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New gold(I) complexes with fluorinated tricyclic NHC ligands: synthesis and catalytic activity

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General Information

All solvents used in reactions were freshly distilled from appropriate drying agents before use. All other reagents were distilled as necessary. All reagents were used as purchased, amberlite IRA-400(Cl) ion exchange resin was obtained from Sigma-Aldrich. Analytical TLC was performed with Merck silica gel 60 F 254 plates; visualization was accomplished with UV light or iodine vapors. Chromatography was carried out using Merck silica gel (Kieselgel 60, 0.063–0.200 mm) and petroleum ether/ethyl acetate as an eluent. Previously known TfO-salts **1a**, **1b** were prepared according to the published methods, analytical data were in accordance with the literature data.[S1] NMR spectra were recorded on a Bruker Avance 400 instrument (400 MHz ^{1}H, 101 MHz ^{13}C, 376 MHz ^{19}F ($CFCl_3$ as reference)). High-resolution mass spectra (HRMS) were recorded on a LCMS-9030 device (Shimadzu, Japan) by electrospray ionization mass spectrometry (ESI-MS). Electrospray ionization (ESI) mass spectra (MS) were obtained from acetonitrile solution.

General procedure A for the synthesis of imidazolinium tetrafluoroborates 2a and 2b

To a solution of the corresponding TfO-salt **1** (0.5 g) in acetone (30 mL) was added a solution of sodium tetrafluoroborate (10 equiv.) in water (30 mL). The resulting mixture was stirred at room temperature for 30 min, concentrated in vacuum to approximately 30 mL, and extracted with dichloromethane (3×20 mL). The organic extract was dried over $MgSO_4$ and evaporated to dryness to give analytically pure products.

2-mesityl-7,9-dimethyl-5,5-bis(trifluoromethyl)-3a,5-dihydro-3H-benzo[d]imidazo[5,1-b][1,3]oxazin-2-ium tetrafluoroborate **2a:** following the general procedure A was obtained as white solid (94%). Analytical data was in accordance with the literature.[S2]

2-(2,6-diisopropylphenyl)-7,9-dimethyl-5,5-bis(trifluoromethyl)-3a,5-dihydro-3H-benzo[d]imidazo[5,1-b][1,3]oxazin-2-ium tetrafluoroborate **2b:** following the general procedure A was obtained as white solid (95%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.75 (s, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.33 (s, 1H), 7.29 – 7.26 (m, 2H), 7.25 – 7.21 (m, 1H), 6.12 (d, *J* = 6.2 Hz, 1H), 4.99 – 4.90 (m, 1H), 4.07 (d, *J* = 14.5 Hz, 1H), 2.99 (p, *J* = 6.7 Hz, 1H), 2.79 (p, *J* = 6.8 Hz, 1H), 2.41 (s, 3H), 2.39 (s, 3H), 1.28 (d, *J* = 6.8 Hz, 3H), 1.23 (d, *J* = 6.6 Hz, 3H), 1.18 (d, *J* = 6.8 Hz, 3H), 1.10 (d, *J* = 6.7 Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -71.9 (d, *J* = 7.5 Hz, 3F, CF_3), -76.4 – -76.5 (d, *J* = 7.6 Hz, 3F, CF_3), -152.6 (s, 4F, CF_3). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.1, 146.7, 145.9, 139.2, 135.5, 132.3, 132.0, 128.7, 128.5, 125.8, 125.1,

124.9, 121.7 (dd, *J* = 287.1, 50.4 Hz), 117.6, 85.8, 59.7, 28.5, 28.4, 24.8, 24.3, 23.9, 23.7, 21.5, 16.5.

General procedure B for the synthesis of imidazolinium chlorides 3a and 3b by anion exchange

In order to exchange the BF_4 ion to Cl according to literature procedure,[S2] the corresponding imidazolinium tetrafluoroborate (0.4 g) was dissolved in methanol and the obtained solution was filtered through a short pad (2×4.5 cm) of Amberlite IRA-400(Cl). The ion exchange resin was washed with an additional volume of methanol. The combined filtrate was concentrated in vacuum to give almost quantitative yield of the chloride salt, which was used on the next step without additional purification.

2-mesityl-7,9-dimethyl-5,5-bis(trifluoromethyl)-3a,5-dihydro-3H-benzo[d]imidazo[5,1-b][1,3]oxazin-2-ium chloride **3a:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.98 (s, 1H), 7.28 (s, 1H), 7.20 (s, 1H), 6.89 (s, 2H), 6.12 (s, 1H), 5.18 (d, *J* = 14.0 Hz, 1H), 3.94 (d, *J* = 13.8 Hz, 1H), 2.57 (s, 3H), 2.35 (s, 6H), 2.25 (s, 3H), 2.18 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -71.84 (d, *J* = 10.0 Hz, 3F, CF_3), -76.16 (d, *J* = 10.1 Hz, 3F, CF_3). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.2, 141.2, 139.0, 135.5, 135.3, 134.6, 132.6, 130.2, 129.6, 128.8, 125.7, 121.7 (dd, *J* = 287.2, 51.8 Hz), 117.4, 85.6, 58.0, 21.5, 21.2, 18.4, 18.1, 17.3. HRMS (ESI+) of $C_{23}H_{23}ClF_6N_2O$, *m*/*z*: calcd for $[M\text{-}Cl]^+$ 457.1709, found 457.1711.

2-(2,6-diisopropylphenyl)-7,9-dimethyl-5,5-bis(trifluoromethyl)-3a,5-dihydro-3H-benzo[d]imidazo[5,1-b][1,3]oxazin-2-ium chloride **3b:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.67 (s, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.37 – 7.27 (m, 4H), 6.23 (d, *J* = 6.3 Hz, 1H), 5.19 (dd, *J* = 14.2, 6.2 Hz, 1H), 4.17 (d, *J* = 14.1 Hz, 1H), 3.29 – 3.22 (m, 1H), 2.88 – 2.81 (m, 1H), 2.72 (s, 3H), 2.42 (s, 3H), 1.37 (d, *J* = 6.8 Hz, 3H), 1.34 (d, *J* = 6.8 Hz, 3H), 1.31 (d, *J* = 6.7 Hz, 3H), 1.23 (d, *J* = 6.7 Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -71.83 (d, *J* = 10.2 Hz, 3F, CF_3), -76.42 (d, *J* = 9.8 Hz, 3F, CF_3). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.0, 146.5, 145.9, 139.3, 135.6, 132.6, 132.0, 129.0, 128.7, 125.8, 125.1, 125.0, 121.7 (dd, *J* = 287.6, 57.5 Hz), 117.6, 85.9, 60.2, 29.0, 28.7, 25.3, 24.9, 23.9, 23.6, 21.6, 17.9. HRMS (ESI+) of $C_{23}H_{23}ClF_6N_2O$, *m*/*z*: calcd for $[M\text{-}Cl]^+$ 499.2179, found 499.2189.

General procedure C for the synthesis of NHC-Au^{I} complexes complexes 4a and 4b

The NHC-Au^{I} complexes **4a** and **4b** were synthesized according to literature procedure[S3] with minor modifications. Under argon in a Schlenk tube with a magnetic stirring bar, the corresponding NHC·HCl **3a** or **3b** (100 mg, 1 equiv), [Au(SMe_2)Cl] (1 equiv) and K_2CO_3 (1 equiv) were suspended in 5 mL of dry and degassed acetone. Then, the reaction mixture was stirred at 60 °C (oil bath temperature) for 3 h. After this time the solvent was removed *in vacuo*. Purification by chromatography (eluent – hexane: ethyl acetate 2:1) gave analytically pure products **4a** and **4b**.

[2-mesityl-7,9-dimethyl-5,5-bis(trifluoromethyl)-2,3,3a,5-tetrahydro-1H-benzo[d]imidazo[5,1-b][1,3]oxazin-1-ylidene]gold(I) chloride **4a**:following the general procedure C **4a** was obtained as white solid (54%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (s, 2H), 6.97 (s, 1H), 6.95 (s, 1H), 5.61 (d, *J* = 5.3 Hz, 1H), 4.11 – 4.05 (m, 1H), 3.93 (d, *J* = 13.7 Hz, 1H), 2.74 (s, 3H), 2.41 (s, 3H), 2.31 (s, 3H), 2.26 (s, 3H), 2.23 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -72.48 (s, 3F, CF_3), -75.76 (s, 3F, CF_3). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.1, 140.0, 137.9, 135.6, 135.5, 134.8, 133.7, 133.6, 132.8, 130.3, 129.8, 125.4, 122.0 (qd, *J* = 287.1, 287.0, 79.5 Hz), 118.6, 85.5, 57.2, 29.8, 21.5, 21.2, 19.9, 17.9, 17.3. HRMS (ESI) of $C_{25}H_{24}AuClF_6O$, *m*/*z*: calcd for $[M\text{-}Cl+MeCN]^+$ 694.1567, found: 694.1588.

