Electronic Supplementary Material (ESI) for ChemComm.

Solvent-controlled selective synthesis of biphenols and quinones via oxidative coupling of phenols

*NagnathYadav More and MasilamaniJeganmohan**

Department of Chemistry, Indian Institute of Science Education and Research, Pune 411008, India

Email: mjeganmohan@iiserpune.ac.in

Electronic Supplementary Information (ESI)

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Experimental Section

General Information

Yields refer to isolated yields of compounds estimated to be > 95 % pure as determined by ^{1}H NMR (25 °C). NMR spectra were recorded on solutions in deuterated chloroform ($CDCl_3$) and deuterated methanol (CD_3OD). Column chromatographically purifications were performed using SiO_2 (130–150 mesh ASTM) from Merck if not indicated otherwise. CF_3COOH, $K_2S_2O_8$, DDQ, CF_3SO_3H, other reagents or chemicals were used as purchased without further purification.

A. General Procedure for the Homocoupling of Phenols and Naphthols **1**.

In a 10-mL Schlenk tube, substituted phenols or naphthols **1** (100 mg) and $K_2S_2O_8$ (2.0 equiv) were taken. To the tube, was then added CF_3COOH (0.5 mL) via syringe. Then, the tube was covered with a septum and stirred at room temperature. The reaction worked very well under an air atmosphere (The whole reaction mixture is an under air atmosphere. Nitrogen purging was not done). The consumption of the substrate was monitored by TLC. The reaction mixture was diluted with CH_2Cl_2 and solvents were evaporated under vacuum. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **2**.

B. General Procedure for Synthesis of Substituted Quinones.

In a 10-mL Schlenk tube, substituted phenols or naphthols **1** (100 mg) and $K_2S_2O_8$ (2.0 equiv) were taken. To the tube, was then added CH_3CN and H_2O (1.0 + 1.0 mL) via syringe (Normal water was used without further distillation). Then, the tube was covered with a septum and stirred at 80 °C for 3 h. The reaction worked very well under an air atmosphere (The whole reaction mixture is an under air atmosphere. Nitrogen purging was not done). After 3 h, the reaction mixture was quenched by water and the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 10mL) and combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **4**, **5** and **6**.

Procedure for the Homocoupling of Sesamol (1e) for 500 mg Scale Reaction.

In a 25-mL round bottom flask, sesamol **1e** (500 mg) and $K_2S_2O_8$ (2.0 equiv) were taken. To the flask, was then added CF_3COOH (5.0 mL) via syringe and the flask was covered with a septum. Then, the reaction mixture was allowed to stir at room temperature for 4 h. The reaction worked very well under an air atmosphere (The whole reaction mixture is an air atmosphere. Nitrogen purging was not done). The reaction mixture was diluted with CH_2Cl_2 and solvents were evaporated under vacuum. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **2e**.

Procedure for the Homocoupling of 4-Methoxy phenol (1f) for 1.0 Gram Scale.

In a 25-mL round bottom flask, 4-methoxy phenol (**1f**) (1.0 gm) and $K_2S_2O_8$ (2.0 equiv) were taken. To the flask, was then added CF_3COOH (5.0 mL) via syringe and the flask was covered with a septum. Then, the reaction mixture was allowed to stir at room temperature for 7 h. The reaction worked very well under an air atmosphere (The whole reaction mixture is an air atmosphere. Nitrogen purging was not done).The reaction mixture was diluted with CH_2Cl_2 and solvents were evaporated under vacuum. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **2f**.

Procedure for the Homocoupling of 2-Naphthol (1j) for 1.0 Gram Scale.

In a 25-mL round bottom flask, 2-naphthol (**1j**) (1.0 gm) and $K_2S_2O_8$ (2.0 equiv) were taken. To the flask, was then added CF_3COOH (5.0 mL) via syringe and the flask was covered with a septum. Then, the reaction mixture was allowed to stir at room temperature for 16 h. The reaction worked very well under an air atmosphere (The whole reaction mixture is an air atmosphere. Nitrogen purging was not done).The reaction mixture was diluted with CH_2Cl_2 and solvents were evaporated under vacuum. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **2j**.

Procedure for the coupling of 1o for 1.0 Gram Scale.

In a 25-mL round bottom flask, 2-methyl phenol (**1o**) (1.0 gm) and $K_2S_2O_8$ (2.0 equiv) were taken. To the tube, was then added CH_3CN and H_2O (8.0 + 8.0 mL) via syringe (Normal water was used without further distillation). Then, the tube was covered with a septum and stirred at 80 °C for 6 h. After 6 h, the reaction mixture was quenched by water and the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 100 mL) and combined organic layers were washed with water and brine, dried

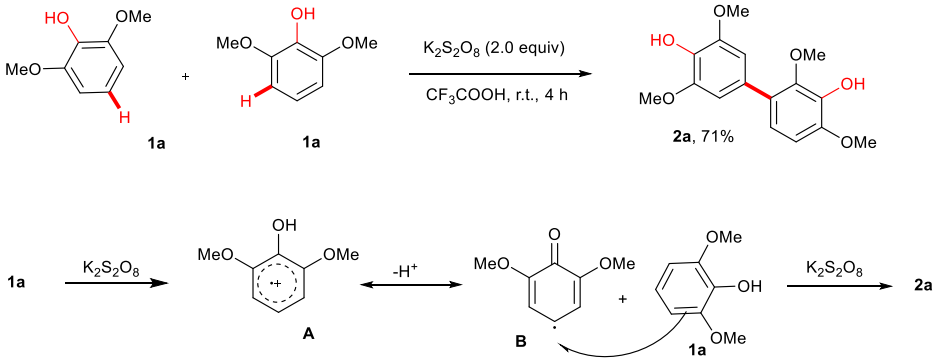
over anhydrous Na_2SO_4 and evaporated under vacuum. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **6a**. (550 mg, 55%)

Procedure for the preparation of Phenazine 8.

In a 25-mL round bottom flask, 2'-hydroxy-[1,1'-binaphthalene]-3,4-dione **6g** (100 mg) and 1,2-diaminobenzene **7** (4.0 equiv) were taken in AcOH (10 mL). Then, the reaction mixture was cover with a septum and allowed to stir at room temperature for 12 h. After 12 h, the reaction mixture was diluted with CH_2Cl_2 and solvents were evaporated under vacuum. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **8**.

UV-Vis Study to Detect a Phenol Cation Radical Intermediate.

To support the formation of a phenol cationic intermediate, the UV-Vis spectroscopy study was done.[1] For 2,6-dimethoxyphenol (**1a**), an intense absorption band was observed at the visible region 456 nm in CF_3COOH solvent which accounts for intermediate **A** and 345 nm in CH_3CN solvent which accounts for intermediate **B**. An intense absorption band was observed at the visible region 415 nm during the reaction of phenol 2,4-dimethylphenol (**1c**) with $K_2S_2O_8$ at room temperature. Similarly, an intense absorption band was observed at the visible region 453 nm for sesamol (**1e**) with $K_2S_2O_8$. Similarly, for 2,6-dimethylphenol (**1n**), an intense absorption band was observed at 425 nm in CF_3COOH solvent which accounts for intermediate **A** and at 410 nm in CH_3CN solvent which accounts for intermediate **B**.



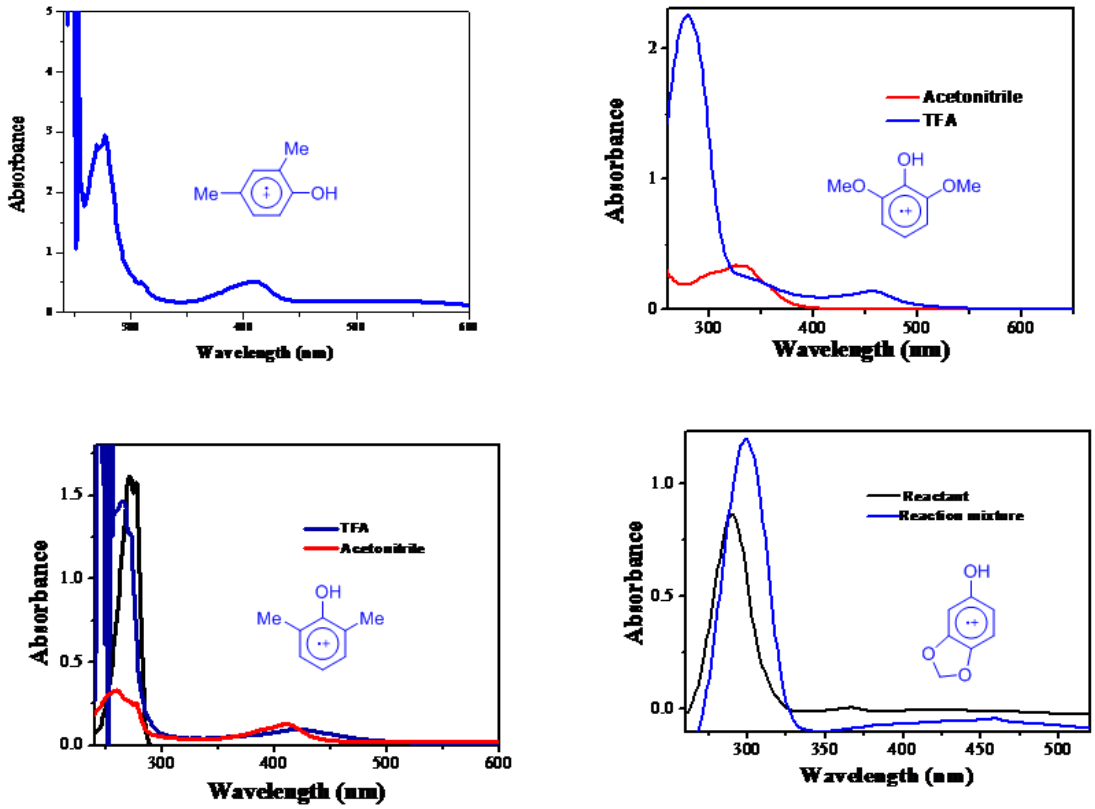


Figure 1: UV-Vis spectroscopy study at ambient temperature.

1. (a) Gadosy, T. A.; Shukla, D.; Johnston, L. J. *J. Phys. Chem. A.* **1999,** *103*, 8834. (b) Joshi, R.; Naumov, S.; Kapoor, S.; Mukherjee,T.; Hermann R.; Brede, O. *J. Phys. Org. Chem.* **2004**, *17*, 665.(c) Sankararaman, S.; Haney, W. A.; Kochi, J. K. *J. Am. Chem. Soc*. **1987**, *109*, 7824. (d) Kita, Y.; Tohma, H.; Hatanaka, K.; Takada, T.; Fujata, S.; Mitoh, S.; Sakurai, H.; Oka, S. *J. Am. Chem. Soc*. **1994**, *116*, 3684.

EPR Analysis

Phenol **1a** was treated with $K_2S_2O_8$ in CF_3COOH under nitrogen atmosphere for 15 min and the EPR analysis was done in the corresponding reaction mixture. A clear very sharp radical signal was at 1.9907 region. This result clearly mentions that the radical intermediate was observed in the reaction. Meanwhile, no signal was observed in the reaction of **1a** without $K_2S_2O_8$ in CF_3COOH and **1a** without $K_2S_2O_8$ and CF_3COOH.

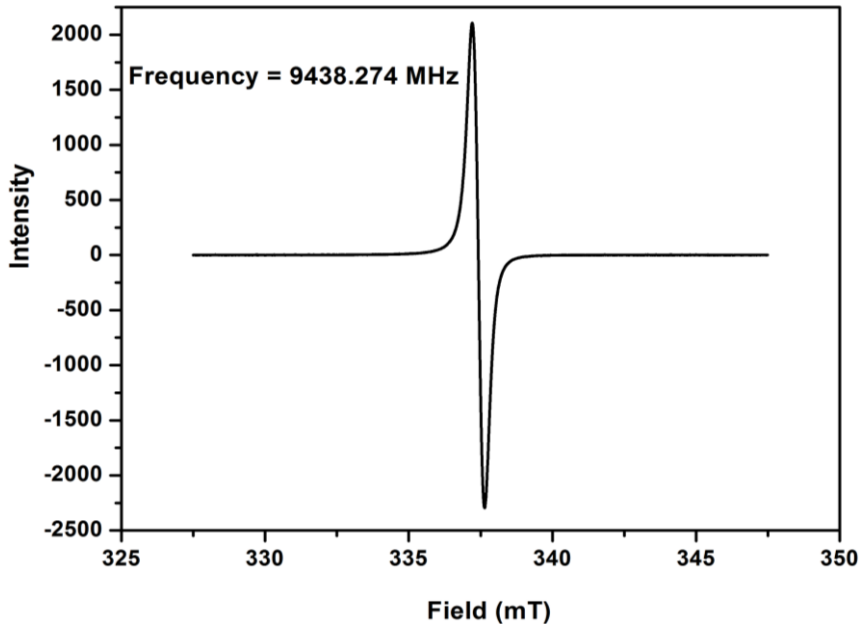


Figure S1: EPR spectrum for the reaction of phenol **1a** with $K_2S_2O_8$ in CF_3COOH under nitrogen atmosphere for 15 min

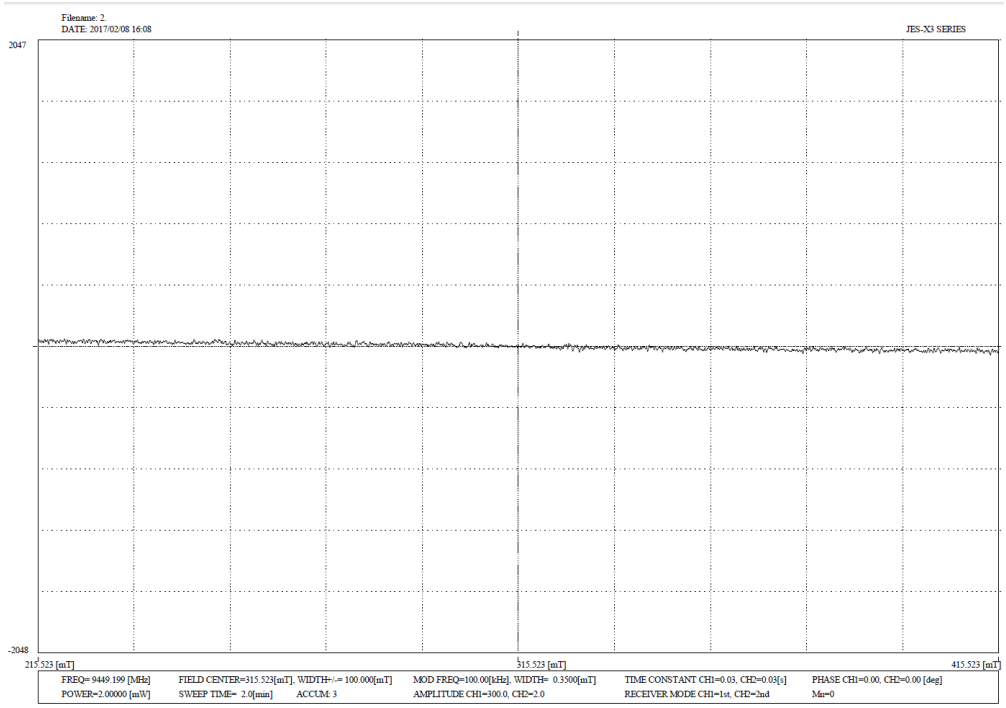


Figure S2: EPR spectrum for the reaction of phenol **1a** in CF_3COOH under nitrogen atmosphere for 15 min

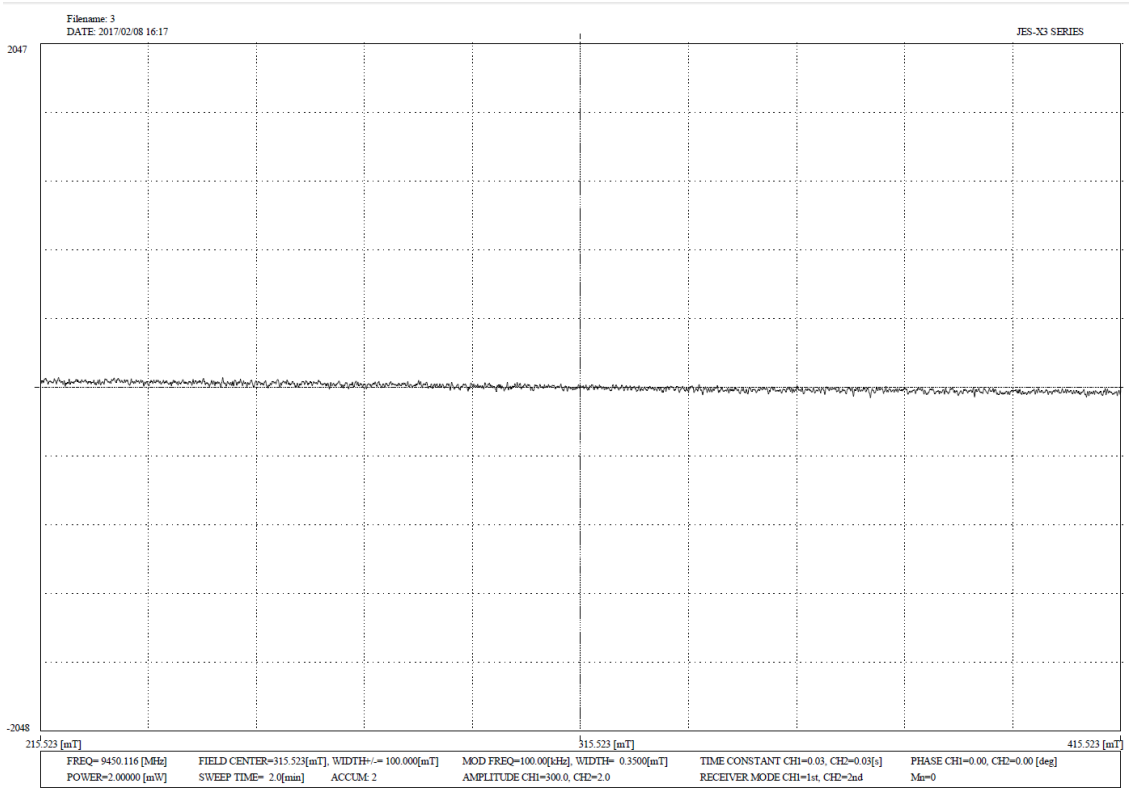
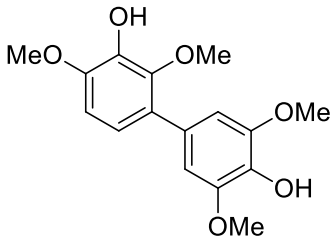


Figure S3: EPR spectrum for phenol **1a** without CF_3COOH

Spectral Data of All Compounds

2,3',4,5'-Tetramethoxy-[1,1'-biphenyl]-3,4'-diol (2a).



The representative general procedure **A** was followed using **1a** (100 mg). The reaction time is 4 h. Product **2a** was isolated in 72 mg and yield is 71%. Dark red solid; mp.156-158 °C; eluent (12 % ethyl acetate in hexanes).

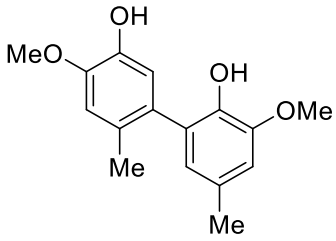
IR (ATR) ṽ (cm^{-1}): 3425, 2932, 1726, 1608, 1493, 1452, 1211, 1109, 1082, 900, 800, 733.

^{1}H NMR (CDCl$_3$, 400 MHz):δ 6.81 (d, *J* = 8.0 Hz, 1 H), 6.77 (s, 2 H), 6.69 (d, *J* = 8.0 Hz, 1 H), 3.90 (d, *J* = 4.0 Hz, 9 H), 3.55 (s, 3 H).

^{13}C NMR (CDCl$_3$, 100 MHz):δ 146.8, 144.5, 138.7, 133.8, 129.2, 127.9, 120.1, 106.9, 105.7, 60.5, 56.3, 56.2.

HRMS (ESI): calc. for [($C_{16}H_{18}O_6$)H] (M+H) 307.1182, measured 307.1181.

3,4'-Dimethoxy-5,6'-dimethyl-[1,1'-biphenyl]-2,3'-diol (2b).



The representative general procedure **A** was followed using **1b** (100 mg). The reaction time is 6 h. Product **2b** was isolated in 31 mg and yield is 31%. Brown semisolid; eluent (12 % ethyl acetate in hexanes).

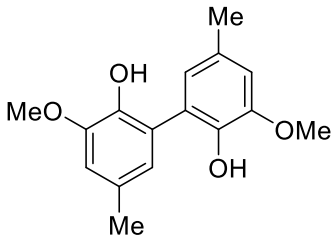
IR (ATR) ṽ (cm-1): 3852, 3671, 3286, 2366, 2319, 1698, 1648, 1477, 1388, 1263, 1222, 1113, 1074, 1018 814, 735.

^{1}H NMR (CDCl$_3$, 400 MHz): δ 6.79 (s, 1H), 6.75 (s, 1H), 6.67 (d, *J* = 4.0 Hz, 1H), 6.54 (d, *J* = 4.0 Hz, 1H), 5.43 (s, 1H), 5.42 (s, 1H), 3.9 (s, 3H), 3.89 (s, 3H), 2.29 (s, 3H), 2.12 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz):δ 146.2, 145.8, 143.2, 140.4, 129.9, 128.7, 128.3, 127.3, 123.3, 116.1, 112.3, 110.4, 56.0, 55.9, 21.1, 19.6.

