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Syntheses of tetrahydroquinoline-based chiral carbene precursors and the related chiral NHC-Au(I) complex having a rare intramolecular Au···H−C(sp^3) interaction

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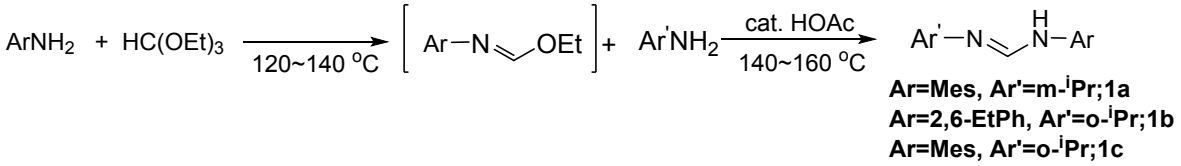
General Information:

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, $(CD_3)_2SO$ 2.50 ppm; ^{13}C NMR $CDCl_3$: 77.0 ppm). Mass spectra were recorded on the HP-5989 instrument by EI/ESI methods. X-ray diffraction analysis was performed by using a Bruker Smart-1000X-ray diffractometer.

Preparation and characterization

Synthesis of various formamidines:



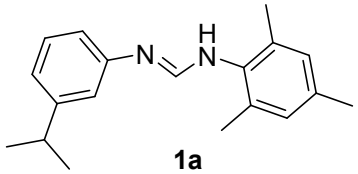
Scheme S-1: Synthesis of various formamidines**.**

General procedure:

The mixture of aromatic amines (1.0 eq.) and triethylorthoformate (1.0 eq.) was heate d at 120~140 °C. After 5 h, the mixture was allowed to cool to room temperature. T hen another aromatic amine (1.0 eq.) and glacial acetic acid (0.05 eq.) was added. Th e mixture was stirred at 140~160 °C for 5 h, then pre-absorbed on silica gel and puri fied by column chromatography (PE/EtOAc = 25:1→20:1) to afford the products.

The formamidines **1c** were prepared as previously reported.[1]

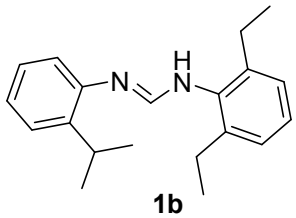
N'-(3-isopropylphenyl)-N-mesitylformimidamide (1a)



1a

Following the general procedure, 2,4,6-trimethylaniline (6.0 g, 44.38 mmol, 1.0 eq.), triethylorthoformate (6.6 g, 44.38 mmol, 1.0 eq.), 3-isopropylaniline (6.0 g, 44.38 mmol, 1.0 eq.) and glacial acetic acid (133 mg, 2.22 mmol, 0.05 eq.) afforded the product as white solid (6.8 g, 55%).The product was obtained as a complex mixture of isomers and the assignment was not possible. In $CDCl_3$ (25 °C) this formamidine exists as a mixture of two isomers in a ratio of 7:3 ratio. ^{1}H NMR chemical shifts that differ between isomers are marked by maj. and min. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (s, 1H), 7.21 (t, J = 8.0 Hz, 0.3H, min.), 7.16 (t, J = 8.0 Hz, 0.7H, maj.), 6.91 (s, 2H), 6.85 (d, J = 7.2 Hz, 1H), 6.76 (d, J = 7.6 Hz, 1H), 6.72 (s, 0.3H, min.), 6.68 (s, 0.7H, maj.), 2.87-2.82 (m, 0.3H, min.), 2.77-2.72 (m, 0.7H, maj.), 2.29 (s, 3H), 2.22 (s, 4H), 2.13 (s, 2H), 1.23 (d, J = 7.2 Hz, 2H), 1.14 (d, J = 6.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.5, 130.7, 129.6, 129.4, 129.2, 129.0, 128.8, 120.4, 115.1, 113.0, 34.0, 23.8, 23.6, 20.7, 18.6, 179; HRMS (EI): m/z $[M]^+$ calcd. for $C_{22}H_{28}N_2^+$: 320.2252, found: 320.2249.

N-(2,6-diethylphenyl)-N'-(2-isopropylphenyl)formimidamide (1b)

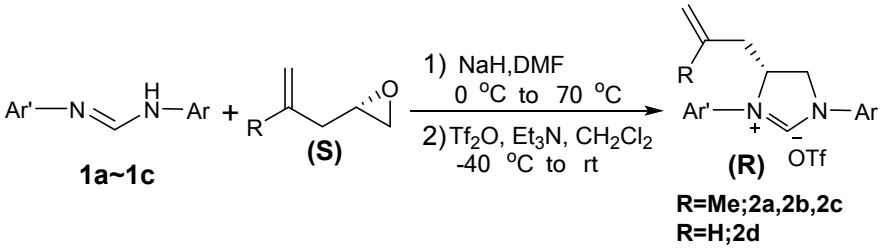


1b

Following the general procedure, 2,6-diethylaniline (6.0 g, 40.27 mmol, 1.0 eq.), triethylorthoformate (6.0 g, 40.27 mmol, 1.0 eq.), 2-isopropylaniline (5.5 g, 40.27 mmol, 1.0 eq.) and glacial acetic acid (121 mg, 2.01 mmol, 0.05 eq.) afforded the product as white solid (6.3 g, 53%).The product was obtained as a complex mixture of isomers and the assignment was not possible. In $CDCl_3$ (25 °C) this formamidine exists as a mixture of two isomers in a ratio of 3:2 ratio. ^{1}H NMR chemical shifts that differ between isomers are marked by maj. and min. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82 (d, J = 11.2 Hz, 0.4H, min.), 7.68 (s, 0.6H, maj.), 7.2-6.95 (m, 7H),3.31-3.23 (m, 1H) 2.68-2.47 (m, 4H), 1.26 (d, J = 6.8 Hz, 4.5H), 1.21 (d, J = 6.0 Hz, 3H), 1.18 (d, J = 6.4 Hz, 3H), 1.05 (d, J = 6.8 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.0, 137.0, 136.2, 134.2, 126.9, 126.5, 126.4, 125.6, 124.0, 123.7, 123.6, 118.8, 117.5, 27.6, 24.9, 24.5, 22.8, 22.3, 14.8, 14.4.

Synthesis of various imidazolinium salts 2a~2d:

The (S)-2-allyloxiranes were prepared as previously reported. [2,3]

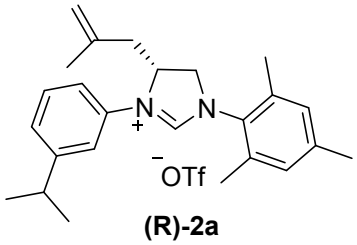


Scheme S-2: Synthesis of various imidazolinium salts **2a~2d.**

General procedure:

Formamidine (1.0 eq.) was dissolved in DMF, and to the suspension NaH (60% suspension in mineral oil, 1.5 eq.) was added portion by portion at 0°C. After 5 mins the resulting mixture was warmed to room temperature and stirred for 30 mins. After cooling to 0°C, (S)- 2-allyloxirane (1.2 eq.) was added dropwise, After 5 mins the mixture was heated to 70°C. The reaction progress was monitored by TLC. 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 Na_2SO_4. The volatiles were removed under vacuum, and the residue was purified by flash chromatography on silica gel (PE/EtOAc = 25:1) to give alcohol intermediate which were used directly. The alcohol intermediate was then dissolved in dry CH_2Cl_2. The mixture was cooled to 0°C, and Et_3N (1.2 eq.) was added dropwise. After 5 mins, Tf_2O (1.2 eq.) was added carefully under -40°C. 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 (CH_2Cl_2-EtOH = 40:1→20:1) to give the product **(R)-2.**

(R)-3-(3-isopropylphenyl)-1-mesityl-4-(2-methylallyl)-4,5-dihydro-1H-imidazol-3-ium trifluoromethanesulfonate ((R)-2a)

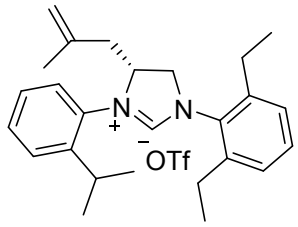


(R)-2a

Following the general procedure, formamidine **1a** (1.0 g, 3.57 mmol, 1.0 eq.) dissolved in DMF 15 mL, NaH (60% suspension in mineral oil, 214 mg, 5.36 mmol, 1.5 eq.), and (S)-2-allyloxirane (420 mg, 4.28 mmol, 1.2 eq.), afforded alcohol intermediate as yellow oill (960

mg, 71%); alcohol intermediate (960 mg, 2.54 mmol, 1.0 eq.) dissolved in CH_2Cl_2 10 mL, Et_3N (308 mg, 3.05 mmol, 1.2 eq.) and Tf_2O (879 mg, 3.05 mmol, 1.2 eq.), afforded **(R)-2a** as white powder (847 mg, 65%). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.67 (s, 1H), 7.42-7.32 (m, 3H) 7.27 (s, 1H), 6.95 (s, 2H), 5.54-5.47 (m, 1H), 4.95 (s, 1H), 4.80 (s, 1H), 4.55 (t, *J* = 11.6 Hz, 1H), 3.98 (dd, *J* = 12.0 Hz, 6.0 Hz, 1H), 3.01-2.94 (m, 1H), 2.65 (dd, *J* = 14.0 Hz, 2.4 Hz, 1H), 2.34 (s, 3H), 2.29 (s, 6H), 1.76 (s, 3H), 1.26 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.5, 151.8, 140.5, 138.6, 133.7, 130.2, 130.1, 129.9, 126.8, 119.8,119.1, 115.8, 60.1, 55.4, 40.5, 34.0, 23.6, 22.3, 21.0, 17.6; HRMS (EI): m/z [M − OTf] calcd for $C_{25}H_{33}N_2^+$: 361.2644; found: 361.2642; $[\alpha]^{25}_D$ +70 (*c* = 0.050, CH_2Cl_2).

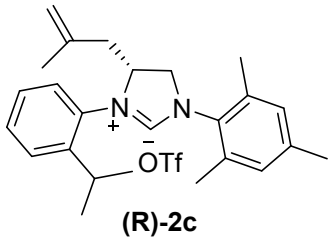
(R)-1-(2,6-diethylphenyl)-3-(2-isopropylphenyl)-4-(2-methylallyl)-4,5-dihydro-1H-imidazol-3-ium trifluoromethanesulfonate ((R)-2b)



(R)-2b

Following the general procedure, formamidine **1b** (1.0 g, 3.40 mmol, 1.0 eq.) dissolved in DMF 15 mL, NaH (60% suspension in mineral oil, 204 mg, 5.10 mmol, 1.5 eq.), and (S)-2-allyloxirane (400 mg, 4.08 mmol, 1.2 eq.), afforded alcohol intermediate as yellow oill (980 mg, 71%); alcohol intermediate (980 mg, 2.50 mmol, 1.0 eq.) dissolved in CH_2Cl_2 10 mL, Et_3N (304 mg, 3.00 mmol, 1.2 eq.) and Tf_2O (865 mg, 3.00 mmol, 1.2 eq.), afforded **(R)-2b** as white powder (983 mg, 75%). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.20 (s, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.50-7.37 (m, 4H), 7.24 (d, *J* = 6.8 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 5.24-5.22 (m, 1H), 4.92 (s, 1H), 4.80 (s, 1H), 4.69 (t, *J* = 11.6 Hz, 1H), 4.00 (dd, *J* = 12.0 Hz, 6.8 Hz, 1H), 3.13-3.07 (m, 1H), 2.77-2.69 (m, 4H), 2.51 (d, *J* = 13.2 Hz, 1H), 2.44 (d, *J* = 11.6 Hz, 1H), 1.70 (s, 3H), 1.37-1.24 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.8, 140.8, 138.4, 131.2, 131.1, 131.0, 130.4, 128.3, 128.1, 128.0, 127.5, 127.3, 127.2, 115.5, 63.2, 56.9, 41.1, 28.3, 24.3, 24.2, 24.1, 23.9, 22.0, 15.2, 14.9; HRMS (EI): m/z $[M - OTf]^+$ calcd. for $C_{26}H_{35}N_2^+$:375.2800, found: 375.5796. $[\alpha]^{25}_D$ +70 (*c* = 0.050, CH_2Cl_2).

