Electronic Supporting Information

for

Pyrazolyl-functionalized 2-Methylimidazolium-based Ionic Liquids and their Palladium(II) Complexes as Recyclable Catalysts

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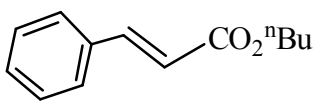
Experimental Sections:

General:

All chemicals were obtained commercially and were used as purchased. A standard Schlenk line system was used 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 for ^{1}H and ^{13}C NMR spectra. GC/MS spectra were determined using an appropriate instrument. 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).

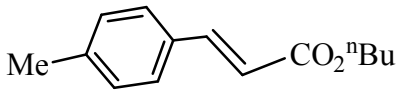
Spectroscopic data:

***trans*-Cinnamic acid *n*-butyl ester (5a):**[1,2]



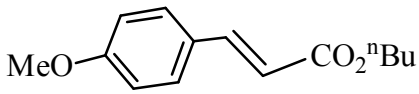
Colorless liquid; ^{1}H NMR: δ 7.67 (d, 1H, *J* = 16.0 Hz), 7.49–7.52 (m, 2H), 7.34–7.37 (m, 3H), 6.42 (d, 1H, *J* = 16.0 Hz), 4.20 (t, 2H, *J* = 6.7 Hz), 1.69 (quint, 2H, *J* = 7.2 Hz), 1.44 (sextet, 2H, *J* = 7.5 Hz), 0.95 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR: δ 167.0, 144.5, 134.5, 130.1, 128.8, 128.0, 118.3, 64.3, 30.8, 19.2, 13.7; GC-MS (EI) m/z (%): 204 (M^+, 100).

***trans*-4-Methylcinnamic acid *n*-butyl ester (5b):** [1]



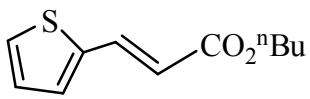
Pale-yellow liquid; ^{1}H NMR: δ 7.64 (d, 1H, *J* = 16.0 Hz), 7.40 (d, 2H, *J* = 8.1 Hz), 7.16 (d, 2H, *J* = 8.0 Hz), 6.37 (d, 1H, *J* = 16.0 Hz), 4.19 (t, 2H, *J* = 6.6 Hz), 2.35 (s, 3H), 1.68 (quint, 2H, *J* = 7.1 Hz), 1.44 (sextet, 2H, *J* = 7.5 Hz), 0.95 (t, 3H, *J* = 7.3 Hz); ^{13}C NMR: δ 167.2, 144.5, 140.5, 131.8, 129.6, 128.0, 117.2, 64.3, 30.8, 21.4, 19.2, 13.7; GC-MS (EI) m/z (%): 218 (M^+, 100).

***trans*-4-Methoxylcinnamic acid *n*-butyl ester (5c):** [1,2]



Pale-yellow liquid; ^{1}H NMR: δ 7.61 (d, 1H, *J* = 16.0 Hz), 7.45 (d, 2H, *J* = 8.7 Hz), 6.87 (d, 2H, *J* = 8.8 Hz), 6.28 (d, 1H, *J* = 15.9 Hz), 4.18 (t, 2H, *J* = 6.8 Hz), 3.80 (s, 3H), 1.66 (quint, 2H, *J* = 5.8 Hz), 1.41 (sextet, 2H, *J* = 7.6 Hz), 0.94 (t, 3H, *J* = 7.3 Hz); ^{13}C NMR: δ 167.3, 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).

