Supporting Information

Cu(II)-catalyzed domino construction of spironaphthalenones by dearomatization of *β*-naphthols and using *N, N*-dimethylaminoethanol as a C1 synthon

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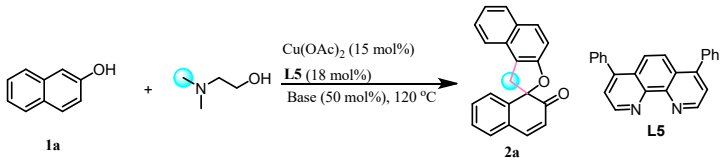
General information

Unless otherwise noted, all the reactions were carried out under air. Glassware was properly dried in an oven before use. Bulk solvents and chemicals were purchased from commercial sources and were used directly without further purification. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker 400 MHz spectrometer (^{1}H: 400 MHz; ^{13}C: 100 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. All ^{1}H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals at 0 ppm (TMS). All ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.0 ppm) and were obtained with ^{1}H-decoupling. Data for ^{1}H NMR are described as following: chemical shift (δ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sep, septet; m, multiplet; br, broad signal), coupling constant (Hz), integration. Data for ^{13}C NMR are described in terms of chemical shift (δ in ppm). Flash column chromatography was performed on commercially available silica gel (200-300 mesh); High resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometer. Melting points were measured on X4 melting point apparatus and uncorrected.

Table S1 Optimization of base.[a]



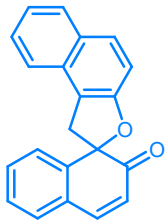
Entry	Base	Temp. (°C)	Yield (%) [b]
1	NaOAc	120	18
2	Na_2HPO_4	120	60
3	KH_2PO_4	120	55
4	$NH_3.H_2O$	120	66
5	Et_3N	120	62
6	$KHCO_3$	120	42
7[c]	$NaHCO_3$	120	53
8[d]	$NaHCO_3$	120	64

[a]Unless otherwise stated, the reaction was carried out with **1a** (1.0 mmol), $Cu(OAc)_2$ (0.15 mmol, 15 mol%), L5 (0.18 mmol, 18 mol%), and base (0.5 mmol.) in DMEA (5 mL) under Air for 3-5 h. [b]Isolated yield the reaction. [c]$NaHCO_3$ (0.3 mmol). [d]$NaHCO_3$ (1 mmol).

General procedure for the synthesis of spiro-cyclohexadienones 2.

To an oven-dried 25-mL Schlenk tube were added 2-Naphthols (1.0 mmol), $Cu(OAc)_2$ (0.15 mmol), 4,7-Diphenyl-1,10-phenanthroline (0.18 mmol), $NaHCO_3$ (0.50 mmol) and DMEA (3mL) under air atmosphere. The resulting mixtures were then stirred at 120 °C for 3-5 h. When the reaction was complete (monitored by TLC), the reaction mixture was cooled to room temperature and diluted with CH_2Cl_2 (25 mL) and washed with H_2O (10 mL × 3). The organic layer was then dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the crude product was purified by flash chromatography on silica gel (PE : EA = 10:1) to afford the corresponding spiro-products **2**.

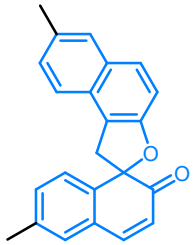
Synthesis and characterization of spiro-cyclohexadienones 2 and 3



1'*H*, 2*H*-spiro[naphthalene-1,2'-naphtho[2,1-*b*]furan]-2-one (2a)[1]

The title compound was obtained as a yellow solid (112 mg, 75%). Mp 168.1-170.4 °C.

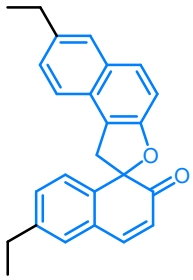
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.54-7.48 (m, 2H), 7.47-7.41 (m, 2H), 7.41-7.29 (m, 5H), 6.25 (d, *J* = 10.0 Hz, 1H), 4.05 (d, *J* = 15.6 Hz, 1H), 3.52 (d, *J* = 15.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.0, 157.8, 145.4, 143.4, 130.8, 130.7, 129.9, 129.7, 129.5, 128.9, 128.8, 128.7, 126.9, 125.6, 123.7, 123.3, 122.5, 115.2, 111.9, 89.4, 42.9; **ESI-MS:** *m/z* 299 $[M+H]^+$.



6,7'-dimethyl-1'*H*,2*H*-spiro[naphthalene-1,2'-naphtho[2,1-*b*]furan]-2-one (2b)

The title compound was obtained as a yellow solid (104 mg, 64%). Mp 88.6-90.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.8 Hz, 1H), 7.61 (s, 1H), 7.44 (d, *J* = 10.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.32-7.25 (m, 2H), 7.16 (s, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 6.22 (d, *J* = 10.0 Hz, 1H), 4.01 (d, *J* = 15.6 Hz, 1H), 3.47 (d, *J* = 15.6 Hz, 1H), 2.47 (s, 3H), 2.36 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.3, 157.1, 145.5, 140.6, 138.6, 132.6, 131.3, 130.1, 129.9, 129.1, 129.0, 129.0, 128.6, 127.8, 125.6, 123.7, 122.3, 115.2, 111.8, 89.1, 42.9, 21.5, 21.0; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{23}H_{19}O_2^+$ $[M+H]^+$: 327.1380; found: 327.1375.

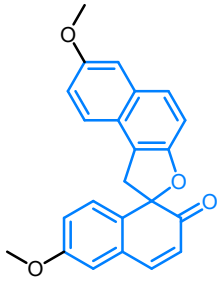


6,7'-diethyl-1'*H*,2*H*-spiro[naphthalene-1,2'-naphtho[2,1-*b*]furan]-2-one (2c)

The title compound was obtained as a yellow solid (149 mg, 84%). Mp 115.8-117.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.8 Hz, 1H), 7.63 (s, 1H), 7.46 (d, *J* = 10.0 Hz, 1H), 7.43-7.35 (m, 2H), 7.35-7.26 (m, 2H), 7.18 (s, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.22 (d, *J* = 9.6 Hz, 1H), 4.02 (d, *J* = 15.6 Hz, 1H), 3.49 (d, *J* = 15.6 Hz, 1H), 2.77 (q, *J* = 7.6 Hz, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.4 Hz, 3H), 1.23 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.3, 157.2, 145.6, 144.9, 140.7, 139.0, 130.2, 129.9, 129.2, 129.0, 128.6, 128.1, 126.5, 125.7, 123.6, 122.4, 115.3, 111.8, 89.1,

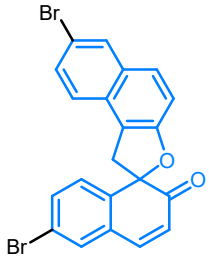
42.9, 28.9, 28.3, 15.7, 15.4; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{25}H_{23}O_2^+$ [M+H]$^+$: 355.1693; found: 355.1697.



6,7'-dimethoxy-1'*H*,2*H*-spiro[naphthalene-1,2'-naphtho[2,1-*b*]furan]-2-one (2d)

The title compound was obtained as a yellow solid (122 mg, 68%). Mp 169.5-171.7 °C.

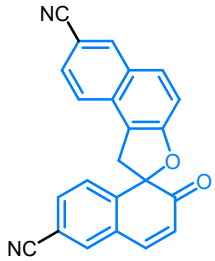
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.8 Hz, 1H), 7.47-7.40 (m, 2H), 7.37 (d, *J* = 8.9 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 1H), 7.17 (d, *J* = 2.4 Hz, 1H), 7.13 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.94-6.79 (m, 2H), 6.25 (d, *J* = 10.0 Hz, 1H), 4.01 (d, *J* = 15.6 Hz, 1H), 3.90 (s, 3H), 3.82 (s, 3H), 3.48 (d, *J* = 15.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.2, 159.8, 156.0, 155.7, 145.2, 135.2, 130.6, 129.9, 128.3, 127.2, 126.2, 124.3, 124.0, 119.6, 115.8, 115.7, 114.8, 112.2, 107.0, 88.6, 55.5, 55.3, 42.7; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{23}H_{19}O_4^+$ [M+H]$^+$: 359.1278; found: 359.1271.



6,7'-dibromo-1'*H*,2*H*-spiro[naphthalene-1,2'-naphtho[2,1-*b*]furan]-2-one (2e)[1]

The title compound was obtained as a yellow solid (28 mg, 12%). Mp 205-209 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 2.0 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.54-7.45 (m, 3H), 7.43 (d, *J* = 10.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 6.29 (d, *J* = 10.0 Hz, 1H), 4.01 (d, *J* = 15.6 Hz, 1H), 3.47 (d, *J* = 16.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.8, 158.0, 143.9, 141.7, 133.4, 132.1, 130.9, 130.8, 130.6, 130.3, 129.21, 129.17, 127.3, 124.8, 124.1, 122.7, 117.0, 115.3, 112.9, 89.0, 42.5; **ESI-MS:** *m/z* 457 [M+H]$^+$.

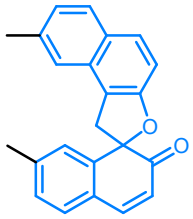


2-oxo-1'*H*,2*H*-spiro[naphthalene-1,2'-naphtho[2,1-*b*]furan]-6,7'-dicarbonitrile (2f)

The title compound was obtained as a yellow solid (79 mg, 44%). Mp 170.9-172.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.70 (s, 1H), 7.69-7.62 (m, 2H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 10.0 Hz, 1H), 7.48 (t, *J* = 8.4 Hz, 2H), 6.39 (d, *J* = 10.0 Hz, 1H), 4.07 (d, *J* = 15.6 Hz, 1H), 3.50 (d, *J* = 16.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.4, 160.1, 146.9, 143.1, 135.1, 133.9, 132.6, 132.1, 131.3, 129.9, 128.7, 127.8, 126.5, 125.4, 123.6, 119.3, 117.5,

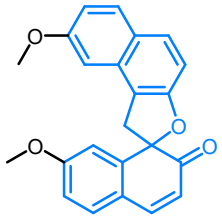
115.4, 113.7, 113.4, 106.9, 89.4, 42.3; **HRMS** (ESI-TOF) *m/z* calcd. For $C_{23}H_{13}N_2O_2^+$ $[M+H]^+$: 349.0972; found: 349.0968.



7,8'-dimethyl-1'*H*,2*H*-spiro[naphthalene-1,2'-naphtho[2,1-*b*]furan]-2-one (2g)

The title compound was obtained as a yellow solid (152 mg, 93%). Mp 179.6-181.5 °C.

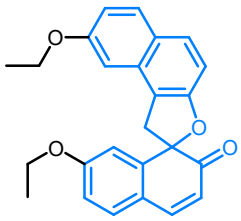
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.70 (m, 2H), 7.46 (d, *J* = 10.0 Hz, 1H), 7.33-7.26 (m, 2H), 7.26-7.20 (m, 2H), 7.19-7.10 (m, 2H), 6.17 (d, *J* = 10.0 Hz, 1H), 4.01 (d, *J* = 15.6 Hz, 1H), 3.48 (d, *J* = 15.6 Hz, 1H), 2.45 (s, 3H), 2.28 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.1, 157.9, 145.4, 143.6, 141.4, 136.7, 131.0, 129.5, 129.3, 128.6, 127.9, 126.2, 126.1, 125.5, 122.6, 121.6, 114.5, 110.9, 89.3, 43.0, 21.9, 21.6; **HRMS** (ESI-TOF) *m/z* calcd. for$C_{23}H_{19}O_2^+$ $[M+H]^+$: 327.1380; found: 327.1384.



7,8'-dimethoxy-1'*H*,2*H*-spiro[naphthalene-1,2'-naphtho[2,1-*b*]furan]-2-one (2h)

The title compound was obtained as a yellow solid (120 mg, 68%). Mp 182.9-184.1 °C.

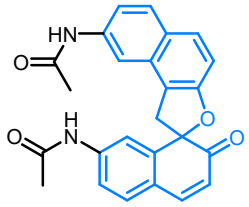
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.69 (m, 2H), 7.45 (d, *J* = 10.0 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 7.06 (d, *J* = 2.8 Hz, 1H), 6.98 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.85 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.67 (d, *J* = 2.8 Hz, 1H), 6.11 (d, *J* = 10.0 Hz, 1H), 4.00 (d, *J* = 15.6 Hz, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 3.47 (d, *J* = 15.2 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.1, 161.8, 158.53, 158.47, 145.9, 145.3, 132.1, 131.2, 130.4, 129.6, 125.1, 121.8, 120.9, 115.8, 114.1, 113.4, 111.8, 109.2, 100.9, 89.6, 55.5, 55.2, 43.2; **HRMS** (ESI-TOF) *m/z* calcd. for$C_{23}H_{19}O_4^+$ $[M+H]^+$: 359.1278; found: 359.1283.



7,8'-diethoxy-1'*H*,2*H*-spiro[naphthalene-1,2'-naphtho[2,1-*b*]furan]-2-one (2i)

The title compound was obtained as a white solid (157 mg, 81%). Mp 152.1-154.7 °C.

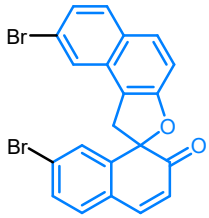
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.68 (m, 2H), 7.43 (d, *J* = 9.6 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.97 (dd, *J* = 9.2, 2.4 Hz, 1H), 6.82 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.66 (d, *J* = 2.8 Hz, 1H), 6.09 (d, *J* = 10.0 Hz, 1H), 4.11-4.01 (m, 2H), 4.01-3.90 (m, 3H), 3.45 (d, *J* = 15.6 Hz, 1H), 1.43 (t, *J* = 7.0 Hz, 3H), 1.34 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.1, 161.2, 158.4, 157.8, 145.9, 145.4, 132.1, 131.2, 130.3, 129.5, 125.0, 121.6, 120.8, 116.1, 114.0, 113.6, 112.4, 109.1, 101.7, 89.5, 63.7, 63.4, 43.3, 14.7, 14.5; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{25}H_{23}O_4^+$ $[M+H]^+$: 387.1591; found: 387.1594.



