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Electronic Supplementary Information

# Activation of C–F Bonds in Fluoroarenes by *N*-Heterocyclic Carbenes as an Effective Route to Abnormal NHC Complexes

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# Materials and Methods

**1. General methods**

All air- and moisture-insensitive reactions were carried out under an ambient atmosphere, magnetically stirred. All air- and moisture-sensitive manipulations were performed using oven-dried glassware, including standard Schlenk and glovebox techniques under an atmosphere of nitrogen.

**2. Reagents**

*2.1. Source of reagents*

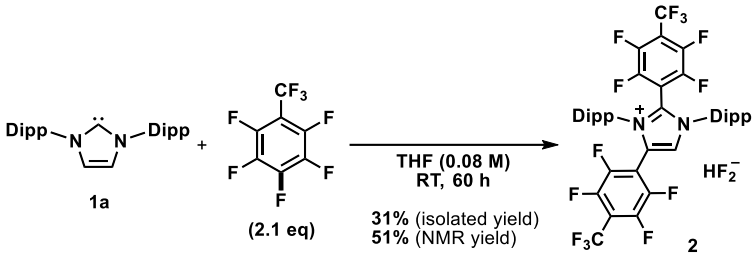
1,3-Bis-(2,6-diisopropylphenyl)imidazolylidene (*I*Pr, **1a**) and 1,3-bis-(2,4,6-trimethylphenyl)-imidazolylidene (*I*Mes, **1b**) were synthesized according to a reference.[1] Octafluorotoluene, 1-fluoro-4-trifluoromethylbenzene, silver(I) oxide, chloro(dimethylsulfide)gold(I) and all other chemicals were purchased from commercial sources and used as received unless otherwise specified. 3Å molecular sieves were activated at 240 ˚C for overnight prior to use.

*2.2. Drying of solvents*

Benzene, benzene-$d_6$, toluene, pentane, diethyl ether and THF (tetrahydrofuran) were distilled from deep purple sodium benzophenone ketyl, and stored over 3Å molecular sieves. DCM (dichloromethane) was dried using calcium hydride, distilled, and stored over 3Å molecular sieves. Chloroform-$d_1$ was dried using 3Å molecular sieves and stored in inert atmosphere.

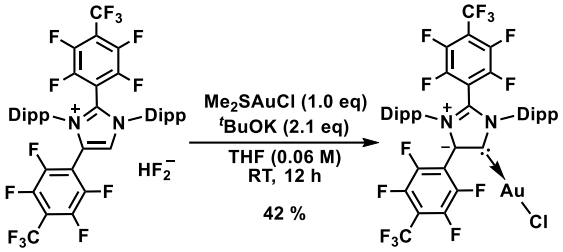
# Experimental Details

**Synthesis of 2**



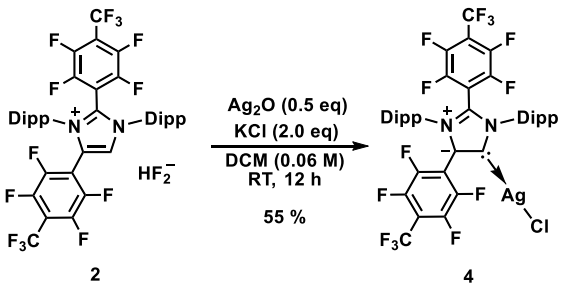

In a $N_2$ atmosphere glovebox, 1,3-bis-(2,6-diisopropylphenyl)imidazolylidene (*I*Pr, 210 mg, 0.540 mmol) were placed in a 20 mL vial and subsequently dry THF (7 mL) and octafluorotoluene (161 $\mu$L, 1.14 mmol) were added to the vial. The solution became green immediately and was stirred at room temperature. Precipitations were formed slowly during the reaction. After 60 hours, dry diethyl ether (14 mL) was added into the reaction mixture, and the green solid formed was collected on a frit, washed with dry diethyl ether (1 × 14 mL) and dry pentane (1 × 14 mL) until the solids become colorless, and dried *in vacuo* to afford 144 mg of the titled compound (31%). Crystals suitable for X-ray crystallography were obtained when the same reaction was performed in benzene instead of THF, without stirring. NMR yield (51%) was determined using hexamethylbenzene as an internal standard. $^{1}$H NMR ($CDCl_3$, 500 MHz): $\delta$ 16.08 (t, $J_{H,F}$ = 129 Hz, 1H), 10.79 (s, 1H), 7.61 (t, $J$ = 7.9 Hz, 1 H), 7.56 (t, $J$ = 7.9 Hz, 1 H), 7.33–7.30 (m, 4 H), 2.48–2.39 (m, 4 H), 1.37 (d, $J$ = 6.7 Hz, 6 H), 1.19 (d, $J$ = 6.6 Hz, 6 H), 0.96 (d, $J$ = 6.5 Hz, 6 H), 0.94 (d, $J$ = 6.6 Hz, 6 H) ppm. $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 214 MHz) $\delta$ 145.53, 145.49, 145.42 (dd, $J$ = 14.7, 255.8 Hz, 1C), 144.70 (dd, $J$ = 18.9, 261.3 Hz), 144.61 (dd, $J$ = 18.4, 262.2 Hz), 144.46 (dd, $J$ = 14.3, 267.7 Hz), 135.29, 135.07 (d, $J$ = 10.1 Hz), 133.41, 133.26, 128.86, 127.39, 127.04, 126.66, 125.52, 120.40 (q, $J$ = 276.3 Hz), 119.54 (q, $J$ = 276.9 Hz), 115.68 (tq, $J$ = 12.1, 36.4 Hz), 113.17 (tq, $J$ = 12.1, 35.4 Hz), 109.11 (t, $J$ = 15.6 Hz), 106.30 (t, $J$ = 15.0 Hz), 29.76, 28.81, 26.60, 24.88, 24.47 (d, $J$ = 4.5 Hz, 1C), 22.34 ppm. $^{19}$F{$^{1}$H} NMR ($CDCl_3$, 282 MHz): $\delta$ –56.5 (t, $J$ = 21.7 Hz, 3F), –56.6 (t, $J$ = 21.6 Hz, 3F), –129.9 (m, 2F), –132.6 (m, 2F), –134.8 (m, 2F), –137.6 (m, 2F), –156.7 (s, 2F) ppm. $^{19}$F NMR ($CDCl_3$, 282 MHz): $\delta$ –56.5 (t, $J$ = 21.7 Hz, 3F), –56.6 (t, $J$ = 21.6 Hz, 3F), –129.9 (m, 2F), –132.7 (m, 2F), –134.8 (m, 2F), –137.6 (m, 2F), –156.7 (d, $J_{F,H}$ = 108 Hz) ppm. Anal. Calcd for $C_{41}H_{36}F_{16}N_2$: C, 57.21; H, 4.22; N, 3.25. Found: C, 53.84; H, 4.34; N, 3.23. (A satisfactory elemental analysis data could not be obtained despite several attempts with analytically pure compound, presumably due to the hygroscopic nature of the compound. *cf.)* Anal. Calcd for $C_{41}H_{36}F_{16}N_2 \cdot 3H_2O$: C, 53.83; H, 4.63; N, 3.06.). HRMS (FAB): m/z calcd for [$C_{41}H_{35}F_{14}N_2$] 821.2577, found 821.2580.