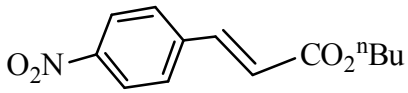
***trans*-3-(2-Thiophenyl)acrylic acid *n*-butyl ester (5d):** [1]



Brown liquid; ^{1}H NMR: δ 7.75 (d, 1H, *J* = 15.7 Hz), 7.34 (d, 1H, *J* = 5.1 Hz), 7.23 (d, 1H,

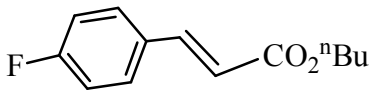
J = 3.6 Hz), 7.03 (t, 1H, J = 4.3 Hz), 6.22 (d, 1H, J = 15.7 Hz), 4.18 (t, 2H, J = 6.7 Hz), 1.67 (quint, 2H, J = 7.1 Hz), 1.40 (sextet, 2H, J = 7.5 Hz), 0.93 (t, 3H, J = 7.4 Hz); ^{13}C NMR: δ 166.8, 139.6, 136.9, 130.7, 128.2, 128.0, 117.1, 64.3, 30.7, 19.1, 13.7; GC-MS (EI) m/z (%): 210 (M^+, 100).

***trans*-4-Nitrocinnamic acid *n*-butyl ester (5e):** [2]



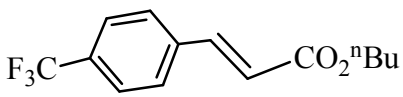
Pale-yellow solid; ^{1}H NMR: δ 8.18 (d, 2H, J = 8.8 Hz), 7.65 (d, J = 16.4 Hz, 1H), 7.65 (d, 2H, J = 8.8 Hz), 6.50 (d, 1H, J = 16.0 Hz), 4.18 (t, 2H, J = 6.7 Hz), 1.65 (quint, 2H, J = 5.4 Hz), 1.42 (sextet, 2H, J = 7.5 Hz), 0.92 (q, 3H, J = 7.3 Hz); ^{13}C NMR: δ 165.9, 148.4, 141.4, 140.5, 128.5, 124.0, 122.5, 64.8, 30.6, 19.1, 13.6; GC-MS (EI) m/z (%): 249 (M^+, 100).

***trans*-4-Fluoro-cinnamic acid *n*-butyl ester (5f):** [2]



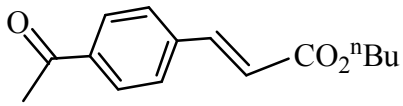
Pale-yellow liquid; ^{1}H NMR: δ = 7.60 (d, 1H, J = 16.0 Hz), 7.48 (dd, 2H, J = 8.7, 5.4 Hz), 7.04 (t, 2H, J = 8.6 Hz), 6.32 (d, 1H, J = 16.0 Hz), 4.18 (t, 2H, J = 6.8 Hz), 1.66 (quint, 2H, J = 6.8 Hz), 1.41 (sextet, 2H, J = 7.4 Hz), 0.94 (q, 3H, J = 7.3 Hz); ^{13}C NMR: δ 166.2 (d, J = 102.1 Hz), 162.2, 143.1, 130.7, 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).

***trans*-4-Trifluoromethylcinnamic acid *n*-butyl ester (5g):** [1,2]



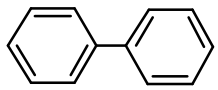
Pale-yellow liquid; ^{1}H NMR: δ 7.66 (d, 1H, *J* = 16.0 Hz), 7.59 (m, 4H), 6.48 (d, 1H, *J* = 16.0 Hz), 4.20 (t, 2H, *J* = 6.8 Hz), 1.67 (quint, 2H, *J* = 6.8 Hz), 1.41 (sextet, 2H, *J* = 7.6 Hz), 0.94 (q, 3H, *J* = 7.4 Hz); ^{13}C NMR: δ 166.4, 142.6, 137.9, 131.6 (q, *J* = 32.4 Hz), 128.1, 125.8 (q, *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).

***trans*-4-Acetylcinnamic acid *n*-butyl ester (5h):** [1]



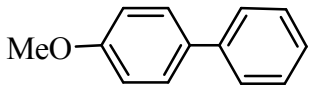
Pale-yellow liquid; ^{1}H NMR: δ 7.89 (d, 2H, *J* = 8.3 Hz), 7.61 (d, 1H, *J* = 16.0 Hz), 7.53 (d, 2H, *J* = 8.3 Hz), 6.45 (d, 1H, *J* = 16.0 Hz), 4.15 (t, 2H, *J* = 6.7 Hz), 2.53 (s, 3H), 1.63 (quint, 2H, *J* = 7.1 Hz), 1.41 (sextet, 2H, *J* = 7.5 Hz), 0.90 (t, 3H, *J* = 7.3 Hz); ^{13}C NMR: δ 197.0, 166.4, 142.8, 138.7, 137.9, 128.7, 128.1, 120.7, 64.5, 30.6, 26.5, 19.0, 13.6; GC-MS (EI) m/z (%): 246 (M^+, 100).