[2-(2,6-diisopropylphenyl)-7,9-dimethyl-5,5-bis(trifluoromethyl)-2,3,3a,5-tetrahydro-1Hbenzo[d]imidazo[5,1-b][1,3]oxazin-1-ylidene]gold(I) chloride **4b**: following the general procedure C **4b** was obtained as white solid (71%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (t, *J* = 7.8 Hz, 1H), 7.31 (s, 2H), 7.25 – 7.20 (m, 2H), 5.62 (d, *J* = 5.1 Hz, 1H), 4.09 (dd, *J* = 13.8, 5.3 Hz, 1H), 3.90 (d, *J* = 13.7 Hz, 1H), 3.01 (p, *J* = 7.0 Hz, 1H), 2.75 (p, *J* = 6.7 Hz, 1H), 2.70 (s, 3H), 2.39 (s, 3H), 1.41 (d, *J* = 6.8 Hz, 3H), 1.25 (d, *J* = 6.9 Hz, 9H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -72.50 (s, 3F, CF_3), -76.06 (s, 3F, CF_3). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.4, 146.7, 146.0, 138.0, 135.5, 133.7, 133.0, 132.8, 130.9, 125.4, 125.2, 124.7, 122.0 (qd, *J* = 287.6, 286.6, 76.0 Hz), 118.5, 85.5, 59.7, 28.9, 28.0, 25.0, 24.9, 24.5, 23.9, 21.5, 19.8. HRMS (ESI) of $C_{28}H_{30}AuClF_6O$, *m*/*z*: calcd for $[M\text{-}Cl+MeCN]^+$ 736.2037, found: 736.2057.

General procedure for intramolecular hydroamination of 2-(phenylethynyl)aniline

According to literature procedure,[S4] AgOTf (0.025 mmol, 5 mol%) was added to a solution of 0.025 mmol (5 mol%) of NHC-Au^{I} complex (**4a** or **4b**) in EtOH (0.5 mL). After stirring for 15 min, 2-(phenylethynyl)aniline (0.5 mmol) in EtOH (1 mL) was added. After 24 h the solvent was evaporated and the product isolated by chromatography with hexane-ethyl acetate mixture.

General procedure for hydration of diphenylacetylene

According to literature procedure,[S5] a screw-cap vial equipped with a magnetic stir bar was charged with 0.02 mmol (2 mol%) of NHC-Au^{I} complex **4a** or **4b** in dioxane (1 mL), 0.02 mmol (2 mol%) of AgOTf, 15 mmol (15 equiv) of H_2O and 1 mmol of diphenylacetylene. The vial was transferred to a preaheated oil bath (80°C). After 24 h reaction mixture was cooled, concentrated *in vacuo*, and the product isolated by chromatography with hexane-ethyl acetate mixture.

General procedure for hydrohydrazination of phenylacetylene

According to literature procedure,[S6] AgOTf (0.01 mmol, 2 mol%) was added to a solution of 0.01 mmol (2 mol%) of NHC-Au^{I} complex (**4a** or **4b**) in $CHCl_3$ (10 mL). After stirring for 15 min, phenylacetylene (0.5 mmol) and *p*-toluenesulfonyl hydrazide (0.5 mmol, 1.0 equiv) were added and the mixture was refluxed for 3 h. After 3 h reaction mixture was cooled, concentrated in vacuum and the product isolated by chromatography with hexane-ethyl acetate mixture.

References

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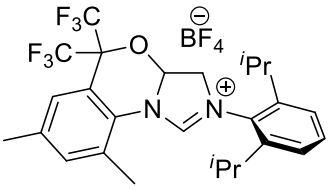
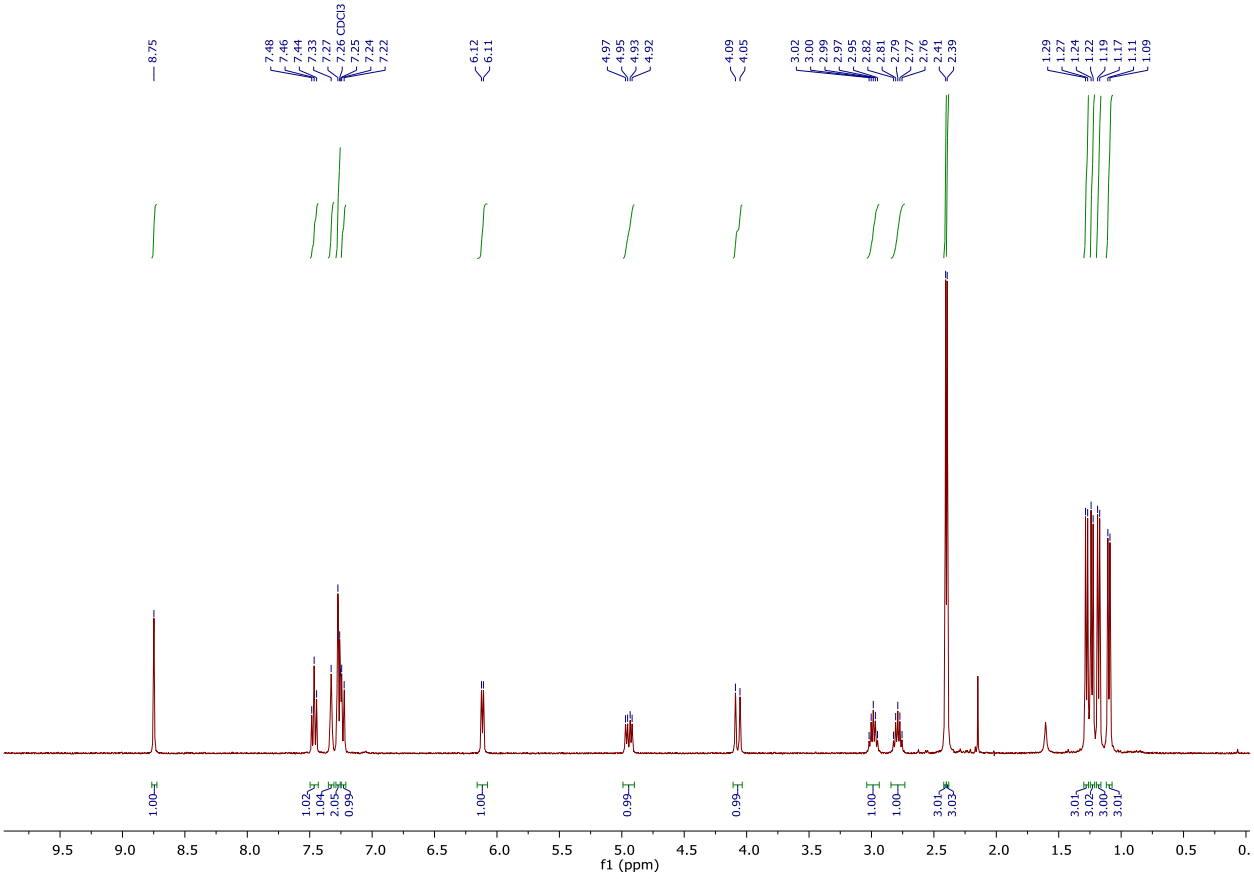
X-ray crystallography of 4a

Table S1. Crystal data and structure refinement parameters for **4a** (CCDC 2479608).

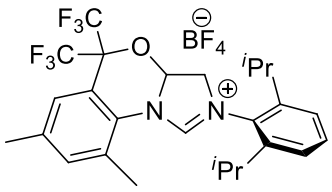
Identification code	**4a**
Empirical formula	$C_{24}H_{23}AuCl_4F_6N_2O$
Formula weight	808.21
Temperature/K	120
Crystal system	triclinic
Space group	P-1
a/Å	13.8599(13)
b/Å	15.0088(14)
c/Å	15.0738(14)
α/°	67.025(4)
β/°	76.166(4)
γ/°	83.821(4)
Volume/Å^3	2802.8(5)
Z	4
ρ_{calc}g/cm^3	1.915
μ/mm^{-1}	5.692
F(000)	1560.0
Crystal size/mm^3	0.27 × 0.15 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.948 to 51.998
Index ranges	$-17 \leq h \leq 17$, $-18 \leq k \leq 18$, $-18 \leq l \leq 18$
Reflections collected	38430
Independent reflections	10970 [R_{int} = 0.0892, R_{sigma} = 0.1144]
Data/restraints/parameters	10970/0/695
Goodness-of-fit on F^2	1.010
Final R indexes [I>=2σ (I)]	R_1 = 0.0545, wR_2 = 0.1195
Final R indexes [all data]	R_1 = 0.0732, wR_2 = 0.1244
Largest diff. peak/hole / e Å^{-3}	3.50/-4.18

