**Palladium-catalyzed Heck arylations of allyl alcohols in ionic liquids:
remarkable base effect on the selectivity**

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SUPPORTING INFORMATION

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General Methods. All chemicals used for synthetic procedures, including the tetraalkylammonium salts, were commercially available. As a number of the reaction products did not furnish suitable chromatographic peaks, the product ratios were evaluated on the basis of their ^1H -NMR signals (see spectra reported in pages S5-S25).

The reaction products were identified by comparison of their spectral data with those reported in the literature. The major unknown isomers have been isolated by silica gel chromatography (eluent petroleum ether/ethyl acetate) and their characterisation data are given below.

Characterisation data of the major unknown isomers.

2-p-Tolyloct-1-en-3-ol (4b): oil. ^1H -NMR (CDCl_3 , 500 MHz): δ = 0.79 (t, J = 7.4 Hz, 3 H), 1.11-1.45 (m, 6 H), 1.50-1.70 (m, 2 H), 2.20 (br s, 1 H), 2.29 (s, 3 H), 4.39 (t, J = 6.3 Hz, 1 H), 5.25 (m, 1 H), 5.29 (m, 1 H), 7.05 (m, 2 H), 7.18 (m, 2 H). ^{13}C -NMR (CDCl_3 , 500 MHz) δ = 14.03, 21.01, 22.40, 22.47, 25.19, 31.56, 73.76, 111.69, 126.64, 129.02, 131.04, 136.58, 143.77. IR (KBr): 3400 (br), 2970, 2932, 695 cm^{-1} . MS: m/z (%) 217 (1), 160 (22), 145 (100), 115 (30), 91 (12). $\text{C}_{15}\text{H}_{22}\text{O}$ (218,16): calcd. C, 82.52; H, 10.16; O, 7.33; found: C, 82.61; H, 10.20; O, 7.19.

2-(4-Methoxyphenyl)oct-1-en-3-ol (5b): yellow oil. ^1H -NMR (CDCl_3 , 500 MHz): δ = 0.80 (t, J = 7.4 Hz, 3 H), 1.10-1.48 (m, 6 H), 1.50-1.68 (m, 2 H), 2.12 (br s, 1 H), 3.76 (s, 3 H), 4.37 (t, J = 6.1 Hz, 1 H), 5.22 (m, 1 H), 5.26 (m, 1 H), 6.81 (d, J = 8.6 Hz, 2 H), 7.09 (d, J = 8.6 Hz, 2 H). ^{13}C -NMR (CDCl_3 , 500 MHz) δ = 13.87, 22.34, 23.36, 25.23, 31.27, 54.98, 73.89, 111.20, 113.38, 127.89, 129.14, 132.12, 142.29, 158.45. IR (KBr): 3400 (br), 2960, 2945, 690 cm^{-1} . MS: m/z (%) 233 (1), 176 (30), 161 (100), 133 (28), 121 (13), 89 (8). $\text{C}_{15}\text{H}_{22}\text{O}_2$ (234,16): calcd. C, 76.88; H, 9.46; O, 13.66; found: C, 76.96; H, 9.52; O, 13.52.

1-[4-((E)-3-Hydroxy-oct-1-enyl)-phenyl]-ethanone (6a): yellow oil. ^1H -NMR (CDCl_3 , 500 MHz): δ = 0.80 (t, J = 7.1 Hz, 3 H), 1.22-1.55 (m, 6 H), 1.57-1.80 (m, 2 H), 2.10 (br s, 1 H), 2.55 (s, 3 H), 4.33 (q, J = 6.4 Hz, 1 H), 6.38 (dd, J = 6.4, 16 Hz, 1 H), 6.61 (d, J = 16 Hz, 1 H), 7.43 (m, 2 H), 7.88 (m, 2 H). ^{13}C -NMR (CDCl_3 , 500 MHz) δ = 13.93, 21.05, 25.03, 29.26, 31.68, 37.17, 73.14, 126.25, 129.12, 130.07, 131.34, 137.23, 143.72, 198.72. IR (KBr): 3400 (br), 2962, 2925, 1680, 690 cm^{-1} . MS: m/z (%) 231

(25), 228 (43), 175 (42), 147 (53), 115 ((100), 105 (35), 77 (22). $C_{16}H_{22}O_2$ (246.16): calcd. C, 78.01; H, 9.00; O, 12.99; found: C, 78.25; H, 9.05; O, 12.7.

1-(4-(3-Hydroxyoct-1-en-2-yl)phenyl)ethanone (6b): oil. 1H -NMR ($CDCl_3$, 500 MHz): δ = 0.86 (t, J = 7.1 Hz, 3 H), 1.20-1.75 (m, 8 H), 2.20 (br s, 1 H), 2.59 (s, 3 H), 4.64 (t, J = 5.9 Hz, 1 H), 5.37 (m, 1 H), 5.47 (m, 1 H), 7.26 (d, J = 8.4 Hz, 2 H), 7.49 (d, J = 8.4 Hz, 2 H). ^{13}C -NMR ($CDCl_3$, 500 MHz) δ = 13.61, 20.72, 22.13, 23.17, 24.71, 31.33, 73.31, 114.19, 126.87, 129.62, 131.15, 135.68, 144.88, 197.89. IR (KBr): 3400 (br), 2968, 2950, 696 cm^{-1} . MS: m/z (%) 243 (1), 188 (89), 145 (100), 131 (94), 115 (20), 91 (15). $C_{16}H_{22}O_2$ (246.16): calcd. C, 78.01; H, 9.00; O, 12.99; found: C, 78.15; H, 9.06; O, 12.79.

