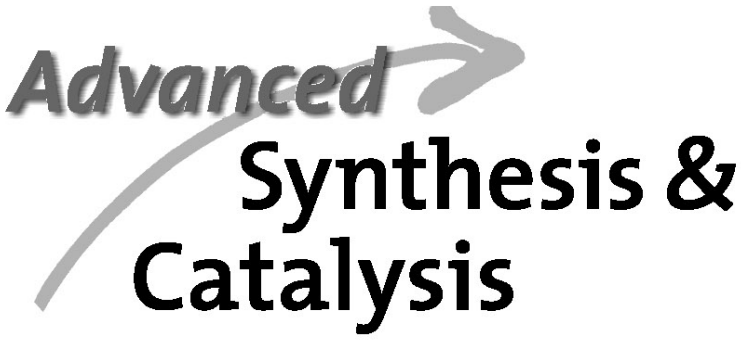

Supporting Information

Supporting Information for

Gold-catalyzed Benzylation of Arenes and Heteroarenes

Kristin Mertins, Irina Iovel, Jette Kischel, Alexander Zapf, Matthias Beller*

Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Str. 29a, 18059 Rostock, Germany

Fax: +49 381 / 12 81 5000, e-mail: matthias.beller@ifok-rostock.de

General remarks: ^{1}H an ^{13}C-NMR spectra were recorded on a Bruker ARX 400 spectrometer. Chemical shifts (d) are given in ppm and refer as the internal standard to the residual solvent ($CDCl_3$: 7.26 ppm) or TMS: 0.00 ppm. Gas chromatography was performed on a Hewlett Packard HP 6890 chromatograph with a HP5 column. Mass spectra were recorded on a AMD 402/3 mass spectrometer.

1-(4-Tolyl)-1-phenylethane (1a):
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): d = 1.55 (d, ^{3}J(H,H) = 7.1 Hz, 3 H; CH_3), 2.22 (s, 3 H; CH_3), 4.04 (q, ^{3}J(H,H) = 7.1 Hz, 1 H; CHCH_3), 7.02–7.29 (m, 9 H; arom. CH) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): d = 21.4, 22.4, 44.8, 126.4, 127.9, 128.8, 129.4, 135.9, 143.8, 147.0 ppm; MS (70 eV): *m/z* (%): 196 (46) [M^+], 181 (100) [M^+–CH_3], 166 (39), 165 (42).

1-(2,5-Dimethylphenyl)-1-phenylethane (1b):
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): d = 1.70 (d, ^{3}J(H,H) = 7.1 Hz, 3 H; CH_3CH), 2.29 (s, 3 H; CH_3), 2.42 (s, 3 H; CH_3), 4.39 (q, ^{3}J(H,H) = 7.1 Hz, 1 H; CHCH_3), 7.03-7.37 (m, 8 H; arom. CH) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): d = 19.3, 21.2, 22.1, 40.9, 125.7, 126.7, 127.6, 128.3, 130.3, 132.9, 135.3, 143.7, 146.3 ppm; IR (kap/KBr): ν~ 1495, 810, 699 cm^{-1}; MS (70 eV): m/z (%): 210 (46) [M^+], 195 (100) [M^+-CH_3], 180 (20), 165 (19); HR-MS (70 eV): calcd for $C_{16}H_{18}$: 210.14085, found 210.1395.

1,2-Dimethyl-4-(1-phenylethyl)-benzene (1c):
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): d = 1.54 (d, ^{3}J (H,H) = 7.2 Hz, 3 H; CH_3CH), 2.12 (s, 6 H, 2 ArCH_3), 4.02 (q, ^{3}J (H,H) = 7.2 Hz, 1 H; CHCH_3), 6.9-7.2 (m, 8 H, CH) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): d = 18.3, 18.8, 20.9, 43.2, 123.8, 124.8, 126.5, 127.3, 127.9, 128.6, 133.1, 135.4, 142.8, 145.6 ppm; IR (kap): ν~ 1494, 1451, 699 cm^{-1}; MS (70 eV): m/z (%): 210 (40) [M^+], 195 (100) [M^+ – CH_3]; HR-MS (70 eV): calcd for $C_{16}H_{18}$: 210.14085, found 210.14085.

