Supporting Information

Radical Addition to 1,4-Benzoquinones:

Addition at *O*- versus *C*-Atom

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General

Catecholborane was distilled under reduced pressure (50 mmHg, 50 °C). Other reagents were obtained from commercial sources and used as received. Solvents for reactions (THF and CH₂Cl₂) were filtered over columns of dried alumina under a positive pressure of argon. Solvents for extractions were of technical grade and were distilled prior to use. All reactions were performed under a nitrogen atmosphere in oven-dried (120 °C) flasks and standard precautions against moisture were taken. A dry ice/acetone bath was used to obtain a temperature of -78 °C. An ice bath was used to obtain 0 °C. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F₂₅₄ analytical plates; visualization under UV light (254 nm) or staining with a solution of phosphomolybdic acid (25 g), CeSO₄ · 4H₂O (10 g), H₂SO₄ 96% (60 mL) in H₂O (940 mL) and subsequent heating. Preparative RP-HPLC was performed with HPLC-grade acetonitrile and MilliQ deionized water in a Waters prepak cartridge 500 g (RP-C18 20 mm, 300 Å pore size) installed on a Waters Prep LC4000 system from Millipore (flow rate 100 mL/min). Solvent systems were: A = 0.1% TFA in H₂O; B = 40% H₂O / 60% CH₃CN, 0.1% TFA. Melting points were measured on a Büchi B-545 apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE-300 spectrometer operating at 300 MHz for ¹H and 75 MHz for ¹³C at rt unless otherwise stated. Some ¹H and ¹³C NMR spectra and two-dimensional NMR spectra were recorded on a Bruker DRX-400 spectrometer. Chemical shift data are reported in units of δ (ppm) using as the internal standard either CHCl₃ (δ = 7.26 for ¹H NMR spectra and δ = 77.00 for ¹³C NMR spectra) or Si(CH₃)₄ (δ = 0 for ¹H NMR and ¹³C NMR spectra). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), hept (heptet), m (multiplet), and bs (broad singlet) for ¹H. Coupling constants, *J*, are reported in Hz. Infrared spectra were recorded on an Jasco FT-IR-460 Plus spectrometer equipped with a Specac MKII Golden Gate Single Reflection Diamond ATR System and are reported in wave numbers (cm⁻¹). Low and high-resolution mass spectra were recorded on a Waters Micromass Autospec Q mass spectrometer in EI mode at 70 eV. Gas chromatographic analyses were carried out on

a CE instruments MEGA Series HRGC fitted with an Optima delta-3 (Macherey-Nagel) capillary column (10 m).

Method A: *N,N*-Dimethylacetamide-catalyzed Hydroboration - Radical Addition. To a solution of olefin (3.0 mmol) and *N,N*-dimethylacetamide (28 μ L, 0.3 mmol) in CH_2Cl_2 (3 mL), catecholborane (400 μ L, 3.75 mmol) was added dropwise at 0 $^\circ\text{C}$ and the reaction mixture was heated under reflux for 5 h. Water (160 μ L, 9 mmol) was added at 0 $^\circ\text{C}$ and the solution was stirred for 15 min at rt. To this solution, CH_2Cl_2 (8 mL), DMPU (360 μ L, 3.0 mmol) and 1,4-benzoquinone (1.5 mmol) were successively added. After 2 h stirring at rt, the reaction mixture was treated with sat. NH_4Cl (10 mL) and extracted with Et_2O (3 x 20 mL). The organic layer was dried (MgSO_4), filtered and concentrated under reduced pressure. Analytically pure samples were obtained either by flash chromatography (FC) or by reverse phase high pressure liquid chromatography (RPC18-HPLC).

