Supporting Information

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

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Measurement

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ operating at 400 MHz and 100 MHz. Proton chemical shifts are reported relative to the residual proton signals of the deuterated solvent $CDCl_3$ (7.26 ppm) or DMSO-d_6 (2.50 and 3.33 ppm) or TMS. Carbon chemical shifts were internally referenced to the deuterated solvent signals in $CDCl_3$ (77.00 ppm) or DMSO-d_6 (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), $Pd_2(dba)_3$ (7.5%), BINAP (5%), NaO*t*Bu (6.0 equiv) and toluene (200 mL) were added in a 1000 mL round-bottomed flask under N_2. The mixture was heated to 110 ^oC overnight. After completion of the reaction (checked by TLC), the reaction mixture was cooled and quenched by addition of sat.NH_4Cl, then extracted with ethyl acetate. The organic layer was washed with brine and dried over Na_2SO_4. 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. $TiCl_4$ (2.0 equiv) was added at 0 ^oC. 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 ^oC. Then, $NaBH_4$ (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 Na_2SO_4. 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_2CO_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 ^oC, K_2CO_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 ^oC. 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_2SO_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_2O (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_3N (1.0-2.0 equiv) and $Cu(OAc)_2 \cdot H_2O$ (0.2-0.5 equiv) were added to it respectively at room temperature. They would

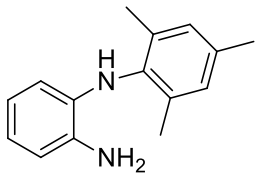
be stirred overnight under the condition of air atmosphere. After completion of the reaction (checked by TLC), the mixture was filtered through Celite and washed with EtOAc. The crude product was purified by silica gel chromatography (hexane:EtOAc = 40:1, 20:1 or 5:1) to give the desired product **9a-b**.

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_2CO_3 (1.0 equiv), benzoic acid (0.5 equiv) and $Cu(OAc)_2 \cdot H_2O$ (20% equiv) were added to it respectively at room temperature. They would be stirred at 80 ^oC 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:

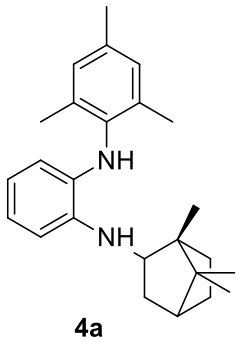
Compound **4a-b** and **9c-e** (50 mg) was dissolved in trimethyl orthoformate (5 mL). Then, concentrated hydrochloric acid (0.1 mL) was added. The mixture was reacted at room temperature for 12 h. Then most solvent was evaporated under reduced pressure. The crude product was purified by silica gel chromatography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

Characterization data of Compounds



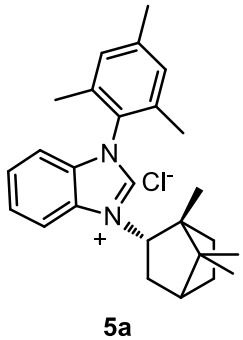
2a

***N*^{1}-Mesitylbenzene-1,2-diamine (2a):** brown liquid, yield 63%; ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $[M+H]^+$.



4a

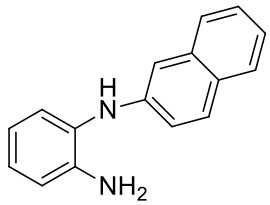
***N*^{1}-Mesityl-*N*^{2}-((1*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)benzene-1,2-diamine (4a):** pale yellow liquid, yield 74%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 2H), 6.87 (t, *J* = 7.6, 1H), 6.76 (d, *J* = 7.6, 1H), 6.59 (t, *J* = 7.6, 1H), 6.32 (d, *J* = 7.6, 1H), 4.65 (br, 1H), 4.13 (br, 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), 0.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $[M+H]^+$.



