Supporting Information

Synthetic and Mechanistic Studies of Indium-Mediated Allylation of Imines in Ionic Liquids.

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Table of contents

Experimental details.....	S3
¹ H NMR and ¹³ C NMR spectra of compound 2a	S4
¹ H NMR spectra of compound 2b	S4
¹³ C NMR spectra of compound 2b	S5
¹ H NMR and ¹³ C NMR spectra of compound 2c	S5
¹ H NMR and ¹³ C NMR spectra of compound 2d	S6
¹ H NMR spectra of compound 2e	S6
¹³ C NMR spectra of compound 2e	S7
¹ H NMR and ¹³ C NMR spectra of compound 2f	S7
¹ H NMR and ¹³ C NMR spectra of compound 2g	S8
¹ H NMR spectra of compound 2h	S8
¹³ C NMR spectra of compound 2h	S9
¹ H NMR and ¹³ C NMR spectra of compound 2i	S9
¹ H NMR and ¹³ C NMR spectra of compound 2j	S10
¹ H NMR spectra of compound 2k	S10
¹³ C NMR spectra of compound 2k	S11
¹ H NMR and ¹³ C NMR spectra of compound 2l	S11
¹ H NMR and ¹³ C NMR spectra of compound 2m	S12
¹ H NMR spectra of compound 3b	S12
¹³ C NMR spectra of compound 3b	S13

Experimental Section

Preparation of ionic liquids. The crude N-butylpyridinium tetrafluoroborate [bpy][BF₄] was prepared by metathesis reaction in acetonitrile (300 mL) from sodium tetrafluoroborate (121 g, 1.1 mol,) (purchased commercially with 98% purity in fine powder form) and its bromide precursor [bpy][Br] (216 g, 1.0 mol) which was in turn prepared from the microwave-assisted method.¹ The mixture was stirred for three days at room temperature and then filtered. The filtrate was evaporated and the residue crude [bpy][BF₄] was vacuum-dried overnight at 70 °C (0.1 mmHg) and stored under nitrogen. Pure [bpy][BF₄] could be obtained by column chromatography of the crude [bpy][BF₄] on silica gel with dichloromethane as eluent.² The recovery of [bpy][BF₄] after chromatography was about 60%.

Typical procedure for the preparation of benzylideneanilines in ionic liquid. To a 50 mL reaction tube was charged with the ionic liquid (2 mL). A mixture of benzaldehyde (1mmol) and aniline (1mmol) was added to ionic liquid (2mL) at room temperature under nitrogen. The reaction mixture was stirred vigorously for the specified time and temperature as indicated in Table 4.

Allylation of imines in ionic liquids. Pure [Bpy][BF₄] (1 mL) with the indicated amount of [bpy][Br] added was used as reaction media. Indium and allylBr (in mmols specified) were added and stirred at r.t. for 1 hr. Imine (0.5 mmol generated *in-situ* in IL) was then added to the reaction mixture and stirred at r.t. overnight. The resulting mixture was quenched with a few drops of saturated ammonium chloride solution followed by extraction with ethyl acetate (3 x 10 mL). After removal of the solvent in vacuum, the residue was purified by flash chromatography on silica gel to yield the pure adduct amine **2**.

(1) Law, M. C.; Wong, K. Y.; Chan, T. H. *Green Chem.* **2002**, 4, 328.

(2) Park, S.; Kazlauskas, R. J. *J. Org. Chem.* **2001**, 66, 8395.

***N*-[1-(4-Chlorophenyl)-3-butenyl]aniline (2a)³:**

¹H NMR (500MHz, CDCl₃) δ7.32-7.29 (m, 4H), 7.10 (t, 2H, *J* = 8Hz), 6.67(t, 1H, *J* = 7.5Hz), 6.47(d, 2H, *J* = 8Hz), 5.79-5.71 (m, 1H), 5.22-5.16 (m, 2H), 4.37 (dd, 1H, *J* = 7.5, 4.5Hz), 4.15 (br s, 1H), 2.61-2.44 (m, 2H).

¹³C NMR (CDCl₃) δ147.0, 142.1, 134.2, 132.5, 129.1, 128.7, 127.7, 118.7, 117.6, 113.5, 56.5, 43.2; MS (ESI) *m/z* 258.19 (M+H)⁺

***4*-Chloro-*N*-(1-phenyl-3-butenyl)aniline (2b)⁴:**

¹H NMR (500MHz, CDCl₃) δ7.32-7.29 (m, 4H), 7.25-7.21 (m, 1H), 7.01-6.98 (m, 2H), 6.41-6.38 (m, 2H), 5.78-5.70 (m, 1H), 5.19-5.13 (m, 2H), 4.33 (dd, 1H, *J* = 7.5, 5Hz), 4.15 (br s, 1H), 2.61-2.44 (m, 2H).

