Supplementary Material (ESI) for New Journal of Chemistry

Heck reaction catalysed by palladium supported with an electron-rich benzimidazolylidene generated *in situ*: Remarkable ligand electronic effects and controllable mono- and di-arylation

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Product characterization for the Heck arylation reactions

***trans*-Cinnamic acid butyl ester:** ^{1}HNMR ($CDCl_3$, 25^{o}C), δ, ppm: 7.68 (1H, d, J = 16Hz, CH=CH), 7.52 (2H, m), 7.39 (2H, m), 6.42 (1H, d, J = 16 Hz, CH=CH), 4.2 (2H, t, J = 6Hz), 1.59 (2H ,m), 1.43 (2H, m), 0.98 (3H, t, J = 7Hz). EI-MS: m/z (relative intensity) 204 (M^+, 78%), 148 (71%), 131 (100%).

4-Methyl-*trans*-cinnamic acid butyl ester: ^{1}HNMR ($CDCl_3$, 25^{o}C), δ, ppm: 7.65 (1H, d, J = 16Hz, CH=CH), 7.41 (2H, d, J = 8Hz), 7.18(2H, d, J = 8Hz), 6.38 (1H, d, J = 16 Hz, CH=CH), 4.20 (2H, t, J = 6Hz), 2.36 (3H, s), 1.67 (2H, m), 1.44 (2H, m), 0.96 (3H, t, J = 7Hz). EI-MS: m/z (relative intensity) 218 (M^+, 58%), 162 (100%).

4-Methoxyl-*trans*-cinnamic acid butyl ester: ^{1}HNMR ($CDCl_3$, 25^{o}C), δ, ppm: 7.61 (1H, d, J = 16Hz, CH=CH), 7.47 (2H, d, J = 8Hz), 6.90 (2H, d, J = 8Hz), 6.29 (1H, d, J = 16 Hz, CH=CH), 4.19 (2H, t, J = 7Hz), 3.83 (3H, s), 1.68(2H, m), 1.47(2H, m), 0.97 (3H, t, J = 8Hz). EI-MS: m/z (relative intensity) 234 (M^+, 74%), 178 (100%).

4-Acetyl-*trans*-cinnamic acid butyl ester: ^{1}HNMR ($CDCl_3$, 25^{o}C), δ, ppm: 7.97 (2H, d, J = 8Hz), 7.69 (1H, d, J = 16Hz, CH=CH), 7.60(2H, d, J = 8Hz), 6.53 (1H, d, J = 16 Hz, CH=CH), 4.22 (2H, t, J = 6Hz), 2.61 (3H, s), 1.69 (2H, m), 1.45 (2H, m), 0.97 (3H, t, J = 7Hz). EI-MS: m/z (relative intensity): 246 (M^+, 23%), 231 (45%), 190 (37%), 175 (100%).

2,5-Dimethyl-*trans*-cinnamic acid butyl ester: ^{1}HNMR ($CDCl_3$, 25^{o}C), δ, ppm: 7.94 (1H, d, J = 16Hz, CH=CH), 7.38 (1H, s), 7.09 (2H, s), 6.36 (1H, d, J = 16 Hz, CH=CH), 4.22 (2H, t, J = 6Hz), 2.39 (3H, s), 2.33 (3H, s), 1.70 (2H, m), 1.45 (2H, m), 0.98 (3H, t, J = 7Hz). EI-MS: m/z (relative intensity) 232 (M^+, 46%), 217 (8%), 159 (100%).

Mesityl-*trans*-cinnamic acid butyl ester: ^{1}HNMR ($CDCl_3$, 25^{o}C), δ, ppm: 7.82 (2H, d, J = 16Hz, CH=CH), 6.86 (2H, s), 6.03 (1H, d, J = 16 Hz, CH=CH), 4.19 (2H, t, J = 7Hz), 2.30 (6H, s), 2.26 (3H, s), 1.67 (2H, m), 1.42 (2H, m), 0.95 (3H, t, J = 8Hz). EI-MS: m/z (relative intensity) 246 (M^+, 49%), 231 (7%), 173 (100%).

