

Supporting Information

Electrochemical Synthesis of Dibenzothiophene *S,S*-Dioxides from Biaryl Sulfonyl Hydrazides

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1. Experimental

General. Nuclear magnetic resonance (NMR) spectra were recorded on Varian 400-MR (^1H 400 MHz), JEOL JNM-ECZ600R (^1H 600 MHz, ^{13}C 150 MHz), and JEOL JNM-ECS400 (^1H 400 MHz, ^{13}C 100 MHz, ^{19}F NMR 376 MHz) spectrometers. Chemical shifts for ^1H NMR are expressed in parts per million (ppm) relative to TMS (δ 0.00 ppm) or residual CHCl_3 in CDCl_3 (δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, dd = double doublet, ddd = double double doublet, td = triple doublet, br = broad, m = multiplet), coupling constants, and integration. Chemical shifts for ^{13}C NMR are expressed in ppm relative to CDCl_3 (δ 77.16 ppm). Chemical shifts for ^{19}F NMR are expressed in ppm relative to α,α,α -trifluorotoluene (δ -63.72 ppm). IR spectra were recorded on a SHIMADZU IRAffinity-1 spectrometer. High-resolution mass spectrometry was performed on a Bruker micrOTOF II-SKA (ESI or APCI-TOF). Cyclic voltammetry (CV) was recorded on Electrochemical Analyzer CHI-600B. Analytic thin layer chromatography (TLC) was performed on Merck, pre-coated plate silica gel 60 F₂₅₄ (0.25 mm thickness). Column chromatography was performed on KANTO CHEMICAL silica gel 60N (40–50 μm). Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Dry tetrahydrofuran (THF) was purchased from FUJIFILM Wako pure chemical corporation. 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) and nitromethane (CH_3NO_2) were dried over MS3A. All reactions were performed under an argon atmosphere. [1,1'-Biaryl]-2-sulfonyl chlorides were synthesized according to the literature.¹¹

General for Electrochemical Reactions. Electrochemical cyclization was carried out using a carbon rod anode and a Pt plate cathode ($1.0 \times 1.5 \text{ cm}^2$) connected to Pt wire (Figure S1a). The electrochemical reactions were performed in a 10 mL two-necked flask equipped with a three-way cock and those electrodes (Figure S1b). The two electrodes are connected to DC power supply (KIKUSUI PMX350-0.2A) and an ammeter (YOKOGAWA 2051 03) (Figure S1c).

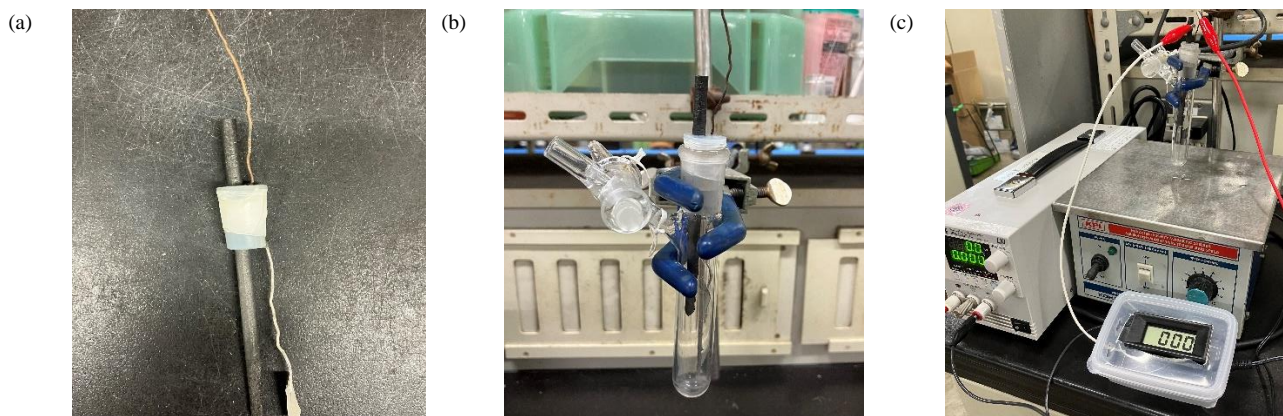
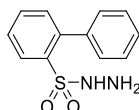


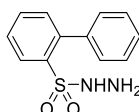
Figure S1. (a) Carbon rod electrode and Pt electrode ($1.0 \times 1.5 \text{ cm}^2$), (b) 10 mL two-necked flask equipped with a three-way cock and a carbon rod electrode and a Pt electrode, (c) electrochemical system.

Cyclic Voltammetry (CV)

A glassy carbon electrode (surface area: 0.071 cm^2 , BAS), a Pt coil electrode, and an Ag/Ag⁺ electrode (Ag wire in 0.01 M AgNO₃/0.10 M Bu₄NPF₆/CH₃CN) were used as a working, counter, and reference electrodes, respectively. The working electrode was polished with 5 μm alumina slurry. After polishing, it was washed with deionized water and acetone, and dried in an oven. A CH₃CN solution of sample including 0.01 M of each sample and 0.10 M of Bu₄NPF₆ was prepared as an electrochemical solution and bubbled with argon for 2 min. Using the electrodes and the solutions, beaker-typed three electrode electrochemical cell were constructed, and were connected with the potentiostat to perform cyclic voltammetry. The redox potentials were calibrated with ferrocene as a standard. CV was performed at a scan rate of 100 mV/s.

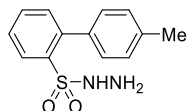


General procedure for the synthesis of Sulfonyl Hydrazides 1.^{20,21} To a solution of [1,1'-biaryl]-2-sulfonyl chloride in THF (0.2 M) was added dropwise H₂NNH₂·H₂O (3 equiv) at 0 °C and the mixture was stirred for 0.5–3 h. The consumption of the substrate was checked by TLC analysis. After the completion of the reaction, the solvent was removed by evaporation, and the mixture was extracted with dichloromethane ($3 \times 15 \text{ mL}$), and the combined organic layer was washed with water, and dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc 5:1 \rightarrow 1:1 with 0.1% Et₃N).

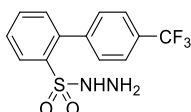


[1,1'-Biphenyl]-2-sulfonylhydrazide (1a). Prepared by the general procedure from [1,1'-biphenyl]-2-sulfonyl chloride (759 mg, 3.00 mmol). After the general work-up, the residue was purified by column

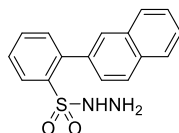
chromatography on silica gel (hexane/EtOAc 5:1 \rightarrow 1:1 with 0.1% Et₃N) to afford the title compound as colorless solid (671 mg, 2.70 mmol, 90%): ¹H NMR (600 MHz, CDCl₃) δ 8.20 (dd, J = 7.8, 1.4 Hz, 1H), 7.66 (td, J = 7.8, 1.4 Hz, 1H), 7.57 (td, J = 7.8, 1.4 Hz, 1H), 7.48–7.46 (m, 5H), 7.39 (dd, J = 7.8, 1.4 Hz, 1H), 4.73 (brs, 1H), 3.28 (brs, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 140.9, 138.4, 134.9, 133.3, 132.5, 131.2, 129.1, 129.0, 128.6, 128.4; IR (KBr) 3359, 3210, 1591, 1465, 1329, 1158, 1078, 870, 763 cm⁻¹; HRMS (ESI) m/z calcd for C₁₂H₁₃N₂O₂S [M + H]⁺ 249.0692, found 249.0696; mp 120.8–121.6 °C.



4'-Methyl-[1,1'-biphenyl]-2-sulfonohydrazide (1b). Prepared by the general procedure from 4'-methyl-[1,1'-biphenyl]-2-sulfonyl chloride (246 mg, 0.92 mmol). After the general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 5:1 \rightarrow 1:1 with 0.1% Et₃N) to afford the title compound as colorless solid (227 mg, 0.87 mmol, 95%): ¹H NMR (600 MHz, CDCl₃) δ 8.15 (dd, J = 7.6, 1.2 Hz, 1H), 7.62 (td, J = 7.6, 1.2 Hz, 1H), 7.53 (td, J = 7.6, 1.2 Hz, 1H), 7.35–7.33 (m, 3H), 7.25 (d, J = 7.6 Hz, 1H), 4.90 (brs, 1H), 3.33 (brs, 2H), 2.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 140.8, 138.7, 135.3, 134.7, 133.1, 132.5, 130.9, 129.1, 128.8, 128.1, 21.3; IR (KBr) 3447, 2361, 1458, 1319, 1157, 764 cm⁻¹; HRMS (ESI) m/z calcd for C₁₃H₁₄N₂NaO₂S [M + Na]⁺ 285.0668, found 285.0672; mp 96.7–97.5 °C.

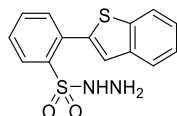


4'-(Trifluoromethyl)-[1,1'-biphenyl]-2-sulfonohydrazide (1c). Prepared by the general procedure from 4'-(trifluoromethyl)-[1,1'-biphenyl]-2-sulfonyl chloride (171 mg, 0.53 mmol). After the general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 5:1 \rightarrow 1:1 with 0.1% Et₃N) to afford the title compound as colorless solid (164 mg, 0.52 mmol, 98%): ¹H NMR (600 MHz, CDCl₃) δ 8.20 (d, J = 7.7 Hz, 1H), 7.71 (d, J = 8.3 Hz, 2H), 7.69 (td, J = 7.7, 1.3 Hz, 1H), 7.61 (td, J = 7.7, 1.3 Hz, 1H), 7.57 (d, J = 8.3 Hz, 2H), 4.92 (brs, 1H), 3.33 (brs, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 142.4, 140.0, 134.9, 133.5, 132.6, 131.2, 130.8 (q, ² J_{C-F} = 33.2 Hz), 129.7, 128.8, 125.3 (q, ³ J_{C-F} = 2.9 Hz), 124.0 (q, ¹ J_{C-F} = 271.7 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -63.6; IR (KBr) 3296, 1260, 1325, 1161, 1107, 1064, 839, 779 cm⁻¹; HRMS (ESI) m/z calcd for C₁₃H₁₁FN₂NaO₂S [M + Na]⁺ 339.0386, found 339.0386; mp 125.2–125.6 °C.

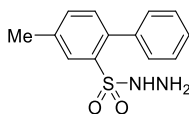


2-(Naphthalen-2-yl)benzenesulfonohydrazide (1d). Prepared by the general procedure from 2-(naphthalen-2-yl)benzenesulfonyl chloride (538 mg, 1.78 mmol). After the general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 5:1 \rightarrow 1:1 with 0.1% Et₃N) to afford the title compound as colorless solid (490 mg, 1.64 mmol, 92%): ¹H NMR (600 MHz, CDCl₃) δ 8.24 (d, J = 7.6 Hz, 1H), 7.95–7.87 (m, 4H), 7.69 (td, J = 7.6, 1.3 Hz, 1H), 7.61–7.54 (m, 4H), 7.46 (dd, J = 7.6, 1.3 Hz, 1H),

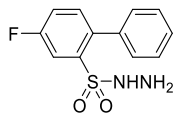
4.74 (brs, 1H), 3.32 (brs, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 141.0, 135.9, 135.0, 133.3, 133.1, 132.9, 132.8, 131.3, 128.44, 128.41, 128.1, 128.2, 128.0, 127.2, 127.1, 126.9; IR (KBr) 3356, 1628, 1329, 1157, 1126, 860, 829, 750 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{NaO}_2\text{S}$ $[\text{M} + \text{Na}]^+$ 321.0668, found 321.0668; mp 131.5–132.3 $^\circ\text{C}$.



2-(Benzo[*b*]thiophen-2-yl)benzenesulfonylhydrazide (1e). Prepared by the general procedure from 2-(benzo[*b*]thiophen-2-yl)benzenesulfonyl chloride (1.62 g, 5.24 mmol). After the general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 5:1 \rightarrow 1:1 with 0.1% Et_3N) to afford the title compound as colorless solid (1.38 g, 4.54 mmol, 87%): ^1H NMR (600 MHz, CDCl_3) δ 8.26 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.68 (t, J = 8.1 Hz, 1H), 7.64–7.60 (m, 3H), 7.44 (t, J = 8.1 Hz, 1H), 7.41 (t, J = 8.1 Hz, 1H), 5.26 (brs, 1H), 3.14 (brs, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 140.2, 139.7, 137.7, 135.8, 133.8, 133.1, 131.8, 129.3, 126.9, 125.5, 125.3, 124.6, 122.2; IR (KBr) 3356, 2361, 1429, 1337, 1161, 772 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{NaO}_2\text{S}_2$ $[\text{M} + \text{Na}]^+$ 327.0232, found 327.0232; mp 134.2–134.9 $^\circ\text{C}$.

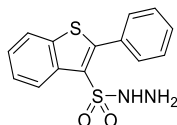


4-Methyl-[1,1'-biphenyl]-2-sulfonylhydrazide (1b'). Prepared by the general procedure from 4-methyl-[1,1'-biphenyl]-2-sulfonyl chloride (240 mg, 0.90 mmol). After the general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 5:1 \rightarrow 1:1 with 0.1% Et_3N) to afford the title compound as yellow solid (233 mg, 0.89 mmol, 99%): ^1H NMR (600 MHz, CDCl_3) δ 7.99 (brs, 1H), 7.45–7.41 (m, 6H), 7.25 (d, J = 8.6 Hz, 1H), 7.48–7.46 (m, 5H), 4.62 (brs, 1H), 3.40 (brs, 2H), 2.47 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 138.6, 138.4, 137.9, 134.4, 133.9, 132.4, 131.3, 129.2, 128.7, 128.4, 21.1; IR (KBr) 3467, 2361, 1474, 1325, 1152, 829, 772 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{NaO}_2\text{S}$ $[\text{M} + \text{Na}]^+$ 285.0668, found 285.0668; mp 88.7–89.5 $^\circ\text{C}$.

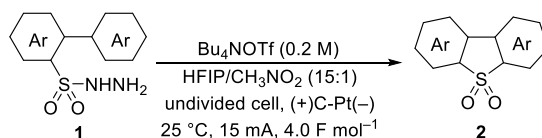


4-Fluoro-[1,1'-biphenyl]-2-sulfonylhydrazide (1f). Prepared by the general procedure from 4-fluoro-[1,1'-biphenyl]-2-sulfonyl chloride (200 mg, 0.74 mmol). After the general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 5:1 \rightarrow 1:1 with 0.1% Et_3N) to afford the title compound as colorless solid (194 mg, 0.73 mmol, 99%): ^1H NMR (600 MHz, CDCl_3) δ 7.92 (dd, J = 2.5 Hz, $^3J_{\text{H-F}}$ = 8.8 Hz, 1H), 7.48–7.43 (m, 5H), 7.39–7.34 (m, 2H), 4.78 (brs, 1H), 2.99 (brs, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 161.7 (d, $^1J_{\text{C-F}}$ = 251.4 Hz), 137.5, 137.0 (d, $^3J_{\text{C-F}}$ = 5.8 Hz), 136.9 (d, $^4J_{\text{C-F}}$ = 2.9 Hz), 134.3 (d, $^3J_{\text{C-F}}$ = 7.2 Hz), 129.3, 129.1, 128.6, 120.2 (d, $^2J_{\text{C-F}}$ = 21.7 Hz), 118.3 (d, $^2J_{\text{C-F}}$ = 24.6 Hz); ^{19}F NMR (376

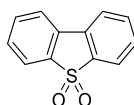
MHz, CDCl₃) δ -112.2; IR (KBr) 3356, 2361, 1476, 1327, 1150, 841, 772 cm⁻¹; HRMS (ESI) m/z calcd for C₁₂H₁₁FN₂NaO₂S [M + Na]⁺ 289.0417, found 289.0424; mp 97.8–98.6 °C.



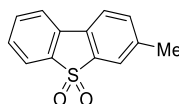
2-Phenylbenzo[*b*]thiophene-3-sulfonohydrazide (1e'). Prepared by the general procedure from 2-phenylbenzo[*b*]thiophene-3-sulfonyl chloride (268 mg, 0.87 mmol). After the general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 5:1 → 1:1 with 0.1% Et₃N) to afford the title compound as colorless solid (60.2 mg, 0.20 mmol, 23%): ¹H NMR (600 MHz, CDCl₃) δ 8.42 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.64–7.63 (m, 2H), 7.52–7.46 (m, 6H), 5.66 (brs, 1H), 3.72 (brs, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 152.2, 138.4, 136.6, 131.6, 130.3, 130.1, 128.6, 126.3, 126.0, 125.1, 124.7, 122.0; HRMS (ESI) m/z calcd for C₁₄H₁₂N₂NaO₂S₂ [M + Na]⁺ 327.0232, found 327.0237.



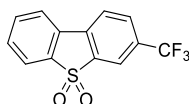
General Procedure for the Synthesis of Dibenzo[*b,d*]thiophene 5,5-Dioxides (2). Electrochemical cyclization was carried out in a 10 mL two-necked flask equipped with a carbon rod anode, and a Pt cathode (1.0 × 1.5 cm²). Substrate **1** (0.2 mmol), Bu₄NOTf (0.63 g, 1.6 mmol) were placed in the flask equipped with a stirring bar. Then, HFIP (7.5 mL) and CH₃NO₂ (0.5 mL) were added with a syringe at room temperature. A constant current (15 mA, 4.0 F mol⁻¹, 1.43 h) was supplied at 25 °C with an oil bath. After the electrolysis, the solvent was removed by evaporation. The reaction mixture was filtered through a short column chromatography on silica gel to remove Bu₄NOTf using Et₂O (50 mL) as an eluent. The combined solution was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc 5:1 → 4:1) to afford compound **2**.



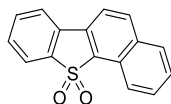
Dibenzob[*b,d*]thiophene 5,5-Dioxide (2a).⁶ Prepared by the general procedure from [1,1'-biphenyl]-2-sulfonohydrazide (**1a**, 49.7 mg, 0.20 mmol). After the general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 5:1 → 4:1) to afford the title compound as colorless solid (14.0 mg, 0.065 mmol, 33%): ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.64 (td, *J* = 7.6, 1.1 Hz, 2H), 7.53 (td, *J* = 7.6, 1.1 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 137.7, 134.0, 131.7, 130.5, 122.2, 121.7; IR (KBr) 1593, 1452, 1289, 1157, 1047, 757 cm⁻¹.



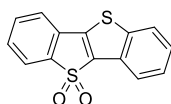
3-Methyldibenzo[*b,d*]thiophene 5,5-Dioxide (2b).²² Prepared by the general procedure from 4'-methyl-[1,1'-biphenyl]-2-sulfonohydrazide (**1b**, 53.2 mg, 0.20 mmol). After the general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 5:1 → 4:1) to afford the title compound as colorless solid (14.8 mg, 0.064 mmol, 32%): ¹H NMR (600 MHz, CDCl₃) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.64 (s, 1H), 7.62 (td, *J* = 7.6, 0.9 Hz, 1H), 7.50 (td, *J* = 7.6, 0.9 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 2.47 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 141.4, 137.9, 137.8, 134.8, 134.0, 132.0, 130.0, 129.2, 122.7, 122.3, 121.5, 121.4, 21.7; IR (KBr) 1458, 1288, 1219, 1155, 772 cm⁻¹.



3-(Trifluoromethyl)dibenzo[*b,d*]thiophene 5,5-Dioxide (2c).⁷ Prepared by the general procedure from 4'-(trifluoromethyl)-[1,1'-biphenyl]-2-sulfonohydrazide (**1c**, 63.4 mg, 0.20 mmol). After the general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 5:1 → 4:1) to afford the title compound as colorless solid (13.9 mg, 0.049 mmol, 24%): ¹H NMR (600 MHz, CDCl₃) δ 8.09 (brs, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.91 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.89–7.87 (m, 2H), 7.72 (td, *J* = 7.9, 1.0 Hz, 1H), 7.63 (td, *J* = 7.9, 1.0 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 138.6, 138.3, 135.0, 134.4, 132.8 (q, ²*J*_{C-F} = 33.2 Hz), 131.7, 131.1 (q, ³*J*_{C-F} = 4.3 Hz), 130.5, 130.3, 122.7, 122.4, 119.9 (d, ³*J*_{C-F} = 2.9 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -63.8; IR (KBr) 2361, 1541, 1327, 1167, 772 cm⁻¹.



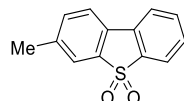
Benzo[*b*]naphtho[2,1-*d*]thiophene 11,11-Dioxide (2d).^{7,23} Prepared by the general procedure from 2-(naphthalen-2-yl)benzenesulfonohydrazide (**1d**, 59.8 mg, 0.20 mmol). After the general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 5:1 → 4:1) to afford the title compound as colorless solid (10.8 mg, 0.041 mmol, 21%): ¹H NMR (600 MHz, CDCl₃) δ 8.44 (dd, *J* = 8.6, 1.0 Hz, 1H), 8.12 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.67 (td, *J* = 7.6, 1.0 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.56 (td, *J* = 7.6, 1.0 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 138.7, 134.8, 134.5, 134.0, 132.2, 131.9, 130.6, 130.4, 129.6, 129.1, 128.0, 126.6, 123.6, 122.3, 121.9, 118.0; IR (KBr) 2361, 1290, 1161, 773, 756 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₆H₁₀NaO₂S [M + Na]⁺ 289.0294, found 289.0294.



