Supporting Information

Asymmetric synthesis with N-heterocyclic carbenes. Application to the copper catalyzed conjugate addition.

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Typical procedure for conjugate addition using imidazolinium salt in Et_2O at –78 °C

A dry Schlenk tube was charged with $Cu(OTf)_2$ (0.04 mmol) and imidazolinium salt (0.04 mmol) and Et_2O (3 mL) was added. The resulting solution was cooled to –78 °C, upon which *n*-BuLi (0.05 mmol as a 2M solution in hexanes) was added. After stirring for 30 minutes at low temperature, the reaction mixture was warmed up to room temperature and stirred for a further 15 minutes to ensure complete deprotonation. After this time, the solution was cooled back to –20 °C and diethyl zinc was added (1.5 mmol as a 1M solution in hexane). The mixture was stirred for 15 minutes before cooling to -78 °C and adding the substrate (1 mmol, either neat if cyclohexenone, or as a solution in toluene). After stirring at –78 °C for 16 hours, the reaction was quenched at low temperature by the addition of HCl (2 mL of a 1M aqueous solution). The resulting mixture was stirred until clear and enantiomeric excesses could be measured directly using chiral GC (capillary column – Lipodex E, 0.2 μm, 50 m, 0.25 mm). The organic phases could be isolated, dried over $MgSO_4$ and the solvent concentrated *in vacuo* to yield the crude product, which could be purified by flash column chromatography to provide the pure product.

Typical procedure for conjugate addition using silver carbene in Et_2O at -78 °C

A dry Schlenk tube was charged with copper salt (0.04 mmol) and silver carbene (0.04 mmol) and Et_2O (3 mL) was added. After stirring for 15 minutes at room temperature, the solution was cooled to –20 °C and diethyl zinc was added (1.5 mmol as a 1M solution in hexane). The mixture was stirred for 15 minutes the reaction mixture was cooled to –78 °C for addition of the substrate (1 mmol, either neat if cyclohexenone, or as a solution in toluene). After stirring at –78 °C for 16 hours, the reaction was quenched at low temperature by the addition of HCl (2 mL of a 1M aqueous solution). The resulting mixture was stirred until clear and enantiomeric excesses could be measured directly using chiral GC (capillary column – Lipodex E, 0.2 μm, 50 m, 0.25 mm). The organic phases could be isolated, dried over $MgSO_4$ and the solvent concentrated *in vacuo* to yield the crude product, which could be purified by flash column chromatography to provide the pure product.

Synthesis of ligands 1, 3 and 4 from known diamines

Into a flask equipped with a magnetic stirrer, was introduced the diamine (1 equiv.), and ammonium tetrafluoroborate (1 equiv.). A distillation cooling head was fitted with a collection head for the second stage of the reaction and the system purged with nitrogen. Triethylorthoformate (2 equiv.) was the added *via* syringe and the resulting mixture was heated at 120 °C for up to 2 hours. After this time, the system was placed under high vacuum and the volatile by-products and excess starting materials were collected. The resulting products were purified as described below.

(4*S*,5*S*)-Diphenyl-1,3-bis-(1(*R*)-phenyl-ethyl)-4,5-dihydro-3*H*-imidazol-1-ium tetraflouroborate 1

The crude product was purified by recrystallisation with an ethanol-ethyl acetate mixture to give the desired compound in 95% yield as a white crystalline product.

^{1}H NMR (400 MHz, $CDCl_3$): 9.18 (s, 1H, NC<u>H</u>N), 7.40-7.11 (m, 16H, Ar<u>H</u>), 7.00-6.90 (m, 4H, Ar<u>H</u>), 4.45 (s, 2H, PhC<u>H</u>N), 4.39 (q, *J* = 6.9 Hz, 2H, PhC<u>H</u>MeN), 2.01 (d, *J* = 6.9 Hz, 6H, CH_3).

^{13}CNMR (100.6 MHz, $CDCl_3$): 153.0 (N<u>C</u>NH), 137.4, 135.4, 130.3, 129.8, 129.4, 129.0, 127.0, 126.9, 72.6, 57.9, 20.1.

α_D –174 (*c* 0.54, $CHCl_3$).