***N*, *N*'-(2-oxo-1'*H*,2*H*-spiro[naphthalene-1,2'-naphtho[2,1-*b*]furan]-7,8'-diyl)diacetamide (2j)**

The title compound was obtained as a yellow solid (133.9 mg, 65%). Mp 182.3-184.5 ℃.

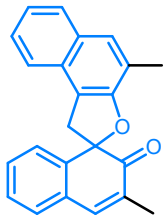
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.75 (s, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.88-7.79 (m, 2H), 7.57-7.46 (m, 3H), 7.38-7.30 (m, 3H), 6.28 (d, *J* = 9.6 Hz, 1H), 4.09 (d, *J* = 16.0 Hz, 1H), 3.74 (d, *J* = 16.0 Hz, 1H), 1.96 (s, 3H), 1.10 (s, 3H); **^{13}C NMR (100 MHz, d^6-DMSO)** δ 197.0, 169.7, 168.5, 158.5, 147.2, 138.1, 136.1, 132.1, 131.5, 131.2, 130.8, 130.5, 129.9, 128.9, 128.8, 128.0, 127.4, 123.3, 123.2, 115.2, 112.9, 87.3, 43.0, 23.6, 22.6; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{25}H_{21}N_2O_4^+$ $[M+H]^+$: 413.1496; found: 413.1493.



7,8'-dibromo-1'*H*,2*H*-spiro[naphthalene-1,2'-naphtho[2,1-*b*]furan]-2-one (2k) [2]

The title compound was obtained as a yellow solid (91 mg, 40%). Mp 200.3-202.5 ℃.

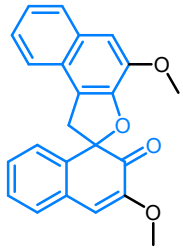
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.48 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.43 (d, *J* = 10.0 Hz, 1H), 7.38 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 6.24 (d, *J* = 10.0 Hz, 1H), 3.98 (d, *J* = 15.6 Hz, 1H), 3.45 (d, *J* = 15.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.5, 158.4, 144.7, 144.3, 132.0, 131.8, 130.8, 130.5, 130.1, 128.7, 128.1, 127.6, 126.7, 125.4, 124.7, 123.8, 121.4, 114.1, 112.2, 89.0, 42.5; **ESI-MS:** *m/z* 457 $[M+H]^+$.



3,4'-dimethyl-1'*H*,2*H*-spiro[naphthalene-1,2'-naphtho[2,1-*b*]furan]-2-one (2l)

The title compound was obtained as a yellow solid (133 mg, 82%). Mp 150.4-151.8 ℃.

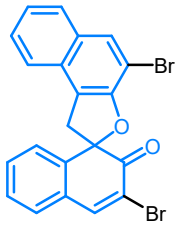
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.57 (s, 1H), 7.47-7.42 (m, 1H), 7.41-7.22 (m, 7H), 3.96 (d, *J* = 15.6 Hz, 1H), 3.49 (d, *J* = 15.2 Hz, 1H), 2.52 (s, 3H), 2.06 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.5, 157.5, 142.8, 141.3, 131.5, 130.0, 129.5, 129.1, 129.0, 128.6, 128.5, 128.0, 125.8, 125.3, 123.1, 122.29, 122.25, 114.4, 89.0, 43.4, 16.2, 15.8; **HRMS** (ESI-TOF) *m/z* calcd. for$C_{23}H_{19}O_2^+$ $[M+H]^+$: 327.1380; found: 327.1385.



3,4'-dimethoxy-1'*H*,2*H*-spiro[naphthalene-1,2'-naphtho[2,1-*b*]furan]-2-one (2m)

The title compound was obtained as a yellow solid (154 mg, 86%). Mp 209.9-211.7 °C.

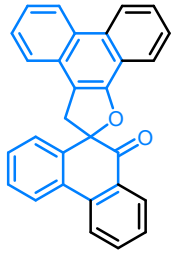
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.71 (m, 1H), 7.44 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.42-7.37 (m, 1H), 7.36-7.26 (m, 3H), 7.22 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.20-7.13 (m, 2H), 6.56 (s, 1H), 4.10 (d, *J* = 15.6 Hz, 1H), 4.03 (s, 3H), 3.85 (s, 3H), 3.57 (d, *J* = 15.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 192.1, 148.8, 148.5, 145.5, 139.0, 130.9, 129.1, 128.6, 128.0, 127.8, 127.4, 125.8, 125.7, 124.5, 123.9, 122.3, 117.0, 115.3, 107.2, 90.3, 55.8, 55.7, 43.1; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{23}H_{19}O_4^+$ $[M+H]^+$: 359.1278; found: 359.1274.



3,4'-dibromo-1'*H*,2*H*-spiro[naphthalene-1,2'-naphtho[2,1-*b*]furan]-2-one (2n)[2]

The title compound was obtained as a yellow solid (114 mg, 50%). Mp 209.1-212.9 °C.

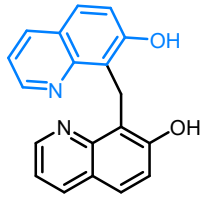
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.93 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.59-7.51 (m, 1H), 7.50-7.28 (m, 6H), 4.11 (d, *J* = 16.0 Hz, 1H), 3.65 (d, *J* = 16.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 190.2, 154.6, 146.8, 141.9, 131.8, 131.2, 130.8, 129.6, 129.4, 129.2, 128.6, 127.9, 127.2, 126.1, 124.4, 122.6, 119.2, 116.5, 104.5, 89.9, 44.2; **ESI-MS:** *m/z* 457 $[M+H]^+$.



3'*H*,10*H*-spiro[phenanthrene-9,2'-phenanthro[9,10-*b*]furan]-10-one (2o)

The title compound was obtained as a yellow solid (149.2 mg, 75%). Mp 196.8-198.3 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70-8.64 (m, 1H), 8.63-8.57 (m, 1H), 8.38-8.30 (m, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.70-7.62 (m, 3H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.45-7.30 (m, 5H), 7.22 (t, *J* = 7.8 Hz, 1H), 4.00 (d, *J* = 15.6 Hz, 1H), 3.53 (d, *J* = 15.2 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.0, 153.6, 139.7, 137.2, 135.0, 131.6, 129.7, 129.5, 129.2, 128.8, 128.6, 128.5, 128.4, 127.3, 127.04, 126.95, 126.8, 126.7, 125.4, 124.3, 123.9, 123.3, 123.0, 122.8, 122.5, 121.6, 110.7, 90.5, 43.8; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{29}H_{19}O_2^+$ $[M+H]^+$: 399.1380; found: 399.1376.



8,8'-methylenebis(quinolin-7-ol) (3)

The title compound was obtained as a yellow solid (120.8 mg, 80%). Mp 229.3-231.5 ℃.

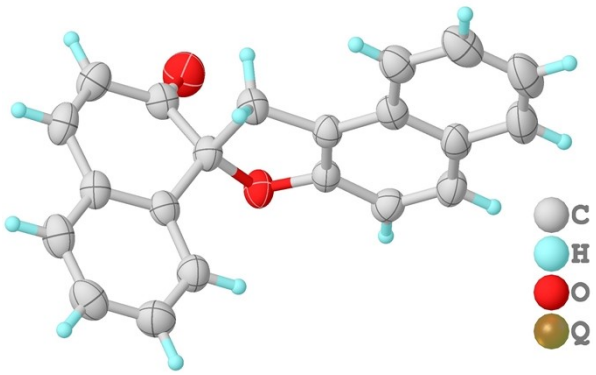
^{1}H NMR (400 MHz, $CDCl_3$) δ 13.79 (s, 2H), 8.86-8.79 (m, 2H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.27-7.22 (m, 2H), 4.83 (s, 2H); **^{13}C NMR (100 MHz, d^6-DMSO)** δ 158.3, 147.9, 147.0, 137.7, 127.3, 123.6, 122.2, 120.5, 117.9, 22.1; **HRMS** (ESI-TOF) *m/z* calcd. for $C_{19}H_{15}N_2O_2^+$ $[M+H]^+$: 303.1128; found: 303.1124.

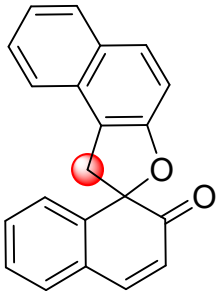
1. References

[1] Dekhici, M.; Plihon, S.; Bar, N.; Villemin, D.; Elsiblani, H.; Cheikh, N. *ChemistrySelect,* **2019**, *4*, 705-708.

[2] Pang, T., Sun, Y., Xue, W. J., Zhu, Y. P., Yu, G. A., & Wu, A. X. *Adv. Synth. Catal.* **2013**, *355*, 2208-2216.

Crystal data and structure refinement for 2a



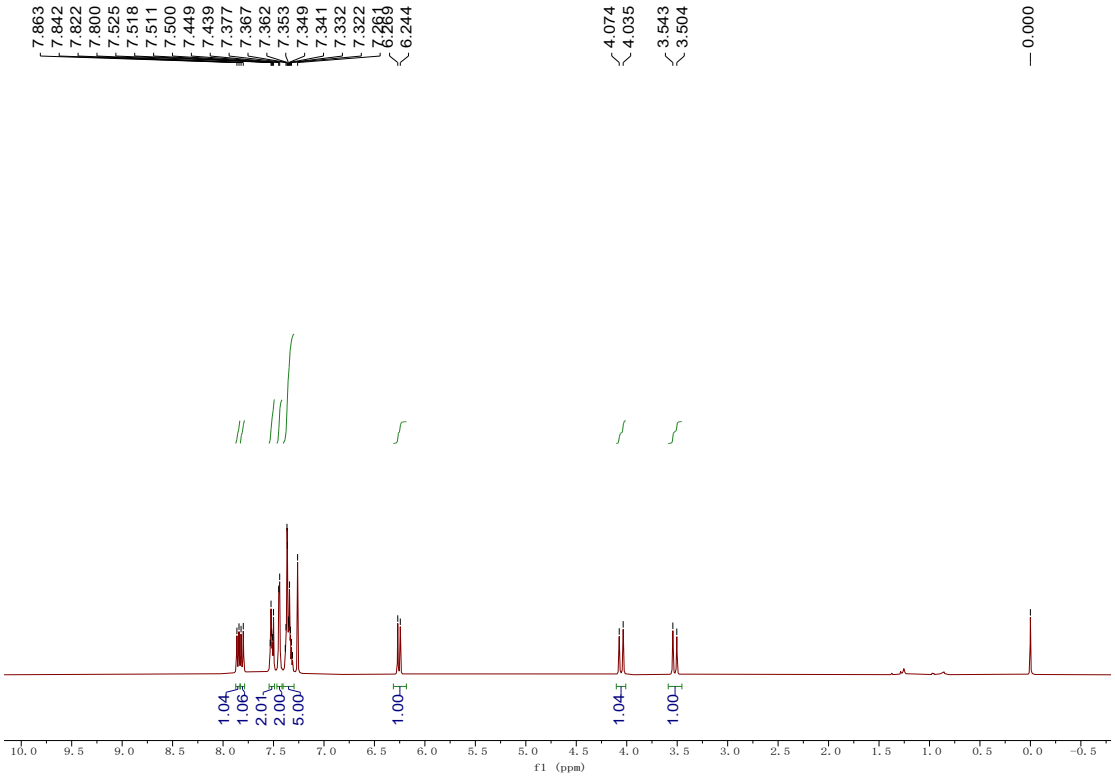


2a

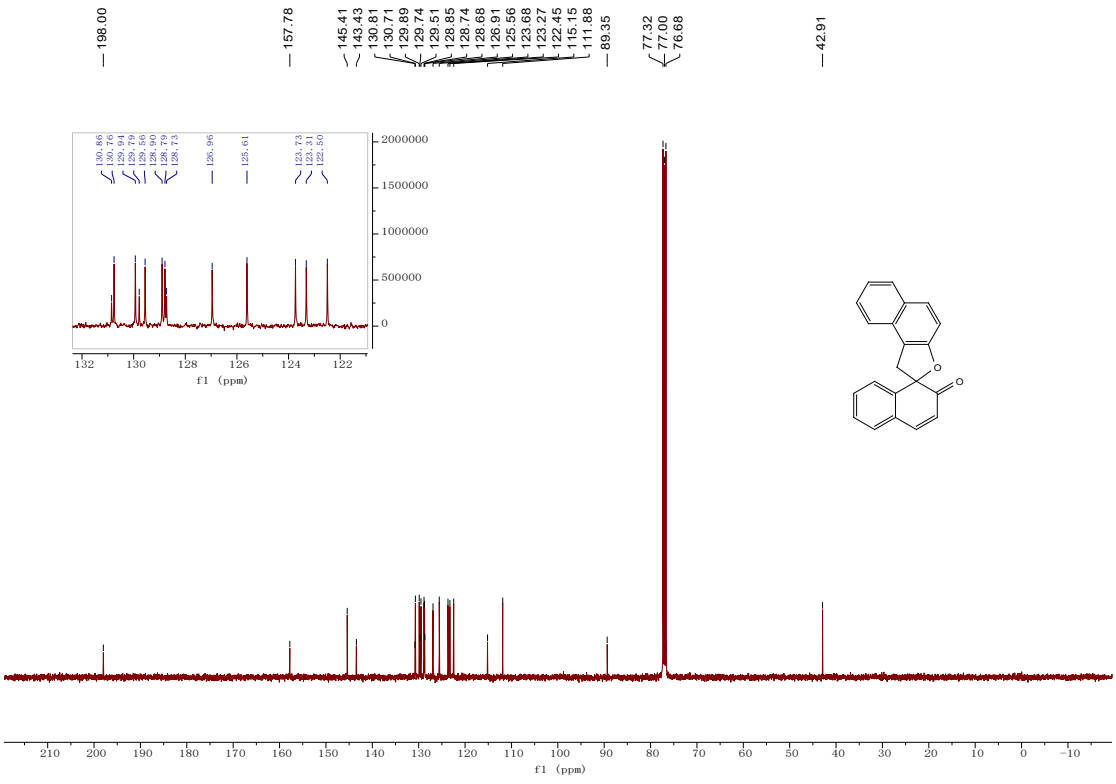
CCDC Number	2208411
Empirical formula	$C_{21}H_{14}O_2$
Formula weight	298.32
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.785(5)
b/Å	8.252(3)
c/Å	12.807(5)
α/°	90
β/°	96.271(7)
γ/°	90
Volume/Å^3	1448.2(9)
Z	4
ρ_{calc}g/cm^3	1.368
μ/mm^{-1}	0.087
F(000)	624.0
Crystal size/mm^3	0.15 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.972 to 58.332
Index ranges	-18 ≤ h ≤ 18, -11 ≤ k ≤ 11, -17 ≤ l ≤ 17
Reflections collected	14650
Independent reflections	3883 [R_{int} = 0.1020, R_{sigma} = 0.1017]
Data/restraints/parameters	3883/0/209
Goodness-of-fit on F^2	0.947
Final R indexes [I>=2σ (I)]	R_1 = 0.0549, wR_2 = 0.1120
Final R indexes [all data]	R_1 = 0.1519, wR_2 = 0.1493
Largest diff. peak/hole / e Å^{-3}	0.18/-0.17