5a

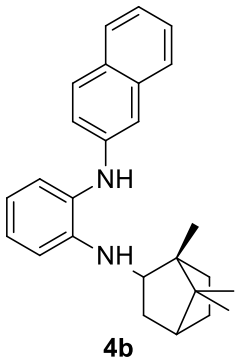
1-Mesityl-3-((1*R*,2*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1*H*-benzo[*d*]imidazol-3-ium

chloride (5a): white solid, yield 66%; mp 206.3-206.8 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 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, 1H), 0.99 (s, 3H), 0.90 (s, 3H), 0.79 (s, 2H); ^{13}C NMR (100 MHz DMSO-d_6) δ 142.6, 141.4, 135.8, 135.5, 133.1, 130.2, 130.1, 127.5, 116.3, 113.6, 66.1, 51.0, 48.4, 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.



2b

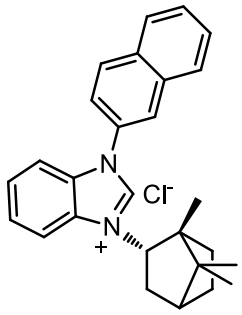
***N*^{1}-(Naphthalen-2-yl)benzene-1,2-diamine (2b)**: brown liquid, yield 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.77 (m, 2H), 7.61 (d, *J* = 8Hz, 1H), 7.39-7.43 (m, 1H), 7.28-7.31 (m, 1H), 7.22-7.24 (m,1H), 7.08-7.12 (m, 2H), 6.96-6.97 (m, 1H), 6.85-6.89 (m, 2H), 5.41 (s, 1H), 3.83 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 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 $[M+H]^+$.



4b

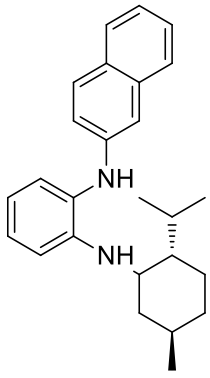
***N*^{1}-(Naphthalen-2-yl)-*N*^{2}-((1*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)benzene-1,2-diamine (4b):** pale yellow liquid, yield 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (t, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.20-7.30 (m, 1H), 7.17 (t, *J* = 7.3 Hz, 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, 127.1, 126.7, 126.3, 126.2, 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 $[M+H]^+$.



5b

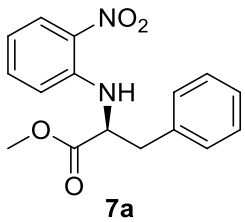
1-(Naphthalen-2-yl)-3-((1*R*,2*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1*H*-benzo[*d*]imidazol-3-ium chloride (5b): white solid, yield 67%; mp 168.3-170.2 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.41 (s, 1H), 8.46 (s, 1H), 8.29 (dd, *J* = 24.0, 8.5 Hz, 2H), 8.16 (d, *J* = 4.9 Hz, 2H), 7.91 (dd, *J* = 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); ^{13}C NMR (100 MHz, DMSO-d_6) 142.1, 133.6, 133.4, 133.1, 132.0, 130.5, 128.9, 128.5, 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 $C_{26}H_{33}N_2^+$ $[M]^+$ 381.2325, Found: 381.2323.



4c

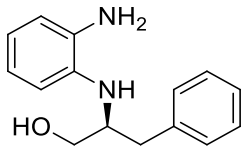
***N*^{1}-((2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl)-*N*^{2}-(naphthalen-2-yl)benzene-1,2-diamine (4c)**: pale green liquid, yield 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.74 (m, 2H), 7.56 (d, *J* = 8Hz, 1H), 7.36-7.40 (m, 1H), 7.16-7.28 (m, 3H), 7.05-7.08 (m, 1H), 6.87-6.88 (m, 1H), 6.78-6.81 (m, 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 143.7, 134.9, 128.9,

127.9, 127.8, 127.4, 126.5, 126.4, 126.2, 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 $[M+H]^+$.



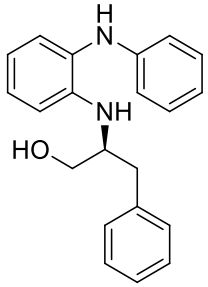
7a

(*S*)-Methyl 2-((2-nitrophenyl)amino)-3-phenylpropanoate (7a): yellow oil, yield 62%; ^{1}H NMR (400 MHz, $CDCl_3$) 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 $[M+H]^+$.



