Chiral NHC/Cu(I)-Catalyzed Asymmetric Hydroboration of Aldimines: Enantioselective Synthesis of $\alpha$-Amido Boronic Esters
Shu-Sheng Zhang, Yi-Shuang Zhao, Ping Tian* and Gio-Qiang Lin*

Key Laboratory of Synthetic Chemistry of Natural Substances, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences
345 Lingling Road, Shanghai, 200032, China
E-mail: tianping@sioc.ac.cn
lingq@sioc.ac.cn

Contents:
1. General considerations...................................................................................................................................... S1
2. General Procedures for NHC/Cu-Catalyzed Enantioselective Hydroboration of Aldimines:...................... S1
3. One-Pot Procedures for NHC/Cu-Catalyzed Enantioselective Hydroboration of $\alpha$-Amido Sulfone Precursors: ........................................................................................................................................ S2
4. Analytical data for $\alpha$-Amido Boronate Esters. ............................................................................................ S2
   Compound 3a ................................................................................................................................................ S2
   Compound 3b ................................................................................................................................................ S3
   Compound 3c ................................................................................................................................................ S4
   Compound 3d ................................................................................................................................................ S4
   Compound 3e ................................................................................................................................................ S5
   Compound 3f ................................................................................................................................................ S5
   Compound 3g ................................................................................................................................................ S6
   Compound 3h ................................................................................................................................................ S7
   Compound 3i ................................................................................................................................................ S8
5. Representative procedure for synthesis of imidazolinium salt: .................................................................... S8
   Scheme 1 Synthesis of Imidazolinium Salt NHC$_2$ ......................................................................................... S8
   imidazolinium salt NHC$_3$ ........................................................................................................................... S10
   imidazolinium salt NHC$_4$ ........................................................................................................................... S10
   imidazolinium salt NHC$_5$ ........................................................................................................................... S11
   imidazolinium salt NHC$_6$ ........................................................................................................................... S11
   imidazolinium salt NHC$_7$ ........................................................................................................................... S12
1. General considerations

Solvents were dried and purified according to the procedure from ‘Purification of Laboratory Chemicals Book’. Unless otherwise indicated, all starting materials were obtained from commercial suppliers and were used without further purification. $^1$H NMR, $^{13}$C NMR spectra were recorded on a Bucker Avance-400 MH spectrometer. Chemical shifts are reported in δ (ppm) referenced to an internal TMS standard for $^1$H NMR and CDCl$_3$ (δ = 77.0 ppm) for $^{13}$C NMR. HRMS of 3a to 3i was based on $^{18}$O (10.01294, 24.8%).

α-Amido sulfone precursors$^1$, N-Benzoyl imine substrates (1)$^1$ and imidazolinium salt NHC$_2$$^2$, NHC$_8$$^3$ are prepared according to the method reported.

2. General Procedures for NHC/Cu-Catalyzed Enantioselective Hydorboration of Aldimines:

In the glovebox, an oven-dried schlenk tube equipped with a stir bar, imidazolinium tetrafluoroborate salt NHC$_6$ (36 mg, 0.06 mmol), NaOt-Bu (12 mg, 0.12 mmol), and CuCl (5 mg, 0.05 mmol) were placed and anhydrous toluene (2.0 mL) was added. After the solution was allowed to stir for two hours at 25 °C under a dry N$_2$ atmosphere, it was filtered through a syringe filter(rinsed with 1.0 mL of toluene) and placed in a separate oven-dried schlenk tube. The resulting solution was charged with B$_2$(Pin)$_2$ (152 mg, 0.6 mmol) and N-benzoyl aldimine (0.5 mmol). The schlenk tube was removed from the glovebox and the mixture was allowed to stir for 12 hours at room temperature. After the reaction completed, the mixture was filtered through a short plug of Celite and rinsed with ethyl acetate, the solution was concentrated under reduced pressure. The products were isolated by rapid silica gel chromatography on deactivated silica gel (containing 35% water) using petroleum ether (PE) / ethyl acetate (EA) = (2/1) mixtures and were visualized with CAM (Ceric Ammonium