HRMS (ESI): calc. for [($C_{16}H_{18}O_4$)H] (M+H) 275.1283, measured 275.1280.

3,3'-Dimethoxy-5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diol (2b').



The representative general procedure **A** was followed using **1b** (100 mg). The reaction time is 6 h. Product **2b'** was isolated in 17 mg and yield is 17%. Brown solid; mp.133-135 °C; eluent (15 % ethyl acetate in hexanes).

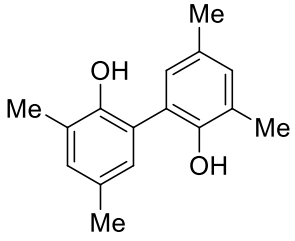
IR (ATR) ṽ (cm^{-1}): 3852, 3671, 3286, 2366, 2319, 1698, 1648, 1477, 1388, 1263, 1222, 1113, 1074, 1018 814, 735.

^{1}H NMR ($CDCl_3$, 400 MHz):δ 6.71 (d, *J* = 4.0 Hz, 4 H), 5.96 (s, 2 H), 3.91 (s, 6 H), 2.32 (s, 6 H).

^{13}C NMR ($CDCl_3$, 100 MHz):δ 147.0, 140.3, 129.6, 124.3, 123.4, 111.3, 56.0, 21.2.

HRMS (ESI): calc. for [($C_{16}H_{18}O_4$)H] (M+H) 275.1283, measured 275.1280.

3,3',5,5'-Tetramethyl-[1,1'-biphenyl]-2,2'-diol (2c).



The representative general procedure **A** was followed using **1c** (100 mg). The reaction time is 16 h. Product **2c** was isolated in 73 mg and yield is 73%.White solid; mp 133-134 °C; eluent (5% ethyl acetate in hexanes).

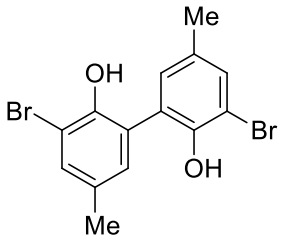
IR (ATR) ṽ (cm^{-1}):3861, 3744, 3535, 2960, 2924, 2369, 1711, 1698, 1477, 1281, 1216, 1122, 1074, 861, 786, 743.

^{1}H NMR ($CDCl_3$, 400 MHz):δ6.98 (s, 2 H), 6.85 (s, 2 H), 5.07 (s, 2 H), 2.26 (s, 12 H).

^{13}C NMR ($CDCl_3$, 100 MHz):δ149.1, 132.0, 130.0, 128.5, 125.2, 122.2, 20.4, 16.2.

HRMS (ESI): calc. for [($C_{16}H_{18}O_2$)H] (M+H) 243.1385, measured 243.1380.

3,3'-Dibromo-5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diol (2d).



The representative general procedure **A** was followed using **1d** (100 mg). The reaction time is 16 h. Product **2d** was isolated in 58 mg and yield is 58%. Pale yellow solid; mp.136-138 °C; eluent (12 % ethyl acetate in hexanes).

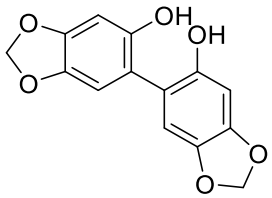
IR (ATR) ṽ (cm^{-1}): 3838, 3744, 3442, 2907, 2366, 2318, 1741, 1541, 1462, 1305, 1231, 1160, 847, 773, 671.

^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.34 (d, *J* = 4.0 Hz, 2 H), 6.99 (d, *J* = 4.0 Hz, 2 H), 5.80 (s, 2 H), 2.29 (s, 6 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ147.1, 132.6, 131.6, 131.4, 125.3, 110.9, 20.2.

HRMS (ESI): calc. for [($C_{14}H_{12}BrO_2$)H] (M+H) 370.9282, measured 370.9279.

[5,5'-bibenzo[*d*][1,3]dioxole]-6,6'-diol (2e).



The representative general procedure **A** was followed using **1e** (100 mg). The reaction time is 4 h. Product **2e** was isolated in 79 mg and yield is 80%.Ash colour solid; mp.202-203 °C; eluent (15 % ethyl acetate in hexanes).

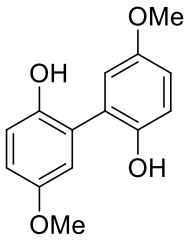
IR (ATR) ṽ (cm^{-1}):3837, 3744, 3210, 2898, 2366, 2318, 1743, 1698, 1634, 1540, 1486, 1229, 1164, 1030, 927, 763.

^{1}H NMR (MeOH-d_4, 400 MHz):δ 6.65 (s, 2 H), 6.47 (s, 2 H), 5.88 (s, 4 H).

^{13}C NMR (MeOH-d_4, 100 MHz):δ 149.6, 148.9, 142.8, 119.2, 111.2, 102.4, 99.4, 49.0.

HRMS (ESI): calc. for [($C_{14}H_{10}O_6$)H] (M+H) 275.0556, measured 275.0554.

5,5'-Dimethoxy-[1,1'-biphenyl]-2,2'-diol (2f).



The representative general procedure **A** was followed using **1f** (100 mg). The reaction time is 7 h. Product **2f** was isolated in 55 mg and yield is 55%.Colourless semisolid; eluent (10 % ethyl acetate in hexanes).

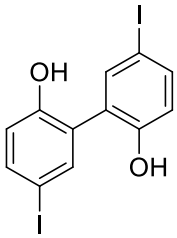
IR (ATR) ṽ (cm^{-1}): 3852, 3671, 3286, 2366, 2319, 1698, 1648, 1477, 1388, 1263, 1222, 1113, 1074, 1018 814, 735.

^{1}H NMR (MeOH-d_4, 400 MHz):δ 6.88 – 6.84 (m, 2 H), 6.81 (m, 4 H), 6.62 (s, 2 H), 3.76 (s, 6 H).

^{13}C NMR (MeOH-d_4, 400 MHz):δ 154.1, 146.4, 125.6, 117.8, 116.0, 115.3, 55.83.

HRMS (ESI): calc. for [($C_{14}H_{14}O_4$)H] (M+H) 247.0970, measured 247.0964.

5,5'-Diiodo-[1,1'-biphenyl]-2,2'-diol (2g).



The representative general procedure **A** was followed using **1g** (100 mg). The reaction time is 16 h. Product **2g** was isolated in 49 mg and yield is 49%.Pale yellow solid; mp.112-115 °C; eluent (12 % ethyl acetate in hexanes).

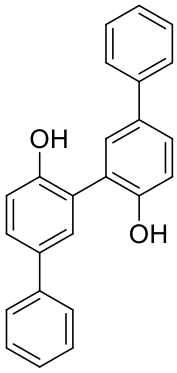
IR (ATR) ṽ (cm^{-1}):3852, 3671, 3286, 2366, 2319, 1698, 1648, 1477, 1388, 1263, 1222, 1113, 1074, 1018 814, 735.

^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.59 (dd, *J* = 8.0, 4.0 Hz, 2 H), 7.54 (d, *J* = 4.0 Hz, 2 H), 6.78 (d, *J* = 8.0 Hz, 2 H), 5.66 (s, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.7, 139.6, 138.9, 125.4, 119.1, 83.6.

HRMS (ESI): calc. for [($C_{12}H_8I_2O_2$)H] (M+H) 438.8692, measured 438.8689.

Compound 2h.



The representative general procedure **A** was followed using **1h** (100 mg). The reaction time is 16 h. Product **2h** was isolated in 69 mg and yield is 69%.Colourless semisolid; eluent (15 % ethyl acetate in hexanes).

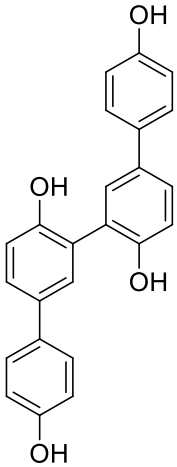
IR (ATR) ṽ (cm^{-1}): 3744, 3441, 3937, 2107, 1727, 1514, 1277, 1212, 1170, 1030, 835.

^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.58 – 7.54 (m, 8 H), 7.41 (t, *J* = 8.0 Hz, 4 H), 7.31 (t, *J* = 8.0 Hz, 2 H), 7.10 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): 152.4, 140.2, 134.9, 130.1, 128.8, 128.6, 127.0, 126.8, 124.3, 117.2.

HRMS (ESI): calc. for [($C_{24}H_{18}O_2$)H] (M+H) 339.1385, measured 339.1382.

Compound 2i.



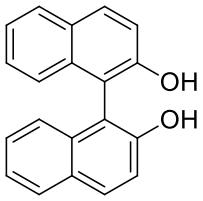
The representative general procedure **A** was followed using **1i** (100 mg). The reaction time is 16 h. Product **2i** was isolated in 79 mg and yield is 79%.Yellow semisolid; eluent (25 % ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3744, 3671, 3441, 3937, 2107, 1727, 1514, 1277, 1212, 1170, 1030, 835.

^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.46 (d, *J* = 4.0 Hz, 2 H), 7.43 – 7.40 (m, 6 H), 6.98 (d, *J* = 8.0 Hz, 2 H), 6.83 (d, *J* = 8.0 Hz, 4 H).

^{13}C NMR ($CDCl_3$, 100 MHz):δ 157.5, 154.1, 134.8, 133.8, 130.7, 128.80, 128.6, 127.8, 117.7, 116.5.**HRMS (ESI):** calc. for [($C_{24}H_{18}O_4$)H] (M+H) 371.1283, measured 371.1291.

[1,1'-Binaphthalene]-2,2'-diol (2j).



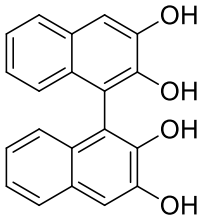
The representative general procedure **A** was followed using **1j** (100 mg). The reaction time is 16 h. Product **2j** was isolated in 80 mg and yield is 80%. Black solid; mp.213-215 °C; eluent (12 % ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3485, 3418, 3059, 1619, 1511, 1382, 1268, 1211, 1180, 1145, 970, 818, 746.

^{1}H NMR ($CDCl_3$, 400 MHz):δ7.94 (d, *J* = 8.0 Hz, 2 H), 7.87 (d, *J* = 8.0 Hz, 2 H), 7.36 (dd, *J* = 8.0, 4.0 Hz, 4 H), 7.29 (t, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 5.06 (s, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz):δ152.7, 133.4, 131.4, 129.4, 128.4, 127.5, 124.2, 124.0, 117.7, 110.8.**HRMS (ESI):** calc. for [($C_{20}H_{14}O_2$)H] (M+H) 287.1072, measured 287.1071.

[1,1'-Binaphthalene]-2,2',3,3'-tetraol (2k).



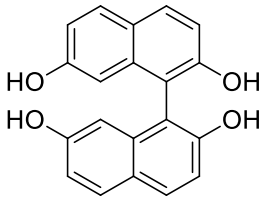
The representative general procedure **A** was followed using **1k** (100 mg). The reaction time is 16 h. Product **2k** was isolated in 70 mg and yield is 70%.Brown solid; eluent (12 % ethyl acetate in hexanes).

IR (ATR) ṽ (cm-1): 3851, 3743, 3395, 2318, 1698, 1341, 1300, 1240, 1146, 941, 725.

^{1}H NMR (MeOH-d_4, 400 MHz):δ7.64 (d, *J* = 8.0 Hz, 2 H), 7.27 (s, 2 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 6.99 (t, *J* = 8.0 Hz, 2 H), 6.93 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (MeOH-d_4, 100 MHz):δ147.4, 145.8, 131.0, 130.3, 127.1, 125.7, 124.3, 124.2, 116.8, 110.3.**HRMS (ESI):** calc. for [($C_{20}H_{14}O_4$)H] (M+H) 319.0970, measured 319.0969.

[1,1'-Binaphthalene]-2,2',7,7'-tetraol (2l).



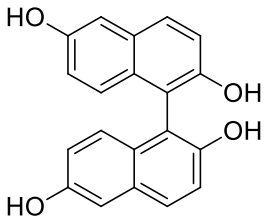
The representative general procedure **A** was followed using **1l** (100 mg). The reaction time is 16 h. Product **2l** was isolated in 72 mg and yield is 72%.Pale red solid; mp.118-120 °C; eluent (20 % ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3851, 3743, 3395, 2318, 1698, 1341, 1300, 1240, 1146, 941, 725.

^{1}H NMR (MeOH-d_4, 400 MHz): δ7.73 (d, *J* = 8.0 Hz, 2 H), 7.67 (d, *J* = 8.0 Hz, 2 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 6.82 (dd, *J* = 8.0, 4.0 Hz, 2 H), 6.40 (d, *J* = 4.0 Hz, 2 H).

^{13}C NMR (MeOH-d_4), 100 MHz):δ164.9, 162.7, 145.5 138.9, 137.7, 132.5, 124.8, 124.3, 123.82, 115.7.**HRMS (ESI):** calc. for [($C_{20}H_{14}O_4$)H] (M+H) 319.0970, measured 319.0967.

[1,1'-Binaphthalene]-2,2',6,6'-tetraol (2m).



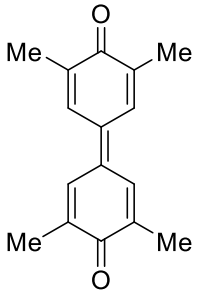
The representative general procedure **A** was followed using **1m** (100 mg). The reaction time is 16 h. Product **2m** was isolated in 78 mg and yield is 78%. Dark grey solid; eluent (12 % ethyl acetate in hexanes).

IR (ATR) ṽ (cm^{-1}): 3851, 3743, 3395, 2318, 1698, 1341, 1300, 1240, 1146, 941, 725.

^{1}H NMR (MeOH-d_4, 400 MHz): δ7.66 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 4.0 Hz, 2 H), 6.91 (d, *J* = 8.0 Hz, 2 H), 6.80 (dd, *J* = 8.0, 4.0 Hz, 2 H).

^{13}C NMR (MeOH-d_4, 100 MHz): δ154.1, 151.9, 131.6, 130.4, 128.8, 127.5, 119.6, 119.2, 116.5, 110.5.**HRMS (ESI):** calc. for [($C_{20}H_{14}O_4$)H] (M+H) 319.0970, measured 319.0971.

3,3',5,5'-Tetramethyl-[1,1'-bi(cyclohexylidene)]-2,2',5,5'-tetraene-4,4'-dione (4a).



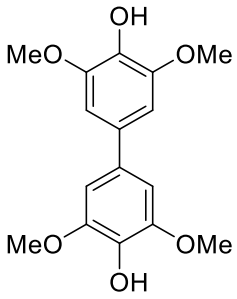
The representative general procedure **B** was followed using **1n** (100 mg). The reaction time is 3 h. Product **4a**[2] was isolated in 62 mg and yield is 62%. Dark red solid, eluent (15% ethyl acetate in hexanes).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (s, 4 H), 2.13 (s, 12 H).

^{13}C NMR ($CDCl_3$, 100 MHz):δ 187.4, 138.9, 135.6, 129.7, 17.2.

HRMS (ESI): calc. for [($C_{16}H_{16}O_2$)H] (M+H) 241.1229, measured 241.1233.

3,3',5,5'-Tetramethoxy-[1,1'-biphenyl]-4,4'-diol (4b).



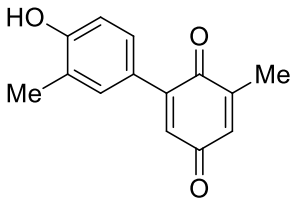
The representative general procedure **B** was followed using **1a** (100 mg). The reaction time is 3 h. Product **4b**[1] was isolated in 81 mg and yield is 81%. Brown semisolid, eluent (20% ethyl acetate in hexanes).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.72 (s, 4 H), 5.61 (s, 2 H), 3.96 (s, 12 H).

^{13}C NMR ($CDCl_3$, 100 MHz):δ 147.2, 134.2, 133.4, 104.1, 56.5.

HRMS (ESI): calc. for [($C_{16}H_{18}O_6$)H] (M+H) 307.1182, measured 307.1184.

4'-Hydroxy-3',6-dimethyl-[1,1'-biphenyl]-2,5-dione (6a).[1]



The representative general procedure **B** was followed using **1o** (100 mg). The reaction time is 3 h. Product **6a** was isolated in 82 mg and yield is 74%. Dark brown solid, eluent (20% ethyl acetate in hexanes).

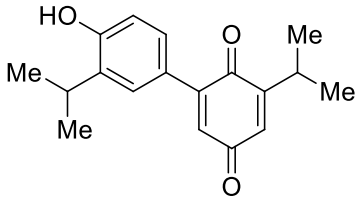
^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.26 (d, *J* = 4.0 Hz, 1 H), 7.21 (dd, *J* = 8.0, 4.0 Hz, 1 H), 6.80 (d, *J* = 8.0 Hz, 1 H), 6.72 (d, *J* = 4.0 Hz, 1 H), 6.63 (m, 1 H), 5.54 (s, 1 H), 2.26 (s, 3H), 2.10 (d, *J* = 4.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz):δ 187.9, 187.6, 155.9, 146.1, 145.7, 133.1, 132.1, 131.1, 128.5, 125.3, 124.2, 115.0, 16.4, 15.8.

HRMS (ESI): calc. for [($C_{14}H_{12}O_3$)H] (M+H) 229.0865, measured 229.0864.

1. Y. Takizawa, T. Munakata, Y. Iwasa, T. Suzuki, and T. Mitsuhashi, *J. Org. Chem*. 1985, **50**, 4383.

4'-Hydroxy-3',6-diisopropyl-[1,1'-biphenyl]-2,5-dione (6b).[1]



The representative general procedure **B** was followed using **1p** (100 mg). The reaction time is 3 h. Product **6b** was isolated in 79 mg and yield is 72%. Dark brown solid, eluent (20% ethyl acetate in hexanes).

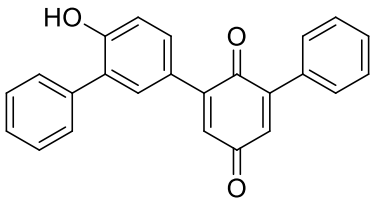
^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.31 (d, *J* = 4.0 Hz, 1H), 7.22 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 4.0 Hz, 1H), 6.56 (m, 1H), 5.24 (s, 1H), 3.22 (m, 1H), 3.12 (m, 1H), 1.26 (d, *J* = 8.0 Hz, 6H), 1.16 (d, *J* = 8.0 Hz, 6H).

^{13}C NMR ($CDCl_3$, 100 MHz):δ 188.4, 187.0, 155.3, 154.8, 146.3, 134.7, 130.7, 130.1, 128.3, 127.9, 125.8, 115.3, 27.1, 27.1, 22.4, 21.6.

HRMS (ESI): calc. for [($C_{18}H_{20}O_3$)H] (M+H) 285.1491, measured 285.1499.

1. Y. Takizawa, T. Munakata, Y. Iwasa, T. Suzuki, and T. Mitsuhashi, *J. Org. Chem*. 1985, **50**, 4383.

4''-Hydroxy-[1,1':2',1'':3'',1'''-quaterphenyl]-3',6'-dione (6c).



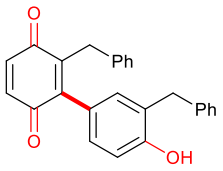
The representative general procedure **B** was followed using **1q** (100 mg). The reaction time is 3 h. Product **6c** was isolated in 63 mg and yield is 58%. Dark brown solid, eluent (25% ethyl acetate in hexanes).

^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.47 (m, 12 H), 7.05 (d, *J* = 8.0 Hz, 1 H), 6.89 (dd, *J* = 8.0, 4.0 Hz, 2 H), 5.63 (s, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz):δ 187.6, 186.5, 154.5, 146.5, 145.7, 136.1, 133.2, 132.7, 131.8, 131.2, 130.5, 130.0, 129.4, 129.3, 129.1, 128.5, 128.5, 128.3, 125.7, 116.2.

HRMS (ESI): calc. for [($C_{24}H_{16}O_3$)H] (M+H) 353.1178, measured 353.1184.

3,3'-Dibenzyl-4'-hydroxy-[1,1'-biphenyl]-2,5-dione (6d).



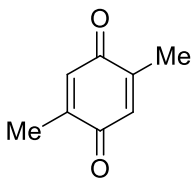
The representative general procedure **B** was followed using **1r** (100 mg). The reaction time is 3 h. Product **6d** was isolated in 53 mg and yield is 51%. Dark brown semisolid, eluent (20% ethyl acetate in hexanes).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34 – 7.25 (m, 7 H), 7.23 – 7.18 (m, 5 H), 6.82 (d, *J* = 8.0 Hz, 1 H), 6.69 (d, *J* = 4.0 Hz, 1 H), 6.38 (m, 1 H), 5.23 (s, 1 H), 4.00 (s, 2H), 3.78 (d, *J* = 4.0 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 187.80, 186.9, 155.8, 148.9, 145.6, 139.3, 136.7, 133.2, 132.1, 131.1, 129.4, 129.3, 128.8, 128.7, 128.7, 127.4, 127.0, 126.6, 125.6, 115.8, 36.3, 35.7.

HRMS (ESI): calc. for [($C_{26}H_{20}O_3$)H] (M+H) 381.1491, measured 381.1489.

2,5-Dimethylcyclohexa-2,5-diene-1,4-dione (6e).



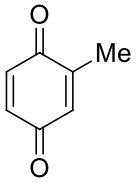
The representative general procedure **B** was followed using **1s** (100 mg). The reaction time is 3 h. Product **6e** was isolated in 41 mg and yield is 73%. Colourless solid, eluent (10% ethyl acetate in hexanes).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.57 (q, *J* = 4.0 Hz, 2 H), 2.01 (d, *J* = 4.0 Hz, 6 H).

