Supporting Information

FACILE SYNTHESIS OF CHIRAL BENZIMIDAZOLIUM SALTS AND THE APPLICATION IN ASYMMETRIC CATALYTIC BORYLATION

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Measurement

1H NMR and 13C NMR spectra were recorded in CDCl3 operating at 400 MHz and 100 MHz. Proton chemical shifts are reported relative to the residual proton signals of the deuterated solvent CDCl3 (7.26 ppm) or DMSO-d6 (2.50 and 3.33 ppm) or TMS. Carbon chemical shifts were internally referenced to the deuterated solvent signals in CDCl3 (77.00 ppm) or DMSO-d6 (40.0 ppm). Data are represented as follows: chemical shift, multiplicity (br = broad singlet, s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant in Hertz (Hz), and integration. Products were identified by comparison to spectral data reported in the literature. Mass spectra (both at low
resolution and at high resolution) were recorded on a time-of-flight mass spectrometer with an ESI source. High performance liquid chromatography (HPLC) was performed using a chromatograph equipped with a Chiral pak column (250 mm × 4.6 mm) with hexane/i-PrOH as the eluent.

General Experimental Methods

General procedure A for synthesis of 2a-b:

1, 2-diaminobenzene (2.0 equiv), bromide (4.0 equiv), Pd2(dba)3 (7.5%), BINAP (5%), NaOtBu (6.0 equiv) and toluene (200 mL) were added in a 1000 mL round-bottomed flask under N2. The mixture was heated to 110 °C overnight. After completion of the reaction (checked by TLC), the reaction mixture was cooled and quenched by addition of sat.NH4Cl, then extracted with ethyl acetate. The organic layer was washed with brine and dried over Na2SO4. The crude product was purified by silica gel chromatography (hexane: EtOAc =5: 1).

General procedure B for synthesis of 3a-d:

A mixture of amine 2a-b (1.0 equiv), ketone (1.0 equiv) and Triethylamine (1.0 equiv) was dissolved in DCM (20-30 mL) in a 100 mL round-bottomed flask equipped with a stir bar. TiCl4 (2.0 equiv) was added at 0 °C. Then, the mixture was stirred at room temperature for about 2-24 h. After completion of the reaction (checked by TLC), DCM was removed under vacuum to give 3a-d. The crude products were used for the next step directly without further purification.

General procedure C for synthesis of 4a-d:

The crude product 3a-d (1.0 equiv) was dissolved in DCM (20-30 mL) in a 100 mL round-bottomed flask and cooled to 0 °C. Then, NaBH4 (1.1 equiv) was added in batches. After completion of the reaction (checked by TLC), the reaction mixture was quenched with saturated NaCl solution, extracted with DCM and dried with Na2SO4. The crude product was purified by silica gel chromatography (hexane: EtOAc =15: 1) to give 4a-c. 4d was used for the next step directly without further purification.

General procedure D for synthesis of 7a-c:
To a stirred solution of amine (1.0 equiv) in 30 mL of anhydrous DMF was added K$_2$CO$_3$ (1.0 equiv) at room temperature followed by addition of ortho-nitrofluorobenzene (1.0 equiv). The mixture was stirred for 4 h at 90 °C, K$_2$CO$_3$ was filtered off and DMF was removed under vacuum. The crude product was purified by silica gel chromatography (hexane: EtOAc = 10:1, 6:1) to give the desired product.

**Procedure E for synthesis of 8a-c:**

**8a:** The crude product 7a (1.0 equiv) was dissolved in anhydrous THF (20-30 mL) in a 100 mL round-bottomed flask and cooled to -20 °C. Then, lithium aluminum hydride (1.2 equiv) was added in batches. Then, the reaction mixture was stirred at rt for about 2 h. After completion of the reaction (checked by TLC), the reaction mixture was quenched with saturated NaCl solution, extracted with DCM and dried with Na$_2$SO$_4$. The crude product was purified by silica gel chromatography (hexane: EtOAc =15: 1 to 10:1).

