Electronic supporting information for

"Effects of an ionic liquid solvent in the synthesis of γ-butyrolactones by conjugate addition using NHC organocatalysts"

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General Experimental

All air sensitive synthetic manipulations were performed using standard Schlenk techniques under an atmosphere of ultra high purity (UHP) argon. Glassware was oven dried at 120°C, followed by flame drying under vacuum prior to use. Solvents were collected in a J. Youngs tapped flask from the MD-7 solvent purification still, and were stored under argon until required. ^{n}BuLi (in hexanes, from Sigma Aldrich) were decanted into J. Youngs tapped ampoule under UHP argon and were standardised using *N*-benzylbenzamide in accordance with Chong *et al.*[1] *trans*-Cinnamaldehyde **3** (Sigma Aldrich) was freeze-thaw degassed and stored in J. Youngs tapped ampoule under UHP argon. Lithium *bis*(trifluoromethanesulfonyl)imide was purchased from the Tokyo Chemical Industry Co. and used as received. *p*-Bromobenzaldehye **4** (Sigma Aldrich) was left under vacuum for 30 minutes to ensure the removal of both water and air from the systems All other reagents were purchased from Sigma Aldrich and used as received.

^{1}H and ^{13}C NMR spectra were all recorded on a Bruker DPX 300 (^{1}H: 300.13 MHz and ^{13}C: 75.47 MHz) or Bruker Avance III 400 (^{1}H: 400.13 MHz and ^{13}C: 100.62 MHz) spectrometer at 298K, unless specified. Spectra were recorded in either benzene-d_6 (C_6D_6), chloroform-d_1 ($CDCl_3$), acetonitrile-d_3 (CD_3CN) or THF-d_8 with chemical shifts referenced to residual non-deuterated solvent peaks. C_6D_6, THF-*d*8 was stored over sodium, and CD_3CN along with $CDCl_3$ were stored over 4 Å molecular sieves; all were freeze thaw degassed prior to use. Multiplicities of signals are denoted as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin), sextet (sext), multiplets (m) or doublet of doublets (dd), with chemical shifts (δ) reported in parts per million (ppm).

Synthesis of 1-butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide ([bmim][NTf$_2$], 1)[2]

1-Butyl-3-methylimidazolium chloride ([bmim][Cl]) was synthesized following a method of Rogers *et al.*[2] To a solution of [bmim][Cl] (6.77 g, 38.8 mmol) in water (20 cm^3), lithium *bis*(trifluoromethanesulfonyl)imide (11.8 g, 41.0 mmol) in water (25 cm^3) was added dropwise, with stirring, over 20 minutes. This was allowed to stand, whereby two layers formed and the pale yellow lower layer was extracted using dichloromethane (4 x 50 cm^3) and washed with water (10 x 50 cm^3). This was dried over anhydrous magnesium sulfate followed and filtered through a plug of fluorisil**.** Volatiles were removed and product dried *in vacuo* at 80°C for 8 hours. This yielded the ionic liquid **1** (11.7 g, 28.0 mmol, 72%) as a colourless viscous liquid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.86 (t, $^3J_{HH}$ = 7.5 Hz, 3H, NCH$_2$CH$_2$CH$_2$C$\underline{H}_3$), 1.27 (m, 2H, NCH$_2$CH$_2$C$\underline{H}_2$CH$_3$), 1.76 (m, 2H, NCH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 3.83 (s, 3H, C$\underline{H}_3$N), 4.07 (t, $^3J_{HH}$ = 7.5 Hz, 2H, NC$\underline{H}_2$CH$_2$CH$_2$CH$_3$), 7.26 (s, 1H, NCHC$\underline{H}$N), 7.28 (s, 1H, NC$\underline{H}$CHN), 8.55 (s, 1H, NC$\underline{H}$N). ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 13.19 (NCH$_2$CH$_2$CH$_2\underline{C}$H$_3$), 19.35 (NCH$_2$CH$_2\underline{C}$H$_2$CH$_3$), 31.97 (NCH$_2\underline{C}$H$_2$CH$_2$CH$_3$), 36.25 (N$\underline{C}$H$_3$), 49.95 (N$\underline{C}$H$_2$CH$_2$CH$_2$CH$_3$), 119.91 (q, $^1J_{CF}$ = 321 Hz, $\underline{C}$F$_3$SO$_2$N), 122.56 (N$\underline{C}$HCHN), 123.88 (NCH$\underline{C}$HN), 135.82 (N$\underline{C}$HN).