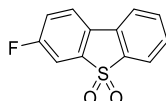
Benzo[*b*]benzo[4,5]thieno[2,3-*d*]thiophene 5,5-Dioxide (2e).⁷

2-(benzo[*b*]thiophen-2-yl)benzenesulfonohydrazide (**1e**, 60.5 mg, 0.20 mmol), Bu₄NOTf (627 mg, 1.60 mmol) were placed in the flask equipped with a stirring bar. Then HFIP (7.5 mL) and CH₃NO₂ (0.5 mL) were added with a syringe at room temperature. A constant current (7.5 mA, 3.0 F mol⁻¹, 2.14 h) was

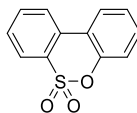
supplied at 25 °C with an oil bath. After the electrolysis, the solvent was removed by evaporation. The reaction mixture was filtered through a short column chromatography on silica gel to remove Bu₄NOTf. The silica gel was washed with Et₂O (50 mL). The combined solution was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc 5:1 → 4:1) to afford the title compound as colorless solid (27.2 mg, 0.10 mmol, 50%): ¹H NMR (600 MHz, CDCl₃) δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.79 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.61 (td, *J* = 8.0, 1.2 Hz, 1H), 7.55–7.51 (m, 3H), 7.46 (t, *J* = 8.0 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 143.8, 142.9, 142.6, 133.8, 130.5, 130.4, 128.5, 126.9, 126.6, 123.9, 122.5, 122.4, 122.1; IR (KBr) 2359, 1541, 1508, 1458, 1298, 1144, 773 cm⁻¹.



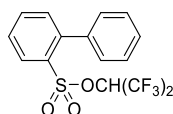
3-Methyldibenzo[*b,d*]thiophene 5,5-Dioxide (2b').²² Prepared by the general procedure from 4-methyl-[1,1'-biphenyl]-2-sulfonohydrazide (**1b'**, 52.6 mg, 0.20 mmol). After the general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 5:1 → 4:1) to afford the title compound as colorless solid (3.40 mg, 0.015 mmol, 7%). All compounds data were consistent with those of **2b**.



3-Fluorodibenzo[*b,d*]thiophene 5,5-Dioxide (2f).⁷ Prepared by the general procedure from 4-fluoro-[1,1'-biphenyl]-2-sulfonohydrazide (**1f**, 55.1 mg, 0.21 mmol). After the general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 5:1 → 4:1) to afford the title compound as colorless solid (23.0 mg, 0.098 mmol, 47%): ¹H NMR (600 MHz, CDCl₃) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.78 (dd, *J* = 8.4 Hz, ⁴*J*_{H-F} = 4.3 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.53–7.51 (m, 2H), 7.33 (ddd, *J* = 8.4, 2.3 Hz, ³*J*_{H-F} = 8.4 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 163.7 (d, ¹*J*_{C-F} = 254.3 Hz), 139.6 (d, ³*J*_{C-F} = 8.7 Hz), 138.1 (d, ⁴*J*_{C-F} = 2.9 Hz), 134.2, 131.0, 127.8 (d, ⁴*J*_{C-F} = 2.9 Hz), 123.5 (d, ³*J*_{C-F} = 7.2 Hz), 122.5, 121.5, 121.3 (d, ²*J*_{C-F} = 23.6 Hz), 110.3 (d, ²*J*_{C-F} = 26.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -108.5; IR (KBr) 2361, 1456, 1298 1155, 773 cm⁻¹.

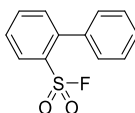


Dibenzo[*c,e*][1,2]oxathiine 6,6-Dioxide (3a).¹¹ The spectral data was consistent with the literature.

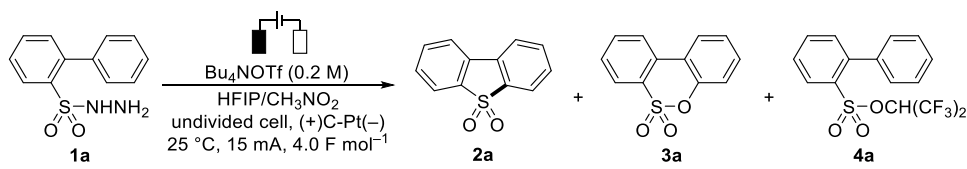


1,1,1,3,3,3-Hexafluoropropan-2-yl [1,1'-Biphenyl]-2-sulfonate (4a). Colorless solid: ¹H NMR (600 MHz, CDCl₃) δ 8.08 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.73 (td, *J* = 7.8, 0.9 Hz, 1H), 7.57 (td, *J* = 7.8, 0.9 Hz, 1H), 7.45 (dd,

$J = 7.8, 0.9$ Hz, 1H), 7.44–7.41 (m, 3H), 7.38–7.35 (m, 2H), 5.19 (sept, $^3J_{\text{H-F}} = 5.5$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 143.1, 138.2, 134.5, 134.2, 133.4, 129.4, 129.2, 128.6, 128.0, 127.9, 119.9 (q, $^1J_{\text{C-F}} = 281.8$ Hz), 72.0 (sept, $^2J_{\text{C-F}} = 36.1$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -74.0 (d, $^3J_{\text{H-F}} = 5.5$ Hz); IR (KBr) 1468, 1385, 1292, 1202, 1188, 1111, 1069, 880, 806 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{10}\text{F}_6\text{NaO}_3\text{S}$ $[\text{M} + \text{Na}]^+$ 407.0147, found 407.0148; mp 45.3–46.1 $^\circ\text{C}$.

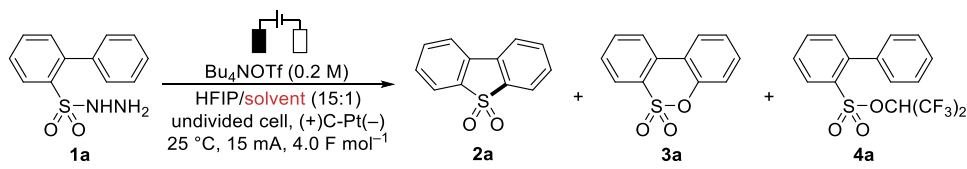


[1,1'-Biphenyl]-2-sulfonyl Fluoride (S1).^{24,25} Colorless solid: ^1H NMR (600 MHz, CDCl_3) δ 8.18 (dd, $J = 7.7, 1.1$ Hz, 1H), 7.66 (td, $J = 7.7, 1.1$ Hz, 1H), 7.61 (t, $J = 7.7$ Hz, 1H), 7.49 (dd, $J = 7.7, 1.1$ Hz, 1H), 7.47–7.43 (m, 3H), 7.39–7.37 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 143.2, 138.0, 134.9, 133.2, 132.4 (d, $^2J_{\text{C-F}} = 21.7$ Hz), 130.1, 129.0, 128.7, 128.2, 128.1; ^{19}F NMR (376 MHz, CDCl_3) δ 66.5; IR (KBr) 2363, 1541, 1396, 1211, 799, 773, 748 cm^{-1} .

Table S1. Screening of the ratio of co-solvent^a


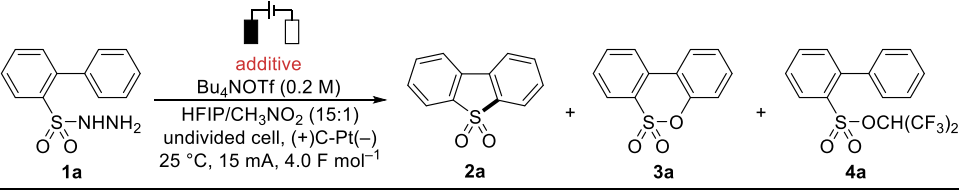
entry	HFIP/CH ₃ NO ₂	2a (%) ^b	3a (%) ^b	4a (%) ^b	1a (%) ^b
1	1:0	41	11	11	26
2	15:1	48 (33) ^c	17	23	16
3	3:1	18	30	14	20
4	1:1	18	44	10	22
5	1:3	12	45	6	14
6	1:15	12	39	trace	trace
7	0:1	N.D. ^d	24	N.D.	N.D.

^a Reaction conditions: **1a** (0.2 mmol), Bu₄NOTf (0.2 M), HFIP/CH₃NO₂, 25 °C, constant current electrolysis, 15 mA, 4.0 F mol⁻¹. ^b NMR yield. ^c Isolated yield. ^d N.D. = Not detected.

Table S2. Screening of solvent^a


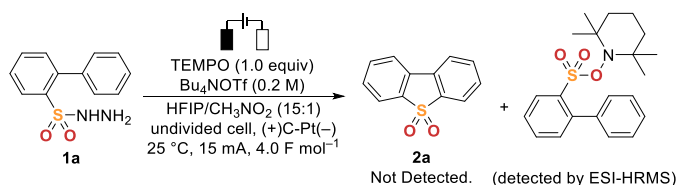
entry	solvent	2a (%) ^b	3a (%) ^b	4a (%) ^b	1a (%) ^b
1	CH ₃ NO ₂	48 (33) ^c	17	23	16
2	DMSO	43	32	17	13
3	sulfolane	38	11	19	11
4	DMF	38	25	15	5
5	DMA	43	18	21	4
6	NMP	43	16	28	19
7	EtOAc	38	10	22	25
8	DME	31	13	18	22
9	1,4-dioxane	40	14	30	28
10	toluene	8	trace	8	16

^a Reaction conditions: **1a** (0.2 mmol), Bu₄NOTf (0.2 M), HFIP/solvent (15:1), 25 °C, constant current electrolysis, 15 mA, 4.0 F mol⁻¹. ^b NMR yield. ^c Isolated yield.

Table S3. Screening of additive^a


entry	additive	2a (%) ^b	3a (%) ^b	4a (%) ^b	1a (%) ^b
1	none	48 (33) ^c	17	23	16
2	MS3A (500 mg)	34	11	17	26
3	MS4A (500 mg)	45	16	22	22
4	MS5A (500 mg)	41	11	16	41
5	2,6-lutidine (1.0 equiv)	35	15	20	10
6	2,6-lutidine (2.0 equiv)	31	13	19	7
7	KO ^t Bu (1.0 equiv)	41	19	23	8

^a Reaction conditions: **1a** (0.2 mmol), Bu₄NOTf (0.2 M), HFIP/CH₃NO₂, 25 °C, constant current electrolysis, 15 mA, 4.0 F mol⁻¹. ^b NMR yield. ^c Isolated yield.



Radical Trapping Experiment Radical trapping experiment was carried out in a 10 mL two-necked flask equipped with a carbon rod anode, and a Pt cathode (1.0 × 1.5 cm²). Substrate **1a** (0.2 mmol), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (0.4 mmol) Bu₄NOTf (1.6 mmol) were placed in the flask equipped with a stirring bar. Then, HFIP (7.5 mL) and CH₃NO₂ (0.5 mL) were added with a syringe at room temperature. A constant current (15 mA, 4.0 F mol⁻¹, 1.43 h) was supplied at 25 °C with an oil bath. After the electrolysis, the solvent was removed by evaporation. The reaction mixture was filtered through a short column chromatography on silica gel to remove Bu₄NOTf using Et₂O (50 mL) as an eluent. The corresponding product **2a** was not obtained. Moreover, high-resolution mass spectra analysis of this reaction mixture showed that TEMPO adduct product was formed. This result strongly suggests that sulfonyl radicals were generated in the reaction system.

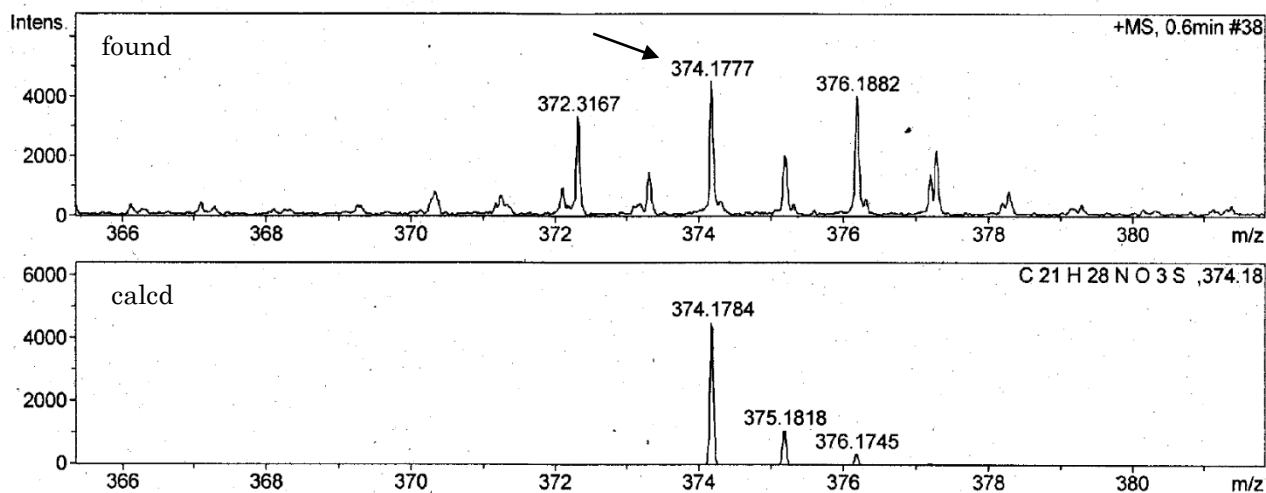
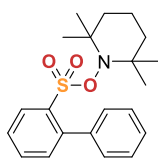


Figure S2. Radical trapping experiment and the ESI-HRMS spectrum



HRMS *m/z* calcd for C₂₁H₂₈NO₃S [M + H]⁺
calcd: 374.1784
found 374.1777

2. X-ray Crystallography

Crystal of **2d** was recrystallized from CH₂Cl₂. The compound was dissolved into the solvent, and the solution was kept at room temperature for slow evaporation to grow the crystals. X-ray single crystal analysis was conducted with Rigaku VariMax with Saturn equipped a Hypix-6000 as a detector. Graphite-monochromated Mo K α radiation ($\lambda = 0.71075$ Å) was used. Details of the crystal data and a summary of the intensity data collection parameters are listed in Tables S4 and Figure S3. The structure was solved with SHELXT and refined by full-matrix least-squares techniques against F^2 (SHELXL).^{26,27} The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions. Calculations were performed by using Olex2.²⁸

Table S4. Crystal data and structure refinement for **2d**

Identification code	CCDC2289413
Empirical formula	C ₁₆ H ₁₀ O ₂ S
Formula weight	266.30
Temperature/K	110
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	11.7679(4)
b/Å	13.7008(5)
c/Å	7.3871(3)
α /°	90
β /°	96.464(4)
γ /°	90
Volume/Å ³	1183.45(8)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.495
μ/mm^{-1}	0.266
F(000)	552.0
Crystal size/mm ³	0.47 × 0.08 × 0.06
Radiation	Mo K α (λ = 0.71073)
2 Θ range for data collection/°	6.888 to 59.362
Index ranges	-15 ≤ h ≤ 14, -17 ≤ k ≤ 19, -9 ≤ l ≤ 10
Reflections collected	7676
Independent reflections	2832 [R_{int} = 0.0328, R_{sigma} = 0.0354]
Data/restraints/parameters	2832/1457/354
Goodness-of-fit on F ²	1.157
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0461, wR_2 = 0.1153
Final R indexes [all data]	R_1 = 0.0575, wR_2 = 0.1196
Largest diff. peak/hole / e Å ⁻³	0.29/-0.35

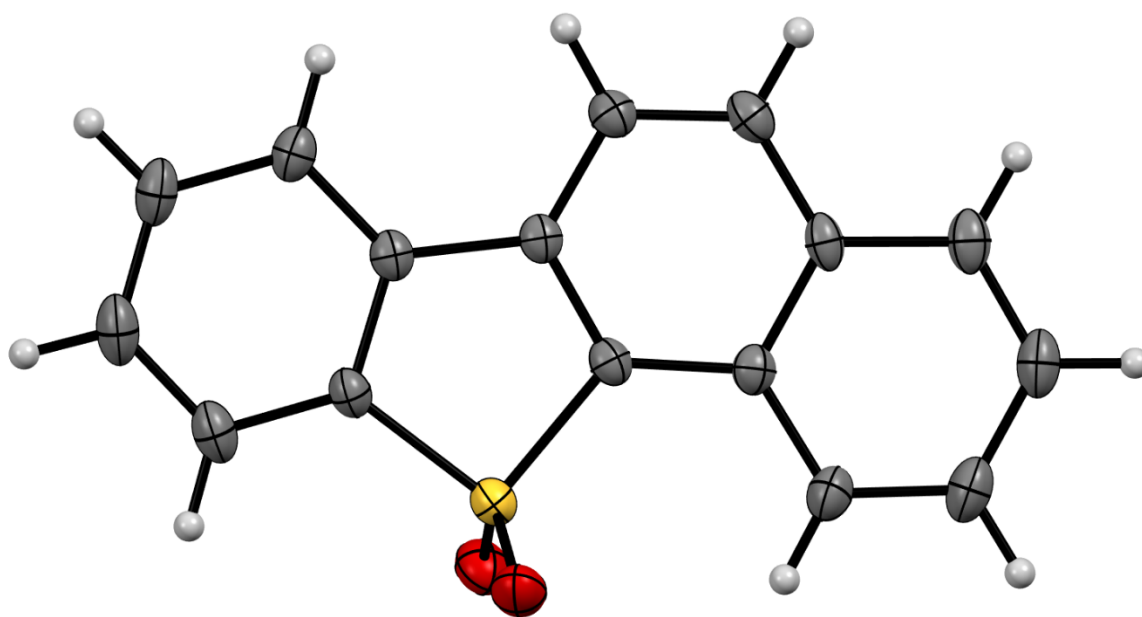


Figure S3. ORTEP drawing of **2d** with 50% thermal ellipsoids. Disorder omitted for clarity.

3. DFT Calculations

Density functional theory (DFT) calculations were performed using the Gaussian 16 program.²⁹ Geometries were optimized at the UM06-2X/6-31+G(d,p).^{30,31} SMD solvation model³² in HFIP^{33,34} was applied. Thermochemical corrections were obtained from frequency calculations at the same level of theory. The energy profile is illustrated in Figure S4 and Figure S5. Calculated structures are illustrated using ChemDraw and CYLView.³⁵

Underneath the Cartesian coordinates for the optimized geometries are listed the following energies:

Electronic energy (E)

Enthalpy at 298.15 K (H)

Gibbs free energy at 298.15 K and 1 mol L⁻¹ (G)

Otherwise noted, all energies are given in Hartree.

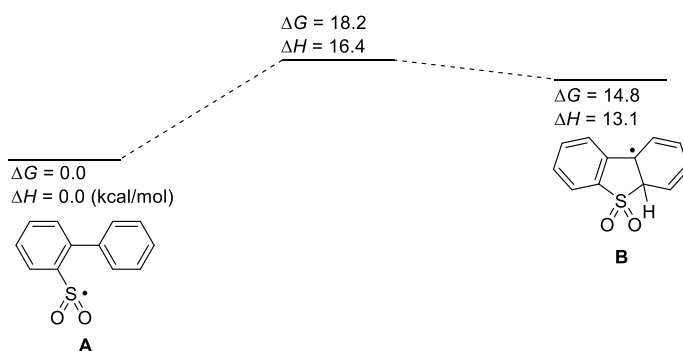


Figure S4. Gibbs free energies (ΔG) and enthalpies (ΔH) of the radical cyclization of **A** to **B** calculated at the UM06-2X/6-31+G(d,p)_{HFIP(SMD)} level of theory. Energies are shown in kcal mol⁻¹ (1 kcal mol⁻¹ = 4.184 kJ).

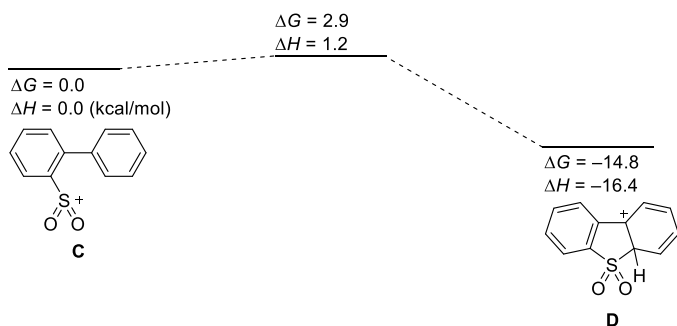
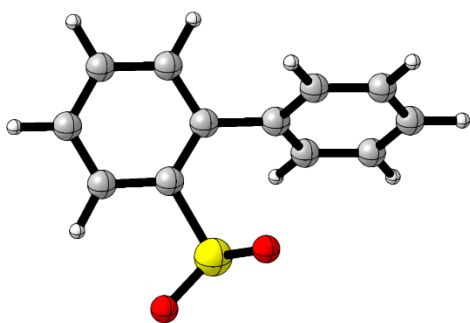


Figure S5. Gibbs free energies (ΔG) and enthalpies (ΔH) of the intramolecular S_EAr from **C** to **D** calculated at the UM06-2X/6-31+G(d,p)_{HFIP(SMD)} level of theory. Energies are shown in kcal mol⁻¹ (1 kcal mol⁻¹ = 4.184 kJ).



