Supporting Information

Cerium(III)-catalyzed regioselective coupling of 2-hydroxychalcones and polyphenols: an efficient domino approach towards synthesis of novel dibenzo-2,8-dioxabicyclo[3.3.1]nonanes

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I. General Information: All chemical reactants were obtained from commercial sources and used without further purification. IR spectra were recorded on Perkin-Elmer FTIR L120-000A. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-400 (400 MHz) spectrometer in $CDCl_3$/DMSO-d_6 with TMS as internal standard (chemical shift in δ). Chemical shifts of common trace impurities ($CDCl_3$, ppm) in some samples: H_2O, 1.56; $CHCl_3$, 7.26 and that of (DMSO-d_6, ppm): H_2O, 2.50; solvent residual peaks ~3.35.[1] Applied Biosystems MDS Sciex API 3200 and QTOF micro™ were used for recording mass spectra of the compounds. AM1 calculations are done using M. J. Frisch *et al Gaussian 09* (*Revision A.02*), Gaussian, Inc., Wallingford CT, 2004 software. Silica gel (60-120 mesh, Spectrochem, India) was used for column chromatography. Melting points were measured by open capillary method in metal bath, and are uncorrected. Light petrol used for chromatographic experiments refers to the fraction boiling at 60-80 °C.

II. Typical experimental procedure for the synthesis of bicyclononane 3a

To a solution of 3-(2-hydroxyphenyl)-1-phenylprop-2-en-1-one (**1a**) (230 mg, 1.03 mmol) and resorcinol (**2a**) (114 mg, 1.04 mmol) in acetonitrile (2 mL) were added $CeCl_3.7H_2O$ (10 mg, 5 mol%) and NaI (4 mg, 5 mol%) and the resulting red coloured solution was heated at reflux for 2 h. After completion of the reaction (TLC monitoring) the cooled reaction mixture was extracted with EtOAc (3X6 mL), washed with water (2X3 mL) and dried (Na_2SO_4). The crude product obtained after removal of solvent from the combined extract was purified by column chromatography using EtOAc: *n*-hexane (1:19) as eluent to give a white solid **3a** (304 mg, 94%), m.p. 230-232 °C (Lit. 231-232 °C)[7b]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.48-7.39 (m, 3H), 7.23 (dd, *J* = 8, 1.2 Hz, 1H), 7.14 (dt, *J* = 8.4, 1.6 Hz, 1H), 7.10 (d, *J* = 8 Hz, 1H), 7.03 (d, *J* = 8 Hz, 1H), 6.92 (dt, *J* = 8, 0.8 Hz, 1H), 6.52 (d, *J* = 2.4 Hz, 1H, H-4), 6.41 (dd, *J* = 8, 2.4 Hz, 1H), 4.74 (s, 1H, O**H**, exchangeable with D_2O), 4.04 (t, *J* = 2.8 Hz, 1H, H-9, nonexchangeable with D_2O), 2.37 (d, *J* = 2.8 Hz, 2H, H-17s) ppm; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.41 (s, 1H, O**H**), 7.70 (d, *J* = 6.8 Hz, 2H), 7.50-7.44 (m, 3H), 7.38 (d, *J* = 6.8 Hz, 1H), 7.19-7.15 (m, 1H), , 7.13 (t, *J* = 6.8 Hz, 1H), 6.96-6.90 (m, 2H), 6.35 (t, *J* = 2.4 Hz, 2H), 4.14 (s, 1H, H-9), 2.36 (s, 2H, H-17s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 152.8, 151.8, 141.4, 128.8, 128.4, 128.0, 127.1, 126.9, 125.8, 121.5, 119.1, 116.8, 108.8, 103.8, 98.7 (C-1), 33.6 (C-17/C-9) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.1, 152.0, 151.3, 141.2, 128.7, 128.3, 128.0, 127.6 (2C), 127.3, 125.5, 121.3, 117.5, 115.9, 108.8, 102.7, 98.2 (C-1), 32.4 (C-17), 31.9 (C-9) ppm; ^{13}C DEPT NMR (100 MHz, DMSO-d_6) δ **C**H: 128.7, 128.3, 128.1, 127.6, 127.3, 125.5, 121.3, 115.9, 108.8, 102.6, 31.8 (C-9), **C**H_2: 32.4 (C-17) ppm; IR (KBr): 3209, 3033, 2937, 2850, 1604, 1487, 1115, 755 cm^{-1}. HRMS (ESI) m/z: Calcd. for $C_{21}H_{17}O_3$ [M+H]: 317.1177. Found: 317.1172.

Bicyclononane 3b: White solid; m.p. 166-168 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8 Hz, 2H), 7.27-7.21 (m, 3H), 7.16-7.11 (m, 1H), 7.09 (d, *J* = 8 Hz, 1H), 7.01 (d, *J* = 8 Hz, 1H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 2.4 Hz, 1H), 6.40 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.68 (s, 1H, O**H**), 4.02 (d, *J* = 2.8 Hz, 1H, H-9), 2.40 (s, 3H), 2.36 (d, *J* = 3.2 Hz, 2H, H-17s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 152.8, 151.9, 138.7, 138.5, 129.0, 127.9, 127.1, 126.9, 125.7, 121.5, 119.1, 116.8, 108.8, 103.8, 98.8 (C-1), 33.6 (C-17), 33.5 (C-9), 21.2 ppm; IR (KBr): 3260, 2937, 1629, 1604, 1588, 1485, 1118, 757 cm^{-1}. HRMS (ESI) m/z: Calcd. for $C_{22}H_{19}O_3$ [M+H]: 331.1334. Found: 331.1328.

Bicyclononane 3c: White solid; m.p. 206-208 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.8 Hz, 2H), 7.51-7.44 (m, 2H), 7.39 (t, *J* = 3.6 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 6.4 Hz, 1H), 7.15-7.11 (m, 1H), 7.09 (d, *J*= 8.4 Hz, 1H), 7.04 (d, *J*= 8.4 Hz, 2H), 7.00 (d, *J*= 8 Hz, 1H), 6.90 (t, *J*= 7.6 Hz, 1H), 6.50 (d, *J*= 2.4 Hz, 1H), 6.40 (dd, *J*= 8, 2.4 Hz, 1H), 5.11 (s, 2H), 4.83 (s, 1H, O**H**), 4.02 (s, 1H, H-9), 2.40-2.35 (m, 2H, H-17s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 155.4, 152.8, 151.9, 136.9, 133.9, 128.6, 128.0, 127.9, 127.5, 127.2, 127.1, 126.9, 121.5, 119.1, 116.7, 114.6, 108.8, 103.8, 98.7 (C-1), 70.1, 33.7 (C-17), 33.6 (C-9) ppm; IR (KBr): 3402, 2869, 1664, 1599, 1584, 1505, 1231, 999, 751 cm^{-1}. HRMS (ESI) m/z: Calcd. for $C_{28}H_{23}O_4$ [M+H]: 423.1596. Found: 423.1563.

Bicyclononane 3d: Pinkish white solid; m.p. 156-158 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.15-7.11 (m, 1H), 7.09 (d, *J* = 8 Hz, 1H), 7.01-6.97 (m, 3H), 6.91 (t, *J*= 7.6 Hz, 1H), 6.50 (d, *J*= 2.4 Hz, 1H), 6.40 (dd, *J*= 8, 2.4 Hz, 1H), 5.11 (s, 1H), 5.00 (s, 1H), 4.67 (s, 1H, O**H**), 4.48 (s, 2H), 4.02 (s, 1H, H-9), 2.35 (d, *J* = 2.8 Hz, 2H, H-17s), 1.84 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 155.4, 152.9, 151.9, 140.8, 133.7, 127.9, 127.0, 126.9, 121.4, 119.1, 116.7, 114.5, 112.9, 108.7, 103.8, 98.7 (C-1), 71.8, 33.7 (C-17), 33.6 (C-9), 19.4 ppm; IR (KBr): 3526, 3207, 1626, 1612, 1594, 1457, 1233, 1149, 758 cm^{-1}. HRMS (ESI) m/z: Calcd. for $C_{25}H_{22}O_4$ [M+H]: 387.1596. Found: 387.1591.

Bicyclononane 3e: Off-white solid; m.p. 172-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.09-7.05 (m, 1H), 7.02 (d, *J* = 8.8 Hz, 1H), 6.86-6.83 (m, 2H), 6.35-6.32 (m, 2H), 4.72 (s, 1H, O**H**), 3.93 (t, *J* = 2.8 Hz, 1H, H-9), 2.21 (d, *J* = 3.2 Hz, 2H, H-17s), 1.84 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 152.6, 151.6, 127.9, 127.8, 127.0, 126.9, 121.2, 119.0, 116.4, 108.5, 103.5, 98.1 (C-1), 33.2 (C-17), 31.3 (C-9), 27.3 ppm; IR (KBr): 3480, 3387, 2936, 1619, 1601, 1508, 1485, 1142, 757 cm^{-1}. HRMS (ESI) m/z: Calcd. for $C_{16}H_{15}O_3$ [M+H]: 255.1021. Found: 255.1016.

Bicyclononane 3f: White solid; m.p. 206-208 °C (Lit. 218-219 °C)[7b]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 4, 0.8 Hz, 1H), 7.32 (dd, *J* = 4, 1.2 Hz, 1H), 7.22 (dd, *J* = 8, 1.2 Hz, 1H), 7.15-7.11 (m, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.08-7.05 (m, 1H), 6.99 (d, *J* = 8 Hz, 1H), 6.94-6.90 (m, 1H), 6.49 (d, *J* = 2.4 Hz, 1H), 6.41 (dd, *J* = 8, 2.4 Hz, 1H), 4.70 (s, 1H, O**H**), 4.05 (t, *J* = 2.8 Hz, 1H, H-9), 2.52 (d, *J*= 2.8 Hz, 2H, H-17s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 152.4, 151.4, 144.9, 128.0, 127.9, 127.1, 126.9, 126.6, 126.0, 125.0, 121.7, 118.9, 116.8, 109.0, 103.8, 97.7 (C-1), 33.7 (C-17), 33.5 (C-9) ppm; IR (KBr): 3518, 3434, 2938, 1622, 1599, 1486, 1236, 1105, 706 cm^{-1}. HRMS (ESI) m/z: Calcd. for $C_{19}H_{15}O_3S$ [M+H]: 323.0742. Found: 323.0703.

Bicyclononane 3g: White solid; m.p. 150-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.17-7.12 (m, 1H), 7.10 (d, *J* = 8 Hz, 1H), 7.01 (d, *J* = 8 Hz, 1H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 6.42 (dd, *J* = 8, 2.4 Hz, 1H), 4.86 (s, 1H, O**H**), 4.04 (d, *J* = 2.4 Hz, 1H, H-9), 2.34 (d, *J* = 3.2 Hz, 2H, H-17s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 152.6, 151.6, 140.0, 134.8, 128.5, 128.0 (2C), 127.4, 127.1, 126.7, 121.7, 118.8, 116.7, 109.0, 103.7, 98.3 (C-1), 33.5 (2C) (C-17 & C-9) ppm; IR (KBr): 3237, 2946, 1600, 1586, 1484, 1227, 1152, 729 cm^{-1}. HRMS (ESI) m/z: Calcd. for $C_{21}H_{16}ClO_3$ [M+H]: 351.0788. Found: 351.0732.

Bicyclononane 3h: White solid; m.p. 164-166 °C (Lit. 164-1652 °C)[7b]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.69 (m, 2H), 7.23 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.16-7.09 (m, 4H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.94-6.90 (m, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 6.41 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.75 (s, 1H, O**H**), 4.03 (t, *J* = 2.8 Hz, 1H, H-9), 2.35 (d, *J* = 3.2 Hz, 2H, H-

17s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 155.5, 152.6, 151.7, 137.3, 128.0, 127.8 (d, $^3J_{C\text{-}F}$ = 9 Hz), 127.1, 126.7, 121.6, 119.0, 116.7, 115.2 (d, $^2J_{C\text{-}F}$ = 21 Hz), 109.0, 103.7, 98.4 (C-1), 33.7 (C-17), 33.5 (C-9) ppm; IR (KBr): 3530, 3252, 2938, 1605, 1506, 1485, 1227, 1119, 755 cm^{-1}. HRMS (ESI) m/z: Calcd. for $C_{21}H_{16}FO_3$ [M+H]: 335.1083. Found: 335.1007.

IV. Typical experimental procedure for the synthesis of bisbicyclononane 4a

To a solution of 3-(2-hydroxyphenyl)-1-phenylprop-2-en-1-one (**1a**) (450 mg, 2.01 mmol) and phloroglucinol (**2b**) (165 mg, 1.02 mmol) in acetonitrile (2 mL) were added $CeCl_3.7H_2O$ (10 mg, 5 mol%) and NaI (4 mg, 5 mol%) and the red coloured solution was heated at reflux temperature for 2 h. After completion of the reaction (TLC monitoring) the cooled reaction mixture was extracted with EtOAc (3X8 mL), washed with water (2X3 mL), dried (Na_2SO_4) and the combined extract was concentrated under reduced pressure. The crude product was purified by column chromatography using EtOAc:light petrol (1:19) as eluent to give a white solid **4a** (427 mg, 79%), which was further recrystallized from EtOAc-*n*-hexane mixture (m.p. 250-252 ^oC). ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 6.4 Hz, 2H), 7.57-7.50 (m, 3H), 7.44-7.35 (m, 4H), 7.25 (d, *J* = 5.6 Hz, 1H), 7.17 (t, *J* = 8 Hz, 2H), 7.11 (d, *J* = 8 Hz, 1H), 7.04 (d, *J* = 8 Hz, 1H), 6.95-6.89 (m, 2H), 6.12 (s, 1H), 4.98 (s, 1H, OH), 4.45 (t, *J* = 2.8 Hz, 1H, H-9/ H-9$^/$), 4.42 (t, *J* = 2.8 Hz, 1H, H-9$^/$/H-9), 2.42 (dd, *J* = 13.2, 3.2 Hz, 1H, H-17/H-17$^/$), 2.26 (dd, *J* =13.2, 3.2 Hz, 1H, H-17/H-17$^/$), 2.20 (dd, *J* = 13.2, 3.2 Hz, 1H, H-17$^/$/ H-17), 2.15 (dd, *J* = 13.2, 3.2 Hz, 1H, H-17$^/$/H-17) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 152.1, 151.5, 151.0, 149.4, 141.4, 141.3, 129.0, 128.7, 128.3, 128.2, 127.7, 127.4, 127.1, 126.1, 125.8, 121.4, 120.9, 116.3, 107.2, 106.9, 99.1 (C-1/C-1$^/$), 98.8 (C-1$^/$/C-1), 96.8, 60.7, 33.4 (C-17/C-17$^/$), 32.8 (C-17$^/$/C-17), 26.7 (C-9/C-9$^/$), 21.2 (C-9$^/$/C-9), 14.2 ppm; IR (KBr): 3411, 3034, 2948, 1614, 1485, 1237, 1111, 1070, 751 cm^{-1}. HRMS (ESI) m/z: Calcd. for $C_{36}H_{27}O_5$ [M+H]: 539.1858. Found: 539.1875.

Bisbicyclononane 4b: White solid; m.p. 256-258 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8 Hz, 2H), 7.53 (d, *J* = 8 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.21-7.14 (m, 4H), 7.09 (d, *J* = 8 Hz, 1H), 7.02 (d, *J* = 8 Hz, 1H), 6.94-6.89 (m, 2H), 6.10 (s, 1H), 4.88 (s, 1H, O**H**), 4.42 (t, *J* = 2.8 Hz, 2H, H-9 & 9$^/$), 2.47 (s, 3H), 2.36 (s, 3H), 2.42-2.13 (m, 4H, H-17s & 17$^/$s) ppm; ^{13}C NMR (100 MHz,

$CDCl_3$) δ 152.6, 152.1, 151.3, 151.1, 149.4, 138.8, 138.6, 138.5 (2C), 129.0, 128.2, 127.7, 127.4, 127.1, 126.0, 125.6, 121.3, 120.8, 116.3, 107.1, 99.1 (C-1/C-1/), 98.8 (C-1/ /C-1), 96.7, 33.3 (C-17/C-17/), 32.9 (C-17//C-17), 26.7, 21.3 (C-9/C-9/), 21.2 (C-9//C-9) ppm; IR (KBr): 3411, 3031, 2949, 1939, 1606, 1485, 1239, 1182, 1068, 751 cm^{-1}. HRMS (ESI) m/z: Calcd. for $C_{38}H_{30}O_5Na$ [M+Na]: 589.1991. Found 589.1991.

