Electronic Supplementary Information for

Tailor-made synthesis of various backboned-substituted imidazolinium salts by triflic anhydride mediated intramolecular cyclisation

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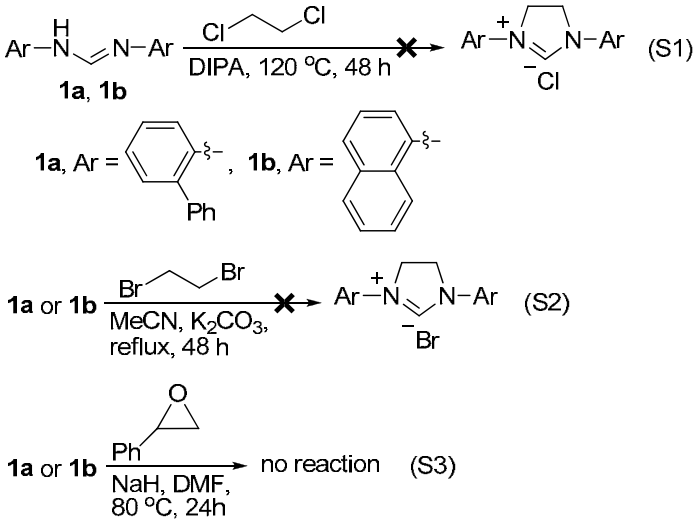
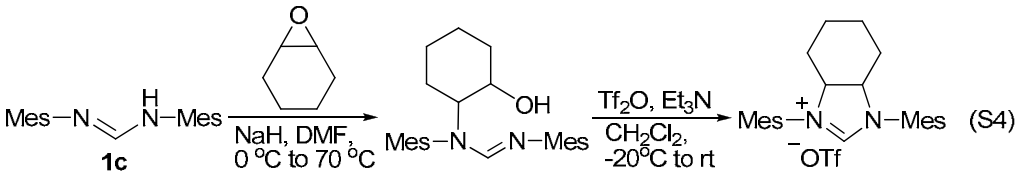
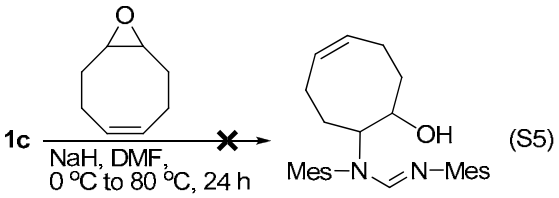
Attempt to synthesize imidazolinium salts from less active formamidines and the imidazolinium salts having a 4,5-disubstituted backbone

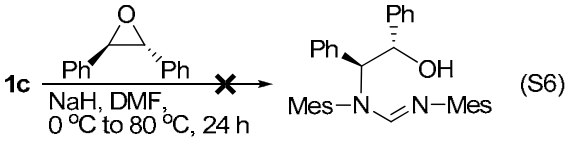


We first attempted to use the established methods to synthesize imidazolinium salts from *N,N′*-di(biphenyl-2-yl)formamidine (**1a**) or *N,N′*-di(naphthalen-1-yl)formamidine (**1b**). Regretfully, by the previous methods, such as Grubbs' [Eq. (S1)],[1] Cavell's [Eq. (S2)],[2] and our previous method [Eq. (S3)],[3] both two formamidines cannot react with either 1,2-dihaloethane or epoxides, probably due to the decreasing electron density and reactivity at their nitrogen atoms, which is attributed to more delocalization of the formamidine anion over the biphenyl ring in **1a** or over the naphthalene ring in **1b**, compared with *N,N′*-dimesitylformamidine **1c**.

1. K. M. Kuhn and R. H. Grubbs, *Org. Lett*., 2008, **10**, 2075.
2. M. Iglesias, D. J. Beetstra, J. C. Knight, L. L. Ooi, A. Stasch, S. Coles, L. Male, M. B. Hursthouse, K. J. Cavell, A. Dervisi and I. A. Fallis, *Organometallics*, 2008, **27**, 3279.
3. J. Zhang, X. Su, J. Fu and M. Shi, *Chem. Commun*., 2011, **47**, 12541.







In our previous work, using **1c** and cyclohexene oxide, we succeeded to synthesize 4,5-disubstituted imidazolinium salt **2** in 68% overall yield [Eq. (S4)].[3] However, our further attempt to prepare other 4,5-disubstituted imidazolinium salts, such as 1,5-cyclooctadiene monoepoxide [Eq. (S5)] and trans-stilbene oxide [Eq. (S6)], failed. It is reasonable that cyclohexene oxide has more ring strain than cyclic epoxides with expanded ring, such as 1,5-cyclooctadiene monoepoxide, and less steric hindrance than other acyclic 2,3-disubstituted epoxides, such as trans-stilbene oxide. Thus an alternative method need to be developed for the modular synthesis of 4,5-disubstituted imidazolinium salt.

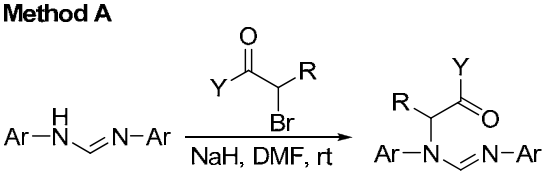
General Information:

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. X-ray diffraction analysis was performed by using a Bruker Smart-1000 X-ray diffractometer. Formamidines **1a-e** were prepared as previously reported[1, 4], and their spectra were consistent with that of the published data.

Preparation and characterization

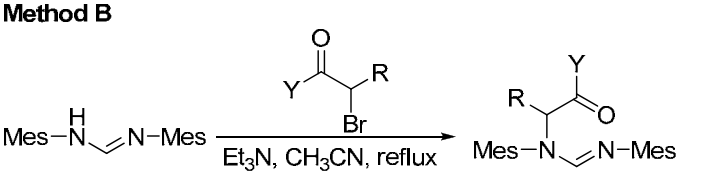
General Procedures for the Synthesis of α-amidino ketone/ester 2a–j.

Method A



Ar = Mes, R = H, Y = ^{t}Bu; **2a**, 71%,
Ar = Mes, R = H, Y = OEt; **2b**, 98%,
Ar = Mes, R = Me, Y = OEt; **2c**, 85%,
Ar = Mes, R = Ph, Y = OEt; **2d**, 99%,
Ar = biphenyl-2-yl, R = H, Y = Ph; **2e**, 39%,
Ar = naphthalen-1-yl, R = H, Y = OEt; **2f**, 94%,

Method B



R = H, Y = Ph; **2g**, 70%,
R = Me, Y = Ph; **2h**, 82%,
R = Ph, Y = Ph; **2i**, 95%,
R = Me, Y = Et; **2j**, 77%,

Method A: NaH (60% suspension in mineral oil, 1.2 eq.) was added to the solution of formamidine (1 eq.) in DMF at 0 °C. After 5 mins, the mixture was warmed to room temperature and stirred for 30

4. K. Hirano, S. Urban, W. Congyang and F. Glorius, *Org. Lett.*, 2009**, 11**, 1019.

mins. α-Bromo ketone or ethylester (1 eq.) was added slowly at -20 °C. Five mins latter, the mixture was warmed to room temperature and stirred for 2-4 h, The reaction progress was monitored by TLC (PE/EA = 8:1). After full consumption of the reagents, H_2O was added and the mixture was extracted with EA, The combined organic layer was washed with brine and dried with anhydrous $MgSO_4$. After evaporating the solvent, the residue was purified by column chromatography on silica gel (PE/EA = 10:1 to 8:1) to afford the product.

Method B: Formamidine (1 eq.) was suspended in acetonitrile. Successively, Et_3N (1.2 eq.) and α-bromo ketone or ethylester (1 eq.) were added and the resulting mixture was refluxed for 2-6 h. The reaction progress was monitored by TLC (PE/EA = 8:1). After full consumption of the reagents, the residue was purified by column chromatography on silica gel (PE/EA = 10:1 to 8:1) to afford the product.

2a: Following the general procedure of method A, **1c** (840 mg, 3.0 mmol), NaH (60% suspension in mineral oil, 145 mg, 3.6 mmol) and 1-bromo-3,3-dimethyl-2-butanone (540 mg, 3.0 mmol) afforded the product **2a** as colourless oil (806 mg, 71%). (Method B afforded a lower yield.) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21 (s, 1H), 6.93 (s, 2H), 6.84 (s, 2H), 4.55 (s, 2H), 2.40 (s, 6H), 2.30 (s, 3H), 2.25 (s, 3H), 2.14 (s, 6H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.9, 150.9, 147.0, 139.6, 137.1, 136.8, 131.0, 129.5, 129.1, 128.3, 53.2, 43.6, 26.7, 26.3, 20.8, 20.6, 18.6, 18.4.

2b: Following the general procedure of method A, **1c** (840 mg, 3.0 mmol), NaH (60% suspension in mineral oil, 145 mg, 3.6 mmol) and ethyl bromoacetate (500 mg, 3.0 mmol) afforded the product **2b** as colourless oil (1.08 g, 98%). (Method B afforded a lower yield.) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25 (s, 1H), 6.93 (s, 2H), 6.83 (s, 2H), 4.35 (s, 2H), 4.26-4.20 (m, 2H), 2.34 (s, 6H), 2.29 (s, 3H), 2.24 (s, 3H), 2.15 (s, 6H), 1.32-1.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.2, 151.6, 146.5, 139.3, 137.3, 136.6, 131.2, 129.4, 129.0, 128.3, 60.8, 50.5, 20.7, 20.5, 18.5, 18.2, 14.0.

2c: Following the general procedure of method A, **1c** (840 mg, 3.0 mmol), NaH (60% suspension in mineral oil, 145 mg, 3.6 mmol) and ethyl 2-bromopropanoate (543 mg, 3.0 mmol) afforded the product **2c** as colourless oil (970 mg, 85%). (Method B afforded a lower yield.) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.19 (s, 1H), 6.94 (s, 1H), 6.89 (s, 1H), 6.81 (s, 2H), 4.67-4.64 (m, 1H), 4.28-4.19 (m, 2H), 2.47 (s, 3H), 2.30 (s, 3H), 2.23-2.22 (m, 6H), 2.15 (s, 6H), 1.29 (t, J = 6.8 Hz, 3H), 1.18 (d, J = 6.8 Hz,

3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.0, 151.6, 147.0, 139.0, 138.3, 137.6, 136.3, 130.9, 129.3, 128.9, 128.7, 128.2, 60.6, 55.4, 20.7, 20.5, 18.7, 18.6, 18.1, 15.2, 13.9.

2d: Following the general procedure of method A, **1c** (840 mg, 3.0 mmol), NaH (60% suspension in mineral oil, 145 mg, 3.6 mmol) and ethyl 2-bromo-2-phenylacetate (730 mg, 3.0 mmol) afforded the product **2d** as colourless oil (1.31 g, 99%). (Method B afforded a lower yield.) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34-7.28 (m, 4H), 7.15 (s, 2H), 6.82 (s, 3H), 6.56 (s, 1H), 5.70 (s, 1H), 4.23-4.12 (m, 2H), 2.54 (s, 3H), 2.23 (s, 3H), 2.18-2.14 (m, 9H), 2.05 (s, 3H), 1.17 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.0, 152.3, 147.0, 138.5, 137.7, 137.3, 136.8, 133.2, 131.2, 129.8, 129.2, 129.1, 129.0, 128.6, 128.5, 128.4, 127.8, 66.3, 61.1, 20.8, 20.6, 18.8, 18.7, 18.6, 13.9.

2e: Following the general procedure of method A, **1a** (1.05 g, 3.0 mmol), NaH (60% suspension in mineral oil, 145 mg, 3.6 mmol) and 2-bromoacetophenone (597 mg, 3.0 mmol) afforded the product **2e** as pale yellow powder (546 mg, 39%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (s, 1H), 7.68-7.65 (m, 2H), 7.51-7.28 (m, 15H), 7.17-7.04 (m, 5H), 6.43-6.41 (m, 1H), 4.72 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 195.1, 151.4, 147.9, 143.4, 141.8, 140.1, 139.5, 139.3, 137.2, 135.6, 135.2, 132.9, 131.2, 130.3, 130.1, 129.9, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.0, 127.9, 127.5, 127.4, 127.3, 127.1, 126.8, 125.9, 123.4, 120.0, 118.5, 115.5, 54.3.

2f: Following the general procedure of method A, **1b** (890 mg, 3.0 mmol), NaH (60% suspension in mineral oil, 145 mg, 3.6 mmol) and ethyl bromoacetate (500 mg, 3.0 mmol) afforded the product **2f** as colourless oil (1.08 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.48-8.46 (m, 1H), 8.20-8.18 (m, 1H), 8.04 (s, 1H), 7.96-7.83 (m, 3H), 7.68-7.51 (m, 7H), 7.39-7.35 (m, 1H), 6.96-6.94 (m, 1H), 5.07 (br, 1H), 4.53 (br, 1H), 4.36 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.4, 151.2, 147.5, 140.3, 134.6, 134.1, 130.1, 129.5, 128.5, 127.9, 127.4, 127.0, 126.5, 126.0, 125.9, 125.6, 125.1, 125.0, 124.3, 123.3, 122.8, 113.2, 61.1, 51.3, 14.2.

2g: Following the general procedure of method B, **1c** (840 mg, 3.0 mmol), Et_3N (365 mg, 3.6 mmol) and 2-bromoacetophenone (597 mg, 3.0 mmol) afforded the product **2g** as white powder (837 mg, 70%). (Method A afforded a lower yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.09-8.07 (m, 2H),

7.59-7.46 (m, 3H), 7.33 (s, 1H), 6.96 (s, 2H), 6.84 (s, 2H), 5.08 (s, 2H), 2.45 (s, 6H), 2.32 (s, 3H), 2.25 (s, 3H), 2.17 (s, 6H); ^{13}C NMR (400 MHz, $CDCl_3$) δ = 194.0, 151.6, 146.6, 139.4, 137.3, 136.8, 136.2, 132.9, 131.3, 129.6, 129.2, 128.5, 128.4, 128.0, 54.6, 20.8, 20.6, 18.6, 18.4.

2h: Following the general procedure of method B, **1c** (840 mg, 3.0 mmol), Et_3N (365 mg, 3.6 mmol) and 2-Bromopropiophenone (640 mg, 3.0 mmol) afforded the product **2h** as pale yellow powder (1.01 g, 82%). (Method A afforded a lower yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12-8.10 (m, 2H), 7.53-7.40 (m, 3H), 7.19 (s, 1H), 6.97 (s, 1H), 6.90 (s, 1H), 6.73 (s, 2H), 5.73 (q, J = 7.2 Hz, 1H), 2.63 (s, 3H), 2.30 (s, 3H), 2.28 (s, 3H), 2.17 (s, 3H), 2.03 (s, 6H), 1.03 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 199.6, 151.2, 147.0, 139.8, 138.6, 137.8, 136.9, 136.0, 132.1, 130.9, 129.4, 129.1, 128.6, 128.4, 128.3, 128.2, 56.2, 20.9, 20.5, 18.6, 18.2, 15.1.

2i: Following the general procedure of method B, **1c** (840 mg, 3.0 mmol), Et_3N (365 mg, 3.6 mmol) and 2-bromo-1,2-diphenylethanone (825 mg, 3.0 mmol) afforded the product **2i** as pale yellow powder (1.35 g, 95%). (Method A afforded a lower yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06-8.05 (m, 2H), 7.35-7.30 (m, 6H), 7.07-7.06 (m, 3H), 6.84-6.82 (m, 2H), 6.77 (s, 2H), 6.55 (s, 1H), 2.75 (s, 3H), 2.19 (s, 3H), 2.14 (s, 6H), 2.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.1, 151.8, 146.9, 138.8, 137.8, 137.2, 137.1, 136.6, 134.8, 132.0, 131.9, 131.0, 130.4, 129.8, 129.4, 129.2, 129.1, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 67.9, 20.7, 20.5, 19.0, 18.7, 18.6.

2j: Following the general procedure of method B, **1c** (840 mg, 3.0 mmol), Et_3N (365 mg, 3.6 mmol) and 2-bromopentan-3-one (495 mg, 3.0 mmol) afforded the product **2j** as pale yellow powder (842 mg, 77%). (Method A afforded a lower yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12 (s, 1H), 6.97 (s, 1H), 6.90 (s, 1H), 6.84 (s, 2H), 4.78 (q, J = 6.8 Hz, 1H), 3.05-2.99 (m, 1H), 2.70-2.60 (m, 1H), 2.56 (s, 3H), 2.32 (s, 3H), 2.26 (s, 3H), 2.23 (s, 3H), 2.13 (s, 6H), 1.14-1.10 (m, 3H), 1.00 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 209.5, 151.1, 146.9, 139.1, 138.0, 137.4, 135.8, 130.6, 129.1, 128.6, 128.3, 128.1, 59.7, 33.1, 20.5, 20.3, 18.3, 18.2, 17.8, 14.1, 7.4.

General Procedures for the Synthesis of backbone-substituted imidazolinlium salts.

Method A: α-Amidino ketone (1 eq.) was dissolved in EtOH, the solution was cooled to 0 ^{o}C, and then

$NaBH_4$ (4 eq.) was added. Five mins latter, the mixture was warmed to room temperature and stirred for 1-4 h, The reaction progress was monitored by TLC (PE/EA = 8:1). After full consumption of the reagents, H_2O was added and the mixture was extracted with EA, the combined organic layers was washed with brine and dried with anhydrous $MgSO_4$. After evaporating the solvent, the residue was purified by flash chromatography (PE/EA = 8:1) to give alcohol which was used without characterization. The alcohol was then dissolved in DCM. The solution was cooled to -40 °C and Et_3N (1.1 eq.) was added dropwise. After 5 mins, Tf_2O (1.1 eq.) was added carefully. The mixture was warmed to room temperature and stirred for 5-8 h. The reaction progress was monitored by TLC (DCM/EtOH = 20:1). The volatiles were removed under vacuum and the residue was purified by chromatography on silica gel (DCM/EtOH = 40:1 to 20:1) to give the product.

Method B: α-Amidino ketone (1 eq.) was dissolved in THF and the solution was added dropwise to the solution of RMgX (2 eq.) in THF at room tempreature. The mixture was refluxed for 2-6 h. The reaction progress was monitored by TLC (PE/EA = 8:1). After full consumption of the ketone, the mixture was quenched with saturated NH_4Cl aqueous solution and extracted with EA, The combined organic layers was washed with brine and dried with anhydrous $MgSO_4$. After evaporating the solvent, the residue was dissolved in DCM. The solution was cooled to -40 °C and Et_3N (1.1 eq.) was added dropwise. After 5 mins, Tf_2O (1.1 eq.) was added carefully. The mixture was warmed to room temperature and stirred for 5-8 h. The reaction progress was monitored by TLC (DCM/EtOH = 20:1). The volatiles were removed under vacuum and the residue was purified by chromatography on silica gel (DCM/EtOH = 40:1 to 20:1) to give the product.

Method C: $LiAlH_4$ (4 eq.) was dissolved in THF and cooled to 0 ^oC, the solution of α-amidino ester (1 eq.) was added dropwise. The mixture was warmed to room tempreature and stirred for 2-6 h. The reaction progress was monitored by TLC (PE/EA = 8:1). After full consumption of the ester, the mixture was quenched with NaOH (4 mol/L) and extracted with EA, The combined organic layers was washed with brine and dried with anhydrous $MgSO_4$. After evaporating the solvent, the residue was purified by flash chromatography (PE/EA = 8:1) to give alcohol which was used without characterization. The alcohol was then dissolved in DCM and cooled to -40 °C, Et_3N (1.1 eq.) was added dropwise. After 5 mins, Tf_2O (1.1 eq.) was added carefully. The mixture was warmed to room

temperature and stirred for 5-8 h. The reaction progress was monitored by TLC (DCM/EtOH = 20:1). The volatiles were removed under vacuum and the residue was purified by chromatography on silica gel (DCM/EtOH = 40:1 to 20:1) to give the product.

Method D: α-Amidino ester (1 eq.) in THF was added dropwise to the solution of RMgX (4 eq.) in THF at room tempreature. The mixture was refluxed for 2-6 h. The reaction progress was monitored by TLC (PE/EA = 8:1). After full consumption of the ester, the mixture was quenched with saturated NH_4Cl and extracted with EA, The combined organic layers was washed with brine and dried with anhydrous $MgSO_4$. After evaporating the solvent, the residue was dissolved in DCM without any purification. The solution was cooled to -40 °C and Et_3N (1.1 eq.) was added dropwise. After 5 mins, Tf_2O (1.1 eq.) was added carefully. The mixture was warmed to room temperature and stirred for 5-8 h. The reaction progress was monitored by TLC (DCM/EtOH = 20:1). The volatiles were removed under vacuum and the residue was purified by chromatography on silica gel (DCM/EtOH = 40:1 to 20:1) to give the product.

3a: Following the general procedure of method C, **2b** (550 mg, 1.5 mmol) and $LiAlH_4$ (228 mg, 6.0 mmol) then Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **3a** as white powder (397 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.20 (s, 1H), 6.98 (s, 4H), 4.51 (s, 4H), 2.53 (s, 12H), 2.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =159.3, 140.6, 134.9, 129.9, 120.4 (q, J = 320 Hz), 51.5, 21.0, 17.5; HRMS (EI): m/z [M – OTf]$^+$ calcd. for $C_{21}H_{27}N_2^+$: 307.2174, found: 307.2175.

3b: Following the general procedure of method C, **2c** (570 mg, 1.5 mmol) and $LiAlH_4$ (228 mg, 6.0 mmol) then Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **3b** as white powder (402 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.33 (s, 1H), 6.98-6.97 (m, 4H), 5.10-5.00 (m, 1H), 4.71 (t, J = 11.6 Hz, 1H), 3.92 (dd, J = 9.2 Hz, 11.6 Hz, 1H), 2.35-2.30 (m, 18H), 1.47 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.8, 140.5, 140.3, 135.4, 135.1, 134.5, 130.3, 130.0, 129.9, 128.4, 120.4 (q, J = 320 Hz), 60.4, 57.9, 21.0, 20.9, 18.3, 17.9, 17.4; HRMS (EI): m/z [M – OTf]$^+$ calcd. for $C_{22}H_{29}N_2^+$: 321.2331, found: 321.2321.

3c: Following the general procedure of method A, **2d** (598 mg, 1.5 mmol) and $NaBH_4$ (227 mg, 6.0 mmol) then Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **3c** as white powder (478 mg, 60%). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.57 (s, 1H), 7.43-7.32 (m, 5H), 7.05 (S, 2H), 6.97 (s, 1H), 6.71 (s, 1H), 5.98 (dd, J = 9.2 Hz, 12.8 Hz, 1H), 4.98 (t, J = 12.8 Hz, 1H), 4.58 (dd, J = 9.2 Hz, 12.8 Hz, 1H), 2.55 (br, 9H), 2.34 (s, 3H), 2.24 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.4, 140.7, 140.2, 135.6, 135.0, 133.3, 130.3, 130.1, 130.0, 129.8, 129.3, 128.6, 128.5, 120.4 (q, J = 320 Hz), 67.1, 56.5, 53.4, 21.0, 20.9, 18.4, 17.7; HRMS (EI): m/z $[M - OTf]^+$ calcd. for $C_{27}H_{31}N_2^+$: 383.2487; found: 383.2487.

3d: Following the general procedure of method A, **2a** (568 mg, 1.5 mmol) and $NaBH_4$ (227 mg, 6.0 mmol) then Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **3d** as white powder (346 mg, 45%). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.54 (s, 1H), 6.98-6.95 (m, 4H), 4.99 (dd, J = 10.4 Hz, 12.4 Hz, 1H), 4.54 (t, J = 12.4 Hz, 1H), 4.07 (dd, J = 10.4 Hz, 12.4 Hz, 1H), 2.44 (s, 6H), 2.36 (s, 6H), 2.30 (s, 6H), 0.96 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.7, 140.3, 139.5, 135.0, 134.2, 134.1, 133.5, 131.4, 130.6, 130.4, 129.9, 129.8, 120.4 (q, J = 320 Hz), 72.0, 53.2, 34.9, 259, 20.8, 20.7, 19.1, 18.7, 17.7, 17.5; HRMS (EI): m/z $[M - OTf]^+$ calcd. for $C_{25}H_{35}N_2^+$: 363.2800, found: 363.2786.

3e: Following the general procedure of method A, **2e** (700 mg, 1.5 mmol) and $NaBH_4$ (227 mg, 6.0 mmol) then Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **3e** as white powder (540 mg, 60%). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.54 (s, 1H), 7.80-7.78 (m, 2H), 7.59-7.52 (m, 9H), 7.39-7.13 (m, 11H), 6.87-6.85 (m, 2H), 5.20 (dd, J = 8.4 Hz, 12.0 Hz, 1H), 4.24 (t, J = 12.0 Hz, 1H), 3.79 (dd, J = 8.4 Hz, 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.1, 137.6, 137.4, 137.3, 134.0, 132.9, 131.4, 131.3, 131.2, 130.1, 129.8, 129.6, 129.5, 129.2, 129.1, 129.0, 128.8, 128.7, 128.5, 128.4, 127.8, 127.0, 126.5, 120.6 (q, J = 320 Hz), 66.4, 58.9; HRMS (EI): m/z $[M - OTf]^+$ calcd. for $C_{33}H_{27}N_2^+$: 451.2174, found: 451.2169.

3f: Following the general procedure of method D, **2f** (574 mg, 1.5 mmol) and PhMgBr (6.0 mL, 1.0 mol/L) then Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **3f** as white powder (281 mg, 30%). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.72 (s, 1H), 8.24-8.23 (m, 1H),

7.97-7.93 (m, 2H), 7.83-7.73 (m, 4H), 7.64-7.56 (m, 7H), 7.42-7.32 (m, 10H), 5.33 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.6, 134.2, 133.7, 131.0, 130.8, 130.6, 129.7, 129.4, 129.1, 128.4, 128.3, 128.2, 128.1, 127.2, 126.7, 126.4, 125.9, 125.6, 124.9, 120.7 (q, J = 320 Hz), 120.5, 120.4, 81.7, 66.5; HRMS (EI): m/z $[M - OTf]^+$ calcd. for $C_{35}H_{27}N_2^+$: 475.2174, found: 475.2181.

3g: Following the general procedure of method A, **2h** (620 mg, 1.5 mmol) and $NaBH_4$ (227 mg, 6.0 mmol) then Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **3g** as white powder (582 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) (A mixture of two isomers with a proportion of cis : trans = 1 : 0.15, chemical shifts differ between them are marked by *maj*. and *min*.) δ = 8.93 (s, 0.15H, *min*.), 8.62 (s, 1H, *maj*.), 7.41-7.33 (m, 5.75H), 7.04-7.00 (m, 2.3H), 6.91 (s, 0.15H, *min*.), 6.84 (s, 2H, *maj*.), 6.72 (s, 0.15H, *min*.), 6.20 (d, J =12.0 Hz, 1H, *maj*.), 5.40-5.32 (m, 1H, *maj*.), 5.29 (d, J = 10.4 Hz, 0.15H, *min*.), 5.05-4.98 (m, 0.15H, *min*.), 2.52 (s, 0.45H, *min*.), 2.47 (s, 6H, *maj*.), 2.45 (s, 3H, *maj*.), 2.42 (s, 0.9H, *min*.), 2.33 (s, 0.9H, *min*.), 2.32 (s, 6H, *maj*.), 2.20 (s, 3H, *maj*.), 1.86 (s, 0.45H, *min*.), 1.51 (d, J = 6.8 Hz, 0.45H, *min*.), 1.04 (d, J = 6.8 Hz, 3H, *maj*.).

3h: Following the general procedure of method A, **2i** (712 mg, 1.5 mmol) and $NaBH_4$ (227 mg, 6.0 mmol) then Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **3h** as white powder (320 mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$) (A mixture of two isomers with a proportion of trans : cis = 1 : 0.33, chemical shifts differ between them are marked by *maj*. and *min*.) δ = 9.16 (s, 1H, *maj*.), 8.85 (s, 0.33H, *min*.), 7.41-7.33 (m, 10H, *maj*.), 7.12-7.09 (m, 3.3H, *min*.), 6.98 (s, 2H, *maj*.), 6.90 (s, 1.32H, *min*.), 6.76 (s, 2H, *maj*.), 6.61 (s, 0.66H, *min*.), 5.96 (s, 2H, *maj*.), 2.67 (s, 6H, *maj*.), 2.51 (s, 1.98H, *min*.), 2.24 (s, 7.98H), 1.96 (s, 6H, *maj*.), 1.59 (s, 1.98H, *min*.).

3i: Following the general procedure of method A, **2j** (547 mg, 1.5 mmol) and $NaBH_4$ (227 mg, 6.0 mmol) then Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **3i** as white powder (307 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) (A mixture of two isomers with a proportion of trans : cis = 1 : 0.76, chemical shifts differ between them are marked by *maj*. and *min*.) δ = 8.75 (s, 1H, *maj*.), 8.46 (s, 0.76H, *min*.), 6.98 (s, 7.04H), 5.03-4.95 (m, 0.76H, *min*.), 4.85-4.79 (m, 0.76H, *min*.), 4.44-4.37 (m, 1H, *maj*), 4.16-4.11 (m, 1H, *maj*), 2.38-2.30 (m, 31.68H), 1.90-1.81 (m, 2H, *maj*), 1.68-1.63 (m, 1.52H, *min*), 1.63 (d, J = 6.8 Hz, 3H, *maj*), 1.35 (d, J = 6.8 Hz, 2.28H, *min*),

0.97-0.89 (m, 5.28H); HRMS (EI): m/z [M – OTf]$^+$ calcd. for $C_{24}H_{33}N_2^+$: 349.2644, found: 349.2640.

