

Supporting Information

Dihydrobenzofurans production from catalytic tandem Claisen rearrangement–intramolecular hydroaryloxylation of allyl phenyl ethers in subcritical water

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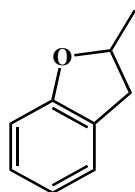
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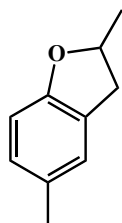
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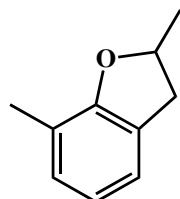
NMR Characterizations



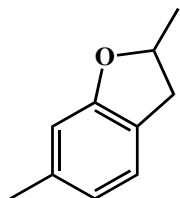
2-methyl-2,3-Dihydro-benzofuran (Table 1, entry 4): ^1H NMR (CDCl_3 , 400 MHz): δ 7.13 (d, $J = 7.6$ Hz, 1 H), 7.09 (t, $J = 7.6$ Hz, 1 H), 6.82 (t, $J = 7.2$ Hz, 1 H), 6.74 (d, $J = 7.6$ Hz, 1 H), 4.91 (m, 1 H), 3.32 (dd, $J = 15.2, 8.8$ Hz, 1 H), 2.81 (dd, $J = 15.2, 7.6$ Hz, 1 H), 1.45 (d, $J = 6.4$ Hz, 3 H).



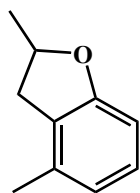
2,5-dimethyl-2,3-dihydrobenzofuran (Table 4, entry 1): ^1H NMR (CDCl_3 , 400 MHz): δ : 6.97 (s, 1 H), 6.90 (d, $J = 8.2$ Hz, 1 H), 6.66 (d, $J = 8.2$ Hz, 1 H), 4.90 (dt, $J = 6.4, 8.0$ Hz, 1 H), 3.26 (dd, $J = 8.6, 15.2$ Hz, 1 H), 2.78 (dd, $J = 7.7, 15.2$ Hz, 1 H), 2.28 (s, 3 H), 1.46 (d, $J = 6.5$ Hz, 3 H).



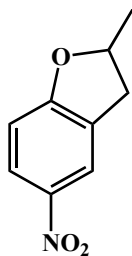
2,7-dimethyl-2,3-dihydrobenzofuran (Table 4, entry 2): ^1H NMR (CDCl_3 , 400 MHz): δ : 6.98 (d, $J = 7.5$ Hz, 1 H), 6.93 (d, $J = 7.5$ Hz, 1 H), 6.73 (t, $J = 7.5$ Hz, 1 H), 4.94 (dt, $J = 6.1, 8.1$ Hz, 1 H), 3.28 (dd, $J = 8.6, 15.3$ Hz, 1 H), 2.81 (dd, $J = 7.7, 15.2$ Hz, 1 H), 2.20 (s, 3 H), 1.46 (d, $J = 6.2$ Hz, 3 H).



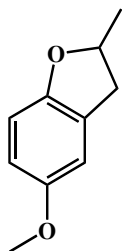
2,6-dimethyl-2,3-dihydro-benzofuran (Table 4, entry 3A): ^1H NMR (CDCl_3 , 400 MHz): δ : 6.89 (d, $J = 7.4$ Hz, 1 H), 6.57 (t, $J = 7.3$ Hz, 1 H), 6.52 (d, $J = 7.5$ Hz, 1 H), 4.25 (dt, $J = 6.4, 8.0$ Hz, 1 H), 3.06 (dd, $J = 8.5, 15.6$ Hz, 1 H), 2.81 (dd, $J = 7.6, 15.1$ Hz, 1 H), 2.35 (s, 3 H), 1.43 (d, $J = 6.1$ Hz, 3 H).



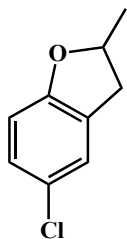
2,4-dimethyl-2,3-dihydrobenzofuran (Table 4, entry 3B): ^1H NMR (CDCl_3 , 400 MHz); δ : 7.05 (t, $J = 8.0$ Hz, 1 H), 6.69 (d, $J = 8.0$ Hz, 1 H), 6.64 (d, $J = 8.0$ Hz, 1 H), 4.95 (br s, $J = 7$ Hz, 1 H), 3.27 (dd, $J = 16.0$ Hz, 1 H), 2.75 (dd, $J = 7.5, 16.0$ Hz, 1 H), 2.27 (s, 3 H), 1.51 (d, $J = 5.9$ Hz, 3 H).



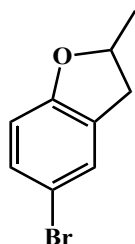
2-methyl-5-nitro-2,3-dihydrobenzofuran (Table 4, entry 4): ^1H NMR (CDCl_3 , 400 MHz); δ : 7.85 (s, 1 H), 7.90 (d, $J = 8.1$ Hz, 1 H), 7.02 (d, $J = 8.3$ Hz, 1 H), 5.10 (m, 1 H); 3.55 (dd, $J = 15.6, 9.3$ Hz, 1 H); 3.18 (dd, $J = 15.6$ Hz, 1 H), 3.03 (dd, $J = 7.5$ Hz, 1 H); 1.82 (d, $J = 6.2$ Hz, 3 H).