Biphenyl (6a): [3]



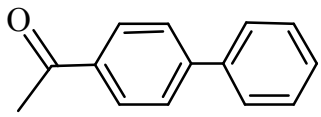
White solid; ^{1}H NMR: δ 7.59–7.62 (m, 4 H), 7.42–7.47 (m, 4 H), 7.33–7.38 (m, 2 H); ^{13}C NMR: 141.3, 128.7, 127.2, 127.2; GC-MS (EI) m/z (%): 154 (M^+, 100).

4-Methoxybiphenyl (6b): [3,4]



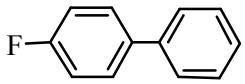
White solid; ^{1}H NMR: δ 7.50–7.58 (m, 4H), 7.39–7.45 (m, 2H), 7.30–7.34 (m, 1H), 6.97–7.03 (m, 2H), 3.86 (s, 3H); ^{13}C NMR: δ 159.2, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3; GC-MS (EI) m/z (%): 184 (M^+, 100).

4-Acetylbiphenyl (6c): [3]



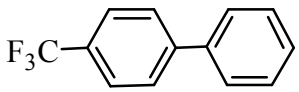
White solid; ^{1}H NMR: δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.58–7.65 (m, 4H), 7.35-7.46 (m, 3H), 2.59 (s, 3H); ^{13}C NMR: δ 197.4, 145.5, 139.6, 135.7, 128.8, 128.7, 128.1, 127.1, 127.0, 26.4; GC-MS (EI) m/z (%): 196 (M^+, 100).

4-Fluoro-biphenyl (6d):[4]



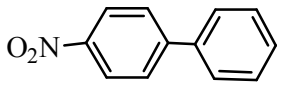
White solid; ^{1}H NMR: δ 7.55-7.65 (m, 4H), 7.44–7.49 (m, 2H), 7.35–7.40 (m, 1H), 7.12–7.18 (m, 2H); ^{13}C NMR: δ 162.5 (d, *J* = 244.7 Hz), 140.3, 137.4, 128.8, 128.7, 128.6, 127.2, 127.1, 126.9, 115.6 (d, *J* = 8.9 Hz); GC-MS (EI) m/z (%): 172 (M^+, 100).

4-Trifluoro-biphenyl (6e): [4]



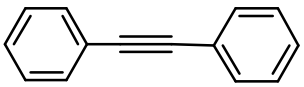
White solid; ^{1}H NMR: δ 7.68 (s, 4H), 7.57–7.60 (m, 2H), 7.39–7.48 (m, 3H); ^{13}C NMR: δ 144.7, 139.8, 129.0, 128.2, 128.0 (q, *J* = 120.3 Hz), 127.4, 127.3, 125.7 (q, *J* = 3.8 Hz); GC-MS (EI) m/z (%): 222 (M^+, 100).

4-Nitro-biphenyl (6f): [3,4]



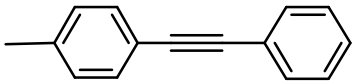
Pale yellow solid; ^{1}H NMR: δ 8.25–8.29 (m, 2H) 7.70–7.74 (m, 2H), 7.59–7.63 (m, 2H), 7.43–7.51 (m, 3H), 7.52–7.41 (m, 3H); ^{13}C NMR: δ 147.6, 147.1,138.8, 129.1, 128.9, 127.8, 127.4, 124.1; GC-MS (EI) m/z (%): 199 (M^+, 100)

Diphenylacetylene (7a) [5]