3. One-Pot Procedures for NHC/Cu-Catalyzed Enantioselective Hydroboration of α-Amido Sulfone Precursors:

In the glovebox, an oven-dried schlenk tube equipped with a stir bar, imidazolinium tetrafluoroborate salt \( \text{NHC}_6 \) (36 mg, 0.06 mmol), NaO\(_t\)-Bu (12 mg, 0.12 mmol), and CuCl (5 mg, 0.05 mmol) were placed and anhydrous toluene (2.0 mL) was added. After the solution was allowed to stir for two hours at 25 °C under a dry \( \text{N}_2 \) atmosphere, it was filtered through a syringe filter (rinsed with 1.0 mL of toluene) and placed in a separate oven-dried schlenk tube. The resulting solution was charged with \( \text{B}_2(\text{pin})_2 \) (152 mg, 0.6 mmol), \( \alpha \)-Amido Sulfone (0.5 mmol, 1 eq) and cesium carbonate (1 mmol, 2 eq). The schlenk tube was removed from the glovebox and the mixture was allowed to stir for 12 hours at room temperature. After the reaction completed, the mixture was filtered through a short plug of Celite and rinsed with ethyl acetate, the solution was concentrated under reduced pressure. The products were isolated by rapid silica gel chromatography on deactivated silica gel (containing 35% water) using PE/EA (2/1) mixtures and were visualized with CAM (Ceric Ammonium Molybdate) stain.

4. Analytical data for \( \alpha \)-Amido Boronate Esters.

Compound 3a

\[ \text{Ph}-\text{B(OH)}_{\text{O}}\text{HN-O} \]

[α]$_{D}^{28}$ $-22.1$ (c 0.95, CHCl$_3$) for 63% ee. $^1$H NMR (400 MHz, CDCl$_3$): δ 3.67 (s, 3H),
3.99 (s, 3H), 4.58 (q, 2H, $J = 10.4$ Hz), 6.54 (s, 4H), 7.13(d, 1H, $J = 8.8$ Hz),
7.32-7.52 (m, 5H), 7.89-7.94 (m, 3H), 9.36 (s, 1H). HPLC: Chiralcel AS-H Column
(250 mm); detected at 220 nm; n-hexane / i-propanol = 95/5; flow = 0.6 mL/min;
Retention time: 8.6 min (minor), 11.5 min (major).

Compound 3b

[α]$_{D}^{28}$ $-1.24$ (c 0.56, DMSO) for 74% ee; m.p. 142-144 °C; $^1$H NMR (400 MHz,
DMSO-$d_6$): δ 10.89 (s, 1H), 8.07 (d, 2H, $J = 7.6$ Hz), 7.73(t, 1H, $J = 7.4$ Hz), 7.62 (t,
2H, $J = 7.6$ Hz), 7.03-7.13 (m, 4H), 3.77 (s, 1H), 1.03 (s, 6H), 0.93 (s, 6H); $^{13}$C NMR
(100 MHz, DMSO-$d_6$): δ 171.53, 160.78 (d, $J = 954.0$ Hz), 138.81 (d, $J = 12.0$ Hz),
134.51, 129.59, 128.86, 128.57 (d, $J = 32.4$ Hz), 126.69, 114.72 (d, $J = 84.8$ Hz),
79.80, 25.65, 25.39; ESI-MS (m/z): 378.2 [M+H]$^+$; HRMS m/z calcd for
[C$_{20}$H$_{23}$BFNO$_3$+Na]$^+$ 377.16890, found: 377.16957; HPLC: Chiralcel AS-H Column
(250 mm), detected at 220 nm, n-hexane / i-propanol = 95/5, flow = 0.6 mL/min,
Retention time: 9.1 min (minor), 11.2 min (major).
Compound 3c