A

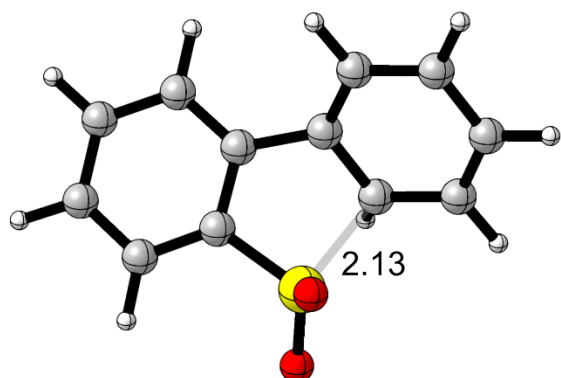
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C	-1.3869300	-0.0402140	-0.0244530
C	-0.3899220	0.9408630	-0.0995710
C	-0.8206990	2.2711600	-0.1308140
C	1.0574400	0.6090430	-0.1526680
C	1.9181840	1.0693640	0.8485920
C	3.2686740	0.7292980	0.8192820
C	3.7691700	-0.0672910	-0.2111350
C	2.9166480	-0.5164330	-1.2189820
C	1.5648030	-0.1798340	-1.1916270
S	-0.9078280	-1.7702480	0.1619510
O	0.1201460	-1.8619760	1.2190070
O	-2.1553630	-2.5491090	0.2984780
H	-2.4845740	3.6271050	-0.1648490
H	-4.1984500	1.8272580	-0.1040140
H	-3.4806030	-0.5568790	-0.0037410
H	-0.0758380	3.0606200	-0.1819420
H	1.5229420	1.6747290	1.6603480
H	3.9294990	1.0806920	1.6065390
H	4.8221380	-0.3331880	-0.2306400
H	3.3036600	-1.1257060	-2.0306190
H	0.9068970	-0.5135700	-1.9917380

Imaginary freq = 0

E = -1010.97007637

H = -1010.776174

G = -1010.829774



TS^{A-B}

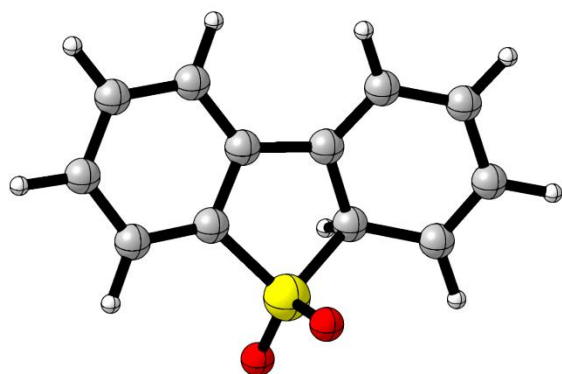
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C	-3.1810940	1.4873810	0.1131890
C	-2.6567990	0.1949020	0.0983180
C	-1.2816560	0.0685340	-0.0176330
C	-0.4087470	1.1572150	-0.1342000
C	-0.9516600	2.4432460	-0.0993460
C	1.0092040	0.7754130	-0.2315480
C	2.0163890	1.3539400	0.5178470
C	3.2607780	0.7217420	0.6359650
C	3.4886660	-0.5246930	0.0160010
C	2.5204890	-1.1187660	-0.7592880
C	1.2331550	-0.4934230	-0.9152670
S	-0.3937660	-1.4810390	0.0418570
O	-0.0469430	-1.8025840	1.4422610
O	-1.1473430	-2.4922150	-0.7274690
H	-2.7573630	3.5944680	0.0338830
H	-4.2535600	1.6321280	0.1990620
H	-3.2954850	-0.6809450	0.1778550
H	-0.3042180	3.3105400	-0.1925540
H	1.8189070	2.2746190	1.0606940
H	4.0426750	1.1789080	1.2334060
H	4.4575240	-1.0035120	0.1241170
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Imaginary freq = 1

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H = -1010.750088

G = -1010.800768



B

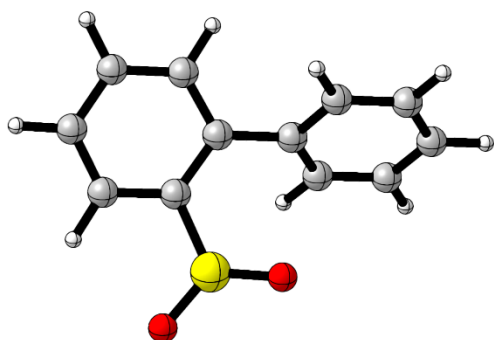
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C	-1.3318210	0.0905740	-0.0703430
C	-0.4467110	1.1781050	-0.0844370
C	-0.9881330	2.4647300	0.0240810
C	0.9548030	0.7844380	-0.1901550
C	2.0506710	1.4767220	0.2670410
C	3.3002880	0.8427960	0.3633840
C	3.4229840	-0.5520190	0.0868580
C	2.3802460	-1.2870850	-0.3838470
C	1.1028310	-0.6107320	-0.7292360
S	-0.4235720	-1.4321050	-0.1137820
O	-0.1940430	-1.9447060	1.2451860
O	-0.9954180	-2.3608770	-1.0981640
H	-2.7911380	3.6088190	0.2015880
H	-4.2988830	1.6490740	0.2045450
H	-3.3523370	-0.6628250	0.0396900
H	-0.3396860	3.3357360	0.0056770
H	1.9321350	2.4965360	0.6244810
H	4.1590140	1.3943640	0.7293830
H	4.3776320	-1.0384890	0.2663160
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C

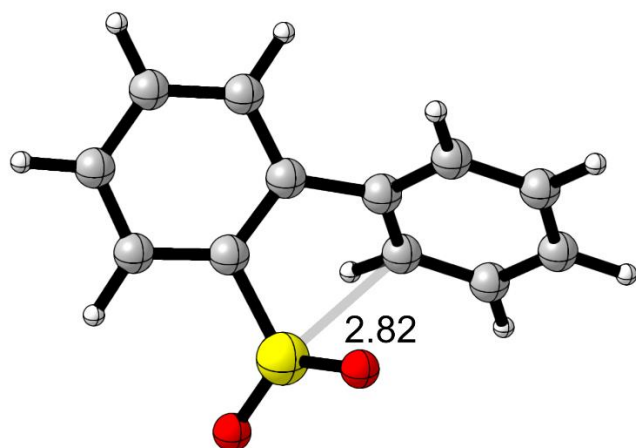
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C	1.9794370	1.1874330	0.7868040
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O	0.3110270	-2.0062320	0.7344470
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H	-0.0404250	3.0500130	-0.1435190
H	1.5899560	1.8373860	1.5658720
H	4.0127950	1.3156130	1.4676890
H	4.8897210	-0.1872540	-0.3031070
H	3.3450320	-1.1513900	-1.9925600
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TS^{C-D}

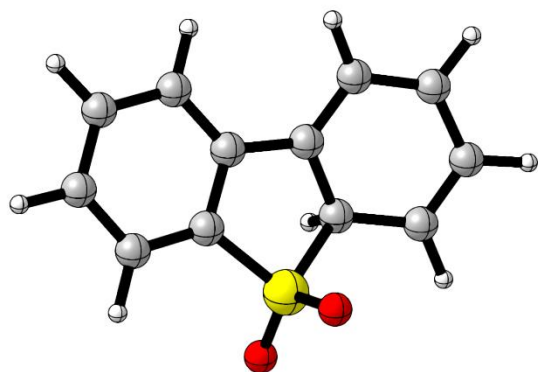
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C	-1.3061590	0.0509050	0.0208360
C	-0.3641660	1.0977400	-0.0169060
C	-0.8846850	2.3895290	-0.0330350
C	1.0526420	0.7303430	-0.1332100
C	2.0073430	1.2092380	0.7687650
C	3.2792850	0.6499460	0.7680870
C	3.6122370	-0.3661000	-0.1372980
C	2.6833700	-0.8042650	-1.0743100
C	1.4005480	-0.2548540	-1.0826540
S	-0.6769460	-1.5245950	0.3325840
O	0.3262600	-1.6912070	1.3390150
O	-1.4604400	-2.5888550	-0.2158750
H	-2.6564650	3.5892240	-0.1224810
H	-4.2295700	1.6805260	-0.1881900
H	-3.3655010	-0.6596190	-0.0955810
H	-0.2061900	3.2359460	-0.0708260
H	1.7313930	1.9621200	1.5013990
H	4.0141180	0.9878870	1.4925200
H	4.6081760	-0.7980280	-0.1174900
H	2.9520350	-1.5585640	-1.8071440
H	0.7040690	-0.5167080	-1.8792590

Imaginary freq = 1

E = -1010.73497977

H = -1010.541258

G = -1010.591296



D

C	-2.3588930	2.6205650	0.0775580
C	-3.2221010	1.5204540	0.0193170
C	-2.7287200	0.2162750	-0.0874920
C	-1.3559010	0.0773990	-0.1227130
C	-0.4659790	1.1619180	-0.0866810
C	-0.9780230	2.4578430	0.0264880
C	0.9248870	0.7633960	-0.1739260
C	2.0293690	1.4691060	0.2554150
C	3.2429480	0.7879050	0.3683300
C	3.4053110	-0.5918630	0.0561270
C	2.3587580	-1.3038960	-0.4369460
C	1.0898480	-0.6104230	-0.7037610
S	-0.4668550	-1.4566960	-0.1907890
O	-0.2431920	-2.0080000	1.1419490
O	-0.9821150	-2.3234840	-1.2416560
H	-2.7754290	3.6196240	0.1562890
H	-4.2950050	1.6785040	0.0659620
H	-3.3918670	-0.6430410	-0.1236580
H	-0.3113290	3.3144760	0.0403230
H	1.9392780	2.4939520	0.6005970
H	4.1010200	1.3275210	0.7609840
H	4.3714240	-1.0590740	0.2101560
H	2.4588650	-2.3456300	-0.7311610
H	0.9883850	-0.5479440	-1.8083800

Imaginary freq = 0

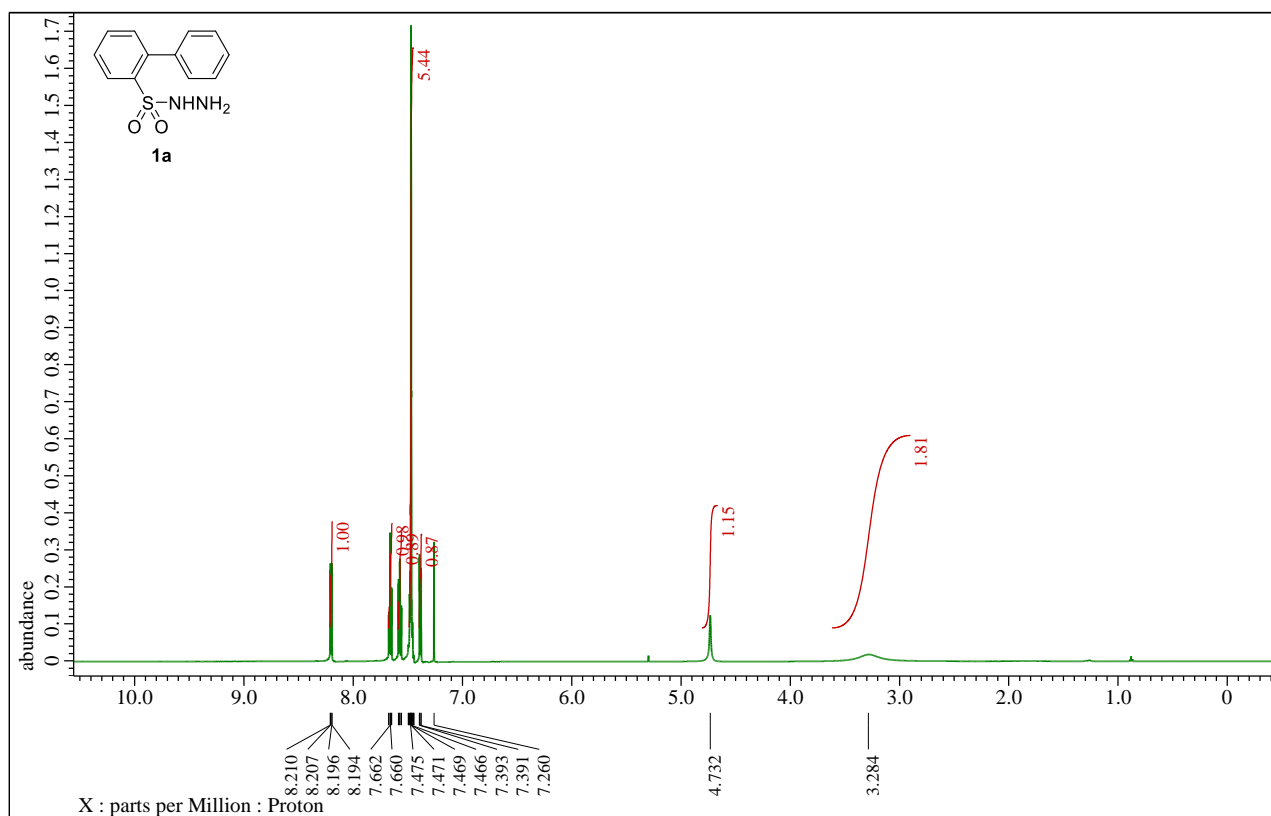
E = -1010.76376526

H = -1010.569286

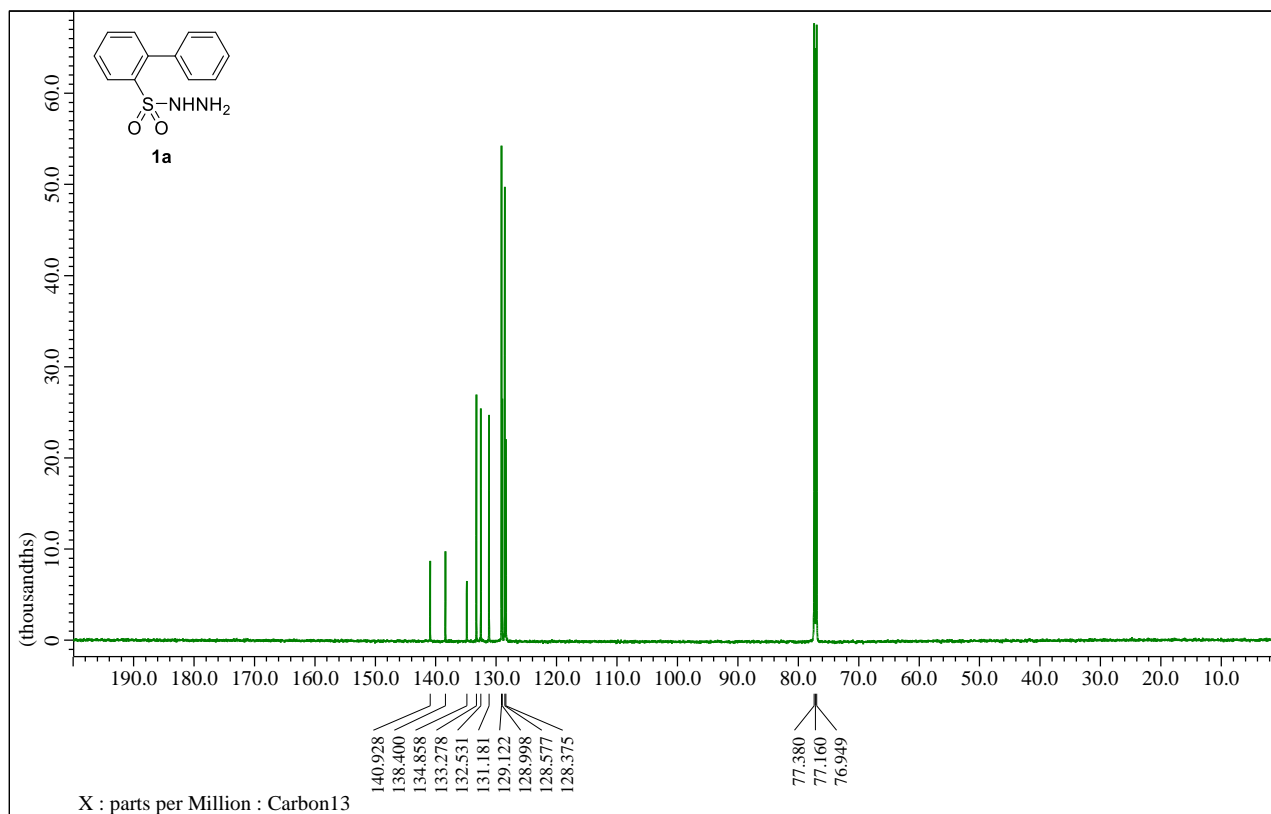
G = -1010.619554

4. NMR Spectra

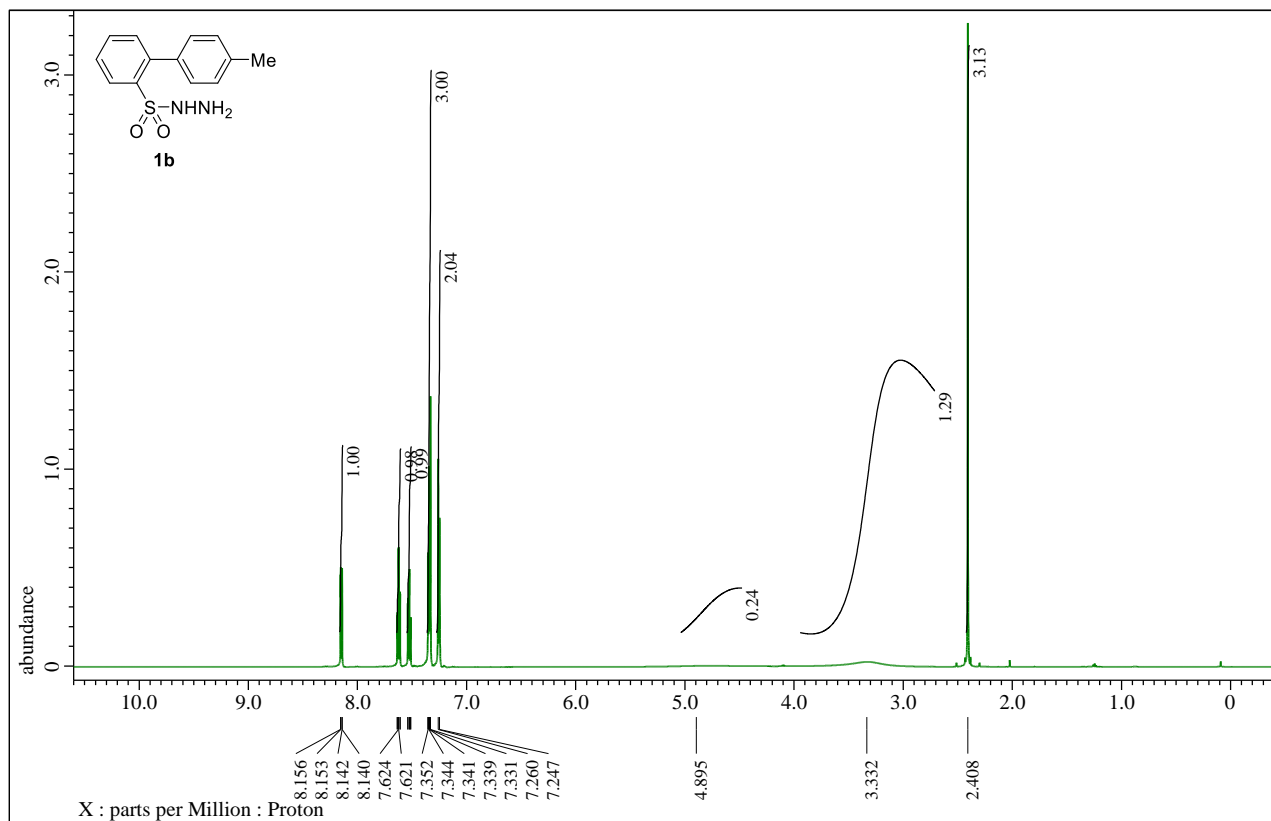
[1,1'-Biphenyl]-2-sulfonohydrazide (1a) ^1H NMR (600 MHz, CDCl_3)



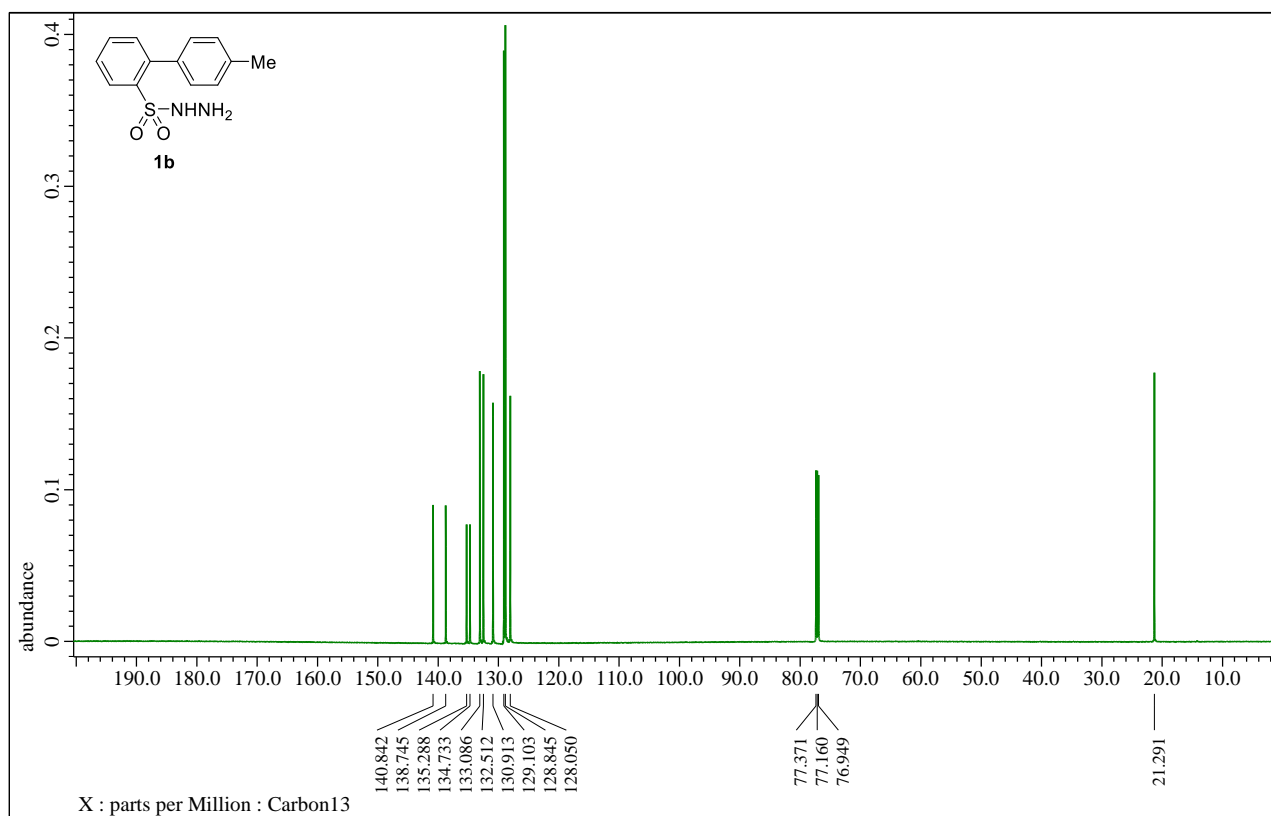
[1,1'-Biphenyl]-2-sulfonohydrazide (1a) ^{13}C NMR (150 MHz, CDCl_3)



