 34.4, 34.3.

HRMS: calculated for $C_{22}H_{29}N_2O_3S$ ($M+H^+$): 401.1893, found 401.1891.



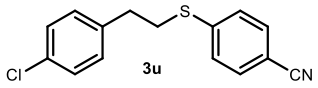
4-((4-Fluorophenethyl)thio)benzonitrile (3t): Synthesized according to the General Procedure A using 2-(4-fluorophenyl)ethan-1-ol (28.0 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 30: 1 as eluent) to afford **3t** (49.5 mg, 90% yield) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 2H), 7.33 – 7.28 (m, 2H), 7.20 – 7.14 (m, 2H), 7.04 – 6.96 (m, 2H), 3.24 – 3.18 (m, 2H), 2.95 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (d, *J* = 246.1 Hz), 144.4, 135.05 (d, *J* = 3.3 Hz), 132.3, 130.0 (d, *J* = 8.0 Hz), 127.0, 118.8, 115.5 (d, *J* = 21.3 Hz), 108.4, 34.2, 33.57 (d, *J* = 1.4 Hz).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -116.1.

HRMS: calculated for $C_{15}H_{12}FNNaS$ ($M+Na^+$): 280.0567, found 280.0571.

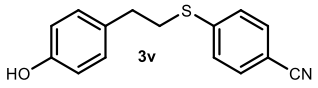


4-((4-Chlorophenethyl)thio)benzonitrile (3u): Synthesized according to the General Procedure A using 2-(4-chlorophenyl)ethan-1-ol (31.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (54.0 mg, 0.4 mmol, 2.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 30: 1 as eluent) to afford **3u** (46.5 mg, 85% yield) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.33 – 7.25 (m, 4H), 7.16 – 7.11 (m, 2H), 3.24 – 3.18 (m, 2H), 2.95 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 137.8, 132.3, 129.9, 128.8, 127.1, 118.8, 108.4, 34.3, 33.3.

HRMS: calculated for $C_{15}H_{12}ClNNaS$ ($M+Na^+$): 296.0271, found 296.0276.

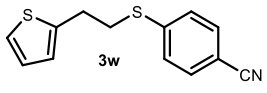


4-((4-Hydroxyphenethyl)thio)benzonitrile (3v): Synthesized according to the General Procedure A using 4-(2-hydroxyethyl)phenol (27.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford **3v** (33.5 mg, 65% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 2H), 7.34 – 7.27 (m, 2H), 7.11 – 7.05 (m, 2H), 6.83 – 6.76 (m, 2H), 5.00 (br, 1H), 3.22 – 3.16 (m, 2H), 2.91 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 144.8, 132.3, 131.6, 129.7, 126.9, 118.9, 115.5, 108.1, 34.1, 33.7.

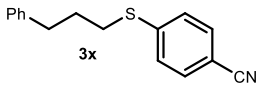
HRMS: calculated for $C_{15}H_{13}NNaOS$ ($M+Na^+$): 278.0610, found 278.0607.



4-((2-(Thiophen-2-yl)ethyl)thio)benzonitrile (3w): Synthesized according to the General Procedure A using 2-(thiophen-2-yl)ethan-1-ol (25.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 150: 1 as eluent) to afford **3w** (40.5 mg, 86% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 2H), 7.34 – 7.29 (m, 2H), 7.18 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.97 – 6.93 (m, 1H), 6.89 – 6.85 (m, 1H), 3.31 – 3.24 (m, 2H), 3.23 – 3.16 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 141.7, 132.4, 127.1, 127.0, 125.4, 124.1, 118.8, 108.5, 33.7, 29.4. HRMS: calculated for $C_{13}H_{12}NS_2$ ($M+H^+$): 246.0406, found 246.0405.

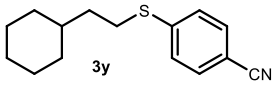


4-((3-Phenylpropyl)thio)benzonitrile (3x): Synthesized according to the General Procedure A using 3-phenylpropan-1-ol (27.2 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 200: 1 as eluent) to afford **3x** (33.0 mg, 65% yield) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.34 – 7.28 (m, 2H), 7.26 – 7.21 (m, 3H), 7.21 – 7.17 (m, 2H), 2.97 (t, *J* = 7.4 Hz, 2H), 2.78 (t, *J* = 7.4 Hz, 2H), 2.02 – 1.97 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 140.7, 132.2, 128.6, 128.5, 126.8, 126.3, 118.9, 108.1, 34.7, 31.0, 30.1.

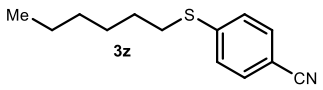
HRMS: calculated for $C_{16}H_{15}NNaS$ ($M+Na^+$): 276.0817, found 276.0824.



4-((2-Cyclohexylethyl)thio)benzonitrile (3y): Synthesized according to the General Procedure A using 2-cyclohexylethan-1-ol (25.6 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford **3y** (33.0 mg, 67% yield) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.30 – 7.26 (m, 2H), 3.01 – 2.95 (m, 2H), 1.78 – 1.64 (m, 5H), 1.60 – 1.56 (m, 2H), 1.45 – 1.37 (m, 1H), 1.26 – 1.14 (m, 3H), 0.98 – 0.90 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 132.2, 126.6, 119.0, 107.8, 37.0, 36.0, 33.0, 29.5, 26.5, 26.2. HRMS: calculated for $C_{15}H_{19}NNaS$ ($M+Na^+$): 268.1130, found 268.1131.

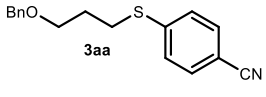


4-(Hexylthio)benzonitrile (3z): Synthesized according to the General Procedure A using hexan-1-ol (20.4 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford **3z** (28.5 mg, 65% yield) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.31 – 7.27 (m, 2H), 2.97 (t, *J* = 8.0 Hz, 2H), 1.72 – 1.66 (m, 2H), 1.48 – 1.41 (m, 2H), 1.33 – 1.28 (m, 4H), 0.91 – 0.87 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 132.2, 126.7, 119.0, 107.9, 31.9, 31.3, 28.6, 28.5, 22.5, 14.0.

HRMS: calculated for $C_{13}H_{17}NNaS$ ($M+Na^+$): 242.0974, found 242.0977.

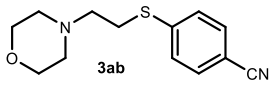


4-((3-(Benzyloxy)propyl)thio)benzonitrile (3aa): Synthesized according to the General Procedure A using 3-(benzyloxy)propan-1-ol (33.2 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 30: 1 as eluent) to afford **3aa** (37.4 mg, 66% yield) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.39 – 7.27 (m, 7H), 4.51 (s, 2H), 3.60 (t, *J* = 5.8 Hz, 2H), 3.12 (t, *J* = 5.8 Hz, 2H), 2.03 – 1.94 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 138.2, 132.2, 128.5, 127.7, 127.6, 126.8, 119.0, 108.0, 73.1, 68.2, 29.1, 28.7.

HRMS: calculated for $C_{17}H_{17}NNaOS$ ($M+Na^+$): 306.0923, found 306.0924.

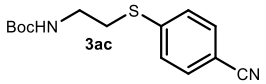


4-((2-Morpholinoethyl)thio)benzonitrile (3ab): Synthesized according to the General Procedure A using 2-morpholinoethan-1-ol (26.2 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 1: 1 as eluent) to afford **3ab**) (31.0 mg, 62% yield) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.34 – 7.28 (m, 2H), 3.74 – 3.68 (m, 4H), 3.15 – 3.08 (m, 2H), 2.70 – 2.64 (m, 2H), 2.54 – 2.44 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 132.3, 126.9, 118.8, 108.3, 66.8, 57.2, 53.5, 29.3.

HRMS: calculated for $C_{13}H_{17}N_2OS$ ($M+H^+$): 249.1056, found 249.1063.

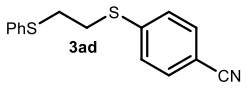


Tert-butyl (2-((4-cyanophenyl)thio)ethyl)carbamate (3ac): Synthesized according to the General Procedure A using tert-butyl (2-hydroxyethyl)carbamate (32.0 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 10: 1 as eluent) to afford **3ac** (28.5 mg, 51% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 2H), 7.40 – 7.34 (m, 2H), 4.89 (br, 1H), 3.38 (q, *J* = 6.6 Hz, 2H), 3.13 (t, *J* = 6.8 Hz, 2H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 143.6, 132.4, 127.2, 118.8, 108.6, 79.8, 39.6, 32.0, 28.4.

HRMS: calculated for $C_{14}H_{18}N_2NaO_2S$ ($M+Na^+$): 301.0981, found 301.0982.

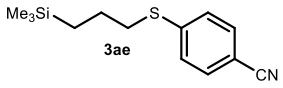


4-((2-(Phenylthio)ethyl)thio)benzonitrile (3ad): Synthesized according to the General Procedure A using 2-(phenylthio)ethan-1-ol (30.8 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 150: 1 as eluent) to afford **3ad** (44.5 mg, 81% yield) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.42 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.24 (m, 1H), 7.22 – 7.15 (m, 2H), 3.18– 3.13(m, 2H), 3.13 – 3.07 (m, 2H).

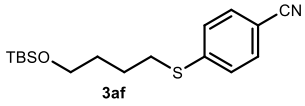
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 134.4, 132.4, 131.1, 129.2, 127.3, 127.3, 118.7, 108.7, 33.5, 31.5.

HRMS: calculated for $C_{15}H_{13}NNaS_2$ ($M+Na^+$): 294.0382, found 294.0387.

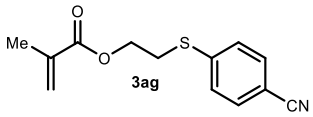


4-((3-(Trimethylsilyl)propyl)thio)benzonitrile (3ae): Synthesized according to the General Procedure A using 3-(trimethylsilyl)propan-1-ol (26.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5

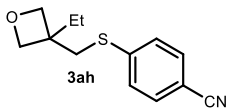
mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford **3ae** (34.0 mg, 68% yield) as a pale yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.31 – 7.26 (m, 2H), 3.01 – 2.94 (m, 2H), 1.72 – 1.64 (m, 2H), 0.69 – 0.61 (m, 2H), 0.01 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 132.2, 126.7, 119.0, 107.9, 35.5, 23.5, 16.5, -1.8.
HRMS: calculated for $C_{13}H_{20}NSSi$ ($M+H^+$): 250.1080, found 250.1076.



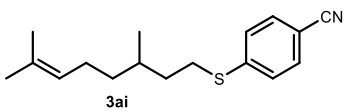
4-((4-((Tert-butyldimethylsilyl)oxy)butyl)thio)benzonitrile (3af): Synthesized according to the General Procedure A using 4-((tert-butyldimethylsilyl)oxy)butan-1-ol (41.0 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 150: 1 as eluent) to afford **3af** (31.0 mg, 48% yield) as a pale yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 2H), 7.32– 7.27 (m, 2H), 3.64 (t, *J* = 6.0 Hz, 2H), 3.00 (t, *J* = 6.0 Hz, 2H),1.82 – 1.73 (m, 2H), 1.69 – 1.63(m, 2H), 0.87 (s, 9H), 0.03 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 132.2, 126.8, 119.0, 108.0, 62.4, 31.8, 31.8, 25.9, 25.3, 18.3, -5.3.
HRMS: calculated for $C_{17}H_{27}NNaOSSi$ ($M+Na^+$): 344.1475, found 344.1482.



2-((4-Cyanophenyl)thio)ethyl methacrylate (3ag): Synthesized according to the General Procedure A using 2-hydroxyethyl methacrylate (26.0 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 20: 1 as eluent) to afford **3ag** (22.5 mg, 45% yield) as a yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 7.44 – 7.37 (m, 2H), 6.09 – 6.05 (m, 1H), 5.61 – 5.55 (m, 1H), 4.36 (t, *J* = 6.9 Hz, 2H), 3.27 (t, *J* = 6.9 Hz, 2H), 1.94 – 1.89 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 143.3, 135.8, 132.4, 127.3, 126.3, 118.7, 108.9, 62.6, 30.5, 18.2. HRMS: calculated for $C_{13}H_{13}NNaO_2S$ ($M+Na^+$): 270.0559, found 270.0558.



4-(((3-Ethyloxetan-3-yl)methyl)thio)benzonitrile (3ah): Synthesized according to the General Procedure A using (3-ethyloxetan-3-yl)methanol (23.2 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 30: 1 as eluent) to afford **3ah** (28.0 mg, 60% yield) as a yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 7.39 – 7.33 (m, 2H), 4.48 – 4.41 (m, 4H), 3.35 (s, 2H), 1.83 (q, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 132.3, 127.5, 118.7, 108.7, 80.0, 43.3, 38.6, 28.3, 8.2.
HRMS: calculated for $C_{13}H_{15}NNaOS$ ($M+Na^+$): 256.0767, found 256.0764.



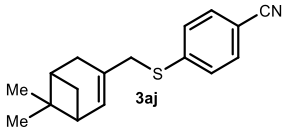
4-((3,7-Dimethyloct-6-en-1-yl)thio)benzonitrile (3ai): Synthesized according to the General Procedure A using 3,7-dimethyloct-6-en-1-ol (31.3 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash

column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford **3ai** (33.0 mg, 60% yield) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.31– 7.26 (m, 2H), 5.11 – 5.04 (m, 1H), 3.05 – 2.89 (m, 2H), 2.05 – 1.90 (m, 2H), 1.76 – 1.68 (m, 4H), 1.60 – 1.48 (m, 5H), 1.40 – 1.32 (m, 1H), 1.24 – 1.16 (m, 1H), 0.94 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 132.2, 131.6, 126.7, 124.4, 119.0, 107.9, 36.7, 35.6, 32.0, 29.8, 25.7, 25.4, 19.2, 17.7.

HRMS: calculated for $C_{17}H_{23}NNaS$ ($M+Na^+$): 296.1443, found 296.1452.

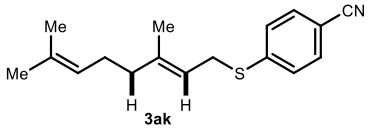


4-(((6,6-Dimethylbicyclo[3.1.1]hept-2-en-3-yl)methyl)thio)benzonitrile (3aj): Synthesized according to the General Procedure A using (6,6-dimethylbicyclo[3.1.1]hept-2-en-3-yl)methanol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 150: 1 as eluent) to afford **3aj** (27.5 mg, 51% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.33 – 7.28 (m, 2H), 5.56 – 5.51 (m, 1H), 3.60 – 3.56 (m, 2H), 2.41 – 2.35 (m, 1H), 2.29 – 2.16 (m, 3H), 2.11 – 2.05 (m, 1H), 1.28 (s, 3H), 1.05 (d, *J* = 8.7 Hz, 1H), 0.73 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 141.7, 132.0, 127.3, 121.7, 119.0, 108.1, 45.2, 40.4, 38.6, 38.2, 31.6, 31.3, 26.1, 21.1.

HRMS: calculated for $C_{17}H_{20}NS$ ($M+H^+$): 270.1311, found 270.1307.

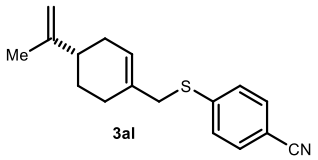


(E)-4-((3,7-Dimethylocta-2,6-dien-1-yl)thio)benzonitrile *(E: Z= 6.5 :1) (major isomer)* (3ak): Synthesized according to the General Procedure A using (E)-3,7-dimethylocta-2,6-dien-1-ol (31.0 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford **3ak** (19.5 mg, 36% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.32– 7.27(m, 2H), 5.32 – 5.25 (m, 1H), 5.07 – 4.99 (m, 1H), 3.64 – 3.59 (m, 2H), 2.12 – 1.98 (m, 4H), 1.69 (s, 3H), 1.66 (s, 3H), 1.59 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 141.4, 132.1, 131.9, 127.2, 123.6, 119.0, 117.8, 108.1, 39.5, 30.5, 26.3, 25.7, 17.7, 16.3.

HRMS: calculated for $C_{17}H_{21}NNaS$ ($M+Na^+$): 294.1287, found 294.1290.

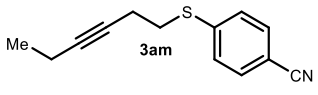


(S)-4-(((4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl)thio)benzonitrile (3al): Synthesized according to the General Procedure A using (S)-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methanol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford **3al** (28.0 mg, 52% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.33 – 7.29 (m, 2H), 5.74 – 5.70 (m, 1H), 4.74 – 4.70 (m, 1H), 4.69 – 4.66(m, 1H), 3.57 (s, 2H), 2.19 – 2.06 (m, 4H), 2.00 – 1.88 (m, 1H), 1.88 – 1.80 (m, 1H), 1.73 – 1.71 (m, 3H), 1.53 – 1.42 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 145.1, 132.1, 131.7, 127.6, 126.0, 119.0, 108.9, 108.3, 40.6, 39.9, 30.7, 27.8, 27.5, 20.8.

HRMS: calculated for $C_{17}H_{19}NNaS$ ($M+Na^+$): 292.1130, found 292.1137.

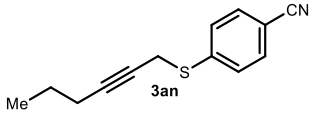


4-(Hex-3-yn-1-ylthio)benzonitrile (3am): Synthesized according to the General Procedure A using hex-3-yn-1-ol (19.6 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 200: 1 as eluent) to afford **3am** (31.0 mg, 72% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.35 – 7.29 (m, 2H), 3.11 (t, *J* = 7.5 Hz, 2H), 2.55 – 2.48 (m, 2H), 2.19 – 2.10 (m, 2H), 1.09 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 132.3, 127.2, 118.8, 108.5, 84.0, 76.5, 31.5, 19.4, 14.0, 12.4.

HRMS: calculated for $C_{13}H_{13}NNaS$ ($M+Na^+$): 238.0661, found 238.0655.

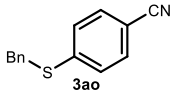


4-(Hex-2-yn-1-ylthio)benzonitrile (3an): Synthesized according to the General Procedure A using hex-2-yn-1-ol (19.6 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford **3an** (13.0 mg, 30% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.44 – 7.39 (m, 2H), 3.70 (t, *J* = 2.4 Hz, 2H), 2.16 – 2.11 (m, 2H), 1.52 – 1.42 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) 143.6, 132.2, 127.3, 118.7, 108.7, 84.8, 74.3, 22.0, 21.3, 20.7, 13.4.

HRMS: calculated for $C_{13}H_{13}NNaS$ ($M+Na^+$): 238.0661, found 238.0653.

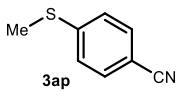


4-(Benzylthio)benzonitrile (3ao): Synthesized according to the General Procedure A using phenylmethanol (21.6 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 100: 1 as eluent) to afford **3ao** (29.0 mg, 64% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.39– 7.26 (m, 7H), 4.2 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 135.8, 132.2, 128.8, 128.7, 127.7, 127.4, 118.8, 108.6, 37.1.

HRMS: calculated for $C_{14}H_{11}NNaS$ ($M+Na^+$): 248.0504, found 248.0509.

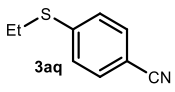


4-(Methylthio)benzonitrile (3ap): Synthesized according to the General Procedure A using methanol (6.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 150: 1 as eluent) to afford **3ap** (27.0 mg, 90% yield) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.27 – 7.23 (m, 2H), 2.50 (s, 3H).

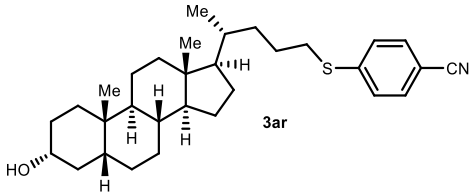
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 132.2, 125.5, 119.0, 107.7, 14.7.

Matching reported literature data[5].

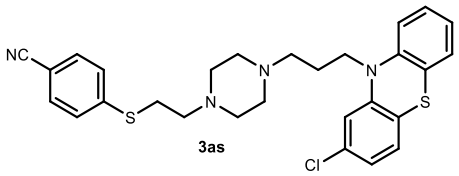


4-(Methylthio)benzonitrile (3aq): Synthesized according to the General Procedure A using ethanol (9.2 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 150: 1 as eluent) to afford **3aq** (16.5 mg, 50% yield) as a yellow liquid.

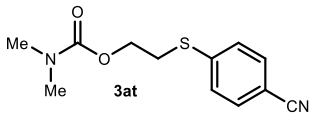
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.31 – 7.27 (m, 2H), 3.01 (q, *J* = 7.4 Hz, 2H), 1.37 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 132.2, 126.7, 119.0, 108.0, 26.0, 13.8.
Matching reported literature data[6].



4-(((4R)-4-((3R,5R,8R,9S,10S,13R)-3-Hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentyl)thio)benzonitrile (3ar): Synthesized according to the General Procedure A using (3R,5R,8R,9S,10S,13R)-17-((R)-5-hydroxypentan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-ol (72.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (DCM as eluent) to afford **3ar** (28.0 mg, 30% yield) as a yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.30 – 7.27 (m, 2H), 3.66 – 3.58 (m, 1H), 3.01 – 2.86 (m, 2H), 1.98 – 1.92 (m, 1H), 1.88 – 1.72 (m, 5H), 1.60 – 1.52 (m, 6H), 1.43 – 1.35 (m, 6H), 1.30 – 1.15 (m, 5H), 1.12 – 1.02 (m, 4H), 1.00 – 0.86 (m, 1H), 0.94 – 0.89 (m, 6H), 0.64 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 132.2, 126.7, 119.0, 107.9, 71.9, 56.5, 56.1, 42.7, 42.1, 40.5, 40.2, 36.5, 35.9, 35.5, 35.4, 35.2, 34.6, 32.4, 30.6, 28.3, 27.2, 26.4, 25.3, 24.2, 23.4, 20.8, 18.6, 12.1. HRMS: calculated for $C_{31}H_{45}NNaOS$ ($M+Na^+$): 502.3114, found 502.3127.



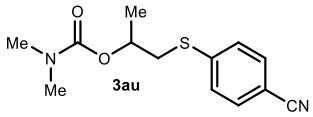
4-((2-(4-(3-(2-Chloro-10H-phenothiazin-10-yl)propyl)piperazin-1-yl)ethyl)thio)benzonitrile (3as): Synthesized according to the General Procedure A using 2-(4-(3-(2-chloro-10H-phenothiazin-10-yl)propyl)piperazin-1-yl)ethan-1-ol (81.0 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (EtOAc as eluent) to afford **3as** (73.0 mg, 72% yield) as a yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.32 – 7.28 (m, 2H), 7.18 – 7.09 (m, 2H), 7.03 – 6.99 (m, 1H), 6.98 – 6.82 (m, 4H), 3.90 (t, *J* = 6.7 Hz, 2H), 3.13 – 3.05 (m, 2H), 2.70 – 2.63 (m, 2H), 2.62 – 2.28 (m, 10H), 2.00 – 1.87 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 144.7, 144.5, 133.2, 132.3, 127.9, 127.5, 127.4, 126.9, 124.9, 123.6, 123.0, 122.3, 118.9, 115.9, 115.9, 108.3, 56.7, 55.4, 53.1, 52.8, 45.2, 29.4, 24.0.
HRMS: calculated for $C_{28}H_{30}ClN_4S_2$ ($M+H^+$): 521.1595, found 521.1600.



2-((4-Cyanophenyl)thio)ethyl dimethylcarbamate (3at): Synthesized according to the General Procedure A using ethane-1,2-diol (12.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 20: 1 as eluent) to afford **3at** (40.5 mg, 90% yield) as a yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 2H), 7.42 – 7.36 (m, 2H), 4.26 (t, *J* = 6.9 Hz, 2H), 3.23 (t, *J* = 6.9 Hz, 2H), 2.89 (s, 3H), 2.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 143.7, 132.4, 127.1, 118.8, 108.6, 63.2, 36.5, 35.9, 30.8.

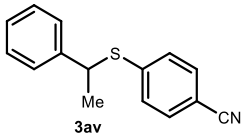
HRMS: calculated for $C_{12}H_{14}N_2NaO_2S$ ($M+Na^+$): 273.0668, found 273.0662.



1-((4-Cyanophenyl)thio)propan-2-yl dimethylcarbamate (3au): Synthesized according to the General Procedure A using propane-1,2-diol (15.2 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 20: 1 as eluent) to afford **3au** (39.0 mg, 74% yield) as a yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.44 – 7.39 (m, 2H), 5.01 – 4.91 (m, 1H), 3.31 (dd, *J* = 13.7, 5.3 Hz, 1H), 3.02 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.88 (s, 3H), 2.79 (s, 3H), 1.36 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 144.2, 132.3, 127.1, 118.8, 108.4, 69.8, 37.3, 36.4, 35.8, 19.4.

HRMS: calculated for $C_{13}H_{16}N_2NaO_2S$ (M+Na$^+$): 287.0825, found 287.0824.



4-((1-Phenylethyl)thio)benzonitrile (3av): Synthesized according to the General Procedure A using 1-phenylethan-1-ol (24.4 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (79.5 mg, 0.6 mmol, 3.0 equiv.) and 4-chlorobenzonitrile (82.5 mg, 0.6 mmol, 3.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 100: 1 as eluent) to afford **3av** (9.6 mg, 20% yield) as a yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.27 (m, 3H), 7.28 – 7.21 (m, 2H), 4.50 (q, *J* = 7.0 Hz, 1H), 1.67 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 142.2, 132.1, 129.4, 128.8, 127.6, 127.1, 118.8, 109.1, 46.6, 22.8. HRMS: calculated for $C_{15}H_{13}NNaS$ (M+Na$^+$): 262.0661, found 262.0668.

C2.4. Unsuccessful Substrates

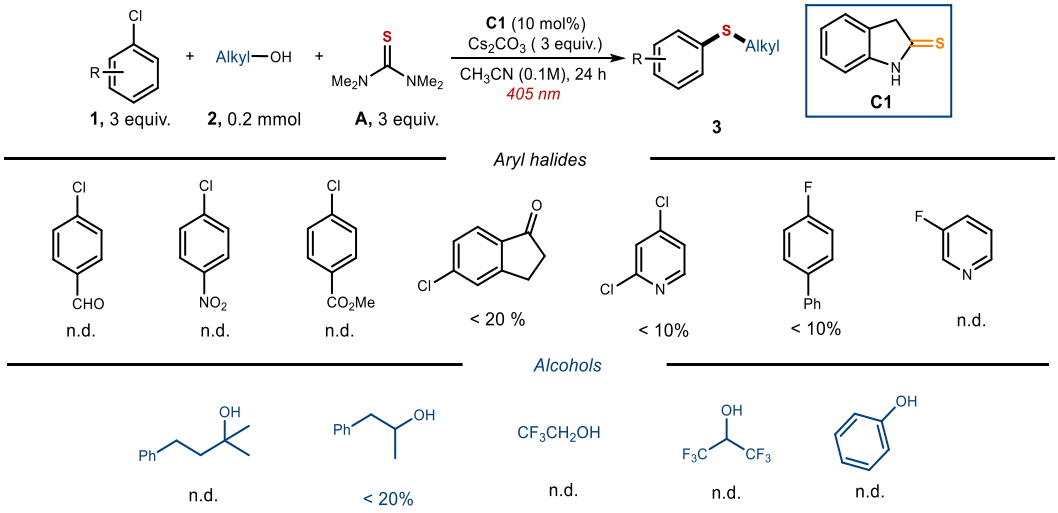


Figure S3. Unsuccessful aryl halides and alcohols; n.d. = product not detected

C2.5. Reactivity of Aryl Halides

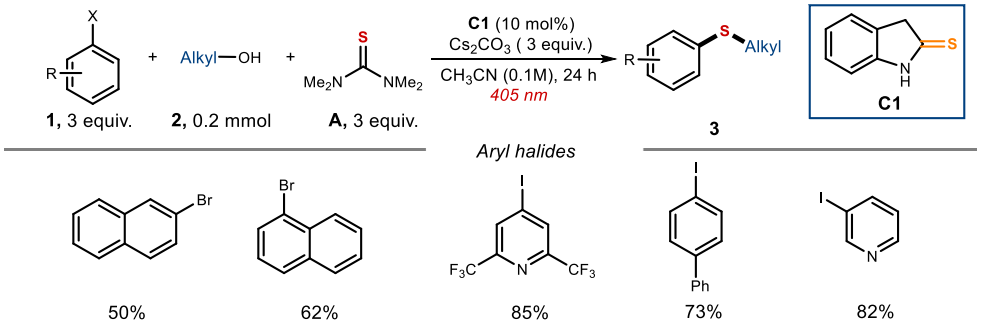
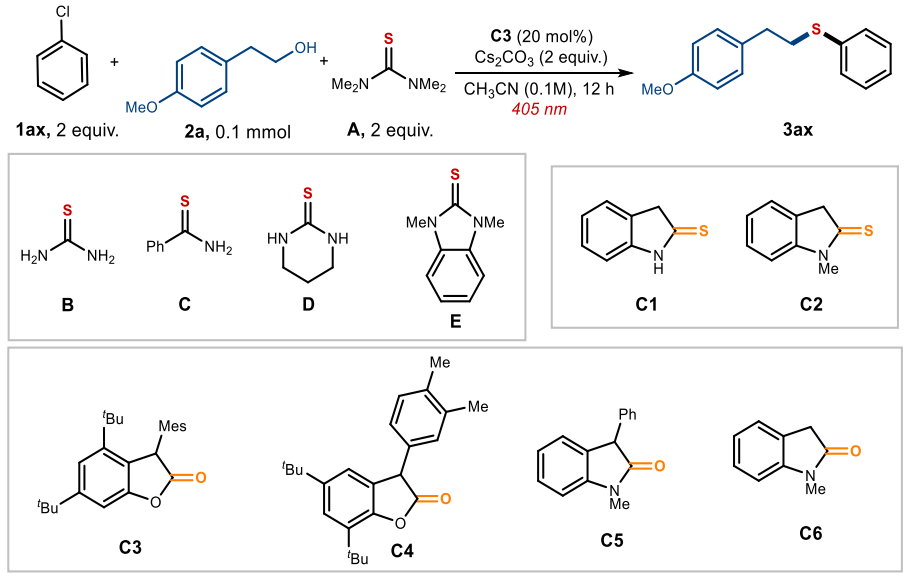


Figure S4. Reactivity of aryl bromides and iodides

C3. Preparation of Thioethers from Alcohols and Aryl Halides Using C3 as Photoreductant

C3.1. Optimization Studies

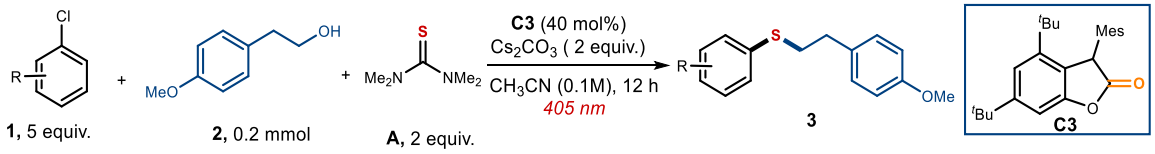
Table S2. Optimization of the thioetherification using **C3** as photoreductant



Entry	Deviations	NMRy **3ax**
1	none	35%
2	No light or No base or No **C3**	0%
3	**E**	5%
4	**B-D**	0%
5	DMSO, DMF, Acetone as solvent	0%
6	$KHCO_3$, K_2CO_3, K_3PO_4, TMG as base	0%
7	**C1** or **C2** (5 mol%) as photocatalyst	5%
8	With TEMPO	0%
9	**C2** (10 mol%) as photocatalyst	5%
10	**C6** (10 mol%) as photocatalyst	0%
11	**C5** (10 mol%) as photocatalyst	10%
12	**C4** (10 mol%), 3 equiv. PhCl	15%
13	**C3** (10 mol%), 3 equiv. PhCl	20%
14	**C3** (20 mol%), 3 equiv. PhCl	45%
15	**C3** (40 mol%), 3 equiv. PhCl	60%
16	**C3** (40 mol%), 5 equiv. PhCl	70% [a]

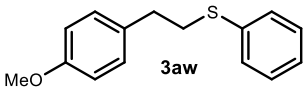
All reactions were performed on a 0.1 mmol scale; yield of **3az** determined by ^{1}H NMR analysis of the crude reaction mixture by comparison with 1,3,5-trimethoxybenzene as internal standard. [a] isolated yield. Mes: mesityl.

C3.2. General Procedure B for neutral and electron-rich aryl halides



To a 7 mL glass vial, **C3** (29.5 mg, 0.08 mmol, 0.4 equiv.), cesium carbonate (130.0 mg, 0.4 mmol, 2 equiv.), 1,1,3,3-tetramethylthiourea **A** (53.0 mg, 0.4 mmol, 2.0 equiv.), alcohol **2** (30.5 mg, 0.2 mmol, 1 equiv.) and aryl chlorides **1** (if solid, 0.6 mmol, 5 equiv.) were sequentially added. The vial was sealed with a screw-top cap with septum and then vacuumed and backfilled with argon for 3 times. Afterwards, aryl chlorides **1** (if liquid, 0.6 mmol, 5 equiv.) followed by argon-sparged acetonitrile (0.1 M, 2.0 mL) were added *via* syringe. The vial was sealed with Parafilm and then stirred under 405 nm for 24 hours using ***Set-up 1*** detailed in **Figure S1**. After completion of the reaction, column chromatography purification afforded the corresponding products **3** with the reported yields (>95% purity according to ^{1}H NMR analysis).

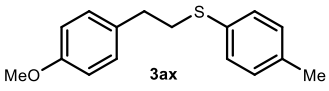
C3.3. Characterization of Products



(4-Methoxyphenethyl)(phenyl)sulfane (3aw): Synthesized according to the General Procedure B using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (54.0 mg, 0.4 mmol, 2.0 equiv.) and chlorobenzene (112.5 mg, 1.0 mmol, 5.0 equiv.) or bromobenzene (157.0 mg, 1.0 mmol, 5.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford **3aw** (34.0 mg, 70% yield with chlorobenzene and 33.2 mg, 68% yield with bromobenzene) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.22 – 7.17 (m, 1H), 7.15 – 7.10 (m, 2H), 6.88 – 6.83 (m, 2H), 3.80 (s, 3H), 3.18 – 3.11 (m, 2H), 2.91 – 2.85 (m, 2H).

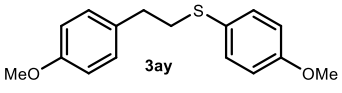
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 136.5, 132.3, 129.5, 129.2, 128.9, 125.9, 114.0, 55.3, 35.4, 34.8. Matching reported literature data[7].



(4-Methoxyphenethyl)(p-tolyl)sulfane (3ax): Synthesized according to the General Procedure B using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (54.0 mg, 0.4 mmol, 2.0 equiv.) and 1-chloro-4-methylbenzene (126.6 mg, 1.0 mmol, 5.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford **3ax** (33.2 mg, 64% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.15 – 7.08 (m, 4H), 6.87 – 6.82 (m, 2H), 3.80 (s, 3H), 3.13 – 3.08 (m, 2H), 2.88 – 2.82 (m, 2H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 136.2, 132.6, 132.5, 130.1, 129.7, 129.5, 113.9, 55.3, 36.1, 34.9, 21.0. Matching reported literature data[8].

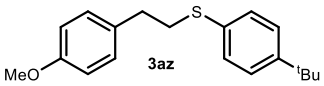


(4-Methoxyphenethyl)(4-methoxyphenyl)sulfane (3ay): Synthesized according to the General Procedure B using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (54.0 mg, 0.4 mmol, 2.0 equiv.) and 1-chloro-4-methoxybenzene (142.5 mg, 1.0 mmol, 5.0 equiv.). The crude mixture was purified by flash column

chromatography on silica gel (Hexane: EtOAc = 100: 1 as eluent) to afford **3ay** (31.0 mg, 56% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.11 – 7.06 (m, 2H), 6.89 – 6.80 (m, 4H), 3.81 (s, 3H), 3.79 (s, 3H), 3.13 – 3.08 (m, 2H), 2.85 – 2.78 (m, 2H).

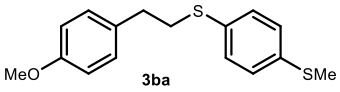
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 158.2, 133.2, 132.5, 129.5, 126.4, 114.6, 113.9, 55.4, 55.3, 37.5, 35.0. HRMS: calculated for $C_{16}H_{18}O_2S$ (M^+): 274.1022, found 274.1021.



(4-(Tert-butyl)phenyl)(4-methoxyphenethyl)sulfane (3az): Synthesized according to the General Procedure B using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (54.0 mg, 0.4 mmol, 2.0 equiv.) and 1-(tert-butyl)-4-chlorobenzene (168.5 mg, 1.0 mmol, 5.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford **3az** (36.5 mg, 60% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 4H), 7.15 – 7.10 (m, 2H), 6.87 – 6.82 (m, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 3.15 – 3.09 (m, 2H), 2.90 – 2.84 (m, 2H), 1.32 (s, 9H).

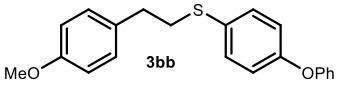
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 149.3, 132.8, 132.5, 129.5, 129.4, 126.0, 113.9, 55.3, 35.8, 34.9, 34.5, 31.3. HRMS: calculated for $C_{19}H_{24}NaOS$ ($M+Na^+$): 323.1440, found 323.1445.



(4-Methoxyphenethyl)(4-(methylthio)phenyl)sulfane (3ba): Synthesized according to the General Procedure B using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (54.0 mg, 0.4 mmol, 2.0 equiv.) and (4-chlorophenyl)(methyl)sulfane (158.5 mg, 1.0 mmol, 5.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford **3bb** (31.4 mg, 54% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.22 – 7.17 (m, 2H), 7.13 – 7.08 (m, 2H), 6.86 – 6.81 (m, 2H), 3.79 (s, 3H), 3.13 – 3.07 (m, 2H), 2.88 – 2.82 (m, 2H), 2.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 136.5, 132.8, 132.3, 130.5, 129.5, 127.3, 113.9, 55.3, 36.0, 34.8, 16.1. HRMS: calculated for $C_{16}H_{18}OS_2$ (M^+): 290.0794, found 290.0791.

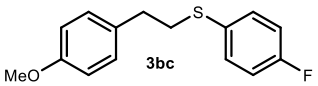


(4-Methoxyphenethyl)(4-phenoxyphenyl)sulfane (3bb): Synthesized according to the General Procedure B using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (54.0 mg, 0.4 mmol, 2.0 equiv.) and 1-chloro-4-phenoxybenzene (204.5 mg, 1.0 mmol, 5.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 200: 1 as eluent) to afford **3bb** (48.0 mg, 71% yield) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 4H), 7.16 – 7.09 (m, 3H), 7.05 – 7.01 (m, 2H), 6.99 – 6.94 (m, 2H), 6.88 – 6.82 (m, 2H), 3.80 (s, 3H), 3.13 – 3.07 (m, 2H), 2.90 – 2.84 (m, 2H).

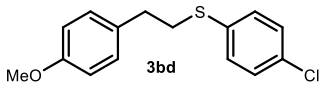
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 157.0, 156.3, 132.3, 132.2, 130.0, 129.8, 129.5, 123.5, 119.4, 119.0, 113.9, 55.3, 36.8, 34.9.

HRMS: calculated for $C_{21}H_{20}NaO_2S$ ($M+Na^+$): 359.1076, found 359.1074.

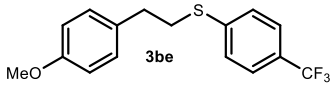


(4-Fluorophenyl)(4-methoxyphenethyl)sulfane (3bc): Synthesized according to the General Procedure B using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (54.0 mg, 0.4 mmol, 2.0 equiv.) and 1-chloro-4-fluorobenzene (130.5 mg, 1.0 mmol, 5.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford **3bc** (43.0 mg, 82% yield) as a pale yellow liquid.

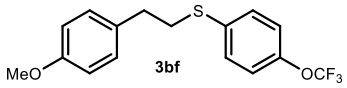
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.12 – 7.07 (m, 2H), 7.05 – 6.97 (m, 2H), 6.87 – 6.81 (m, 2H), 3.79 (s, 3H), 3.12 – 3.06 (m, 2H), 2.88 – 2.81 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (d, *J* = 246.1 Hz), 158.3, 132.3(d, *J* = 8.1 Hz), 132.2, 131.2(d, *J* = 4.0 Hz), 129.5, 116.0 (d, *J* = 22.2 Hz), 113.9, 55.27, 36.75, 34.82.
^{19}F{^{1}H} NMR (376 MHz, CDCl3) δ -115.8.
HRMS: calculated for $C_{15}H_{15}FOS$ (M^+): 262.0822, found 262.0826.



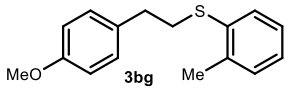
(4-Chlorophenyl)(4-methoxyphenethyl)sulfane (3bd): Synthesized according to the General Procedure B using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (54.0 mg, 0.4 mmol, 2.0 equiv.) and 1-bromo-4-chlorobenzene (191.5 mg, 1.0 mmol, 5.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 200: 1 as eluent) to afford **3bd** (27.9 mg, 50% yield) as a yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 4H), 7.13 – 7.08 (m, 2H), 6.87 – 6.82 (m, 2H), 3.79 (s, 3H), 3.14 – 3.09 (m, 2H), 2.89 – 2.83 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 135.0, 132.0, 131.9, 130.5, 129.5, 129.0, 114.0, 55.3, 35.7, 34.6.
HRMS: calculated for $C_{15}H_{15}ClNaO_2S$ ($M+Na^+$): 317.0373, found 317.0365.
The HRMS was shown is the oxidized form of the product, the desired mass can be found in GC-MS (calculated: 278.0, found 277.9).



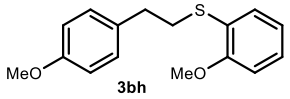
(4-Methoxyphenethyl)(4-(trifluoromethyl)phenyl)sulfane (3be): Synthesized according to the General Procedure B using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (54.0 mg, 0.4 mmol, 2.0 equiv.) and 1-chloro-4-(trifluoromethyl)benzene (180.5 mg, 1.0 mmol, 5.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 200: 1 as eluent) to afford **3be** (34.0 mg, 54% yield) as a pale yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.39 – 7.34 (m, 2H), 7.16 – 7.11 (m, 2H), 6.88 – 6.53 (m, 2H), 3.80 (s, 3H), 3.23 – 3.17 (m, 2H), 2.95 – 2.89 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 142.2, 131.8, 129.5, 127.5, 125.7 (q, *J* = 3.9 Hz). 124.2 (q, *J* = 273.7 Hz), 114.0, 55.3, 34.4, 34.3.
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.5.
HRMS: calculated for $C_{16}H_{16}F_3OS$ ($M+H^+$): 313.0868, found 313.0855.



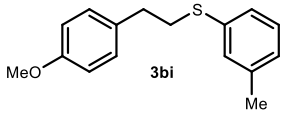
(4-Methoxyphenethyl)(4-(trifluoromethoxy)phenyl)sulfane (3bf): Synthesized according to the General Procedure B using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (54.0 mg, 0.4 mmol, 2.0 equiv.) and 1-chloro-4-(trifluoromethoxy)benzene (196.5 mg, 1.0 mmol, 5.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 200: 1 as eluent) to afford **3bf** (37.0 mg, 56% yield) as a pale yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.17 – 7.09 (m, 4H), 6.87 – 6.82 (m, 2H), 3.79 (s, 3H), 3.17 – 3.11 (m, 2H), 2.91 – 2.84 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 147.47 (q, *J* = 1.9 Hz), 135.4, 132.0, 130.5, 129.5, 121.6, 120.5 (q, *J* = 258.6 Hz), 114.0, 55.3, 36.7, 34.7.
^{19}F{^{1}H} NMR (376 MHz, CDCl3) δ -58.1.
HRMS: calculated for $C_{16}H_{16}F_3O_2S$ ($M+H^+$): 329.0818, found 329.0804.



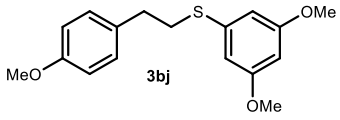
(4-Methoxyphenethyl)(p-tolyl)sulfane (3bg): Synthesized according to the General Procedure B using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (54.0 mg, 0.4 mmol, 2.0 equiv.) and 1-chloro-2-methylbenzene (126.5 mg, 1.0 mmol, 5.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford **3bg** (33.5 mg, 65% yield) as a yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 1H), 7.20 – 7.08 (m, 5H), 6.88 – 6.83 (m, 2H), 3.80 (s, 3H), 3.15 – 3.09 (m, 2H), 2.93 – 2.87 (m, 2H), 2.38 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 137.6, 135.8, 132.4, 130.1, 129.5, 127.8, 126.4, 125.6, 113.9, 55.3, 34.6, 20.4.
HRMS: calculated for $C_{16}H_{18}OS$ (M^+): 258.1073, found 258.1076.



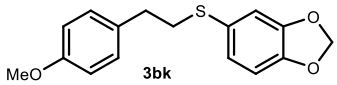
(4-Methoxyphenethyl)(2-methoxyphenyl)sulfane (3bh): Synthesized according to the General Procedure B using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (54.0 mg, 0.4 mmol, 2.0 equiv.) and 1-chloro-2-methoxybenzene (142.6 mg, 1.0 mmol, 5.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 100: 1 as eluent) to afford **3bh** (36.5 mg, 66% yield) as a yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.23 – 7.17 (m, 1H), 7.16 – 7.11 (m, 2H), 6.97 – 6.91 (m, 1H), 6.88 – 6.82 (m, 3H), 3.90 (s, 3H), 3.79 (s, 3H), 3.15 – 3.08 (m, 2H), 2.91 – 2.85 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 157.4, 132.6, 129.5, 129.5, 127.2, 124.5, 121.1, 113.9, 110.5, 55.8, 55.3, 34.7, 33.8.
HRMS: calculated for $C_{16}H_{18}NaO_2S$ ($M+Na^+$): 297.0920, found 297.0922.



(4-Methoxyphenethyl)(p-tolyl)sulfane (3bi): Synthesized according to the General Procedure B using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (54.0 mg, 0.4 mmol, 2.0 equiv.) and 1-chloro-3-methylbenzene (126.5 mg, 1.0 mmol, 5.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford **3bi** (30.0 mg, 58% yield) as a yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.10 (m, 5H), 7.02 – 6.98 (m, 1H), 6.87 – 6.82 (m, 2H), 3.80 (s, 3H), 3.16 – 3.11 (m, 2H), 2.91 – 2.84 (m, 2H), 2.33 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 138.7, 136.2, 132.4, 129.8, 129.5, 128.8, 126.8, 126.1, 113.9, 55.3, 35.4, 34.8, 21.4.
HRMS: calculated for $C_{16}H_{18}OS$ (M^+): 258.1073, found 258.1079.



(3,5-Dimethoxyphenyl)(4-methoxyphenethyl)sulfane (3bj): Synthesized according to the General Procedure B using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (54.0 mg, 0.4 mmol, 2.0 equiv.) and 1-chloro-3,5-dimethoxybenzene (172.5 mg, 1.0 mmol, 5.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 100: 1 as eluent) to afford **3bj** (26.8 mg, 44% yield) as a yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.11 (m, 2H), 6.88 – 6.82 (m, 2H), 6.50 (d, *J* = 2.2 Hz, 2H), 6.29 (t, *J* = 2.2 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 6H), 3.17 – 3.11 (m, 2H), 2.92 – 2.87 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 158.3, 138.6, 132.3, 129.5, 113.9, 106.5, 98.3, 55.4, 55.3, 35.0, 34.7. HRMS: calculated for $C_{17}H_{21}O_3S$ ($M+H^+$): 305.1206, found 305.1194.

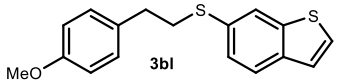


5-((4-Methoxyphenethyl)thio)benzo[d][1,3]dioxole (3bk): Synthesized according to the General Procedure B using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (54.0 mg, 0.4 mmol, 2.0 equiv.) and 5-chlorobenzo[d][1,3]dioxole (156.5 mg, 1.0 mmol, 5.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 100: 1 as eluent) to afford **3bk** (32.5 mg, 56% yield) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.06 (m, 1H), 6.94 – 6.90 (m, 2H), 6.86 – 6.81 (m, 2H), 6.78 – 6.74 (m, 2H), 5.97 (s, 2H), 3.79 (s, 3H), 3.07 – 3.01(m, 2H), 2.86 – 2.79 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 148.0, 147.0, 132.3, 129.5, 128.1, 125.3, 113.9, 112.0, 108.7, 101.3, 55.3, 37.5, 34.9.

HRMS: calculated for $C_{16}H_{16}O_3S$ (M^+): 288.0815, found 288.0816.



6-((4-Methoxyphenethyl)thio)benzo[b]thiophene (3bl): Synthesized according to the General Procedure B using 2-(4-methoxyphenyl)ethan-1-ol (30.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea (54.0 mg, 0.4 mmol, 2.0 equiv.) and 6-chlorobenzo[b]thiophene (168.5 mg, 1.0 mmol, 5.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 100: 1 as eluent) to afford **3bl** (26.0 mg, 43% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 1.9 Hz, 1H), 7.82 – 7.78 (m, 1H), 7.46 (dd, J = 5.4, 0.5 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.28 (dd, *J* = 5.5, 0.8 Hz, 1H), 7.14 – 7.09 (m, 2H), 6.86 – 6.81 (m, 2H), 3.79 (s, 3H), 3.21 – 3.15 (m, 2H), 2.91 – 2.85 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 140.4, 138.0, 132.4, 131.9, 129.5, 127.4, 126.7, 125.2, 123.4, 122.8, 113.9, 55.3, 36.6, 34.9.

HRMS: calculated for $C_{17}H_{17}OS_2$ ($M+H^+$): 301.0715, found 301.0706.

C3.4. Unsuccessful Substrates

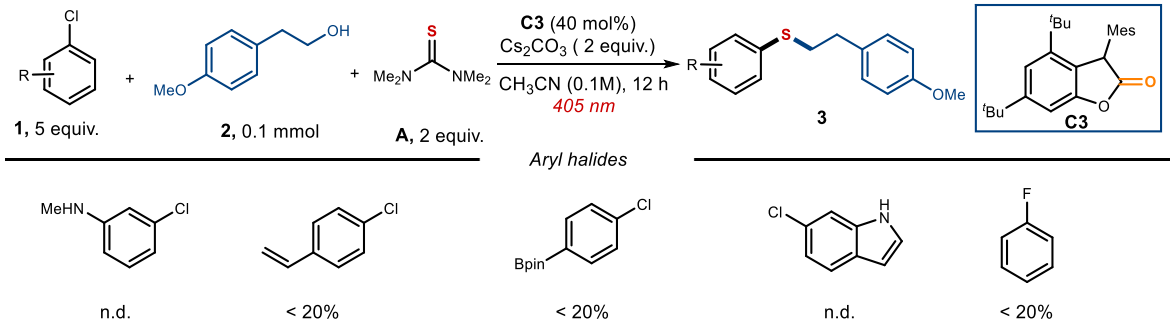


Figure S5. Unsuccessful aryl halides; n.d. = product not detected.

D. Mechanistic Studies

D1. Deprotonation Experiments for catalysts C1 and C3

- *Deprotonation of catalyst **C1**:*

To a 7 mL glass vial, catalyst **C1** (0.1 mmol, 1 equiv.) and cesium carbonate (0.3 mmol, 3 equiv.) were added. The vial was sealed with a screw-top cap with septum, then vacuumed and backfilled with argon for 3 times and CD_3CN (0.1 M) was added *via* syringe. The solution was stirred at ambient temperature for 10 min, transferred into an argon filled NMR tube *via* syringe and then the ^{1}H NMR spectrum was recorded (**Figure S5**).

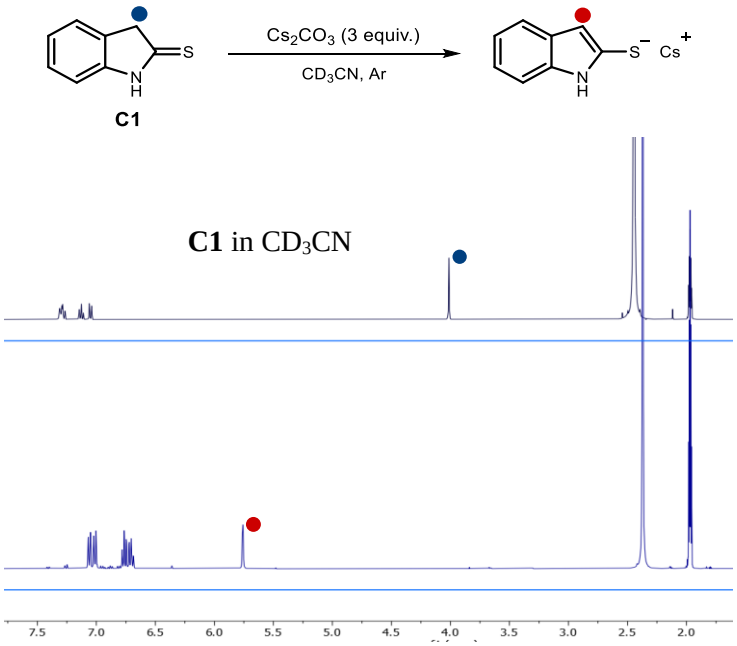
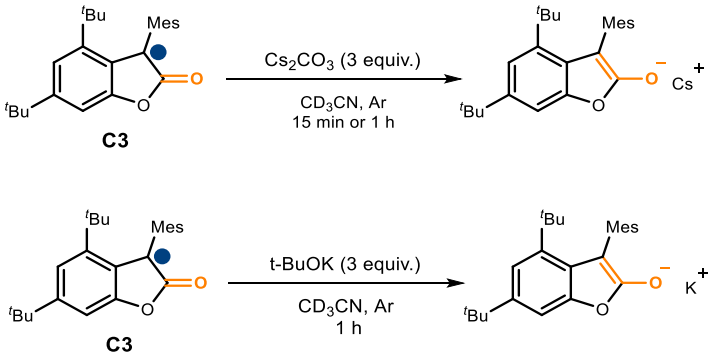


Figure S6. ^{1}H NMR analysis of catalyst **C1** before (up) and after (bottom) treatment with Cs_2CO_3.

- *Deprotonation of catalyst **C3**:*

To a 7 mL glass vial, catalyst **C3** (0.1 mmol, 1 equiv.) and cesium carbonate (0.3 mmol, 3 equiv.) or potassium *tert*-butoxide were added. The vial was sealed with a screw-top cap with septum, then vacuumed and backfilled with argon for 3 times and CD_3CN (0.1 M) were added *via* syringe. The solution was stirred at room temperature for 15 min or 1 h, transferred into an argon filled NMR tube *via* syringe and then the ^{1}H NMR spectrum was recorded (**Figure S6-7**).



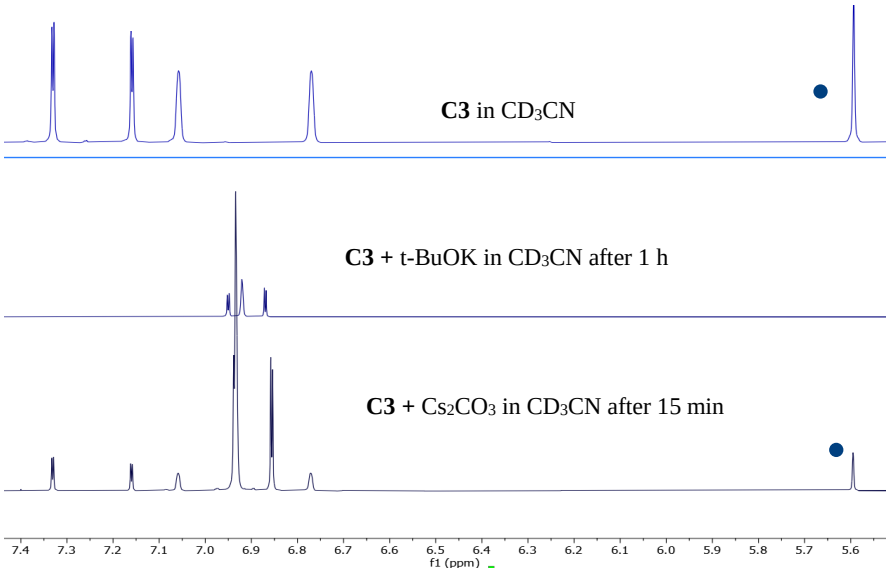


Figure S7. ^{1}H NMR analysis of catalyst **C1** before (top), after (middle) treatment with t-BuOK in 1hour and after (bottom) treatment with Cs_2CO_3 in 15 min.

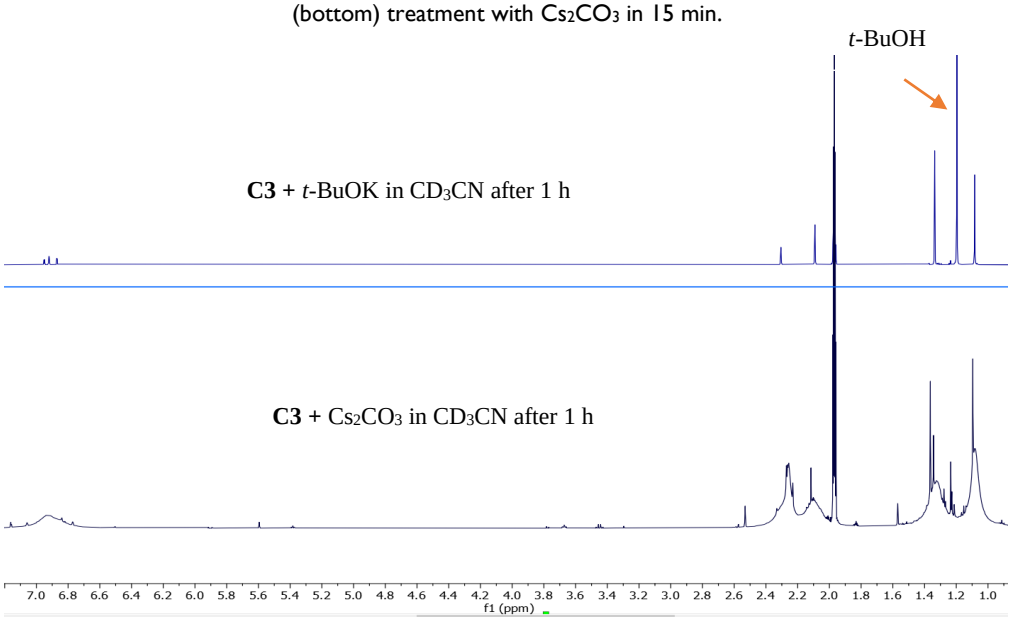


Figure S8. ^{1}H NMR analysis of catalyst **C1** after treatment with t-BuOK (top) and Cs_2CO_3 (bottom) in 1 hour.

D2. Hydrodechlorination of Aryl Halides Catalyzed by C1 and C3

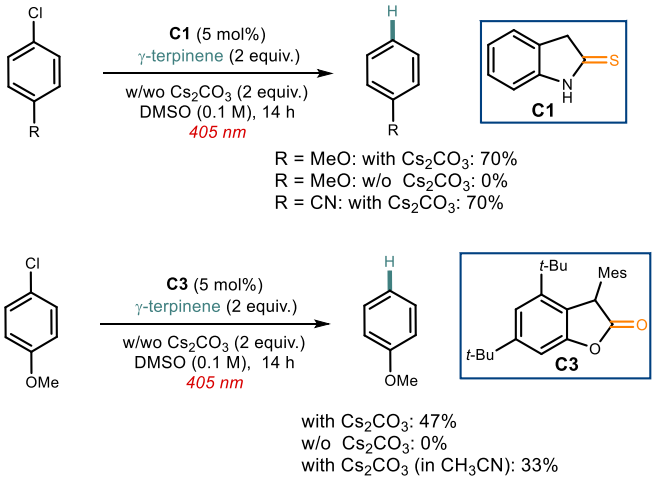


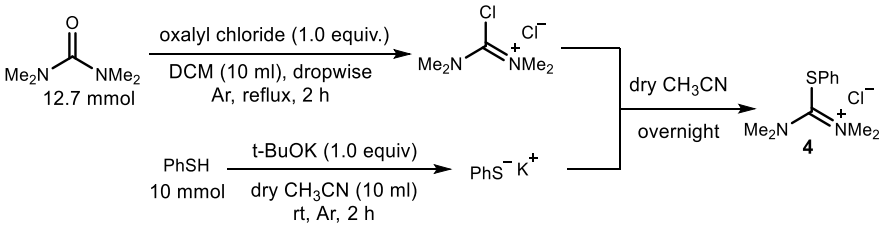
Figure S9. Effect of the base on the reactivity of catalysts **C1** and **C3** in the hydrodechlorination of aryl halides

We compared the reactivity of photocatalysts **C1** and **C3** in the hydrodechlorination of aryl halides.[2] The results in Figure S8 demonstrate the necessity of Cs_2CO_3 to deprotonate **C1** and **C3**, which are the active photoreductants.

D3. Evidence of a Polar Substitution Process

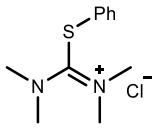
D3.1 Reactions Between Prepared Aryl Isothiourea Salts and Alcohols

- preparation of Aryl Isothiouronium salts **4**[9]:



All manipulations were performed in anhydrous conditions under argon. Oxalyl chloride (1.1 mL, 1.0 equiv.) was added dropwise via syringe to a stirred solution of tetramethylurea (15.25 mL, 12.7 mmol) in DCM (10 mL). The reaction was refluxed for 2 hours, cooled to room temperature, and anhydrous ether (30 mL) was added. The tightly stoppered flask was refrigerated for 2 hours, then the precipitated intermediate was isolated by filtration under argon, and washed 3 times with anhydrous ether. In a separate flask, thiophenol (1.05 mL, 10 mmol) in dry acetonitrile (10 mL) was stirred vigorously and treated with potassium *tert*-butoxide (1.2 g). After 2 hours, the deprotonation reaction of thiophenol was evaporated to dryness in vacuo, and dried for a further 2 hours.

The filtered chloro-uronium salt without further drying, was mixed with newly obtained thiolate and washed in with 10 mL dry acetonitrile, and stirred vigorously. An exothermic reaction started immediately. The reaction was stirred overnight and resulting mixture was filtered (to remove precipitated KCl), and the residue washed 3 x with 5 mL dry acetonitrile. The filtrates were evaporated, anhydrous ether (~20 mL) added to the oily residue, and then refrigerated. After 2 hours, the crude product was isolated and washed with dry ether. The material was suspended in acetone (15 mL), sonicated and vortexed, which effectively extracted a yellow impurity from the product. The mixture was refrigerated, and the product isolated by filtration was washed with cold acetone and dried. The isothiourea salt was obtained as white solid in 82% yield (*which is sensitive to moisture, and therefore should be stored carefully under dry condition*).



1,1,3,3-tetramethyl-2-phenylisothiouronium chloride (4):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.42 – 7.32 (m, 3H), 3.30 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 131.7, 130.6, 130.0, 127.8, 44.8.

Matching reported literature data[9].

- *thioetherification from preformed phenyl isothiouronium salt **4** and alcohol **2a***:

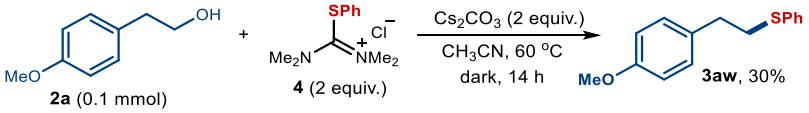


Figure S10. Thioetherification from prepared aryl Isothiouronium salts and alcohols

As shown above, primary alcohol **2a** can be converted into corresponding thioether by reacting with isothiouronium salt **4** under dark condition, while accompanying with 1,2-diphenyldisulfane and 1,1,3,3-tetramethylurea as by-products. This confirmed that the polar *S_N2 substitution* reaction can provide the desired product. However, more hindered secondary alcohol **8** failed to convert even at higher temperature.

D3.2 Stereospecific Displacement: Configuration Inversion

To verify the occurrence of *S_N2 substitution* process in the photochemical thioetherification, we subjected an enantioenriched alcohol to the standard condition and observed inversion of configuration (96% ee), which is consistent with an S_N2 polar manifold being opertaive. The optical rotation was in good agreement with the value reported in the literature[10].

