Supporting Information

$NaIO_4$-Driven Oxidative Dimerization and Cu(I)-Catalyzed Oxidative Decarbonylation: Modular Synthesis of 1,2-Naphthoquinones and Aryl Naphtho[2,b]furans

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Section I. General information:

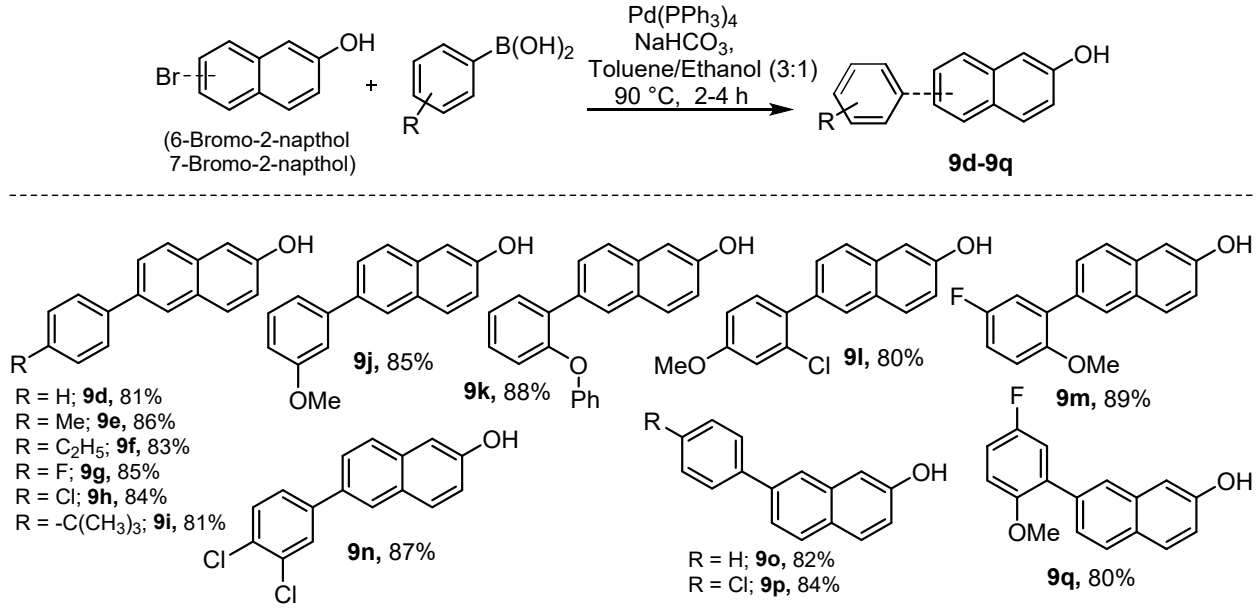
All reagents were purchased from commercial suppliers (Sigma Aldrich, TCI, BLD-Pharma, and Spectrochem) and used without further purification unless otherwise stated. All the reactions were performed in oven-dried glassware and monitored by thin-layer chromatography (TLC). Visualization of the spots on TLC plates was done by exposure to iodine vapor, under UV light or by spraying with Anisaldehyde-H_2SO_4-methanol solution and heating the plates at ~120 °C. Column chromatographic purifications were performed on silica gel (100-200 mesh). Spectroscopic characterizations were carried out at the Central Instrumentation Facility (CIF), CSIR-Indian Institute of Integrative Medicine Jammu. **^{1}H NMR** spectra were recorded on Bruker Avance-III FT-NMR spectrometers at 400 MHz and **^{13}C NMR** spectra at 100 MHz. ^{1}H NMR chemical shifts are reported in ppm relative to the TMS (δ = 0) and are abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), and m (multiplet). ^{13}C NMR chemical shifts are reported in ppm relative to the residual signal, DMSO-d_6 (δ = 39.52), $CDCl_3$ signal (δ = 77.16), CD_3OD signal (δ = 49.00). High-resolution mass spectrometry (**HRMS**) was measured on an electrospray ionization (ESI) apparatus using the time-of-flight (TOF) mass spectrometry. X-ray crystallographic data were collected using a **Bruker APEX-II CCD** diffractometer.

Section II. General procedure for the synthesis of substituted 2-Naphthols:

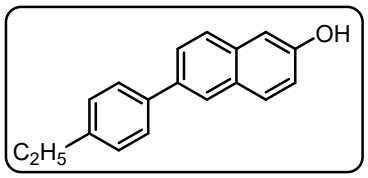
All substituted 2-Naphthols were synthesized according to the reported literature, via Suzuki coupling from commercially available 6-Bromo-2-napthol (**9d-9n**) and 7-Bromo-2-napthol (**9o-9q**).[1]

To a solution of 6-bromo-2-naphthol, **9d** (1000 mg, 4.48 mmol, 1.0 equiv.) and Tetrakis(triphenylphosphine) palladium[0] (258.0 mg, 0.224 mmol, 0.05 equiv.) in toluene (15 mL) was added aqueous 2 M sodium bicarbonate solution (5 mL, 1mL/200mg of 6-bromo-2-naphthol). The reaction mixture was stirred at room temperature for 10 minutes under nitrogen atmosphere. Afterwards, phenyl boronic acid (547.0 mg, 4.48 mmol, 1 .0 equiv.) in 5 mL ethanol was added to the reaction mixture and the mixture was stirred at 90 °C for 3 hours under nitrogen atmosphere. After completion, monitored by TLC analysis, the reaction mixture was allowed to cool to room temperature, diluted with water and the aqueous layer was extracted with ethyl acetate (20 mL x 3). The combined organic layer was dried over anhydrous sodium sulphate, concentrated under reduced pressure and purified by column chromatography using Hexanes: Ethyl acetate (90:10, v/v) as eluent to afford product **9d** (800 mg, 81% yield).

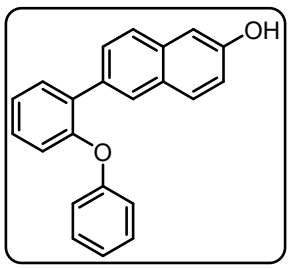
Similar procedure was followed for the synthesis of compounds **9e-9q** (81-89% yield). Some of these compounds are reported in literature and for new compounds, the analytical data is given below.[2]



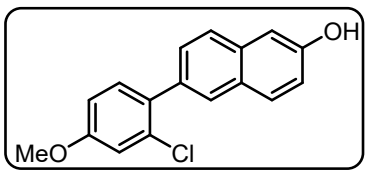
Analytical data for compounds 9f, 9k, 9l, 9m, 9q:



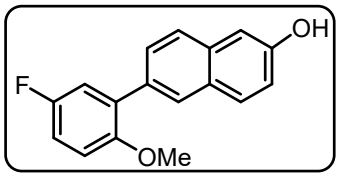
6-(4-ethylphenyl)naphthalen-2-ol (9f): White solid, (Melting point: 143-146 °C), yield (83%); **^{1}H NMR** (400 MHz, MeOD) δ 7.93 – 7.60 (m, 6H), 7.23 – 7.07 (m, 4H), 2.69 – 2.65 (m, 2H), 1.29 –1.25 (m, 3H). **^{13}C NMR** (100 MHz, MeOD) δ 156.5, 144.3, 139.8, 136.9, 135.4, 130.8, 130.2, 129.4, 130.0, 127.8, 127.7, 126.6, 126.1, 119.6, 109.8, 109.5, 29.5, 16.2. **ESI HRMS** m/z calcd. for $C_{18}H_{17}O$ $[M+H]^+$: 249.1279, Found 249.1279.



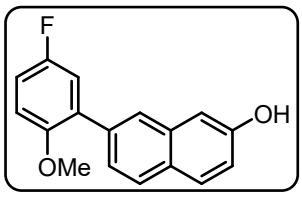
6-(2-phenoxyphenyl)naphthalen-2-ol (9k): Yellowish liquid, yield (88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.69- 7.63 (m, 2H), 7.58- 7.56 (m, 1H), 7.35- 7.25 (m, 3H), 7.26- 7.24 (m,1H), 7.12 – 6.96 (m, 6H), 5.38 (s, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ ^{13}C 157.9, 153.9, 153.7, 133.8, 133.8, 133.2, 131.6, 130.3, 129.7, 129.0, 128.7, 128.3, 128.1, 126.1, 124.1, 122.8, 120.3, 118.3, 118.0, 109.4. **ESI HRMS** m/z calcd. for $C_{22}H_{17}O_2$ $[M+H]^+$: 313.1229, Found 313.1228.



6-(2-chloro-4-methoxyphenyl)naphthalen-2-ol (9l): Yellowish liquid, yield (80%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.7 Hz, 2H), 7.72 (d, J = 8.5 Hz, 1H), 7.53 (d, J = 8.5, 1.4 Hz, 1H), 7.34 (d, J = 8.5 Hz, 1H), 7.19-7.12 (m, 2H), 7.06 (d, J = 2.5 Hz, 1H), 6.92- 6.89 (m, 1H), 5.16 (s, 1H), 3.86 (s, 3H). **^{13}C NMR** (100, MHz, $CDCl_3$) δ 159.5, 153.8, 134.7, 133.8, 133.3, 133.1, 132.2, 130.2, 128.8, 128.7, 128.4, 126.0, 118.2, 115.3, 113.3, 109.5, 55.8. **ESI HRMS** m/z calcd. for $C_{17}H_{14}ClO_2$ $[M+H]^+$: 285.0682, Found 285.0688.



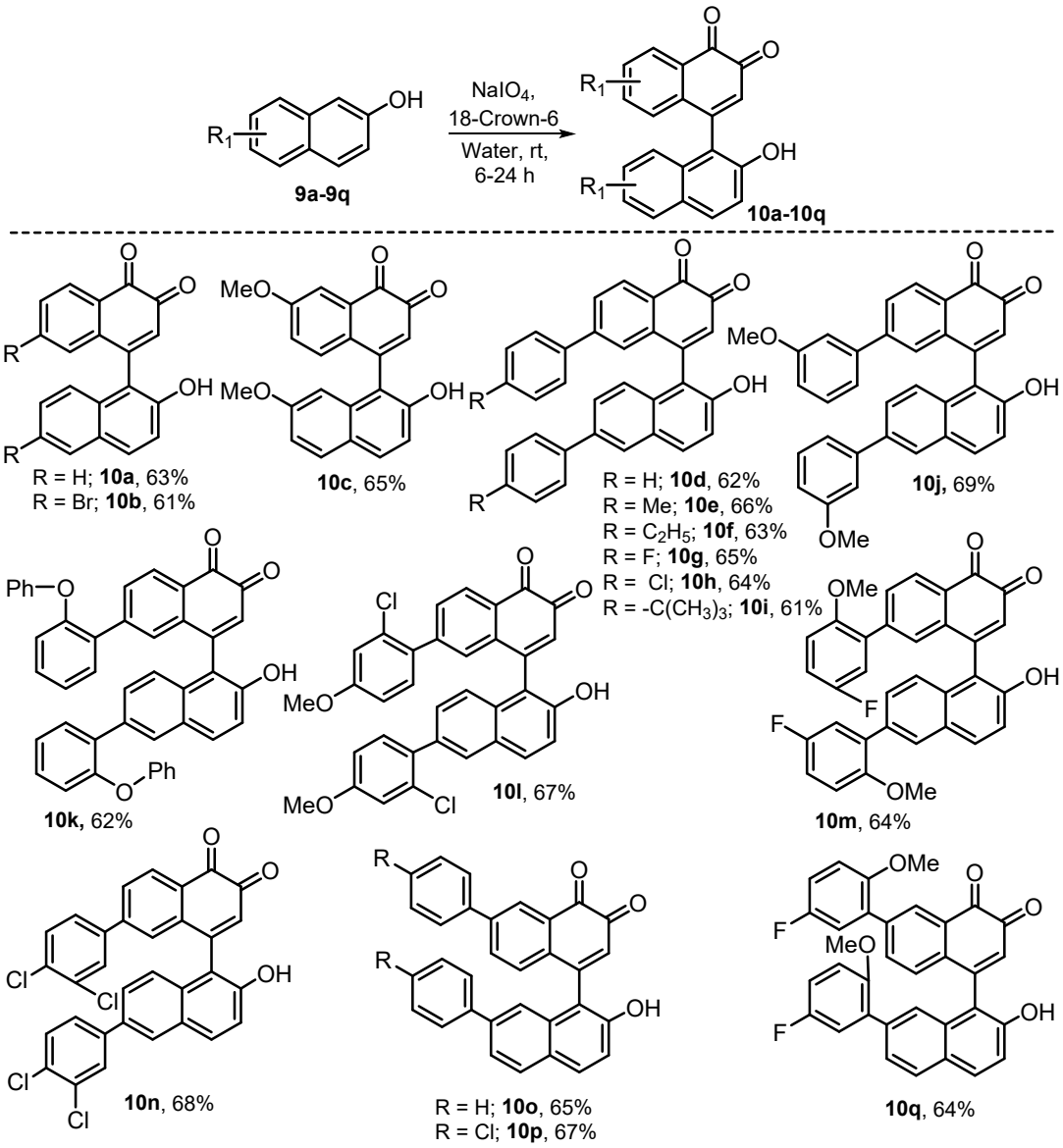
6-(5-fluoro-2-methoxyphenyl)naphthalen-2-ol (9m): Yellowish liquid, yield (89%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.70 (d, J = 8.6 Hz, 1H), 7.63- 7.61 (m, 1H), 7.16- 7.10 (m, 3H), 7.05- 7.00 (m, 1H), 6.94 (m,1H), 3.80 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.4, 156.1, 153.7, 152.8, 152.8, 133.8, 132.9, 132.1, 132.0, 130.2, 128.8, 128.3, 128.1, 126.0, 118.0, 117.7, 117.5, 114.4, 114.1, 112.5, 112.4, 109.3, 56.3. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -123.8. **ESI HRMS** m/z calcd. for $C_{17}H_{14}FO_2$ $[M+H]^+$: 269.0978, Found 269.0984.



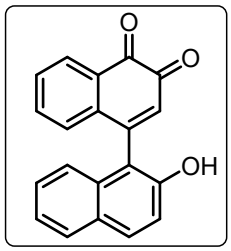
7-(5-fluoro-2-methoxyphenyl)naphthalen-2-ol (9q): Yellowish liquid, yield (80%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.5 Hz, 1H), 7.75 (d, J = 9.2 Hz, 2H), 7.54- 7.51 (m, 1H), 7.17- 7.02 (m, 4H), 6.96-6.93 (m, 1H), 5.54- 5.44 (m, 1H), 3.80 (s, 3H). **^{13}C NMR** (100, DMSO-d_6) δ 158.5, 156.1, 153.7, 152.9, 152.9, 135.9, 134.6, 132.3, 132.2, 129.7, 128.2, 127.4, 126.8, 125.5, 118.1, 117.9, 117.6, 114.7, 114.5, 112.8, 112.7, 109.9, 77.2, 56.5. **^{19}F NMR** (377 MHz, DMSO-d_6) δ -123.7. **ESI HRMS** m/z calcd. for $C_{17}H_{14}FO_2$ $[M+H]^+$: 269.0978, Found 269.0977.

Section III. General procedure for the synthesis of substituted 1,2-naphthoquinones (10a-10q):

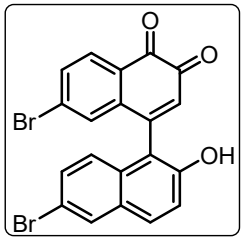
A round bottomed flask equipped with a magnetic stir bar was charged with 2-napthol (800 mg, 5.549 mmol, 1.0 equiv.) and 18-crown-6 (293.00 mg, 1.11 mmol, 0.2 equiv.) in water (40 mL).The reaction mixture was stirred at room temperature for 10 minutes followed by the addition of sodium periodate (3.5 g, 16.65 mmol, 3 equiv.) and was allowed to stir at room temperature for 6 hours. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was quenched with water and extracted with ethyl acetate (30 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure and subjected to column chromatography using Hexanes: Ethyl acetate (80:20, v/v) as eluent to afford **10a** product (525 mg, 63% yield). A similar procedure was followed for the synthesis of remaining compounds **10b-10q** (61-69% yield).



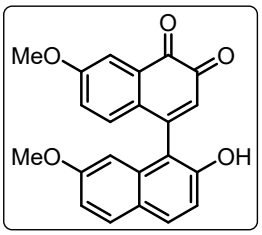
Analytical data for compounds 10a-10q:



2'- hydroxy-[1,1'-binaphthalene]-3,4-dione (10a): Brownish solid (Melting point: 205-207 °C), yield (63%); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.86 (s, 1H), 8.07 (d, J = 6.0 Hz, 1H), 7.95-7.88 (m, 2H), 7.73 (d, J = 7.4 Hz, 1H), 7.62-7.47 (m, 2H), 7.41-7.26 (m, 3H), 6.71 (d, J = 6.5 Hz, 1H), 6.36 (s, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 179.9, 179.0, 151.8, 151.7, 135.5, 135.2, 132.5, 132.0, 130.5, 130.4, 128.9, 128.2, 128.1, 127.8, 126.9, 124.1, 123.2, 118.4, 115.5. **ESI HRMS** m/z calcd. for $C_{20}H_{13}O_3$ $[M+H]^+$: 301.0865, Found 301.0867.

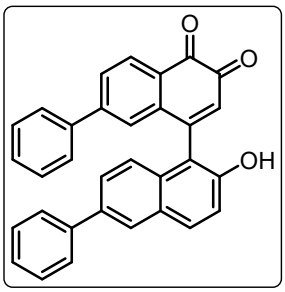


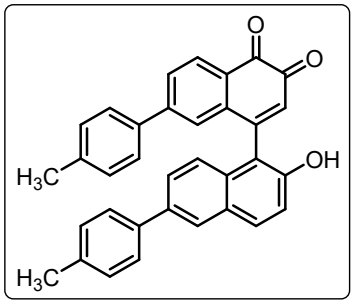
6',7-dibromo-2'-hydroxy-[1,1'-binaphthalene]-3,4-dione (10b): Brownish solid (Melting point: 275-277 °C), yield (61%); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.18 (s, 1H), 8.18 (d, J = 1.5 Hz, 1H), 7.97 (m, 2H), 7.88 -7.71 (m, 2H), 7.52-7.49 (m,1H), 7.37 (d, J = 8.9 Hz, 1H), 6.74 (d, J = 1.5 Hz, 1H), 6.41 (s, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 179.3, 178.0, 152.3, 149.1, 137.1, 133.2, 131.9, 131.3, 131.1, 130.7, 130.1, 130.0, 130.0, 129.9, 129.1, 129.0, 126.4, 119.6, 116.3, 115.1. **ESI HRMS** m/z calcd. for $C_{20}H_{11}Br_2O_3$ $[M+H]^+$: 456.9075, Found 456.9068.



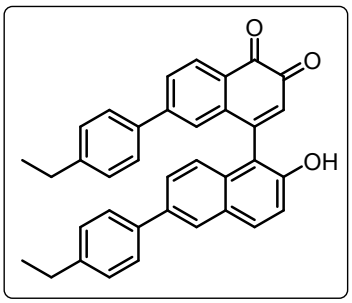
2'-hydroxy-6,7'-dimethoxy-[1,1'-binaphthalene]-3,4-dione (10c): Brownish solid (Melting point: 239-242 °C), yield (65%); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.75 (s, 1H), 7.83-7.78 (m, 2H), 7.54 (d, J = 2.7 Hz, 1H), 7.13-6.98 (m, 4H), 6.69-6.63 (m, 1H), 6.22-6.10 (m, 1H), 3.84 (s, 3H), 3.67 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 180.1, 179.1, 160.9, 158.2, 152.2, 152.2, 133.8, 133.6, 130.1, 130.0, 129.8, 128.3, 127.7, 123.2, 120.1, 115.6, 115.1, 114.8, 113.9, 103.6, 55.8, 55.4. **ESI HRMS** m/z calcd. for $C_{22}H_{17}O_5$ $[M+H]^+$: 361.1076, Found 361.1081.

2'-hydroxy-6',7-diphenyl-[1,1'-binaphthalene]-3,4-dione (10d): Brownish solid (Melting point: 241-244 °C), yield (62%); **^{1}H NR** (400 MHz, DMSO-d_6) δ 10.04 (s, 1H), 8.30-8.14 (m, 2H), 8.05 (d, J = 8.9 Hz, 1H), 7.92-7.85 (m, 2H), 7.79-7.69 (m, 3H), 7.49-7.46 (m, 2H), 7.40-7.30 (m, 7H), 6.98 (s, 1H), 6.44 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.8, 179.3, 152.8, 150.5, 149.0, 140.6, 139.1, 137.1, 135.8, 131.8, 131.6, 131.3, 130.4, 129.6, 129.5, 129.3, 129.1, 129.1, 129.1, 128.0, 127.6, 127.4, 127.3, 127.3, 126.4, 124.8, 118.5, 115.6. **ESI HRMS** m/z calcd. for $C_{32}H_{21}O_3$ $[M+H]^+$: 453.1491, Found 453.1484.

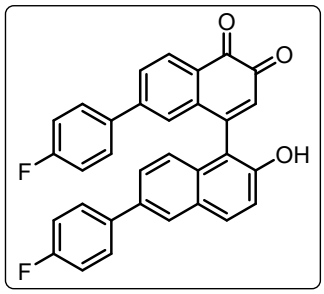




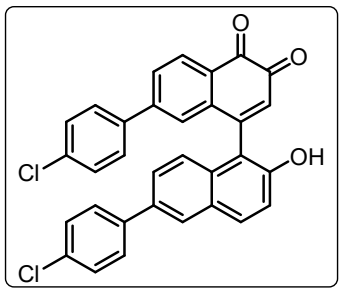
2'-hydroxy-6',7-di-p-tolyl-[1,1'-binaphthalene]-3,4-dione (10e): Brownish solid (Melting point: 163-166 °C),, yield (66%); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.98 (s, 1H), 8.19-8.13 (m, 2H), 8.03 (d, J = 9.0 Hz, 1H), 7.91-7.77 (m, 2H), 7.65 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.9 Hz, 1H), 7.31-7.11 (m, 7H), 6.96 (s, 1H), 6.43 (s, 1H), 2.33 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 180.1, 178.6, 151.9, 151.4, 146.3, 138.6, 137.0, 136.6, 136.0, 135.5, 134.8, 131.6, 131.0, 130.8, 130.6, 129.9, 129.6, 128.2, 126.6, 126.4, 126.0, 125.9, 125.3, 124.8, 118.7, 115.3, 20.7, 20.7. **ESI HRMS** m/z calcd. for $C_{34}H_{25}O_3$ $[M+H]^+$: 481.1804, Found 481.1798.



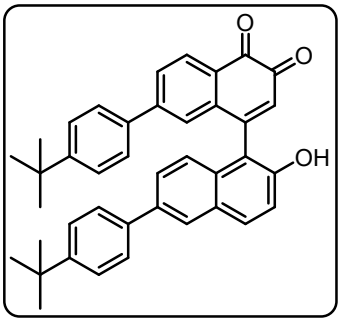
6',7-bis(4-ethylphenyl)-2'-hydroxy-[1,1'-binaphthalene]-3,4-dione (10f): Brownish solid (Melting point: 170-173 °C), yield (63%); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.00 (s, 1H), 8.19-8.11 (m, 2H), 8.03 (d, J = 8.9 Hz, 1H), 7.89-7.82 (m, 2H), 7.72-7.73 (m, 3H), 7.39-7.17 (m, 7H), 6.96 (s, 1H), 6.44-6.40 (m, 1H), 2.67-2.60 (m, 2H), 2.58-2.51 (m, 2H), 1.22- 1.18 (m, 3H), 1.12-1.08 (m, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 180.1, 178.6, 151.9, 151.5, 146.4, 144.9, 143.0, 137.3, 136.0, 135.8, 134.9, 131.6, 131.0, 130.9, 130.7, 129.8, 128.7, 128.4, 128.2, 128.2, 126.7, 126.6, 126.1, 126.0, 125.3, 124.8, 118.7, 115.3, 27.9, 27.8, 15.7, 15.4. **ESI HRMS** m/z calcd. for $C_{36}H_{29}O_3$ [M+H]$^+$: 509.2117, Found 509.2106.



6',7-bis(4-fluorophenyl)-2'-hydroxy-[1,1'-binaphthalene]-3,4-dione (10g): Brownish solid (Melting point: 180-182 °C), yield (65%); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.05 (s, 1H), 8.17 (d, J = 10.7 Hz, 2H), 8.04 (d, J = 8.2 Hz, 1H), 7.95-7.66 (m, 5H), 7.46-7.15 (m, 7H), 6.95 (s, 1H), 6.43 (s, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 180.0, 178.6, 163.8, 163.1, 161.4, 160.6, 152.1, 151.3, 145.3, 136.4, 136.4, 136.0, 134.9, 134.9, 133.9, 131.7, 131.1, 131.0, 130.9, 129.9, 128.9, 128.8, 128.7, 128.5, 128.1, 126.0, 126.0, 125.7, 124.9, 118.9, 116.4, 116.2, 115.9, 115.7, 115.3. **^{19}F NMR** (377 MHz, DMSO-d_6) δ -113.0, -115.7. **ESI HRMS** m/z calcd. for $C_{32}H_{19}F_2O_3$ [M+H]$^+$: 489.1302, Found 489.1298.

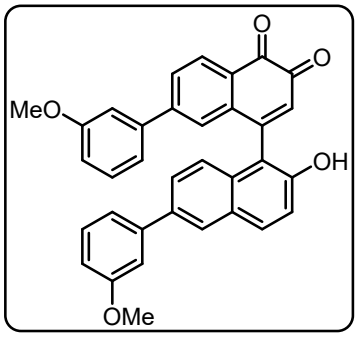


6',7-bis(4-chlorophenyl)-2'-hydroxy-[1,1'-binaphthalene]-3,4-dione (10h): Brownish solid (Melting point: 190-192 °C), yield (64%); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.07 (s, 1H), 8.22 (s, 1H), 8.17 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.9 Hz, 1H), 7.91 (d, J = 8.8 Hz, 1H), 7.84 (d, J = 7.7 Hz, 1H), 7.78 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.5 Hz, 1H), 7.51 (d, J = 8.3 Hz, 2H), 7.44-7.32 (m, 5H), 6.96 (s, 1H), 6.43 (s, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 179.9, 178.5, 152.2, 151.1, 145.0, 138.7, 137.2, 136.0, 133.9, 133.5, 132.1, 131.9, 131.2, 131.0, 129.8, 129.3, 128.9, 128.5, 128.5, 128.4, 128.4, 128.1, 126.0, 125.8, 125.8, 125.0, 118.9, 115.2. **ESI HRMS** m/z calcd. for $C_{32}H_{19}Cl_2O_3$ [M+H]$^+$: 521.0711, Found 521.0696.

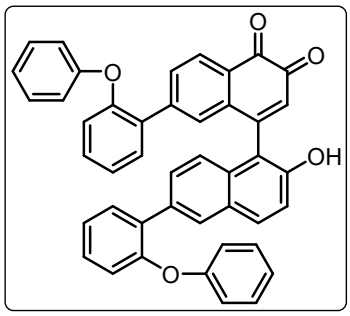


6',7-bis(4-(tert-butyl)phenyl)-2'-hydroxy-[1,1'-binaphthalene]-3,4-dione (10i): Brownish solid (Melting point: 195-197 °C), yield (61%); **^{1}H NMR** (400 MHz, DMSO- d_6) δ 10.00 (s, 1H), 8.16 (d, J = 7.9 Hz, 2H), 8.04 (d, J = 9.0 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.85-7.82 (m,1H), 7.76-7.62 (m, 3H), 7.48 (d, J = 8.5 Hz, 2H), 7.40-7.35 (m, 3H), 7.26 (d, J = 8.5 Hz, 2H), 6.97 (d, J =

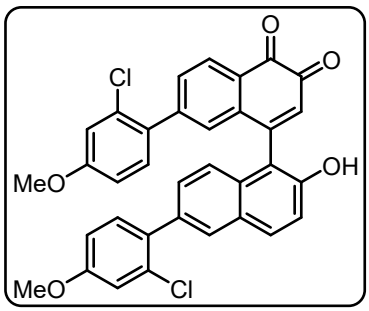
1.6 Hz, 1H), 6.44 (s, 1H). 1.30 (s, 9H), 1.20 (s, 9H). **^{13}C NMR** (100 MHz, DMSO- d_6) δ 180.1, 178.6, 151.9, 151.6, 151.5, 149.7, 146.3, 137.0, 136.0, 135.5, 134.8, 131.6, 131.0, 130.8, 130.7, 129.8, 128.2, 128.2, 126.4, 126.3, 126.1, 125.7, 125.3, 124.8, 118.7, 115.3, 34.3, 34.2, 31.1, 30.9. **ESI HRMS** m/z calcd. for $C_{40}H_{37}O_3$ $[M+H]^+$: 565.2743, Found 565.2737.



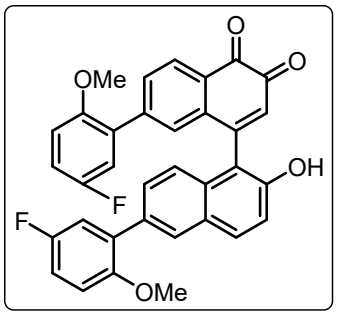
2'-hydroxy-6',7-bis(3-methoxyphenyl)-[1,1'-binaphthalene]-3,4-dione (10j): Brownish solid (Melting point: 220-222 °C), yield (69%); **^{1}H NMR** (400 MHz, DMSO- d_6) δ 10.04 (s, 1H), 8.22 (s, 1H), 8.16 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.9 Hz, 1H), 7.92-7.84 (m, 2H), 7.72 (d, J = 8.5 Hz, 1H), 7.45-7.25 (m, 5H), 6.96-6.81 (m, 5H), 6.45 (s, 1H), 3.83 (s, 3H), 3.67 (s, 3H). **^{13}C NMR** (100 MHz, DMSO- d_6) δ 180.0, 178.6, 159.8, 159.7, 152.1, 151.2, 146.1, 141.5, 139.8, 135.9, 134.8, 131.9, 131.2, 131.1, 130.9, 130.5, 130.1, 129.7, 128.6, 128.1, 126.4, 126.2, 125.9, 124.9, 119.1, 118.8, 118.8, 115.3, 114.3, 112.8, 112.4, 112.3, 55.2, 55.1. **ESI HRMS** m/z calcd. for $C_{34}H_{25}O_5$ $[M+H]^+$: 513.1702, Found 513.1695.



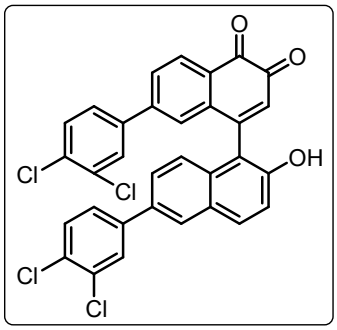
2'-hydroxy-6',7-bis(2-phenoxyphenyl)-[1,1'-binaphthalene]-3,4-dione (10k): Brownish solid (Melting point: 127-129 °C), yield (62%); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.84 (s, 1H), 8.08 (d, J = 8.0 Hz, 1H), 8.03 (s, 1H), 7.90 (d, J = 9.0 Hz, 1H), 7.77-7.67 (m, 2H), 7.62-7.60 (m,1H), 7.51 (d, J = 8.8 Hz, 1H), 7.42-7.29 (m, 4H), 7.29-7.16 (m, 4H), 7.13-6.95 (m, 5H), 6.93-6.89 (m, 3H), 6.83 (d, J = 8.2 Hz, 1H), 6.35-6.30 (m, 3H). **^{13}C NMR** (100 MHz, DMSO- d_6) δ 180.0, 178.6, 157.4, 156.2, 153.1, 152.7, 151.9, 151.6, 143.6, 135.3, 132.9, 132.1, 131.6, 131.4, 130.8, 130.8, 130.7, 130.5, 130.4, 130.0, 129.8, 129.2, 129.2, 129.1, 128.1, 128.0, 127.7, 124.7, 124.7, 123.9, 122.9, 122.9, 120.3, 120.1, 118.5, 117.7, 117.2, 115.3. **ESI HRMS** m/z calcd. for $C_{44}H_{29}O_5$ $[M+H]^+$: 637.2015, Found 637.2011.



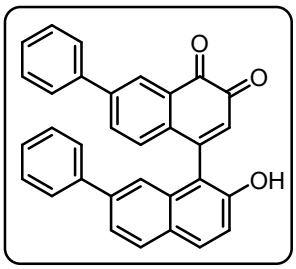
6',7-bis(2-chloro-4-methoxyphenyl)-2'-hydroxy-[1,1'-binaphthalene]-3,4-dione (10l): Brownish solid (Melting point: 266-269 °C), yield (67%); **^{1}H NMR** (400 MHz, DMSO- d_6) δ 9.98 (s, 1H), 8.15 (d, J = 7.9 Hz, 1H), 7.96 (d, J = 9.0 Hz, 1H), 7.87 (s, 1H), 7.83 (d, J = 8.7 Hz, 1H), 7.59 (d, J = 7.9 Hz, 1H), 7.41 (t, J = 8.6 Hz, 2H), 7.32 (d, J = 8.9 Hz, 1H), 7.19 (d, J = 8.6 Hz, 1H), 7.14 (d, J = 2.1 Hz, 1H), 7.03-6.99 (m, 2H), 6.91 (dd, J = 8.6, 2.0 Hz, 1H), 6.83 (s, 1H), 6.47 (s, 1H), 3.81 (s, 3H), 3.73 (s, 3H). **^{13}C NMR** (100 MHz, DMSO- d_6) δ 180.0, 178.6, 160.0, 159.3, 159.3, 152.1, 151.3, 144.6, 135.2, 133.4, 132.3, 132.1, 132.0, 131.7, 131.5, 130.9, 130.8, 130.0, 129.9, 129.4, 129.2, 128.6, 128.3, 127.5, 123.9, 118.6, 115.4, 115.2, 115.0, 114.0, 113.7, 55.7, 55.7. **ESI HRMS** m/z calcd. for $C_{34}H_{23}Cl_2O_5$ $[M+H]^+$: 581.0923, Found 581.0906.



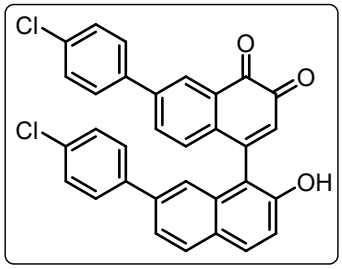
6',7-bis(5-fluoro-2-methoxyphenyl)-2'-hydroxy-[1,1'-binaphthalene]-3,4-dione (10m): Brownish solid (Melting point: 197-199 °C), yield (64%); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.98 (s, 1H), 8.13 (d, J = 7.9 Hz, 1H), 8.04-7.94 (m, 2H), 7.80 (d, J = 8.8 Hz, 1H), 7.68- 7.65 (m,1H), 7.57-7.55 (m,1H), 7.35 (d, J = 8.9 Hz, 1H), 7.24- 7.23 (m,1H), 7.20- 7.06 (m, 4H), 7.02 (d, J = 1.2 Hz, 1H), 6.96 - 6.93 (m,1H), 6.46 (s, 1H), 3.73 (s, 3H), 3.33 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 180.1, 178.8, 157.7, 157.5, 155.3, 155.2, 152.8, 152.7, 152.4, 152.4, 152.1, 151.8, 143.2, 135.1, 132.0, 131.6, 131.2, 131.1, 130.8, 130.7, 130.6, 129.6, 129.1, 128.7, 128.7, 128.5, 128.3, 127.6, 123.8, 118.5, 117.0, 116.8, 116.3, 116.2, 116.1, 116.0, 115.4, 114.6, 114.4, 113.6, 113.5, 113.2, 113.1, 56.1, 55.5. **^{19}F NMR** (377 MHz, DMSO d_6) δ -123.3, -123.8. **ESI HRMS** m/z calcd. for $C_{34}H_{23}F_2O_5$ $[M+H]^+$: 549.1514, Found 549.1503.



6',7-bis(3,4-dichlorophenyl)-2'-hydroxy-[1,1'-binaphthalene]-3,4-dione (10n): Brownish solid (Melting point: 258-260 °C), yield (68%); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.14 (s, 1H), 8.28 (s, 1H), 8.16 (d, J = 7.5 Hz, 1H), 8.09-7.97 (m, 2H), 7.93-7.86 (m, 2H), 7.76-7.66 (m, 3H), 7.66-7.56 (m, 2H), 7.39 (d, J = 8.8 Hz, 1H), 7.22 (d, J = 7.5 Hz, 1H), 6.94 (s, 1H), 6.44 (s, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 179.8, 178.5, 152.5, 150.8, 143.6, 140.5, 139.0, 136.0, 132.2, 132.1, 132.0, 131.8, 131.7, 131.6, 131.4, 131.4, 131.2, 131.0,129.9, 129.7, 128.9, 128.6, 128.4, 128.0, 126.9, 126.8, 126.3, 126.2, 125.6, 125.1, 119.0, 115.2. **ESI HRMS** m/z calcd. for $C_{32}H_{17}Cl_4O_3$ $[M+H]^+$: 588.9932, Found 588.9951.

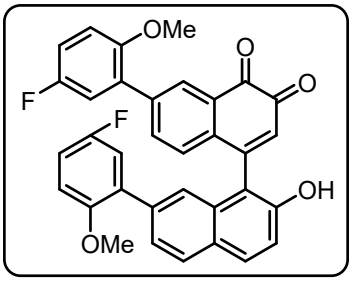


2'-hydroxy-6,7'-diphenyl-[1,1'-binaphthalene]-3,4-dione (10o): Brownish solid (Melting point: 176-178 °C), yield (65%);**^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.94 (s, 1H), 8.31 (s, 1H), 8.01- 7.98 (m, 3H), 7.84- 7.82 (m, 1H), 7.69 (m, 5H), 7.48 (m, 2H), 7.72- 7.64 (m, 5H), 6.45- 6.44 (m, 1H), 6.44 (m, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 179.9, 179.0, 152.2, 151.0, 141.8, 140.1, 138.8, 138.2, 134.5, 132.9, 132.8, 132.7, 130.5, 130.2, 129.3, 129.0, 129.0, 128.9, 128.6, 127.5, 127.3, 127.1, 126.7, 126.6, 122.6, 121.3, 118.5, 116.0. **ESI HRMS** m/z calcd. for $C_{32}H_{21}O_3$ $[M+H]^+$: 453.1491, Found 453.1491.



6,7'-bis(4-chlorophenyl)-2'-hydroxy-[1,1'-binaphthalene]-3,4-dione (10p): Brownish solid (Melting point: 240-242 °C), yield (67%); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.94 (s, 1H), 8.31 (s, 1H), 8.02- 7.98 (m, 3H), 7.84 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 8.2 Hz, 2H), 7.69- 7.84 (m,3H), 7.54 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.9 Hz, 1H), 6.82 (d, J = 8.0 Hz,

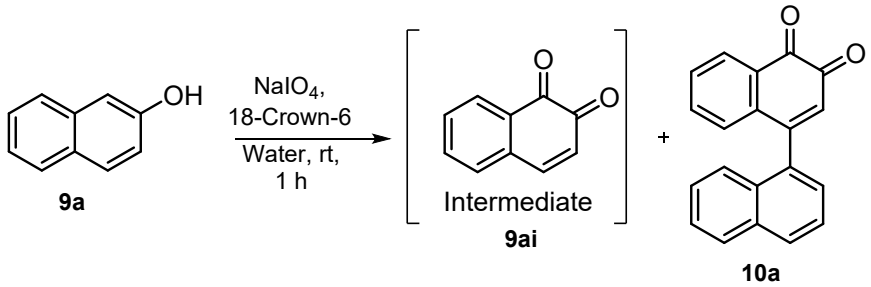
1H), 6.44 (s, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 179.8, 179.0, 152.2, 150.8, 140.4, 138.8, 137.4, 136.9, 134.8, 133.5, 132.8, 132.8, 132.7, 132.4, 130.6, 130.2, 129.2, 129.1, 129.0, 128.9, 128.8, 128.6, 127.2, 126.5, 122.3, 121.3, 118.6, 115.9. **ESI HRMS** m/z calcd. for $C_{32}H_{19}Cl_2O_3$ $[M+H]^+$: 521.0711, Found 521.0692.



6,7'-bis(5-fluoro-2-methoxyphenyl)-2'-hydroxy-[1,1'-binaphthalene]-3,4-dione (10q): Brownish solid (Melting point: 155-159 °C), yield (64%); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.98 (s, 1H), 8.24 (d, J = 1.9 Hz, 1H), 8.04-7.97 (m, 3H), 7.74- 7.72 (m, 1H), 7.53-7.51(m, 1H), 7.40 (m, 1H), 7.31- 7.27 (m, 2H), 7.23-7.09 (m, 4H), 6.88-6.86 (m,1H), 6.47 (s, 1H), 3.81 (s, 3H), 3.65 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 179.9, 179.0, 157.6, 157.4, 155.2, 155.1, 152.7, 152.7, 152.6, 152.6, 152.0, 151.1, 138.8, 135.7, 135.5, 134.5, 132.3, 131.9, 131.3, 131.2, 130.5, 130.1, 129.5, 129.1, 129.0, 128.3, 127.6, 126.9, 124.9, 124.4, 118.6, 117.2, 117.0, 116.7, 116.4, 115.9, 115.8, 115.7, 114.8, 114.5, 113.4, 113.1, 56.2, 55.9. **^{19}F NMR** (377 MHz, DMSO-d_6) δ -123.4, -123.7. **ESI HRMS** m/z calcd. for $C_{34}H_{23}F_2O_5$ $[M+H]^+$: 549.1514, Found 549.1495.

Section IV. Isolation and characterization of intermediate 9ai:

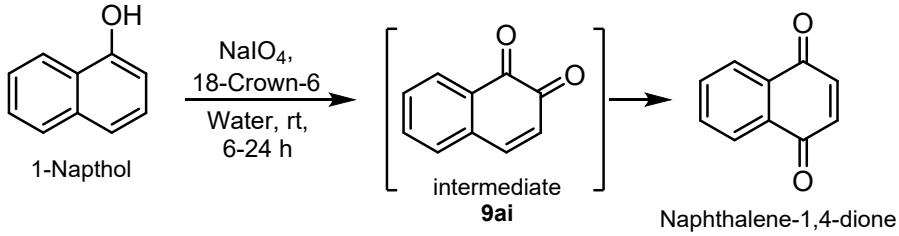
A round bottomed flask equipped with a magnetic stir bar was charged with 2-napthol (100 mg, 0.694 mmol, 1.0 equiv.) and 18-crown-6 (37 mg, 0.139 mmol, 0.2 equiv.) in water (10 mL). The reaction mixture was stirred at room temperature for 10 minutes followed by the addition of sodium periodate (297 mg, 1.388 mmol, 2 equiv.) and was allowed to stir at room temperature under open atmosphere for 1 hour. The progress of the reaction was monitored by TLC. As soon as the starting material disappeared, the reaction mixture was quenched with water and extracted with ethyl acetate (10 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure and subjected to column chromatography using Hexanes: Ethyl acetate (90:10, v/v) as eluent to afford intermediate **9ai** (60 mg, 55% yield) along with compound **10a** (24 mg, 12% yield).



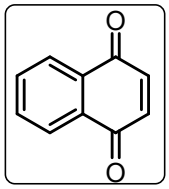
Naphthalene-1,2-dione intermediate (9ai): Black solid (Melting point: 191-193 °C), yield (55%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.1 Hz, 1H), 7.67- 7.63 (m, 1H), 7.53- 7.49 (m, 1H), 7.44 (d, J = 10.0 Hz, 1H), 7.36 (d, J = 7.5 Hz, 1H), 6.43 (d, J = 10.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.0, 179.0, 145.5, 136.0, 134.9, 131.7, 131.0, 130.4, 130.0, 128.1. **ESI HRMS** m/z calcd. for $C_{10}H_7O_2$ $[M+H]^+$: 159.0446, Found 159.0454.