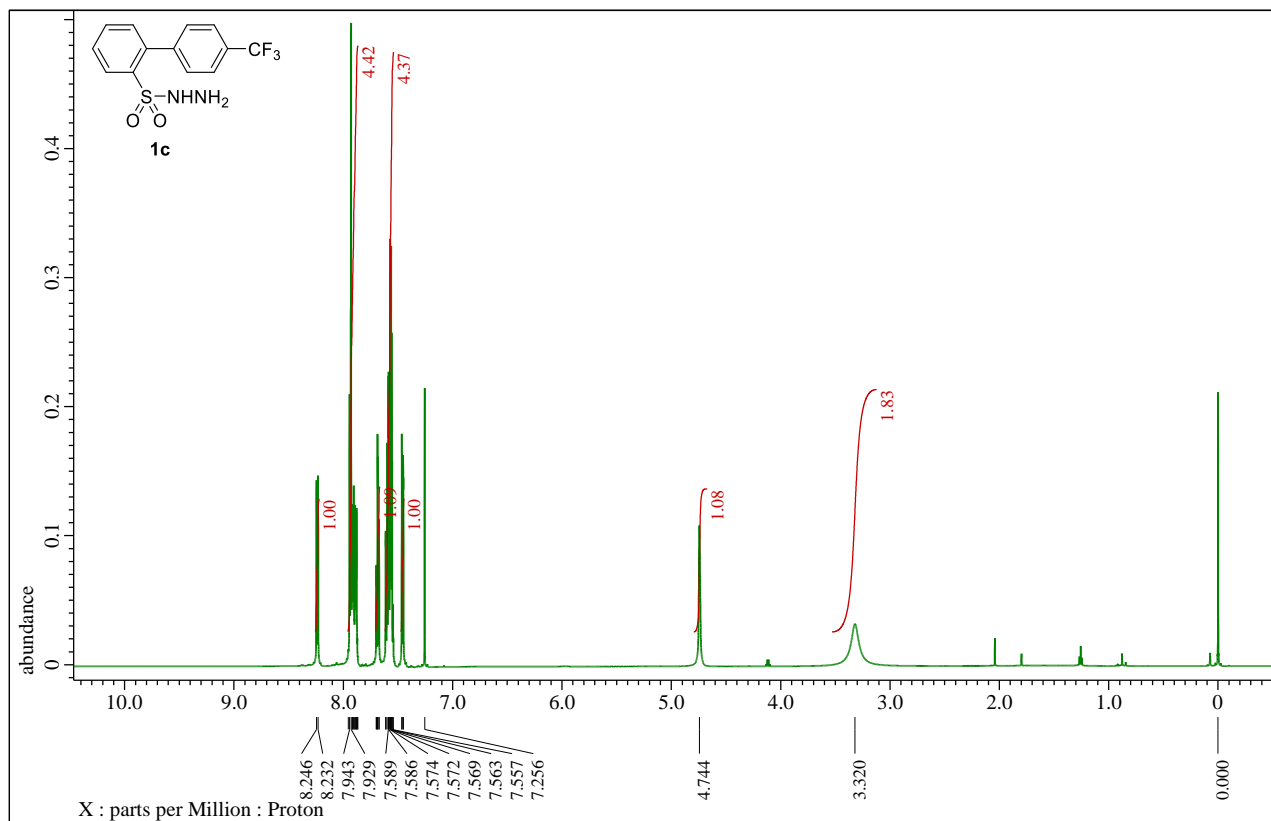
4'-Methyl-[1,1'-biphenyl]-2-sulfonohydrazide (1b) ^1H NMR (600 MHz, CDCl_3)



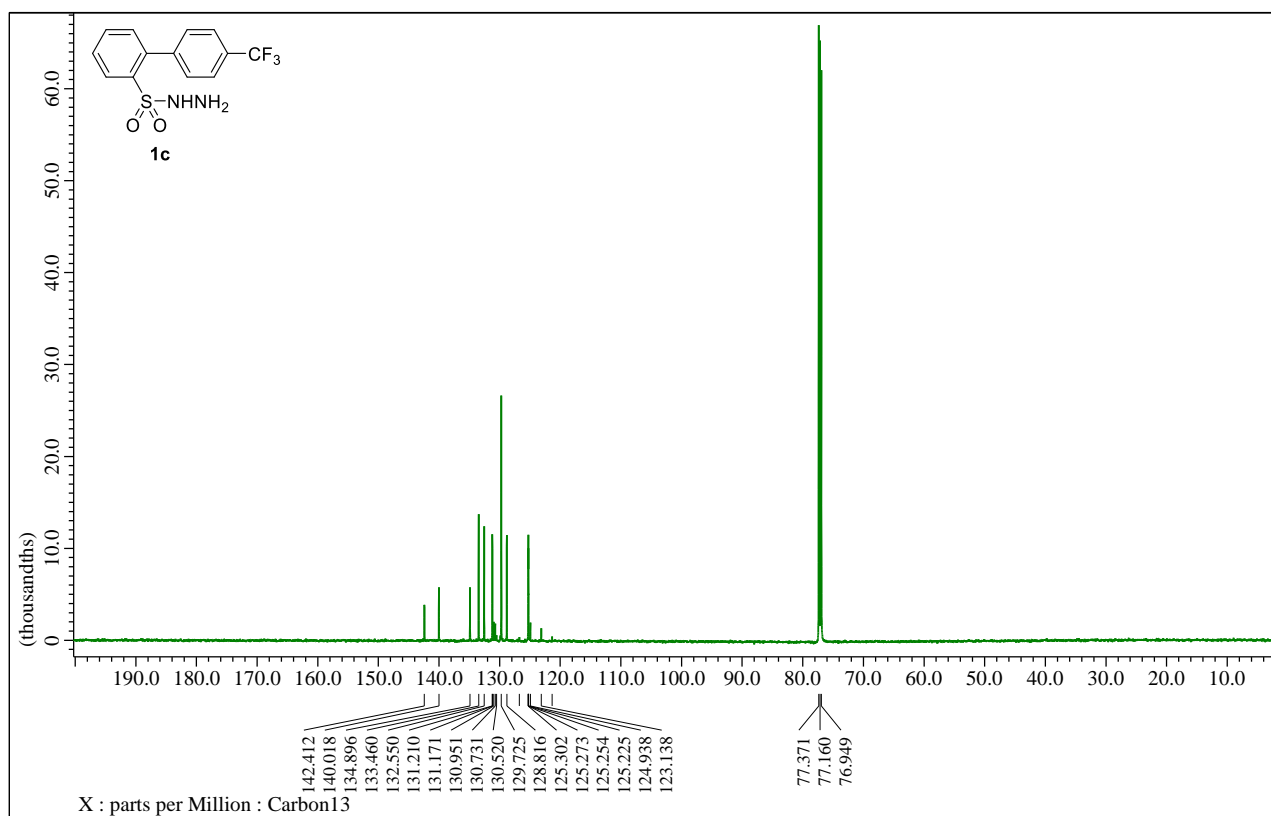
4'-Methyl-[1,1'-biphenyl]-2-sulfonohydrazide (1b) ^{13}C NMR (150 MHz, CDCl_3)



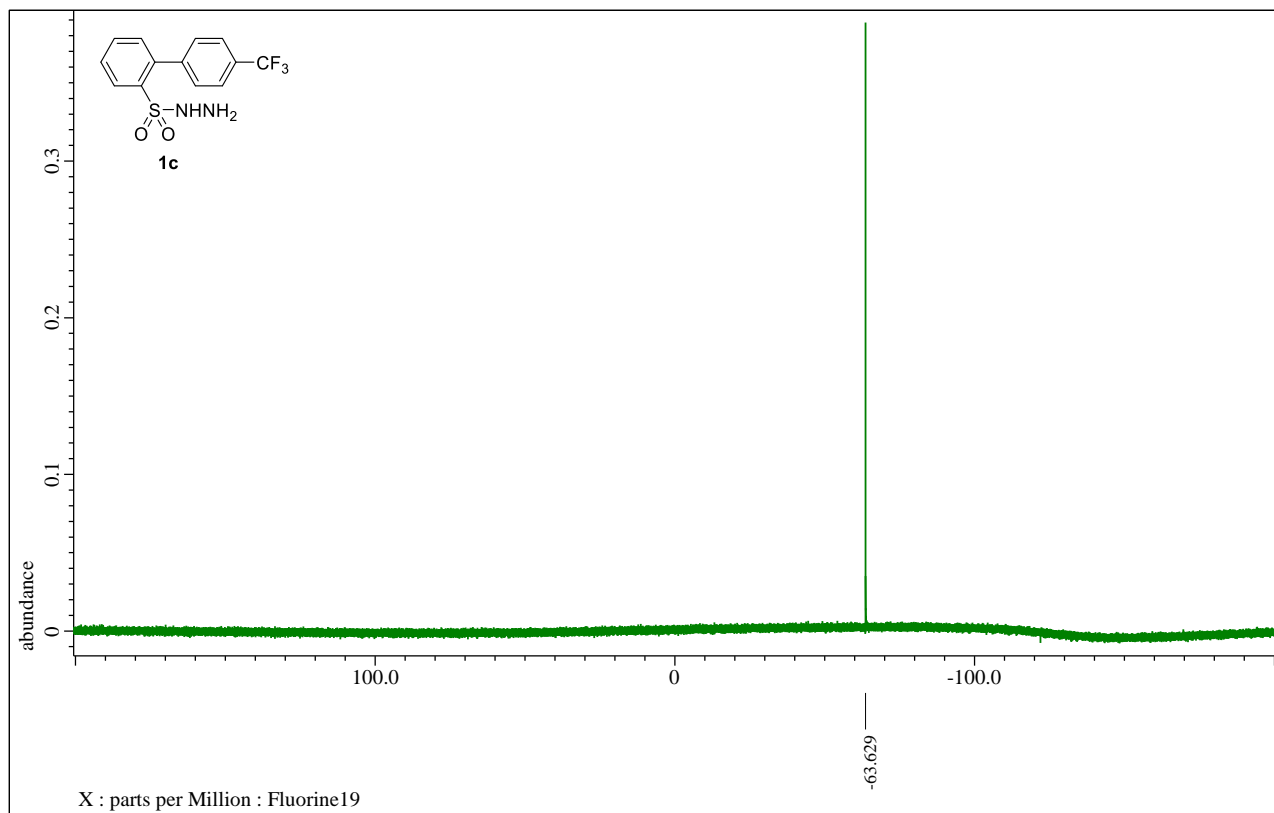
4'-(Trifluoromethyl)-[1,1'-biphenyl]-2-sulfonohydrazide (1c) ^1H NMR (600 MHz, CDCl_3)



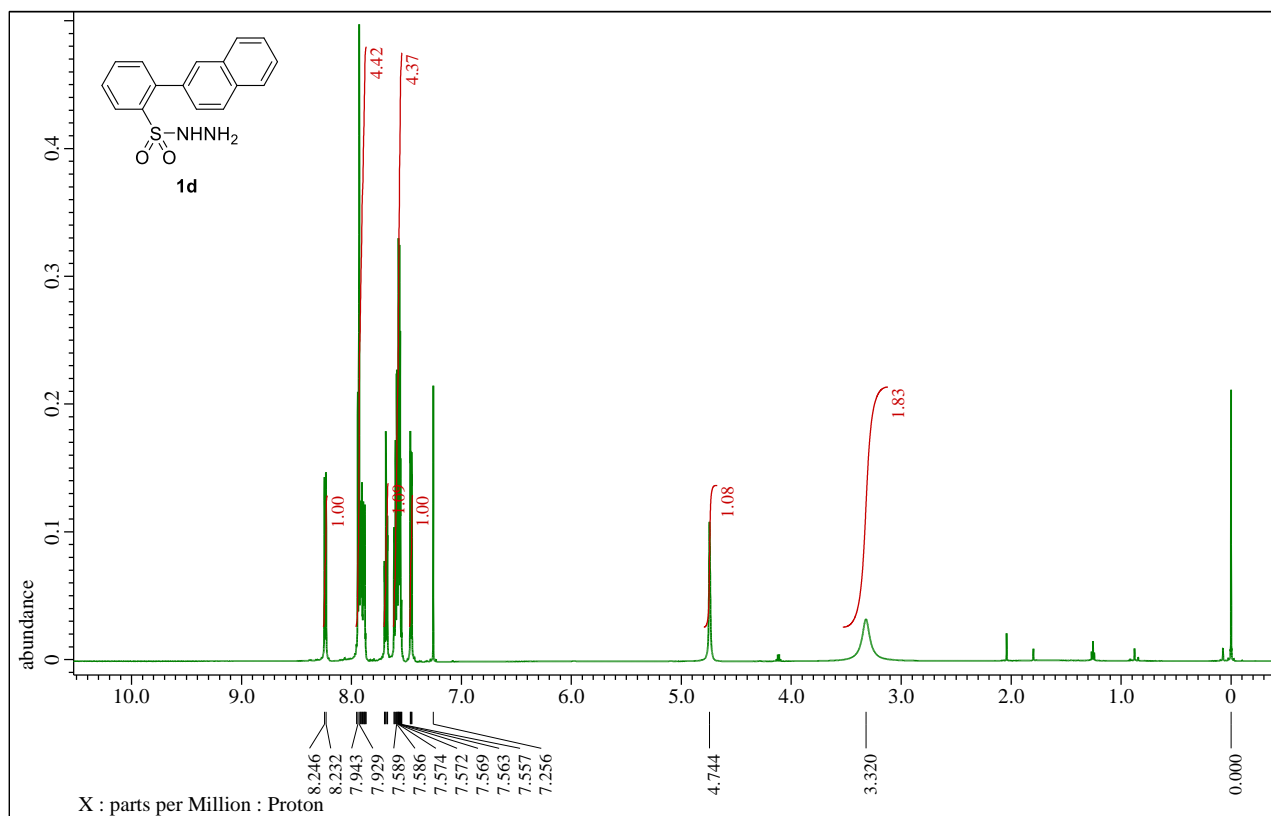
4'-(Trifluoromethyl)-[1,1'-biphenyl]-2-sulfonohydrazide (1c) ^{13}C NMR (150 MHz, CDCl_3)



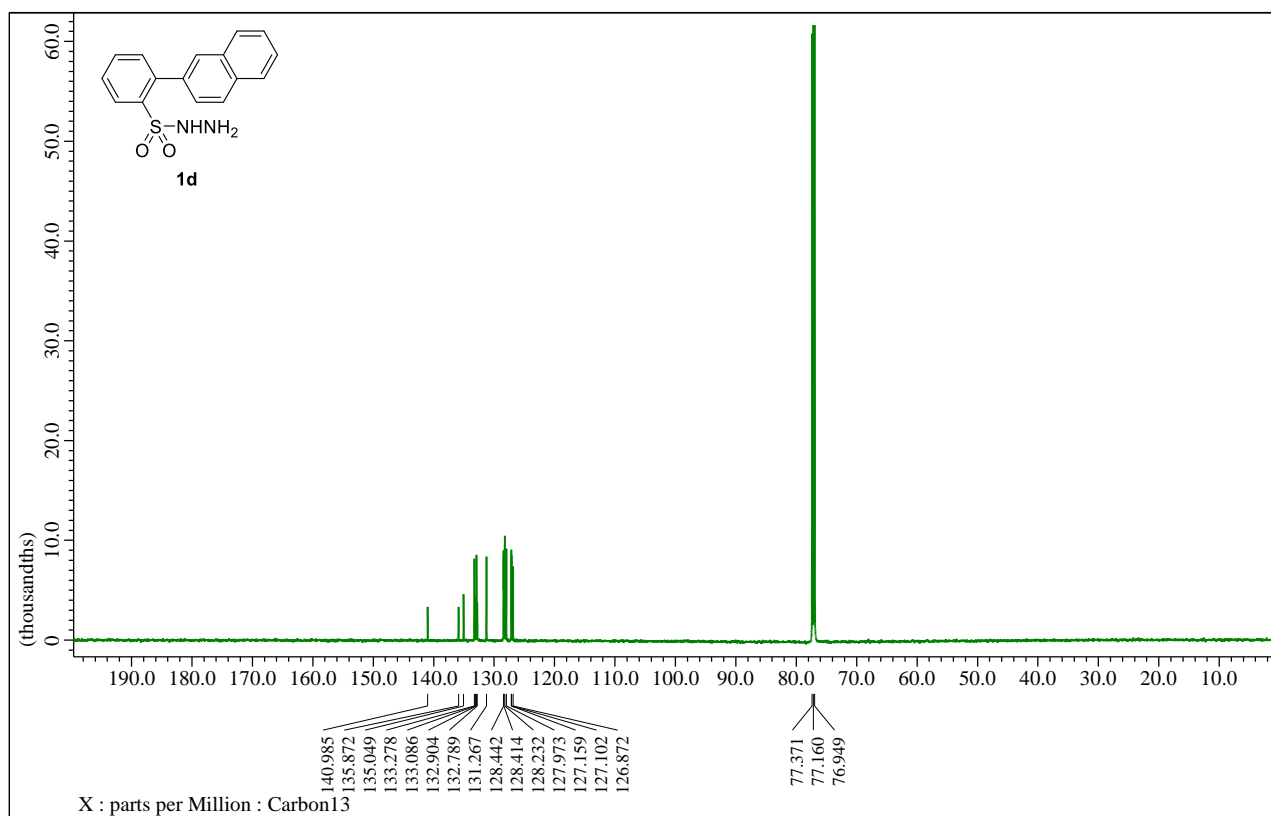
4'-(Trifluoromethyl)-[1,1'-biphenyl]-2-sulfonohydrazide (1c) ^{19}F NMR (376 MHz, CDCl_3)



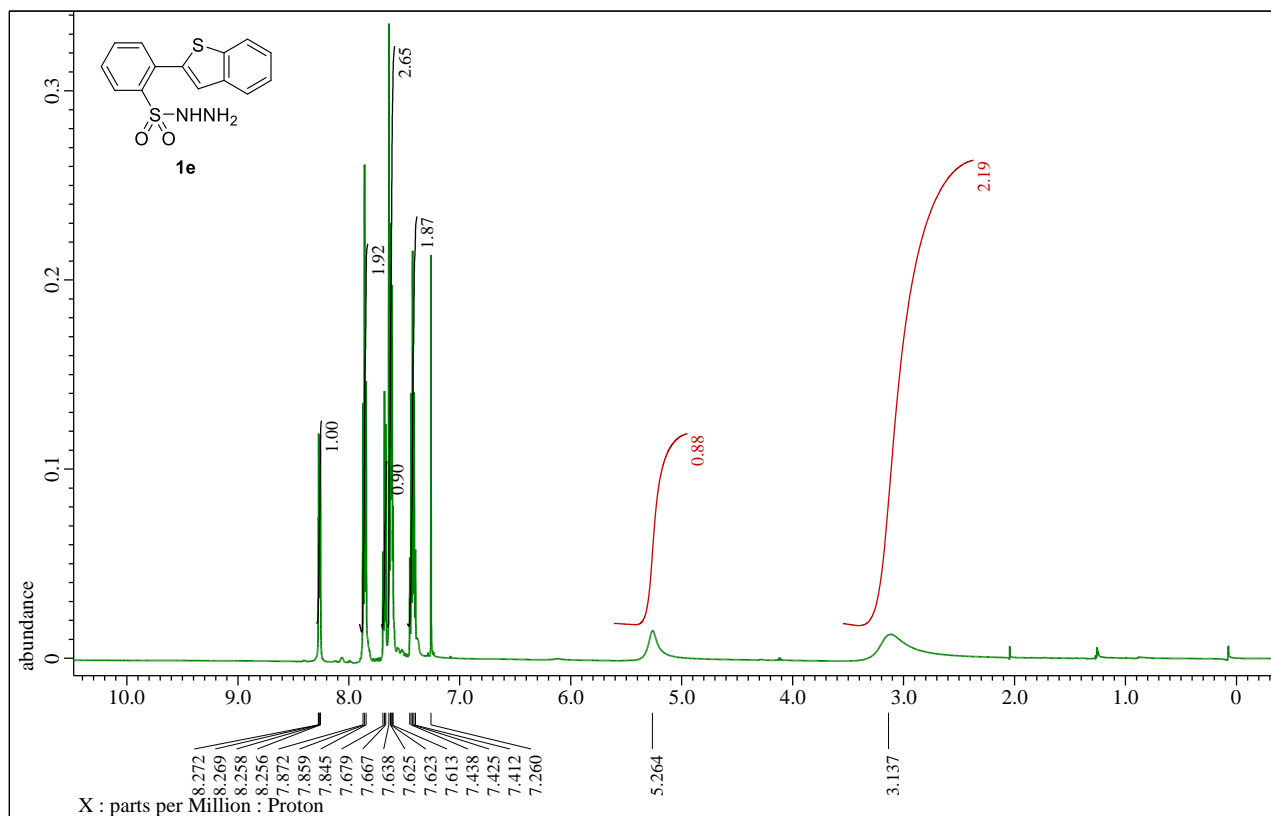
2-(Naphthalen-2-yl)benzenesulfonylhydrazide (1d) ^1H NMR (600 MHz, CDCl_3)