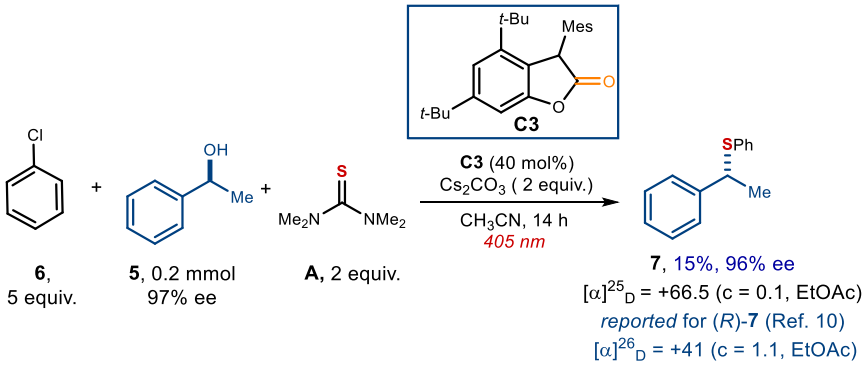
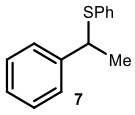


Figure S11. Stereospecific displacement of enantiopure alcohol **5**

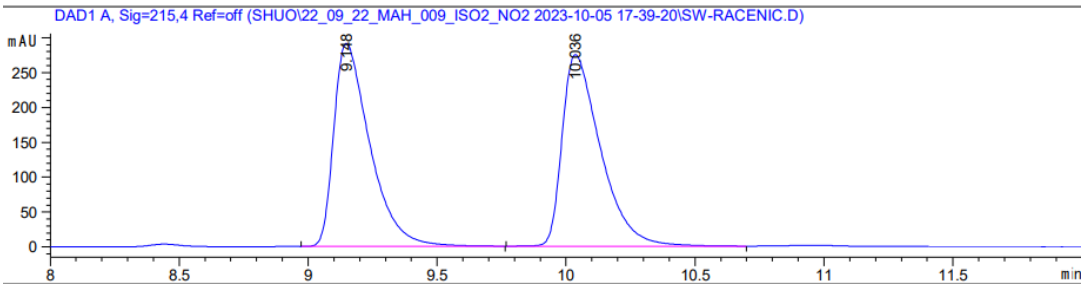


(*rac*)-**Phenyl(1-phenylethyl)sulfane (7):** Synthesized according to the General Procedure using (*rac*)-1-phenylethan-1-ol **5** (24.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea **A** (79.5 mg, 0.6 mmol, 3.0 equiv.) and chlorobenzene **6** (112.5 mg, 1.0 mmol, 5.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford (*rac*)-**7** (5.5 mg, 13% yield) as a yellow liquid.

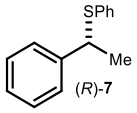
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 6H), 7.27 – 7.20 (m, 4H), 4.37 (qd, J = 7.0, 1.8 Hz, 1H), 1.66 (dd, J = 7.0, 1.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 135.2, 132.5, 128.7, 128.4, 127.3, 127.2, 127.2, 48.0, 22.4.

Matching reported literature data[10].



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.148	BB	0.1454	2829.27246	291.16721	49.8440
2	10.036	BB	0.1569	2846.97754	274.71118	50.1560



(*R*)-Phenyl(1-phenylethyl)sulfane (7): Synthesized according to the General Procedure using (*S*)-1-phenylethan-1-ol (*S*)-**5** (24.5 mg, 0.2 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea **A** (79.5 mg, 0.6 mmol, 3.0 equiv.) and chlorobenzene **6** (112.6 mg, 1.0 mmol, 5.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 300: 1 as eluent) to afford (*R*)-**7** (6.5 mg, 15% yield) as a yellow liquid.

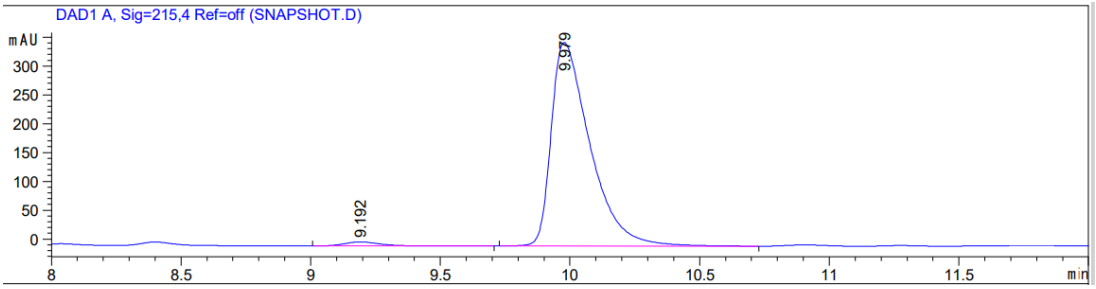
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 6H), 7.27 – 7.20 (m, 4H), 4.37 (qd, J = 7.0, 1.8 Hz, 1H), 1.66 (dd, J = 7.0, 1.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 135.2, 132.5, 128.7, 128.4, 127.3, 127.2, 127.2, 48.0, 22.4.

Matching reported literature data[10].

The enantiomeric excess of the corresponding product was determined to be 96% by Agilient 1200 series HPLC, using Daicel Chiralpak IB-3 column (eluent: *n*-hexane; flow rate 1.0 mL/min; λ = 215 nm: t_R(major) = 9.98 min, t_R(minor) = 9.19 min)

$[\alpha]_D^{25}$ = +66.5 (c = 0.1, EtOAc), reported:[10] $[\alpha]_D^{26}$ = +41 (c = 1.1, EtOAc)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.192	BB	0.1485	66.13474	6.85553	1.7704
2	9.979	BB	0.1562	3669.54980	353.21246	98.2296

D4. Photophysical Studies

*The photophysical properties of **C2** have been presented in our previous reports*[2].

Sample Preparation:

- Neutral catalysts **C1 and C3**

A 25 mL glass vial containing catalysts **C1** or **C3** (0.01 mmol) was sealed with a septum, vacuumed and backfilled with argon for 3 times, then degassed acetonitrile (5 mL, HPLC grade) was added via syringe to provide a $2\cdot10^{-3}$ M stock solution of catalyst. 20 μL of the stock solution were taken and diluted further with acetonitrile (4 mL) to obtain a $1\cdot10^{-5}$ M solution (200 μL were taken for a $1\cdot10^{-4}$ M solution). 2.5 mL of the solution was transferred into an argon filled quartz cuvette (10 x 10 mm light path) equipped with a septum.

- Deprotonated **C1 and C3**

A 25 mL glass vial containing Cs_2CO_3 (130 mg) was sealed with a septum, vacuumed and backfilled with argon for 3 times, then degassed acetonitrile (8 mL, HPLC grade) was added via syringe. Addition of 40 µL of freshly prepared neutral **C1** or **C3** solution ($2 \cdot 10^{-3}$ M) gave a $1 \cdot 10^{-5}$ M solution (400 µL were taken for a $1 \cdot 10^{-4}$ M solution). The vial was sealed with Parafilm and stirred at room temperature for 1 hour. 2.5 mL of the solution was transferred into an argon filled quartz cuvette (10 x 10 mm light path) equipped with a septum.

D4.1. Absorption Studies

UV-Vis measurements were carried out on an Agilent Cary 60 UV-Vis spectrophotometer equipped with two silicon diode detectors, double beam optics and Xenon pulse light (**Figure S11**).

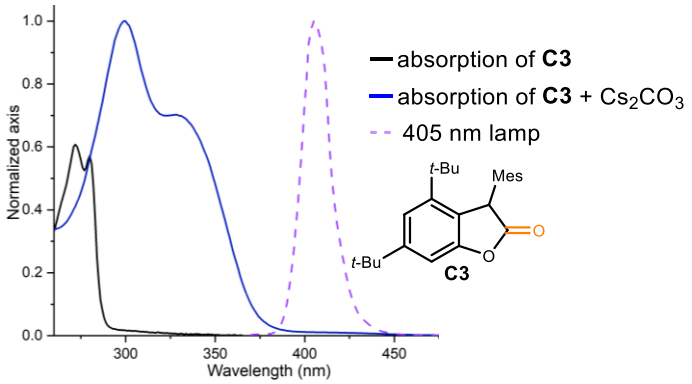


Figure S12. Normalized absorption spectra recorded for catalyst **C3** in CH_3CN, in absence (black line) or in presence (blue line) of Cs_2CO_3 in a $1 \cdot 10^{-4}$ M solution and 405 nm lamp spectrum (purple line).

D4.2. Emission Studies

Fluorescence measurements were carried out on an Fluorolog Horiba Jobin Yvon spectrofluorimeter equipped with a photomultiplier detector, a double monochromator, and a 450W xenon light source. The emission spectrum of the deprotonated **C1** and **C3** (formed in situ upon addition of Cs_2CO_3 in degassed CH_3CN according to the same procedure in page S31) was recorded from 340 nm to 550 nm and 370 nm to 600 nm after excitation with 350 nm and 360 nm lasers.

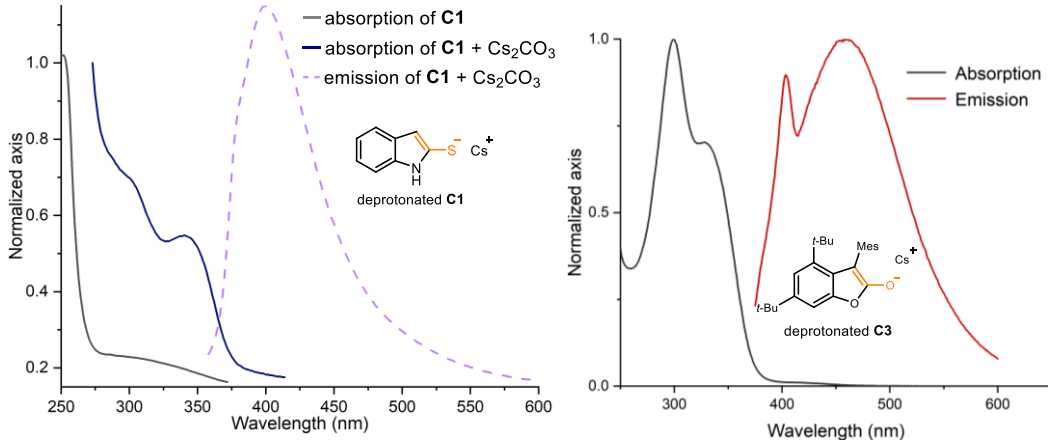


Figure S13. *left*) Normalized absorption of catalyst **C1**, absorption and emission spectra of the deprotonated **C1** (formed upon deprotonation with Cs_2CO_3) in CH_3CN in a $1 \cdot 10^{-5}$ M solution; *right*) Normalized absorption and emission spectra of the deprotonated catalyst **C3** (formed upon deprotonation with Cs_2CO_3 (3 equiv.)) in CH_3CN in a $1 \cdot 10^{-4}$ M solution.

D4.3. Stern-Volmer Quenching Studies

Fluorescence measurements were carried out on an Fluorolog Horiba Jobin Yvon spectrofluorimeter equipped with a photomultiplier detector, a double monochromator, and a 450W xenon light source. A 1.0 M solution of the quencher substrate in degassed ACN (HPLC grade) was prepared and 20 µL of this stock solution were added to the solution of the deprotonated catalyst, prepared according to the procedure detailed in page S34. The addition of the substrate solution (the quencher) was repeated for four/five times. After each addition, the solution was mixed and the emission spectra of the excited catalyst was acquired from 365 nm to 500 nm (the excitation wavelength was fixed at 350 nm, slit width= 5 nm). A solvent blank was subtracted from all the measurements. The excitation wavelength was chosen in order to avoid saturation of the emission detector.

The results shown in **Figure S13** indicates that 4-chlorobenzonitrile quenched the excited state emission of the deprotonated catalyst **C1**. The Stern-Volmer plot shows a linear correlation between the amounts of substrates and the ratio I_0/I, following the relationship: $I_0/I = 1 + K_{SV}[Q]$ (Q = Quencher).

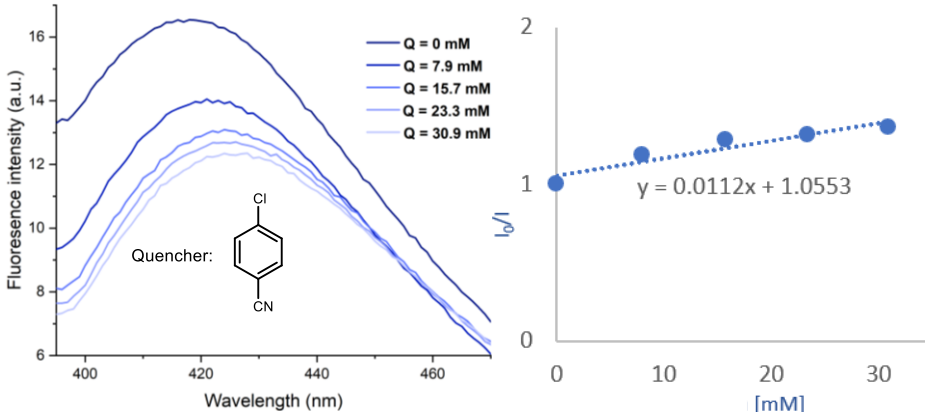


Figure S14. Stern-Volmer quenching studies with 4-chlorobenzonitrile (**1a**).

D4.4. Quantum Yield Determination

-Experimental Setup

The experiments for the quantum yield determination were conducted under illumination by a 405 nm high-power single LED (setup depicted in **Figure S14**), using an aluminum block on a 3D-printed holder, fitted with a 405 nm high-power single LED. The irradiance was fixed at 60±2 mW/cm^2, as controlled by an external power supply and measured using a photodiode light detector at the start of each reaction. This setup secured a reliable irradiation while keeping a distance of 1 cm between the reaction vessel and the light source.

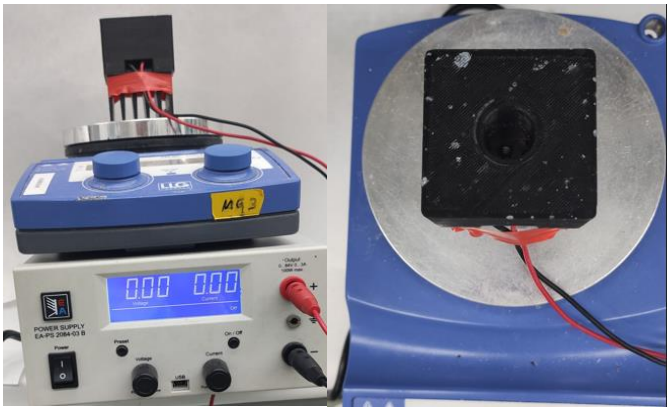


Figure S15. High-power single LED setup

-General Procedure for photon Flux (F) determination[11]

$$\Phi = M/(F \bullet t \bullet f) \quad (1)$$

$$f = 1 - 10^{-A} \quad (2)$$

M is the moles of product formed (mol), **F** is the number of photons emitted per second (einstein s^{-1}), **t** is the time (s) and ***f*** is fraction of light absorbed which can be calculated using eq. 2, where **A** is the measured absorbance at 405 nm.

The number of photons emitted per second was determined using azobenzene as actinometer[12-13]. Using the reaction setup depicted in **Figure S14**, a glass vial was filled with a solution of *trans*-azobenzene (0.1 mmol) in CD_3OD (0.1M) and irradiated with a 405 nm light. The *trans-cis* isomerization was followed in time in ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard.

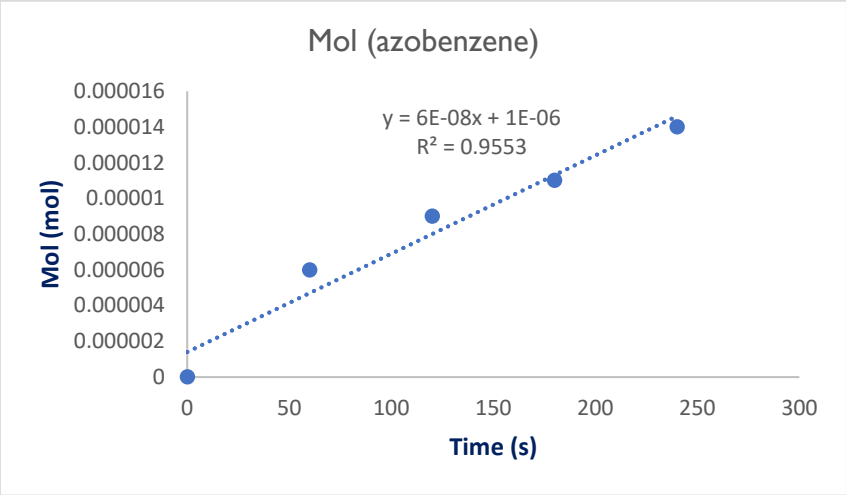


Figure S16. Plot of moles of *cis*-azobenzene formed vs irradiation time

The actinometer solution was irradiated for 0 min, 1 min, 2 min, 3 min and 4 min. According to the eq. 1-2 and reported quantum yield of trans-cis isomerization process (Φ = 0.288)[13], the number of photons emitted per time unit (**F**) was determined (3.0×10^{-7} mol s^{-1}).

*-Quantum Yield Determination Using **C1** as Photocatalyst*

Following the general procedure A, five model thioetherification reactions between **1a** and **2a** were performed separately using catalyst **C1**. Each reaction mixture was irradiated for 0 min, 30 min, 60 min, 90 min and 120 min. After irradiation, the amount of product **3a** formed was determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard. An absorbance of 0.216 was determined for the model reaction mixture (1:4 dilution). The moles of the formed product **3a** are plotted against the number of incident photons (**Figure S16**). The quantum yield (Φ) was calculated to be Φ = 0.017 based on the slope and eq. 1-2.

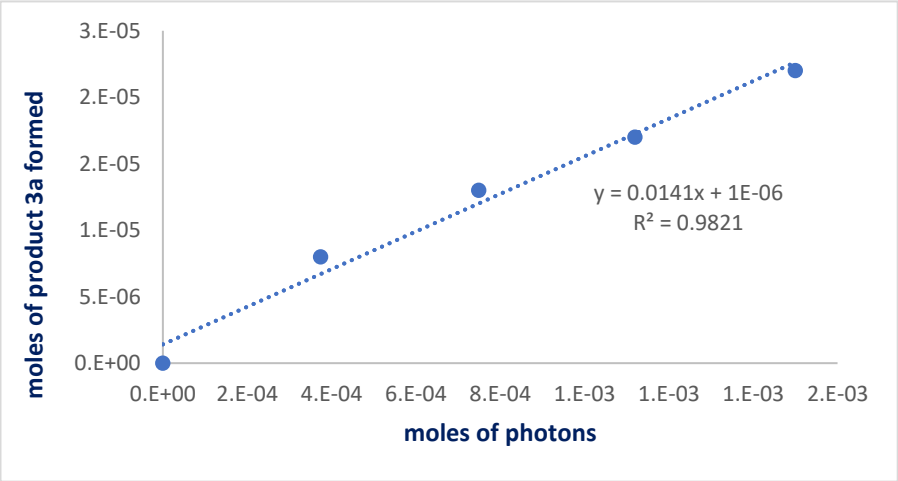


Figure S17. Plot of moles of incident photons vs moles of product **3a** formed

*-Quantum Yield Determination Using **C3** as Photoreductant*

Following the general procedure B, five model thioetherification reactions between **1aw** and **2a** were performed separately under **C3** catalysis. Each reaction mixture was irradiated for 0 min, 30 min, 60 min, 90 min and 120 min. After irradiation, the amount of product **3aw** formed was determined by ^{1}H NMR measurement using 1,3,5-trimethoxybenzene as the internal standard. An absorbance of 0.084 was determined for the model reaction mixture (1:4 dilution). The moles of the formed product are plotted against the number of incident photons (**Figure S17**). The quantum yield (Φ) was calculated to be Φ = 0.052 based on the slope and eq. 1-2.

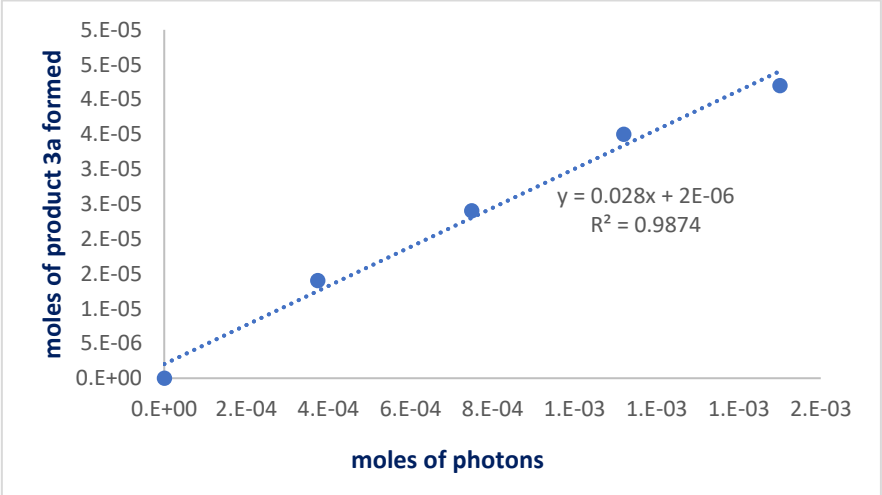


Figure S18. Plot of moles of incident photons vs moles of product **3aw** formed

D4.5. Light On-off Experiment

Experiments with successive intervals of irradiation and dark periods were performed following the general procedure A (page S7), using alcohol **2a** as model substrate in the presence of aryl halide **1a**, photocatalyst **C1**, thiourea **A1** and Cs_2CO_3 ([**2a**] = 0.1 M in CH_3CN). Formation of product **3a** was determined by means of ^{1}H NMR analysis from aliquots taken under nitrogen atmosphere from the reaction mixture.

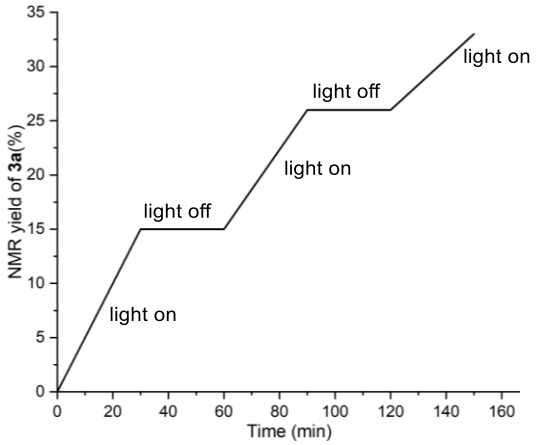


Figure S19. Light on-off experiment according to formation of **3a**

D5. Electrochemical Studies

Cyclic voltammetry (CV) measurements were carried out on a Princeton Applied Research PARSTAT 2273 instrument with a glassy carbon disk electrode (diameter: 3 mm) as working electrode. A silver wire coated with AgCl immersed in a 3.0 M aqueous solution of NaCl and separated from the analyte by a fritted glass disk was employed as the reference electrode and a Pt wire counter-electrode completed the electrochemical setup. The scan rate was 100 mV/s unless otherwise stated. The substrates were measured at concentration of 0.02 M in acetonitrile with $TBAPF_6$ (0.1 M) as electrolyte. The preparation of the deprotonated catalyst solutions was carried out as described in the photophysical studies section (page S31, at a concentration of 0.02 M).

Potentials are quoted with the following notation: E_p^C (E_{Red}) refers to the cathodic peak potential, E_p^A (E_{Ox}) refers to the anodic peak potential.

D5.1. Cyclic Voltammetry Measurements of the Model Substrates

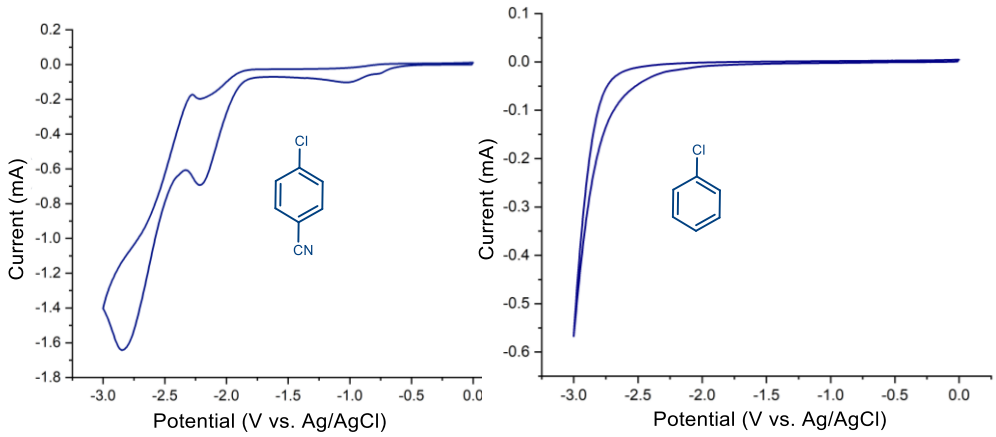


Figure S20. *left*) CV of 4-chlorobenzonitrile [0.02M] in [0.1 M] TBAPF6 in CH_3CN. Measurement started by reduction from 0 to -3.0 V and finishing at 0 V. Platinum disk working electrode, Ag/AgCl (NaCl 3 M) referenceelectrode, Pt wire auxiliary electrode. irreversible reduction E_p = -2.2 V, E_p = -2.8 V. *right*) CV of chlorobenzene [0.02M] in [0.1 M] TBAPF6 in CH_3CN. Measurement started by reduction from 0 to -3.0 V and finishing at 0 V. Platinum disk working electrode, Ag/AgCl (NaCl 3 M) referenceelectrode, Pt wire auxiliary electrode.), reduction was not observed in the registered potential window.

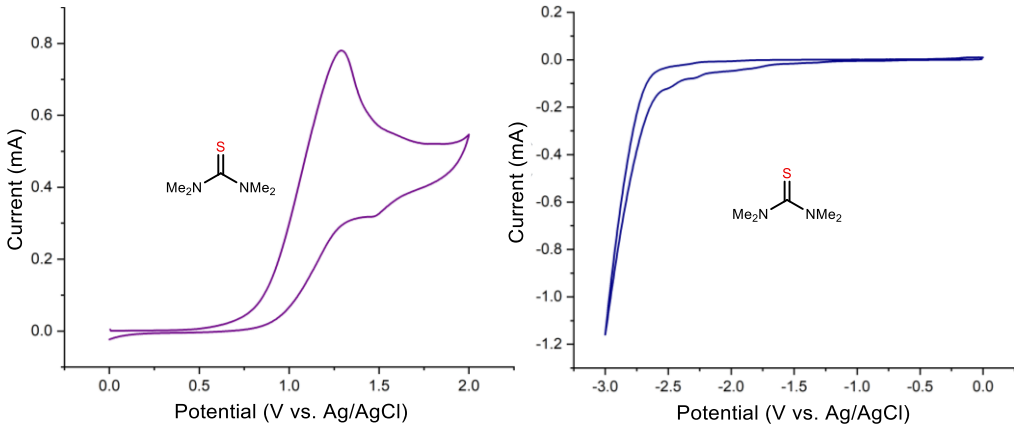


Figure S21. *left*) CV of 1,1,3,3-tetramethylthiourea [0.02M] in [0.1 M] TBAPF6 in CH_3CN. Measurement started by oxidation from 0 to +2.0 V and finishing at 0 V. Platinum disk working electrode, Ag/AgCl (NaCl 3 M) referenceelectrode, Pt wire auxiliary electrode, one irreversible oxidation E_p = 1.29 V. *right*) CV of 1,1,3,3-tetramethylthiourea [0.02M] in [0.1 M] TBAPF6 in CH_3CN. Measurement started by reduction from 0 to -3.0 V and finishing at 0 V. Platinum disk working electrode, Ag/AgCl (NaCl 3 M) referenceelectrode, Pt wire auxiliary electrode, reduction was not observed in the registered potential window.

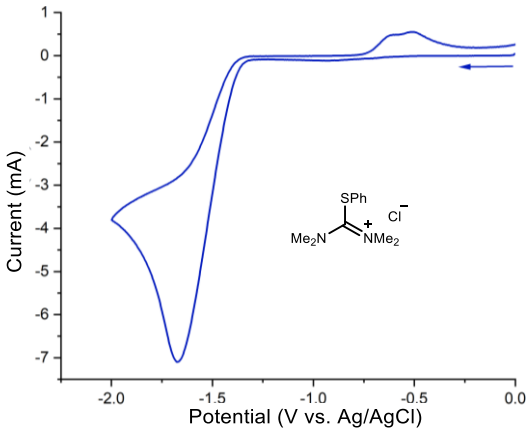


Figure S22. CV of 1,1,3,3-tetramethyl-2-phenylisothiouronium chloride [0.02M] in [0.1 M] TBAPF6 in CH_3CN. Measurement started by reduction from 0 to -2.5 V and finishing at 0 V. Platinum disk working electrode, Ag/AgCl (NaCl 3 M) referenceelectrode, Pt wire auxiliary electrode, one irreversible reduction E_p = -1.68 V.

D5.2. Cyclic Voltammetry Measurements of Pre-catalysts and Catalytic Active Species

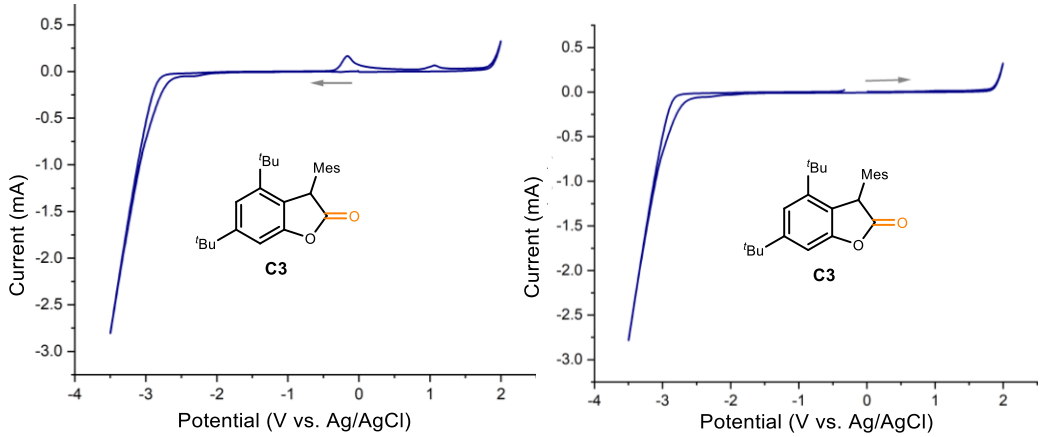


Figure S23. *left*) CV of **C3** [0.02M] in [0.1 M] TBAPF6 in CH_3CN. Measurement started by reduction from 0 to -4.0 to +2.0 V and finishing at 0 V. Platinum disk working electrode, Ag/AgCl (NaCl 3 M) referenceelectrode, Pt wire auxiliary electrode, reduction was not observed in the registered potential window and irreversible oxidation E_p^A = -0.16 V; *right*) CV of **C3** [0.02M] in [0.1 M] TBAPF6 in CH_3CN. Measurement started by oxidation from 0 to +2.0

to -4.0 V and finishing at 0 V. Platinum disk working electrode, Ag/AgCl (NaCl 3 M) referenceelectrode, Pt wire auxiliary electrode, oxidation was not observed in the registered potential window.

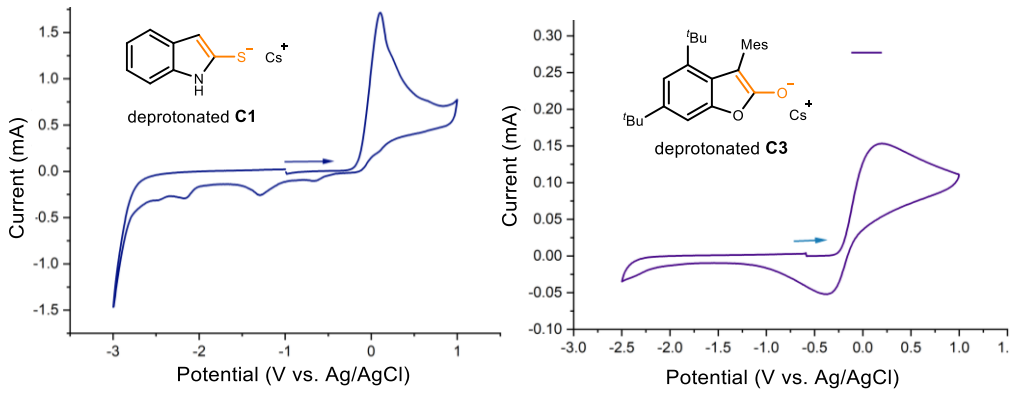


Figure S24. *left*) CV of the deprotonated catalyst **C1** [0.02M] in [0.1 M] TBAPF6 in CH_3CN. Measurement started by oxidation from -1V to +1.5 to -3.0 V and finishing at -1 V. Platinum disk working electrode, Ag/AgCl (NaCl 3 M) referenceelectrode, Pt wire auxiliary electrode, irreversible oxidation E_p^A = 0.1 V; *right*) CV of the deprotonated catalyst **C3** [0.02M] in [0.1 M] TBAPF6 in CH_3CN. Measurement started by oxidation from -0.5 to 1.0 to -2.5 V and finishing at -0.5 V. Platinum disk working electrode, Ag/AgCl (NaCl 3 M) referenceelectrode, Pt wire auxiliary electrode, irreversible oxidation E_p^A = 0.17 V.

D5.3. Conversion of the Potential from Ag/AgCl to SCE

The conversion of the redox potential from Ag/AgCl to SCE was done according to the literature by measuring the redox potential of ferrocene as reference in CH_3CN.[14]

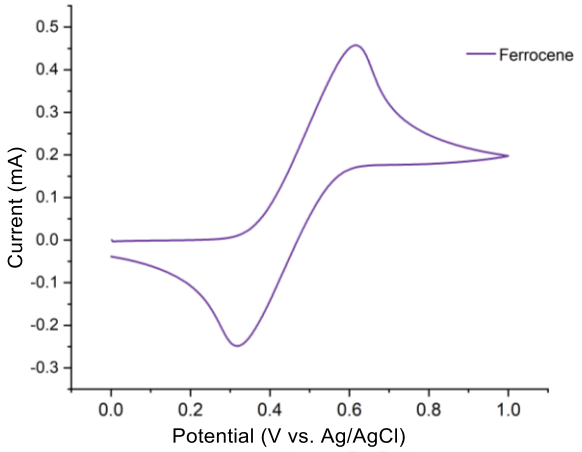


Figure S25. CV of ferrocene [0.02M] in [0.1 M] TBAPF6 in CH_3CN. Measurement started by oxidation from 0 V to +1.0 and finishing at -1 V. Platinum disk working electrode, Ag/AgCl (NaCl 3 M) referenceelectrode, Pt wire auxiliary electrode, one reversible reduction and oxidation $E_{1/2}$ = 0.46 V.

With the reference CV, the redox potential *vs.* SCE in CH_3CN was calculated using the following equations:

*For deprotonated **C1:***

$$E_p^A \text{ (Ag/AgCl to Fc/Fc}^+\text{)} = 0.1 - 0.46 = -0.36 \text{ V } \textit{vs.}\text{ Fc/Fc}^+$$
$$E_p^A \text{ (Fc/Fc}^+\text{ to SCE)} = (-0.36) + 0.38 = 0.02 \text{ V } \textit{vs.}\text{ SCE}$$

*For deprotonated **C3:***

$$E_p^A \text{ (Ag/AgCl to Fc/Fc}^+\text{)} = 0.17 - 0.46 = -0.29 \text{ V } \textit{vs.}\text{ Fc/Fc}^+$$
$$E_p^A \text{ (Fc/Fc}^+\text{ to SCE)} = (-0.29) + 0.38 = 0.09 \text{ V } \textit{vs.}\text{ SCE}$$

D6. Evaluation of the Excited-State Potential of the Deprotonated Catalyst C1 and C3

Using the data collected from the CV studies (**Figure S22**) and from the absorption and emission spectra (**Figure S12**) of the deprotonated **C1** and**C3**, we could estimate the redox potential of the excited state with the following Equation:[15]

$$E(Pc^{\bullet}/Pc^{-*}) = E(Pc^{\bullet}/Pc^{-}) - E_{0\text{-}0}(Pc^{-*})/(Pc^{-})$$

Since the electrochemical oxidation of deprotonated **C1** and **C3** is irreversible (**Figure S22**), the irreversible peak potential E_p anode was used for $E(Pc^{\bullet}/Pc^{-})$. The oxidation potential was calculated to be 0.02 V *vs.* SCE (in ACN) and 0.09 V *vs.* SCE (in ACN) respectively. $E_{0\text{-}0}(Pc^{-*})/(Pc^{-})$ was approximately determined spectroscopically from the intersection of the normalized absorbance and emission spectra (roughly at 373 nm for deprotonated **C1** and 360 nm for deprotonated **C3**) to have values of 3.3 eV and 3.44 eV.

The oxidation potential of the excited deprotonated catalyst **C1**:

$$E(Pc^{\bullet}/Pc^{-*}) = 0.1 - 3.3 = \textit{-3.2 V vs. Ag/AgCl}$$
$$E(Pc^{\bullet}/Pc^{-*}) = 0.02 - 3.3 = \textit{-3.28 V vs. SCE}$$

The oxidation potential of excited deprotonated catalyst **C3**:

$$E(Pc^{\bullet}/Pc^{-*}) = 0.17 - 3.44 = \textit{-3.27 V vs. Ag/AgCl}$$
$$E(Pc^{\bullet}/Pc^{-*}) = 0.09 - 3.44 = \textit{-3.35 V vs. SCE}$$

D7. GC-MS Analyses of the Reaction Mixture

Figure S26 shows the product distribution for the model reaction, including the recovery of substrates and by-products, providing an indication of the compounds formed in our process. In addition to cesium chloride and 1,1,3,3-tetramethylurea, which are the expected by-products, we also observed the formation of 4,4'-thiodibenzonitrile (0.15 mmol) and traces of dehalogenation of the aryl chloride **1a**, as detected by GC-MS analysis of the crude mixture. Unconverted thiourea **A** and alcohol **2a** were also recovered. *These by-products were particularly prevalent in the low-efficiency processes* (yield < 50%). After completion of reaction, the reaction mixture was diluted and injected into GC-MS.

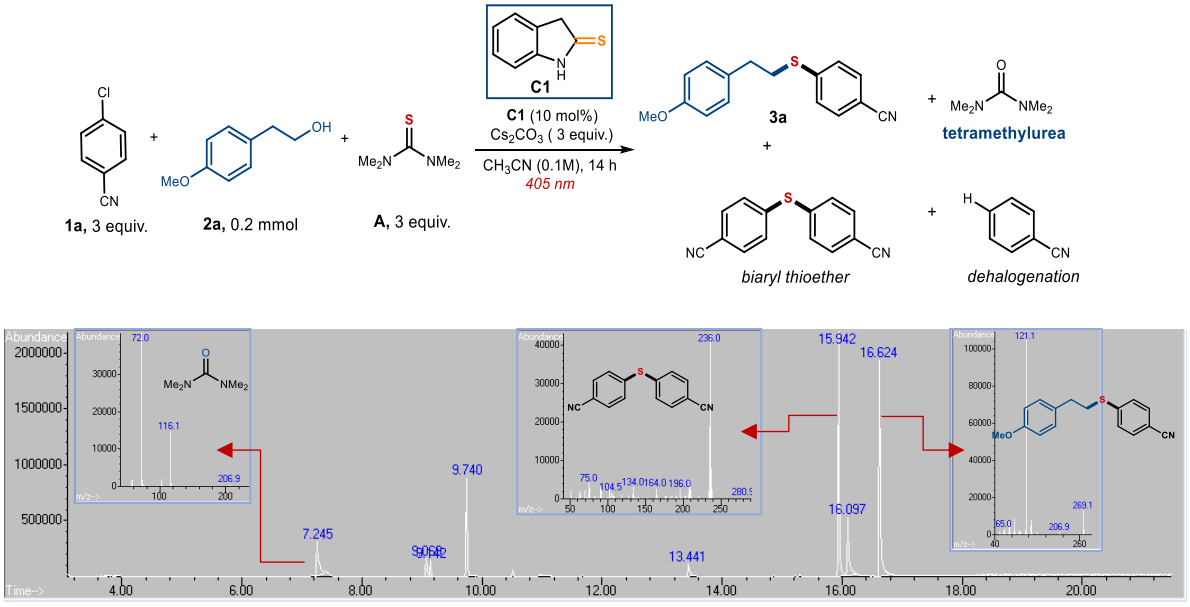


Figure S26. Product distribution in the model reaction and assignment of species by GC-MS analyses

D8. Rationale for the Higher Reactivity of Catalyst C3.

As illustrated in Figure S27, and based on the redox potentials of the excited catalysts **C1-3** reported in Figure 1 of the main manuscript, the difference in efficiency among these catalysts is likely not dependent on their ability to activate electron-rich aryl chlorides via SET reduction. All of them could be capable of reducing the substrates and generating the relatively electron-rich aryl radicals along with intermediates **V** or **VI** (Figure S27). However, the polarity mismatch between the generated electron-rich aryl radicals and the electron-rich tetramethylthiourea **A** may impede a fast radical trap (*step I* in Fig. S27 below), slowing down the formation of the radical intermediate **IV**. Consequently, the SET reduction of radical **V** from **IV**, which secures the turnover of the catalyst (*step II*), may become problematic. This could lead to the deactivation of the catalyst since the reactive intermediate **V** could engage in different pathways. The more hindered lactone catalyst **C3** may circumvent this problem by means of the bulky mesitylene group at the C3 position, which could stabilize the radical in the corresponding intermediate **VI**, making it long-lived.

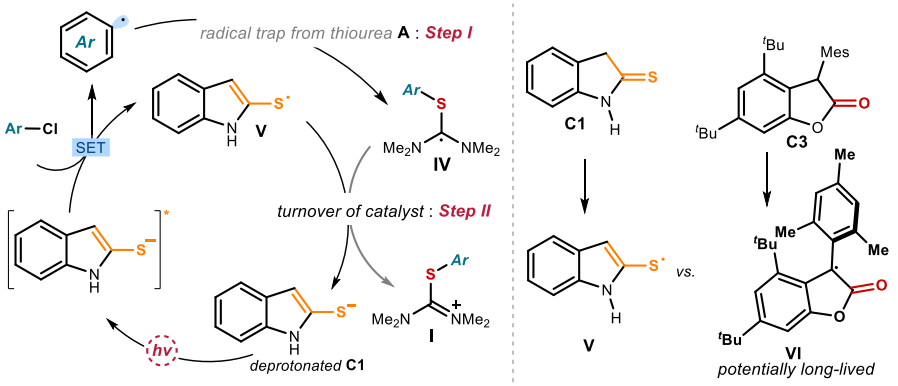


Figure S27. Rationale for the higher reactivity of catalyst **C3** in activating electron-rich aryl chlorides.

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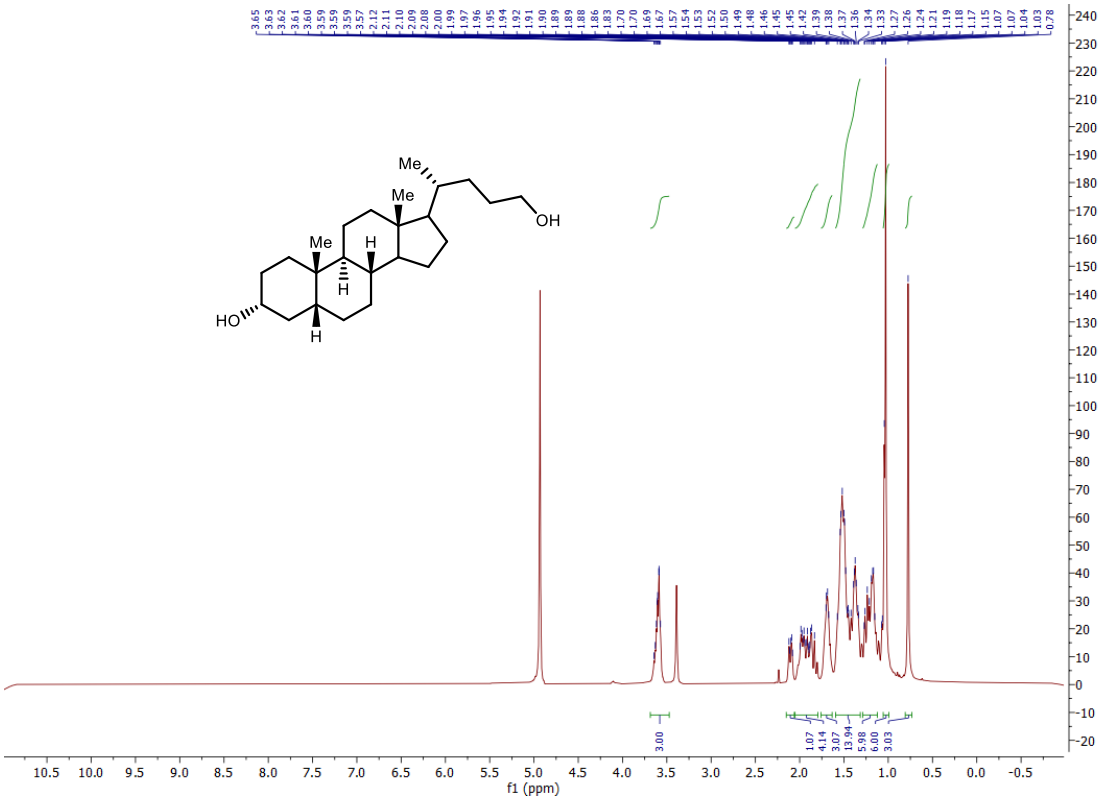
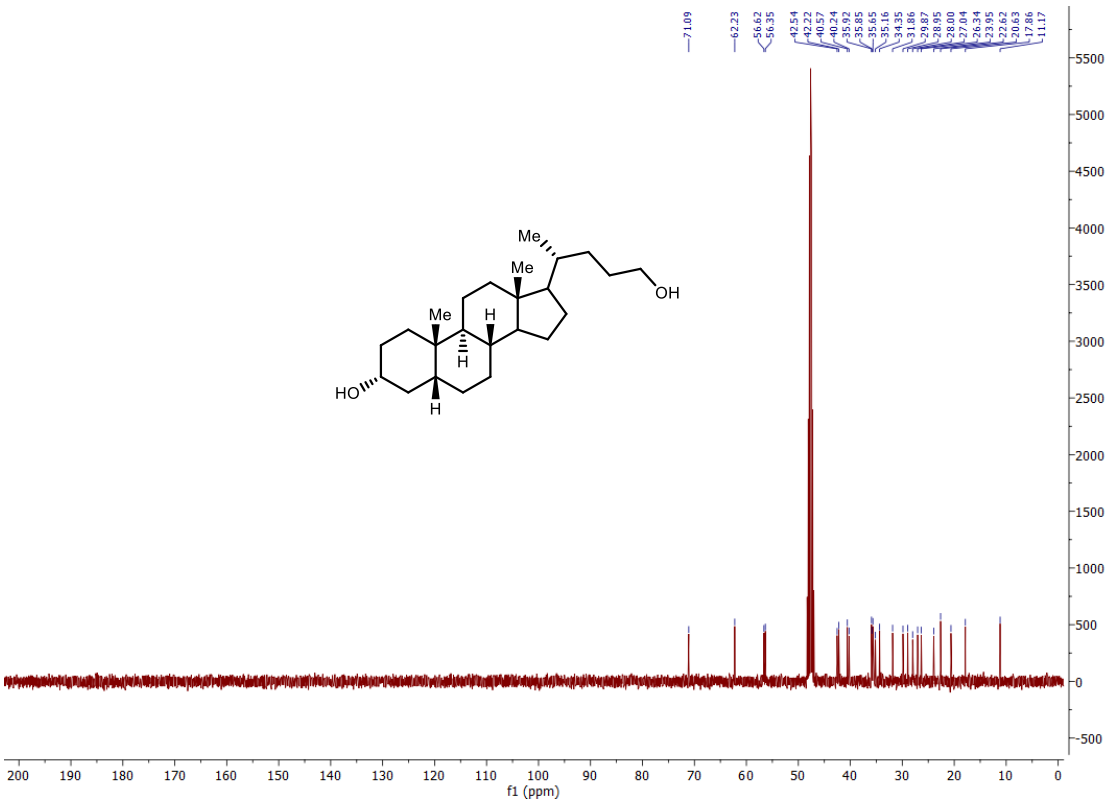
NMR Spectra

Substrates and catalysts

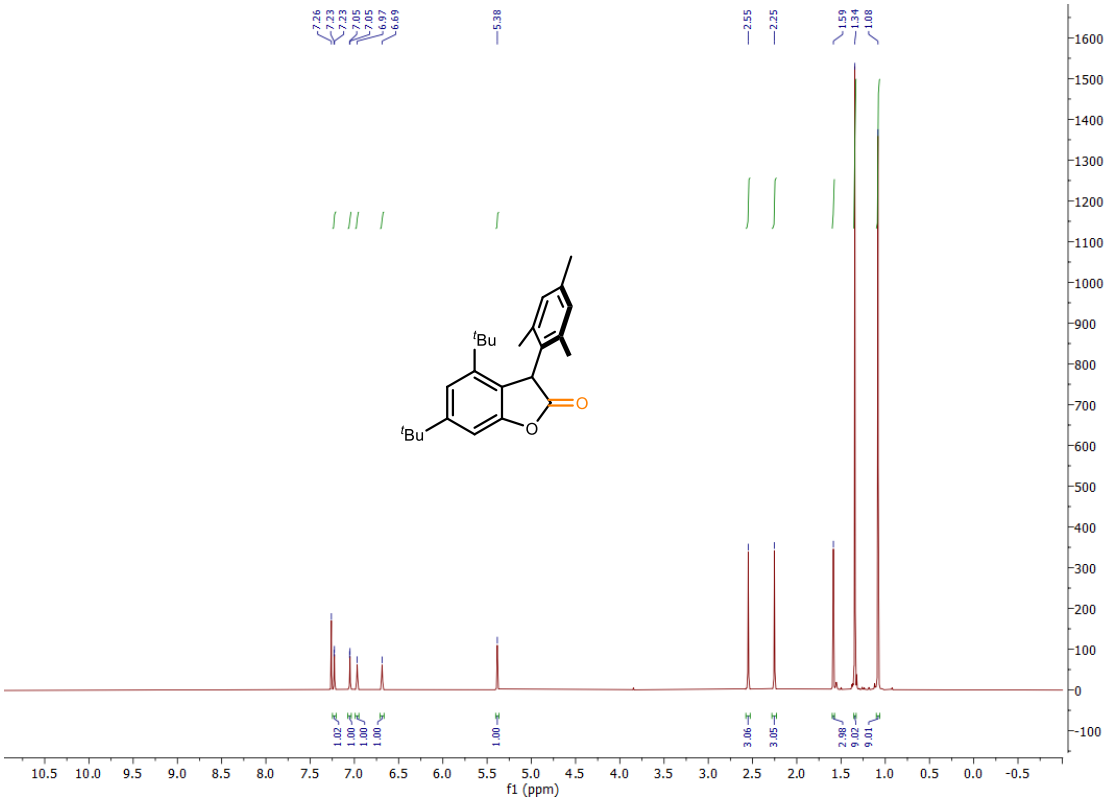
^{1}H NMR (400 MHz, CD_3OD) of **2ar**:



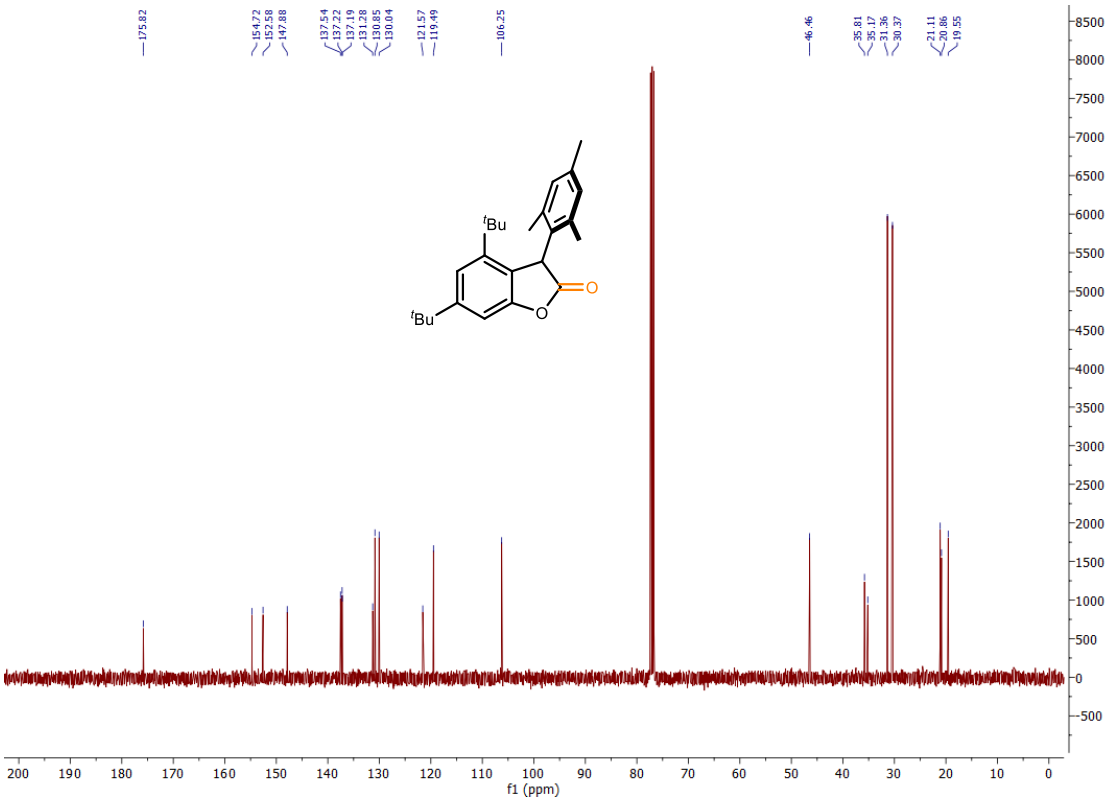
^{13}C NMR (101 MHz, CD_3OD) of **2ar:**



^{1}H NMR (400 MHz, $CDCl_3$) of **C3**:

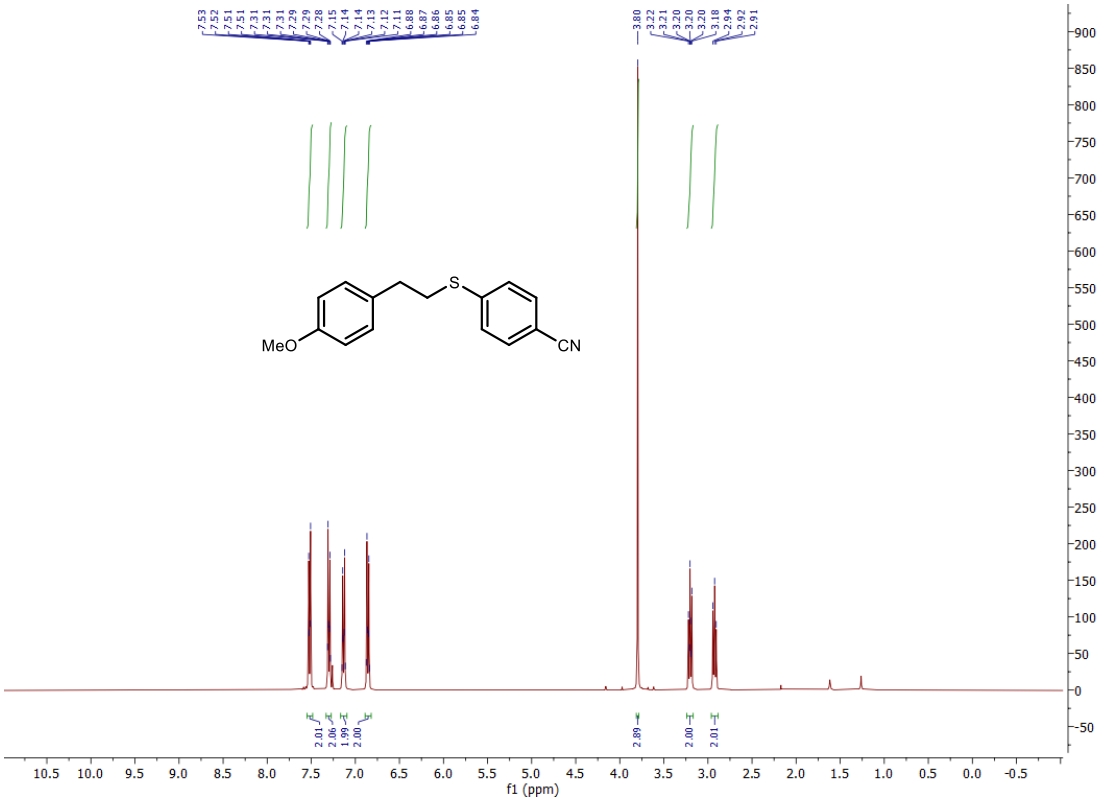


^{13}C NMR (101 MHz, $CDCl_3$) of **C3:**

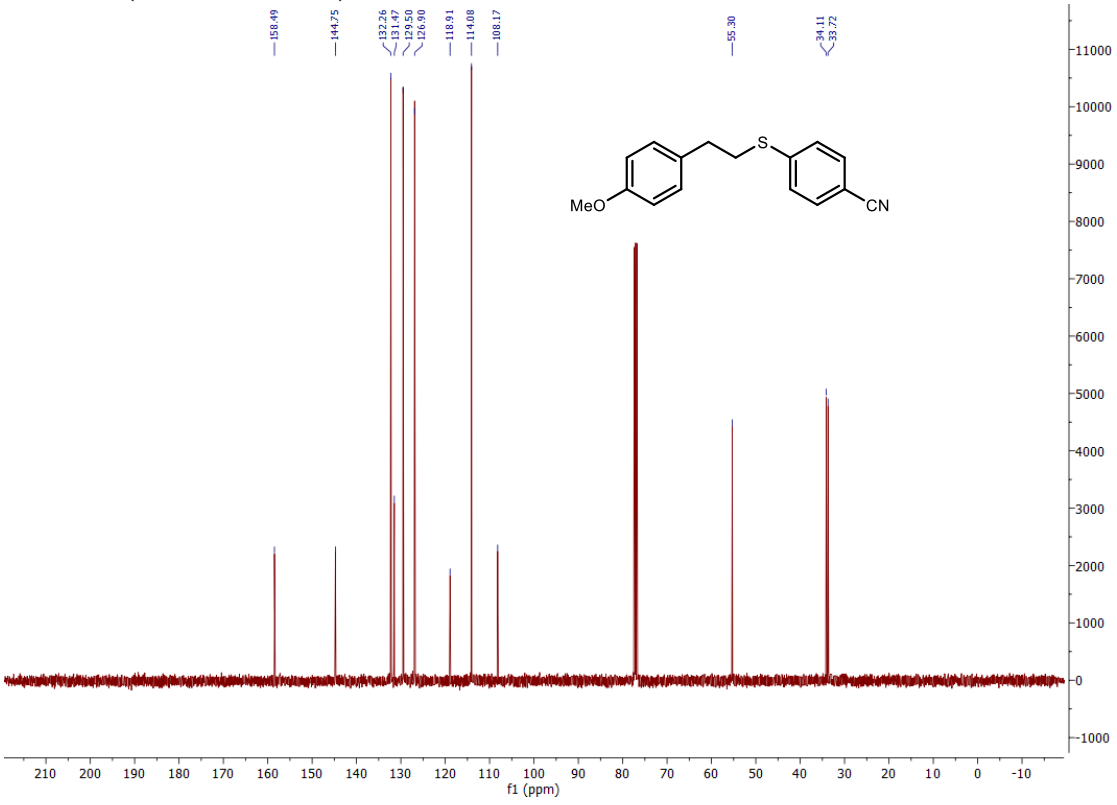


Products

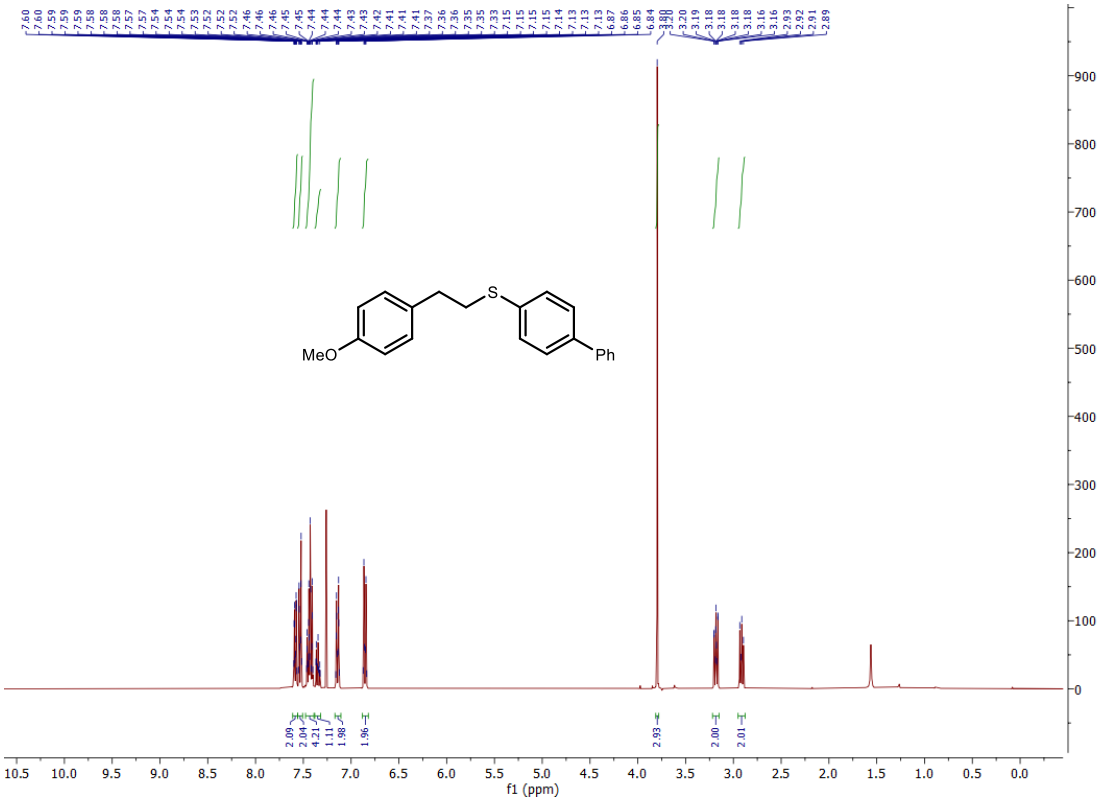
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**:



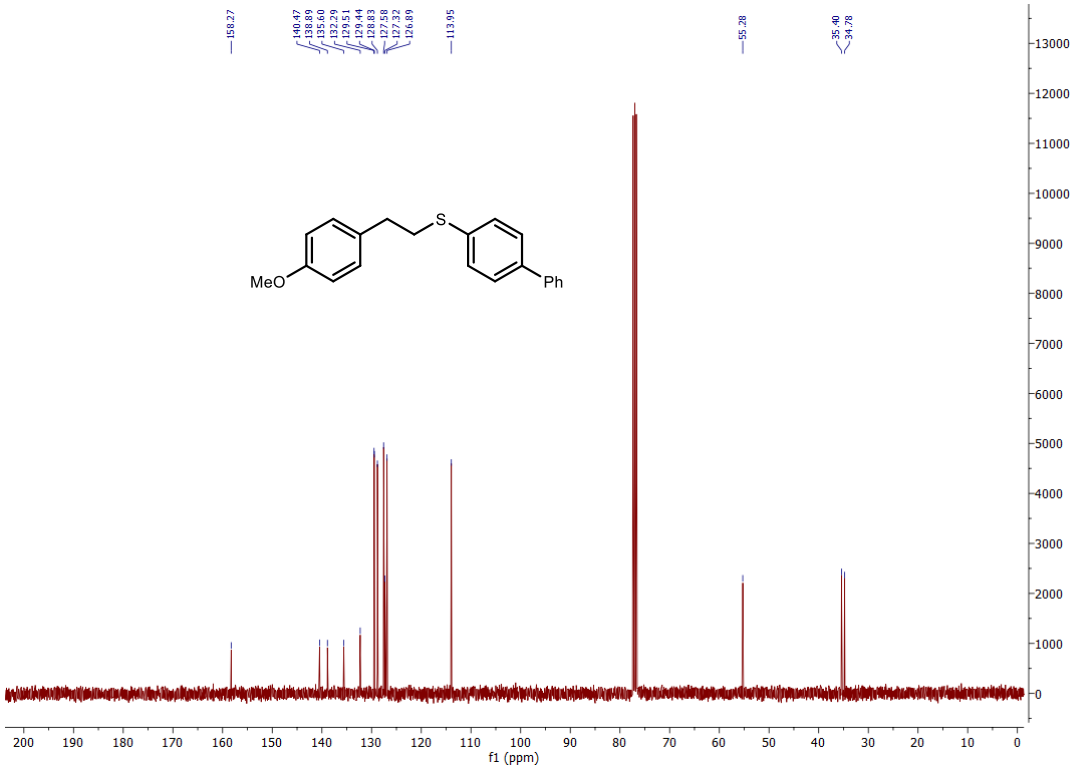
^{13}C NMR (101 MHz, $CDCl_3$) of **3a:**