3j: Following the general procedure of method B, **2g** (598 mg, 1.5 mmol) and EtMgBr (3.0 mL, 1.0 mol/L) then Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **3j** as white powder (303 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.77-8.75 (m, 1H), 7.45-7.35 (m, 3H), 7.11-7.10 (m, 2H), 7.02 (s, 3H), 6.69 (s, 1H), 4.98 (d, J = 12.4 Hz, 1H), 4.34 (d, J = 12.4 Hz, 1H), 2.53-2.42 (m, 11H), 2.32 (s, 3H), 2.28 (s, 3H), 1.13 (s, 3H), 0.70 (t, 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.4, 140.5, 140.4, 138.4, 136.3, 134.9, 134.3, 132.3, 130.3, 130.1, 130.0, 129.7, 129.6, 129.2, 129.1, 128.5, 127.3, 126.7, 120.3 (q, J = 320 Hz), 78.6, 58.0, 32.4, 20.9, 20.8, 19.5, 17.8, 17.7, 17.1, 8.0; HRMS (EI): m/z [M – OTf]$^+$ calcd. for $C_{29}H_{35}N_2^+$: 411.2800, found: 411.2809.

3k: Following the general procedure of method D, **2b** (550 mg, 1.5 mmol) and EtMgBr (6.0 mL, 1.0 mol/L) then Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **3k** as white powder (269 mg, 37%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.66 (s, 1H), 6.98 (s, 4H), 4.04 (s, 2H), 2.40 (s, 6H), 2.37 (s, 6H), 2.30 (s, 6H), 2.27-2.18 (m, 2H), 2.06-1.97 (m, 2H), 0.86 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.0, 140.3, 140.1, 136.4, 134.6, 130.3, 129.9, 129.8, 129.6, 120.3 (q, J = 320 Hz), 77.6, 61.2, 28.8, 20.8, 20.7, 19.5, 17.5, 7.6; HRMS (EI): m/z [M – OTf]$^+$ calcd. for $C_{25}H_{35}N_2^+$: 363.2800, found: 363.2785.

3l: Following the general procedure of method D, **2b** (550 mg, 1.5 mmol) and PhMgBr (6.0 mL, 1.0 mol/L) then Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **3l** as white powder (730 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.17 (s, 1H), 7.45-7.34 (m, 6H), 7.26-7.23 (m, 4H), 7.00 (s, 2H), 6.76 (s, 2H), 4.94 (s, 2H), 2.43 (s, 6H), 2.31 (s, 3H), 2.22 (s, 3H), 1.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.5, 140.7, 140.6, 137.6, 137.2, 134.9, 130.5, 130.4, 130.1, 130.0, 129.6, 128.5, 128.3, 120.4 (q, J = 320 Hz), 79.0, 64.1, 20.9, 20.7, 20.3, 18.7; HRMS (EI): m/z [M – OTf]$^+$ calcd. for $C_{33}H_{35}N_2^+$: 459.2800, found: 459.2795.

3m: Following the general procedure of method B, **2h** (620 mg, 1.5 mmol) and MeMgBr (3.0 mL, 1.0 mol/L) then Et_3N (167 mg, 1.65 mmol) and Tf_2O (167 mg, 1.65 mmol) afforded the product **3m** as white powder (278 mg, 33%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.10 (s, 1H), 7.66-7.64 (m, 2H),

7.52-7.47 (m, 3H), 7.00-6.96 (m, 3H), 6.79 (s, 1H), 5.02 (q, J = 6.8 Hz, 1H), 2.52 (s, 3H), 2.50 (s, 3H), 2.41 (s, 3H), 2.30 (s, 3H), 2.25 (s, 3H), 1.84 (s, 3H), 1.56 (s, 3H), 0.83 (d, J = 6.8 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ = 161.6, 140.4, 140.0, 136.7, 136.4, 136.2, 135.0, 134.9, 131.5, 130.7, 130.6, 130.3, 129.8, 129.5, 128.6, 128.5, 127.8, 120.4 (q, J = 320 Hz), 74.5, 71.8, 22.4, 21.3, 20.8, 20.6, 20.4, 20.0, 18.8, 12.1; HRMS (EI): m/z $[M - OTf]^+$ calcd. for $C_{29}H_{35}N_2^+$: 411.2800, found: 411.2796.

3n: Following the general procedure of method B, **2j** (547 mg, 1.5 mmol) and EtMgBr (3.0 mL, 1.0 mol/L) then Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **3n** as white powder (277 mg, 37%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.60 (s, 1H), 6.98 (s, 4H), 4.52 (q, J = 6.8 Hz, 1H), 2.41-2.22 (m, 19 H), 2.16-2.08 (m, 2H), 1.92-1.85 (m, 1H), 1.33 (d, J = 6.8 Hz, 3H), 0.96 (t, J = 7.2 Hz, 3H), 0.67 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.1, 140.2, 140.1, 136.5, 136.3, 135.2, 134.9, 130.7, 130.5, 130.2, 130.1, 130.0, 128.4, 120.4 (q, J = 320 Hz), 78.5, 67.4, 29.6, 22.9, 20.8, 20.7, 19.8, 19.2, 18.5, 18.1, 13.5, 7.2, 7.1; HRMS (EI): m/z $[M - OTf]^+$ calcd. for $C_{26}H_{37}N_2^+$: 377.2957, found: 377.2949.

3o: Following the general procedure of method D, **2c** (570 mg, 1.5 mmol) and PhMgBr (6.0 mL, 1.0 mol/L) then Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **3o** as white powder (626 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.29 (s, 1H), 7.43-7.26 (m, 7H), 7.26-7.24 (m, 1H), 7.00-6.95 (m, 4H), 6.89 (s, 1H), 6.61 (s, 1H), 5.88 (q, J = 6.8 Hz, 1H), 2.47 (s, 3H), 2.41 (s, 3H), 2.31 (s, 6H), 2.21 (s, 3H), 1.66 (s, 3H), 0.83 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.9, 140.5, 140.4, 137.8, 137.3, 137.1, 135.5, 134.6, 133.5, 131.2, 130.7, 130.5, 130.4, 129.8, 129.7, 129.5, 129.4, 128.4, 128.2, 127.9, 120.4 (q, J = 320 Hz), 81.1, 67.8, 53.4, 22.3, 20.8, 20.7, 19.8, 19.1, 18.7, 12.3; HRMS (EI): m/z $[M - OTf]^+$ calcd. for $C_{34}H_{37}N_2^+$: 473.2957, found: 473.2954.

3p: Following the general procedure of method D, **2d** (664 mg, 1.5 mmol) and MeMgBr (6.0 mL, 1.0 mol/L) then Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **3p** as white powder (395 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.01 (s, 1H), 7.36-7.35 (m, 3H), 7.24-7.22 (m, 2H), 7.05-7.03 (m, 2H), 6.95 (s, 2H), 6.77 (s, 1H), 5.86 (s, 1H), 2.59 (s, 3H), 2.47 (s, 3H), 2.43 (s, 3H), 2.32-2.31 (m, 6H), 2.21 (s, 3H), 1.63 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ = 159.6, 140.2, 139.4, 137.3, 135.8, 133.9, 133.6, 130.7, 130.5, 130.4, 130.3, 129.8, 129.2, 129.0, 128.2, 127.5, 120.4 (q, J = 320 Hz), 77.4, 74.8, 25.7, 22.9, 20.7, 20.6, 19.6, 19.4, 19.0; HRMS (EI): m/z [M – OTf]$^+$ calcd. for $C_{29}H_{35}N_2^+$: 411.2800, found: 411.2799.

3q: Following the general procedure of method B, **2h** (620 mg, 1.5 mmol) and EtMgBr (3.0 mL, 1.0 mol/L) then Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **3q** as white powder (418 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.62 (s, 1H), 7.40-7.36 (m, 5H), 7.02-7.00 (m, 2H), 6.85 (s, 2H), 6.21 (d, J =12.0 Hz, 1H), 5.40-5.32 (m, 1H), 2.47 (s, 6H), 2.45 (s, 3H), 2.32 (s, 6H), 2.20 (s, 3H), 1.04 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.1, 140.4, 139.6, 135.6, 135.2, 134.6, 133.8, 130.5, 130.2, 130.1, 129.8, 129.5, 129.3, 128.7, 128.6, 120.5 (q, J = 320 Hz),, 70.3, 63.4, 20.9, 20.7, 19.0, 18.1, 13.4; HRMS (EI): m/z [M – OTf]$^+$ calcd. for $C_{28}H_{33}N_2^+$: 397.2644, found: 397.2628.

3r: Following the general procedure of method B, **2i** (712 mg, 1.5 mmol) and EtMgBr (3.0mL, 1.0 mol/L) then Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **3r** as white powder (410 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.85 (s, 1H), 7.14-7.07 (m, 10H), 6.91 (s, 4H), 6.61 (s, 2H), 2.51 (s, 6H), 2.24 (s, 6H), 1.58 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.3, 139.7, 130.7, 130.6, 130.5, 129.8, 129.4, 128.9, 128.8, 128.7, 128.2, 120.6 (q, J = 320 Hz), 71.1, 20.7, 19.4; HRMS (EI): m/z [M – OTf]$^+$ calcd. for $C_{33}H_{35}N_2^+$: 459.2800, found: 459.2795.

General Procedures for the Synthesis of imidazolinlium salts from unsymmetrical formamidines.

Method A: Formamidine (1 eq.) was dissolved in DMF, and to the suspension NaH (60% suspension in mineral oil, 1.2 eq.) was added at 0 °C. After 5 mins the resulting mixture was warmed to room temperature and stirred for 1-2 h. Then olefin oxide (1 eq.) was added dropwise to the solution at 0 °C. After 5 mins the mixture was warmed to room temperature and stirred for 8-12 h. The reaction progress was monitored by TLC (PE/EA = 8:1/4:1). After full conversion of the corresponding olefin oxide, H_2O was added and the mixture was extracted with EA, The combined organic layer was dried over anhydrous $MgSO_4$. The volatiles were removed under vacuum, and the residue was purified by flash chromatography (PE/EA = 8:1/4:1) to give the alcohol which was used without characterization. The alcohol was then dissolved in DCM and cooled to -40 °C, 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 reaction progress was monitored by TLC (DCM/EtOH = 20:1). The volatiles were removed under vacuum, and the residue was purified by chromatography on silica gel (DCM/EtOH = 40:1 to 20:1) to give the product.

Method B: The mixture of formamidine (1 eq.), α-bromo ketone (1 eq.) and K_2CO_3 (1.2 eq.) in acetone was refluxed for 10-14 h, then filtered. The volatiles were removed under vacuum, and the residue was purified by flash chromatography on silica gel (PE/EA = 8:1/4:1) to give the crude α-amidino ketone which was then dissolved in EtOH without any characterization. The mixture was cooled to 0 °C and $NaBH_4$ (4 eq.) was added. 5 mins latter, it was warmed to room tempreature and stirred for 1-4 h. Then H_2O was added and the mixture was extracted with EA, the combined organic layers was washed with brine and dried with anhydrous $MgSO_4$. After evaporating the solvent, the residue was dissolved in DCM without any purification. The solution was cooled to -40 °C, and Et_3N (1.1 eq.) was added dropwise. After 5 mins, Tf_2O (1.1 eq.) was added carefully. The mixture was warmed to room temperature and stirred for 5-8 h. The reaction progress was monitored by TLC (DCM/EtOH = 20:1). The volatiles were removed under vacuum, and the residue was purified by chromatography on silica gel (DCM/EtOH = 40:1 to 20:1) to give the product.

4b: Following the general procedure of method B, **1d** (440 mg, 1.5 mmol), 2-bromoacetophenone (300 mg, 1.5 mmol) and K_2CO_3 (250 mg, 1.8 mmol) affored the crude α-amidino ketone, then $NaBH_4$ (227 mg, 6.0 mmol) subsequently Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **4b** as white powder (377 mg, 46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.24 (s, 1H), 7.76-7.74 (m, 1H), 7.42-7.35 (m, 7H), 7.32-7.26 (m, 3H), 5.83 (dd, J = 8.4 Hz, 12.4 Hz, 1H), 5.42 (t, J = 12.4 Hz, 1H), 4.74 (dd, J = 8.4 Hz, 12.4 Hz, 1H), 3.37 (sept, J = 6.8 Hz, 1H), 2.53 (s, 3H), 2.48 (sept, J = 6.8 Hz, 1H), 1.53 (d, J = 6.8 Hz, 3H), 1.31 (d, J = 6.8 Hz, 3H), 1.06 (d, J = 6.8 Hz, 3H), 0.35 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.4, 147.0, 146.7, 134.0, 132.7, 132.6, 132.1, 131.3, 130.5, 130.4, 129.6, 128.7, 128.4, 127.6, 126.1, 125.4, 124.6, 120.6 (q, J = 320 Hz), 69.2, 57.5, 29.7, 29.0, 28.9, 25.9, 25.3, 24.2, 22.4, 18.0; HRMS (EI): m/z $[M - OTf]^+$ calcd. for $C_{28}H_{33}N_2^+$: 397.2644, found: 397.2641.

4c: Following the general procedure of method B, **1e** (400 mg, 1.5 mmol), 2-bromoacetophenone (300 mg, 1.5 mmol) and K_2CO_3 (250 mg, 1.8 mmol) afforded the crude α-amidino ketone, then $NaBH_4$ (227 mg, 6.0 mmol) subsequently Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **4c** as white powder (366 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) (A mixture of two enantiomers with a proportion of 1 : 1) δ = 9.02 (s, 1H), 8.14 (s, 1H), 7.49-7.29 (m, 18H), 7.18-7.15 (m, 2H), 6.95 (s, 2H), 6.91 (s, 2H), 5.78 (dd, J = 8.4 Hz, 12.4 Hz, 1H), 5.12 (dd, J = 8.4 Hz, 12.4 Hz, 1H), 4.95 (q, J = 6.8 Hz, 1H), 4.68 (t, J = 12.4 Hz, 1H), 4.47-4.44 (m, 2H), 3.99-3.89 (m, 2H), 3.96 (dd, J = 8.4 Hz, 12.4 Hz, 1H), 3.89 (dd, J = 8.4 Hz, 12.4 Hz, 1H), 2.33-2.25 (m, 18H), 1.82 (d, J = 6.8 Hz, 3H), 1.59 (d, J = 6.8 Hz, 3H).

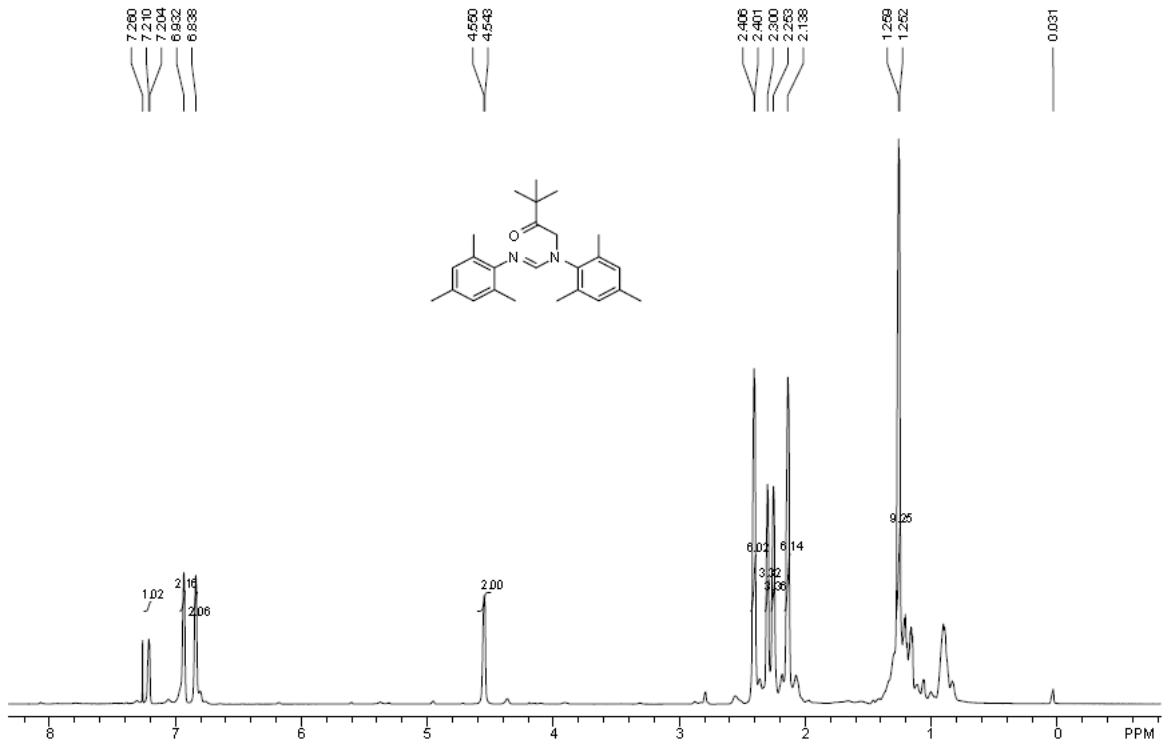
4d: Following the general procedure of method A, **1e** (400 mg, 1.5 mmol), NaH (60% suspension in mineral oil, 72 mg, 1.8 mmol) and styrene oxide (180 mg, 1.5 mmol) then Et_3N (167 mg, 1.65 mmol) and Tf_2O (465 mg, 1.65 mmol) afforded the product **4d** as white powder (303 mg, 39%). ^{1}H NMR (400 MHz, $CDCl_3$) (A mixture of two enantiomers with a proportion of 1 : 0.66, chemical shifts differ between them are marked by *maj*. and *min*.) δ = 8.48 (s, 1H, *maj*.), 8.37 (s, 0.66H, *min*.), 7.56-7.45 (m, 8.3H), 7.34-7.19 (m, 4.98H), 7.04-7.02 (m, 1.66H), 6.94-6.90 (m, 3.32H), 6.68-6.66 (m, 1.66H), 5.57 (q, J = 6.8 Hz, 1H, *maj*.), 5.50-5.36 (m, 2.32H), 4.56-4.49 (m, 1.66H), 4.19-4.11 (m, 1.66H), 2.42-2.41 (m, 4.98H), 2.21-2.20 (m, 4.98H), 1.91 (d, J = 6.8 Hz, 1.98H, *min*.), 1.88 (d, J = 6.8 Hz, 3H, *maj*.), 1.66-1.64 (m, 4.98H).

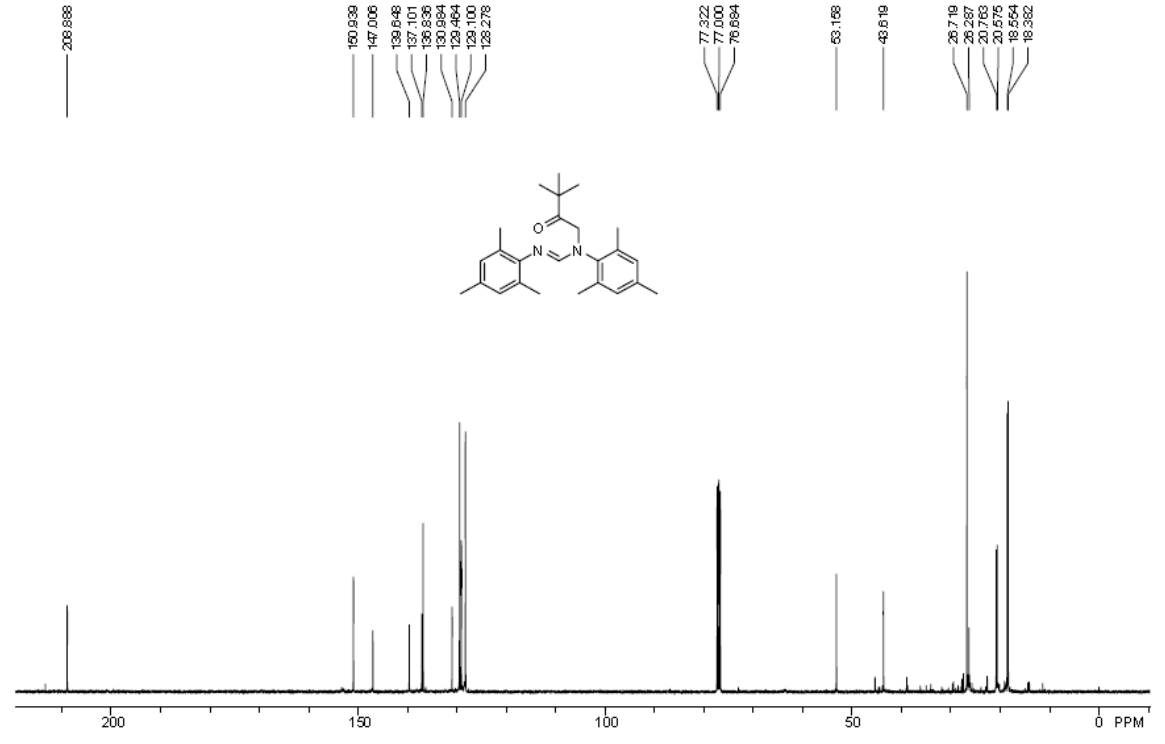
(*S*, *S*)-**5a** and (*R*, *S*)-**5b**: KHMDS (0.6 mL, 1.0 M in hexane) was added dropwise to a suspension of **4d** (260 mg, 0.5 mmol) and CS_2 (152 mg, 2.0 mmol) in THF (5 mL) at -78°C. After 10 mins, the mixture was warmed to room temperature and stirred for 4 h. Evacuated the solvent in vacuo and the residue was purified by column chromatography on silica gel (PE/EA = 4:1) to give the product (*S*, *S*)-**5a** and (*R*, *S*)-**5b** as brownish red powders ((*S*, *S*)-**5a** 67 mg, 30%, (*R*, *S*)-**5b** 66 mg, 30%). (*S*, *S*)-**5a:** ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62-7.60 (m, 2H), 7.45-7.34 (m, 7H), 6.85 (s, 1H), 6.57 (s, 1H), 5.72 (q, J = 6.8 Hz, 1H), 4.93 (dd, J = 7.6 Hz, 11.6 Hz, 1H), 4.02 (dd, J = 7.6 Hz, 11.6 Hz, 1H), 3.79 (t, J = 11.6 Hz, 1H), 2.52 (s, 3H), 2.17 (s, 3H), 1.92 (d, J = 6.8 Hz, 1H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.5, 139.3, 138.0, 137.0, 136.2, 136.0, 129.9, 129.8, 129.7, 129.6, 129.0, 128.9, 128.8, 128.2, 127.7, 64.6, 54.5, 48.4, 20.9, 19.3, 19.0, 15.0; HRMS (EI): m/z [M^+] calcd. for $C_{27}H_{28}N_2S_2^+$: 444.1694,

found: 444.1685; $[\alpha]^{20}_{D}$ –218.4 (*c* = 1.000, $CHCl_3$). (*R*, *S*)-**5b:** ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74-7.72 (m, 2H), 7.52-7.40 (m, 3H), 7.33-7.20 (m, 3H), 6.96-6.94 (m, 2H), 6.86 (s, 1H), 6.57 (s, 1H), 5.78 (q, *J* = 6.8 Hz, 1H), 4.98 (dd, *J* = 6.4 Hz, 11.6 Hz, 1H), 4.29 (t, *J* = 11.6 Hz, 1H), 3.66 (dd, *J* = 6.4 Hz, 11.6 Hz, 1H), 2.58 (s, 3H), 2.17 (s, 3H), 1.82 (d, *J* = 6.8 Hz, 1H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.5, 139.3, 138.0, 137.0, 136.2, 136.0, 129.9, 129.8, 129.7, 129.6, 129.0, 128.9, 128.8, 128.2, 127.7, 64.6, 54.5, 48.4, 20.9, 19.3, 19.0, 15.0; HRMS (EI): m/z [M^+] calcd. for $C_{27}H_{28}N_2S_2^+$: 444.1694, found: 444.1692; $[\alpha]^{20}_{D}$ –92.3 (*c* = 0.950, $CHCl_3$).

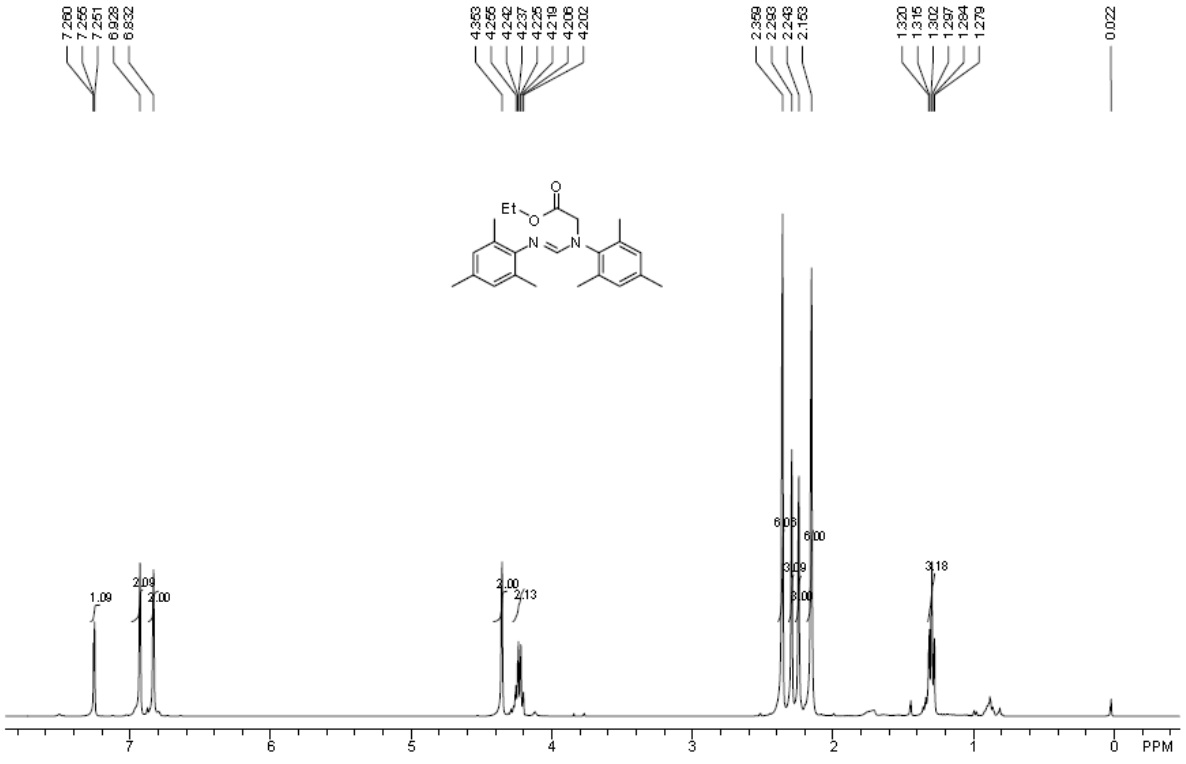
NMR Spectra:

2a





2b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4.202
2.399
2.293
2.243
2.163
1.320
1.315
1.302
1.297
1.284
1.279
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O
N
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2.09
2.00
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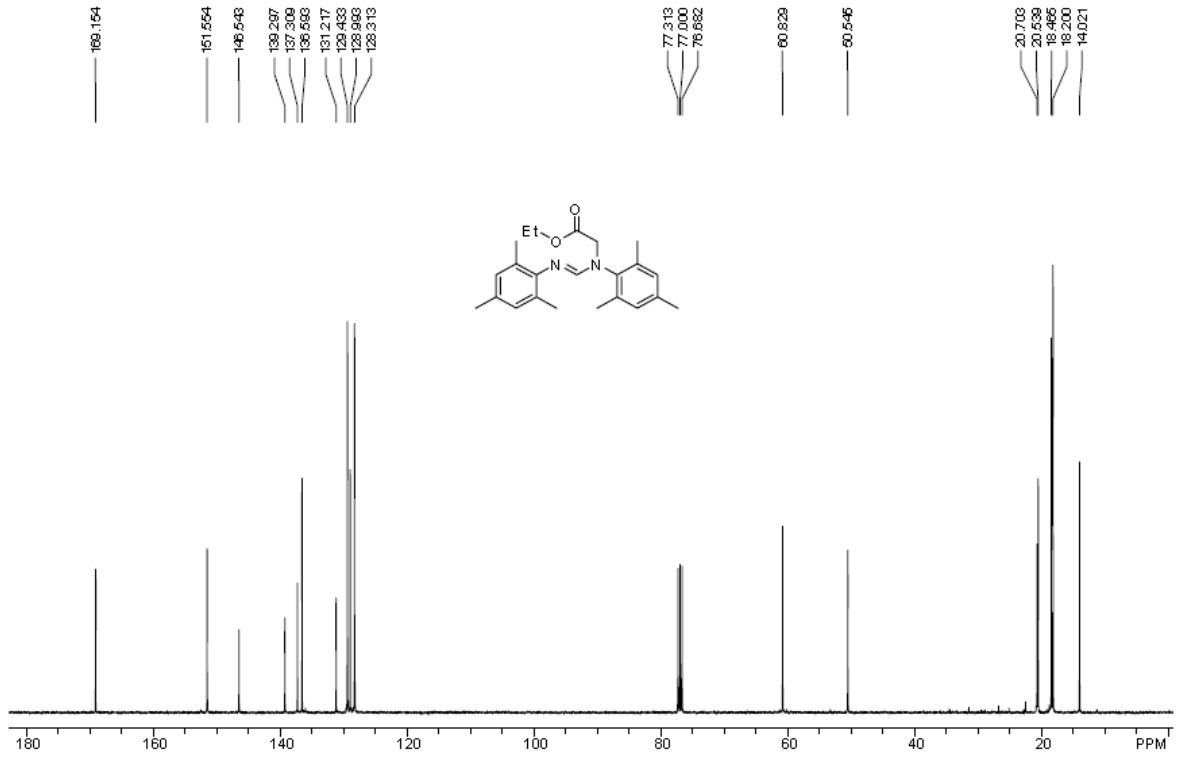
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20.703
20.539
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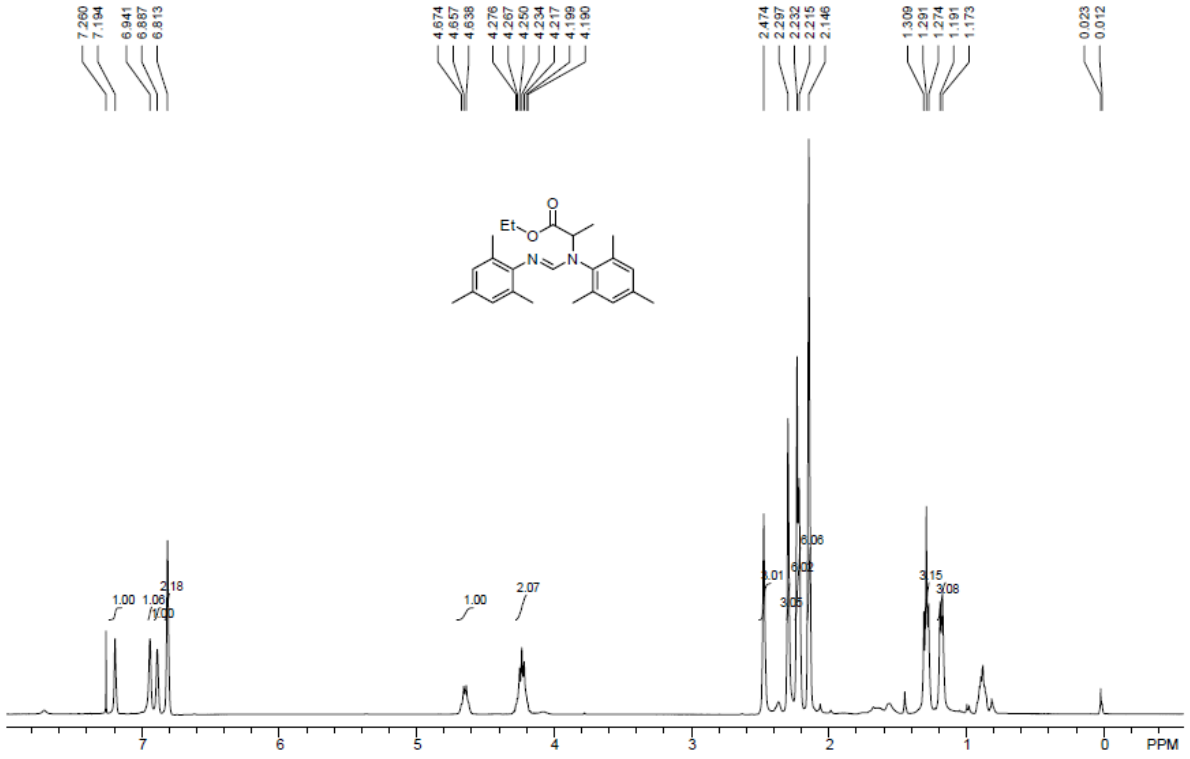
140
120
100
80
60
40
20
PPM