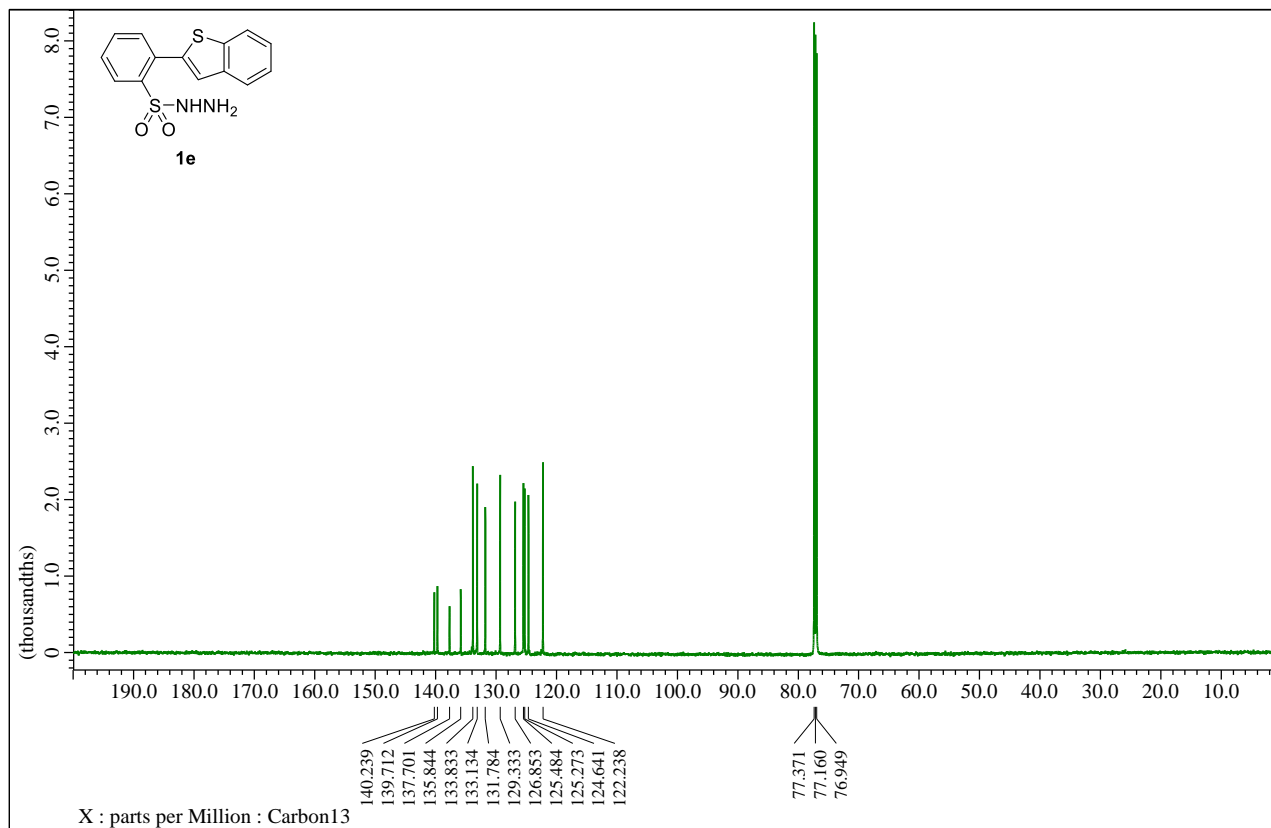
2-(Naphthalen-2-yl)benzenesulfonylhydrazide (1d) ^{13}C NMR (150 MHz, CDCl_3)



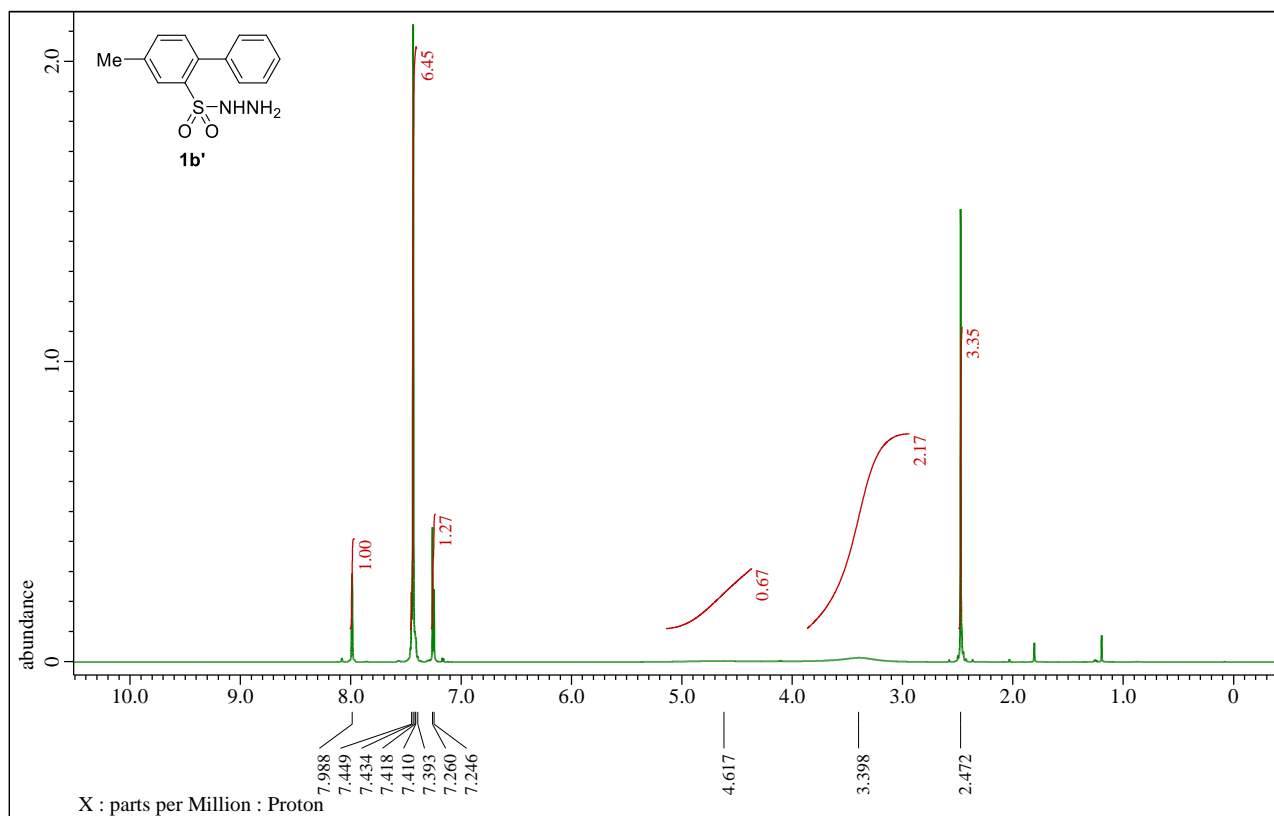
2-(Benzo[*b*]thiophen-2-yl)benzenesulfonohydrazide (1e) ^1H NMR (600 MHz, CDCl_3)



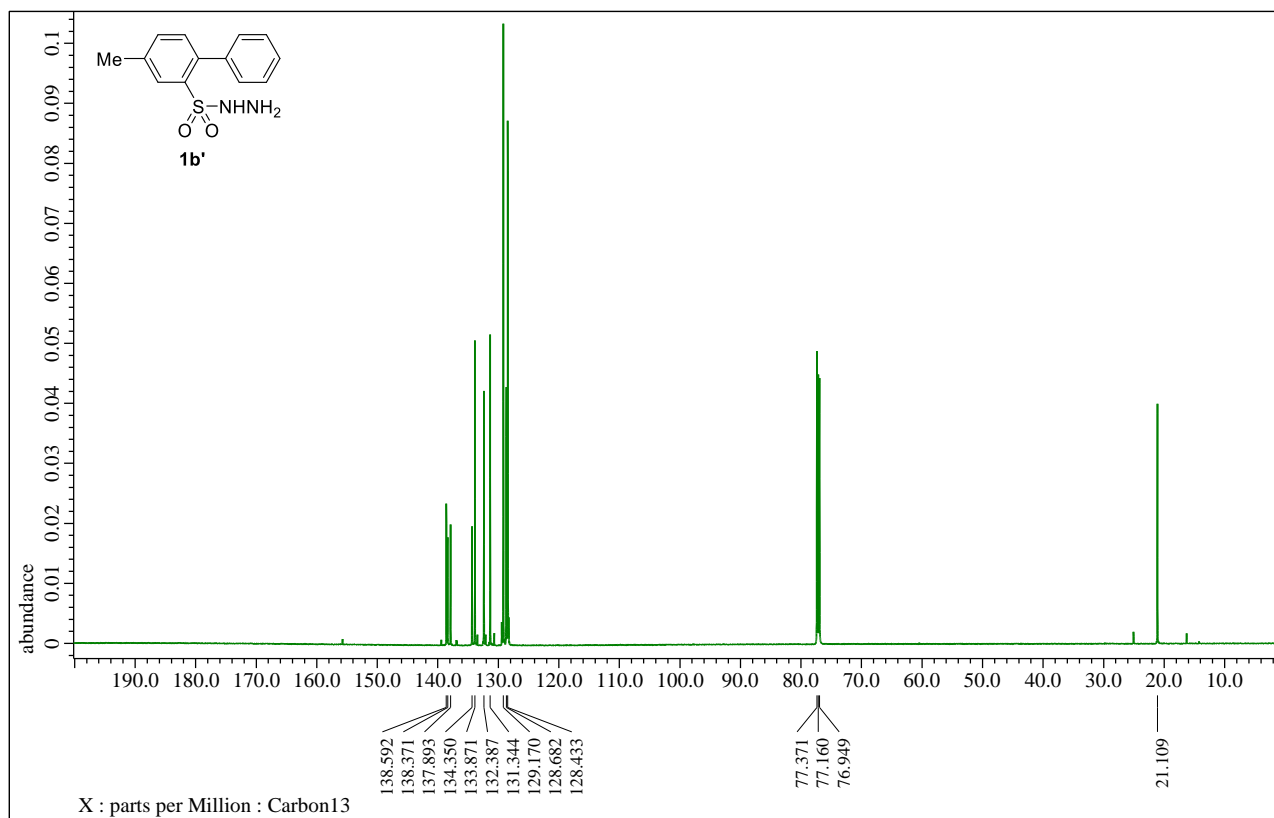
2-(Benzo[*b*]thiophen-2-yl)benzenesulfonohydrazide (1e) ^{13}C NMR (150 MHz, CDCl_3)



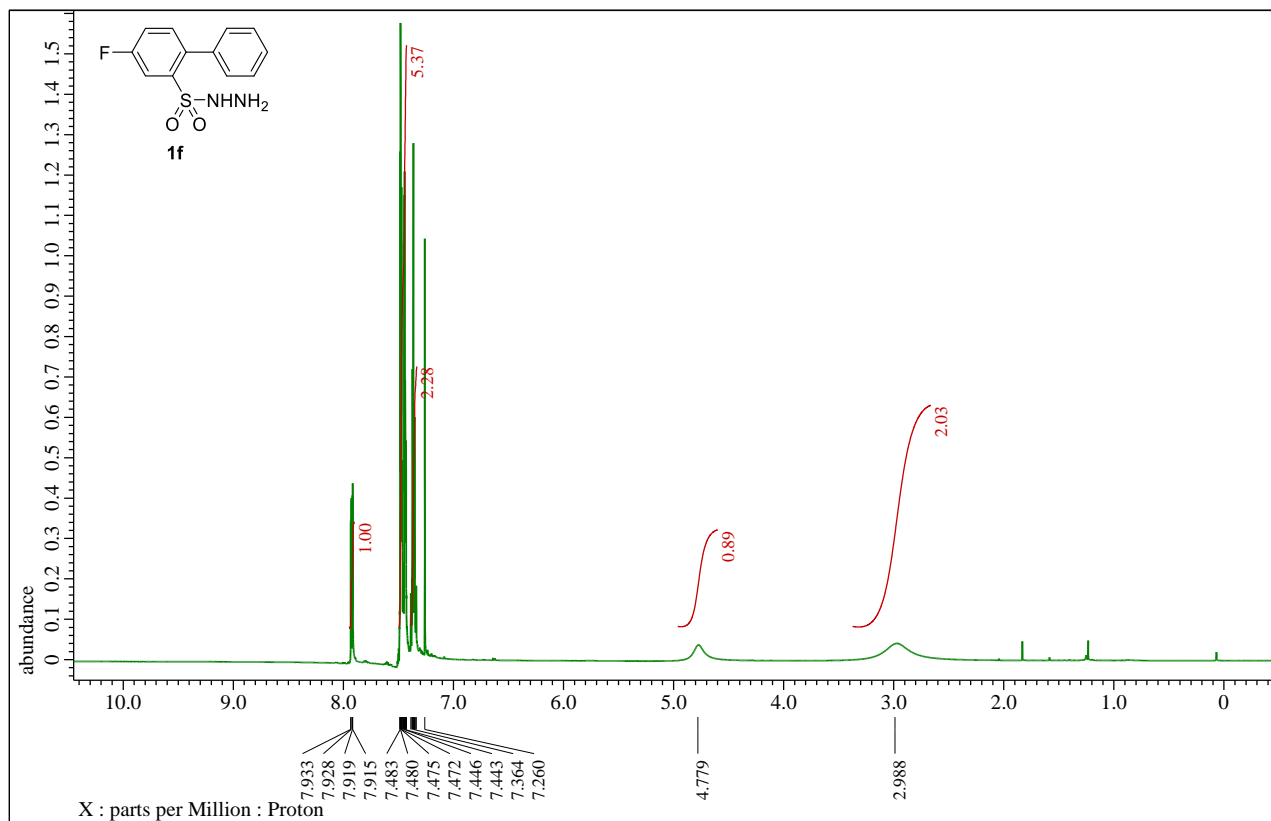
4-Methyl-[1,1'-biphenyl]-2-sulfonohydrazide (1b') ^1H NMR (600 MHz, CDCl_3)



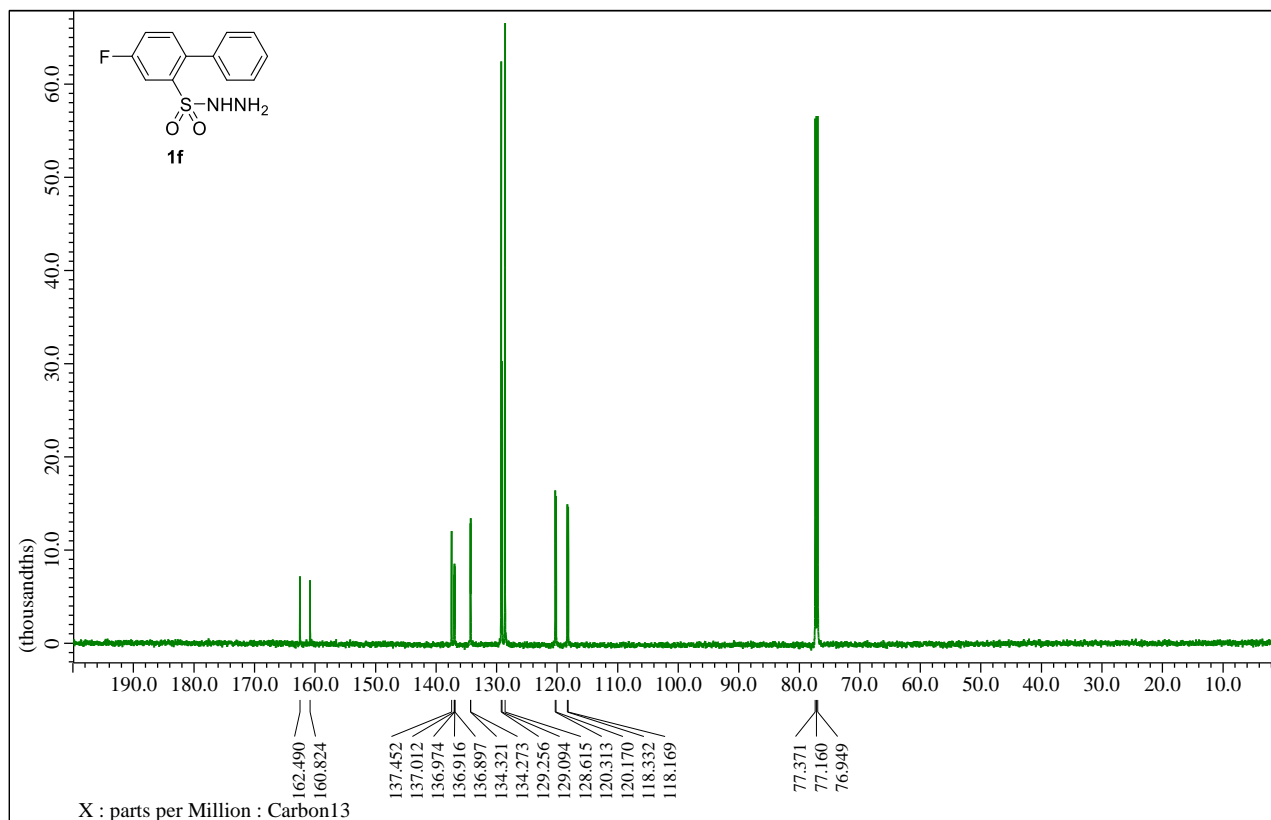
4-Methyl-[1,1'-biphenyl]-2-sulfonohydrazide (1b') ^{13}C NMR (150 MHz, CDCl_3)



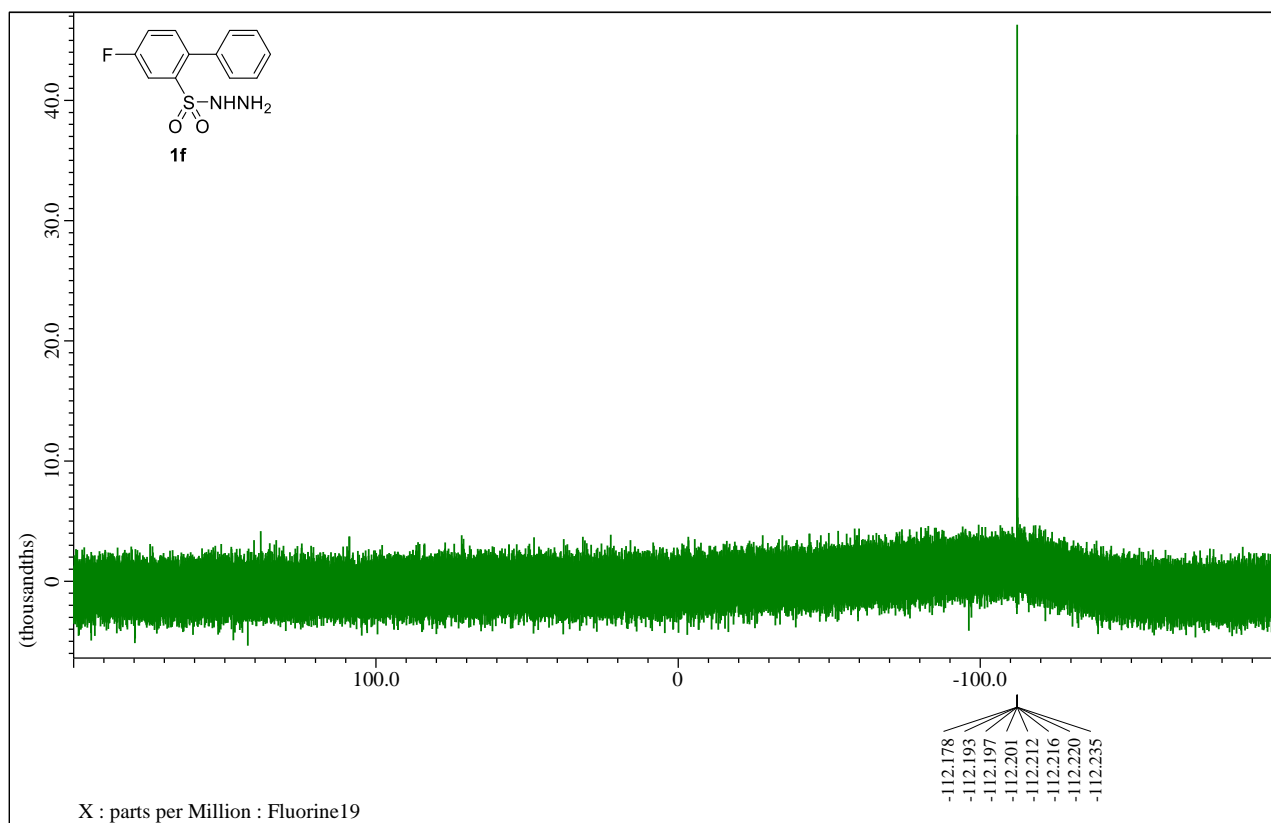
4-Fluoro-[1,1'-biphenyl]-2-sulfonylhydrazide (1f) ^1H NMR (600 MHz, CDCl_3)



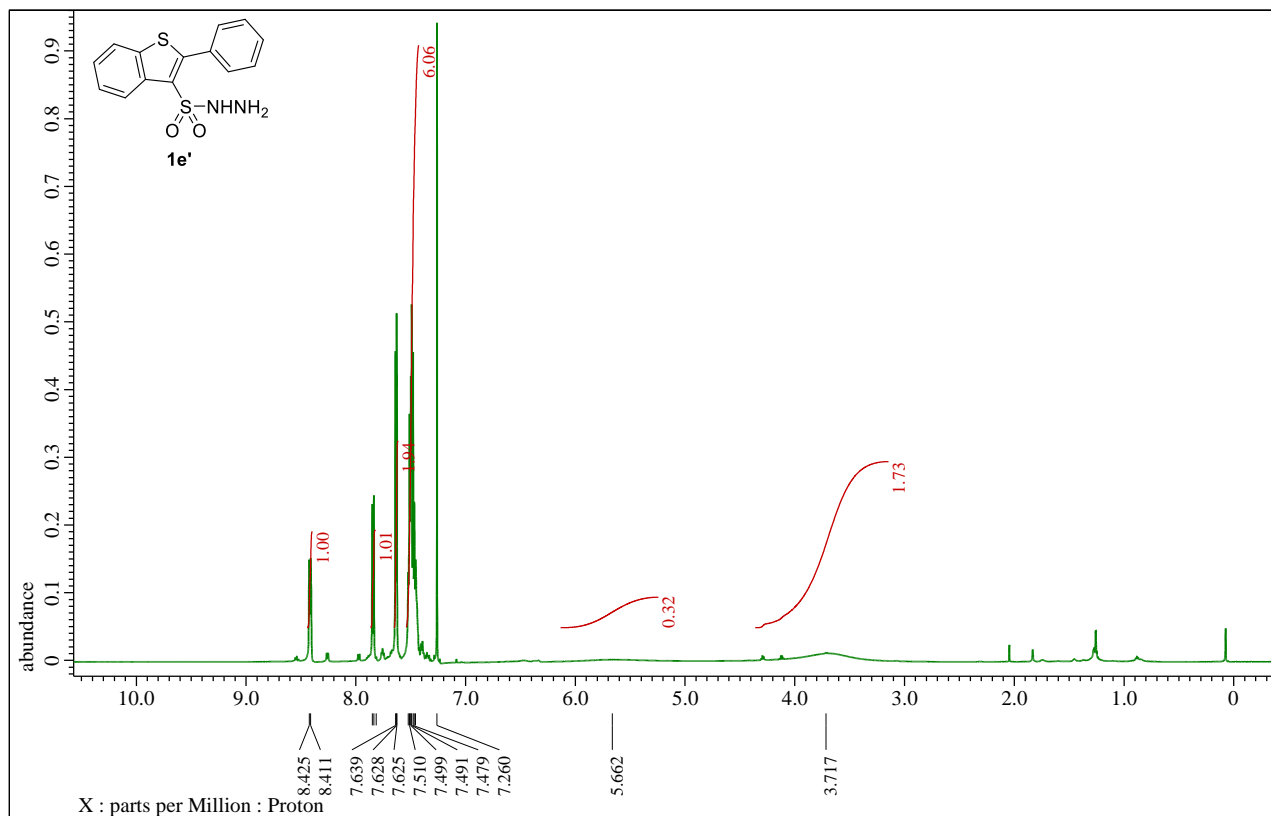
4-Fluoro-[1,1'-biphenyl]-2-sulfonylhydrazide (1f) ^{13}C NMR (150 MHz, CDCl_3)



