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Supporting Information

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# Synthesis of Aryl-Substituted 1,4-Benzoquinone via Water-Promoted and In(OTf)<sub>3</sub>-Catalyzed Conjugate Addition of Aromatic Compounds to 1,4-Benzoquinone in Water

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## Supporting Information

### Experimental Section

IR spectra were recorded on a Bruker Tensor 27 infra-red spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured by Bruker AV-300 spectrometers in CDCl<sub>3</sub> with tetramethylsilane as an internal standard. Mass spectra were recorded on a GCT-MS Micromass spectrometer. Elemental analyses were performed on a Carlo Flash 1112 Elemental Analysis instrument. Melting points were measured by a Beijing-Tike X-4 apparatus and were uncorrected. The X-ray crystal structures were measured on a Rigaku R-axis RAPID IP. Recrystallizations were performed by using a co-solvent of CH<sub>2</sub>Cl<sub>2</sub>/hexane. Common reagents and materials were purchased from commercial sources and purified before use.

**Typical experimental procedure:** A mixture of *N,N*-dimethyl-3-methoxyaniline (**1a**, 15.1 mg, 0.1 mmol), 1,4-benzoquinone (**2a**, 21.6 mg, 0.2 mmol), and In(OTf)<sub>3</sub> (2.8 mg, 0.005 mmol) in water (2 mL) was stirred at room temperature. The reaction was monitored by TLC. After **1a** disappeared, the reaction mixture was extracted by dichloromethane (10 mL × 3). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to remove the solvent. The crude product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6 : 1) to give **3a** as a blue solid (24 mg, 93%).

**2-(4'-*N,N*-dimethylamino-2'-methoxyphenyl)-1,4-benzoquinone (3a):** As a blue solid, mp: 130-131°C. IR (KBr): ν 2923, 1648, 1617, 1603, 1576, 1549, 1369, 1268, 796 cm<sup>-1</sup>. <sup>1</sup>H NMR

(CDCl<sub>3</sub>): d 3.03 (6H, s), 3.79 (3H, s), 6.23 (1H, d,  $J = 2.3$  Hz), 6.34 (1H, dd,  $J = 8.6, 2.3$  Hz), 6.74 (1H, dd,  $J = 10.1, 2.5$  Hz), 6.82 (1H, d,  $J = 10.1$  Hz), 6.86 (1H, d,  $J = 2.5$  Hz), 7.10 (1H, d,  $J = 8.6$  Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): d 40.3, 55.4, 95.4, 104.4, 110.1, 132.1, 132.2, 136.1, 137.1, 145.3, 153.1, 158.9, 186.9, 188.2. MS (EI)  $m/z$  (%): 257 (M<sup>+</sup>, 100). Anal. calcd. for C<sub>15</sub>H<sub>15</sub>NO<sub>3</sub>: C, 70.02; H, 5.88; N, 5.44; found: C, 69.92; H, 5.92; N, 5.40.

**2-(1'-N,N-Dimethylamino-naphthalen-4'-yl)-1,4-benzoquinone (3c)**: As a blue solid, mp: 35-36°C. IR (KBr):  $\nu$  2939, 2830, 1656, 1574, 1510, 1424, 1278, 1199, 1096, 910, 840 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): d 2.94 (6H, s), 6.87-6.95 (3H, m), 7.06 (1H, d,  $J = 7.8$ Hz), 7.27 (1H, d,  $J = 7.8$ Hz), 7.42-7.51 (1H, m), 7.59 (1H, dd,  $J = 8.7, 1.5$ Hz), 8.26 (1H, dd,  $J = 8.1, 1.5$ Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): d 44.98, 112.9, 124.9, 125.2, 125.3, 125.7, 126.4, 128.0, 128.6, 132.7, 135.1, 136.5, 137.1, 147.5, 152.8, 186.9, 187.7. HRMS (EI)  $m/z$  calcd. for C<sub>18</sub>H<sub>15</sub>NO<sub>2</sub> (M<sup>+</sup>): 277.1103; found: 277.1103.