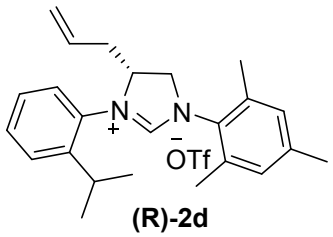
(R)-3-(2-isopropylphenyl)-1-mesityl-4-(2-methylallyl)-4,5-dihydro-1H-imidazol-3-ium trifluoromethanesulfonate ((R)-2c)



(R)-2c

Following the general procedure, formamidine **1c** (1.0 g, 3.57 mmol, 1.0 eq.) dissolved in DMF 15 mL, NaH (60% suspension in mineral oil, 214 mg, 5.36 mmol, 1.5 eq.), and (S)-2-allyloxirane (420 mg, 4.28 mmol, 1.2 eq.), afforded alcohol intermediate as yellow oill (820 mg, 60%); alcohol intermediate (820 mg, 2.17 mmol, 1.0 eq.) dissolved in CH_2Cl_2 10 mL, Et_3N (264 mg, 2.60 mmol, 1.2 eq.) and Tf_2O (750 mg, 2.60 mmol, 1.2 eq.), afforded **(R)-2c** as white powder (819 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (s, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.45 (d, J = 7.2 Hz, 1H), 7.39 (t, J = 7.2 Hz, 1H), 6.99 (s, 2H), 5.20-5.12 (m, 1H), 4.93 (s, 1H), 4.80 (s, 1H), 4.63 (t, J = 12.0 Hz, 1H), 3.98 (dd, J = 11.6 Hz, 6.8 Hz, 1H), 3.13-3.06 (m, 1H), 2.51 (dd, J = 14.0 Hz, 3.6 Hz, 1H), 2.46 (d, J = 11.6 Hz, 1H), 2.40 (s, 6H), 2.31 (s, 3H), 1.71 (s, 3H), 1.33 (d, J = 6.4 Hz, 3H), 1.32 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.9, 145.3, 140.4, 138.3, 135.2, 130.9, 130.4, 129.9, 128.3, 127.6, 127.2, 62.9, 55.5, 53.4, 40.7, 30.8, 28.1, 24.1, 23.9, 21.9, 20.9, 17.5; HRMS (EI): m/z [M – OTf]$^+$ calcd. for $C_{25}H_{33}N_2^+$:361.2644, found: 361.2645. $[\alpha]^{25}_D$ +35 (c = 0.100, CH_2Cl_2).

(R)-4-allyl-3-(2-isopropylphenyl)-1-mesityl-4,5-dihydro-1H-imidazol-3-ium trifluoromethanesulfonate ((R)-2d)

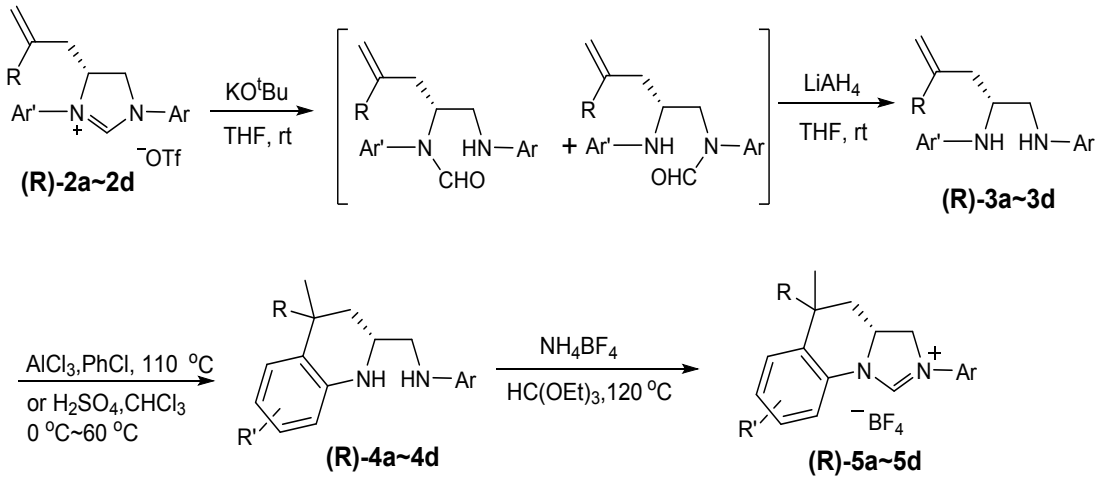


(R)-2d

Following the general procedure, formamidine **1a** (1.0 g, 3.57 mmol, 1.0 eq.) dissolved in DMF 15 mL, NaH (60% suspension in mineral oil, 214 mg, 5.36 mmol, 1.5 eq.), and (S)-2-allyloxirane (360 mg, 4.28 mmol, 1.2 eq.), afforded alcohol intermediate as yellow oill (770 mg, 59%); alcohol intermediate (770 mg, 2.11 mmol, 1.0 eq.) dissolved in CH_2Cl_2 10 mL, Et_3N (256 mg, 2.53 mmol, 1.2 eq.) and Tf_2O (730 mg, 2.53 mmol, 1.2 eq.), afforded **(R)-2d** as white powder (718 mg, 69%) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.20 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.45 (d, J = 6.4 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 6.98 (s, 2H), 5.75-5.65 (m, 1H), 5.27 (t, J = 12.0 Hz, 2H), 5.20-5.12 (m, 1H), 4.64 (t, J = 12.0 Hz, 1H), 4.03 (dd, J = 12.0 Hz, 7.6 Hz, 1H), 3.11-3.04 (m, 1H), 2.61-2.56 (m, 1H), 2.55-2.47 (m, 1H),

2.38 (s, 6H), 2.31 (s, 3H), 1.33 (d, J = 6.8 Hz, 3H), 1.30 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.2, 145.1, 140.8, 131.1, 130.4, 130.1, 130.0, 129.9, 128.1, 127.8, 127.4, 121.5, 64.1, 55.1, 36.1, 28.3, 24.3, 24.1, 21.0, 17.7; HRMS (EI): m/z [M – OTf]$^+$ calcd. for $C_{24}H_{31}N_2^+$:347.2487, found: 347.2491. $[\alpha]^{25}_D$ +82 (c = 0.050, CH_2Cl_2).

Synthesis of various imidazolinium salts 6a~6d:



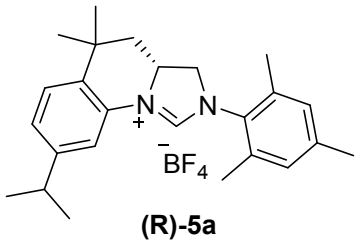
Scheme S-3: Synthesis of various imidazolinium salts **5a~5d.**

General procedure:

Imidazolinium salts **(R)-2** (1.0 eq.) was dissolved in THF, and KO^{t}Bu (1.5 eq.) was added. The mixture was stirred at room temperature for 3h, the reaction progress was monitored by TLC. After full conversion of the corresponding imidazolinium salts **2**, H_2O was added and the mixture was extracted with EtOAc (15 mL x 3), the combined organic layers was dried over anhydrous Na_2SO_4. The volatiles were removed under vacuum, and the residue were used for the next step directly. The intermediate was then dissolved in dry THF and $LiAlH_4$ (1.5 eq) was added under 0°C, then the mixture was stirred at room temperature for 2 h, then 10% NaOH was added and the mixture was extracted with EtOAc (15 mL x 3), The combined organic layers was dried over anhydrous Na_2SO_4. The volatiles were removed under vacuum, and the residue was purified by flash chromatography to give diamine intermediate **3** which were used without characterization. The diamine intermediate **3** was then dissolved in PhCl and $AlCl_3$ (2.5 eq) was added, then the mixture was heated to 110°C for 2 h（or the diamine intermediate **3** was dissolved in $CHCl_3$ and H_2SO_4 was added under 0°C carefully, then the mixture was heated to 60°C for 3 h), then ice water was added and the mixture was extracted with EtOAc (15 mL x 3), The combined organic layers was dried over anhydrous Na_2SO_4. The volatiles were removed under vacuum, and the residue was purified by flash chromatography to give diamine intermediate **4** which were used without characterization.

The diamine intermediate **4** was then dissolved in $HC(OEt)_3$ and NH_4BF_4 (1.2 eq) was added, and the mixture was heated to 120°C for 4 h, then pre-absorbed on silica gel and purified by chromatography on silica gel to give the product **(R)-5.**

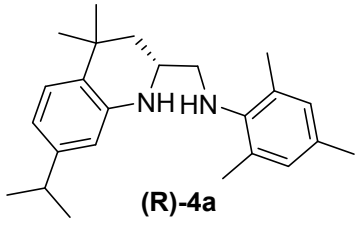
(R)-8-isopropyl-2-mesityl-5,5-dimethyl-3,3a,4,5-tetrahydro-2H-imidazo[1,5-a]quinolin-10-ium tetrafluoroborate ((R)-5a)



(R)-5a

Following the general procedure, imidazolinium salts **2a** (1.0 g, 1.96 mmol, 1.0 eq.) dissolved in THF 10 mL, and KO^{t}Bu (330 mg, 2.94 mmol, 1.5 eq.); THF 10 mL, KO^{t}Bu (263 mg, 2.35 mmol, 1.2 eq.) and $LiAlH_4$ (112 mg, 2.94 mmol, 1.5 eq), afforded **3a** as yellow oill (452 mg, 66%); **3a** (450 mg, 1.29 mmol, 1.0 eq.) dissolved in PhCl 10 mL, amd $AlCl_3$ (430 mg, 3.21 mmol, 2.5 eq), afforded **4a** as yellow oill (250 mg, 55%); **4a** (250 mg, 0.71 mmol, 1.0 eq) dissolved in $HC(OEt)_3$ 6 mL, and NH_4BF_4 (90 mg, 0.86 mmol, 1.2 eq), afforded **(R)-5a** as yellow powder (200 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71 (s, 1H), 7.42 (d, J = 1.6 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.18 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 6.97 (s, 2H), 5.06-4.97 (m, 1H), 4.64 (t, J = 12.0 Hz, 1H), 3.86 (dd, J = 11.6 Hz, 10.0 Hz, 1H), 2.99-2.92 (m, 1H), 2.38 (s, 3H), 2.30 (s, 3H), 2.27 (s, 3H), 2.22-2.1 (m, 1H), 2.13 (t, J = 13.2 Hz, 1H), 1.48 (s, 3H), 1.41 (s, 3H), 1.25 (d, J = 1.6 Hz, 3H), 1.23 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.8, 149.7, 140.7, 133.3, 130.2, 129.7, 127.8, 126.2, 115.7, 56.8, 56.3, 43.2, 33.7, 33.4, 31.7, 30.6, 23.6, 23.5, 21.0, 17.5; HRMS (ESI): m/z $[M - BF_4]^+$ calcd. for $C_{25}H_{33}N_2^+$:361.2638, found: 361.2639. $[\alpha]^{25}_D$ +503 (c = 0.035, CH_2Cl_2).