**Synthesis of 3**




In a $N_2$ atmosphere glovebox, **2** (50 mg, 0.058 mmol), chloro(dimethylsulfide)gold(I) (17 mg, 0.058 mmol) and potassium *tert*-butoxide (14 mg, 0.13 mmol) were placed in a 4 mL vial and subsequently dry THF (1 mL) was added to the vial. The reaction mixture was stirred at room temperature for 12 hours in the absence of light. The mixture was then filtered through dry Celite and subsequently eluted with dry dichloromethane (2 × 1 mL). The filtrate was concentrated *in vacuo* and then dry diethyl ether (2 mL) was added to solidify the product. The solid were collected on a frit, washed with dry diethyl ether (2 × 1 mL), and dried *in vacuo* to afford **3** as white solid (26 mg, 42%). Crystals suitable for X-ray crystallography were obtained by recrystallization in THF/pentane. $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.51 (t, $J$ = 7.7 Hz, 1 H), 7.50 (t, $J$ = 7.7 Hz, 1 H), 7.25 (d, $J$ = 7.5 Hz, 2 H), 7.24 (d, $J$ = 7.9 Hz, 2 H), 2.58 (m, 2 H), 2.46 (m, 2 H), 1.55 (d, $J$ = 6.7 Hz, 6 H), 1.17 (d, $J$ = 5.7 Hz, 6 H), 1.01 (d, $J$ = 6.5 Hz, 6 H), 0.96 (d, $J$ = 6.4 Hz, 6 H) ppm. $^{13}$C{$^1$H} NMR ($CDCl_3$, 214 MHz): $\delta$ 164.38, 146.04, 145.75, 145.55 (dd, $J$ = 11.4, 253.8 Hz), 144.62 (dd, $J$ = 16.0, 262.9 Hz), 144.41 (dd, $J$ = 16.3, 259.7 Hz), 144.17 (dd, $J$ = 14.3, 264.3 Hz), 135.08, 132.66, 132.55, 132.06, 128.72, 127.88, 126.32, 125.24, 120.50 (q, $J$ = 275.1 Hz), 119.75 (q, $J$ = 276.1 Hz), 114.5, 114.24 (t, $J$ = 16.3 Hz), 111.97, 108.34 (t, $J$ = 15.6 Hz), 29.28, 28.44, 27.28, 25.13 (d, $J$ = 5.7 Hz), 24.99 (d, $J$ = 6.1 Hz), 22.87 (d, $J$ = 3.5 Hz) ppm. $^{19}$F{$^1$H} NMR ($CDCl_3$, 282 MHz): $\delta$ –59.6 (t, $J$ = 21.7 Hz, 3F), –56.8 (t, $J$ = 21.6 Hz, 3F), –132.1 (m, 2F), –134.7 (m, 2F), –139.8 (m, 2F), –141.7 (m, 2F) ppm. Anal. Calcd for $C_{41}H_{34}AuClF_{14}N_2$: C, 46.76; H, 3.25; N, 2.66. Found: C, 48.13; H, 3.44; N, 2.51. (A satisfactory elemental analysis data could not be obtained despite several attempts with analytically pure compound. *cf.)* Anal. Calcd for $C_{41}H_{34}AuClF_{14}N_2{\cdot}C_4H_8O$ (a THF molecule): C, 48.03; H, 3.76; N, 2.49.). HRMS (FAB): m/z calcd for [$C_{41}H_{34}AuF_{14}N_2$] 1017.2164, found 1017.2168.

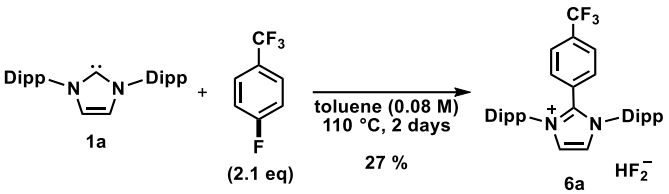
**Synthesis of 4**




In a $N_2$ atmosphere glovebox, **2** (50 mg, 0.058 mmol), silver(I) oxide (6.7 mg, 0.029 mmol) and potassium chloride (8.5 mg, 0.11 mmol) were placed in a 4 mL vial and subsequently dry

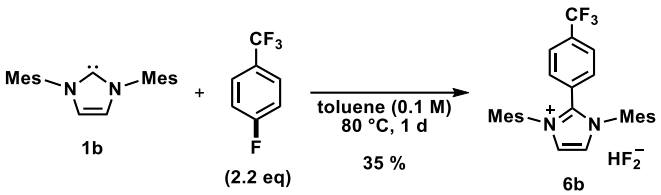
dichloromethane (1 mL) was added to the vial. The reaction mixture was stirred at room temperature for 12 hours in the absence of light. The mixture was then filtered through dry Celite and subsequently eluted with dry dichloromethane (2 × 1 mL). The filtrate was concentrated *in vacuo* to afford a yellow oil. The yellow oil was further diluted with dry dichloromethane (0.5 mL), and then dry pentane (3 mL) was slowly added to solidify the product as light yellow solid. The solid was collected on a frit, washed with dry pentane (2 × 1 mL), and dried *in vacuo* to afford 30.9 mg of the titled compound as light yellow microcrystalline solid (55%). $^{1}$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.51 (t, $J$ = 7.9 Hz, 1 H), 7.49 (t, $J$ = 7.8 Hz, 1 H), 7.26 (d, $J$ = 7.9 Hz, 2 H), 7.24 (d, $J$ = 7.9 Hz, 2 H), 2.57–2.52 (m, 2 H), 2.48–2.42 (m, 2 H), 1.42 (d, $J$ = 6.7 Hz, 6 H), 1.16 (d, $J$ = 6.4 Hz, 6 H), 0.97 (d, $J$ = 5.7 Hz, 6 H), 0.95 (d, $J$ = 6.5 Hz, 6 H) ppm. $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 214 MHz): 172.25 (d, $J_{C,Ag}$ = 230.2 Hz), 145.87, 145.55 (dd, $J$ = 16.3, 272.4 Hz), 145.47, 144.67 (dd, $J$ = 13.8, 264.4 Hz), 144.35 (dd, $J$ = 15.9, 275.8 Hz), 144.20 (dd, $J$ = 15.1, 265.8 Hz), 136.05, 133.58, 132.44, 132.03, 130.38 (d, $J$ = 15.9 Hz), 127.95, 126.27, 125.26, 120.46 (q, $J$ = 274.3 Hz), 119.76 (q, $J$ = 276.8 Hz), 114.92 (t, $J$ = 16.0 Hz), 114.26 (d, $J$ = 30.9 Hz), 111.77 (d, $J$ = 35.3 Hz), 108.54 (t, $J$ = 15.2 Hz), 29.09, 28.40, 27.49, 25.05, 24.90, 22.68 ppm. $^{19}$F{$^{1}$H} NMR ($CDCl_3$, 282 MHz): $\delta$ –59.6 (t, $J$ = 21.8 Hz, 3F), –59.8 (t, $J$ = 21.5 Hz, 3F), –132.6 (m, 2F), –136.0 (m, 2F), –139.8 (m, 2F), –141.3 (m, 2F) ppm. Anal. Calcd for $C_{41}H_{34}AgClF_{14}N_2$: C, 51.08; H, 3.56; N, 2.91. Found: C, 50.97; H, 3.64; N, 3.03.

