Supporting Information

"Thiol-free Synthesized" and Sustainable Thiolating Synthons for Nickel-catalyzed Reductive Assembling Sulfides

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14 May 2024

Note added after first publication: This supplementary information file replaces that originally published on 04 Oct 2022. This updated file provides corrected ^{1}H and ^{13}C NMR data for compound **6b**. This does not affect the results or conclusions of the work.

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I. General information

General procedures. General Information Unless specifically stated, all reagents were commercially obtained and where appropriate, purified prior to use. For example, dichloromethane (DCM) was freshly distilled from CaH_2; toluene, ether (Et_2O) was dried and distilled from metal sodium and benzophenone. Other commercially available reagents and solvents were used directly without purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica (200 – 300 mesh). ^{1}H, ^{13}C, ^{19}F NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer in $CDCl_3$, CD_3COCD_3 or d_6-DMSO. Multiplicities were given as: s (singlet); d (doublet); dd (doublets of doublet); t (triplet); q (quartet); td (triplet of doublets); tt (triplet of triplets) ddd (doublet of doublet of doublets) or m (multiplets). High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOF-spectrometer.

Reagents. The following chemicals were used as received: Bis(4-chlorophenyl)disulfide (Energy-Chemical), Bis(triphenylphosphine)nickel(II) chloride (Adamas), 1-(2-Bromo-ethyl)-4-chloro-benzene (Energy-Chemical), 1-Bromo-4-iodobenzene (Energy-Chemical), 1-(4-Bromophenyl)ethanone (Leyan.com), 2-Bromopyridine (Energy-Chemical), 2-(2-Bromoethyl)-1,3-dioxolane (Energy-Chemical), 3-Bromobenzoate (Energy-Chemical), 3-Bromoquinoline (Energy-Chemical), 3-Bromobenzoate (Energy-Chemical), 4-Bromobenzoyl chloride (Energy-Chemical), 4-Bromobenzotrifluoride (Leyan.com), 5-Bromopyrimidine (Energy-Chemical), 5-bromobenzofuran (Energy-Chemical), Copper(II) trifluoromethanesulfonate (Energy-Chemical), 1-Chloro-4-iodobenzene (Energy-Chemical), 1,4-Dibromobenzene (Leyan.com), 4,4'-Dimethyl-2,2'-dipyridyl (Energy-Chemical), 5,5'-Dimethyl-2,2'-bipyridyl (Energy-Chemical), 1-Fluoro-2-[(2-fluorophenyl)disulfanyl]benzene (Energy-Chemical), Iodine (Energy-Chemical), Iodobenzene (Energy-Chemical), 4-Iodoanisole (Energy-Chemical), 4-

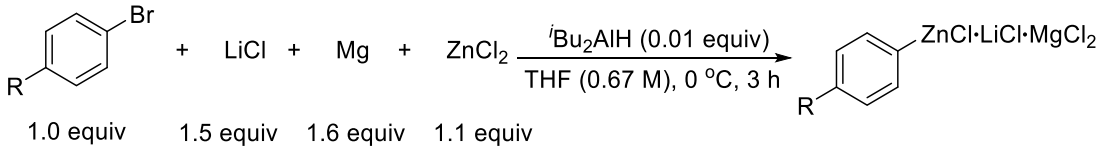
Iodobenzotrifluoride (Leyan.com), 5-Iodoindole (Adamas), lithium chloride (Leyan.com), Methyl cyclopropylcarbinol (Adamas), Methyl 2-bromobenzoate (Energy-Chemical), Methyl 3-pyridyl bromide (Energy-Chemical), Methyl 4-bromobenzoate (Energy-Chemical), Methyl 4-iodobenzoate (Energy-Chemical), Nickel bromide (Adamas), Phenyl disulfide (Energy-Chemical), phthalimide (Energy-Chemical), 1,10-Phenanthroline (Energy-Chemical), 3-Phenylpropyl bromide (Energy-Chemical), *p*-Tolyl disulfide (Energy-Chemical), Sodium iodide (Leyan.com), Sulfuryl chloride (aladdin), Sulfur monochloride (Adamas), 2,2,6,6-Tetramethylpiperidinyl-1-oxidezinc (Leyan.com).

II. Synthesis of starting materials

1. Synthesis of aryl(hetero) iodides 5c-e, 5g, 5h, 5x, 5y,:

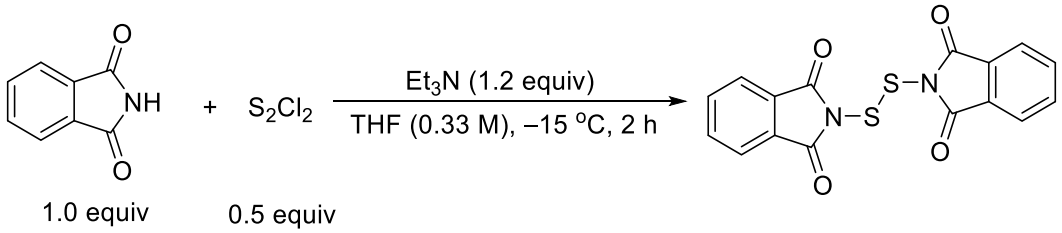
The aryl(hetero) iodides **5c-e**, **7g**, **7h**, **5x**, **5y**, were synthesized according to our previous report[1].

2. Synthesis of organozinc halides from aryl halides



An oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with with magnesium turnings (583 mg, 24.0 mmol, 1.60 equiv), LiCl (954 mg, 22.5 mmol, 1.50 equiv), $ZnCl_2$ (2.25 g, 16.5 mmol, 1.10 equiv) was added, then the bottom was dried at 150 °C under vacuum for 3 h. After cooling to room temperatureand dry THF (23.0 mL) was added, the magnesium was activated with $^{i}Bu_2AlH$ (1.50 mL, 0.100 M in THF, 0.150 mmol, 0.0100 equiv) in 0 °C. After 5 min of stirring, the aryl bromide (15.0 mmol, 1.00 equiv) was added in one portion at 0 °C. The mixture was allowed to stir for 3 h at 0 °C. The organozinc chlorides were titrated against iodine before use[1]. Round-bottom flask and the yield of the zinc reagent was determined by iodometric titration. (0.33 M, **3a**), (0.29 M, **3b**), (0.36 M, **3c**), (0.36 M, **3d**), (0.35 M, **3e**), (0.36 M, **3f**).

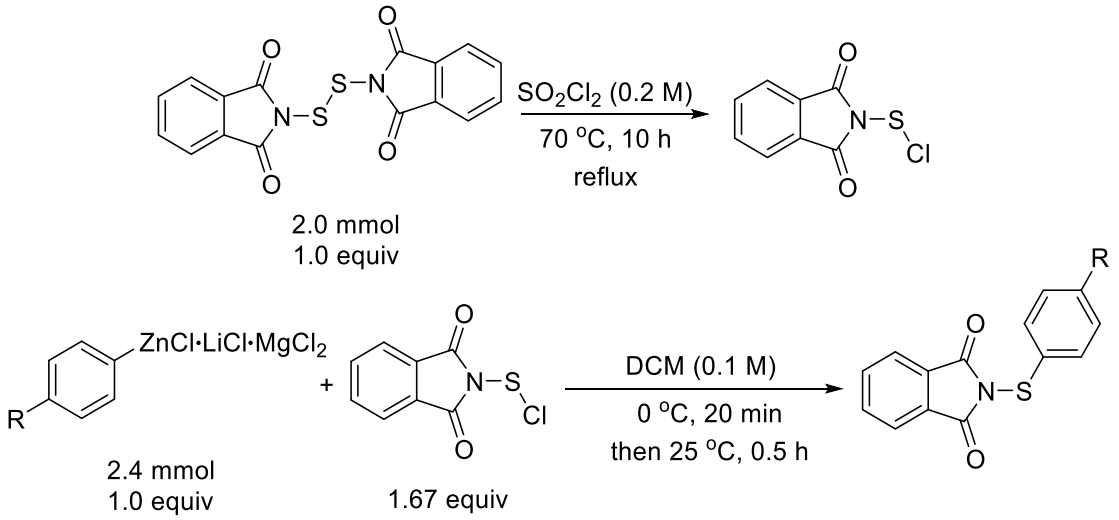
3. Synthesis of di(1-phthalimidyl)disulfane



An oven-dried 500-mL round-bottom flask, equipped with a stir bar, phthalimide (5.88 g, 40.0 mmol, 1.00 equiv) was dissolved in THF (120 mL) and triethylamine (4.86 g, 48.0 mmol, 1.20 equiv). The mixture was cooled in –15 °C, and then sulfur monochloride (1.35 g, 20.0 mmol, 0.500 equiv) was added dropwise. The mixture was

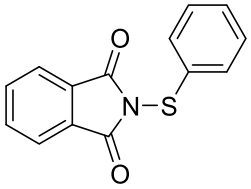
stirred for 2 h, and then quenched with 150 mL of H_2O. The resulting precipitate was filtered and washed with diethyl ether. Recrystallization from $CHCl_3$:MeOH (2:1, v:v) yielded di(1-phthalimidy1)disulfane as a white solid (6.04 g, 85% yield). Spectra were consistent with literature data[2].

4. General Method A: Synthesis of *N*-thiophthalimides 4a-4f

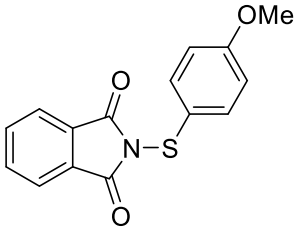


An oven-dried 100-mL round-bottom flask, equipped with a stir bar, di(1-phthalimidy1) disulfane (713 mg, 2.00 mmol, 1.00 equiv) and SO_2Cl_2 (10.0 mL) were added under N_2. The reaction was heated to 70 °C reflux for 10 h. After cooling to room temperature, the insoluble precipitate was removed, and the filtrate was concentrated to give a yellow solid of Phth-SCl. The product was subsequently used for next step.

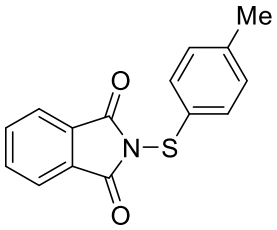
DCM (25.0 mL) was added to the round-bottom flask at 25 °C under N_2. The mixture was subsequently cooled to 0 °C followed by addition of the THF solution of the above arylzinc chloride (2.40 mmol, 1.00 equiv) over 10 min. The reaction was stirred at the same temperature for another 10 min and then allowed to warm up to 25 °C. The mixture was stirred for 0.5 h. Upon the completion of reaction, the solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 1:1 petroleum ether: DCM)[2].



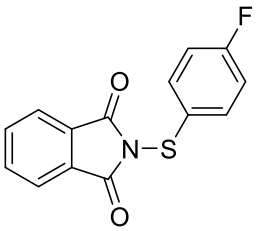
2-(Phenylthio)isoindoline-1,3-dione 4a: Prepared according to **General Method A** (Eluent: 50:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (346.9 mg, 1.36 mmol, 56.6% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.92 (2H, m), 7.79 – 7.77 (2H, m), 7.62 – 7.59 (2H, m) 7.33 – 7.31 (3H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.8, 135.1, 134.8, 132.0, 131.0, 129.4, 124.2. Spectra were consistent with literature data[2].



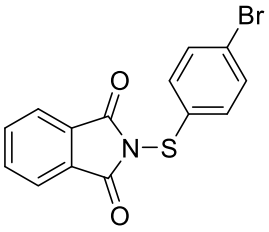
2-((4-Methoxyphenyl)thio)isoindoline-1,3-dione 4b: Prepared according to **General Method A** (Eluent: 50:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (494.5 mg, 1.73 mmol, 72.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.88 (2H, m), 7.79 – 7.73 (4H, m), 6.85 (2H, d, J = 8.8 Hz), 3.79 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.0, 161.6, 136.9, 134.7, 132.2, 125.5, 124.0, 114.8, 55.5. Spectra were consistent with literature data[2].



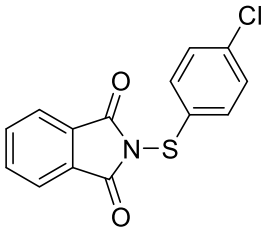
2-(*p*-Tolylthio)isoindoline-1,3-dione 4c: Prepared according to **General Method A** (Eluent: 50:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (545.1 mg, 2.02 mmol, 84.3% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 – 7.90 (2H, m), 7.77 – 7.75 (2H, m), 7.60 (2H, d, J = 8.2 Hz), 7.14 (2H, d, J = 8.2 Hz), 2.32 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.9, 140.4, 134.7, 132.8, 132.1, 131.5, 130.2, 124.1, 21.4. Spectra were consistent with literature data[2].



2-((4-Fluorophenyl)thio)isoindoline-1,3-dione 4d: Prepared according to **General Method A** (Eluent: 50:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (396.2 mg, 1.45 mmol, 60.4% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.91 (2H, m), 7.79 – 7.73 (4H, m), 7.05 – 7.01 (2H, m); **^{19}F NMR** (471 MHz, $CDCl_3$) δ –110; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.8, 163.9 (d, $J_{C\text{-}F}$ = 252.2 Hz), 162.6, 135.7(d, $J_{C\text{-}F}$ = 88.3 Hz), 134.9, 132.1, 130.2 (d, $J_{C\text{-}F}$ = 2.9 Hz), 124.2, 116.7 (d, $J_{C\text{-}F}$ = 22.1 Hz). Spectra were consistent with literature data[3].



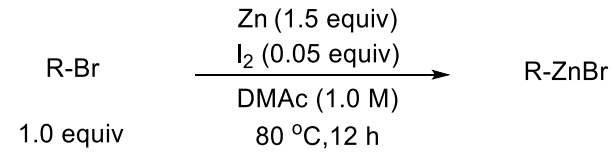
2-((4-Bromophenyl)thio)isoindoline-1,3-dione 4e: Prepared according to **General Method A** (Eluent: 50:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (616.0 mg, 1.84 mmol, 76.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.92 (2H, m), 7.80 – 7.78 (2H, m), 7.50 – 7.44 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.7, 135.0, 134.2, 132.9, 132.7, 132.0, 124.3, 124.1. Spectra were consistent with literature data[2].



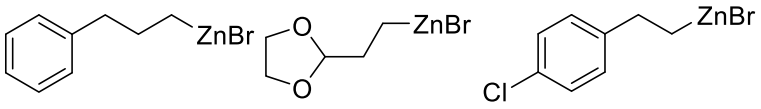
2-((4-Chlorophenyl)thio)isoindoline-1,3-dione 4f: Prepared according to **General Method A** (Eluent: 50:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (513.6 mg, 1.77 mmol, 73.9% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.92 (2H, m), 7.80 – 7.78 (2H, m), 7.58 (2H, d, J =

8.6 Hz), 7.30 (2H, d, J = 8.6 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.7, 136.0, 135.0, 133.5, 133.0, 132.0, 129.7, 124.3. Spectra were consistent with literature data[2].

5. Synthesis of Alkylzinc Reagents

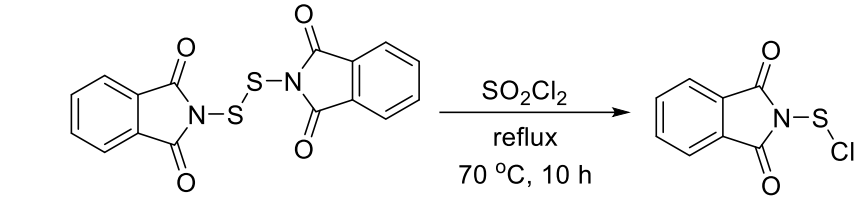


An 25-mL of Schlenk tube, equipped with a stir bar, and charged with zinc powder (1.47 g, 22.5 mmol, 1.50 equiv) and heated to 80 °C under vacuum for 30 min. After the tube was back-filled with argon and cooled to room temperature, iodine (190 mg, 0.750 mmol, 0.0500 equiv) and DMAc (15.0 mL) were added. The resulting mixture was stirred until the brown color disappeared, alkyl bromide (15.0 mmol, 1.00 equiv) was added. The reaction mixture was heated to 80 °C. After stirring for 12 h at 80 °C, the mixture was cooled to room temperature. The gray solution was filtered and the filtrate was stored under argon in a Schlenk tube, the solution of the alkylzinc reagent was titrated with I_2 according to Knochel's method. This alkylzinc solution can be stored at room temperature under argon for several weeks without deterioration[4].

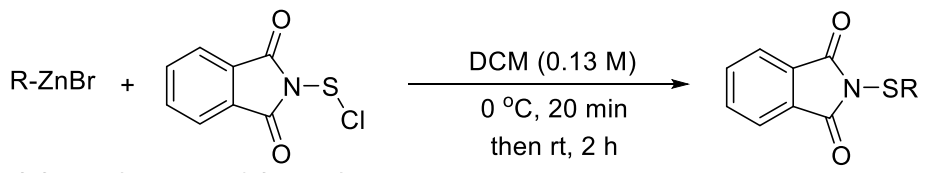


0.445 M (**3g**) 0.667 M (**3h**) 0.559 M (**3i**)

6. <u>General Method B</u>: Synthesis of *N*-thiophthalimides 4g-4i



2.0 mmol
1.0 equiv

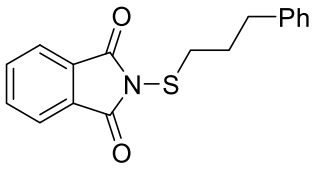


3.3 mmol
1.0 equiv

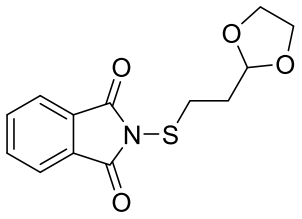
4.0 mmol
1.2 equiv

An oven-dried 100-mL round-bottom flask, equipped with a stir bar, di(1-phthalimidy1) disulfane (713 mg, 2.00 mmol, 1.00 equiv) and SO_2Cl_2 (10.0 mL) were added under N_2. The reaction was heated to 70 °C reflux for 10 h. After cooling to room temperature, the insoluble precipitate was removed, and the filtrate was concentrated to give a yellow solid of Phth-SCl. The product was subsequently used for next step.

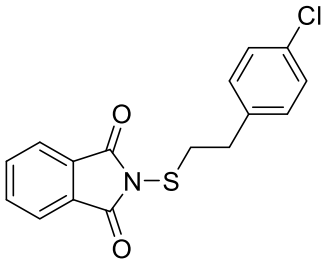
DCM (25.0 ml) was added to the round-bottom flask at 25 °C under N_2. The mixture was subsequently cooled to 0 °C followed by addition of the solution of R-ZnBr (3.30 mmol, 1.00 equiv) in DMF over 10 min. The reaction was stirred at the same temperature for another 10 min and then allowed to warm up to 25 °C. The mixture was stirred for 2 h. Upon the completion of reaction, the organic layer was separated and the aqueous layer extracted with DCM (50.0 mL x 3). The organic phase was separated, dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated, and the resulting residue was purified by column chromatography (Eluent: 50:1 to 2:1 petroleum ether: ethyl acetate) to provide the product[2].



2-((3-Phenylpropyl)thio)isoindoline-1,3-dione 4g: Prepared according to **General Method B** (Eluent: 50:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (613.6 mg, 2.06 mmol, 62.5% yield). **M.p.** = 79.9 – 80.5 °C; **IR** (thin film) 1785 (w), 1743 (s), 1715 (s), 1454 (w), 1342 (m), 1283 (s), 1051 (s), 868 (m), 800 (w), 745 (m), 711 (s), 693 (s) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.91 (2H, m), 7.79 – 7.77 (2H, m), 7.27 – 7.24 (2H, m), 7.18 – 7.15 (3H, m), 2.88 (2H, t, J = 7.2 Hz), 2.80 (2H, t, J = 7.5 Hz), 1.94 – 1.86 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.7, 141.1, 134.7, 132.2, 128.7, 128.6, 126.2, 124.0, 38.2, 34.3, 29.8; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{17}H_{15}NaNO_2S$: 320.0716, found: 320.0708.

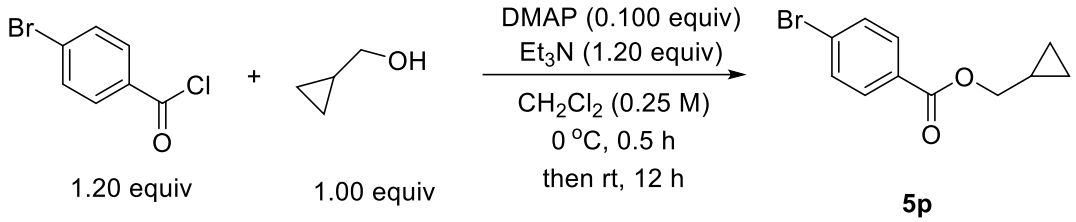


2-((2-(1,3-Dioxolan-2-yl)ethyl)thio)isoindoline-1,3-dione 4h: Prepared according to **General Method B** (Eluent: 50:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (730.7 mg, 2.62 mmol, 79.3% yield). **M.p.** = 90.1 – 90.9 ºC; **IR** (thin film) 1730 (m), 1706 (m), 1341 (w), 1278 (m), 1232 (w), 1045 (m), 865 (m), 712 (s) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.89 (2H, m), 7.77 – 7.75 (2H, m), 5.00 (1H, t, J = 4.1 Hz), 3.92 – 3.88 (2H, m), 3.81 – 3.78 (2H, m), 2.98 – 2.95 (2H, m), 2.02 – 1.98 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.6, 134.7, 132.1, 124.0, 102.6, 65.2, 33.2, 33.0; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{13}H_{14}NO_4S$: 280.0638, found: 280.0635.



2-((4-Chlorophenethyl)thio)isoindoline-1,3-dione 4i: Prepared according to **General Method B** (Eluent: 50:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (662.1 mg, 1.96 mmol, 59.5% yield). **M.p.** = 123.2 – 124.7 ºC; **IR** (thin film) 1781 (w), 1733 (s), 1709 (s), 1489 (w), 1466 (w), 1341 (w), 1280 (s), 1092 (m), 1051 (s), 1012 (m), 866 (m), 803 (m), 710 (s) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.89 (2H, m), 7.80 – 7.77 (2H, m), 7.19 – 7.13 (4H, m), 3.15 (2H, t, J = 7.3 Hz), 2.94 (2H, t, J = 7.4 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.6, 137.6, 134.8, 132.5, 132.1, 130.0, 128.7, 124.0, 39.4, 34.7; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{16}H_{12}ClNaNO_2S$: 340.0169, found: 340.0164.

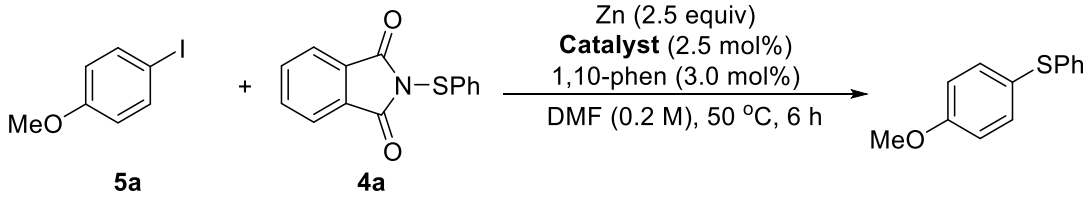
7. Synthesis of cyclopropylmethyl 4-bromobenzoate 5p:



An oven-dried 25-mL Schlenk tube, equipped with a stir bar, was charged with cyclopropylmethanol (505 mg, 7.00 mmol, 1.00 equiv), Et_3N (0.850 g, 8.40 mmol, 1.20 equiv), DMAP (8.55 mg,0.0700 mmol, 0.100 equiv), and DCM (14.0 mL). The mixture was cooled to 0 °C and 4-bromobenzoyl chloride (1.84 g, 8.40 mmol, 1.20 equiv) in DCM (14.0 mL) was added dropwise at 0 °C for 0.5 h under N_2. The reaction mixture was allowed to stir at room temperature for 12 h and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (Eluent: 50:1 to 20:1 petroleum ether: ethyl acetate) to obtain the product as a white solid (1.59 g, 6.23 mmol, 89.0% yield). **M.p.** = 49.2 – 50.8 °C; **IR** (thin film) 1698 (s), 1588 (m), 1484 (w), 1395 (w), 1345 (m), 1262 (s), 1173 (m), 1119 (s), 1101 (s), 1069 (m), 1011 (s), 959 (s), 849 (s), 751 (s), 681 (m) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (2H, d, J = 8.6 Hz), 7.57 (2H, d, J = 8.5 Hz), 4.14 (2H, d, J = 7.3 Hz), 1.28 – 1.21 (1H, m), 0.64 – 0.59 (2H, m), 0.38 – 0.34 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.1, 131.8, 131.3, 130.0, 128.0, 70.1, 10.0, 3.5; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{11}H_{11}NaO_2Br$: 276.9835, found: 276.9832.

III. Optimization of the reaction conditions

Table S1. Evaluation of different catalysts

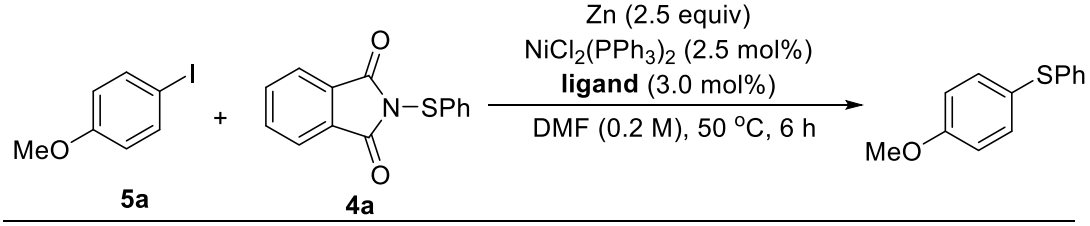


5a **4a**

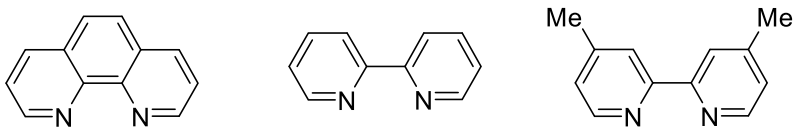
Entry	Catalyst	^{1}H NMR yield (%)
1	$Cu(OTf)_2$	<5
2	$CrCl_3$	<5
3	$PdCl_2(PPh_3)_2$	<5
4	$NiCl_2(PPh_3)_2$	>99
5	$NiBr_2$	98
6	$CoBr_2$	<5
7	$Ni(OAc)_2$	95

Reaction conditions: **5a** (0.500 mmol), Phth-SPh **4a** (1.00 mmol), **catalyst** (2.50 mol%), 1,10-phen (3.00 mol%), Zn (2.50 equiv), DMF (2.50 mL) at 50 °C for 6 h. Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table S2. Evaluation of different ligands

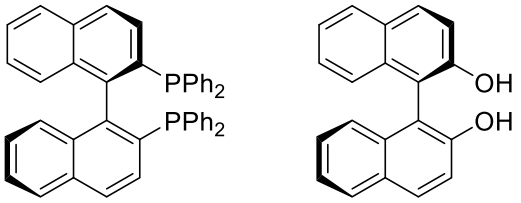


5a **4a**



DMAP

L1 99% yield | **L2** 88% yield | **L3** 92% yield | **L4** 7% yield

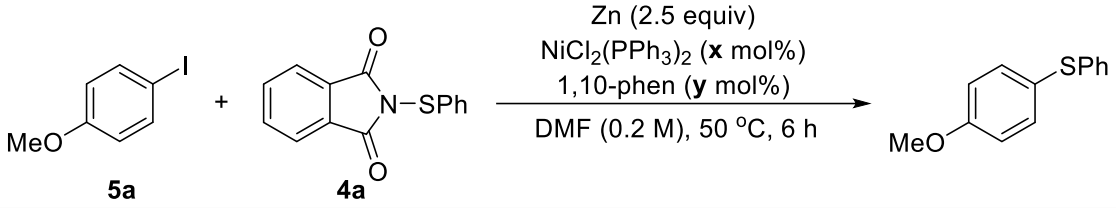


PPh_3 none

L5 29% yield | **L6** 10% yield | **L7** 6% yield | <5% yield

Reaction conditions: **5a** (0.500 mmol), Phth-SPh **4a** (1.00 mmol), $NiCl_2(PPh_3)_2$ (2.50 mol%), **ligand** (3.00 mol%), Zn (2.50 equiv), DMF (2.50 mL) at 50 °C for 6 h. Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table S3. Evaluation of different amounts of catalysts and ligands

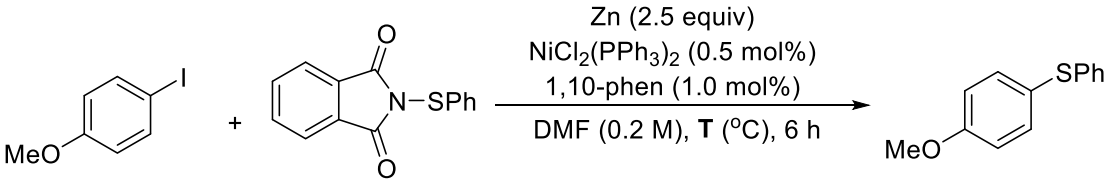


5a **4a**

Entry	**x**	**y**	^{1}H NMR yield (%)
1	2.5	3.0	>99
2	1.0	2.0	>99
3	0.5	1.0	>99
4	2.5	0	<1

Reaction conditions: **5a** (0.500 mmol), Phth-SPh **4a** (0.750 mmol), $NiCl_2(PPh_3)_2$ (**x** mol%), 1,10-phen (**y** mol%), Zn (2.50 equiv), DMF (2.50 mL) at 50 °C for 6 h. Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table S4. Evaluation of different temperature

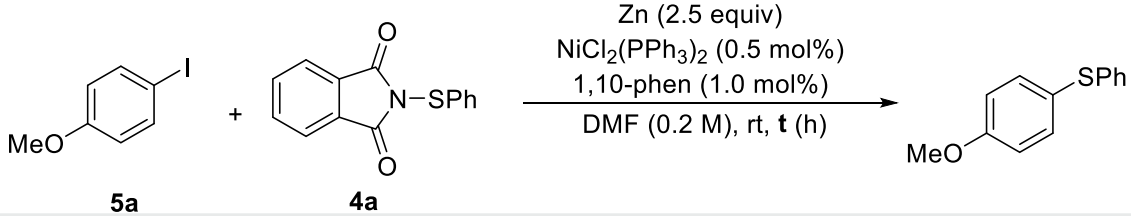


5a **4a**

Entry	**T** (°C)	^{1}H NMR yield (%)
1	50	>99
2	rt	>99

Reaction conditions: **5a** (0.500 mmol), Phth-SPh **4a** (0.600 mmol), $NiCl_2(PPh_3)_2$ (0.500 mol%), 1,10-phen (1.00 mol%), Zn (2.50 equiv), DMF (2.50 mL) at **T** °C for 2 h. Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table S5. Evaluation of different reaction time

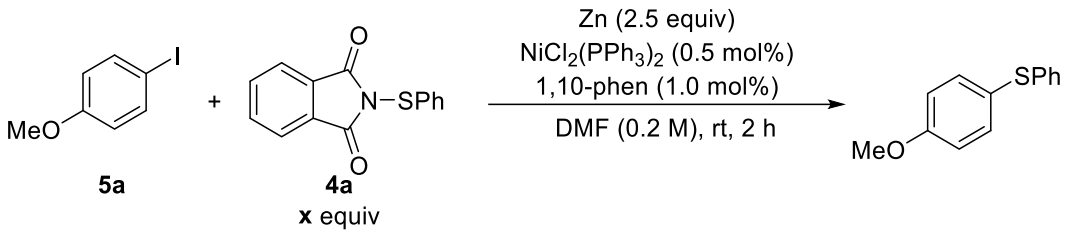


5a **4a**

Entry	**t** (h)	^{1}H NMR yield (%)
1	6	>99
2	2	>99
3	1	98
4	0.5	50

Reaction conditions: **5a** (0.500 mmol), Phth-SPh **4a** (0.600 mmol), $NiCl_2(PPh_3)_2$ (0.500 mol%), 1,10-phen (0.100 mol%), Zn (2.50 equiv), DMF (2.50 mL) at rt for **t** h. Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table S6. Evaluation of different amounts of reagent

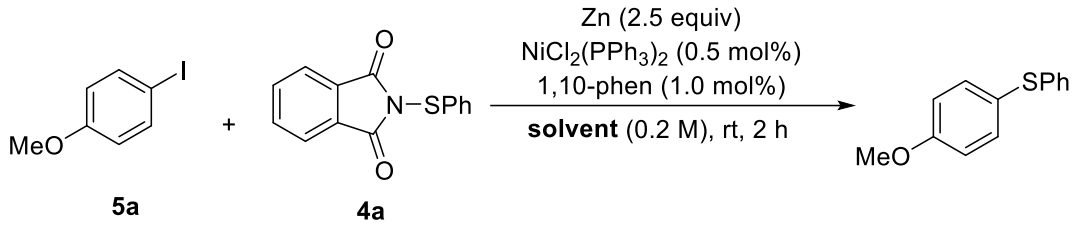


5a **4a** **x** equiv

Entry	**x** (equiv)	^{1}H NMR yield (%)
1	1.5	>99
2	1.2	>99

Reaction conditions: **5a** (0.500 mmol), Phth-SPh **4a** (**x** equiv), $NiCl_2(PPh_3)_2$ (0.500 mol%), 1,10-phen (1.00 mol%), Zn (2.50 equiv), DMF (2.50 mL) at rt for 2 h. Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table S7. Evaluation of different solvents

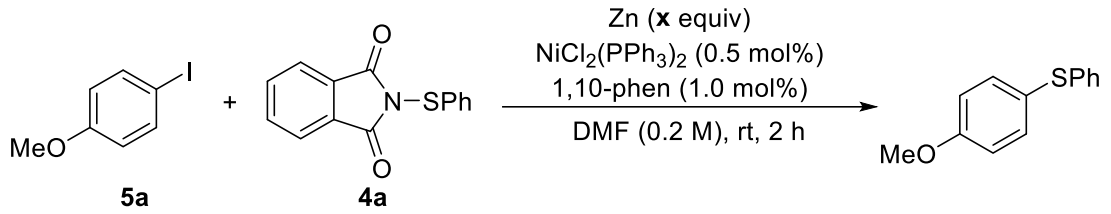


5a **4a**

Entry	**solvent**	^{1}H NMR yield (%)
1	THF	<5
2	MeOH	57
3	DMAc	>99
4	1,4-Dioxane	<5
5	DMSO	45
6	DCM	<5
7	DMF	>99

Reaction conditions: **5a** (0.500 mmol), Phth-SPh **4a** (0.600 mmol), $NiCl_2(PPh_3)_2$ (0.500 mol%), 1,10-phen (1.00 mol%), Zn (2.50 equiv), **solvent** (2.50 mL) at rt for 2 h. Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table S8. Evaluation of different amounts of Zinc

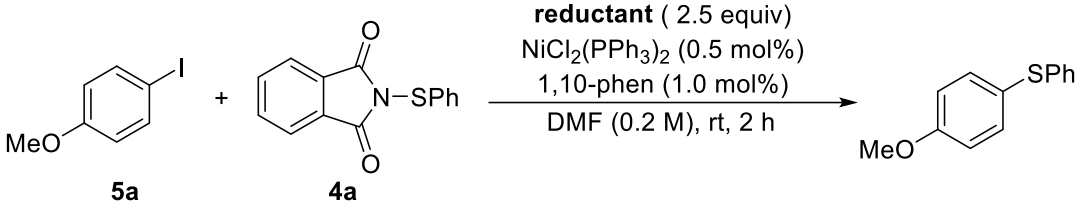


5a **4a**

Entry	**x** (equiv)	^{1}H NMR yield (%)
1	2.5	99
2	1.0	<5
3	0	<5

Reaction conditions: **5a** (0.500 mmol), Phth-SPh **4a** (0.600 mmol), $NiCl_2(PPh_3)_2$ (0.500 mol%), 1,10-phen (1.00 mol%), Zn (**x** equiv), DMF (2.50 mL) at rt for 2 h. Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table S9. Evaluation of different reductant



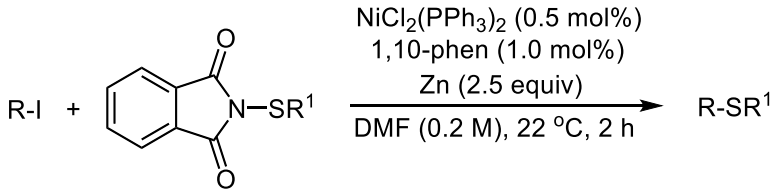
5a **4a**

Entry	**reductant**	^{1}H NMR yield (%)
1	Mn	<5
2	Fe	<5
3	Cu	<5
4	Zn	>99

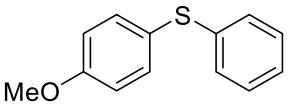
Reaction conditions: **5a** (0.500 mmol), Phth-SPh **4a** (0.600 mmol), $NiCl_2(PPh_3)_2$ (0.500 mol%), 1,10-phen (1.00 mol%), **reductant** (2.50 equiv), DMF (2.50 mL) at rt for 2 h. Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

IV. Substrate scope

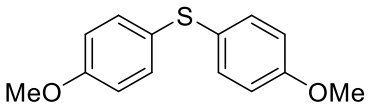
1. General Method C:



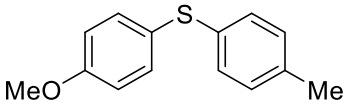
An 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with aryl(hetero)iodide (0.500 mmol, 1.00 equiv), Phth-SR^1 (0.600 mmol, 1.20 equiv), Zn (81.8 mg, 1.25 mmol, 2.50 equiv), $NiCl_2(PPh_3)_2$ (1.64 mg, 0.00250 mmol, 0.00500 equiv), 1,10-phenanthroline (0.900 mg, 0.00500 mmol, 0.0100 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for 2 h at 22 °C. After the addition was complete, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography.



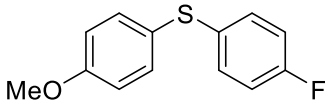
(4-Methoxyphenyl)(phenyl)sulfane 6a: Prepared according to **General Method C** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (94.0 mg, 0.435 mmol, 86.9% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (2H, m, J = 8.8 Hz), 7.23 – 7.09 (5H, m), 6.87 (2H, m, J = 8.8 Hz), 3.78 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.9, 138.7, 135.5, 129.0, 128.2, 125.8, 124.3, 115.1, 55.4. Spectra were consistent with literature data[5].



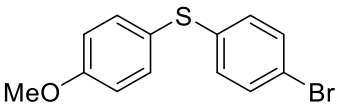
Bis(4-methoxyphenyl)sulfane 6b: Prepared according to **General Method C** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (112.3 mg, 0.456 mmol, 91.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (4H, d, J = 8.8 Hz), 6.86 (4H, d, J = 8.8 Hz), 3.80 (6H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.0, 132.8, 127.4, 114.8, 55.4. Spectra were consistent with literature data[6].



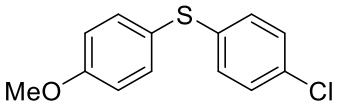
(4-Methoxyphenyl)(*p*-tolyl)sulfane 6c: Prepared according to **General Method C** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (102.0 mg, 0.443 mmol, 88.6% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (2H, d, J = 8.8 Hz), 7.12 (2H, d, J = 8.2 Hz), 7.05 (2H, d, J = 8.0 Hz), 6.85 (2H, d, J = 8.8 Hz), 3.78 (3H, s), 2.29 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.5, 136.2, 134.5, 134.5, 129.9, 129.5, 125.7, 115.0, 55.4, 21.1. Spectra were consistent with literature data[5].



(4-Chlorophenyl)(4-methoxyphenyl)sulfane 6d: Prepared according to **General Method C** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (103 mg, 0.440 mmol, 87.9% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (2H, d, J = 8.7 Hz), 7.21 – 7.17 (2H, m), 6.97 – 6.93 (2H, m), 6.87 (2H, d, J = 8.7 Hz), 3.80 (3H, s); **^{19}F NMR** (471 MHz, $CDCl_3$) δ –116 – –111 (1F, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.7 (d, $J_{C\text{-}F}$ = 246.9 Hz), 159.8, 134.6, 133.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 131.1 (d, $J_{C\text{-}F}$ = 8.1 Hz), 125.3, 116.2 (d, $J_{C\text{-}F}$ = 22.0 Hz), 115.1, 55.5. Spectra were consistent with literature data[5].

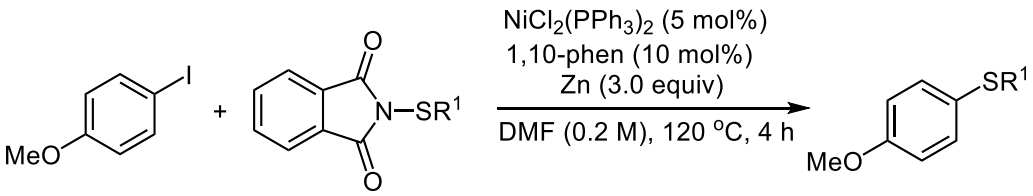


(4-Bromophenyl)(4-methoxyphenyl)sulfane 6e: Prepared according to **General Method C** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (119.6 mg, 0.405 mmol, 81.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (2H, d, J = 8.8 Hz), 7.33 (2H, d, J = 8.5 Hz), 7.00 (2H, d, J = 8.5 Hz), 6.91 (2H, d, J = 8.8 Hz), 3.83 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.2, 138.3, 135.8, 132.0, 129.6, 123.6, 119.5, 115.3, 55.5. Spectra were consistent with literature data[7].



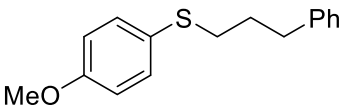
(4-Chlorophenyl)(4-methoxyphenyl)sulfane 6f: Prepared according to **General Method C** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (100.5 mg, 0.401 mmol, 80.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (2H, d, J = 8.7 Hz), 7.18 (2H, d, J = 8.6 Hz), 7.06 (2H, d, J = 8.6 Hz), 6.89 (2H, d, J = 8.7 Hz), 3.81 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.5, 137.8, 136.0, 132.0, 129.7, 129.4, 124.1, 115.5, 55.8. Spectra were consistent with literature data[7].

2. General Method D:

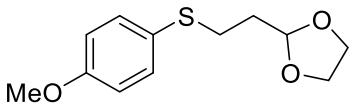


An 120 ºC oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with 4-iodoanisole (23.4 mg, 0.100 mmol, 1.00 equiv), Phth-SR^1 (0.200 mmol, 2.00 equiv), Zn (19.6 mg, 0.300 mmol, 3.00 equiv), $NiCl_2(PPh_3)_2$ (3.27 mg, 0.00500 mmol, 0.0500 equiv), 1,10-phenanthroline (1.80 mg, 0.0100 mmol, 0.100 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for 4 h at 120 ºC. After cooling to room temperature, the mixture was diluted with saturated

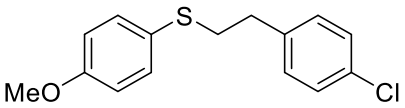
NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography.



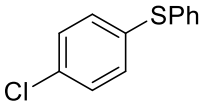
(4-Methoxyphenyl)(3-phenylpropyl)sulfane 6g: Prepared according to **General Method D** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (25.3 mg, 0.0979 mmol, 97.9% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (2H, d, J = 8.8 Hz), 7.30 – 7.24 (2H, m), 7.21 – 7.11 (3H, m), 6.82 (2H, d, J = 8.7 Hz), 3.77 (3H, s), 2.82 (2H, t, J = 7.2 Hz), 2.72 (2H, t, J = 7.6 Hz), 1.89 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 141.6, 133.3, 128.6, 128.5, 126.6, 126.0, 114.6, 55.4, 35.2, 34.7, 30.9. Spectra were consistent with literature data[5].



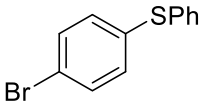
2-(2-((4-Methoxyphenyl)thio)ethyl)-1,3-dioxolane 6h: Prepared according to **General Method D** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (19.4 mg, 0.0810 mmol, 81.0% yield). **IR** (thin film) 2883 (w), 1592 (w), 1493 (s), 1284 (m), 1243 (s), 1174 (m), 1129 (s), 1029 (s), 878 (w), 825 (s), 638 (w) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (2H, d, J = 8.8 Hz), 6.84 (2H, d, J = 8.7 Hz), 4.95 (1H, t, J = 4.6 Hz), 3.97 – 3.82 (4H, m), 3.79 (3H, s), 2.93 – 2.89 (2H, m), 1.95 – 1.90 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.1, 133.4, 126.2, 114.7, 103.2, 65.1, 55.5, 33.8, 30.2; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{12}H_{16}NaO_3S$: 263.0712, found: 263.0723.



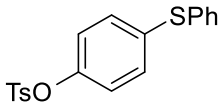
(4-Chlorophenethyl)(4-methoxyphenyl)sulfane 6i: Prepared according to **General Method D** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (26.8 mg, 0.961mmol, 96.1% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (2H, d, J = 8.8 Hz), 7.24 (2H, d, J = 8.4 Hz), 7.08 (2H, d, J = 8.4 Hz), 6.86 (2H, d, J = 8.7 Hz), 3.80 (3H, s), 3.03 (2H, t, J = 7.7 Hz), 2.82 (2H, t, J = 7.7 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 138.8, 133.6, 132.2, 130.0, 128.7, 126.1, 114.7, 55.5, 37.3, 35.3. Spectra were consistent with literature data[5].



(4-Chlorophenyl)(phenyl)sulfane 7a: Prepared according to **General Method C** (1.00 mol% $NiCl_2(PPh_3)_2$ and 2.00 mol% 1,10-phen were used) (Eluent: 500:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (102.7 mg, 0.465 mmol, 93.1% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.24 (9H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.2, 134.8, 133.1, 132.1, 131.5, 129.5, 129.5, 127.6. Spectra were consistent with literature data[5].

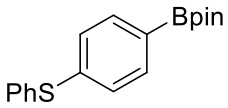


(4-Bromophenyl)(phenyl)sulfane 7b: Prepared according to **General Method C** (Eluent: 500:0 to 500:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (97.4 mg, 0.367 mmol, 73.5% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (2H, d, J = 8.5 Hz), 7.35 – 7.22 (5H, m), 7.15 (2H, d, J = 8.5 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.6, 134.9, 132.3, 132.2, 131.7, 129.5, 127.7, 121.0. Spectra were consistent with literature data[5].

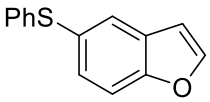


4-(Phenylthio)phenyl 4-methylbenzenesulfonate 7c: Prepared according to **General Method C** (1.00 mol% $NiCl_2(PPh_3)_2$, 2.00 mol% 1,10-phen were used.) (Eluent: 500:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white

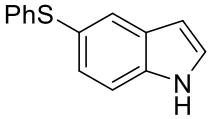
solid (151.1 mg, 0.424 mmol, 84.8 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (2H, d, J = 8.4 Hz), 7.35 – 7.28 (7H, m), 7.18 (2H, d, J = 8.8 Hz), 6.89 (2H, d, J = 8.8 Hz), 2.45 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.4, 145.6, 135.7, 134.5, 132.3, 132.0, 131.3, 129.9, 129.5, 128.6, 127.9, 123.2, 21.9. Spectra were consistent with literature data[5].



4,4,5,5-Tetramethyl-2-(4-(phenylthio)phenyl)-1,3,2-Dioxaborolane 7d: Prepared according to **General Method C** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (102.6 mg, 0.329 mmol, 65.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (2H, m, J = 8.2 Hz), 7.32 – 7.29 (2H, m), 7.25 – 7.15 (5H, m), 1.24 (12H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.5, 135.5, 134.6, 132.2, 129.4, 129.1, 127.7, 84.0, 25.0 (the signal of one carbon connected to B atom was not observed). Spectra were consistent with literature data[5].

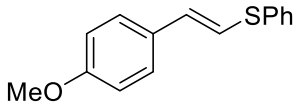


5-(Phenylthio)benzofuran 7e: Prepared according to **General Method C** (Eluent: 500:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (109.6 mg, 0.484 mmol, 96.9% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (1H, d, J = 1.3 Hz), 7.61 (1H, d, J = 2.2 Hz), 7.47 – 7.45 (1H, m), 7.38 (1H, dd, J = 8.6, 1.9 Hz), 7.23 – 7.22 (4H, m), 7.16 – 7.12 (1H, m), 6.71 (1H, d, J = 2.2 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.8, 146.0, 138.3, 129.8, 129.1, 129.0, 128.7, 127.9, 126.5, 126.2, 112.5, 106.6. Spectra were consistent with literature data[5].

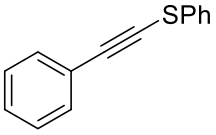


6-(Phenylthio)-1H-indole 7f: Prepared according to **General Method C** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (100 mg, 0.444 mmol, 88.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (1H, s), 7.85 – 7.84 (1H, m), 7.34 – 7.29 (2H, m), 7.21 – 7.14 (5H, m), 7.11 – 7.07 (1H,

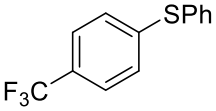
m), 6.53 – 6.51 (1H, m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.8, 135.7, 128.9, 128.9, 128.3, 127.7, 127.5, 125.4, 125.3, 123.0, 112.2, 102.9. Spectra were consistent with literature data[5].



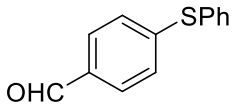
(*E*)-(4-methoxystyryl)(phenyl)sulfane 7g: Prepared according to **General Method C** (Eluent: petroleum ether) and the title compound was isolated as a colorless oil (98.6 mg, 0.407 mmol, 81.4 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (2H, d, J = 7.0 Hz), 7.33 – 7.27 (4H, m), 7.24 – 7.20 (1H, d, J = 8.0 Hz), 6.84 (2H, d, J = 8.8 Hz), 6.77 – 6.68 (2H, m), 3.79 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.5, 136.1, 132.9, 129.5, 129.3, 129.2, 127.5, 126.7, 120.1, 114.2, 55.4. Spectra were consistent with literature data[5].



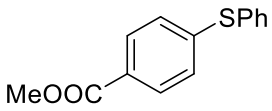
Phenyl(phenylethynyl)sulfane 7h: Prepared according to **General Method C** (Eluent: 500:0 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (30.1 mg, 0.143 mmol, 28.6% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (4H, m), 7.36 – 7.32 (5H, m), 7.24 – 7.20 (1H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.1, 132.6, 129.4, 129.2, 128.6, 127.6, 127.3, 121.9, 81.7, 74.0. Spectra were consistent with literature data[5].



Phenyl(4-(trifluoromethyl)phenyl)sulfane 7i: Prepared according to **General Method C** (Eluent: 500:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (105.3 mg, 0.414 mmol, 82.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.46 (4H, m), 7.41 – 7.38 (3H, m), 7.26 (2H, d, J = 9.0 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ – 62.5; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.0, 133.7, 132.6, 129.8, 129.2 128.8, 128.1 (q, $J_{C\text{-}F}$ = 33.0 Hz), 126.0 (q, $J_{C\text{-}F}$ = 3.8 Hz), 125.9 (q, $J_{C\text{-}F}$ = 272.8 Hz). Spectra were consistent with literature data[5].

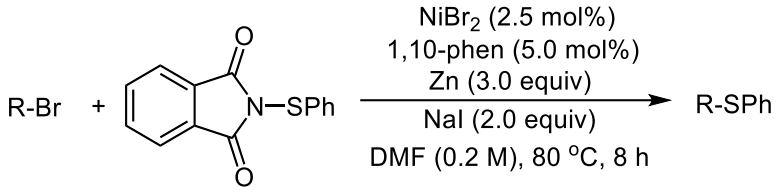


4-(Phenylthio)benzaldehyde 7j: Prepared according to **General Method C** (Eluent: 500:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (84.4 mg, 0.394 mmol, 78.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.89 (1H, s), 7.70 (2H, d, J = 8.4 Hz), 7.53 – 7.51 (2H, m), 7.43 – 7.40 (3H, m), 7.22 (2H, d, J = 8.4 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.2, 147.3, 134.4, 133.7, 131.3, 130.2, 129.9, 129.2, 127.2. Spectra were consistent with literature data[5].



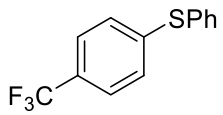
Methyl 4-(phenylthio)benzoate 7k: Prepared according to **General Method C** (Eluent: 500:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (113.1 mg, 0.463 mmol, 92.6% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (2H, d, J = 8.6 Hz), 7.49 – 7.47 (2H, m), 7.39 – 7.37 (3H, m), 7.19 (2H, d, J = 8.5 Hz), 3.88 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 144.5, 133.8, 132.4, 130.2, 129.7, 128.7, 127.6, 127.5, 52.2. Spectra were consistent with literature data[5].

3. General Method E:

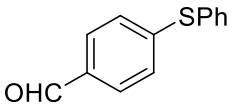


An 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with aryl(hetero)bromide (0.500 mmol, 1.00 equiv), Phth-SPh (255 mg, 1.00 mmol, 2.00 equiv), Zn (98.1 mg, 1.50 mmol, 3.00 equiv), $NiBr_2$ (2.73 mg, 0.0125 mmol, 0.0250 equiv), 1,10-phenanthroline (4.51 mg, 0.0250 mmol, 0.0500 equiv), NaI (149.9 mg, 1.00 mmol, 2.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for 8 h at 80 °C. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers

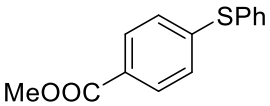
were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography.



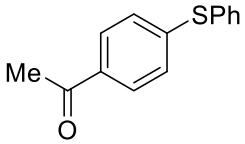
Phenyl(4-(trifluoromethyl)phenyl)sulfane 7l: Prepared according to **General Method E** (Eluent: 500:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (104.6 mg, 0.411 mmol, 82.2% yield). The structure of compound **7l** was the same with compound **7i**.



4-(Phenylthio)benzaldehyde 7m: Prepared according to **General Method E** (Eluent: 500:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (45.2 mg, 0.211 mmol, 42.2% yield). The structure of compound **7m** was the same with compound **7j**.

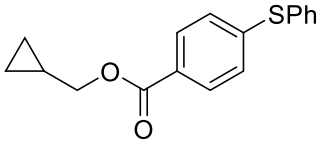


Methyl 4-(phenylthio)benzoate 7n: Prepared according to **General Method E** (Eluent: 500:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (98.4 mg, 0.403 mmol, 80.6% yield). The structure of compound **7n** was the same with compound **7k**.