Method B: Rhodium-catalyzed Hydroboration - Radical Addition. To a solution of olefin (3.0 mmol) and $(\text{Ph}_3\text{P})_3\text{RhCl}$ (56 mg, 2 mol%) in THF (11 mL), catecholborane (400 μ L, 3.75 mmol) was added dropwise at -78°C . The reaction mixture was stirred overnight at rt. Water (160 μ L, 9 mmol) was added at 0 $^\circ\text{C}$ and the solution was stirred for 15 min at rt. To this solution, THF (8 mL), DMPU (360 μ L, 3.0 mmol) and 1,4-benzoquinone (1.5 mmol) were successively added. After 2 h stirring at rt, the reaction mixture was treated with sat. NH_4Cl (10 mL) and extracted with Et_2O (3 x 20 mL). The organic layer was dried (MgSO_4), filtered and concentrated under reduced pressure. Analytically pure samples were obtained by RPC18-HPLC.

Method C: Barton Decarboxylation Radical Addition. In a flask protected from light 2,2-dimethyl-propionic acid 2-thioxo-2,3-dihydro-pyridin-1-yl ester (634 mg, 3.0 mmol) and 1,4-benzoquinone (162 mg, 1.5 mmol) were added in CH_2Cl_2 (10 mL) at 0 $^\circ\text{C}$. The reaction mixture was exposed to light using a 300 W sun lamp from a distance of 10 cm, while maintaining the temperature at 0 $^\circ\text{C}$. After 2 h the crude reaction mixture was concentrated and the residue purified by FC (pentane/ EtOAc 10:1–5:1).

2-Octylbenzene-1,4-diol (3a).

Prepared according to method A from 1,4-benzoquinone (162 mg, 1.50 mmol) and 1-octene (470 μ L, 3.00 mmol). Yield 72% (GC); retention time (t_r = 5.76 min, 180 $^\circ\text{C}$ -250 $^\circ\text{C}$, rate: 10 $^\circ\text{C}/\text{min}$, 45 kPa helium, l = 10 m). RP-HPLC (A/B = 50:50 to A/B = 10:90 in 40 min).

Mp 92-94 $^\circ\text{C}$. FT-IR (ATR): 3264, 2952, 2917, 2848, 1456, 1380, 1194 cm^{-1} . ^1H -NMR (400 MHz, CDCl_3): δ = 6.65-6.62 (2H, m), 6.55 (1H, dd, J = 8.5, 3.0 Hz), 4.43 (1H, bs), 4.38 (1H, bs), 2.56-2.52 (2H, dd, J = 7.8, 7.8 Hz), 1.64-1.55 (2H, m), 1.37-1.27 (10H, m), 0.88 (3H, t, J = 7.1 Hz). ^{13}C -NMR (100 MHz, CDCl_3): δ = 149.3, 147.4, 130.0, 116.8, 116.0, 113.2, 31.9, 30.0, 29.7, 29.5, 29.5, 29.3, 22.7, 14.1. MS (EI, 70 eV): m/z (%) = 222 (69) (M^+), 149 (6), 137 (17), 123 (100), 110 (13), 95 (20), 77 (13). HRMS-EI: m/z (M^+) calcd for $\text{C}_{14}\text{H}_{22}\text{O}_2$: 222.16198; found: 222.16144.

2-(6,6-Dimethylbicyclo[3.1.1]hept-2-ylmethyl)benzene-1,4-diol (3b).

Prepared according to method A from 1,4-benzoquinone (162 mg, 1.50 mmol) and β -pinene (470 μ L, 3.00 mmol). Yield 95% (GC); retention time (t_r = 5.77 min, 180 °C-250 °C, rate: 10 °C/min, 45 kPa helium, l = 10 m). RP-HPLC (A/B = 30:70 to A/B = 0:100 in 40 min).

Mp 134 °C. FT-IR (ATR): 3313, 2981, 2931, 2900, 1508, 1196, 1154, 872, 803 cm^{-1} . ^1H -NMR (400 MHz, CDCl_3): δ = 6.63 (1H, d, J = 8.5 Hz), 6.58 (1H, d, J = 2.9 Hz), 6.54 (1H, dd, J = 8.5, 3.0 Hz), 2.65-2.58 (2H, m), 2.35-2.28 (2H, m), 2.00-1.81 (5H, m), 1.73-1.56 (1H, m), 1.20 (3H, s), 1.15 (3H, s), 0.85-0.79 (1H, m). ^{13}C -NMR (75 MHz, CDCl_3): δ = 149.1, 147.6, 129.1, 117.7, 116.0, 113.3, 45.3, 41.7, 41.5, 38.8, 37.2, 33.8, 28.2, 26.5, 23.4, 22.3. MS (EI, 70 eV): m/z (%) = 246 (25) (M^+), 203 (6), 123 (100), 81 (26), 67 (34), 41 (25). HRMS-EI: m/z (M^+) calcd for $\text{C}_{16}\text{H}_{22}\text{O}_2$: 246.16198; found: 246.16194.