Bisbicyclononane 4g: White solid; m.p. 284-286 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.20-7.15 (m, 3H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 8 Hz, 1H), 6.96-6.90 (m, 2H), 6.10 (s, 1H), 5.00 (s, 1H, O**H**), 4.45 (s, 1H, H-9/ H-9/), 4.38 (s, 1H, H-9//H-9), 2.40-2.10 (m, 4H, H-17 & H-17/s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 151.8, 151.3, 150.9, 149.3, 139.9, 139.8, 135.0, 134.7, 128.5, 128.0, 127.9, 127.8, 127.7 (2C), 127.3, 127.1, 126.8, 121.6, 121.0, 116.3, 107.2, 106.9, 98.7(C-1/C-1/), 98.4 (C-1// C-1), 96.8, 33.3 (C-17/C-17/), 32.7 (C-17//C-17), 26.7 (C-9/C-9/), 26.6 (C-9//C-9) ppm; IR (KBr): 3315, 3039, 2975, 1627, 1484, 1458, 1234, 1116, 1014, 754 cm^{-1}. HRMS (ESI) m/z: Calcd. for $C_{36}H_{25}O_5Cl_2$ [M+H]: 607.1079. Found: 607.1094.

Bisbicyclononane 4h: White solid; m.p. above 290 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.62 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.24-7.16 (m, 6H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.03 (t, *J* = 8.8 Hz, 1H), 6.96-6.85 (m, 2H), 6.11 (s, 1H), 4.98 (s, 1H, O**H**), 4.45 (s, 1H, H-9/H-9/), 4.39 (s, 1H, H-9//H-9), 2.40 (dd, *J* = 13.2, 3.2 Hz, 1H, H-17/H-17/), 2.24 (dd, *J* = 13.2, 2.8 Hz, 1H, H-17/H-17/), 2.18 (dd, *J* = 13.6, 3.2 Hz, 1H, H-17//H-17), 2.13 (dd, *J* = 13.2, 2.8 Hz, 1H, H-17//H-17) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.4 (d, $^1J_{C-F}$ = 245 Hz), 162.2 (d, $^1J_{C-F}$ = 247 Hz), 153.1, 151.7, 151.4, 150.3, 148.4, 137.5, 137.3, 128.0 (d, $^3J_{C-F}$ = 9Hz), 127.8 (d, $^3J_{C-F}$ = 9 Hz), 127.6, 127.5, 127.4, 127.0, 121.1, 120.9, 115.8, 115.1 (d, $^2J_{C-F}$ = 21 Hz), 115.0 (d, $^2J_{C-F}$ = 22 Hz), 114.9, 107.1, 104.9, 98.3 (C-1/C-1/), 98.0 (C-1//C-1), 95.7, 32.0 (C-17/C-17/), 31.0 (C-17//C-17), 25.9 (C-9/C-9/), 25.8 (C-9//C-9) ppm; IR (KBr): 3315, 3039, 2975, 1627, 1484, 1458, 1234, 1116, 1014, 754 cm^{-1}. HRMS (ESI) m/z: Calcd. for $C_{36}H_{24}O_5F_2$ [M]: 574.1592. Found: 574.1592.

Bisbicyclononane 4i: White solid; m.p. 242-244 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72-7.66 (m, 4H), 7.54-7.52 (m, 4H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.20-7.17 (m, 3H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 8 Hz, 1H), 6.94 (t, *J* = 7.2 Hz, 2H), 6.11 (s, 1H), 5.02 (s, 1H,

OH), 4.45 (s, 1H, H-9/H-9′), 4.39 (s, 1H, H-9′/H-9), 2.40-2.13 (m, 4H, H-17s & H-17′s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 152.1, 151.8, 150.7, 148.8, 141.0, 140.8, 132.0, 131.8 (2C), 131.7, 128.6, 128.5, 128.3, 128.1, 128.0, 127.4, 122.9, 122.6, 121.6, 116.3, 107.6, 105.5, 98.9 (C-1/C-1′), 98.8 (C-1′/C-1), 98.5, 96.3, 32.3 (C-17/C-17′), 31.5 (C-17′/C-17), 26.3 (C-9/C-9′) ppm; IR (KBr): 3309, 3038, 2938, 1627, 1485, 1234, 1115, 1071, 1010, 753 cm^{-1}. HRMS (ESI) m/z: Calcd. for $C_{36}H_{25}O_5Br_2$ [M+H]: 695.0068. Found: 695.0063.

Bisbicyclononane 4j: White solid; m.p. 240-242 ^oC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dt, *J* = 7.6, 1.2 Hz, 2H), 7.10-7.05 (m, 2H), 6.90-6.82 (m, 4H), 5.90 (s, 1H), 4.78 (s, 1H, O**H**), 4.39 (t, *J* = 2.8 Hz, 1H, H-9/H-9′), 4.30 (t, *J* = 2.8 Hz, 1H, H-9′/H-9), 2.33-2.18 (m, 2H, H-17/H-17′s), 2.13-1.94 (m, 6H, H-17′/H-17s & four C**H₂**CH₃ protons), 1.25 (t, *J* = 7.6 Hz, 3H) 1.04 (t, *J* = 7.6Hz, 3H,) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 152.2, 151.0, 149.0, 127.6, 127.5, 127.4, 127.3, 120.8, 120.6, 116.1, 116.0, 107.1, 107.0, 99.9 (2C) **(**C-1 & C-1′**)**, 96.0, 33.3 (C-17/C-17′), 33.0 (C-17′/C-17), 28.4, 28.3, 26.0 (C-9/C-9′), 25.9 (C-9′/C-9), 8.0, 7.9 ppm; IR (KBr): 3409, 2979, 2940, 1623, 1485, 1459, 1234, 1108, 1061, 931, 864, 749 cm^{-1}. HRMS (ESI) m/z: Calcd. for $C_{28}H_{27}O_5$ [M+H]: 443.1858. Found: 443.1875.

Bicyclononane 5: White solid; m.p. 130-132 ^oC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 1H), 7.36 (dd, *J* = 5.2, 0.8 Hz, 1H), 7.31 (d, *J* = 3.6 Hz, 1H), 7.15-7.11 (m, 1H), 7.07-7.04 (m, 1H), 6.99 (d, *J* = 8 Hz, 1H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.07 (d, *J* = 2 Hz, 1H, H-4), 5.82 (d, *J* = 2.4 Hz, 1H, H-6), 5.09 (s, 1H, O**H** of C-5), 4.81 (s, 1H, O**H** of C-7), 4.43 (d, *J* = 2.4 Hz, 1H, H-9), 2.45 (d, *J*= 2.8 Hz, 2H, H-17) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 154.6, 152.8, 151.8, 145.4, 127.9, 127.5, 127.3, 126.8, 125.7, 124.8, 121.1, 116.1, 105.6, 97.7 (C-1), 96.6, 95.3, 33.7 (C-17), 26.5 (C-9) ppm; IR (KBr): 3604, 3533, 3423, 3343, 1619, 1484, 1464, 1230, 1140, 1017, 702 cm^{-1}. HRMS (ESI) m/z: Calcd. for $C_{19}H_{16}O_4S$ [M+H]: 339.0691. Found: 339.0703.

VI. *O*-allylation of the bisbicyclononane 4a to 6

To a solution of **4a** (150mg, 0.358 mmol) in dry acetone (10 mL) were added allyl bromide (65mg, 0.537 mmol) and K_2CO_3 (200mg, 1.44 mmol). The resulting solution was refluxed in water bath for 10 h (TLC monitoring) and filtered after cooling. The residual solid was extracted with acetone (2X3 mL) and the combined extract and filtrate was concentrated to give a thick liquid. It was subjected to column chromatography over silica gel (60-120 mesh) using light petrol-ethyl acetate (19:1) as eluent to afford **6** which was further recrystallized from EtOAc-*n*-hexane to give a white crystalline solid (153 mg, 95%), m.p. 204-206 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.59-7.51 (m, 3H), 7.46-7.38 (m, 4H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.23-7.18 (m, 2H), 7.13 (d, *J* = 8 Hz, 1H), 7.07 (d, *J* = 8 Hz, 1H), 6.96-6.92 (m, 2H), 6.26 (s, 1H), 6.21-6.12 (m, 1H), 5.52 (d, *J* = 17.2 Hz, 1H), 5.37 (d, *J* = 10.4 Hz, 1H), 4.61-4.55 (m, 2H), 4.54-4.41 (m, 2H, H-9 & 9$^{/}$), 2.43 (dd, *J* = 13.2, 2.8 Hz, 1H, H-17/H-17$^{/}$), 2.26 (dd, *J* = 13.2, 2.8 Hz, 1H, H-17/H-17$^{/}$), 2.23-2.18 (m, 2H, H-17$^{/}$/H-17s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 152.6, 152.1, 151.3, 141.5, 141.3, 133.2, 129.0, 128.7, 128.3, 128.2, 127.7, 127.6, 127.4, 127.1, 126.1, 125.7, 121.3, 120.8, 117.7, 116.3, 108.2, 106.8, 99.0 (C-1/C-1$^{/}$), 98.8 (C-1$^{/}$/C-1), 94.0, 69.1, 33.4 (C-17/C-17$^{/}$), 32.8 (C-17$^{/}$/C-17), 26.7 (C-9/ C-9$^{/}$), 26.6 (C-9$^{/}$/C-9) ppm; IR (KBr): 2936, 1622, 1602, 1484, 1237, 1118, 753 cm^{-1}. HRMS (ESI) m/z: Calcd. for $C_{39}H_{31}O_5$ [M+H]: 579.2171. Found: 579.2413.

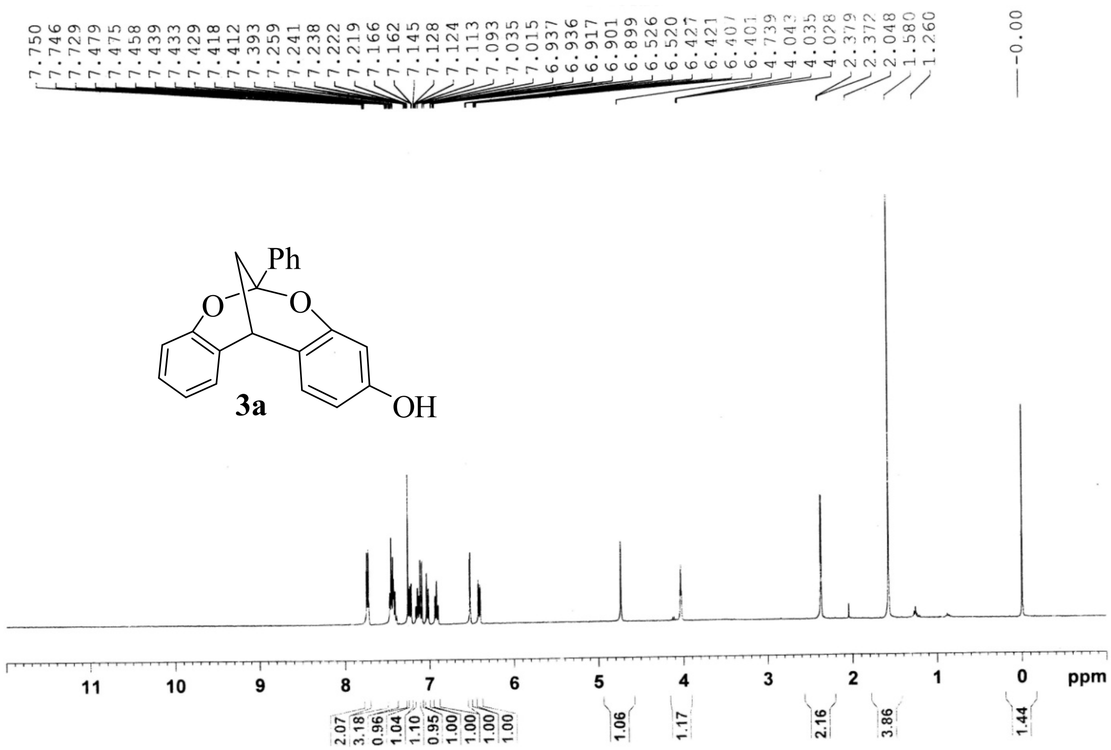
VII. Claisen rearrangement of 6

Compound **6** (100 mg, 0.173 mmol) was added to 1,2-dichlorobenzene (2 mL) and heated to reflux for 16 h (TLC monitoring). The reaction mixture was cooled and directly subjected to column chromatography over silica gel (60-120 mesh) using *n*-hexane-ethyl acetate (9:1) as eluent to afford **7** which was recrystallized from EtOAc-*n*-hexane mixture to give a white crystalline solid (85 mg, 85%), m.p. 216-218 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.86 (m, 2H), 7.67-7.65 (m, 2H), 7.59-7.50 (m, 3H), 7.47-7.40 (m, 4H), 7.32-7.30 (m, 1H), 7.22-7.18 (m, 2H), 7.13 (d, *J* = 8 Hz, 1H), 7.06 (d, *J* = 8 Hz, 1H), 6.98-6.92 (m, 2H), 6.04-5.94 (m, 1H), 5.47 (s, 1H, O**H**), 5.31 (d, *J* = 17.2 Hz, 1H), 5.23 (d, *J* = 10 Hz, 1H), 4.49 (s, 1H, H-9/H-9$^{/}$), 4.49 (s, 1H, H-9$^{/}$/H-9), 3.64 (dd, *J* = 16.4, 5.6 Hz, 1H), 3.49 (dd, *J* = 16.4, 6.4 Hz, 1H, H-17/H-17$^{/}$), 2.44 (dd, *J* = 13.2, 3.2 Hz, 1H, H-17/H-17$^{/}$), 2.27 (dd, *J* = 13.6, 2.8 Hz, 1H, H-17$^{/}$/H-17), 2.21 (dd, *J* = 13.2, 2.8 Hz, 1H, H-17$^{/}$/H-17), 2.16 (dd, *J* = 13.2, 3.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 152.1, 151.0, 148.3, 147.6, 141.7, 141.4, 136.8, 129.0, 128.7, 128.3 (2C), 127.8, 127.7 (2 C), 127.4, 127.0, 126.1, 125.7, 121.3, 120.9, 116.9, 116.3 (2 C), 107.5, 106.8, 105.0, 99.0 (C-1/C-1$^{/}$), 98.8 (C-1$^{/}$/C-1), 33.4 (C-17/C-17$^{/}$), 32.9 (C-17$^{/}$/C-17), 28.1, 26.8 (2 C) (C-9

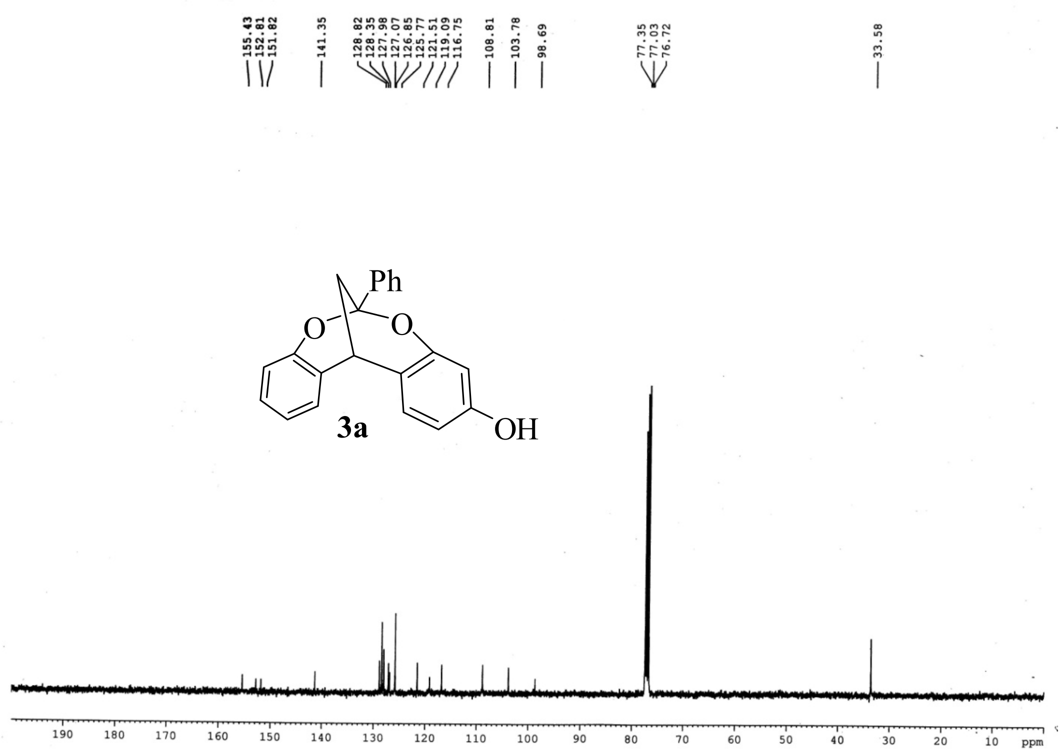
&-9$^{/}$) ppm; IR (KBr): 3492 (OH), 2940, 1618, 1459, 1232, 1103, 757 cm^{-1}. HRMS (ESI) m/z: Calcd. for $C_{39}H_{31}O_5$ [M+H]: 579.2171. Found: 579.2530.