(3) Shen, K. H.; Yao, C. F. *J. Org. Chem.* **2006**, *71*, 3980.

(4) Das, B.; Ravikanth, B.; Thirupathi, P. and Vittal Rao, B. *Tetrahedron Lett.* **2006**, *47*, 5041.

^{13}C NMR (CDCl_3) δ 145.7, 142.9, 134.4, 128.8, 128.6, 127.1, 126.2, 121.9, 118.5, 114.5, 57.1, 43.2; MS (ESI) m/z 258.11 ($\text{M}+\text{H}$) $^+$

N-[1-(2-Pyridyl)-3-butenyl]aniline (2c) 5 :

^1H NMR (500MHz, CDCl_3) δ 8.60-8.59 (m, 1H), 7.62-7.59 (m, 1H), 7.34 (d, 1H, J = 8Hz), 7.17-7.14 (m, 1H), 7.10 (t, 2H, J = 8Hz), 6.68-6.65 (m, 1H), 6.54 (d, 2H, J = 8.5Hz), 5.80-5.72 (m, 1H), 5.18-5.11 (m, 2H), 4.55-4.52 (m, 1H), 4.44 (br s, 1H), 2.77-2.72 (m, 2H).

^{13}C NMR (CDCl_3) δ 162.3, 149.3, 147.0, 136.6, 134.4, 129.1, 122.0, 120.9, 118.2, 117.5, 113.4, 58.4, 42.2; MS (ESI) m/z 225.07 ($\text{M}+\text{H}$) $^+$

(5) Degrand, C.; Compagnon, P. L.; Belot, G. and Jacquin, D. *J. Org. Chem.* **1980**, *45*, 1189.

4-[1-(Phenylamino)-3-butenyl]benzonitrile (2d)⁶:

¹H NMR (500MHz, CDCl₃) δ 7.62 (d, 2H, *J* = 8Hz), 7.45 (d, 2H, *J* = 8Hz), 7.10-7.07 (m, 2H), 6.68 (t, 1H, *J* = 7.5Hz), 6.42 (d, 1H, *J* = 8Hz), 5.76-5.68 (m, 1H), 5.22-5.18 (m, 2H), 4.44-4.40 (m, 1H), 4.17 (d, 1H, *J* = 3Hz), 2.63-2.44 (m, 2H).

¹³C NMR (CDCl₃) δ 149.4, 146.6, 133.5, 132.5, 129.2, 127.1, 119.2, 118.9, 118.0, 113.4, 110.9, 56.9, 42.9; MS (ESI) *m/z* 249.05 (M+H)⁺

***N*-[1-(2-Furyl)-3-butenyl]aniline (2e)⁴:**

¹H NMR (500MHz, CDCl₃) δ 7.35 (d, 1H, *J* = 2Hz), 7.15 (t, 2H, *J* = 8Hz), 6.79 (t, 1H, *J* = 8Hz), 6.62 (d, 2H, *J* = 8Hz), 6.29 (dd, 1H, *J* = 2, 1.5Hz), 6.16 (d, 1H, *J* = 3.5Hz), 5.20-5.12 (m, 1H), 4.56 (t, 2H, *J* = 6.3Hz), 3.99 (br s, 1H), 2.71-2.62 (m, 2H).

(6) Hilt, G.; Smolko, K. I.; Waloch, C. *Tetrahedron Lett.* **2002**, 43, 1437.

^{13}C NMR (CDCl_3) δ 155.6, 146.9, 141.5, 134.0, 129.1, 118.4, 117.8, 113.5, 110.1, 106.1, 51.2, 39.2; MS (ESI) m/z 214.03 ($\text{M}+\text{H}$) $^+$

***N*-[1-(4-Methoxyphenyl)-3-butenyl]aniline (**2f**) 4 :**

^1H NMR (500MHz, CDCl_3) δ 7.30 (d, 2H, J = 8Hz), 7.08 (t, 2H, J = 7.8Hz), 6.86 (d, 2H, J = 8.5Hz), 6.64 (t, 1H, J = 7.3Hz), 6.50 (d, 2H, J = 8Hz), 5.80-5.72 (m, 1H), 5.20-5.13 (m, 2H), 4.34 (dd, 1H, J = 8, 5.5Hz), 4.13 (br s, 1H), 3.80 (s, 3H), 2.60-2.44 (m, 2H).