Section-V. Reaction of 1-Napthol in presence of $NaIO_4$:

A round bottomed flask equipped with a magnetic stir bar was charged with 1-napthol (200 mg, 1.387 mmol, 1.0 equiv.) and 18-crown-6 (73.00 mg, 0.277 mmol, 0.2 equiv.) in water (15 mL).The reaction mixture was stirred at room temperature for 10 minutes followed by the addition of sodium periodate (890 mg, 4.16 mmol, 3 equiv.) and was allowed to stir at room temperature under open atmosphere for 12 hours. The progress of the reaction was monitored by TLC and after completion, the reaction mixture was quenched with water and extracted with ethyl acetate (15 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure and subjected to column chromatography using Hexanes: Ethyl acetate (95:05, v/v) as eluent to afford **Naphthalene-1,4-dione** product (180 mg, 84% yield).



Analytical Data of Naphthalene-1,4-dione:

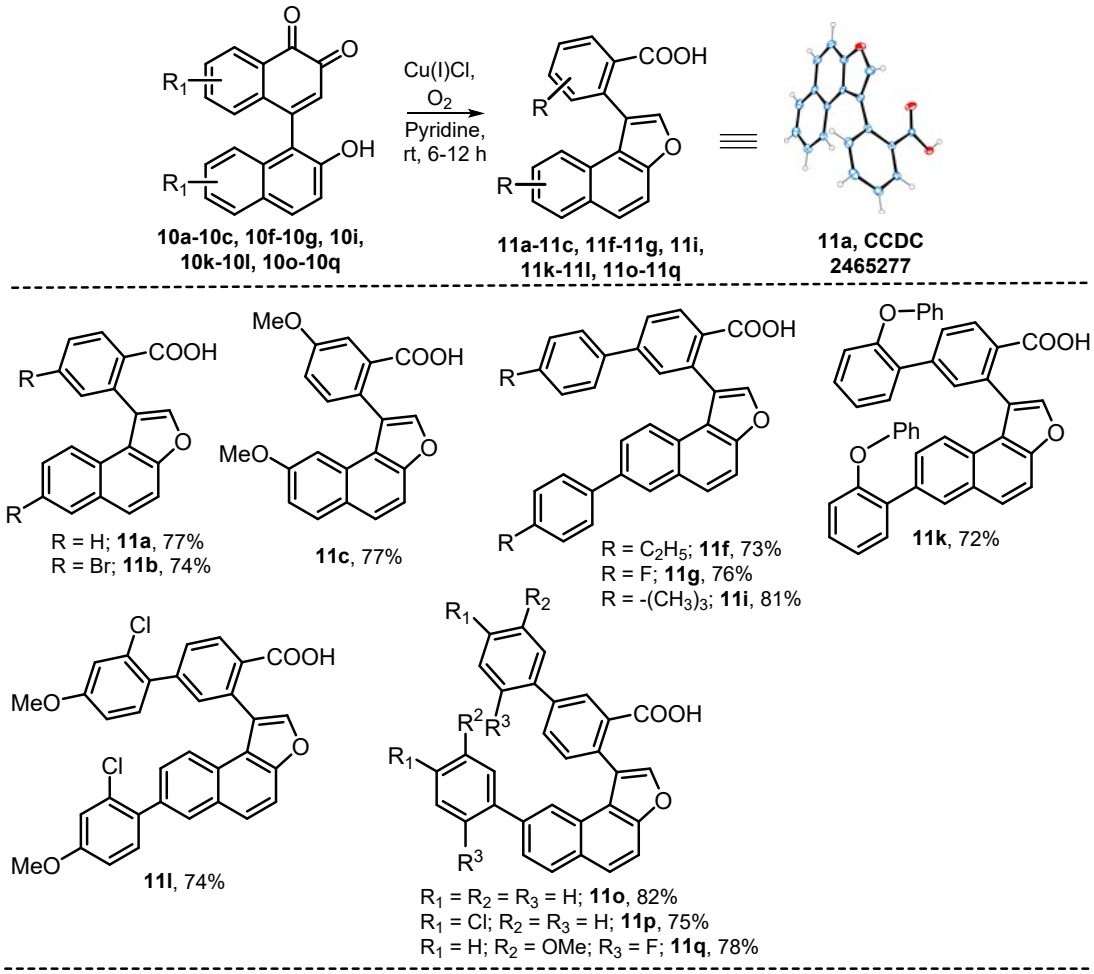


Naphthalene-1,4-dione: Greenish solid (Melting point: 125-127 °C), yield (84%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, J = 3.3 Hz, 1H), 8.05 (d, J = 3.3 Hz, 1H), 7.75 (d, J = 3.3 Hz, 1H), 7.73 (d, J = 3.3 Hz, 1H), 6.96 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.1, 138.8, 134.0, 132.0, 126.5. **ESI HRMS** m/z calcd. for $C_{10}H_7O_2$ $[M+H]^+$: 159.0446, Found 159.0438.

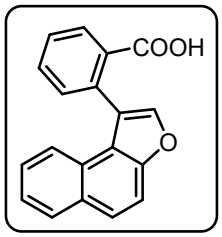
Section VI. General procedure for the synthesis of substituted naphtho[2,*b*]furans:

To a stirred solution of **10a** (500 mg, 1.665 mmol, 1.0 equiv.) in pyridine (15 mL) was added copper(I) chloride (165 mg, 1.665 mmol, 1.0 equiv.). The reaction mixture was stirred at room temperature under oxygen for 6 hours. The completion of reaction was monitored by TLC. After completion, the reaction mixture was quenched with a saturated aqueous solution of copper(II)sulfate and extracted with ethyl acetate (15 mL x 3). Combined organic layer was dried over anhydrous sodium sulphate and concentrated under reduced pressure to obtain the crude mixture which was further purified by column chromatography to afford the desired product **11a** (370mg, 77%).

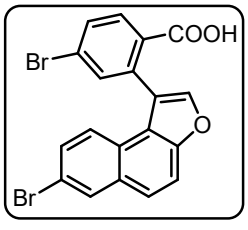
Similar procedure was followed for compounds **11b, 11c, 11f-11g, 11i, 11k-11m, 11o-11q** (72-82% yield).



Analytical data of compounds 11a-11c, 11f-11g, 11i, 11k-11l, 11o-11q:

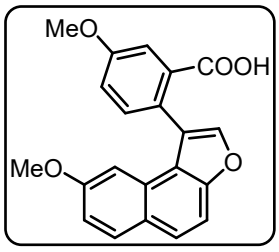


4-(2-hydroxynaphthalen-1-yl)-1H-isochromen-1-one (11a): White crystalline solid (Melting Point 170 °C), yield (77%); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.60 (s, 1H), 8.10-7.95 (m, 3H), 7.89-7.80 (m, 2H), 7.76-7.61 (m, 2H), 7.54 (d, J = 7.4 Hz, 1H), 7.48-7.39 m, 2H), 7.35- 7.31 (m,1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 167.8, 151.9, 141.8, 132.8, 132.5, 132.2, 131.9, 130.3, 130.3, 128.9, 128.7, 127.9, 126.1, 125.5, 124.3, 123.2, 122.3, 121.6, 112.7. **ESI HRMS** m/z calcd. for $C_{19}H_{11}O_3$ [M-H]$^+$: 287.0708, Found 287.0707.

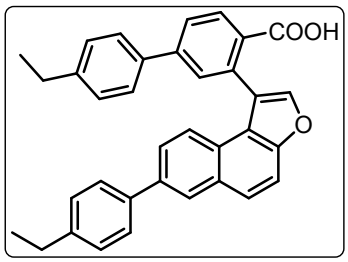


6-bromo-4-(6-bromo-2-hydroxynaphthalen-1-yl)-1H-isochromen-1-one (11b): White solid (Melting point: 175-178 °C), yield (74%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06

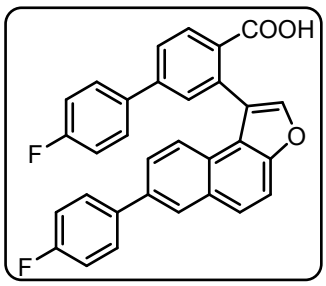
(d, *J* = 2.0 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.72- 7.70 (m, 1H), 7.69- 7.62 (m, 3H), 7.61 (s, 1H), 7.37- 7.35 (m, 1H), 7.29 (d, *J* = 8.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 169.0, 152.7, 141.8, 136.1, 135.6, 133.1, 132.1, 132.0, 131.1, 129.6, 129.0, 127.9, 126.7, 125.1, 124.4, 121.8, 121.8, 118.2, 113.9. **ESI HRMS** m/z calcd. for $C_{19}H_{11}Br_2O_3$ $[M+H]^+$: 444.9075, Found 442.9081.



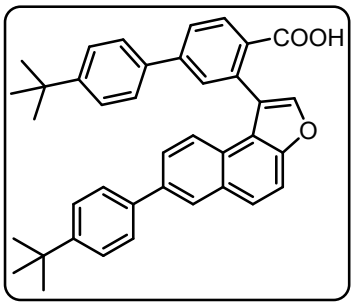
4-(2-hydroxy-7-methoxynaphthalen-1-yl)-7-methoxy-1H-isochromen-1-one (11c): White solid (Melting point: 188-190 °C), yield (77%); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.76 (d, *J* = 8.9 Hz, 1H), 7.65-7.60 (m, 2H), 7.57- 7.50 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.18- 7.15 (m, 1H), 7.00- 6.98 (m, 1H), 6.82 (d, *J* = 2.5 Hz, 1H), 3.88 (s, 3H), 3.47 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 171.0, 159.5, 157.8, 153.2, 140.8, 134.2, 131.5, 130.3, 129.6, 126.5, 125.7, 125.4, 122.5, 121.2, 119.0, 116.2, 115.8, 110.3, 102.3, 55.8, 54.9. **ESI HRMS** m/z calcd. for $C_{21}H_{15}O_5$ $[M-H]^+$: 347.0919, Found 347.0920.



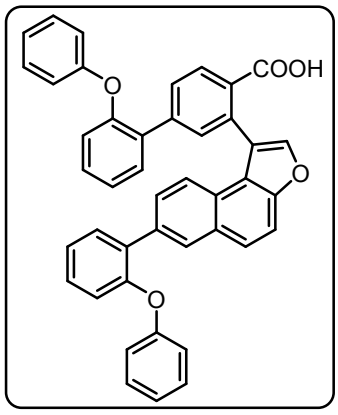
4'-ethyl-3-(7-(4-ethylphenyl)naphtho[2,1-b]furan-1-yl)-[1,1'-biphenyl]-4-carboxylic acid (11f): White solid (Melting point: 172-174 °C), yield (73%); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.27 (d, *J* = 8.2 Hz, 1H), 8.10 (d, *J* = 1.7 Hz, 1H), 7.83- 7.78 (m, 3H), 7.75 – 7.69 (m, 2H), 7.67 – 7.50 (m, 6H), 7.30- 7.27 (m, 4H), 2.72- 2.66 (m, 4H), 1.29 – 1.24 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 169.3, 152.7, 145.4, 144.9, 143.3, 141.3, 138.5, 137.0, 136.5, 134.9, 132.2, 131.0, 131.0, 128.6, 128.4, 128.3, 127.3, 127.2, 127.2, 126.6, 126.6, 126.0, 125.7, 123.2, 123.1, 121.8, 113.0, 28.6, 28.5, 15.6, 15.5. **ESI HRMS** m/z calcd. for $C_{35}H_{29}O_3$$[M+H]^+$: 497.2117, Found 497.2112.



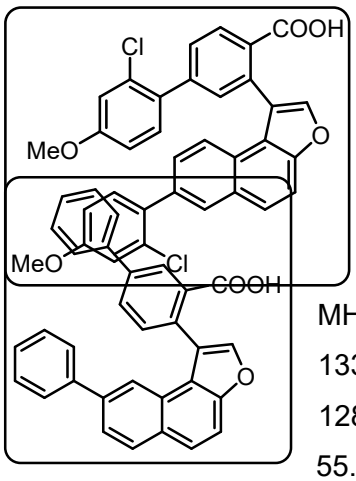
4'-fluoro-3-(7-fluoronaphtho[2,1-b]furan-1-yl)-[1,1'-biphenyl]-4-carboxylic acid (11g): White solid (Melting point: 190-192 °C), yield (76%); **^{1}H NMR** (400 MHz, DMSO-d_6) *δ* 8.33 (s, 1H), 8.19- 8.15 (m, 2H), 7.98- 7.94 (m, 2H), 7.90- 7.79 (m, 6H), 7.71- 7.62 (m, 2H), 7.34- 7.28 (m, 4H). **^{13}C NMR** (100 MHz, DMSO-d_6) *δ* 167.9, 164.1, 163.5, 161.7, 161.1, 152.5, 142.8, 142.7, 136.8, 136.8, 135.4, 135.4, 135.3, 134.1, 131.8, 131.5, 131.5, 131.2, 130.7, 129.7, 129.7, 129.3, 129.2, 127.5, 127.1, 126.8, 126.4, 125.6, 123.7, 123.5, 122.0, 116.6, 116.3, 116.1, 113.7. **^{19}F NMR** (377 MHz, DMSO-d_6) *δ* -113.9, -115.6. **ESI HRMS** m/z calcd. for $C_{31}H_{19}F_2O_3$ $[M+H]^+$: 477.1302, Found 477.1290.



4'-(tert-butyl)-3-(7-(4-(tert-butyl)phenyl)naphtho[2,1-b]furan-1-yl)-[1,1'-biphenyl]-4-carboxylic acid (11i): White solid (Melting point: 193-196 °C), yield (81%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.1 Hz, 1H), 8.10 (d, J = 1.5 Hz, 1H), 7.80- 7.76 (m, 3H), 7.71 (d, J = 9.0 Hz, 1H), 7.63 (s, 1H), 7.62-7.58 (m, 5H), 7.55- 7.53 (m, 1H), 7.47 (m, 4H), 1.36 (s, 9H), 1.34 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.28, 152.78, 151.89, 150.25, 145.34, 141.39, 138.29, 136.92, 136.33, 135.04, 132.31, 131.14, 128.48, 127.42, 127.08, 127.02, 126.73, 126.14, 125.90, 125.81, 123.37, 123.17, 121.89, 113.11, 34.79, 34.67, 31.51, 31.41. **ESI HRMS** m/z calcd. for $C_{39}H_{37}O_3$ $[M+H]^+$: 553.2743, Found 553.2747.



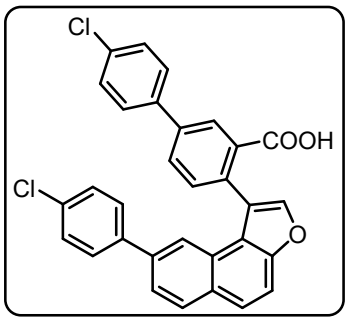
4-(2-hydroxy-6-(2-phenoxyphenyl)naphthalen-1-yl)-6-(2-phenoxyphenyl)-1H-isochromen-1-one (11k): White solid (Melting point: 188-192 °C), yield (72%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.2 Hz, 1H), 8.06 (s, 1H), 7.77-7.67 (m, 3H), 7.64 (d, J = 9.0 Hz, 1H), 7.53 (s, 1H), 7.50-7.43 (m, 4H), 7.37-7.28 (m, 2H), 7.24-7.16 (m, 6H), 7.05 – 6.90 (m, 6H), 6.83 (d, J = 7.7 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.3, 157.8, 157.5, 154.0, 153.7, 152.8, 142.4, 141.4, 134.3, 133.8, 133.6, 133.5, 132.1, 131.7, 131.5, 131.3, 130.7, 129.9, 129.8, 129.7, 129.3, 129.2, 128.7, 128.7, 127.8, 127.5, 126.1, 124.4, 124.1, 123.0, 123.0, 122.9, 122.7, 121.7, 120.6, 120.0, 118.5, 118.1, 112.8. **ESI HRMS** m/z calcd. for $C_{43}H_{29}O_5$ $[M+H]^+$: 625.2015, Found 625.2008.



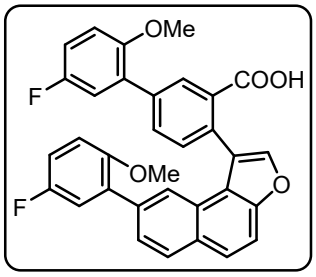
2'-chloro-3-(7-(2-chloro-4-methoxyphenyl)naphtho[2,1-b]furan-1-yl)-4'-methoxy-[1,1'-biphenyl]-4-carboxylic acid (11l): White solid (Melting point: 220-224 °C), yield (74%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.9 Hz, 1H), 7.92 (d, J = 1.6 Hz, 1H), 7.76- 7.69 (m, 2H), 7.66- 7.62 (m, 4H), 7.39- 7.37 (m, 1H), 7.31- 7.28 (m, 2H), 7.03- 7.00 (m, 2H), 6.88- 6.84 (m, 2H), 3.84 (s, 3H), 3.82 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 160.1, 159.5, 153.0, 143.8, 141.5, 135.2, 134.2, 134.0, 133.3, 133.1, 133.0, 132.3, 131.9, 131.4, 131.3, 130.6, 129.7, 129.5, 128.9, 128.1, 127.4, 126.0, 122.8, 122.7, 121.8, 115.5, 115.3, 113.4, 113.2, 113.1, 55.8, 55.7. **ESI HRMS** m/z calcd. for $C_{33}H_{23}Cl_2O_5$ $[M+H]^+$: 569.0923, Found 569.0930.

4-(8-phenylnaphtho[2,1-b]furan-1-yl)-[1,1'-biphenyl]-3-carboxylic acid (11o): White solid (Melting point: 225-228 °C), yield (82%); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.39 (d, J = 1.8 Hz, 1H), 8.17 (s, 1H), 8.11 (d, J = 9.2 Hz, 1H), 8.04 – 7.99 (m, 1H), 7.91 – 7.86 (m, 2H), 7.85 – 7.81 (m, 2H), 7.79 – 7.75 (m, 2H), 7.66 (d, J = 7.9 Hz, 1H), 7.59- 7.55 (m, 2H), 7.52 – 7.45 (m, 3H), 7.36-7.26 (m, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 167.9, 152.3, 141.8, 140.6, 140.0, 138.9, 137.5, 133.4, 133.1, 131.8, 130.1, 129.7,

129.6, 129.3, 129.0, 128.3, 128.2, 128.1, 127.7, 126.9, 126.7, 125.3, 123.3, 122.9, 121.8, 120.1, 112.9. **ESI HRMS** m/z calcd. for $C_{31}H_{20}O_3$ $[M+H]^+$: 441.1491, Found 441.1491.



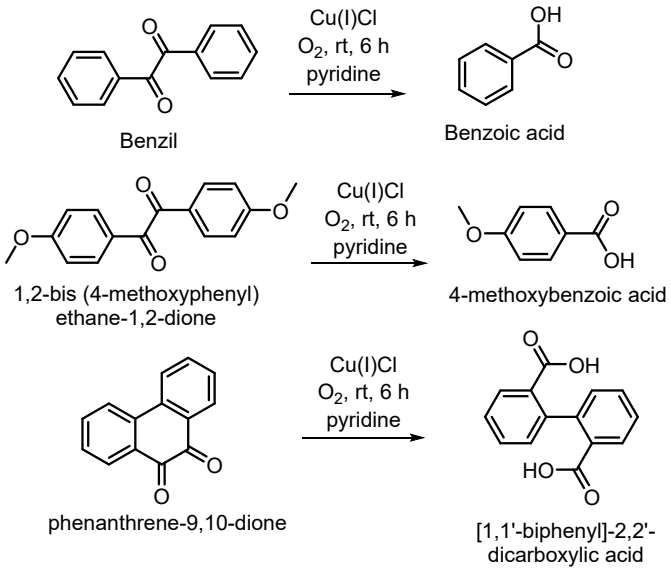
7-(4-chlorophenyl)-4-(7-(4-chlorophenyl)-2-hydroxynaphthalen-1-yl)-1H-isochromen-1-one (11p): White solid (Melting point: 252-254 °C), yield (75%); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.86 (s, 1H), 8.37 (d, J = 1.9 Hz, 1H), 8.20-8.10 (m, 2H), 8.05 (dd, J = 7.9, 2.0 Hz, 1H), 7.94-7.85 (m, 4H), 7.78-7.72 (m, 2H), 7.69 (d, J = 7.9 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 167.9, 152.3, 142.0, 139.2, 138.9, 137.6, 136.3, 133.5, 133.2, 133.1, 132.6, 131.9, 130.0, 129.8, 129.7, 129.2, 129.2, 129.0, 128.7, 128.4, 128.0, 125.3, 123.2, 122.8, 121.7, 120.1, 113.1. **ESI HRMS** m/z calcd. for $C_{31}H_{19}Cl_2O_3$ $[M+H]^+$: 509.0711, Found 509.0711.



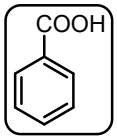
5'-fluoro-4-(8-(5-fluoro-2-methoxyphenyl)naphtho[2,1-b]furan-1-yl)-2'-methoxy-[1,1'-biphenyl]-3-carboxylic acid (11q): White solid (Melting point: 230-234 °C), yield (78%); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.71 (s, 1H), 8.16 (d, J = 1.9 Hz, 1H), 8.12 (s, 1H), 8.05 (d, J = 8.5 Hz, 1H), 7.91 – 7.81 (m, 3H), 7.78 (d, J = 1.7 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.29 – 7.16 (m, 3H), 7.16 – 7.09 (m, 2H), 7.08 – 7.00 (m, 1H), 3.76 (s, 3H), 3.58 (s, 3H).**^{13}C NMR** (100 MHz, DMSO-d_6) δ 167.8, 157.7, 155.3, 152.6, 152.6, 152.6, 152.1, 142.0, 137.2, 134.5, 132.5, 132.4, 132.2, 131.8, 130.9, 130.8, 130.7, 129.7, 129.6, 129.4, 128.4, 127.6, 125.8, 125.2, 123.1, 123.0, 121.8, 116.8, 116.6, 115.5, 115.3, 114.8, 114.6, 113.5, 113.4, 113.2, 113.1, 113.0, 56.2, 55.9. **^{19}F NMR** (377 MHz, DMSO-d_6) δ -123.6, -123.8. **ESI HRMS** m/z calcd. for $C_{33}H_{21}F_2O_5$ $[M-H]^+$: 535.1357, Found 535.1382.

Section VII. Reactions of acyclic diketones and phenanthrene-9,10-dione:

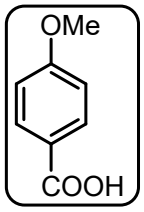
A similar procedure as reported in the **Section VI** was followed in these cases also and corresponding carboxylic acids were encountered as shown below-



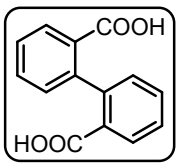
Analytical data:



Benzoic acid White solid (Melting point: 122-124 °C), yield (80%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.37 (s, 1H), 8.18 – 8.13 (m, 2H), 7.67– 7.60 (m, 1H), 7.51- 7.47 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 134.0, 130.4, 129.5, 128.6. **ESI HRMS** m/z calcd. for $C_7H_5O_2$ $[M-H]^+$: 121.0290, Found 121.0361.



4-methoxybenzoic acid White solid (Melting point: 182-185 °C), yield (81%); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.63 (s, 1H), 7.92 – 7.86 (m, 2H), 7.00 (d, J = 8.9 Hz, 2H), 3.81 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6)) δ 167.1, 162.9, 131.44, 123.1, 113.9, 55.5. **ESI HRMS** m/z calcd. for $C_8H_7O_3$ $[M-H]^+$: 151.0395, Found 151.0461.

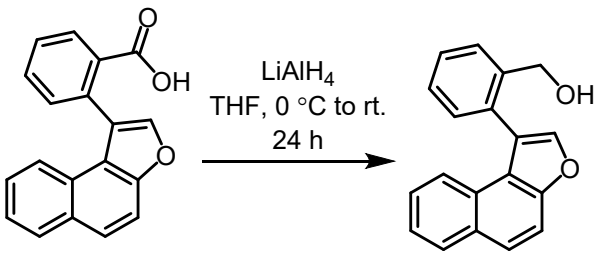


[1,1'-biphenyl]-2,2'-dicarboxylic acid White solid (Melting point: 232-234 °C), yield (74%); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.44 (s, 1H), 7.89 (dd, J = 7.8, 1.2 Hz, 1H), 7.56-7.52 (m, 1H), 7.41- 7.45 (m, 1H), 7.16 (m,1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 167.9, 143.1, 131.1, 130.4, 130.4, 129.5, 127.0. **ESI HRMS** m/z calcd. for $C_{14}H_{09}O_4$ $[M-H]^+$: 241.0501, Found 241.0565.

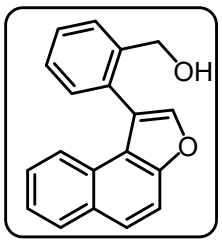
Section VIII. Post-synthetic transformations of biaryl acid 11a:

a) $LiAlH_4$ mediated reduction:

A two necked round bottomed flask, equipped with a magnetic stir bar was charged with $LiAlH_4$ (18 mg, 0.48 mmol, 2.0 equiv.) taken in dry THF (5 mL) under nitrogen atmosphere and cooled to 0 ℃. Compound **11a** (70 mg, 0.24 mmol, 1.0 equiv.) dissolved in dry THF (5 mL) was added drop wise to the above solution. After addition, the reaction mixture was allowed to stir at room temperature for 24 h. The progress of the reaction was monitored by TLC and after completion, the reaction mixture was quenched with the dropwise addition of water (5 mL) and 15% NaOH (10 mL). Extraction was done with ethyl acetate (10 mL x 3) and the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Column chromatography using Hexanes: Ethyl acetate (95:5, v/v) as eluent afforded the required alcohol, **12** (61 mg, 91% yield).



11a **12, 91%**

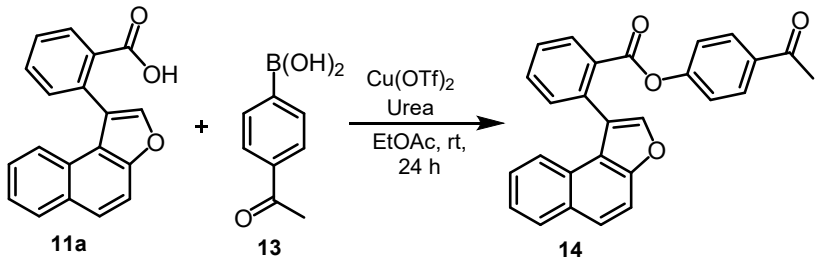


(2-(naphtho[2,1-b]furan-1-yl)phenyl)methanol (12):

Colourless oil, yield (75%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.1 Hz, 1H), 7.80 – 7.77 (m,1H), 7.74 – 7.69 (m, 3H), 7.57 – 7.50 (m, 2H), 7.47 – 7.40 (m, 3H), 7.32 – 7.28 (m,1H), 4.57 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.9, 141.8, 140.4, 131.2, 131.2, 130.8, 129.0, 128.9, 128.3, 127.9, 127.8, 126.5, 126.1, 124.5, 122.5, 121.5, 121.2, 112.7, 63.2. **ESI HRMS** m/z calcd. for $C_{19}H_{15}O_2$ $[M+H]^+$: 275.1072, Found 275.1082.

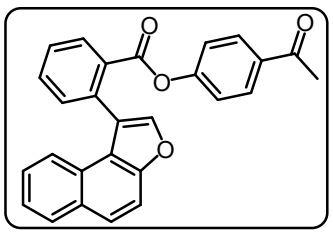
b) Esterification using $Cu(OTf)_2$:

A round bottomed flask equipped with a magnetic stir bar was charged with **11a** (80 mg, 0.27 mmol, 1.0 equiv.), 4-Acetyl phenyl boronic acid (**13**, 110 mg, 0.67 mmol, 2.5 equiv.), $Cu(OTf)_2$ (49 mg, 0.35 mmol, 0.5 equiv.), urea (17 mg, 0.2 mmol, 1.1 equiv.), and ethyl acetate (8 mL). The mixture was allowed to stir under air at 60 °C for 24 h. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was quenched with water (20 mL) and extracted with ethyl acetate (10 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure and subjected to column chromatography using Hexanes: Ethyl acetate (95:5, v/v) as eluent to afford ester **14** (93 mg, 85% yield).



11a 13 14

4-acetylphenyl 2-(3H-cyclopenta[a]naphthalen-1-yl)benzoate (14):

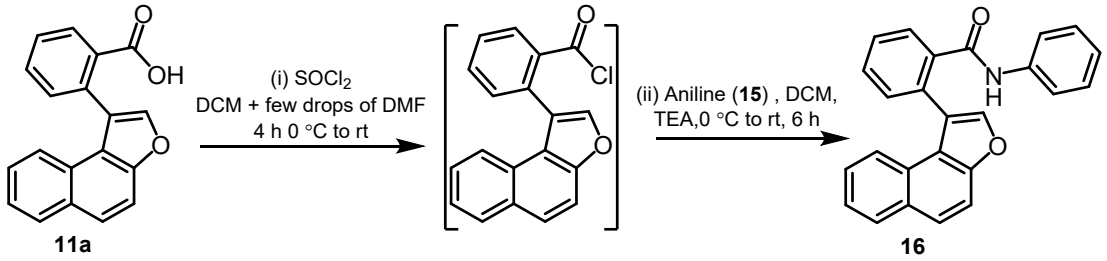


Colourless oil, yield (73%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (d, J = 7.6 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.79 – 7.61 (m, 9H), 7.45 – 7.35 (m, 2H), 6.57 (d, J = 8.6 Hz, 2H), 2.46 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.8, 165.0, 154.1, 152.7, 141.2, 134.4, 134.3, 133.1, 132.6, 131.4, 130.8, 130.6, 129.7, 129.1, 128.7, 128.3, 126.3, 126.0, 124.5, 123.2, 122.7, 121.7, 121.3, 112.7, 26.5. **ESI HRMS** m/z calcd. for $C_{27}H_{19}O_4$ $[M+H]^+$: 407.1283, Found 407.1274.

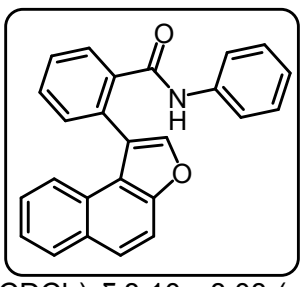
c) Amidation for the Synthesis of aryl amide:

Synthesis of acyl chloride: To an ice-cold solution of the **11a** (100 mg, 0.34 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (10 mL) was added Thionyl chloride (42 mg, 0.45 mmol, 1.3 equiv.) followed by a catalytic amount of DMF under continuous stirring. The reaction temperature was increased to room temperature and the stirring was continued for further 4 h. The solvent was concentrated under vacuum to afford the corresponding acyl chloride which was directly used for next step, without further purification.

Synthesis of amide: To a round-bottom flask containing 10 mL of dry CH_2Cl_2, aniline (**15**, 42 mg, 0.45 mmol, 1.3 equiv.) and triethylamine (100 µL, 0.69 mmol, 2.0 equiv.), was dropwise added acyl chloride at 0 °C and the resulting mixture was stirred for 6 h at room temperature. After reaction completion, the reaction mixture was quenched with saturated NH_4Cl (10 mL), and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic was dried over anhydrous Na_2SO4, and concentrated under reduced pressure. Column chromatography using Hexanes: Ethyl acetate (95:5, v/v) as eluent resulted in the isolation of amide **16** (111 mg, 88% yield).



11a 16



2-(naphtho[2,1-b]furan-1-yl)-N-phenylbenzamide:

Off white solid (Melting Point 198-200 °C), yield (85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 - 8.08 (m, 1H), 7.97 (d, J = 8.1 Hz, 1H), 7.83 – 7.80 (m, 2H), 7.73 – 7.55 (m, 6H), 7.50 –

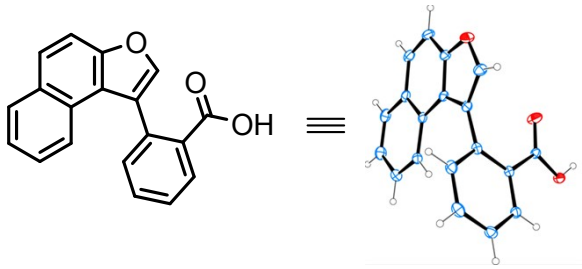
7.36 (m, 2H), 7.06 – 7.04 (m, 2H), 6.93 – 6.90 (m, 1H), 6.74 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 166.2, 153.2, 142.3, 137.4, 136.9, 132.1, 131.0, 131.0, 130.0, 129.9, 129.4, 129.2, 128.8, 127.9, 127.1, 126.9, 125.0, 124.4, 122.3, 121.6, 120.9, 119.7, 112.8. **ESI HRMS** m/z calcd. for $C_{25}H_{18}NO_2$ $[M+H]^+$: 364.1338, Found 364.1325.

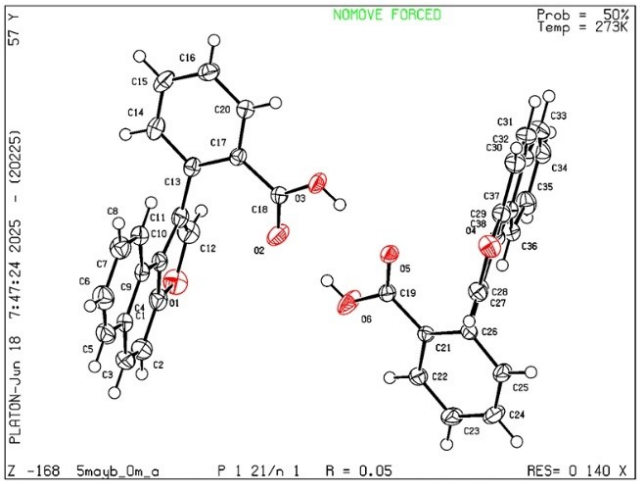
Section IX. Single crystal X-ray data:

Sample preparation for crystallization of 11a:

15 mg of **11a** was dissolved in 1 mL of ethyl acetate, after that 9 mL of hexane was added dropwise into the above solution and was left for slow evaporation for about 60 h which led to the formation of block shaped crystals which were used for data collection. The crystals were mounted on a glass tip for diffraction experiments. Intensity data were collected on a Bruker Apex II CCD diffractometer with Mo K*α* radiation (0.71073 Å) below room temperature**.**

ORTEP representation of **11a** (**CCDC No. 2465277**): Thermal ellipsoids are drawn at 50% probability in this ORTEP representation:





Crystal data and structure refinement for 11a:

Compound	**11a**
Identification code	5mayb_0m_a
Empirical formula	$C_{19}H_{12}O_3$

Formula weight	288.29
Temperature/K	273.15
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	16.8830(6)
b/Å	7.0571(2)
c/Å	24.4179(8)
α/°	90
β/°	94.6180(10)
γ/°	90
Volume/Å^3	2899.83(16)
Z	8
ρ_{calc}g/cm^3	1.321
μ/mm^{-1}	0.089
F(000)	1200.0
Crystal size/mm^3	0.13 × 0.12 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.396 to 56.576
Index ranges	-22 ≤ h ≤ 22, -9 ≤ k ≤ 9, -32 ≤ l ≤ 32
Reflections collected	43732
Independent reflections	7200 [R_{int} = 0.0555, R_{sigma} = 0.0401]
Data/restraints/parameters	7200/0/399
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0483, wR_2 = 0.1064
Final R indexes [all data]	R_1 = 0.0731, wR_2 = 0.1228
Largest diff. peak/hole / e Å^{-3}	0.28/-0.29

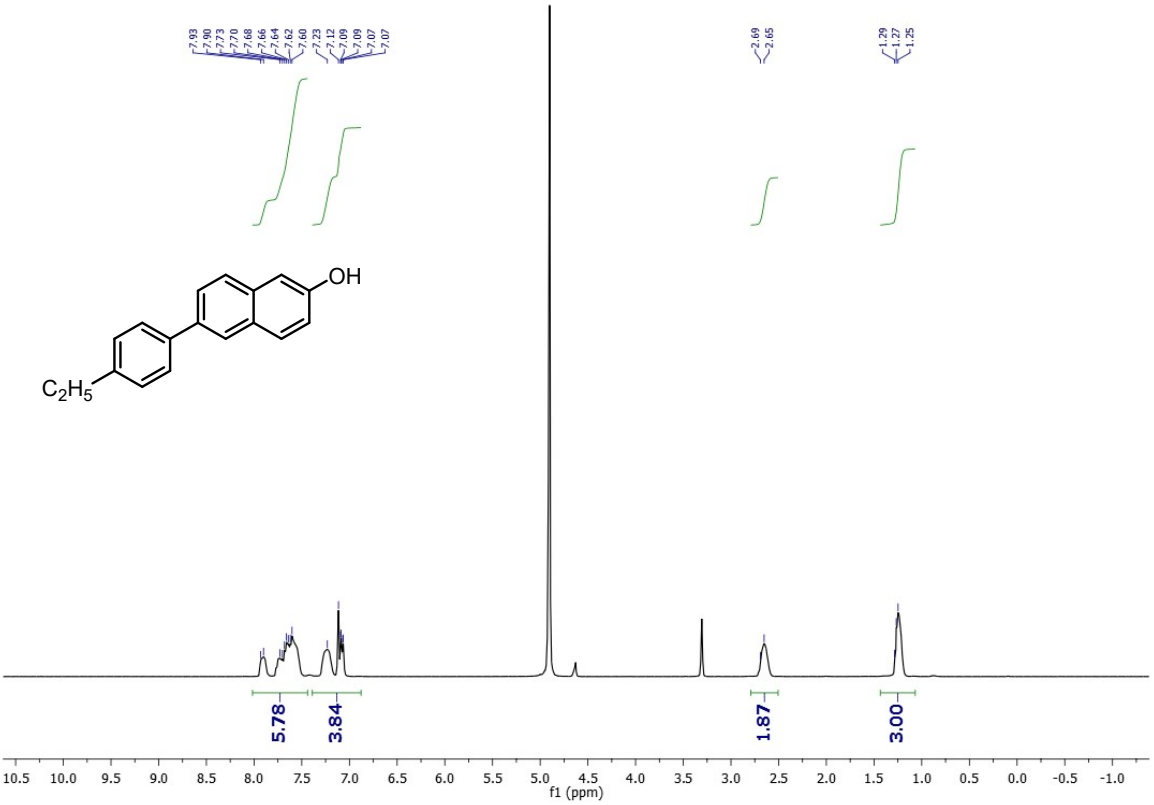
Section X. References:

1. A. Kamal, M. K. Reddy, M. J. Ramaiah, Y. V. V. Srikanth, Rajender, V. S. Reddy, G. B. Kumar, S. N. C. V. L. Pushpavalli, I. Bag, A. Juvekar, S. Sen, S. M. Zingde, and M. Pal-Bhadra, *Chem. Med. Chem.*, 2011, **6**, 1665-1679.
2. (a) C. A. Sojdak, and M. C. Kozlowski, *Org. lett.*, 2022, **24**, 8326-8330. (b) Y. H. Park, H. R. Ahn,

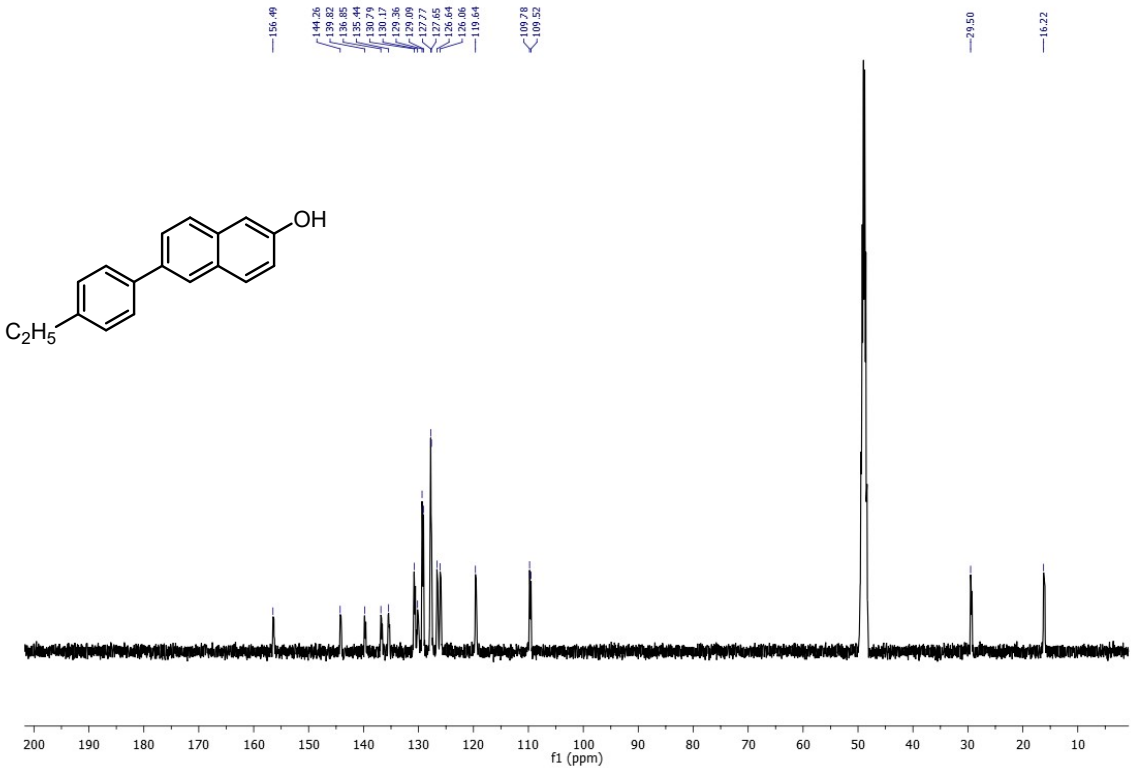
B. Canturk, S. I. Jeon, S. Lee, H. Kang, and J. Ham, *Org. Lett.,* 2008, **10**, 1215-1218. (c) W. Zhang, T. Li, Q. Wang, and W. Zhao, *Adv. Synth. Catal.,* 2019, **361**, 4914-4918. (d) S. Narute, R. Parnes, F. D. Toste, and D. Pappo, *J. Am. Chem. Soc.,* 2016, **138**, 16553-16560. (e) C. Xu, H. Zheng, B. Hu, X. Liu, L. Lin, and X. Feng, *Chem. Commun.,* 2017, **53**, 9741-9744. (f) F. Fan, J. Tang, M. Luo, and X. Zeng, *J. Org. Chem.*, 2018, **83**, 13549-13559. (g) T. Horibe, K. Nakagawa, T. Hazeyama, K. Takeda, and K. Ishihara, *Chem. Commun.*, 2019, **55**, 13677-13680.