VIII. NMR spectra copies:

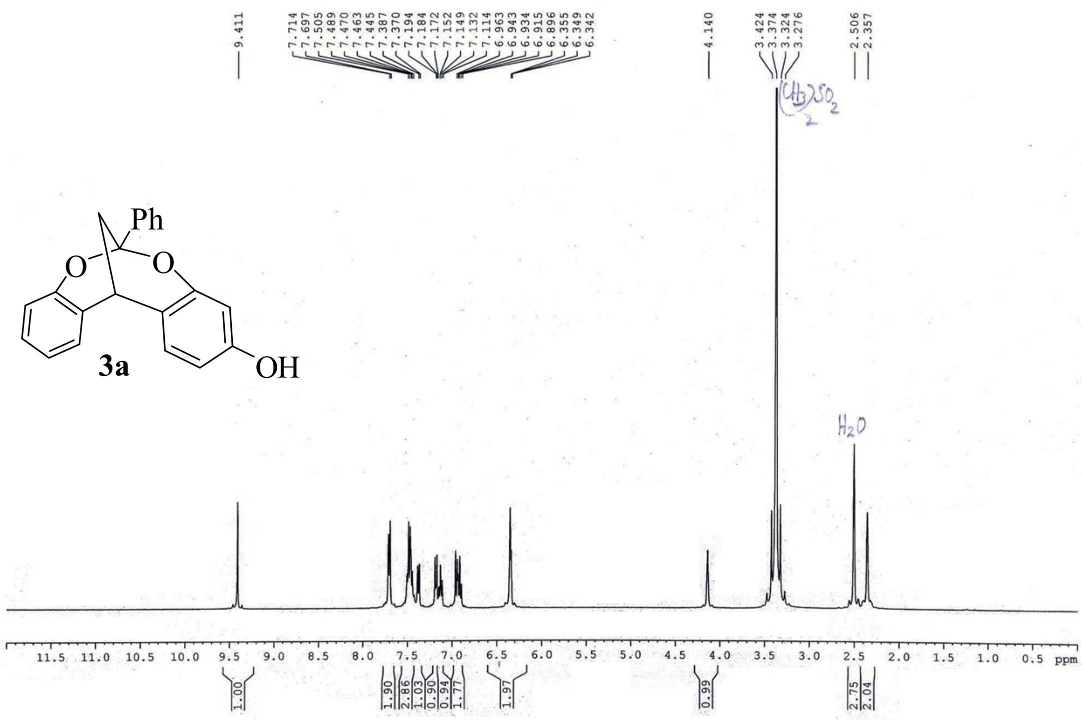
^{1}H-NMR of 3a in CDCl$_3$



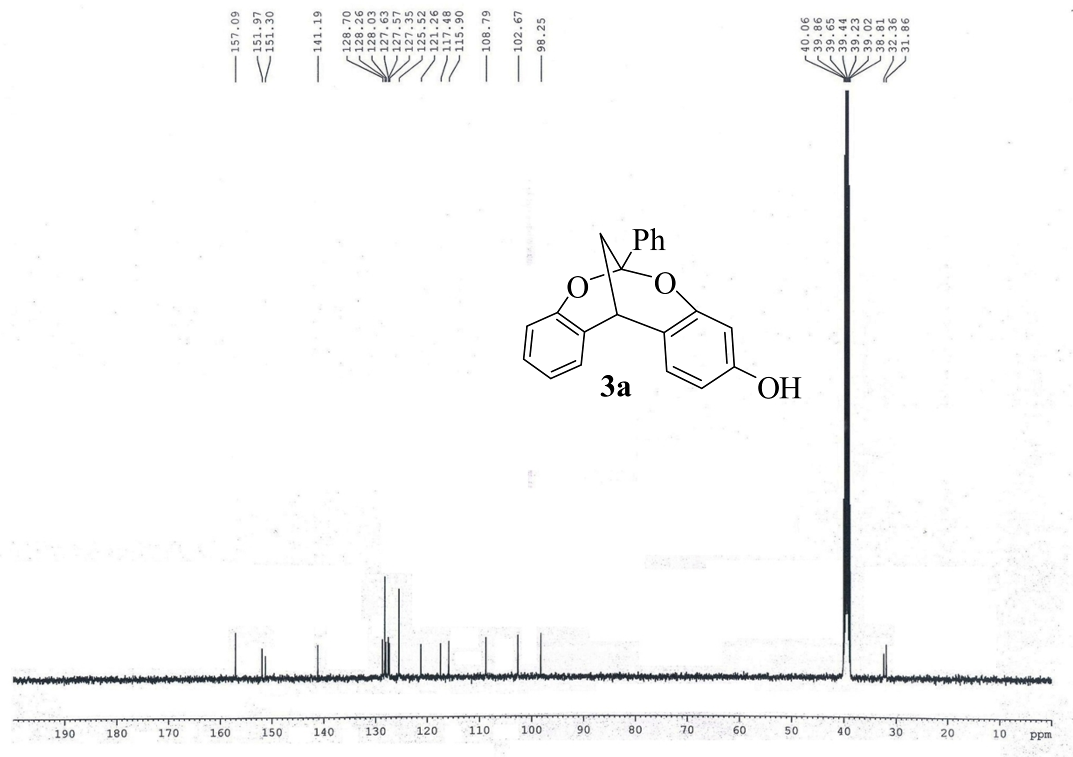
^{13}C-NMR of 3a in CDCl$_3$



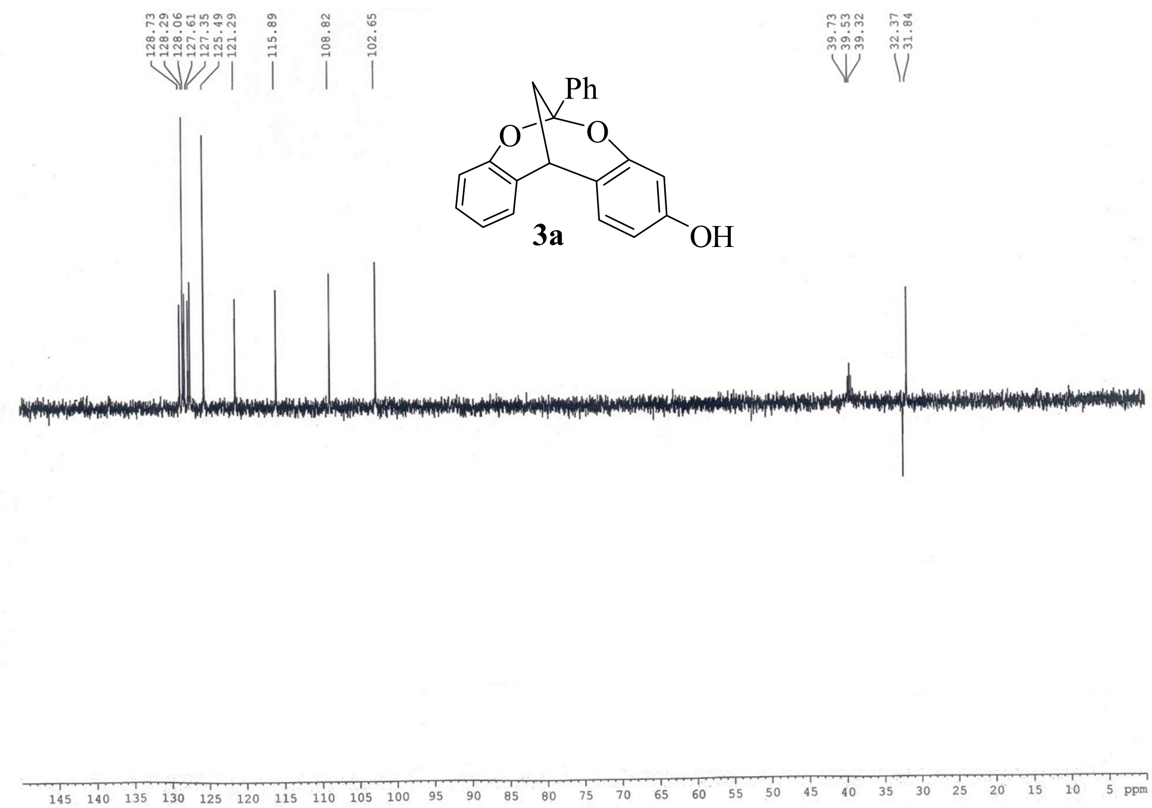
[1]H-NMR of 3a in DMSO-d_6



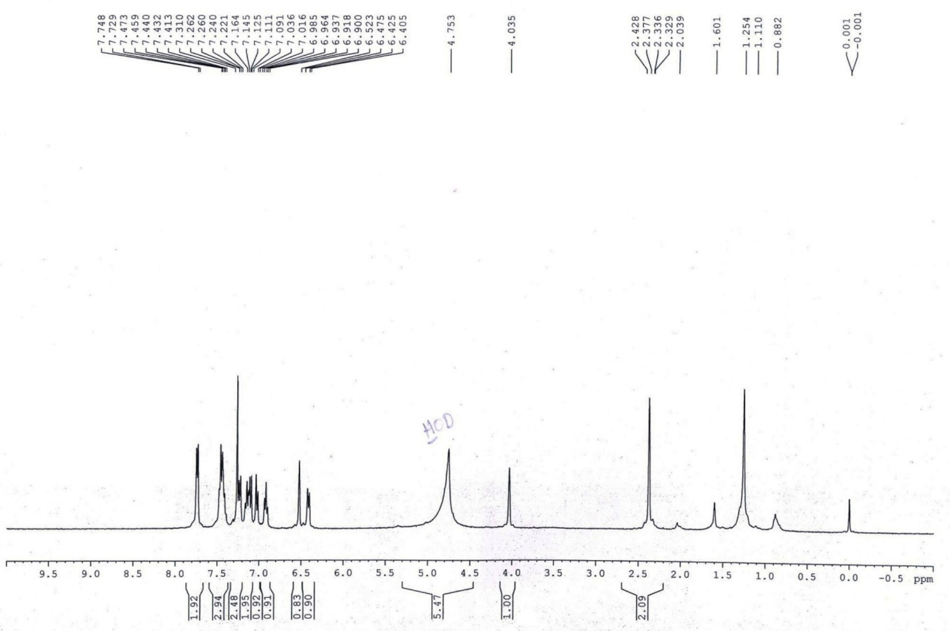
[13]C-NMR of 3a in DMSO-d_6



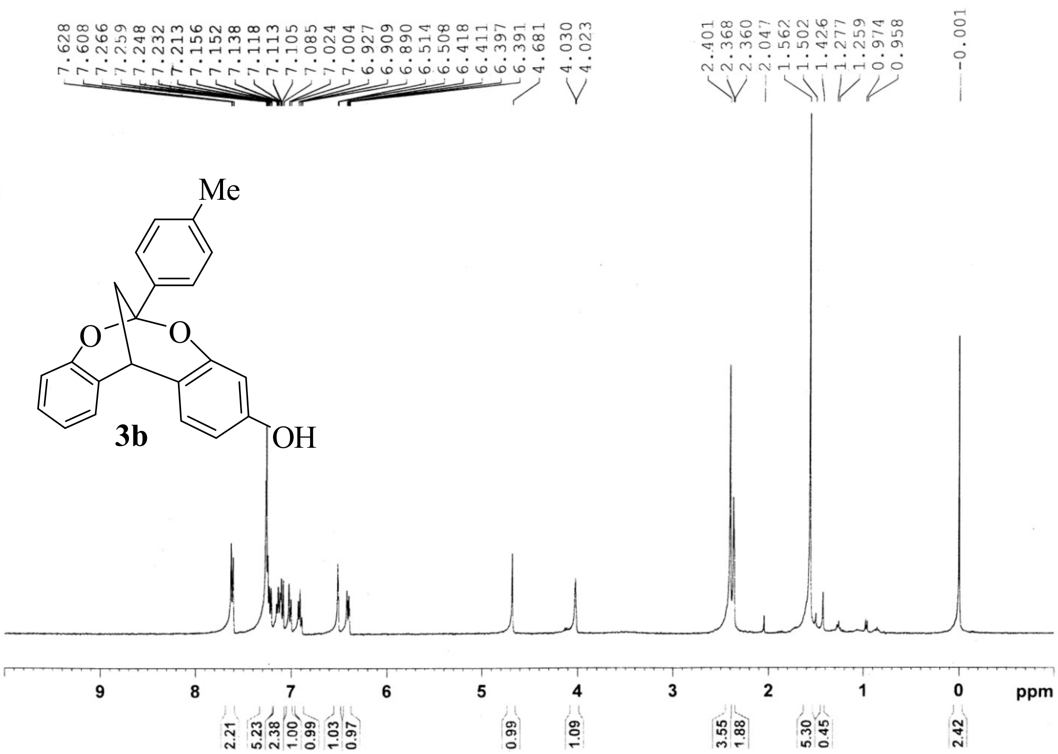
^{13}C DEPT NMR of 3a in DMSO-d_6



^{1}H-NMR of 3a after D_2O exchange in $CDCl_3$



[1]H-NMR of 3b



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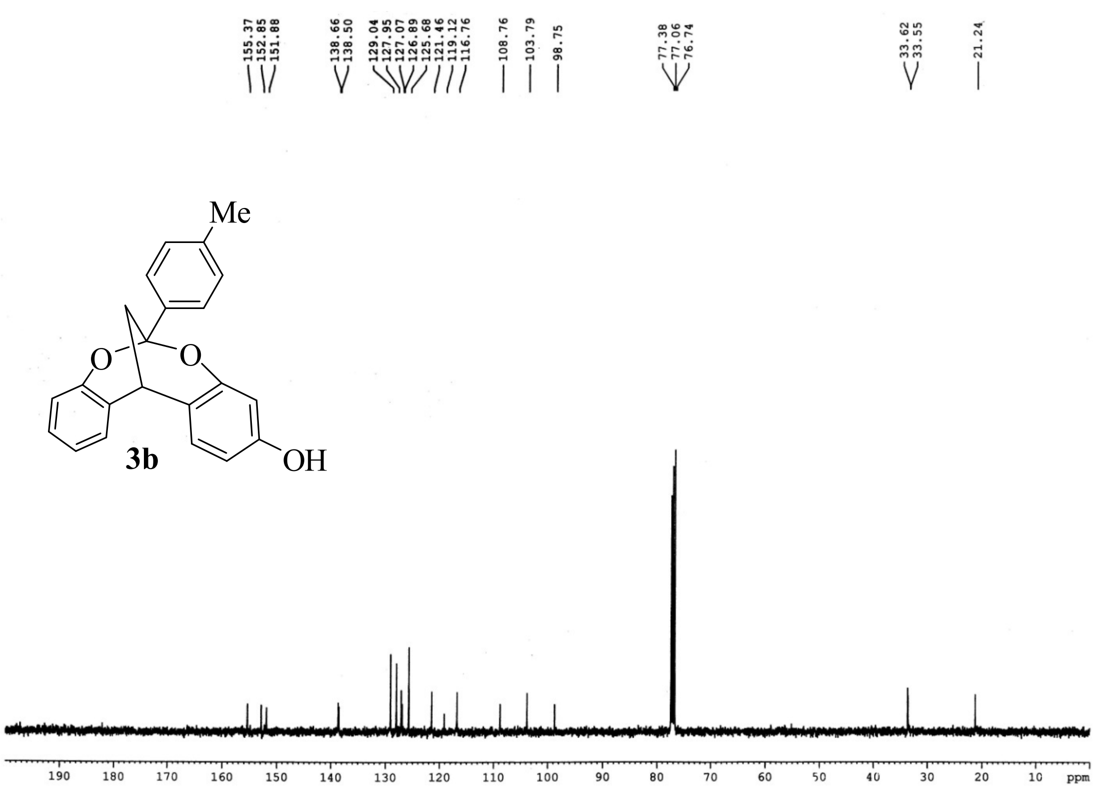