^{13}C NMR (CDCl_3) δ 158.5, 147.4, 135.5, 134.7, 129.0, 127.3, 118.2, 117.3, 113.9, 113.4, 56.5, 55.2, 43.4; MS (ESI) m/z 254.16 ($\text{M}+\text{H}$) $^+$

***N*-[1-(1-Naphthyl)-3-butenyl]aniline (2g)⁷:**

¹H NMR (500MHz, CDCl₃) δ 8.19 (d, 1H, *J* = 8.5Hz), 7.93 (d, 1H, *J* = 7.5Hz), 7.76 (d, 1H, *J* = 8.5Hz), 7.64 (d, 1H, *J* = 7Hz), 7.61-7.57 (m, 1H), 7.55-7.52 (m, 1H), 7.41 (t, 1H, *J* = 7.5Hz), 7.04 (t, 2H, *J* = 8Hz), 6.63 (t, 1H, *J* = 7.3Hz), 6.46 (t, 2H, *J* = 8Hz), 5.90-5.82 (m, 1H), 5.28-5.19 (m, 3H), 2.88-2.83 (m, 1H), 2.60-2.54 (m, 1H).

¹³C NMR (CDCl₃) δ 147.1, 138.0, 134.8, 134.2, 130.6, 129.2, 129.1, 127.5, 126.1, 125.8, 125.4, 123.2, 122.3, 118.3, 117.3, 113.4, 53.0, 41.6; MS (ESI) *m/z* 274.17 (M+H)⁺

5-[1-(Benylamino)-3-butenyl]thiazole (2h):

¹H NMR (500MHz, CDCl₃) δ 7.74 (d, 1H, *J* = 3Hz), 7.33-7.24 (m, 6H), 5.79-5.71 (m, 1H), 5.14-5.10 (m, 2H), 4.16 (dd, 1H, *J* = 8.5, 5Hz), 3.84 (d, 1H, *J* = 13Hz), 3.72 (d, 1H, *J* = 13Hz), 2.70-2.46 (m, 2H).

(7) Yadav, J. S.; Reddy, B. V. S.; Raju, A. K. *Synthesis*. **2003**, 6, 883.

^{13}C NMR (CDCl_3) δ 176.6, 142.5, 139.8, 134.0, 128.4, 128.2, 127.1, 118.8, 118.7, 59.3, 51.8, 41.7; MS (ESI) m/z 245.14 ($\text{M}+\text{H}$) $^+$; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{N}_2\text{S}$ 245.1112 ($\text{M}+\text{H}$) $^+$; found: 245.1121.

4-Methoxy-*N*-(1-phenyl-3-butenyl)benzylamine (2i)⁸:

^1H NMR (500MHz, CDCl_3) δ 7.36-7.33 (m, 4H), 7.28-7.25 (m, 1H), 7.17 (d, 2H, J = 9Hz), 6.85 (d, 2H, J = 8.5Hz), 5.74-5.67 (m, 1H), 5.08-5.02 (m, 2H), 3.80 (s, 3H), 3.68 (dd, 1H, J = 7, 6.5Hz), 3.61 (d, 1H, J = 13Hz), 3.46 (d, 1H, J = 13Hz), 2.45-2.36 (m, 2H).

^{13}C NMR (CDCl_3) δ 158.5, 143.8, 135.4, 132.7, 129.2, 128.3, 127.3, 127.0, 117.5, 113.7, 61.4, 55.2, 50.7, 43.0; MS (ESI) m/z 268.07 ($\text{M}+\text{H}$) $^+$

(8) Fernandes, R. A.; Stimac, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **2003**, 125, 14133.

***N*-[1-(4-Bromophenyl)-3-butenyl]benylamine (2j):**

^1H NMR (500MHz, CDCl_3) δ 7.47 (d, 2H, $J = 7\text{Hz}$), 7.33-7.30 (m, 2H), 7.26-7.23 (m, 5H), 5.72-5.63 (m, 1H), 5.08-5.04 (m, 2H), 3.67-3.64 (m, 2H), 3.50 (d, 1H, $J = 13.5\text{Hz}$), 2.41-2.32 (m, 2H).