\[
\begin{align*}
\text{[\(\alpha\)]}^{28}_D \, &\, -2.26 \, (c \, 0.52, \, \text{DMSO}) \, \text{for} \, 74\% \, \text{ee}; \, \text{m.p.} \, 178-180 \, ^\circ\text{C}; \, ^1\text{H NMR} \, (400 \, \text{MHz,} \, \text{DMSO-}d_6): \, \delta \, 10.92 \, (s, \, 1\text{H}), \, 8.07 \, (d, \, 2\text{H}, \, J = 8.0 \text{Hz}), \, 7.75 \, (t, \, 1\text{H}, \, J = 7.4 \text{Hz}), \, 7.63 \, (t, \, 2\text{H}, \, J = 7.6 \text{Hz}), \, 7.30 \, (d, \, 2\text{H}, \, J = 8.4 \text{Hz}), \, 7.04 \, (d, \, 2\text{H}, \, J = 8.4 \text{Hz}), \, 3.75 \, (s, \, 3\text{H}), \, 1.03 \, (s, \, 6\text{H}), \, 0.94 \, (s, \, 6\text{H}); \, ^{13}\text{C NMR} \, (100 \, \text{MHz,} \, \text{DMSO-}d_6): \, \delta \, 171.71, \, 142.43, \, 134.59, \, 132.81, \, 130.91, \, 129.61, \, 126.59, \, 118.21, \, 79.85, \, 55.57, \, 25.68, \, 25.43; \, \text{ESI-MS (m/z):} \, 438.2 \, [\text{M+Na}^+]^\circ; \, \text{HRMS m/z calcld for} \, [\text{C}_{20}\text{H}_{23}\text{BBrNO}_3+\text{Na}]^\circ \, 437.08884, \, \text{found:} \, 437.08949; \, \text{HPLC:} \, \text{Chiralcel AS-H Column (250 mm), detected at} \, 220 \, \text{nm;} \, \text{n-hexane / i-propanol} \, = \, 95/5, \, \text{flow} \, = \, 0.6 \, \text{mL/min, Retention time:} \, 8.8 \, \text{min (minor), 11.4 \, min (major).}
\end{align*}
\]

Compound 3d

\[
\begin{align*}
\end{align*}
\]
[α]²⁸D -17.9 (c 0.57, DMSO) for 69% ee; m.p. 144-146 °C; ¹H NMR (400 MHz, DMSO-d₆): δ 10.80 (s, 1H), 8.06 (d, 2H, J = 7.6 Hz), 7.73 (t, 1H, J = 7.2 Hz), 7.61 (t, 2H, J = 7.6 Hz), 7.01 (d, 2H, J = 8.4 Hz), 6.83 (d, 2H, J = 8.4 Hz), 3.71 (s, 1H), 1.03 (s, 6H), 0.93 (s, 6H); ¹³C NMR (100 MHz, DMSO-d₆): δ 171.18, 157.60, 134.52, 134.37, 129.56, 128.79, 128.11, 126.91, 113.61, 79.75, 55.44, 25.66, 25.42; ESI-MS (m/z): 390.2 [M+Na]⁺. HRMS m/z calcd for [C₂₁H₂₆BNO₄⁺Na]⁺ 389.18889, found: 389.18906; HPLC: Chiralcel AS-H Column (250 mm), detected at 220 nm, n-hexane / i-propanol = 95/5, flow = 0.6 mL/min, Retention time: 14.0 min (minor), 20.9 min (major).

Compound 3e

[α]²⁸D 4.14 (c 0.69, DMSO) for 41% ee; m.p. 95-96 °C; ¹H NMR (400 MHz, DMSO-d₆): δ 10.88 (s, 1H), 8.08 (d, 2H, J = 7.6 Hz), 7.74 (t, 1H, J =7.4 Hz), 7.62 (t, 2H, J = 7.6 Hz), 6.61-6.71 (m, 3H), 3.74 (s, 1H), 3.71 (s, 3H), 1.05 (s, 6H), 0.96 (s, 6H); ¹³C NMR (100 MHz, DMSO-d₆): δ 171.46, 159.40, 144.48, 134.47, 129.60, 129.08, 128.84, 126.74, 119.02, 112.54, 110.70, 79.80, 55.32, 25.73, 25.45. ESI-MS (m/z): 390.2 [M+Na]⁺. HRMS m/z calcd for [C₂₁H₂₆BNO₄⁺Na]⁺ 389.18889, found: 389.18948; HPLC: Chiralcel AS-H Column (250 mm), detected at 220 nm, n-hexane / i-propanol = 95/5, flow = 0.6 mL/min, Retention time: 11.6 min (minor), 15.3 min (major).

