Supporting information

for

A Highly Efficient, Recyclable Catalyst for C–C Coupling Reactions in Ionic Liquids: Pyrazolyl-functionalized N-Heterocyclic Carbene Complex of Palladium(II)

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Experimental Procedures:

General:

The compounds 1-(chloromethyl)-pyrazole hydrochloride,¹ 1-mesitylimidazole² and Pd(cod)MeCl³ and the ionic liquid [bmim][PF₆]⁴ were prepared via literature methods. DMF was distilled prior to use. The other chemicals were obtained commercially and were used as received. A standard Schlenk line system was used for handling air- and moisture-sensitive reactions under nitrogen. IR spectra were recorded as KBr pellets. ¹H and ¹³C spectra were recorded on spectrometers at 300, 75 and 282 MHz, respectively. Chemical shifts were reported in ppm relative to TMS for ¹H and ¹³C NMR spectra. DMSO-*d*₆ was used as the NMR solvent for **1** and **2**. CDCl₃ was used as NMR solvent for catalytic products. Thin-layer chromatography (TLC) analysis was performed with Al backed plates pre-coated with silica gel and examined under UV (254 nm) irradiation. Flash column chromatography was executed on silica gel (60–200 μm, 60 Å). Elemental analyses were obtained in our laboratories.

Spectroscopic data:

trans-Cinnamic acid *n*-butyl ester (**3a**):^{5,6}

Colorless liquid; ¹H NMR: δ 7.67 (d, *J* = 16.0 Hz, 1H), 7.52-7.49 (m, 2H), 7.37-7.35 (m, 3H), 6.42 (d, *J* = 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); ¹³C NMR: δ 167.0, 144.5, 134.5, 130.1, 128.8, 128.0, 118.3, 64.4, 30.8, 19.2, 13.7; GC-MS (EI) *m/z* (%): 204 (*M*⁺, 100).

***trans*-4-Methylcinnamic acid *n*-butyl ester (3b):** ⁵

Pale-yellow liquid; ¹H NMR: δ 7.64 (d, J = 16.0 Hz, 1H), 7.40 (d, J = 8.1 Hz, 2H), 7.17 (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); ¹³C 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-Methoxycinnamic acid *n*-butyl ester (3c):** ^{5,6}

Pale-yellow liquid; ¹H NMR: δ 7.60 (d, J = 16.0 Hz, 1H), 7.45 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.30 (d, J = 16.0 Hz, 1H), 4.18 (t, J = 6.8 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); ¹³C 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).

***trans*-4-Nitrocinnamic acid *n*-butyl ester (3d):** ⁶

Pale-yellow solid; ¹H NMR: δ 8.23 (d, J = 8.8 Hz, 2H), 7.68 (d, J = 16.0 Hz, 1H), 7.65 (d, J = 8.8 Hz, 2H), 6.54 (d, J = 16.0 Hz, 1H), 4.21 (t, J = 6.8 Hz, 2H), 1.66 (quint, J = 6.8 Hz, 2H), 1.42 (sextet, J = 7.6 Hz, 2H), 0.95 (q, J = 7.4 Hz, 3H); ¹³C NMR: δ 166.1, 148.4, 141.6, 140.6, 128.8, 124.1, 122.6, 64.9, 30.7, 19.1, 13.7; GC-MS (EI) m/z (%): 249 (M^+ , 100).

***trans*-4-Fluoro-cinnamic acid *n*-butyl ester (3e):**⁶

Pale-yellow liquid; ¹H NMR: δ = 7.62 (d, *J* = 16.0 Hz, 1H), 7.48 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.04 (t, *J* = 8.6 Hz, 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); ¹³C NMR: δ 166.2 (d, *J* = 102.2 Hz), 162.2, 143.2, 130.7, 129.9, 129.8, 116.0 (d, *J* = 21.8 Hz), 64.9, 30.7, 19.1, 13.7; GC-MS (EI) *m/z* (%): 222 (*M*⁺, 100).