1,3-Dimethyl-(4*S*,5*S*)-diphenyl-4,5-dihydro-3*H*-imidazol-1-ium tetrafluoroborate 3

The pale yellow crude product was recrystallised with an ethyl acetate-chloroform mixture to give the desired product in 88% yield as a white crystalline product with melting point = 223-224 °C.

^{1}H NMR (200 MHz, $CDCl_3$): 8.16 (s, 1H, NC<u>H</u>N), 7.55-7.45 (m, 6H, Ar<u>H</u>), 7.40-7.30 (m, 4H, Ar<u>H</u>), 5.00 (s, 2H, NC<u>H</u>Ph), 2.97 (s, 6H, C<u>H</u>$_3$).

^{13}CNMR (50 MHz, $CDCl_3$): 159.6 (N<u>C</u>NH), 135.8, 131.0, 130.6, 128.8, 75.8, 33.8.

α_D +253 (*c* 0.59, $CHCl_3$).

1,3-Bis-(1(*S*)-phenyl-ethyl)-4,5-dihydro-3*H*-imidazol-1-ium tetraflouroborate 4

The resulting oil was triturated with ethyl acetate and the resulting white solid collected by filtration. After recrystallisation with an ethanol-water mixture, the desired product was obtained in 80% yield as a white crystalline solid with melting point = 118 °C.

^{1}H NMR (200 MHz, $CDCl_3$): 8.13 (s, 1H, NC<u>H</u>N), 7.50-7.30 (m, 10H, Ar<u>H</u>), 4.80 (q, *J* = 7.0 Hz, 2H, NC<u>H</u>Me), 3.70-3.55 (m, 4H, NC<u>H</u>$_2$C<u>H</u>$_2$N), 1.67 (d, *J* = 7.0 Hz, 6H, C<u>H</u>$_3$).

^{13}CNMR (50 MHz, $CDCl_3$): 155.6 (N<u>C</u>NH), 139.2, 130.1, 129.8, 128.0, 59.0, 47.7, 19.9.

α_D +23 (*c* 0.51, $CHCl_3$).

General method for preparation of unsaturated tetrafluoroborate-imidazolium salts (Ligands 5-8)[1]

A 50 mL flask was charged with (*R*)- or (*S*)-chiral amine (10 mmol) in toluene. Under vigorous stirring and slight cooling, was added paraformaldehyde (10 mmol). After 30 minutes, a second equivalent of the amine was added at 0 °C. Under constant cooling, HBF_4 (10 mmol as a 32% aqueous solution) was added dropwise. After stirring for 15 minutes, the ice bath was removed and glyoxal was slowly added (10 mmol as a 40% aqueous solution). The resulting mixture was stirred for 30 minutes at room temperature, then for 12 hours at 35-40 °C. After this time, the mixture was cooled to room temperature and the mixture was diluted with diethyl ether (10 mL) and a saturated solution of Na_2CO_3 (5 mL). The phases were then separated and the aqueous layer washed with dichloromethane (2 x 10 mL). The combined organic layers were washed with brine (25 mL), dried over $MgSO_4$ then concentrated under reduced pressure. The crude product in each case was isolated as a viscous brown/orange oil which could be purified by trituration using diethyl ether.

[1] Herrman, W. A.; Elison M.; Fischer, J.; Kocher, C.; Artus, G. R. J. *Chem. Eur. J.,* **1996**, *2*, 780.

1,3-Bis-(1(*R*)-phenyl-ethyl)-imidazolium tetraflouroborate 5

The desired product was obtained as a hygroscopic, yellow powder in 60 % yield.

^{1}H NMR (400 MHz, $CDCl_3$): 9.26 (s, 1H, NC<u>H</u>N), 7.39-7.37 (m, 10H, Ar<u>H</u>), 7.13 (s, 2H, NC<u>H</u>=C), 5.75 (q, *J* = 7.0 Hz, 2H, NC<u>H</u>(CH_3)Ph), 1.96 (d, *J* = 7.0 Hz, 6H, C<u>H</u>$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 137.8, 133.7, 129.0, 126.9, 121.1, 60.1, 20.6.

α_D +18.5 (*c* 0.96, $CHCl_3$).