(R)-N-((7-isopropyl-4,4-dimethyl-1,2,3,4-tetrahydroquinolin-2-yl)methyl)-2,4,6-trimethylaniline ((R)-4a)

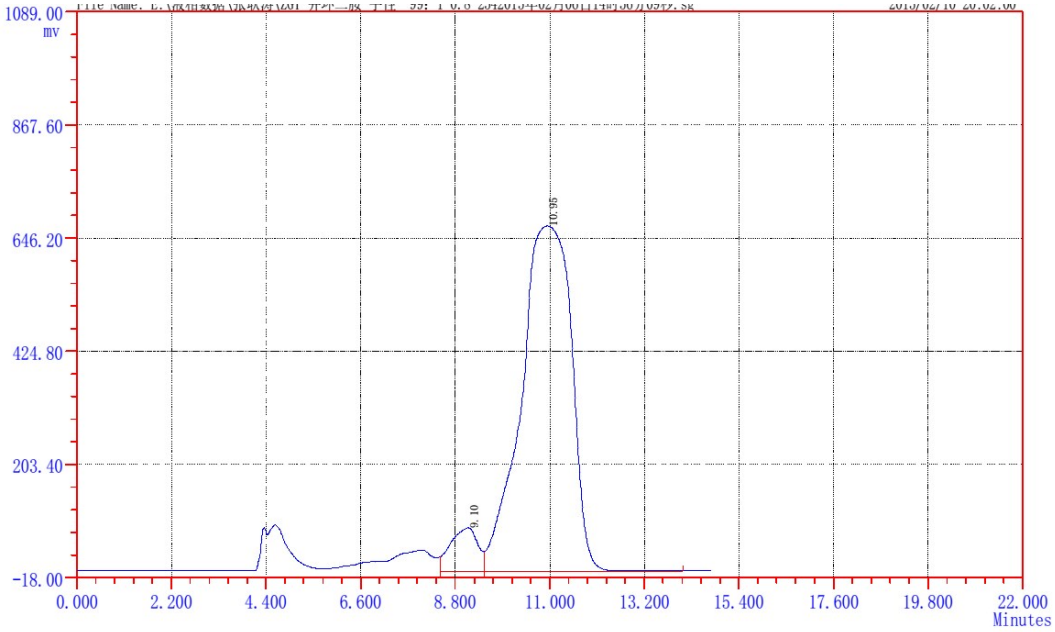


(R)-4a

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12 (d, J = 8.0 Hz, 1H), 6.85 (s, 2H), 6.56 (dd, J = 7.6 Hz, 1.6 Hz, 1H), 6.41 (d, J = 1.6 Hz, 1H), 3.59-3.52 (m, 1H), 3.01 (dd, J = 12.0 Hz, 4.0 Hz, 1H), 2.92 (dd, J = 12.0 Hz, 8.0 Hz, 1H), 2.81-2.74 (m, 1H), 2.31 (s, 6H), 2.24 (s, 3H), 1.64 (d, J =

3.2 Hz, 1H), 1.62 (s, 1H), 1.35 (s, 3H), 1.28 (s, 3H), 1.21 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.4, 143.2, 143.0, 131.9, 130.3, 129.5, 127.8, 126.2, 115.8, 112.3, 54.5, 49.1, 42.2, 33.6, 32.9, 32.2, 30.3, 24.0, 23.9, 20.6, 18.3; HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_{24}H_{35}N_2^+$:351.2795, found: 351.2795. $[\alpha]^{25}_D$ +96.8 (c = 0.080, CH_2Cl_2).

HPLC for **(R)-4a**: Chiralcel OD-H, 99:1 Hexanei-PrOH, 25°C, 254 nm, 0.8 mL/min.



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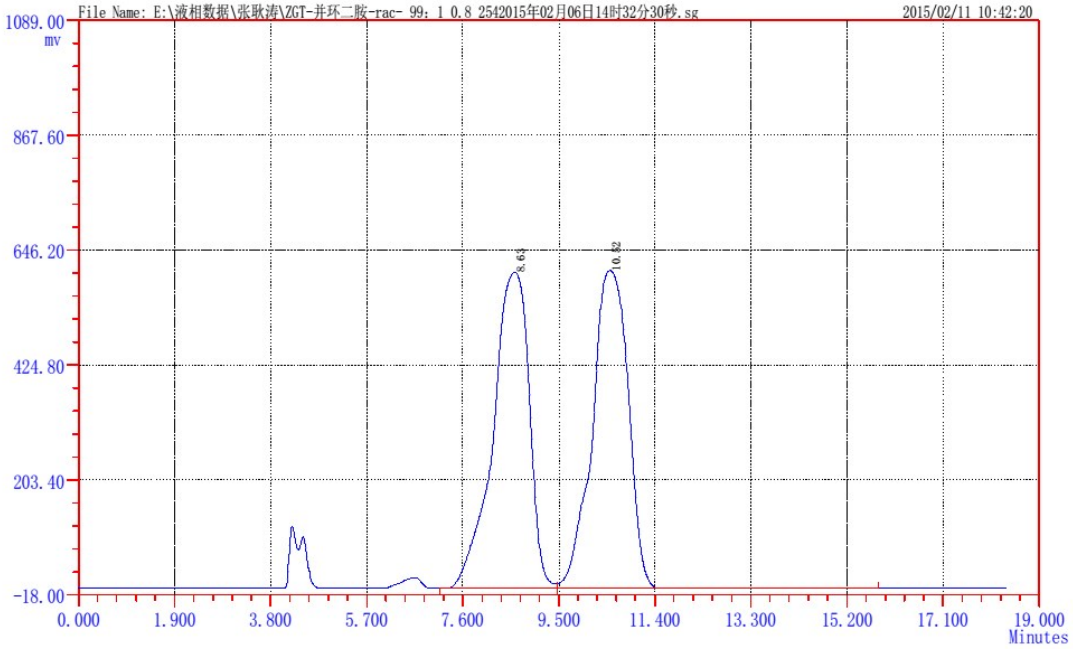

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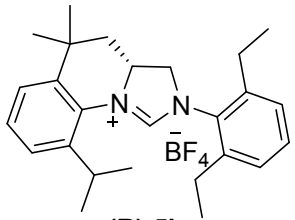
2		10.515	612150	30439690.0	49.9515	0.92	891
	Σ:		1221388	60938457.6	100.0000		

(R)-2-(2,6-diethylphenyl)-9-isopropyl-5,5-dimethyl-3,3a,4,5-tetrahydro-2H-imidazo[1,5-a]quinolin-10-ium tetrafluoroborate ((R)-5b)

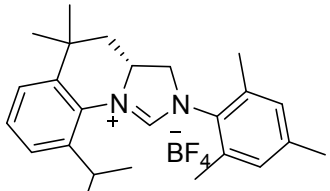


(R)-5b

Following the general procedure, imidazolinium salts **2b** (1.8 g, 3.43 mmol, 1.0 eq.) dissolved in THF 15 mL, and KO^{t}Bu (576 mg, 5.15 mmol, 1.5 eq.); THF 15 mL, KO^{t}Bu (461 mg, 4.12 mmol, 1.2 eq.) and $LiAlH_4$ (196 mg, 5.15 mmol, 1.5 eq), afforded **3b** as yellow oill (640 mg, 52%); **3b** (640 mg, 1.76 mmol, 1.0 eq.) dissolved in PhCl 10 mL, amd $AlCl_3$ (586 mg, 4.40 mmol, 2.5 eq), afforded **4b** as yellow oill (300 mg, 49%); **4b** (300 mg, 0.82 mmol, 1.0 eq) dissolved in $HC(OEt)_3$ 6 mL, and NH_4BF_4 (103 mg, 0.98 mmol, 1.2 eq), afforded **(R)-5b** as brown powder (205 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (s, 1H), 7.47-7.42 (m, 2H), 7.35-7.27 (m,1H), 5.18-5.10 (m, 1H), 4.80 (t, J = 11.6 Hz, 1H), 4.04 (dd, J = 12.0 Hz, 4.0 Hz, 1H), 3.07-3.00 (m, 1H), 2.76-2.66 (m, 4H), 2.56 (d, J = 5.2 Hz, 1H), 2.45 (d, J = 4.8 Hz, 1H), 1.51 (s, 3H), 1.44 (s, 3H), 1.35-1.29 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =

155.0, 141.2, 141.0, 139.8, 139.5, 131.0, 128.4, 128.1, 127.7, 127.3, 126.9, 125.6, 125.4, 115.0, 63.0, 58.3, 57.7, 53.4, 44.2, 34.6, 32.3, 31.1, 31.0, 27.5, 24.4, 24.1, 23.8, 15.6, 14.6; HRMS (EI): m/z $[M - BF_4]^+$ calcd. for $C_{26}H_{35}N_2^+$:375.2800, found: 375.2785. $[\alpha]^{25}_D$ +192 (*c* = 0.050, CH_2Cl_2).

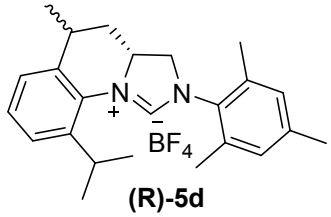
(R)-9-isopropyl-2-mesityl-5,5-dimethyl-3,3a,4,5-tetrahydro-2H-imidazo[1,5-a]quinolin-10-ium ((R)-5c)



(R)-5c

Following the general procedure, imidazolinium salts **2c** (1.0 g, 1.96 mmol, 1.0 eq.) dissolved in THF 10 mL, and KO^{t}Bu (330 mg, 2.94 mmol, 1.5 eq.); THF 10 mL, KO^{t}Bu (263 mg, 2.35 mmol, 1.2 eq.) and $LiAlH_4$ (112 mg, 2.94 mmol, 1.5 eq), afforded **3c** as yellow oill (464 mg, 68%); **3c** (464 mg, 1.32 mmol, 1.0 eq.) dissolved in PhCl 10 mL, amd $AlCl_3$ (440 mg, 3.31 mmol, 2.5 eq), afforded **4c** as yellow oill (282 mg, 61%); **4c** (282 mg, 0.80 mmol, 1.0 eq) dissolved in $HC(OEt)_3$ 6 mL, and NH_4BF_4 (101 mg, 0.96 mmol, 1.2 eq), afforded **(R)-5c** as brown powder (214 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (s, 1H), 7.34-7.28 (m, 3H), 7.02 (s, 2H), 5.15-5.08 (m, 1H), 4.77 (t, *J* = 11.6 Hz, 1H), 4.00 (dd, *J* = 12.4 Hz, 4.0 Hz, 1H), 3.09-3.02 (m, 1H), 2.37 (s, 6H), 2.34 (s, 3H), 2.28 (d, *J* = 12.0 Hz 1H), 2.21 (dd, *J* = 13..2 Hz, 2.8 Hz, 1H), 1.50 (s, 3H), 1.44 (s, 3H), 1.34 (d, *J* = 2.4 Hz, 3H), 1.32 (d, *J* = 4.0 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.0, 141.1, 139.9, 139.4, 134.9, 130.3, 129.9, 128.5, 128.1, 125.7, 125.6, 58.4, 56.6, 44.3, 34.7, 32.5, 31.2, 31.0, 27.7, 24.5, 24.3, 17.7; HRMS (EI): m/z $[M - BF_4]^+$ calcd. for $C_{25}H_{33}N_2^+$:361.2644, found: 361.2642. $[\alpha]^{25}_D$ +88.3 (*c* = 0.050, CH_2Cl_2).