1,4-Di(2-butoxycarbonyl-*trans*-vinyl)-*p*-xylene: Mp.: 98-100^{o}C. Anal. Found: C, 73.76; H, 8.52; requires for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44. ^{1}HNMR ($CDCl_3$, 25^{o}C), δ, ppm: 7.89 (2H, d, J = 16Hz, CH=CH), 7.39 (2H, s), 6.38 (2H, d, J = 16 Hz, CH=CH), 4.22 (4H, t, J = 6Hz), 2.41 (6H, s), 1.69 (4H, m), 1.45 (4H, m), 0.97 (6H, t, J = 7Hz). ^{13}C NMR ($CDCl_3$, 25^{o}C), δ, ppm: 166.95, 141.31, 135.37, 134.85, 128.61, 119.84, 64.46, 30.74, 19.29, 19.27, 13.70. EI-MS: m/z (relative intensity) 358 (M^+, 75%), 343 (7%), 285 (100%).

2-Cyano-*trans*-cinnamic acid n-butyl ester: ^{1}HNMR ($CDCl_3$, 25^{o}C), δ, ppm: 7.96 (1H, d, J = 16Hz, CH=CH), 7.72 (2H, t, J = 9Hz), 7.62 (1H, t, J = 8Hz), 7.47 (1H, t, J = 8Hz), 6.63 (2H, d, J = 16 Hz, CH=CH), 4.24 (2H, t, J = 7Hz), 1.69 (2H ,m), 1.45 (2H, m), 0.97 (3H, t, J = 8Hz). EI-MS: m/z (relative intensity) 229 (M^+, 12%), 184(36%), 156 (100%).

***trans*-Stilbene:** ^{1}HNMR ($CDCl_3$, 25^{o}C), δ, ppm: 7.55-7.57 (m, 4H), 7.39-7.42 (m, 4H), 7.28-7.32 (m, 2H), 7.16 (s, 2H). EI-MS: m/z (relative intensity):180 (M^+, 100%), 165(42%).

4-Methoxy-*trans*-stilbene: ^{1}H NMR ($CDCl_3$, 25^{o}C), δ, ppm: 7.49 (d, J = 7 Hz, 2H), 7.45 (d, J = 9 Hz, 2H), 7.34 (t, J = 8Hz, 2H), 7.23 (t, J = 8Hz, 1H), 7.06 (d, J = 16Hz, 1H), 6.98 (d, J = 16 Hz, 1H), 6.90 (d, J = 8 Hz, 2H), 3.83 (s, 3H). EI-MS: m/z (relative intensity): 210 (M^+, 100%), 195 (34%).

4-Acetyl-*trans*-stilbene: ^{1}H NMR ($CDCl_3$, 25^{o}C), δ, ppm: 7.95 (d, J = 9 Hz, 2H), 7.58 (d, J = 8 Hz, 2H), 7.54 (d, J = 8Hz, 2H), 7.38 (t, J = 7Hz, 2H), 7.30 (t, J = 7Hz, 1H), 7.23 (d, J = 16 Hz, 1H), 7.12 (d, J = 16 Hz, 1H), 2.61 (s, 3H). EI-MS: m/z (relative intensity): 222 (M^+, 78%), 207 (100%), 178 (67%).

N,N-Dimethyl-*trans*-cinnamamide: ^{1}HNMR ($CDCl_3$, 25^{o}C), δ, ppm: 7.68 (d, 1H, J = 15Hz), 7.52-7.54 (m, 2H), 7.34-7.39(m, 3H), 6.89 (d, 1H, J = 15Hz), 3.12 (s, 3H). EI-MS: m/z (relative intensity): 175 (M^+, 58%), 131 (100%).

Butyl 3,3-bisphenyl acrylate: ^{1}HNMR ($CDCl_3$, 25^{o}C), δ, ppm: 7.29-7.38 (m, 8H), 7.20-7.22 (m, 2H), 6.37(s, 1H), 4.00 (t, 2H. J = 7Hz), 1.42-1.48 (m, 2H), 1.20-1.25(m, 2H), 0.86 (t, 3H, J = 7Hz). EI-MS: m/z (relative intensity): 280 (M^+, 61%), 224 (77%), 207 (83%), 178 (100%).

