Supplementary Information

Carbon nanotube-ruthenium hybrid towards mild oxidation of sulfides to sulfones: Efficient synthesis of diverse sulfonyl compounds

Renata G. Almeida,[a] Renato L. de Carvalho,[a] Mateus P. Nunes,[a] Roberto S. Gomes,[b] Leandro F. Pedrosa,[c] Carlos A. de Simone,[d] Elumalai Gopi,[e] Valérie Geertsen,[f] Edmond Gravel,[e] Eric Doris[e]* and Eufrânio N. da Silva Júnior[a]*

[a.] *Institute of Exact Sciences, Department of Chemistry, Federal University of Minas Gerais, Belo Horizonte, MG, 31270-901, Brazil;*

[b.] *Department of Chemistry and Chemical Biology, Harvard University, USA;*

[c.] *Fluminense Federal University, Volta Redonda, RJ, 27213-145, Brazil.*

[d.] *Institute of Physics, University of São Paulo, São Carlos, SP, 13560-160, Brazil.*

[e.] *Service de Chimie Bioorganique et de Marquage (SCBM) CEA, Université Paris-Saclay 91191 Gif-sur-Yvette, France.*

[f.] *NIMBE, CEA, CNRS, Université Paris-Saclay, 91191, Gif-sur-Yvette, France*

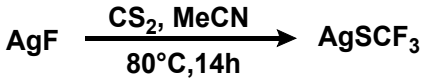
Corresponding authors: eufranio@ufmg.br, eric.doris@cea.fr

Contents

General experimental details

Unless otherwise indicated, all common reagents and solvents were used as obtained from commercial suppliers without further purification. Flash column chromatography (FCC) was performed using silica gel (Aldrich 40-63 μm, 230-400 mesh). Thin layer chromatography (TLC) was performed using aluminium backed 60 F254 silica plates. Visualization was achieved by UV fluorescence. Proton nuclear magnetic resonance spectra (NMR) were recorded using Bruker DRX 400, Bruker AVANCE 400 or Bruker AVANCE NEO ASCEND 600. ^{13}C NMR spectra were recorded at 100 MHz or at 150 MHz as stated. Chemical shifts (δ) are given in parts per million (ppm). Peaks are described as singlets (s), doublets (d), double doublets (dd), triplets (t), double triplets (dt), and multiplets (m). ^{1}H and ^{13}C NMR spectra were referenced to the appropriate residual solvent peak or TMS peak. Coupling constants (J) were quoted to the nearest 0.5 Hz. Mass spectra were recorded using a Bruker microTOFII ESI spectrometer (ESI^+ mode). Infrared spectra were recorded on a Perkin Elmer Spectrum One FTIR spectrometer as thin films or solids compressed on a diamond plate. IR bands ($\bar{\nu}$, cm^{-1}) are described as strong (s), medium (m) and weak (w). Melting points were determined using Stuart SMP30 melting point apparatus and are uncorrected.

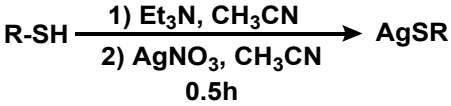
Synthesis of $AgSCF_3$[1]



To an oven dried 30 mL Schlenk flask equipped with a stir bar 2.5 g (19,7 mmol) of dry AgF was added. The flask was evacuated and refilled with Argon (three times) until inert atmosphere was achieved. 15 mL of dry MeCN was injected into the flask followed by 2.5 mL of CS_2. The flask was then placed into a pre-heated at 80 °C oil bath with efficient stirring. After 14 h, the reaction mixture was black, and the mixture was allowed to cool to room temperature. MeCN and the excess of CS_2 were removed under reduced pressure with the aid of a rotary evaporator to produce a black residue, which was then dissolved in EtOAc and filtered through a pad of celite. The solvent was once again removed under reduced pressure and the resulting yellow solid was dissolved in a minimum amount of MeCN to produce a clear yellow solution. 30 mL of

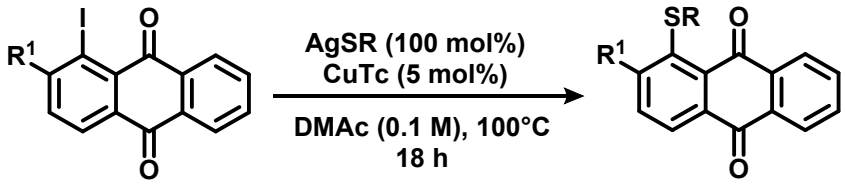
Et_2O was carefully layered on top of the yellow solution. The flask was placed in a freezer set to -10°C for 24 h to produce off-white crystals. The crystals were collected by filtration, dried under reduced pressure, affording $AgSCF_3$ (1.25 g, 5.98 mmol, 90%). **m.p. (°C)** = 224.8-225.9 (degrades) (Et_2O/CH_3CN).

General procedure for the synthesis of AgSR salts:[2]



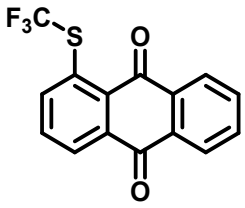
A 50 mL round bottom flask was charged with the corresponding thiol (2.0 mmol), EtN_3 (2.0 mmol, 279 μL) and acetonitrile (5 mL). The mixture was stirred and a solution of $AgNO_3$ (339.7 mg, 2 mmol) in acetonitrile (10 mL) was added dropwise. The suspension was stirred for 30 min under vigorous stirring, and the resulting solid was filtered, washed with acetonitrile (30 mL) and dried under reduced pressure. Yields for all AgSR salts were quantitative.

General procedure for the thiolation reactions:[3]

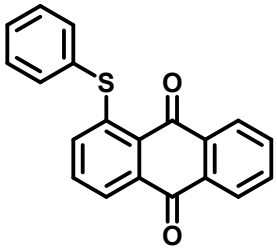


R^1 = H ref. 4
R^1 = I ref. 5

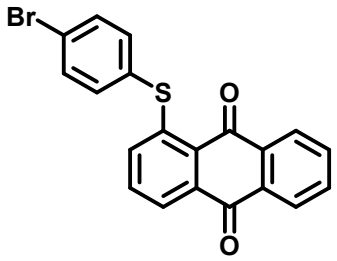
An oven dried re-sealable reaction tube was charged with the corresponding iodinated quinone (0.20 mmol), AgSR (0.20 mmol) and CuTc (1.6 mg, 5 mol%). Anhydrous DMAc (2.0 mL) was added and the tube was sealed. The mixture was heated at 100 °C for 18 h. After cooling and solvent removal by reduced pressure, the residue was purified by FCC, under the conditions noted.



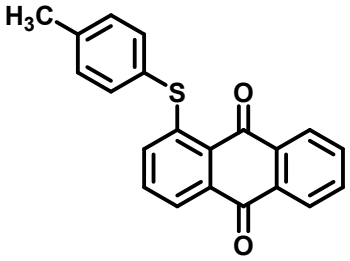
7-((Trifluoromethyl)thio)-1,6-anthraquinone (1a): Purification by FCC (toluene) afforded product **1a** (56.7 mg, 0.18 mmol, 92% yield) as yellow solid; **m.p. (°C)** = 173-175; **IR (solid, cm^{-1}) *v*:** 1671 (w), 1274 (m), 1098 (s), 698 (s); **HRMS (ESI$^+$):** Calcd for $C_{15}H_8F_3O_2SNa$ $[M+Na]^+$ 331.0011, found 331.0011; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.27 (d, *J* = 7.5 Hz, 3H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.91-7.70 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 183.9, 182.1, 135.3, 134.6, 134.5, 133.9, 133.2, 132.5, 132.2 (dd, *J* = 6.1, 3.1 Hz), 131.1, 129.7, 128.0, 127.5, 127.2, 126.2. The data are consistent with those reported in the literature.[3]



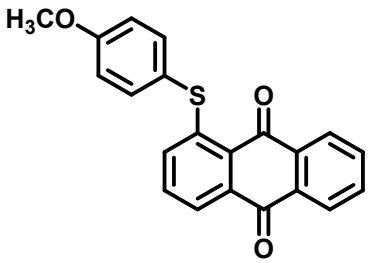
1-(Phenylthio)anthracene-9,10-dione (1b): Purification by FCC (toluene) afforded product **1b** (53.8 mg, 0.17 mmol, 85% yield) as orange solid; **m.p. (°C)** = 173-175; **IR (solid, cm^{-1}) *v*:** 3068 (s), 2165 (w), 1979 (w), 1666 (s), 1442 (m), 1417 (m), 962 (w), 698 (w); **HRMS (ESI$^+$):** Calcd for $C_{20}H_{12}O_2SNa$ $[M+Na]^+$ 339.0455, found 339.0457; **HRMS (ESI$^+$):** Calcd for $C_{20}H_{13}O_2S$ $[M+H]^+$ 317.0636, found 317.0640; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.38 (d, *J* = 7.5 Hz, 1H), 8.28 (d, *J* = 7.4 Hz, 1H), 8.09 (d, *J* = 7.5 Hz, 1H), 7.90-7.71 (m, 2H), 7.64 (dd, *J* = 6.3, 2.9 Hz, 2H), 7.57-7.47 (m, 3H), 7.44 (t, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) *δ*:** 183.6, 183.1, 146.5, 136.1, 135.1, 134.4, 134.0, 133.8, 132.8, 132.7, 131.9, 131.9, 130.1, 129.8, 128.1, 127.5, 126.9, 124.1.



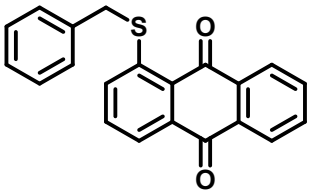
1-((4-Bromophenyl)thio)anthracene-9,10-dione (1c): Purification by FCC (toluene) afforded product **1c** (53.7 mg, 0.14 mmol, 68% yield) as orange solid; **m.p. (°C) =** 192-195; **IR (solid, cm^{-1}) *v*:** 3075 (w), 1662 (s), 1647 (m), 1567 (s), 704 (s), 658 (s); **HRMS (ESI$^+$):** Calcd for $C_{20}H_{11}BrO_2SNa$ $[M+Na]^+$ 416.9560, found 416.9558; **HRMS (ESI$^+$):** Calcd for $C_{20}H_{12}BrO_2S$ $[M+H]^+$ 394.9741, found 394.9745; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.36 (d, *J* = 7.5 Hz, 1H), 8.28 (d, *J* = 7.2 Hz, 1H), 8.10 (d, *J* = 7.5 Hz, 1H), 7.92-7.70 (m, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.48 (dd, *J* = 15.1, 7.7 Hz, 3H), 7.09 (d, *J* = 8.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) *δ*:** 183.6, 182.9, 145.5, 137.6, 135.1, 134.4, 133.9, 133.3, 132.9, 132.7, 131.7, 131.2, 128.2, 127.5, 127.4, 126.9, 124.6, 124.3.



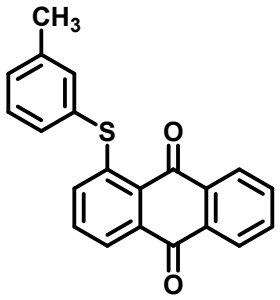
1-(*p*-Tolylthio)anthracene-9,10-dione (1d): Purification by FCC (toluene) afforded product **1d** (64.9 mg, 0.19 mmol, 97% yield) as orange solid; **m.p. (°C) =** 213-215; **IR (solid, cm^{-1}) *v*:** 3040 (w), 1664 (s), 1569 (s), 1417 (w), 802 (s), 705 (s); **HRMS (ESI$^+$):** Calcd for $C_{21}H_{14}O_2SNa$ $[M+Na]^+$ 353.0612, found 353.0616; **HRMS (ESI$^+$):** Calcd for $C_{21}H_{15}O_2S$ $[M+H]^+$ 331.0792, found 331.0799; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.37 (d, *J* = 7.4 Hz, 1H), 8.27 (d, *J* = 7.4 Hz, 1H), 8.06 (d, *J* = 7.5 Hz, 1H), 7.95-7.72 (m, 2H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 1H), 2.44 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 183.5, 183.1, 146.9, 140.1, 136.1, 135.1, 134.3, 134.1, 134.0, 133.7, 132.7, 132.7, 131.8, 130.8, 128.3, 128.0, 127.5, 127.2, 126.9, 123.9, 21.4.



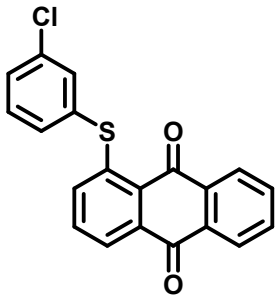
1-((4-Methoxyphenyl)thio)anthracene-9,10-dione (1e): Purification by FCC (toluene) afforded product **1e** (62.3 mg, 0.18 mmol, 90% yield) as red solid; **m.p. (°C)** = 210-213; **IR (solid, cm^{-1}) *ν*:** 2919 (w), 1665 (s), 1592 (s), 1568 (s), 1493 (m), 802 (s), 701 (s); **HRMS (ESI$^+$):** Calcd for $C_{21}H_{14}O_3SNa$ $[M+Na]^+$ 369.0561, found 369.0559; **HRMS (ESI$^+$):** Calcd for $C_{21}H_{15}O_3S$ $[M+H]^+$ 347.0741, found 347.0739; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.38 (d, *J* = 7.7 Hz, 1H), 8.28 (d, *J* = 7.3 Hz, 1H), 8.08 (d, *J* = 7.5 Hz, 1H), 7.81 (dt, *J* = 15.7, 7.9 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 183.6, 183.2, 161.0, 147.5, 137.7, 135.1, 134.4, 134.1, 134.0, 133.8, 132.7, 132.7, 131.7, 127.9, 127.5, 126.9, 123.9, 122.4, 115.7, 55.5.



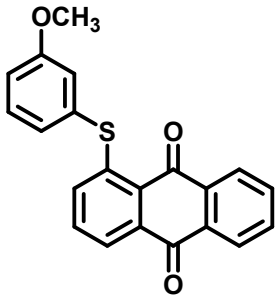
1-(Benzylthio)anthracene-9,10-dione (1f): Purification by FCC (toluene) afforded product **1f** (44.3 mg, 0.13 mmol, 67% yield) as orange solid; **m.p. (°C)** = 173-175; **IR (solid, cm^{-1}) *ν*:** 2923 (m), 1668 (m), 1271 (m), 704 (s); **HRMS (ESI$^+$):** Calcd for $C_{21}H_{15}O_2SNa$ $[M+Na]^+$ 353.0612, found 353.0613; **HRMS (ESI$^+$):** Calcd for $C_{21}H_{15}O_2S$ $[M+H]^+$ 331.0792, found 331.0781; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.31 (dd, *J* = 17.7, 7.5 Hz, 2H), 8.16 (d, *J* = 7.4 Hz, 1H), 7.81 (dd, *J* = 13.9, 7.2 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 7.3 Hz, 1H), 4.28 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 183.5, 183.1, 145.3, 135.4, 134.3, 133.9, 133.7, 133.1, 132.5, 130.1, 129.2, 128.8, 127.8, 127.6, 127.5, 126.8, 124.9, 123.6, 37.5. The data are consistent with those reported in the literature.[3]



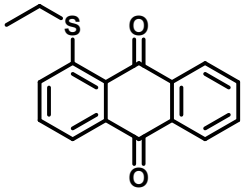
1-(*m*-Tolylthio)anthracene-9,10-dione (1g): Purification by FCC (toluene) afforded product **1g** (52.8 mg, 0.16 mmol, 80% yield) as orange solid; **m.p. (°C)** = 167-169; **IR (solid, cm^{-1}) *v*:** 2920 (m), 1669 (s), 1569 (m), 1309 (m), 697 (s); **HRMS (ESI$^+$):** Calcd for $C_{21}H_{14}O_2SNa$ $[M+Na]^+$ 353.0612, found 353.0615; **HRMS (ESI$^+$):** Calcd for $C_{21}H_{15}O_2S$ $[M+H]^+$ 331.0792, found 331.0797; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.36 (d, *J* = 7.5 Hz, 1H), 8.27 (d, *J* = 7.4 Hz, 1H), 8.06 (d, *J* = 7.5 Hz, 1H), 7.88-7.69 (m, 2H), 7.54-7.34 (m, 4H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ:*** 183.4, 183.0, 146.6, 140.0, 136.6, 135.0, 134.3, 133.9, 133.7, 133.0, 132.7, 132.6, 131.9, 131.5, 130.6, 129.8, 127.9, 127.4, 126.8, 124.0, 21.3.



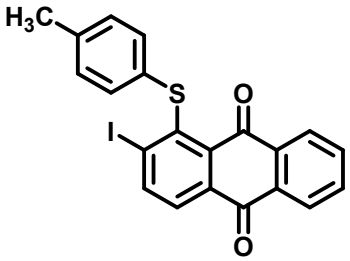
1-((3-Chlorophenyl)thio)anthracene-9,10-dione (1h): Purification by FCC (toluene) afforded product **1h** (53.3 mg, 0.15 mmol, 76% yield) as orange solid; **m.p. (°C)** = 159-161; **IR (solid, cm^{-1}) *v*:** 3061 (w), 1668 (s), 1592 (m), 1567 (s), 725 (s), 699 (s); **HRMS (ESI$^+$):** Calcd for $C_{20}H_{11}ClO_2SNa$ $[M+Na]^+$ 373.0066, found 373.0071; **HRMS (ESI$^+$):** Calcd for $C_{20}H_{12}ClO_2S$ $[M+H]^+$ 351.0246, found 351.0251; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.36 (d, *J* = 7.7 Hz, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 8.10 (d, *J* = 7.5 Hz, 1H), 7.90-7.74 (m, 2H), 7.64 (s, 1H), 7.58-7.39 (m, 4H), 7.10 (d, *J* = 8.2 Hz, 1H).**^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 183.6, 182.9, 145.3, 135.7, 135.6, 135.1, 134.4, 134.2, 134.0, 133.9, 133.8, 133.0, 132.6, 131.8, 131.1, 130.1, 128.2, 127.5, 127.0, 124.4.



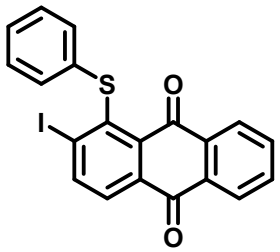
1-((3-Methoxyphenyl)thio)anthracene-9,10-dione (1i): Purification by FCC (toluene) afforded product **1i** (62.3 mg, 0.18 mmol, 90% yield) as orange solid; **m.p. (°C) =** 118-121; **IR (solid, cm^{-1}) *v*:** 3071 (w), 1668 (s), 1587 (m), 1569 (s), 802 (s), 701 (s); **HRMS (ESI$^+$):** Calcd for $C_{21}H_{14}O_3SNa$ $[M+Na]^+$ 369.0561, found 369.0567; **HRMS (ESI$^+$):** Calcd for $C_{21}H_{15}O_3S$ $[M+H]^+$ 347.0741, found 347.0747; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.37 (d, *J* = 7.6 Hz, 1H), 8.27 (d, *J* = 7.3 Hz, 1H), 8.08 (d, *J* = 7.5 Hz, 1H), 7.94-7.67 (m, 2H), 7.49-7.36 (m, 2H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.20-7.13 (m, 2H), 7.04 (dd, *J* = 8.2, 1.7 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 183.5, 183.0, 160.6, 146.3, 135.0, 134.3, 134.0, 133.8, 132.9, 132.8, 132.7, 132.0, 130.9, 128.2, 127.5, 126.9, 124.1, 120.8, 116.0, 55.4.



1-(Ethylthio)anthracene-9,10-dione (1j): Purification by FCC (toluene) afforded product **1j** (26.3 mg, 0.01 mmol, 49% yield) as orange solid; **m.p. (°C) =** 165-167; **IR (solid, cm^{-1}) *v*:** 3071 (w), 2925 (m), 1662 (s), 1595 (w), 1567 (s), 1311 (s); **HRMS (ESI$^+$):** Calcd for $C_{16}H_{12}O_2SNa$ $[M+Na]^+$ 291.0455, found 291.0450; **HRMS (ESI$^+$):** Calcd for $C_{16}H_{13}O_2S$ $[M+H]^+$ 269.0636, found 269.0639; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.30 (d, *J* = 7.7 Hz, 1H), 8.24 (d, *J* = 7.3 Hz, 1H), 8.08 (dd, *J* = 5.9, 2.7 Hz, 1H), 7.85-7.71 (m, 2H), 7.69-7.59 (m, 2H), 3.01 (q, *J* = 7.4 Hz, 2H), 1.46 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 183.4, 183.1, 145.5, 135.5, 134.3, 134.0, 133.6, 132.9, 132.5, 129.8, 128.7, 127.4, 126.7, 123.3, 26.1, 12.8.



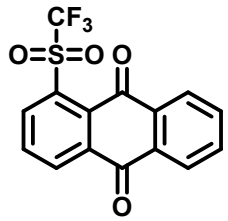
2-Iodo-1-(p-tolylthio)anthracene-9,10-dione (1k): Purification by FCC (hexane:toluene) afforded product **1k** (77.6 mg, 0.17 mmol, 85% yield) as red solid; **m.p. (°C)** = 170-173; **IR (solid, cm^{-1}) *v*:** 3062 (w), 1665 (s), 1584 (m), 1549 (s), 1489 (m), 708 (s); **HRMS (ESI$^+$):** Calcd for $C_{21}H_{13}IO_2SNa$ $[M+Na]^+$ 478.9578, found 478.9573; **HRMS (ESI$^+$):** Calcd for $C_{21}H_{14}IO_2S$ $[M+H]^+$ 456.9759, found 456.9765; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.35 (d, *J* = 8.2 Hz, 1H), 8.21 (dd, *J* = 5.7, 3.3 Hz, 1H), 8.04 (dd, *J* = 5.6, 3.4 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.79-7.70 (m, 2H), 7.02 (s, 4H), 2.26 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 182.6, 182.3, 145.0, 141.4, 136.6, 136.3, 136.2, 135.3, 134.6,7 134.5, 133.8, 133.7, 132.2, 129.9, 128.7, 128.3, 127.4, 126.6, 119.4, 21.0.



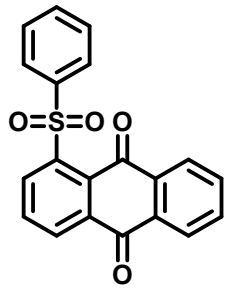
2-Iodo-1-(phenylthio)anthracene-9,10-dione (1l): Purification by FCC (hexane:toluene) afforded product **1l** (69.8 mg, 0.16 mmol, 79.0% yield) as red solid; **m.p. (°C)** = 148-150; **IR (solid, cm^{-1}) *v*:** 2922 (s), 1671 (s), 1662 (s), 1582 (m), 1547 (s), 707 (s); **HRMS (ESI$^+$):** Calcd for $C_{20}H_{11}IO_2SNa$ $[M+Na]^+$ 464.9422, found 464.9425; **HRMS (ESI$^+$):** Calcd for $C_{20}H_{12}IO_2S$ $[M+H]^+$ 442.9602, found 442.9609; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.37 (d, *J* = 8.2 Hz, 1H), 8.26-8.17 (m, 1H), 8.08-7.96 (m, 2H), 7.74 (dd, *J* = 5.7, 3.3 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.12 (dd, *J* = 15.1, 7.3 Hz, 3H).**^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 182.5, 182.3, 145.1, 140.7, 137.4, 136.7, 135.4, 134.6, 134.6, 133.7, 132.2, 129.2, 128.5, 128.3, 127.4, 126.6, 126.2, 119.7.

General procedure for oxidation with RuCNT/$NaIO_4$

To a solution of the corresponding sulfide (0.1 mmol) in H_2O:ACN:DCM (2:1:1, 4 mL) was added RuCNT (0.1 mol%, 333 μL of 0.3 mM aqueous suspension). The mixture was kept under vigorous stirring, and $NaIO_4$ (63.9 mg, 0.3 mmol) was added. The mixture was heated at 75 °C for 1 h, washed with a saturated solution of $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The organic phase was dried with Na_2SO_4 and submitted to purification by column chromatography over silica-gel, eluting with toluene.

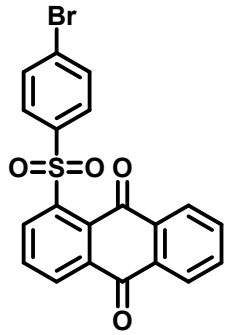


7-((Trifluoromethyl)sulfonyl)-1,6-anthraquinone (2a): Purification by FCC (toluene) afforded product **2a** (33.0 mg, 0.097 mmol, 97% yield) as yellow solid; **m.p. (°C)** = 214.9-216.0; **IR (solid, cm^{-1}) *v*:** 2923 (w), 1685 (m), 1190 (s), 704 (s); **HRMS (ESI^+):** Calcd for $C_{15}H_7F_3O_4SNa$ $[M+Na]^+$ 362.9914, found 362.9913; **HRMS (ESI^+):** Calcd for $C_{15}H_8F_3O_4S$ $[M+H]^+$ 341.0095, found 341.0099; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.78 (d, *J* = 7.8 Hz, 1H), 8.73 (d, *J* = 7.9 Hz, 1H), 8.38-8.28 (m, 2H), 8.07 (t, *J* = 7.9 Hz, 1H), 7.97-7.81 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 181.0, 180.8, 138.3, 135.9, 135.1, 134.9, 134.6, 134.0, 133.4, 132.1, 128.0, 127.3. The data are consistent with those reported in the literature.[3]

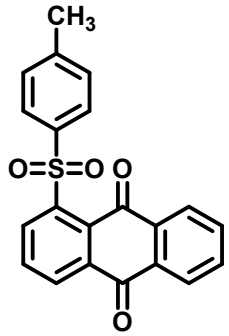


1-(Phenylsulfonyl)anthracene-9,10-dione (2b): Purification by FCC (toluene) afforded product **2b** (34.8 mg, 0.1 mmol, >99% yield) as yellow solid; **m.p. (°C)** = 218-

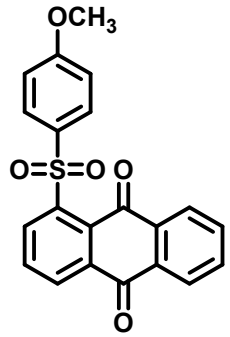
221; **IR (solid, cm^{-1}) *v*:** 3074 (s), 1684 (s), 1670 (m), 1578 (m), 1304 (s), 1153 (s), 748 (w), 688 (s); **HRMS (ESI$^+$):** Calcd for $C_{20}H_{12}O_4SNa$ $[M+Na]^+$ 371.0354, found 371.0353; **HRMS (ESI$^+$):** Calcd for $C_{20}H_{13}O_4S$ $[M+H]^+$349.0534, found 349.0533; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.96 (d, *J* = 7.8 Hz, 1H), 8.68 (d, *J* = 7.8 Hz, 1H), 8.22 (dd, *J* = 5.7, 2.9 Hz, 1H), 8.15 (dd, *J* = 5.7, 3.1 Hz, 1H), 8.04 (dd, *J* = 7.0, 5.0 Hz, 3H), 7.81-7.71 (m, 2H), 7.63-7.46 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 181.8, 181.0, 141.8, 141.5, 136.8, 135.8, 134.7, 134.3, 133.8, 133.5, 132.7, 132.0, 128.6, 127.8, 127.5, 126.9.



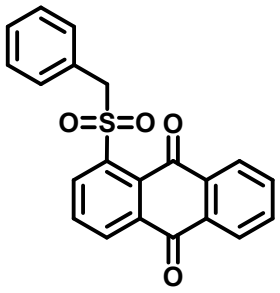
1-((4-Bromophenyl)sulfonyl)anthracene-9,10-dione (2c): Purification by FCC (toluene) afforded product **2c** (33.3 mg, 0.78 mmol, 78% yield) as yellow solid; **m.p. (°C) =** 215-218; **IR (solid, cm^{-1}) *v*:** 3080 (s), 1673 (s), 1573 (s), 1388 (m), 808 (s), 701 (s), 664 (w); **HRMS (ESI$^+$):** Calcd for $C_{20}H_{11}O_4BrSNa$ $[M+Na]^+$ 448.9459, found 448.9458; **HRMS (ESI$^+$):** Calcd for $C_{20}H_{12}O_4BrS$ $[M+H]^+$ 425.9561, found 425.9568; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.95 (d, *J* = 7.8 Hz, 1H), 8.69 (d, *J* = 7.7 Hz, 1H), 8.30-8.19 (m, 1H), 8.18-8.13 (m, 1H), 8.05 (t, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.83-7.76 (m, 2H), 7.67 (d, *J* = 8.3 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 181.7, 181.1, 141.1, 140.9, 136.8, 135.9, 134.8, 134.4, 133.7, 133.6, 133.0, 132.7, 132.0, 131.8, 129.2, 127.8, 127.0.



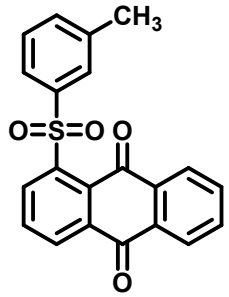
1-Tosylanthracene-9,10-dione (2d): Purification by FCC (toluene) afforded product **2d** (31.8 mg, 0.088 mmol, 88% yield) as yellow solid; **m.p. (°C)** = 210-212; IR **(solid, cm^{-1}) *v*:** 3082 (s), 1675 (s), 1580 (m), 1462 (w), 815 (m), 704 (s); **HRMS (ESI$^+$):** Calcd for $C_{21}H_{14}O_4SNa$ $[M+Na]^+$ 385.0510, found 385.0508; **HRMS (ESI$^+$):** Calcd for $C_{21}H_{15}O_4S$ $[M+H]^+$363.0691, found 363.0692; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.93 (d, *J* = 7.9 Hz, 1H), 8.66 (d, *J* = 7.8 Hz, 1H), 8.26-8.20 (m, 1H), 8.17 (dt, *J* = 7.5, 3.7 Hz, 1H), 8.01 (t, *J* = 7.9 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.83-7.68 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 2.41 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 181.9, 181.1, 143.7, 142.0, 138.8, 136.7, 135.8, 134.7, 134.2, 133.9, 133.4, 132.8, 132.6, 132.0, 129.2, 127.8, 126.9, 21.6.



1-((4-Methoxyphenyl)sulfonyl)anthracene-9,10-dione (2e): Purification by FCC (toluene) afforded product **2e** (34.4 mg, 0.091 mmol, 91% yield) as yellow solid; **m.p. (°C)** = 220-222; **IR (solid, cm^{-1}) *v*:** 2920 (s), 1685 (s), 1666 (m), 1576 (s), 1308 (s), 836 (s), 703 (s); **HRMS (ESI$^+$):** Calcd for $C_{21}H_{14}O_5SNa$ $[M+Na]^+$ 401.0459, found 401.0459; **HRMS (ESI$^+$):** Calcd for $C_{21}H_{15}O_5S$ $[M+H]^+$379.0640, found 379.0639; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.90 (dd, *J* = 7.9, 1.2 Hz, 1H), 8.65 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.30-8.15 (m, 2H), 8.10-7.95 (m, 3H), 7.86-7.72 (m, 2H), 7.10-6.94 (m, 2H), 3.86 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 182.0, 181.2, 163.1, 142.5, 136.6, 135.7, 134.7, 134.2, 134.0, 133.4, 133.0, 132.7, 132.5, 132.0, 130.5, 127.8, 126.9, 113.8, 55.6.

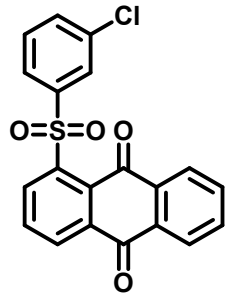


5-(Benzylsulfonyl)-1,6-anthraquinone (2f): Purification by FCC (toluene) afforded product **2f** (24.6 mg, 0.068 mmol, 68% yield) as a yellow solid; **m.p. (°C)** = 210-212; **IR (solid, cm^{-1}) *v*:** 1680 (m), 1303 (s), 1110 (m), 692 (s); **HRMS (ESI$^+$):** Calcd for $C_{21}H_{15}O_4SNa$ $[M+Na]^+$ 385.0510 found 385.0513; **HRMS (ESI$^+$):** Calcd for $C_{21}H_{15}O_4S$ $[M+H]^+$ 363.0686 found 363.0680; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.53 (d, *J* = 7.8 Hz, 1H), 8.34 (d, *J* = 7.6 Hz, 1H), 8.29-8.23 (m, 1H), 8.16 (d, *J* = 7.9 Hz, 1H), 7.92-7.81 (m, 2H), 7.71 (t, *J* = 7.9 Hz, 1H), 7.37-7.31 (m, 2H), 7.25 (t, *J* = 5.9 Hz, 3H), 5.25 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 183.4, 181.7, 139.8, 137.8, 135.4, 134.9, 134.5, 134.4, 134.1, 133.1, 132.4, 132.2, 131.1, 128.9, 128.7, 128.2, 127.8, 127.1, 62.4. The data are consistent with those reported in the literature.[3]

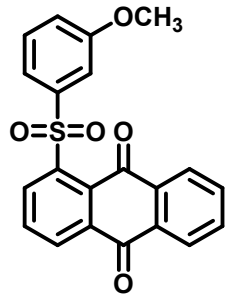


1-(*m*-Tolylsulfonyl)anthracene-9,10-dione (2g): Purification by FCC (toluene) afforded product **2g** (21.7 mg, 0.06 mmol, 60% yield) as a yellow solid; **m.p. (°C)** = 204-206; **IR (solid, cm^{-1}) *v*:** 3075 (s), 1684 (s), 1670 (m), 1576 (m), 1315 (s), 1148 (m), 787 (s); **HRMS (ESI$^+$):** Calcd for $C_{21}H_{14}O_4SNa$ $[M+Na]^+$ 385.0510, found 385.0510; **HRMS (ESI$^+$):** Calcd for $C_{21}H_{15}O_4S$ $[M+H]^+$ 363.0691, found 363.0697; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.94 (d, *J* = 7.9 Hz, 1H), 8.67 (d, *J* = 7.8 Hz, 1H), 8.27-8.20 (m, 1H), 8.18-8.13 (m, 1H), 8.03 (t, *J* = 7.9 Hz, 1H), 7.88-7.72 (m, 4H), 7.48-7.34 (m, 2H), 2.43 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 181.9, 181.0, 141.7, 141.5, 138.8, 136.8,

135.8, 134.7, 134.3, 133.8, 133.6, 133.5, 132.8, 132.7, 132.0, 128.4, 127.8, 127.5, 126.9, 124.6, 21.4.

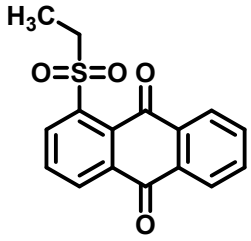


1-((3-Chlorophenyl)sulfonyl)anthracene-9,10-dione (2h): Purification by FCC (toluene) afforded product **2h** (32.2 mg, 0.084 mmol, 84% yield) as a yellow solid; **m.p. (°C)** = 200-203; **IR (solid, cm^{-1}) *v*:** 3078 (s), 1682 (s), 1578 (s), 1316 (s), 955 (m), 790 (s); **HRMS (ESI$^+$):** Calcd for $C_{20}H_{11}O_4ClSNa$ $[M+Na]^+$ 404.9964, found 404.9967; **HRMS (ESI$^+$):** Calcd for $C_{20}H_{12}O_4ClS$ $[M+H]^+$ 383.0144, found 383.0149; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.96 (d, *J* = 7.9 Hz, 1H), 8.71 (d, *J* = 7.8 Hz, 1H), 8.27-8.21 (m, 1H), 8.21-8.13 (m, 1H), 8.06 (t, *J* = 7.9 Hz, 1H), 8.00-7.89 (m, 2H), 7.85-7.74 (m, 2H), 7.51 (dt, *J* = 15.6, 7.9 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 181.7, 180.9, 143.7, 140.7, 136.9, 135.9, 134.8, 134.5, 133.7, 133.1, 132.8, 131.9, 129.8, 127.8, 127.4, 127.0, 125.6.

