Electronic Supplementary Information for

A Facile Preparation of Backbone-substituted, Functionalized and Chiral Imidazolinium Salts

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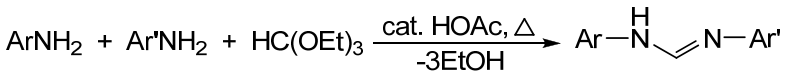
1. General Information:

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:

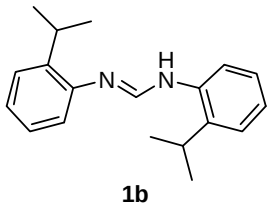
In general, formamidines were prepared following the method described by Grubbs et al[1].



Scheme S1. Synthesis of various formamidines

The formamidines **1a, 1c, 1d, 1e, 1g** were prepared as previously reported[2].

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



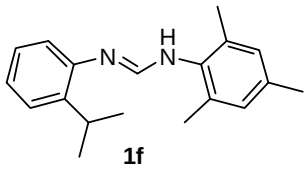
1b

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.) and glacial acetic acid (22.2 mg, 21 µL, 0.37 mmol, 0.05 eq.) were mixed and stirred at 140 °C for 3 h. The crude 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, $CDCl_3$): δ = 8.00 (s, 1H, NC*H*N), 7.28-7.09 (m, 8H, 8×Ar-*H*), 3.29 (sept, *J* = 6.8 Hz, 2H, 2×CH_3C*H*CH_3), 1.26 (d, *J* = 6.8 Hz, 12H, 4×CH_3CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 149.1, 142.8,

1. K. M. Kuhn, R. H. Grubbs, *Org. Lett.*, 2008, **10**, 2075.
2. K. Hirano, S. Urban, W. Congyang, F. Glorius, *Org. Lett.*, 2009**, 11**, 1019.

139.7, 126.5, 125.6, 123.9, 118.9, 27.5, 22.9. HRMS (ESI-MS): m/z [M + H^+] calcd for $C_{19}H_{25}N_2^+$: 281.2012; found: 281.2023.

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

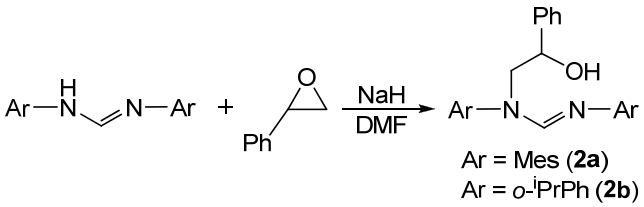


1f

The mixtuer 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%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (s, 1H, NC*H*N), 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, CH_3CHCH_3), 2.28 (s, 3H, $ArCH_3$), 2.26 (s, 6H, 2×$ArCH_3$), 1.24 (d, *J* = 6.8 Hz, 6H, 2×CH_3CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 144.2, 129.3, 129.0, 128.1, 126.9, 126.5, 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 $C_{19}H_{25}N_2^+$: 281.2018; found: 281.2019.

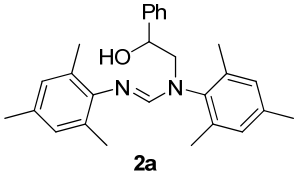
3. Synthesis of intermediate alcohols:

Method A:



Scheme S2. Synthesis of intermediate alcohols from formamidines

Alcohol 2a

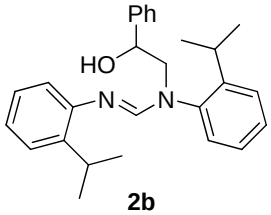


2a

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 H_2O 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 column chromatography on silica gel (PE-EtOAc = 12:1→10:1) to afford the product **2a** as a pale yellow oil (737 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (s, 1H, NC*H*N), 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, ArC*H*OH), 4.49 (dd, *J* = 9.2 Hz, 14.4 Hz, 1H, NCH_2CH), 3.35 (d, *J* = 14.4 Hz, 1H, NCH_2CH), 2.46 (s, 3H, ArCH_3), 2.29 (s, 3H, ArCH_3), 2.25 (s, 3H, ArCH_3), 2.22 (s, 6H, ArCH_3), 2.10 (s, 3H, ArCH_3), 2.02 (s, 3H, ArCH_3). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 156.3, 145.2, 143.1, 140.1, 137.7, 136.6, 135.7, 132.2, 129.6, 129.6, 129.5, 128.7, 128.2, 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$^+$] calcd for $C_{27}H_{33}N_2O^+$: 401.2593, found : 401.2587.

Alcohol 2b

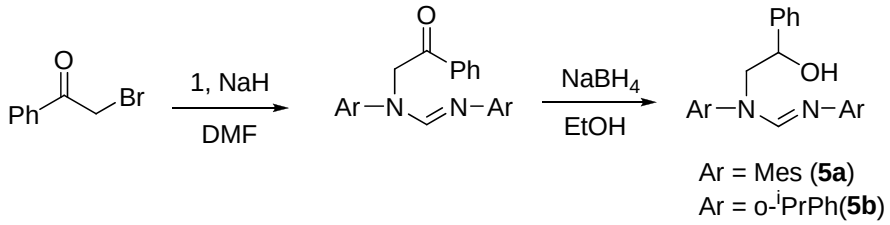


2b

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 H_2O 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 column chromatography on silica gel (PE-EtOAc = 12：1→10：1) to afford the product **2b** as a pale yellow oil (454 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (s, 1H, NC*H*N), 7.41-7.27 (m, 7H, 7×Ar-*H*), 7.16-7.10 (m, 3H, 3×Ar-*H*), 7.04-7.01 (m, 1H, ArC*H*OH), 6.81-6.68 (m, 3H, 3×Ar-*H*), 5.14 (d, *J* = 9.6 Hz, 1H, NCH_2CH), 3.95 (brs, 2H, NCH_2CH, O*H*), 3.56 (sept, *J* = 6.8 Hz, 1H, CH_3CHCH_3), 2.91 (sept, *J* = 6.8 Hz, 1H, CH_3CHCH_3), 1.33 (d, *J* = 6.8 Hz, 3H, CH_3CH), 1.31 (d, *J* = 6.8 Hz, 3H, CH_3CH), 1.27 (d, *J* = 6.8 Hz, 6H, 2×CH_3CH). ^{13}C NMR (400 MHz, $CDCl_3$): 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$^+$] calcd for $C_{27}H_{33}N_2O^+$: 401.2593, found :

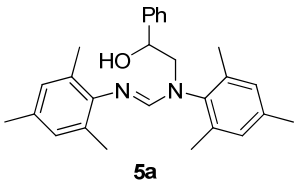
401.2587.

Method B:



Scheme S3. Synthesis of intermediate alcohols from 2-bromoacetophenone

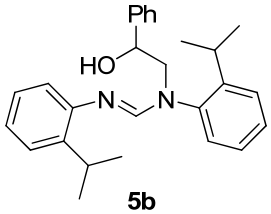
Alcohol 5a



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 H_2O 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→8:1) to afford the crude product which was then dissolved in 40 mL of EtOH. The solution was cooled to 0 °C and $NaBH_4$ (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%). ^{1}H NMR shows that it is same as **3a**.

Alcohol 5b

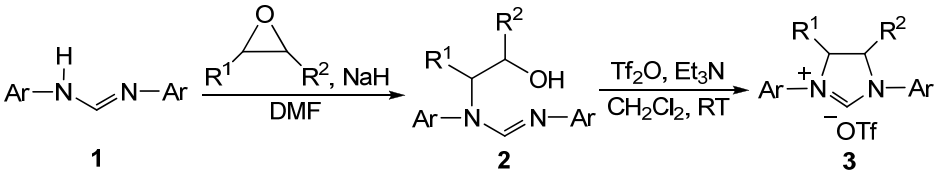


5b

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 H_2O 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 40 mL of EtOH. The solution was cooled to 0 °C and $NaBH_4$ (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%). ^{1}H NMR shows that it is same as **3b**.

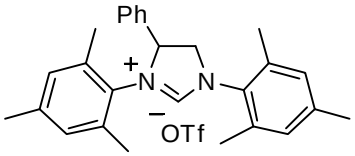
4. General procedure for the synthesis of backbone-substituted imidazolinlium salts:



Scheme S4. Synthesis of backbone-substituted imidazolinlium 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^{o}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, H_2O was added and the mixture was extracted with EtOAc (30 mL x 3), The combined organic layers was dried over anhydrous $MgSO_4$. 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 CH_2Cl_2. The mixture was cooled to 0 °C, and Et_3N (1.1 eq.) was added dropwise. After 5 mins, Tf_2O (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**.

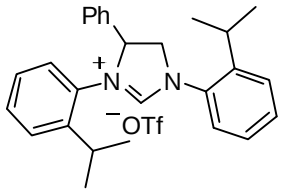
Imidazolinlium trifluoromethanesulfonate 3a



3a

2a (737 mg) was dissolved in 10 mL of dry CH_2Cl_2, the mixture was cooled to 0 °C and Et_3N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) was added dropwise. After 5 mins Tf_2O (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 (CH_2Cl_2/EtOH = 40:1→20:1) to give **3a** as a white powder (884 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (s, 1H, NC*H*N), 7.43-7.32 (m, 5H, 5×Ar-*H*), 7.05 (s, 2H, 2×Ar-*H*), 6.97 (s, H, Ar-*H*), 6.71 (s, H, Ar-*H*), 5.98 (dd, *J* = 9.2 Hz, 12.8 Hz, 1H, ArC*H*CH_2), 4.99 (t, *J* = 12.8 Hz, 1H, NCH_2CH), 4.58 (dd, *J* = 9.2 Hz, 12.8 Hz, 1H, NCH_2CH), 2.55-2.49 (brs, 9H, 3×ArCH_3) 2.34 (s, 3H, ArCH_3), 2.24 (s, 3H, ArCH_3), 1.73 (s, 3H, ArCH_3). ^{13}C NMR (400 MHz, $CDCl_3$): 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 $C_{27}H_{31}N_2^+$: 383.2487; found: 383.2487.

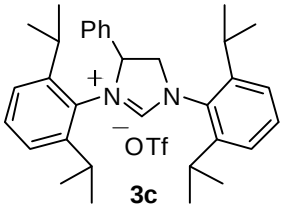
Imidazolinlium trifluoromethanesulfonate 3b



3b

2b (454 mg) was dissolved in 10 mL of dry CH_2Cl_2, the mixture was cooled to 0 °C and Et_3N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) was added dropwise. After 5 mins Tf_2O (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 (CH_2Cl_2/EtOH = 40:1→20:1) to give **3b** as a white powder (543 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93-7.91 (m, 1H, Ar-*H*), 7.85 (s, 1H, NC*H*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, ArC*H*CH_2), 5.33 (t, *J* = 12.0 Hz, 1H, NCH_2CH), 4.45 (dd, *J* = 8.8 Hz, 12.0 Hz, 1H, NCH_2CH), 3.24 (sept, *J* = 6.8 Hz, 1H, CH_3C*H*CH_3), 2.87 (sept, 1H, *J* = 6.8 Hz, CH_3C*H*CH_3), 1.42 (d, *J* = 6.8 Hz, 6H, 2×CH_3CH), 1.40 (d, *J* = 6.8 Hz, 6H, 2×CH_3CH), 1.22 (d, *J* = 6.8 Hz, 3H, CH_3CH), 0.85 (d, *J* = 6.8 Hz, 3H, CH_3CH). ^{13}C NMR (400 MHz, $CDCl_3$): 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 $C_{27}H_{31}N_2^+$: 383.2482; found: 383.2487.

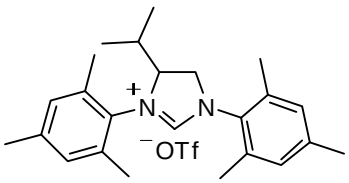
Imidazolinlium trifluoromethanesulfonate 3c



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 H_2O was added and the mixture was extracted 3 times with 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_2Cl_2. The mixture was cooled to 0 °C and Et_3N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) was added dropwise. After 5 mins Tf_2O (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 (CH_2Cl_2/EtOH = 40:1→20:1) to give **3c** as a white powder (968 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (s, 1H, NC*H*N), 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, ArC*H*CH_2), 5.31 (t, *J* = 12.8 Hz, 1H, NC*H*$_2$CH), 4.63 (dd, *J* = 10.4 Hz, 12.8 Hz, 1H, NC*H*$_2$CH), 3.30 (sept, *J* = 6.8 Hz, 2H, 2×CH_3C*H*CH_3), 3.16 (sept, *J* = 6.8 Hz, 1H, CH_3C*H*CH_3), 2.50 (sept, *J* = 6.8 Hz, 1H, CH_3C*H*CH_3), 1.54 (d, *J* = 6.8 Hz, 3H, C*H*$_3$CH), 1.46 (d, *J* = 6.8 Hz, 3H, C*H*$_3$CH), 1.39 (d, *J* = 6.8 Hz, 3H, C*H*$_3$CH), 1.31 (d, *J* = 6.8 Hz, 3H, C*H*$_3$CH), 1.29 (d, *J* = 6.8 Hz, 3H, C*H*$_3$CH), 1.21 (d, *J* = 6.8 Hz, 3H, C*H*$_3$CH), 1.04 (d, *J* = 6.8 Hz, 3H, C*H*$_3$CH), 0.39 (d, *J* = 6.8 Hz, 3H, C*H*$_3$CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 157.8, 146.9, 146.7, 146.7, 145.4, 132.1, 131.6, 131.3, 130.4, 129.5, 129.3, 128.8, 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, 22.2. HRMS (ESI-MS): m/z [M – OTf^-] calcd for $C_{33}H_{43}N_2^+$: 467.3421; found: 467.3428.

Imidazolinlium trifluoromethanesulfonate 3d

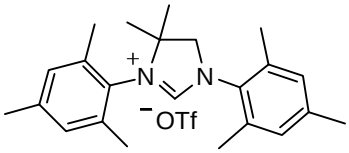


3d

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 °C. 5 mins latter, the mixture was heated to 70 °C. After stirring for 10 h, 50 mL of H_2O 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→8：1) to afford the crude product which was then dissolved in 10 mL of dry CH_2Cl_2. The mixture was cooled to 0 °C and Et_3N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) was added dropwise. After 5 mins Tf_2O (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 (CH_2Cl_2/EtOH = 40:1→20:1) to give **3d** as a white powder (808 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (s, 1H, NC*H*N), 6.97 (s, 4H, 4×Ar-*H*), 4.86 (dt, *J* = 5.6 Hz, 11.2 Hz, 1H, CHC*H*CH_2), 4.50 (t, *J* = 12.0 Hz, 1 H, NCH_2CH), 4.05 (t, *J* = 11.2Hz, 1H, NCH_2CH), 2.39 (s, 3H, ArCH_3), 2.38 (s, 3H, ArCH_3), 2.35 (s, 6H, 2×ArCH_3), 2.30 (s, 6H, 2×ArCH_3), 2.09 (sept, *J* = 6.8Hz, 1H, CH_3C*H*CH_3), 1.07 (d, *J* = 6.8 Hz, 3H, CH_3CH), 0.84 (d, *J* = 6.8 Hz, 3H, CH_3CH). ^{13}C NMR (400 MHz, $CDCl_3$): 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 $C_{24}H_{33}N_2^+$: 349.2644; found: 349.2639.

Imidazolinlium trifluoromethanesulfonate 3e

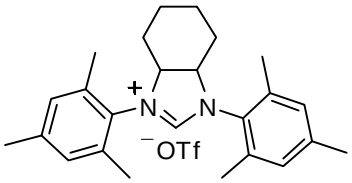


3e

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 H_2O 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 disolved in 10 mL of dry

CH_2Cl_2 and Et_3N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) were added. The mixture was cooled to 0°C before Tf_2O (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 5h. The volatiles were removed under vacuum, and the residue was purified by column chromatography (CH_2Cl_2/EtOH = 40:1→20:1) to give the product **3e** as a white powder (600 mg, 62.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (s, 1H, NC*H*N), 7.0 (s, 2H, 2×Ar-*H*), 6.96 (s, 2H, 2×Ar-*H*), 4.17 (s, 2H, CH_2), 2.34 (s, 12H, 4×ArCH_3), 2.30 (s, 3H, ArCH_3), 2.29 (s, 3H, ArCH_3), 1.62 (s, 6H, CH_3C). ^{13}C NMR (400 MHz, $CDCl_3$): 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 $C_{23}H_{31}N_2^+$: 335.2487; found: 335.2479.

Imidazolinlium trifluoromethanesulfonate 3f

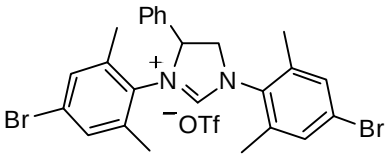


3f

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 H_2O 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 disolved in 10 mL of dry CH_2Cl_2 and Et_3N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) were added. The mixture was cooled to 0°C before Tf_2O (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 (CH_2Cl_2/EtOH = 40:1→20:1) to give the product **3f** as a white powder (694 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (s, 1H, NC*H*N), 6.98 (s, 4H, 4×Ar-*H*), 4.88 (t, *J* = 4.0 Hz, 2H, 2×C*H*), 2.39 (s, 6H, 2×ArCH_3), 2.37 (s, 6H, 2×ArCH_3), 2.30 (s, 6H, 2×ArCH_3), 1.90-1.89 (m, 2H, CH_2), 1.80-1.78 (m, 2H, CH_2), 1.64-1.62 (m, 2H, CH_2), 1.51-1.48 (m, 2H, CH_2). ^{13}C NMR (400 MHz, $CDCl_3$): 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.

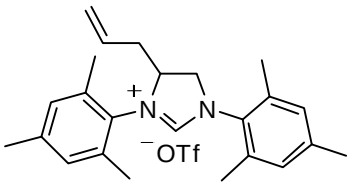
Imidazolinlium trifluoromethanesulfonate 3g



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 (240mg, 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_2O 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_2Cl_2, the mixture was cooled to 0 °C and Et_3N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) was added dropwise. After 5 mins Tf_2O (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_2Cl_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, NC*H*N), 7.45-7.27 (m, 8H, Ar-*H*), 7.04 (s, 1H, Ar-*H*), 5.95 (dd, *J* = 9.2, 12.4 Hz, 1H, ArC*H*CH_2), 4.93 (t, *J* = 12.4 Hz, 1 H, NCH_2CH), 4.51 (dd, *J* = 9.2 Hz, *J* = 12.4 Hz, 1H, NCH_2CH), 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 $C_{25}H_{25}N_2Br_2^+$: 511.0384; found: 511.0388.

Imidazolinlium trifluoromethanesulfonate 3h

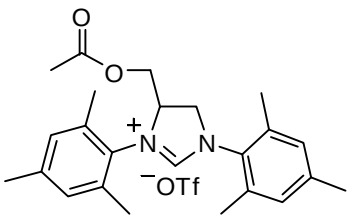


3h

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 H_2O 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 disolved in 10 mL of dry CH_2Cl_2 and Et_3N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) were added. The mixture was cooled to 0°C before Tf_2O (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_2Cl_2/EtOH = 40:1→20:1) to give the product **3h** as a white powder (606 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (s, 1H, NC*H*N), 6.98 (s, 2H, 2×Ar-*H*), 6.96 (s, 2H, 2×Ar-*H*), 5.64-5.57 (m, 1H, CH_2=C*H*), 5.19-5.15 (m, 2H, C*H*$_2$=CH), 4.96-4.93 (m, 1H, CH_2CHCH_2), 4.57 (t, *J* = 12.0 Hz, 1H, NC*H*$_2$CH), 3.98 (dd, *J* = 8.8 Hz, 12.0 Hz, 1H, NC*H*$_2$CH), 2.61-2.49 (m, 2H, CHC*H*$_2$CH), 2.38 (s, 3H, ArC*H*$_3$), 2.34 (s, 9H, 3×ArC*H*$_3$), 2.30 (s, 6H, 2×ArC*H*$_3$). ^{13}C NMR (400 MHz, $CDCl_3$): 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 $C_{24}H_{31}N_2^+$: 347.2566, found: 347.2560.