N,N-Dimethyl-3,3-diphenylacrylamide: ^{1}HNMR ($CDCl_3$, 25^{o}C), δ, ppm: 7.29-7.34 (m, 8H), 7.24-7.26 (m, 2H), 6.35 (s, 1H), 2.79 (s, 6H). EI-MS: m/z (relative intensity): 251 (M^+, 52%), 207 (100%).

Butyl-3,3-bis(4-fluorophenyl)acrylate: ^{1}HNMR ($CDCl_3$, 25^{o}C), δ, ppm: 7.24-7.28 (m, 2H), 7.17-7.19 (m, 2H), 7.05-7.09 (m, 2H), 6.99-7.03 (m, 2H), 6.30 (s, 1H), 4.01 (t, 2H. J = 6Hz), 1.45-1.50 (m, 2H), 1.23-1.27 (m, 2H), 0.86 (t, 3H, J = 6Hz). EI-MS: m/z (relative intensity): 316 (M^+, 41%), 260 (100%), 243 (93%), 214 (79%).

Butyl-3,3-bis(4-methylphenyl)acrylate: ^{1}HNMR ($CDCl_3$, 25^{o}C), δ, ppm: 7.17-7.25 (m, 4H), 7.08-7.12 (m, 4H), 6.30 (s, 1H), 4.00 (t, 2H. J = 7Hz), 2.38 (s, 3H), 2.35 (s, 3H), 1.45-1.48 (m, 2H), 1.20-1.25 (m, 2H), 0.86 (t, 3H, J = 7Hz). EI-MS: m/z (relative intensity): 308 (M^+, 100%), 252 (82%), 235 (97%).

Butyl-3,3-bis(4-methoxylphenyl)acrylate: ^{1}HNMR ($CDCl_3$, 25^{o}C), δ, ppm: 7.25 (d, 2H, J = 9Hz), 7.15 (d, 2H, J = 9Hz), 6.91 (d, 2H, J = 9Hz), 6.84 (d, 2H, J = 9Hz), 6.23 (s, 1H, C=CH), 4.01 (t, 2H, J = 6Hz), 3.83 (s, 3H), 3.81 (s, 3H), 1.47-1.50 (m, 2H), 1.25-1.28 (m, 2H), 0.87 (t, 3H, J = 6Hz). EI-MS: m/z (relative intensity): 340 (M^+, 100%), 284 (39%), 267 (51%), 240 (97%).

1,1,2-Triphenylethene:[3] ^{1}HNMR ($CDCl_3$, 25^{o}C), δ, ppm: 7.25-7.34 (m, 8H), 7.19-7.21 (m, 2H), 7.07-7.15 (m, 3H), 7.02-7.03 (m, 2H), 6.96 (s, 1H). EI-MS: m/z (relative intensity): 256 (M^+, 100%), 24 1(25%), 207 (83%).

Butyl-3,3-bis(4-acetylphenyl)acrylate: Mp.: 66-68^{o}C. Anal. Found: C, 75.73; H, 6.68; requires for $C_{22}H_{30}O_4$: C, 75.80; H, 6.64. ^{1}HNMR ($CDCl_3$, 25^{o}C), δ, ppm: 7.98 (d, 2H, J = 8Hz), 7.85 (d, 2H, J = 8Hz), 7.35 (d, 2H, J = 8Hz), 7.30 (d, 2H, J = 8Hz), 6.48 (s, 1H, C=CH), 4.01 (t, 2H, J = 6Hz), 2.62 (s, 3H, $COCH_3$), 2.58 (s, 3H, $COCH_3$), 1.47-1.50 (m, 2H) , 1.20-1.25 (m, 2H), 0.84 (t, 3H, J = 6Hz). ^{13}C NMR ($CDCl_3$, 25^{o}C), δ, ppm: 198.82, 198.64, 166.83, 155.21, 145.62, 144.73, 138.98, 138.14, 130.65, 129.84, 129.65, 129.51, 121.33, 65.83, 31.83, 28.02, 27.98, 20.42, 15.00. EI-MS: m/z (relative intensity): 364 (M^+, 55%), 349 (42%), 308 (27%), 293 (100%).