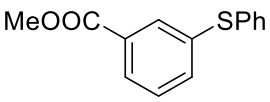


1-(4-(Phenylthio)phenyl)ethan-1-one 7o: Prepared according to **General Method E** (Eluent: 500:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (63.3 mg, 0.277 mmol, 55.5% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (2H, d, J = 8.5 Hz), 7.51 – 7.48 (2H, m), 7.41 – 7.39 (3H, m), 7.20 (2H,

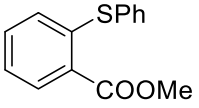
d, J = 8.5 Hz), 2.55 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.2, 145.0, 134.5, 134.0, 132.1, 129.8, 129.0, 128.9, 127.5, 26.6. Spectra were consistent with literature data[5].



Cyclopropylmethyl 4-(phenylthio)benzoate 7p: Prepared according to **General Method E** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (119.4 mg, 0.420 mmol, 84.0% yield). **IR** (thin film) 1712 (s), 1594 (m), 1475 (w), 1400 (w), 1345 (w), 1266 (s), 1177 (m), 1101 (s), 1014 (m), 962 (m), 846 (w), 746 (s), 689 (s) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (2H, d, J = 8.5 Hz), 7.49 – 7.47 (2H, m), 7.40 – 7.37 (3H, m), 7.22 (2H, d, J = 8.5 Hz), 4.13 (2H, d, J = 7.2 Hz), 1.27 – 1.21 (1H, m), 0.62 – 0.57 (2H, m), 0.36 – 0.33 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 144.3, 133.7, 132.6, 130.3, 129.8, 128.7, 128.0, 127.8, 69.8, 10.0, 3.4; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{17}H_{16}NaO_2S$: 307.0763, found: 307.0773.

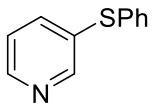


Methyl 3-(phenylthio)benzoate 7q: Prepared according to **General Method E** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (75.7 mg, 0.310 mmol, 62.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 – 8.00 (1H, m), 7.90 – 7.87 (1H, m), 7.47 – 7.45 (1H, m), 7.38 – 7.28 (6H, m), 3.89 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 137.2, 134.8, 134.7, 131.8, 131.5, 131.2, 129.5, 129.3, 128.1, 127.8, 52.4. Spectra were consistent with literature data[8].

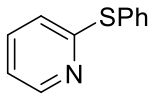


Methyl 2-(phenylthio)benzoate 7r: Prepared according to **General Method E** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (61.2 mg, 0.251 mmol, 50.1% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (1H, dd, J = 7.8, 1.6 Hz), 7.61 – 7.53 (2H, m), 7.47 – 7.39 (3H, m), 7.26 – 7.21 (1H,

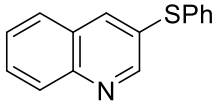
m), 7.14 – 7.10 (1H, m), 6.81 (1H, dd, J = 8.2, 1.2 Hz), 3.95 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 143.4, 135.7, 132.6, 132.5, 131.2, 129.9, 129.2, 127.5, 126.8, 124.4, 52.3. Spectra were consistent with literature data[9].



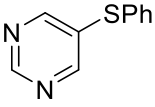
3-(Phenylthio)pyridine 7s: Prepared according to **General Method E** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow oil (58.6 mg, 0.313 mmol, 62.6% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 – 8.55 (1H, m), 8.47 – 8.45 (1H, m), 7.61 – 7.58 (1H, m), 7.39 – 7.30 (5H, m), 7.23 – 7.20 (1H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.1, 148.0, 138.0, 134.0, 133.8, 131.9, 129.6, 128.0, 124.0. Spectra were consistent with literature data[10].



2-(Phenylthio)pyridine 7t: Prepared according to **General Method E** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow oil (75.1 mg, 0.401 mmol, 80.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 – 8.40 (1H, m), 7.59 – 7.57 (2H, m), 7.42 – 7.39 (4H, m), 6.99 – 6.95 (1H, m), 6.87 (1H, d, J = 8.1 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.5, 149.5, 136.7, 134.9, 131.0, 129.6, 129.1, 121.3, 119.9. Spectra were consistent with literature data[5].

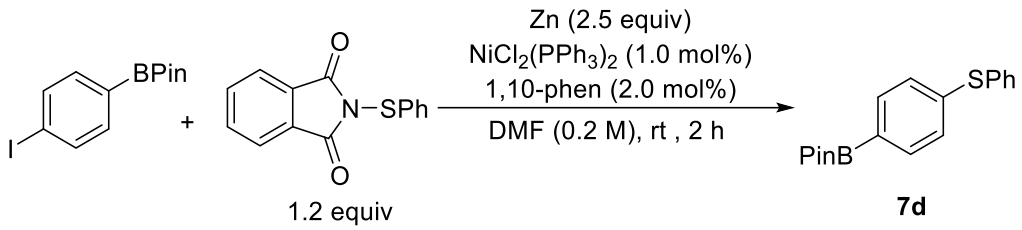


3-(Phenylthio)quinoline 7u: Prepared according to **General Method E** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow oil (61.8 mg, 0.260 mmol, 52.1% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.82 – 8.81 (1H, m), 8.09 – 8.06 (2H, m), 7.72 – 7.67 (2H, m), 7.56 – 7.52 (1H, m), 7.41 – 7.30 (5H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.3, 146.8, 137.2, 134.4, 131.5, 130.2, 129.7, 129.7, 129.4, 128.3, 127.9, 127.4, 127.4. Spectra were consistent with literature data[5].



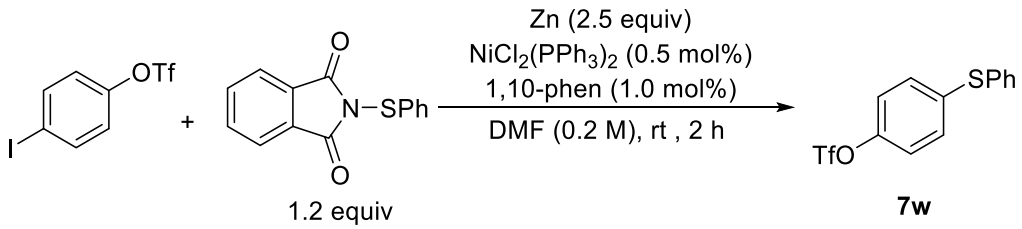
5-(Phenylthio)pyrimidine 7v: Prepared according to **General Method E** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (43.1 mg, 0.229 mmol, 45.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.03 (1H, s), 8.59 (2H, s), 7.46 – 7.37 (5H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.1, 156.3, 133.7, 132.8, 131.7, 130.0, 128.9. Spectra were consistent with literature data[11].

4. Synthesis of 4,4,5,5-tetramethyl-2-(4-(phenylthio)phenyl)-1,3,2-dioxaborolane 7d



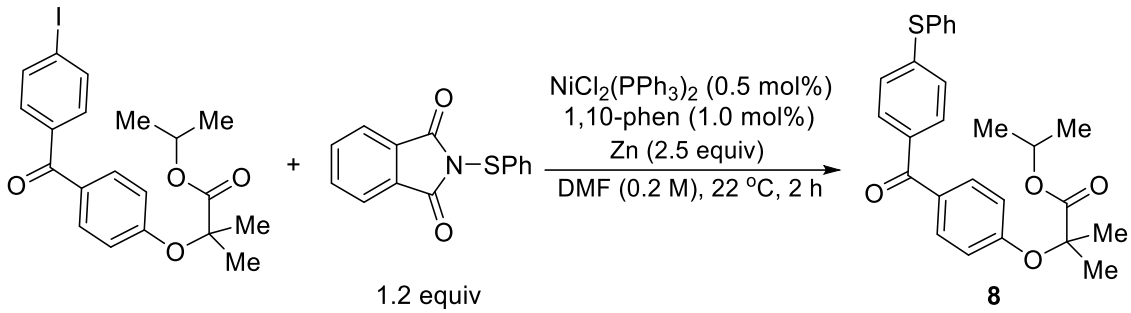
An 120 ºC oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.16 g, 3.50 mmol, 1.00 equiv), Phth-SPh (1.07 g, 4.20 mmol, 1.20 equiv), Zn (572 mg, 8.75 mmol, 2.50 equiv), $NiCl_2(PPh_3)_2$ (22.9 mg, 0.0350 mmol, 0.0100 equiv), 1,10-phenanthroline (12.6 mg, 0.0700 mmol, 0.0200 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (17.5 mL) was added under N_2 and the mixture was allowed to stir for 2 h at 22 ºC. After the addition was complete, the mixture was diluted with saturated NaCl aqueous solution (50.0 mL) and ethyl acetate (50.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (40.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (50.0 mL x 3), dried over Na_2SO_4 and filtered. The residue was purified by column chromatography on silica gel (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) to obtain the product as a white solid (819.6 mg, 2.62 mmol, 75.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (2H, m, J = 8.2 Hz), 7.32 – 7.29 (2H, m), 7.25 – 7.15 (5H, m), 1.24 (12H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.5, 135.5, 134.6, 132.2, 129.4, 129.1, 127.7, 84.0, 25.0 (the signal of one carbon connected to B atom was not observed). Spectra were consistent with literature data.

5. Synthesis of 5-(Phenylthio)phenyl trifluoromethanesulfonate 7w

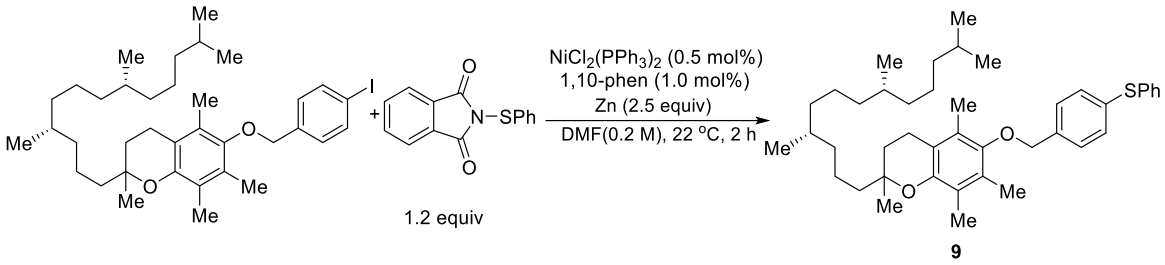


An 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with 4-iodophenyl trifluoromethanesulfonate (975 mg, 3.00 mmol, 1.00 equiv), Phth-SPh (919 mg, 3.60 mmol, 1.20 equiv), Zn (491 mg, 7.50 mmol, 2.50 equiv), $NiCl_2(PPh_3)_2$ (9.81 mg, 0.0150 mmol, 0.00500 equiv), 1,10-phenanthroline (5.40 mg, 0.0300 mmol, 0.0100 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (15.0 mL) was added under N_2 and the mixture was allowed to stir for 2 h at 22 °C. After the addition was complete, the mixture was diluted with saturated NaCl aqueous solution (50.0 mL) and ethyl acetate (50.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (40.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (50.0 mL x 3), dried over Na_2SO_4 and filtered. The residue was purified by column chromatography on silica gel (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) to obtain the product as a colorless oil (840.9 mg, 2.52 mmol, 83.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.42 (2H, m), 7.38 – 7.34 (3H, m), 7.27 (2H, d, J = 8.8 Hz), 7.15 (2H, d, J = 8.9 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ –72.8; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.0, 138.5, 133.3, 133.0, 130.7, 129.8, 128.6, 122.1, 118.8 (q, $J_{C\text{-}F}$ = 322.1 Hz). Spectra were consistent with literature data[5].

V. Late-stage thiolation of complex molecules

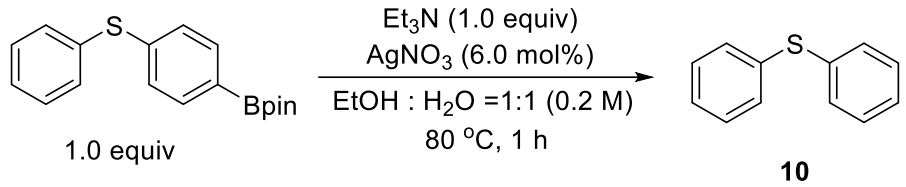


An 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with isopropyl 2-(4-(4-iodobenzoyl)phenoxy)-2-methylpropanoate (226 mg, 0.500 mmol, 1.00 equiv), Phth-SPh (153 mg, 0.600 mmol, 1.20 equiv), Zn (81.8 mg, 1.25 mmol, 2.50 equiv), $NiCl_2(PPh_3)_2$ (1.64 mg, 0.00250 mmol, 0.00500 equiv), 1,10-phenanthroline (0.900 mg, 0.00500 mmol, 0.0100 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for 2 h at 22 °C. After the addition was complete, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel (Eluent: 500:1 to 20:1 petroleum ether: ethyl acetate) to obtain the product as a white solid (212.8 mg, 0.490 mmol, 97.9% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (2H, d, J = 8.8 Hz), 7.65 (2H, d, J = 8.4 Hz), 7.51 – 7.48 (2H, m), 7.40 – 7.36 (3H, m), 7.24 (2H, d, J = 8.4 Hz), 6.86 (2H, d, J = 8.8 Hz), 5.11 – 5.05 (1H, m), 1.65 (6H, s), 1.20 (6H, d, J = 6.3 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.6, 173.2, 159.5, 143.4, 135.5, 133.7, 132.5, 132.0, 130.6, 130.6, 129.7, 128.7, 127.6, 117.2, 79.4, 69.4, 25.4, 21.6. Spectra were consistent with literature data[5].

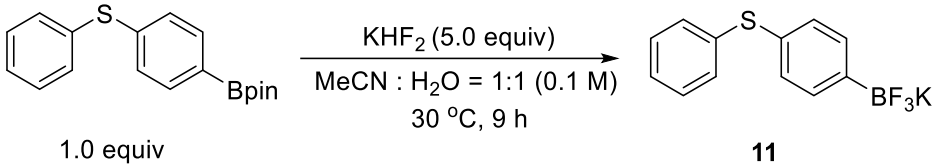


An 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with 6-((4-iodobenzyl)oxy)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8, 12-trimethyltridecyl) chromane (323 mg, 0.500 mmol, 1.00 equiv), Phth-SPh (153 mg, 0.600 mmol, 1.20 equiv), Zn (81.8 mg, 1.25 mmol, 2.50 equiv), $NiCl_2(PPh_3)_2$ (1.64 mg, 0.00250 mmol, 0.00500 equiv), 1,10-phenanthroline (0.900 mg, 0.00500 mmol, 0.0100 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for 2 h at 22 °C. After the addition was complete, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel (Eluent: 500:1 to 20:1 petroleum ether: ethyl acetate) to obtain the product as a colorless oil (273.3 mg, 0.434 mmol, 86.9% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (2H, d, J = 8.1 Hz), 7.36 – 7.31 (4H, m), 7.27 – 7.23 (2H, m), 7.20 – 7.19 (1H, m), 4.64 (2H, s), 2.56 (2H, t, J = 6.8 Hz), 2.19 (3H, s), 2.14 (3H, s), 2.10 (3H, s), 1.84 – 1.70 (2H, m), 1.54 – 1.08 (24H, m), 0.87 – 0.84 (12H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.1, 148.0, 137.2, 136.1, 135.1, 131.4, 130.9, 129.2, 128.6, 127.9, 127.0, 125.9, 123.0, 117.7, 74.9, 74.2, 40.1, 39.5, 37.6, 37.5, 37.4, 32.9, 32.8, 31.4, 28.1, 24.9, 24.6, 24.0, 22.9, 22.8, 21.1, 20.8, 19.9, 19.8, 13.0, 12.1, 12.0. Spectra were consistent with literature data[5].

VI. Derivations of the products

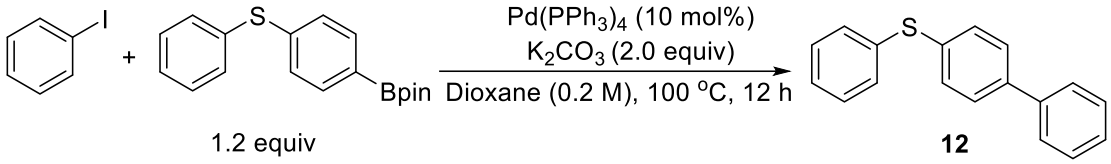


An 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with 4,4,5,5-tetramethyl-2-(4-(phenylthio)phenyl)-1,3,2-dioxaborolane (62.4 mg, 0.200 mmol, 1.00 equiv), $AgNO_3$ (2.04 mg, 0.0120 mmol, 0.0600 equiv), Et_3N (20.2 mg, 0.200 mmol, 1.00 equiv) and EtOH/H_2O (0.500 mL/0.500 mL). The mixture was stirred at 80 °C for 1 h in air. The aqueous solution was then washed with ethyl acetate (2.00 mL x 3). The combined organic layers were dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 500:1 to 100:1 petroleum ether: ethyl acetate)[12]. The product was isolated as colorless oil (34.9 mg, 0.187 mmol, 93.7% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.32 (4H, m), 7.32 – 7.27 (4H, m), 7.26 – 7.22 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.9, 131.1, 129.3, 127.1. Spectra were consistent with literature data[11].

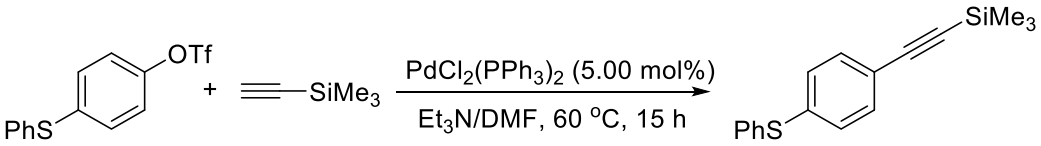


An oven-dried 25-mL Schlenk tube, equipped with a stir bar, was charged with 4,4,5,5-tetramethyl-2-(4-(phenylthio)phenyl)-1,3,2-dioxaborolane (62.4 mg, 0.200 mmol, 1.00 equiv), KHF_2 (78.1 mg, 1.00 mmol, 5.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. MeCN/H_2O (1.00 mL/1.00 mL) was added under N_2. The mixture was vigorously stirred 9 h at 30 °C. Then the mixture concentrated under reduced pressure. The remaining solids were extracted with boiling acetone (5.00 mL x 2) and twice with acetone at room temperature (5.00 mL x 2). The acetone was removed under reduced pressure and the remaining solid was dissolved in a minimum amount of boiling acetone, before being treated with

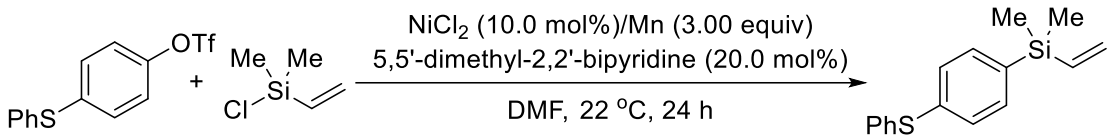
diethyl ether, which resulted in precipitation of a white solid. The solids were filtered, washed with diethyl ether and dried in vacuo to product. The product was isolated as a white solid (31.5 mg, 0.108 mmol, 53.9% yield)[13]. **M.p.** = 193.6 – 194.3 °C; **IR** (thin film) 1592 (w), 1477 (w), 1222 (m), 1080 (w), 966 (s), 828 (s), 811 (s), 735 (s), 689 (s) cm^{-1}; **^{1}H NMR** (400 MHz, CD_3COCD_3) δ 7.53 (2H, d, J = 7.7 Hz), 7.28 – 7.23 (4H, m), 7.17 – 7.13 (3H, m); **^{19}F NMR** (471 MHz, CD_3COCD_3) δ –143.0; **^{13}C NMR** (101 MHz, CD_3COCD_3) δ 139.8, 133.9, 133.9, 132.5, 129.9, 129.8, 129.1, 126.5; **HRMS** (ESI^+) $[M+K]^+$ calc'd for $C_{12}H_9BF_3SK_2$: 329.9775, found: 329.9767.



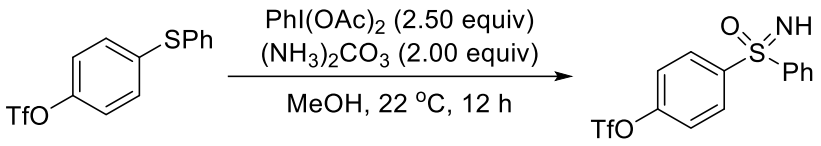
An 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with 4,4,5,5-tetramethyl-2-(4-(phenylthio)phenyl)-1,3,2-dioxaborolane (74.9 mg, 0.240 mmol, 1.20 equiv), iodobenzene (40.8 mg, 0.200 mmol, 1.00 equiv), $Pd(PPh_3)_4$ (14.0 mg, 0.0200 mmol, 0.100 equiv), K_2CO_3 (55.3 mg, 0.400 mmol, 2.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. The dry dioxane (1.00 mL) was added under N_2 and the mixture was allowed to stir for 12 h at 100 °C. After completion of the reaction, the mixture was diluted with H_2O (15.0 mL) and extracted with ethyl acetate (15.0 mL x 3). The combined organic layers were washed with H_2O (15.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) to provide the desired product as a white solid (38.4 mg, 0.146 mmol, 73.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.56 (2H, m), 7.54 – 7.52 (2H, m), 7.45 – 7.36 (6H, m), 7.34 – 7.24 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.4, 140.1, 135.8, 135.0, 131.4, 131.3, 129.4, 129.0, 128.0, 127.6, 127.3, 127.1. Spectra were consistent with literature data[8].



An 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with 4-(phenylthio)phenyl trifluoromethanesulfonate (167.0 mg, 0.500 mmol, 1.00 equiv), and bis(triphenylphosphine)palladium (II) dichloride (21.1 mg, 0.0250 mmol, 0.0500 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry Et_3N (0.500 mL) and DMF (1.50 mL) was added under N_2. After standing for 5 min at room temperature, the ethynyltrimethylsilane (58.5 mg, 0.600 mmol, 1.20 equiv) was added into the reaction mixture and the mixture was allowed to stir for 15 h at 60 °C. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (15.0 mL × 3). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 mL × 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) to provide the desired product as a colorless oil (95.5 mg, 0.428 mmol, 86.7% isolated yield). D-inc. >99% (determined by ^{1}H NMR). **IR** (thin film) 2155 (m), 1489 (m), 1249 (m), 1094 (w), 841 (s), 759 (m), 697 (m), 664 (w) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (2H, d, J = 8.5 Hz), 7.06 (2H, d, J = 8.5 Hz), 0.19 (9H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.7, 132.3, 125.6, 119.4, 105.0, 94.2, 15.0 – 14.3 (m, C-D_3), 0.1; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{12}H_{14}D_3SSi$: 224.1003, found: 224.1008.

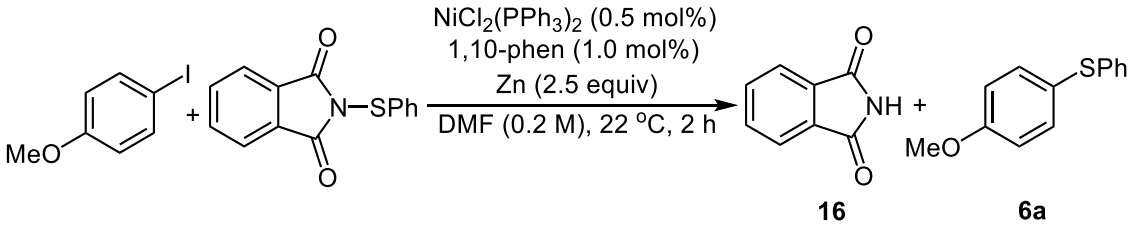


A 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with 4-(phenylthio)phenyl trifluoromethanesulfonate (167.0 mg, 0.500 mmol, 1.00 equiv), Mn (82.5 mg, 1.25 mmol, 2.50 equiv), $NiCl_2$ (6.50 mg, 0.0500 mmol, 0.0100 equiv), 5,5'-dimethyl-2,2'-bipyridine (18.5 mg, 0.100 mmol, 0.0200 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) and chlorosilane (180.0 mg, 1.50 mmol, 3.00 equiv) were added under N_2 and the mixture was allowed to stir for 24 h at 22 °C. After the addition was complete, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL × 3). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 mL × 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) to provide the desired product as a colorless oil (126.5 mg, 0.449 mmol, 89.7% yield). **IR** (thin film) 1577 (w), 1477 (w), 1249 (w), 1074 (w), 1007 (w), 954 (w), 818 (s), 773 (s), 738 (m), 690 (s), 619 (w) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.41 (2H, m), 7.39 – 7.37 (2H, m), 7.32 – 7.25 (5H, m), 7.30 – 7.21 (1H, m), 6.06 – 6.02 (1H, m), 5.77 – 5.71 (1H, m), 0.32 (6H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.8, 137.6, 136.8, 135.0, 134.7, 133.2, 131.9, 129.5, 129.4, 127.5, –2.8; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{16}H_{19}SSi$: 271.0971, found: 271.0968.



An 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 4-(phenylthio)phenyl trifluoromethanesulfonate (167 mg, 0.500 mmol, 1.00 equiv), $PhI(OAc)_2$ (403 mg, 1.25 mmol. 2.50 equiv) and ammonium carbamate (78.1 mg, 1.00 mmol, 2.00 equiv) and methanol (1.25 mL). The mixture was stirred at 22 °C for 12 h. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 30:1 to 1:4 petroleum ether: ethyl acetate) to provide the desired product as a yellow solid (167.2 mg, 0.458 mmol, 73.0% yield). M.p. = 81.0 – 81.6 °C; IR (thin film) 1483 (w), 1418 (s), 1227 (s), 1200 (s), 1131 (s), 1092 (s), 985 (m), 890 (s), 784 (m), 757 (m), 706 (m), 688 (m), 652 (s) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (2H, d, J = 8.9 Hz), 8.06 – 8.03 (2H, m), 7.58 – 7.50 (3H, m), 7.38 (2H, d, J = 8.9 Hz), 3.18 (1H, s); **^{19}F NMR** (471 MHz, $CDCl_3$) δ –72.7; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.9, 143.9, 142.5, 133.2, 130.5, 129.4, 128.1, 122.2, 118.6 (q, $J_{C\text{-}F}$ = 322.3 Hz); HRMS (ESI+) $[M+K]^+$ calc'd for $C_{13}H_{10}O_4F_3S_2NK$: 403.9635, found: 403.9646.

VII. Scale up reaction and recycle of phthalimide

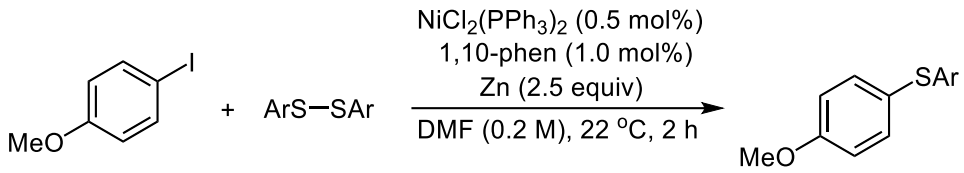


An 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with 4-iodoanisole (468 mg, 2.00 mmol, 1.00 equiv), Phth-SPh (613 mg, 2.40 mmol, 1.20 equiv), Zn (327 mg, 5.00 mmol, 2.50 equiv), $NiCl_2(PPh_3)_2$ (6.54 mg, 0.0100 mmol, 0.00500 equiv), 1,10-phenanthroline (3.60 mg, 0.0200 mmol, 0.0100 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (10.0 mL) was added under N_2 and the mixture was allowed to stir for

2 h at 22 °C. After the addition was complete, the mixture was diluted with saturated NaCl aqueous solution (30.0 mL) and ethyl acetate (30.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (30.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation to get the mixture. The mixture is washed with petroleum ether and filtered through aCelite pad to obtain the product (4-methoxyphenyl)(phenyl)sulfane (426.3 mg, 1.97 mmol, 98.5% yield) and the white solid (293.8 mg, 1.99 mmol, 99.9% yield) isoindoline-1,3-dione. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.87 (2H, m), 7.78 – 7.76 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.1, 134.5, 132.8, 123.8. Spectra were consistent with literature data[14].

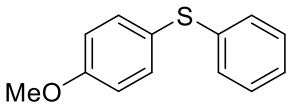
VIII. Reductive thiolation utilizing disulfides

General Method E:

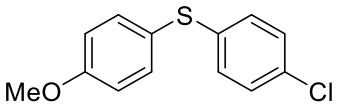


An 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with 4-iodoanisole (117 mg,0.500 mmol, 1.00 equiv), ArS-SAr (0.600 mmol, 1.20 equiv), Zn (81.8 mg, 1.25 mmol, 2.50 equiv), $NiCl_2(PPh_3)_2$ (1.64 mg, 0.00250 mmol, 0.00500 equiv), 1,10-phenanthroline (0.0900 mg, 0.00500 mmol, 0.0100 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for 2 h at 22 °C. After the addition was complete, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 2). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 mL x 2), dried over Na_2SO_4 and filtered.

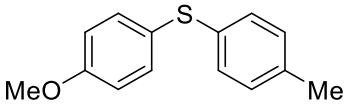
The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography.



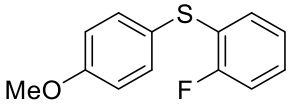
(4-Methoxyphenyl)(phenyl)sulfane 18a: Prepared according to **General Method E** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (107.9 mg, 0.499 mmol, 99.8% yield). The structure of compound **18a** was the same with compound **6a**.



(4-Chlorophenyl)(4-methoxyphenyl)sulfane 18b: Prepared according to **General Method E** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (86.4 mg, 0.345 mmol, 68.9% yield). The structure of compound **18b** was the same with compound **6f**.



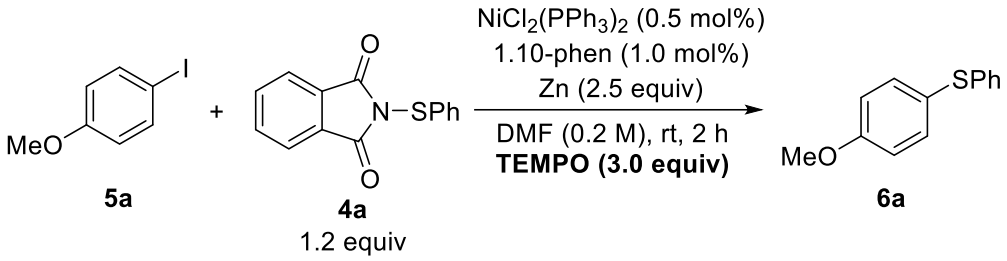
(4-Methoxyphenyl)(p-tolyl)sulfane 18c: Prepared according to **General Method E** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (96.0 mg, 0.417 mmol, 83.4% yield). The structure of compound **18c** was the same with compound **6c**.



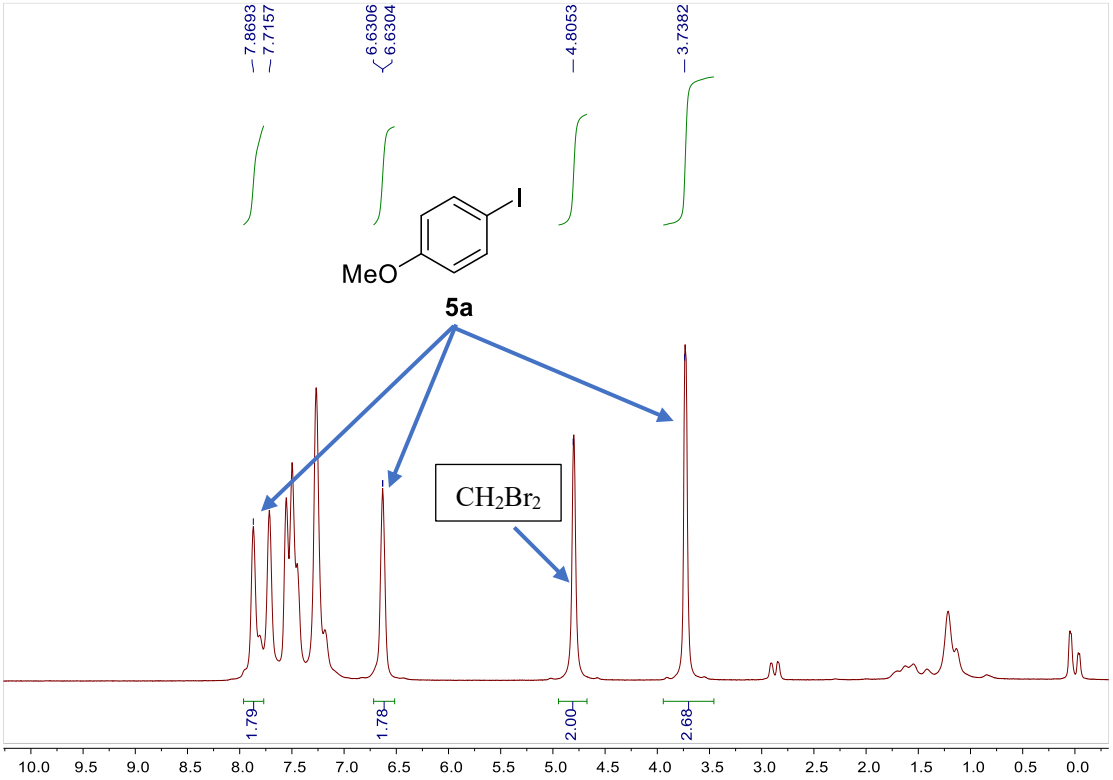
(2-Fluorophenyl)(4-methoxyphenyl)sulfane 18d: Prepared according to **General Method E** (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (101.3 mg, 0.432 mmol, 86.5% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (2H, d, J = 8.8 Hz), 7.14 – 7.11 (1H, m), 7.04 – 6.96 (3H, m), 6.89 (2H, d, J = 8.8 Hz), 3.80 (3H, s); **^{19}F NMR** (471 MHz, $CDCl_3$) δ –111; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.1, 159.8 (d, $J_{C\text{-}F}$ = 246.0 Hz) , 135.6, 130.5 (d, $J_{C\text{-}F}$ = 2.1 Hz), 127.8 (d, $J_{C\text{-}F}$ = 7.7 Hz), 125.8 (d, $J_{C\text{-}F}$ = 17.2 Hz), 124.6 (d, $J_{C\text{-}F}$ = 3.6 Hz), 122.6 (d, $J_{C\text{-}F}$ =

1.4 Hz), 115.6 (d, $J_{C\text{-}F}$ = 21.8 Hz), 115.2, 55.4. Spectra were consistent with literature data[5].

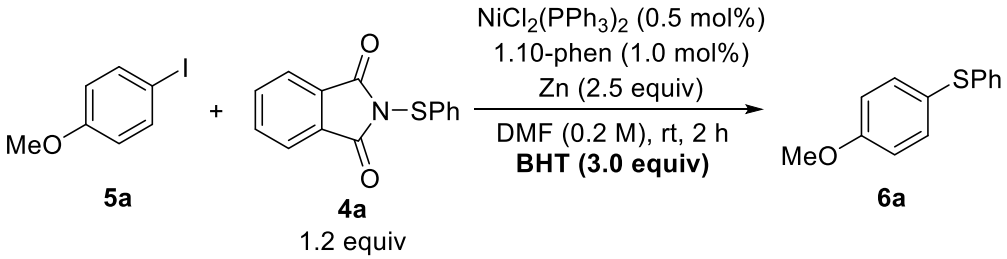
IX. Mechanistic studies



An 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with 4-iodoanisole (117 mg, 0.500 mmol, 1.00 equiv), Phth-SPh (153 mg, 0.600 mmol, 1.20 equiv), Zn (81.8 mg, 1.25 mmol, 2.50 equiv), $NiCl_2(PPh_3)_2$ (1.64 mg, 0.00250 mmol, 0.00500 equiv), 1,10-phenanthroline (0.900 mg, 0.00500 mmol, 0.0100 equiv), 2,2,6,6-tetramethyl-1-piperidinyloxy (Tempo) (234 mg, 1.50 mmol, 3.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for 2 h at 25 °C. After the addition was complete, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 2). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 mL x 2), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^1H NMR spectroscopy in the presence of CH_2Br_2 (86.9 mg, 0.500 mmol).

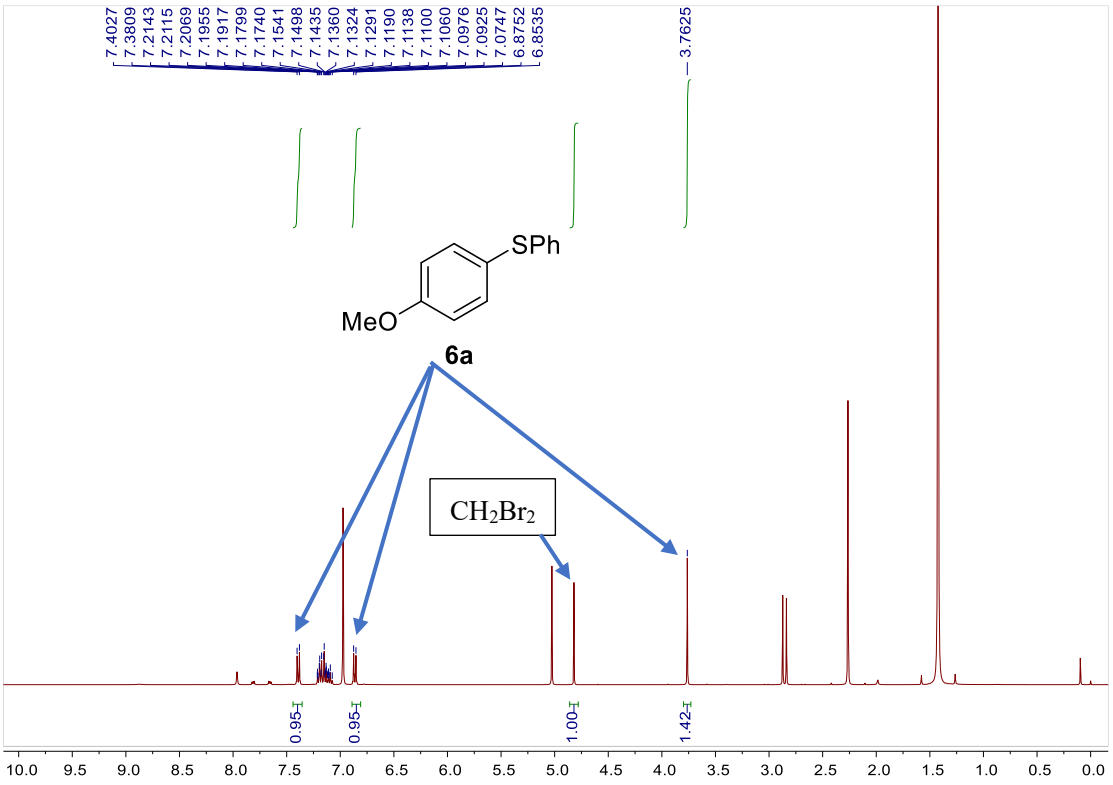


Tempo as the additive in the reductive coupling

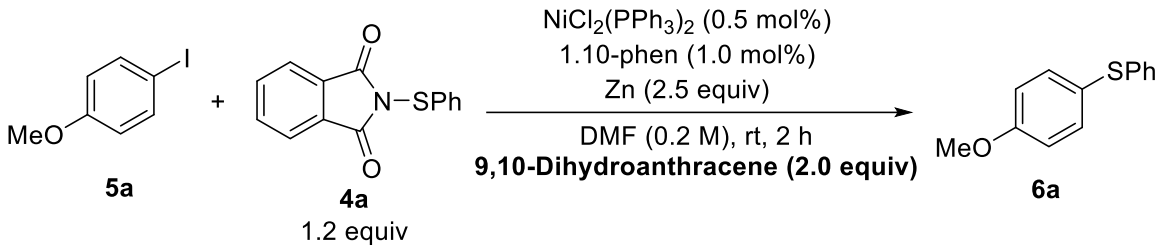


An 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with 4-iodoanisole (117 mg, 0.500 mmol, 1.00 equiv), Phth-SPh (153 mg, 0.600 mmol, 1.20 equiv), Zn (81.8 mg, 1.25 mmol, 2.50 equiv), $NiCl_2(PPh_3)_2$ (1.64 mg, 0.00250 mmol, 0.00500 equiv), 1,10-phenanthroline (0.900 mg, 0.00500 mmol, 0.0100 equiv), 2,6-di-*tert*-butyl-4-methylphenol (BHT) (331 mg, 1.50 mmol, 3.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for 2 h at 22 °C. After the addition was complete, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 2). The combined organic layers were

washed with saturated NaCl aqueous solution (15.0 mL x 2), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^1H NMR spectroscopy in the presence of CH_2Br_2 (86.9 mg, 0.500 mmol).

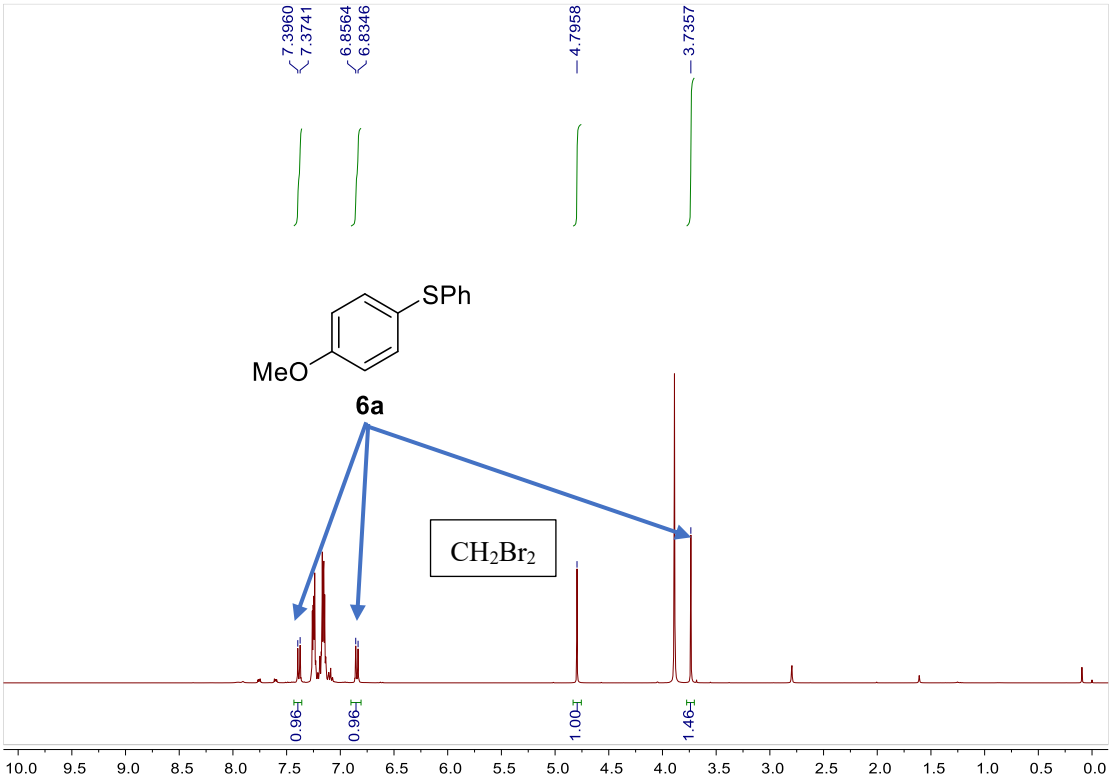


BHT as the additive in the reductive coupling

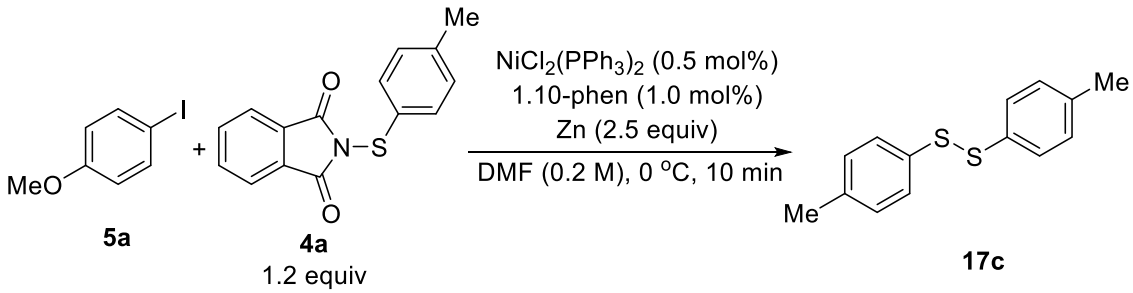


An 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with 4-iodoanisole (117 mg, 0.500 mmol, 1.00 equiv), Phth-SPh (153 mg, 0.600 mmol, 1.20 equiv), Zn (81.8 mg, 1.25 mmol, 2.50 equiv), $NiCl_2(PPh_3)_2$ (1.64 mg, 0.00250 mmol, 0.00500 equiv), 1,10-phenanthroline (0.900 mg, 0.00500 mmol, 0.0100 equiv), 9,10-Dihydroanthracene (180 mg, 1.00 mmol, 2.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for

2 h at 22 °C. After the addition was complete, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 2). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 mL x 2), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^1H NMR spectroscopy in the presence of CH_2Br_2 (86.9 mg, 0.500 mmol).

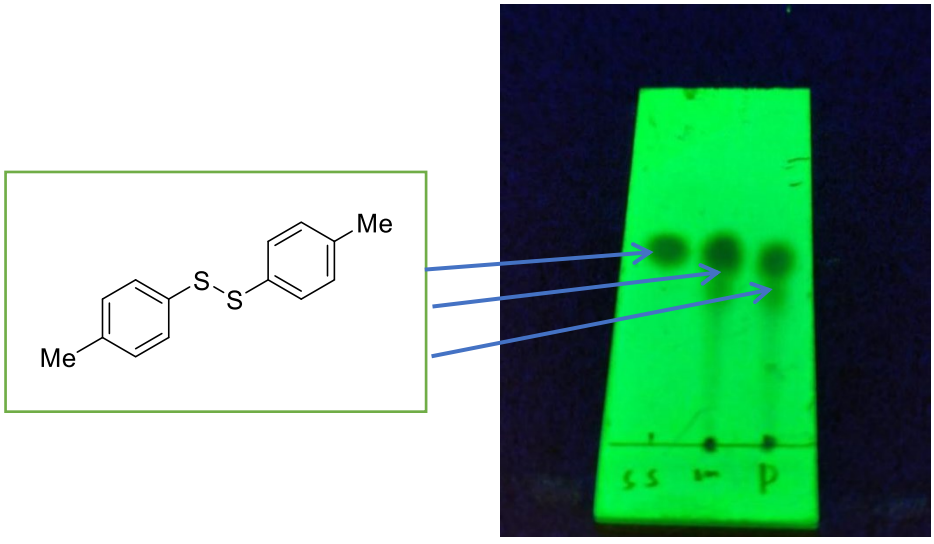


9,10-Dihydroanthracene as the additive in the reductive coupling

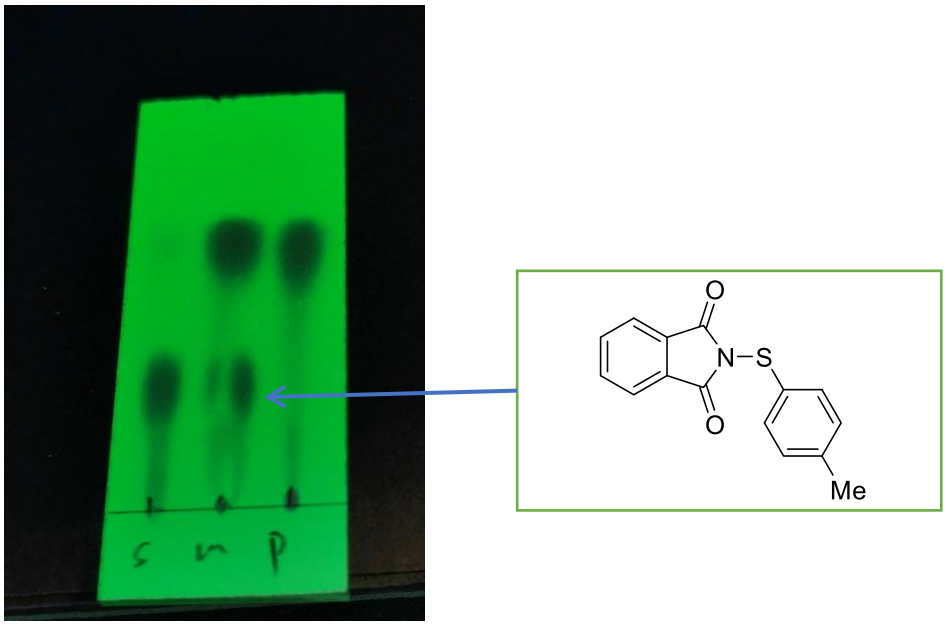


An 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with 4-iodoanisole (117 mg, 0.500 mmol, 1.00 equiv), 2-(*p*-tolylthio)isoindoline-1,3-dione (171 mg, 0.600 mmol, 1.20 equiv), Zn (81.8 mg, 1.25 mmol, 2.50 equiv),

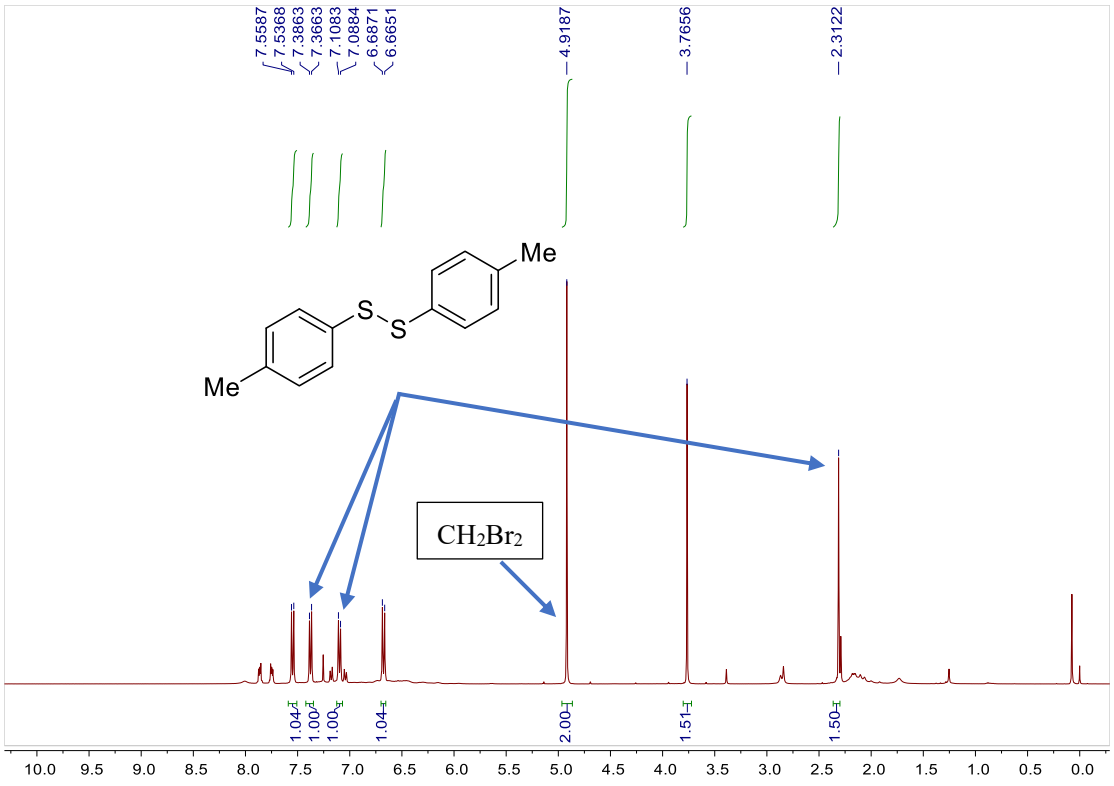
$NiCl_2(PPh_3)_2$ (1.64 mg, 0.00250 mmol, 0.00500 equiv), 1,10-phenanthroline (0.900 mg, 0.00500 mmol, 0.0100 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for 10 min at 0 °C. After the addition was complete, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 2). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 mL x 2), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to GC-MS and ^1H NMR spectroscopy in the presence of CH_2Br_2 (86.9 mg, 0.500 mmol).