**8b:** The crude product 7b (1.0 equiv) was dissolved in anhydrous MeOH (5-10 mL) in a sealed tube and Pd/C was added. Then, the reaction mixture was stirred at rt for about 2 h under H$_2$. After completion of the reaction (checked by TLC), the resulting suspension was filtered through a plug of Celite (diatomaceous earth), and the filter cake was washed with MeOH. MeOH was removed under vacuum and the crude product was purified by silica gel chromatography (hexane: EtOAc =15: 1 to 10:1).

**8c:** The crude product 7c (1.0 equiv) was dissolved in EtOH: H$_2$O (20-30 mL) in a 100 mL round-bottomed flask and iron powder (5.0 equiv). Then, the reaction mixture was heated to reflux. After completion of the reaction (checked by TLC), the resulting suspension was filtered through a plug of Celite (diatomaceous earth) and washed with EtOH. Then, EtOH was removed under vacuum and the water layer was extracted with DCM. The crude product was used for the next step directly without further purification.

**General procedure F for synthesis of 9a-c:**

**9a-b:** A mixture of diamine 8a-b (1.0 equiv), phenylboronic acid (2.1 equiv) was dissolved in DCM (20-30 mL) in a 100 mL round-bottomed flask equipped with a stir bar. Then, Et$_3$N (1.0-2.0 equiv) and Cu(OAc)$_2$·H$_2$O (0.2-0.5 equiv) were added to it respectively at room temperature. They would
be stirred overnight under the condition of air atmosphere. After completion of the reaction (checked by TLC), the mixture was filtered through Celite and washed with EtOAc. The crude product was purified by silica gel chromatography (hexane:EtOAc = 40:1, 20:1 or 5:1) to give the desired product 9a-b.

9c: A mixture of diamine 8c (1.0 equiv), phenylboronic acid (2.1 equiv) was dissolved in DCM (20-30 mL) in a 100 mL round-bottomed flask equipped with a stir bar. Then, K$_2$CO$_3$ (1.0 equiv), benzoic acid (0.5 equiv) and Cu(OAc)$_2$·H$_2$O (20% equiv) were added to it respectively at room temperature. They would be stirred at 80 °C for 4 h under the condition of air atmosphere. After completion of the reaction (checked by TLC), the mixture was filtered through Celite and washed with EtOAc. The crude product was purified by silica gel chromatography (hexane:EtOAc = 40:1, 20:1 or 5:1) to give the desired product 9c.

General procedure G for synthesis of N-heterocyclic Carbene precursors:
Compound 4a-b and 9c-e (50 mg) was dissolved in trimethyl orthoformate (5 mL). Then, concentrated hydrochloric acid (0.1 mL) was added. The mixture was reacted at room temperature for 12 h. Then most solvent was evaporated under reduced pressure. The crude product was purified by silica gel chromatography (DCM: MeOH = 10:1) to give the desired product 5a-e.

Characterization data of Compounds
N\textsuperscript{1}-Mesitylbenzene-1,2-diamine (2a): brown liquid, yield 63%; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 6.91 (s, 2H), 6.75-6.83 (m, 2H), 6.66-6.70 (m, 1H), 6.26-6.28 (m, 1H), 4.80 (br, 1H), 3.67 (br, 1H), 2.34 (s, 3H), 2.16 (s, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 137.0, 135.6, 134.8, 133.9, 133.3, 129.3, 120.2, 120.1, 116.3, 15.0, 20.82, 18.07. MS (ESI-TOF) m/z: 227.1 [M+H]\textsuperscript{+}.

N\textsuperscript{1}-Mesityl-N\textsuperscript{2}-(1R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl)benzene-1,2-diamine (4a): pale yellow liquid, yield 74%; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 6.94 (s, 2H), 6.87 (t, J = 7.6, 1H), 6.76 (d, J = 7.6, 1H), 6.59 (t, J = 7.6, 1H), 6.32 (d, J = 7.6, 1H), 4.65 (br, 1H), 4.13 (br, 1H), 3.41 (d, J = 4.12, 1H), 2.33 (s, 3H), 2.13 (s, 6H), 1.93-1.98 (m, 1H), 1.80-1.83 (m, 2H), 1.66-1.72 (m, 1H), 1.22-1.41 (m, 3H), 1.03 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 138.7, 137.8, 133.7, 133.4, 129.2, 121.1, 117.4, 115.7, 111.4, 61.2, 48.7, 47.2, 45.4, 40.5, 36.8, 31.6, 27.5, 22.6, 20.6, 20.5, 14.07, 18.0. MS (ESI-TOF) m/z: 363.3 [M+H]\textsuperscript{+}.