Compound 3f
$[\alpha]^2_D$ $-0.35$ (c 0.885, DMSO) for 58\% ee; m.p. 99 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): δ 10.62 (s, 1H), 8.07 (d, 2H, $J = 8.0$ Hz), 7.74 (t, 1H, $J = 7.4$ Hz), 7.63 (t, 2H, $J = 7.6$ Hz), 7.12 (td, 2H, $J = 7.6$ Hz, 1.2 Hz), 6.85-6.94 (m, 3H), 4.16 (s, 1H), 3.76 (s, 3H), 1.06 (s, 6H), 0.97 (s, 6H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 171.29, 156.60, 134.20, 131.14, 129.54, 128.68, 127.34, 126.75, 120.34, 110.64, 79.90, 55.57, 25.62, 25.35. ESI-MS (m/z): 390.1 [M+Na]$^+$. HRMS m/z calcd for [C$_{21}$H$_{26}$BNO$_4$+Na]$^+$ 389.18889, found: 389.18963; HPLC: Chiralcel AS-H Column (250 mm), detected at 220 nm, n-hexane / i-propanol = 95/5, flow = 0.6 mL/min, Retention time: 9.4 min (minor), 11.2 min (major).

Compound 3g

$[\alpha]^2_D$ $-11.85$ (c 0.65, DMSO) for 71\% ee; m.p. 102 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): δ 10.91 (s, 1H), 8.08 (d, 2H, $J = 7.6$ Hz), 7.76 (t, 1H, $J = 7.4$ Hz), 7.64 (t, 2H, $J = 7.4$ Hz), 7.06-7.21 (m, 4H), 4.00 (s, 1H), 1.05 (s, 6H), 0.96 (s, 6H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 171.94, 160.18 (d, $J = 965.0$ Hz), 134.60, 129.88 (d,
J=55.0 Hz), 129.63, 128.86, 128.84, 128.57 (d, J = 20.4 Hz), 127.14 (d, J = 28.8 Hz), 126.55, 124.19 (d, J = 12.0 Hz), 115.12 (d, J = 87.6 Hz), 79.84, 25.56, 25.29; ESI-MS (m/z): 356.3 \[C_{20}H_{23}BFNO_3+Na]^+; HRMS m/z calcd for \[C_{20}H_{23}BFNO_3+Na]^+ 377.16890, found: 377.16960; HPLC: Chiralcel AS-H Column (250 mm), detected at 220 nm, n-hexane / i-propanol = 95/5, flow = 0.6 mL/min, Retention time: 8.5 min (minor), 10.4 min (major).

Compound 3h

\[
\begin{align*}
\text{H} & \quad \text{N} \\
\text{O} & \\
\text{O} & \\
\text{H} & \\
\end{align*}
\]

[\(\alpha\)]$_D^{23}$ -29.7 (c 0.21, DMSO) for 80% ee; m.p. 156-157 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): \(\delta\) 9.84 (s, 1H), 7.99 (d, 2H, J = 7.6 Hz), 7.68 (t, 1H, J = 7.4 Hz), 7.58 (t, 2H, J = 7.8 Hz), 2.38 (m, 4H), 1.50-1.83 (m, 7H), 0.99-1.32 (m, 4H), 0.913 (s, 12H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): \(\delta\) 170.39, 133.66, 129.27, 128.60, 79.88, 39.69, 31.21, 29.49, 26.73, 26.68, 26.66, 26.02, 25.83; ESI-MS (m/z): 366.3 [M+H]$^+$; HRMS m/z calcd for \[C_{20}H_{30}BNO_3+Na]^+ 365.22528, found: 365.22450; HPLC: Chiralpak AD-H Column (250 mm), detected at 220 nm, n-hexane / i-propanol = 95/5, flow = 0.6 mL/min, Retention time: 5.4 min (minor), 6.9 min (major).
Compound 3i