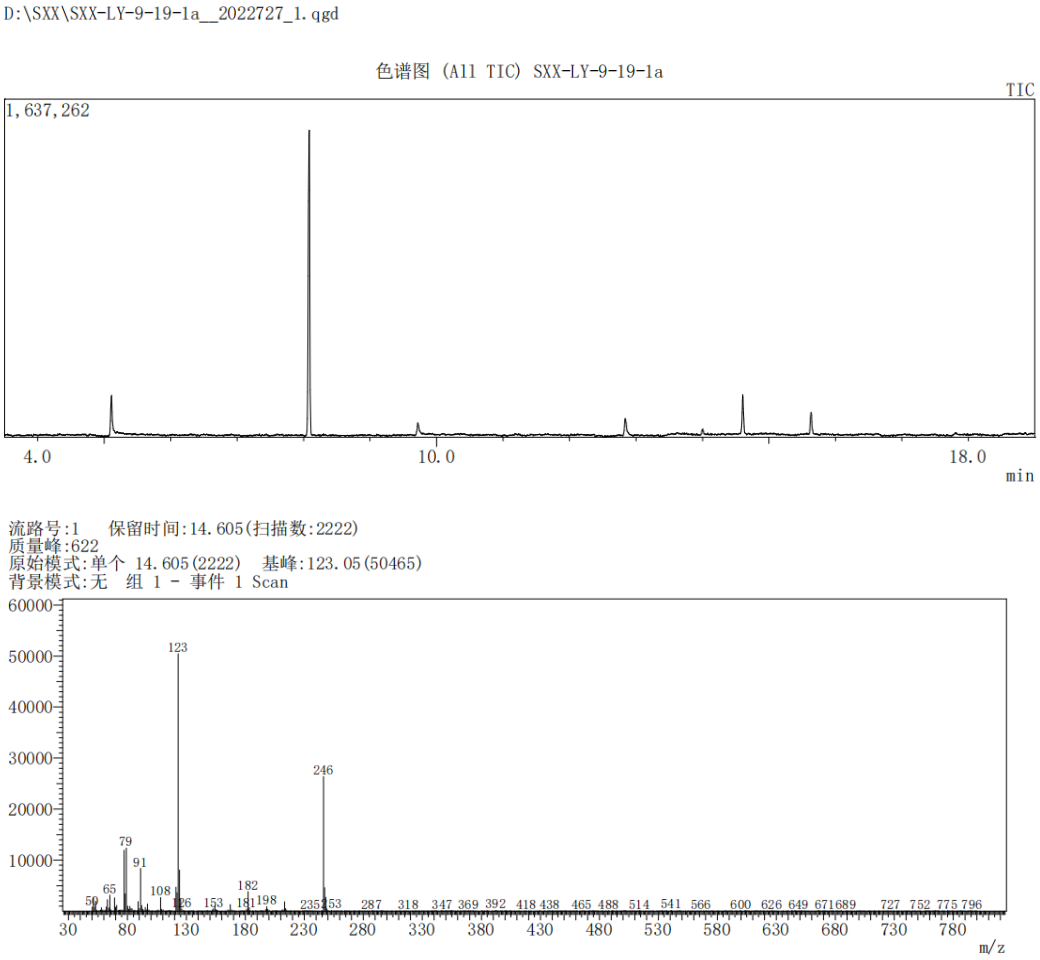


(PE)

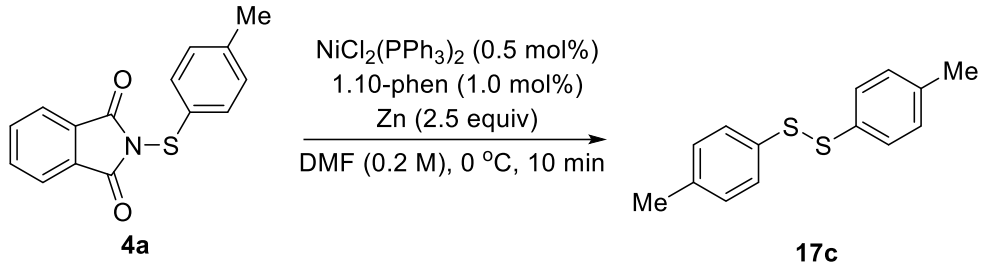

O
N–S
O
Me

(PE:EA=5:1)


7.5587
7.5368
7.3863
7.3663
7.1083
7.0884
6.6871
6.6651
4.9187
3.7656
2.3122
Me
S
S
Me
CH2Br2
1.04
1.00
1.00
1.04
2.00
1.51
1.50
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0



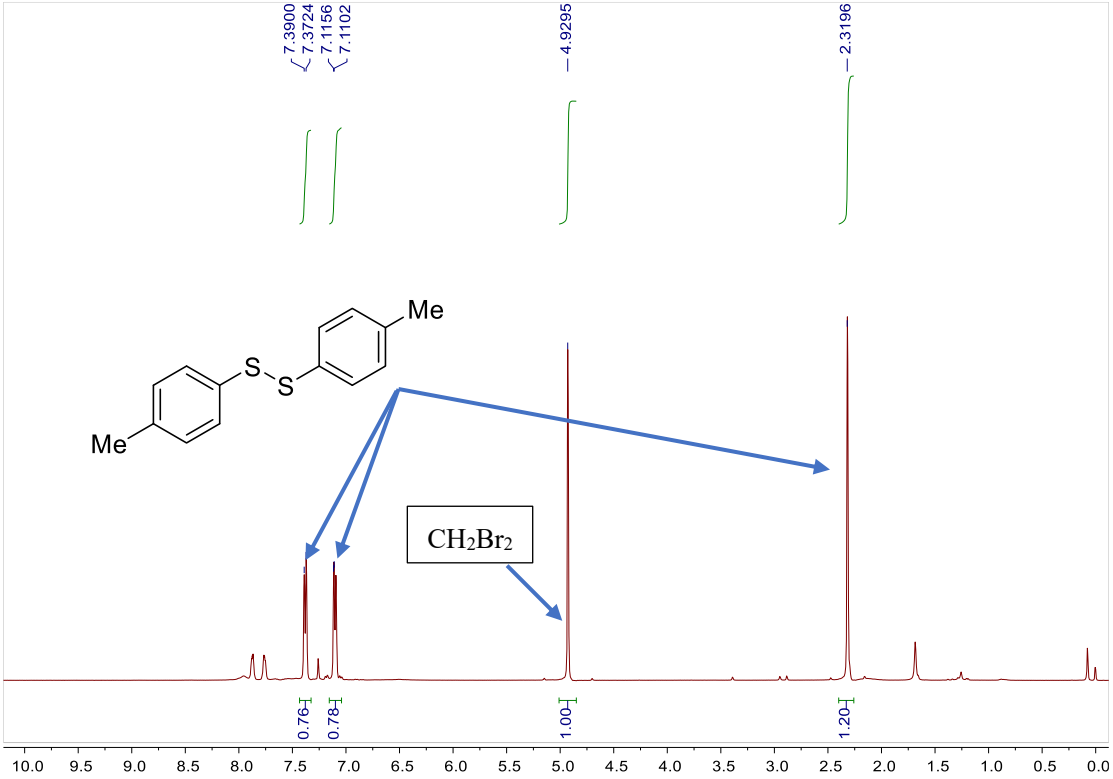
Evidence on GC-MS of 1,2-di-*p*-tolyldisulfane

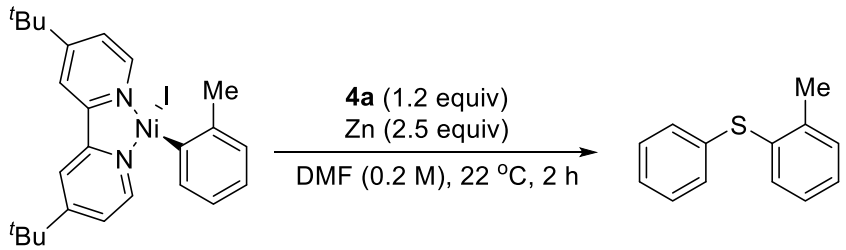


4a **17c**

An 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with2-(p-tolylthio)isoindoline-1,3-dione (143 mg, 0.500 mmol, 1.00 equiv), Zn (81.8 mg, 1.25 mmol, 2.50 equiv), $NiCl_2(PPh_3)_2$ (1.64 mg, 0.00250 mmol, 0.00500 equiv), 1,10-phenanthroline (0.900 mg, 0.00500 mmol, 0.0100 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for 10 min at 0 °C. After the addition was complete, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a

Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 2). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 mL x 2), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^1H NMR spectroscopy in the presence of CH_2Br_2 (86.9 mg, 0.500 mmol).

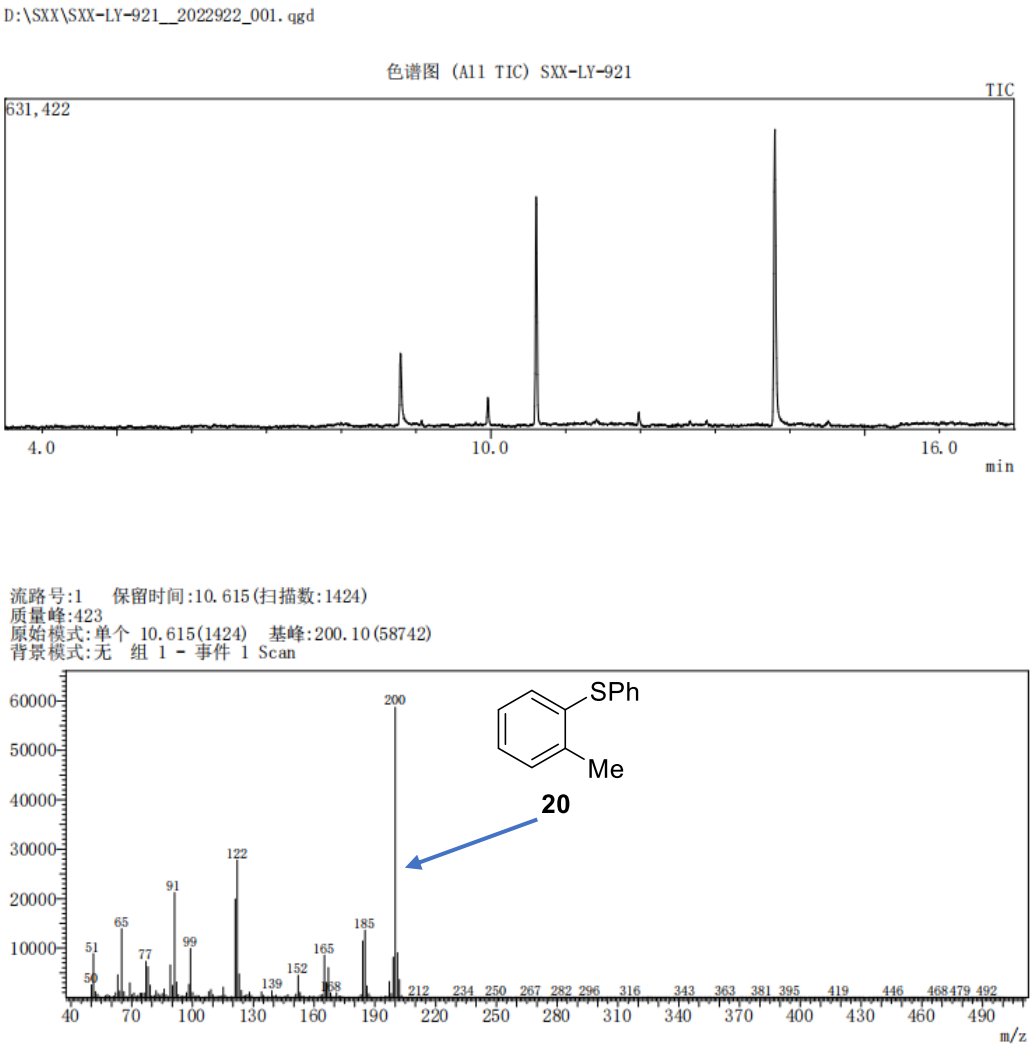




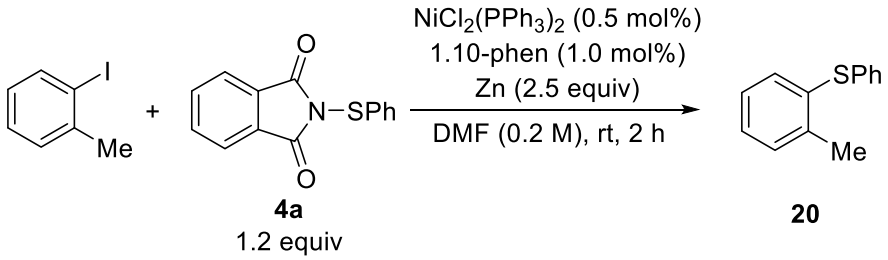
19 **20**

The nickel-complex **19**[15] (54.4 mg, 0.100 mmol, 1.0 equiv), Phth-SPh (30.6 mg, 0.120 mmol, 1.20 equiv), Zn (16.4 mg, 0.250 mmol, 2.50 equiv) and DMF (0.500 mL) were added to the reaction mixture. After that, the reaction mixture was stirred at 22 °C for 2 h. After the addition was complete, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed

with saturated NaCl aqueous solution (15.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^1H NMR spectroscopy in the presence of CH_2Br_2 (17.4 mg, 0.100 mmol) and the crude ^1H NMR yield of **20** is 57.3%.



GC-MS of phenyl(o-tolyl)sulfane



An 120 ºC oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged

with 2-iodotoluene (109 mg, 0.500 mmol, 1.00 equiv), Phth-SPh (153 mg, 0.600 mmol, 1.20 equiv), Zn (81.8 mg, 1.25 mmol, 2.50 equiv), $NiCl_2(PPh_3)_2$ (1.64 mg, 0.00250 mmol, 0.00500 equiv), 1,10-phenanthroline (0.900 mg, 0.00500 mmol, 0.0100 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for 2 h at 22 °C. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a Celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 2). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 mL x 2), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel (Eluent: 500:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (99.3 mg, 0.496 mmol, 99.3% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.23 (8H, m), 7.21 – 7.18 (1H, m), 2.44 (3H, s); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.1, 136.3, 133.9, 133.1, 130.7, 129.8, 129.3, 128.0, 126.9, 126.5, 20.7. Spectra were consistent with literature data[9].

X. References

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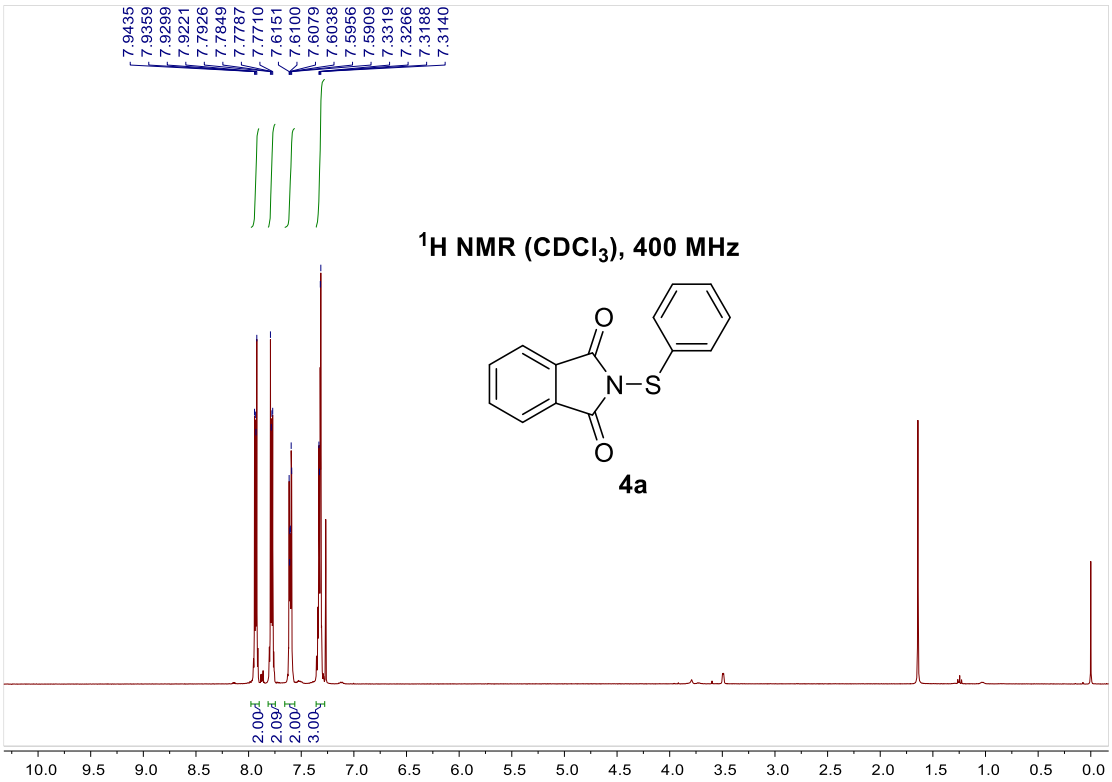
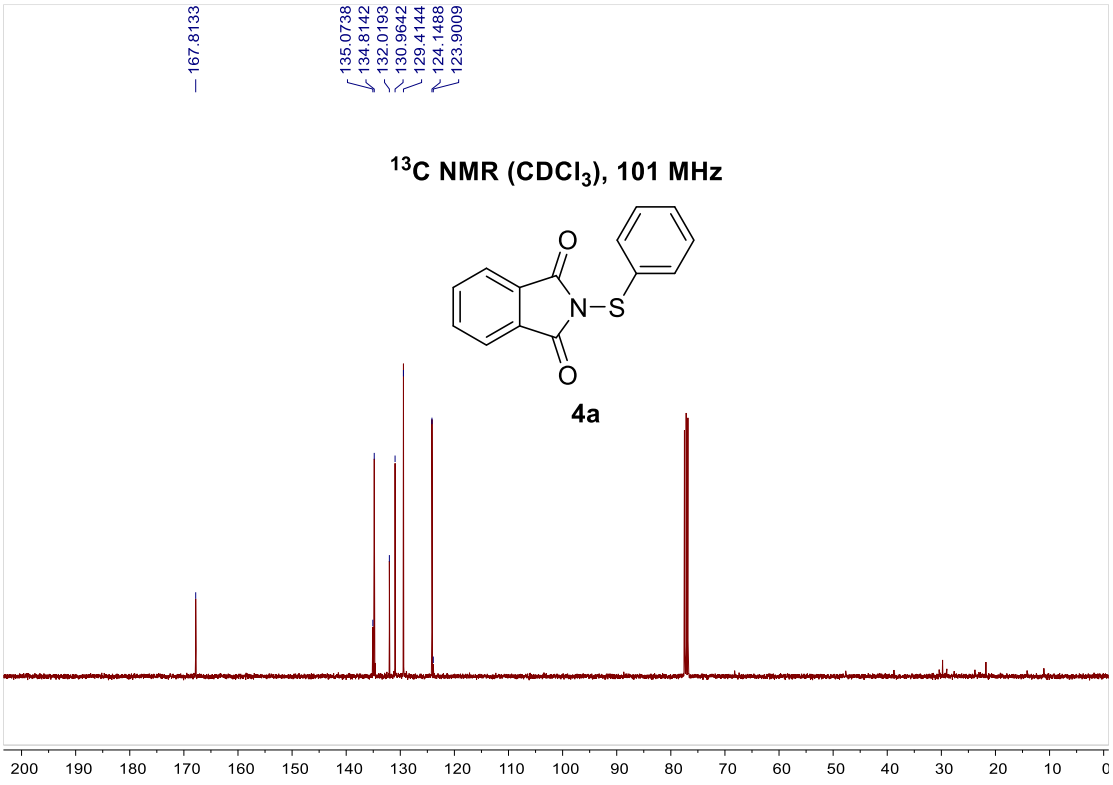
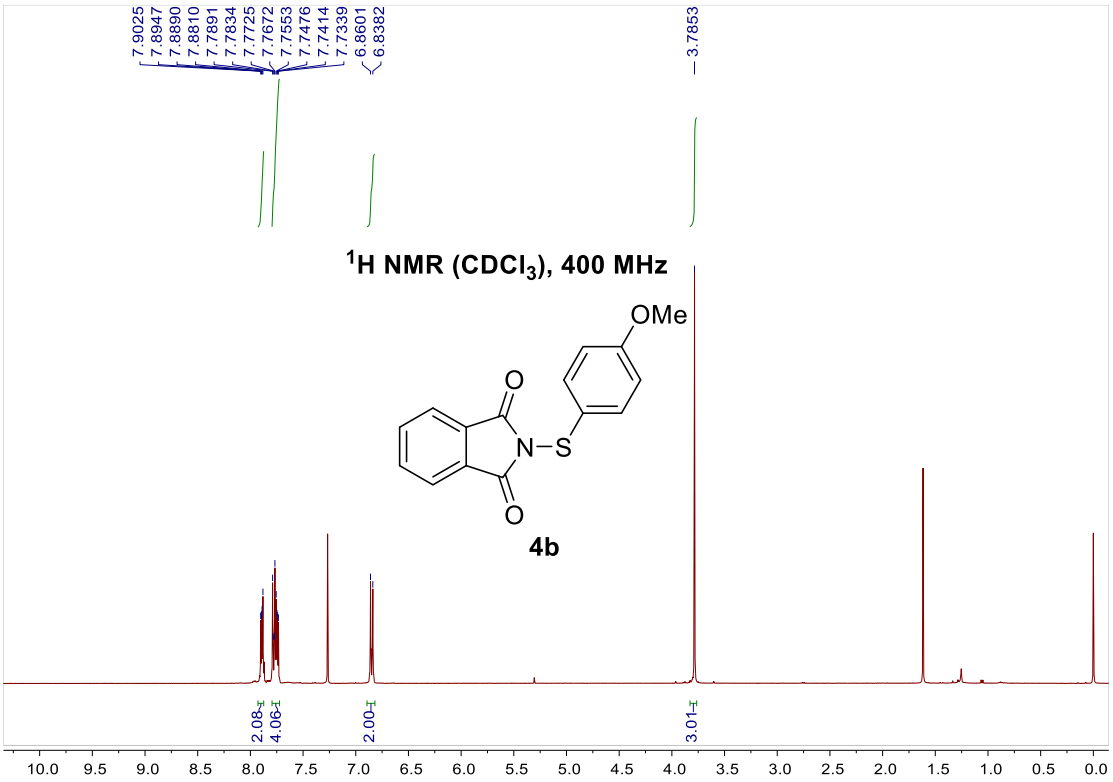
XI. NMR spectra



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7.8890
7.8810
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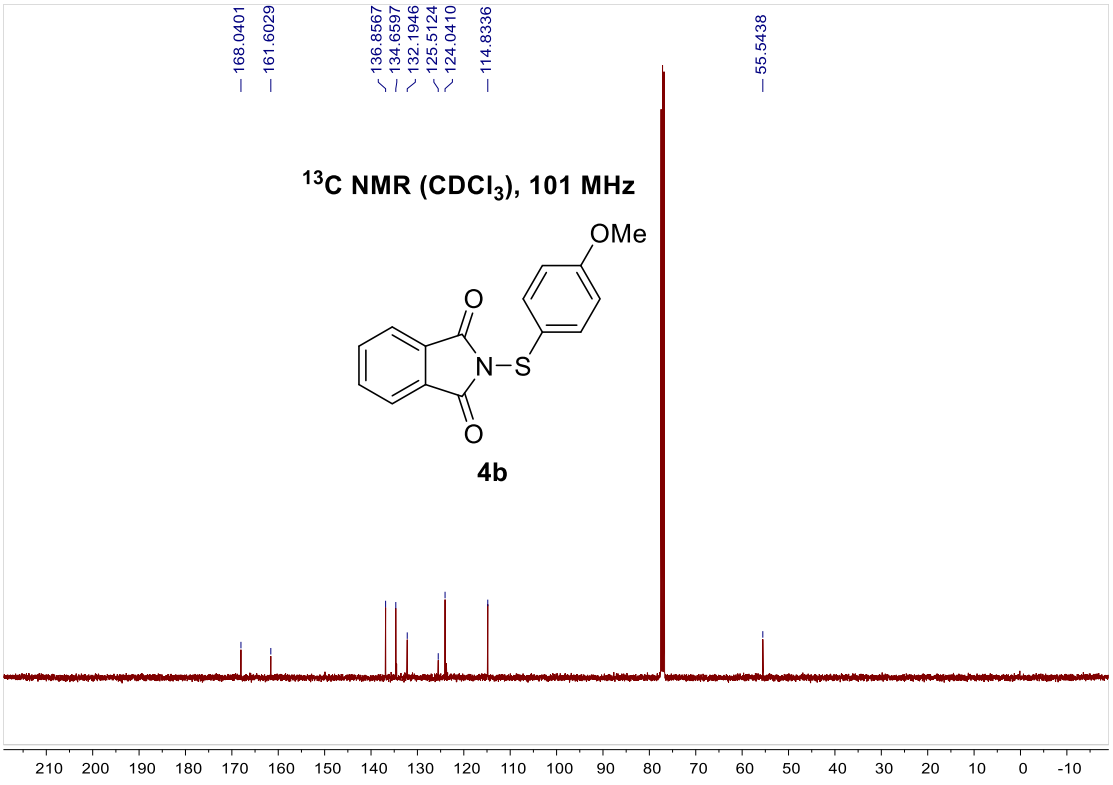
7.7834
7.7725
7.7672
7.7553
7.7476
7.7414
7.7339
6.8601
6.8382
3.7853
1H NMR (CDCl3), 400 MHz
OMe
O
N–S
O
4b
2.08
4.06
2.00
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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OMe
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4b
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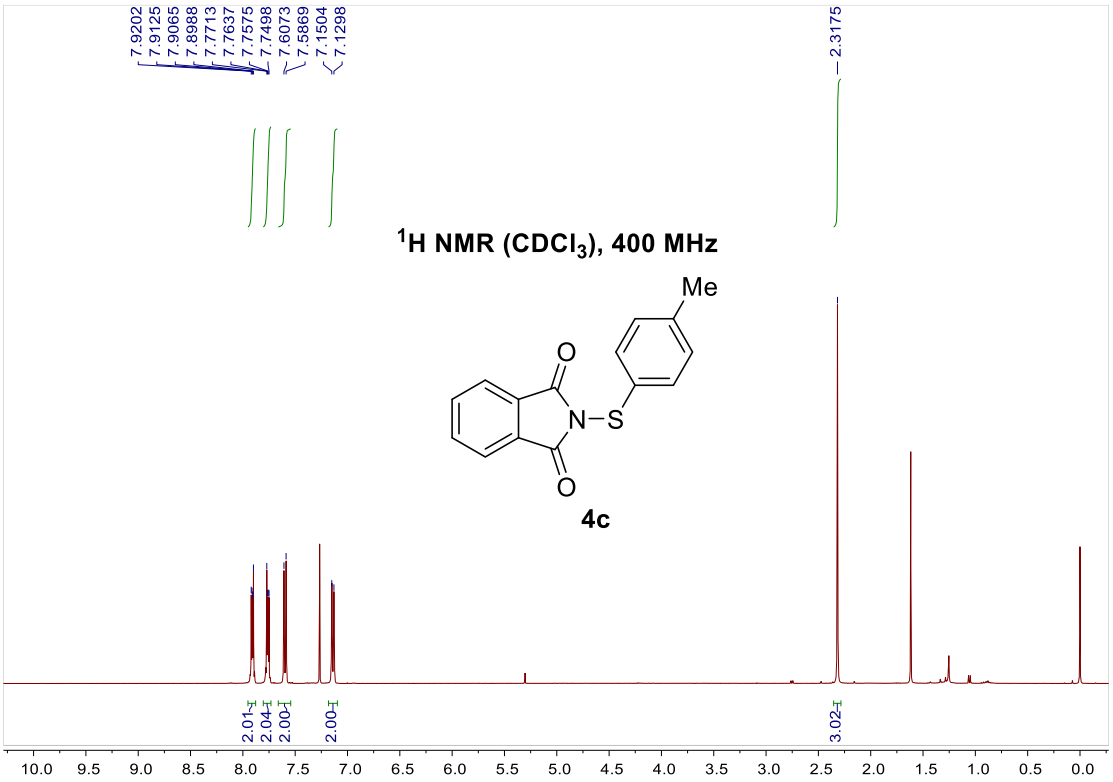
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7.7713
7.7637
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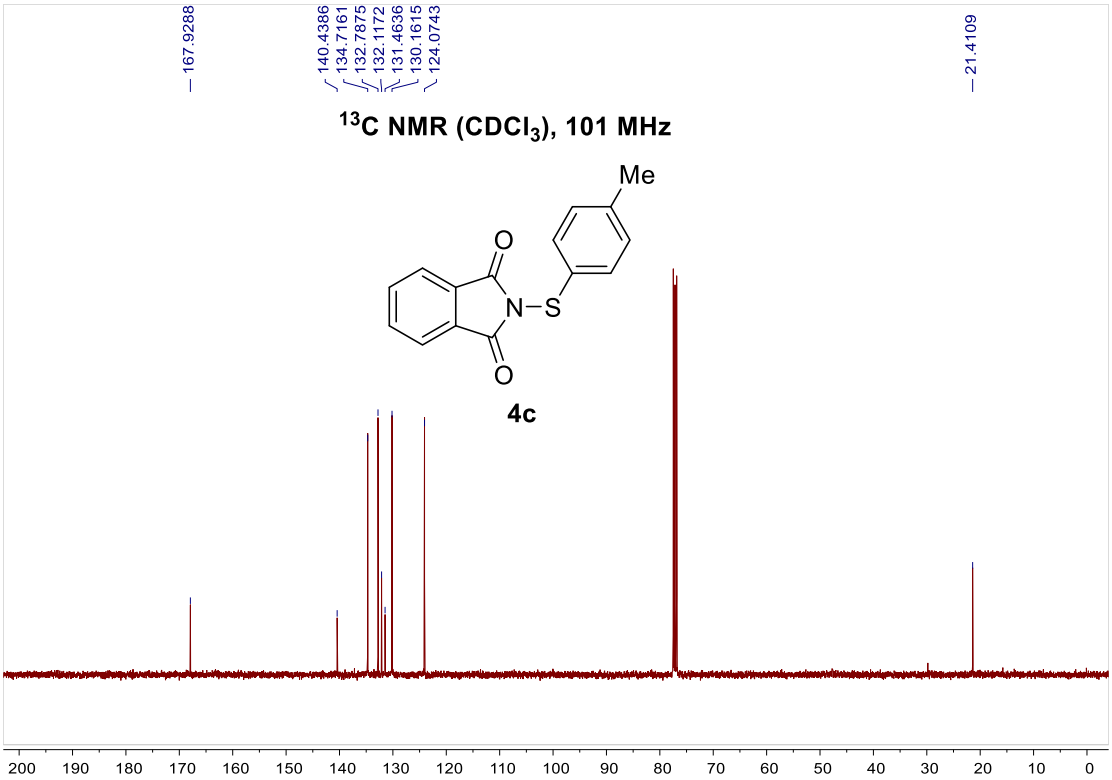
7.1504
7.1298
2.3175
^{1}H NMR ($CDCl_3$), 400 MHz
Me
O
N–S
O
4c
2.01
2.04
2.00
2.00
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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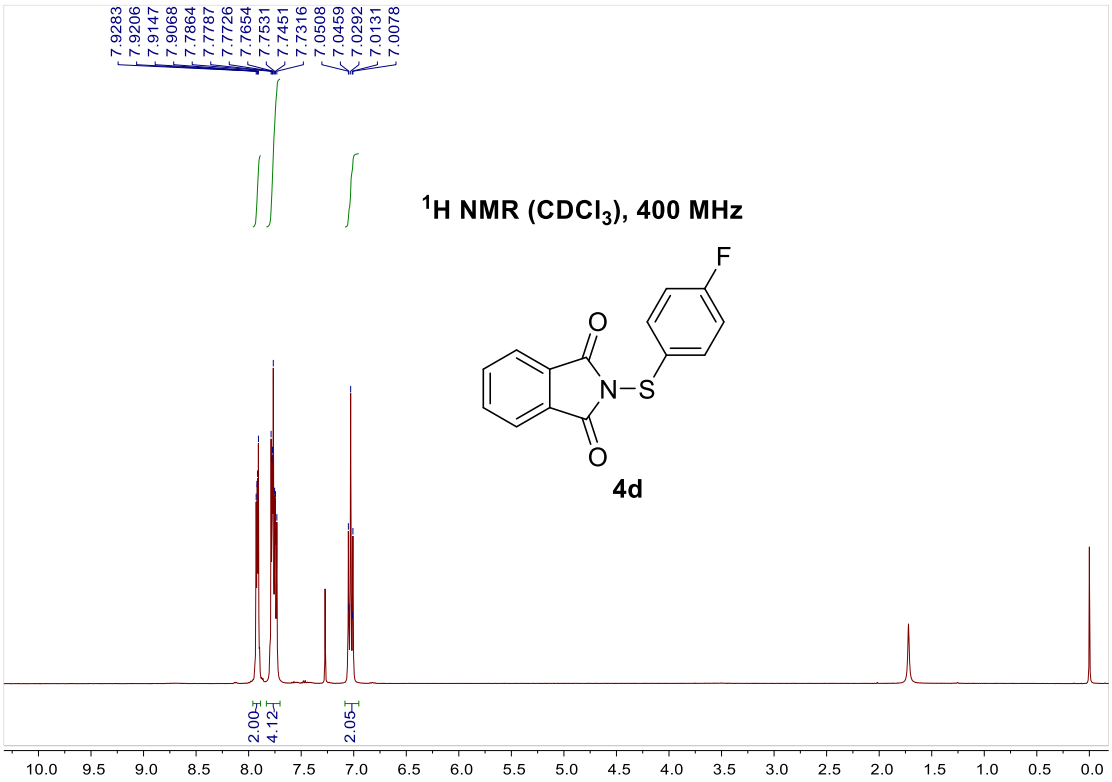
^{13}C NMR ($CDCl_3$), 101 MHz
Me
O
N–S
O
4c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.9147
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7.7864
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7.7726
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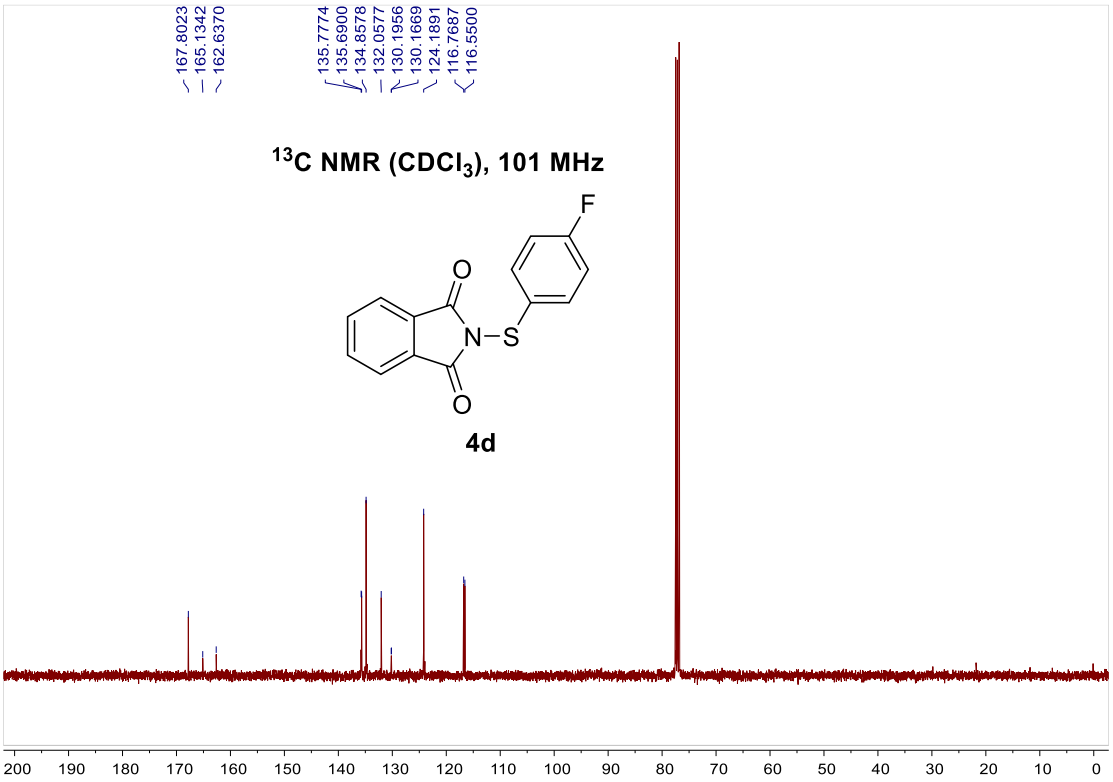
7.7531
7.7451
7.7316
7.0508
7.0459
7.0292
7.0131
7.0078
^{1}H NMR (CDCl$_3$), 400 MHz
F
O
N–S
O
4d
2.00
4.12
2.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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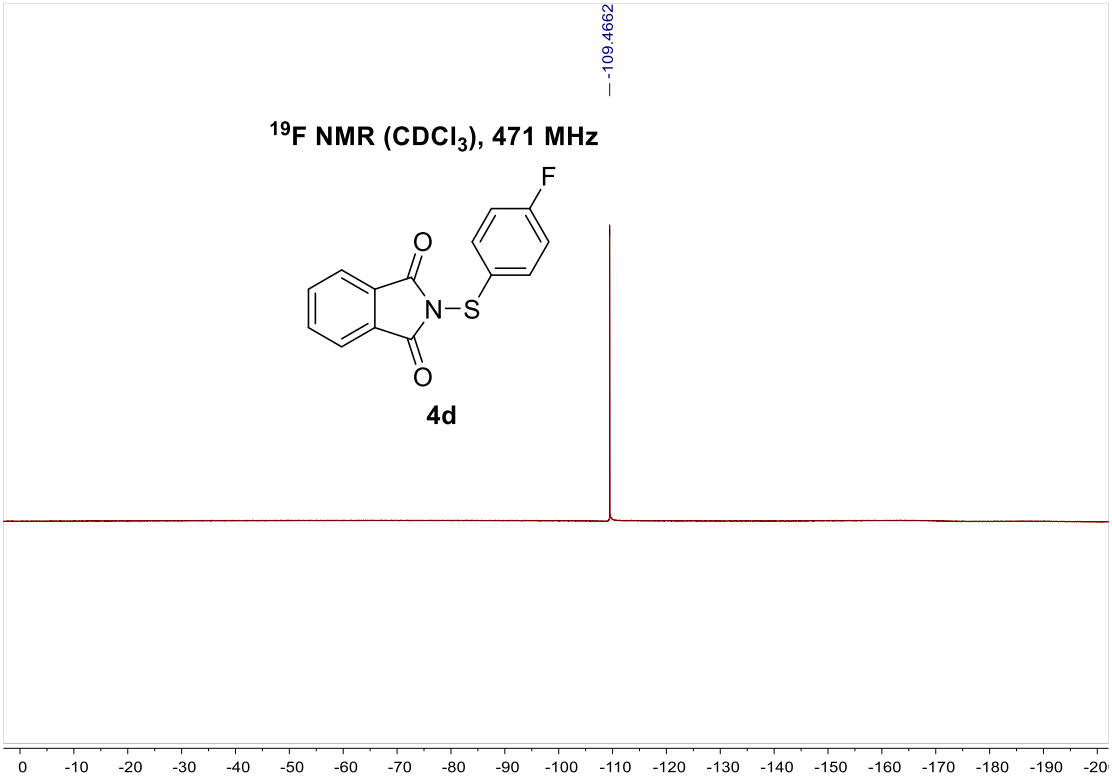
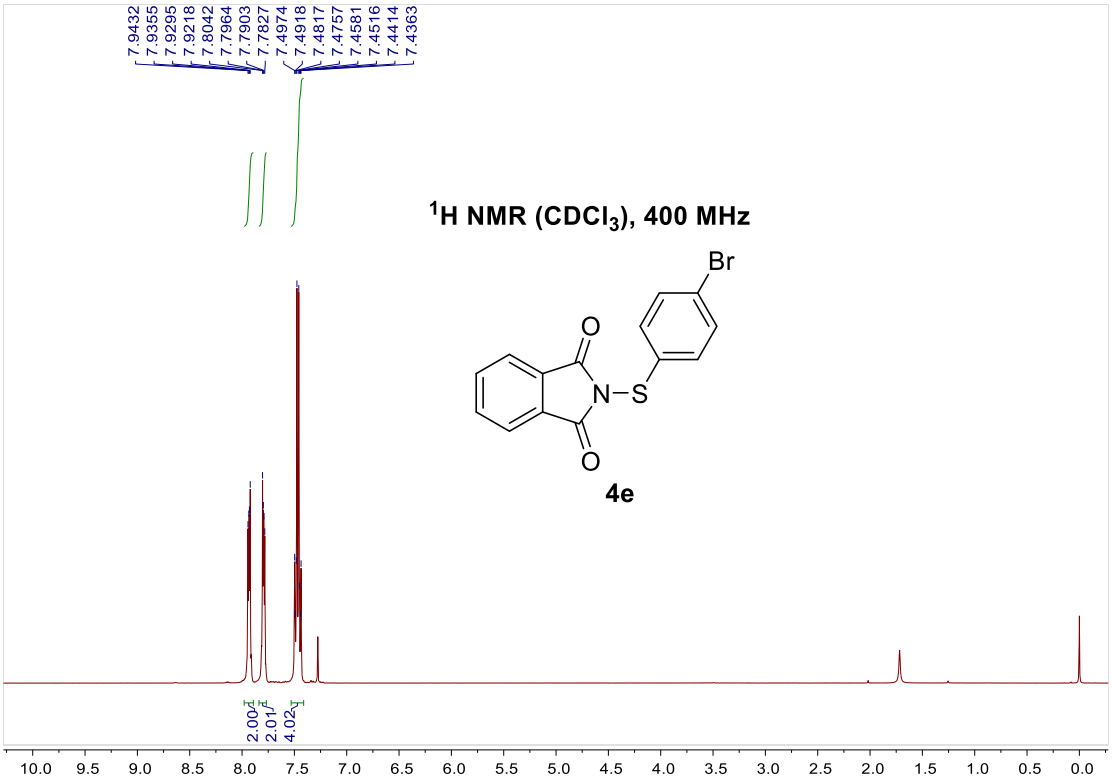
162.6370
135.7774
135.6900
134.8578
132.0577
130.1956
130.1669
124.1891
116.7687
116.5500
^{13}C NMR (CDCl$_3$), 101 MHz
F
O
N–S
O
4d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


-109.4662
19F NMR (CDCl3), 471 MHz
F
O
N–S
O
4d
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20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7.9295
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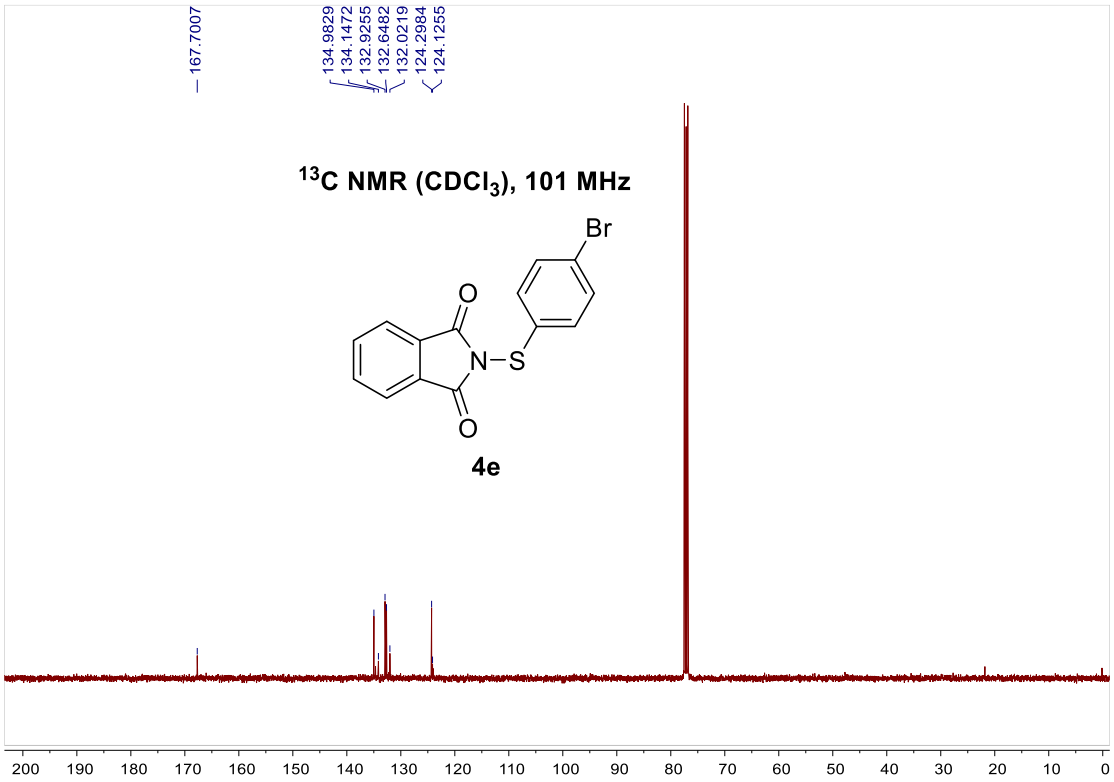
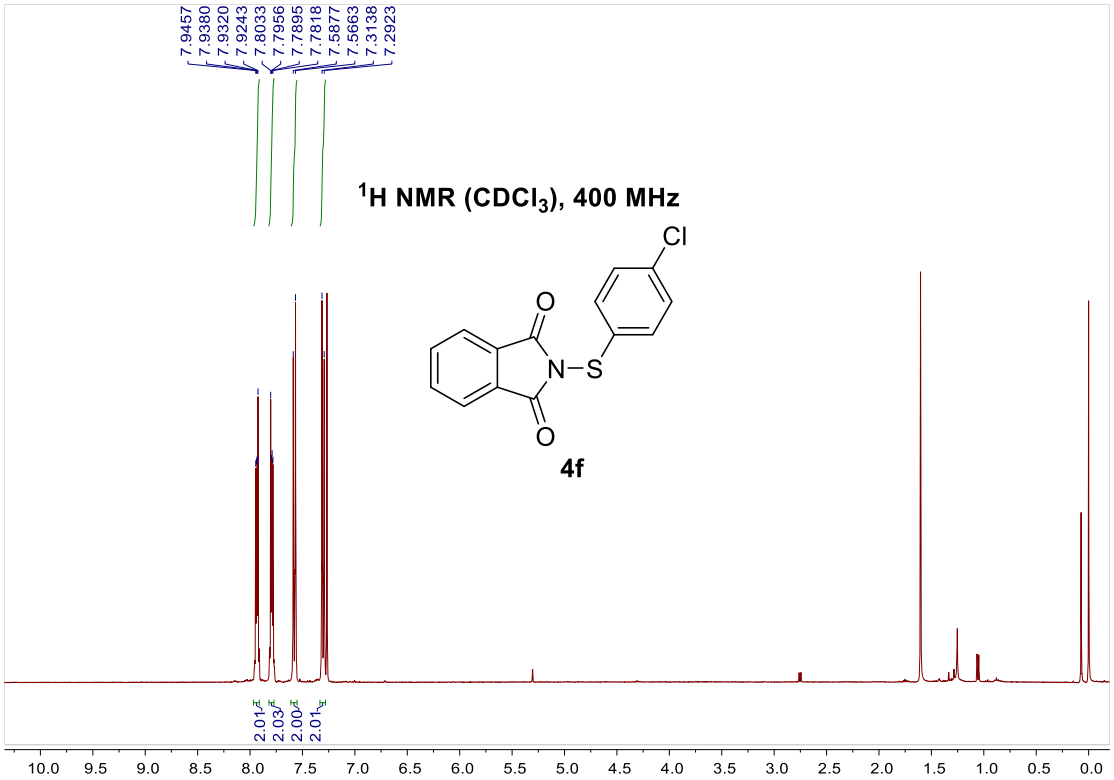
7.7903
7.7827
7.4974
7.4918
7.4817
7.4757
7.4581
7.4516
7.4414
7.4363
1H NMR (CDCl3), 400 MHz
Br
O
N–S
O
4e
2.00
2.01
4.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


167.7007
134.9829
134.1472
132.9255
132.6482
132.0219
124.2984
124.1255
13C NMR (CDCl3), 101 MHz
Br
O
N–S
O
4e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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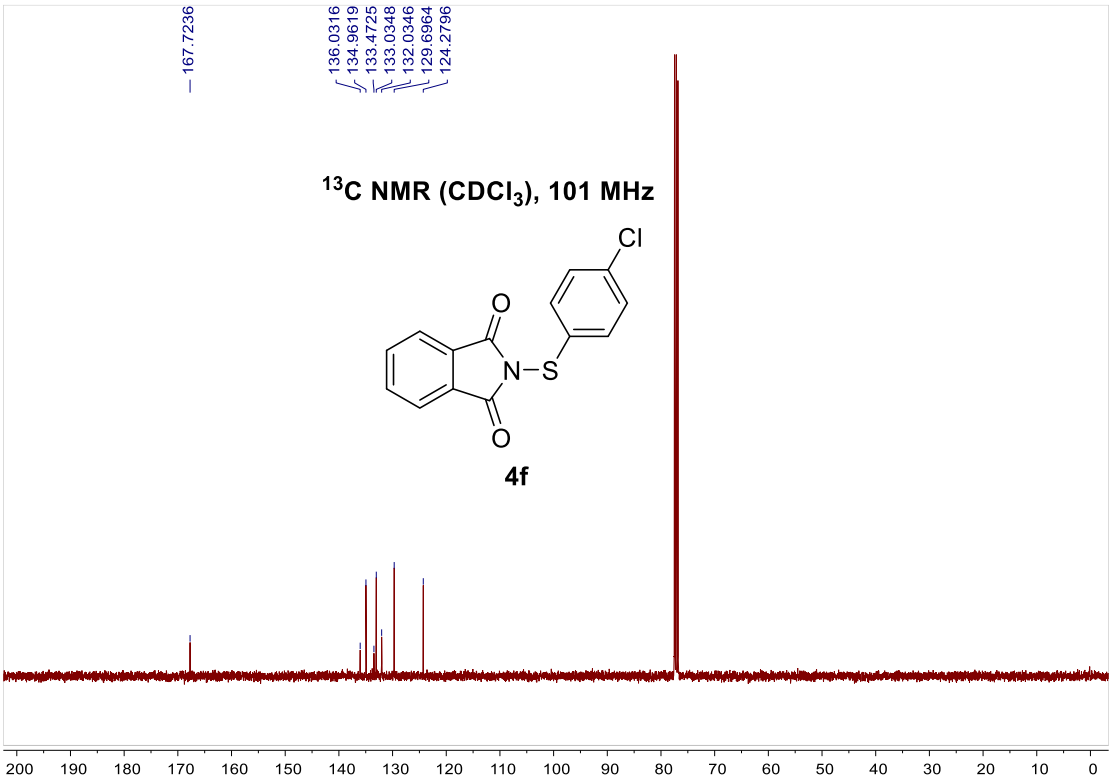
7.9320
7.9243
7.8033
7.7956
7.7895
7.7818
7.5877
7.5663
7.3138
7.2923
1H NMR (CDCl3), 400 MHz
Cl
O
N–S
O
4f
2.01
2.03
2.00
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


167.7236
136.0316
134.9619
133.4725
133.0348
132.0346
129.6964
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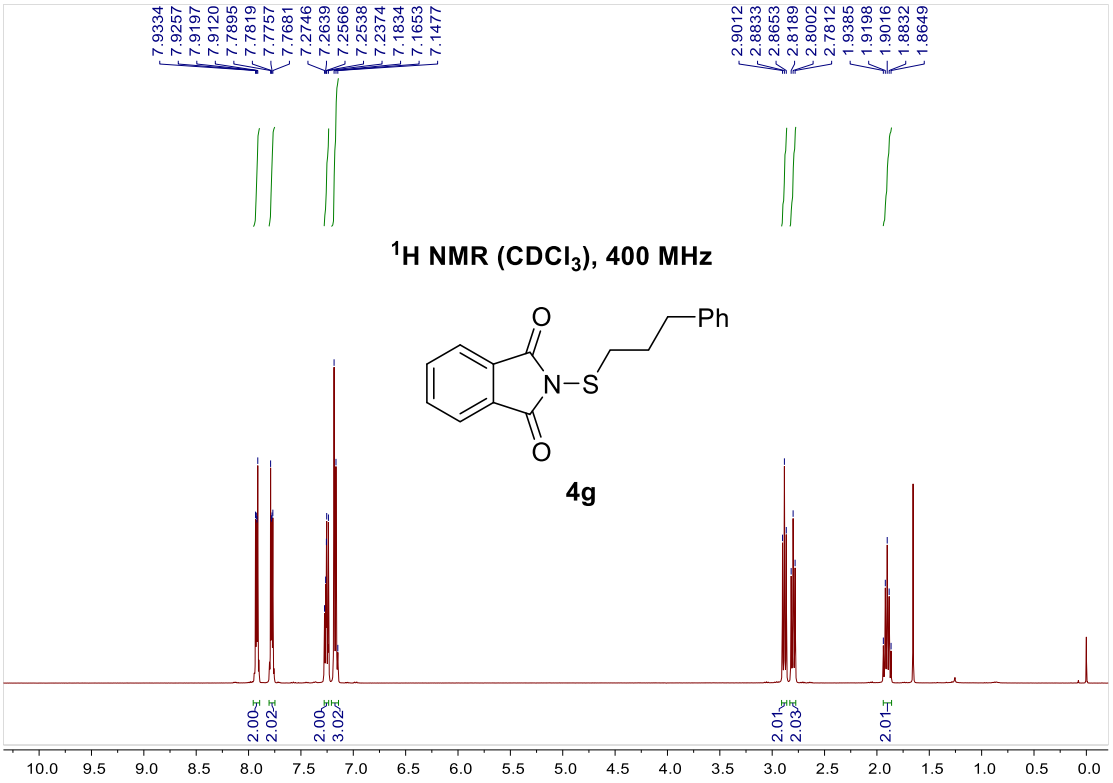
13C NMR (CDCl3), 101 MHz
Cl
O
N–S
O
4f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.9197
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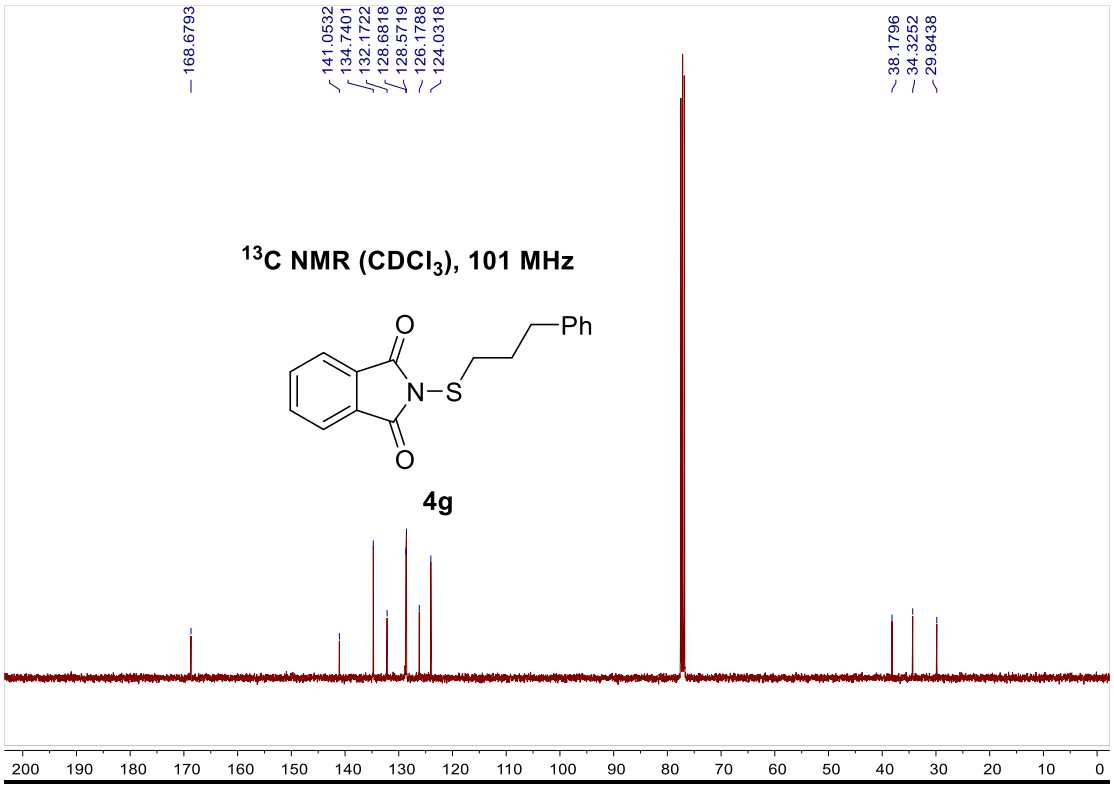
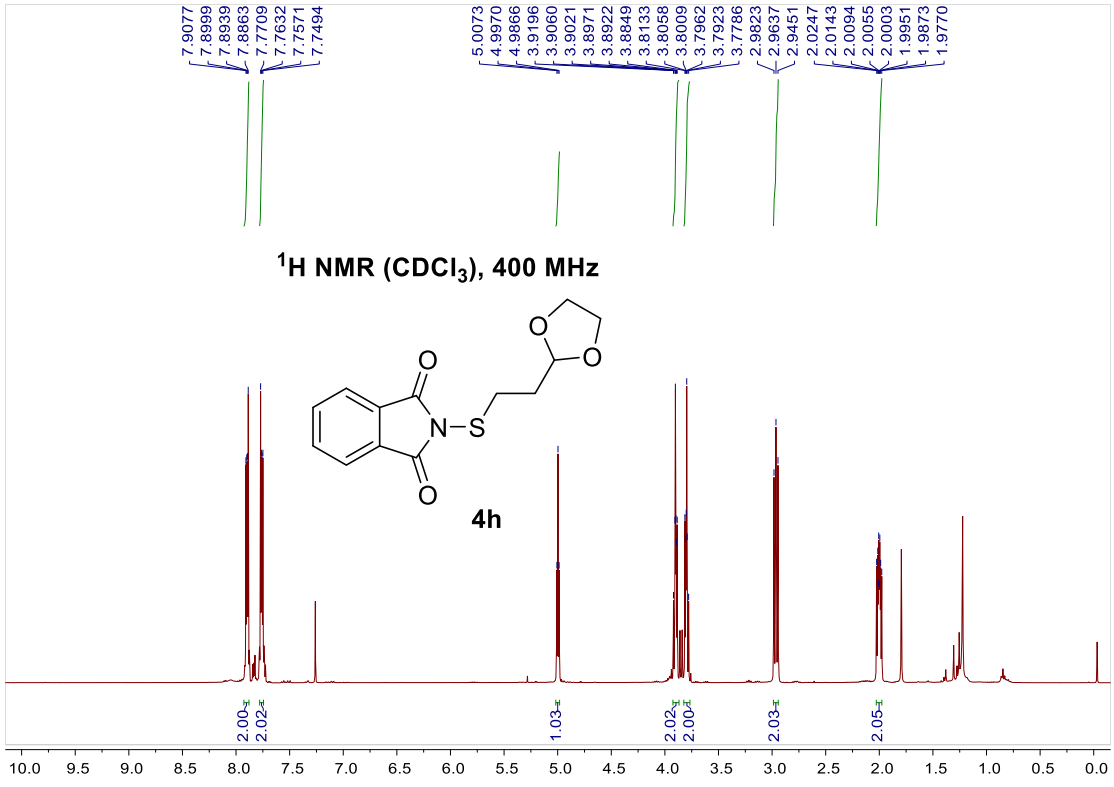
7.7895
7.7819
7.7757
7.7681
7.2746
7.2639
7.2566
7.2538
7.2374
7.1834
7.1653
7.1477
2.9012
2.8833
2.8653
2.8189
2.8002
2.7812
1.9385
1.9198
1.9016
1.8832
1.8649
1H NMR (CDCl3), 400 MHz
O
Ph
N–S
O
4g
2.00
2.02
2.00
3.02
2.01
2.03
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