^{1}H NMR and ^{13}C NMR spectra of spiro-cyclohexadienones 2 and 3

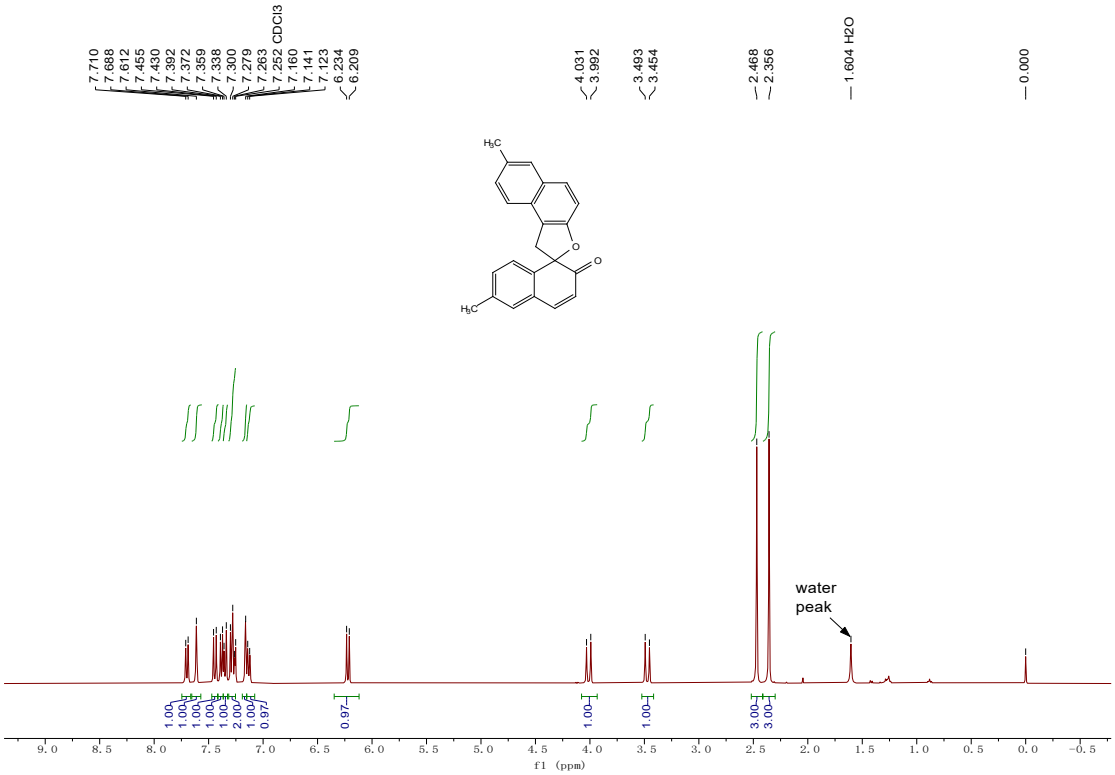
^{1}H NMR of Compound **2a** (400 MHz, $CDCl_3$)



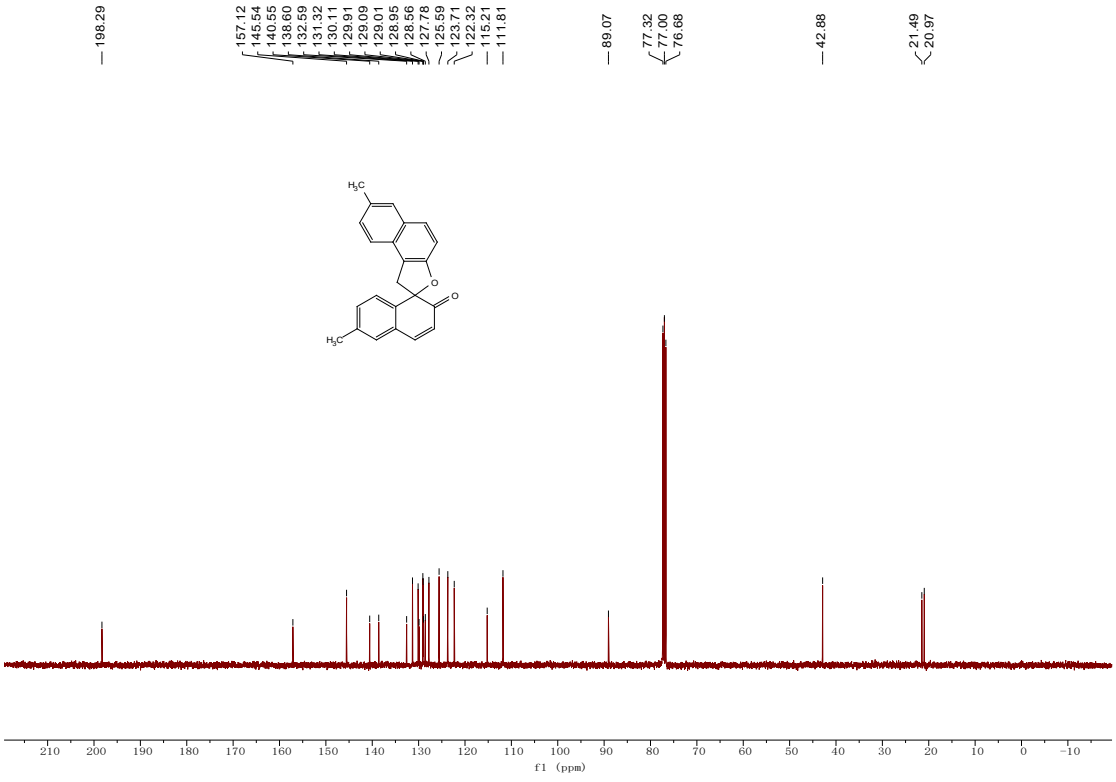
^{13}C NMR of Compound **2a** (100 MHz, $CDCl_3$)



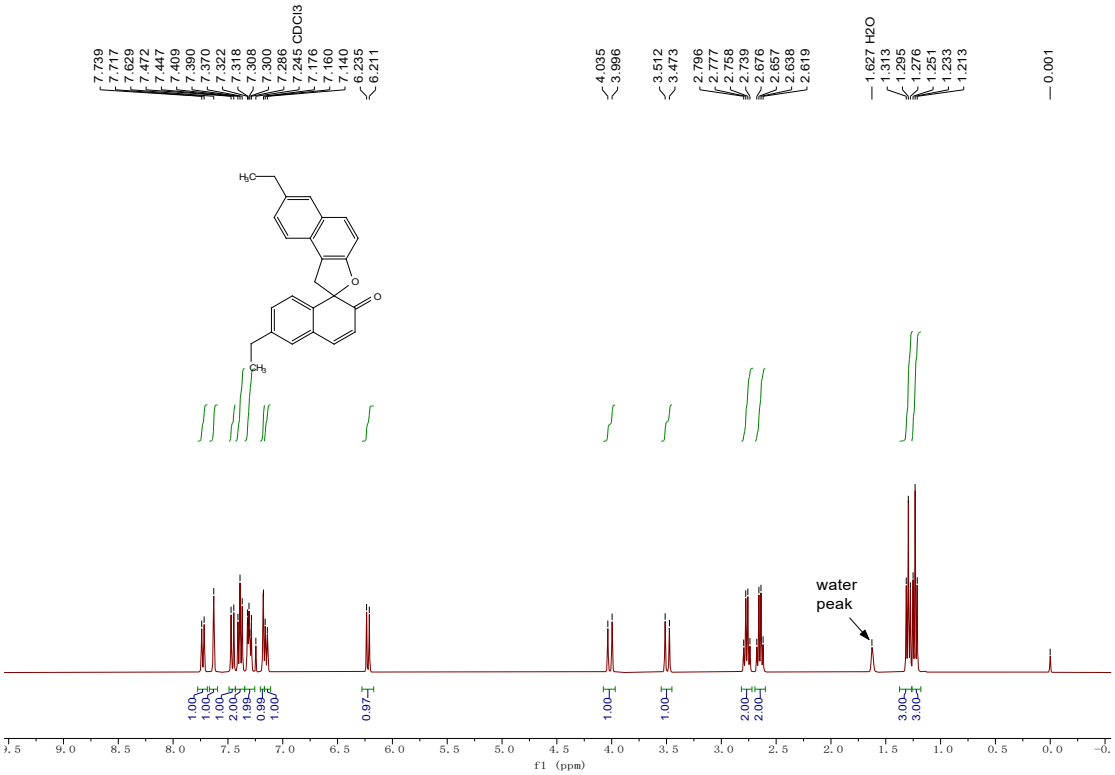
^{1}H NMR of Compound **2b** (400 MHz, $CDCl_3$)



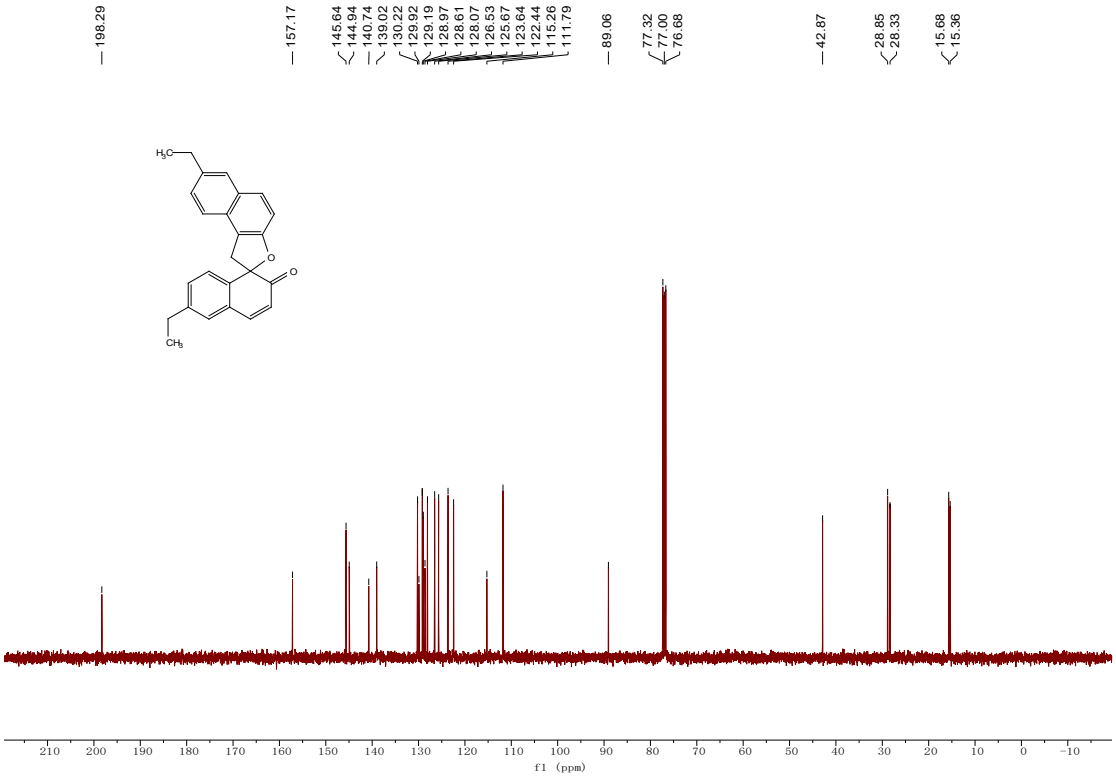
^{13}C NMR of Compound **2b** (100 MHz, $CDCl_3$)