Section XI. NMR Spectra:

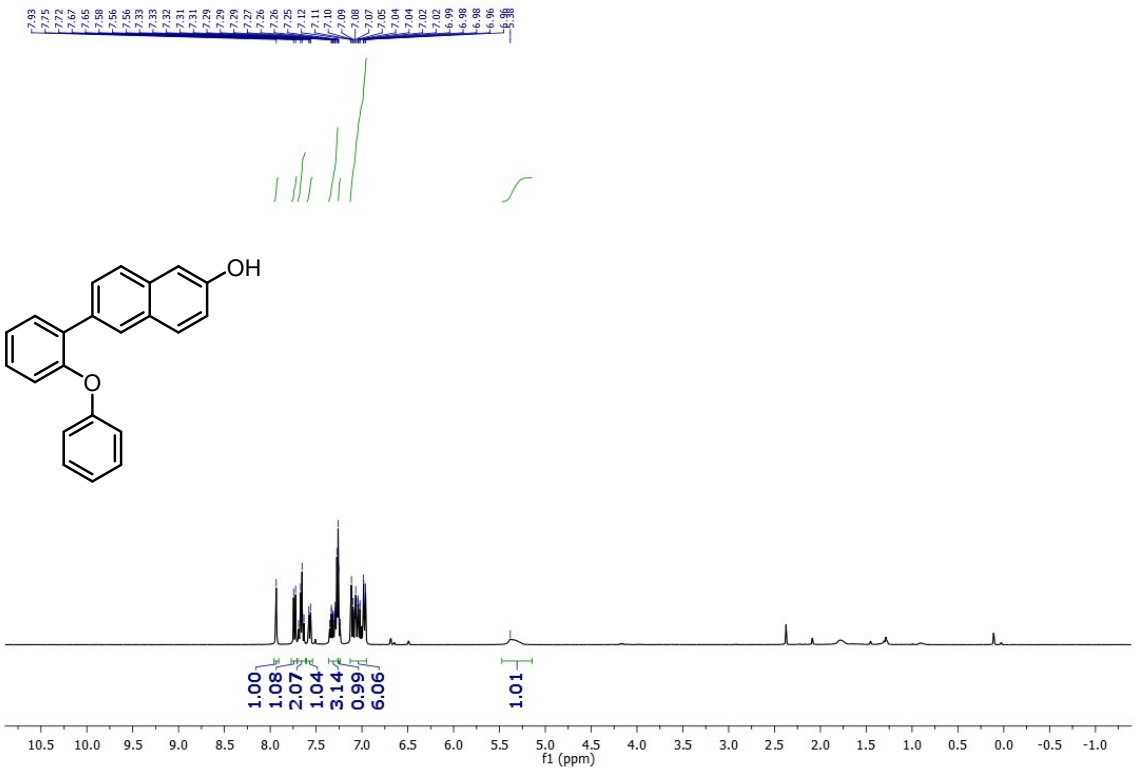
^{1}H NMR Spectrum of **9f** (400 MHz, CD_3OD)



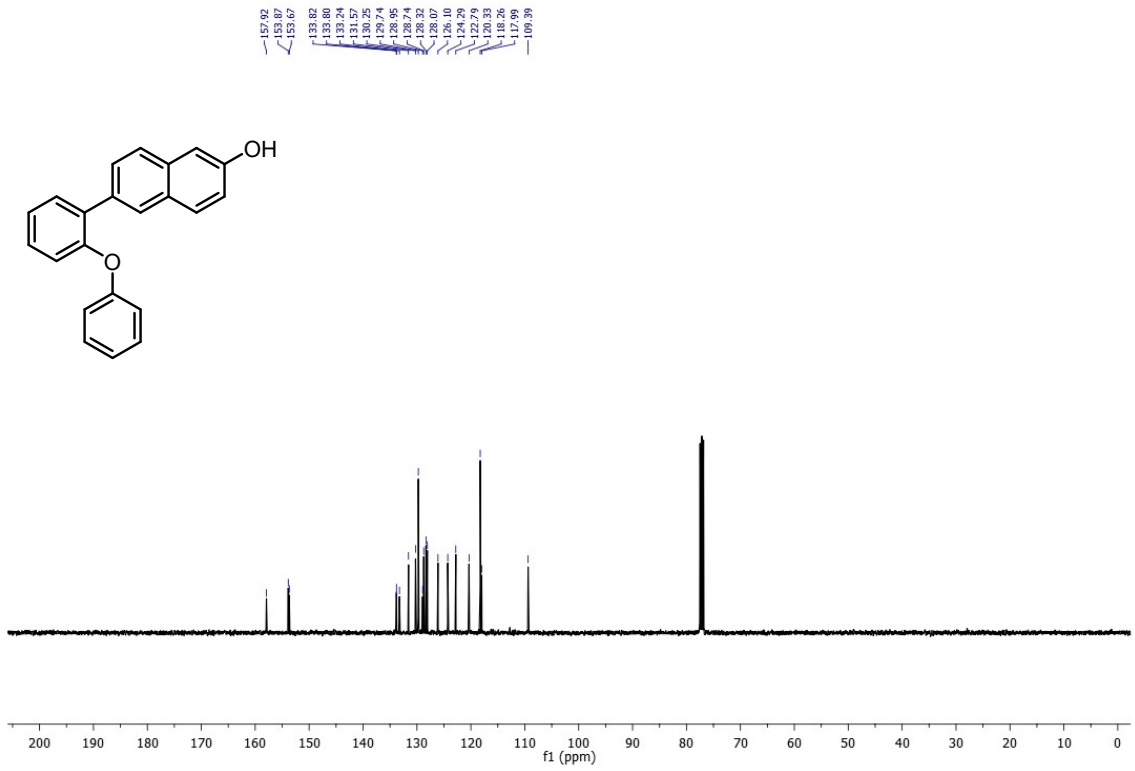
^{13}C NMR Spectrum of **9f** (100 MHz, CD_3OD)



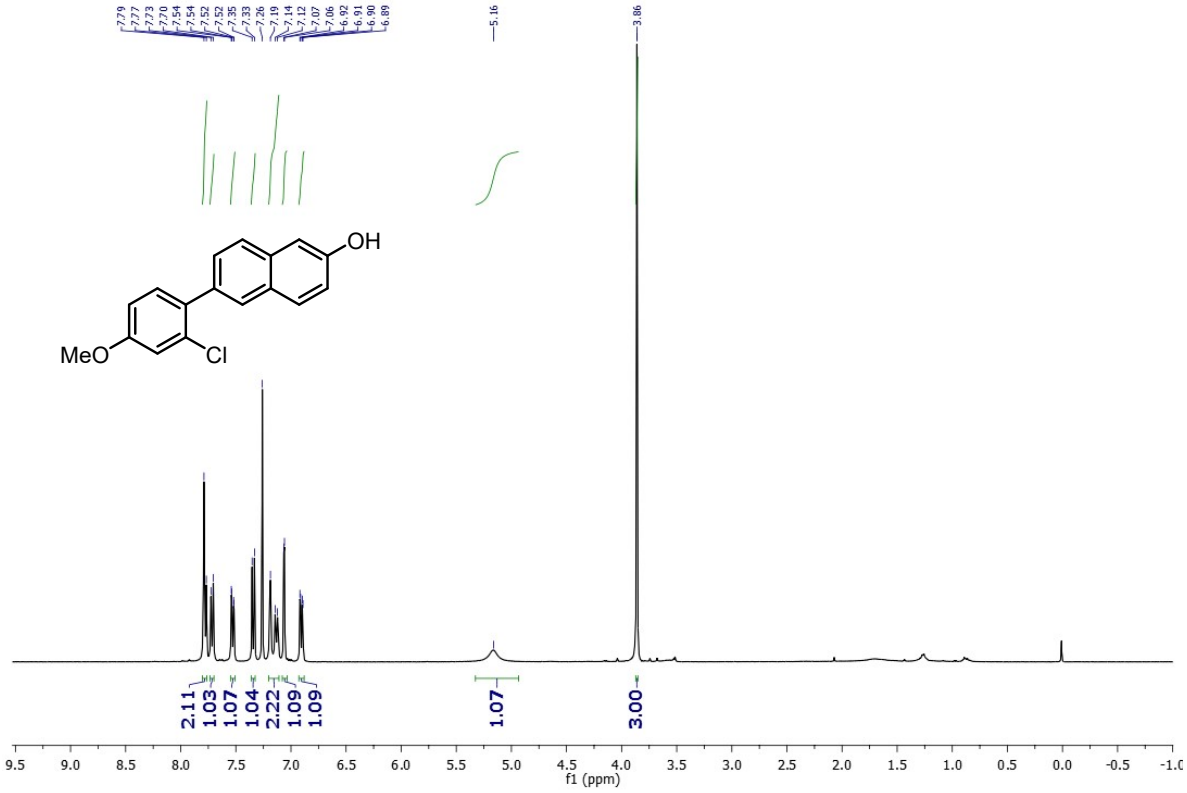
^{1}H NMR Spectrum of **9k** (400 MHz, $CDCl_3$)



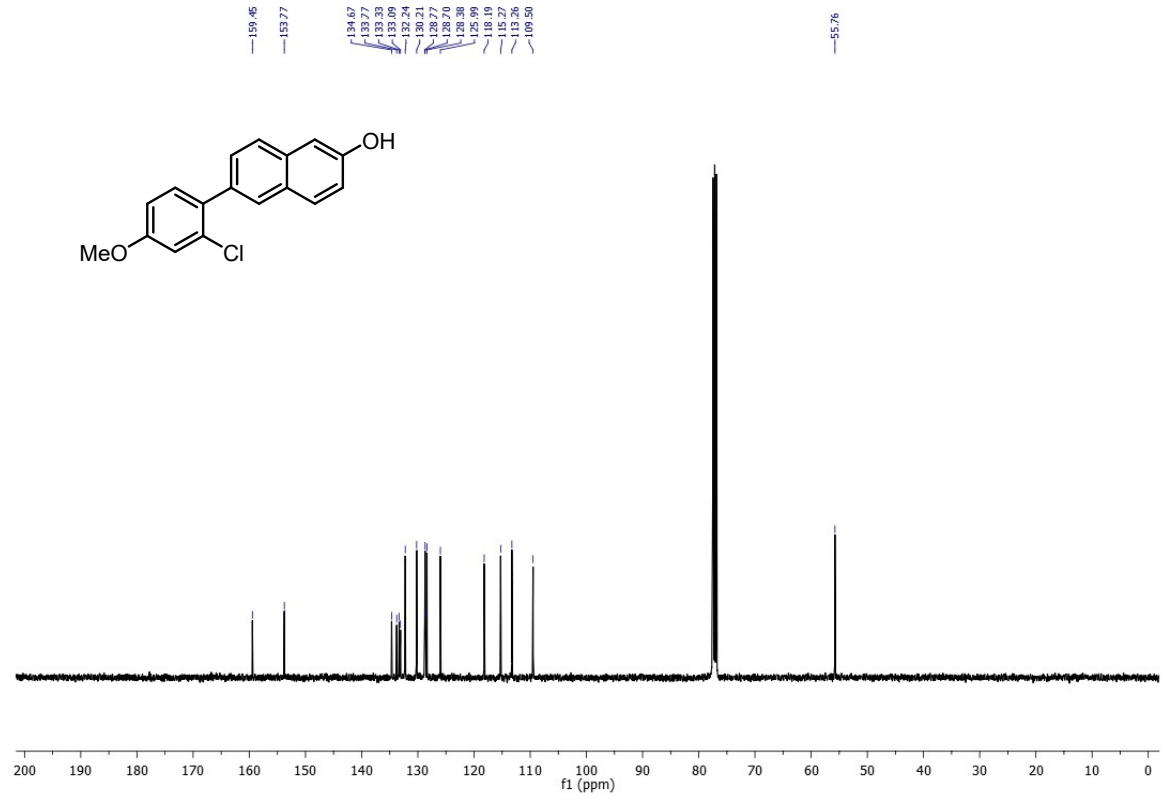
^{13}C NMR Spectrum of **9k** (100 MHz, $CDCl_3$)



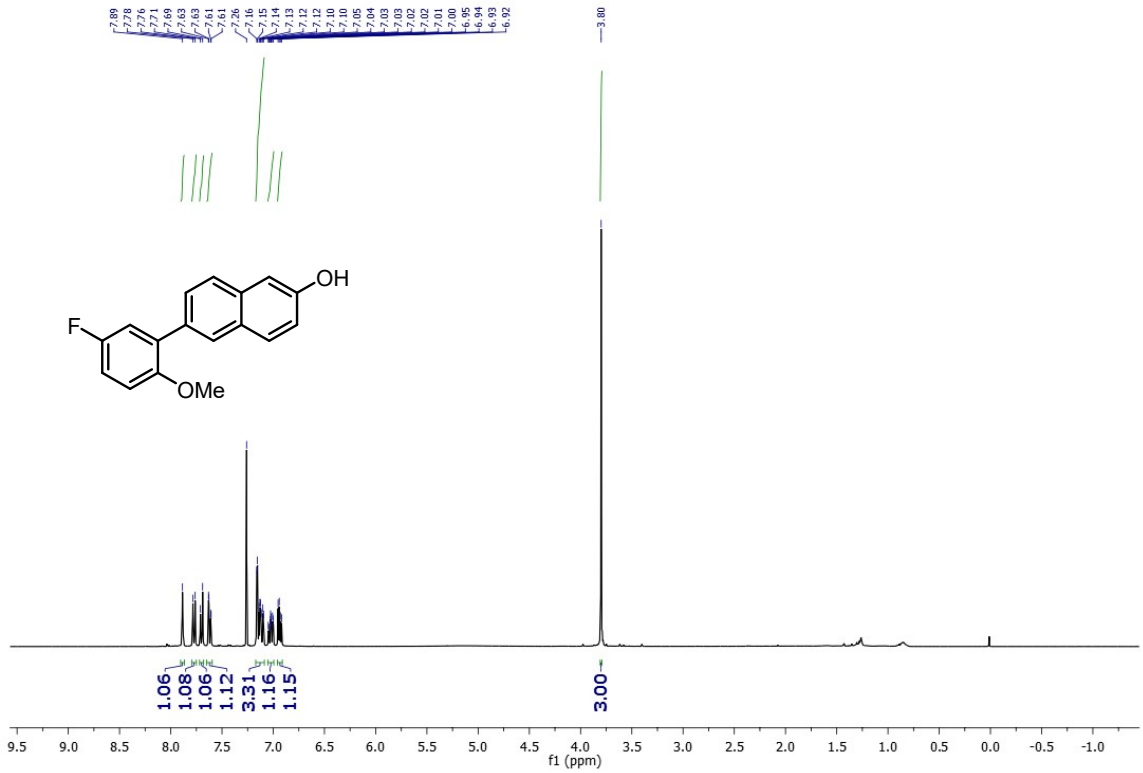
^{1}H NMR Spectrum of **9l** (400 MHz, $CDCl_3$)



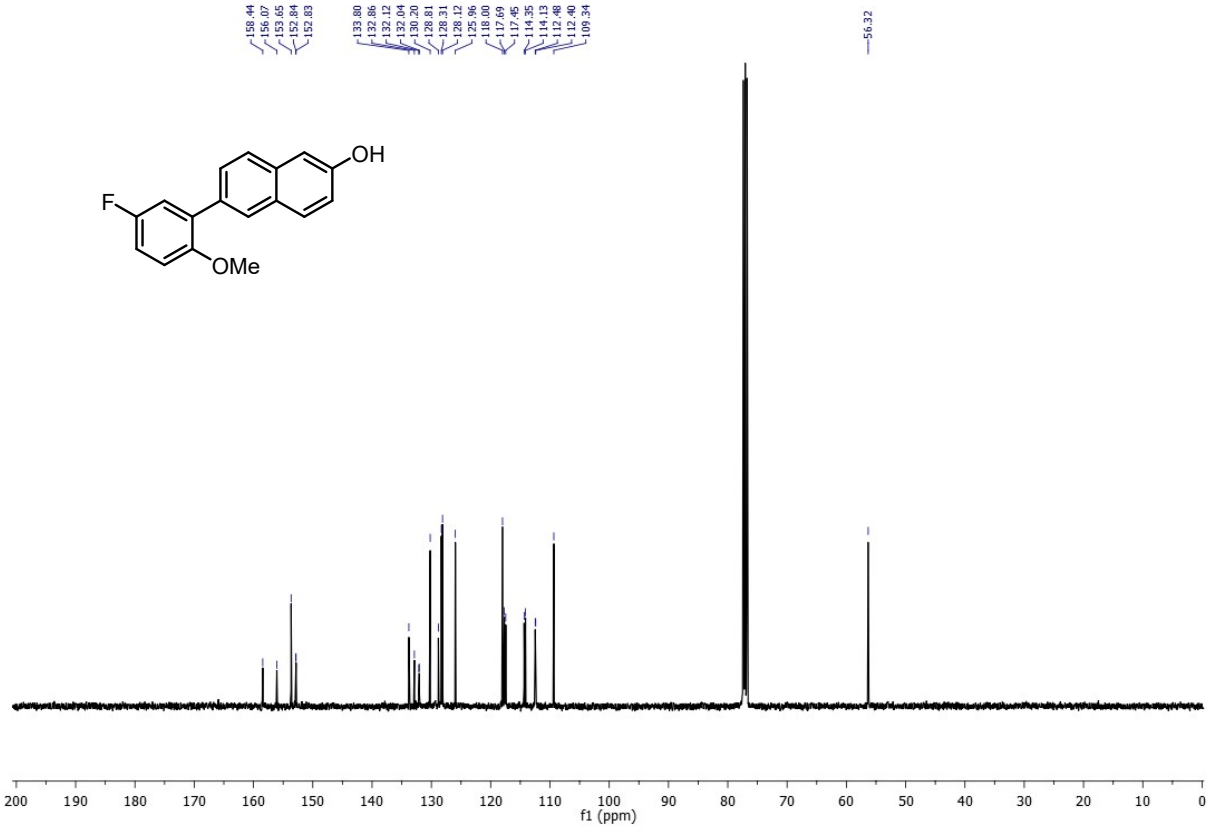
^{13}C NMR Spectrum of **9l** (100 MHz, $CDCl_3$)



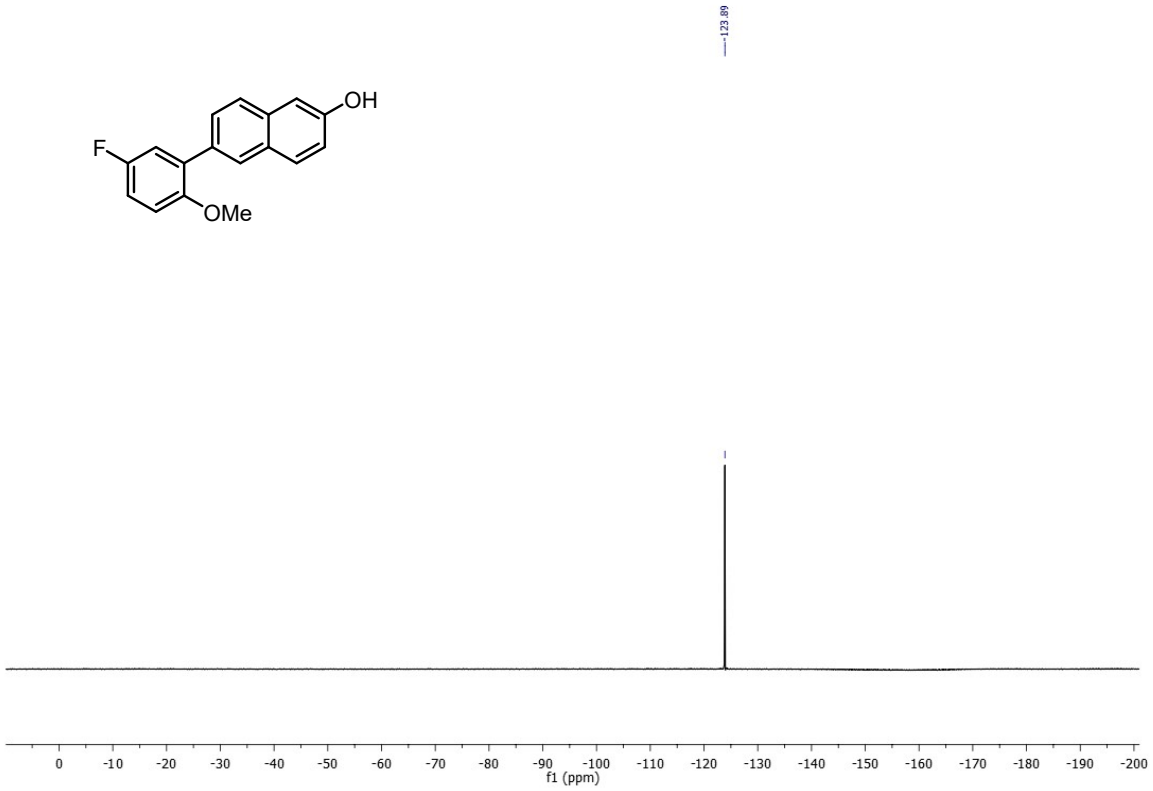
^{1}H NMR Spectrum of **9m** (400 MHz, $CDCl_3$)



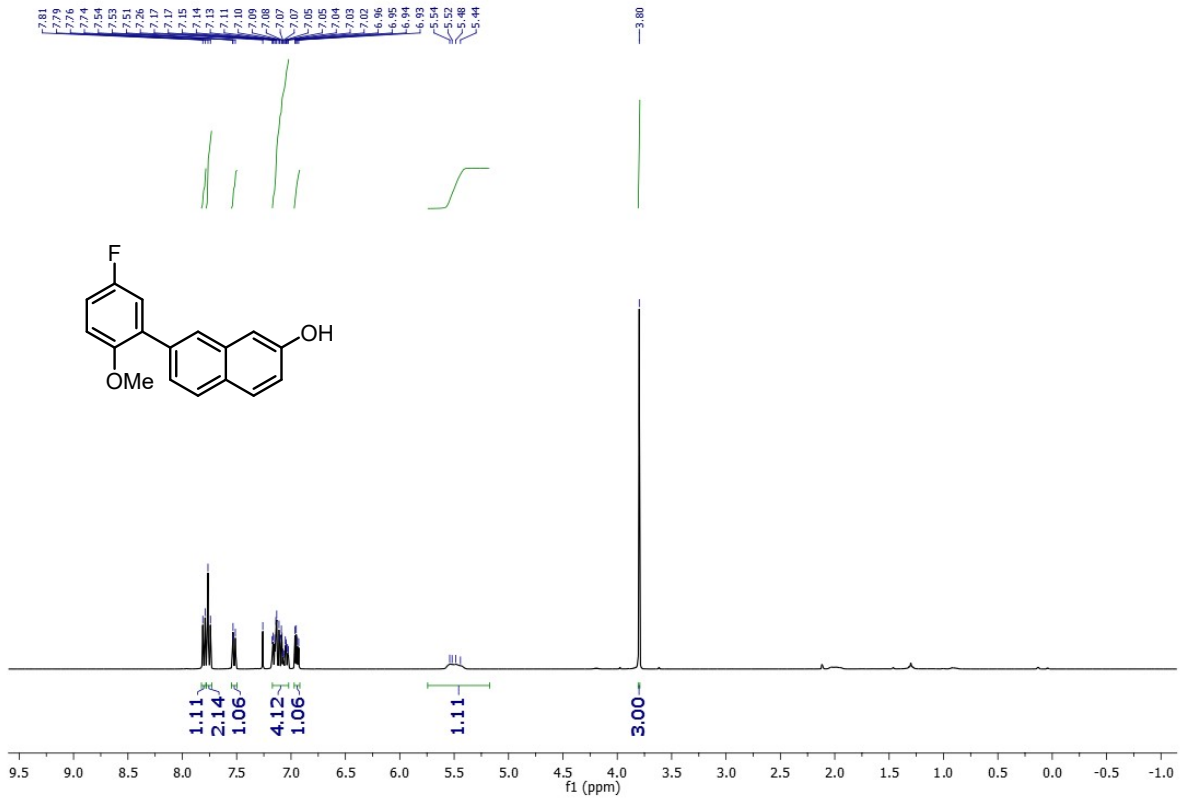
^{13}C NMR Spectrum of **9m** (100 MHz, $CDCl_3$)



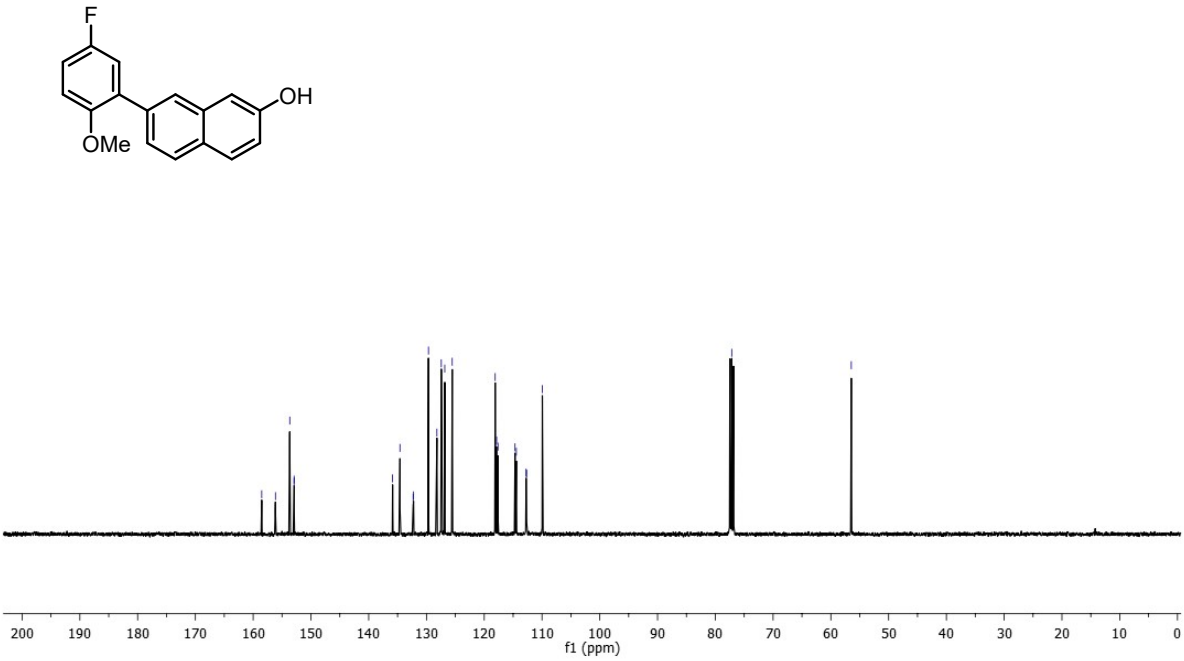
^{19}F NMR Spectrum of **9m** (377 MHz, $CDCl_3$)



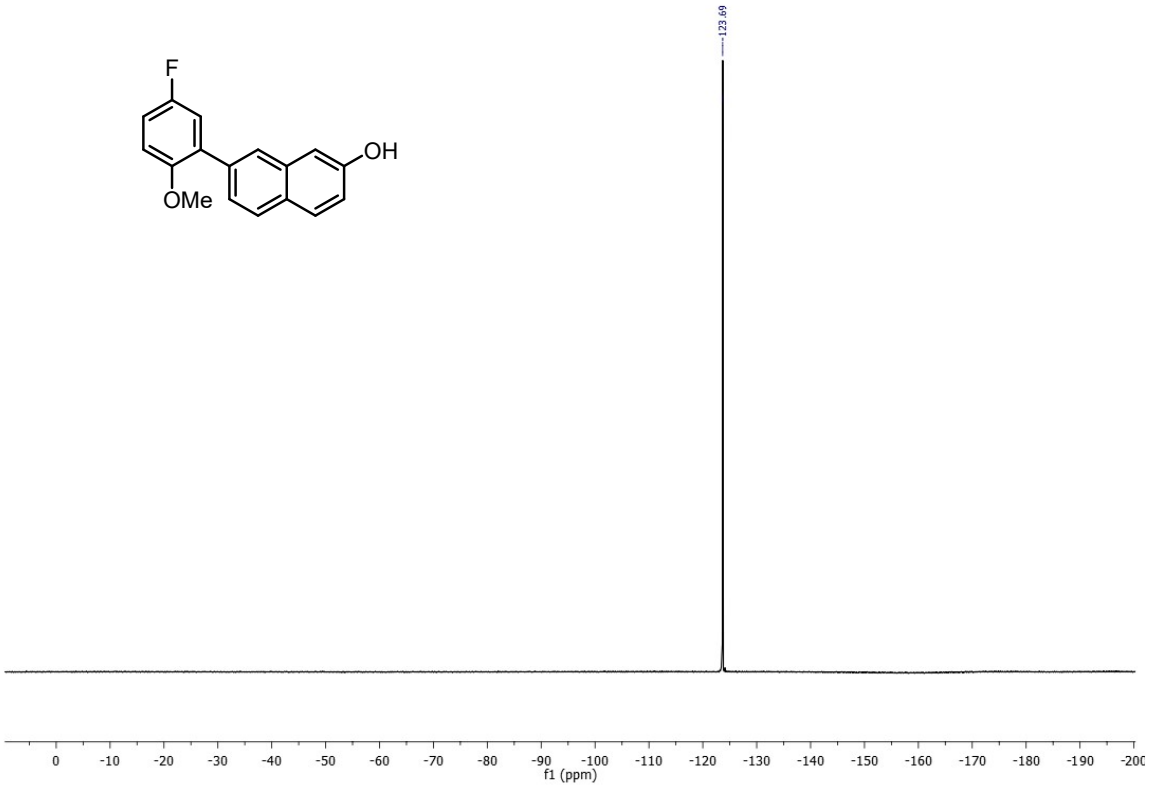
^{1}H NMR Spectrum of **9q** (400 MHz, $CDCl_3$)



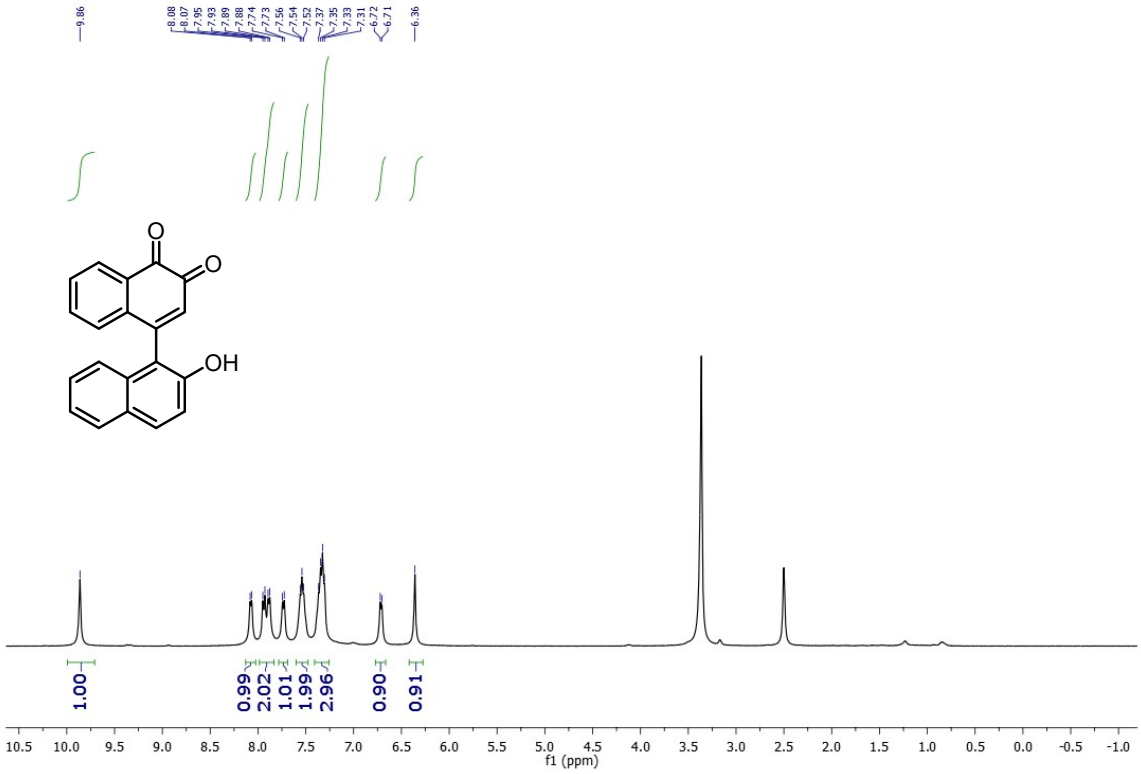
^{13}C NMR Spectrum of **9q** (100 MHz, $CDCl_3$)



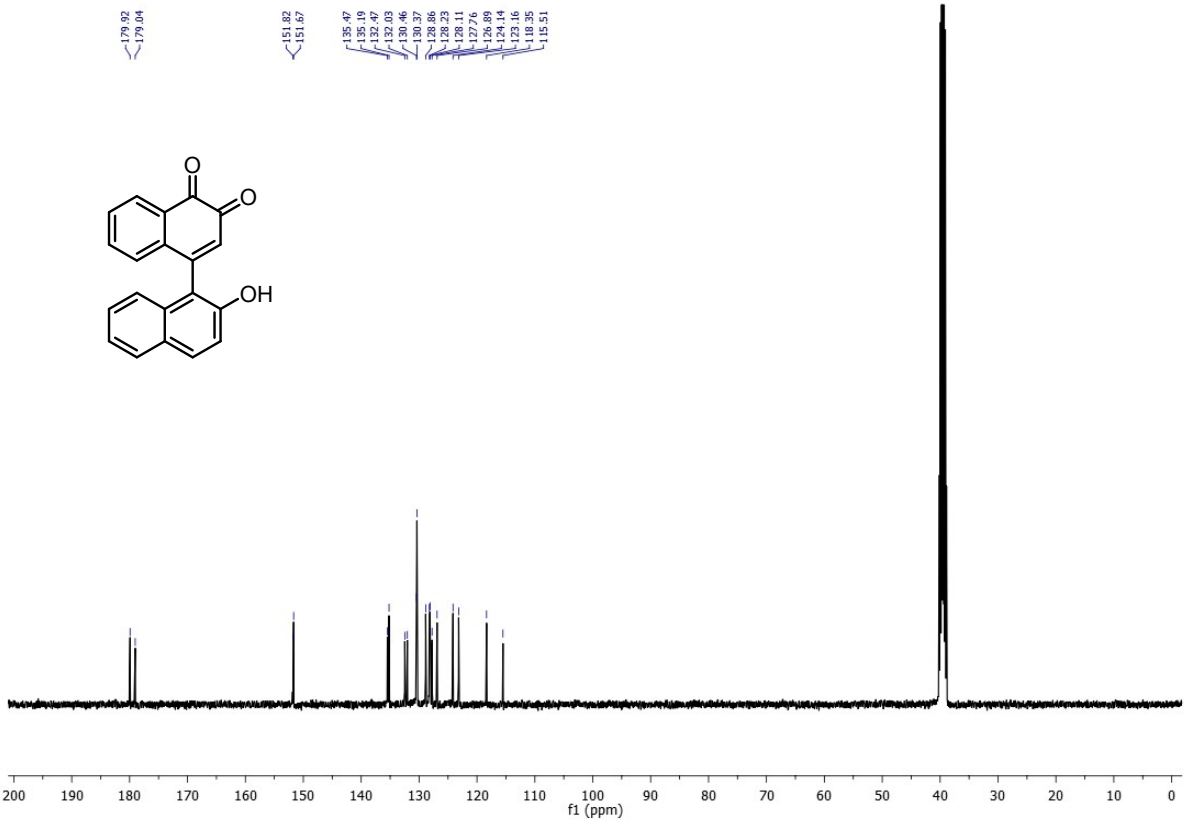
^{19}F NMR Spectrum of **9q** (377 MHz, $CDCl_3$)



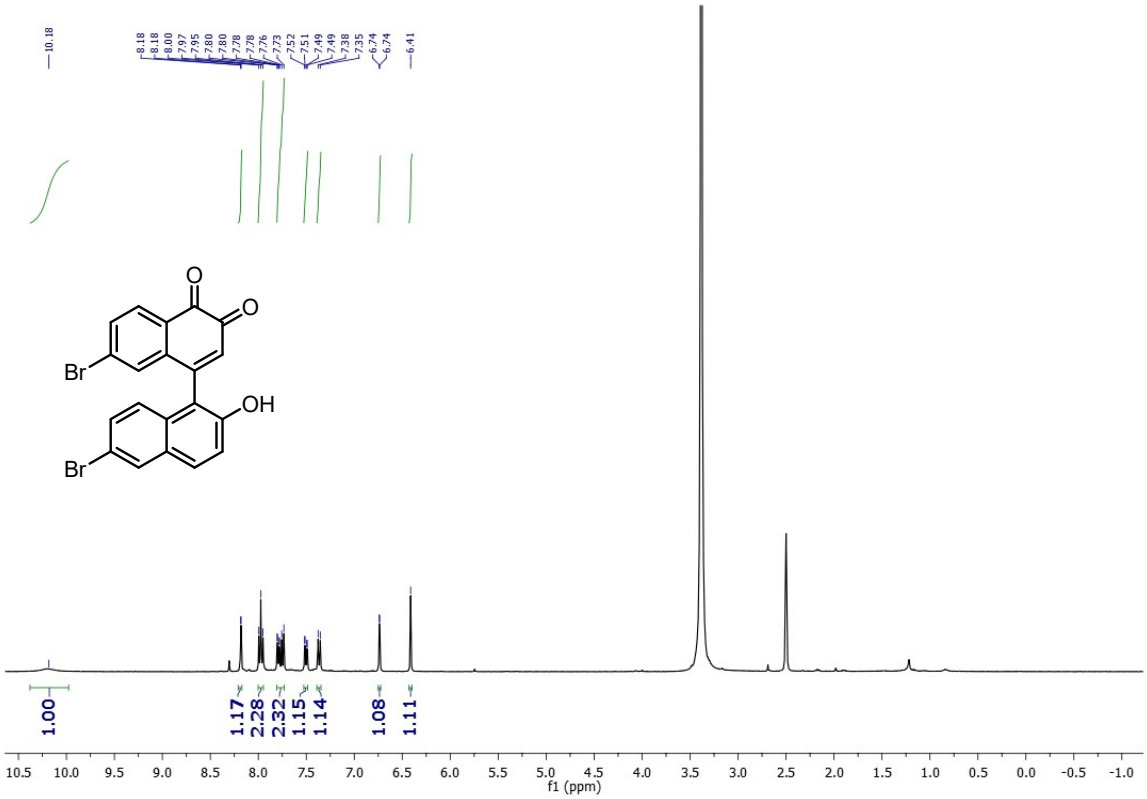
^{1}H NMR Spectrum of **10a** (400 MHz, DMSO-d_6)



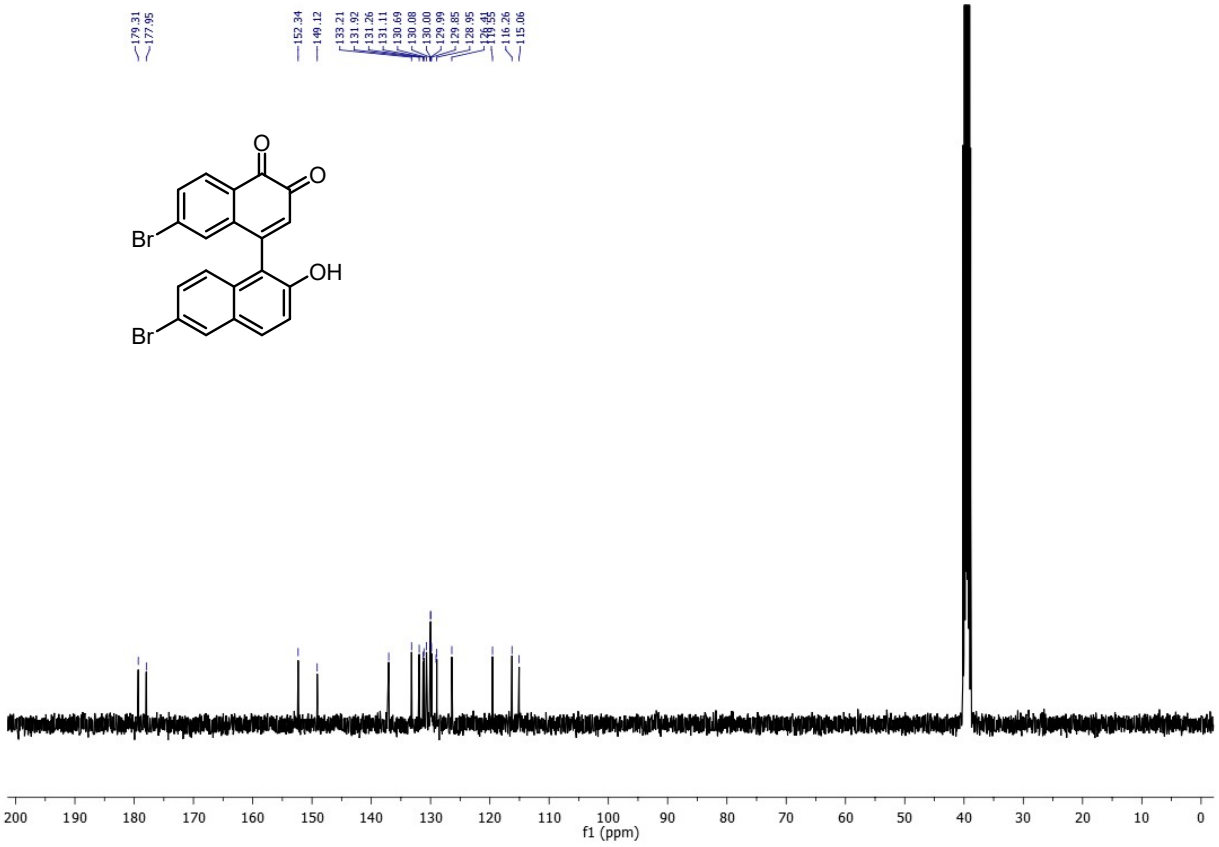
^{13}C NMR Spectrum of **10a** (100 MHz, DMSO-d_6)



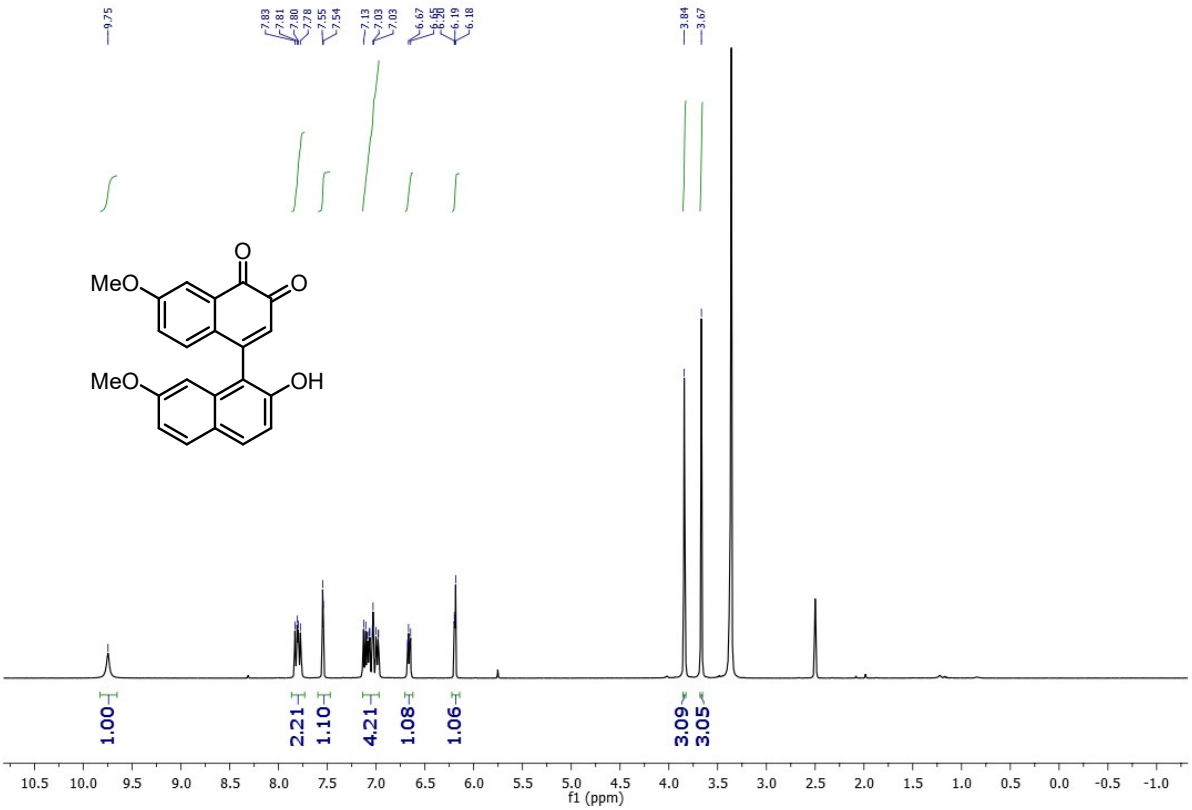
^{1}H NMR Spectrum of **10b** (400 MHz, DMSO-d_6)