^{13}C NMR (CDCl_3) δ 142.2, 139.6, 134.7, 131.5, 129.1, 128.3, 128.2, 127.0, 120.8, 118.0, 60.9, 51.2, 42.7; MS (ESI) m/z 315.92 ($\text{M}+\text{H}$) $^+$

***N*-[1-(4-Methoxyphenyl)-3-butenyl]benylamine (2k)⁹:**

^1H NMR (500MHz, CDCl_3) δ 7.32-7.22 (m, 7H), 6.89 (d, 2H, $J = 9\text{Hz}$), 5.73-5.65 (m, 1H), 5.08-5.02 (m, 2H), 3.82 (s, 3H), 3.68-3.63 (m, 2H), 3.51 (d, 1H, $J = 13\text{Hz}$), 2.41-2.39 (m, 2H).

(9) Yadav, J. S.; Reddy, B. V. S.; Reddy, P. S. R.; Shesha Rao, M. *Tetrahedron Lett.* **2002**, 43, 6245.

^{13}C NMR (CDCl_3) δ 158.6, 140.6, 135.7, 135.5, 128.3, 128.2, 128.1, 126.8, 117.4, 113.7, 60.9, 55.2, 51.3, 43.1; MS (ESI) m/z 268.07 ($\text{M}+\text{H}$) $^+$

4-[1-(benzylamino)-3-butenyl]benzonitrile (2l):

^1H NMR (500MHz, CDCl_3) δ 7.64 (d, 2H, J = 8.5Hz), 7.49 (d, 2H, J = 8Hz), 7.33-7.30 (m, 2H), 7.25-7.22 (m, 2H), 5.70-5.62 (m, 1H), 5.08-5.05 (m, 2H), 3.75 (dd, 1H, J = 8, 5.5Hz), 3.63 (d, 1H, J = 13.5Hz), 3.50 (d, 1H, J = 13.5Hz), 2.42-2.31 (m, 2H).

^{13}C NMR (CDCl_3) δ 149.6, 139.9, 134.3, 132.3, 128.4, 128.1, 128.0, 127.1, 119.0, 118.5, 110.9, 61.3, 51.5, 42.9; MS (ESI) m/z 263.20 ($\text{M}+\text{H}$) $^+$; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{19}\text{N}_2$ 263.1548 ($\text{M}+\text{H}$) $^+$; found: 263.1559.

4-Chloro-*N*-[1-(2-Phenylethenyl)-3-butenyl]aniline (2m):

^1H NMR (500MHz, CDCl_3) δ 7.34-7.23 (m, 4H), 7.24-7.21 (m, 1H), 7.11 (d, 2H, J = 8.5Hz), 6.58-6.55 (m, 3H), 6.16 (dd, 1H, J = 16, 6.5Hz), 5.86-5.78 (m, 1H), 5.20-5.15 (m, 2H), 4.02-3.98 (m, 1H), 2.53-2.42 (m, 2H).

^{13}C NMR (CDCl_3) δ 146.0, 136.7, 134.1, 130.9, 130.5, 128.9, 128.5, 127.5, 126.3, 122.0, 118.5, 114.6, 54.8, 40.4; MS (ESI) m/z 284.12 ($\text{M}+\text{H}^+$); HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{19}\text{NCl}$ 284.1206 ($\text{M}+\text{H}^+$); found: 284.1201.

***N,N*-[1-(Phenyl)-3-butenyl-1'-propenyl]benzylamine (3b):**

^1H NMR (500MHz, CDCl_3) δ 7.36-7.22 (m, 10H), 5.89-5.73 (m, 2H), 5.17 (d, 1H, J = 17.5Hz), 5.11 (d, 1H, J = 10Hz), 5.02 (d, 1H, J = 17.5Hz), 4.96 (d, 1H, J = 10Hz), 3.85 (t, 1H, J = 7.5Hz), 3.80 (d, 1H, J = 14Hz), 3.28-3.20 (m, 2H), 2.83-2.74 (m, 2H), 2.57-2.51 (m, 1H).

^{13}C NMR (CDCl_3) δ 140.3, 139.4, 136.8, 136.4, 128.7, 128.5, 128.0, 127.8, 126.9, 126.6, 116.8, 115.9, 62.7, 53.6, 52.5, 36.0; MS (ESI) m/z 278.20 ($\text{M}+\text{H}^+$); HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{24}\text{N}$ 278.1909 ($\text{M}+\text{H}^+$); found: 278.1915.