1-(4-Acetyl-phenyl)-octan-3-one (6c): yellow oil. 1H -NMR ($CDCl_3$, 500 MHz): δ = 0.87 (t, J = 7.1 Hz, 3 H), 1.18-1.33 (m, 4 H), 1.50-1.59 (m, 2 H), 2.38 (t, J = 7.4 Hz, 2 H), 2.57 (s, 3 H), 2.76 (t, J = 7.4 Hz, 2 H), 2.95 (t, J = 7.4 Hz, 2 H), 7.28 (m, 2 H), 7.87 (m, 2 H). IR (KBr): 3080, 2955, 1699, 1677, 825 cm^{-1} . ^{13}C -NMR ($CDCl_3$, 500 MHz) δ = 13.78, 22.30, 23.30, 26.43, 29.49, 32.21, 42.85, 43.41, 128.46, 129.71, 135.08, 146.91, 197.63, 209.60. MS: m/z (%) 246 (M^+ , 5), 231 (47), 190 (56), 147 (100), 133 (85), 105 (87), 103 (19), 89 (16). $C_{16}H_{22}O_2$ (246.16): calcd. C, 78.01; H, 9.00; O, 12.99; found: C, 78.20; H, 8.95; O, 12.85.

1-(4-((Z)-3-hydroxy-1-phenylprop-1-en-2-yl)phenyl)ethanone (8b): yellow oil. 1H -NMR ($CDCl_3$, 500 MHz): δ = 2.10 (br s, 1 H), 2.56 (s, 3 H), 4.72 (s, 2 H), 7.06 (s, 1 H), 7.11 (m, 1 H), 7.28 (m, 2 H), 7.34 (m, 2 H), 7.58 (m, 2 H), 7.79 (m, 2 H). IR (KBr): 3400 (br), 2982, 1675, 690 cm^{-1} . ^{13}C -NMR ($CDCl_3$, 500 MHz) δ = 30.38, 64.20, 126.50, 127.22, 128.13, 128.27, 128.43, 128.83, 133.00, 135.52, 136.56, 146.85, 197.16. MS: m/z (%) 252 (M^+ , 2), 221 (10), 209 (20), 179 (11), 78 (5). $C_{17}H_{16}O_2$ (252.115): calcd. C, 80.93; H, 6.39; O, 12.68; found: C, 80.99; H, 6.35; O, 12.66.

2-(4-acetylphenyl)-3-phenylpropanal (8d): yellow oil. 1H -NMR ($CDCl_3$, 500 MHz): δ = 2.54 (s, 3 H), 2.98 (dd, J = 8.4, 14.0 Hz, 1 H), 3.47 (dd, J = 6.4, 14.0 Hz, 1 H), 3.94 (m, 1 H), 6.93-7.49 (m, 7 H), 7.89 (m, 2 H), 9.75 (d, J = 1.2 Hz, 1 H). IR (KBr): 3089, 2855, 2752, 1722, 1680, 692 cm^{-1} . ^{13}C -NMR ($CDCl_3$, 500 MHz) δ = 29.30, 35.70, 60.20,

126.30, 127.55, 128.72, 129.45, 129.60, 135.04, 139.50, 140.68, 199.20, 200.71. MS: m/z (%) 252 (M^+ , 12), 223 (100), 209 (25), 135 (21), 91 (5). $C_{17}H_{16}O_2$ (252,115): calcd. C, 80.93; H, 6.39; O, 12.68; found: C, 80.98; H, 6.30; O, 12.72.

2-(4-methoxyphenyl)-3-phenylpropanal (9d): yellow oil. 1H -NMR ($CDCl_3$, 500 MHz): δ = 2.90 (dd, J = 7.9, 14.0 Hz, 1 H), 3.40 (dd, J = 6.6, 14.0 Hz, 1 H), 3.73 (s, 3 H), 4.53 (m, 1 H), 6.70-6.86 (m, 2 H), 6.98-7.37 (m, 7 H), 9.67 (d, J = 1.7 Hz, 1 H). IR (KBr): 3070, 2850, 2756, 1720, 660 cm^{-1} . ^{13}C -NMR ($CDCl_3$, 500 MHz) δ = 36.58, 55.94, 58.12, 114.06, 126.05, 127.48, 128.33, 129.84, 129.90, 136.35, 141.16, 159.62, 200.80. MS: m/z (%) 240 (M^+ , 25), 239 (36), 211 (56), 149 (100), 91 (38). $C_{16}H_{16}O_2$ (240,12): calcd. C, 79.97; H, 6.71; O, 13.32; found: C, 79.89; H, 6.71; O, 13.40.

2c (85%)

2d (15%)

catalytic
method **B**

7d 7c