**Synthesis of 6a**




In a $N_2$ atmosphere glovebox, 1,3-bis-(2,6-diisopropylphenyl)imidazolylidene (*I*Pr, 60 mg, 0.154 mmol) were placed in a 4 mL vial and subsequently dry toluene (2 mL) and 1-fluoro-4-trifluoromethylbenzene (41 $\mu$L, 0.32 mmol) were added to the vial. The solution was heated to 110 ˚C for 2 days. The solution became brown and colorless crystals (which were suitable for X-ray crystallography) were formed. The solution was decanted and remaining crystals were washed with dry toluene (2 × 1 mL) and dry pentane (2 × 1 mL). The crystals were further dried *in vacuo* to afford 24 mg of the titled compound (27%). $^{1}$H NMR ($CDCl_3$, 500 MHz): $\delta$ 16.64 (t, $J_{HF}$ = 127 Hz, 1H), 8.77 (s, 2H), 7.57 (t, $J$ = 7.8 Hz, 2 H), 7.48 (d, $J$ = 8.5 Hz, 2 H), 7.31 (d, $J$ = 7.9 Hz, 4 H), 7.06 (d, $J$ = 8.3 Hz, 2 H), 2.46–2.40 (m, 4 H), 1.31 (d, $J$ = 6.8 Hz, 12 H), 0.98 (d, $J$ = 6.9 Hz, 12 H) ppm. $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 214 MHz): $\delta$ 144.85, 142.30, 134.27 (q, $J$ = 34.8 Hz), 132.68, 129.95, 129.80, 129.24, 126.21, 125.57, 124.64, 122.72 (q, $J$ = 273.7 Hz), 29.53, 25.68, 22.75 ppm. $^{19}$F{$^{1}$H} NMR ($CDCl_3$, 470 MHz): $\delta$ –63.6 (s, 3F), –157.4 (s, 2F) ppm. $^{19}$F NMR ($CDCl_3$, 470 MHz): $\delta$ –63.6 (s, 3F), –157.4 (d, $J_{F,H}$ = 125 Hz, 2F) ppm. Anal. Calcd for $C_{34}H_{41}F_5N_2$: C, 71.31; H, 7.22; N, 4.89. Found: C, 71.09; H, 6.81; N, 4.61.

**Synthesis of 6b**




In a $N_2$ atmosphere glovebox, 1,3-bis-(2,4,6-trimethylphenyl)imidazolylidene (*I*Mes, 60 mg, 0.197 mmol) were placed in a 4 mL vial and subsequently dry toluene (2 mL) and 1-fluoro-4-trifluoromethylbenzene (55 $\mu$L, 0.43 mmol) were added to the vial. The solution was heated to 80 ˚C for 1 day. The solution became yellow and colorless crystals were formed. The solution was decanted and remaining crystals were washed with dry toluene (2 × 1 mL) and dry pentane (2 × 1 mL). The crystals were further dried *in vacuo* to afford 34 mg of the titled compound (35%). $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 16.61 (t, $J_{HF}$ = 121 Hz, 1 H), 8.50 (s, 2H), 7.52 (d, $J$ = 8.4 Hz, 2 H), 7.07 (d, $J$ = 8.2 Hz, 2 H), 7.00 (s, 4H), 2.34 (s, 6H), 2.07 (s, 12H) ppm. $^{13}$C{$^1$H} NMR ($CDCl_3$, 214 MHz): $\delta$ 142.03, 141.38, 134.17 (q, $J$ = 33.7 Hz), 134.03, 130.51, 130.35, 129.22, 127.79, 126.53 (indistinct q), 124.86, 122.92 (q, $J$ = 272.3 Hz), 21.32, 17.84 ppm. $^{19}$F{$^1$H} NMR ($CDCl_3$, 470 MHz): $\delta$ –63.5 (s, 3F), –158.1 (s, 2F) ppm. $^{19}$F NMR ($CDCl_3$, 470 MHz): $\delta$ –63.5 (s, 3F), –158.1 (d, $J_{F,H}$ = 124 Hz, 2F) ppm. Anal. Calcd for $C_{28}H_{29}F_5N_2$: C, 68.84; H, 5.98; N, 5.73. Found: C, 68.72; H, 6.27; N, 5.95.

# NMR

## General information

$^{1}$H NMR spectra were recorded using a Bruker DRX 500 spectrometer operating at 500 MHz for $^{1}$H acquisitions. Proton decoupled $^{13}$C NMR spectra ($^{13}$C{$^{1}$H}) were recorded using a AVANCE III HD 850 spectrometer operating at 214 MHz for $^{13}$C acquisitions. $^{1}$H–$^{13}$C polarization transfer experiments (DEPT45 and DEPT90) were performed using the same 850 spectrometer to allocate the $^{13}$C NMR signals. Proton decoupled $^{19}$F NMR spectra ($^{19}$F{$^{1}$H}) and proton coupled $^{19}$F NMR spectra ($^{19}$F) were recorded using either a Bruker DRX 500 spectrometer operating at 470 MHz for $^{19}$F acquisitions, or a AVANCE 300MHz FT-NMR spectrometer operating at 282 MHz for $^{19}$F acquisitions.

Chemical shifts of $^{1}$H and $^{13}$C acquisitions were referenced to the residual proton solvent peaks ($^{1}$H: $CDCl_3$, $\delta$ = 7.26 ppm), solvent $^{13}$C signals ($CDCl_3$, $\delta$ = 77.16 ppm).[2] Chemical shifts of $^{19}$F acquisitions were internally referenced using hexafluorobenzene ($\delta$ = –164.9 ppm relative to $CFCl_3$).