**2-(4'-N,N-Dimethylamino-2'-methylphenyl)-1,4-benzoquinone (3d)**: As a blue solid, mp: 159-160°C. IR (KBr):  $\nu$  2890, 2804, 1656, 1610, 1585, 1512, 1444, 1367, 1286, 1086, 835 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): d 2.19 (3H, s), 2.99 (3H, s), 6.56-6.59 (2H, m), 6.68 (1H, d,  $J = 2.3$ Hz), 6.80 (1H, dd,  $J = 10.1, 2.3$ Hz), 6.85 (1H, d,  $J = 10.1$ Hz), 7.00-7.03 (1H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>): d 21.4, 40.3, 109.6, 114.2, 120.9, 131.2, 133.4, 136.4, 137.0, 137.6, 148.4, 151.4, 187.1, 188.1. MS (EI)  $m/z$  (%): 241 (M<sup>+</sup>, 100). Anal calcd for C<sub>15</sub>H<sub>15</sub>NO<sub>2</sub>: C, 74.67; H, 6.27; N, 5.81; found: C, 74.51; H, 6.21; N, 5.83.

**2-(4'-N,N-Dimethylamino-2'-methylphenyl)-1,4-hydroquinone (3d-1)**: As a white solid, mp: 140-141°C. IR (KBr):  $\nu$  3100, 2921, 2858, 1606, 1499, 1444, 1358, 1233, 1199, 823 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): d 2.17 (3H, s), 2.91 (6H, s), 5.66 (1H, br), 6.59-6.70 (6H, m), 6.83 (1H, d,  $J = 8.7$ Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>): d 16.7, 41.5, 112.2, 116.0, 116.3, 117.3, 121.1, 130.8, 146.4, 147.6, 150.3, 152.8. MS (EI):  $m/z$  (%): 243 (M<sup>+</sup>, 100). Anal calcd for C<sub>15</sub>H<sub>17</sub>NO<sub>2</sub>: C, 74.05; H, 7.04; N, 5.76; found: C, 74.12; H, 7.14; N, 5.78.

**2-(4'-N,N-dimethylamino-2'-methoxyphenyl)-1,4-naphthoquinone (3e)**: As a blue solid, mp: 155-156°C. IR (KBr):  $\nu$  2904, 2814, 1663, 1611, 1516, 1452, 1245, 1141, 783 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): d 3.04 (6H, s), 3.81 (3H, s), 6.27 (1H, d,  $J = 2.4$ Hz), 6.37 (1H, dd,  $J = 8.6, 2.4$ Hz), 7.08 (1H, s), 7.20 (1H, d,  $J = 8.6$ Hz) 7.71-7.74 (2H, m), 8.11 (2H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>): d 40.4, 55.5, 95.5, 104.4, 110.9, 125.7, 126.9, 132.1, 132.3, 133.0, 133.29, 133.32, 134.8, 147.5, 153.1, 158.9,

184.7, 185.6. MS (EI):  $m/z$  (%): 307 ( $M^+$ , 100). Anal calcd for  $C_{19}H_{17}NO_3$ : C, 74.25; H, 5.88; N, 4.56; found: C, 73.97; H, 5.61; N, 4.52.

**2,5-Dichloro-3-(4'-*N,N*-dimethylamino-2'-methoxyphenyl)-1,4-benzoquinone (3f)**: As a blue solid, mp: 184-185°C. IR (KBr):  $\nu$  2935, 1684, 1659, 1609, 1564, 1515, 1367, 1263, 1122, 1040  $cm^{-1}$ .  $^1H$ NMR ( $CDCl_3$ ):  $\delta$  3.04 (6H, s), 3.77 (3H, s), 6.23 (1H, d,  $J = 2.3$ Hz), 6.37 (1H, dd,  $J = 8.6, 2.3$ Hz), 7.03 (1H, d,  $J = 8.6$ Hz), 7.15 (1H, s).  $^{13}C$ NMR ( $CDCl_3$ ):  $\delta$  40.3, 55.5, 95.2, 104.2, 108.3, 131.4, 132.9, 140.0, 143.1, 144.6, 153.3, 158.3, 176.7, 178.1. MS (EI):  $m/z$  (%): 325 ( $M^+$ , 100). Anal calcd for  $C_{15}H_{13}Cl_2NO_3$ : C, 55.23; H, 4.02; N, 4.29; found: C, 55.09; H, 4.06; N, 4.24.

