Supplementary Material (ESI) for Chemical Communications


**Supporting Information for**

# Mechanistic evidence for the remote π-aryl participation in acid-catalyzed ring opening of homobenzoquinone epoxides

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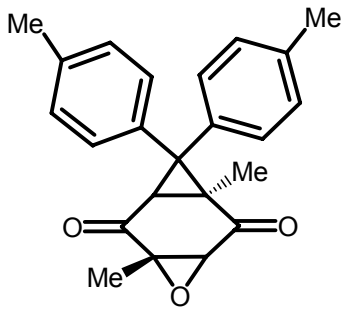
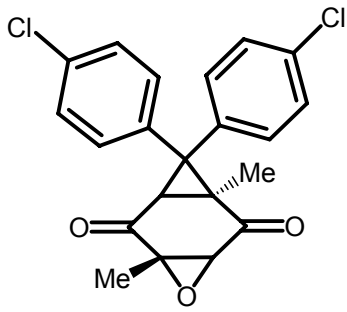
**General procedures for the synthesis of homobenzoquinone epoxides.** To a mixture of homobenzoquinone (0.5 mmol) and 30% $H_2O_2$ (0.75 mmol) in DMSO (1 mL) was added dropwisely (10 min) a solution of $Bu_4NF$ (1M solution in THF, 0.5 mmol) at room temperature. After the addition of the reagent the reaction mixture was stirred for 2h. Then, the epoxide **1** was extracted with ethyl acetate (3 mL × 3). The organic layer was washed with water (3 mL × 3) and dried over magnesium sulfate. The solvent was evaporated *in vacuo*. The epoxide **1** was purified by column chromatography on silica gel (benzene as an eluent) and recrystallization from hexane-ether or hexane-benzene. The structures of all epoxides were deduced from the $^1H$ and $^{13}C$ NMR, and IR spectra.

**General procedures for acid-catalyzed reaction of homobenzoquinone epoxides.** To a $CDCl_3$ solution (650 μl) of **1** (0.02 mmol) in a NMR tube was added the requisite amount of $BF_3{\cdot}OEt_2$ or $MeSO_3H$ at room temperature by using a micro syringe. The progress of reaction was monitored by $^1H$ NMR. After a period of requisit time, the reaction solution was transferred into a separate funnel, diluted with chloroform (10 mL) and then washed with water (3 mL × 3). The aqueous layer was extracted with chloroform (5 mL × 2). The combined organic layer was washed with water (3 mL × 3), then dried over magnesium sulfate. After the evaporation of the solvent *in vacuo*, the residue was submitted for a $^1H$ NMR analysis to determine the product distribution. The column chromatographic treatment of the reaction mixtures on silica gel gave **2c**, **3a-c**, and **4c** with a mixture of hexane-ethyl acetate as an elurnt. These compounds were purified by recrystallization from hexane-ether. The structures of all products were deduced from the $^1H$ and $^{13}C$ NMR, and IR spectra. The structures of **2c** was also confirmed by the X-ray crystallographic analyses.



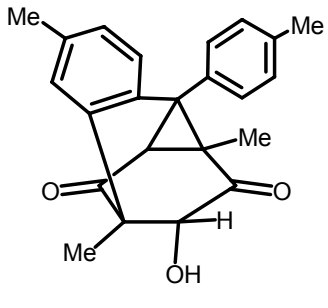

**1a**

**1,3-Dimethyl-8,8-ditolyl-4-oxa-tricyclo[5.1.0.0$^{3,5}$]octane-2,6-dione** (**1a**): **mp** 139.9-140.8 $^{o}$C (from chloroform/*n*-hexane); **$^{1}$H NMR**(270 MHz, $CDCl_3$) δ 0.94 (s, 3H), 1.17 (s, 3H), 2.24 (s, 3H), 2.27 (s, 3H), 2.77 (s, 1H), 2.81 (s, 1H), 7.02-7.14 (m, 6H), 7.22-7.26 (m, 2H); ); **$^{13}$C NMR** (67 MHz, $CDCl_3$) δ 13.8, 16.9, 21.1, 21.1, 37.7, 39.8, 49.3, 60.1, 60.4, 128.0, 129.2, 129.5, 129.7, 135.3, 137.3, 137.3, 137.6, 198. 4, 200.5; **IR** (KBr) : 3390, 3025, 2992, 2979, 2930, 2868, 1915, 1702, 1610, 1513, 1454, 1411, 1381, 1328, 1253, 1226, 1185, 1157, 1121, 1072cm$^{-}$1; **HRMS** : Calculated for $C_{23}H_{22}O_3$, 346.1569, found 346.1572



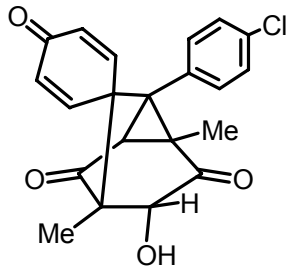

**1c**

**1,5-Dimethyl-8,8-bis(4-chlorophenyl)-4-oxa-tricyclo[5.1.0.0$^{3,5}$]octa ne-2,6-dione** (**1c**): **mp** 142.7-143.5 $^{o}$C (from chloroform/*n*-hexane); **$^{1}$H NMR**(270 MHz, $CDCl_3$) δ 1.01 (s, 3H), 1.19 (s, 3H), 2.75 (s, 1H), 2.89 (s, 1H), 7.14-7.19 (m, 2H), 7.22-7.27 (m, 2H), 7.29 (s, 4H); **$^{13}$C NMR** (67 MHz, $CDCl_3$) δ 13.8, 17.0, 37.2, 39.2, 47.4, 60.4, 129.3, 129.4, 129.6, 130.8, 133.9, 134.3, 136.1, 138.0, 197.8, 200.0; **IR** (KBr): 2977, 2936, 1702, 1591, 1490, 1448, 1402, 1382, 1332, 1252, 1225, 1156, 1092, 1065, 1011 cm$^{-1}$; **HRMS** : Calculated for $C_{21}H_{16}Cl_2O_3$, 386.0476, found 386.0479