2-Cyclohexylbenzene-1,4-diol (3c).

Prepared according to method A from 1,4-benzoquinone (162 mg, 1.50 mmol) and cyclohexene (310 μ L, 3.06 mmol). Yield 74% (GC); retention time (t_r = 4.89 min, 180 °C-250 °C, rate: 10 °C/min, 45 kPa helium, l = 10 m). RP-HPLC (A/B = 70:30 to A/B = 30:70 in 40 min).

FT-IR (ATR): 3264, 2925, 2856, 1476, 1445, 1187, 858, 809 cm^{-1} . ^1H -NMR (400 MHz, CDCl_3): δ = 6.68 (1H, d, J = 2.9 Hz), 6.64 (1H, d, J = 8.6 Hz), 6.53 (1H, dd, J = 8.5, 3.0 Hz), 4.56 (1H, bs), 4.50 (1H, bs), 2.76 (1H, tt, J = 11.5, 2.9 Hz), 1.86-1.73 (5H, m), 1.44-1.22 (4H, m). ^{13}C -NMR (75 MHz, CDCl_3): δ = 149.4, 146.6, 135.2, 116.2, 114.0, 112.9, 37.3, 33.0, 26.9, 26.2. MS (EI, 70 eV): m/z (%) = 192 (67) (M^+), 166 (26), 149 (23), 135 (100), 123 (54), 77 (33). HRMS-EI: m/z (M^+) calcd for $\text{C}_{12}\text{H}_{16}\text{O}_2$: 192.11503; found: 192.11510.

2-(2,6,6-Trimethylbicyclo[3.1.1]hept-3-yl)benzene-1,4-diol (3d).

Prepared according to method A from 1,4-benzoquinone (162 mg, 1.50 mmol) and α -pinene (480 μ L, 3.02 mmol). Yield 36% (GC); retention time (t_r = 7.15 min, 180 °C-250 °C, rate: 10 °C/min, 45 kPa helium, l = 10 m). RP-HPLC (A/B = 30:70 to A/B = 0:100 in 40 min).

FT-IR (ATR): 3229, 2923, 2900, 1497, 1451, 1182, 809 cm^{-1} . ^1H -NMR (500 MHz, CDCl_3): δ = 6.80 (1H, d, J = 3.0 Hz), 6.63 (1H, d, J = 8.4 Hz), 6.53 (1H, dd, J = 8.4, 3.0 Hz), 4.37 (2H, bs), 3.43 (1H, q, J = 9.3 Hz), 2.48-2.36 (2H, m), 2.18-2.11 (1H, m), 2.04-2.00 (1H, m), 1.90-1.88 (1H, m), 1.82 (1H, ddd, J = 13.6, 7.8, 2.2 Hz), 1.28 (3H, s), 1.19 (3H, s), 1.19-1.17 (1H, m), 1.00 (3H, d, J = 7.0 Hz). ^{13}C -NMR (125 MHz, CDCl_3): δ = 149.7, 147.2, 136.4, 116.2, 116.1, 113.0, 48.4, 44.7, 42.1, 39.2, 36.6, 36.3, 34.7, 28.6, 23.1, 21.3. MS (EI, 70 eV): m/z (%) = 246 (42) (M^+), 203 (18), 191 (100), 177 (42), 163 (58), 149 (51), 136 (77), 123 (61), 107 (28), 83 (52). HRMS-EI: m/z (M^+) calcd for $\text{C}_{16}\text{H}_{22}\text{O}_2$: 178.09938; found: 178.09941.

4-(2,6,6-Trimethylbicyclo[3.1.1]hept-3-yloxy)phenol (4d).