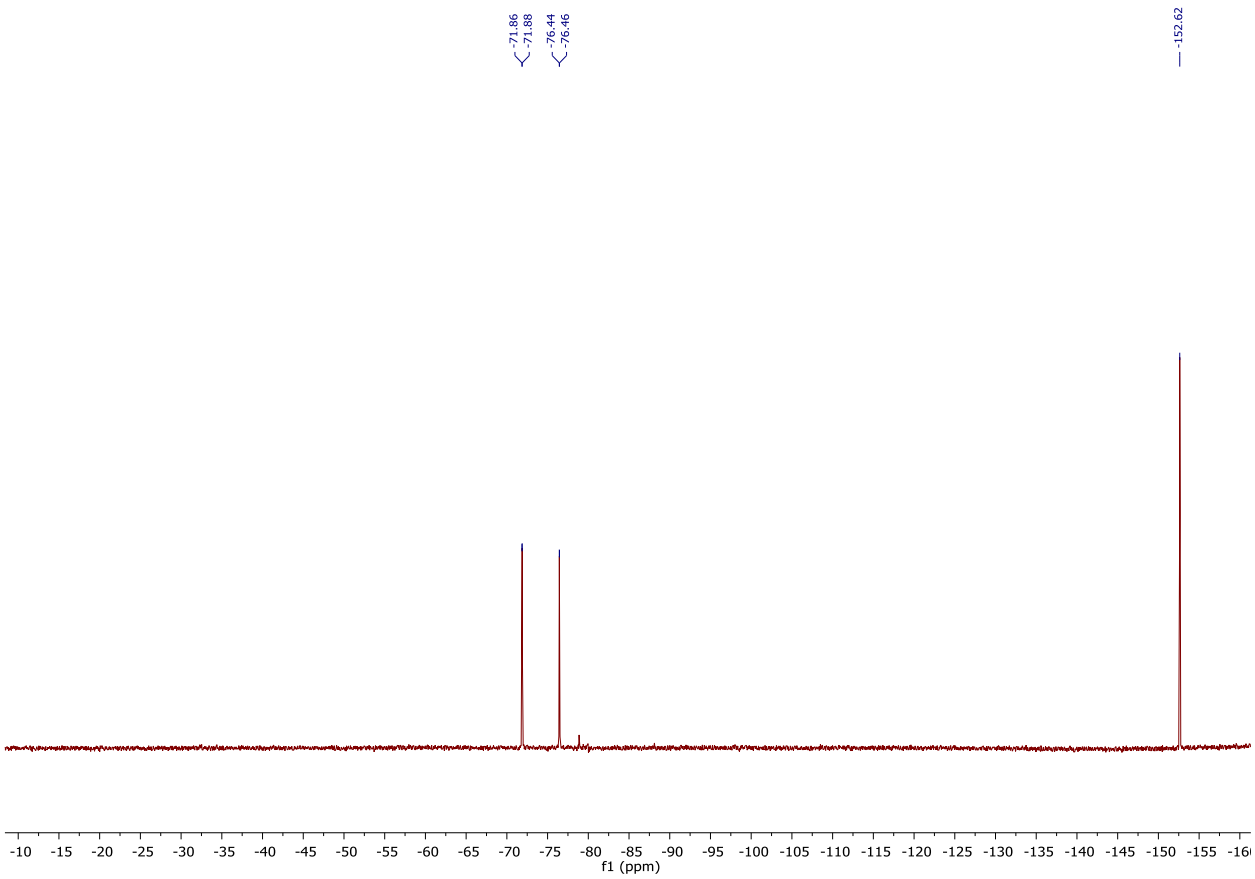
NMR spectra



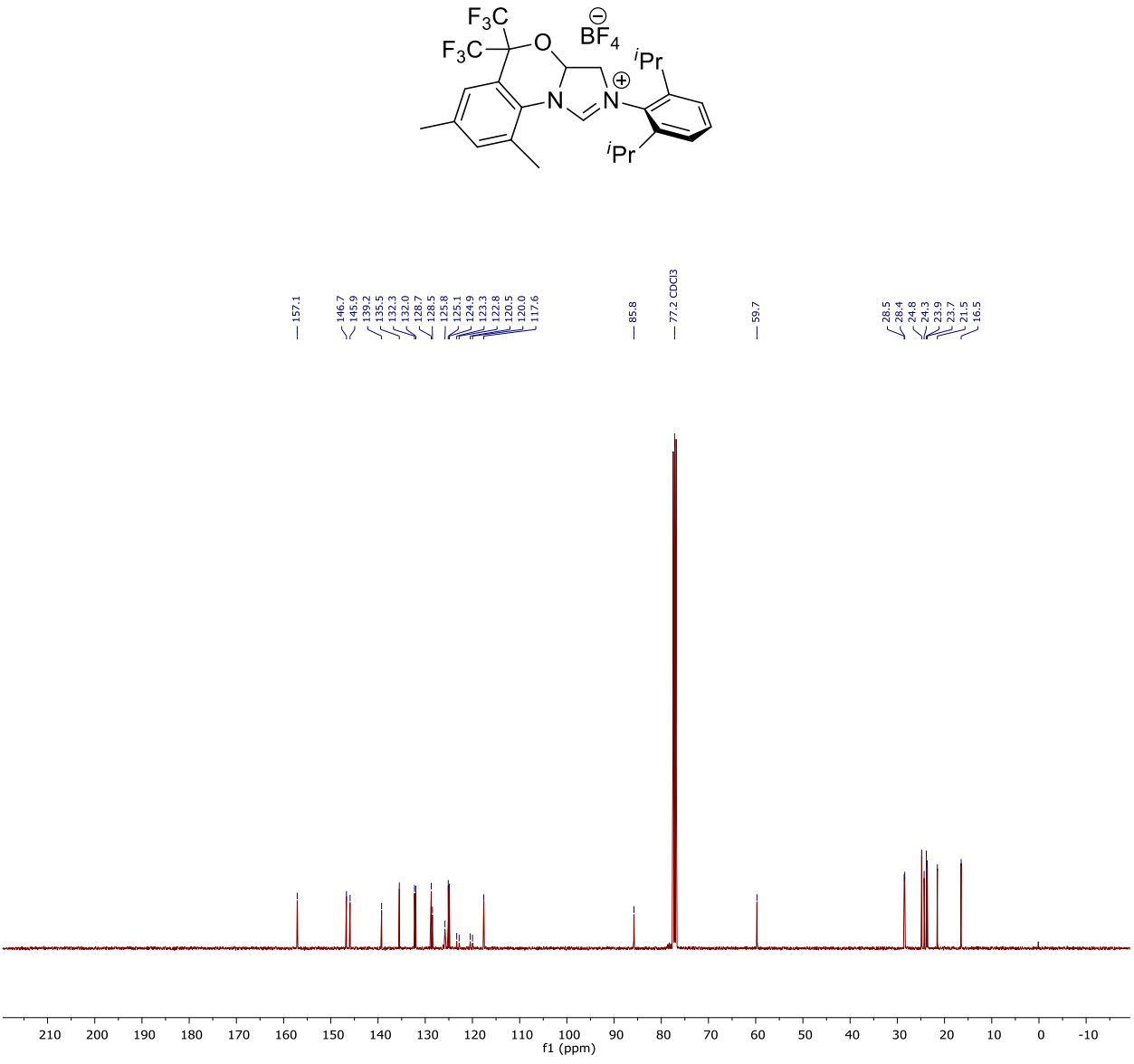


^{1}H NMR (400 MHz, Chloroform-d) of 2b

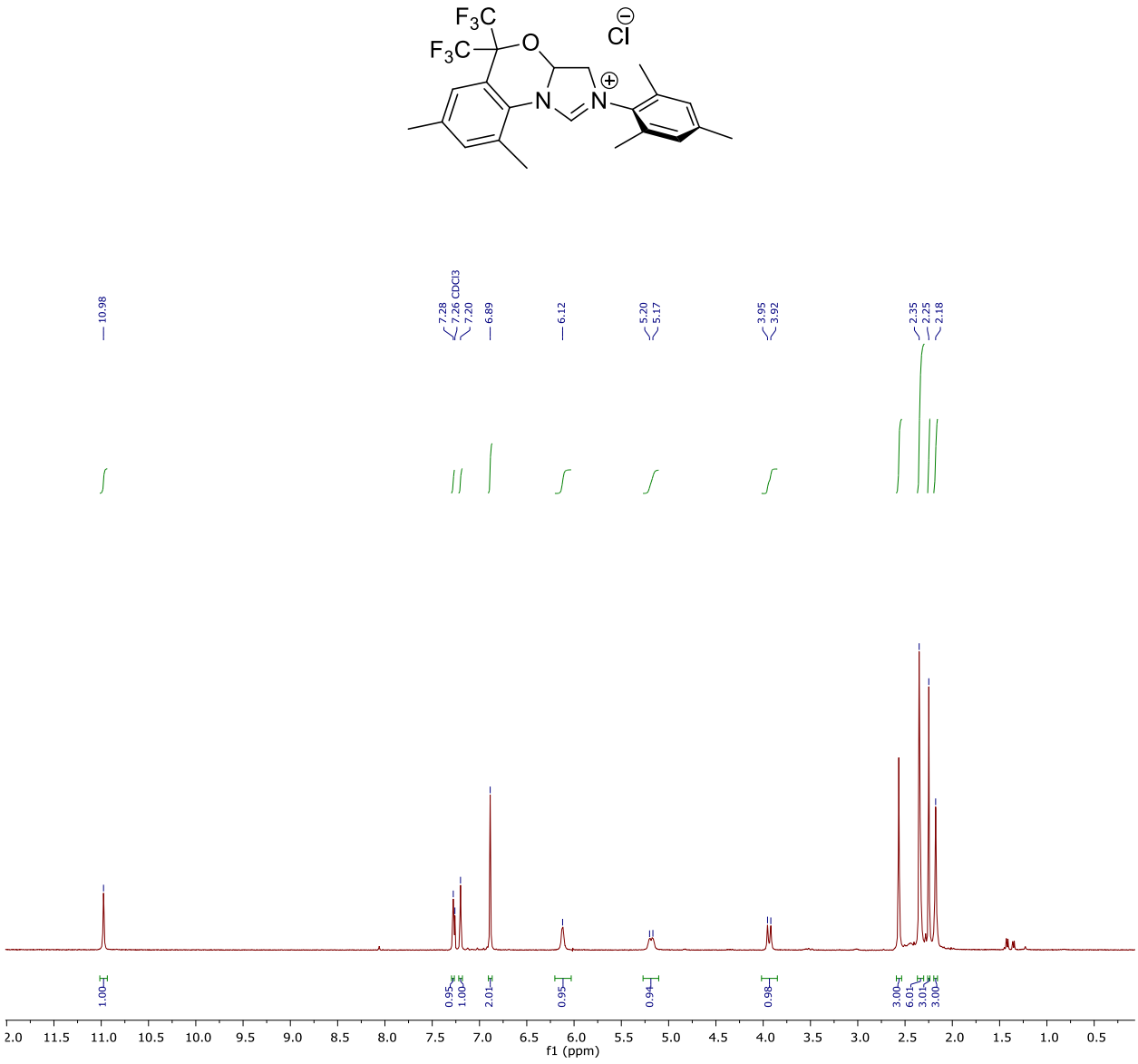




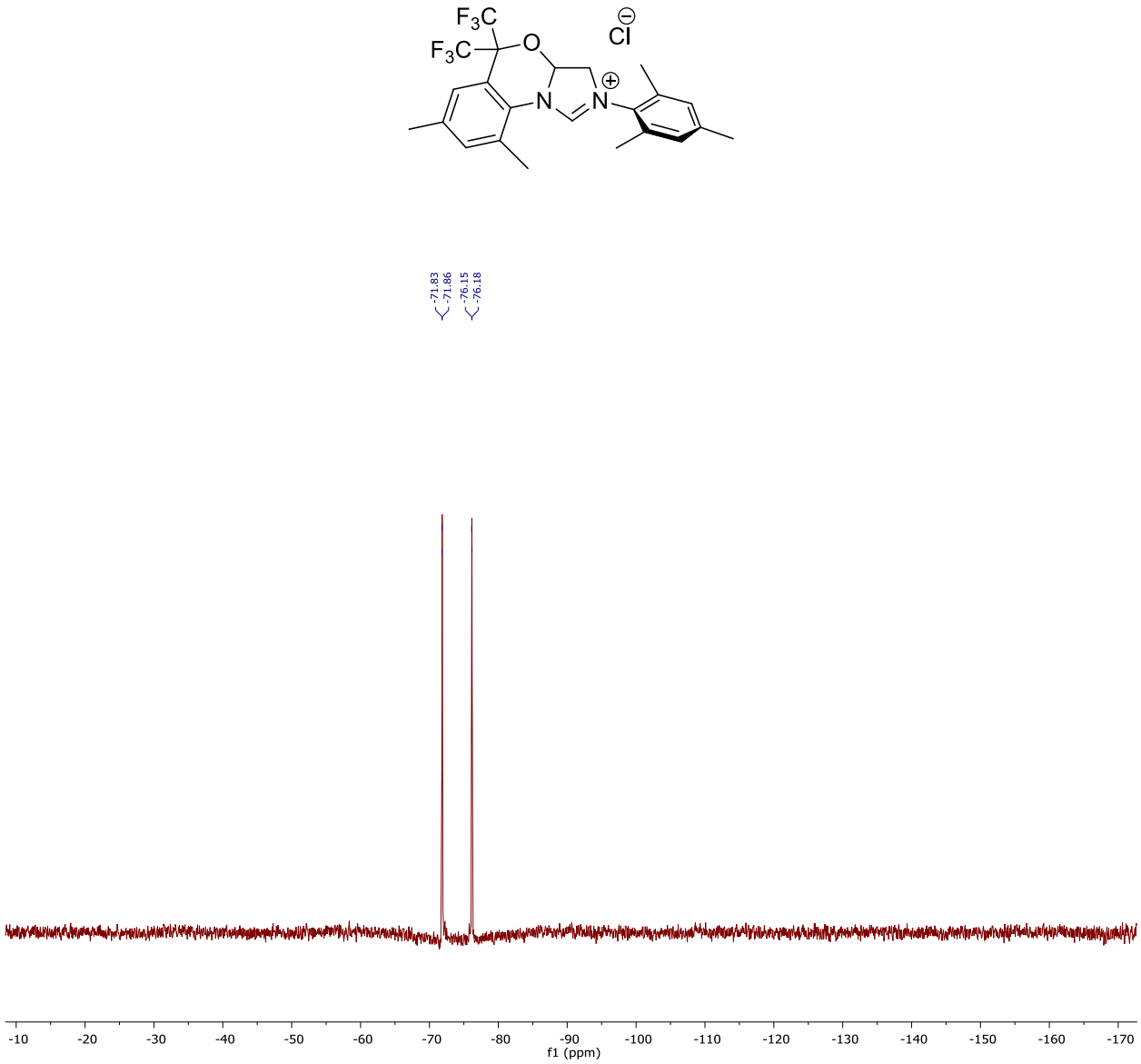