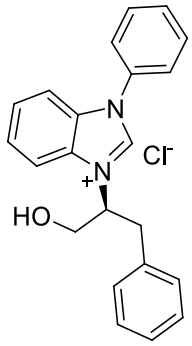
8a

(*S*)-2-((2-Aminophenyl)amino)-3-phenylpropan-1-ol (8a): brown oil, yield 71%; ^{1}H NMR (400 MHz, $CDCl_3$) 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).



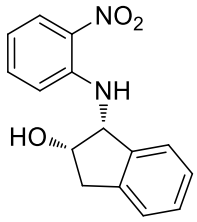
9a

(*S*)-3-Phenyl-2-((2-(phenylamino)phenyl)amino)propan-1-ol (9a): brown oil, yield 62%; ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (100 MHz, $CDCl_3$) 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 $[M+H]^+$.



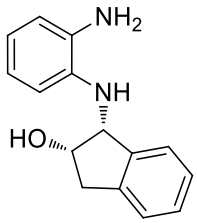
5c

(*S*)-3-(1-Hydroxy-3-phenylpropan-2-yl)-1-phenyl-1*H*-benzo[*d*]imidazol-3-ium chloride (5c): brown solid, yield 72%; mp 147.2-148.7 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 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) δ 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 $C_{22}H_{21}ClN_2O^+$ $[M]^+$ 329.1648, Found: 329.1649.



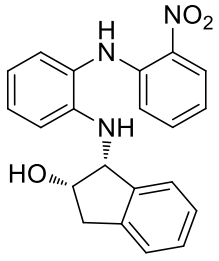
7b

(1*R*,2*S*)-1-((2-Nitrophenyl)amino)-2,3-dihydro-1*H*-inden-2-ol (7b): yellow solid, yield 65%; mp 141.0-142.4 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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$[M+H]^+$.



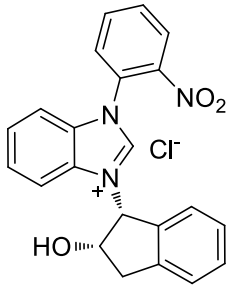
8b

(1*R*,2*S*)-1-((2-Aminophenyl)amino)-2,3-dihydro-1*H*-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$[M+H]^+$.



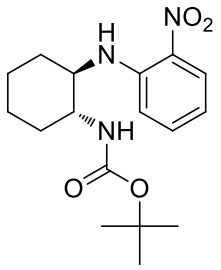
9b

(1*R*, 2*S*)-1-((2-((2-Nitrophenyl)amino)phenyl)amino)-2,3-dihydro-1*H*-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 $[M+H]^+$.



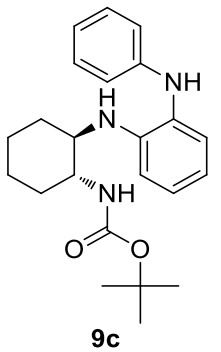
5d

3-((1*R*,2*S*)-2-Hydroxy-2,3-dihydro-*1H*-inden-1-yl)-1-(2-nitrophenyl)-1*H*-benzo[*d*]imidazol-3-ium chloride (5d): white solid, yield 71%; mp 137.5-139.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 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) δ 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, 126.2, 125.0, 115.1, 113.6. MS (ESI-TOF) *m/z*: 372.2 $[M+H]^+$. HRMS (ESI-TOF) calcd for $C_{22}H_{18}N_3O_3^+$ $[M]^+$ 372.1343, Found: 372.1341.



7c

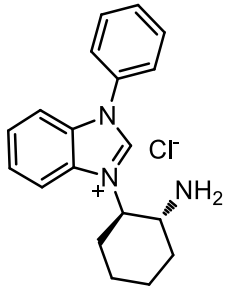
***tert*-butyl ((1*R*,2*R*)-2-((2-Nitrophenyl)amino)cyclohexyl)carbamate (7c):** yellow solid, yield 64%; mp 148.0-149.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 6.8 Hz, 1H), 8.18 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.63 (t, *J* = 7.7 Hz, 1H), 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, $CDCl_3$) δ 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 $[M+H]^+$.