1-Mesityl-3-((1R,2S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-benzo[d]imidazol-3-ium
chloride (5a): white solid, yield 66%; mp 206.3-206.8 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 10.41 (s, 1H), 8.18-8.49 (m, 1H), 7.79 (t, \(J = 7.7\) Hz, 1H), 7.70 (t, \(J = 7.7\) Hz, 1H), 7.42 (d, \(J = 8.2\) Hz, 1H), 7.27 (d, \(J = 7.2\) Hz, 2H), 4.85-5.10 (m, 1H), 2.67 (d, \(J = 13.2\) Hz, 1H), 2.41 (d, \(J = 4.9\) Hz, 3H), 2.24 (dd, \(J = 13.3, 9.4\) Hz, 1H), 1.94-2.09 (m, 5H), 1.92 (d, \(J = 13.1\) Hz, 3H), 1.66-1.86 (m, 2H), 1.32-1.46 (m, 1H), 1.18 (s, 3H), 0.99 (s, 3H), 0.90 (s, 3H), 0.79 (s, 2H); \(^{13}\)C NMR (100 MHz DMSO-\(d_6\)) \(\delta\) 142.6, 141.4, 135.8, 135.5, 133.1, 130.2, 130.1, 127.5, 116.3, 113.6, 112.1, 66.1, 51.0, 44.8, 44.8, 44.8, 36.0, 26.7, 21.4, 21.2, 19.9, 17.5. MS (ESI-TOF) \(m/z\): 373.3 [M+H]+. HRMS (ESI-TOF) calcd for C\(_{26}\)H\(_{33}\)N\(_2\)+ [M]+ 373.2638, Found 373.2641.

\(N^1\)-(Naphthalen-2-yl)benzene-1,2-diamine (2b): brown liquid, yield 65%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.74-7.77 (m, 2H), 7.61 (d, \(J = 8\) Hz, 1H), 7.39-7.43 (m, 1H), 7.28-7.31 (m, 1H), 7.22-7.24 (m,1H), 7.08-7.12 ( m, 2H), 6.96-6.97 ( m, 1H), 6.85-6.89 ( m, 2H), 5.41 ( s, 1H), 3.83 (br, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.0, 142.1, 134.9, 129.2, 128.5, 128.3, 127.7, 126.5, 126.2, 126.0, 125.3, 122.9, 119.2, 118.5, 116.3, 108.5. MS (ESI-TOF) \(m/z\): 235.2 [M+H]+.

\(N^1\)-(Naphthalen-2-yl)-N\(^2\)-((1\(R\))-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)benzene-1,2-diamine (4b): pale yellow liquid, yield 63%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.71 (t, \(J = 8.1\) Hz, 2H), 7.58 (d, \(J = 8.3\) Hz, 1H), 7.37 (t, \(J = 7.2\) Hz, 1H), 7.20-7.30 (m, 1H), 7.17 (t, \(J = 7.3\) Hz, 2H), 7.05 (d, \(J = 8.7\) Hz, 1H), 6.90 (s, 1H), 6.79 (d, \(J = 7.8\) Hz, 1H), 6.70 (t, \(J = 7.3\) Hz, 1H), 3.34 (dd, \(J = 7.3, 4.5\) Hz, 1H), 1.89 (dd, \(J = 12.6, 8.3\) Hz, 1H), 1.53-1.68 (m, 3H), 1.31-1.39 (m, 1H), 1.12-1.27 (m, 1H), 0.79 (s, 1H), 0.76 (s, 1H), 0.71 (s, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) 144.2, 143.5,
134.9, 129.0, 128.5, 127.6, 126.7, 126.3, 126.0, 122.7, 118.2, 116.2, 110.9, 108.8, 61.2, 48.8, 47.0, 45.2, 40.7, 36.7, 27.4, 20.3, 20.0, 12.1.

MS (ESI-TOF) m/z: 371.2 [M+H]⁺.