^{19}F NMR (376 MHz, Chloroform-d) of 2b



^{13}C NMR (101 MHz, Chloroform-d) of 2b



^{1}H NMR (400 MHz, Chloroform-d) of 3a



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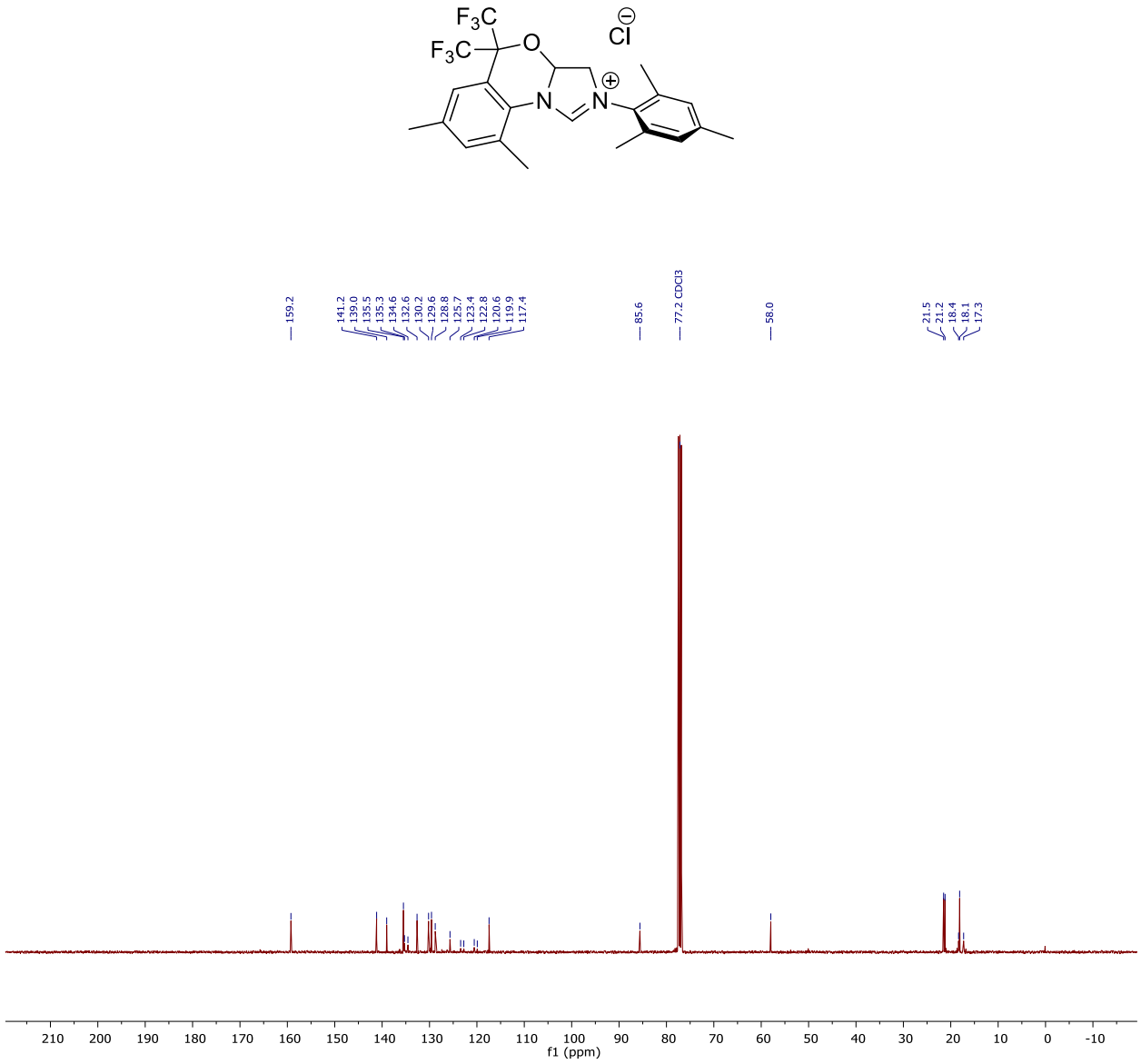