Prepared according to method A from 1,4-benzoquinone (162 mg, 1.50 mmol) and α -pinene (480 μ L, 3.02 mmol). Yield 39% (GC); retention time (t_r = 5.89 min, 180 °C-250 °C, rate: 10 °C/min, 45 kPa helium, l = 10 m). RP-HPLC (A/B = 30:70 to A/B = 0:100 in 40 min).

FT-IR (ATR): 3377, 2952, 2907, 2868, 1505, 1448, 1208, 995, 823 cm^{-1} . ^1H -NMR (400 MHz, CDCl_3): δ = 6.82-6.79 (2H, m), 6.77-6.73 (2H, m), 4.63 (1H, bs), 4.42-4.37 (1H, m), 2.56-2.49 (1H, m), 2.40-2.26 (2H, m), 1.99-1.94 (1H, m), 1.88-1.83 (2H, m), 1.24 (3H, s), 1.18 (1H, d, J = 9.8 Hz), 1.13 (3H, d, J = 7.5 Hz), 0.97 (3H, s). ^{13}C -NMR (75 MHz, CDCl_3): δ = 152.6, 149.4, 117.6, 116.0, 78.6, 47.5, 44.6, 41.5, 38.3, 35.9, 33.2, 27.4, 23.8, 21.1. MS (EI, 70 eV): m/z (%) = 246 (4) (M^+), 136 (15), 121 (13), 110 (100), 93 (33), 81 (59), 69 (26), 55 (21), 41 (30). HRMS-EI: m/z (M^+) calcd for $\text{C}_{16}\text{H}_{22}\text{O}_2$: 246.16198; found: 246.16127.

2-(1-Phenylethyl)benzene-1,4-diol (3e).

Prepared according to method B from 1,4-benzoquinone (162 mg, 1.50 mmol) and styrene (350 μL , 3.05 mmol). Yield 9% (GC); retention time (t_r = 6.01 min, 180 $^\circ\text{C}$ -250 $^\circ\text{C}$, rate: 10 $^\circ\text{C}/\text{min}$, 45 kPa helium, l = 10 m). RP-HPLC (A/B = 50:50 to A/B = 0:100 in 30 min).

FT-IR (ATR): 3332, 2967, 2931, 2872, 1491, 1447, 1195, 928 cm^{-1} . ^1H -NMR (400 MHz, CDCl_3): δ = 7.32-7.19 (5H, m), 6.73 (1H, d, J = 2.9 Hz), 6.65 (1H, d, J = 8.4 Hz), 6.59 (1H, dd, J = 8.5, 2.9 Hz), 4.32 (1H, q, J = 7.2 Hz), 1.60 (3H, d, J = 7.2 Hz), OH signal missing. ^{13}C -NMR (100 MHz, CDCl_3): δ = 149.5, 147.2, 145.0, 133.5, 128.7, 127.5, 126.5, 116.9, 114.9, 113.8, 38.8, 20.9. MS (EI, 70 eV): m/z (%) = 214 (92) (M^+), 199 (100), 181 (31), 153 (22), 136 (66), 77 (23). HRMS-EI: m/z (M^+) calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2$: calc. 214.09938; found: 214.09865.

4-(1-Phenylethoxy)phenol (4e).

Prepared according to method B from 1,4-benzoquinone (162 mg, 1.50 mmol) and styrene (350 μL , 3.05 mmol). Yield 61% (GC); retention time (t_r = 4.63 min, 180 $^\circ\text{C}$ -250 $^\circ\text{C}$, rate: 10 $^\circ\text{C}/\text{min}$, 45 kPa helium, l = 10 m). RP-HPLC (A/B = 50:50 to A/B = 0:100 in 30 min).