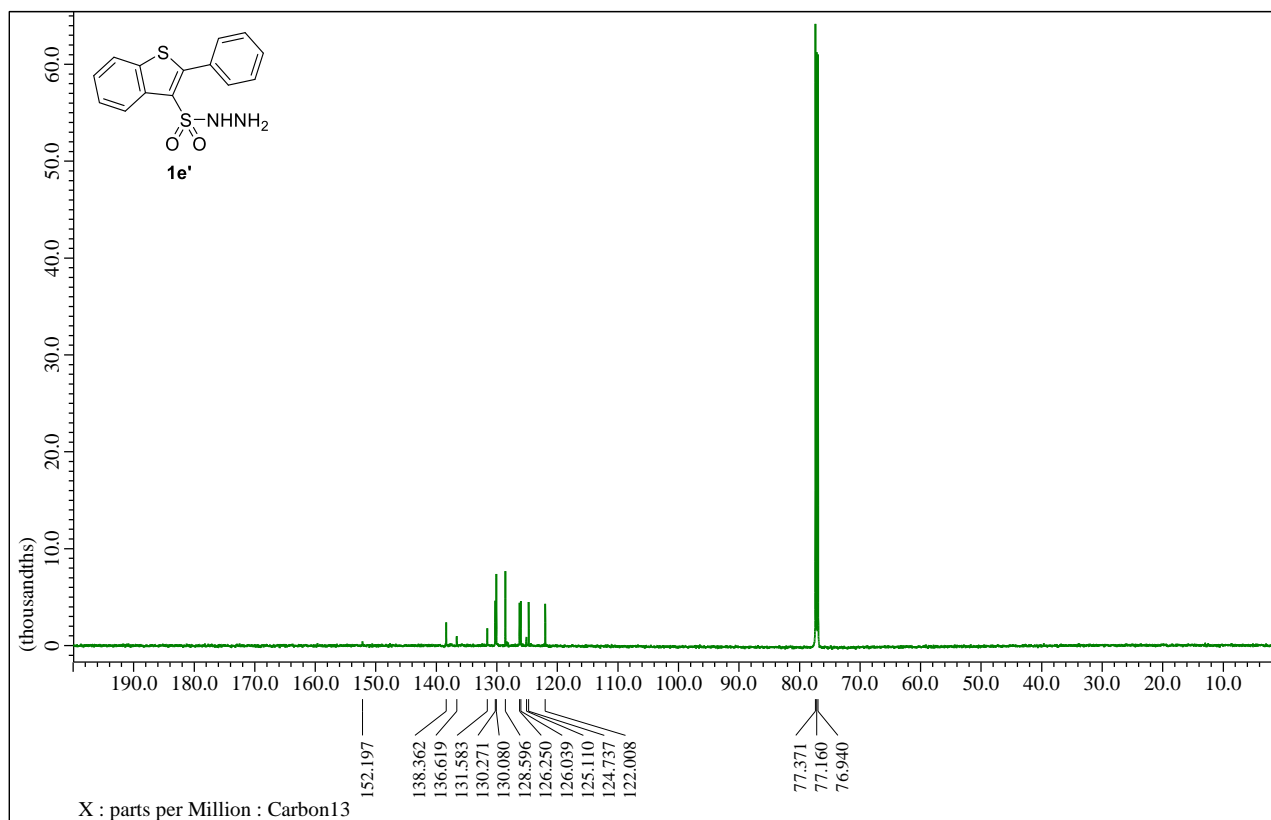
4-Fluoro-[1,1'-biphenyl]-2-sulfonohydrazide (1f) ^{19}F NMR (376 MHz, CDCl_3)



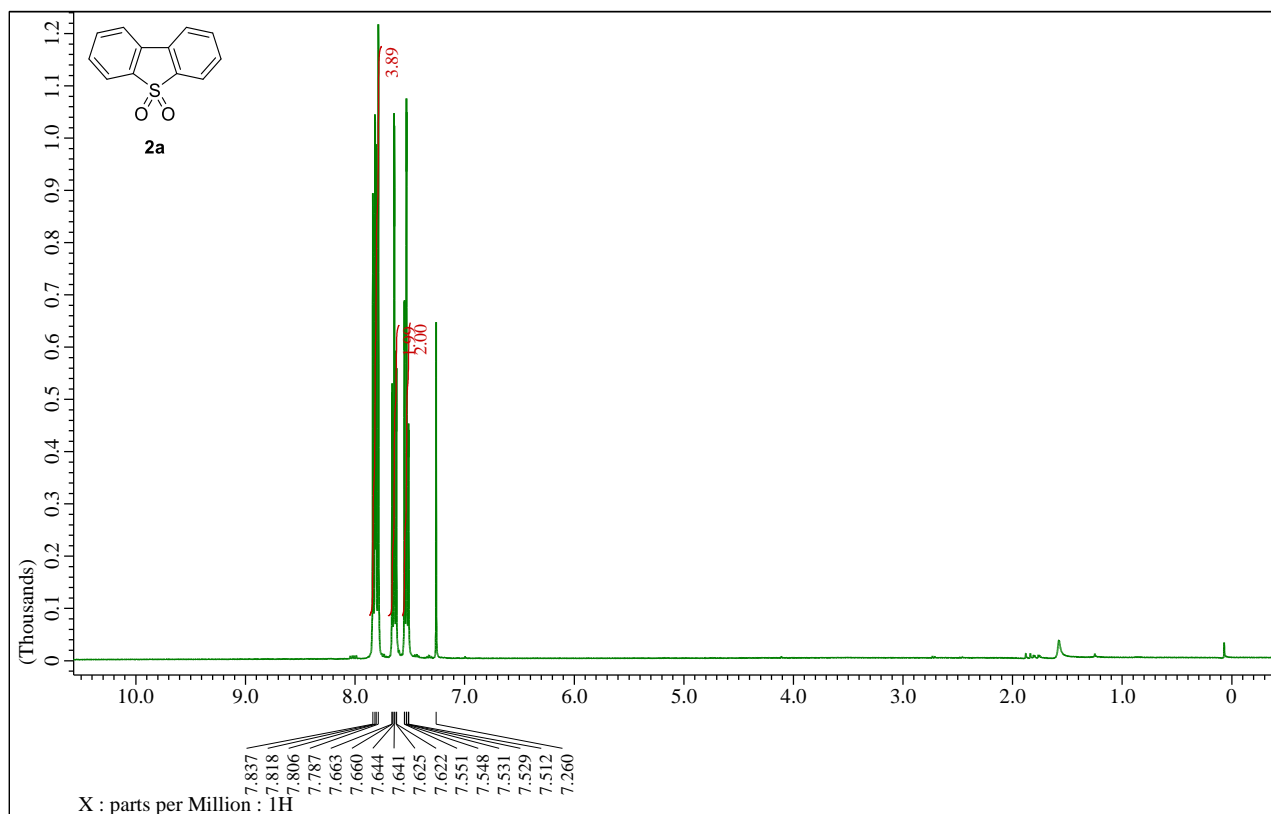
2-Phenylbenzo[*b*]thiophene-3-sulfonohydrazide (1e') ¹H NMR (600 MHz, CDCl₃)



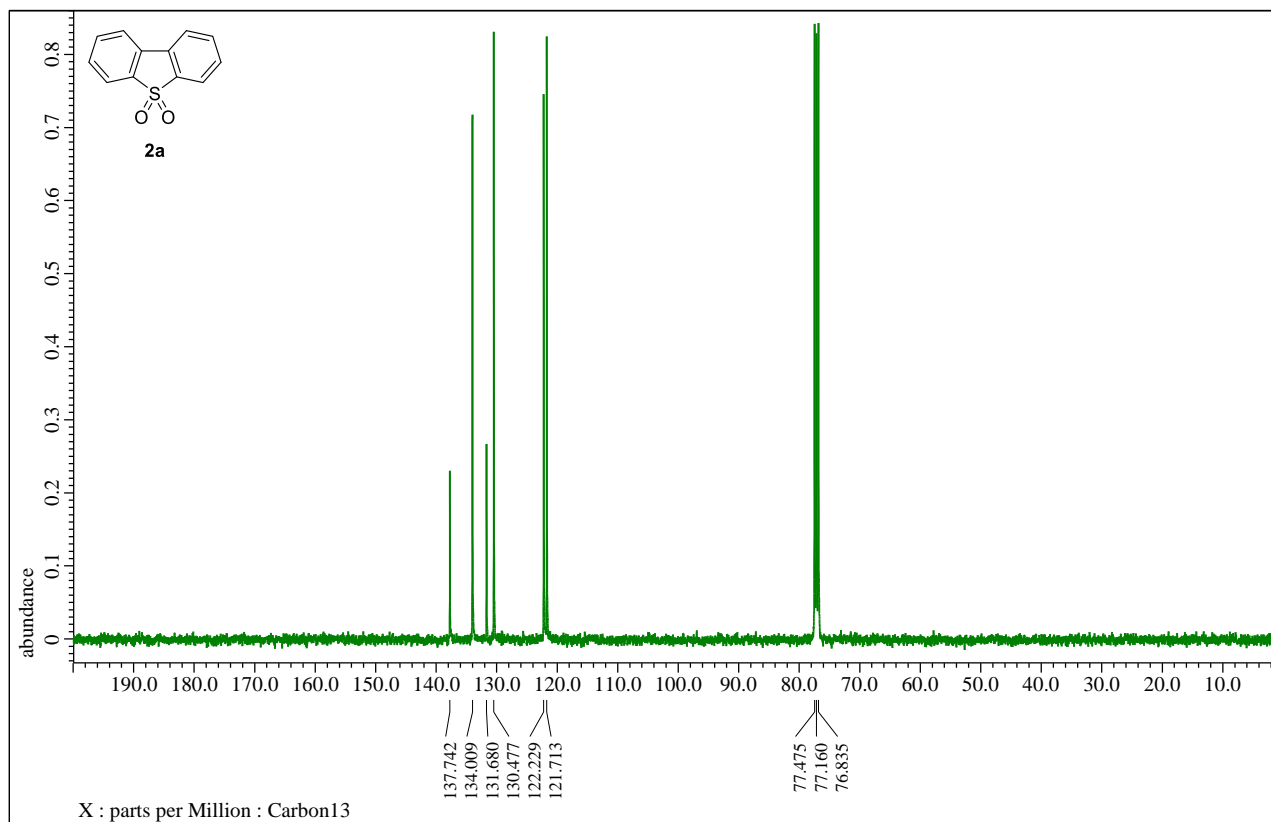
2-Phenylbenzo[*b*]thiophene-3-sulfonohydrazide (1e') ¹³C NMR (150 MHz, CDCl₃)



Dibenzo[*b,d*]thiophene 5,5-Dioxide (2a) ^1H NMR (400 MHz, CDCl_3)



Dibenzo[*b,d*]thiophene 5,5-Dioxide (2a) ^{13}C NMR (100 MHz, CDCl_3)



Chemical structure of **2b** (2-methyl-1,1'-biphenyl-4,4'-diyl sulfone) is shown in the top left corner.

The ^1H NMR spectrum (CDCl₃) shows the following peaks and integrations:

Chemical Shift (ppm)	Integration
7.813, 7.801, 7.760, 7.748, 7.682, 7.669, 7.636, 7.625, 7.623, 7.511, 7.510, 7.498, 7.497, 7.447, 7.260	1.00, 0.98, 1.08, 0.89, 2.05
2.469	3.22

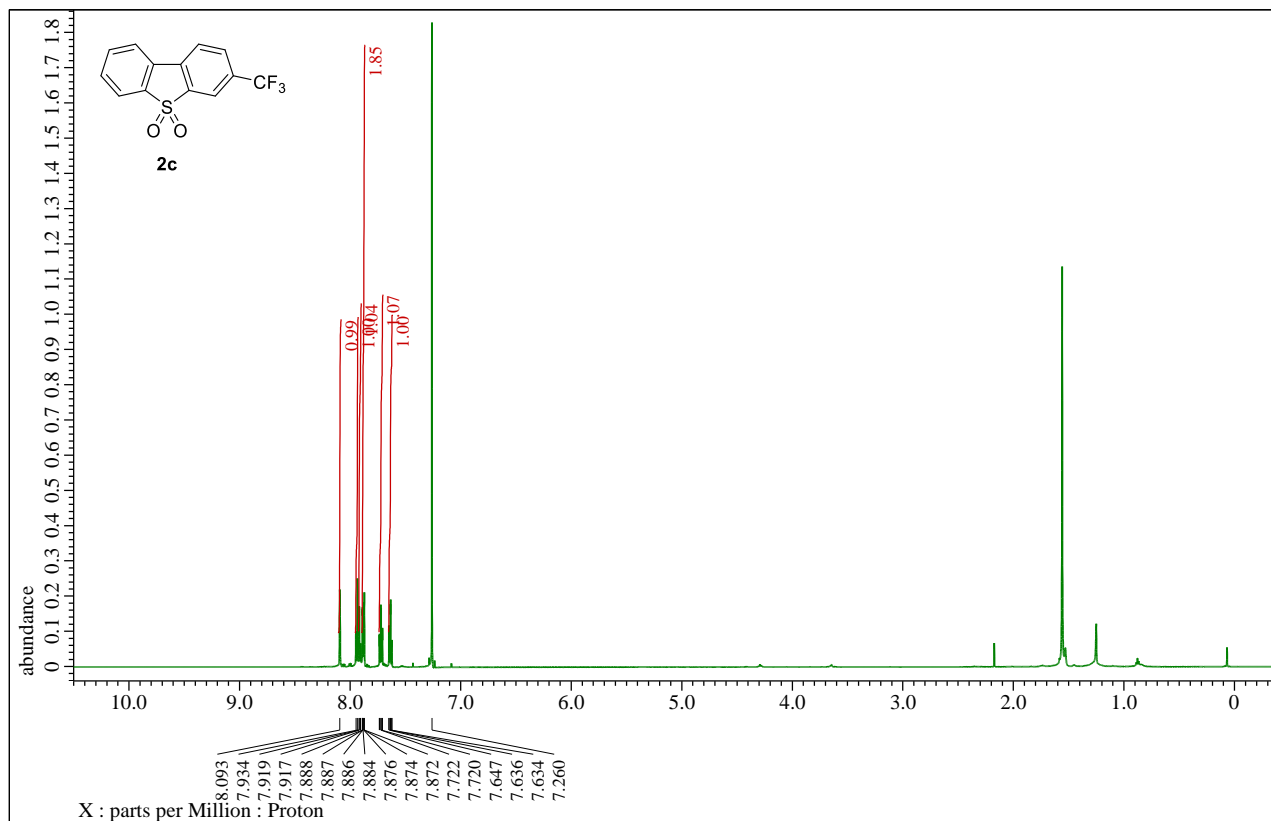
X : parts per Million : Proton

Chemical structure of **2b** (2-methyl-1,1'-biphenyl-4,4'-diyl sulfone) is shown in the top left corner.

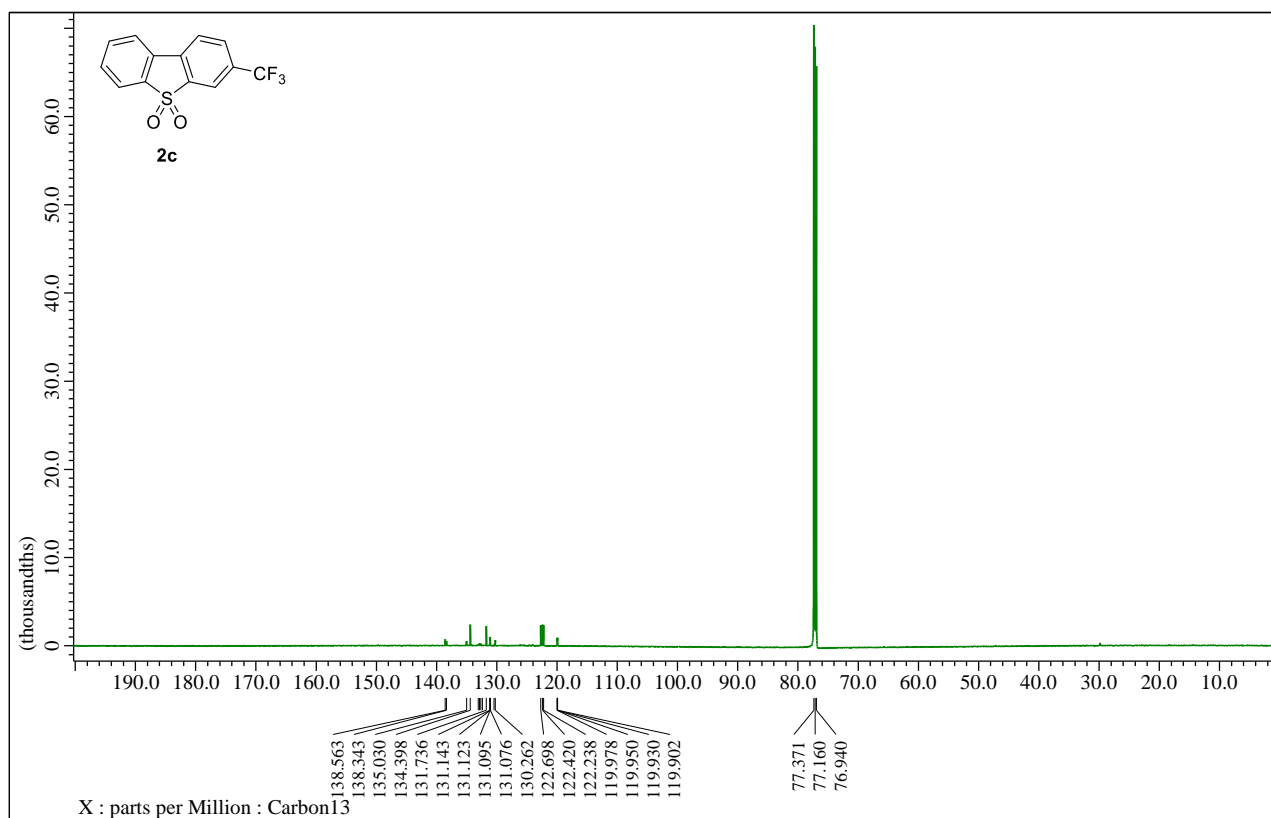
The ^{13}C NMR spectrum (X : parts per Million : Carbon13) displays the following chemical shifts (ppm):

- 141.407
- 137.921
- 137.787
- 134.762
- 133.977
- 131.976
- 130.022
- 129.161
- 122.650
- 122.295
- 121.520
- 121.415
- 77.371
- 77.160
- 76.949
- 21.665

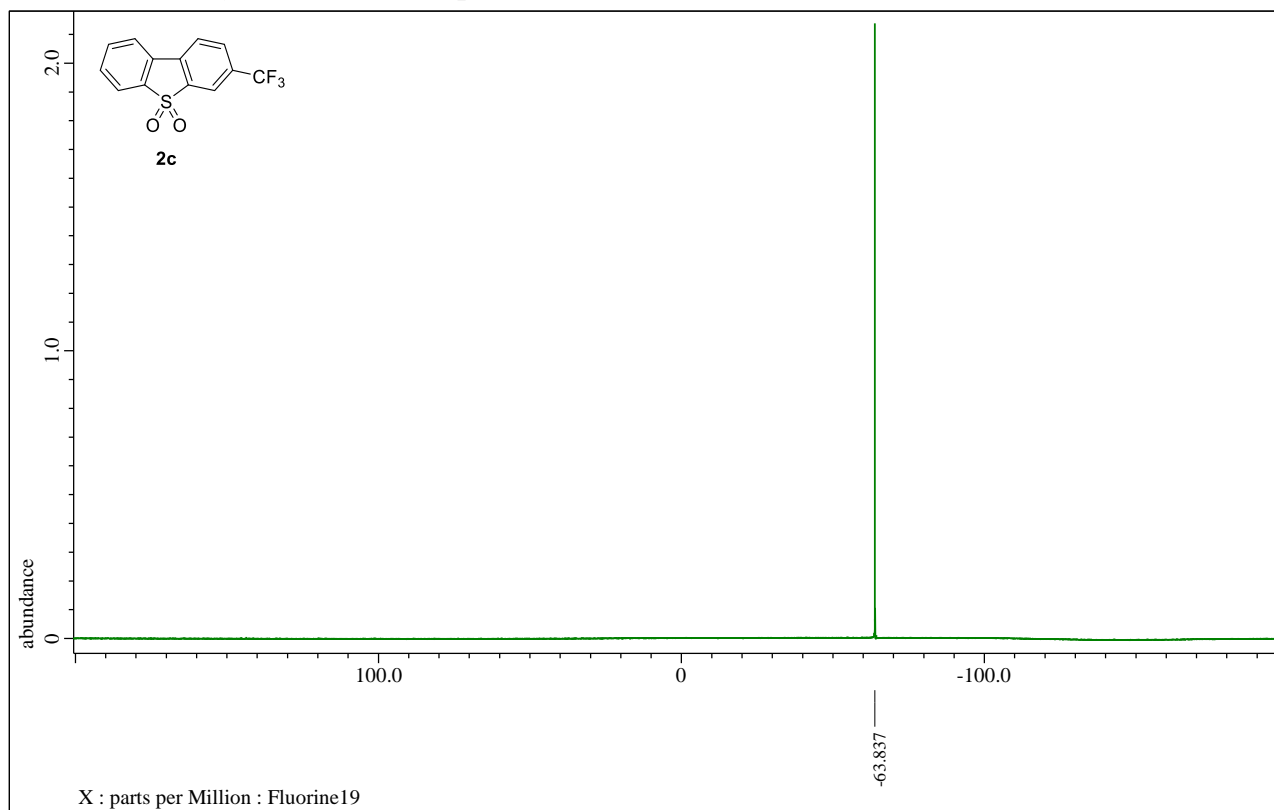
3-(Trifluoromethyl)dibenzo[*b,d*]thiophene 5,5-Dioxide (2c) ^1H NMR (600 MHz, CDCl_3)