Imidazolinlium trifluoromethanesulfonate 3i

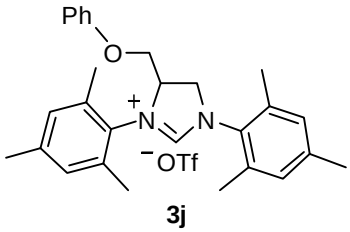


3i

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 H_2O 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 disolved in 10 mL of dry CH_2Cl_2 and Et_3N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) were added. The mixture was cooled to 0°C before Tf_2O (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_2Cl_2/EtOH = 40:1→20:1) to give the product **3i** as a white powder (793 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (s, 1H, NC*H*N), 6.96 (s, 4H, 4×Ar-*H*), 5.31-5.26 (m, 1H, CH_2CHCH_2), 4.75 (t, *J* =12.8 Hz, 1H, NCH_2CH), 4.32 (dd, *J* = 3.2 Hz, 9.2 Hz, 1H, OCH_2CH), 4.22 (dd, *J* = 8.0 Hz, 12.8 Hz, 1H, NCH_2CH), 4.07 (dd, *J* = 2.0 Hz, 13.2 Hz, 1H, OCH_2CH), 2.37 (s, 6H, 2×ArCH_3), 2.29 (s, 12H, 12×ArCH_3), 2.07 (s, 3H, CH_3CO). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 169.7, 159.8, 140.9, 140.6, 140.5, 135.4, 135.2, 130.5, 130.4, 130.3, 130.2, 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 $C_{24}H_{31}N_2O_2^+$: 379.2446, found: 379.2439.

Imidazolinlium trifluoromethanesulfonate 3j



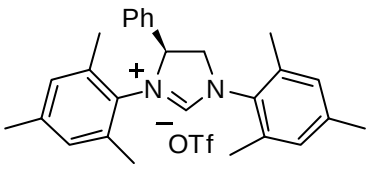
3j

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_2O 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 disolved in 10 mL of dry CH_2Cl_2 and Et_3N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) were added. The mixture was cooled to 0°C before Tf_2O (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_2Cl_2/EtOH = 40:1→20:1) to give the product **3j** as a white powder (821 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (s, 1H, NC*H*N), 7.33-6.85 (m, 9H, 9×Ar-*H*), 5.56-5.53 (m, 1H, CH_2CHCH_2), 4.91 (t, *J* = 12.4, 1H, NCH_2CH), 4.50 (dd, *J* = 8.0 Hz, 12.4 Hz, 1H, NCH_2CH), 4.29 (dd, *J* = 2.0 Hz, 11.2 Hz, 1H, OCH_2CH), 3.96 (d, *J* = 11.2 Hz, 1H, OCH_2CH), 2.52 (s, 3H,

ArCH_3), 2.46 (s, 3H, ArCH_3), 2.38 (s, 3H, ArCH_3), 2.33 (s, 3H, ArCH_3), 2.28 (s, 3H, ArCH_3), 2.26 (s, 3H, ArCH_3). ^{13}C NMR (400 MHz, $CDCl_3$): 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 $C_{28}H_{33}N_2O^+$: 413.2593, found: 413.2588.

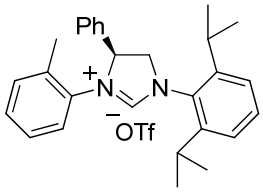
5. Synthesis of chiral imidazolium salts:

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



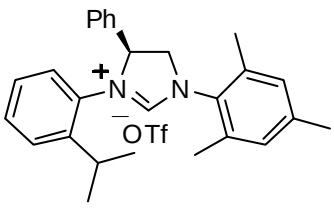
According to the general procedure, NaH (60% suspension in mineral oil, 120 mg, 3.0 mmol, 1.5 eq.) was added portion by portion to the solution of **1a** (673 mg, 2.4 mmol, 1.2 eq.) in DMF (15 mL) at 0 °C. After 5 mins, the mixture was warmed to room temperature and stirred for 30 mins. *R*-(+)-styrene 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 H_2O 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→8：1) to afford the crude product which was then dissolved in 10 mL of dry CH_2Cl_2. The mixture was cooled to 0 °C and Et_3N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) was added dropwise. After 5 mins Tf_2O (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 (CH_2Cl_2/EtOH = 40:1→20:1) to give (*S*)**-4a-OTf** as a white powder (884 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (s, 1H, NC*H*N), 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, ArC*H*CH_2), 4.99 (t, *J* = 12.8 Hz, 1H, NCH_2CH), 4.58 (dd, *J* = 9.2 Hz, 12.8 Hz, 1H, NCH_2CH), 2.55-2.49 (brs, 9H, 3×ArCH_3), 2.34 (s, 3H, ArCH_3), 2.24 (s, 3H, ArCH_3), 1.73 (s, 3H, ArCH_3). ^{13}C NMR (400 MHz, $CDCl_3$): 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 $C_{27}H_{31}N_2^+$: 383.2487; found: 383.2487. $[\alpha]^{20}_D$ –85.4 (*c* = 0.645, $CHCl_3$).

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 H_2O 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 disolved in 10 mL of dry CH_2Cl_2 and Et_3N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) were added. The mixture was cooled to 0°C before Tf_2O (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 (CH_2Cl_2/EtOH = 40:1→20:1) to give the product (*S*)**-4b-OTf** as a white powder (490 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 1H, NC*H*N), 7.52-7.18 (m, 12H, 12×Ar-*H*), 6.48 (dd, *J* = 9.2 Hz, 12.4 Hz, 1H, ArC*H*CH_2), 5.09 (t, *J* = 12.4 Hz, 1H, NCH_2CH), 4.23 (dd, *J* = 9.2 Hz, 12.4 Hz, 1H, NCH_2CH), 3.33 (sept, *J* = 6.8 Hz, 1H, CH_3C*H*CH_3), 3.15 (sept, *J* = 6.8 Hz, 1H, CH_3C*H*CH_3), 2.36 (s, 3H, ArCH_3), 1.43 (d, *J* = 6.8 Hz, 3H, CH_3CH), 1.38 (d, *J* = 6.8 Hz, 6H, 2×CH_3CH), 1.27 (d, *J* = 6.8 Hz, 3H, CH_3CH). ^{13}C NMR (400 MHz, $CDCl_3$): 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 $C_{28}H_{33}N_2^+$: 397.2644, found: 397.2638. $[\alpha]^{20}_D$ –108.6 (*c* = 0.575, $CHCl_3$).

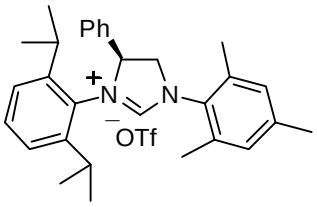
Imidazolinium trifluoromethanesulfonate (*S*)**-4c-OTf**



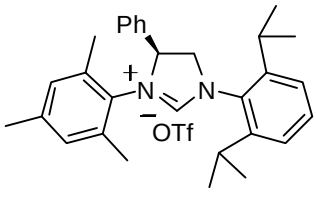
Following the general procedure, **1f** (673 mg, 2.4 mmol, 1.2 eq.) was dissolved in 15 mL of DMF. The mixture was cooled to 0 °C and NaH (60% suspension in mineral oil, 120 mg, 3.0 mmol, 1.5 eq.) was added portion by portion. After 5 mins, the mixture was warmed to room temperature and stirred for 30 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 H_2O 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_2Cl_2, the mixture was cooled to 0 °C and Et_3N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) was added dropwise. After 5 mins Tf_2O (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_2Cl_2-EtOH = 40:1→20:1) to give (*S*)-**4c-OTf** as a white powder (458 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 1H, NC*H*N), 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, ArC*H*CH_2), 5.05 (t, *J* = 12.4 Hz, 1H, NCH_2CH), 4.33 (dd, *J* = 9.2 Hz, 12.4 Hz, 1H, NCH_2CH), 2.99 (sept, *J* = 6.8 Hz, 1H, CH_3C*H*CH_3), 2.50 (s, 6H, 2×ArCH_3), 2.33 (s, 3H, ArCH_3), 1.29 (d, *J* = 6.8 Hz, 3H, CH_3CH), 0.85 (d, *J* = 6.8 Hz, 3H, CH_3CH). ^{13}C NMR (400 MHz, $CDCl_3$): 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, 24.3, 24.0, 21.0, 17.8. HRMS (ESI-MS): m/z [M – OTf^-] calcd for $C_{27}H_{31}N_2^+$: 383.2487; found: 383.2487. $[\alpha]^{20}_D$ –113.1 (*c* = 0.500, $CHCl_3$).

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



(*S*)-**4d-OTf**

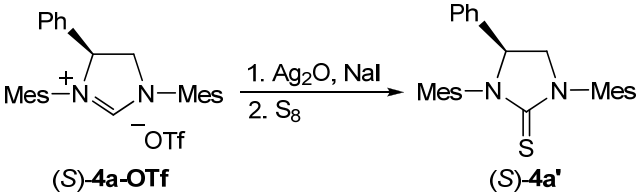


(*S*)-**4e-OTf**

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 H_2O 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

dissolved in 10 mL of dry CH_2Cl_2, the mixture was cooled to 0 °C and Et_3N (223 mg, 0.31 mL, 2.2 mmol, 1.1 eq.) was added dropwise. After 5 mins Tf_2O (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_2Cl_2-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** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (s, 1H, NC*H*N), 7.40-7.28 (m, 7H, 7×Ar-*H*), 7.05 (s, 2H, 2×Ar-*H*), 7.00-6.98 (m, 1H, Ar-*H*), 5.97-5.91 (m, 1H, ArC*H*CH_2), 5.19-5.12 (m, 1H, NCH_2CH), 4.65-4.58 (m, 1H, NCH_2CH), 3.25 (sept, 1H, *J* = 6.8 Hz, CH_3CHCH_3), 2.50 (s, 6H, 2×ArCH_3), 2.47(sept, *J* = 6.8 Hz, 1H, CH_3CHCH_3), 2.34 (s, 3H, ArCH_3), 1.56-1.54 (m, 3H, CH_3CH), 1.32-1.29 (m, 3H, CH_3CH), 1.05-1.03 (m, 3H, CH_3CH), 0.35 (d, *J* = 6.8 Hz, 3H, CH_3CH). ^{13}C NMR (400 MHz, $CDCl_3$): 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 $C_{30}H_{37}N_2^+$: 425.2957; found: 425.2954. $[\alpha]^{20}_D$ –2.7 (*c* = 0.485, $CHCl_3$). (*S*)-**4e-OTf** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (s, 1H, NC*H*N), 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, ArC*H*CH_2), 5.13 (t, *J* = 12.8 Hz, 1H, NCH_2CH), 4.57 (dd, *J* = 9.6 Hz, 12.8Hz, 1H, NCH_2CH), 3.20 (sept, *J* = 6.8 Hz, 2H, 2×CH_3CHCH_3), 2.57 (s, 3H, ArCH_3), 2.24 (s, 3H, ArCH_3), 1.72 (s, 3H, ArCH_3), 1.50 (d, *J* = 6.8 Hz, 3H, CH_3CH), 1.43 (d, *J* = 6.8 Hz, 3H, CH_3CH), 1.39 (d, *J* = 6.8 Hz, 3H, CH_3CH), 1.29 (d, *J* = 6.8 Hz, 3H, CH_3CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 158.0, 146.9, 145.6, 140.3, 135.4, 135.1, 132.9, 131.4, 130.3, 130.2, 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 $C_{30}H_{37}N_2^+$: 425.2957; found: 425.2954. $[\alpha]^{20}_D$ –55.8 (*c* = 0.585, $CHCl_3$).

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



(*S*)-**4a-OTf** (*S*)-**4a'**

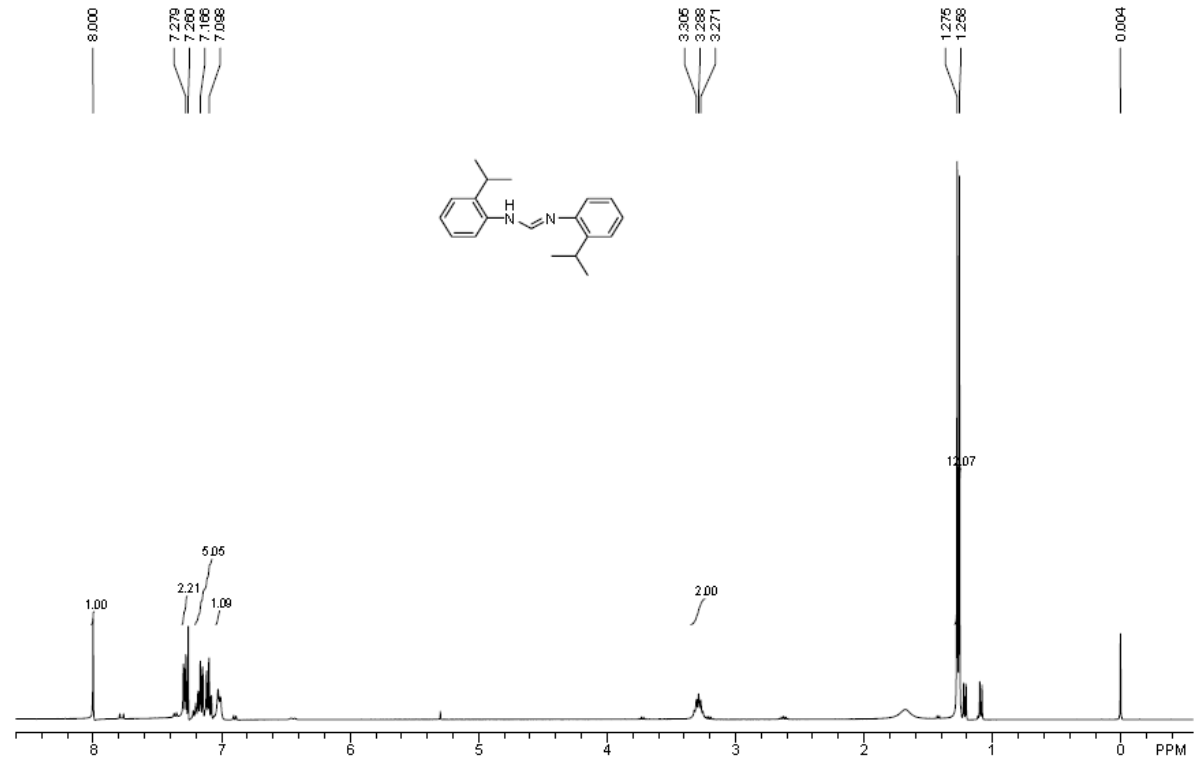
Scheme S5. Synthesis of imidazolidin-2-thione (*S*)-**4a'**

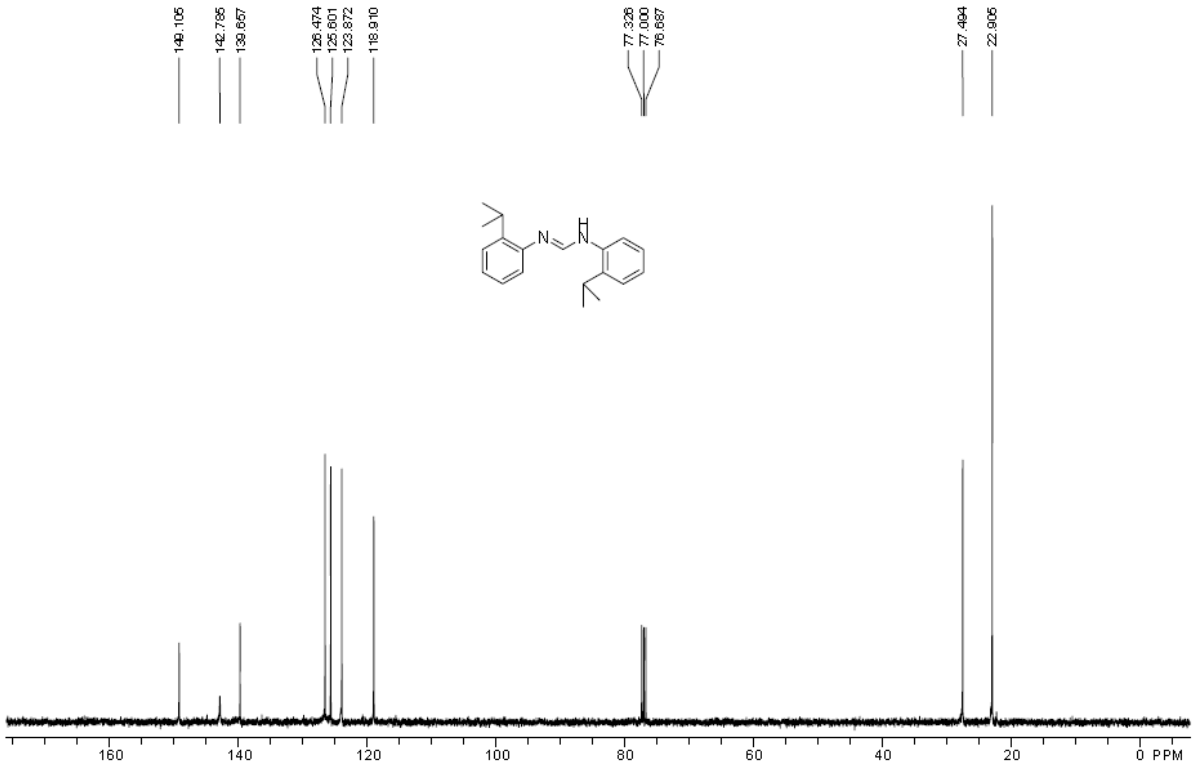
A suspension of (*S*)-**4a-OTf** (54.7 mg, 0.1 mmol), NaI (60mg, 0.4 mmol) and Ag_2O (23.2 mg, 0.1

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, $CDCl_3$): δ = 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, ArC*H*CH_2), 4.33 (d, *J* = 10.8 Hz, 1H, NCH_2CH), 4.25 (dd, *J* = 9.2 Hz, 10.8 Hz, 1H, NCH_2CH), 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, $CDCl_3$): δ =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, 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 $C_{27}H_{31}N_2S^+$: 415.2163, found : 415.2058. $[\alpha]^{20}_D$ +27.0 (*c* = 0.140, $CHCl_3$).

