Electronic supporting information for

"Ionic liquids effects on Mizoroki-Heck reactions: More than just carbene complex formation"

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Synthesis of [Bmim][NTf$_2$]–d_3

Prepared following the procedure of Dupont[1] with modification. All of the following operations were conducted under an argon atmosphere. Sodium metal (944 mg, 41.1 mmol) was added to D$_2$O (30 cm^3) with stirring. The resulting solution was transferred by cannula to a Schlenk flask containing [bmim]Cl (30.03 g, 171.9 mmol) and stirred for 48 hours under argon. The yellow solution was then neutralised with a solution of DCl (35% in D$_2$O) and the volatiles removed *in vacuo*. The oily residue was redissolved in CH$_2$Cl$_2$ (100 cm^3), filtered and the volatiles again removed *in vacuo*. The resulting solid was again treated with a fresh solution of sodium (95 mg, 4.1 mmol) in D$_2$O (20 cm^3) and stirred for a further 48 hours before neutralisation with DCl (35% in D$_2$O). Volatiles were again removed *in vacuo*, the crude product redissolved CH$_2$Cl$_2$ (100 cm^3), filtered and the solvent removed and redissolved in D$_2$O (10 cm^3). To this was added a solution of Li[NTf$_2$] (g, mmol) in D$_2$O (10 cm^3). After stirring for three hours, the reaction mixture was diluted with CH$_2$Cl$_2$ (200 cm^3) and the lower layer removed by decanting. The organic phase was washed with water (5 x 150 cm^3), dried over MgSO$_4$ and volatiles removed *in vacuo* to afford [bmim][N(CF$_3$SO$_2$)$_2$]-d_3 as a pale yellow highly viscous liquid. (39.22 g, 93.52 mmol, 54%) ^{1}H NMR (500.13 MHz, (CD$_3$)$_2$SO) δ 0.90 (t, $^3J_{HH}$ = 7.4 Hz, 3H, NCH$_2$CH$_2$CH$_2$C*H$_3$*), 1.25 (m, 2H, NCH$_2$CH$_2$C*H$_2$*CH$_3$), 1.76 (m, 2H, NCH$_2$C*H$_2$*CH$_2$CH$_3$), 3.86 (s, 3H, C*H$_3$*N), 4.18 (t, $^3J_{HH}$ = 7.3 Hz, 2H, NC*H$_2$*CH$_2$CH$_2$CH$_3$), 7.74 (s, 1H, NCHC*H*N, 99% D), 7.81 (s, 1H, NC*H*CHN, 99% D), 9.34 (s, 1H, NC*H*N, 95% D).

Kinetic Data

The following charts display the extent of consumption of butyl acrylate as well as the rate of formation of the cinnamate product, as measured using ^{1}H NMR Spectroscopy. Each data point is the average of data points for that particular point in time. Each average was determined from two or three independent iterations of a particular experiment. The error bars displayed represent the 95% confidence interval calculated using the inverse of the Student's t-distribution and are presented for the experiments with three iterations. For experiments where only duplicates were performed, a 95% confidence interval is meaningless - in such cases the data are displayed as the average of conducted experiments and it is noted that the range in such cases is *ca*. 10%. Control experiments conducted in the absence of a palladium pre-catalyst displayed no observable cinnamate formation.

[1]J. D. Scholten, G. Ebeling and J. Dupont, *Dalton Trans.* 2007, 5554-5560.

[PdCl2(IBuMe)2]/ DMF-d7

[PdCl2(CH3CN2)2]/ DMF-d7

[PdCl2(CH3CN)2] + 2[AgCl(IBuMe)]/ DMF-d7

[PdCl2(IBuMe)2]/ [bmim][Tf2N]

PdCl2(CH3CN2)2]/ [bmim][Tf2N]

PdCl2(CH3CN)2] + 2[AgCl(IBuMe)]/ [bmim][Tf2N]