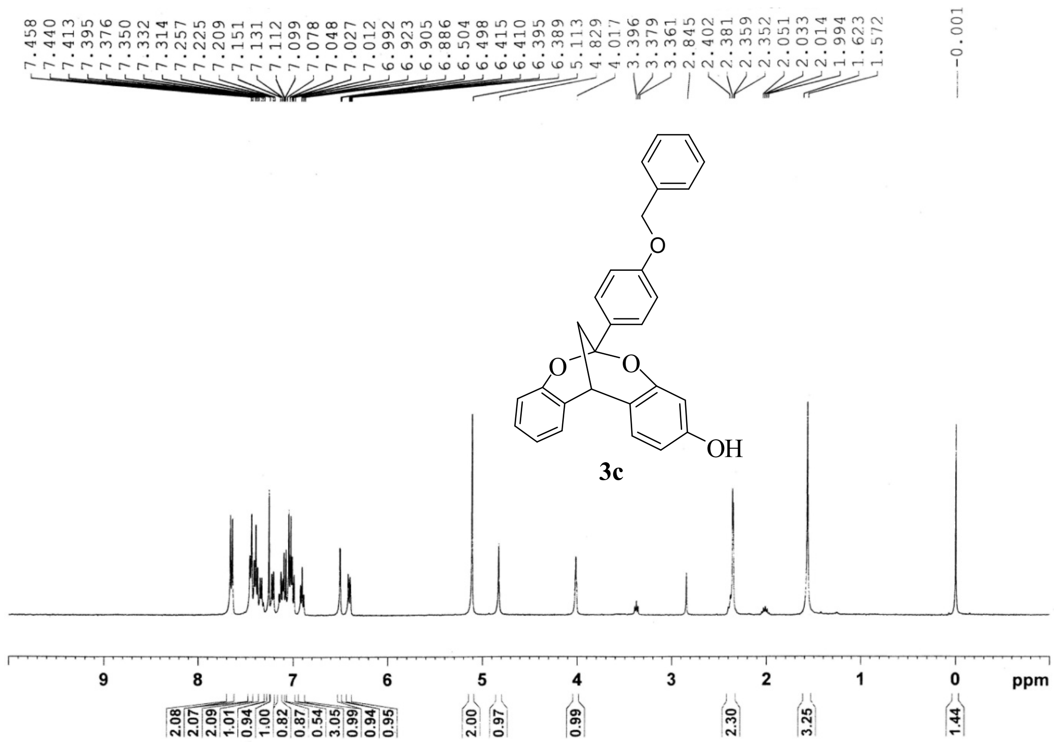


^{1}H-NMR of 3c



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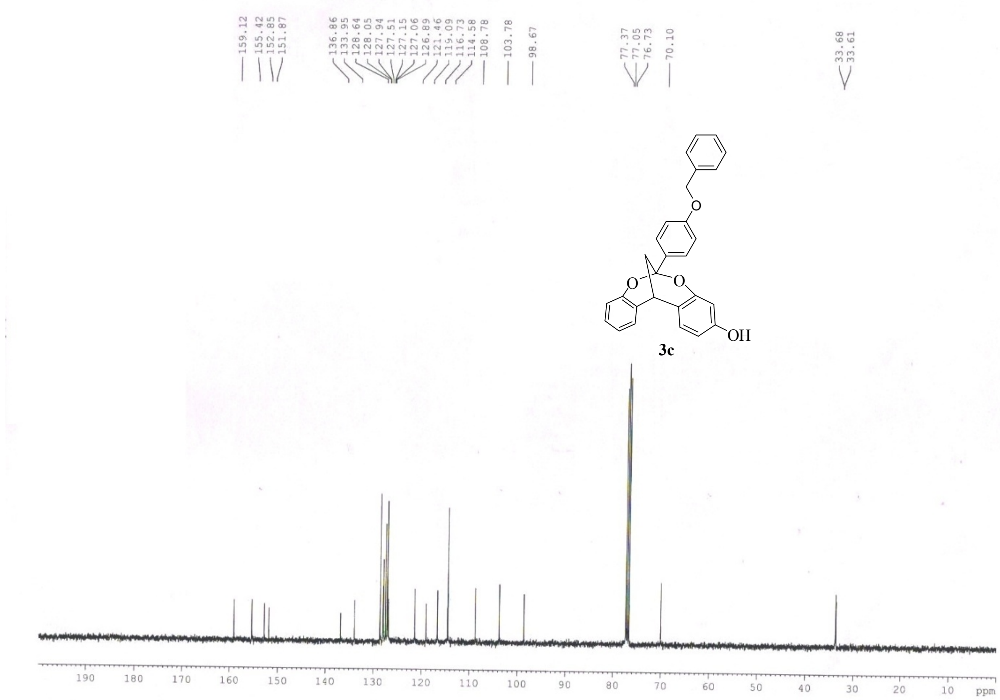

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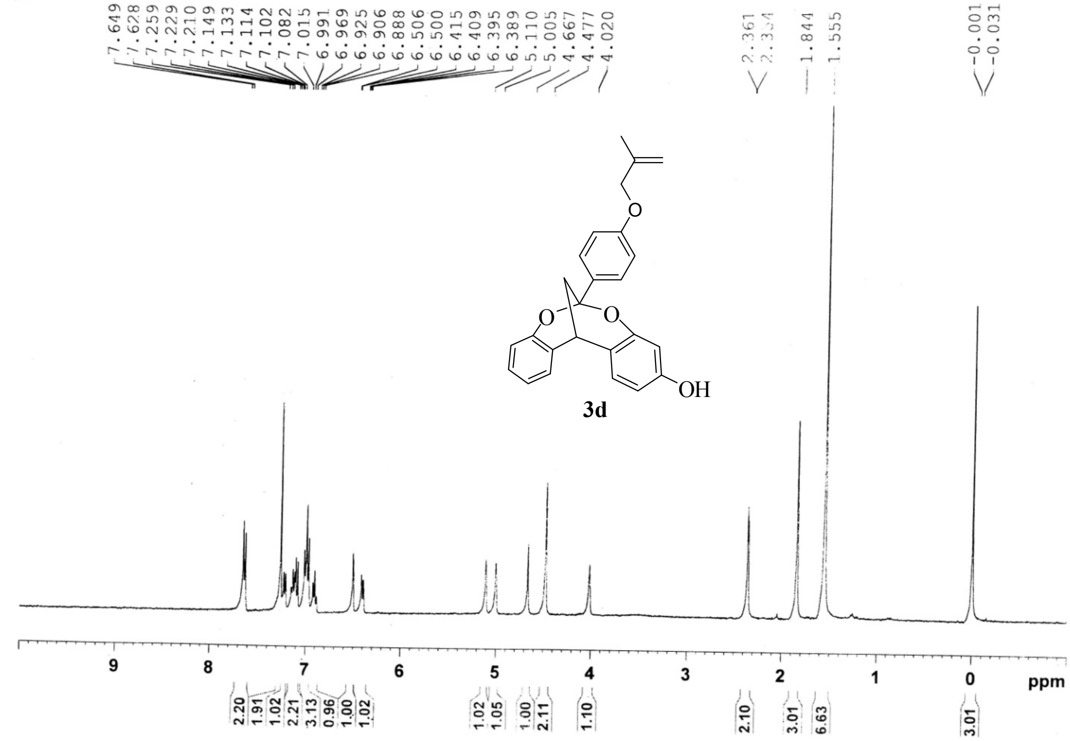

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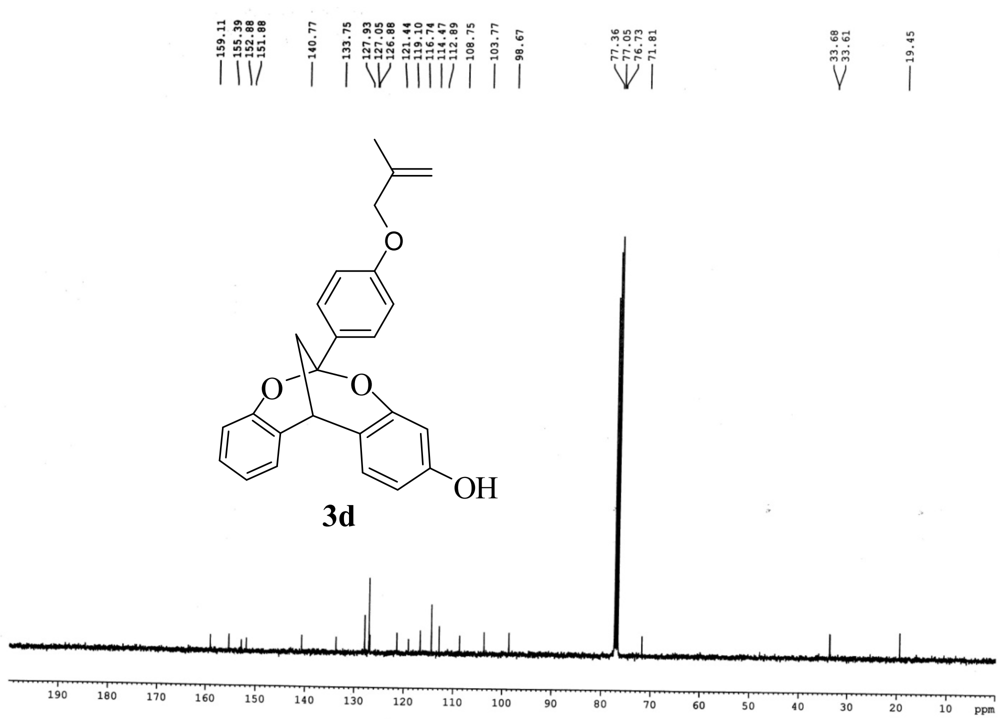

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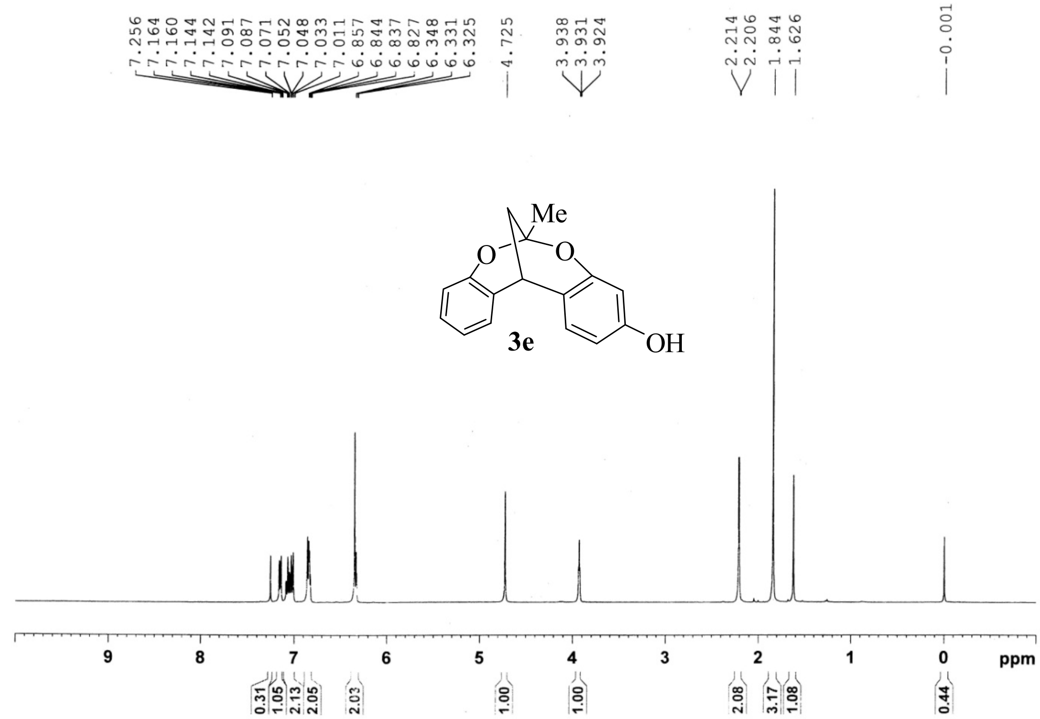
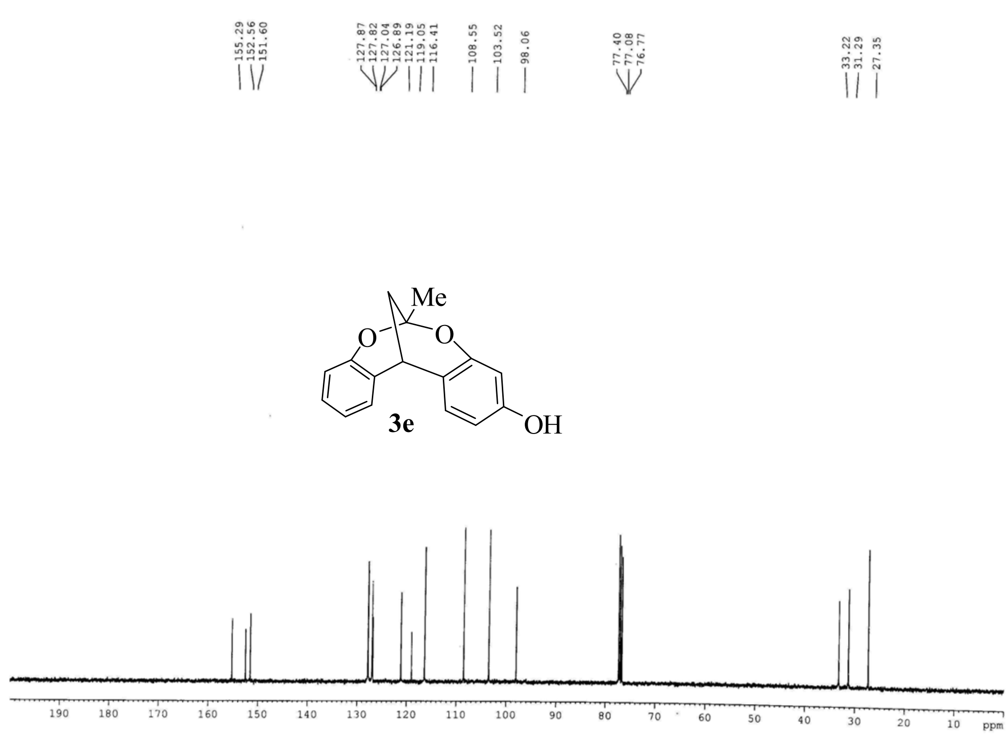
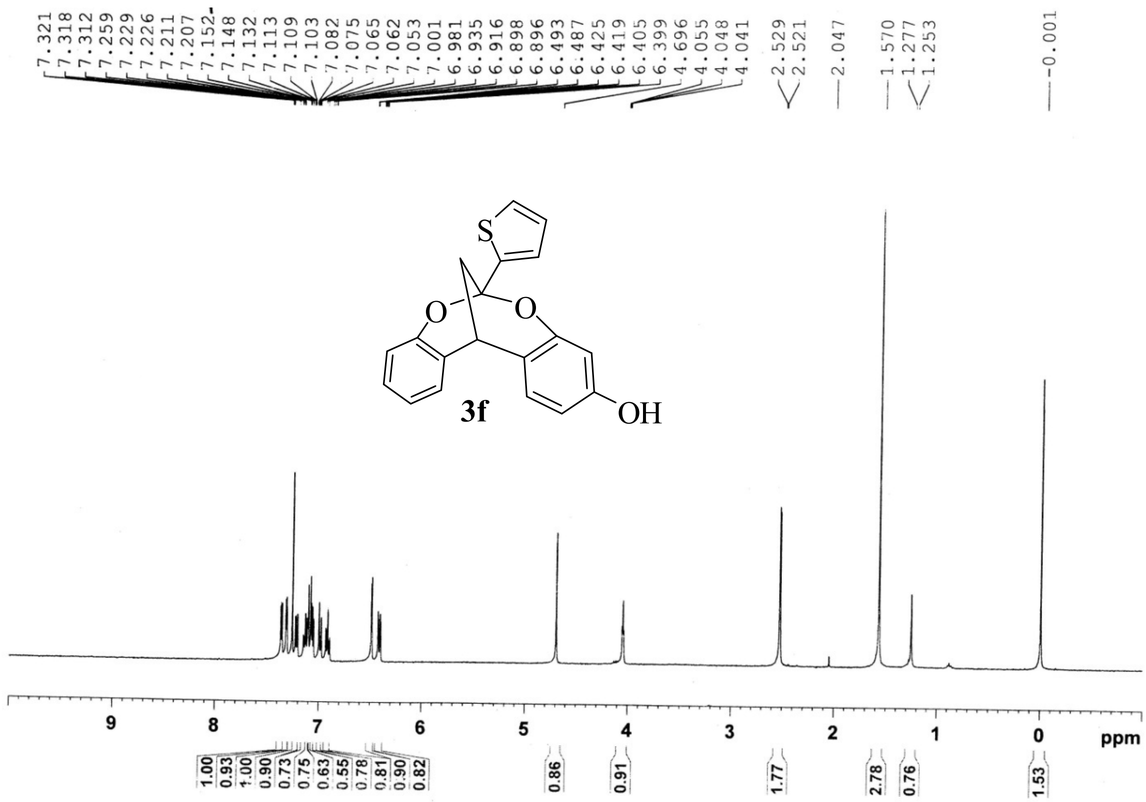