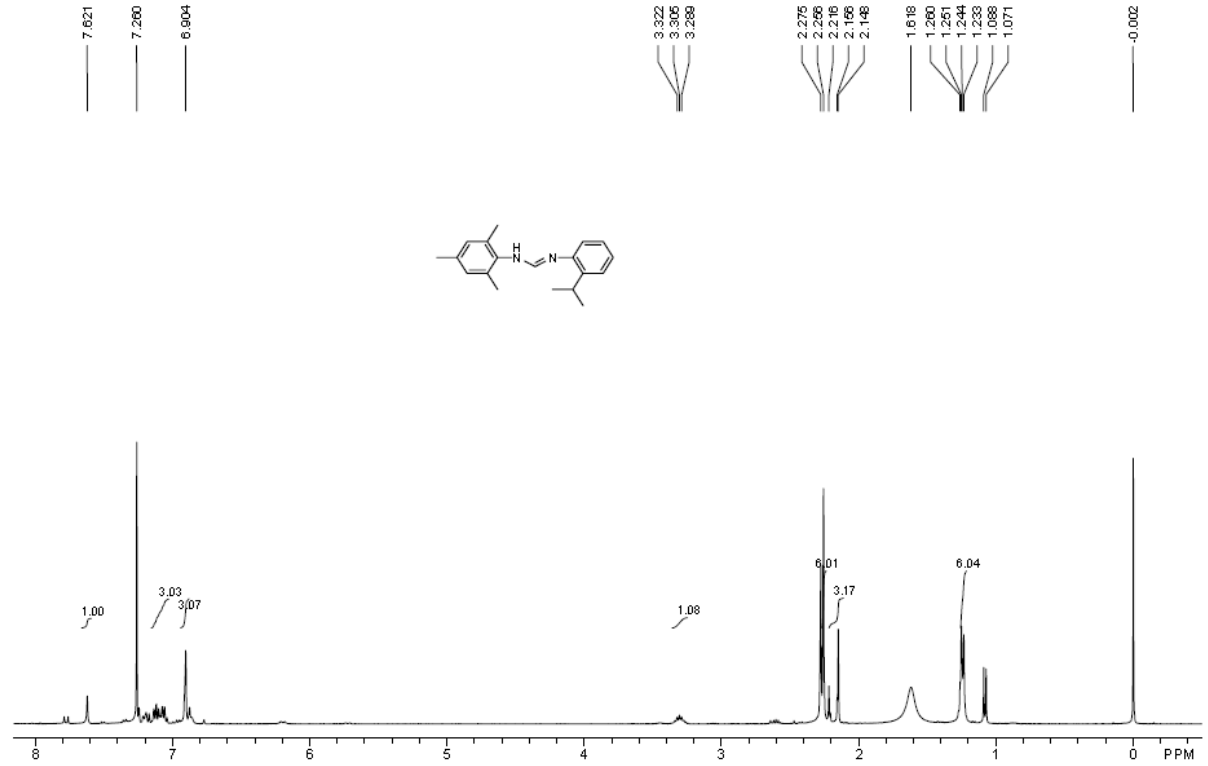
7. NMR Spectra:

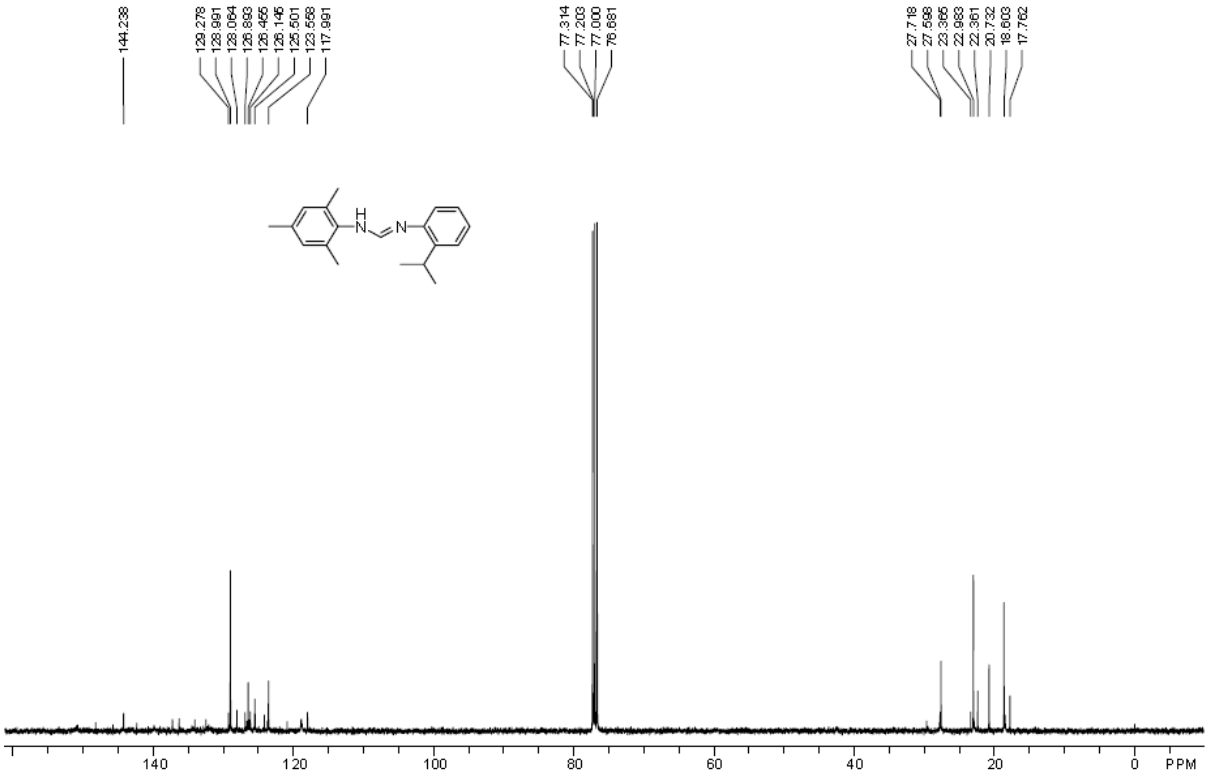
N,*N*'-Bis(2-isopropylphenyl)formamidine (1b)



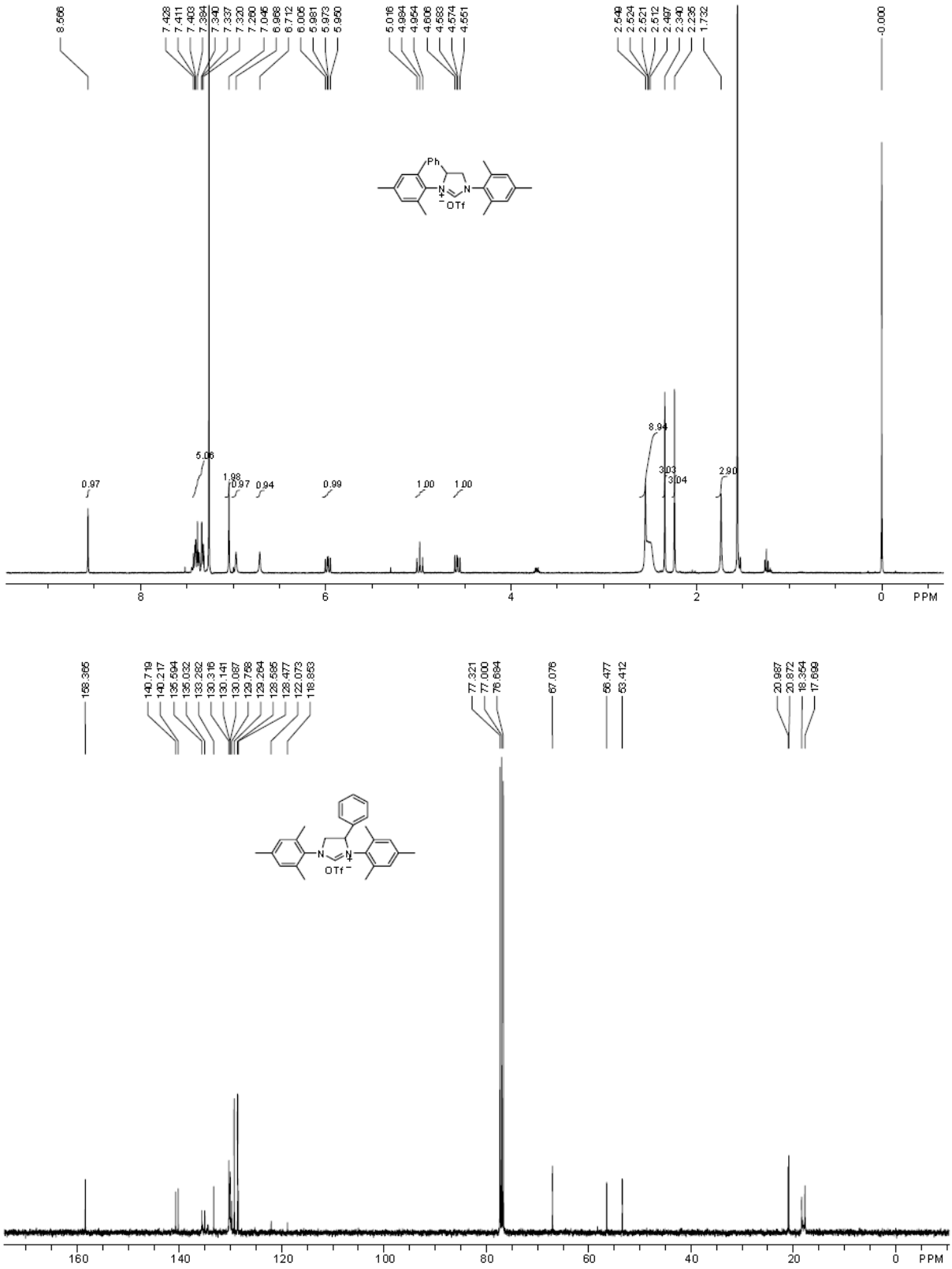


_N_-(2-isopropylphenyl)-_N'_-(2,4,6-trimethylphenyl)formamidine (1f)