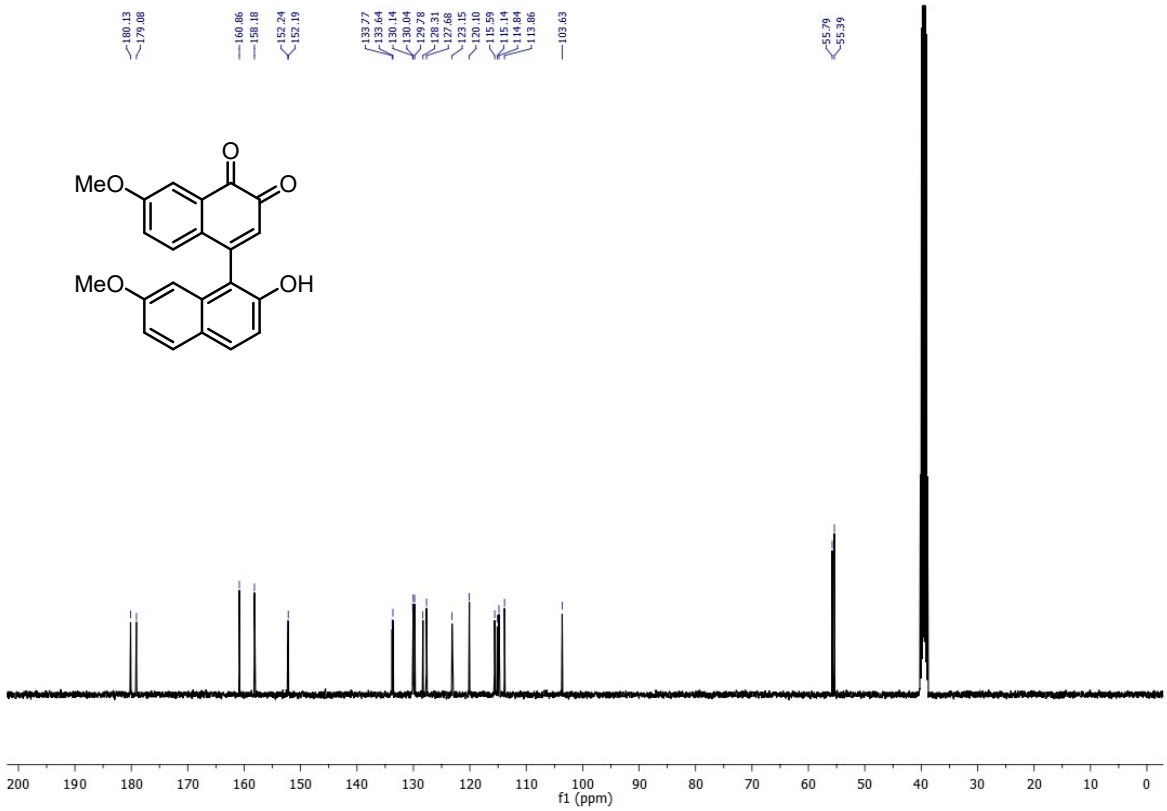
^{13}C NMR Spectrum of **10b** (100 MHz, DMSO-d_6)



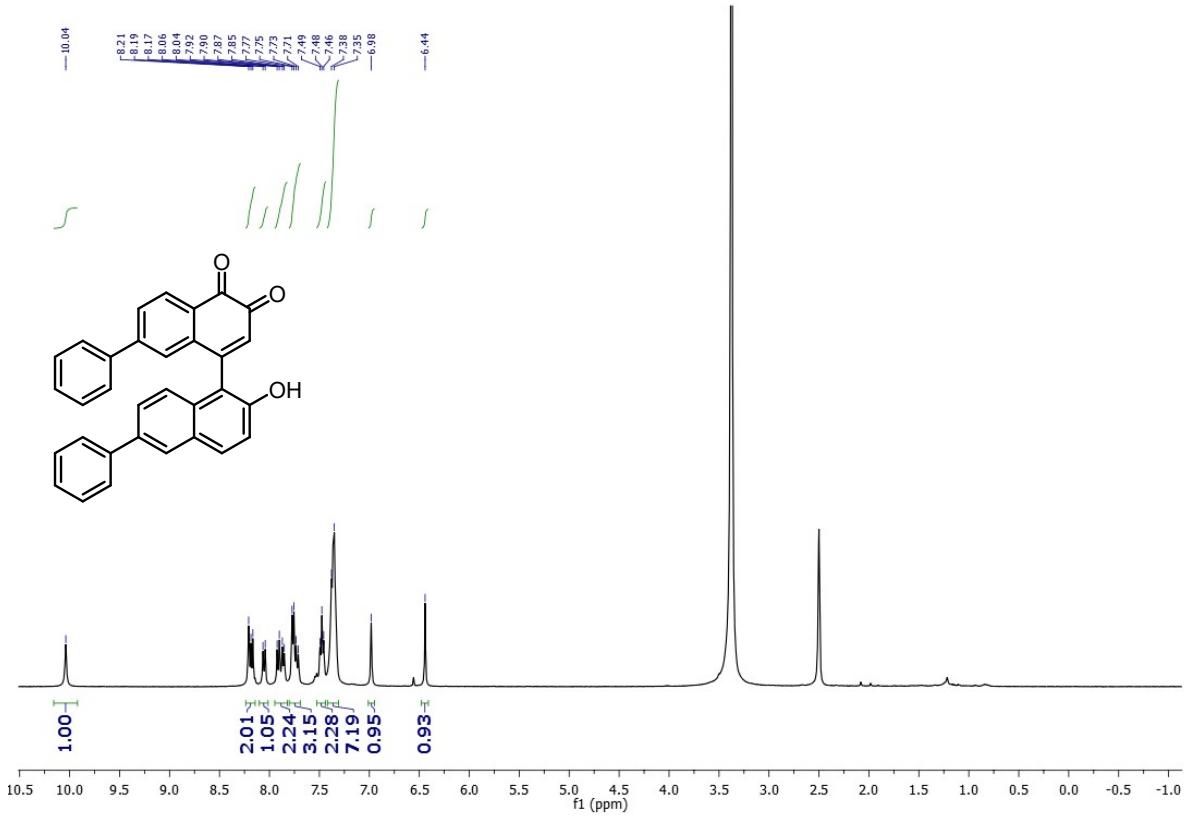
^{1}H NMR Spectrum of **10c** (400 MHz, DMSO-d_6)



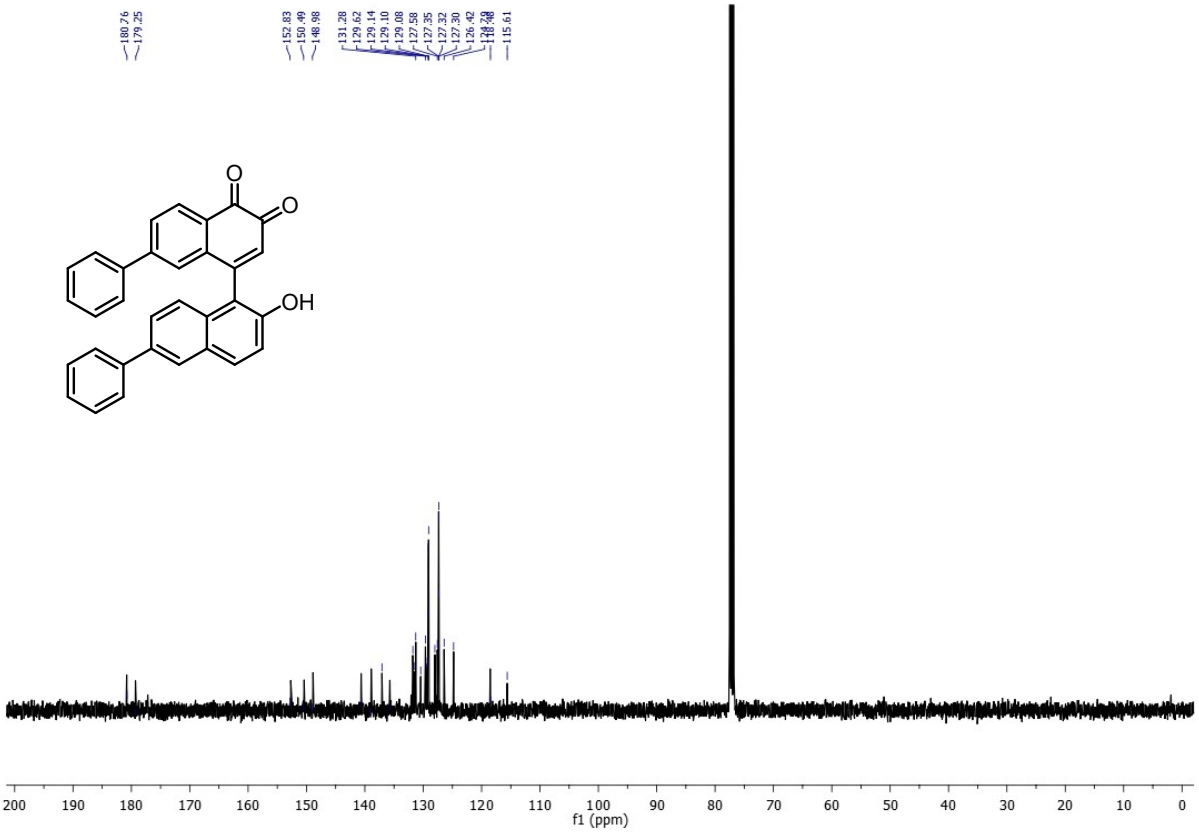
^{13}C NMR Spectrum of **10c** (100 MHz, DMSO-d_6)



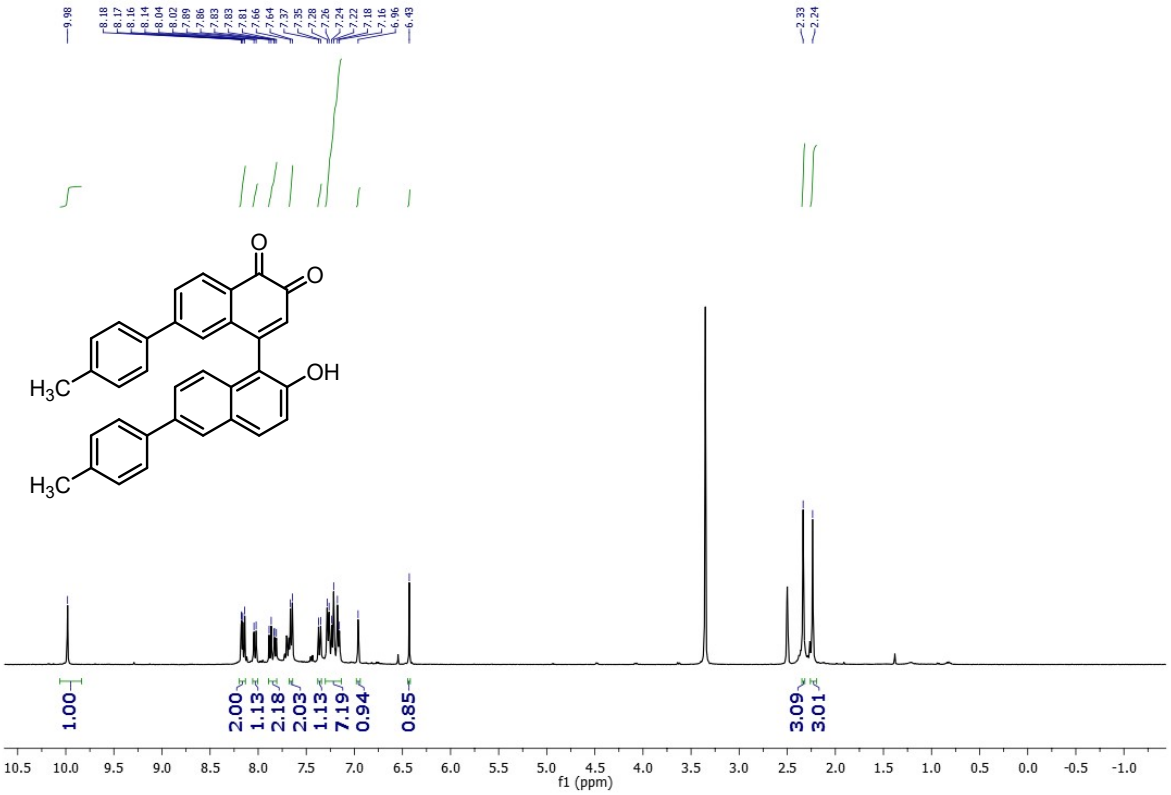
^{1}H NMR Spectrum of **10d** (400 MHz, DMSO-d_6)



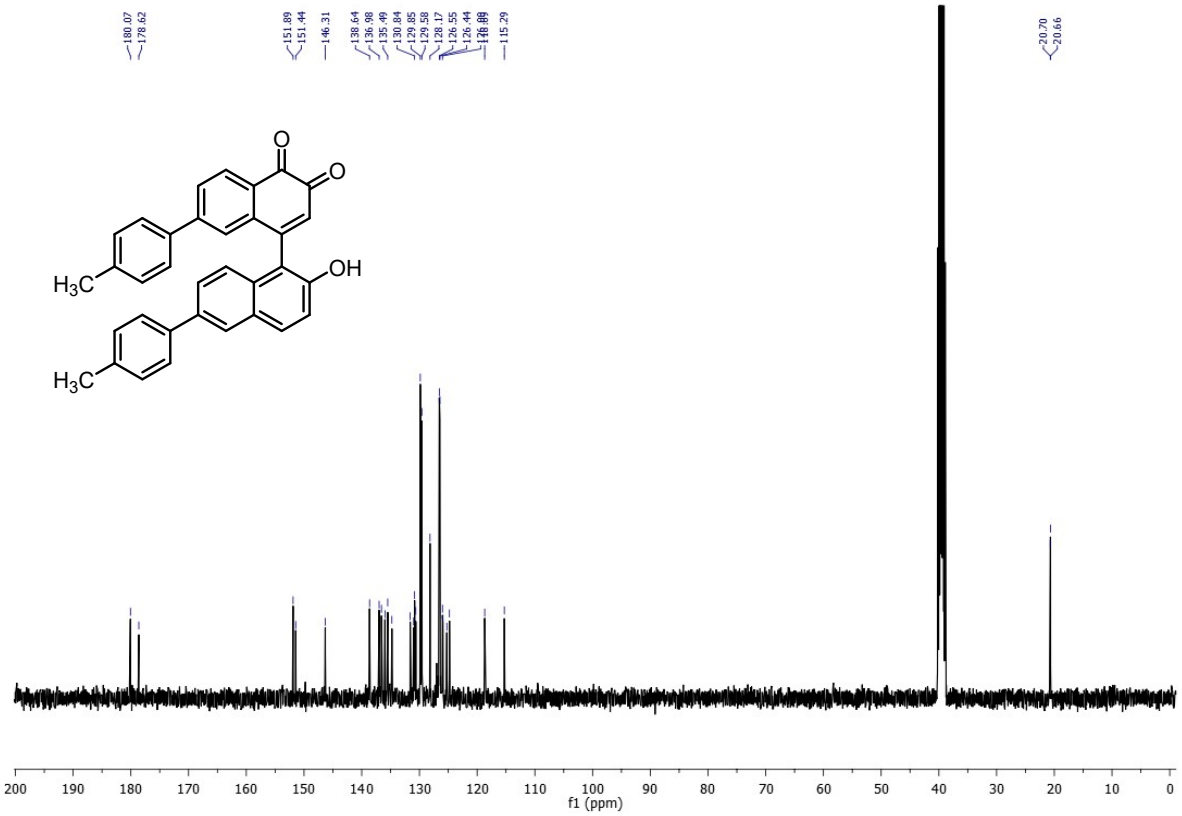
^{13}C NMR Spectrum of **10d** (100 MHz, DMSO-d_6)



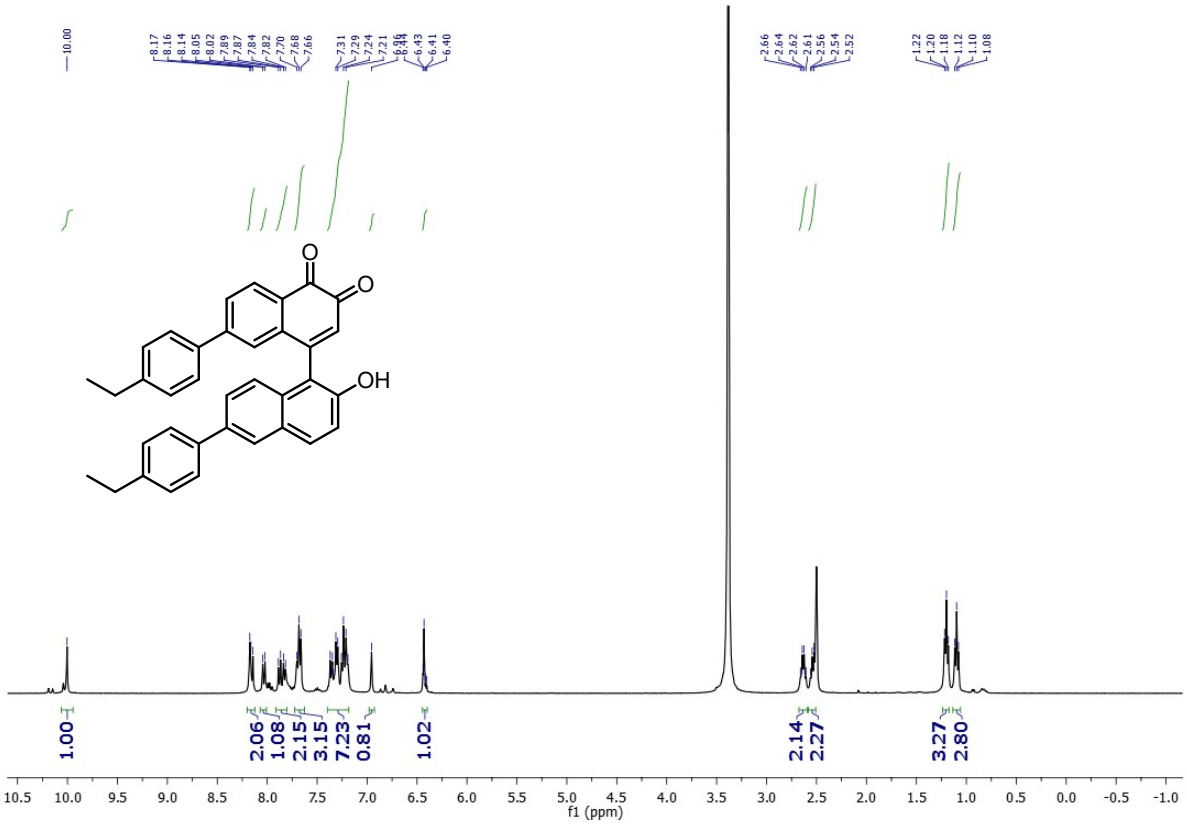
^{1}H NMR Spectrum of **10e** (400 MHz, DMSO-d_6)



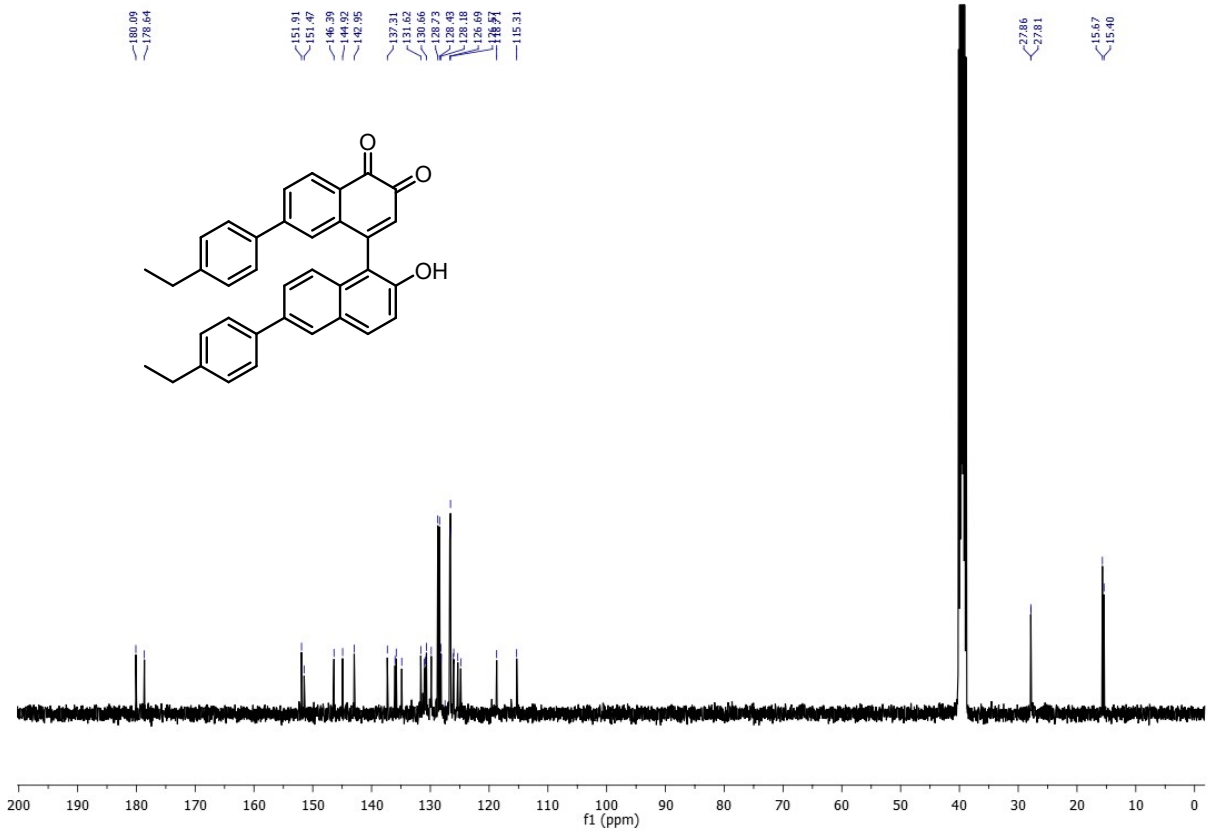
^{13}C NMR Spectrum of **10e** (100 MHz, DMSO-d_6)



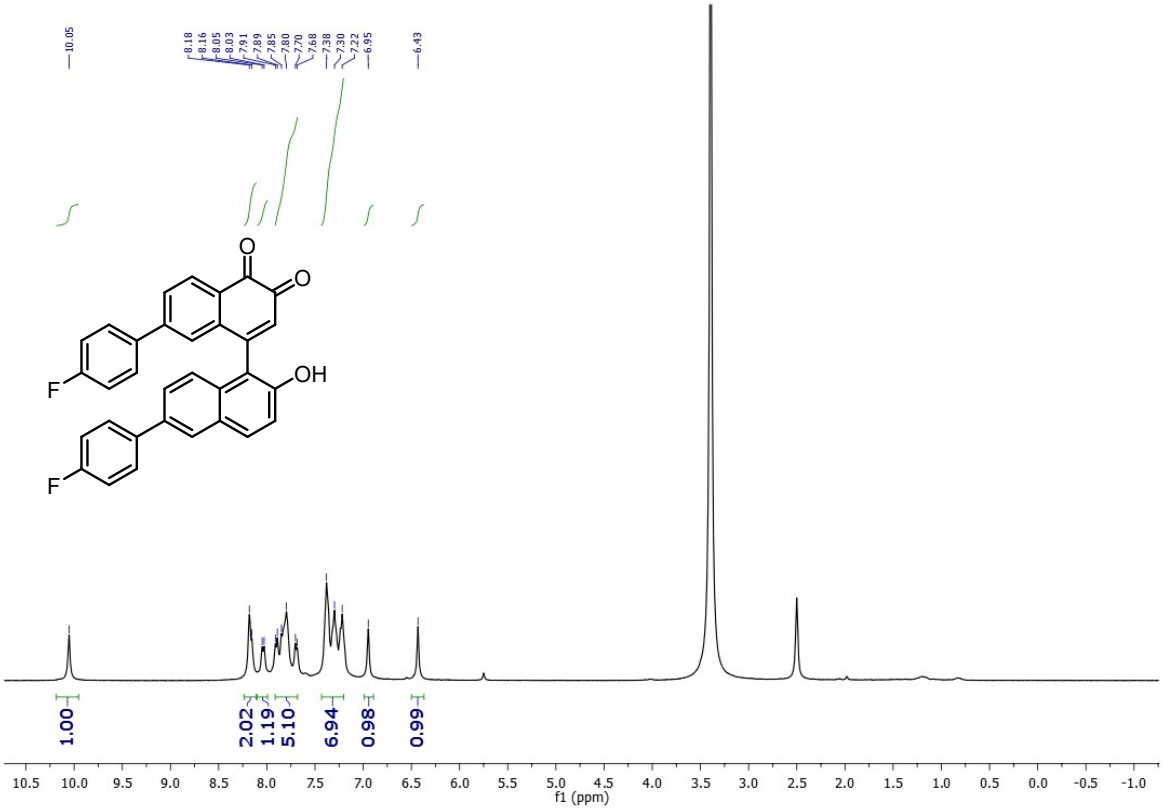
^{1}H NMR Spectrum of **10f** (400 MHz, DMSO-d_6)



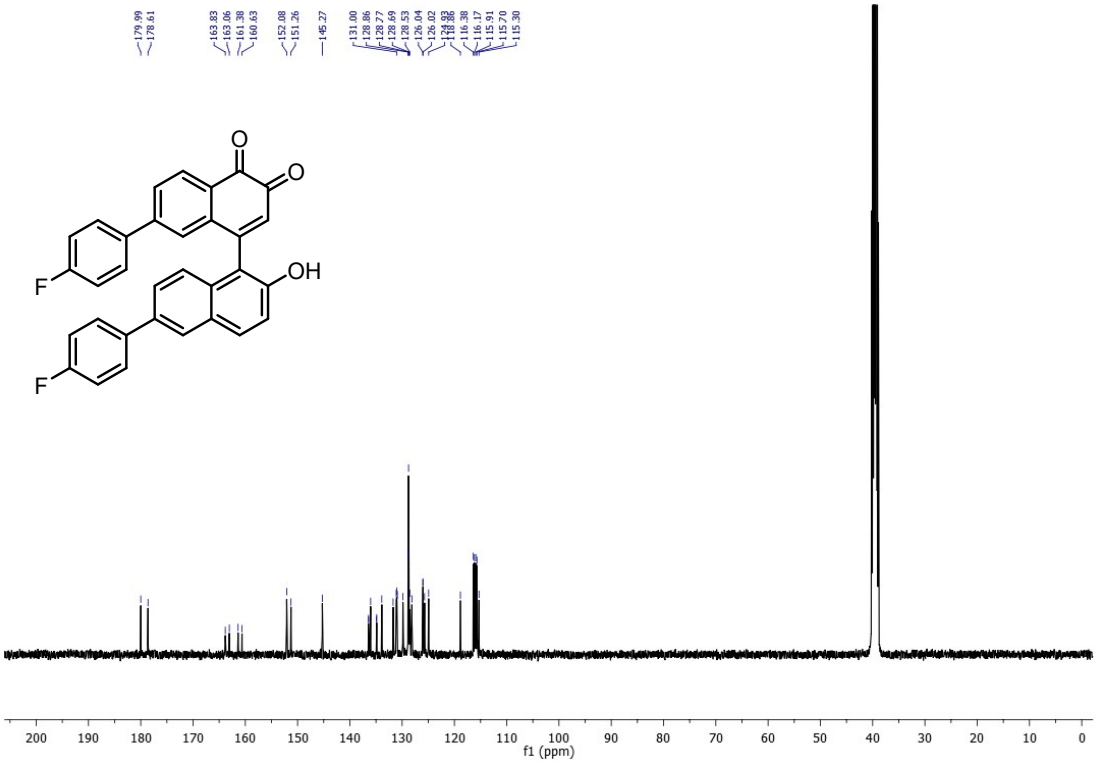
^{13}C NMR Spectrum of **10f** (100 MHz, DMSO-d_6)



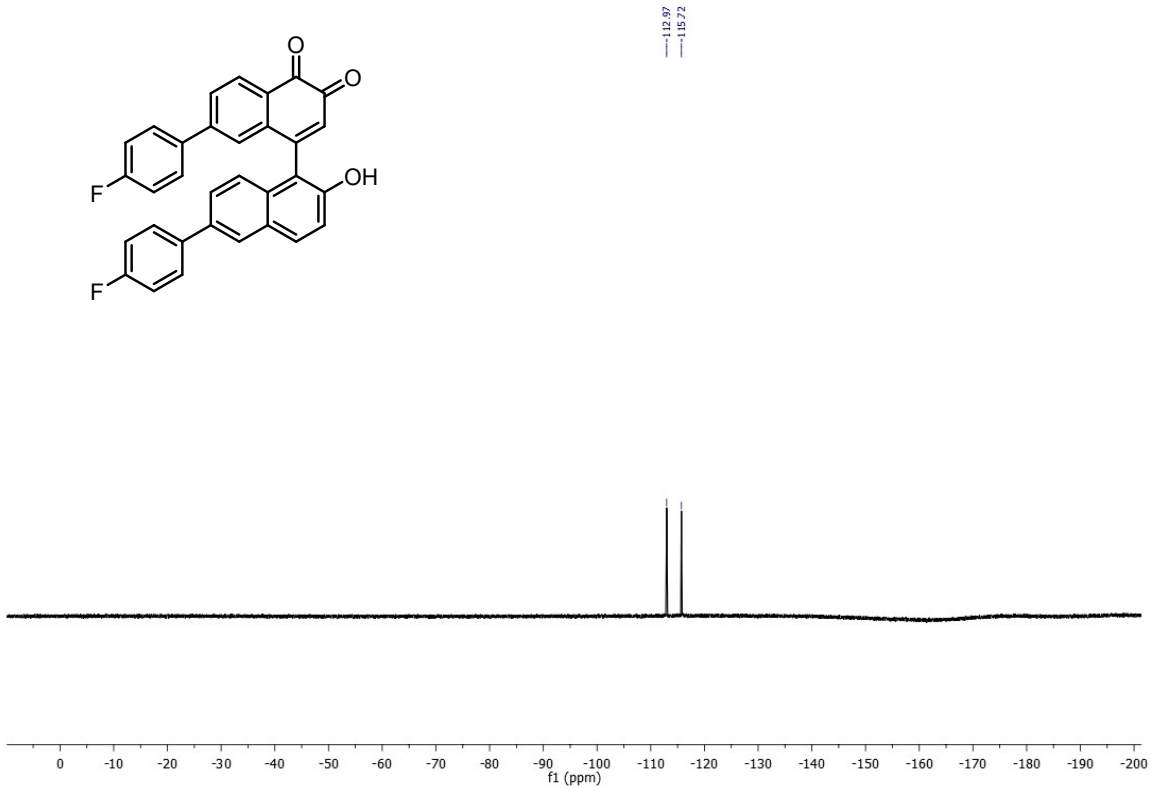
^{1}H NMR Spectrum of **10g** (400 MHz, DMSO-d_6)



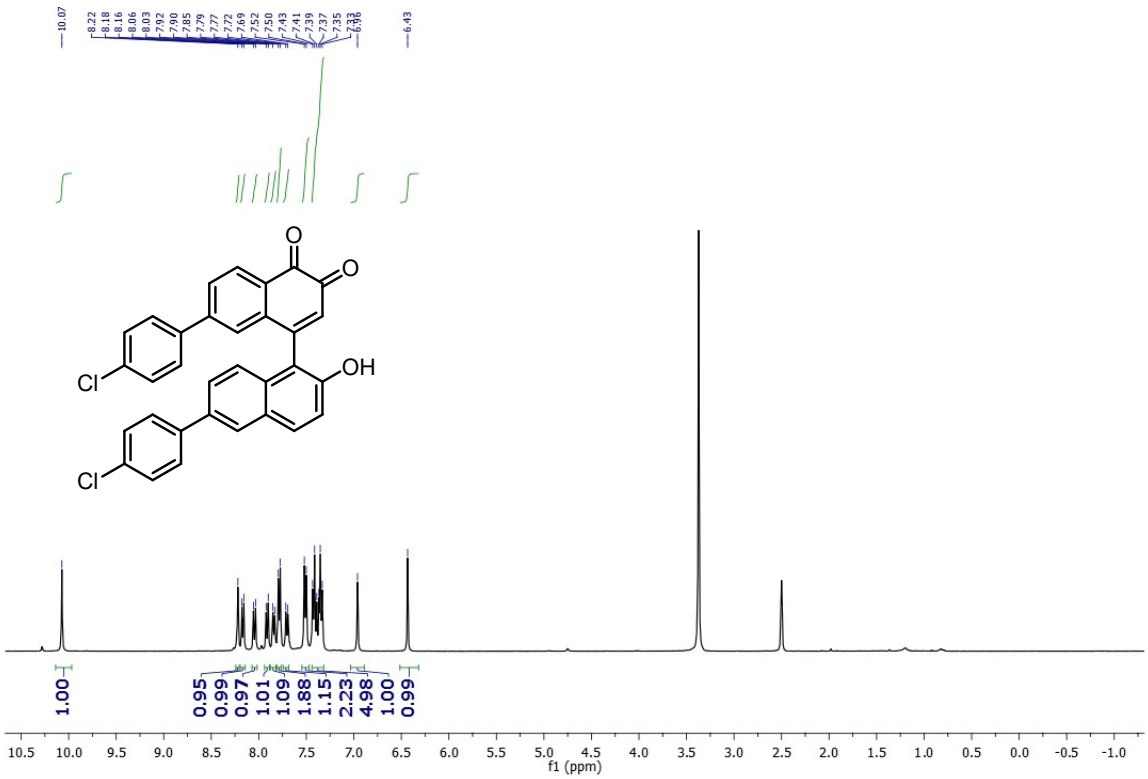
^{13}C NMR Spectrum of **10g** (100 MHz, DMSO-d_6)



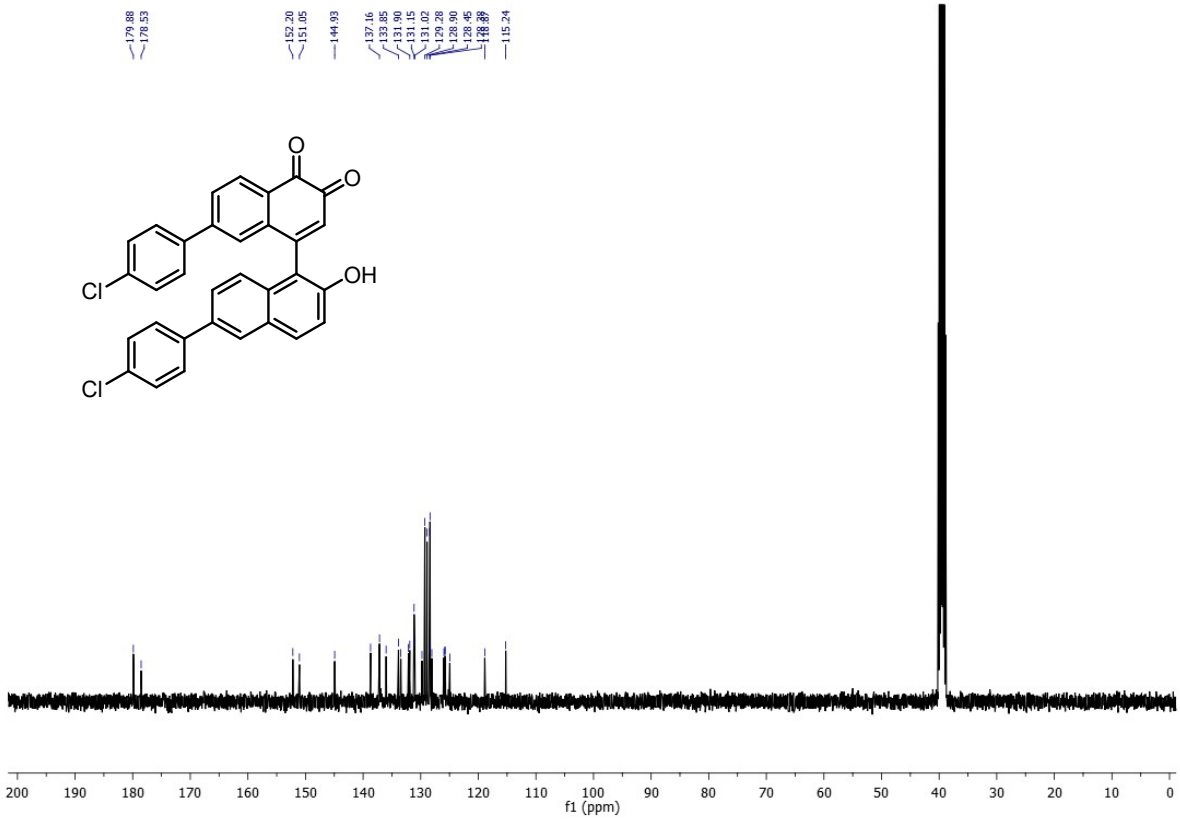
^{19}F NMR Spectrum of **10g** (377 MHz, DMSO-d_6)



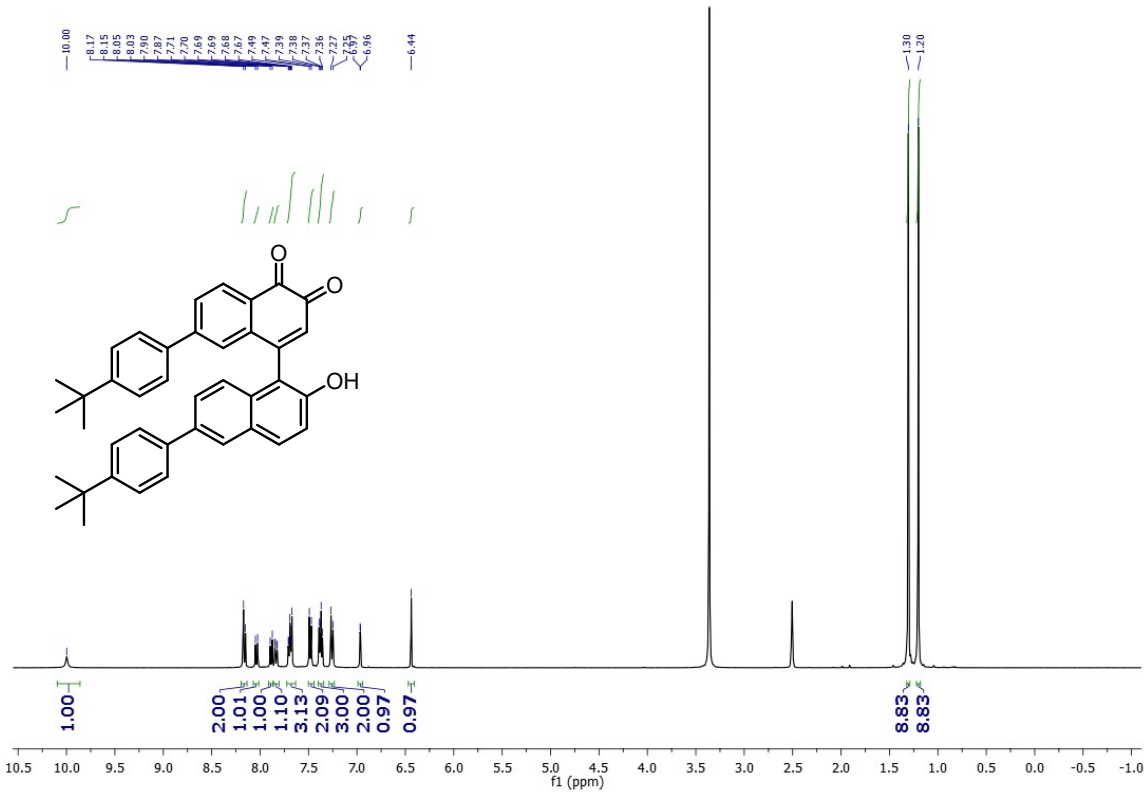
^{1}H NMR Spectrum of **10h** (400 MHz, DMSO-d_6)



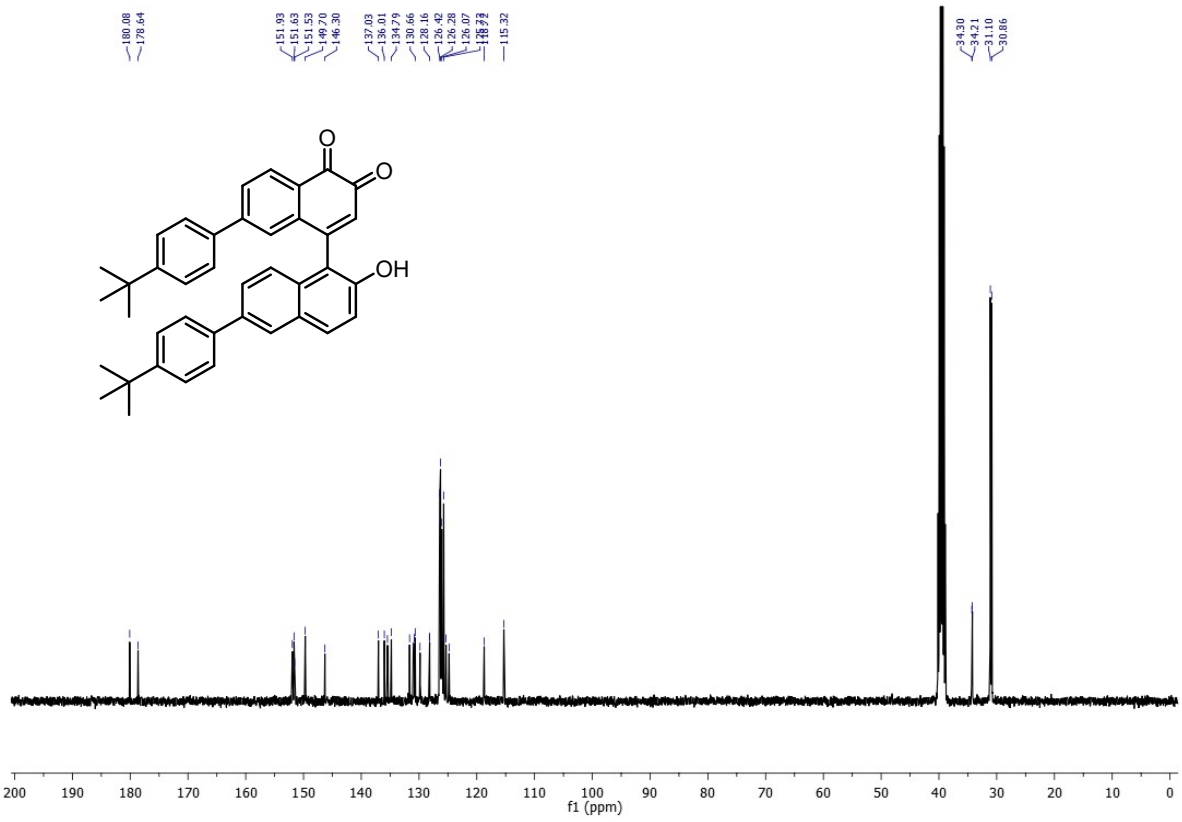
^{13}C NMR Spectrum of **10h** (100 MHz, DMSO-d_6)



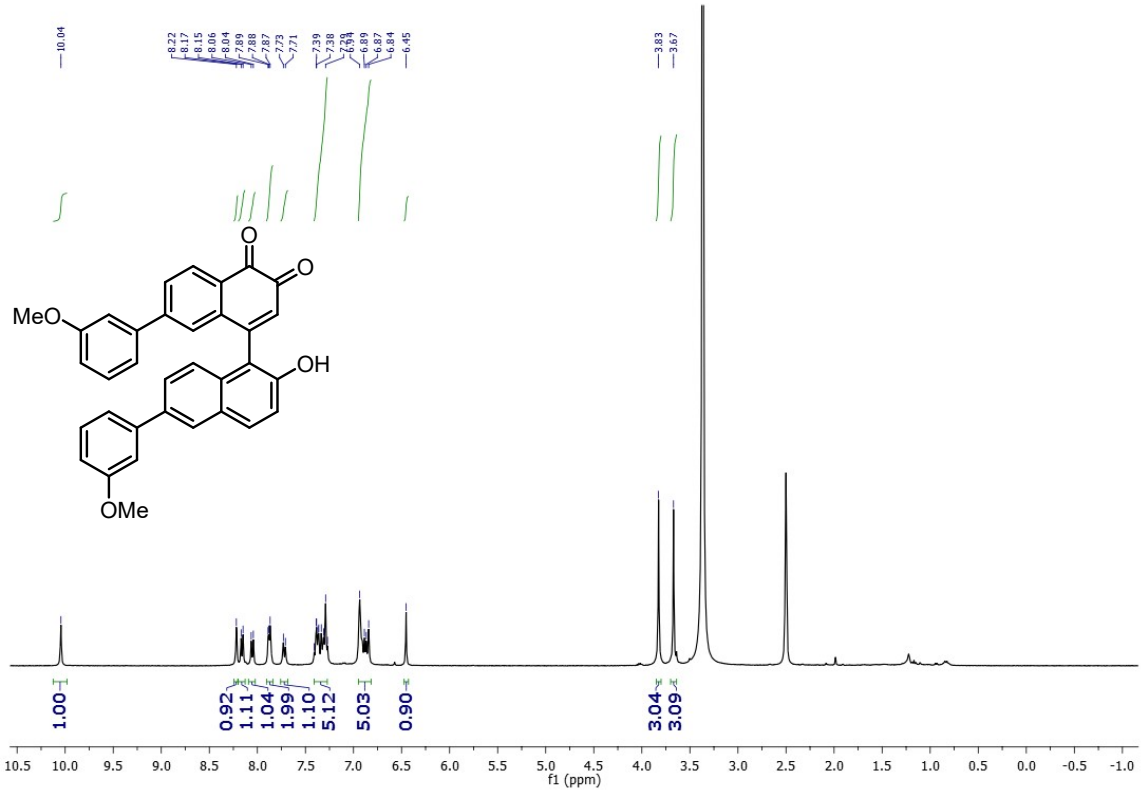
^{1}H NMR Spectrum of **10i** (400 MHz, DMSO-d_6)



