Electronic Supplementary Information for

A Facile Preparation of Backbone-substituted, Functionalized and Chiral

Imidazolinium Salts

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1. **General Information:**

Unless otherwise stated, all reactions and manipulations were performed using standard Schlenk techniques. All solvents were purified by distillation using standard methods. Commercially available reagents were used without further purification. NMR spectra were recorded by using a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (\(^{1}\)H NMR CDCl\(_3\): 7.26 ppm; \(^{13}\)C NMR CDCl\(_3\): 77.0 ppm). Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer 341 MC digital polarimeter with a 10 cm cell (\(c\) given in g per 100 mL) and \([\alpha]_D\) values are given in 10\(^{-1}\) deg cm\(^2\) g\(^{-1}\). Mass spectra were recorded on the HP-5989 instrument by EI/ESI methods. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm\(^{-1}\). X-ray diffraction analysis was performed by using a Bruker Smart-1000 X-ray diffractometer. Chiral HPLC was performed by using a SHIMADZU SPD-10A vp series instrument with chiral columns (Chiralpak AD-H column, 4.6 × 250 mm, Daicel Chemical Co. Ltd).

2. **Preparation of formamidines:**

In general, formamidines were prepared following the method described by Grubbs et al\(^1\).

\[
\begin{align*}
\text{ArNH}_2 + \text{Ar'NH}_2 + \text{HC(OEt)}_3 & \xrightarrow{\text{cat. HOAc, } \Delta} \text{Ar}-\overset{\text{N}}{\text{N}}\text{Ar'} \\
\text{Scheme S1. Synthesis of various formamidines}
\end{align*}
\]

The formamidines 1a, 1c, 1d, 1e, 1g were prepared as previously reported\(^2\).

**N,N’-Bis(2-isopropylphenyl)formamidine (1b)**

\[
\begin{align*}
\begin{array}{c}
\text{2-isopropylamine (2.0 g, 2.1 mL, 14.80 mmol, 2 eq.), triethylorthoformate} \\
(1.1 g, 1.2 mL, 7.40 mmol, 1 eq.) \text{ and glacial acetic acid (22.2 mg, 21 \(\mu\)L, 0.37 mmol, 0.05 eq.) were mixed and stirred at 140 °C for 3 h. The crude} \\
\text{solid was triturated in cold PE and filtered through a glassfrit. The solid was} \\
washed with PE and dried in vacuum to give the product 1b as a white solid (1.40 g, 67%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.00\) (s, 1H, NCHN), 7.28-7.09 (m, 8H, 8\(\times\)Ar-H), 3.29 (sept, \(J = 6.8\) Hz, 2H, 2\(\times\)CH\(_3\)CH\(_3\)), 1.26 (d, \(J = 6.8\) Hz, 12H, 4\(\times\)CH\(_2\)CH\(_3\)). \(^{13}\)C NMR (400 MHz, CDCl\(_3\)): \(\delta = 149.1, 142.8, 105.6\).
\end{array}
\end{align*}
\]

139.7, 126.5, 125.6, 123.9, 118.9, 27.5, 22.9. HRMS (ESI-MS): m/z [M + H+] calcd for C₁₉H₂₅N₂⁺: 281.2012; found: 281.2023.

**N-(2-isopropylphenyl)-N’-(2,4,6-trimethylphenyl)formamidine (1f)**

The mixture of 2-isopropylaniline (2.0 g, 2.1 mL, 14.79 mmol, 1 eq.), glacial acetic acid (44.4 mg, 42 μL, 0.74 mmol, 0.05 eq.) and triethylorthoformate (2.2 g, 2.5 mL, 14.79 mmol, 1 eq.) was heated at 140 °C. After 1 h, the mixture was allowed to cool to ambient temperature and mesitylamine (2.0 g, 2.1 mL, 14.79 mmol, 1 eq.) was added. The mixture was stirred at 140 °C for 8 h and 160 °C for additional 2 h. The propylamine in the residue was distilled under reduced pressure, then pre-absorbed on silica gel and purified by column chromatography (PE/EtOAc = 20:1→15:1→10:1). The fractions containing the desired product were collected and concentrated under reduced pressure, then recrystallized from acetone to yield the product 1f as a white solid (490 mg, 12%).

**1H NMR (400 MHz, CDCl₃):** δ = 7.62 (s, 1H, NCH), 7.25-7.06 (m, 3H, 3×Ar-H), 6.90-6.88 (m, 3H, 3×Ar-H), 3.30 (sept, J = 6.8 Hz, 1H, CH₃CH₂CH₃), 2.28 (s, 3H, ArCH₃), 2.26 (s, 6H, 2×ArCH₃), 1.24 (d, J = 6.8 Hz, 6H, 2×CH₃CH).

**13C NMR (400 MHz, CDCl₃):** δ = 144.2, 129.3, 129.0, 128.1, 126.9, 126.1, 125.5, 123.6, 118.0, 27.7, 27.6, 23.4, 23.0, 22.4, 20.7, 18.6, 17.8. HRMS (ESI-MS): m/z [M + H⁺] calcd for C₁₉H₂₅N₂⁺: 281.2018; found: 281.2019.

### 3. Synthesis of intermediate alcohols:

**Method A:**

![Scheme S2](image)

**Scheme S2.** Synthesis of intermediate alcohols from formamidines

**Alcohol 2a**

NaH (60% suspension in mineral oil, 120 mg, 3.0 mmol, 1.5 eq.) was added portion by portion to the solution of 1a (673 mg, 2.4 mmol, 1.2 eq.) in DMF (15 mL) at 0 °C. After 5 mins, the mixture was warmed to room temperature and stirred for 30 mins. Styrene oxide (240mg, 0.24 mL, 2.0
mmol, 1 eq.) was added dropwise at 0 °C. 5 mins latter, the mixture was warmed to room temperature. After stirring for 12 h, 50 mL of H₂O was added and the mixture was extracted 3 times with 30 mL of EtOAc. The combined organic layers was washed with saturated NaCl and dried with anhydrous MgSO₄. After evaporating the solvent, the residue was purified by column chromatography on silica gel (PE-EtOAc = 12:1→10:1) to afford the product 2a as a pale yellow oil (737 mg, 92%).

**1H NMR (400 MHz, CDCl₃):** δ = 7.64 (s, 1H, NC₆H₄), 7.43-7.23 (m, 5H, 5×Ar-H), 6.96 (s, 1H, Ar-H), 6.90 (s, 1H, Ar-H), 6.86 (s, 2H, 2×Ar-H), 5.15 (d, J = 9.2 Hz, 1H, ArCHOH), 4.49 (dd, J = 9.2 Hz, 14.4 Hz, 1H, NCH₂CH), 3.56 (sept, J = 6.8 Hz, 1H, CH₃C₆H₄CH₃), 2.91 (sept, J = 6.8 Hz, 1H, CH₃C₆H₄CH₃), 1.33 (d, J = 6.8 Hz, 3H, CH₃CH₃), 1.31 (d, J = 6.8 Hz, 3H, CH₃CH₃), 1.27 (d, J = 6.8 Hz, 6H, 2×CH₂CH₃).

**13C NMR (400 MHz, CDCl₃):** δ = 156.3, 145.2, 143.1, 140.1, 137.7, 136.6, 135.7, 132.2, 129.6, 129.6, 129.5, 128.6, 128.0, 127.3, 125.9, 75.3, 65.8, 60.7, 20.8, 18.8, 18.6, 17.8, 15.2. HRMS (ESI-MS): m/z [M+H⁺] calced for C₂₇H₃₃N₂O⁺: 401.2593, found: 401.2587.