**$^{1}$H, $^{13}$C, and $^{19}$F NMR spectra of 2**

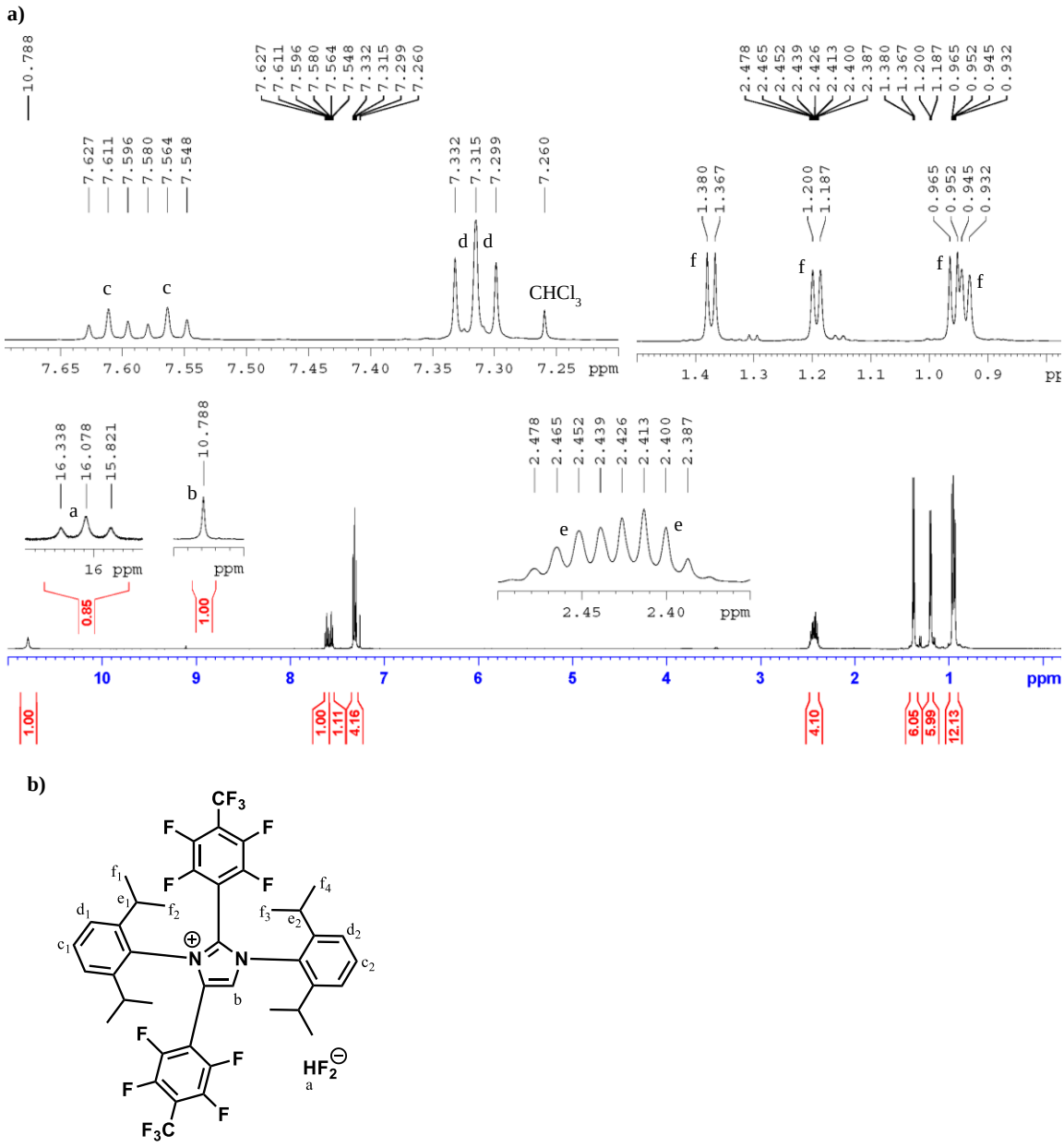



**Figure S1.** a) $^{1}$H NMR spectrum and b) assignment of the signals for the compound **2**.

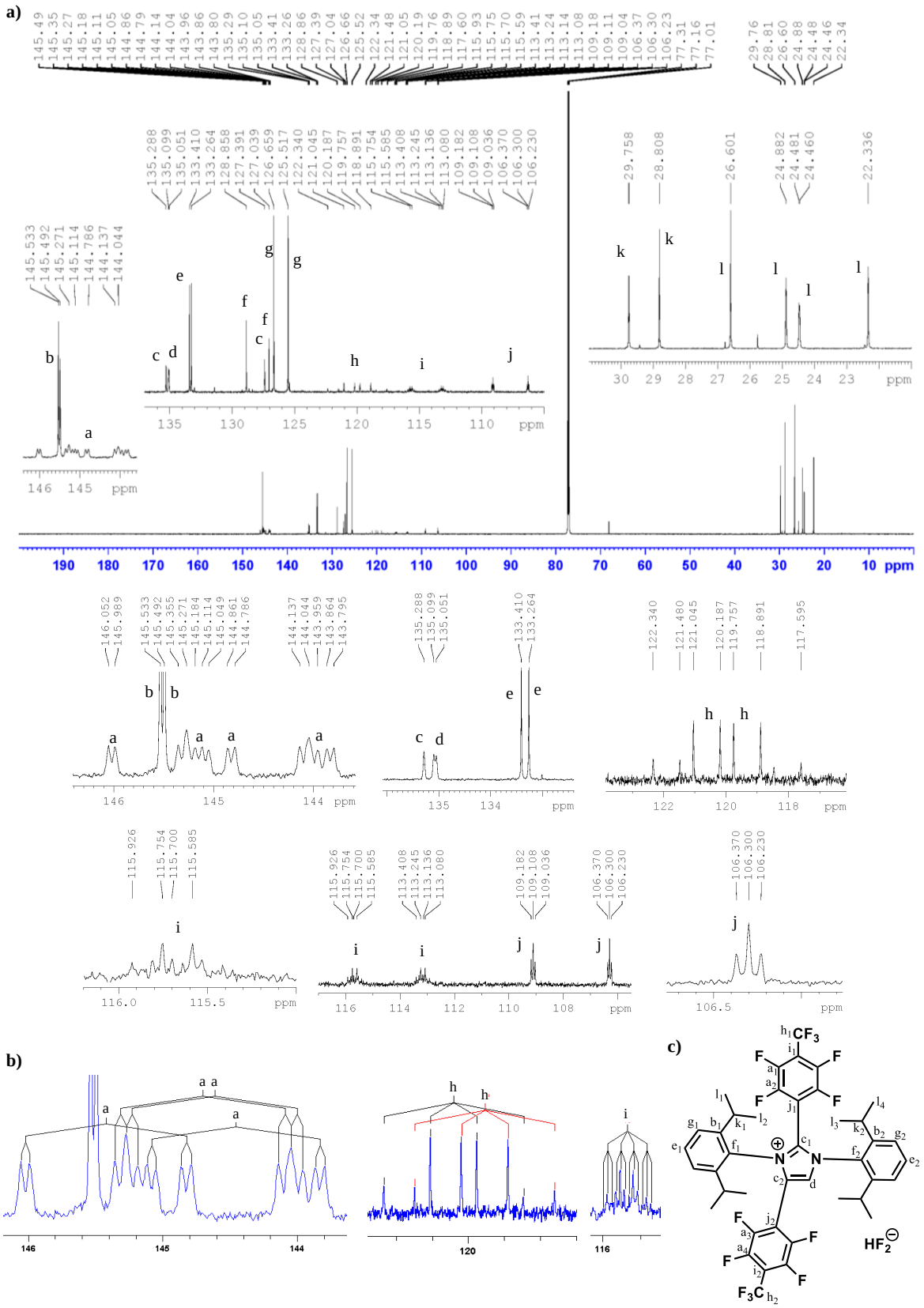



**Figure S2.** a) Proton decoupled $^{13}C$ NMR spectrum ($^{13}C\{^{1}H\}$), b) labelled expansions of the multiplets, and c) assignment of the signals for the compound **2**.