1-(Naphthalen-2-yl)-3-((1R,2S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-benzo[d]imidazol-3-ium chloride (5b): white solid, yield 67%; mp 168.3-170.2 °C; ¹H NMR (400 MHz, DMSO-d₆) δ 10.41 (s, 1H), 8.46 (s, 1H), 8.29 (dd, J = 24.0, 8.5 Hz, 2H), 8.16 (d, J = 4.9 Hz, 2H), 7.91 (dd, J = 14.3, 9.2 Hz, 2H), 7.63-7.85 (m, 4H), 4.94 (t, J = 7.8 Hz, 1H), 2.78-2.81 (m, 1H), 2.21 (dd, J = 13.1, 9.5 Hz, 1H), 2.03 (s, 1H), 1.66-1.94 (m, 3H), 1.42 (s, 1H), 1.08 (s, 3H), 0.92 (t, J = 9.0 Hz, 6H); ¹³C NMR (100 MHz, DMSO-d₆) 142.1, 133.6, 133.4, 133.1, 132.0, 130.5, 128.9, 128.1, 127.3, 125.6, 123.7, 115.9, 114.1, 66.2, 51.1, 48.4, 44.9, 36.5, 36.0, 26.8, 21.5, 20.3, 12.8. MS (ESI-TOF) m/z: 381.2 [M+H]⁺. HRMS (ESI-TOF) calcd for C₂₆H₃₃N₂⁺ [M]⁺ 381.2325, Found: 381.2323.

N¹-((2S,5R)-2-Isopropyl-5-methylcyclohexyl)-N²-(naphthalen-2-yl)benzene-1,2-diamine (4c): pale green liquid, yield 76%; ¹H NMR (400 MHz, CDCl₃) δ 7.71-7.74 (m, 2H), 7.56 (d, J = 8Hz, 1H), 7.36-7.40 (m, 1H), 7.16-7.28 (m, 3H), 7.05-7.08 (m, 1H), 6.87-6.88 (m, 1H), 6.78-6.81 (m, 1H), 6.67-6.71 (m, 1H), 5.27 (s, 1H), 4.39 (s, 1H), 3.87 (s, 1H), 2.03-2.09 (m, 1H), 1.65-1.67 (m, 1H), 1.54-1.58 (m, 2H), 1.38-1.48 (m, 1H), 1.23-1.31 (m, 1H), 0.91-1.08 (m, 4H), 0.85 (d, J = 6.5 Hz, 3H), 0.77 (dd, J = 6.6, 9.96 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 145.0, 143.7, 134.9, 128.9,
127.9, 127.8, 127.4, 126.5, 126.4, 126.0, 122.3, 118.9, 115.7, 110.5, 107.0, 52.1, 46.8, 43.7, 36.1, 30.7, 29.6, 26.8, 22.4, 21.9, 21.8. MS (ESI-TOF) m/z: 373.4 [M+H]^+.

(S)-Methyl 2-((2-nitrophenyl)amino)-3-phenylpropanoate (7a): yellow oil, yield 62%; ^1H NMR (400 MHz, CDCl₃) δ 8.37 (d, J = 7.1 Hz, 1H), 8.19 (dd, J = 8.5, 1.5 Hz, 1H), 7.39-7.44 (m, 1H), 7.30-7.37 (m, 2H), 7.23-7.27 (m, 2H), 6.47-6.89 (m, 2H), 4.50 (dd, J = 12.9, 7.3 Hz, 1H), 3.76 (s, 3H), 3.27 (dd, J = 27.2, 6.4 Hz, 2H). MS (ESI-TOF) m/z: 301.1 [M+H]^+.

(S)-2-((2-Aminophenyl)amino)-3-phenylpropan-1-ol (8a): brown oil, yield 71%; ^1H NMR (400 MHz, CDCl₃) δ 7.30-7.38 (m, 2H), 7.23-7.25 (m, 3H), 6.78-6.90 (m, 2H), 6.75 (d, J = 3.5 Hz, 2H), 3.70-3.78 (m, 2H), 3.53-3.57 (m, 1H), 2.97-3.08 (m, 2H).