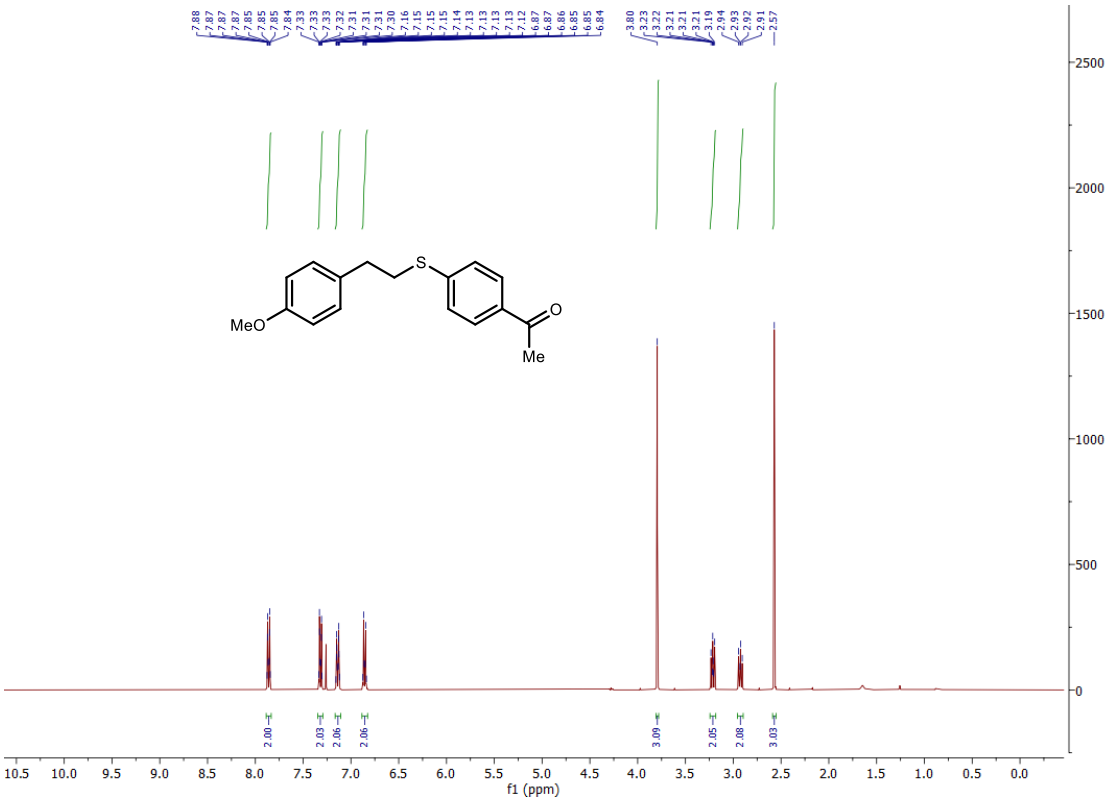
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**:



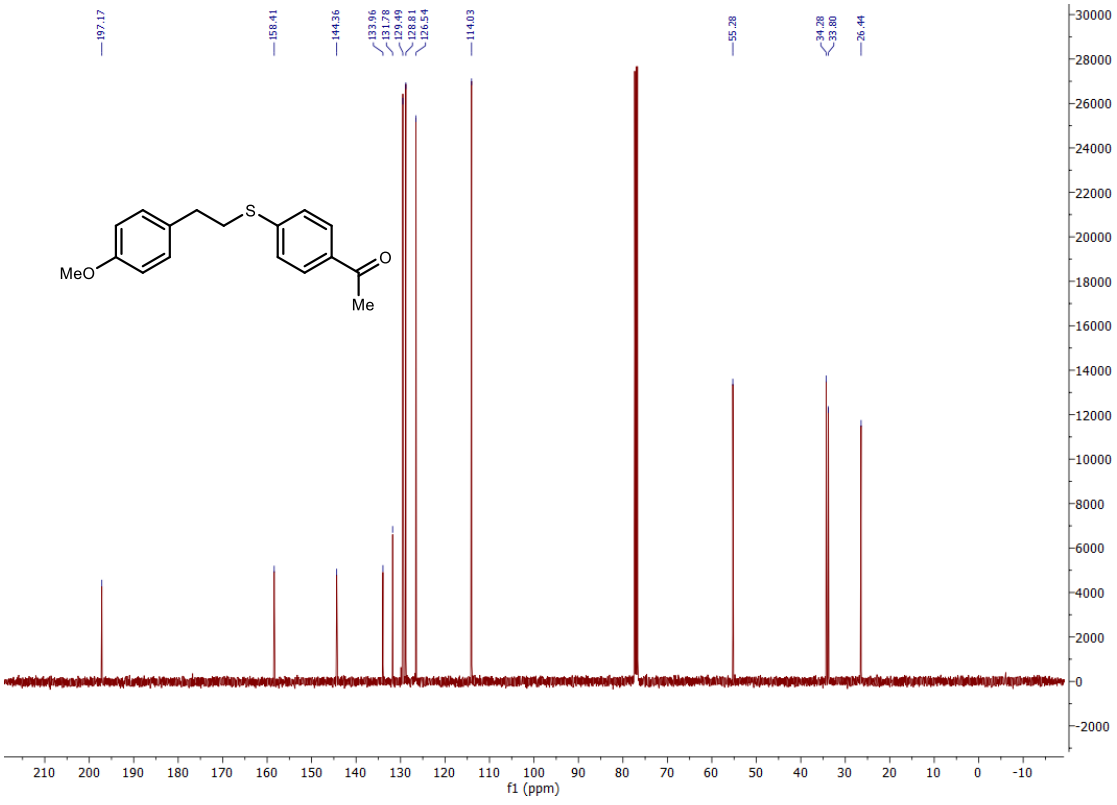
^{13}C NMR (101 MHz, $CDCl_3$) of **3b:**



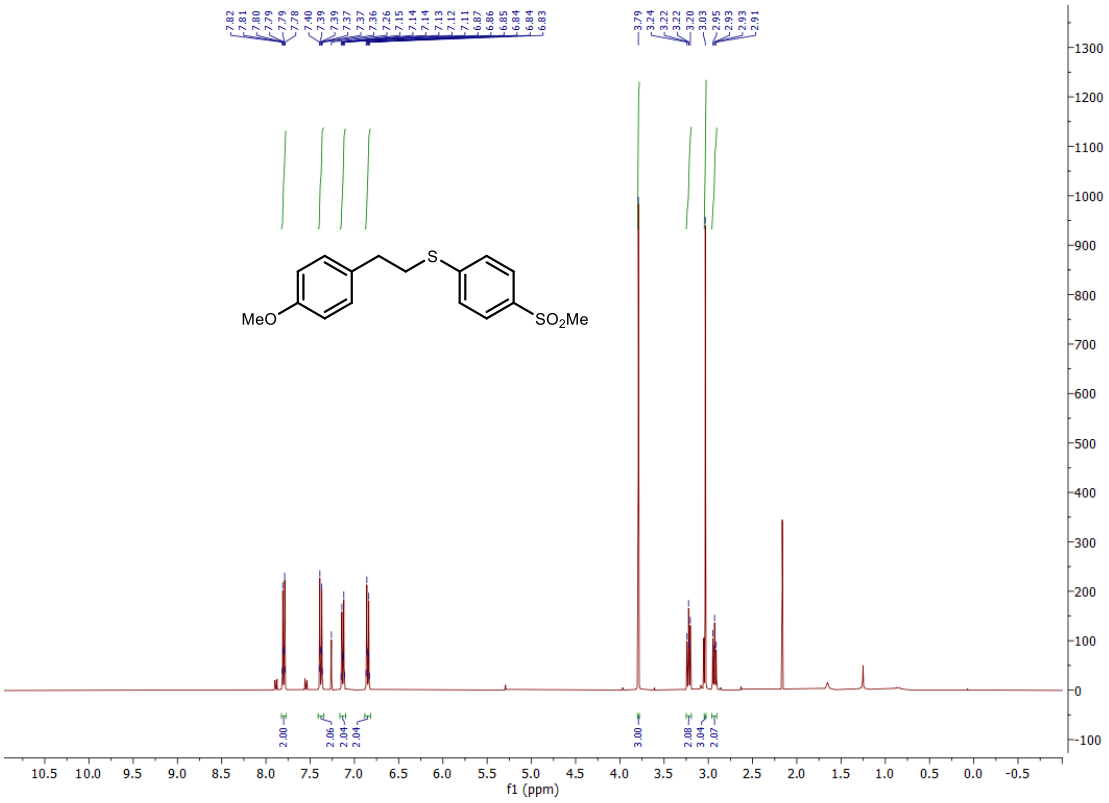
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**:



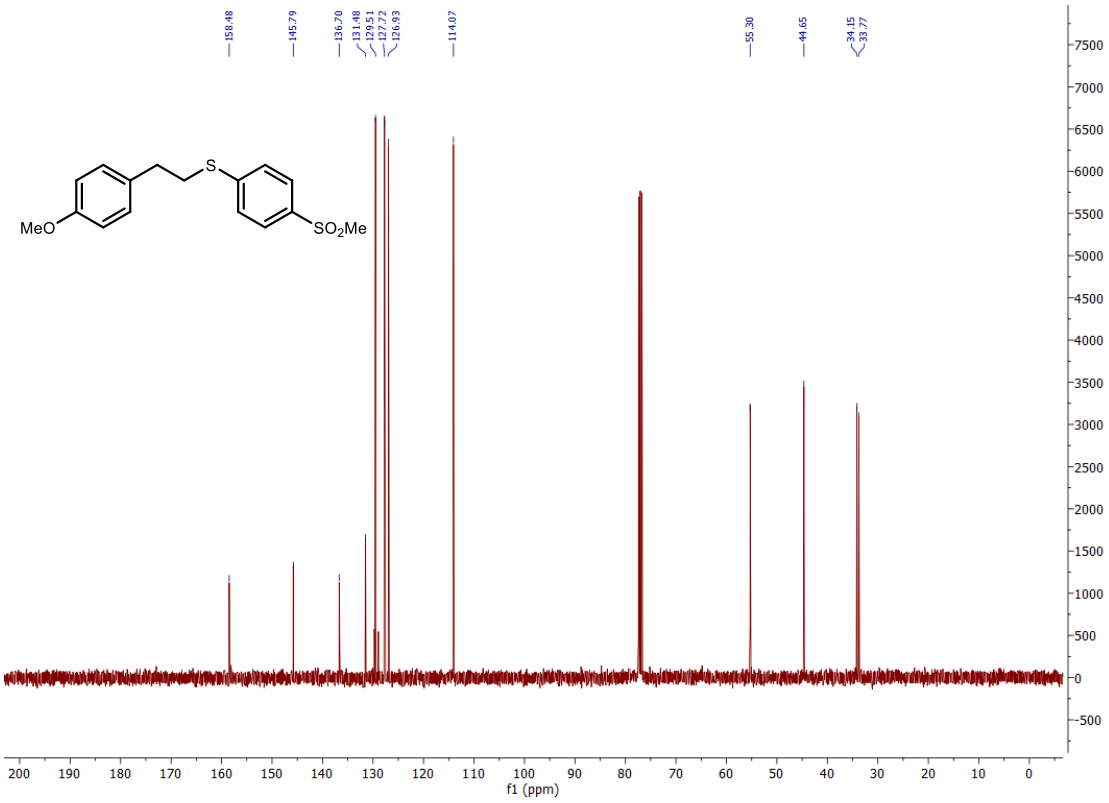
^{13}C NMR (101 MHz, $CDCl_3$) of **3c:**



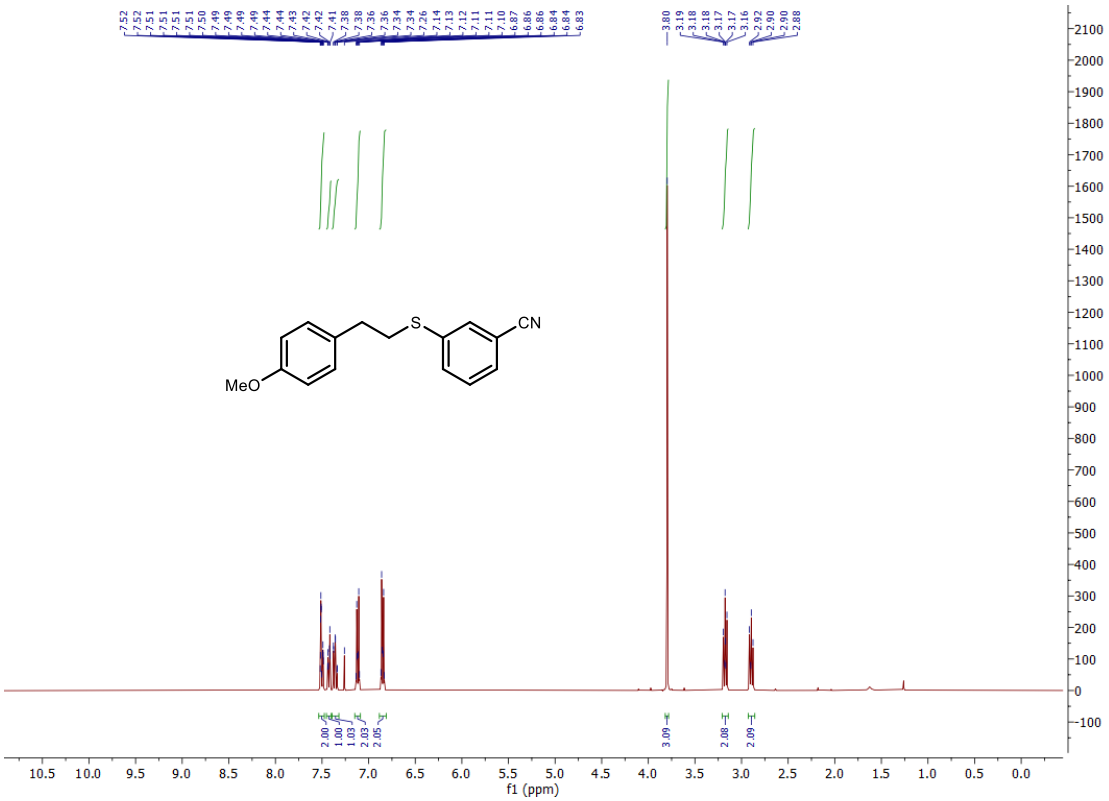
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**:



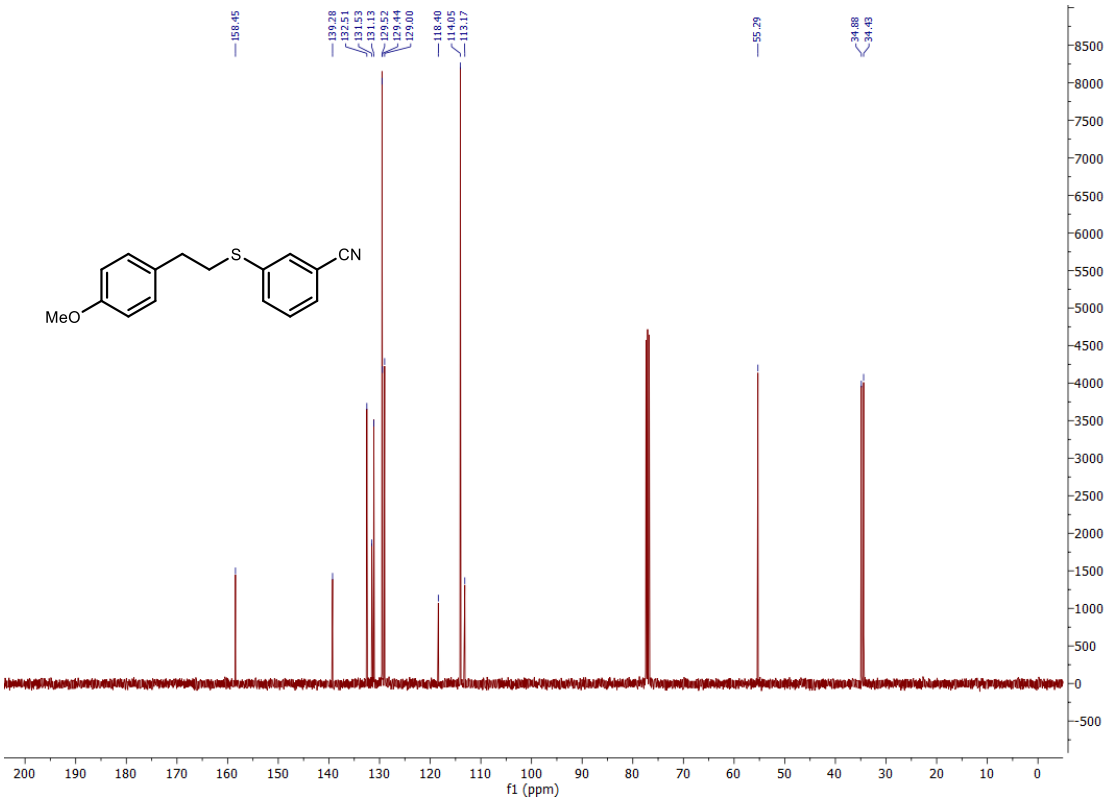
^{13}C NMR (101 MHz, $CDCl_3$) of **3d:**



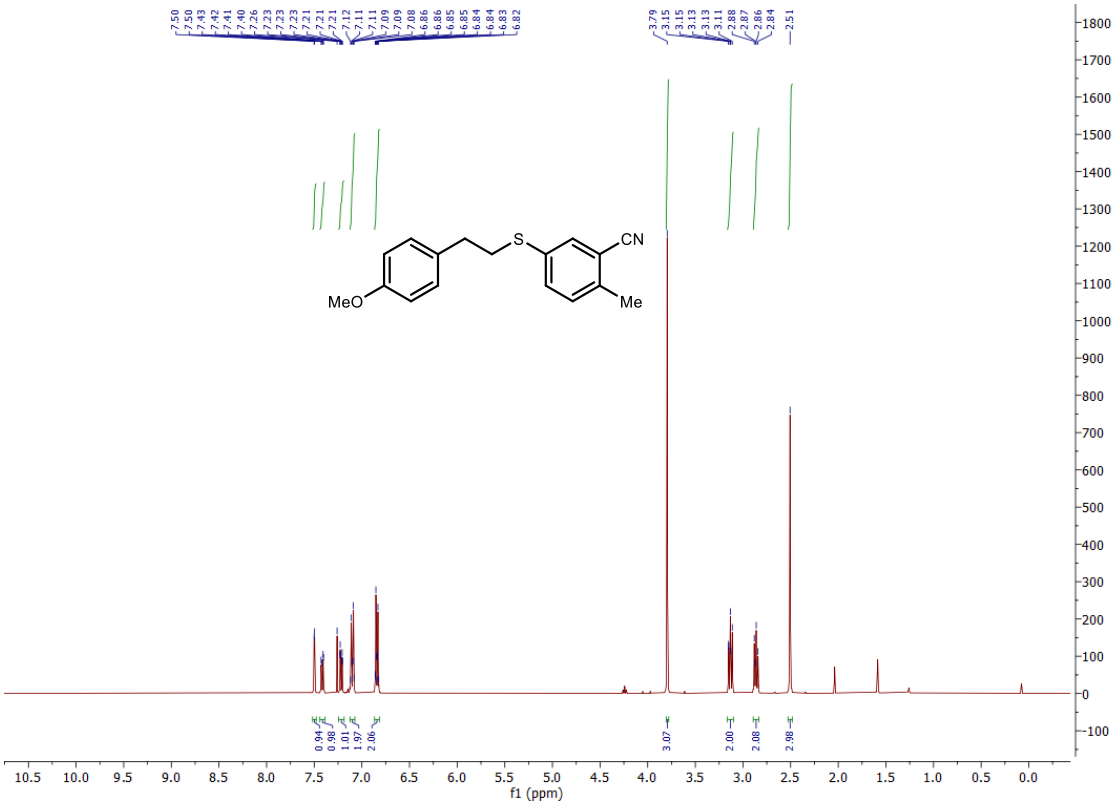
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**:



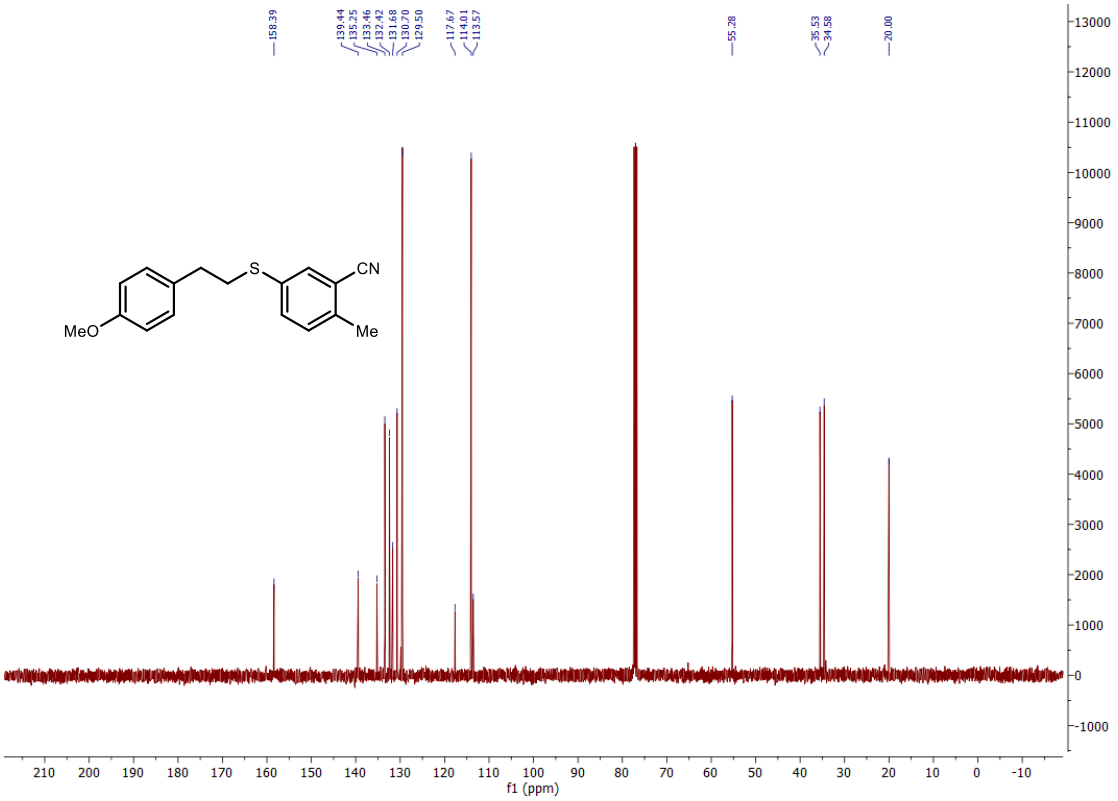
^{13}C NMR (101 MHz, $CDCl_3$) of **3e:**



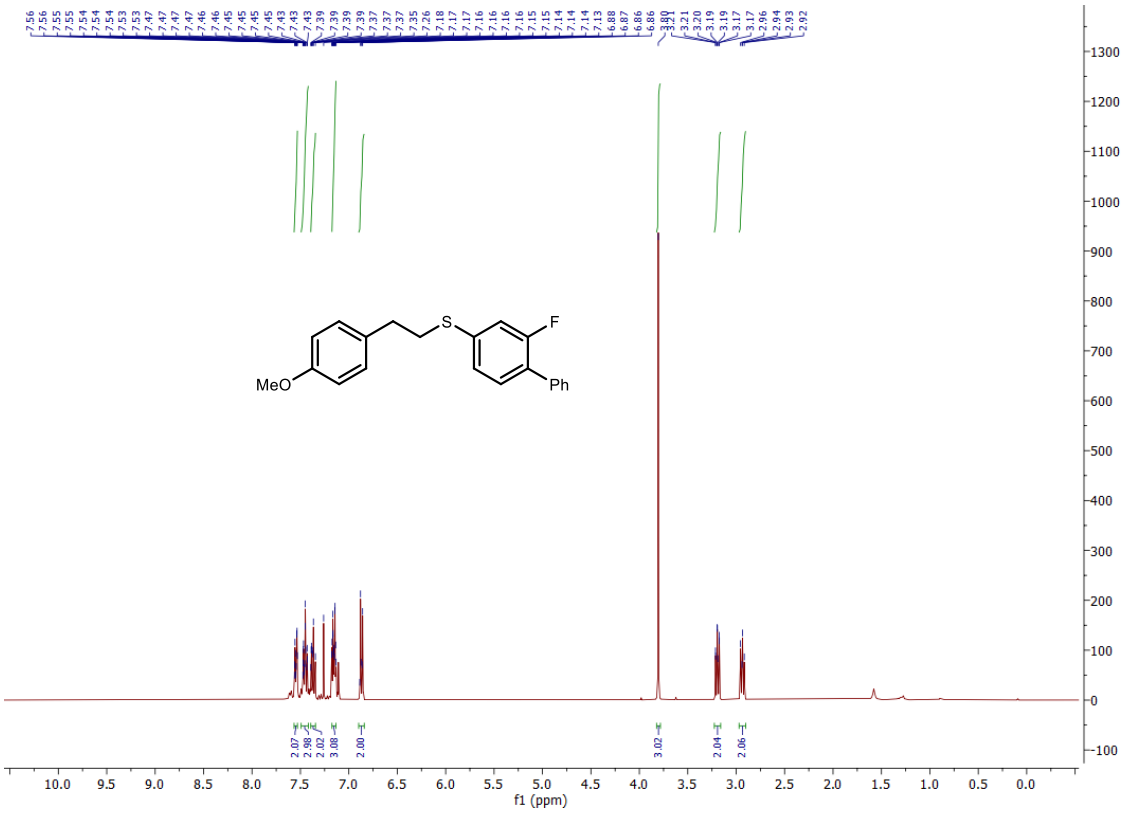
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**:



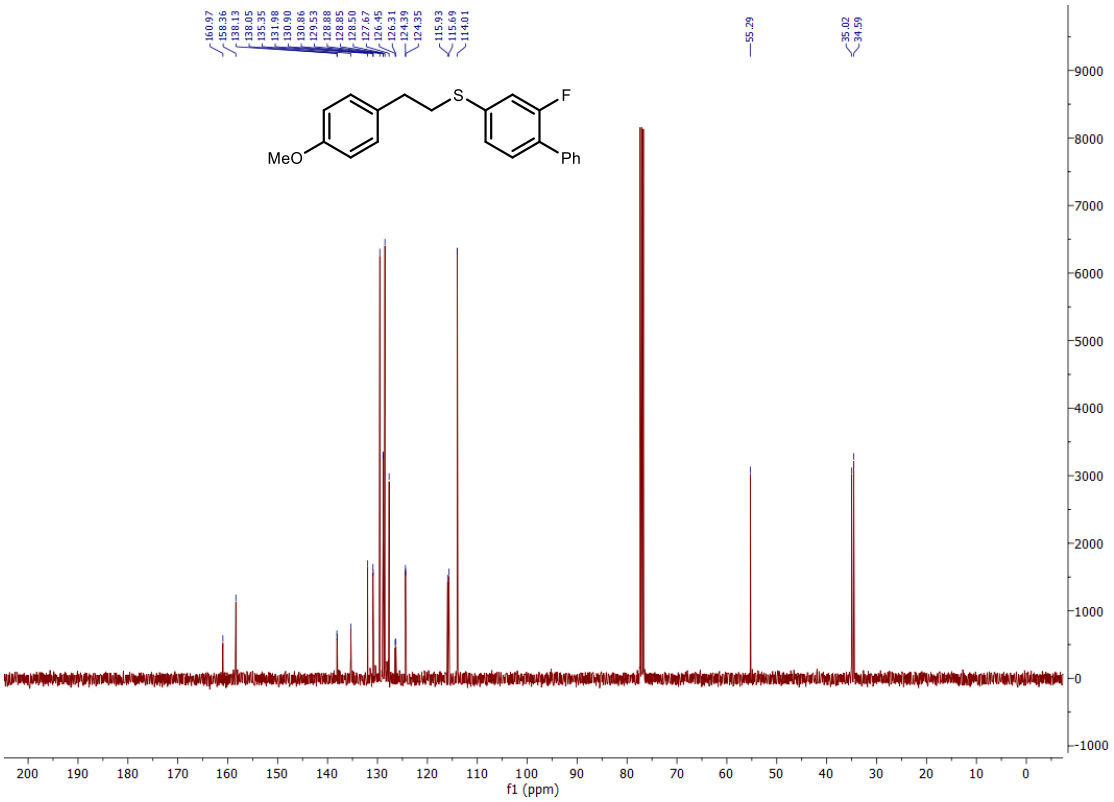
^{13}C NMR (101 MHz, $CDCl_3$) of **3f:**



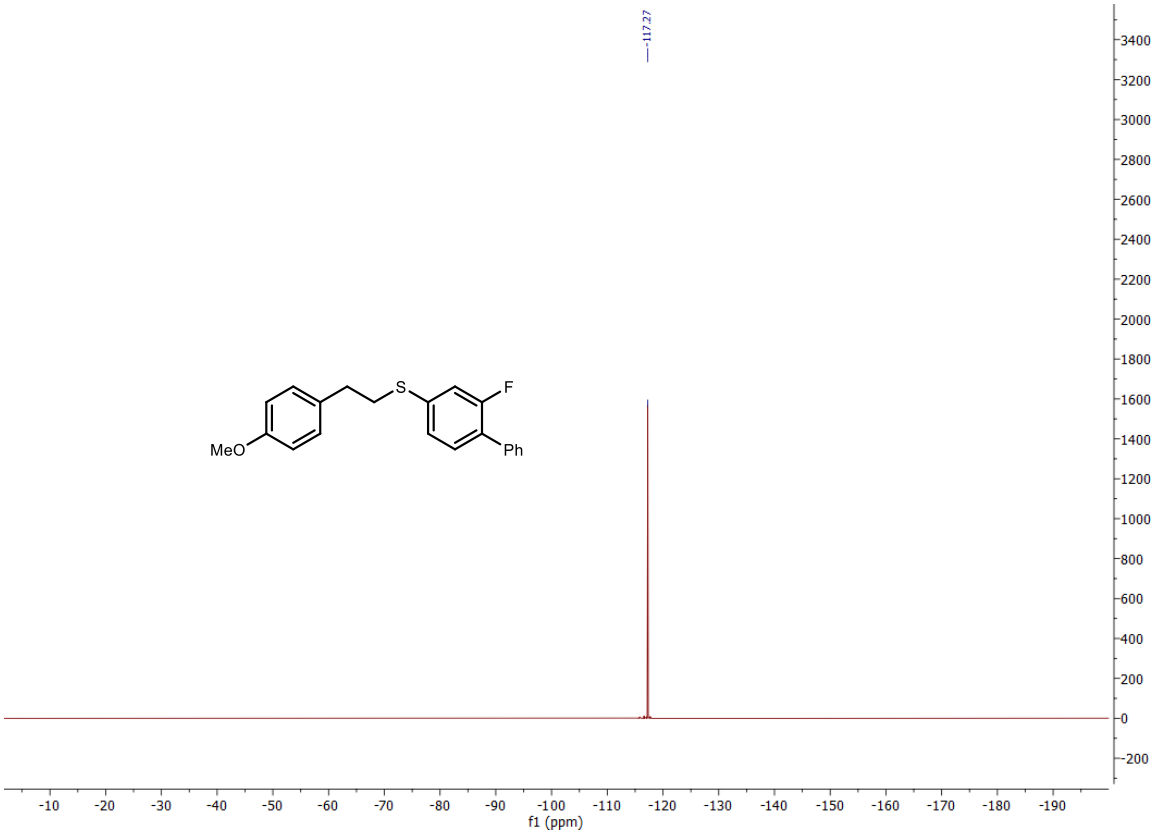
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**:



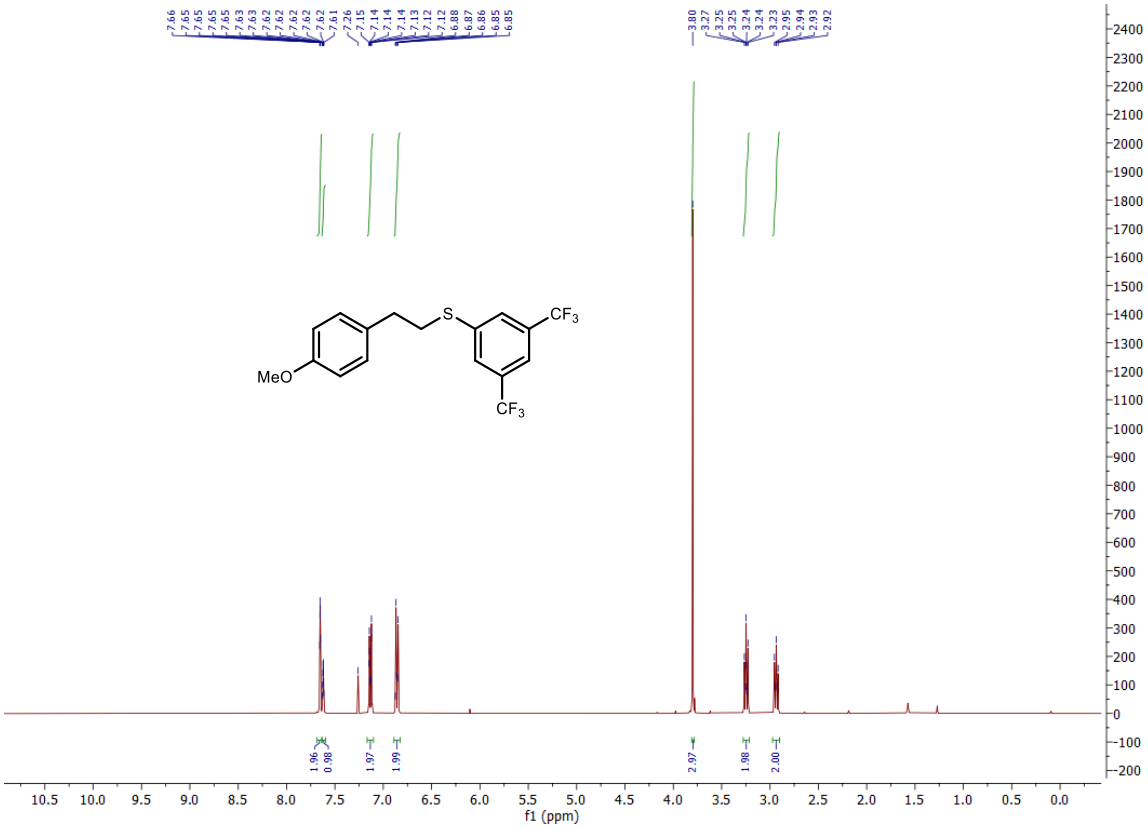
^{13}C NMR (101 MHz, $CDCl_3$) of **3g:**



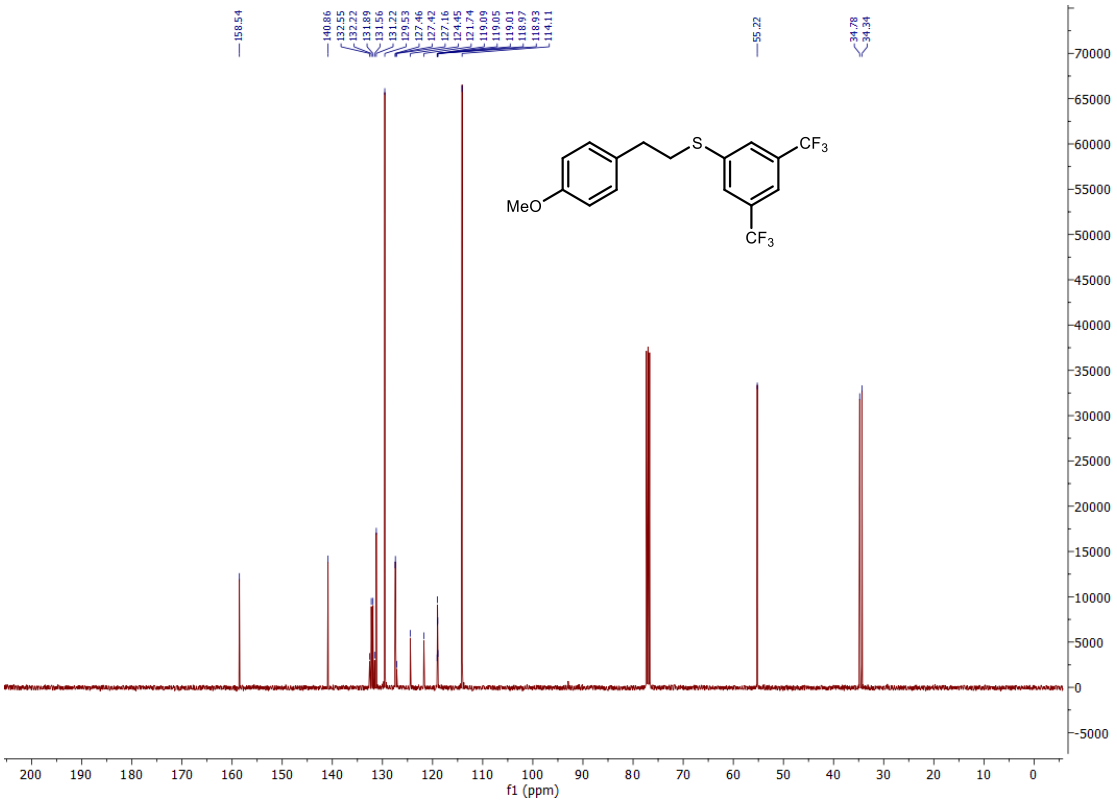
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) of **3g:**



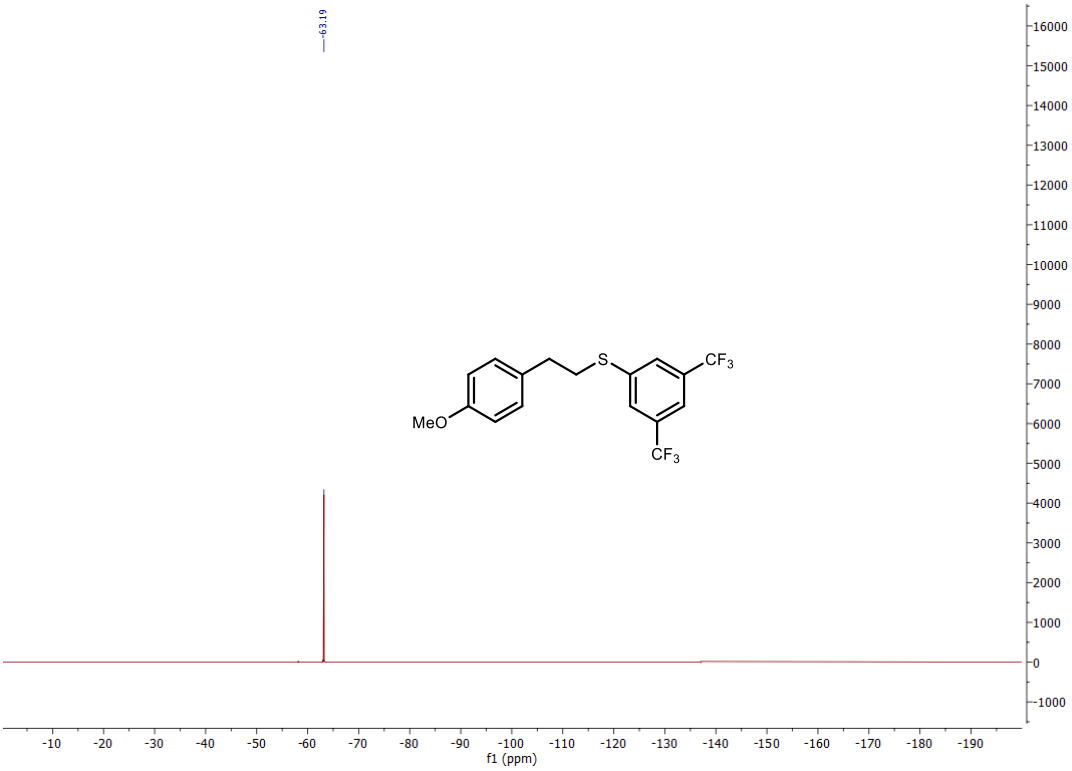
^{1}H NMR (400 MHz, $CDCl_3$) of **3h**:



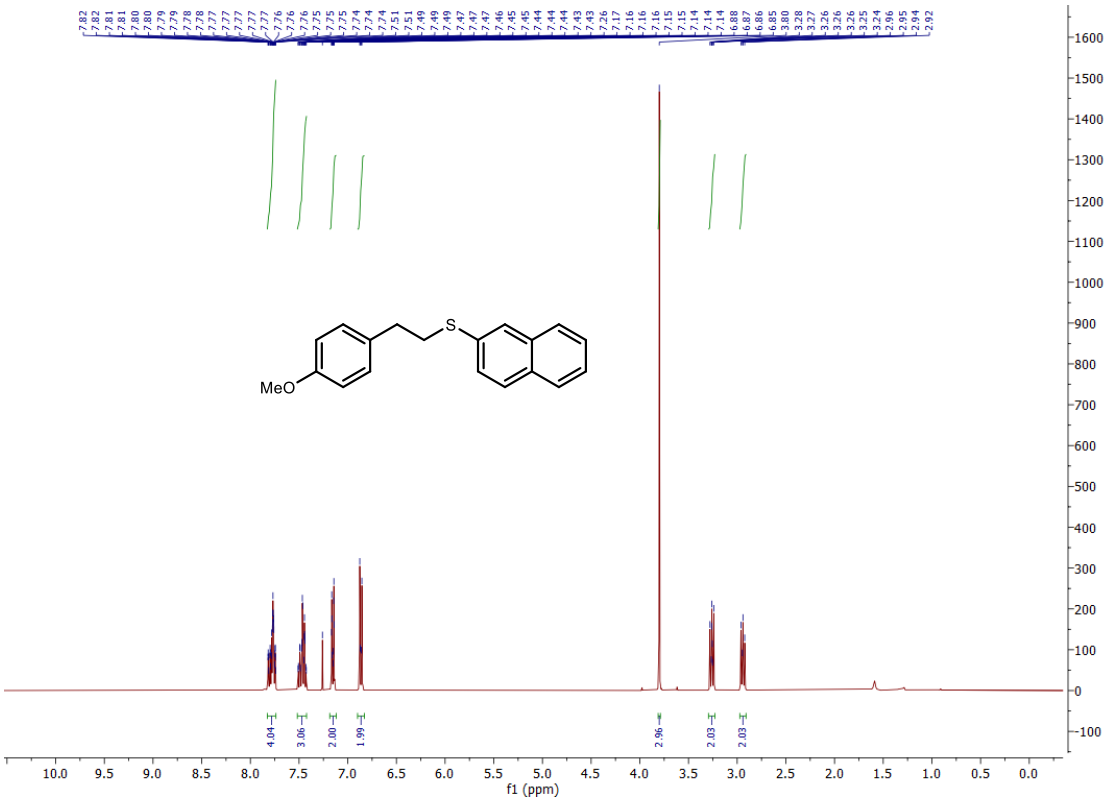
^{13}C NMR (101 MHz, $CDCl_3$) of **3h:**



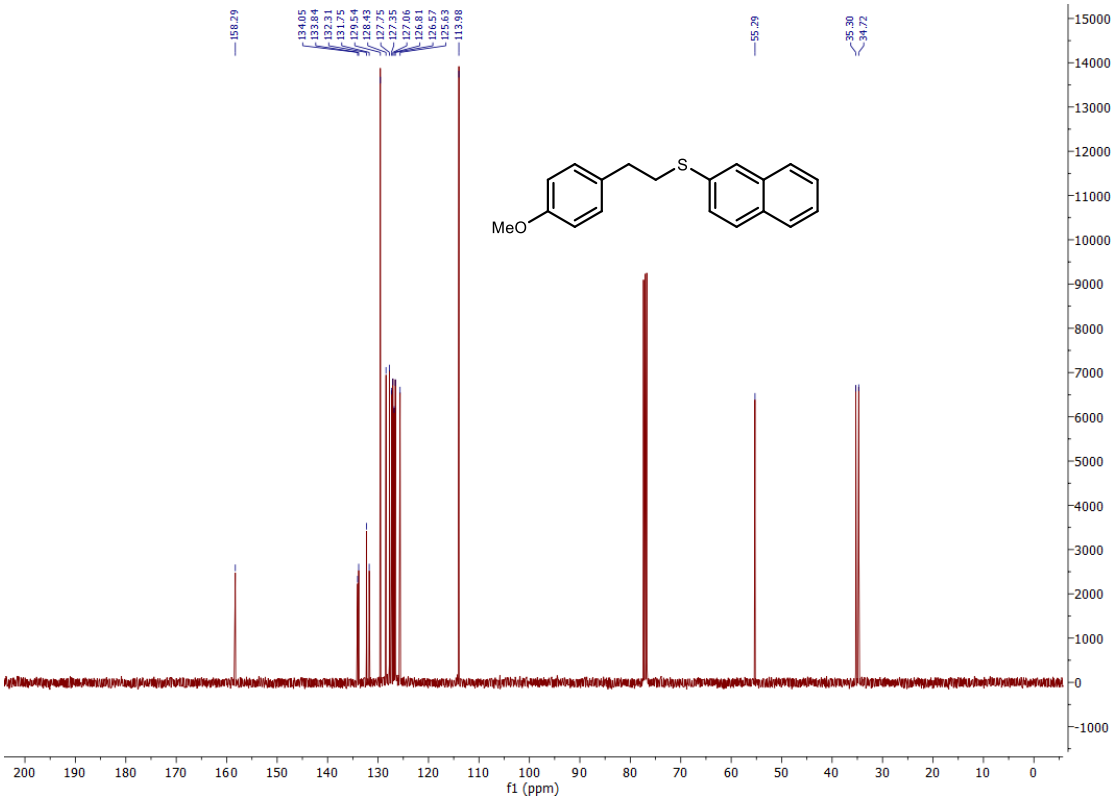
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) of **3h:**



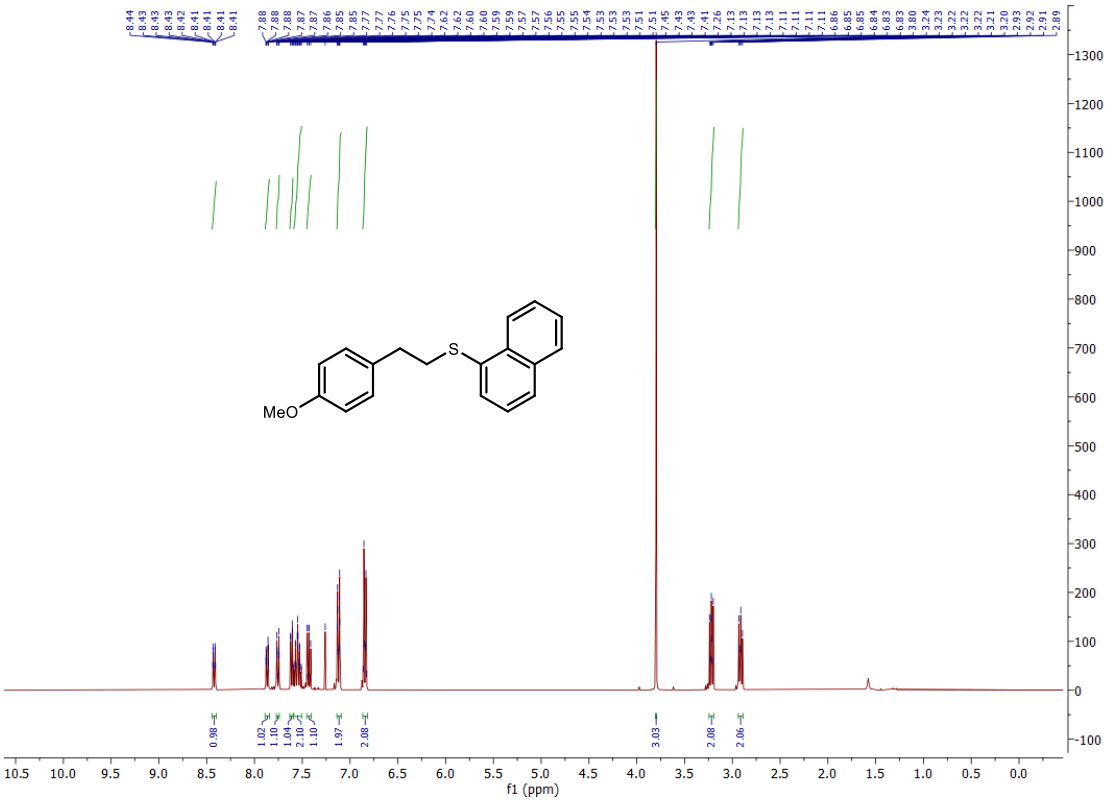
^{1}H NMR (400 MHz, $CDCl_3$) of **3i**:



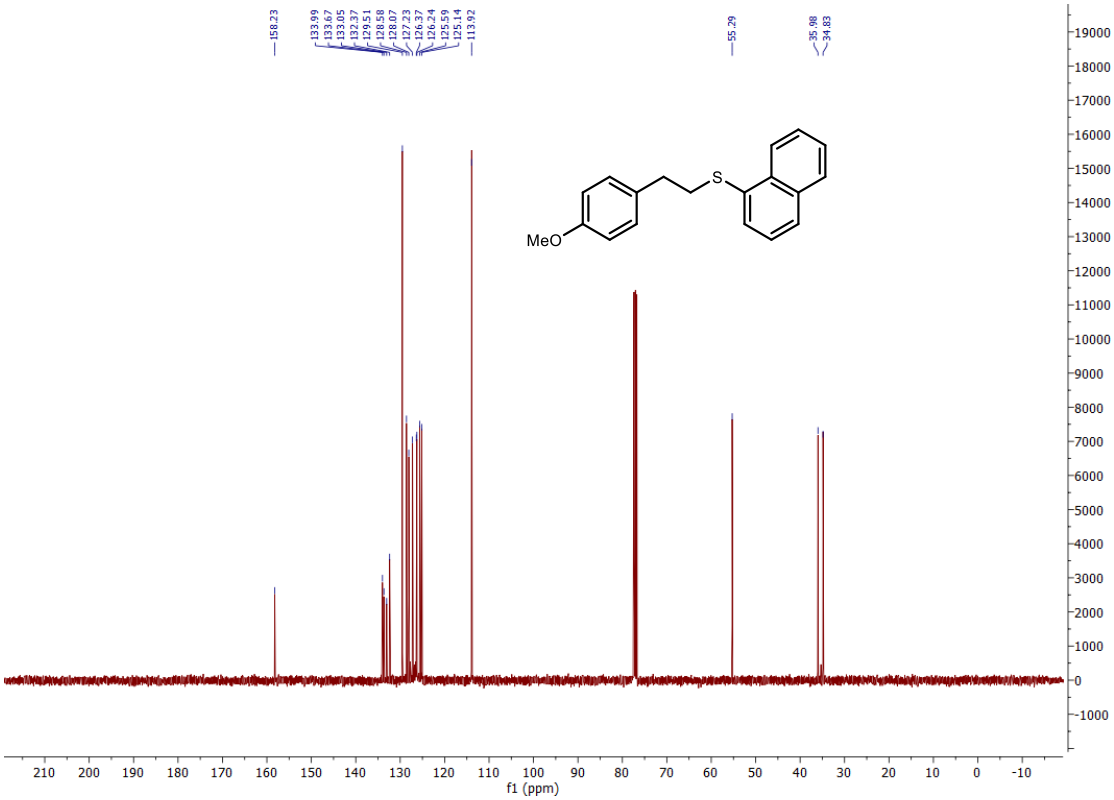
^{13}C NMR (101 MHz, $CDCl_3$) of **3i:**



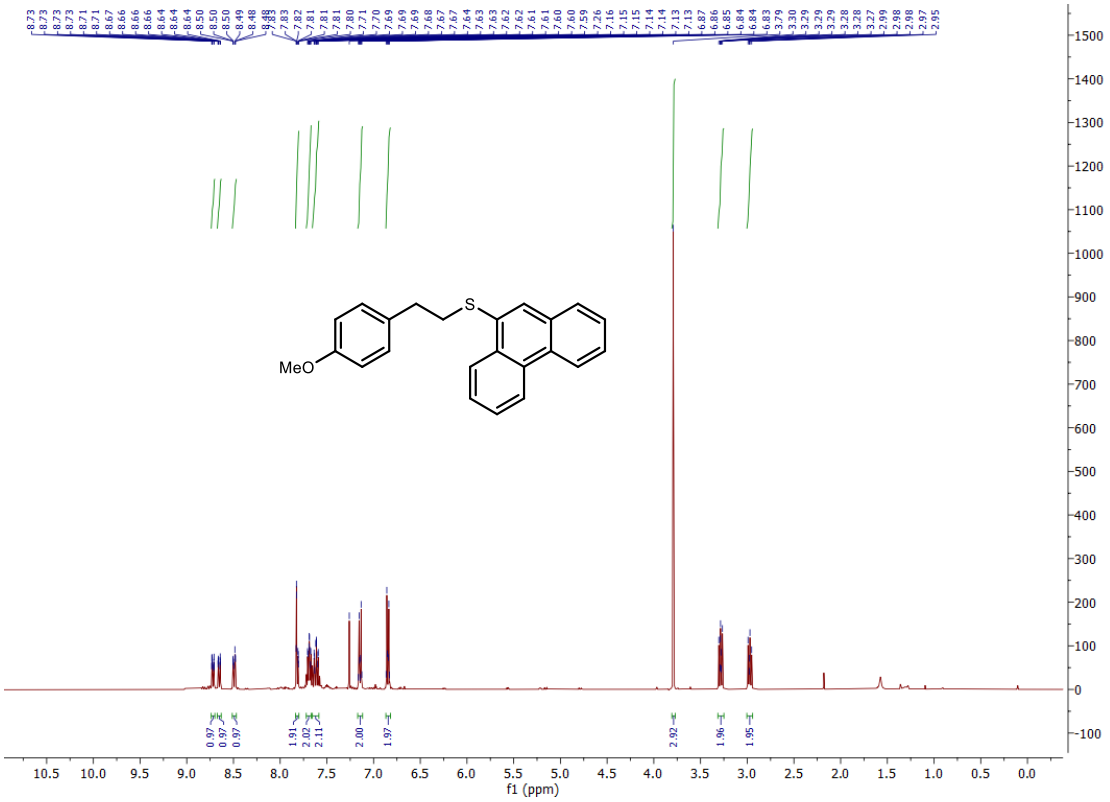
^{1}H NMR (400 MHz, $CDCl_3$) of **3j:**



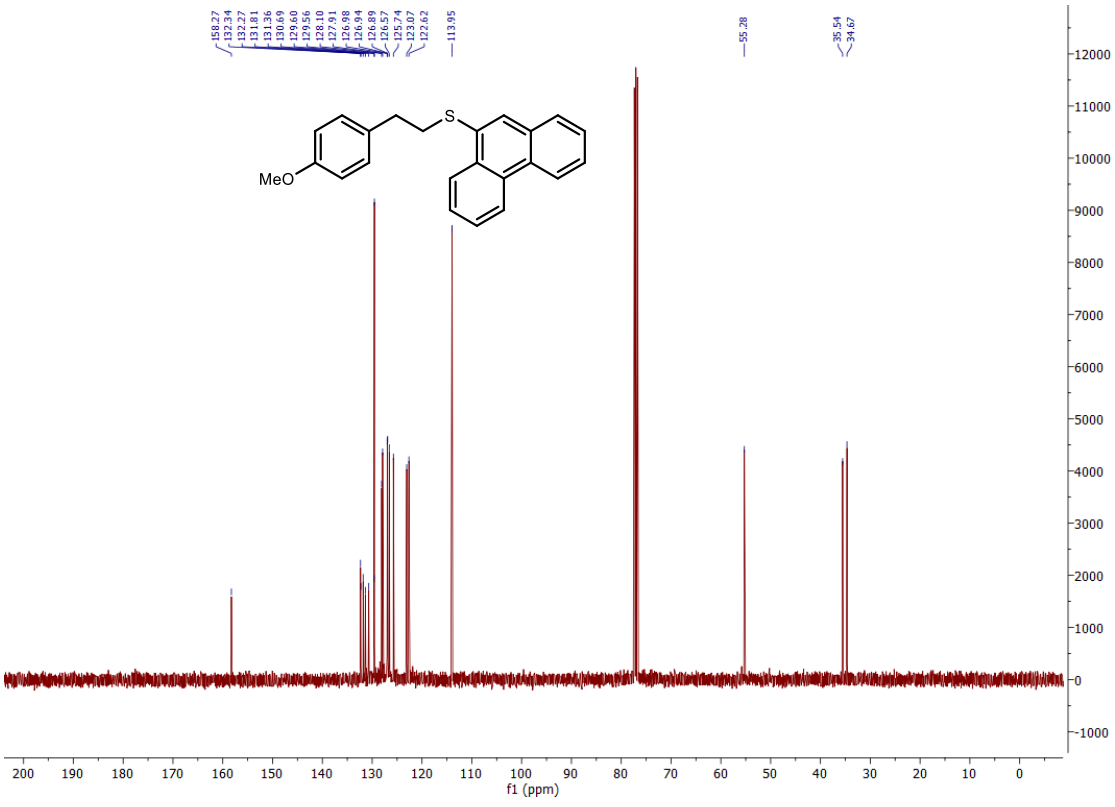
^{13}C NMR (101 MHz, $CDCl_3$) of **3j:**



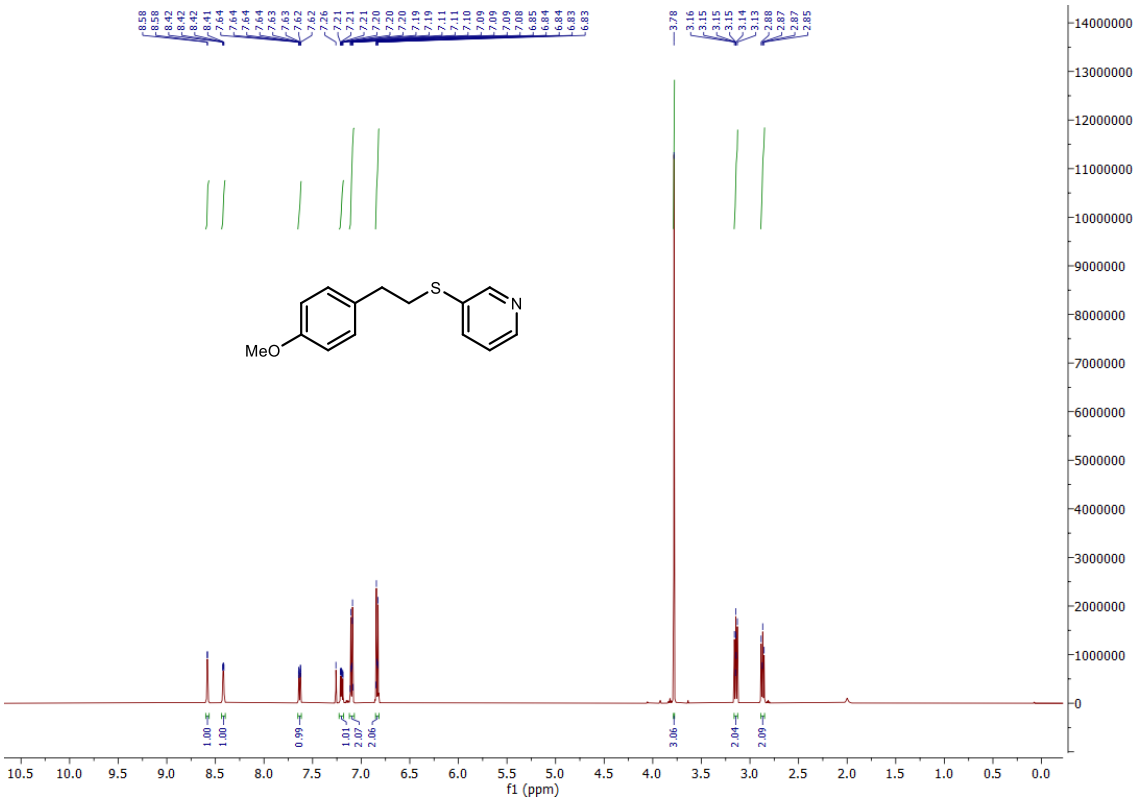
^{1}H NMR (400 MHz, $CDCl_3$) of **3k:**



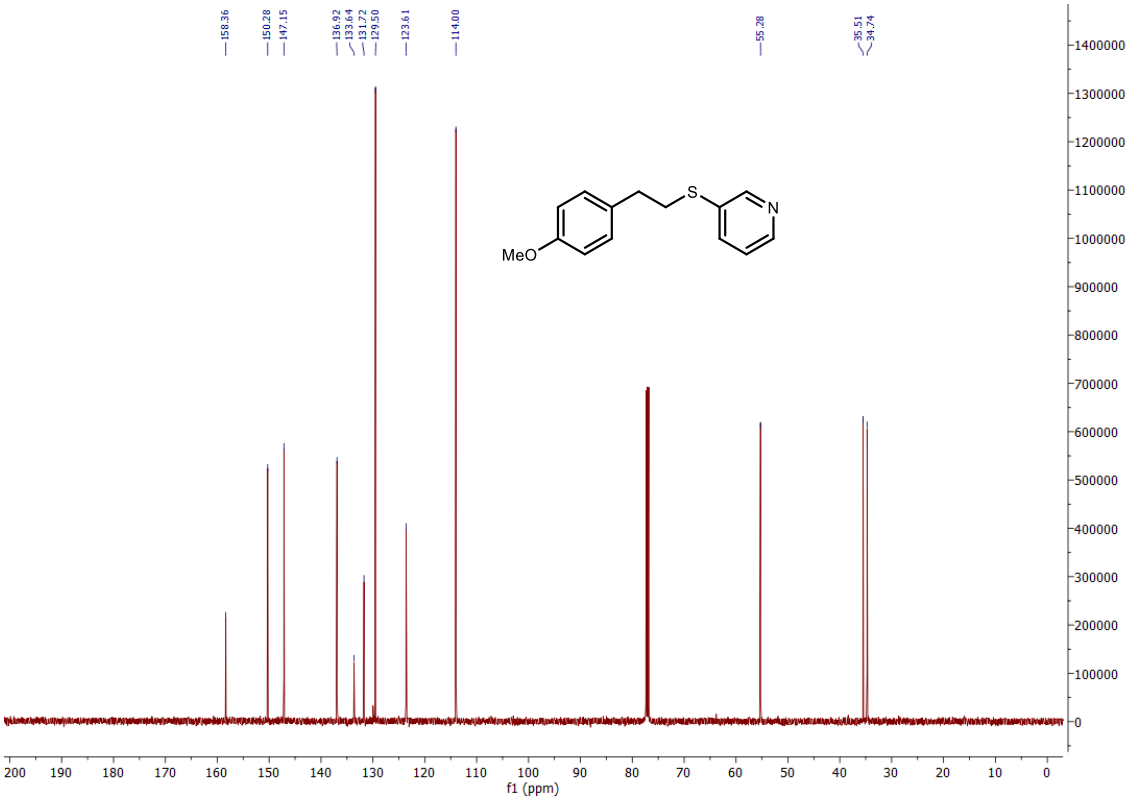
^{13}C NMR (101 MHz, $CDCl_3$) of **3k:**