^{13}C NMR ($CDCl_3$, 100 MHz):δ 188.0, 145.8, 133.4, 15.5.

HRMS (ESI): calc. for [($C_8H_8O_2$)H] (M+H) 137.0603, measured 137.0600.

2-Methylcyclohexa-2,5-diene-1,4-dione (6f).



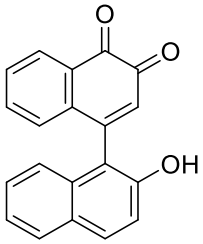
The representative general procedure **B** was followed using **1t** (100 mg). The reaction time is 3 h. Product **6f** was isolated in 44 mg and yield is 89%. Yellow solid, eluent (5% ethyl acetate in hexanes).

^{1}H NMR ($CDCl_3$, 400 MHz):δ 6.72 (d, *J* = 8.0 Hz, 1H), 6.67 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.57 (m, 1H), 2.01 (d, *J* = 4.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz):δ 187.7, 187.5, 145.8, 136.5, 136.4, 133.3, 15.8.

HRMS (ESI): calc. for [($C_7H_6O_2$)H] (M+H) 123.0446, measured 123.0444.

2'-Hydroxy-[1,1'-binaphthalene]-3,4-dione (6g).[1]



The representative general procedure **B** was followed using **1j** (100 mg). The reaction time is 3 h. Product **6g** was isolated in 84 mg and yield is 80%. Dark brown solid, eluent (25% ethyl acetate in hexanes).

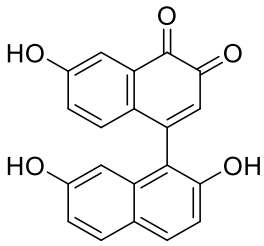
^{1}H NMR ($CDCl_3$, 400 MHz)δ 8.16 (d, *J* = 8.0 Hz, 1 H), 7.89 (d, *J* = 8.0 Hz, 1 H), 7.84 (d, *J* = 8.0 Hz, 1 H), 7.61 (d, *J* = 8.0 Hz, 1 H), 7.52 (t, *J* = 8.0 Hz, 1 H), 7.45 (t, *J* = 8.0 Hz, 1 H), 7.38 – 7.29 (m, 2 H), 7.25 (d, *J* = 8.0 Hz, 1 H), 6.83 (d, *J* = 8.0 Hz, 1 H), 6.41 (s, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): 181.8, 181.0, 155.5, 152.9, 137.2, 136.5, 134.0, 133.2, 131.9, 131.7, 131.3, 130.5, 130.1, 129.8, 129.3, 128.2, 124.9, 124.5, 118.9, 117.1.

HRMS (ESI): calc. for [($C_{20}H_{12}O_3$)H] (M+H) 301.0865, measured 301.0871.

1. Y. Takizawa, T. Munakata, Y. Iwasa, T. Suzuki, and T. Mitsuhashi, *J. Org. Chem.* 1985, **50**, 4383.

2',6,7'-Trihydroxy-[1,1'-binaphthalene]-3,4-dione (6h).



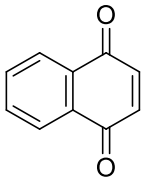
The representative general procedure **A** was followed using **1l** (100 mg). The reaction time is 3 h. Product **6h** was isolated in 76 mg and yield is 73%. Dark brown solid, eluent (25% ethyl acetate in hexanes).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (d, *J* = 8.0 Hz, 1 H), 7.70 (d, *J* = 8.0 Hz, 1 H), 7.56 (d, *J* = 4.0 Hz, 1 H), 7.03 (d, *J* = 8.0 Hz, 1 H), 6.88 (m, 3 H), 6.74 (d, *J* = 8.0 Hz, 1 H), 6.24 (s, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz):δ 182.4, 181.4, 161.6, 157.6, 157.2, 153.0, 135.5, 134.7, 132.5, 131.5, 131.0, 128.79, 127.8, 124.7, 122.6, 117.5, 116.6, 116.2, 115.7, 106.7.

HRMS (ESI): calc. for [($C_{20}H_{12}O_5$)H] (M+H) 333.0763, measured 333.0759.

Naphthalene-1,4-dione (6i).



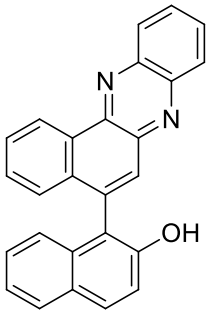
The representative general procedure **A** was followed using **1u** (100 mg). The reaction time is 3 h. Product **6i** was isolated in 51% yield. Ash colour solid, eluent (5% ethyl acetate in hexanes).

^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.92 (d, *J* = 8.0 Hz, 2H), 6.98 (s, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz):δ 185.0, 138.6, 133.9, 131.8, 126.3.

HRMS (ESI): calc. for [($C_{10}H_6O_2$)H] (M+H) 159.0446, measured 159.0448.

1-(Benzo[a]phenazin-5-yl)naphthalen-2-ol (8).



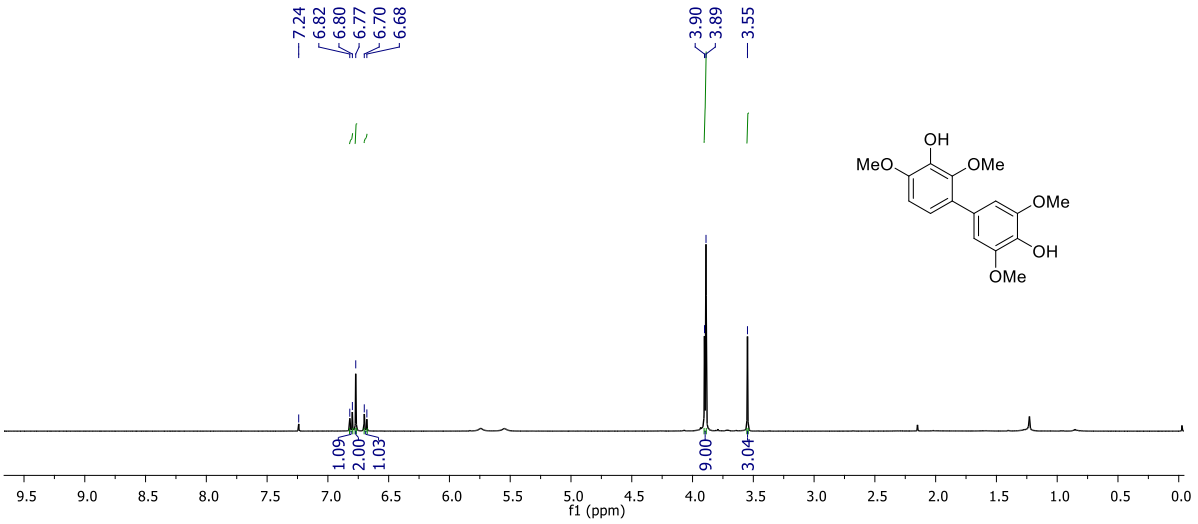
The representative general procedure **C** was followed using **6g** (100 mg). The reaction time is 12 h. Product **8** was isolated in 97 mg and yield is 78%. Yellow solid, mp.229-231 °C eluent (10% ethyl acetate in hexanes).

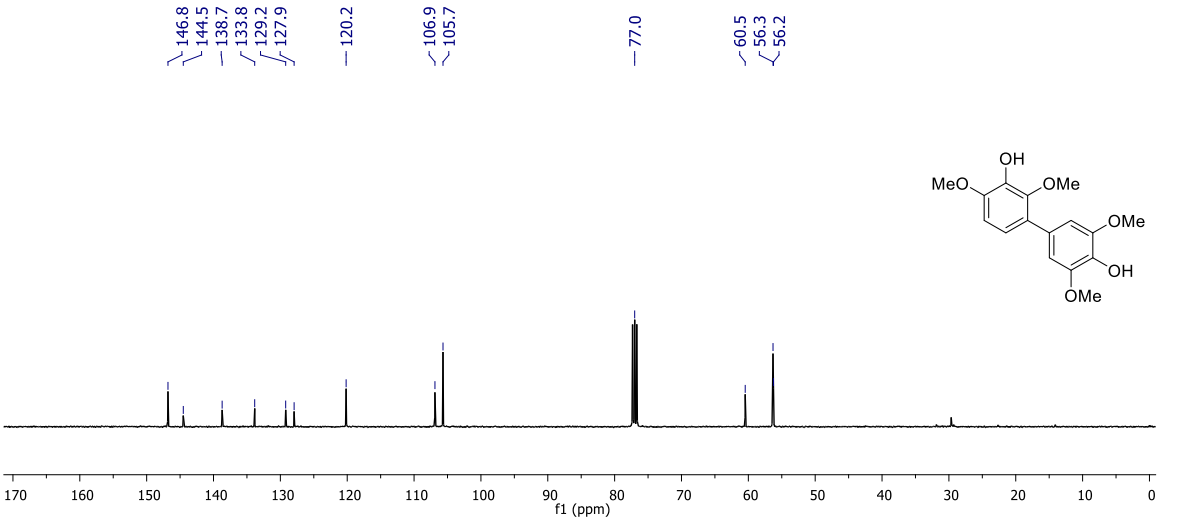
IR (ATR) ṽ (cm^{-1}): 3412, 3050, 1707, 1434, 1363, 750, 700

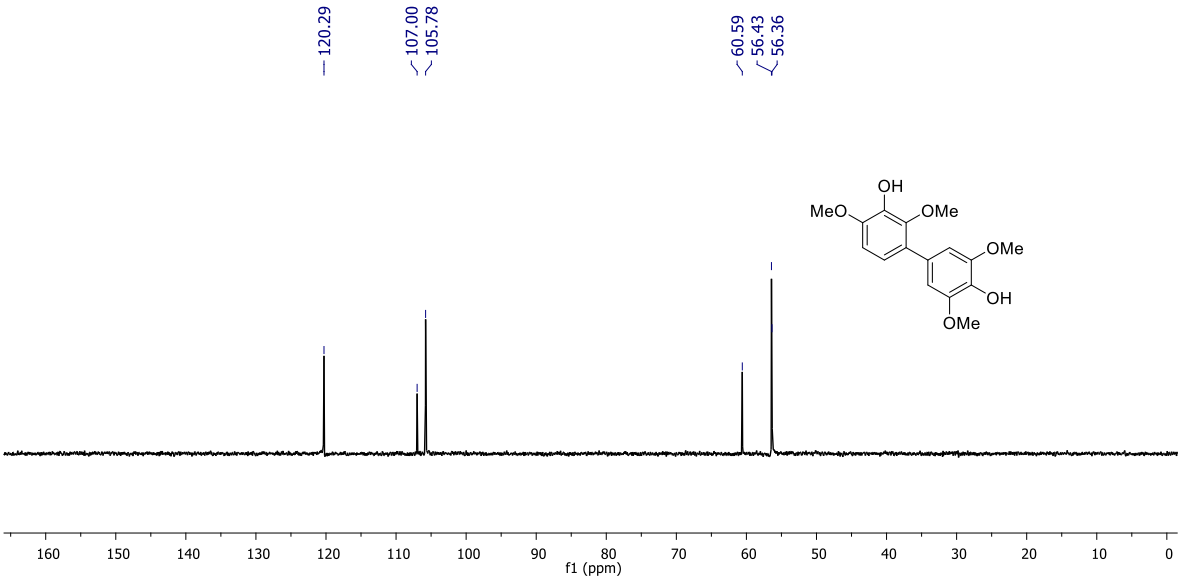
^{1}H NMR (DMSO-D6**, 400 MHz)**δ 9.83 (s, 1 H), 9.44 (d, *J* = 8.0 Hz, 1 H), 8.37 (dd, *J* = 8.0, 4.0 Hz, 2 H), 8.00 (m, 3 H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR (DMSO-D6**, 100 MHz):**δ 152.7, 143.1, 142.6, 141.9, 141.4, 140.6, 133.7, 133.4, 130.84, 130.8, 130.7, 130.3, 130.0, 129.5, 129.0, 129.0, 128.3, 128.0, 126.8, 126.8, 125.1, 124.1, 123.0, 118.5, 117.4.**HRMS (ESI):** calc. for [($C_{26}H_{16}O$)H] (M+H) 373.1341, measured 373.1340.

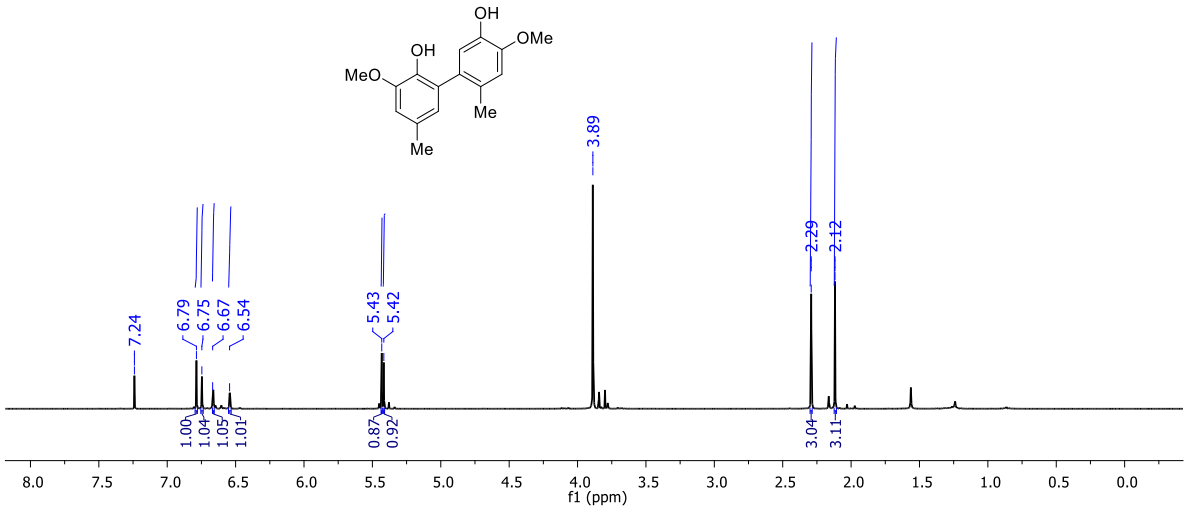
^{1}H and ^{13}C NMR Spectra of Compound 2a.

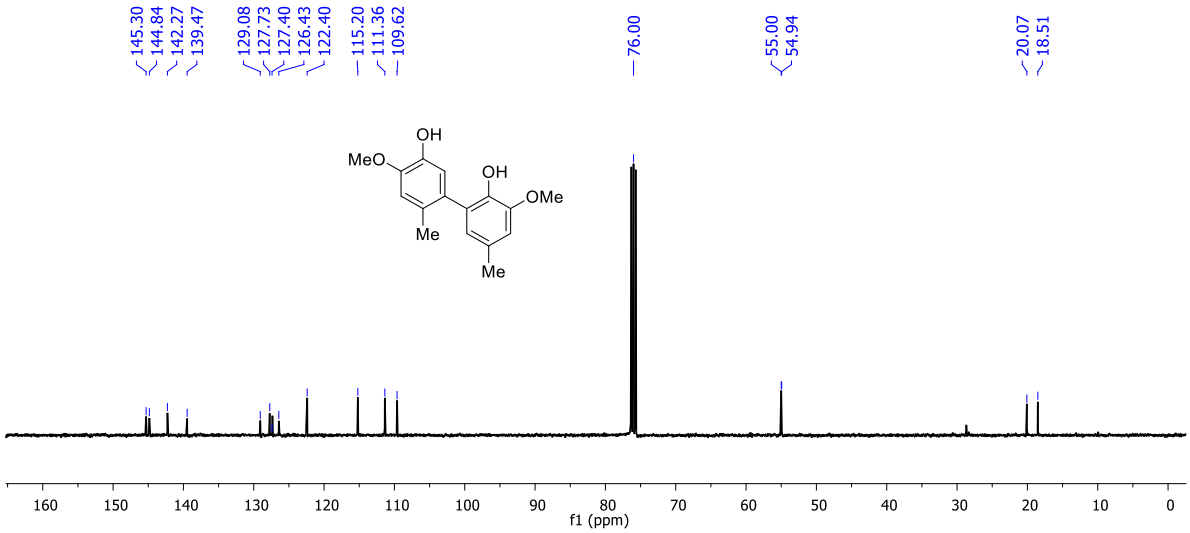


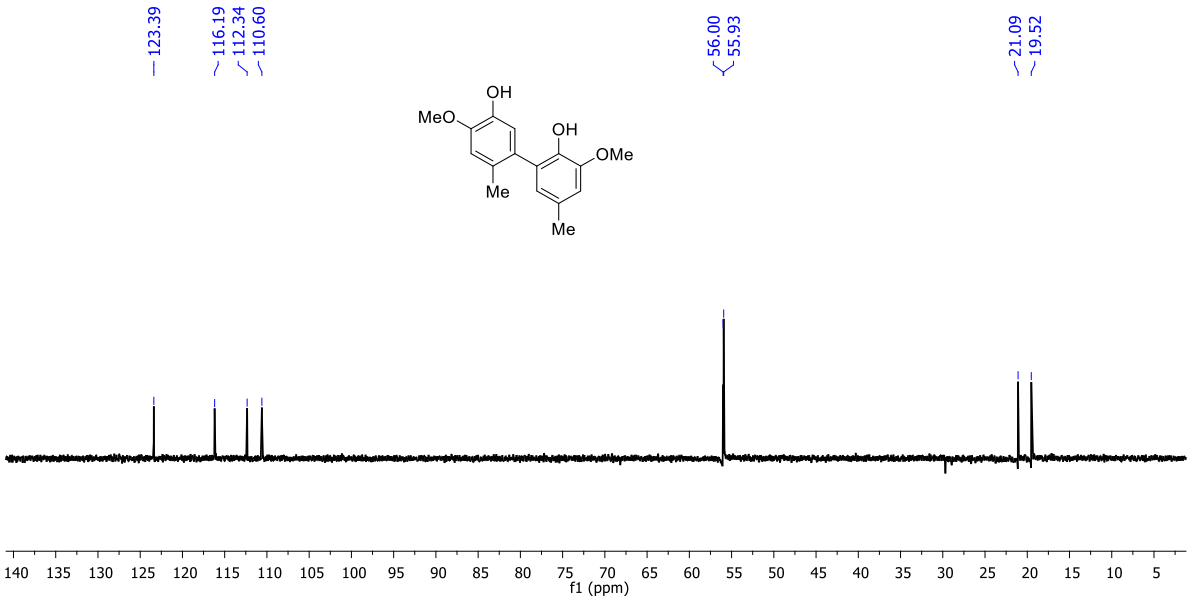




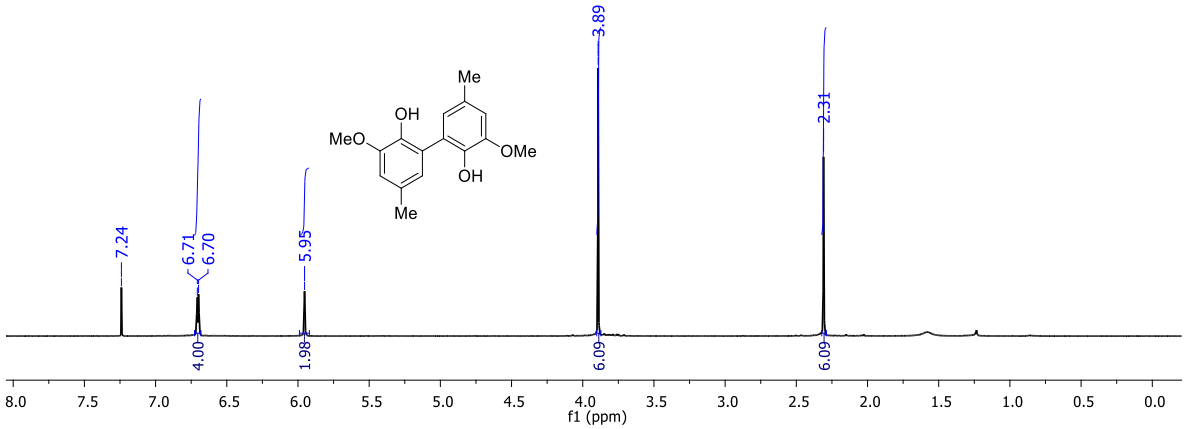
^{1}H and ^{13}C NMR Spectra of Compound **2b**.