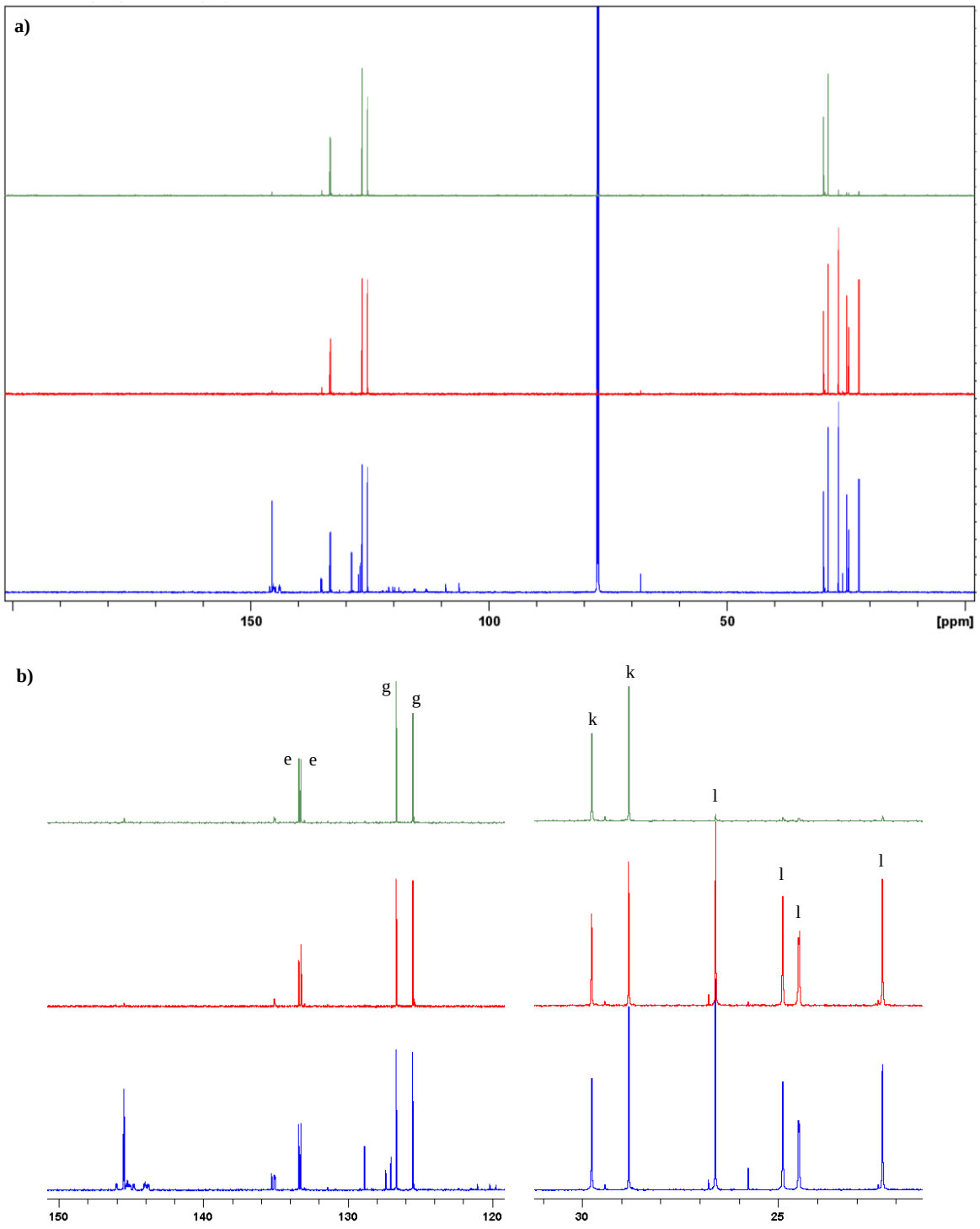



**Figure S3.** a) DEPT90 $^{13}$C NMR (top, green), DEPT45 $^{13}$C NMR (middle, red), and $^{13}$C NMR (bottom, blue) spectra of **2**. b) Expanded spectra with labels.

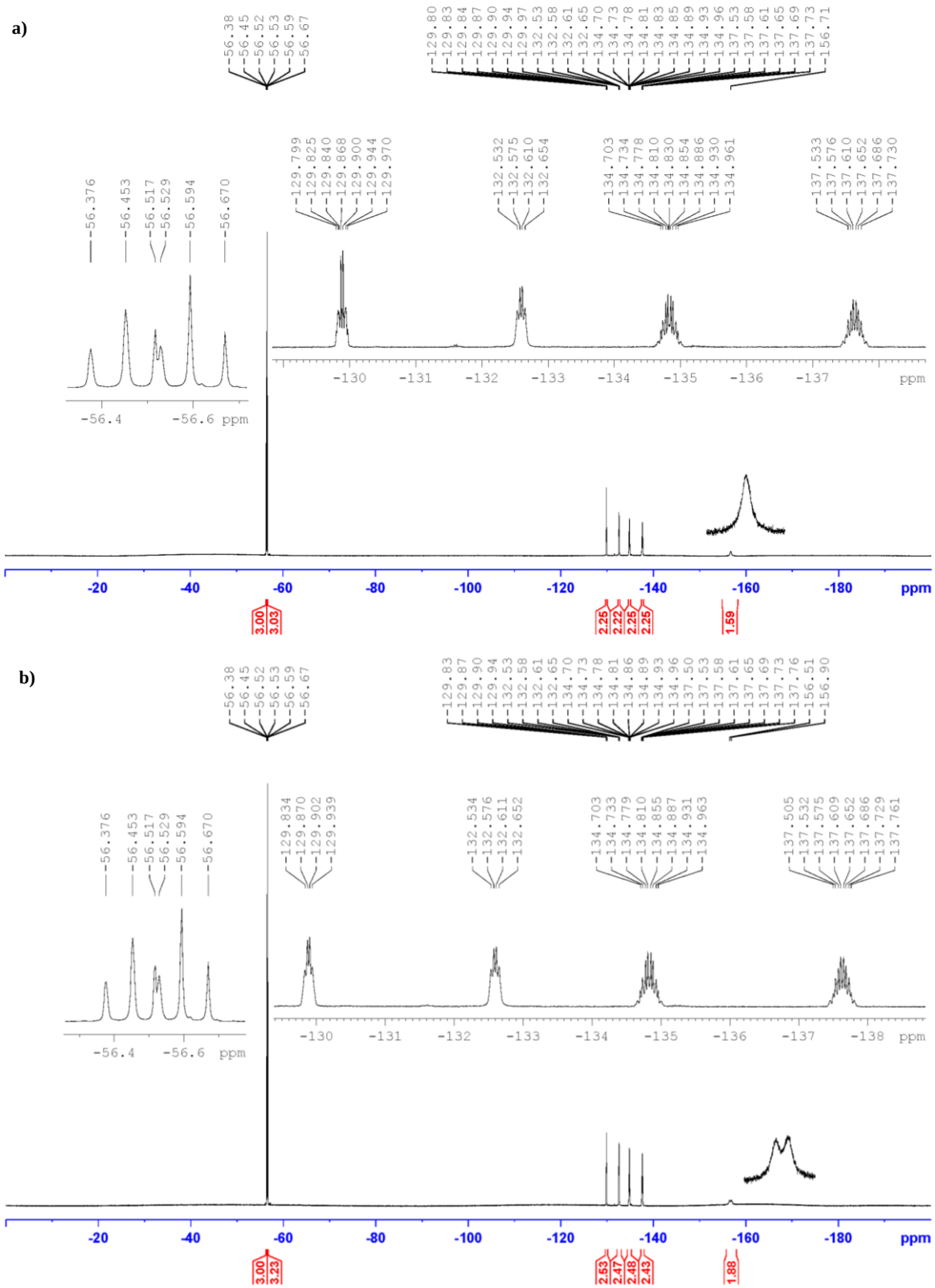
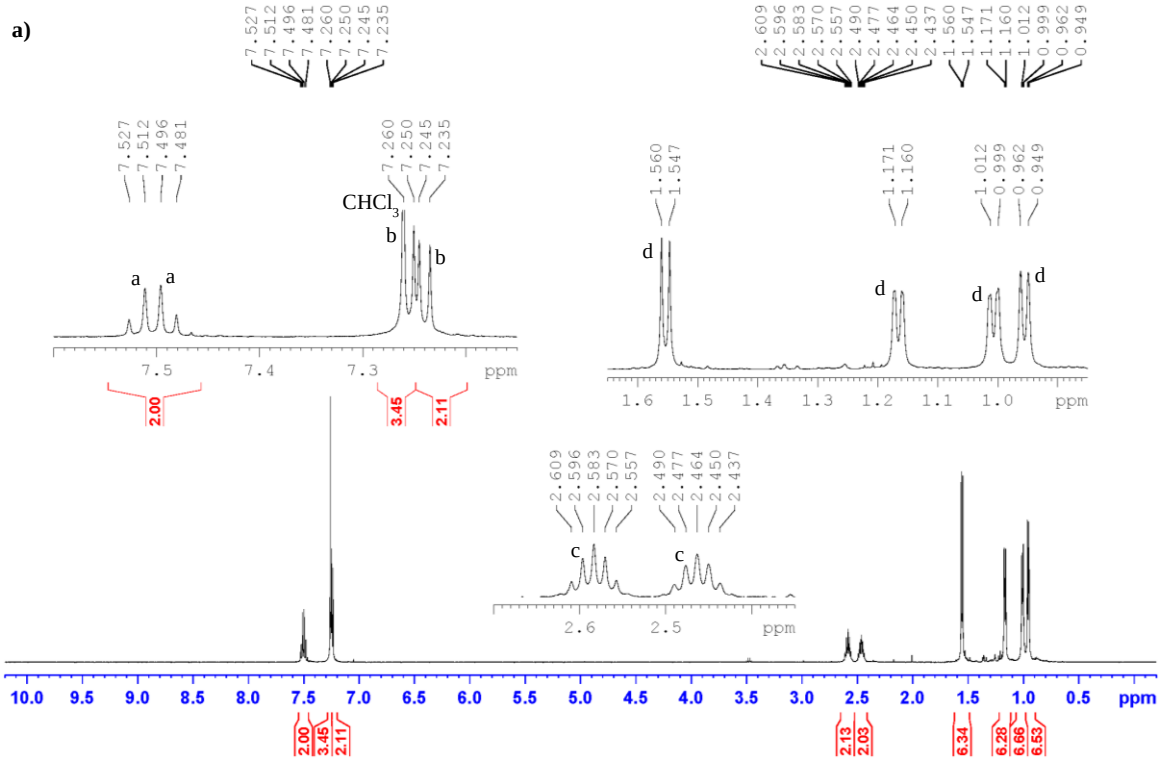