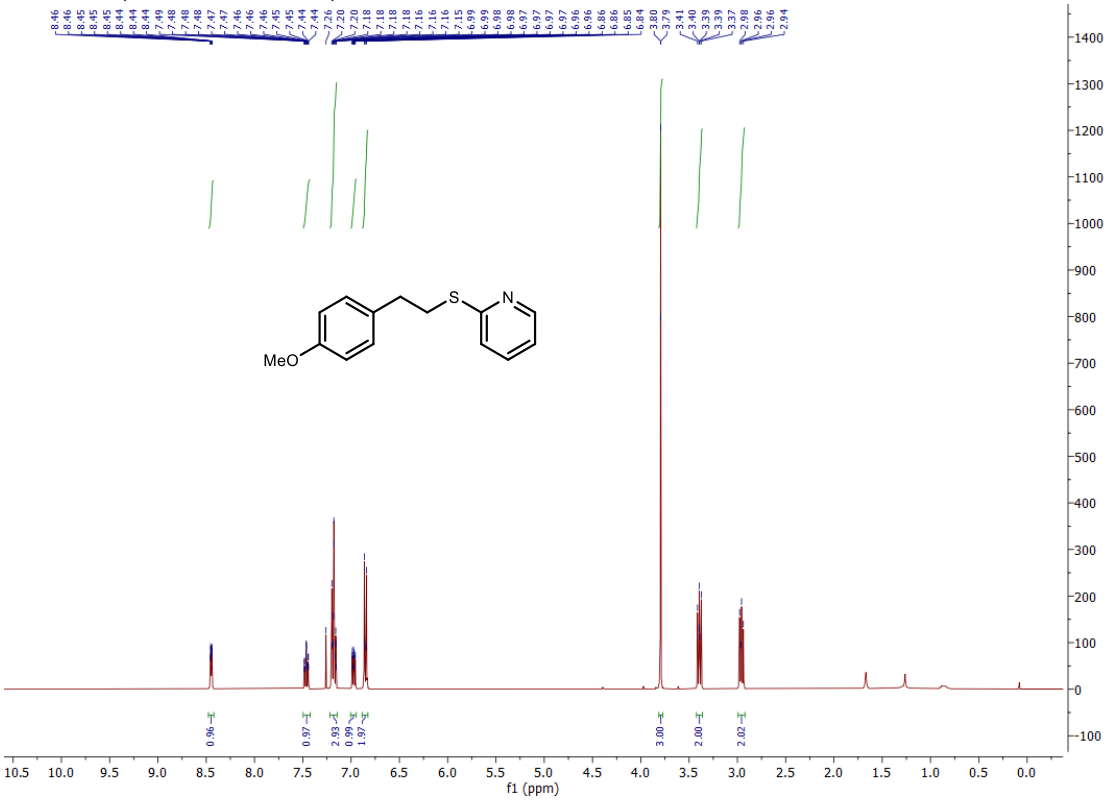
^{1}H NMR (400 MHz, $CDCl_3$) of **3l:**



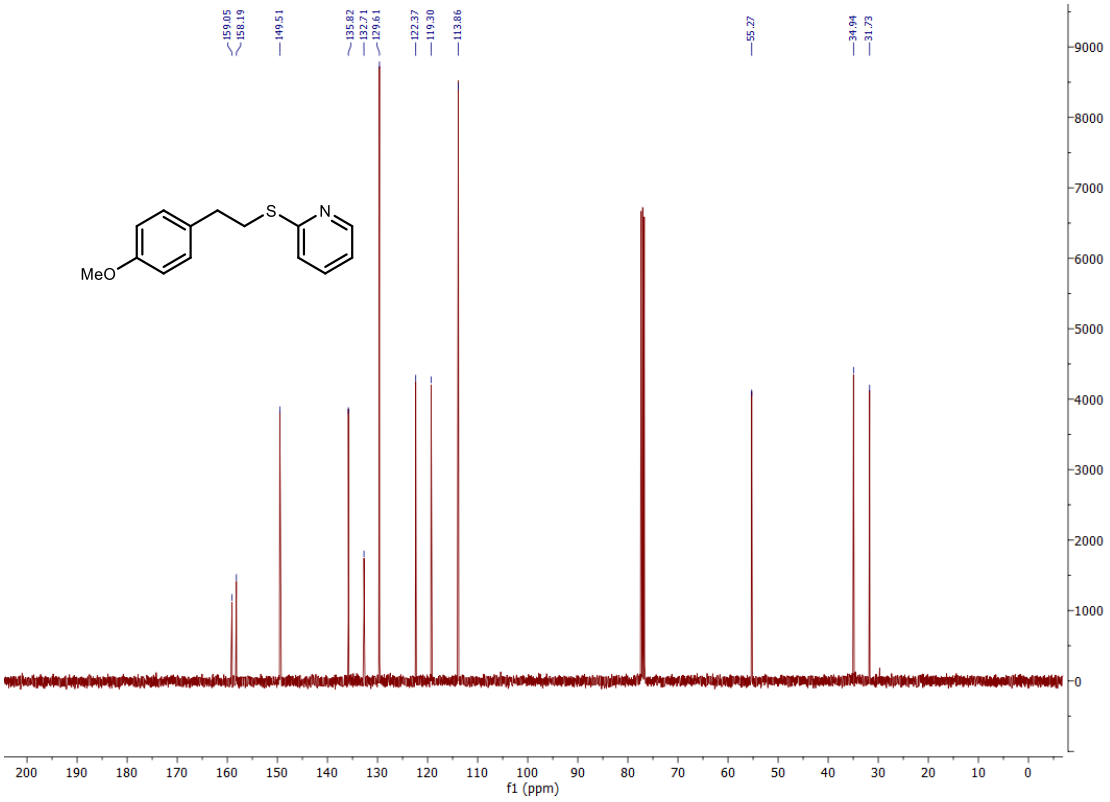
^{13}C NMR (101 MHz, $CDCl_3$) of **3l:**



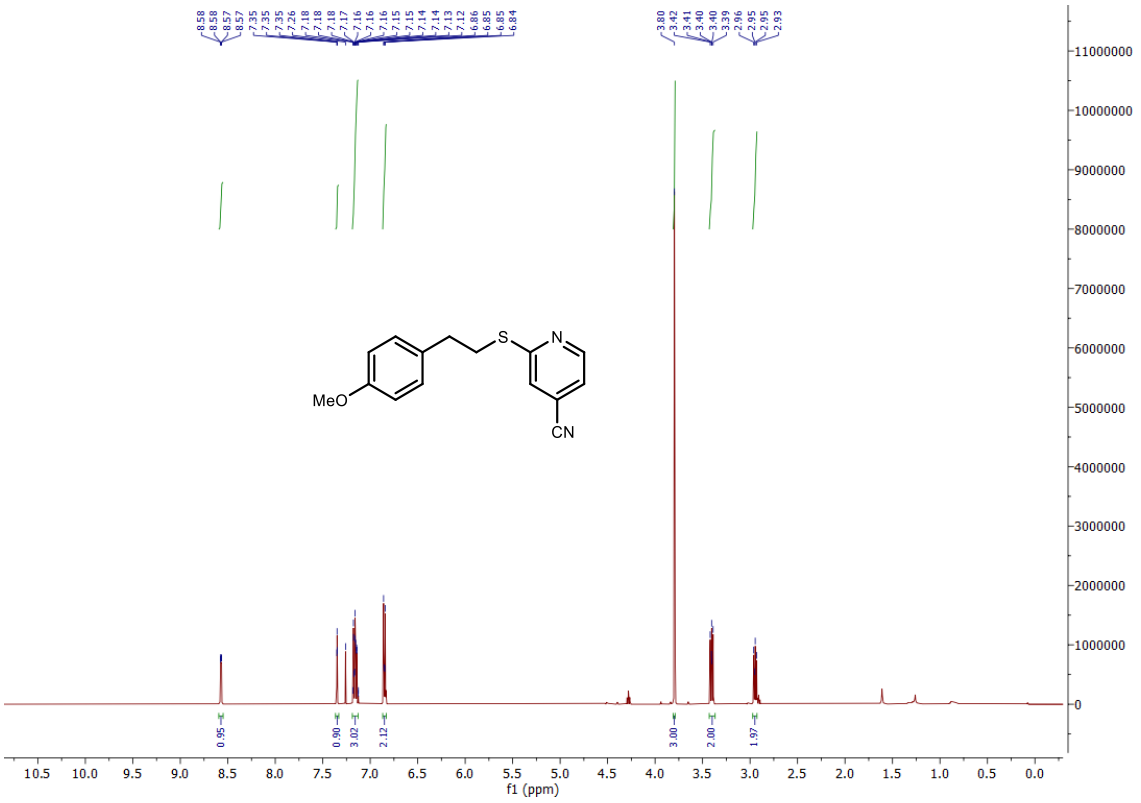
^{1}H NMR (400 MHz, $CDCl_3$) of **3m:**



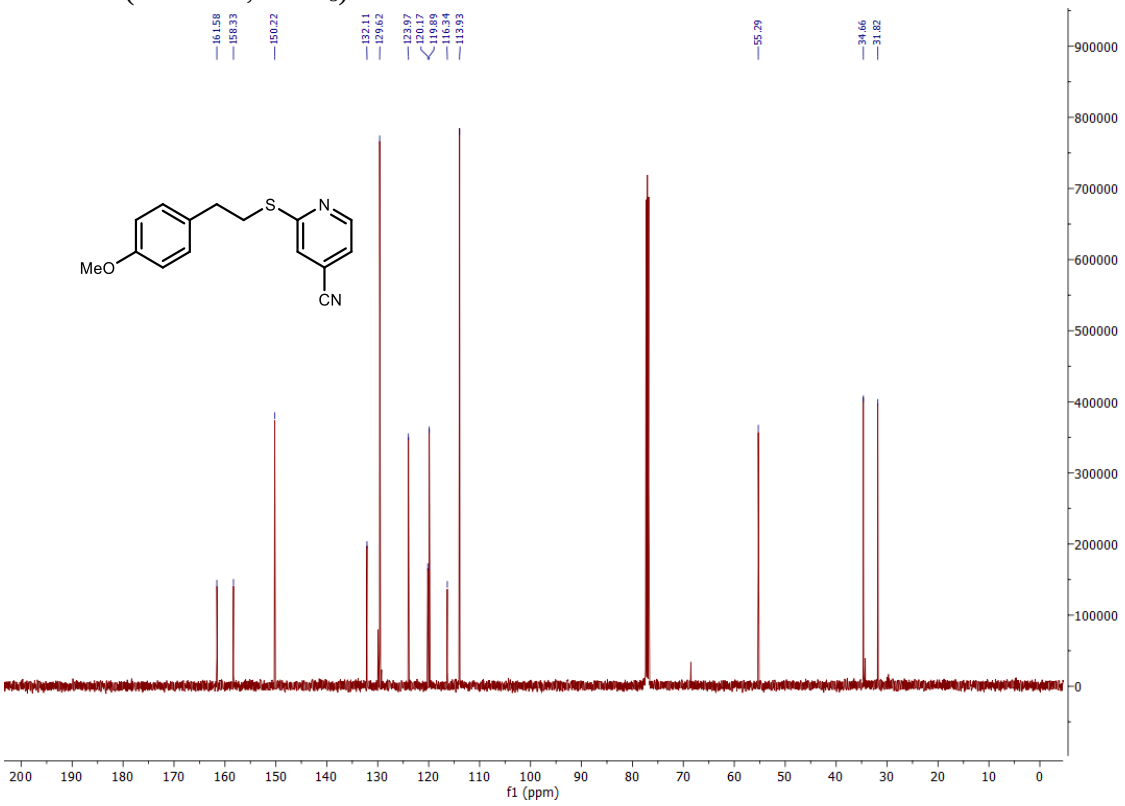
^{13}C NMR (101 MHz, $CDCl_3$) of **3m:**



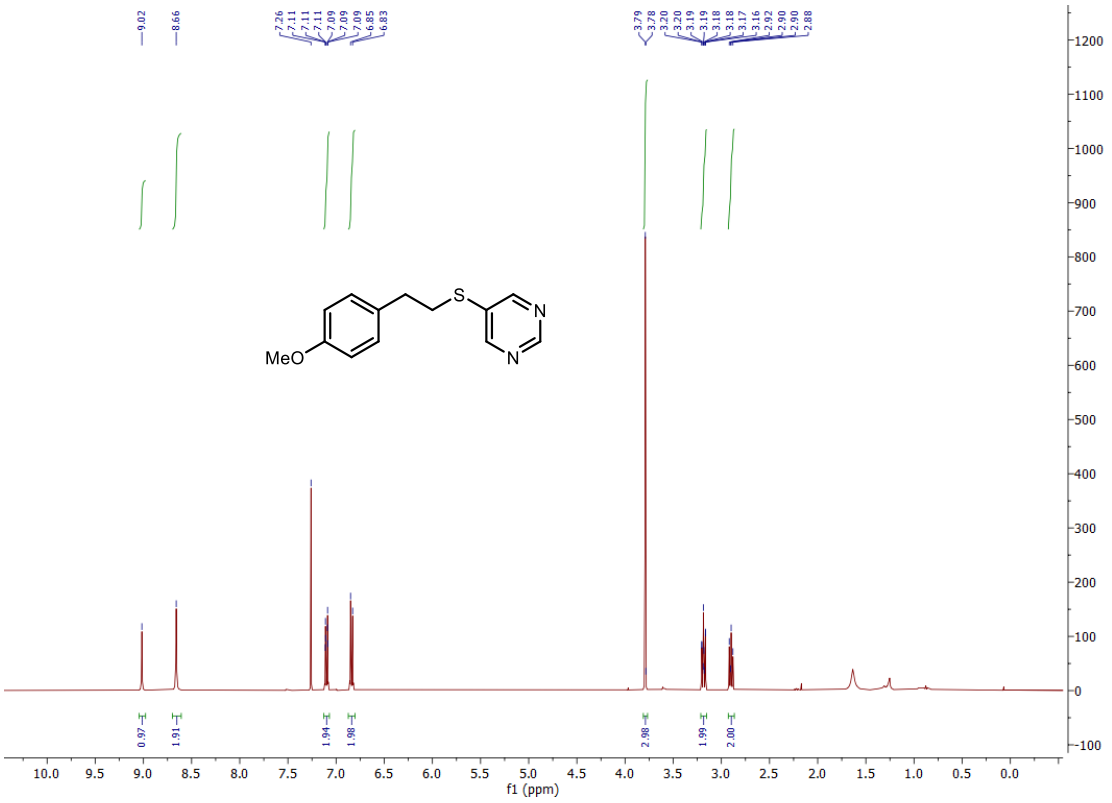
^{1}H NMR (400 MHz, $CDCl_3$) of **3n:**



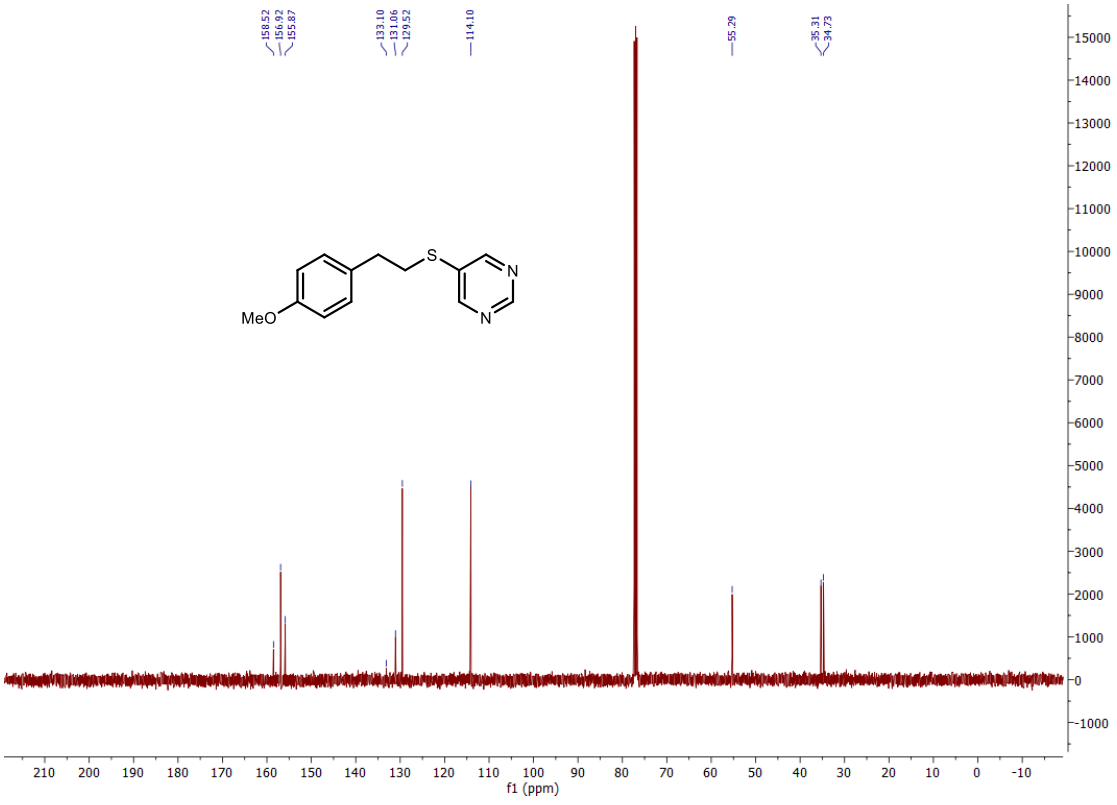
^{13}C NMR (101 MHz, $CDCl_3$) of **3n:**



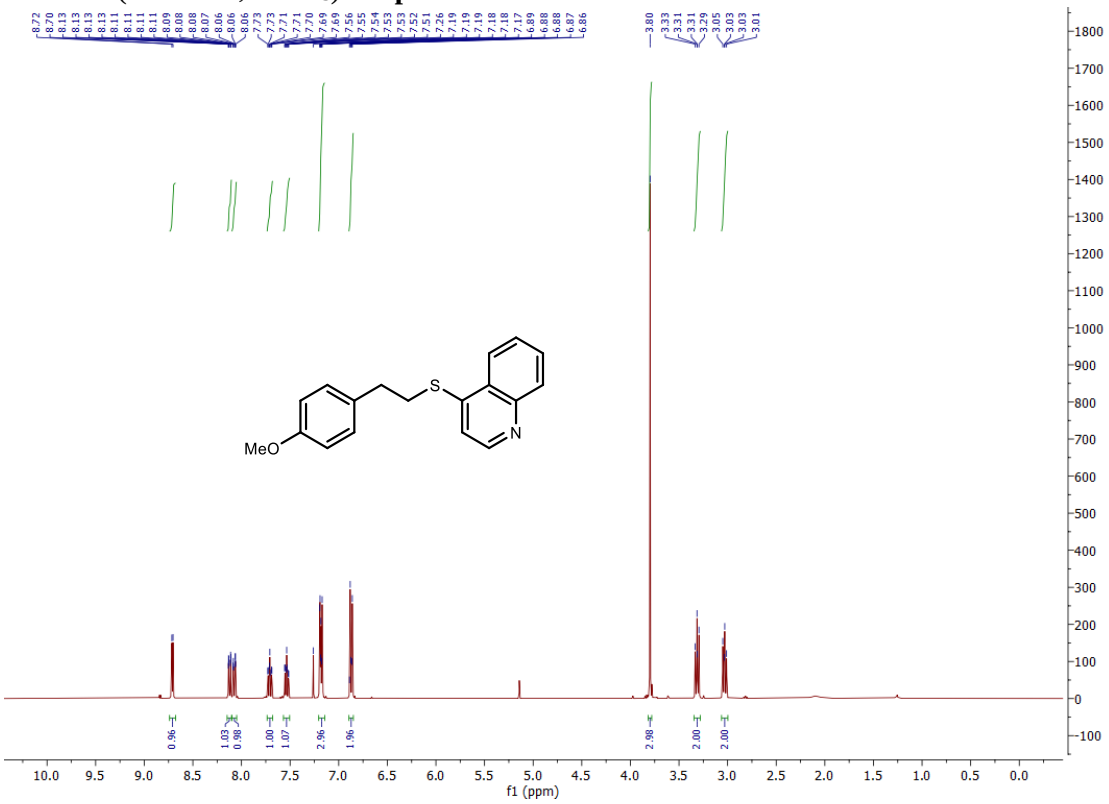
^{1}H NMR (400 MHz, $CDCl_3$) of **3o:**



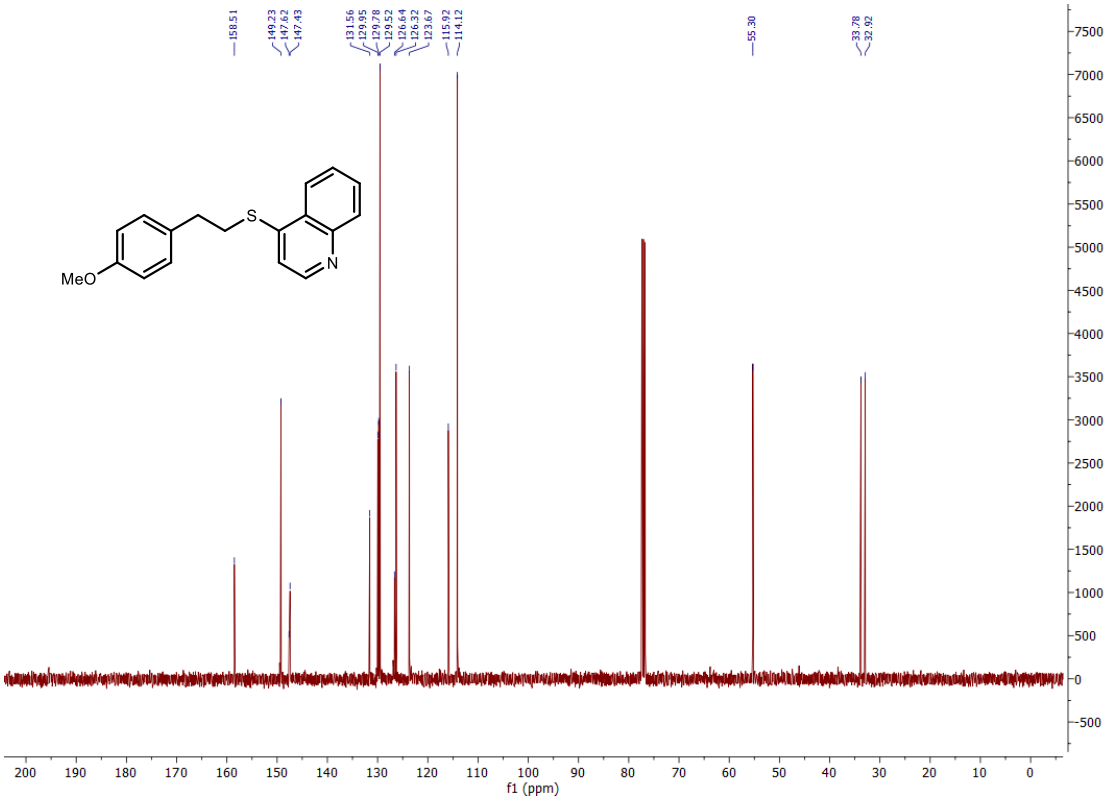
^{13}C NMR (101 MHz, $CDCl_3$) of **3o:**



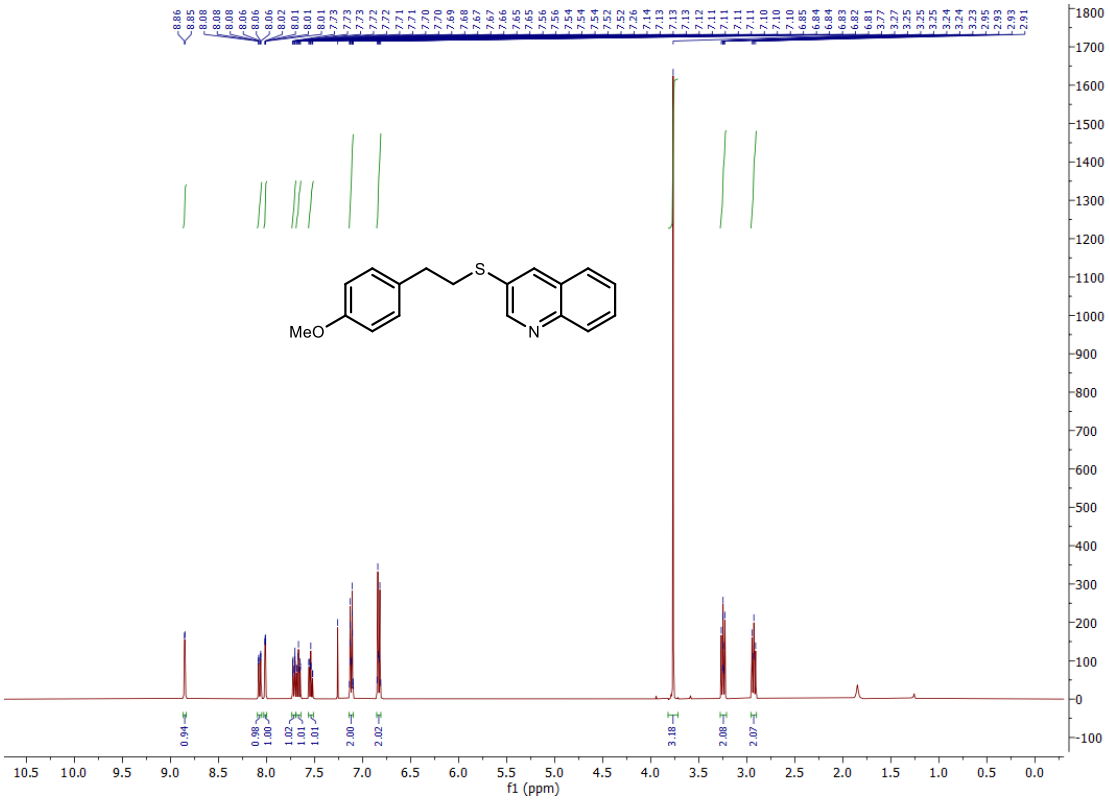
^{1}H NMR (400 MHz, $CDCl_3$) of **3p:**



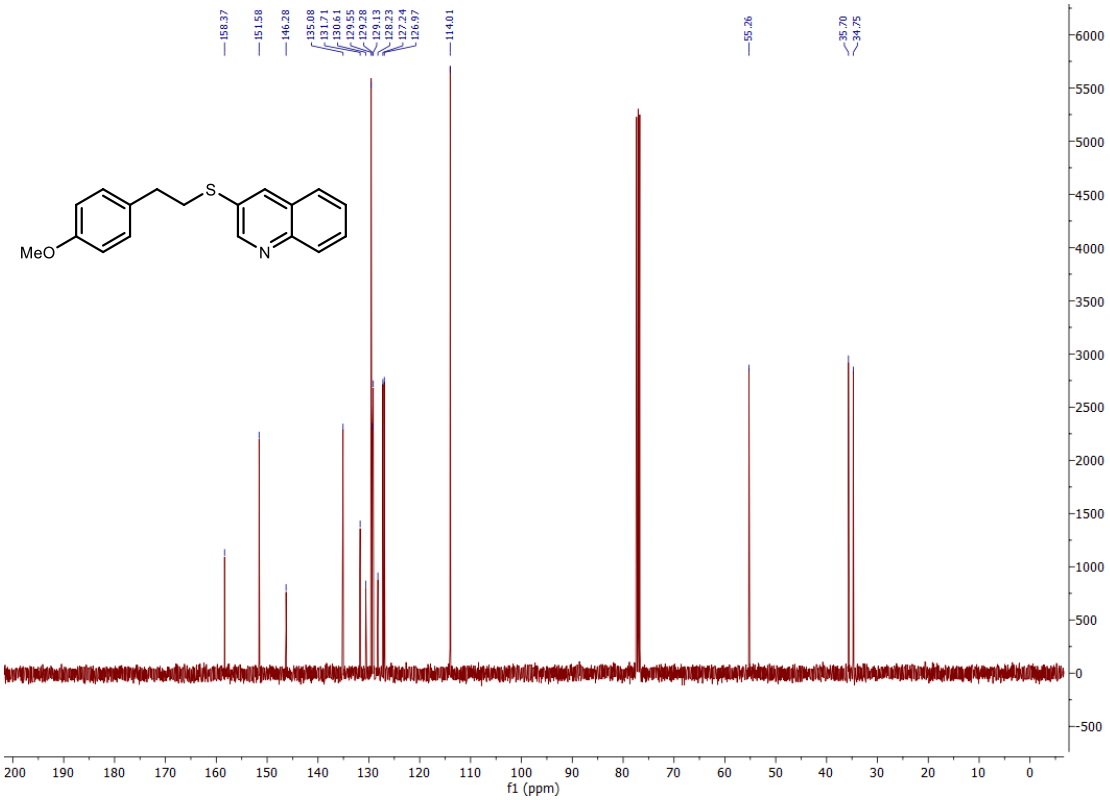
^{13}C NMR (101 MHz, $CDCl_3$) of **3p:**



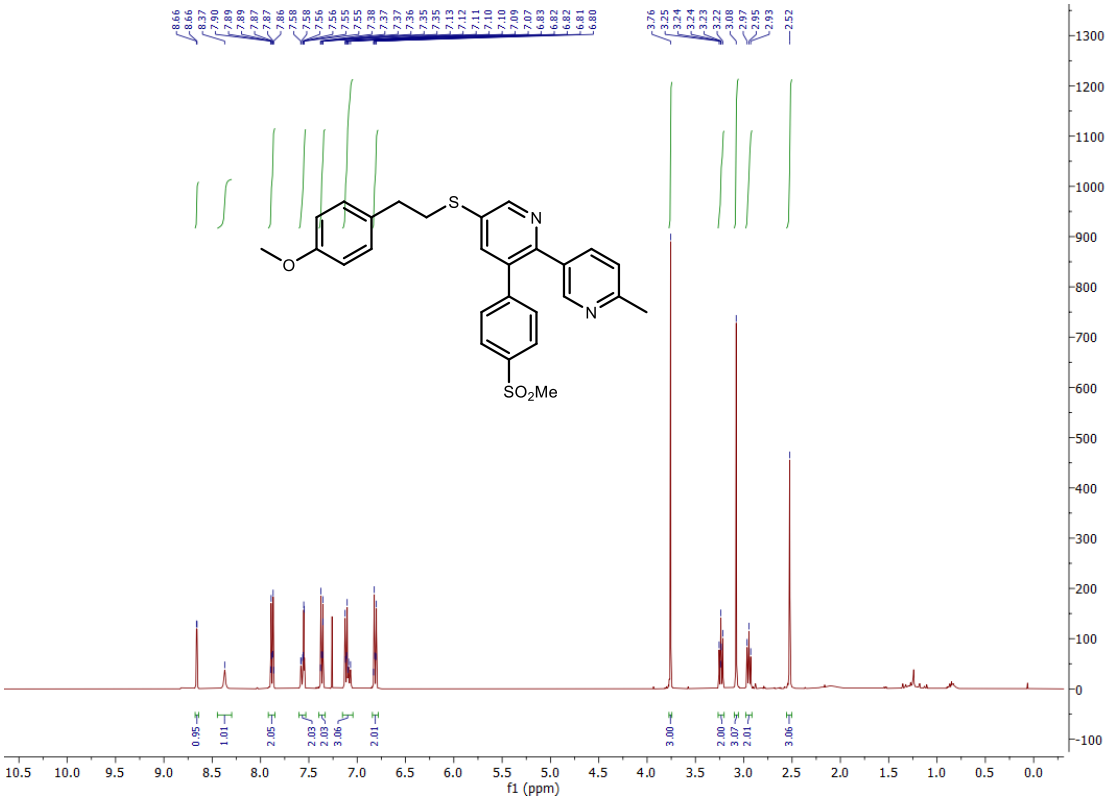
^{1}H NMR (400 MHz, $CDCl_3$) of **3q:**



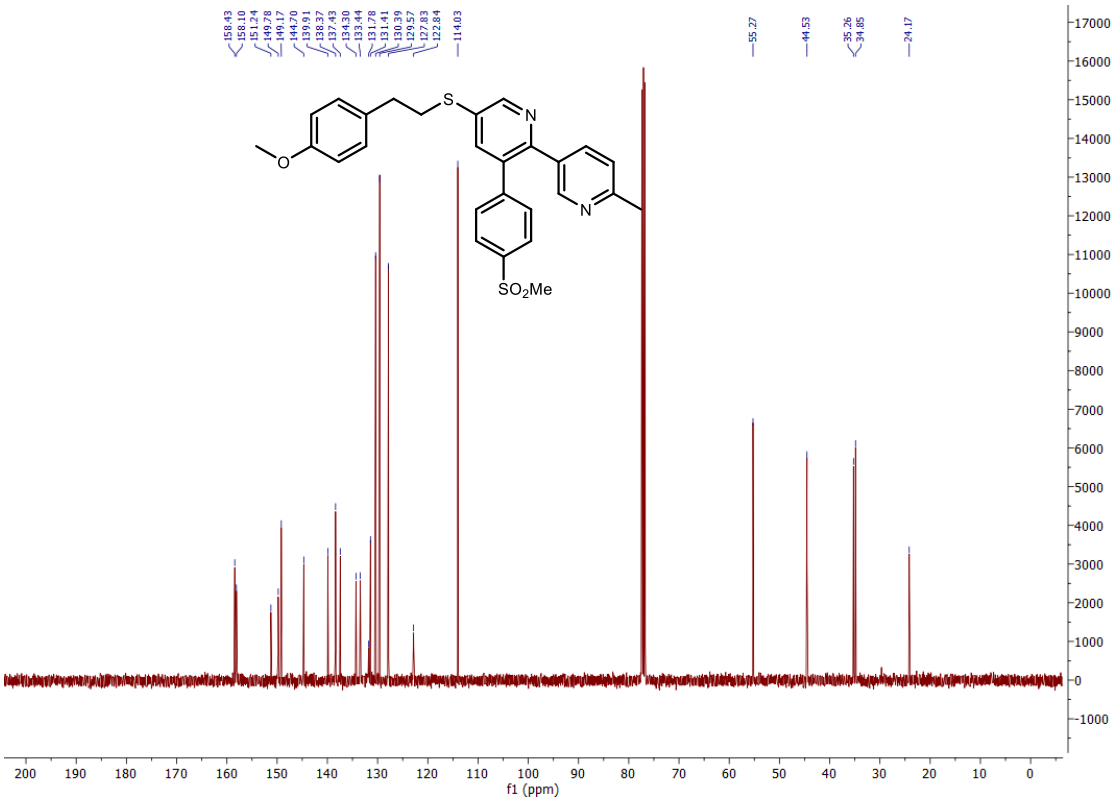
^{13}C NMR (101 MHz, $CDCl_3$) of **3q:**



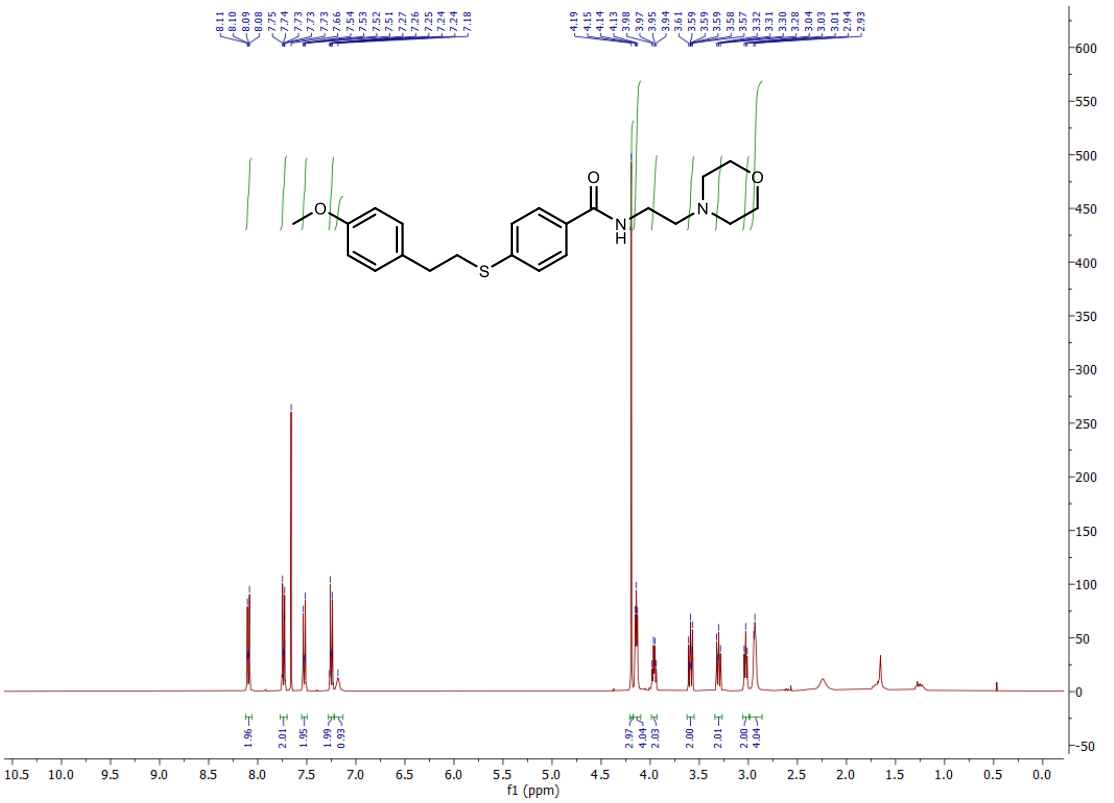
^{1}H NMR (400 MHz, $CDCl_3$) of **3r:**



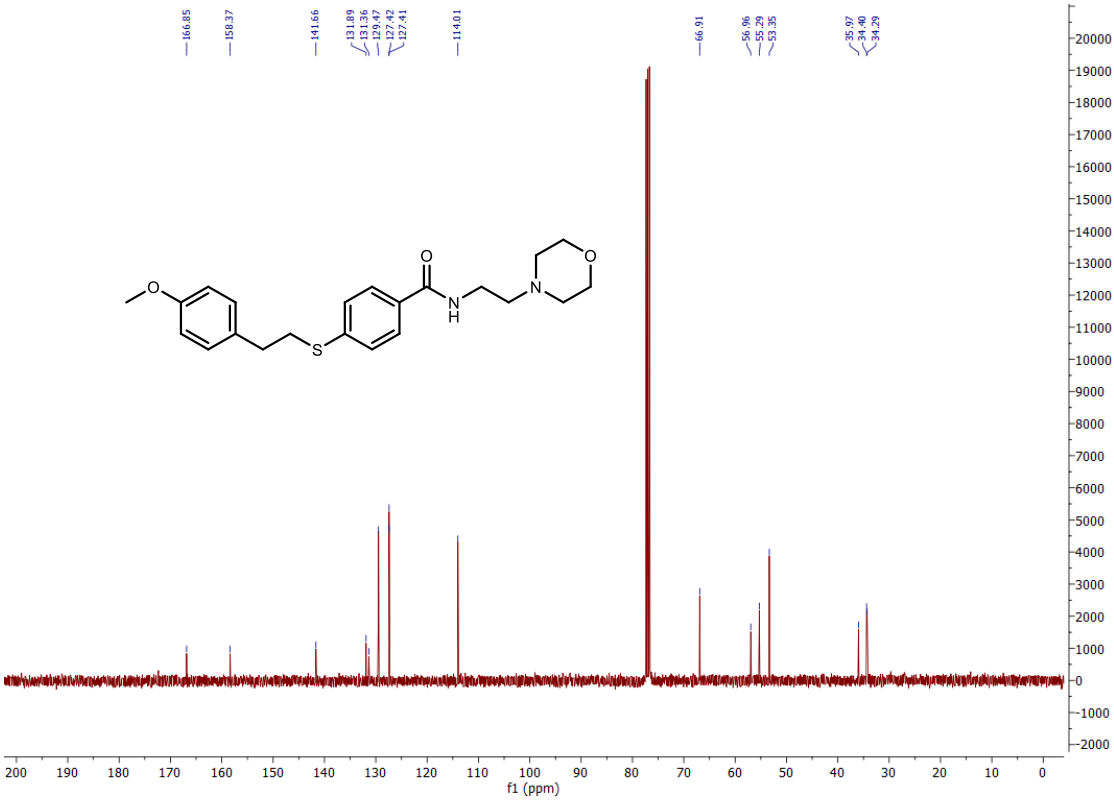
^{13}C NMR (101 MHz, $CDCl_3$) of **3r:**



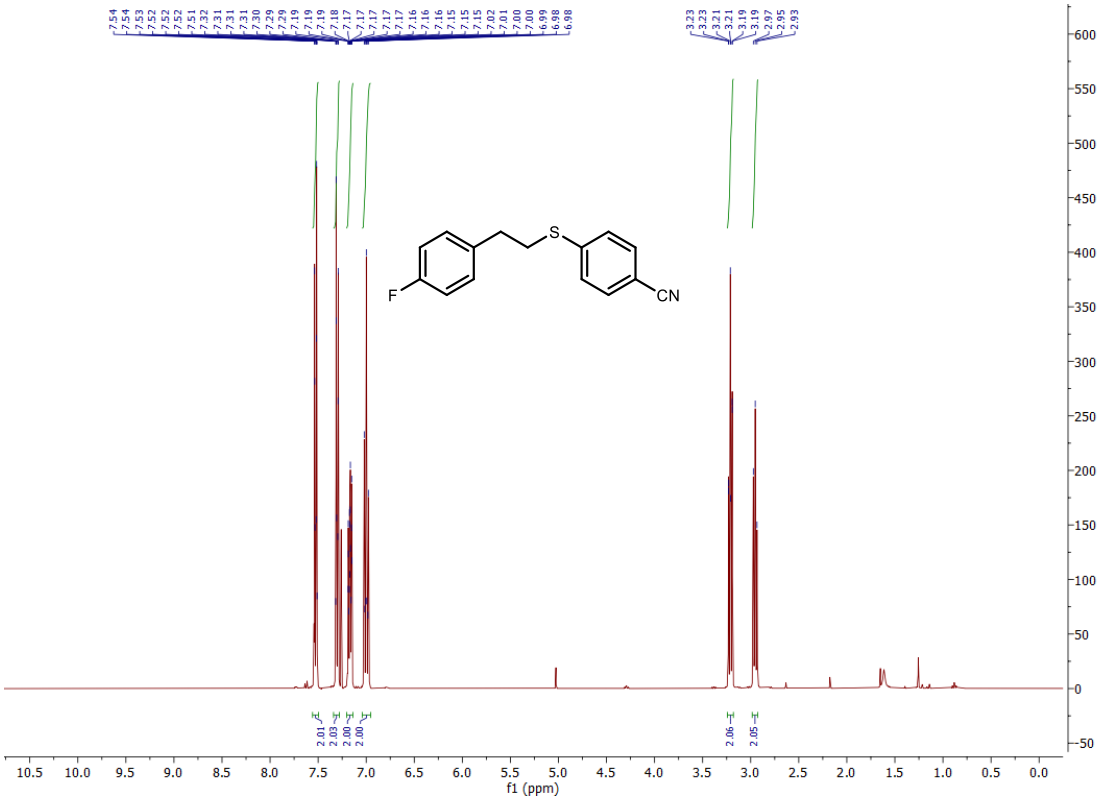
^{1}H NMR (400 MHz, $CDCl_3$) of **3s:**



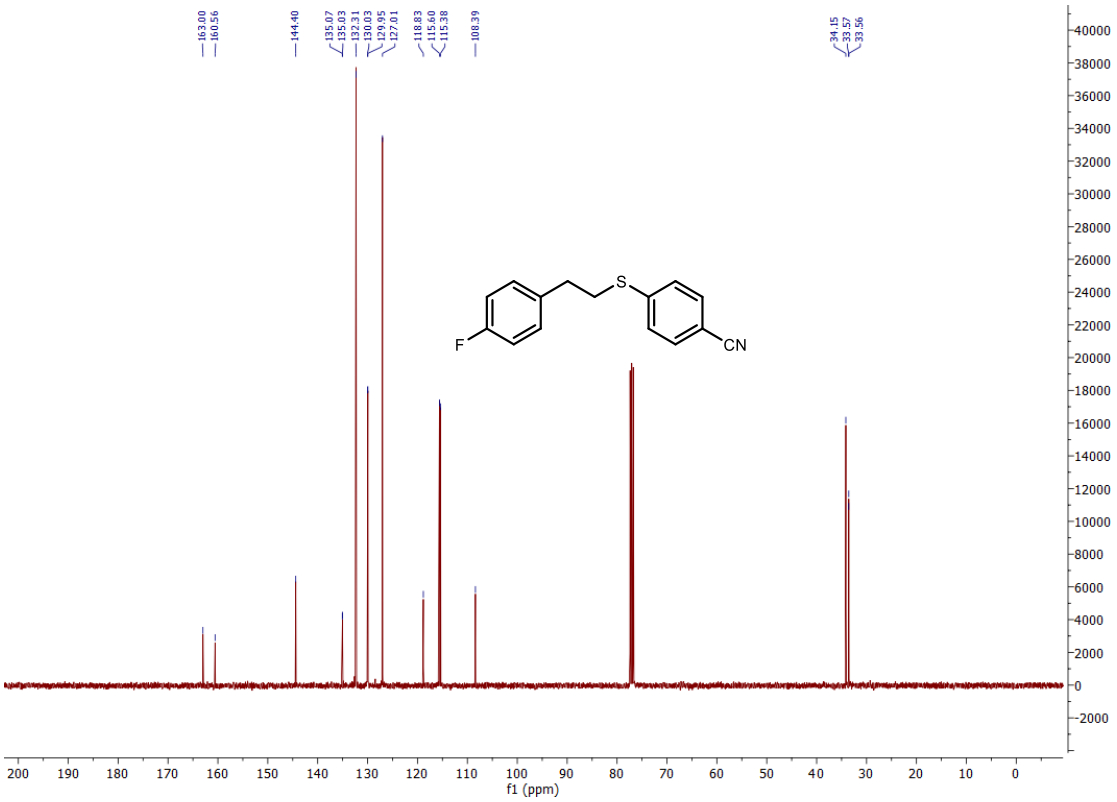
^{13}C NMR (101 MHz, $CDCl_3$) of **3s:**



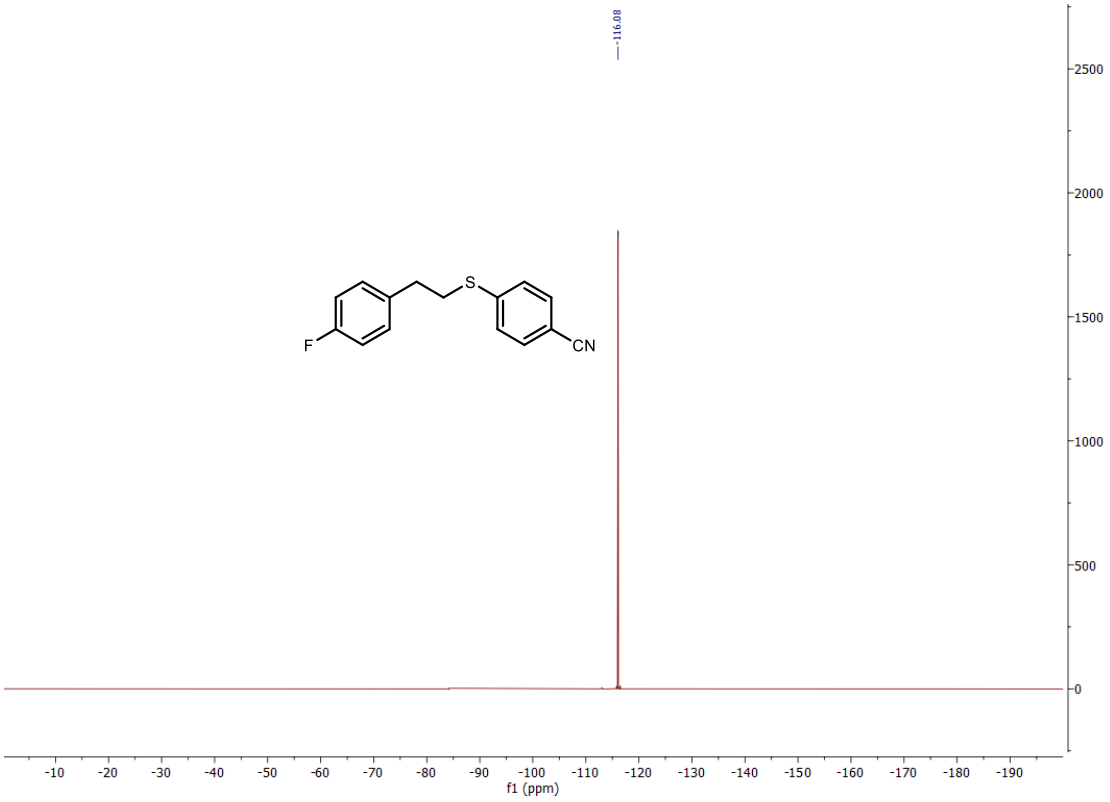
^{1}H NMR (400 MHz, $CDCl_3$) of **3t:**



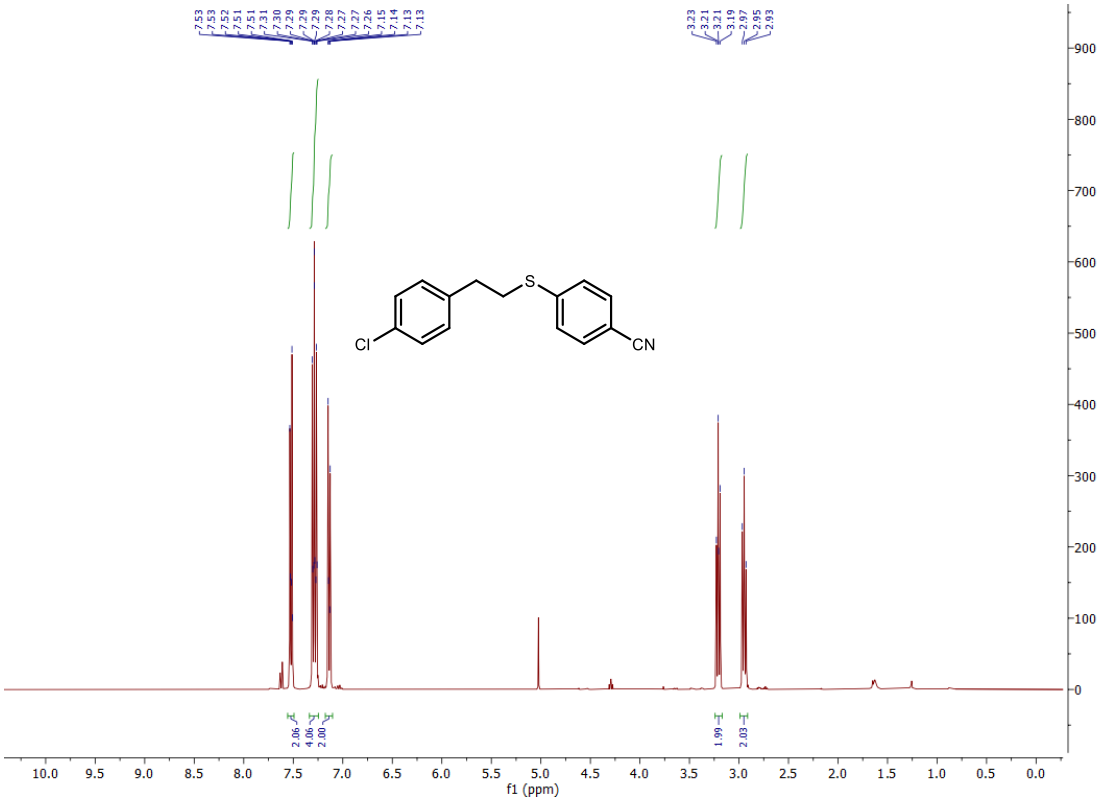
^{13}C NMR (101 MHz, $CDCl_3$) of **3t:**



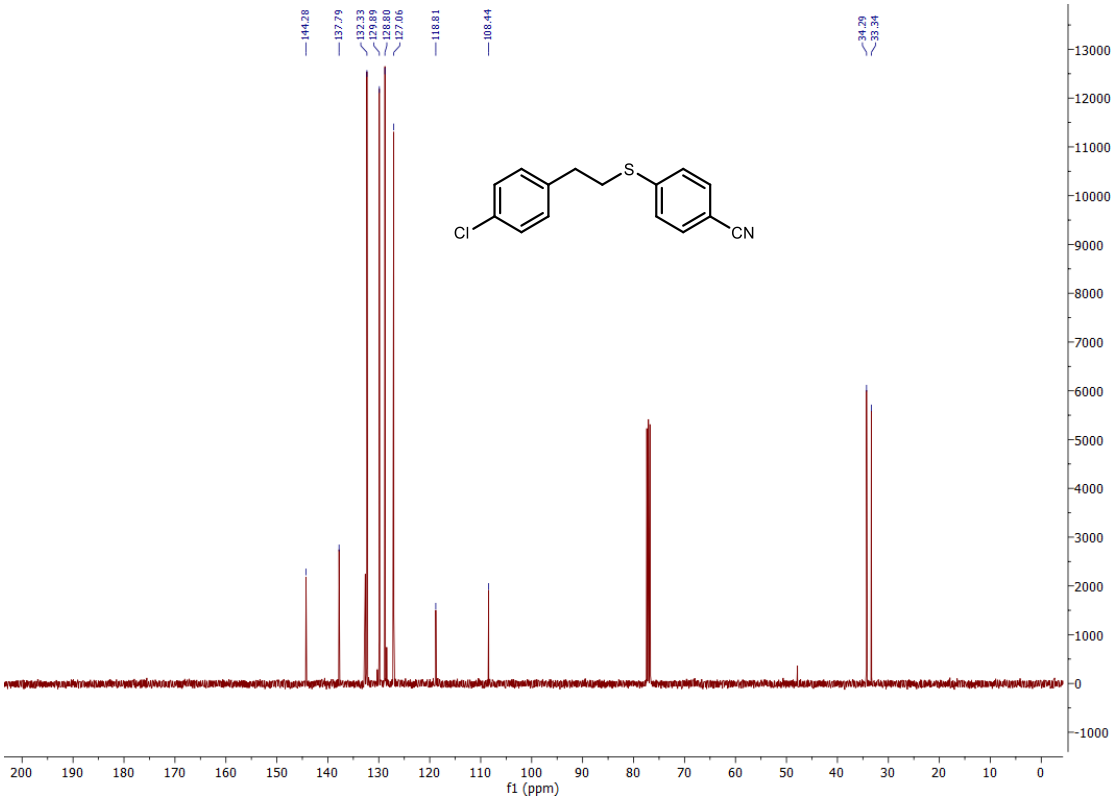
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) of **3t:**



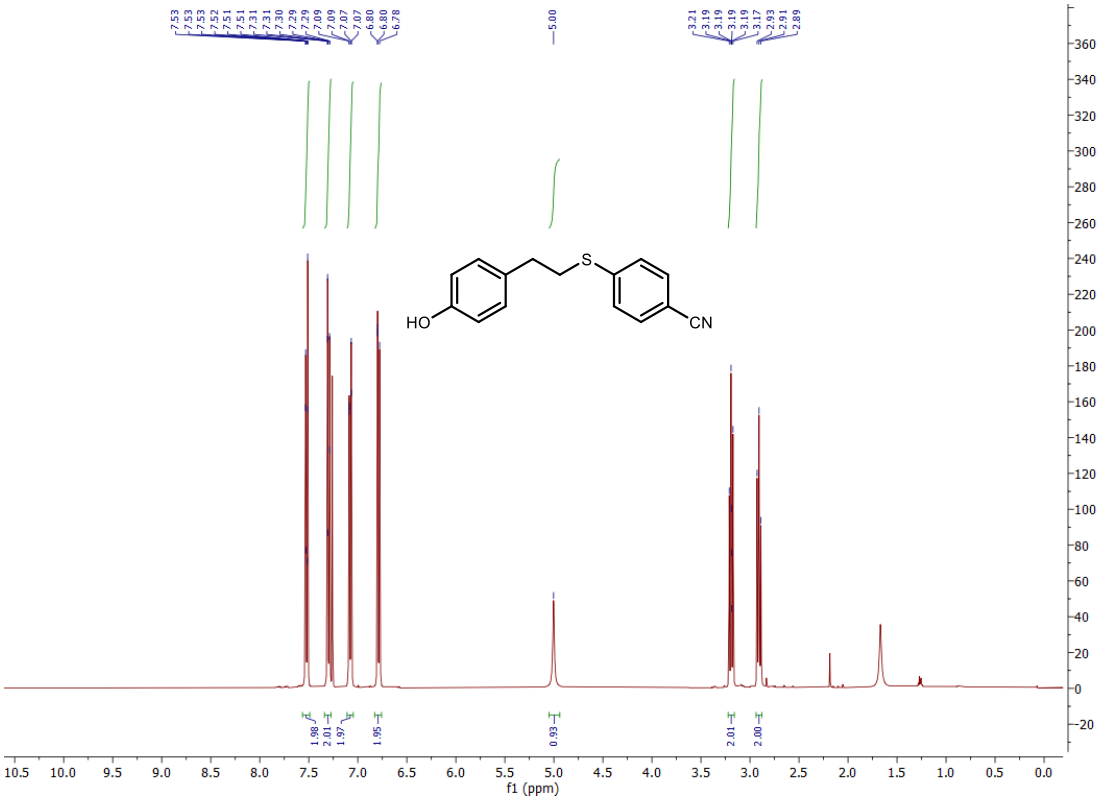
^{1}H NMR (400 MHz, $CDCl_3$) of **3u:**



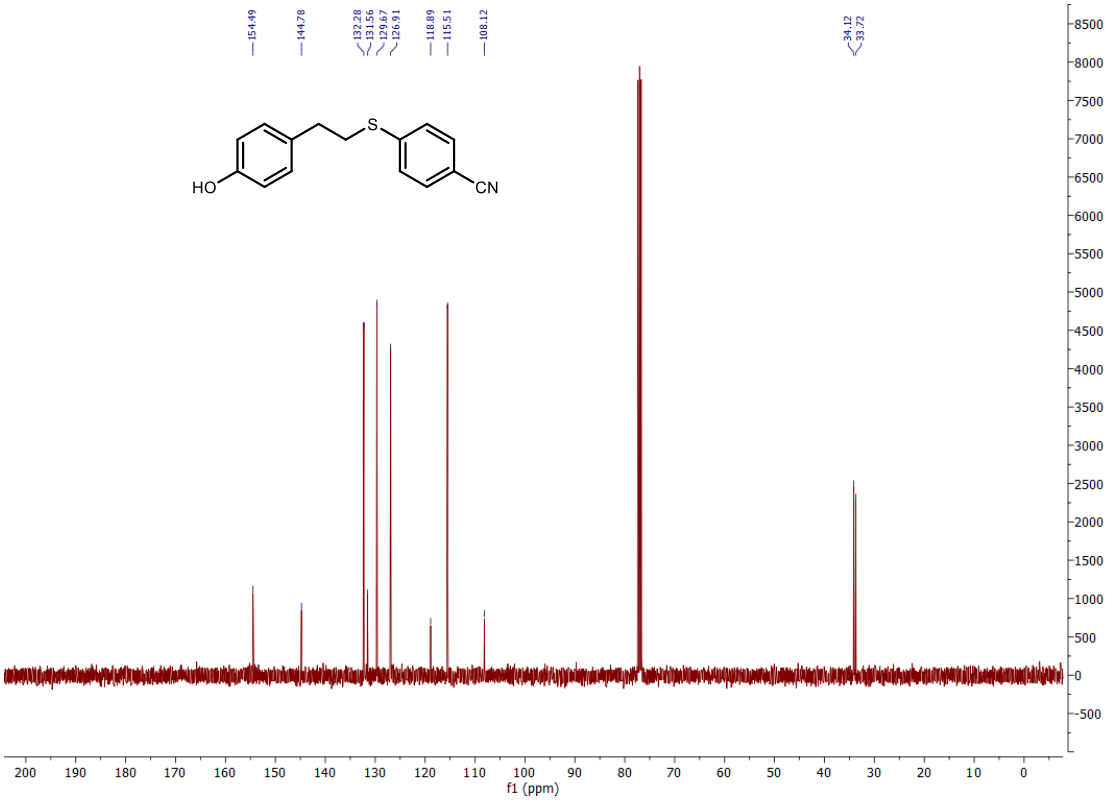
^{13}C NMR (101 MHz, $CDCl_3$) of **3u:**



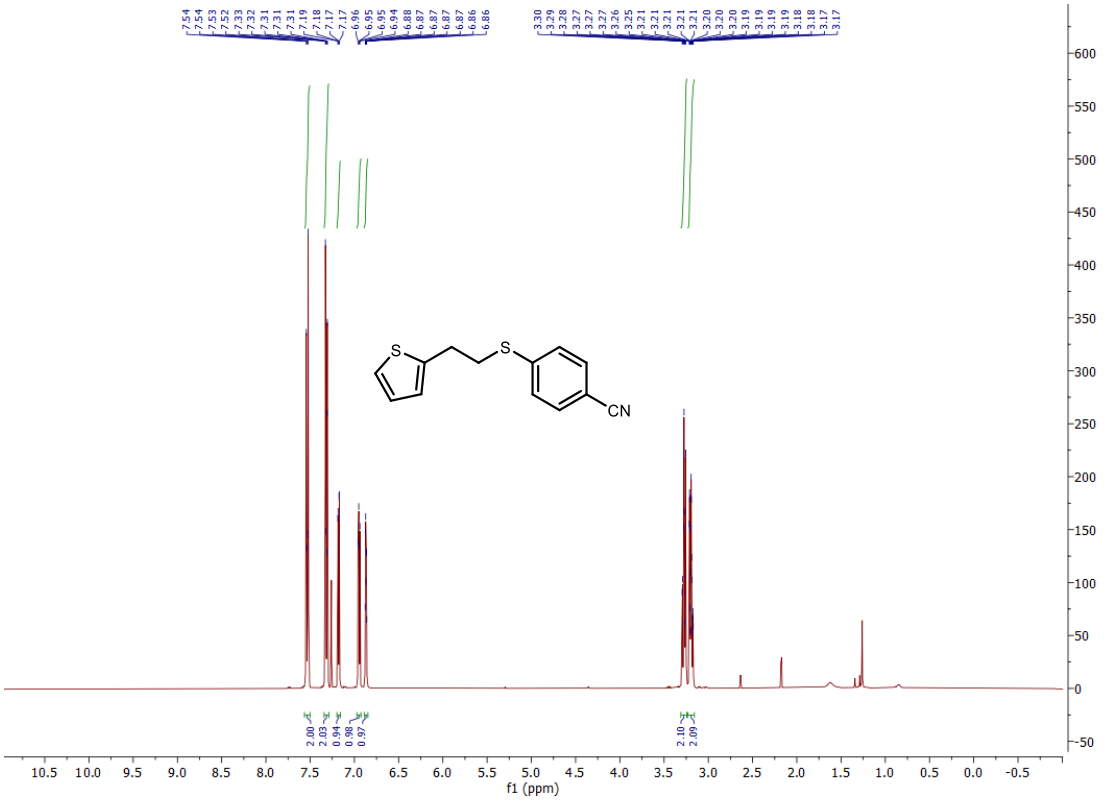
^{1}H NMR (400 MHz, $CDCl_3$) of **3v:**