^{13}C-NMR of 3e



[1]H-NMR of 3f



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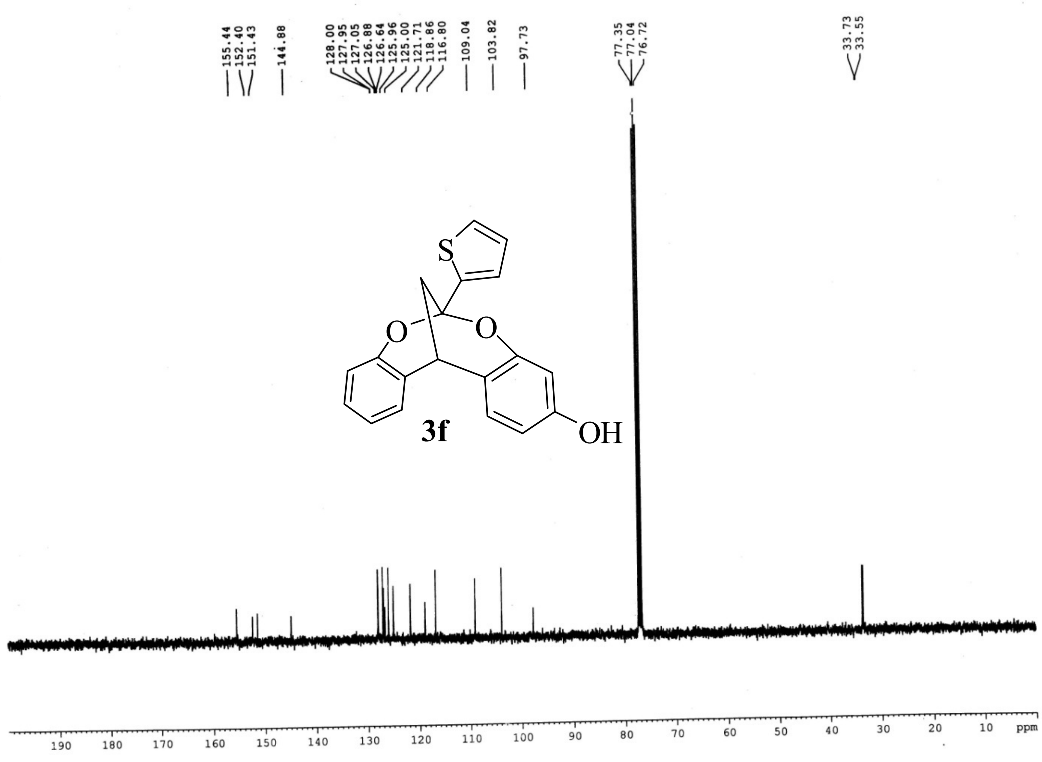
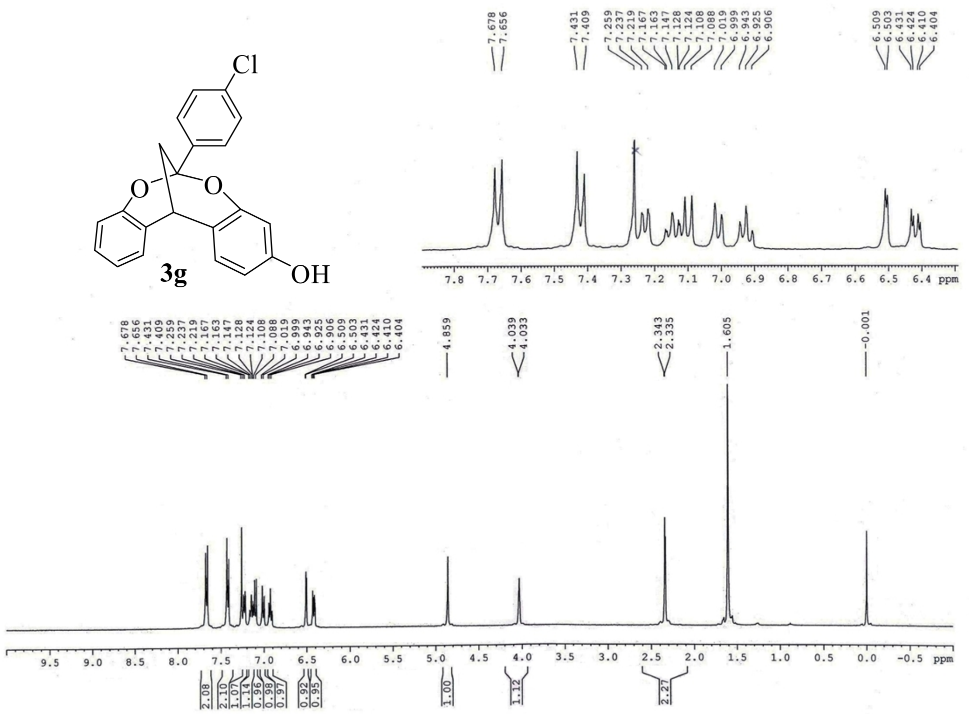
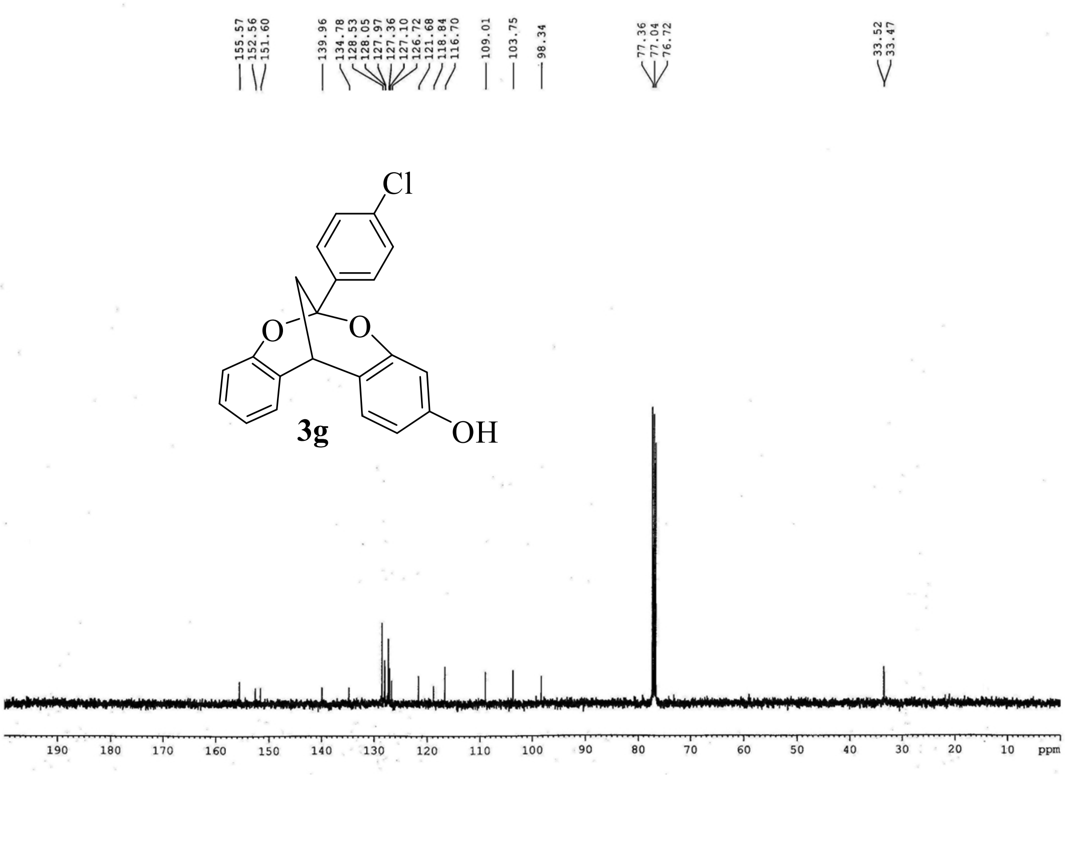