2c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4.180
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2.297
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1.291
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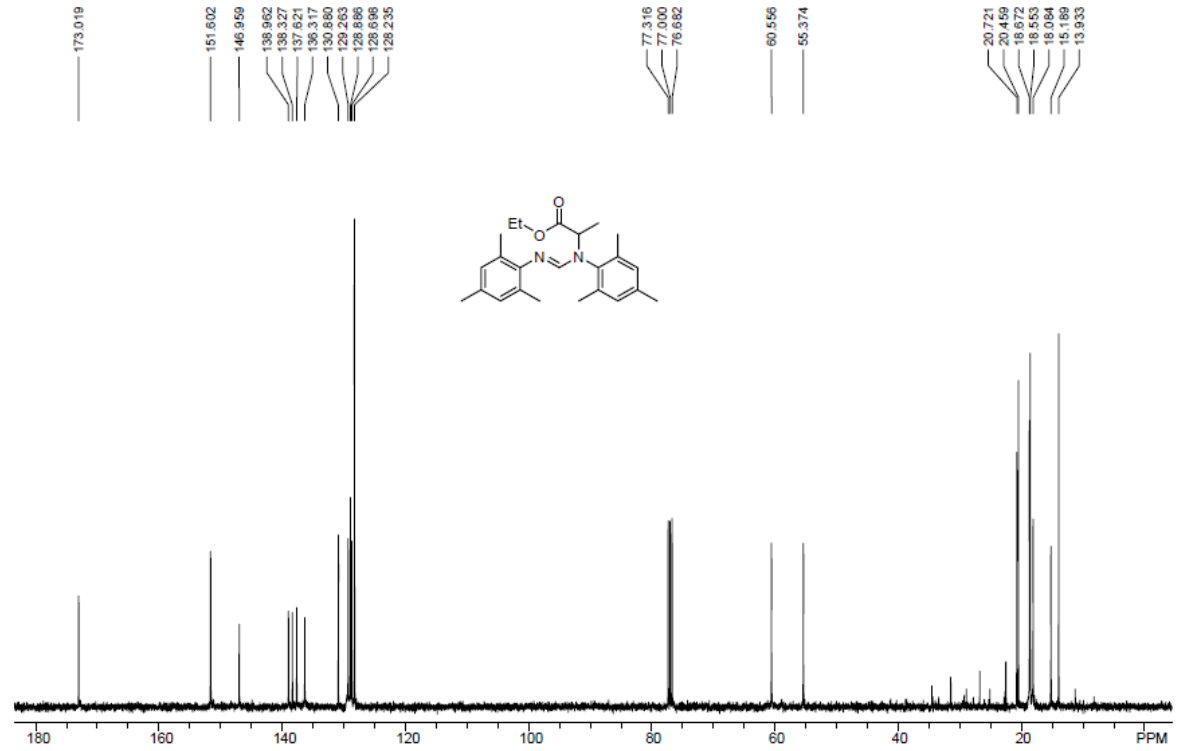
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77.000
76.682
60.556
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20.721
20.459
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20
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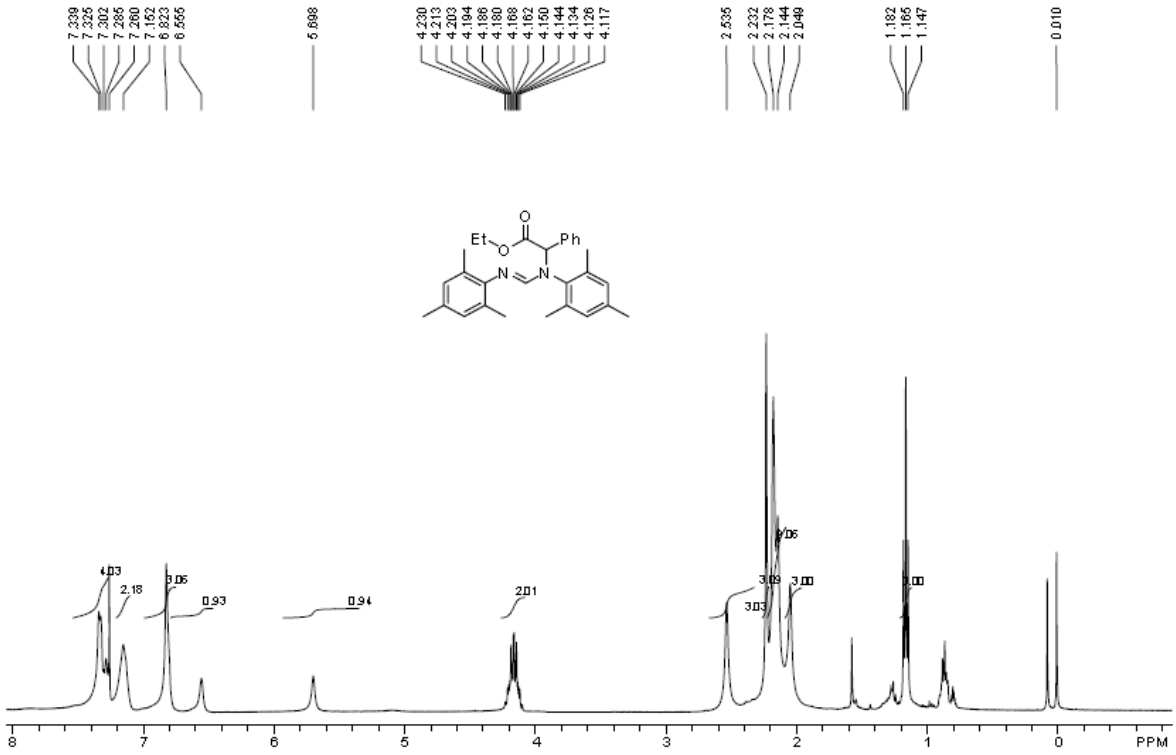
2d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4.180
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4.162
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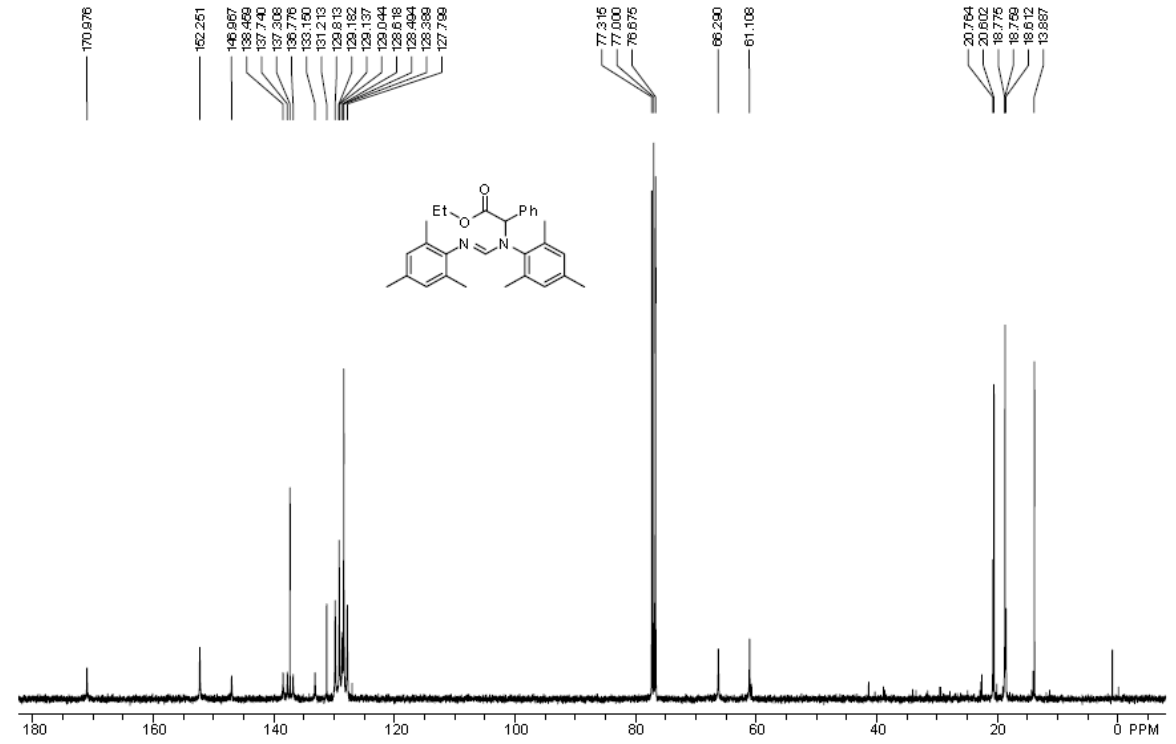
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77.000
76.675
66.290
61.108
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20.602
18.776
18.759
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20
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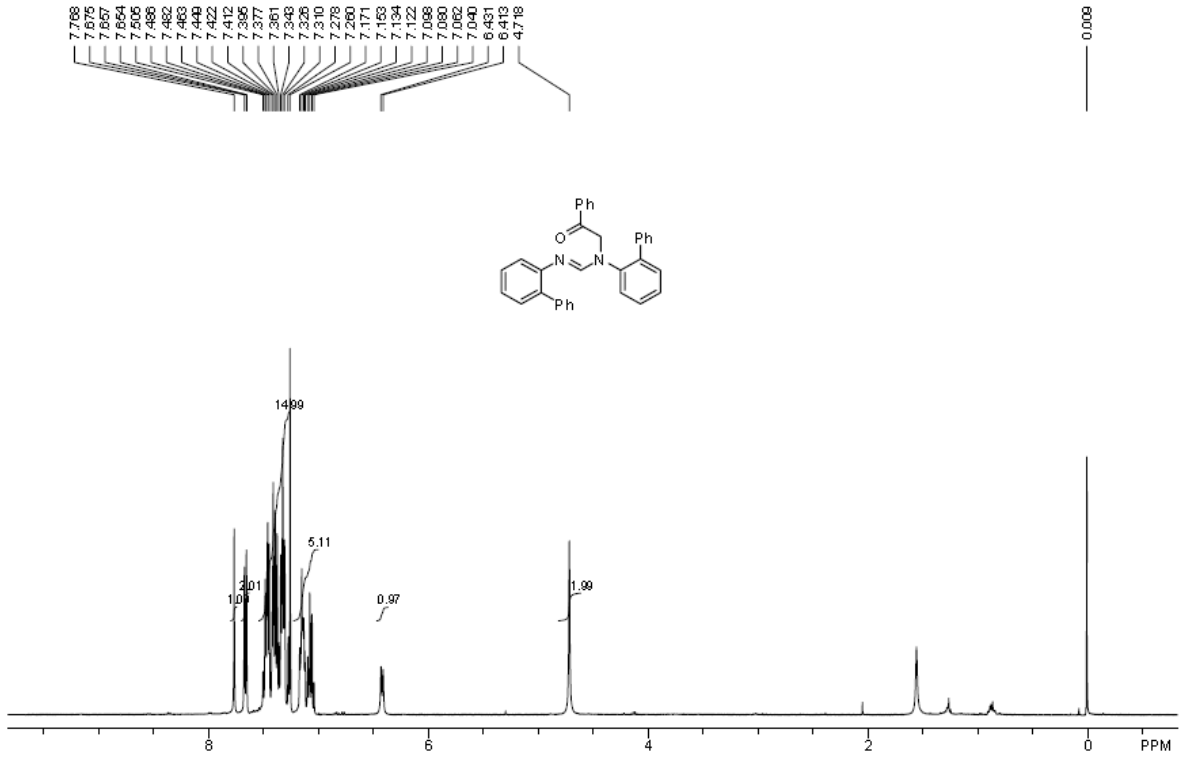
2e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7.310
7.278
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7.122
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7.040
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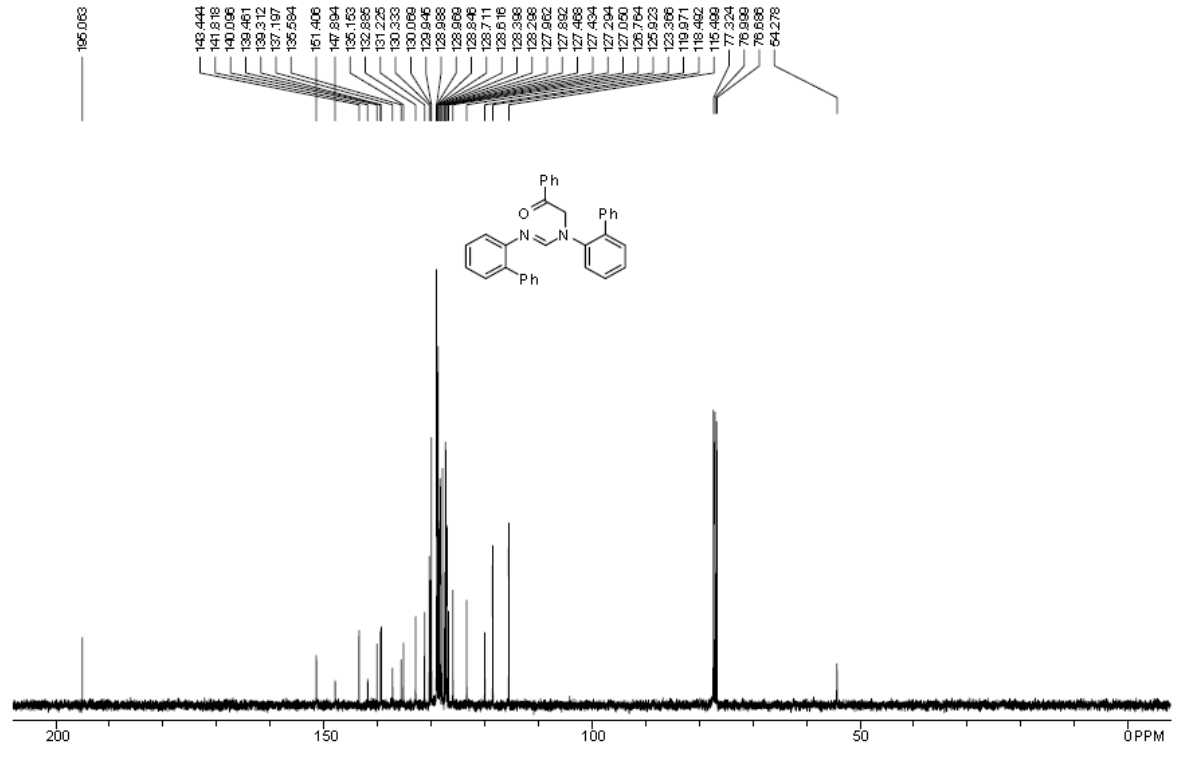
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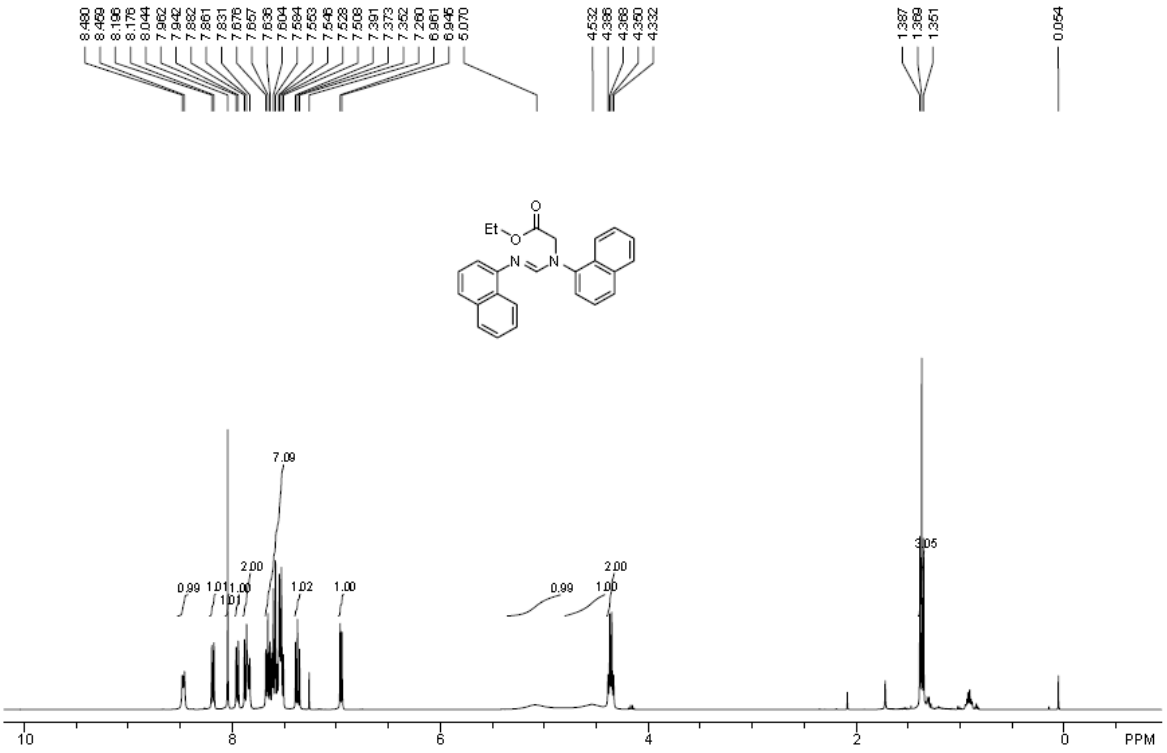
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7.508
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7.260
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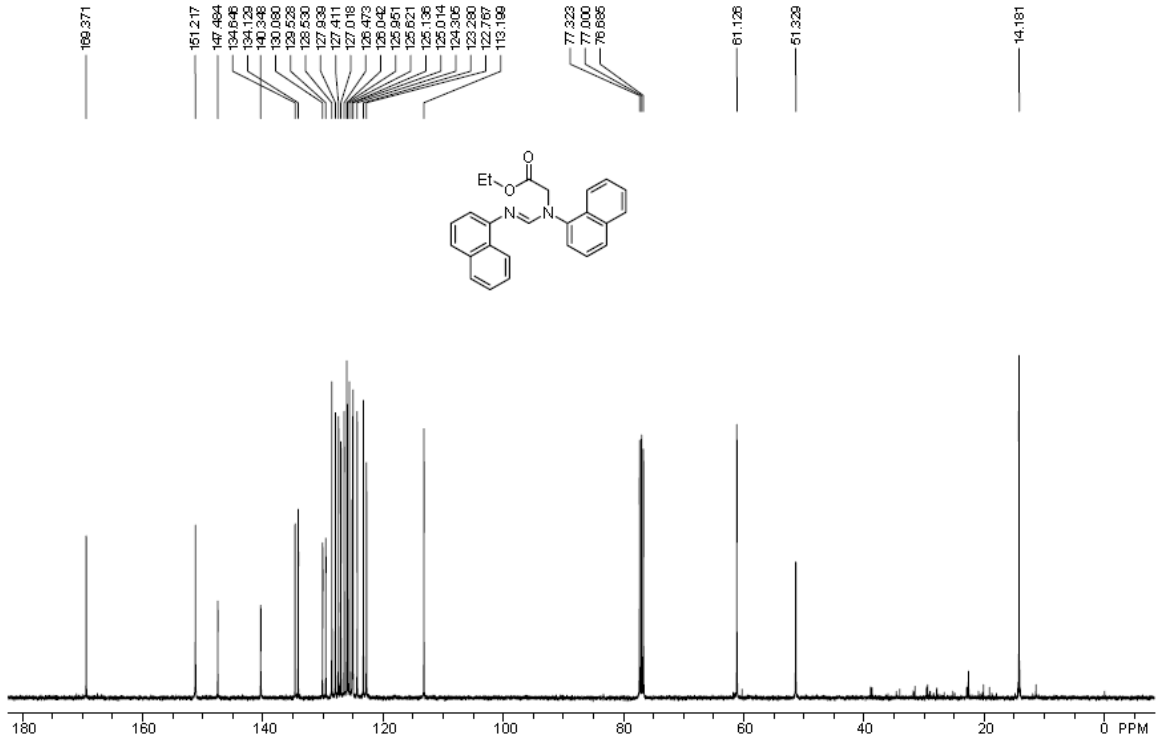
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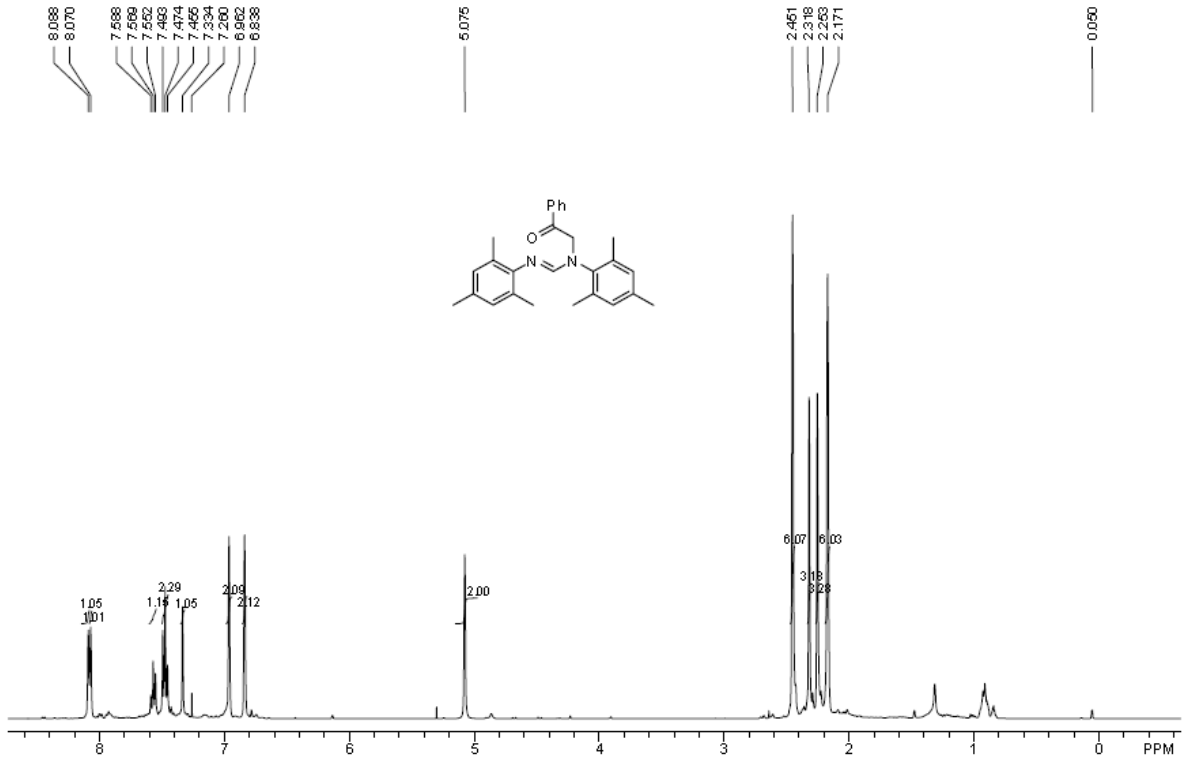
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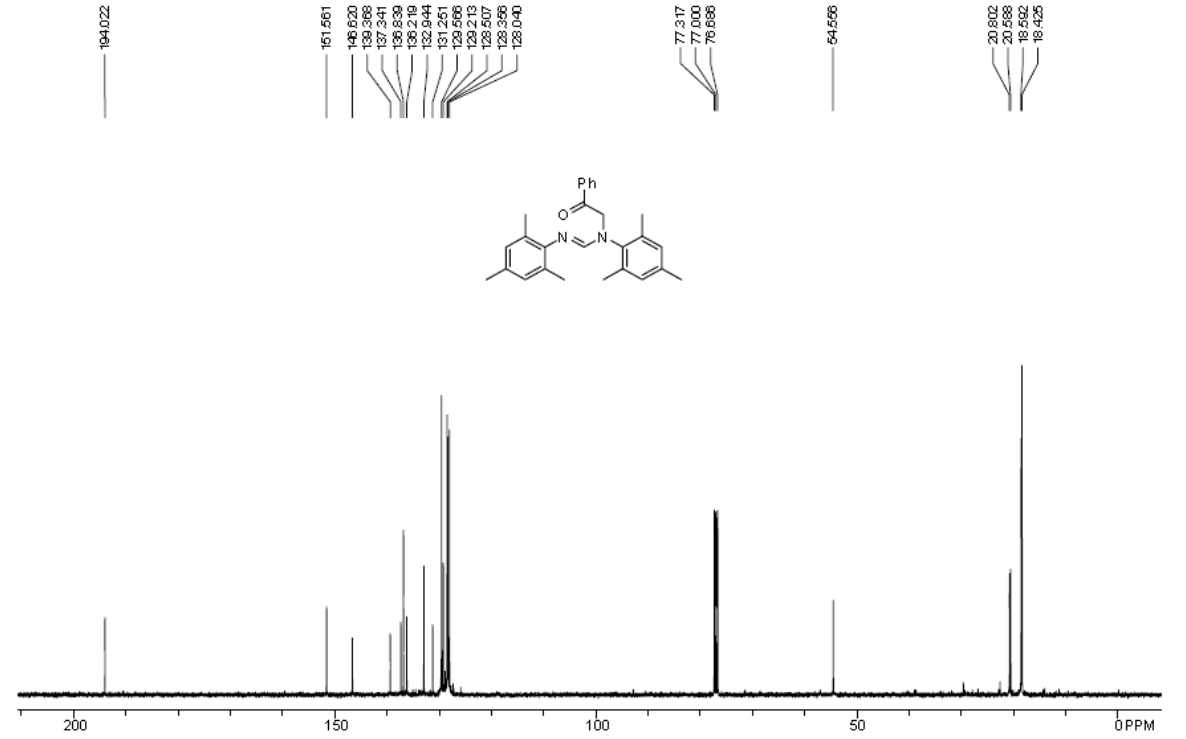
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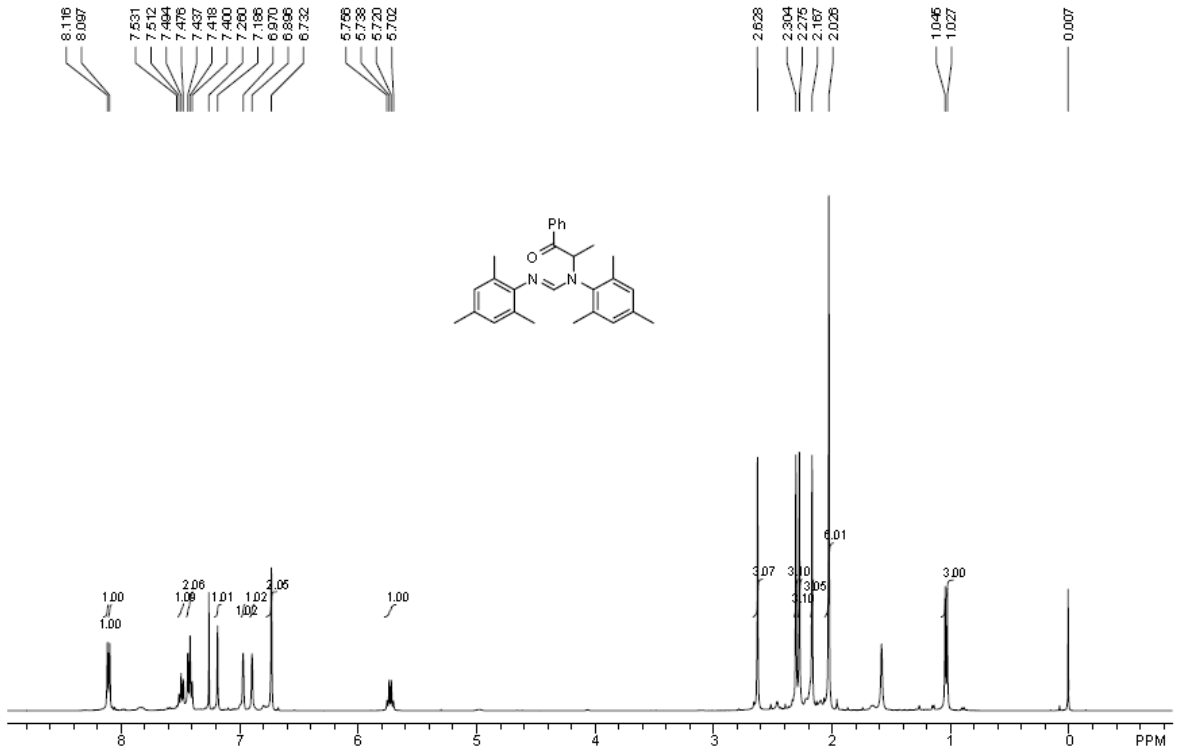
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6.732
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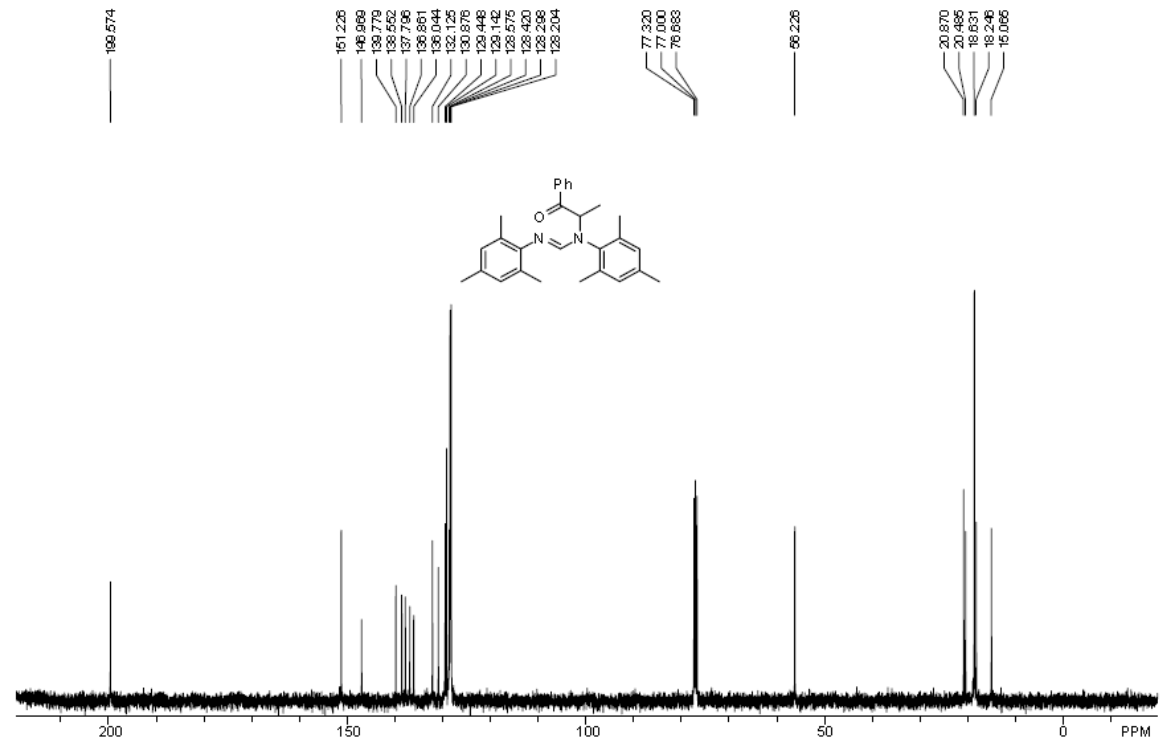
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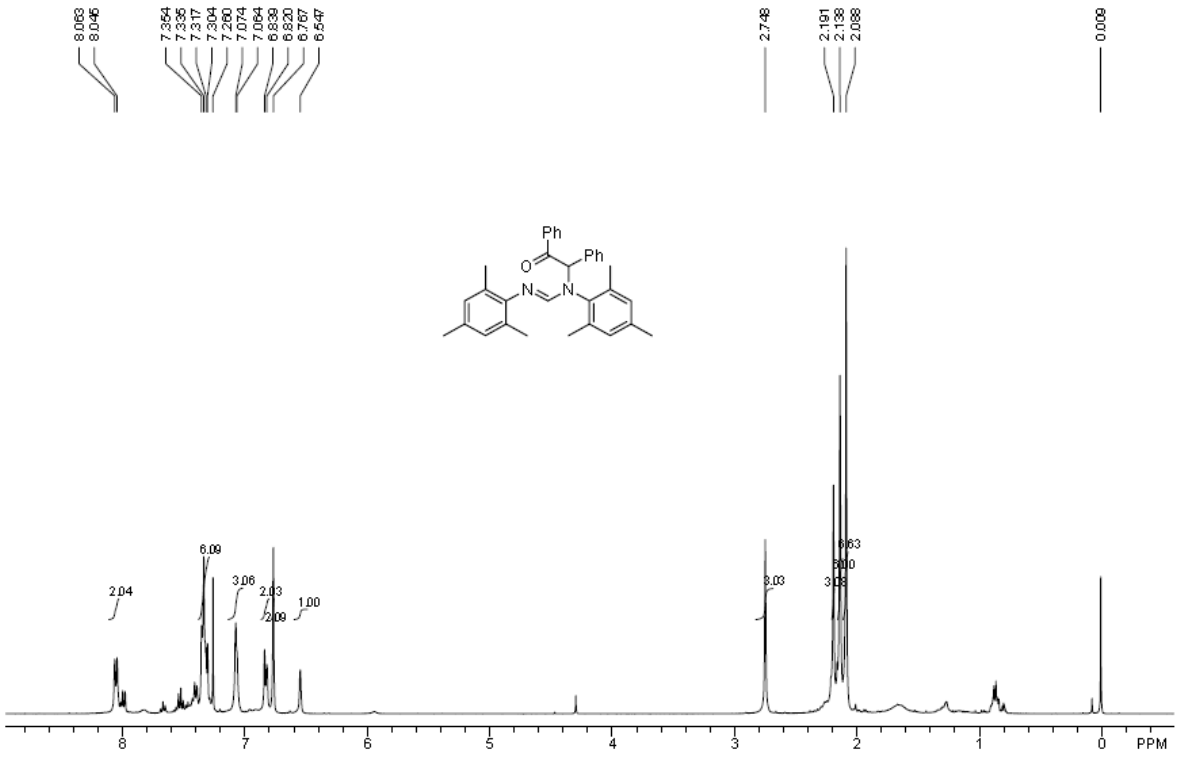
2i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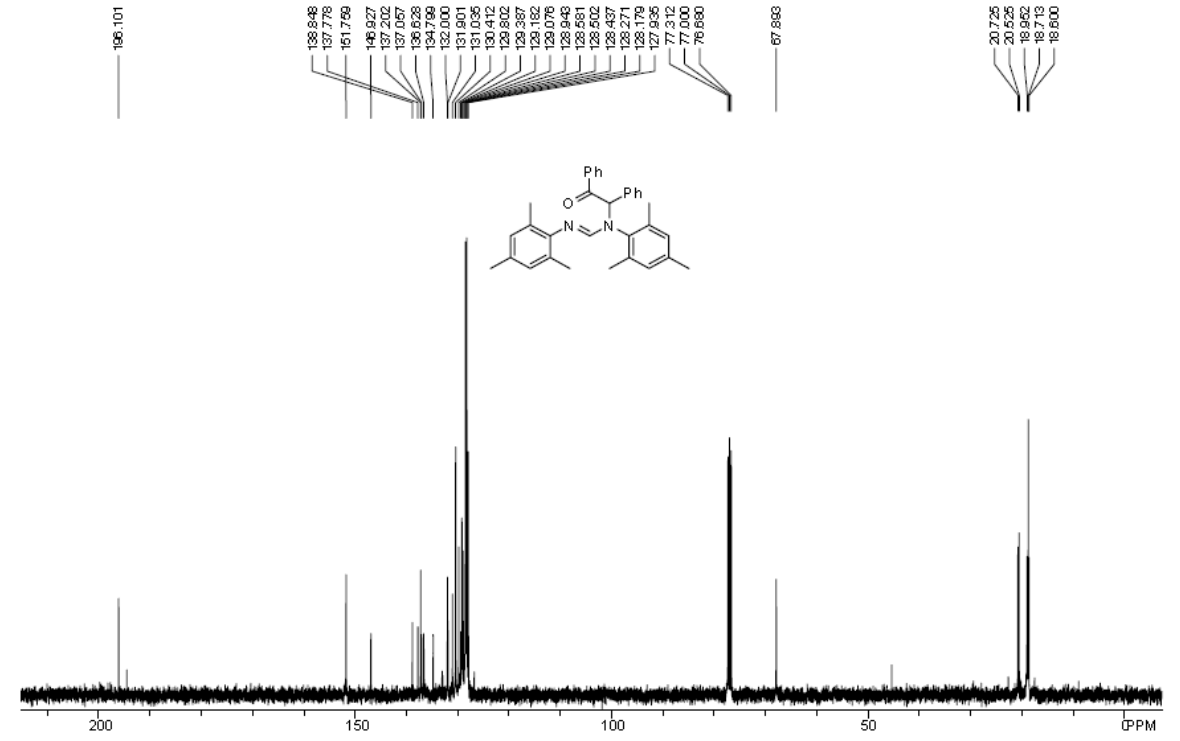
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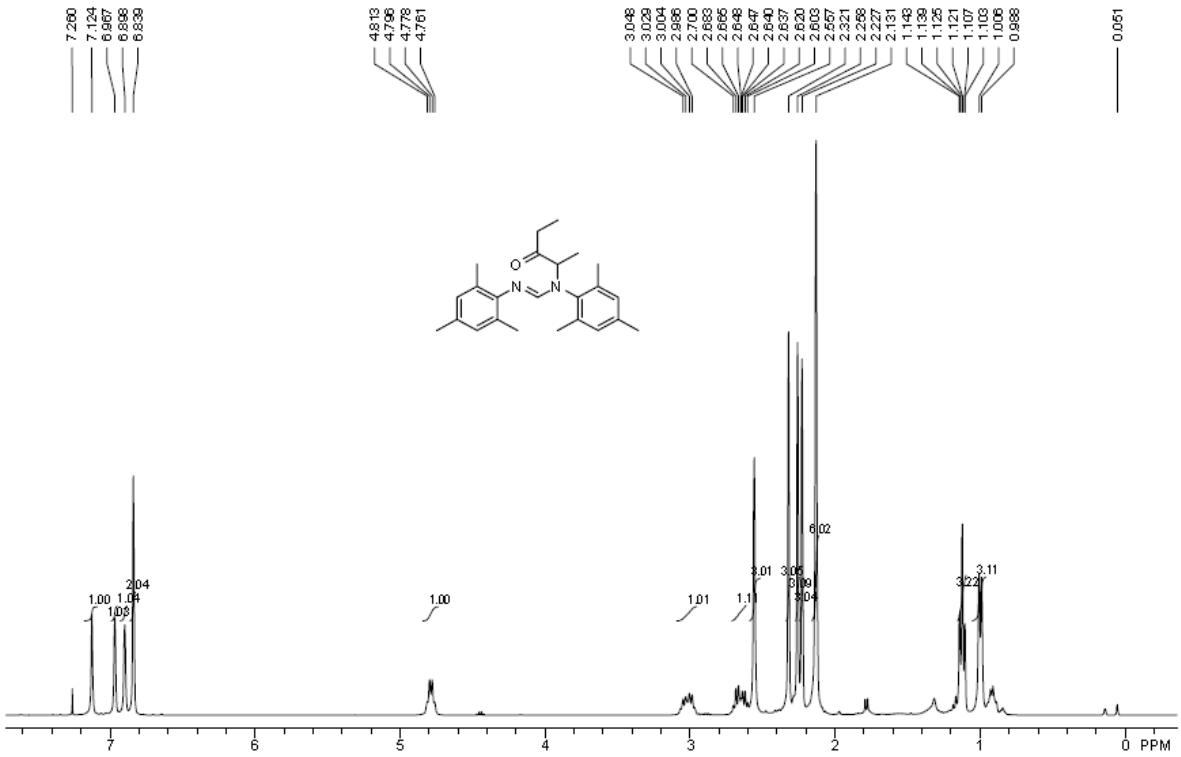
2j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2.04
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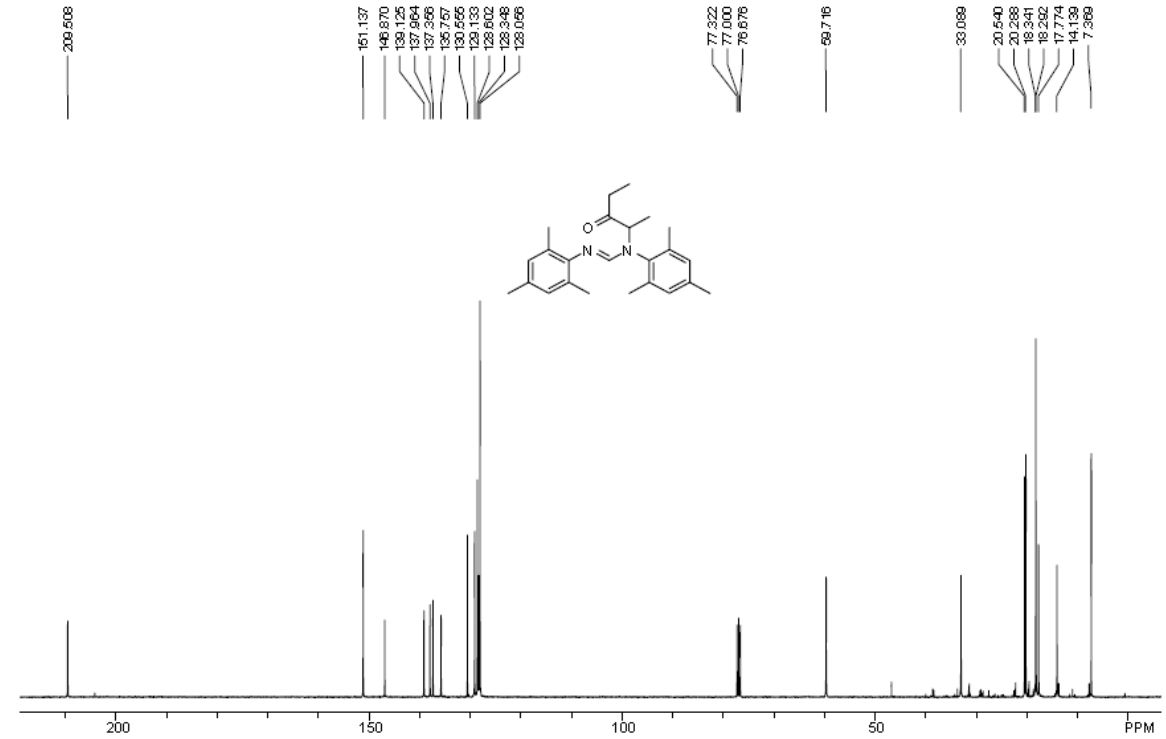
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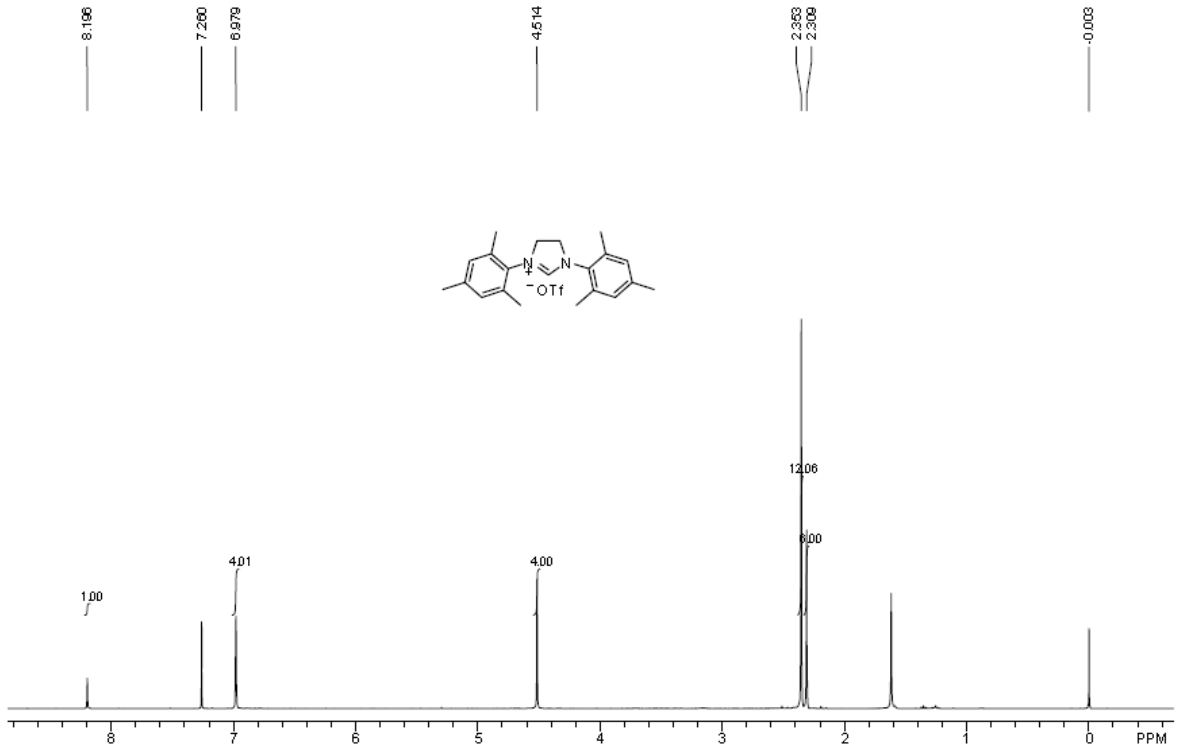
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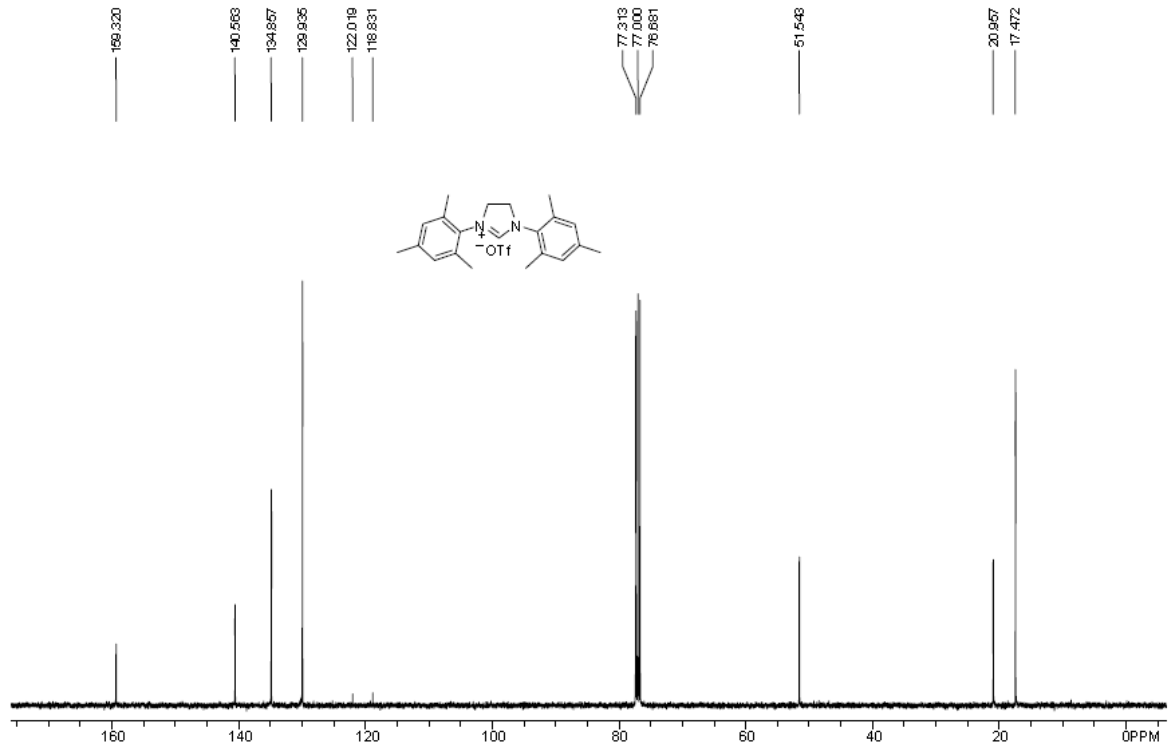
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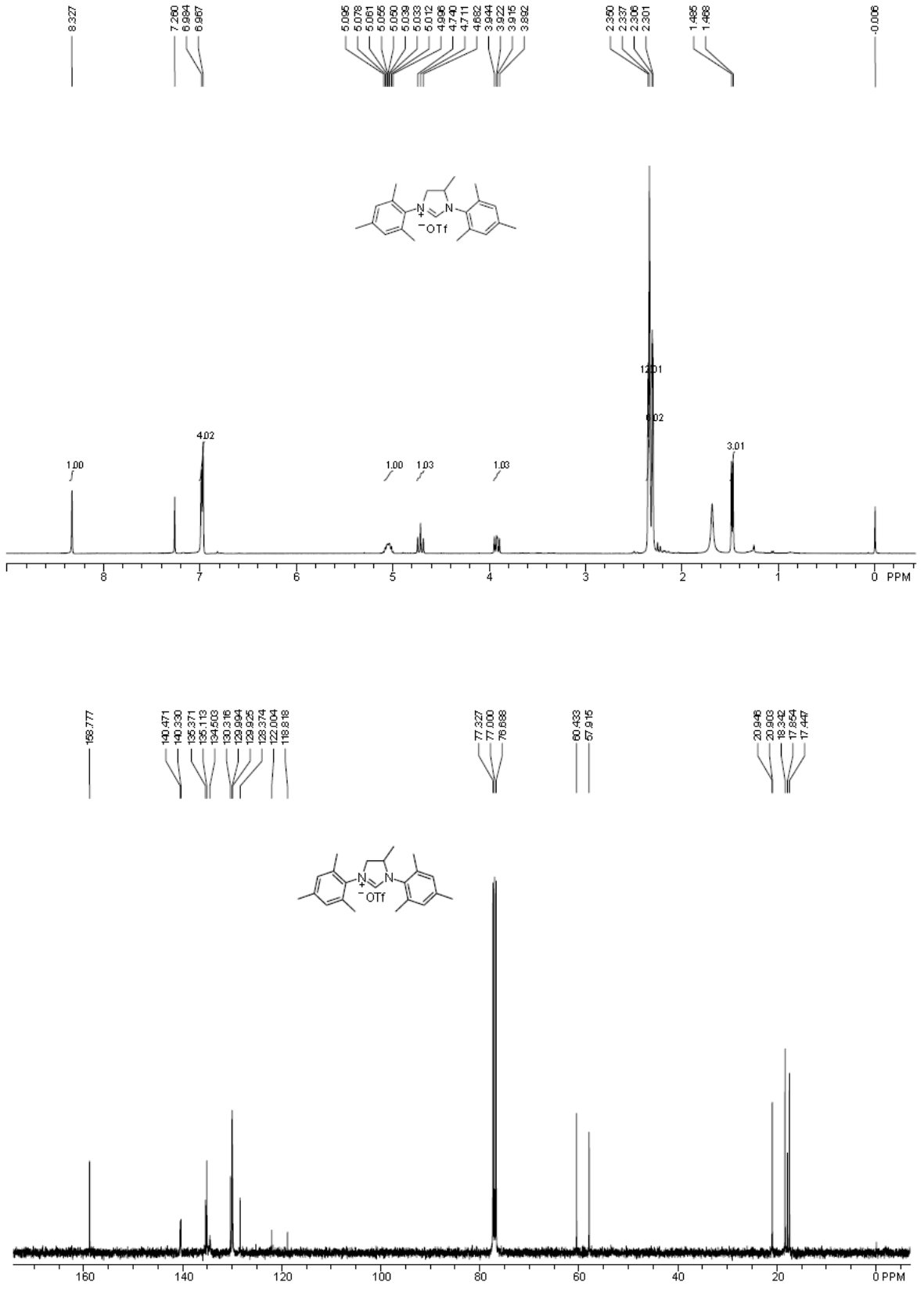
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1.00
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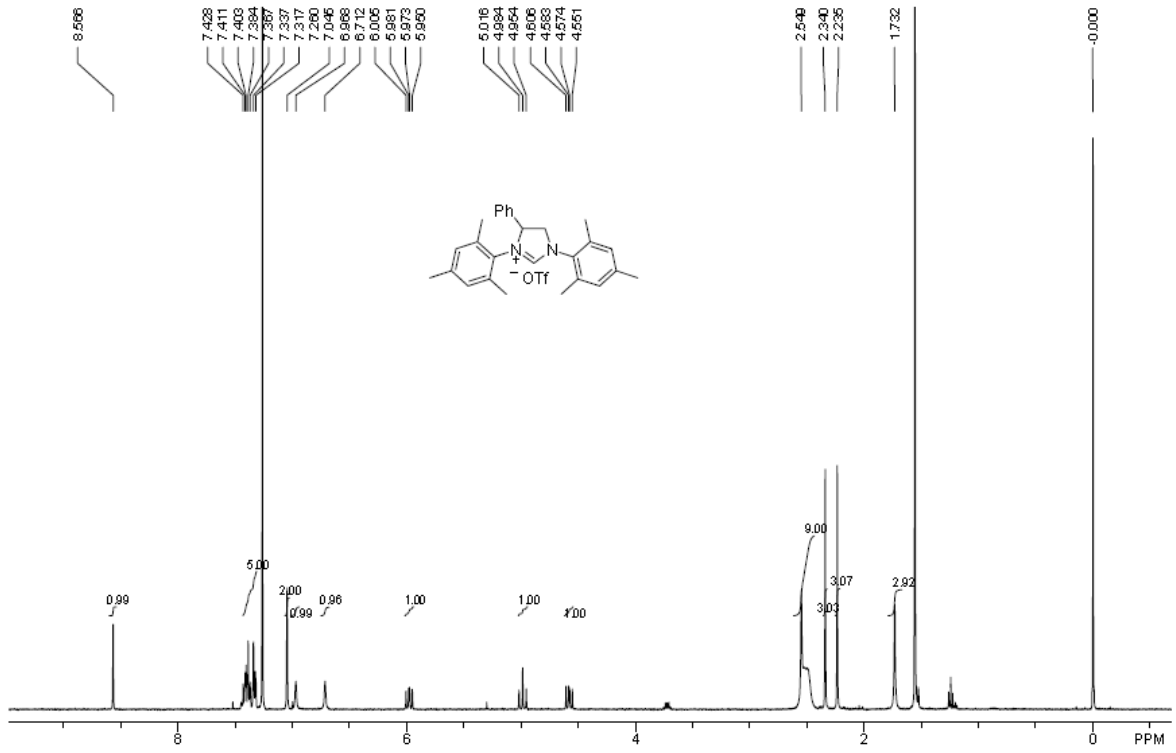
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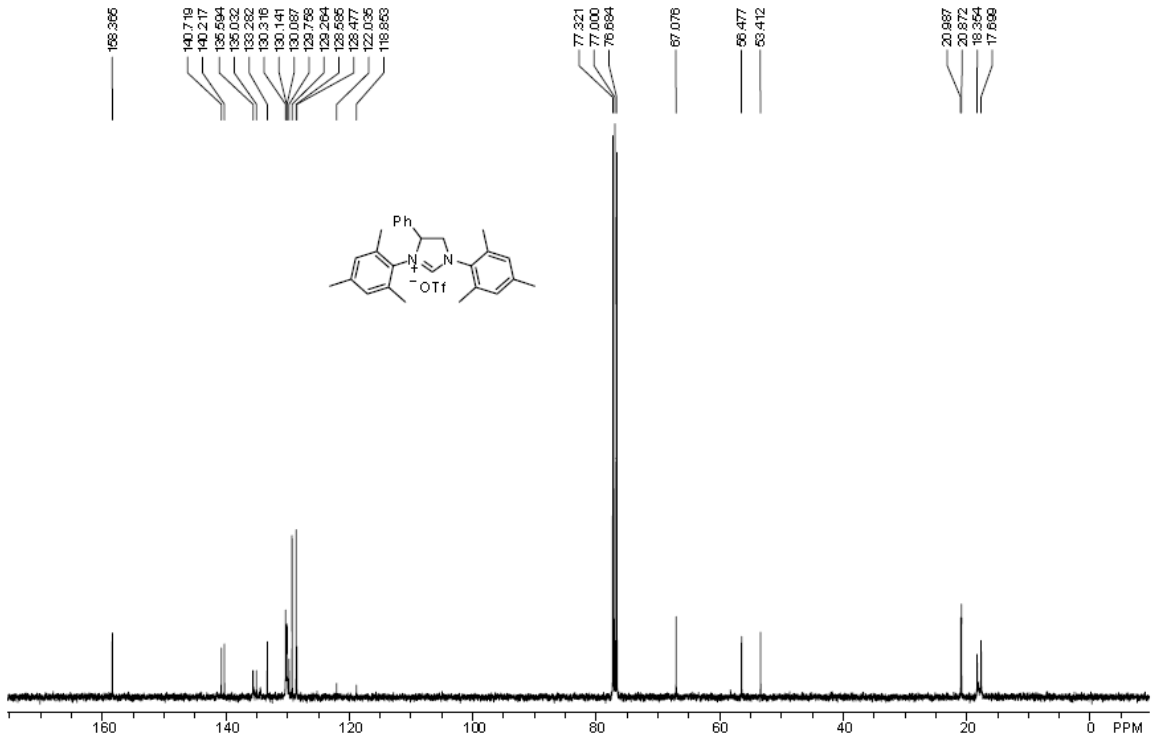
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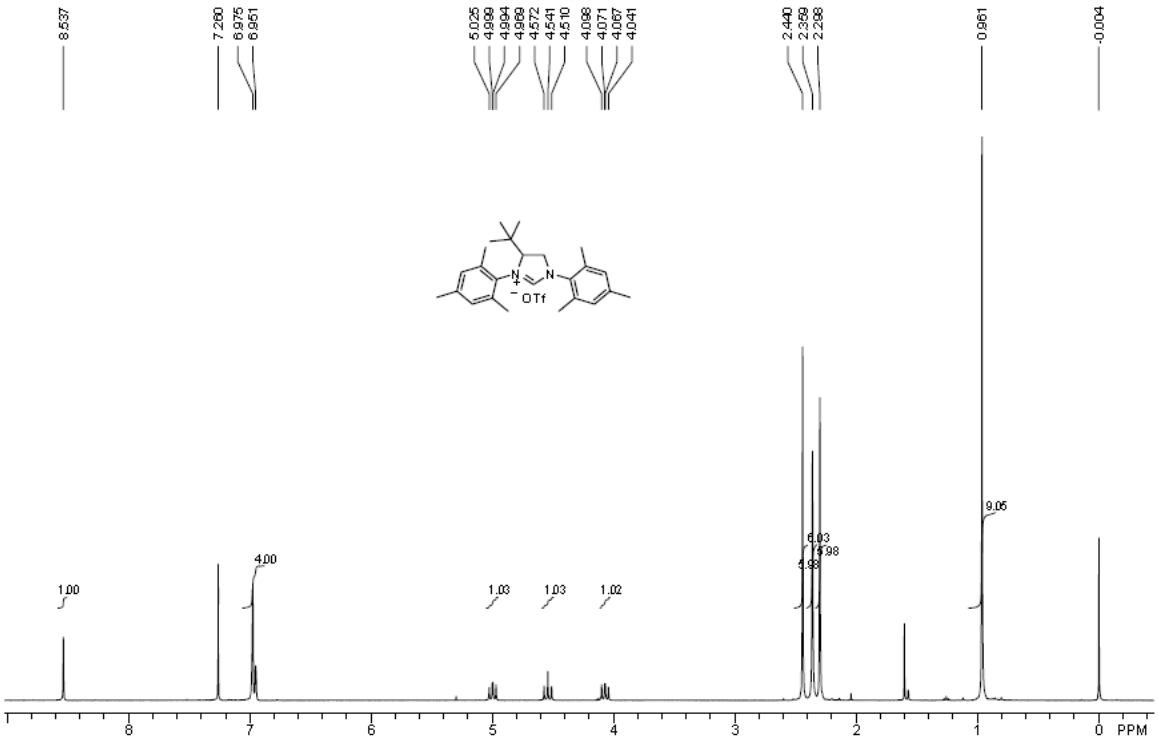
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OTf
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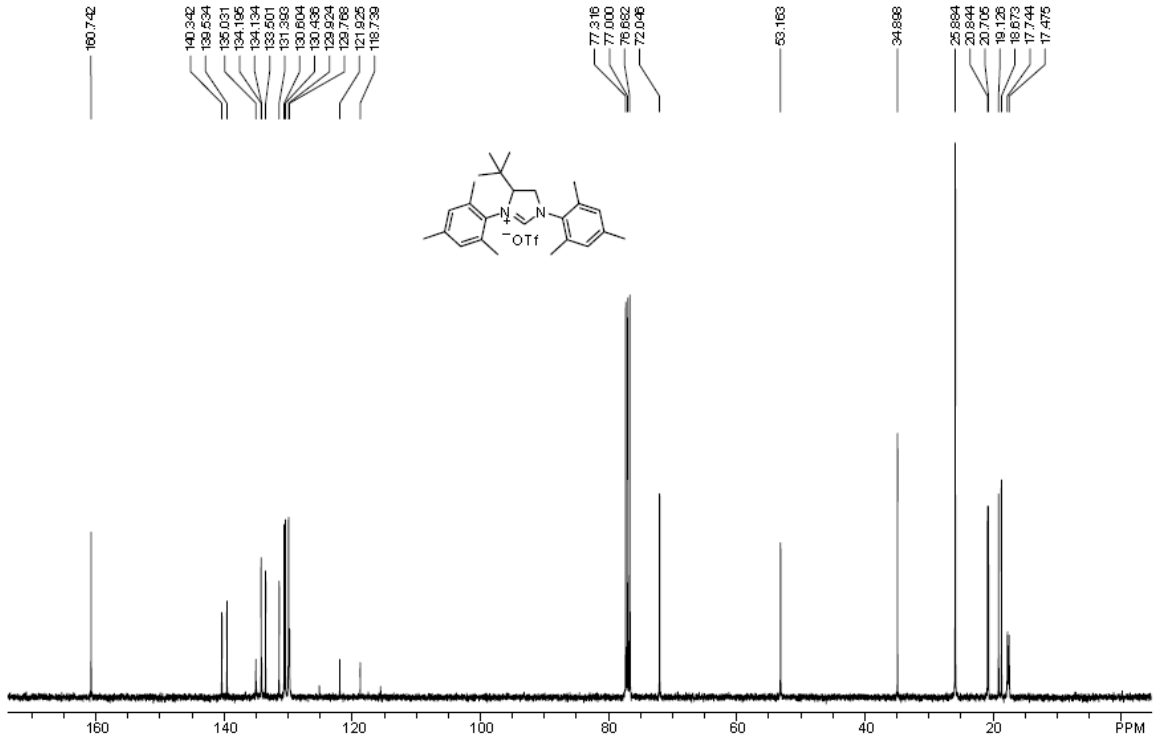
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121.925
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77.000
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72.046
53.163
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25.884
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20
PPM

