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Pd-Nanoparticles Catalyzed Stereospecific Synthesis of β -Aryl Cinnamic Esters in Ionic Liquids

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Supporting information section

Catalyst **1** and other cinnamic esters used as substrates were prepared according to our procedures.^{20,21} TEM images were obtained at 100 KV under a PHILIPS 400T microscope.

Arylation of cinnamates in TBAB and in the presence of different bases: a 50 mL three-necked round flask, equipped with a condenser and a magnetic stirrer, was charged with tetrabutylammonium bromide (3 g) and heated at 130 °C. To the stirred molten salt were added ethyl cinnamate (5.68 mmol), aryl halide (5.68 mmol), catalyst **1** (0.085 mmol), sodium formate (0.18 mmol), base (14.3 mmol) and monitoring the reaction by glc until the disappearance of the starting materials. The reaction products were extracted with ethyl ether leaving the ionic liquid and the catalyst which were further utilized.

Arylation of cinnamates catalysed by nanoparticles: a 50 mL three-necked round flask, equipped with a condenser and a magnetic stirrer, was charged with tetrabutylammonium bromide (3 g) and heated at 130 °C. To the stirred molten salt were added ethyl cinnamate (5.68 mmol), aryl halide (5.68 mmol), catalyst **1** or Pd(OAc)₂ (0.085 mmol) and tetrabutylammonium acetate (14.2 mmol). The colour of the solution turned rapidly from red to black. The work-up procedure was performed as before.

The E/Z configuration of β -aryl cinnamates **2-6** was established by comparison of their NMR and mass spectra with those reported previously.^{22a} β -aryl cinnamates **7-8** were isolated and characterized as follows:

(E)-Ethyl 3-(p-methoxyphenyl)-3-(p-tolyl)-propenoate (7). ¹H NMR δ 1.12 (t, J =7.1 Hz, 3H, CH₃ ethyl), 2.34 (s, 3H, CH₃ tolyl), 3.82 (s, 3H, OMe), 4.02 (q, J = 7.1 Hz, 2H, CH₂ ethyl), 6.26 (s, 1H, vinyl proton), 6.86-6.92 (m, 2H, aromatic protons), 7.07-7.26 (m, 4H, aromatic protons), 7.45-7.48 (m, 2H, aromatic protons) – ¹³C NMR δ 13.74, 19.05, 55.08, 64.16, 114.22, 115.70, 128.39, 128.94, 129.72, 130.76, 139.44, 144.13, 156.35, 159.58, 167.34 – MS (EI) m/z 296 (M⁺, 53), 268 (39), 251

(59), 224 (100), 209 (44), 193 (9), 178 (21), 165 (38), 135 (55), 119 (24), 105 (11), 91 (14), 77 (9), 41 (76) – IR (KBr) ν = 1718, 1635, 1604, 1510 cm^{-1} – $\text{C}_{19}\text{H}_{20}\text{O}_3$ (296.14), calcd. C, 77.00; H, 6.80; O, 16.20; found C, 76.85; H, 6.71; O, 16.32.

(Z)-Ethyl 3-(*p*-methoxyphenyl)-3-(*p*-tolyl)-propenoate (**8**). ^1H NMR δ 1.15 (t, J =7.1 Hz, 3H, CH_3 ethyl), 2.28 (s, 3H, CH_3 tolyl), 3.81 (s, 3H, OMe), 3.99 (q, J = 7.1 Hz, 2H, CH_2 ethyl), 6.23 (s, 1H, vinyl proton), 6.81-6.85 (m, 2H, aromatic protons), 7.08-7.25 (m, 4H, aromatic protons), 7.34-7.37 (m, 2H, aromatic protons) ^{13}C NMR δ 13.67, 19.18, 55.32, 63.80, 113.65, 115.67, 128.51, 129.09, 129.77, 130.81, 139.47, 144.50, 156.40, 159.64, 166.44 – MS (EI) 296 (M^+ , 47), 268 (31), 251 (56), 224 (85), 209 (40), 193 (9), 178 (23), 165 (38), 135 (48), 119 (35), 105 (12), 91 (14), 77 (9), 41 (100) – IR (KBr) ν = 1718, 1636, 1604, 1500 cm^{-1} – $\text{C}_{19}\text{H}_{20}\text{O}_3$ (296.14), calcd. C, 77.00; H, 6.80; O, 16.20; found C, 76.72; H, 6.65; O, 16.35.

2-oxo-3-methylbenzothiazole A

To tetrabutylammonium bromide (3 g) heated at 130 °C were added the catalyst **1** (1 g, 1.52 mmol) and tetrabutylammonium acetate (1.15 g, 3.80 mmol). The red colour of the solution turned to black and after 1h, the cooled solution, diluted with 50 mL of water, was extracted with ether. After filtration, evaporation of the solvent leaved a pale yellow oil which solidified. Yield 85%, mp 66-68 °C, lit.⁴⁵ 67°C.