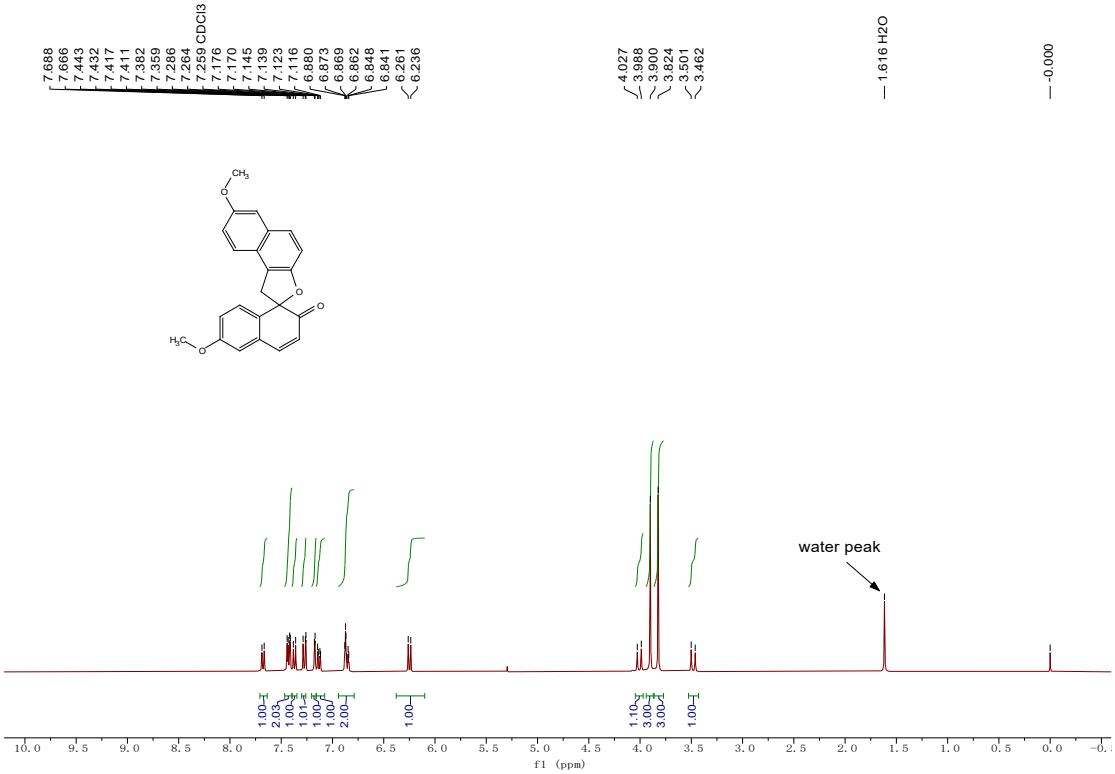
^{1}H NMR of Compound **2c** (400 MHz, $CDCl_3$)



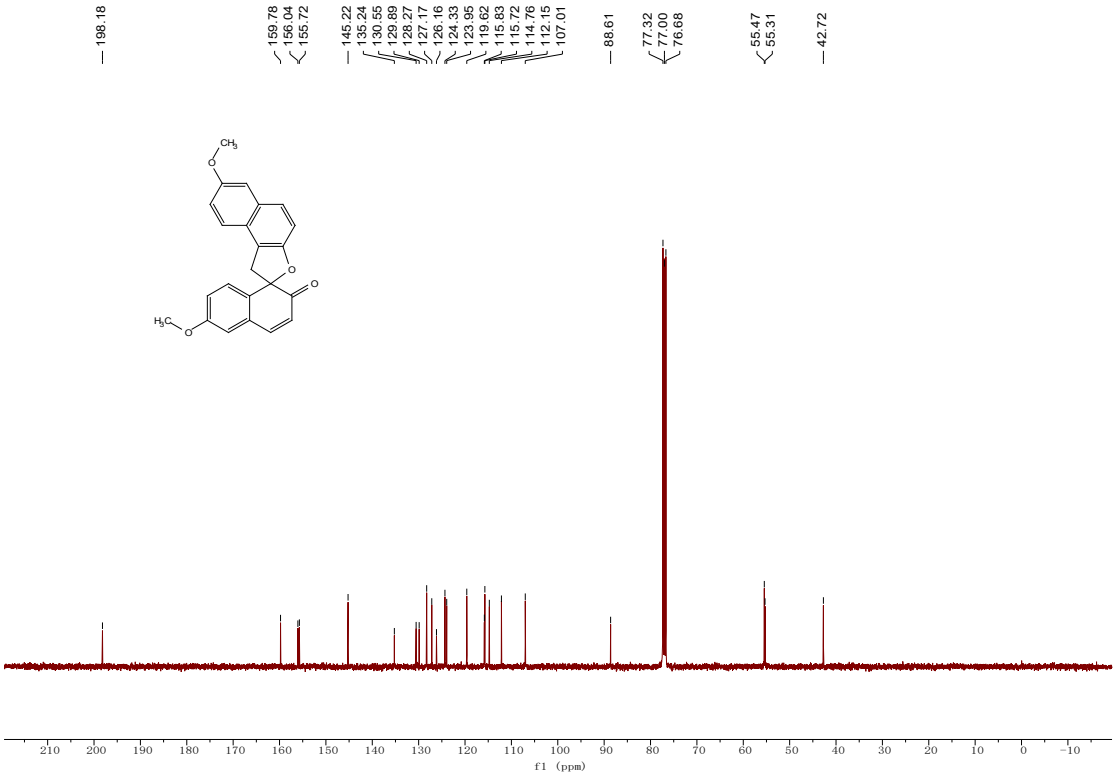
^{13}C NMR of Compound **2c** (100 MHz, $CDCl_3$)



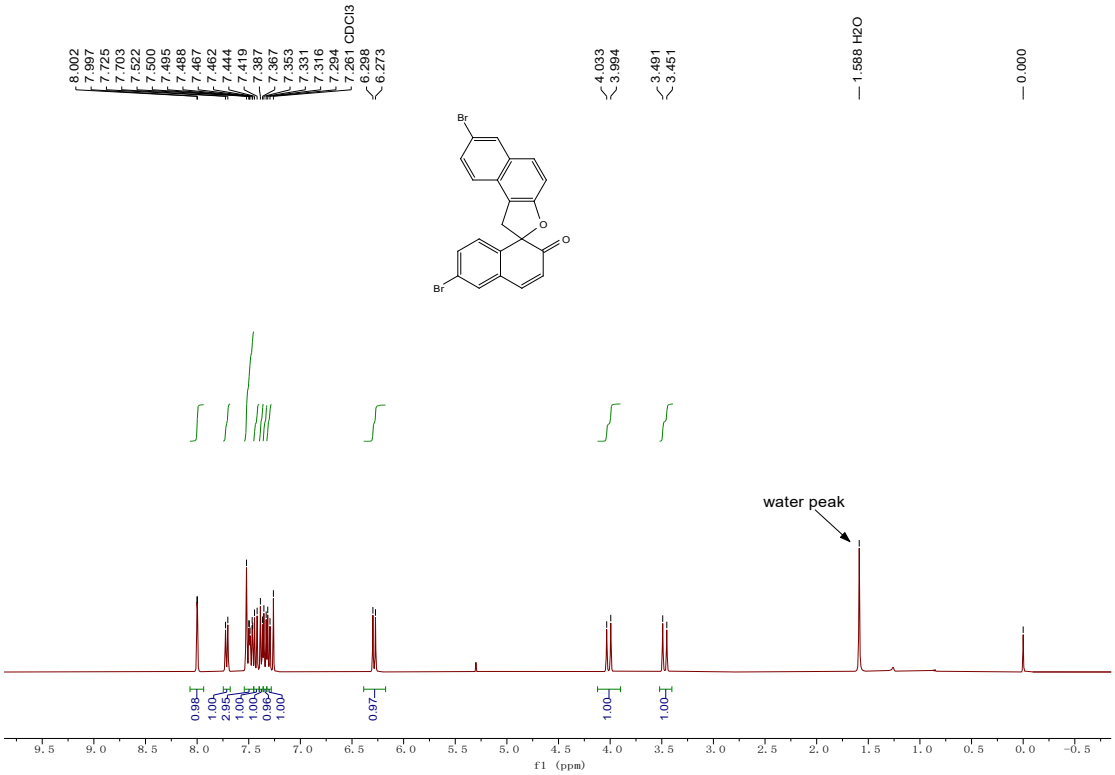
^{1}H NMR of Compound **2d** (400 MHz, $CDCl_3$)



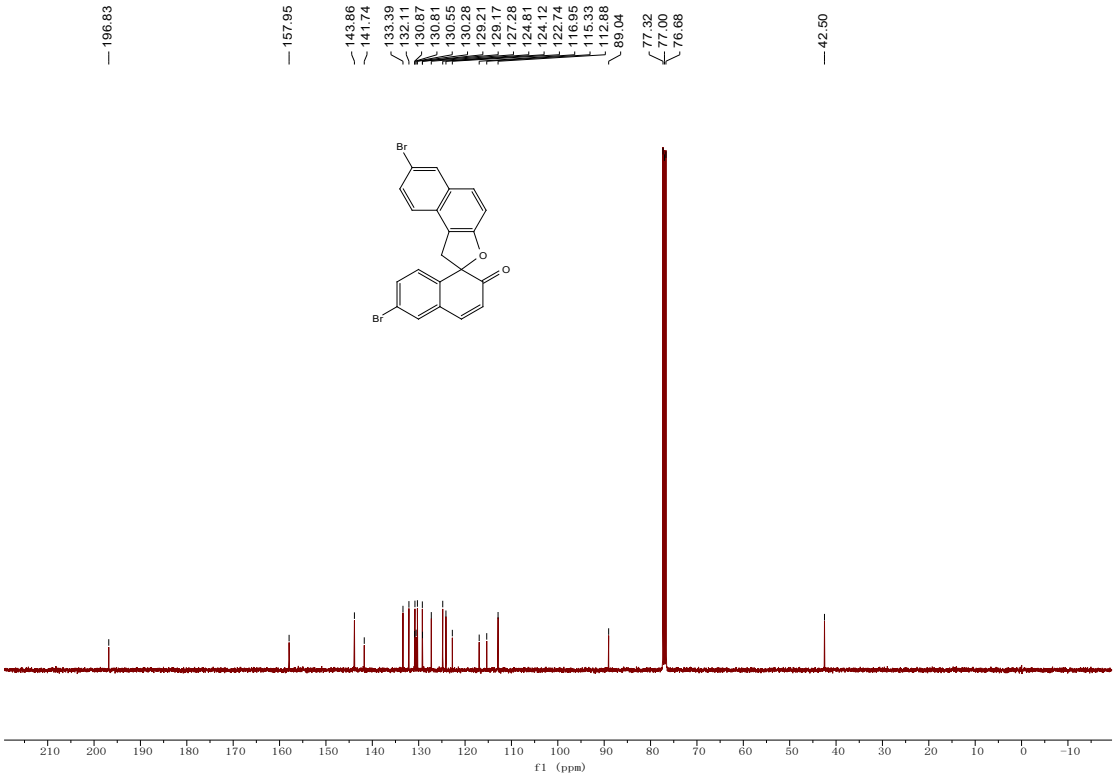
^{13}C NMR of Compound **2d** (100 MHz, $CDCl_3$)



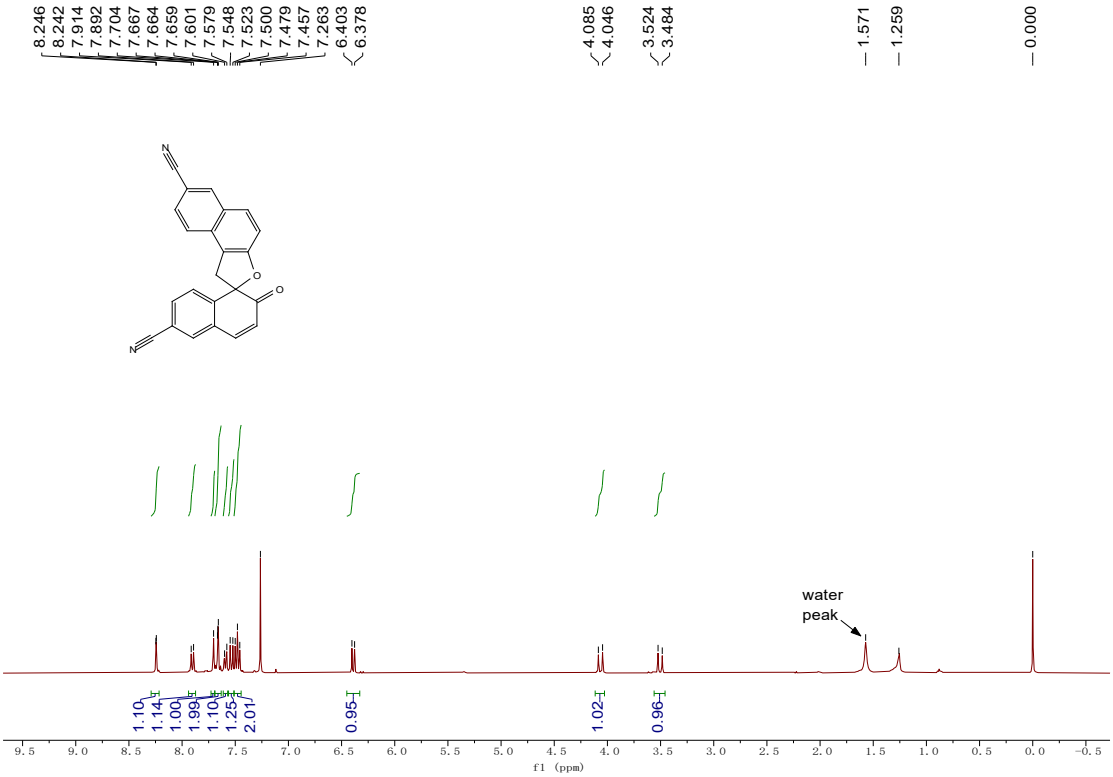
^{1}H NMR of Compound **2e** (400 MHz, $CDCl_3$)