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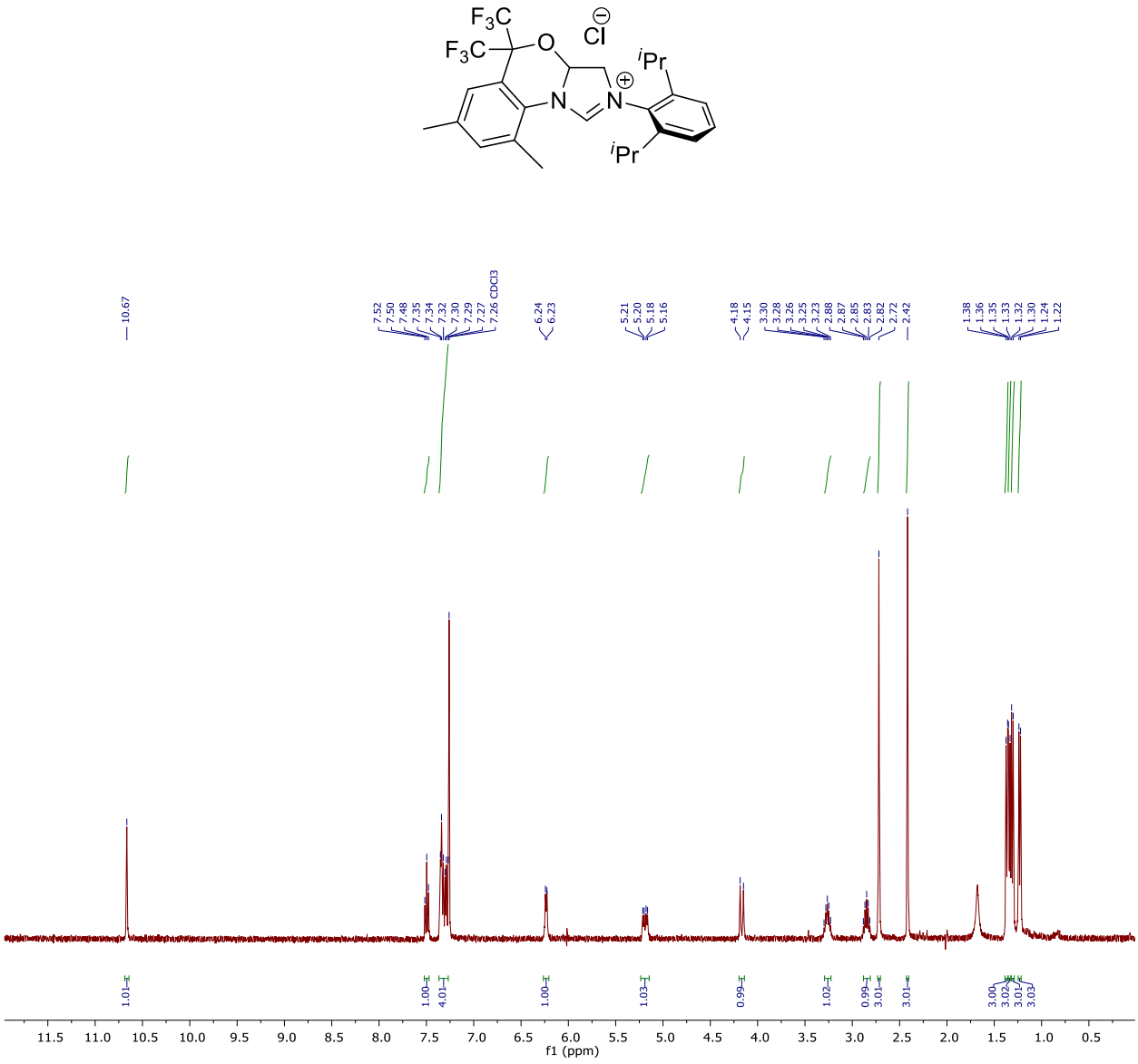

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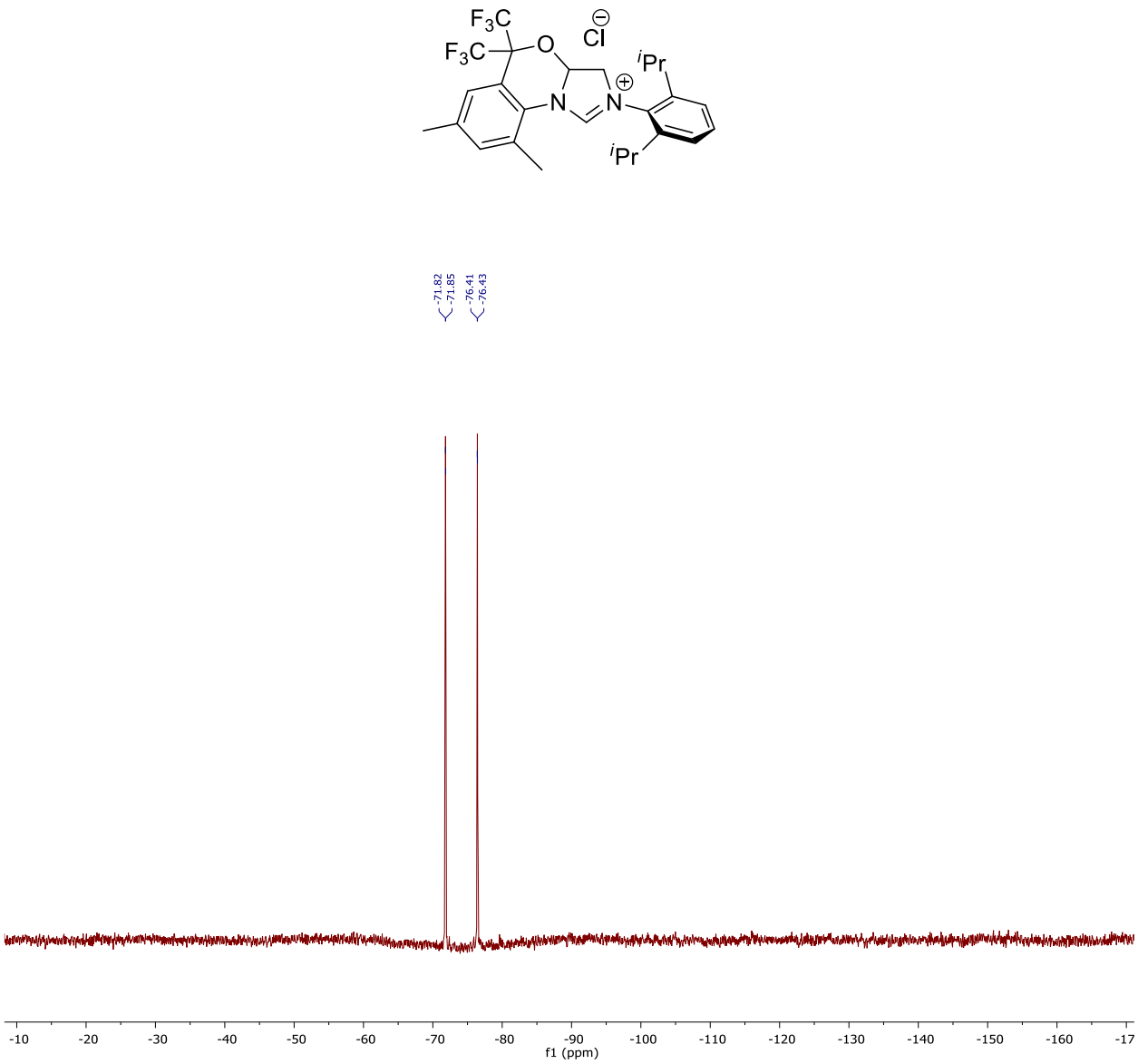