1-Methoxy-4-(1-phenylethyl)-benzene (1d):
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): d = 1.51 (d, ^{3}J(H,H) = 7.1 Hz, 3 H; CH_3CH), 3.63 (s, 3 H; OCH_3), 3.98 (q, ^{3}J(H,H) = 7.1 Hz, 1 H; CHCH_3), 6.70 (dt, ^{3}J(H,H) = 8.7 Hz, ^{4}J(H,H) = 2.2 Hz, 2 H; CH), 7.01 (m, ^{3}J(H,H) = 8.7 Hz, ^{4}J(H,H) = 2.2 Hz, 2 H; CH), 7.05–7.2 (m, 5 H; arom. CH) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): d = 22.6, 44.5, 55.7, 114.3, 126.5, 128.1, 128.9, 129.1, 139.1, 147.3, 158.4 ppm; MS (70 eV): *m/z* (%): 212 (47) [M^+], 197 (100) [M^+–CH_3], 182 (12), 165 (22), 153 (22).

1,4-Dimethoxy-2-(1-phenylethyl)-benzene (1e):
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): d = 1.46 (d, ^{3}J(H,H) = 7.1 Hz, 3 H; CH_3CH), 3.58 (s, 3 H; OCH_3), 3.60 (s, 3 H; OCH_3), 4.45 (q, ^{3}J(H,H) = 7.1 Hz, 1 H; CHCH_3), 6.57 (dd, ^{3}J(H,H) = 8.7 Hz, ^{4}J(H,H) = 3.0 Hz, 1 H), 6.64 (d, ^{3}J(H,H) = 8.7 Hz, 1 H), 6.65 (d, ^{4}J(H,H) = 3.0 Hz, 1 H), 7.05–7.15

(m, 5 H; arom. C*H*) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): d = 21.4, 38.1, 56.0, 56.6, 110.9, 112.1, 115.1, 115.2, 126.3, 128.2, 128.6, 136.8, 146.6, 151.7, 154.1 ppm; MS (70 eV): *m/z* (%): 242 (100) [M^+], 227 (45) [M^+–CH_3], 211 (15), 165 (20), 152 (16), 103 (20), 91 (90).

4-Chloro-1-methoxy-2-(1-phenylethyl)-benzene (1f):
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): d = 1.59 (d, ^3J(H,H) = 7,1 Hz, 3 H, CH_3CH), 3.76 (s, 3 H; OCH_3), 4.56 (q, ^3J(H,H) = 7,1 Hz, 1 H, C*H*CH_3), 6.76 (d, ^3J(H,H) = 9,3 Hz, 1 H, C*H*), 7.14-7.33 (m, 7 H, arom. C*H*) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): d = 20.7, 37.4, 55.6, 11.7, 125.4 (CCl), 125.9, 126.7, 127.6, 127.7, 128.2, 136.7, 145.4, 155.4 ppm; IR (kap/KBr): ν~= 1487, 1245, 1131, 1029, 808, 699, 646; MS (70 eV): m/z (%): 246 (55) [M^+], 231 (43), 165 (17), 152 (12), 91 (100); HR-MS (70 eV): calcd for $C_{15}H_{15}ClO$: 246.08115, found 246.08134.

2-Chloro-1-methoxy-4-(1-phenylethyl)-benzene (1g):
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): d = 1.57 (d, ^3J(H,H) = 7,2 Hz, 3 H, CH_3CH), 3.82 (s, 3 H, OCH_3), 4.04 (q, ^3J(H,H) = 7,2 Hz, 1 H, C*H*CH_3), 6.80 (d, ^3J(H,H) = 8,5 Hz, 1 H, C*H*CH), 7.03 (dd, ^3J(H,H) = 8,5 Hz, 1 H, CHC*H*), 7.15-7.27 (m, 6 H, arom. C*H*) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): d = 21.8, 43.7, 56.1, 111.9, 122.1, 126.1, 126.7, 127.4, 128.4, 129.3, 139.6, 145.9, 153.2 ppm; IR (kap/KBr): ν~= 1501, 1254, 1066, 700 cm^{-1}; MS (70 eV): m/z (%): 246 (41) [M^+], 231 (100) [M^+-CH_3], 196 (15), 181 (11), 165 (13), 152 (18); HR-MS (70 eV): calcd for $C_{15}H_{15}ClO$: 246.08115, found 246.08103.