(3aR)-9-isopropyl-2-mesityl-5-methyl-3,3a,4,5-tetrahydro-2H-imidazo[1,5-a]quinolin-10-ium tetrafluoroborate ((R)-5d)

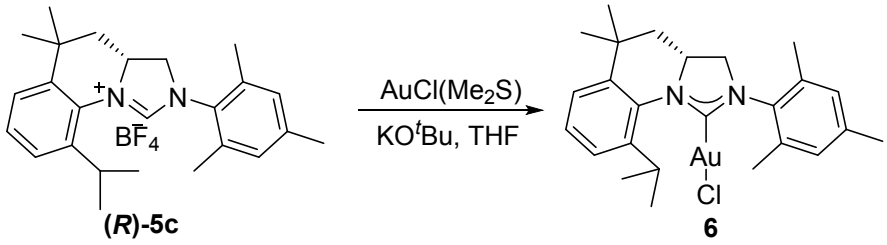


(R)-5d

Following the general procedure, imidazolinium salts **2d** (620 mg, 1.25 mmol, 1.0 eq.) dissolved in THF 10 mL, and KO^{t}Bu (210 mg, 1.88 mmol, 1.5 eq.); THF 10 mL, KO^{t}Bu (168

mg, 1.50 mmol, 1.2 eq.) and $LiAlH_4$ (72 mg, 1.88 mmol, 1.5 eq), afforded **3d** as yellow oill (291 mg, 69%); **3d** (291 mg, 0.86 mmol, 1.0 eq.) dissolved in $CHCl_3$ 5 mL, amd H_2SO_4 1.0 mL, afforded **4d** as yellow oill (214 mg, 74%); **4d** (214 mg, 0.64 mmol, 1.0 eq) dissolved in $HC(OEt)_3$ 5 mL, and NH_4BF_4 (80 mg, 0.76 mmol, 1.2 eq), afforded **(R)-5d** as yellow powder (200 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (s, 1H), 7.35-7.28 (m, 3H), 7.02 (s, 2H), 5.04-4.97 (m, 1H), 4.73 (t, J = 12.0 Hz, 1H), 4.02 (dd, J = 12.4 Hz, 3.6 Hz, 1H), 3.38-3.27 (m, 1H), 3.07-3.00 (m, 1H), 2.58-2.53 (m, 1H), 2.37 (s, 3H), 2.34 (s, 6H), 2.09-2.00 (m 1H), 1.48 (d, J = 7.2 Hz, 3H), 1.33 (d, J = 3.6 Hz, 3H), 1.31 (d, J = 3.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.1, 141.0, 140.0, 135.2, 134.9, 130.3, 129.9, 129.2, 128.5, 126.4, 125.5, 60.9, 56.5, 38.1, 31.2, 27.5, 24.3, 24.1, 21.7, 21.0, 17.6; HRMS (EI): m/z $[M - BF_4]^+$ calcd. for $C_{24}H_{31}N_2^+$:347.2487, found: 347.2486. $[\alpha]^{25}_D$ +100 (c = 0.035, CH_2Cl_2).

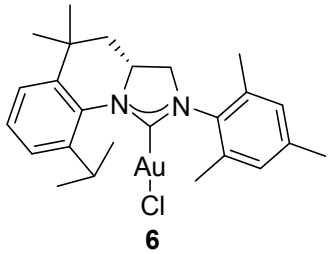
Synthesis of NHC-Au complex 6



(*R*)-5c 6

Scheme S-4: Synthesis of NHC-Au complex**.**

((3aR)-9-isopropyl-2-mesityl-5,5-dimethyl-1,2,3,3a,4,5-hexahydroimidazo[1,5-a]quinolin-1-yl)gold(II) chloride (6)



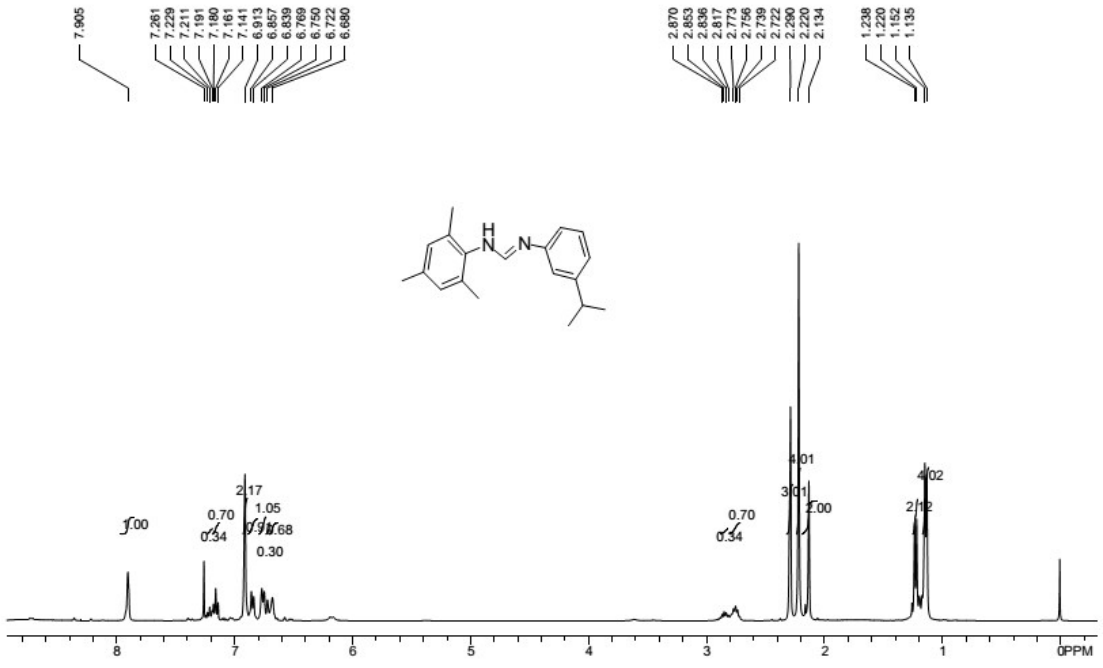
6

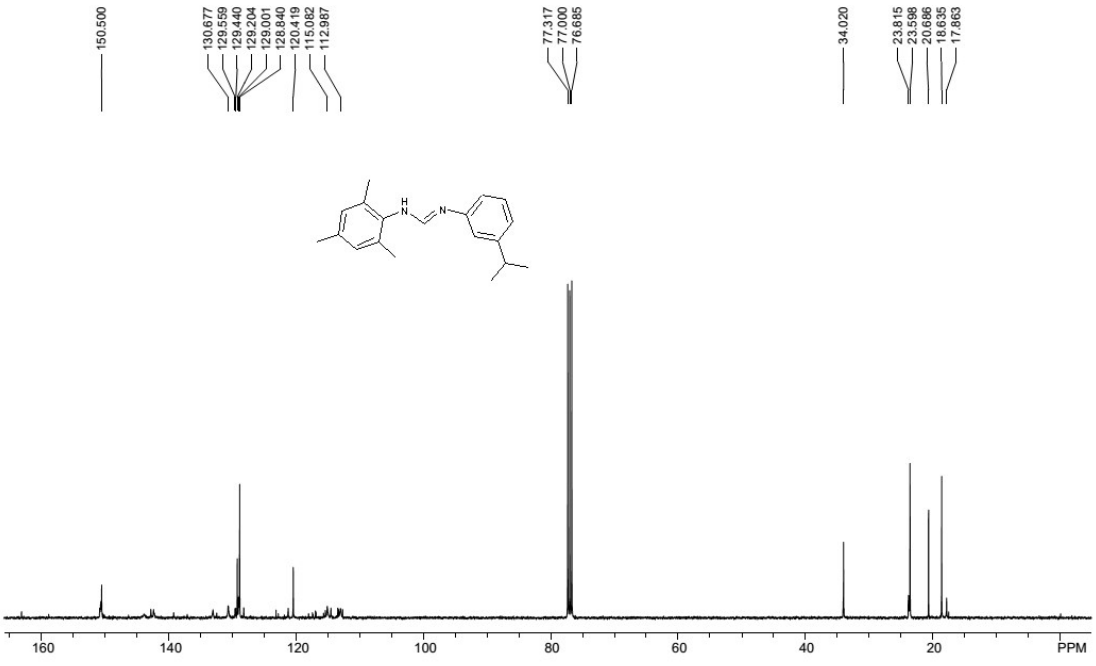
Imidazolinium salts **(R)-5c** (50 mg, 0.11 mmol, 1.0 eq.) was dissolved in dry THF in 25 mL Schlenk tube, and KO^{t}Bu (14 mg, 0.12 mmol, 1.1 eq.) was added, the added $AuCl(Me_2S)$ (33

mg, 0.11 mmol, 1.0 eq.), The mixture was stirred at room temperature for 5h. After full conversion of the **(R)-5c**, monitored by TLC, then pre-absorbed on silica gel and purified by chromatography on silica gel to give the product **6** as yellow solid (40 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29-7.26 (m, 2H), 7.24-7.20 (m,1H), 6.95 (s,1H), 4.34-4.26 (m, 1H), 4.13-4.01 (m, 2H), 3.56 (dd, J = 10.4 Hz, 2.8 Hz, 1H), 2.31 (s, 3H), 2.30 (s, 3H), 2.29 (s, 3H), 2.14 (dd, J = 13.6 Hz, 10.4 Hz, 1H), 1.94 (dd, J = 13.2 Hz, 4.8 Hz, 1H), 1.53 (d, J = 6.8 Hz, 3H), 1.44 (s, 3H), 1.38 (s, 3H), 1.08 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 195.7, 143.3, 140.2, 139.0, 135.4, 135.2, 134.6, 133.5, 129.9, 129.8, 127.4, 124.9, 123.7, 58.0, 56.8, 53.4, 46.0, 34.3, 32.1, 31.5, 28.7, 25.7, 21.5, 21.0, 18.2, 17.9; HRMS (ESI): m/z [M – Cl + MeCN]$^{+}$ calcd. for $C_{27}H_{35}AuN_3^{+}$:598.2491, found: 598.2486. $[\alpha]^{25}_{D}$ +128 (c = 0.050, CH_2Cl_2).

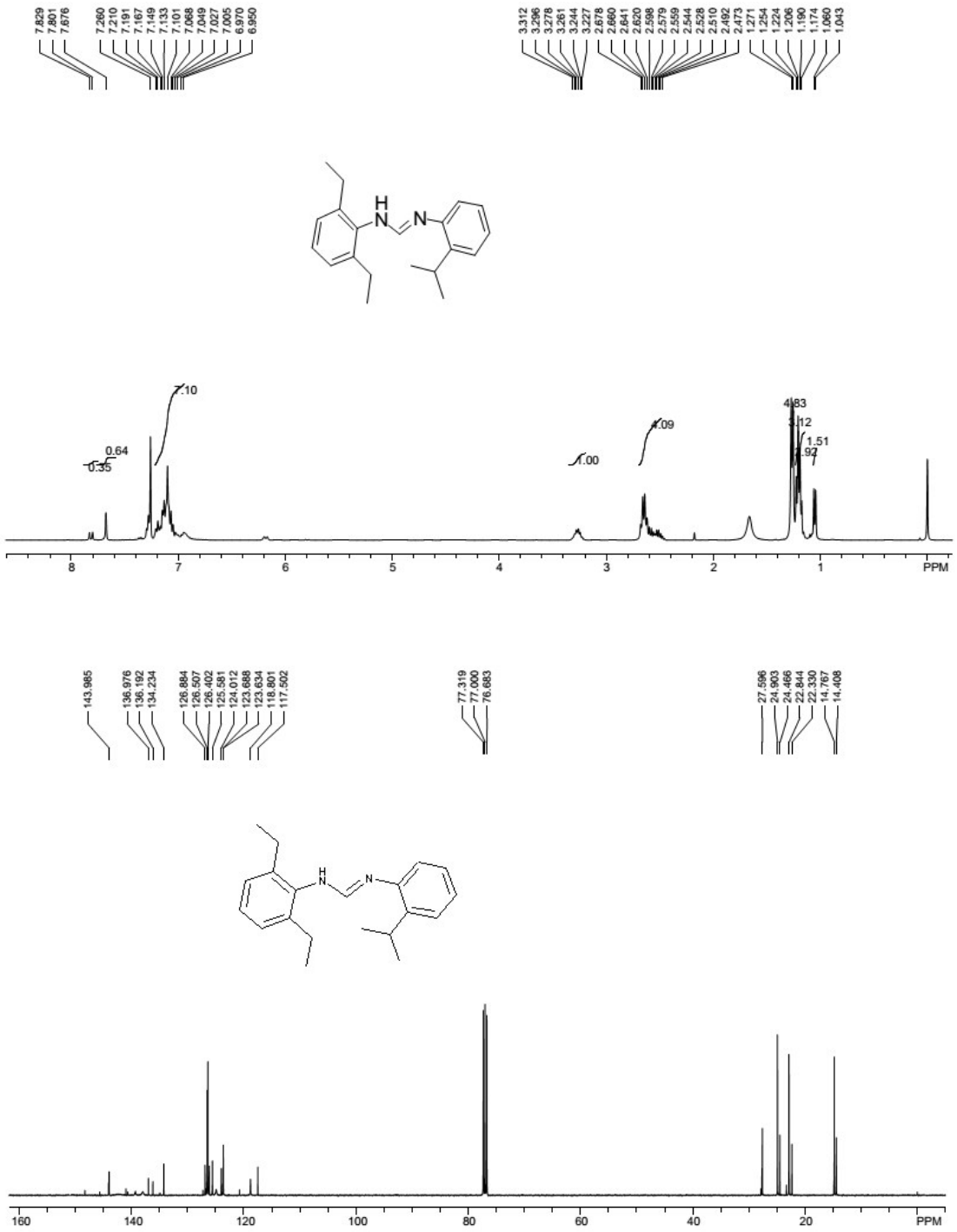
NMR Spectra:

1a





1b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6.970
6.950
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3.261
3.244
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2.641
2.620
2.598
2.579
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2.528
2.510
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1.254
1.224
1.206
1.190
1.174
1.060
1.043
H
N
N
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1.00
4.09
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3.12
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1.92
8
7
6
5
4
3
2
1
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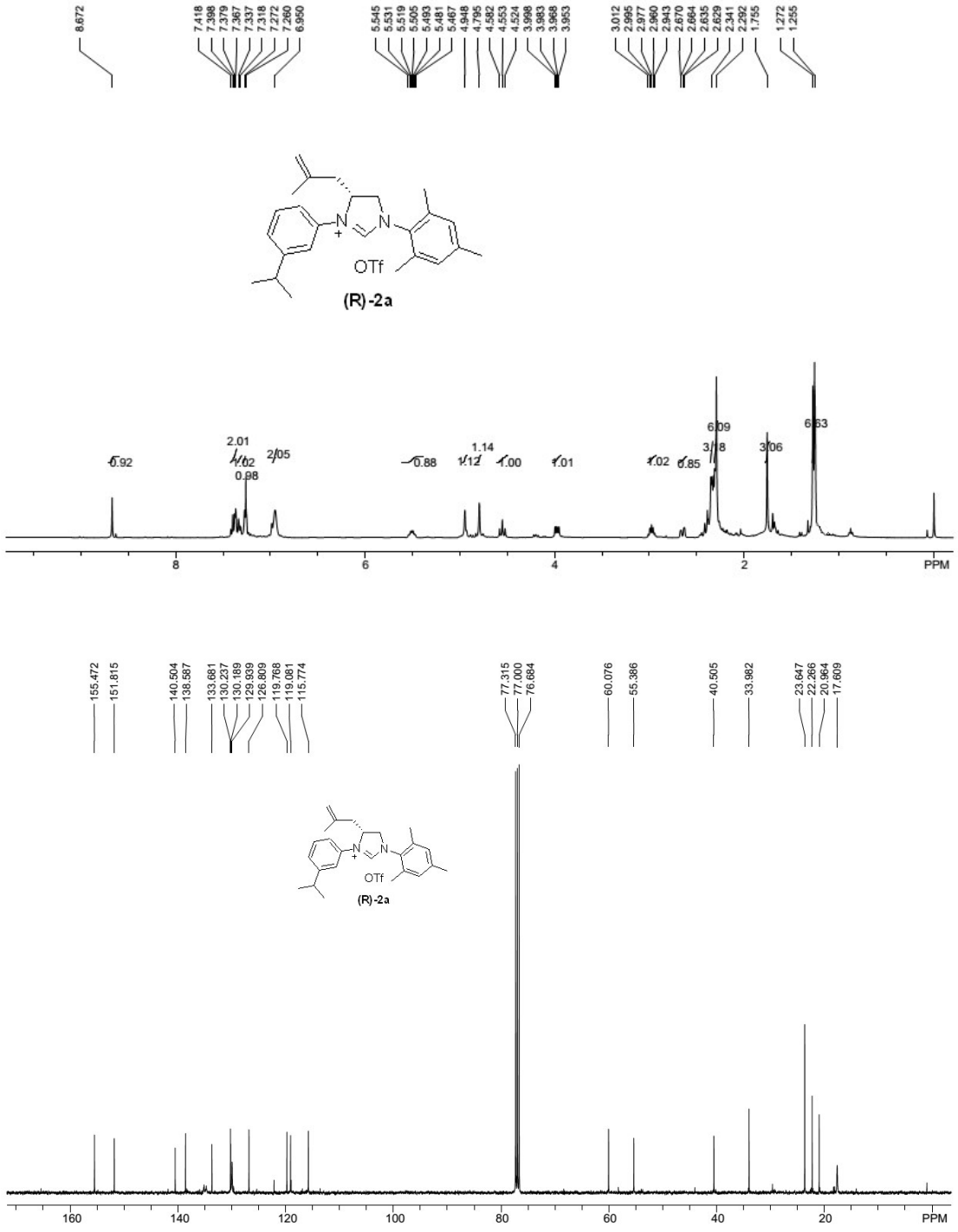
20
PPM

2a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5.467
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4.795
4.582
4.553
4.524
3.998
3.983
3.968
3.953
3.012
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2.977
2.960
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1.01
1.02
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3.18
3.06
6.63
8
6
4
2
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OTf
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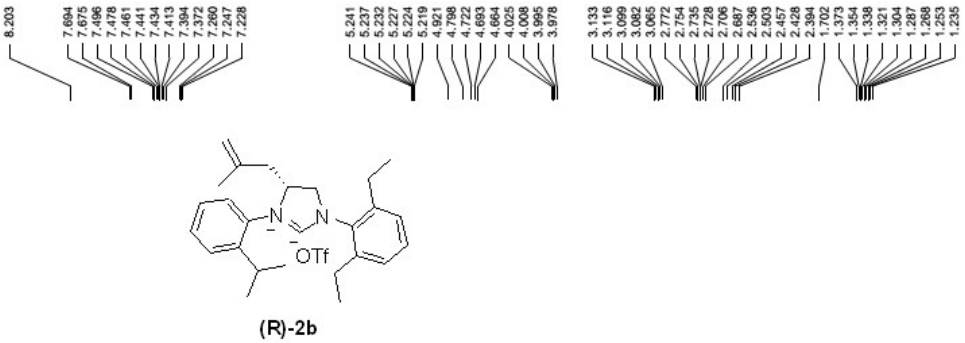
120
100
80
60
40
20
PPM

2b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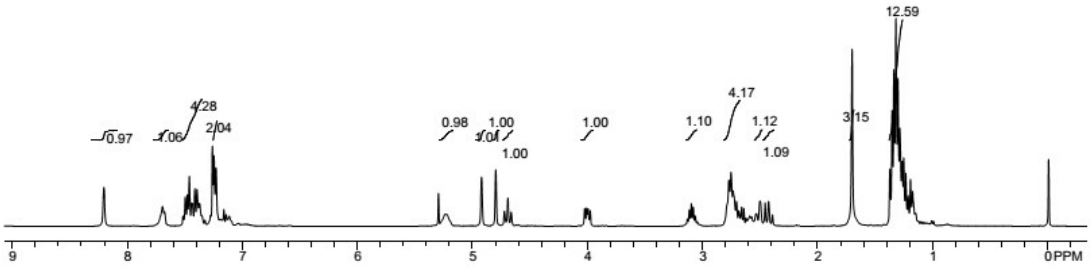
OTf

(R)-2b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7
6
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4
3
2
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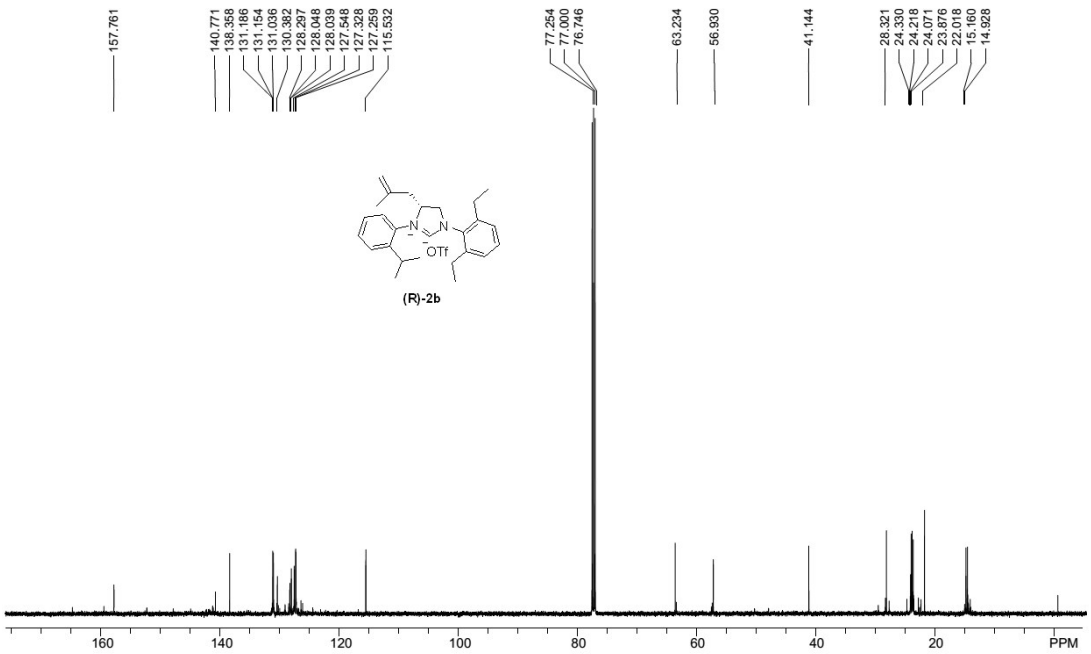
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28.321
24.330
24.218
24.071
23.876
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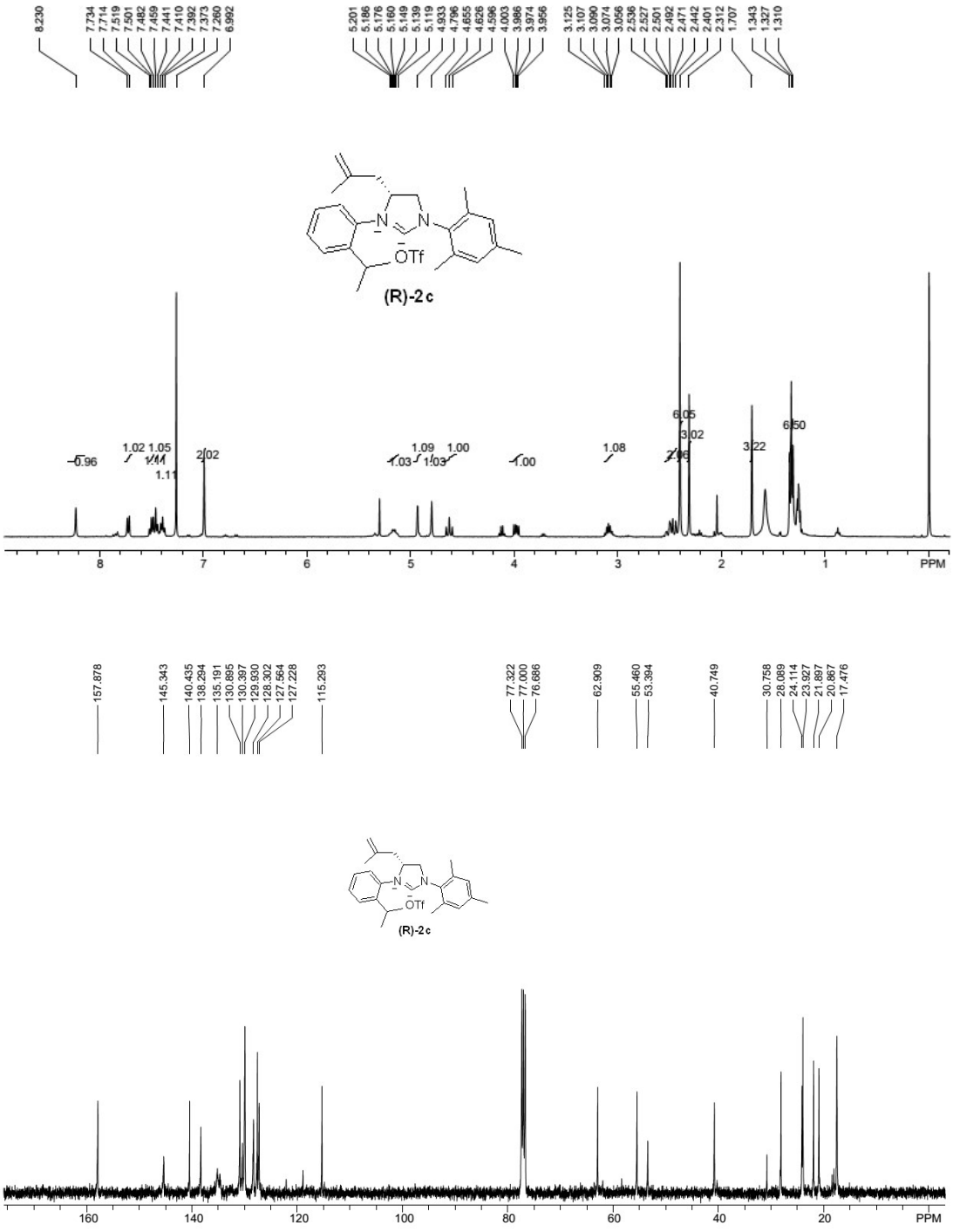
60
40
20
PPM