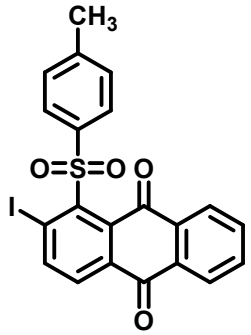


1-((3-Methoxyphenyl)sulfonyl)anthracene-9,10-dione (2i): Purification by FCC (toluene) afforded product **2i** (21.2 mg, 0.056 mmol, 56% yield) as a yellow solid; **m.p. (°C)** = 189-191; **IR (solid, cm^{-1}) *v*:** 3077 (s), 1682 (s), 1578 (m), 1478 (m), 1311 (s), 956 (m), 703 (s); **HRMS (ESI$^+$):** Calcd for $C_{21}H_{14}O_5SNa$ $[M+Na]^+$ 401.0459, found 401.0457; **HRMS (ESI$^+$):** Calcd for $C_{21}H_{15}O_5S$ $[M+H]^+$ 379.0640, found 379.0638; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 8.92 (d, *J* = 7.9 Hz, 1H), 8.67 (d, *J* = 7.8 Hz, 1H), 8.31-

8.20 (m, 1H), 8.19-8.12 (m, 1H), 8.03 (t, J = 7.9 Hz, 1H), 7.77 (dd, J = 5.3, 3.8 Hz, 2H), 7.61 (s, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.09 (dd, J = 8.1, 2.1 Hz, 1H), 3.90 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ:** 181.8, 180.9, 159.5, 143.1, 141.3, 136.6, 135.8, 134.7, 134.3, 133.8, 133.5, 132.8, 132.7, 131.9, 129.6, 127.8, 126.9, 119.3, 119.0, 112.4, 55.8.

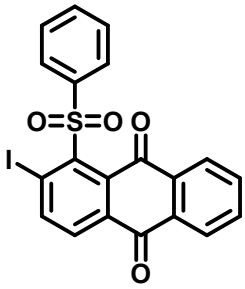


1-(Ethylsulfonyl)anthracene-9,10-dione (2j): Purification by FCC (toluene) afforded product **2j** (21.0 mg, 0.07 mmol, 70% yield) as a yellow solid; **m.p. (°C)** = 208-210; **IR (solid, cm^{-1}) ν:** 3092 (s), 1683 (s), 1662 (m), 1575 (m), 1112 (s); **HRMS (ESI$^+$):** Calcd for $C_{16}H_{12}O_4SNa$ $[M+Na]^+$ 323.0354, found 323.0358; **HRMS (ESI$^+$):** Calcd for $C_{16}H_{13}O_4S$ $[M+H]^+$ 301.0534, found 301.0537; **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 8.65 (dd, J = 7.8, 1.9 Hz, 2H), 8.30-8.24 (m, 2H), 7.98 (t, J = 7.9 Hz, 1H), 7.89-7.81 (m, 2H), 3.99 (q, J = 7.5 Hz, 2H), 1.42 (t, J = 7.5 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ:** 182.9, 181.6, 140.1, 137.5, 135.7, 134.9, 134.5, 134.3, 134.0, 133.5, 132.7, 132.0, 127.7, 127.0, 50.7, 7.6.

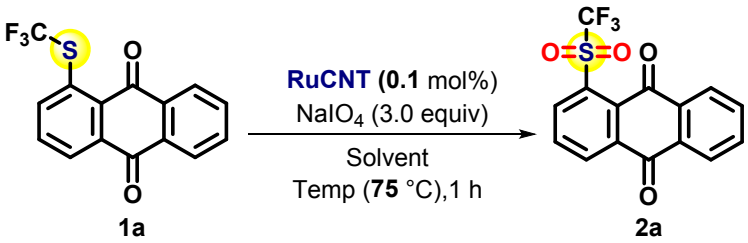


2-Iodo-1-tosylanthracene-9,10-dione (2k): Purification by FCC (toluene) afforded product **2k** (29.3 mg, 0.06 mmol, 60% yield) as a light yellow solid; **m.p. (°C)** = 220-223; **IR (solid, cm^{-1}) ν:** 3075 (s), 1673 (s), 1596 (m), 1554 (m), 1302 (s), 814 (s), 706 (s); **HRMS (ESI$^+$):** Calcd for $C_{21}H_{13}IO_4SNa$ $[M+Na]^+$ 510.9477, found 510.9470; **HRMS (ESI$^+$):** Calcd for $C_{21}H_{14}IO_4S$ $[M+H]^+$488.9657, found 488.9655; **^{1}H NMR**

(400 MHz, $CDCl_3$) δ: 8.44 (d, J = 8.2 Hz, 1H), 8.28 (d, J = 8.2 Hz, 2H), 8.21-8.14 (m, 1H), 8.12-8.06 (m, 2H), 7.84-7.78 (m, 2H), 7.40 (d, J = 8.0 Hz, 2H), 2.47 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ:** 185.1, 181.2, 147.2, 145.9, 144.5, 140.9, 138.0, 135.6, 134.9, 134.6, 133.9, 132.0, 131.1, 129.5, 128.8, 127.0, 126.8, 104.5, 21.7.



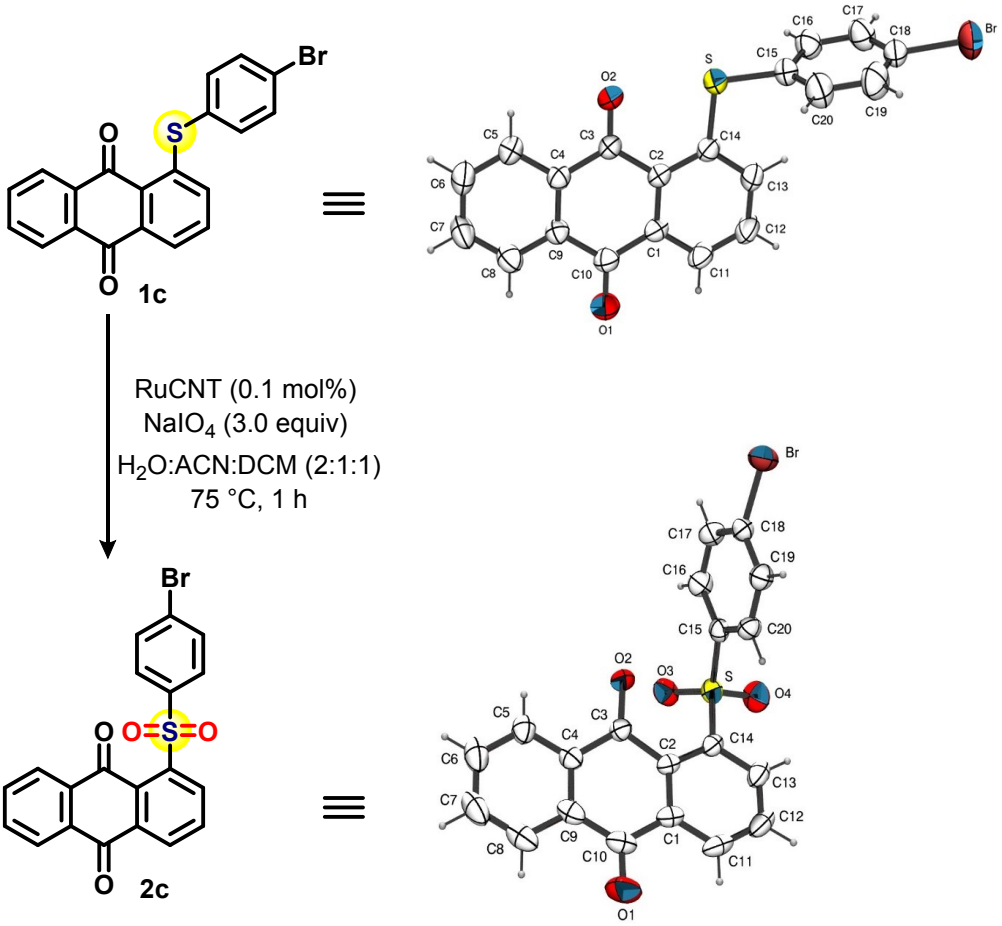
2-Iodo-1-(phenylsulfonyl)anthracene-9,10-dione (2l): Purification by FCC (toluene) afforded product **2l** (16.6 mg, 0.035 mmol, 84% yield) as a light yellow solid; **m.p. (°C)** = 228-230; **IR (solid, cm^{-1}) ν:** 3054 (s), 1681 (s), 1575 (m), 1446 (m), 1303 (s), 706 (s); **HRMS (ESI^+):** Calcd for $C_{20}H_{11}IO_4SNa$ $[M+Na]^+$ 496.9320, found 496.9322; **HRMS (ESI^+):** Calcd for $C_{20}H_{12}IO_4S$ $[M+H]^+$ 474.9501, found 474.9501; **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 8.46 (d, J = 8.2 Hz, 1H), 8.37 (d, J = 7.5 Hz, 2H), 8.25-8.15 (m, 1H), 8.09 (d, J = 8.2 Hz, 1H), 8.06-8.01 (m, 1H), 7.87-7.73 (m, 2H), 7.73-7.60 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ:** 182.5, 182.3, 145.1, 140.6, 137.4, 135.3, 134.6, 133.7, 132.2, 129.2, 128.9, 128.5, 128.3, 127.4, 126.6, 126.2, 119.7.

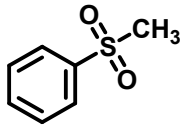


Entry	RuCNT (mol%)	Solvent	Yield (%)[b]
1	0.1	H_2O	NR
2	0.1	ACN:H_2O (1:1)	NR
3	0.1	DCM:H_2O (1:1)	9
4	0.1	H_2O:ACN:DCM (2:1:1)	97

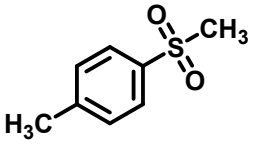
Table S1. Oxidation reaction performed with H_2O, ACN:H_2O (1:1), DCM:H_2O (1:1) and H_2O:ACN:DCM (2:1:1) as solvents.

Example of substrate and its respective product of oxidation solved by X-ray crystallography.

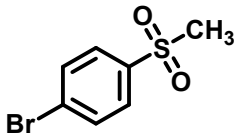




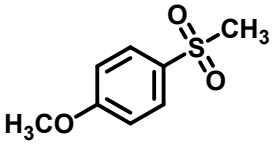
(methylsulfonyl)benzene (4a): Purification by recrystallization (hexane/$CHCl_3$) afforded product **4b** (31.2 mg, 0.2 mmol, >99% yield) as a crystalline white solid; **m.p. (°C)** = 85-87; **IR (solid, cm^{-1}) *v*:** 3024 (s), 1448 (m), 1282 (s), 1143 (s), 788 (s), 746 (s), 687 (w); **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 7.95 (d, *J* = 7.7 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 3.06 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 140.6, 133.7, 129.4, 127.3, 44.5. The data are consistent with those reported in the literature.[6]



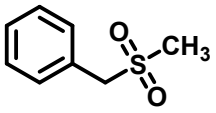
1-methyl-4-(methylsulfonyl)benzene (4b): Purification by recrystallization (hexane/$CHCl_3$) afforded product **4b** (31.0 mg, 0.18 mmol, 91% yield) as a crystalline white solid; **m.p. (°C)** = 82-84; **IR (solid, cm^{-1}) *v*:** 3010 (s), 1448 (m), 1287 (s), 1143 (s), 780 (s), 680 (w); **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 7.76 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.97 (s, 3H), 2.39 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 151.1, 144.6, 129.9, 127.4, 44.6, 21.6. The data are consistent with those reported in the literature.[7]



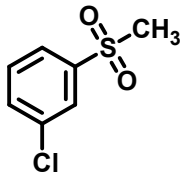
1-bromo-4-(methylsulfonyl)benzene (4c): Purification by recrystallization (hexane/$CHCl_3$) afforded product **4c** (47.1 mg, 0.2 mmol, >99% yield) as a crystalline white solid; **m.p. (°C)** = 100-102; **IR (solid, cm^{-1}) *v*:** 3093 (s), 1572 (m), 1464 (w), 1306 (s), 823 (s), 660 (w); **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 7.82 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.6 Hz, 2H), 3.06 (s, 3H).**^{13}C NMR (150 MHz, $CDCl_3$) *δ*:** 139.5, 132.6, 129.0, 128.9, 127.4, 44.4. The data are consistent with those reported in the literature.[8]



1-methoxy-4-(methylsulfonyl)benzene (4d): Purification by recrystallization (hexane/$CHCl_3$) afforded product **4d** (37.2 mg, 0.2 mmol, >99% yield) as a crystalline white solid; **m.p. (°C)** = 113-115; **IR (solid, cm^{-1}) *ν*:** 3010 (s), 1593 (m), 1499 (m), 1290 (s), 833 (s); **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 7.87 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 3.04 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 163.6, 132.2, 129.4, 114.4, 55.6, 44.8. The data are consistent with those reported in the literature.[6]

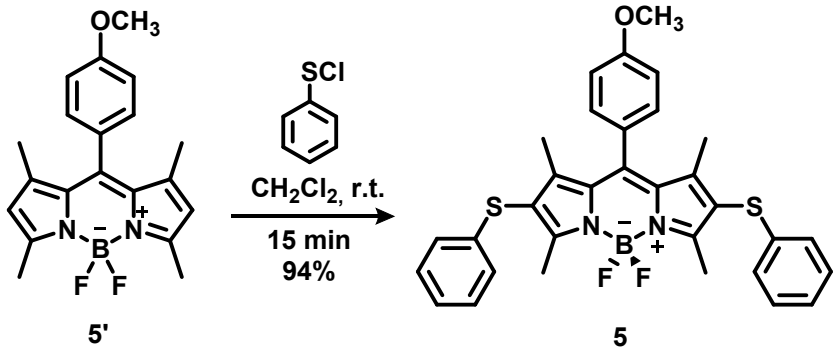


((methylsulfonyl)methyl)benzene (4e): Purification by recrystallization (hexane/$CHCl_3$) afforded product **4e** (22.8 mg, 0.13 mmol, 87% yield) as a crystalline white solid; **m.p. (°C)** = 123-125; **IR (solid, cm^{-1}) *ν*:** 3013 (s), 1603 (w), 1458 (m), 1412 (m), 1299 (s); **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 7.41 (s, 5H), 4.25 (s, 2H), 2.76 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 130.5, 129.1, 128.2, 61.2, 38.9. The data are consistent with those reported in the literature.[8]

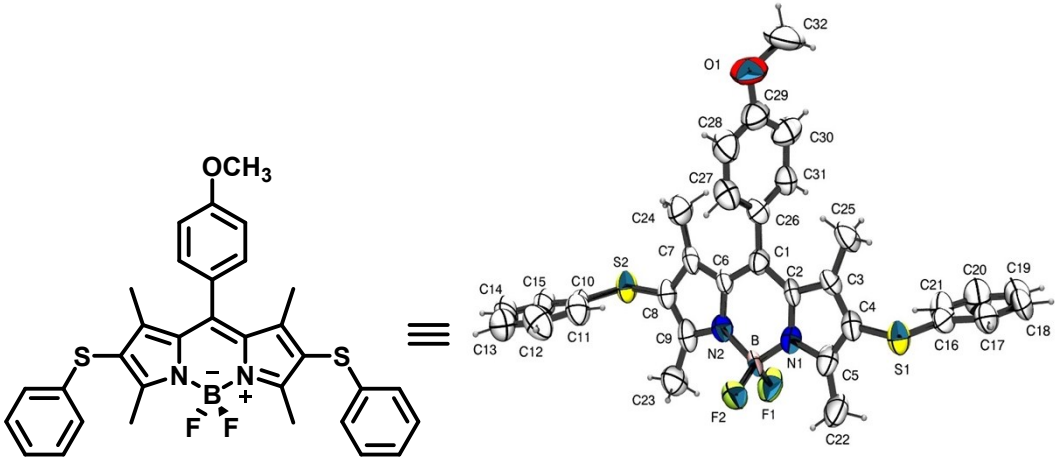


1-chloro-3-(methylsulfonyl)benzene (4f): Purification by recrystallization (hexane/$CHCl_3$) afforded product **4f** (25.6 mg, 0.2 mmol, 67% yield) as a crystalline white solid; **m.p. (°C)** = 55-57; **IR (solid, cm^{-1}) *ν*:** 3028 (s), 1570 (m), 1450 (w), 1306 (s), 823 (s); **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 7.95 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 1H), 3.08 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 142.2, 135.6, 133.9, 130.7, 127.5, 125.5, 44.4. The data are consistent with those reported in the literature.[6]

Synthesis of BODIPY 5[9]

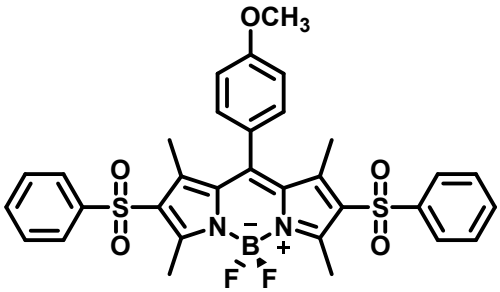


5,5-difluoro-10-(4-methoxyphenyl)-1,3,7,9-tetramethyl-2,8-bis(phenylthio)-5*H*-4λ⁴,5λ⁴-dipyrrolo[1,2-*c*:2',1'-f][1,3,2]diazaborinine: To a suspension of *N*-chlorosuccinimide (267 mg, 2 mmol) in CH_2Cl_2 (10 mL) at room temperature was dropwise addition of a solution of thiophenol (220,4 mg, 2 mmol) in dry CH_2Cl_2 (10 mL). After stirring for 30 min, the orange solution of the phenyl-sulfenyl chloride was used *in situ* assuming a complete conversion. The solution the phenyl-sulfenyl chloride at 0 ºC, a solution of BODIPY **5'** (50,0 mg, 0,135 mmol) in 10 mL of in dry CH_2Cl_2 was added dropwise within 15 min. The mixture of was stirred at room temperature for 15 min. H_2O (20 mL) was added to the deep red reaction mixture. After phase separation, the organic phase was washed with H_2O (20 mL), dried over Na_2SO_4, and the solvent was evaporated under vacuum. The residue was purified through column chromatography on silica, using hexane/CH_2Cl_2 (8:1) as eluent to give the desired product **5**.



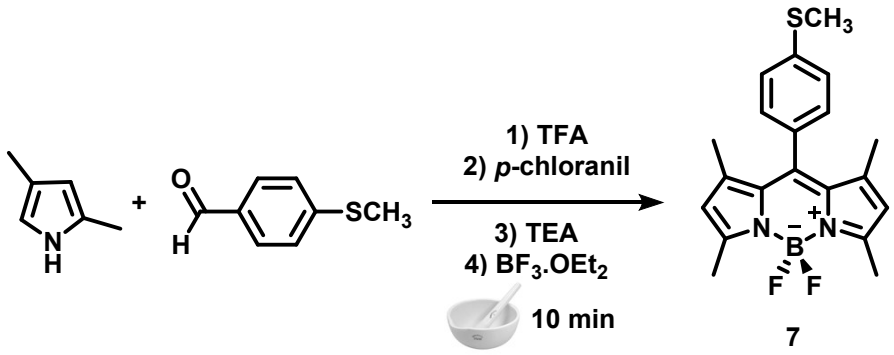
5,5-difluoro-10-(4-methoxyphenyl)-1,3,7,9-tetramethyl-2,8-bis(phenylsulfonyl)-5*H*-4λ⁴,5λ⁴-dipyrrolo[1,2-*c*:2',1'-f][1,3,2]diazaborinine (5): Purification by FCC

(hexane/CH_2Cl_2) afforded product **5** (1.07 g, 1.87 mmol, 94% yield) as an pink solid; **m.p. (°C) =** 225-228; **IR (solid, cm^{-1}) *v*:** 2930 (m), 1606 (m), 1517 (s), 1289 (s), 1243 (s), 1173 (s), 991 (s), 726 (m), 681 (w); **HRMS (ESI$^+$):** Calcd for $C_{32}H_{30}BF_2N_2OS_2$ $[M+H]^+$ 571.1860, found 571.1842; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 7.24-7.17 (m, 6H), 7.10 (ddd, *J* = 6.9, 2.1, 1.1 Hz, 2H), 7.06-7.02 (m, 2H), 7.00 (dt, *J* = 8.4, 1.6 Hz, 4H), 3.87 (s, 3H), 2.62 (s, 6H), 1.54 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 160.5, 159.9, 148.4, 143.2, 137.4, 131.7, 129.0, 128.9, 126.6, 125.9, 125.9, 125.2, 120.6, 114.9, 55.3, 13.4, 13.2.

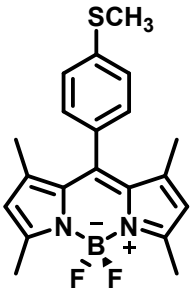


5,5-difluoro-10-(4-methoxyphenyl)-1,3,7,9-tetramethyl-2,8-bis(phenylsulfonyl)-5*H*-4λ^4,5 λ^4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (6): This compound was prepared following the oxidation method herein described. Purification by FCC (hexane/EtOAc) afforded product **6** (21.3 mg, 0.033 mmol, 67% yield) as an orange solid; **m.p. (°C) =** 198-200; **IR (solid, cm^{-1}) *v*:** 2922 (m), 1738 (m), 1538 (s), 1464 (s), 1305 (s), 1150 (s), 1055 (m), 963 (m), 835 (w), 749 (w); **HRMS (ESI$^+$):** Calcd for $C_{32}H_{29}BF_2N_2O_5S_2Na$ $[M+Na]^+$ 657.1476, found 657.1467; **HRMS (ESI$^+$):** Calcd for $C_{32}H_{30}BF_2N_2O_5S_2$ $[M+H]^+$ 635.1657, found 635.1657; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 7.83 (d, *J* = 7.5 Hz, 4H), 7.58 (t, *J* = 7.3 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 4H), 7.06 (q, *J* = 8.7 Hz, 4H), 3.88 (s, 3H), 2.88 (s, 6H), 1.71 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 161.2, 158.0, 147.1, 146.9, 142.6, 133.3, 131.8, 129.3, 128.7, 126.6, 125.0, 115.4, 102.3, 55.5, 14.3, 13.4. **^{19}F NMR (470 MHz, $CDCl_3$) *δ*:** 143.11 (q, *J* = 31,7 Hz).

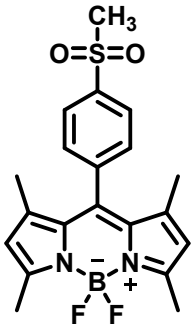
Synthesis of BODIPY 7



4-(methylthio)benzaldehyde (0.67 mL, 5.0 mmol) and 2,4-dimethylpyrrole (1.03 mL, 10.0 mmol) were mixed with a pestle and mortar. Trifluoroacetic acid (TFA) (5 drops) was added via a pipette, while the mixture was ground with the pestle for about 2 minutes. To the resulting paste, $CHCl_3$ (2.0 mL) was added, followed immediately by the addition of *p*-chloranil (1.81 g, 7.4 mmol). The purple paste was ground for 2 minutes, after which triethylamine (TEA) (6.0 mL, 43.0 mmol) was added via a syringe. The resulting dark brown paste was ground with the pestle for 3 minutes. Subsequently, $BF3{\cdot}OEt_2$ (6.0 mL, 47.4 mmol) was added slowly, dropwise, via a syringe and the mixture was ground for 2 minutes until a thick dark red paste was formed. The reaction mixture was dissolved in $CHCl_3$ (200 mL), transferred to a separation funnel, and washed with saturated Na_2CO_3 (3 × 200 mL) followed by brine (2 × 200 mL). The solvent was evaporated under reduced pressure and the crude solid was purified by column chromatography (silica gel) using hexane:chloroform (9:1) as the eluent to give the desired product **7**.



5,5-difluoro-1,3,7,9-tetramethyl-10-(4-(methylthio)phenyl)-5*H*-4λ^4,5λ^{4}dipyrrolo[1,2-c:2',1'-*f*][1,3,2]diazaborinine (7): Purification by FCC (hexane/CH_2Cl_2) afforded product **7** (778 mg, 2.1 mmol, 42% yield) as an pink solid; **m.p. (°C) =** 186-187; **IR (solid, cm^{-1}) *v*:** 3021 (s), 1538 (s), 1460 (m), 1300 (s), 1158 (s), 1055 (w), 850 (m), 725 (m); **HRMS (ESI$^+$):** Calcd for $C_{20}H_{21}BF_2N_2SNa$ $[M+Na]^+$ 393.1384, found 393.1382; **HRMS (ESI$^+$):** Calcd for $C_{20}H_{22}BF_2N_2S$ $[M+H]^+$ 371.1564, found 371.1563; **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 7.35 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 5.98 (s, 2H), 2.55 (d, *J* = 3.7 Hz, 9H), 1.43 (s, 6H).**^{13}C NMR (100 MHz, $CDCl_3$) *δ*:** 155.6, 143.2, 140.9, 140.2, 131.5, 128.6, 126.6, 121.4, 119.0, 77.2, 29.9, 15.5, 14.8. **^{19}F NMR (470 MHz, CDCl3) *δ*:** 143.70 (q, *J* = 32.8 Hz).



5,5-difluoro-1,3,7,9-tetramethyl-10-(4-(methylsulfonyl)phenyl)-5*H*-4λ^4,5λ^{4}dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (8): This compound was prepared following the oxidation method herein described. Purification by FCC (hexane/EtOAc) afforded product **8** (25.7 mg, 0.064 mmol, 64% yield) as an orange solid; **m.p. (°C) =** 193-196; **IR (solid, cm^{-1}) *v*:** 2922 (s), 1538 (s), 1464 (m), 1305 (s), 1150 (s), 1055 (w), 835 (m), 749 (m); **HRMS (ESI$^+$):** Calcd for $C_{20}H_{21}BF_2N_2O_2SNa$ $[M+Na]^+$ 425.1282, found 425.1281; **HRMS (ESI$^+$):** Calcd for $C_{20}H_{22}BF_2N_2O_2S$ $[M+H]^+$403.1463, found 403.1461; **^{1}H NMR (400 MHz, $CDCl_3$) *δ:*** 8.14 (t, *J* = 7.8 Hz, 2H), 7.58 (dd, *J* = 8.1, 3.9 Hz, 2H), 6.08 (s, 1H), 6.03 (s, 1H), 3.16 (d, *J* = 3.9 Hz, 3H), 2.59 (d, *J* = 5.7 Hz,

6H), 1.36 (t, J = 6.1 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$) δ:** 159.0, 156.6, 151.3, 144.3, 142.5, 141.8, 141.5, 141.1, 140.6, 138.9, 138.7, 130.8, 129.6, 129.5, 128.3, 128.2, 122.6, 121.8, 44.6, 14.7, 14.6, 12.3, 11.9.

Procedure for the recycling experiments

To a solution of **3a** (0.1 mmol) in H_2O:ACN:DCM (2:1:1, 4 mL) was added RuCNT (0.1 mol%). The mixture was kept under vigorous stirring, and $NaIO_4$ (63.9 mg, 0.3 mmol) was added. The mixture was heated at 75 °C for 1 h, after this period, the reaction mixture was cooled to room temperature and methanol (4 mL) was added. The mixture was then transferred to *Eppendorf tube* (single tube) and centrifuged to give a pellet consisting of nanohybrid and inorganic salts. The supernatant was collected and the pellet was dispersed/centrifuged with fresh methanol (2×2 mL). All supernatants were combined, dried, and purified by chromatography over silica-gel, eluting with a gradient mixture of hexane/AcOEt with increasing polarity to quantitatively yield pure sulfone **4a**. The pellet was washed with water (2×2 mL) to remove inorganic salts from the nanohybrid. The recovered RuCNT catalyst was used without further treatment in subsequent recycling experiments.

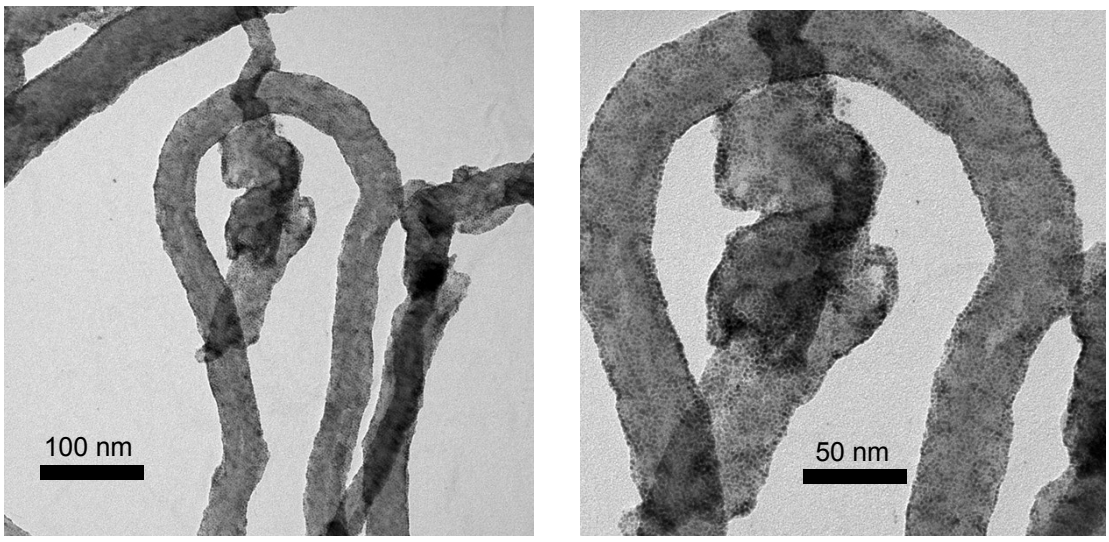
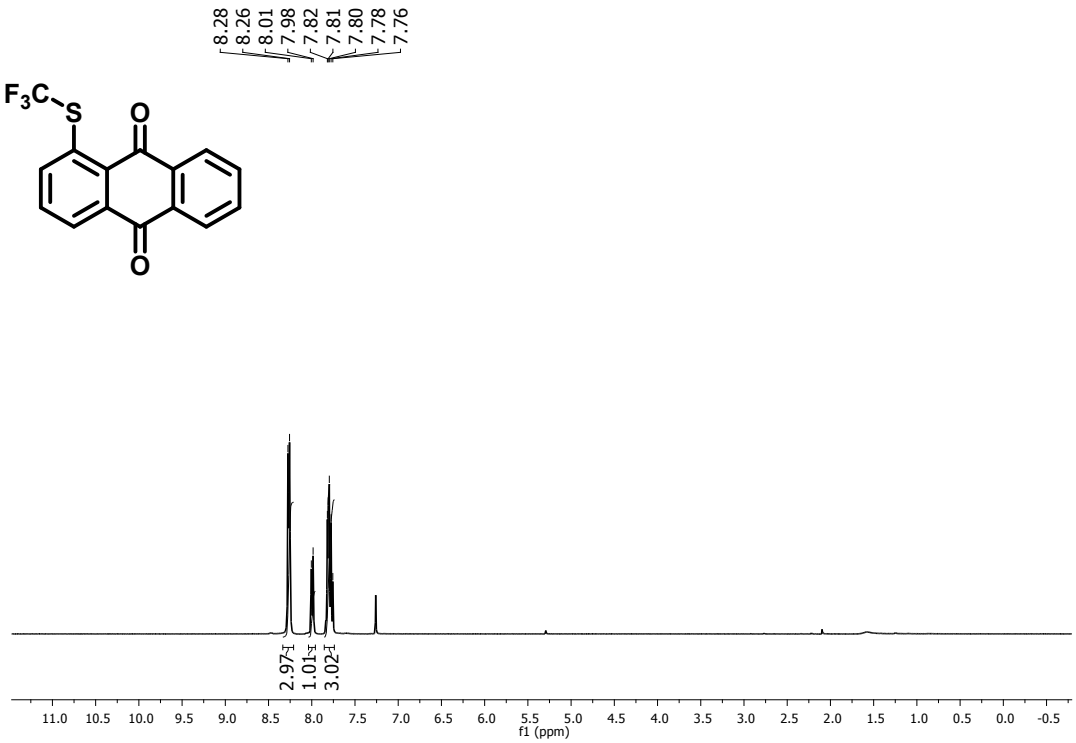
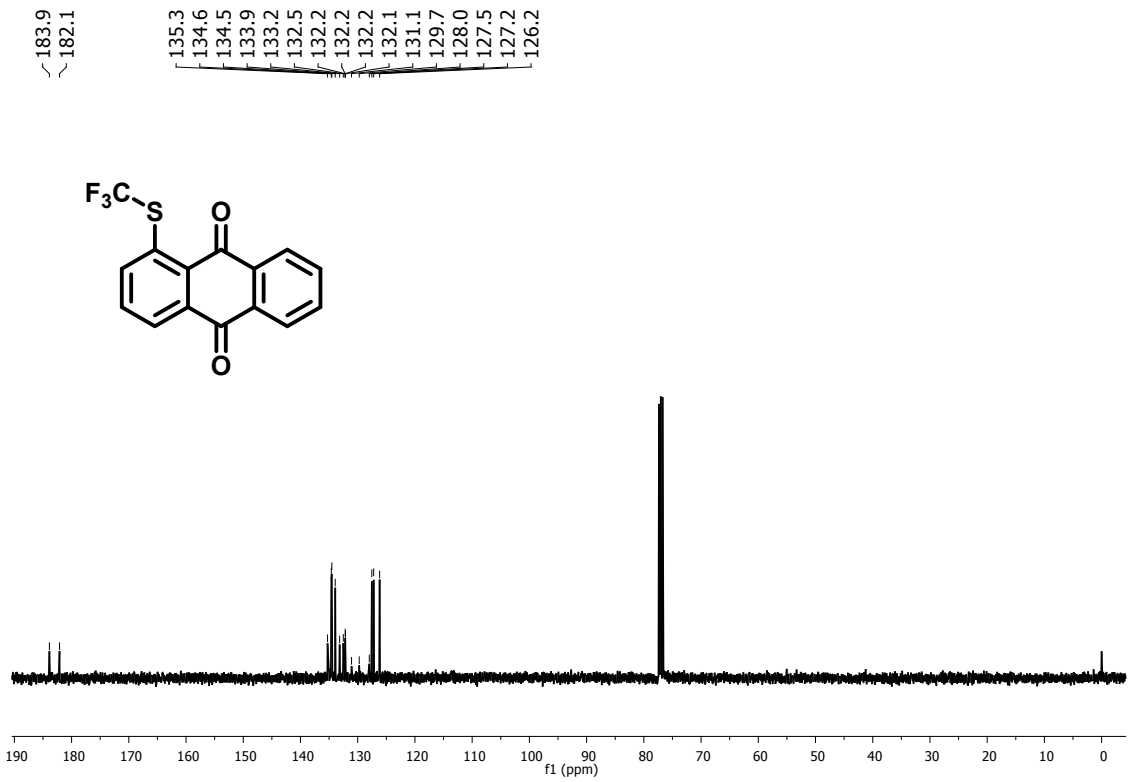


Figure S1. Transmission electron microscopy image of the RuCNT hybrid.

