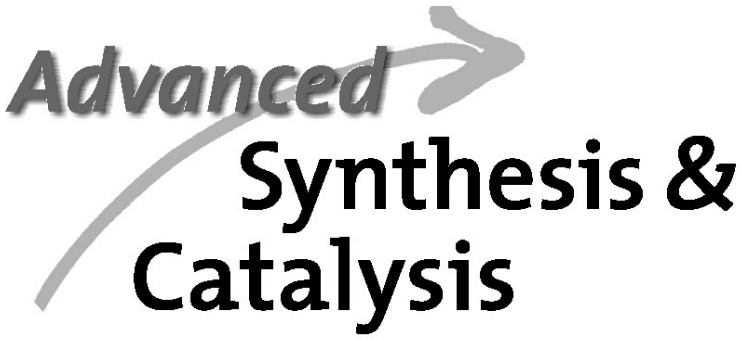

Supporting Information

Supporting information

Synthesis of 3-Substituted Furans by Hydroformylation

Perli Nanayakkara and Howard Alper*

Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa, Ontario, K1N 6N5, Canada

Fax: 1-613-562-5871, email: howard.alper@science.uottawa.ca

1-[4-(3-Hydroxy-1-propynyl)-phenyl]-ethanone (1b): ^{1}H NMR (300 MHz, $CDCl_3$) d 7.86 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 4.50 (s, 2H), 2.56 (s, 3H), 2.02, (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) d 197.6, 136.3, 131.7, 128.2, 127.5, 90.7, 84.7, 51.3, 26.6; MS (m/e) 174 (M^+); EIHRMS calcd for $C_{11}H_{10}O_2$ 174.0681, found 174.0695.

3-(4-Trifluoromethyl-phenyl)-2-propyn-1-ol (1c): ^{1}H NMR (300 MHz, $CDCl_3$) d 7.56-7.48 (dd, *J* = 7.5 Hz, 7.4 Hz, 4H), 4.49 (s, 2H), 2.02 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) d 131.9, 130.4, 126.3, 125.3, 125.2, 89.6, 84.3, 51.5; MS (m/e) 200 (M^+); EIHRMS calcd for $C_{10}H_7O_1F_3$ 200.0449, found 200.0456.

3-(Naphthalen-1-yl)-2-propyn-1-ol (1d): ^{1}H NMR (300 MHz, $CDCl_3$) d 8.34-7.37 (m, 7H), 4.64 (s, 2H), 2.14 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) d 133.2, 133.0, 130.6, 128.9, 128.2, 126.8, 126.4, 125.9, 125.1, 120.1, 92.0, 83.7, 51.8; MS (m/e) 182 (M^+); EIHRMS calcd for $C_{13}H_{10}O_1$ 182.0732, found 182.0713.

3-(Thiophen-2-yl)-2-propyn-1-ol (1e): ^{1}H NMR (300 MHz, $CDCl_3$) d 7.24-6.93 (m, 3H), 4.48 (s, 2H), 2.2 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) d 132.3, 127.4, 126.9, 122.4, 91.2, 78.9, 51.6; MS (m/e) 138 (M^+); EIHRMS calcd for $C_7H_6O_1S_1$ 138.0139, found 138.0169.

3-(4-Aminophenyl)-2-propyn-1-ol (1f): ^{1}H NMR (300 MHz, $CDCl_3$) d 7.35 (d, *J* = 8.6 Hz, 2H), 6.57 (d, *J* = 7.1 Hz, 2H), 4.44 (s, 2H), 3.81 (s, 2H), 2.0 (s, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) d 148.5, 133.1, 114.6, 112.8, 90.4, 84.3, 51.8; MS (m/e) 147 (M^+); EIHRMS calcd for $C_9H_9O_1N_1$ 147.0684, found 147.0714.

2-(3-Hydroxy-1-propynyl)phenol (1g): ^{1}H NMR (300 MHz, $CDCl_3$) d 7.52-6.61 (m, 4H), 5. 12 (s, 1H), 4.75 (s, 2H), 2.19 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) d 156.4, 128.1, 124.3, 122.8, 121.1, 111.2, 104.1, 90.2, 58.1; MS (m/e) 148 (M^+); EIHRMS calcd for $C_9H_8O_2$ 148.0524, found 148.0543.