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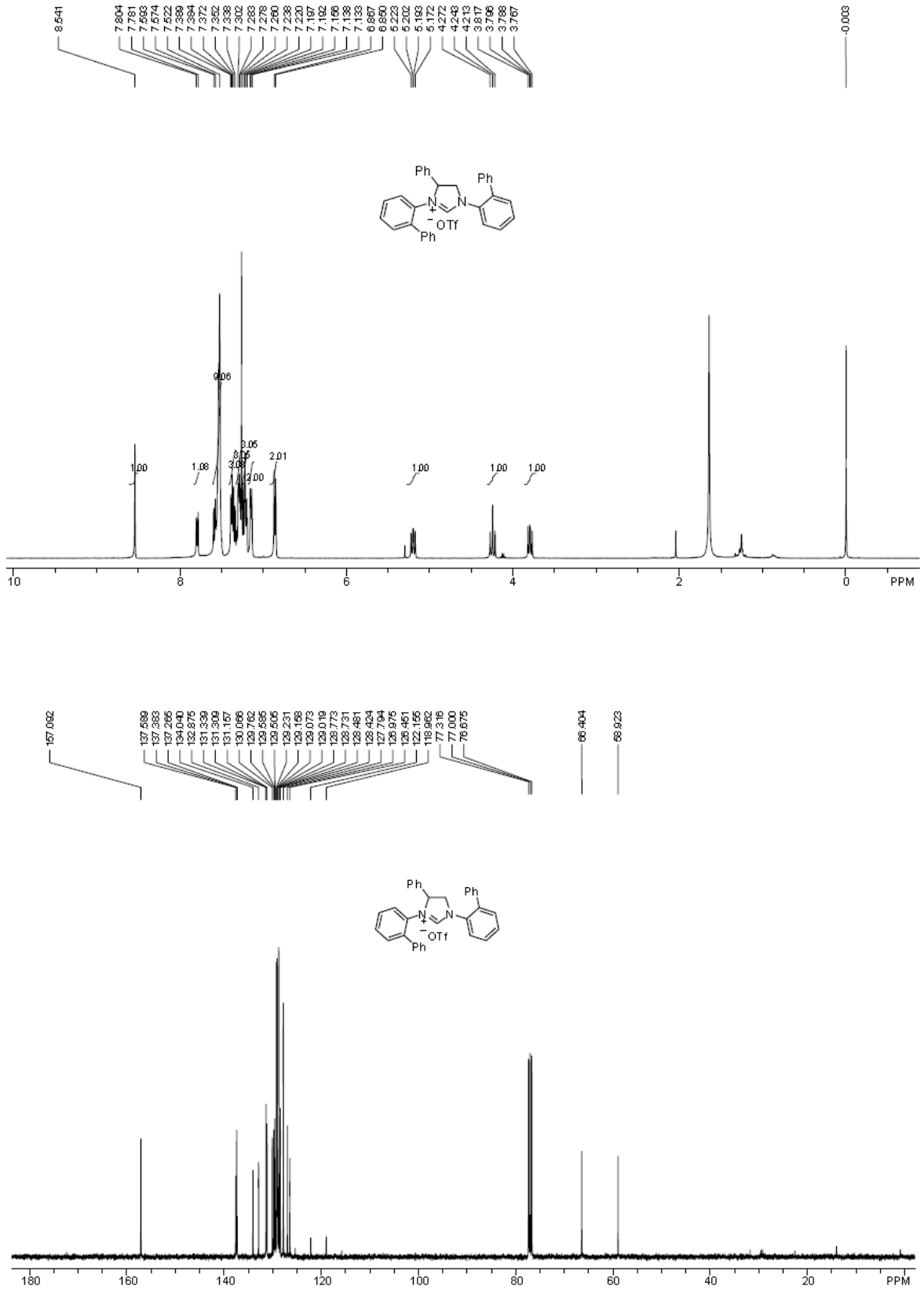
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7.283
7.278
7.260
7.238
7.220
7.197
7.192
7.158
7.138
7.133
6.867
6.850
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5.193
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4.246
4.213
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3.788
3.767
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Ph
N
N
OTf
Ph
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3.05
3.05
3.03
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1.08
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1.00
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10
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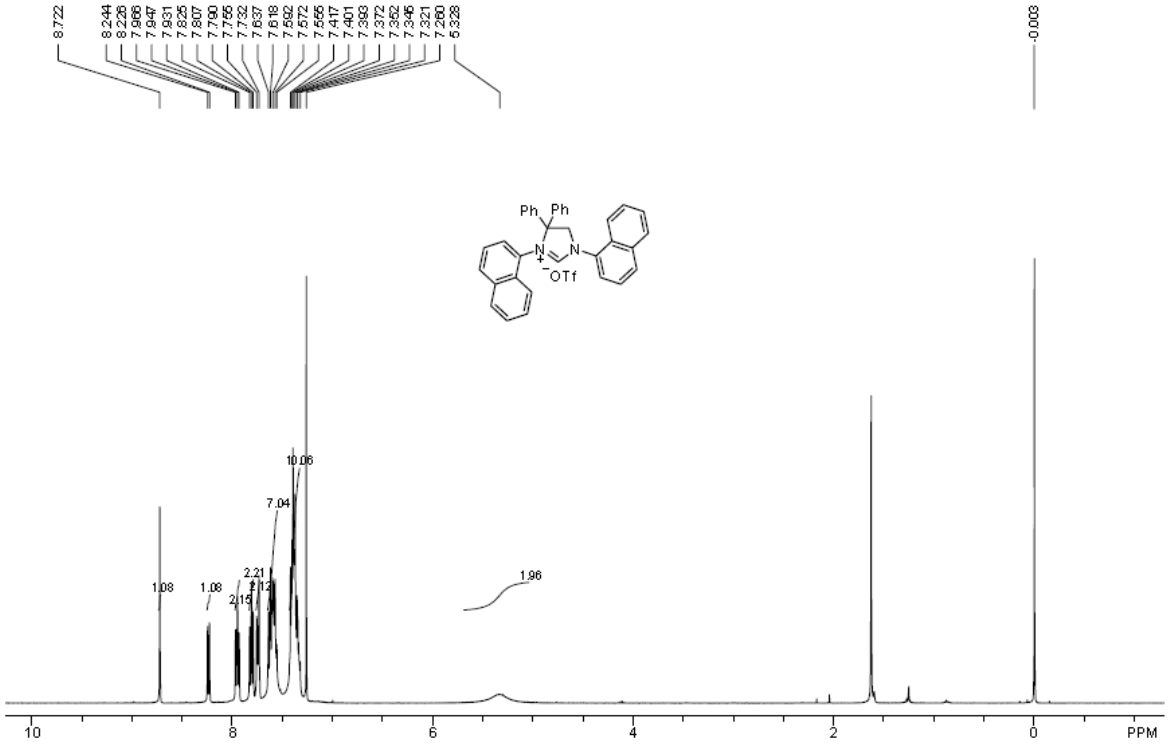
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7.592
7.572
7.555
7.417
7.401
7.393
7.372
7.352
7.346
7.321
7.260
6.328
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Ph Ph
N
N
OTf
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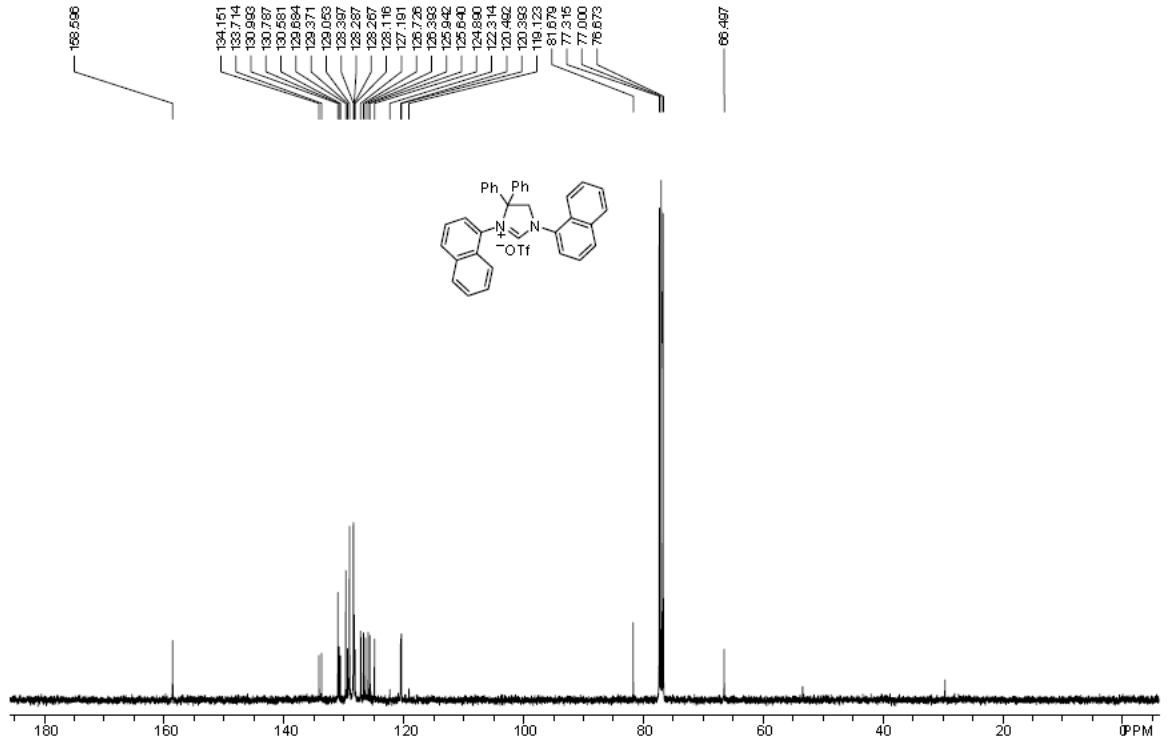
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20
0
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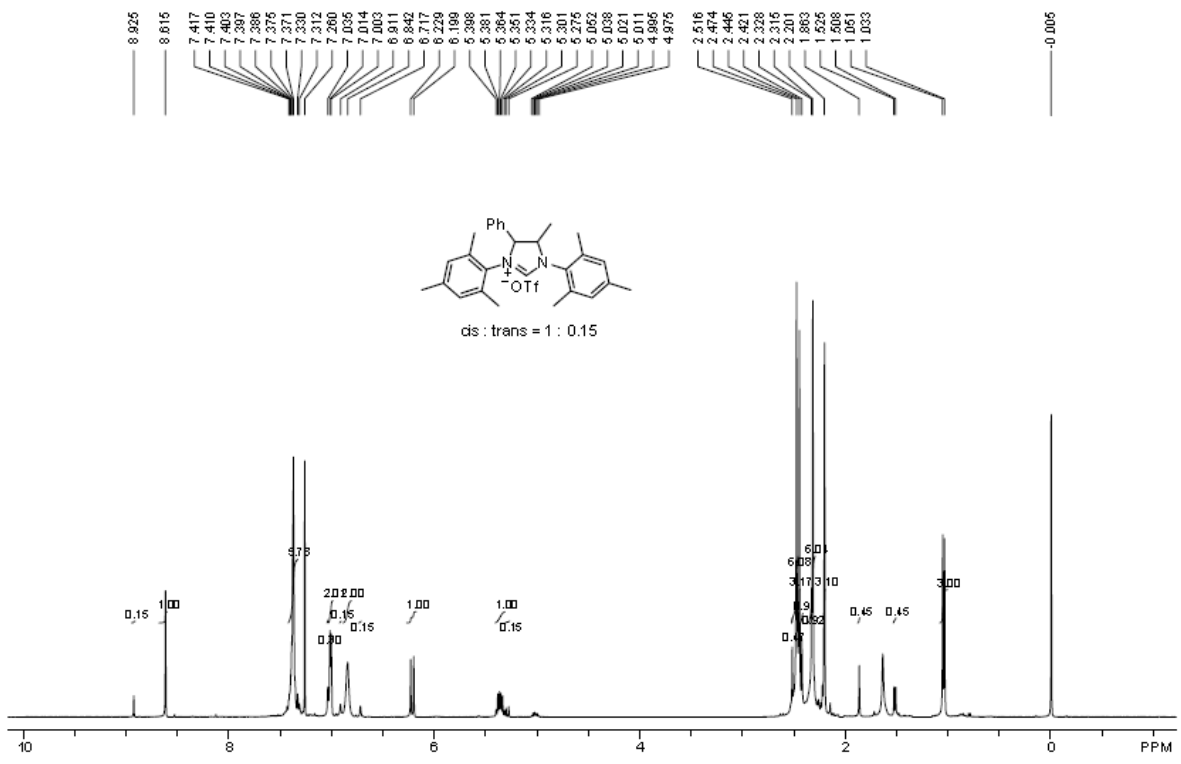