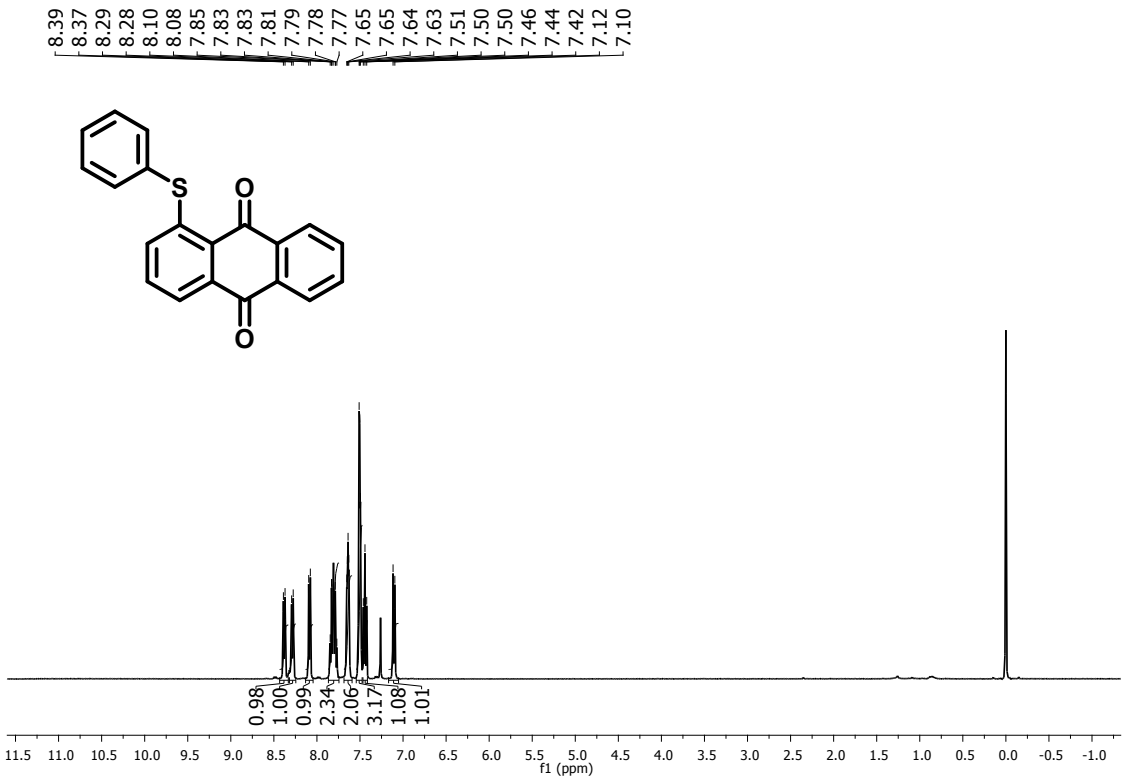
Copies of NMR spectra of novel compounds



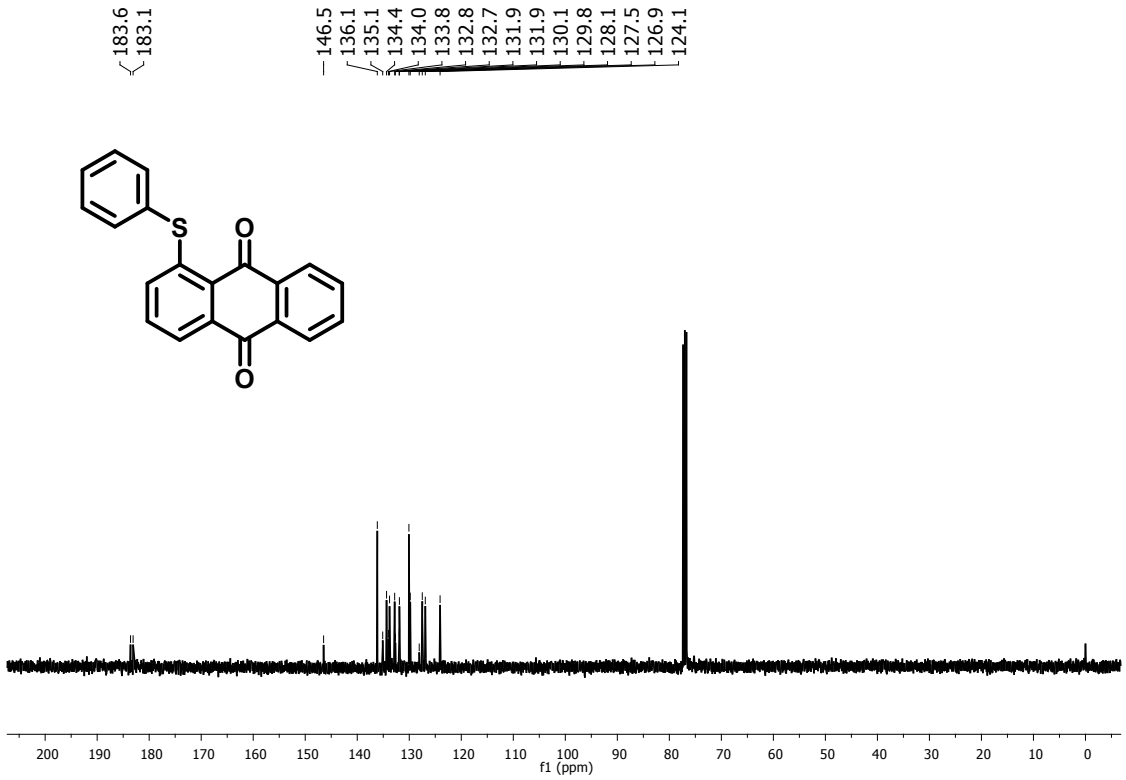
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1a**.



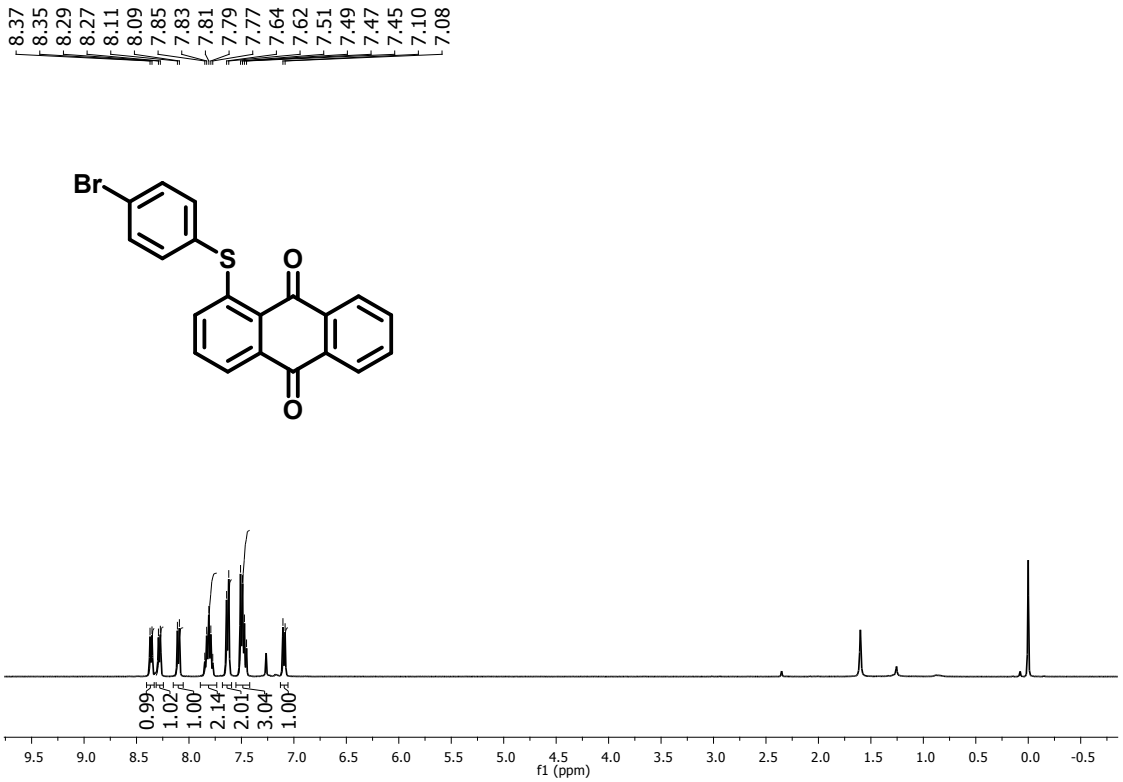
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **1a**.



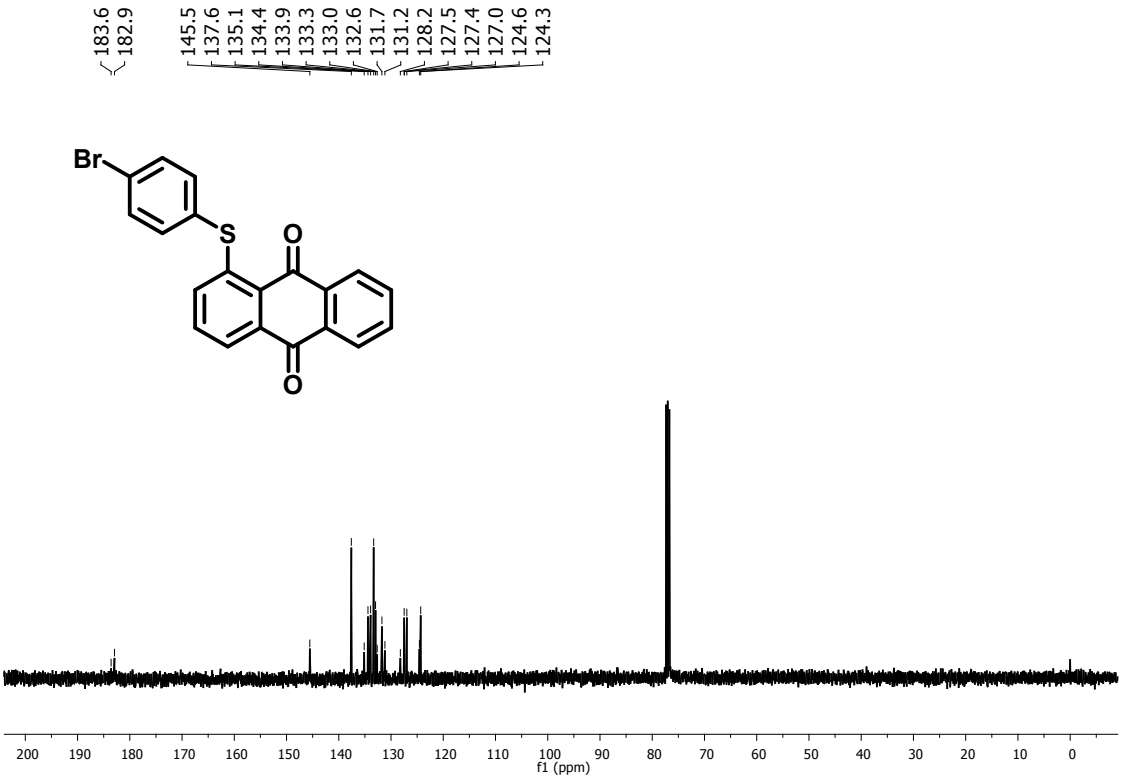
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1b**.



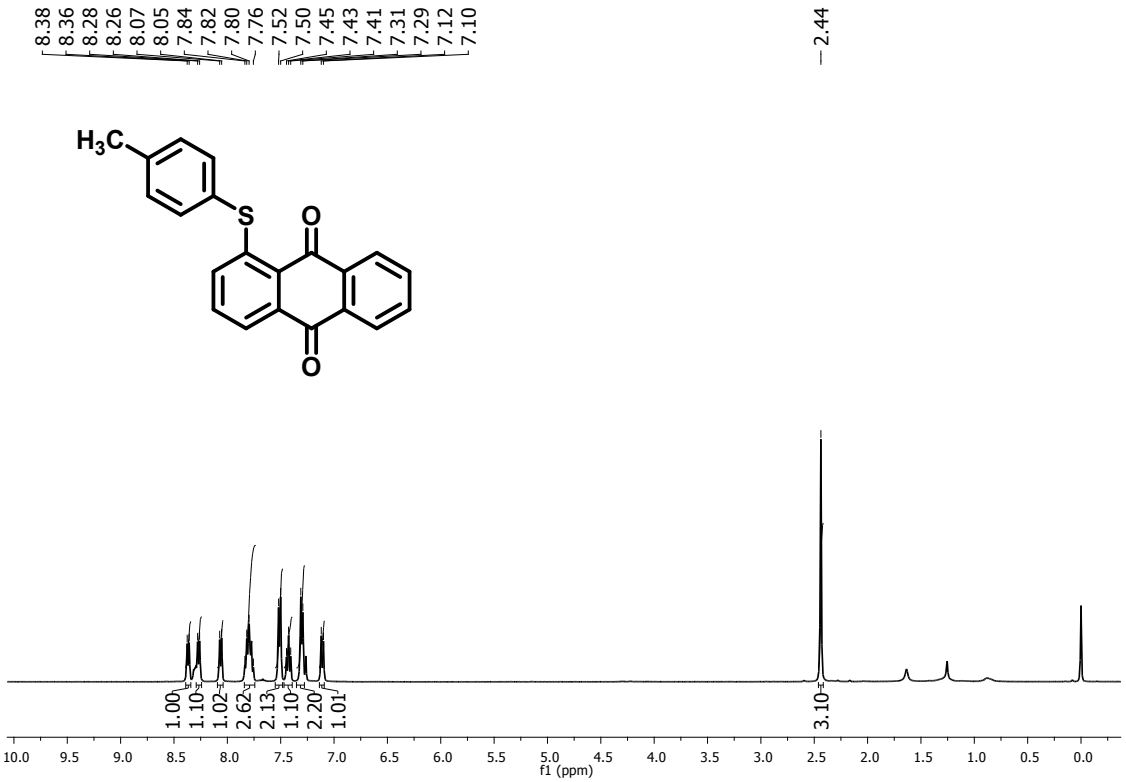
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **1b**.



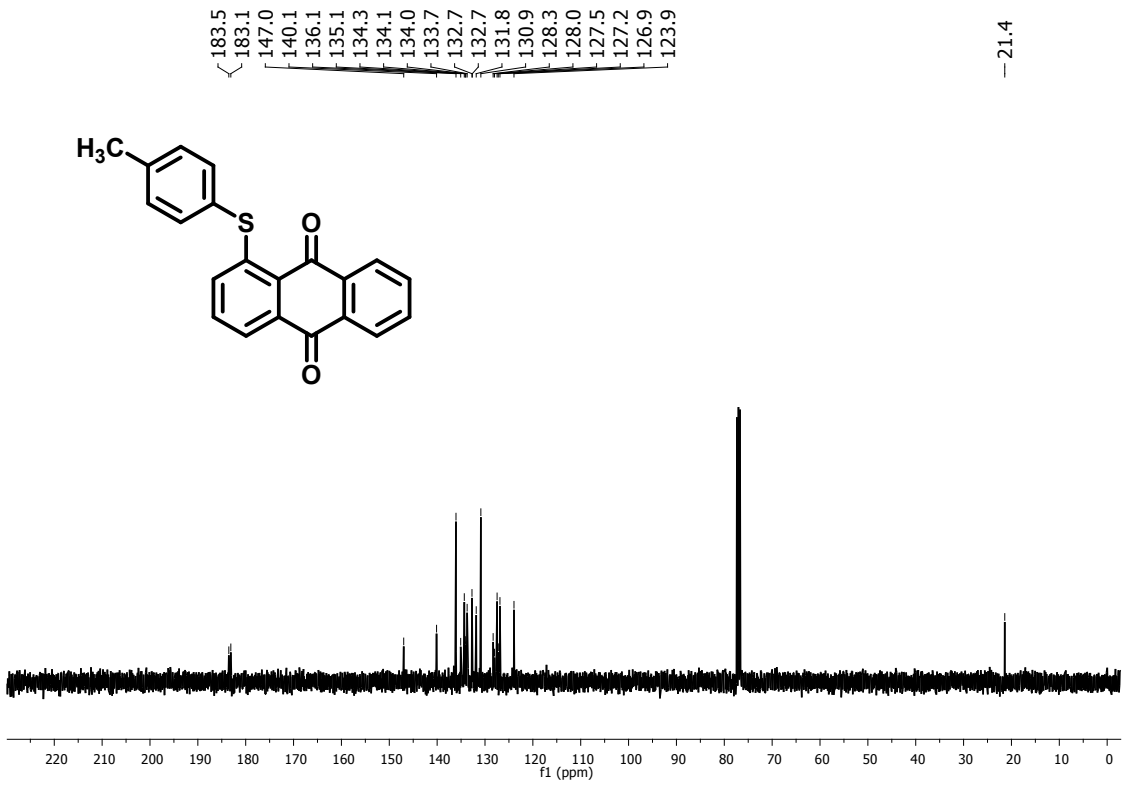
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1c**.



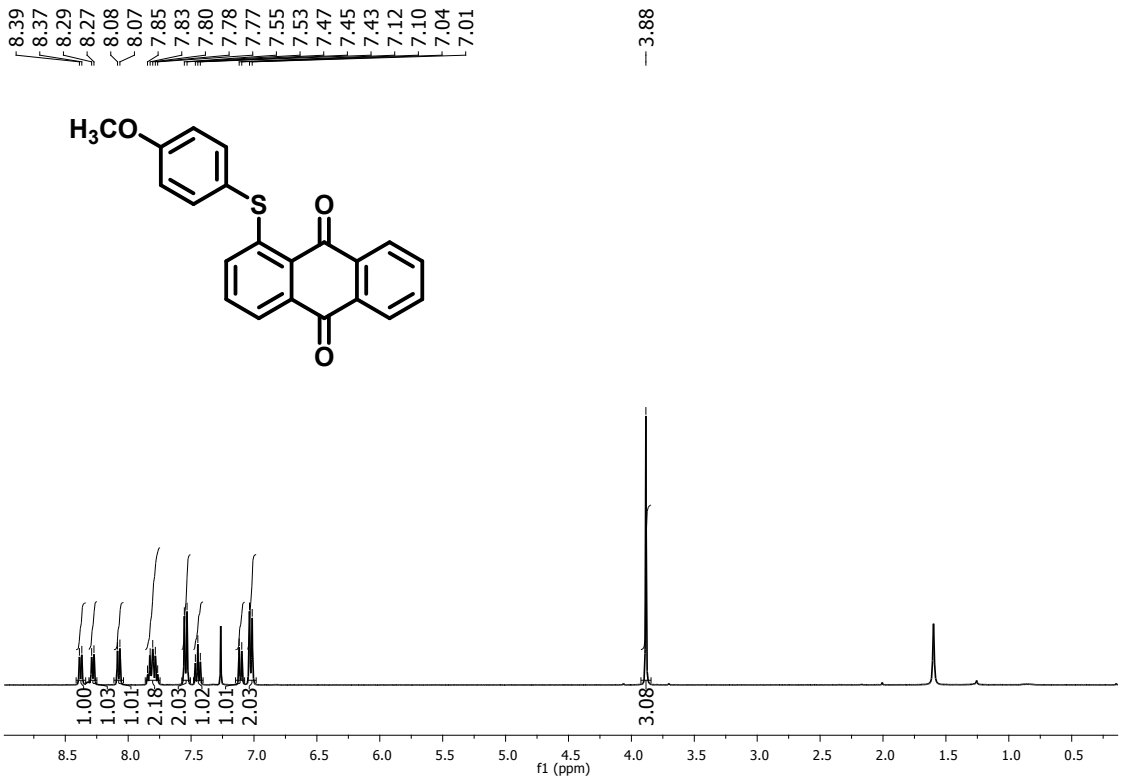
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **1c**.



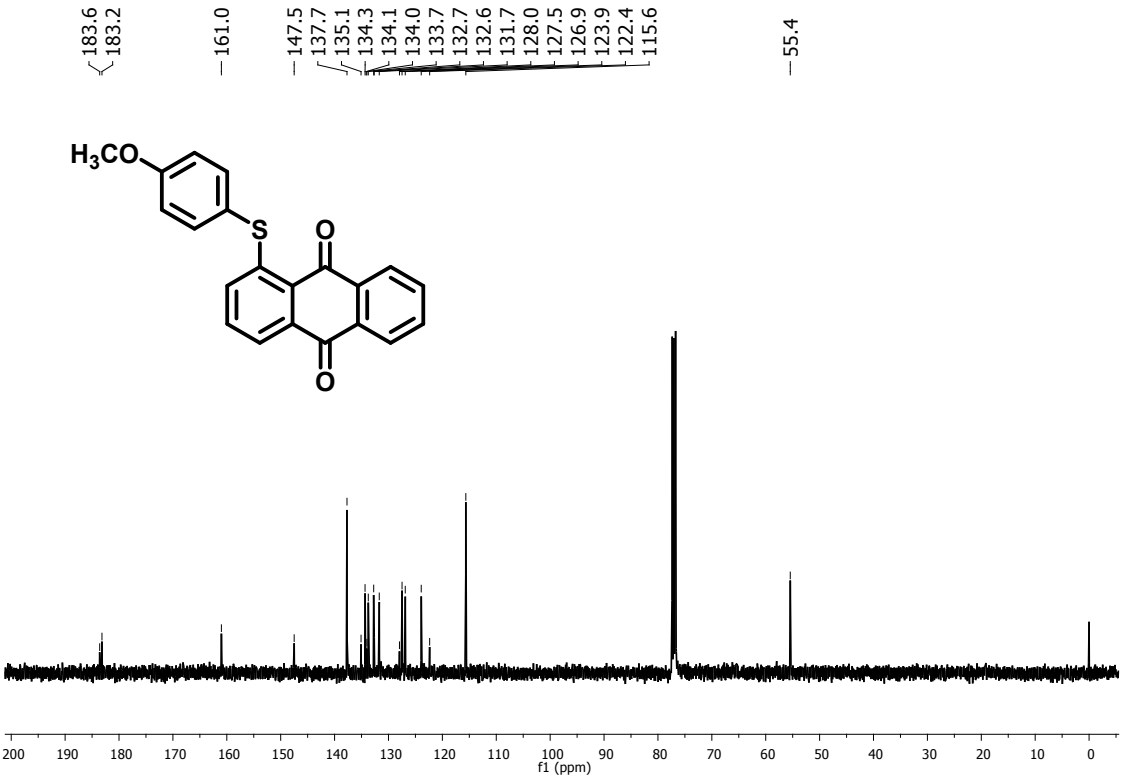
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1d**.



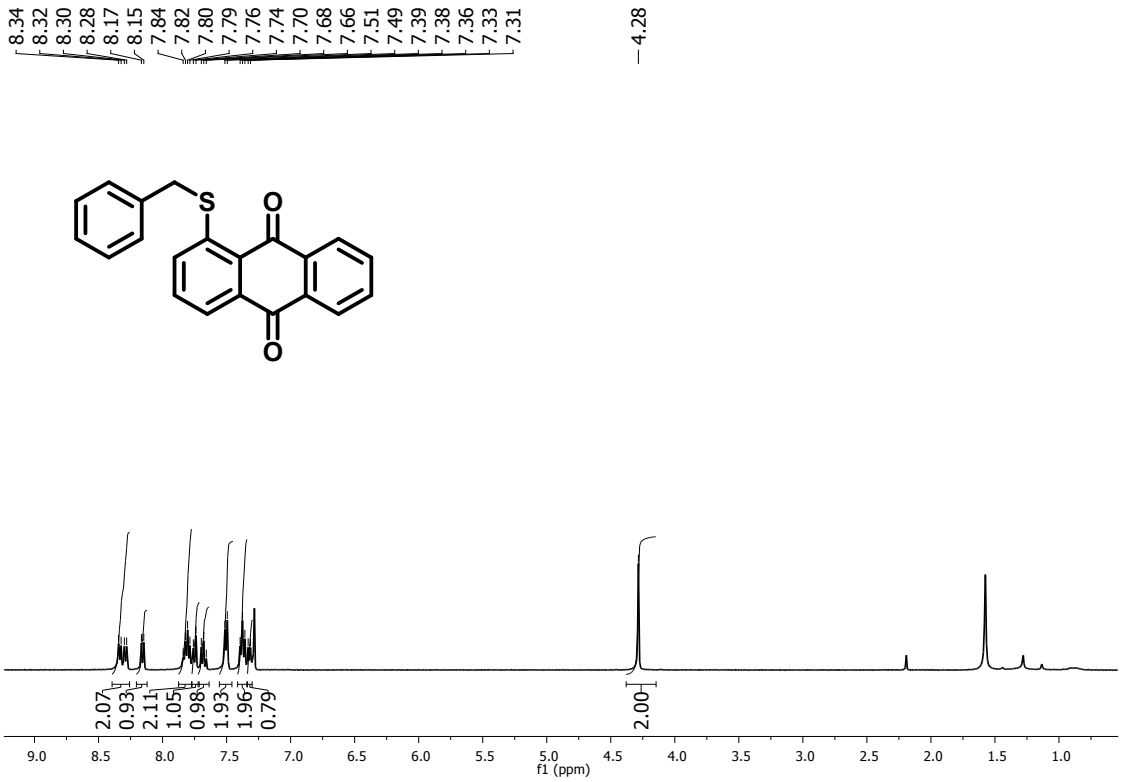
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **1d**.



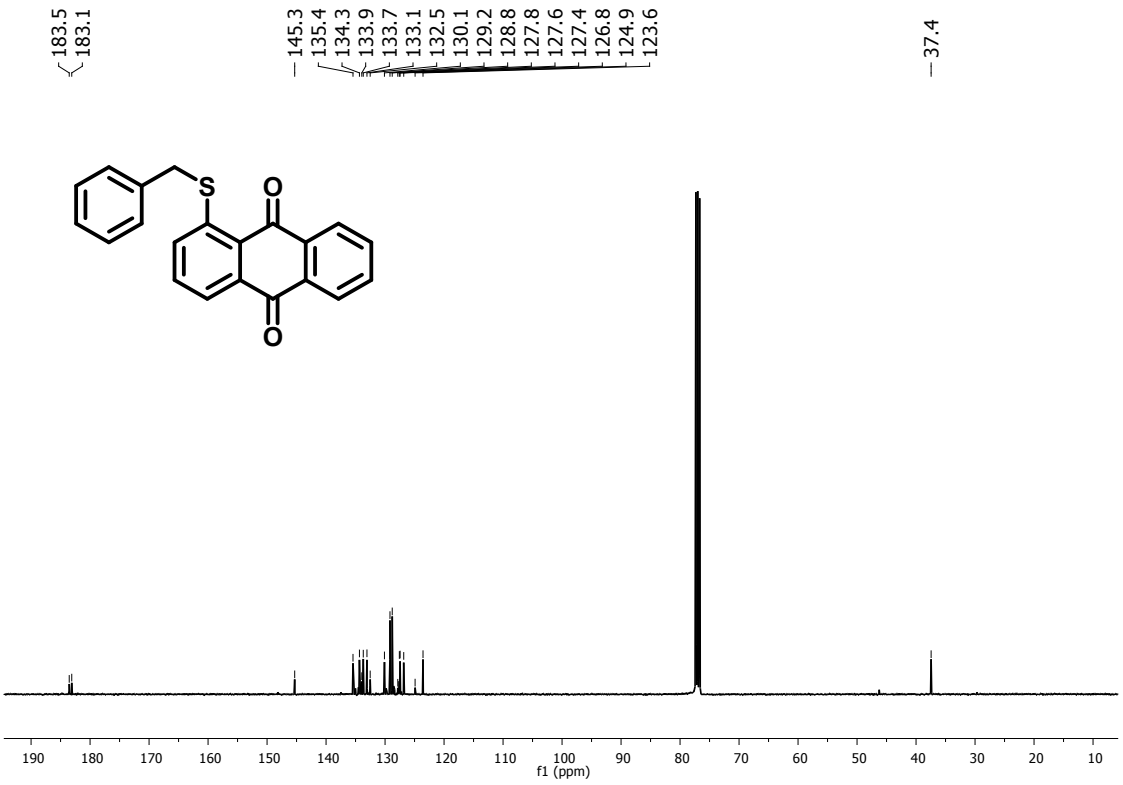
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1e**.



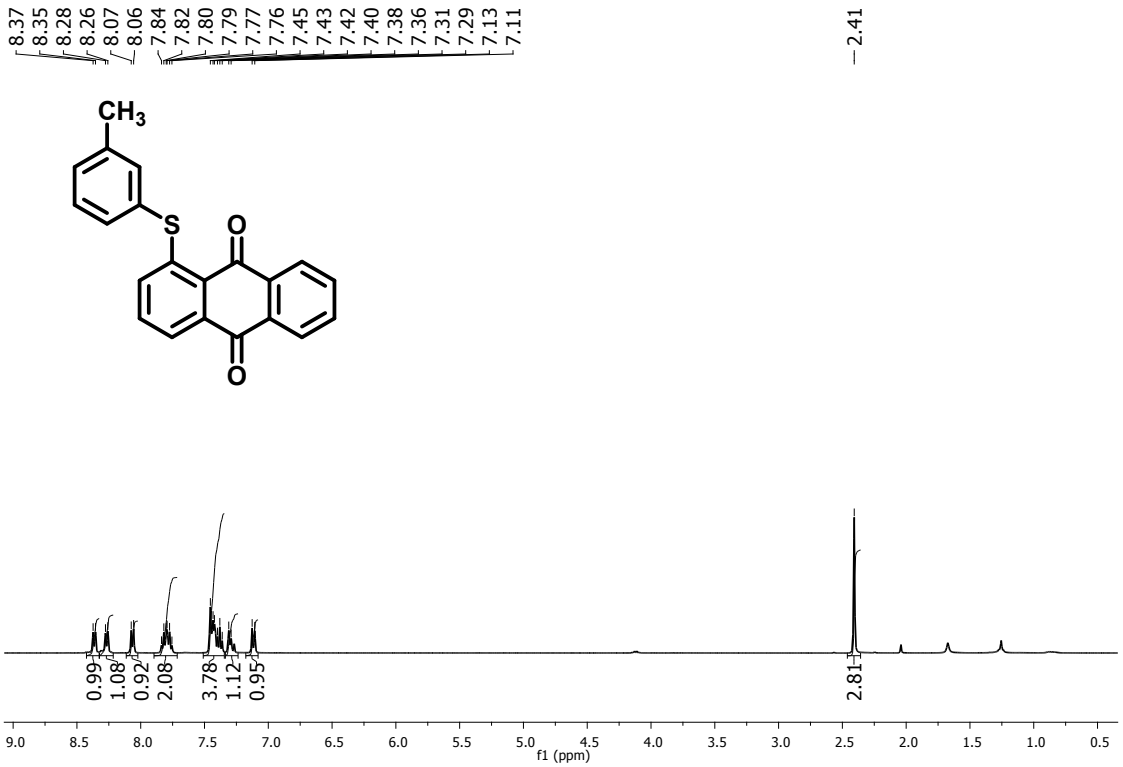
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **1e**.



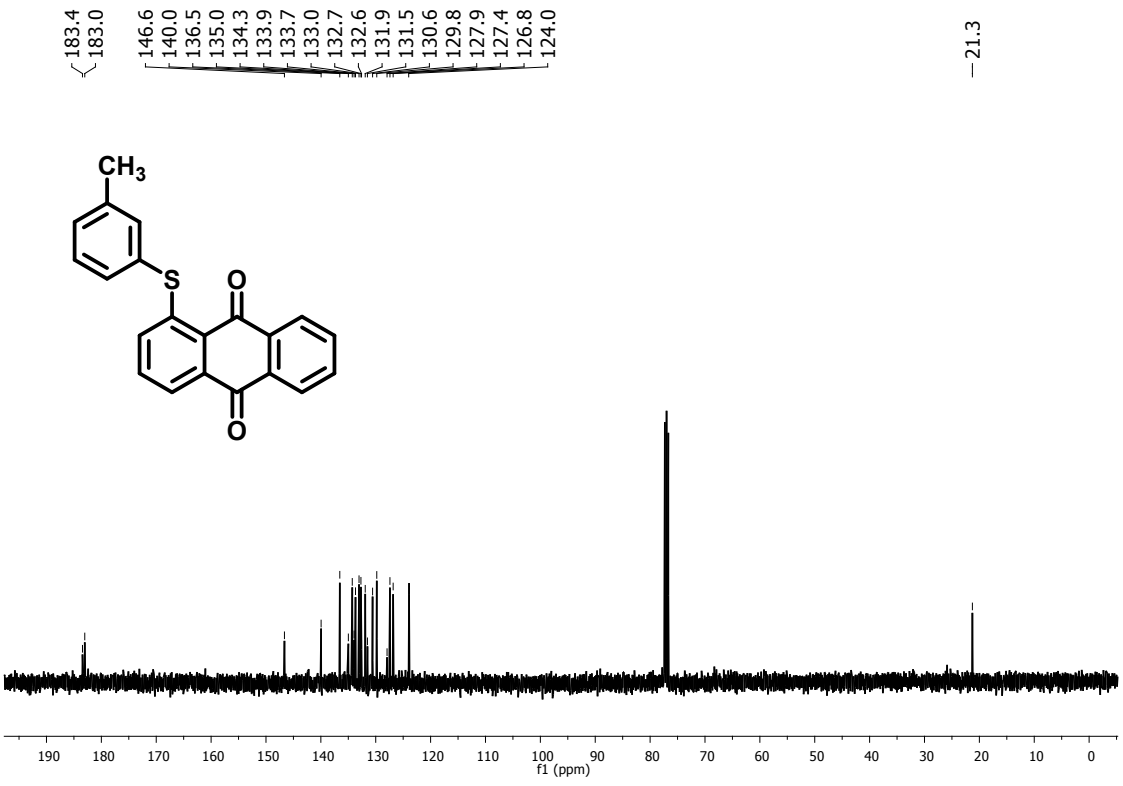
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1f**.



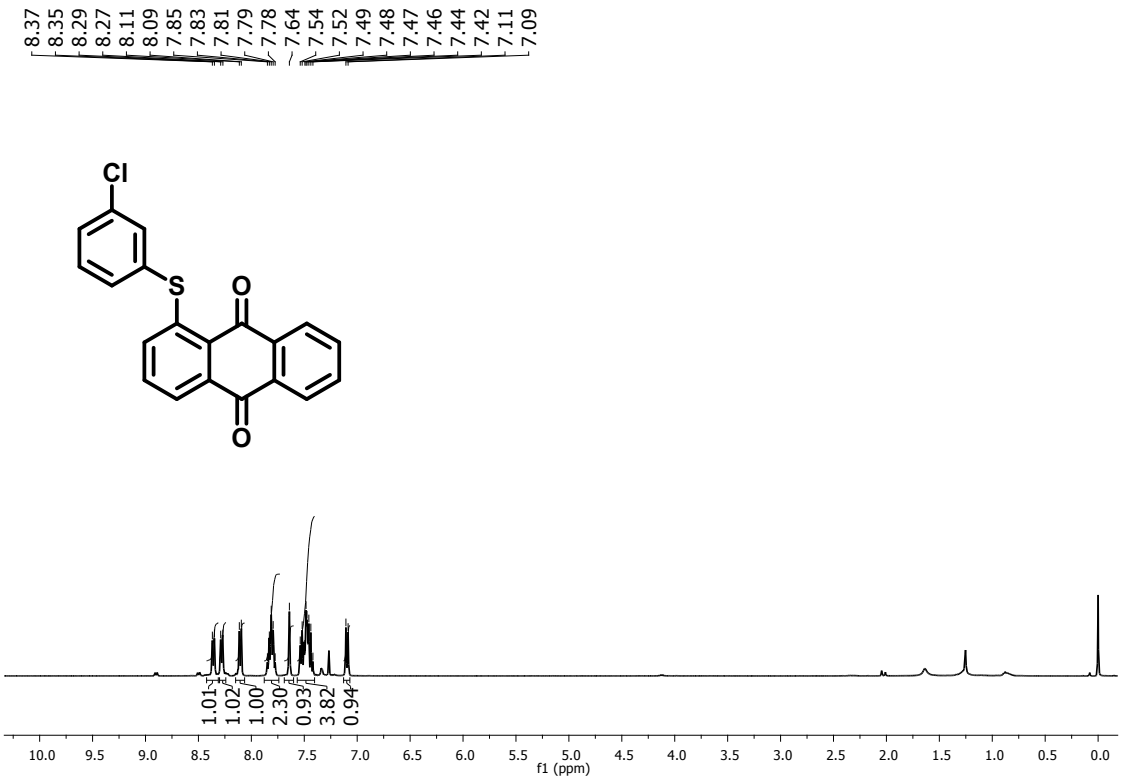
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **1f**.