***trans*-3-(2-Thiophenyl)acrylic acid *n*-butyl ester (3f):**⁵

Brown liquid; ¹H NMR: δ 7.76 (d, *J* = 15.8 Hz, 1H), 7.34 (d, *J* = 4.8 Hz, 1H), 7.23 (d, *J* = 3.6 Hz, 1H), 7.03 (t, *J* = 4.3 Hz, 1H), 6.23 (d, *J* = 15.7 Hz, 1H), 4.18 (t, *J* = 6.7 Hz, 2H), 1.67 (quint, *J* = 7.1 Hz, 2H), 1.42 (sextet, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ¹³C NMR: δ 166.9, 139.7, 136.9, 128.3, 117.1, 64.4, 30.8, 19.1, 13.7; GC-MS (EI) *m/z* (%): 210 (*M*⁺, 100).

***trans*-4-Trifluoromethylcinnamic acid *n*-butyl ester (3g):**^{5,6}

Pale-yellow liquid; ¹H NMR: δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.59 (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), 0.94 (q, *J* = 7.4 Hz, 3H); ¹³C NMR: δ 166.5, 142.6, 137.8, 131.6 (q, *J* = 32.4 Hz), 128.1, 125.8 (q, *J* = 3.8 Hz), 121.4 (q, *J* = 270.5 Hz), 120.8, 64.7, 30.7, 19.1, 13.7; GC-MS (EI) *m/z* (%): 272 (*M*⁺, 100).

***trans*-4-Acetylcinnamic acid *n*-butyl ester (3h):**⁵

Pale-yellow liquid; ¹H NMR: δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 16.0 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.19 (t, *J* = 6.8 Hz, 2H), 2.57 (s, 3H), 1.64 (quint, *J* = 5.8 Hz, 2H), 1.41 (sextet, *J* = 7.6 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); ¹³C NMR: δ 197.1, 166.5, 142.3, 138.8, 138.0, 128.8, 128.1, 120.8, 64.6, 30.7, 26.6, 19.1, 13.7; GC-MS (EI) *m/z* (%): 246 (*M*⁺, 100).

***trans*-Stilbene (4a):**⁷

White solid; ¹H NMR: δ 7.61 (d, *J* = 7.4 Hz, 4H), 7.46 (t, *J* = 7.6 Hz, 4H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.21 (s, 2H); ¹³C NMR: δ 137.4, 128.8, 128.7, 127.7, 126.6; GC-MS (EI) *m/z* (%): 180 (*M*⁺, 100).

***trans*-4-Methylstilbene (4b):**^{5,7,8}

White solid; ¹H NMR: δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.08 (s, 2H), 2.37 (s, 3H); ¹³C NMR: δ 137.6, 137.5, 134.6, 129.4, 128.7, 127.7, 127.4, 126.5, 126.4, 21.2; GC-MS (EI) *m/z* (%): 194 (*M*⁺, 100).

***trans*-2-Methoxystilbene (4c):**^{5,7}

White solid; ^1H NMR: δ 7.52 (d, J = 7.8 Hz, 2H), 7.48 (d, J = 8.7 Hz, 2 H), 7.38 (t, J = 7.5 Hz, 2H), 7.27 (t, J = 7.6 Hz, 1 H), 7.05 (dd, J = 30.5, 16.3 Hz, 2 H), 6.93 (d, J = 8.6 Hz, 2 H), 3.85 (s, 3 H); ^{13}C NMR: δ 159.3, 137.7, 130.18, 128.6, 128.2, 127.7, 127.2, 126.6, 126.2, 114.2, 55.3; GC-MS (EI) m/z (%): 210 (M^+ , 100).

***trans*-4-Fluorostilbene (4d):**⁷

White solid; ^1H NMR: δ 7.55-7.47 (m, 4H), 7.40 (t, J = 7.6 Hz, 2H), 7.33-7.30 (m, 1H), 7.14-7.06 (m, 4H); ^{13}C NMR: δ 162.4 (d), 137.3, 133.6, 128.8, 128.6 (d, J = 2.3 Hz), 128.0 (d, J = 0.4 Hz), 127.7, 127.6, 126.5, 115.6 (d, J = 21.45 Hz); GC-MS (EI) m/z (%): 198 (M^+ , 100).