**2,5-Dichloro-3-(4-(dimethylamino)-2-methoxyphenyl)-1,4-hydroquinone (3f-1)**: As a white solid, mp: 232-233°C. IR (KBr):  $\nu$  3459, 2904, 1609, 1525, 1451, 1367, 1247, 1133  $cm^{-1}$ .  $^1H$ NMR ( $CDCl_3$ ):  $\delta$  3.04 (6H, s), 3.79 (3H, s), 5.24 (1H, s), 5.29 (1H, s), 6.33 (1H, d,  $J = 2.4$ Hz), 6.42 (1H, dd,  $J = 8.5, 2.4$ Hz), 7.03 (1H, d,  $J = 8.5$ Hz), 7.04 (1H, s).  $^{13}C$ NMR ( $CDCl_3$ ):  $\delta$  40.4, 55.6, 95.8, 104.7, 109.2, 115.3, 119.4, 119.7, 125.7, 132.1, 144.2, 145.2, 152.6, 157.9. MS (EI)  $m/z$  (%): 327 ( $M^+$ , 100). Anal calcd for  $C_{15}H_{15}Cl_2NO_3$ : C, 54.90; H, 4.61; N, 4.27; found: C, 54.90; H, 4.67; N, 4.11.

**2-(2',4'-Dimethoxyphenyl)-1,4-benzoquinone (3h)**: As a red solid; mp: 111-112 °C. IR (KBr):  $\nu$  2975, 2940, 2843, 1655, 1608, 1504, 1460, 1306, 1271, 835  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  3.77 (3H, s), 3.85 (3H, s), 6.52 (1H, d,  $J = 2.3$ Hz), 6.55 (1H, dd,  $J = 8.3, 2.3$ Hz), 6.78 (1H, dd,  $J = 10.0, 2.4$ Hz), 6.82 (1H, d,  $J = 2.4$ Hz), 6.85 (1H, d,  $J = 10.0$ Hz) 7.12 (1H, d,  $J = 8.3$ Hz);  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  55.5, 55.7, 99.0, 104.8, 115.1, 131.7, 133.8, 136.6, 137.1, 145.2, 158.5, 162.4, 186.1, 188.0. MS (EI):  $m/z$  (%) = 244 ( $M^+$ , 100); Anal calcd for  $C_{14}H_{12}NO_4$ : C, 68.85; H, 4.95; found: C, 68.75; H, 5.01.

**2-(2,4-Dimethoxyphenyl)-1,4-naphthoquinone (3i)**: As a red crystal; mp: 98-100 °C. IR (KBr):  $\nu$  2924, 2853, 1660, 1611, 1574, 1505, 1456, 1299, 1250, 1207, 1159, 818  $cm^{-1}$ .  $^1H$  NMR( $CDCl_3$ ):  $\delta$  3.78 (3H, s), 3.86 (3H, s), 6.54-6.59 (2H, m), 7.03 (1H, s), 7.21 (1H, d,  $J = 8.22$ ), 7.74-7.76 (2H, m), 8.09-8.16 (2H, m).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  55.5, 55.7, 99.1, 104.7, 115.9, 125.9, 126.9, 131.7, 132.2, 132.7, 133.5, 133.6, 136.3, 147.4, 158.6, 162.3, 184.0, 185.5. HRMS (EI):  $m/z$ : calcd. for  $C_{18}H_{14}O_4$ , [ $M^+$ ], 294.0892, found 294.0888.

**2-(2'-Methylfuran-3'-yl)-1,4-benzoquinone (3j)**: As a red solid, mp: 31-32 °C. IR (KBr):  $\nu$

2921, 1671, 1648, 1631, 1592, 1564, 1339, 1288, 1105, 1028, 894, 795  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): d 2.38 (3H, s), 6.20 (1H, d,  $J = 3\text{Hz}$ ), 6.72 (2H, s), 6.97 (1H, s), 7.37 (1H, d,  $J = 3.0\text{Hz}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): d 13.9, 110.4, 120.5, 123.9, 133.4, 136.4, 136.6, 144.9, 156.6, 185.7, 187.3. Anal calcd for  $\text{C}_{11}\text{H}_8\text{O}_3$ : C, 70.21; H, 4.29. found: C, 69.80; H, 4.34.