**Figure S4.** a) Proton decoupled $^{19}F$ NMR spectra ($^{19}F\{^{1}H\}$) and b) proton coupled $^{19}F$ NMR spectra ($^{19}F$) for the compound **2**.

**$^{1}$H, $^{13}$C, and $^{19}$F NMR spectra of 3**




b)

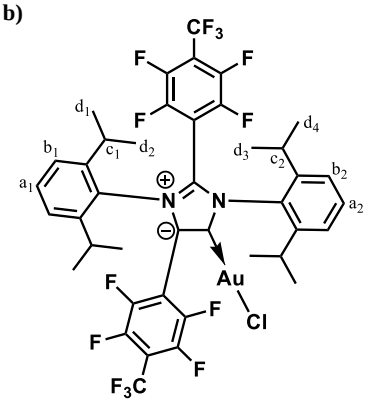



**Figure S5.** a) $^{1}$H NMR spectrum and b) assignment of the signals for the compound **3**.

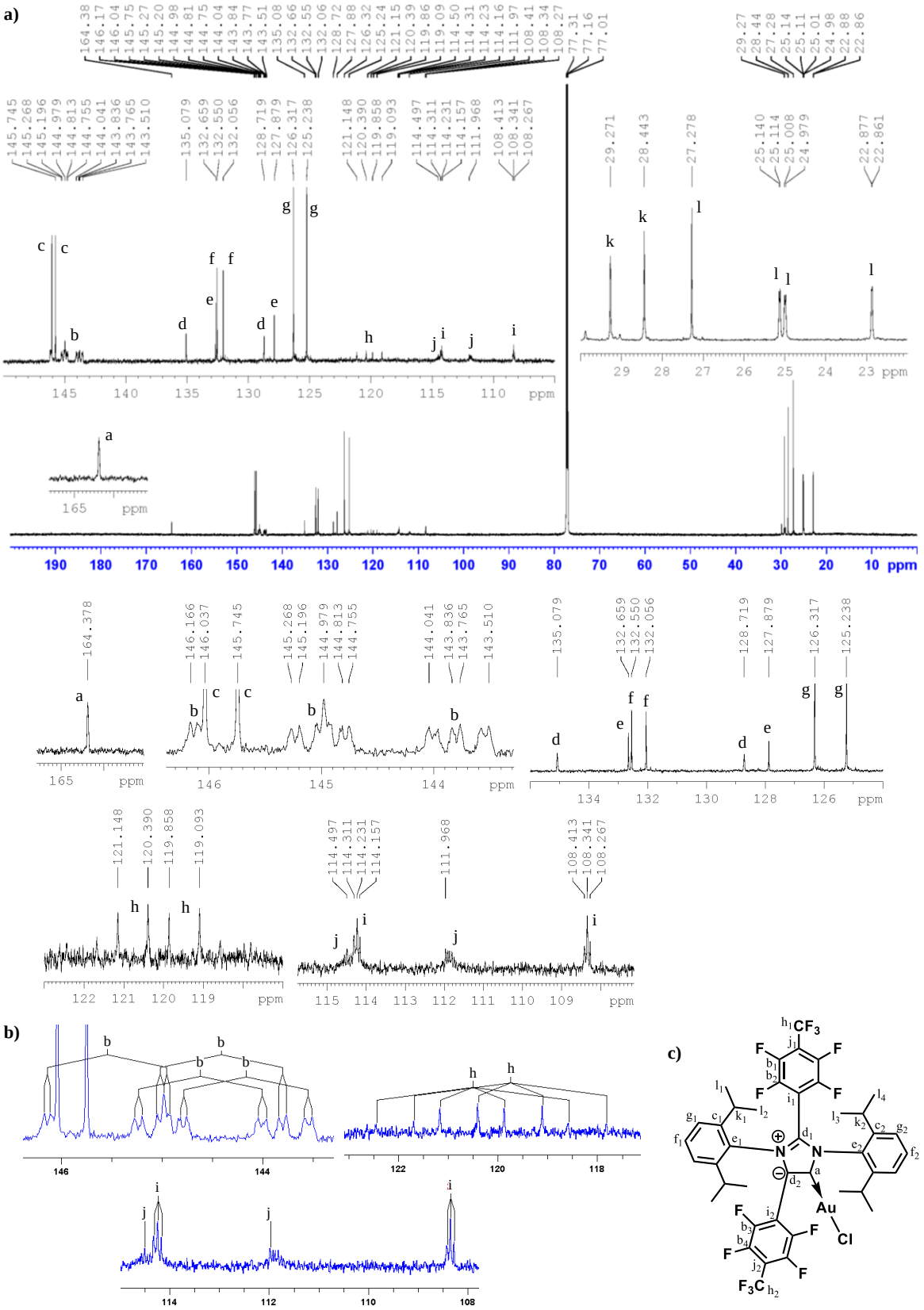



**Figure S6.** a) Proton decoupled $^{13}C$ NMR spectrum ($^{13}C\{^{1}H\}$), b) labelled expansions of the multiplets, and c) assignment of the signals for the compound **3**.