\[ \alpha \]^{23}_D -48.66 (c 0.385, DMSO) for 84% ee; m.p. 144-146 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 10.00 (s, 1H), 7.97 (d, 2H, \(J = 7.2\) Hz), 7.67 (t, 1H, \(J = 7.2\) Hz), 7.56 (t, 2H, \(J = 7.6\) Hz), 2.57 (m, 1H), 1.83 (m, 1H), 1.31 (m, 2H), 1.11 (s, 12H), 0.90 (d, 6H, \(J = 6.4\) Hz); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)): \(\delta\) 170.19, 133.76, 129.28, 128.61, 127.89, 79.89, 44.36, 25.86, 25.73, 25.49, 23.91, 22.57. ESI-MS (m/z): 340.2 [M+Na]++; HRMS m/z calcd for \([\text{C}_{18}\text{H}_{28}\text{BNO}_3+\text{Na}]^+\) 339.20963, found: 339.20870; HPLC: Chiralpak AD-H Column (250 mm), detected at 220 nm, n-hexane / i-propanol = 95/5, flow = 0.6 mL/min, Retention time: 7.8 min (minor), 8.9 min (major).

5. Representative procedure for synthesis of imidazolinium salt:

Scheme 1 Synthesis of Imidazolium Salt \(\text{NHC}_2\)

A flame-dried schlenk flask equipped with a stir bar and a reflux condenser was
charged with 2-bromobiphenyl (1.4 g), (S,S)-1,2-diphenyl ethylenediamine A (1.65g, 7.77 mmol), Pd(OAc)$_2$ (135 mg), rac-BINAP (747 mg) and NaO-t-Bu (1.2 g), under a dry N$_2$ atmosphere. Toluene (100 mL) was added to the mixture. After 10 hours at 100 °C, the solution was allowed to cool to room temperature, filtered through Celite, concentrated, and purified by silica gel chromatography (PE/EtOAc:1/1) to afford 1.74 g(90% yield) of diamine B as a light yellow oil.  

A 25 mL round-bottom flask charged with diamine B (365 mg), NaBH(OAc)$_3$ (296 mg), 1,2-dichloroethane (8 mL) was added to the mixture. After 12 hours at 110 °C, the solution was allowed to cool to 22 °C and passed through a plug of Celite, concentrated, and purified by silica gel column chromatography (hexanes/Et2O:20/1) to afford 400 mg (90% yield) of the corresponding diamine C as a light yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.40-7.52(m, 4H), 7.38-7.40(m, 1H), 6.90-7.19(m, 10H), 6.66-6.92 (m, 3H), 6.65 (t, 1H, $J = 7.2$ Hz), 6.23 (d, 1H, $J = 7.6$ Hz), 5.66(s, 1H), 4.22(s, 1H), 3.80 (d, 1H, $J = 7.6$ Hz), 2.32(m, 1H), 0.85-1.60 (m, 10H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 144.80, 141.53, 141.43, 139.79, 129.80, 129.72, 129.57, 128.67, 128.34, 128.29, 128.16, 127.99, 127.63, 127.09, 127.03, 126.94, 116.62, 111.74, 65.28, 64.35, 52.29, 34.48, 31.85, 26.03, 24.66, 24.12; ESI-MS (m/z): 447.3 (M+H)$^\oplus$; HRMS (MALDI) m/z calcld for [C$_{32}$H$_{34}$N$_2$+H]$^\oplus$ 447.28002, found: 447.2800 ±0.002.

A 25mL round-bottom flask equipped with reflux condenser was charged with diamine C (300 mg), HC(OEt)$_3$ (5 mL), and NH$_4$BF$_4$ (126). After 4 hours at 110 °C, the solution was concentrated and purified by silica gel column chromatography (hexanes/EtOAc:2/3) to afford 440 mg (98% yield) of the corresponding imidazolinium salt NH$_2$C$_2$.[α]$^{23}_{D}$ +430.1 (c 1.00, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): δ 8.79 (s, 1H), 7.30-7.57 (m, 14H), 7.19-7.22 (m, 1H), 7.05 (m, 2H), 6.87 (d, 2H, $J = 7.2$ Hz), 5.07 (d, 1H, $J = 8.4$ Hz), 4.48 (d, 1H, $J = 8.4$ Hz), 3.38 (tt, 1H, $J = 12.0$ Hz, $J = 3.4$ Hz), 1.70-2.0 (m, 5H), 1.08-1.42 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 156.13, 138.09, 137.83, 15.40, 134.71, 132.01, 130.92, 129.89, 129.58, 129.52, 129.49, 129.24, 129.01, 128.56, 128.31, 127.56, 127.22, 75.15, 72.49, 58.06, 31.39,
30.36, 25.06, 24.88, 24.48; ESI-MS (m/z): 457.3 (C_{33}H_{33}BF_{4}N_{2}-BF_{4})\textsuperscript{6}; HRMS (MALDI) m/z calcd for [C_{33}H_{33}N_{2}]\textsuperscript{6} 457.26437, found: 457.2645 \pm 0.002.