(S)-3-Phenyl-2-((2-(phenylamino)phenyl)amino)propan-1-ol (9a): brown oil, yield 62%; ^1H NMR (400 MHz, CDCl₃) δ 7.20-7.27 (m, 5H), 7.12-7.17 (m, 4H), 6.86 (dd, J = 14.8, 7.5 Hz, 1H), 6.76 (t, J = 7.2 Hz, 1H), 6.71 (d, J = 7.7 Hz, 1H), 3.78-3.81 (m, 1H), 3.72 (dd, J = 11.0, 4.2 Hz, 1H), 3.51 (dd, J = 11.0, 5.6 Hz, 1H), 2.80-2.94 (m, 2H). ^13C NMR (100 MHz, CDCl₃) δ 145.8, 143.0, 137.9, 129.3, 129.0, 128.9, 128.5, 126.5, 126.3, 125.7, 119.4, 118.1, 115.2, 112.5, 63.4, 56.1, 37.7. MS (ESI-TOF) m/z: 319.2 [M+H]^+. 

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(S)-3-(1-Hydroxy-3-phenylpropan-2-yl)-1-phenyl-1H-benzo[d]imidazol-3-ium chloride (5c): brown solid, yield 72%; mp 147.2-148.7 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\) ) \(\delta\) 10.45 (s, 1H), 8.21 (d, \(J = 7.8\) Hz, 1H), 7.62-7.92 (m, 8H), 7.34 (d, \(J = 7.3\) Hz, 2H), 7.27 (t, \(J = 7.5\) Hz, 2H), 7.18 (t, \(J = 7.3\) Hz, 1H), 5.47 (t, \(J = 6.0\) Hz, 1H), 5.36 (br, 1H), 3.77-4.05 (m, 2H), 3.49 (d, \(J = 7.2\) Hz, 1H); \(^13\)C NMR (100 MHz, DMSO-\(d_6\) ) \(\delta\) 142.1, 137.0, 134.5, 133.5, 132.1, 131.3, 131.1, 130.9, 129.5, 129.0, 128.0, 127.4, 127.3, 125.8, 114.8, 113.9. MS (ESI-TOF) \(m/z\): 329.2 [M+H]+. HRMS (ESI-TOF) calcd for C\(_{22}\)H\(_{21}\)ClN\(_2\)O\(_2\) [M]+ 329.1648, Found: 329.1649.

(1R,2S)-1-((2-Nitrophenyl)amino)-2,3-dihydro-1H-inden-2-ol (7b): yellow solid, yield 65%; mp 141.0-142.4 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\) ) \(\delta\) 8.61 (s, 1H), 8.27 (dd, \(J = 8.6, 1.5\) Hz, 1H), 7.51-7.55 (m, 1H), 7.23-7.44 (m, 4H), 7.18 (d, \(J = 8.6\) Hz, 1H), 6.67-6.91 (m, 1H), 5.12 (s, 1H), 4.80-4.83 (m, 1H), 3.29 (dd, \(J = 16.7, 4.8\) Hz, 1H), 3.12 (d, \(J = 16.2\) Hz, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\) ) \(\delta\) 145.3, 140.4, 139.9, 136.3, 132.8, 128.7, 127.5, 124.3, 116.3, 114.6, 73.4, 61.6, 39.9. MS (ESI-TOF) \(m/z\): 271.2[M+H]+.
(1R,2S)-1-((2-Aminophenyl)amino)-2,3-dihydro-1H-inden-2-ol (8b): brown oil, yield 64%; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, $J = 7.0$ Hz, 1H), 7.22-7.37 (m, 3H), 6.87-7.03 (m, 2H), 6.74-6.86 (m, 2H), 4.90 (d, $J = 4.6$ Hz, 1H), 4.73 (t, $J = 4.1$ Hz, 1H), 3.21 (dd, $J = 16.6$, 5.0 Hz, 2H), 3.09 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 141.8, 140.6, 137.0, 134.3, 128.3, 127.1, 125.5, 124.2, 121.2, 119.9, 117.7, 113.6, 72.3, 63.0, 39.6. MS (ESI-TOF) $m/z$: 241.1 [M+H]$^+$. 