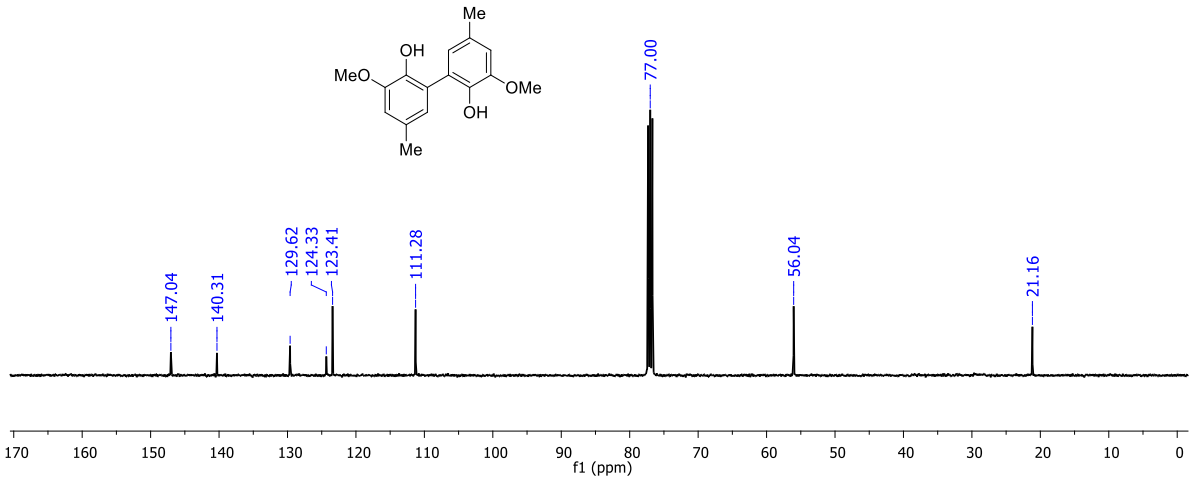


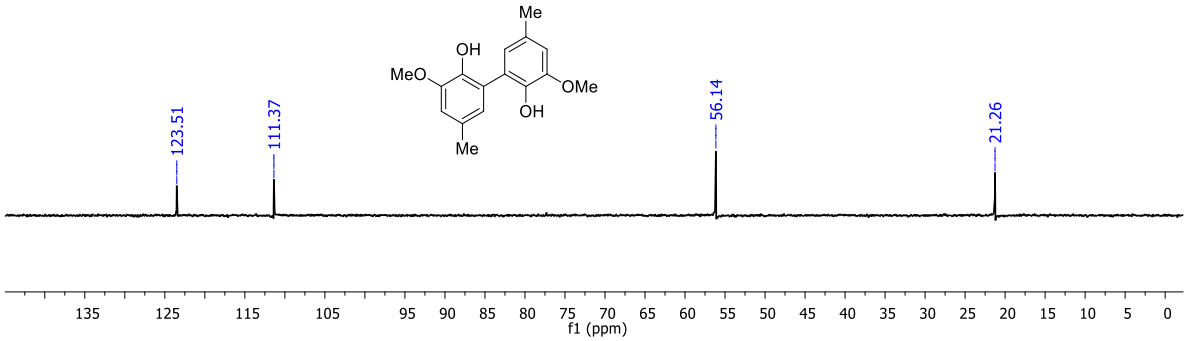




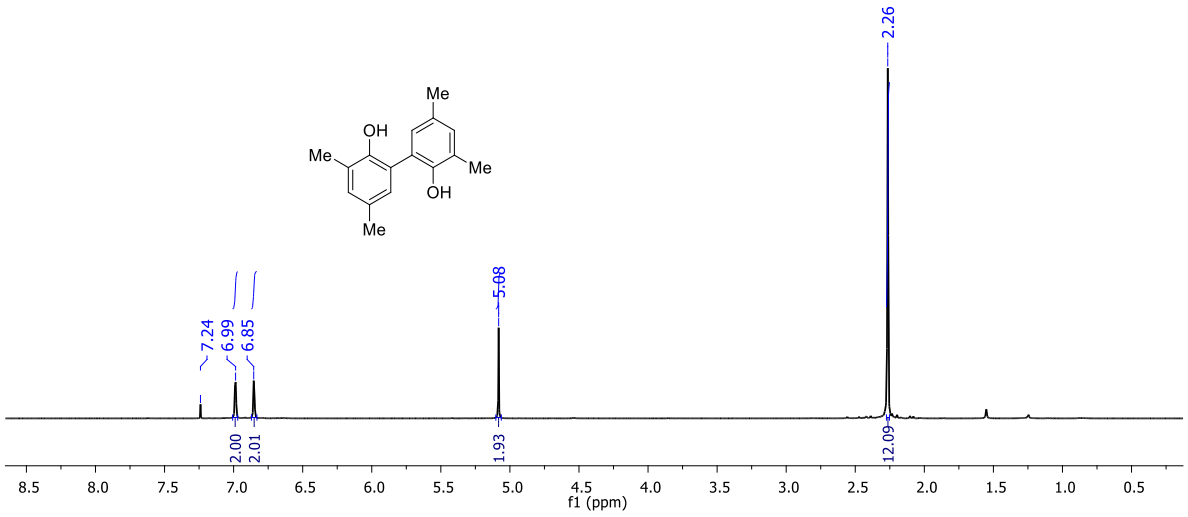
^{1}H and ^{13}C NMR Spectra of Compound **2b**'.

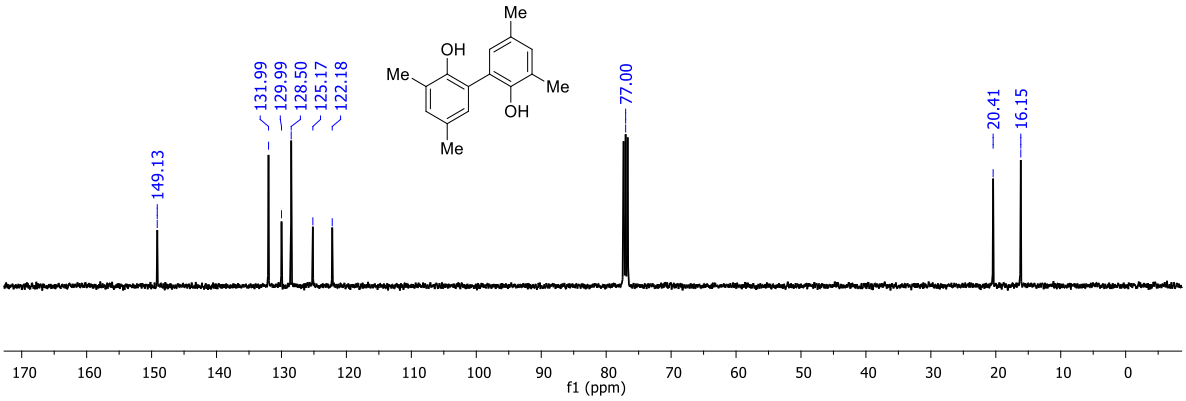




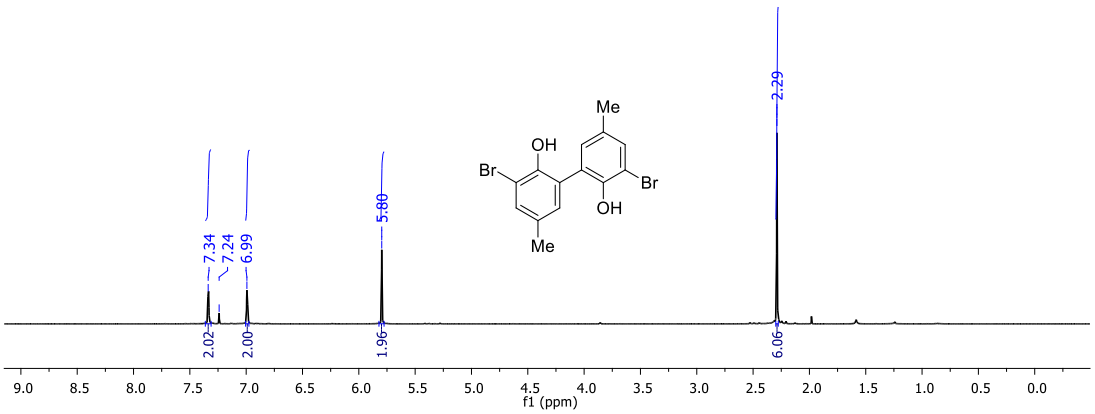


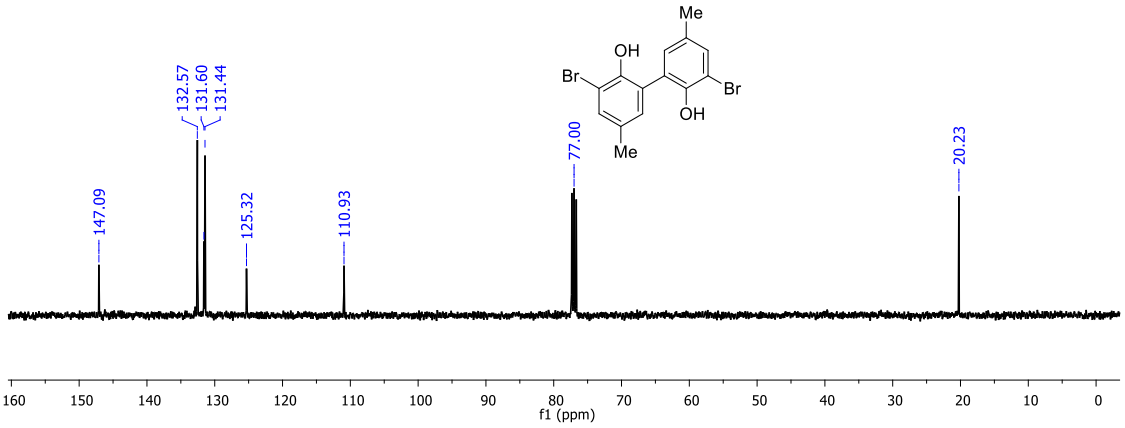
^{1}H and ^{13}C NMR Spectra of Compound **2c**.

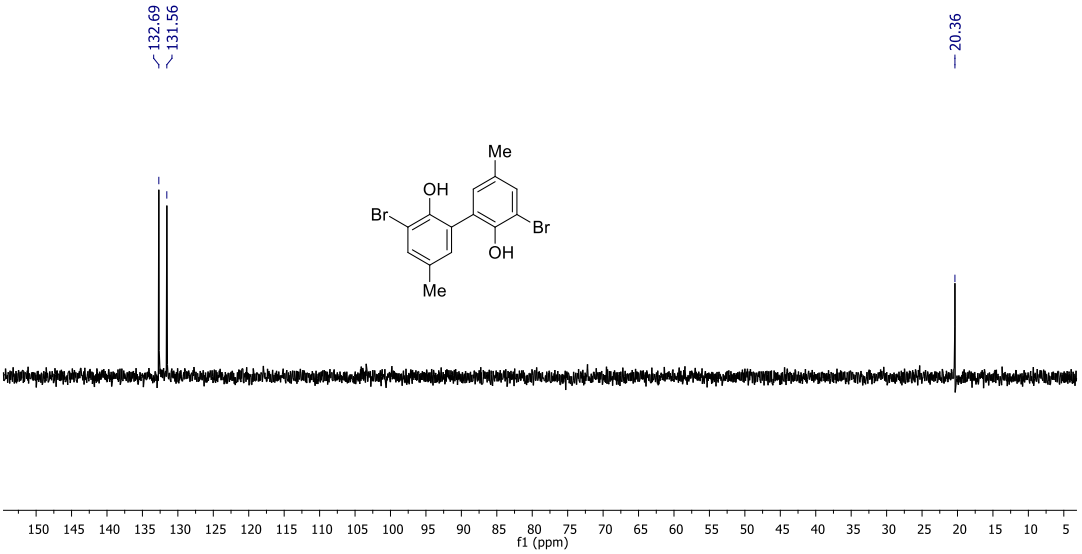




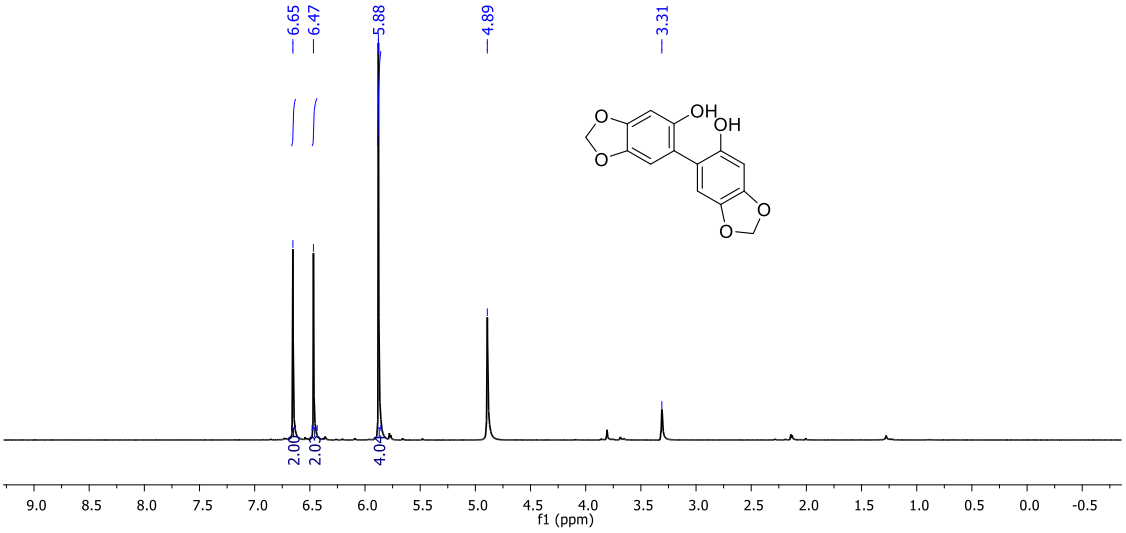
^{1}H and ^{13}C NMR Spectra of Compound **2d**.

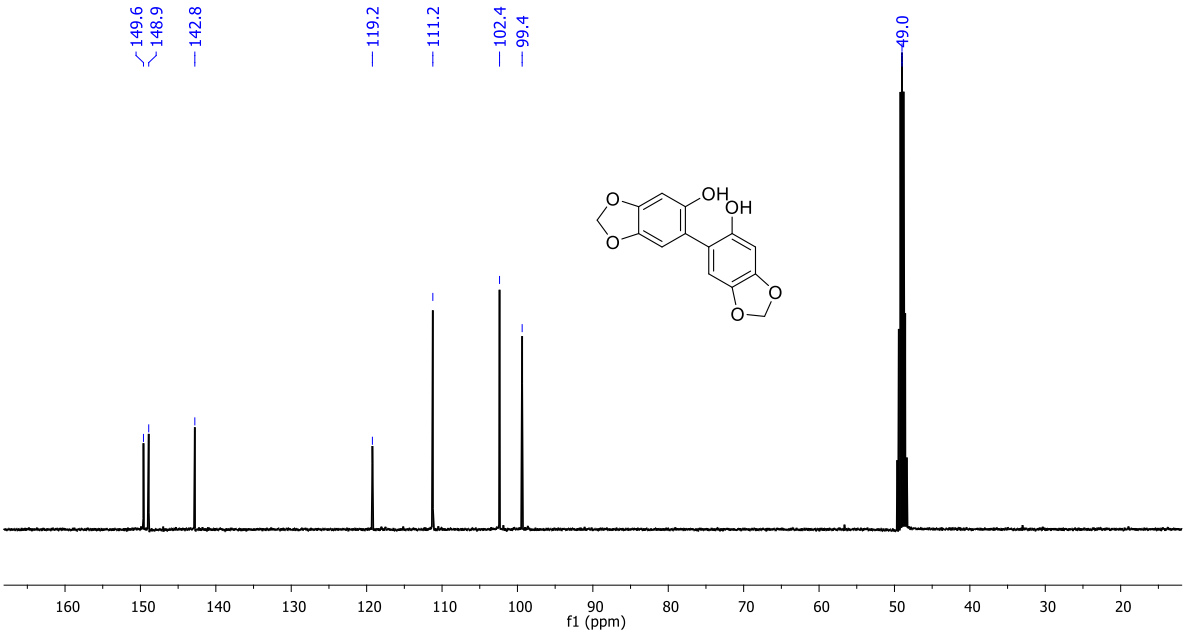




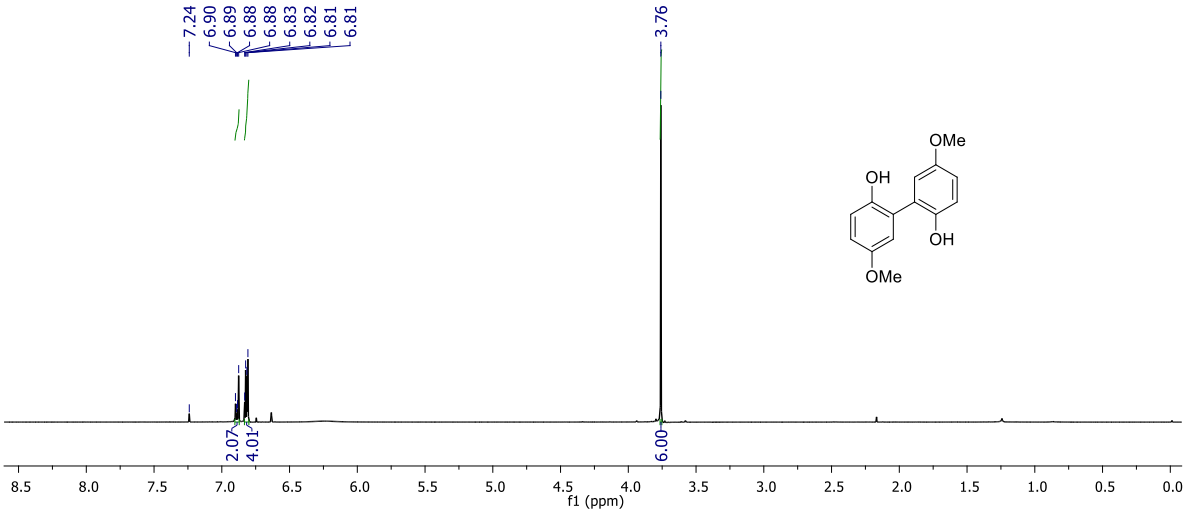


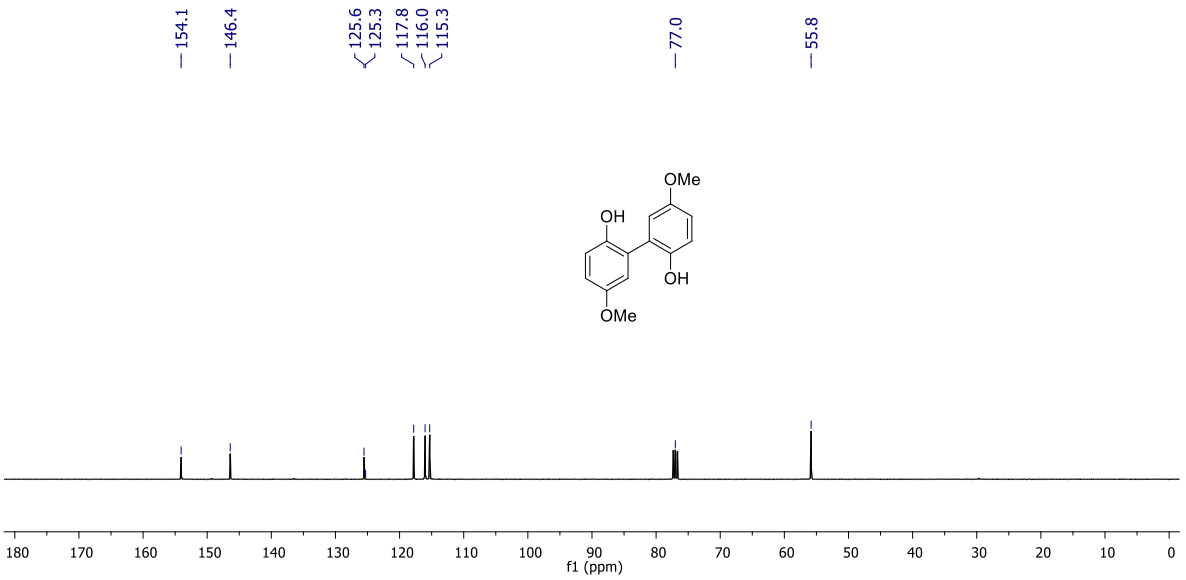
^{1}H and ^{13}C NMR Spectra of Compound 2e.

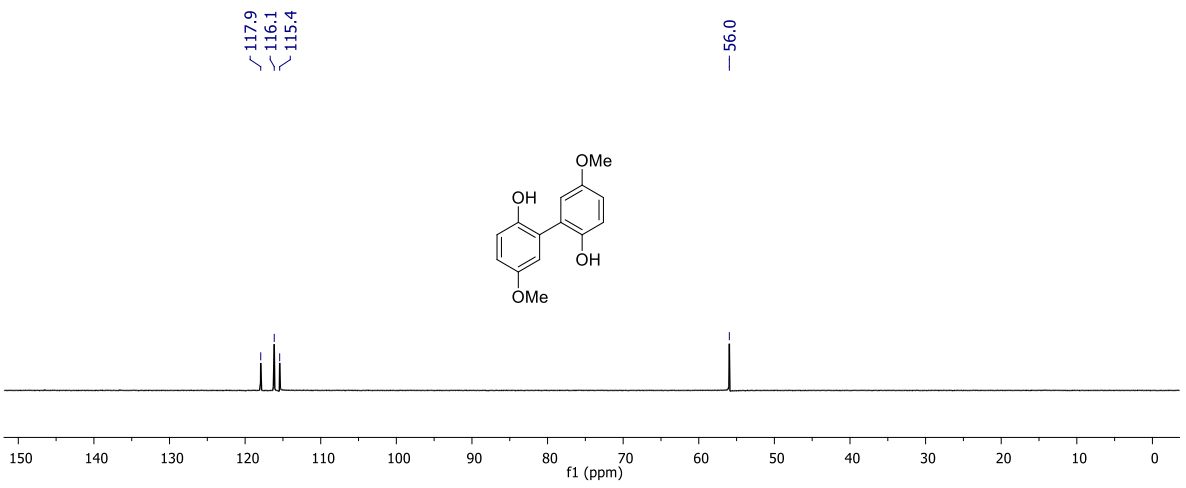




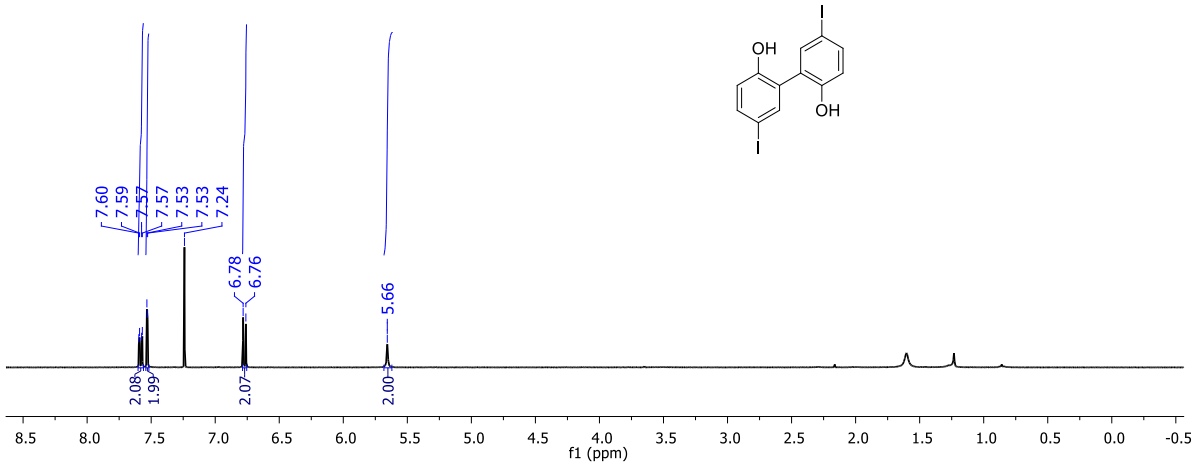
^{1}H and ^{13}C NMR Spectra of Compound 2f.

