

Supplementary information

Simple halogen-free synthesis of aryl cinnamates using Mo-Keggin heteropoly acids as catalyst*

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Phenyl cinnamate (3.1), colorless solid, mp 75–75.5 °C (Lit. [18] 75–76 °C); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.64 (1H, d, J = 16 Hz), 7.18 (2H, br d, J = 7.5 Hz), 7.25 (1H, br t, J = 7.3 Hz), 7.38–7.46 (5H, m), 7.56–7.62 (2H, m), 7.88 (1H, d, J = 16 Hz); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 117.4, 121.6, 125.8, 128.3, 129.0, 129.4, 130.7, 134.2, 146.6, 150.8, 165.4; MS (m/z, I%): 224 (M⁺, 8.5); 77 (7.9); 103 (30.3); 131 (100).

2-Methylphenyl cinnamate (3.3), colorless solid, mp 84–85°C (Lit. [32]: 84–85°C); ¹H NMR (400 MHz, CDCl₃), δ (ppm): 2.38 (3H, s), 6.63 (1H, d, J = 16 Hz), 6.96–7.30 (5H, m), 7.41–7.43 (3H, m), 7.57–7.60 (2H, m), 7.86 (1H, d, J = 16 Hz). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 21.3, 117.5, 118.0, 122.2, 126.6, 128.2, 128.9, 129.1, 130.6, 134.2, 146.4, 150.8, 165.5. MS (m/z, I%): 238 (M⁺, 24.3), 77 (14.2), 103 (42.7), 131 (100).

4-Methoxyphenyl cinnamate (3.4), colorless solid, mp 99–101 °C (Lit. [33] 100–102 °C); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 3.74 (3H, s), 6.55 (1H, d, J = 16 Hz), 6.81–6.87 (2H, m), 6.99–7.05 (2H, m), 7.32–7.38 (3H, m), 7.48–7.54 (2H, m), 7.78 (1H, d, J = 16 Hz); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 55.6, 114.5, 117.4, 122.4, 128.3, 129.0, 130.6, 134.2, 144.3, 146.4, 157.3, 165.8; MS (m/z, I%): 254 (M⁺, 28.0); 77 (28.3); 103 (38.8); 131 (100); 181 (13.3); 211 (14).

4-Chlorophenyl cinnamate (3.6), colorless solid, mp 103–104 °C (Lit. [34]: 105°C); ¹H NMR (400 MHz, CDCl₃), δ (ppm): 6.61 (1H, d, J = 16 Hz), 7.08–7.12 (2H, m), 7.35–7.36 (2H, m), 7.41–7.43 (3H, m), 7.57–7.59

(2H, m), 7.85 (1H, d, $J = 16$ Hz); ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 116.9, 123.0, 128.3, 129.0, 129.5, 130.8, 131.1, 134.1, 147.0, 149.3, 165.1; MS (m/z , I%): 258 (M^+ , 6.7), 77 (13.7), 103 (40.7), 131 (100).

4-Bromophenyl cinnamate (**3.7**). colorless solid, mp 111-112°C (Lit. [35]: 113-115°C); ^1H NMR (400 MHz, CDCl_3): 6.60 (1H, d, $J = 16$ Hz), 7.02-7.10 (2H, d, $J = 8.9$ Hz), 7.25-7.38 (3H, m), 7.40-7.45 (2H, d, $J = 8.8$ Hz), 7.57-7.62 (2H, m), 7.86 (1H, d, $J = 16$ Hz); ^{13}C NMR (100 MHz, CDCl_3): 117.1, 119.1, 123.7, 128.6, 129.3, 131.1, 132.7, 134.3, 147.3, 150.1, 165.3, MS (m/z , I%): 304 (M^+ , 6.7); 77 (34.8); 103 (32.4); 131 (100).

