

Supporting Information

Copper-catalyzed 1,3-aminothiocyanation of arylcyclopropanes

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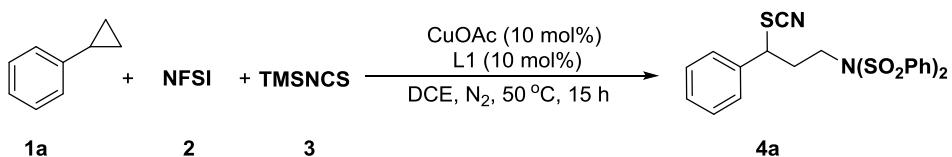
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1. General information

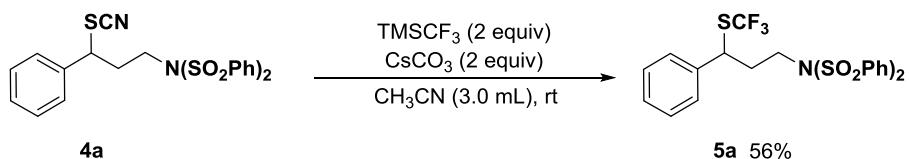
All reactions were performed under nitrogen atmosphere unless otherwise stated. Commercially available reagents were used without further purification. Cyclopropane substrates were synthesized according to procedures described in the literature.^{1,2} All reactions were monitored by thin layer chromatography (TLC) using Macherey-Nagel 0.20 mm silica gel 60 plates. ¹H NMR spectra were recorded on 600 MHz spectrometer, ¹³C NMR spectra were recorded on a 150 MHz instrument, and ¹⁹F NMR spectra were recorded on a 470, and 565 MHz instrument. ¹H and ¹³C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm for ¹H NMR) and CHCl₃ (77.0 ppm for ¹³C NMR), respectively. High-resolution mass spectra (HRMS) were recorded on Bruck microtof or Hybrid Quadrupole-Orbitrap GC-MS/MS system (Q Exactive GC).

2. General procedure for the synthesis of 4a-4ab

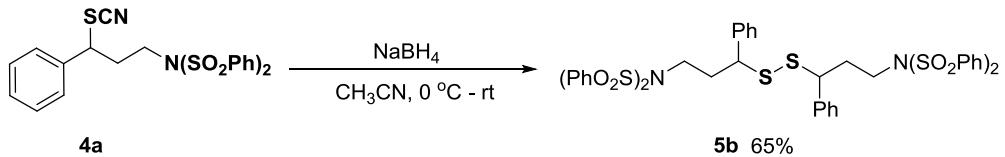


Take 4a as an example: In a nitrogen-filled glove box, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with CuOAc (10 mol%) and **L1** (10 mol%). Anhydrous DCE (2.0 mL) was added and the reaction mixture was stirred for 20 min and NFSI (2.0 equiv.) was added. Then cyclopropanes **1a** (0.3 mmol), TMSNCS (0.45 mmol, 1.5 equiv) was added at room temperature. The tube was sealed and removed from the glove box. The reaction mixture was stirred at 30 °C. After 15 h the reaction mixture was quenched with water and extracted with CH₂Cl₂ (3×10 mL) and the combined organic layers were concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (PE/EA, 1:10, PE = petroleum ether, EA = ethyl acetate) to obtain product **4a**.

3. Transformation of **4a**

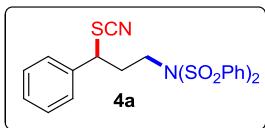


In a 25 mL round-bottom flask, **4a** (94.4 mg, 0.2 mmol) in CH₃CN (3 mL) was added CsCO₃ (130.3 mg, 0.4 mmol) and cooled to 0 °C. Then TMSCF₃ (56.9 mg, 0.4 mmol) was added at once and the mixture was then stirred at room temperature for 16 h and transformed to 30 °C over 2 h. The resulting mixture was filtered through a short pad of celite and extracted with Et₂O. The resulting organic solution was washed with water (10 mL) and brine (10 mL) and dried over MgSO₄. After the removal of solvent, the residue was further purified by flash chromatography affording **5a** (57.7 mg, 56%).



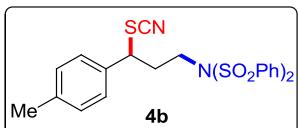
To a solution of **4a** (94.4 mg, 0.2 mmol) in 2 mL of MeCN was added NaBH₄ (11.3 mg, 0.3 mmol) at 0 °C. After the mixture had been stirred at 0 °C for 4 h and transferred to room temperature overnight, the reaction was quenched with 20 mL of saturated aqueous NaHCO₃. The aqueous layer was extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄, and concentrated. Column chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave 115.9 mg of **5b** (65%).

4. Characterization data of all products



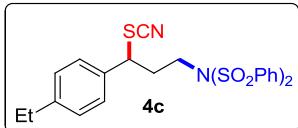
N-(3-phenyl-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4a)

Yellow oil (94%, 133.1 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); **^1H NMR** (600 MHz, CDCl_3) $\delta = 7.94$ (dd, $J = 7.8$ Hz, 1.2 Hz, 4H), 7.66 (t, $J = 7.8$ Hz, 2H), 7.53 (t, $J = 8.4$ Hz, 4H), 7.42-7.36 (m, 3H), 7.32-7.30 (m, 2H), 4.32 (t, $J = 7.2$ Hz, 1H), 3.78-3.73 (m, 1H), 3.61-3.55 (m, 1H), 2.66-2.60 (m, 1H), 2.57-2.51 (m, 1H); **^{13}C NMR** (150 MHz, CDCl_3) $\delta = 139.3$, 136.9, 134.2, 129.4, 129.3, 129.3, 128.2, 127.6, 110.9, 50.1, 46.4, 35.2; **HRMS** (ESI) calcd for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{NaO}_4\text{S}_3$ ($[\text{M} + \text{Na}]^+$), 495.0477, found 495.0471.



N-(phenylsulfonyl)-N-(3-thiocyanato-3-(p-tolyl)propyl)benzenesulfonamide (4b)

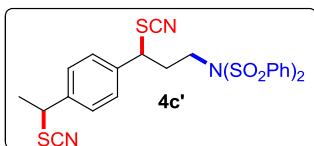
White solid (80%, 116.7 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); mp 93-94 °C; **^1H NMR** (600 MHz, CDCl_3) $\delta = 7.95$ (d, $J = 7.8$ Hz, 4H), 7.66 (t, $J = 7.2$ Hz, 2H), 7.54 (t, $J = 7.8$ Hz, 4H), 7.20 (s, 4H), 4.31 (t, $J = 7.8$ Hz, 1H), 3.77-3.72 (m, 1H), 3.61-3.56 (m, 1H), 2.63-2.59 (m, 1H), 2.55-2.52 (m, 1H); **^{13}C NMR** (150 MHz, CDCl_3) $\delta = 139.5$, 139.4, 134.3, 133.8, 130.0, 129.4, 128.3, 127.5, 111.1, 50.2, 46.5, 35.3, 21.3; **HRMS** (ESI) calcd for $\text{C}_{23}\text{H}_{22}\text{N}_2\text{NaO}_4\text{S}_3$ ($[\text{M} + \text{Na}]^+$), 509.0634, found 509.0642.



N-(3-(4-ethylphenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4c)

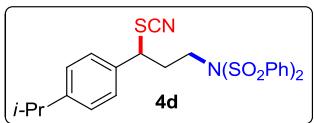
Yellow oil (41%, 61.5 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); **^1H NMR** (600 MHz, CDCl_3) $\delta = 7.95$ (d, $J = 7.8$ Hz, 4H), 7.67 (t, $J = 7.8$ Hz, 2H), 7.54 (t, $J = 7.8$ Hz, 4H), 7.32 (s, 4H), 4.32 (dd, $J = 7.2$, 1.2 Hz, 1H), 3.77-3.72 (m, 1H), 3.60-3.55 (m, 1H), 2.87-2.60 (m, 3H), 2.57-2.52 (m, 1H), 1.26 (t, $J = 7.2$ Hz, 3H); **^{13}C NMR** (150 MHz, CDCl_3) $\delta = 145.6$, 139.2,

134.1, 133.8, 129.2, 128.7, 128.1, 127.4, 110.9, 49.9, 46.3, 35.1, 28.5, 15.3; **HRMS** (ESI) calcd for C₂₄H₂₄N₂NaO₄S₃ ([M + Na]⁺), 523.0790, found 523.0788.



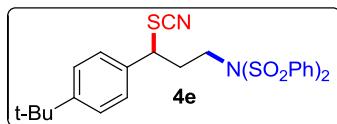
***N*-(phenylsulfonyl)-*N*-(3-thiocyanato-3-(4-(1-thiocyanatoethyl)phenyl)propyl)benzenesulfonamide (4c')**

Yellow oil (25%, 41.8 mg,); R_f = 0.5 (petroleum ether/ethyl acetate = 6:1, v/v); **¹H NMR** (600 MHz, CDCl₃) δ = 7.95 (d, J = 7.2 Hz, 4H), 7.67 (t, J = 7.8 Hz, 2H), 7.56 (t, J = 7.8 Hz, 4H), 7.45 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 4.62 (q, J = 7.2 Hz, 1H), 4.32 (t, J = 7.8 Hz, 1H), 3.80-3.76 (m, 1H), 3.66-3.63 (m, 1H), 2.66-2.62 (m, 1H), 2.56-2.53 (m, 1H), 1.89 (d, J = 6.6 Hz, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ = 140.5, 139.1, 137.8, 134.2, 129.3, 128.2, 128.1, 127.9, 111.2, 110.5, 49.2, 47.8, 46.2, 34.8, 21.7; **HRMS** (ESI) calcd for C₂₄H₂₄N₂NaO₄S₃ ([M + Na]⁺), 580.0464, found 580.0460.



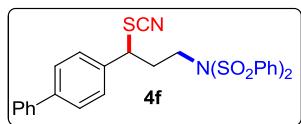
***N*-(3-(4-isopropylphenyl)-3-thiocyanatopropyl)-*N*-(phenylsulfonyl)benzenesulfonamide (4d)**

White solid (75%, 115.6 mg), R_f = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v), mp 103-104 °C; **¹H NMR** (600 MHz, CDCl₃) 7.95 (d, J = 7.2 Hz, 4H), 7.66 (t, J = 7.8 Hz, 2H), 7.54 (t, J = 7.2 Hz, 4H), 7.27 (q, J = 7.8 Hz, 4H), 4.32-4.30 (t, J = 7.8 Hz, 1H), 3.77-3.72 (m, 1H), 3.59-3.54 (m, 1H), 2.95-2.91 (m, 1H), 2.68-2.61 (m, 1H), 2.57-2.53 (m, 1H), 1.27 (d, J = 6.6 Hz, 6H); **¹³C NMR** (150 MHz, CDCl₃) δ = 150.2, 139.2, 134.1, 133.9, 129.2, 128.1, 127.5, 127.3, 110.0, 49.9, 46.3, 35.1, 33.8, 23.8; **HRMS** (ESI) calcd for C₂₅H₂₆N₂NaO₄S₃ ([M + Na]⁺), 537.0947, found 537.0931.



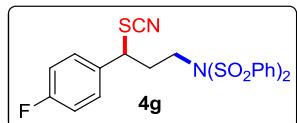
***N*-(3-(4-(tert-butyl)phenyl)-3-thiocyanatopropyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**4e**)**

Light yellow solid (85%, 134.6 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); mp 103-104 °C; **¹H NMR** (600 MHz, CDCl₃) δ = 7.95 (d, J = 8.4 Hz, 4H), 7.66 (t, J = 7.2 Hz, 2H), 7.54 (t, J = 8.4 Hz, 4H), 7.42 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 4.32 (t, J = 7.2 Hz, 1H), 3.77-3.72 (m, 1H), 3.59-3.54 (m, 1H), 2.68-2.63 (m, 1H), 3.59-3.54 (m, 1H), 1.33 (s, 1H); **¹³C NMR** (150 MHz, CDCl₃) δ = 152.6, 139.3, 134.2, 133.7, 129.3, 128.2, 127.3, 126.2, 111.1, 49.9, 46.4, 35.2, 34.8, 31.3; **HRMS** (ESI) calcd for C₂₆H₂₈N₂NaO₄S₃ ([M + Na]⁺), 551.1103, found 551.1101.



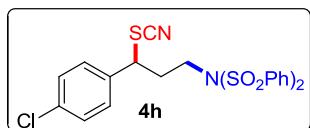
***N*-(3-((1,1'-biphenyl)-4-yl)-3-thiocyanatopropyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**4f**)**

Light yellow oil (69%, 113.4 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); **¹H NMR** (600 MHz, CDCl₃) δ = 7.96 (d, J = 7.8 Hz, 4H), 7.67-7.63 (m, 4H), 7.61 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 8.4 Hz, 4H), 7.48 (t, J = 7.8 Hz, 2H), 7.40-7.38 (m, 3H), 4.38 (t, J = 7.2 Hz, 1H), 3.82-3.77 (m, 1H), 3.65-3.60 (m, 1H), 2.71-2.66 (m, 1H), 2.61-2.56 (m, 1H); **¹³C NMR** (150 MHz, CDCl₃) δ = 142.2, 139.9, 139.1, 135.6, 134.1, 129.2, 128.8, 128.1, 127.9, 127.8, 127.7, 127.0, 110.7, 49.8, 46.2, 35.0; **HRMS** (ESI) calcd for C₂₈H₂₄N₂NaO₄S₃ ([M + Na]⁺), 571.0790, found 571.0792.



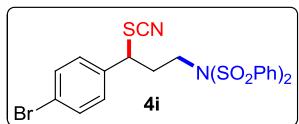
***N*-(3-(4-fluorophenyl)-3-thiocyanatopropyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**4g**)**

Pale yellow oil (79%, 116.1 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); **¹H NMR** (600 MHz, CDCl₃) δ = 7.95 (d, J = 7.2 Hz, 4H), 7.68 (t, J = 7.2 Hz, 2H), 7.56 (t, J = 7.8 Hz, 4H), 7.31-7.30 (m, 2H), 7.11 (t, J = 8.4 Hz, 2H), 4.32 (t, J = 7.8 Hz, 1H), 3.79-3.74 (m, 1H), 3.63-3.58 (m, 1H), 2.62-2.52 (m, 2H); **¹³C NMR** (150 MHz, CDCl₃) δ = 163.8 (d, J = 247.95 Hz), 139.2, 134.2, 132.9 (d, J = 3.3 Hz), 129.4 (d, J = 8.25 Hz), 129.3, 128.1, 116.4 (d, J = 21.75 Hz), 110.6, 49.3, 46.3, 35.1; **¹⁹F NMR** (565 MHz, CDCl₃) δ = -111.18 -- -111.24 (m, 1F); **HRMS** (ESI) calcd for C₂₂H₁₉FN₂NaO₄S₃ ([M + Na]⁺), 513.0383, found 513.0379.



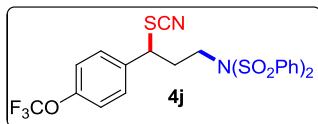
N-(3-(4-chlorophenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4h)

Light yellow oil (yield 109.3 mg, 72%); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); **¹H NMR** (600 MHz, CDCl₃) δ = 7.95 (d, J = 7.8 Hz, 4H), 7.68 (t, J = 7.2 Hz, 2H), 7.56 (t, J = 7.8 Hz, 4H), 7.40 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 4.29 (t, J = 7.2 Hz, 1H), 3.79-3.74 (m, 1H), 3.62-3.57 (m, 1H), 2.62-2.56 (m, 1H), 2.54-2.49 (m, 1H); **¹³C NMR** (150 MHz, CDCl₃) δ = 139.3, 134.2, 133.8, 130.2, 129.3, 128.1, 127.7, 127.7, 110.3, 46.3, 45.4, 34.3; **HRMS** (ESI) calcd for C₂₂H₁₉ClN₂NaO₄S₃ ([M + Na]⁺), 529.0088, found 529.0078.



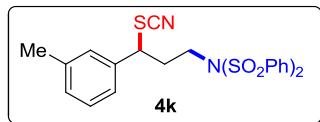
N-(3-(4-bromophenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4i)

Light yellow oil (64%, 105.6 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); **¹H NMR** (600 MHz, CDCl₃) δ = 7.87 (d, J = 7.8 Hz, 4H), 7.61 (t, J = 7.2 Hz, 2H), 7.49-7.46 (m, 6H), 7.13 (d, J = 8.4 Hz, 2H), 4.21 (t, J = 7.8 Hz, 1H), 3.71-3.67 (m, 1H), 3.54-3.49 (m, 1H), 2.55-2.49 (m, 1H), 2.47-2.41 (m, 1H); **¹³C NMR** (150 MHz, CDCl₃) δ = 139.1, 136.1, 134.2, 132.5, 129.3, 129.1, 128.1, 123.5, 110.4, 49.2, 46.2, 34.8; **HRMS** (ESI) calcd for C₂₂H₁₉BrN₂NaO₄S₃ ([M + Na]⁺), 572.9583, found 572.9587.



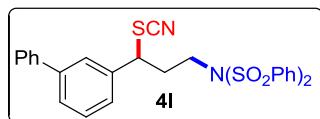
N-(phenylsulfonyl)-N-(3-thiocyanato-3-(trifluoromethoxy)phenyl)propylbenzenesulfonamide (4j)

Yellow oil (yield 135.1 mg, 81%); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); **¹H NMR** (600 MHz, CDCl₃) δ = 7.94 (d, J = 8.4 Hz, 4H), 7.67 (t, J = 7.2 Hz, 2H), 7.54 (t, J = 7.8 Hz, 4H), 7.37 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 7.8 Hz, 1H), 4.32 (t, J = 7.8 Hz, 1H), 3.80-3.76 (m, 1H), 3.62-3.57 (m, 1H), 2.63-2.60 (m, 1H), 2.56-2.53 (m, 1H). **¹³C NMR** (150 MHz, CDCl₃) δ = 149.7, 139.1, 135.8, 134.3, 129.4, 129.2, 129.0 (q, J = 256.2 Hz), 128.2, 121.6, 110.4, 48.9, 46.1, 34.9; **¹⁹F NMR** (565 MHz, CDCl₃) δ = -57.76 (s, 1CF₃O); **HRMS** (ESI) calcd for C₂₃H₁₉F₃N₂NaO₅S₃ ([M + Na]⁺), 579.0300, found 579.0300.



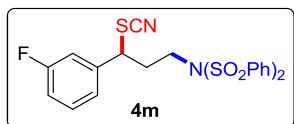
N-(phenylsulfonyl)-N-(3-thiocyanato-3-(m-tolyl)propyl)benzenesulfonamide (4k)

White solid (65%, 94.7 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); mp 144-145 °C; **¹H NMR** (600 MHz, CDCl₃) δ = 7.95 (d, J = 7.8 Hz, 4H), 7.67 (t, J = 7.8 Hz, 2H), 7.55 (t, J = 7.8 Hz, 4H), 7.31 (t, J = 7.8 Hz, 1H), 7.20 (d, J = 7.8 Hz, 1H), 7.11 (s, 1H), 4.29 (t, J = 7.8 Hz, 1H), 3.78-3.73 (m, 1H), 3.60-3.55 (m, 1H), 2.65-2.59 (m, 1H), 2.56-2.51 (m, 1H), 2.38 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ = 139.3, 139.2, 136.7, 134.2, 130.2, 129.3, 129.2, 128.2, 124.6, 111.0, 50.2, 46.4, 35.3, 21.5; **HRMS** (ESI) calcd for C₂₂H₂₃N₂NaO₄S₃ ([M + Na]⁺), 509.0634, found 509.0630.



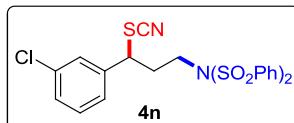
N-(3-([1,1'-biphenyl]-3-yl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4l)

Pale yellow oil (80%, 132.1 mg); $R_f = 0.5$ (petroleum ether); **$^1\text{H NMR}$** (600 MHz, CDCl_3) $\delta = 7.94$ (d, $J = 7.2$ Hz, 4H), 7.63 (t, $J = 7.8$ Hz, 5H), 7.52-7.45 (m, 8H), 7.39 (t, $J = 7.2$ Hz, 1H), 7.29 (d, $J = 7.8$ Hz, 1H), 4.38 (t, $J = 7.2$ Hz, 1H), 3.82-3.77 (m, 1H), 3.64-3.59 (m, 1H), 2.71-2.69 (m, 1H), 2.63-2.59 (m, 1H); **$^{13}\text{C NMR}$** (150 MHz, CDCl_3) $\delta = 142.4, 140.2, 139.2, 137.4, 134.2, 129.3, 129.0, 128.2, 127.9, 127.2, 126.4, 126.3, 110.9, 50.0, 46.4, 35.2$; **HRMS (ESI)** calcd for $\text{C}_{28}\text{H}_{24}\text{N}_2\text{NaO}_4\text{S}_3$ ($[\text{M} + \text{Na}]^+$), 571.0790, found 571.0791.



***N*-(3-(3-fluorophenyl)-3-thiocyanatopropyl)-*N*-(phenylsulfonyl)benzenesulfonamide (4m)**

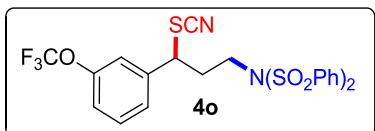
Light yellow oil (62%, 91.1 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); **$^1\text{H NMR}$** (600 MHz, CDCl_3) $\delta = 7.96$ (d, $J = 7.8$ Hz, 4H), 7.68 (t, $J = 7.8$ Hz, 2H), 7.56 (t, $J = 7.8$ Hz, 4H), 7.41-7.37 (m, 1H), 7.12-7.08 (m, 2H), 7.02-7.00 (m, 1H), 4.29 (t, $J = 7.8$ Hz, 1H), 3.81-3.76 (m, 1H), 3.75-3.71 (m, 1H), 3.65-3.60 (m, 1H), 2.60-2.54 (m, 1H), 2.53-2.49 (m, 1H); **$^{13}\text{C NMR}$** (150 MHz, CDCl_3) $\delta = 163.7$ (d, $J = 246.9$ Hz), 139.6 (d, $J = 7.05$ Hz), 139.2, 134.2, 131.0 (d, $J = 8.25$ Hz), 129.3, 128.2, 123.2 (d, $J = 3.0$ Hz), 116.5 (d, $J = 20.85$ Hz), 114.6 (d, $J = 22.35$ Hz), 110.3, 49.2, 46.2, 34.9; **$^{19}\text{F NMR}$** (565 MHz, CDCl_3) $\delta = -111.75$ - -111.80 (m, 1F); **HRMS (ESI)** calcd for $\text{C}_{22}\text{H}_{19}\text{FN}_2\text{NaO}_4\text{S}_3$ ($[\text{M} + \text{Na}]^+$), 513.0383, found 513.0380.



***N*-(3-(3-chlorophenyl)-3-thiocyanatopropyl)-*N*-(phenylsulfonyl)benzenesulfonamide (4n)**

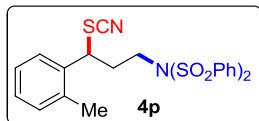
White solid (56%, 85.0 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); **$^1\text{H NMR}$** (600 MHz, CDCl_3) $\delta = 7.96$ (d, $J = 7.8$ Hz, 4H), 7.69 (t, $J = 8.4$ Hz, 2H), 7.57 (t, $J = 7.8$ Hz, 4H), 7.37-7.34 (m, 2H), 7.27 (s, 1H), 7.23 (d, $J = 6.6$ Hz, 1H), 4.26 (t, $J = 7.2$ Hz, 1H), 3.78-3.76 (m, 1H), 3.63-3.59 (m, 1H), 2.59-2.50 (m, 2H); **$^{13}\text{C NMR}$** (150 MHz, CDCl_3) $\delta = 139.2, 139.1,$

135.1, 134.2, 130.6, 129.6, 129.3, 128.2, 127.7, 125.6, 110.3, 49.1, 46.1, 34.9; **HRMS** (ESI) calcd for C₂₂H₁₉ClN₂NaO₄S₃ ([M + Na]⁺), 529.0088, found 529.0084.



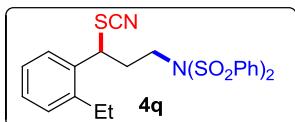
N-(phenylsulfonyl)-N-(3-thiocyanato-3-(trifluoromethoxy)phenyl)propylbenzenesulfonamide (4o)

Light yellow oil (61%, 100 mg); R_f = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); **¹H NMR** (600 MHz, CDCl₃) δ = 7.96 (d, J = 7.8 Hz, 4H), 7.68 (t, J = 7.8 Hz, 2H), 7.56 (t, J = 7.2 Hz, 4H), 7.47 (t, J = 7.2 Hz, 1H), 7.28 (t, J = 8.4 Hz, 2H), 7.15 (s, 1H), 4.30 (t, J = 7.2 Hz, 1H), 3.80-3.78 (m, 1H), 3.68-3.63 (m, 1H), 2.61-2.50 (m, 2H); **¹³C NMR** (150 MHz, CDCl₃) δ = 149.7, 139.6, 139.2, 134.3, 130.8, 129.5 (q, J = 239.3 Hz), 129.3, 128.2, 125.8, 121.7, 120.1, 110.2, 49.1, 46.2, 34.8; **¹⁹F NMR** (565 MHz, CDCl₃) δ = -57.83 (s, 1CF₃O); **HRMS** (ESI) calcd for C₂₃H₁₉F₃N₂NaO₅S₃ ([M + Na]⁺), 579.0300, found 579.0304.



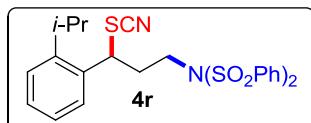
N-(phenylsulfonyl)-N-(3-thiocyanato-3-(o-tolyl)propyl)benzenesulfonamide (4p)

White solid (82%, 119.6 mg); R_f = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); mp 111-112 °C; **¹H NMR** (600 MHz, CDCl₃) δ = 7.96 (d, J = 8.4 Hz, 4H), 7.66 (t, J = 7.8 Hz, 2H), 7.54 (t, J = 7.2 Hz, 4H), 7.34-7.28 (m, 3H), 7.21 (d, J = 7.2 Hz, 1H), 4.54 (dd, J = 7.2 Hz, 1H), 3.83-3.79 (m, 1H), 3.69-3.64 (m, 1H), 2.73-2.69 (m, 1H), 3.69-3.64 (m, 1H), 2.30(s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ = 139.2, 136.3, 134.6, 134.1, 131.1, 129.3, 129.1, 128.1, 127.0, 126.2, 110.9, 46.3, 45.8, 34.9, 19.2; **HRMS** (ESI) calcd for C₂₅H₂₂N₂NaO₄S₃ ([M + Na]⁺), 509.0634, found 509.0634.