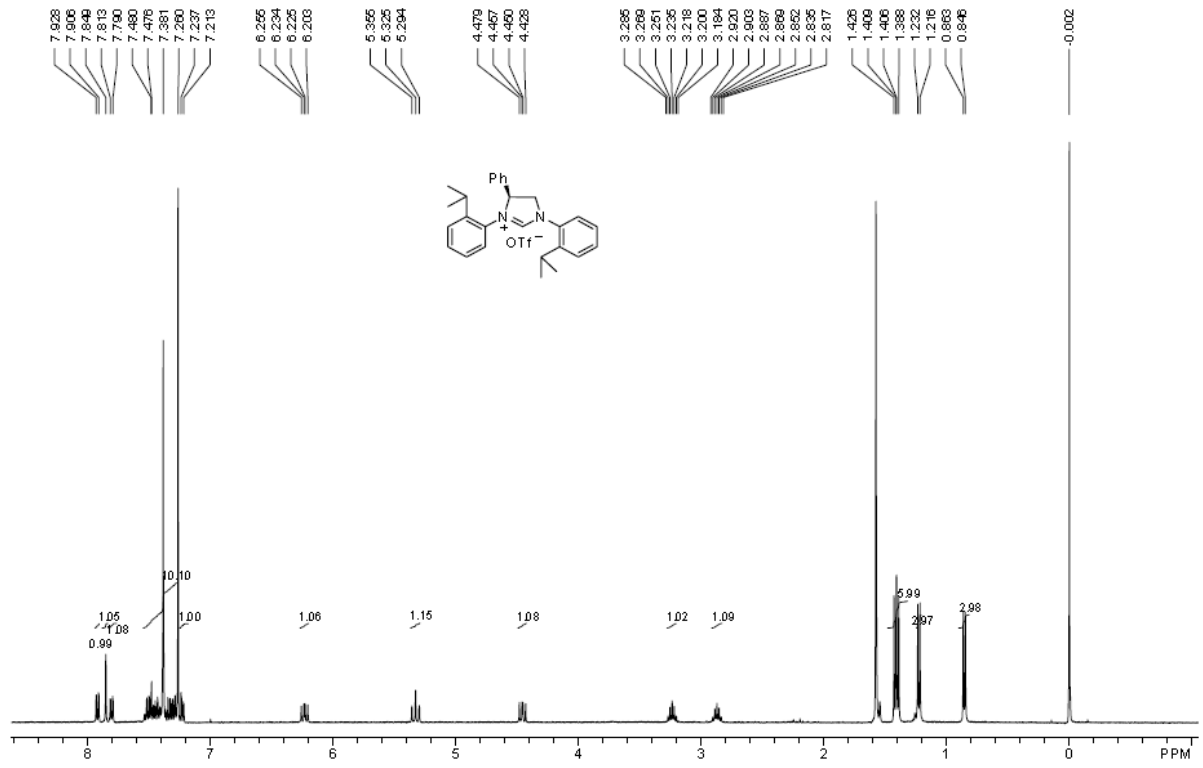


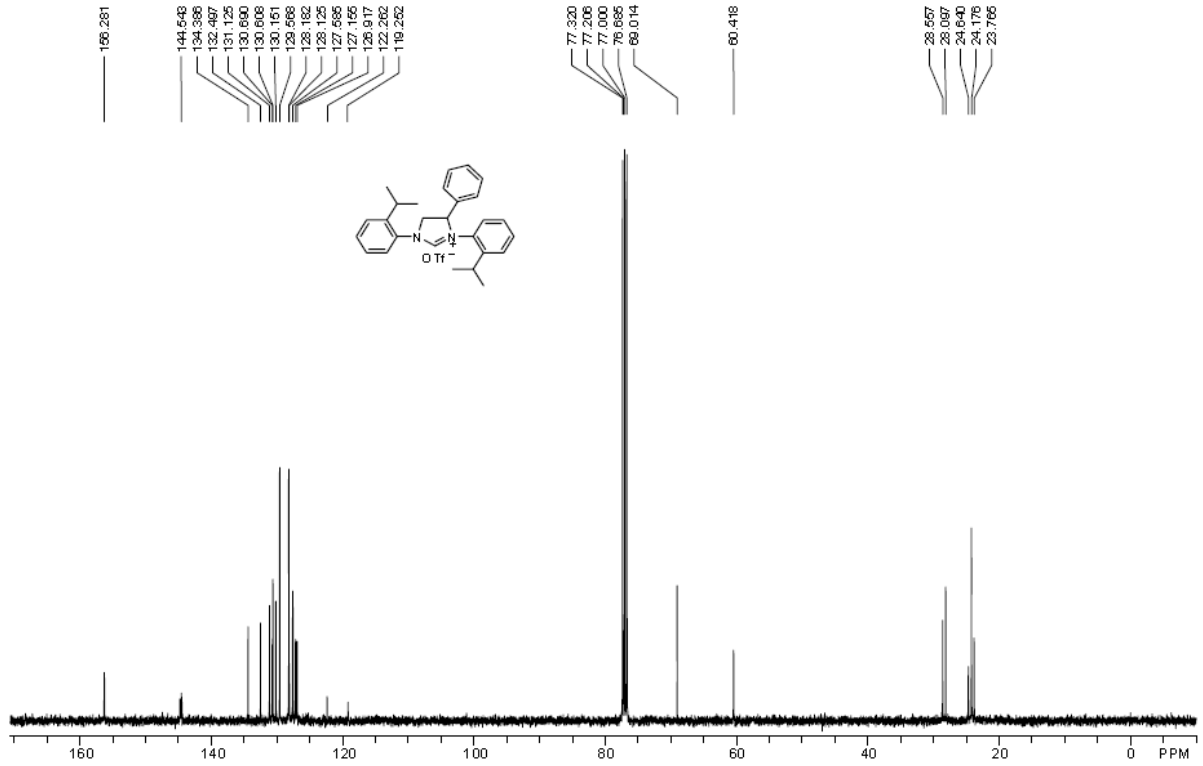


Imidazolinlium trifluoromethanesulfonate 3a

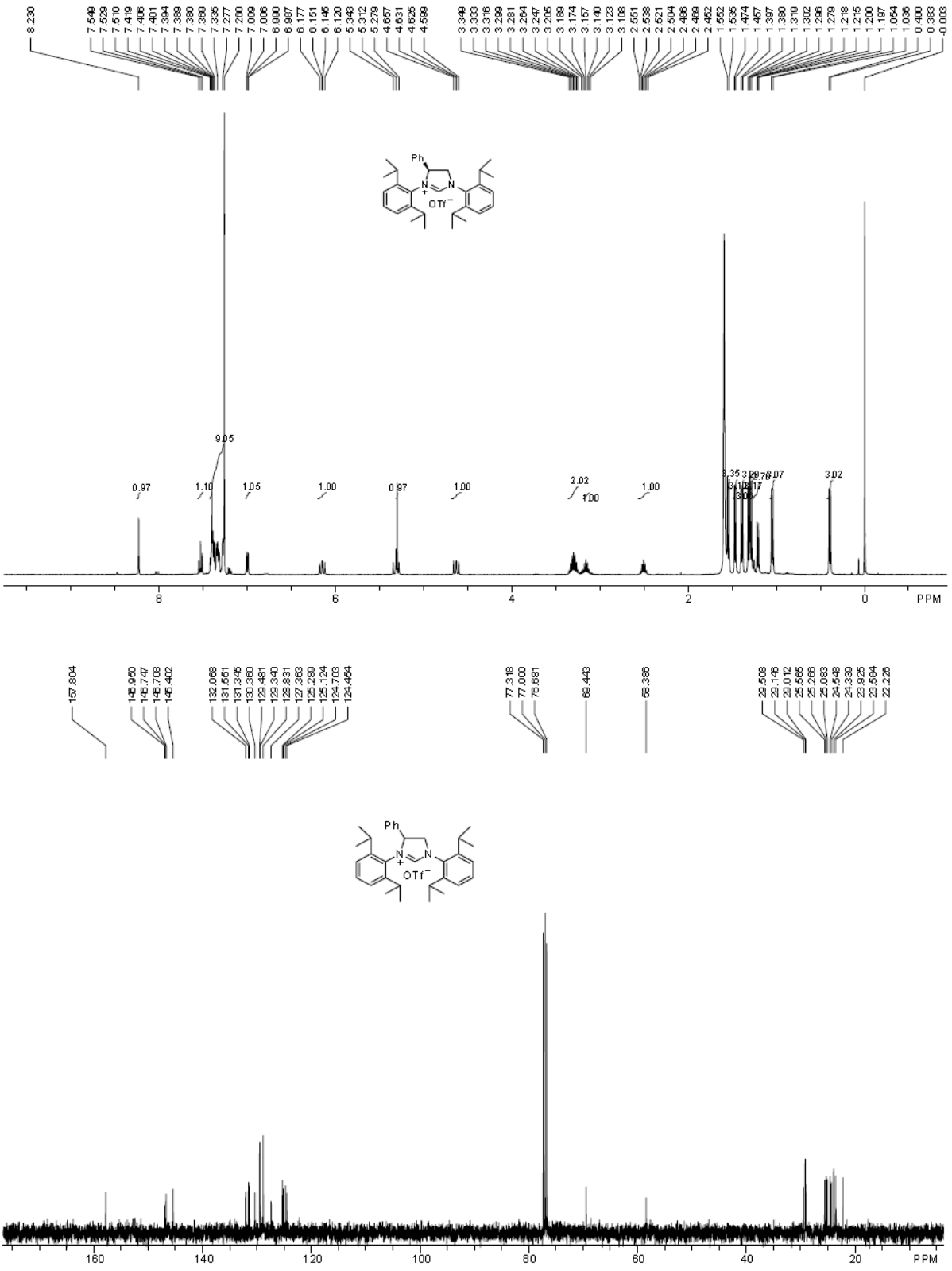


Imidazolinlium trifluoromethanesulfonate 3b

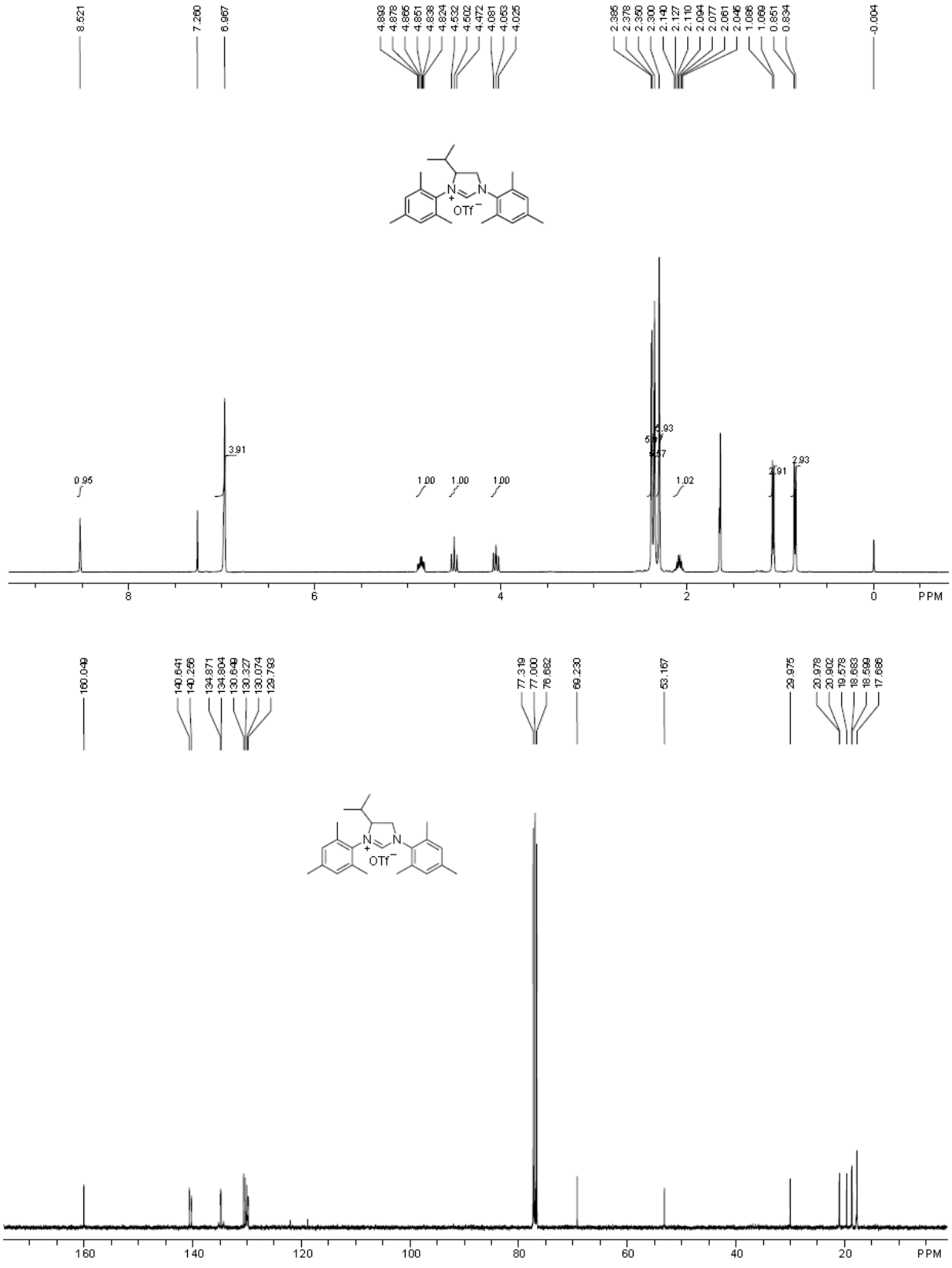




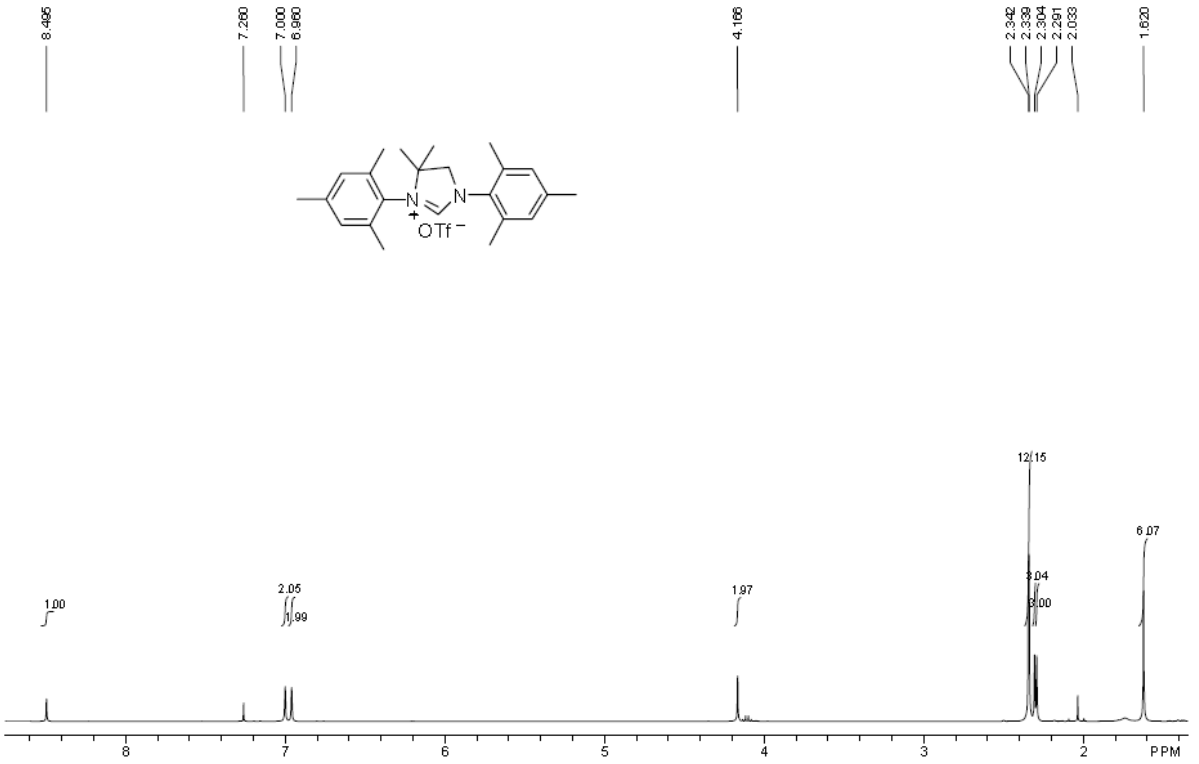
Imidazolinlium trifluoromethanesulfonate 3c

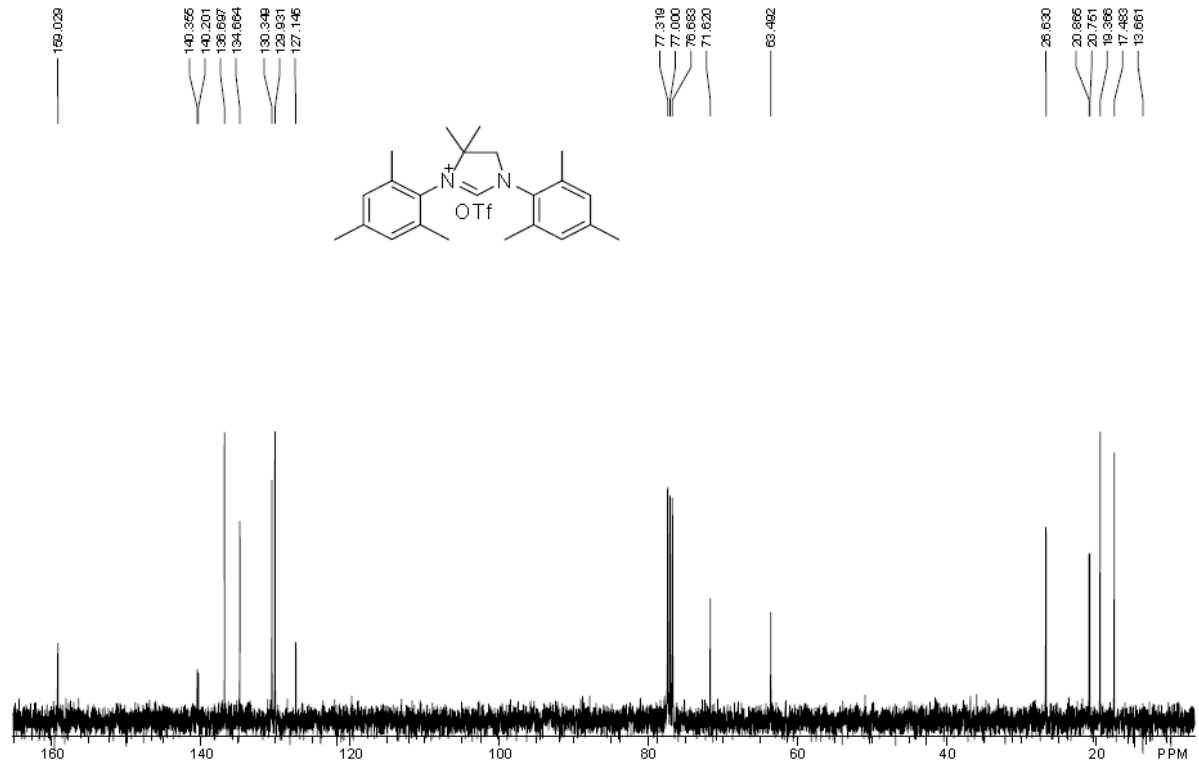


Imidazolinlium trifluoromethanesulfonate 3d

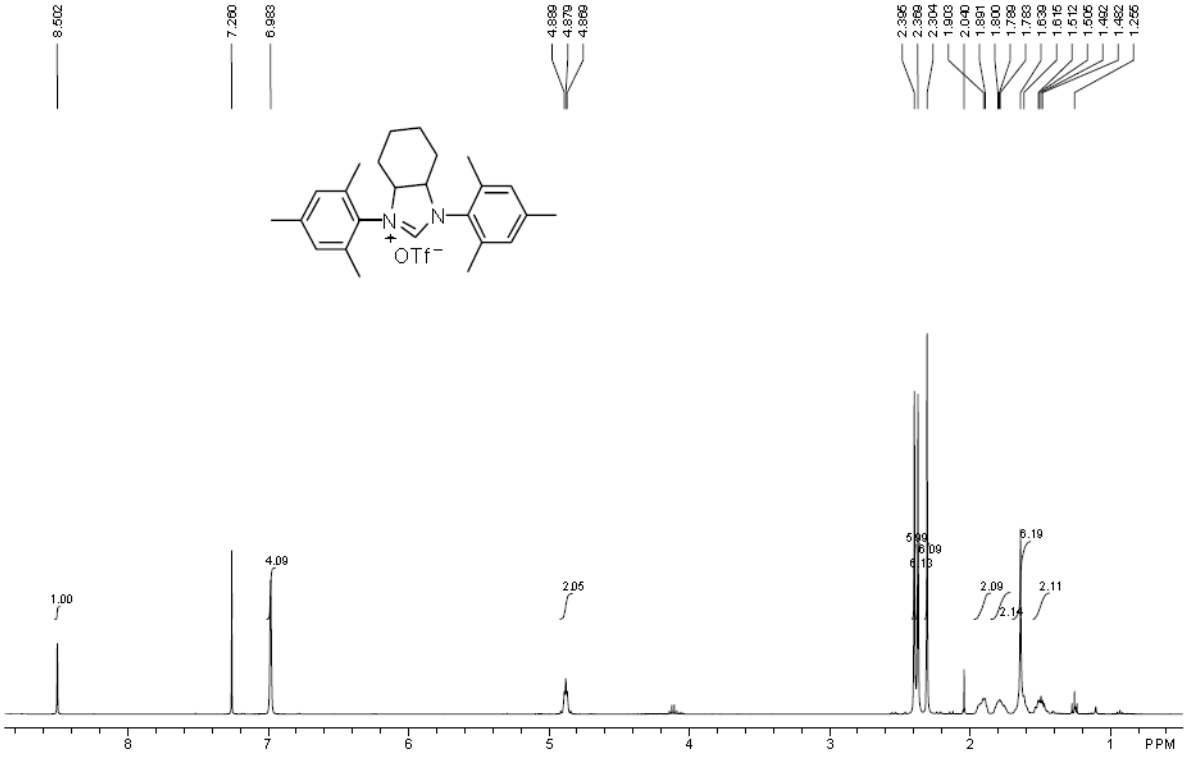


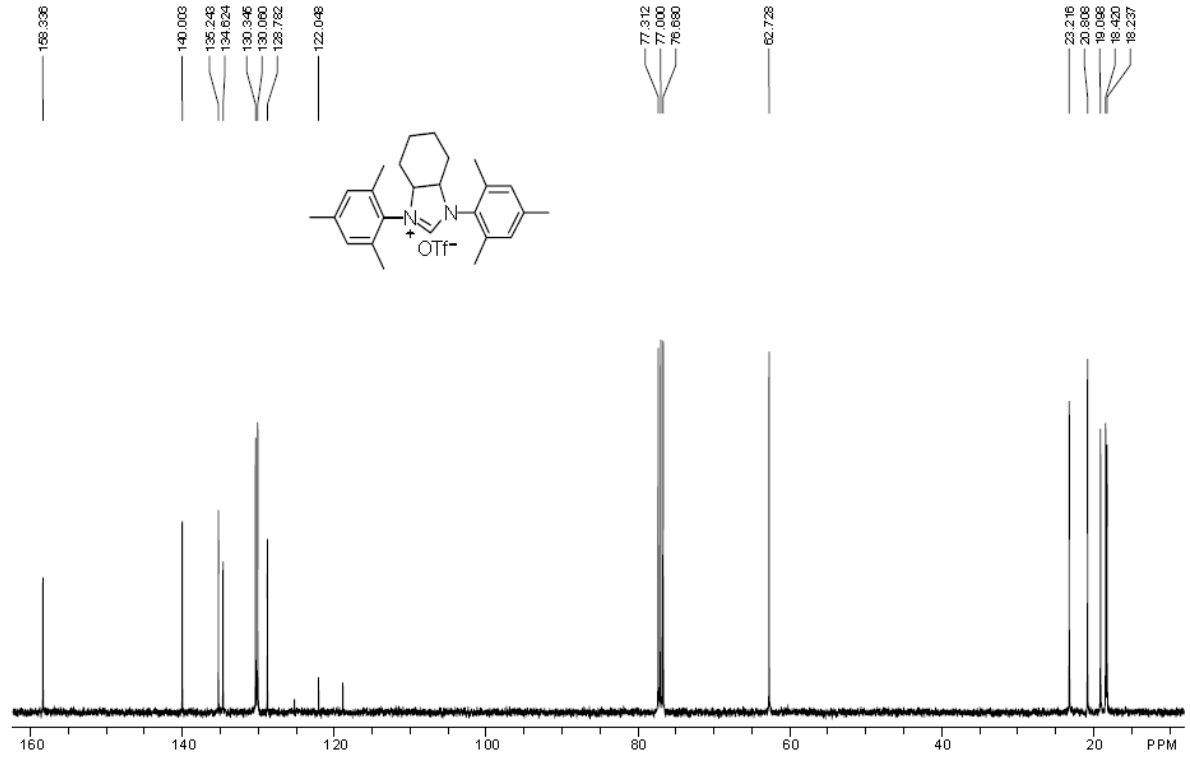
Imidazolinlium trifluoromethanesulfonate 3e