(R)-2b

2c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5.139
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4.003
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3.974
3.956
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1.343
1.327
1.310
OTf
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1.03
1.09
1.03
1.00
1.00
1.08
2.06
6.05
3.02
3.22
6.50
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7
6
5
4
3
2
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OTf
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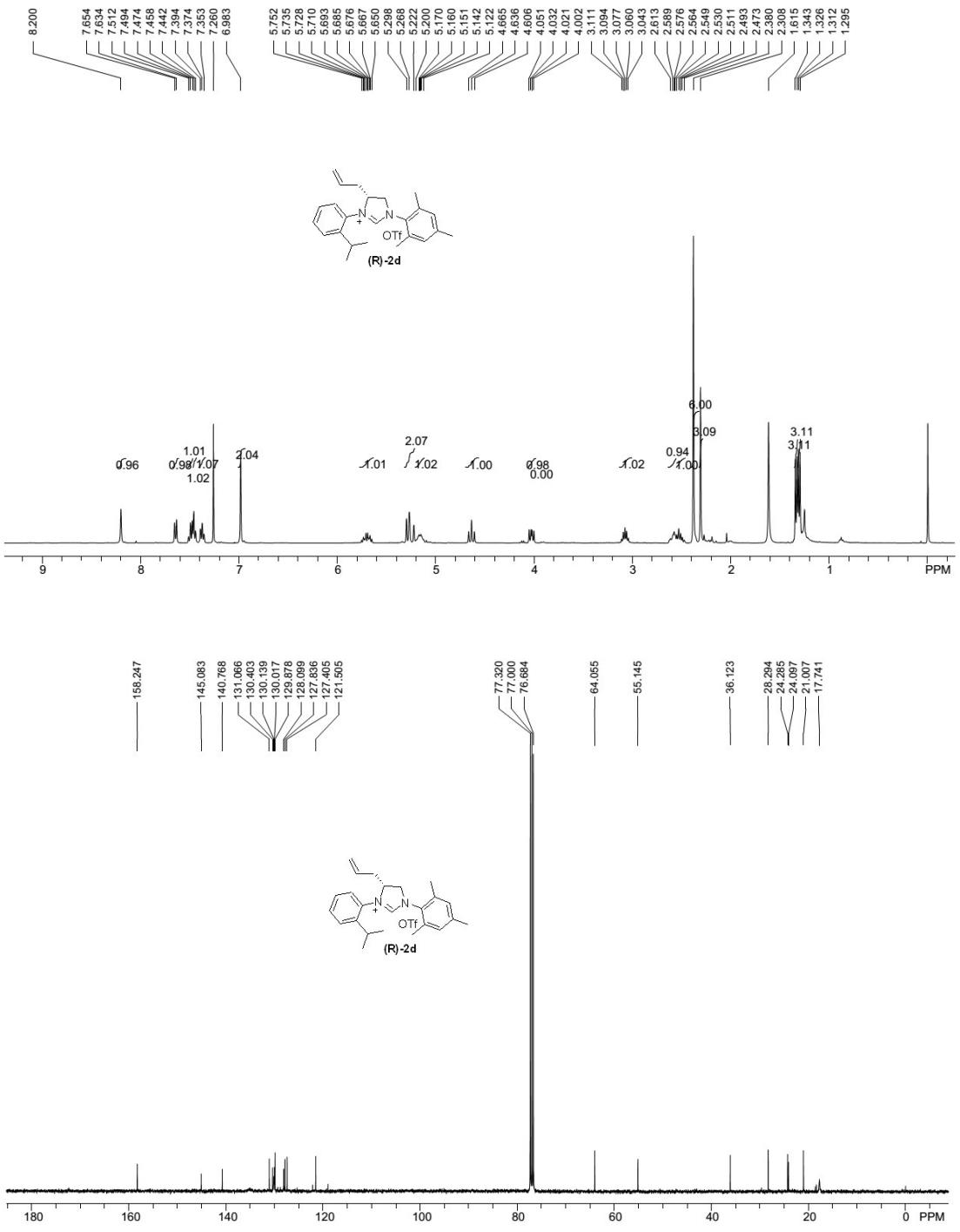
120
100
80
60
40
20
PPM

2d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3.11
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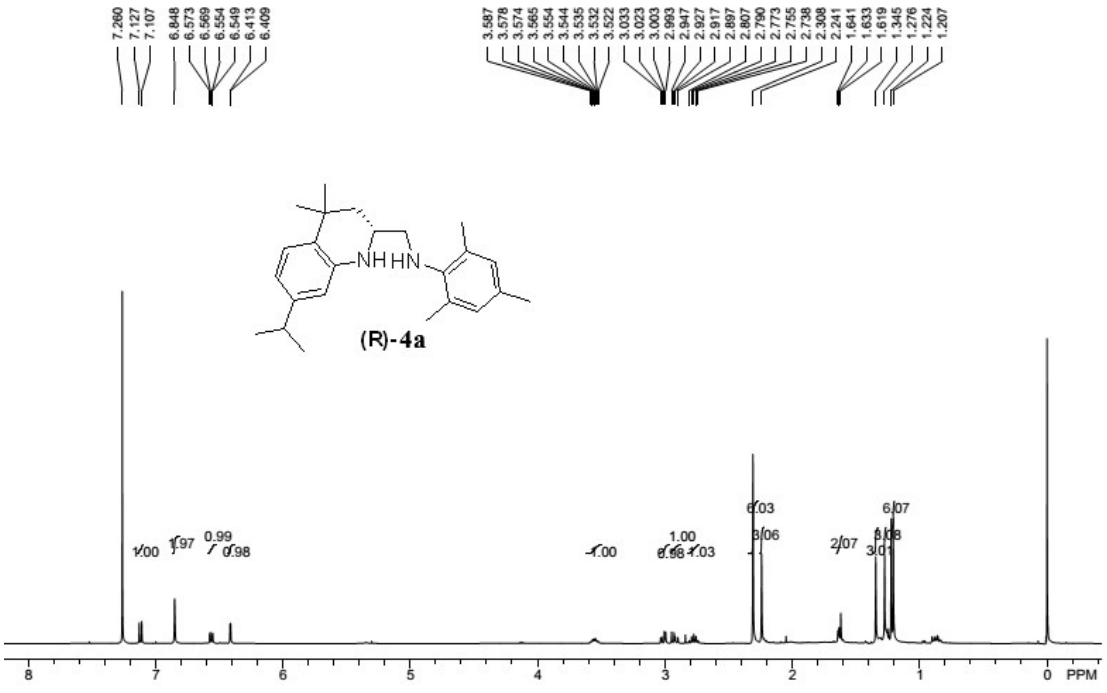
OTf
(R)-2d
PPM