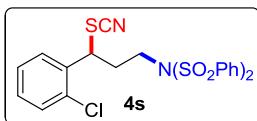
N-(3-(2-ethylphenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4q)

White solid (75%, 112.5 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); mp 110-111 °C; **¹H NMR** (600 MHz, CDCl₃) δ = 7.95 (d, J = 7.8 Hz, 4H), 7.66 (t, J = 7.8 Hz, 2H), 7.54 (t, J = 7.8 Hz, 4H), 7.37 (dd, J = 6.0, 1.8 Hz, 1H), 7.33-7.30 (m, 2H), 7.24-7.23 (m, 1H), 4.62 (t, J = 7.8 Hz, 1H), 3.83-3.78 (m, 1H), 3.63-3.59 (m, 1H), 2.71-2.66 (m, 1H), 2.65-2.60 (m, 3H), 1.21 (t, J = 7.2 Hz, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ = 142.1, 139.2, 134.1, 133.9, 129.3, 129.2, 128.1, 126.9, 126.3, 111.0, 46.3, 45.2, 35.4, 25.4, 15.1; **HRMS** (ESI) calcd for C₂₄H₂₄N₂NaO₄S₃ ([M + Na]⁺), 523.0790, found 523.0761.



N-(3-(2-isopropylphenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4r)

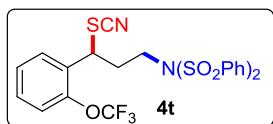
White solid (92%, 141.8 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); mp 111-112 °C; **¹H NMR** (600 MHz, CDCl₃) δ = 7.96 (dd, J = 7.2, 1.2 Hz, 4H), 7.67 (t, J = 7.8 Hz, 2H), 7.55 (t, J = 7.8 Hz, 4H), 7.36-7.33 (m, 3H), 7.30-7.27 (m, 2H), 7.66 (t, J = 7.8 Hz, 1H), 3.82-3.77 (m, 1H), 3.62-3.57 (m, 1H), 3.13-3.09 (m, 1H), 2.72-2.67 (m, 1H), 2.65-2.61 (m, 1H), 1.29 (d, J = 7.2 Hz, 3H), 1.16 (d, J = 6.6 Hz, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ = 147.0, 139.3, 134.2, 133.0, 129.5, 129.3, 128.2, 126.7, 126.4, 126.3, 111.0, 46.4, 35.7, 28.6, 24.4, 23.6; **HRMS** (ESI) calcd for C₂₅H₂₆N₂NaO₄S₃ ([M + Na]⁺), 537.0947, found 537.0948.



N-(3-(2-chlorophenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4s)

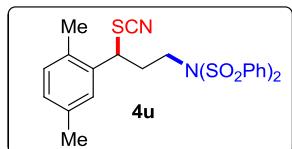
Light yellow oil (67%, 101.9 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); **¹H NMR** (600 MHz, CDCl₃) δ = 7.99 (d, J = 7.8 Hz, 4H), 7.67 (t, J = 7.2 Hz, 2H), 7.56 (t, J = 7.8 Hz,

4H), 7.41-7.32 (m, 4H), 4.71 (t, $J = 7.8$ Hz, 1H), 3.91-3.86 (m, 1H), 3.73-3.68 (m, 1H), 2.66-2.56 (m, 2H); **^{13}C NMR** (150 MHz, CDCl_3) δ = 139.3, 134.6, 134.2, 133.8, 130.3, 130.2, 129.3, 128.1, 127.7, 127.7, 110.3, 46.3, 45.4, 34.3; **HRMS** (ESI) calcd for $\text{C}_{22}\text{H}_{19}\text{ClN}_2\text{NaO}_4\text{S}_3$ ($[\text{M} + \text{Na}]^+$), 529.0088, found 529.0088.



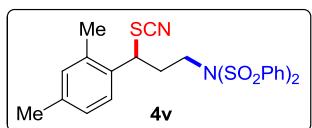
***N*-(phenylsulfonyl)-*N*-(3-thiocyanato-3-(trifluoromethoxy)phenyl)propylbenzenesulfonamide (**4t**)**

White solid (65%, yield 105.3 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 25:1, v/v); mp 52-53 °C; **^1H NMR** (600 MHz, CDCl_3) δ = 7.98 (dd, $J = 7.2, 1.2$ Hz, 4H), 7.68 (t, $J = 7.8$ Hz, 2H), 7.56 (t, $J = 7.8$ Hz, 4H), 7.50 (dd, $J = 6.0, 1.8$ Hz, 1H), 7.46-7.43 (m, 1H), 7.32-7.31 (m, 1H), 4.61 (t, $J = 7.2$ Hz, 1H), 3.86-3.81 (m, 1H), 3.64-3.60 (m, 1H), 2.63-2.56 (m, 2H); **^{13}C NMR** (150 MHz, CDCl_3) δ = 146.6, 139.3, 134.2, 130.6, 129.4, 129.2 (q, $J = 260.9$ Hz), 129.3, 129.2, 128.2, 127.4, 120.2, 110.1, 46.2, 42.2, 34.6; **^{19}F NMR** (565 MHz, CDCl_3) δ = -56.71 (s, $1\text{CF}_3\text{O}$); **HRMS** (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{F}_3\text{N}_2\text{NaO}_5\text{S}_3$ ($[\text{M} + \text{Na}]^+$), 579.0300, found 579.0304.



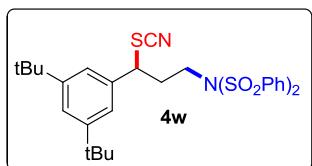
***N*-(3-(2,5-dimethylphenyl)-3-thiocyanatopropyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**4u**)**

Yellow oil (yield 93 mg, 62%); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); **^1H NMR** (600 MHz, CDCl_3) δ = 7.96 (dd, $J = 8.4, 1.8$ Hz, 4H), 7.67 (t, $J = 7.2$ Hz, 2H), 7.55 (t, $J = 8.4$ Hz, 4H), 7.15 (s, 1H), 7.09 (s, 2H), 4.53 (t, $J = 7.2$ Hz, 1H), 3.81-3.76 (m, 1H), 3.67-3.62 (m, 1H), 2.72-2.67 (m, 1H), 2.63-2.58 (m, 1H), 2.37 (s, 3H), 2.27 (s, 3H); **^{13}C NMR** (150 MHz, CDCl_3) δ = 139.3, 136.6, 134.2, 134.1, 133.2, 131.1, 129.9, 129.3, 128.2, 126.9, 111.0, 46.4, 46.0, 35.0, 21.1, 18.8; **HRMS** (ESI) calcd for $\text{C}_{24}\text{H}_{24}\text{N}_2\text{NaO}_4\text{S}_3$ ($[\text{M} + \text{Na}]^+$), 523.0790, found 523.0786.



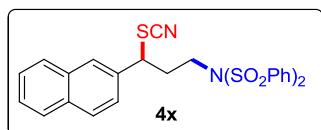
N-(3-(2,4-dimethylphenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4v)

Yellow oil (52%, 78 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); **^1H NMR** (600 MHz, CDCl_3) $\delta = 7.93$ (dd, $J = 7.2, 1.2$ Hz, 4H), 7.66 (t, $J = 7.2$ Hz, 2H), 7.53 (t, $J = 7.8$ Hz, 4H), 7.15 (d, $J = 7.2$ Hz, 1H), 7.08 (d, $J = 7.8$ Hz, 1H), 7.02 (d, $J = 7.8$ Hz, 1H), 5.10 (t, $J = 7.8$ Hz, 1H), 3.80-3.75 (m, 1H), 3.53-3.48 (m, 1H), 2.76-2.69 (m, 1H), 2.58-2.53 (m, 1H), 2.47 (s, 3H), 2.33 (s, 3H); **^{13}C NMR** (150 MHz, CDCl_3) $\delta = 142.1, 139.2, 134.1, 133.9, 129.3, 129.2, 128.2, 126.9, 126.3, 111.0, 46.3, 45.2, 35.4, 25.4, 15.1; **HRMS** (ESI) calcd for $\text{C}_{24}\text{H}_{24}\text{N}_2\text{NaO}_4\text{S}_3$ ($[\text{M} + \text{Na}]^+$), 523.0790, found 523.0794.$



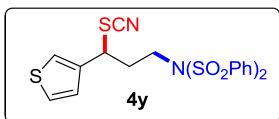
N-(3-(3,5-di-tert-butylphenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4w)

Light yellow solid (50%, 74.7 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 25:1, v/v); mp 108-109 °C; **^1H NMR** (600 MHz, CDCl_3) $\delta = 7.96$ (d, $J = 8.4$ Hz, 4H), 7.65 (t, $J = 7.8$ Hz, 2H), 7.53 (t, $J = 7.8$ Hz, 4H), 7.44 (s, 1H), 7.14 (s, 1H), 4.34 (t, $J = 7.8$ Hz, 1H), 3.77-3.74 (m, 1H), 3.58-3.53 (m, 1H), 2.73-2.68 (m, 1H), 2.60-2.55 (m, 1H), 1.34 (s, 18H); **^{13}C NMR** (150 MHz, CDCl_3) $\delta = 152.0, 139.4, 135.7, 134.1, 129.3, 128.2, 123.5, 111.2, 51.0, 46.5, 35.4, 35.0, 31.4; **HRMS** (ESI) calcd for $\text{C}_{30}\text{H}_{36}\text{N}_2\text{NaO}_4\text{S}_3$ ($[\text{M} + \text{Na}]^+$), 607.1729, found 607.1749.$



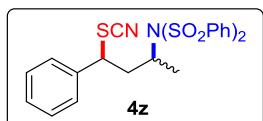
N-(3-(naphthalen-2-yl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4x)

Light yellow oil (66%, 103.3 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); **¹H NMR** (600 MHz, CDCl₃) δ = 7.92 (dd, J = 7.8 Hz, 5H), 7.87-7.85 (m, 2H), 7.77 (s, 1H), 7.64 (t, J = 8.4 Hz, 2H), 7.56-7.55 (q, J = 3.6 Hz, 2H), 7.50 (t, J = 7.8 Hz, 4H), 7.44 (dd, J = 6.6, 1.8 Hz, 1H), 4.51(t, J = 7.2 Hz, 1H), 3.83-3.78 (m, 1H), 3.63-3.58 (m, 1H), 2.78-2.73 (m, 1H), 2.67-2.62 (m, 1H); **¹³C NMR** (150 MHz, CDCl₃) δ = 139.2, 134.1, 134.0, 133.5, 133.0, 129.5, 129.2, 128.20, 128.16, 127.8, 127.11, 127.09, 126.9, 124.5, 110.8, 50.4, 46.3, 35.1; **HRMS** (ESI) calcd for C₂₆H₂₂N₂NaO₄S₃ ([M + Na]⁺), 545.0634, found 545.0621.



***N*-(phenylsulfonyl)-*N*-(3-thiocyanato-3-(thiophen-3-yl)propyl)benzenesulfonamide (**4y**)**

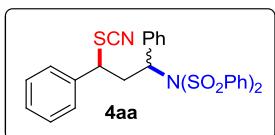
Light yellow oil (49%, 70.2 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); **¹H NMR** (600 MHz, CDCl₃) δ = 7.98 (dd, J = 7.8, 1.2 Hz, 4H), 7.69 (t, J = 7.8 Hz, 2H), 7.57 (t, J = 7.2 Hz, 4H), 7.41-7.40 (m, 1H), 7.34-7.33 (m, 1H), 7.11 (dd, J = 3.6, 1.2 Hz, 1H), 4.48 (t, J = 7.8 Hz, 1H), 3.81-3.76 (m, 1H), 3.70-3.65 (m, 1H), 2.66-2.61 (m, 1H), 2.56-2.53 (m, 1H); **¹³C NMR** (150 MHz, CDCl₃) δ = 139.2, 137.5, 134.2, 129.3, 128.2, 127.5, 126.1, 124.2, 110.7, 46.3, 45.3, 35.5; **HRMS** (ESI) calcd for C₂₀H₁₈N₂NaO₄S₄ ([M + Na]⁺), 501.0042, found 501.0039.



***N*-(4-phenyl-4-thiocyanatobutan-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (**4z**)**

A mixture of two diastereoisomers which are inseparable. The ratio of the two diastereoisomers was determined by **¹H NMR** spectroscopy (d.r. = 1:2). The mixture was white solid (65%, 94.7 mg); mp 94-95 °C; $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); **¹H NMR** (600 MHz, CDCl₃) δ = 7.91 (d, J = 7.8 Hz, 4.19H), 7.68-7.65 (m, 3.25H), 7.57-7.54 (m, 3.03H), 7.51-7.48 (m, 3.08H), 7.43-7.35 (m, 5.41H), 7.30 (d, J = 6.6 Hz, 1.14H), 7.25-7.23 (m, 2.22H), 4.24-4.17 (m, 2.58H), 4.15-4.11 (m, 0.57H), 3.01-2.96 (m, 1H), 2.82-2.77 (m, 0.57H), 2.74-2.71 (m, 0.55H), 2.68-2.63 (m, 1.01H), 1.32 (d, J = 7.2 Hz, 3.14H), 1.28 (d, J = 6.6 Hz, 1.60H); **¹³C NMR** (150

MHz, CDCl₃) δ = 137.8, 137.4, 134.1, 129.3, 129.2, 128.3, 127.6, 127.5, 110.8, 57.3, 50.1, 39.7, 19.6; **HRMS** (ESI) calcd for C₂₃H₂₂N₂NaO₄S₃ ([M + Na]⁺), 509.0634, found 509.0643.



N-(1,3-diphenyl-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4aa)

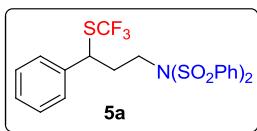
4aa and **4aa'** are diastereomers and can be separated by column chromatography.

White solid (41%, 67.4 mg); mp 146-147 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v);

¹H NMR (600 MHz, CDCl₃) δ = 7.60 (s, 2H), 7.46 (d, J = 7.2 Hz, 6H), 7.41-7.31(m, 8H), 7.17-7.16 (m, 2H), 5.86(dd, J = 12, 3.0 Hz, 1H), 4.04 (dd, J = 10.8, 1.8 Hz, 1H), 3.70-3.65 (m, 1H), 2.37-2.32 (m, 1H); **¹³C NMR** (150 MHz, CDCl₃) δ = 138.5, 133.4, 130.0, 129.2, 129.0, 128.8, 128.3, 127.2, 110.3, 62.2, 51.3, 37.7; **HRMS** (ESI) calcd for C₂₈H₂₄N₂NaO₄S₃ ([M + Na]⁺), 571.0790, found 571.0785.

White solid (29%, 44.2 mg); R_f = 0.5 (petroleum ether/ethyl acetate = 8:1, v/v); mp 144-145 °C;

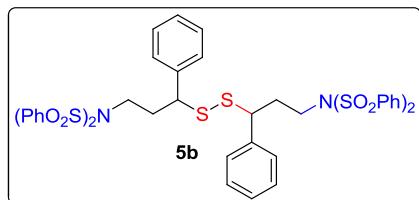
¹H NMR (600 MHz, CDCl₃) δ = 7.57 (s, 2H), 7.46-7.33 (m, 15H), 6.92 (d, J = 7.8 Hz, 2H), 5.08 (dd, J = 11.4, 3.6 Hz, 1H), 4.18 (dd, J = 10.8, 4.2 Hz, 1H), 3.73-3.69 (m, 1H), 2.45-2.40 (m, 1H); **¹³C NMR** (150 MHz, CDCl₃) δ = 136.4, 133.7, 133.5, 129.9, 129.43, 129.36, 129.1, 128.9, 128.1, 127.6, 110.9, 61.6, 50.0, 38.8; **HRMS** (ESI) calcd for C₂₈H₂₄N₂NaO₄S₃ ([M + Na]⁺), 571.0790, found 571.0784.



N-(3-phenyl-3-((trifluoromethyl)thio)propyl)-N-(phenylsulfonyl)benzenesulfonamide (5a)

Light yellow solid (56%, 57.7 mg); R_f = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); mp 76-77 °C; **¹H NMR** (600 MHz, CDCl₃) δ = 7.91 (d, J = 8.4 Hz, 4H), 7.69 (t, J = 7.8 Hz, 2H), 7.57 (t, J = 7.2 Hz, 4H), 7.41-7.40 (m, 1H), 7.34-7.33 (m, 1H), 7.11(dd, J = 3.6, 1.2 Hz, 1H), 4.48 (t, J = 7.8 Hz, 1H), 3.81-3.76 (m, 1H), 3.70-3.65 (m, 1H), 2.66-2.61 (m, 1H), 2.56-2.53 (m, 1H); **¹³C NMR**

(150 MHz, CDCl₃) δ = 139.2, 137.5, 134.2, 129.3, 128.2, 127.5, 126.1, 124.1, 110.7, 46.3, 45.3, 35.5; **¹⁹F NMR** (565 MHz, CDCl₃) δ = -39.69 (s, 1SCF₃); **HRMS** (ESI) calcd for C₂₀H₁₈N₂NaO₄S₄ ([M + Na]⁺), 501.0042, found 501.0039.



***N,N'*-disulfanediylbis(3-phenylpropane-3,1-diyl))bis(N-(phenylsulfonyl)benzenesulfonamide)**
(5b)

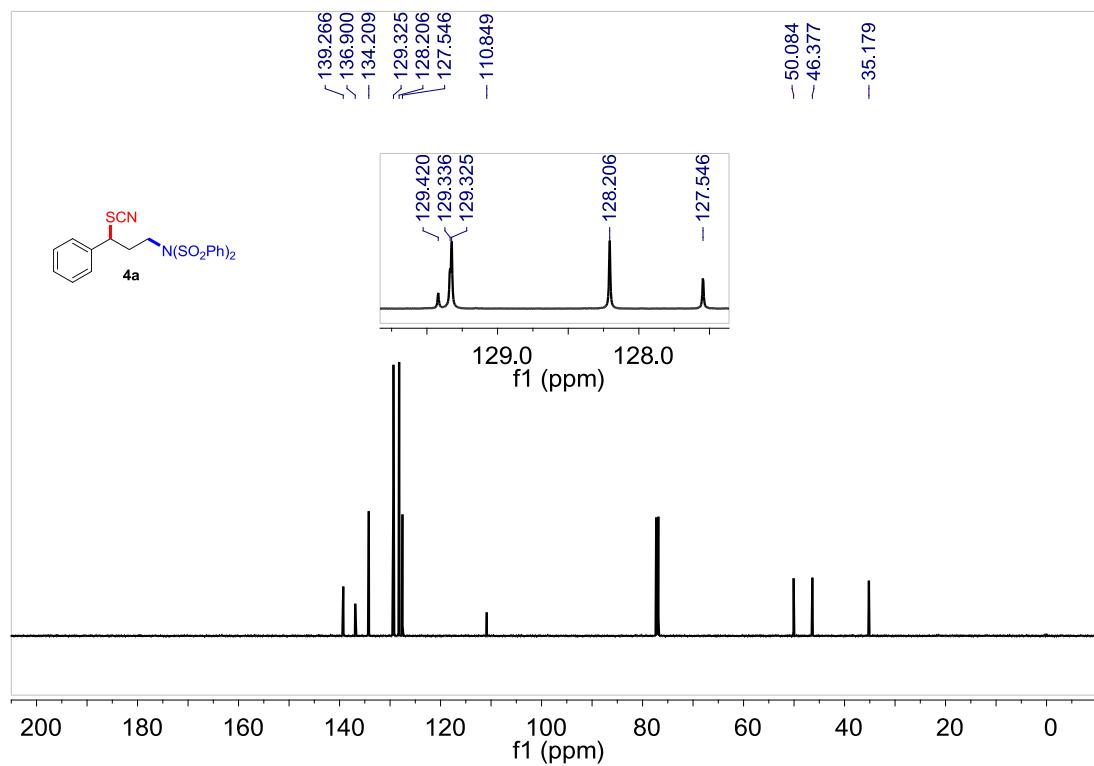
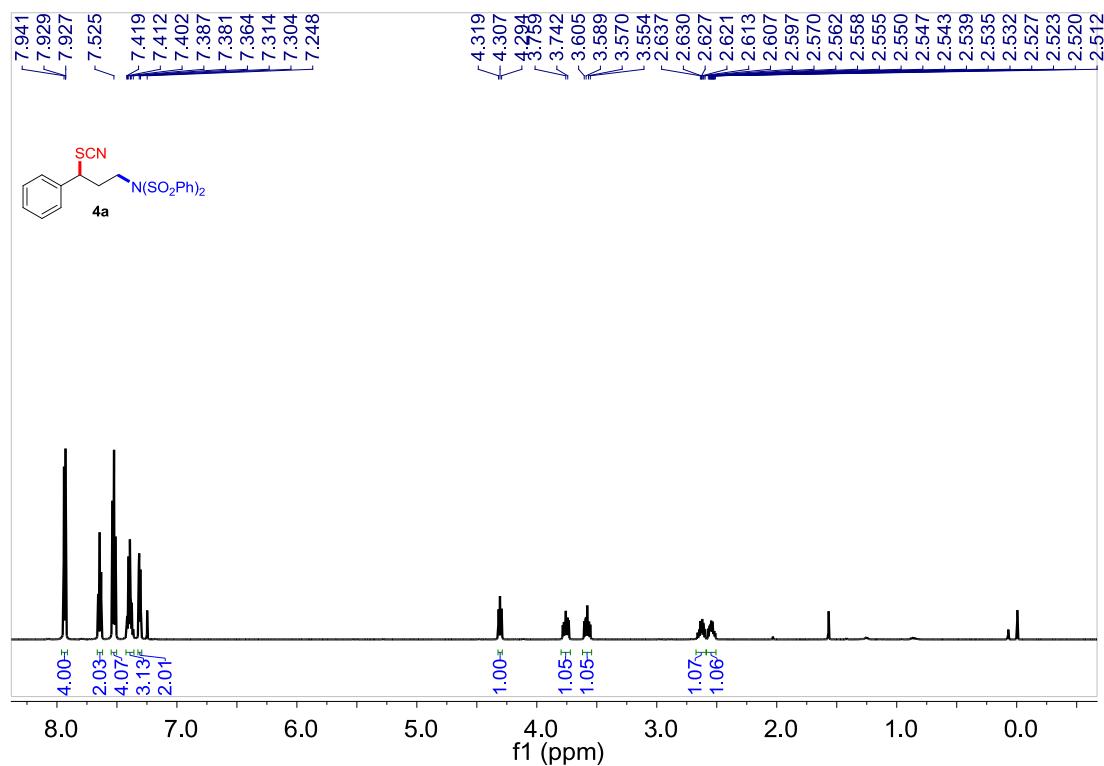
Yellow oil (65%, 115.9 mg); R_f = 0.5 (petroleum ether/ethyl acetate = 4:1, v/v); **¹H NMR** (600 MHz, CDCl₃) δ = 7.93 (t, J = 7.8 Hz, 8H), 7.60 (q, J = 7.2 Hz, 4H), 7.54-7.48 (m, 8H), 7.36-7.29 (m, 6H), 7.15-7.12 (m, 4H), 3.57-3.52 (m, 2H), 3.39-3.31 (m, 2H), 3.20-3.18 (m, 1H), 3.13-3.10 (m, 1H), 5.69 (dd, J = 9.6, 4.8 Hz, 1H), 3.81-3.76 (m, 1H), 3.65-3.60 (m, 1H), 3.07-3.00 (m, 1H), 2.42-2.34 (m, 2H), 2.26-2.21 (m, 2H); **¹³C NMR** (150 MHz, CDCl₃) δ = 139.51, 139.49, 139.3, 139.2, 133.90, 133.86, 129.11, 129.08, 128.7, 128.6, 128.3, 128.2, 128.1, 128.0, 127.9, 51.5, 51.3, 47.02, 47.01, 34.0, 33.8; **HRMS** (ESI) calcd for C₄₂H₄₀N₂NaO₈S₈ ([M + Na]⁺), 915.1001, found 915.0996.

5. Reference

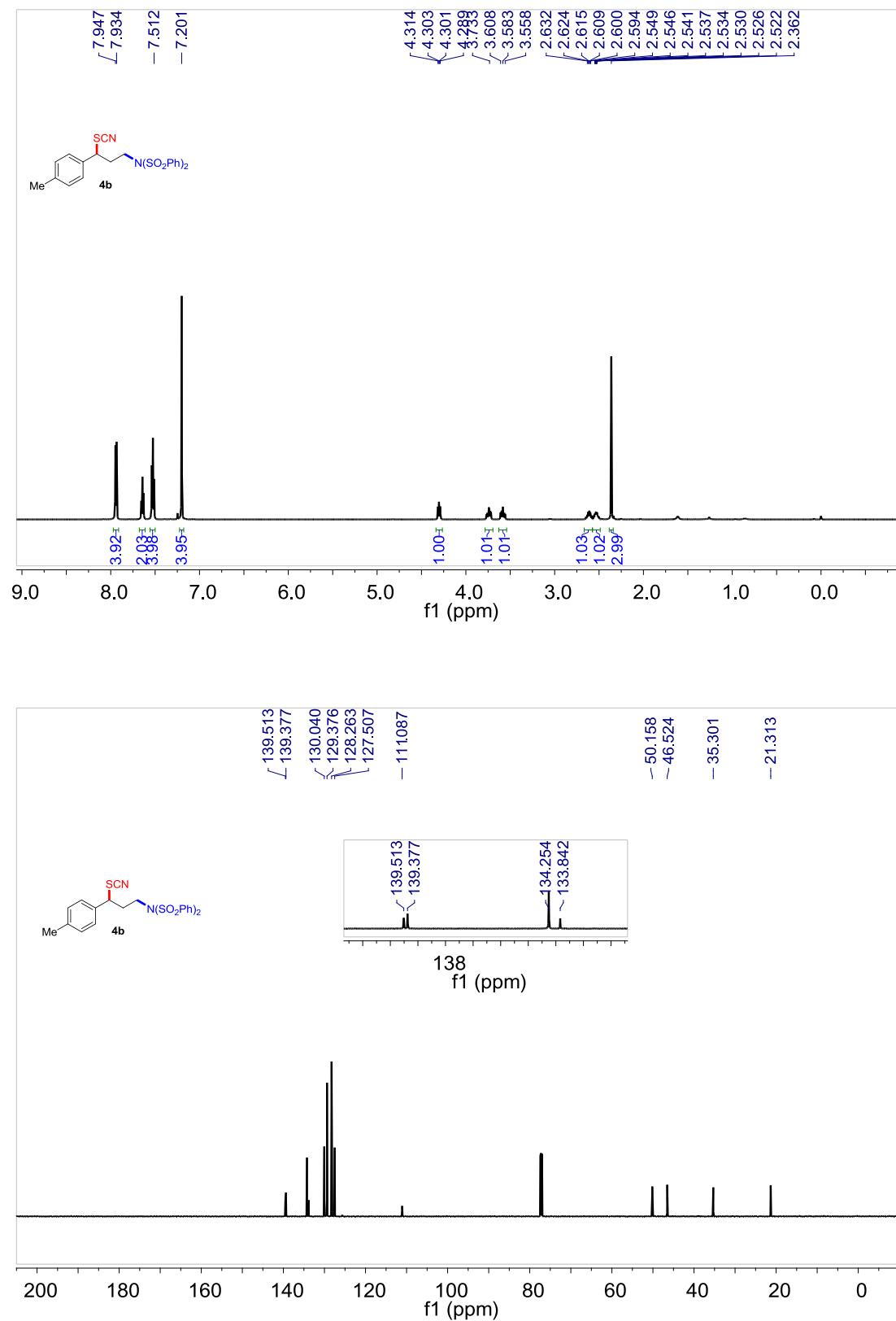
- 1 C. R. Pitts, B. Ling, J. Snyder, A. Bragg and T. Lectka, *J. Am. Chem. Soc.*, 2016, **138**, 6598.
- 2 Z. Yang, J. C. Lorenz and Y. Shi, *Tetrahedron Lett.*, 1998, **39**, 8621.