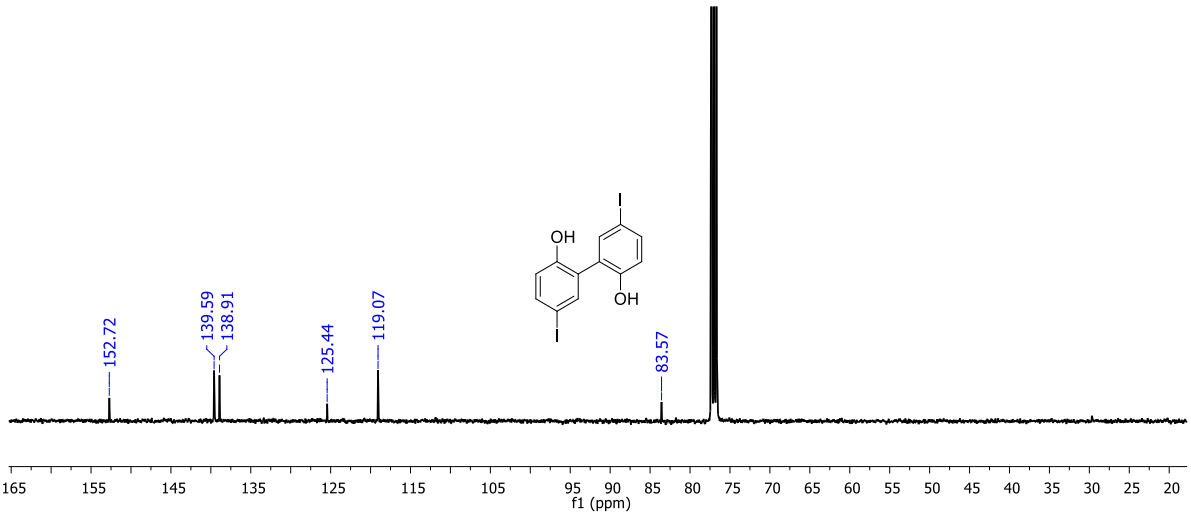


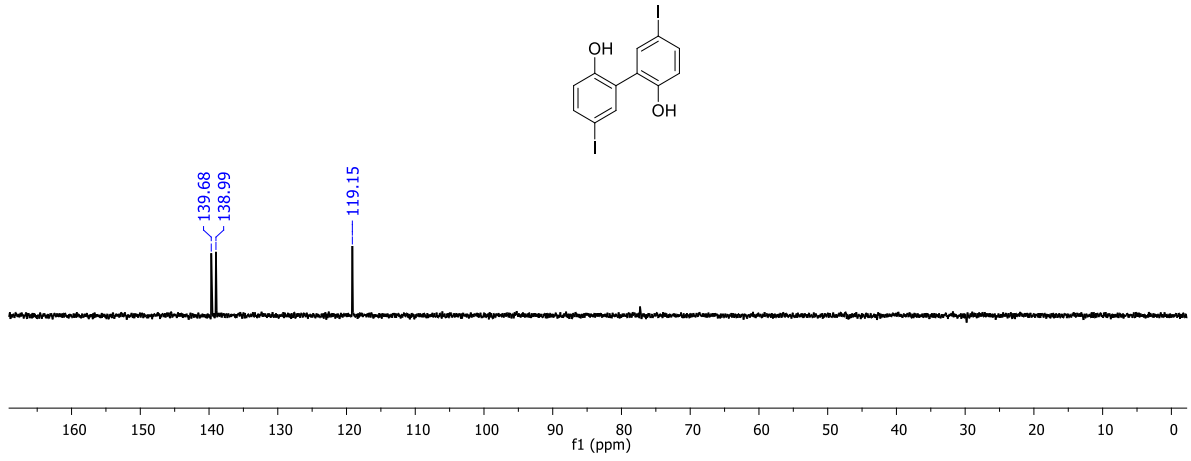




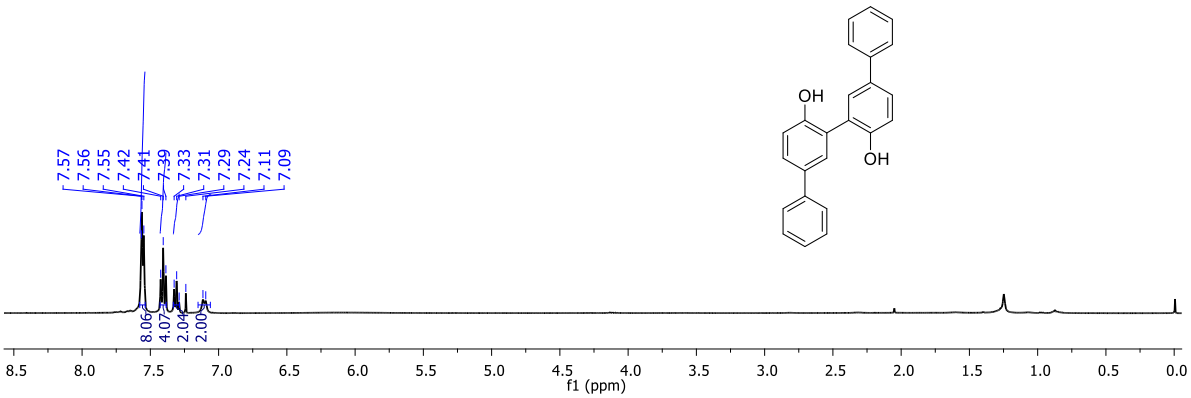
^{1}H and ^{13}C NMR Spectra of Compound 2g.

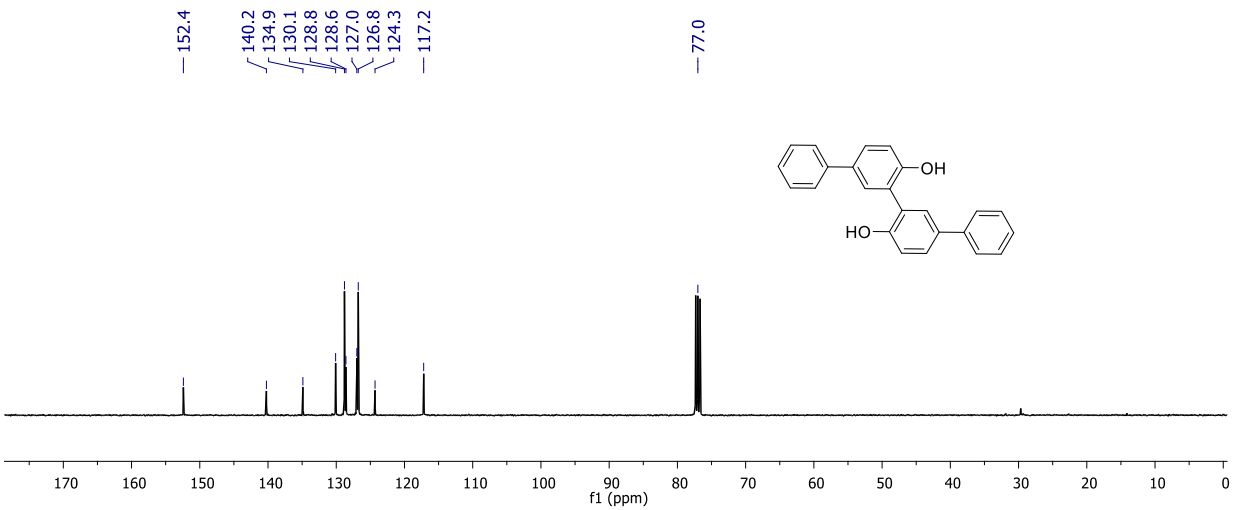


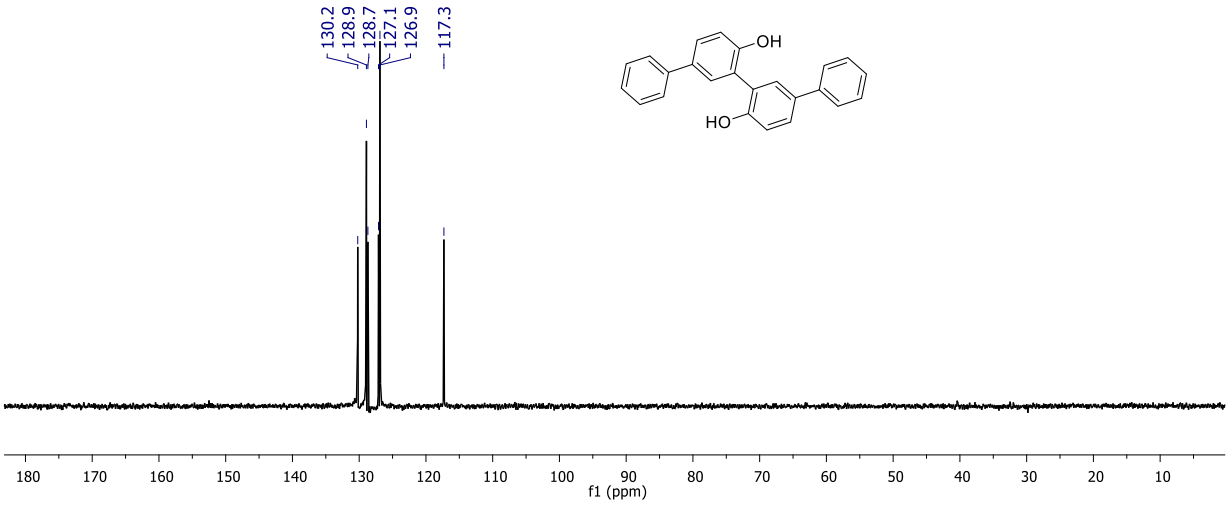




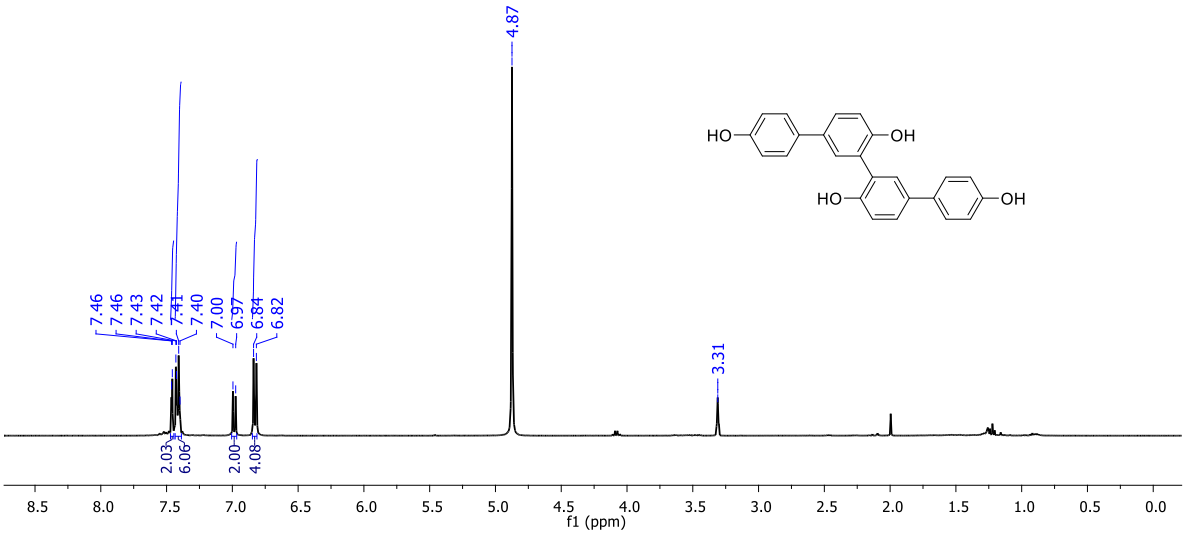
^{1}H and ^{13}C NMR Spectra of Compound 2h.

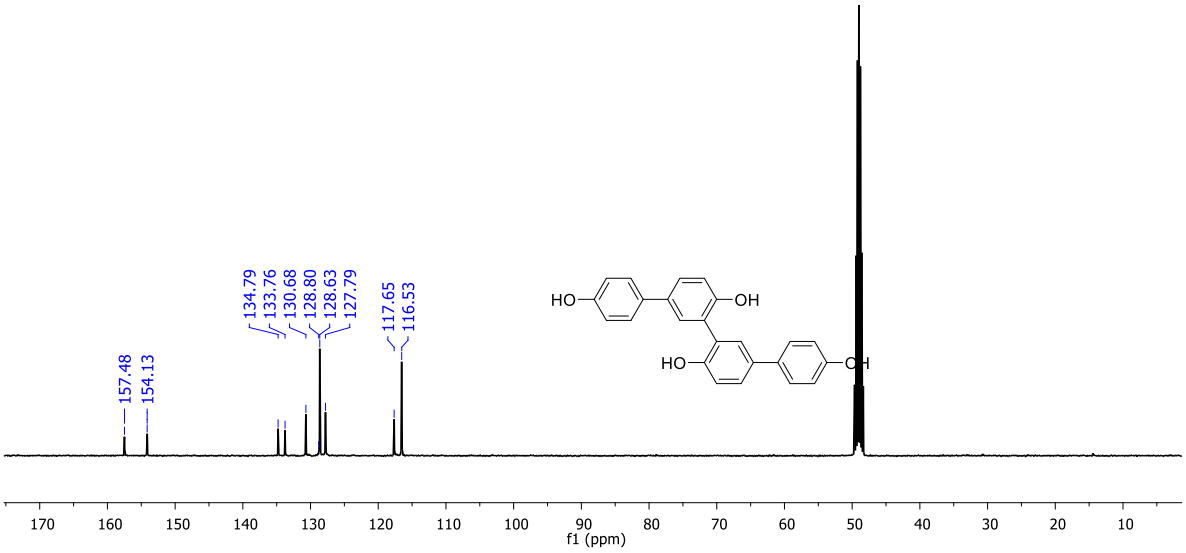


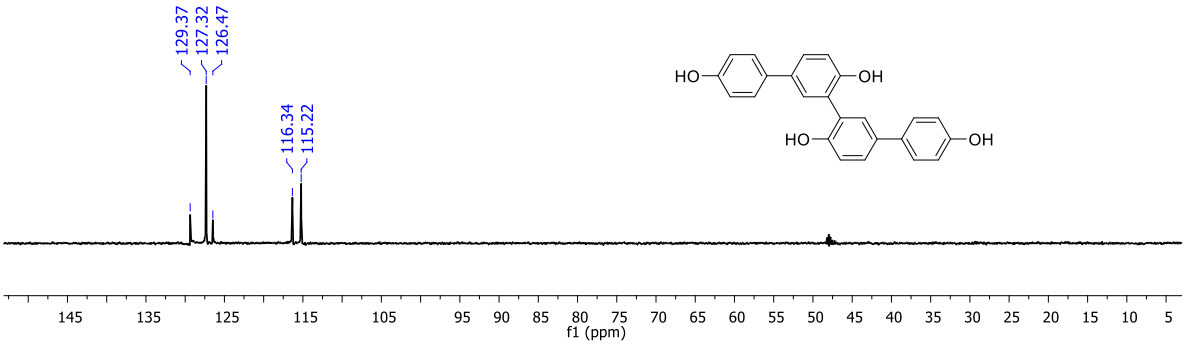




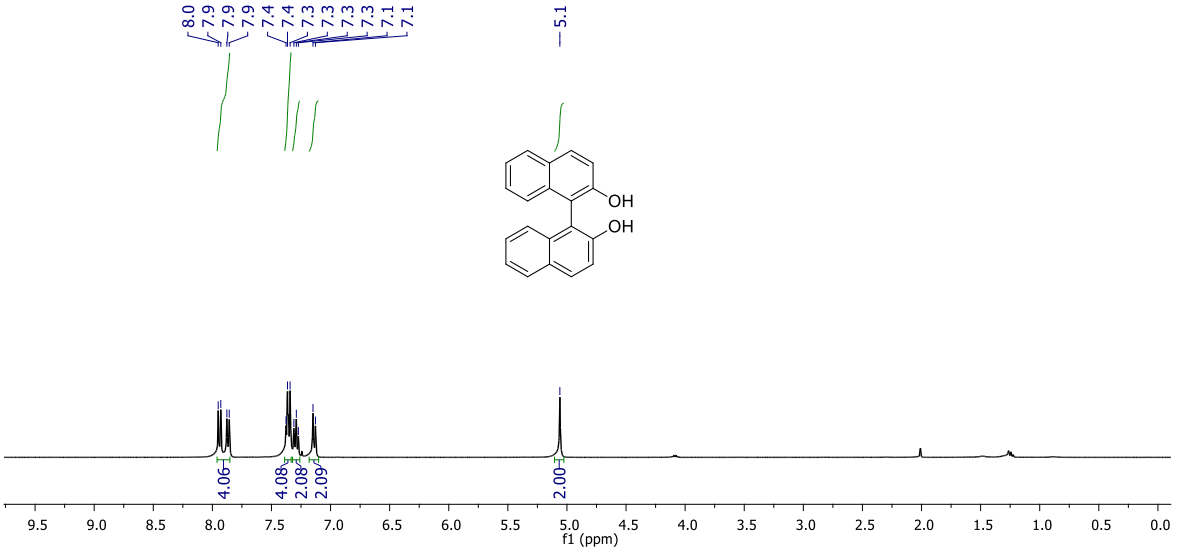
^{1}H and ^{13}C NMR Spectra of Compound 2i.