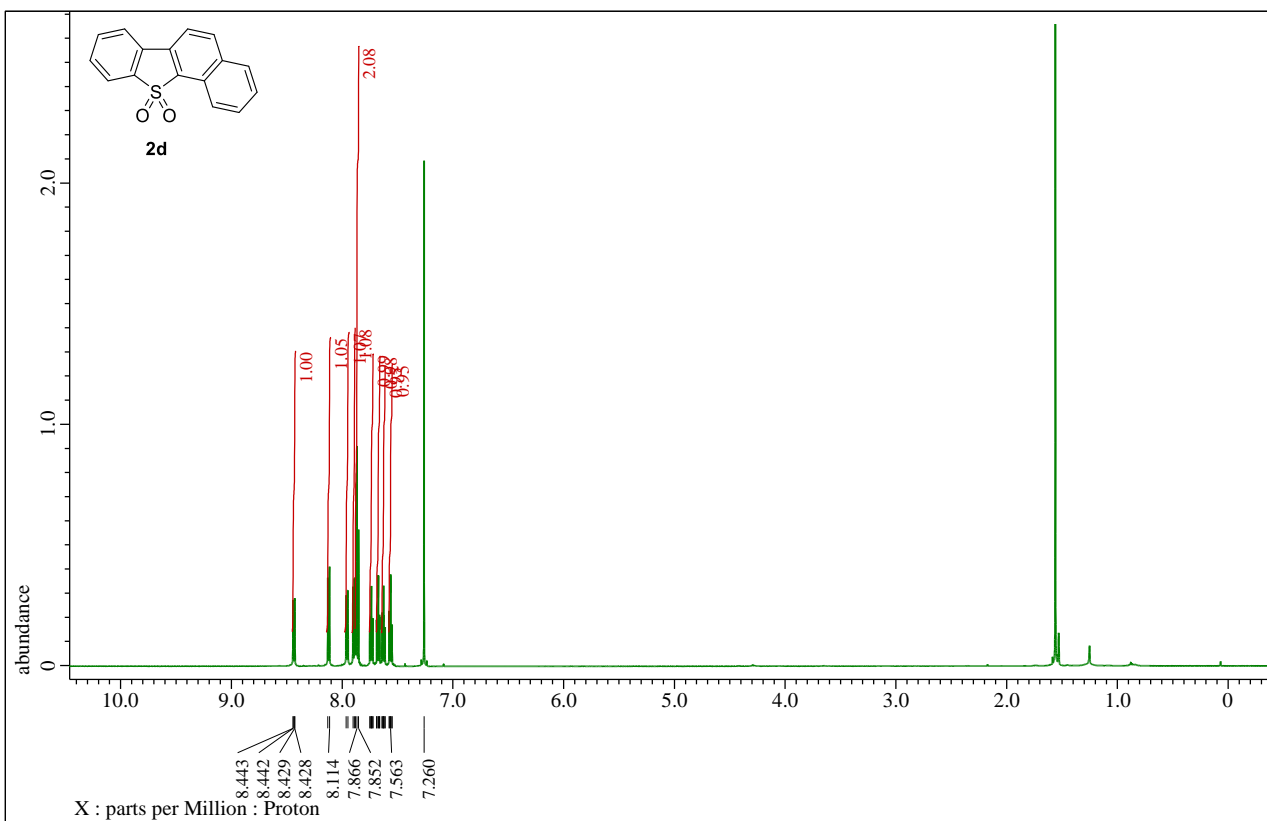
3-(Trifluoromethyl)dibenzo[*b,d*]thiophene 5,5-Dioxide (2c) ^{13}C NMR (150 MHz, CDCl_3)



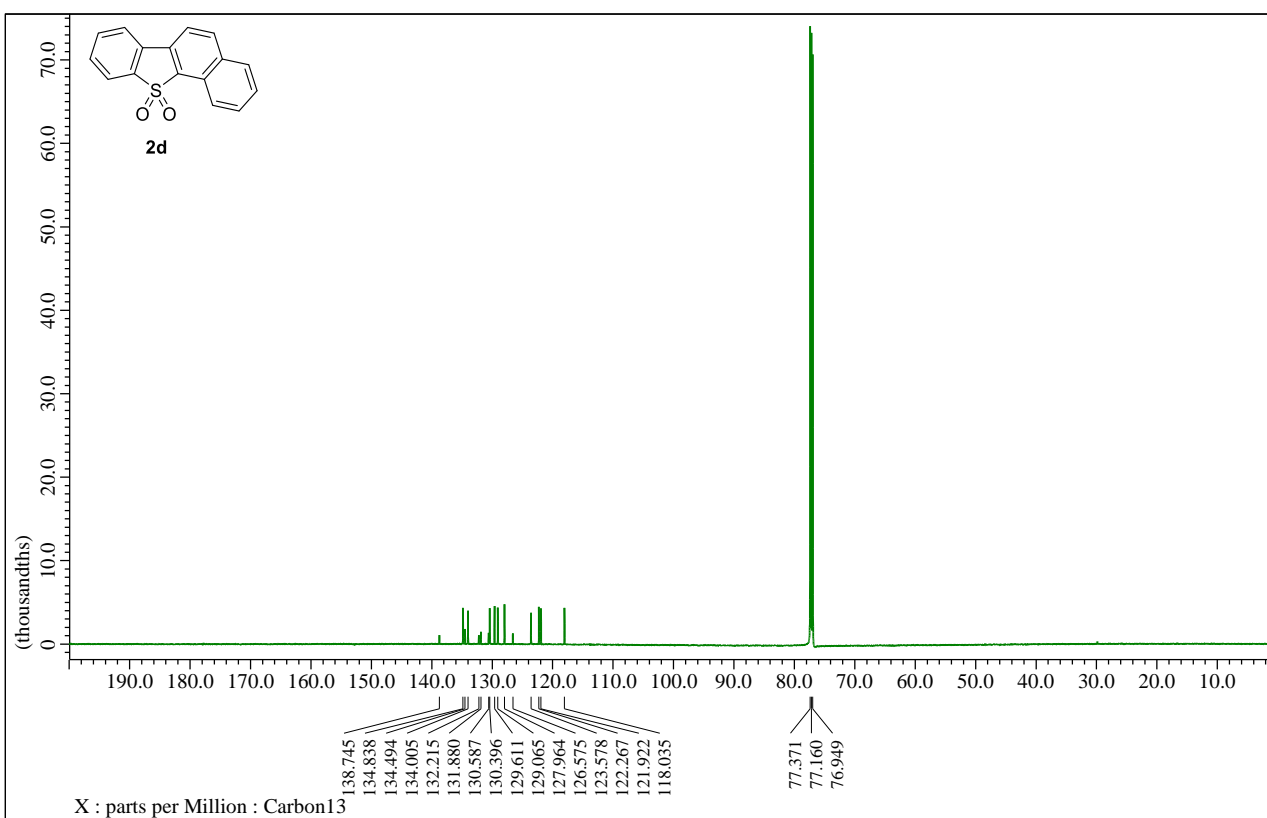
3-(Trifluoromethyl)dibenzo[*b,d*]thiophene 5,5-Dioxide (2c) ^{19}F NMR (376 MHz, CDCl_3)



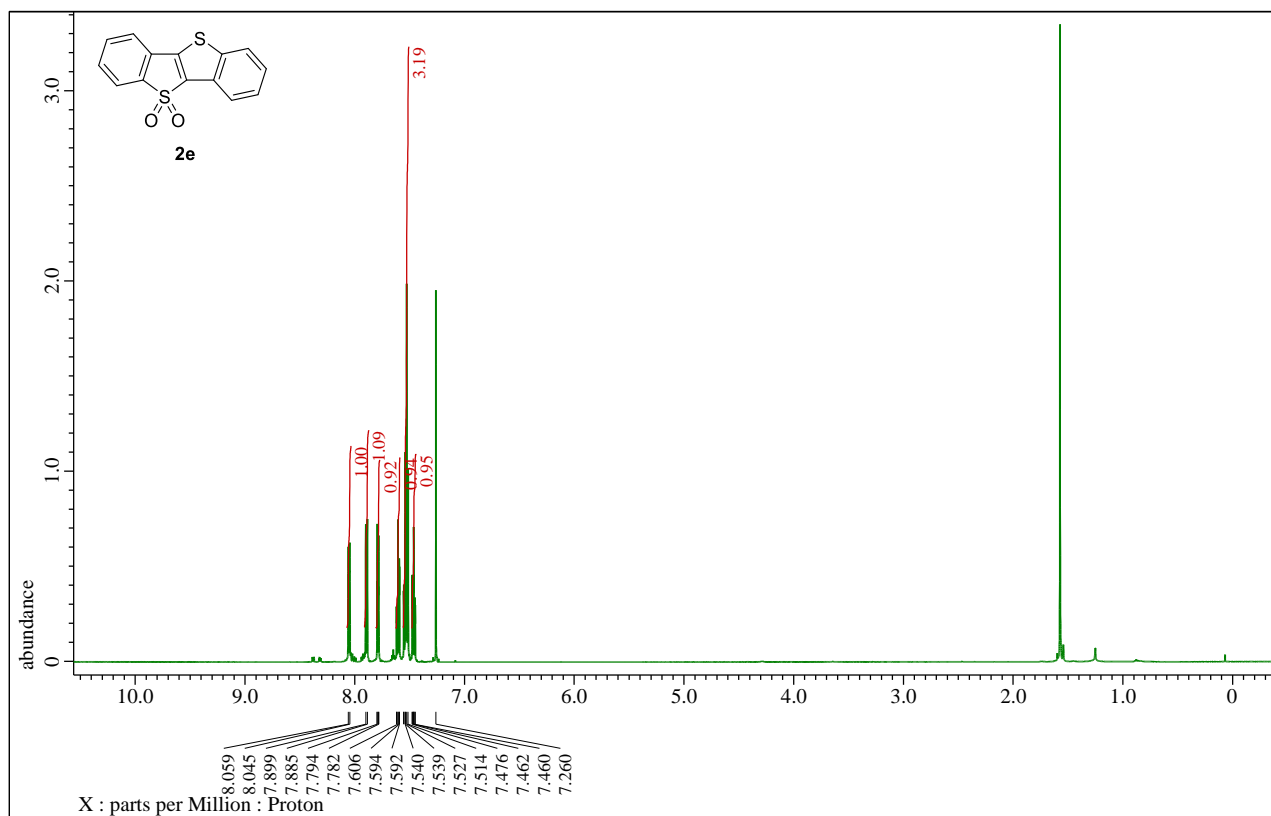
Benzo[*b*]naphtho[2,1-*d*]thiophene 11,11-Dioxide (2d) ¹H NMR (600 MHz, CDCl₃)



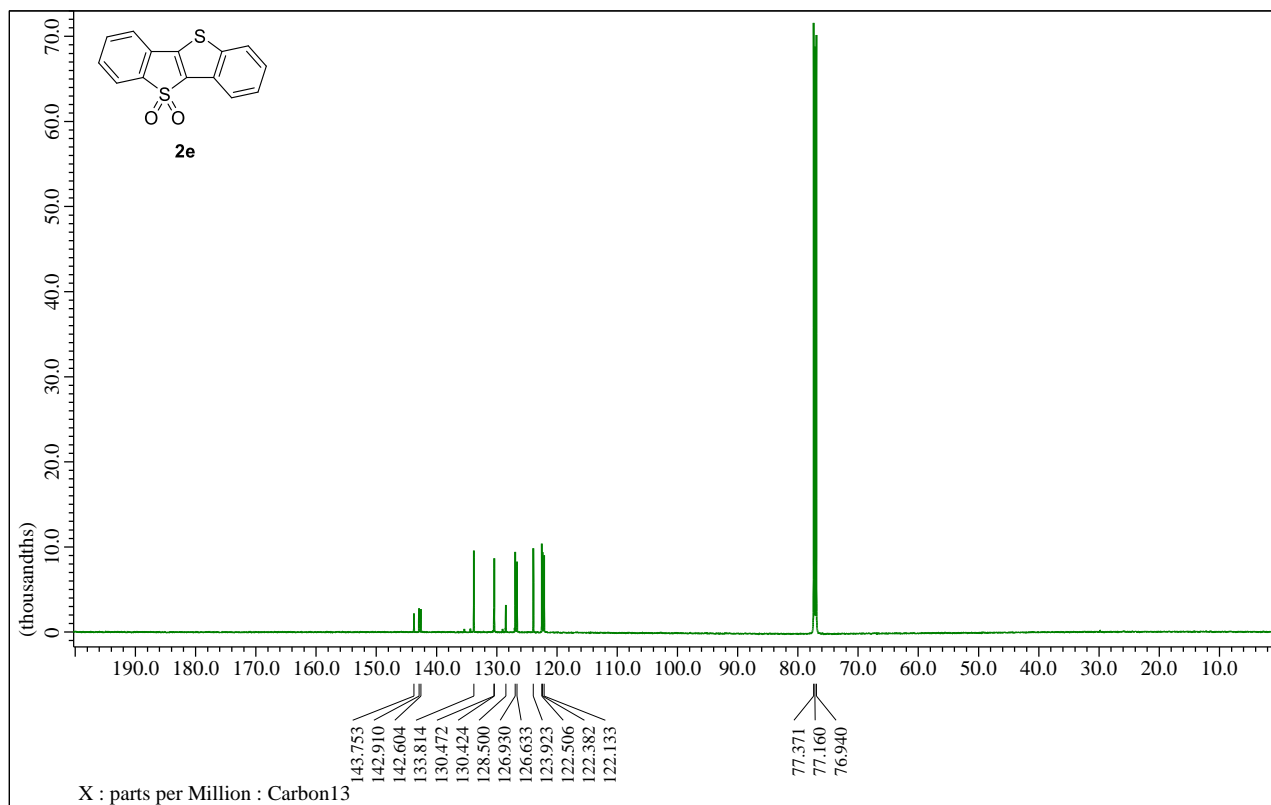
Benzo[*b*]naphtho[2,1-*d*]thiophene 11,11-Dioxide (2d) ¹³C NMR (150 MHz, CDCl₃)



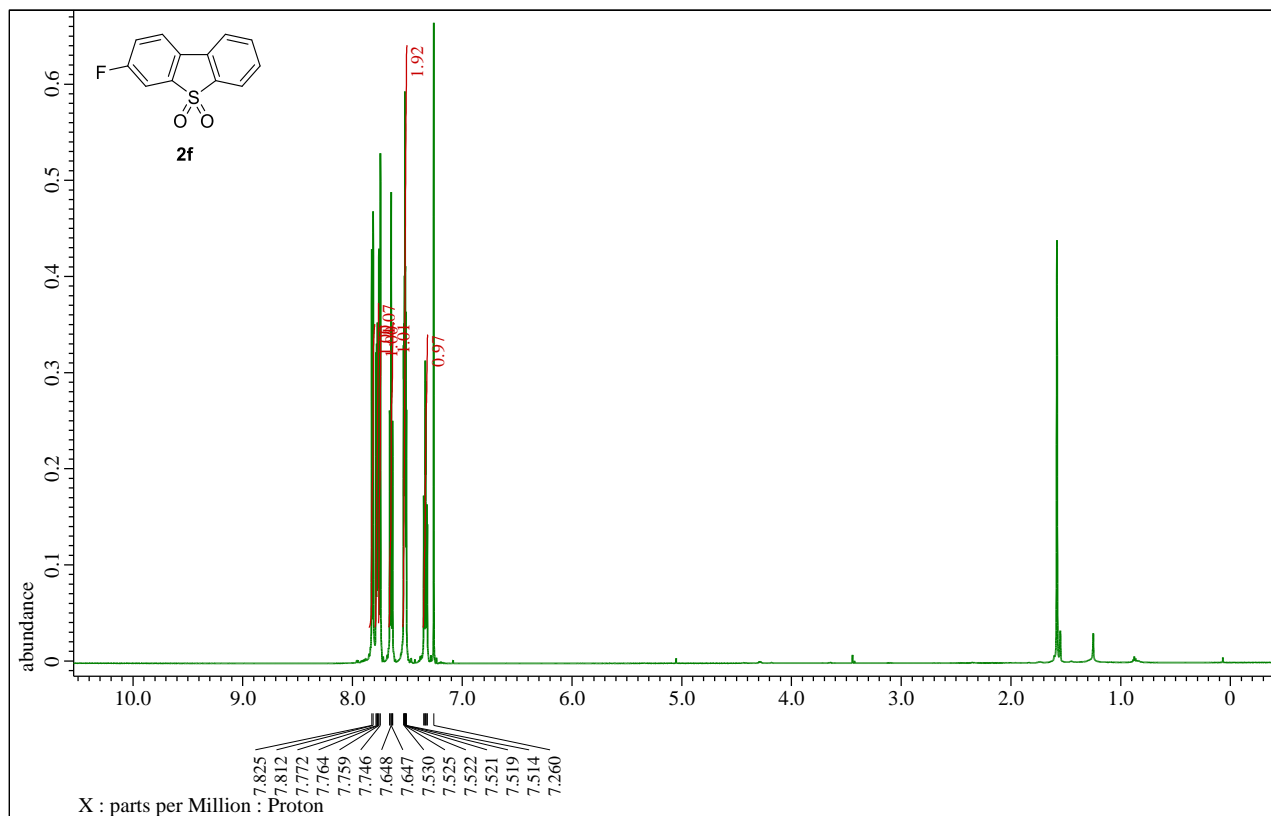
Benzo[*b*]benzo[4,5]thieno[2,3-*d*]thiophene 5,5-Dioxide (2e) ^1H NMR (600 MHz, CDCl_3)



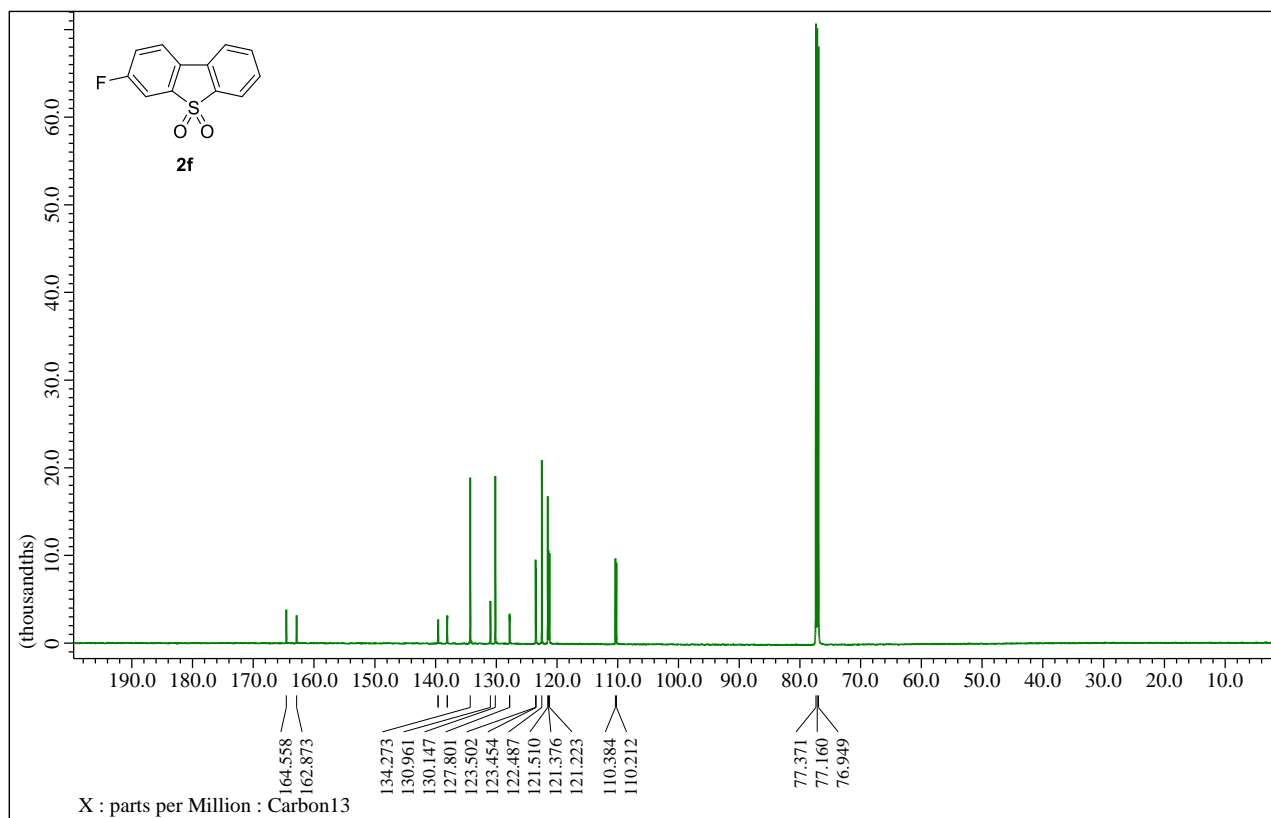
Benzo[*b*]benzo[4,5]thieno[2,3-*d*]thiophene 5,5-Dioxide (2e) ^{13}C NMR (150 MHz, CDCl_3)



