

## Nitrene transfer reactions catalysed by copper(I) complexes in ionic liquid using chloramine-T

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### Supplementary Information

**General Methods.** All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents and hydrocarbons were dried and degassed before use. Chloramine-T trihydrate was purchased from Aldrich and was dried by heating at 60 °C in an oil bath under vacuum for 6 h without decomposition. Ionic liquid [bmim]PF<sub>6</sub><sup>1</sup> and the complexes [Tpm<sup>X</sup>Cu(NCMe)]BF<sub>4</sub><sup>2</sup> were prepared according to literature procedure. NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer. <sup>1</sup>H chemical shifts were measured relative to partially deuterated solvent peaks but are reported relatively to tetramethylsilane.

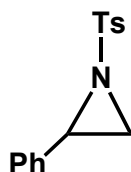
**General Catalytic Procedure for Aziridination Reactions.** The catalyst (0.025 mmol, 5 mol%) was dissolved in [bmim]PF<sub>6</sub> (3 mL) in an ampoule containing molecular sieves. The olefin (2.5 mmol) and dried chloramine-T (0.5 mmol) were added to the solution under a nitrogen atmosphere. The reaction mixture is stirred at room temperature for 24h. The product was extracted with diethyl ether (4 x 4 mL) and the organic solvent was evaporated to dryness to yield a crude solid residue which was investigated by <sup>1</sup>H NMR to determine the conversion using trimethyl vinyl silane (0.5 mmol) as internal standard. The crude residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (5:1) as eluent to afford the aziridination product.

Aziridines and allylic amination products were characterized by comparison of their spectroscopic data with those previously reported.

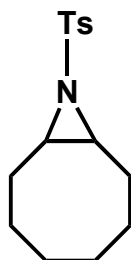
**General Catalytic Procedure for Amidation Reactions of Cyclic Ethers.** The catalyst (0.025 mmol, 5 mol%) was dissolved in [bmim]PF<sub>6</sub> (3 mL) in an ampoule containing molecular sieves. The substrate (2 mL) and dried chloramine-T (0.5 mmol) were added to the solution under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for the specified time period (see Table 5). Diethyl ether (4 mL) was added to separate the organic layer. The ionic liquid phase was washed with diethyl ether (3 x 4 mL). The combined organic solution was evaporated to dryness and the residue was investigated by <sup>1</sup>H NMR to determine the conversion (using trimethyl vinyl silane as internal standard). We observed that the amidation products decomposed on chromatography. To avoid decomposition, the crude residue was treated with hexane and filtered to remove *p*-toluenesulfonamide. The filtrates were evaporated and dried under vacuum to yield the pure amidation products. Compounds were characterized by comparing their <sup>1</sup>H NMR with the previously reported data.

**Study of Reuse of the Catalytic System.** The aziridination or amidation reaction was performed as described above. Once the product was extracted with diethyl ether the ionic liquid phase was dried under vacuum and charged with a second load of the substrate and chloramine-T (0.5 mmol) under nitrogen. The mixture was stirred at room temperature for a specific reaction period. After this time, the products were extracted with diethyl ether and the remaining solution of the catalyst in the IL was reused following the same method (see Tables 2 and 4).

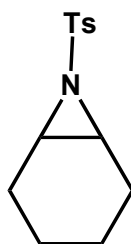
**Characterization Data:**



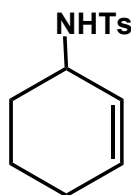
***N*-(*p*-Toluenesulfonyl)-2-phenylaziridine:**<sup>3</sup> Yield: 84%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 (d, 2H,  $J$  = 8.3 Hz), 7.33 (d, 2H,  $J$  = 8.3 Hz), 7.30-7.20 (m, 5H), 3.77 (dd, 1H,  $J$  = 7.1, 4.6 Hz), 2.98 (d, 1H,  $J$  = 7.3 Hz), 2.43 (s, 3H), 2.39 (d, 1H,  $J$  = 4.8 Hz).