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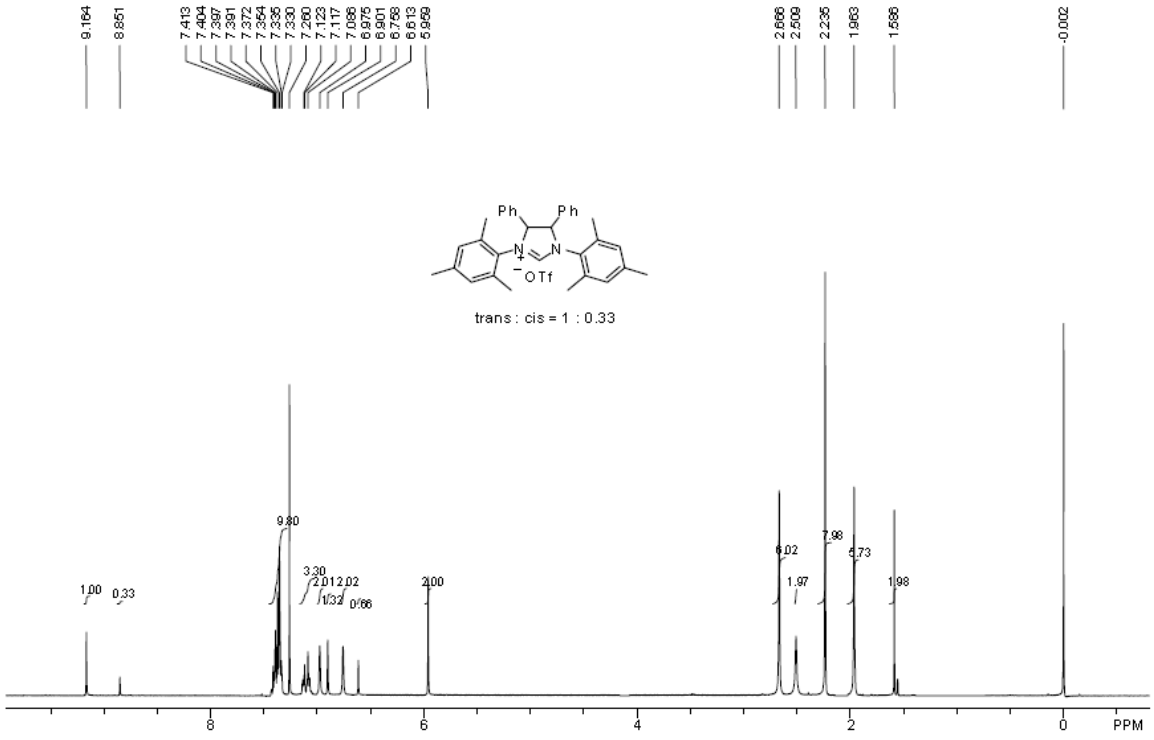