168.6793
141.0532
134.7401
132.1722
128.6818
128.5719
126.1788
124.0318
38.1796
34.3252
29.8438
13C NMR (CDCl3), 101 MHz
O
Ph
N–S
O
4g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.8999
7.8939
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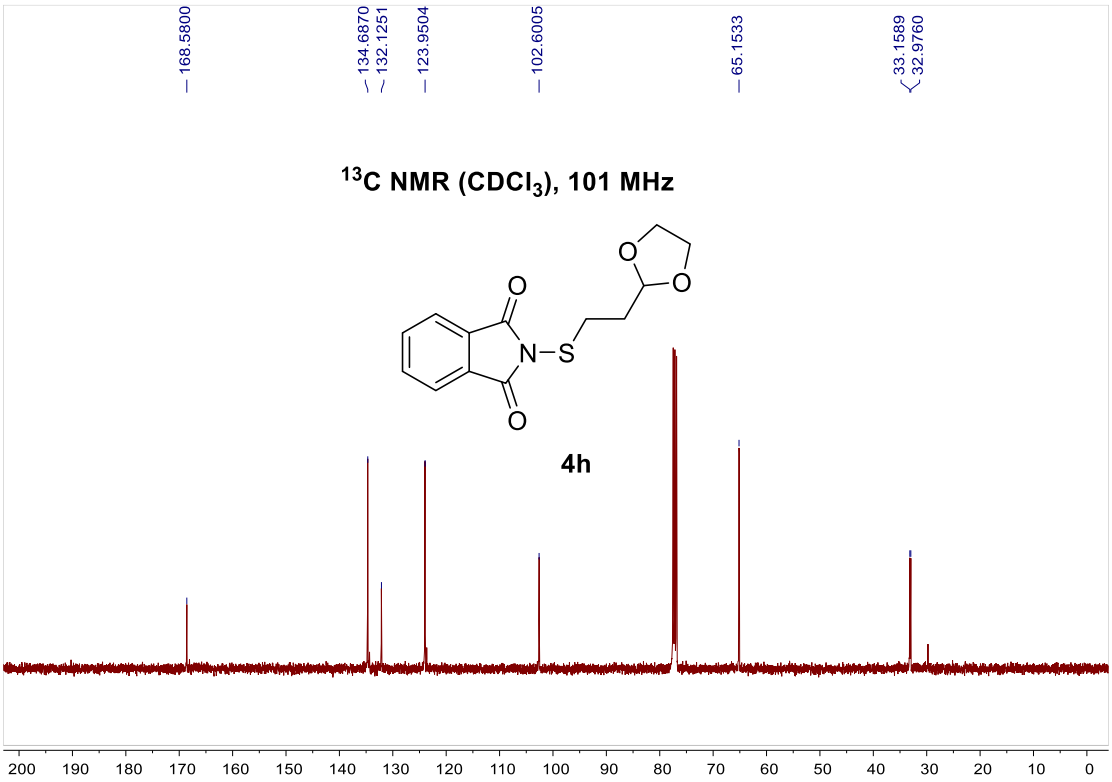
7.7709
7.7632
7.7571
7.7494
5.0073
4.9970
4.9866
3.9196
3.9060
3.9021
3.8971
3.8922
3.8849
3.8133
3.8058
3.8009
3.7962
3.7923
3.7786
2.9823
2.9637
2.9451
2.0247
2.0143
2.0094
2.0055
2.0003
1.9951
1.9873
1.9770
1H NMR (CDCl3), 400 MHz
O
O
O
N–S
O
4h
2.00
2.02
1.03
2.02
2.00
2.03
2.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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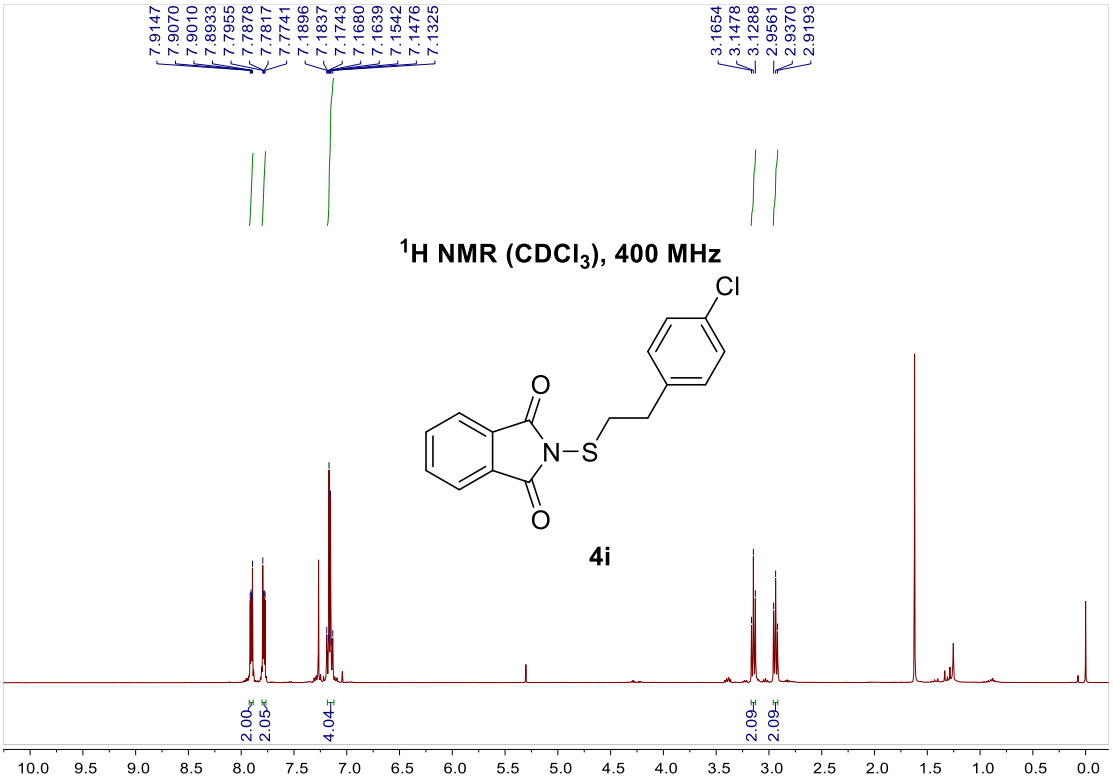
134.6870
132.1251
123.9504
102.6005
65.1533
33.1589
32.9760
13C NMR (CDCl3), 101 MHz
O
O
O
N–S
O
4h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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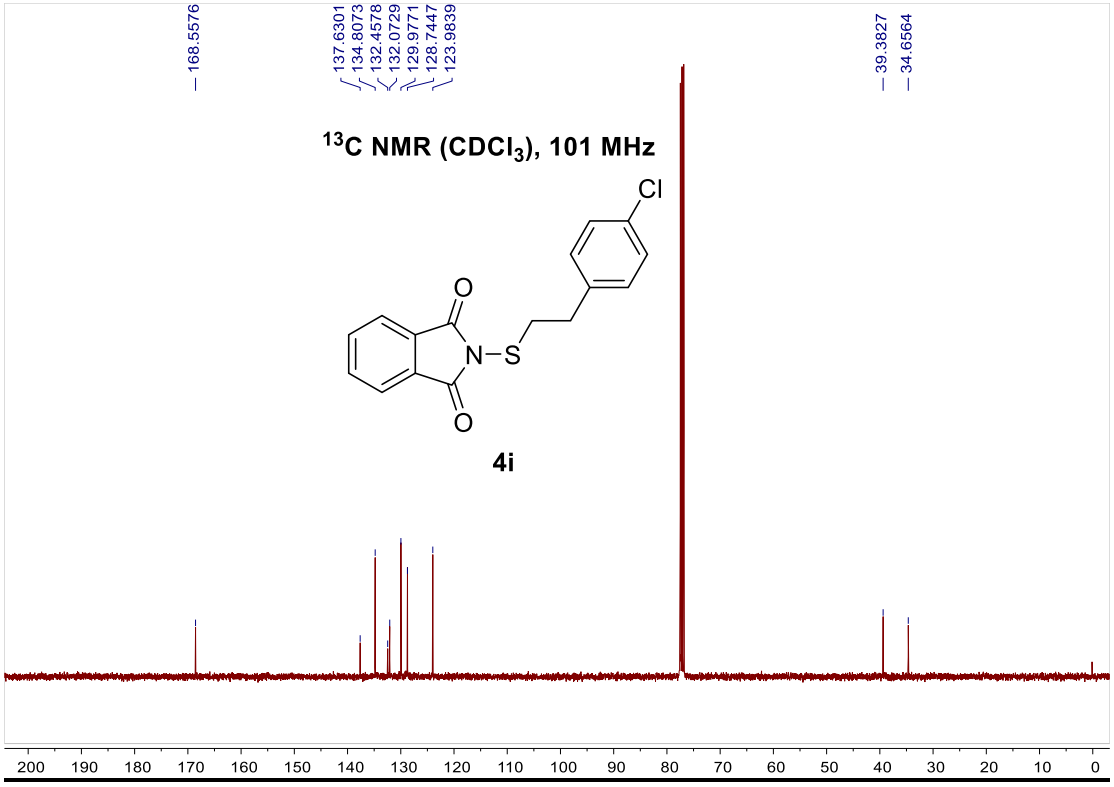
7.9010
7.8933
7.7955
7.7878
7.7817
7.7741
7.1896
7.1837
7.1743
7.1680
7.1639
7.1542
7.1476
7.1325
3.1654
3.1478
3.1288
2.9561
2.9370
2.9193
1H NMR (CDCl3), 400 MHz
Cl
O
O
N–S
O
4i
2.00
2.05
4.04
2.09
2.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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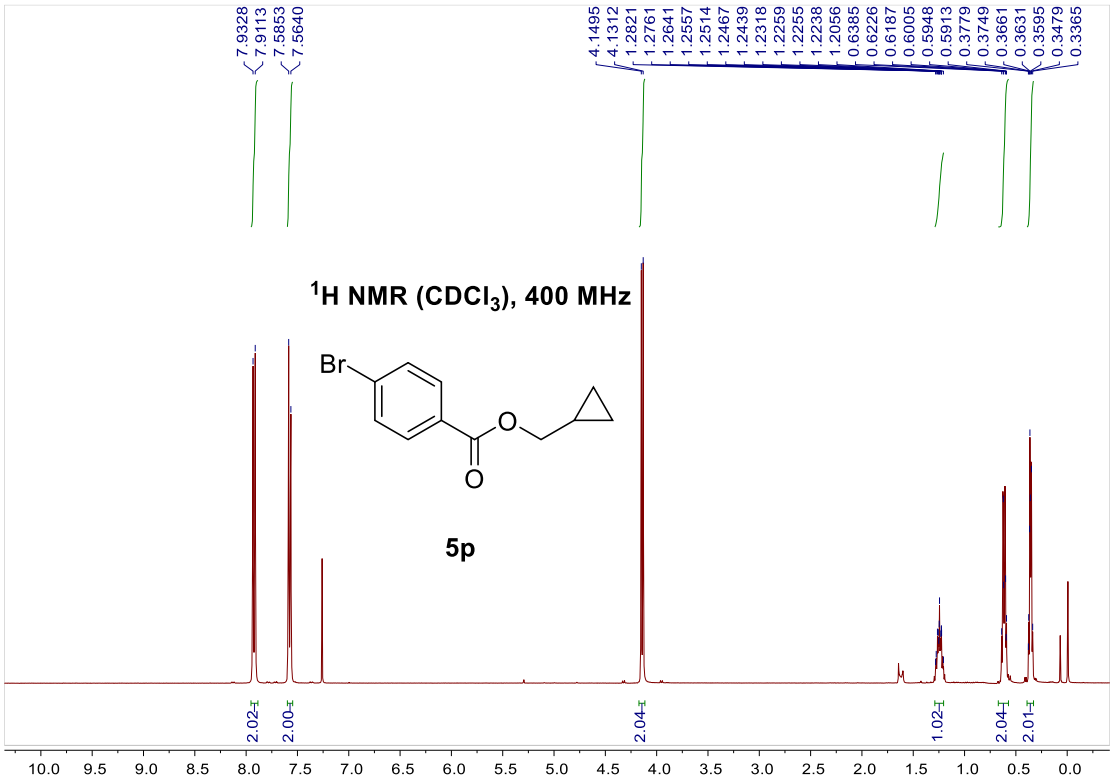
137.6301
134.8073
132.4578
132.0729
129.9771
128.7447
123.9839
39.3827
34.6564
13C NMR (CDCl3), 101 MHz
Cl
O
N–S
O
4i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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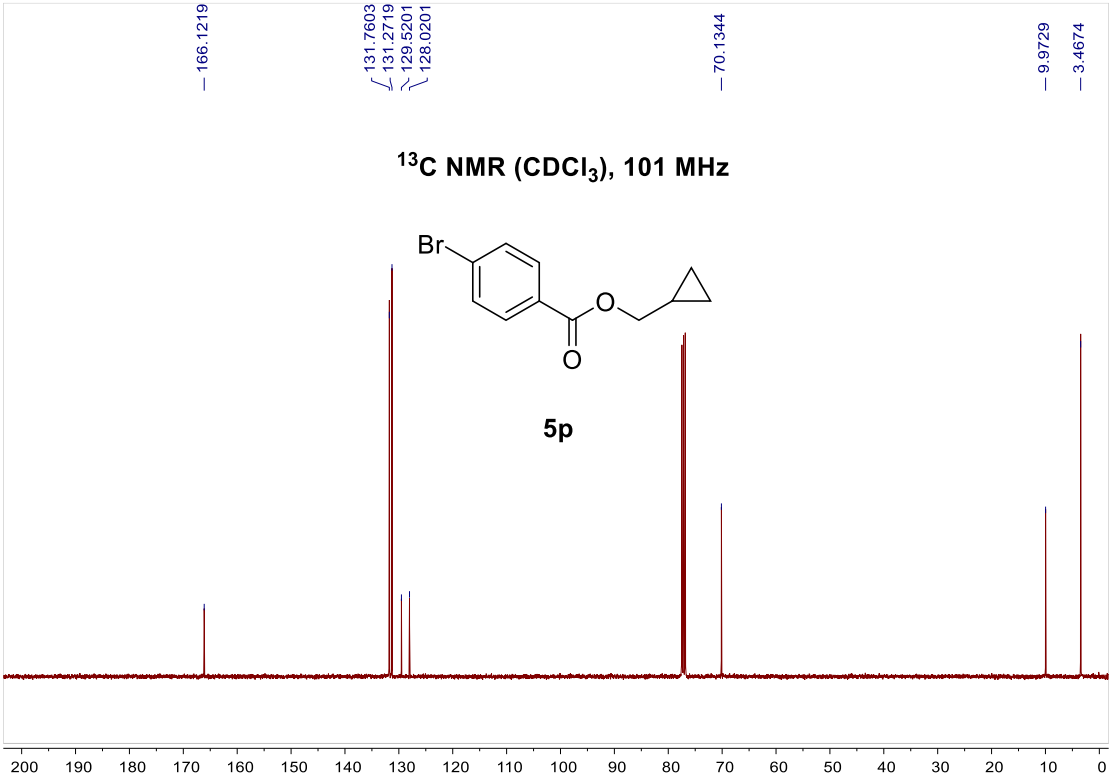
7.5853
7.5640
4.1495
4.1312
1.2821
1.2761
1.2641
1.2557
1.2514
1.2467
1.2439
1.2318
1.2259
1.2255
1.2238
1.2056
0.6385
0.6226
0.6187
0.6005
0.5948
0.5913
0.3779
0.3749
0.3661
0.3631
0.3595
0.3479
0.3365
1H NMR (CDCl3), 400 MHz
Br
O
O
5p
2.02
2.00
2.04
1.02
2.04
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


166.1219
131.7603
131.2719
129.5201
128.0201
70.1344
9.9729
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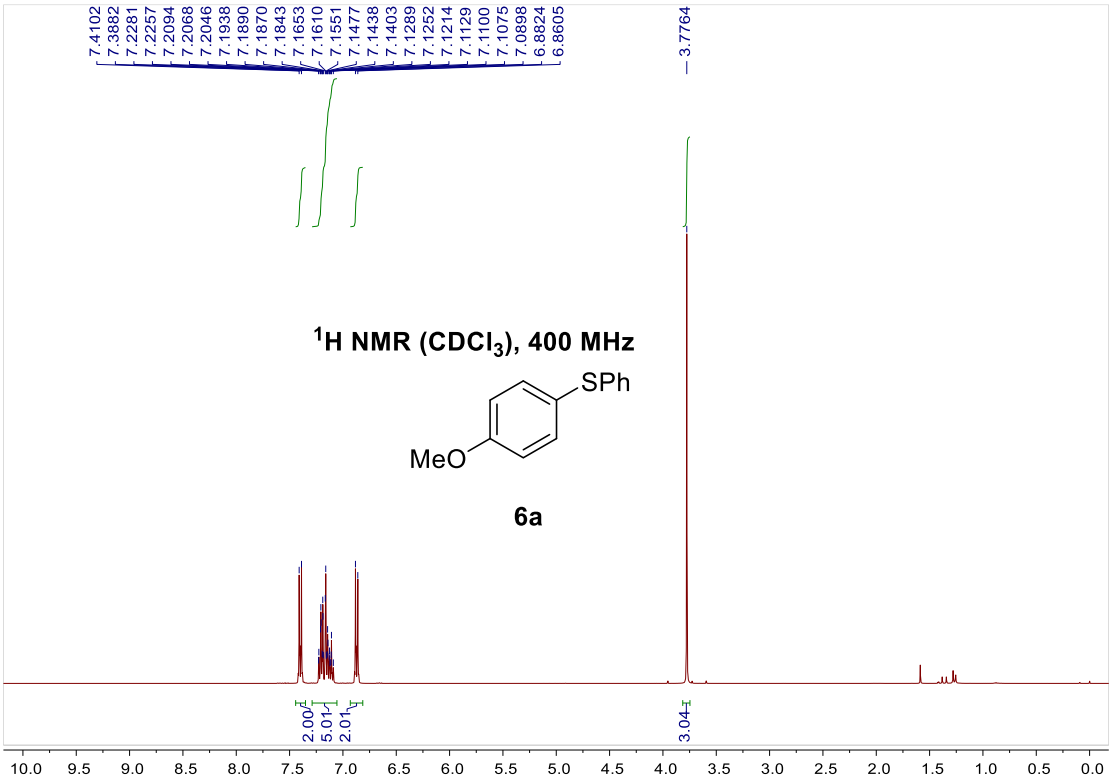
13C NMR (CDCl3), 101 MHz
Br
O
O
5p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.2281
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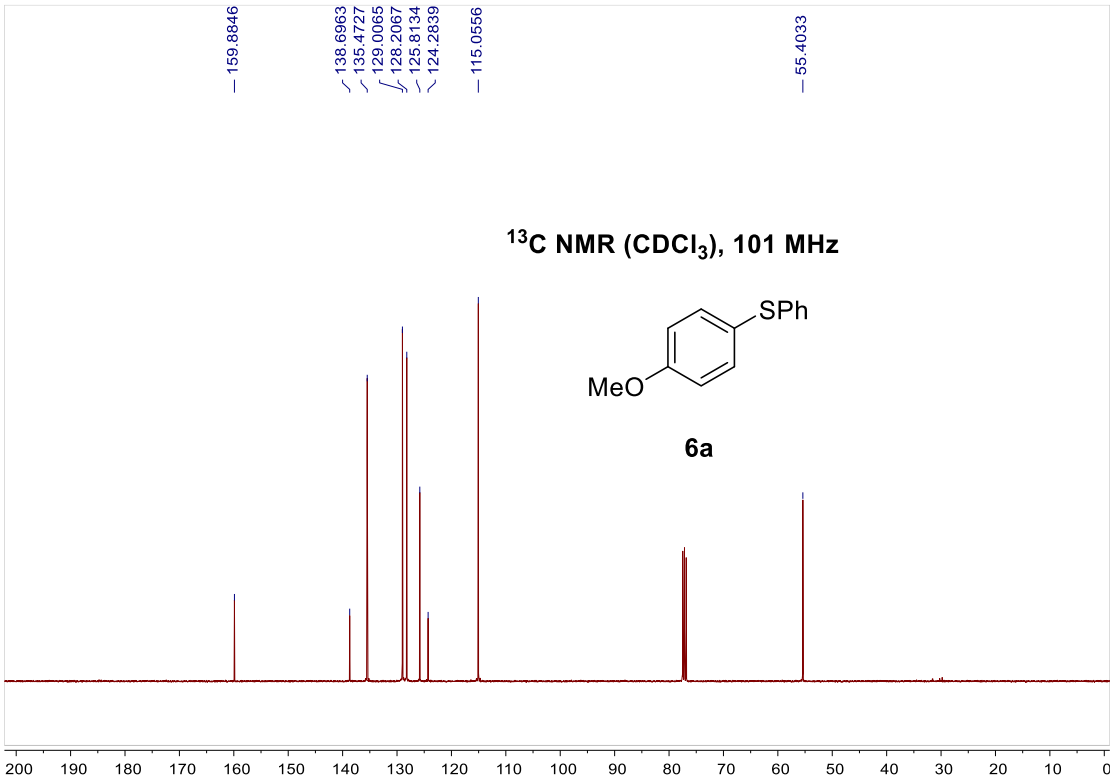
7.2094
7.2068
7.2046
7.1938
7.1890
7.1870
7.1843
7.1653
7.1610
7.1551
7.1477
7.1438
7.1403
7.1289
7.1252
7.1214
7.1129
7.1100
7.1075
7.0898
6.8824
6.8605
3.7764
1H NMR (CDCl3), 400 MHz
SPh
MeO
6a
2.00
5.01
2.01
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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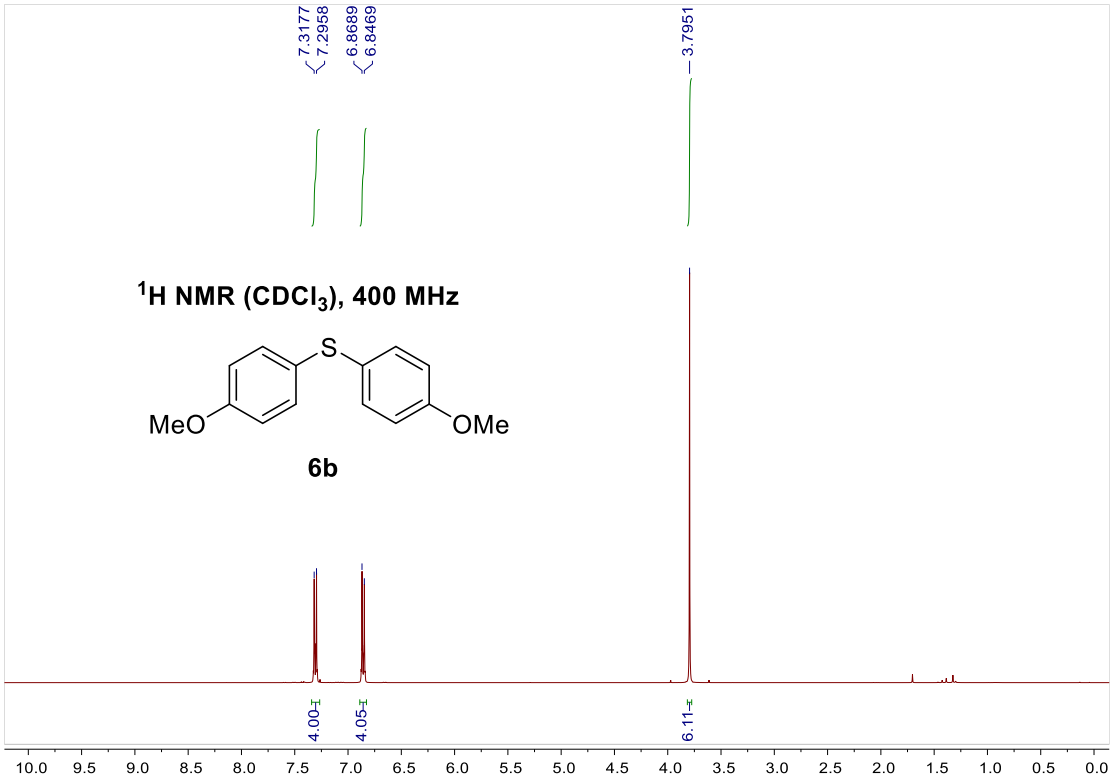
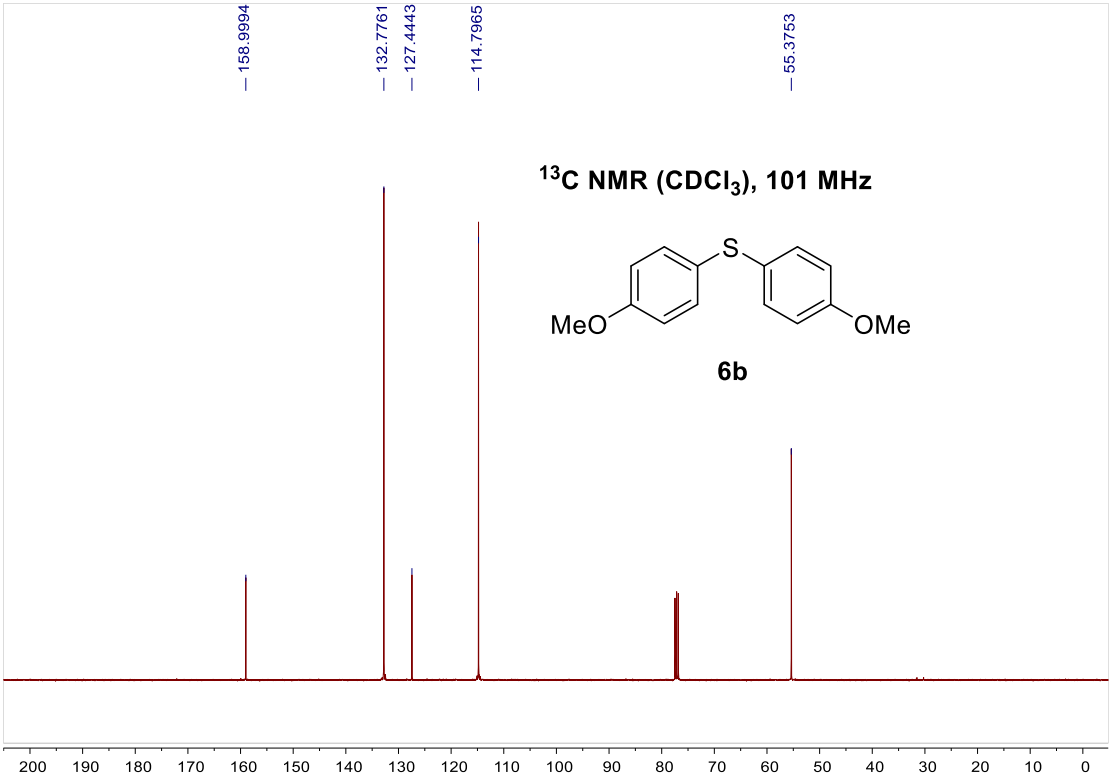
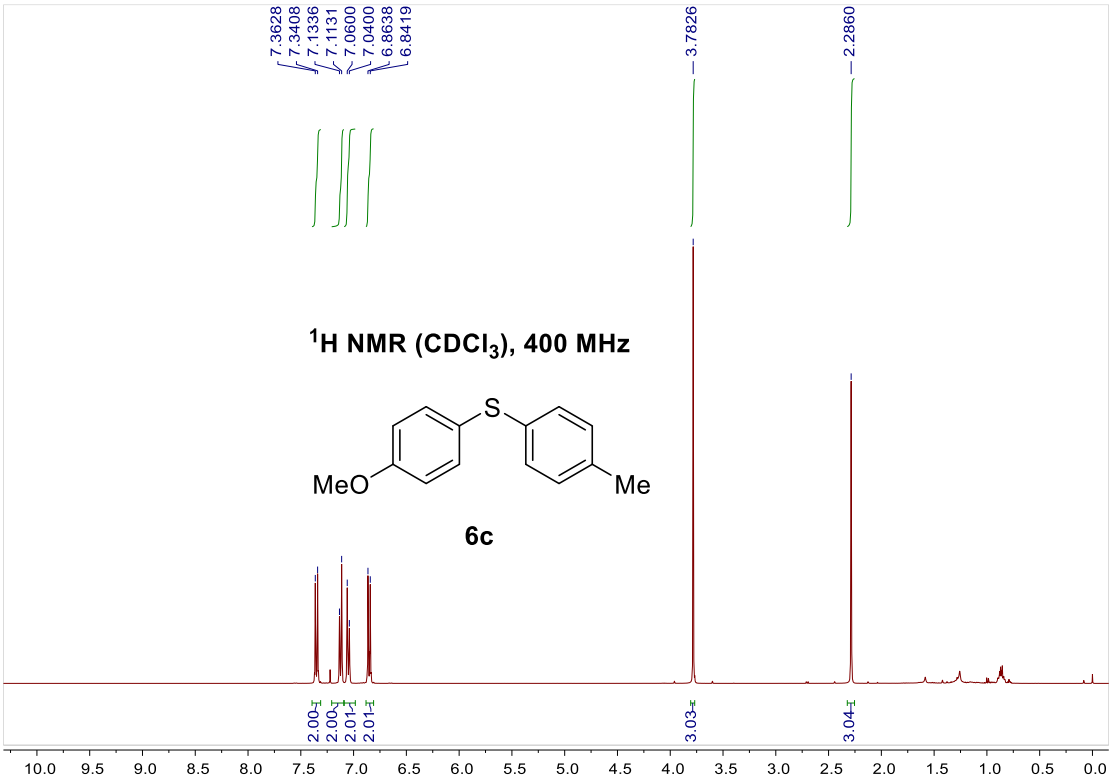
135.4727
129.0065
128.2067
125.8134
124.2839
115.0556
55.4033
13C NMR (CDCl3), 101 MHz
SPh
MeO
6a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.3177
7.2958
6.8689
6.8469
3.7951
1H NMR (CDCl3), 400 MHz
S
MeO
OMe
6b
4.00
4.05
6.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