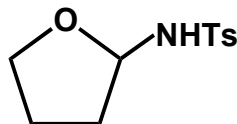
***N*-(*p*-Toluenesulfonyl)-3-azatricyclo[3.2.1]octane:**<sup>4</sup> Yield: 53%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.81 (d, 2H,  $J$  = 8.3 Hz), 7.32 (d, 2H,  $J$  = 7.8 Hz), 2.78 (m, 2H), 2.44 (s, 3H), 2.01 (m, 2H), 1.56-1.25 (m, 10 H).



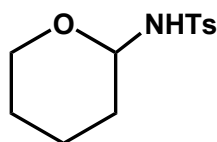
***N*-(*p*-Toluenesulfonyl)-7-azabicyclo[4.1.0]heptane:**<sup>4</sup> Yield: 8%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (d, 2H,  $J$  = 8.2 Hz), 7.32 (d, 2H,  $J$  = 8.0 Hz), 2.97 (br s, 2H), 2.44 (s, 3H), 1.79 (m, 4H), 1.38 (m, 2H), 1.21 (m, 2H).



***N*-(*p*-Toluenesulfonyl)-1-amino-2-cyclohexene:**<sup>5</sup> Yield: 18%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.78 (d, 2H, *J* = 7.8 Hz), 7.30 (d, 2H, *J* = 7.8 Hz), 5.75 (m, 1H), 5.34 (m, 1H), 4.46 (d, 1H, *J* = 8.2 Hz), 3.83 (m, 1H), 2.43 (s, 3H), 2.0-1.4 (m, 6H).



***N*-(Tetrahydrofuran-2-yl)-*p*-toluenesulfonamide:**<sup>6</sup> Yield: 83%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.78 (d, 2H, *J* = 8.3 Hz), 7.26 (d, 2H, *J* = 8.3 Hz), 5.94 (d, 1H, *J* = 8.8 Hz), 5.31 (m, 1H), 3.65 (m, 2H), 2.39 (s, 3H), 2.09 (m, 1H), 1.86-1.76 (m, 3H).



***N*-(Tetrahydropyran-2-yl)-*p*-toluenesulfonamide:**<sup>7</sup> The compound could not be isolated pure. NMR Yield: 40%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79 (d, 2H, *J* = 8.3 Hz), 7.28 (d, 2H, *J* = 8.3 Hz), 5.54 (d, 1H, *J* = 9.8 Hz), 4.73 (br t, 1H, *J* = 8.1 Hz), 3.69 (m, 1H), 3.35 (m, 1H), 2.40 (s, 3H), 1.78 (m, 2H), 1.45 (m, 1H), 1.40 (m, 2H).

## References

1. (a) J. S. Wilkes, J. A. Levisky, R. A. Wilson and C. L. Hussey, *Inorg. Chem.*, 1982, **21**, 1263; (b) P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. de Souza and J. Dupont, *Polyhedron*, 1996, **15**, 1217.
2. (a) Tpm<sup>X</sup> = Tpm\* (see Figure 1): D. L. Reger, J. E. Collins, A. L. Rheingold and L. M. Liable-Sands, *Organometallics*, 1996, **15**, 2029; (b) Tpm<sup>X</sup> = Tpm<sup>\*,Br</sup>: M. Cvetkovic, S. R. Batten, B. Moubaraki, K. S. Murray and L. Spiccia, *Inorg. Chim. Acta*, 2001, **324**, 131; (c) Tpm<sup>X</sup> = Tpm<sup>Ms</sup>: P. Rodríguez, E. Álvarez, M. C. Nicasio and P. J. Pérez, *Organometallics*, 2007, **26**, 6661.
3. T. P. Seden and T. W. Turner, *J. Chem. Soc. (C)*, 1968, 876.

4. D. A. Evans, M. M. Faul and M. T. Bilodeau, *J. Am. Chem. Soc.*, 1994, **116**, 2742.
5. M. C. McIntosh and S. M. Weinreb, *J. Org. Chem.*, 1993, **58**, 4823.
6. S. K.-Y. Leung, W.-M. Tsui, J.-S. Huang, C.-M. Che, J.-L. Liang and N. Zhu, *J. Am. Chem. Soc.*, 2005, **127**, 16629.
7. D. H. R. Barton, M. R. Britten-Kelly and D. J. Ferreira, *Chem. Soc., Perkin Trans. 1*, 1978, 1682.