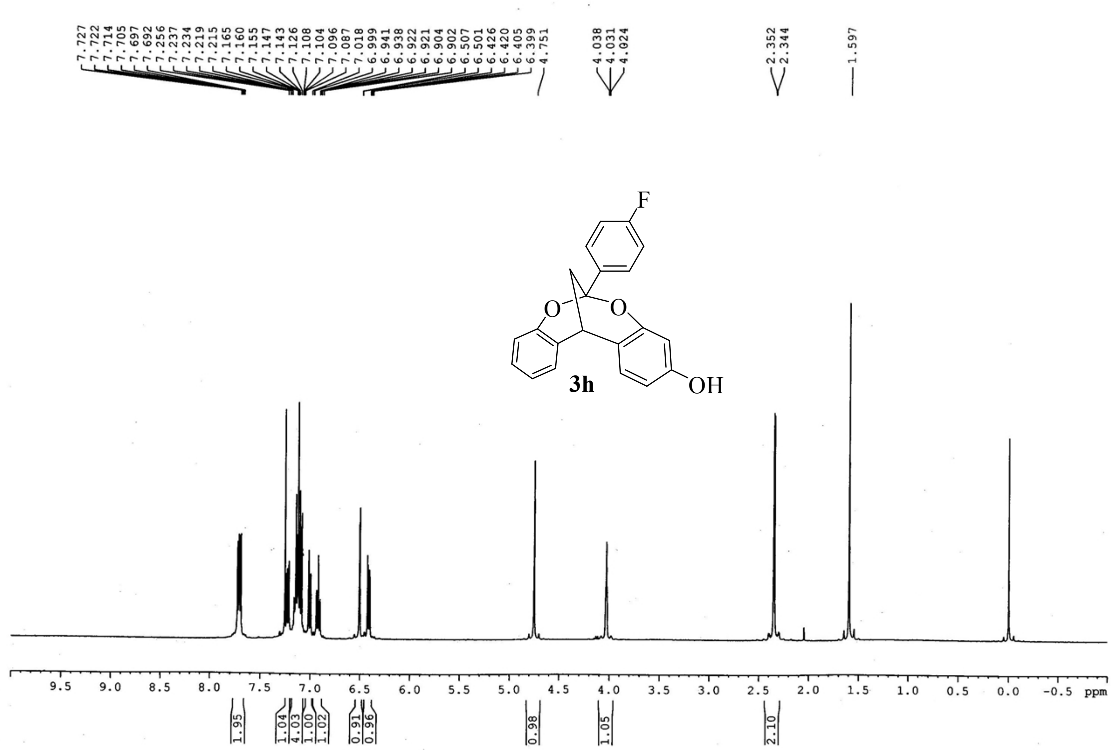
[1]H-NMR of 3g



[13]C-NMR of 3g



[1]H-NMR of 3h



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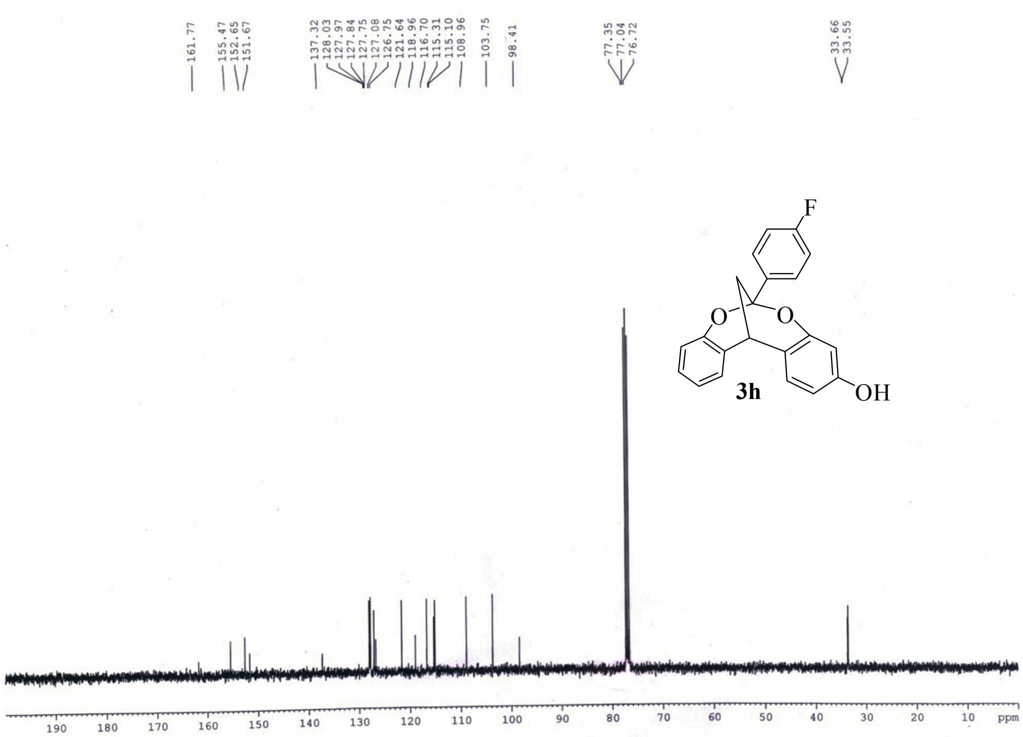
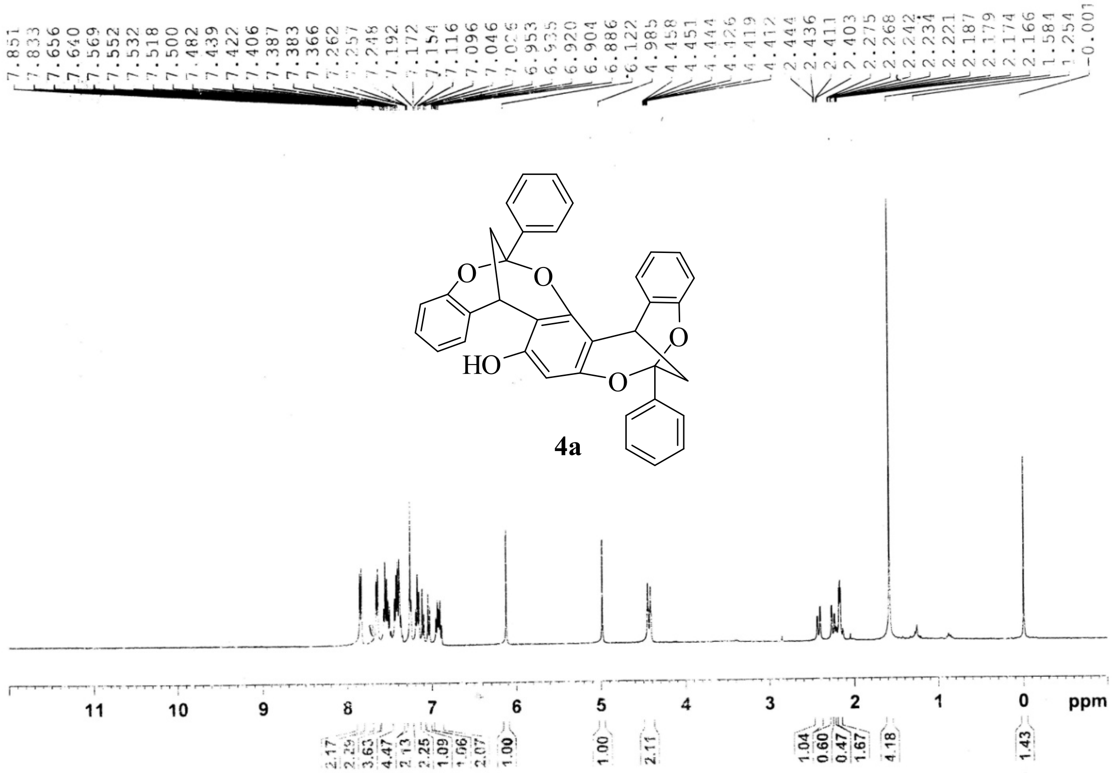


[1]H-NMR of 4a



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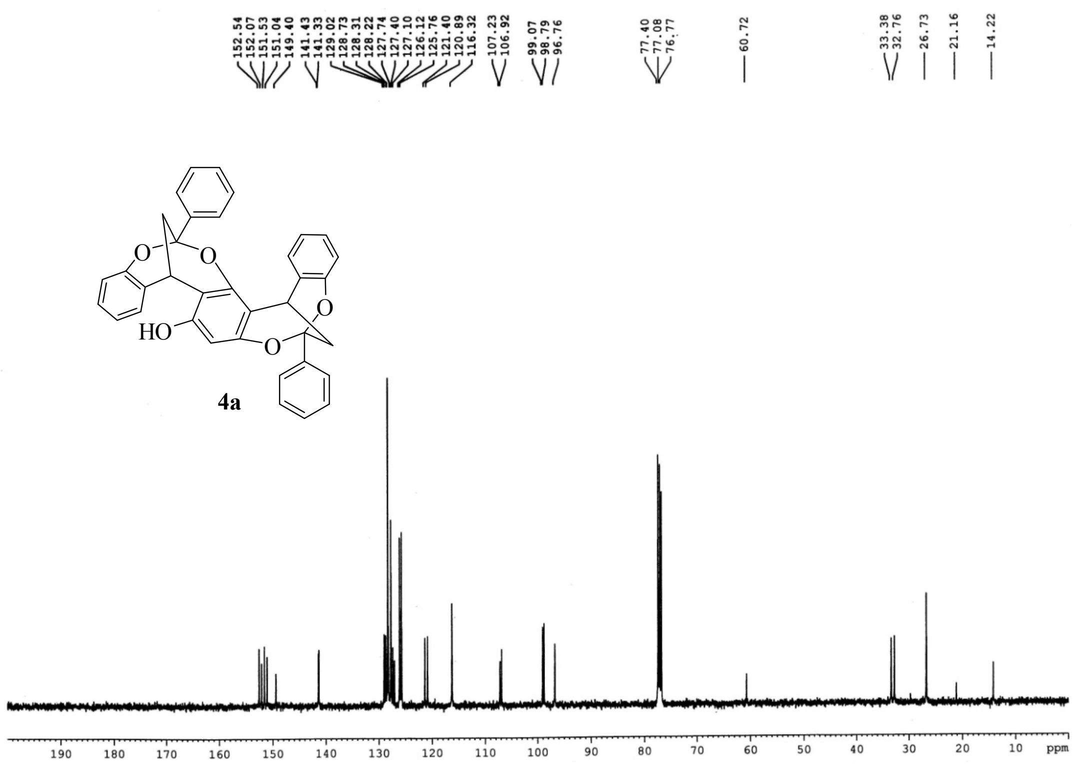
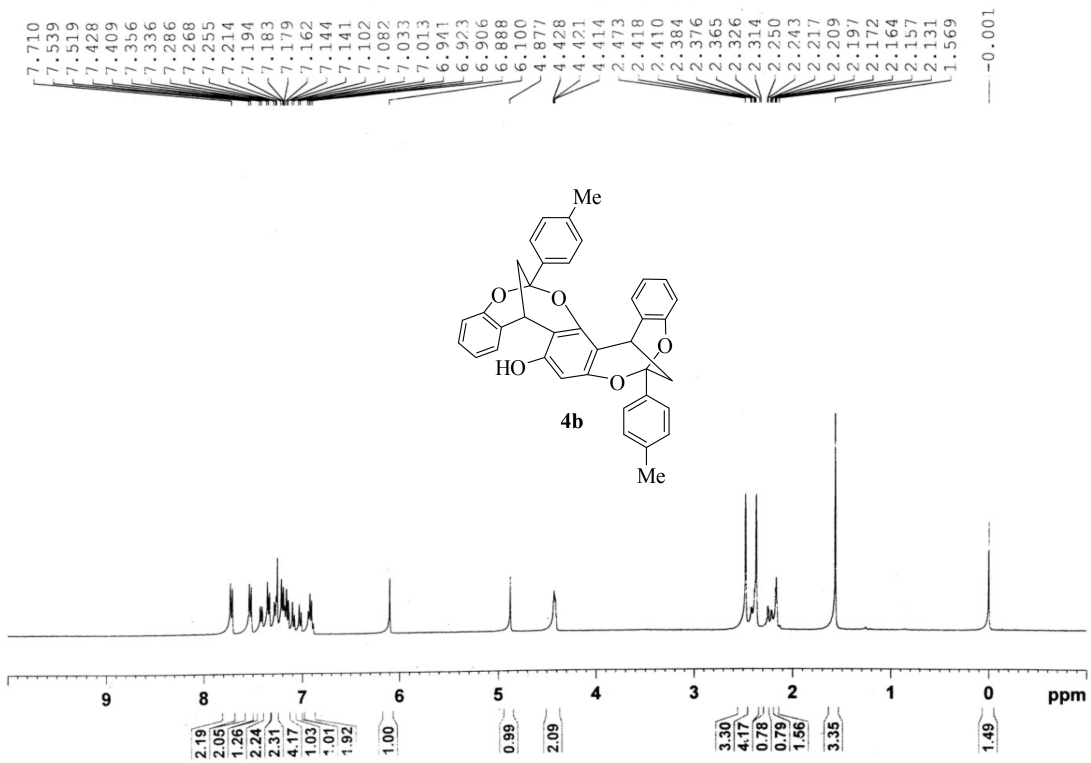


^{1}H-NMR of 4b



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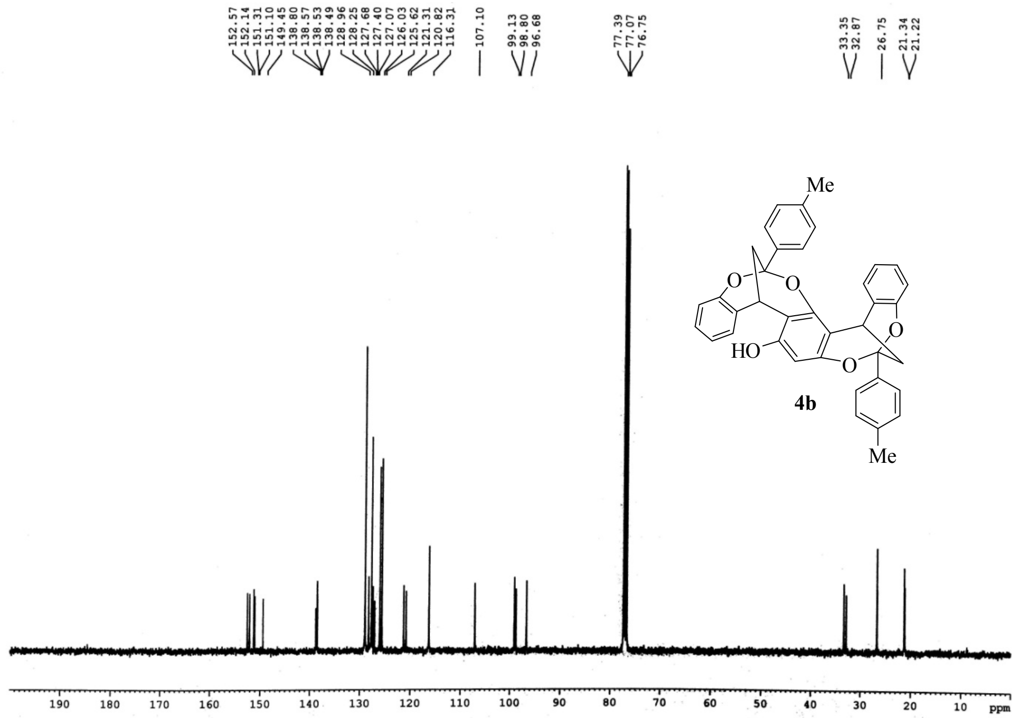

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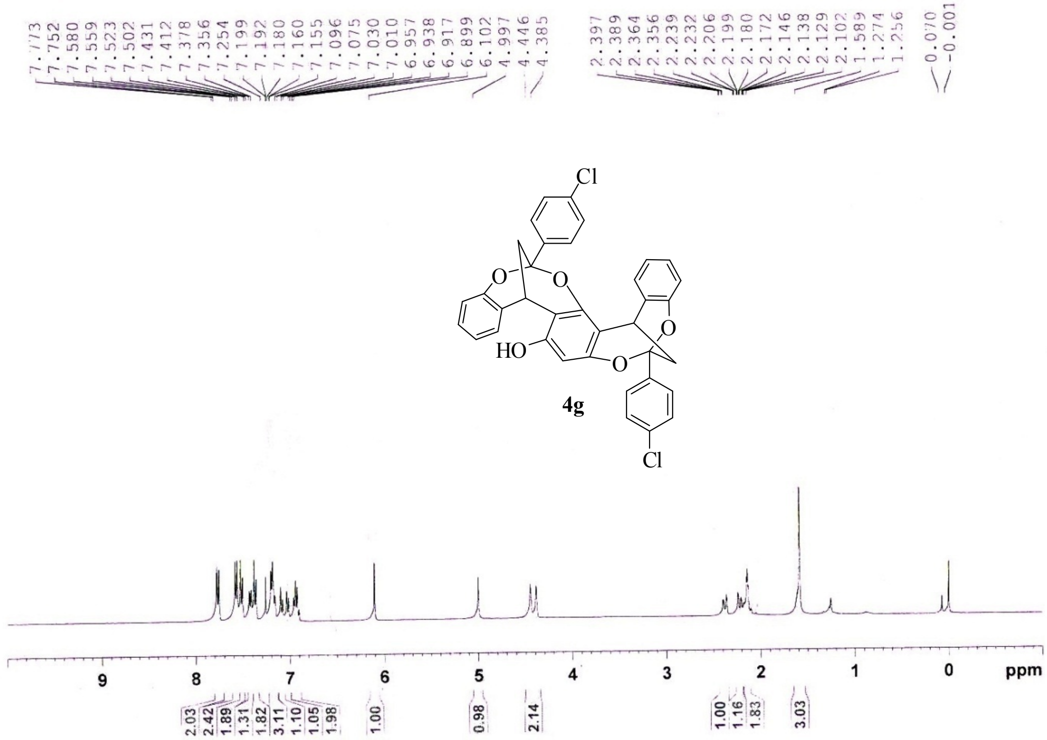

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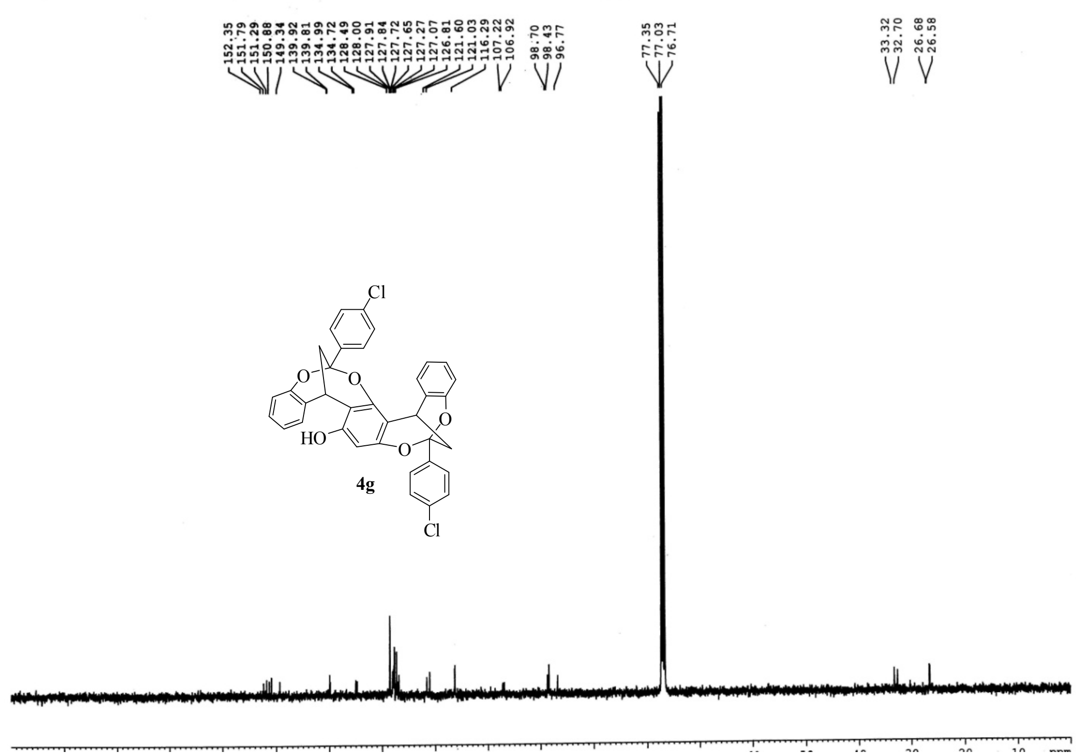
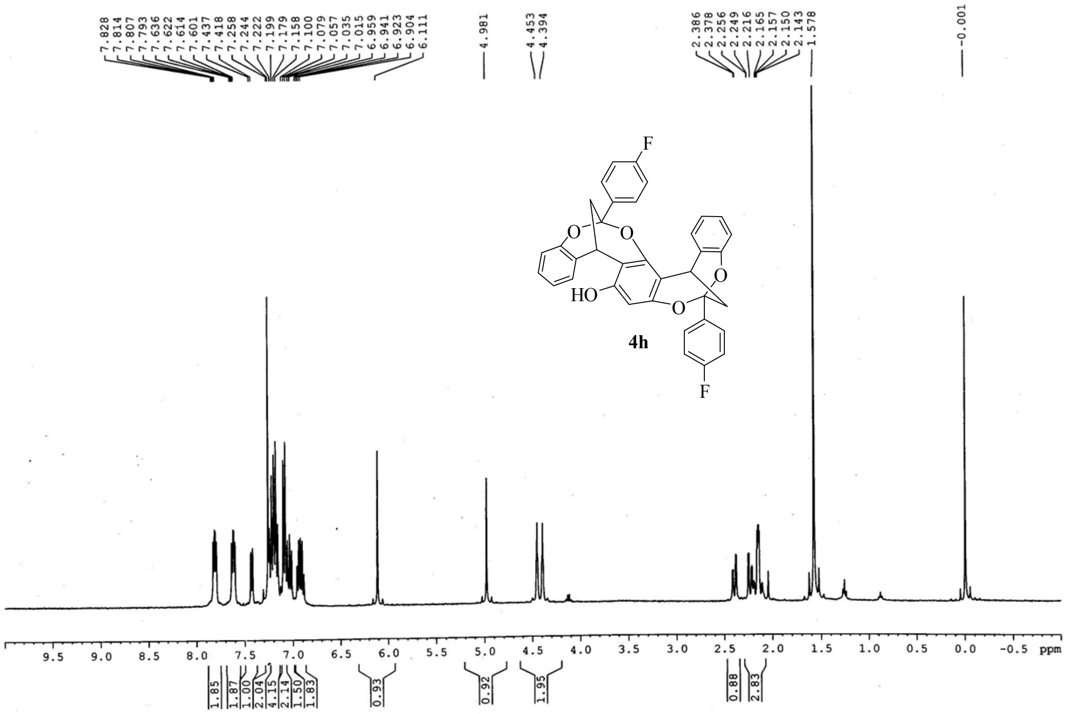