**2-Methoxy-5-(4'-*N,N*-dimethylamino-2'-methoxyphenyl)-1,4-benzoquinone [(2,5)-4b]:** As a blue solid; mp: 190-191  $^\circ\text{C}$ . IR (KBr):  $\nu$  2926, 1652, 1611, 1549, 1452, 1360, 1253, 1194, 808  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): d 3.03 (6H, s), 3.80 (3H, s), 3.84 (3H, s), 5.99 (1H, s), 6.23 (1H, d,  $J = 2.3\text{Hz}$ ), 6.34 (1H, dd,  $J = 8.6, 2.3\text{Hz}$ ), 6.86 (1H, s), 7.13 (1H, d,  $J = 8.6\text{Hz}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): d 40.3, 55.4, 56.1, 95.4, 104.5, 107.9, 110.1, 130.3, 132.7, 145.4, 153.1, 158.5, 159.3, 182.6, 187.2. MS (EI)  $m/z$  (%): 287 ( $\text{M}^+$ , 100); Anal calcd for  $\text{C}_{16}\text{H}_{17}\text{NO}_4$ : C, 66.89; H, 5.96; N, 4.88; found: C, 66.65; H, 5.95; N, 4.96.

**2-Methoxy-5-(4'-*N,N*-dimethylaminophenyl)-1,4-benzoquinone [(2,5)-4c]:** As a blue solid; mp: 240-241  $^\circ\text{C}$ . IR (KBr):  $\nu$  2909, 1655, 1632, 1618, 1602, 1572, 1362, 1186, 816  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): d 3.04 (6H, s), 3.85 (3H, s), 5.97 (1H, s), 6.72 (2H, dd,  $J = 7.1, 1.9\text{Hz}$ ), 6.73 (1H, s), 7.51 (2H, dd,  $J = 7.1, 1.9\text{Hz}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): d 40.1, 56.2, 107.9, 111.8, 120.0, 126.5, 131.2, 145.9, 151.9, 158.8, 182.1, 187.9. Anal calcd for  $\text{C}_{15}\text{H}_{15}\text{NO}_3$ : C, 70.02; H, 5.88; N, 5.44; found: C, 69.71; H, 5.73; N, 5.42. The crystal used for the X-ray study had the dimension 0.75 x 0.26 x 0.15  $\text{mm}^3$ . Crystal data:  $\text{C}_{15}\text{H}_{15}\text{NO}_3$ , Mr 257.28; Monoclinic; space group, P2(1)/c;  $a = 11.714(2)\text{\AA}$ ,  $b = 6.5339(13)\text{\AA}$ ,  $c = 16.581(3)\text{\AA}$ ;  $\alpha = 90\text{deg}$ ,  $\beta = 91.51(3)\text{deg}$ ,  $\gamma = 90\text{deg}$ .  $V = 1268.6(4)\text{\AA}^3$ ,  $Z = 4$ ,  $d_{\text{calcd}} = 1.347\text{g/cm}^3$ ;  $F_0 = 544$ ; Final R indices [ $I > 2s(I)$ ]  $R_1 = 0.0562$ ,  $wR_2 = 0.1540$ ; R indices (all data)  $R_1 = 0.1028$ ,  $wR_2 = 0.1782$ ; Goodness of fit 0.954.

**2-Methoxy-5-(4'-*N,N*-dimethylamino-2'-methylphenyl)-1,4-benzoquinone [(2,5)-4d]:** As a blue solid; mp: 147-148  $^\circ\text{C}$ . IR (KBr):  $\nu$  2935, 1665, 1647, 1592, 1513, 1363, 1205, 1114, 1006, 801  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): d 2.20 (3H, s), 2.99 (6H, s), 3.86 (3H, s), 6.02 (1H, s), 6.56-6.59 (2H, m), 6.62 (1H, s), 7.01-7.04 (1H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): d 21.4, 40.2, 56.2, 107.8, 109.4, 114.1, 120.8, 131.2, 131.3, 137.7, 148.9, 151.3, 158.6, 182.4, 187.1. Anal calcd for  $\text{C}_{16}\text{H}_{17}\text{NO}_3$ : C, 70.83; H, 6.32; N, 5.16; found: C, 70.54; H, 6.25; N, 5.00.