4a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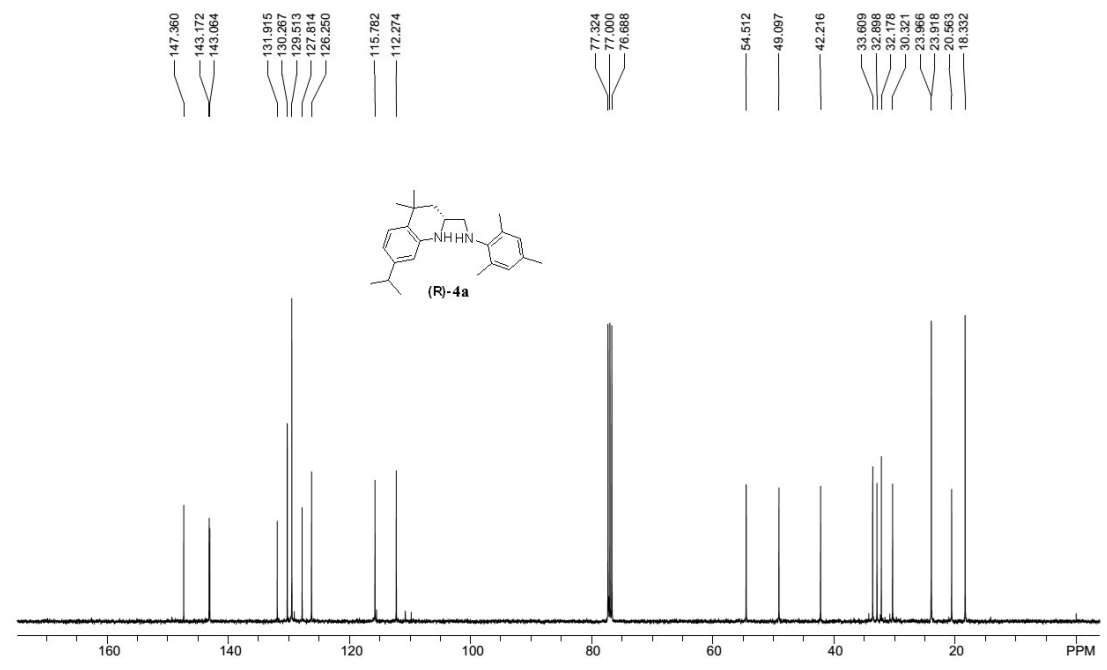
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54.512
49.097
42.216
33.609
32.898
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30.321
23.966
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NH HN
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20
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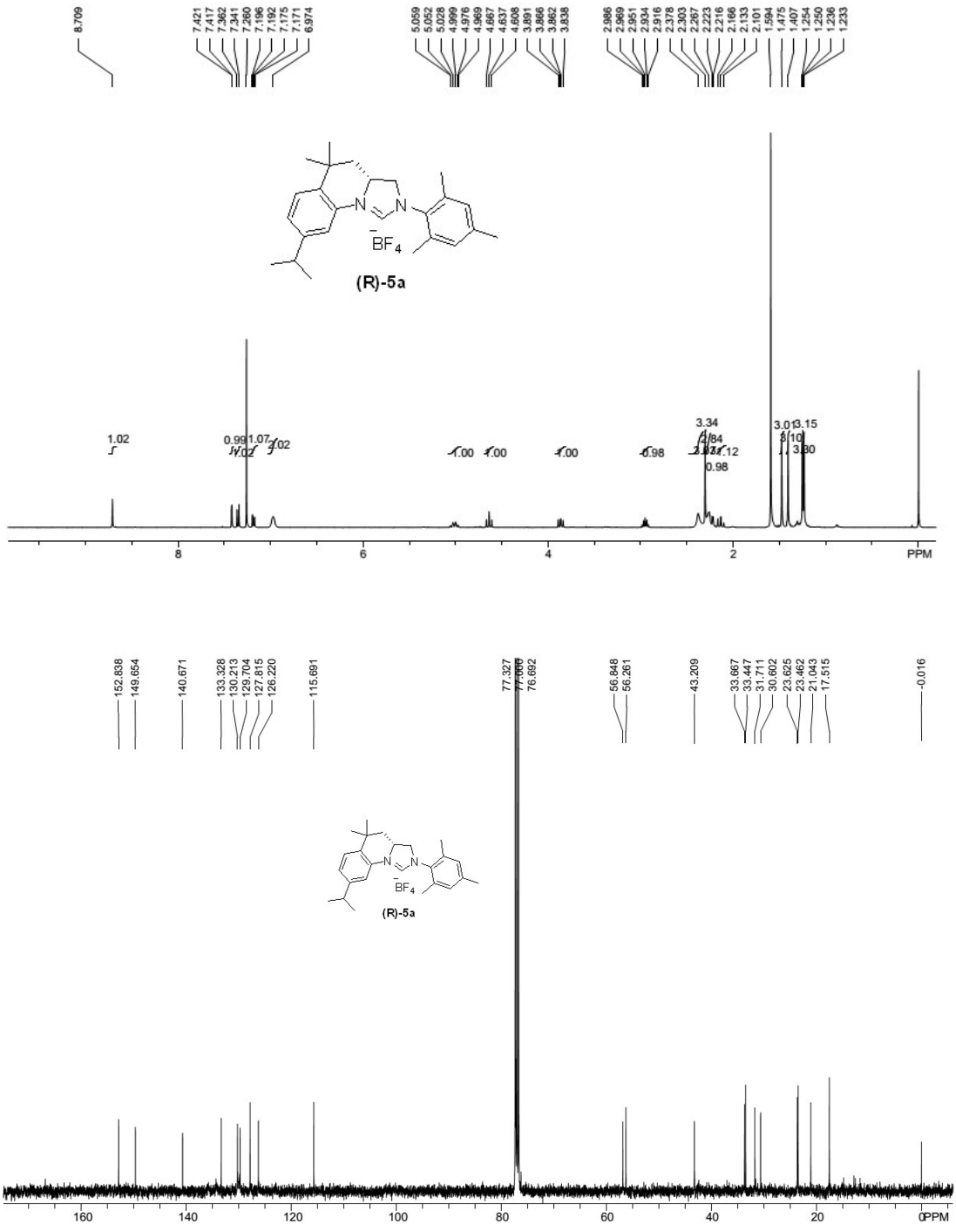
5a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5.028
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4.969
4.667
4.637
4.608
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3.866
3.862
3.838
2.986
2.969
2.951
2.934
2.916
2.378
2.303
2.267
2.223
2.216
2.166
2.133
2.101
1.594
1.475
1.407
1.254
1.250
1.236
1.233
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1.00
1.00
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3.01
3.15
3.10
3.30
8
6
4
2
PPM
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31.711
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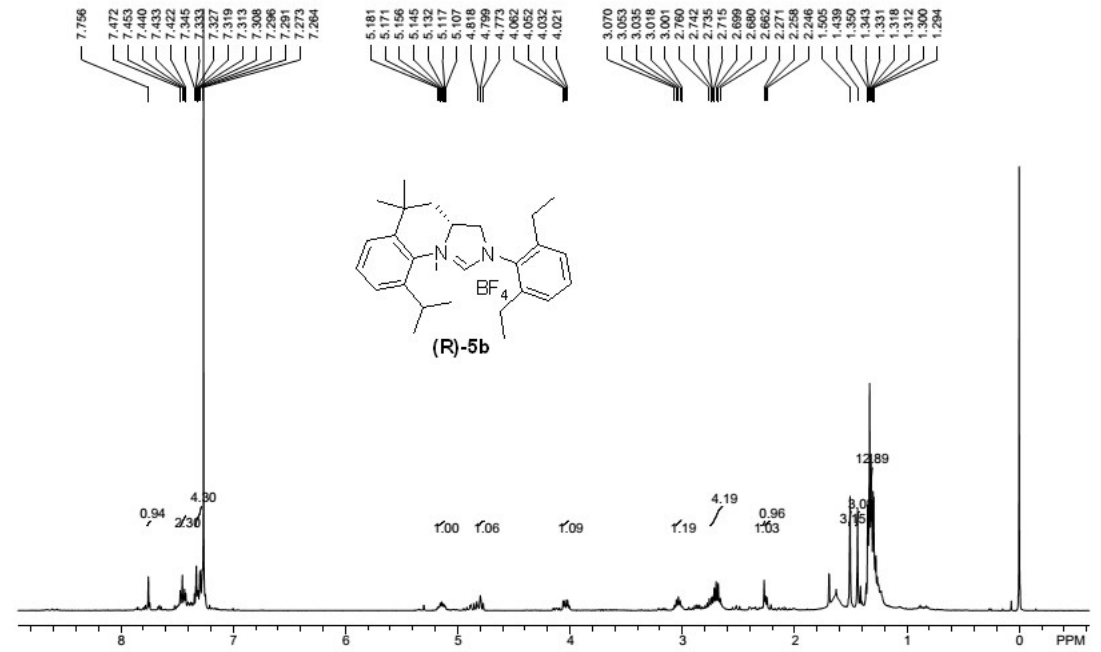
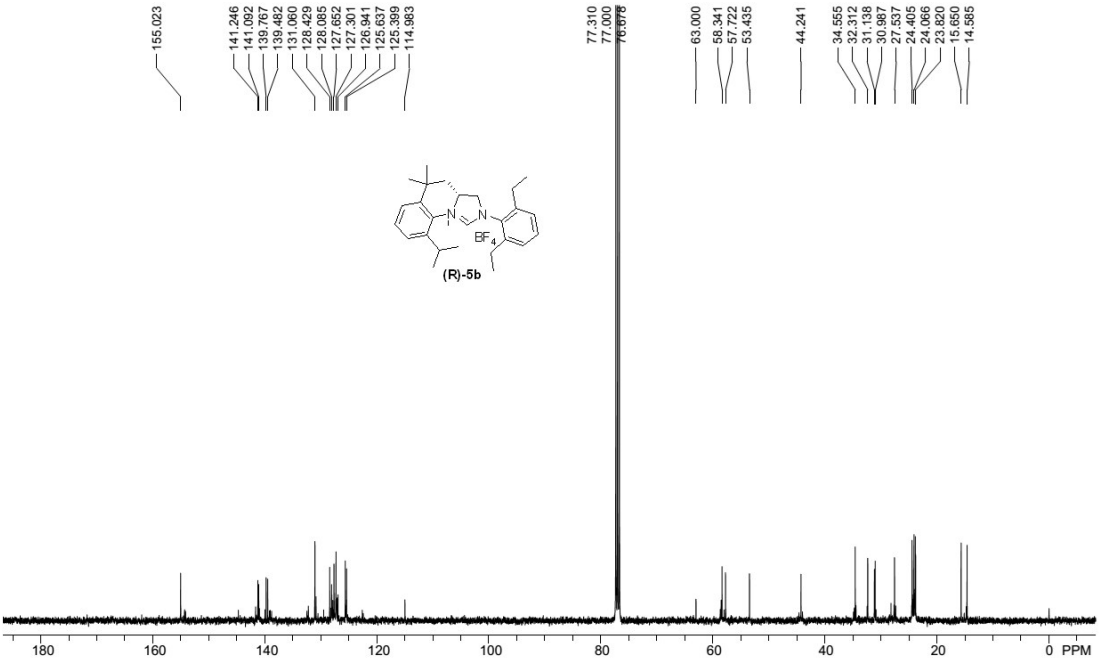
PPM