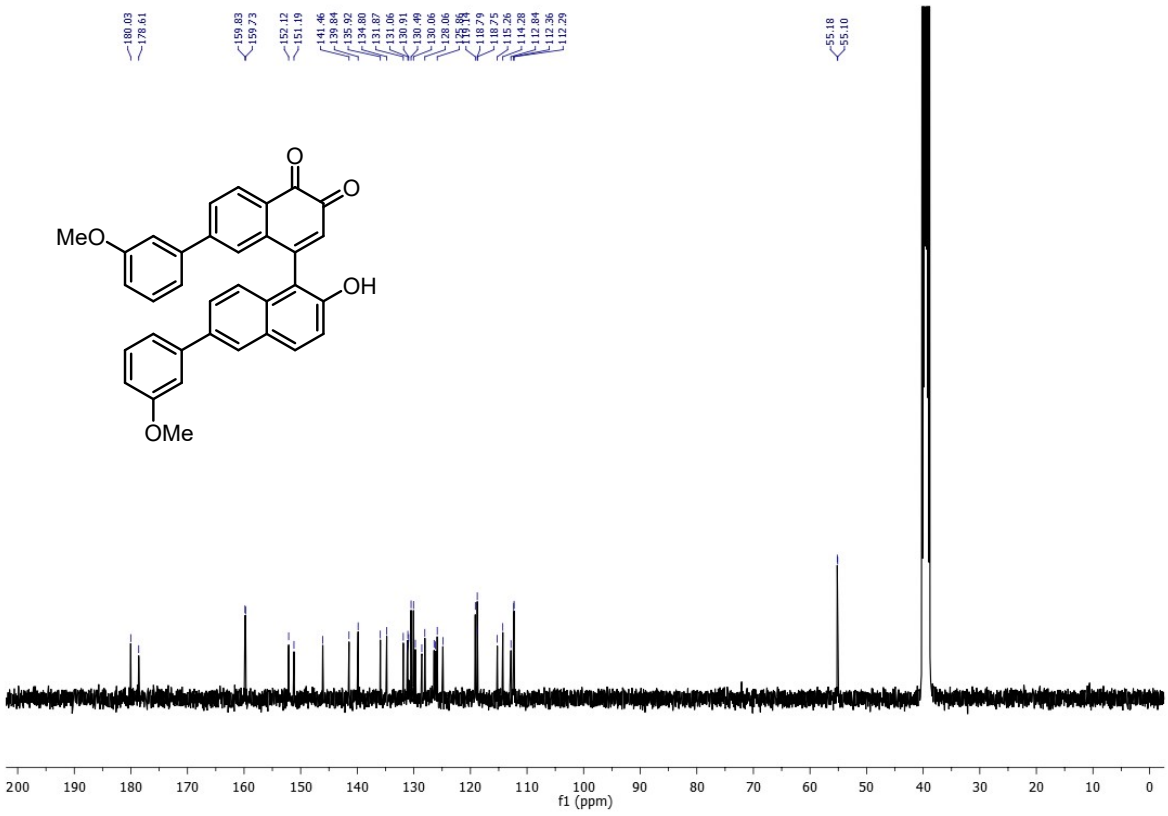
^{13}C NMR Spectrum of **10i** (100 MHz, DMSO-d_6)



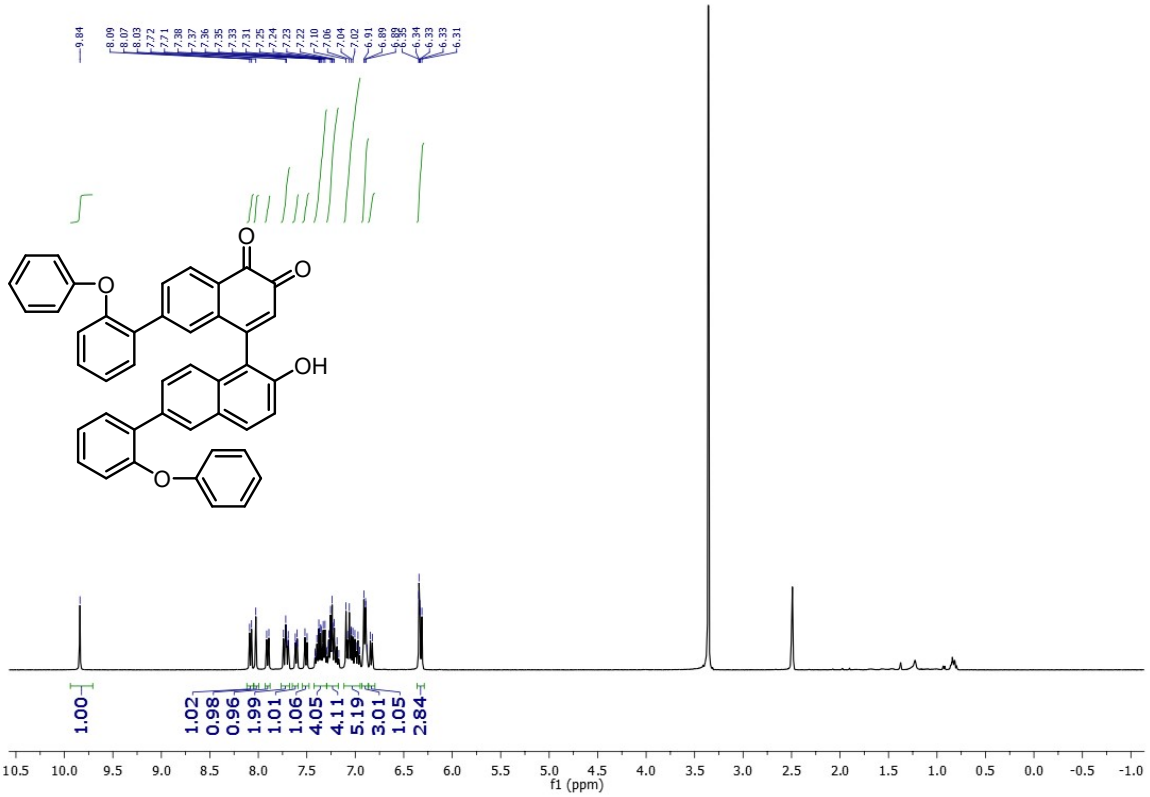
^{1}H NMR Spectrum of **10j** (400 MHz, DMSO-d_6)



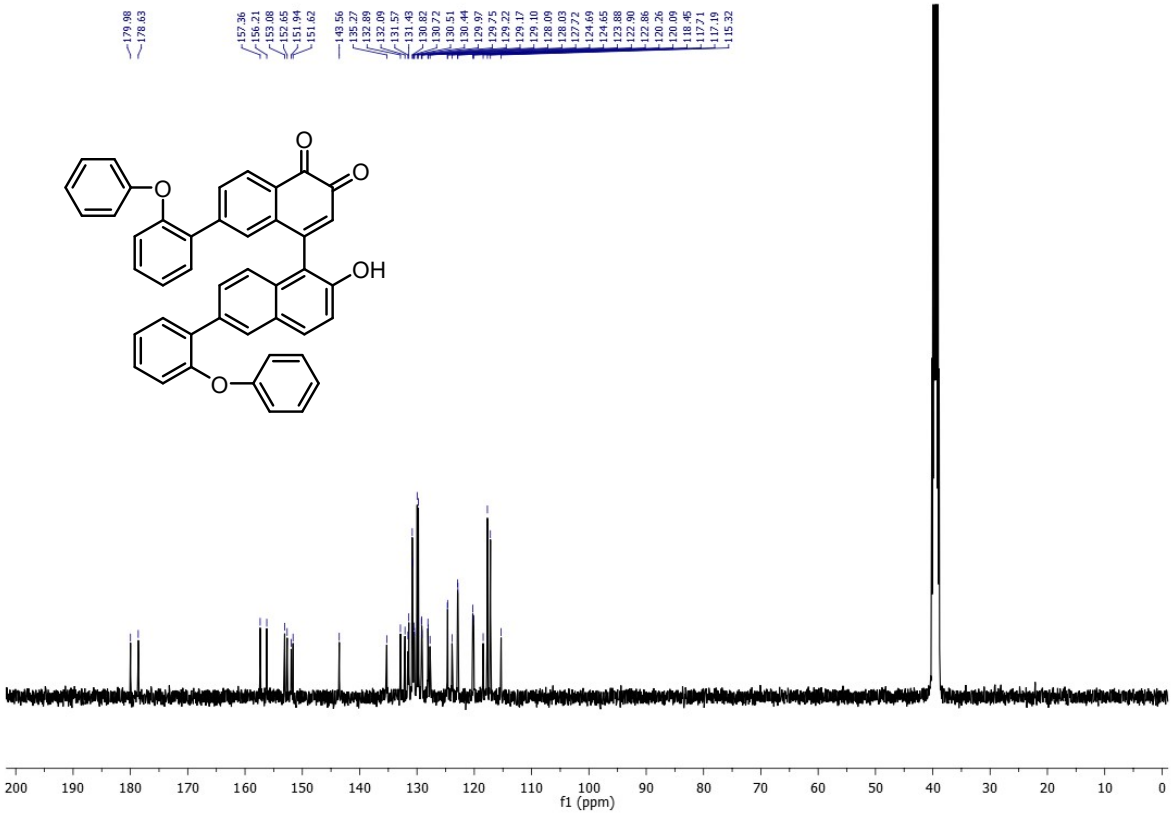
^{13}C NMR Spectrum of **10j** (100 MHz, DMSO-d_6)



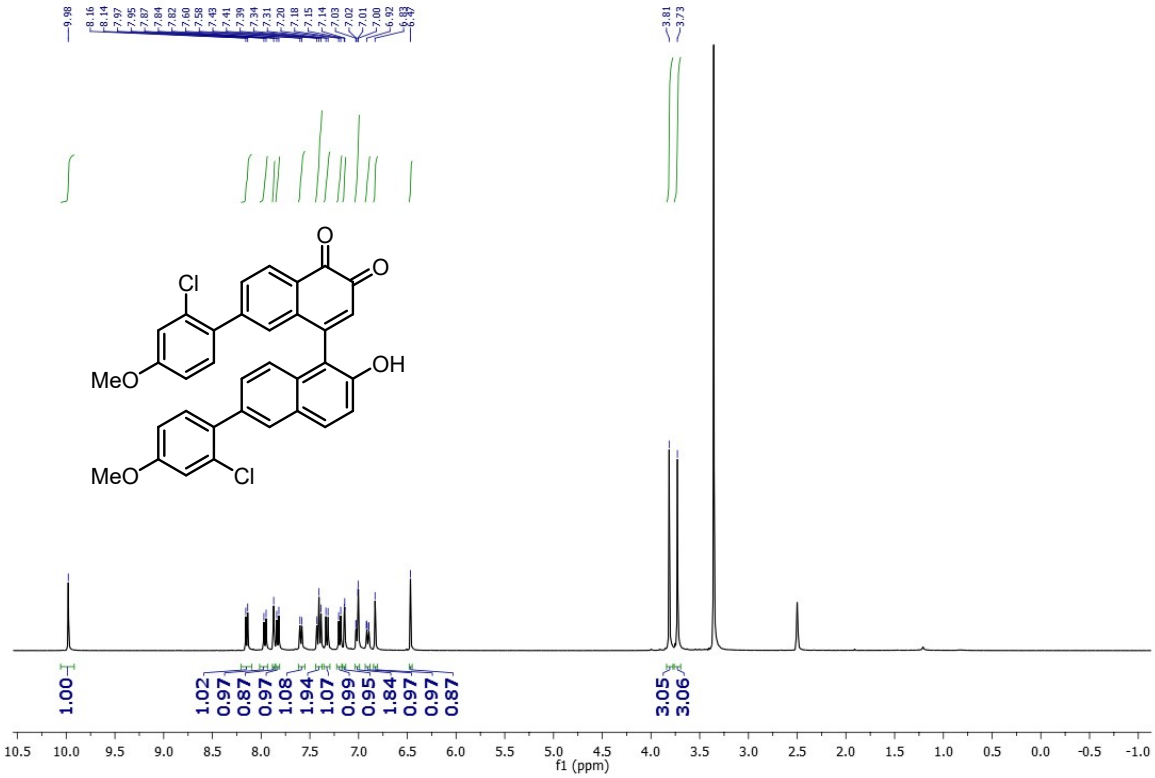
^{1}H NMR Spectrum of **10k** (400 MHz, DMSO-d_6)



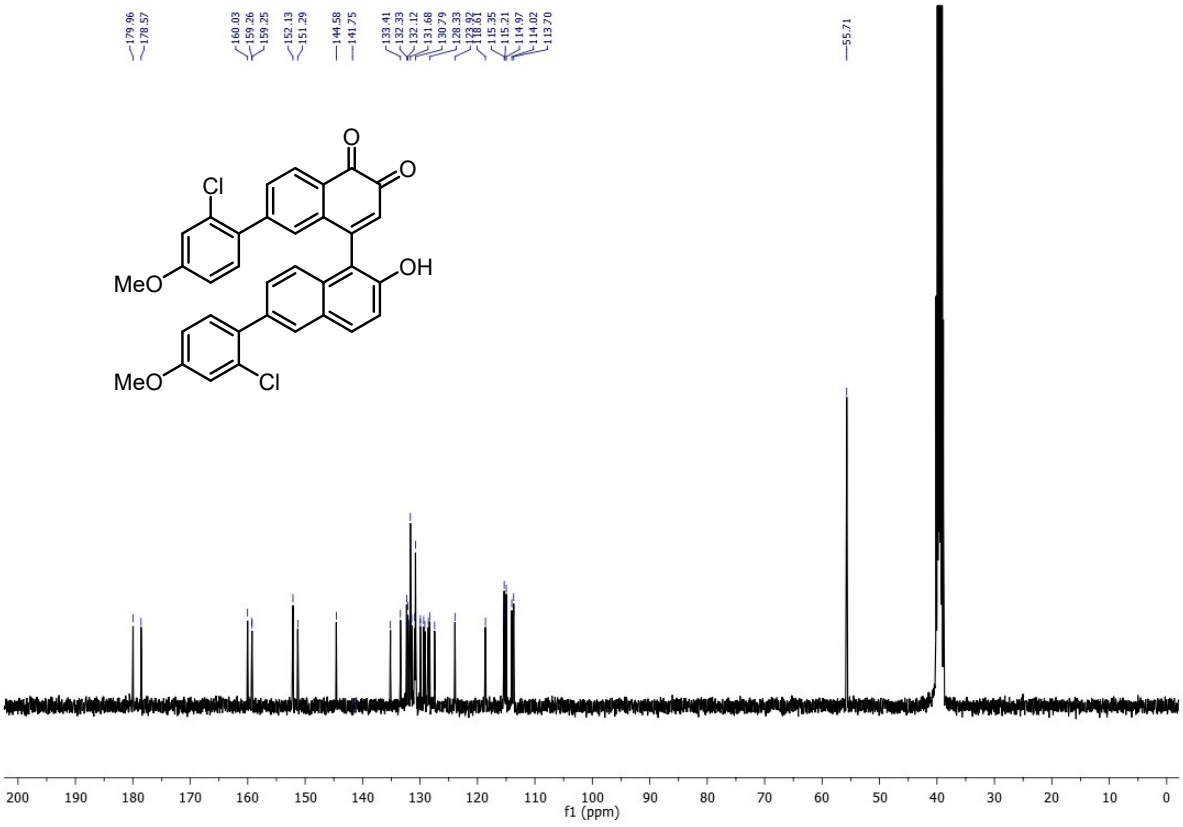
^{13}C NMR Spectrum of **10k** (100 MHz, DMSO-d_6)



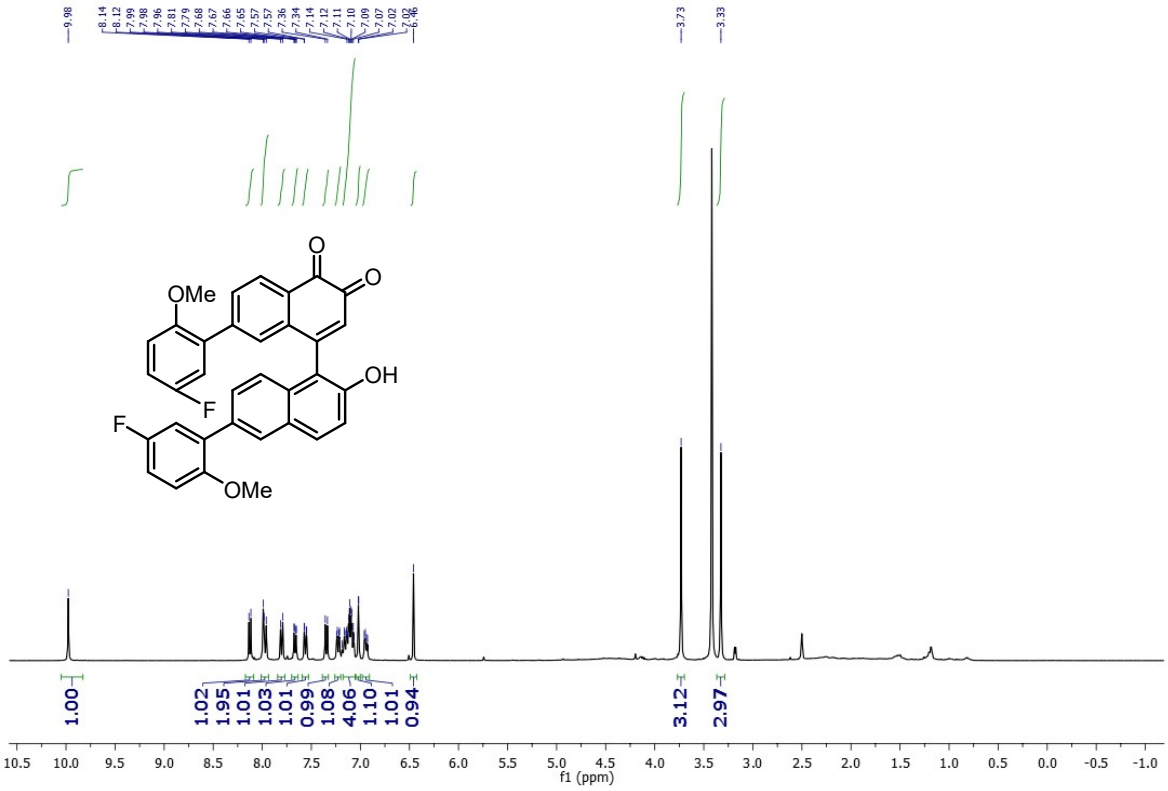
^{1}H NMR Spectrum of **10l** (400 MHz, DMSO-d_6)



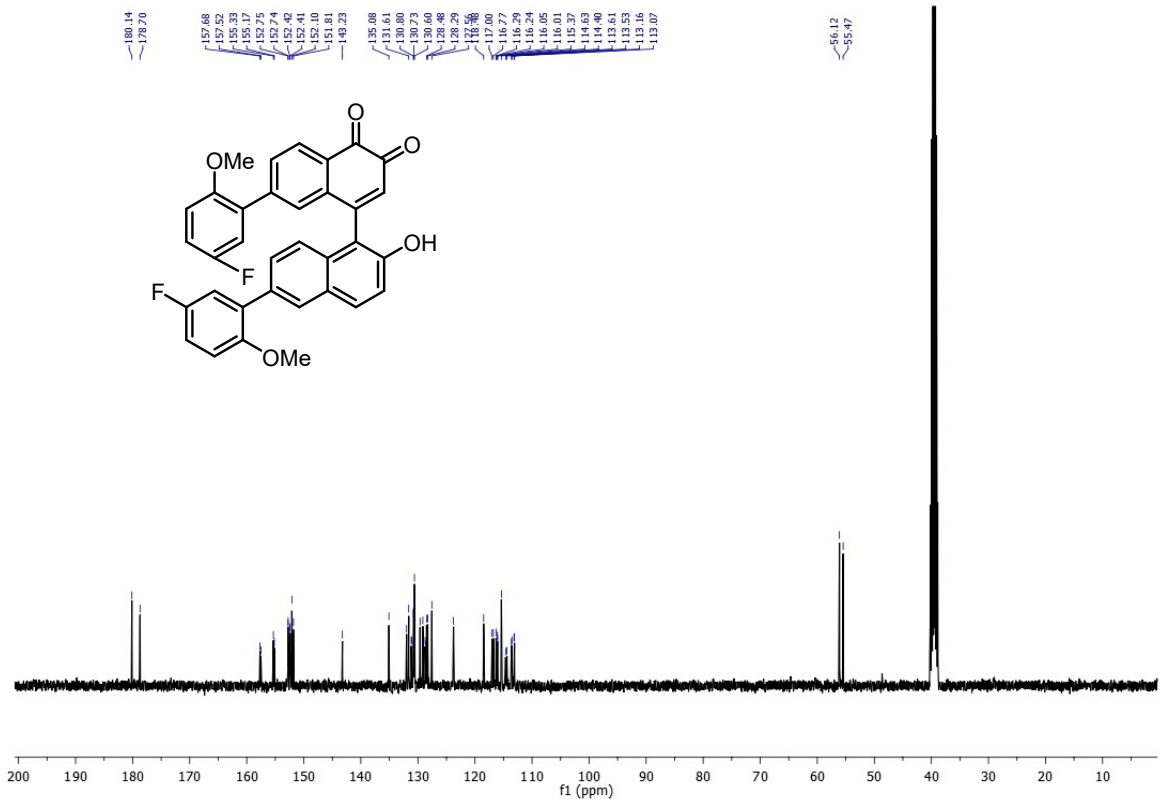
^{13}C NMR Spectrum of **10l** (100 MHz, DMSO-d_6)



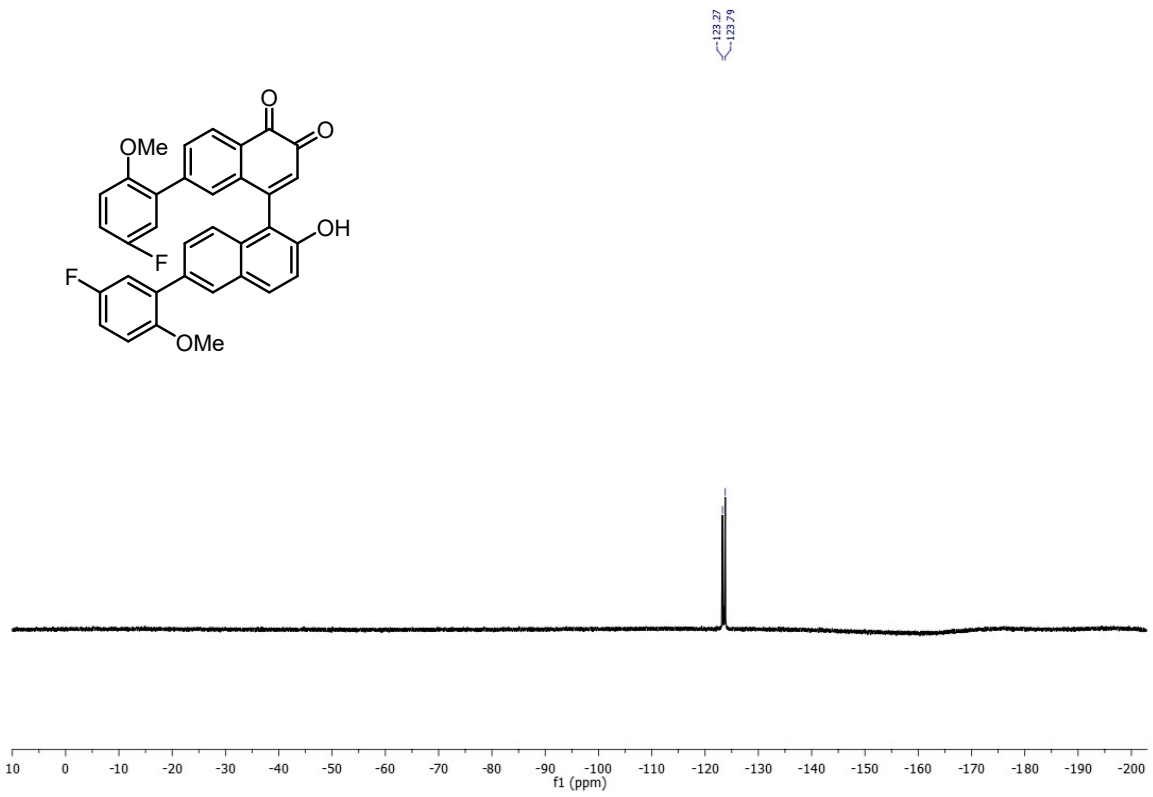
^{1}H NMR Spectrum of **10m** (400 MHz, DMSO-d_6)



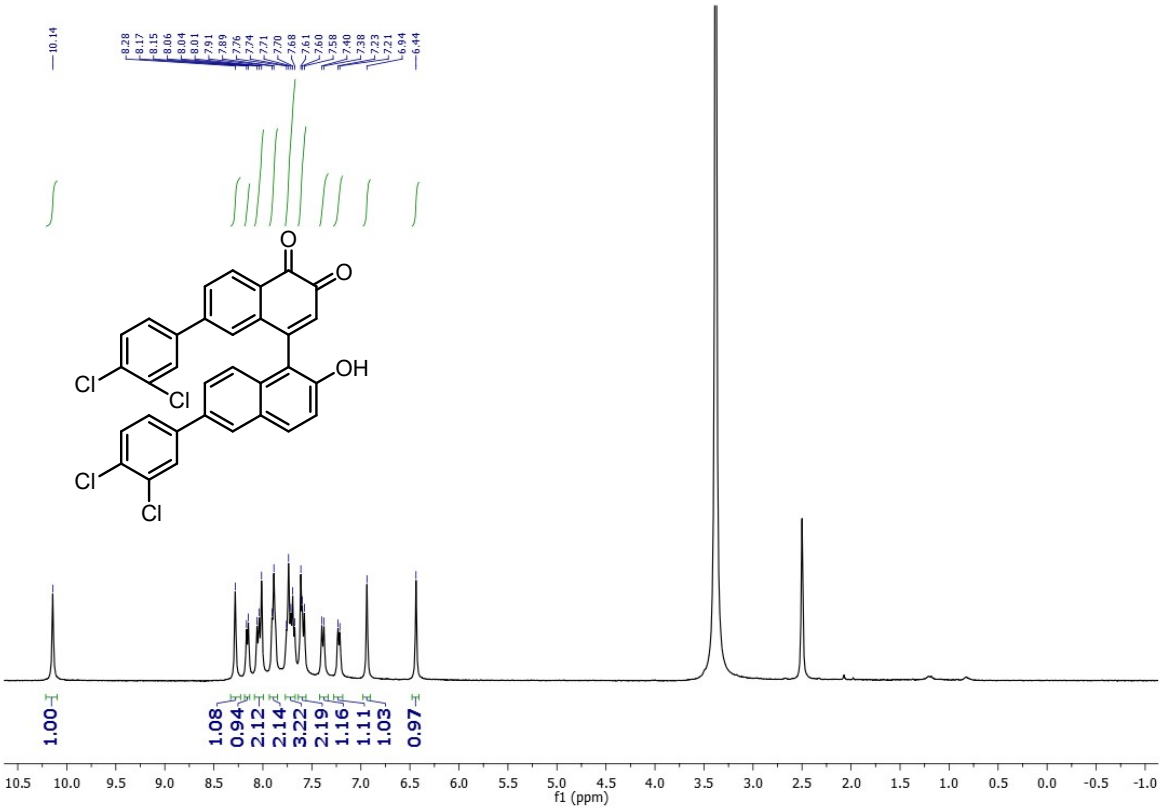
^{13}C NMR Spectrum of **10m** (100 MHz, DMSO-d_6)



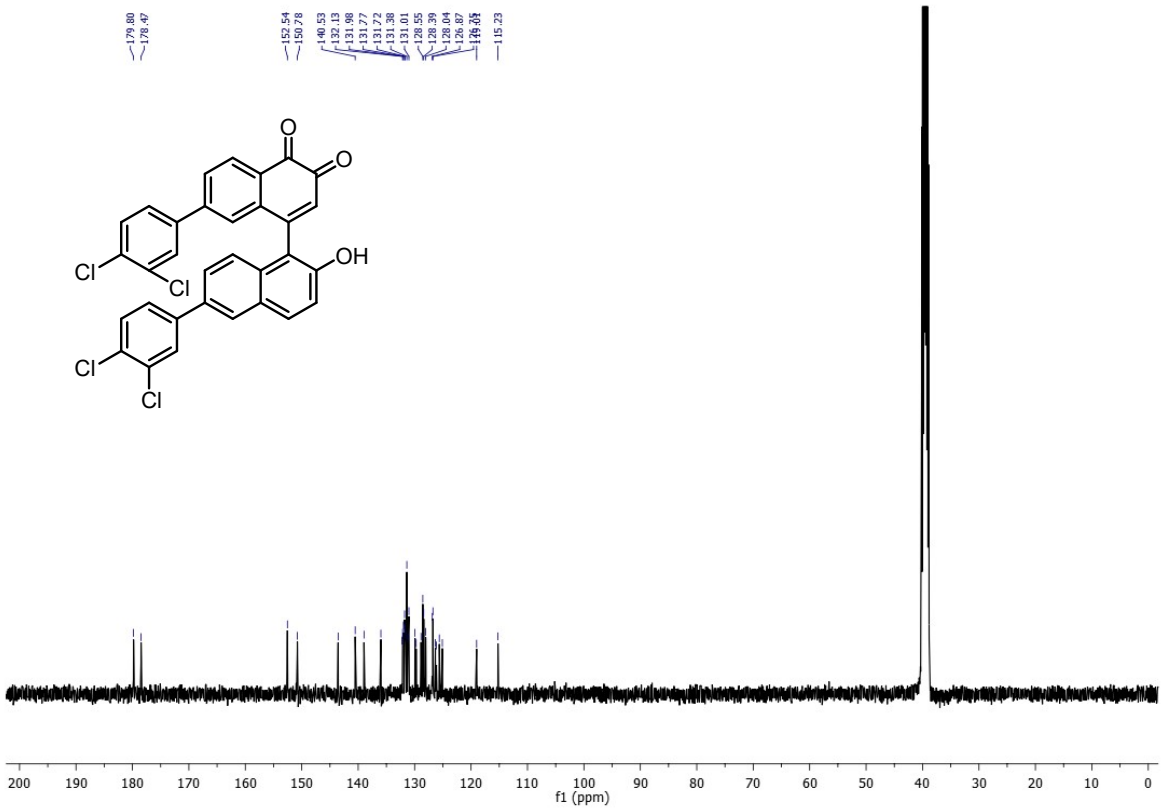
^{19}F NMR Spectrum of **10m** (377 MHz, DMSO-d_6)



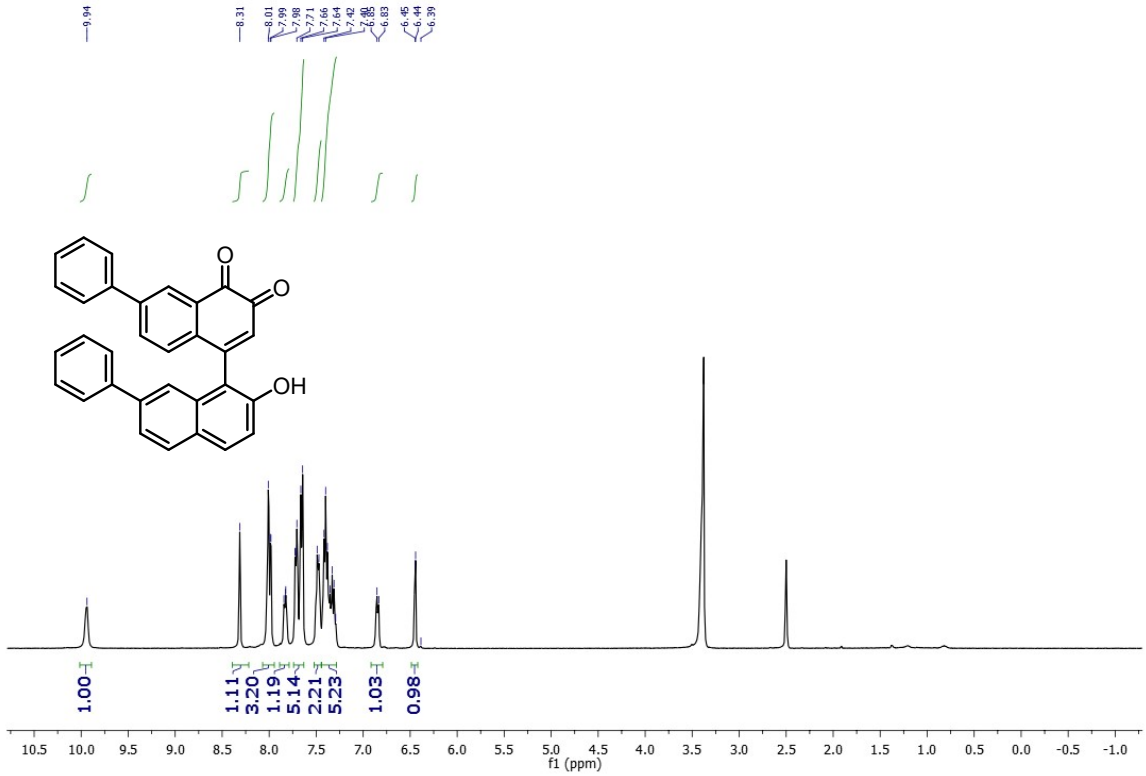
^{1}H NMR Spectrum of **10n** (400 MHz, DMSO-d_6)



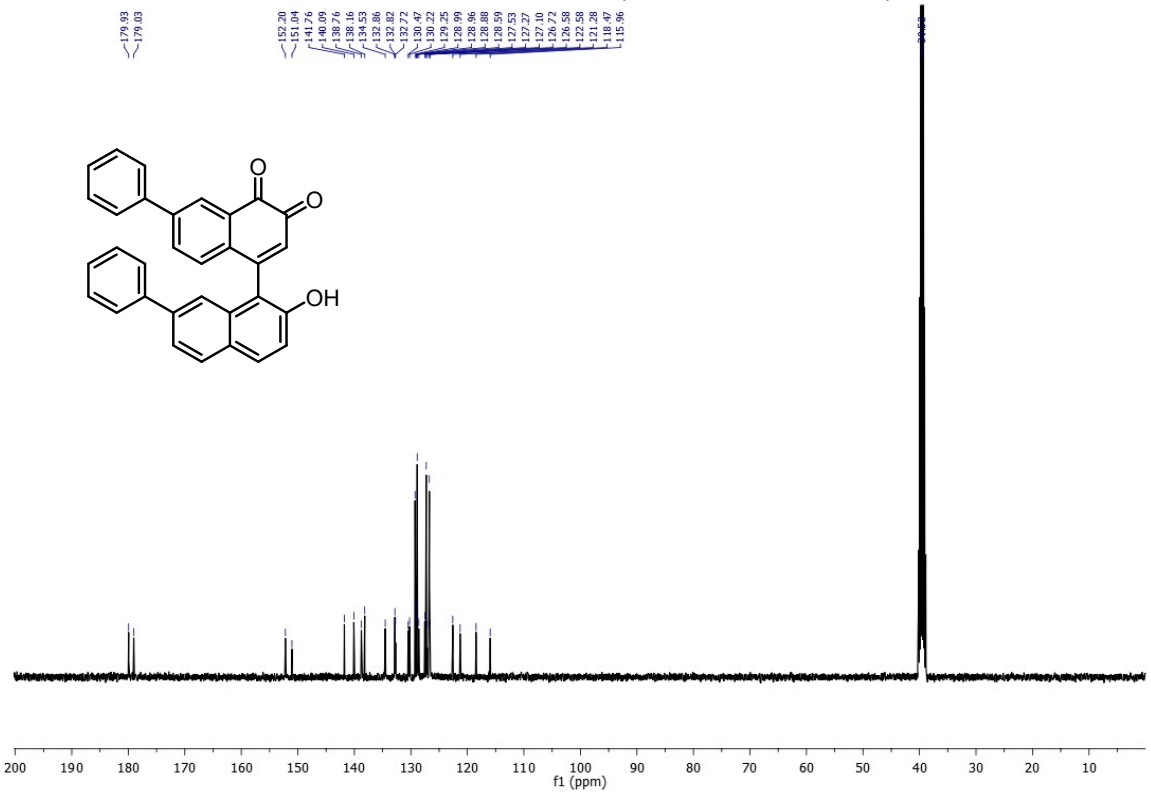
^{13}C NMR Spectrum of **10n** (100 MHz, DMSO-d_6)



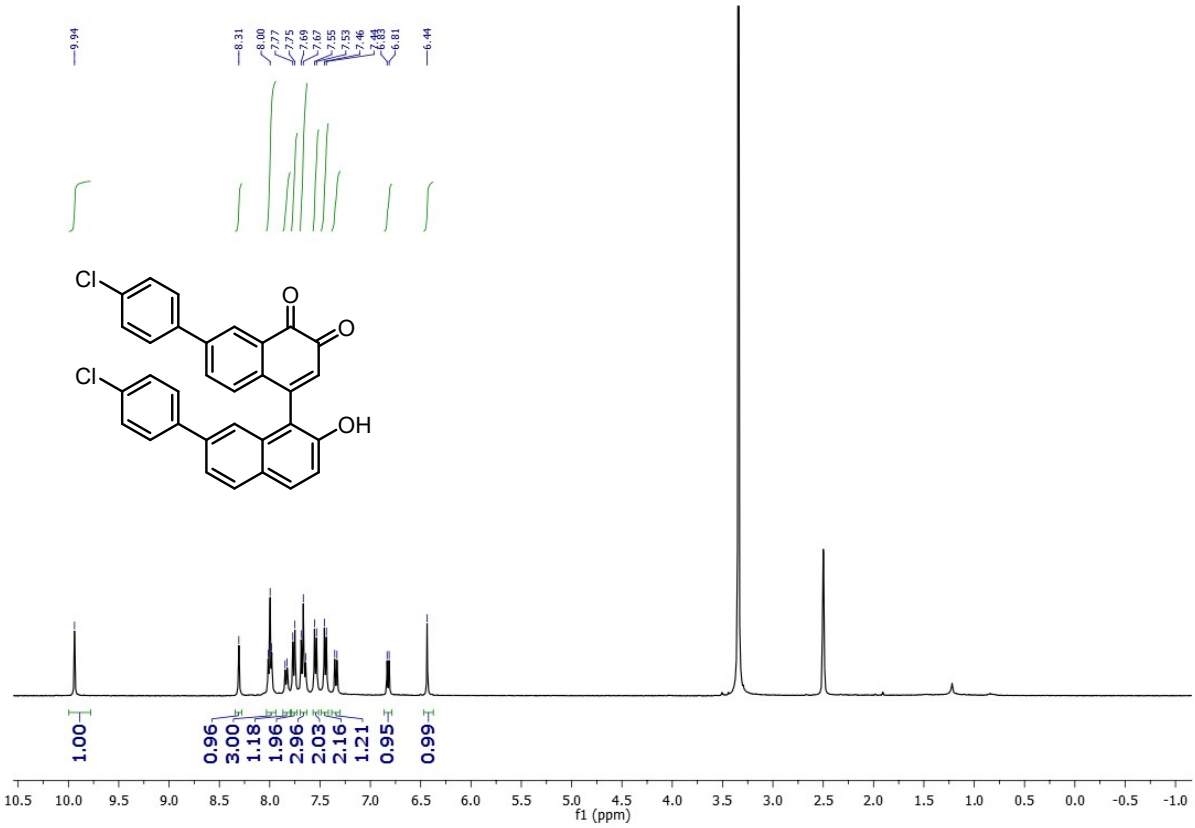
^{1}H NMR Spectrum of **10o** (400 MHz, DMSO-d_6)



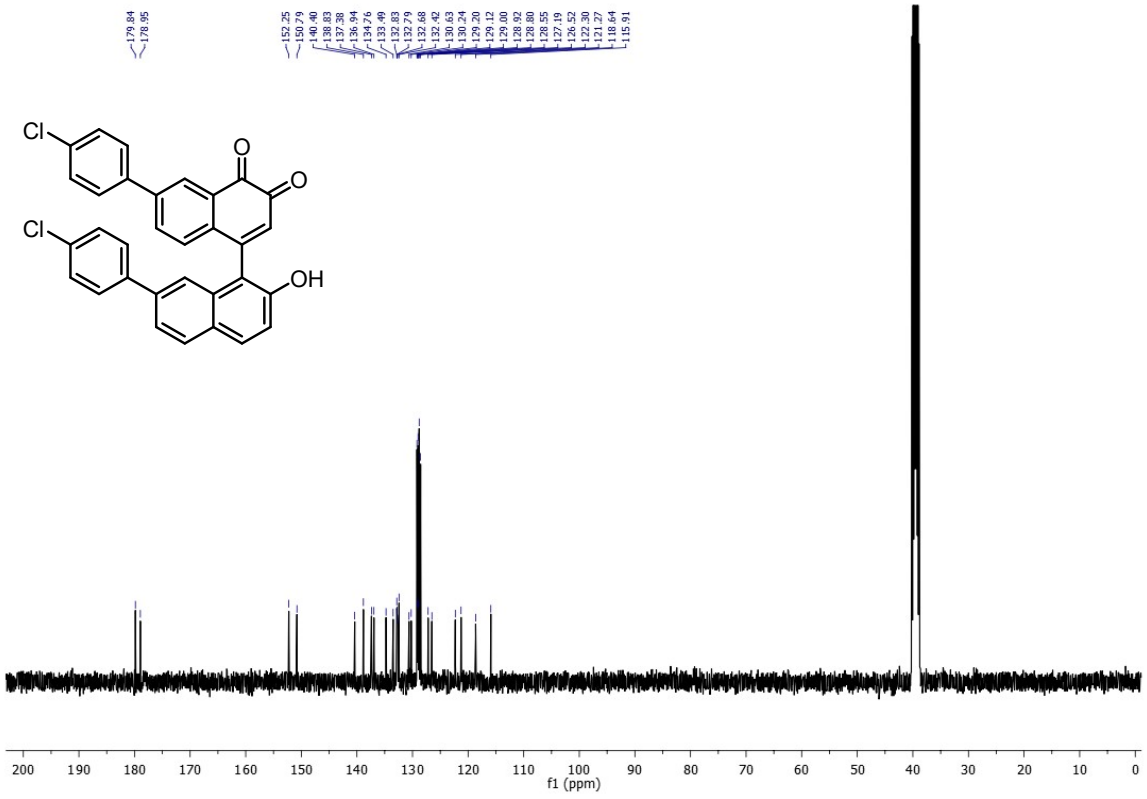
^{13}C NMR Spectrum of **10o** (100 MHz, DMSO-d_6)