Mp 70-71 $^\circ\text{C}$. FT-IR (ATR): 3212, 2973, 1507, 1449, 1223, 1200, 1069, 930, 822 cm^{-1} . ^1H -NMR (400 MHz, CDCl_3): δ = 7.36-7.30 (4H, m), 7.26-7.22 (1H, m), 6.75-6.71 (2H, m), 6.66-6.62 (2H, m), 5.18 (1H, q, J = 6.5 Hz), 4.48 (1H, bs), 1.61 (3H, d, J = 6.5 Hz), OH signal missing. ^{13}C -NMR (100 MHz, CDCl_3): δ = 152.1, 149.4, 143.3, 128.5, 127.4, 125.7, 117.3, 115.9, 76.9, 24.3. MS (EI, 70 eV): m/z (%) = 214 (24) (M^+), 110 (100), 77 (59), 103 (45). HRMS-EI: m/z (M^+) calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2$: calc. 214.09938; found: 214.09859.

2-(1,1,2-Trimethylpropyl)benzene-1,4-diol (3f).

Prepared according to method A from 1,4-benzoquinone (162 mg, 1.50 mmol) and 2,3-dimethyl-2-butene (360 μL , 3.03 mmol). Yield 16% (GC); retention time (t_r = 3.65 min, 180 $^\circ\text{C}$ -250 $^\circ\text{C}$, rate: 10 $^\circ\text{C}/\text{min}$, 45 kPa helium, l = 10 m). RP-HPLC (A/B = 60:40 to A/B = 10:90 in 40 min).

Mp 112-115 $^\circ\text{C}$. FT-IR (ATR): 3312, 2958, 2872, 1682, 1596, 1375, 1193, 1132, 809 cm^{-1} . ^1H -NMR (400 MHz, CDCl_3): δ = 6.72 (1H, m), 6.53 (2H, m), 2.60 (1H, hept, J = 6.9 Hz), 1.29 (6H, s), 0.76 (3H, d, J = 6.9 Hz). ^{13}C -NMR (75 MHz, CDCl_3): δ = 149.0, 147.9, 137.6, 117.3, 115.7, 112.8, 41.0, 32.8, 23.5, 18.1. MS (EI, 70 eV): m/z (%) = 194 (11) (M^+), 151 (44), 123 (89), 44 (100), 40 (68). HRMS-EI: m/z (M^+) calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2$: calc. 194.13068; found: 194.12993.

4-(1,1,2-Trimethylpropoxy)phenol (4f).

Prepared according to method A from 1,4-benzoquinone (162 mg, 1.50 mmol) and 2,3-dimethyl-2-butene (360 μ L, 3.03 mmol). Yield 60% (GC); retention time (t_r = 2.69 min, 180 °C-250 °C, rate: 10 °C/min, 45 kPa helium, l = 10 m). RP-HPLC (A/B = 60:40 to A/B = 10:90 in 40 min).

Mp 45-47 °C. FT-IR (ATR): 3276, 2976, 2931, 2872, 1681, 1504, 1205, 1132, 1094, 849 cm^{-1} . ^1H -NMR (400 MHz, CDCl_3): δ = 6.86-6.83 (2H, m), 6.73-6.69 (2H, m), 1.92 (1H, hept, J = 6.9 Hz), 1.14 (6H, s), 1.01 (6H, d, J = 6.9 Hz). ^{13}C -NMR (100 MHz, CDCl_3): δ = 151.4, 148.8, 125.5, 115.3, 82.9, 37.4, 23.2, 17.8. MS (EI, 70 eV): m/z (%) = 194 (12) (M^+), 179 (20), 151 (75), 123 (36), 110 (98), 84 (62), 69 (89), 55 (70), 41 (100). HRMS-EI: m/z (M^+) calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2$: 194.13068; found: 194.13060.

4-(2,3-Dimethylbutan-2-yloxy)-2,3,5,6-tetramethylphenol (7).

According to method A from duroquinone (246 mg, 1.5 mmol) and 2,3-dimethyl-2-butene (0.18 ml, 3.0 mmol), FC ($\text{CH}_2\text{Cl}_2/\text{AcOEt}$ 3:1, pentane/ Et_2O 4:1) afforded the desired product (302 mg, 80%) as a pale yellow oil.