2-Methoxyphenyl cinnamate (**3.5**). Colorless solid, mp 138-139°C (lit [36]: 139-140°C); ^1H NMR (400 MHz, CDCl_3): 3.88 (3H, s), 6.63 (1H, d, $J = 16$ Hz), 6.89-7.01 (2H, m), 7.03-7.09 (1H, m), 7.23-7.31 (1H, m), 7.39-7.46 (3H, m), 7.55-7.62 (2H, m), 7.86 (1H, d, $J = 16$ Hz); ^{13}C NMR (100 MHz, CDCl_3): 55.9, 112.5, 117.1, 120.8, 122.9, 126.9, 128.3, 128.9, 130.6, 134.3, 139.9, 146.5, 151.3, 164.9, MS (m/z , I%): 254 (M^+ , 5.7); 77 (5.4); 103 (27.2); 131 (100); 211 (1.1).

2-Isopropyl-5-methylphenyl cinnamate (**3.8**). Colorless solid mp 70-71°C (Lit [37]: 69-70°C); ^1H NMR (400 MHz, CDCl_3): 1.20 (3H, s), 1.22 (3H, s), 2.34 (3H, s), 3.04 (1H, m), 6.67 (1H, d, $J = 16$ Hz), 6.89 (1H, br s), 7.04 (1H, d, $J = 8$ Hz), 7.22 (1H, d, $J = 8$ Hz), 7.39-7.48 (3H, m), 7.57-7.63 (2H, m), 7.88 (1H, d, $J = 16$ Hz); ^{13}C NMR (100 MHz, CDCl_3): 116.2, 122.5, 125.2, 128.5, 129.1, 129.5, 133.8, 148.0, 155.6, 164.3, MS (m/z , I%): 280 (M^+ , 10.9); 77 (3.6); 103 (29.54); 131 (100).

2-Biphenyl cinnamate (**3.9**). Colorless solid mp 101-103°C (lit [38]: 103-104°C); ^1H NMR (400 MHz, CDCl_3): 6.47 (1H, d, $J = 16$ Hz), 7.22 -7.26 (1H, dd, $J = 8, 1.3$ Hz), 7.28-7.41 (8H, m), 7.43-7.47 (3H, m), 7.48-7.53 (2H, m), 7.70 (1H, d, $J = 16$ Hz); ^{13}C NMR (100 MHz, CDCl_3): 117.1, 123.0, 126.3, 127.4, 128.3, 128.5, 128.9, 130.6, 131.0, 134.2, 134.9, 137.6, 146.5, 147.9, 165.3, MS (m/z , I%): 300 (M^+ , 15.4); 77 (9.3); 103 (38.8); 131 (100).

1-Naphthyl cinnamate (3.13). Colorless solid mp 106-107°C (Lit [39]: 105-108°C); ¹H NMR (400 MHz, CDCl₃): 1.24 (3H, t, J = 7.3 Hz), 3.01 (2H, qt, J = 7.3 Hz), 6.64 (1H, d, J = 16 Hz), 7.26-7.29 (2H, m), 7.45-7.43 (3H, m), 7.59-7.61 (2H, m), 7.90 (1H, d, J = 16 Hz), 8.04 (2H, d, J = 8.7 Hz); ¹³C NMR (100 MHz, CDCl₃): 117.0, 118.1, 121.3, 125.4, 126.0, 126.4, 127.0, 128.0, 128.4, 129.0, 130.8, 134.2, 134.7, 146.7, 147.0, 165.4, MS (m/z, I%): 274 (M⁺, 8.7); 77 (12.2); 103 (16.8); 131 (100)

Phenyl α-phenylcinnamate (3.17). Colorless solid mp 137-138°C (lit [40]: 138,5-139,5°C); ¹H NMR (400 MHz, CDCl₃): 1.24 (3H, t, J = 7.3 Hz), 3.01 (2H, qt, J = 7.3 Hz), 6.64 (1H, d, J = 16 Hz), 7.26-7.29 (2H, m), 7.45-7.43 (3H, m), 7.59-7.61 (2H, m), 7.90 (1H, d, J = 16 Hz), 8.04 (2H, d, J = 8.7 Hz); ¹³C NMR (100 MHz, CDCl₃): 121.6, 125.7, 128.0, 128.3, 128.7, 129.3, 129.4, 129.8, 129.9, 130.8, 132.0, 134.5, 135.5, 142.0, 151.2, 162.0, MS (m/z, I%): 300 (M⁺, 10.6); 77 (7.6); 131 (8.7); 152 (15.1); 179 (100); 207 (75.8).

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