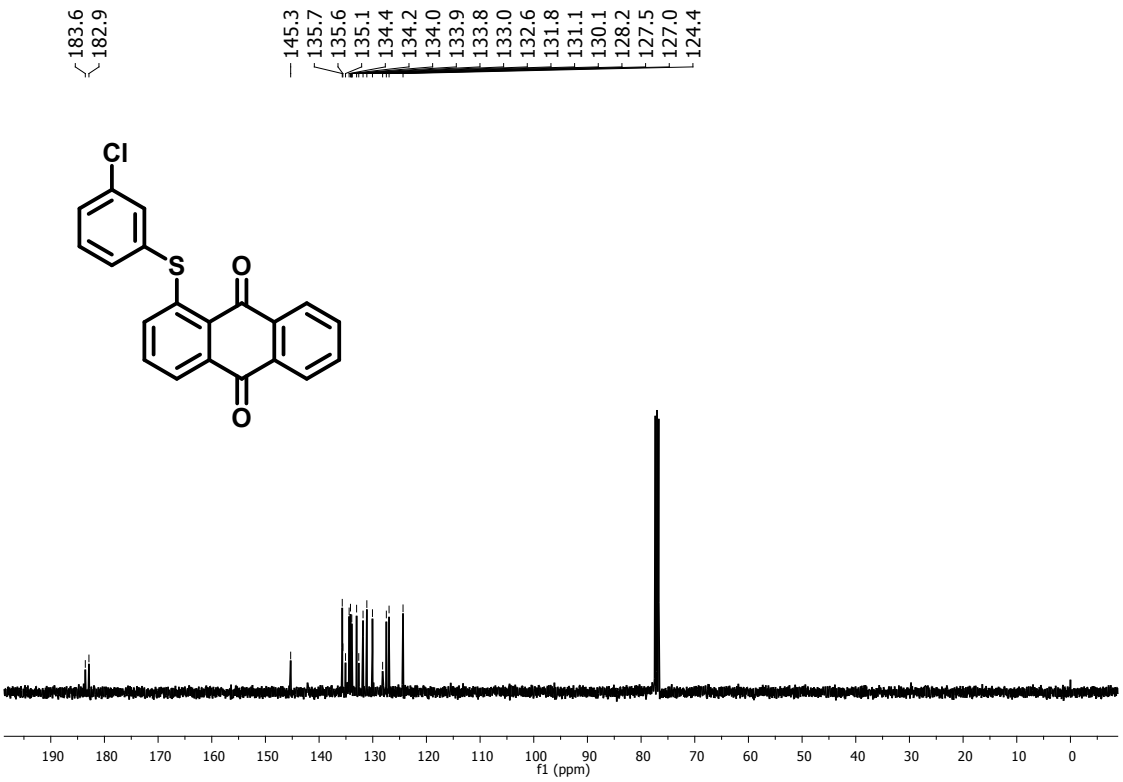
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1g**.



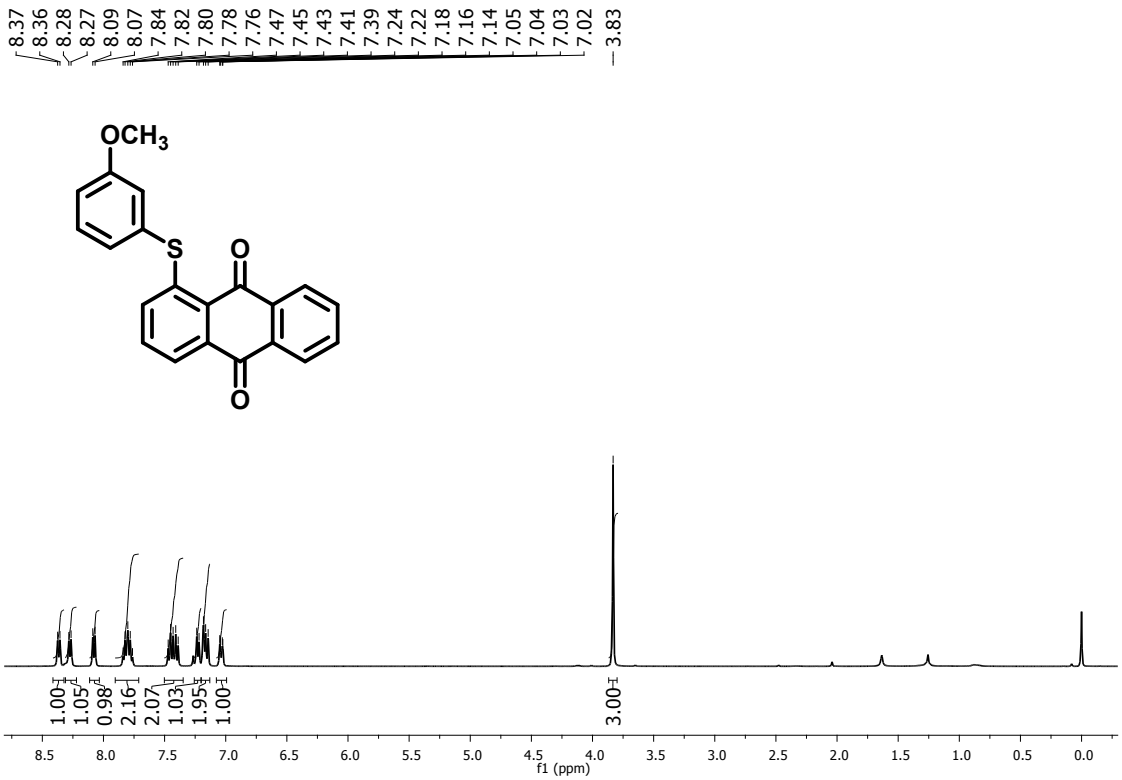
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **1g**.



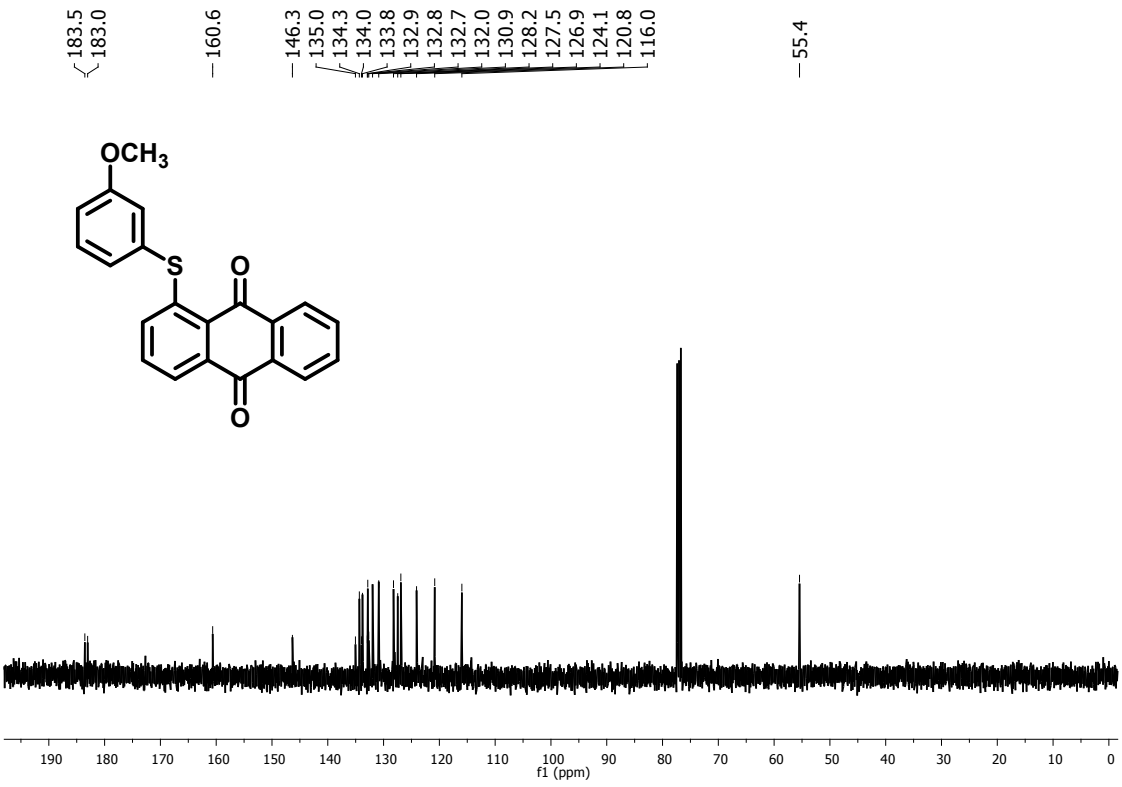
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1h**.



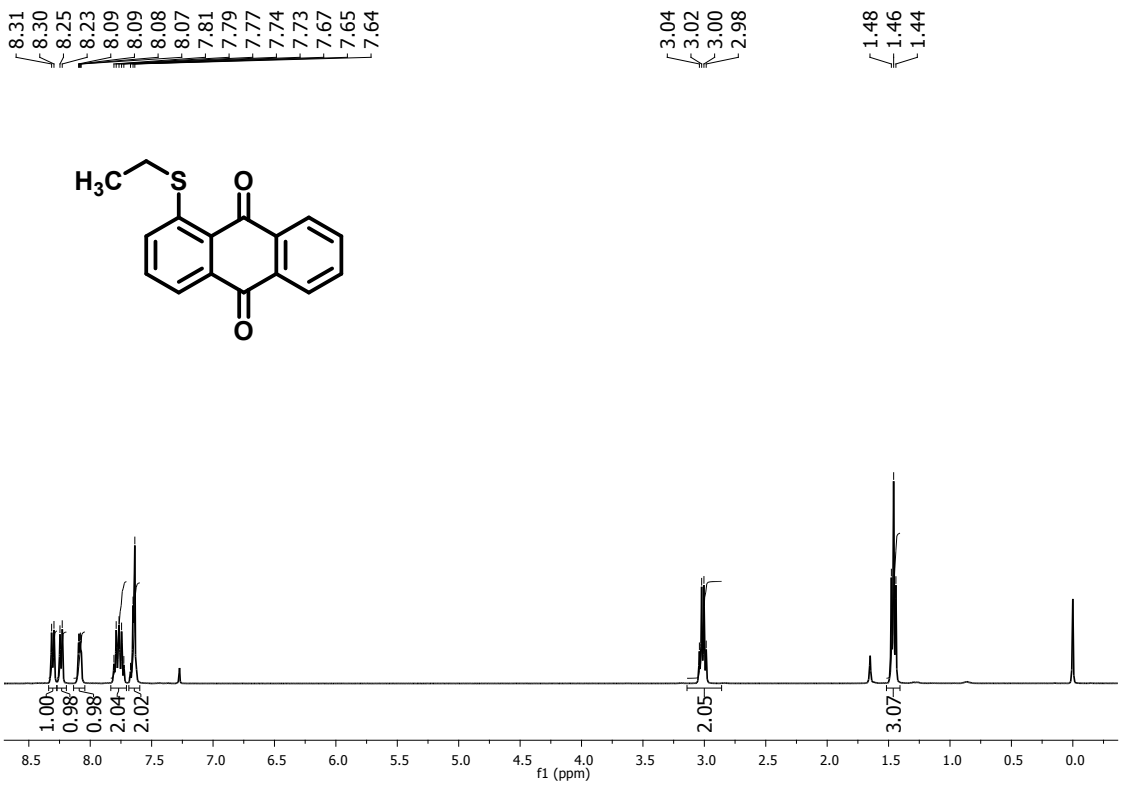
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **1h**.



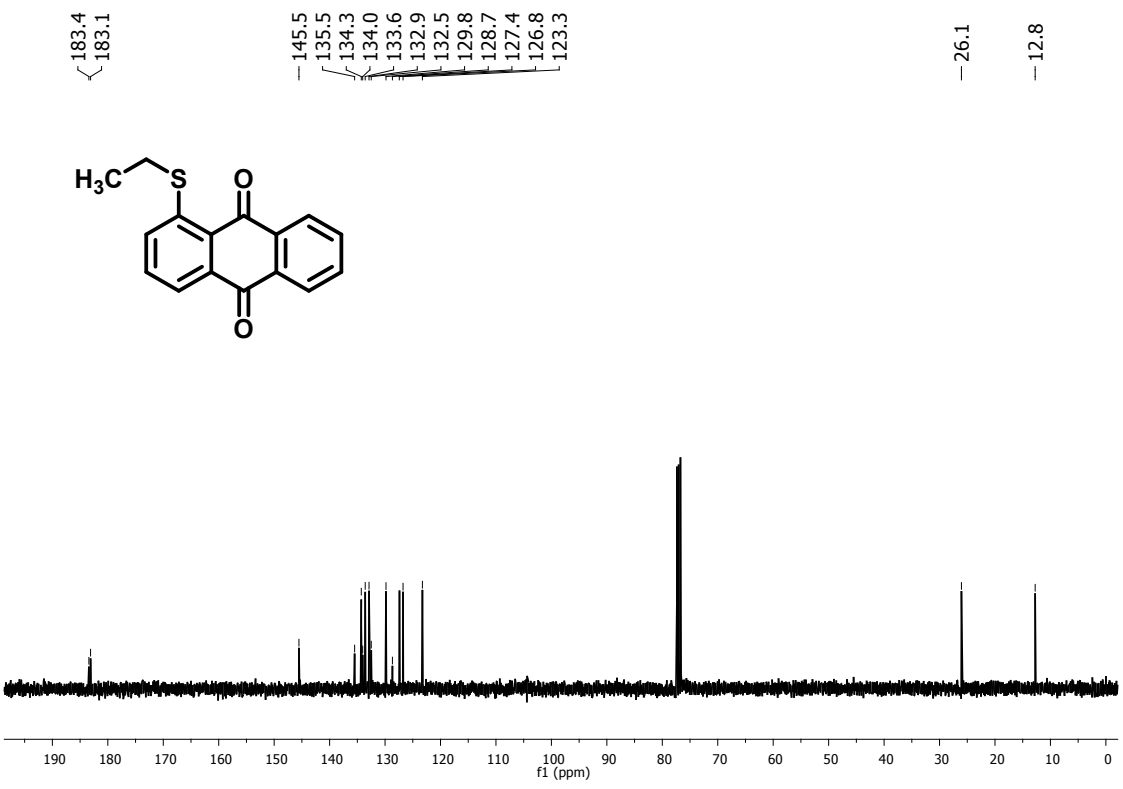
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1i**.



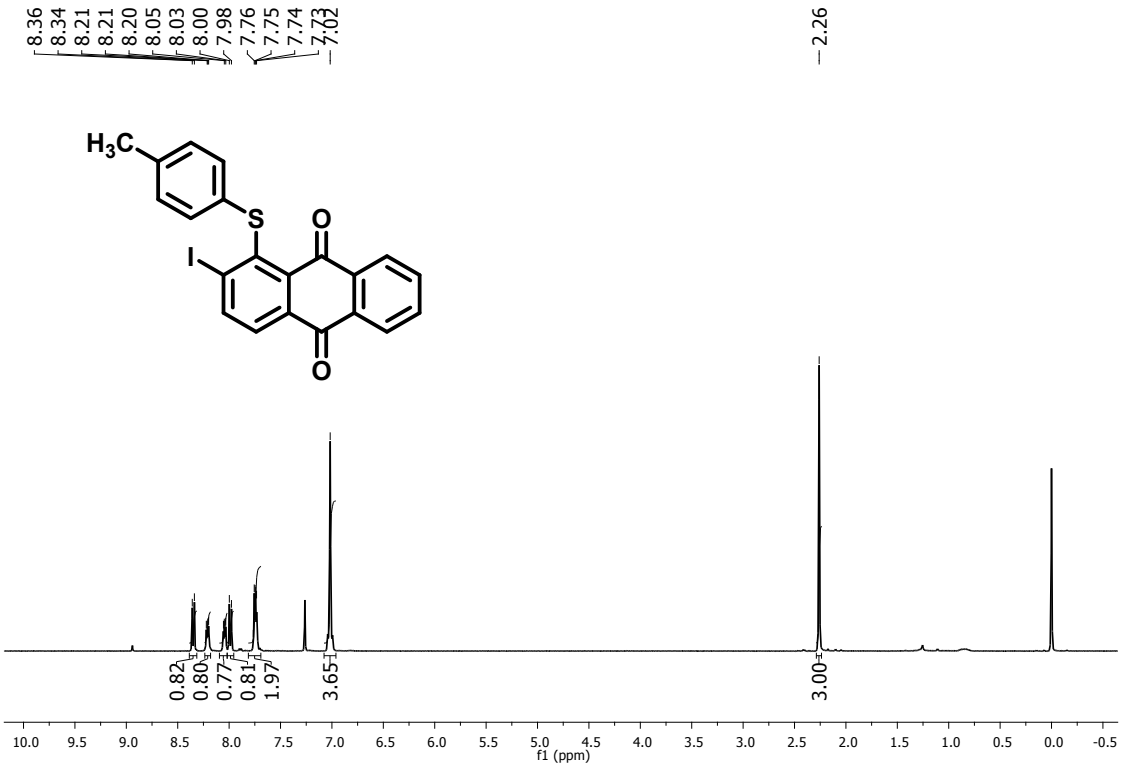
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **1i**.



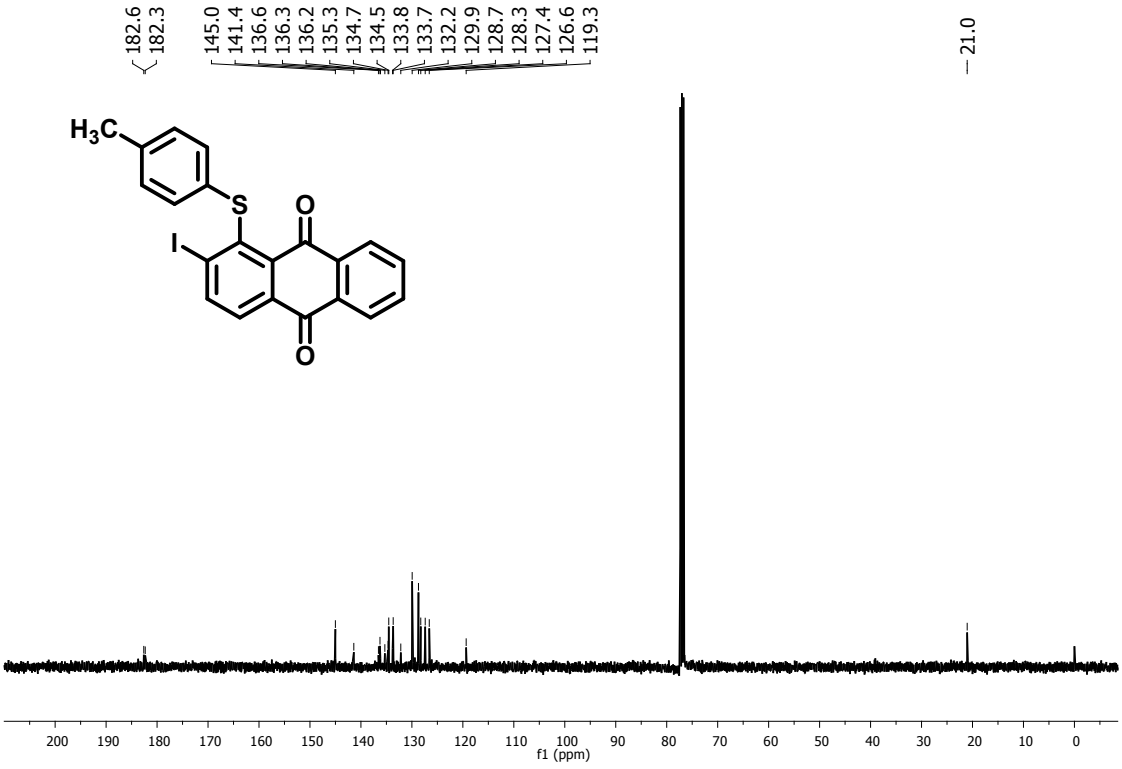
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1j**.



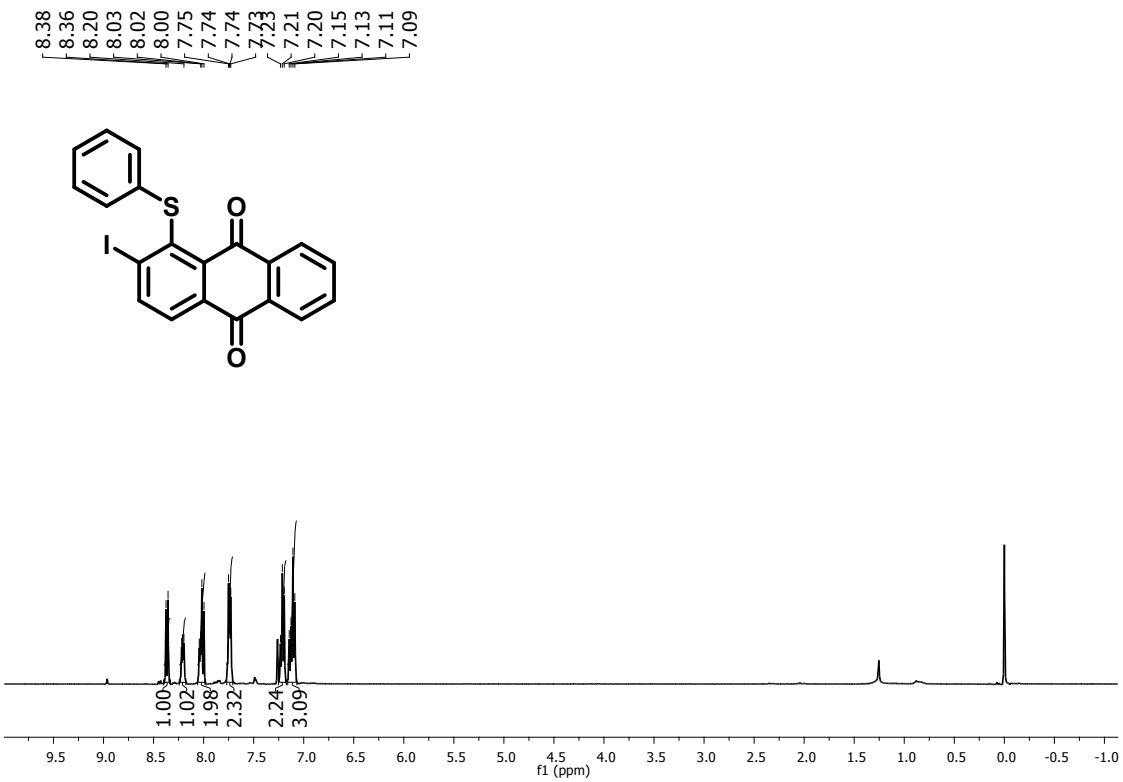
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **1j**.



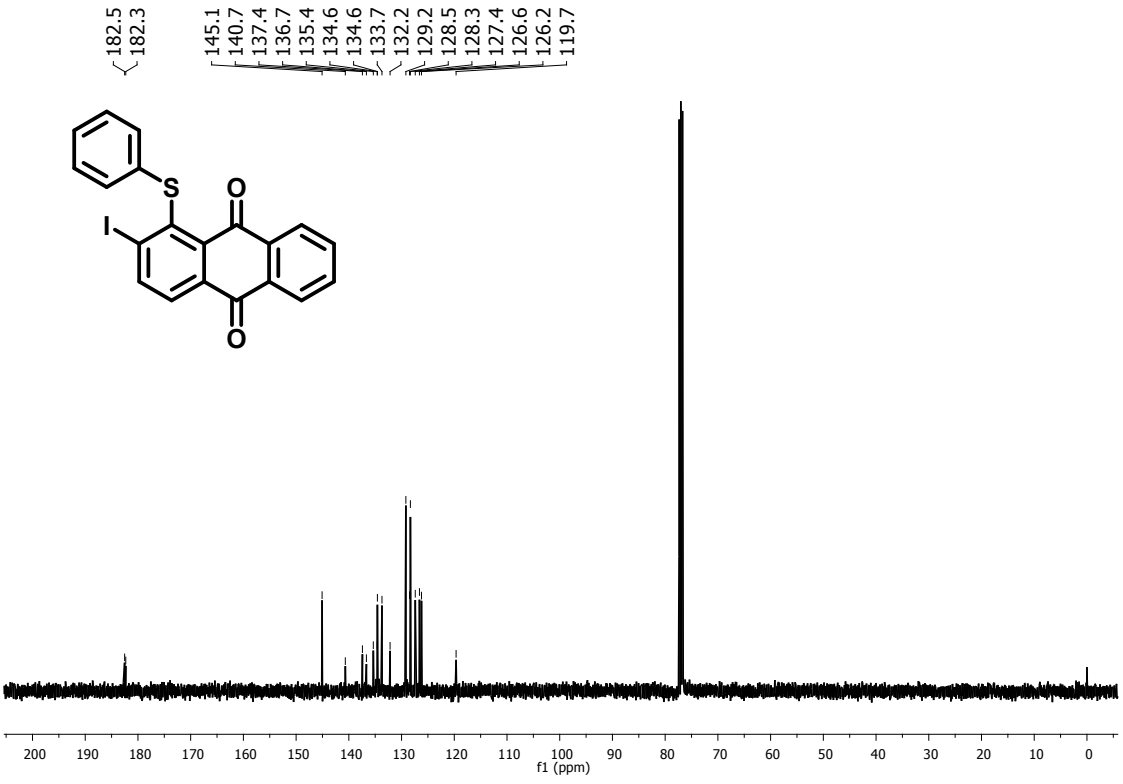
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1k**.



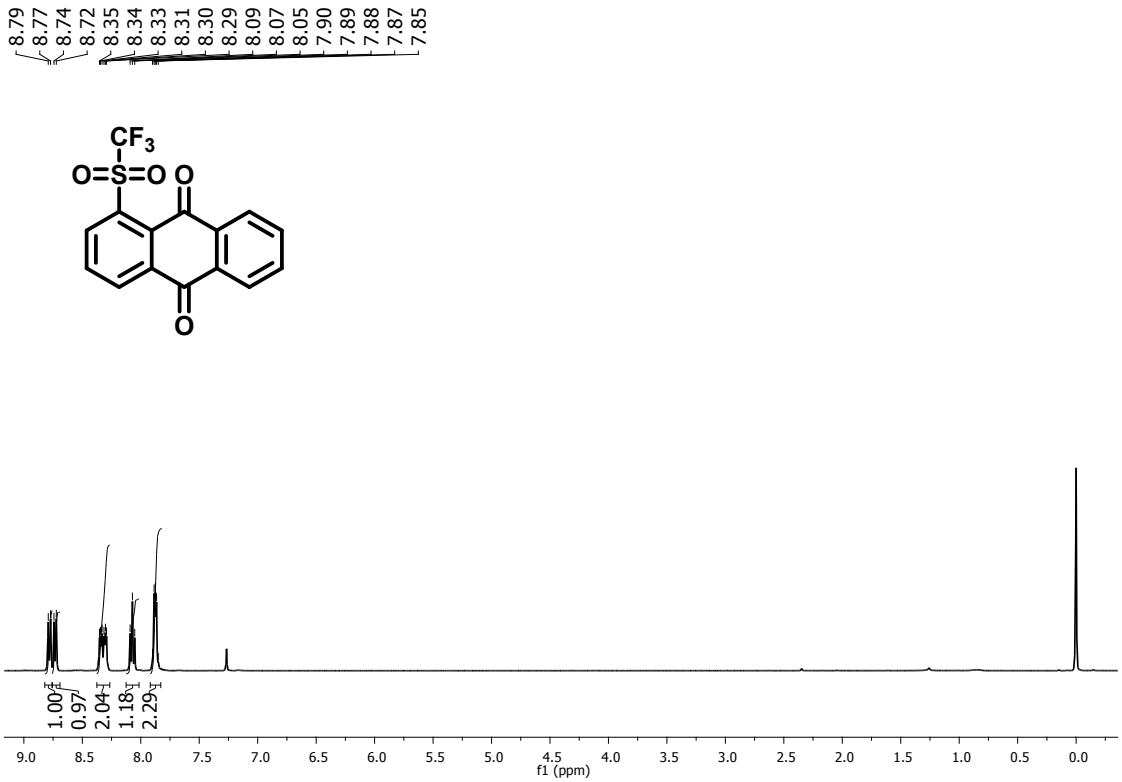
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **1k**.



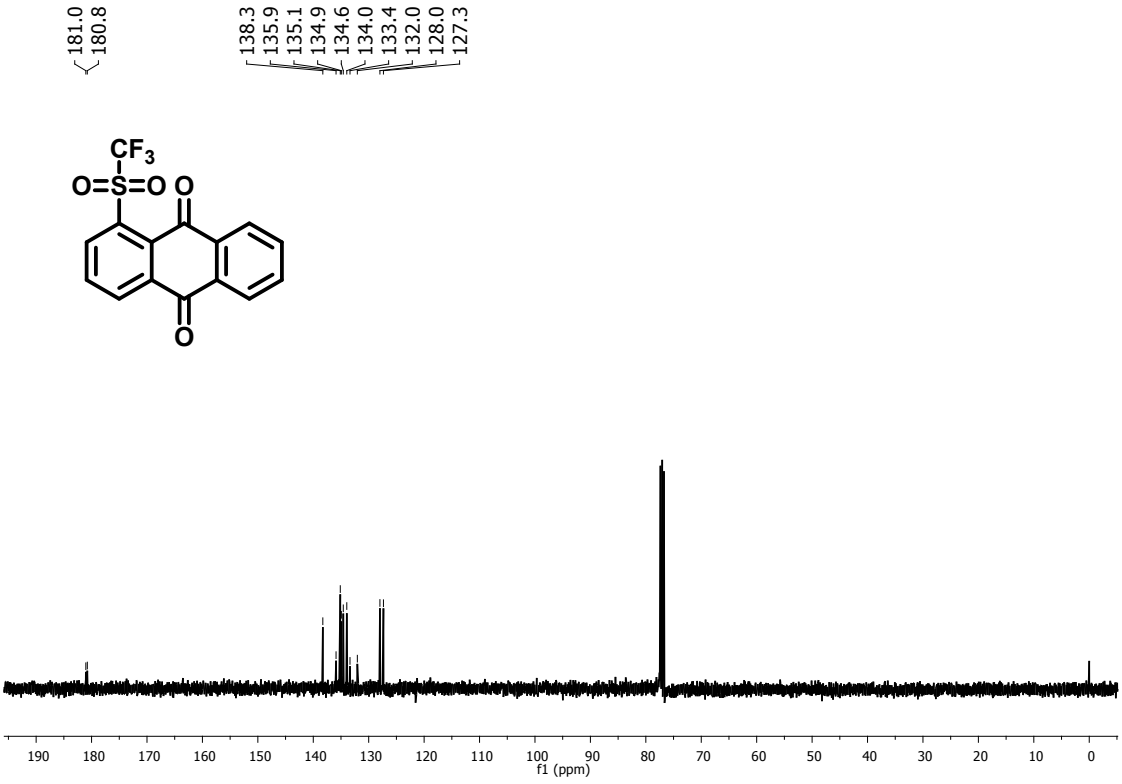
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1l**.



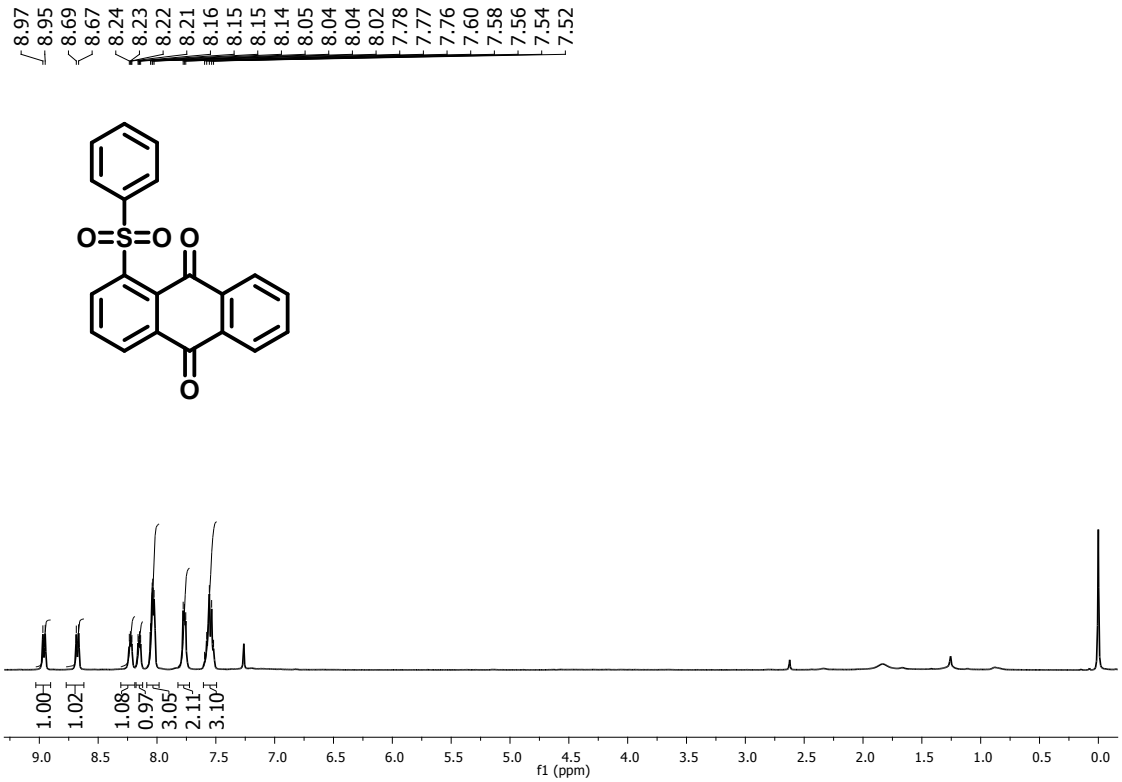
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **1l**.



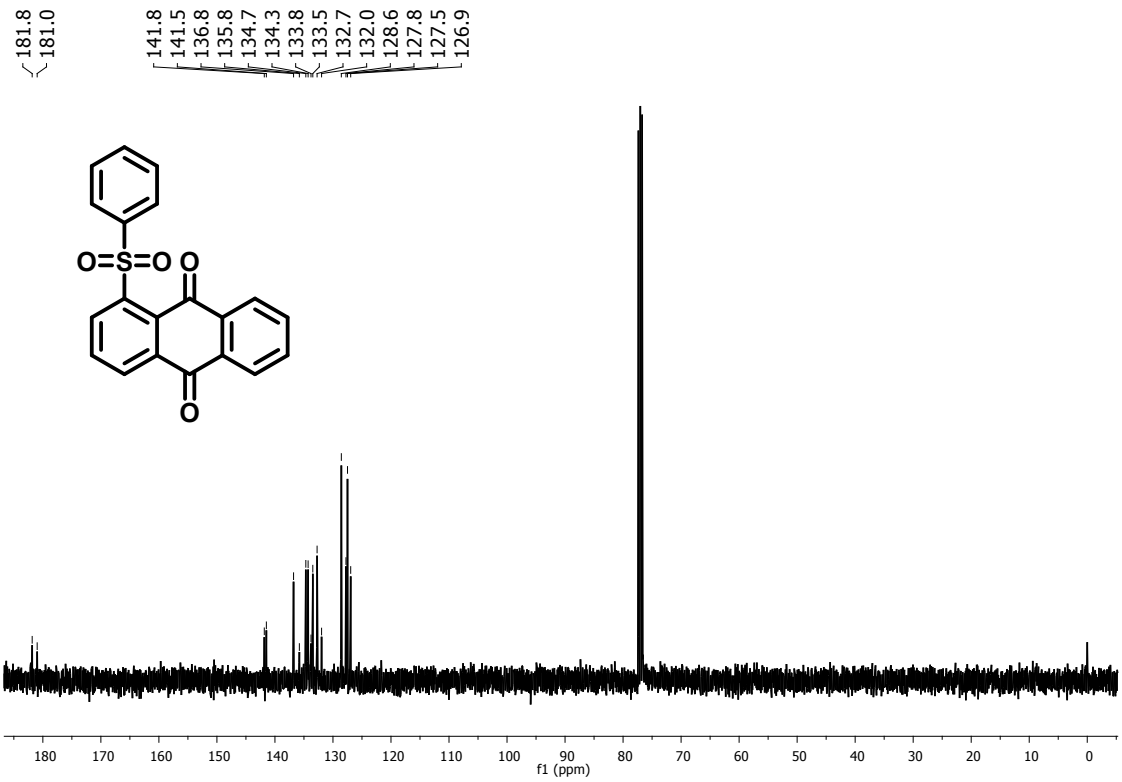
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2a**.