**2-(*N*-methyl-*N*-phenylamino)-5-methoxy-1,4-benzoquinone [(2,5)-4e]:** As a red solid, mp: 242-243  $^\circ\text{C}$ . IR (KBr):  $\nu$  3057, 2980, 1664, 1618, 1570, 1494, 1238, 1043, 703  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): d 3.38 (3H, s), 3.80 (3H, s), 5.65 (1H, s), 5.71 (1H, s), 7.08 (2H, dd,  $J = 7.6, 1.2\text{Hz}$ ),

7.26-7.29 (1H, m), 7.35-7.41 (2H, m).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): d 43.2, 56.2, 105.5, 106.4, 125.4, 126.7, 129.7, 147.6, 151.1, 160.0, 179.9, 183.7. MS (EI):  $m/z$  (%) = 243 ( $\text{M}^+$ , 100); Anal calcd for  $\text{C}_{14}\text{H}_{13}\text{NO}_3$ : C, 69.12; H, 5.39; N, 5.76. found: C, 68.65; H, 5.48; N, 5.72. The crystal used for the X-ray study had the dimension 0.54 x 0.32 x 0.04  $\text{mm}^3$ . Crystal data:  $\text{C}_{14}\text{H}_{13}\text{NO}_3$ , Mr 243.25; Monoclinic; space group, P2(1)/c; a = 7.1495(14)Å, b = 6.6785(13)Å, c = 24.313(5)Å; a = 90deg,  $\beta$  = 95.63(3)deg,  $\gamma$  = 90deg. V = 1155.3(4)Å<sup>3</sup>, Z = 4,  $d_{\text{calcd}}$  = 1.399  $\text{g}/\text{cm}^3$ ;  $F_0$  = 512; Final R indices [ $I > 2s(I)$ ]  $R_1$  = 0.0483,  $wR_2$  = 0.1357; R indices (all data)  $R_1$  = 0.0733,  $wR_2$  = 0.1452; Goodness of fit 1.009.

**2-(4'-N,N-Dimethylaminophenyl)-5-methyl-1,4-benzoquinone [(2,5)-4f]**: As a blue crystal, mp: 179-181 °C. IR (KBr):  $\nu$  2911, 2821, 1647, 1602, 1566, 1526, 1173, 1006, 820  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): d 2.08 (3H, d,  $J$  = 1.5Hz), 3.03 (6H, s), 6.64 (1H, d,  $J$  = 1.5Hz), 6.71-6.78 (3H, m), 7.48-7.51 (2H, m).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): d 15.5, 40.2, 111.9, 120.0, 128.6, 130.8, 133.8, 145.3, 145.6, 151.7, 188.2, 188.3. HRMS(EI):  $m/z$  calcd. for  $\text{C}_{15}\text{H}_{15}\text{NO}_2$  ( $\text{M}^+$ ): 241.1103, found 241.1099.

**2-(4'-N,N-Dimethylaminophenyl)-6-methyl-1,4-benzoquinone [(2,6)-4f]**: As a blue crystal, mp: 57-59 °C. IR (KBr):  $\nu$  2956, 2925, 2855, 1648, 1604, 1573, 1523, 1188, 1078, 819  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): d 2.12 (3H, d,  $J$  = 1.5Hz), 3.03 (6H, s), 6.62 (1H, m), 6.71-6.74 (3H, m), 7.46-7.48 (2H, m).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): d 16.4, 40.1, 111.7, 120.4, 128.7, 130.6, 133.2, 145.6, 145.9, 151.6, 187.9, 188.2. HRMS(EI):  $m/z$  calcd. for  $\text{C}_{15}\text{H}_{15}\text{NO}_2$  ( $\text{M}^+$ ): 241.1103, found 241.1104.

**2-tert-Butyl-6-(4-(dimethylamino)-2-methoxyphenyl)-1,4-benzoquinone [(2,6)-4g]**: As a blue crystal, mp: 98-100 °C. IR(KBr):  $\nu$  2960, 2905, 2813, 1668, 1645, 1610, 1516, 1359, 1296, 1246, 1125, 1047, 823  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR( $\text{CDCl}_3$ ): d 1.32 (9H, s), 3.02 (6H, s), 3.77 (3H, s), 6.23 (1H, d,  $J$  = 2.28Hz), 6.33 (1H, dd,  $J$  = 8.4, 2.3Hz), 6.57 (1H, d,  $J$  = 2.7Hz), 6.68 (1H, d,  $J$  = 2.7Hz), 7.07(1H, d,  $J$  = 8.4Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): d 29.3, 35.5, 40.4, 55.4, 95.5, 104.6, 111.7, 130.1, 130.9, 131.4, 148.7, 153.2, 157.1, 158.6, 187.4, 188.7. HRMS (EI):  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{23}\text{NO}_3$  [ $\text{M}^+$ ] 313.1678, found 313.1677.