5b





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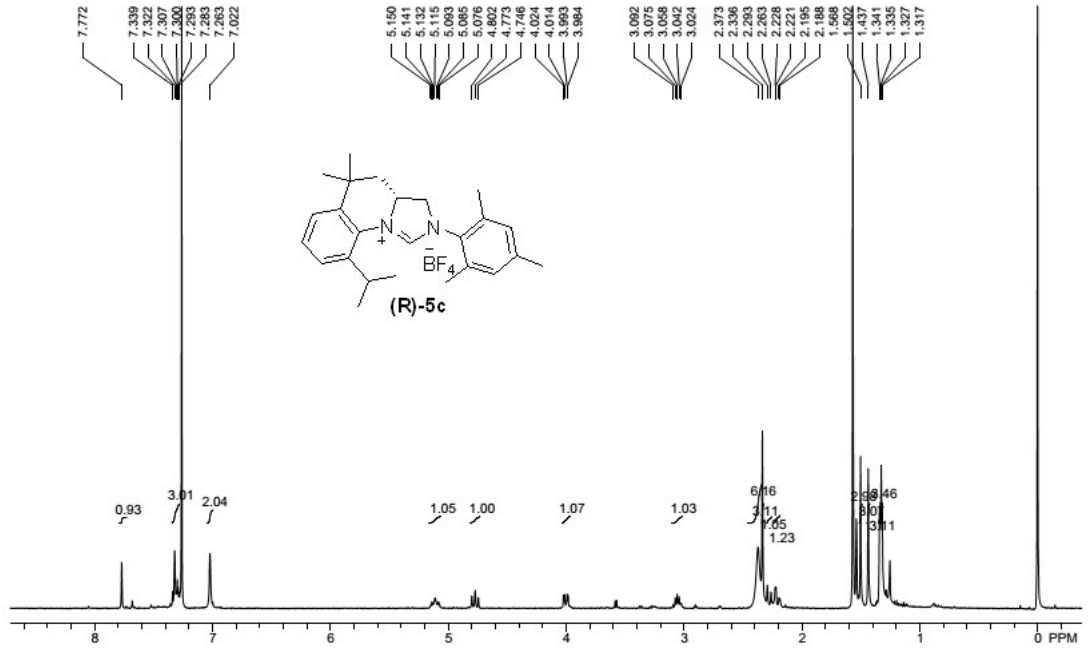
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2.293
2.263
2.228
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1.05
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1.07
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4
3
2
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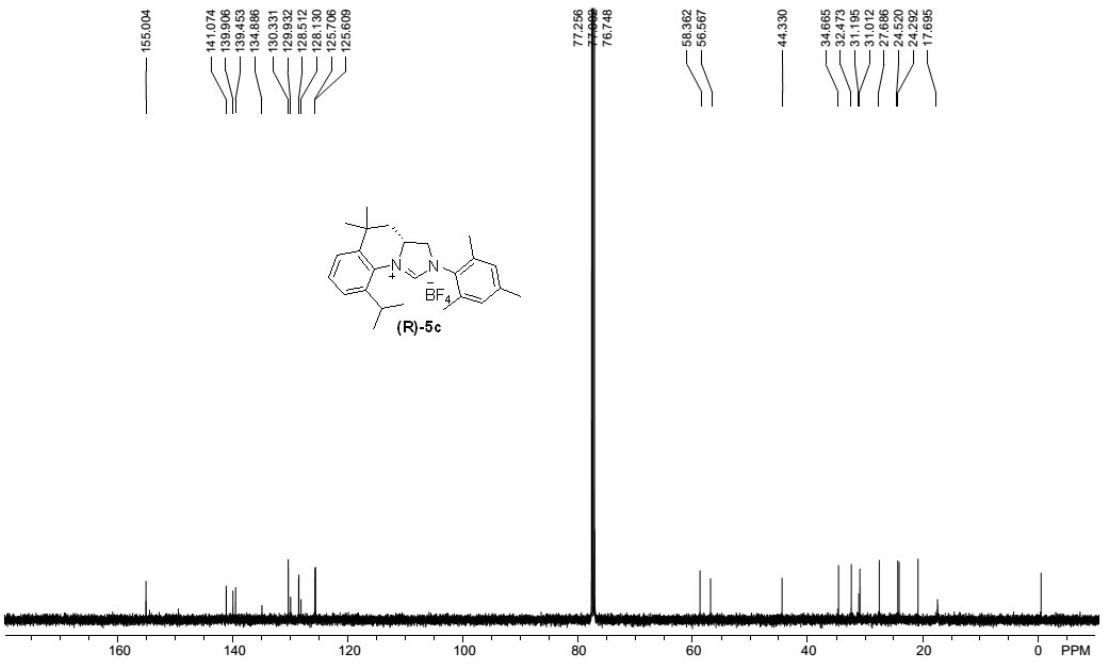
0 PPM
(R)-5c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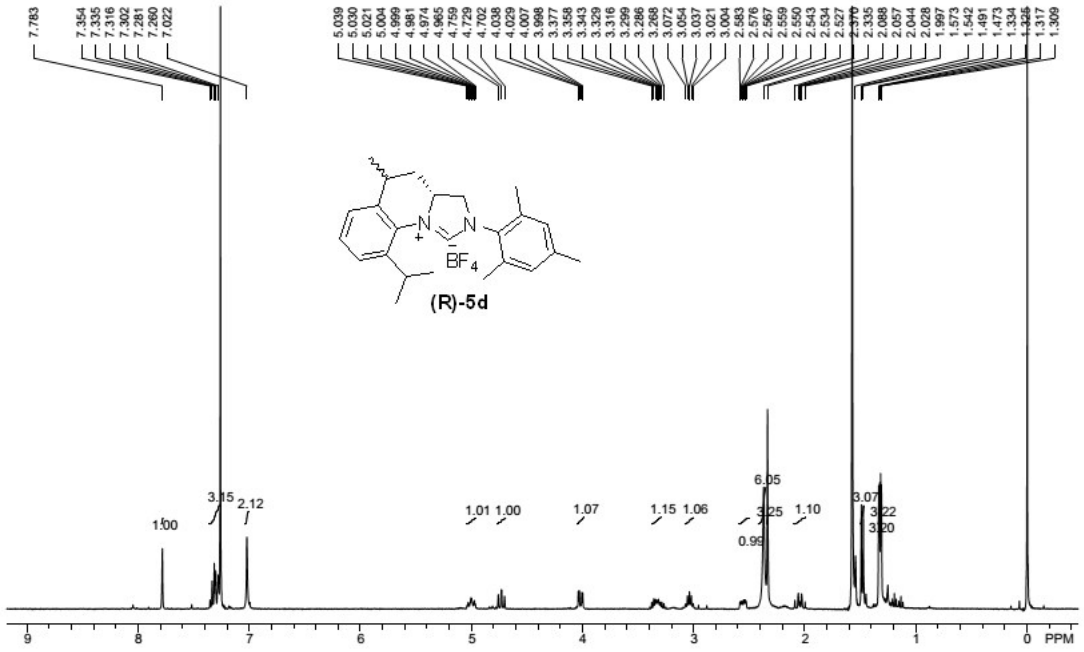
5d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3.998
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1.317
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BF4
(R)-5d
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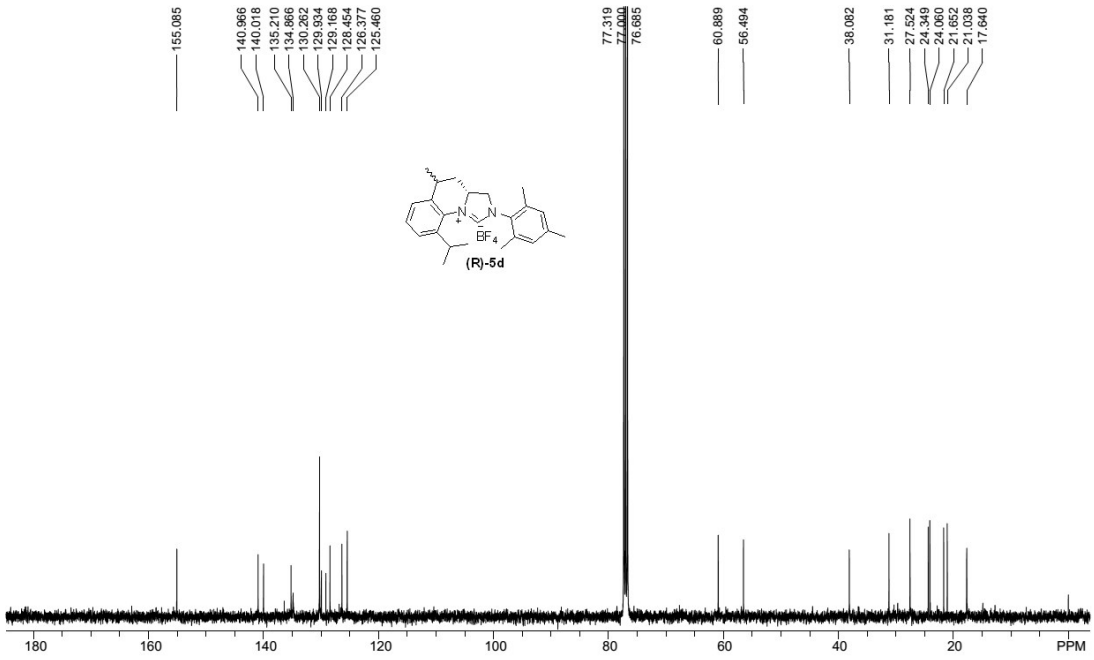
PPM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76.685
60.889
56.494
38.082
31.181
27.524
24.349
24.060
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BF4
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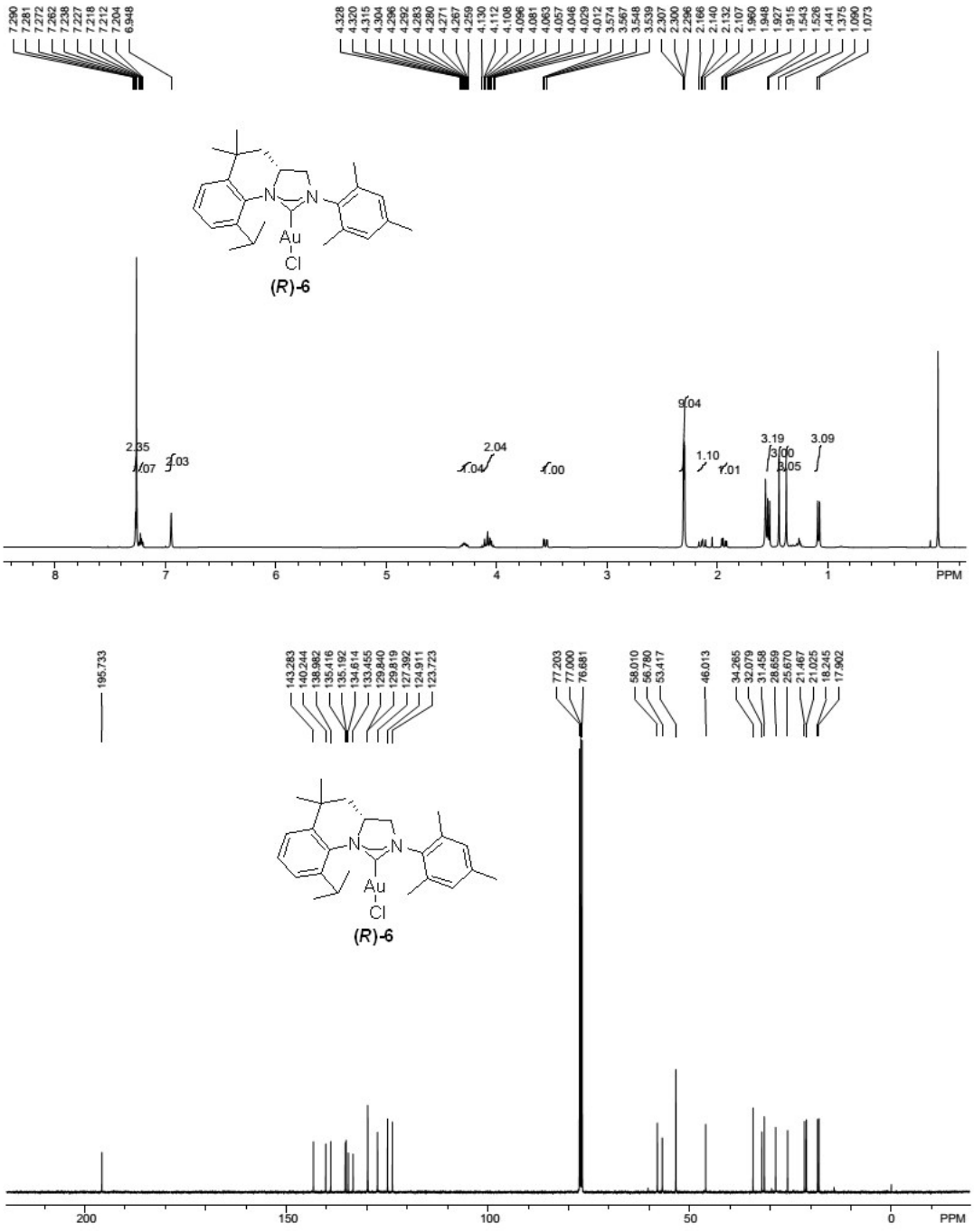
180
160
140
120
100
80
60
40
20
PPM

6



X-Ray Crystallography

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-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.

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. CCDC-2011334 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal Data, Data Collection, and Structure Refinement for **6**.

	6
Identification code	a21113a
Formula	$C_{25}H_{32}AuClN_2$
Formula weight	592.94
T, K	293(2)
crystal system	Orthorhombic
space group	P2(1)2(1)2(1)
a, Å	12.530(6)
b, Å	12.767(6)
c, Å	15.210(7)
α, deg	90
β, deg	90
γ, deg	90
Volume, Å ^{3}	2433.3(19)
Z	4
D_{calc}, Mg / m^3	1.619
absorption coefficient, mm^{-1}	6.169
F(000)	1168
crystal size, mm	0.31 x 0.16 x 0.12
2θ range, deg	2.08 to 26.00
reflections collected /unique	10930 / 4778 [R(int) = 0.0587]
data / restraints/ parameters	4778 / 0 / 269
goodness of fit on F^2	0.974
final R indices [I >2σ(I)]^a	R1 = 0.0330, wR2 = 0.0715
R indices (all data)	R1 = 0.0386, wR2 = 0.0730
largest diff. peak and hole, e/Å^3	1.418 and -1.030

References：

[1] J. Zhang, X. Su, J. Fu, M. Shi, Chem. Commun., 2011, **47**, 12541-12543.
[2] M. Dai, I. J. Krauss, S. J. Danishefsky, J. Org. Chem., 2008, **73**, 9576-9583.
[3] T. Spangenberg, S. Aubry, Y. Kishi, Tetrahedron Lett., 2010, **51**, 1782-1785.