**Alcohol 2b**

Following the procedure of 2a, 1b (673 mg, 2.4 mmol, 1.2 eq.) was dissolved in 15 mL of DMF. The mixture was cooled to 0 °C and NaH (60% suspension in mineral oil, 120 mg, 3.0 mmol, 1.5 eq.) was added portion by portion. After 5 mins, the mixture was warmed to room temperature and stirred for 30 mins. Styrene oxide (240mg, 0.24 mL, 2.0 mmol, 1 eq.) was added dropwise and the temperature of the mixture was rised to 70 °C. After stirring for 10 h, 50 mL of H₂O was added and the mixture was extracted 3 times with 30 mL of EtOAc. The combined organic layers was washed with saturated NaCl and dried with anhydrous MgSO₄. After evaporating the solvent, the residue was purified by column chromatography on silica gel (PE-EtOAc = 12:1→10:1) to afford the product 2b as a pale yellow oil (454 mg, 57%).

**1H NMR (400 MHz, CDCl₃):** δ = 7.63 (s, 1H, NC₆H₄), 7.41-7.27 (m, 7H, 7×Ar-H), 7.16-7.10 (m, 3H, 3×Ar-H), 7.04-7.01 (m, 1H, ArCHOH), 6.81-6.68 (m, 3H, 3×Ar-H), 5.14 (d, J = 9.6 Hz, 1H, NCH₂CH), 3.95 (brs, 2H, NCH₂CH, OH), 3.56 (sept, J = 6.8 Hz, 1H, CH₃CH₂CH₃), 2.91 (sept, J = 6.8 Hz, 1H, CH₃CH₂CH₃), 1.33 (d, J = 6.8 Hz, 3H, CH₃CH₃), 1.31 (d, J = 6.8 Hz, 3H, CH₃CH₃), 1.27 (d, J = 6.8 Hz, 6H, 2×CH₂CH₃).

**13C NMR (400 MHz, CDCl₃):** δ = 154.6, 147.3, 142.8, 141.9, 128.3, 127.4, 126.9, 126.5, 126.4, 125.9, 124.1, 119.7, 119.0, 115.8, 29.7, 28.1, 27.8, 27.6, 23.2, 23.0, 22.2. HRMS (ESI-MS): m/z [M + H⁺] calced for C₂₇H₃₃N₂O⁺: 401.2593, found:
Method B:

Scheme S3. Synthesis of intermediate alcohols from 2-bromoacetophenone

Alcohol 5a

NaH (60% suspension in mineral oil, 120 mg, 3.0 mmol, 1.5 eq.) was added portion by portion to the solution of 1a (560 mg, 2.0 mmol, 1 eq.) in DMF (15 mL) at 0 °C. After 5 mins, the mixture was warmed to room temperature and stirred for 30 mins. 2-bromoacetophenone (796 mg, 4.0 mmol, 2 eq.) was dissolved in 10 mL of DMF and added dropwise to the mixture in 10 mins, the mixture was then warmed to room temperature. After stirring for 8 h, 50 mL of H2O was added and the mixture was extracted 3 times with 30 mL of EtOAc. The combined organic layers was washed with saturated NaCl and dried with anhydrous MgSO4. After evaporating the solvent, the residue was purified by flash column chromatography on silica gel (PE-EtOAc = 12:1→8:1) to afford the crude product which was then dissolved in 40 mL of EtOH. The solution was cooled to 0 °C and NaBH4 (227mg, 6 mmol, 3 eq.) was added carefully with vigorous stirring. The mixture was warmed to room temperature and stirred for 1 h. The volatiles were removed under vacuum, and the residue was purified by chromatography on silica gel (PE/EtOAc = 12:1→8:1) to give 5a as a pale yellow oil (448 mg, 56%). 1H NMR shows that it is same as 3a.

Alcohol 5b

Following the procedure of 5a, 1b (560 mg, 2.0 mmol, 1 eq.) was dissolved in 15 mL of DMF. The mixture was cooled to 0 °C and NaH (60% suspension in mineral oil, 120 mg, 3.0 mmol, 1.5 eq.) was added portion by portion. After 5 mins, the mixture was warmed to room temperature and stirred for 30 mins. 2-Bromoacetophenone (796 mg, 4.0 mmol, 2 eq.) was dissolved in 10 mL of DMF and added dropwise to the mixture in 10 mins, the mixture was then warmed to room temperature.
After stirring for 8 h, 50 mL of H₂O was added and the mixture was extracted 3 times with 30 mL of EtOAc. The combined organic layers was washed with saturated NaCl and dried with anhydrous MgSO₄. After evaporating the solvent, the residue was purified by flash column chromatography on silica gel (PE-EtOAc = 12:1→10:1) to afford the crude product which was then dissolved in 40 mL of EtOH. The solution was cooled to 0 °C and NaBH₄ (227mg, 6 mmol, 3 eq.) was added carefully with vigorous stirring. The mixture was warmed to room temperature and stirred for 1 h. The volatiles were removed under vacuum, and the residue was purified by chromatography on silica gel (PE/EtOAc = 12:1→8:1) to give 5b as a pale yellow oil (385 mg, 48%). ¹H NMR shows that it is same as 3b.

4. General procedure for the synthesis of backbone-substituted imidazolinium salts:

Formamidine (2.0 mmol 1 (1.2 eq.) was dissolved in DMF, and to the suspension NaH (60% suspension in mineral oil, 1.5 eq.) was added portion by portion at 0 °C. After 5 mins the resulting mixture was warmed to room temperature and stirred for 30 mins. After cooling to 0°C, olefin oxide (1 eq.) was added dropwise over 5 mins, and then the mixture was warmed to room temperature. The reaction progress was monitored by TLC or ESI. After full conversion of the corresponding formamidine, H₂O was added and the mixture was extracted with EtOAc (30 mL x 3), The combined organic layers was dried over anhydrous MgSO₄. The volatiles were removed under vacuum, and the residue was purified by flash chromatography to give alcohol 2 which were used without characterization. The alcohol 2 was then dissolved in dry CH₂Cl₂. The mixture was cooled to 0 °C, and Et₃N (1.1 eq.) was added dropwise. After 5 mins, Tf₂O (1.1 eq.) was added carefully. The solution was warmed to room temperature and stirred for 5-8 h. The volatiles were removed under vacuum, and the residue was purified by chromatography on silica gel to give the product 3.
Imidazolinium trifluoromethanesulfonate 3a

2a (737 mg) was dissolved in 10 mL of dry CH₂Cl₂, the mixture was cooled to 0 °C and Et₃N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) was added dropwise. After 5 mins Tf₂O (621 mg, 0.36 mL, 2.2 mmol, 1.1 eq.) was added carefully. The solution was warmed to room temperature and stirred for 5 h. The volatiles were removed under vacuum, and the residue was purified by chromatography on silica gel (CH₂Cl₂/EtOH = 40:1→20:1) to give 3a as a white powder (884 mg, 83%). ¹H NMR (400 MHz, CDCl₃): δ = 8.57 (s, 1H, NC₃H𝑁), 7.43-7.32 (m, 5H, 5×Ar-H), 7.05 (s, 2H, 2×Ar-H), 6.97 (s, H, Ar-H), 5.98 (dd, J = 9.2 Hz, 12.8 Hz, 1H, ArCHCH₃), 4.99 (t, J = 12.8 Hz, 1H, NCH₂CH), 4.58 (dd, J = 9.2 Hz, 12.8 Hz, 1H, NCH₂CH), 2.55-2.49 (brs, 9H, 3×ArCH₃) 2.34 (s, 3H, ArCH₃), 2.24 (s, 3H, ArCH₃), 1.73 (s, 3H, ArCH₃). ¹³C NMR (400 MHz, CDCl₃): δ = 158.4, 140.7, 140.2, 135.6, 135.0, 133.3, 130.3, 130.1, 130.1, 129.8, 129.3, 128.6, 128.5, 122.1, 118.9, 67.1, 56.5, 53.4, 20.9, 18.4, 17.7. HRMS (ESI-MS): m/z [M – OTf⁻] calcd for C₂₇H₃₁N₂⁺: 383.2487; found: 383.2487.