9c

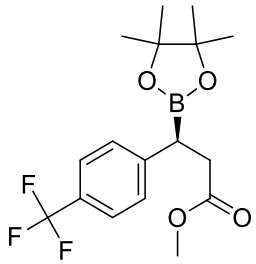
***tert*-butyl((1*R*,2*R*)-2-((2-(phenylamino)phenyl)amino)cyclohexyl)carbamate (9c):** pale yellow oil, yield 68%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.7 Hz, 3H), 7.04 (t, *J* = 7.7 Hz, 1H), 6.82 (dd, *J* = 14.3, 7.4 Hz, 3H), 6.59-6.77 (m, 2H), 4.53 (br, 1H), 3.47 (br, 1H), 3.12 (br, 1H), 2.25

(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, $CDCl_3$) δ 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/z*: 382.2 $[M+H]^+$.



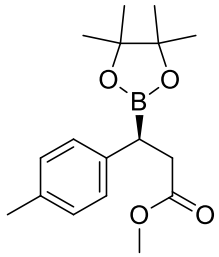
5e

3-((1*R*,2*R*)-2-Aminocyclohexyl)-1-phenyl-1*H*-benzo[*d*]imidazol-3-ium chloride (5e): white solid, yield 61%; mp 108.3-109.6 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.44 (s, 1H), 8.38 (d, *J* = 7.8 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 Hz, 1H), 1.99-2.29 (m, 3H), 1.71-1.95 (m, 2H), 1.38-1.61 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 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/z*: 292.1 $[M+H]^+$. HRMS (ESI-TOF) calcd for $C_{19}H_{22}N_3^+$ $[M]^+$ 292.1808, Found: 292.1809.



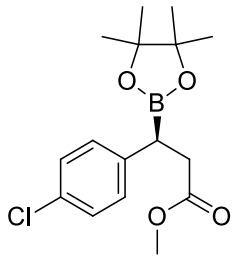
D1

(*S*)-Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(4-(trifluoromethyl)phenyl) propanoate D1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 3.68 (s, 3H), 2.68-2.95 (m, 2H), 2.71 (dd, *J* =15.9, 5.8 Hz, 1H), 1.24 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 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.



D2

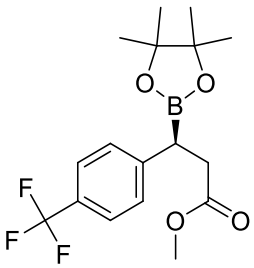
(S)-Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(4-(trifluoromethyl)phenyl) propanoate D2: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (q, *J* = 8.1 Hz, 4H), 3.67 (s, 3H), 2.89 (dd, *J* = 15.6, 9.4 Hz, 1H), 2.69 (ddd, *J* = 21.6, 12.4, 6.0 Hz, 1H), 2.32 (s, 3H), 1.25 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 138.2, 135.1, 129.2, 128.1, 83.5, 51.5, 37.3, 24.6, 24.5, 20.9.



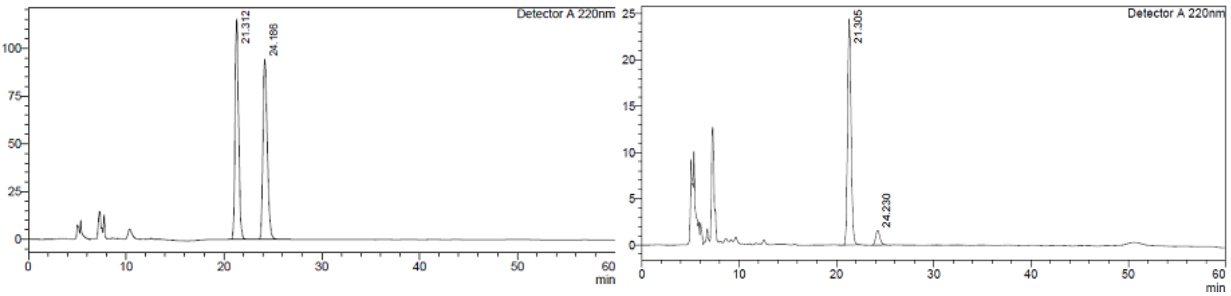
D3

(*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, $CDCl_3$) δ 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, $CDCl_3$) δ 173.5, 139.9, 131.5, 129.5, 128.6, 83.7, 51.6, 36.9, 24.6, 24.5.