3-(4-Ethylphenyl)-2-propyn-1-ol (1h): ^{1}H NMR (300 MHz, $CDCl_3$) d 6.63 (d, *J* = 7.6 Hz, 2H), 5.99 (d, *J* = 7.7 Hz, 2H), 4.15 (s, 2H), 2.79 (q, *J* = 7.4 Hz, 2H), 2.0 (s, 1H), 1.23 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) d 138.9, 131.8, 128.9, 119.2, 87.6, 86.1, 51.2, 21.3, 16.7; MS (m/e) 160 (M^+); EIHRMS calcd for $C_{11}H_{12}O_1$ 160.0888, found 160.0897.

3-*p*-Tolyl-2-propyn-1-ol (1i): ^{1}H NMR (300 MHz, $CDCl_3$) d 7.30 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 4.46 (s, 2H), 2.32 (s, 3H), 2.03 (s, 1H); ^{13}C NMR (75 MHz,

$CDCl_3$) d 139.2, 131.9, 129.4, 119.7, 87.1, 86.3, 51.7, 21.8; MS (m/e) 146 (M^+); EIHRMS calcd for $C_{11}H_{12}O_1$ 146.0732, found 146.0743.

3-(4-Methoxyphenyl)-2-propyn-1-ol (1j): ^{1}H NMR (300 MHz, $CDCl_3$) d 7.21 (d, *J* = 7.4 Hz, 2H), 6.42 (d, *J* = 7.6 Hz, 2H), 4.22 (s, 2H), 3.69 (s, 3H), 2.0 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) d 159.2, 138.7, 118.5, 114.2, 89.7, 86.5, 57.5, 51.3; MS (m/e) 162 (M^+); EIHRMS calcd for $C_{10}H_{10}O_2$ 162.0681, found 162.0694.

3-(3-Methoxyphenyl)-2-propyn-1-ol (5.19j): ^{1}H NMR (300 MHz, $CDCl_3$) d 6.62-7.22 (m, 4H), 4.33 (s, 2H), 3.65 (s, 3H)); ^{13}C NMR (75 MHz, $CDCl_3$) d 160.1, 132.1, 121.2, 118.5, 115.2, 89.2, 86.4, 57.3, 51.1; MS (m/e) 162 (M^+); EIHRMS calcd for $C_{10}H_{10}O_2$ 162.0681, found 162.0698.

3-(3-Bromophenyl)-2-propyn-1-ol (5.19k): ^{1}H NMR (300 MHz, $CDCl_3$) d 7.56 (s, 1H), 7.45-7.16 (m, 3H), 4.47 (s, 2H), 1.65 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) d 134.4, 131.7, 130.2, 129.8, 124.5, 122.1, 88.5, 84.2, 51.5; MS (m/e) 210 (M^+); EIHRMS calcd for $C_9H_7O_1Br_1$ 209.9680, found 209.9673.

3-Phenylfuran (2a): ^{1}H NMR (300 MHz, $CDCl_3$) d 7.72-7.22 (m, 7H), 6.69 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) d 144.1, 138.5, 132.5, 129.2, 127.3, 126.8, 125.9, 109.3; MS (m/e) 144 (M^+); EIHRMS calcd for $C_{10}H_8O_1$144.0575, found 144.0584.

1-(4-Furan-3-yl-phenyl)ethanone (2b): ^{1}H NMR (300 MHz, $CDCl_3$) d 7.94-7.49 (m, 6H), 6.73 (m, 1H), 2.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) d 197.5, 144.1, 139.6,

137.2, 135.5, 129.0, 125.7, 125.6, 108.6, 26.6; MS (m/e) 186 (M^+), 171, 143, 115; EIHRMS calcd for $C_{12}H_{10}O_2$ 186.0681, found 186.0664.

3-(4-Trifluoromethylphenyl)furan (2c): ^{1}H NMR (300 MHz, $CDCl_3$) d 7.78-7.49 (m, 6H), 6.71 (dd, *J* = 1.8 Hz, 2.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) d 144.1, 139.3, 137.1, 129.2, 125.9, 125.9, 125.8, 125.7, 108.6; MS (m/e) 212 (M^+), 193, 183, 162, 133, 115; EIHRMS calcd for $C_{11}H_7O_1F_3$ 212.0449, found 212.0446.