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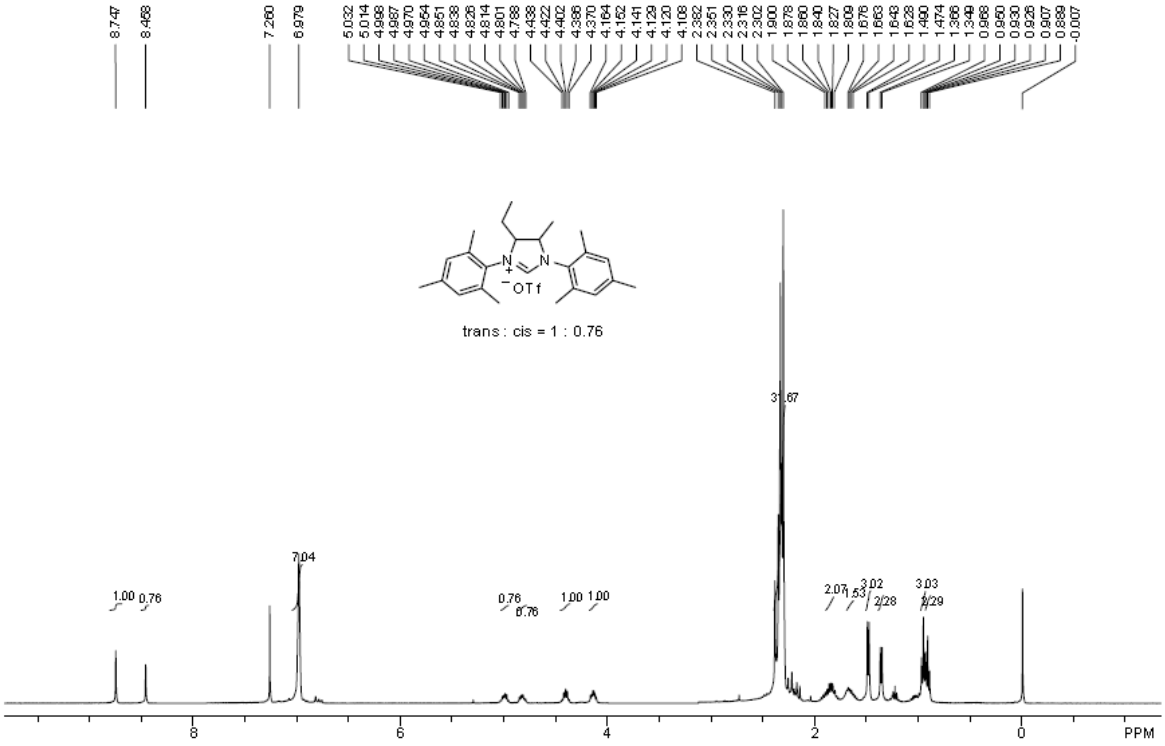
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4.402
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4.129
4.120
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2.351
2.330
2.316
2.302
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0.950
0.930
0.926
0.907
0.889
-0.007
OTf
trans : cis = 1 : 0.76
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0.76
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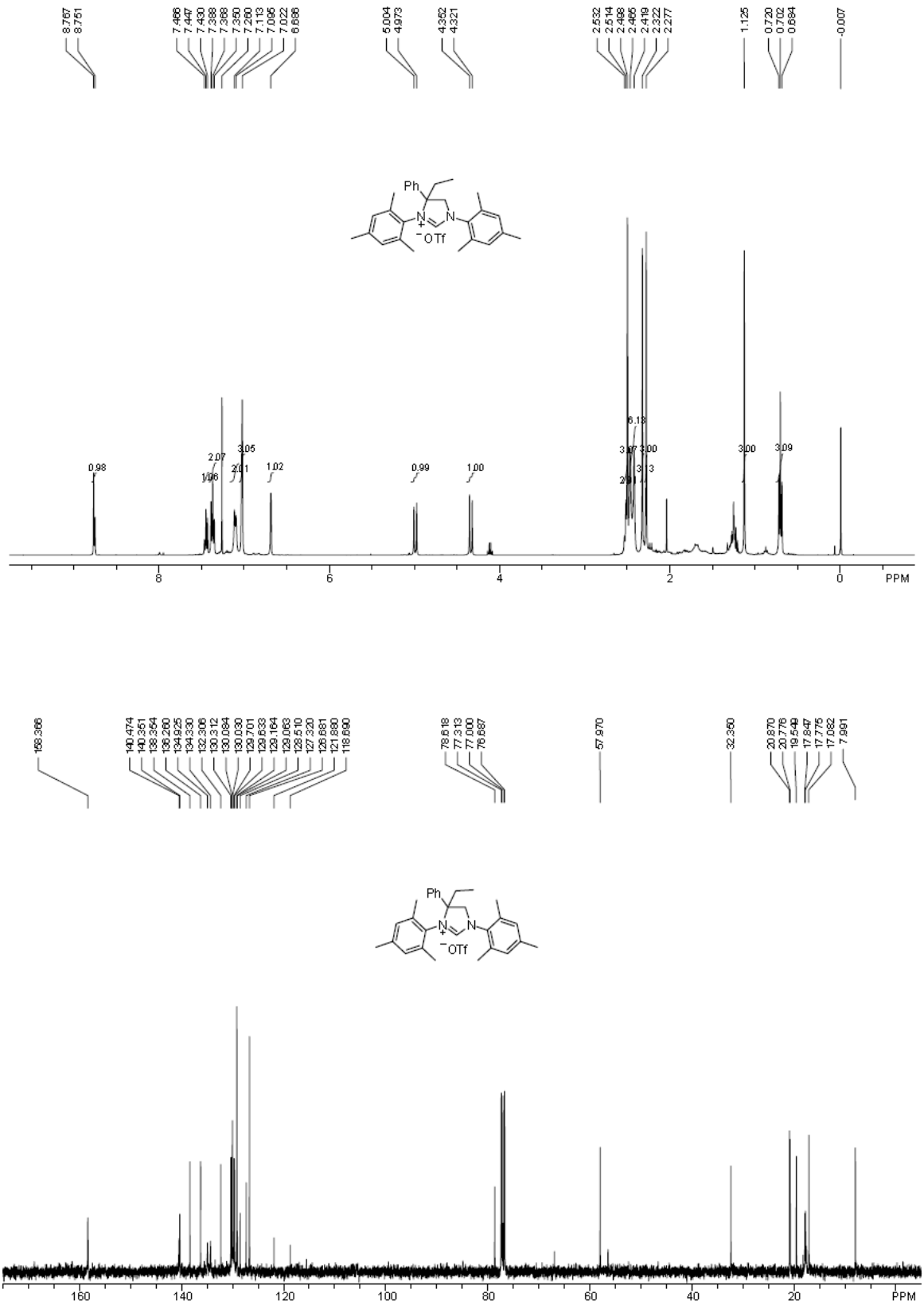
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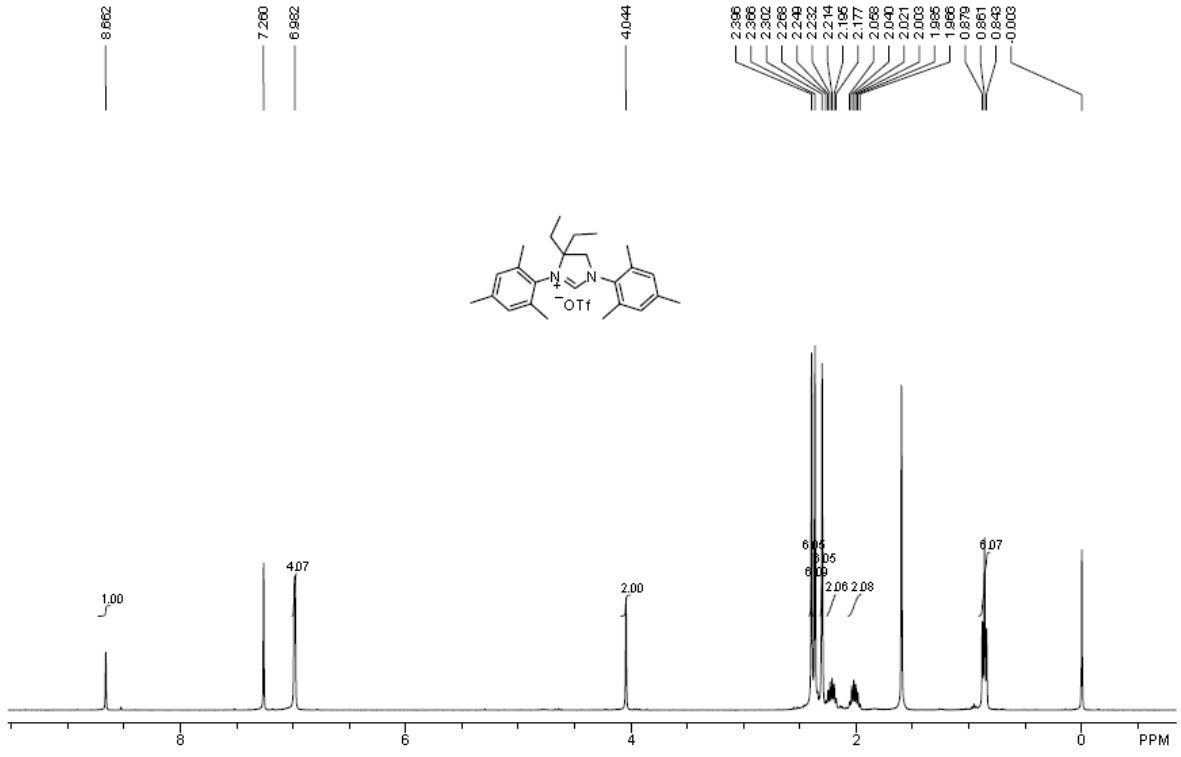
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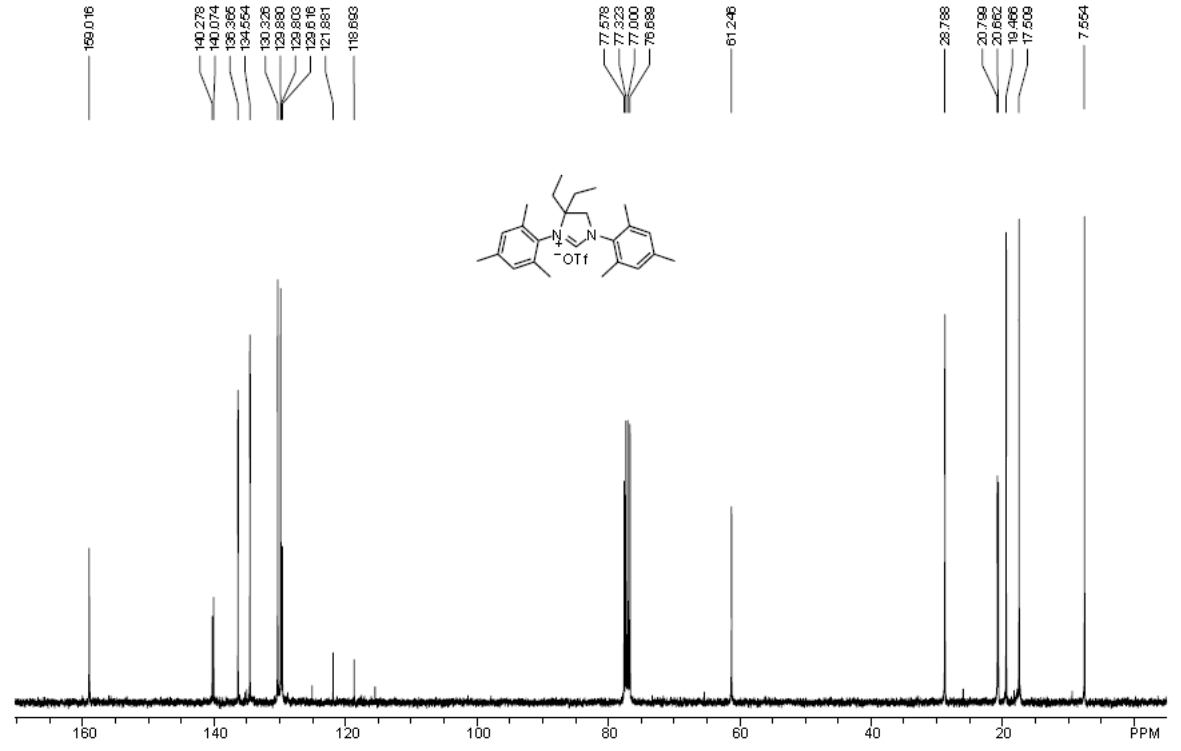
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20
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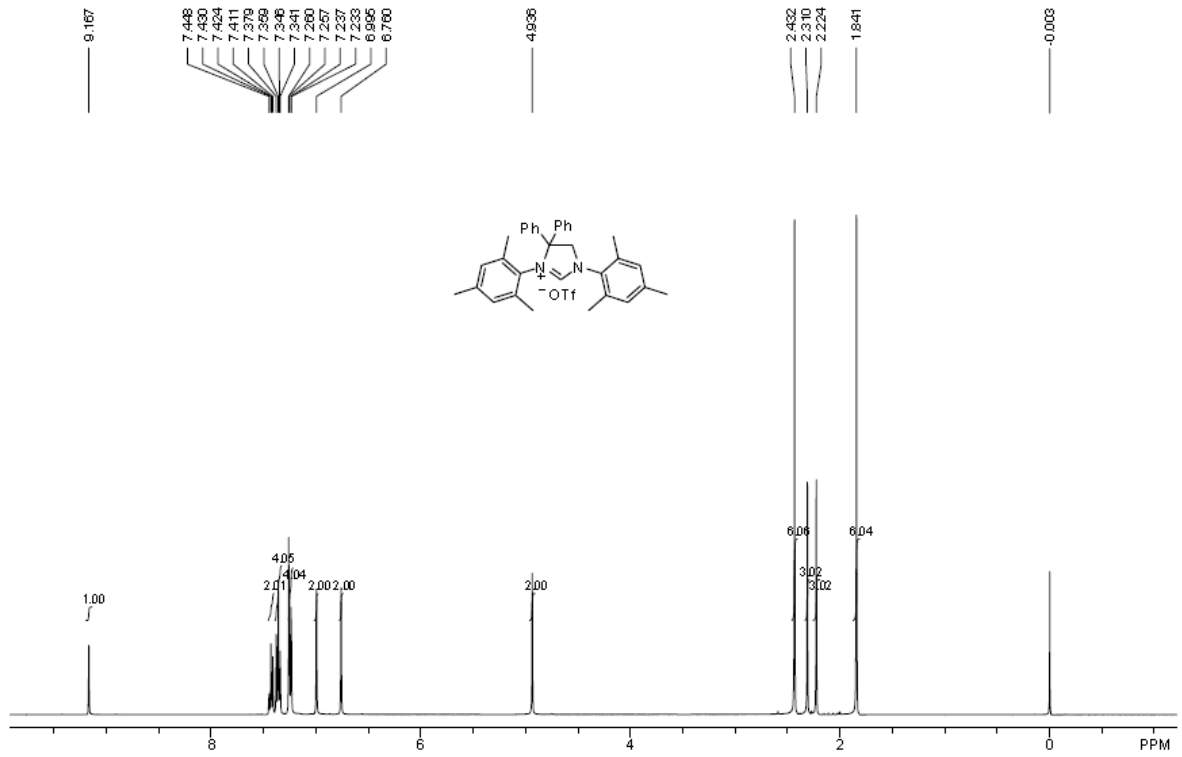
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Ph
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OTf
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4.05
4.04
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2.00
2.00
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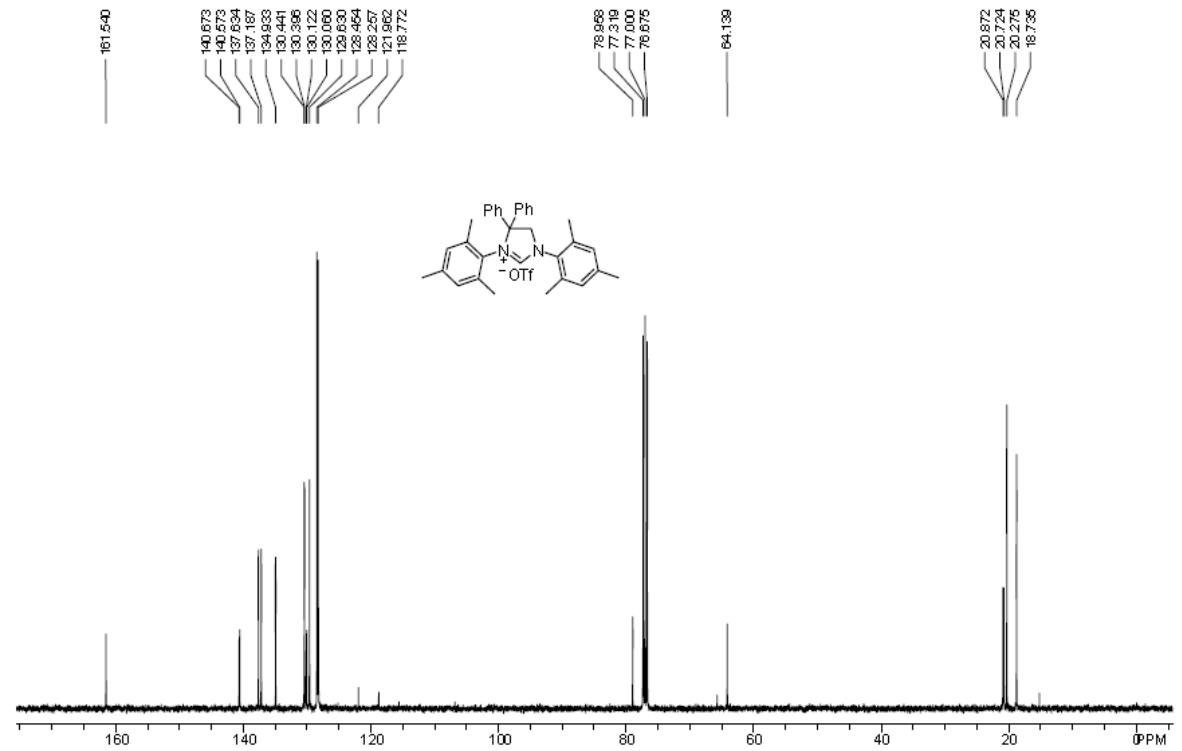
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40
20
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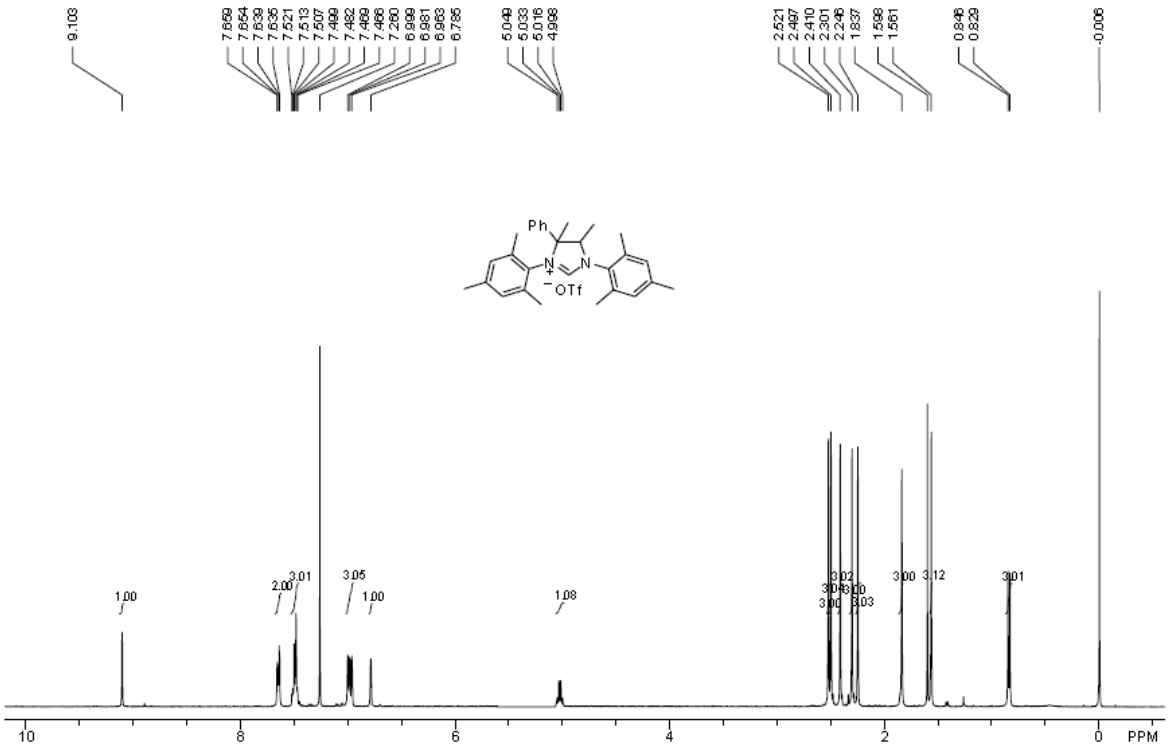
3m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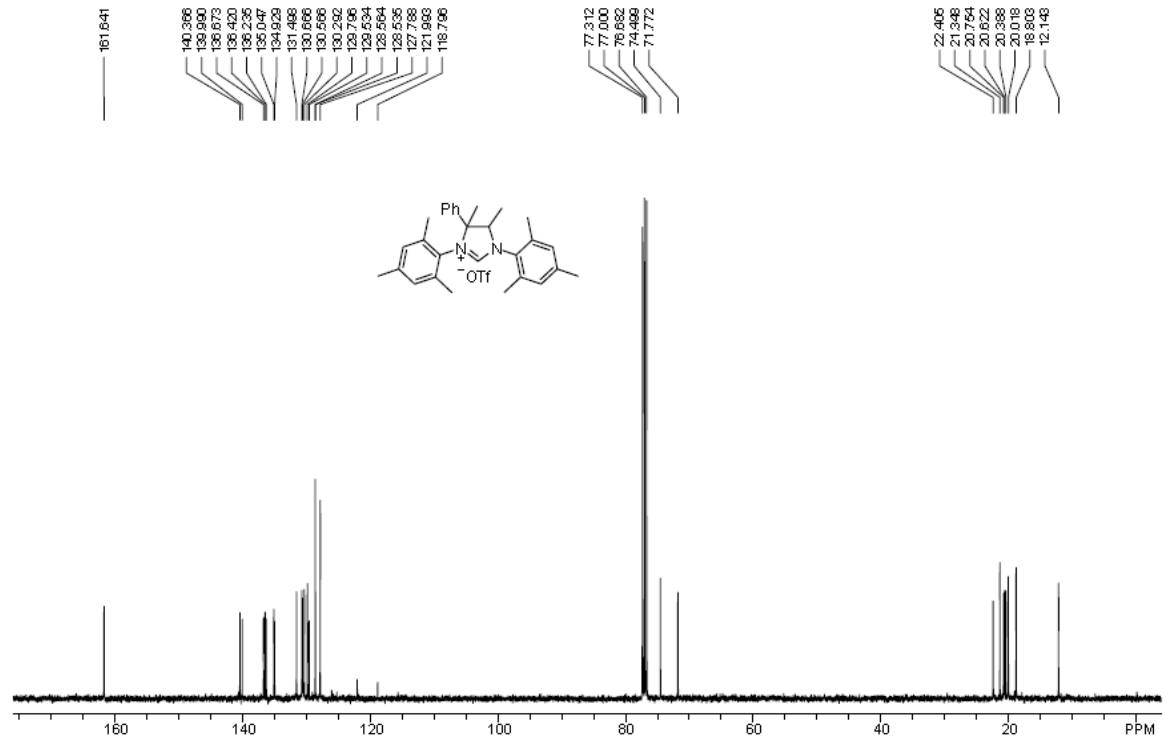
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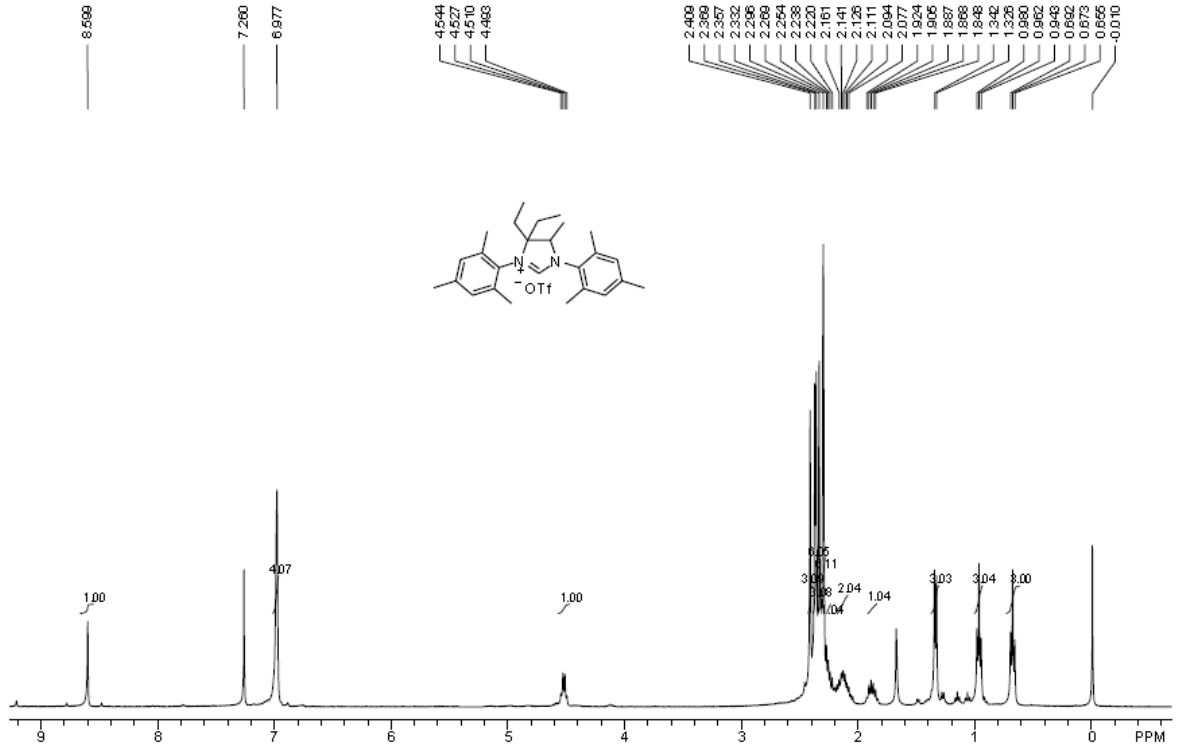
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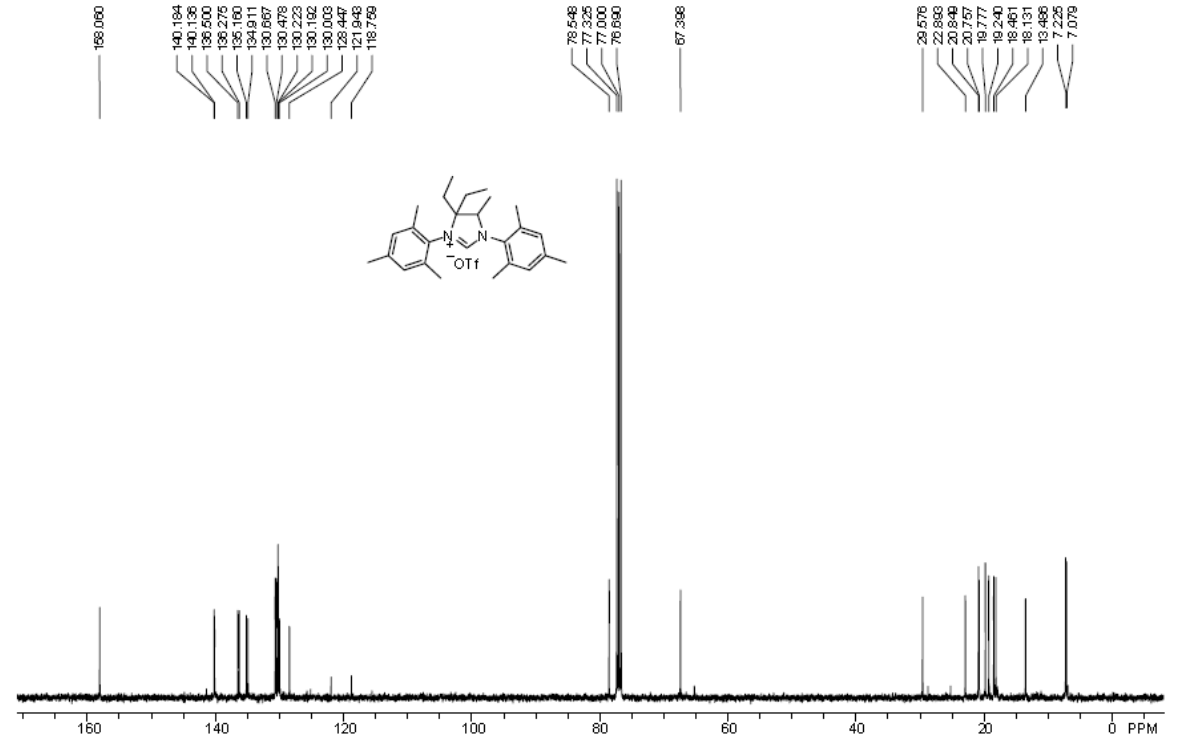
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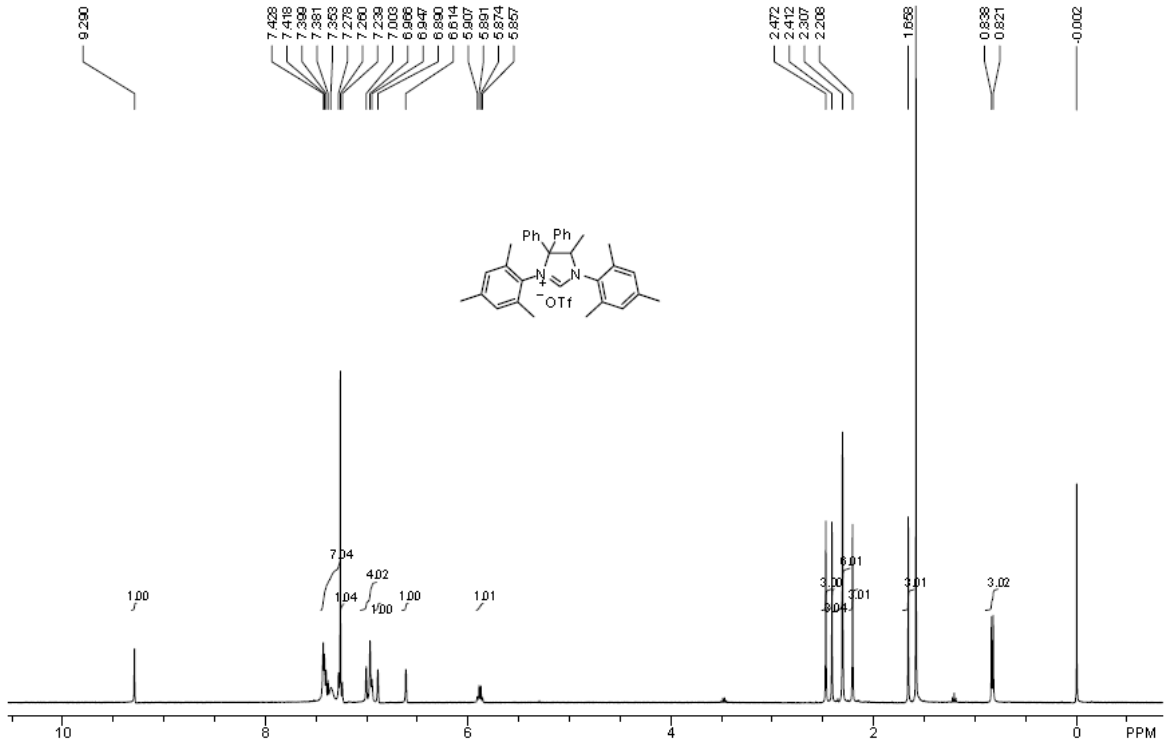
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Ph
N
N
OTf
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1.04
4.02
1.00
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3.04
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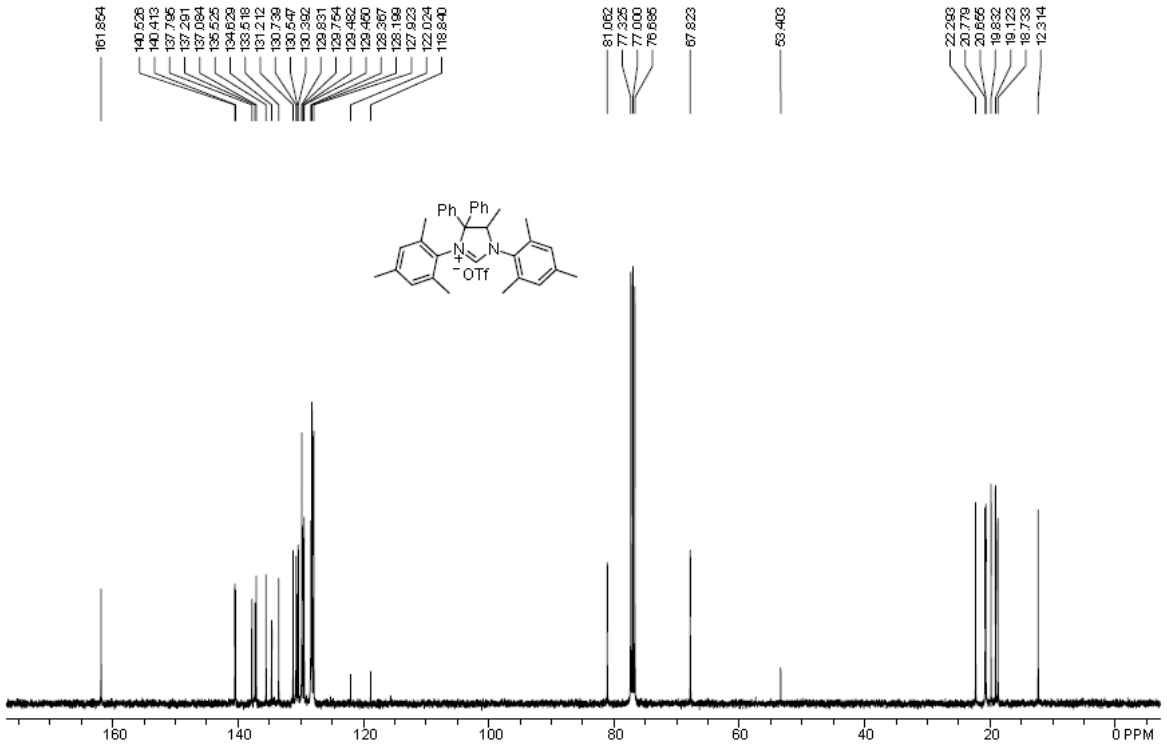
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81.062
77.325
77.000
76.685
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22.293
20.779
20.656
19.832
19.123
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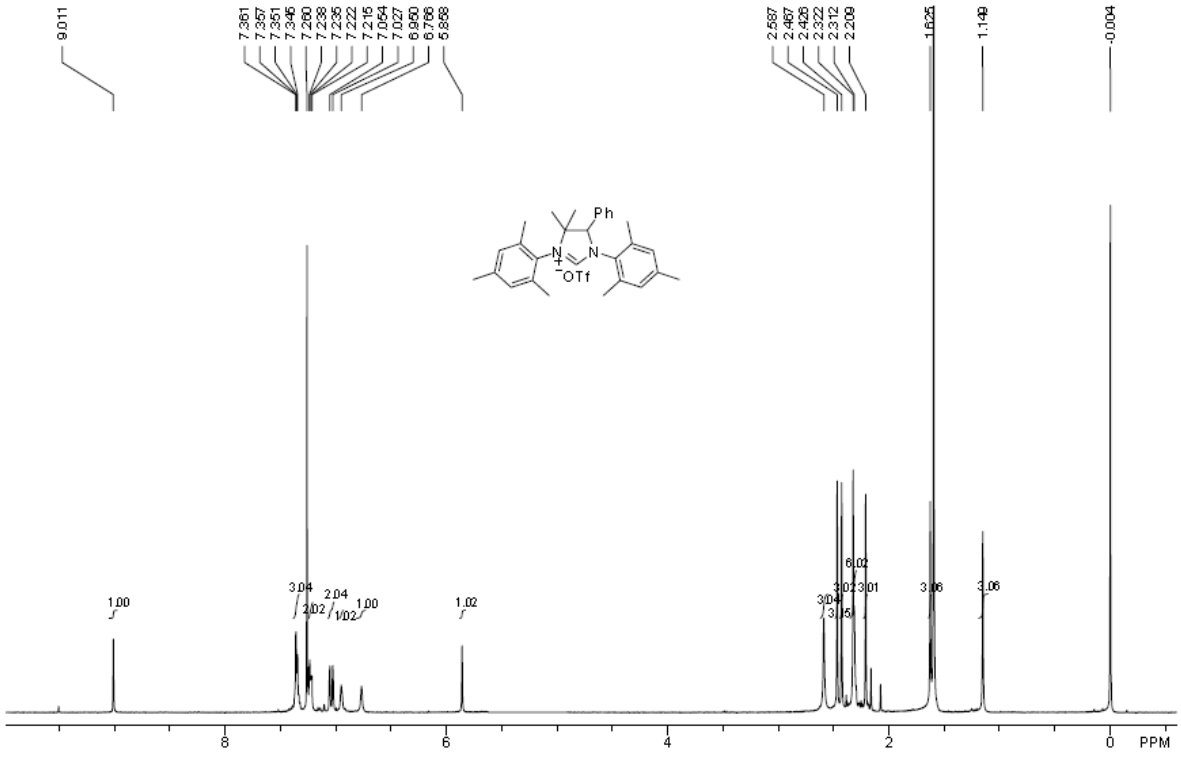
Ph
Ph
N
N
OTf
160
140
120
100
80
60
40
20
0 PPM