6. Copies of NMR Spectra

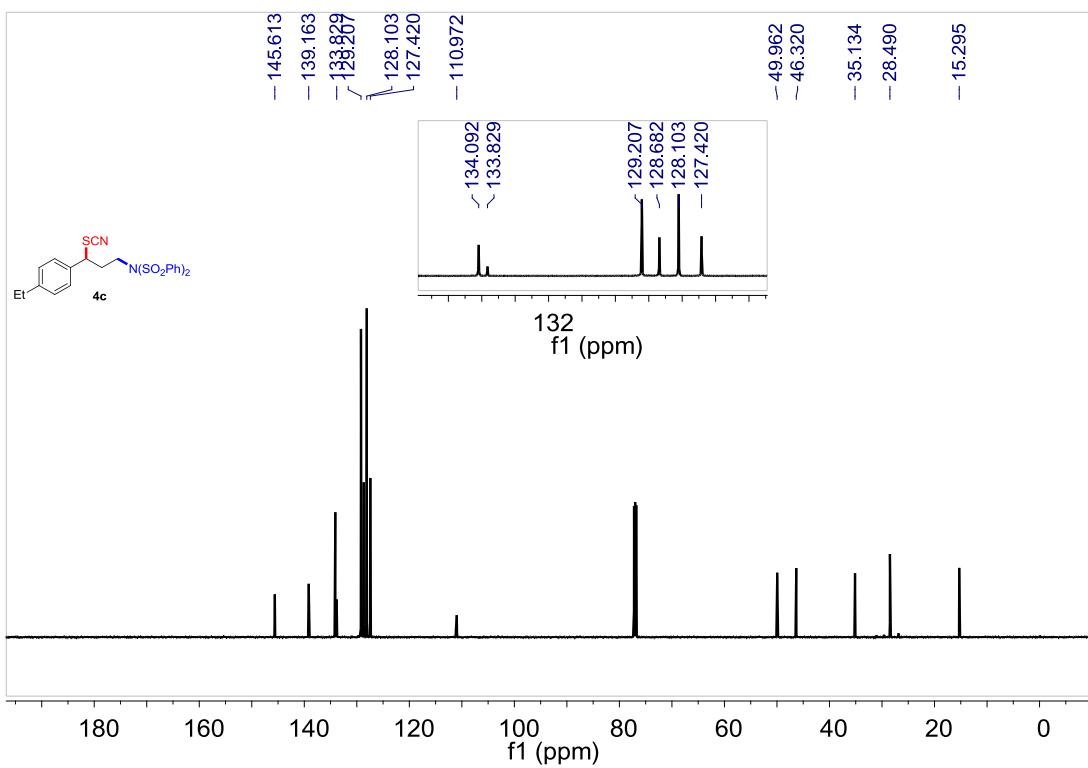
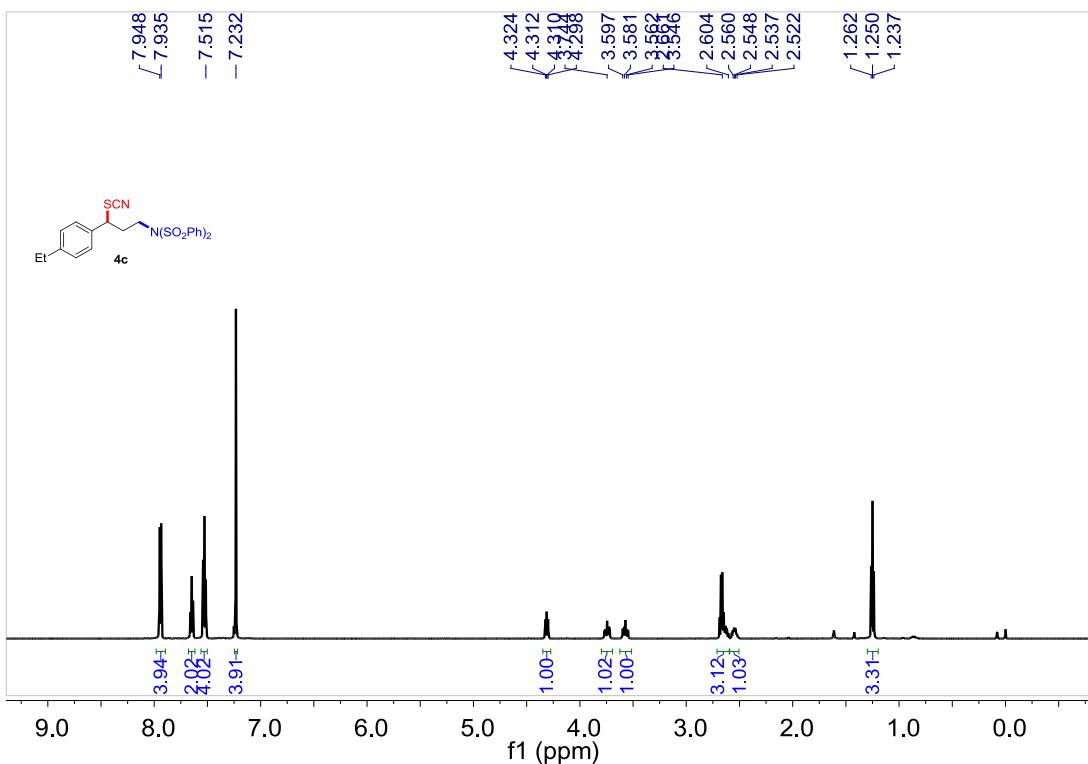
Compound 4a



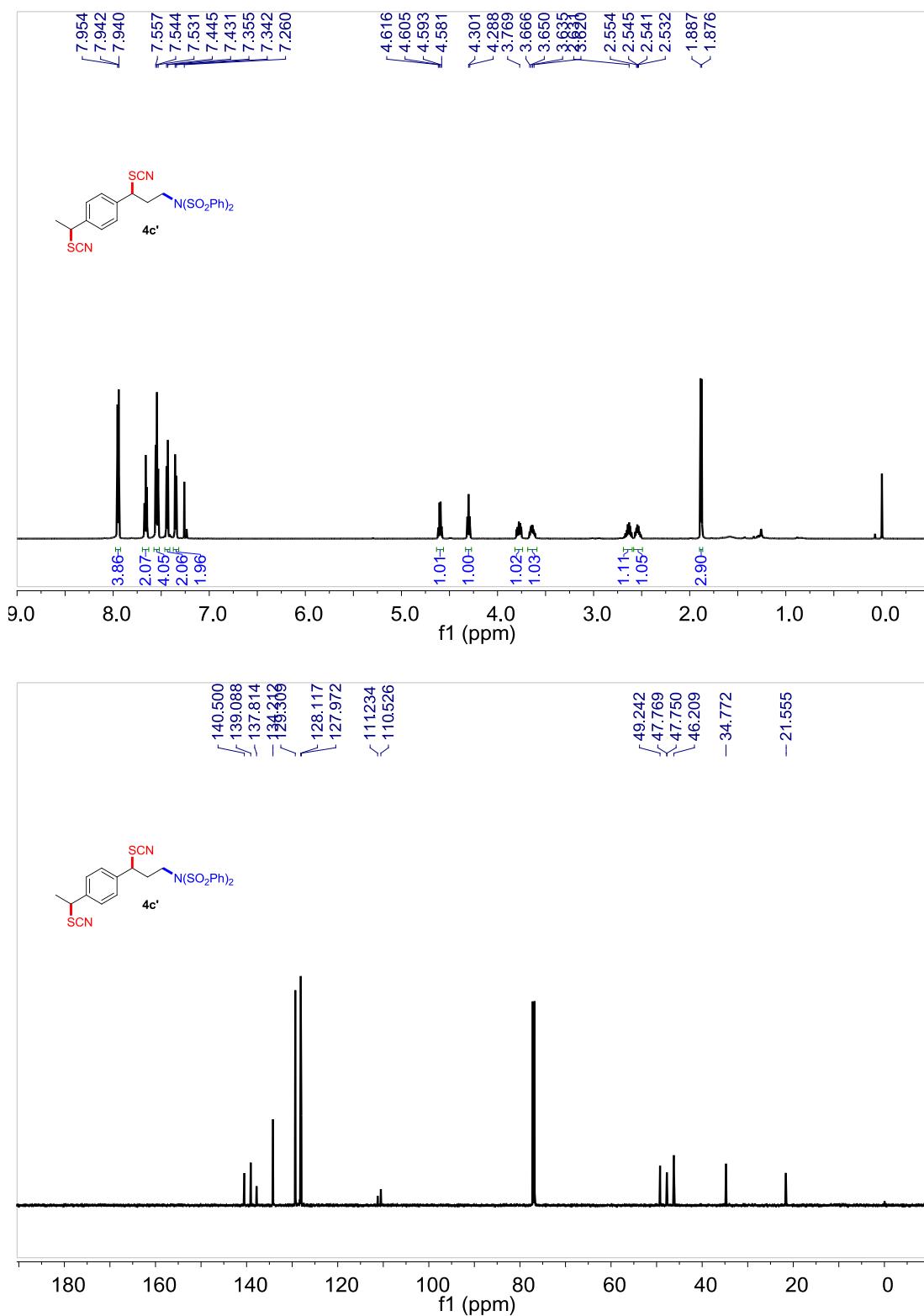
Compound 4b



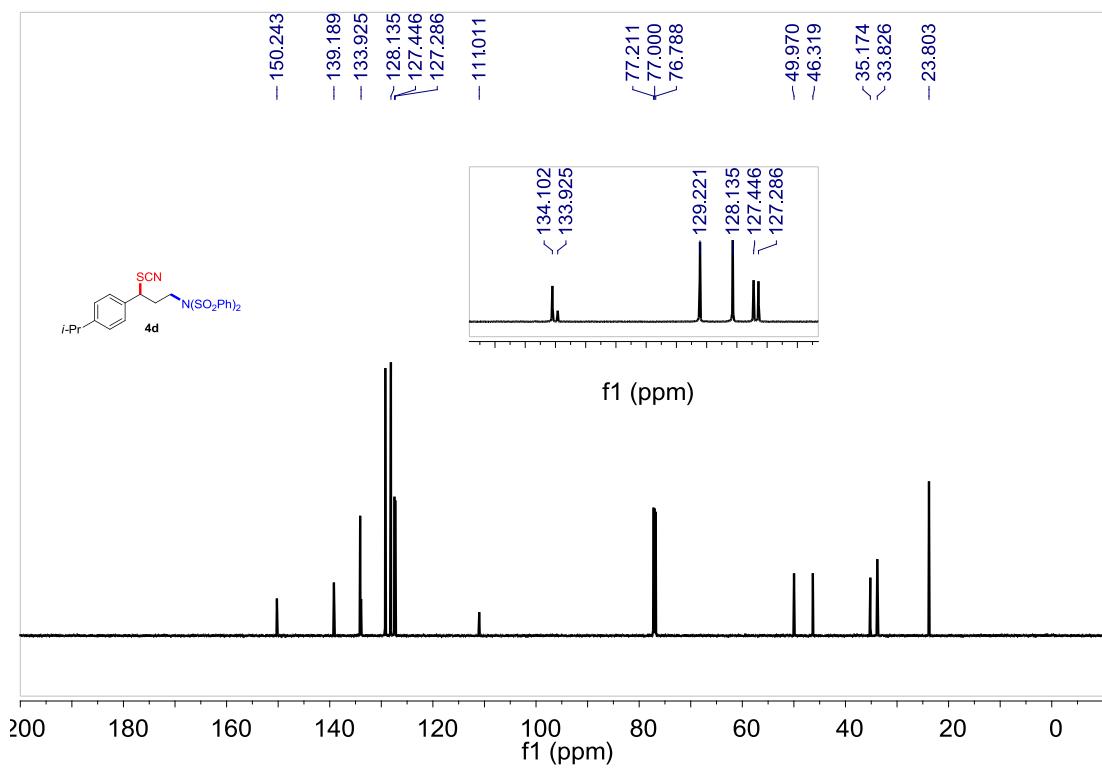
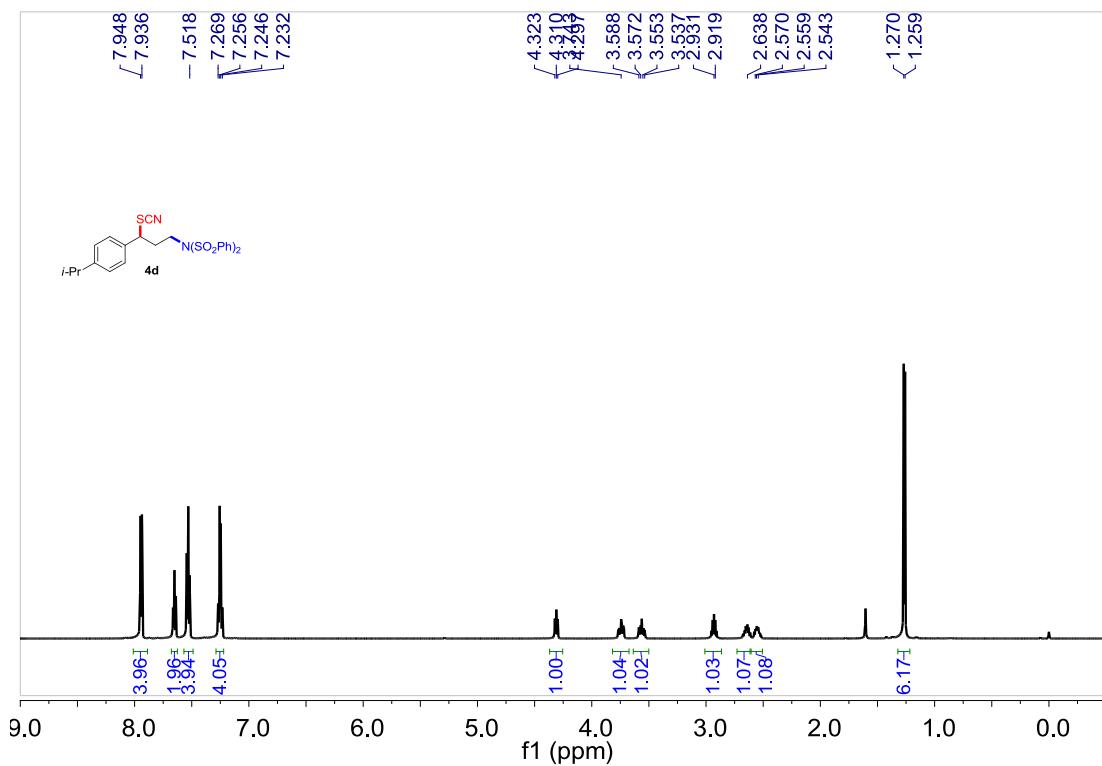
Compound 4c



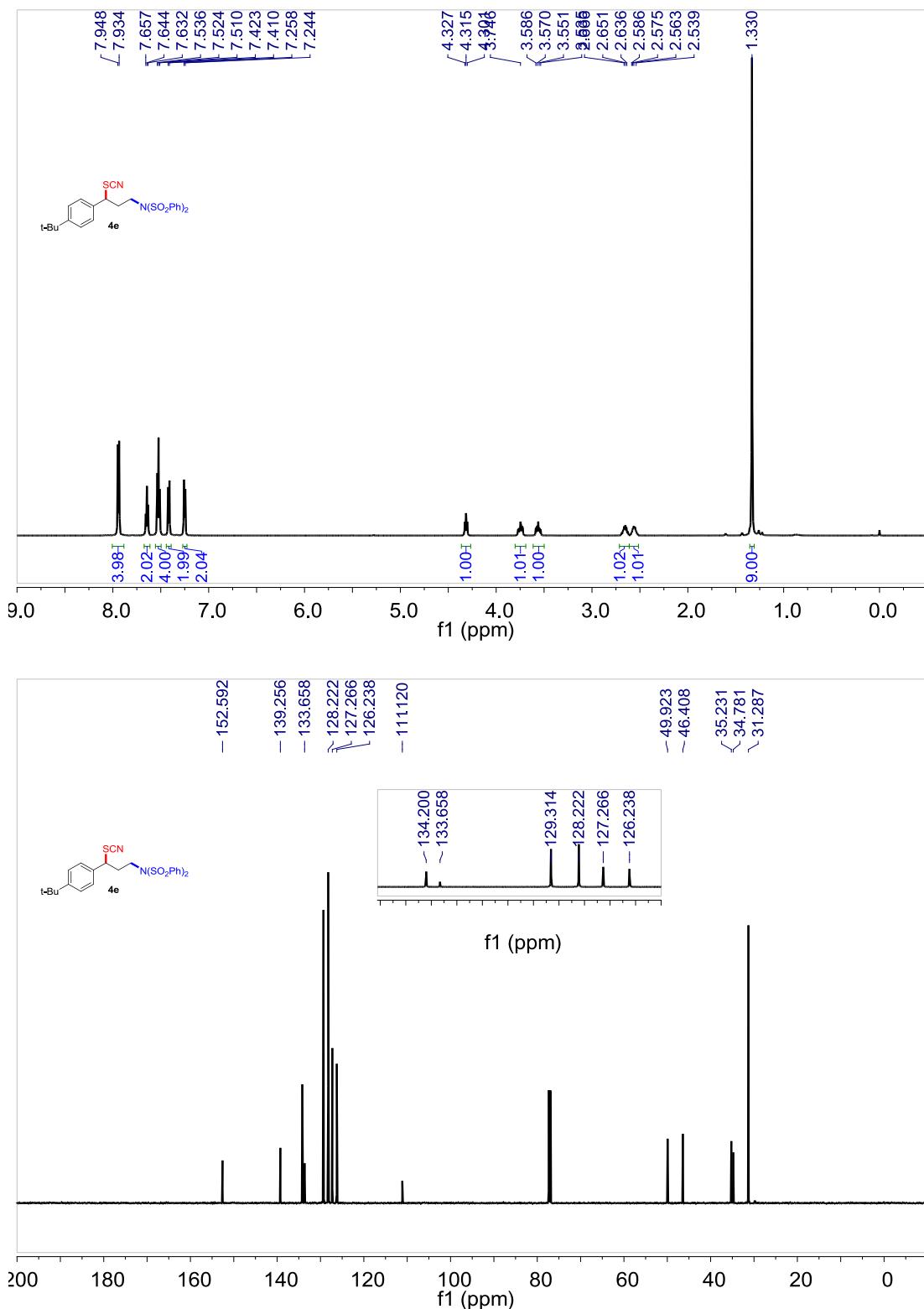
Compound 4c'



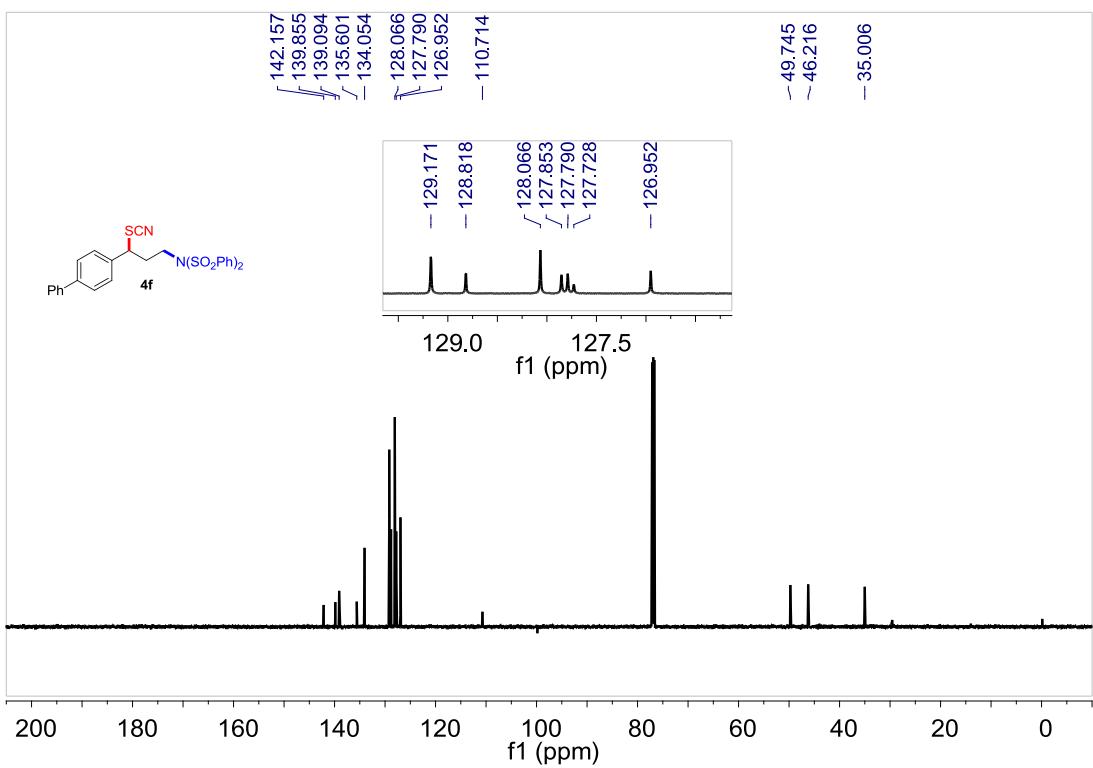
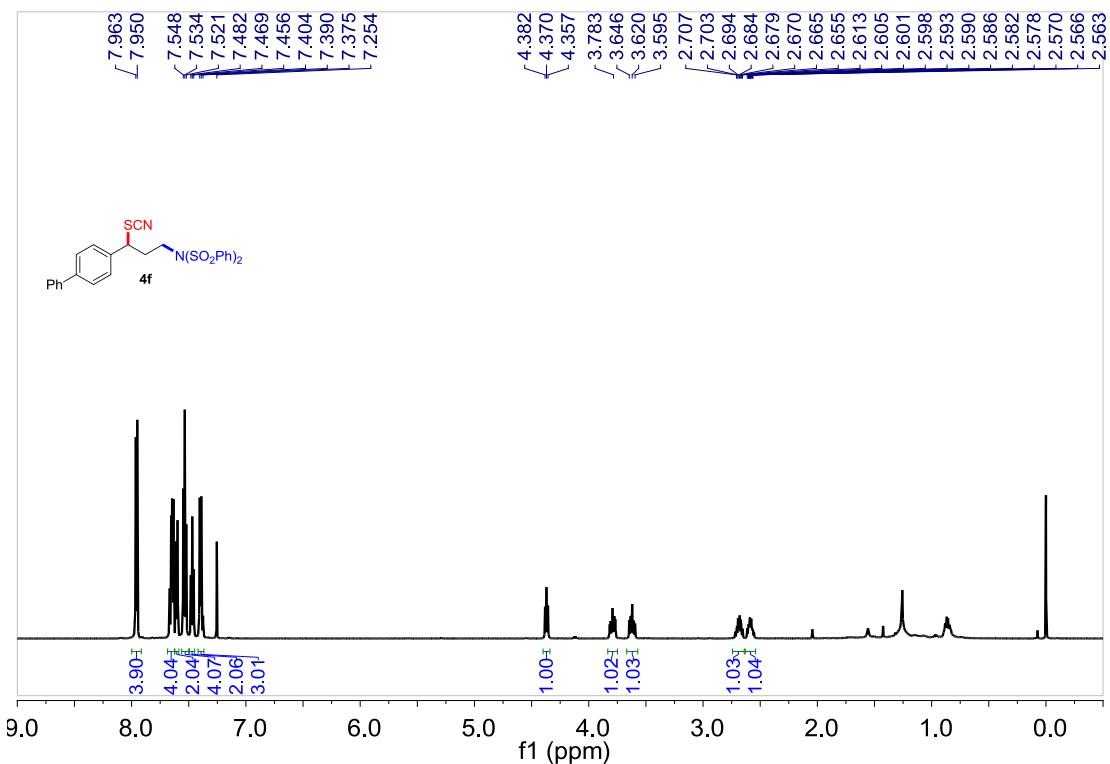
Compound 4d