3-(Naphthalen-1-yl)furan (2d): ^{1}H NMR (300 MHz, $CDCl_3$) d 8.14-7.46 (m, 9H), 6.69 (m, 1H);^{13}C NMR (75 MHz, $CDCl_3$) d 143.8, 138.5, 136.3, 134.5, 132.1, 130.1, 128.4, 126.5, 125.8, 124.4, 109.2; MS (m/e) 194 (M^+), 165, 115, 82; EIHRMS calcd for $C_{14}H_{10}O_1$ 194.0732, found 194.0722.

3-(Thiophen-2-yl)furan (2e): ^{1}H NMR (300 MHz, $CDCl_3$) d 7.66-7.0 (m, 5H), 6.6 (dd, *J* = 2.7 Hz, 3.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) d 143.5, 138.1, 137.3, 129.1, 127.5, 123.6, 123.3 109.4; MS (m/e) 150 (M^+), 121, 112, 69; EIHRMS calcd for $C_8H_6O_1S_1$ 150.0139, found 150.0143.

3-(4-Ethylphenyl)furan (2h): ^{1}H NMR (300 MHz, $CDCl_3$) d 7.68-6.67 (m, 6H), 6.67 (m, 1H), 2.64 (q, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) d 142.4, 141.1, 138.2, 133.6, 130.3, 127.9, 125.9, 109.3; MS (m/e) 172 (M^+), 157, 128, 115; EIHRMS calcd for $C_{12}H_{12}O$ 172.0888, found 172.0892.

3-p-Tolylfuran (2i): ^{1}H NMR (300 MHz, $CDCl_3$) d 7.68-7.16 (m, 6H), 6.66 (m, 1H) ,2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) d 143.6, 138.5, 137.1, 133.4, 129.9, 127.7, 126.2, 109.3, 22.7; MS (m/e) 158 (M^+), 143; EIHRMS calcd for $C_{11}H_{10}O$ 158.0732 , found 158.0699.

3-(4-methoxyphenyl)furan (2j): ^{1}H NMR (300 MHz, $CDCl_3$) d 7.64-6.89 (m, 6H), 6.64 (m, 1H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) d 143.9, 138.0, 128.7, 127.4, 126.4, 125.4, 114.6, 109.2, 55.7; MS (m/e) 174 (M^+), 159, 131, 102, 77, 51; EIHRMS calcd for $C_{11}H_{10}O_2$ 174.0681, found 174.0699.

3-(3-Methoxyphenyl)furan (2k): ^{1}H NMR (300 MHz, $CDCl_3$) d 7.71-6.78 (m, 6H), 6.67 (m, 1H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) d 163.2, 143.6, 138.6, 133.8, 129.8, 126.4, 118.4, 112.2, 111.7, 108.9, 55.2; MS (m/e) 174 (M^+), 131, 115, 102, 77, 51; EIHRMS calcd for $C_{11}H_{10}O_2$ 174.0681, found 174.0698.

3-(3-Bromophenyl)furan (2l): ^{1}H NMR (300 MHz, $CDCl_3$) d 7.70-7.19 (m, 4H), 6.65 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) d 144.3, 139.3, 134.9, 130.7, 130.2, 129.2, 125.6, 124.8, 123.3, 109.0; MS (m/e) 222 (M^+), 193, 115; EIHRMS calcd for $C_{10}H_7O_1Br_1$ 221.9680, found 221.9664.

3-(3,5-Bis-trifluoromethylphenyl)furan (2m): ^{1}H NMR (300 MHz, $CDCl_3$) d 7.86-7.53 (m, 5H), 6.73 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) d 144.6, 139.7, 134.7, 132.2, 131.9, 125.7, 120.5, 120.3, 108.4; MS (m/e) 280 (M^+), 251, 232, 183, 133; EIHRMS calcd for $C_{12}H_6O_1F_6$ 280.0323, found 280.0329.

4-(Furan-3-yl)benzonitrile (2n): ^{1}H NMR (300 MHz, $CDCl_3$) d 7.79-7.49 (m, 7H), 6.68 (m, 1H) ; ^{13}C NMR (75 MHz, $CDCl_3$) d 144.4, 139.8, 137.0, 132.6, 126.1, 125.1, 118.9, 110.3, 108.4; MS (m/e) 169 (M^+), 140, 114; EIHRMS calcd for $C_{11}H_7O_1N_1$ 169.0528, found 169.0529.