^1H NMR (300MHz, CDCl_3) : δ 4.39 (s, 1H), 2.16 (s, 6H), 2.13 (s, 6H), 2.10 (m, 1H), 1.08 (d, J = 6.8 Hz, 6H), 1.05 (s, 6H). ^{13}C NMR (75MHz, CDCl_3) : δ 145.7, 130.1, 119.7, 85.9, 39.1, 22.6, 18.1, 16.1, 12.4. IR (cm^{-1}) : 2947, 1456, 1409, 1365, 1254, 1141, 1097, 1069, 834, 797, 733, 663. (EI) : m/z : 250 [M^+], 240, 207, 166, 151, 136, 121, 105, 93, 84, 77, 69, 53, 41. HRMS-EI: m/z (M^+) calcd. for $\text{C}_{16}\text{H}_{26}\text{O}_2$: 250.19328; found : 250.19350.

4-[1-Methyl-1-(4-methyl-cyclohex-2-enyl)ethoxy]phenol (9).

Prepared according to method A from 1,4-benzoquinone (162 mg, 1.50 mmol) and (+)-2-carene (480 μ L, 3.04 mmol). Yield 69% (GC); retention time (t_r = 6.09 min, 180 °C-250 °C, rate: 10 °C/min, 45 kPa helium, l = 10 m). RP-HPLC (A/B = 30:70 to A/B = 0:100 in 30 min).

Mp 112 °C. FT-IR (ATR): 3332, 3195, 2944, 2920, 1506, 1216, 1198, 1138, 1116, 845 cm^{-1} . ^1H -NMR (400 MHz, CDCl_3): δ = 6.88-6.84 (2H, m), 6.74-6.69 (2H, m), 5.91-5.87 (1H, m), 5.79-5.74 (1H, m), 2.43-2.37 (1H, m), 2.26-2.18 (1H, m), 1.78-1.46 (4H, m), 1.19 (3H, s), 1.16 (3H, s), 1.00 (3H, d, J = 7.2 Hz). ^{13}C -NMR (100 MHz, CDCl_3): δ = 151.5, 148.5, 134.6, 127.1, 125.6, 115.3, 82.6, 44.9, 29.0, 28.7, 24.4, 23.2, 21.0, 20.5. MS (EI, 70 eV): m/z (%) = 246 (5) (M^+), 151 (63), 136 (79), 121 (57), 110 (100), 95 (67), 81 (96). HRMS-EI: m/z (M^+) calcd for $\text{C}_{16}\text{H}_{22}\text{O}_2$: 246.16198; found: 246.16167.

2,3,5,6-Tetramethyl-4-[1-Methyl-1-(4-methylcyclohex-2-enyl)ethoxy]phenol (10).

According to method A from duroquinone (246 mg, 1.5 mmol) and (+)-2-carene (0.48 ml, 3.0 mmol), FC ($\text{CH}_2\text{Cl}_2/\text{AcOEt}$ 3:1, pentane/ Et_2O 4:1) afforded the desired product (355 mg, 78%) as a pale yellow oil.

^1H NMR (300MHz, CDCl_3): δ 6.01-5.97 (m, 1H), 5.81-5.75 (m, 1H), 4.40 (s, 1H), 2.66-2.60 (m, 1H), 2.25-2.22 (m, 1H), 2.17 (s, 6H), 2.14 (s, 6H), 1.80-1.76(m, 2H), 1.56 (m, 2H), 1.09 (s, 3H), 1.04 (s, 3H), 1.0 (d, J = 7.2, 3H). ^{13}C NMR (75MHz,

CDCl_3 : δ 147.3, 145.6, 140.4, 134.4, 130.1, 127.5, 119.7, 85.4, 47.2, 29.2, 28.9, 23.6, 23, 21, 20.6, 16.2, 12.4.

IR (cm^{-1}): 2936, 1632, 1453, 1365, 1255, 1100, 1071, 883, 858, 812, 730, 693. MS (EI): m/z : 302 $[\text{M}^+]$, 207, 166, 151, 136, 121, 107, 93, 79, 67, 53, 41. HRMS-EI: m/z (M^+) calcd. for $\text{C}_{20}\text{H}_{30}\text{O}_2$: 302.22458; found : 302.22440.

3,5-Dichloro-2-cyclohexyl benzene-1,4-diol (12).