Synthesis of 1-butyl-3-methylimidazol-2-ylidene (IBuMe, 2)

^{n}BuLi (1.22 M in hexane, 3.3 cm^3, 4.03 mmol) was added dropwise to a dried solution of [bmim][Cl] (701 mg, 4.01 mmol, prepared by the method of of Rogers *et al.*[2]) in THF (10 cm^3), and the resulting mixture stirred overnight. This mixture was washed with diethyl ether (10 cm^3), the volatiles were removed and the product was dried *in vacuo*. Care needed to be taken due to the volatility of the product. The product IBuMe **2** (527 mg, 3.81 mmol, 95%) was isolated as yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.87 (t, $^3J_{HH}$ = 7.5 Hz, 3H, NCH$_2$CH$_2$CH$_2$C$\underline{H}_3$), 1.36 (sext, $^3J_{HH}$ = 7.5 Hz, 2H, NCH$_2$CH$_2$C$\underline{H}_2$CH$_3$), 1.72 (quin, $^3J_{HH}$ = 7.5 Hz, 2H, NCH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 4.74 (s, 3H,

$C\underline{H}_3N$), 4.20 (t, $^3J_{HH}$ = 7.5 Hz, 3H, $NC\underline{H}_2CH_2CH_2CH_3$), 6.12 (s, 1H, $NCHC\underline{H}N$), 6.27 (s, 1H, $NC\underline{H}CHN$).

Synthesis of 1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes, 6)

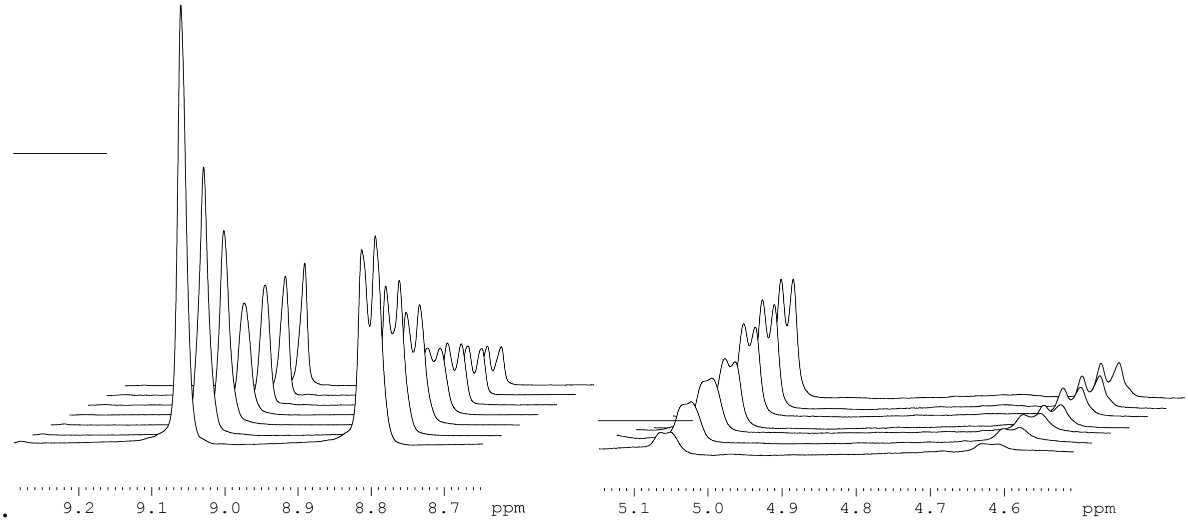
1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride ([IMes·H][Cl]) was synthesized following a method by Hintermann *et al.*[3] To a dried solution of [IMes·H][Cl] (10.6 g, 31.0 mmol) in THF, ^{t}BuOK (3.65 g, 32.5 mmol) was added and the resulting mixture was stirred for 2 hours. The solution was filtered and volatiles removed *in vacuo*. The resulting solid was extracted into toluene (100 cm^3), the solution halved in volume *in vacuo* and then placed in the freezer overnight. This yielded a crop of IMes **6** (1.91 g, 6.29 mmol, 20%) as brown crystals, which were washed with cold pentane and dried *in vacuo*. A second crop (0.26 g, 0.86 mmol, 3%) was isolated from the filtrate. This gave a total yield of IMes **1** (2.17 g, 7.15 mmol, 23%) that was stored in an argon glovebox until required. ^1H NMR (400 MHz, C_6D_6); δ 2.25 (s, 18H, *o*-, *p*-$C\underline{H}_3$), 6.57 (s, 2H, $NC\underline{H}$), 6.79 (s, 4H, Ar-H).