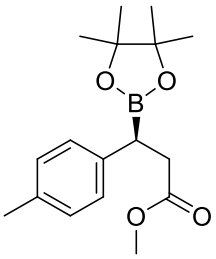
HPLC analysis in catalysts screening for borylation of α, β-unsaturated ester



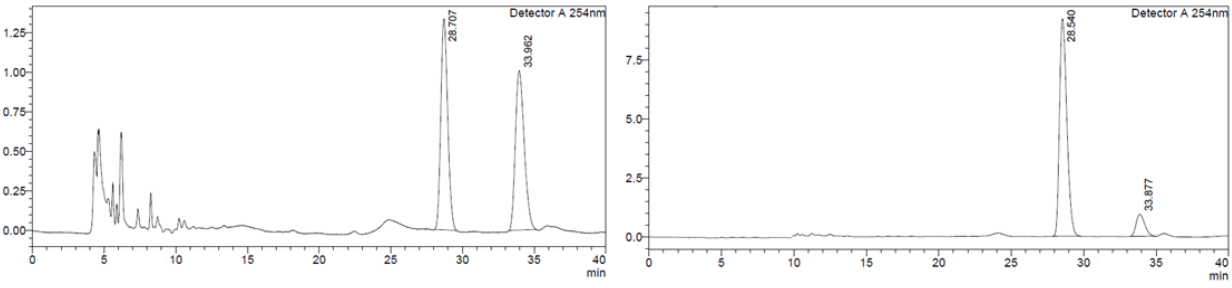
D1



D1(Racemic)				**D1**			
D1(Racemic)	Peak #	Time (min)	Area (%)	**D1**	Peak #	Time (min)	Area (%)
	1	21.312	49.979		1	21.305	92.701
	2	24.186	50.021		2	24.23	7.299

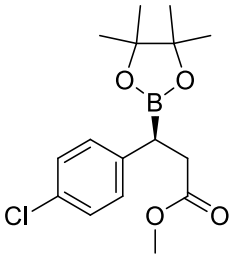


D2

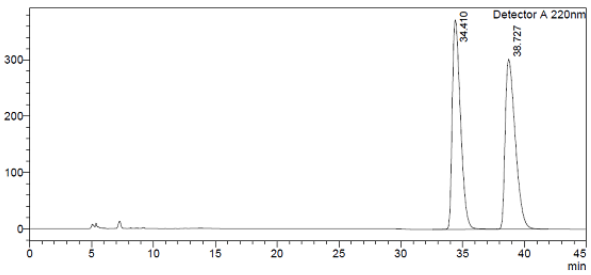


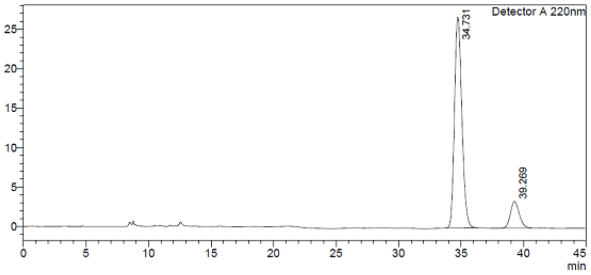
D2(Racemic)	**D2**

D2(Racemic)	Peak #	Time (min)	Area (%)	**D2**	Peak #	Time (min)	Area (%)
	1	28.707	50.704		1	28.54	89.406
	2	33.962	49.296		2	33.877	10.594



D3





D3(Racemic)				**D3**			
D3(Racemic)	Peak #	Time(min)	Area (%)	**D3**	Peak #	Time (min)	Area (%)
	1	34.41	50.19		1	34.731	86.979
	2	38.727	49.81		2	39.269	13.021