158.9994
132.7761
127.4443
114.7965
55.3753
^{13}C NMR ($CDCl_3$), 101 MHz
S
MeO
OMe
6b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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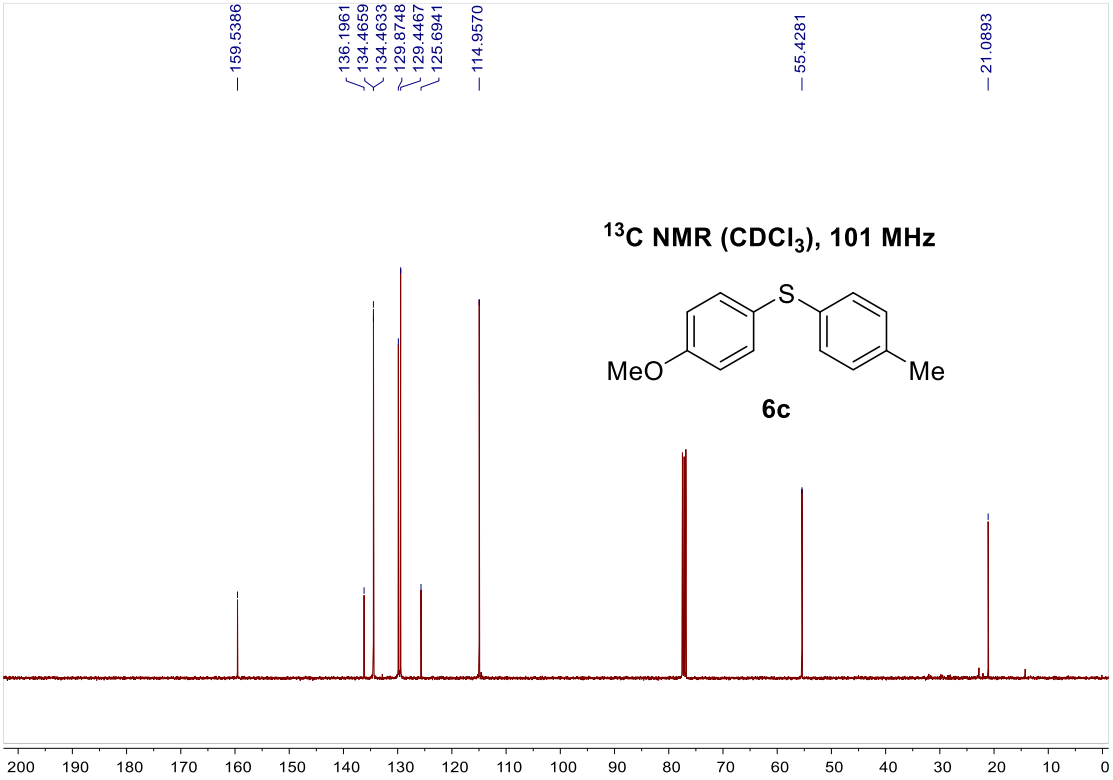
7.1336
7.1131
7.0600
7.0400
6.8638
6.8419
3.7826
2.2860
^{1}H NMR ($CDCl_3$), 400 MHz
S
MeO
Me
6c
2.00
2.00
2.01
2.01
3.03
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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125.6941
114.9570
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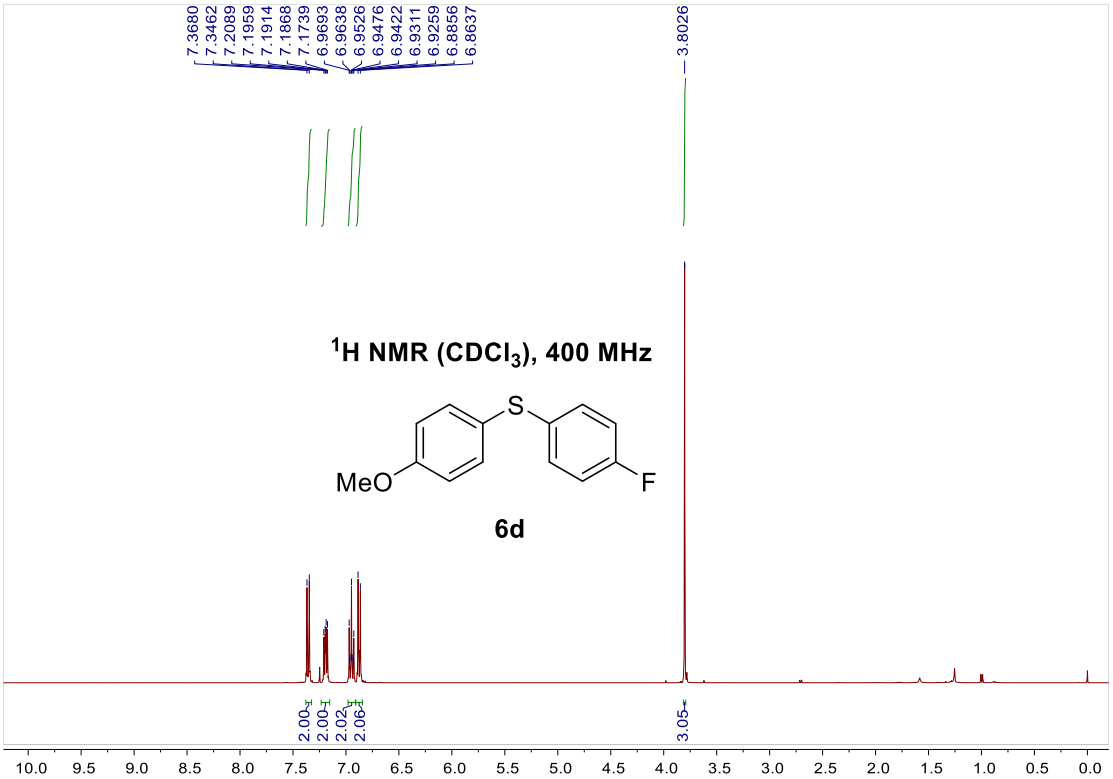
13C NMR (CDCl3), 101 MHz
S
MeO
Me
6c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.2089
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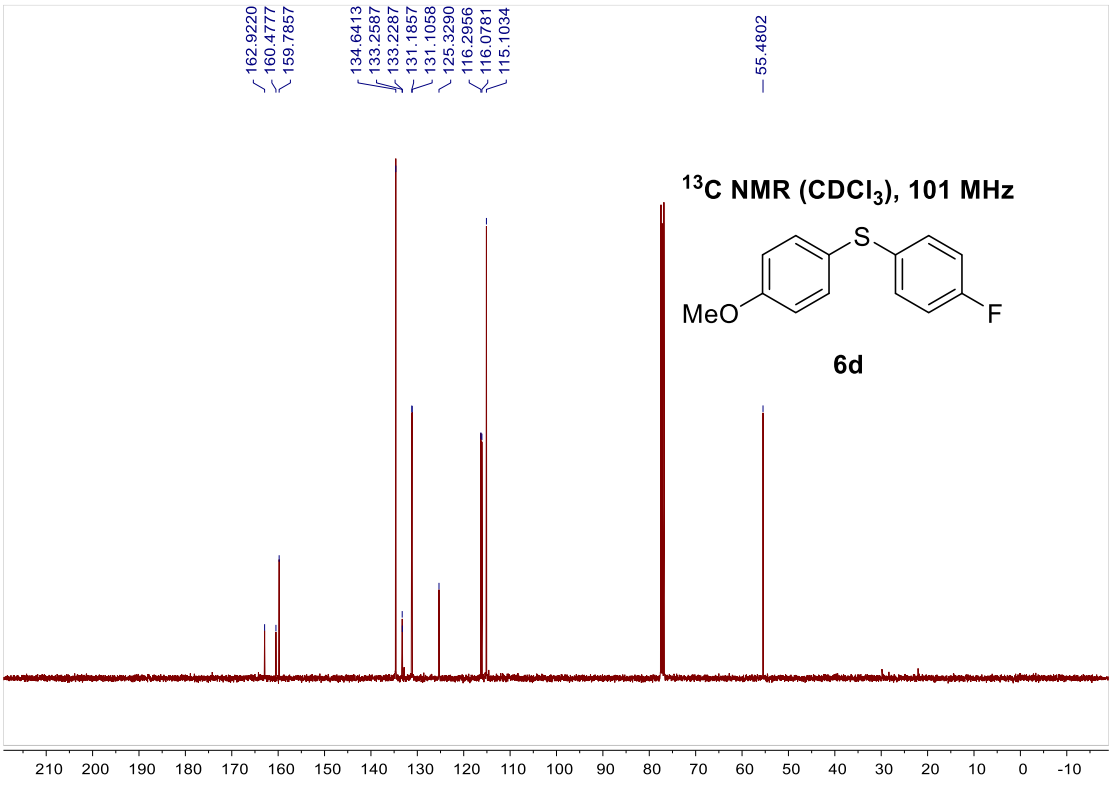
7.1914
7.1868
7.1739
6.9693
6.9638
6.9526
6.9476
6.9422
6.9311
6.9259
6.8856
6.8637
3.8026
1H NMR (CDCl3), 400 MHz
S
MeO
F
6d
2.00
2.00
2.02
2.06
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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134.6413
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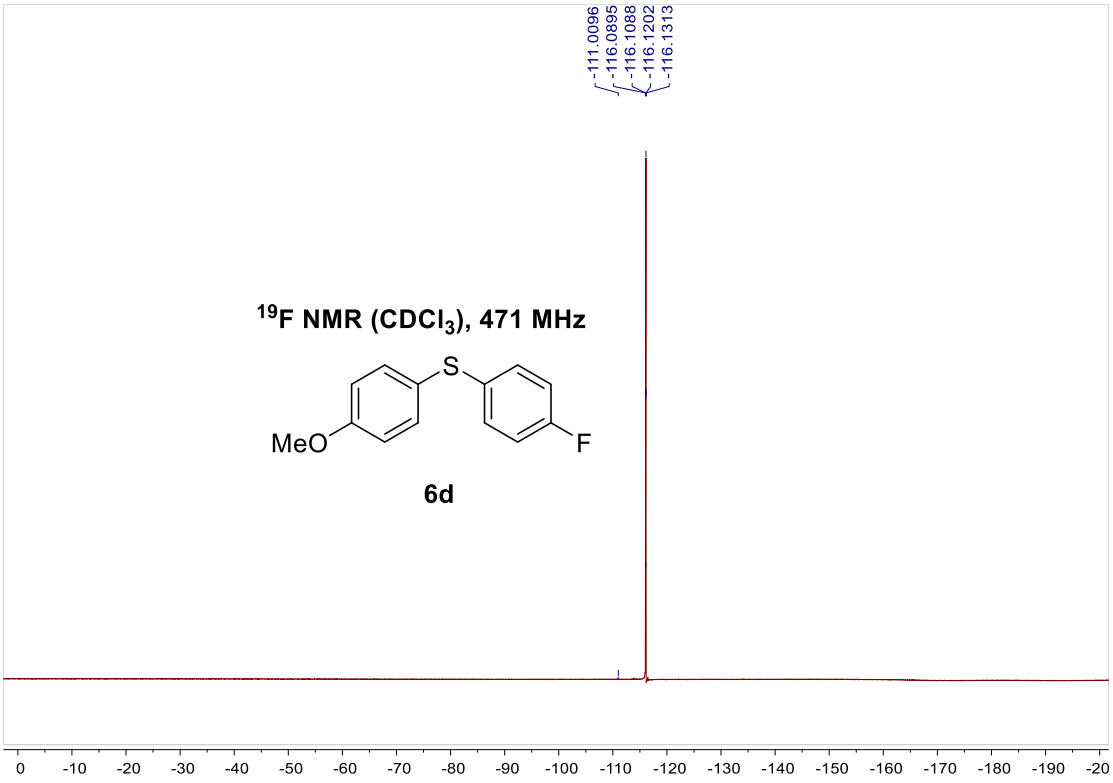
133.2287
131.1857
131.1058
125.3290
116.2956
116.0781
115.1034
55.4802
^{13}C NMR ($CDCl_3$), 101 MHz
S
MeO
F
6d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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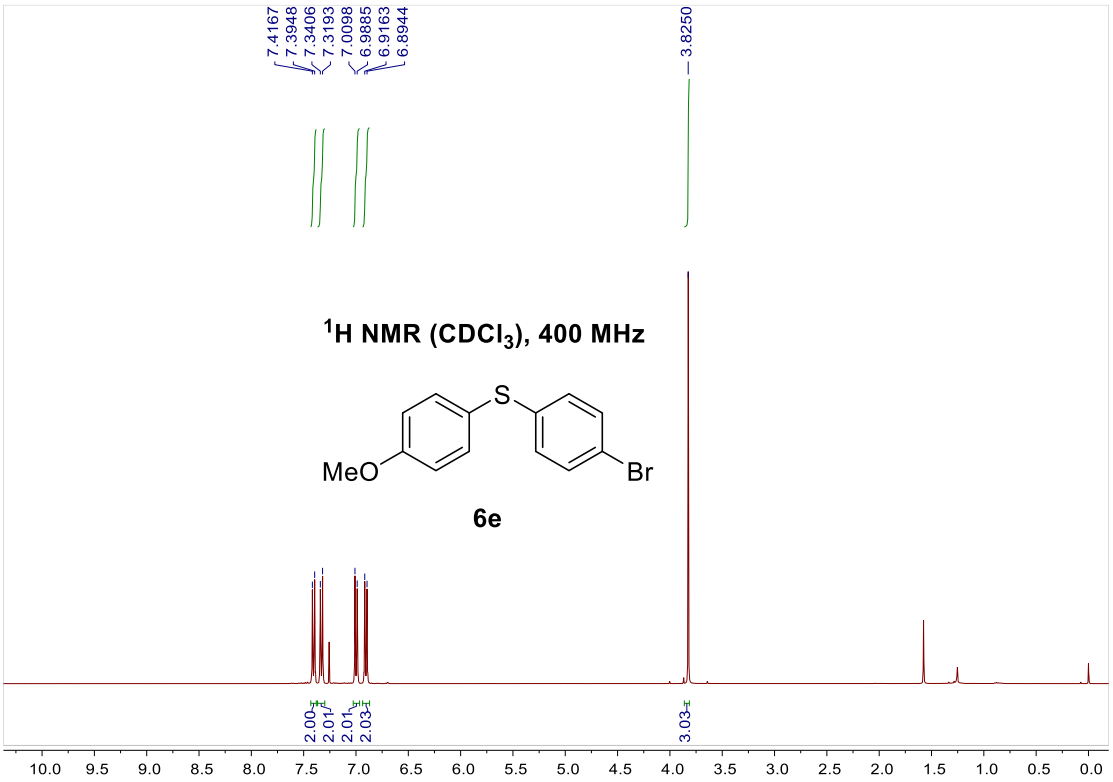
-116.0895
-116.1088
-116.1202
-116.1313
^{19}F NMR ($CDCl_3$), 471 MHz
S
MeO
F
6d
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20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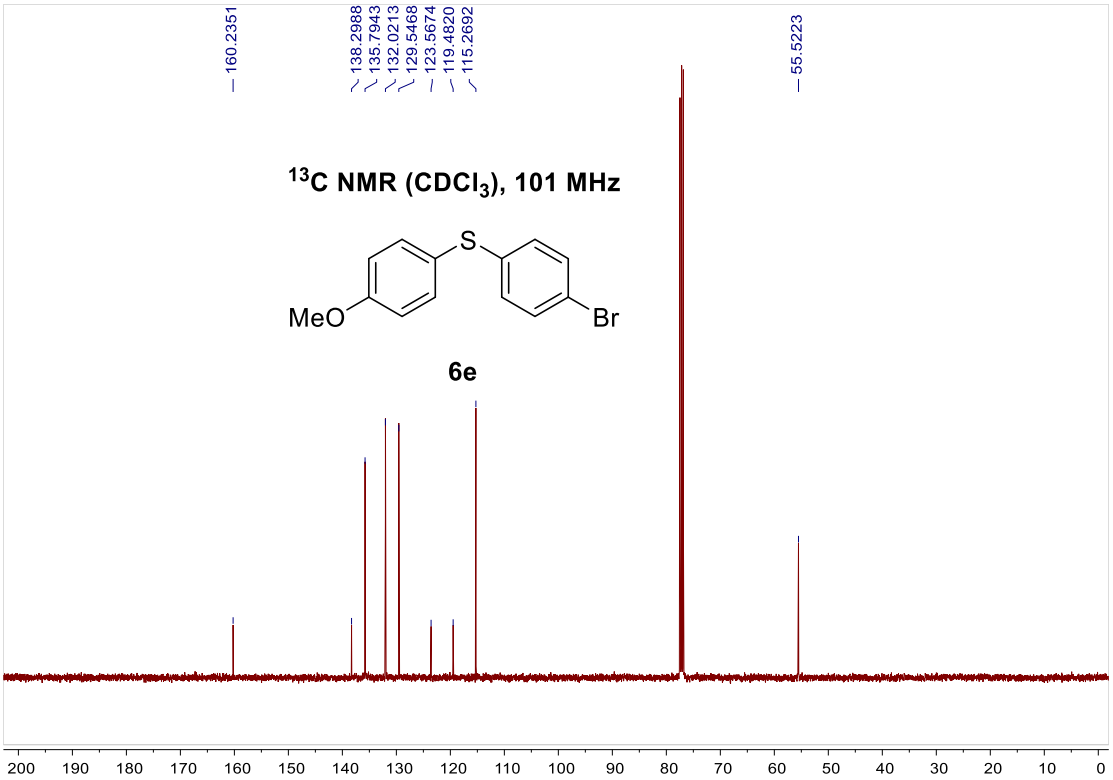
7.3948
7.3406
7.3193
7.0098
6.9885
6.9163
6.8944
3.8250
^{1}H NMR (CDCl$_3$), 400 MHz
S
MeO
Br
6e
2.00
2.01
2.01
2.03
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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138.2988
135.7943
132.0213
129.5468
123.5674
119.4820
115.2692
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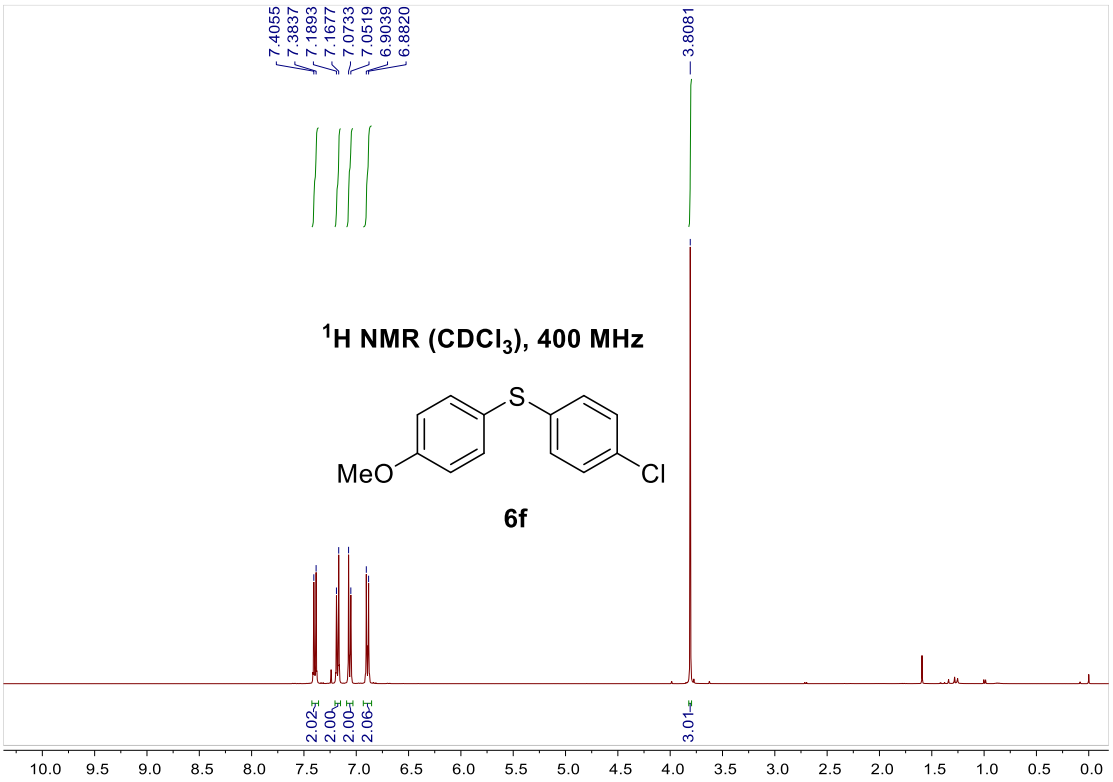
S
MeO
Br
6e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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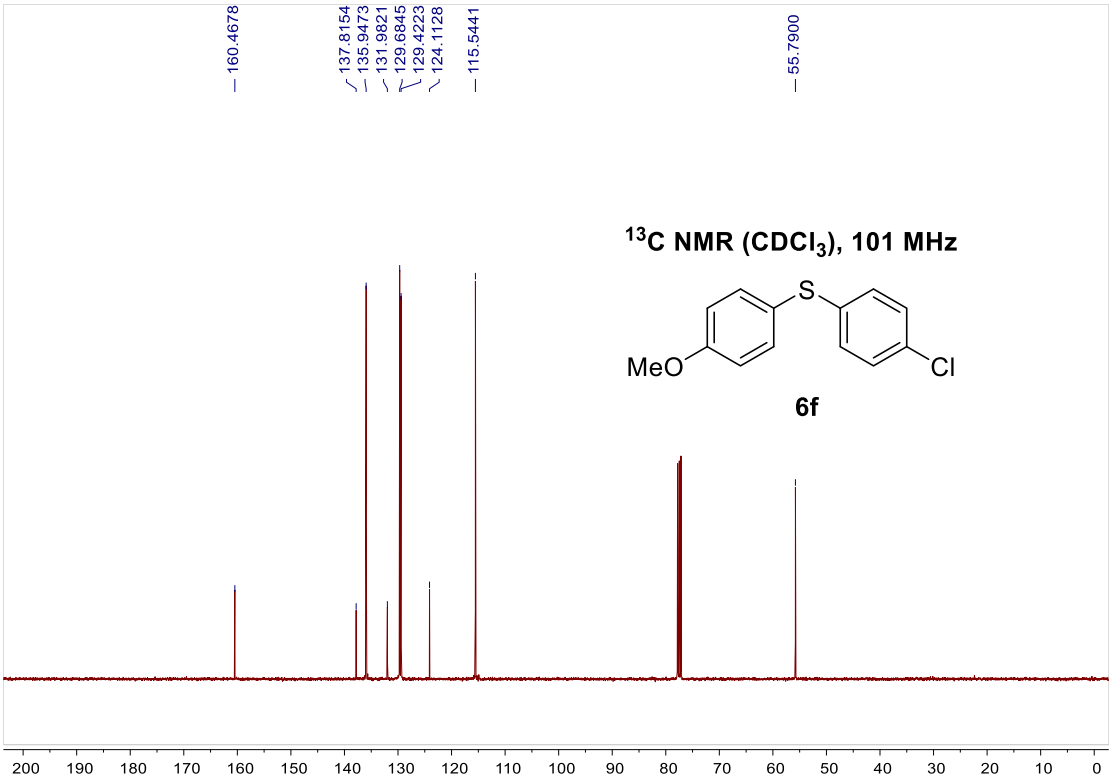
7.3837
7.1893
7.1677
7.0733
7.0519
6.9039
6.8820
3.8081
^{1}H NMR (CDCl$_3$), 400 MHz
S
MeO
Cl
6f
2.02
2.00
2.00
2.06
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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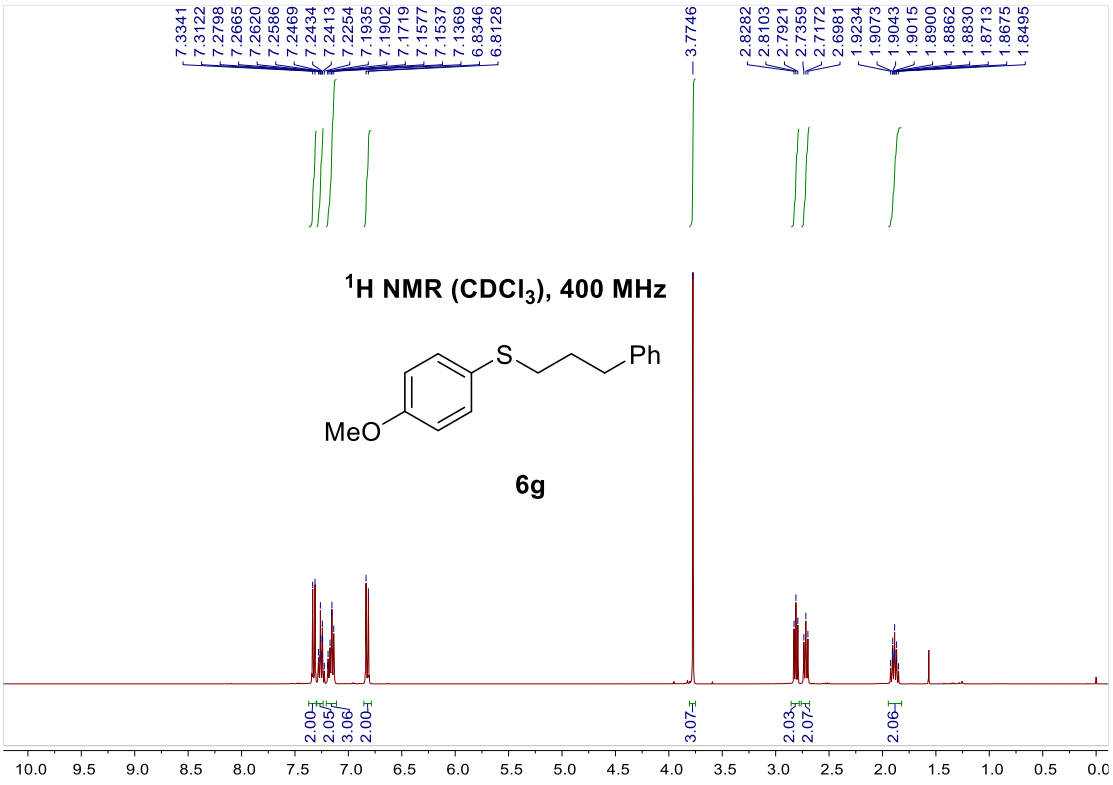
115.5441
55.7900
^{13}C NMR (CDCl$_3$), 101 MHz
S
MeO
Cl
6f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.2798
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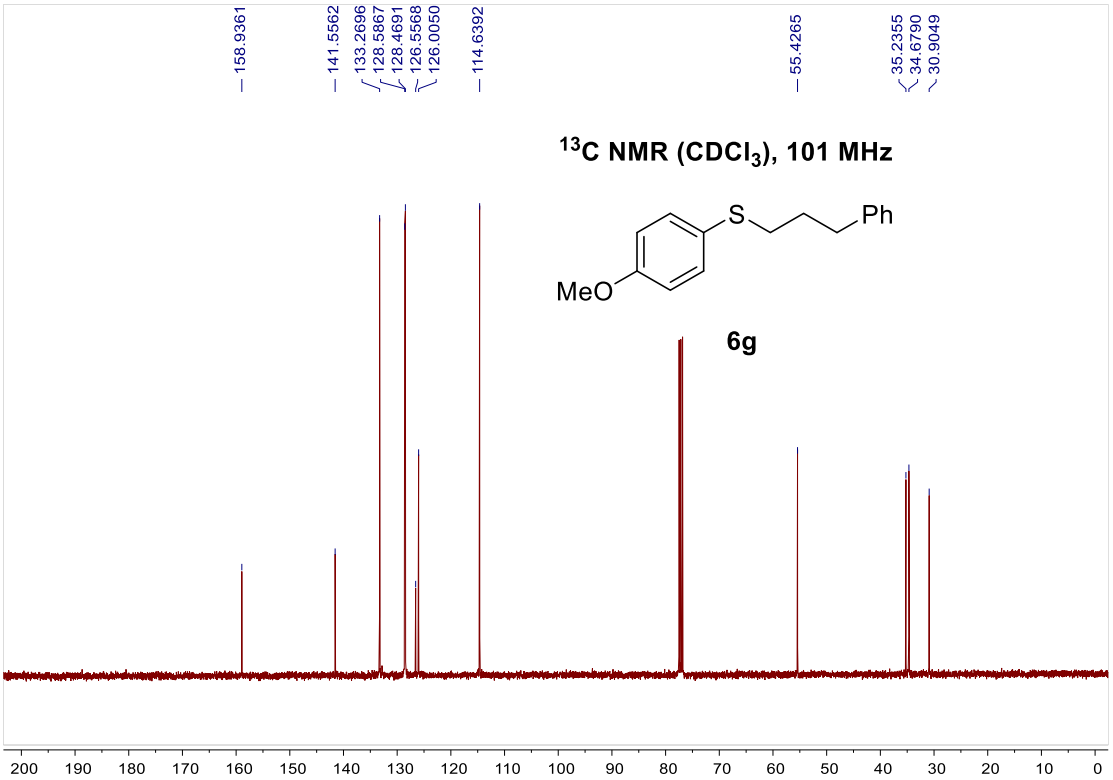
7.2620
7.2586
7.2469
7.2434
7.2413
7.2254
7.1935
7.1902
7.1719
7.1577
7.1537
7.1369
6.8346
6.8128
3.7746
2.8282
2.8103
2.7921
2.7359
2.7172
2.6981
1.9234
1.9073
1.9043
1.9015
1.8900
1.8862
1.8830
1.8713
1.8675
1.8495
^{1}H NMR ($CDCl_3$), 400 MHz
S
Ph
MeO
6g
2.00
2.05
3.06
2.00
3.07
2.03
2.07
2.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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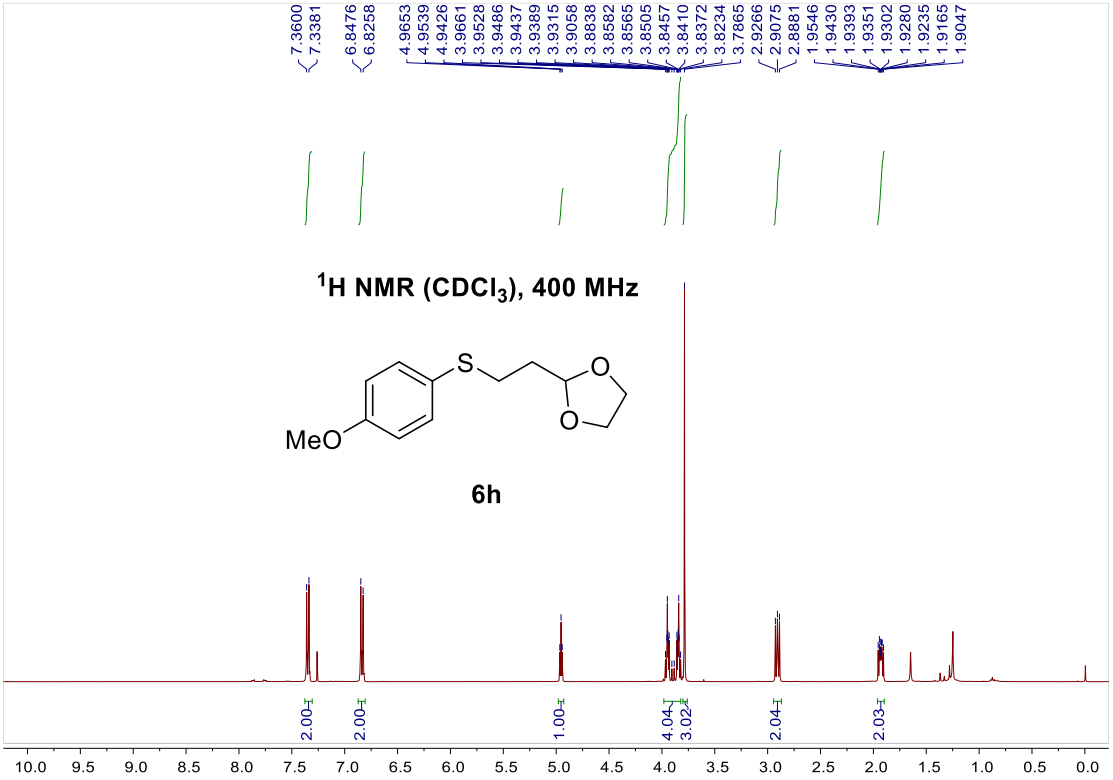
141.5562
133.2696
128.5867
128.4691
126.5568
126.0050
114.6392
55.4265
35.2355
34.6790
30.9049
^{13}C NMR ($CDCl_3$), 101 MHz
S
Ph
MeO
6g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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6.8476
6.8258
4.9653
4.9539
4.9426
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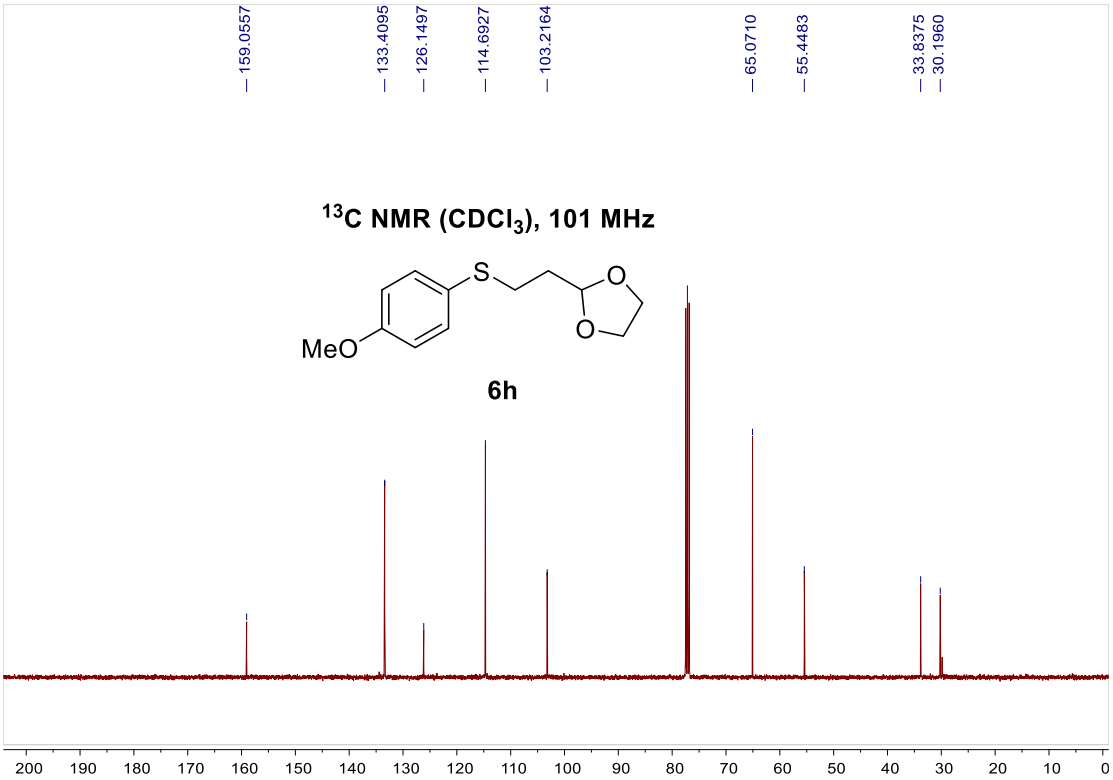
3.9528
3.9486
3.9437
3.9389
3.9315
3.9058
3.8838
3.8582
3.8565
3.8505
3.8457
3.8410
3.8372
3.8234
3.7865
2.9266
2.9075
2.8881
1.9546
1.9430
1.9393
1.9351
1.9302
1.9280
1.9235
1.9165
1.9047
^{1}H NMR ($CDCl_3$), 400 MHz
S
O
O
MeO
6h
2.00
2.00
1.00
4.04
3.02
2.04
2.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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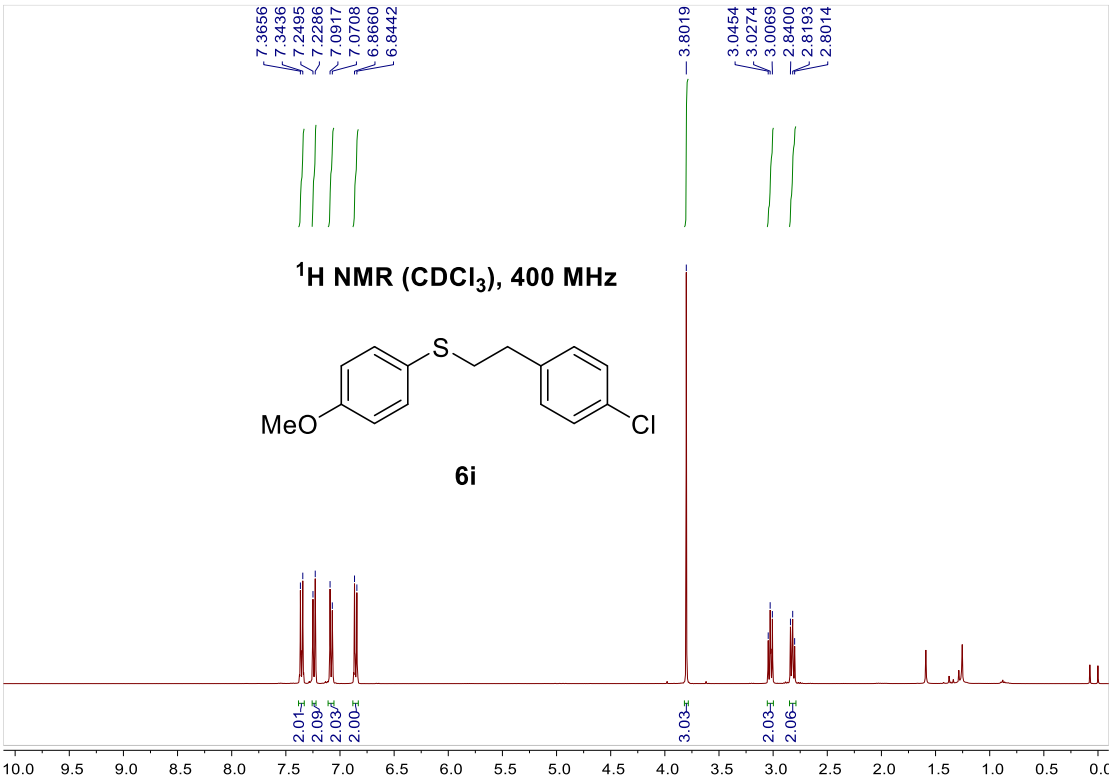
133.4095
126.1497
114.6927
103.2164
65.0710
55.4483
33.8375
30.1960
^{13}C NMR ($CDCl_3$), 101 MHz
S
O
O
MeO
6h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.2495
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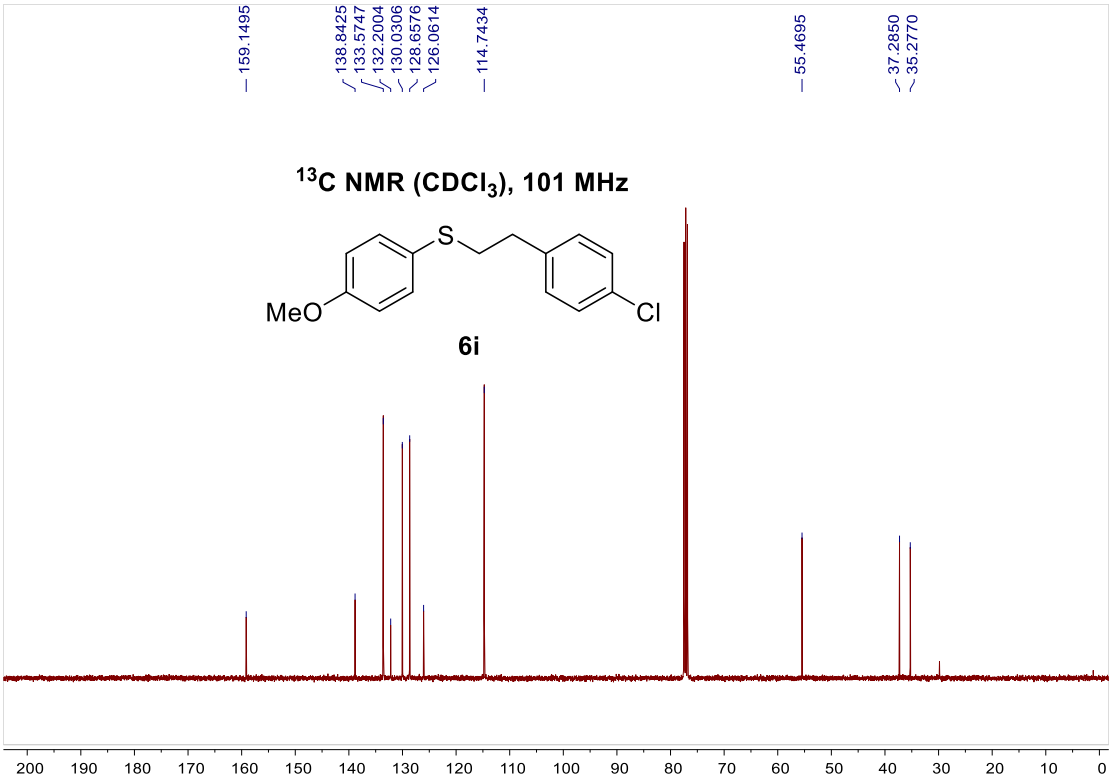
7.0917
7.0708
6.8660
6.8442
3.8019
3.0454
3.0274
3.0069
2.8400
2.8193
2.8014
1H NMR (CDCl3), 400 MHz
S
MeO
Cl
6i
2.01
2.09
2.03
2.00
3.03
2.03
2.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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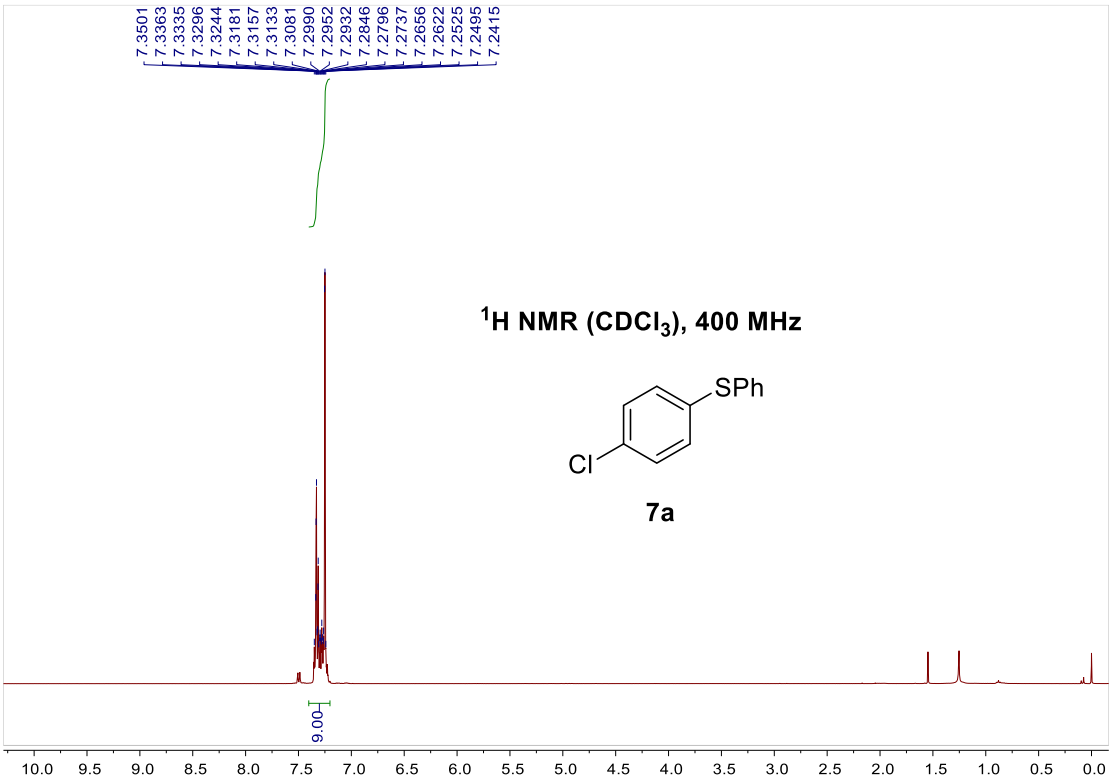
138.8425
133.5747
132.2004
130.0306
128.6576
126.0614
114.7434
55.4695
37.2850
35.2770
13C NMR (CDCl3), 101 MHz
S
MeO
Cl
6i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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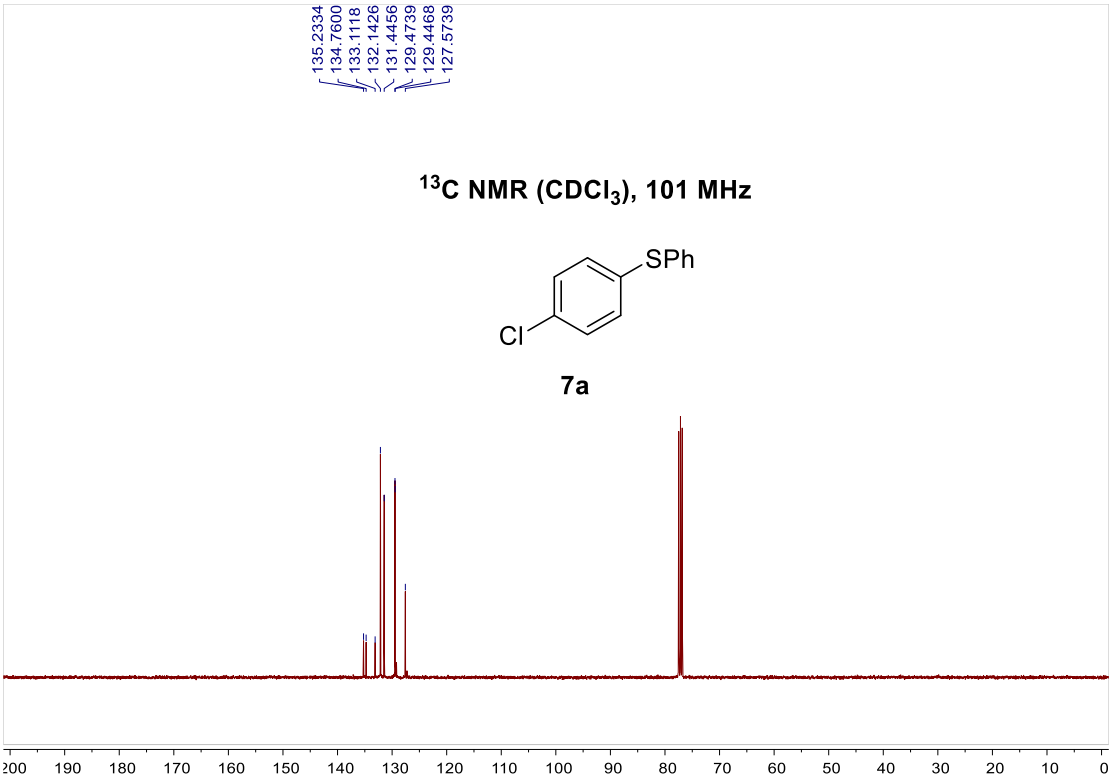
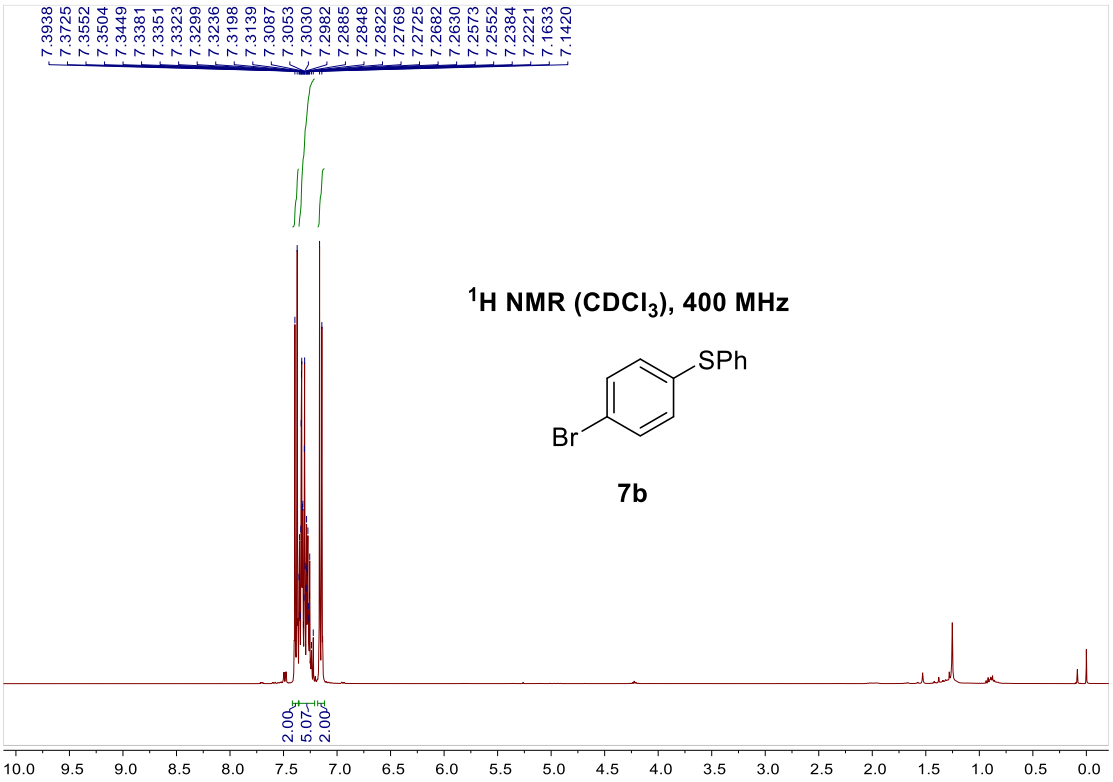
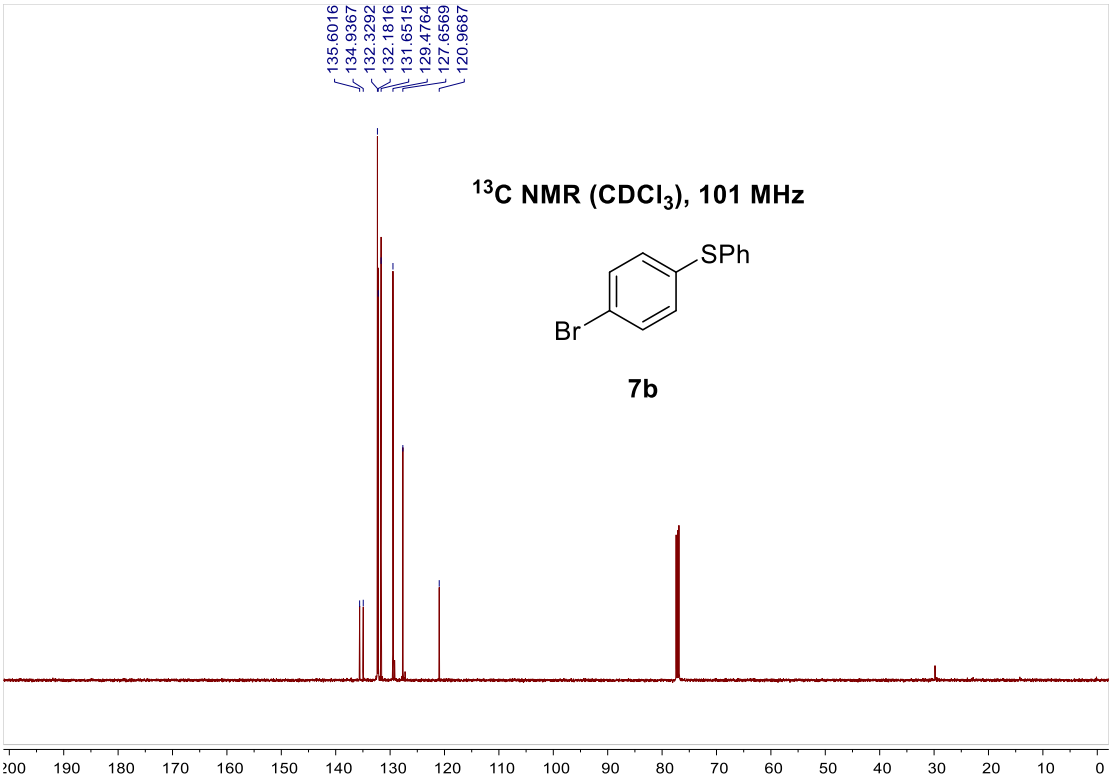
7.3363
7.3335
7.3296
7.3244
7.3181
7.3157
7.3133
7.3081
7.2990
7.2952
7.2932
7.2846
7.2796
7.2737
7.2656
7.2622
7.2525
7.2495
7.2415
^{1}H NMR ($CDCl_3$), 400 MHz
SPh
Cl
7a
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


135.2334
134.7600
133.1118
132.1426
131.4456
129.4739
129.4468
127.5739
^{13}C NMR ($CDCl_3$), 101 MHz
SPh
Cl
7a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



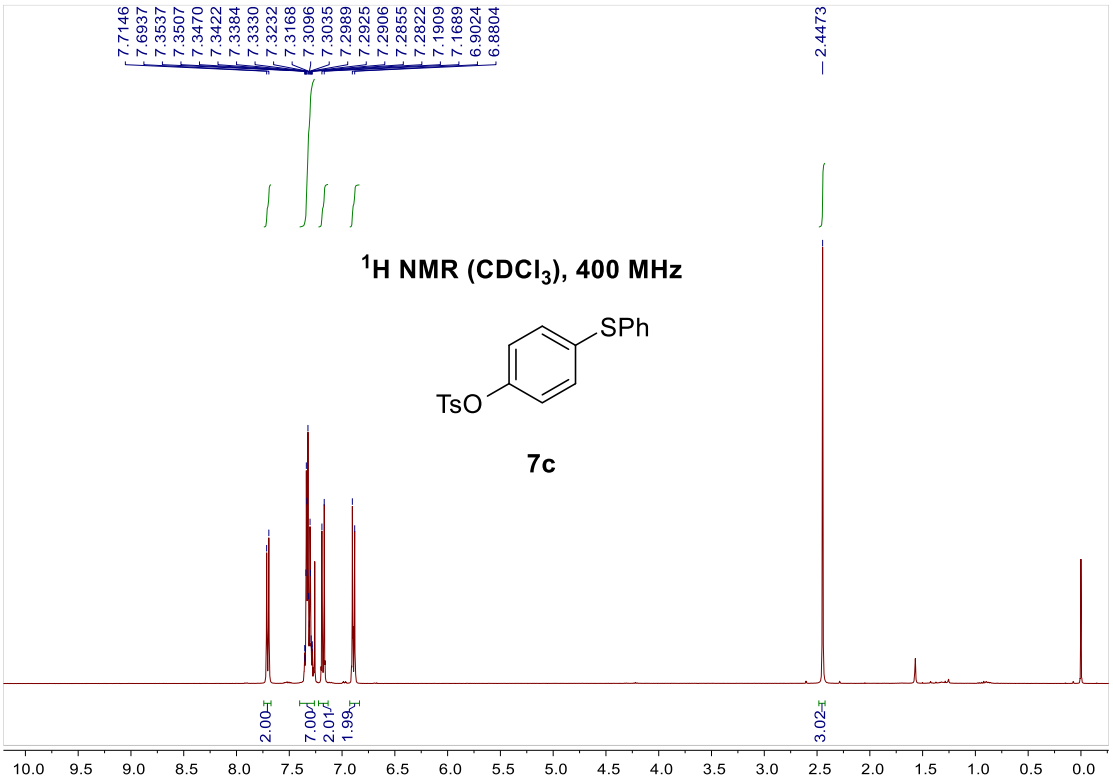
^{1}H NMR ($CDCl_3$), 400 MHz

7b



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

7b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7.3537
7.3507
7.3470
7.3422
7.3384
7.3330
7.3232
7.3168
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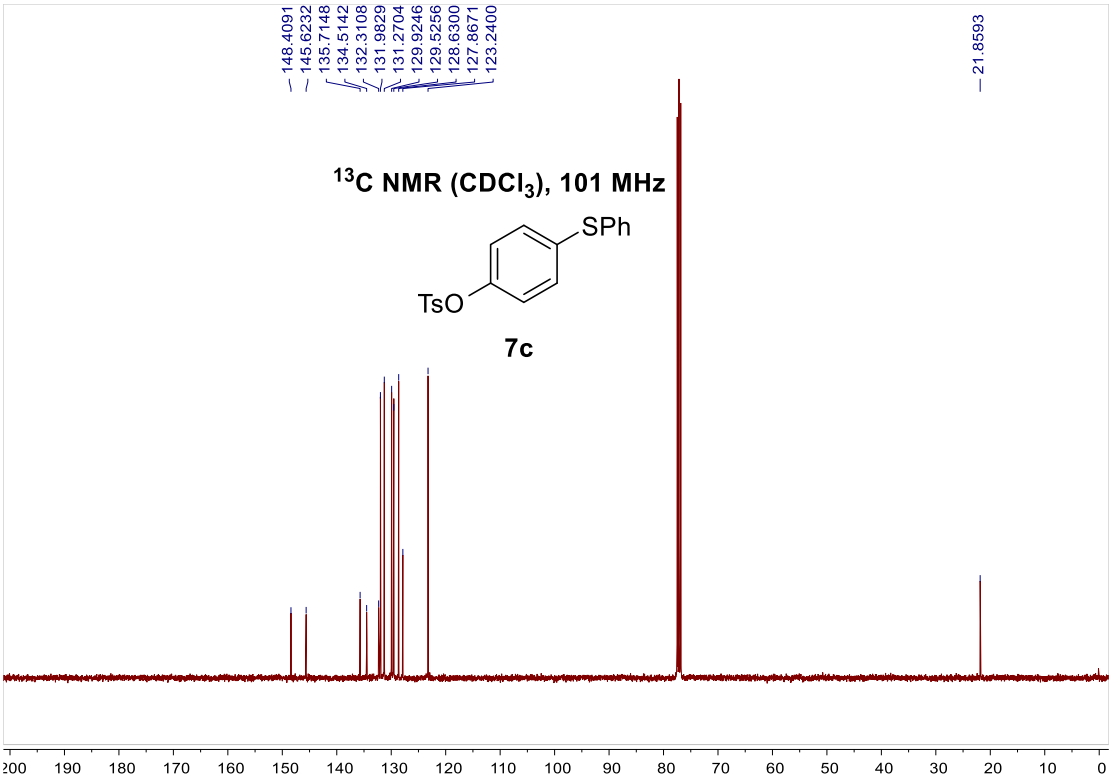
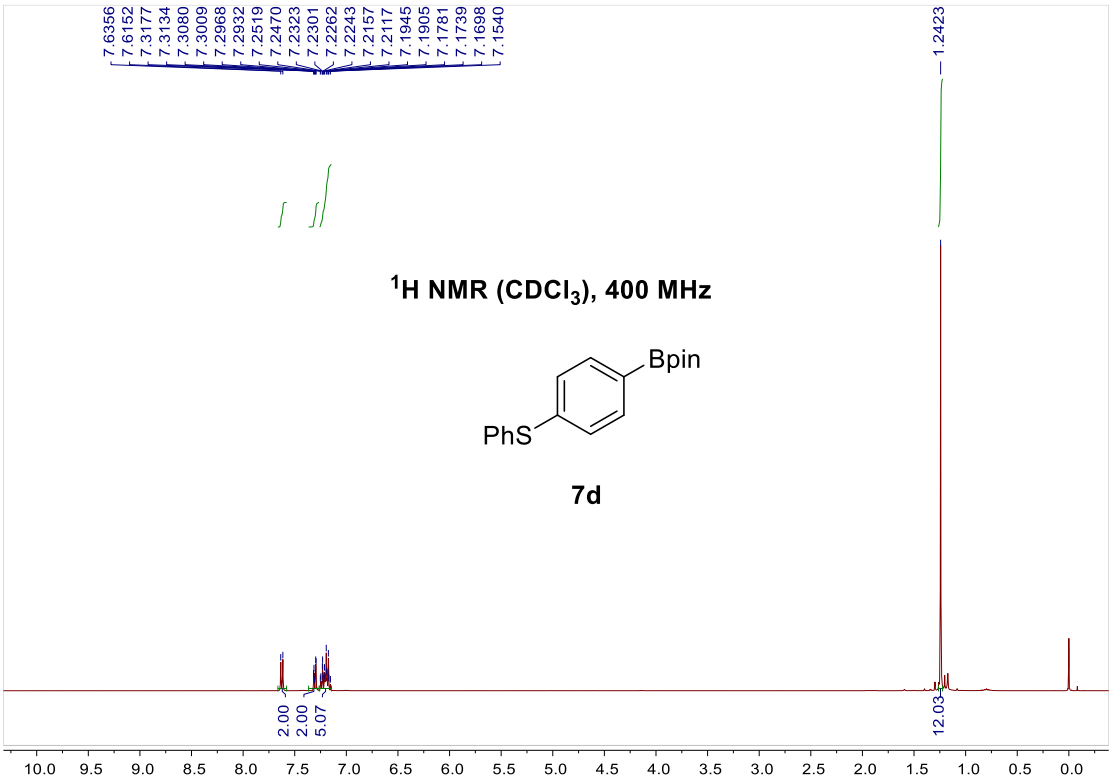
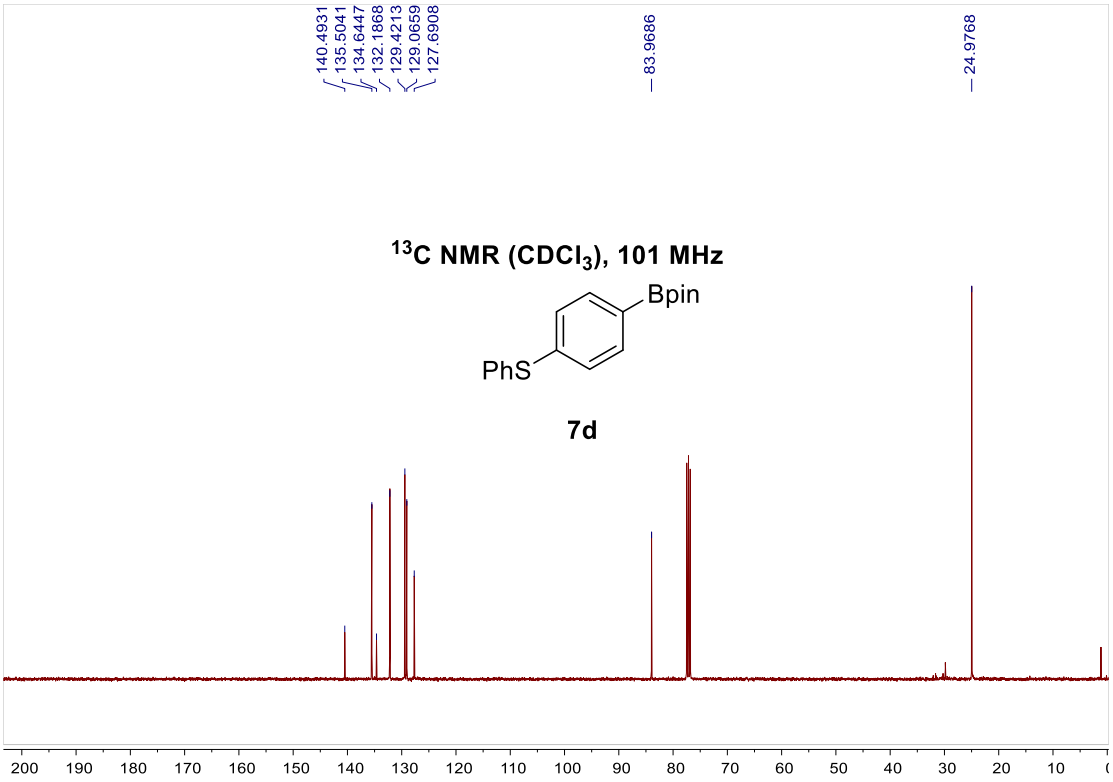
7.3035
7.2989
7.2925
7.2906
7.2855
7.2822
7.1909
7.1689
6.9024
6.8804
2.4473
^{1}H NMR ($CDCl_3$), 400 MHz
SPh
TsO
7c
2.00
7.00
2.01
1.99
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


148.4091
145.6232
135.7148
134.5142
132.3108
131.9829
131.2704
129.9246
129.5256
128.6300
127.8671
123.2400
21.8593
^{13}C NMR ($CDCl_3$), 101 MHz
SPh
TsO
7c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