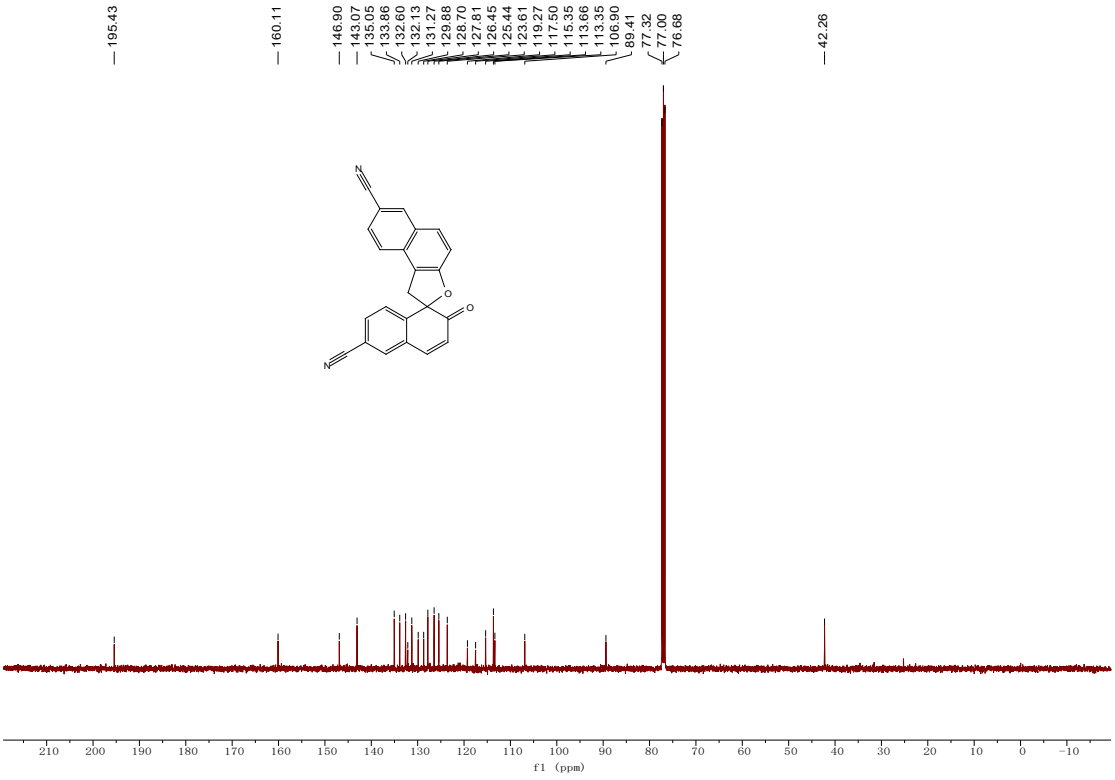
^{13}C NMR of Compound **2e** (100 MHz, $CDCl_3$)



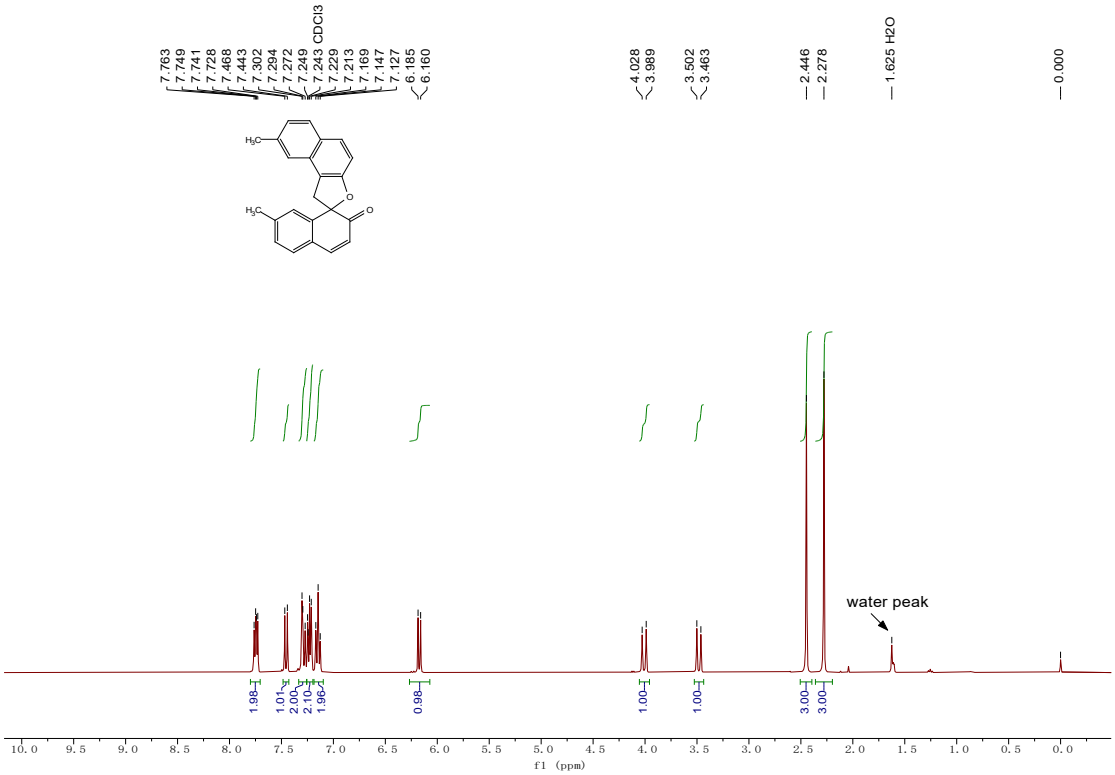
^{1}H NMR of Compound **2f** (400 MHz, $CDCl_3$)



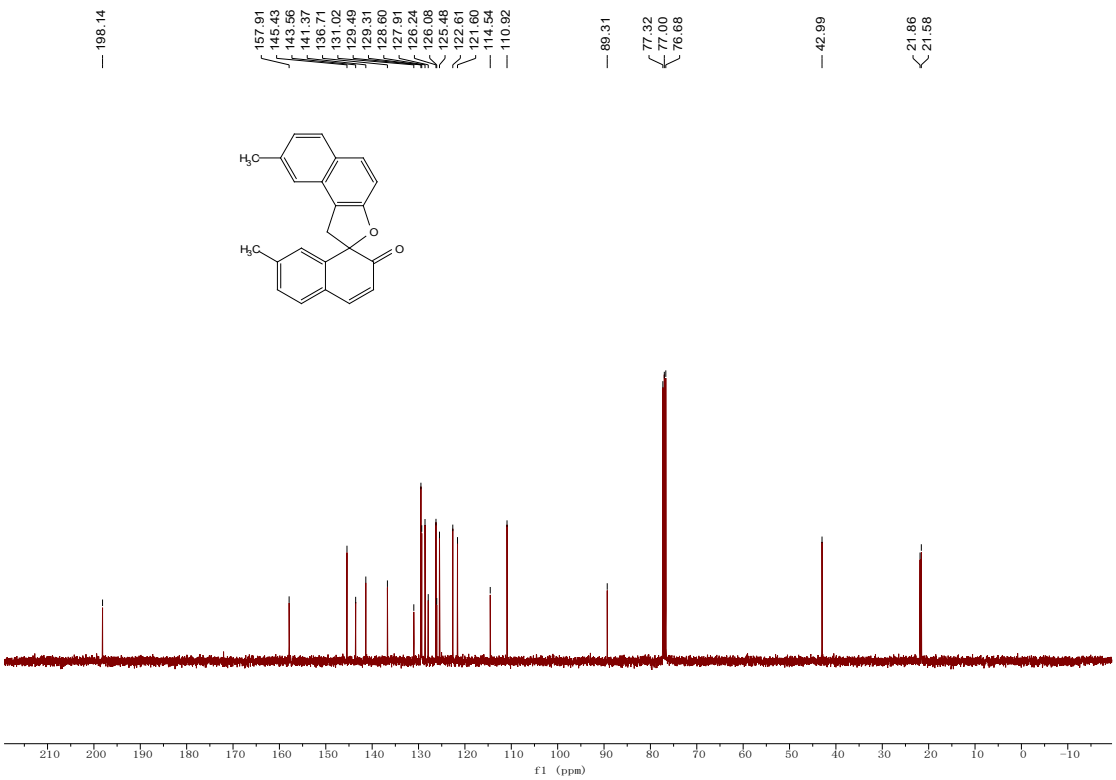
^{13}C NMR of Compound **2f** (100 MHz, $CDCl_3$)



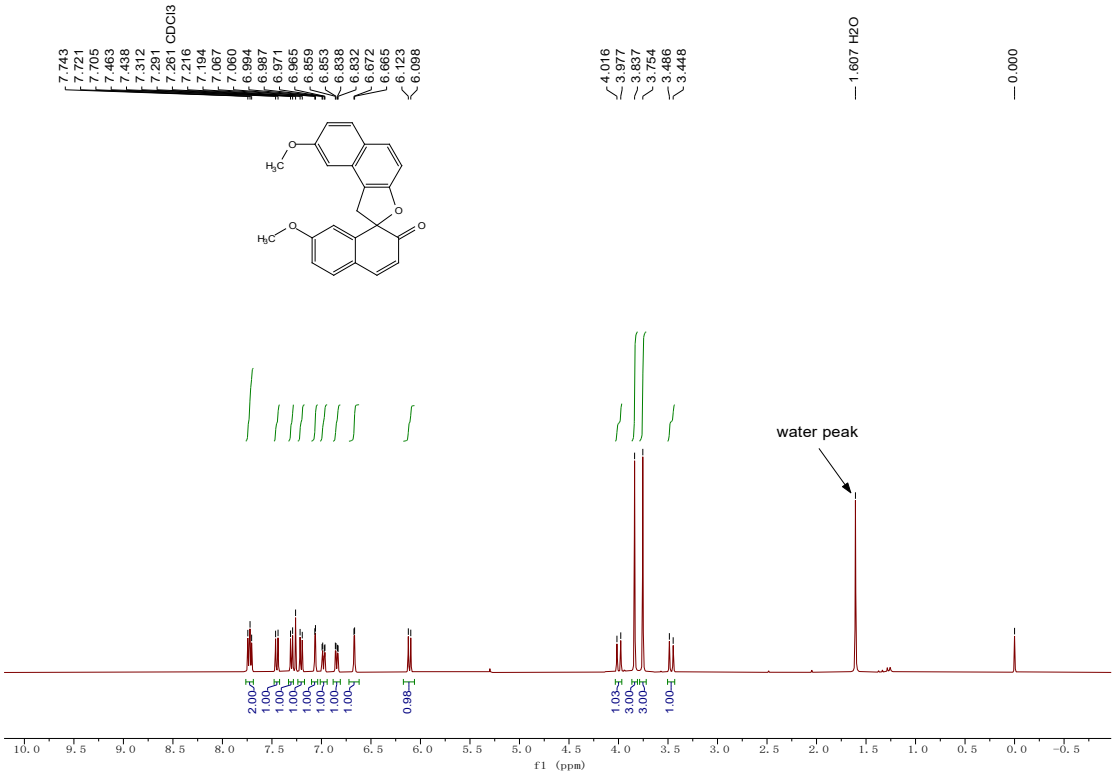
^{1}H NMR of Compound **2g** (400 MHz, $CDCl_3$)



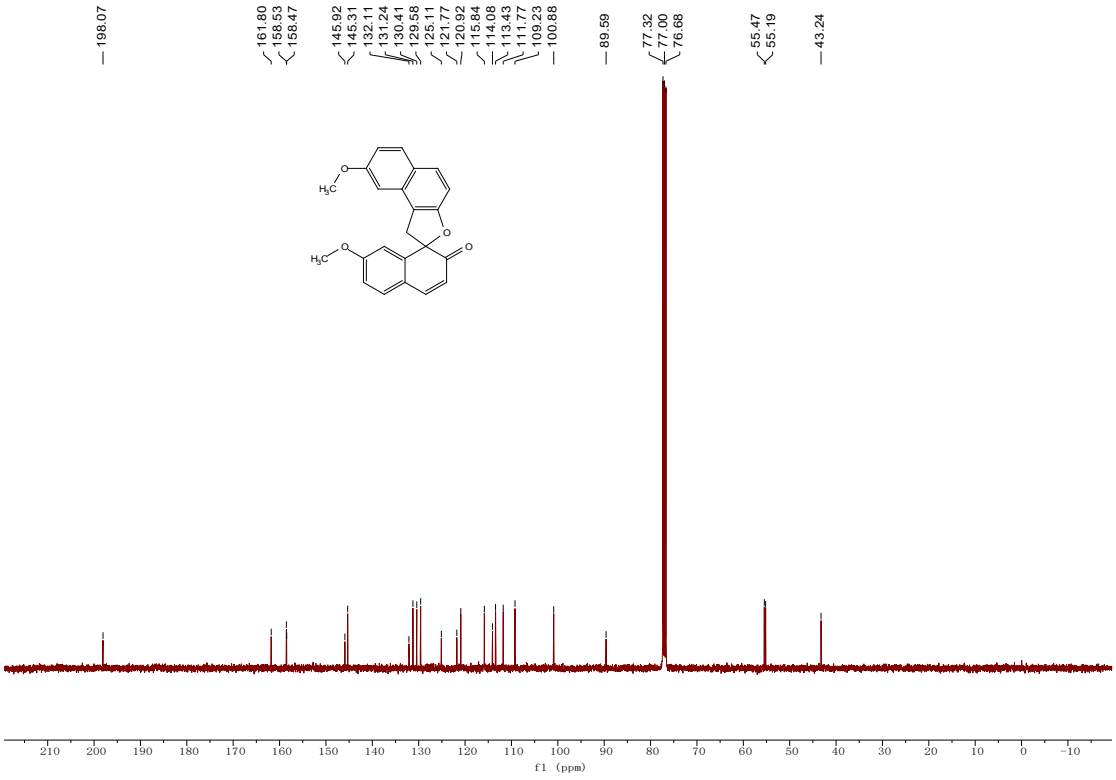
^{13}C NMR of Compound **2g** (100 MHz, $CDCl_3$)