Prepared according to method A from 2,6-dichloro-1,4-benzoquinone (265 mg, 1.50 mmol) and cyclohexene (310 μL , 3.06 mmol). FC (pentane/*t*-BuOMe 10:1). Yield 72%.

FT-IR (ATR): 3447, 2924, 2851, 1704, 1592, 1414, 1171, 798 cm^{-1} . ^1H -NMR (300 MHz, CDCl_3): δ = 6.70 (1H, s), 5.57 (1H, bs), 4.69 (1H, bs), 3.20 (1H, tt, J = 12.2, 3.4 Hz) 2.12-1.97 (2H, m), 1.86-1.62 (5H, m), 1.44-1.23 (3H, m). ^{13}C -NMR (75 MHz, CDCl_3): δ = 142.2, 130.7, 121.6, 117.4, 116.1, 115.9, 29.4, 27.1 (2xC), 25.9. MS (EI, 70 eV): m/z (%) = 260 (29) (M^+), 217 (5), 204 (13), 191 (37), 178 (13), 110 (17), 84 (33), 43 (100). HRMS-EI: m/z (M^+) calcd for $\text{C}_{12}\text{H}_{16}\text{Cl}_2\text{O}_2$: 260.03708; found: 260.03693.

2,6-Dichloro-4-(1,1,2-trimethyl propoxy)phenol (13).

Prepared according to method A from 2,6-dichloro-1,4-benzoquinone (260 mg, 1.50 mmol) and 2,3-dimethyl-2-butene (360 μL , 3.03 mmol). FC (pentane/*t*-BuOMe 10:1). Yield 41%.

FT-IR (ATR): 3374, 3220, 2968, 2876, 1726, 1586, 1469, 1433, 1203, 790 cm^{-1} . ^1H -NMR (400 MHz, CDCl_3): δ = 6.92 (2H, s), 5.58 (1H, bs), 1.91 (1H, hept, J = 6.8 Hz), 1.16 (6H, s), 1.00 (6H, d, J = 6.8 Hz). ^{13}C -NMR (100 MHz, CDCl_3): δ = 148.4, 144.1, 124.3, 120.2, 84.5, 37.4, 23.2, 17.7. MS (EI, 70 eV): m/z (%) = 262 (15) (M^+), 219 (42), 178 (86), 114 (13), 84 (81), 69 (64), 43 (100). HRMS-EI: m/z (M^+) calcd for $\text{C}_{12}\text{H}_{16}\text{Cl}_2\text{O}_2$: 262.05273; found: 262.05182.

2,5-Dichloro-4-(1,1,2-trimethylpropoxy)phenol (15).

Prepared according to method A from 2,5-dichloro-1,4-benzoquinone (261 mg, 1.48 mmol) and 2,3-dimethyl-2-butene (360 μL , 3.03 mmol). FC (pentane/*t*-BuOMe 10:1). Yield 46%.

FT-IR (ATR): 3441, 2976, 2881, 1475, 1200, 1135, 1072, 848 cm^{-1} . ^1H -NMR (300 MHz, CDCl_3): δ = 7.05 (2H, s), 5.50 (1H, bs), 2.04 (1H, hept, J = 6.9 Hz), 1.22 (6H, s) 1.05 (6H, d, J = 6.9 Hz). ^{13}C -NMR (75 MHz, CDCl_3): δ = 147.3, 145.5, 129.0, 124.6, 117.5, 117.2, 86.6, 38.2, 22.9, 17.8. MS (EI, 70 eV): m/z (%) = 262 (10) (M^+), 219 (47), 178 (84), 144 (7), 114 (17), 84 (84), 69 (68), 43 (100). HRMS-EI: m/z (M^+) calcd for $\text{C}_{12}\text{H}_{16}\text{Cl}_2\text{O}_2$: 262.05273; found: 262.05200.

4-*tert*-Butoxyphenol.

Prepared according to method C from 1,4-benzoquinone (162 mg, 1.50 mmol) and 2,2-dimethyl-propionic acid 2-thioxo-2H-pyridin-1-yl ester¹ (634 mg, 3.00 mmol). FC (pentane/*t*-BuOMe 10:1). Yield 24%.

