Electronic Supporting Information

for

Pyridyl-functionalized Imidazolium-based Ionic liquids and Palladium (II) Complex Catalyzed Highly Recyclable and Efficient Heck Reactions

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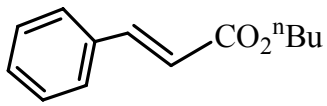
General:

All the reagents were purchased from commercial sources and used without further purification. A standard Schlenk line system was used for handling the reactions under nitrogen. ^{1}H, and ^{13}C NMR spectra were recorded on spectrometers at 300 and 75 MHz, respectively, by using deuterated $CDCl_3$ as locking solvent. Chemical shifts were reported in ppm relative to TMS. GC/MS spectra were determined using an appropriate instrument. M^+ is the mass of the cation. Thin-layer chromatography (TLC) analysis was performed with Al backed plates pre-coated with silica gel and examined under UV (254 nm). Flash column chromatography was executed on silica gel (60–200 μm, 60 A).

Spectroscopic data:

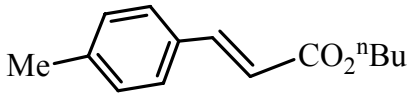
***n*-Butyl *trans*-cinnamater:** [1,2]



Pale-yellow liquid; ^{1}H NMR: δ 7.67 (d, J = 16.0 Hz, 1H), 7.49–7.52 (m, 2H), 7.34–7.37 (m, 3H), 6.42 (AB, J = 0.4, 16.0 Hz, 1H), 4.20 (t, J = 6.7 Hz, 2H), 1.68 (quint, J = 7.2 Hz,

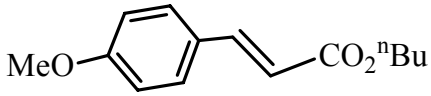
2H), 1.43 (sextet, J = 7.5 Hz, 2H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR: δ 167.0, 144.5, 134.5, 130.1, 128.8, 128.0, 118.3, 64.3, 30.8, 19.2, 13.7; GC-MS (EI) m/z (%): 204 (M^+, 100).

***n*-Butyl *trans*-4-methylcinnamate:** [1]



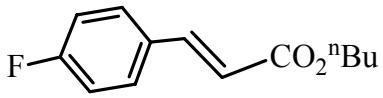
Pale-yellow liquid; ^{1}H NMR: δ 7.64 (d, J = 16.0 Hz, 1H), 7.40 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.37 (d, J = 16.0 Hz, 1H), 4.19 (t, J = 6.6 Hz, 2H), 2.35 (s, 3H), 1.68 (quint, J = 7.1 Hz, 2H), 1.44 (sextet, J = 7.5 Hz, 2H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR: δ 167.2, 144.5, 140.5, 131.8, 129.5, 128.0, 117.2, 64.3, 30.8, 21.4, 19.2, 13.7; GC-MS (EI) m/z (%): 218 (M^+, 100).

***n*-Butyl *trans*-4-methoxylcinnamate:** [1,2]



Pale-yellow liquid; ^{1}H NMR: δ 7.61 (d, J = 16.0 Hz, 1H), 7.43–7.46 (m, 2H), 6.86–6.90 (m, 2H), 6.29 (AB, J = 0.5, 16.0 Hz, 1H), 4.18 (t, J = 6.7 Hz, 2H), 3.81 (s, 3H), 1.67 (quint, J = 5.8 Hz, 2H), 1.41 (sextet, J = 7.6 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR: δ 167.4, 161.3, 144.1, 129.6, 127.2, 115.8, 114.3, 64.2, 55.3, 30.8, 19.2, 13.7; GC-MS (EI) m/z (%): 234 (M^+, 100).

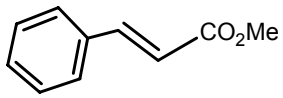
***n*-Butyl *trans*-4-fluorocinnamate:** [2]



Pale-yellow liquid; ^{1}H NMR: δ = 7.61 (d, J = 16.0 Hz, 1H), 7.45–7.50 (m, 2H), 7.01–7.06 (m, 2H), 6.33 (d, J = 16.0 Hz, 1H), 4.18 (t, J = 6.8 Hz, 2H), 1.66 (quint, J = 6.8

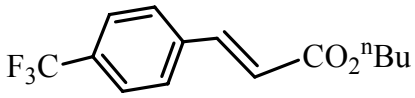
Hz, 2H), 1.41 (sextet, J = 7.5 Hz, 2H), 0.94 (q, J = 7.4 Hz, 3H); ^{13}C NMR: δ 166.2 (d, J = 102.1 Hz), 162.2, 143.1, 130.8, 130.7, 129.9, 129.8, 118.1, 116.0 (d, J = 21.8 Hz), 64.4, 30.8, 19.2, 13.7; GC-MS (EI) m/z (%): 222 (M^+, 100).

Methyl *trans*-cinnamate: [2]



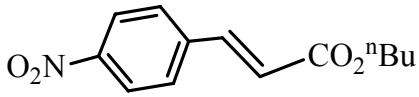
Pale-yellow liquid; ^{1}H NMR: δ 7.67 (d, J = 16.0 Hz, 1H), 7.48–7.51 (m, 2H), 7.34–7.36 (m, 3H), 6.42 (d, J = 16.0 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR: δ 167.3, 144.7, 134.3, 130.2, 128.8, 128.0, 117.8, 51.5; GC-MS (EI) m/z (%): 162 (M^+, 100).