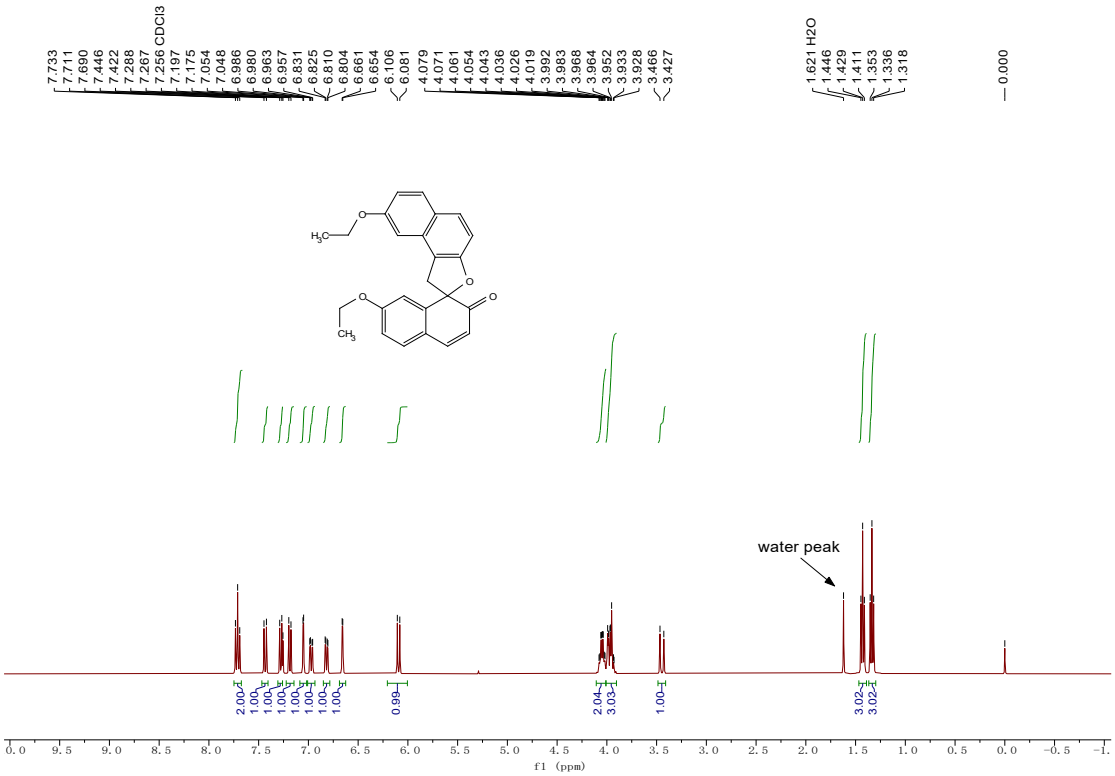
^{1}H NMR of Compound **2h** (400 MHz, $CDCl_3$)



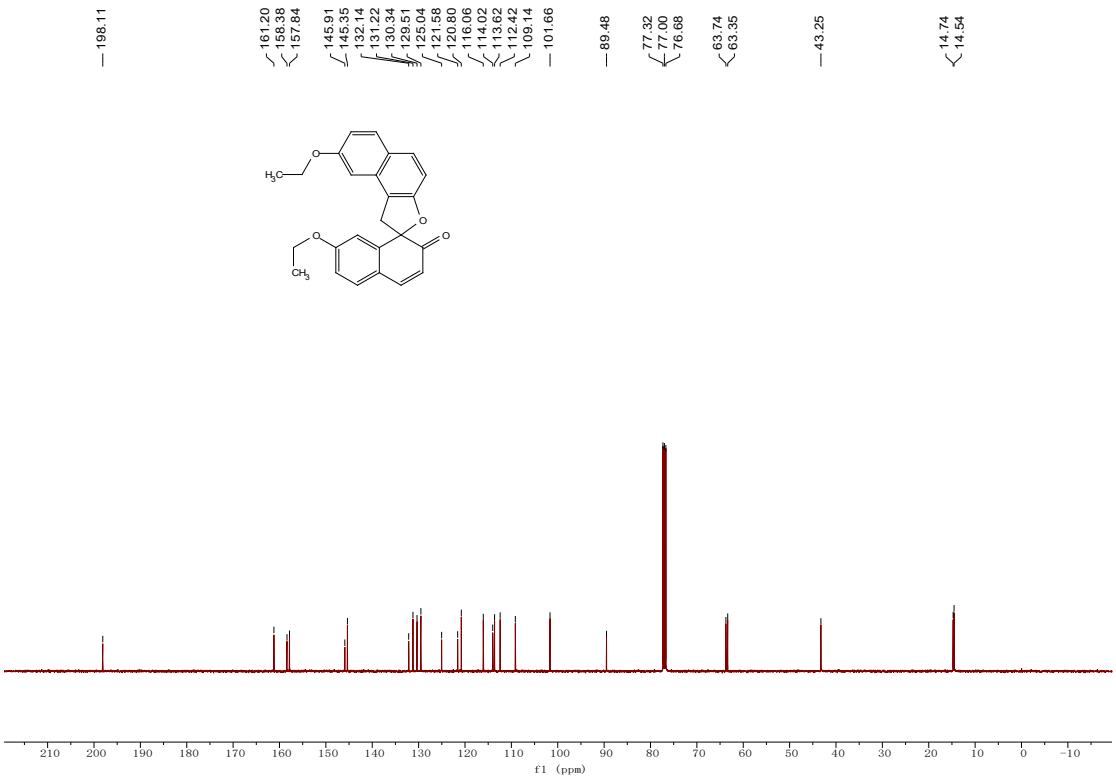
^{13}C NMR of Compound **2h** (100 MHz, $CDCl_3$)



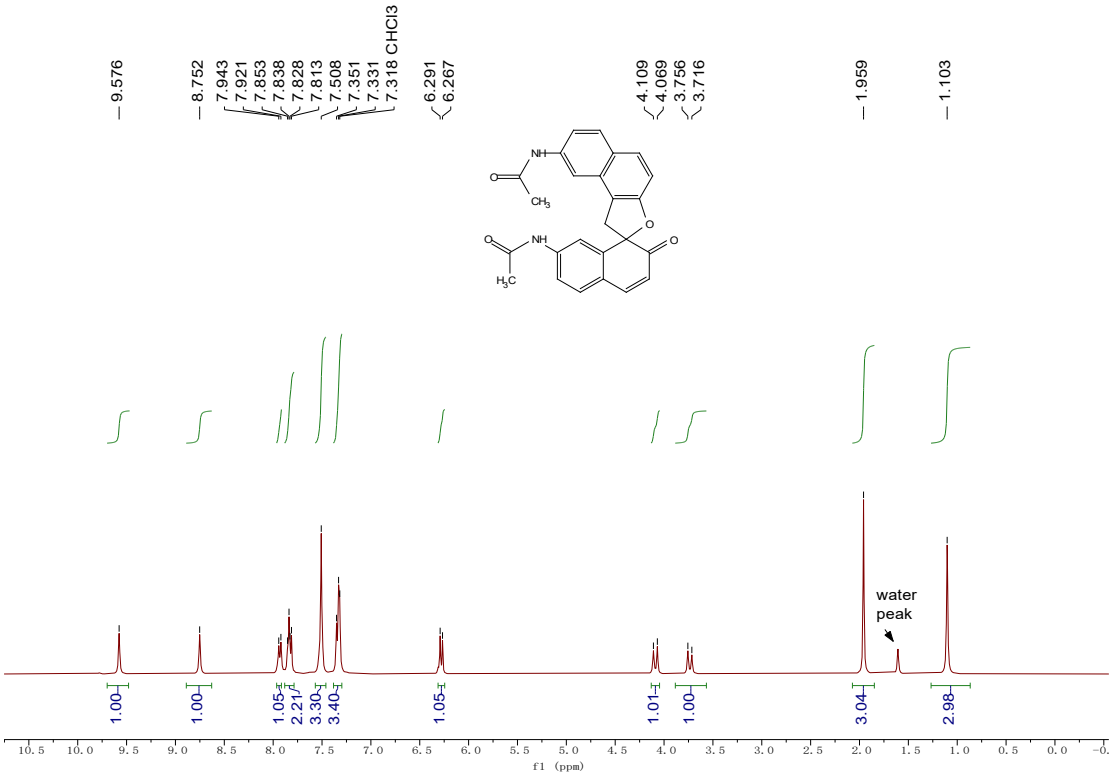
^{1}H NMR of Compound **2i** (400 MHz, $CDCl_3$)



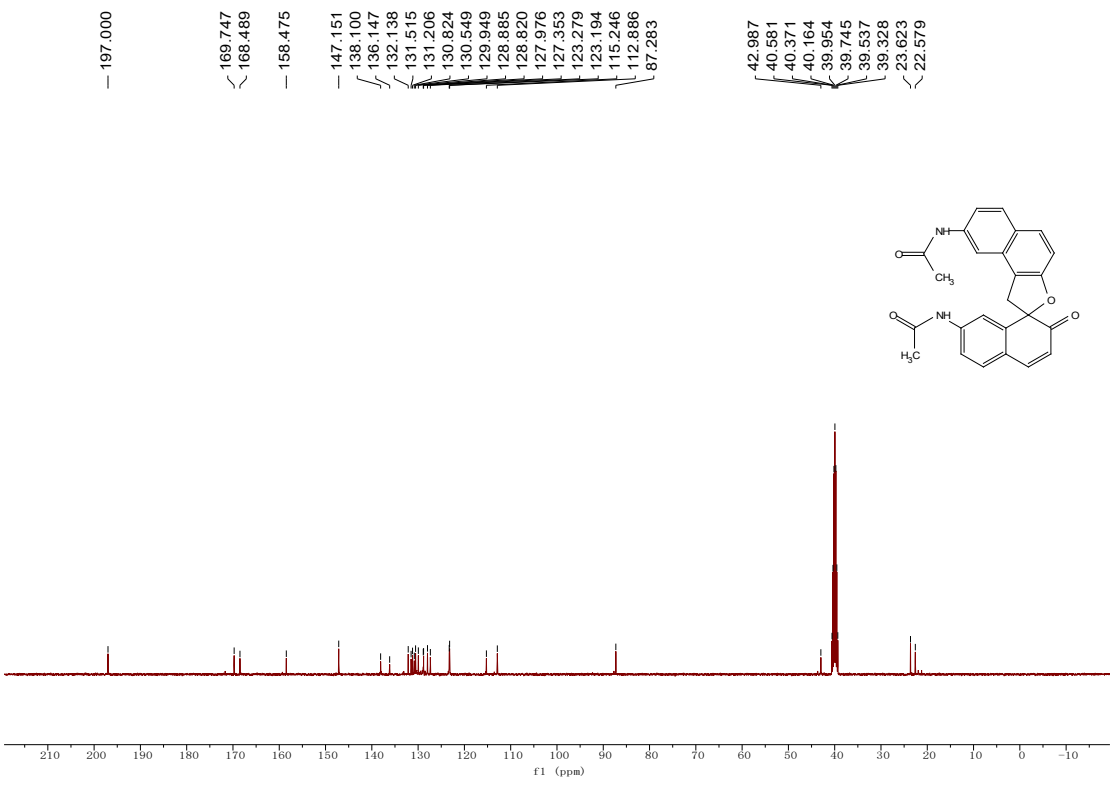
^{13}C NMR of Compound **2i** (100 MHz, $CDCl_3$)



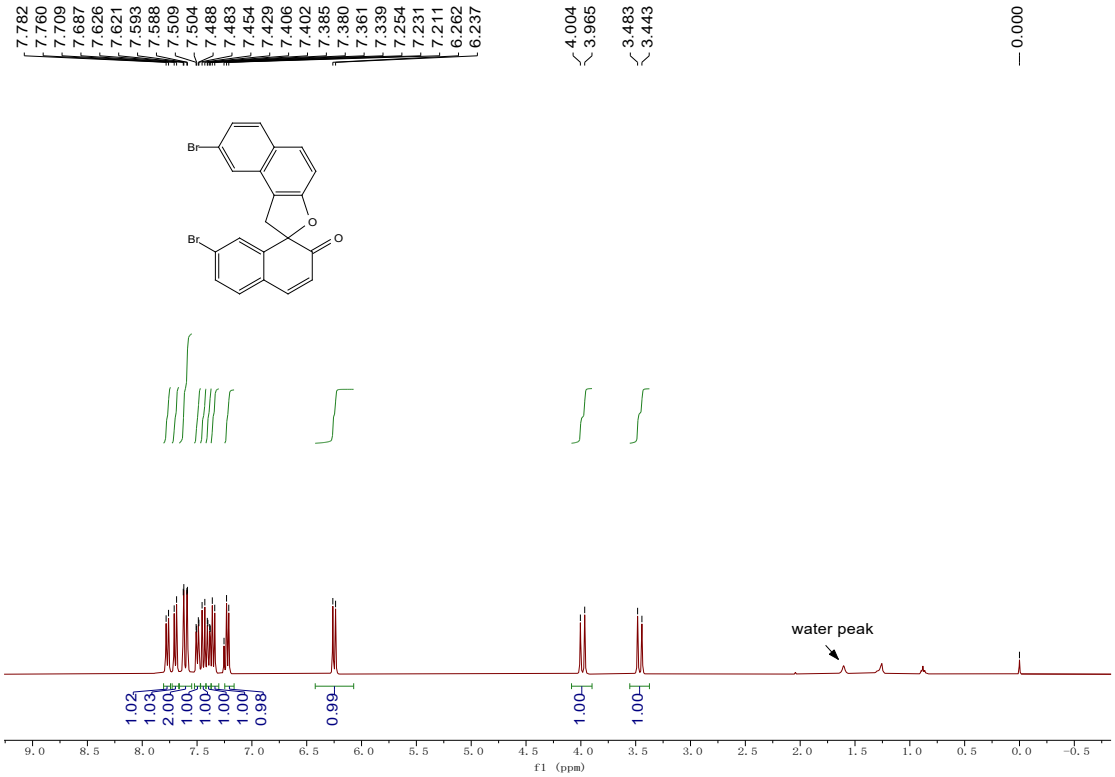
^{1}H NMR of Compound **2j** (400 MHz, $CDCl_3$)