2-Iodo-1-methoxy-4-(1-phenylethyl)-benzene (1h):
^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): d = 1.50 (d, ^3J(H,H) = 7.3 Hz, 3 H; CH_3CH), 3.73 (s, 3 H; OCH_3), 3.96 (q, ^3J(H,H) = 7.3 Hz, 1 H; C*H*CH_3), 6.63 (d, ^3J(H,H) = 8.5 Hz, 1 H; C*H*), 7.03 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.4 Hz, 1 H; C*H*), 7.0–7.2 (m, 5 H; arom. C*H*), 7.55 (d, ^4J(H,H) = 2.4 Hz, 1 H; C*H*) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$, 25 °C): d = 22.4, 44.0, 56.8, 86.5, 111.2, 122.9, 126.6, 127.9, 128.9, 138.9, 141.1, 146.5, 156.8 ppm; IR (kap/KBr): ν~= 1489, 1249, 1051, 699 cm^{-1}; MS (70 eV): *m/z* (%): 338 (72) [M^+], 323 (100) [M^+–CH_3], 195 (10), 181 (14), 165 (39), 152 (24); HR-MS (70 eV): calcd for $C_{15}H_{15}IO$: 338.01675, found 338,.01655.

2-Methoxy-5-(1-phenylethyl)-benzaldehyde (1i):
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): d = 1.54 (d, ^3J(H,H) = 7.3 Hz, 3 H; CH_3CH), 3.79 (s, 3 H; OCH_3), 4.04 (q, ^3J(H,H) = 7.3 Hz, 1 H; C*H*CH_3), 6.80 (d, ^3J(H,H) = 8.7 Hz, 1 H; C*H*), 7.1–7.2 (m, 5 H; arom. C*H*), 7.28 (dd, ^3J(H,H) = 8.7 Hz, ^4J(H,H) = 2.4 Hz, 1 H; C*H*), 7.66 (d, ^4J(H,H) = 2.4 Hz, 1 H; C*H*), 10.36 (s, 1 H; C*H*O) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): d = 22.2, 44.3, 56.1, 112.2, 124.9, 126.6, 127.4, 127.9, 128.9, 135.8, 139.2, 146.4, 160.8, 190.4 ppm; IR (kap/KBr): ν~= 1682, 1495, 1252, 1025, 700 cm^{-1}; MS (70 eV): *m/z* (%): 240 (70) [M^+], 225 (100) [M^+–CH_3], 210 (10), 195 (14), 182 (18), 181 (20), 152 (21); HR-MS (70 eV): calcd for $C_{16}H_{16}O_2$: 240.11504, found 240.11455.

3-Methyl-2-(1-phenylethyl)-thiophene (1j):
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1,75 (d, ^3J(H,H) = 7,1 Hz, 3 H; CH_3CH); 2.15 (s, 3 H; CH_3), 4.45 (q, ^3J(H,H) = 7,1 Hz, 1 H; C*H*CH_3); 6.86 (d, ^3J(H,H) = 5.0 Hz, 1 H; C*H*) 7.13 (d, ^3J(H,H) = 5.0 Hz, 1 H; C*H*) 7.19-7.40 (m, 5 H; arom. C*H*) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 13.8, 23.5, 38.8, 121.2, 125.9 – 150.4 (m, C-Ar) ppm; IR (kap/KBr): ν~= 2968 (m), 1493 (m), 1451 (m), 699 (vs) cm^{-1}; MS (70 eV): *m/z* (%): 202 (31) [M^+], 187 (100) [M^+- CH_3], 171 (7) [M^+- 2 CH_3], 153 (6), 139 (3), 125 (6), 103 (3), 90 (3), 77 (5) [$C_6H_5^+$]; HR-MS (70 eV): calcd for $C_{13}H_{14}S$: 202.08162, found 202.08347.

2,5-Dimethyl-3-(1-phenylethyl)-furane (1k):
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): d = 1.42 (d, ^3J(H,H) = 7.3 Hz, 3 H; CH_3CH), 2.05 (s, 3 H; CH_3), 2.12 (s, 3 H; CH_3), 3.81 (q, ^3J(H,H) = 7.3 Hz, 1 H; C*H*CH_3), 5.75 (s, 1 H; C*H*), 7.05–7.21 (m,

5 H; arom. C*H*) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): d = 12.1, 14.0, 22.5, 36.0, 106.4, 124.5, 126.3, 127.5, 128.8, 145.1, 147.0 ppm; MS (70 eV): *m/z* (%): 200 (52) [M^+], 185 (100) [M^+–CH_3], 141 (12), 115 (11).