Imidazolinium trifluoromethanesulfonate 3b

2b (454 mg) was dissolved in 10 mL of dry CH₂Cl₂, the mixture was cooled to 0 °C and Et₃N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) was added dropwise. After 5 mins Tf₂O (621 mg, 0.36 mL, 2.2 mmol, 1.1 eq.) was added carefully. The solution was warmed to room temperature and stirred for 5 h. The volatiles were removed under vacuum, and the residue was purified by chromatography on silica gel (CH₂Cl₂/EtOH = 40:1→20:1) to give 3b as a white powder (543 mg, 51%). ¹H NMR (400 MHz, CDCl₃): δ = 7.93-7.91 (m, 1H, Ar-H), 7.85 (s, 1H, NCH,N), 7.81-7.79 (m, 1H, Ar-H), 7.48-7.27 (m, 10H, Ar-H), 7.24-7.21 (m, 1H, Ar-H), 6.23 (dd, J = 8.8 Hz, 12.0 Hz, 1H, ArCHCH₃), 5.33 (t, J = 12.0 Hz, 1H, NCH₂CH), 4.45 (dd, J = 8.8 Hz, 12.0 Hz, 1H, NCH₂CH), 3.24 (sept, J = 6.8 Hz, 1H, CH₃CHCH₃), 2.87 (sept, 1H, J = 6.8 Hz, CH₃CHCH₃), 1.42 (d, J = 6.8 Hz, 6H, 2×CH₃CH), 1.40 (d, J = 6.8 Hz, 6H, 2×CH₃CH), 1.22 (d, J = 6.8 Hz, 3H, CH₃CH), 0.85 (d, J = 6.8 Hz, 3H, CH₃CH). ¹³C NMR (400 MHz, CDCl₃): δ = 156.3, 144.5, 134.4, 132.5, 131.1, 130.7, 130.6, 130.2, 129.6, 128.2, 128.1, 127.6, 127.2, 126.9, 122.3, 119.3, 69.0, 60.4, 28.6, 28.1, 24.6, 24.2, 23.8. HRMS (ESI-MS): m/z [M – OTf⁻] calcd for C₂₇H₃₁N₂⁺: 383.2482; found: 383.2487.
Imidazolinium trifluoromethanesulfonate 3c

According to the general procedure, 1c (875 mg, 2.4 mmol, 1.2 eq.) was dissolved in 15 mL of DMF and the mixture was cooled to 0°C before NaH (60% suspension in mineral oil, 120 mg, 3.0 mmol, 1.5 eq.) was added portion by portion. After 5 mins it was warmed to room temperature and stirred for 30 mins then cooled to 0 °C again. Styrene oxide (240mg, 0.24 mL, 2.0 mmol, 1 eq.) was added dropwise. 5 mins latter, the mixture was warmed to room temperature. After stirring for 12 h, 50 mL of H2O was added and the mixture was extracted 3 times with EtOAc. The combined organic layers was washed with saturated NaCl and dried with anhydrous MgSO4. After evaporating the solvent, the residue was purified by flash column chromatography on silica gel (PE-EtOAc = 12:1→10:1) to afford the crude product which was then dissolved in 10 mL of dry CH2Cl2. The mixture was cooled to 0 °C and Et3N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) was added dropwise. After 5 mins Tf2O (621 mg, 0.36 mL, 2.2 mmol, 1.1 eq.) was added carefully. The solution was warmed to room temperature and stirred for 5 h. The volatiles were removed under vacuum, and the residue was purified by chromatography on silica gel (CH2Cl2/EtOH = 40:1→20:1) to give 3c as a white powder (968 mg, 78%). 1H NMR (400 MHz, CDCl3): δ = 8.23 (s, 1H, NCH2N), 7.55-7.28 (m, 9H, Ar-H), 7.00-6.99 (m, 1H, Ar-H), 6.15 (dd, J = 10.4 Hz, 12.8 Hz, 1H, ArCH2CH3), 5.31 (t, J = 12.8 Hz, 1H, NCH2CH3), 4.63 (dd, J = 10.4 Hz, 12.8 Hz, 1H, NCH2CH3), 3.30 (sept, J = 6.8 Hz, 2H, 2×CH3CH2CH3), 3.16 (sept, J = 6.8 Hz, 1H, CH3CH2CH3), 2.50 (sept, J = 6.8 Hz, 1H, CH3CH2CH3), 1.54 (d, J = 6.8 Hz, 3H, CH3CH2CH3), 1.46 (d, J = 6.8 Hz, 3H, CH3CH2CH3), 1.39 (d, J = 6.8 Hz, 3H, CH3CH2CH3), 1.31 (d, J = 6.8 Hz, 3H, CH3CH2CH3), 1.29 (d, J = 6.8 Hz, 3H, CH3CH2CH3), 1.21 (d, J = 6.8 Hz, 3H, CH3CH2CH3), 1.04 (d, J = 6.8 Hz, 3H, CH3CH2CH3), 0.39 (d, J = 6.8 Hz, 3H, CH3CH2CH3). 13C NMR (400 MHz, CDCl3): δ = 157.8, 146.9, 146.7, 146.7, 145.4, 132.1, 131.6, 131.3, 130.4, 129.5, 129.3, 128.9, 127.4, 125.3, 125.1, 124.7, 124.5, 69.4, 58.4, 29.5, 29.1, 29.0, 25.6, 25.3, 25.1, 24.5, 24.3, 23.9, 23.6, 22.6. HRMS (ESI-MS): m/z [M – OTf ] calcd for C33H43N2+: 467.3421; found: 467.3428.

Imidazolinium trifluoromethanesulfonate 3d

According to the general procedure, NaH (60% suspension in mineral oil, 120 mg, 3.0 mmol, 1.5 eq.) was added portion by portion to the solution of 1a (673 mg, 2.4 mmol, 1.2 eq.) in DMF (15 mL) at 0 °C.
After 5 mins, the mixture was warmed to room temperature and stirred for 30 mins. (R)-Isopropyloxirane (172mg, 0.19 mL, 2.0 mmol, 1 eq.) was added dropwise at 0 ºC. 5 mins latter, the mixture was heated to 70 ºC. After stirring for 10 h, 50 mL of H2O was added and the mixture was extracted 3 times with 30 mL of EtOAc. The combined organic layers was washed with saturated NaCl and dried with anhydrous MgSO4. After evaporating the solvent, the residue was purified by flash column chromatography on silica gel (PE-EtOAc = 12: 1→8: 1) to afford the crude product which was then dissolved in 10 mL of dry CH2Cl2. The mixture was cooled to 0 ºC and Et3N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) was added dropwise. After 5 mins Tf2O (621 mg, 0.36 mL, 2.2 mmol, 1.1 eq.) was added carefully. The solution was warmed to room temperature and stirred for 5 h. The volatiles were removed under vacuum, and the residue was purified by chromatography on silica gel (CH2Cl2/EtOH = 40:1→20:1) to give 3d as a white powder (808 mg, 81%). 1H NMR (400 MHz, CDCl3): δ = 8.52 (s, 1H, NCCH), 6.97 (s, 4H, 4×Ar-H), 4.86 (dt, J = 5.6 Hz, 11.2 Hz, 1H, CHCH2), 4.50 (t, J = 12.0 Hz, 1H, NCH2CH), 4.05 (t, J = 11.2Hz, 1H, NCH2CH), 2.39 (s, 3H, ArCH3), 2.38 (s, 3H, ArCH3), 2.35 (s, 6H, 2×ArCH3), 2.30 (s, 6H, 2×ArCH3), 2.09 (sept, J = 6.8Hz, 1H, CH3CHCH2), 1.07 (d, J = 6.8 Hz, 3H, CH3CH). 13C NMR (400 MHz, CDCl3): δ = 160.0, 140.6, 140.3, 134.9, 134.8, 130.6, 130.3, 130.1, 129.8, 122.0, 118.9, 69.2, 53.2, 30.0, 21.0, 20.9, 19.6, 18.7, 18.6, 17.7. HRMS (ESI-MS): m/z [M – OTf ] calcd for C24H33N2+: 349.2644; found: 349.2639.