3p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7.357
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7.027
6.950
6.766
6.858
2.587
2.467
2.426
2.322
2.312
2.209
1.625
1.149
-0.004
Ph
N
N
OTf
1.00
3.04
2.02
2.04
1.02
1.00
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3.15
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3.06
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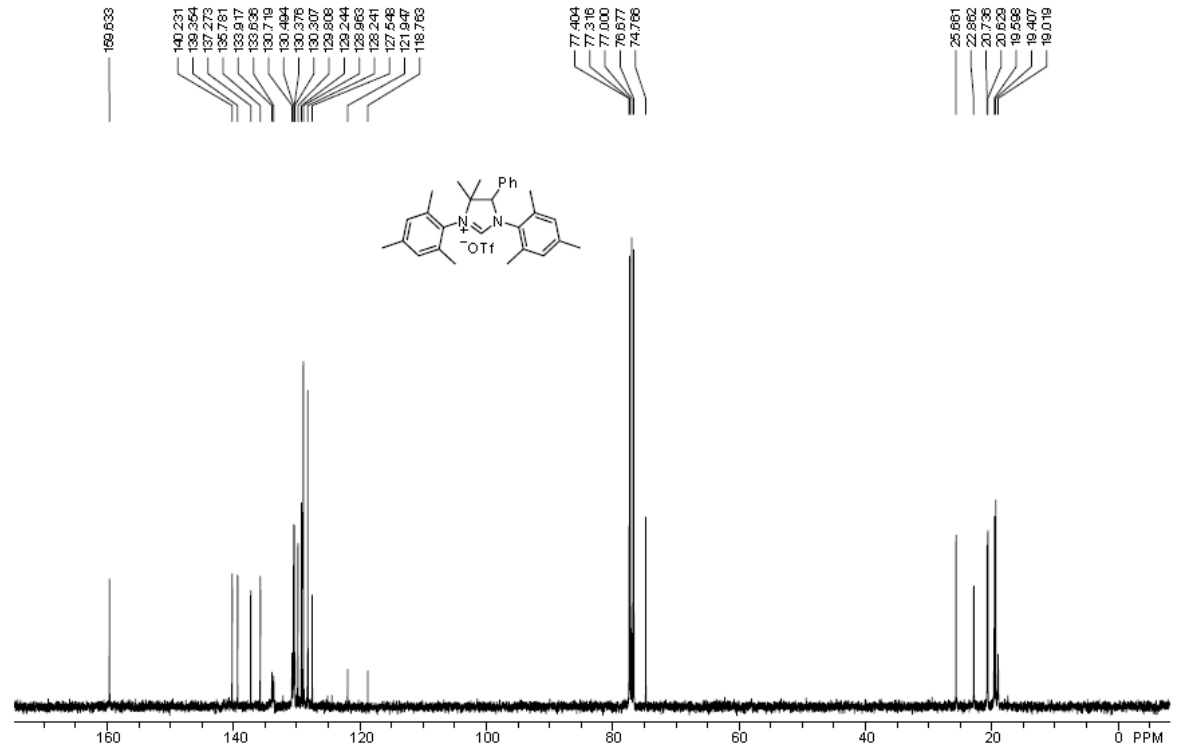
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128.963
128.241
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121.947
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77.316
77.000
76.677
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25.661
22.862
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20.629
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Ph
N
N
OTf
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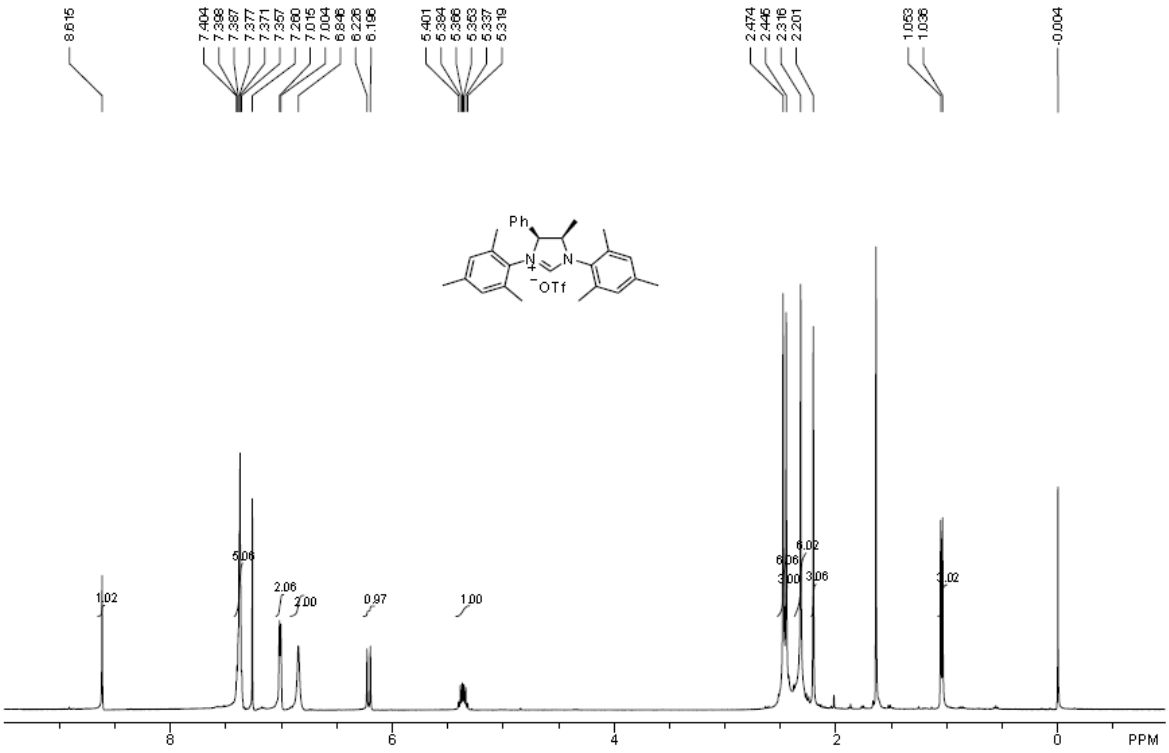
80
60
40
20
0
PPM

3q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5.401
5.384
5.366
5.353
5.337
5.319
2.474
2.445
2.316
2.201
1.053
1.036
-0.004
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N
OTf
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5.06
2.06
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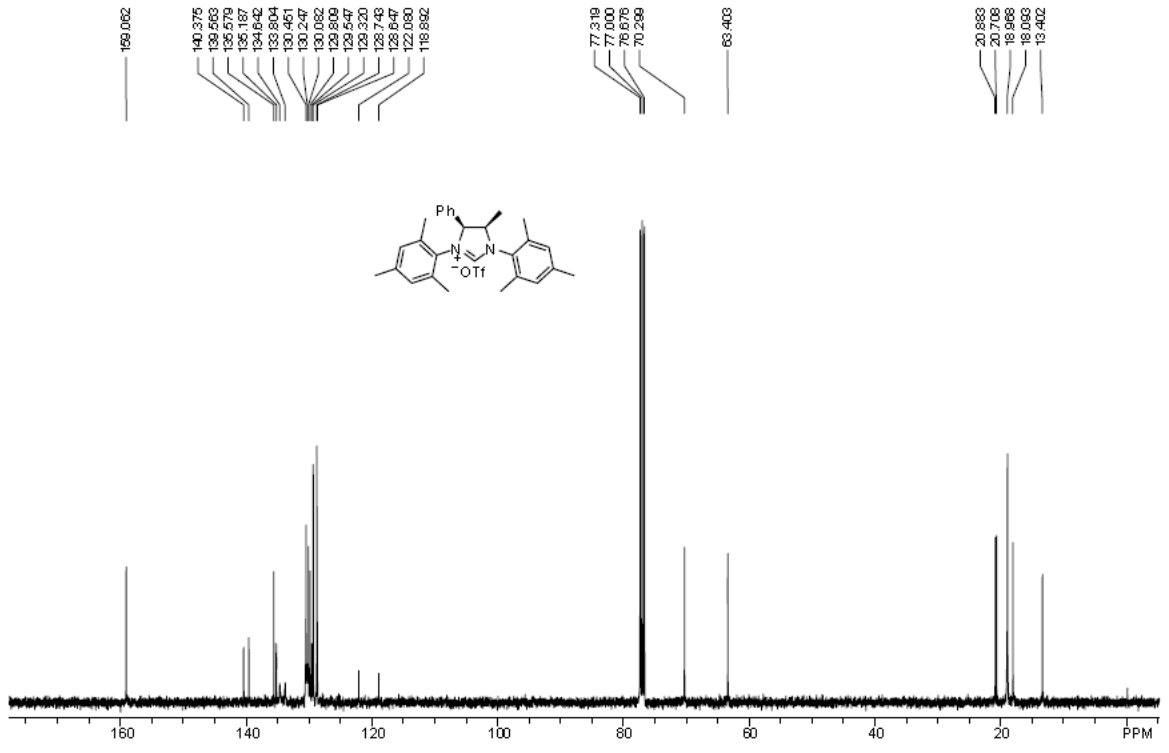
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128.743
128.647
122.080
118.892
77.319
77.000
76.676
70.299
63.403
20.883
20.708
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Ph
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OTf
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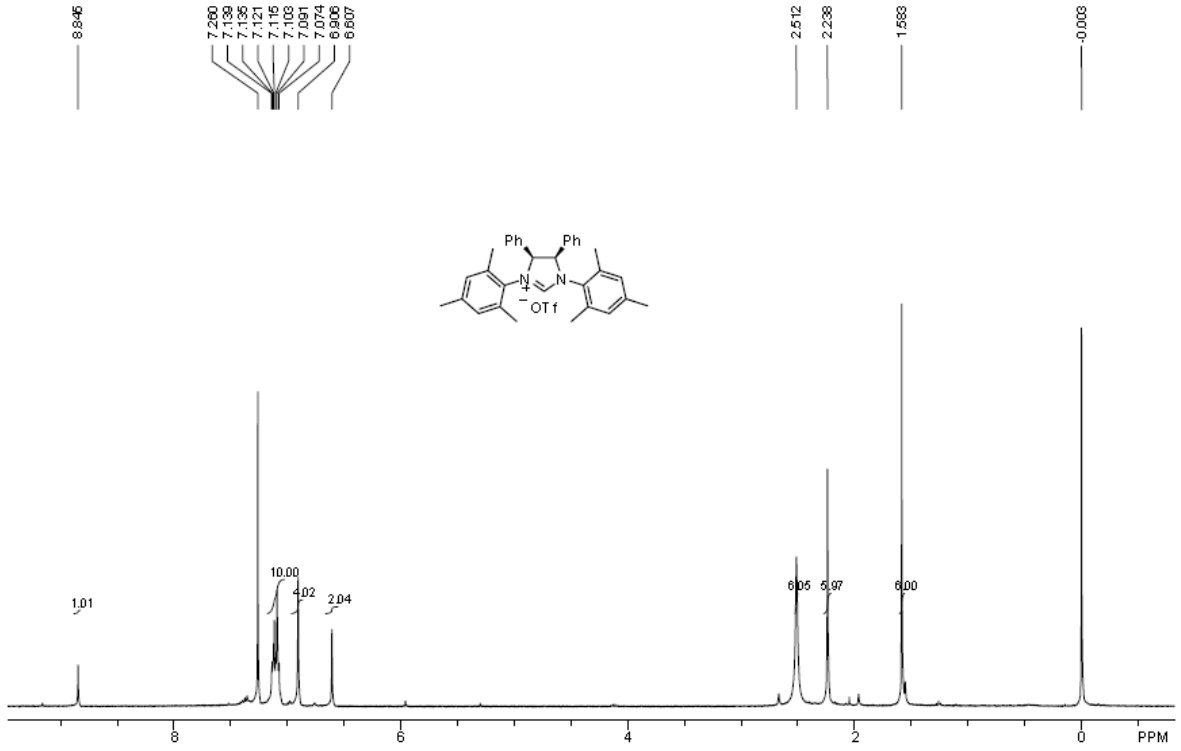
100
80
60
40
20
PPM

3r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2.238
1.583
-0.003
Ph
Ph
N
N
+
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6.00
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6
4
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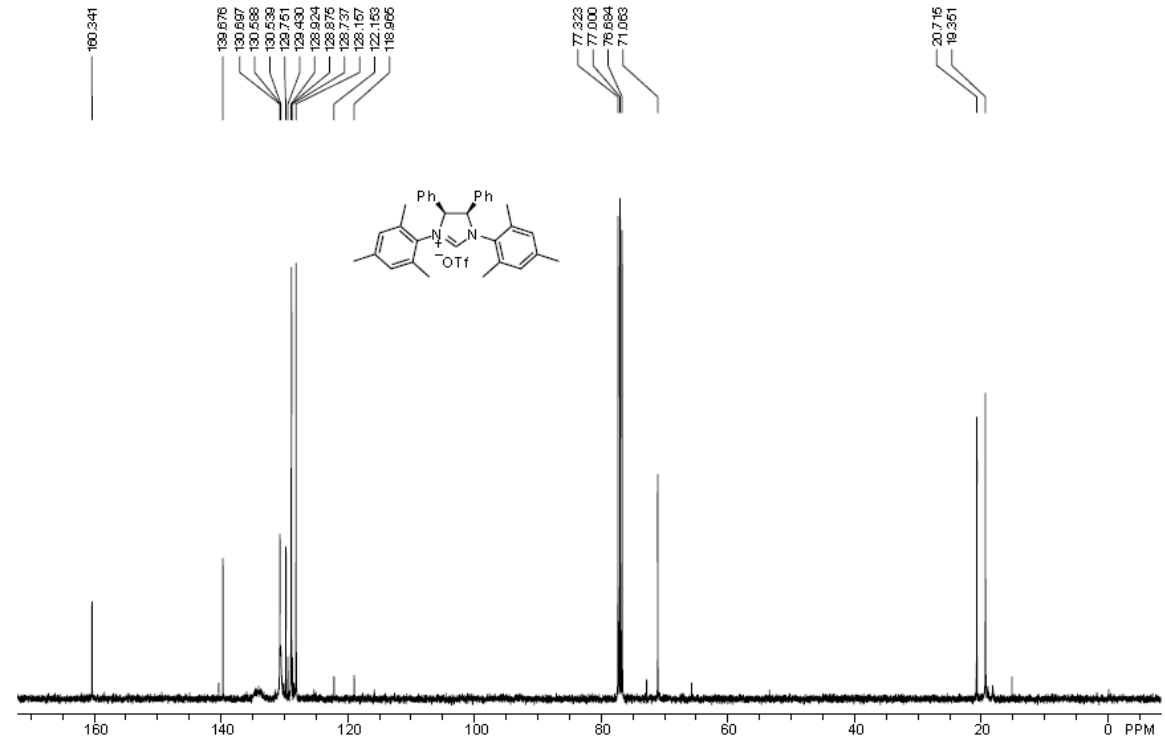
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128.737
128.157
122.153
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77.323
77.000
76.694
71.063
20.715
19.351
Ph
Ph
N
N
+
−OTf
160
140
120
100
80
60
40
20
0
PPM

4c

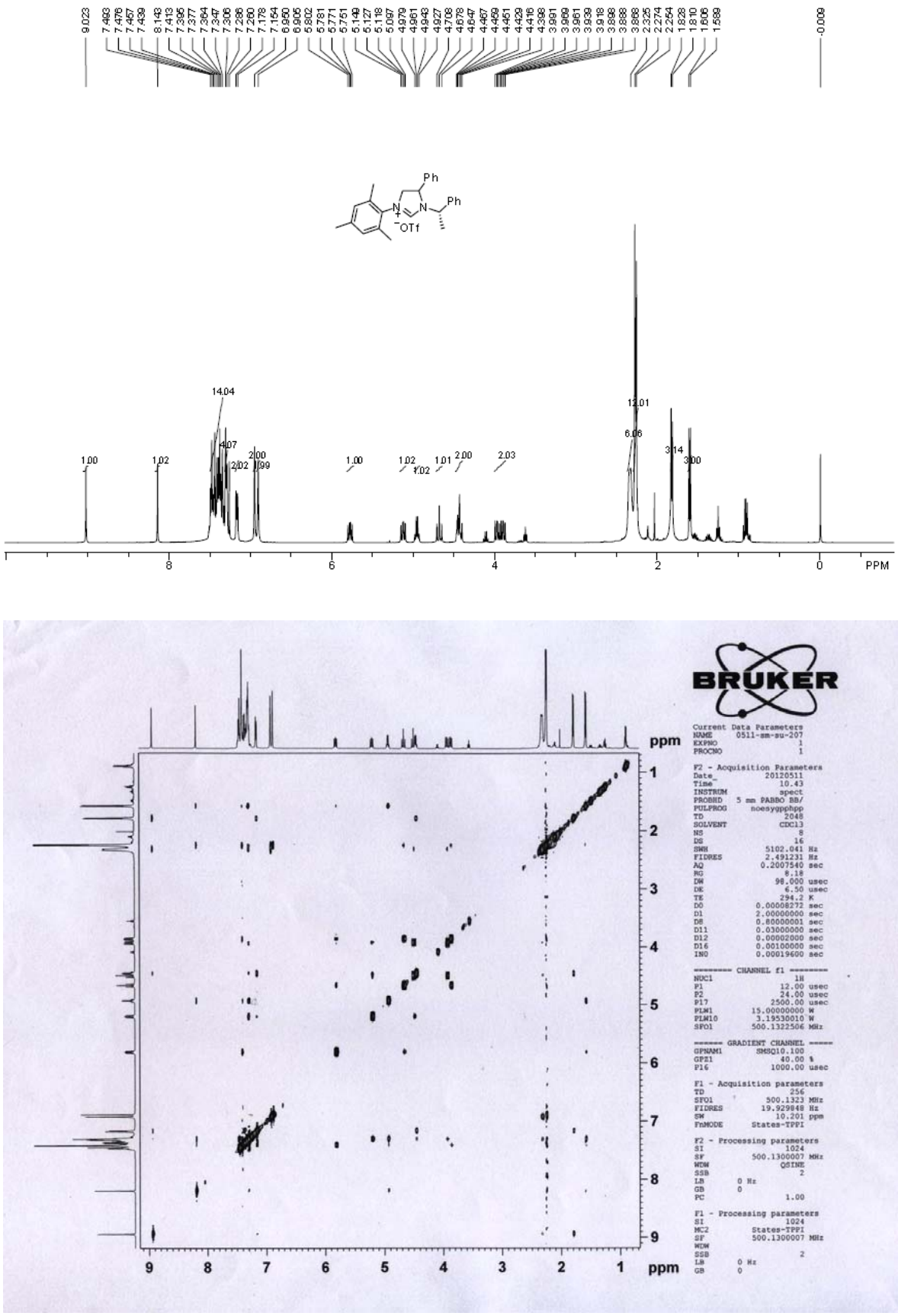
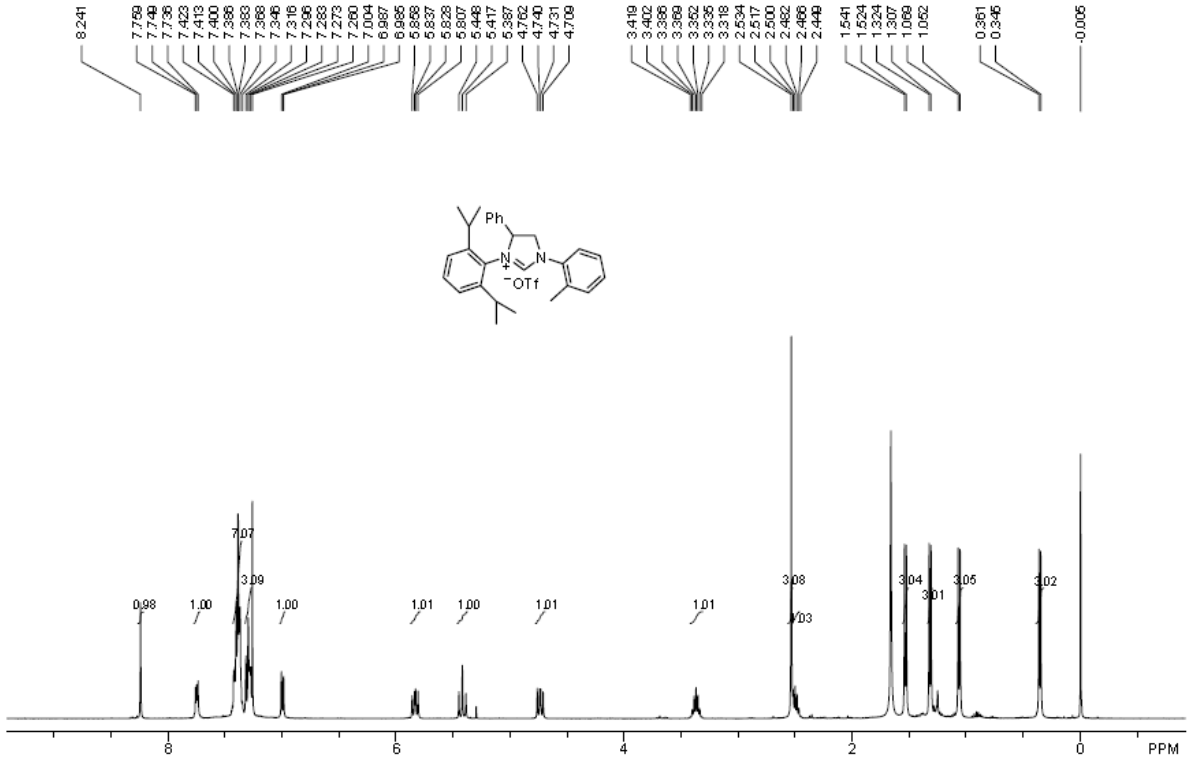


Figure S1. 2D NMR spectrum of **4c**

4b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7.286
7.283
7.273
7.260
7.004
6.987
6.985
5.858
5.837
5.828
5.807
5.448
5.417
5.387
4.762
4.740
4.731
4.709
3.419
3.402
3.386
3.369
3.352
3.335
3.318
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2.517
2.500
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2.466
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1.307
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0.345
-0.005
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N
OTf
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3.09
0.98
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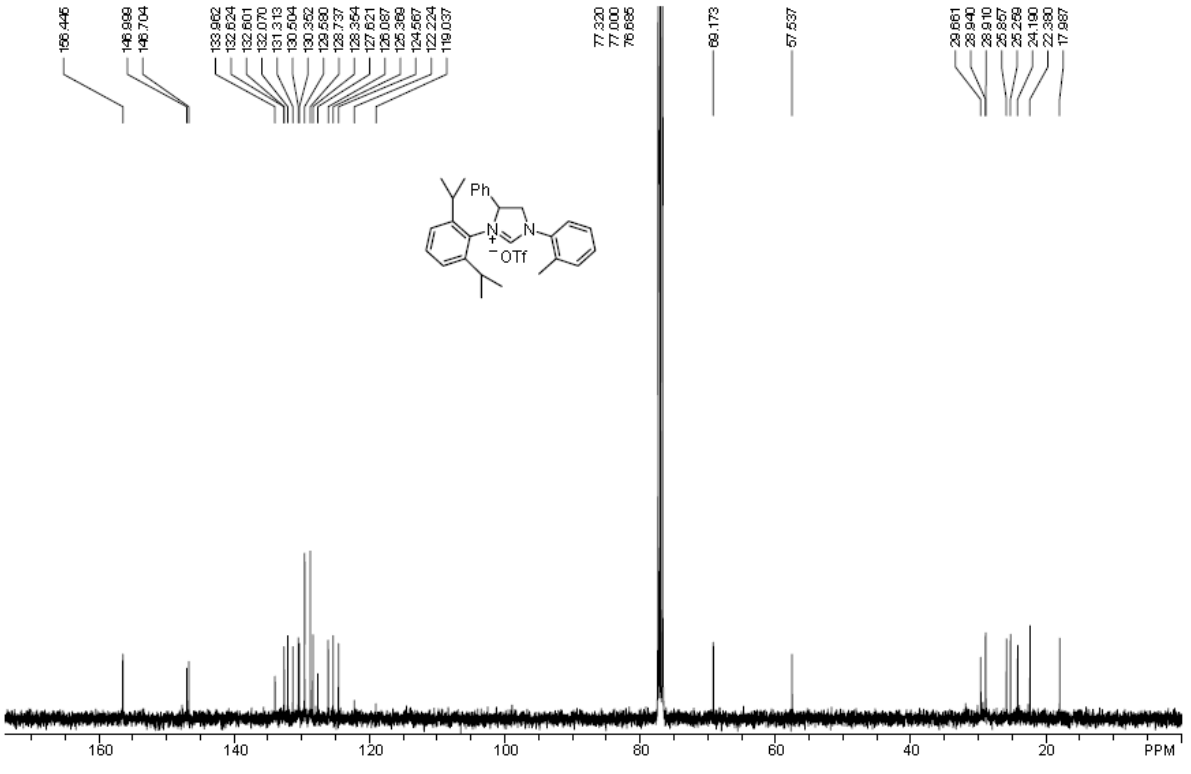
1.00
1.01
1.00
1.01
1.01
3.08
3.03
3.04
3.01
3.05
3.02
8
6
4
2
0
PPM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128.354
127.621
126.087
125.369
124.567
122.224
119.037
77.320
77.000
76.685
69.173
57.537
29.661
28.940
28.910
25.857
25.259
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Ph
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OTf
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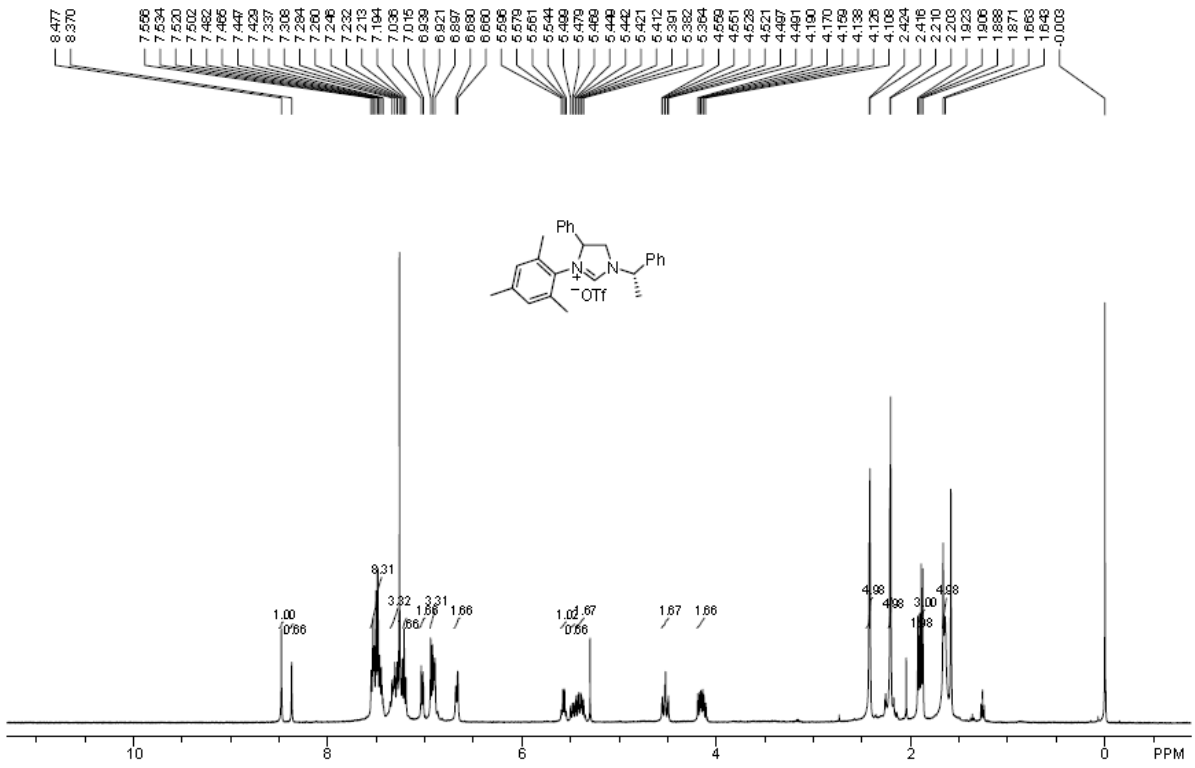
100
80
60
40
20
PPM