***trans*-4-Nitrostilbene (4e):**⁸

Pale-yellow solid; ^1H NMR: δ 8.22 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.7 Hz, 2 H), 7.55 (d, J = 7.5 Hz, 2H), 7.43-7.25 (m, 4 H), 7.14 (d, J = 16.1 Hz, 1H); ^{13}C NMR: δ 147.8, 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).

Biphenyl (5a):⁹

White solid; ^1H NMR: δ 7.60 (d, 4 H, J = 7.5 Hz), 7.44 (t, 4 H, J = 7.2 Hz), 7.35 (t, 2 H, J = 7.2 Hz); ^{13}C NMR: 141.3, 128.7, 127.2, 127.2; GC-MS (EI) m/z (%): 154 (M^+ , 100).

4-Methylbiphenyl (5b):⁹

White solid; ^1H NMR: δ 7.60 (d, $J = 7.2$ Hz, 2H), 7.51 (d, 2 H, $J = 13.4$ Hz), 7.45 (t, 2 H, $J = 7.5$ Hz), 7.33 (t, 1 H, $J = 7.3$ Hz), 7.26 (d, 2 H, $J = 7.8$ Hz), 2.42 (s, 3H); ^{13}C NMR: δ 141.2, 138.4, 137.0, 129.5, 128.7, 127.0, 126.9, 21.1; GC-MS (EI) m/z (%): 168 (M^+ , 100).

4-Methoxybiphenyl (5c): ^{9,10}

White solid; ^1H NMR: δ 7.57-7.50 (m, 4H), 7.42 (t, $J = 7.7$ Hz, 2H), 7.32 (t, $J = 7.4$, 1H), 6.98 (d, $J = 8.8$, 2H), 3.85 (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-Fluoro-biphenyl (5d): ¹⁰

White solid; ^1H NMR: δ 7.58-7.54 (m, 4H), 7.48 (t, $J = 7.3$ Hz, 2H), 7.36 (t, $J = 7.1$ Hz, 1H), 7.14 (t, $J = 8.6$ Hz, 2H); ^{13}C NMR: δ 162.5 (d, $J = 244.8$ Hz), 161.2, 140.3, 137.4, 128.8, 128.6, 128.5, 127.2, 127.0, 115.6 (d, $J = 21.3$ Hz); GC-MS (EI) m/z (%): 172 (M^+ , 100).

4-Nitro-biphenyl (5e): ^{9,10}

Pale yellow solid; ^1H NMR: δ 8.29 (d, $J = 8.8$ Hz, 2H), 7.72 (d, $J = 8.8$ Hz, 2H), 7.63 (d, $J = 7.2$ Hz, 2H), 7.52-7.41 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) 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)

X-ray crystallography: Crystals of compound **2** 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.¹¹ Data for **2** were collected at 87(2) K using a Bruker/Siemens SMART APEX instrument (Mo K α 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 5 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 SMART¹² software and refined using SAINTPlus¹³ on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.¹⁴ The structure was solved by direct methods and refined by least squares method on F² using the SHELXTL program package.¹⁵ The structure was solved in the space group P2(1)/c (# 14) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. The CH₂Cl₂ solvent molecule is symmetry disordered and only half occupied. No decomposition was observed during data collection.

FIGURE 1. Crystal structure of **2** with thermal ellipsoids at 30% probability. Selected bond lengths (Å) and angles (°): C(11)–Pd(1) 1.981(3), C(21)–Pd(1) 2.035(3), N(1)–Pd(1) 2.151(3), Cl(1)–Pd(1) 2.3699(7); C(11)–Pd(1)–Cl(1) 176.31(8), C(21)–Pd(1)–N(1) 178.34(10), C(11)–Pd(1)–C(21) 91.47(11), C(11)–Pd(1)–N(1) 87.67(10), C(21)–Pd(1)–Cl(1) 92.18(8), N(1)–Pd(1)–Cl(1) 88.69(7).

Fig. 2. Packing diagram for **2** to show no other short contacts or worthwhile weak interactions among adjacent molecules.

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