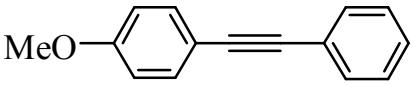
White solid; ^{1}H NMR: δ 7.50–7.55 (m, 4H), 7.31–7.37 (m, 6H); ^{13}C NMR: δ 131.6, 128.3, 128.2, 123.3, 89.4; GC-MS (EI) m/z (%): 178 (M^{+}, 100)

4-(Phenylethynyl)toluene (7b)[5,6]



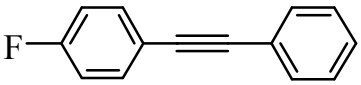
White solid; ^{1}H NMR: δ 7.50–7.54 (m, 2H), 7.43 (d, 2H, J = 8.1 Hz), 7.30–7.35 (m, 3H), 7.15 (d, 2H; J = 7.9 Hz), 2.36 (s, 3H); ^{13}C NMR: δ 138.4, 131.6, 131.5, 129.1, 128.3, 128.1, 123.5, 120.2, 89.6, 88.7, 21.5; GC-MS (EI) m/z (%): 192 (M^{+}, 100).

4-(Phenylethynyl)anisole (7c) [5,6]



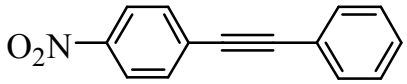
White solid; ^{1}H NMR: δ 7.54–7.52 (m, 4H), 7.28–7.36 (m, 2H), 6.84–6.89 (m, 2H), 3.81, (s, 3H); ^{13}C NMR: δ 159.6, 133.0, 131.4, 128.3, 127.9, 123.6, 115.4, 114.0, 89.4, 88.1, 55.3; GC-MS (EI) m/z (%):208 (M^{+}, 100).

4-(Fluorophenyl)phenylacetylene (7d)[6]



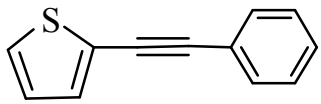
White solid; ^{1}H NMR: δ 7.51–7.58 (m,4H), 7.34–7.39 (m, 3H), 7.03–7.09 (m, 2H); ^{13}C NMR: δ 162.5, (d, J = 248.1 Hz), 133.4 (d, J = 8.3 Hz), 131.5, 128.3 (d, J = 3.8 Hz), 123.1, 119.4 (d, J = 3.4 Hz), 115.6 (d, J = 22.1 Hz), 89.0, 88.3; GC-MS (EI) m/z (%):196 (M^{+}, 100)

4-(Phenylethynyl)nitrobenzene (7e)[6]



Pale-yellow soilid; ^{1}H NMR: δ 8.18–8.22 (m, 2H), 7.62–7.67 (m, 2H), 7.52–7.56 (m, 2H), 7.35–7.39 (m, 3H); ^{13}C NMR: 147.0, 132.3, 131.9, 130.2, 129.3, 128.5, 123.6, 122.1, 94.7, 87.5; GC-MS (EI) m/z (%):223 (M^{+}, 100)

2-(Phenylethynyl)thiophene (7f)[6]



White solid; ^{1}H NMR: δ 7.57–7.59 (m, 2H), 7.34–7.42 (m, 3H), 7.29–7.32 (m, 2H), 7.03–7.06 (m, 1H); ^{13}C NMR: 131.8, 131.3, 128.3, 128.3, 127.2, 127.0, 123.3, 122.9, 93.1, 82.7; GC-MS (EI) m/z (%):184 (M^{+}, 100).

References:

(1) Yao, Q.; Kinney, E. P.; Zheng C. *Org. Lett.* **2004**, *6*, 2997.

(2) Feuerstein, M.; Doucet, H.; Santelli, M. *J. Org. Chem.* **2001**, *66*, 5923.

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(5) Gujadhur, R. K.; Bates, C. G.; Venkataraman, D. *Org. Lett.* **2001**, *3*, 4315.

(6) Sakai, N.; Annaka, K.; Konakahara, T. *Org. Lett.* **2004**, *6*, 1527.