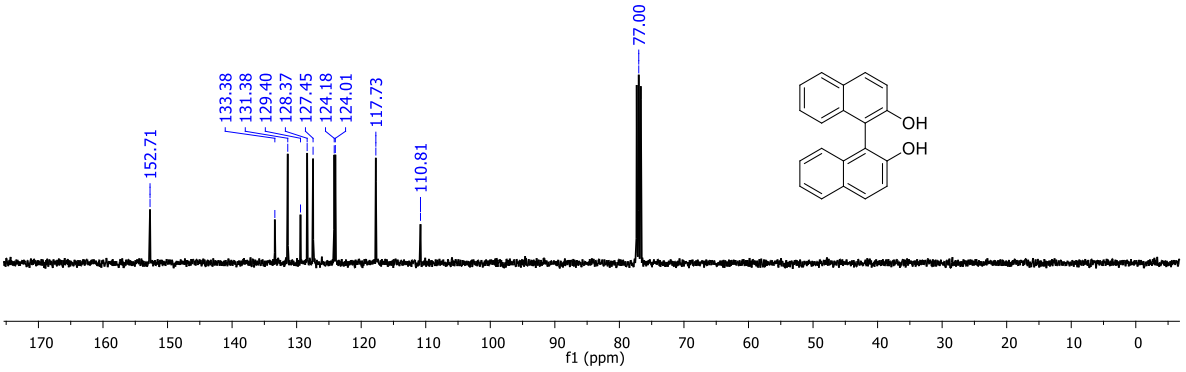




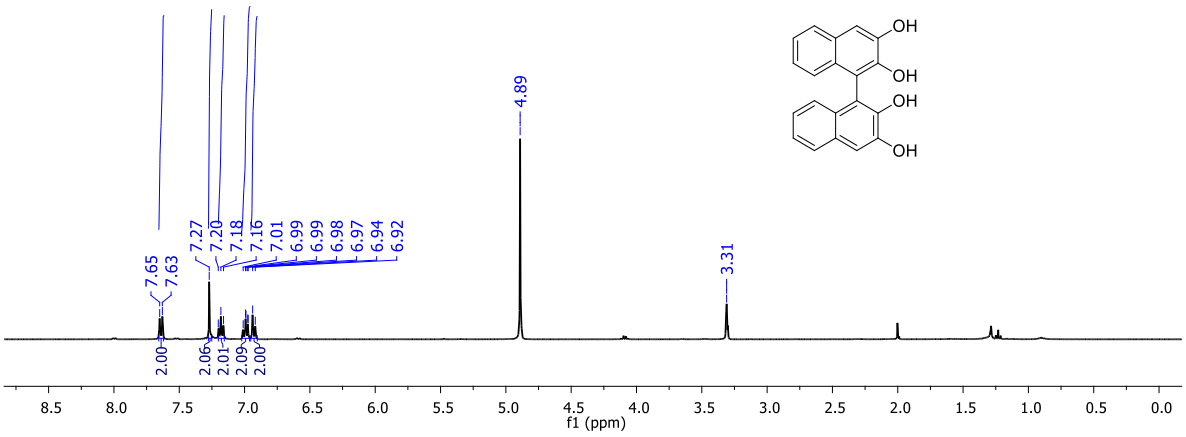


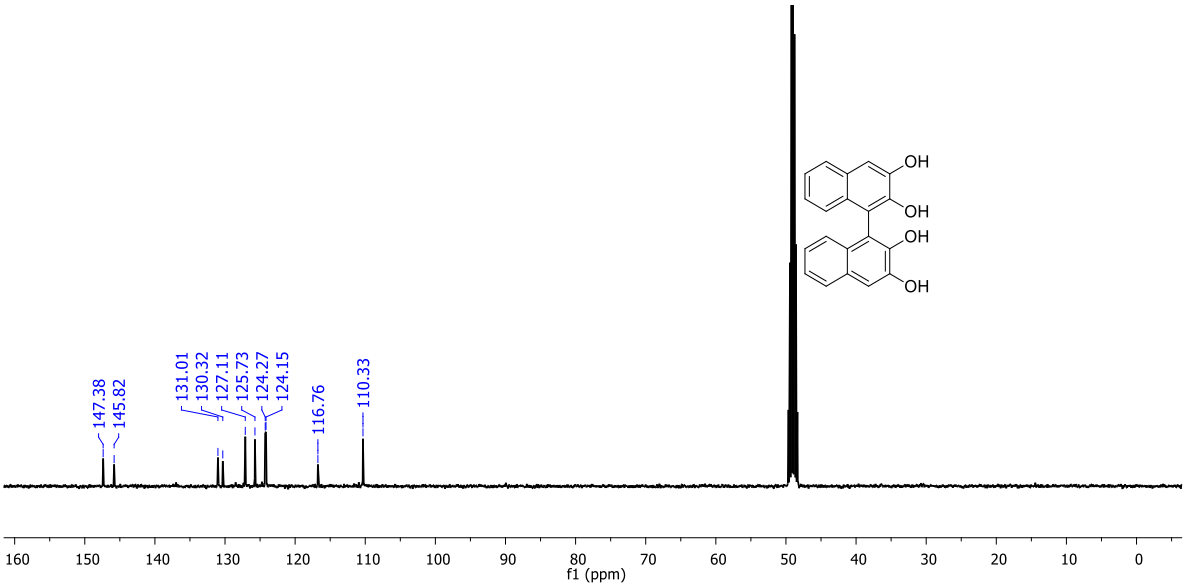
^{1}H and ^{13}C NMR Spectra of Compound 2j.

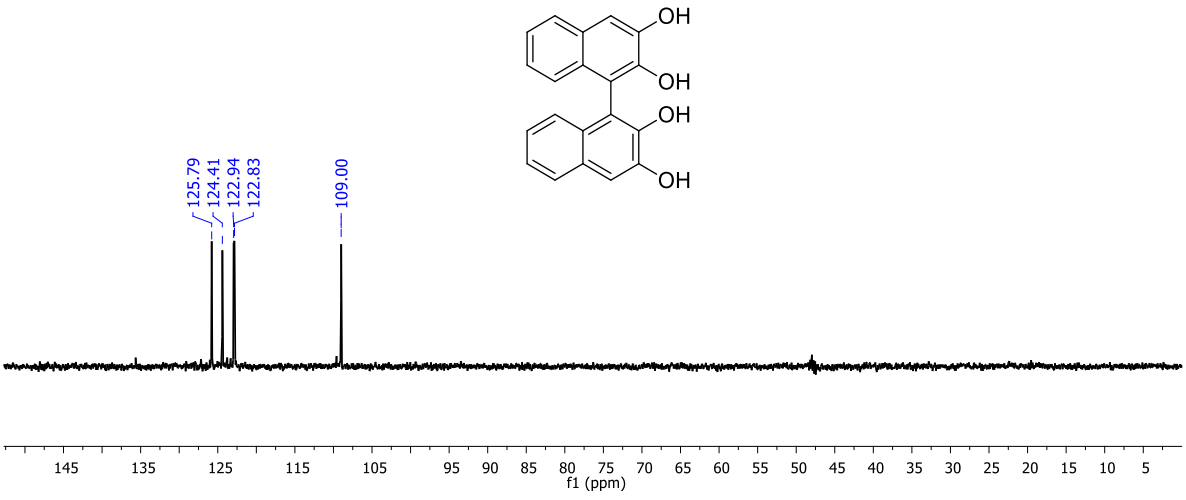




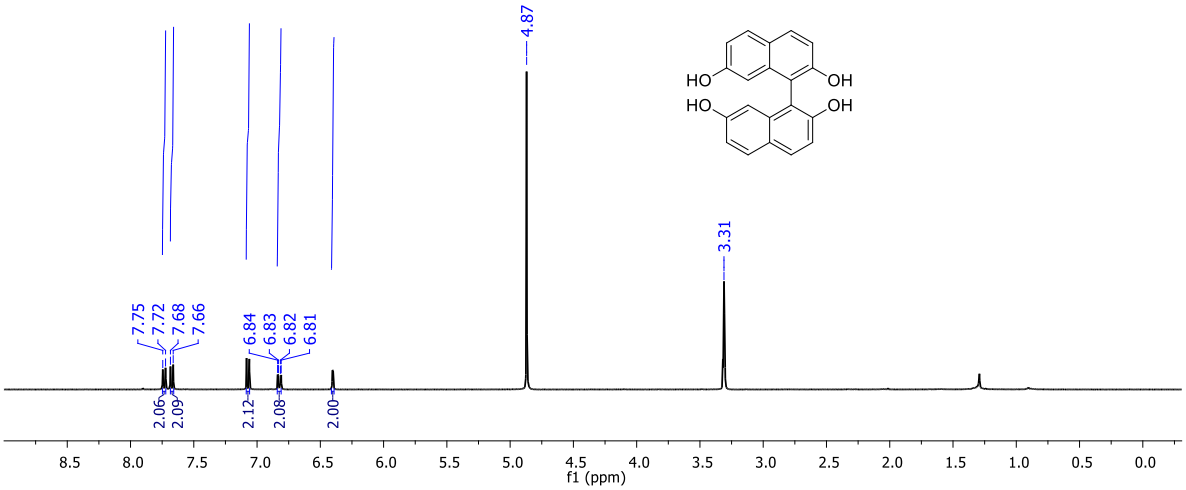
^{1}H and ^{13}C NMR Spectra of Compound 2k.

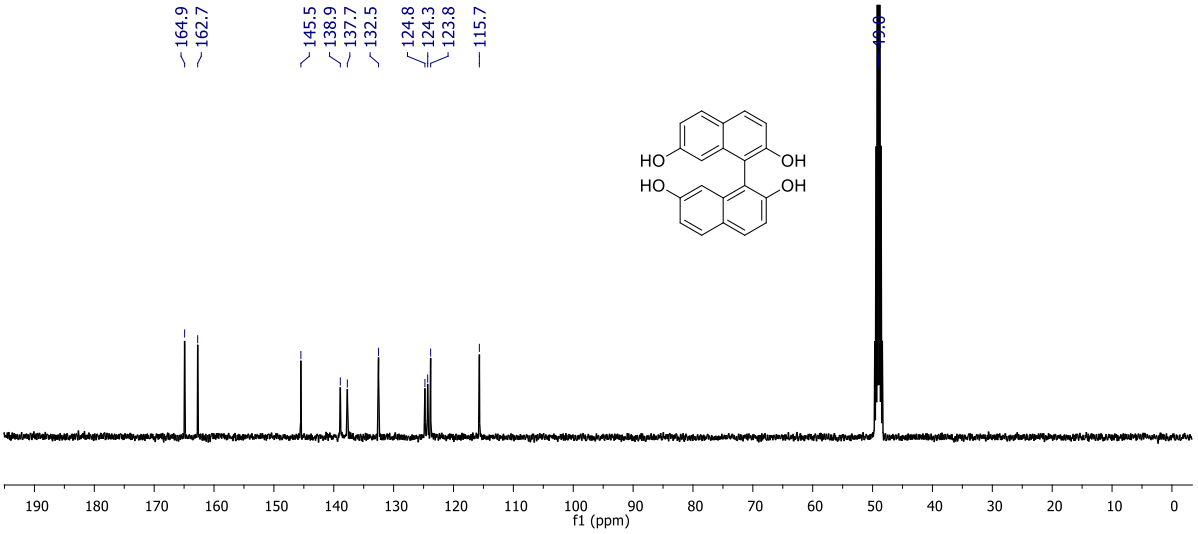


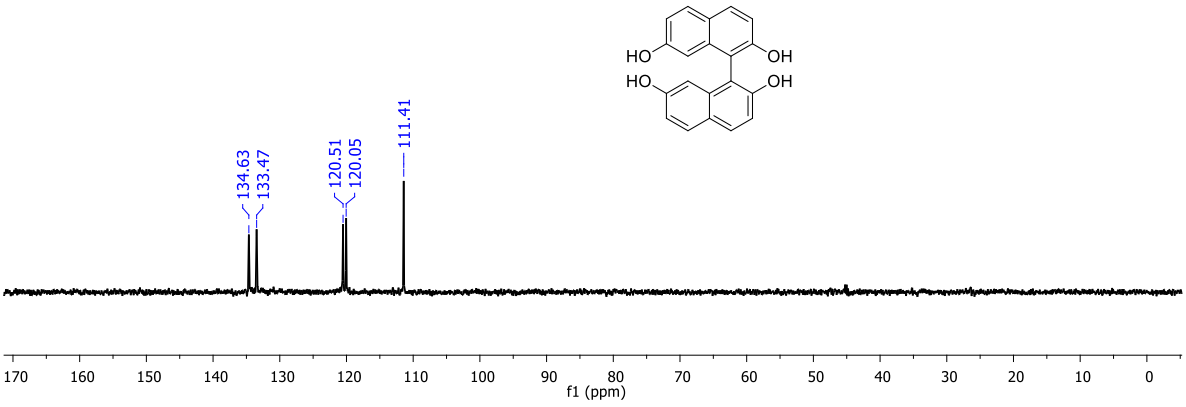




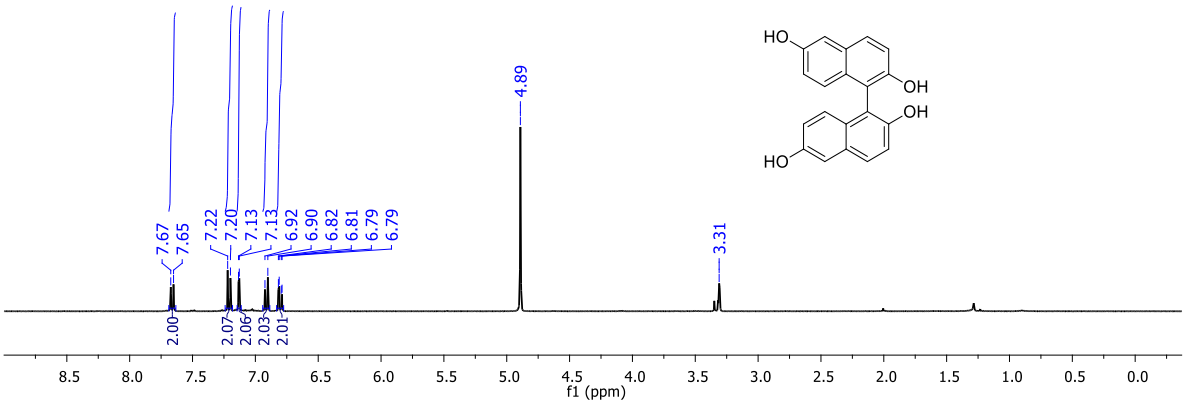
^{1}H and ^{13}C NMR Spectra of Compound 2l.

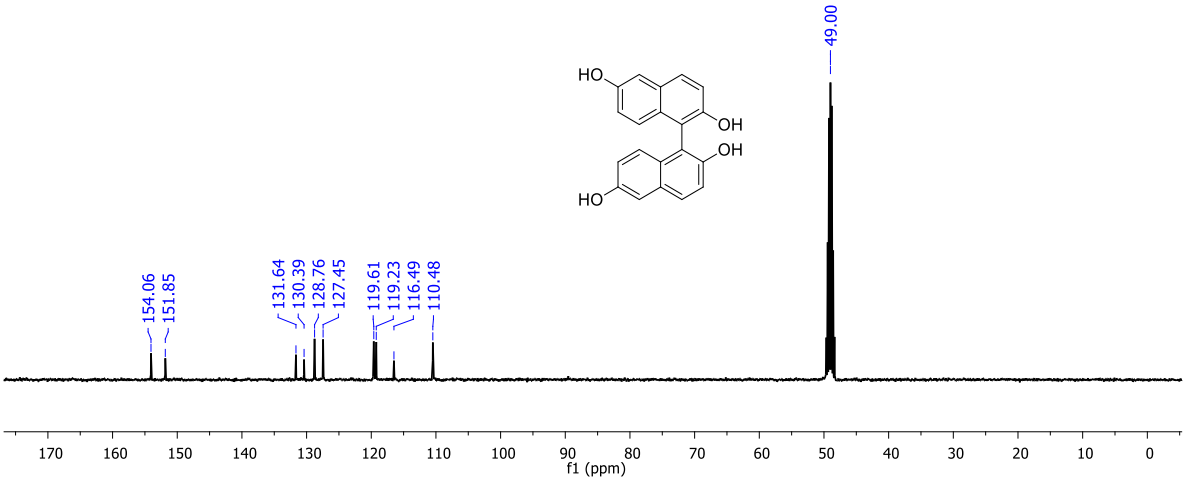


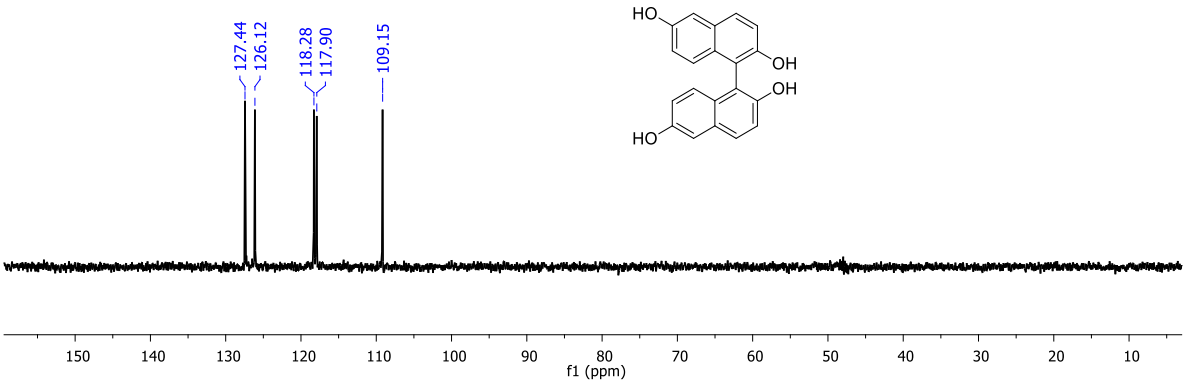




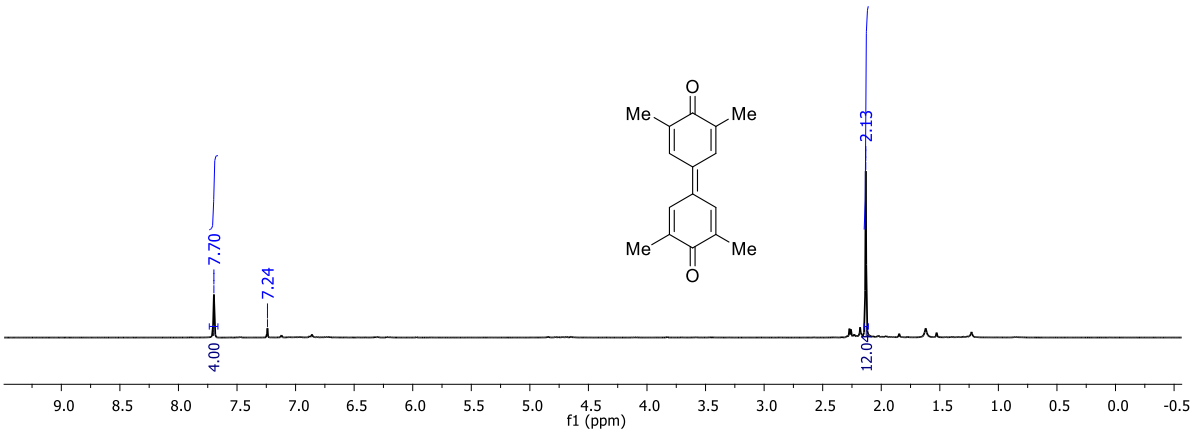
^{1}H and ^{13}C NMR Spectra of Compound 2m.

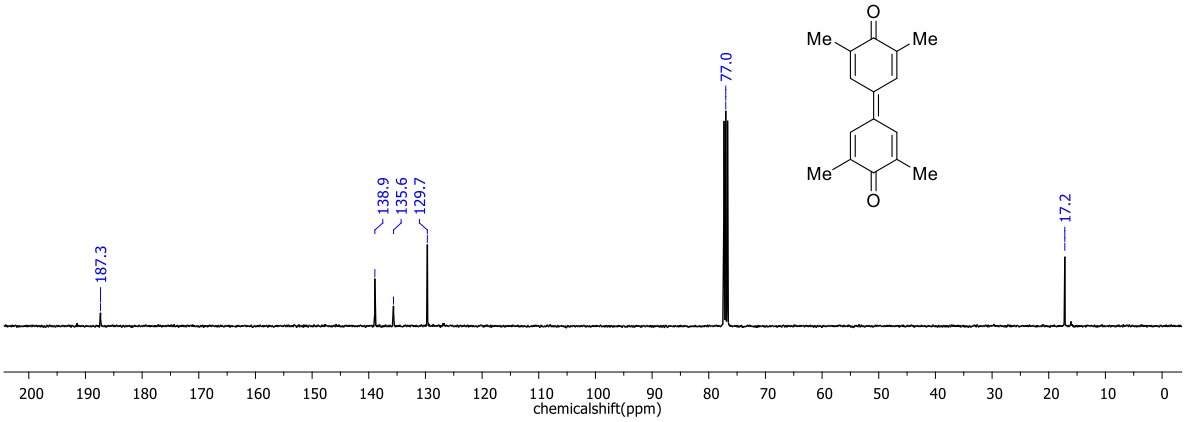


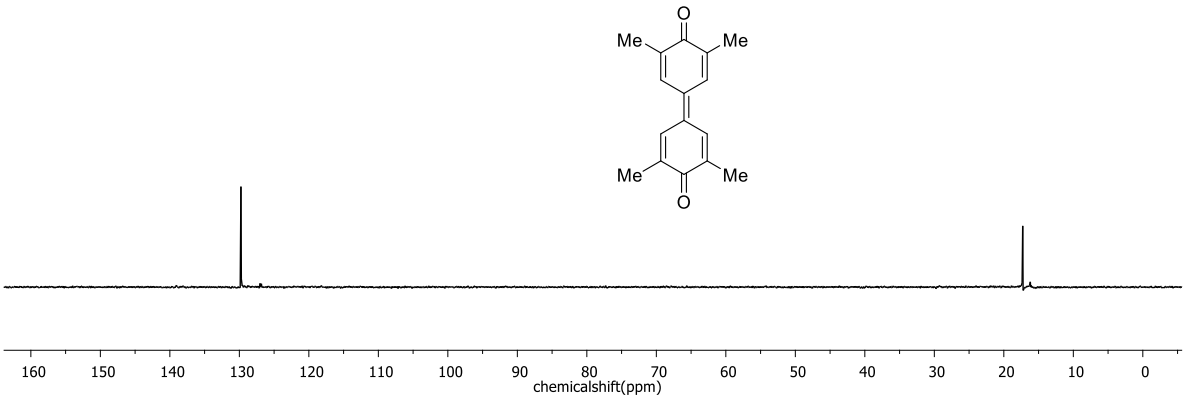




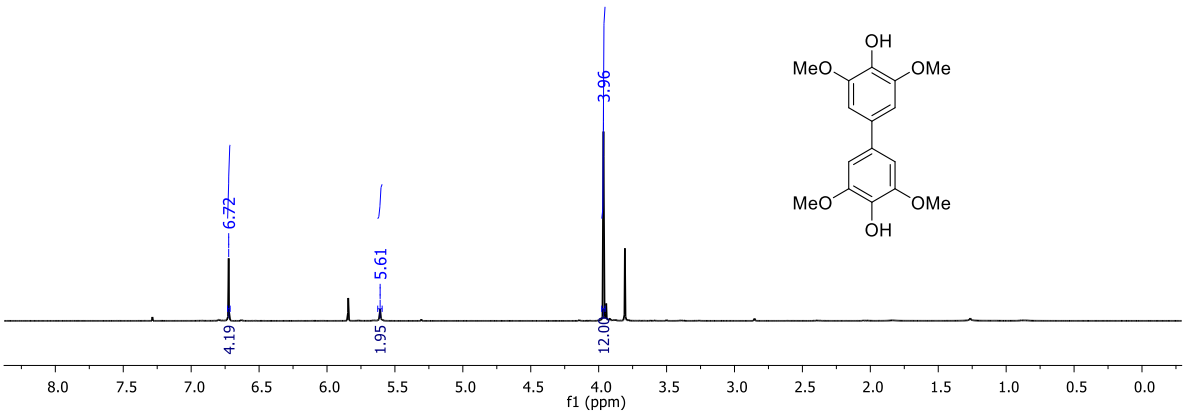
^{1}H and ^{13}C NMR Spectra of Compound **4a-5a** (isomer).