**Imidazolinium trifluoromethanesulfonate 3e**

According to the general procedure, 1a (673 mg, 2.4 mmol, 1.2 eq.) was dissolved in 15 mL of DMF and the mixture was cooled to 0°C before NaH (60% suspension in mineral oil, 120 mg, 3.0 mmol, 1.5 eq.) was added portion by portion. After 5 mins, the mixture was warmed to room temperature and stirred for 0.5 h. Isobutylene oxide (144 mg, 0.18 ml, 2.0 mmol, 1.0 eq.) was added dropwise at 0°C, 5 mins latter, the mixture was warmed to room temperature. After stirring for 12 h, 50 mL of H2O was added and the reaction solution was extracted with 30 mL of EtOAc for 3 times. The combined organic layers was washed with saturated NaCl and dried over anhydrous MgSO4. After evaporating the solvent, the residue was purified by flash column chromatography on silica gel (PE-EtOAc = 12:1→10:1). The resulting crude product was then dissolved in 10 mL of dry
CH₂Cl₂ and Et₃N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) were added. The mixture was cooled to 0°C before Tf₂O (621 mg, 0.36 mL, 2.2 mmol, 1.1 eq.) was added dropwise. 5 mins later, the mixture was heated to room temperature and stirred about 5h. The volatiles were removed under vacuum, and the residue was purified by column chromatography (CH₂Cl₂/EtOH = 40:1→20:1) to give the product 3e as a white powder (600 mg, 62.0%). ¹H NMR (400 MHz, CDCl₃): δ = 8.49 (s, 1H, NC₃H₅), 7.0 (s, 2H, 2×Ar-H), 6.96 (s, 2H, 2×Ar-H), 4.17 (s, 2H, CH₂), 2.34 (s, 12H, 4×ArCH₃), 2.30 (s, 3H, ArCH₃), 2.29 (s, 3H, ArCH₃), 2.30 (s, 3H, ArCH₃). ¹³C NMR (400 MHz, CDCl₃): δ = 159.0, 140.3, 140.2, 136.7, 134.6, 130.3, 129.9, 127.1, 71.6, 63.5, 26.6, 20.8, 20.7, 19.3, 17.5, 13.6. HRMS (ESI-MS): m/z [M – TfO⁻] calcd. for C₂₃H₃₁N₂⁺: 335.2487; found: 335.2479.

Imidazolinium trifluoromethanesulfonate 3f

According to the general procedure, 1a (673 mg, 2.4 mmol, 1.2 eq.) was dissolved in 15 mL of DMF and the mixture was cooled to 0°C before NaH (60% suspension in mineral oil, 120 mg, 3.0 mmol, 1.5 eq.) was added portion by portion. After 5 mins, the mixture was allowed to warm to ambient temperature for 0.5 h. Then Cyclohexene oxide (196 mg, 0.20 ml, 2.0 mmol, 1.0 eq.) was added dropwise at 0°C. 5 mins latter, the mixture was heated to 70 °C. After stirring for 12 h, 50 mL of H₂O was added and the reaction solution was extracted with 30 mL of EtOAc for 3 times. The combined organic layers was washed with saturated NaCl and dried over anhydrous MgSO₄. After evaporating the solvent, the residue was purified by flash column chromatography on silica gel (PE-EtOAc = 12:1→10:1). The resulting crude product was then dissolved in 10 mL of dry CH₂Cl₂ and Et₃N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) were added. The mixture was cooled to 0°C before Tf₂O (621 mg, 0.36 mL, 2.2 mmol, 1.1 eq.) was added dropwise. 5 mins later, the mixture was warmed to room temperature and stired for about 5h. The volatiles were removed under vacuum, and the residue was purified by column chromatography (CH₂Cl₂/EtOH = 40:1→20:1) to give the product 3f as a white powder (694 mg, 68%). ¹H NMR (400 MHz, CDCl₃): δ = 8.50 (s, 1H, NC₃H₅), 6.98 (s, 4H, 4×Ar-H), 4.88 (t, J = 4.0 Hz, 2H, 2×CH₂), 2.39 (s, 6H, 2×ArCH₃), 2.37 (s, 6H, 2×ArCH₃), 2.30 (s, 6H, 2×ArCH₃), 1.90-1.89 (m, 2H, CH₂), 1.80-1.78 (m, 2H, CH₂), 1.64-1.62 (m, 2H, CH₂), 1.51-1.48 (m, 2H, CH₂). ¹³C NMR (400 MHz, CDCl₃): δ = 158.3, 140.0, 135.2, 134.6, 130.3, 130.0, 128.7, 122.0, 62.7, 23.2, 20.8, 19.1, 19.4, 18.4, 18.2. HRMS (ESI-MS):
m/z [M – TfO–] calcd. for C_{25}H_{33}N_{2}^+: 361.2644, found: 361.2646.

**Imidazolinium trifluoromethanesulfonate 3g**

Following the general procedure, 1d (984 mg, 2.4 mmol, 1.2 eq.) was dissolved in 15 mL of DMF. The mixture was cooled to 0 °C and NaH (60% suspension in mineral oil, 120 mg, 3.0 mmol, 1.5 eq.) was added portion by portion. After 5 mins, the mixture was warmed to room temperature and stirred for 30 mins. Styrene oxide (240 mg, 0.24 mL, 2.0 mmol, 1 eq.) was added dropwise and the temperature of the mixture was warmed to room temperature. After stirring for 12 h, 50 mL of H_{2}O was added and the mixture was extracted 3 times with 30 mL of EtOAc. The combined organic layers was washed with saturated NaCl and dried with anhydrous MgSO_{4}. After evaporating the solvent, the residue was purified by flash column chromatography on silica gel (PE-EtOAc = 12:1→10:1) to afford the crude product which was then dissolved in 10 mL of dry CH_{2}Cl_{2}, the mixture was cooled to 0 °C and Et_{3}N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) was added dropwise. After 5 mins Tf_{2}O (621 mg, 0.36 mL, 2.2 mmol, 1.1 eq.) was added carefully. The solution was warmed to room temperature and stirred for 5 h. The volatiles were removed under vacuum, the residue was purified by chromatography on silica gel (CH_{2}Cl_{2}-EtOH = 40:1→20:1) to give 3g as a white powder (1.13 g, 85%). ^{1}H NMR (400 MHz, CDCl_{3}): δ = 8.84 (s, 1H, NCH_{2}), 7.04 (s, 1H, Ar-H), 7.04 (s, 1H, Ar-H), 5.95 (dd, J = 9.2, 12.4 Hz, 1H, ArCH_{2}CH_{2}), 4.93 (t, J = 12.4 Hz, 1 H, NCH_{2}CH), 4.51 (dd, J = 9.2 Hz, J = 12.4 Hz, 1H, NCH_{2}CH), 2.51 (s, 3H, ArCH_{3}), 2.48 (s, 3H, ArCH_{3}), 2.41 (s, 3H, ArCH_{3}), 1.72 (s, 3H, ArCH_{3}). ^{13}C NMR (400 MHz, CDCl_{3}): δ = 158.8, 138.3, 138.0, 137.6, 137.0, 132.8, 132.3, 132.1, 132.0, 131.8, 130.5, 130.2, 129.3, 128.5, 124.3, 123.9, 121.8, 118.6, 67.0, 56.1, 18.2, 18.0, 17.6, 17.5. HRMS (ESI-MS): m/z [M – OTf–] calcd. for C_{25}H_{33}N_{2}Br_{2}: 511.0384; found: 511.0388.