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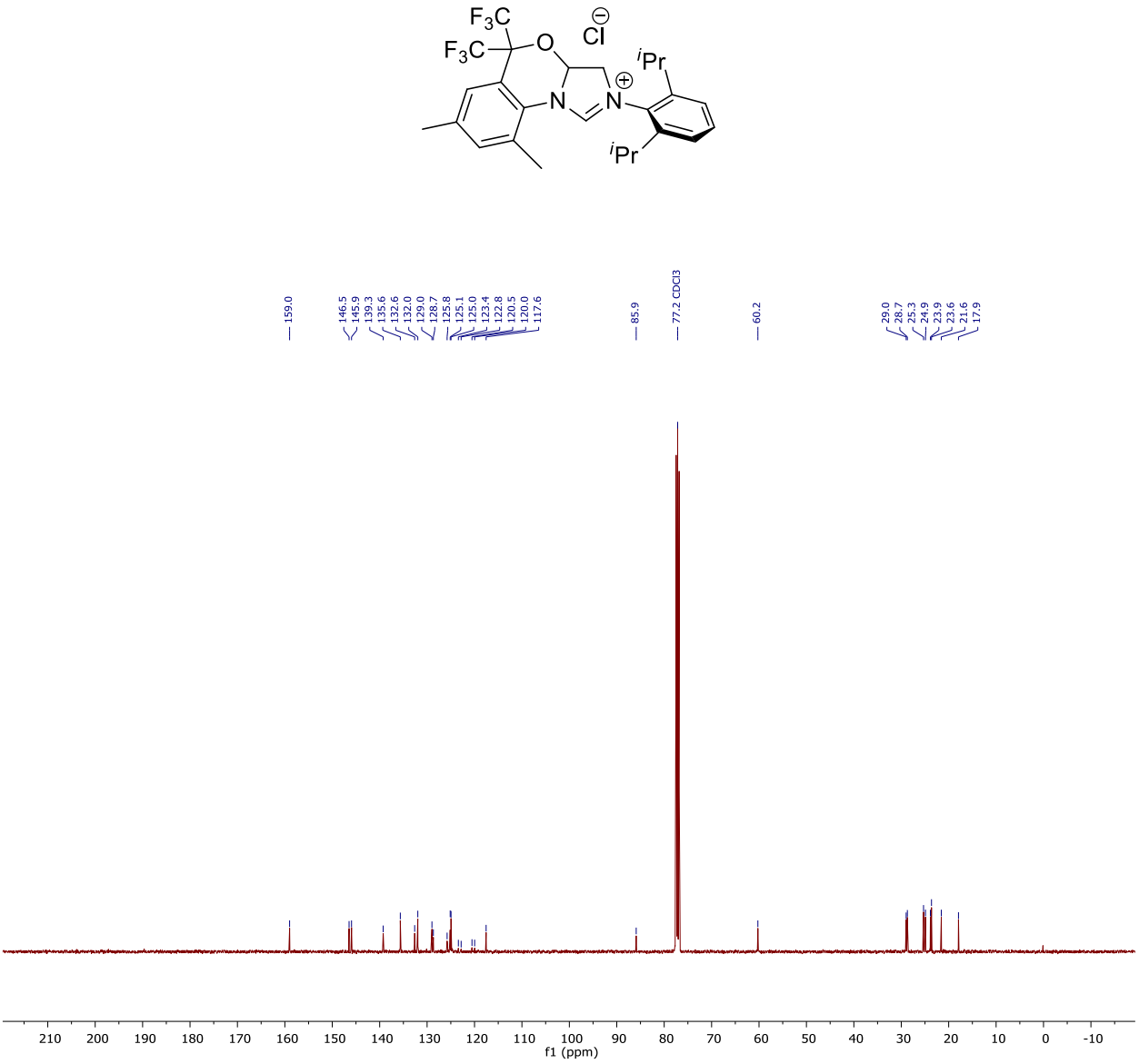

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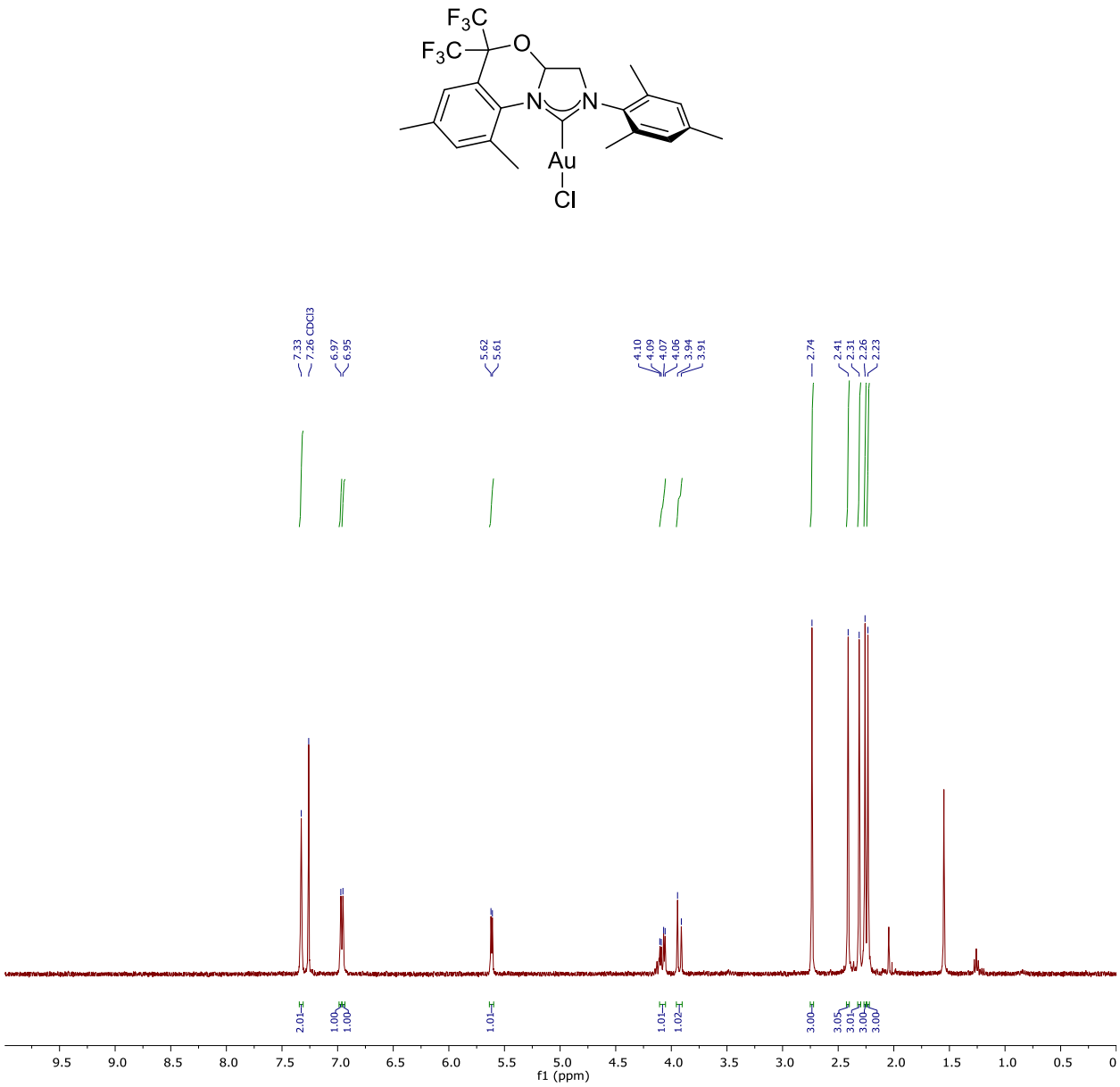