(1R, 2S)-1-((2-(2-Nitrophenyl)amino)phenyl)amino)-2,3-dihydro-1H-inden-2-ol (9b): brown oil, yield 63%; $^1$H NMR (400 MHz, CDCl$_3$) δ 9.11 (s, 1H), 8.23 (d, $J = 8.8$ Hz, 1H), 7.29-7.38 (m, 2H), 7.16-7.30 (m, 4H), 7.12 (dd, $J = 16.4$, 7.8 Hz, 2H), 6.91 (t, $J = 7.6$ Hz, 1H), 6.79 (dd, $J = 5.0$, 3.6 Hz, 2H), 4.95 (d, $J = 4.2$ Hz, 1H), 4.73 (d, $J = 4.6$ Hz, 1H), 3.20 (dd, $J = 16.7$, 4.6 Hz, 1H), 3.04 (d, $J = 16.7$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.4, 144.2, 141.0, 140.3, 136.0, 133.1, 129.0, 128.6, 128.5, 127.3, 126.7, 125.6, 124.4, 123.9, 118.9, 117.5, 116.0, 112.8, 72.4, 62.8, 39.6. MS (ESI-TOF) $m/z$: 362.1 [M+H]$^+$. 

5d
3-((1R,2S)-2-Hydroxy-2,3-dihydro-1H-inden-1-yl)-1-(2-nitrophenyl)-1H-benzo[d]imidazol-3-ium chloride (5d): white solid, yield 71%; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 9.95 (s, 1H), 8.50 (s, 1H), 8.25 (d, \(J = 33.6\) Hz, 1H), 8.03-8.13 (m, 3H), 7.75 (dd, \(J = 23.3, 15.7\) Hz, 2H), 7.64 (d, \(J = 8.2\) Hz, 1H), 7.39-7.57 (m, 3H), 7.35 (t, \(J = 7.2\) Hz, 1H), 6.71 (s, 1H), 5.74-5.98 (m, 1H), 4.86 (s, 1H), 3.31 (d, \(J = 5.1\) Hz, 1H), 3.11 (d, \(J = 16.3\) Hz, 1H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 144.7, 144.2, 142.4, 139.9, 136.4, 133.3, 132.2, 131.4, 130.0, 128.2, 127.9, 127.4, 127.1, 126.5, 126.2, 126.5, 125.0, 115.1, 113.6. MS (ESI-TOF) \(m/z\): 372.2 [M+H]⁺. HRMS (ESI-TOF) calcd for C\(_{22}\)H\(_{18}\)N\(_3\)O\(_3\)⁺ [M]⁺ 372.1343, Found: 372.1341.

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\begin{align*}
\text{7c} & \quad \text{tert-butyl ((1R,2R)-2-((2-Nitrophenyl)amino)cyclohexyl)carbamate (7c): yellow solid, yield 64%; mp 148.0-149.0 °C; \(^1\)H NMR (400 MHz, CDCl}_3) \(\delta\) 8.30 (d, \(J = 6.8\) Hz, 1H), 8.18 (dd, \(J = 8.6, 1.4\) Hz, 1H), 7.42 (t, \(J = 7.2\) Hz, 1H), 6.97 (d, \(J = 8.5\) Hz, 1H), 6.63 (t, \(J = 7.7\) Hz, 1H), 4.52 (d, \(J = 6.8\) Hz, 1H), 3.69 (s, 1H), 3.46 (s, 1H), 2.17 (d, \(J = 16.5\) Hz, 1H), 1.99-2.13 (m, 1H), 1.72-1.83 (m, 1H), 1.42-1.53 (m, 3H), 1.40 (s, 9H), 1.29 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl}_3) \(\delta\) 155.5, 145.0, 135.9, 132.2, 127.1, 55.9, 31.1, 29.7, 28.4, 28.3, 24.1, 23.7. MS (ESI-TOF) \(m/z\): 336.2 [M+H]⁺.
\end{align*}
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\begin{align*}
\text{9c} & \quad \text{tert-butyl((1R,2R)-2-((2-(phenylamino)phenyl)amino)cyclohexyl)carbamate (9c): pale yellow oil, yield 68%; \(^1\)H NMR (400 MHz, CDCl}_3) \(\delta\) 7.21 (t, \(J = 7.7\) Hz, 3H), 7.04 (t, \(J = 7.7\) Hz, 1H), 6.82 (dd, \(J = 14.3, 7.4\) Hz, 3H), 6.59-6.77 (m, 2H), 4.53 (br, 1H), 3.47 (br, 1H), 3.12 (br, 1H), 2.25
\end{align*}
\]
(d, J = 13.3 Hz, 1H), 2.09 (dd, J = 11.4, 4.3 Hz, 1H), 1.75 (s, 2H), 1.38 (s, 9H), 1.23-1.34 (m, 4H), 1.04-1.25 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 156.5, 145.6, 129.1, 125.0, 123.8, 119.1, 115.6, 79.5, 54.4, 32.9, 32.2, 29.7, 28.3, 24.9, 24.5. MS (ESI-TOF) \(m/\ell\): 382.2 [M+H]+.