**Imidazolinium trifluoromethanesulfonate 3h**

According to the general procedure, 1a (673 mg, 2.4 mmol, 1.2 eq.) was dissolved in 15 mL of DMF and the mixture was cooled to 0°C before NaH (60% suspension in mineral oil, 120 mg, 3.0 mmol, 1.5 eq.) was added portion by portion. After 5 mins, the mixture was allowed to warm to ambient temperature for 0.5 h. Then 1,2-epoxy-3-vinylpropane (170 mg, 2.0 mmol,
1.0 eq.) was added dropwise at 0°C. 5 mins latter, the mixture was warmed to room temperature. After stirring for 12 h, 50 mL of H₂O was added and the reaction solution was extracted with 30 mL of EtOAc for 3 times. The combined organic layers was washed with saturated NaCl and dried over anhydrous MgSO₄. After evaporating the solvent, the residue was purified by flash column chromatography on silica gel (PE-EtOAc = 12:1→10:1). The resulting crude product was then dissolved in 10 mL of dry CH₂Cl₂ and Et₃N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) were added. The mixture was cooled to 0°C before Tf₂O (621 mg, 0.36 mL, 2.2 mmol, 1.1 eq.) was added dropwise. 5 mins later, the mixture was heated to room temperature and stirred about 8 h. The volatiles were removed under vacuum, and the residue was purified by column chromatography (CH₂Cl₂/EtOH = 40:1→20:1) to give the product 3h as a white powder (606 mg, 61%). ¹H NMR (400 MHz, CDCl₃): δ = 8.56 (s, 1H, NCH), 6.98 (s, 2H, 2×Ar-H), 6.96 (s, 2H, 2×Ar-H), 5.64-5.57 (m, 1H, CH₂=CH), 5.19-5.15 (m, 2H, CH₃=CH), 4.96-4.93 (m, 1H, CH₂CH₂CH₂), 4.57 (t, J = 12.0 Hz, 1H, NCH₂CH), 3.98 (dd, J = 8.8 Hz, 12.0 Hz, 1H, NCH₂CH), 2.61-2.49 (m, 2H, CHCH₂CH), 2.38 (s, 3H, ArCH₃), 2.34 (s, 9H, 3×ArCH₃), 2.30 (s, 6H, 2×ArCH₃). ¹³C NMR (400 MHz, CDCl₃): δ = 159.2, 140.4, 140.23, 135.1, 130.4, 130.3, 129.9, 129.8, 128.6, 120.2, 62.9, 55.6, 36.8, 20.9, 20.8, 18.3, 17.9, 17.4, 17.3. HRMS (ESI-MS): m/z [M – TfO⁻] calcd. for C₂₄H₃₁N₂⁺: 347.2566, found: 347.2560.

**Imidazolinium trifluoromethanesulfonate 3i**

According to the general procedure, 1a (673 mg, 2.4 mmol, 1.2 eq.) was dissolved in 15 mL of DMF and the mixture was cooled to 0°C before NaH (60% suspension in mineral oil, 120 mg, 3.0 mmol, 1.5 eq.) was added portion by portion. After 5 mins, the mixture was allowed to warm to ambient temperature for 0.5 h. Then 1,2-epoxy-3-acetoxylpropane (230 mg, 2.0 mmol, 1.0 eq.) was added dropwise at 0°C. 5 mins latter, the mixture was warmed to room temperature. After stirring for 12 h, 50 mL of H₂O was added and the reaction solution was extracted with 30 mL of EtOAc for 3 times. The combined organic layers was washed with saturated NaCl and dried over anhydrous MgSO₄. After evaporating the solvent, the residue was purified by flash column chromatography on silica gel (PE-EtOAc = 12:1→10:1). The resulting crude product was then dissolved in 10 mL of dry CH₂Cl₂ and Et₃N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) were added. The mixture was cooled to 0°C before Tf₂O (621 mg, 0.36 mL, 2.2 mmol,
1.1 eq.) was added dropwise. 5 mins later, the mixture was heated to room temperature and stirred about 8 h. The volatiles were removed under vacuum, and the residue was purified by column chromatography (CH$_2$Cl$_2$/EtOH = 40:1→20:1) to give the product 3i as a white powder (793 mg, 75%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.40$ (s, 1H, NCHN), $6.96$ (s, 4H, 4×Ar-H), $5.31$-$5.26$ (m, 1H, CH$_2$CH$_2$), $4.75$ (t, $J = 12.8$ Hz, 1H, NCH$_2$CH), $4.32$ (dd, $J = 3.2$ Hz, 9.2 Hz, 1H, OCH$_2$CH), $4.22$ (dd, $J = 8.0$ Hz, 12.8 Hz, 1H, NCH$_2$CH), $4.07$ (dd, $J = 2.0$ Hz, 13.2 Hz, 1H, OCH$_2$CH), $2.37$ (s, 6H, 2×ArCH$_3$), $2.29$ (s, 12H, 12×ArCH$_3$), $2.07$ (s, 3H, CH$_3$CO). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta = 169.7$, $159.8$, $140.9$, $140.6$, $140.5$, $135.4$, $135.2$, $130.5$, $130.4$, $130.3$, $130.0$, $129.9$, $128.1$, $62.1$, $61.4$, $52.7$, $20.9$, $20.8$, $20.5$, $18.1$, $17.4$, $17.3$, $16.8$. HRMS (ESI-MS): m/z [M – TfO$^-$] calcd. for C$_{24}$H$_{31}$N$_2$O$_2$: 379.2446, found: 379.2439.

**Imidazolinium trifluoromethanesulfonate 3j**

According to the general procedure, 1a (673 mg, 2.4 mmol, 1.2 eq.) was dissolved in 15 mL of DMF and the mixture was cooled to 0°C before NaH (60% suspension in mineral oil, 120 mg, 3.0 mmol, 1.5 eq.) was added portion by portion. After 5 mins, the mixture was warmed to room temperature for 0.5 h. Then 1,2-epoxy-3-phenoxypropane (300 mg, 2.0 mmol, 1.0 eq.) was added dropwise at 0°C. 5 mins latter, the mixture was warmed to room temperature. After stirring for 12 h, 50 mL of H$_2$O was added and the reaction solution was extracted with 30 mL of EtOAc for 3 times. The combined organic layers was washed with saturated NaCl and dried over anhydrous MgSO$_4$. After evaporating the solvent, the residue was purified by flash column chromatography on silica gel (PE-EtOAc = 12:1→10:1). The resulting crude product was then dissolved in 10 mL of dry CH$_2$Cl$_2$ and Et$_3$N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) were added. The mixture was cooled to 0°C before Tf$_2$O (621 mg, 0.36 mL, 2.2 mmol, 1.1 eq.) was added dropwise. 5 mins later, the mixture was heated to room temperature and stired about 8 h. The volatiles were removed under vacuum, and the residue was purified by column chromatography (CH$_2$Cl$_2$/EtOH = 40:1→20:1) to give the product 3j as a white powder (821 mg, 73%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.02$ (s, 1H, NCHN), $7.33$-$6.85$ (m, 9H, 9×Ar-H), $5.56$-$5.53$ (m, 1H, CH$_2$CH$_2$), $4.91$ (t, $J = 12.4$ Hz, 1H, NCH$_2$CH), $4.50$ (dd, $J = 8.0$ Hz, 12.4 Hz, 1H, NCH$_2$CH), $4.29$ (dd, $J = 2.0$ Hz, 11.2 Hz, 1H, OCH$_2$CH), $3.96$ (d, $J = 11.2$ Hz, 1H, OCH$_2$CH), $2.52$ (s, 3H, ...
ArCH₃), 2.46 (s, 3H, ArCH₃), 2.38 (s, 3H, ArCH₃), 2.33 (s, 3H, ArCH₃), 2.28 (s, 3H, ArCH₃), 2.26 (s, 3H, ArCH₃). ¹³C NMR (400 MHz, CDCl₃): δ = 159.1, 157.0, 140.5, 140.3, 135.8, 135.2, 135.0, 134.9, 130.3, 130.1, 129.8, 129.7, 127.9, 122.0, 121.9, 118.8, 114.1, 63.8, 63.0, 52.4, 20.9, 20.8, 18.0, 17.6, 17.4, 17.1. HRMS (ESI-MS): m/z [M – TfO ] calcd. for C₂₈H₃₃N₂O+: 413.2593, found: 413.2588.