^{1}H-NMR of 4h



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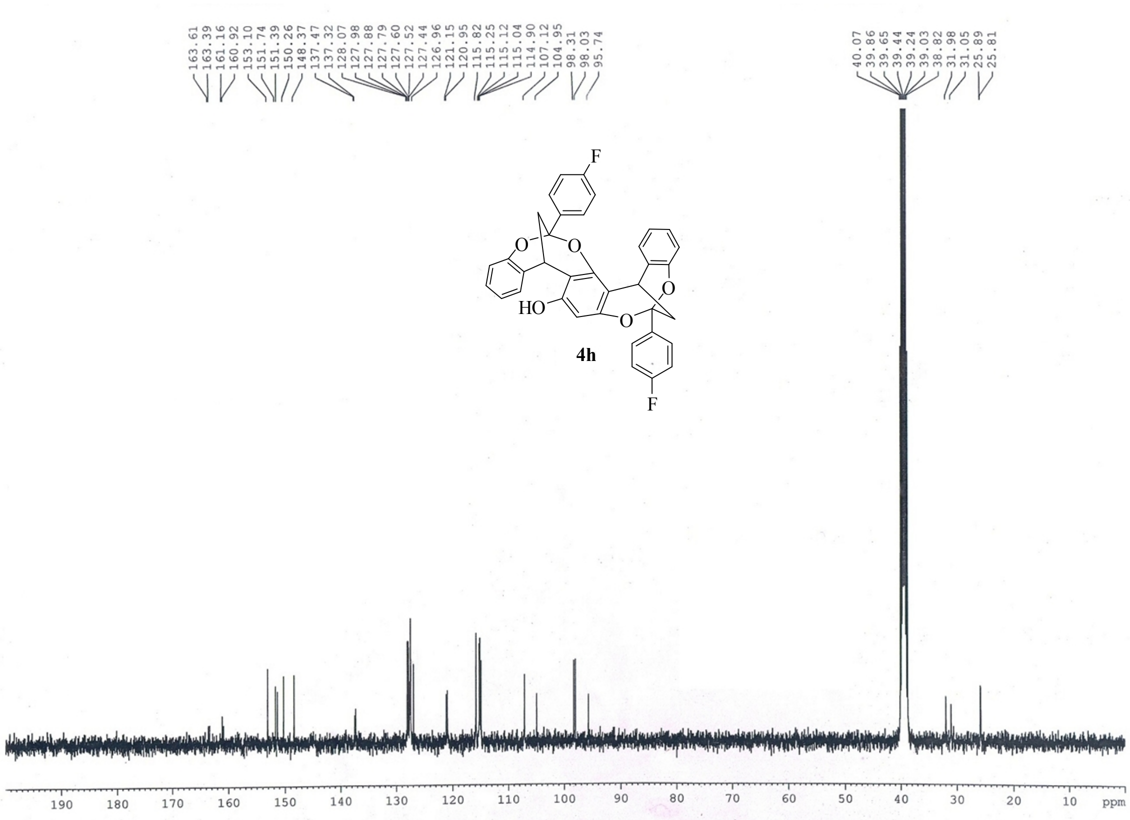
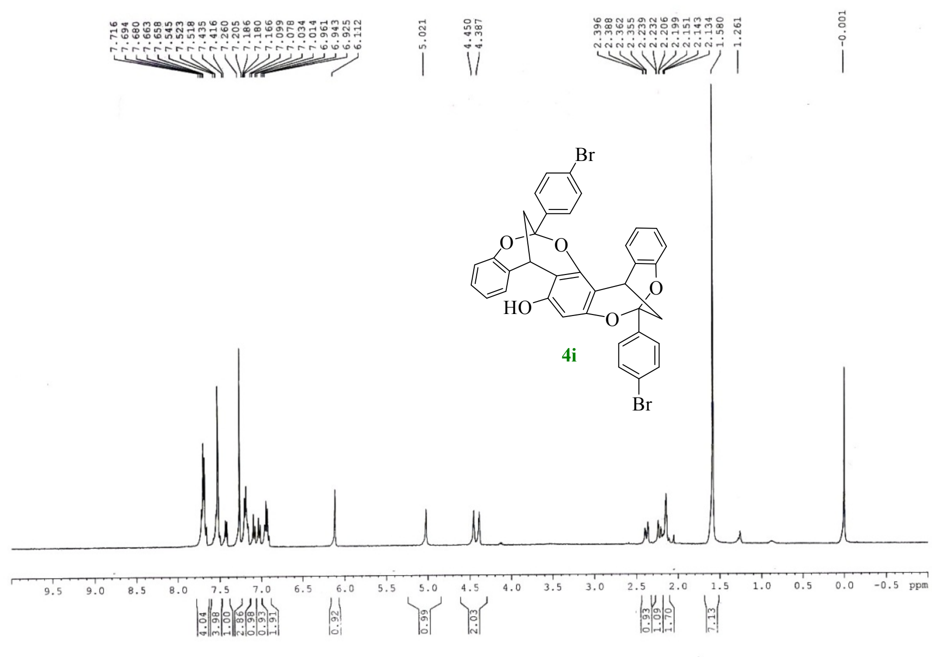


[1]H-NMR of 4i



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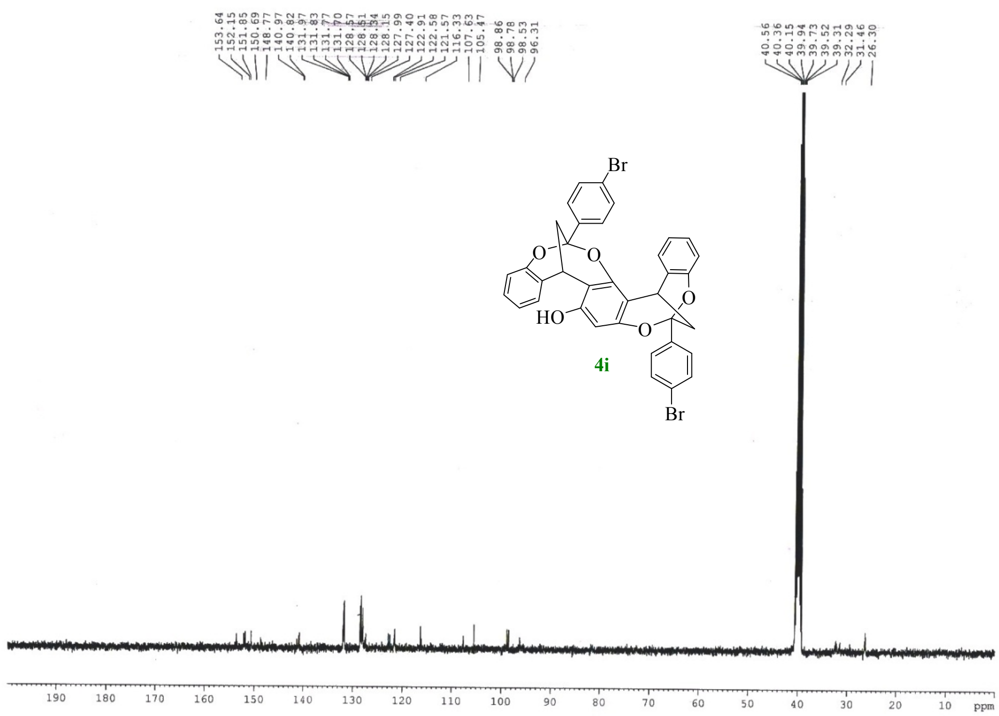

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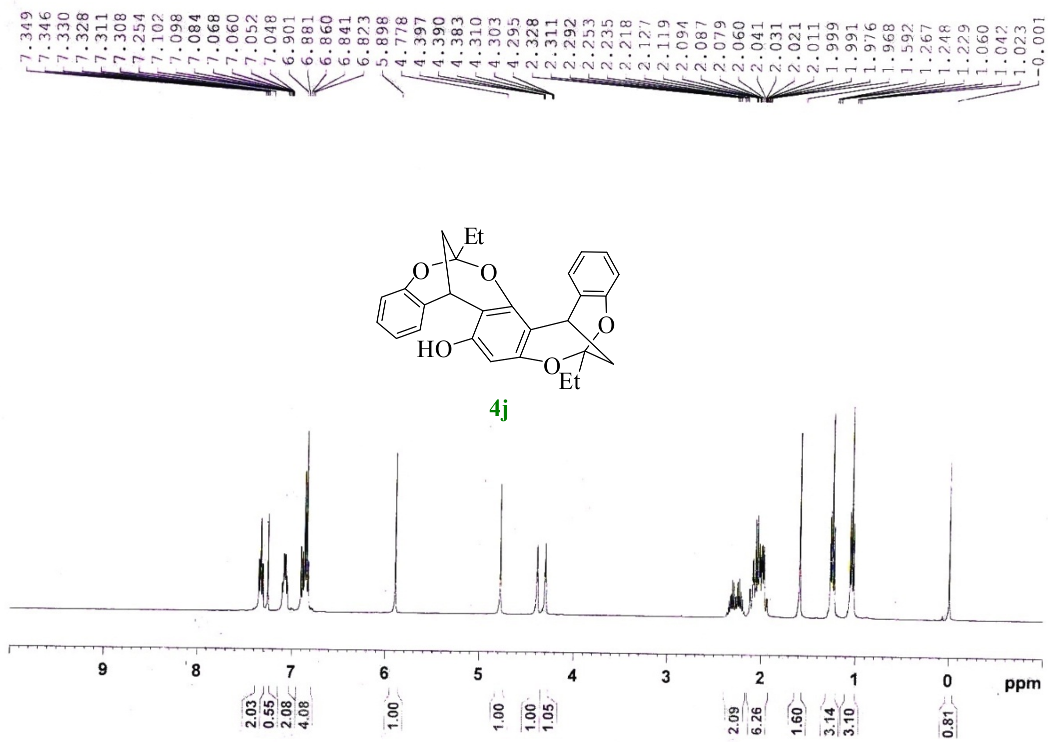

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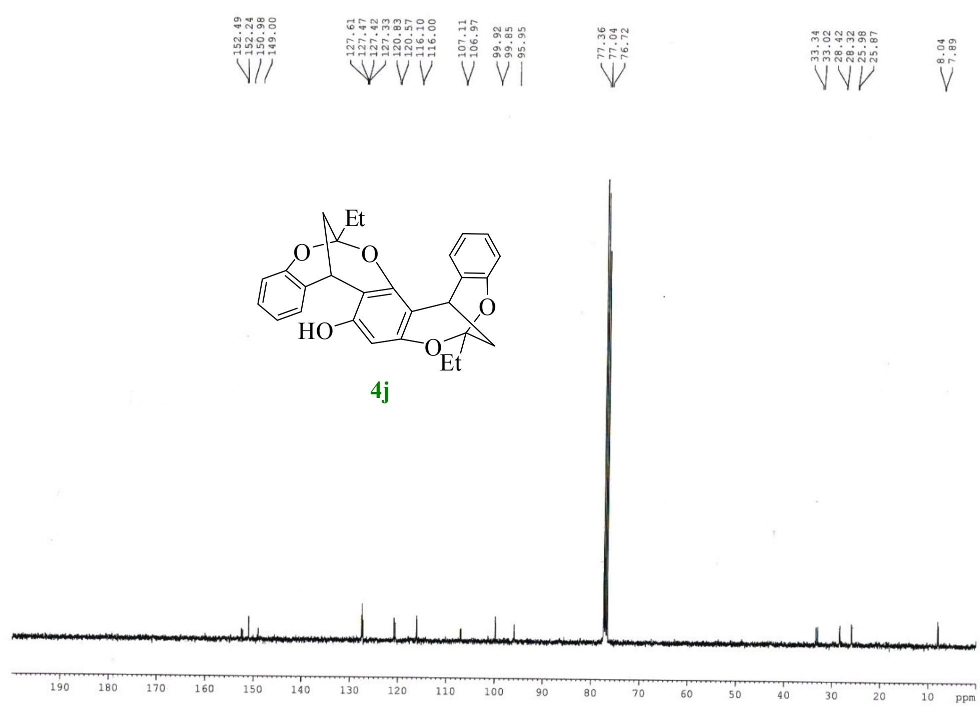
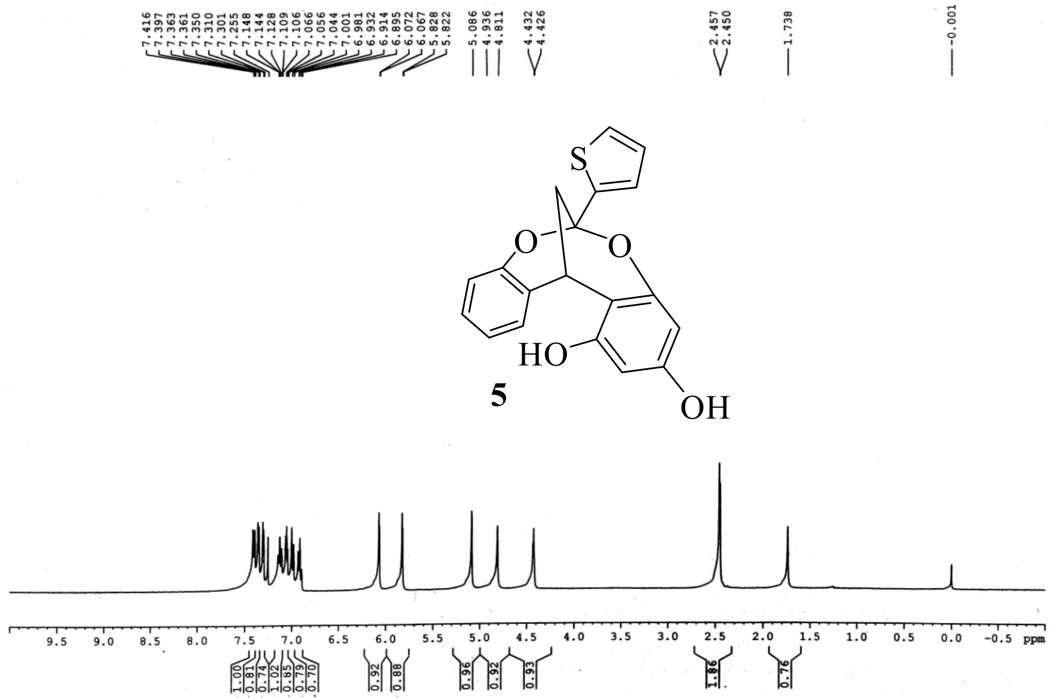