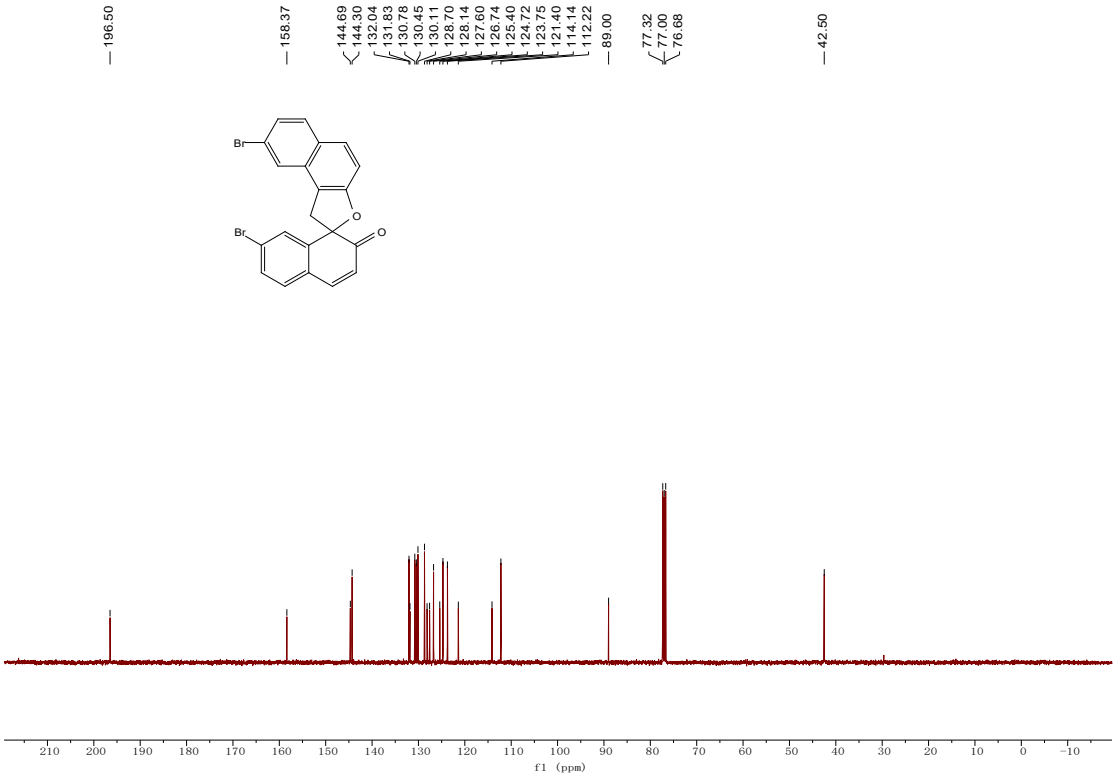
^{13}C NMR of Compound **2j** (100 MHz, d^{6}-DMSO)



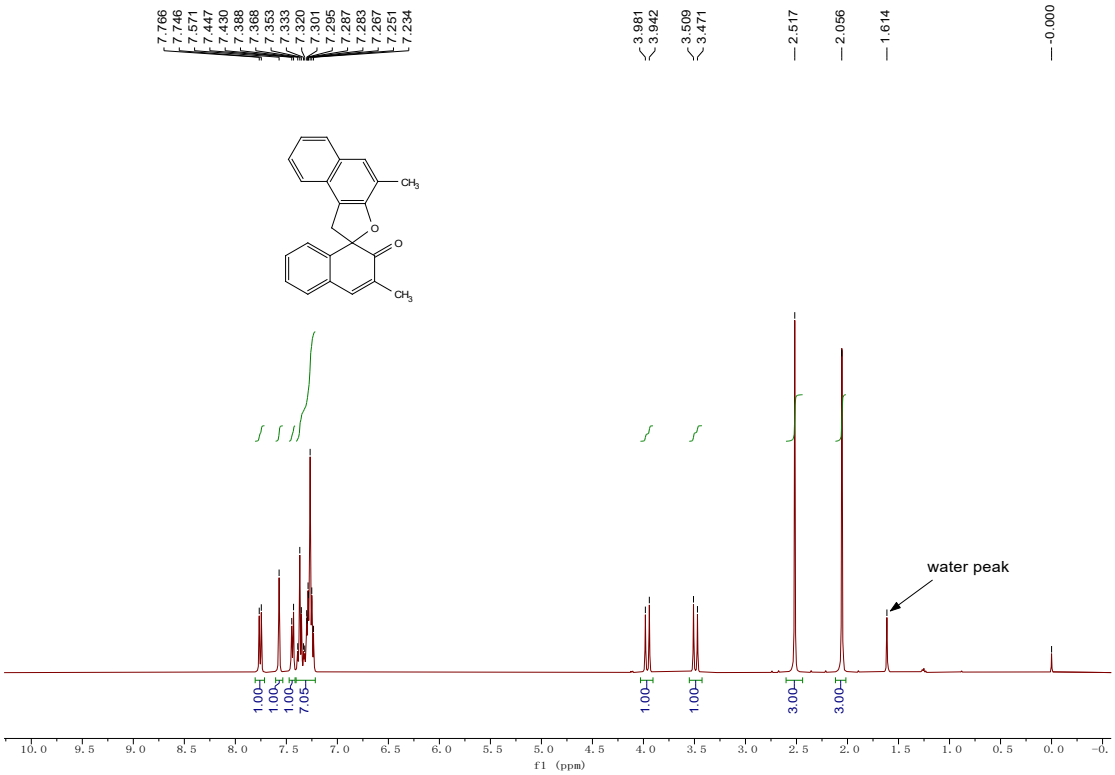
^{1}H NMR of Compound **2k** (400 MHz, $CDCl_3$)



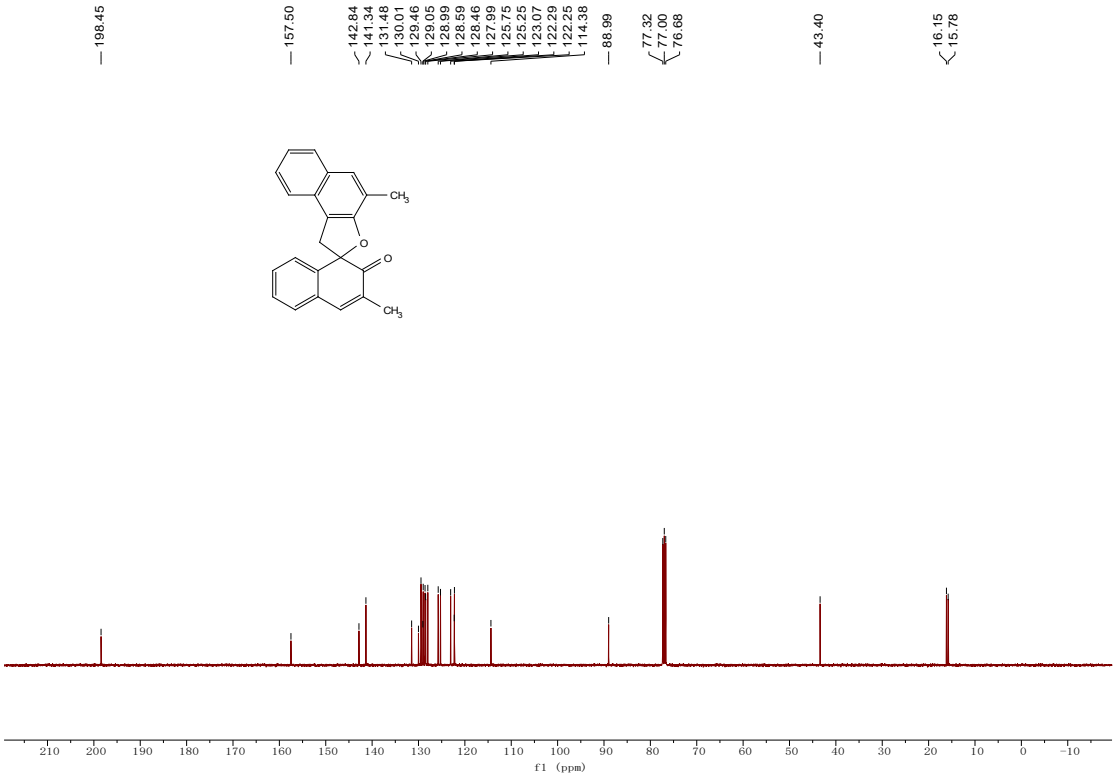
^{13}C NMR of Compound **2k** (100 MHz, $CDCl_3$)



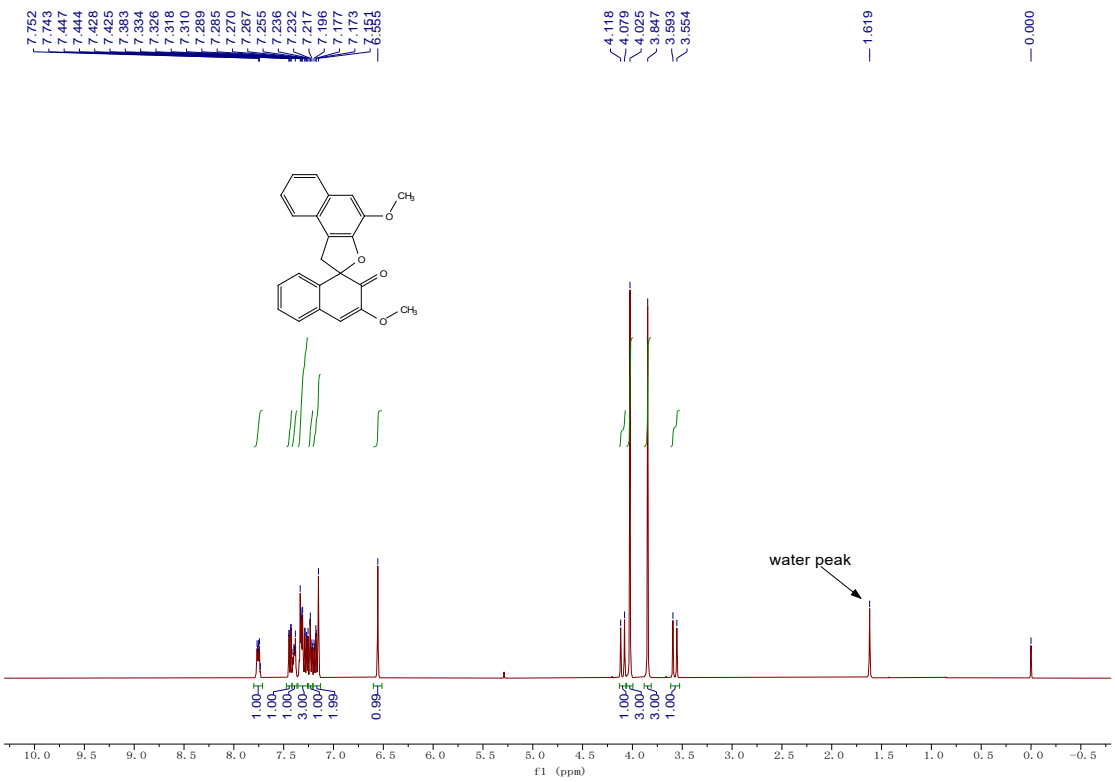
^{1}H NMR of Compound **2l** (400 MHz, $CDCl_3$)



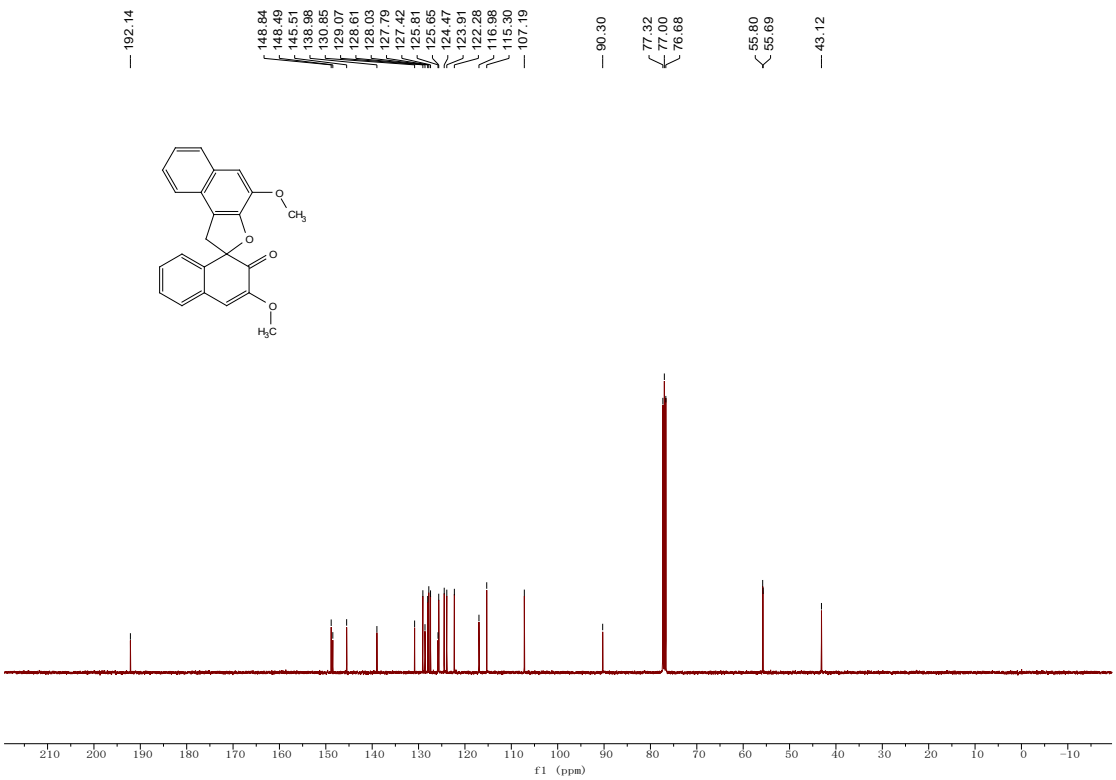
^{13}C NMR of Compound **2l** (100 MHz, $CDCl_3$)