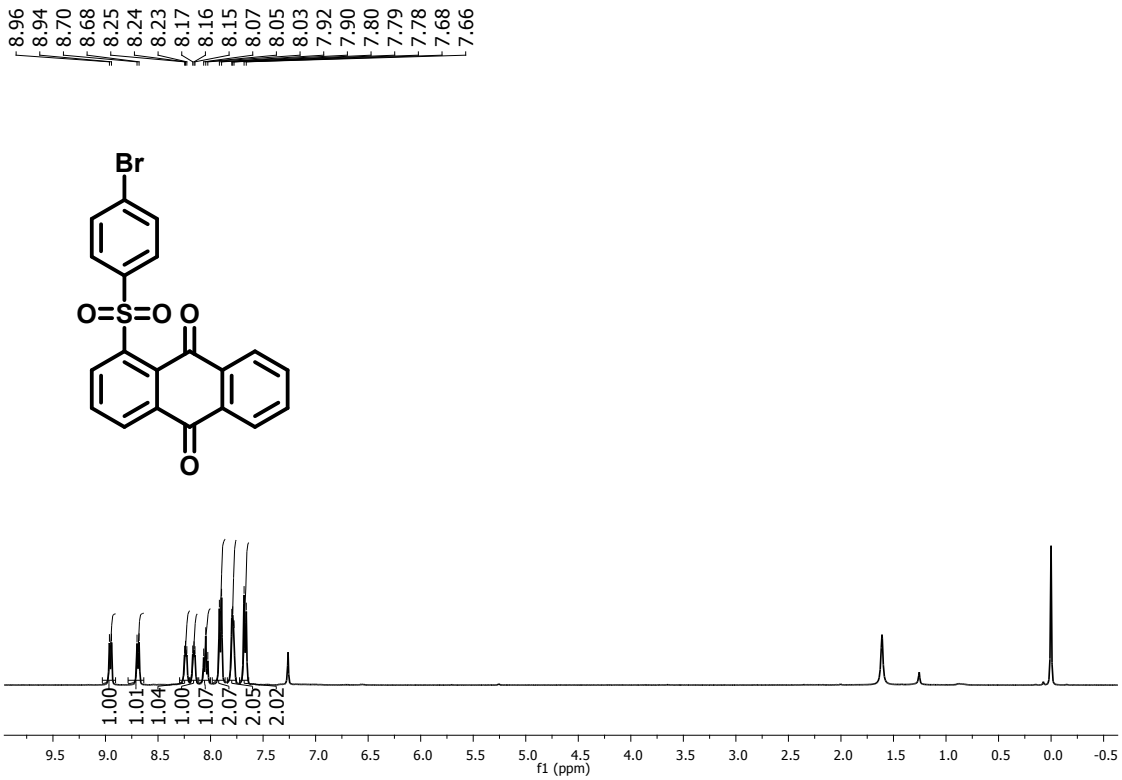
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2a**.



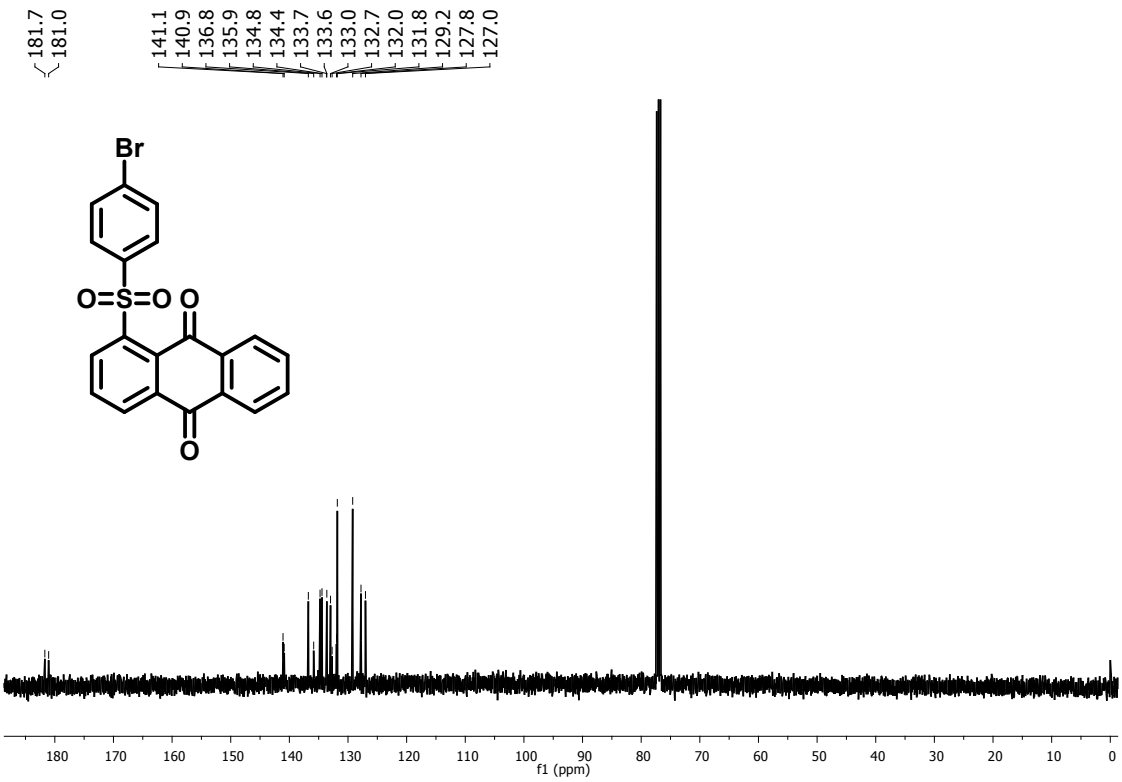
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2b**.



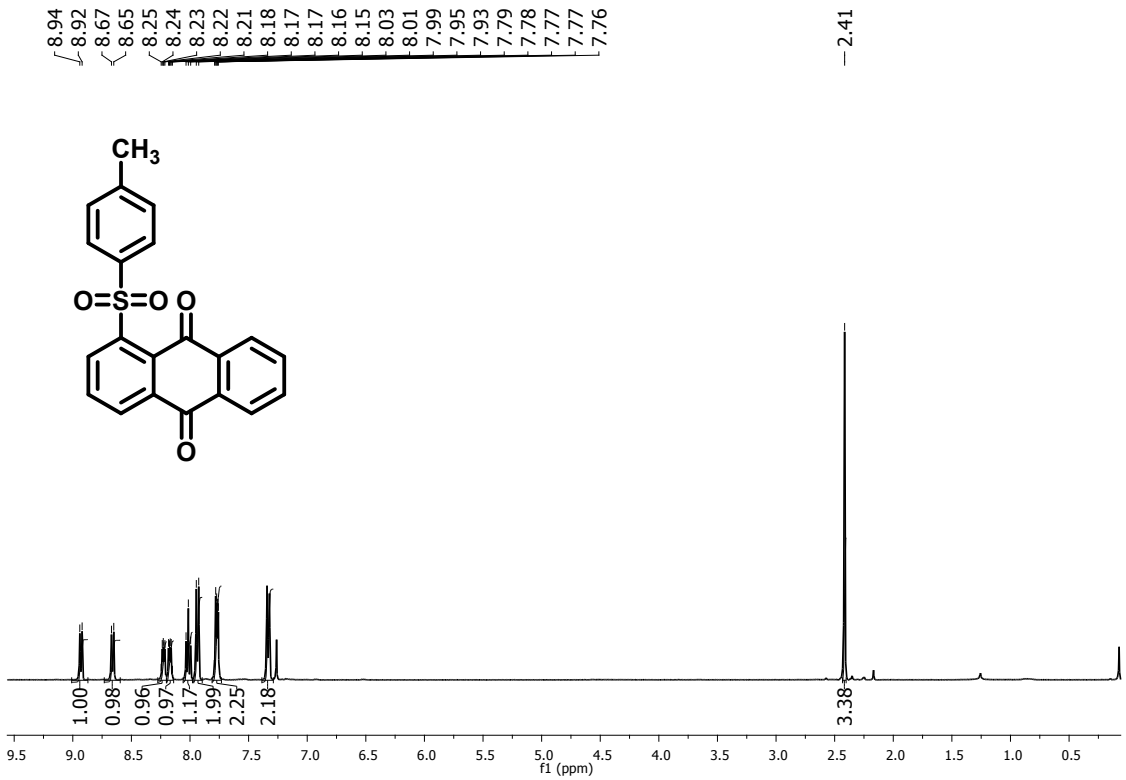
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2b**.



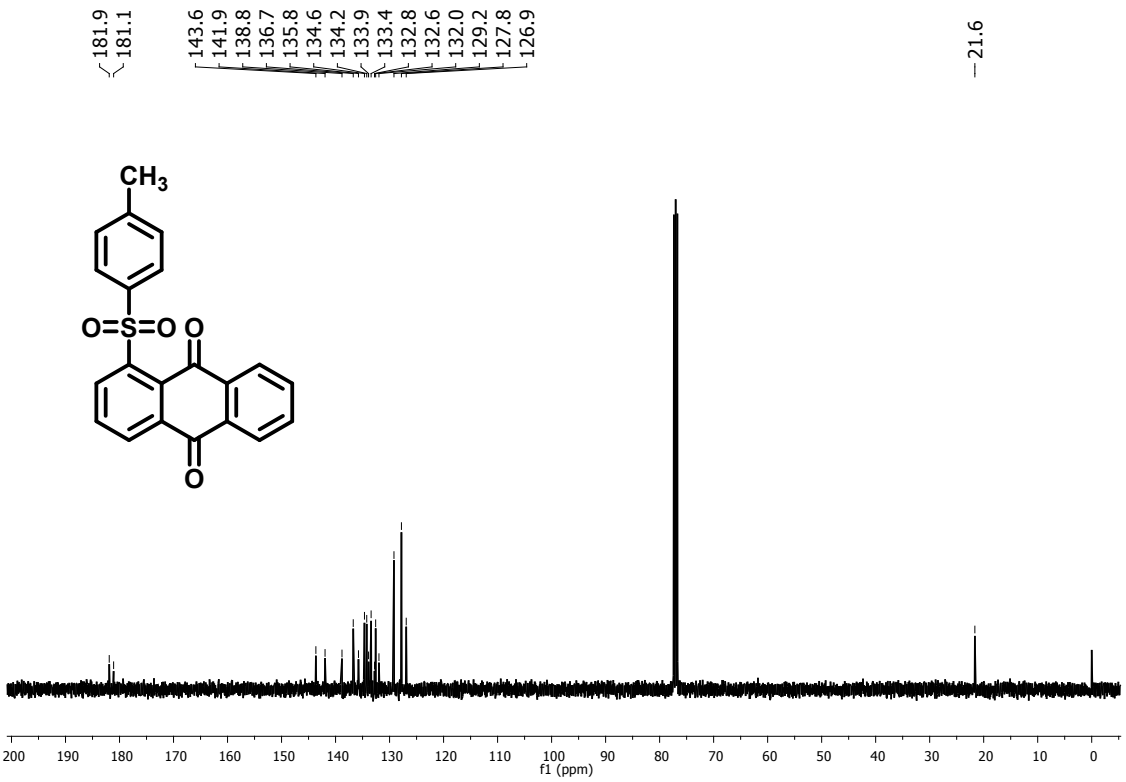
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2c**.



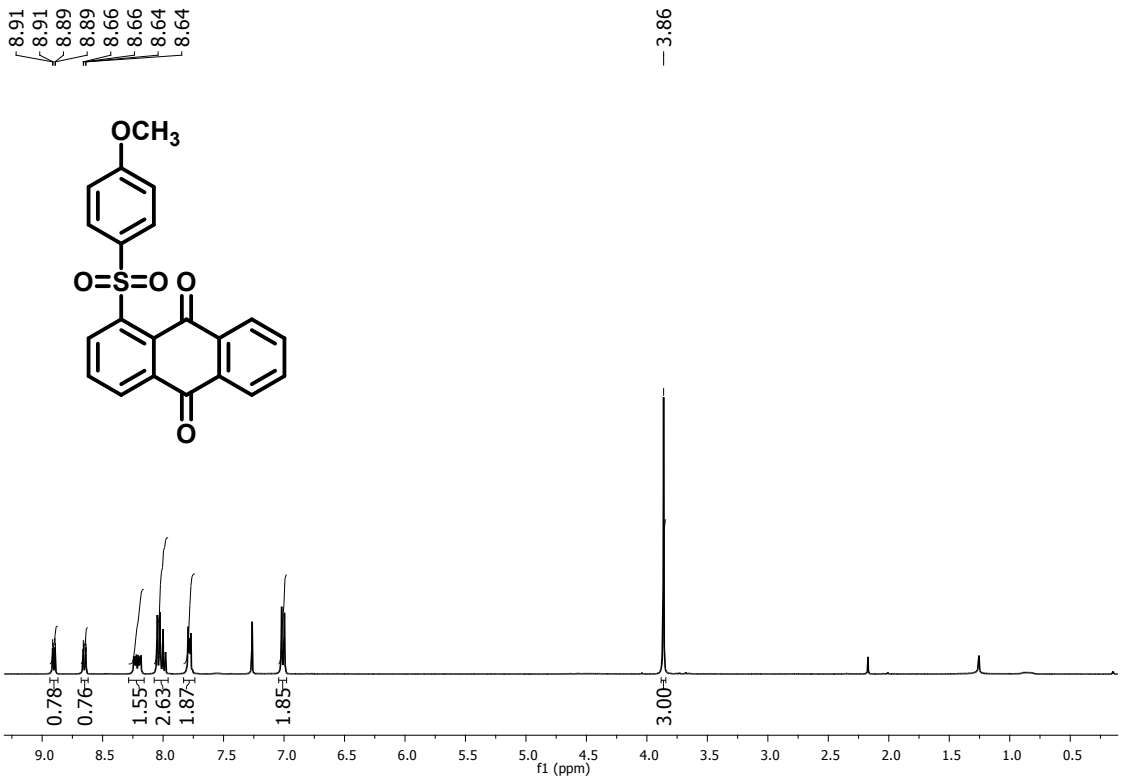
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2c**.



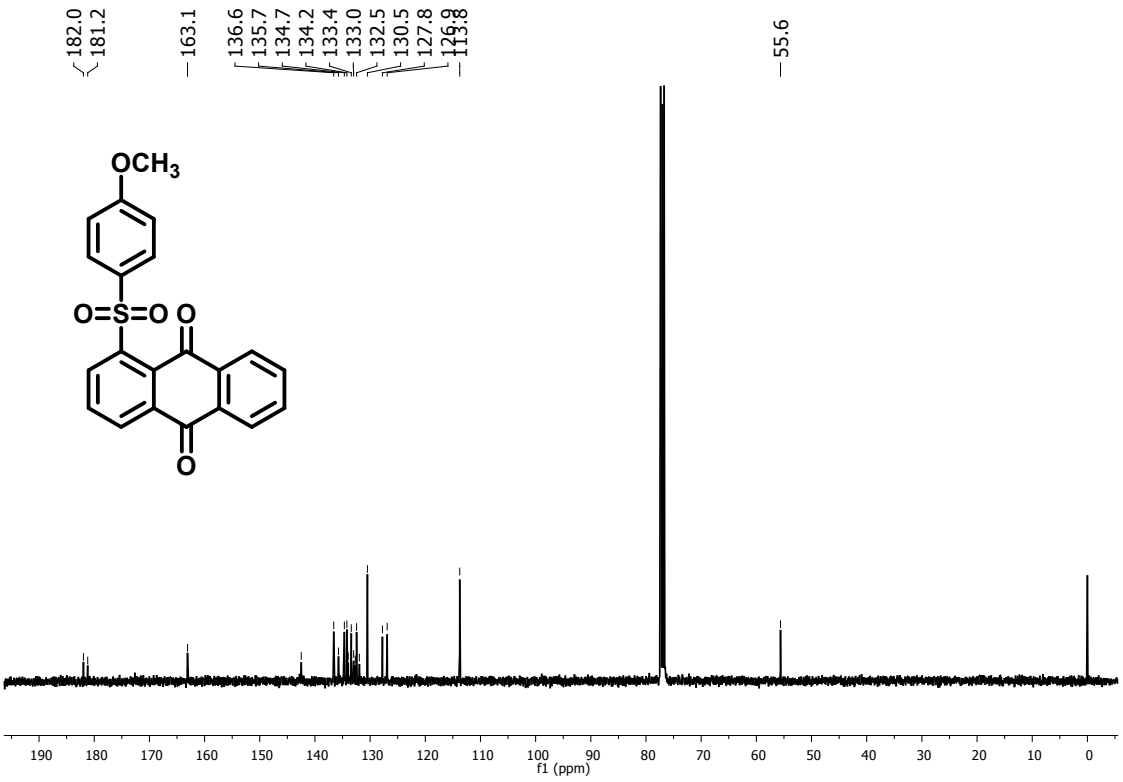
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2d**.



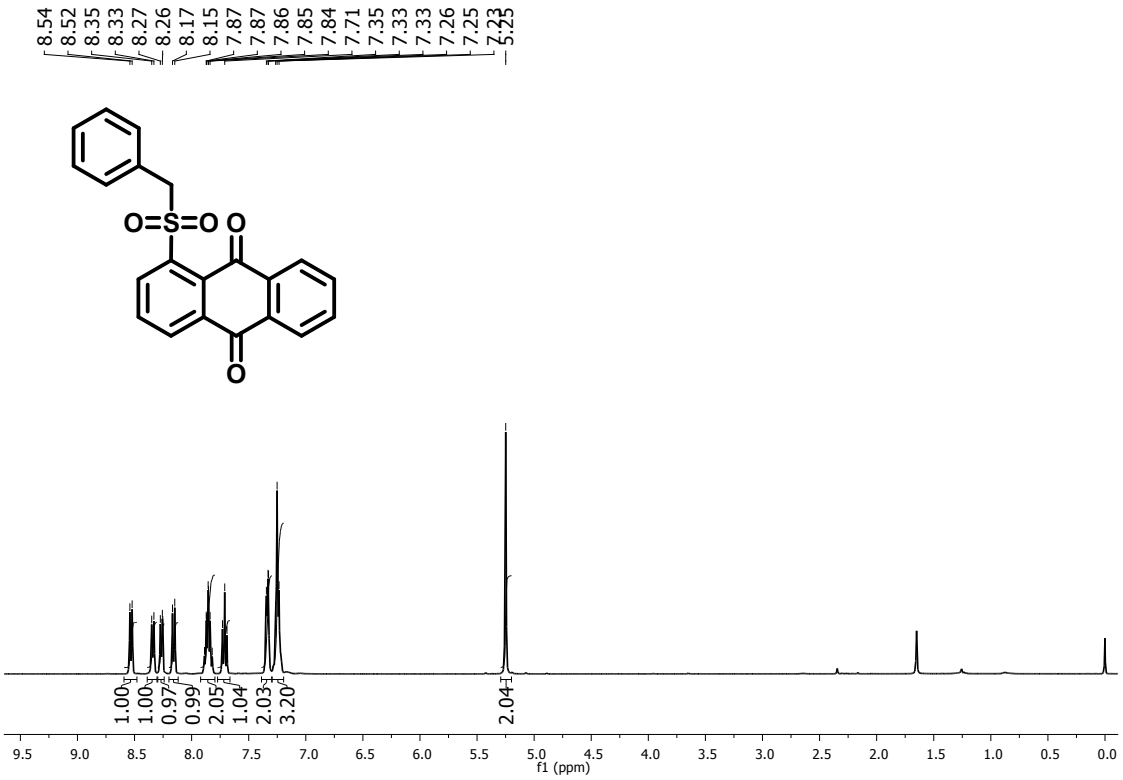
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2d**.



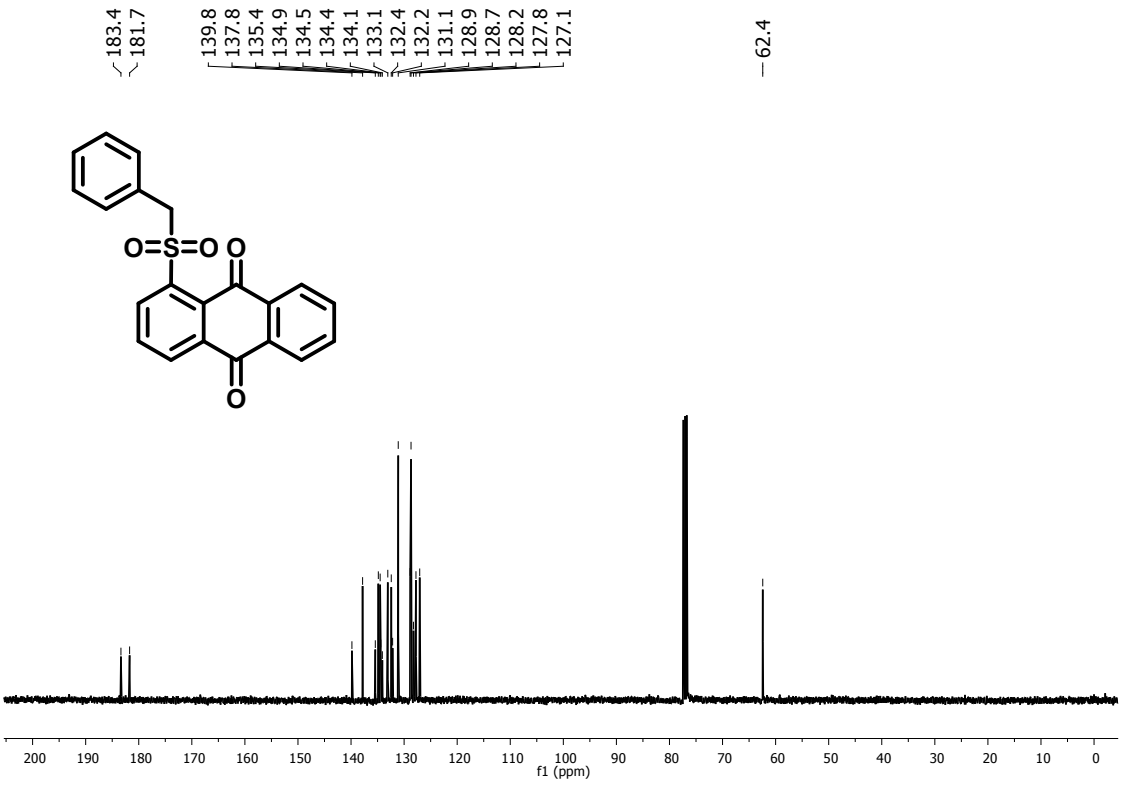
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2e**.



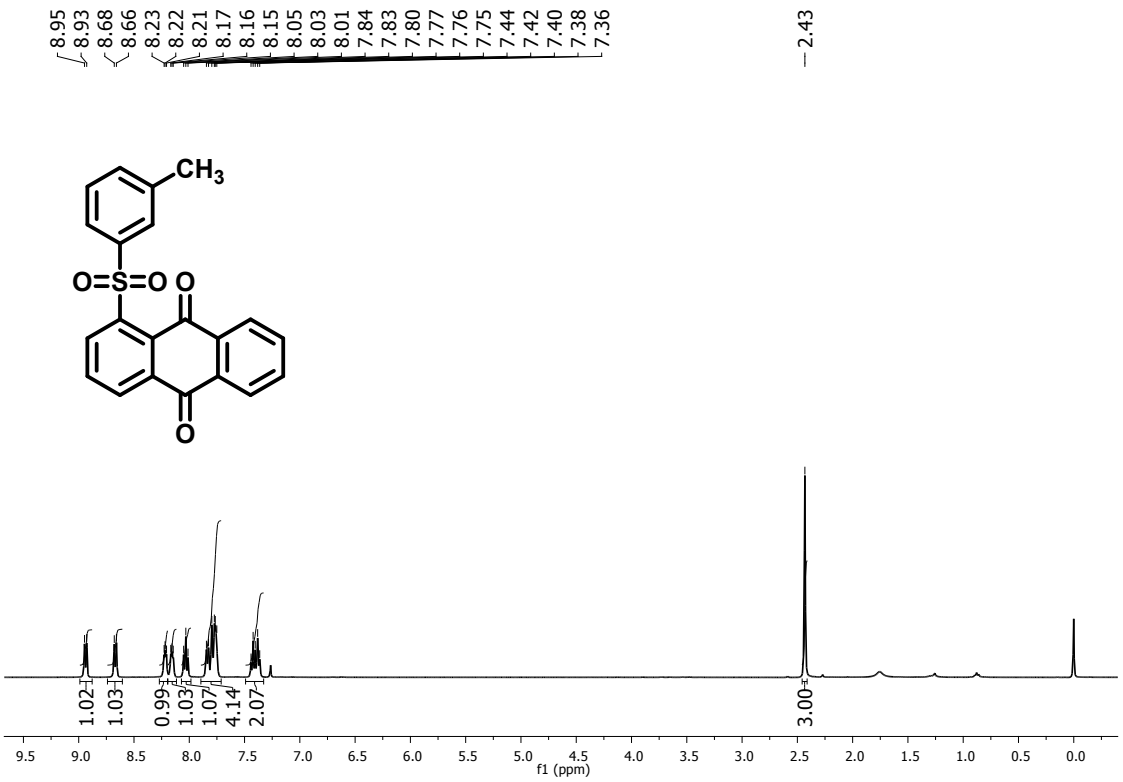
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2e**.



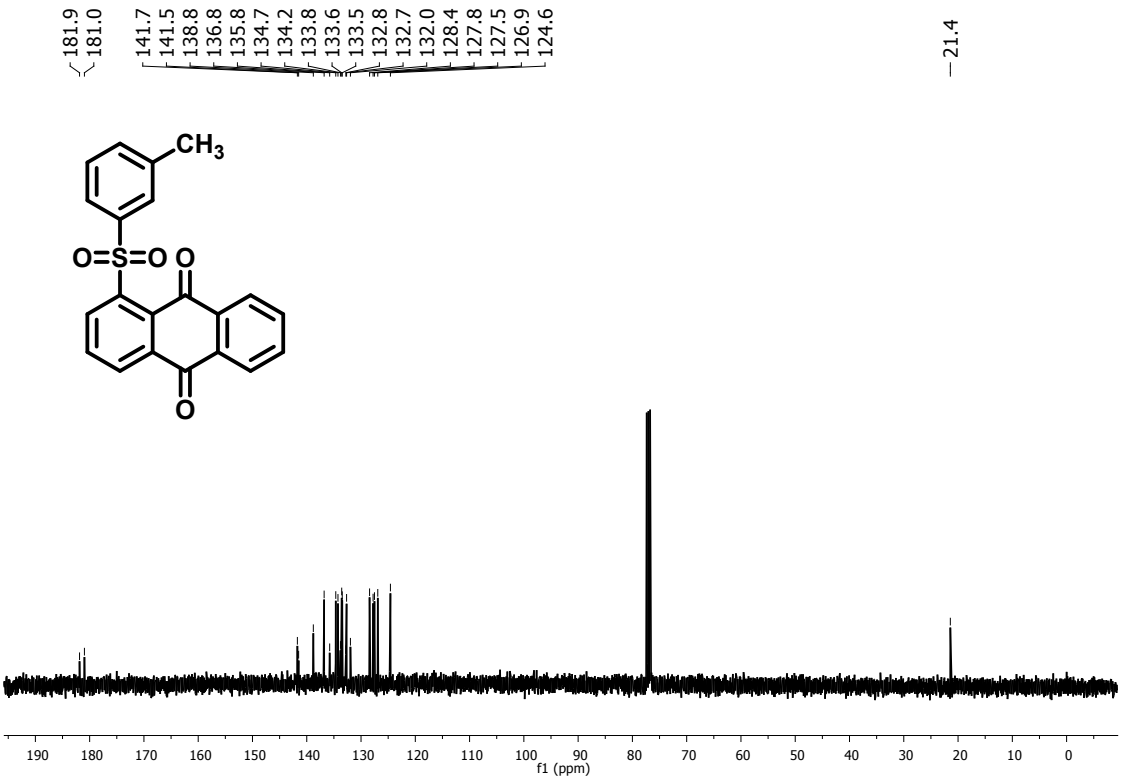
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2f**.



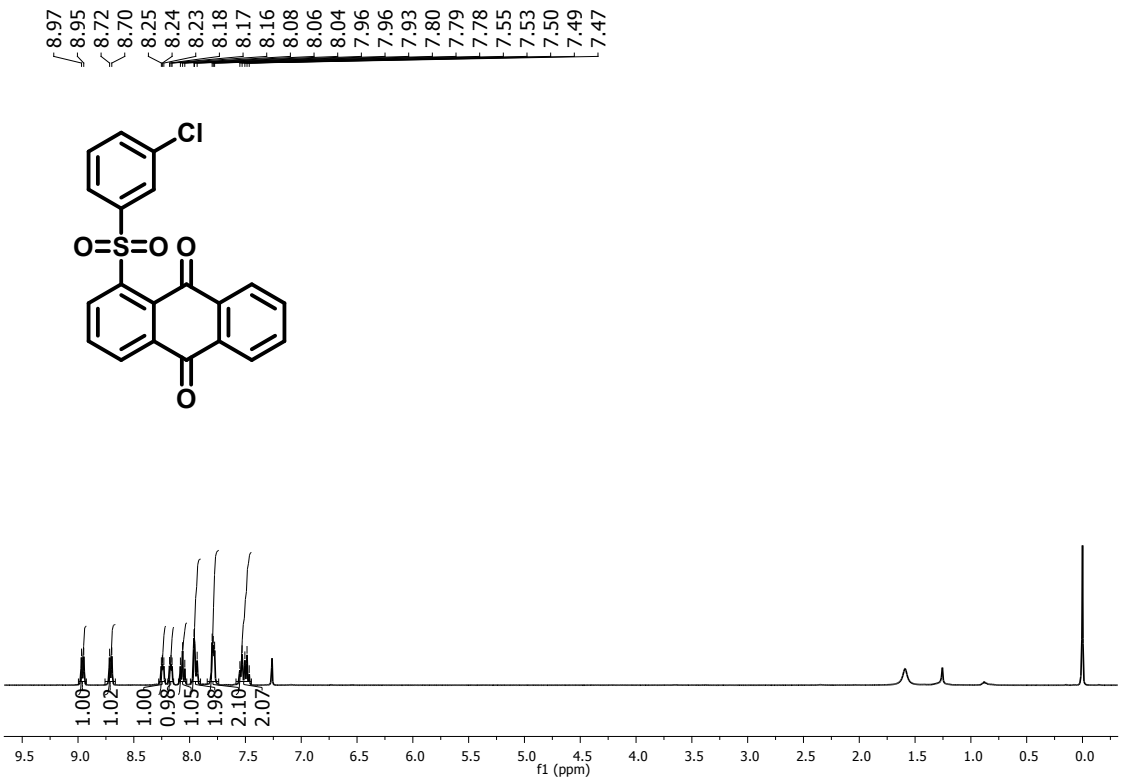
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2f**.



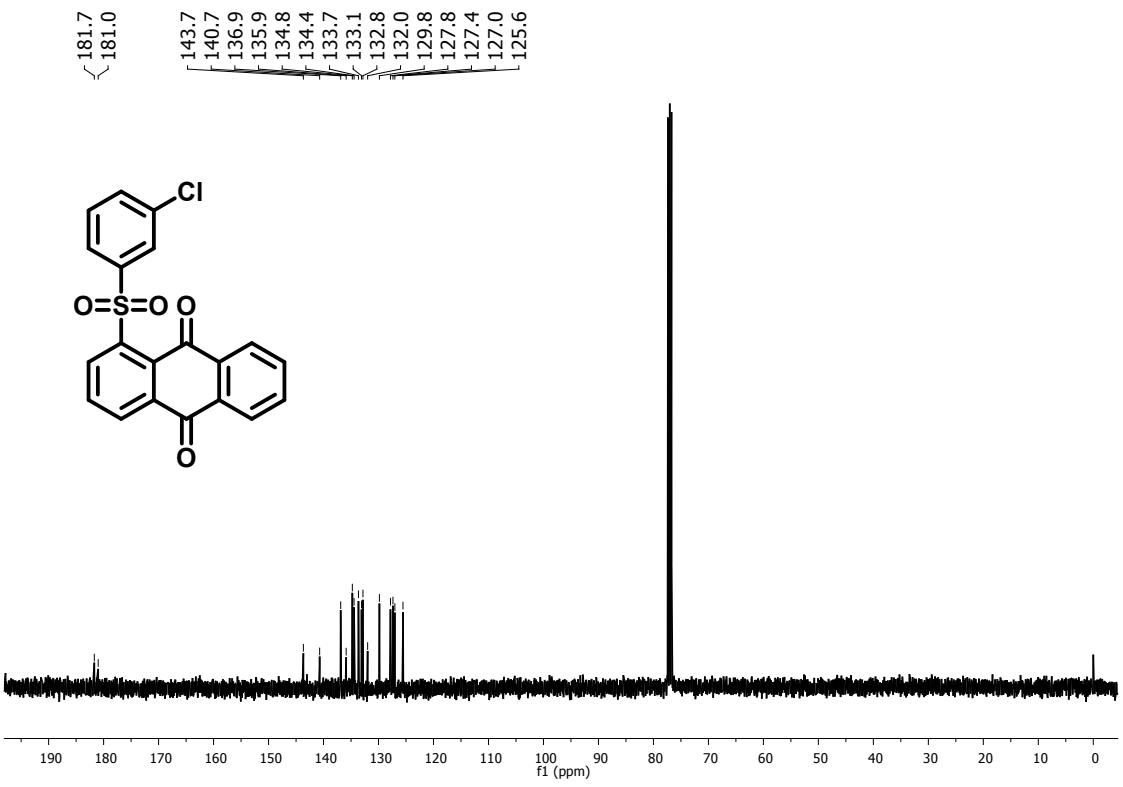
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2g**.