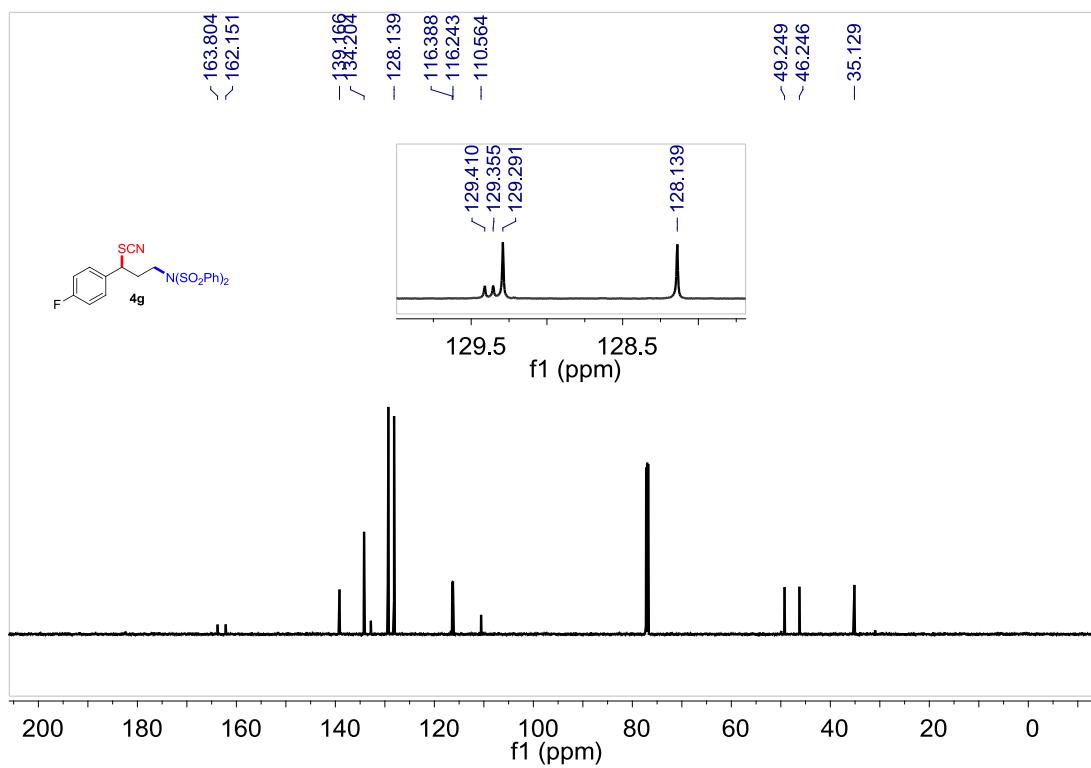
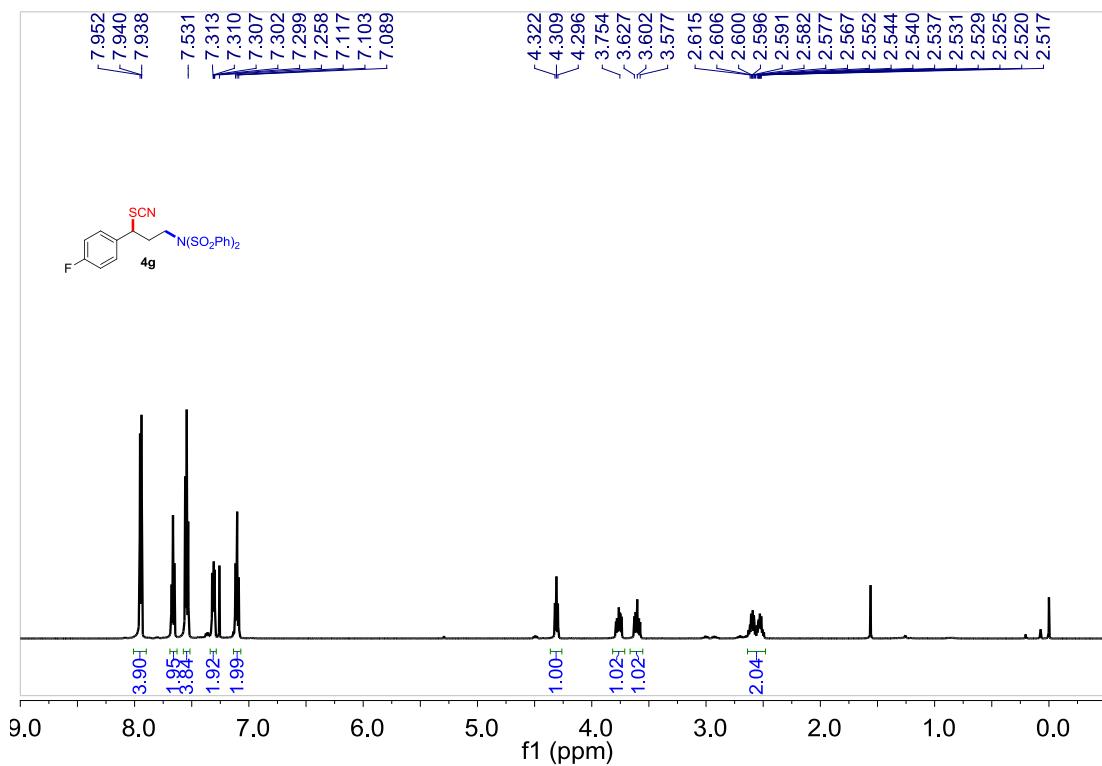
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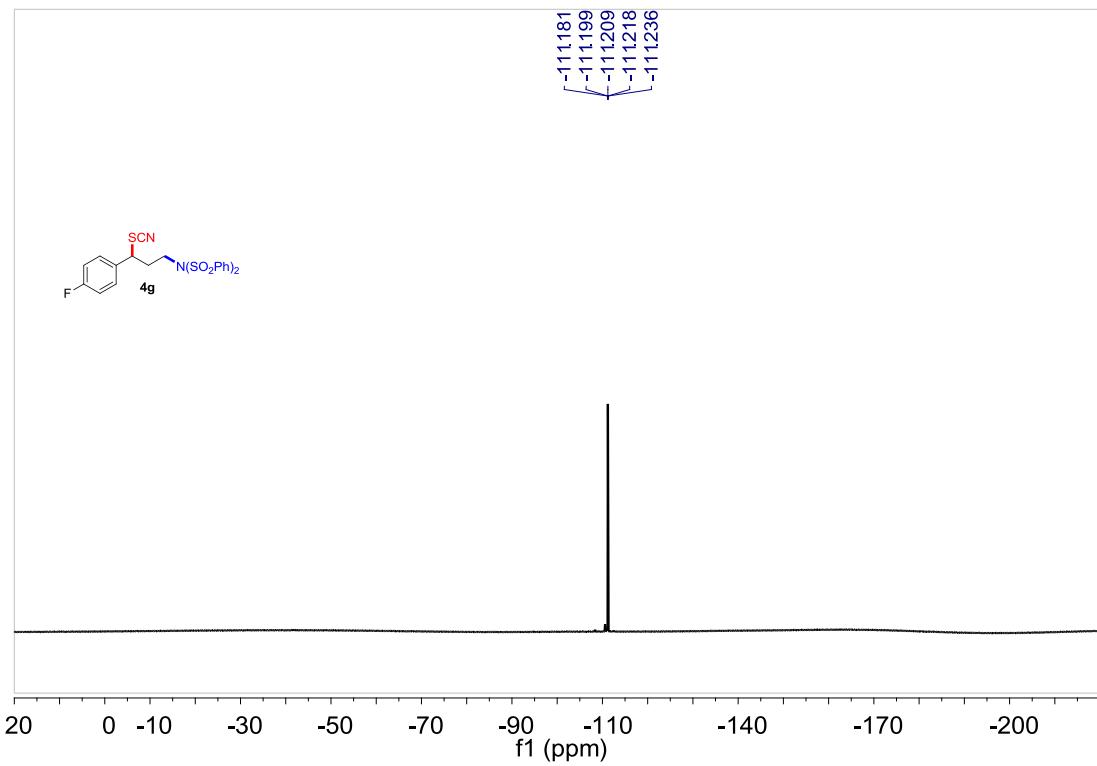


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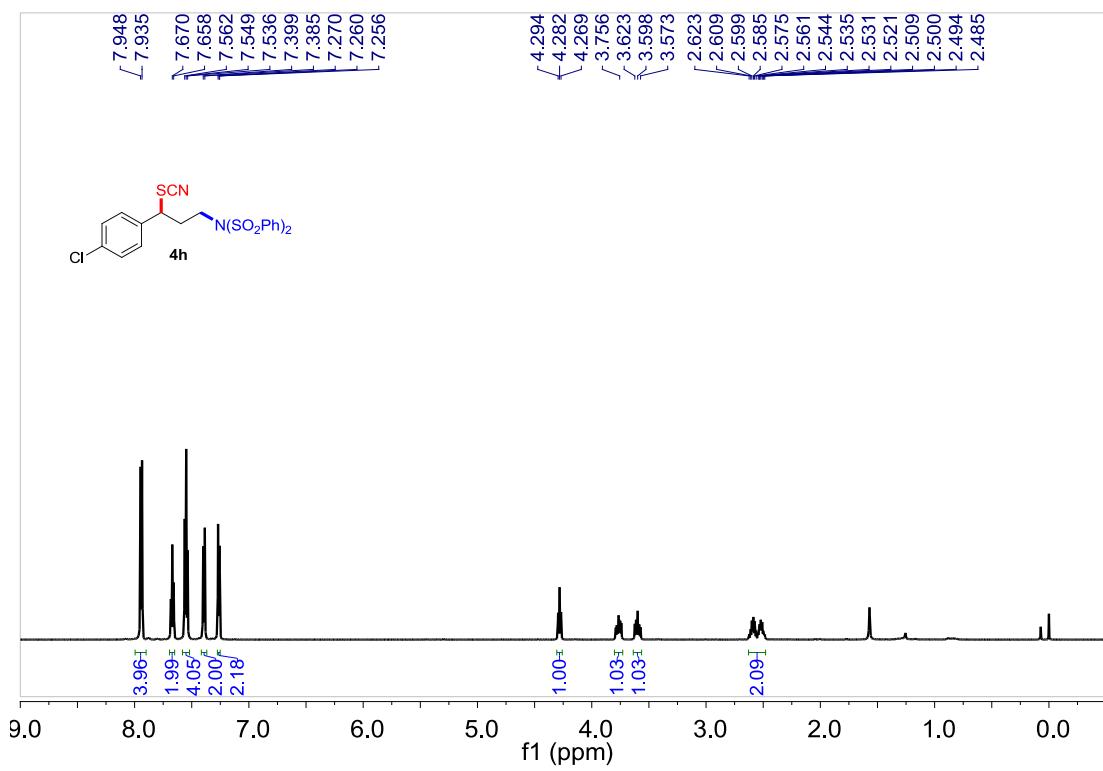


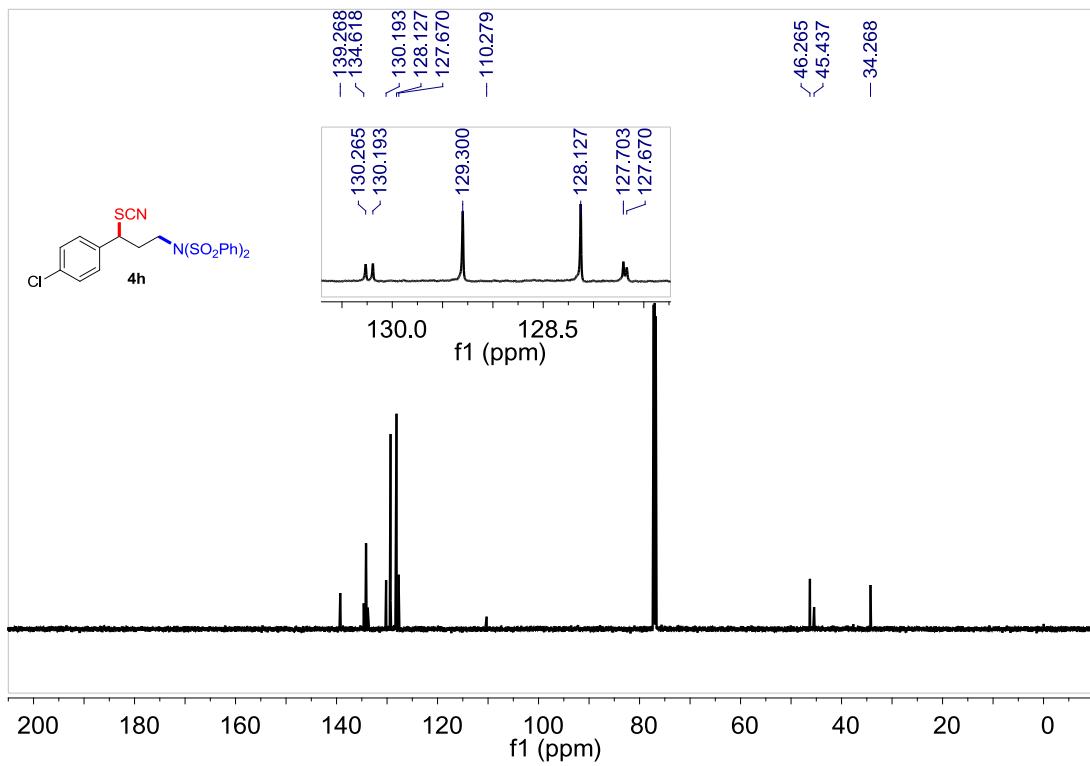
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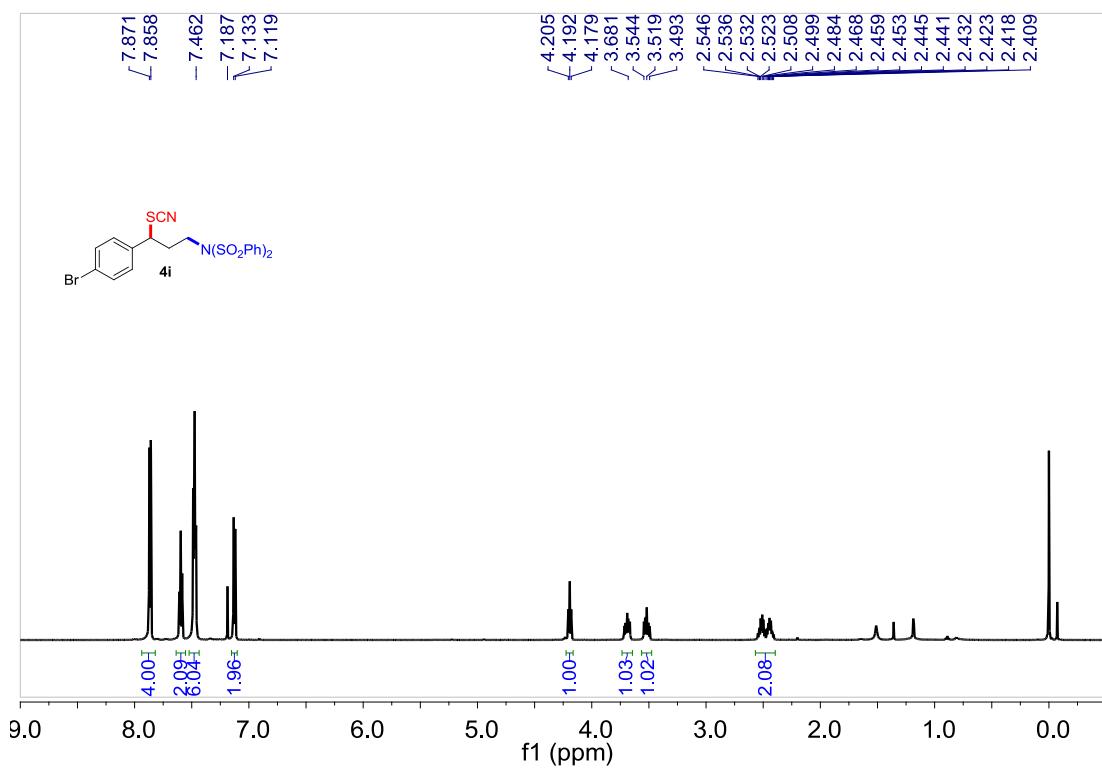


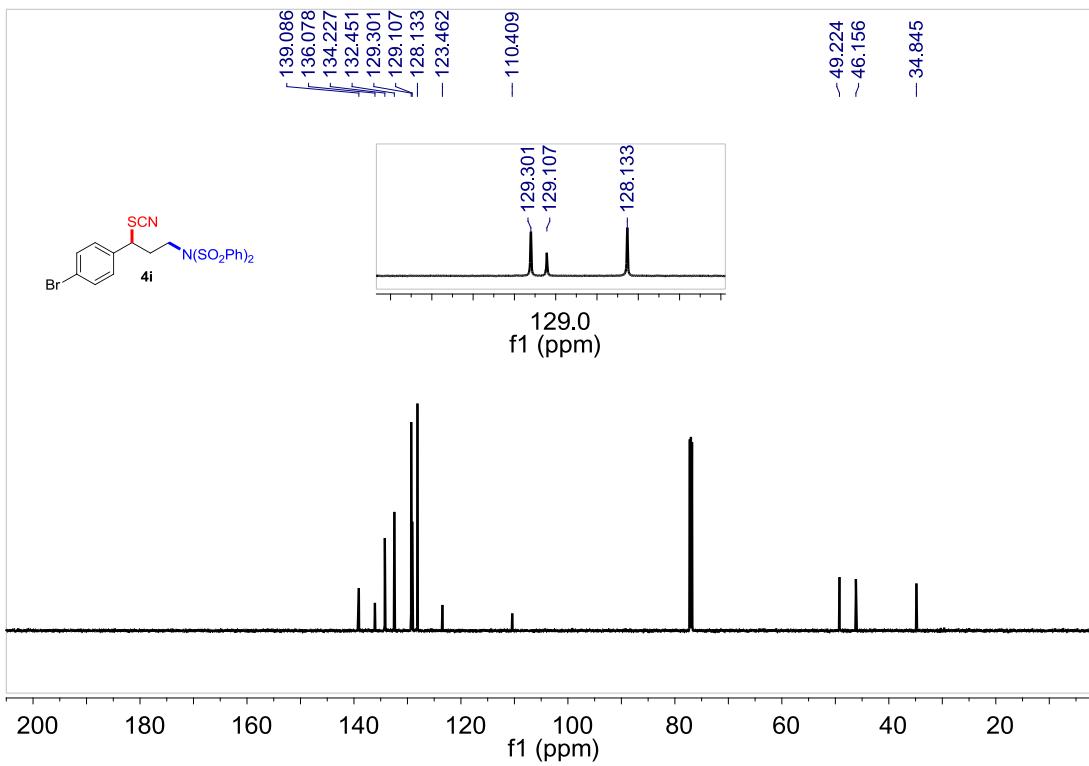
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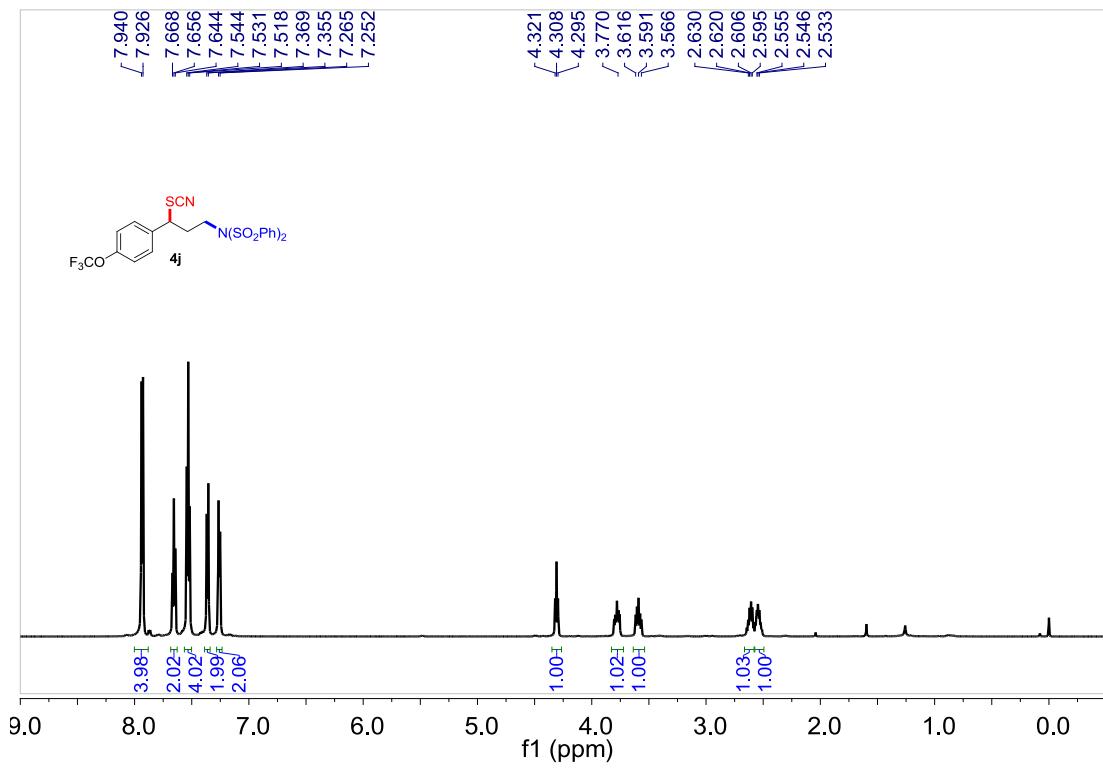


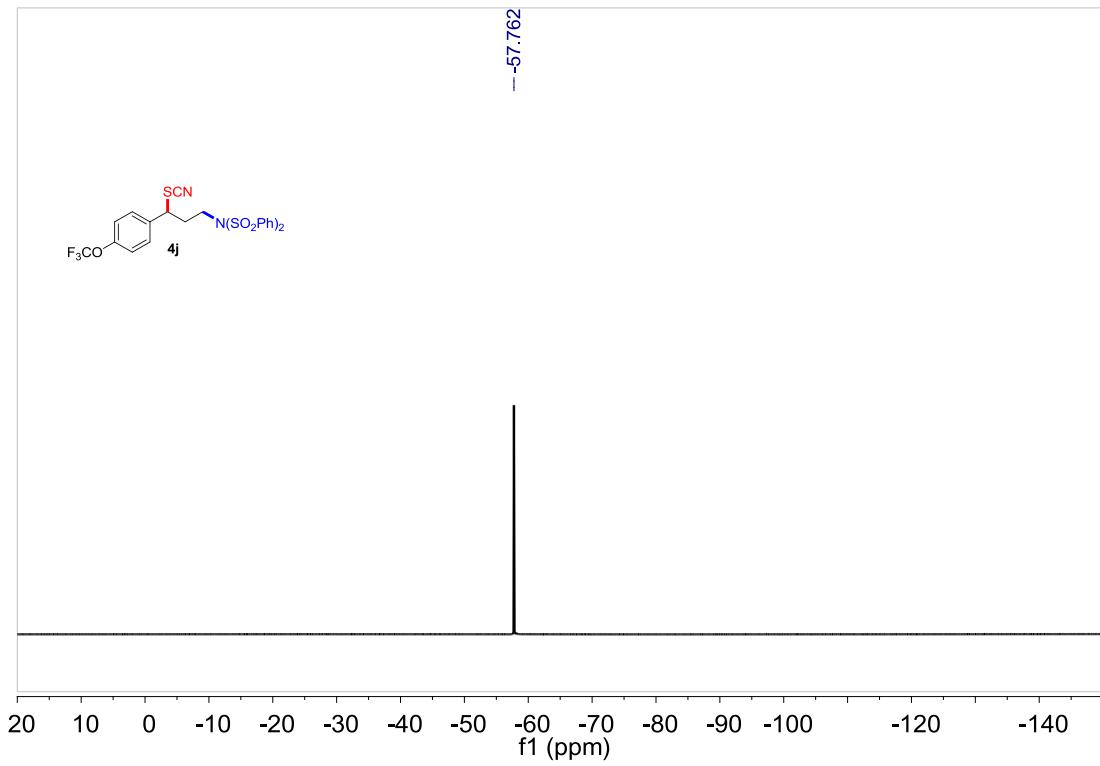
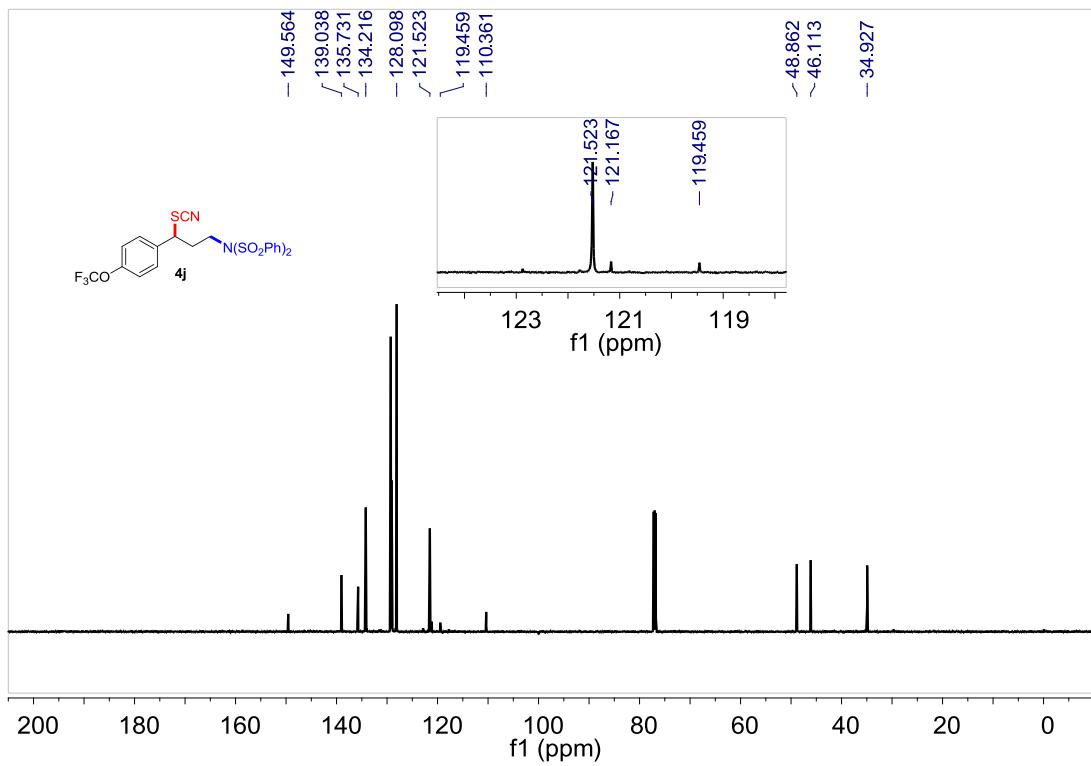
Compound 4i