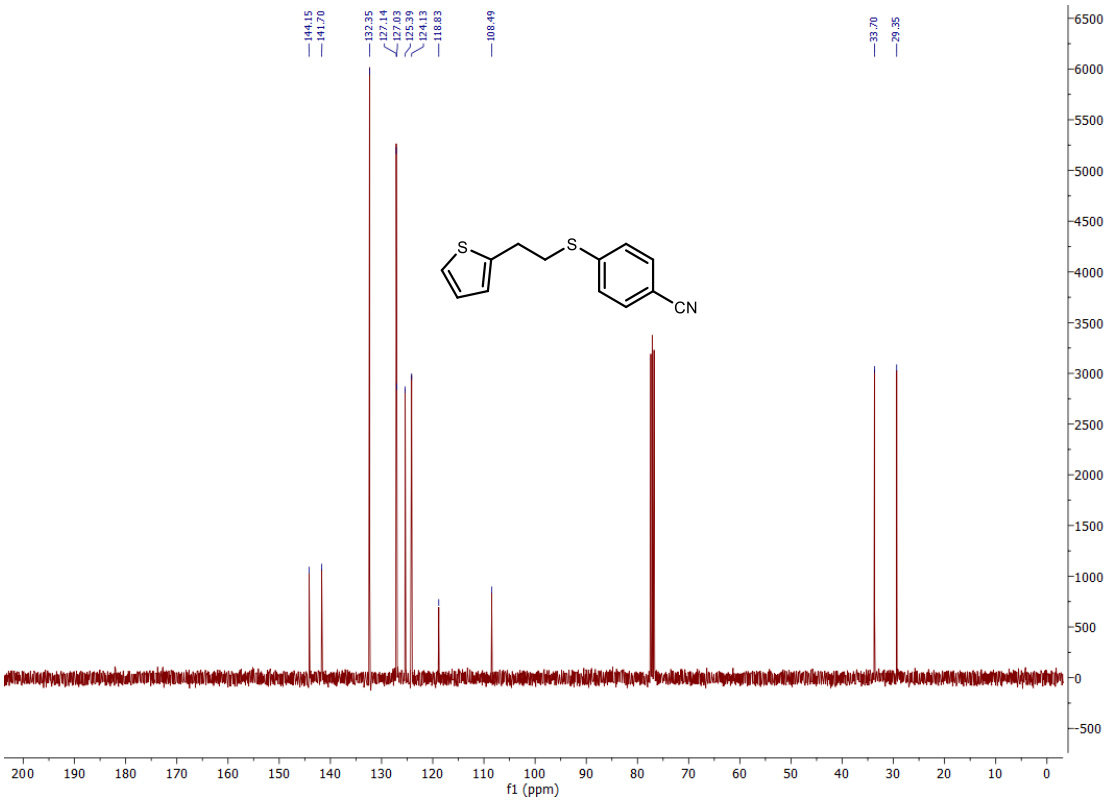
^{13}C NMR (101 MHz, $CDCl_3$) of **3v:**



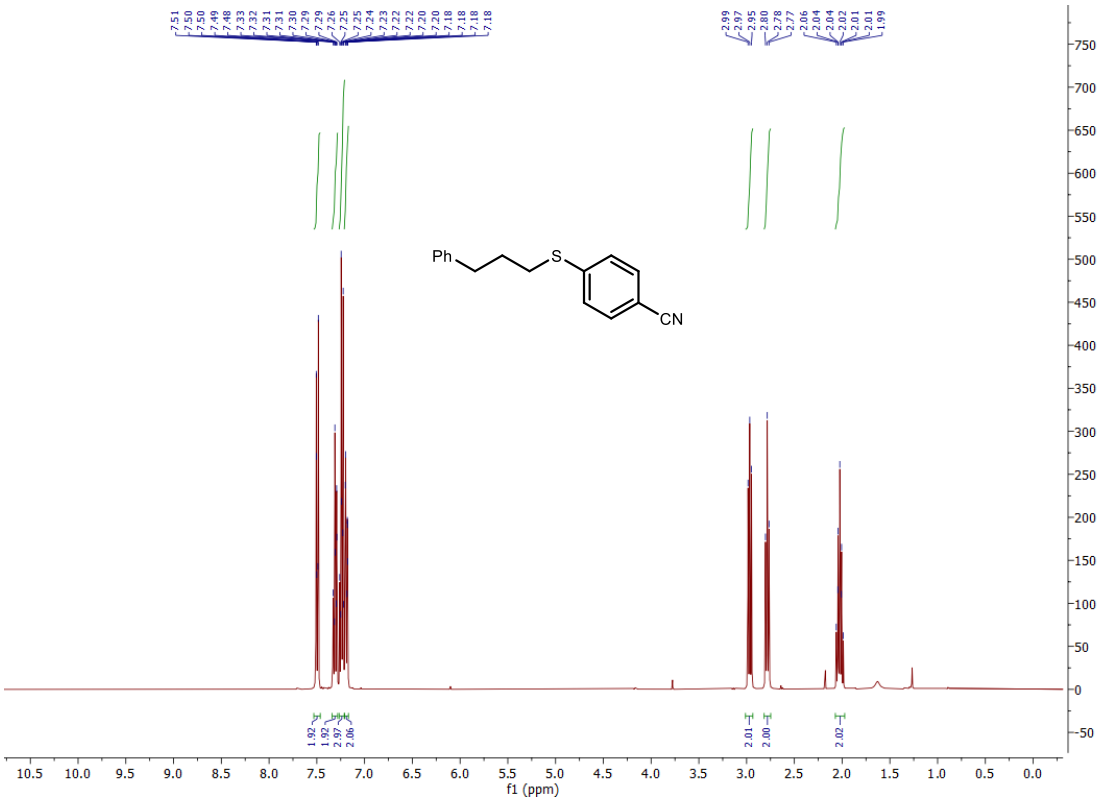
^{1}H NMR (400 MHz, $CDCl_3$) of **3w:**



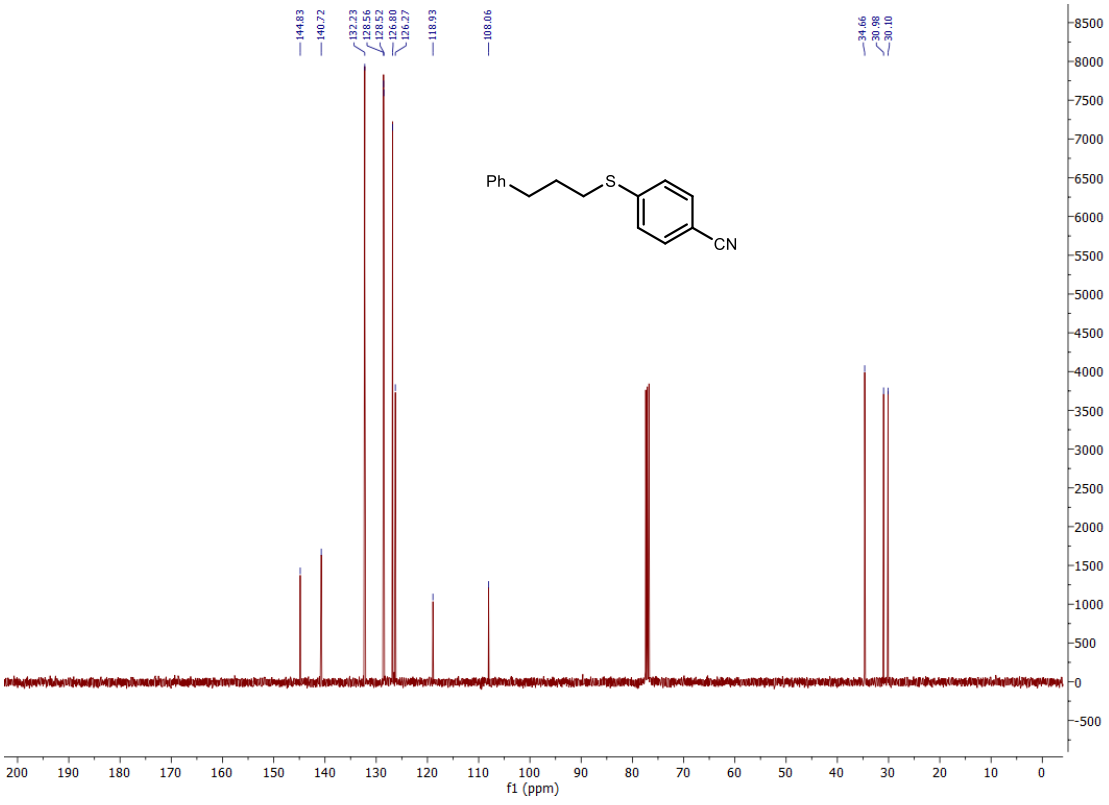
^{13}C NMR (101 MHz, $CDCl_3$) of **3w:**



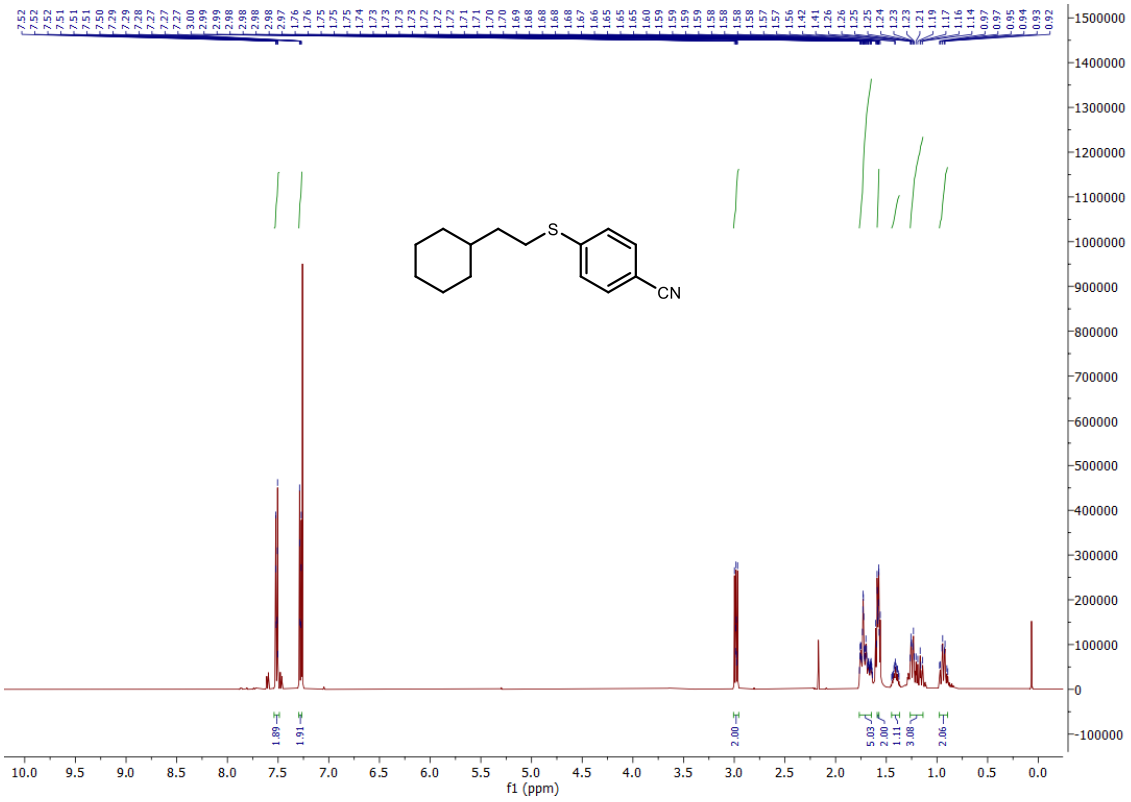
^{1}H NMR (400 MHz, $CDCl_3$) of **3x:**



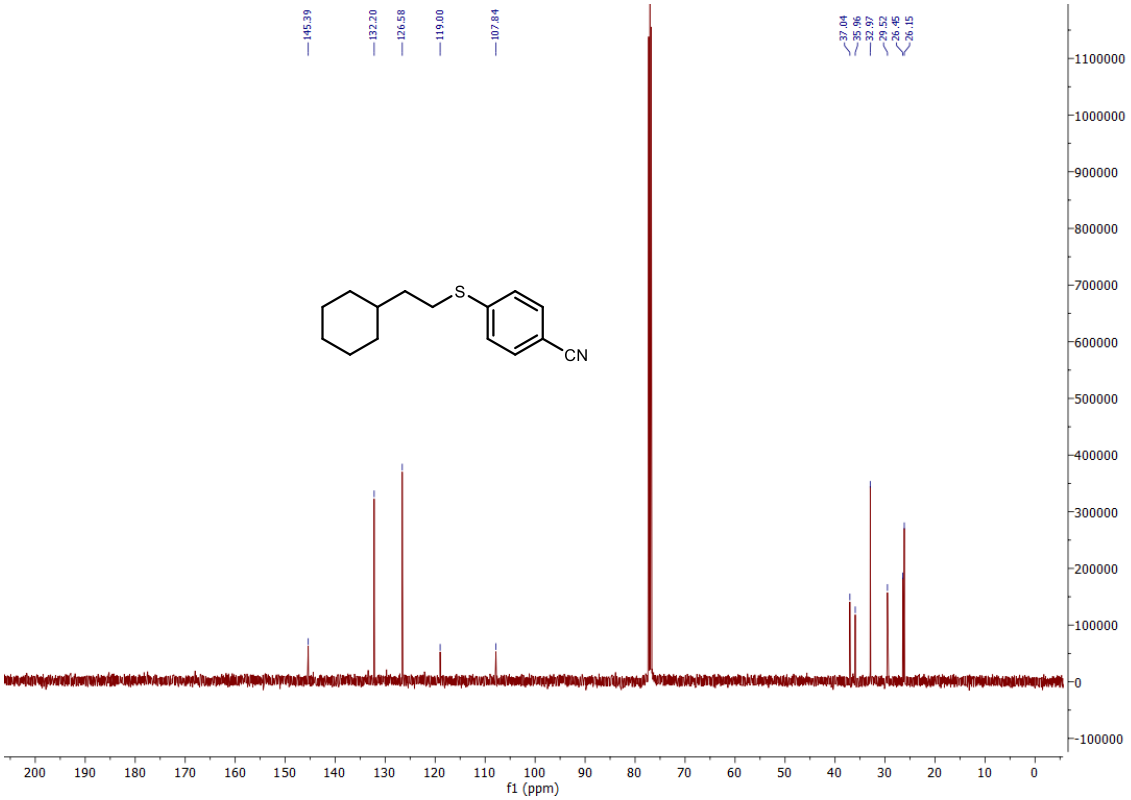
^{13}C NMR (101 MHz, $CDCl_3$) of **3x:**



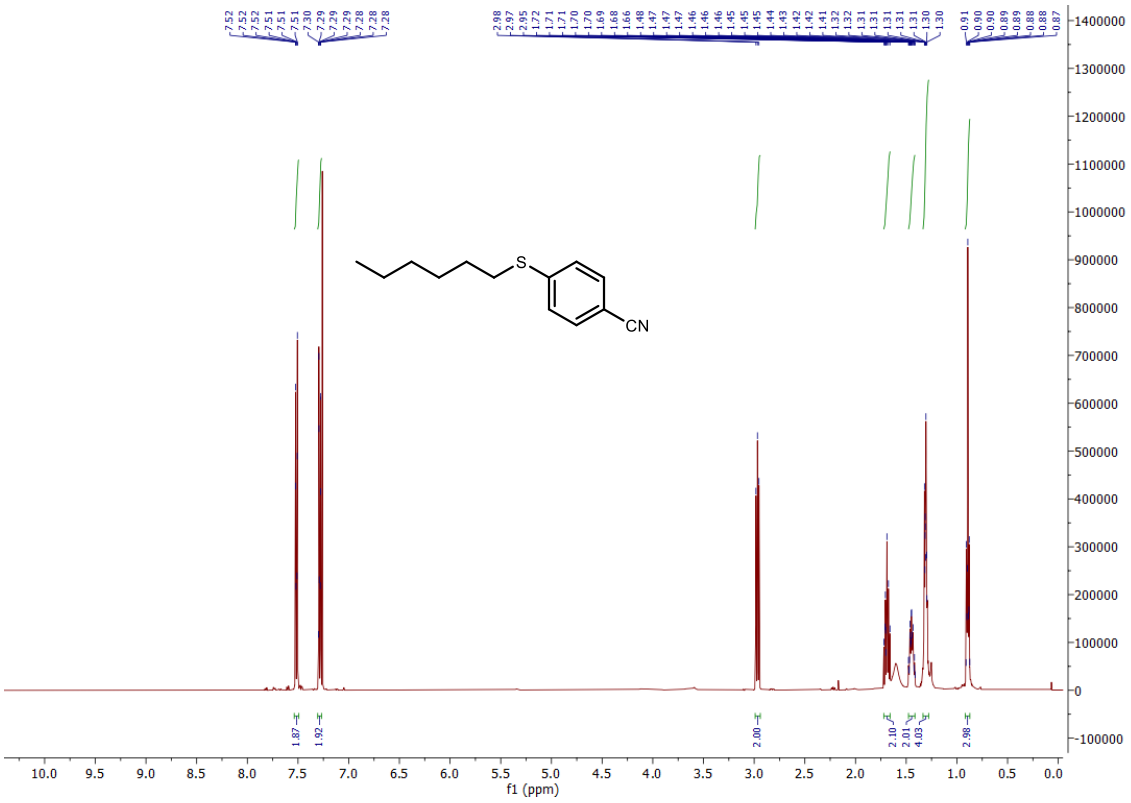
^{1}H NMR (400 MHz, $CDCl_3$) of **3y:**



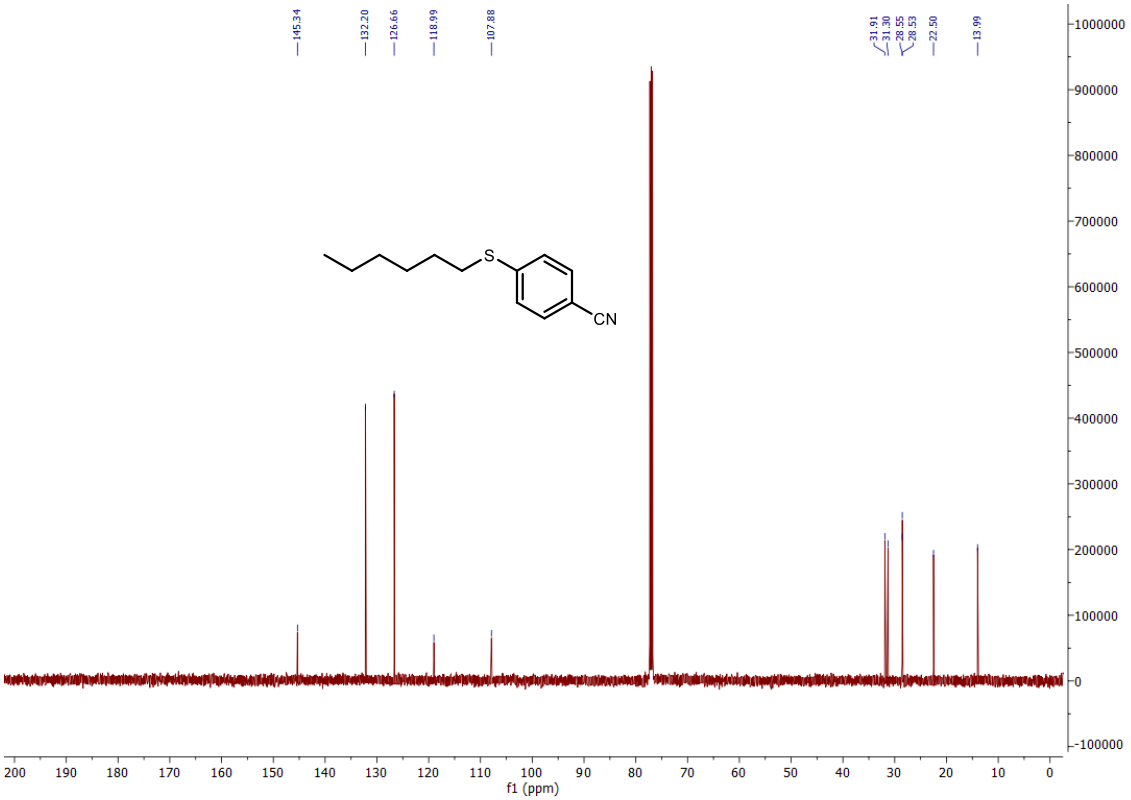
^{13}C NMR (101 MHz, $CDCl_3$) of **3y:**



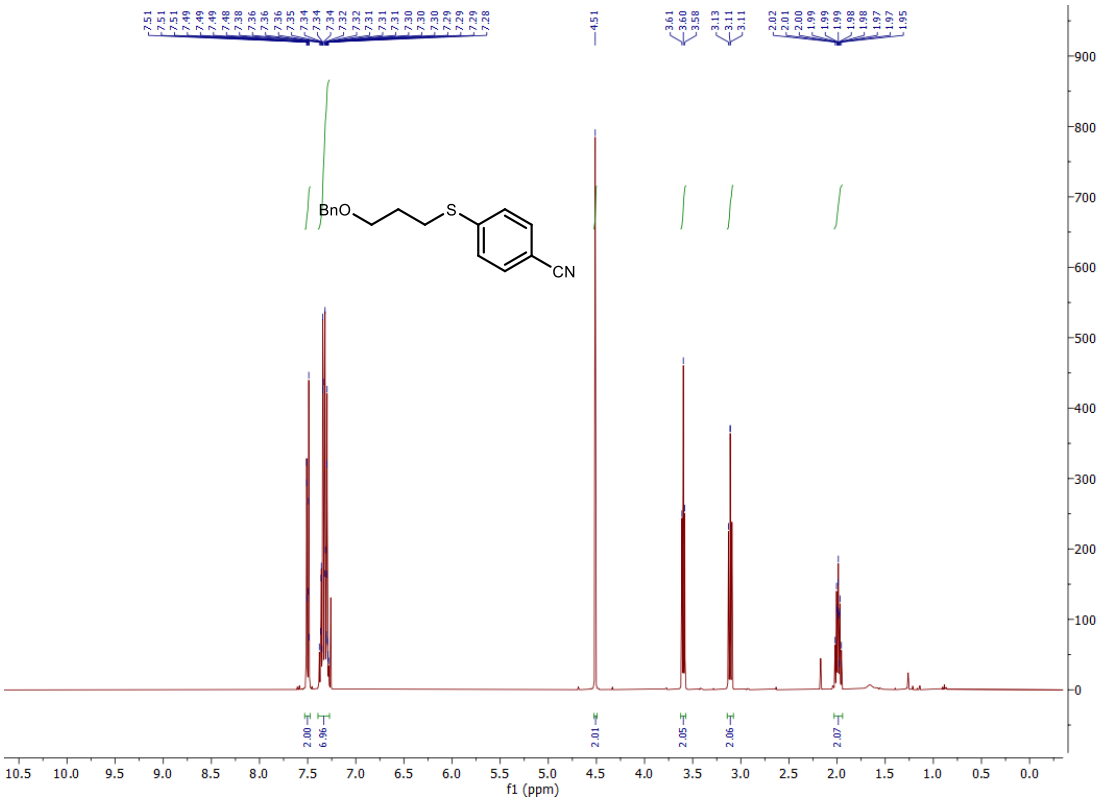
^{1}H NMR (400 MHz, $CDCl_3$) of **3z:**



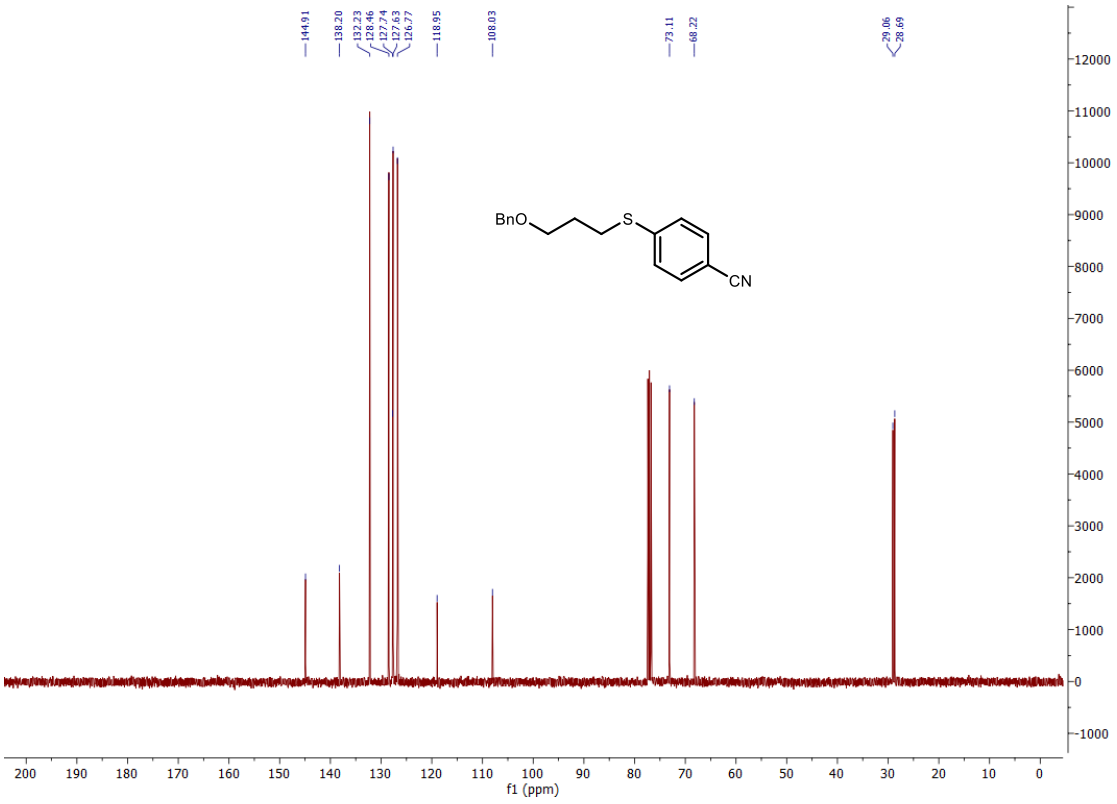
^{13}C NMR (101 MHz, $CDCl_3$) of **3z:**



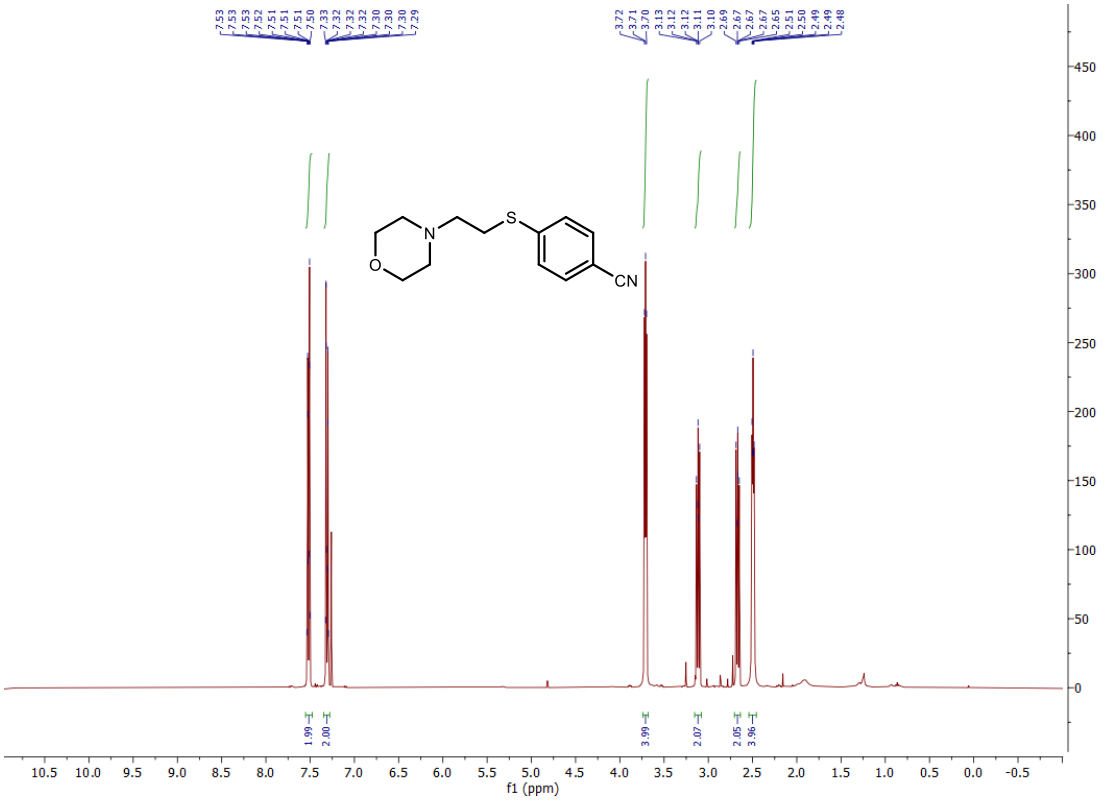
^{1}H NMR (400 MHz, $CDCl_3$) of **3aa:**



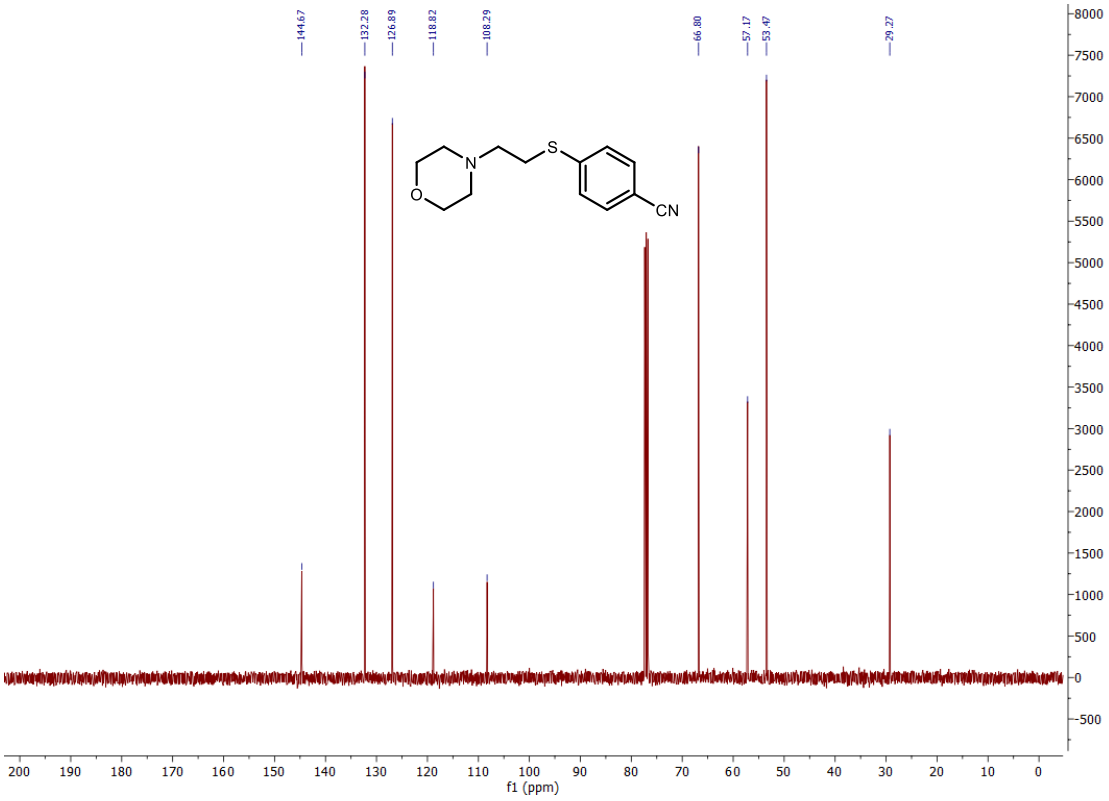
^{13}C NMR (101 MHz, $CDCl_3$) of **3aa:**



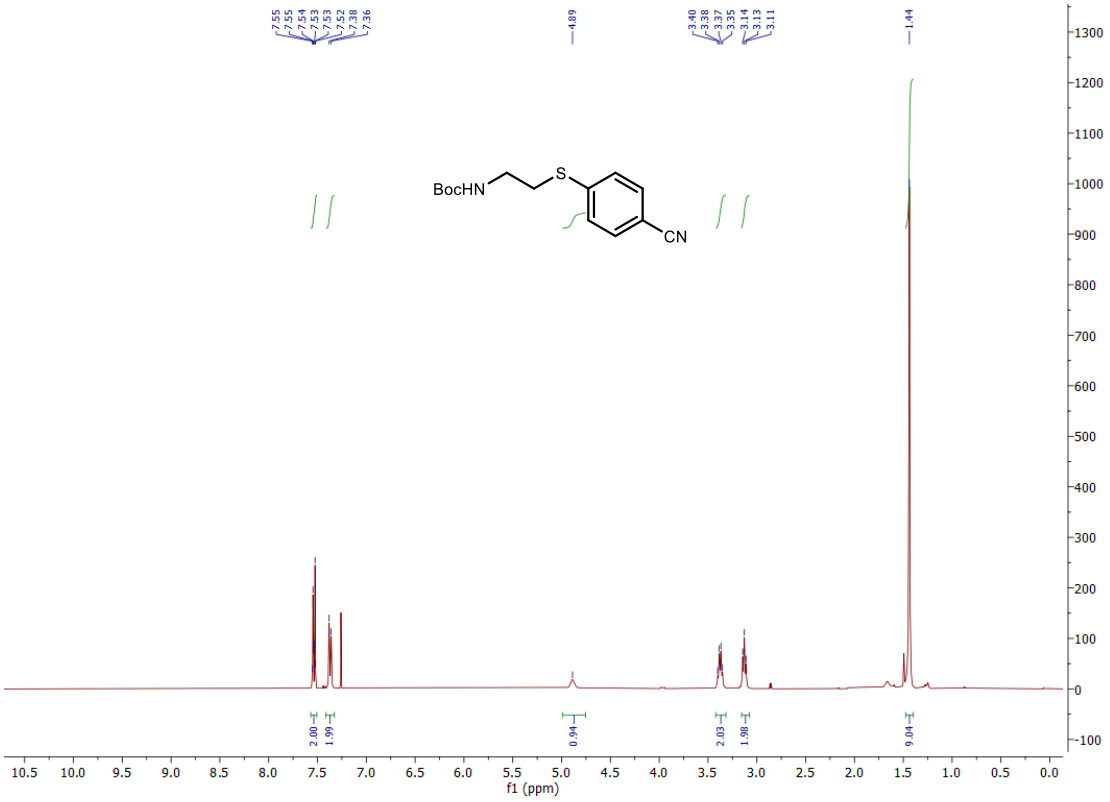
^{1}H NMR (400 MHz, $CDCl_3$) of **3ab:**



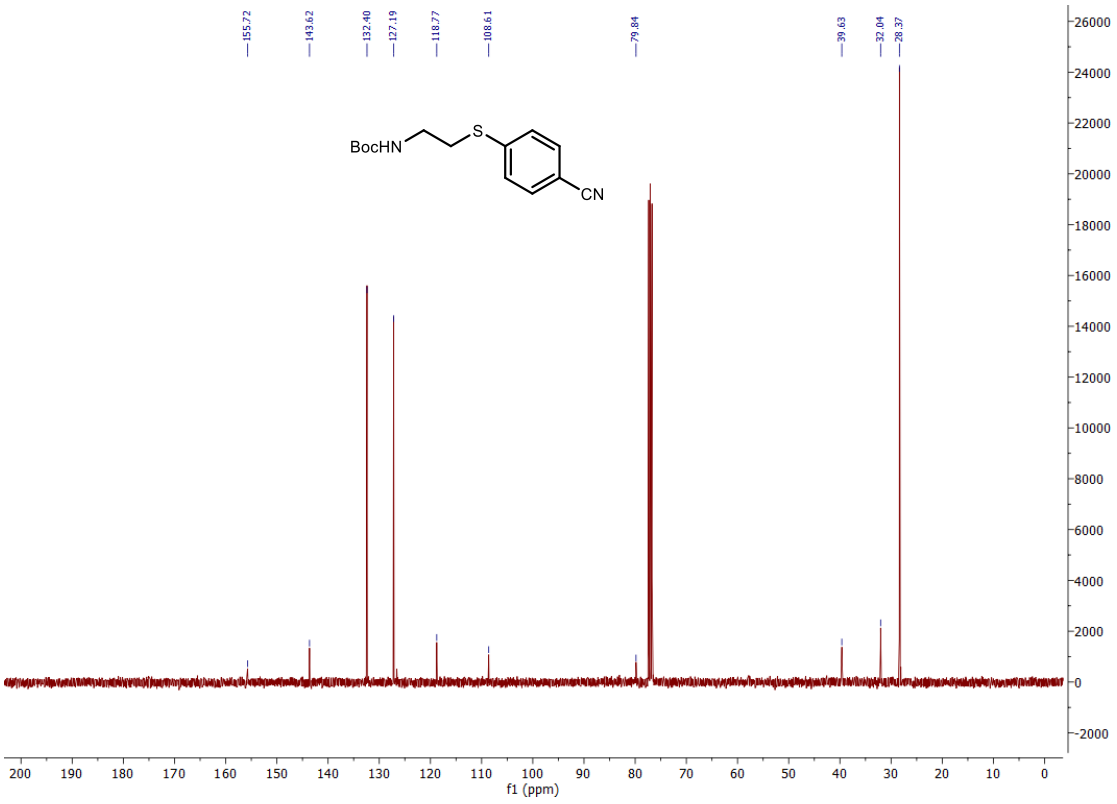
^{13}C NMR (101 MHz, $CDCl_3$) of **3ab:**



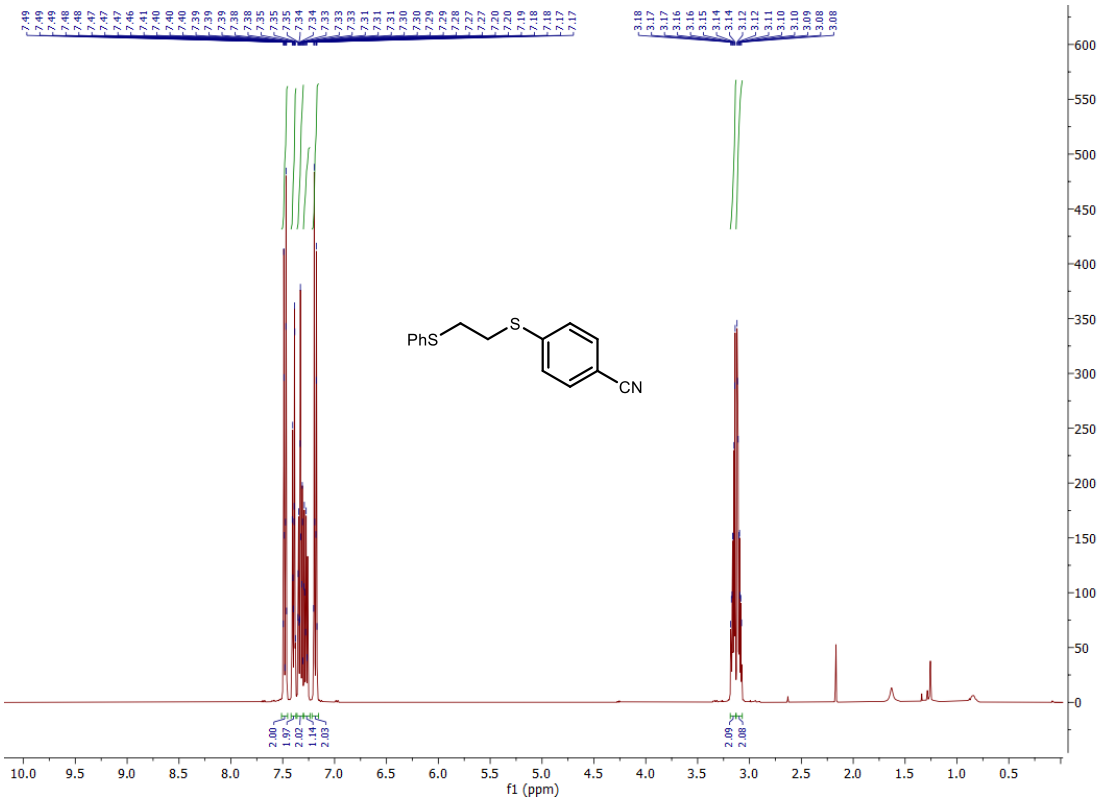
^{1}H NMR (400 MHz, $CDCl_3$) of **3ac:**



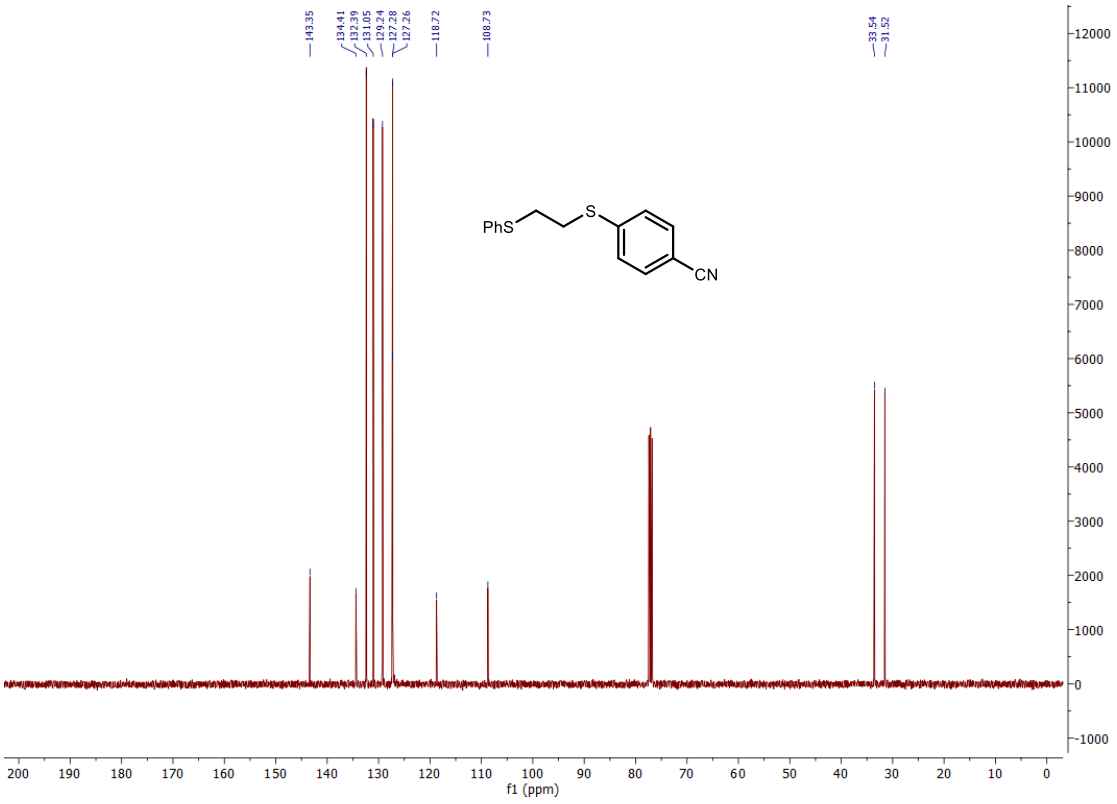
^{13}C NMR (101 MHz, $CDCl_3$) of **3ac:**



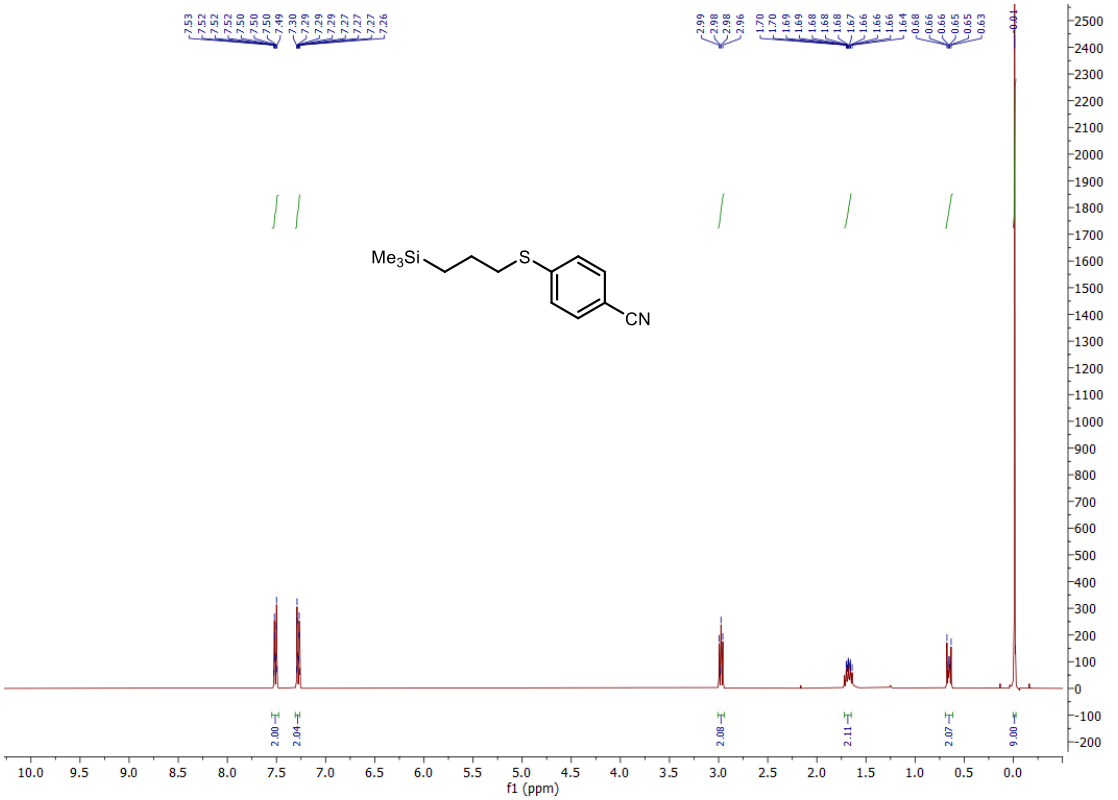
^{1}H NMR (400 MHz, $CDCl_3$) of **3ad:**



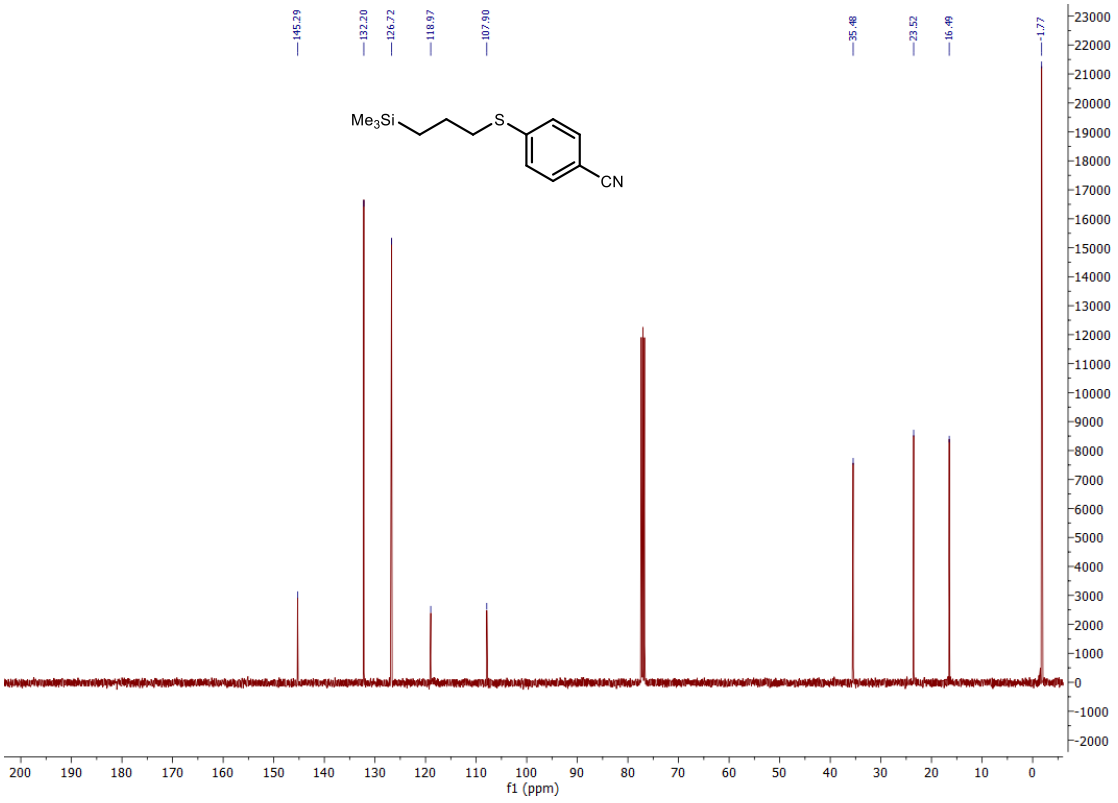
^{13}C NMR (101 MHz, $CDCl_3$) of **3ad:**



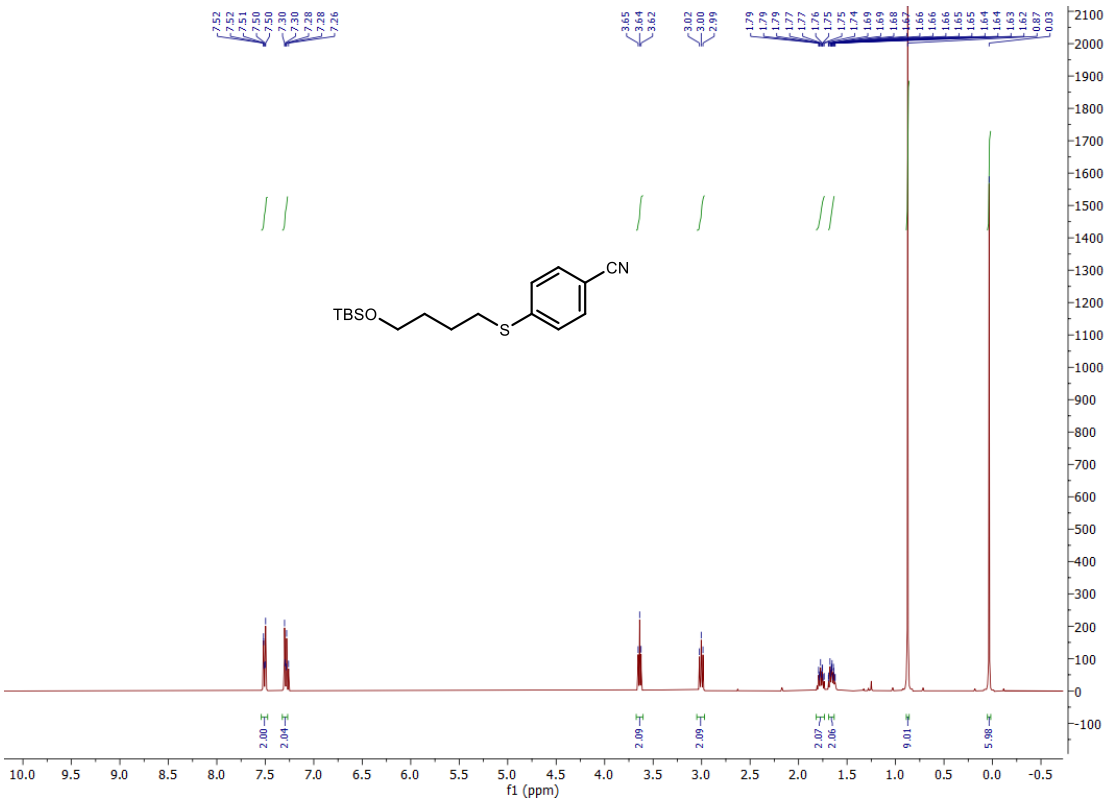
^{1}H NMR (400 MHz, $CDCl_3$) of **3ae:**



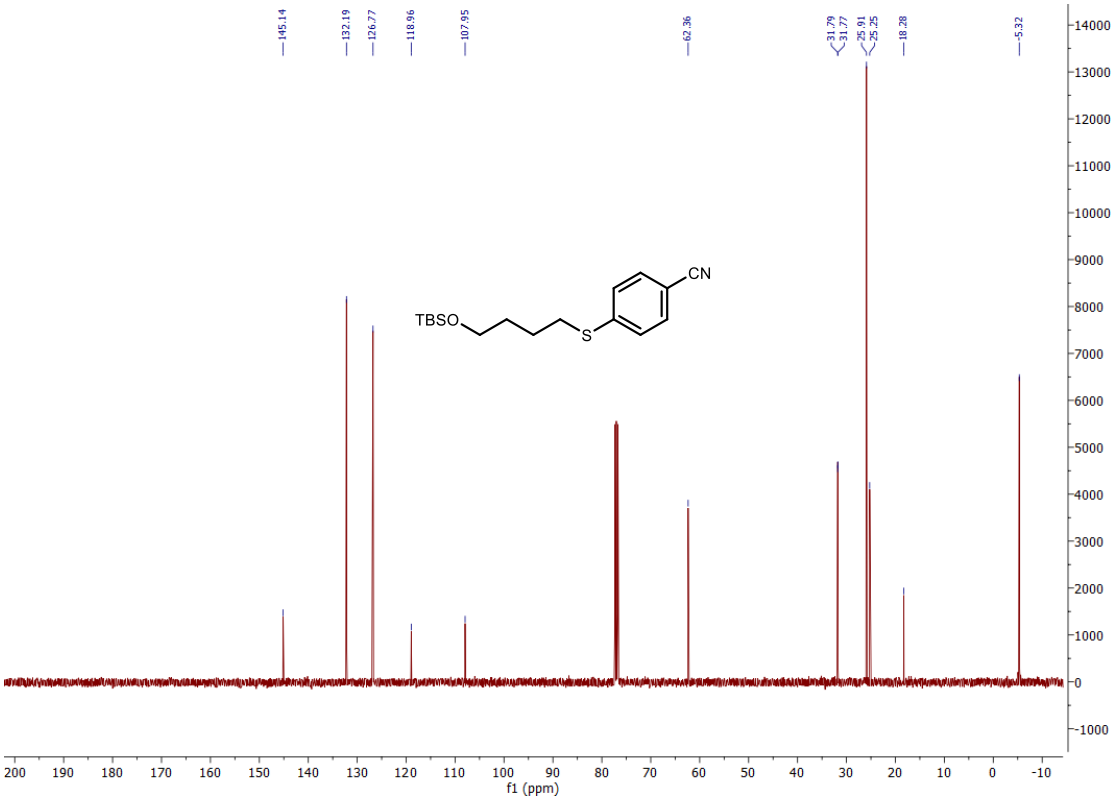
^{13}C NMR (101 MHz, $CDCl_3$) of **3ae:**



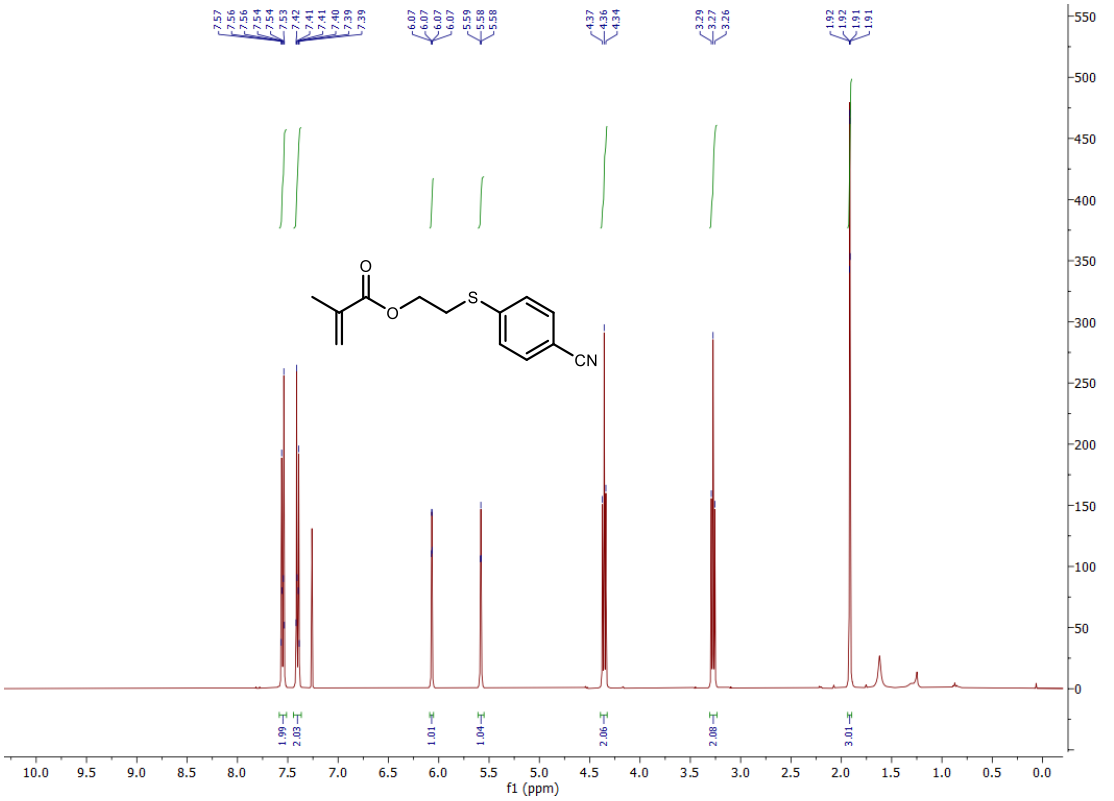
^{1}H NMR (400 MHz, $CDCl_3$) of **3af:**



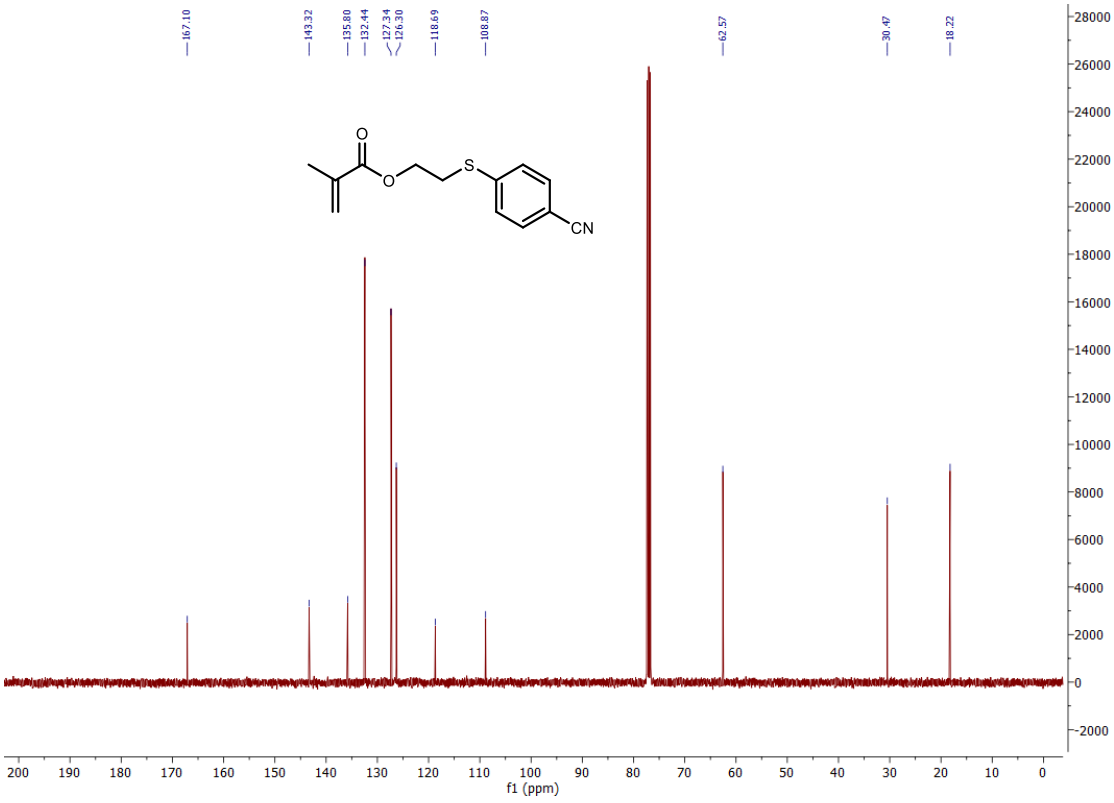
^{13}C NMR (101 MHz, $CDCl_3$) of **3af:**



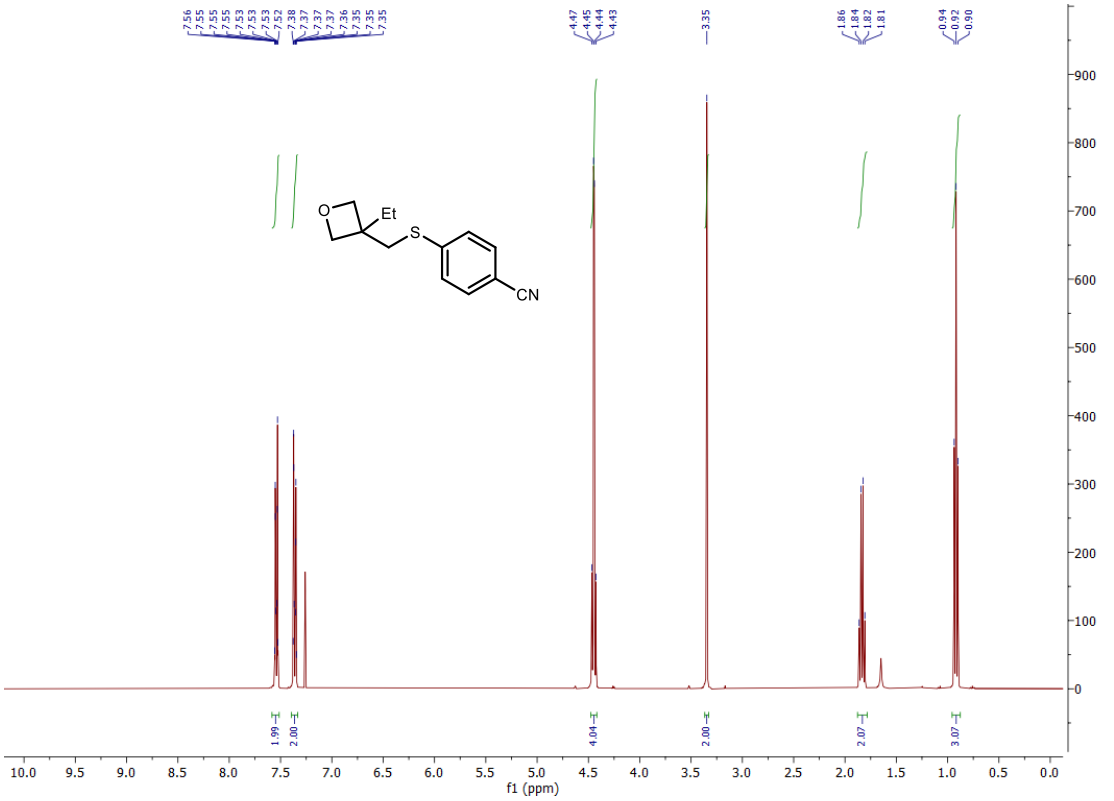
^{1}H NMR (400 MHz, $CDCl_3$) of **3ag:**



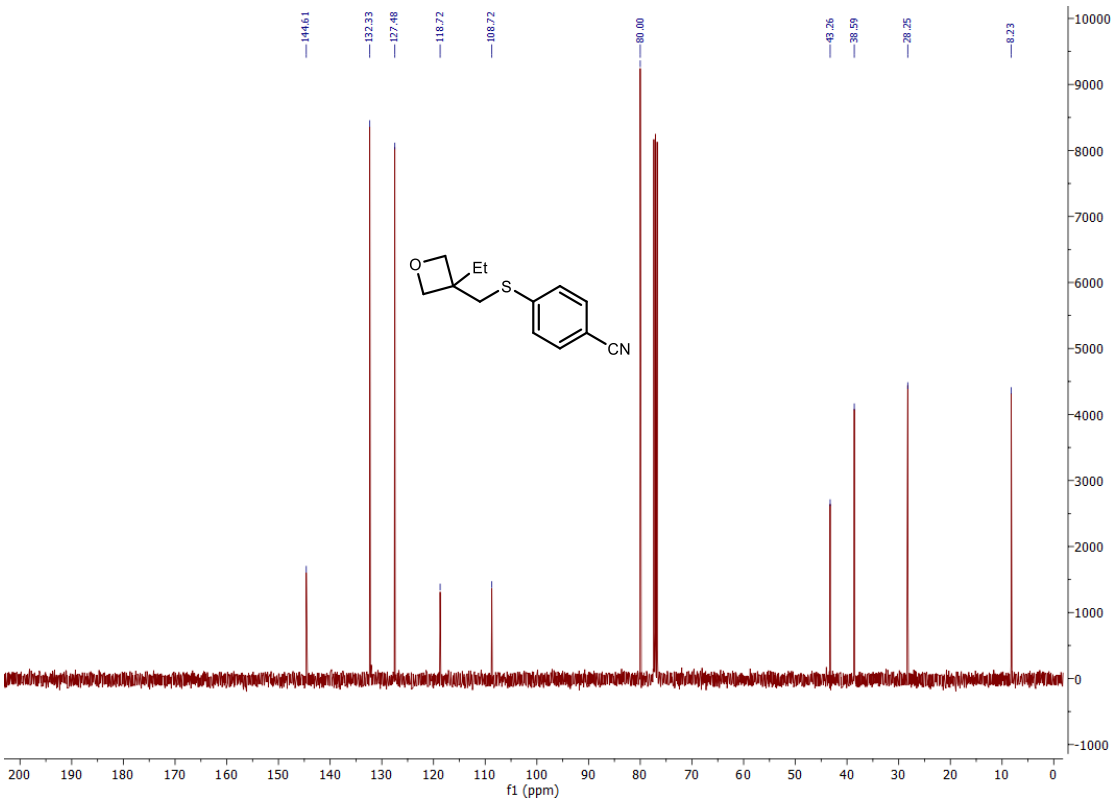
^{13}C NMR (101 MHz, $CDCl_3$) of **3ag:**