FT-IR (ATR): 3233, 2969, 1507, 1369, 1205, 1154, 849 cm^{-1} . ^1H -NMR (400 MHz, CDCl_3): δ = 6.88-6.84 (2H, m), 6.74-6.70 (2H, m), 1.30 (9H, s). ^{13}C -NMR (75 MHz, CDCl_3): δ = 151.8, 148.4, 125.5, 115.4, 78.2, 28.7. MS (EI, 70 eV): m/z (%) = 166 (15) (M^+), 151 (6), 110 (100), 81 (9). HRMS-EI: m/z (M^+) calcd for $\text{C}_{10}\text{H}_{14}\text{O}_2$: 166.09938; found: 166.09935.

1. Ling, T; Poupon, E.; Rueden, E. J.; Kim, S. H.; Theodorakis, E. A. *J. Am. Chem. Soc.* **2002**, *124*, 12261.

— 152.5999
— 149.4326

— 117.5868
— 115.9907

— 78.5464

— 47.5357
— 44.5587
— 41.4825
— 38.3400
— 35.9419
— 33.1716
— 27.4408
— 23.8105
— 21.0485

149.5200
147.1957
144.9661

133.4681
128.7205
127.5089
126.5281

116.8887
114.9146
113.7484

38.7804

20.9152

— 152.1040
— 149.4376
— 143.3094

— 128.5351
— 127.3976
— 125.6503

— 117.3420
— 115.8708

— 76.9217

— 24.3399

2D-NMR spectrum: $^{13}\text{C}/^1\text{H}$ -HMBC

$^1\text{H}\{^1\text{H}\}$ -NOE spectra

fm480 Proton_ns16 CDCl3 :disk0 service 22

*** Current Data Parameters ***

NAME : ga_33220

EXPNO : 10

PROCNO : 1

*** Acquisition Parameters ***

BF1 : 300.1800000 MHz

DATE_d : Mar 30 2006

EXP : Proton_ns16

*** Current Data Parameters ***

NAME : ga_33220
EXPNO : 11
PROCNO : 1

*** Acquisition Parameters ***

BFI : 75.4803210 MHz
DATE_d : Mar 30 2006
EXP : Carbon_ns256

22.5637
18.0824
16.1477
12.4105

39.0669

85.8646
77.4393
77.0177
76.5960

119.6564

130.1487

145.7010

(ppm)

10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160

*** Current Data Parameters ***

NAME : ga_33175
EXPNO : 10
PROCNO : 1

*** Acquisition Parameters ***

BF1 : 300.180000 MHz
DATE_d : Mar 30 2006
EXP : Proton_ns32

7.2600
6.0118
5.9773
5.9697
5.8053
5.8028
5.7972
5.7928
5.7884
5.7834
5.7802
5.7714
5.7689
5.7633
5.7589
5.7545
5.7488
5.7457

4.3990

3.5160
3.4928
3.4689
3.4457
2.6588
2.6506
2.6399
2.6318
2.6280
2.6192
2.6098
2.6010
2.2546
2.2458
2.2295
2.2257
2.1699
2.1391
2.0149
1.8053
1.7971
1.7795
1.7626
1.7431
1.5643
1.2329
1.2097
1.1865
1.0961
1.0497
1.0346
1.0114
0.9976
0.9731
0.9066
0.8840
0.8790
0.8602
0.8577

Integral

1.0000
1.1121

0.9700

0.7934

1.0015

1.0786

5.8390

5.8949

2.8714

2.2667

2.0129

1.6114

3.0485

2.9841

2.0197

*** Current Data Parameters ***

NAME : gb_1735
EXPNO : 10
PROCNO : 1

*** Acquisition Parameters ***

BF1 : 75.4677490 MHz
DATE_d : Mar 30 2006
EXP : dept135std

29.1666
28.8523
23.5846
23.0471
21.0542
20.6076
16.2248
15.2820
12.4208

47.1610

65.8584

76.6005
77.0222
77.4440

85.4323

119.6846

127.5489

130.1290

134.4374

140.3997

145.6095

147.2965

(ppm)