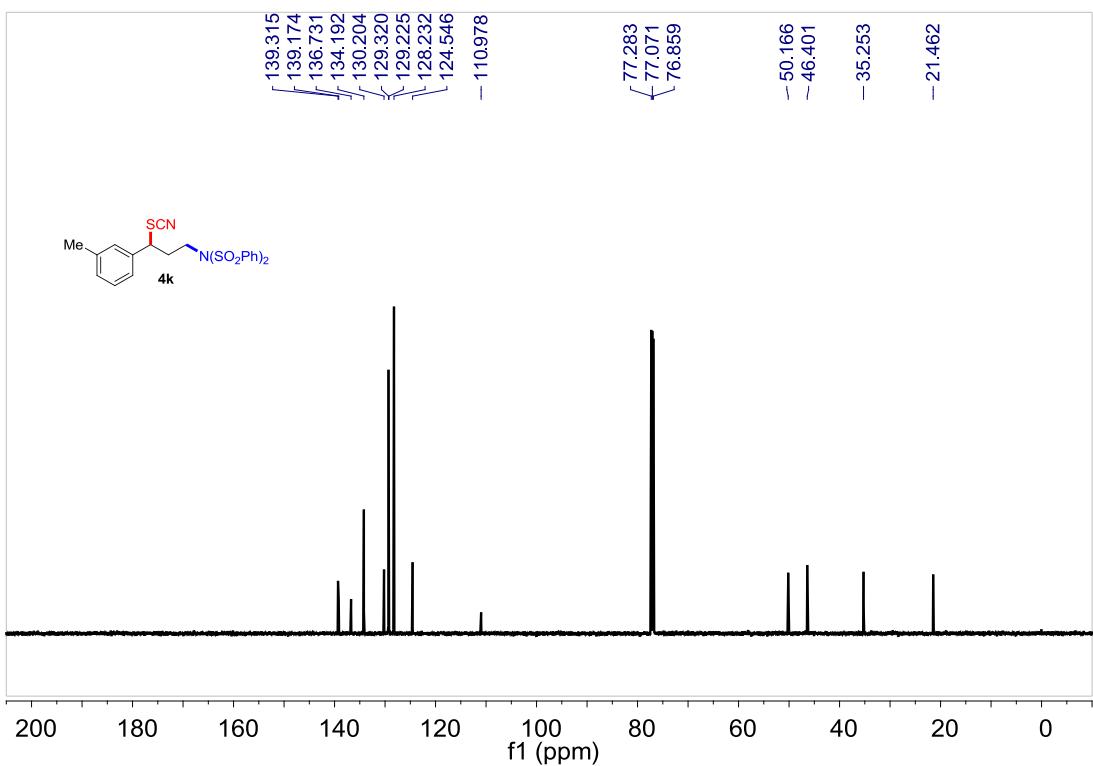
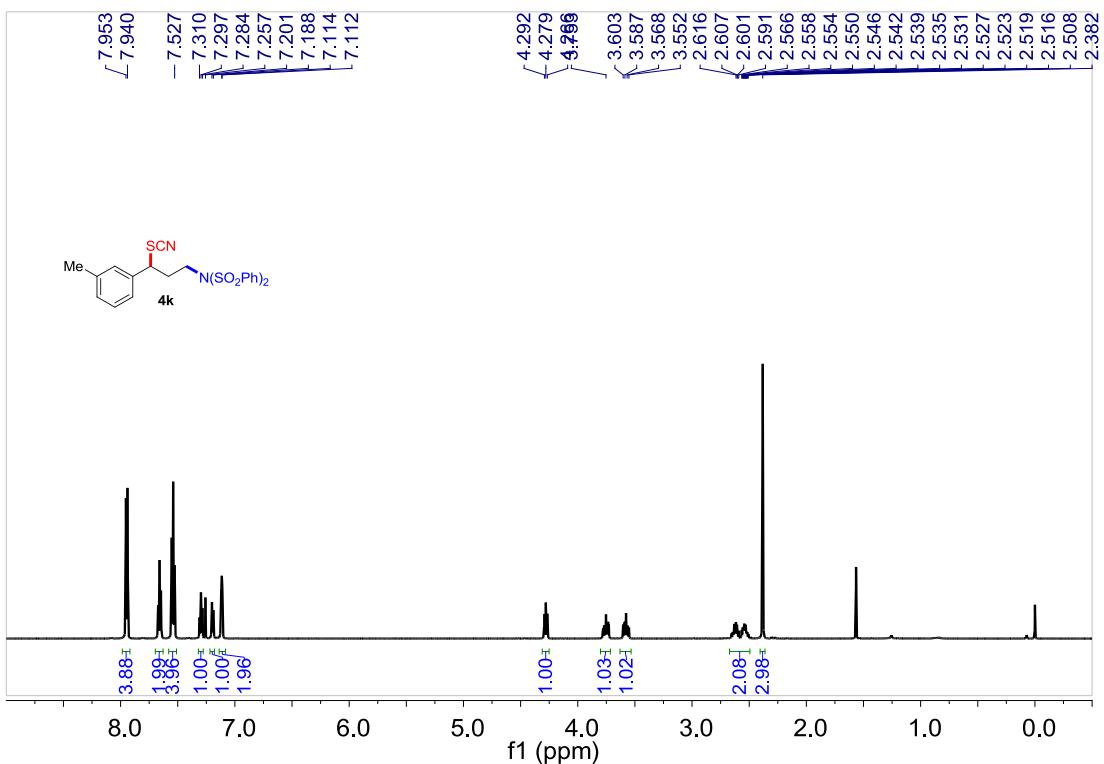


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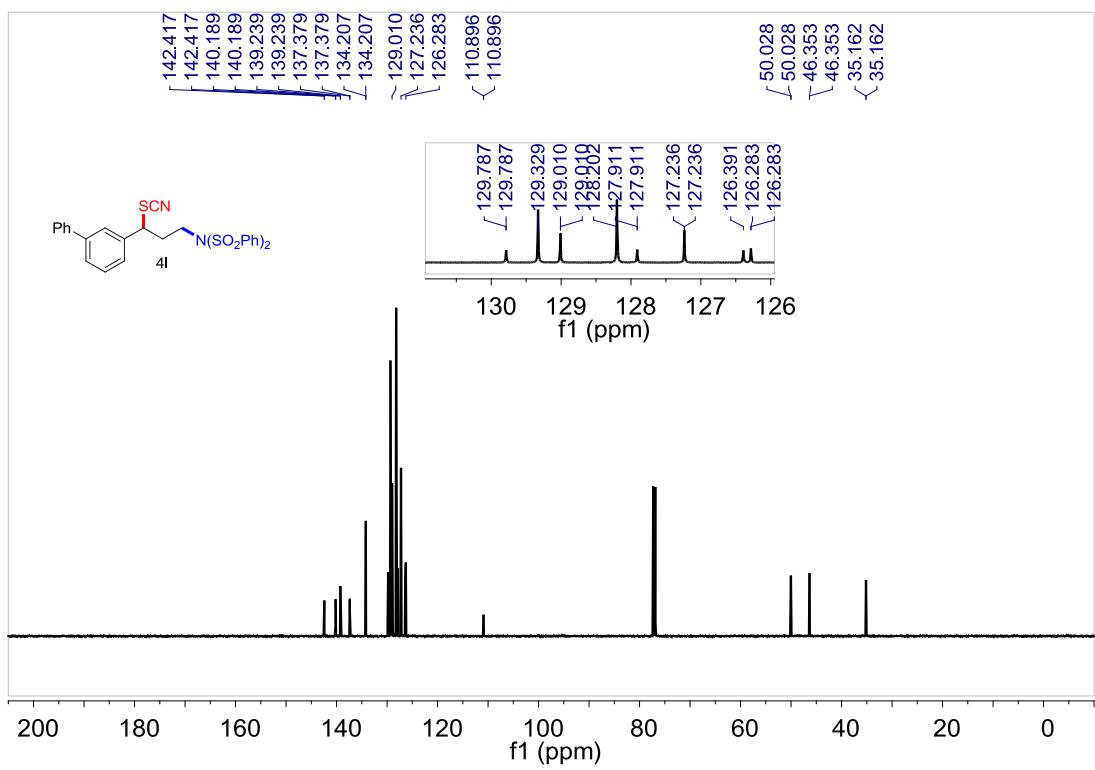
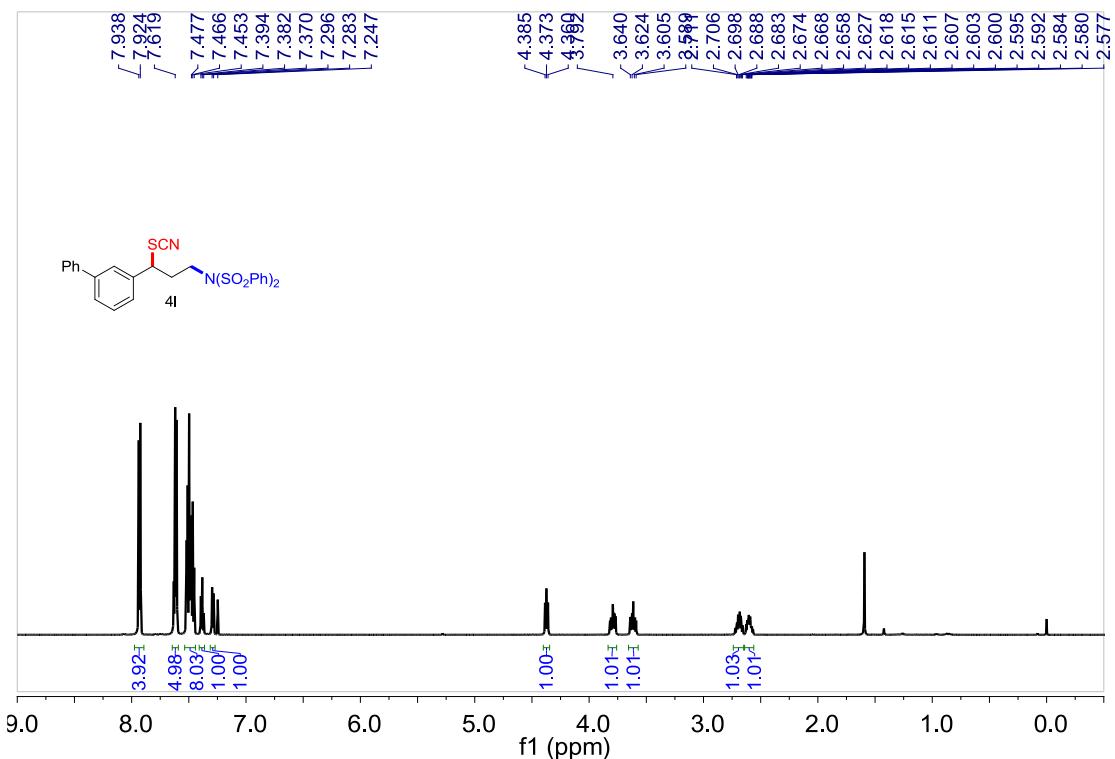




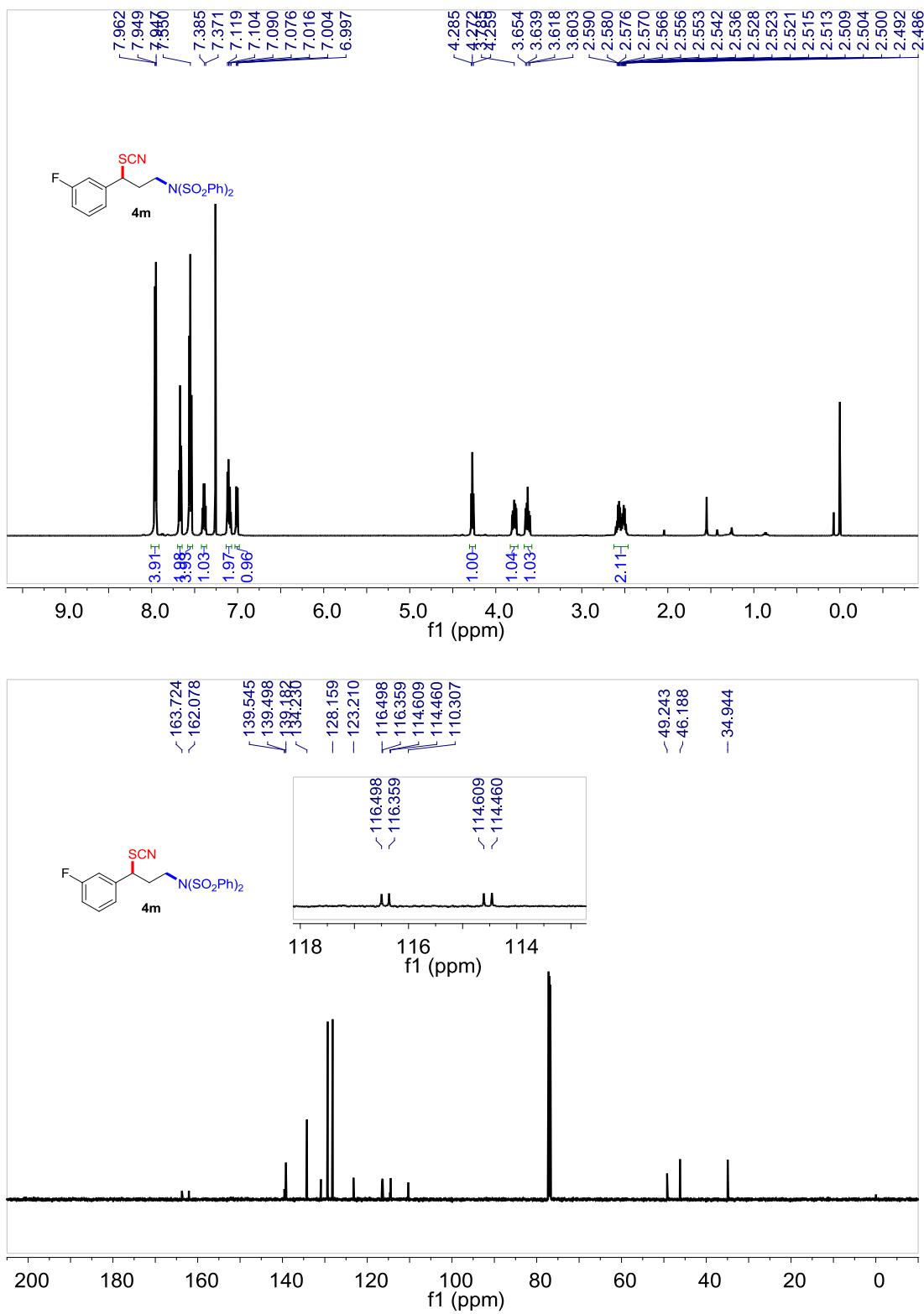
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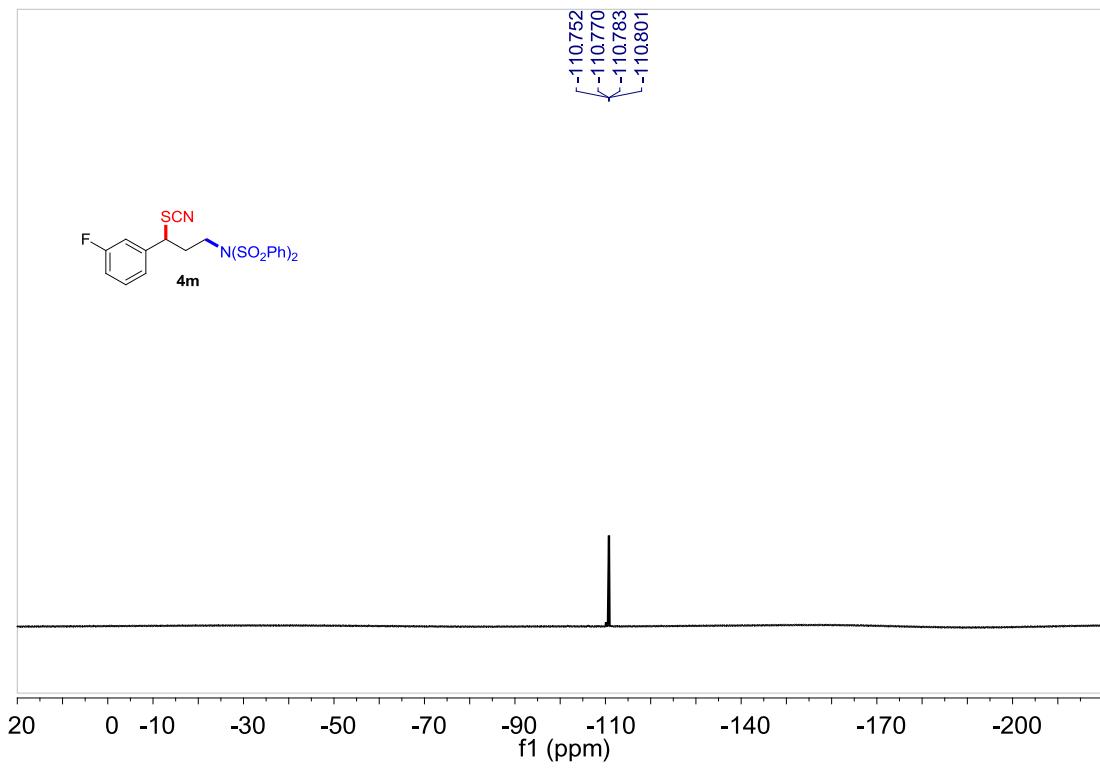


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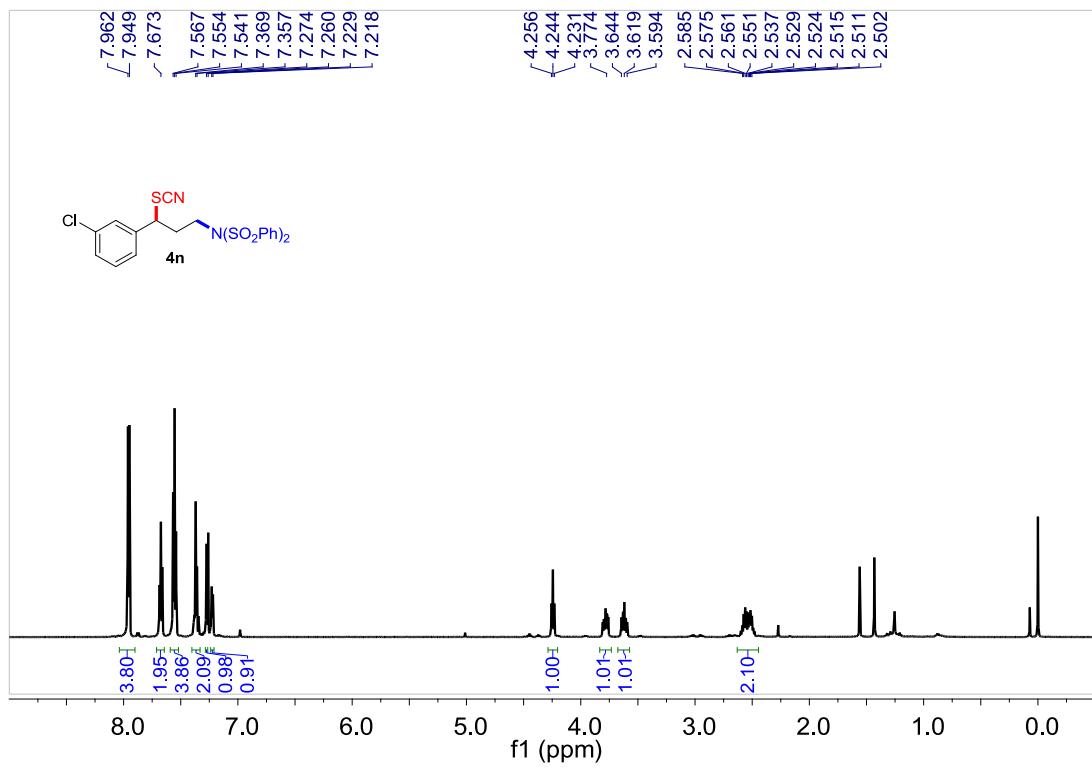


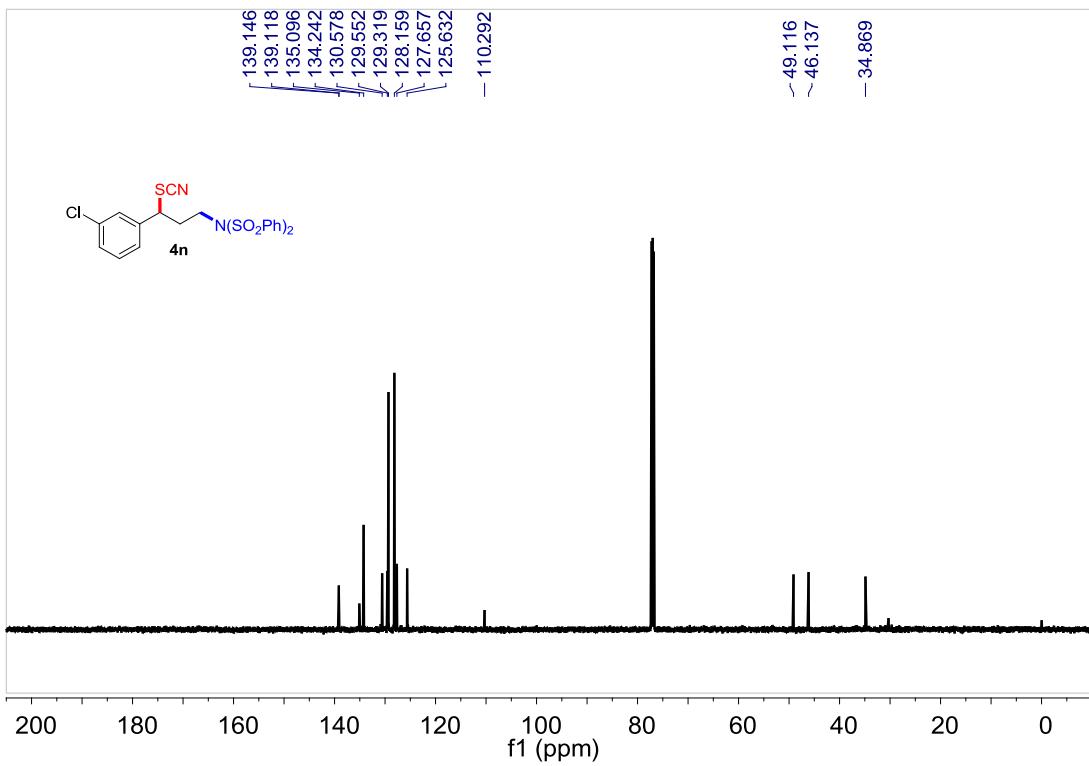
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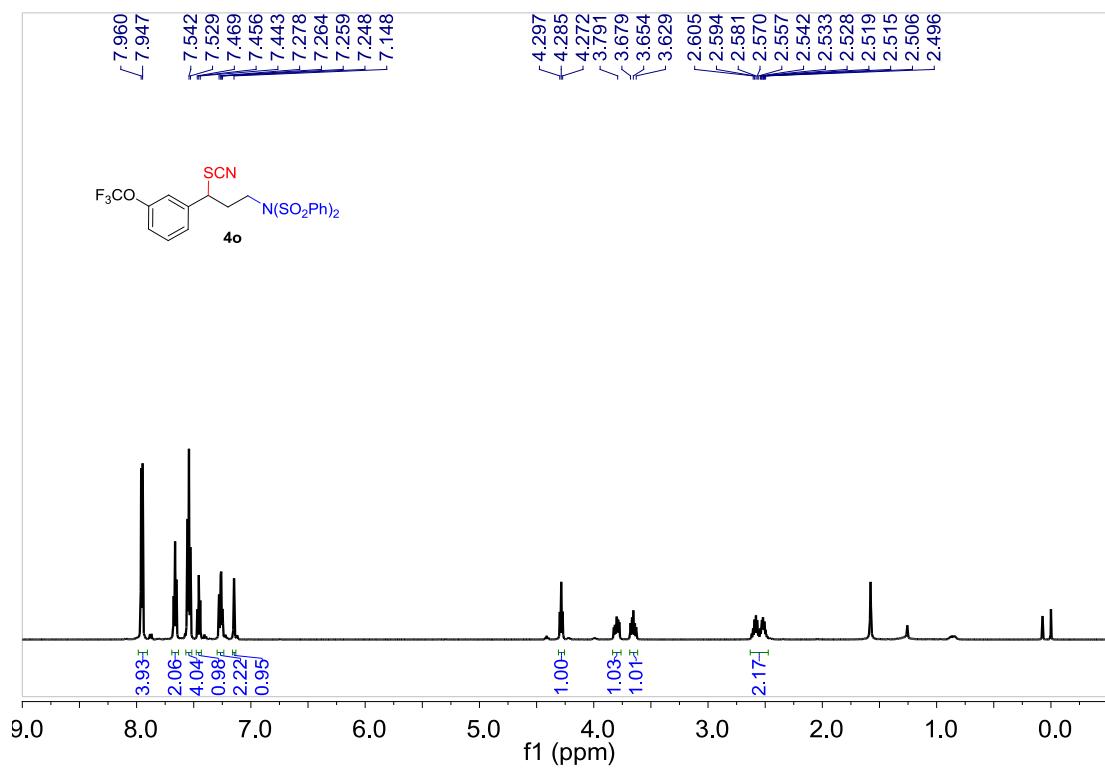