Synthesis of 1-butyl-2,3-dimethylimidazolium *bis*(trifluoromethanesulfonyl)imide, ([bm_2im][NTf_2], 7)[4]

1-Butyl-2,3-dimethylimidazolium chloride ([bm_2im]Cl]) was synthesized following the method of Welton *et al.*[4] To a solution of [bm_2im][Cl] (16.8 g, 89.4 mmol) in water (50 cm^3), lithium *bis*(trifluoromethanesulfonyl)imide (27.5 g, 95.8 mmol) in water (60cm^3) was added dropwise, with stirring, over 20 minutes. The resulting solution was allowed to stand overnight whereupon two layers formed. The lower layer was extracted using dichloromethane (4 x 50 cm^3) and washed with water (10 x 50 cm^3). This organic solution was dried with anhydrous magnesium sulfate, the volatiles removed *in vacuo* and the residual oil dried *in vacuo* over 4 hours. This yielded the ionic liquid **7** (32.0 g, 73.7 mmol, 82%) as a colourless viscous liquid. ^1H NMR (300 MHz, $CDCl_3$) δ 0.85 (t, $^3J_{HH}$ = 7.5 Hz, 3H, $NCH_2CH_2CH_2C\underline{H}_3$), 1.27 (sext, $^3J_{HH}$ = 7.5 Hz, 2H, $NCH_2CH_2C\underline{H}_2CH_3$), 1.67 (m, 2H, $NCH_2C\underline{H}_2CH_2CH_3$), 2.49 (s, 3H, $NC(C\underline{H}_3)N$), 3.68 (s, 3H, $C\underline{H}_3N$), 3.95 (t, $^3J_{HH}$ = 7.5 Hz, 2H, $NC\underline{H}_2CH_2CH_2CH_3$), 7.12 (s, 2H, $NC\underline{H}C\underline{H}N$), 7.28 (s, 1H, $NC\underline{H}CHN$). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 9.13 ($NC(\underline{C}H_3)N$), 13.03 ($NCH_2CH_2CH_2\underline{C}H_3$), 19.17 ($NCH_2CH_2\underline{C}H_2CH_3$), 31.22 ($NCH_2\underline{C}H_2CH_2CH_3$), 34.90 ($N\underline{C}H_3$), 48.30 ($N\underline{C}H_2CH_2CH_2CH_3$), 119.61 (q, $^1J_{CF}$ = 321 Hz, $\underline{C}F_3SO_2N$), 120.70 ($N\underline{C}HCHN$), 122.26 ($NCH\underline{C}HN$), 143.53 ($N\underline{C}HN$).