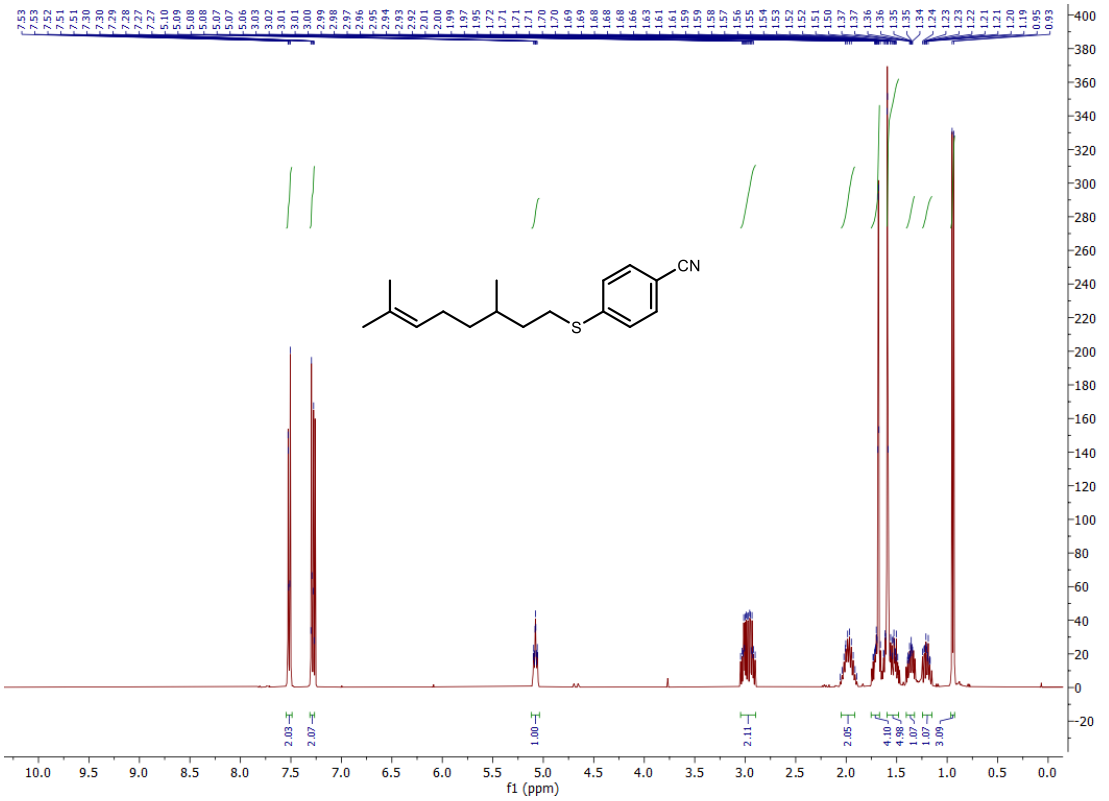
^{1}H NMR (400 MHz, $CDCl_3$) of **3ah:**



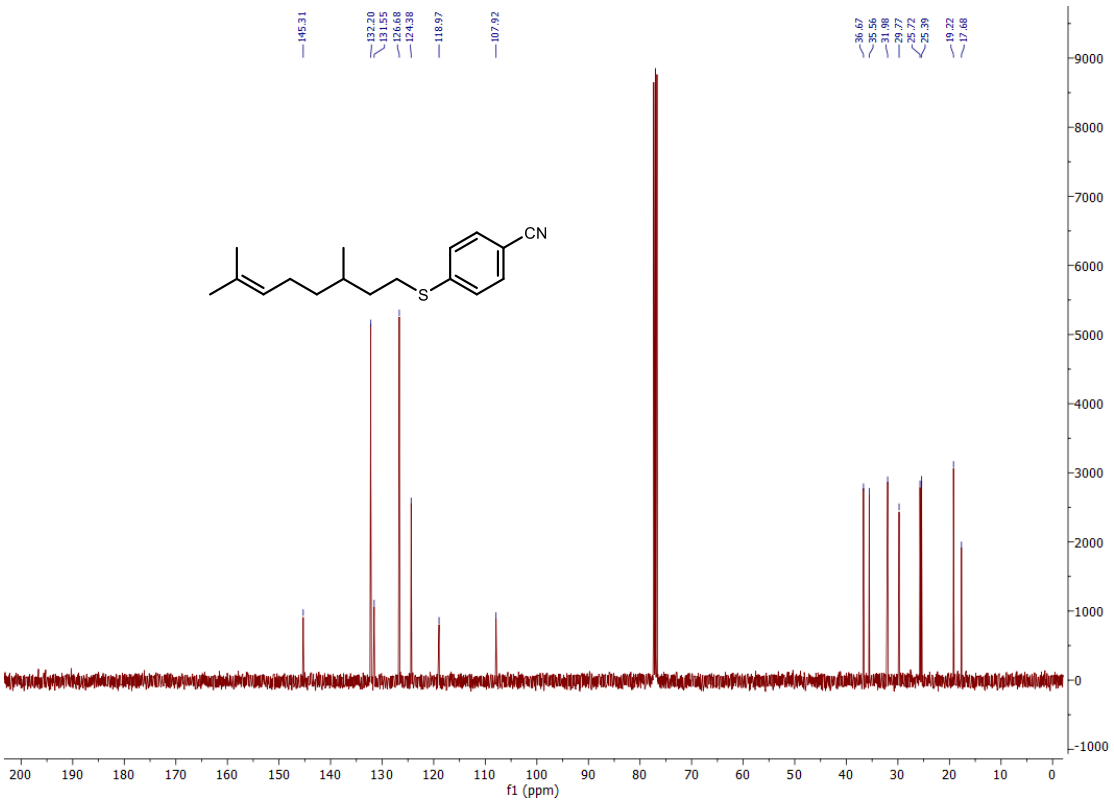
^{13}C NMR (101 MHz, $CDCl_3$) of **3ah:**



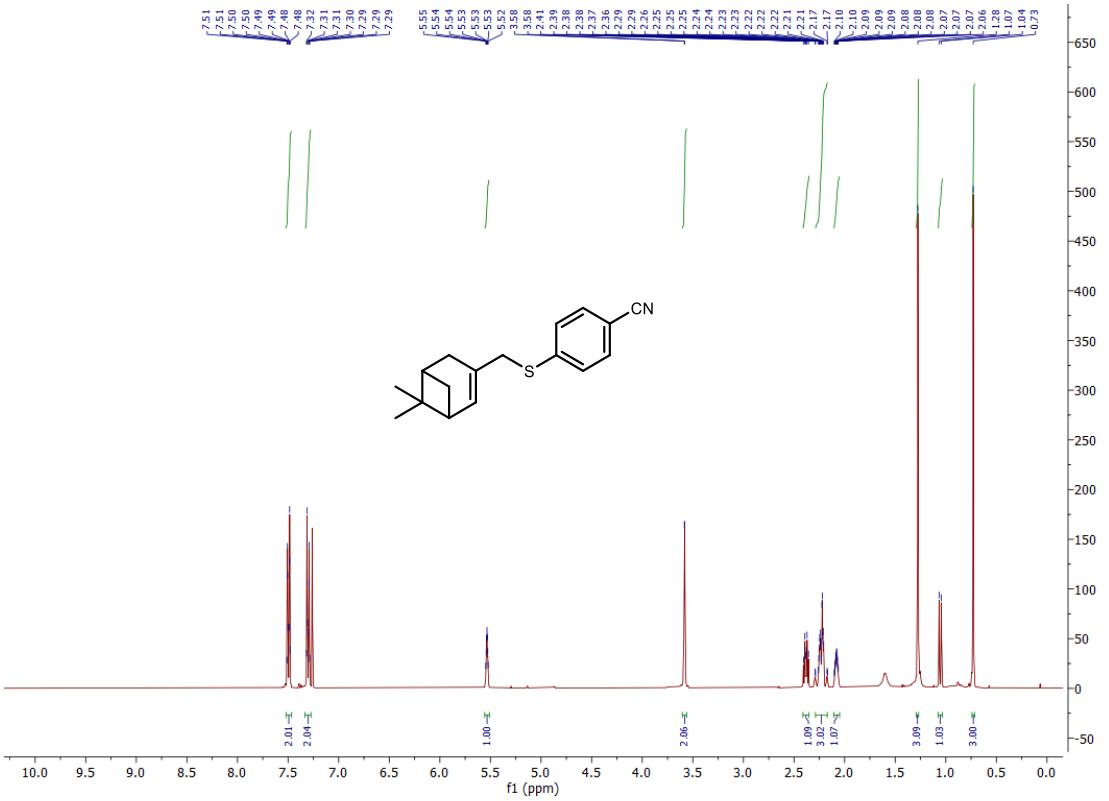
^{1}H NMR (400 MHz, $CDCl_3$) of **3ai:**



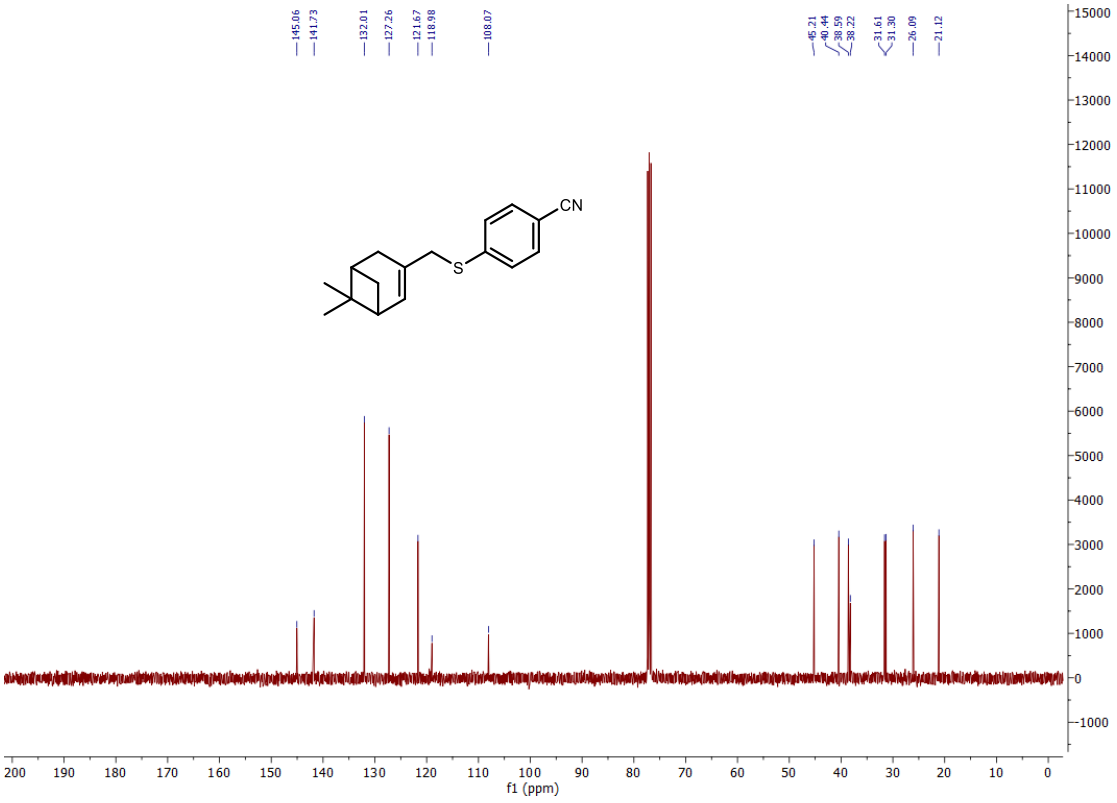
^{13}C NMR (101 MHz, $CDCl_3$) of **3ai:**



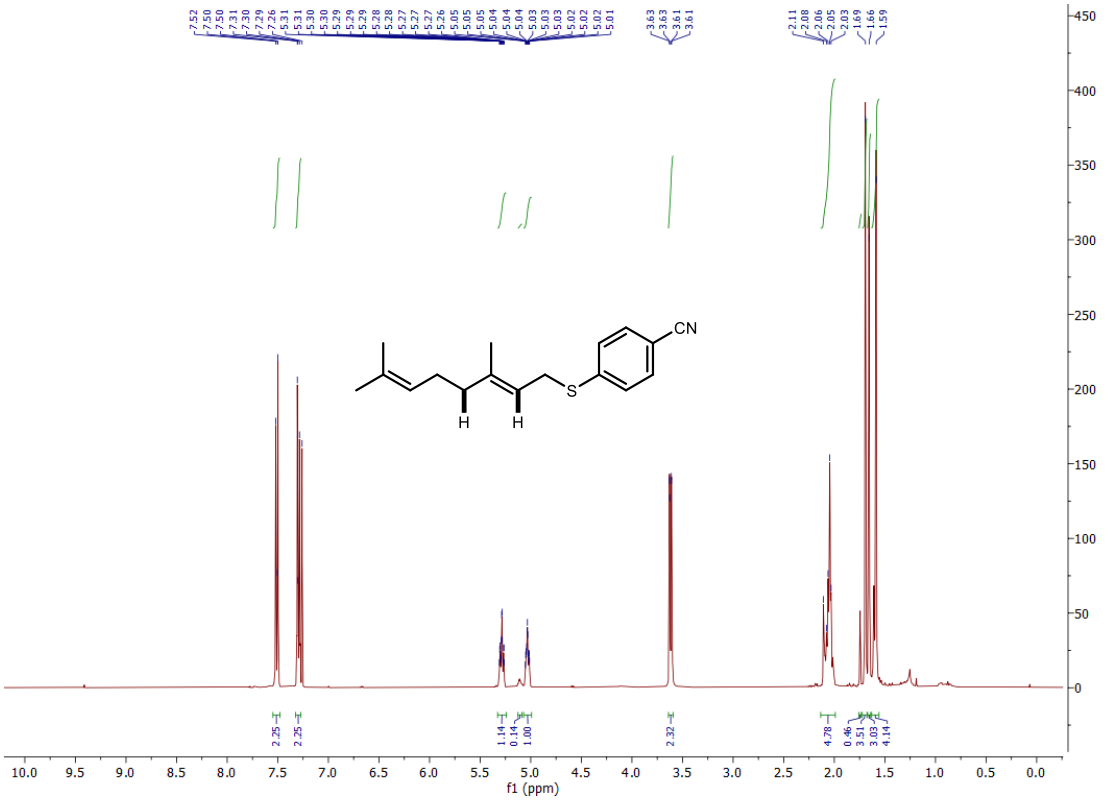
^{1}H NMR (400 MHz, $CDCl_3$) of **3aj:**



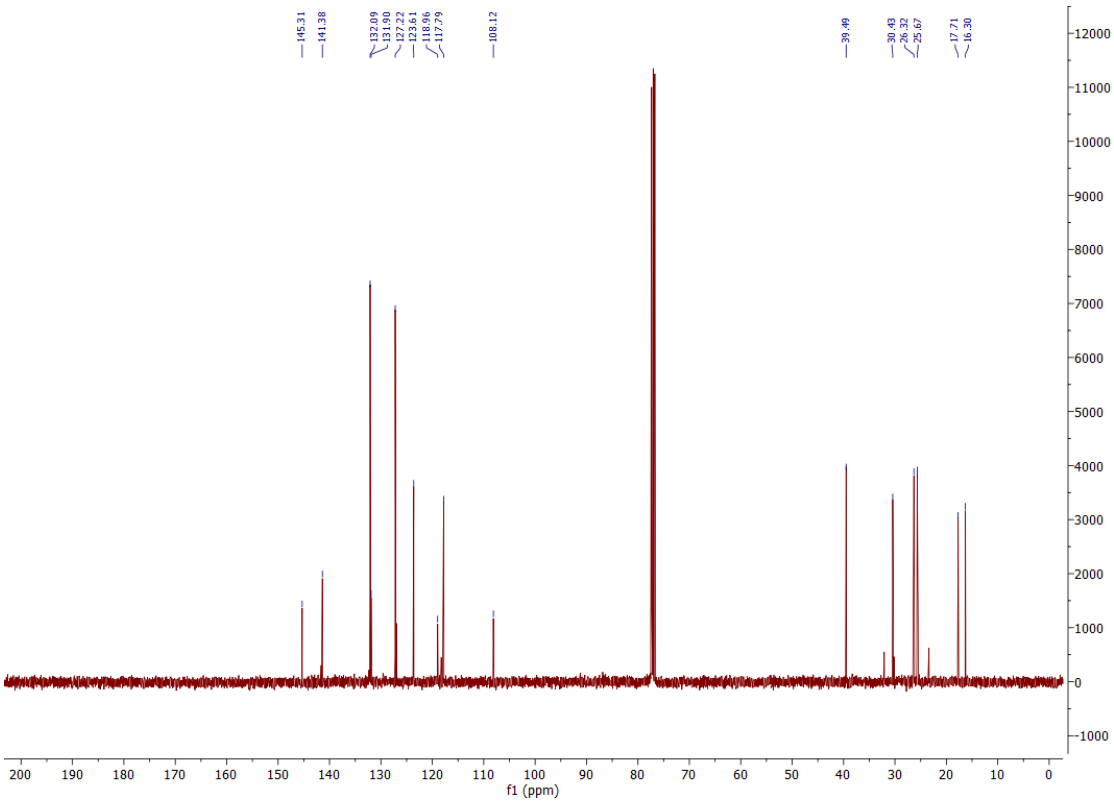
^{13}C NMR (101 MHz, $CDCl_3$) of **3aj:**



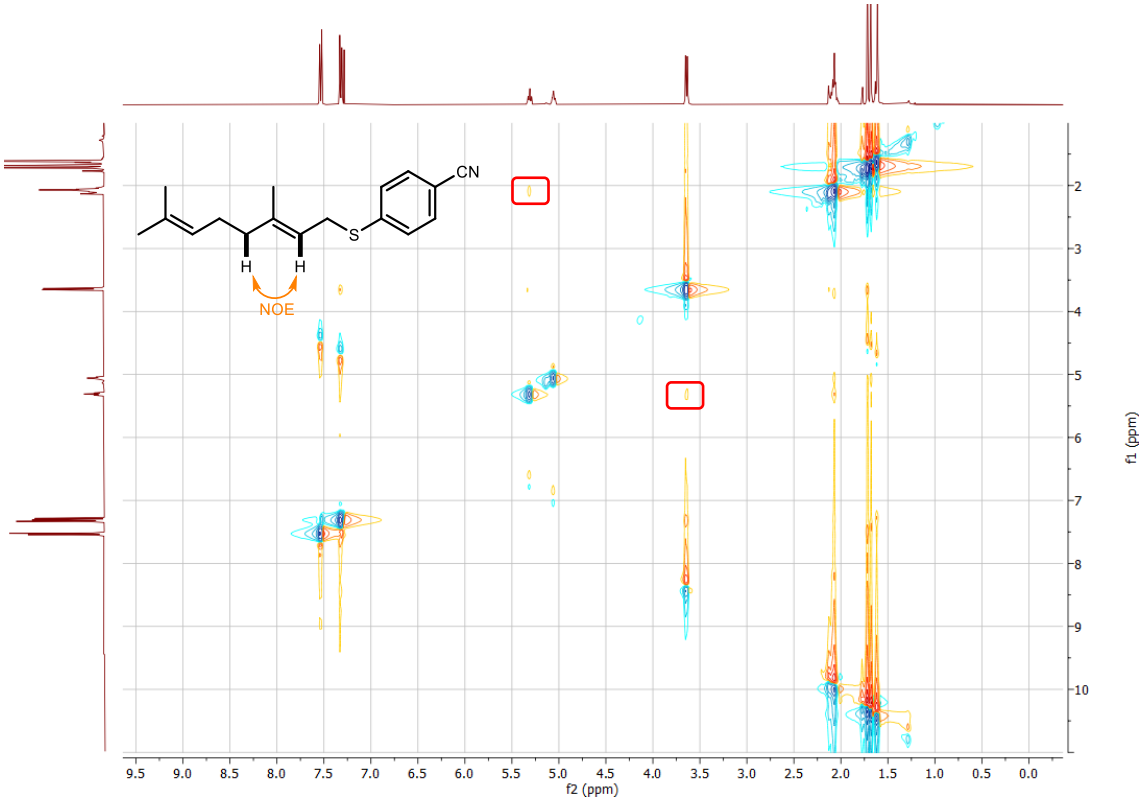
^{1}H NMR (400 MHz, $CDCl_3$) of **3ak:**



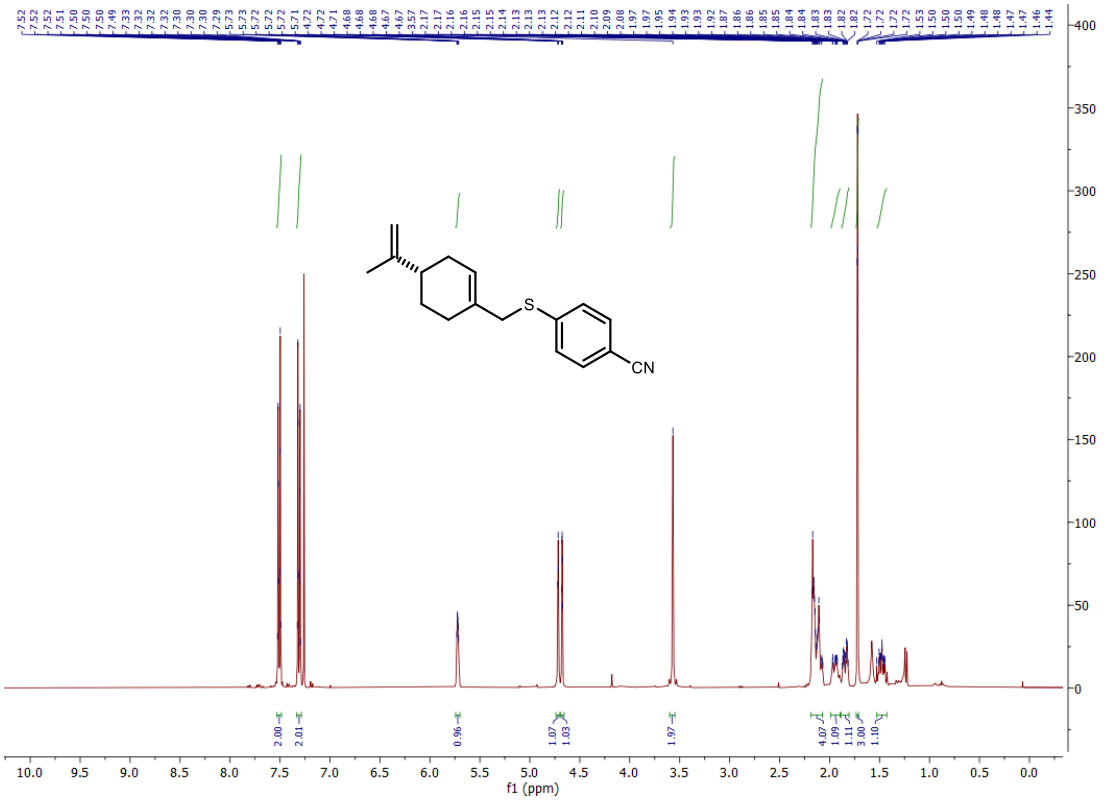
^{13}C NMR (101 MHz, $CDCl_3$) of **3ak:**



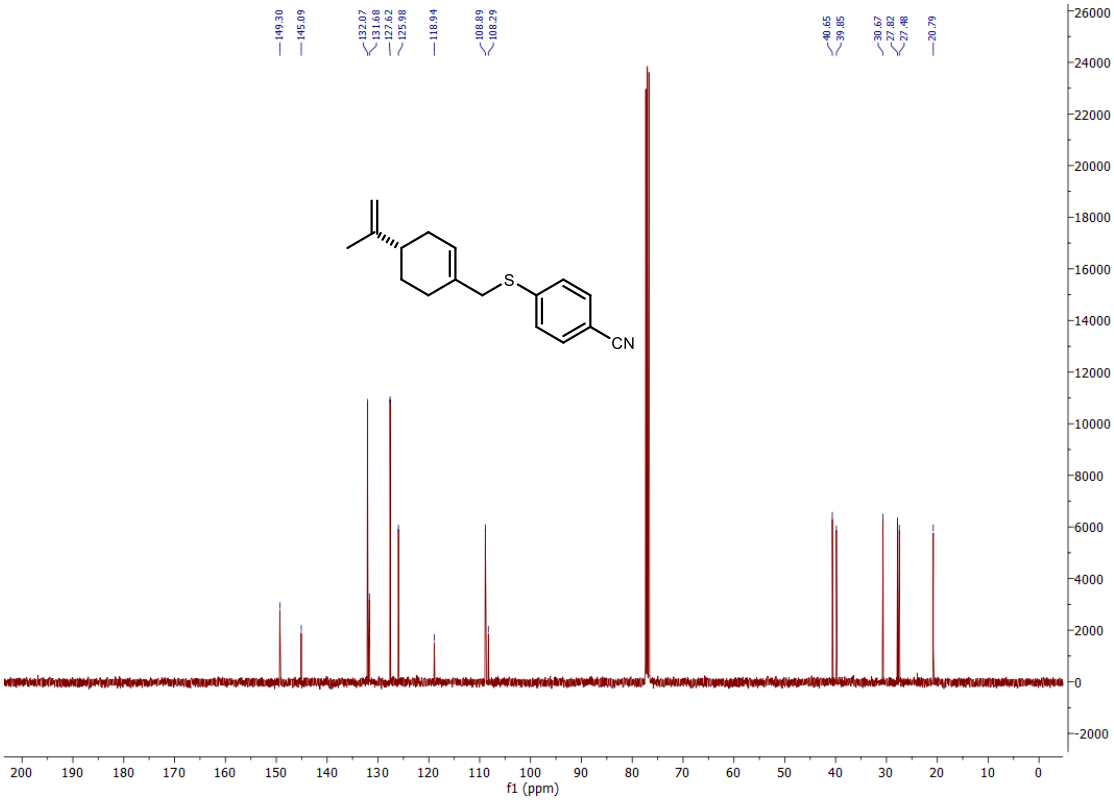
NOESYof **3ak:**



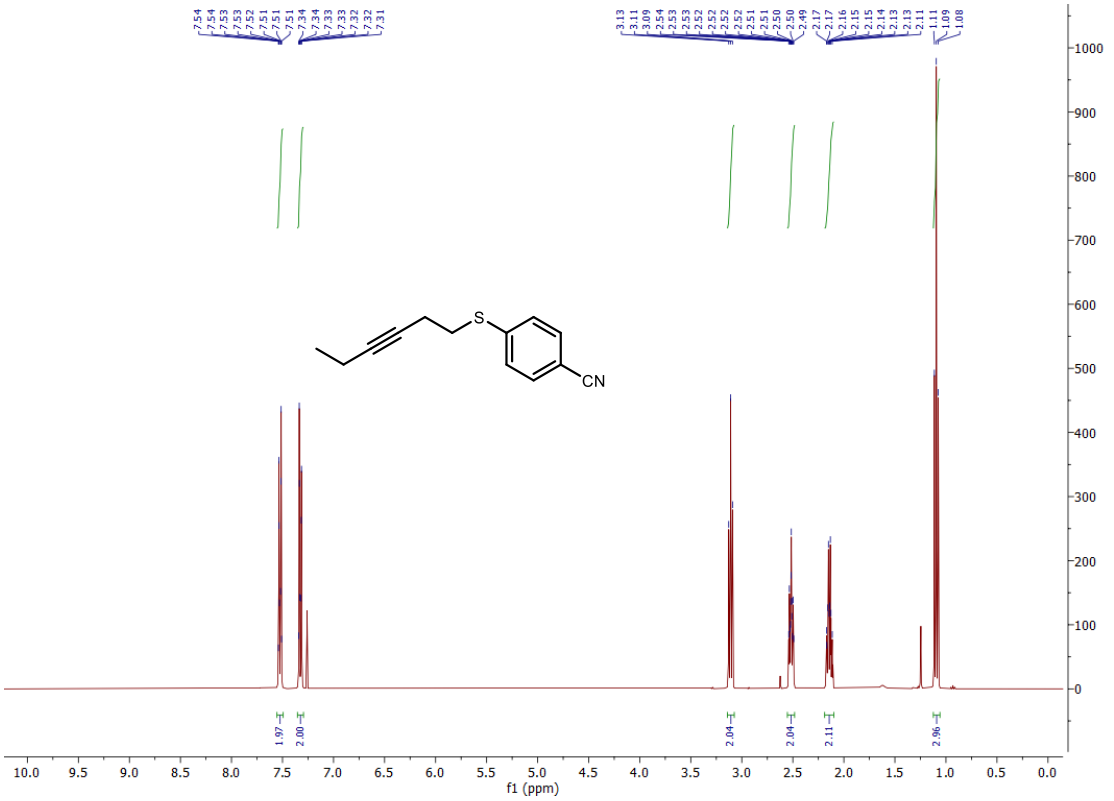
^{1}H NMR (400 MHz, $CDCl_3$) of **3al:**



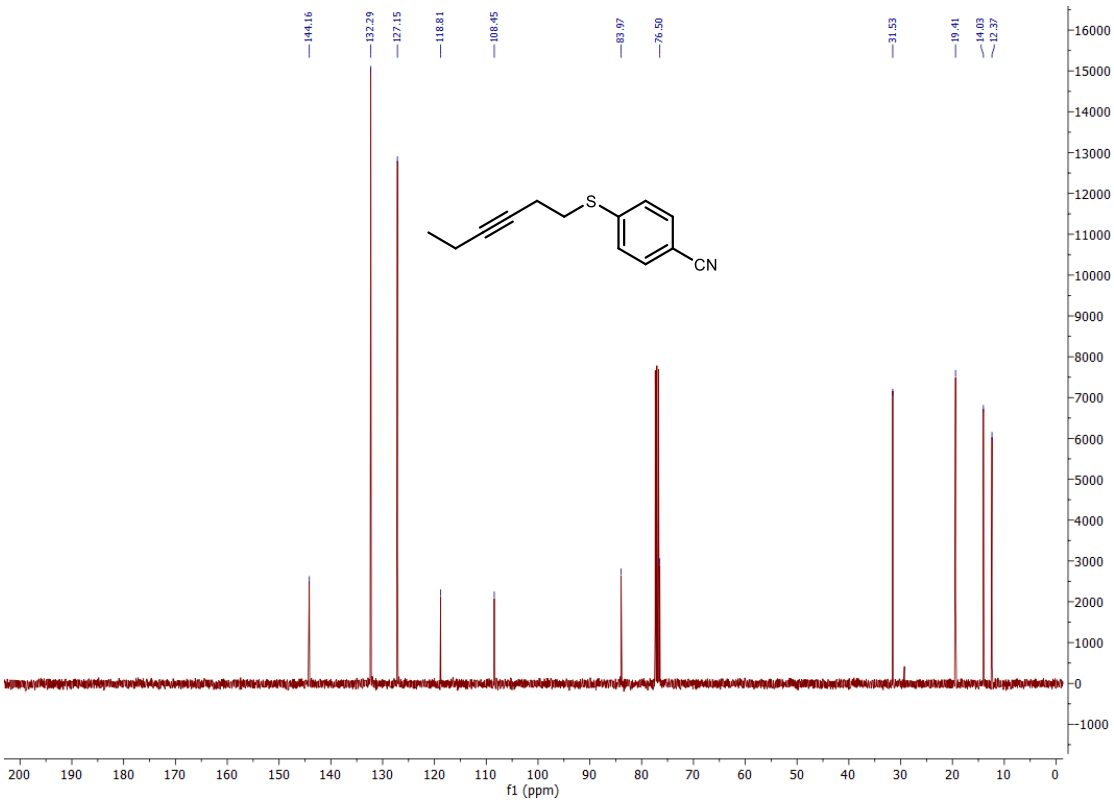
^{13}C NMR (101 MHz, $CDCl_3$) of **3al:**



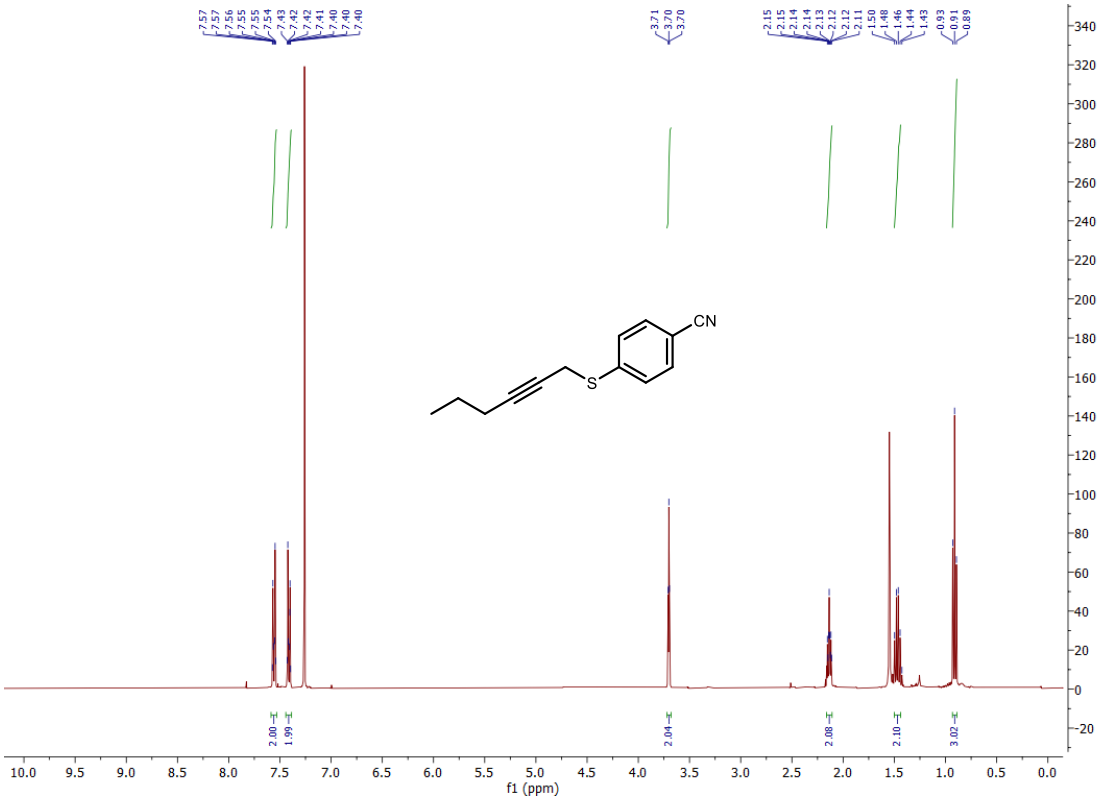
^{1}H NMR (400 MHz, $CDCl_3$) of **3am:**



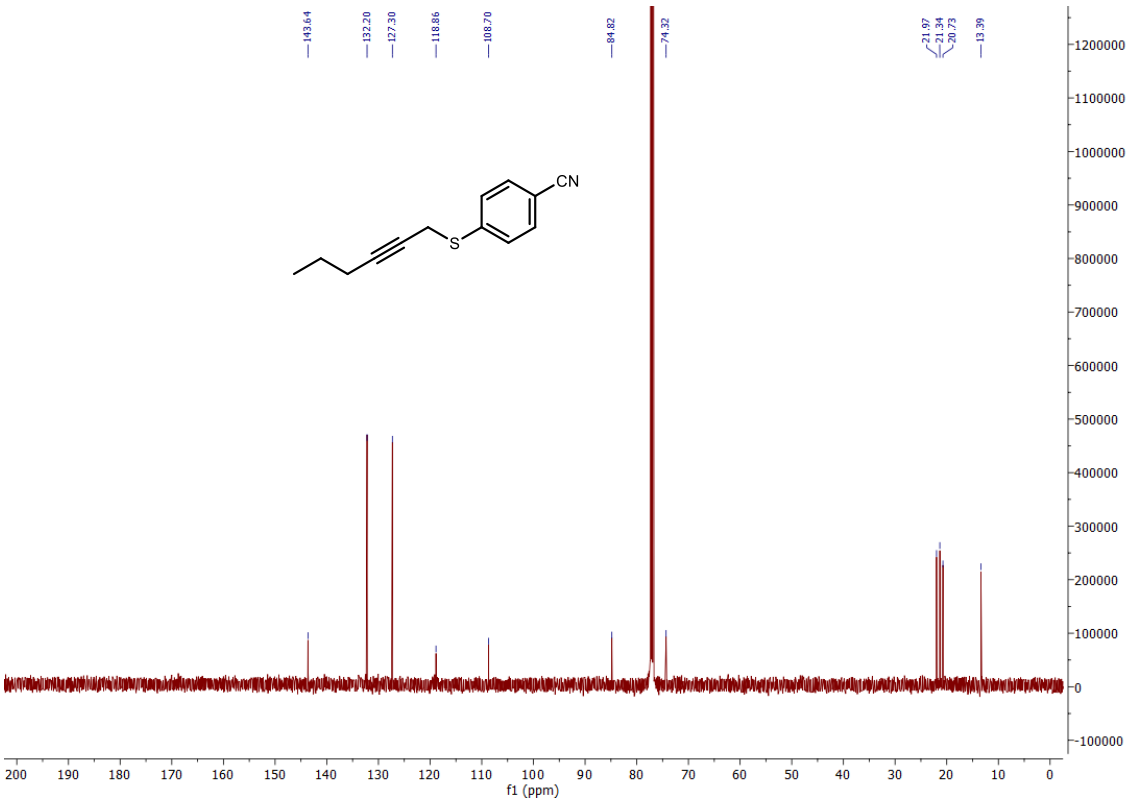
^{13}C NMR (101 MHz, $CDCl_3$) of **3am:**



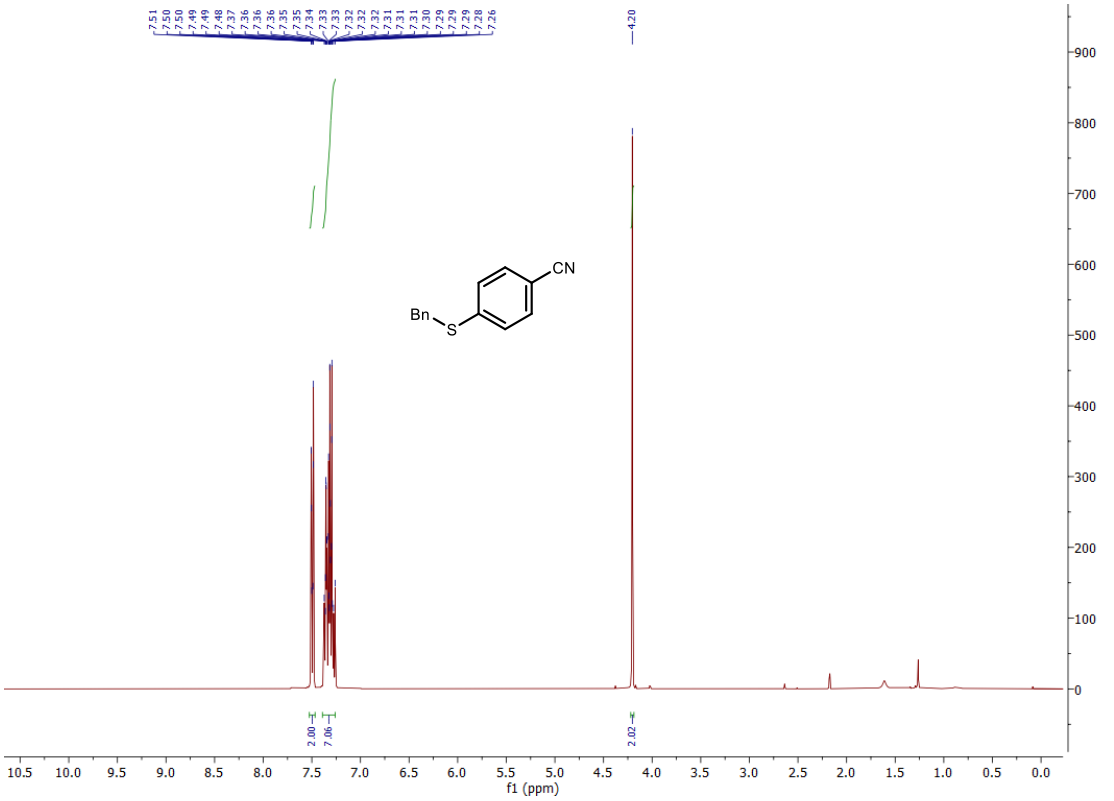
^{1}H NMR (400 MHz, $CDCl_3$) of **3an:**



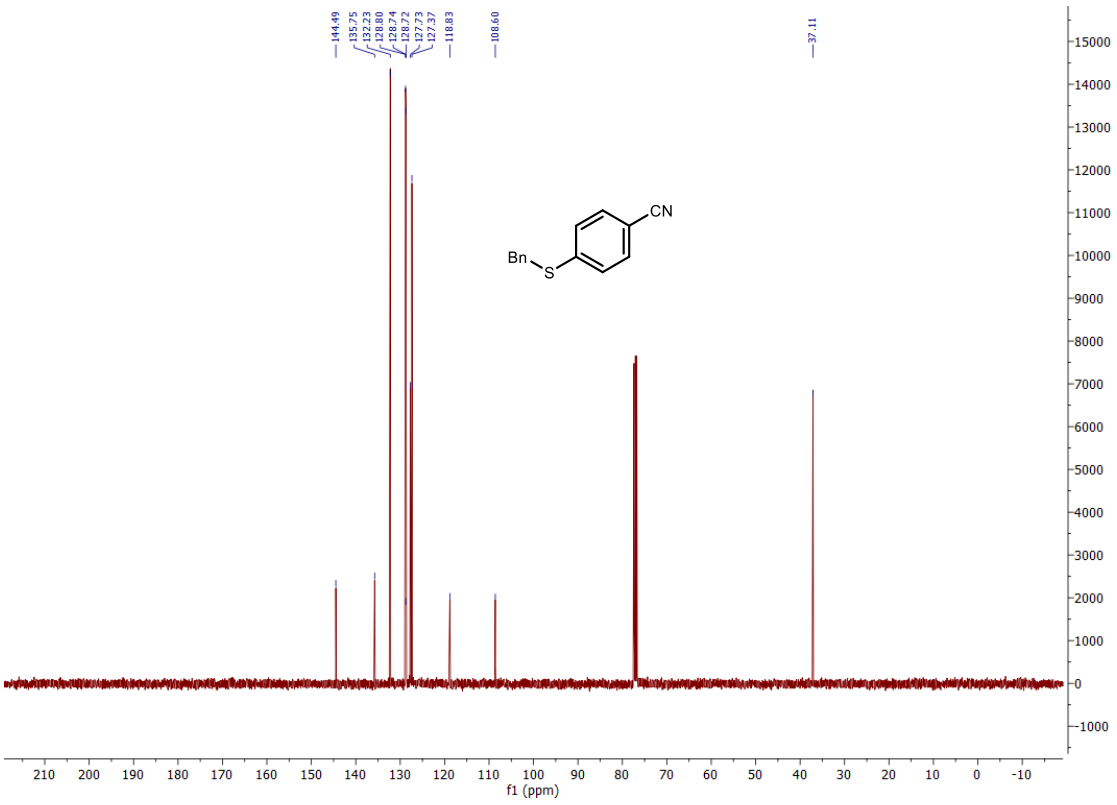
^{13}C NMR (101 MHz, $CDCl_3$) of **3an:**



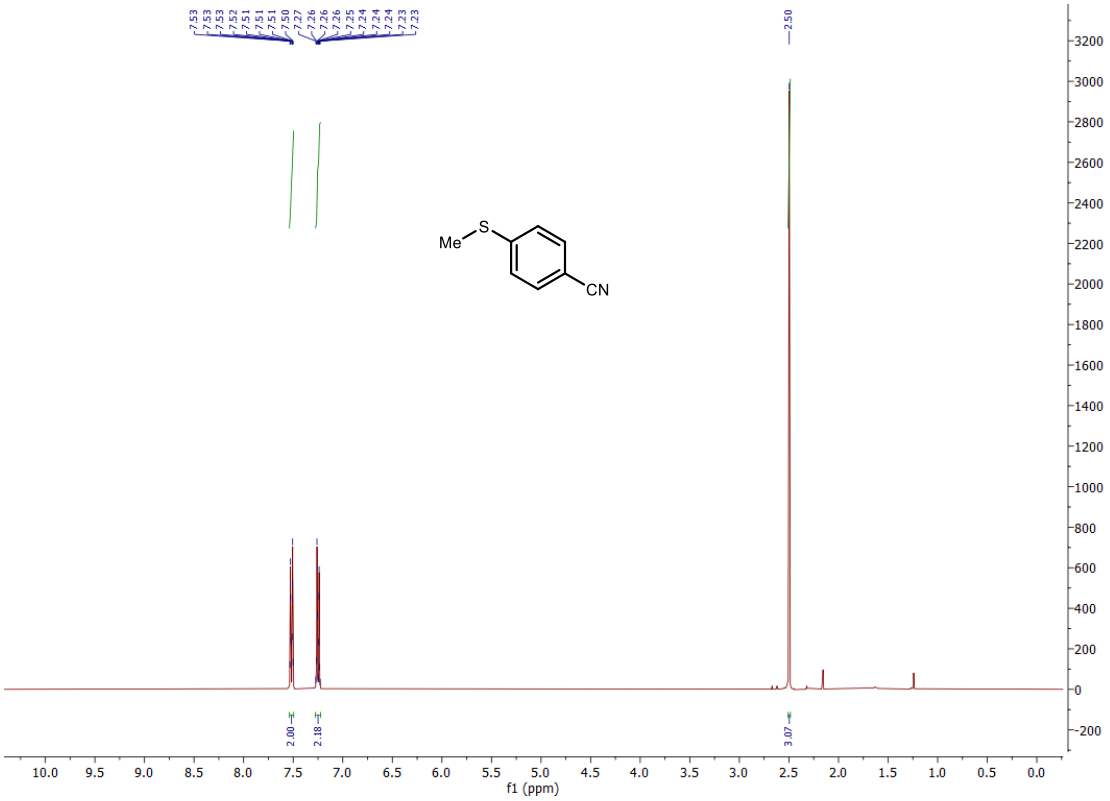
^{1}H NMR (400 MHz, $CDCl_3$) of **3ao:**



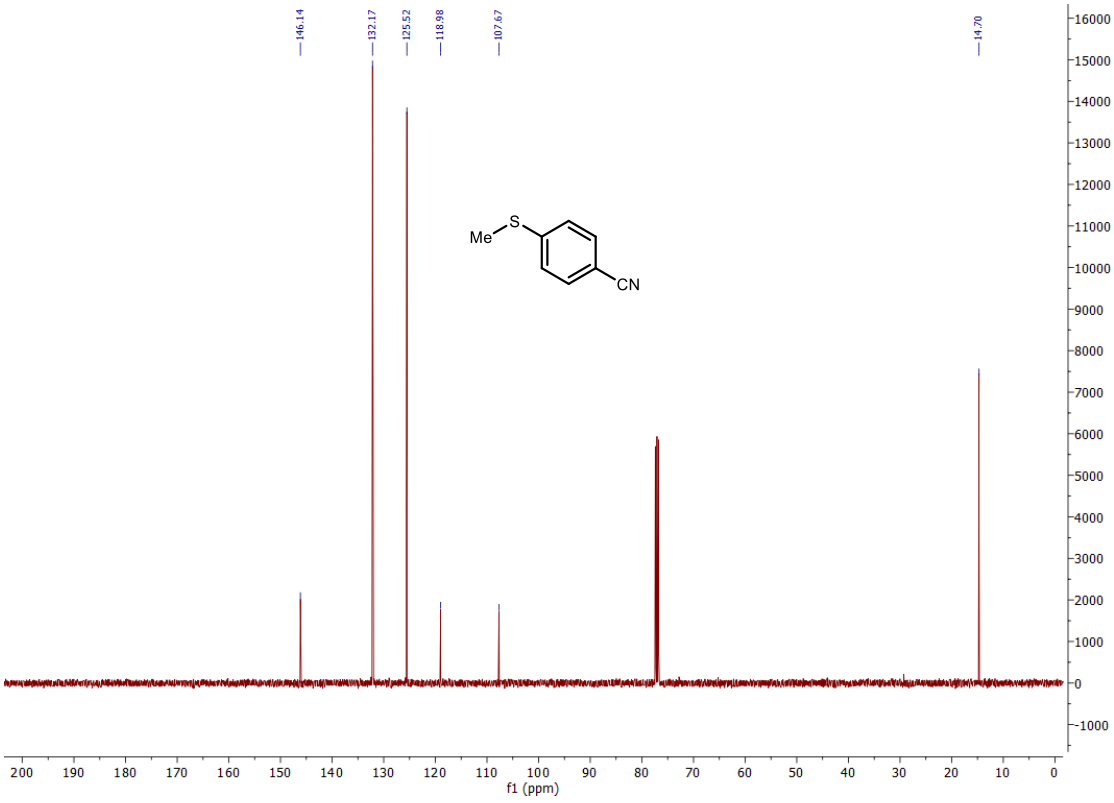
^{13}C NMR (101 MHz, $CDCl_3$) of **3ao:**



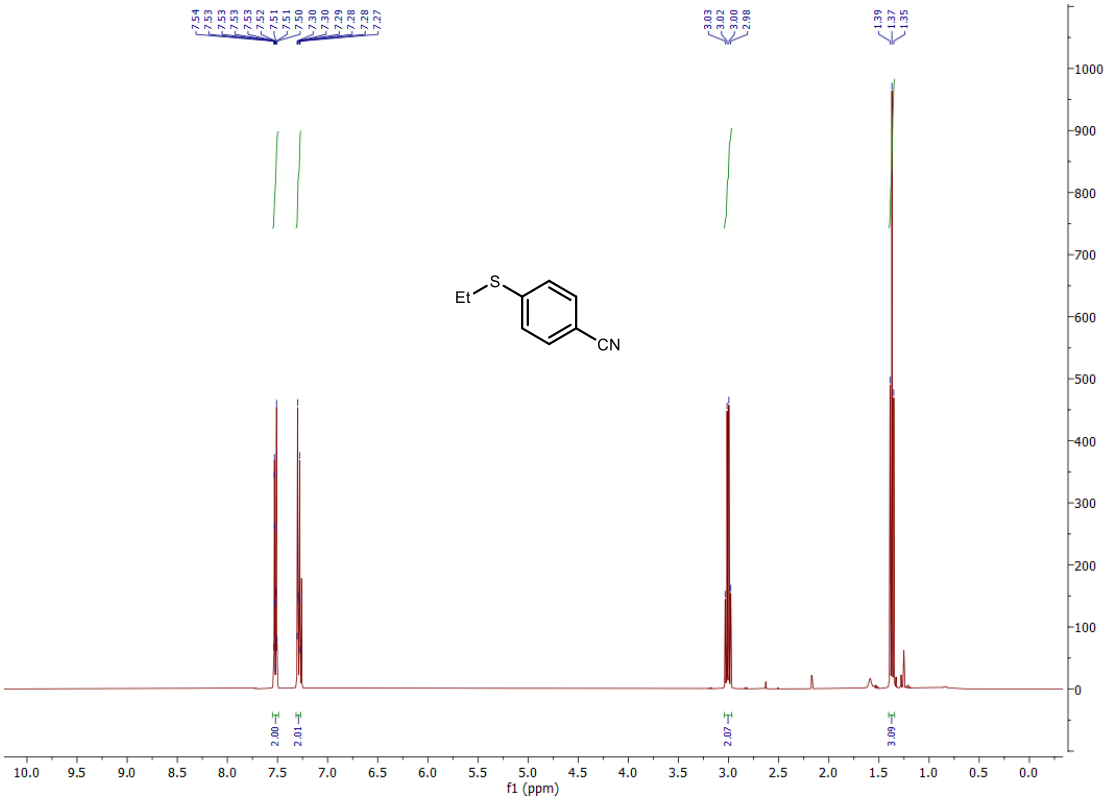
^{1}H NMR (400 MHz, $CDCl_3$) of **3ap:**



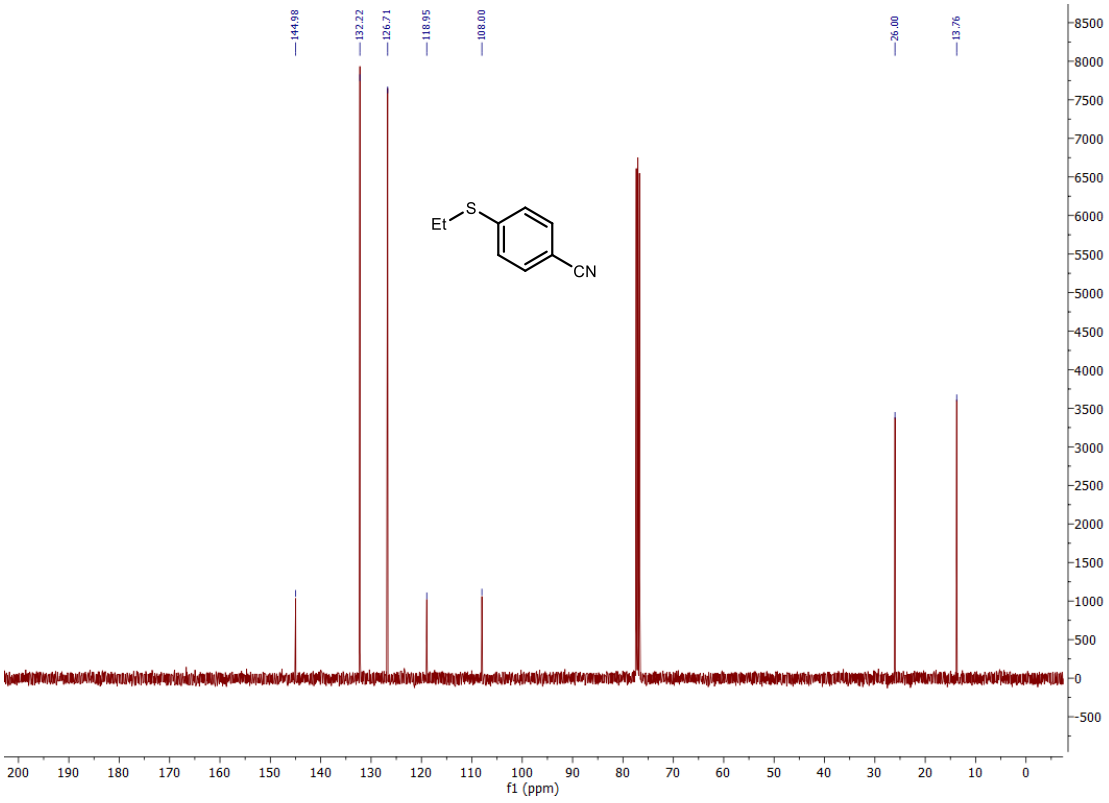
^{13}C NMR (101 MHz, $CDCl_3$) of **3ap:**



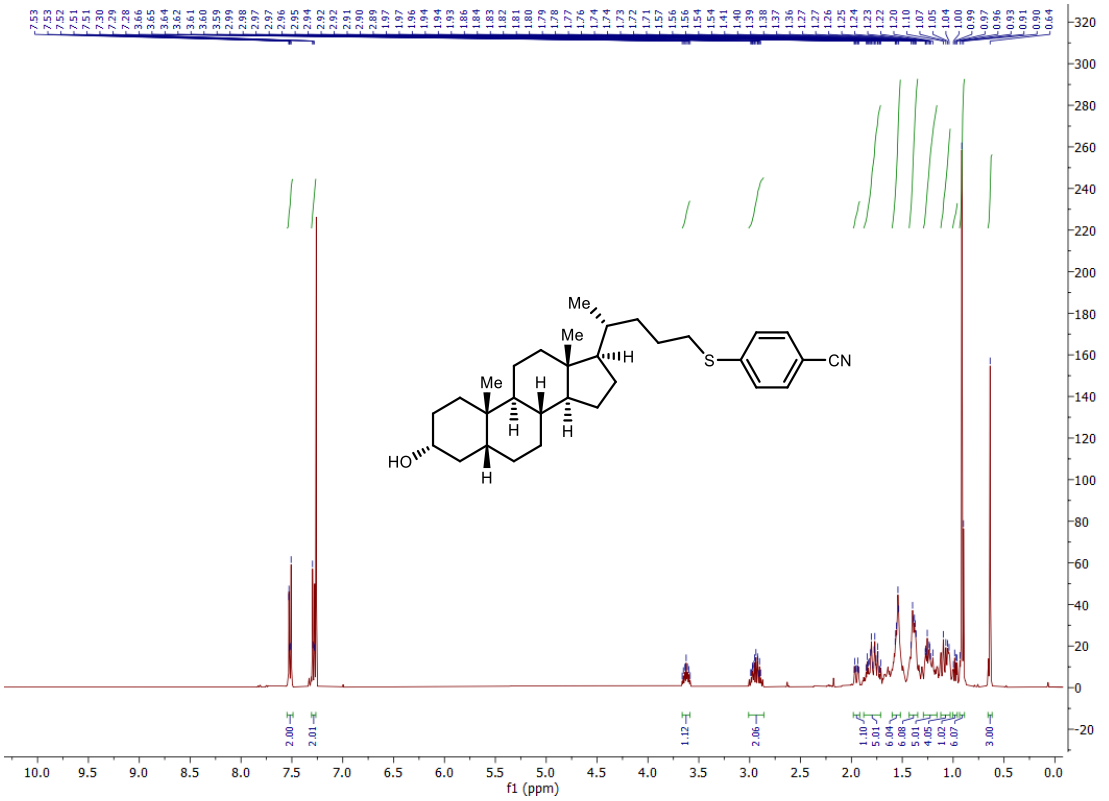
^{1}H NMR (400 MHz, $CDCl_3$) of **3aq:**



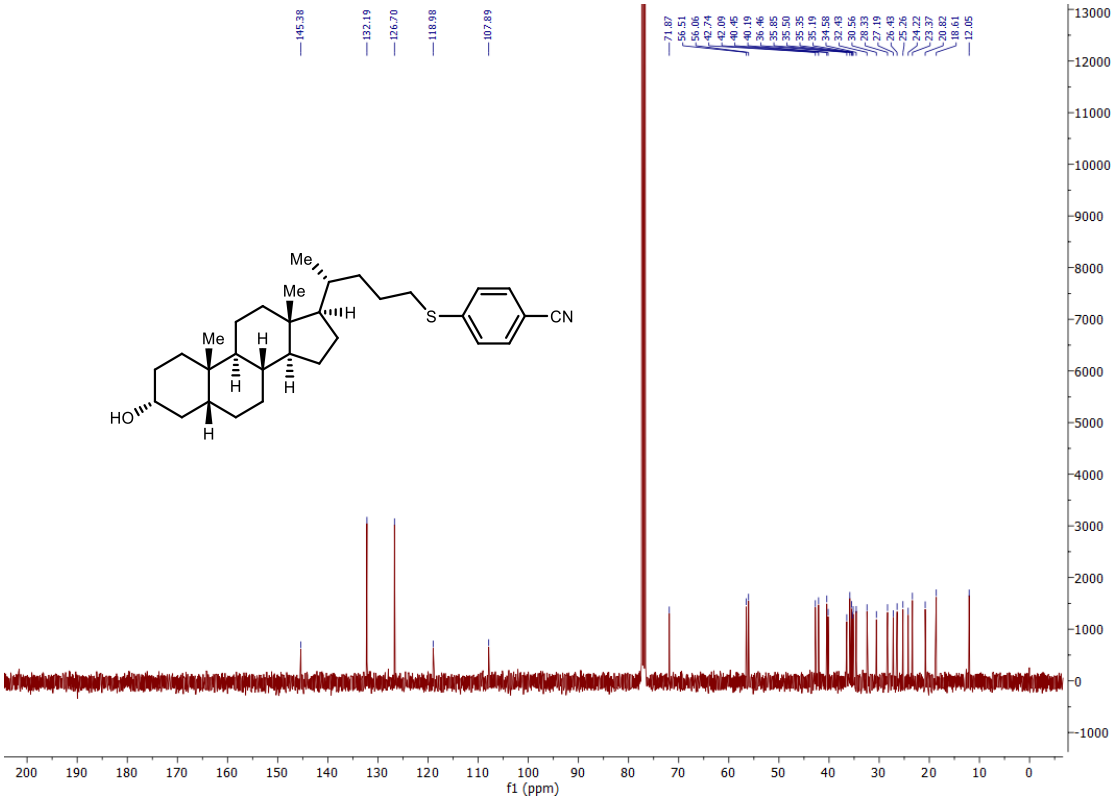
^{13}C NMR (101 MHz, $CDCl_3$) of **3aq:**



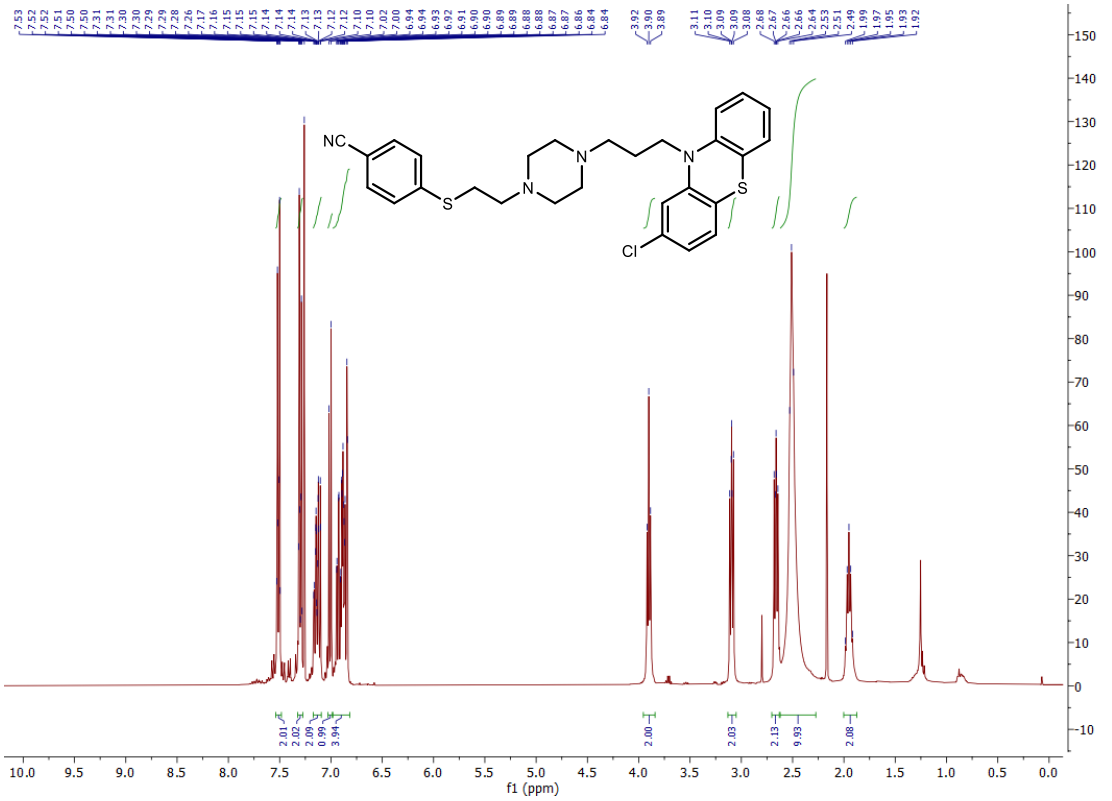
^{1}H NMR (400 MHz, $CDCl_3$) of **3ar:**



