Electronic Supporting Information

for

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

Ruihu Wang, Ji-Chang Xiao, Brendan Twamley and Jean’ne M. Shreeve*

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-cinnamate: $^{1,2}$

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: $\delta$ 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:**

\[
\begin{array}{c}
\text{Me} \\
\text{CO}_2 \text{Bu} \\
\end{array}
\]

Pale-yellow liquid; $^1$H NMR: $\delta$ 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: $\delta$ 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-methoxycinnamate:**

\[
\begin{array}{c}
\text{MeO} \\
\text{CO}_2 \text{Bu} \\
\end{array}
\]

Pale-yellow liquid; $^1$H NMR: $\delta$ 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: $\delta$ 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:**

\[
\begin{array}{c}
\text{F} \\
\text{CO}_2 \text{Bu} \\
\end{array}
\]

Pale-yellow liquid; $^1$H NMR: $\delta$ 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), 1.43 (sextet, $J = 7.5$ Hz, 2H), 0.95 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR: 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).
Hz, 2H), 1.41 (sextet, $J = 7.5$ Hz, 2H), 0.94 (q, $J = 7.4$ Hz, 3H); $^{13}$C NMR: $\delta$ 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:**

![Methyl trans-cinnamate structure]

Pale-yellow liquid; $^1$H NMR: $\delta$ 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: $\delta$ 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:**

![n-Butyl trans-4-trifluoromethylcinnamate structure]

Pale-yellow liquid; $^1$H NMR: $\delta$ 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: $\delta$ 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:**

![n-Butyl trans-4-nitrocinnamate structure]

Pale-yellow solid; $^1$H NMR: $\delta$ 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: $\delta$ 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

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).
Pale-yellow solid; $^1$H NMR: $\delta$ 8.20 (d, $J = 8.8$ Hz, 2H), 7.61 (d, $J = 8.7$ Hz, 2H), 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: $\delta$ 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. Data for 4 were collected at 87(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, $\lambda = 0.71073$ 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 and refined using SAINTPlus on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS. The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package. 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
7. SAINTPlus: v. 6.45a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, 2003.