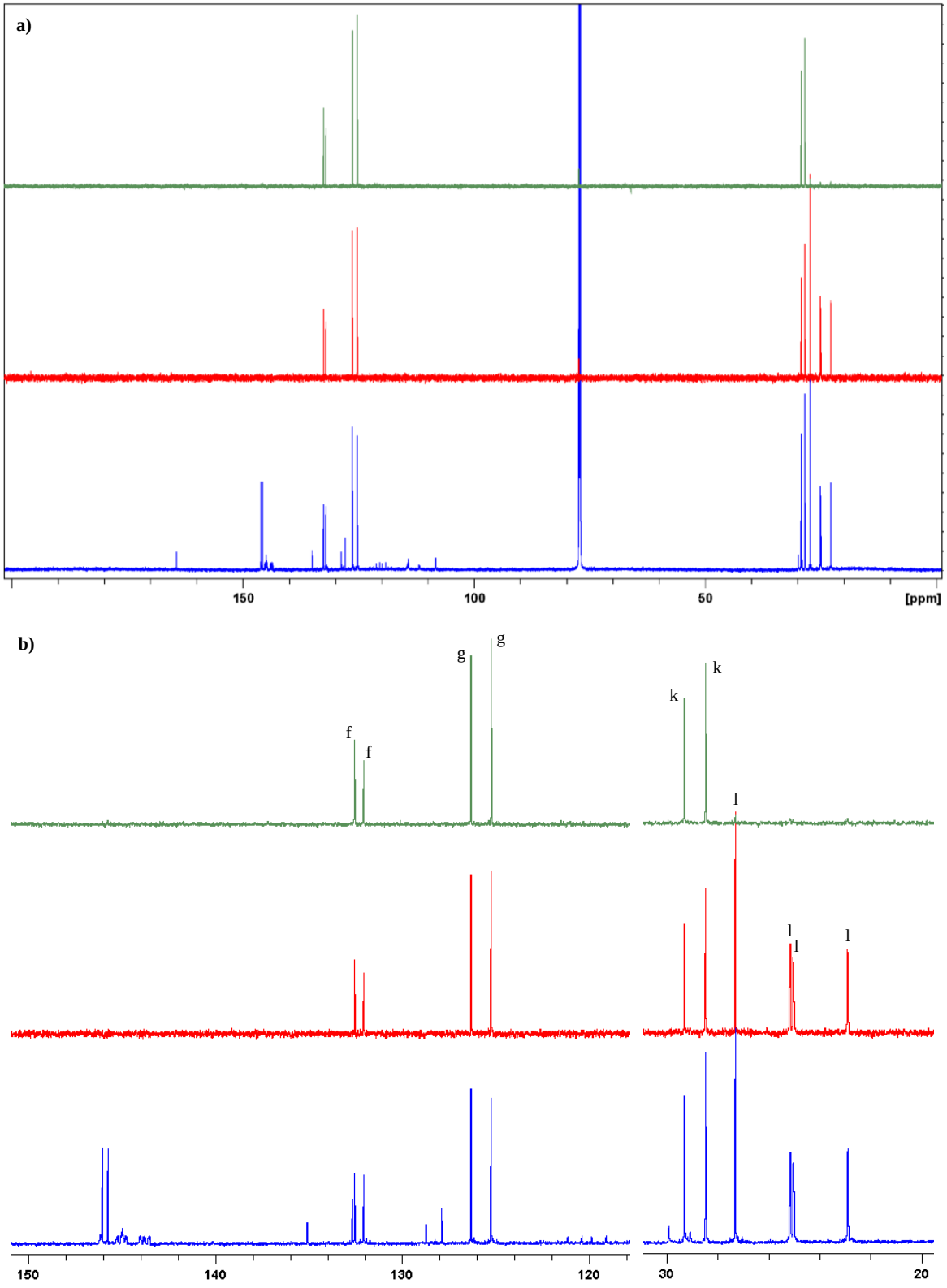



**Figure S7.** a) DEPT90 $^{13}$C NMR (top, green), DEPT45 $^{13}$C NMR (middle, red), and $^{13}$C NMR (bottom, blue) spectra of **3**. b) Expanded spectra with labels.