\[\text{3-}((1R,2R)-2-\text{Aminocyclohexyl})-1-\text{phenyl}\text{-1H-benzo[}d\text{]imidazol-3-ium chloride (5e)}:\text{ white solid, yield 61%; mp 108.3-109.6 °C; }^{1}\text{H NMR (400 MHz, DMSO-}d_{6}\text{) }\delta\text{ 10.44 (s, 1H), 8.38 (d, } J = 7.8 \text{ Hz, 1H), 7.88-7.93 (m, 2H), 7.82-7.87 (m, 1H), 7.69-7.80 (m, 5H), 4.73 (t, } J = 9.3 \text{ Hz, 1H), 1.99-2.29 (m, 3H), 1.71-1.95 (m, 2H), 1.38-1.61 (m, 4H); }^{13}\text{C NMR (100 MHz, DMSO-}d_{6}\text{) }\delta\text{ 142.1, 133.8, 132.2, 131.6, 130.9, 130.7, 127.8, 127.1, 125.8, 115.2, 113.8, 63.7, 53.9, 34.0, 32.2, 25.1, 24.4. MS (ESI-TOF) }m/\ell:\text{ 292.1 [M+H]+. HRMS (ESI-TOF) calcd for C}_{19}\text{H}_{22}\text{N}_{3}^{+} [M]^+ 292.1808, Found: 292.1809.}\]

\[\text{(S)-Methyl 3-}((4,4,5,5-\text{tetramethyl-1,3,2-dioxaborolan-2-yl})-3-\text{(4-} \text{(trifluoromethyl)phenyl})\text{ propanoate D1: }^{1}\text{H NMR (400 MHz, CDCl}3\text{) }\delta\text{ 7.54 (d, } J = 8.1 \text{ Hz, 2H), 7.35 (d, } J = 8.1 \text{ Hz, 2H), 3.68 (s, 3H), 2.68-2.95 (m, 2H), 2.71 (dd, } J = 15.9, 5.8 \text{ Hz, 1H), 1.24 (s, 6H), 1.20 (s, 6H); }^{13}\text{C NMR (100 MHz, CDCl}3\text{) }\delta\text{ 173.4, 145.7, 128.4, 125.4, 125.4, 83.9, 51.6, 36.6, 31.4, 30.2, 29.7, 24.6, 24.47.}\]
(S)-Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(4-(trifluoromethyl)phenyl)propanoate D2: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.11 (q, \(J = 8.1\) Hz, 4H), 3.67 (s, 3H), 2.89 (dd, \(J = 15.6, 9.4\) Hz, 1H), 2.69 (ddd, \(J = 21.6, 12.4, 6.0\) Hz, 1H), 2.32 (s, 3H), 1.25 (s, 6H), 1.20 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 173.8, 138.2, 135.1, 129.2, 128.1, 83.5, 51.5, 37.3, 24.6, 24.5, 20.9.

(S)-Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(4-(trifluoromethyl)phenyl)propanoate D3: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.21-7.27 (m, 2H), 7.13-7.21 (m, 2H), 3.67 (s, 3H), 2.87 (dd, \(J = 15.7, 9.1\) Hz, 1H), 2.70 (ddd, \(J = 21.9, 12.2, 6.2\) Hz, 2H), 1.24 (s, 6H), 1.20 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 173.5, 139.9, 131.5, 129.5, 128.6, 83.7, 51.6, 36.9, 24.6, 24.5.

HPLC analysis in catalysts screening for borylation of \(\alpha, \beta\)-unsaturated ester
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