**2-(4'-N-Dimethylamino-2'-methoxyphenyl)-6-(2',4'-dimethoxyphenyl)-1,4-benzoquinone [(2,6)-4j]**: As a blue crystal, mp: 169-170 °C. IR(KBr): 2926, 1641, 1606, 1525, 1448, 1366, 1247, 1206, 1100, 1028, 816, 796  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): d 3.01 (6H, s), 3.79 (3H, s), 3.82 (3H,

s), 3.83 (3H, s), 6.23 (1H, d,  $J = 2.3\text{Hz}$ ), 6.33 (1H, dd,  $J = 8.61, 2.3\text{Hz}$ ), 6.51-6.56 (2H, m), 6.81 (1H, d,  $J = 2.7\text{Hz}$ ), 6.91 (1H, d,  $J = 2.7\text{Hz}$ ), 7.11-7.17 (2H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): d 40.3, 55.4, 55.5, 55.7, 95.5, 99.0, 104.5, 104.8, 111.2, 116.5, 131.3, 131.8, 132.3, 132.9, 146.2, 146.3, 153.0, 158.6, 159.1, 162.2, 186.4, 188.4. HRMS(EI):  $m/z$ : calcd. for  $\text{C}_{23}\text{H}_{23}\text{NO}_5$  ( $\text{M}^+$ ): 393.1576, found: 393.1559

**2-(*N*-Methyl-*N*-phenylamino)-5-(4'-dimethylamino-2'-methoxyphenyl)-1,4-benzoquinone [(2,5)-4k]:** As a dark brown crystal, mp: 130-131 °C. IR (KBr):  $\nu$  2930, 1647, 1620, 1601, 1561, 1369, 1201, 1145, 891  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): d 3.01 (6H, s), 3.34 (3H, s), 3.80 (3H, s), 5.91 (1H, s), 6.23 (1H, d,  $J = 2.3\text{Hz}$ ), 6.34 (1H, dd,  $J = 8.7, 2.3\text{Hz}$ ), 6.65 (1H, s), 7.10-7.25 (4H, m), 7.34-7.39 (2H, m).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): d 40.3, 42.6, 55.5, 95.7, 104.5, 110.2, 125.3, 126.0, 129.5, 131.2, 132.6, 145.0, 147.9, 150.1, 152.8, 159.2, 184.4, 185.8. HRMS(EI):  $m/z$  calcd. for  $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_3$  ( $\text{M}^+$ ): 362.1630, found 362.1628.

**2-(*N*-Methyl-*N*-phenylamino)-6-(4'-dimethylamino-2'-methoxyphenyl)-1,4-benzoquinone [(2,6)-4k]:** As a blue crystal, mp: 168-169 °C. IR (KBr):  $\nu$  2903, 2818, 1685, 1626, 1607, 1564, 1494, 1286, 1105, 905, 765  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): d 2.97 (6H, s), 3.32 (3H, s), 3.67 (3H, s), 5.85 (1H, d,  $J = 2.6\text{Hz}$ ), 6.14 (1H, d,  $J = 2.3\text{Hz}$ ), 6.27 (1H, dd,  $J = 8.6, 2.3\text{Hz}$ ), 6.64 (1H, d,  $J = 2.6\text{Hz}$ ), 6.99 (1H, d,  $J = 8.6\text{Hz}$ ), 7.15-7.23 (3H, m), 7.33-7.38 (2H, m).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): d 40.4, 42.4, 55.2, 95.4, 104.6, 108.9, 111.4, 125.3, 125.8, 129.3, 131.2, 131.9, 145.5, 147.7, 152.6, 153.0, 158.2, 183.9, 186.8. HRMS(EI):  $m/z$  calcd. for  $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_3$  ( $\text{M}^+$ ): 362.1630, found 362.1627?

#### **Synthesis of diaryl-substituted 1,4-quinone in one-pot:**

A mixture of **1a** (30.2 mg, 0.2 mmol), **2a** (21.6 mg, 0.2 mmol) and  $\text{In}(\text{OTf})_3$  (5.6 mg, 0.01 mmol) in water (2 mL) was stirred at room temperature for 24 h. The reaction was monitored by TLC. After **1a** disappeared, the reaction mixture was extracted by dichloromethane (6 mL  $\times$  3). The organic layer was dried over  $\text{Na}_2\text{SO}_4$  and evaporated to remove the solvent. The crude product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6 : 1) to give (2,6)-**4a** as a red solid (32 mg, 79% yield).