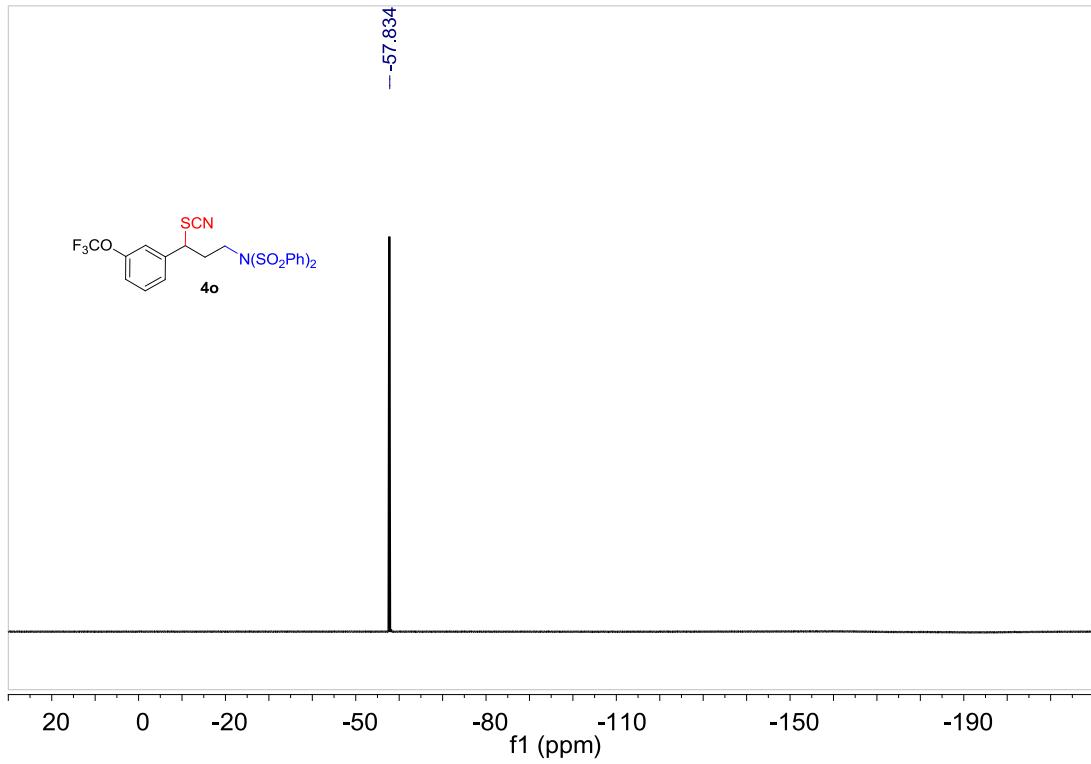
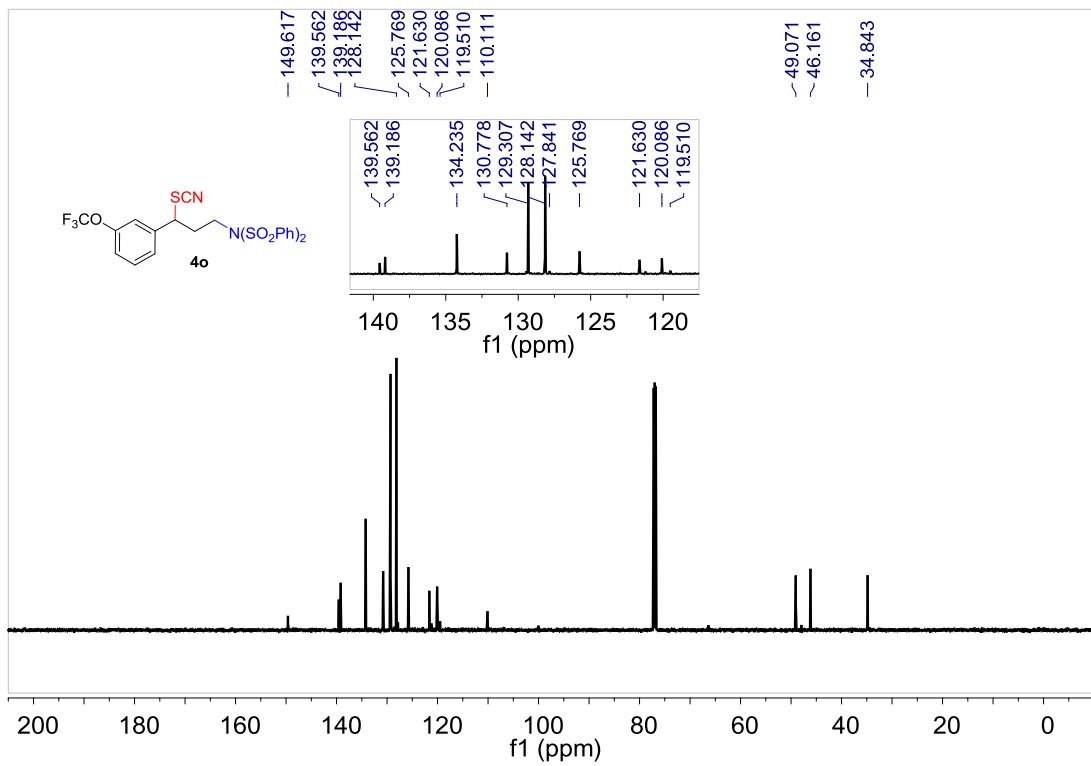
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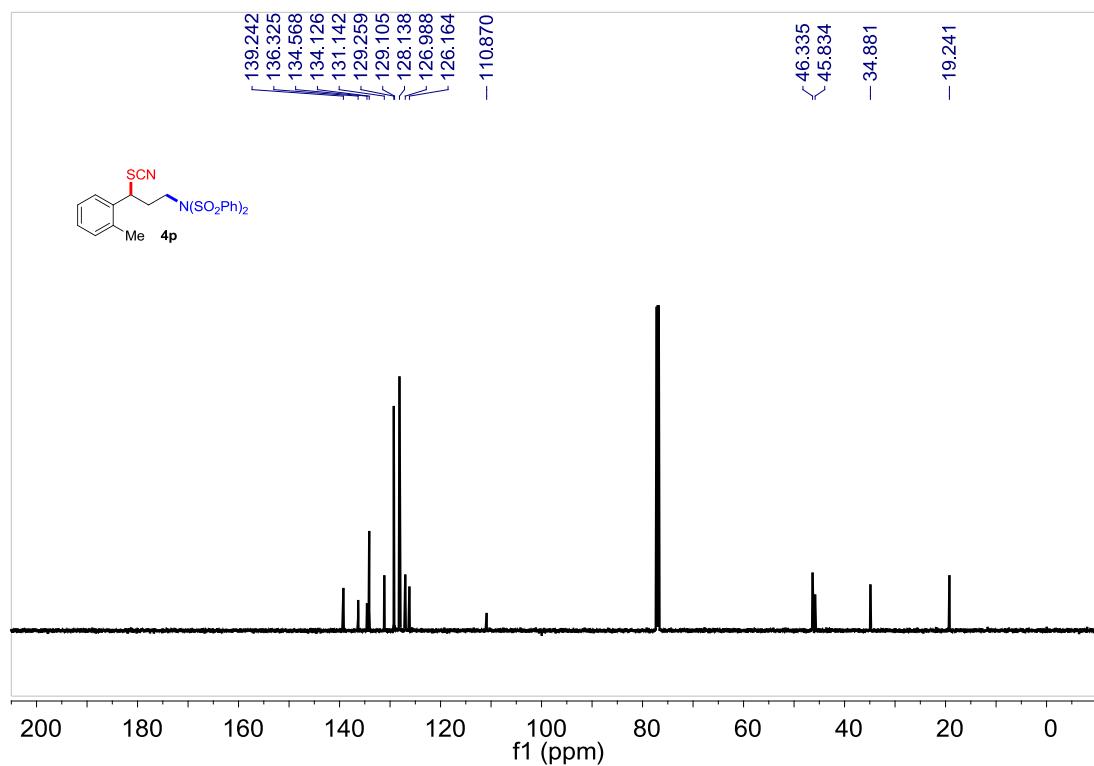
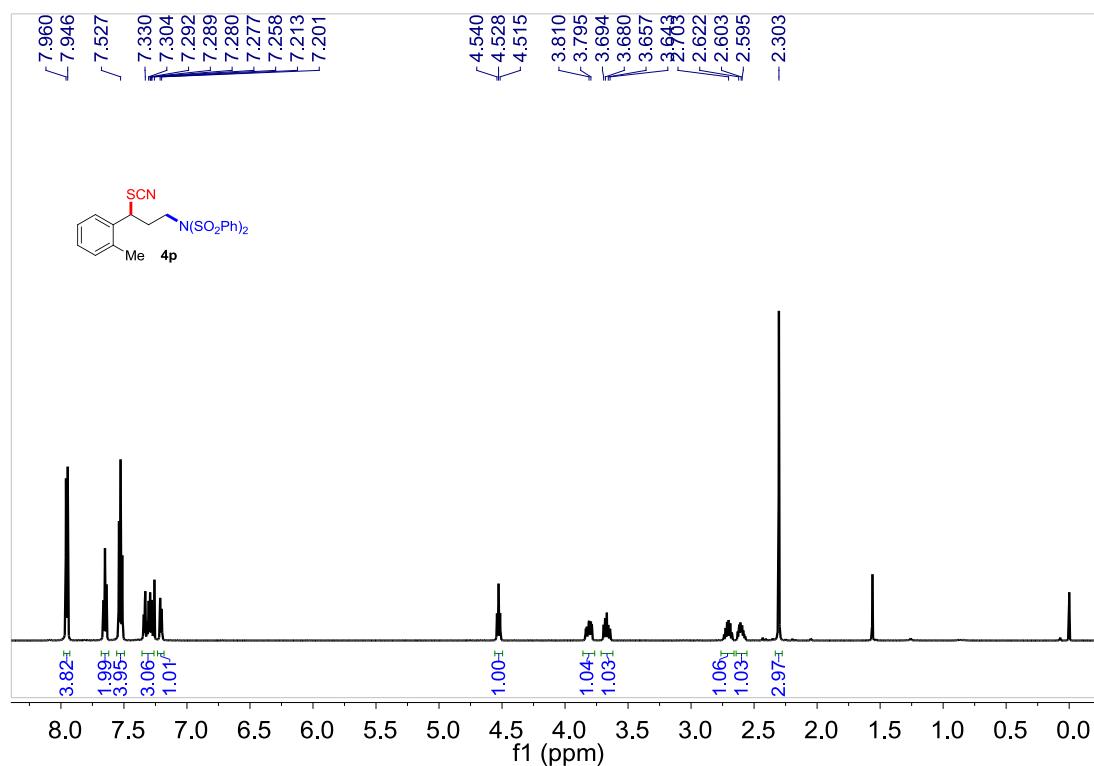


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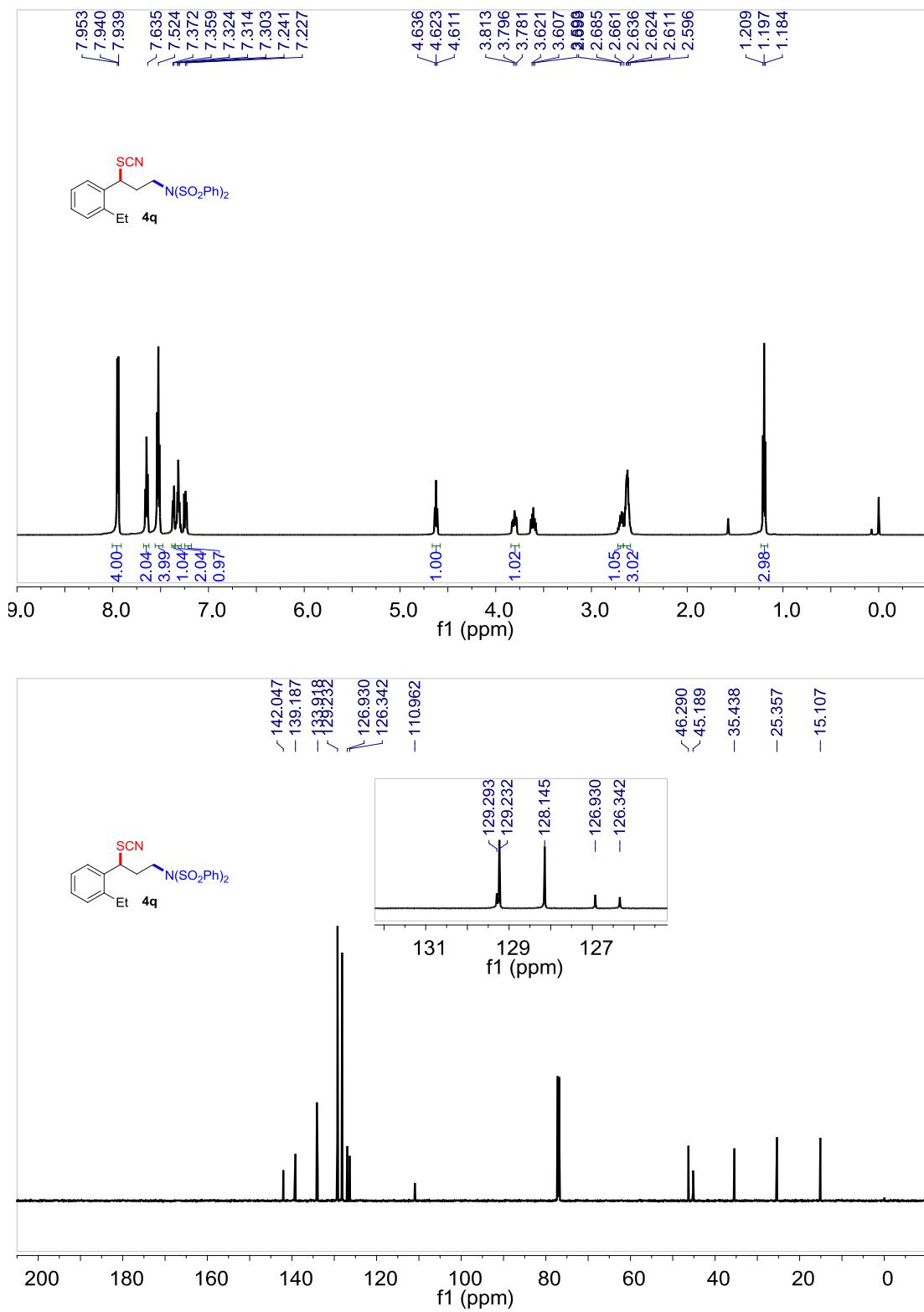




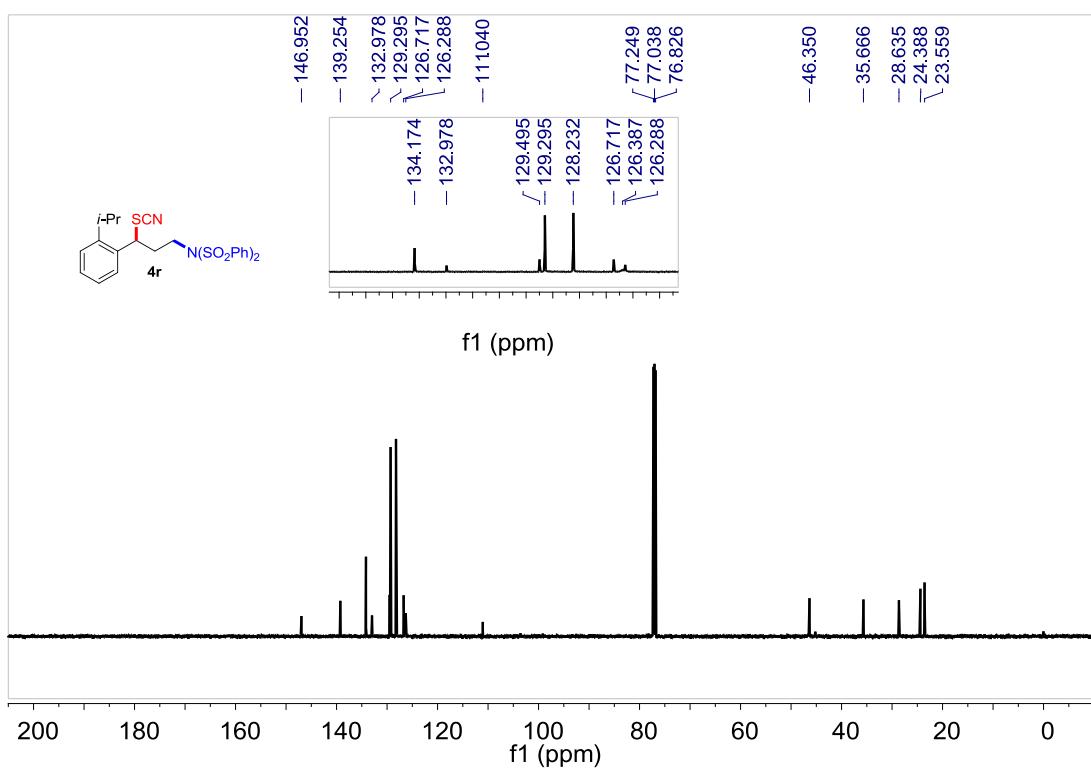
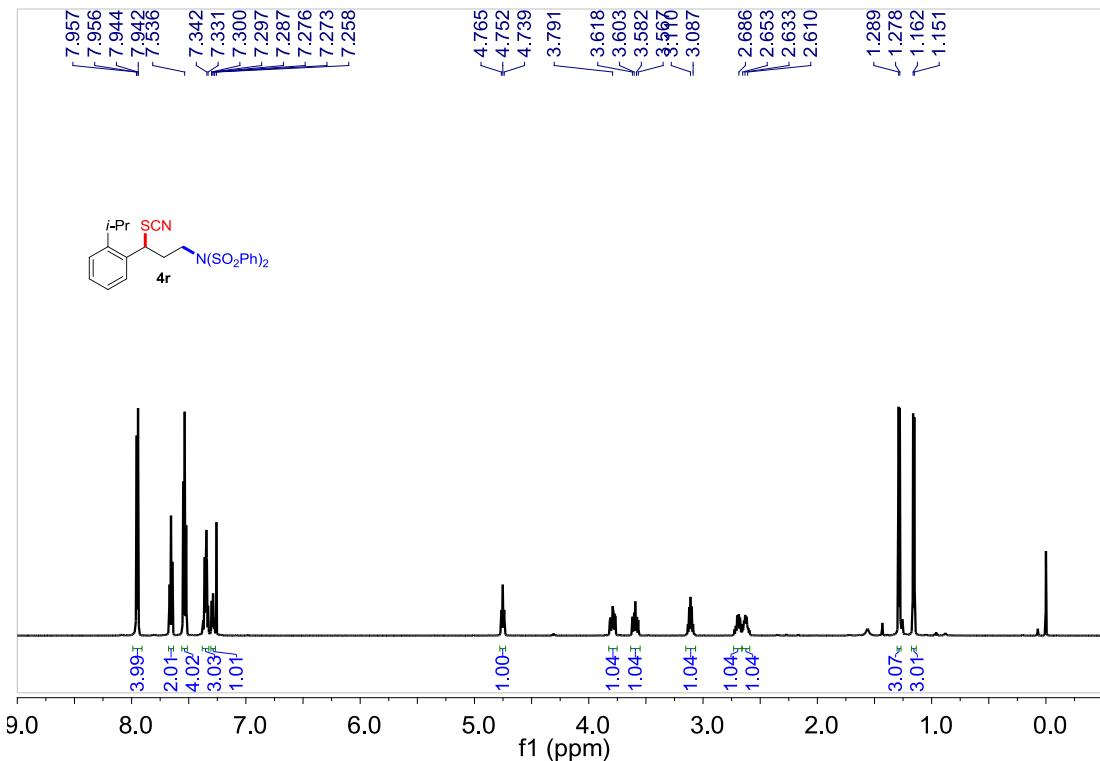
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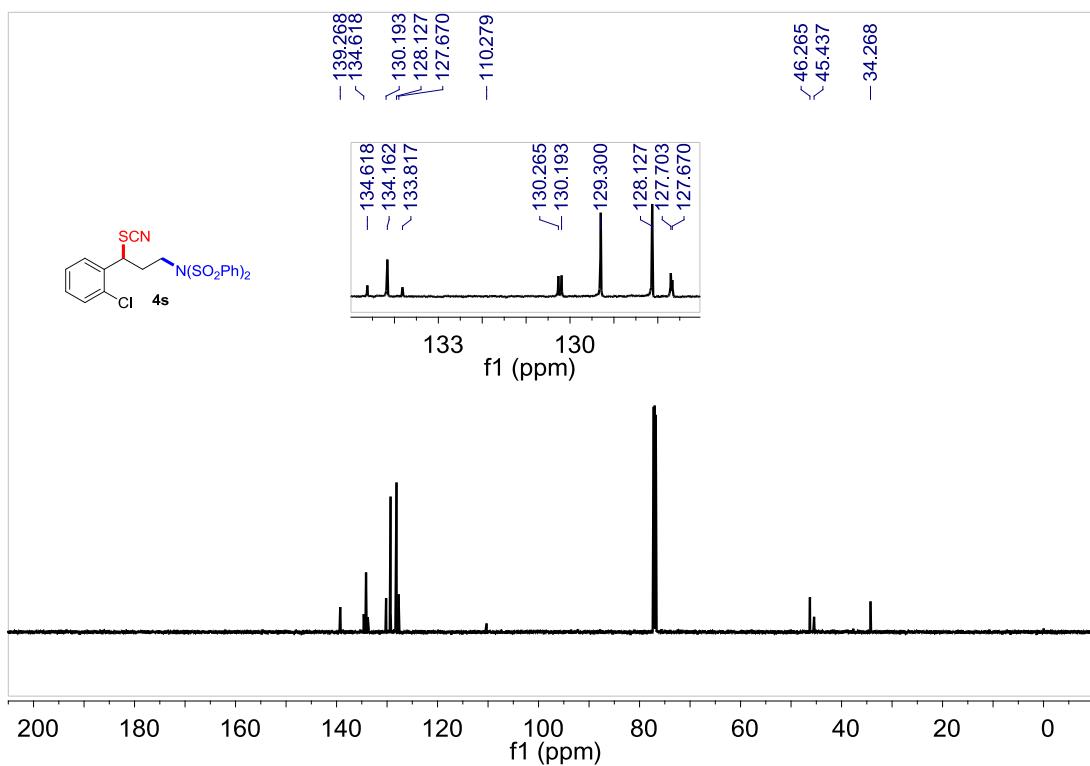
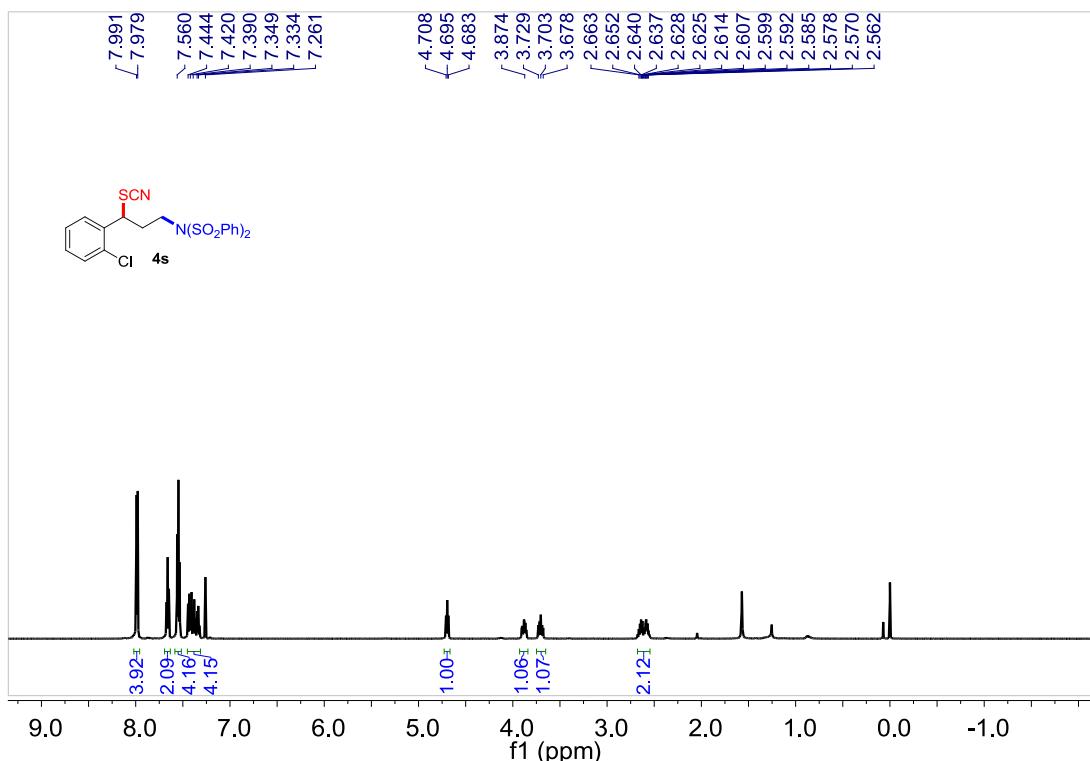
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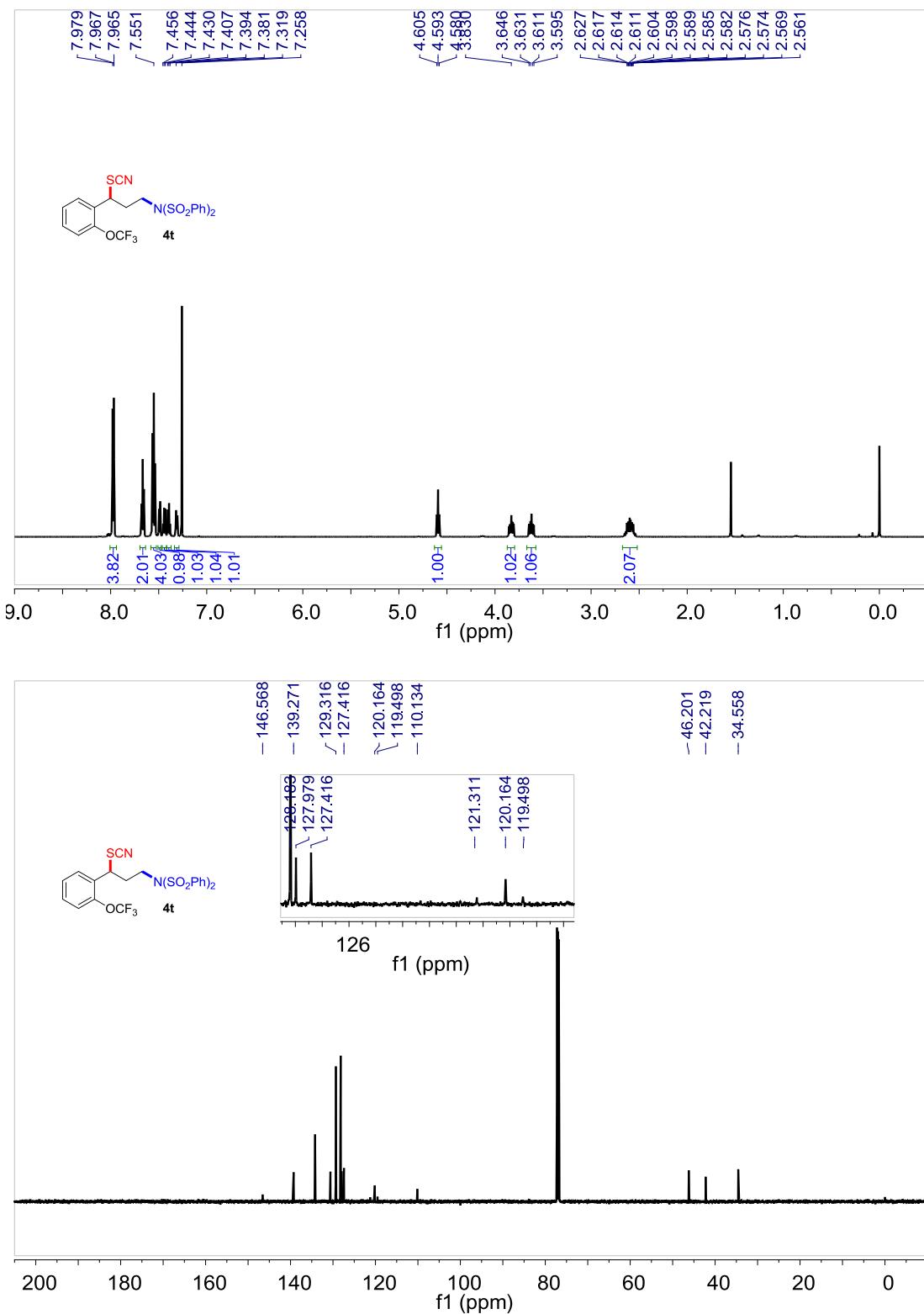
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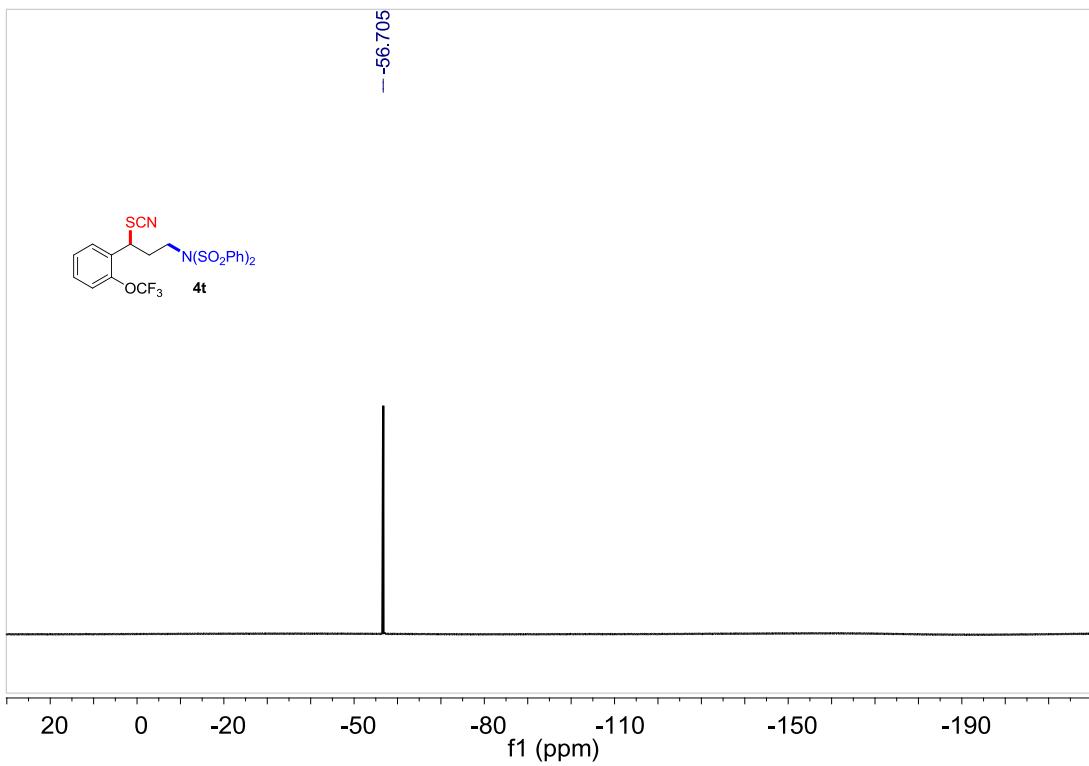