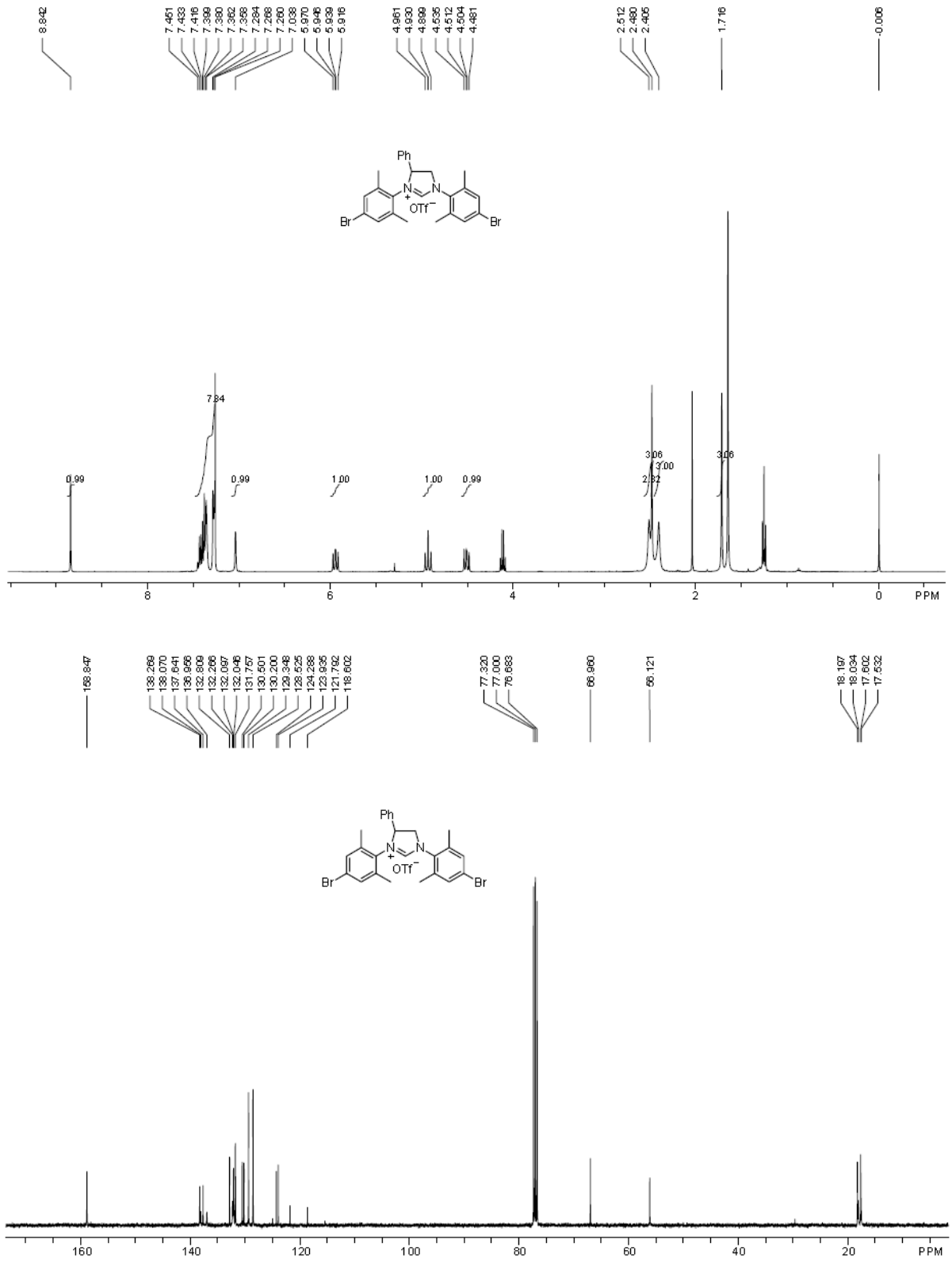


Imidazolinlium trifluoromethanesulfonate 3f

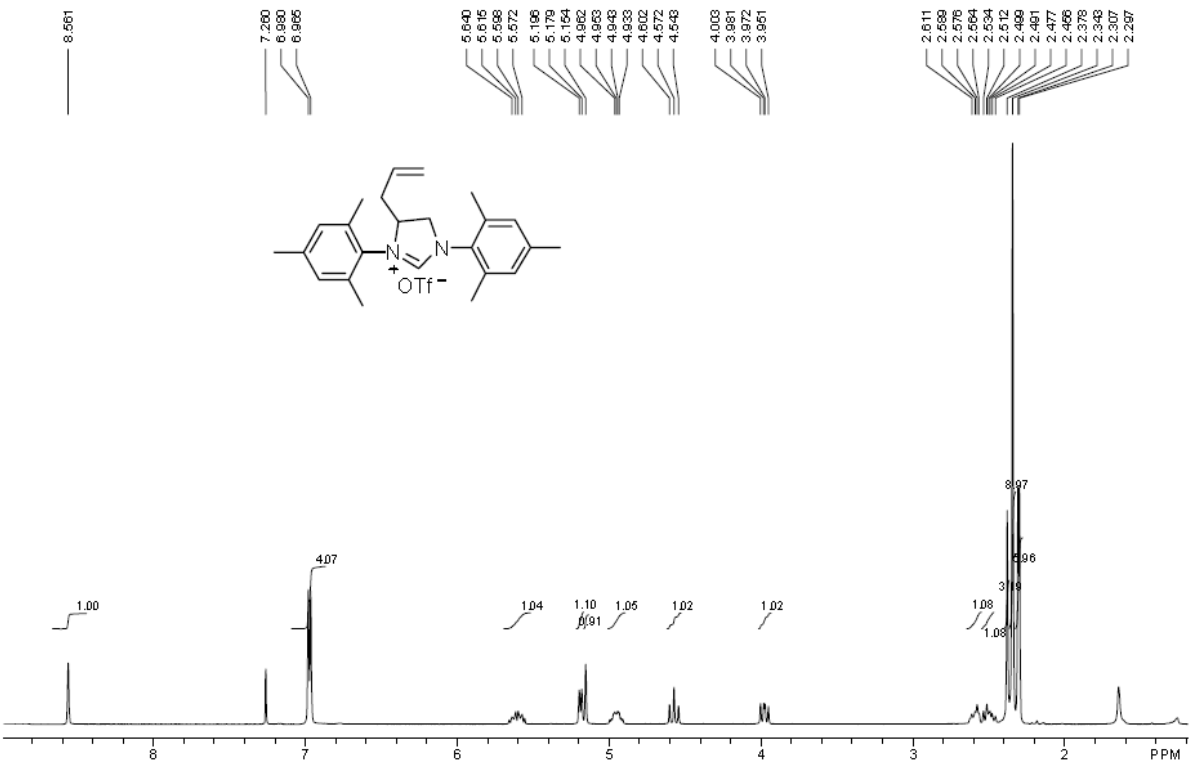


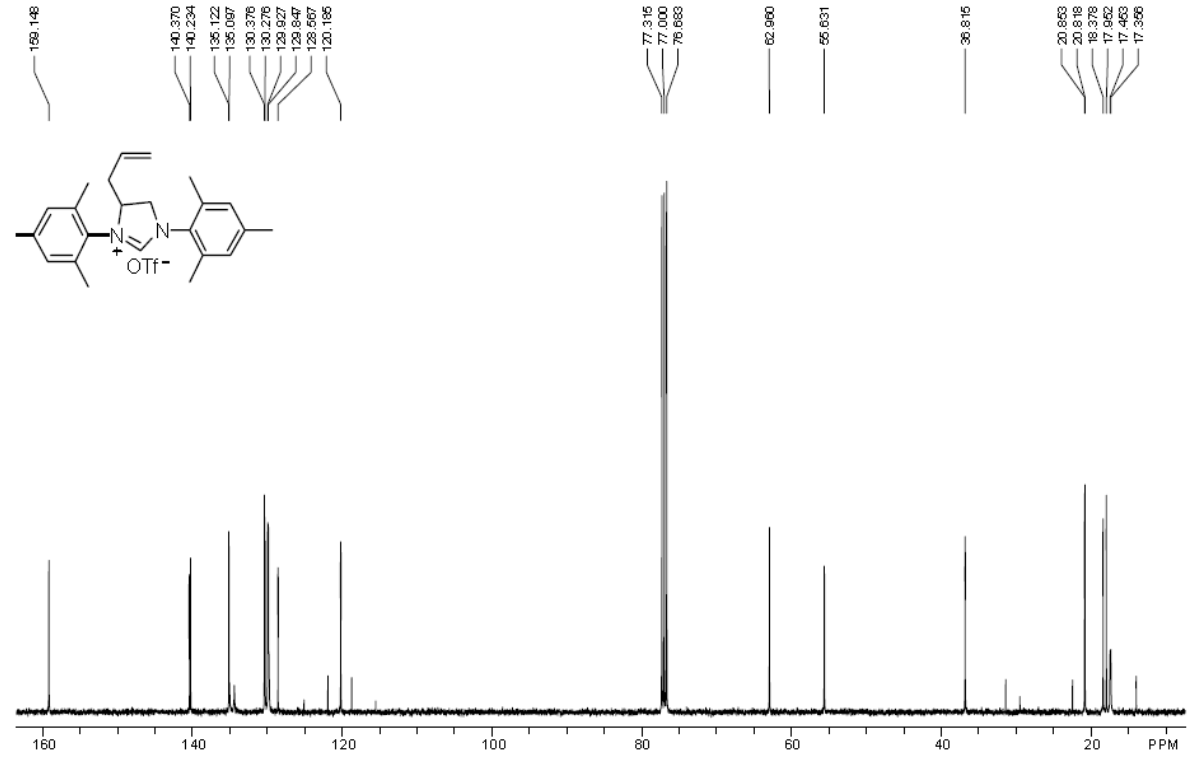


Imidazolinlium trifluoromethanesulfonate 3g

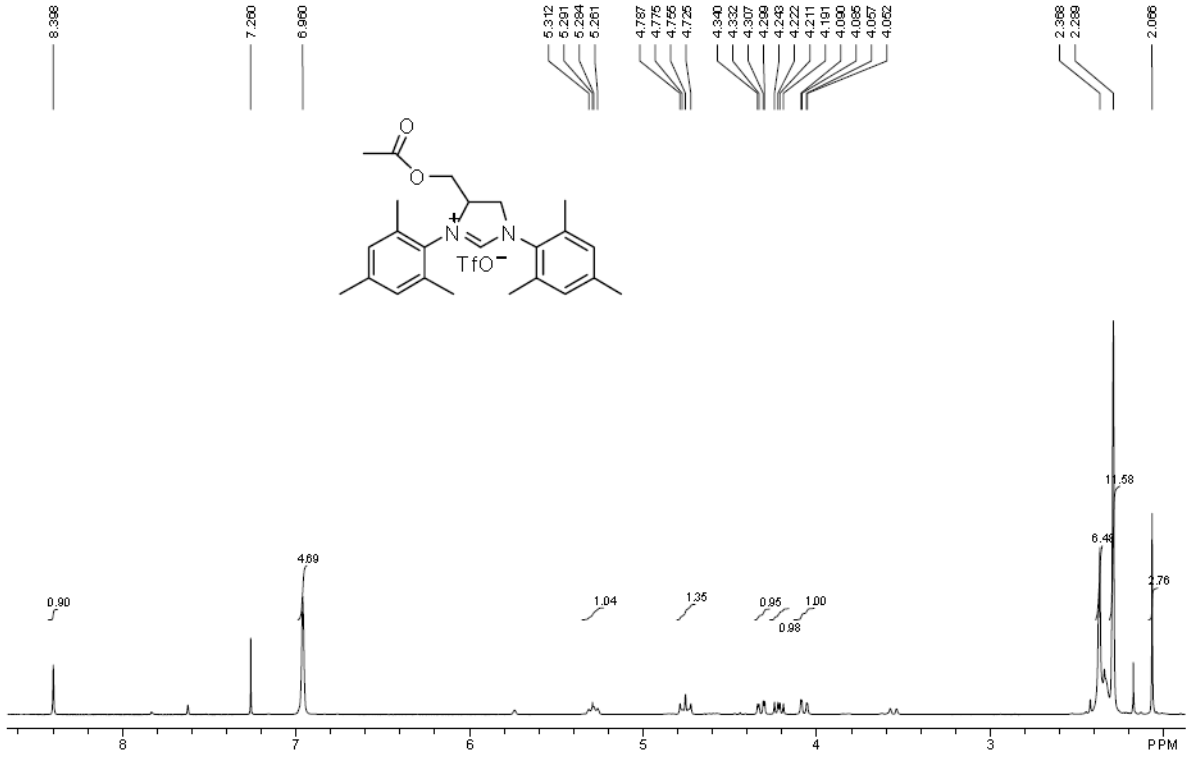


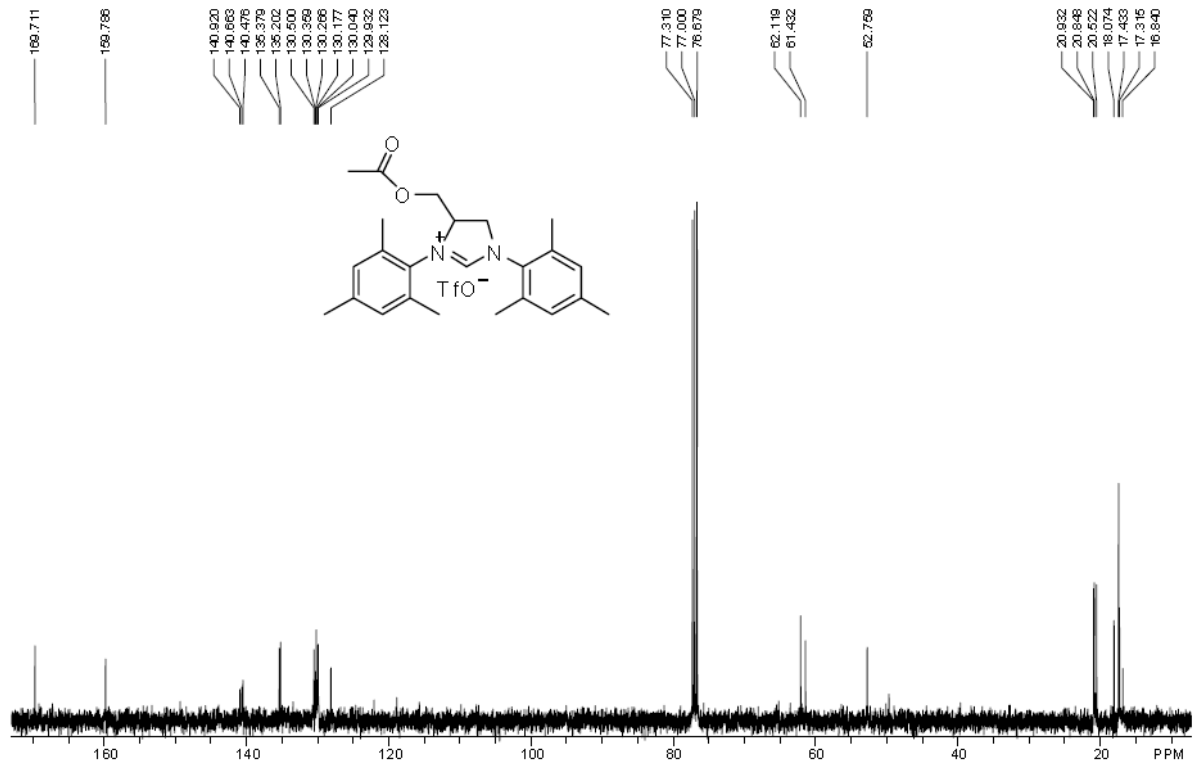
Imidazolinlium trifluoromethanesulfonate 3h