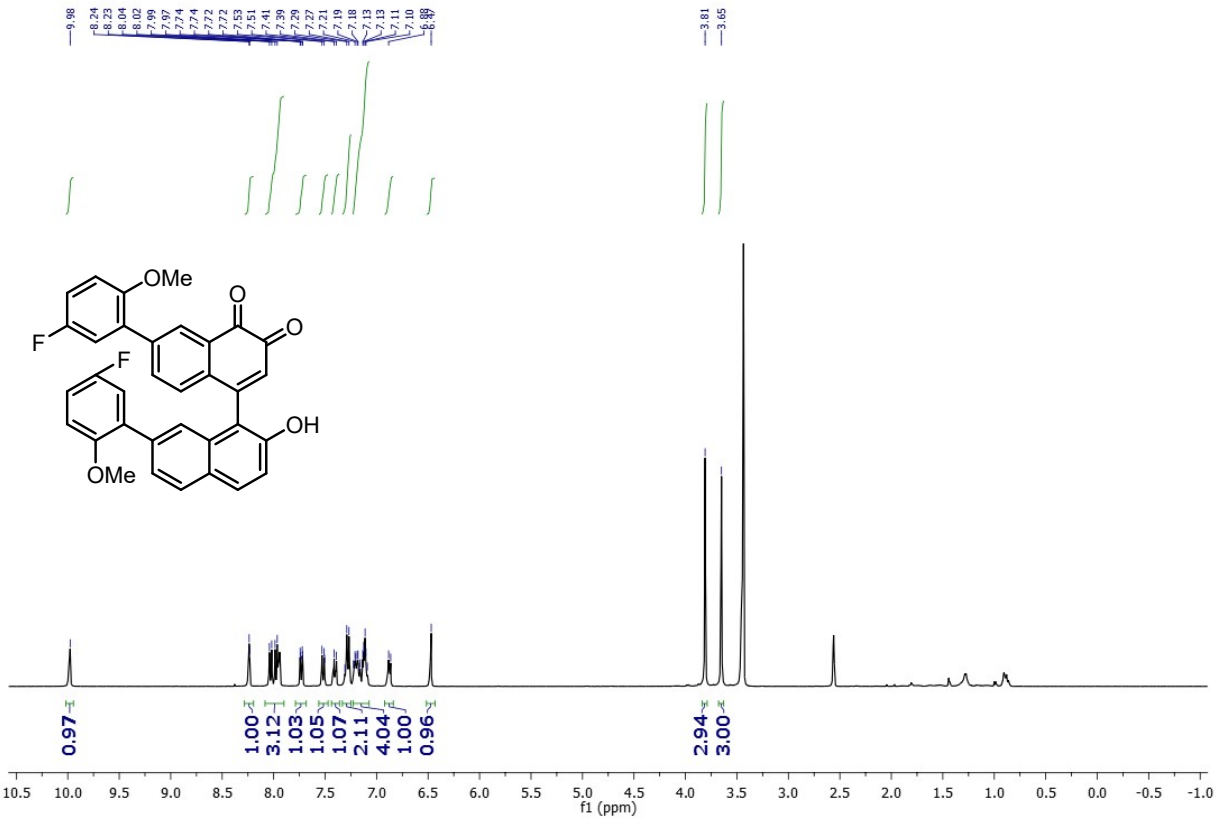
^{1}H NMR Spectrum of **10p** (400 MHz, DMSO-d_6)



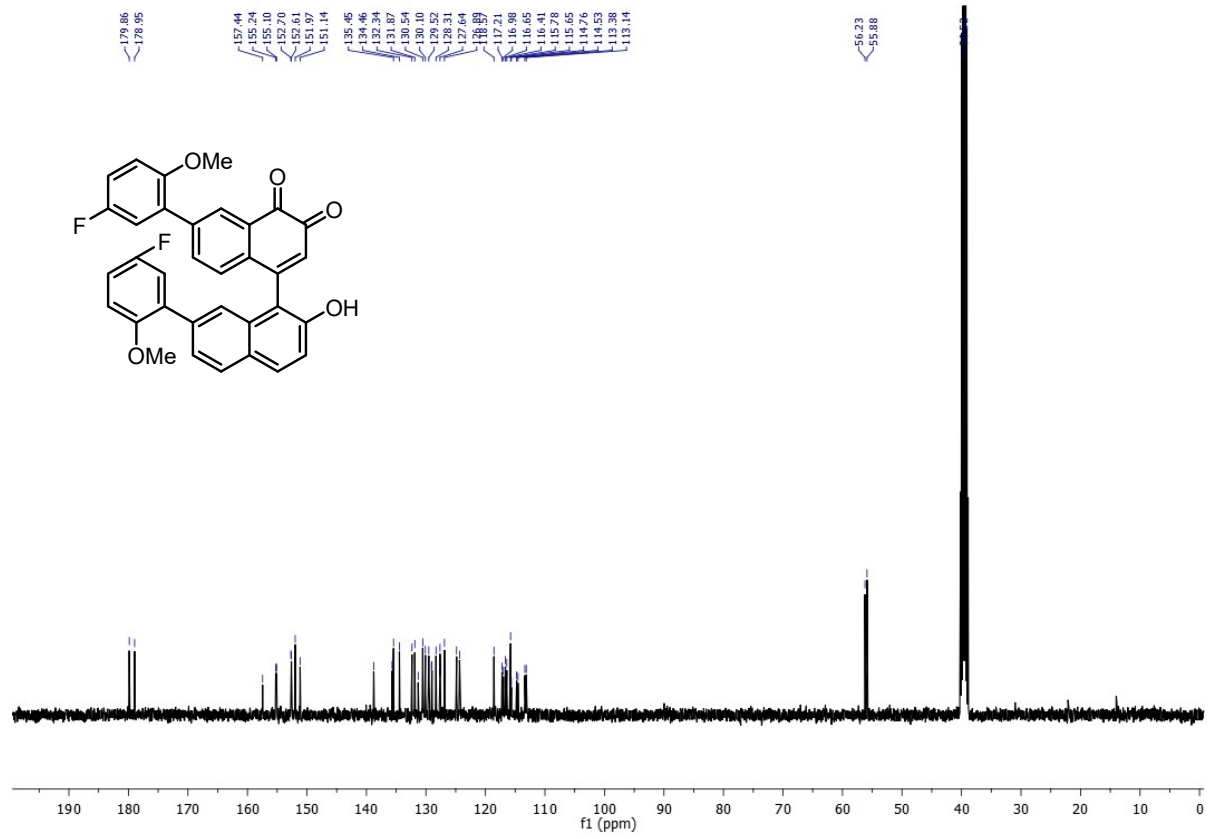
^{13}C NMR Spectrum of **10p** (100 MHz, DMSO-d_6)



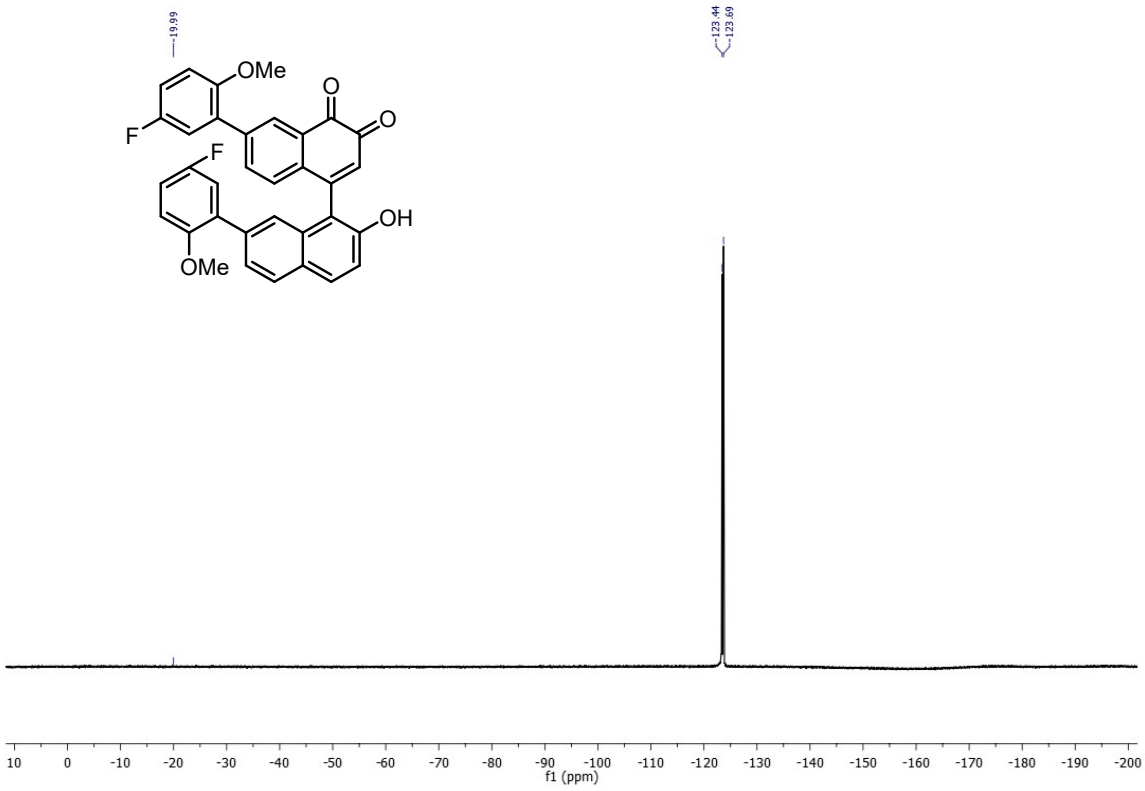
^{1}H NMR Spectrum of **10q** (400 MHz, DMSO-d_6)



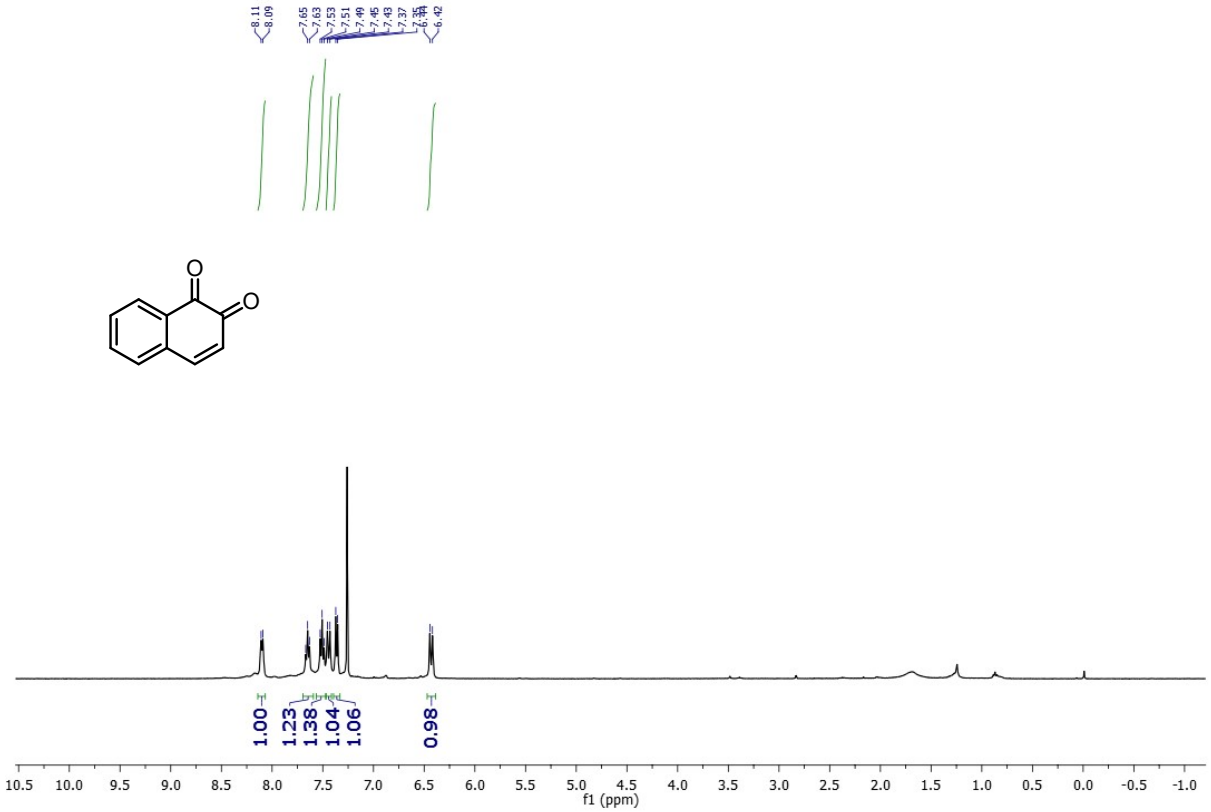
^{13}C NMR Spectrum of **10q** (100 MHz, DMSO-d_6)



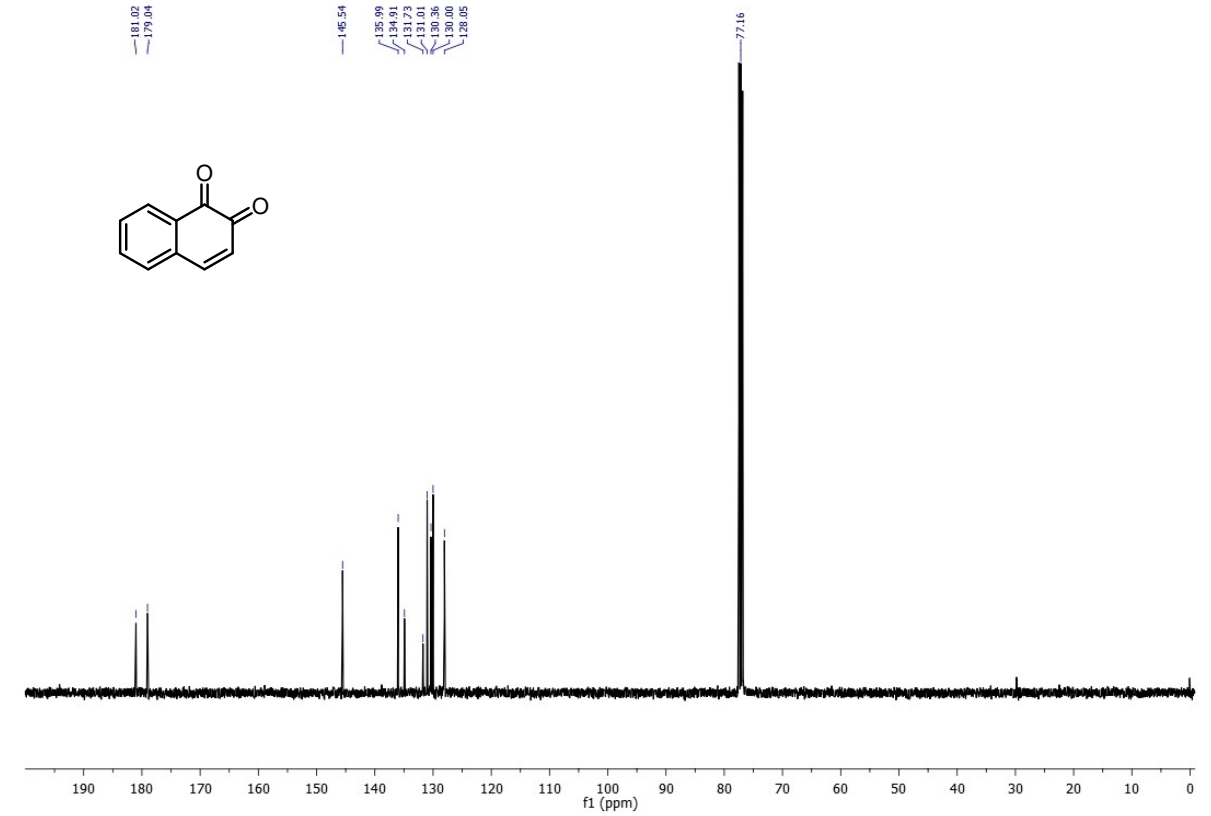
^{19}F NMR Spectrum of **10q** (377 MHz, DMSO-d_6)



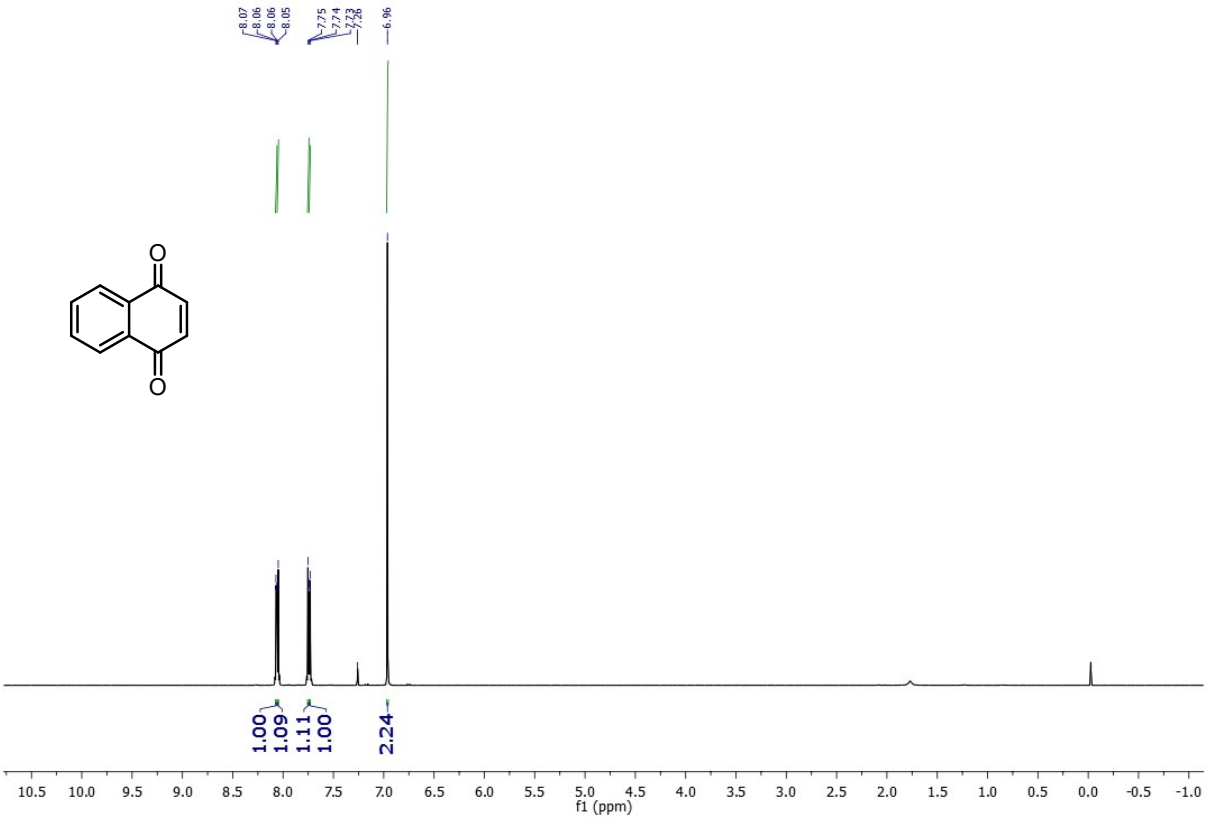
^{1}H NMR Spectrum of intermediate **9ai** (400 MHz, $CDCl_3$)



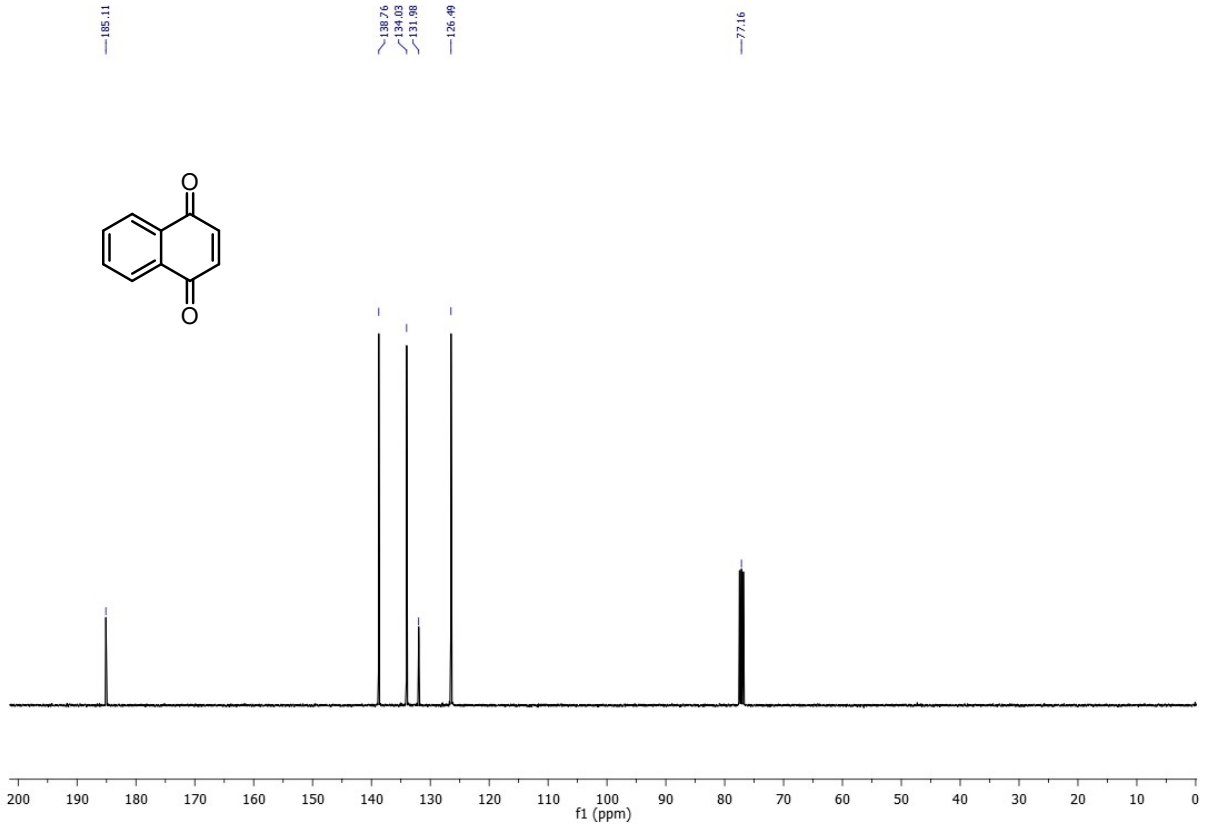
^{13}C NMR Spectrum of intermediate **9ai** (100 MHz, $CDCl_3$)



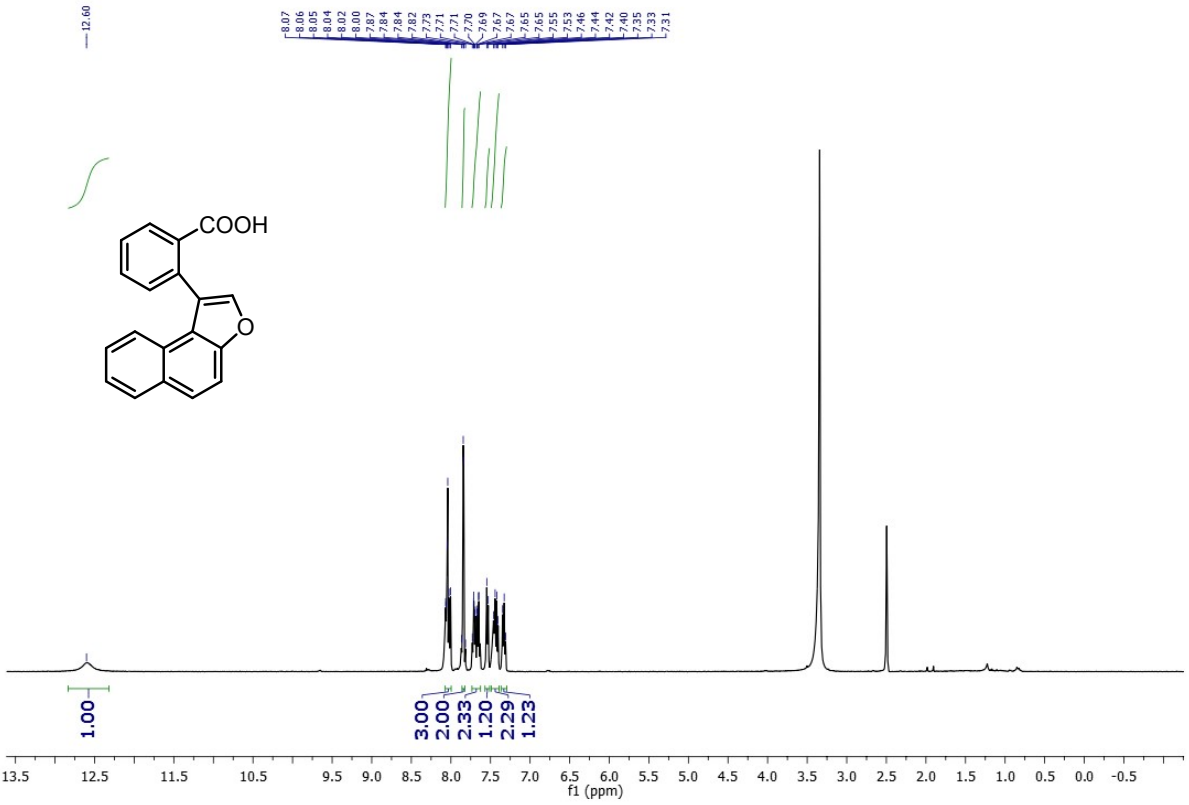
^{1}H NMR Spectrum of **Naphthalene-1,4-dione** (400 MHz, $CDCl_3$)



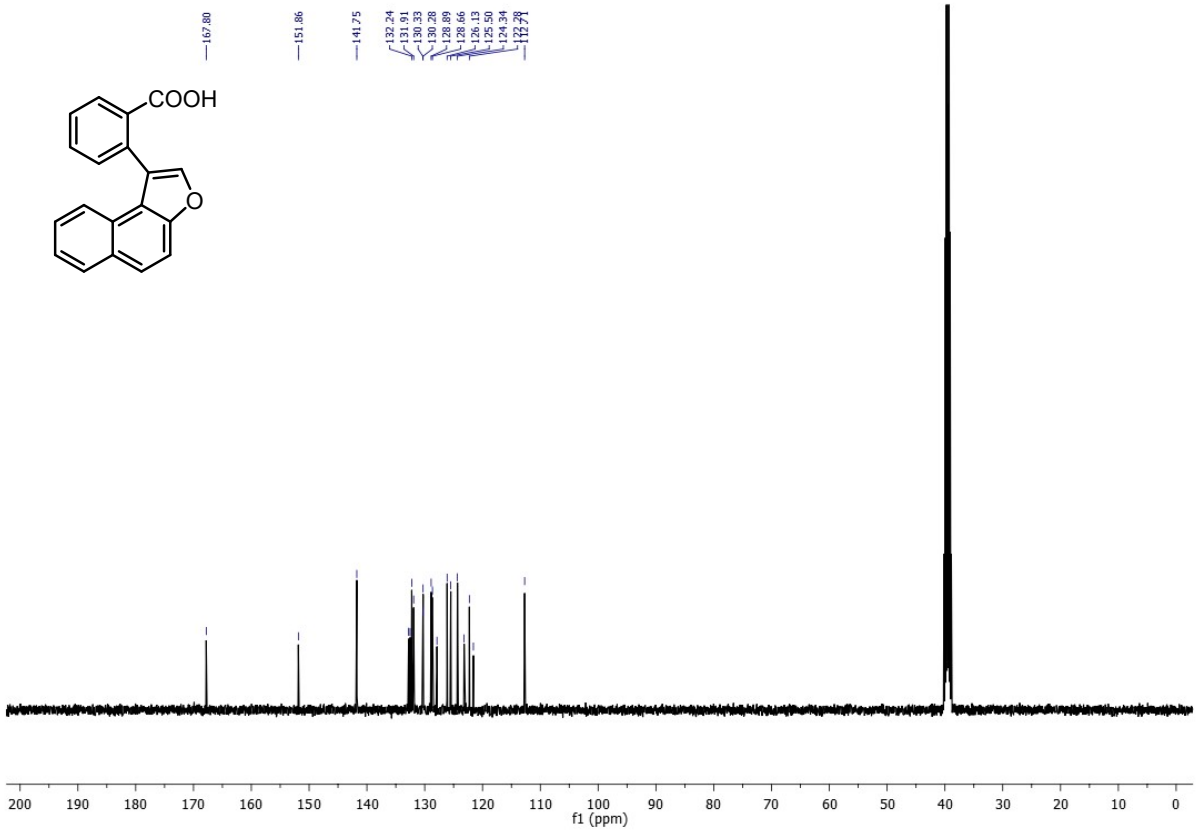
^{13}C NMR Spectrum of **Naphthalene-1,4-dione** (100 MHz, $CDCl_3$)



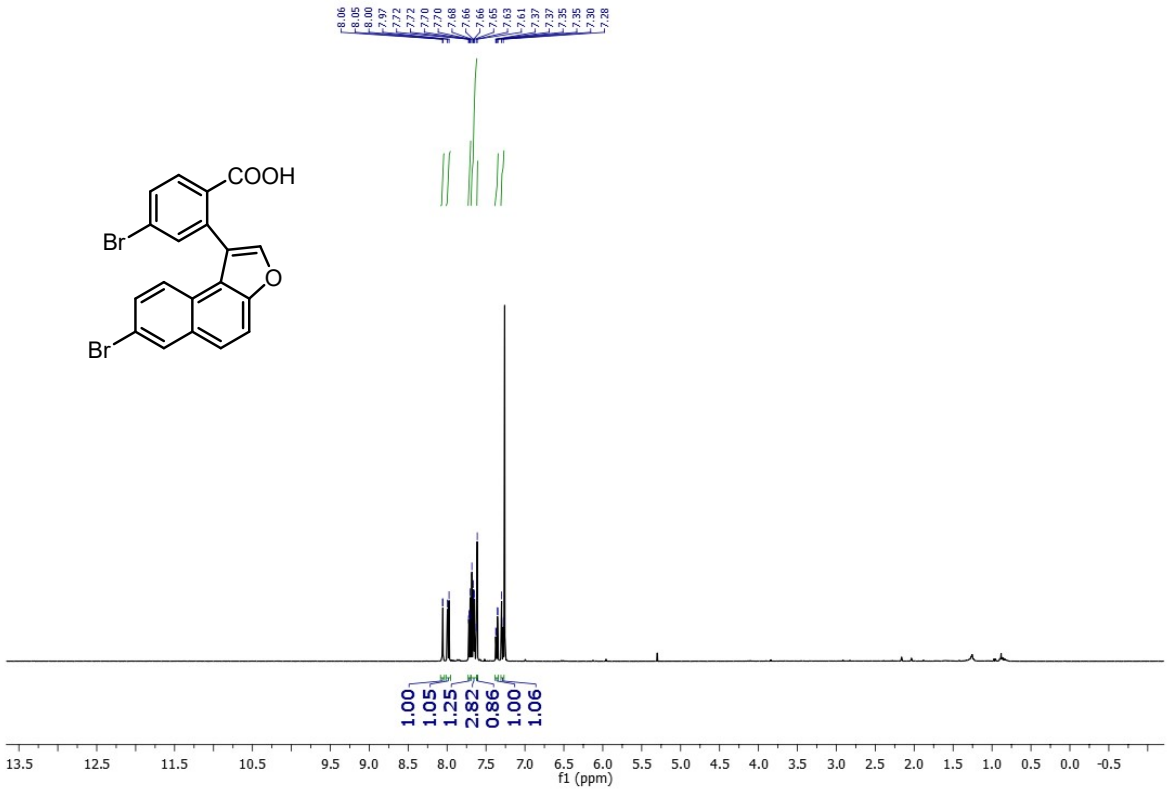
^{1}H NMR Spectrum of **11a** (400 MHz, $CDCl_3$)



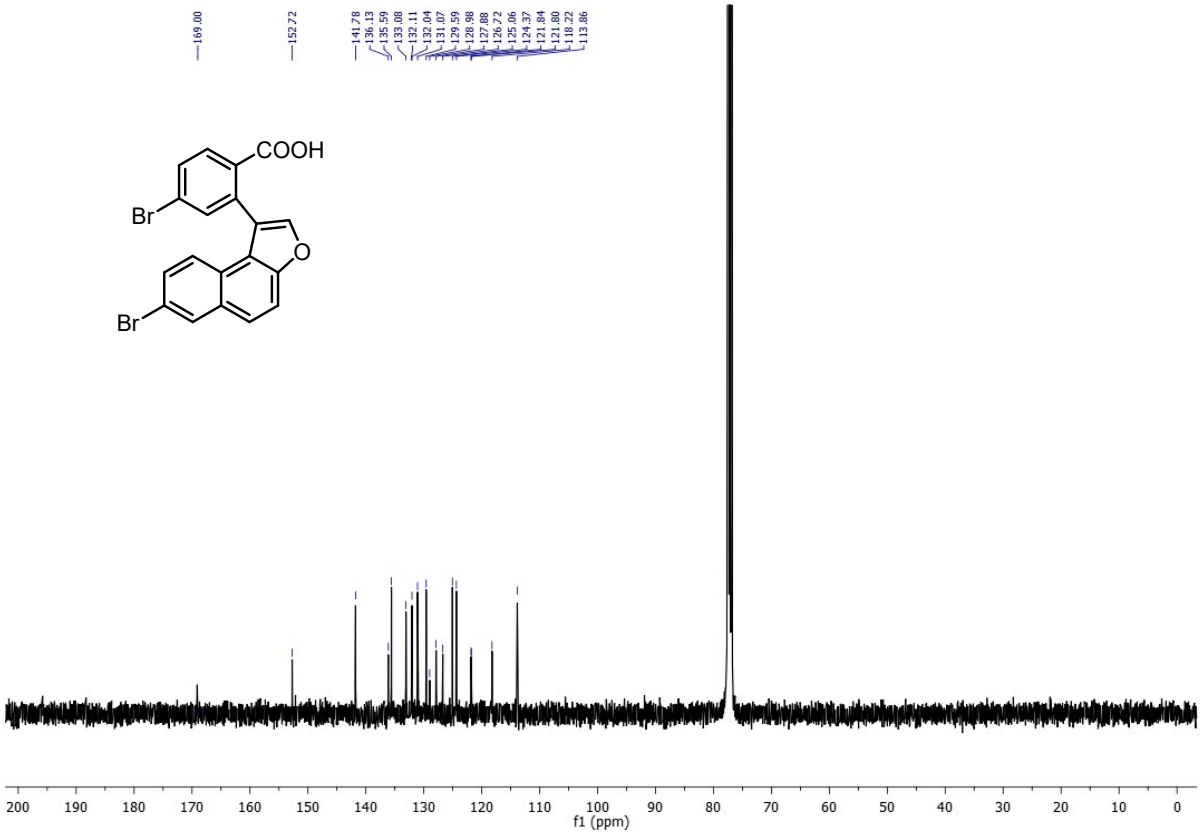
^{13}C NMR Spectrum of **11a** (100 MHz, DMSO-d_6)



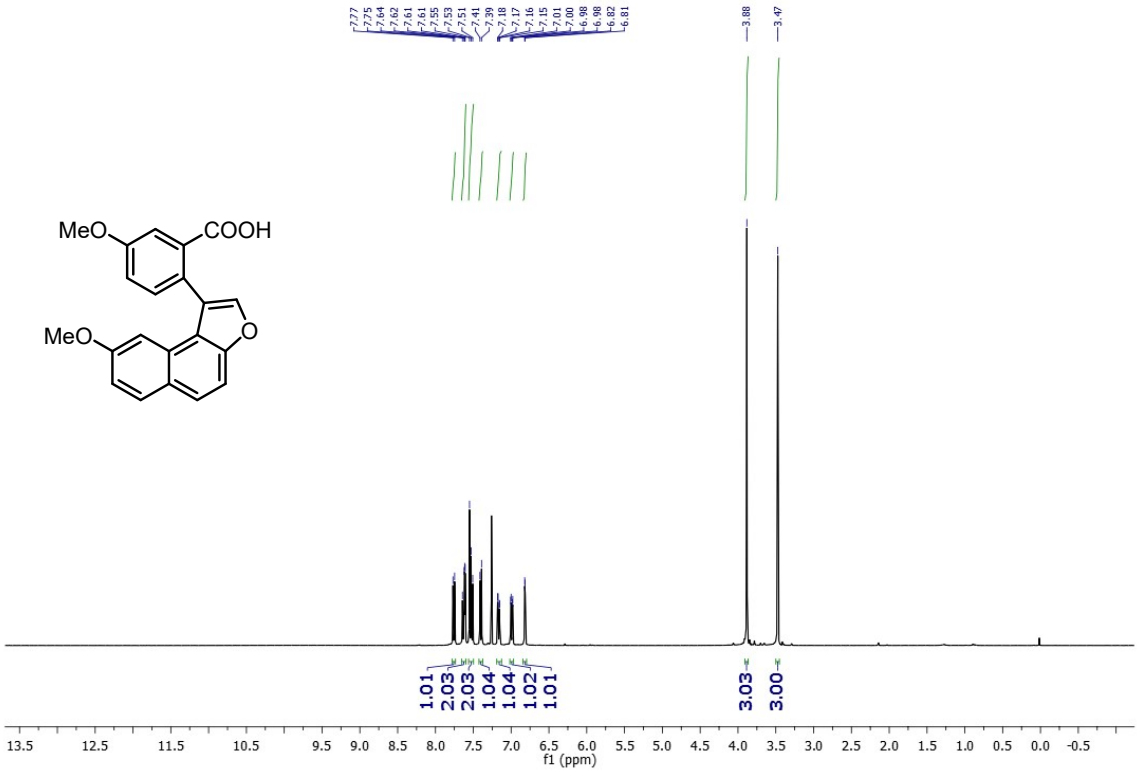
^{1}H NMR Spectrum of **11b** (400 MHz, $CDCl_3$)



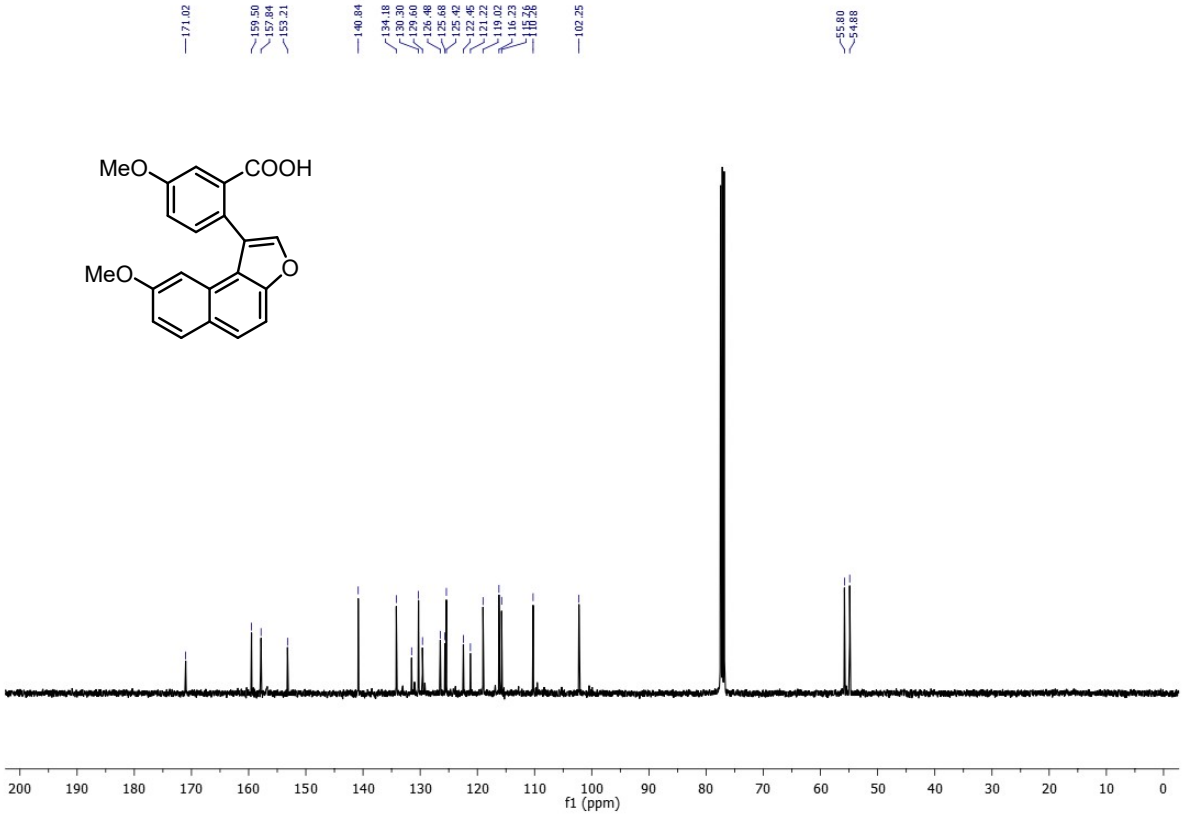
^{13}C NMR Spectrum of **11b** (100 MHz, $CDCl_3$)



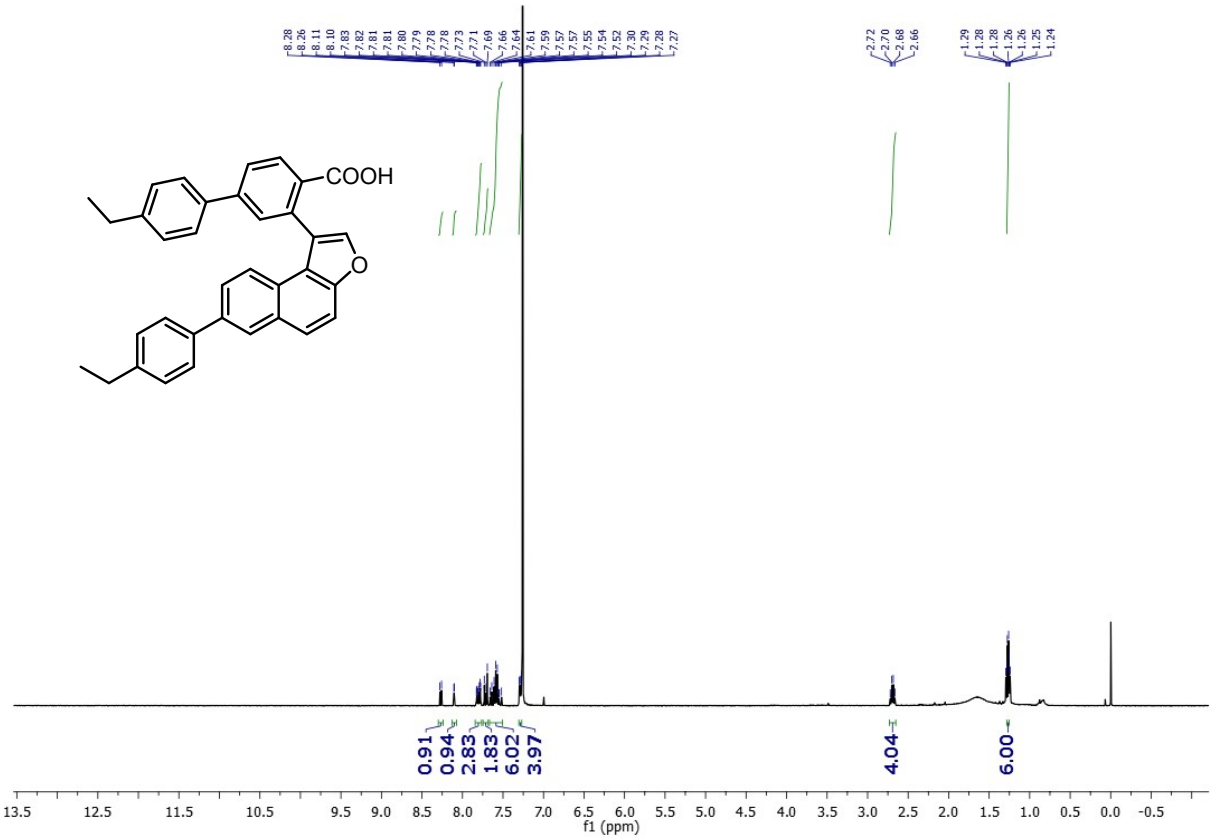
^{1}H NMR Spectrum of **11c** (400 MHz, $CDCl_3$)