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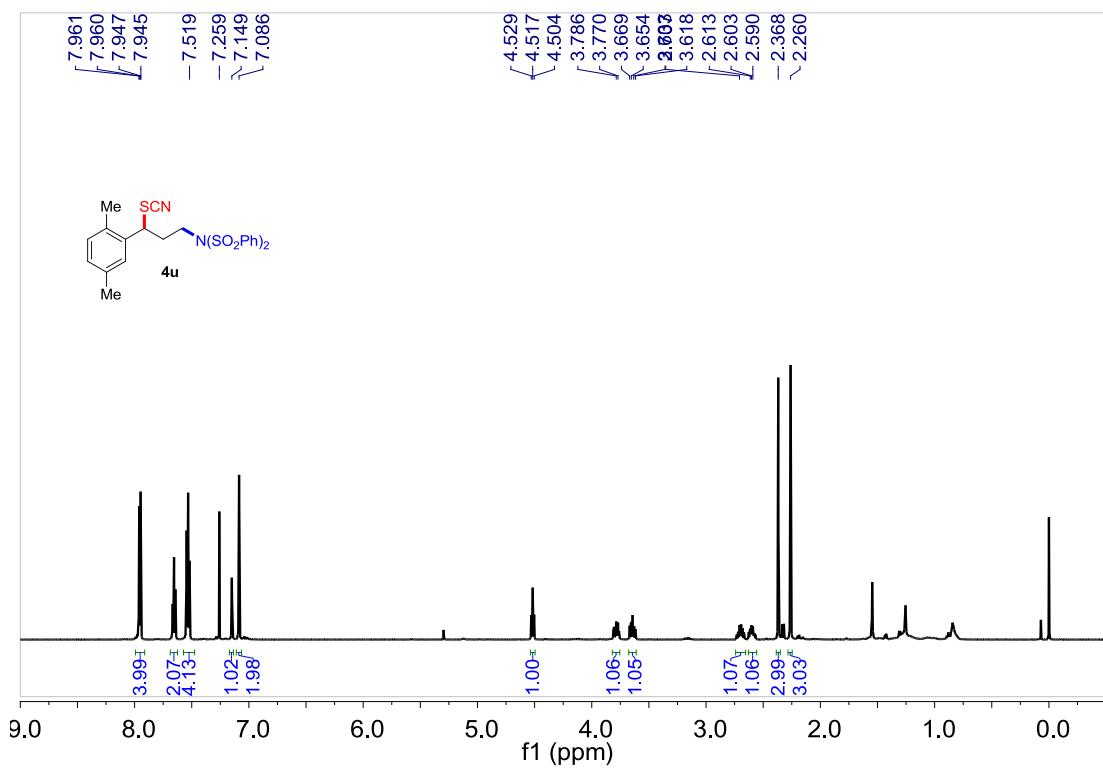


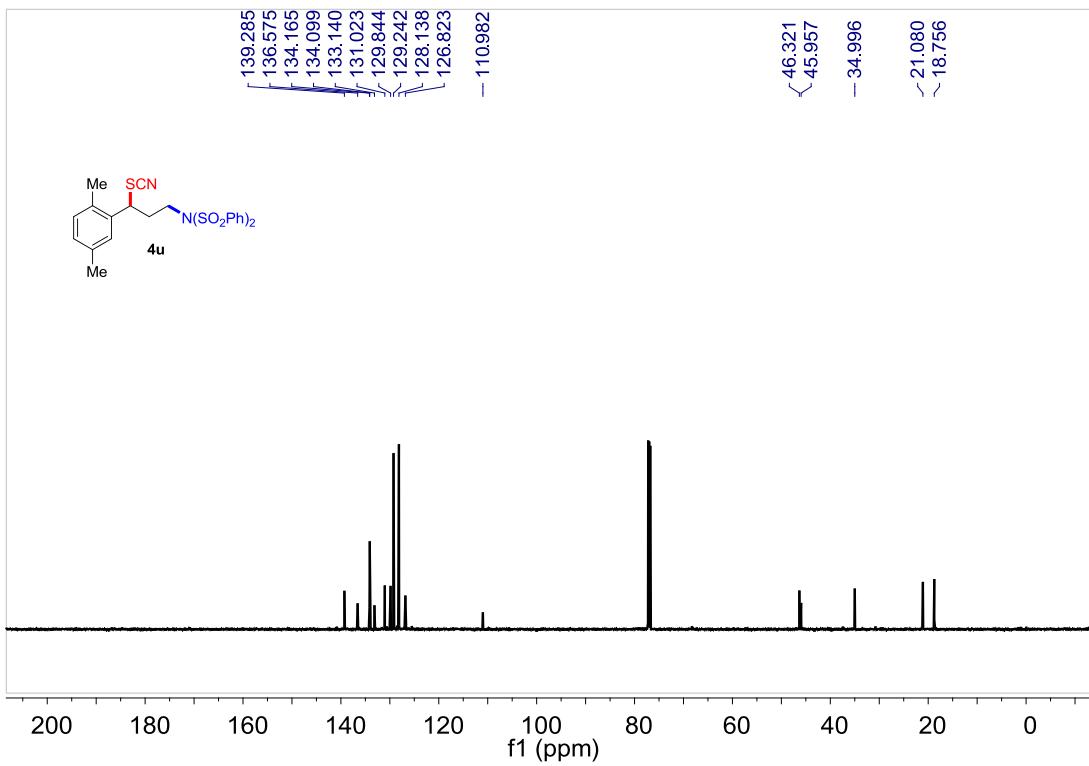
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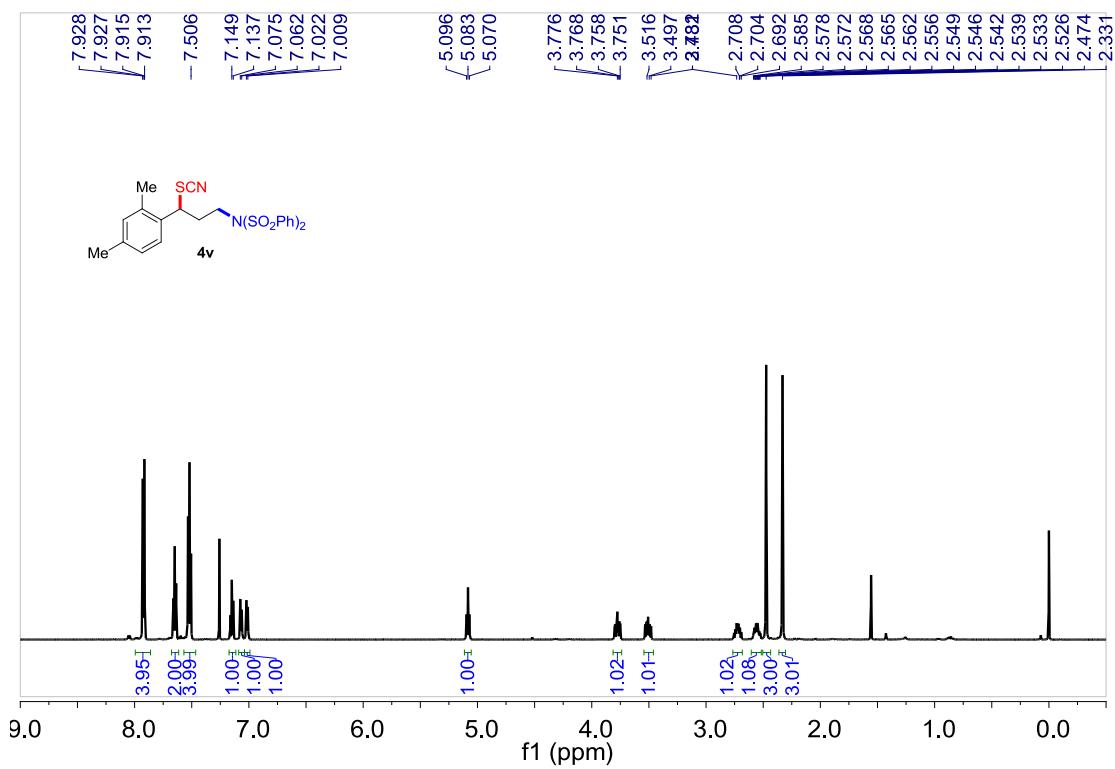


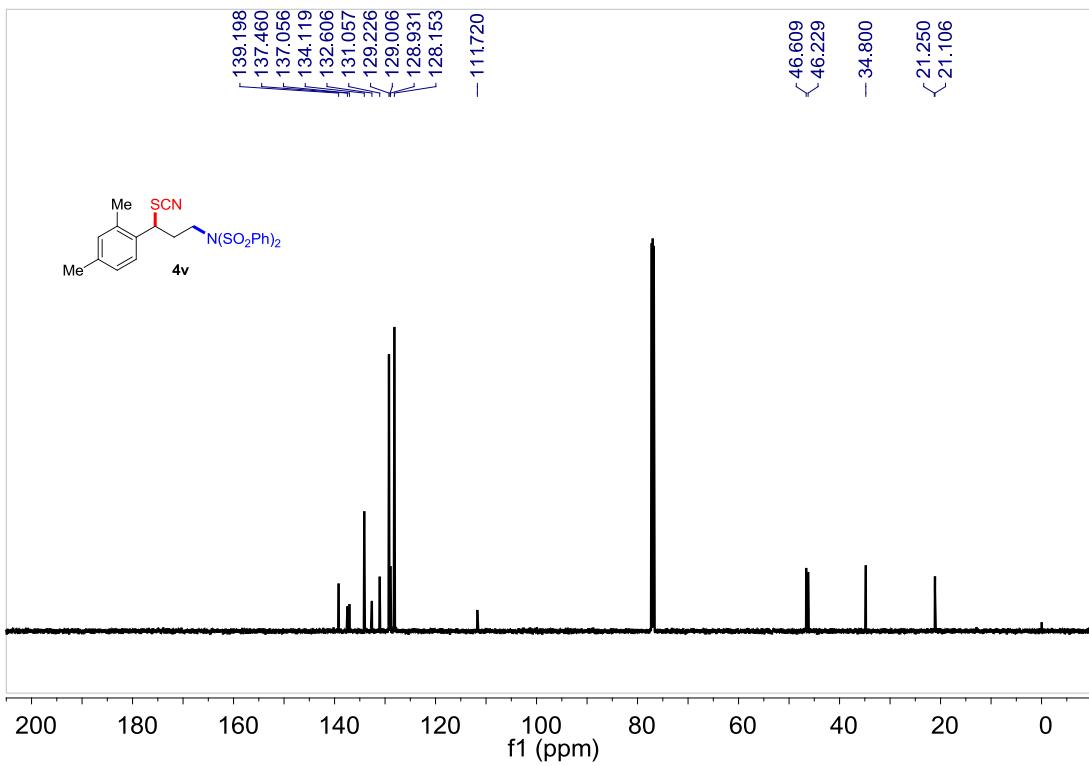
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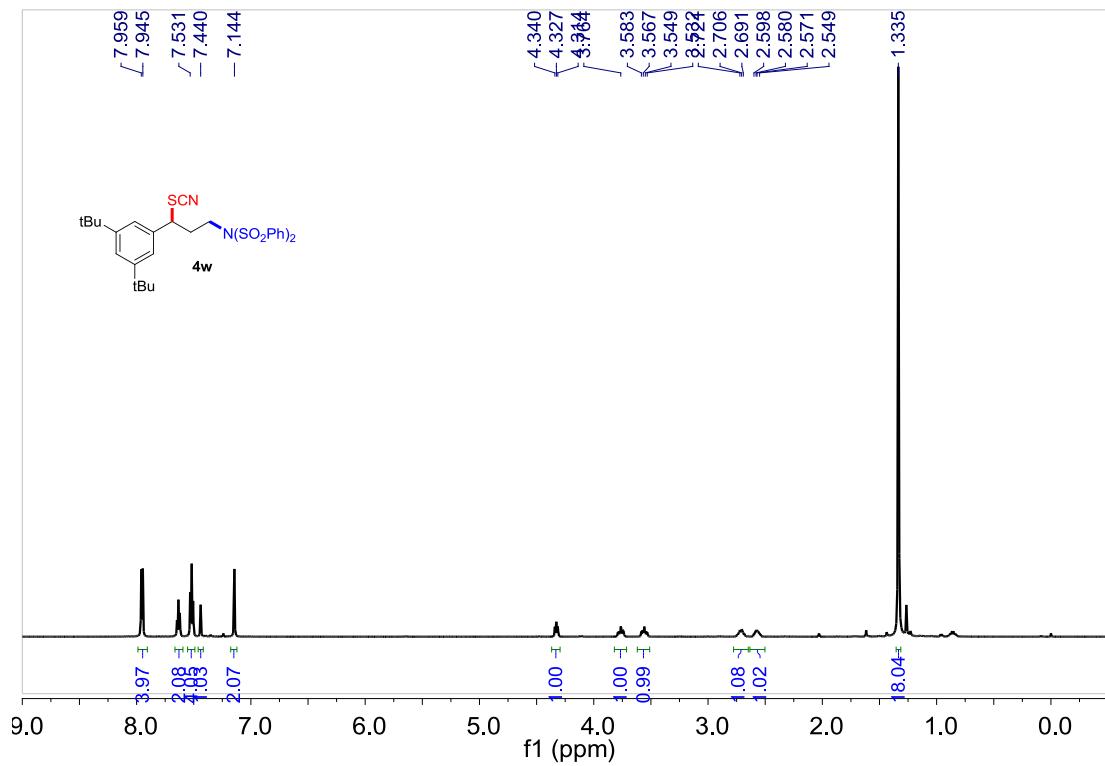


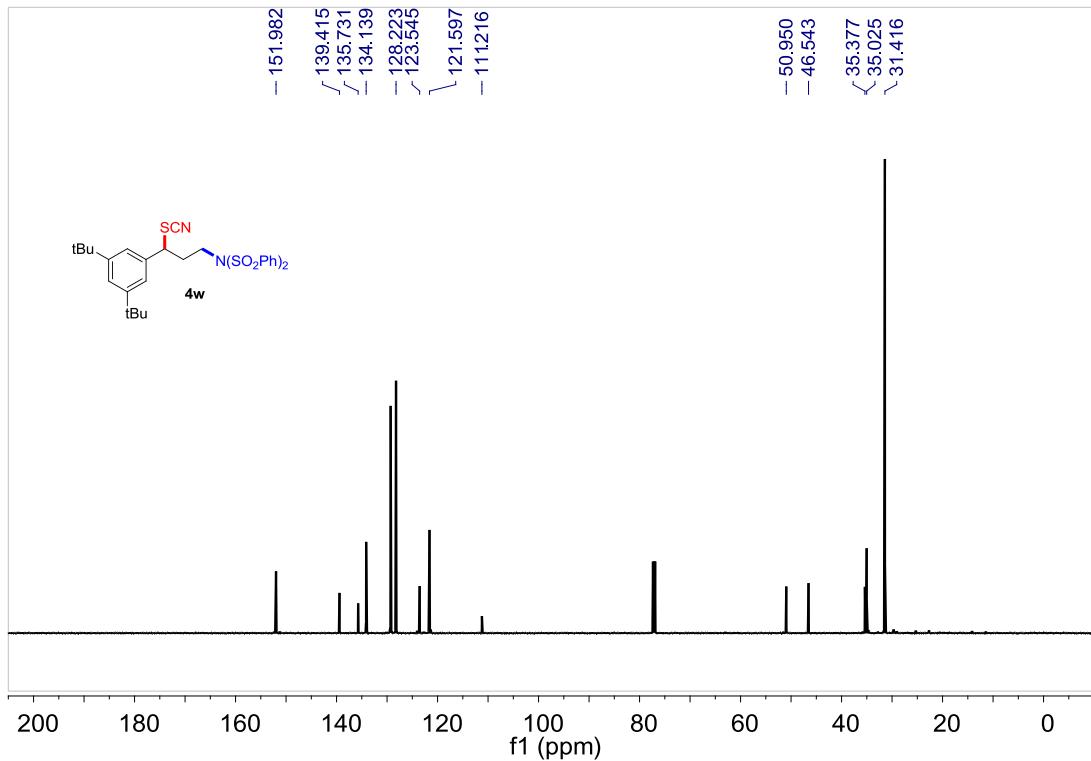
Compound 4v



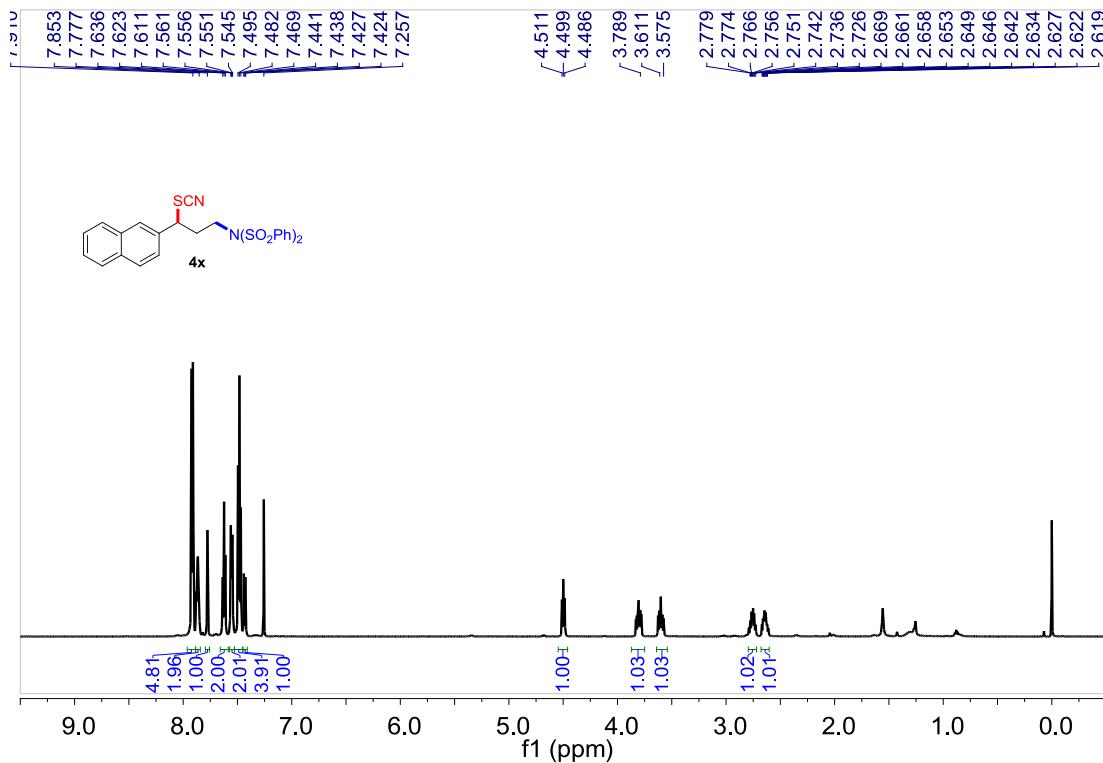


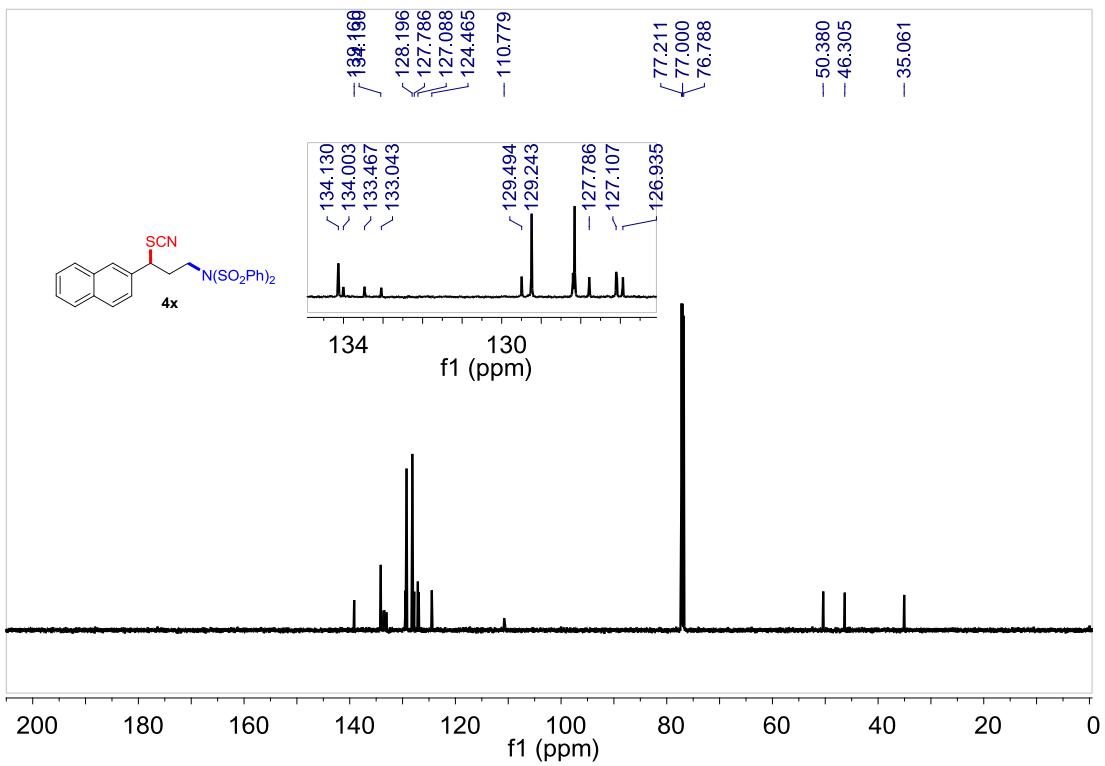
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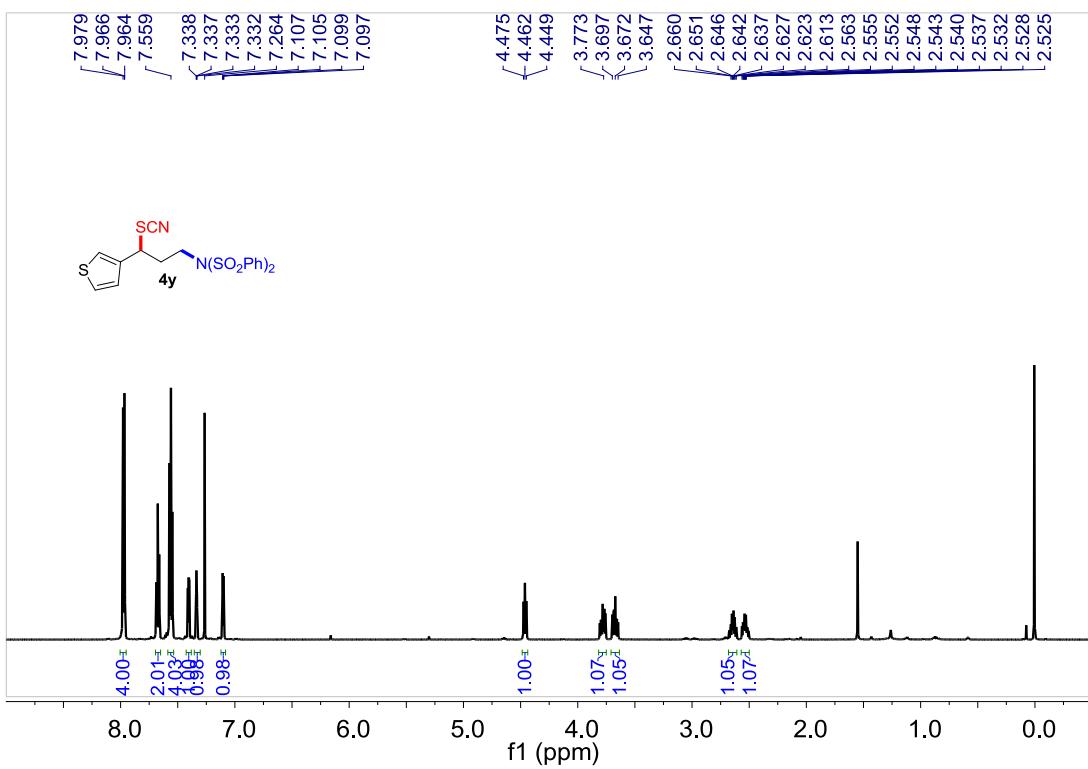