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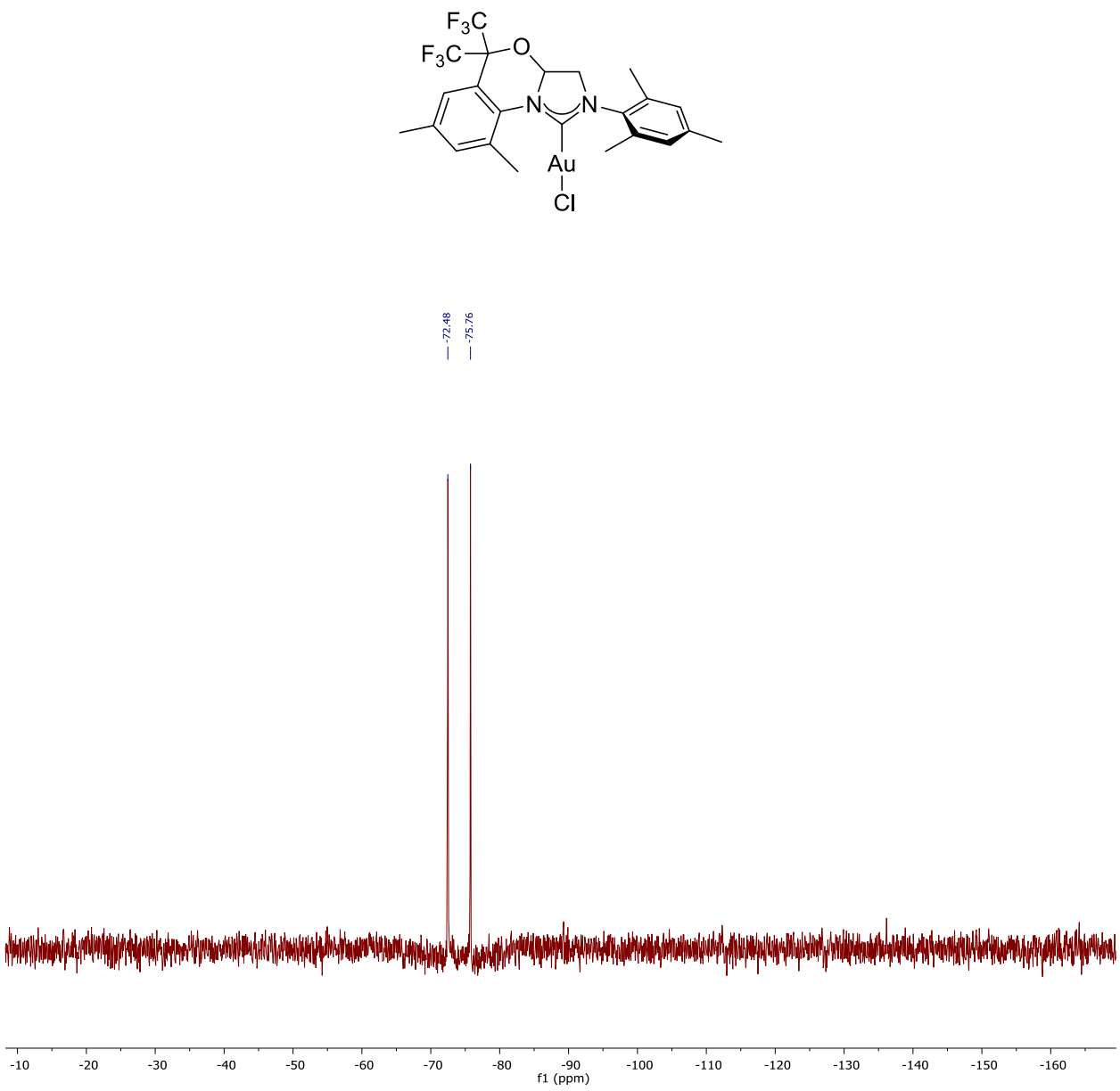
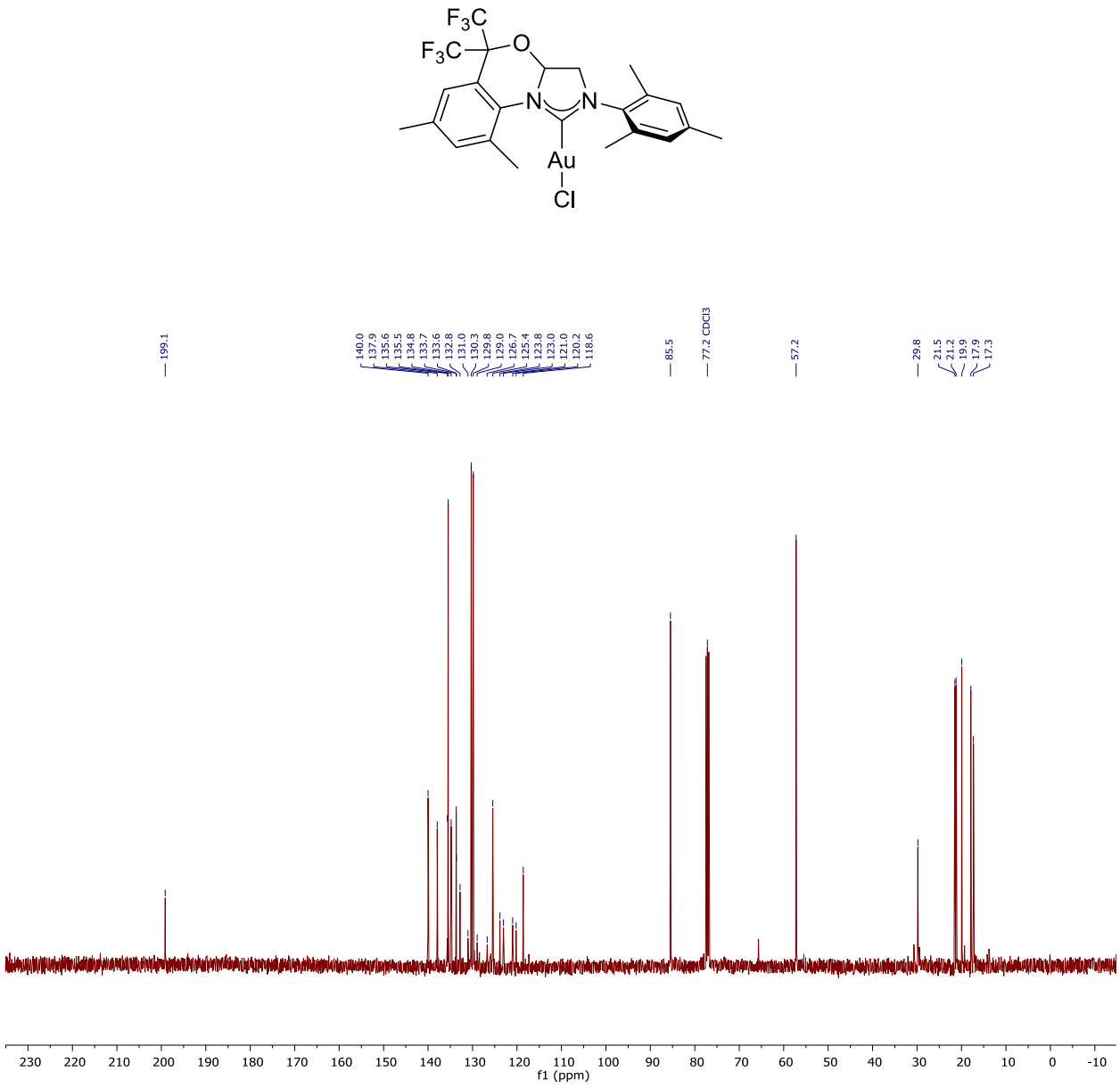


^{19}F NMR (376 MHz, Chloroform-d) of 4a



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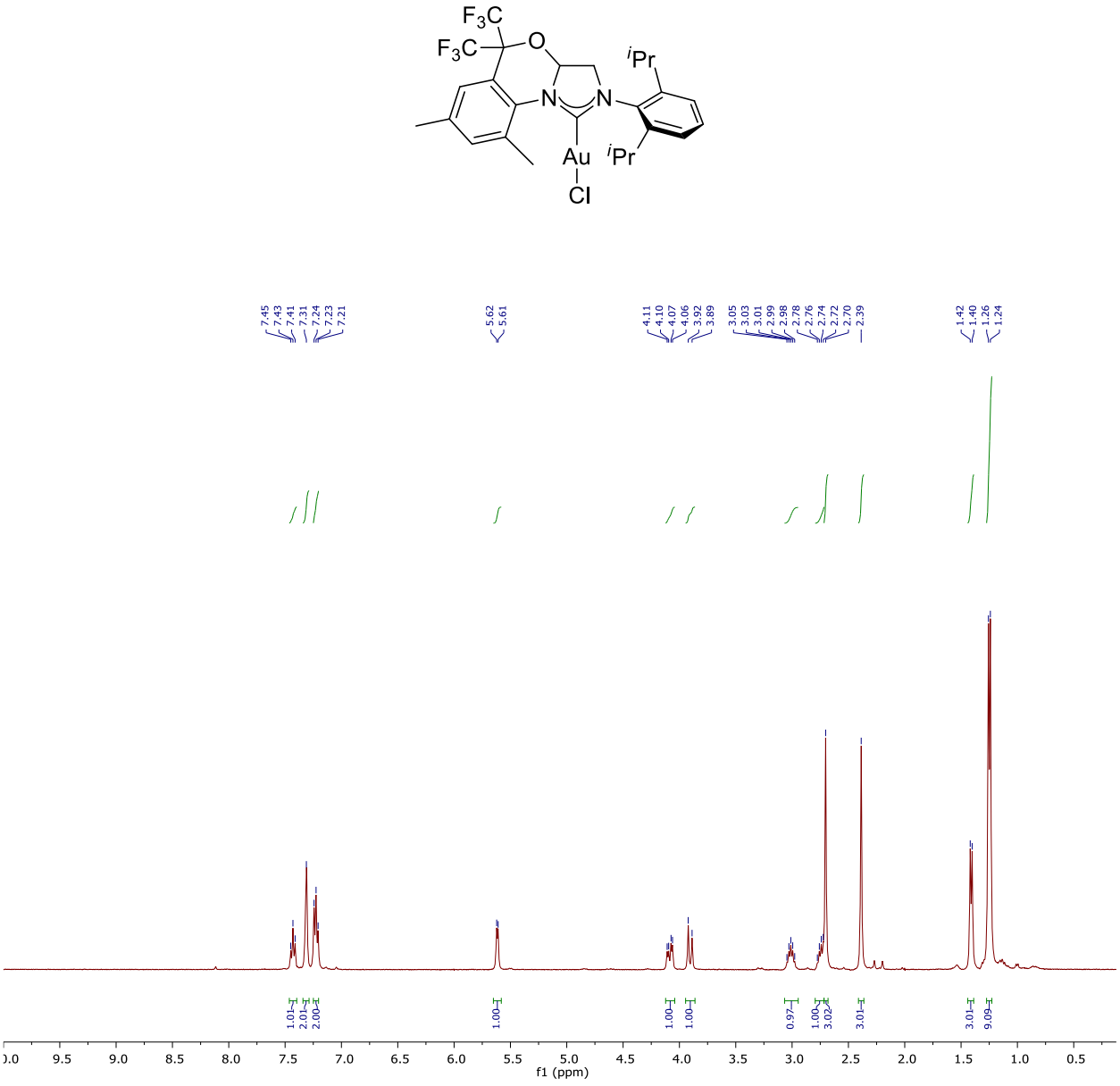