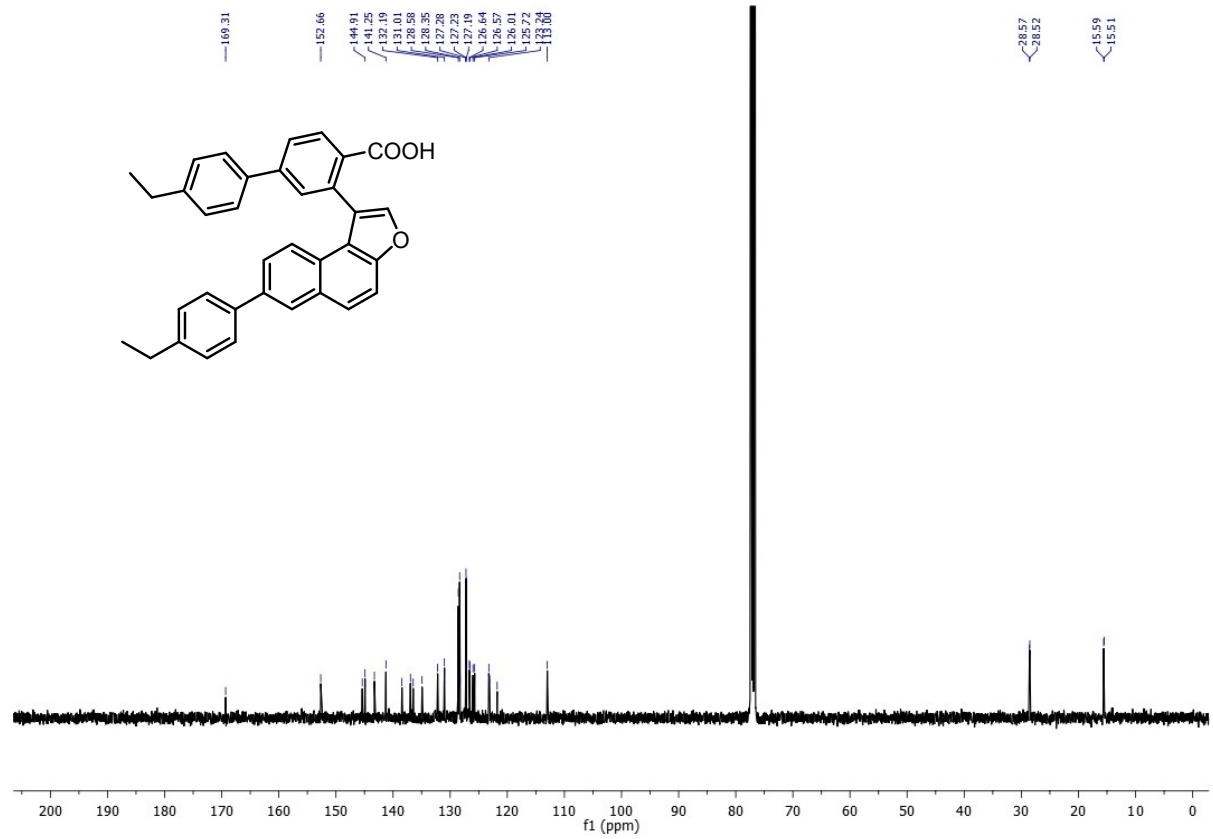
^{13}C NMR Spectrum of **11c** (100 MHz, $CDCl_3$)



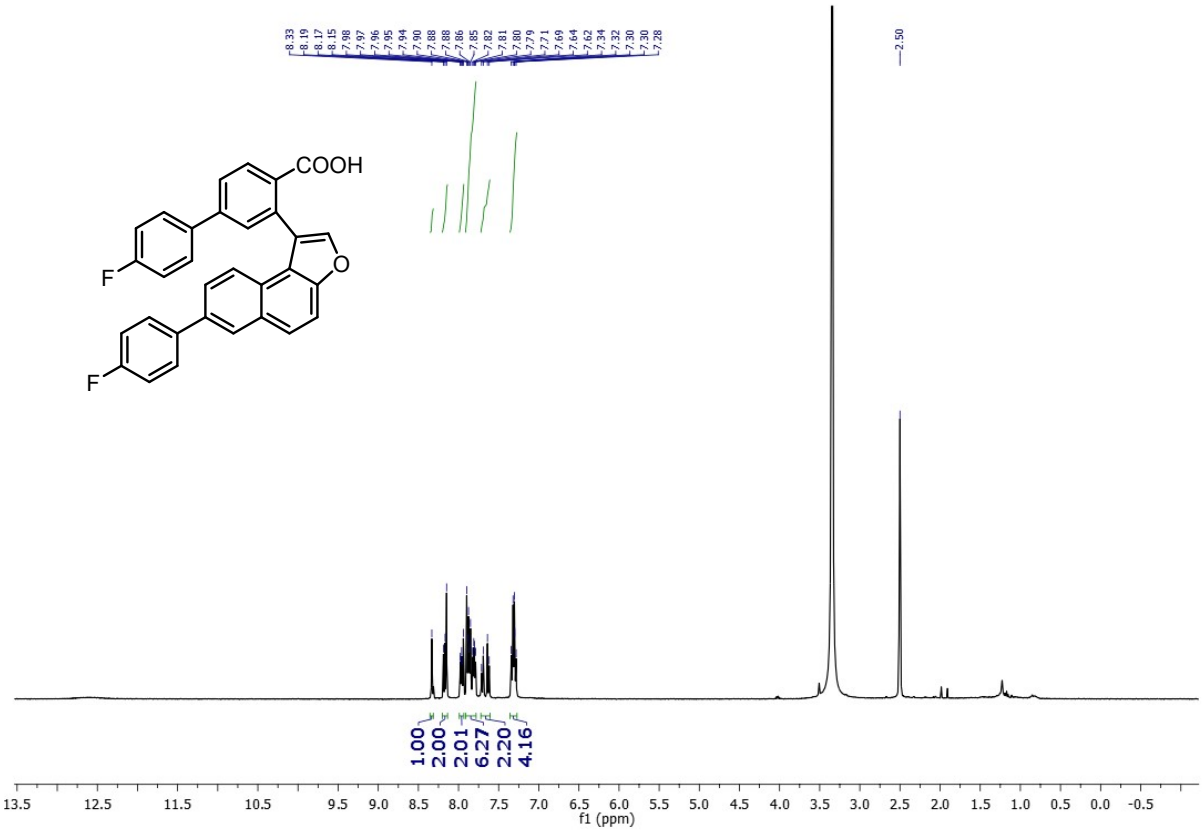
^{1}H NMR Spectrum of **11f** (400 MHz, $CDCl_3$)



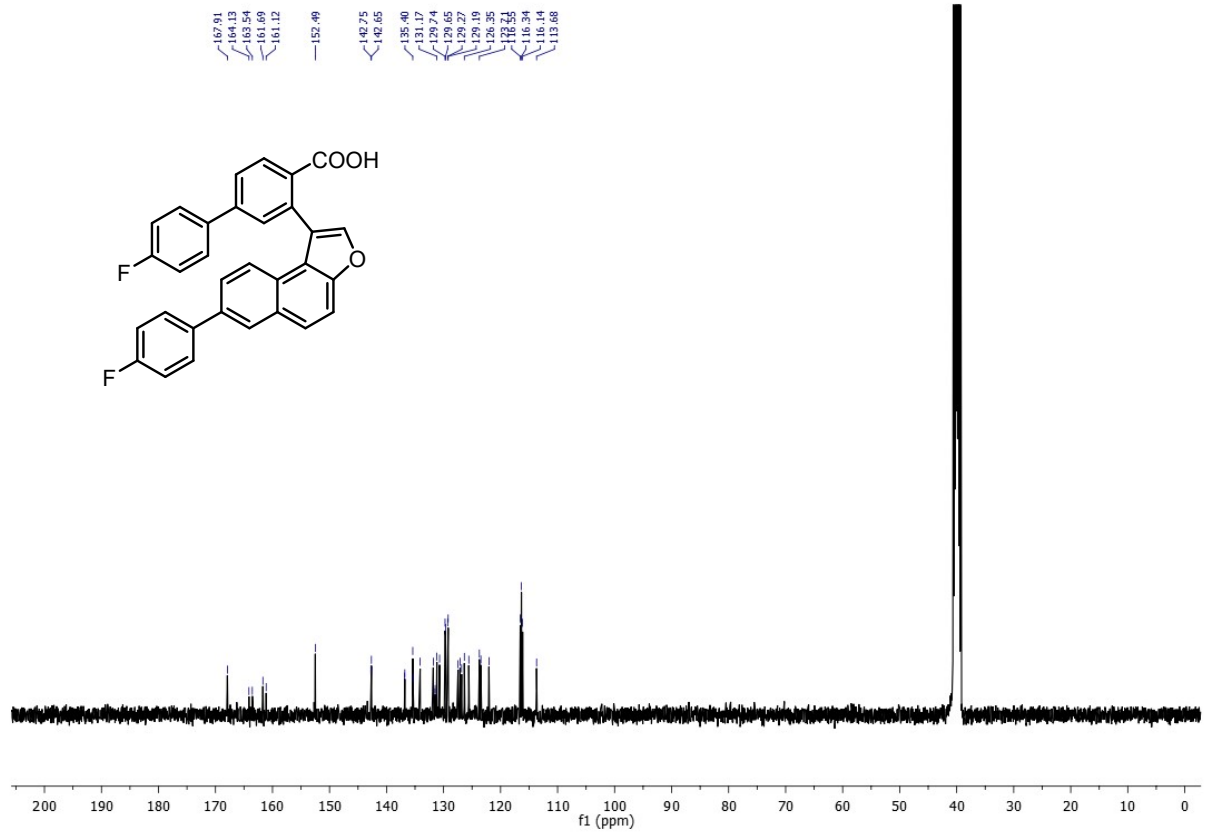
^{13}C NMR Spectrum of **11f** (100 MHz, $CDCl_3$)



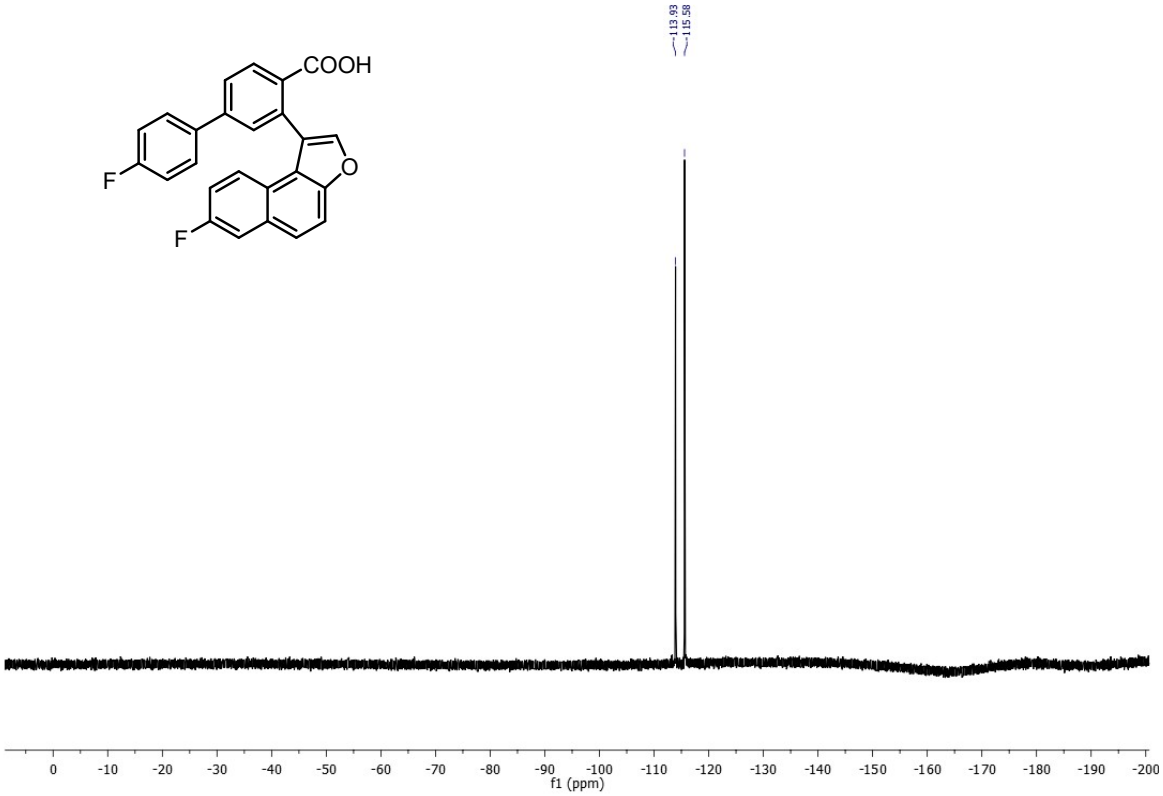
^{1}H NMR Spectrum of **11g** (400 MHz, DMSO-d_6)



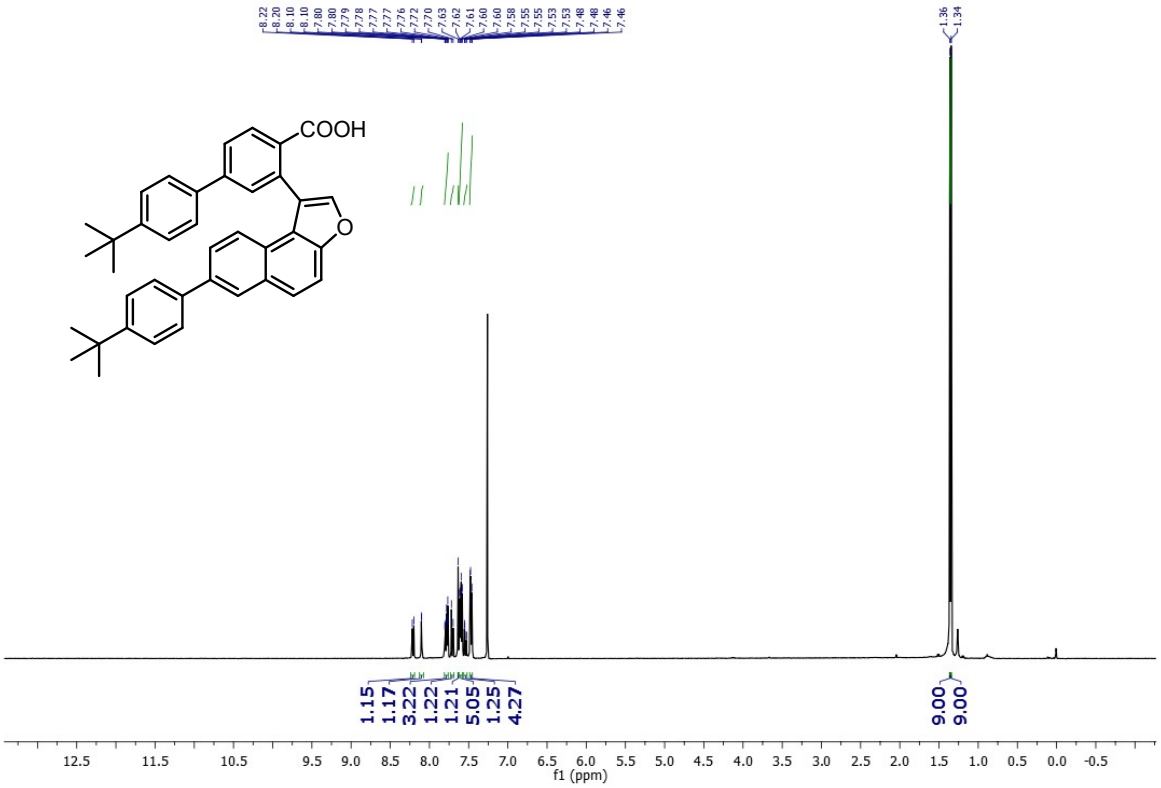
^{13}C NMR Spectrum of **11g** (100 MHz, DMSO-d_6)



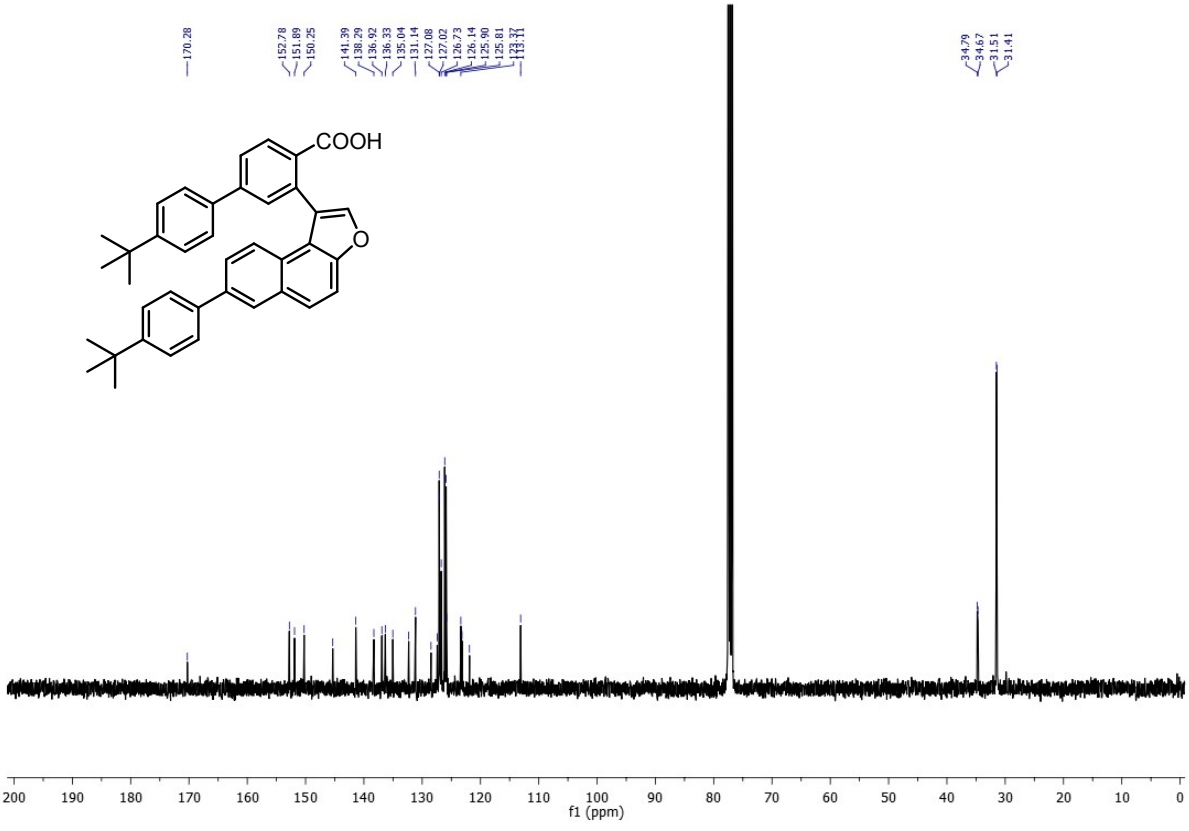
^{19}F NMR Spectrum of **11g** (377 MHz, DMSO-d_6)



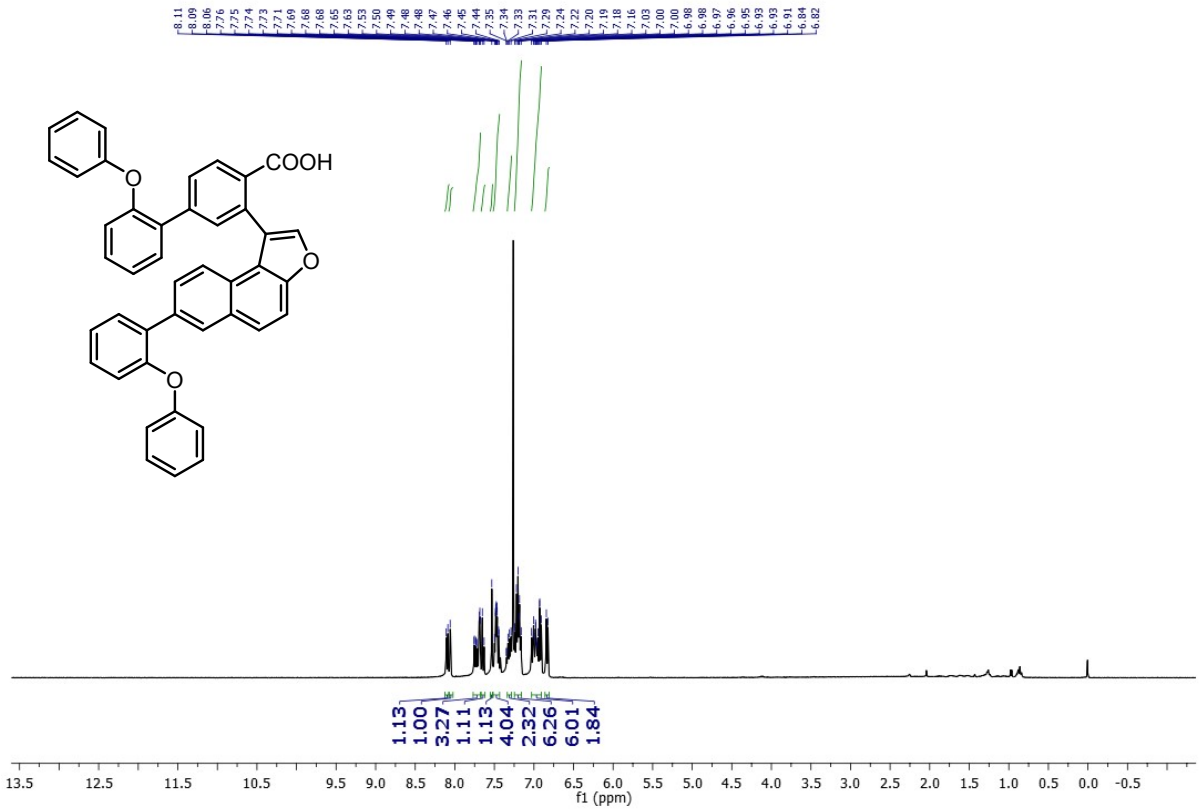
^{1}H NMR Spectrum of **11i** (400 MHz, $CDCl_3$)



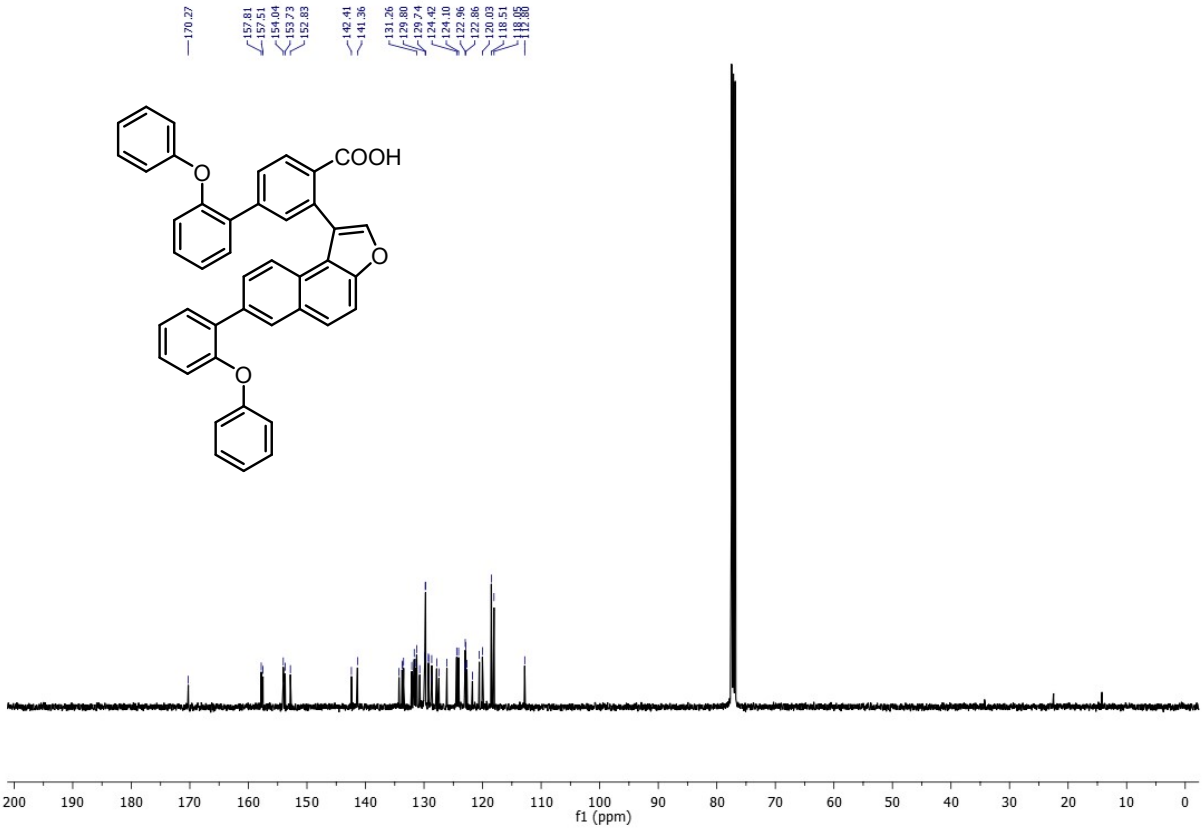
^{13}C NMR Spectrum of **11i** (100 MHz, $CDCl_3$)



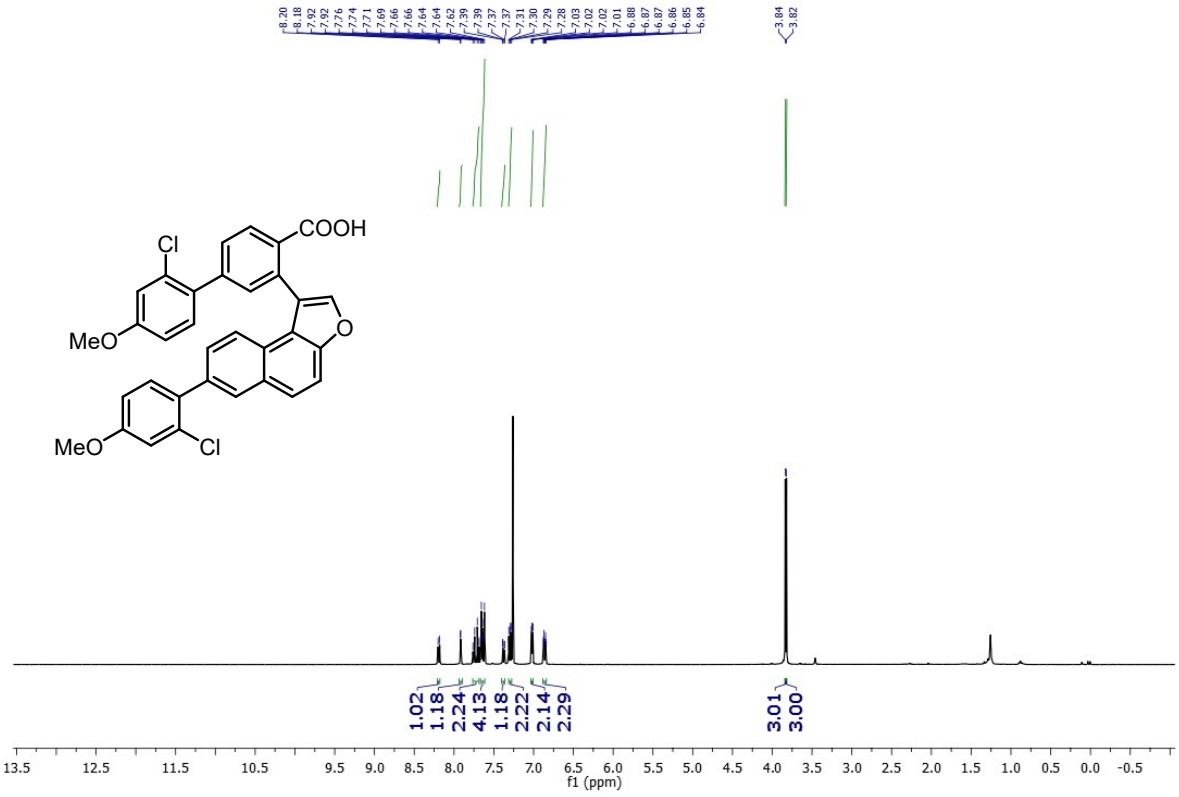
^{1}H NMR Spectrum of **11k** (400 MHz, $CDCl_3$)



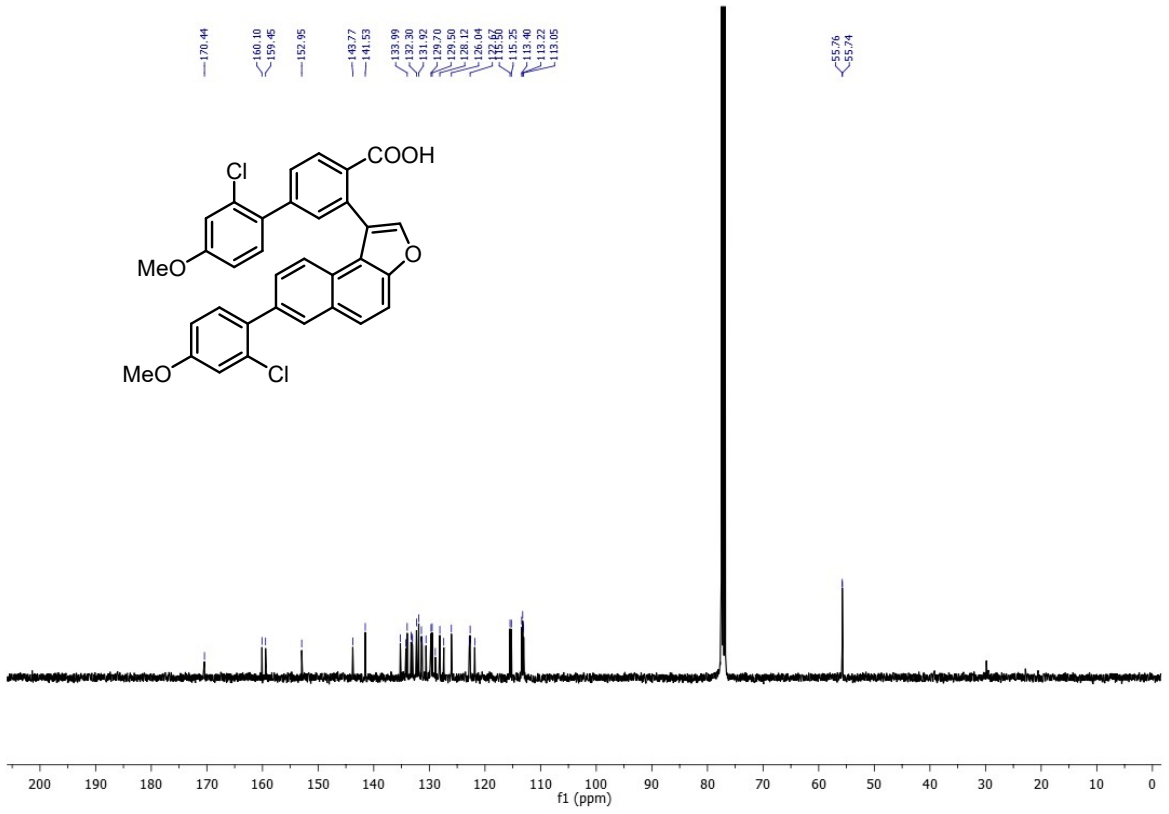
^{13}C NMR Spectrum of **11k** (100 MHz, $CDCl_3$)



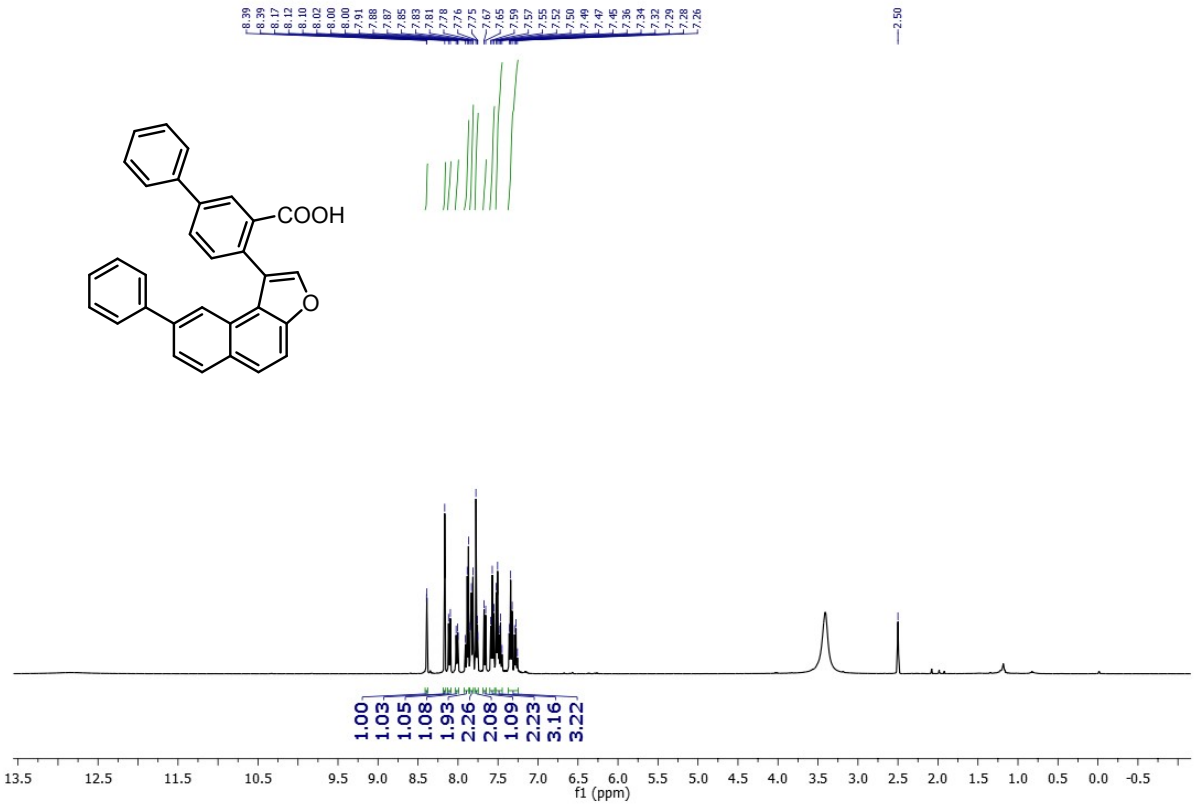
^{1}H NMR Spectrum of **11l** (400 MHz, $CDCl_3$)



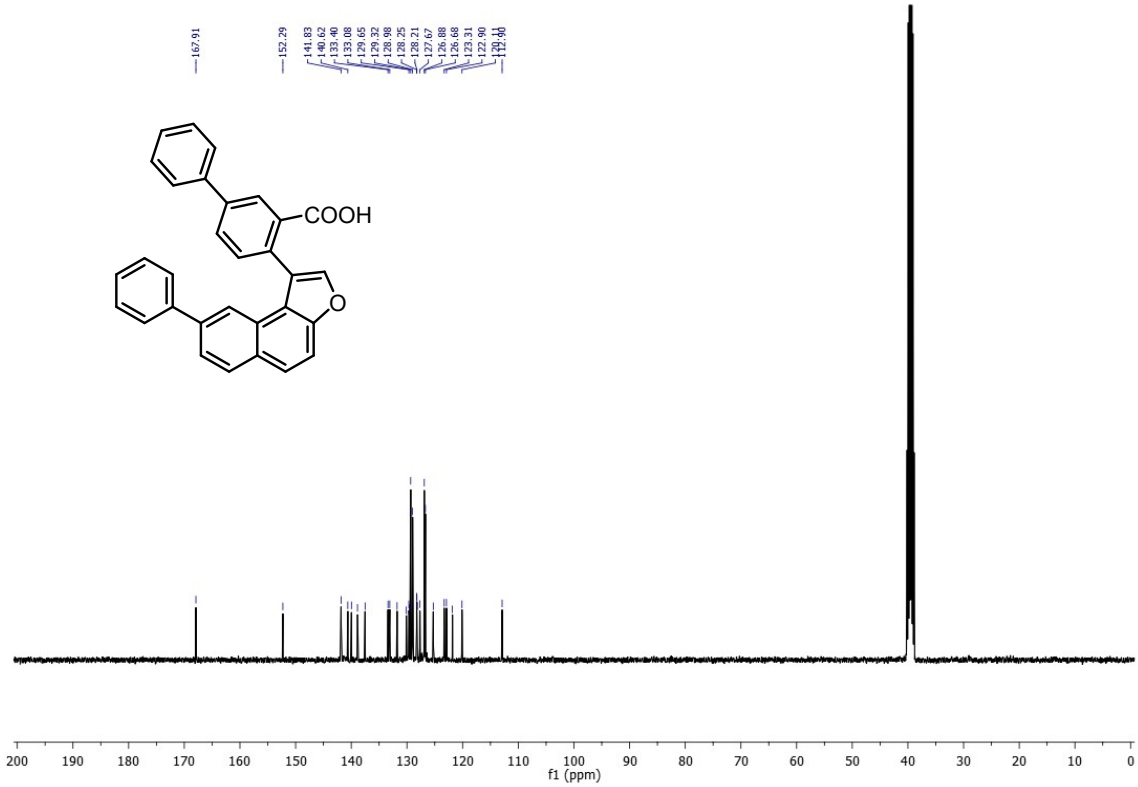
^{13}C NMR Spectrum of **11l** (100 MHz, $CDCl_3$)



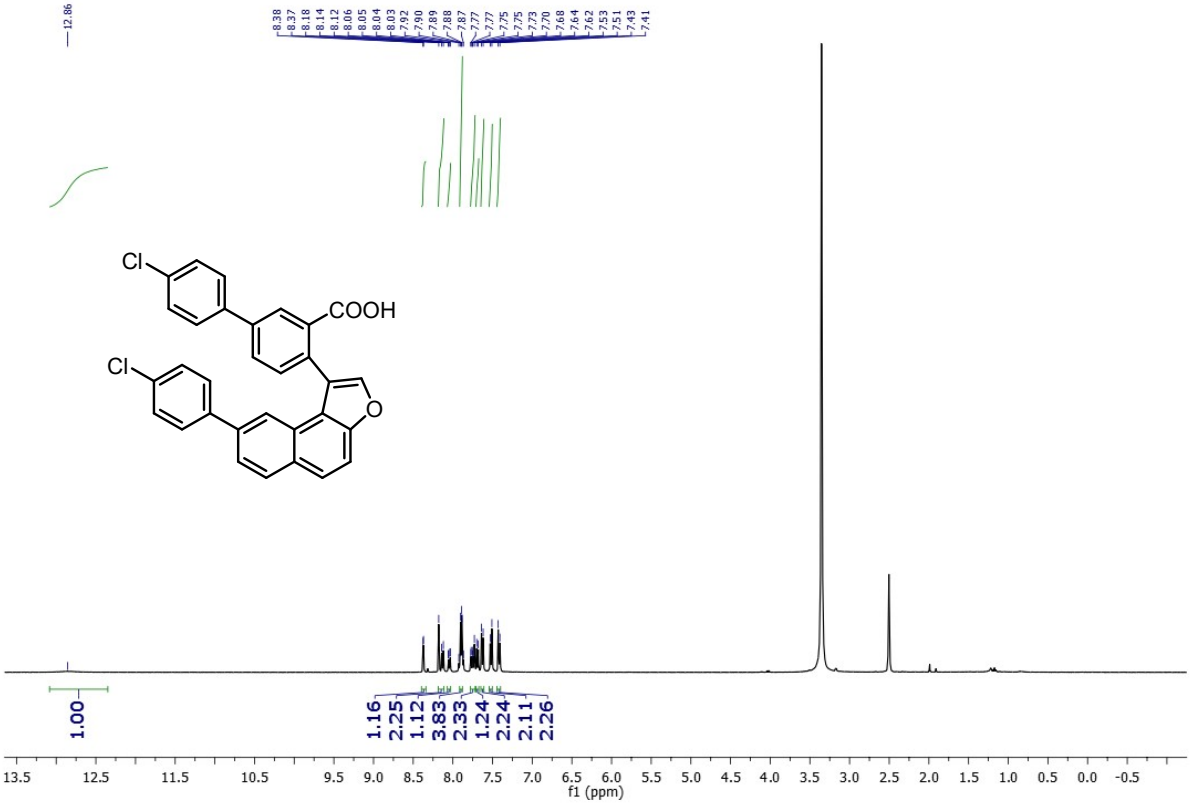
^{1}H NMR Spectrum of **11o** (400 MHz, DMSO-d_6)



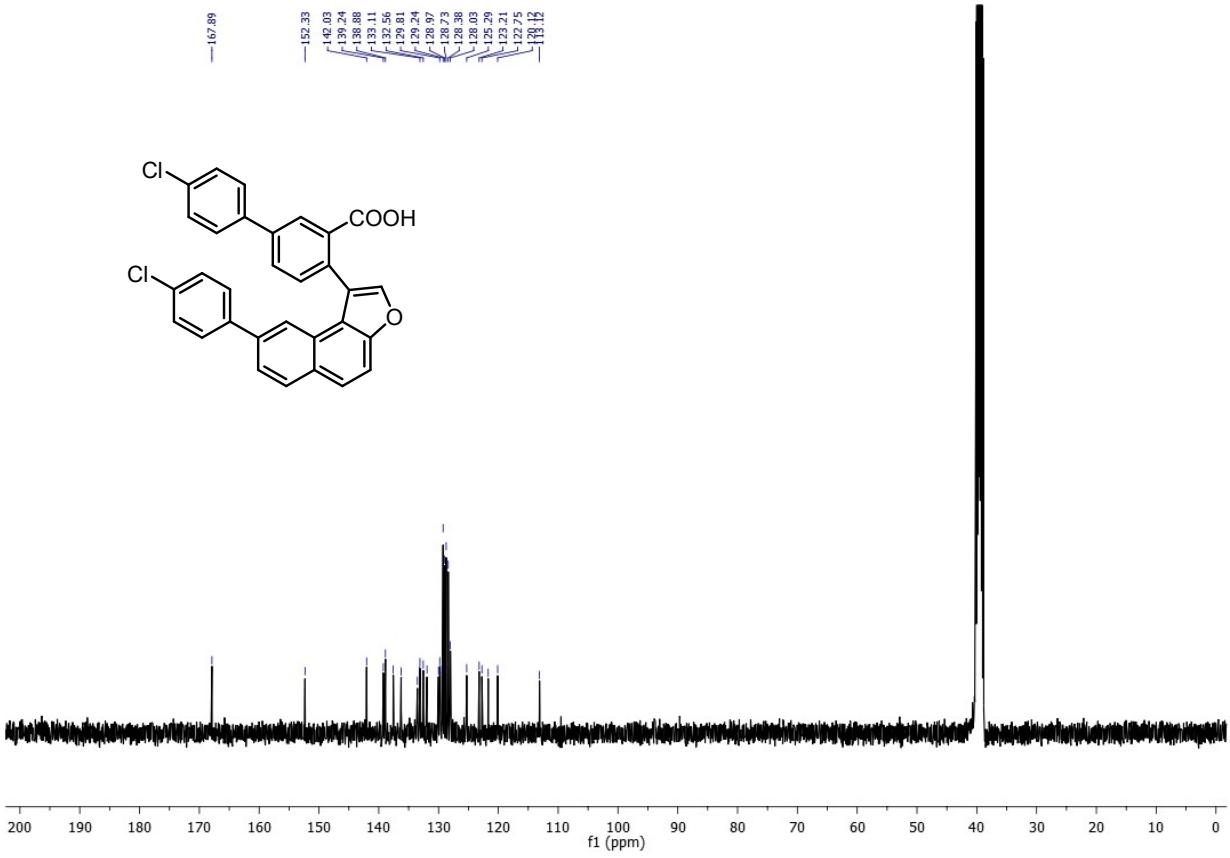
^{13}C NMR Spectrum of **11o** (100 MHz, DMSO-d_6)