Imidazolinium salt NHC\textsubscript{3}

![Diagram of NHC3]

[α]\textsubscript{23}D +267.8 (c 1.505, CHCl\textsubscript{3}); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 8.71 (s, 1H), 7.49-7.58 (m, 3H), 7.26-7.45 (m, 1H), 7.17-7.20 (m, 1H), 7.04-7.06 (m, 2H), 6.98 (d, 2H, J = 7.2 Hz), 5.04 (d, 1H, J = 8.8 Hz), 4.52 (d, 1H, J = 8.8 Hz), 3.79 (m, 1Hz), 1.40-2.04 (m, 8H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 156.15, 138.09, 137.33, 135.21, 134.46, 132.03, 131.04, 129.92, 129.87, 129.55, 129.68, 129.23, 129.04, 128.35, 128.31, 127.70, 127.40, 75.20, 73.92, 59.67, 30.71, 30.09, 22.86, 22.56; ESI-MS (m/z): 443.2 (C\textsubscript{32}H\textsubscript{31}BF\textsubscript{4}N\textsubscript{2}-BF\textsubscript{4})\textsuperscript{6}; HRMS m/z calcd for [C\textsubscript{33}H\textsubscript{31}N\textsubscript{2}]\textsuperscript{6} 443.24872, found: 443.24899.

Imidazolinium salt NHC\textsubscript{4}

![Diagram of NHC4]

[α]\textsubscript{23}D +301.9 (c 1.49, CHCl\textsubscript{3}); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 8.77 (s, 1H), 7.46-7.55 (m, 4H), 7.26-7.42 (m, 10H), 7.18-7.21 (m, 1H), 7.04-7.06 (m, 2H), 6.92 (d, 2H, J = 7.2 Hz), 5.05 (d, 1H, J = 8.8 Hz), 4.60 (d, 1H, J = 8.8 Hz), 3.51 (m, 1Hz), 1.28-2.08 (m, 14H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 156.15, 138.09, 137.33, 135.21, 134.46, 132.03, 131.04, 129.92, 129.87, 129.55, 129.48, 129.23, 129.04, 128.35, 128.31, 127.70, 127.40, 75.20, 73.92, 59.67, 30.71, 30.09, 22.86, 22.56; ESI-MS (m/z): 485.3 [C\textsubscript{35}H\textsubscript{37}BF\textsubscript{4}N\textsubscript{2}-BF\textsubscript{4}]\textsuperscript{6}; HRMS m/z calcd for [C\textsubscript{35}H\textsubscript{37}N\textsubscript{2}]\textsuperscript{6} 485.29567, found:
485.29393.

Imidazolinium salt NHC₅

\[
\begin{align*}
\text{Ph} & \quad \text{NHC}_5 \\
\text{Ph} & \quad \text{BF}_4
\end{align*}
\]

\([\alpha]^{23}_D +318.7 \, (c \, 1.37, \text{CHCl}_3)\); \(^1\)H NMR (400 MHz, CDCl₃): \(\delta 9.86 \, (s, 1H), \ 8.17 \, (d, 1H, \ J = 7.6 \, \text{Hz}), \ 7.17-7.56 \, (m, 16H), \ 6.97 \, (d, 1H, \ J = 7.6 \, \text{Hz}), \ 4.99 \, (d, 1H, \ J = 10.0 \, \text{Hz}), \ 4.39 \, (d, 1H, \ J = 10.0 \, \text{Hz}), \ 3.88 \, (s, 3H); \ \text{C}^{13} \text{NMR} (100 \, \text{MHz, CDCl}_3): \ \delta 158.04, \ 137.94, \ 137.77, \ 134.10, \ 133.95, \ 132.02, \ 130.82, \ 129.83, \ 129.64, \ 129.51, \ 129.42, \ 129.16, \ 129.10, \ 129.04, \ 128.58, \ 128.28, \ 127.48, \ 75.83, \ 74.60, \ 35.20; \ \text{ESI-MS (m/z):} 389.2 \ \text{[C}_{28}\text{H}_{25}\text{IN}_2\text{-I]}^\oplus; \ \text{HRMS m/z} \ \text{calcd for [C}_{28}\text{H}_{25}\text{N}_2]^\oplus 389.20177, \ \text{found: 389.20140.}
\]