5. Synthesis of chiral imidazolium salts:

**Imidazolium trifluoromethanesulfonate (S)-4a-OTf**

According to the general procedure, NaH (60% suspension in mineral oil, 120 mg, 3.0 mmol, 1.5 eq.) was added portion by portion to the solution of 1a (673 mg, 2.4 mmol, 1.2 eq.) in DMF (15 mL) at 0 °C. After 5 mins, the mixture was warmed to room temperature and stirred for 30 mins. R- (+)-styrene oxide (240mg, 0.24 mL, 2.0 mmol, 1 eq.) was added dropwise at 0 °C. 5 mins latter, the mixture was warmed to room temperature. After stirring for 10 h, 50 mL of H₂O was added and the mixture was extracted 3 times with 30 mL of EtOAc. The combined organic layers was washed with saturated NaCl and dried with anhydrous MgSO₄. After evaporating the solvent, the residue was purified by flash column chromatography on silica gel (PE-EtOAc = 12: 1→8: 1) to afford the crude product which was then dissolved in 10 mL of dry CH₂Cl₂. The mixture was cooled to 0 °C and Et₃N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) was added dropwise. After 5 mins Tf₂O (621 mg, 0.36 mL, 2.2 mmol, 1.1 eq.) was added carefully. The solution was warmed to room temperature and stirred for 5 h. The volatiles were removed under vacuum, and the residue was purified by chromatography on silica gel (CH₂Cl₂/EtOH = 40:1→20:1) to give (S)-4a-OTf as a white powder (884 mg, 83%). ¹H NMR (400 MHz, CDCl₃): δ = 8.57 (s, 1H, NCH₃), 7.43-7.32 (m, 5H, 5×Ar-H), 7.05 (s, 2H, 2×Ar-H), 6.97 (s, 1H, Ar-H), 6.71 (s, 1H, Ar-H), 5.98 (dd, J = 9.2 Hz, 12.8 Hz, 1H, ArCH₂CH₂), 4.99 (t, J = 12.8 Hz, 1H, NCH₂CH₂), 4.58 (dd, J = 9.2 Hz, 12.8 Hz, 1H, NCH₂CH₂), 2.55-2.49 (brs, 9H, 3×ArCH₃), 2.34 (s, 3H, ArCH₃), 2.24 (s, 3H, ArCH₃), 1.73 (s, 3H, ArCH₃). ¹³C NMR (400 MHz, CDCl₃): δ = 158.4, 140.7, 140.2, 135.6, 135.0, 133.3, 130.3, 130.1, 130.1, 129.8, 129.3, 128.6, 128.5, 122.1, 118.9, 67.1, 56.5, 53.4, 20.9, 18.4, 17.7. HRMS (ESI-MS): m/z [M – OTf⁻] calcd for C₂₇H₃₁N₂⁺: 383.2487; found: 383.2487. [α]₂⁰D =85.4 (c = 0.645, CHCl₃).
Imidazolinium trifluoromethanesulfonate (S)-4b-OTf

According to the general procedure, 1e (706 mg, 2.4 mmol, 1.2 eq.) was dissolved in 15 mL of DMF and the mixture was cooled to 0°C before NaH (60% suspension in mineral oil, 120 mg, 3.0 mmol, 1.5 eq.) was added portion by portion. After 5 mins, the mixture was allowed to heat to ambient temperature for 0.5 h. R-(+)-styrene oxide (240mg, 0.24 mL, 2.0 mmol, 1 eq.) was added dropwise at 0 °C. 5 mins latter, the mixture was heated to 70 °C. After stirring for 10 h, 50 mL of H2O was added and the reaction solution was extracted with 30 mL of EtOAc for 3 times. The combined organic layers was washed with saturated NaCl and dried over anhydrous MgSO4. After evaporating the solvent, the residue was purified by flash column chromatography on silica gel (PE-EtOAc = 12:1→10:1). The resulting crude product was then dissolved in 10 mL of dry CH2Cl2 and Et3N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) were added. The mixture was cooled to 0°C before Tf2O (621 mg, 0.36 mL, 2.2 mmol, 1.1 eq.) was added dropwise. 5 mins later, the mixture was heated to room temperature and stirred for about 5 h. The volatiles were removed under vacuum, and the residue was purified by column chromatography (CH2Cl2/EtOH = 40:1→20:1) to give the product (S)-4b-OTf as a white powder (490 mg, 45%). 1H NMR (400 MHz, CDCl3): δ = 8.32 (s, 1H, NCH), 7.52-7.18 (m, 12H, 12×Ar-H), 6.48 (dd, J = 9.2 Hz, 12.4 Hz, 1H, ArCHCH3), 5.09 (t, J = 12.4 Hz, 1H, NCH2CH), 4.23 (dd, J = 9.2 Hz, 12.4 Hz, 1H, NCH2CH), 3.33 (sept, J = 6.8 Hz, 1H, CH3CH2CH3), 3.15 (sept, J = 6.8 Hz, 1H, CH3CH2CH3), 2.36 (s, 3H, ArCH3), 1.43 (d, J = 6.8 Hz, 3H, CH2CH3), 1.38 (d, J = 6.8 Hz, 6H, 2×CH2CH3), 1.27 (d, J = 6.8 Hz, 3H, CH2CH3). 13C NMR (400 MHz, CDCl3): δ = 157.7, 147.2, 145.6, 134.9, 133.4, 132.5, 131.8, 131.4, 130.0, 129.8, 129.5, 129.4, 127.8, 127.5, 126.6, 125.3, 124.7, 67.6, 61.1, 29.1, 28.6, 24.8, 24.5, 24.3, 23.9, 17.7. HRMS (ESI-MS): m/z [M – TfO ] calcd. for C28H33N2: 397.2644, found: 397.2638. [α]20 D = 108.6 (c = 0.575, CHCl3).