4d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7.260
7.246
7.232
7.213
7.194
7.036
7.015
6.939
6.921
6.897
6.680
6.660
5.596
5.579
5.561
5.544
5.499
5.479
5.469
5.449
5.442
5.421
5.412
5.391
5.382
5.364
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4.551
4.528
4.521
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4.126
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2.210
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1.906
1.888
1.871
1.663
1.643
0.003
Ph
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N
Ph
OTf
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3.32
3.31
1.66
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4
2
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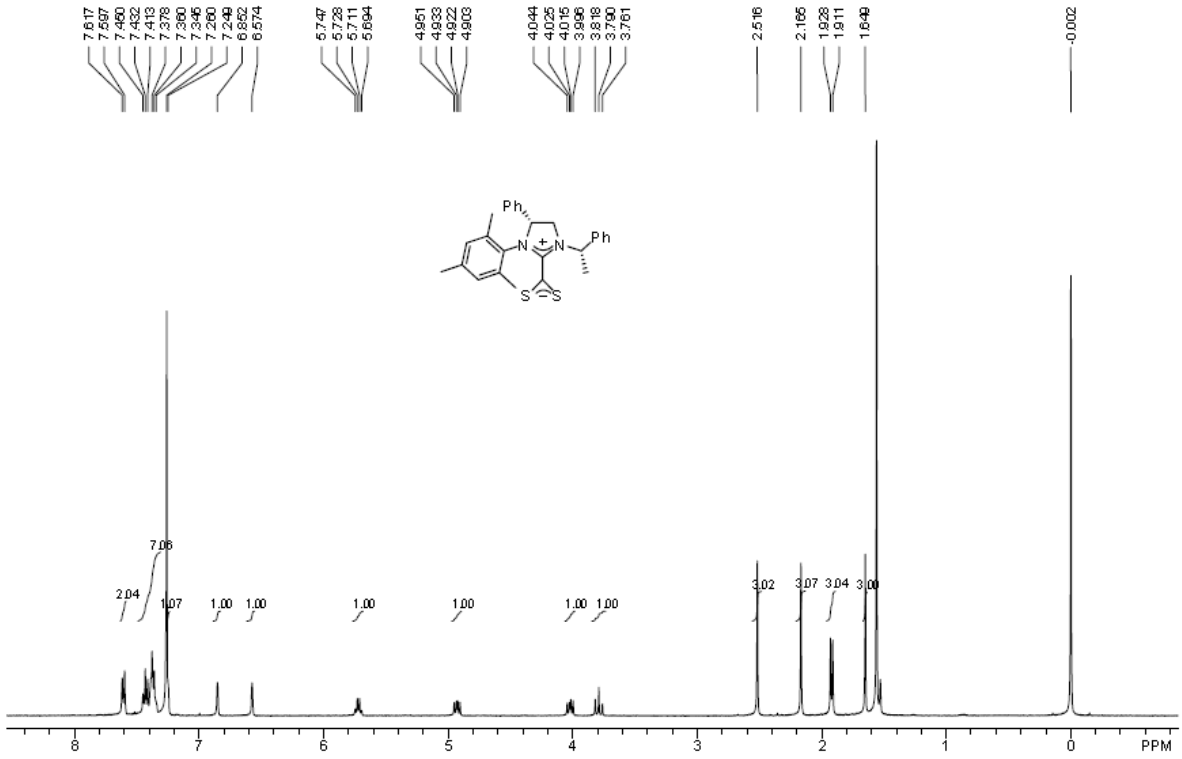
PPM

(*S*, *S*)-**5a**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5.728
5.711
5.694
4.951
4.933
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4.903
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4.025
4.015
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3.818
3.790
3.761
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1.928
1.911
1.649
-0.002
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N
N
Ph
S
S
2.04
7.06
1.07
1.00
1.00
1.00
1.00
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1.00
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3.04
3.00
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6
5
4
3
2
1
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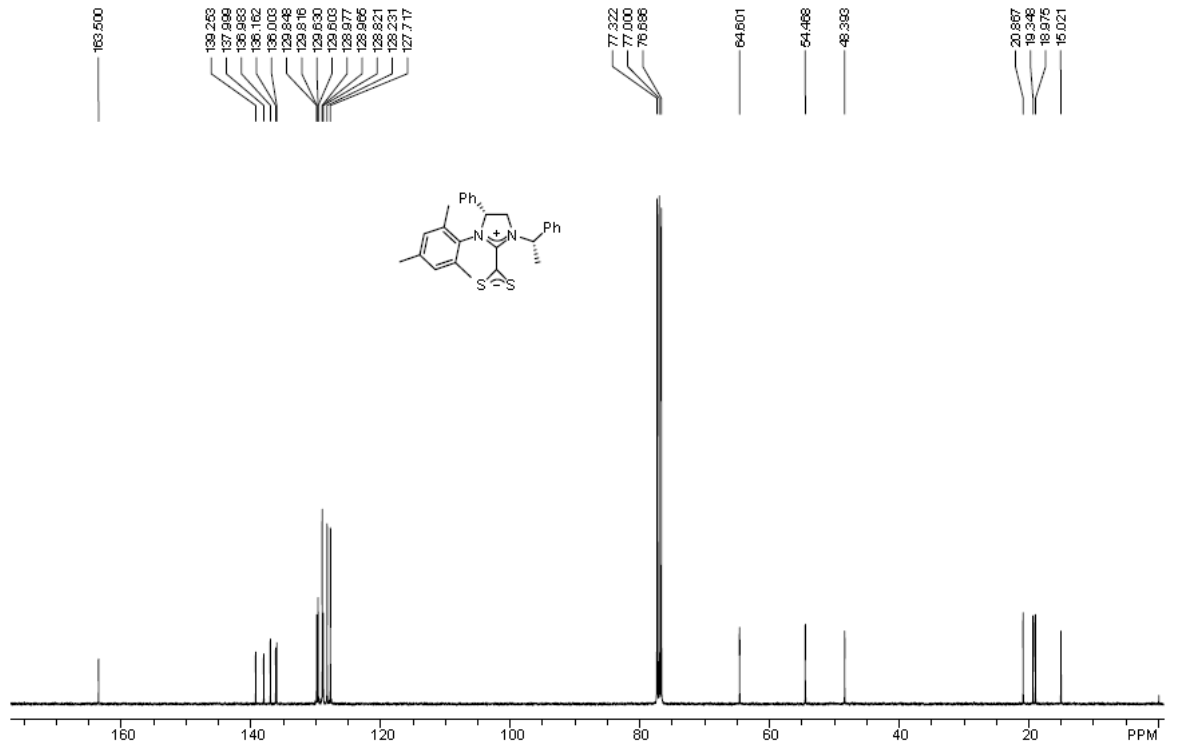
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128.231
127.717
77.322
77.000
76.686
64.601
54.468
48.393
20.867
19.348
18.975
15.021
Ph
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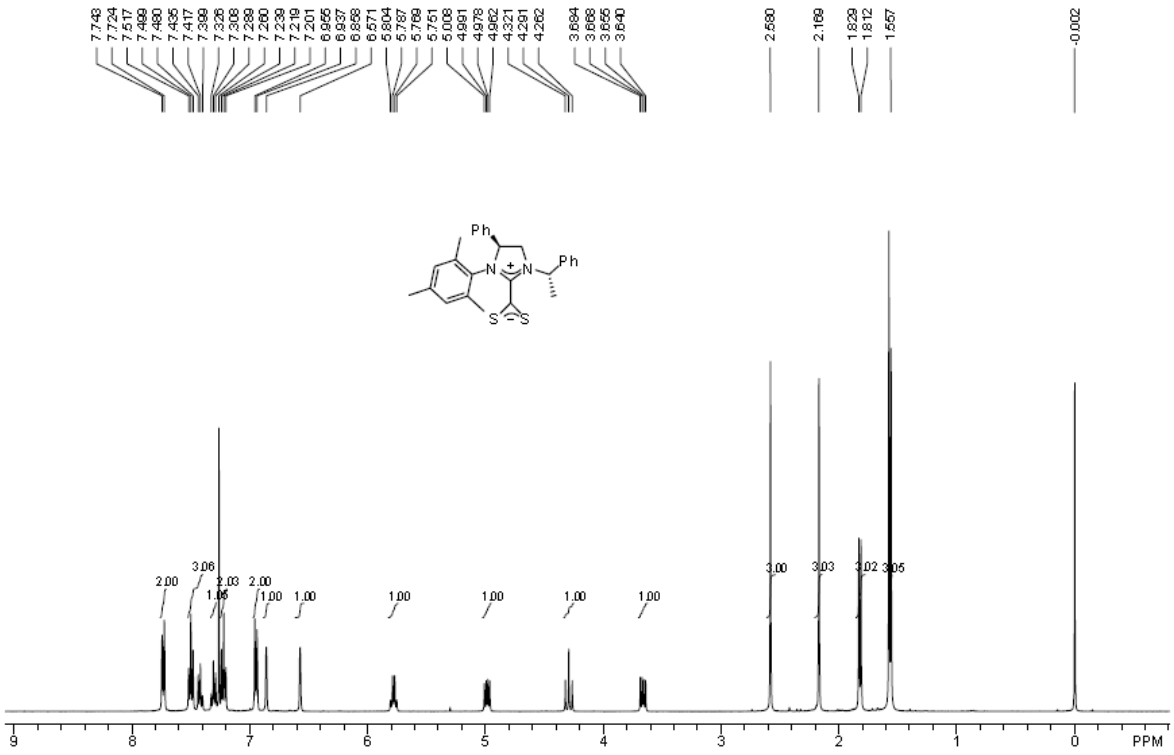
N
Ph
S
S
160
140
120
100
80
60
40
20
PPM

(*R*, *S*)-**5b**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7.239
7.219
7.201
6.855
6.837
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6.571
5.804
5.787
5.769
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4.978
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4.321
4.291
4.262
3.684
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N
Ph
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S
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3.06
2.03
2.00
1.05
1.00
1.00
1.00
1.00
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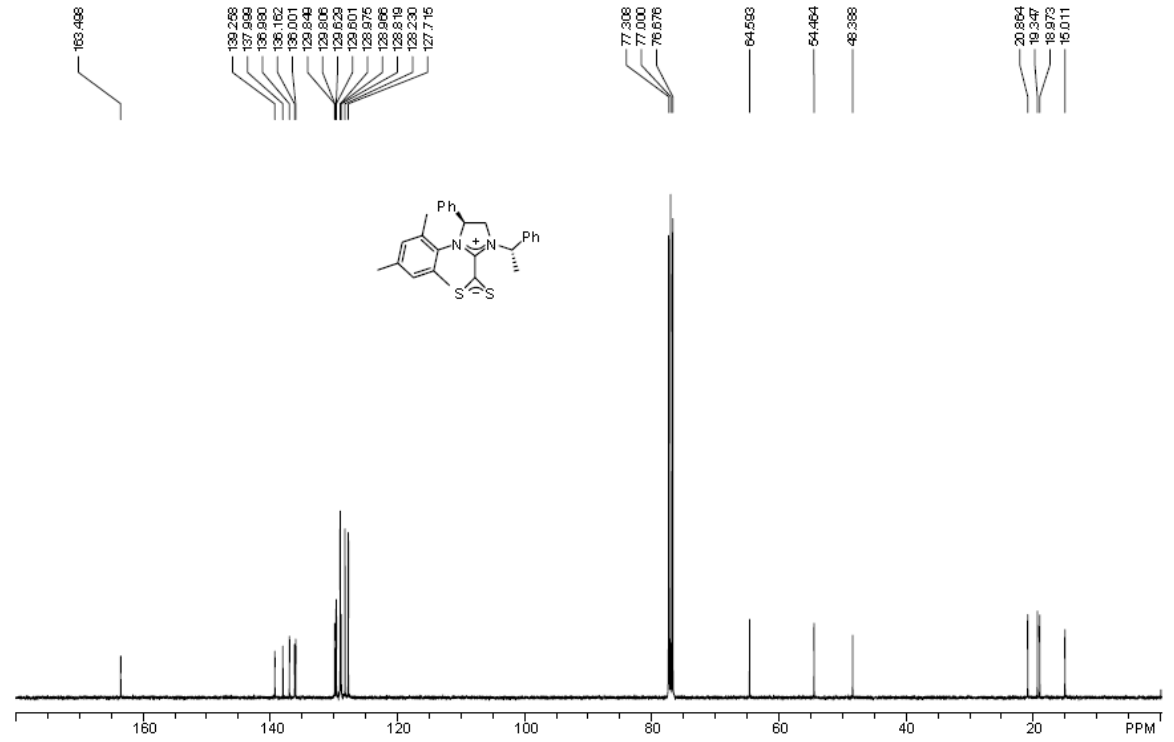
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77.000
76.676
64.593
54.464
48.388
20.864
19.347
18.973
15.011
Ph
N
N
Ph
S
S
160
140
120
100
80
60
40
20
PPM

X-Ray Crystallography.

Crystallographic measurements were made on a Bruker Smart Apex 100 CCD area detector using graphite monochromated Mo-Kαradiation ($\lambda_{\text{Mo-K}\alpha}$ = 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.[5]

Key details of the crystal and structure refinement data are summarized in Table S1–S2. 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 **3l**, **3p**, **3q**, **3r**, **4b**, and (*R*,*S*)-**5b** were assigned as 887382, 887379, 887378, 887383, 887380, and 887381, respectively.

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

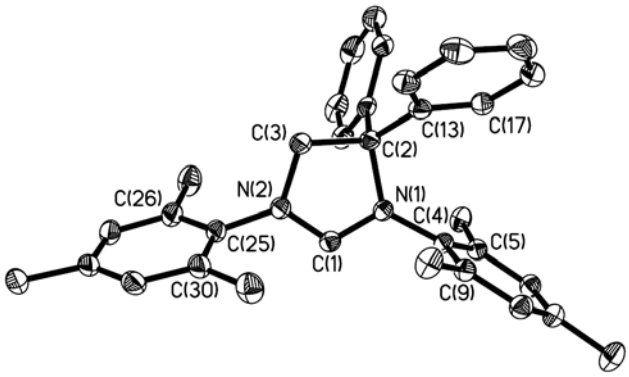

Figure S2. Molecular structure of **3l** with 30% probability ellipsoids. H atoms and the anion (OTf^-) have been omitted for clarity. Selected bond distances (Å) and angles (°): N(1)-C(1) 1.310(4), N(1)-C(4) 1.461(3), N(1)-C(2) 1.527(3), N(2)-C(1) 1.300(4), N(2)-C(25) 1.453(4), N(2)-C(3) 1.476(4), C(2)-C(13) 1.516(4), C(2)-C(3) 1.558(4), C(4)-C(5) 1.394(4), C(25)-C(30) 1.382(4), C(1)-N(1)-C(4) 121.2(2), C(1)-N(1)-C(2) 108.9(2), C(4)-N(1)-C(2) 127.9(2), C(1)-N(2)-C(25) 127.1(2), C(1)-N(2)-C(3) 109.3(2), C(25)-N(2)-C(3) 121.8(2), N(2)-C(1)-N(1) 115.1(3), C(13)-C(2)-N(1) 110.6(2), C(13)-C(2)-C(19) 111.6(2), N(1)-C(2)-C(19) 110.7(2), C(13)-C(2)-C(3) 115.8(2), N(1)-C(2)-C(3) 99.9(2), C(19)-C(2)-C(3) 107.6(2), N(2)-C(3)-C(2) 102.9(2).

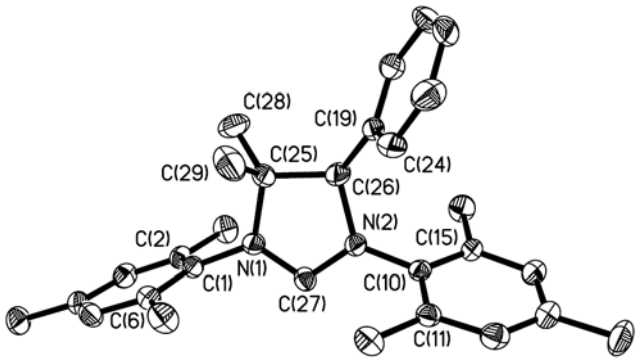

Figure S3. Molecular structure of **3p** with 30% probability ellipsoids. H atoms and the anion (OTf^-) have been omitted for clarity. Selected bond distances (Å) and angles (°): N(1)-C(27) 1.306(7), N(1)-C(1) 1.456(7), N(1)-C(25) 1.505(7), N(2)-C(27) 1.323(6), N(2)-C(10) 1.437(6), N(2)-C(26) 1.497(8), C(1)-C(6) 1.392(8), C(1)-C(2) 1.393(7), C(2)-C(3) 1.370(8), C(19)-C(24) 1.370(9), C(2)-C(7) 1.523(8), C(25)-C(29) 1.471(10), C(25)-C(28) 1.496(11), C(25)-C(26) 1.520(8), C(27)-N(1)-C(1) 125.7(4), C(27)-N(1)-C(25) 110.8(4), C(1)-N(1)-C(25) 123.1(4), C(27)-N(2)-C(10) 126.2(4), C(27)-N(2)-C(26) 108.8(5), C(10)-N(2)-C(26) 124.9(4),

C(2)-C(1)-N(1) 118.6(4), C(28)-C(25)-N(1) 115.0(5), C(29)-C(25)-C(26) 114.0(6), N(1)-C(25)-C(26) 100.4(4), N(2)-C(26)-C(25) 103.0(5), C(19)-C(26)-C(25) 119.7(5), N(1)-C(27)-N(2) 112.6(5).

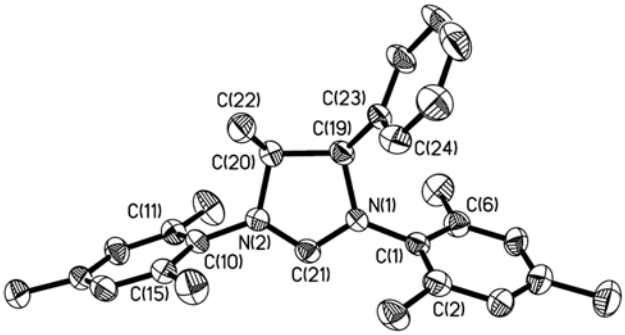

Figure S4. Molecular structure of **3q** with 30% probability ellipsoids. H atoms and the anion (OTf^-) have been omitted for clarity. Selected bond distances (Å) and angles (°): N(1)-C(21) 1.289(8), N(1)-C(1) 1.433(8), N(1)-C(19) 1.515(8), N(2)-C(21) 1.312(9), N(2)-C(10) 1.439(8), N(2)-C(20) 1.492(9), C(1)-C(2) 1.367(10), C(1)-C(6) 1.41(1), C(2)-C(3) 1.408(12), C(2)-C(9) 1.511(11), C(19)-C(23) 1.512(9), C(3)-C(4) 1.381(13), C(19)-C(20) 1.555(9), C(4)-C(5) 1.354(12), N(1)-C(21)-N(2) 115.0(6), C(21)-N(1)-C(1) 126.2(6), C(21)-N(1)-C(19) 109.7(6), C(1)-N(1)-C(19) 124.1(5), C(21)-N(2)-C(10) 126.9(6), C(21)-N(2)-C(20) 110.4(5), C(10)-N(2)-C(20) 122.6(5), C(2)-C(1)-C(6) 121.2(7), C(2)-C(1)-N(1) 119.6(6), C(6)-C(1)-N(1) 118.9(6), C(1)-C(2)-C(3) 118.2(7), C(1)-C(2)-C(9) 124.0(8), C(3)-C(2)-C(9) 117.5(8), C(4)-C(3)-C(2) 121.3(8), C(23)-C(19)-N(1) 113.4(6), N(1)-C(19)-C(20) 102.2(5).

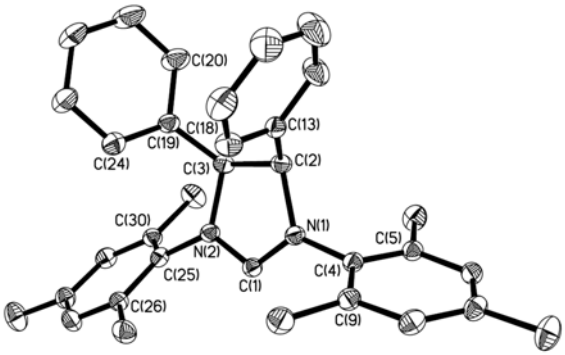

Figure S5. Molecular structure of **3r** with 30% probability ellipsoids. H atoms and the anion (OTf^-)

have been omitted for clarity. Selected bond distances (Å) and angles (°): N(1)-C(1) 1.302(4), N(1)-C(4) 1.440(4), N(1)-C(2) 1.499(3), N(2)-C(1) 1.307(4), N(2)-C(25) 1.448(4), N(2)-C(3) 1.502(4), C(2)-C(13) 1.507(4), C(2)-C(3) 1.554(4), C(3)-C(19) 1.493(4), C(4)-C(9) 1.394(4), C(4)-C(5) 1.396(4), C(1)-N(1)-C(4) 126.3(2), C(1)-N(1)-C(2) 110.5(2), C(4)-N(1)-C(2) 123.1(2), C(1)-N(2)-C(25) 124.7(3), C(1)-N(2)-C(3) 109.7(2), C(25)-N(2)-C(3) 125.6(2), N(1)-C(1)-N(2) 114.8(3), N(1)-C(2)-C(13) 112.9(2), N(1)-C(2)-C(3) 102.0(2), C(13)-C(2)-C(3) 118.8(2), C(19)-C(3)-N(2) 115.7(2), C(19)-C(3)-C(2) 115.3(2), N(2)-C(3)-C(2) 102.6(2), C(9)-C(4)-C(5) 121.7(3), C(9)-C(4)-N(1) 120.4(3), C(5)-C(4)-N(1) 117.9(3), C(6)-C(5)-C(4) 117.7(3).

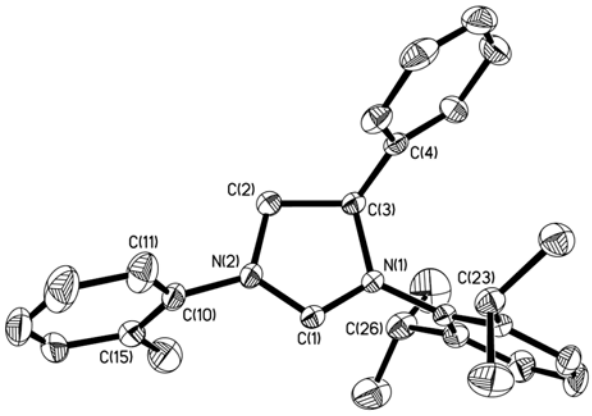

Figure S6. Molecular structure of **4d** with 30% probability ellipsoids. H atoms and the anion (OTf^-) have been omitted for clarity. Selected bond distances (Å) and angles (°): N(1)-C(1) 1.302(3), N(1)-C(17) 1.448(2), N(1)-C(3) 1.505(2), N(2)-C(1) 1.310(2), N(2)-C(10) 1.438(3), N(2)-C(2) 1.466(3), C(2)-C(3) 1.536(3), C(3)-C(4) 1.504(3), C(8)-C(9) 1.375(4), C(13)-C(14) 1.365(6), C(17)-C(22) 1.395(3), C(18)-C(19) 1.392(3), C(1)-N(1)-C(17) 125.43(16), C(1)-N(1)-C(3) 110.43(15), C(17)-N(1)-C(3) 123.76(16), C(1)-N(2)-C(10) 127.78(18), C(1)-N(2)-C(2) 109.96(18), C(10)-N(2)-C(2) 122.24(17), N(1)-C(1)-N(2) 113.87(18), N(2)-C(2)-C(3) 104.09(17), C(4)-C(3)-N(1) 113.02(16), C(4)-C(3)-C(2) 115.82(18), N(1)-C(3)-C(2) 101.02(16), C(9)-C(4)-C(3) 118.94(19).

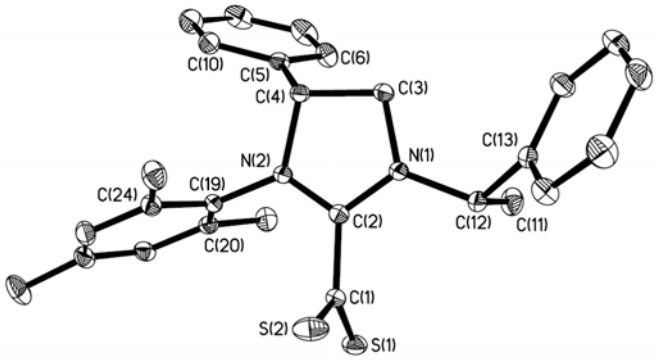

Figure S7. Molecular structure of (*R*,*S*)-**5b** with 30% probability ellipsoids. H atoms and the anion (OTf^-) have been omitted for clarity. Selected bond distances (Å) and angles (°): S(1)-C(1) 1.6595(13), S(2)-C(1) 1.6717(13), N(1)-C(2) 1.3313(15), N(1)-C(3) 1.4735(15), N(1)-C(12) 1.4776(16), N(2)-C(2) 1.3255(16), N(2)-C(19) 1.4397(16), N(2)-C(4) 1.4964(15), C(1)-C(2) 1.4920(16), C(3)-C(4) 1.5415(17), C(4)-C(5) 1.5136(17), C(5)-C(6) 1.3901(19), C(6)-C(7) 1.392(2), C(2)-N(1)-C(3) 110.41(10), C(2)-N(1)-C(12) 123.49(11), C(3)-N(1)-C(12) 122.34(10), C(2)-N(2)-C(19) 125.68(10), C(2)-N(2)-C(4) 110.89(10), C(19)-N(2)-C(4) 123.18(10), C(2)-C(1)-S(1) 115.78(9), C(2)-C(1)-S(2) 113.19(9), S(1)-C(1)-S(2) 131.02(7), N(2)-C(2)-N(1) 112.21(10), N(2)-C(2)-C(1) 123.56(11), N(1)-C(2)-C(1) 124.20(11), N(1)-C(3)-C(4) 103.64(9), N(2)-C(4)-C(5) 111.18(10), N(2)-C(4)-C(3) 101.51(9), C(5)-C(4)-C(3) 117.86(11).

Table S1. Crystal Data, Data Collection, and Structure Refinement for **3l**, **3p**, **3q**, and **3r**

	3l	**3p**	**3q**	**3r**
Identification code	a20104a	z-1659	z-1649	a11230a
Formula	$C_{34}H_{35}F_3N_2O_3S$	$C_{30}H_{35}F_3N_2O_3S$	$C_{29}H_{33}F_3N_2O_3S$	$C_{34}H_{35}F_3N_2O_3S$
Formula weight	608.70	560.66	510.44	608.70
T, K	293(2)	296(2)	173(2)	293(2)
crystal system	Triclinic	Orthorhombic	Orthorhombic	Monoclinic
space group	P-1	P2(1)2(1)2(1)	P2(1)2(1)2(1)	P2(1)/c
a, Å	10.433(4)	11.5154(5)	11.6191(11)	9.301(4)
b, Å	17.320(7)	14.5123(6)	14.5312(14)	16.385(8)
c, Å	19.236(8)	17.4192(7)	17.0220(16)	20.954(10)
α, deg	66.656(5)	90	90	90
β, deg	84.785(5)	90	90	101.758(7)
γ, deg	88.956(5)	90	90	90
Volume, Å ^{3}	3178(2)	2911.0(2)	2874.0(5)	3126(3)
Z	4	4	4	4
D_{calc}, Mg / m^3	1.272	1.279	1.263	1.293
absorption coefficient, mm^{-1}	0.156	0.164	0.164	0.158
F(000)	1280	1184	1152	1280
crystal size, mm	0.45 x 0.30 x 0.21	0.36 x 0.18 x 0.12	0.46 x 0.32 x 0.22	0.25 x 0.15 x 0.15
2θ range, deg	1.34 to 25.01	1.83 to 25.01	1.84 to 25.01	1.59 to 25.01
reflections collected /unique	13216 / 10966 [R(int) = 0.0399]	34247 / 5127 [R(int) = 0.0840]	32907 / 5056 [R(int) = 0.1089]	12757 / 5482 [R(int) = 0.0661]
data / restraints / parameters	10966 / 14 / 795	5127 / 0 / 352	5056 / 0 / 343	5482 / 1 / 398
goodness of fit on F^2	1.042	1.037	1.031	0.908
final R indices [I >2σ(I)][a]	R1 = 0.0694, wR2 = 0.2017	R1 = 0.0797, wR2 = 0.2218	R1 = 0.0858, wR2 = 0.2280	R1 = 0.0591, wR2 = 0.1237
R indices (all data)	R1 = 0.0945, wR2 = 0.2275	R1 = 0.1271, wR2 = 0.2624	R1 = 0.1654, wR2 = 0.2978	R1 = 0.1247, wR2 = 0.1472
lgst diff peak and hole, e/Å^3	0.620 and -0.429	0.494 and -0.347	0.565 and -0.235	0.284 and -0.191

Table S2. Crystal Data, Data Collection, and Structure Refinement for **4b** and (*R*,*S*)-**5b**

	4b	(*R*,*S*)-**5b**
Identification code	cd212276	mo_dm12279_0m
Formula	$C_{29}H_{33}F_3N_2O_3S$	$C_{27}H_{28}N_2S_2$
Formula weight	546.63	444.63
T, K	293(2)	173(2)
crystal system	Orthorhombic	Orthorhombic
space group	Pbca(61)	P2(1)2(1)2(1)
a, Å	16.6967(11)	10.0291(10)
b, Å	18.3660(12)	15.1285(15)
c, Å	18.5592(12)	15.5536(15)
α, deg	90	90
β, deg	90	90
γ, deg	90	90
Volume, Å ^{3}	5691.2(6)	2359.9(4)
Z	8	4
D_{calc}, Mg / m^3	1.276	1.251
absorption coefficient, mm^{-1}	0.165	0.243
F(000)	2304	944
crystal size, mm	0.312 x 0.212 x 0.145	0.28 x 0.25 x 0.22
2θ range, deg	1.98 to 25.50	1.88 to 29.24
reflections collected /unique	31583 / 5307 [R(int) = 0.0539]	21311 / 6400 [R(int) = 0.0840]
data / restraints / parameters	5307 / 86 / 420	6400 / 0 / 284
goodness of fit on F^2	1.023	1.034
final R indices [I >2σ(I)]^a	R1 = 0.0521, wR2 = 0.1317	R1 = 0.0303, wR2 = 0.0804
R indices (all data)	R1 = 0.0860, wR2 = 0.1532	R1 = 0.0347, wR2 = 0.0835
lgst diff peak and hole, e/Å^3	0.185 and -0.138	0.248 and -0.256