***n*-Butyl *trans*-4-trifluoromethylcinnamate:** [1,2]



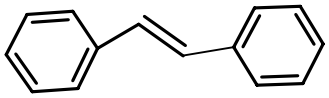
Pale-yellow liquid; ^{1}H NMR: δ 7.66 (d, J = 16.0 Hz, 1H), 7.57–7.62 (m, 4H), 6.48 (d, J = 16.0 Hz, 1H), 4.20 (t, J = 6.8 Hz, 2H), 1.67 (quint, J = 6.8 Hz, 2H), 1.41 (sextet, J = 7.6 Hz, 2H), 0.95 (q, J = 7.4 Hz, 3H); ^{13}C NMR: δ 166.4, 142.6, 137.9, 131.6 (q, J = 32.4 Hz), 128.1, 125.8 (q, J = 3.8 Hz), 121.4 (q, J = 270.5 Hz), 120.9, 64.7, 30.7, 19.2, 13.6; GC-MS (EI) m/z (%): 272 (M^+, 100).

***n*-Butyl *trans*-4-nitrocinnamate:** [2]



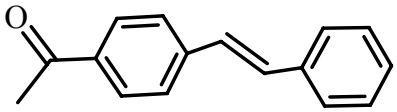
Pale-yellow solid; ^{1}H NMR: δ 8.18 (d, J = 8.7 Hz, 2H), 7.61–7.67 (m, 3H), 6.50 (d, J = 16.0 Hz, 1H), 4.19 (t, J = 6.6 Hz, 2H), 1.66 (quint, J = 6.8 Hz, 2H), 1.39 (sextet, J = 7.6 Hz, 2H), 0.92 (q, J = 7.4 Hz, 3H); ^{13}C NMR: δ 165.9, 148.2, 141.4, 140.5, 128.5, 124.0, 122.5, 64.8, 30.6, 19.1, 13.6; GC-MS (EI) m/z (%): 249 (M^+, 100).

***trans*-Stilbene:** [3]



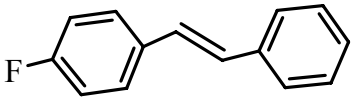
White solid; ^{1}H NMR: δ 7.52–7.55 (m, 4H), 7.35–7.40 (m, 4H), 7.25-7.30 (m, 2H), 7.13 (s, 2H); ^{13}C NMR: δ 137.4, 128.7, 128.6, 127.6, 126.5; GC-MS (EI) m/z (%): 180 (M^{+}, 100).

***trans*-4-Acetylstilbene:** [3]



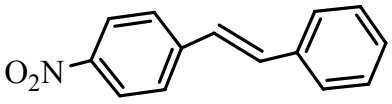
White solid; ^{1}H NMR: δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.50–7.57 (M, 4 H), 7.28–7.39 (m, 3H), 7.15 (dd, *J* = 15.8, 32.2 Hz, 2H), 2.58 (s, 3 H); ^{13}C NMR: δ 197.3, 141.9, 136.7, 135.9, 131.4, 128.7, 128.6, 128.2, 127.4, 126.8, 126.4, 26.5; GC-MS (EI) m/z (%): 222 (M^{+}, 100).

***trans*-4-Fluorostilbene:** [3]



White solid; ^{1}H NMR: δ 7.45–7.51 (m, 4H), 7.33–7.38 (m, 2H), 7.24–7.29 (m, 1H), 7.02–7.08 (m, 4H); ^{13}C NMR: δ 162.4 (d, *J* = 245.6 Hz), 137.2, 133.6, 128.7, 128.6 (d, *J* = 2.3 Hz), 128.0 (d, *J* = 0.4 Hz), 127.7, 127.5, 126.4, 115.6 (d, *J* = 21.6 Hz); GC-MS (EI) m/z (%): 198 (M^{+}, 100).

***trans*-4-Nitrostilbene:** [4]



Pale-yellow solid; ^{1}H NMR: δ 8.20 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.7 Hz, 2 H), 7.53 (d, J = 7.5 Hz, 2H), 7.28–7.41 (m, 3H), 7.14 (dd, J = 16.3, 40.0 Hz, 2H); ^{13}C NMR: δ 146.8, 143.9, 136.2, 133.3, 128.9, 128.8, 127.0, 126.9, 126.3, 124.1; GC-MS (EI) m/z (%): 225 (M^{+}, 100).

X-ray crystallography:

Crystals of compound **4** were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber and placed in the low-temperature nitrogen stream.[5] Data for **4** were collected at 87(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3° per frame for 30 seconds, and a full sphere of data was collected. A total of 2450 frames were collected with a final resolution of 0.83 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART software [6] and refined using SAINTPlus [7] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[8] The structure was solved by direct methods and refined by least squares method on F^2 using the SHELXTL program package.[9] The structure was solved in the space group P2(1)/n (# 14) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection.

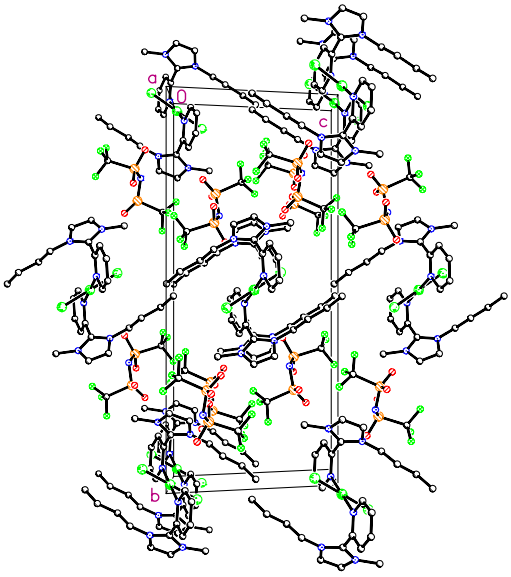


Figure 2 Packing diagram of compound **4**

References

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