Imidazolinium trifluoromethanesulfonate (S)-4c-OTf

Following the general procedure, 1f (673 mg, 2.4 mmol, 1.2 eq.) was dissolved in 15 mL of DMF. The mixture was cooled to 0 °C and NaH (60% suspension in mineral oil, 120 mg, 3.0 mmol, 1.5 eq.) was added portion by portion. After 5 mins, the mixture was warmed to room temperature and stirred for 30 mins. R-(+)-styrene oxide (240mg, 0.24 mL, 2.0 mmol, 1 eq.) was
added dropwise and the temperature of the mixture was heated to 70 °C. After stirring for 10 h, 50 mL of H₂O was added and the mixture was extracted 3 times with 30 mL of EtOAc. The combined organic layers was washed with saturated NaCl and dried with anhydrous MgSO₄. After evaporating the solvent, the residue was purified by flash column chromatography on silica gel (PE-EtOAc = 12:1→10:1) to afford the crude product which was then dissolved in 10 mL of dry CH₂Cl₂, the mixture was cooled to 0 °C and Et₃N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) was added dropwise. After 5 mins Tf₂O (621 mg, 0.36 mL, 2.2 mmol, 1.1 eq.) was added carefully. The solution was warmed to room temperature and stirred for 5 h. The volatiles were removed under vacuum, the residue was purified by chromatography on silica gel (CH₂Cl₂-EtOH = 40:1→20:1) to give (S)-4c-OTf as a white powder (458 mg, 43%). ¹H NMR (400 MHz, CDCl₃): δ = 8.19 (s, 1H, NCHN), 7.56-7.19 (m, 9H, 9×Ar-H), 7.03 (s, 2H, 2×Ar-H), 6.23 (dd, J = 9.2 Hz, 12.4 Hz, 1H, ArCH₂CH₂), 5.05 (t, J = 12.4 Hz, 1H, NCH₂CH₂), 4.33 (dd, J = 9.2 Hz, 12.4 Hz, 1H, NCH₂CH₂), 2.99 (sept, J = 6.8 Hz, 1H, CH₃CH₂CH₂), 2.50 (s, 6H, 2×ArCH₂), 2.33 (s, 3H, ArCH₃), 1.29 (d, J = 6.8 Hz, 3H, CH₃CH₂), 0.85 (d, J = 6.8 Hz, 3H, CH₃CH₂). ¹³C NMR (400 MHz, CDCl₃): δ = 157.8, 145.0, 144.9, 140.9, 140.8, 134.7, 130.7, 130.3, 130.1, 130.1, 129.6, 128.1, 128.0, 127.4, 127.4, 127.0, 122.2, 119.0, 68.8, 58.4, 53.4, 28.2, 24.3, 24.0, 21.0, 17.8. HRMS (ESI-MS): m/z [M – OTf⁻] calcd for C₂₇H₃₁N₂⁺: 383.2487; found: 383.2487. [α]²⁰D –113.1 (c = 0.500, CHCl₃).

**Imidazolinium trifluoromethanesulfonates (S)-4d-OTf and (S)-4e-OTf**

According to the general procedure, NaH (60% suspension in mineral oil, 120 mg, 3.0 mmol, 1.5 eq.) was added portion by portion to the solution of 1g (774 mg, 2.4 mmol, 1.2 eq.) in DMF (15 mL) at 0 °C. After 5 mins, the mixture was warmed to room temperature and stirred for 30 mins. R-(+)-styrene oxide (240mg, 0.24 mL, 2.0 mmol, 1 eq.) was added dropwise at 0 °C. 5 mins latter, the mixture was warmed to room temperature. After stirring for 10 h, 50 mL of H₂O was added and the mixture was extracted 3 times with 30 mL of EtOAc. The combined organic layers was washed with saturated NaCl and dried with anhydrous MgSO₄. After evaporating the solvent, the residue was purified by flash column chromatography on silica gel (PE-EtOAc = 12:1→10:1) to afford the crude product which was
dissolved in 10 mL of dry CH2Cl2, the mixture was cooled to 0 °C and Et3N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) was added dropwise. After 5 mins Tf2O (621 mg, 0.36 mL, 2.2 mmol, 1.1 eq.) was added carefully. The solution was warmed to room temperature and stirred for 5 h. The volatiles were removed under vacuum, the residue was purified by chromatography on silica gel (CH2Cl2-EtOH = 40:1→20:1) to give (S)-4d-OTf (587 mg, 51%) and (S)-4e-OTf (127 mg, 11%) as light brown powder. 
(S)-4d-OTf 1H NMR (400 MHz, CDCl3): δ = 8.37 (s, 1H, NC6H5), 7.40-7.28 (m, 7H, 7×Ar-H), 7.05 (s, 2H, 2×Ar-H), 7.00-6.98 (m, 1H, Ar-CH2), 6.87-6.83 (m, 1H, Ar-CH2), 6.59-6.52 (m, 1H, ArCH3), 4.65-4.58 (m, 1H, NC6H5CH2), 3.25 (sept, 1H, J = 6.8 Hz, CH3C6H4CH3), 2.50 (s, 6H, 2×ArCH3), 2.47 (sept, J = 6.8 Hz, 1H, CH3C6H4CH3), 2.34 (s, 3H, ArCH3), 1.56-1.54 (m, 3H, CH3CH), 1.32-1.29 (m, 3H, CH3CH), 1.05-1.03 (m, 3H, CH3CH), 0.35 (d, J = 6.8 Hz, 3H, CH3CH). 13C NMR (400 MHz, CDCl3): δ = 157.9, 146.8, 146.6, 140.7, 135.5, 134.1, 132.5, 131.2, 130.3, 130.2, 129.9, 129.4, 128.8, 127.5, 125.2, 125.0, 124.4, 122.0, 118.8, 69.2, 56.2, 53.4, 28.9, 28.9, 25.3, 25.1, 23.8, 22.1, 20.9, 17.9, 17.5. HRMS (ESI-MS): m/z [M – OTf –] calcd for C30H37N2+: 425.2957; found: 425.2954. [α]20 D –2.7 (c = 0.485, CHCl3). (S)-4e-OTf 1H NMR (400 MHz, CDCl3): δ = 8.38 (s, 1H, NC6H5), 7.43-7.31 (m, 8H, 8×Ar-H), 6.98 (s, 1H, Ar-H), 6.72 (s, 1H, Ar-H), 6.18 (dd, J = 9.6 Hz, 12.8Hz, 1H, ArCH2CH3), 5.13 (t, J = 12.8 Hz, 1H, NCH2CH3), 4.57 (dd, J = 9.6 Hz, 12.8Hz, 1H, NCH2CH3), 3.20 (sept, J = 6.8 Hz, 2H, 2×CH3CH2CH3), 2.57 (s, 3H, ArCH3), 2.24 (s, 3H, ArCH3), 1.72 (s, 3H, ArCH3), 1.50 (d, J = 6.8 Hz, 3H, CH3CH), 1.43 (d, J = 6.8 Hz, 3H, CH3CH), 1.39 (d, J = 6.8 Hz, 3H, CH3CH), 1.29 (d, J = 6.8 Hz, 3H, CH3CH). 13C NMR (400 MHz, CDCl3): δ = 158.0, 146.9, 145.6, 140.3, 135.4, 135.1, 132.9, 131.4, 130.3, 129.7, 129.5, 129.3, 128.6, 128.3, 125.2, 124.7, 122.1, 118.9, 67.2, 58.7, 53.4, 29.3, 28.9, 24.9, 24.5, 24.3, 23.6, 20.9, 18.2, 17.5. HRMS (ESI-MS): m/z [M – OTf –] calcd for C30H37N2+: 425.2957; found: 425.2954. [α]20 D –55.8 (c = 0.585, CHCl3).