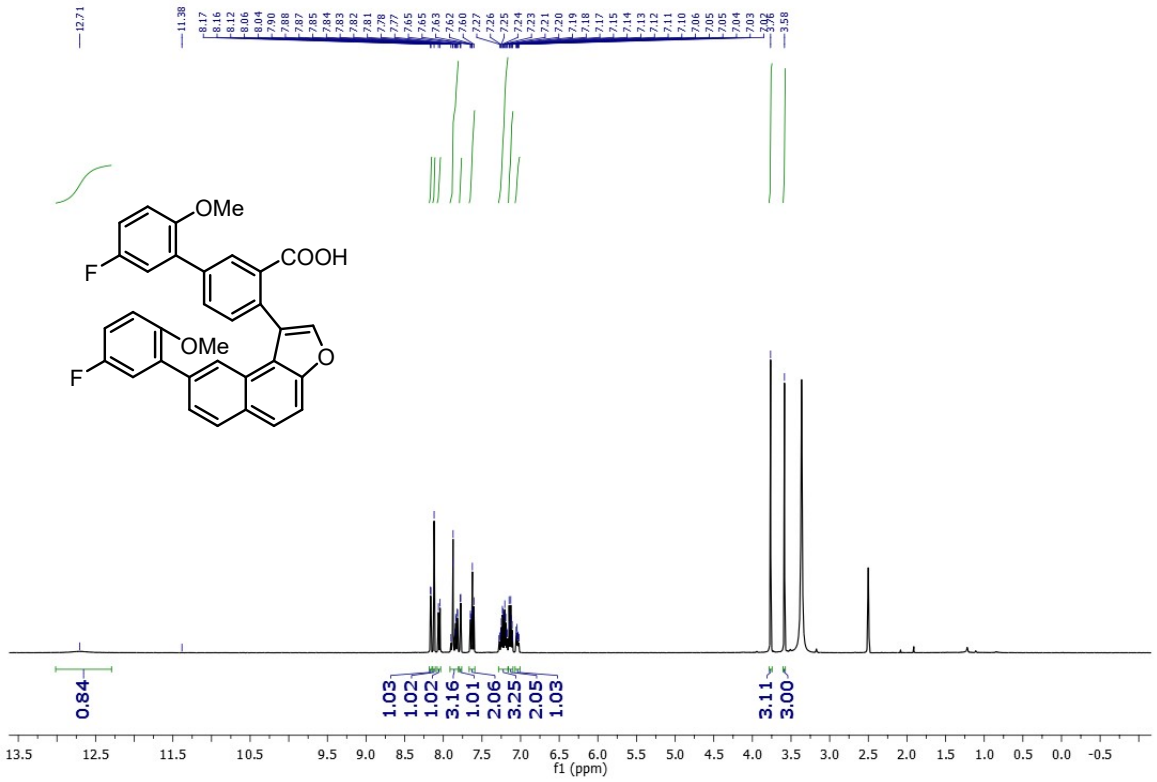
^{1}H Spectrum of **11p** (400 MHz, DMSO-d_6)



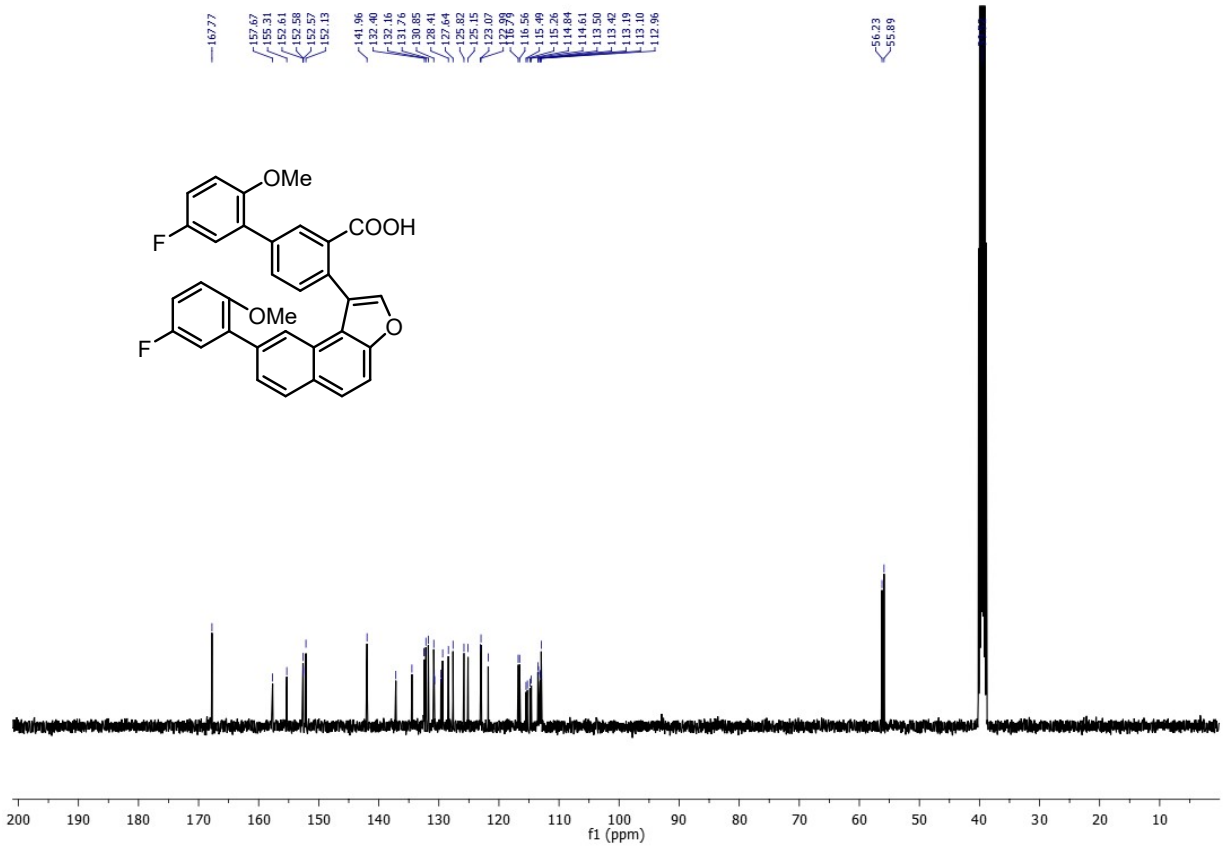
^{13}C NMR Spectrum of **11p** (100 MHz, DMSO-d_6)



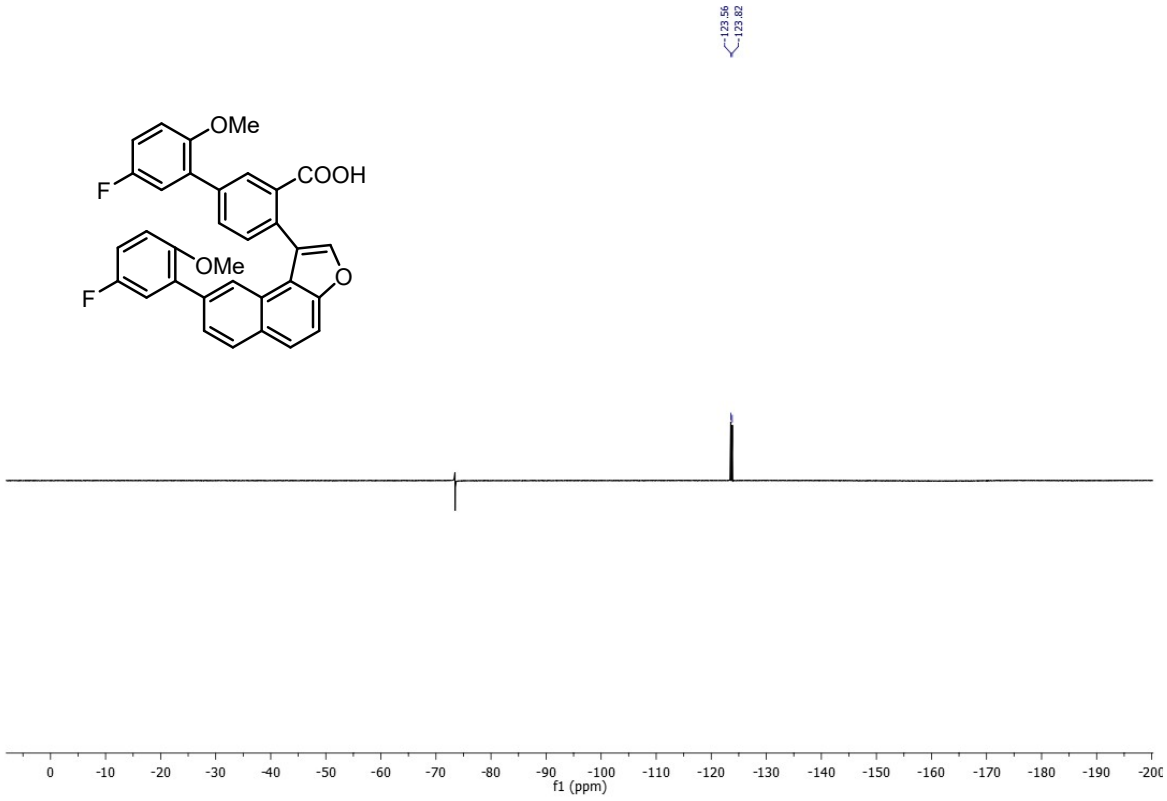
^{1}H NMR Spectrum of **11q** (400 MHz, DMSO-d_6)



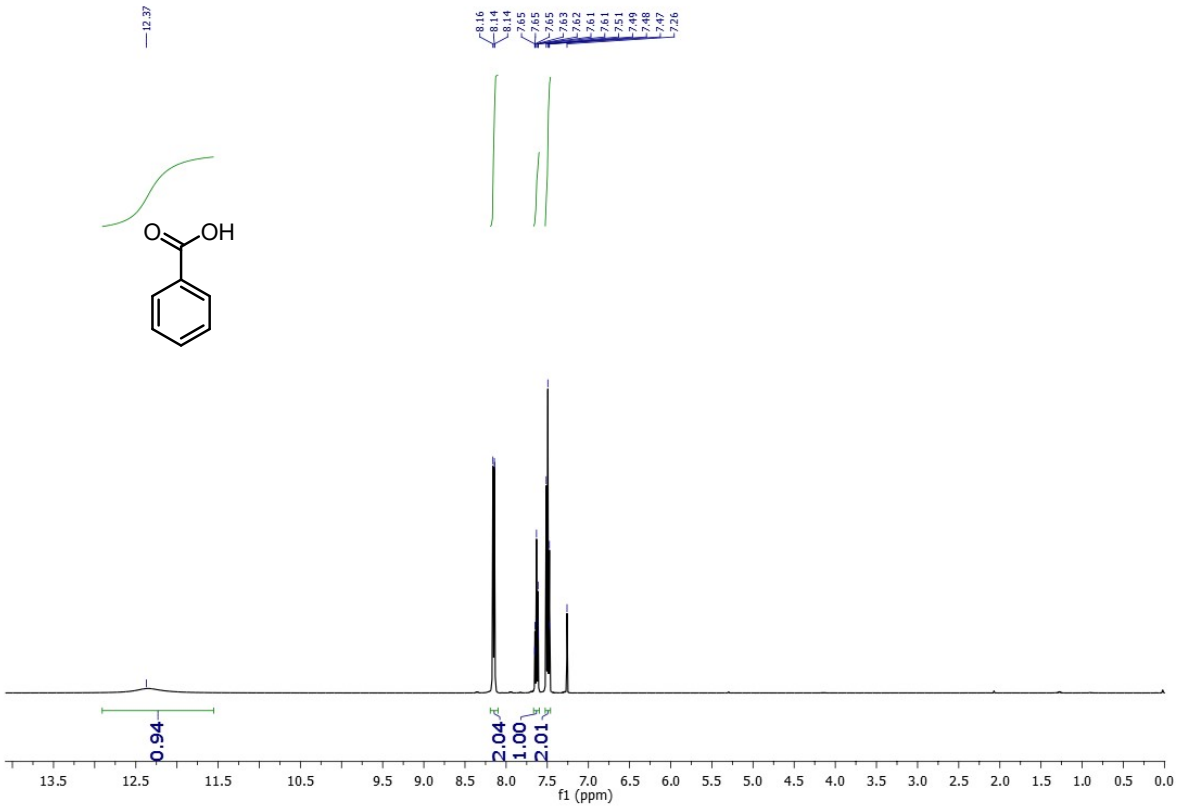
^{13}C NMR Spectrum of **11q** (100 MHz, DMSO-d_6)



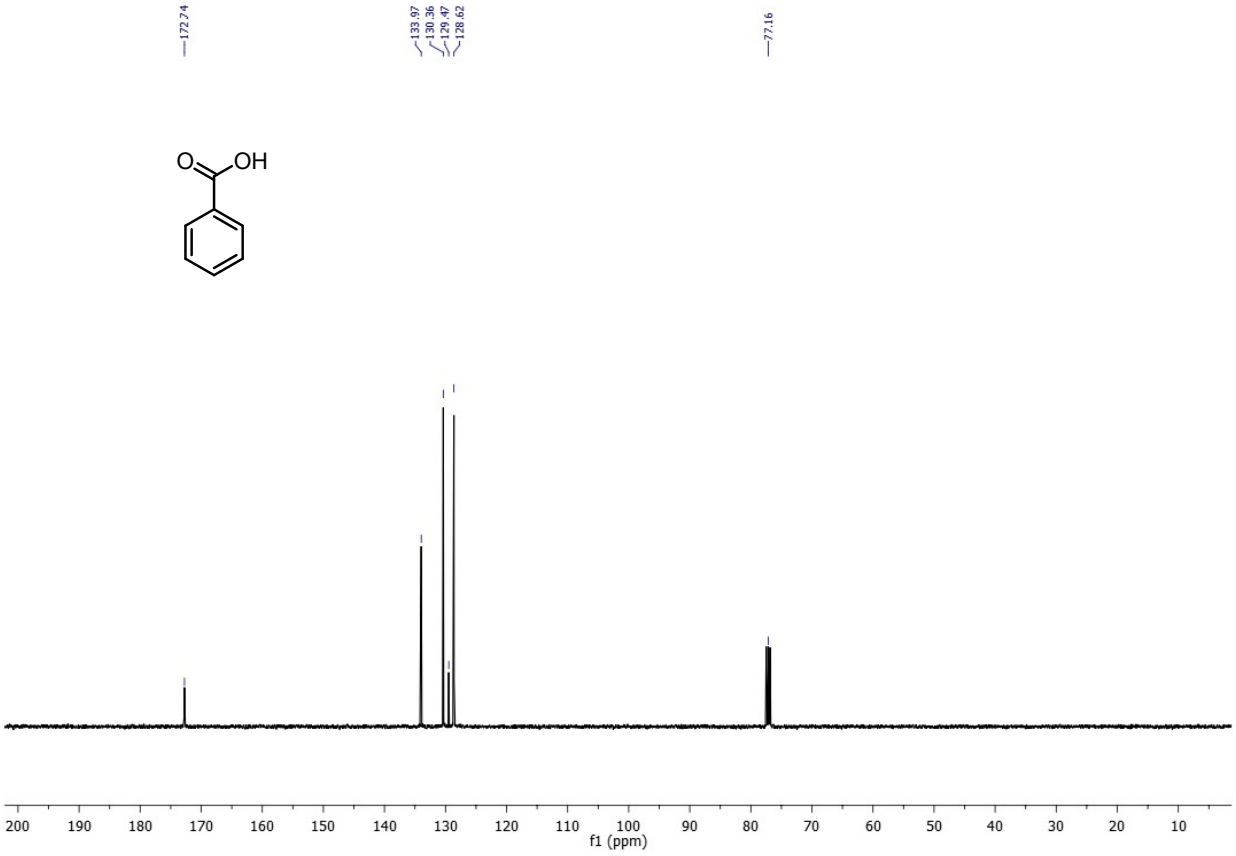
^{19}F NMR Spectrum of **11q** (377 MHz, DMSO-d_6)



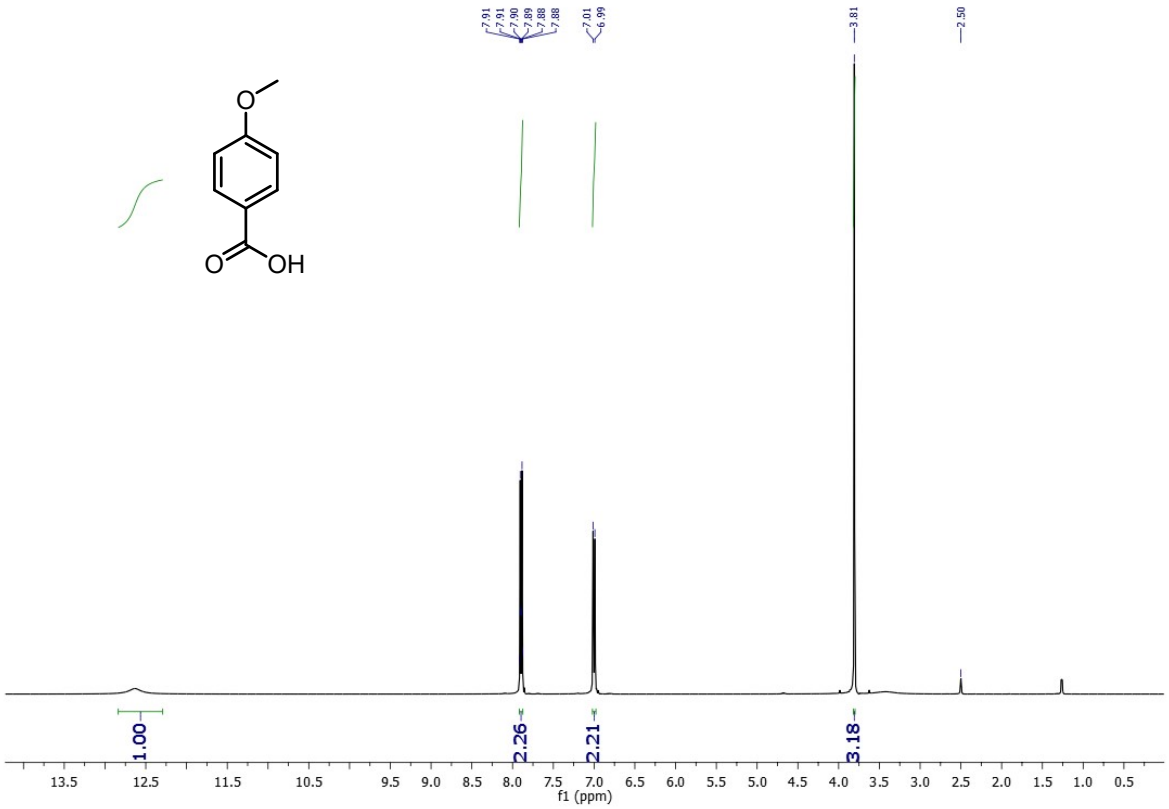
^{1}H NMR Spectrum of **Benzoic Acid** (400 MHz, $CDCl_3$)



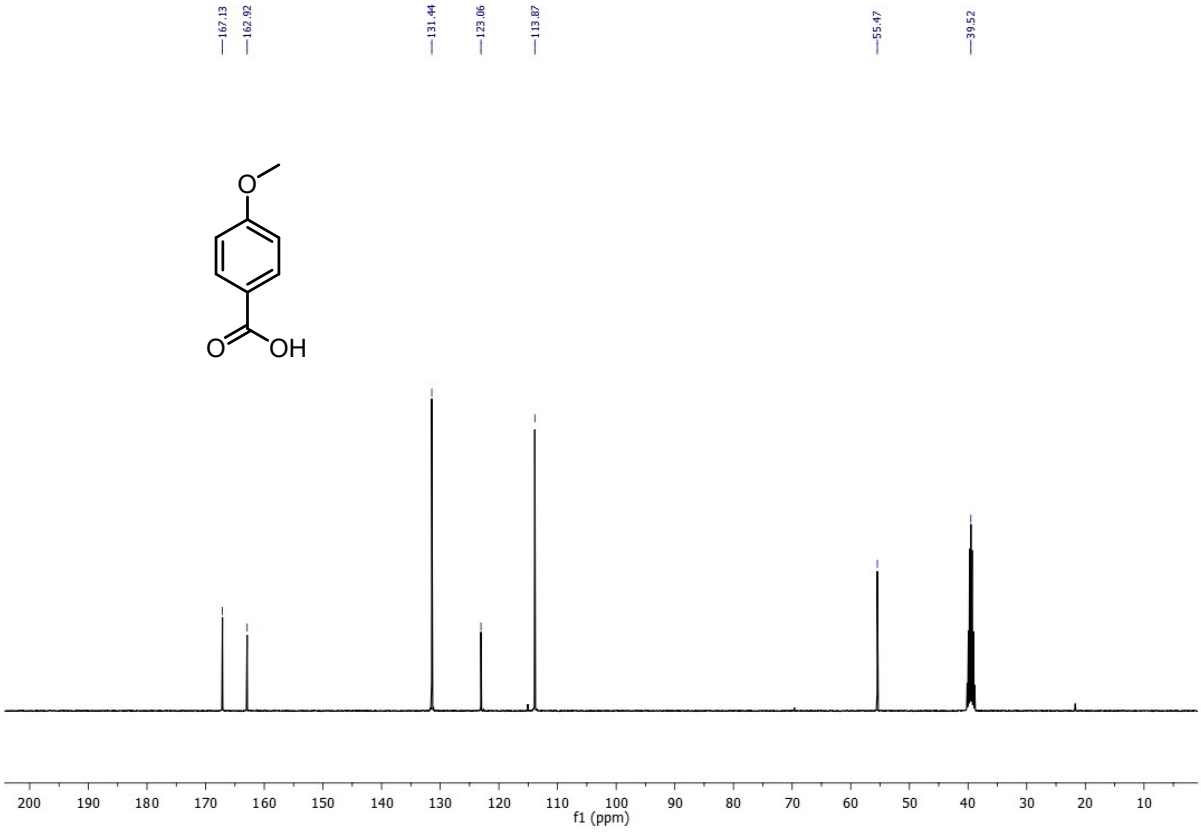
^{13}C NMR Spectrum of **Benzoic Acid** (100 MHz, $CDCl_3$)



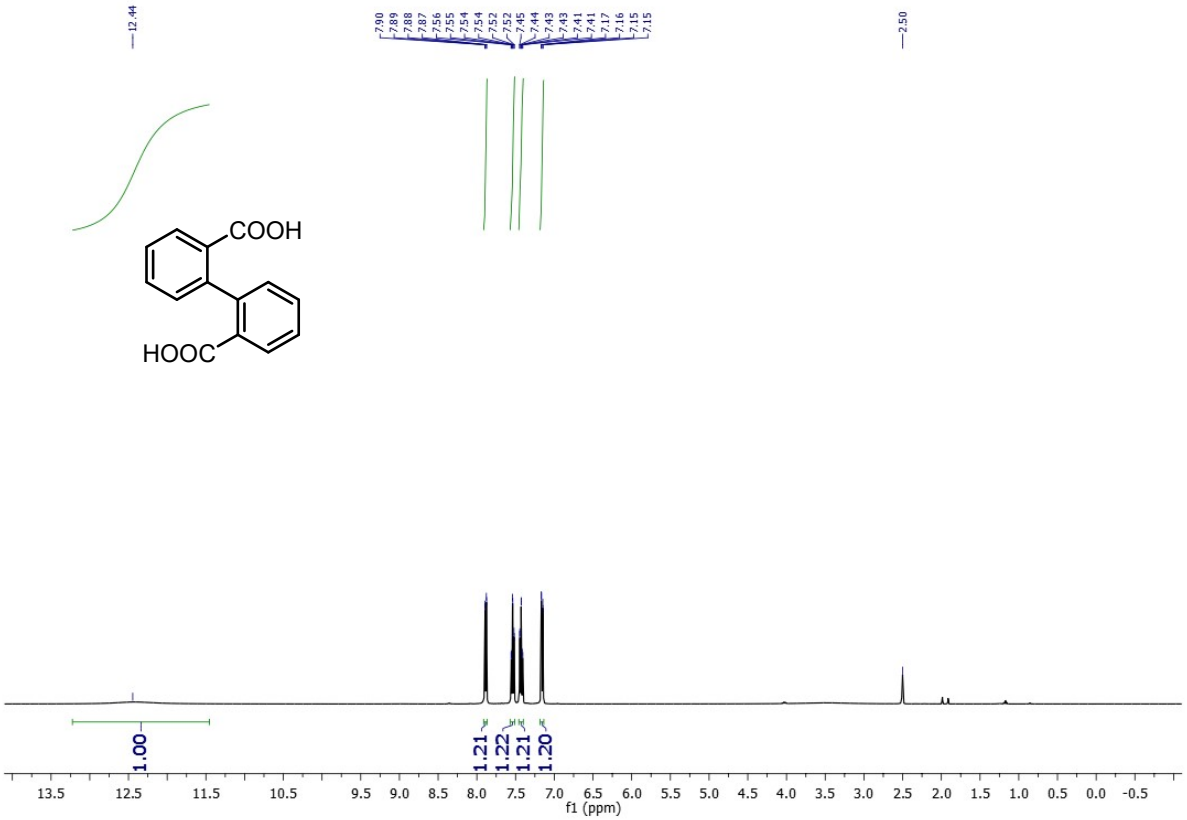
^{1}H NMR Spectrum of **4-methoxybenzoic acid** (400 MHz, DMSO-d_6)



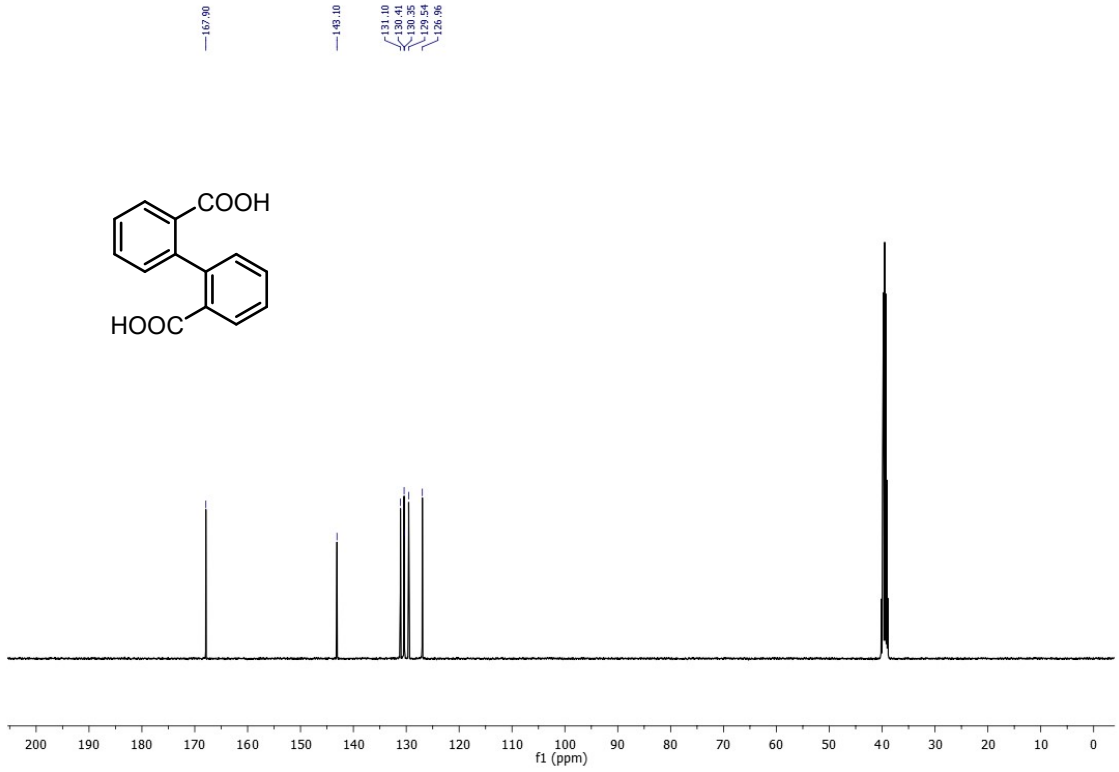
^{13}C NMR Spectrum of **4-methoxybenzoic acid** (100 MHz, DMSO-d_6)



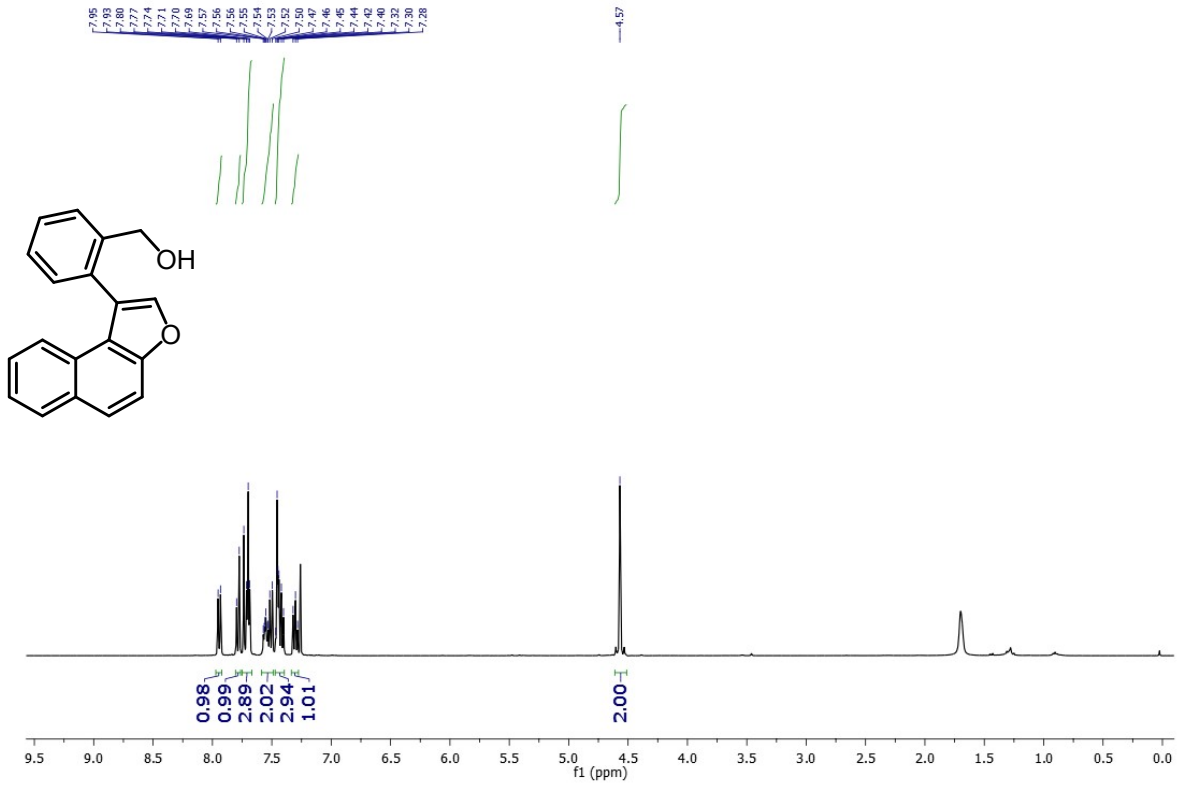
^{1}H NMR Spectrum of **[1,1'-biphenyl]-2,2'-di- acid**(400 MHz, DMSO-d_6)



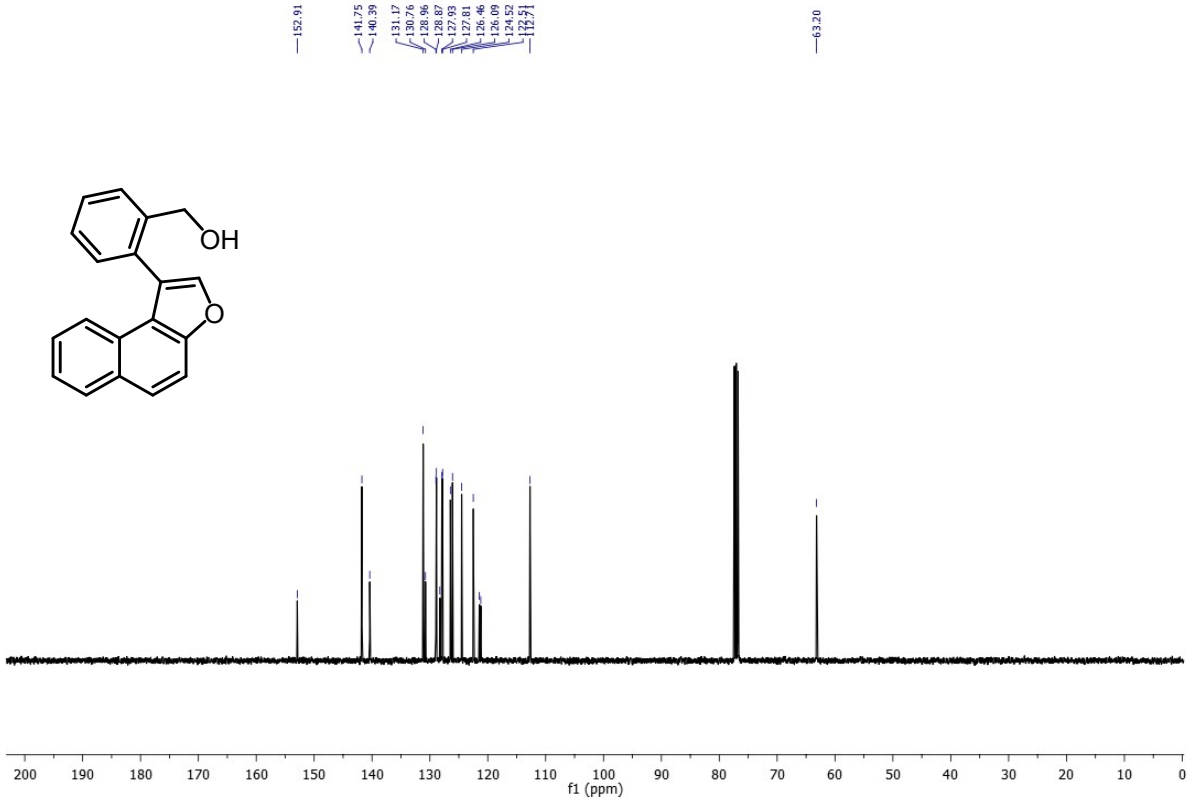
^{13}C NMR Spectrum of **[1,1'-biphenyl]-2,2'-di- acid**(100 MHz, DMSO-d_6)



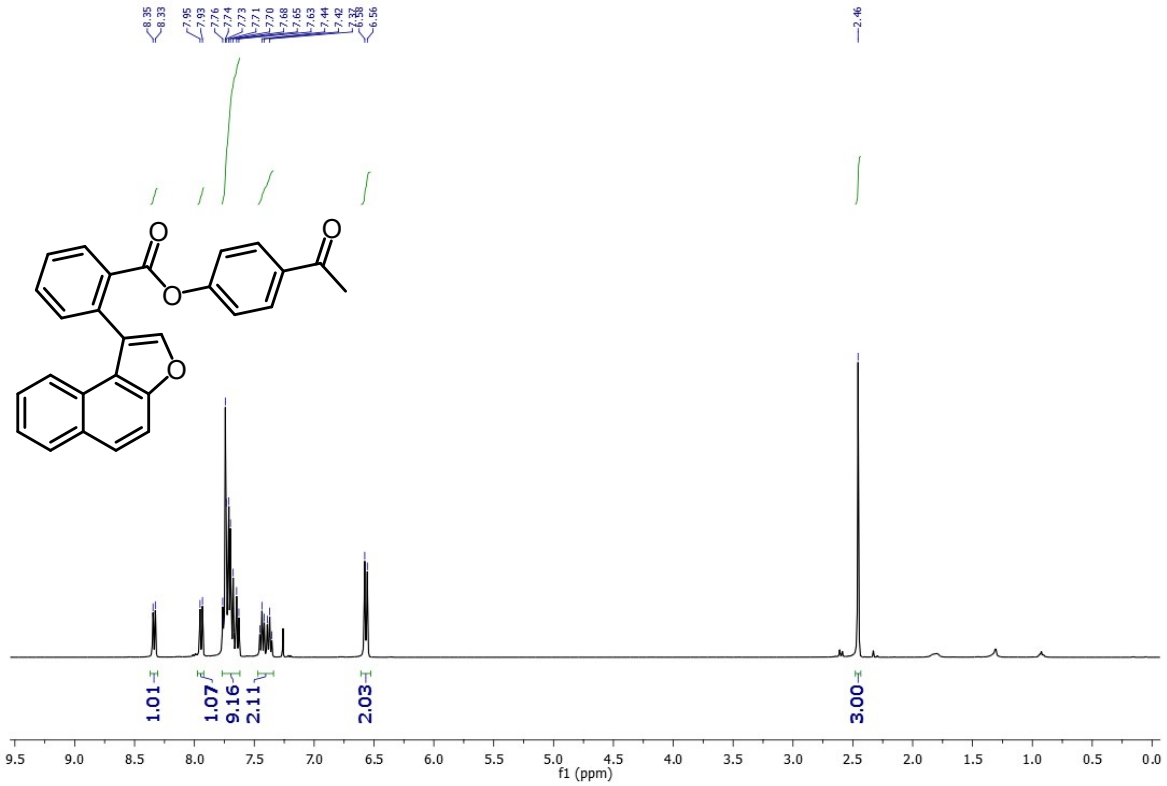
^{1}H NMR Spectrum of **12** (400 MHz, $CDCl_3$)



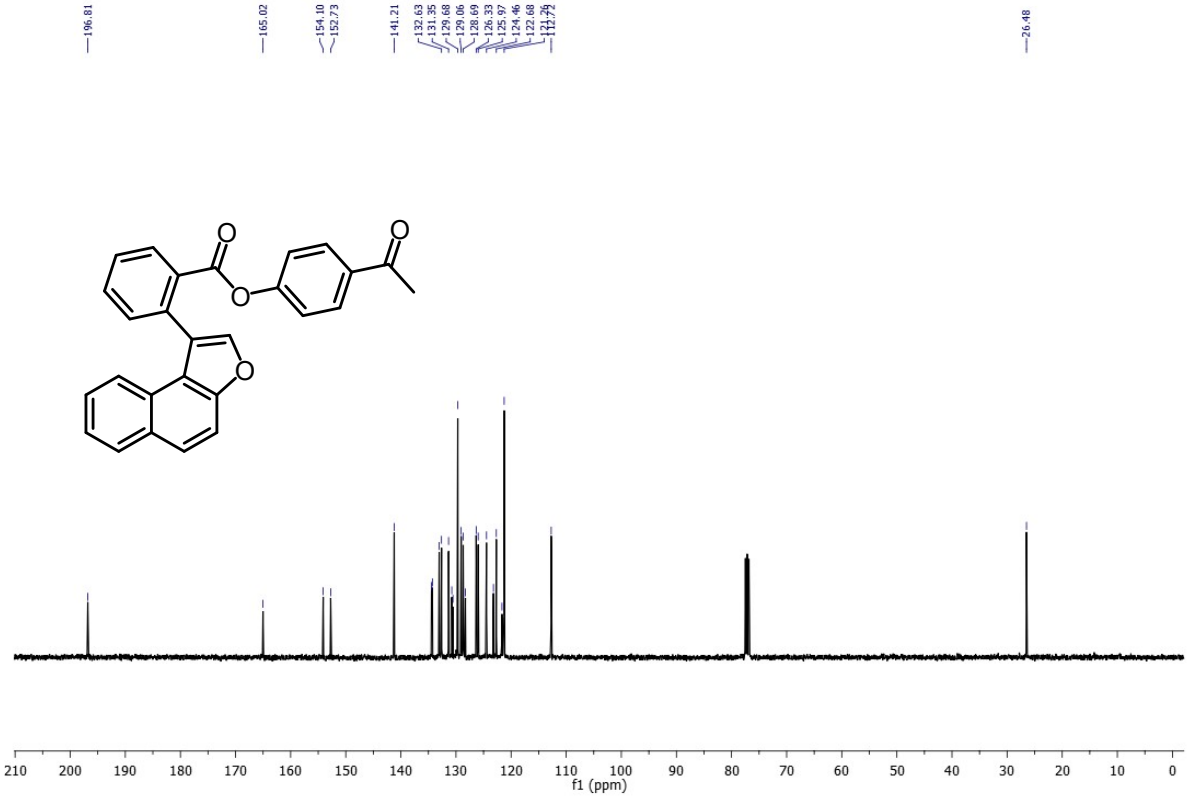
^{13}C NMR Spectrum of **12** (400 MHz, $CDCl_3$)



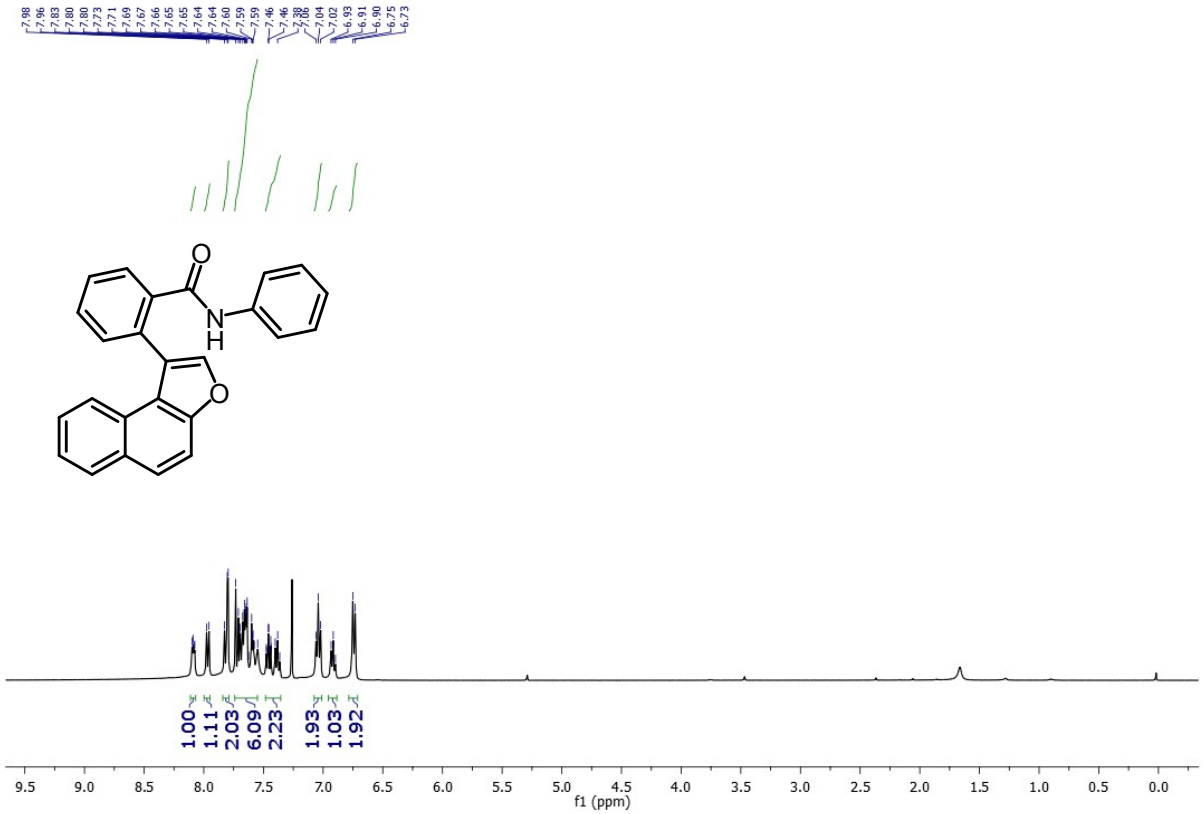
^{1}H NMR Spectrum of **14** (400 MHz, $CDCl_3$)



^{13}C NMR Spectrum of **14** (400 MHz, $CDCl_3$)



^{1}H NMR Spectrum of **16** (400 MHz, $CDCl_3$)



^{13}C NMR Spectrum of **16** (400 MHz, $CDCl_3$)