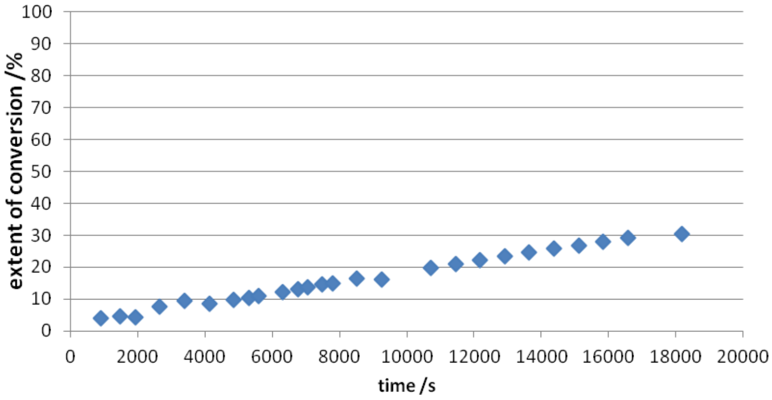
Extent of conversion *vs* time data

Reactions were carried out as described in the manuscript. It was observed that there was only a small degree of variation between individual spectra for a given experiment (± 2%) and between replicate experiments (± 5%). Representative stacked plots showing the change in ^1H NMR resonances with time for the starting material **3** and the isomers of the products *cis*-**5** and *trans*-**5**.

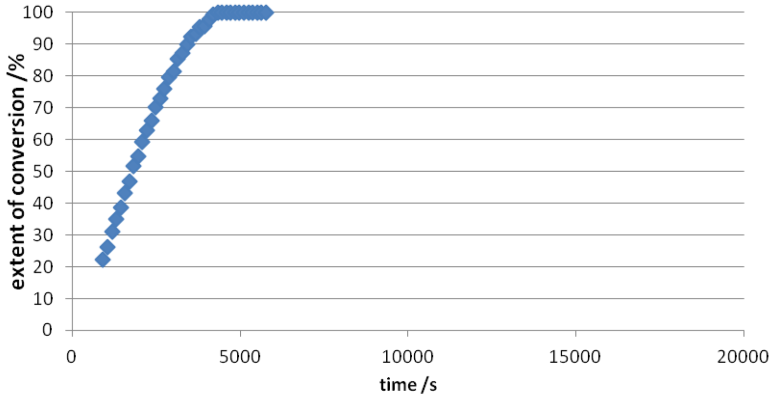


Examples of catalytic effect of IMes 6 in THF at three different temperatures

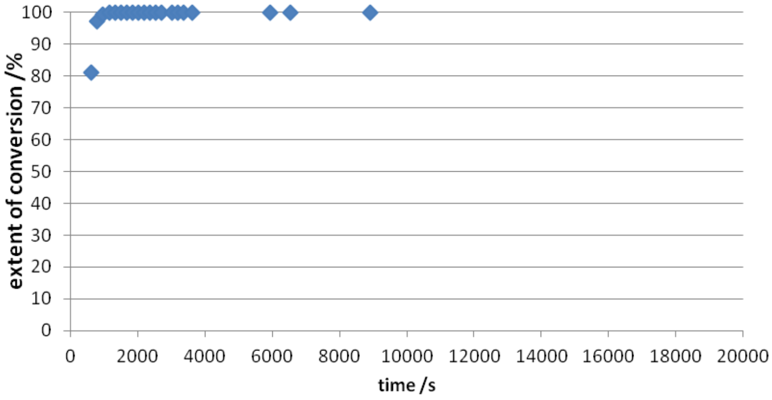
Extent of reaction of the process carried out at -10 ^{o}C in THF with 10 mol% IMes **6**



Extent of reaction of the process carried out at 5 ^{o}C in THF with 10 mol% IMes **6**

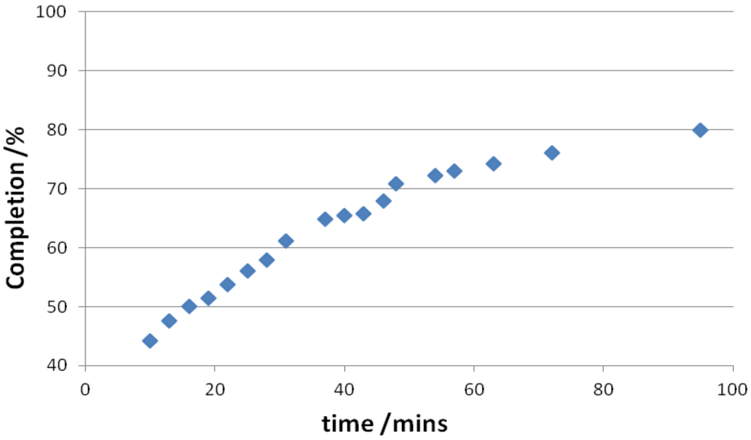


Extent of reaction of the process carried out at 25 ^{o}C in THF with 10 mol% IMes **6**