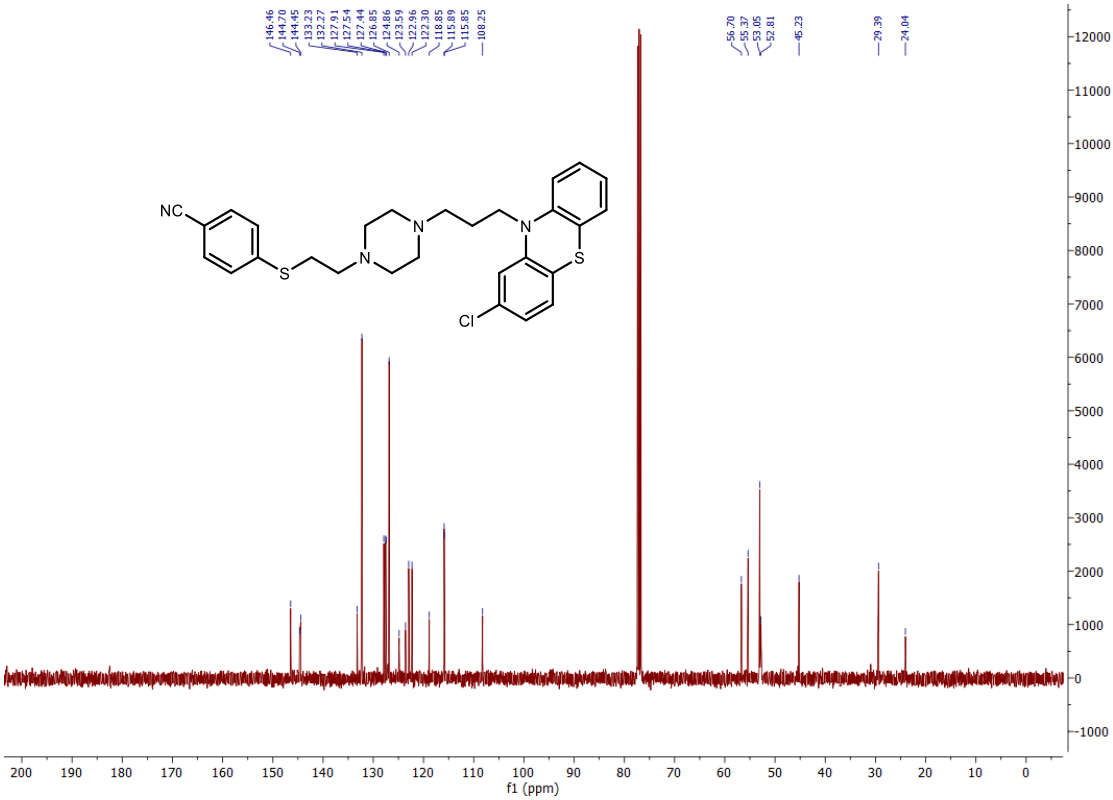
^{13}C NMR (101 MHz, $CDCl_3$) of **3ar:**



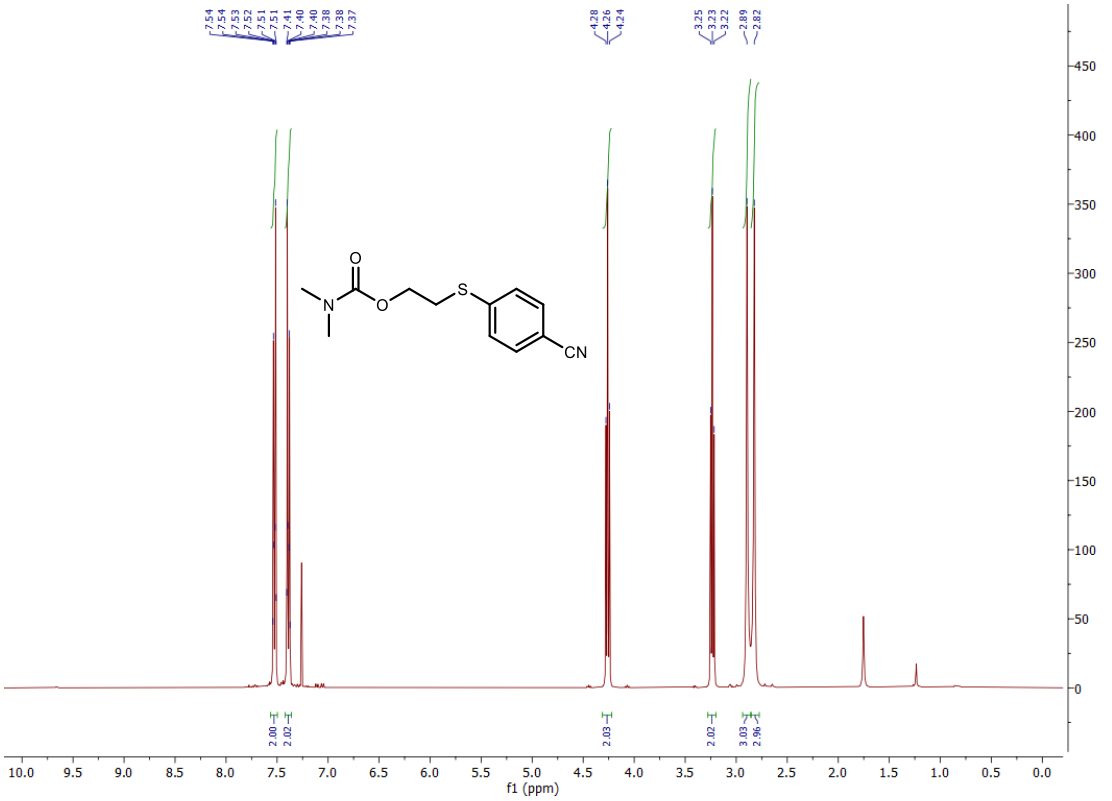
^{1}H NMR (400 MHz, $CDCl_3$) of **3as:**



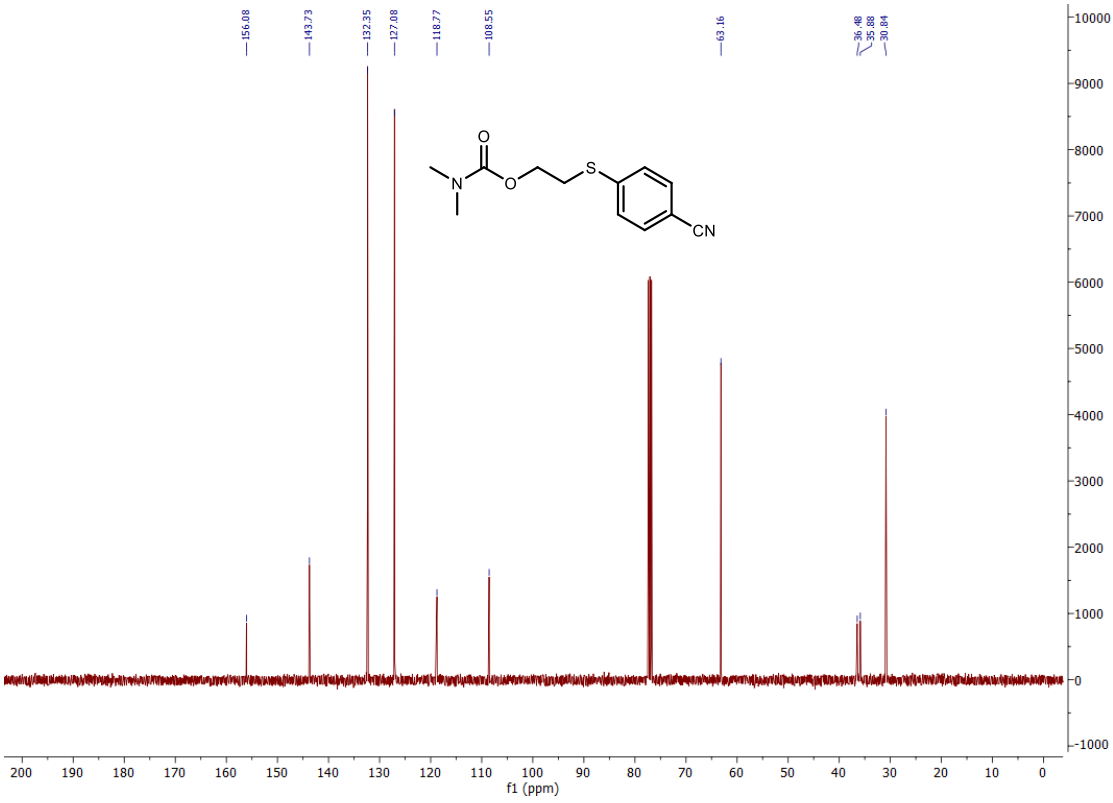
^{13}C NMR (101 MHz, $CDCl_3$) of **3as:**



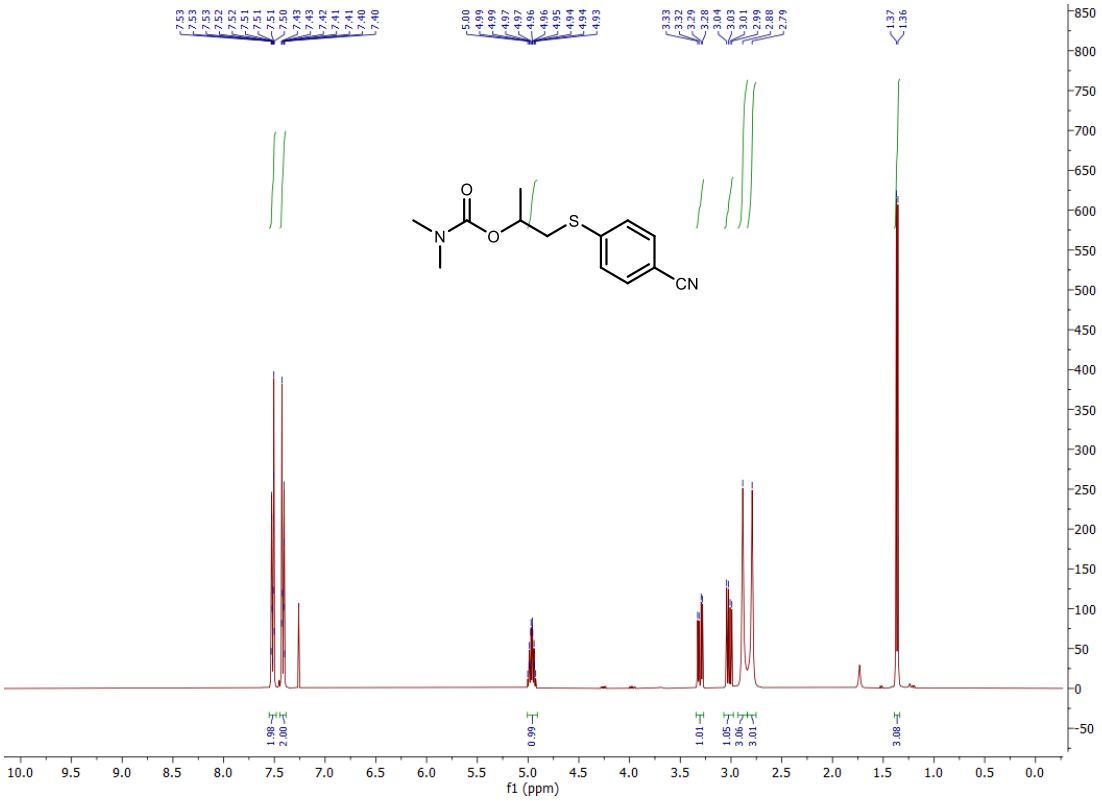
^{1}H NMR (400 MHz, $CDCl_3$) of **3at:**



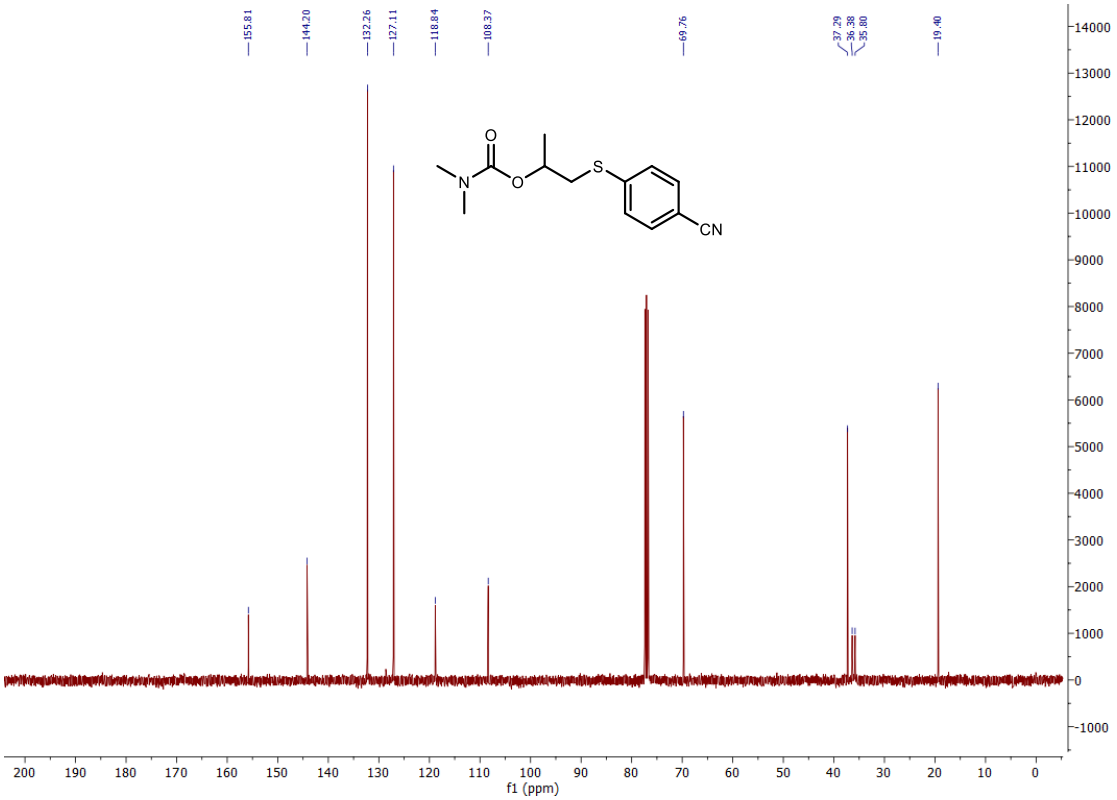
^{13}C NMR (101 MHz, $CDCl_3$) of **3at:**



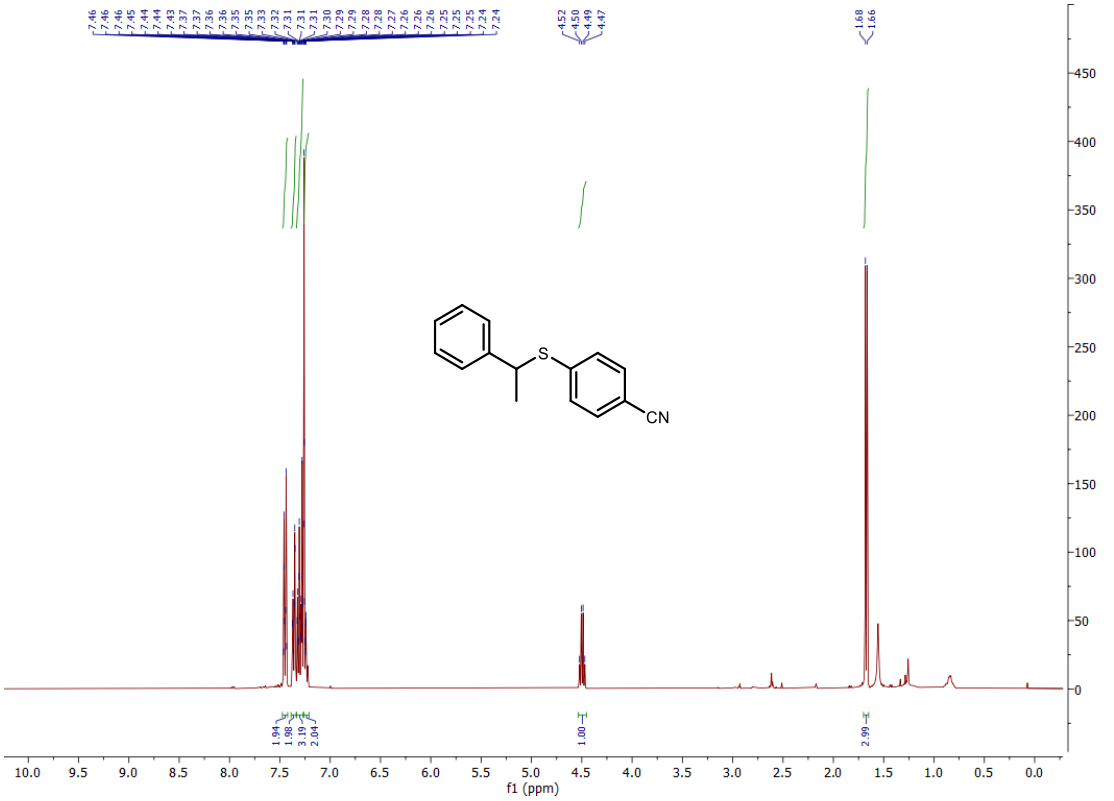
^{1}H NMR (400 MHz, $CDCl_3$) of **3au:**



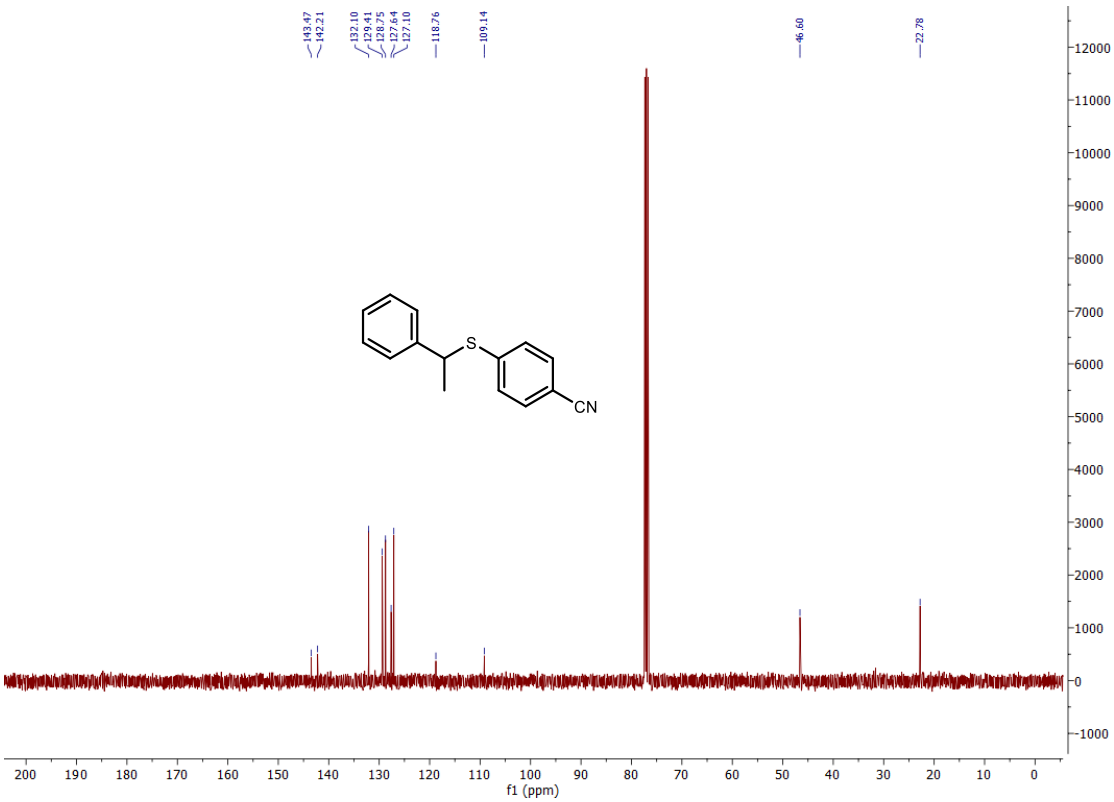
^{13}C NMR (101 MHz, $CDCl_3$) of **3au:**



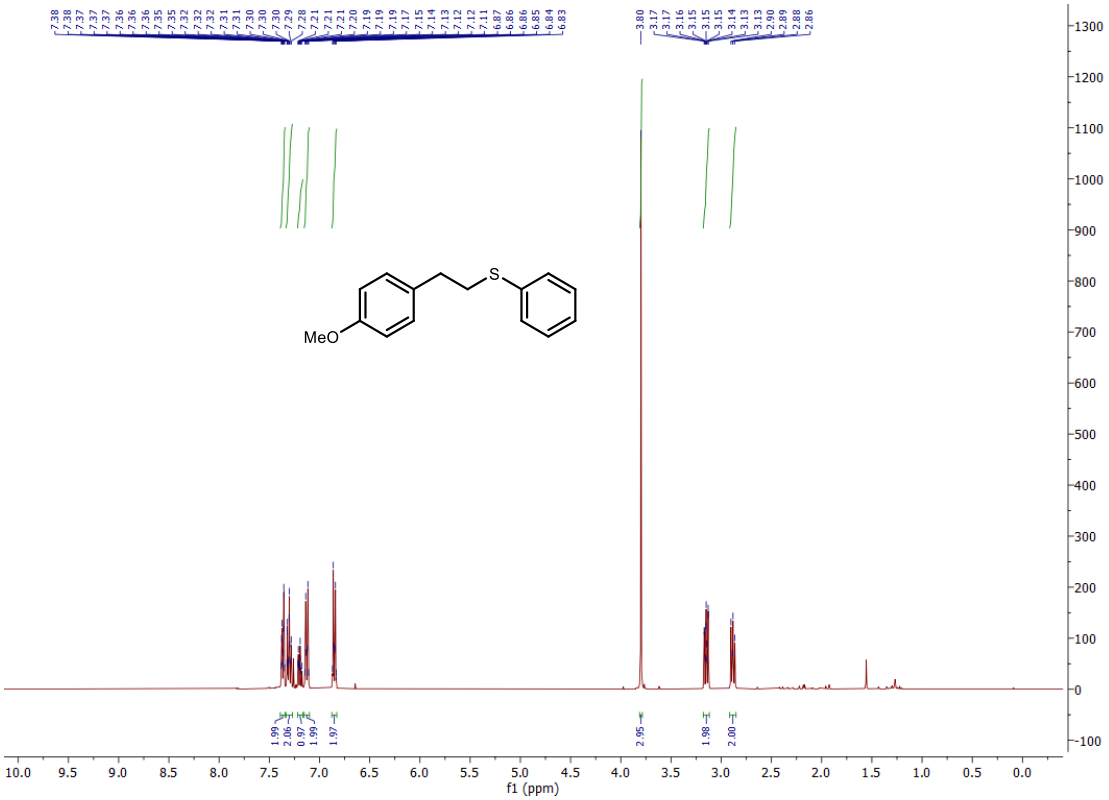
^{1}H NMR (400 MHz, $CDCl_3$) of **3av:**



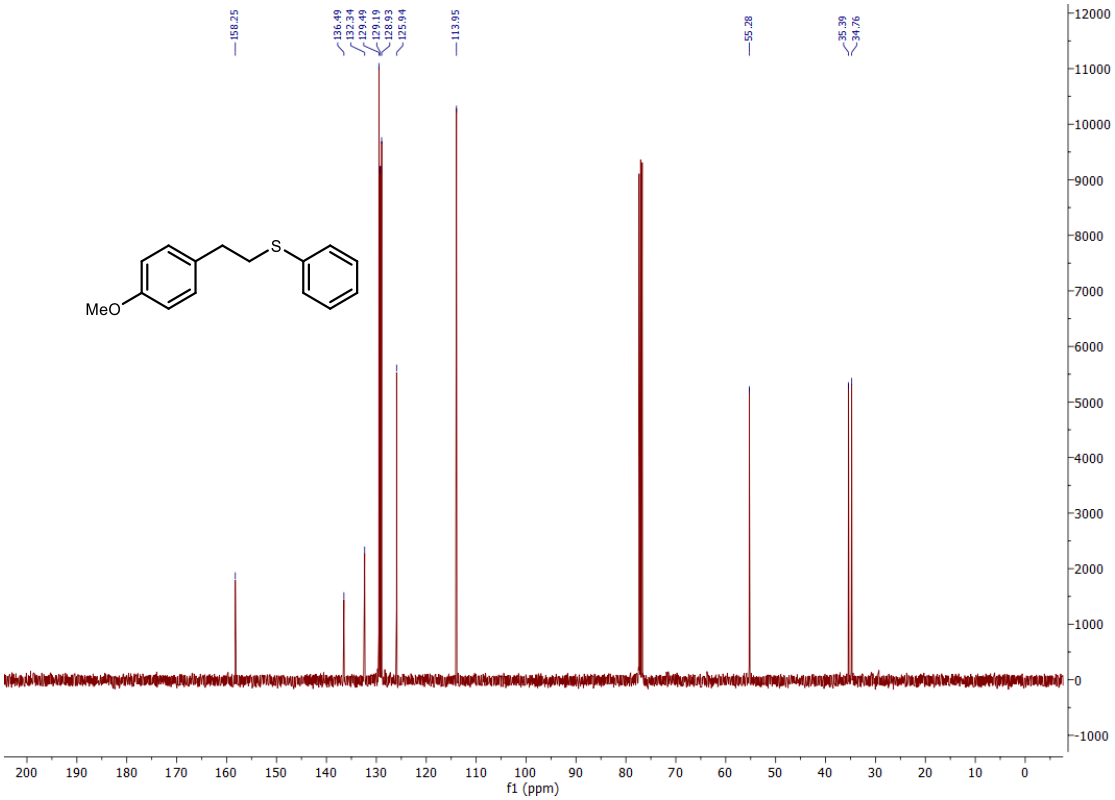
^{13}C NMR (101 MHz, $CDCl_3$) of **3av:**



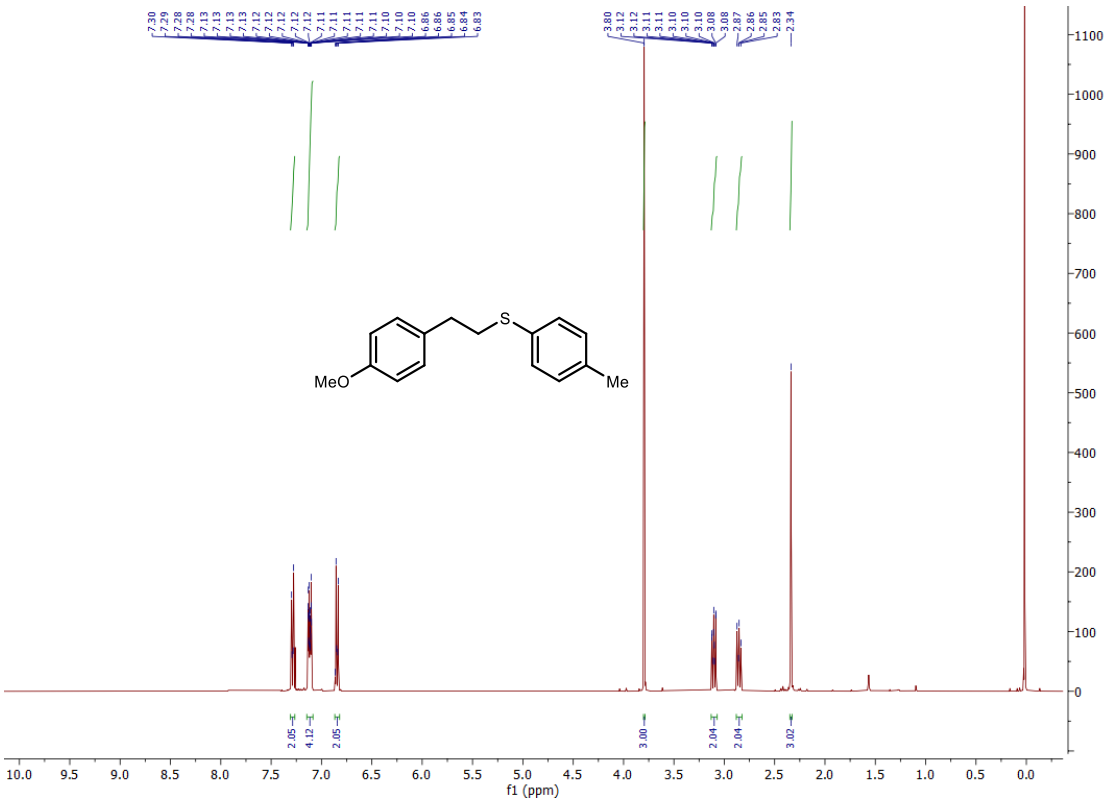
^{1}H NMR (400 MHz, $CDCl_3$) of **3aw:**



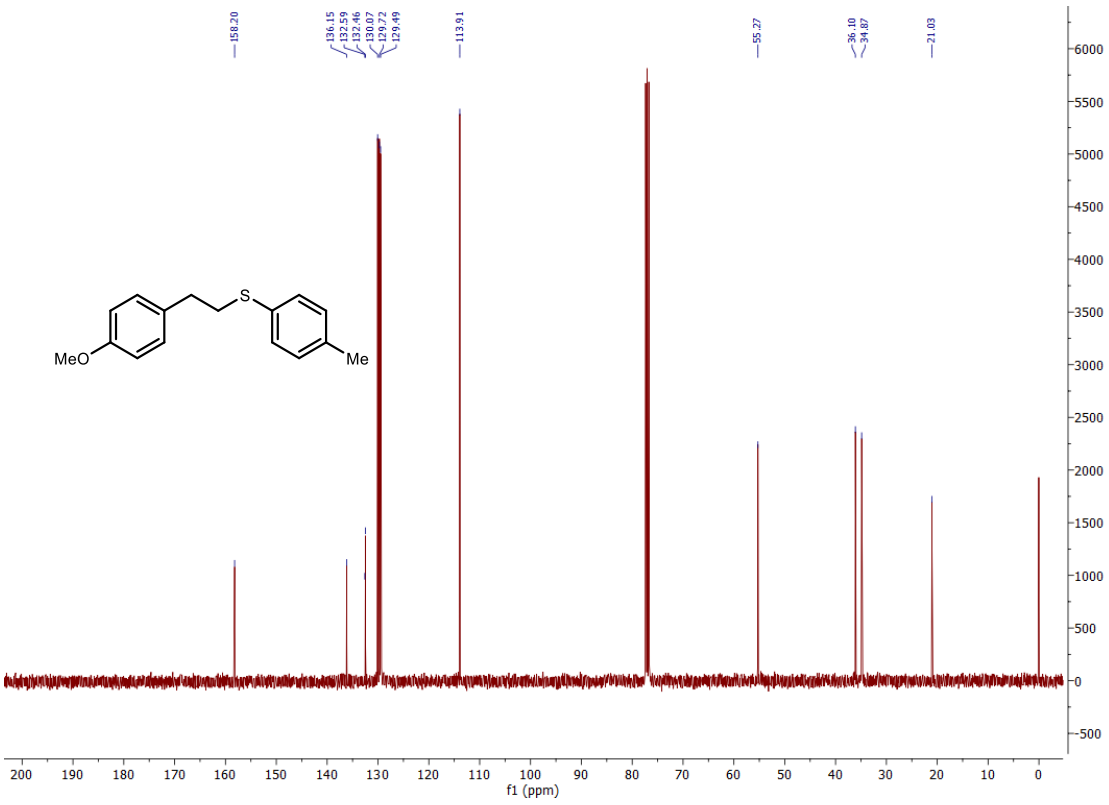
^{13}C NMR (101 MHz, $CDCl_3$) of **3aw:**



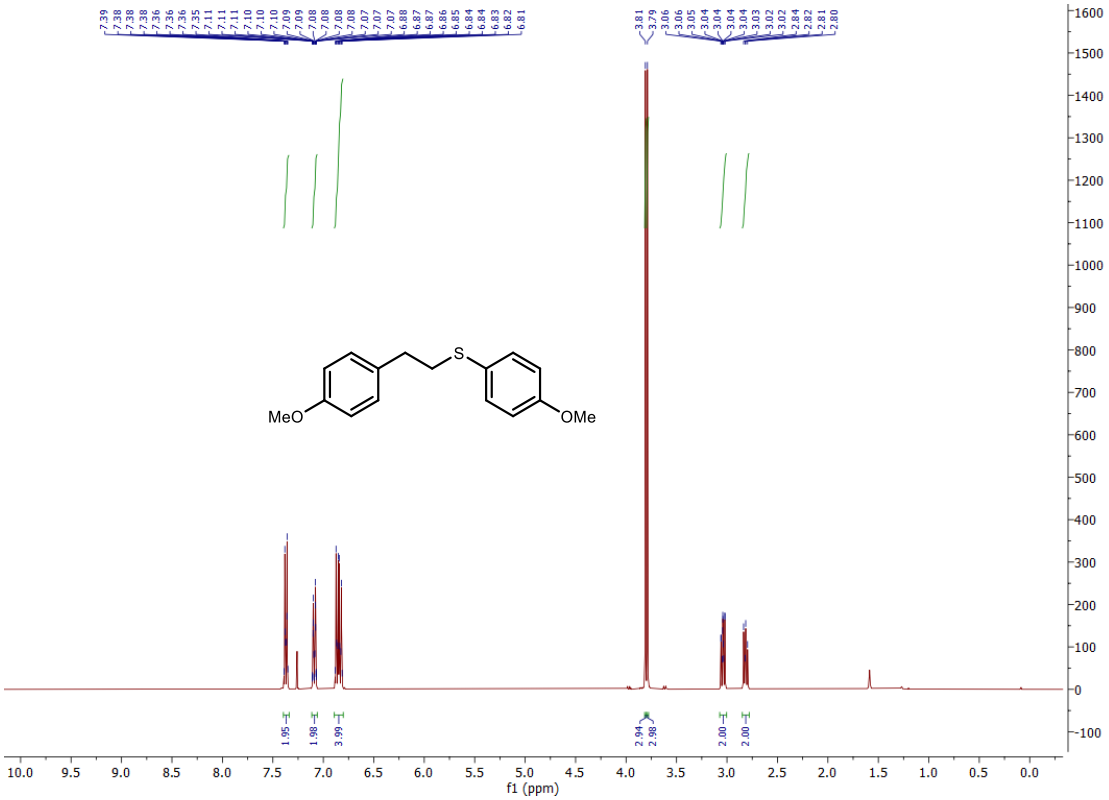
^{1}H NMR (400 MHz, $CDCl_3$) of **3ax:**



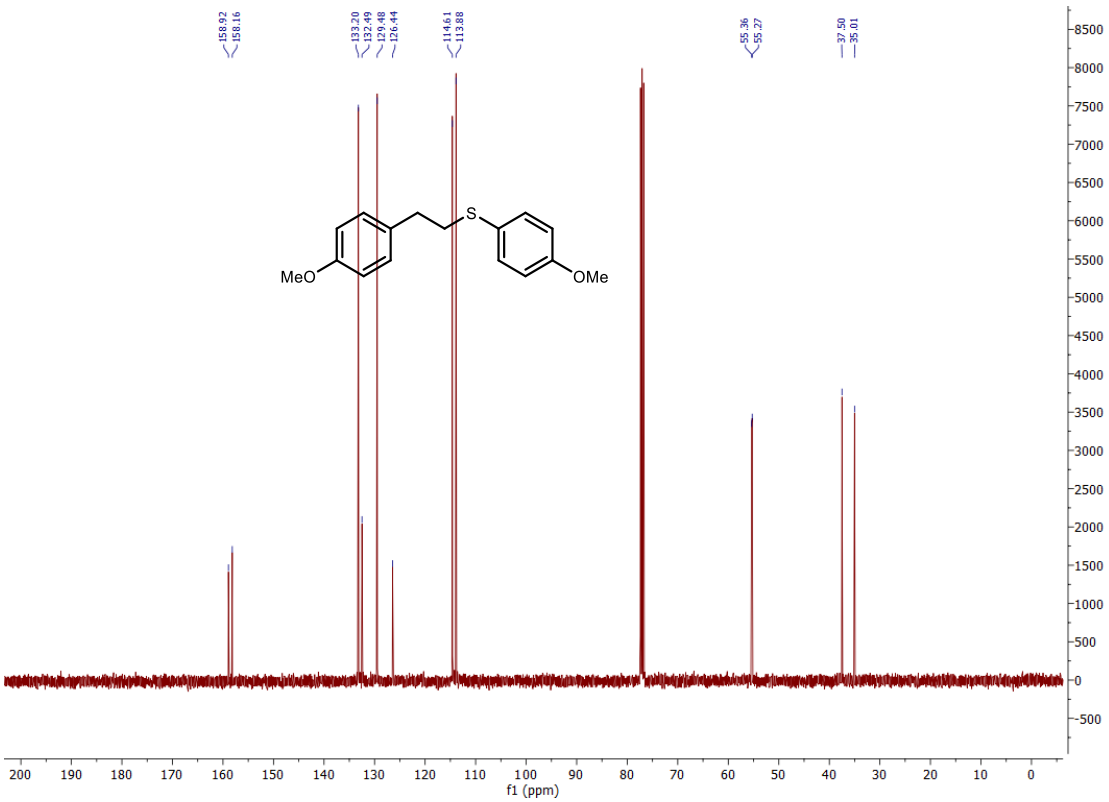
^{13}C NMR (101 MHz, $CDCl_3$) of **3ax:**



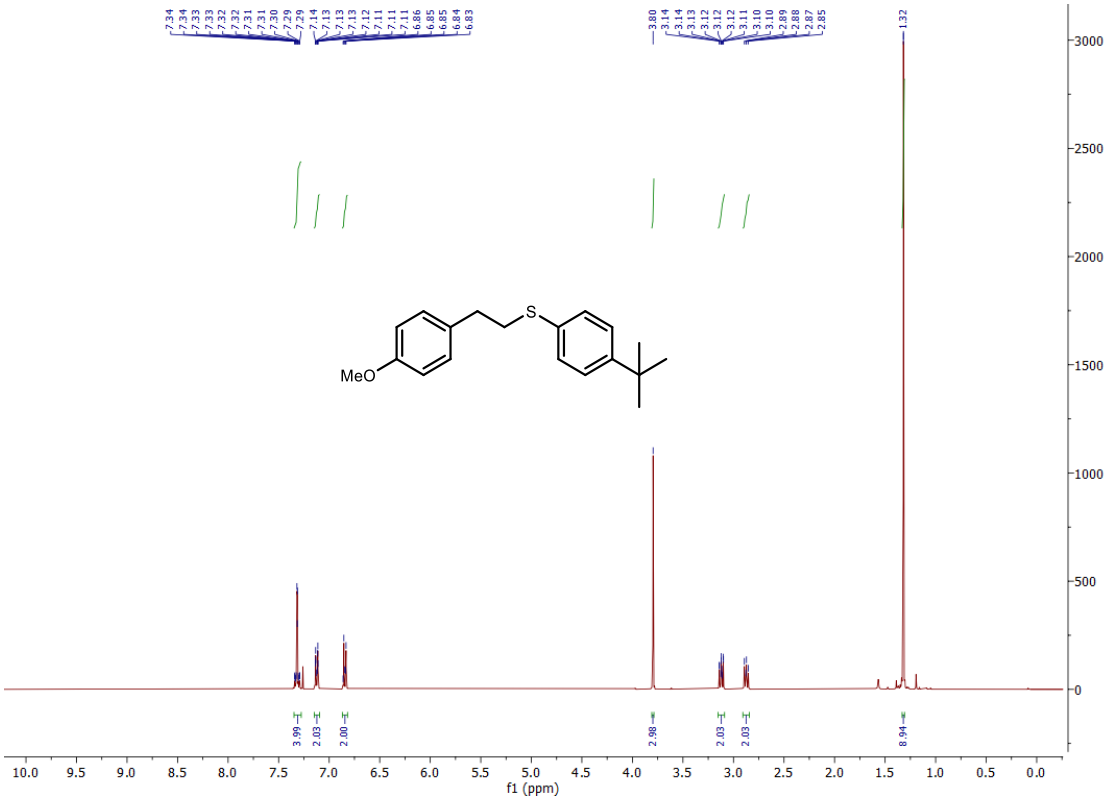
^{1}H NMR (400 MHz, $CDCl_3$) of **3ay:**



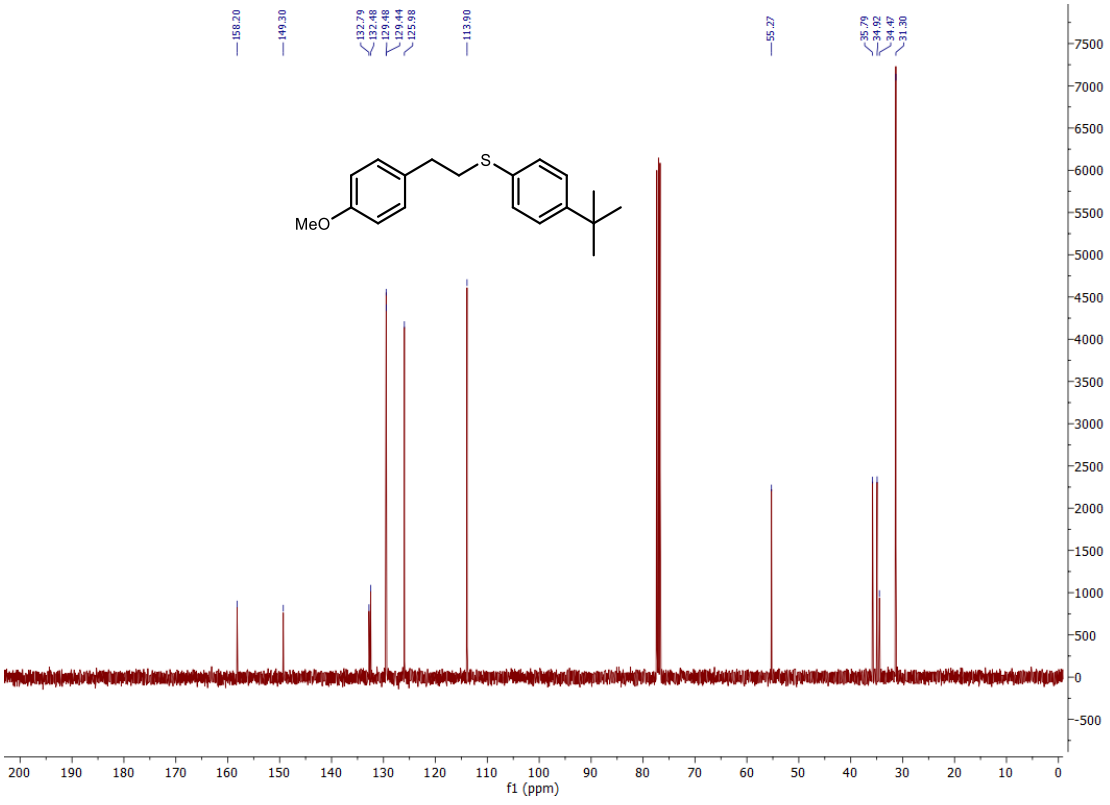
^{13}C NMR (101 MHz, $CDCl_3$) of **3ay:**



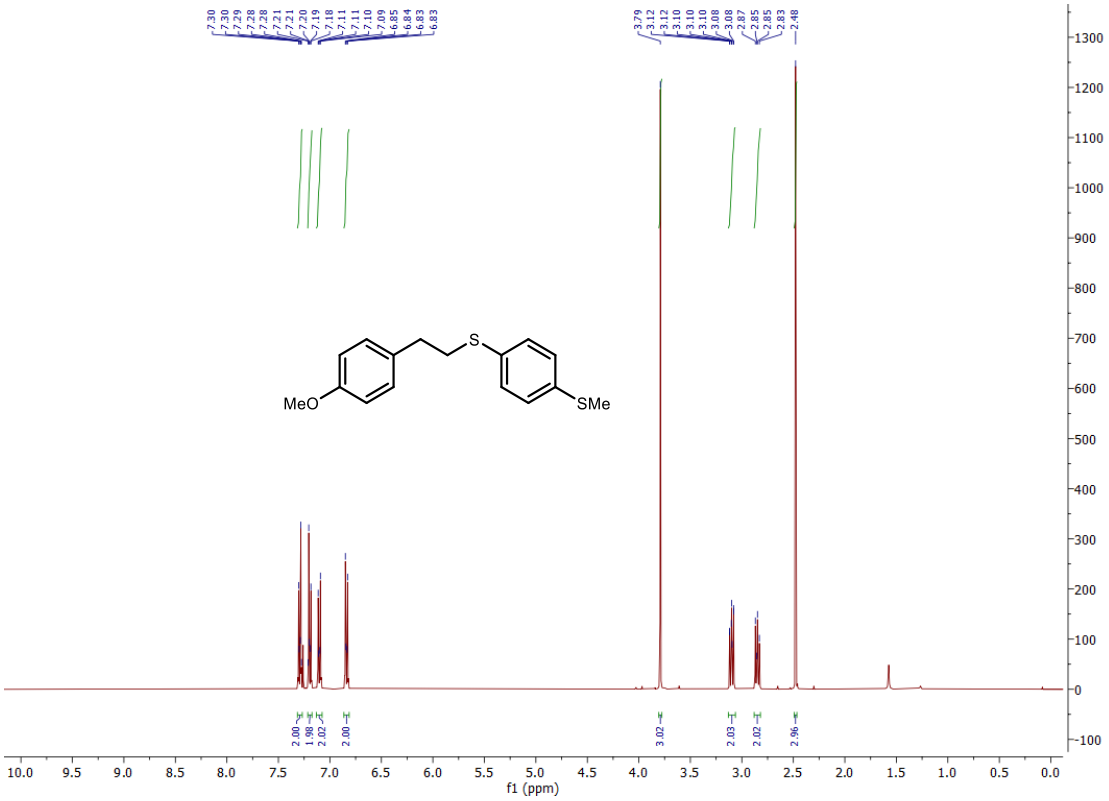
^{1}H NMR (400 MHz, $CDCl_3$) of **3az:**



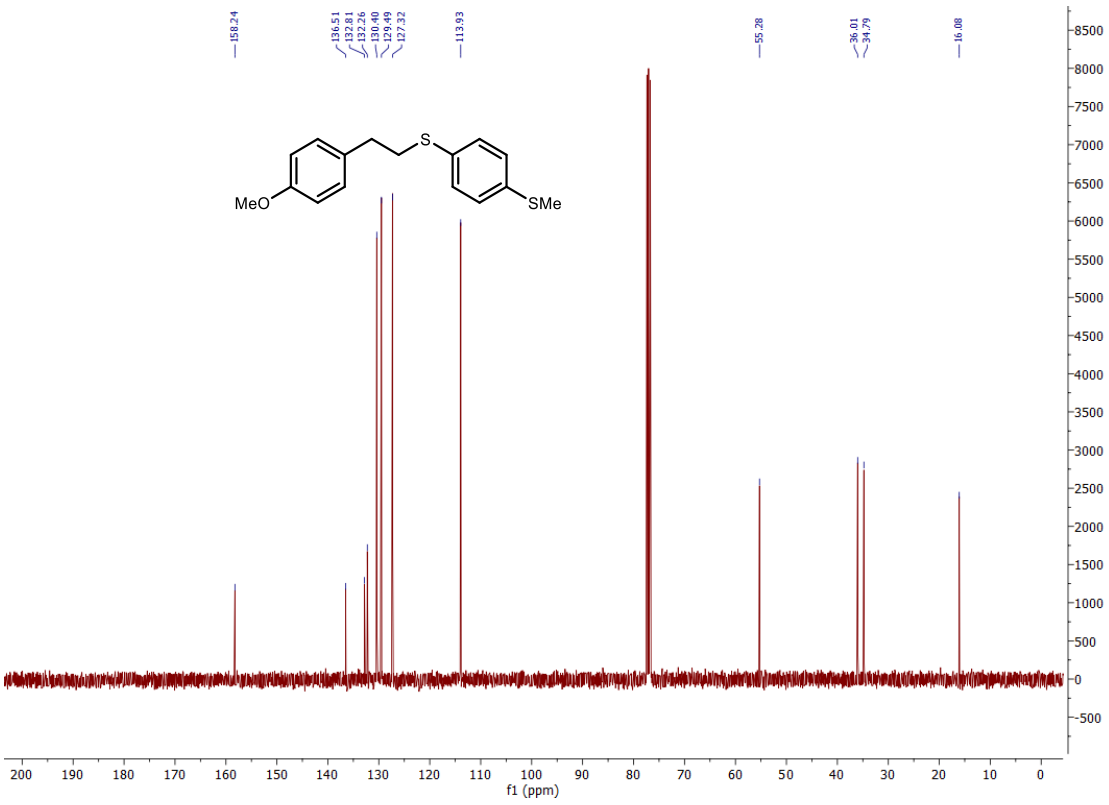
^{13}C NMR (101 MHz, $CDCl_3$) of **3az:**



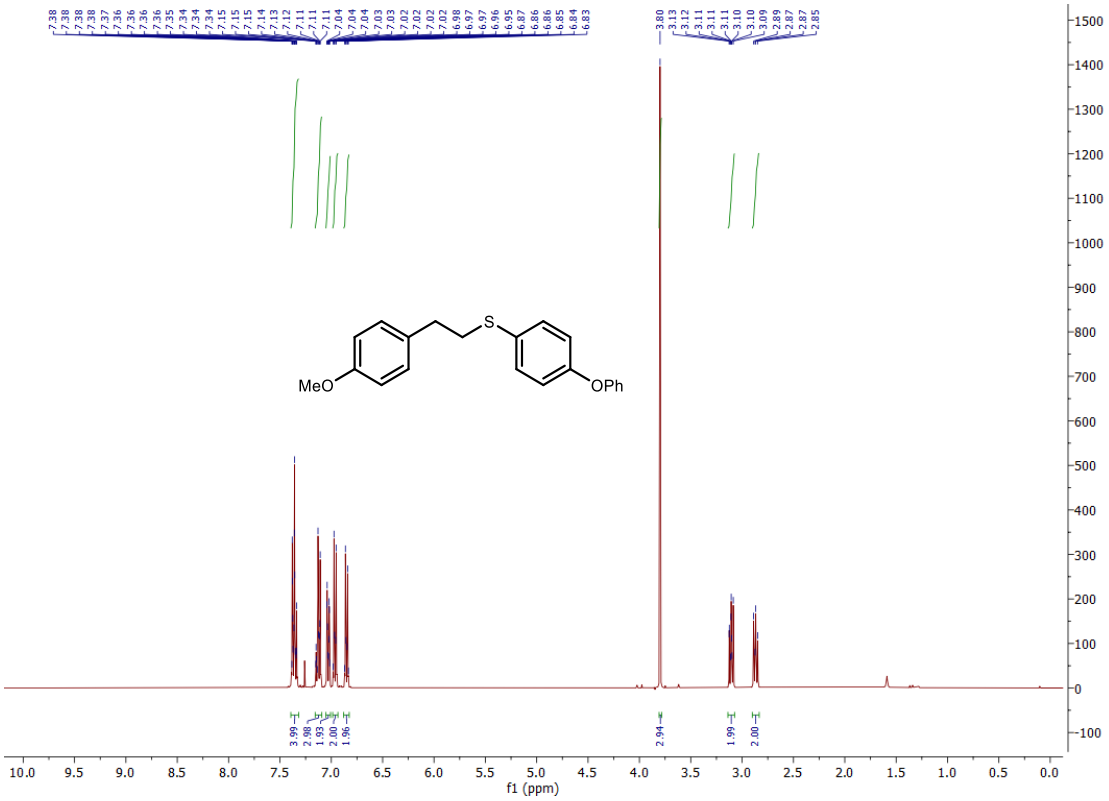
^{1}H NMR (400 MHz, $CDCl_3$) of **3ba:**



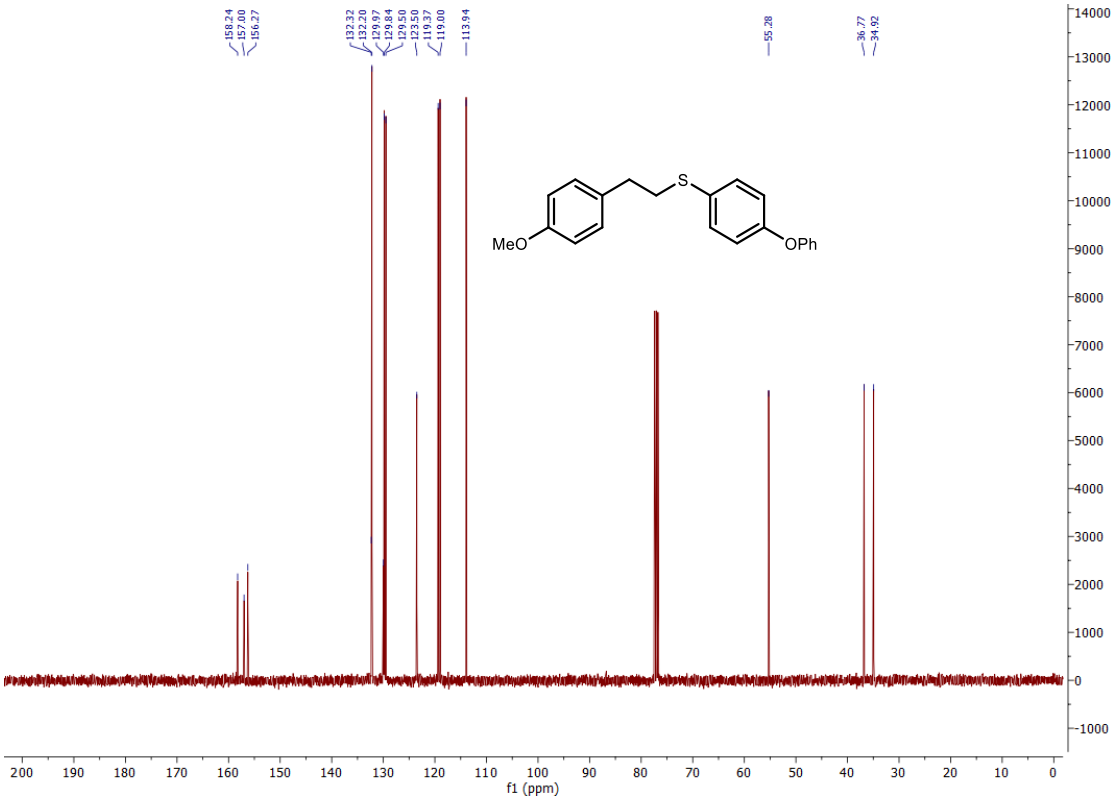
^{13}C NMR (101 MHz, $CDCl_3$) of **3ba:**



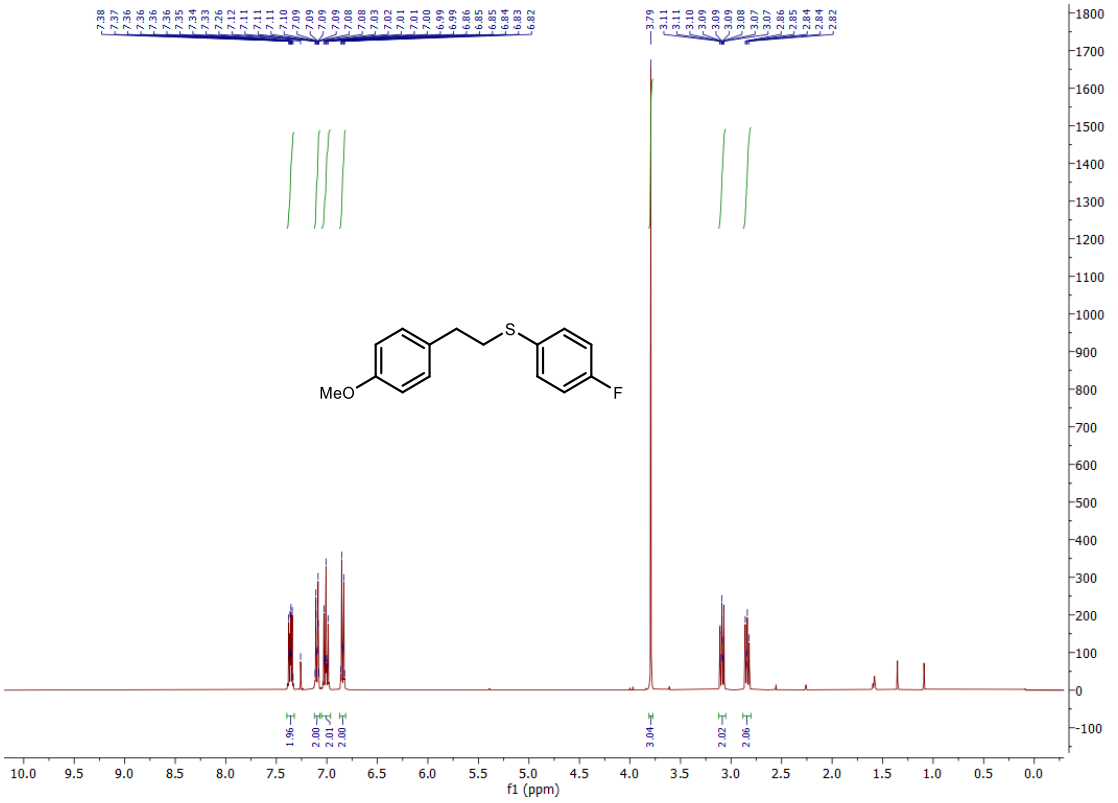
^{1}H NMR (400 MHz, $CDCl_3$) of **3bb:**



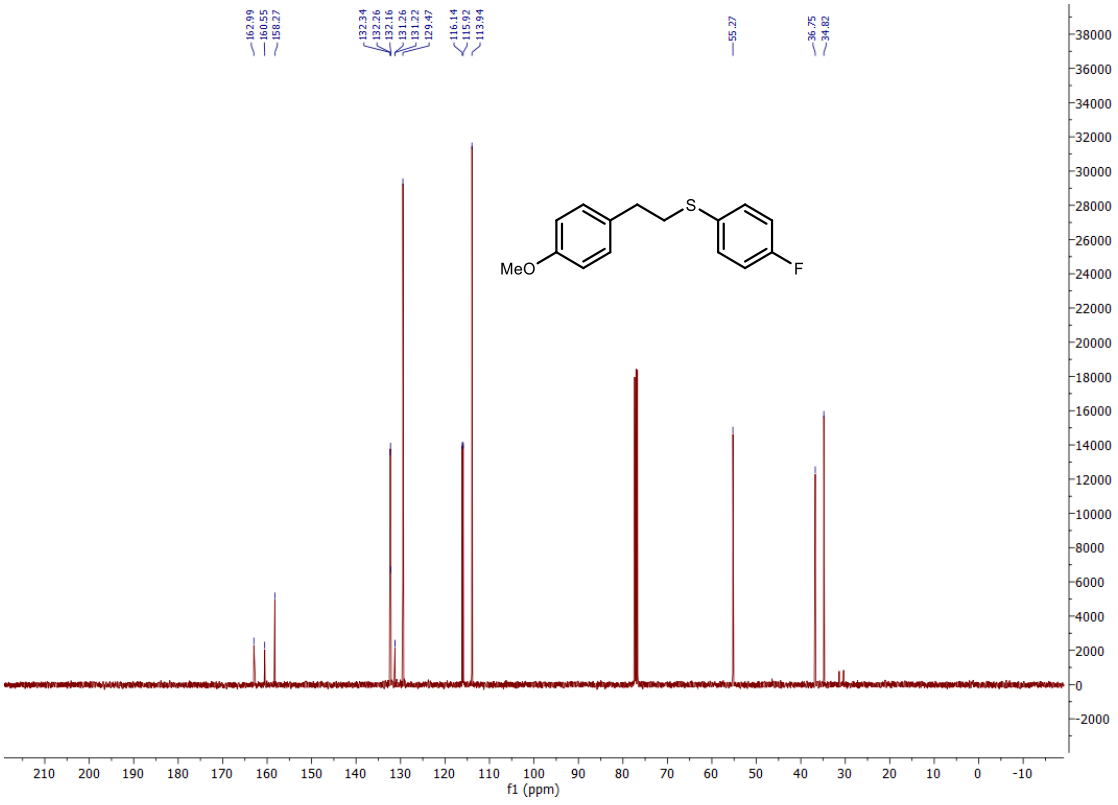
^{13}C NMR (101 MHz, $CDCl_3$) of **3bb:**



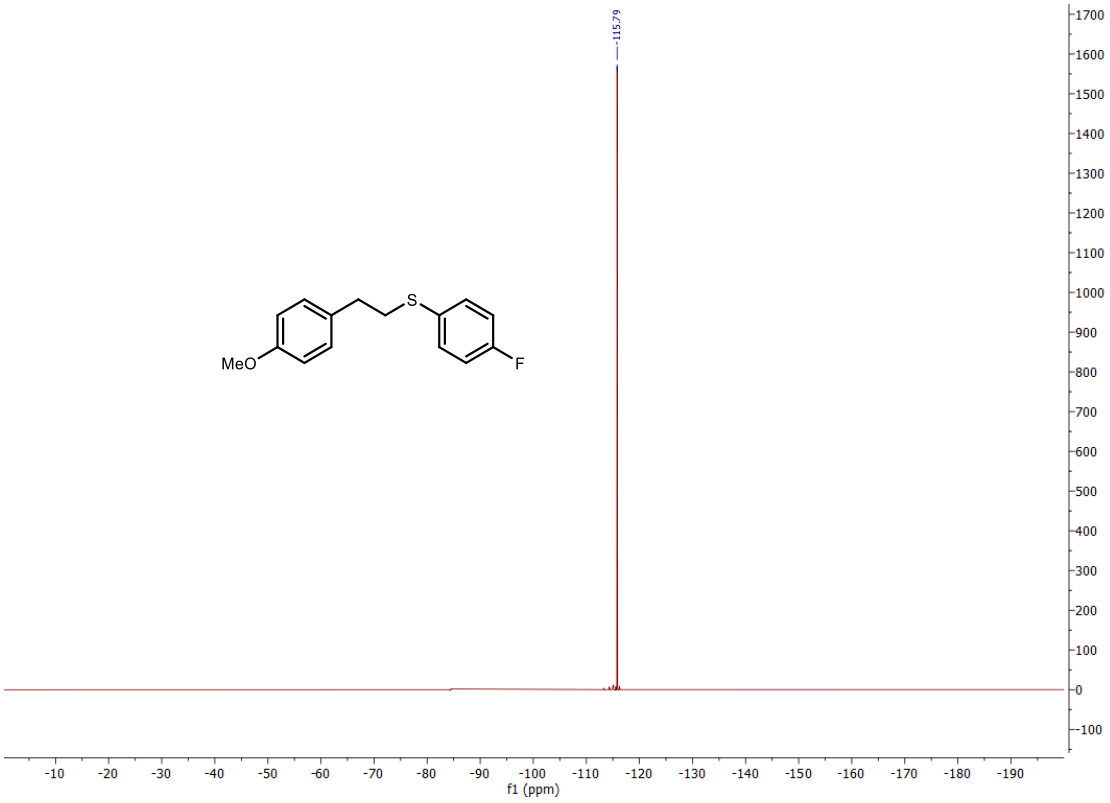
^{1}H NMR (400 MHz, $CDCl_3$) of **3bc:**



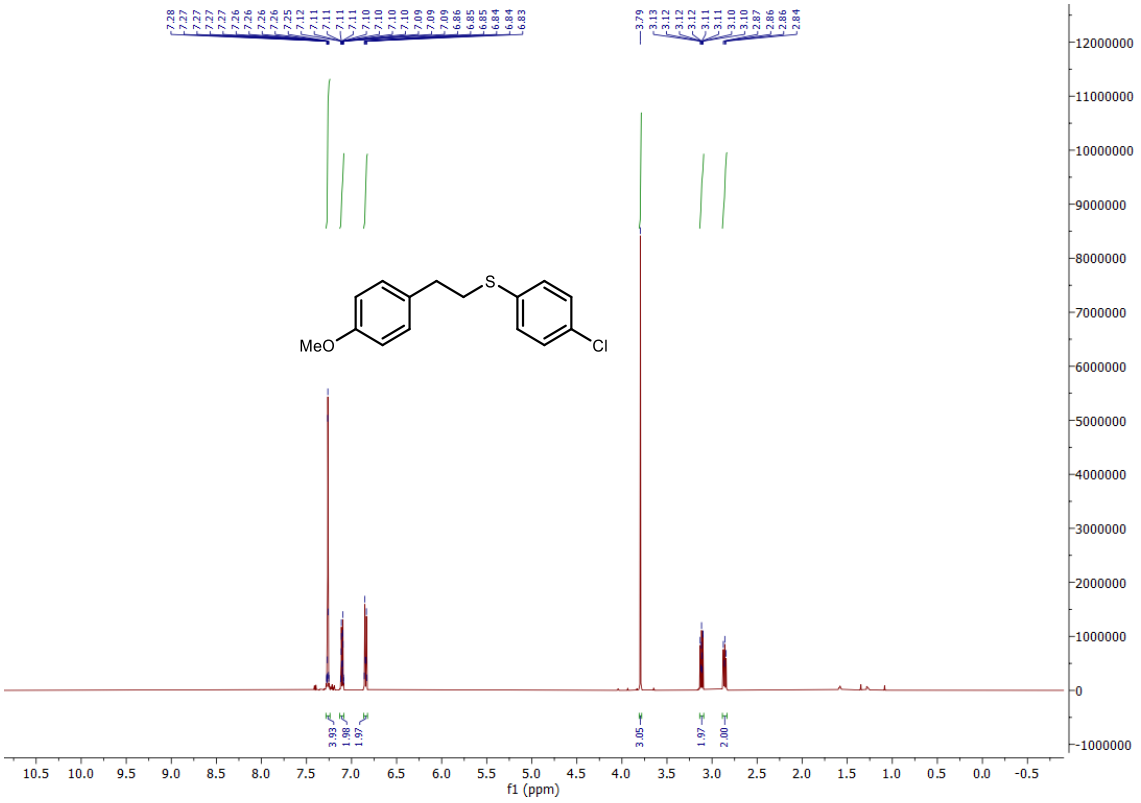
^{13}C NMR (101 MHz, $CDCl_3$) of **3bc:**