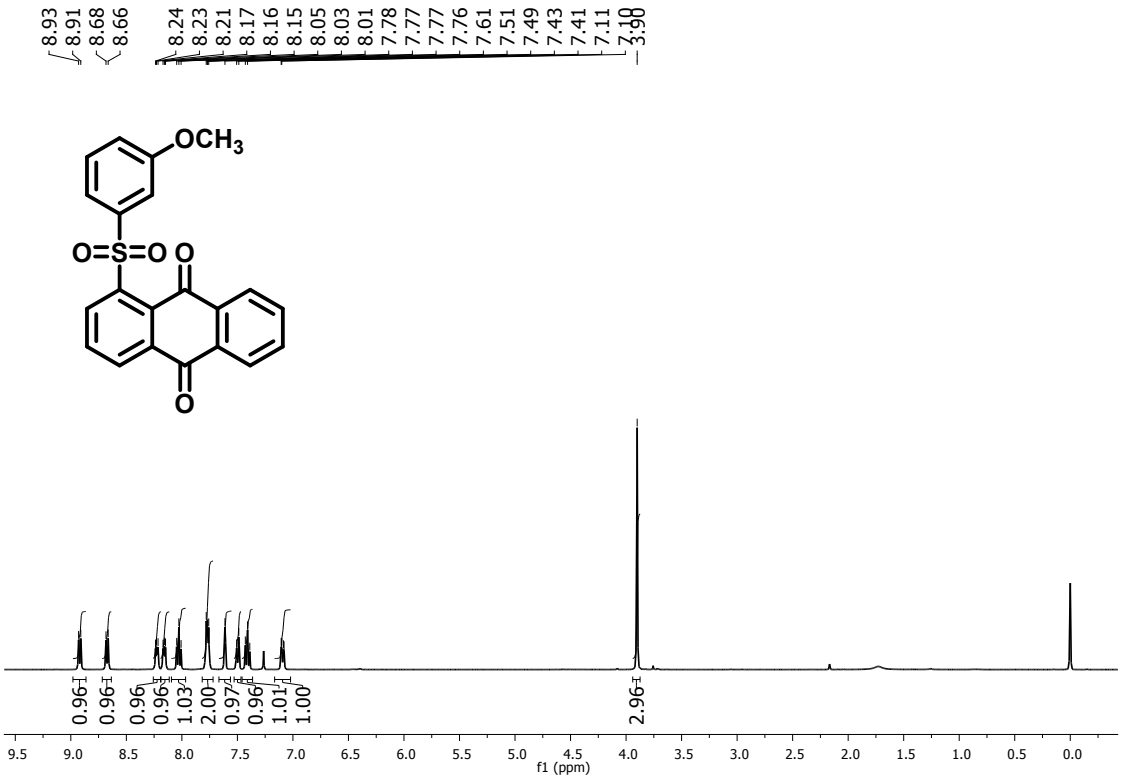
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2g**.



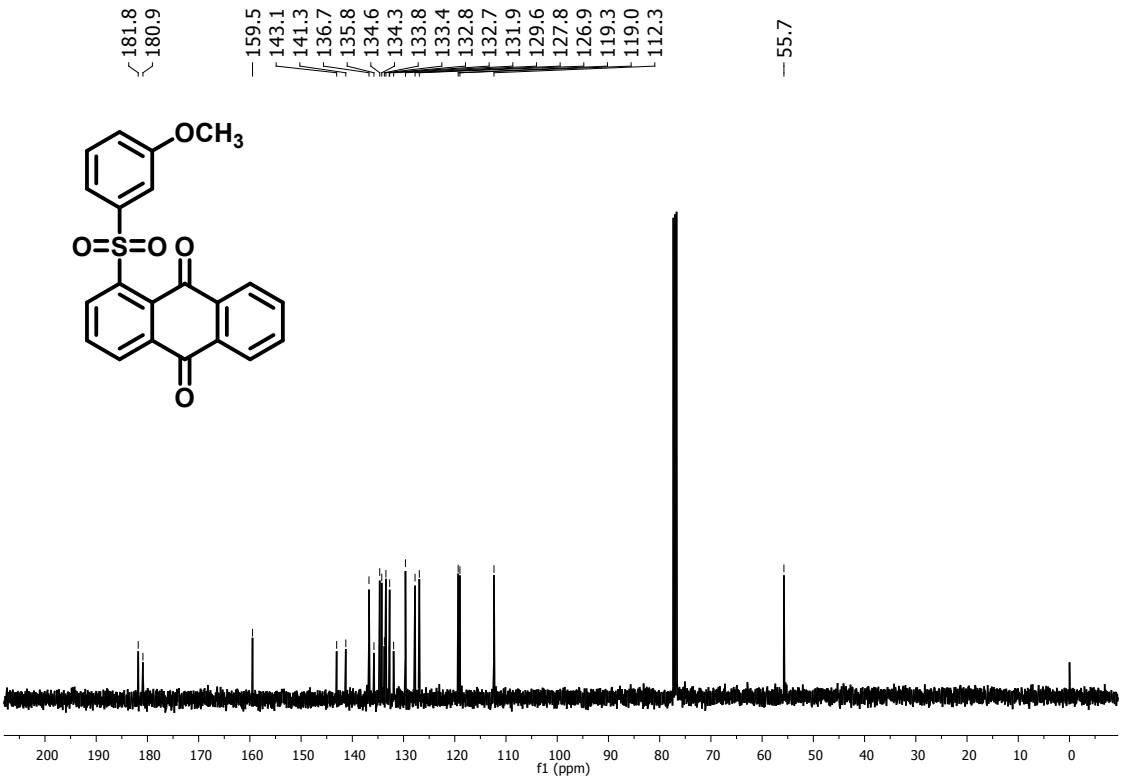
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2h**.



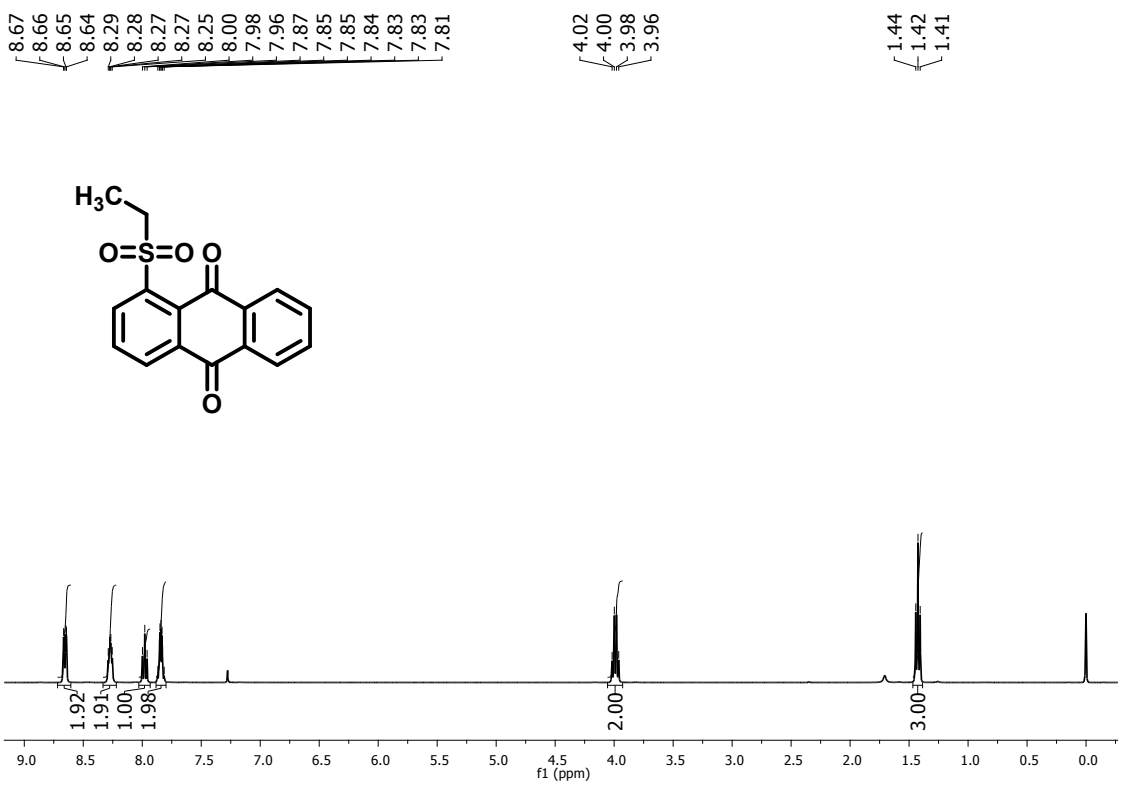
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2h**.



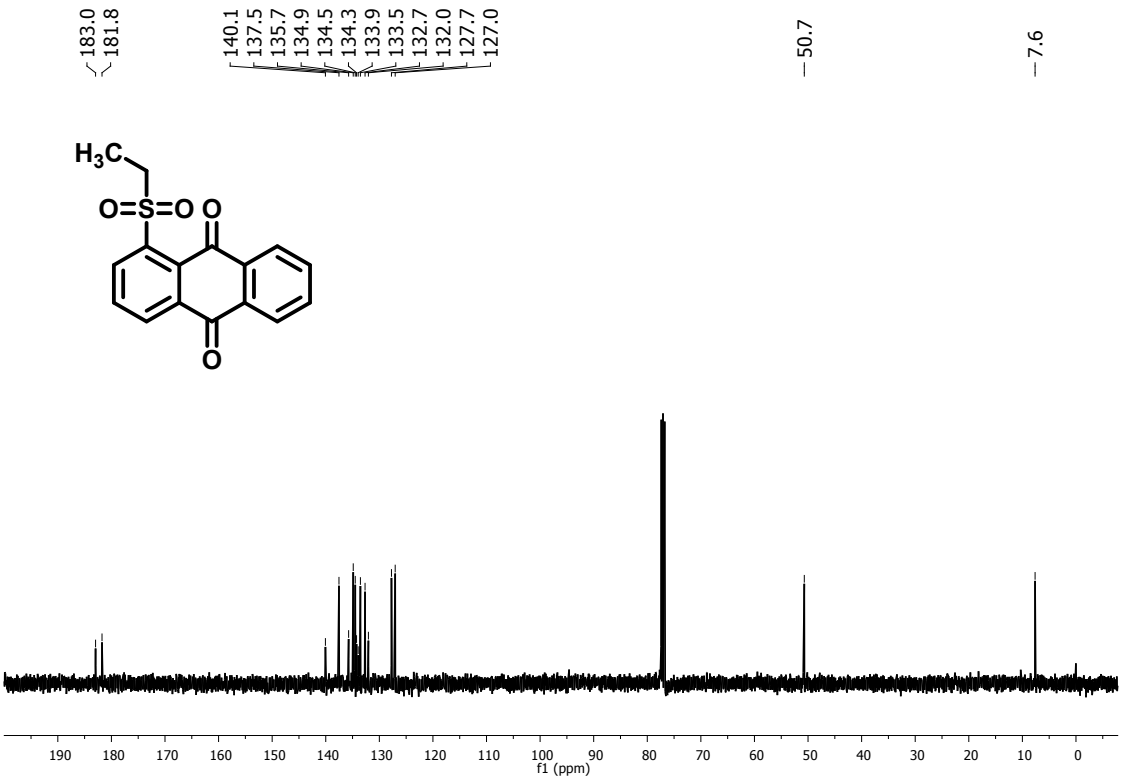
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2i**.



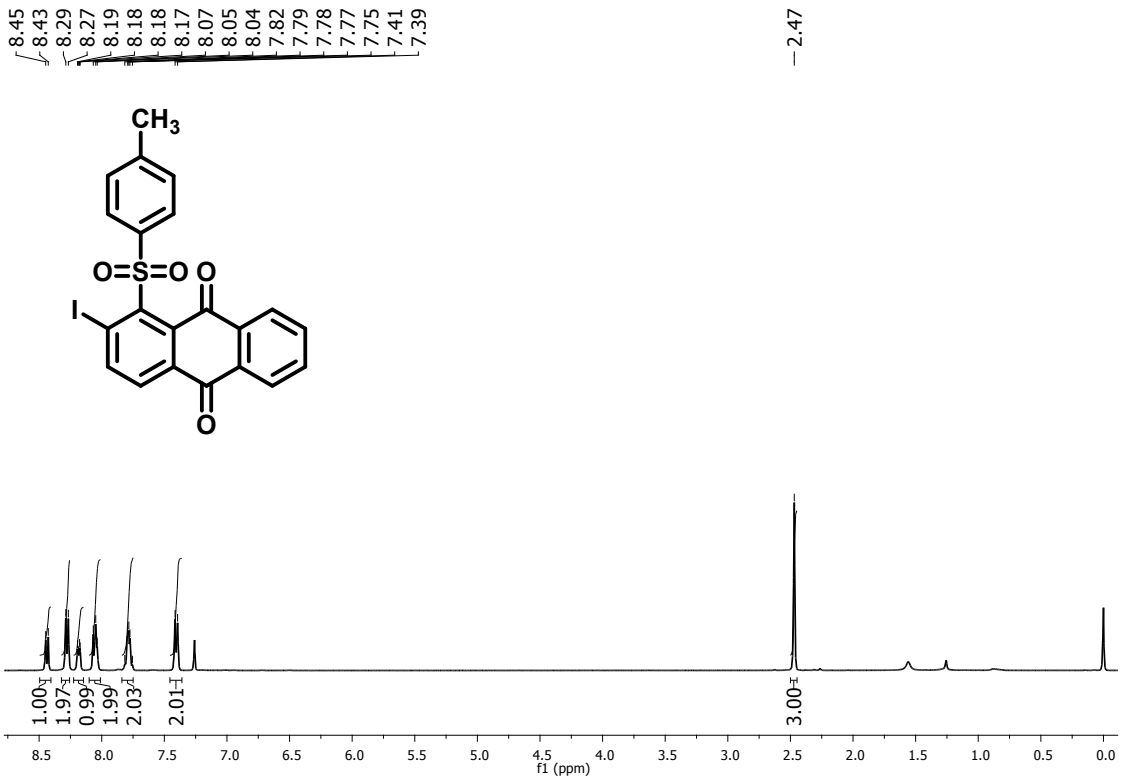
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2i**.



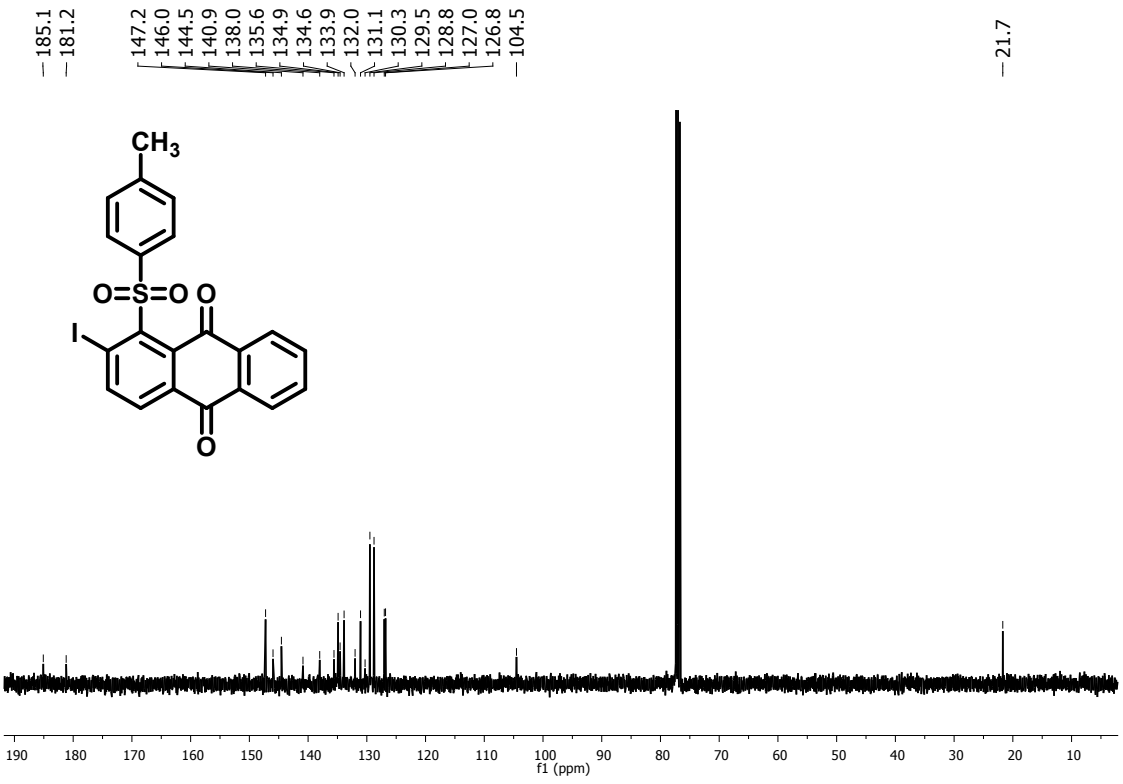
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2j**.



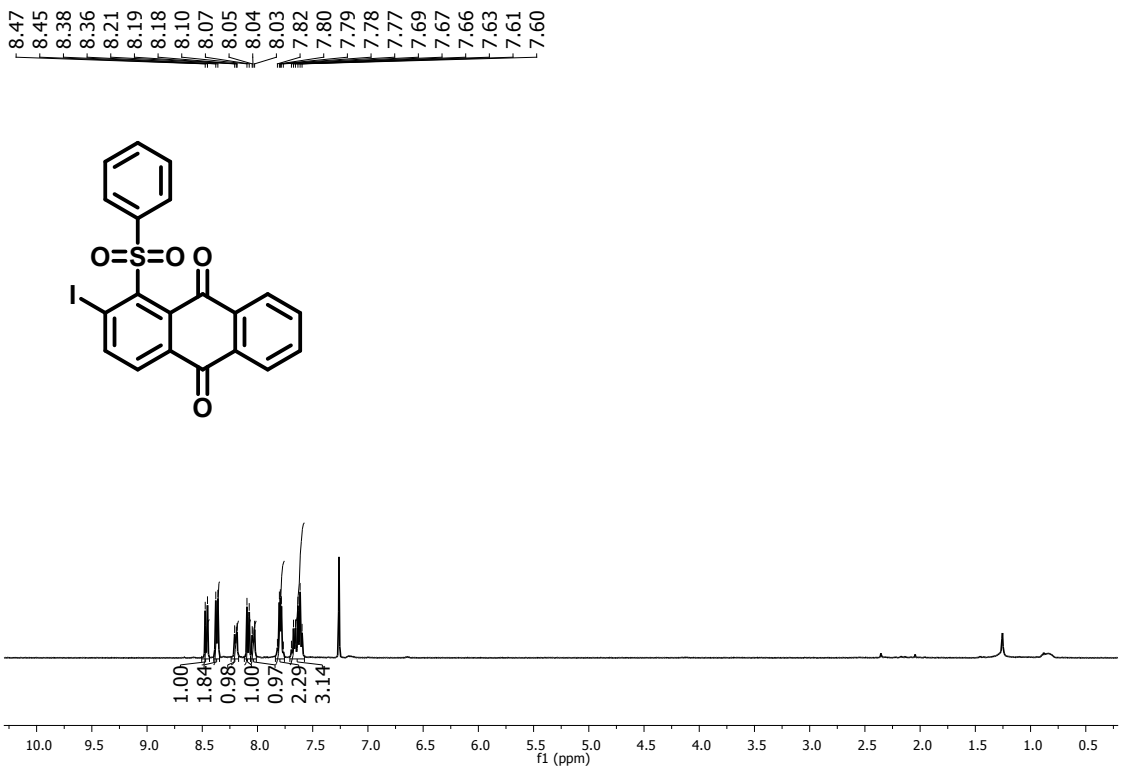
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2j**.



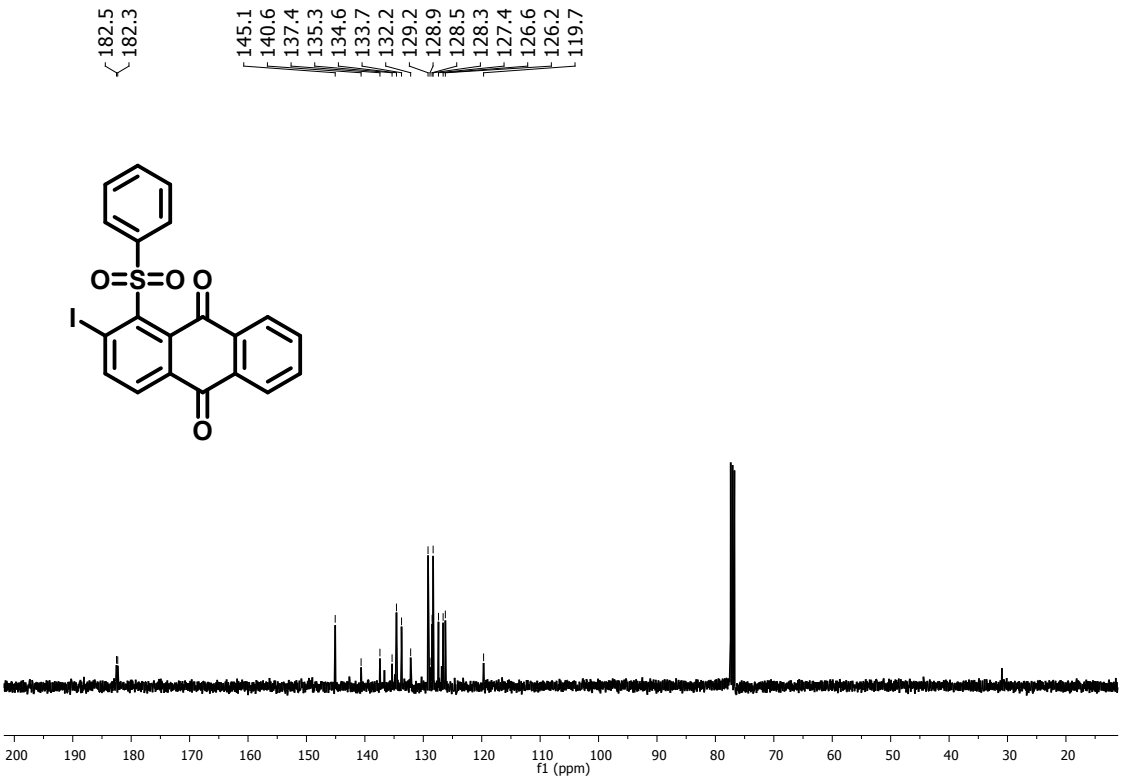
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2k**.



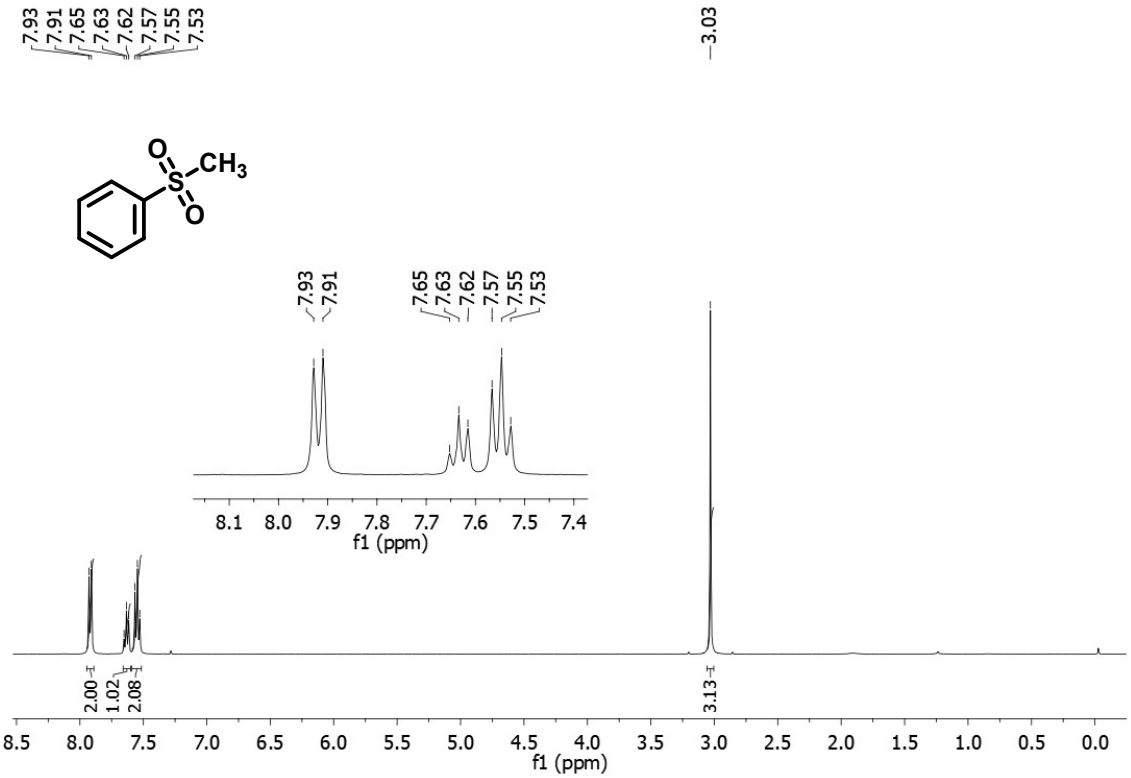
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2k**.



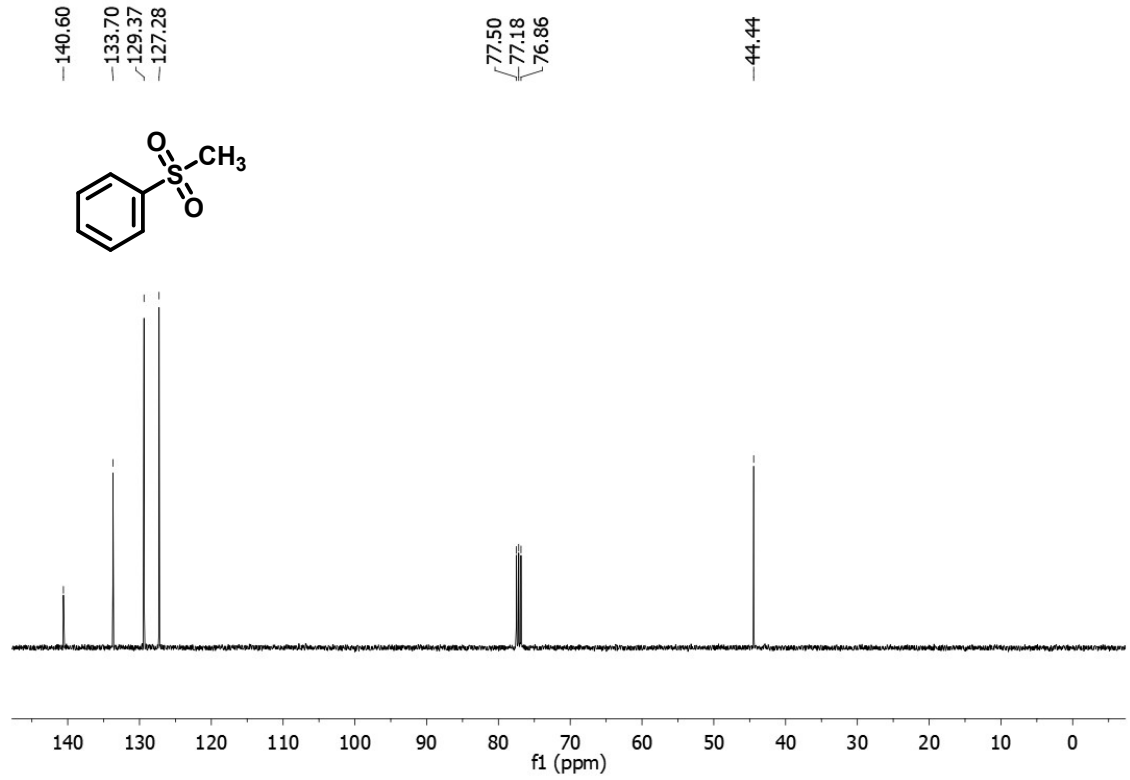
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2l**.



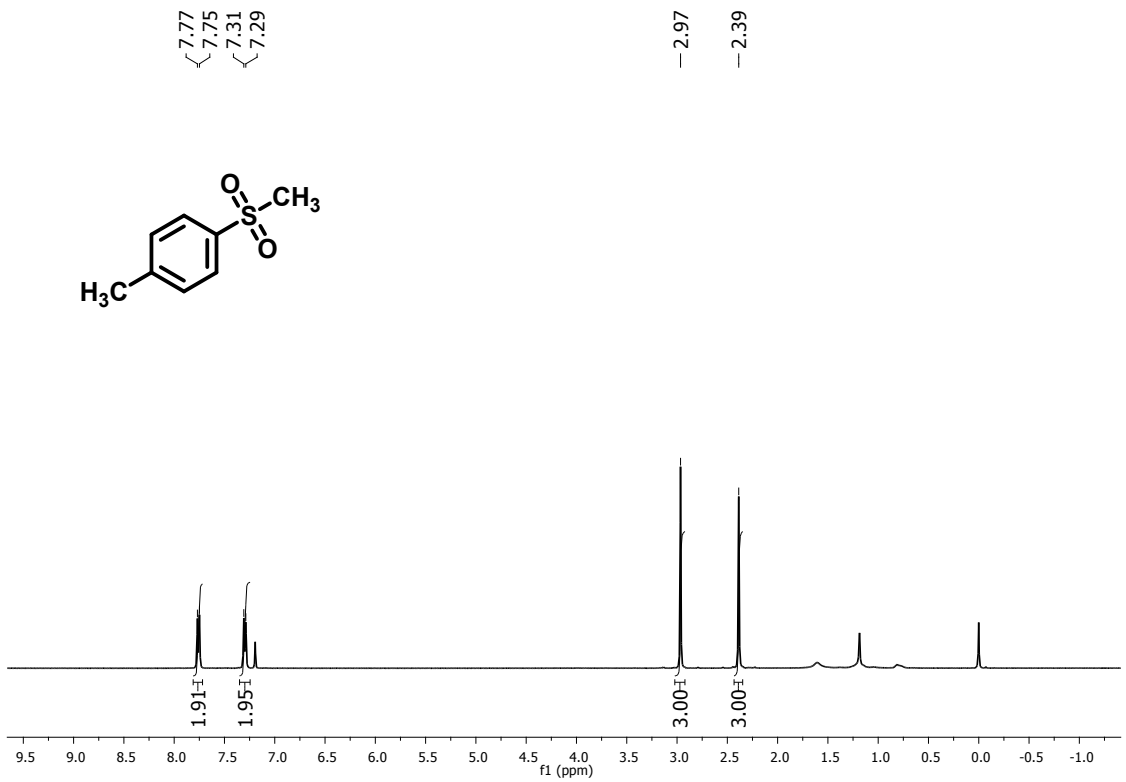
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2l**.



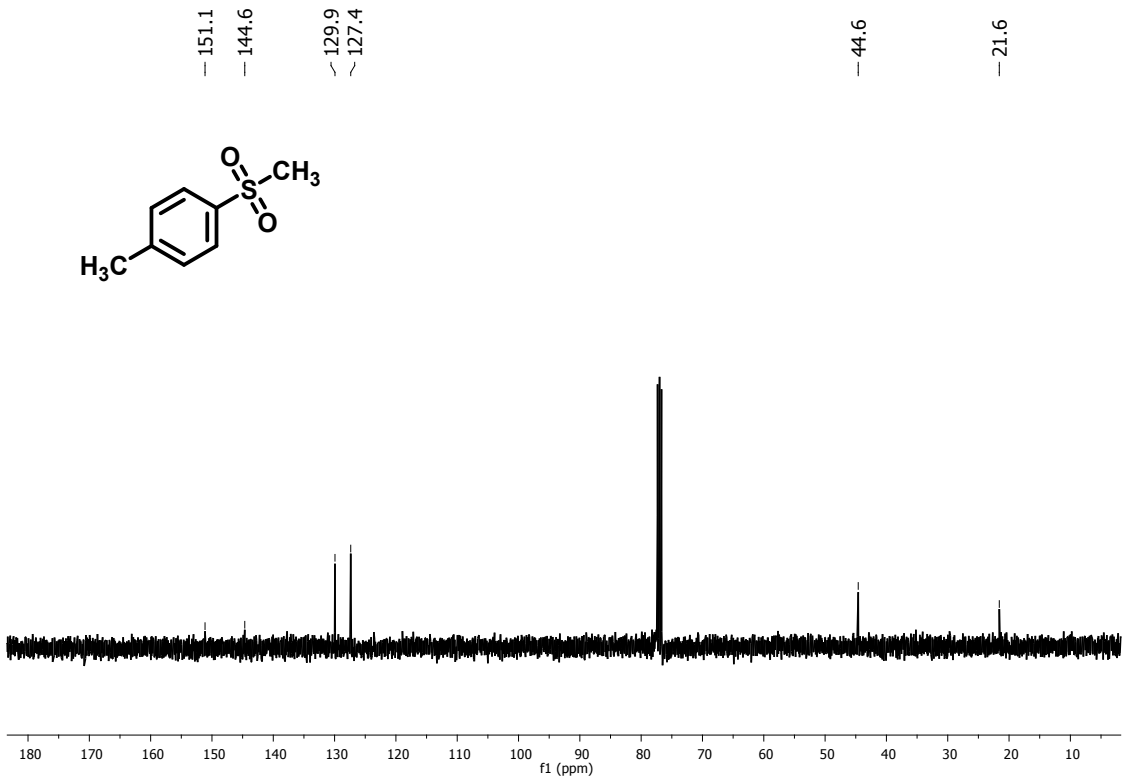
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4a**.



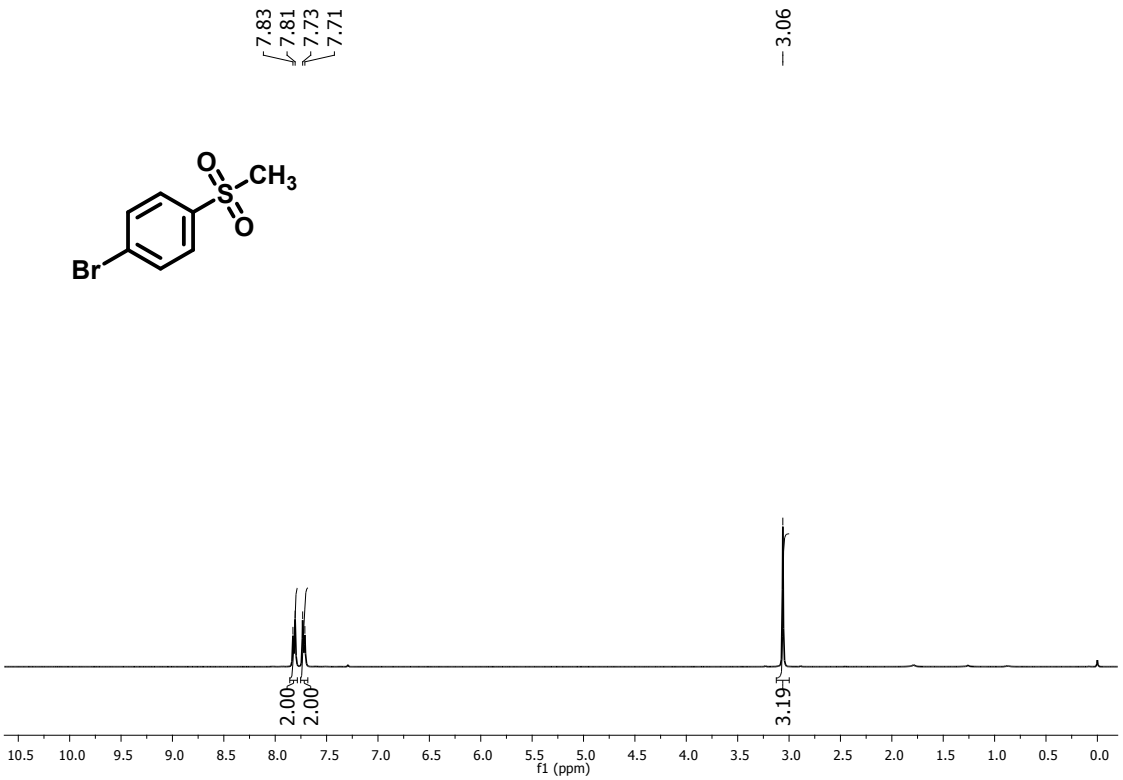
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4a**.