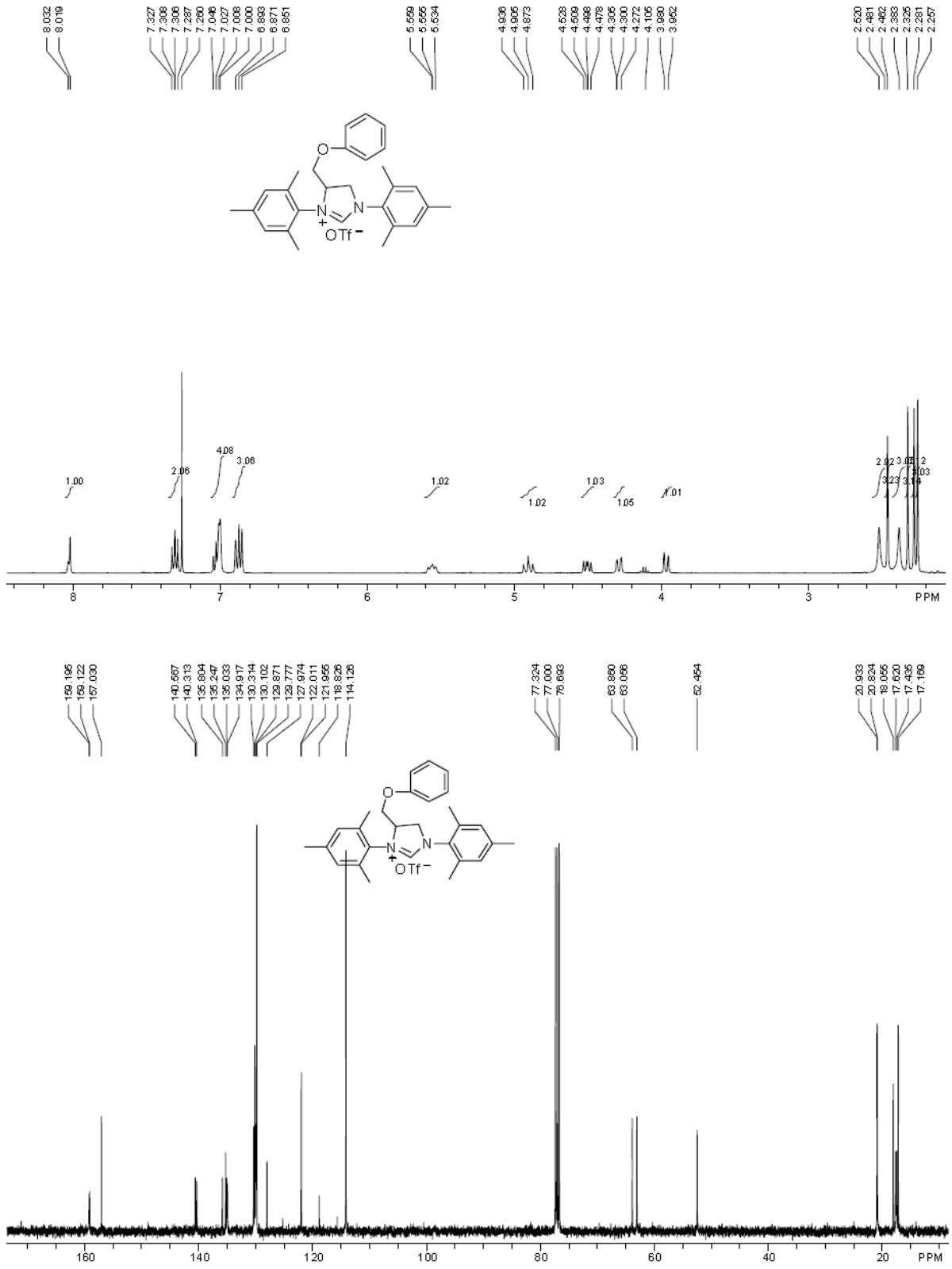


Imidazolinlium trifluoromethanesulfonate 3i

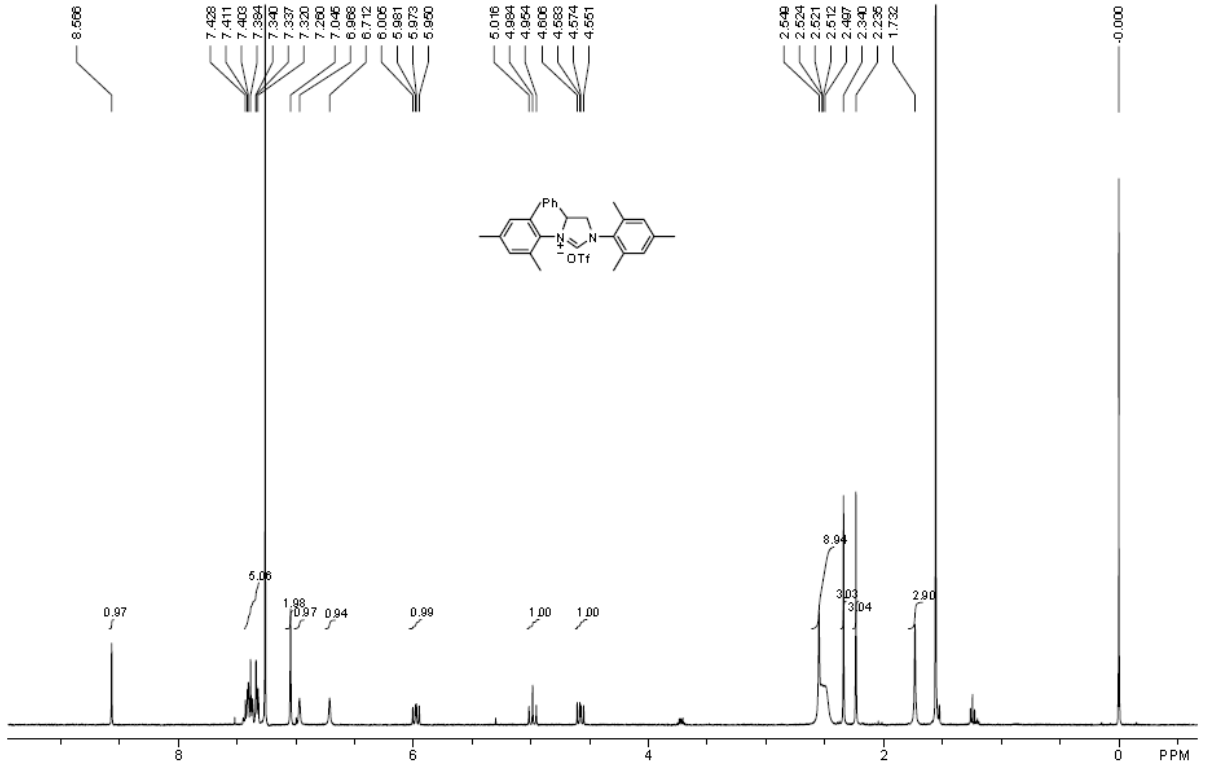


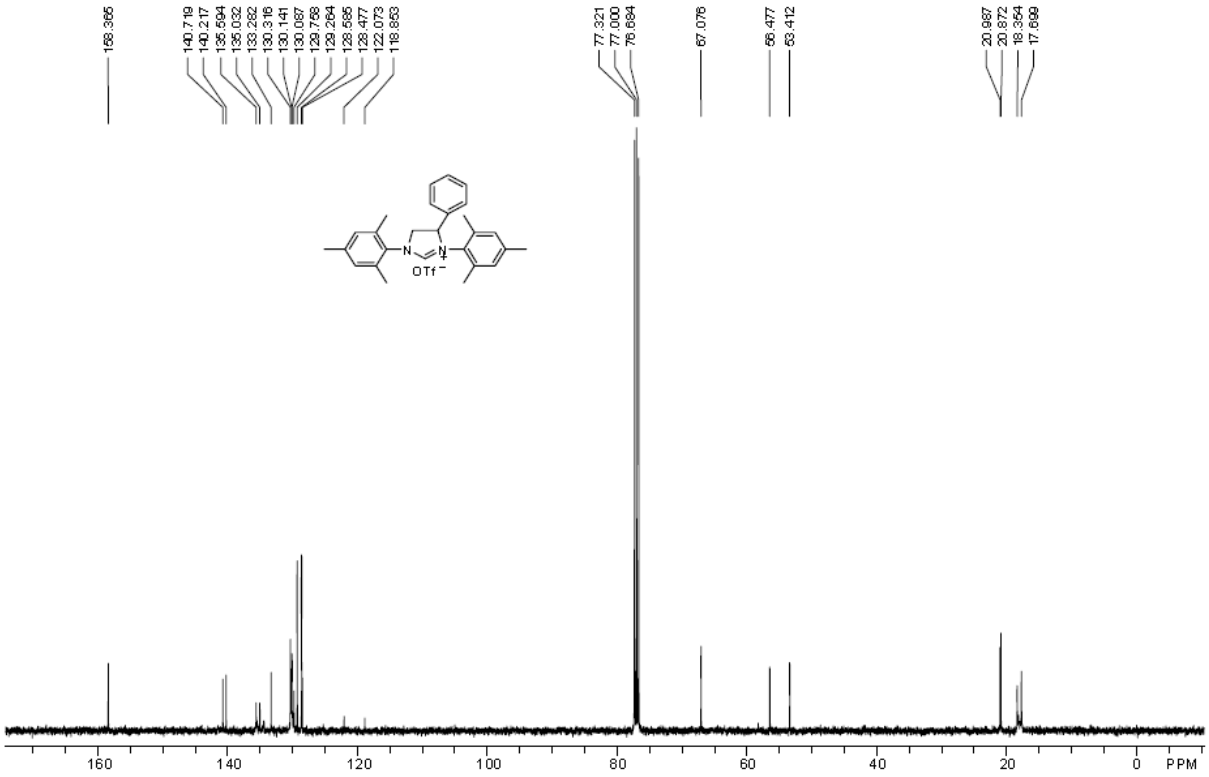


Imidazolinlium trifluoromethanesulfonate 3j

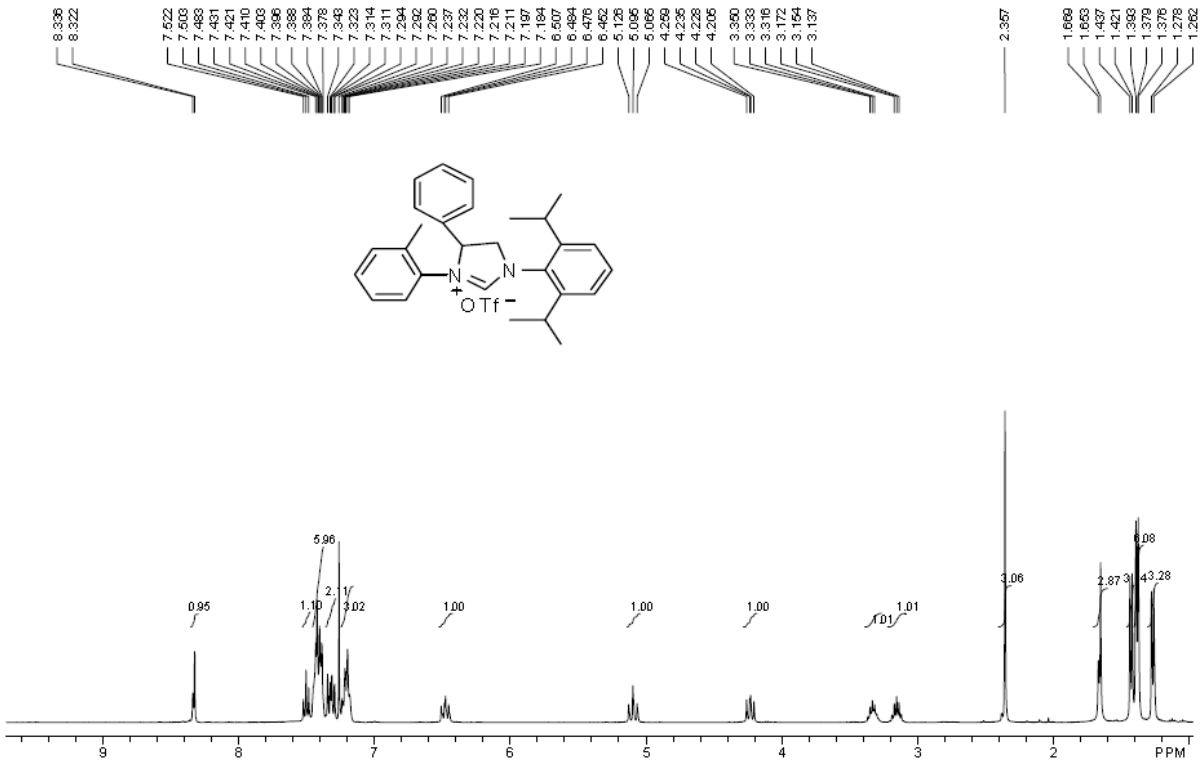


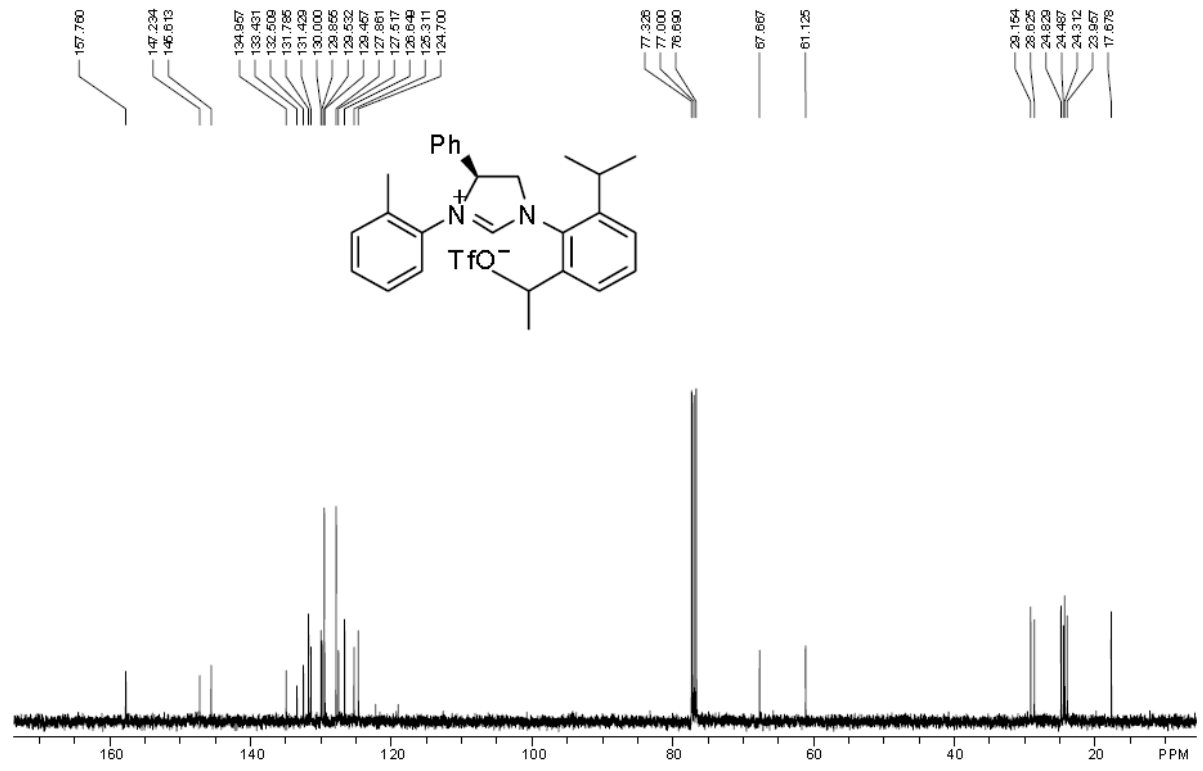
Imidazolinlium trifluoromethanesulfonate (*S*)**-4a-OTf**