6. Synthesis of Imidazolidin-2-thione (S)-4a’

![Scheme S5](image)

**Scheme S5.** Synthesis of imidazolidin-2-thione (S)-4a’

A suspension of (S)-4a-OTf (54.7 mg, 0.1 mmol), NaI (60 mg, 0.4 mmol) and Ag2O (23.2 mg, 0.1
mmol) in dry dichloromethane (15 mL) was stirred at room temperature for 24 h with exclusion of light. The suspension was then filtered, and sulfur (4.8 mg, 0.15 mmol) was added to the filtrate. The resultant mixture was stirred for 24 h at room temperature. After filtration, the solvent was evaporated in vacuo. The crude product was purified by chromatographically on silica gel (PE/EtOAc = 8:1) to give \((S)-4a'\) as a white solid (32.3 mg, 78%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.33$ (s, 5H, 5×Ar-H), 7.01 (s, 2H, Ar-H), 7.00 (s, 1H, Ar-H), 6.91 (s, H, Ar-H), 6.67 (s, H, Ar-H), 5.28 (dd, $J = 9.2$ Hz, 10.8 Hz, 1H, ArCH$_2$CH$_2$), 4.33 (d, $J = 10.8$ Hz, 1H, NCH$_2$CH), 4.25 (dd, $J = 9.2$ Hz, 10.8 Hz, 1H, NCH$_2$CH), 2.49 (s, 3H, ArCH$_3$), 2.41 (s, 3H, ArCH$_3$), 2.38 (s, 3H, ArCH$_3$), 2.32 (s, 6H, ArCH$_3$), 2.21 (s, 3H, Ar-CH)$_3$, 1.74 (s, 3H, Ar-CH$_3$). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta =$180.9, 138.3, 138.3, 137.7, 137.4, 136.6, 136.4, 135.3, 134.4, 133.6, 129.6, 129.6, 129.3, 128.9, 128.6, 128.6, 128.6, 63.7, 54.4, 21.1, 21.0, 18.5, 18.4, 18.2, 18.0. HRMS (ESI-MS): m/z [M+H$^+$] calcd for C$_{27}$H$_{31}$N$_2$S$^+$ : 415.2163, found : 415.2058. [α]$^{20}_{D} +27.0$ ($c = 0.140$, CHCl$_3$).
7. NMR Spectra:

*N,N*-Bis(2-isopropylphenyl)formamidine (1b)
N-(2-isopropylphenyl)-N’-(2,4,6-trimethylphenyl)formamidine (1f)
Imidazolinium trifluoromethanesulfonate 3a
Imidazolinium trifluoromethanesulfonate 3b
Imidazolinium trifluoromethanesulfonate 3c
Imidazolinium trifluoromethanesulfonate 3d
Imidazolinium trifluoromethanesulfonate 3e
Imidazolinium trifluoromethanesulfonate 3f
Imidazolinium trifluoromethanesulfonate 3g
Imidazolinium trifluoromethanesulfonate 3h
Imidazolinium trifluoromethanesulfonate 3i
Imidazolinium trifluoromethanesulfonate 3j
Imidazolinium trifluoromethanesulfonate (S)-4a-OTf
Imidazolinium trifluoromethanesulfonate (S)-4b-OTf
Imidazolinium trifluoromethanesulfonate (S)-4c-OTf
Imidazolinium trifluoromethanesulfonate (S)-4d-OTf
Imidazolinium trifluoromethanesulfonate (S)-4e-OTf
Alcohol 2a/5a
Alcohol 2b/5b
Imidazolidin-2-thione (S)-4a"
Figure S1. 2D NMR spectrum of (S)-4b-OTf

Figure S2. 2D NMR spectrum of (S)-4c-OTf
8. HPLC for (S)-4a: Chiralcel AD, 90:10 Hexane-PrOH, 25 °C, 254 nm, 0.7 mL/min.

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(S)-4a-OTf was treated with 8 equiv. NaI in acetone. After it was stirred for 8 h, the solvent was removed under vacuum and the residue was extracted with CH$_2$Cl$_2$. Layering the CH$_2$Cl$_2$ solution with diethyl ether afforded (S)-4a-I as colorless single crystals. Colorless single crystals of (S)-4d-I were obtained as described above for (S)-4a-I, starting from (S)-4d-OTf. The single crystals of (S)-4b-OTf were obtained from slow diffusion of diethyl ether into CH$_2$Cl$_2$ solution of (S)-4b-OTf. Each crystal was mounted on a glass fiber. Crystallographic measurements were made on a Bruker Smart Apex 100 CCD area detector using graphite monochromated Mo-K$_\alpha$ radiation (\(\lambda = 0.71073\) Å). The structures were solved by directed methods (SHELXS-97) and refined on \(F^2\) by full-matrix least squares (SHELX-97) using all unique data. All the calculations were carried out with the SHELXTL18 program.\(^3\)

Key details of the crystal and structure refinement data are summarized in Table S1. Further crystallographic details may be found in the respective CIF files, which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The CCDC reference numbers for (S)-4a-I, (S)-4b-OTf, and (S)-4d-I were assigned as 841930, 841928, and 841931, respectively.

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Figure S3. Molecular structure of (S)-4a-I with 30% probability ellipsoids. H atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): N(1)-C(1) 1.312(5), N(1)-C(4) 1.452(6), N(1)-C(3) 1.465(6), N(2)-C(1) 1.297(5), N(2)-C(13) 1.437(5), N(2)-C(2) 1.508(5), C(2)-C(3) 1.542(6), C(2)-C(22) 1.497(7), C(4)-C(5) 1.381(7), C(1)-N(1)-C(4) 124.7(4), C(1)-N(1)-C(3) 111.1(3), C(4)-N(1)-C(3) 124.2(3), C(1)-N(2)-C(13) 125.0(3), C(1)-N(2)-C(2) 110.6(3), C(13)-N(2)-C(2) 124.4(3), N(2)-C(1)-N(1) 113.5(4), C(22)-C(2)-N(2) 112.2(4), C(22)-C(2)-C(3) 116.5(4), N(2)-C(2)-C(3) 101.5(3), N(1)-C(3)-C(2) 103.3(3), C(5)-C(4)-C(9) 122.9(4), C(5)-C(4)-N(1) 119.5(4), C(9)-C(4)-N(1) 117.6(4).

Figure S4. Molecular structure of (S)-4b-OTf with 30% probability ellipsoids. H atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): N(1)-C(1) 1.304(6), N(1)-C(4) 1.455(6), N(1)-C(3) 1.466(6), N(2)-C(1) 1.312(6), N(2)-C(16) 1.442(6), N(2)-C(2) 1.481(6), C(2)-C(23) 1.517(7), C(2)-C(3) 1.536(7), C(1)-N(1)-C(4) 126.5(4), C(1)-N(1)-C(3) 110.7(4), C(4)-N(1)-C(3) 122.3(4), C(1)-N(2)-C(16) 125.2(4), C(1)-N(2)-C(2) 111.0(4), C(16)-N(2)-C(2) 123.1(4),
Figure S5. Molecular structure of (S)-4d-I with 30% probability ellipsoids. H atoms and anion have been omitted for clarity. Selected bond distances (Å) and angles (°): N(1)-C(1) 1.297(7), N(1)-C(4) 1.437(8), N(1)-C(3) 1.489(8), N(2)-C(1) 1.324(8), N(2)-C(13) 1.445(7), N(2)-C(2) 1.503(7), C(2)-C(25) 1.517(8), C(2)-C(3) 1.521(8), C(4)-C(9) 1.370(9), C(1)-N(1)-C(4) 127.0(5), C(1)-N(1)-C(3) 109.6(5), C(4)-N(1)-C(3) 122.1(5), C(1)-N(2)-C(2) 109.8(5), C(13)-N(2)-C(2) 125.1(5), N(1)-C(1)-N(2) 114.2(5), N(2)-C(2)-C(25) 114.6(4), N(2)-C(2)-C(3) 101.9(5), C(25)-C(2)-C(3) 117.0(5), N(1)-C(3)-C(2) 104.3(5), C(9)-C(4)-C(5) 123.2(6), C(9)-C(4)-N(1) 118.6(6), C(5)-C(4)-N(1) 118.2(5).
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