**2,6-Bis(4'-*N,N*-dimethylamino-2'-methoxyphenyl)-1,4-benzoquinone [(2,6)-4a]:** As a blue

solid, mp: 181-182 °C. IR (KBr):  $\nu$  2926, 1668, 1635, 1608, 1366, 1242, 1091, 811  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): d 3.02 (12H, s), 3.83 (6H, s), 6.24 (2H, d,  $J = 2.1$  Hz), 6.34 (2H, dd,  $J = 8.6, 2.1$  Hz), 6.87 (2H, s), 7.14 (2H, d,  $J = 8.6$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): d 40.4, 55.5, 95.6, 104.5, 111.6, 131.2, 132.2, 146.6, 152.9, 159.0, 187.2, 188.6. MS (EI):  $m/z$  (%): 406 ( $\text{M}^+$ , 100); Anal. calcd. for  $\text{C}_{24}\text{H}_{26}\text{N}_2\text{O}_4$ : C, 70.92; H, 6.45; N, 6.89; found: C, 70.65; H, 6.38; N, 6.99. The crystal used for the X-ray study had the dimension 0.56 x 0.07 x 0.06  $\text{mm}^3$ . Crystal data:  $\text{C}_{24}\text{H}_{26}\text{N}_2\text{O}_4$ , Mr 406.47; Orthorhombic; space group, P2(1)2(1)2(1);  $a = 9.2670(19)\text{\AA}$ ,  $b = 14.627(3)\text{\AA}$ ,  $c = 15.143(3)\text{\AA}$ ;  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ .  $V = 2052.6(7)\text{\AA}^3$ ,  $Z = 4$ ,  $d_{\text{calcd}} = 1.315\text{g/cm}^3$ ;  $F_0 = 864$ ; Final R indices [ $I > 2s(I)$ ]  $R_1 = 0.0507$ ,  $wR_2 = 0.0478$ ; R indices (all data)  $R_1 = 0.1012$ ,  $wR_2 = 0.0524$ ; Goodness of fit 0.912.

**2,6-Bis(2,4-dimethoxyphenyl)-1,4-benzoquinone [(2,6)-4h]:** As a red solid, mp: 204-205 °C. IR (KBr):  $\nu$  2936, 2835, 1669, 1645, 1607, 1502, 1460, 1299, 1207, 1037, 837  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): d 3.80 (6H, s), 3.84 (6H, s), 6.53 (2H, d,  $J = 2.2\text{Hz}$ ), 6.54 (2H, dd,  $J = 8.4, 2.2\text{Hz}$ ), 6.85 (2H, s), 7.16 (2H, d,  $J = 8.4\text{Hz}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): d 55.5, 55.7, 99.0, 104.7, 116.0, 131.8, 133.1, 145.9, 158.6, 162.3, 185.4, 188.3. MS (EI):  $m/z$  (%): 380 ( $\text{M}^+$ , 100); Anal calcd for  $\text{C}_{22}\text{H}_{20}\text{O}_6$ : C, 69.46; H, 5.30; found: C, 69.30; H, 5.34. The crystal used for the X-ray study had the dimension 0.723 x 0.440 x 0.200  $\text{mm}^3$ . Crystal data:  $\text{C}_{22}\text{H}_{20}\text{O}_6$ , Mr 380.38; Monoclinic; space group, P2(1)/n;  $a = 13.525(3)\text{\AA}$ ,  $b = 9.870(2)\text{\AA}$ ,  $c = 15.173(3)\text{\AA}$ ;  $\alpha = 90^\circ$ ,  $\beta = 115.28(3)^\circ$ ,  $\gamma = 90^\circ$ .  $V = 1831.6(6)\text{\AA}^3$ ,  $Z = 4$ ,  $d_{\text{calcd}} = 1.379\text{g/cm}^3$ ;  $F_0 = 800$ ; Final R indices [ $I > 2s(I)$ ]  $R_1 = 0.0399$ ,  $wR_2 = 0.1031$ ; R indices (all data)  $R_1 = 0.0584$ ,  $wR_2 = 0.1084$ ; Goodness of fit 1.007.