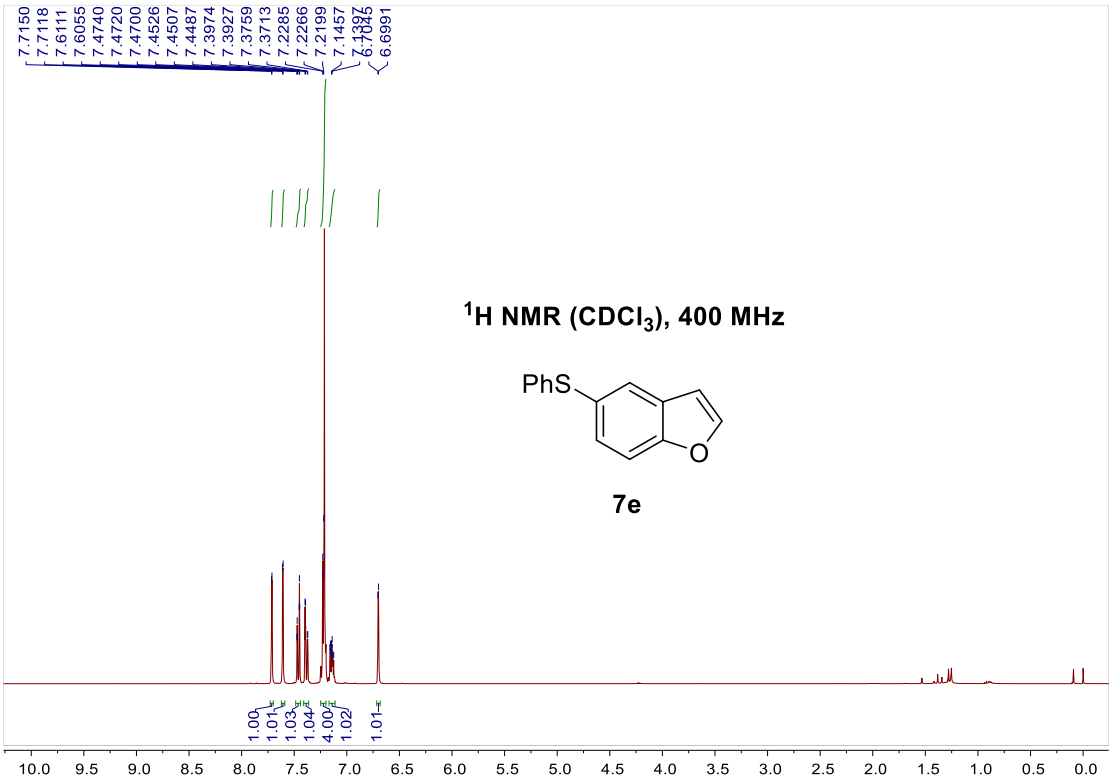
^{1}H NMR ($CDCl_3$), 400 MHz

7d



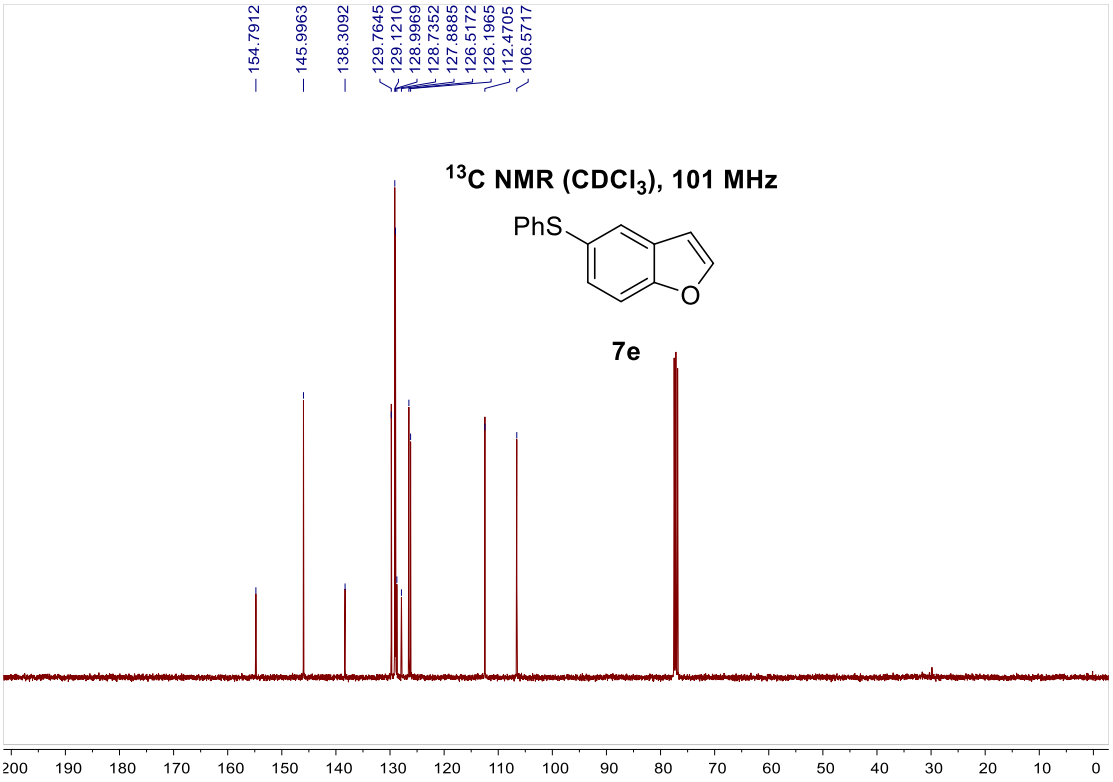
^{13}C NMR ($CDCl_3$), 101 MHz

7d



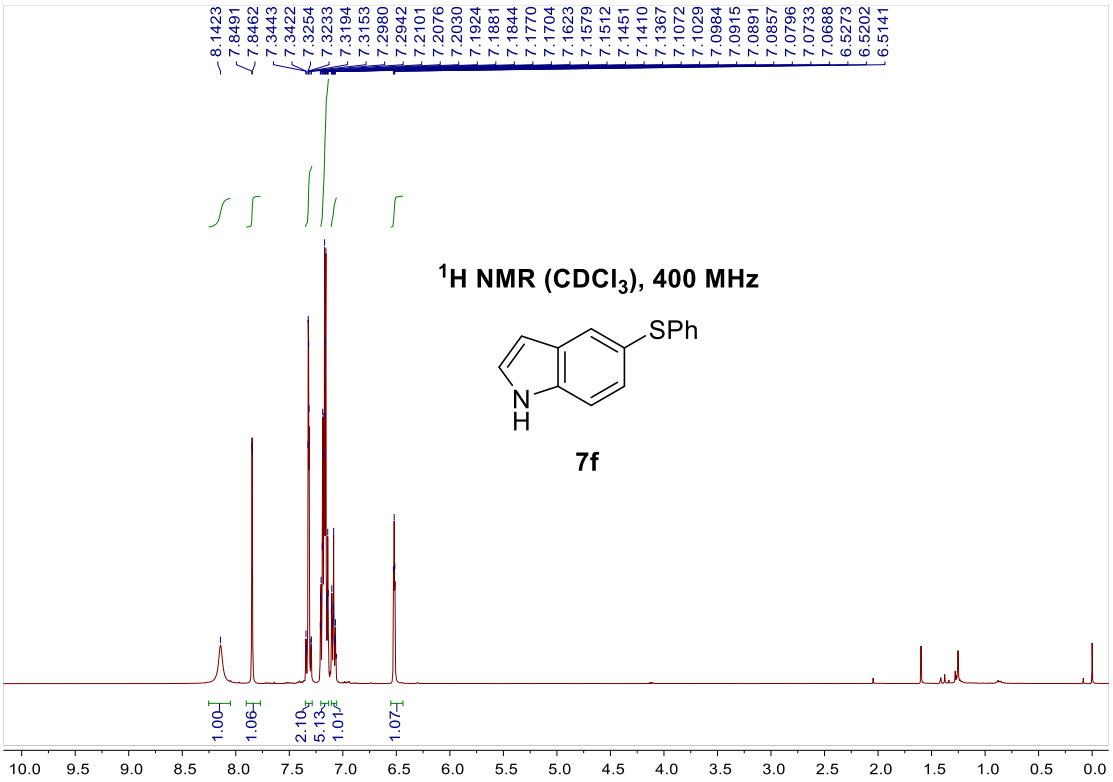
^{1}H NMR ($CDCl_3$), 400 MHz

7e



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

7e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7.3422
7.3254
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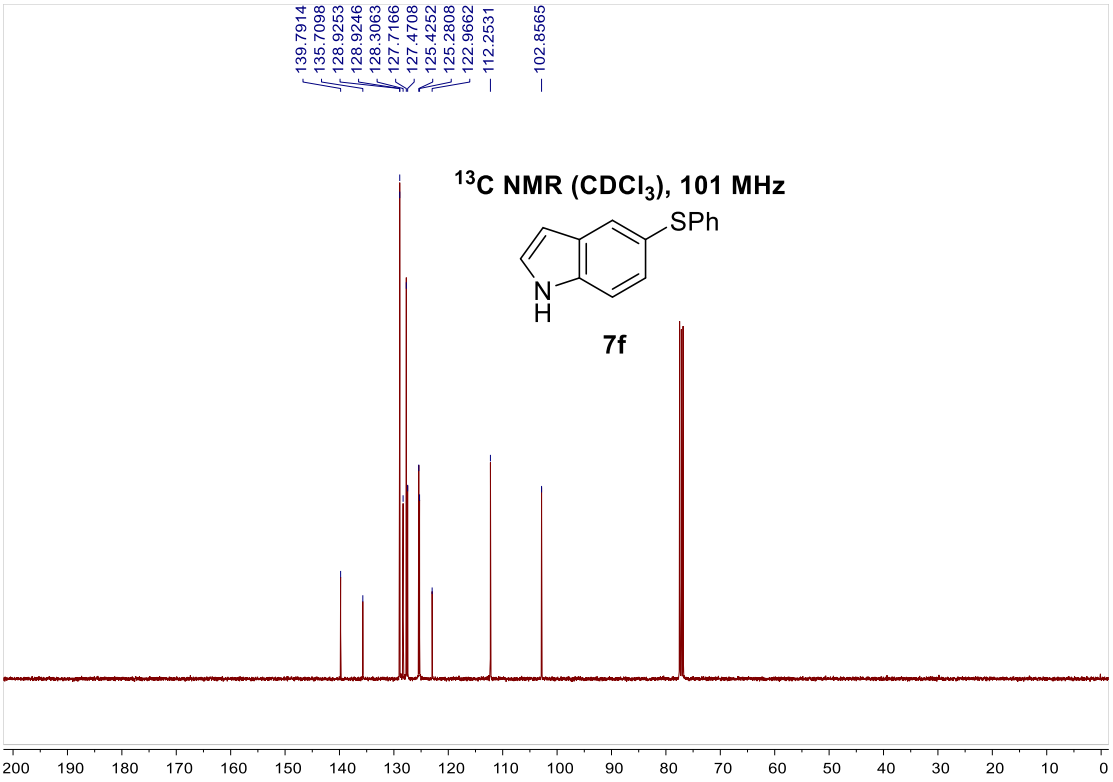
7.3153
7.2980
7.2942
7.2101
7.2076
7.2030
7.1924
7.1881
7.1844
7.1770
7.1704
7.1623
7.1579
7.1512
7.1451
7.1410
7.1367
7.1072
7.1029
7.0984
7.0915
7.0891
7.0857
7.0796
7.0733
7.0688
6.5273
6.5202
6.5141
1H NMR (CDCl3), 400 MHz
SPh
N
H
7f
1.00
1.06
2.10
5.13
1.01
1.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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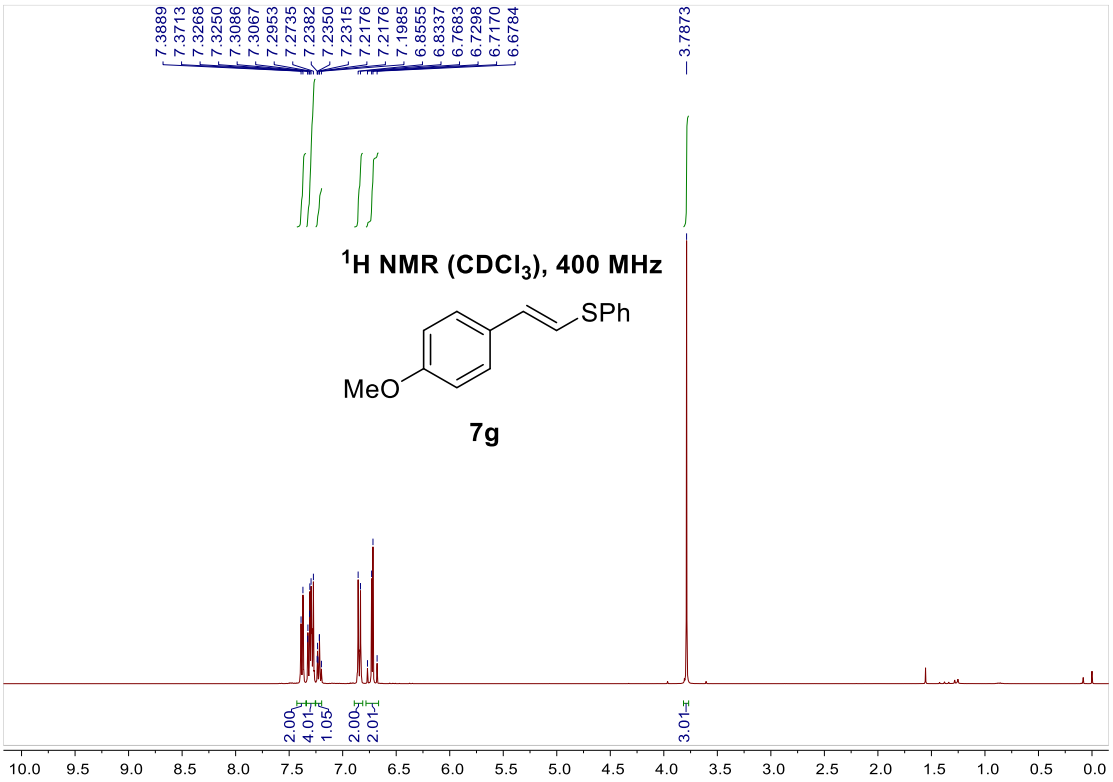
135.7098
128.9253
128.9246
128.3063
127.7166
127.4708
125.4252
125.2808
122.9662
112.2531
102.8565
13C NMR (CDCl3), 101 MHz
SPh
N
H
7f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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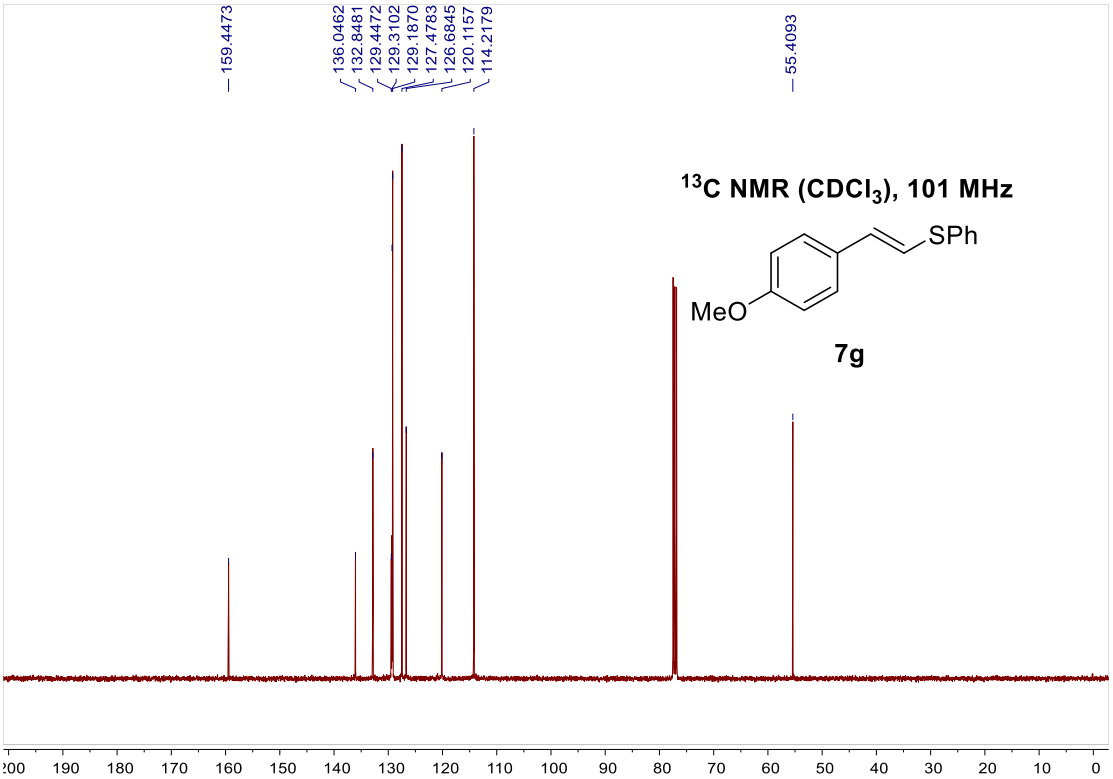
7.3268
7.3250
7.3086
7.3067
7.2953
7.2735
7.2382
7.2350
7.2315
7.2176
7.2176
7.1985
6.8555
6.8337
6.7683
6.7298
6.7170
6.6784
3.7873
^{1}H NMR (CDCl$_3$), 400 MHz
SPh
MeO
7g
2.00
4.01
1.05
2.00
2.01
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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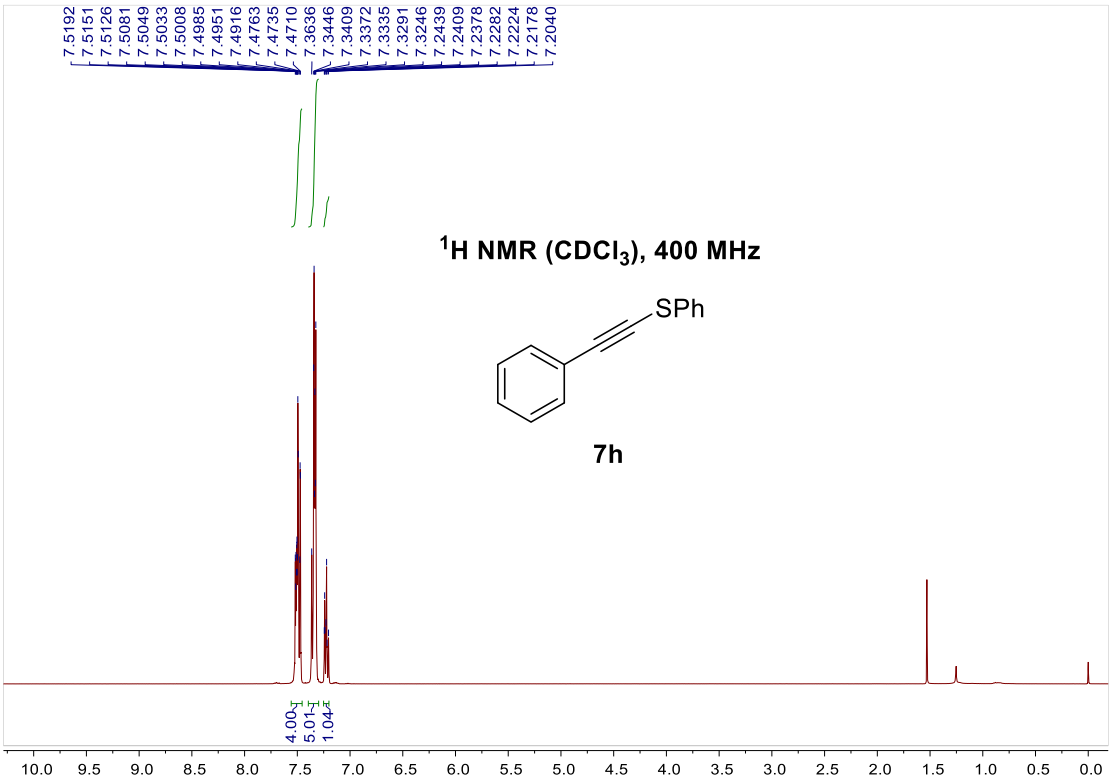
132.8481
129.4472
129.3102
129.1870
127.4783
126.6845
120.1157
114.2179
55.4093
^{13}C NMR (CDCl$_3$), 101 MHz
SPh
MeO
7g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.5081
7.5049
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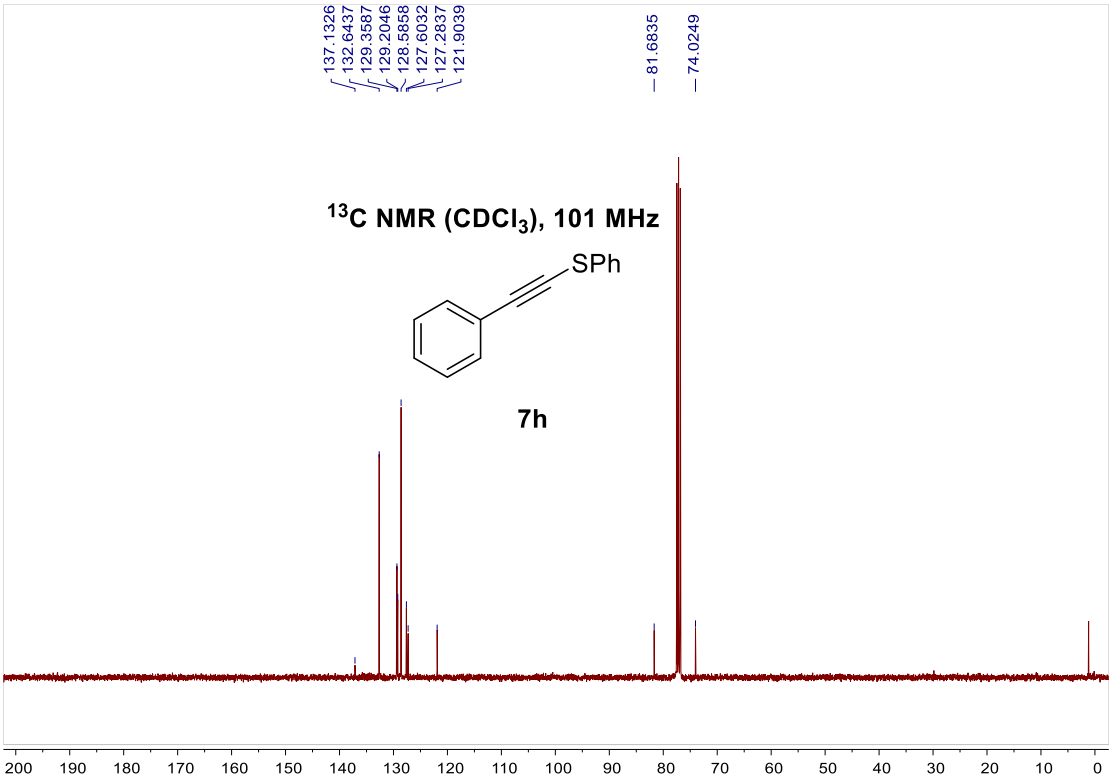
7.4916
7.4763
7.4735
7.4710
7.3636
7.3446
7.3409
7.3372
7.3335
7.3291
7.3246
7.2439
7.2409
7.2378
7.2282
7.2224
7.2178
7.2040
^{1}H NMR (CDCl$_3$), 400 MHz
SPh
7h
4.00
5.01
1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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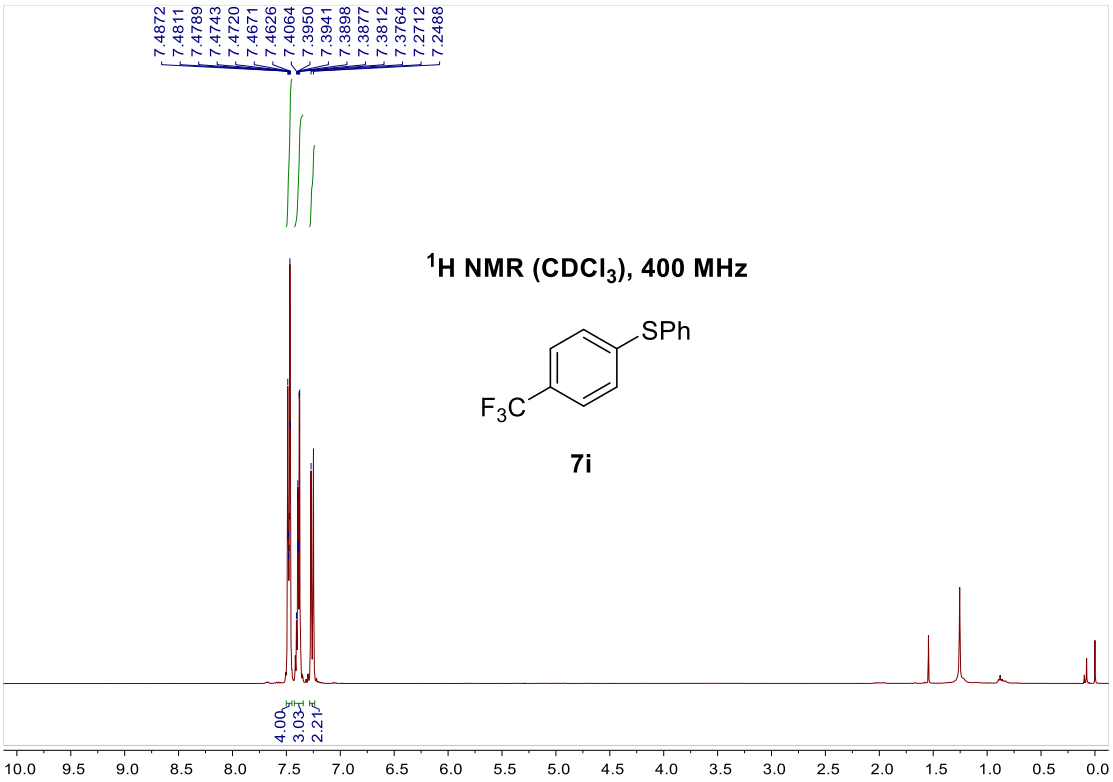
129.3587
129.2046
128.5858
127.6032
127.2837
121.9039
81.6835
74.0249
^{13}C NMR (CDCl$_3$), 101 MHz
SPh
7h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.4720
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7.4626
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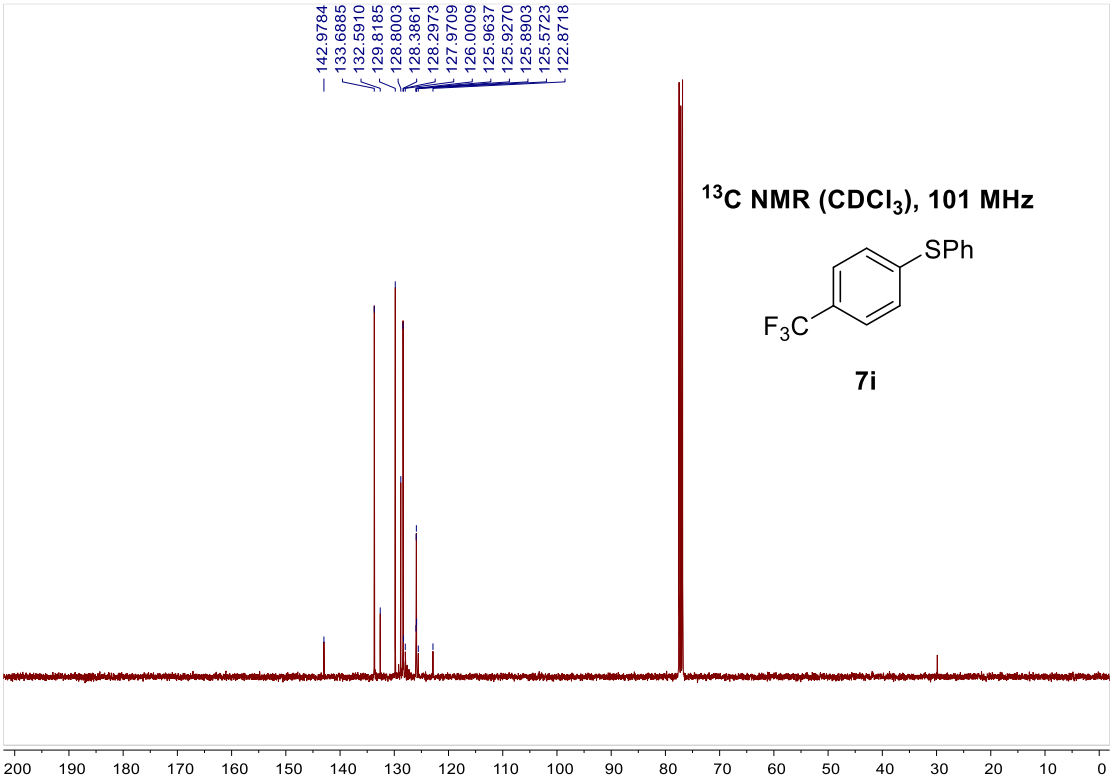
7.3950
7.3941
7.3898
7.3877
7.3812
7.3764
7.2712
7.2488
^{1}H NMR ($CDCl_3$), 400 MHz
SPh
F_3C
7i
4.00
3.03
2.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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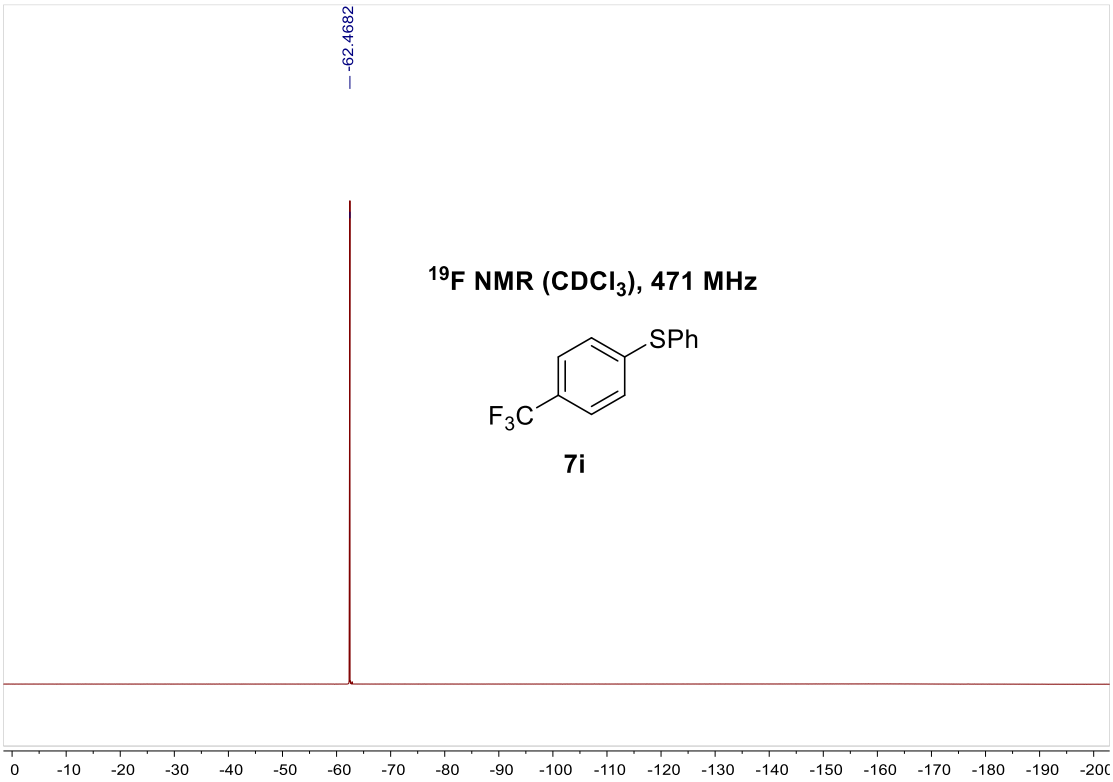
128.8003
128.3861
128.2973
127.9709
126.0009
125.9637
125.9270
125.8903
125.5723
122.8718
^{13}C NMR ($CDCl_3$), 101 MHz
SPh
F_3C
7i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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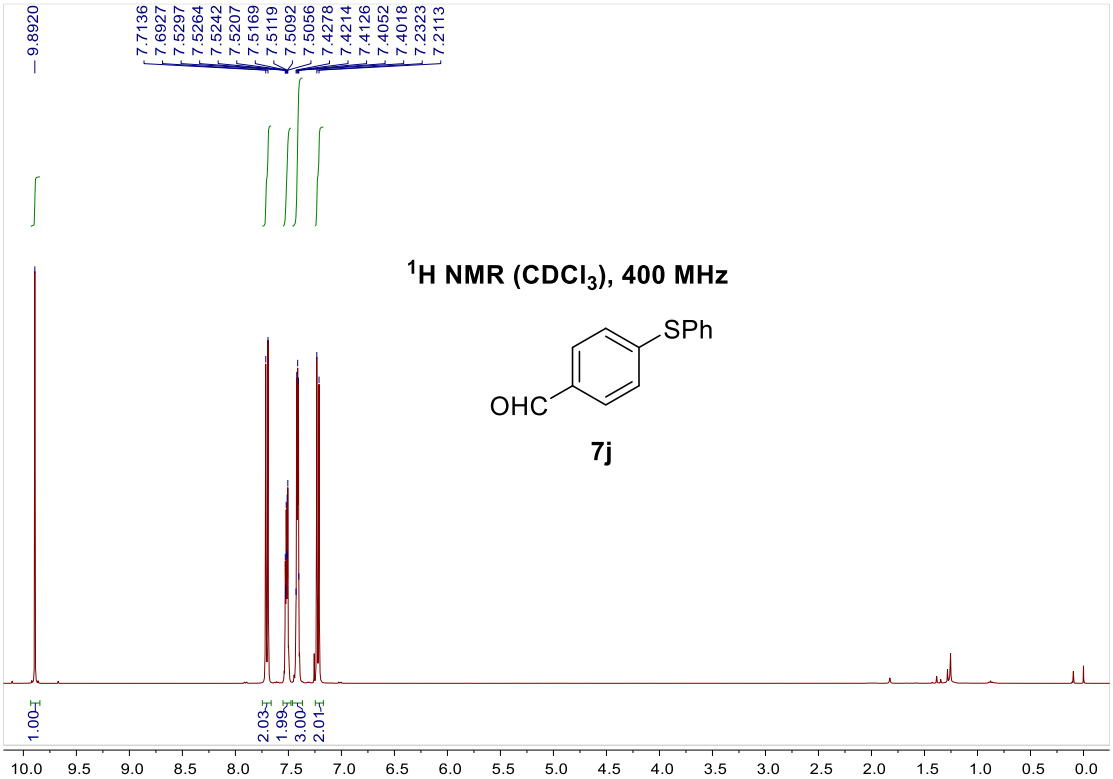
SPh
F$_3$C
7i
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200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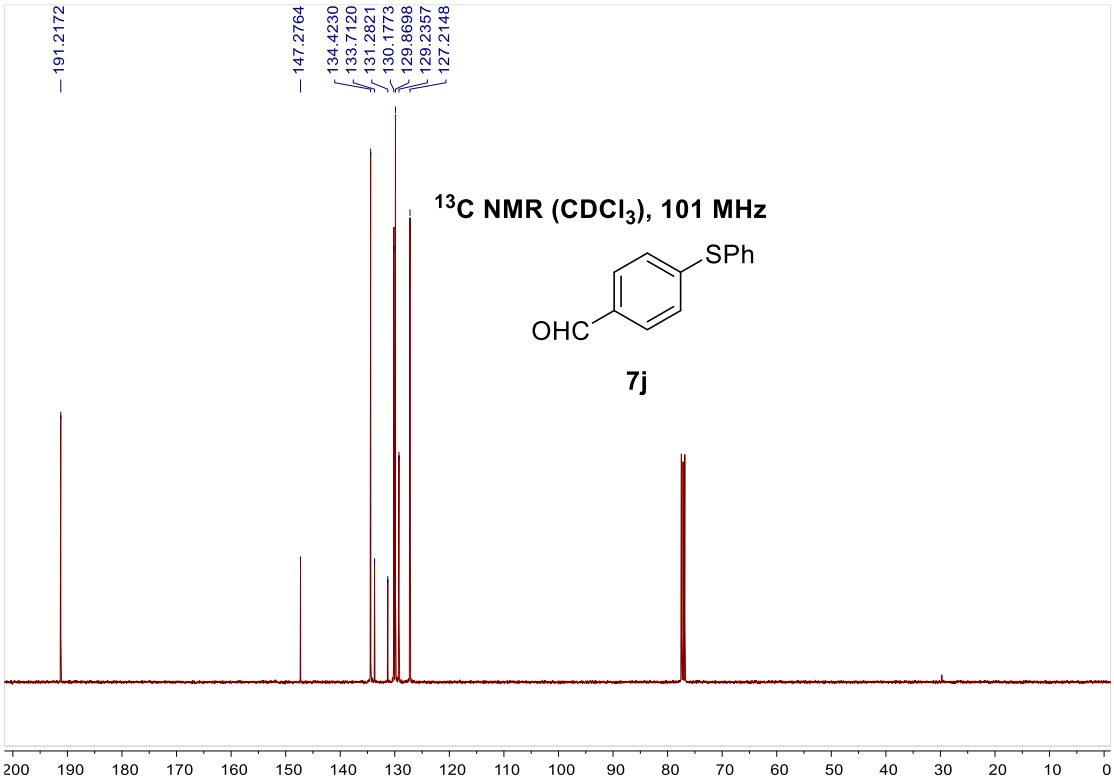
7.6927
7.5297
7.5264
7.5242
7.5207
7.5169
7.5119
7.5092
7.5056
7.4278
7.4214
7.4126
7.4052
7.4018
7.2323
7.2113
^{1}H NMR (CDCl$_3$), 400 MHz
SPh
OHC
7j
1.00
2.03
1.99
3.00
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


191.2172
147.2764
134.4230
133.7120
131.2821
130.1773
129.8698
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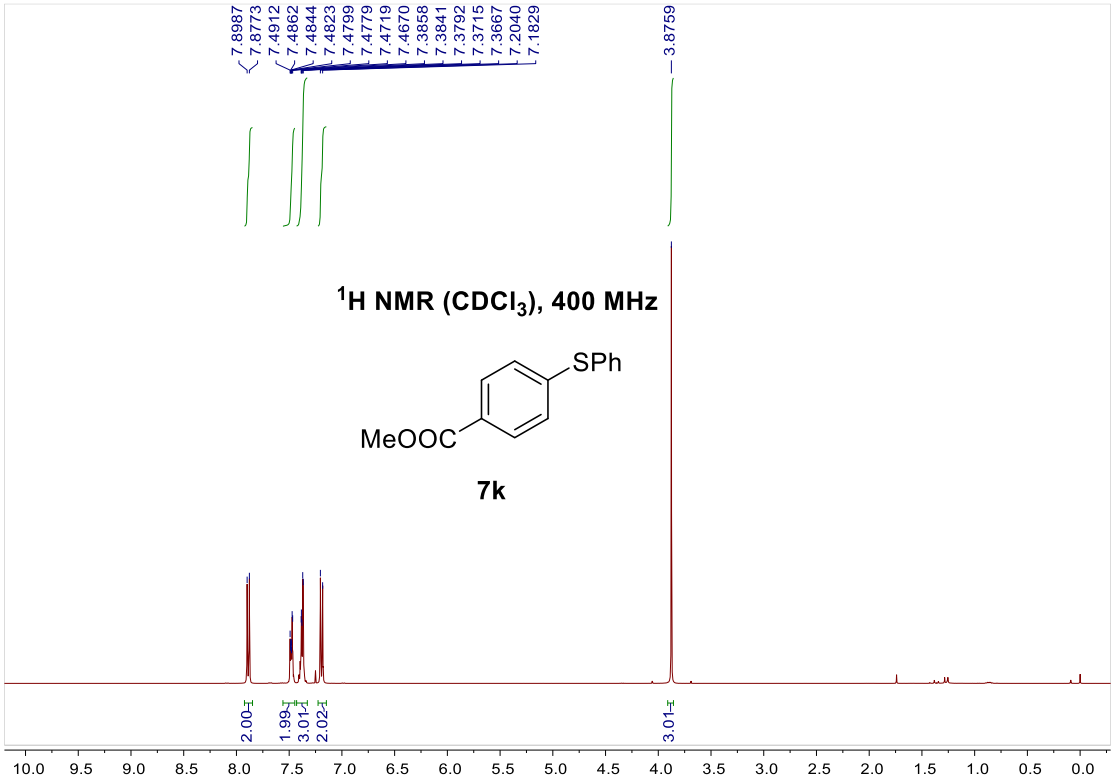
13C NMR (CDCl3), 101 MHz
SPh
OHC
7j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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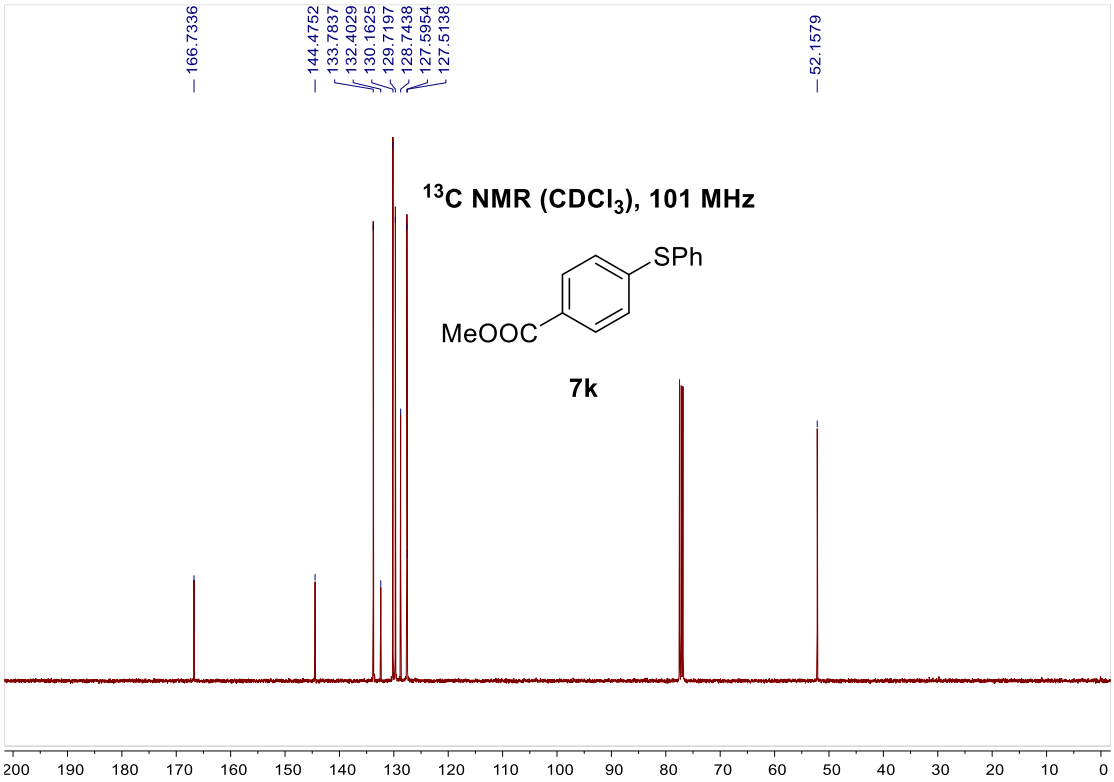
7.4912
7.4862
7.4844
7.4823
7.4799
7.4779
7.4719
7.4670
7.3858
7.3841
7.3792
7.3715
7.3667
7.2040
7.1829
3.8759
1H NMR (CDCl3), 400 MHz
SPh
MeOOC
7k
2.00
1.99
3.01
2.02
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


166.7336
144.4752
133.7837
132.4029
130.1625
129.7197
128.7438
127.5954
127.5138
52.1579
13C NMR (CDCl3), 101 MHz
SPh
MeOOC
7k
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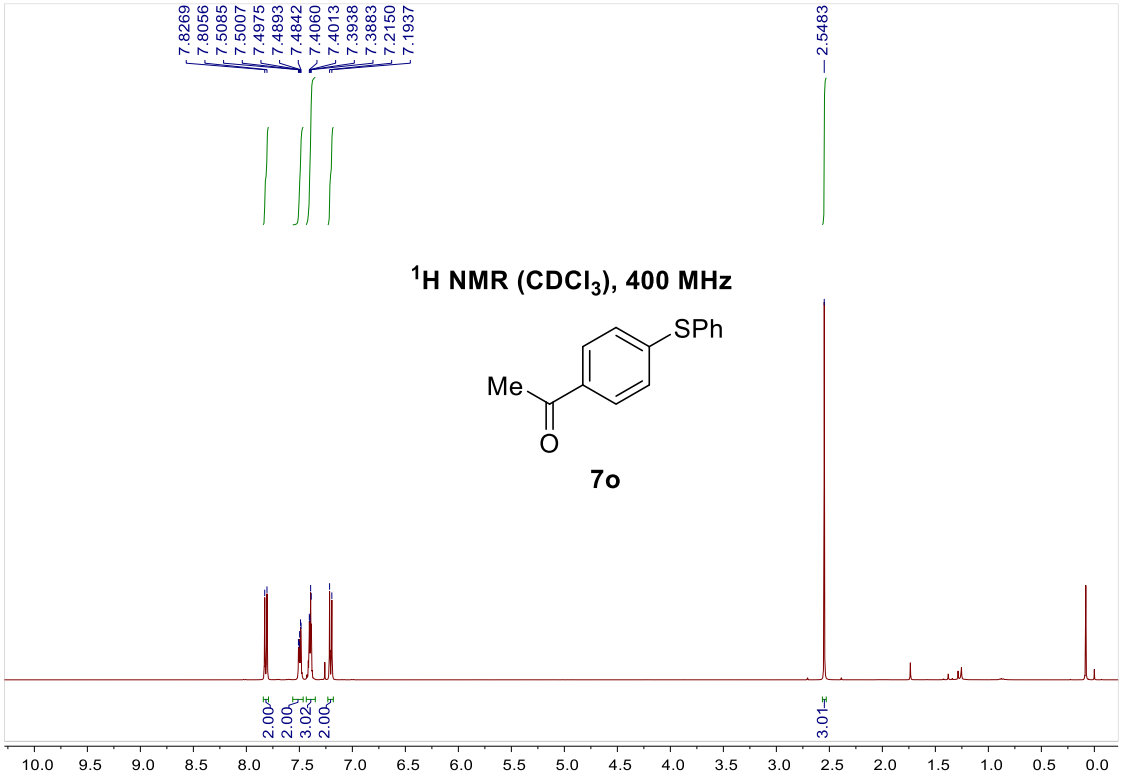
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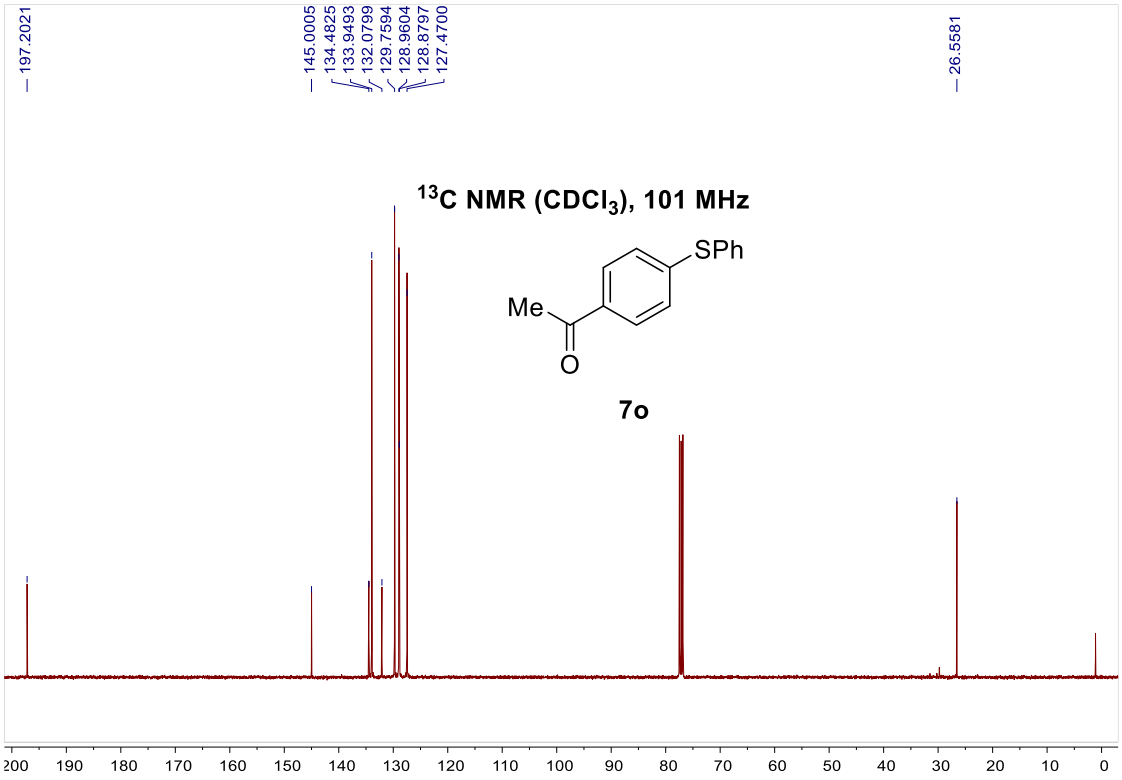
7.5085
7.5007
7.4975
7.4893
7.4842
7.4060
7.4013
7.3938
7.3883
7.2150
7.1937
2.5483
1H NMR (CDCl3), 400 MHz
SPh
Me
O
7o
2.00
2.00
3.02
2.00
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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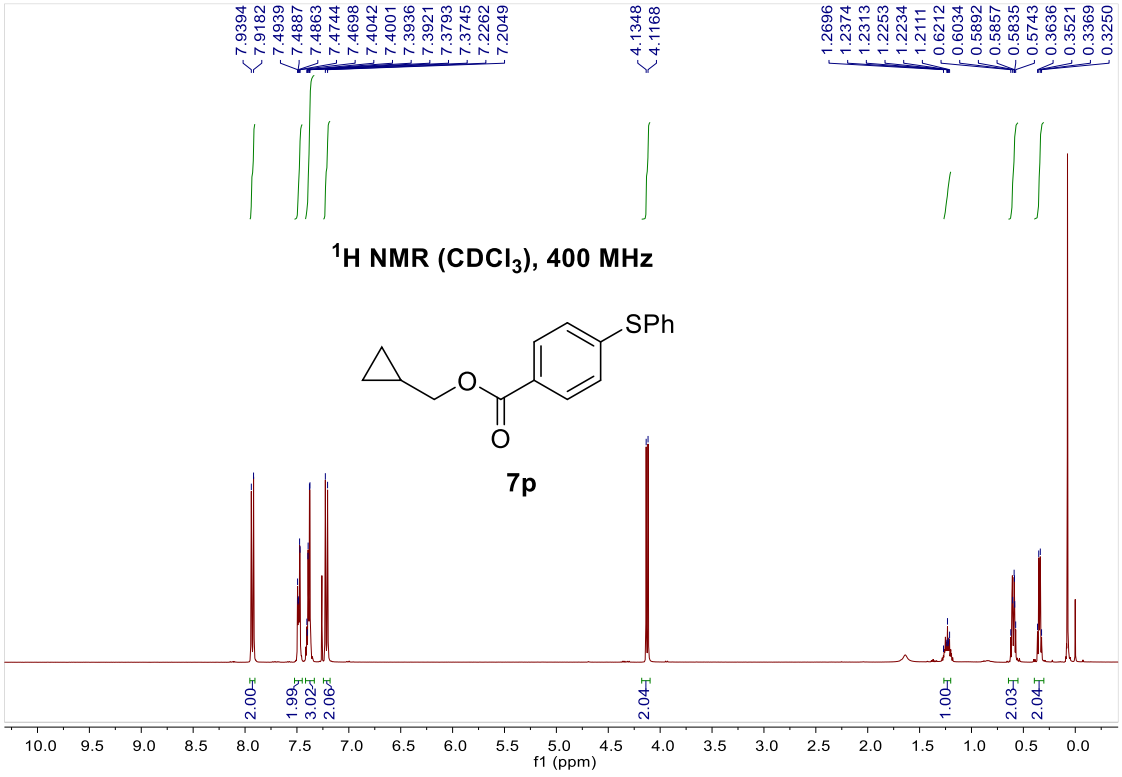
145.0005
134.4825
133.9493
132.0799
129.7594
128.9604
128.8797
127.4700
26.5581
13C NMR (CDCl3), 101 MHz
SPh
Me
O
7o
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.4939
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7.4863
7.4744
7.4698
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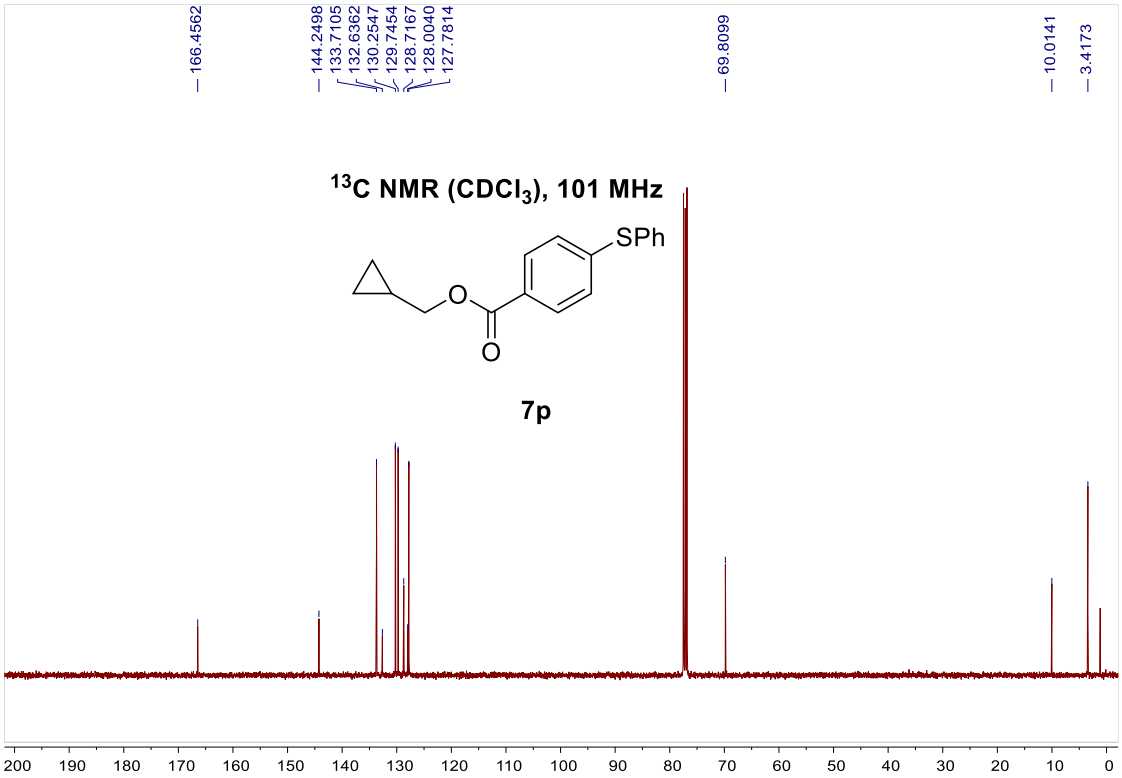
7.4001
7.3936
7.3921
7.3793
7.3745
7.2262
7.2049
4.1348
4.1168
1.2696
1.2374
1.2313
1.2253
1.2234
1.2111
0.6212
0.6034
0.5892
0.5857
0.5835
0.5743
0.3636
0.3521
0.3369
0.3250
1H NMR (CDCl3), 400 MHz
SPh
O
O
7p
2.00
1.99
3.02
2.06
2.04
1.00
2.03
2.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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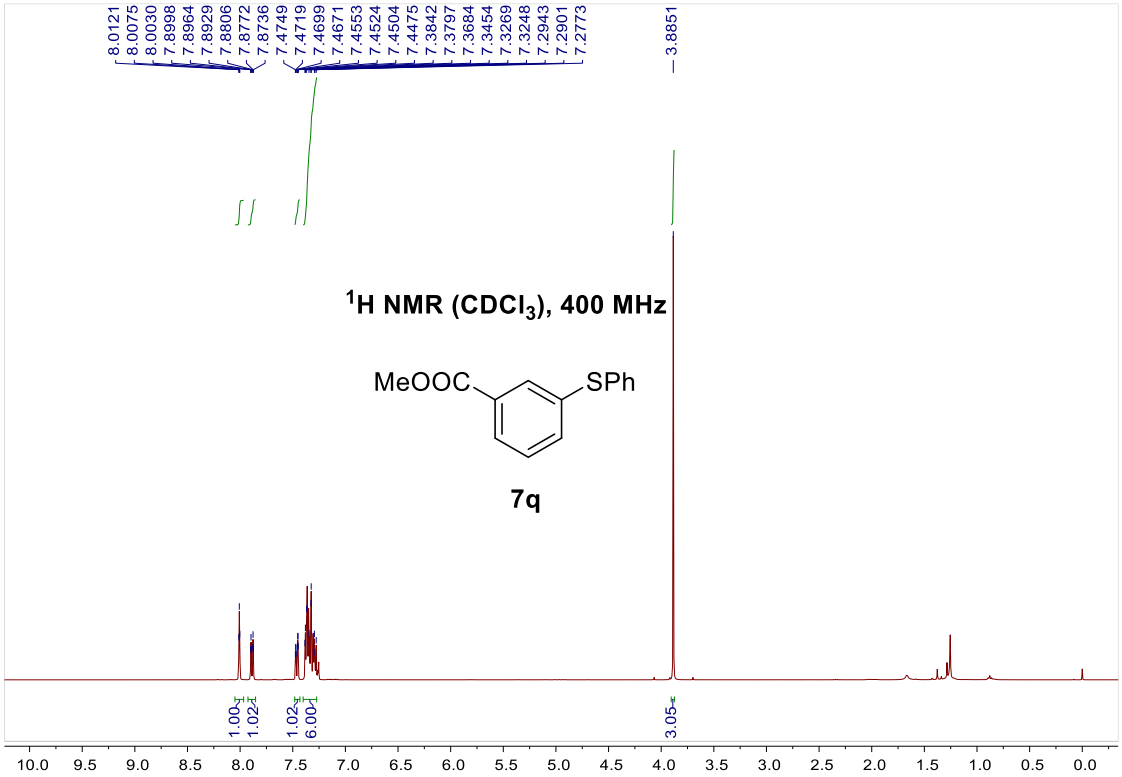
144.2498
133.7105
132.6362
130.2547
129.7454
128.7167
128.0040
127.7814
69.8099
10.0141
3.4173
13C NMR (CDCl3), 101 MHz
SPh
O
O
7p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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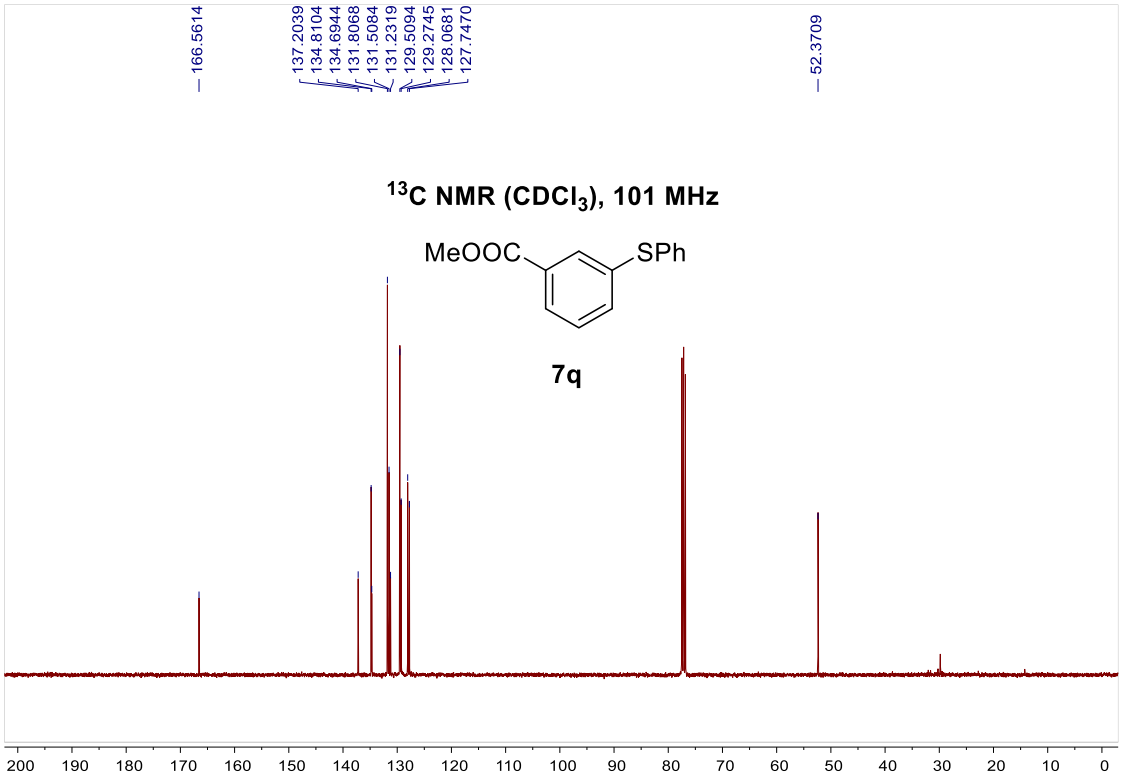
8.0075
8.0030
7.8998
7.8964
7.8929
7.8806
7.8772
7.8736
7.4749
7.4719
7.4699
7.4671
7.4553
7.4524
7.4504
7.4475
7.3842
7.3797
7.3684
7.3454
7.3269
7.3248
7.2943
7.2901
7.2773
3.8851
1H NMR (CDCl3), 400 MHz
MeOOC
SPh
7q
1.00
1.02
1.02
6.00
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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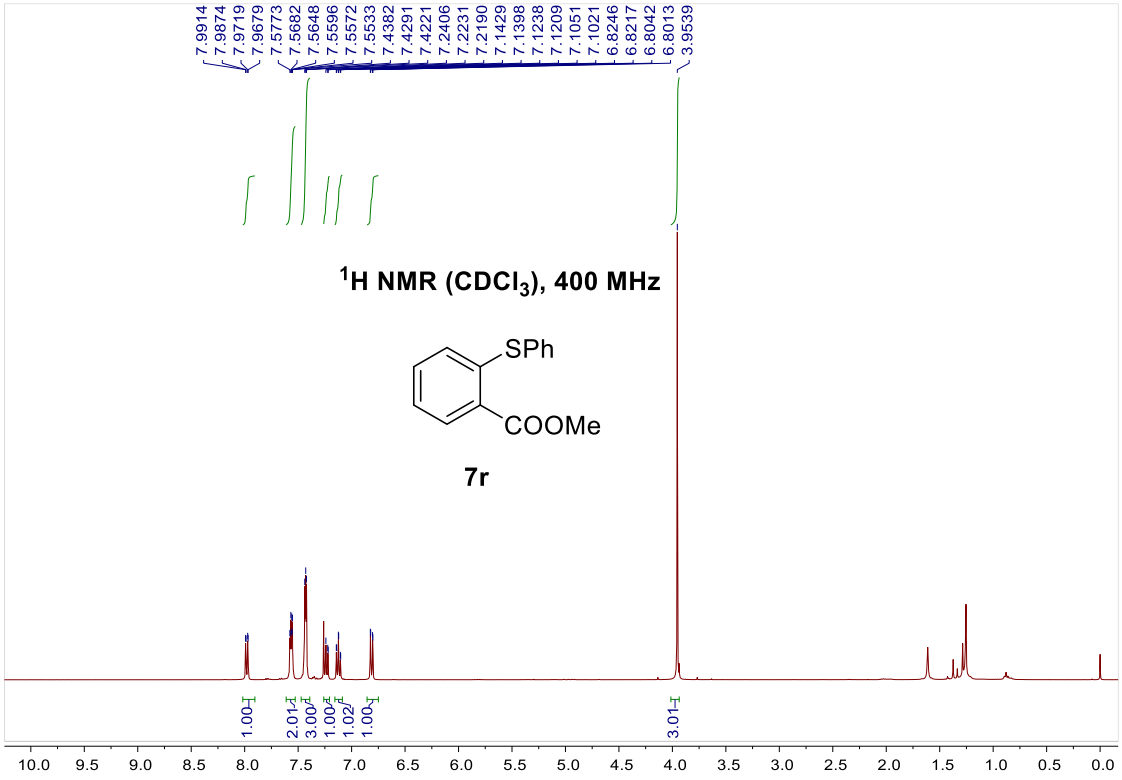
137.2039
134.8104
134.6944
131.8068
131.5084
131.2319
129.5094
129.2745
128.0681
127.7470
52.3709
13C NMR (CDCl3), 101 MHz
MeOOC
SPh
7q
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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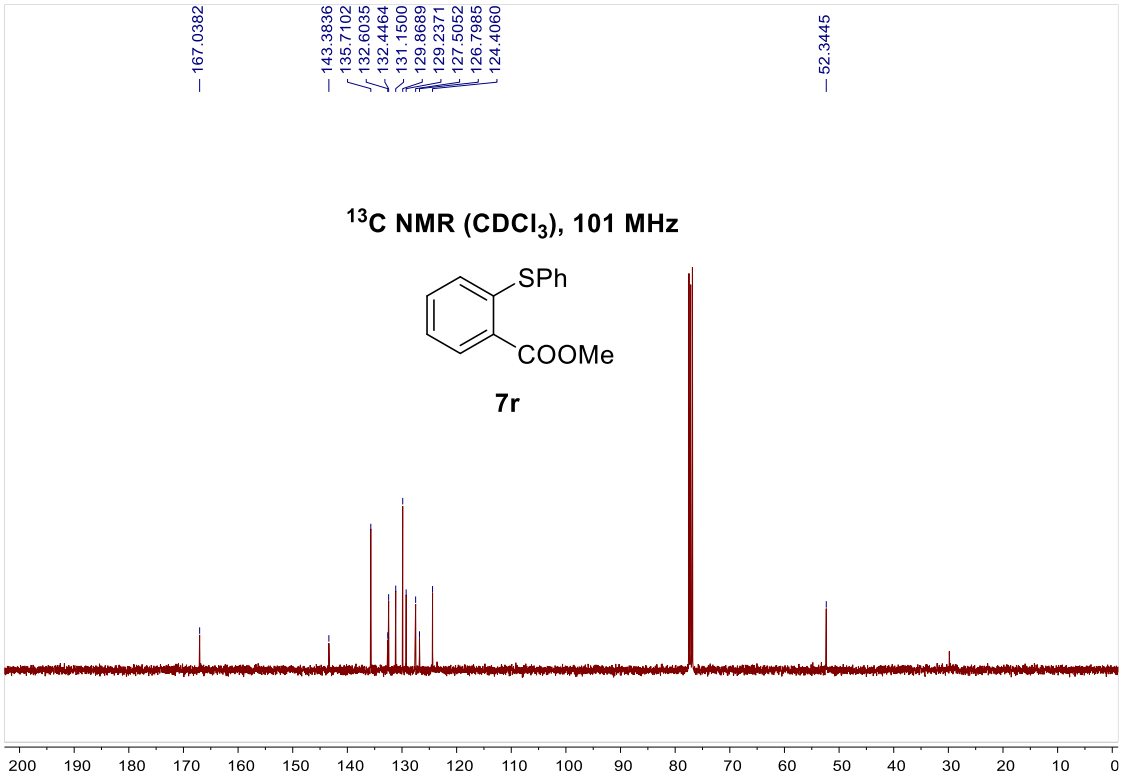
7.9719
7.9679
7.5773
7.5682
7.5648
7.5596
7.5572
7.5533
7.4382
7.4291
7.4221
7.2406
7.2231
7.2190
7.1429
7.1398
7.1238
7.1209
7.1051
7.1021
6.8246
6.8217
6.8042
6.8013
3.9539
1H NMR (CDCl3), 400 MHz
SPh
COOMe
7r
1.00
2.01
3.00
1.00
1.02
1.00
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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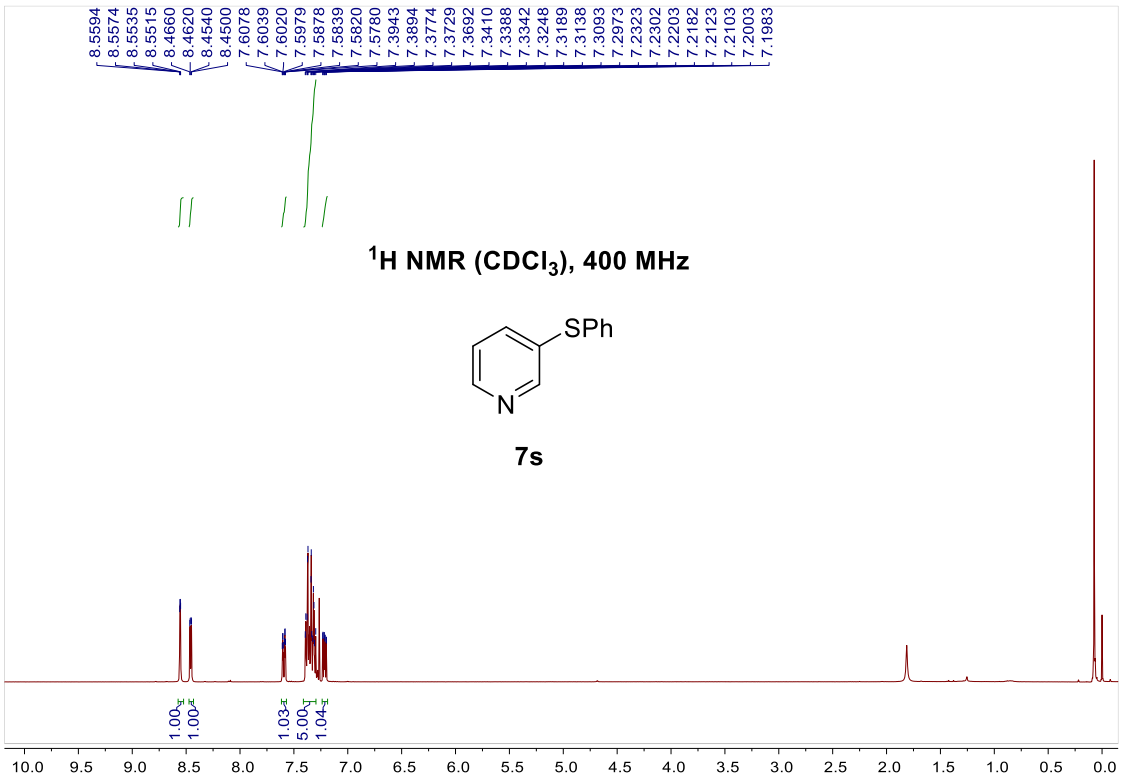
143.3836
135.7102
132.6035
132.4464
131.1500
129.8689
129.2371
127.5052
126.7985
124.4060
52.3445
13C NMR (CDCl3), 101 MHz
SPh
COOMe
7r
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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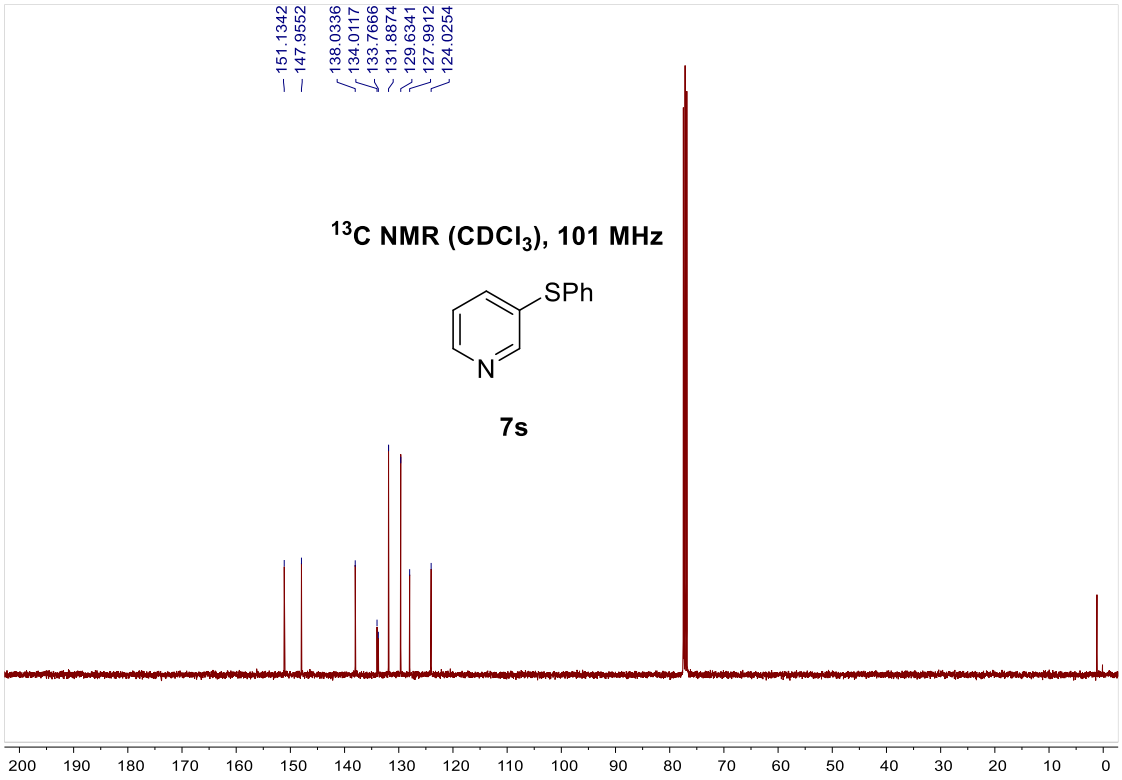
8.5574
8.5535
8.5515
8.4660
8.4620
8.4540
8.4500
7.6078
7.6039
7.6020
7.5979
7.5878
7.5839
7.5820
7.5780
7.3943
7.3894
7.3774
7.3729
7.3692
7.3410
7.3388
7.3342
7.3248
7.3189
7.3138
7.3093
7.2973
7.2323
7.2302
7.2203
7.2182
7.2123
7.2103
7.2003
7.1983
1H NMR (CDCl3), 400 MHz
SPh
N
7s
1.00
1.00
1.03
5.00
1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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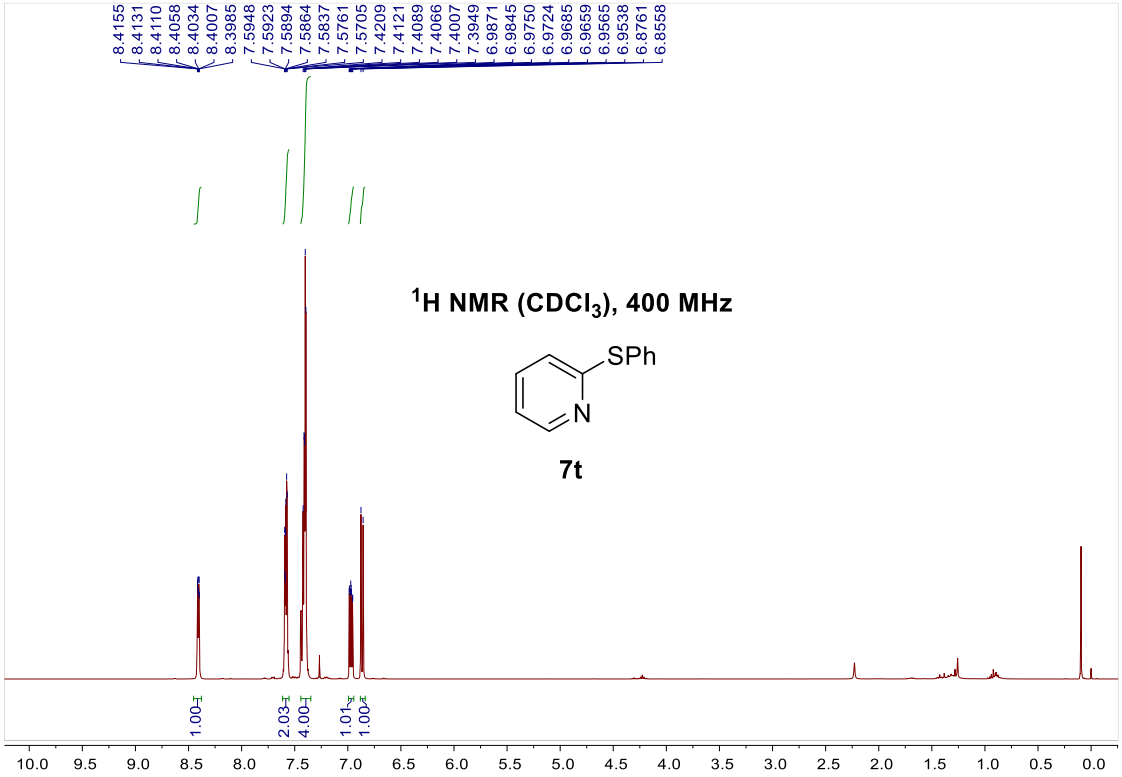
138.0336
134.0117
133.7666
131.8874
129.6341
127.9912
124.0254
13C NMR (CDCl3), 101 MHz
SPh
N
7s
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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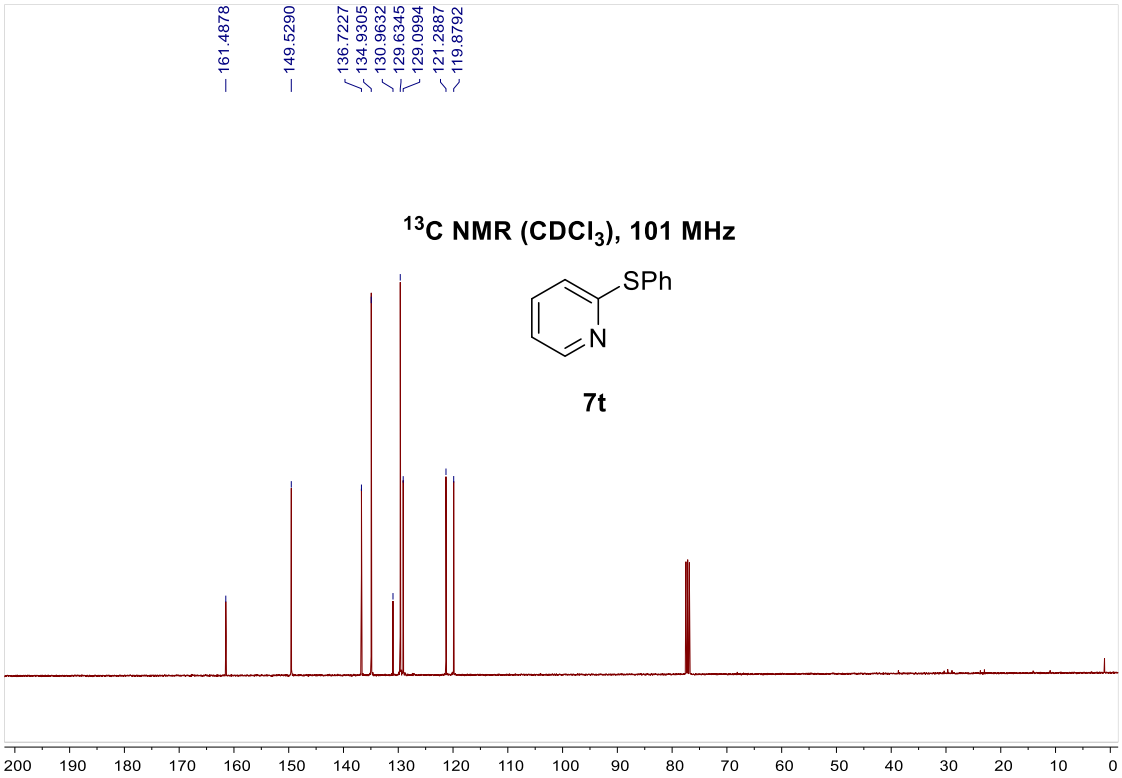
8.4110
8.4058
8.4034
8.4007
8.3985
7.5948
7.5923
7.5894
7.5864
7.5837
7.5761
7.5705
7.4209
7.4121
7.4089
7.4066
7.4007
7.3949
6.9871
6.9845
6.9750
6.9724
6.9685
6.9659
6.9565
6.9538
6.8761
6.8558
1H NMR (CDCl3), 400 MHz
SPh
N
7t
1.00
2.03
4.00
1.01
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