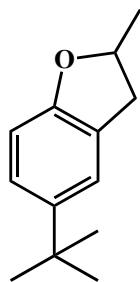
5-methoxy-2-methyl-2,3-dihydrobenzofuran (Table 4, entry 5): ^1H NMR (CDCl_3 , 400 MHz); δ : 6.75 (s, 1H), 6.64 (s, 2H), 4.91 (dt, $J = 6.0, 8.2$ Hz, 1H), 3.75 (s, 3H), 3.29 (dd, $J = 8.6, 14.7$ Hz, 1 H), 2.78 (dd, $J = 7.7, 14.7$ Hz, 1 H), 1.46 (d, $J = 6.0$ Hz, 3 H).



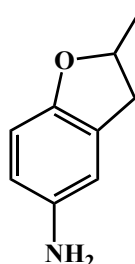
2,3-Dihydro-5-chloro-2-methylbenzofuran (Table 4, entry 6): ^1H NMR (CDCl_3 , 400 MHz); δ : 1.45 (d, $J = 6.3$ Hz, 3 H), 2.74 (dd, $J = 15.5$ Hz, 1 H), 2.85 (dd, $J = 7.5$ Hz, 1 H), 3.27 (dd, $J = 8.8, 15.5$ Hz, 1 H), 4.91 (m, 1 H), 6.65 (d, $J = 8.3$ Hz, 1 H), 7.04 (d, $J = 8.3$ Hz, 1 H), 7.10 (s, 1 H).



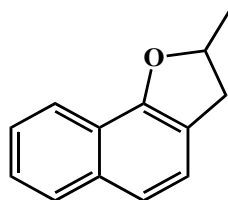
5-bromo-2-methyl-2,3-dihydrobenzofuran (Table 4, entry 7): ^1H NMR (CDCl_3 , 400 MHz) δ : 7.22 (s, 1 H), 7.18 (d, $J=8.1$ Hz, 1 H), 6.62 (d, $J=8.3$ Hz, 1 H), 4.94 (m, 1 H), 3.28 (dd, 1 H), 2.78 (dd, $J=15.4$ Hz, 1 H), 1.45 (d, $J=6.7$ Hz, 3 H).



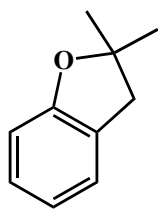
5-tert-Butyl-2,3-dihydro-2-methylbenzofuran (Table 4, entry 8): ^1H NMR (CDCl_3 , 400 MHz): δ : 7.26 (s, 1 H), 7.12 (d, $J=8.41$ Hz, 1 H), 6.67 (d, $J=8.36$ Hz, 1 H), 4.90 (m, 1 H), 3.29 (dd, $J=8.74, 6.55$ Hz, 1 H), 2.80 (dd, $J=7.87, 7.42$ Hz, 1 H), 1.46 (d, $J=6.31$ Hz, 3 H), 1.29 (s, 9 H).



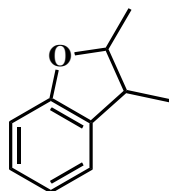
2-methyl-2,3-dihydrobenzofuran-5-amine (Table 4, entry 9): ^1H NMR (CDCl_3 , 400 MHz): δ : 6.92 (s, 1 H), 6.67 (d, $J=7.9$ Hz, 1 H), 6.43 (d, $J=8.1$ Hz, 1 H), 4.25 (m, 1 H), 4.0 (s, 2 H), 3.36 (dd, $J=15.5$ Hz, 1 H), 2.93 (dd, $J=15.4$ Hz, 1 H), 1.43 (d, $J=6.7$ Hz, 3 H).



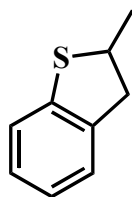
2,3-Dihydro-2-methylnaphthofuran (Table 4, entry 10): ^1H NMR (CDCl_3 , 400 MHz) δ : 7.98 (d, $J=2.5$ Hz, 1 H), 7.80 (d, $J=2.5$ Hz, 1 H), 7.45-7.31 (m, 4 H), 5.19-5.13 (m, 1 H), 3.51 (dd, $J=9.1, 15.0$ Hz, 1 H), 2.98 (dd, $J=7.5, 15.0$ Hz, 1 H), 1.58 (d, $J=6.3$ Hz, 3 H).



2,2-dimethyl-2,3-Dihydrobenzofuran (Table 4, entry 11) ^1H NMR (CDCl_3 , 400 MHz) δ : 7.17 (m, 1H), 7.11(m, 1H), 6.84 (t, J = 7.3 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 3.01 (s, 2H), 1.50 (s, 6H).



2,3-dimethyl-2,3-dihydrobenzofuran (Table 4, entry 12): ^1H NMR (CDCl_3 , 400 MHz): δ : 7.15 (m, 1 H), 7.11(d, J = 8.0 Hz, 1H), 6.88 (m, 1H), 6.79 (m, 1 H), 4.35 (dq, J = 8.3, 6.3 Hz, 1H), 3.09 (m, 1 H), 1.49 (d, J = 6.3 Hz, 3H), 1.32 (d, J = 6.9 Hz, 3H).



2-methyl-2,3-dihydrobenzothiophene (Table 4, entry 13): ^1H NMR (CDCl_3 , 400 MHz): δ : 7.28 (s, 1 H), 7.10 (d, J = 7.5 Hz, 1 H), 7.15(d, J = 8.1 Hz, 1 H), 6.94 (m, 1 H), 3.96 (m, 1H), 3.36 (dd, J = 15.5 Hz, 1H), 2.93 (dd, J = 15.3 Hz, 1 H), 1.43 (d, J = 6.7 Hz, 3H).