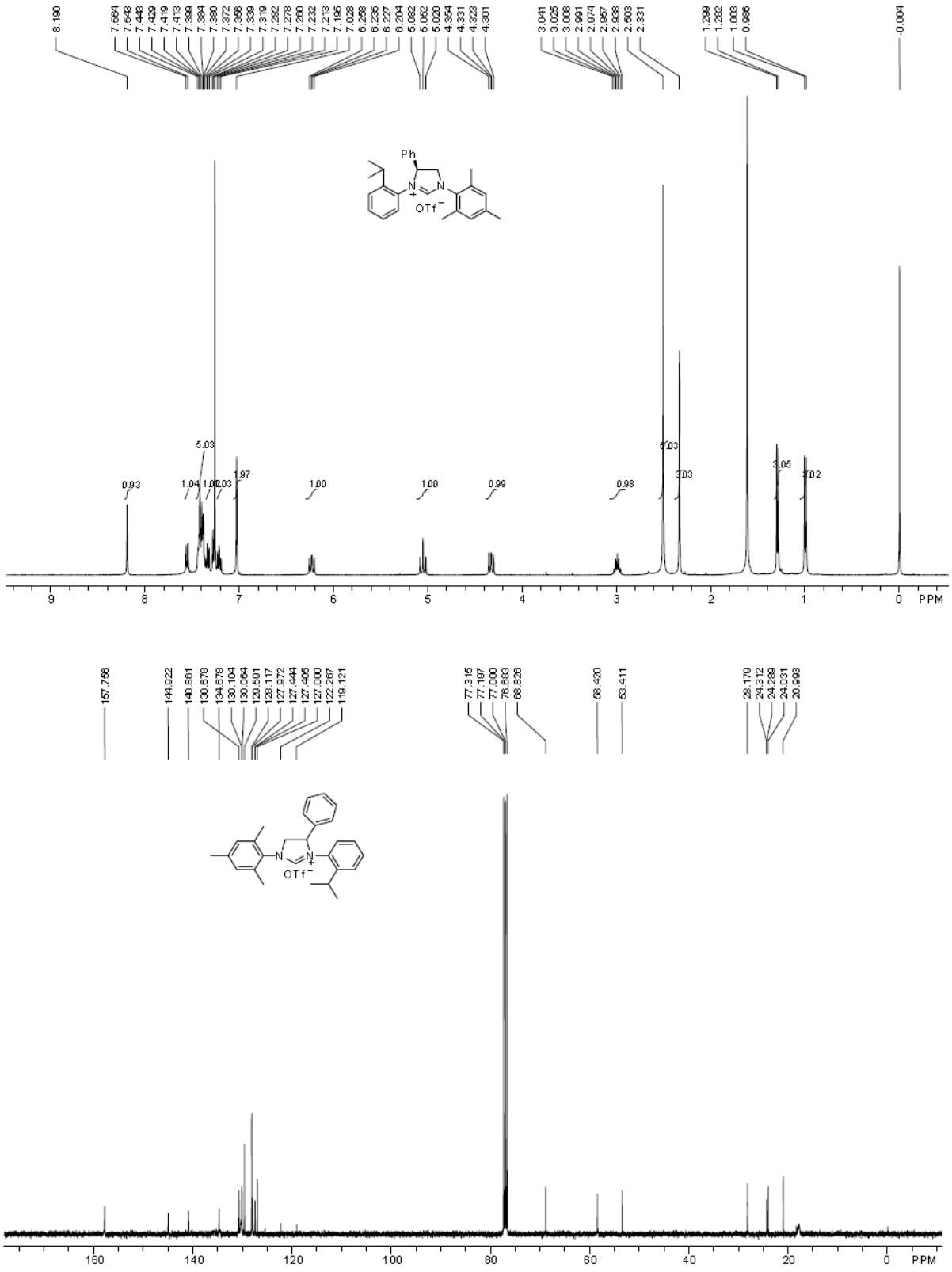


Imidazolinlium trifluoromethanesulfonate (*S*)**-4b-OTf**

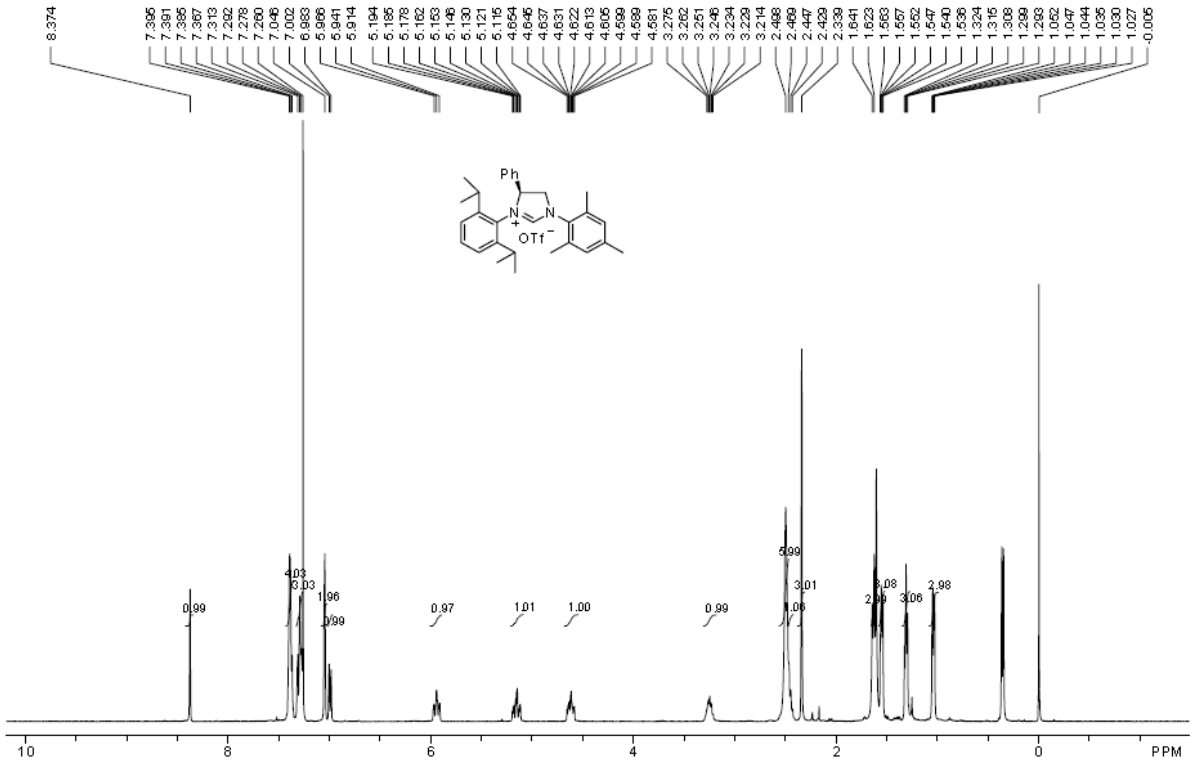


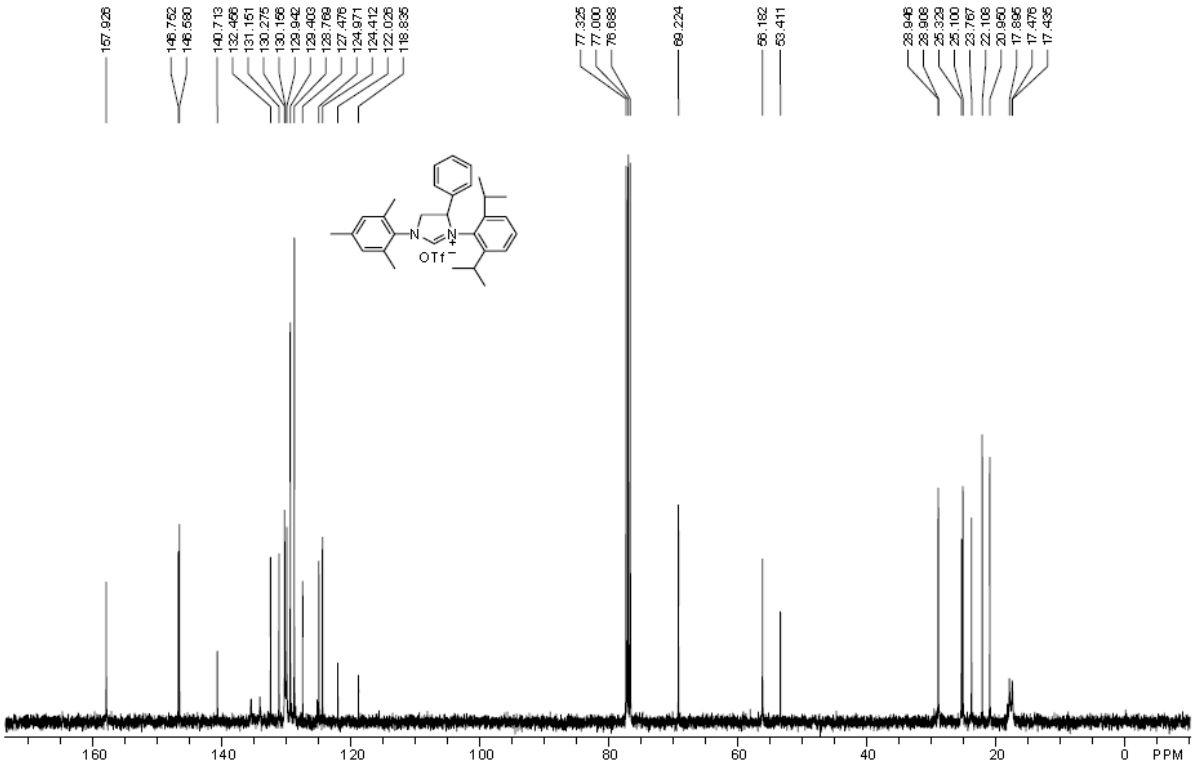


Imidazolinlium trifluoromethanesulfonate (*S*)-4c-OTf

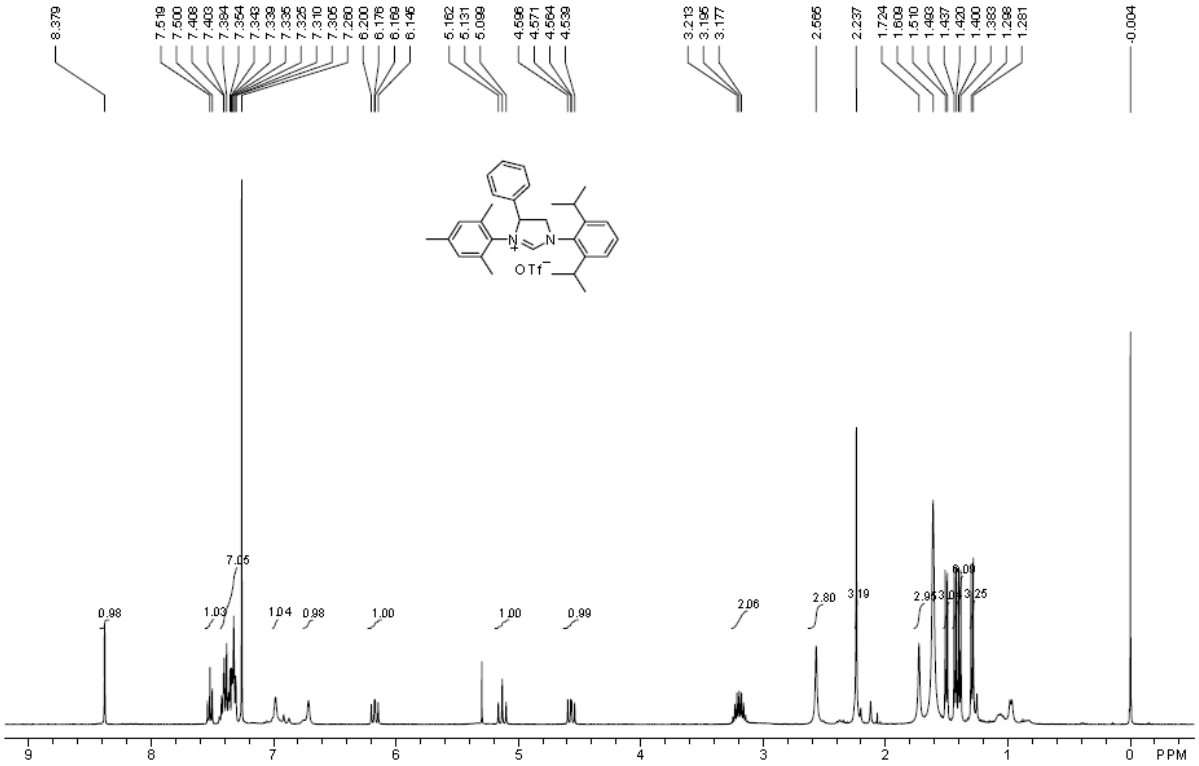


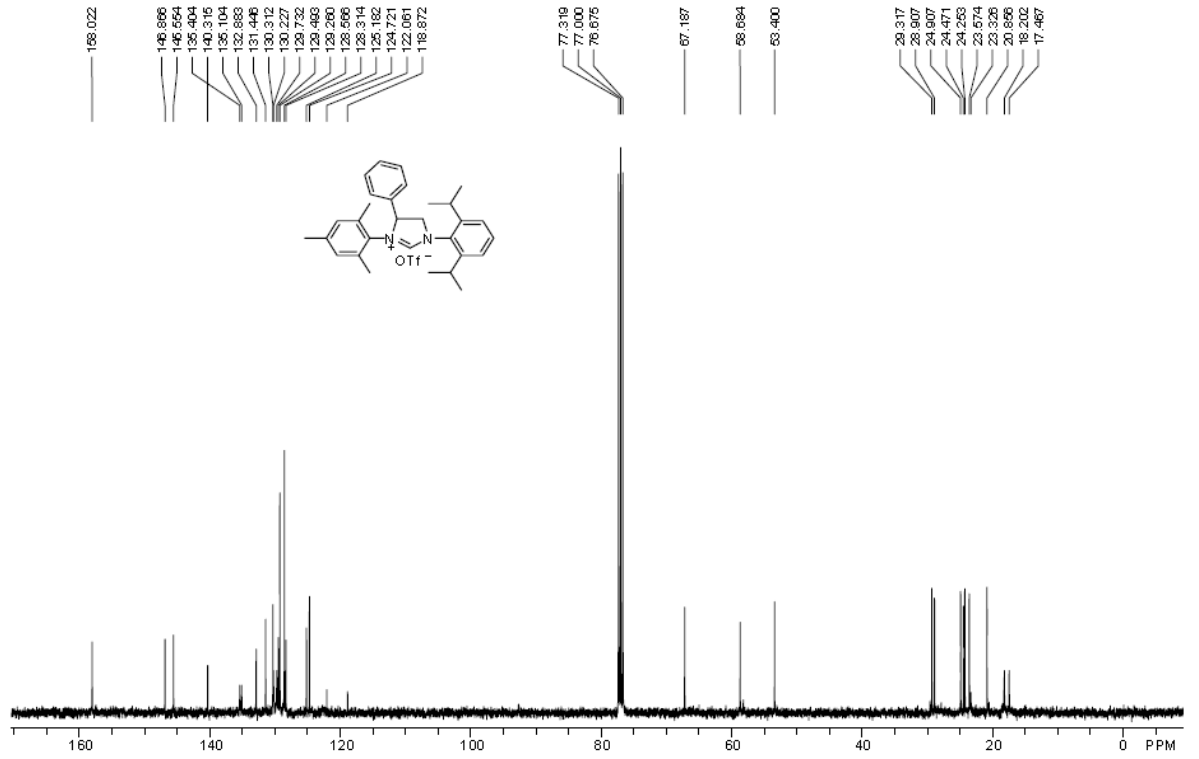
Imidazolinlium trifluoromethanesulfonate (*S*)-4d-OTf



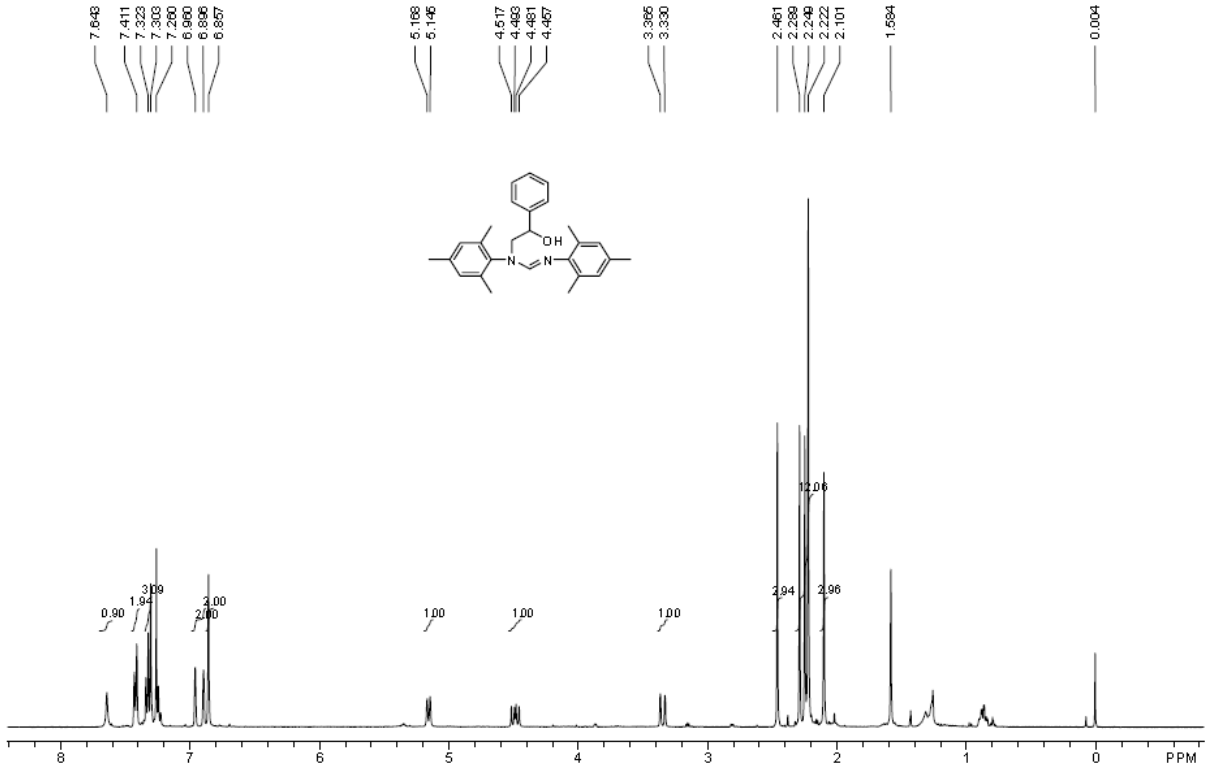


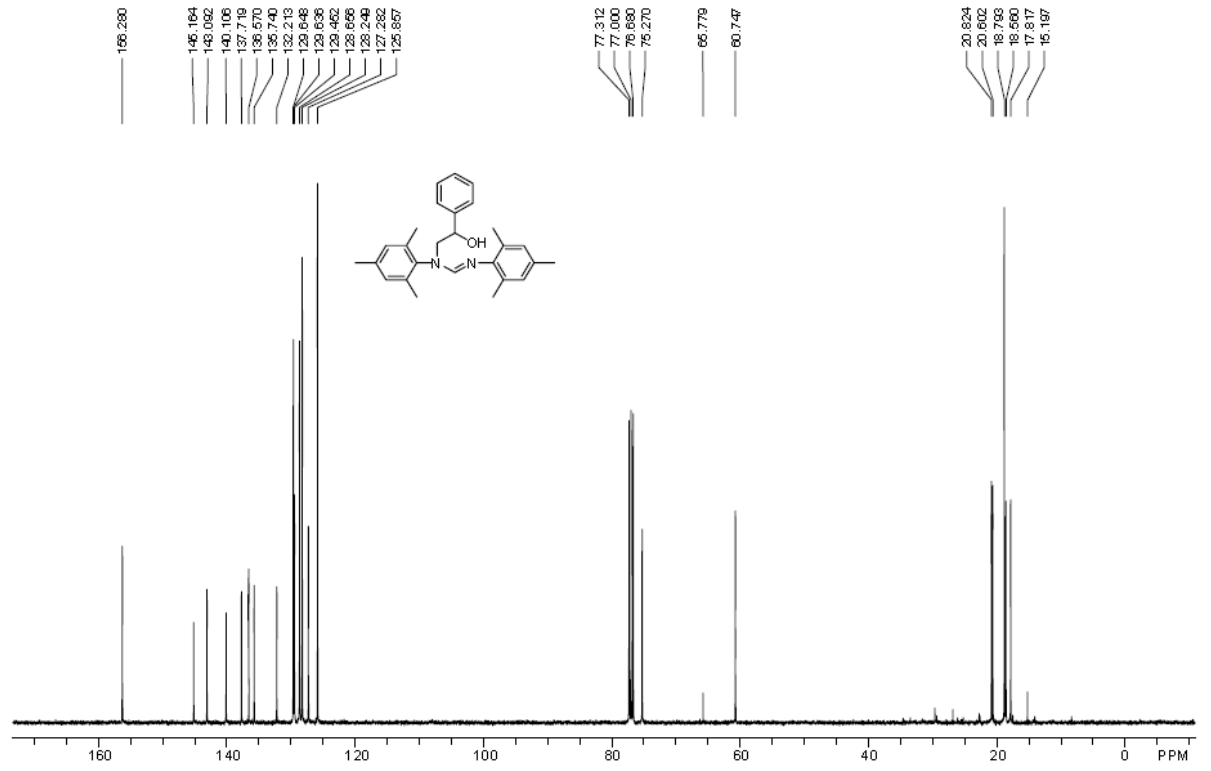
Imidazolinlium trifluoromethanesulfonate (*S*)-4e-OTf