1,3-Bis-(1(*S*)-phenyl-propyl)-imidazolium tetraflouroborate 6

The desired product was obtained as a hygroscopic, pale yellow powder in 48 % yield.

^{1}H NMR (400 MHz, $CDCl_3$): 9.54 (s, 1H, NC<u>H</u>N), 7.45-7.38 (m, 10H, Ar<u>H</u>), 7.17 (s, 2H, NC<u>H</u>=C), 5.51 (t, *J* = 7.9 Hz, 2H, NC<u>H</u>(CH_2CH_3)Ph), 2.35 (qd, *J* = 13.6 Hz, *J* = 7.4 Hz, 4H, C<u>H</u>$_2$CH$_3$), 0.94 (t, *J* = 7.3 Hz, 6H, C<u>H</u>$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 136.4, 134.9, 129.5, 127.5, 120.6, 66.3, 27.5, 10.6.

α_D –34.2 (*c* 1.13, $CHCl_3$).

1,3-Bis-(1(*S*)-1-naphthyl-ethyl)-imidazolium tetraflouroborate 7

The desired product was obtained as a hygroscopic, pale orange powder in 100% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 9.42 (s, 1H, NC<u>H</u>N), 8.15-7.19 (m, 14H, Ar<u>H</u>), 6.89 (s, 2H, NC<u>H</u>=C), 6.56 (q, *J* = 6.9 Hz, 2H, NC<u>H</u>(CH_3)Naphth), 2.12 (d, *J* = 6.9 Hz, 6H, C<u>H</u>$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 139.4, 133.9, 132.6, 130.4, 129.2, 128.2, 127.8, 126.5, 126.1, 125.5, 124.5, 123.3.

α_D +91.7 (*c* 0.98, $CHCl_3$).

1,3-Bis-(1(*S*)-2-naphthyl-ethyl)-imidazolium tetraflouroborate 8

The desired product was obtained as a hygroscopic yellow powder in 53% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 9.47 (s, 1H, NC<u>H</u>N), 7.92-42 (m, 14H, Ar<u>H</u>), 7.10 (s, 2H, NC<u>H</u>=C), 5.94 (q, *J* = 6.9 Hz, 2H, NC<u>H</u>(CH_3)Naphth), 2.07 (d, *J* = 7.0 Hz, 6H, C<u>H</u>$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 135.0, 134.7, 133.4, 133.1, 129.7, 128.3, 127.7, 127.2, 127.0, 126.7, 123.9, 120.6, 60.5, 20.7.

α_D +6.90 (*c* 1.02, $CHCl_3$).

General procedure for synthesis of silver carbene

The silver carbenes 9, 10 and 11 were prepared from their corrseponding chloro-imidazolinium salts which in turn, were prepared as described above, substituting HBF_4 for HCl (as a 32% aqueous solution).[1]

To a solution of the appropriate chloro-imidazolinium salt (1 mmol) in DCM (15 mL), was added Ag_2O (0.5 mmol). The mixture was stirred at room temperature for 16 hours then filtered through celite and concentrated under reduced pressure to yield the desired compound as a crystalline solid.

1,3-Bis-(1(*S*)-1-phenyl-ethyl)-imidazolin-2-ylidene silver (I) chloride 9

The desired product was isolated in quantitative yield and required no further purification.

^{1}H NMR (400 MHz, $CDCl_3$): 7.40-7.30 (m, 6H, Ar<u>H</u>), 7.30-7.20 (m, 4H, Ar<u>H</u>), 6.95 (s, 2H, NC<u>H</u>=C), 5.76 (q, *J* = 7.1 Hz, 2H, NC<u>H</u>(CH_3)Ph), 1.84 (d, *J* = 7.1 Hz, 6H, C<u>H</u>$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 139.7, 129.1, 128.6, 126.6, 61.0, 21.4.

α_D +32.7 (*c* 1.09, $CHCl_3$).

1,3-Bis-(1(*S*)-phenyl-propyl)-imidazolin-2-ylidene silver (I) chloride 10

The desired product was isolated in quantitative yield and required no further purification.