Imidazolinium salt NHC₆

\[
\begin{align*}
\text{Ph} & \quad \text{NHC}_6 \\
\text{Ph} & \quad \text{BF}_4
\end{align*}
\]

\([\alpha]^{23}_D +454.0 \, (c \, 0.845, \text{CHCl}_3); \ \text{H NMR} (400 \, \text{MHz, CDCl}_3): \ \delta 8.67 \, (s, 1H), \ 7.54 \, (m, 3H), \ 7.32-7.42 \, (m, 10H), \ 7.12-7.17 \, (m, 3H), \ 6.81 \, (d, 2H, \ J = 7.6 \, \text{Hz}), \ 5.14 \, (d, 1H, \ J = 8.8 \, \text{Hz}), \ 3.88 \, (m, 1H), 1.69-1.94 \, (m, 6H), \ 1.54 \, (m, 1H), 1.32-1.42 \, (m, 1H), 1.09-1.27 \, (m, 3H), 1.19 \, (s, 9H); \ \text{C}^{13} \text{NMR} (100 \, \text{MHz, CDCl}_3): \ \delta 155.83, \ 152.92, \ 138.12, \ 135.44, \ 135.39, \ 134.82, \ 131.53, \ 130.44, \ 129.94, \ 129.58, \ 129.44, \ 129.22, \ 129.18, \ 128.21, \ 127.92, \ 127.23, \ 126.46, \ 75.96, \ 72.09, \ 57.94, \ 34.65, \ 31.44, \ 30.75, \ 25.08, \ 24.90, \ 24.44; \ \text{ESI-MS (m/z):} 513.3 \ \text{[C}_{37}\text{H}_{41}\text{BF}_2\text{N}_2\text{-BF}_4]^\oplus; \ \text{HRMS m/z} \ \text{calcd for [C}_{37}\text{H}_{41}\text{N}_2]^\oplus 513.32697, \ \text{found: 513.32435.}
Imidazolinium salt $\text{NHC}_7$

\[
\begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{BF}_4 \\
\text{NHC}_7
\end{array}
\]

$\lbrack \alpha \rbrack_{D}^{23} +326.1 \ (c \ 1.095, \ \text{CHCl}_3)$; $^1\text{H NMR (400 MHz, CDCl}_3\rbrack$: $\delta$ 8.67 (s, 1H), 7.54 (m, 3H), 7.32-7.42 (m, 10H), 7.12-7.17 (m, 3H), 6.81 (d, 2H, $J = 7.6 \text{ Hz}$), 5.14 (d, 1H, $J = 8.8 \text{ Hz}$), 3.88 (m, 1H), 1.69-1.94 (m, 6H), 1.54 (m, 1H), 1.32-1.42 (m, 1H), 1.09-1.27 (m, 3H), 1.19 (s, 9H); $^{13}\text{C NMR (100 MHz, CDCl}_3\rbrack$: $\delta$ 155.83, 152.92, 138.12, 135.44, 135.39, 134.82, 131.53, 130.44, 129.94, 129.58, 129.44, 129.22, 129.18, 128.21, 127.92, 127.23, 126.46, 75.96, 72.09, 57.94, 34.65, 31.44, 30.75, 25.08, 24.90, 24.44; ESI-MS (m/z): 541.4 [C$_{30}$H$_{45}$BF$_4$N$_2$-BF$_4$]; HRMS m/z calcd for [C$_{30}$H$_{45}$N$_2$]$^+$ 541.35827, found: 541.35712.