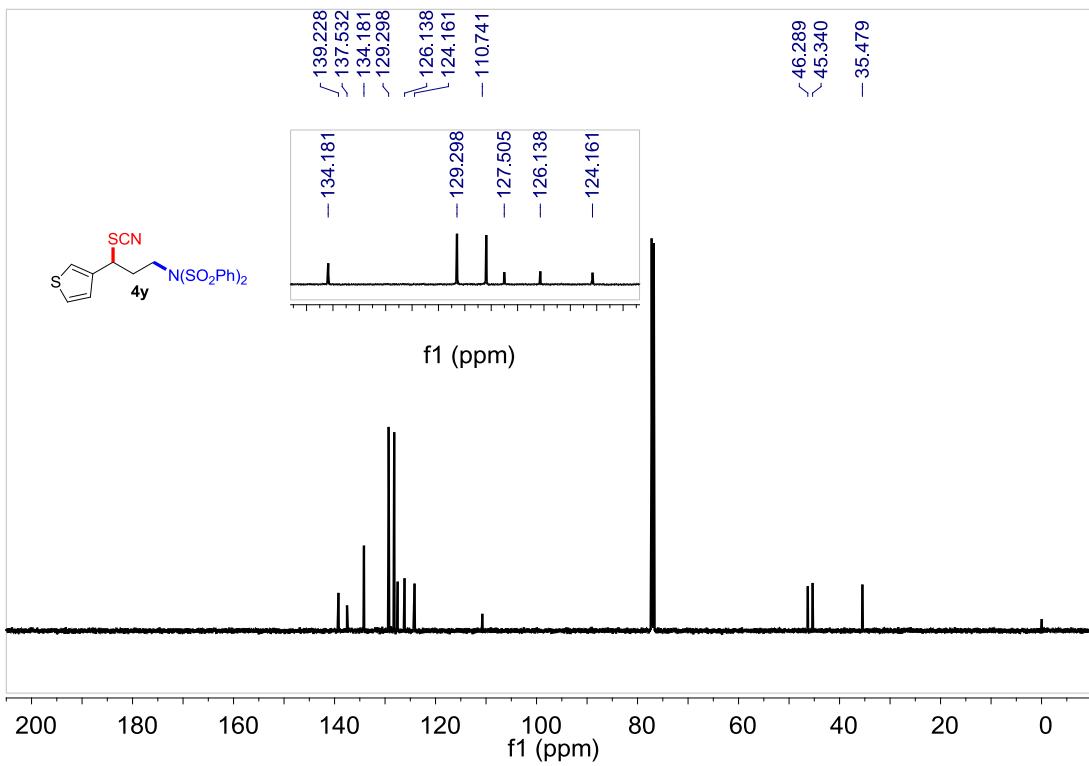
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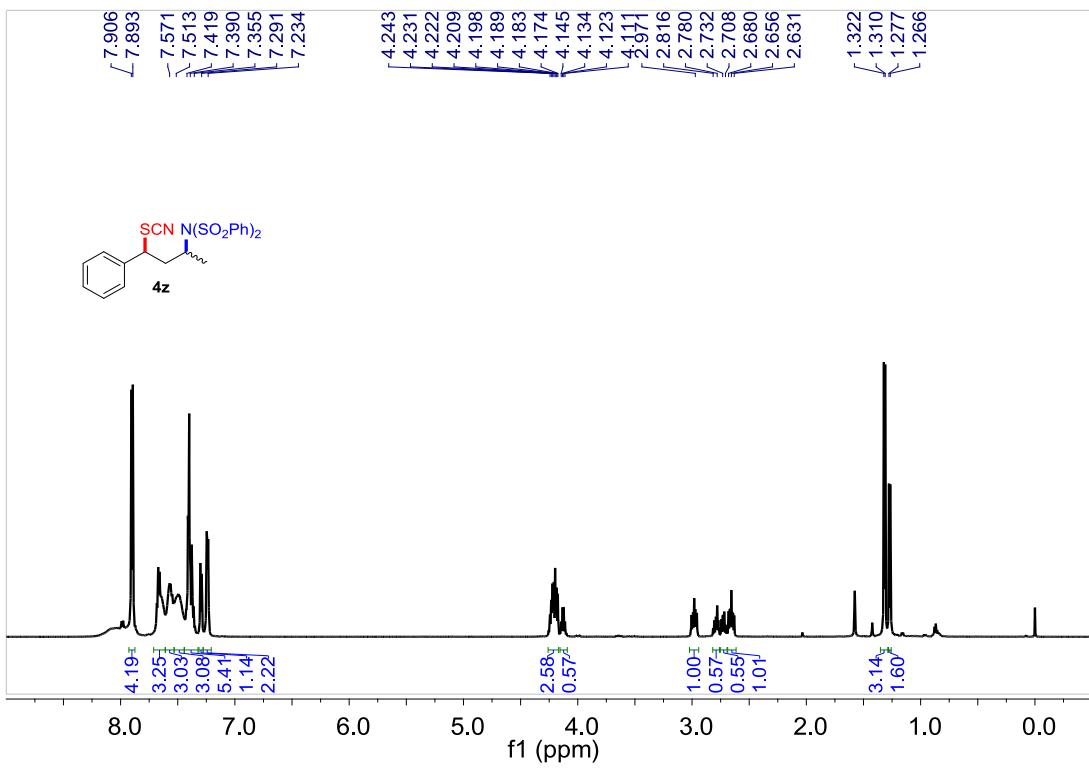


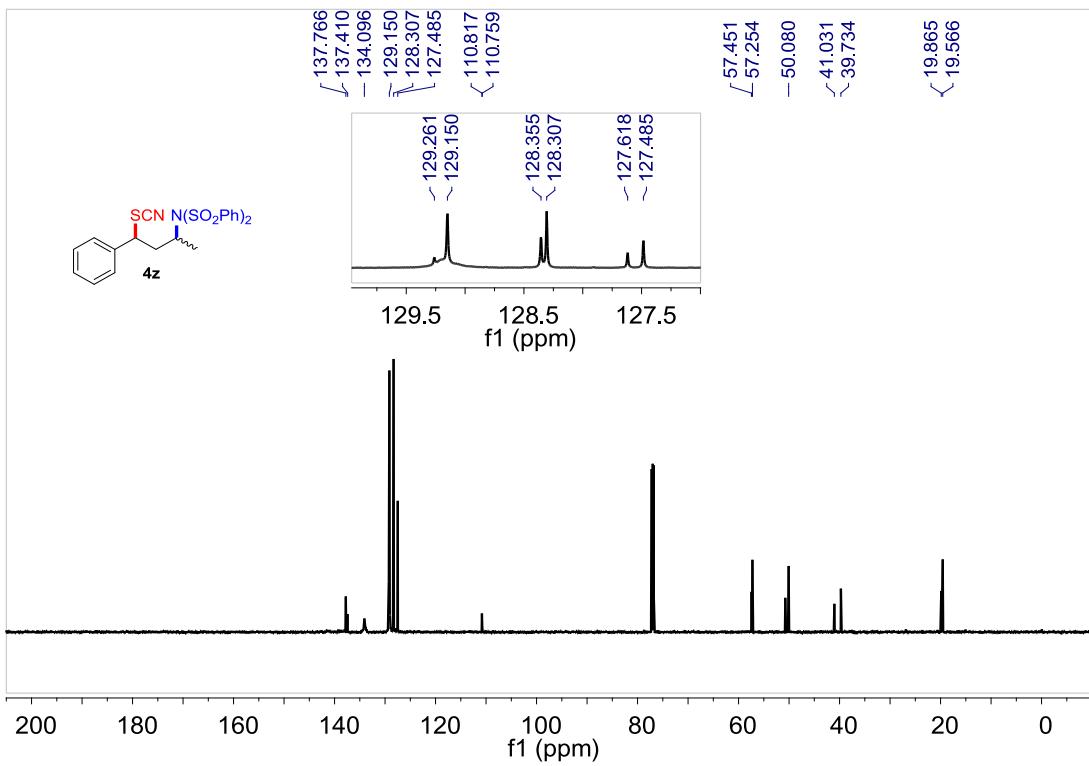
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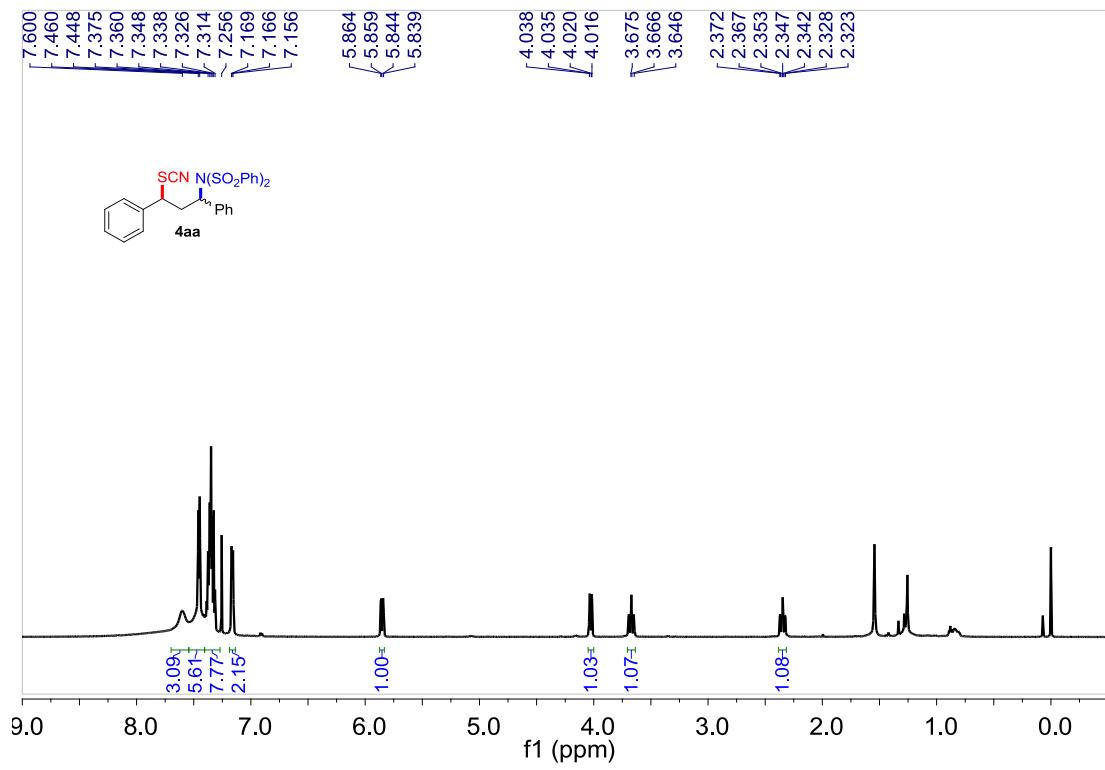


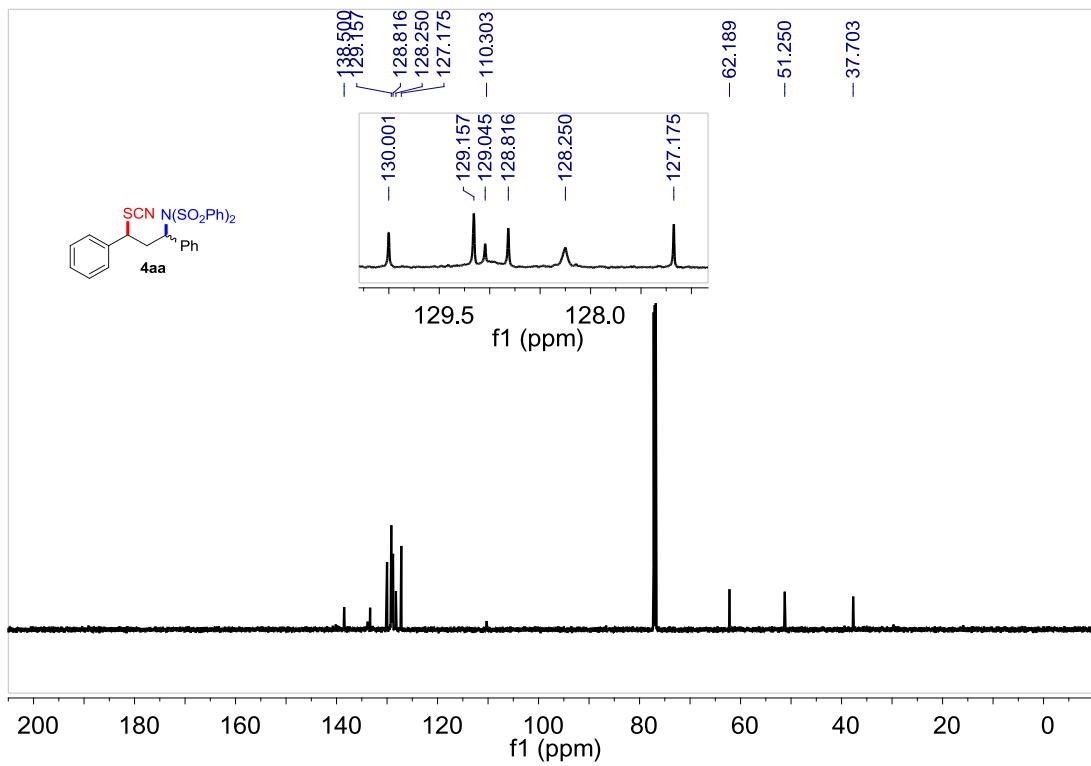
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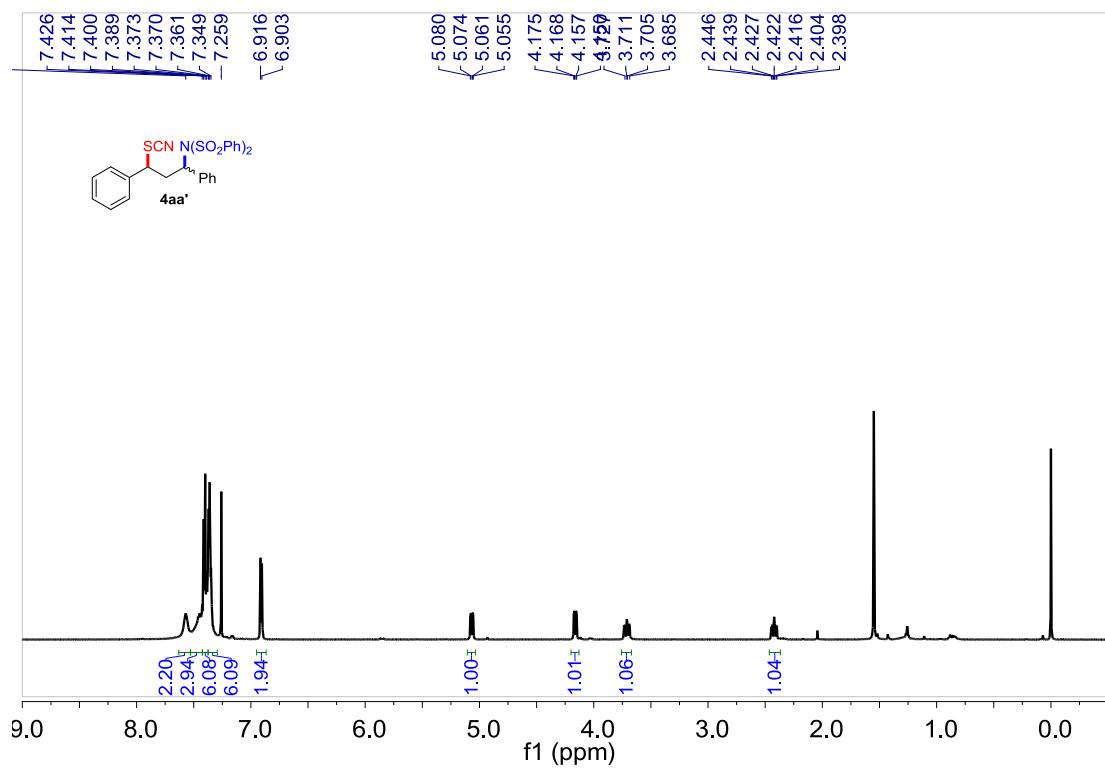


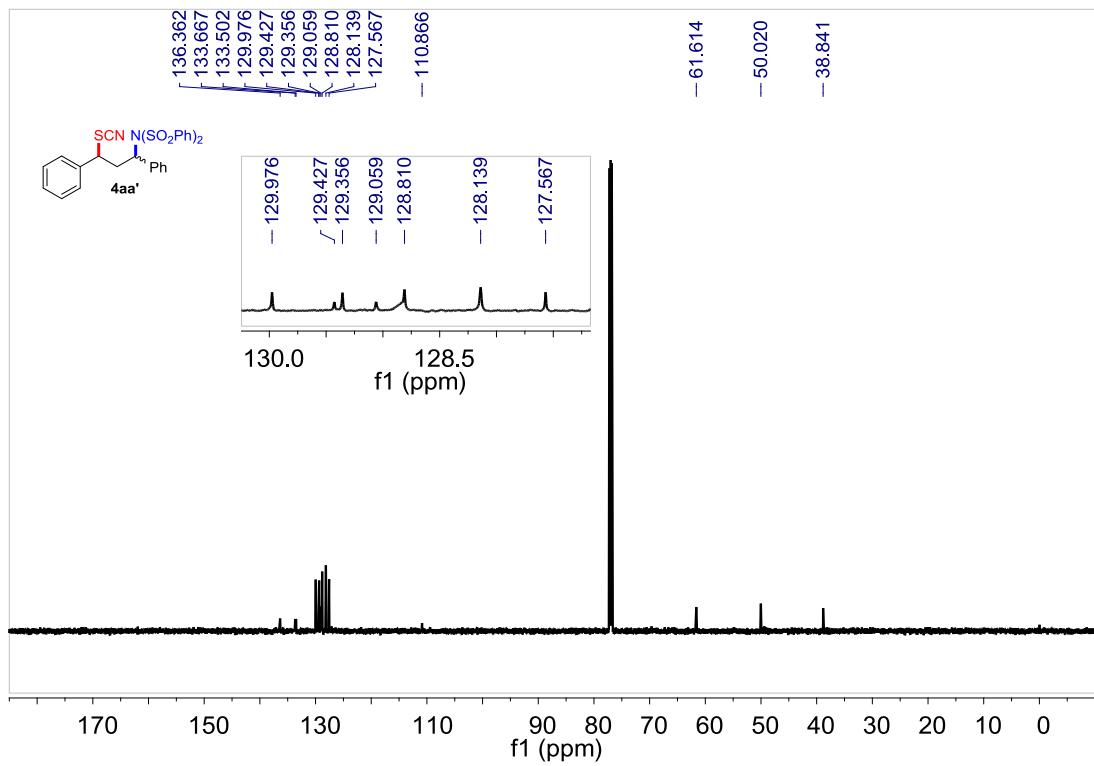
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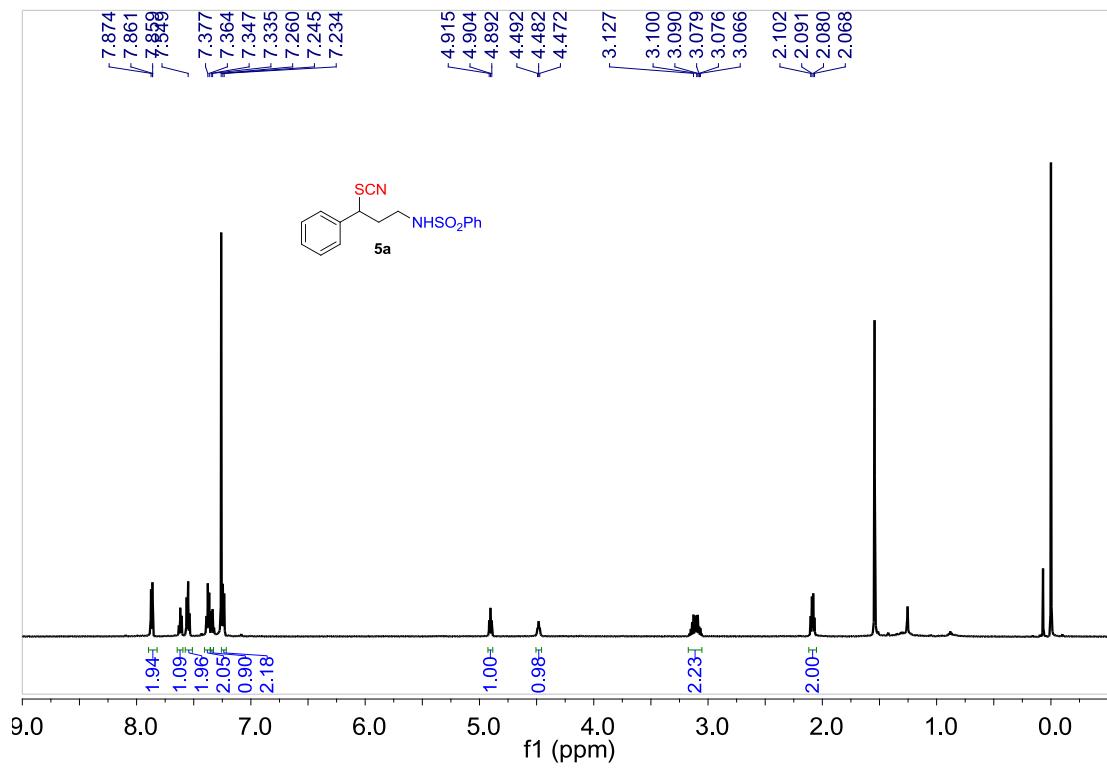


Compound 4aa'

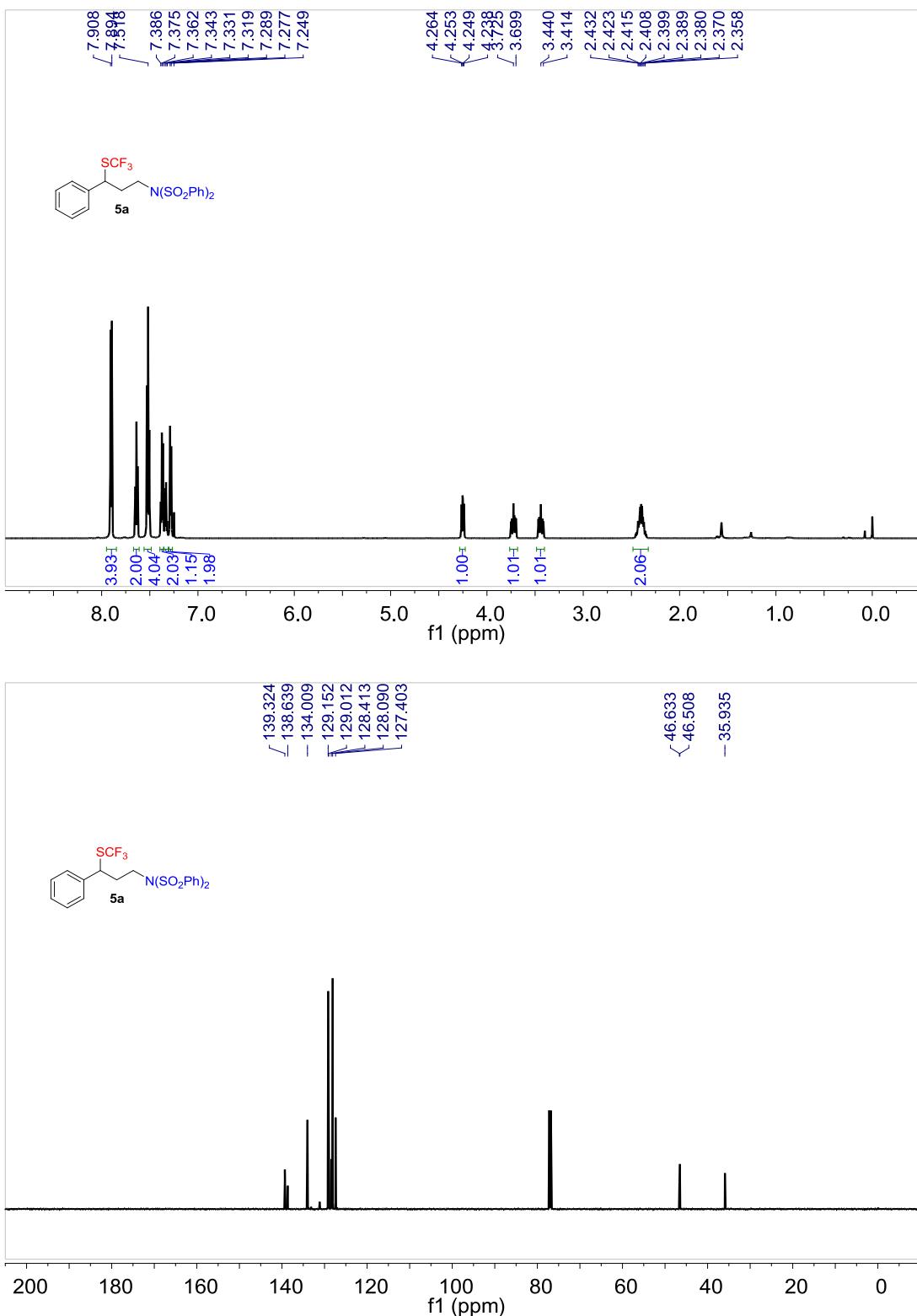


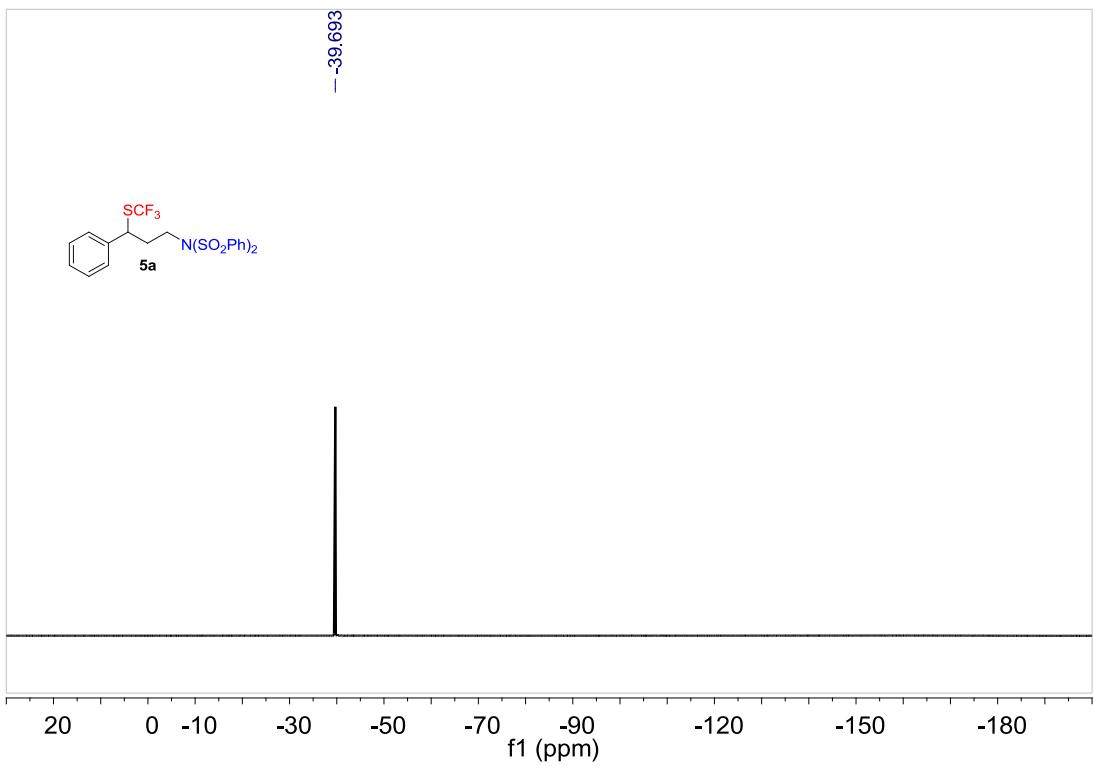


Compound 5a



Compound 5a





Compound 5b