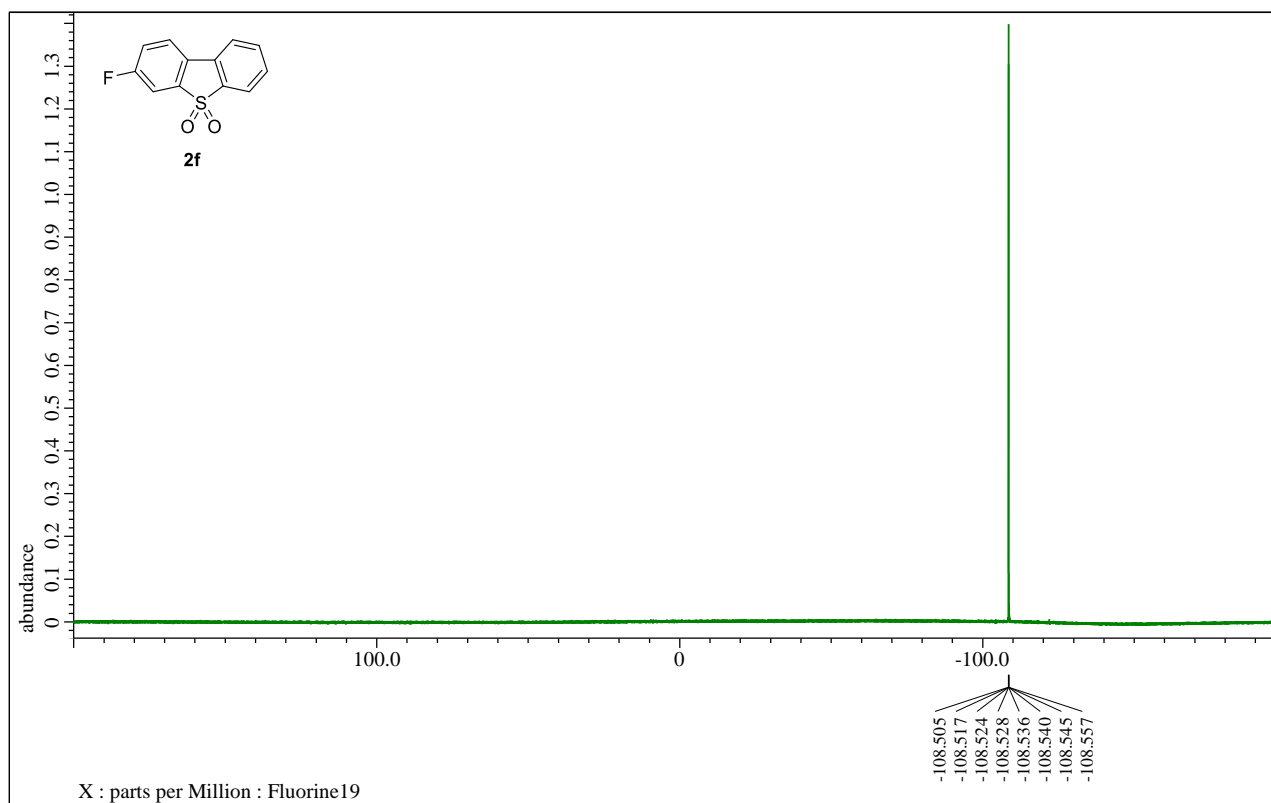
3-Fluorodibenzo[*b,d*]thiophene 5,5-Dioxide (2f) ^1H NMR (600 MHz, CDCl_3)



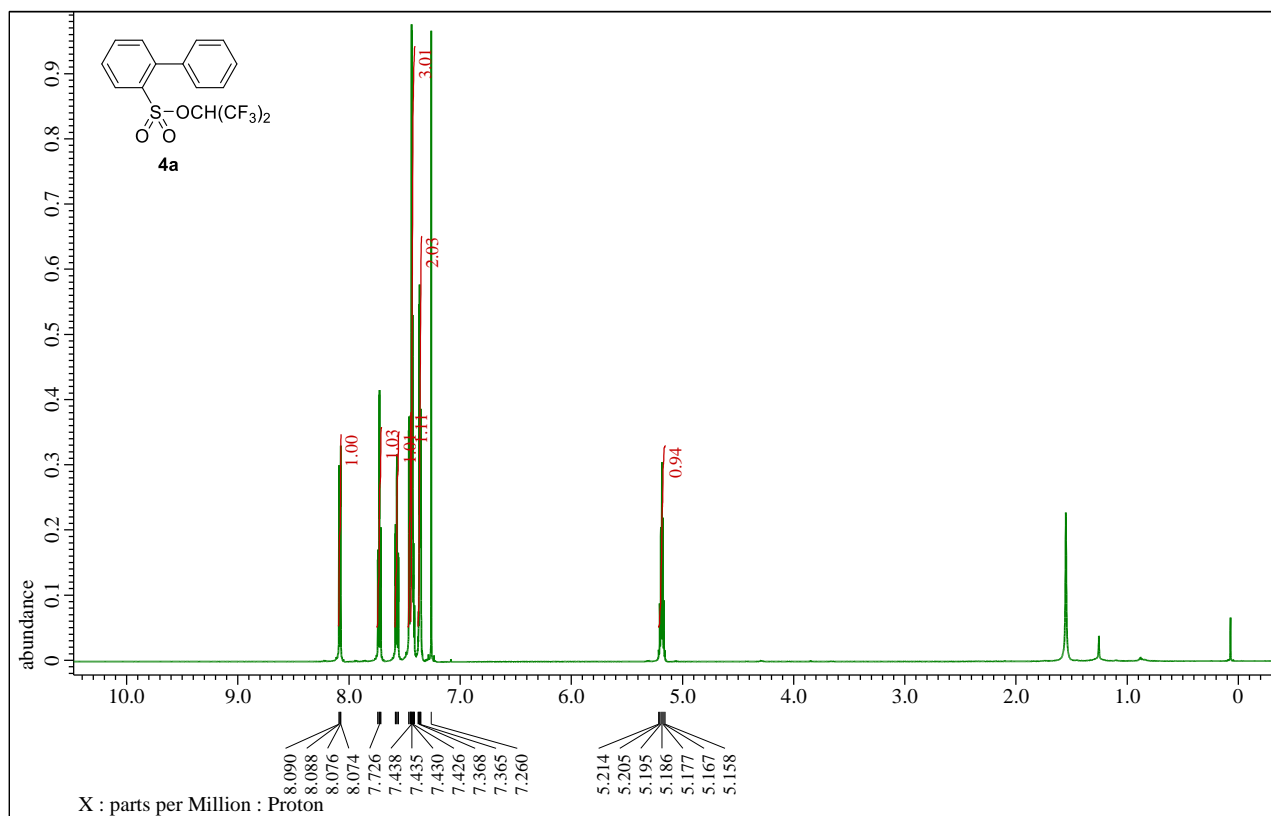
3-Fluorodibenzo[*b,d*]thiophene 5,5-Dioxide (2f) ^{13}C NMR (150 MHz, CDCl_3)



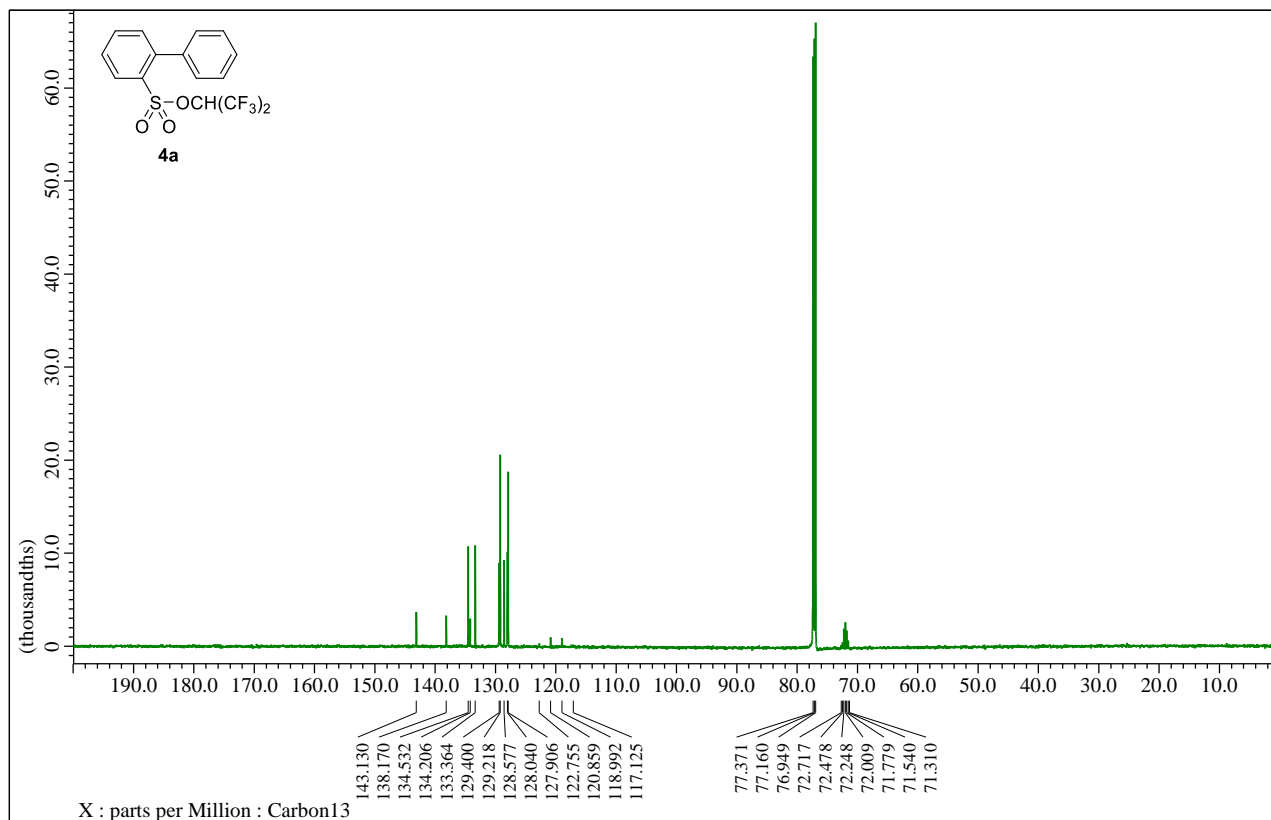
3-Fluorodibenzo[*b,d*]thiophene 5,5-Dioxide (2f) ^{19}F NMR (376 MHz, CDCl_3)



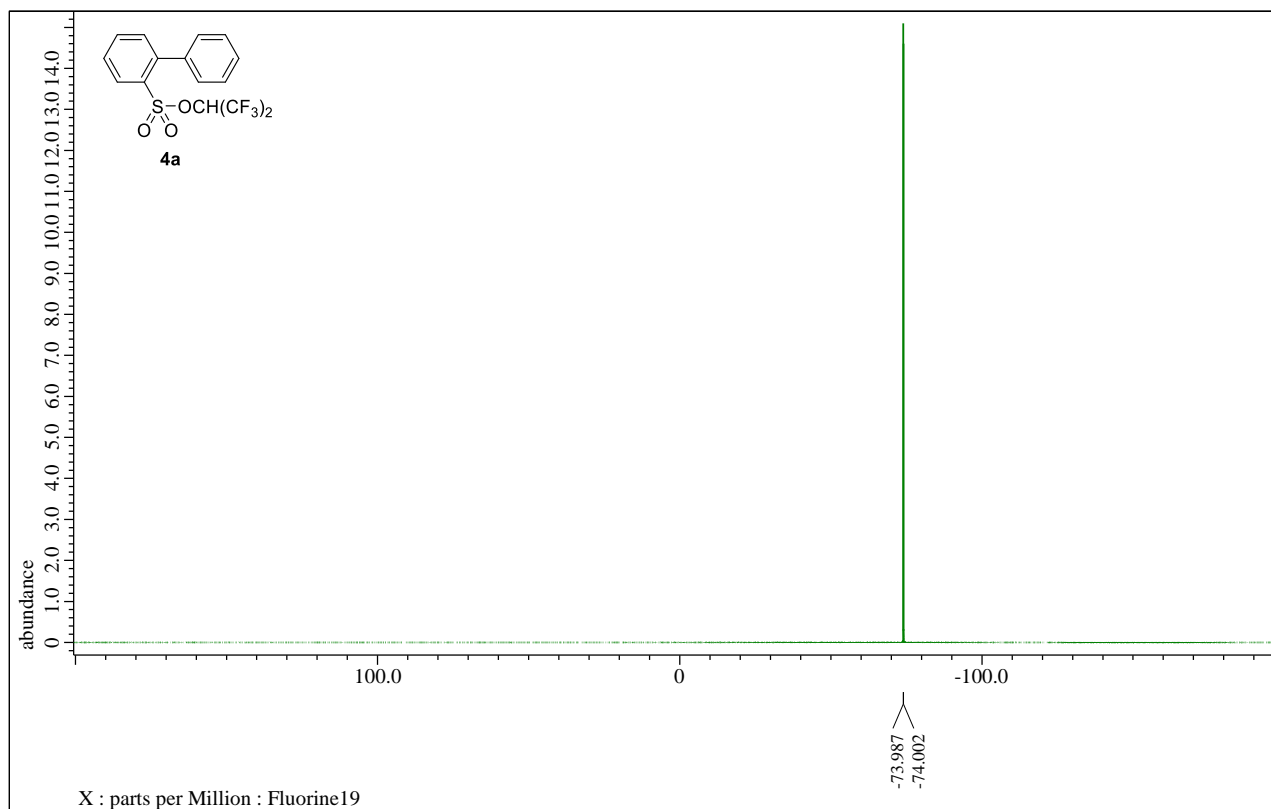
1,1,1,3,3,3-Hexafluoropropan-2-yl [1,1'-Biphenyl]-2-sulfonate (4a) ^1H NMR (600 MHz, CDCl_3)



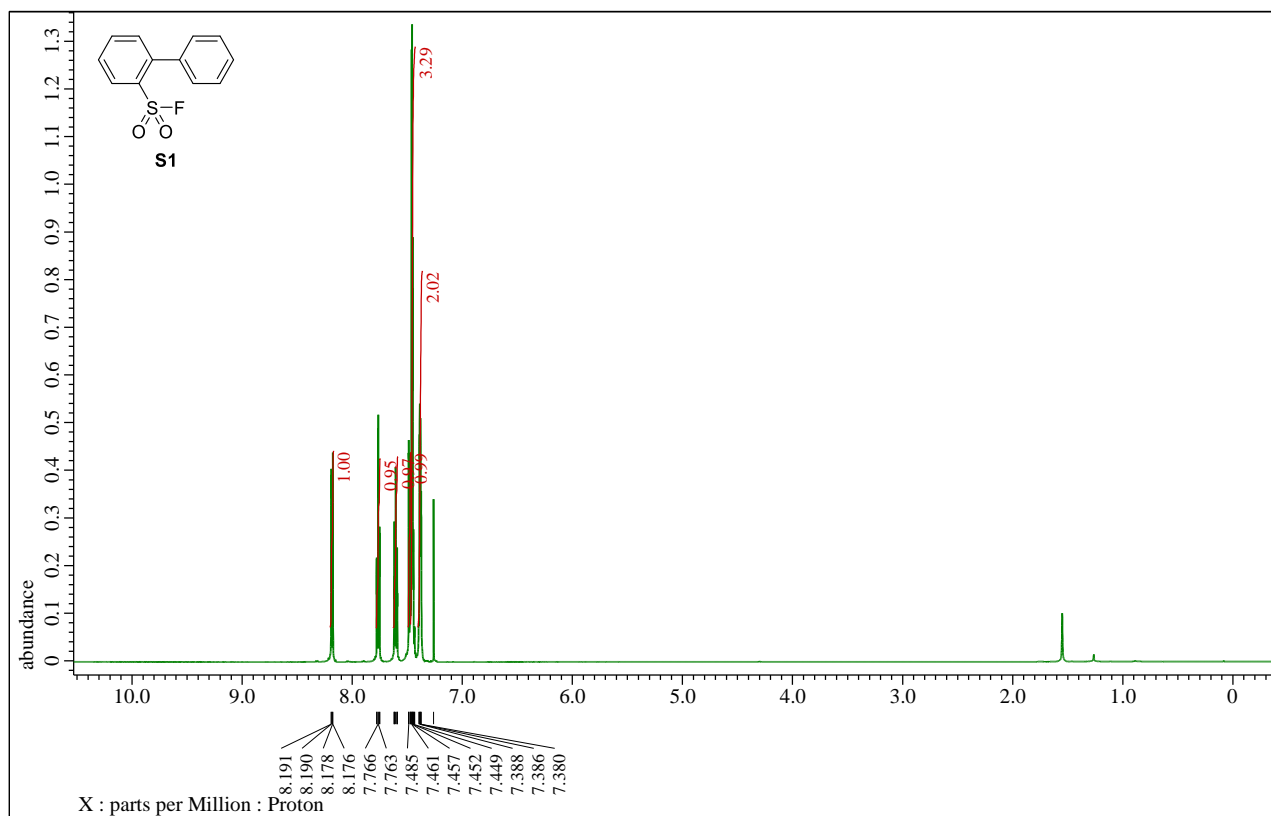
1,1,1,3,3,3-Hexafluoropropan-2-yl [1,1'-Biphenyl]-2-sulfonate (4a) ^{13}C NMR (150 MHz, CDCl_3)



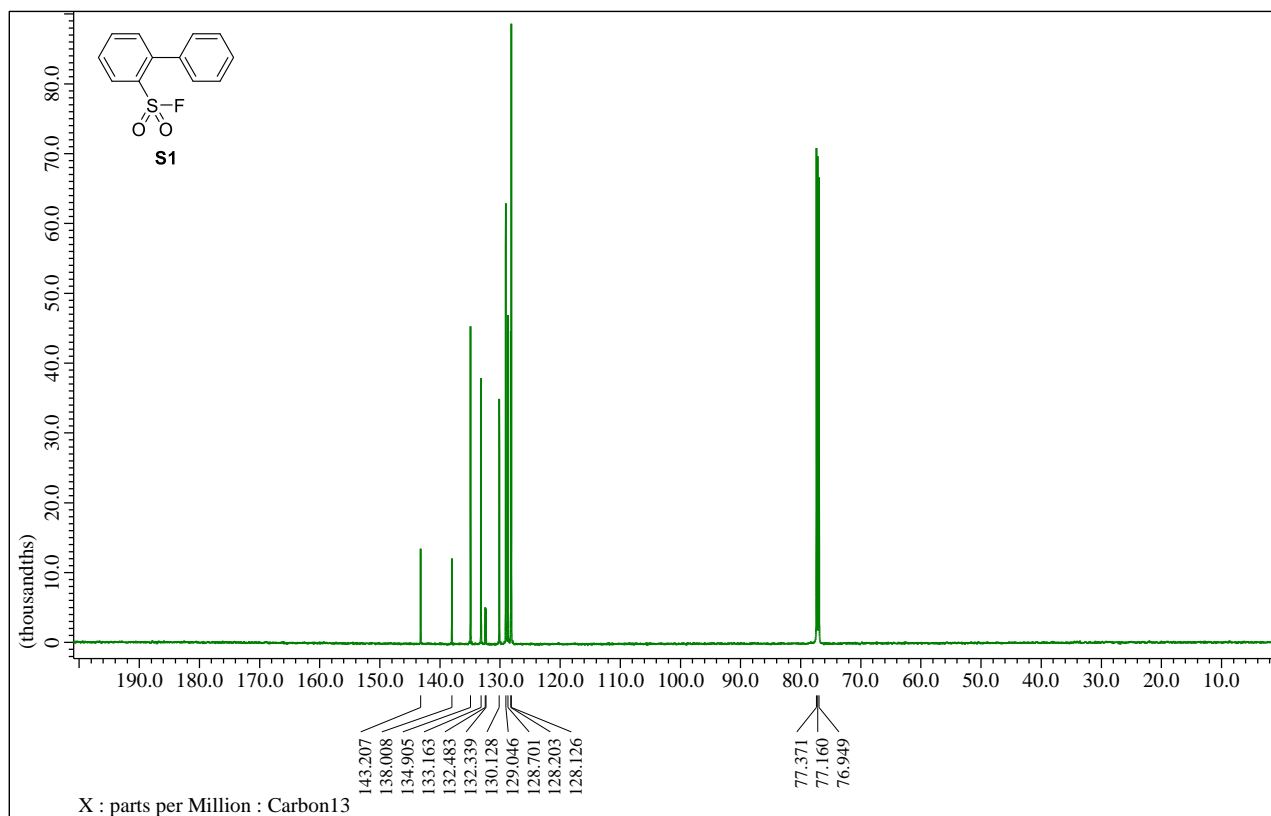
1,1,1,3,3,3-Hexafluoropropan-2-yl [1,1'-Biphenyl]-2-sulfonate (4a) ^{19}F NMR (376 MHz, CDCl_3)



[1,1'-Biphenyl]-2-sulfonyl Fluoride (S1) ^1H NMR (600 MHz, CDCl_3)



[1,1'-Biphenyl]-2-sulfonyl Fluoride (S1) ^{13}C NMR (150 MHz, CDCl_3)



[1,1'-Biphenyl]-2-sulfonyl Fluoride (S1) ^{19}F NMR (376 MHz, CDCl_3)