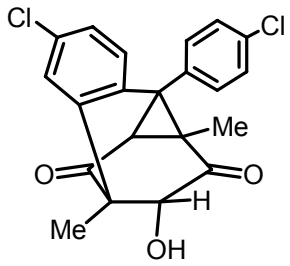

**3a**

(**3a**): **mp.** 237.5-238.4 $^{o}$C (from chloroform/*n*-hexane); **$^{1}$H NMR**(270 MHz, $CDCl_3$) δ 1.24 (s, 3H), 1.61 (s, 3H), 2.13 (s, 3H), 2.41 (s, 3H), 2.68 (s, 1H), 3.09 (d, 1H, *J* = 3.63 Hz), 3.81 (d, 1H, *J* = 3.63) 6.64 (d, 1H, *J* = 1.65 Hz), 6.97-7.00 (m, 1H), 7.13-7.16 (m, 2H), 7.22-7.33 (m, 3H); **$^{13}$C NMR** (67 MHz, $CDCl_3$) δ 14.5, 19.3, 21.2, 21.3, 42.0, 47.4, 52.5, 53.3, 85.6, 125.5, 128.4, 128.6, 129.1, 129.9, 130.4, 131.6, 133.1, 133.4, 136.1, 137.9, 138.0, 205.5, 205.9; **IR** (KBr): 3357, 2921, 1707, 1493, 1458, 1393, 1327, 1069, 1041, 942cm$^{-}$1; **HRMS** : Calculated for $C_{23}H_{22}O_3$, 346.1569, found 346.1573



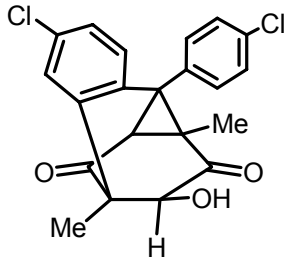

**2c**

**Spiro[cyclohexa-2,5-dienone-4,8'-7-(4-chlorophenyl)-1,4-dimethyl-3-hydroxy-tricyclo[2.2.2.0$^{6,7}$]octane-2,5-dione]** (**2c**): **mp** 206.6-206.9 $^{o}$C (from chloroform/*n*-hexane); **$^{1}$H NMR**(270 MHz, $CDCl_3$) δ 1.00 (s, 3H), 1.08 (s, 3H), 2.75 (s, 1H), 2.93 (s, 1H), 4.00 (s,1H), 6.17 (dd, 1H, *J* = 1.81, 10.4 Hz), 6.52 (dd, 1H, *J* = 1.81, 10.2 Hz), 6.54 (dd, 1H, *J* = 3.13, 10.4 Hz), 6.82 (dd, 1H, *J* = 3.13, 10.2 Hz), 7.00-7.10 (m, 2H), 7.25-7.26 (m, 2H); **$^{13}$C NMR** (67 MHz, $CDCl_3$) δ 10.9, 14.8, 29.8, 43.1, 46.0, 52.8, 56.0, 75.4, 128.9, 129.7, 130.5, 131.3, 134.4, 135.3, 142.7, 147.5, 184.0, 203.0, 204.0; **IR** (KBr): 3417, 2925, 1745, 1664, 1261, 1091, 801 cm$^{-}$1;




**3c**

(**3c**): **$^{1}$H NMR**(270 MHz, $CDCl_3$) δ 1.31 (s, 3H), 1.76 (s, 3H), 2.73 (s, 1H), 3.23 (d, 1H, *J* = 3.13 Hz), 4.20 (d, 1H, *J* = 3.13 Hz), 6.72 (d, 1H, *J* = 1.32), 7.20-7.52 (m, 6H). **$^{13}$C NMR** (67 MHz, $CDCl_3$) δ 14.6, 17.7, 41.8, 45.9, 50.3, 55.1, 84.7, 127.2, 127.6, 128.5, 128.7, 128.9, 130.5, 131.6, 132.9, 133.2, 134.2, 135.0, 136.3, 203.7, 205.0;




**4c**

(**4c**): **mp** 238.5-239.5 $^{o}$C (from chloroform/*n*-hexane); **$^{1}$H NMR**(270 MHz, $CDCl_3$) δ 1.26 (s, 3H), 1.62 (s, 3H), 2.70 (s, 1H), 2.80 (d, 1H, *J* = 3.63 Hz), 3.84 (d, 1H, *J* = 3.63 Hz), 6.76 (d, 1H, *J* = 1.32 Hz), 7.18 (d, 1H, *J* = 1.32 Hz), 7.19-7.31 (m. 1H), 7.32-7.52 (m, 5H); **$^{13}$C NMR** (67 MHz, $CDCl_3$) δ 14.4, 19.1, 41.2, 47.0, 51.0, 53.3, 85.4, 127.2, 127.6, 128.2, 128.5, 128.8, 130.5, 131.6, 132.9, 133.9, 134.6, 134.9, 135.0, 137.9, 204.1, 204.2; **IR** (KBr): 3417, 2360, 1707, 1489, 1401, 1094, 1015, 832 cm$^{-}$1; **HRMS** : Calculated for $C_{21}H_{16}Cl_2O_3$, 386.0476, found 386.0474