[1]H-NMR of 5



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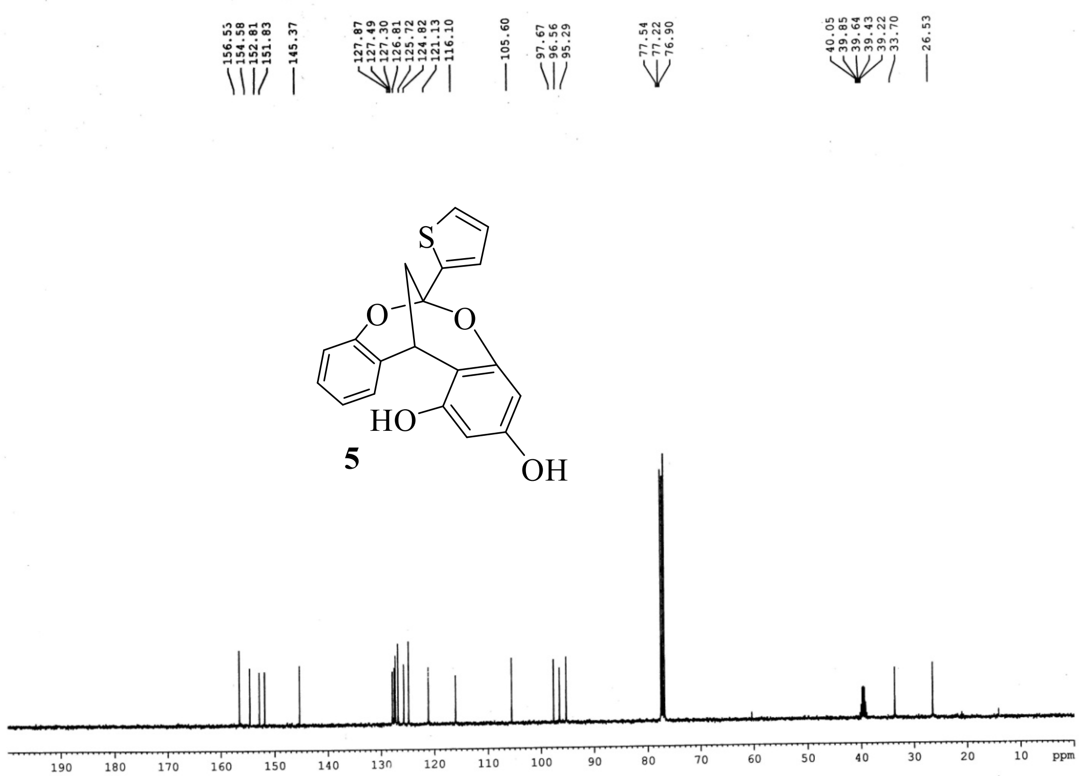
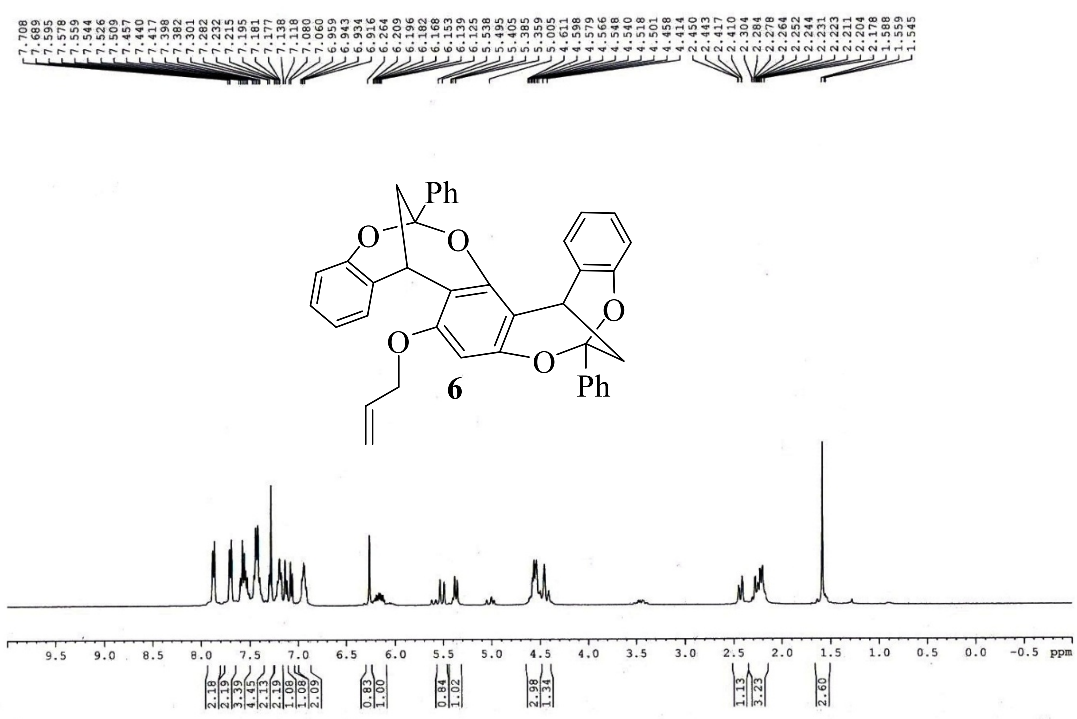


[1]H-NMR of 6



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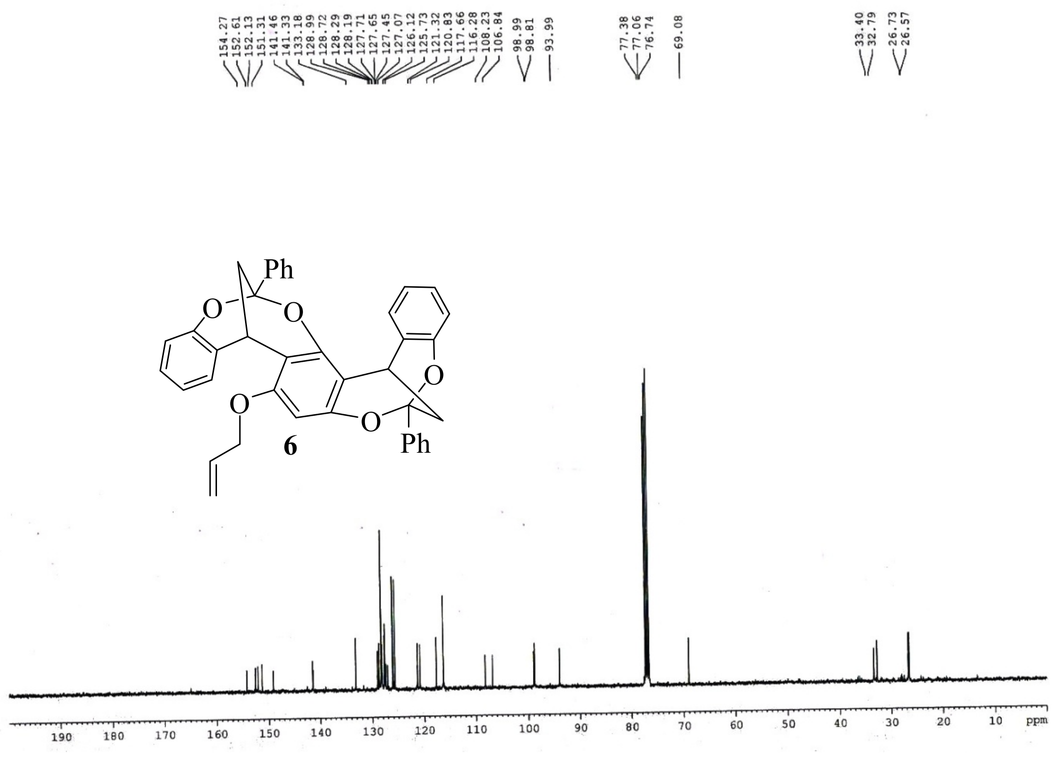
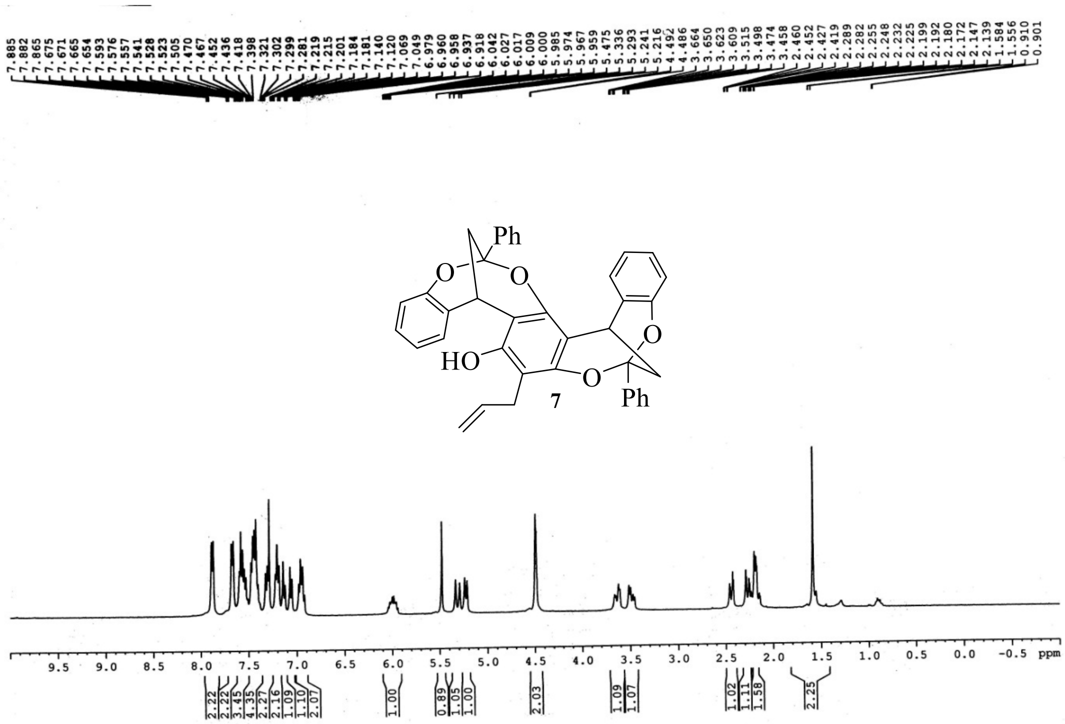
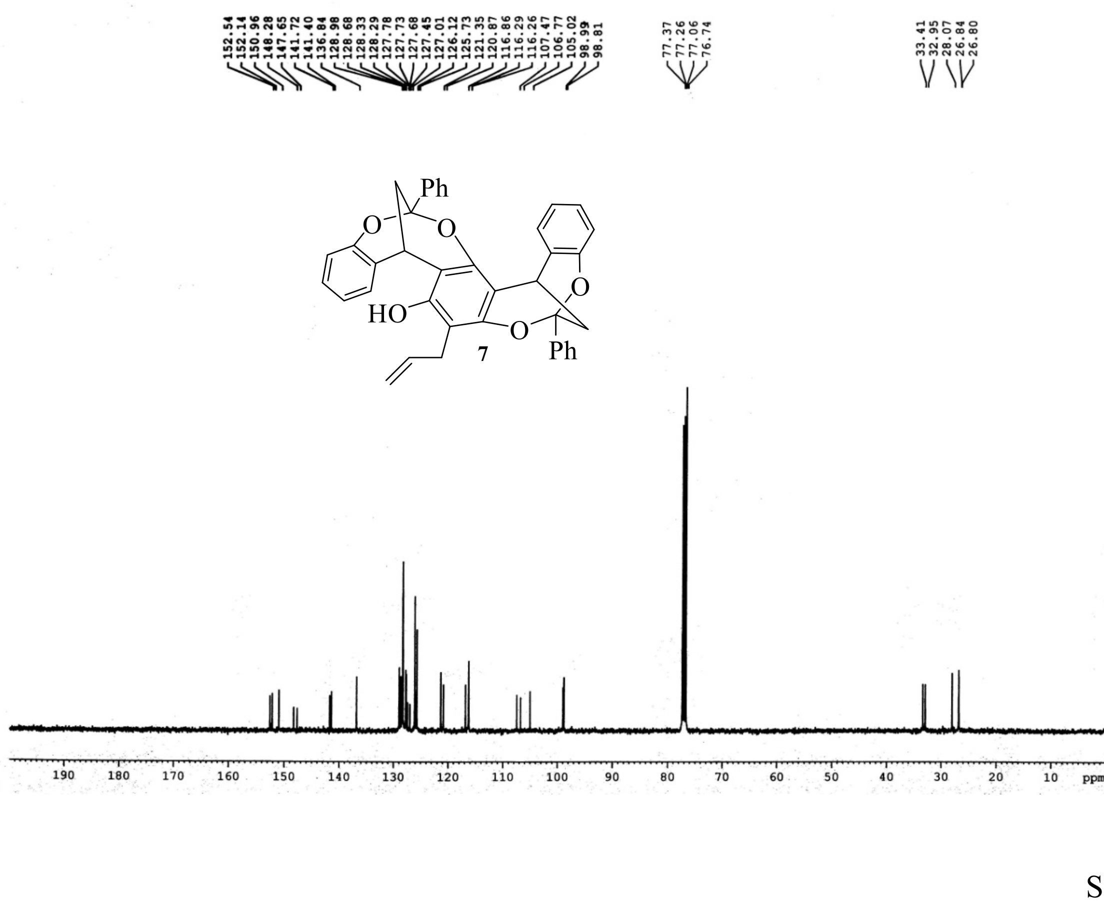


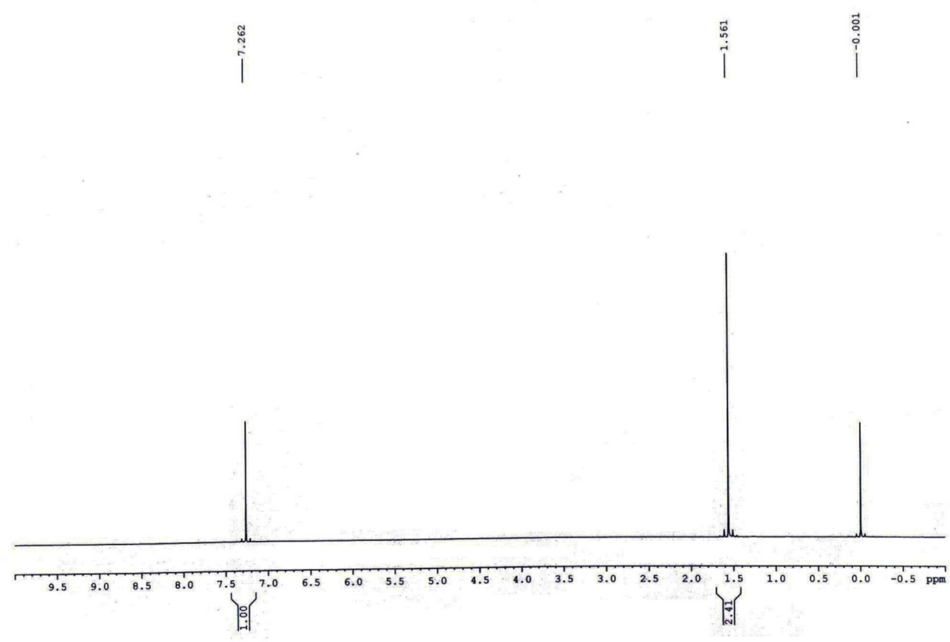
[1]H-NMR of 7



[13]C-NMR of 7



^{1}H-NMR of $CDCl_3$



IX. AM1 optimized structures of 4a and 4a$^{/}$ and 4a$^{//}$

X. References:

1 H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512-7515**.**