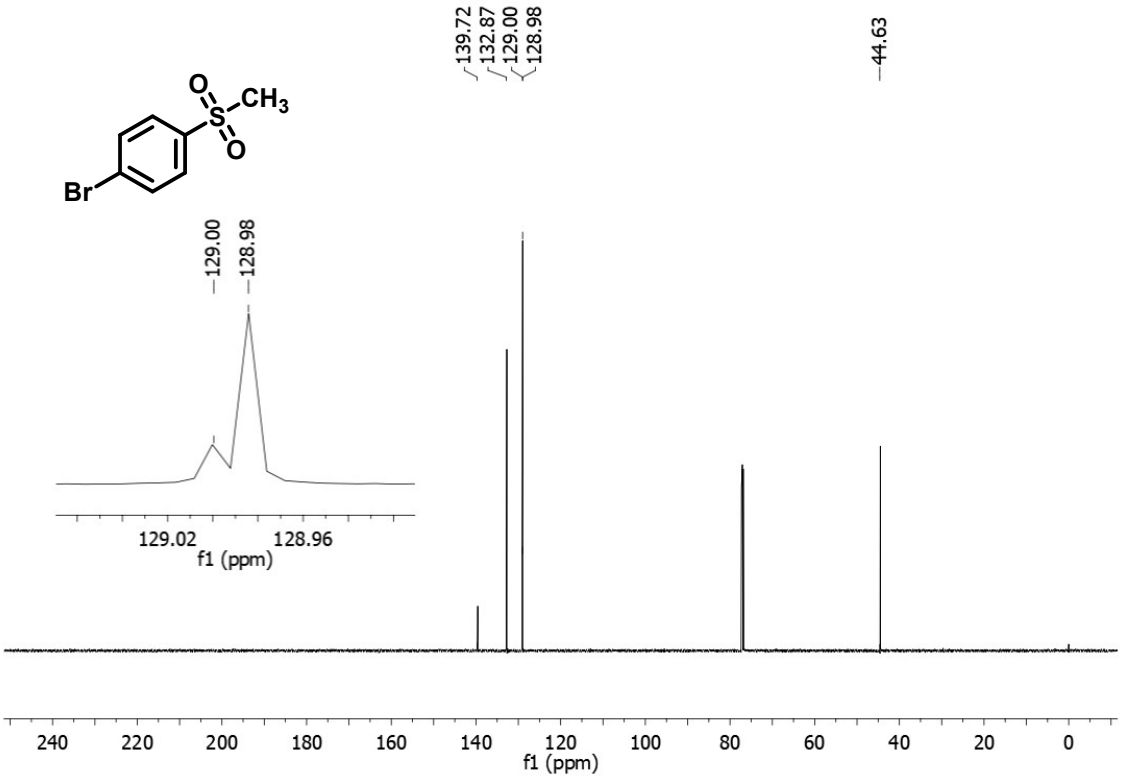
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4b**.



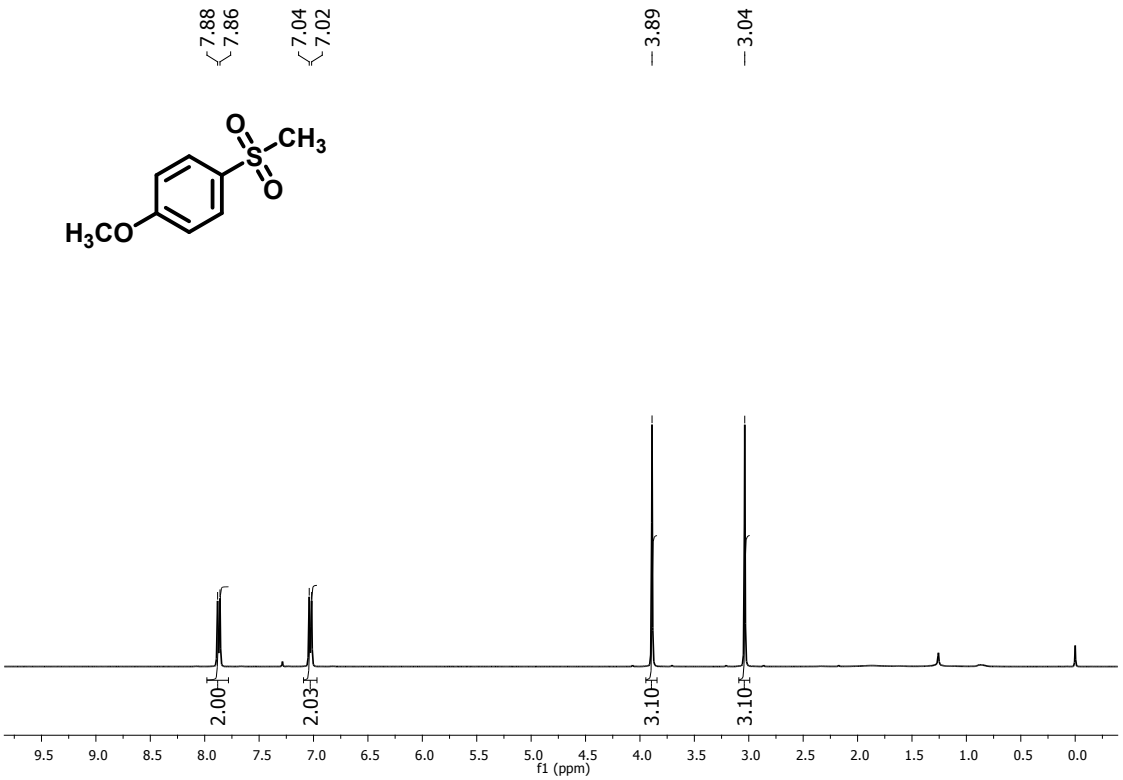
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4b**.



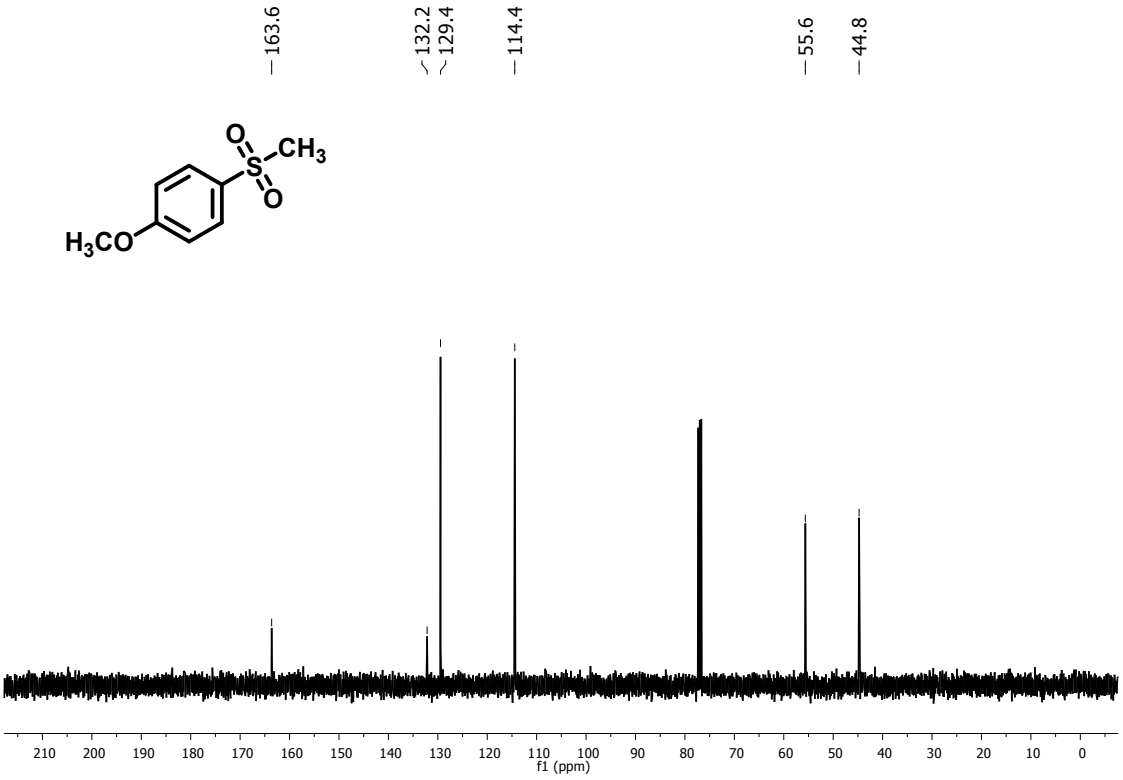
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4c**.



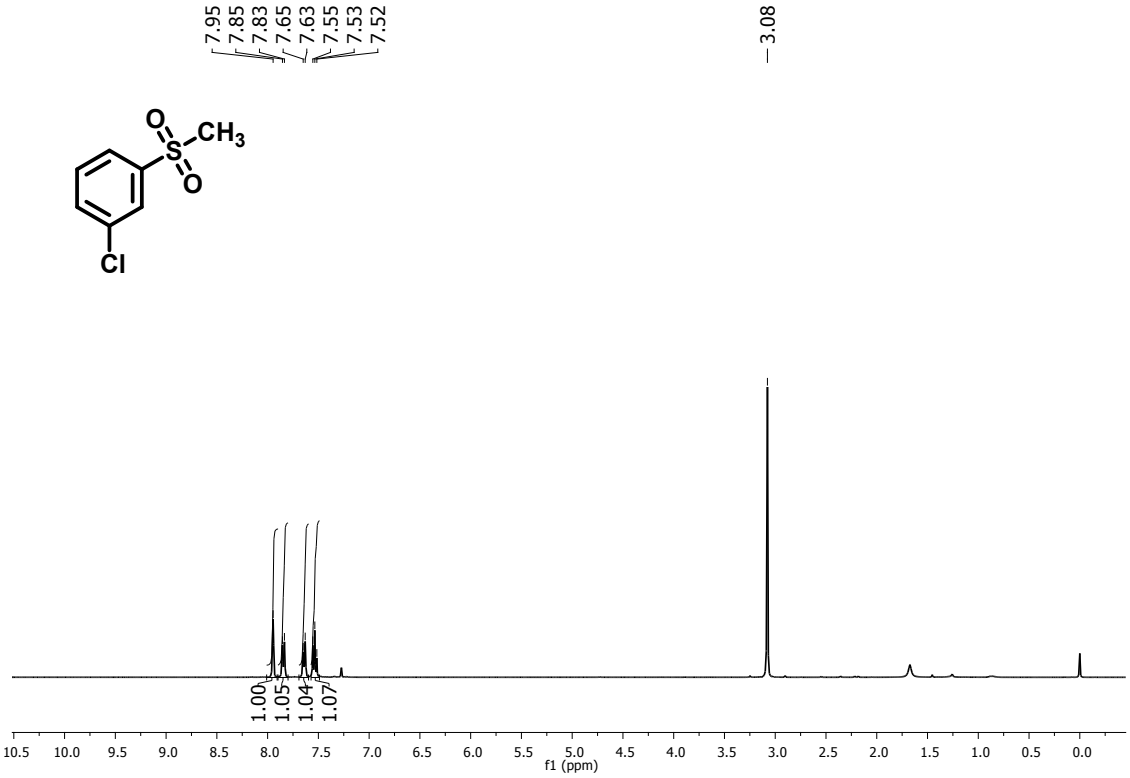
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound **4c**.



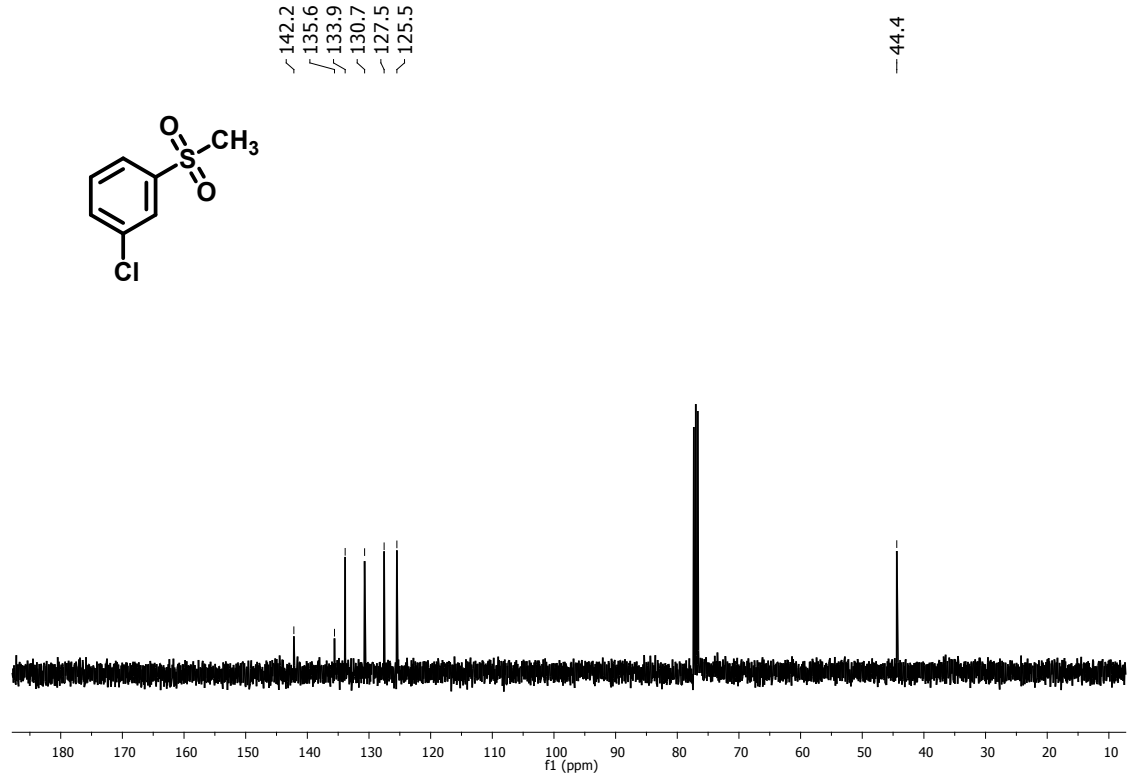
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4d**.



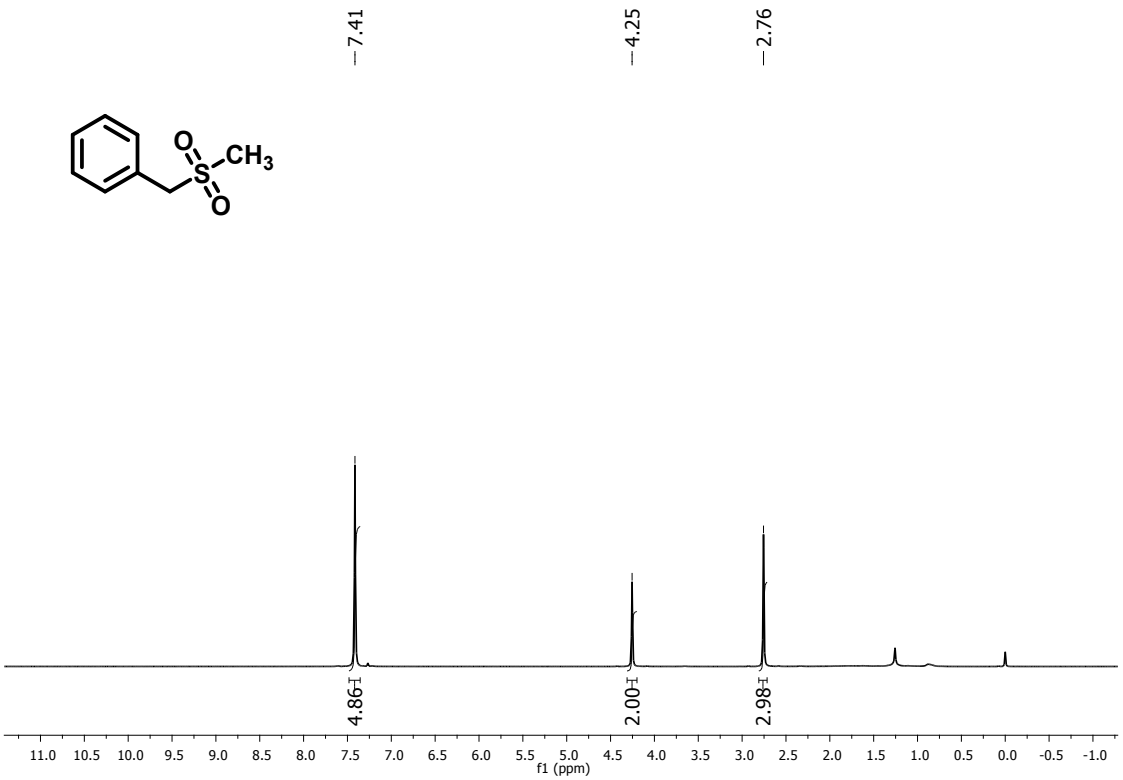
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4d**.



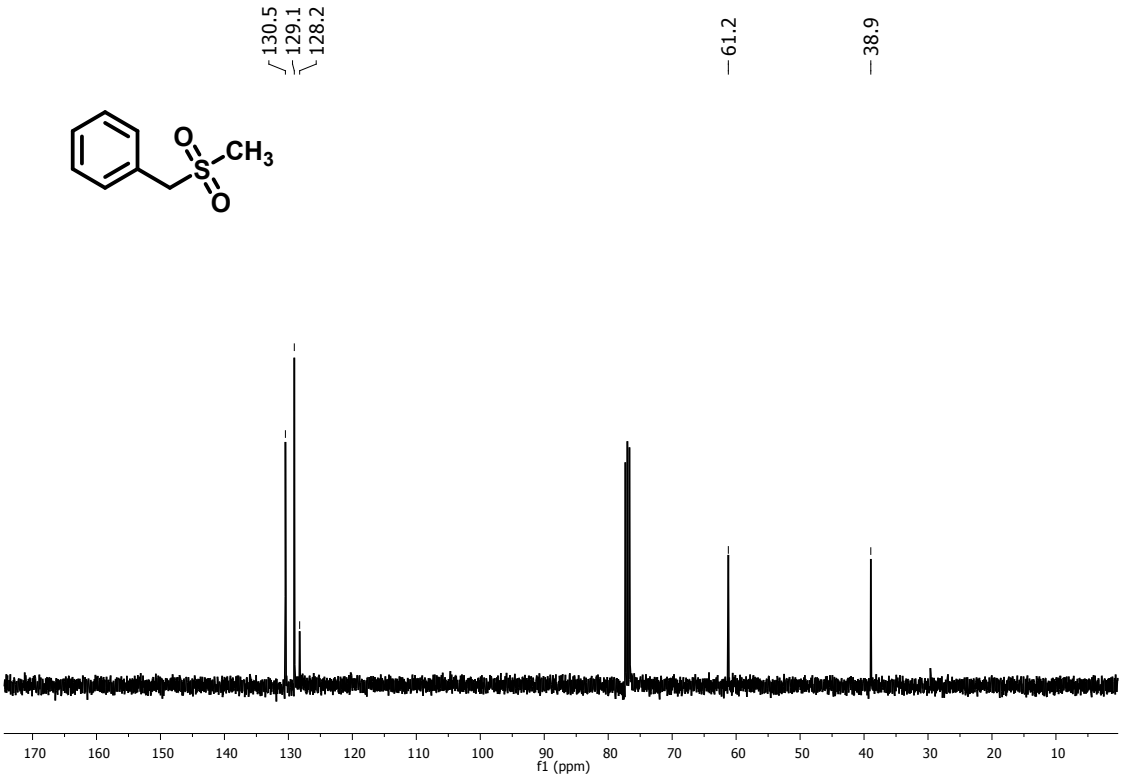
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4e**.



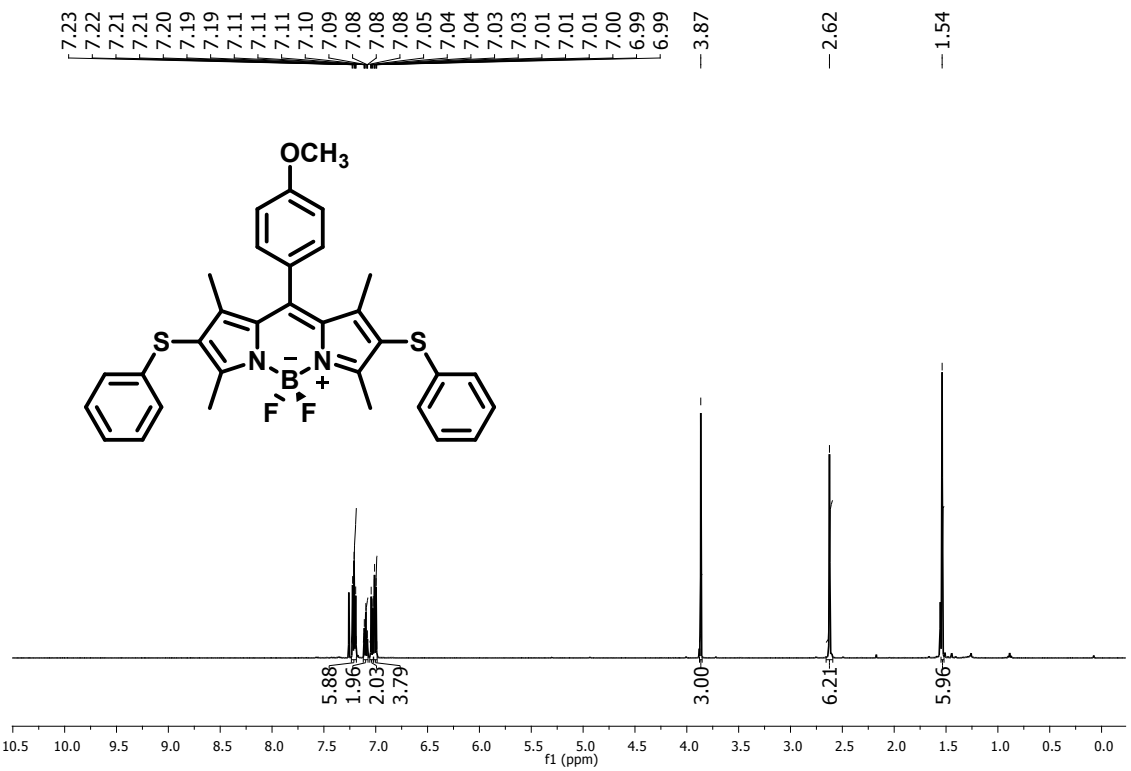
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4e**.



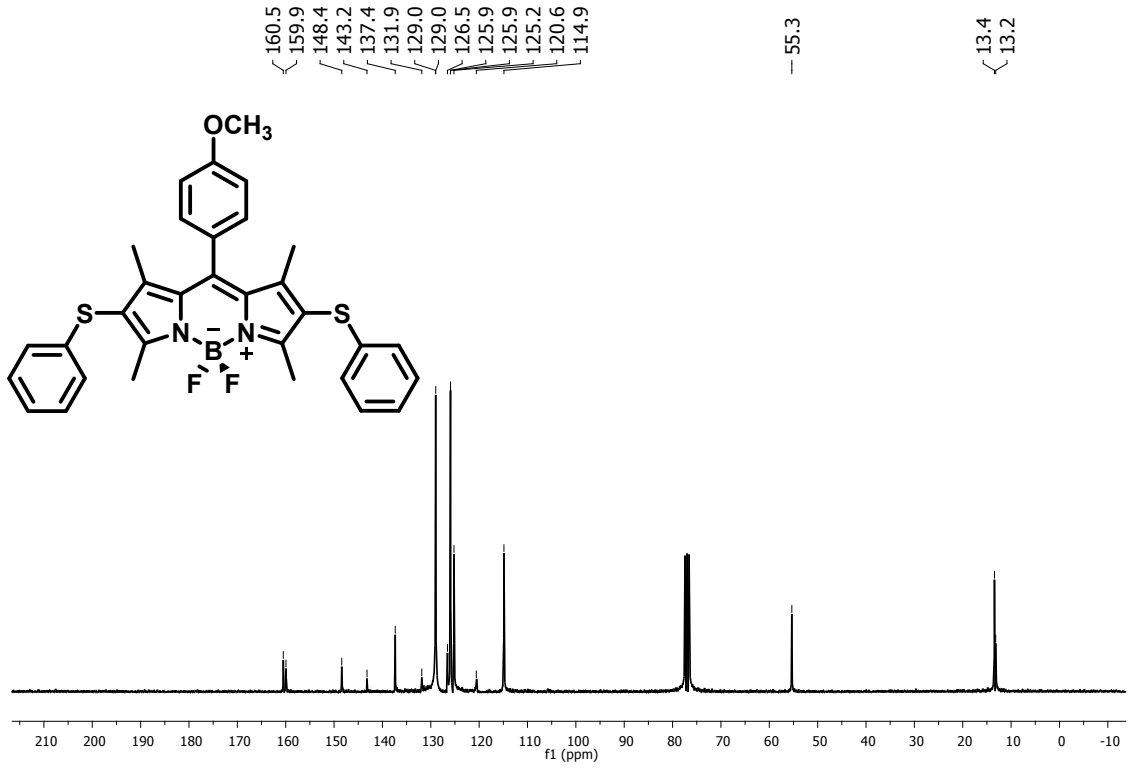
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4f**.



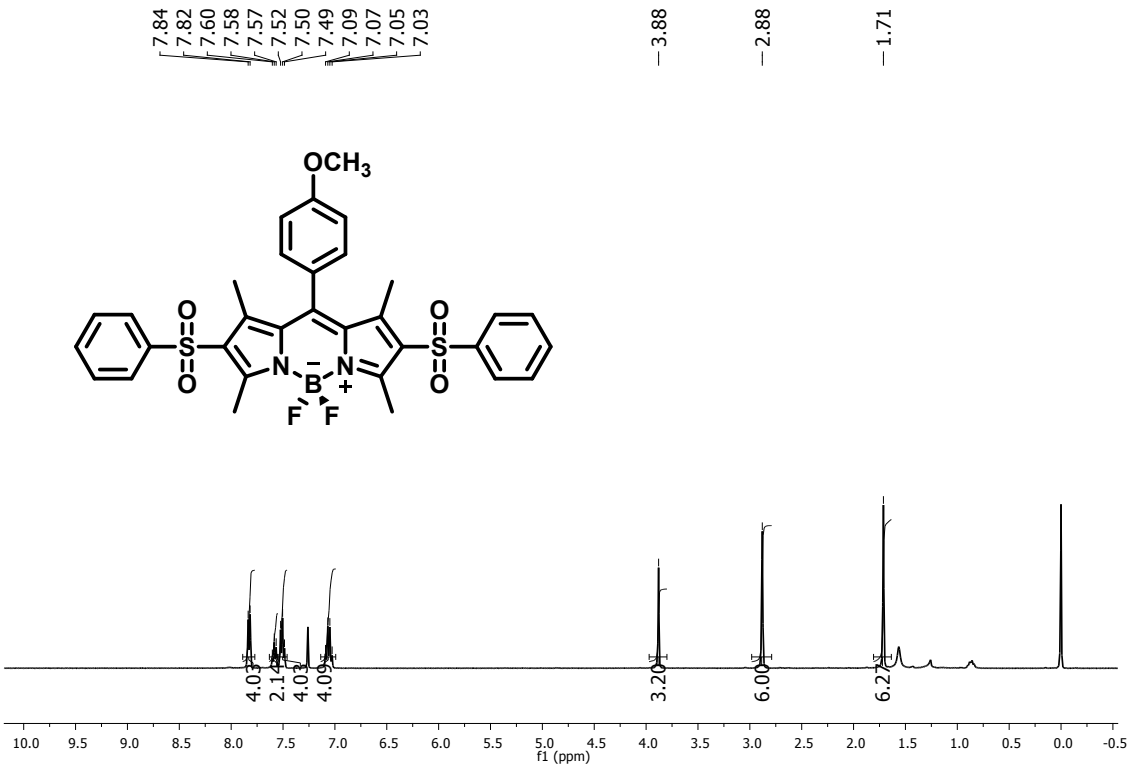
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4f**.



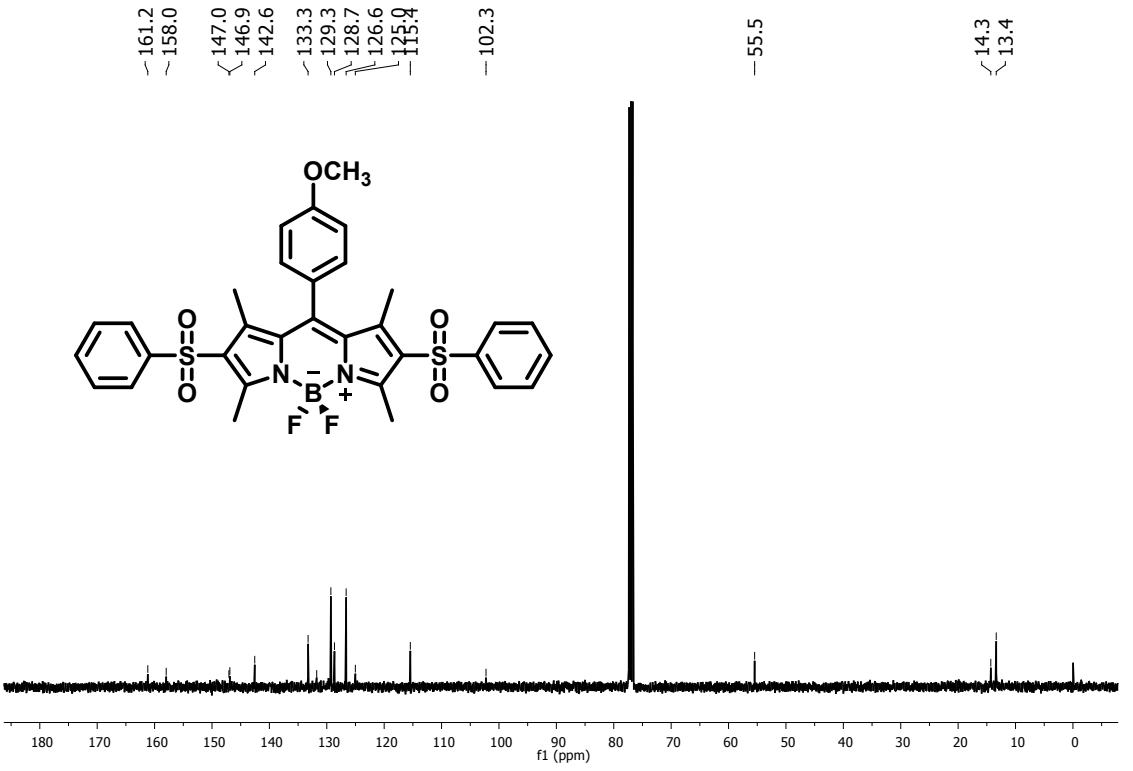
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5**.



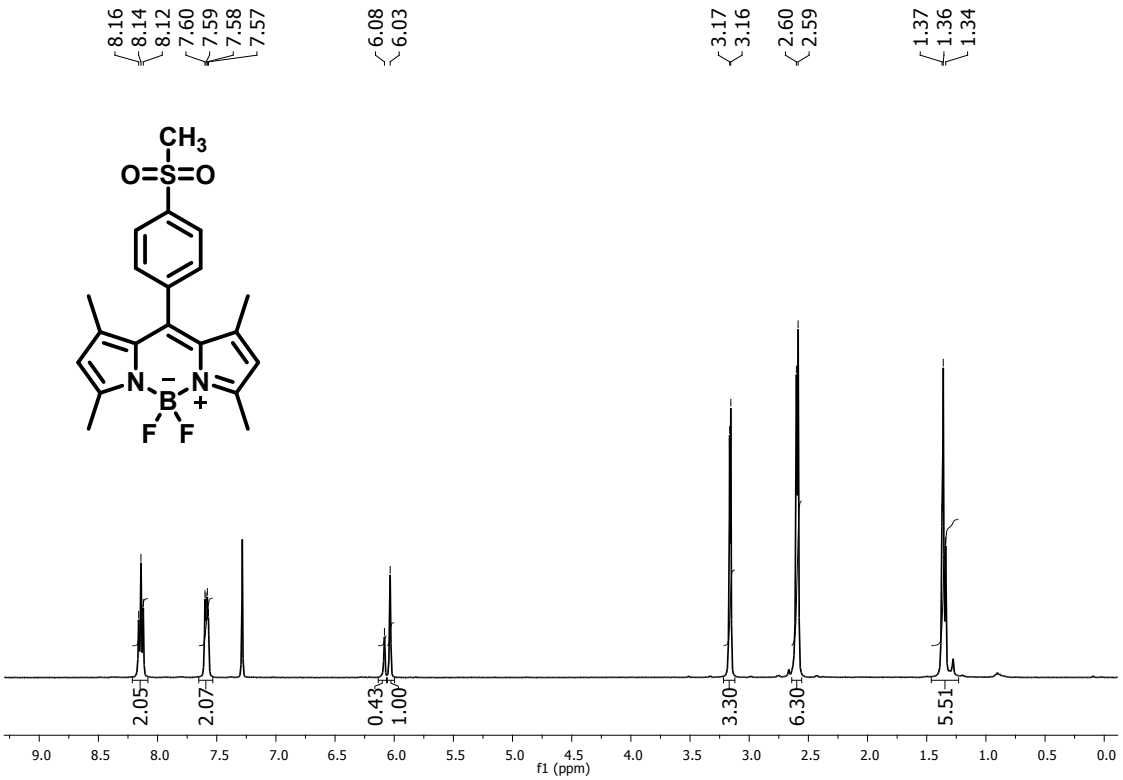
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **5**.



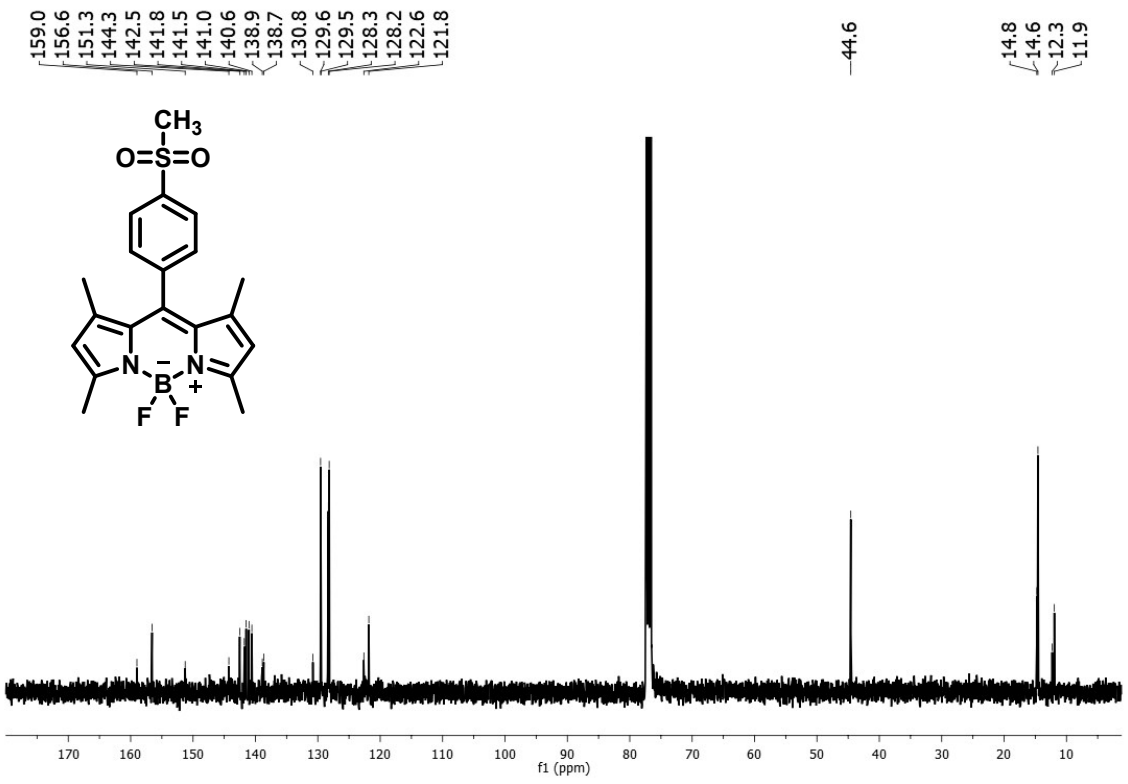
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **6**.