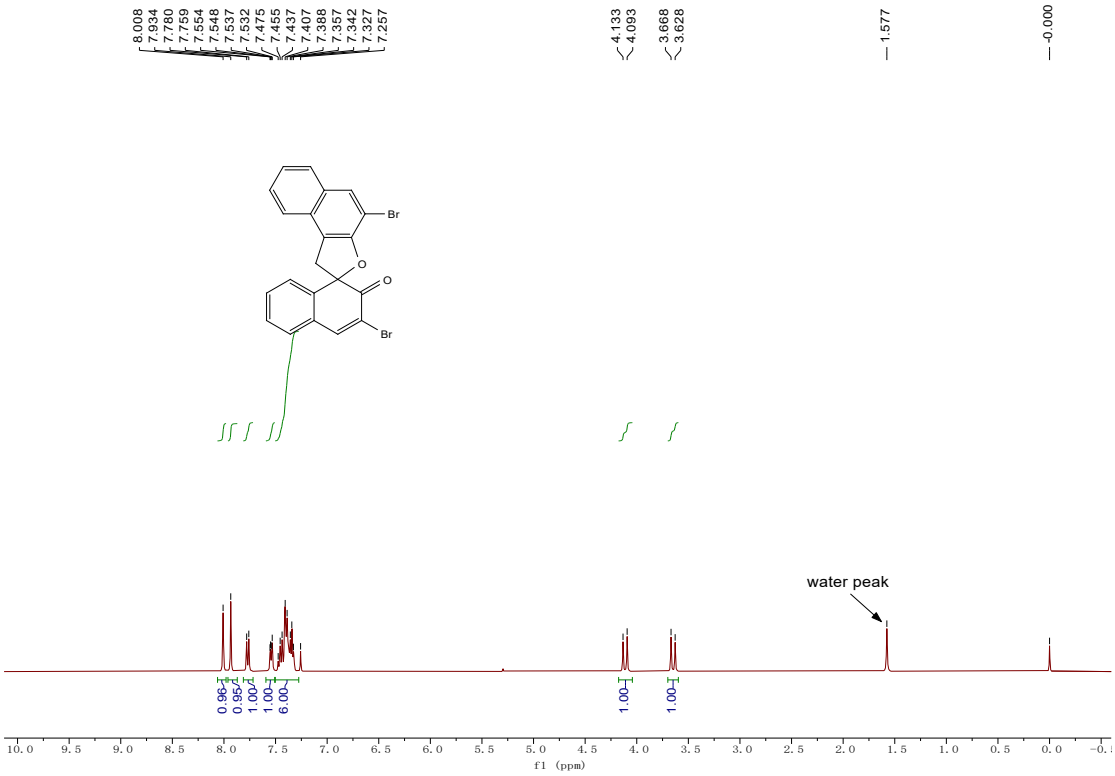
^{1}H NMR of Compound **2m** (400 MHz, $CDCl_3$)



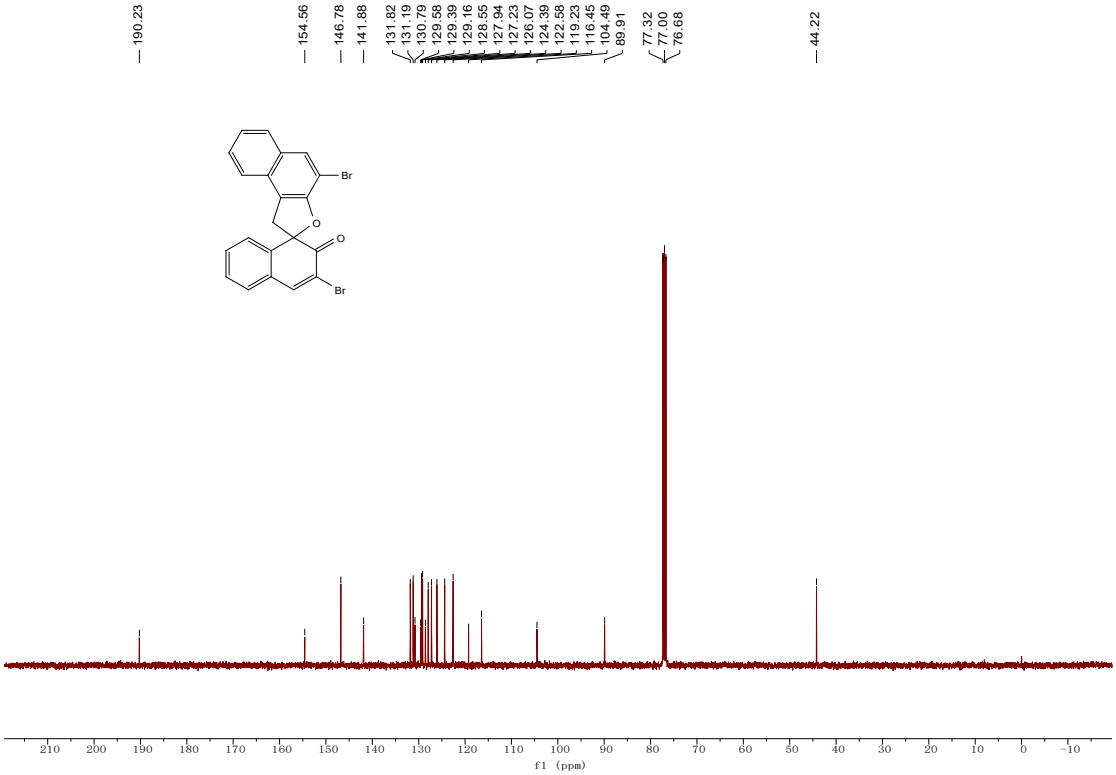
^{13}C NMR of Compound **2m** (100 MHz, $CDCl_3$)



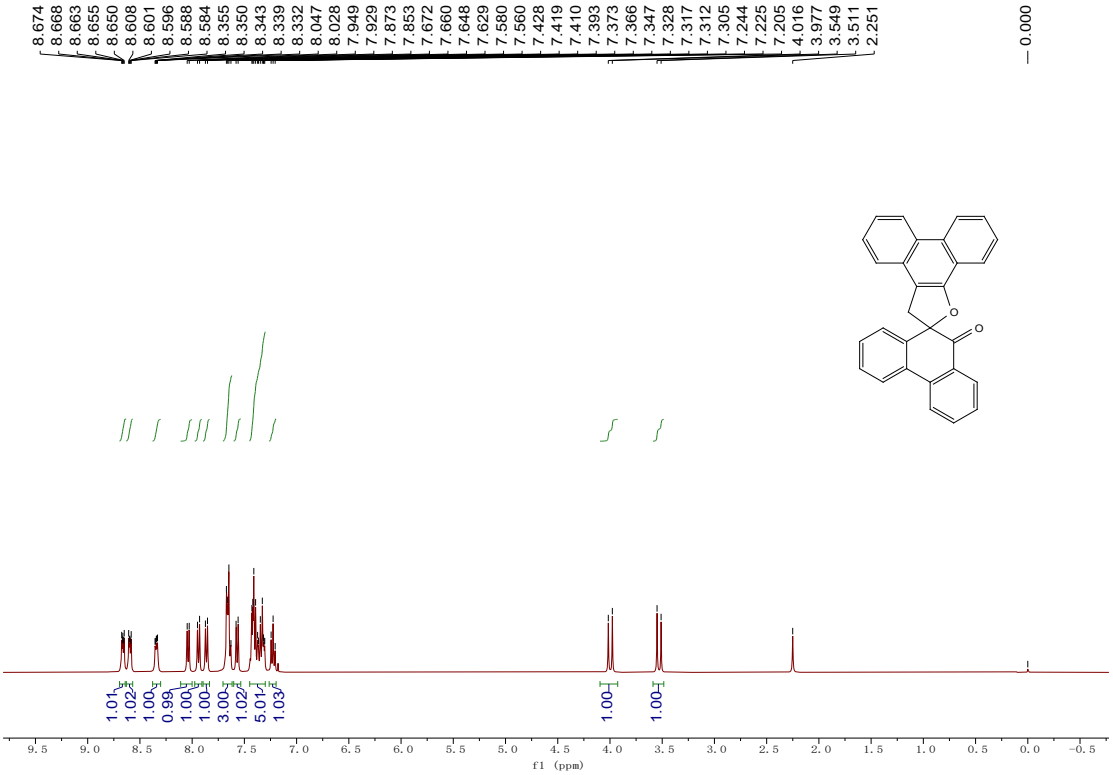
^{1}H NMR of Compound **2n** (400 MHz, $CDCl_3$)



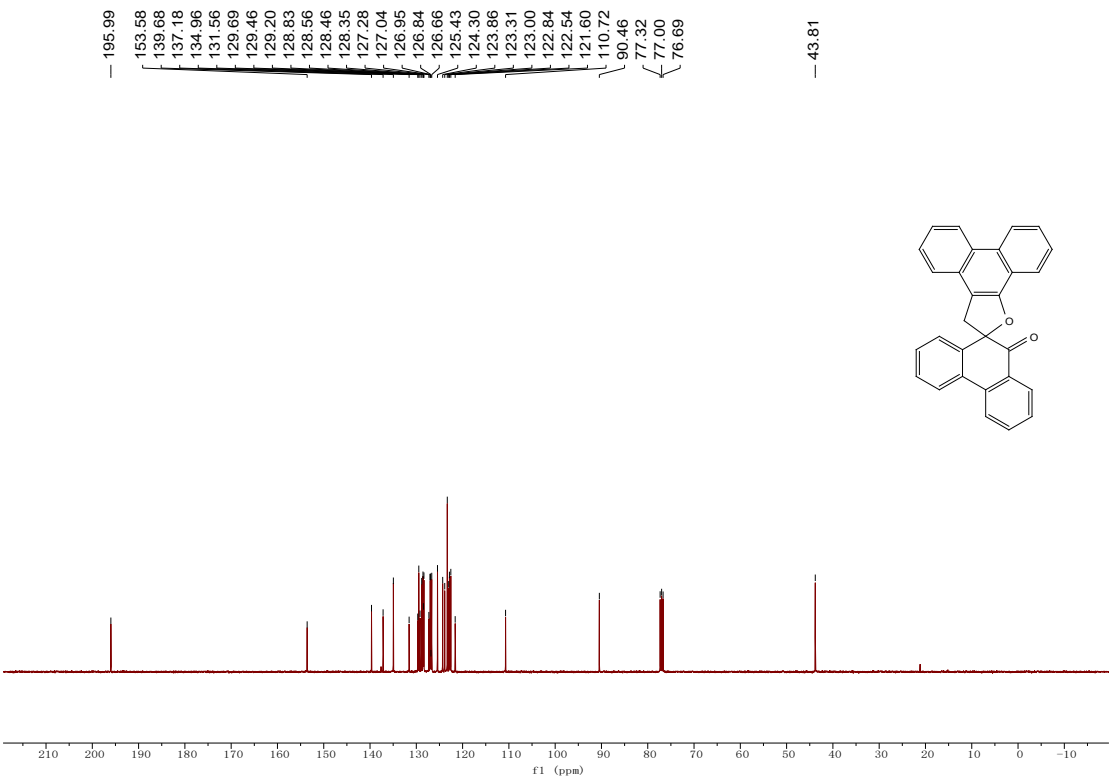
^{13}C NMR of Compound **2n** (100 MHz, $CDCl_3$)



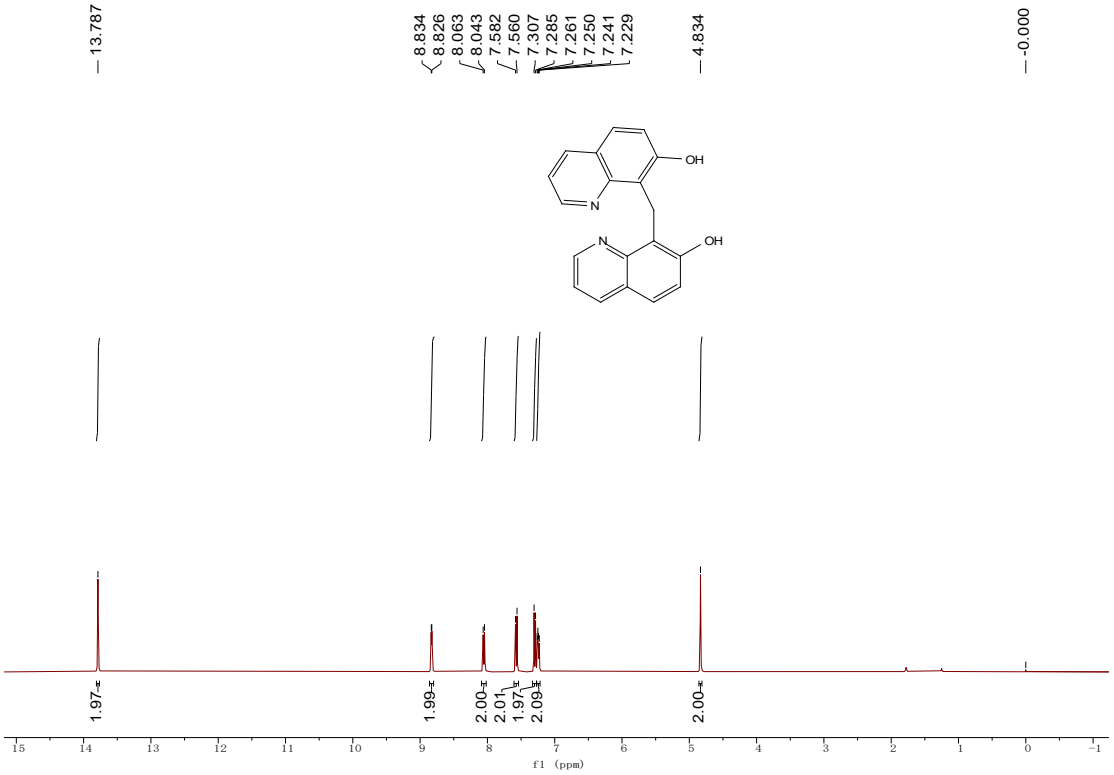
^{1}H NMR of Compound **2o** (400 MHz, $CDCl_3$)



^{13}C NMR of Compound **2o** (100 MHz, $CDCl_3$)



^{1}H NMR of Compound **3** (400 MHz, $CDCl_3$)



^{13}C NMR of Compound **3** (100 MHz, $CDCl_3$)