161.4878
149.5290
136.7227
134.9305
130.9632
129.6345
129.0994
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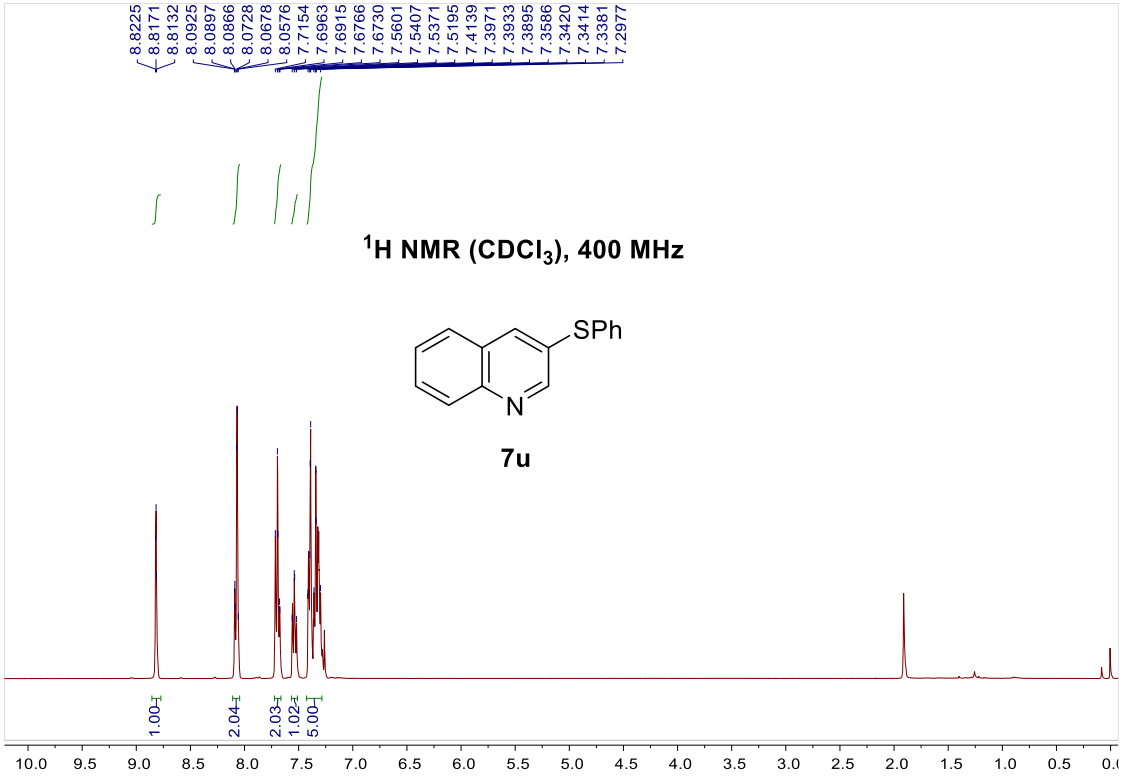
119.8792
13C NMR (CDCl3), 101 MHz
SPh
N
7t
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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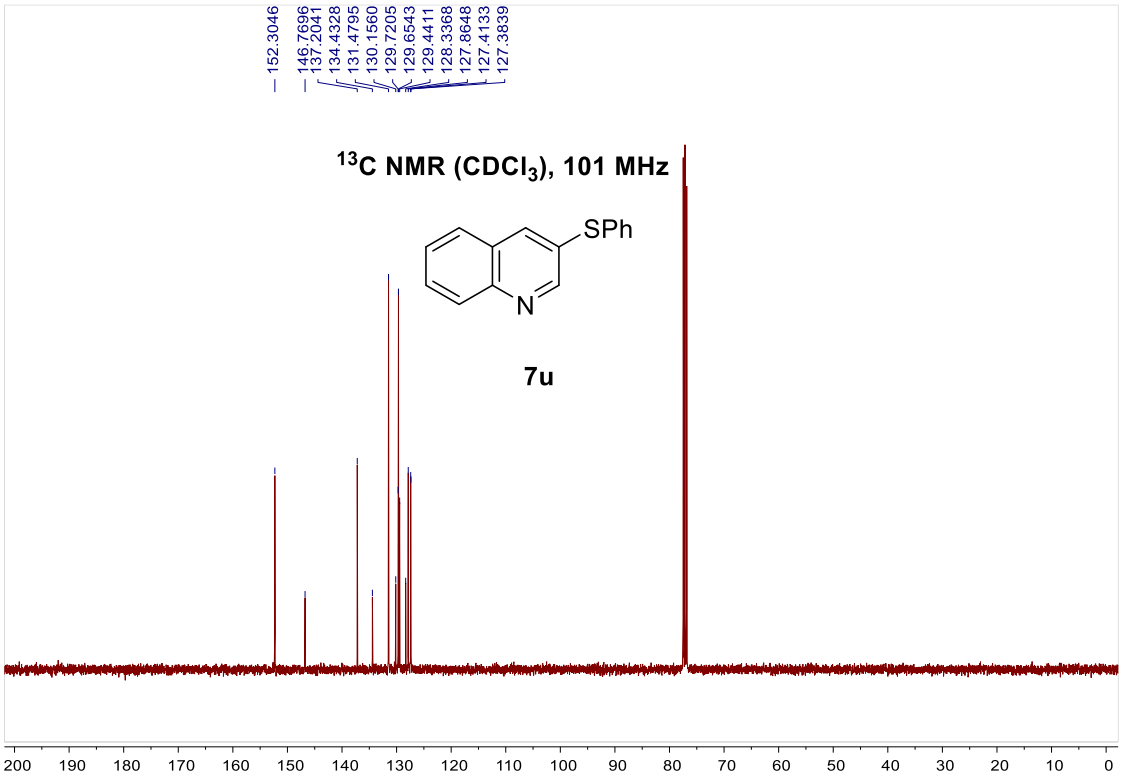
8.8132
8.0925
8.0897
8.0866
8.0728
8.0678
8.0576
7.7154
7.6963
7.6915
7.6766
7.6730
7.5601
7.5407
7.5371
7.5195
7.4139
7.3971
7.3933
7.3895
7.3586
7.3420
7.3414
7.3381
7.2977
1H NMR (CDCl3), 400 MHz
SPh
N
7u
1.00
2.04
2.03
1.02
5.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5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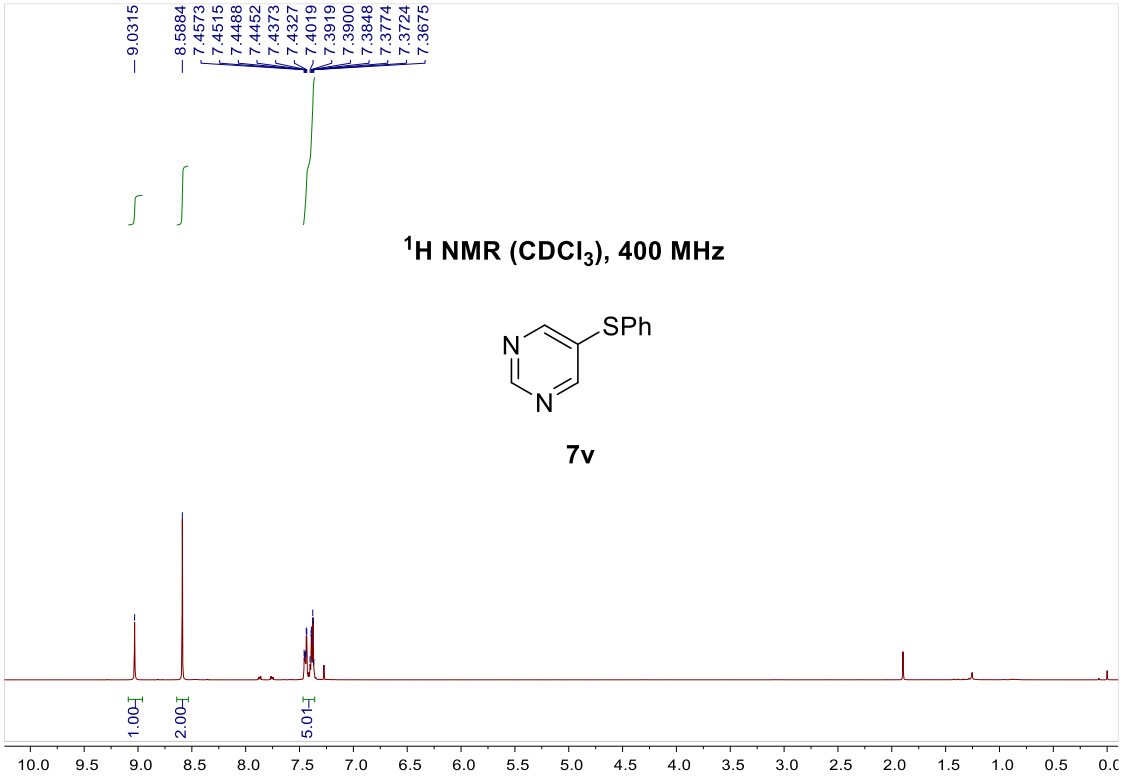
134.4328
131.4795
130.1560
129.7205
129.6543
129.4411
128.3368
127.8648
127.4133
127.3839
13C NMR (CDCl3), 101 MHz
SPh
N
7u
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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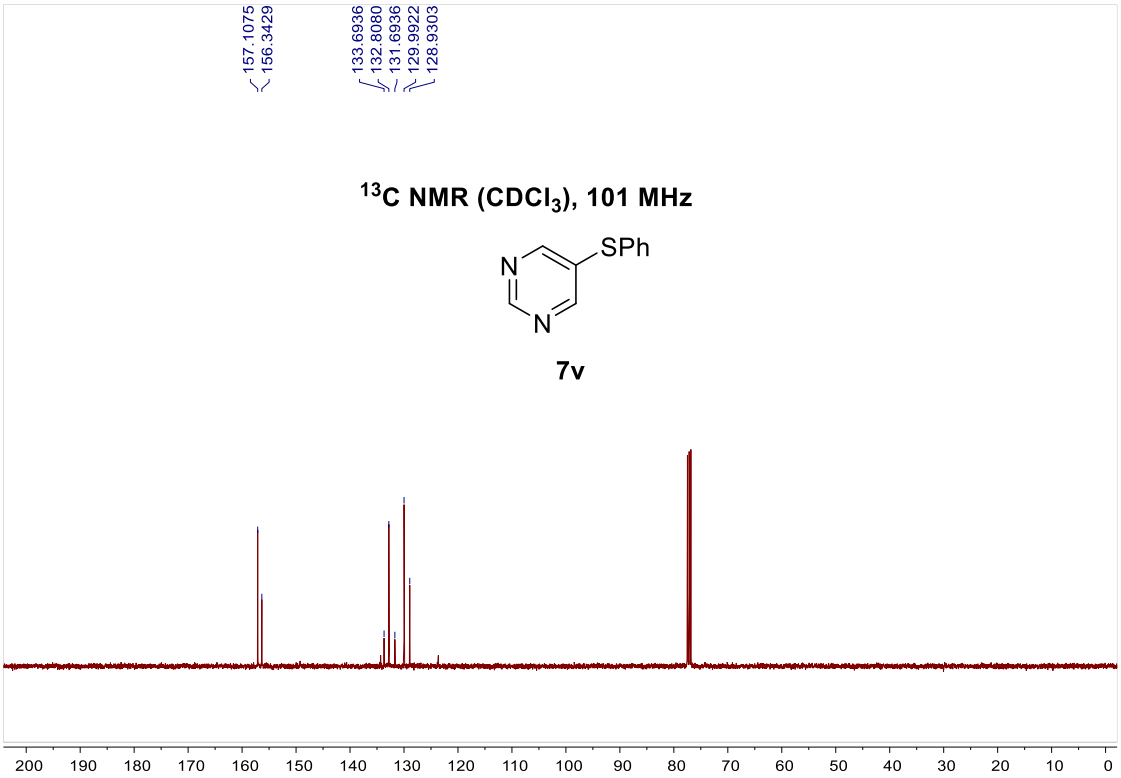
7.4573
7.4515
7.4488
7.4452
7.4373
7.4327
7.4019
7.3919
7.3900
7.3848
7.3774
7.3724
7.3675
1H NMR (CDCl3), 400 MHz
N
SPh
N
7v
1.00
2.00
5.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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133.6936
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131.6936
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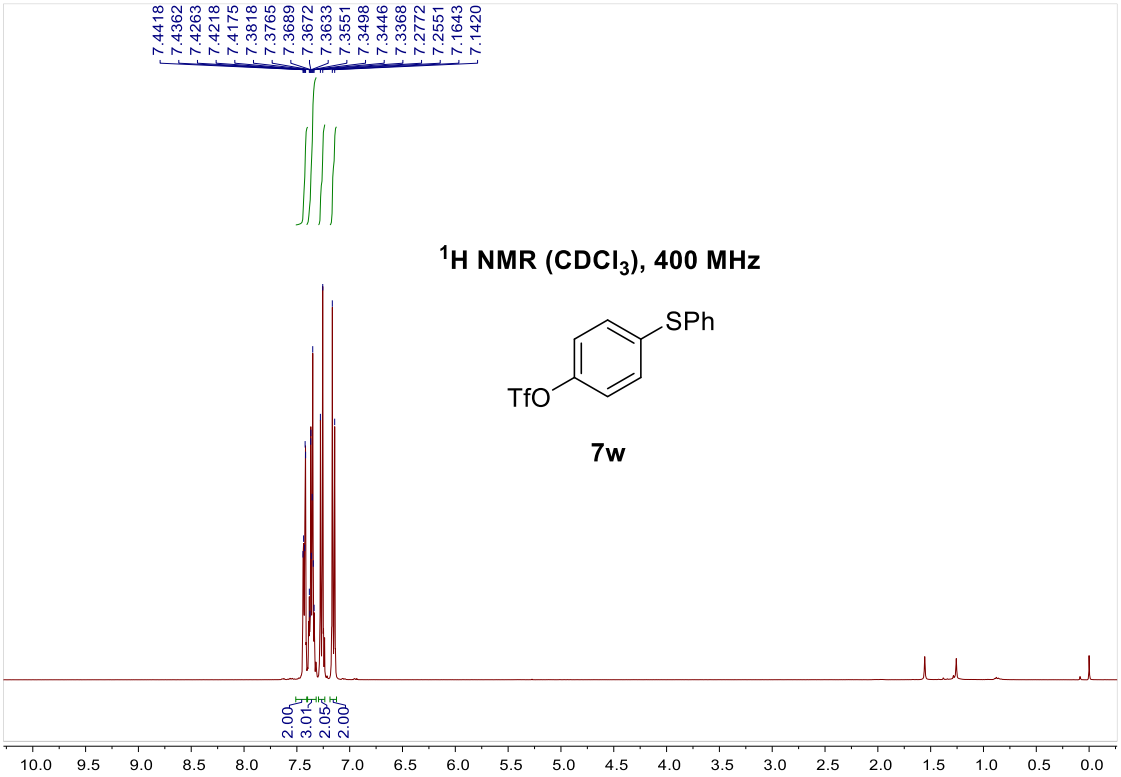
SPh
N
N
7v
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.4263
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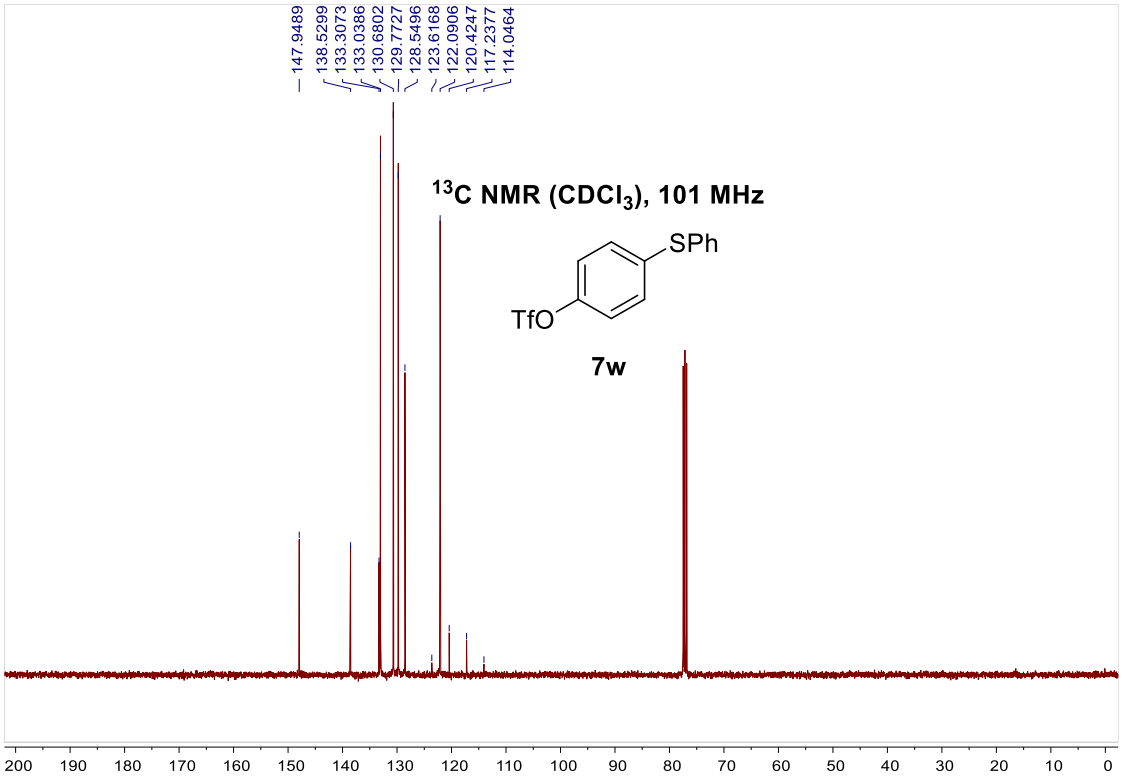
7.4175
7.3818
7.3765
7.3689
7.3672
7.3633
7.3551
7.3498
7.3446
7.3368
7.2772
7.2551
7.1643
7.1420
1H NMR (CDCl3), 400 MHz
SPh
TfO
7w
2.00
3.01
2.05
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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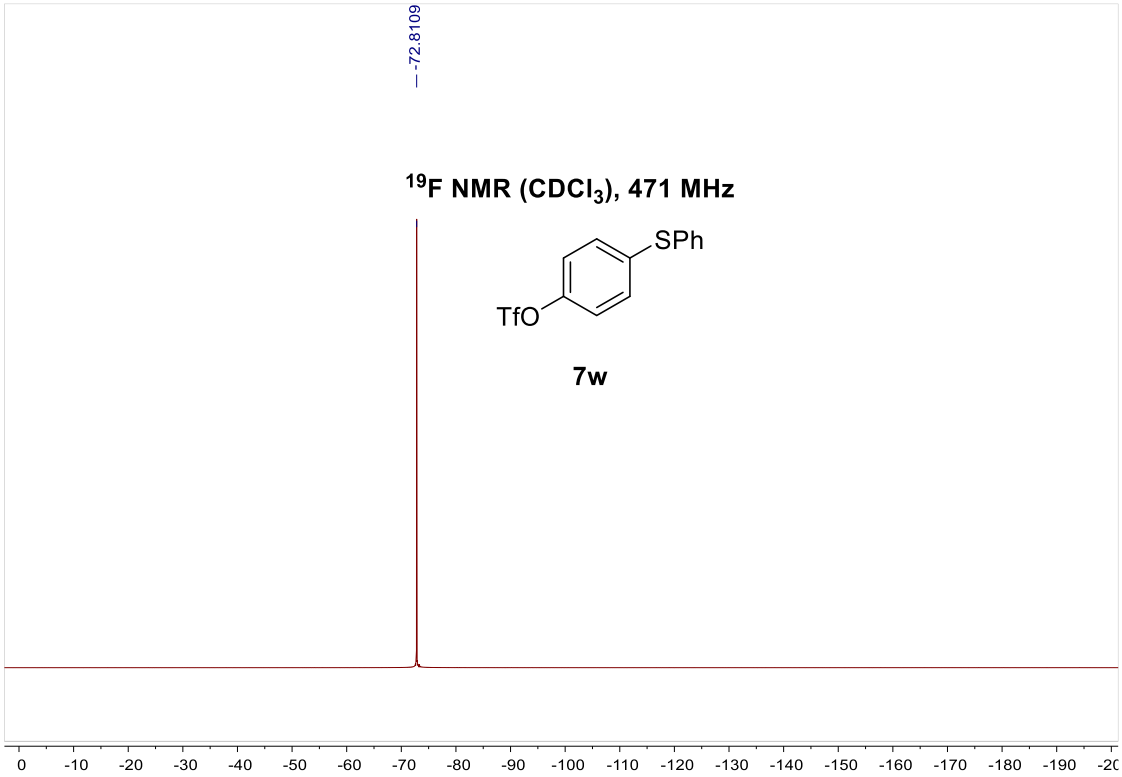
133.3073
133.0386
130.6802
129.7727
128.5496
123.6168
122.0906
120.4247
117.2377
114.0464
13C NMR (CDCl3), 101 MHz
SPh
TfO
7w
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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19F NMR (CDCl3), 471 MHz
SPh
TfO
7w
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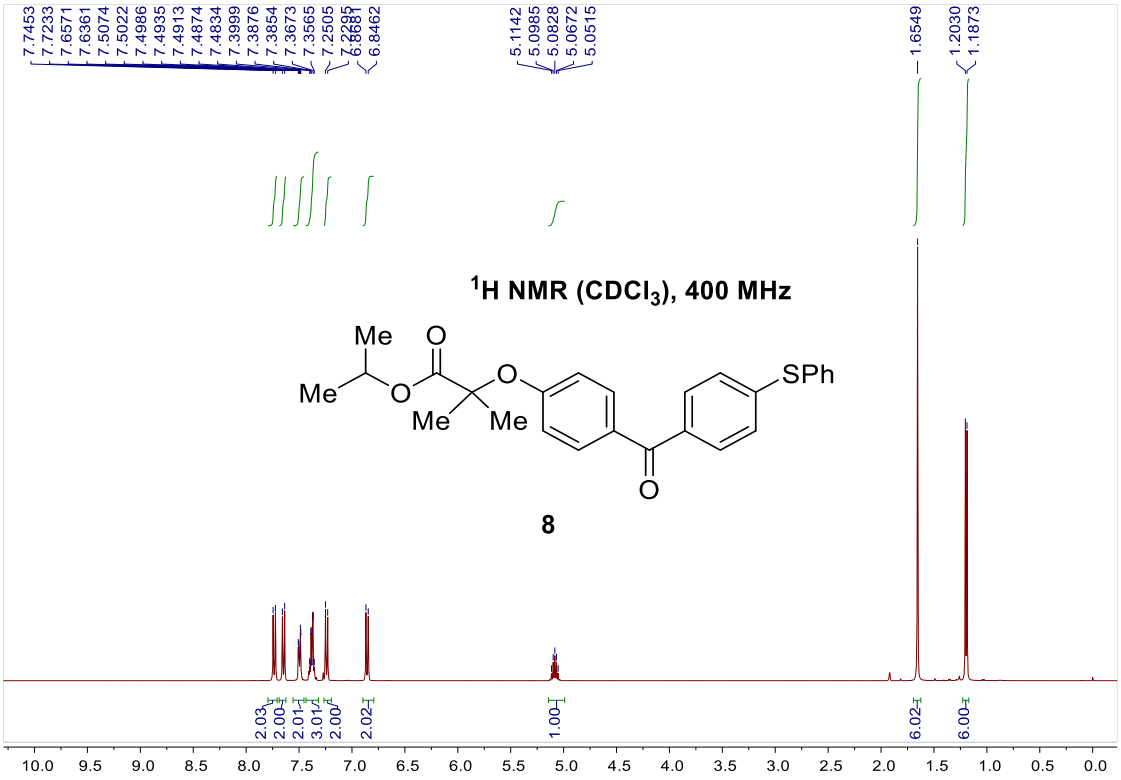
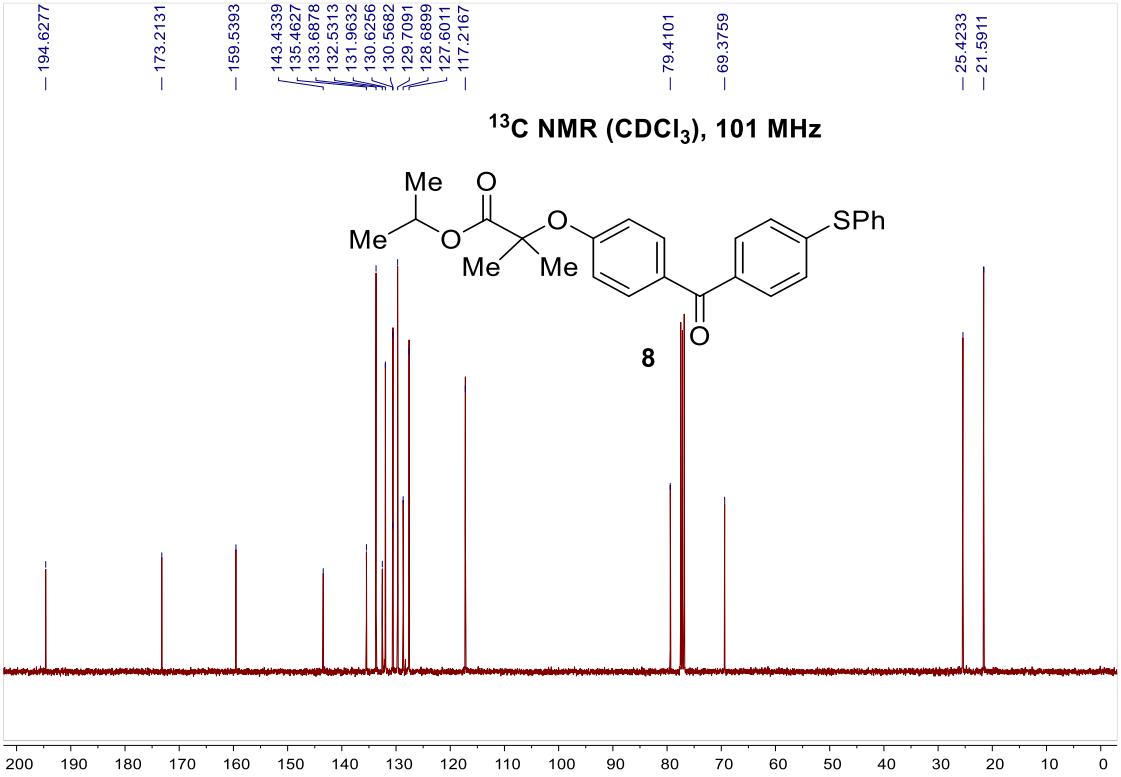


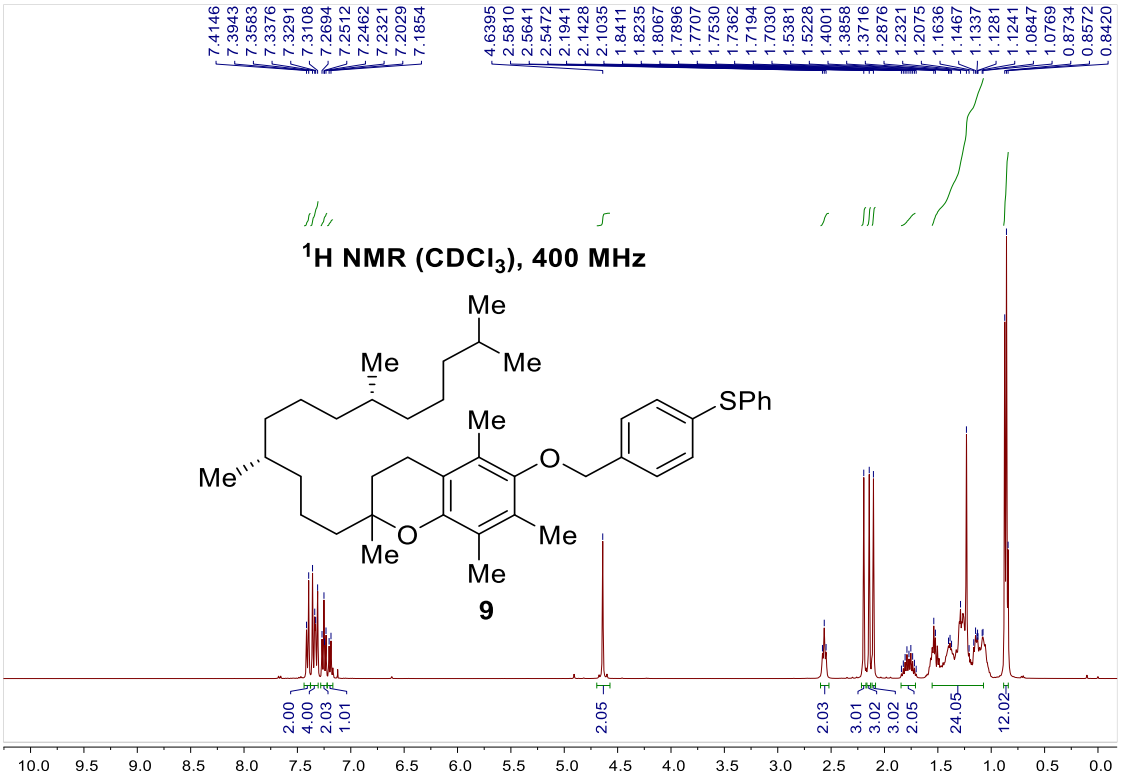
^{1}H NMR ($CDCl_3$), 400 MHz

8



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

8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7.3583
7.3376
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7.2694
7.2512
7.2462
7.2321
7.2029
7.1854
4.6395
2.5810
2.5641
2.5472
2.1941
2.1428
2.1035
1.8411
1.8235
1.8067
1.7896
1.7707
1.7530
1.7362
1.7194
1.7030
1.5381
1.5228
1.4001
1.3858
1.3716
1.2876
1.2321
1.2075
1.1636
1.1467
1.1337
1.1281
1.1241
1.0847
1.0769
0.8734
0.8572
0.8420
^{1}H NMR (CDCl$_3$), 400 MHz
Me
Me
Me
SPh
Me
O
Me
O
Me
Me
Me
9
2.00
4.00
2.03
1.01
2.05
2.03
3.01
3.02
3.02
2.05
24.05
12.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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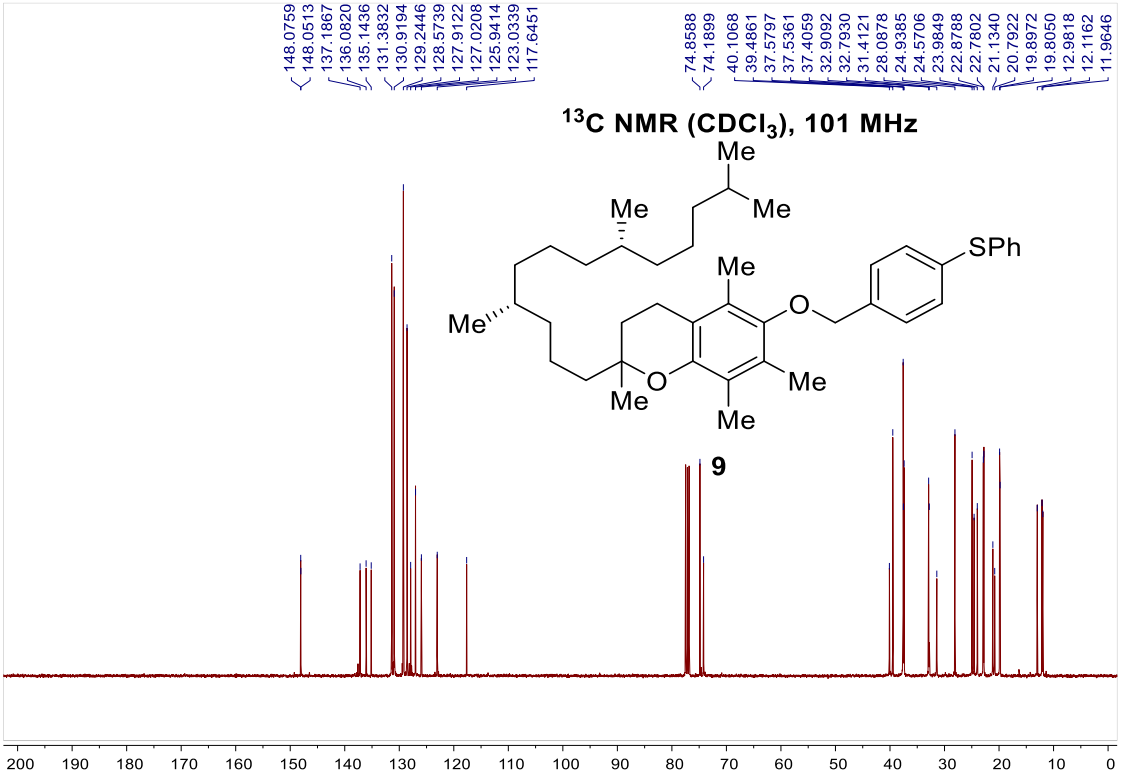
0.0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148.0513
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136.0820
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131.3832
130.9194
129.2446
128.5739
127.9122
127.0208
125.9414
123.0339
117.6451
74.8588
74.1899
40.1068
39.4861
37.5797
37.5361
37.4059
32.9092
32.7930
31.4121
28.0878
24.9385
24.5706
23.9849
22.8788
22.7802
21.1340
20.7922
19.8972
19.8050
12.9818
12.1162
11.9646
^{13}C NMR (CDCl$_3$), 101 MHz
Me
Me
Me
SPh
Me
O
Me
O
Me
Me
Me
9
200
190
180
170
160
150
140
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10
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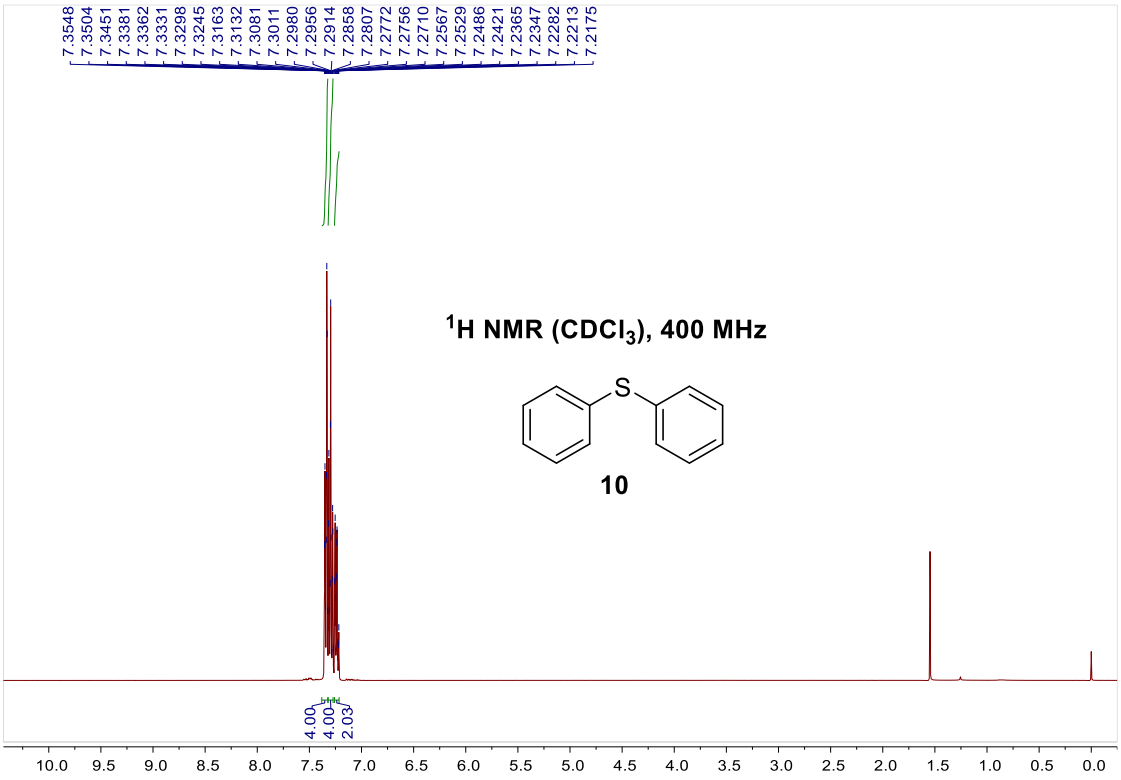
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7.3381
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7.3298
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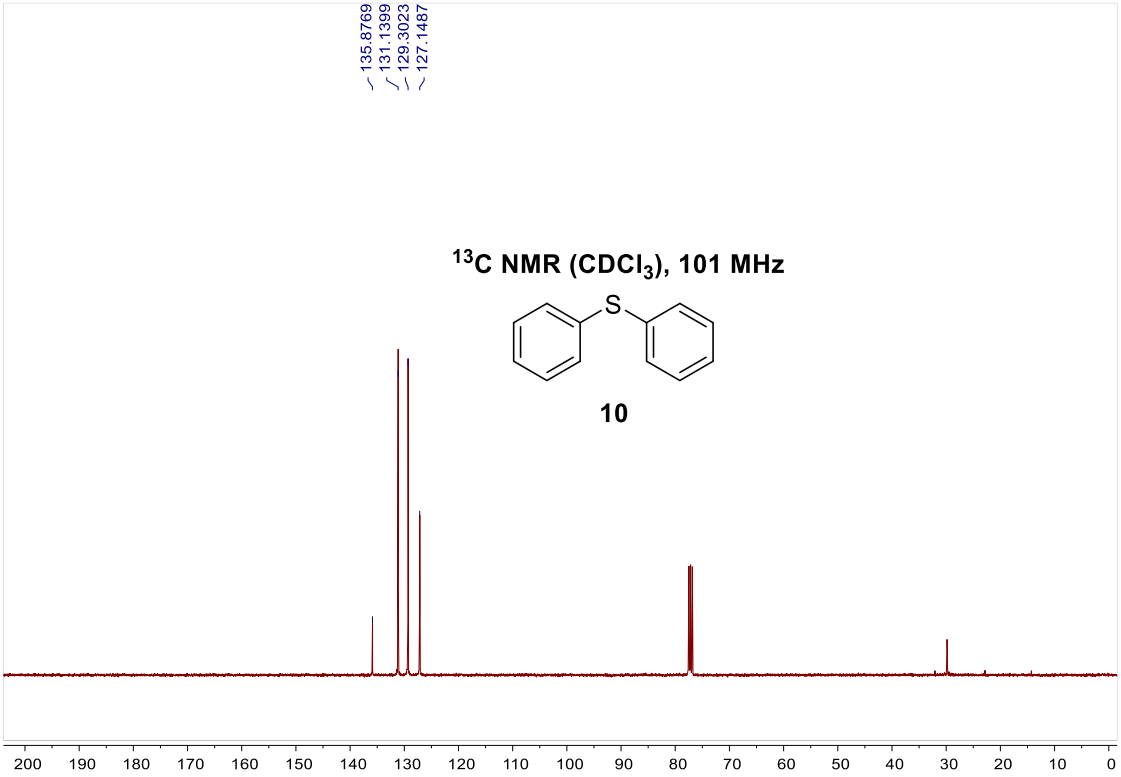
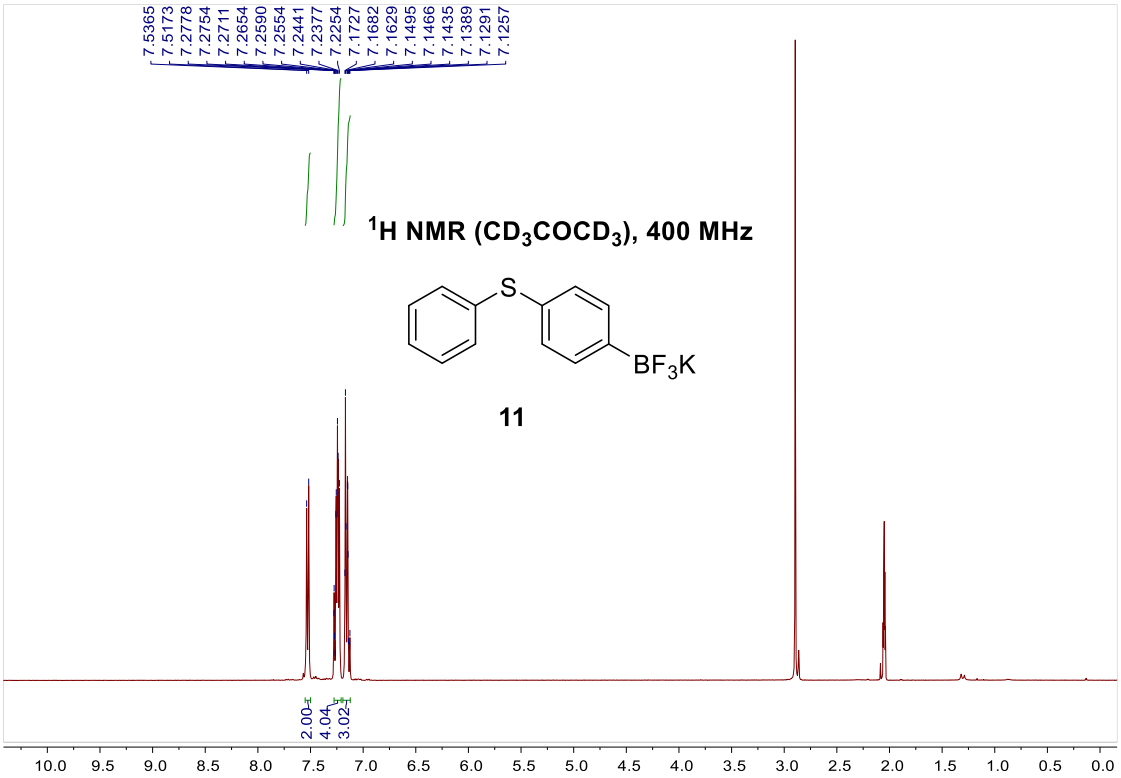
7.3163
7.3132
7.3081
7.3011
7.2980
7.2956
7.2914
7.2858
7.2807
7.2772
7.2756
7.2710
7.2567
7.2529
7.2486
7.2421
7.2365
7.2347
7.2282
7.2213
7.2175
^{1}H NMR (CDCl$_3$), 400 MHz
S
10
4.00
4.00
2.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