^{1}H NMR (400 MHz, $CDCl_3$): 7.40-7.33 (m, 10H, Ar<u>H</u>), 7.01 (s, 2H, NC<u>H</u>=C), 5.45 (m, 2H, NC<u>H</u>(CH_2CH_3)Ph), 2.31-2.14 (m, 4H, C<u>H</u>$_2$CH$_3$), 0.89 (t, *J* = 7.3 Hz, 6H, C<u>H</u>$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 139.1, 129.1, 128.5, 126.8, 118.9, 67.4, 27.8, 11.1.

α_D +48.1 (*c* 0.75, $CHCl_3$).

1,3-Bis-(1(*S*)-1-naphthyl-ethyl)-imidazolin-2-ylidene silver (I) chloride 11

The desired product was isolated in 82% yield and required no further purification.

^{1}H NMR (400 MHz, $CDCl_3$): 8.15-7.42 (m, 14H, Ar<u>H</u>), 6.55 (s, 2H, NC<u>H</u>=C), 6.42 (q, *J* = 6.2 Hz, 2H, NC<u>H</u>(CH_3)Ar), 2.0 (d, *J* = 6.9 Hz, 6H, C<u>H</u>$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 134.0, 131.0, 130.0, 129.1, 127.3, 126.2, 125.1, 124.4, 122.8, 119.0, 57.4, 22.4.

α_D +49.8 (*c* 0.72, $CHCl_3$).

Typical procedure for the synthesis of 2, 12 and 13

To a solution of the corresponding imidazolinium salt[2] (1 mmol) in DCM (15 mL) was added Ag_2O (0.5 mmol). The mixture was stirred at 20 °C (unless otherwise indicated) until complete consumption of the precipitate (4-20 hours), filtered through celite and concentrated to give quantitatively the expected compounds as crystalline solids.

(4*R*, 5*R*)-1,3-Dimethyl-4,5-di-*tert*-butyl-imidazolin-2-ylidene silver (I) chloride 2

^{1}H NMR (400 MHz, DMSO-D_6): 3.34 (s, 2H, C<u>H</u>tBu), 3.21 (s, 6H, NC<u>H</u>$_3$), 0.87 (s, 18H, C(C<u>H</u>$_3$)$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 213.7, 80.5, 45.8, 41.7, 32.9.

α_D -93 (*c* 1.0, $CHCl_3$).

(4R,5R)-1,3-Dibenzyl-4,5-di-tert-butylimidazolin-2-ylidene silver (I) chloride 12

The single crystals of 12 suitable for X-ray diffraction analysis were obtained by recrystallisation from DCM and hexane mixture.

^{1}H-NMR (200 MHz, $CDCl_3$): 7.42-7.3 (m, 10H, Ar<u>H</u>), 5.12 (d, *J* = 14.5 Hz, 2H, NC(H')<u>H</u>Ph), 4.50 (d, *J* = 4.5 Hz, 2H, NC(H)<u>H'</u>Ph), 3.24 (s, 2H, NC<u>H</u>tBu), 0.68 (s, 18H, C(C<u>H</u>$_3$)$_3$).

^{13}C-NMR ($CDCl_3$): 135.4, 129.7, 129.2, 128.8, 71.2, 56.5, 35.7, 27.3.

α_D –57 (*c* 0.68, DCM).

(4R,5R)-1,3-Di-(3-methoxybenzyl)-4,5-di-tert-butylimidazolin-2-ylidene silver (I) chloride 13

The mixture was refluxed for 12hours, filtered through celite and concentrated to give 470 mg (95%) of the desired compound as a white crystalline solid.

^{1}H-NMR (400 MHz, $CDCl_3$): 7.30-6.80 (m, 8H, Ar<u>H</u>), 5.06 (d, *J* = 15.2 Hz, 2H, NC(H)<u>H'</u>Ph), 4.49 (d, *J* = 15.2 Hz, 2H, NC(H')<u>H</u>Ph), 3.81 (s, 6H, OC<u>H</u>$_3$), 3.28 (s, 2H, NC<u>H</u>tBu), 0.75 (s, 18H, C(C<u>H</u>$_3$)$_3$.

α_D +192.8 (*c* 0.66, $CHCl_3$).

[2] For general method of preparation of imidazolinium salts, see Pytkowicz, J.; Roland, S.; Mangeney, P. *J. Organomet. Chem.,* **2001**, *631*, 157.