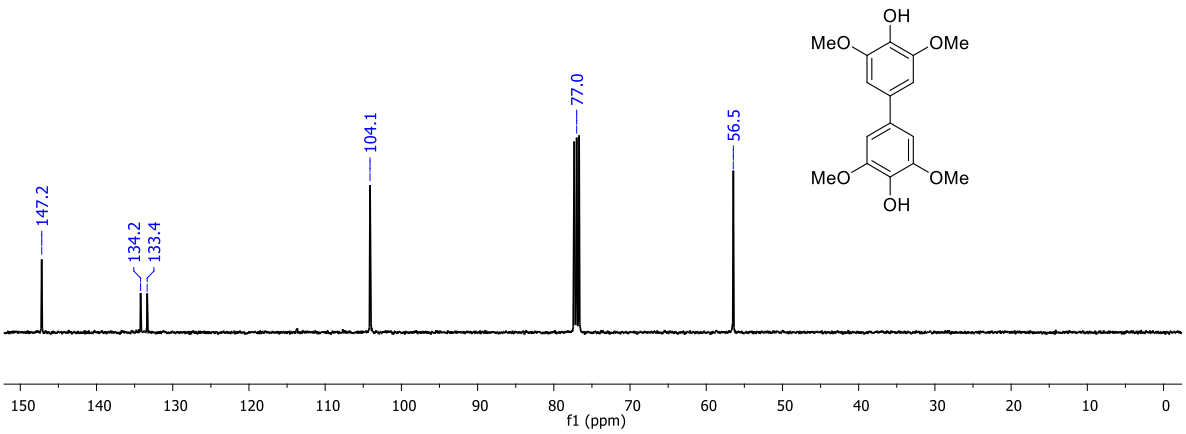




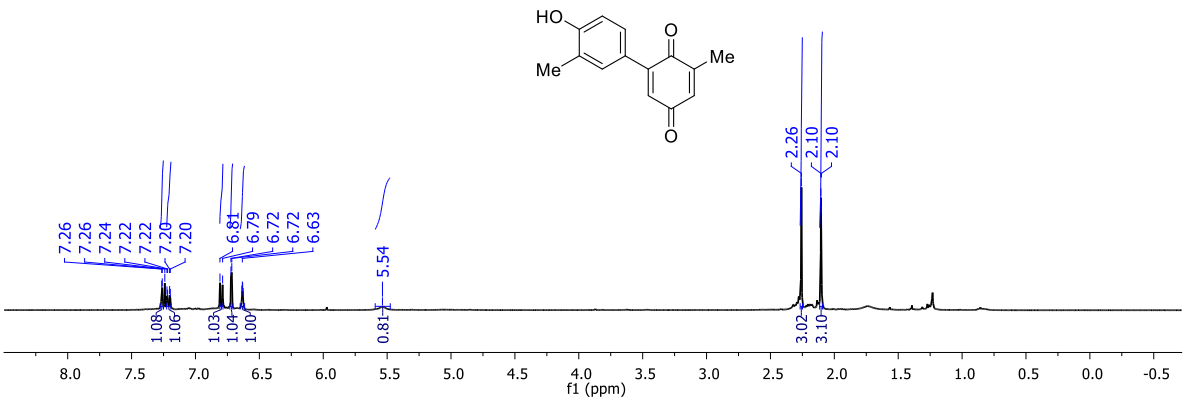


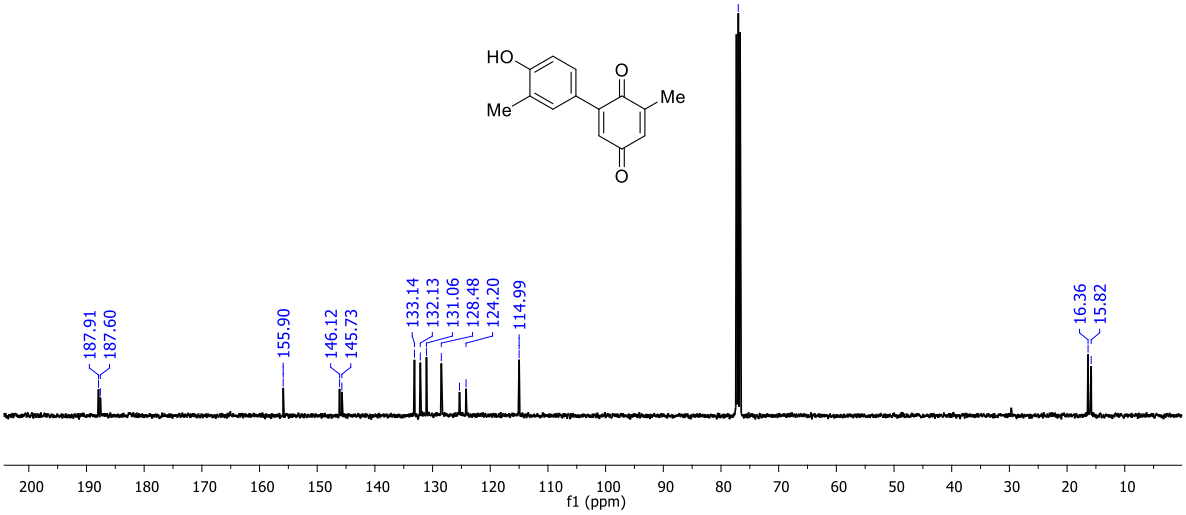
^{1}H and ^{13}C NMR Spectra of Compound **4b**.

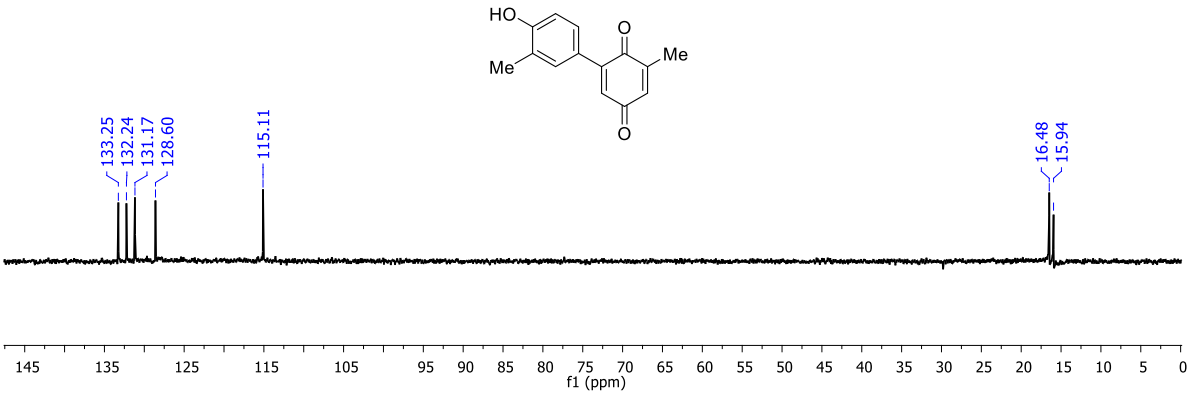




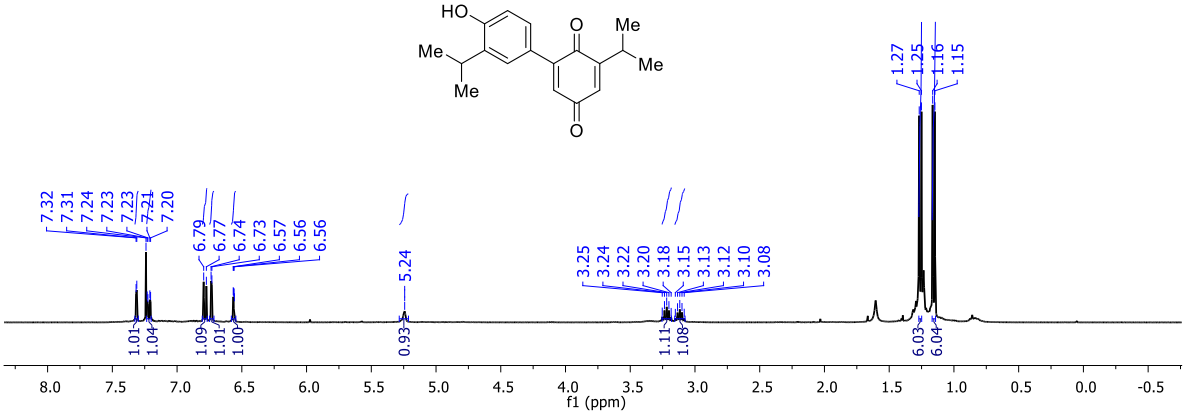
^{1}H and ^{13}C NMR Spectra of Compound **6a**.

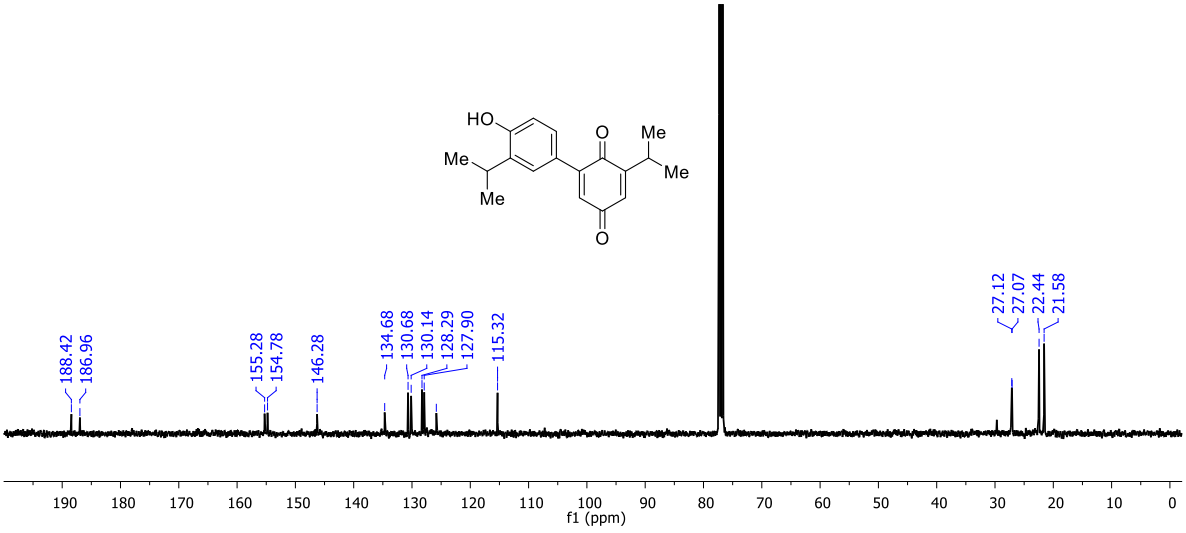




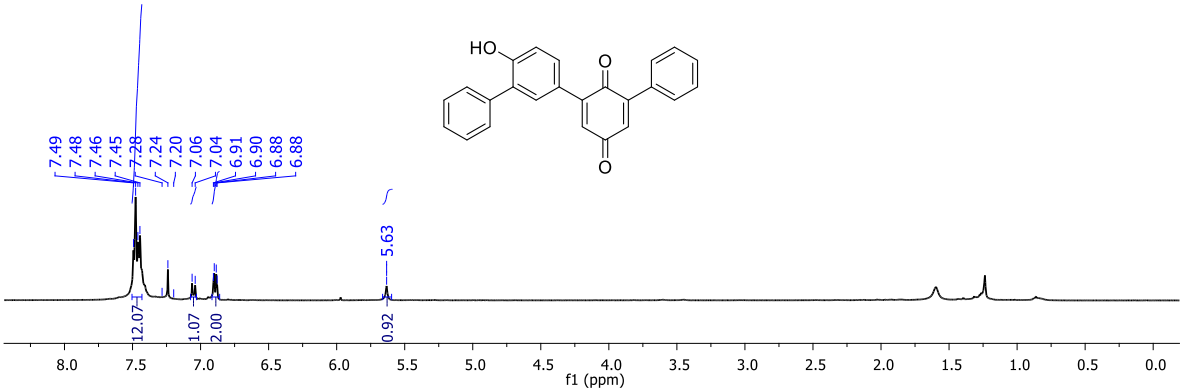


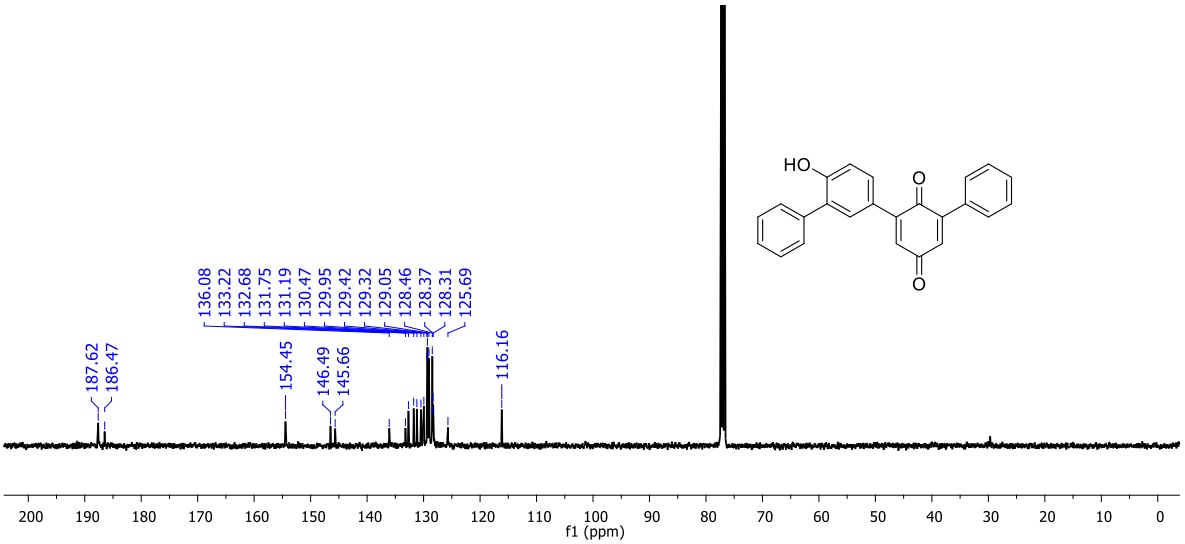
^{1}H and ^{13}C NMR Spectra of Compound **6b**.

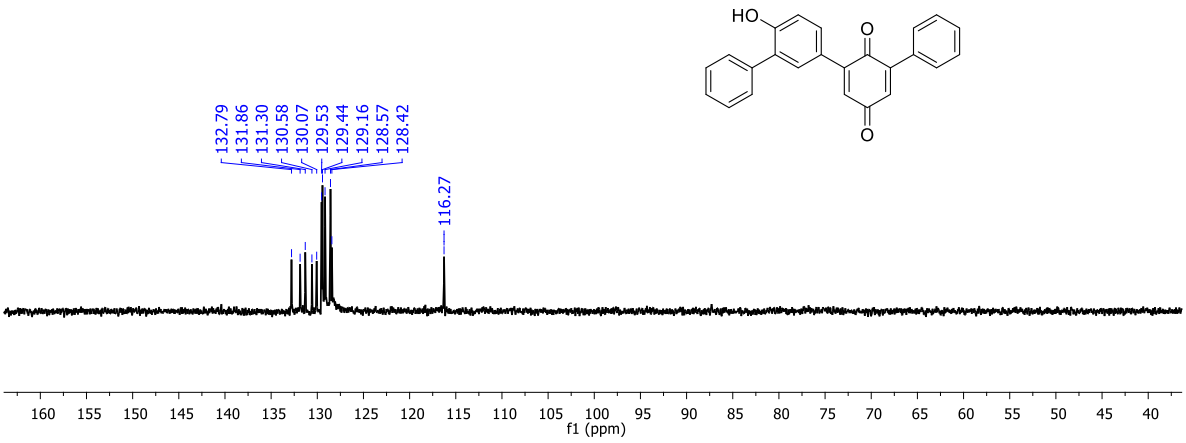




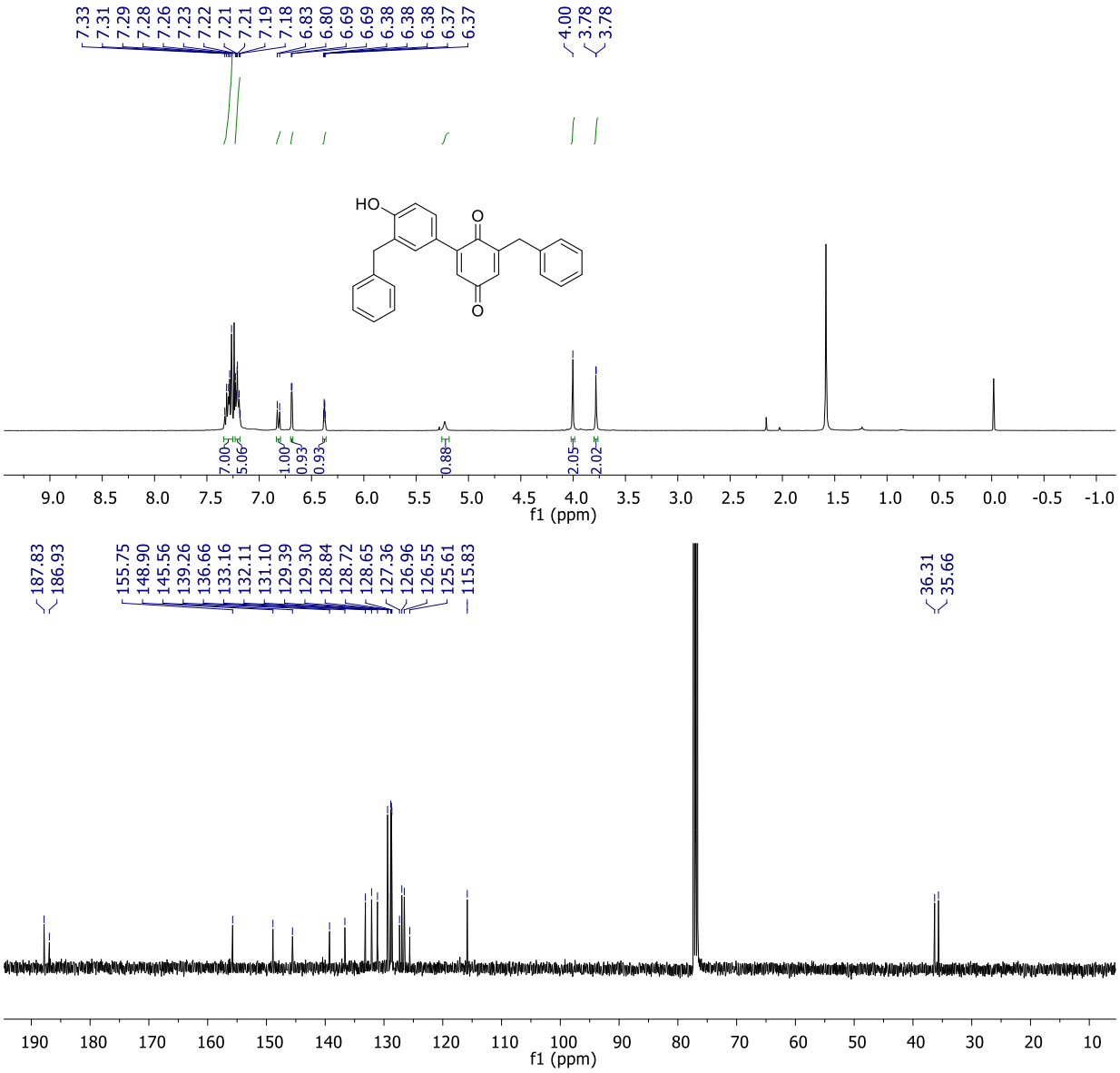
^{1}H and ^{13}C NMR Spectra of Compound **6c**.