135.8769
131.1399
129.3023
127.1487
^{13}C NMR (CDCl$_3$), 101 MHz
S
10
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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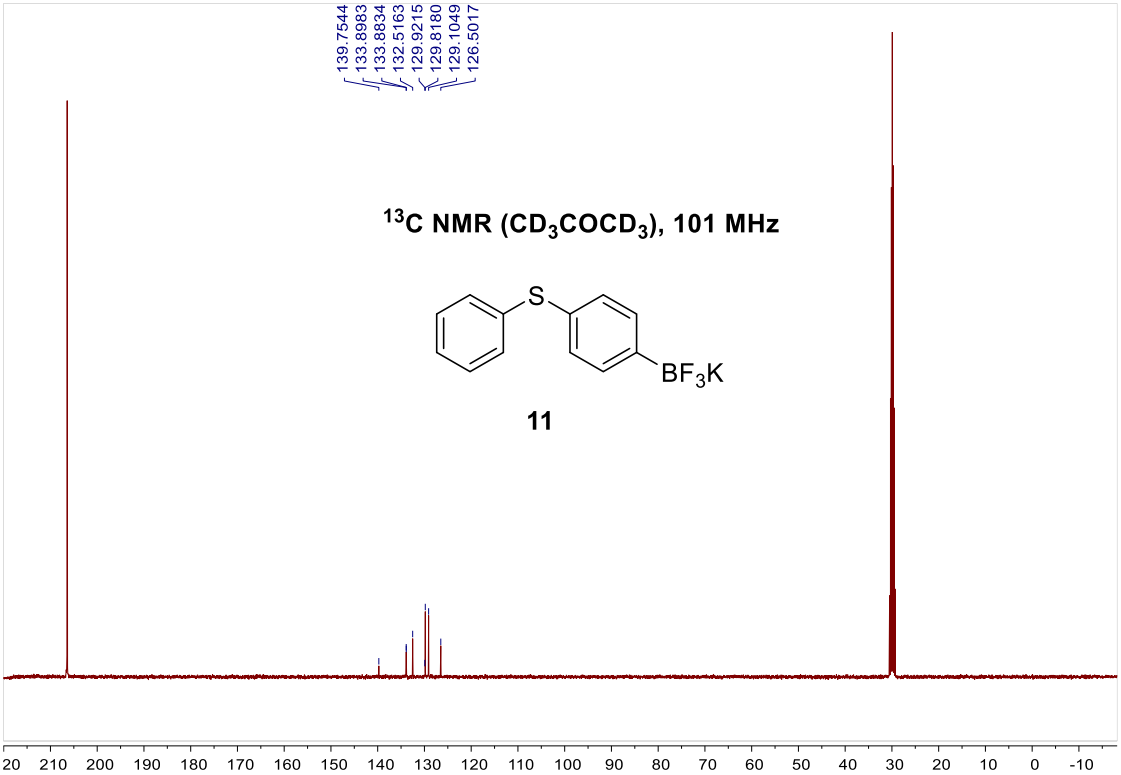
7.5173
7.2778
7.2754
7.2711
7.2654
7.2590
7.2554
7.2441
7.2377
7.2254
7.1727
7.1682
7.1629
7.1495
7.1466
7.1435
7.1389
7.1291
7.1257
^{1}H NMR (CD_3COCD_3), 400 MHz
S
BF_3K
11
2.00
4.04
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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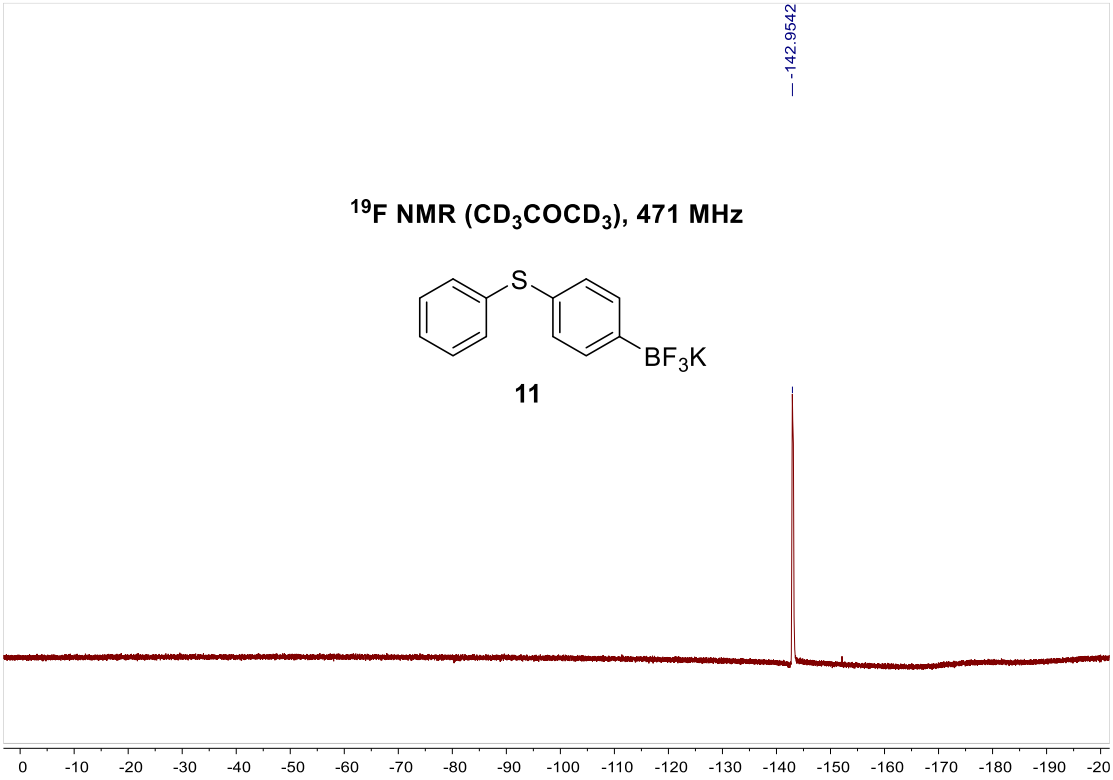
133.8983
133.8834
132.5163
129.9215
129.8180
129.1049
126.5017
^{13}C NMR (CD_3COCD_3), 101 MHz
S
BF_3K
11
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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19F NMR (CD3COCD3), 471 MHz
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BF3K
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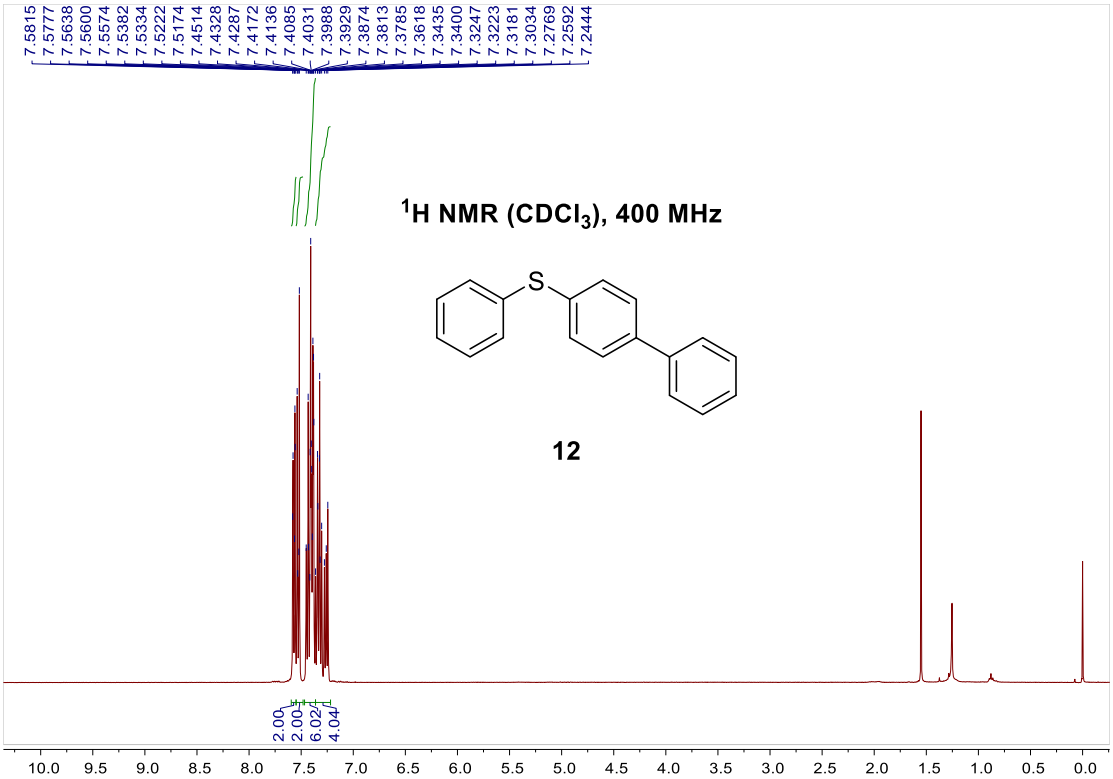
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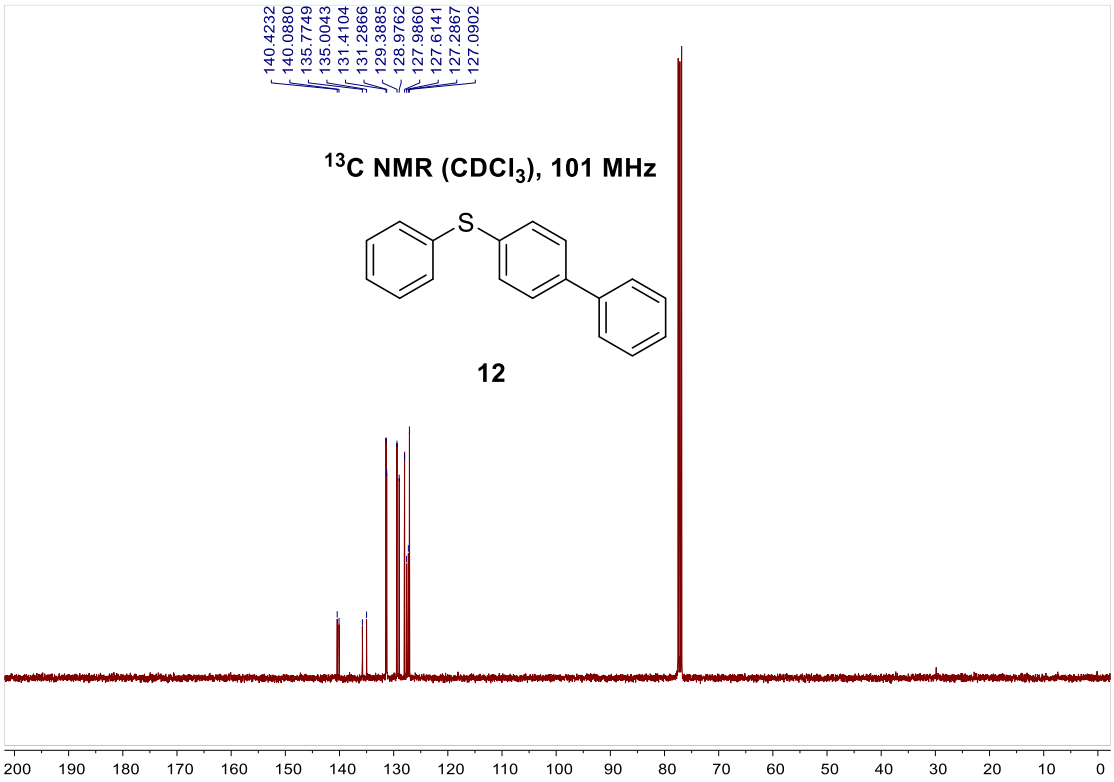
7.5638
7.5600
7.5574
7.5382
7.5334
7.5222
7.5174
7.4514
7.4328
7.4287
7.4172
7.4136
7.4085
7.4031
7.3988
7.3929
7.3874
7.3813
7.3785
7.3618
7.3435
7.3400
7.3247
7.3223
7.3181
7.3034
7.2769
7.2592
7.2444
1H NMR (CDCl3), 400 MHz
S
12
2.00
2.00
6.02
4.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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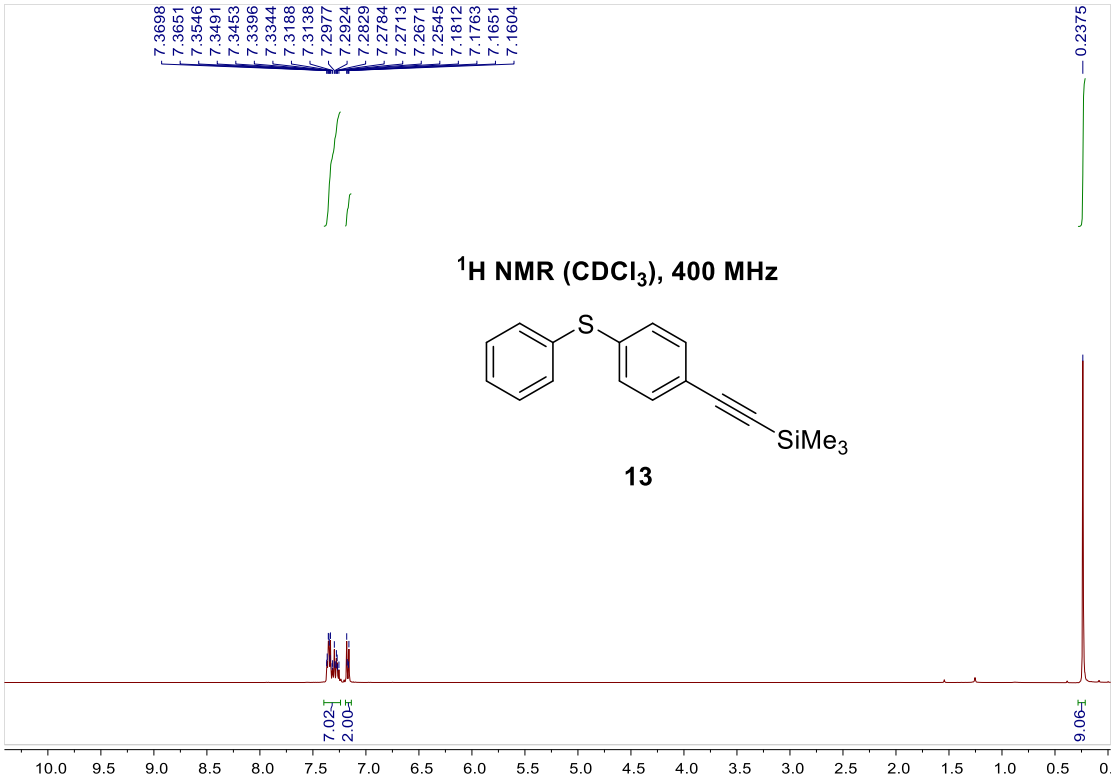
140.0880
135.7749
135.0043
131.4104
131.2866
129.3885
128.9762
127.9860
127.6141
127.2867
127.0902
13C NMR (CDCl3), 101 MHz
S
12
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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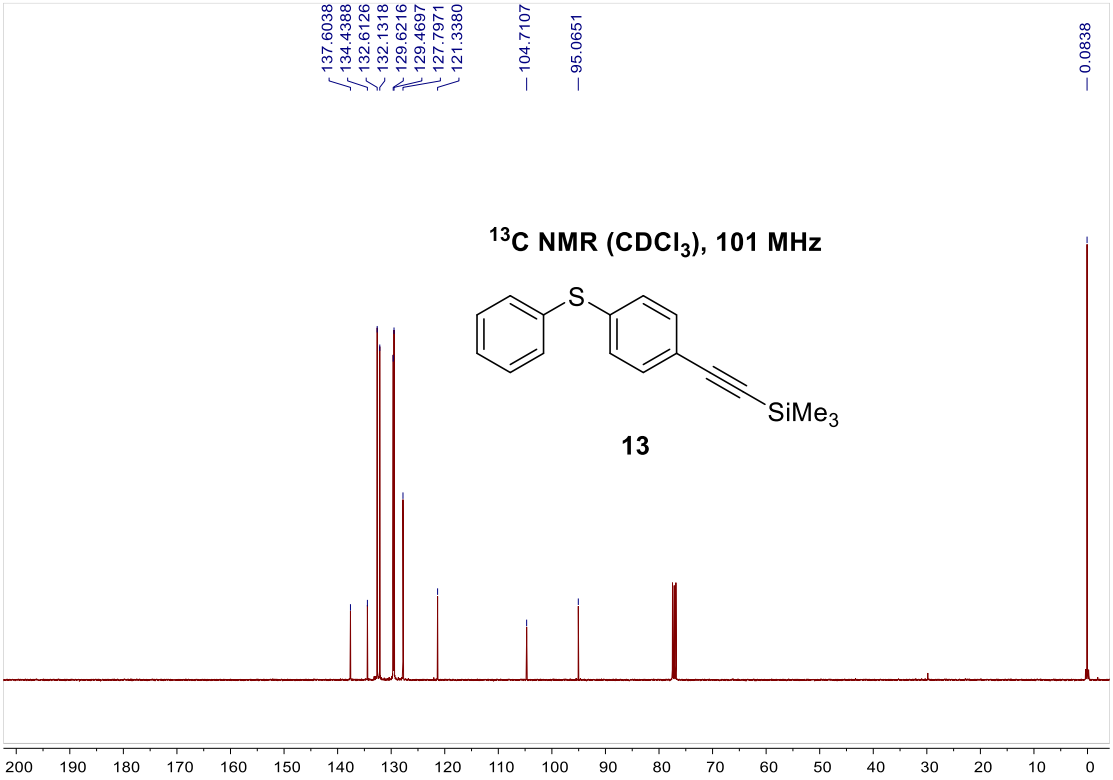
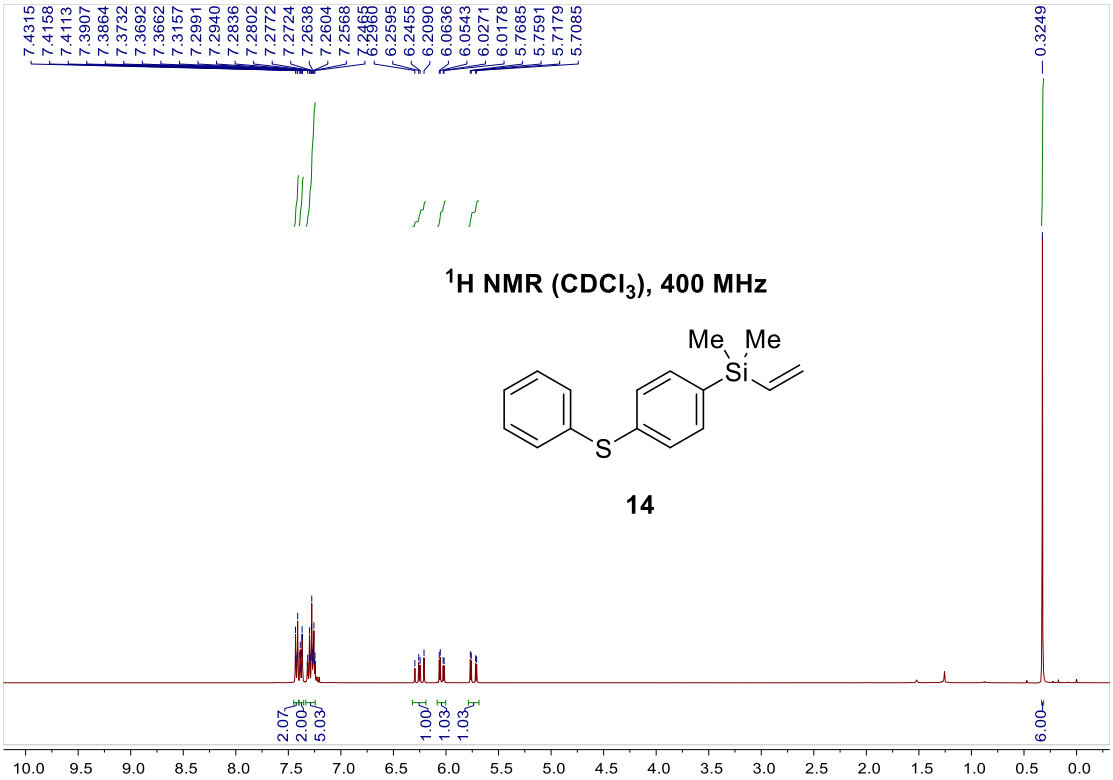
7.3651
7.3546
7.3491
7.3453
7.3396
7.3344
7.3188
7.3138
7.2977
7.2924
7.2829
7.2784
7.2713
7.2671
7.2545
7.1812
7.1763
7.1651
7.1604
0.2375
1H NMR (CDCl3), 400 MHz
S
SiMe3
13
7.02
2.00
9.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5


137.6038
134.4388
132.6126
132.1318
129.6216
129.4697
127.7971
121.3380
104.7107
95.0651
0.0838
13C NMR (CDCl3), 101 MHz
S
SiMe3
13
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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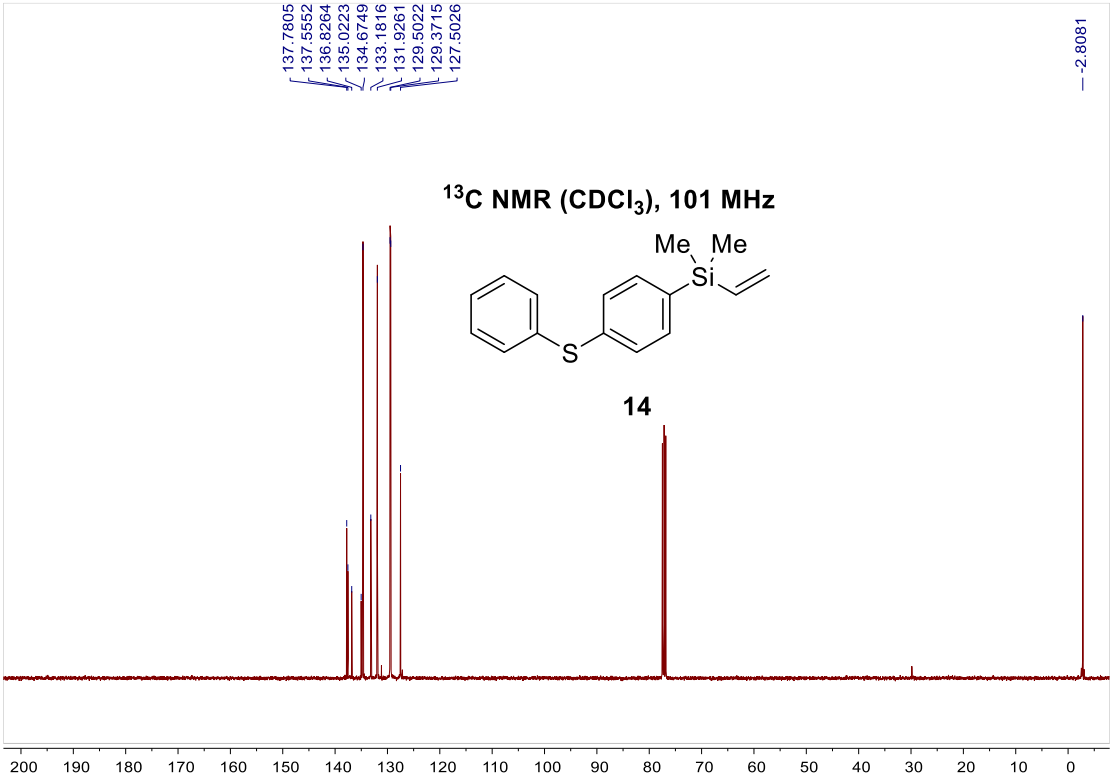
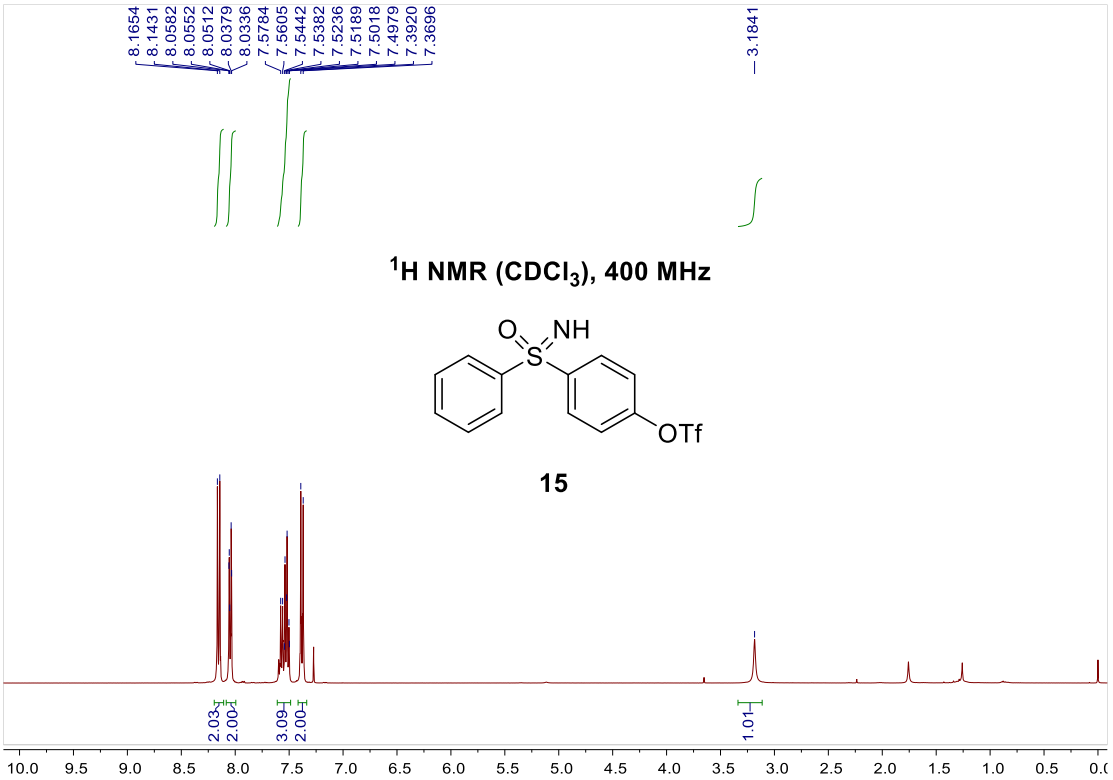
7.4158
7.4113
7.3907
7.3864
7.3732
7.3692
7.3662
7.3157
7.2991
7.2940
7.2836
7.2802
7.2772
7.2724
7.2638
7.2604
7.2568
6.2595
6.2455
6.2090
6.0636
6.0543
6.0271
6.0178
5.7685
5.7591
5.7179
5.7085
0.3249
1H NMR (CDCl3), 400 MHz
Me
Me
Si
S
14
2.07
2.00
5.03
1.00
1.03
1.03
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


137.7805
137.5552
136.8264
135.0223
134.6749
133.1816
131.9261
129.5022
129.3715
127.5026
-2.8081
13C NMR (CDCl3), 101 MHz
Me
Me
Si
S
14
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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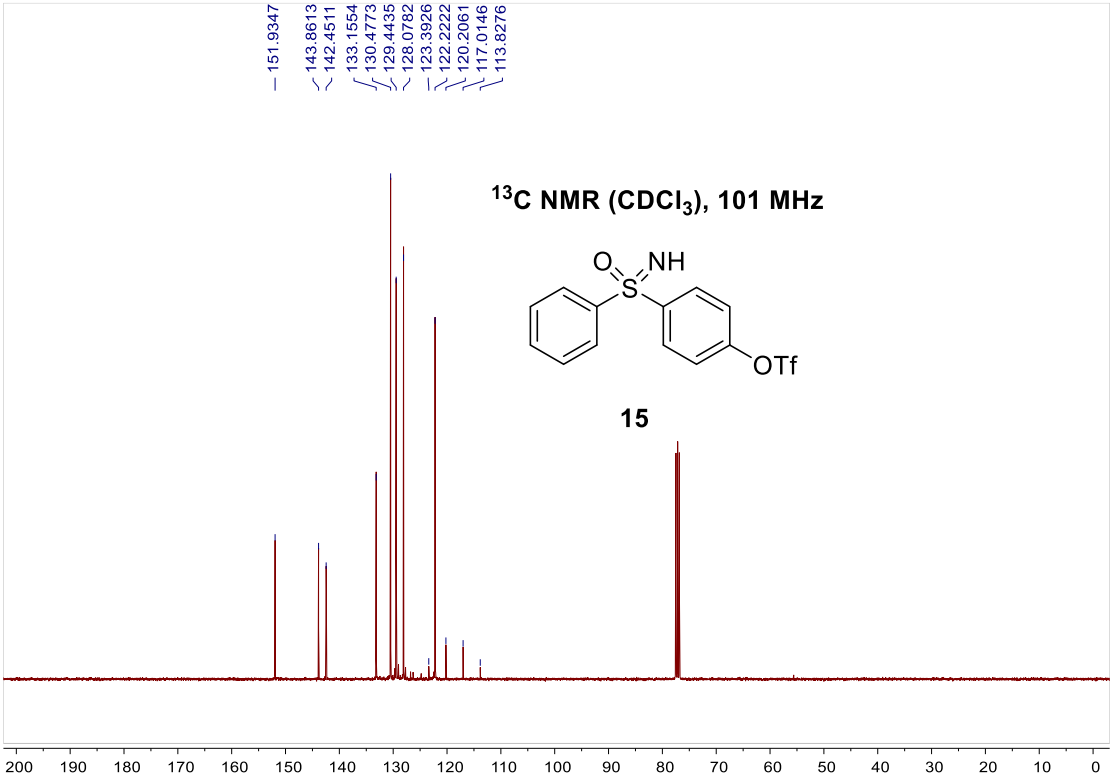
8.1431
8.0582
8.0552
8.0512
8.0379
8.0336
7.5784
7.5605
7.5442
7.5382
7.5236
7.5189
7.5018
7.4979
7.3920
7.3696
3.1841
1H NMR (CDCl3), 400 MHz
O
NH
S
OTf
15
2.03
2.00
3.09
2.00
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5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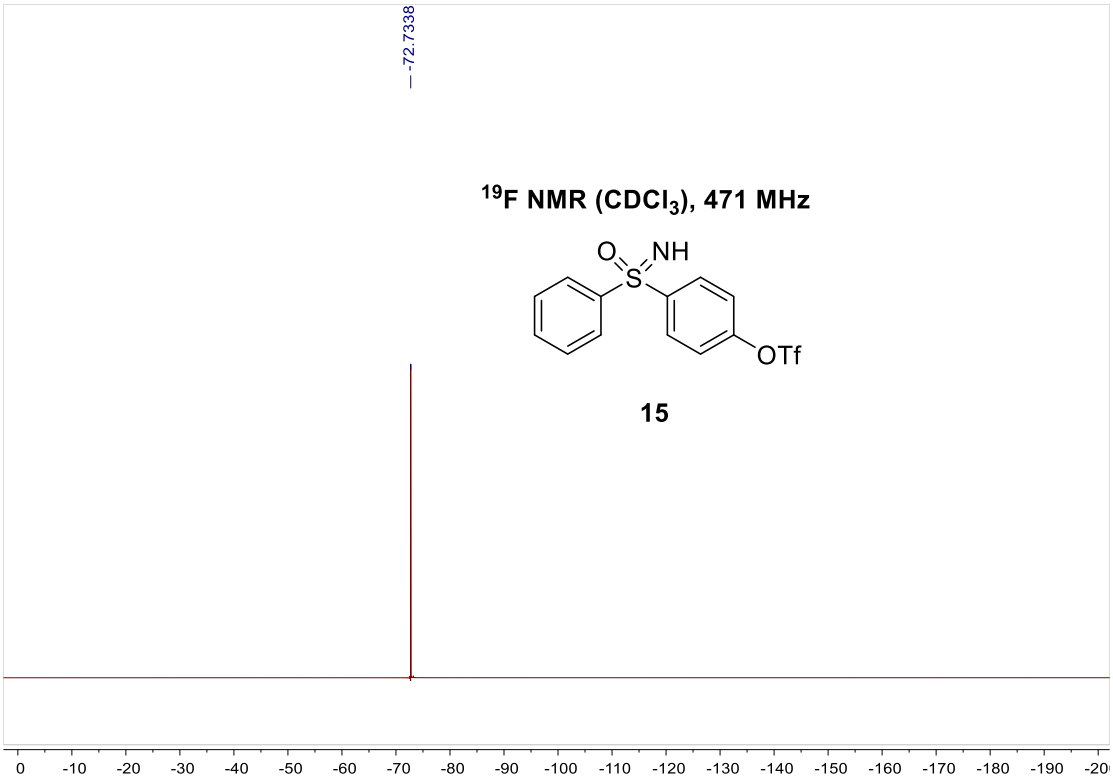
143.8613
142.4511
133.1554
130.4773
129.4435
128.0782
123.3926
122.2222
120.2061
117.0146
113.8276
13C NMR (CDCl3), 101 MHz
O
S
NH
OTf
15
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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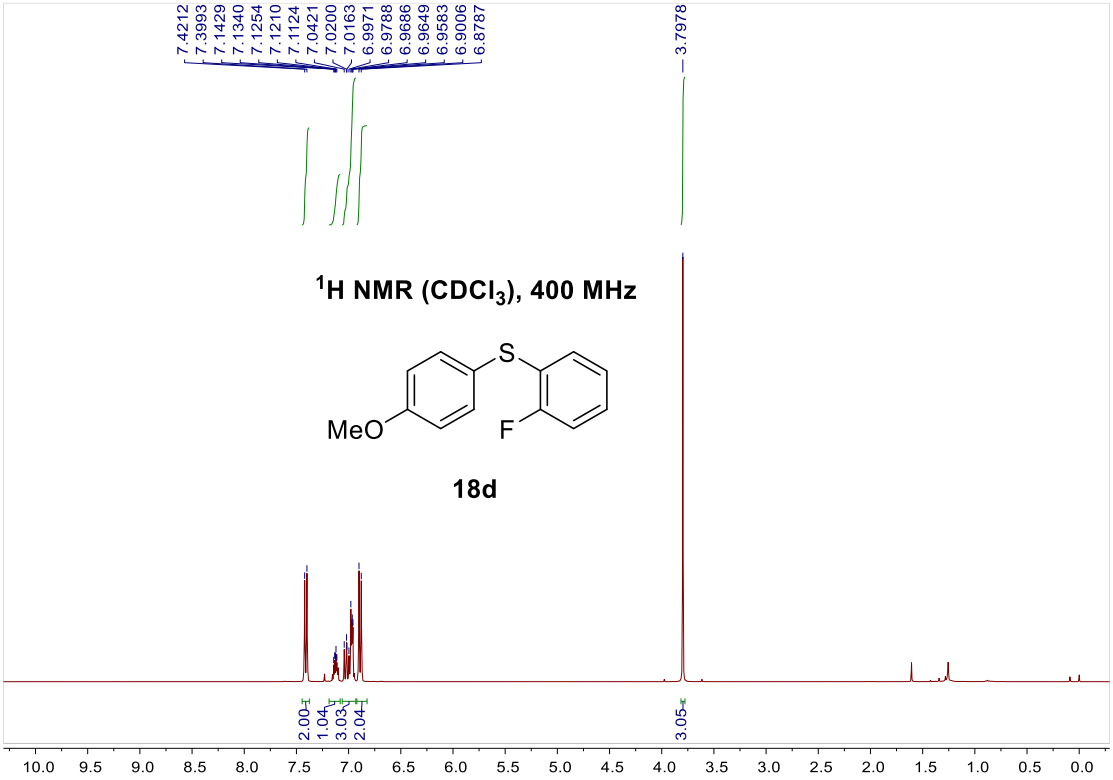
19F NMR (CDCl3), 471 MHz
O
S
NH
OTf
15
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20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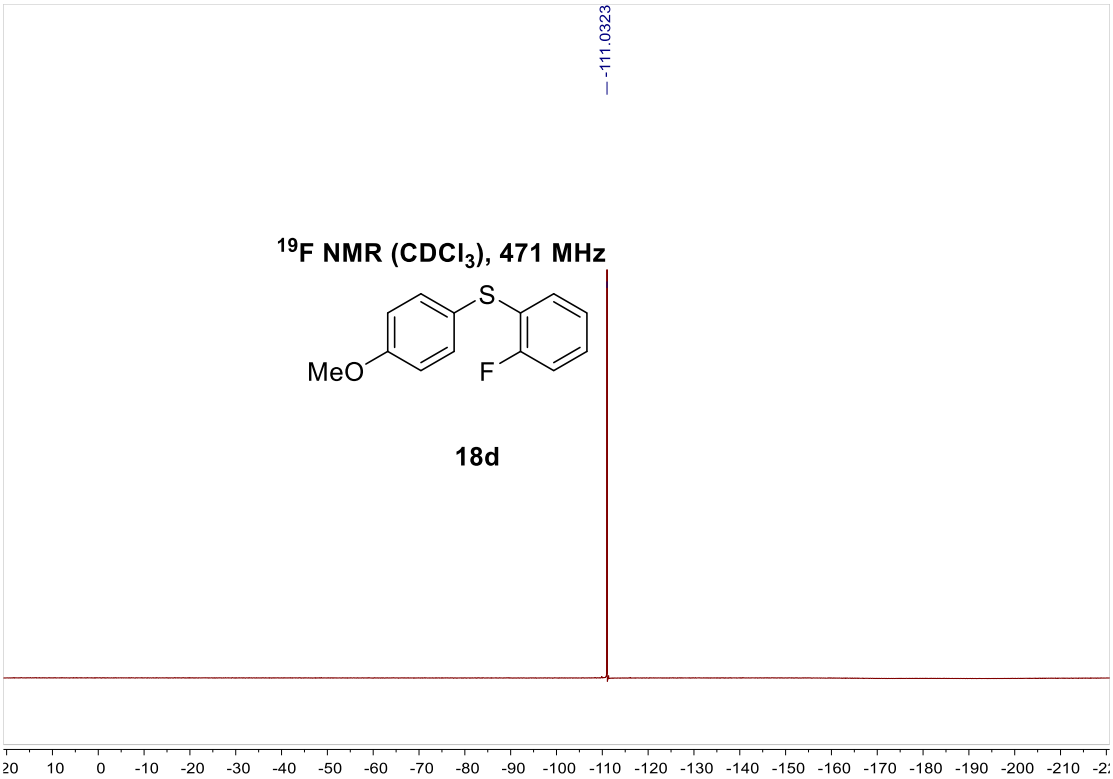
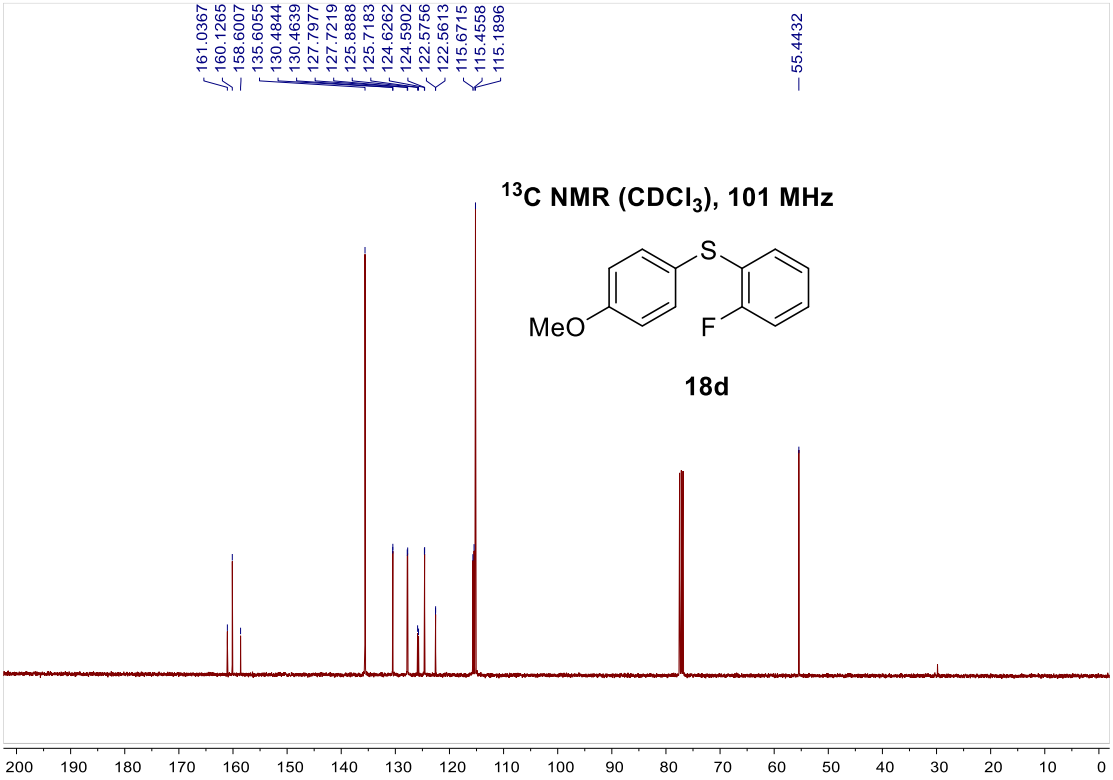
7.3993
7.1429
7.1340
7.1254
7.1210
7.1124
7.0421
7.0200
7.0163
6.9971
6.9788
6.9686
6.9649
6.9583
6.9006
6.8787
3.7978
^{1}H NMR ($CDCl_3$), 400 MHz
S
MeO
F
18d
2.00
1.04
3.03
2.04
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


-111.0323
^{19}F NMR ($CDCl_3$), 471 MHz
S
MeO
F
18d
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210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135.6055
130.4844
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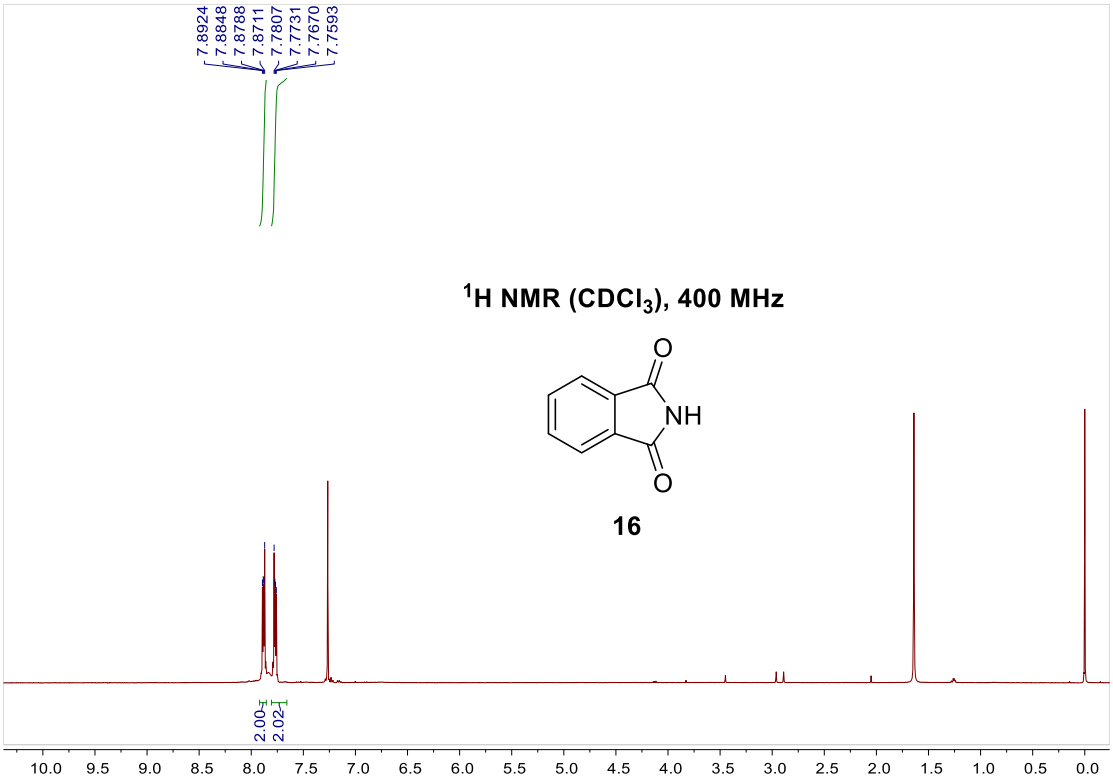
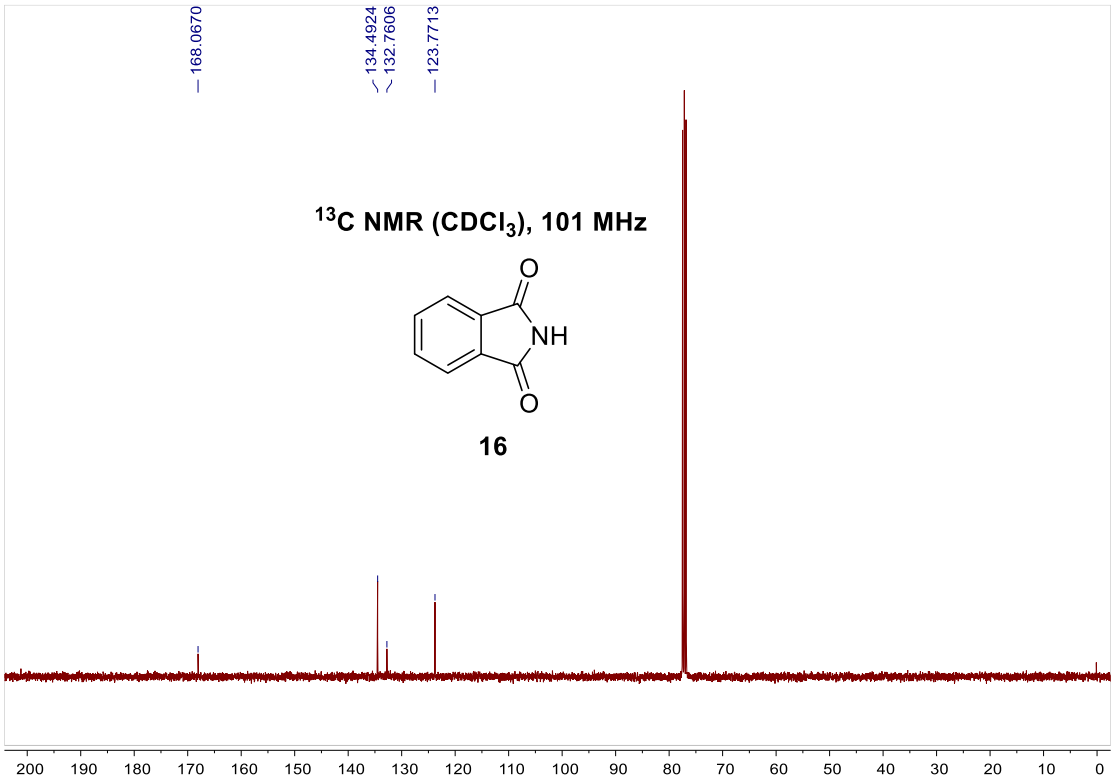
127.7219
125.8888
125.7183
124.6262
124.5902
122.5756
122.5613
115.6715
115.4558
115.1896
55.4432
^{13}C NMR (CDCl$_3$), 101 MHz
S
MeO
F
18d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.8924
7.8848
7.8788
7.8711
7.7807
7.7731
7.7670
7.7593
^{1}H NMR (CDCl$_3$), 400 MHz
O
NH
O
16
2.00
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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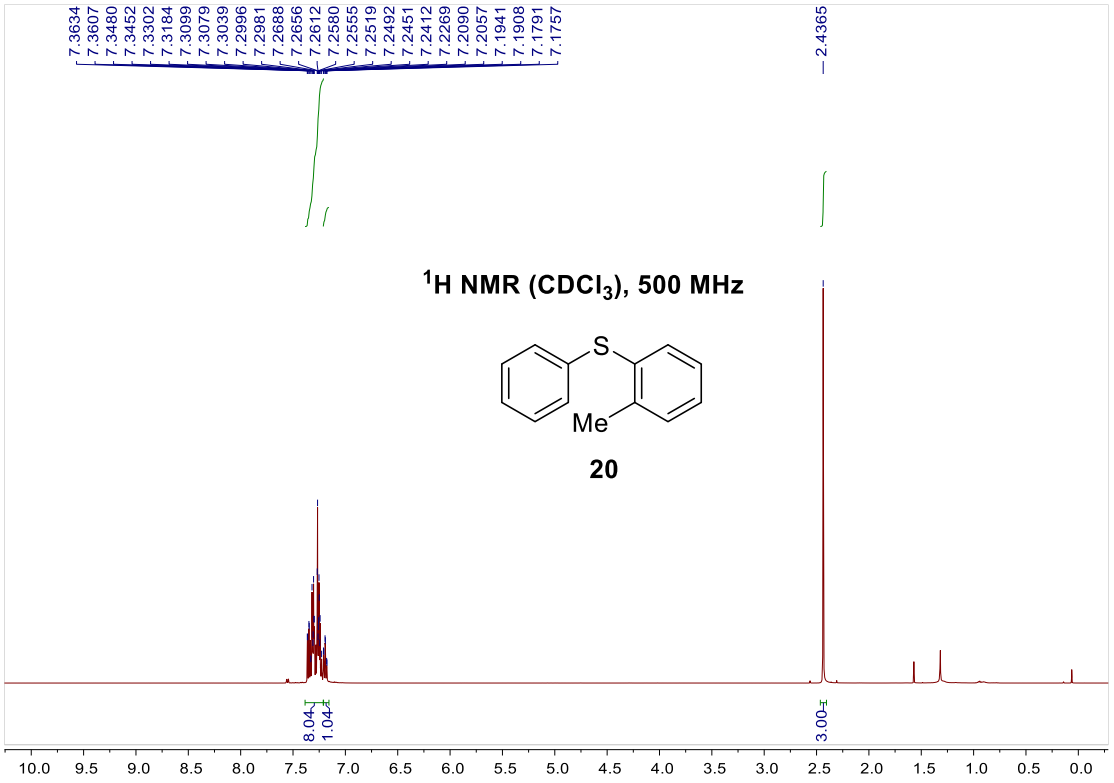
134.4924
132.7606
123.7713
13C NMR (CDCl3), 101 MHz
O
NH
O
16
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.3480
7.3452
7.3302
7.3184
7.3099
7.3079
7.3039
7.2996
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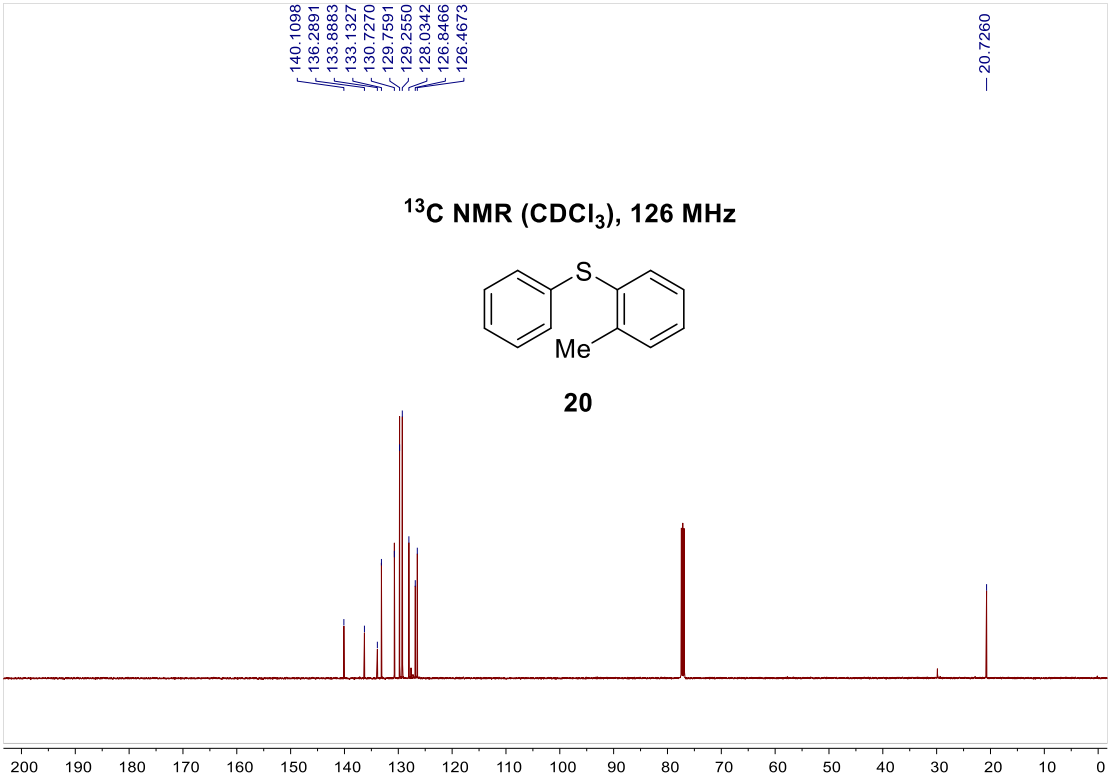
7.2688
7.2656
7.2612
7.2580
7.2555
7.2519
7.2492
7.2451
7.2412
7.2269
7.2090
7.2057
7.1941
7.1908
7.1791
7.1757
2.4365
1H NMR (CDCl3), 500 MHz
S
Me
20
8.04
1.04
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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136.2891
133.8883
133.1327
130.7270
129.7591
129.2550
128.0342
126.8466
126.4673
20.7260
13C NMR (CDCl3), 126 MHz
S
Me
20
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0