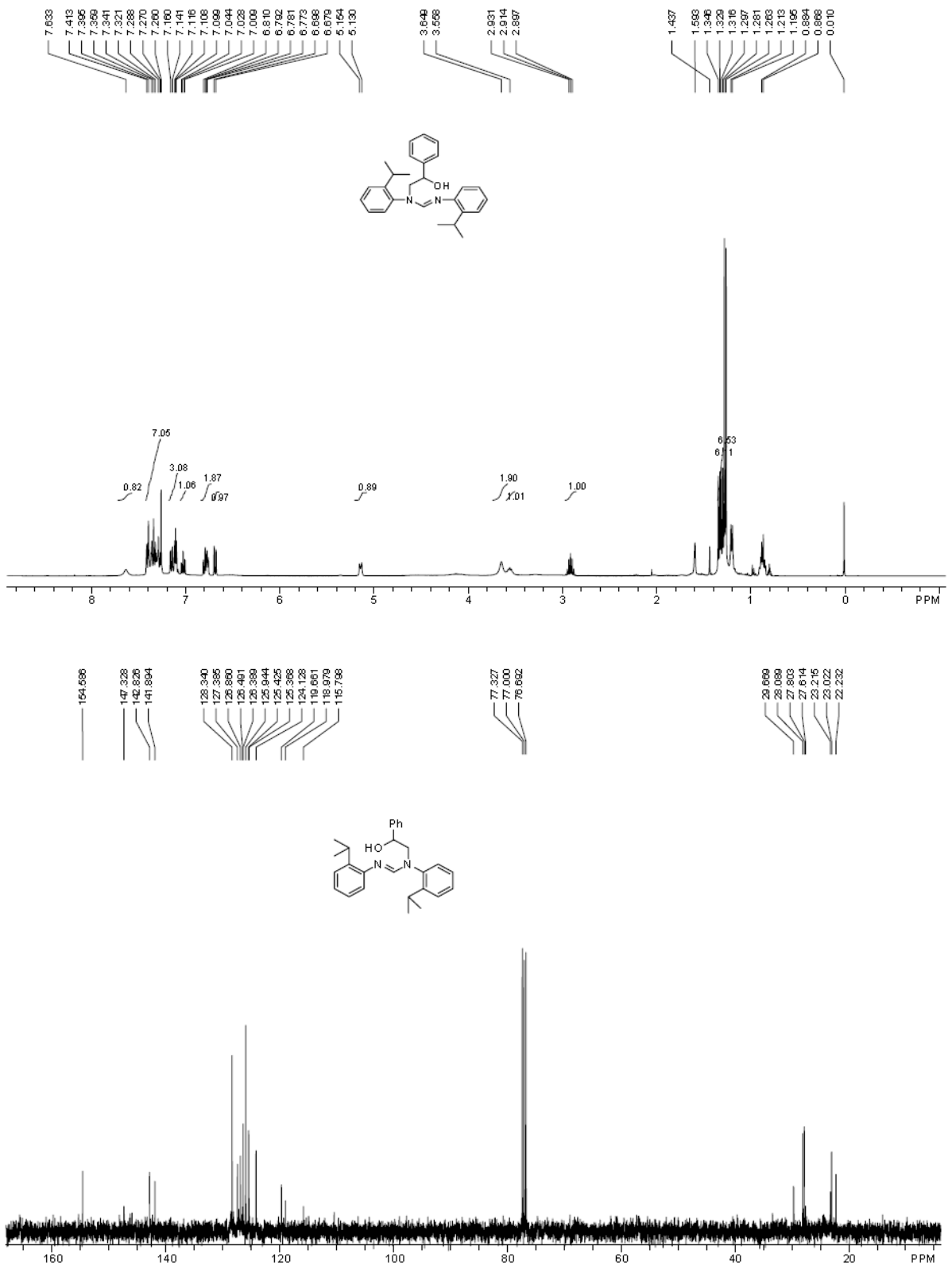


Alcohol 2a/5a

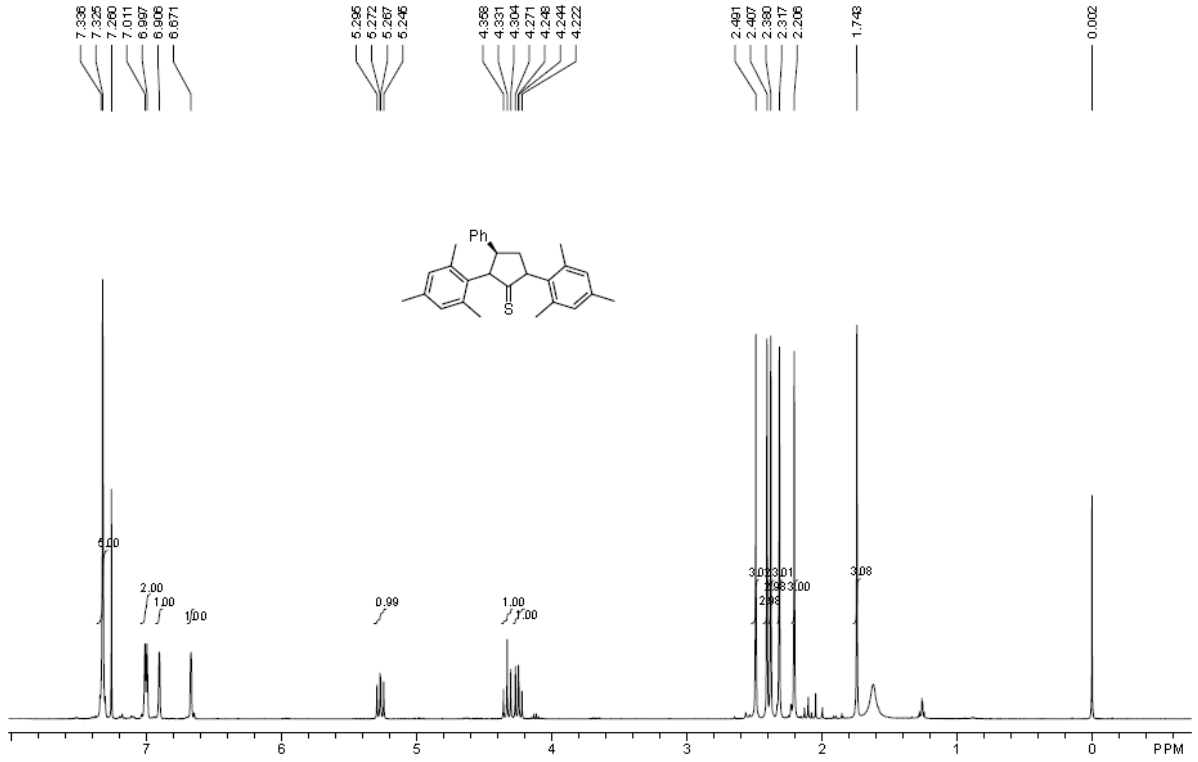


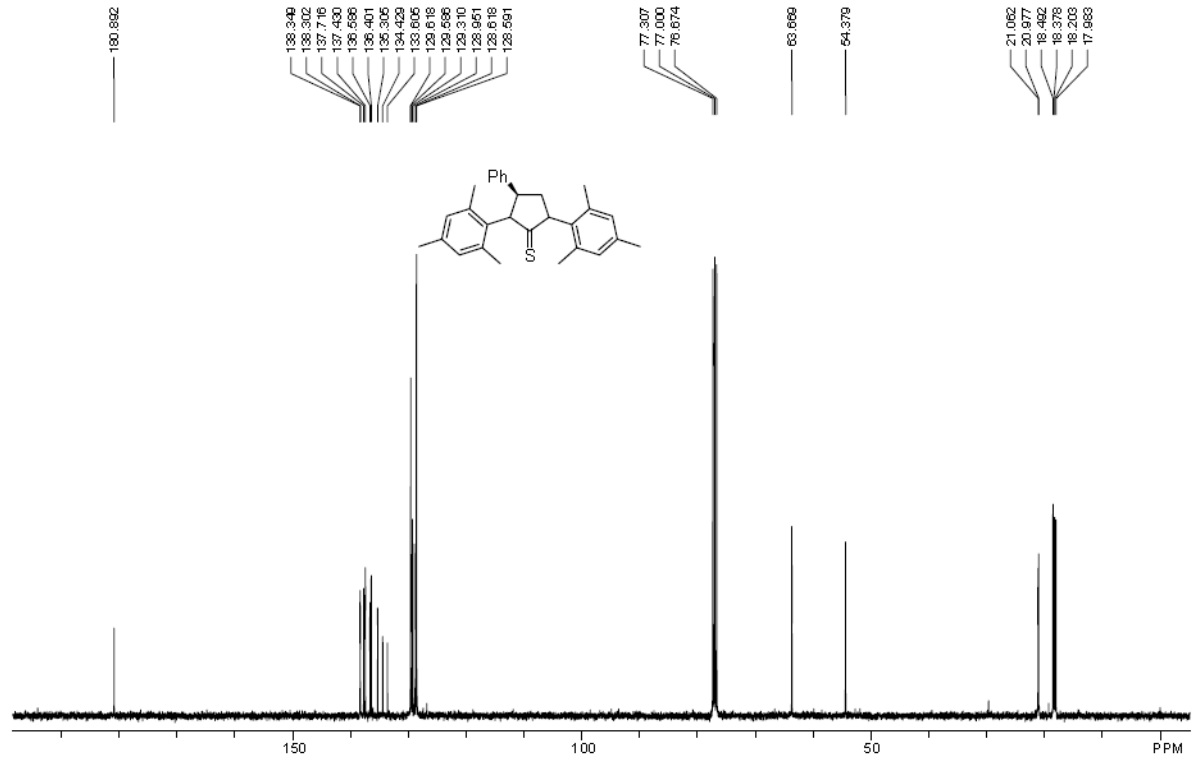


Alcohol 2b/5b



Imidazolidin-2-thione (*S*)**-4a'**





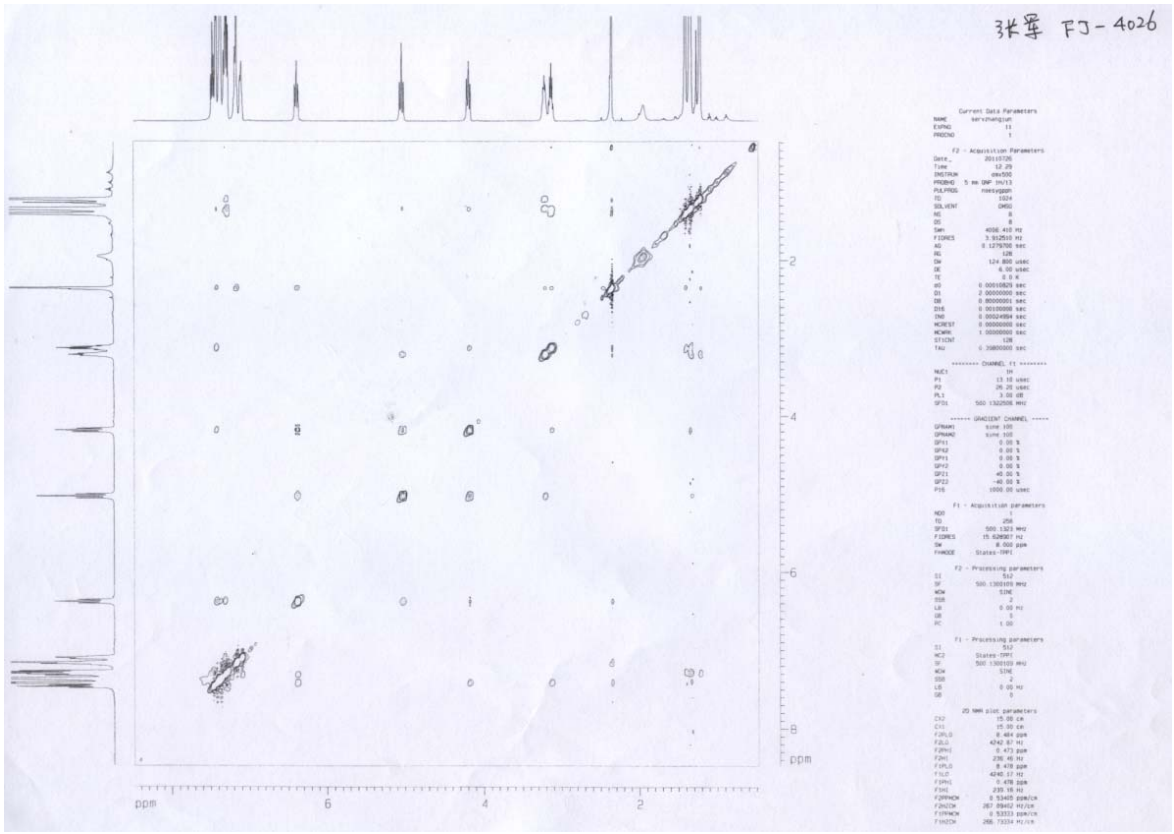


Figure S1. 2D NMR spectrum of (*S*)-**4b-OTf**

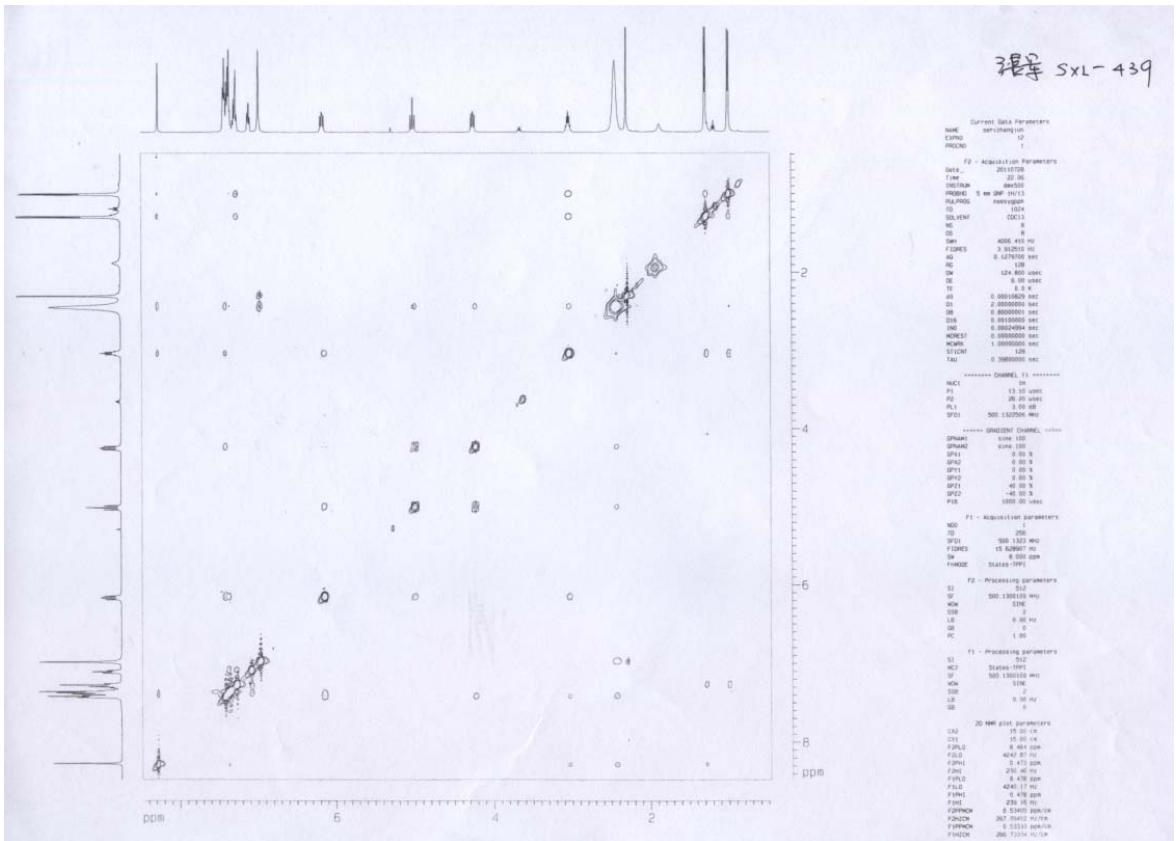
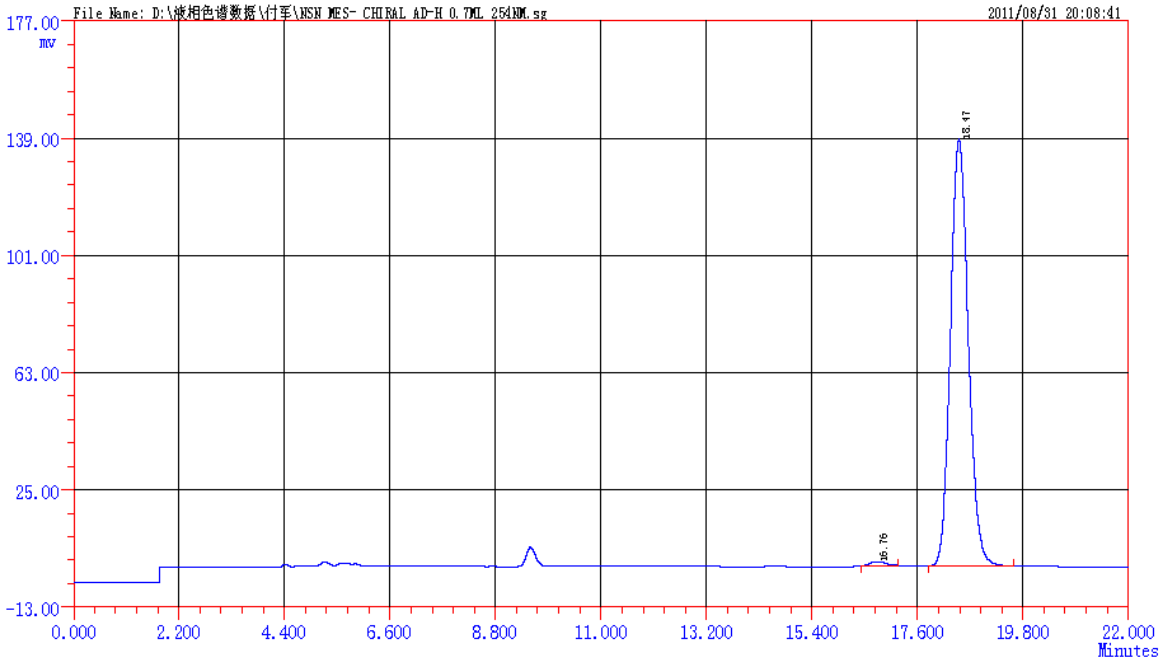
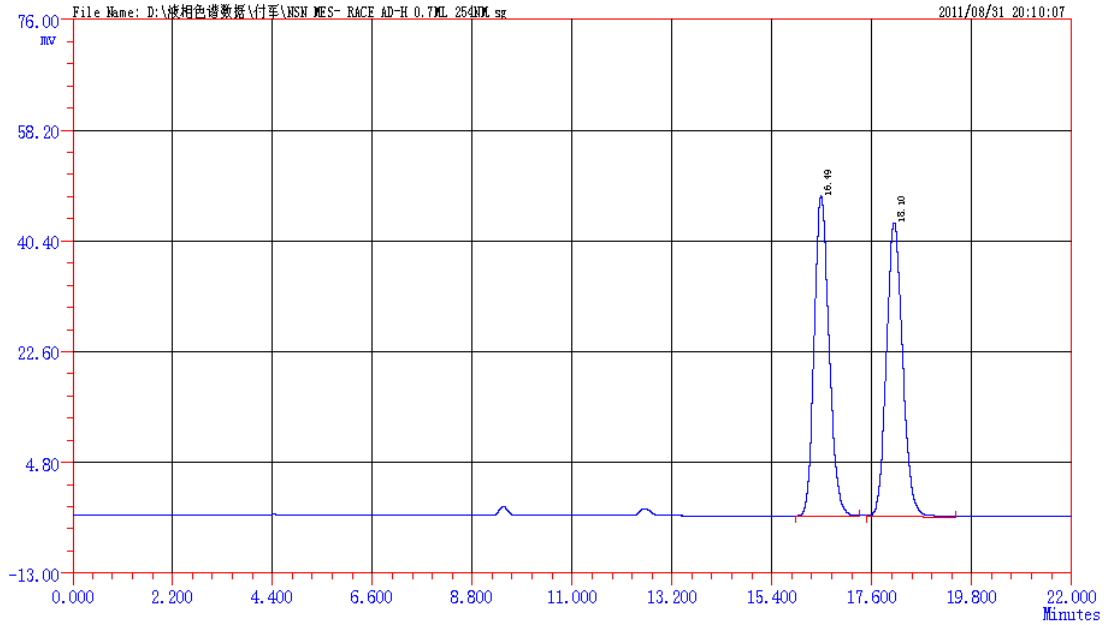


Figure S2. 2D NMR spectrum of (*S*)-**4c-OTf**

8. HPLC for (*S*)-**4a'**: Chiralcel AD, 90:10 Hexane-^{i}PrOH, 25 °C, 254 nm, 0.7 mL/min.



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		16.760	1424	36230.9	1.0001	1.19	8648
2		18.472	138444	3586471.5	98.9999	1.12	10133
	Σ:		139868	3622702.3	100.0000		



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		16.488	51468	1173989.5	49.7949	1.16	10414
2		18.100	47258	1183658.5	50.2051	1.10	10408
	Σ:		98726	2357648.0	100.0000		

9. X-Ray Crystallography.

(*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_2Cl_2. Layering the CH_2Cl_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_2Cl_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-Kα radiation (□ = 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.

3. G. M. Sheldrick, SHELL-97, Program for crystal structure refinement, University of Göttingen: Göttingen, Germany, 1997.

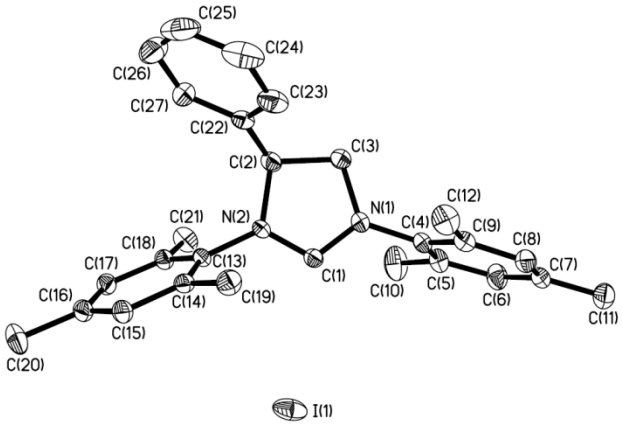


Figure S3. Molecular structure of (*S*)-**4a-I** with 30% probability ellipsoids. H atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): N(1)-C(1) 1.312(5), N(1)-C(4) 1.452(6), N(1)-C(3) 1.465(6), N(2)-C(1) 1.297(5), N(2)-C(13) 1.437(5), N(2)-C(2) 1.508(5), C(2)-C(3) 1.542(6), 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).

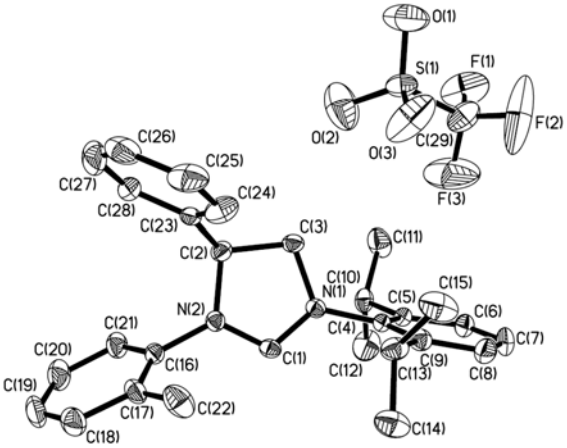


Figure S4. Molecular structure of (*S*)-**4b-OTf** with 30% probability ellipsoids. H atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): N(1)-C(1) 1.304(6), N(1)-C(4) 1.455(6), N(1)-C(3) 1.466(6), N(2)-C(1) 1.312(6), N(2)-C(16) 1.442(6), N(2)-C(2) 1.481(6), C(2)-C(23) 1.517(7), 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),

N(1)-C(1)-N(2) 112.9(5), N(2)-C(2)-C(23) 111.0(4), N(2)-C(2)-C(3) 101.6(4), C(23)-C(2)-C(3) 116.8(4), N(1)-C(3)-C(2) 103.5(4), C(9)-C(4)-C(5) 124.2(4), C(9)-C(4)-N(1) 118.6(4), C(5)-C(4)-N(1) 117.1(4), C(6)-C(5)-C(4) 116.0(5).

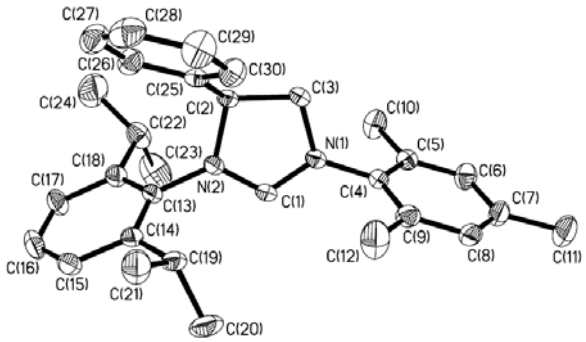


Figure S5. Molecular structure of (*S*)-**4d-I** with 30% probability ellipsoids. H atoms and anion have been omitted for clarity). Selected bond distances (Å) and angles (°): N(1)-C(1) 1.297(7), N(1)-C(4) 1.437(8), N(1)-C(3) 1.489(8), N(2)-C(1) 1.324(8), N(2)-C(13) 1.445(7), N(2)-C(2) 1.503(7), C(2)-C(25) 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(13) 125.0(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).

Table S1. Crystal Data, Data Collection, and Structure Refinement for (*S*)-**4b-OTf**, (*S*)-**4a-I**, and (*S*)-**4d-I**

	(*S*)-**4b-OTf**	(*S*)-**4a-I**	(*S*)-**4d-I**
Identification code	a10707a	mo_10726a	mo_10727b
Formula	$C_{29}H_{33}F_3N_2O_3S$	$C_{30}H_{37}IN_2$	$C_{27}H_{31}IN_2$
Formula weight	546.63	552.52	510.44
T, K	293(2)	173(2)	173(2)
crystal system	Orthorhombic	Orthorhombic	Orthorhombic
space group	P2(1)2(1)2(1)	P2(1)2(1)2(1)	P2(1)2(1)2(1)
a, Å	8.521(3)	13.2441(17)	15.2391(17)
b, Å	14.946(6)	15.930(2)	15.3799(18)
c, Å	22.415(9)	27.319(3)	22.066(3)
α, deg	90	90	90
β, deg	90	90	90
γ, deg	90	90	90
Volume, Å ^{3}	2855(2)	5763.9(13)	5171.8(10)
Z	4	8	8
D_{calc}, Mg / m^3	1.272	1.273	1.311
absorption coefficient, mm^{-1}	0.165	1.129	1.253
F(000)	1152	2272	2080
crystal size, mm	0.40 x 0.35 x 0.25	0.50 x 0.20 x 0.20	0.35 x 0.20 x 0.20
2θ range, deg	1.64 to 25.01	1.48 to 27.43	1.61 to 27.50
reflections collected /unique	11878 / 5023 [R(int) = 0.0581]	41229 / 13047 [R(int) = 0.0430]	37272 / 11769 [R(int) = 0.0268]
data / restraints / parameters	5023 / 6 / 352	13047 / 0 / 617	11769 / 2 / 561
goodness of fit on F^2	0.998	1.024	1.022
final R indices [I >2σ(I)][a]	R1 = 0.0774, wR2 = 0.1995	R1 = 0.0643, wR2 = 0.1781	R1 = 0.0481, wR2 = 0.1444
R indices (all data)	R1 = 0.1151, wR2 = 0.2232	R1 = 0.1057, wR2 = 0.2095	R1 = 0.0737, wR2 = 0.1672
lgst diff peak and hole, e/Å^3	0.547 and -0.271	1.863 and -1.113	1.100 and -0.678