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **6**.

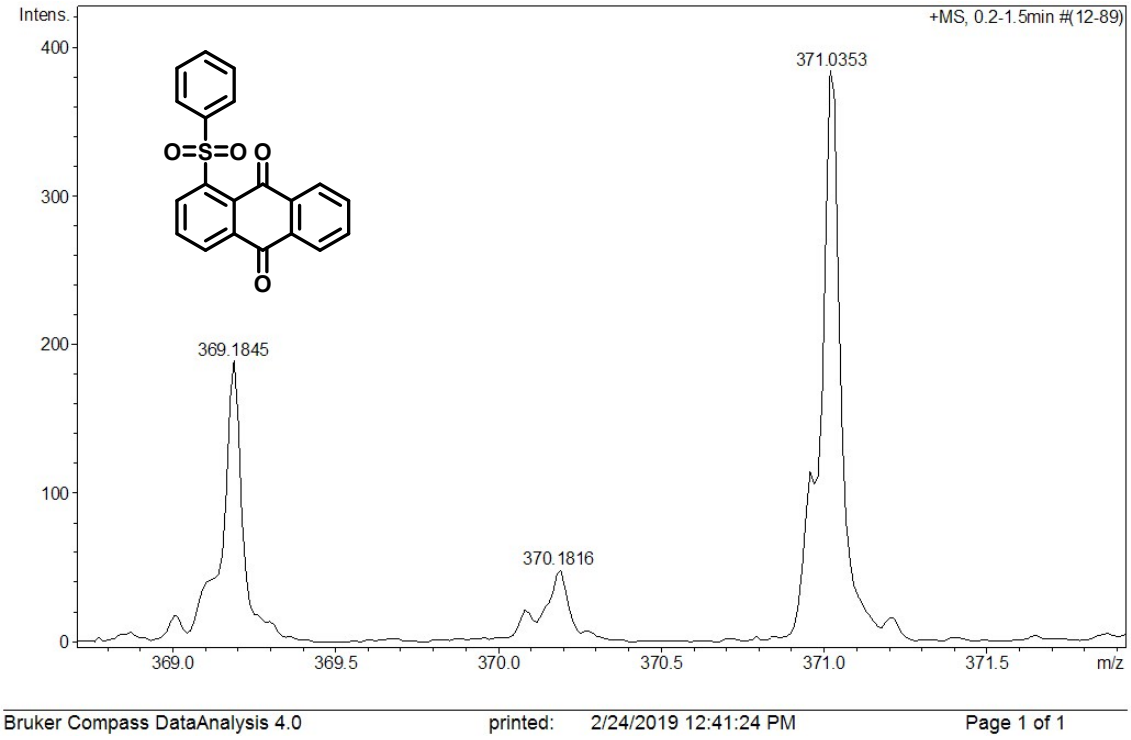


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **8**.

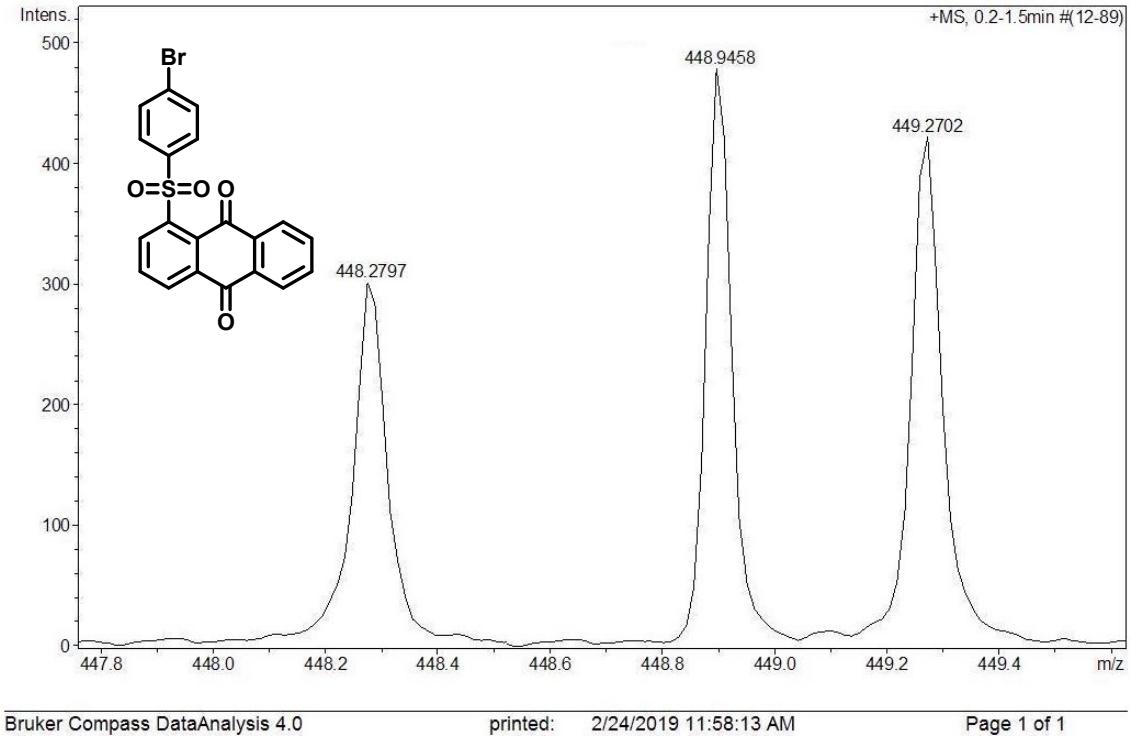


^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **8**.

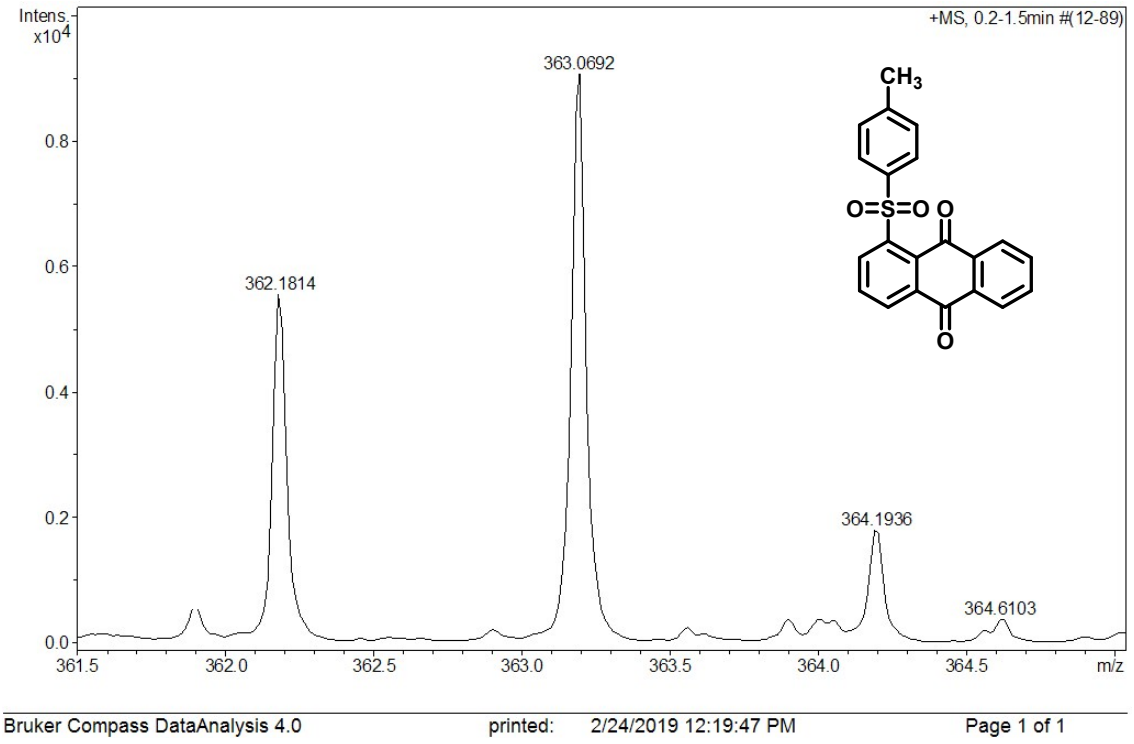
Copies of HRMS of novel compounds



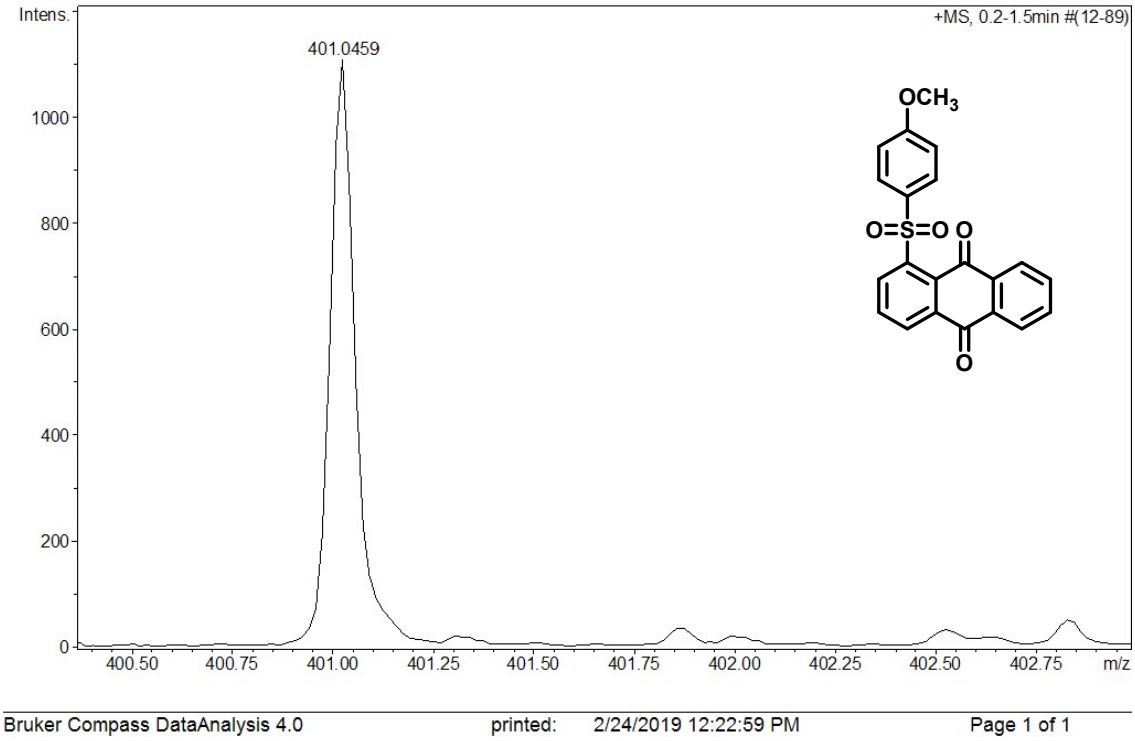
HRMS (ESI$^+$) of compound **2b**.



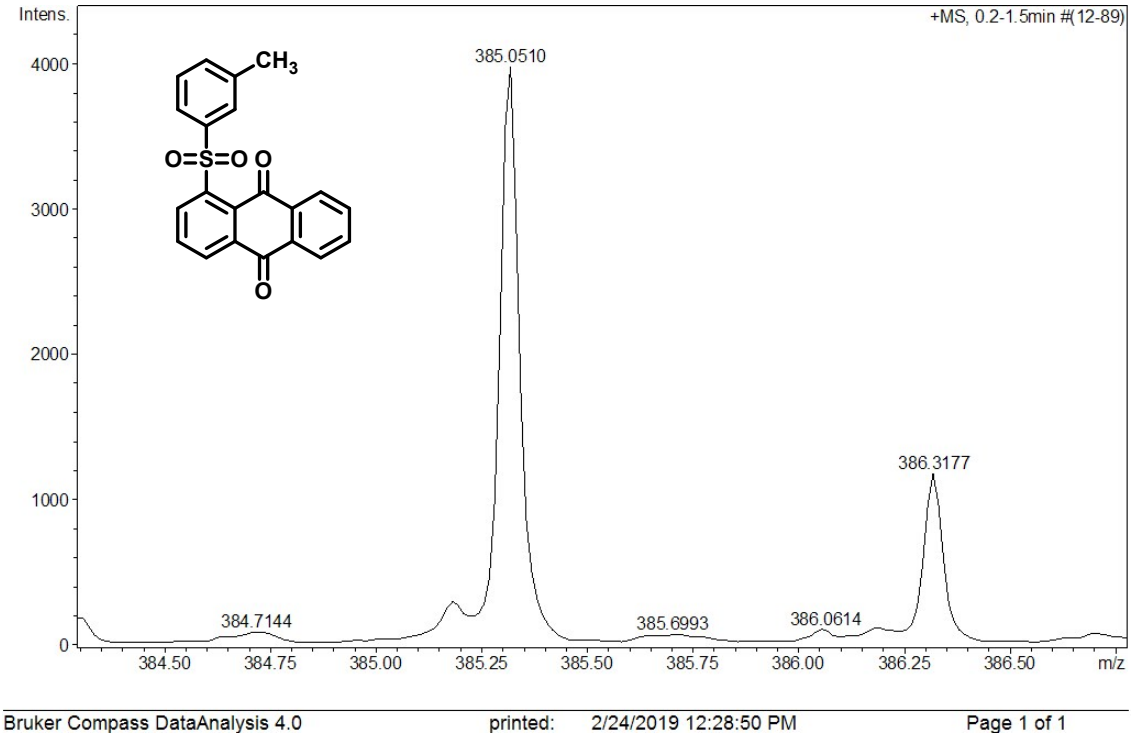
HRMS (ESI$^+$) of compound **2c**.



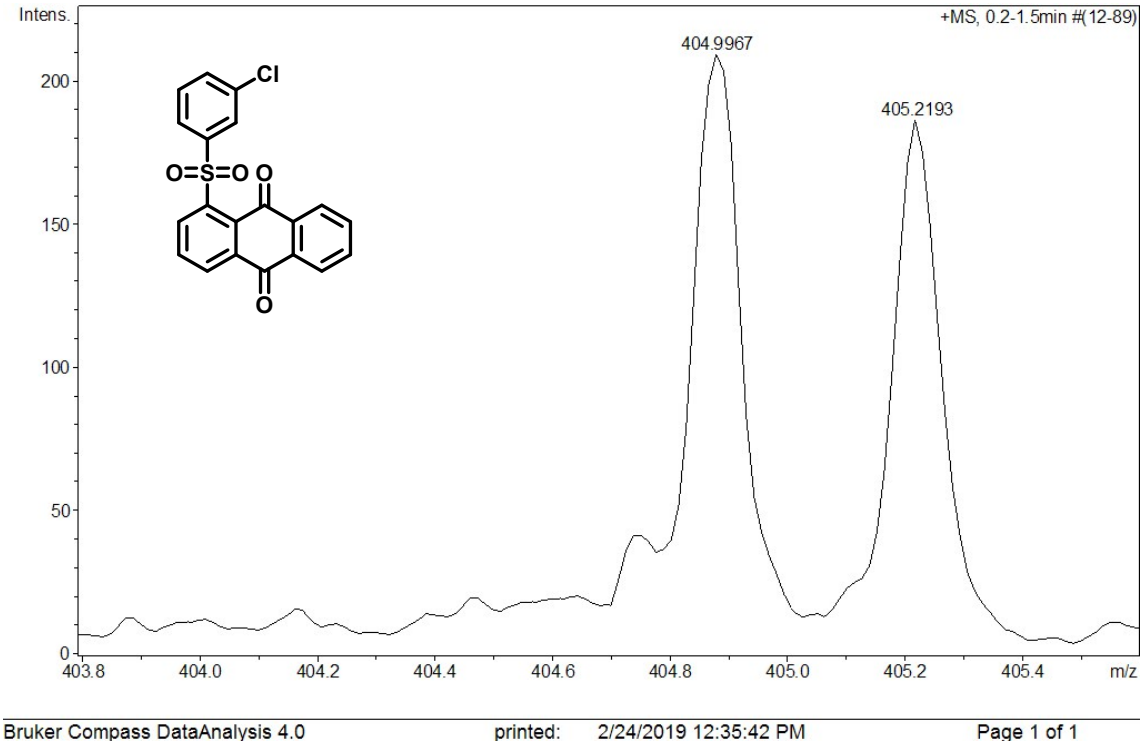
HRMS (ESI$^+$) of compound **2d**.



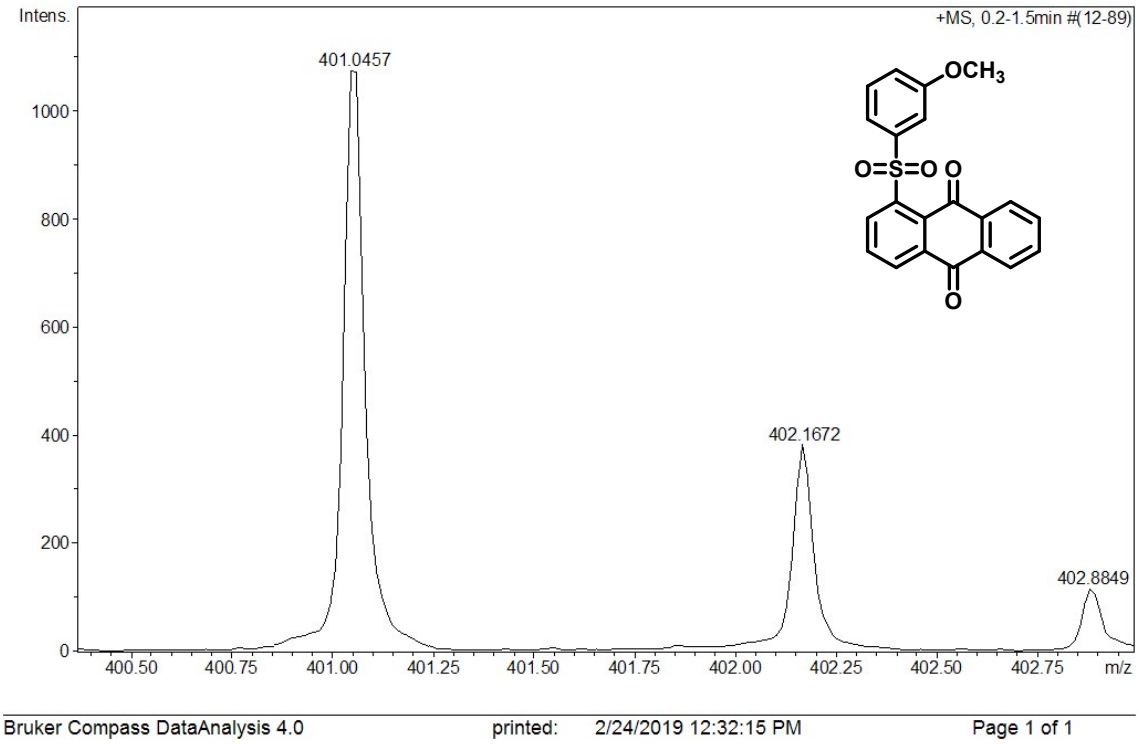
HRMS (ESI$^+$) of compound **2e**.



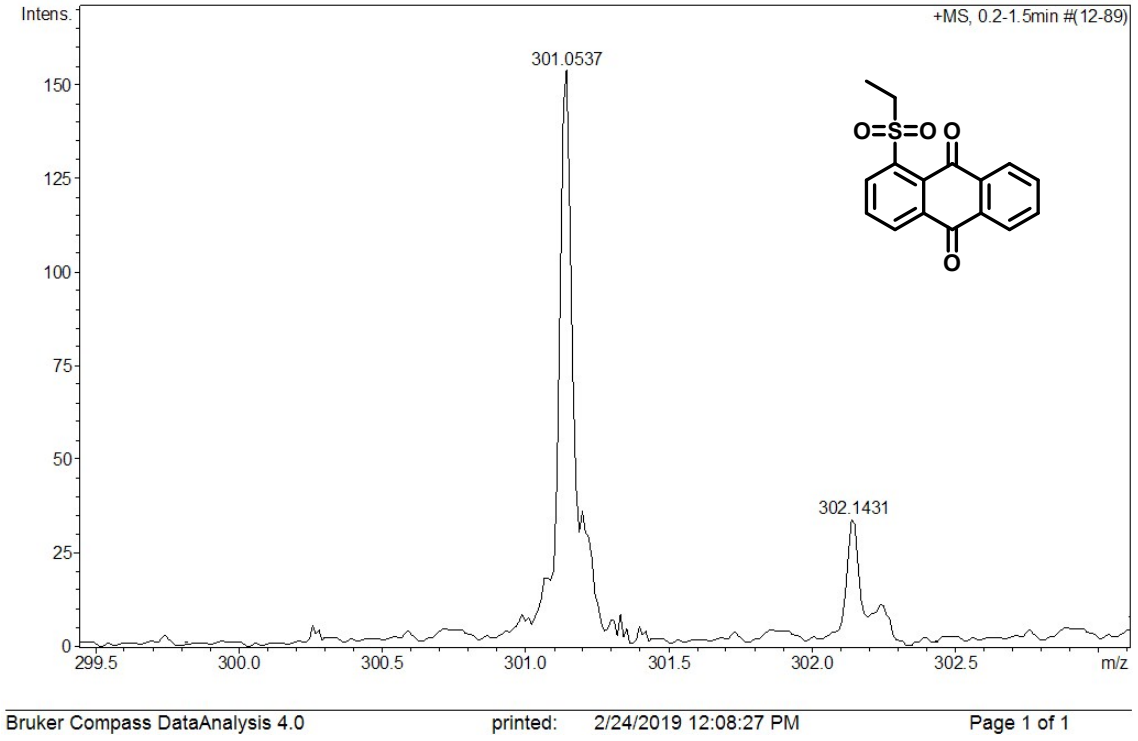
HRMS (ESI$^+$) of compound **2g**.



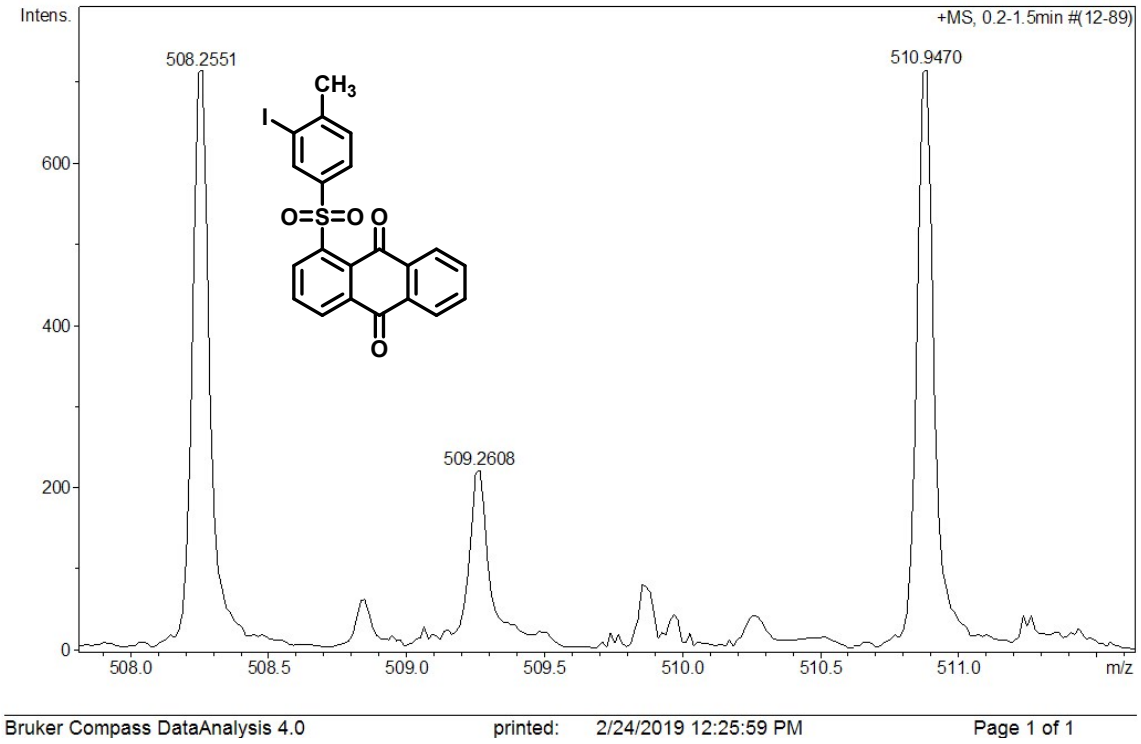
HRMS (ESI$^+$) of compound **2h**.



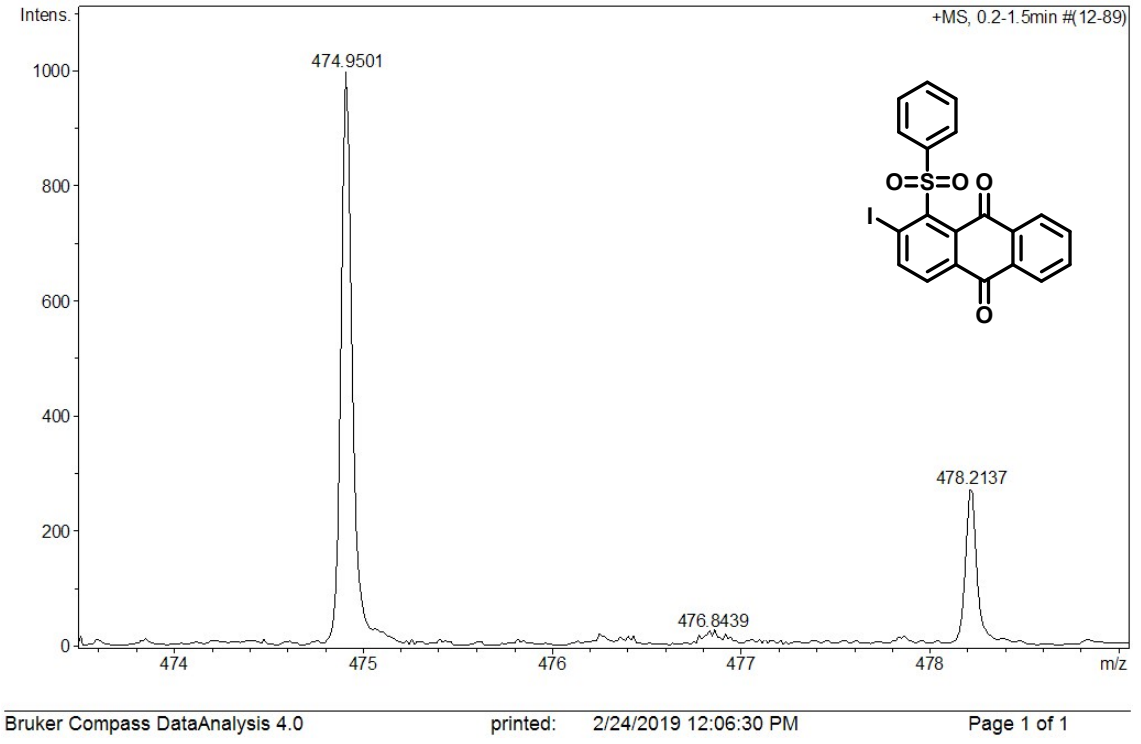
HRMS (ESI$^+$) of compound **2i**.



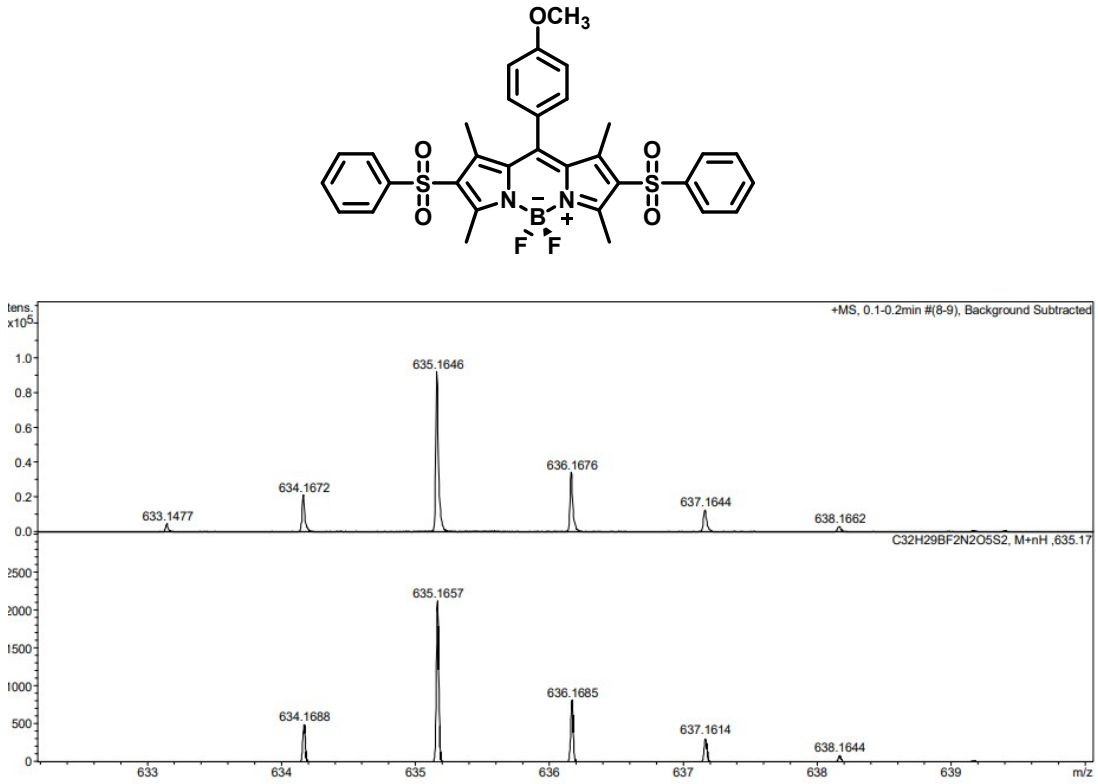
HRMS (ESI$^+$) of compound **2j**.



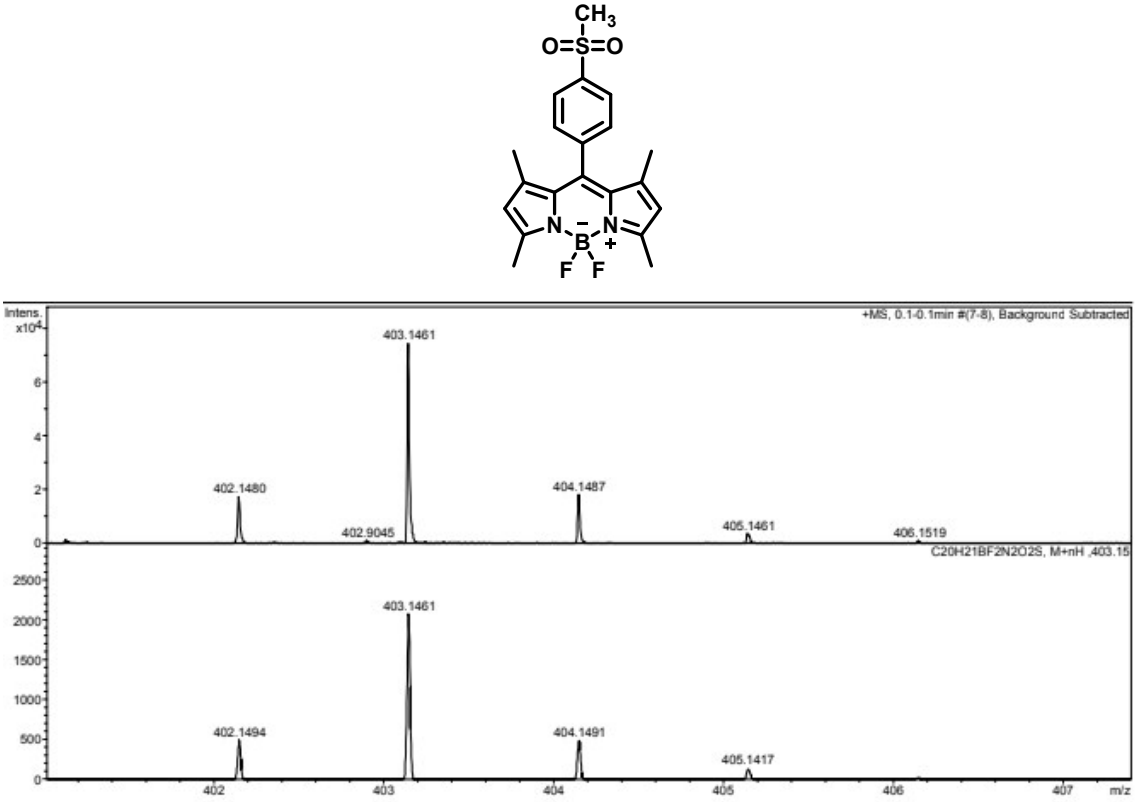
HRMS (ESI$^+$) of compound **2k**.



HRMS (ESI$^+$) of compound **2l**.



HRMS (ESI$^+$) of compound **6**.



HRMS (ESI$^+$) of compound **8**.

References

1. (a) G. Teverovskiy, D. S. Surry, S. L. Buchwald, *Angew. Chem. Int. Ed.*, 2011, **50**, 7312. (b) J. H. Clark, C. W. Jones, A. P. Kybett, M. A. Mcclinton, J. M. Miller, D. Bishop, R. J. Blade, *J. Fluorine Chem.*, 1990, **48**, 249.

2. (a) M. J. Baena, P. Espinet, M. C. Lequerica, A. M. Levelut, *J. Am. Chem. Soc.*, 1992, **114**, 4182. (b) I. G. Dance, K. J. Fisher, R. M. H. Banda, M. L. Scudder, *Inorg. Chem.*, 1991, **30**, 183.

3. G. A. M. Jardim, W. X. C. Oliveira, R. P. de Freitas, R. F. S. Menna-Barreto, T. L. Silva, M. O. F. Goulart, E. N. da Silva Júnior, *Org. Biomol. Chem.*, 2018, **16**, 1686.

4. N. V. Ivashkina, V. S. Romanov, A. A. Moroz, M. S. Shvartsberg, *Russ. Chem. B.*, 1984, **33**, 2345**.**

5. M. Gouda, M. Berghot, A. Shoeip, K. Elattar, A. E. G. Khalil, *Turk. J. Chem.,* 2010, **34**, 651-709.

6. A. Kar, I. A. Sayyed, W. F. Lo, H. M. Kaiser, M. Beller, M. K. *Org. Lett.,* 2007, **9**, 3405-3408.

7. M. Lutz, M. Wenzler, I. Likhotvorik, *Synthesis*., 2018, **50**, 2231-2234.

8. G. Laudadio, N. J. Straathof, M. D. Lanting, B. Knoops, V. Hessel, T. Noël, T. *Green Chem*., 2017, **19**, 4061-4066.

9. J. Ahrens, B. Böker, K. Brandhorst, M. Funk, M. Bröring, *Chem. Eur. J*. 2013, *19*, 11382-11395.