Demonstration of the autocatalytic effect of lactones 5 in the presence of IBuMe 2

To a J. Youngs tap NMR tube containing *p*-bromobenzaldehyde (22.5 mg, 0.12 mmol), *trans*-cinnemaldehyde **3** (15 μL, 0.12 mmol) and the GBL product mixture **5** (22.6 mg, 0.07 mmol), a stock solution of IBuMe in THF (0.8 mL, 0.071 mol/L, 0.06 mmol) was added. The reaction was followed as per other experiments using ^{1}H NMR spectroscopy.



Extent of reaction of the process carried out at 25 °C in THF with 5 mol% IMes **6** and 5 mol % of GBL **5**.

Deuterium exchange experiment for IMes 6 / bmimCl

IMes **6** (7 mg, 0.02 mmol) and acetonitrile-d_3 (0.6 cm^3) were placed in a J. Youngs tap NMR tube. ^{1}H NMR spectra showed the presense of the hydrogen atoms on the mesityl groups, however resonances due to the C4/C5 protons were not present. This is consistent with observations by Cole[5] and Denk[6] that deuteration of the 4,5-heterocyclic carbons on imidazol-2-ylidenes occurs rapidly when placed in a weakly acidic deuterated medium. This exchange was also noted when IBuMe **2** (7 mg) and acetonitrile-d_3 were placed in a J. Youngs NMR tube, with C4/C5 backbone proton signals not observed. As a control, NMR spectra of IMes.HCl in acetonitrile-d_3 and [bmim][Cl] in acetonitrile-d_3 showed the signals due to the C2 proton and C4/C5 backbone protons.

IMes **6** (7 mg, 0.02 mmol), [bmim][Cl] (5.1 mg, 0.027 mmol) and acetonitrile (0.6 cm^3) were placed into a J. Youngs tap NMR tube. It was noted that no resonances due to either C2 protons or

C4/C5 backbone protons of *any* species were present. This indicates that the carbene **2** must be forming *in situ*, most likely through a proton exchange mechanism with IMes **6**.

Demonstration that IBuMe 2 was present in the reaction mixture in ionic liquid 1.

The ionic liquid [bmim][NTf$_2$] **1** (15 mg, 0.035 mmol) and acetonitrile-d$_3$ (0.6 cm^3) were placed in a J. Youngs NMR tube and a ^{1}H NMR spectrum taken; resonances due to all protons were observed. To a solution of [bmim][NTf$_2$] **1** in THF, ^{n}BuLi (1.5 eq.) was added dropwise and allowed to stir for 2 hours at room tempreture. Solvents (THF/hexane) were removed *in vacuo*, and residual product dissolved into acetonitrile-d$_3$. A ^{1}H NHR spectra in showed no signals due to the C4,C5 protons, indicating that IBuMe **2** had been formed.

Determination of equilibrium constant for proton exchange of IMes 6 in ionic liquid 1

To a J. Youngs tapped NMR tube containing a saturated solution of ionic liquid **1** (10 μL in 0.3 cm^3 of benzene-*d*$_6$), an aliquot (0.3 cm^3) of a stock solution of IMes **6** in benzene-*d*$_6$ (20 mg in 0.6 cm^3) was added and an NMR spectra obtained. Another three aliquots (20 μL each) of the IMes **6** stock solution were added and NMR spectra obtained after each addition. The C2 proton resonances corresponding to the cations **2·H**$^+$ and **6.H**$^+$ and the C4/5 proton resonances corresponding to the carbenes **2** and **6** were integrated and scaled to the number of protons in each of the environments. These values allowed determination of the equilibrium constant as 0.0216, corresponding to a ΔpK_a of 0.79.

References

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