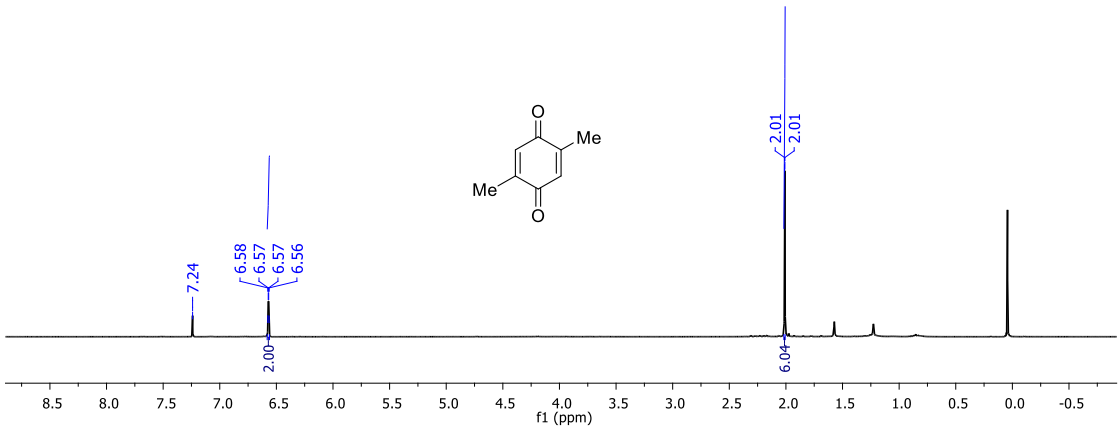


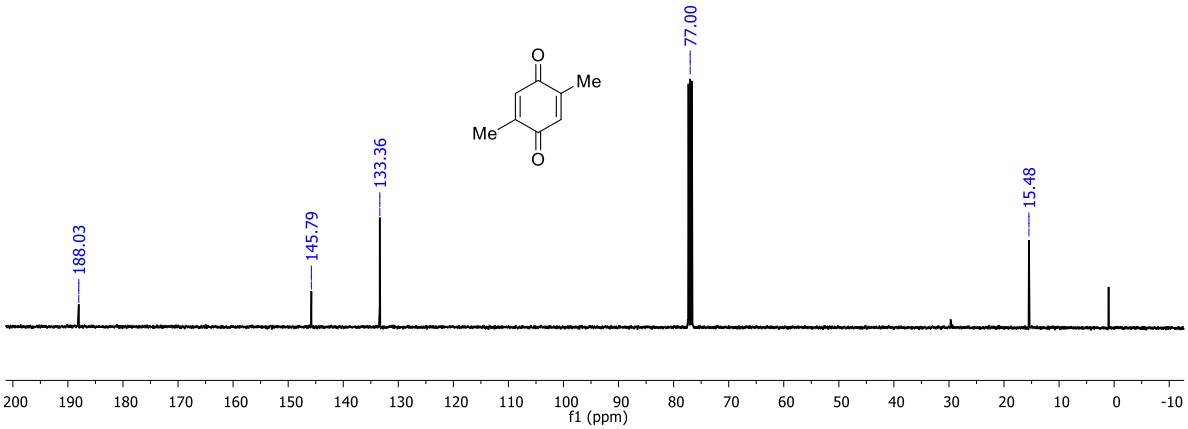


^{1}H and ^{13}C NMR Spectra of Compound **6d**.

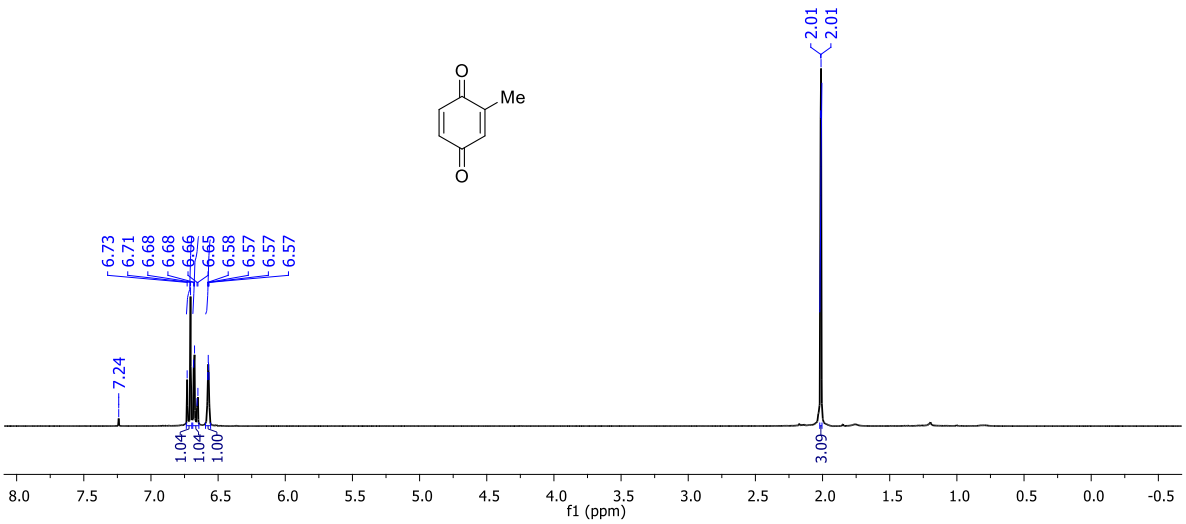


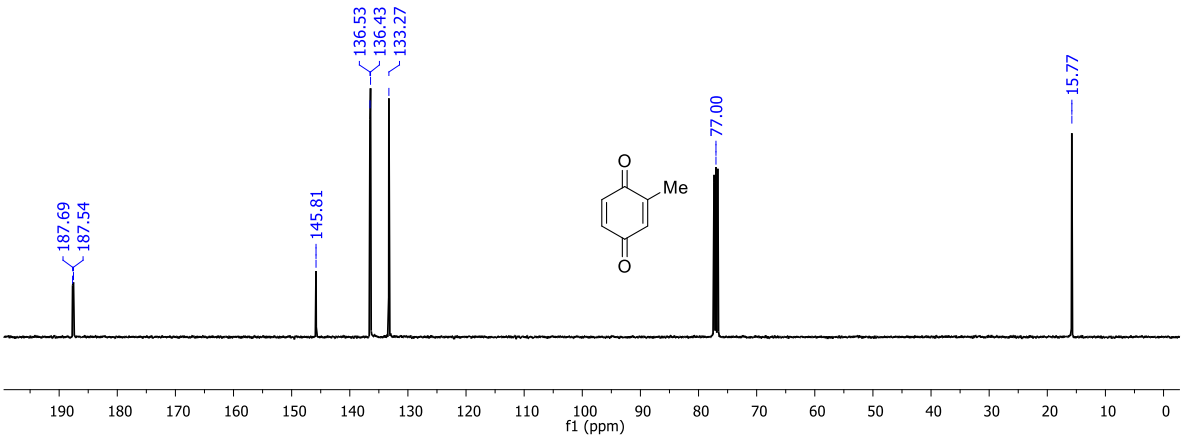
^{1}H and ^{13}C NMR Spectra of Compound **6e**.

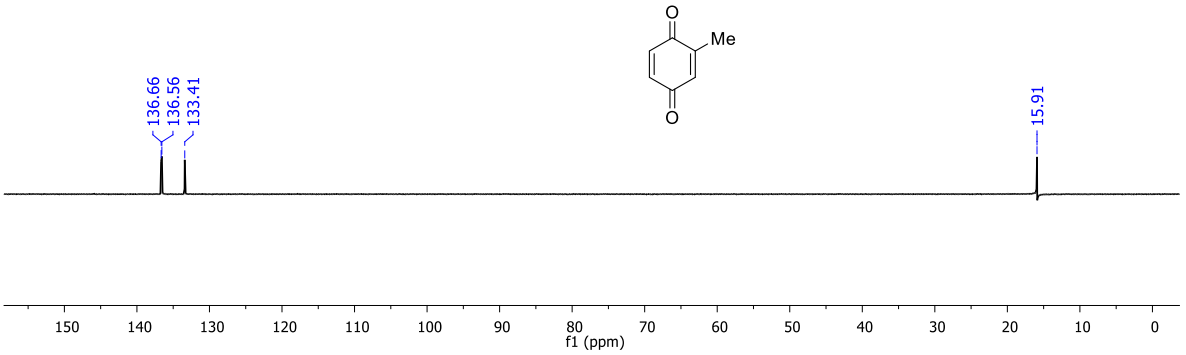




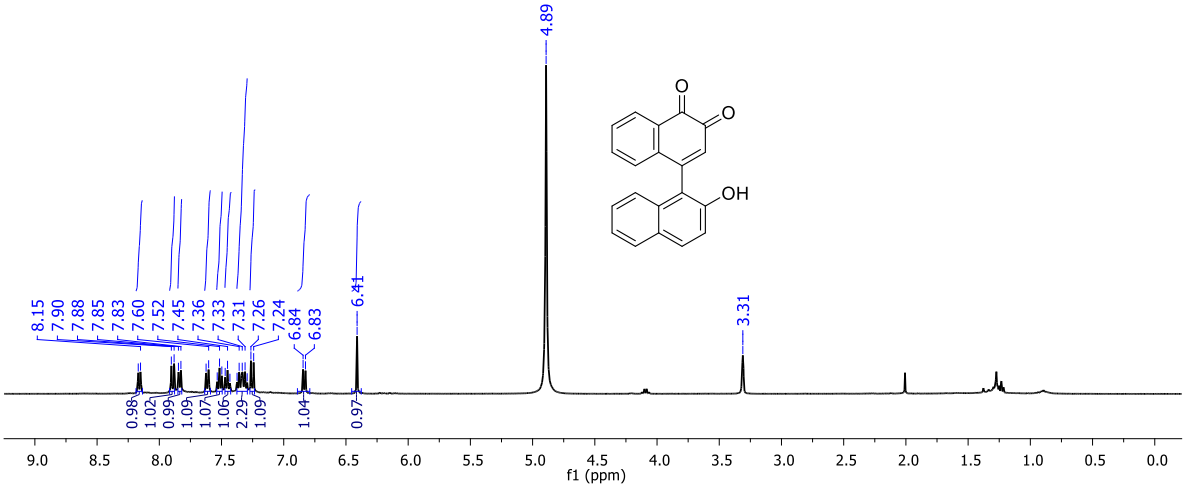
^{1}H and ^{13}C NMR Spectra of Compound **6f**.

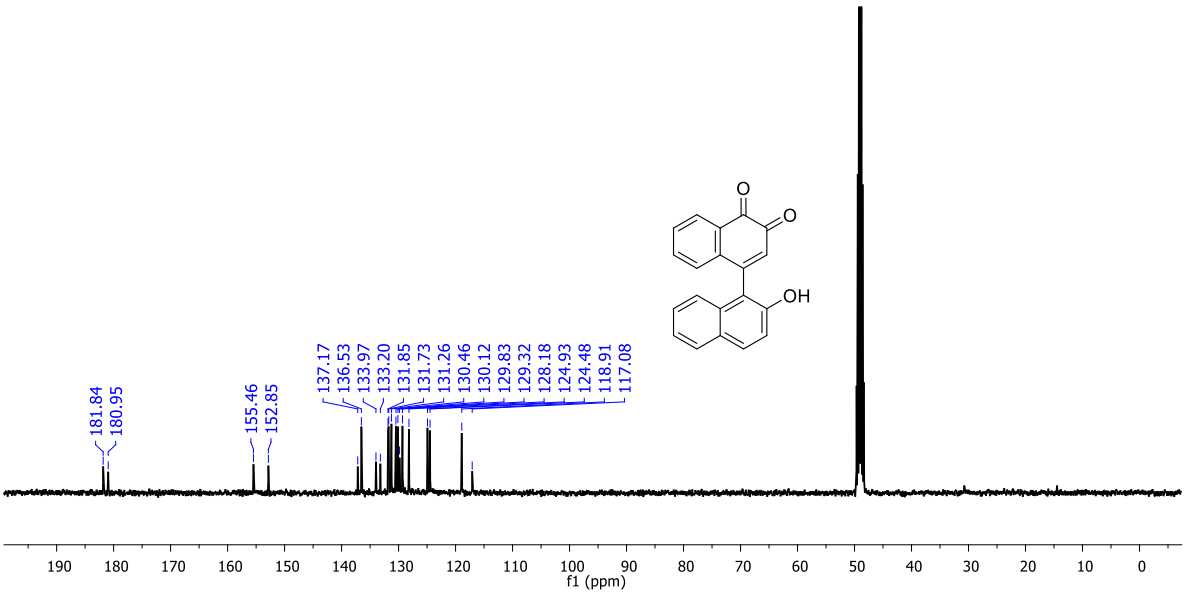


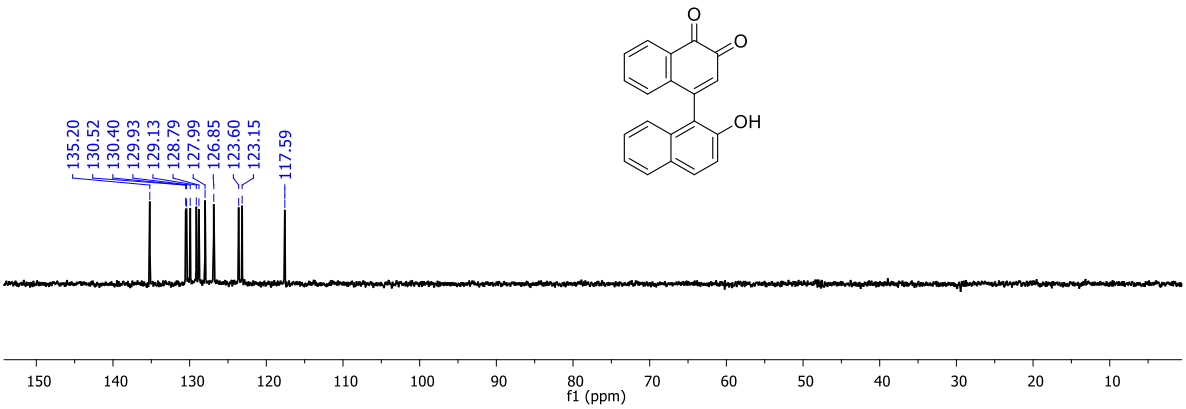




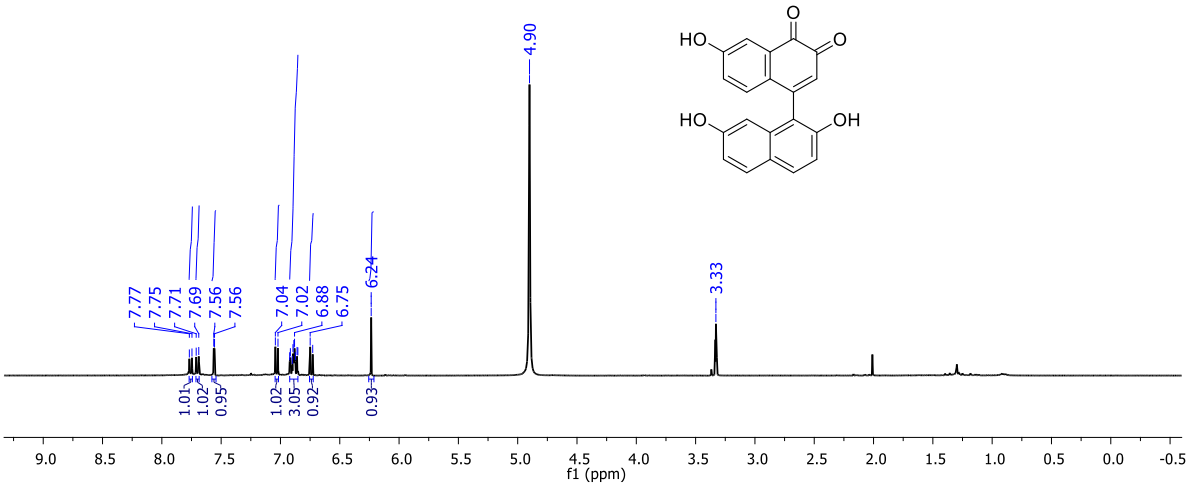
^{1}H and ^{13}C NMR Spectra of Compound **6g**.

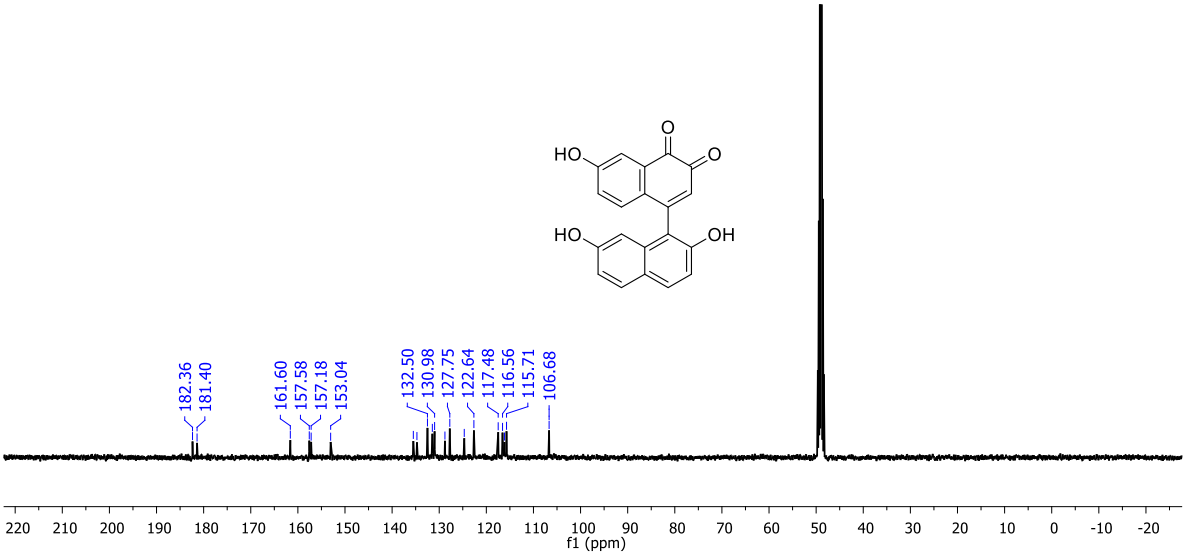




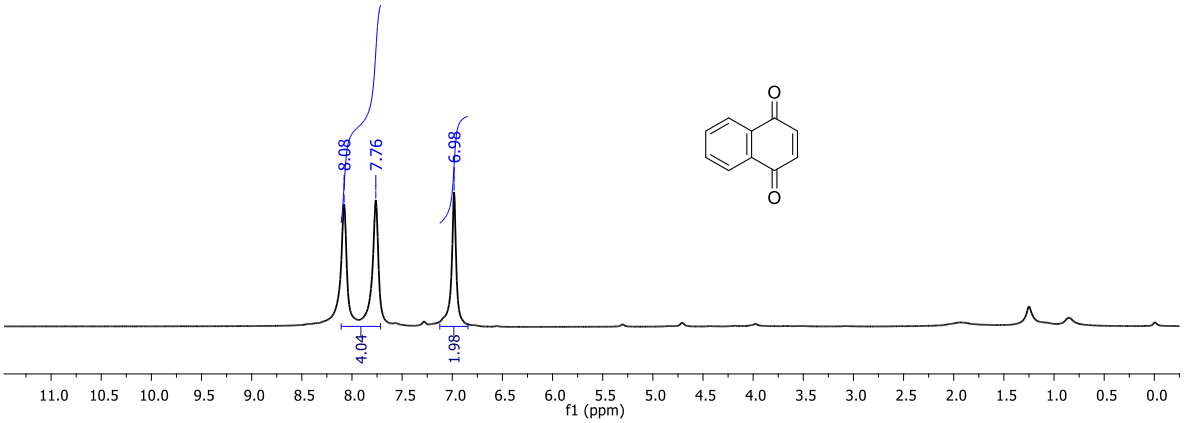


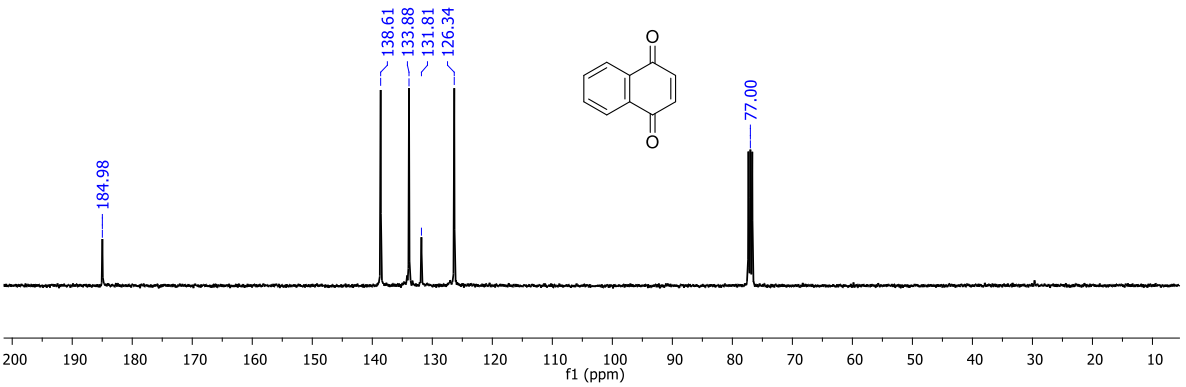
^{1}H and ^{13}C NMR Spectra of Compound **6h**.

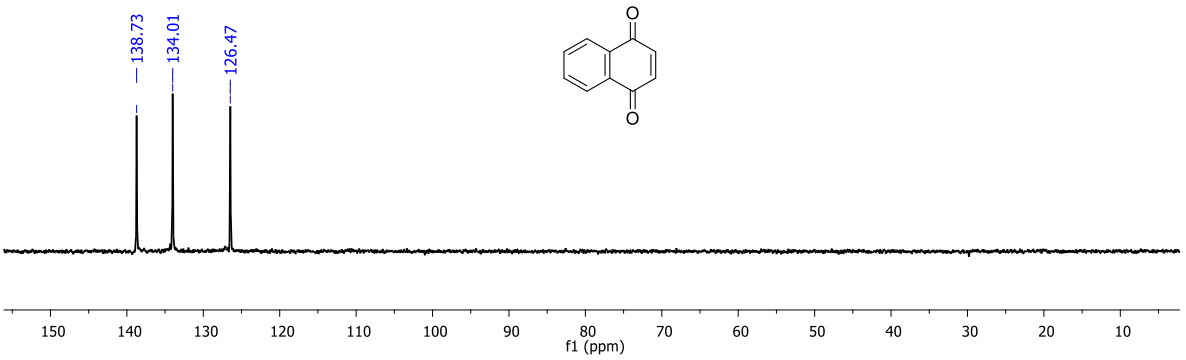




^{1}H and ^{13}C NMR Spectra of Compound **6i**.







^{1}H and ^{13}C NMR Spectra of Compound **8**.