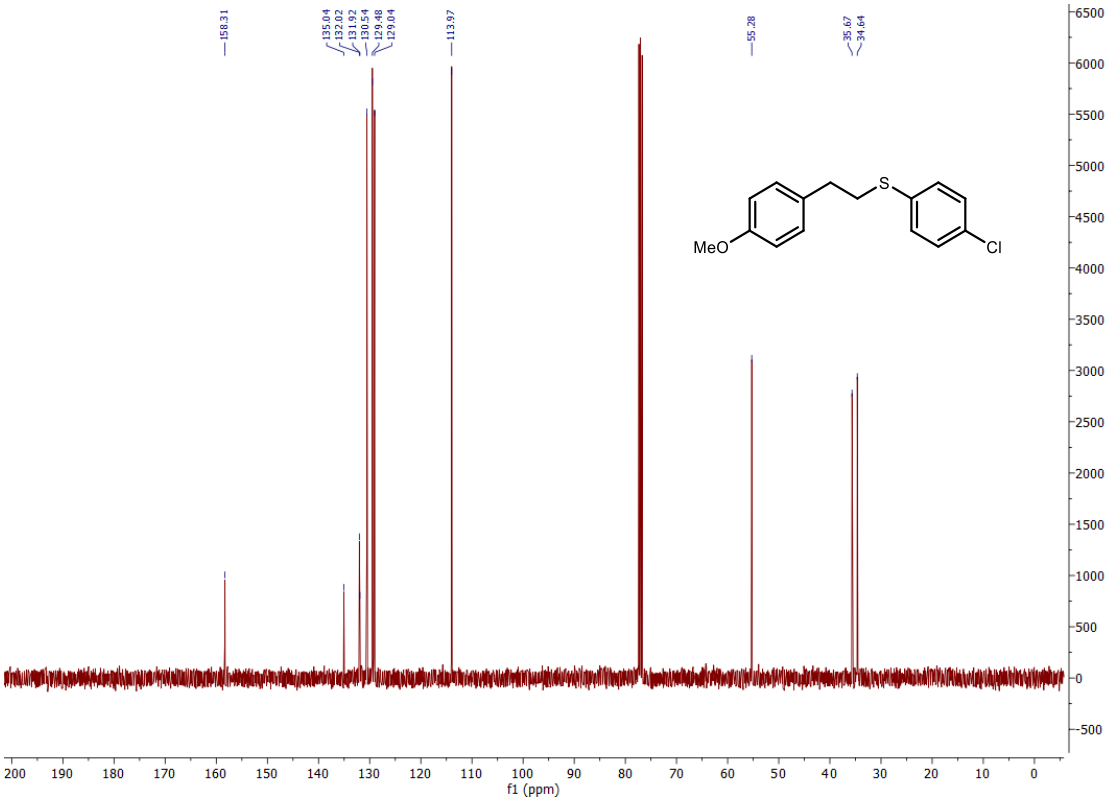
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) of **3bc:**



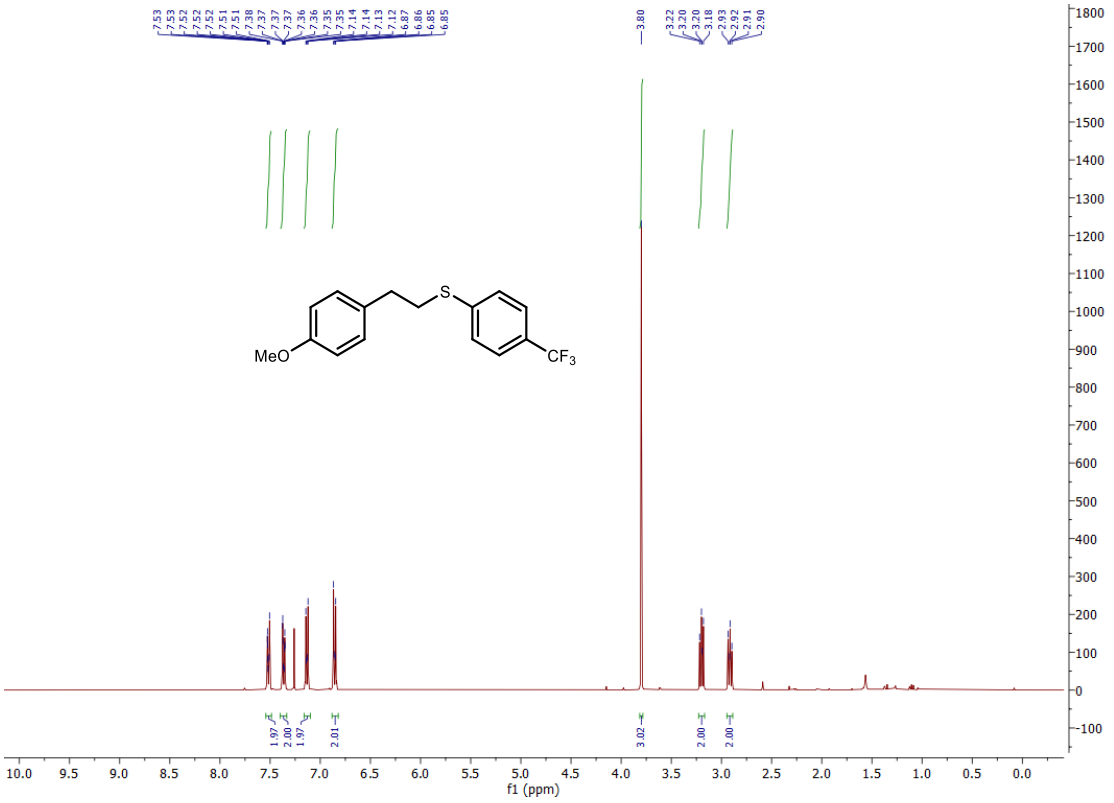
^{1}H NMR (400 MHz, $CDCl_3$) of **3bd:**



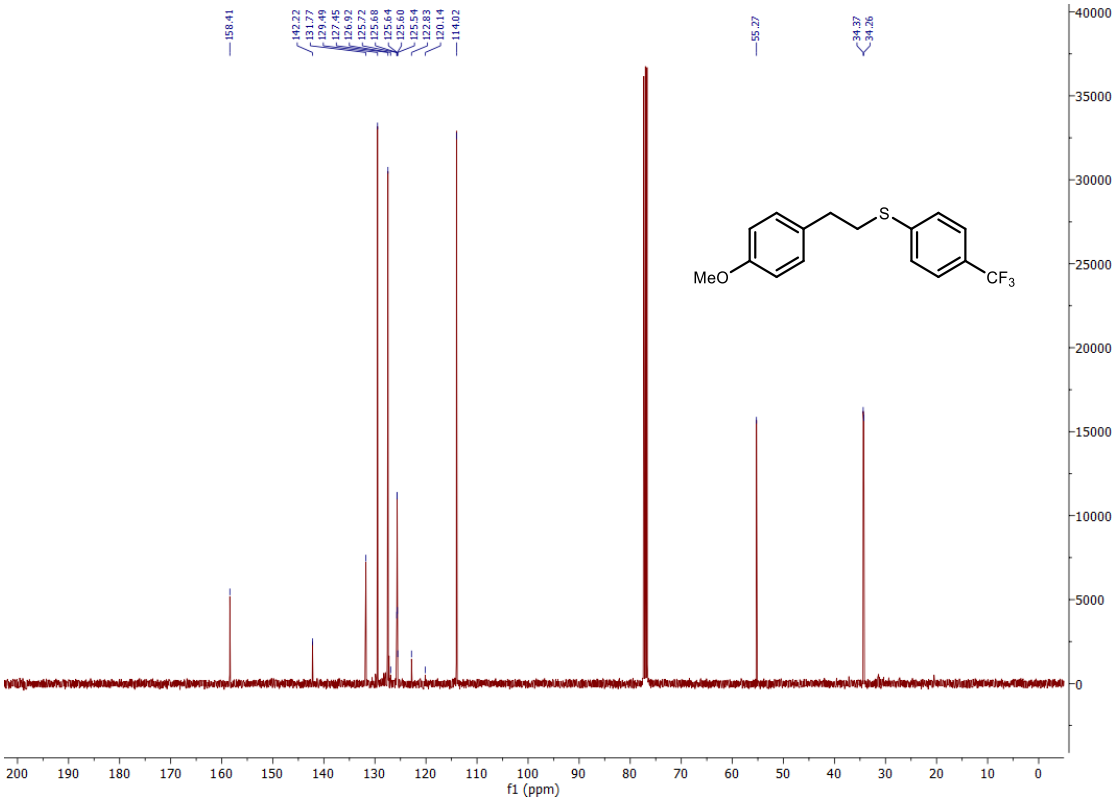
^{13}C NMR (101 MHz, $CDCl_3$) of **3bd:**



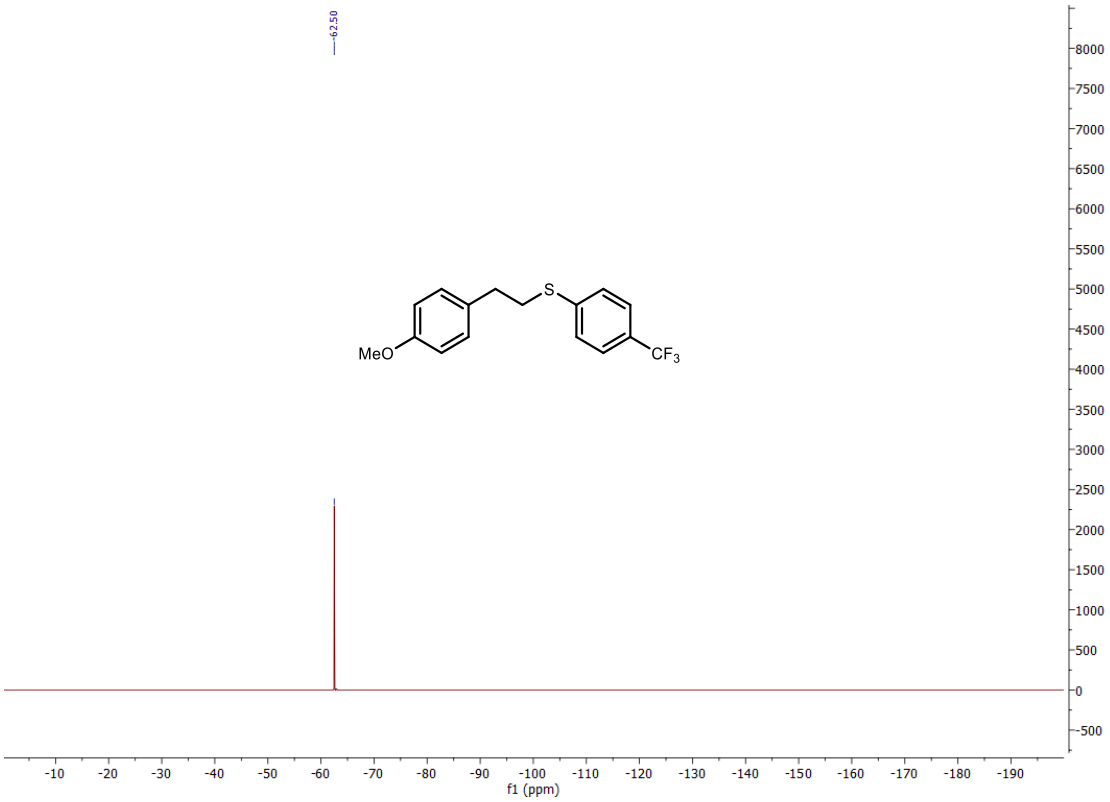
^{1}H NMR (400 MHz, $CDCl_3$) of **3be:**



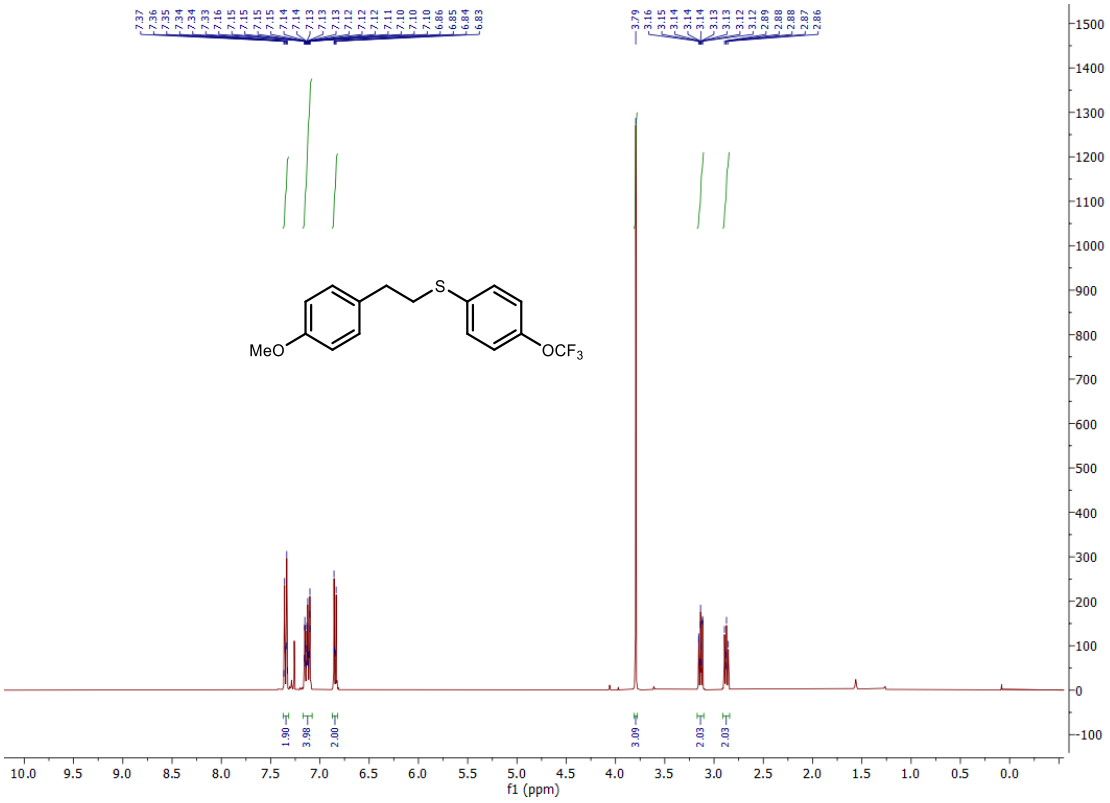
^{13}C NMR (101 MHz, $CDCl_3$) of **3be:**



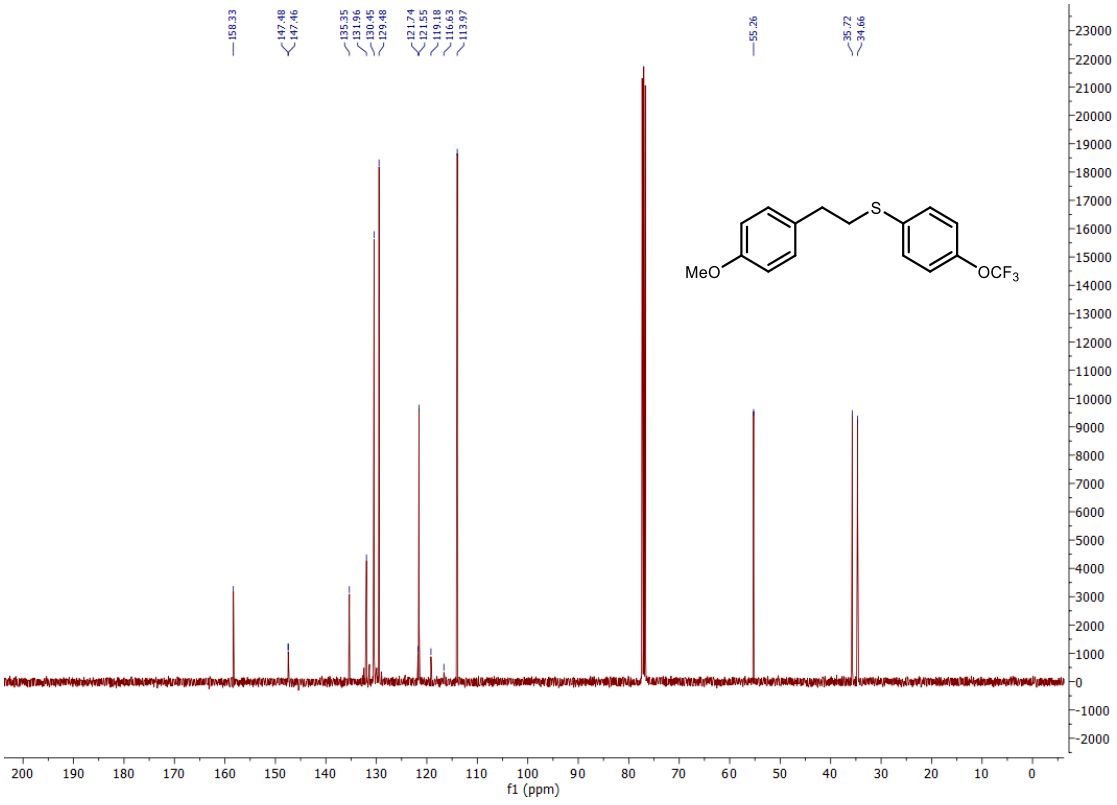
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) of **3be:**



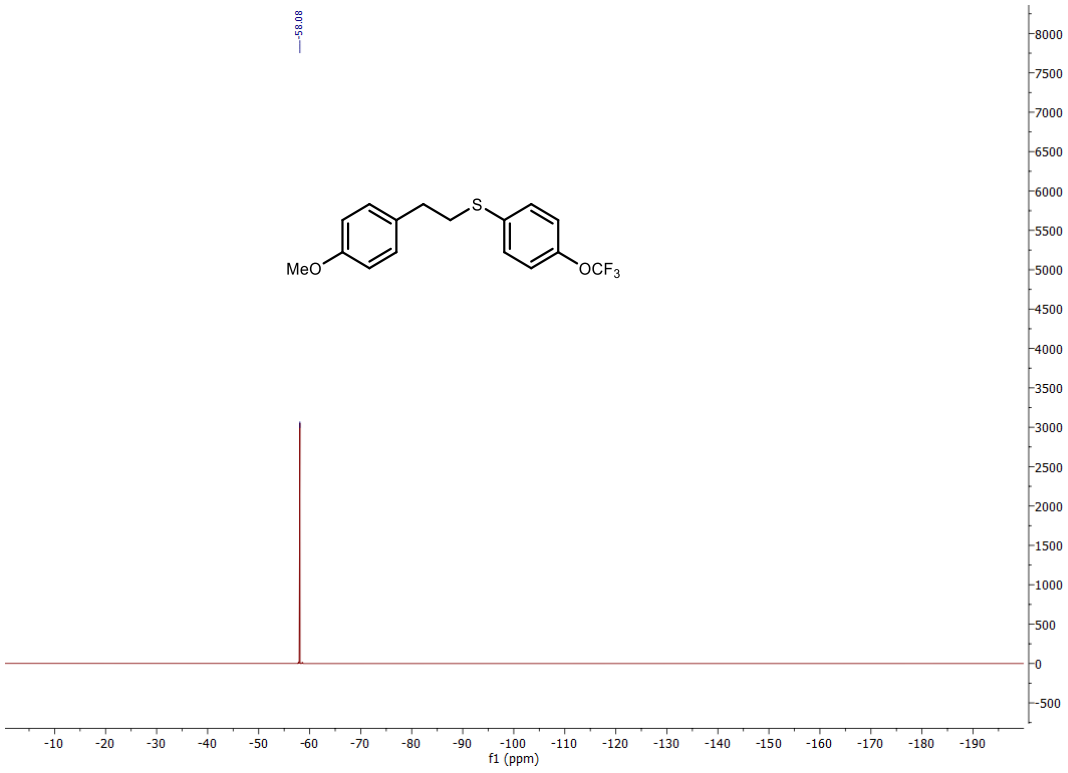
^{1}H NMR (400 MHz, $CDCl_3$) of **3bf:**



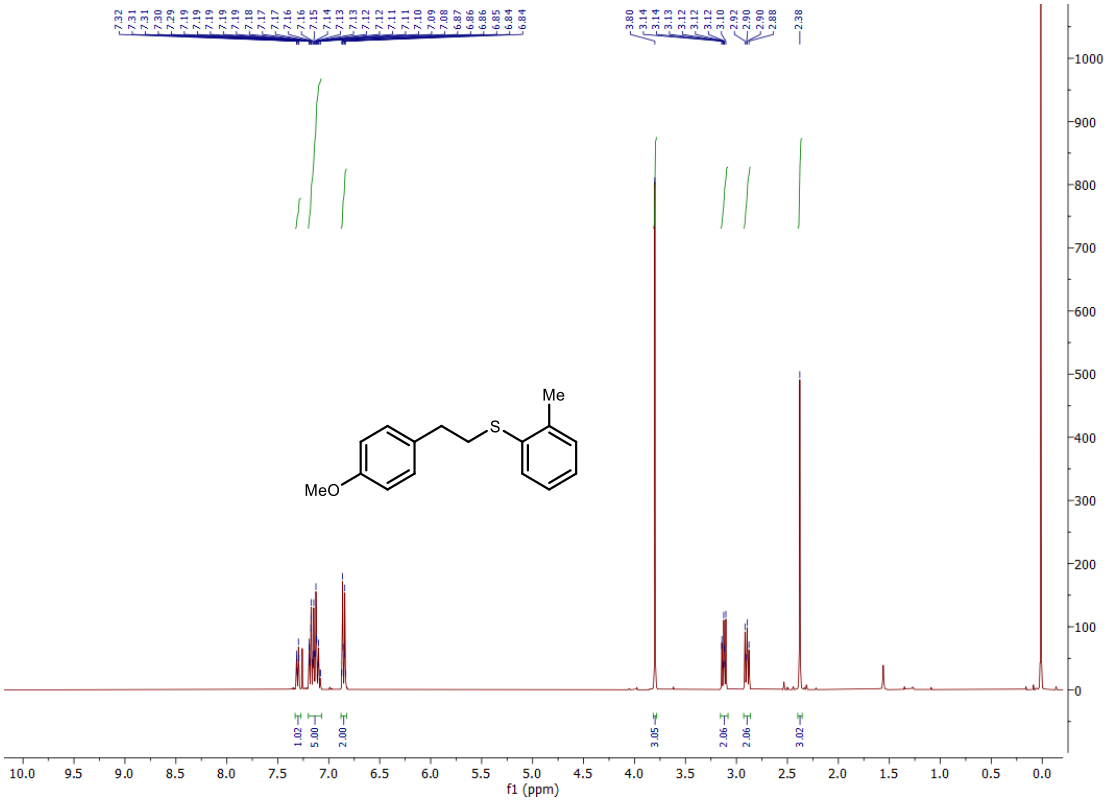
^{13}C NMR (101 MHz, $CDCl_3$) of **3bf:**



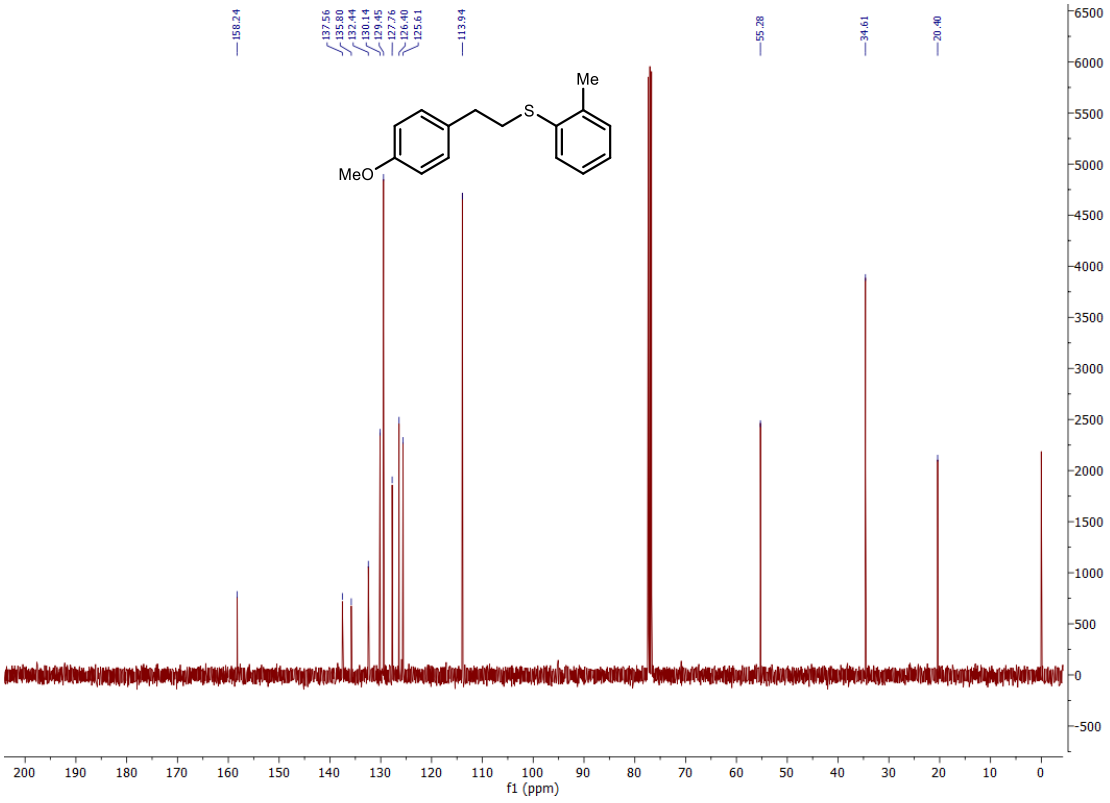
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) of **3bf:**



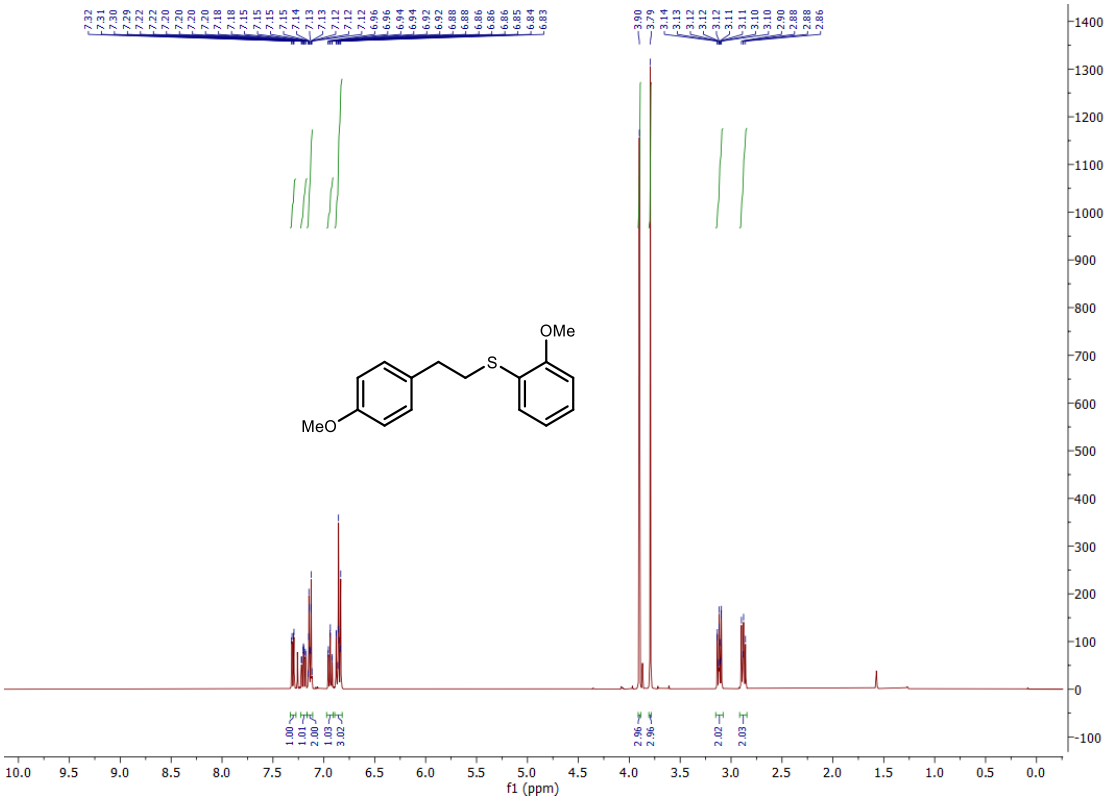
^{1}H NMR (400 MHz, $CDCl_3$) of **3bg:**



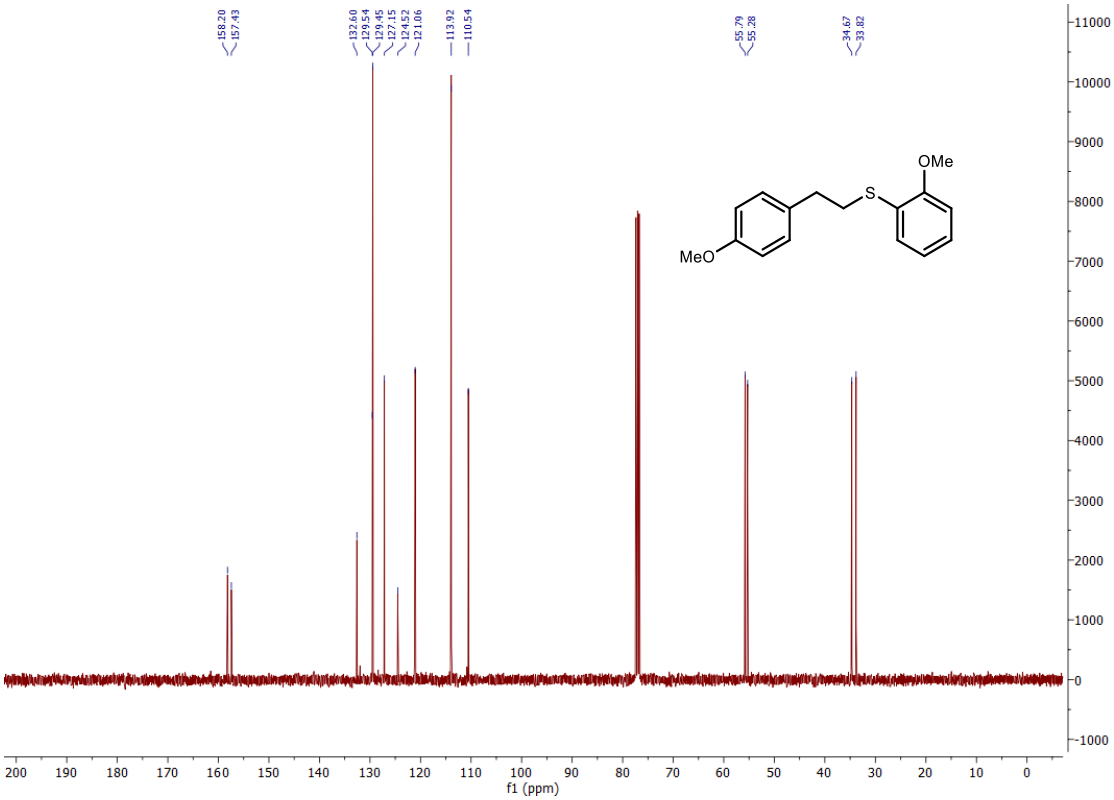
^{13}C NMR (101 MHz, $CDCl_3$) of **3bg:**



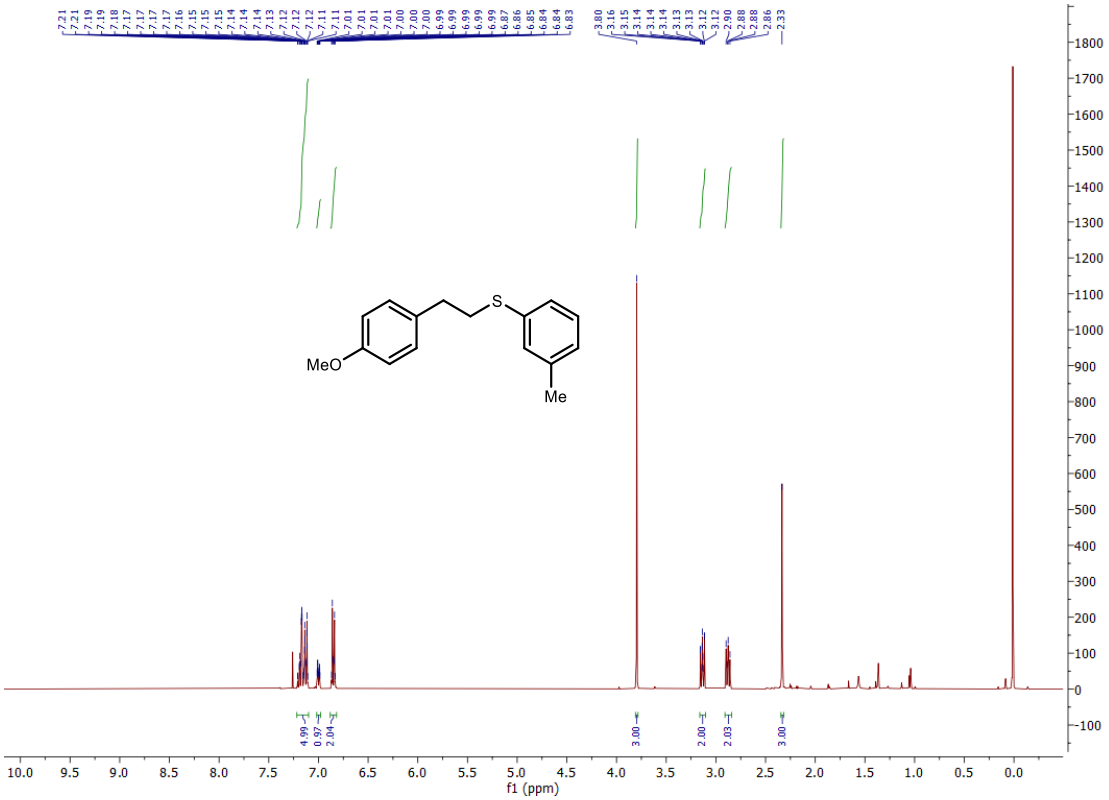
^{1}H NMR (400 MHz, $CDCl_3$) of **3bh:**



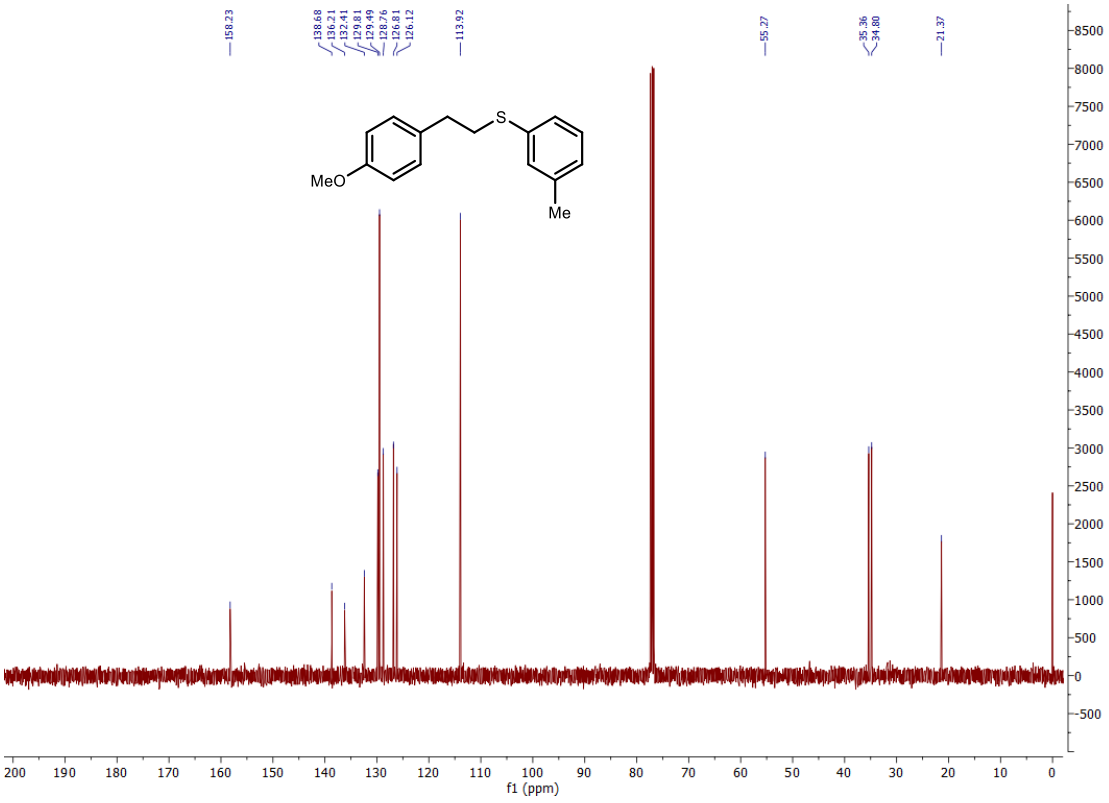
^{13}C NMR (101 MHz, $CDCl_3$) of **3bh:**



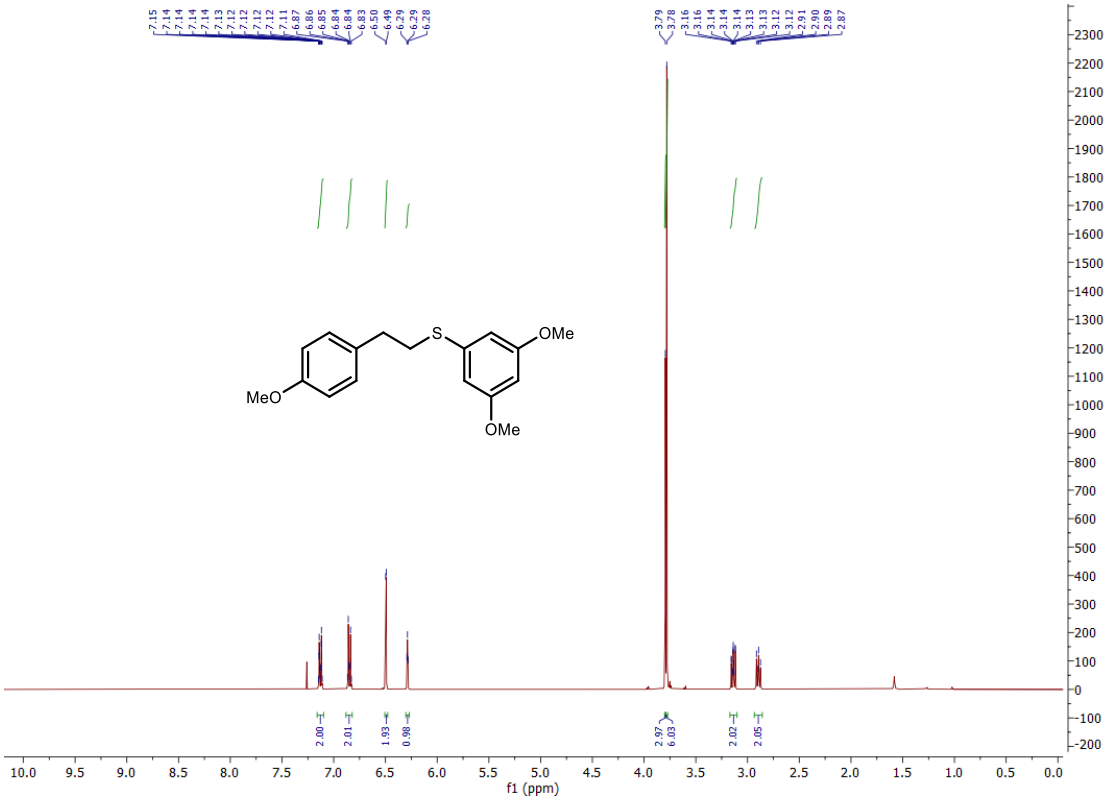
^{1}H NMR (400 MHz, $CDCl_3$) of **3bi:**



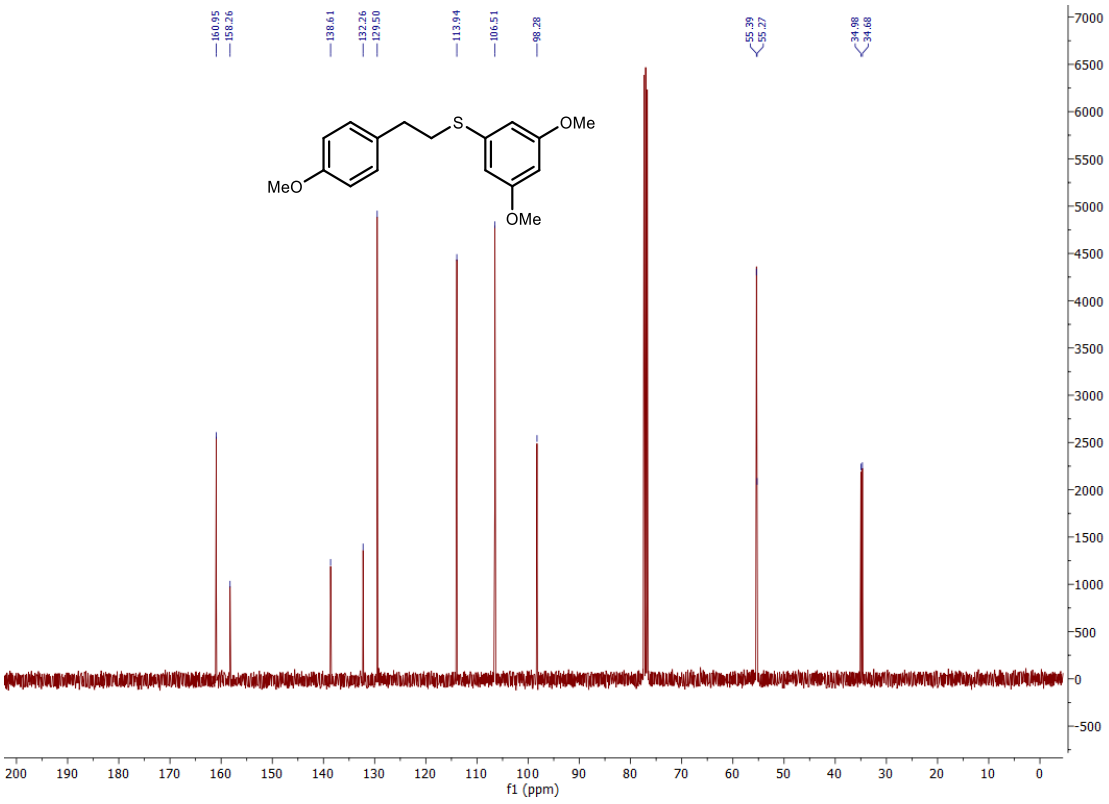
^{13}C NMR (101 MHz, $CDCl_3$) of **3bi:**



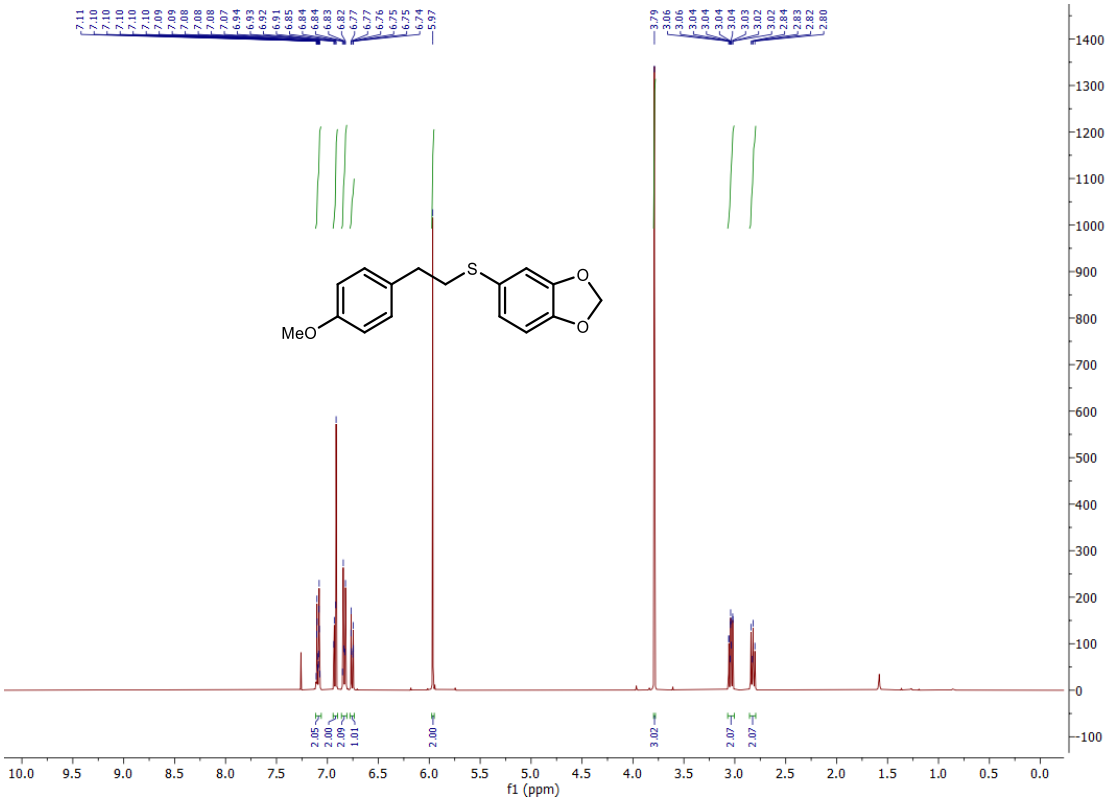
^{1}H NMR (400 MHz, $CDCl_3$) of **3bj:**



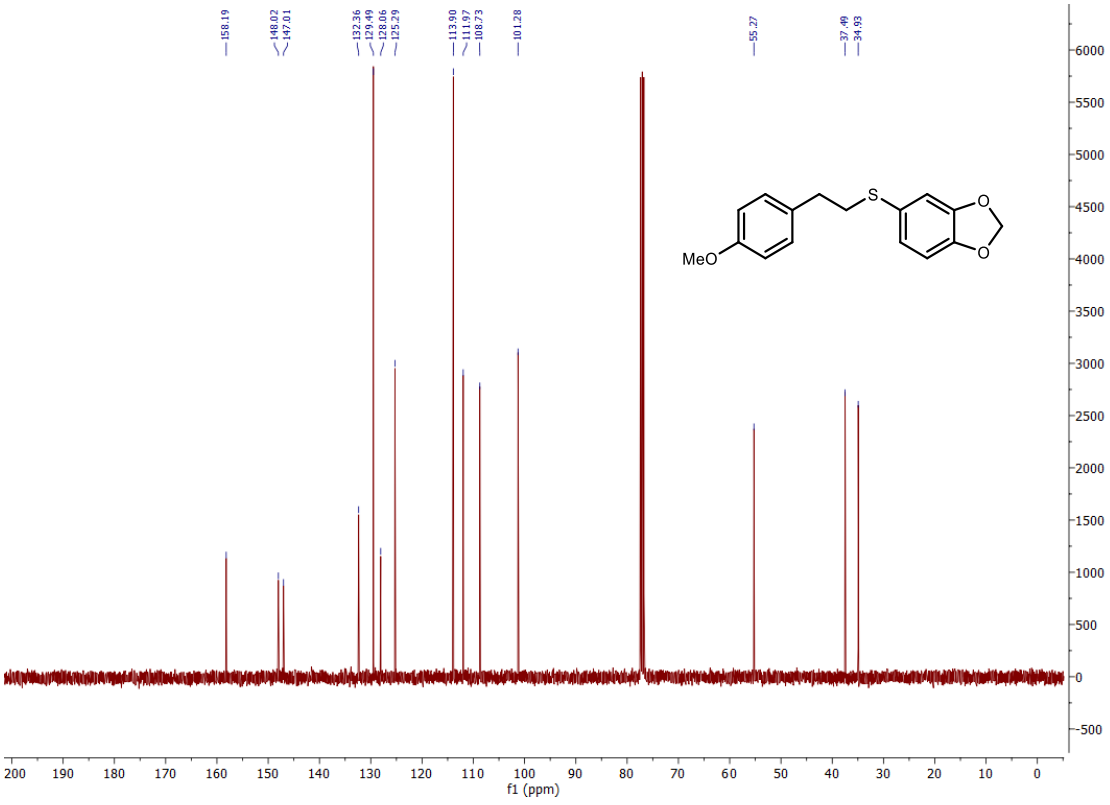
^{13}C NMR (101 MHz, $CDCl_3$) of **3bj:**



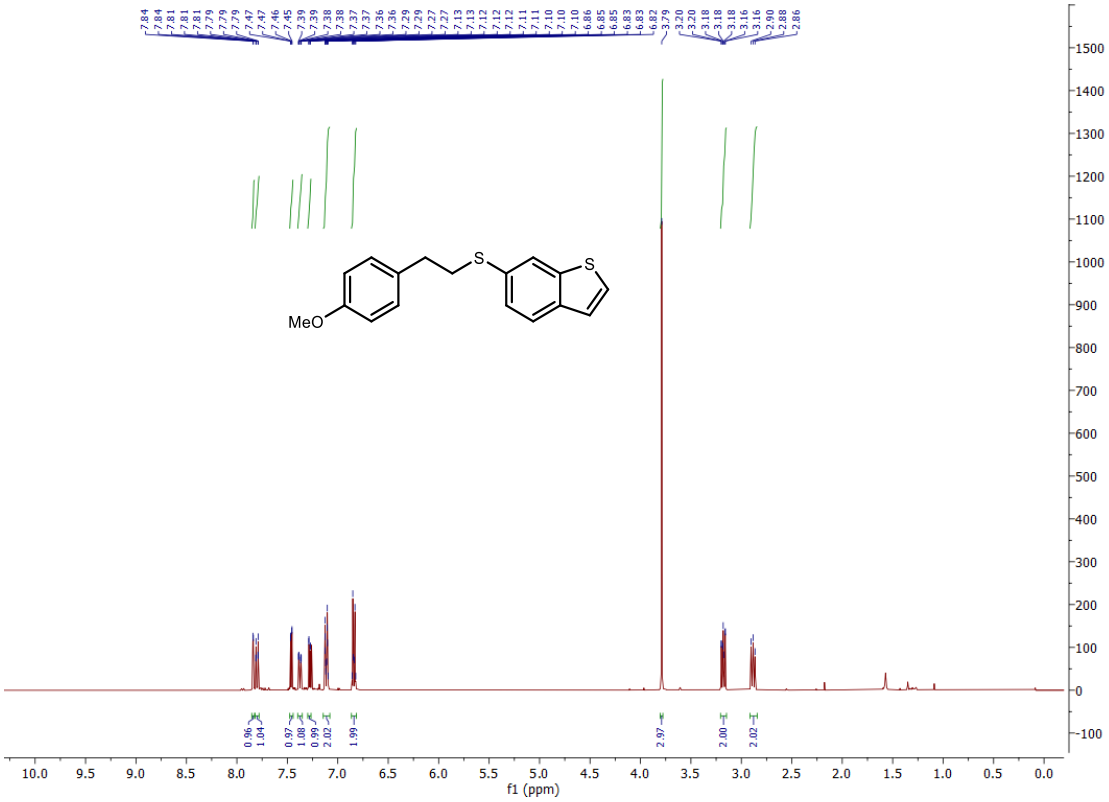
^{1}H NMR (400 MHz, $CDCl_3$) of **3bk:**



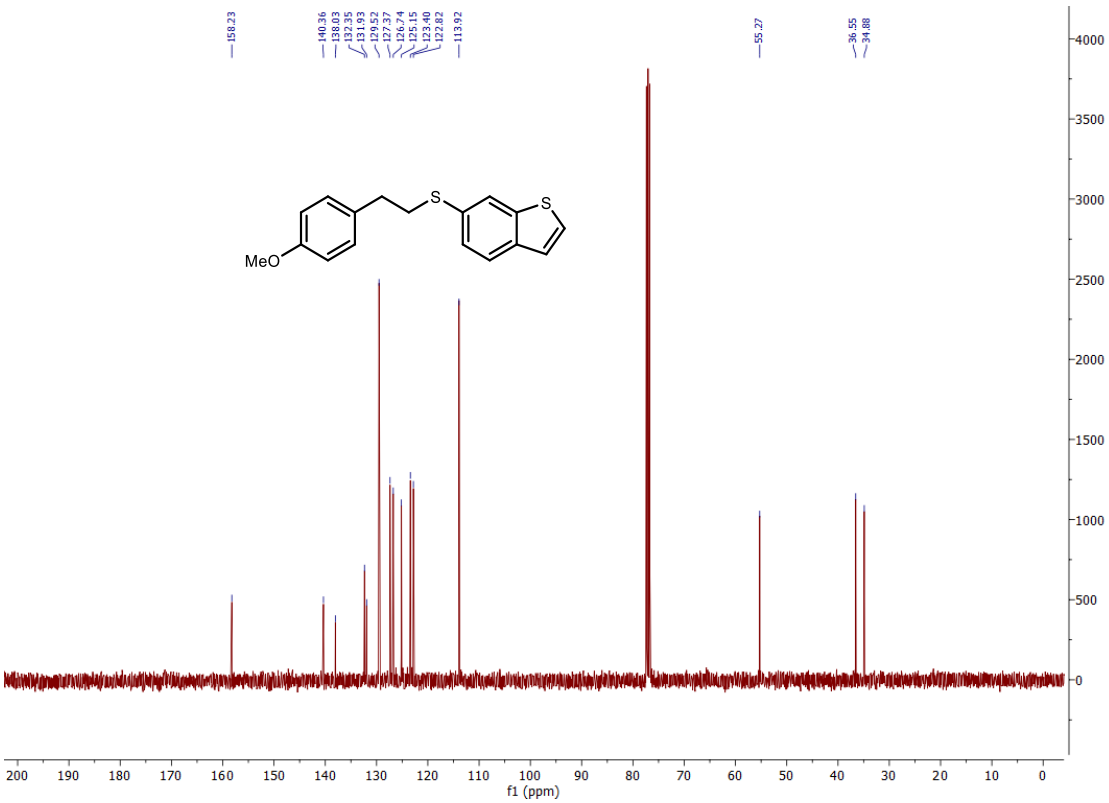
^{13}C NMR (101 MHz, $CDCl_3$) of **3bk:**



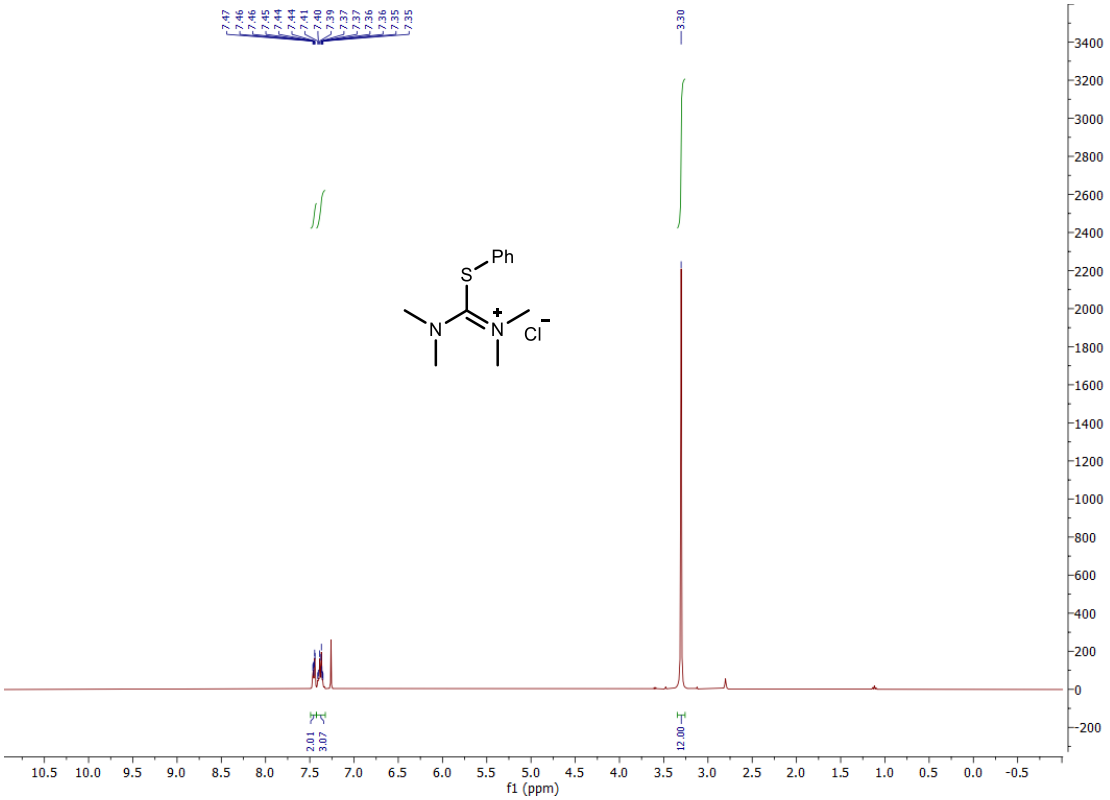
^{1}H NMR (400 MHz, $CDCl_3$) of **3bl:**



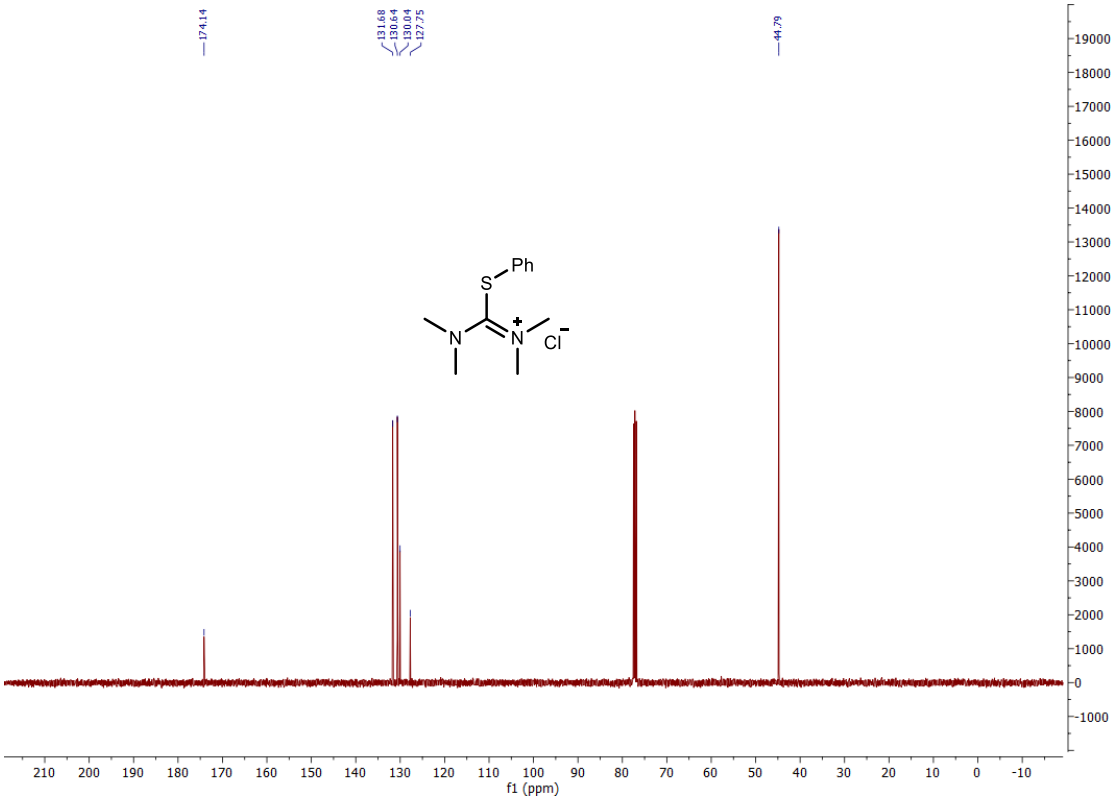
^{13}C NMR (101 MHz, $CDCl_3$) of **3bl:**



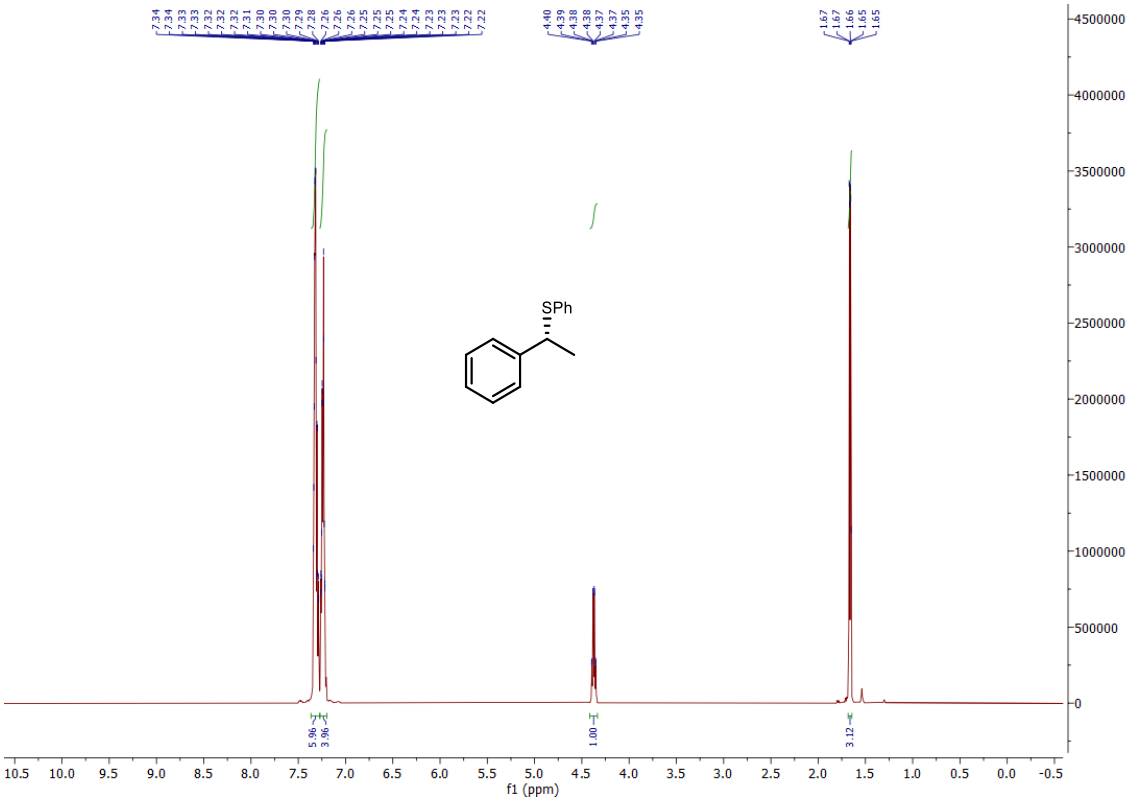
^{1}H NMR (400 MHz, $CDCl_3$) of **4:**



^{13}C NMR (101 MHz, $CDCl_3$) of **4:**



^{1}H NMR (400 MHz, $CDCl_3$) of **7:**



^{13}C NMR (101 MHz, $CDCl_3$) of **7:**