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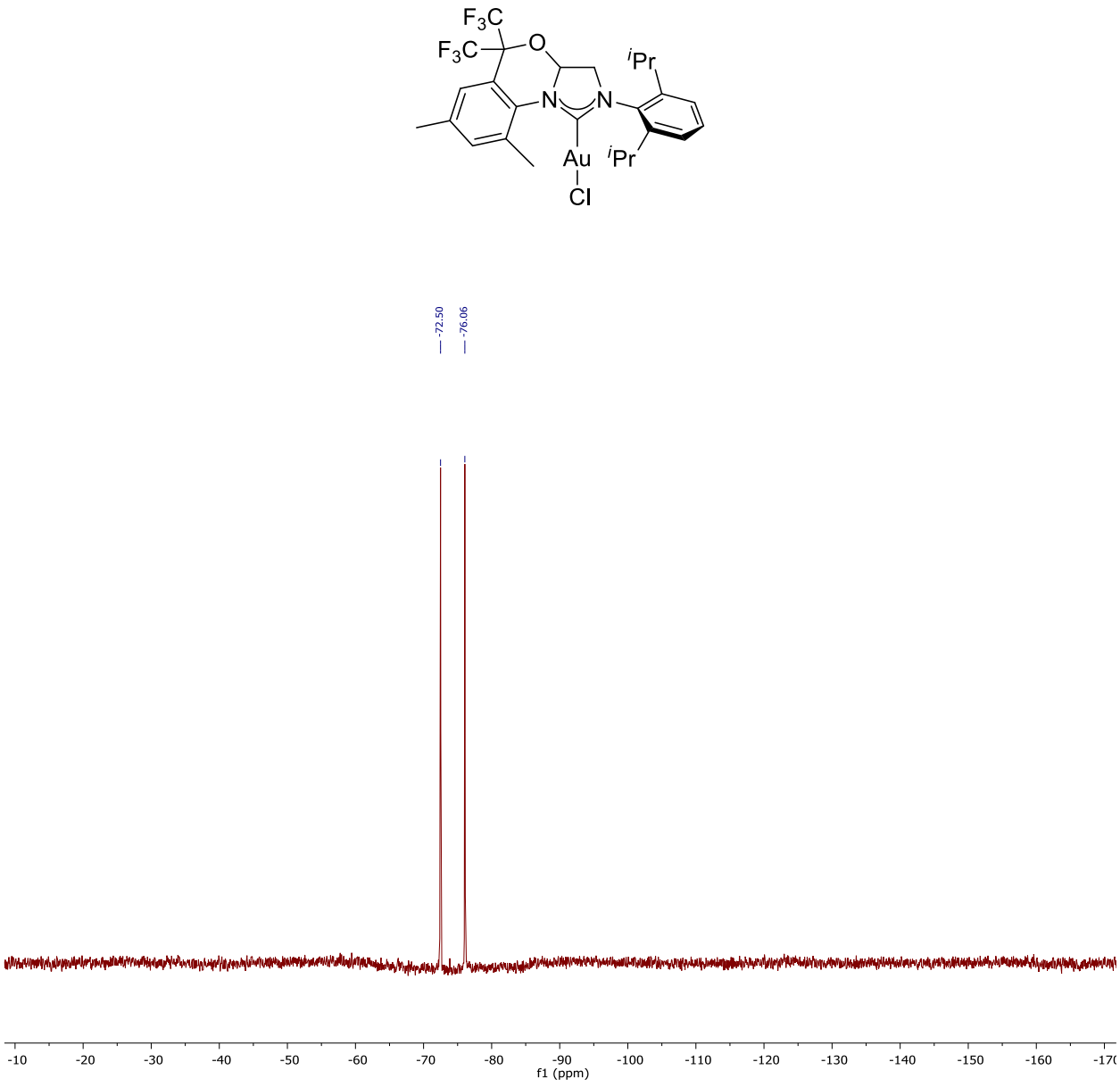

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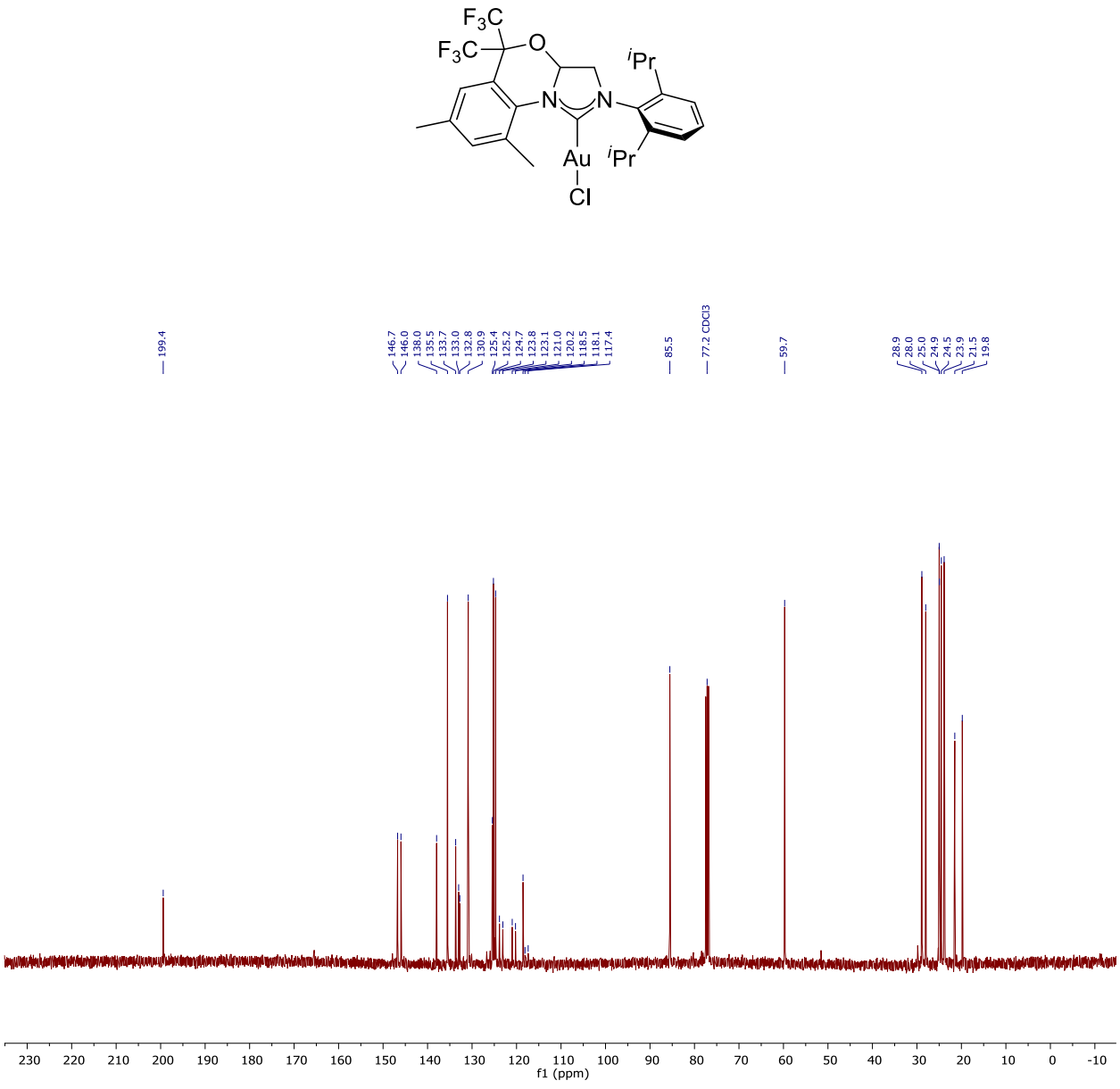

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