2-Acetyl-[5-(1-phenylethyl)-furane (1l):
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): d = 1.56 (d, ^3J(H,H) = 7.1 Hz, 3 H; CH_3CH), 2.32 (m, 3 H; COCH_3), 4.10 (q, ^3J(H,H) = 7.1 Hz, 1 H; C*H*CH_3), 6.07 (d, ^3J(H,H) = 3.6 Hz, 1 H; C*H*), 7.02 (d, ^3J(H,H) = 3.6 Hz, 1 H; C*H*), 7.0–7.3 (m, 5 H; arom. C*H*) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): d = 20.6, 26.2, 40.0, 108.6, 119.1, 127.3, 127.8, 129.1, 143.0, 152.2, 164.6, 186.8 ppm; IR (kap/KBr): ν~= 1511, 1675 cm^{-1}; MS (70 eV): *m/z* (%): 214 (55) [M^+], 199 (100) [M^+–CH_3], 171 (42), 128 (41), 115 (16); HR-MS (70 eV): calcd for $C_{14}H_{14}O_2$: 214.09938, found 214. 09925.

4-Benzyl-1,2-dimethyl-benzene (2a):
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): d = 2.16 (s, 6 H; 2 ArCH_3), 3.85 (s, 2 H; CH_2), 6.81-7.19 (m, 8 H, arom. C*H*) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): d = 18.2, 18.7, 40.5, 124.8, 127.3, 127.8, 128.6, 129.2, 133.0, 135.4, 137.4, 140.4 ppm; MS (70 eV): m/z (%): 196 (61) [M^+], 181 (100) [M^+–CH_3], 165 (33).

4-(4-Methoxybenzyl)-1,2-dimethyl-benzene (2b):
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): d = 2.13 (s, 6 H, 2 ArCH_3), 3.68 (s, 3 H; OCH_3), 3.82 (s, 2 H; CH_2), 6.71-7.02 (m, 7 H, arom. C*H*) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): d = 18.3, 39.6, 54.2, 112.8, 125.1, 128.6, 129.1, 131.8, 132.6, 133.0, 135.5, 137.9, 156.8 ppm; MS (70 eV): m/z (%): 226 (71) [M^+], 211 (100) [M^+–CH_3].

4-(4-Chlorobenzyl)-1,2-dimethyl-benzene (2c):
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): d = 2.14 (s, 6 H; 2 ArCH_3), 3.90 (s, 2 H; CH_2), 6.80 (d, ^3J(H,H) = 8.5 Hz, 1 H; C*H*), 6.85 (s, 1 H; C*H*), 6.97 (d, ^3J(H,H) = 8.5 Hz, 1 H; C*H*), 7.06 (dd, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 2.0 Hz, 2 H; C*H*), 7.31 (dd, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 2.0 Hz, 2 H; C*H*) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): d = 19.8, 20.2, 38.6, 116.2, 127.5, 129.6, 130.2, 130.6, 132.1, 135.1, 136.7, 137.2, 138.1 ppm; IR (kap/KBr): ν~= 1490, 1440, 1091, 1015, 800 cm^{-1}; MS (70 eV): *m/z* (%): 230 (85) [M^+], 215 (100) [M^+–CH_3], 195 (55) [M^+–Cl], 180 (55), 165 (53), 89 (28); HR-MS (70 eV): calcd for $C_{15}H_{15}Cl$: 230.08623, found 230.08619.

4-(4-Chlorobenzyl)-phenol (2d):
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): d = 3.95 (s, 2 H; CH_2), 6.69-6.91 (m, 2 H; arom. C*H*), 6.98-7.12 (m, 2 H; arom. C*H*), 7.18-7.27 (m, 4 H; arom. C*H*), 8.45 (s, 1 H; O*H*) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): d = 35.8, 115.9, 128.4, 128.8, 131.3, 131.8, 141.4, 155.9 ppm.

2-[4-(4-Chlorobenzyl)-phenoxy]-2-methylbutyrate (3)
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): d = 0.85 (t, ^3J (H,H) = 7.5 Hz, 3 H; CH_2CH_3), 1.18 (t, ^3J (H,H) = 7.1 Hz, 3 H; CH_2CH_3), 1.42 (s, 3 H; CCH_3), 1.90 (q, ^3J (H,H) = 5.2 Hz, 2 H; CH_2CH_3), 3.93 (s, 2 H; CH_2), 4.17 (q, ^3J (H,H) = 7.1 Hz, 2 H; CH_2CH_3), 6.54-6.64 (m, 1 H; arom. C*H*), 6.79-6.93 (m, 1 H; arom. C*H*), 7.04-7.23 (m, 6 H; arom. C*H*) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): d = 6.6, 12.9, 19.7, 32.6, 39.6, 60.9, 81.1, 115.1, 126.6, 127.6, 127.9, 129.8, 130.1, 139.9, 153.2, 173.8 ppm.