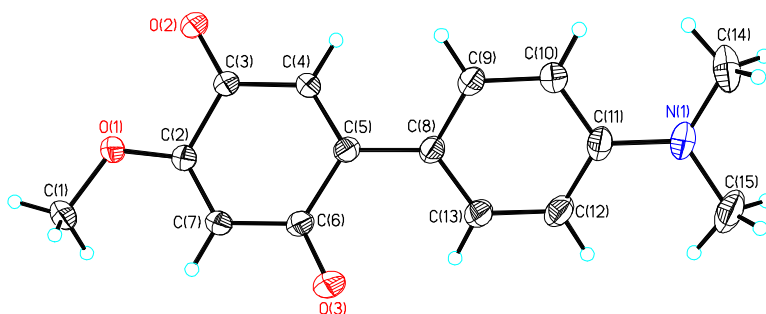


Fig. 1. X-ray analysis for determining the structure of (2,5)-4c.

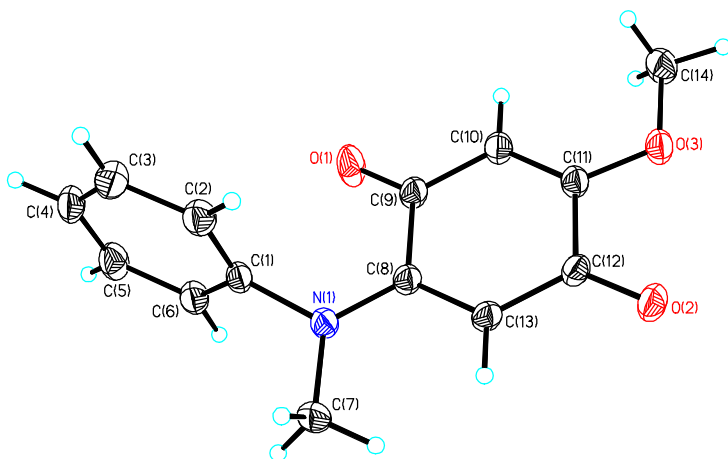


Fig. 2. X-ray analysis for determining the structure of (2,5)-4e.

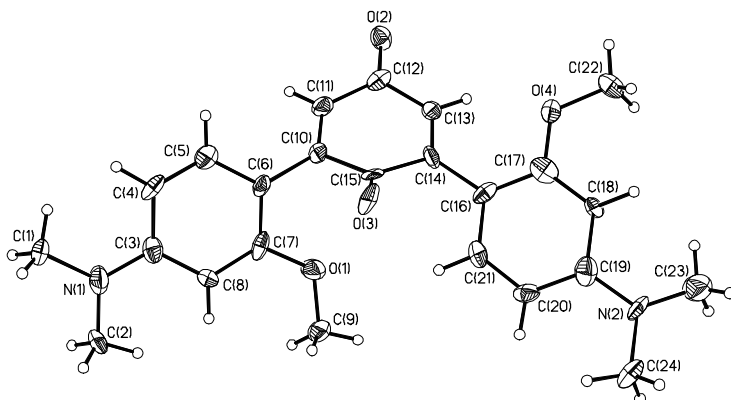


Fig. 3. X-ray analysis for determining the structure of (2,6)-**4a**.

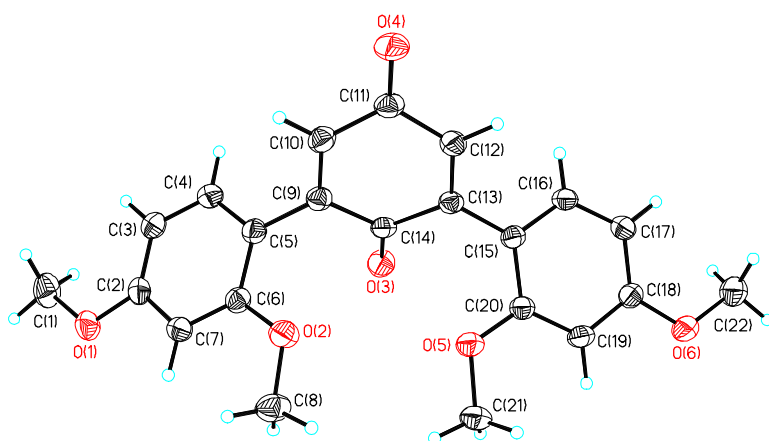


Fig 4. X-ray analysis for determining the structure of (2,6)-**4h**.