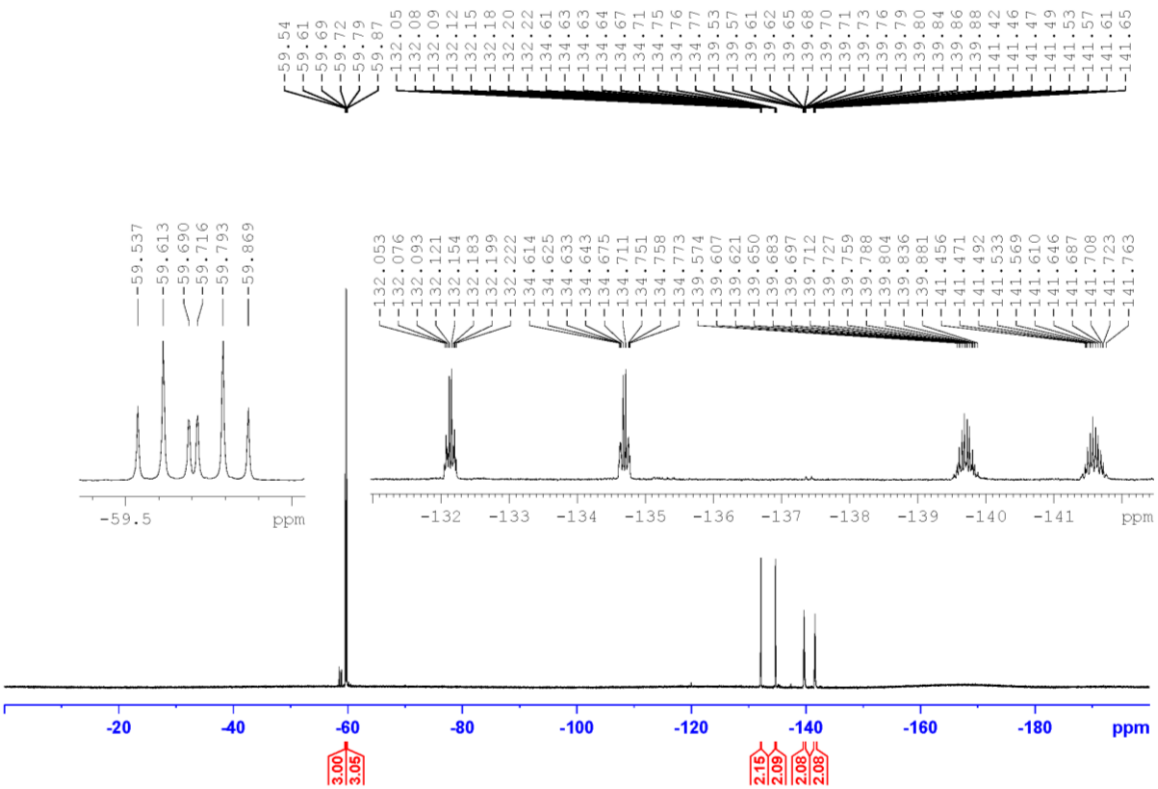



**Figure S8.** Proton decoupled $^{19}F$ NMR spectra ($^{19}F\{^{1}H\}$) of **3**.

**$^{1}$H, $^{13}$C, and $^{19}$F NMR spectra of 4**

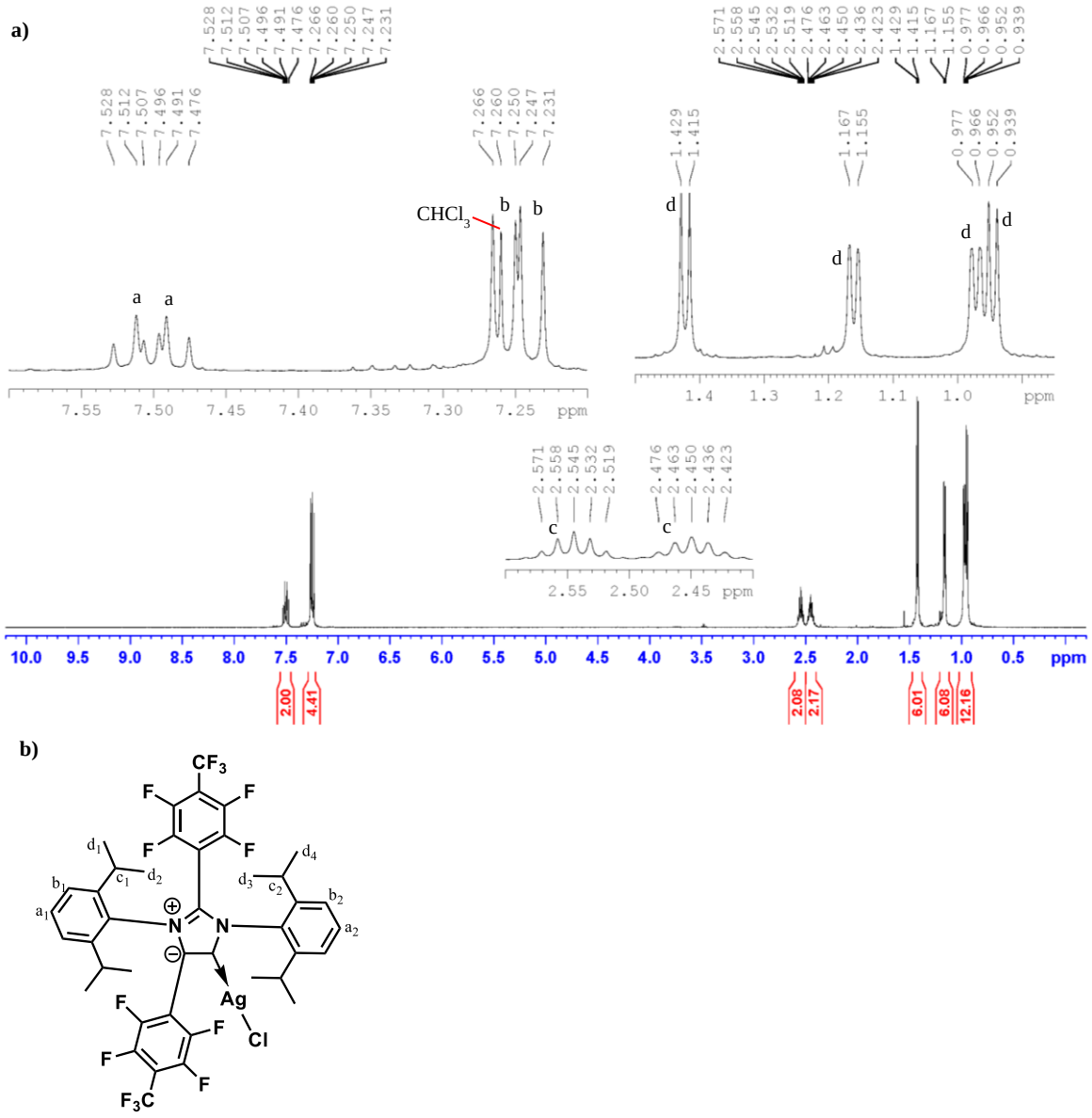



**Figure S9.** a) $^{1}$H NMR spectrum and b) assignment of the signals for the compound **4**.

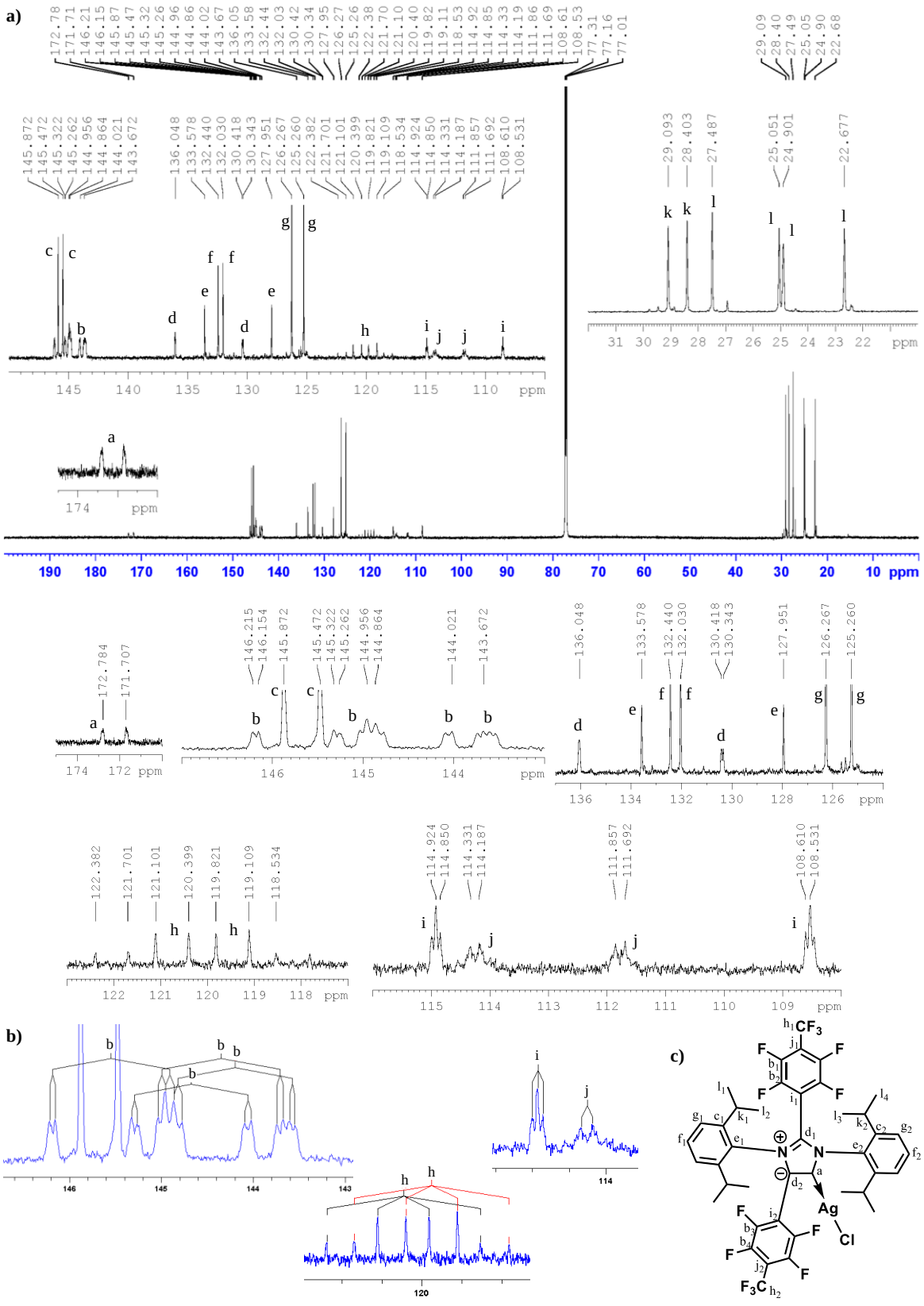



**Figure S10.** a) Proton decoupled $^{13}C$ NMR spectrum ($^{13}C\{^{1}H\}$), b) labelled expansions of the multiplets, and c) assignment of the signals for the compound **4**.

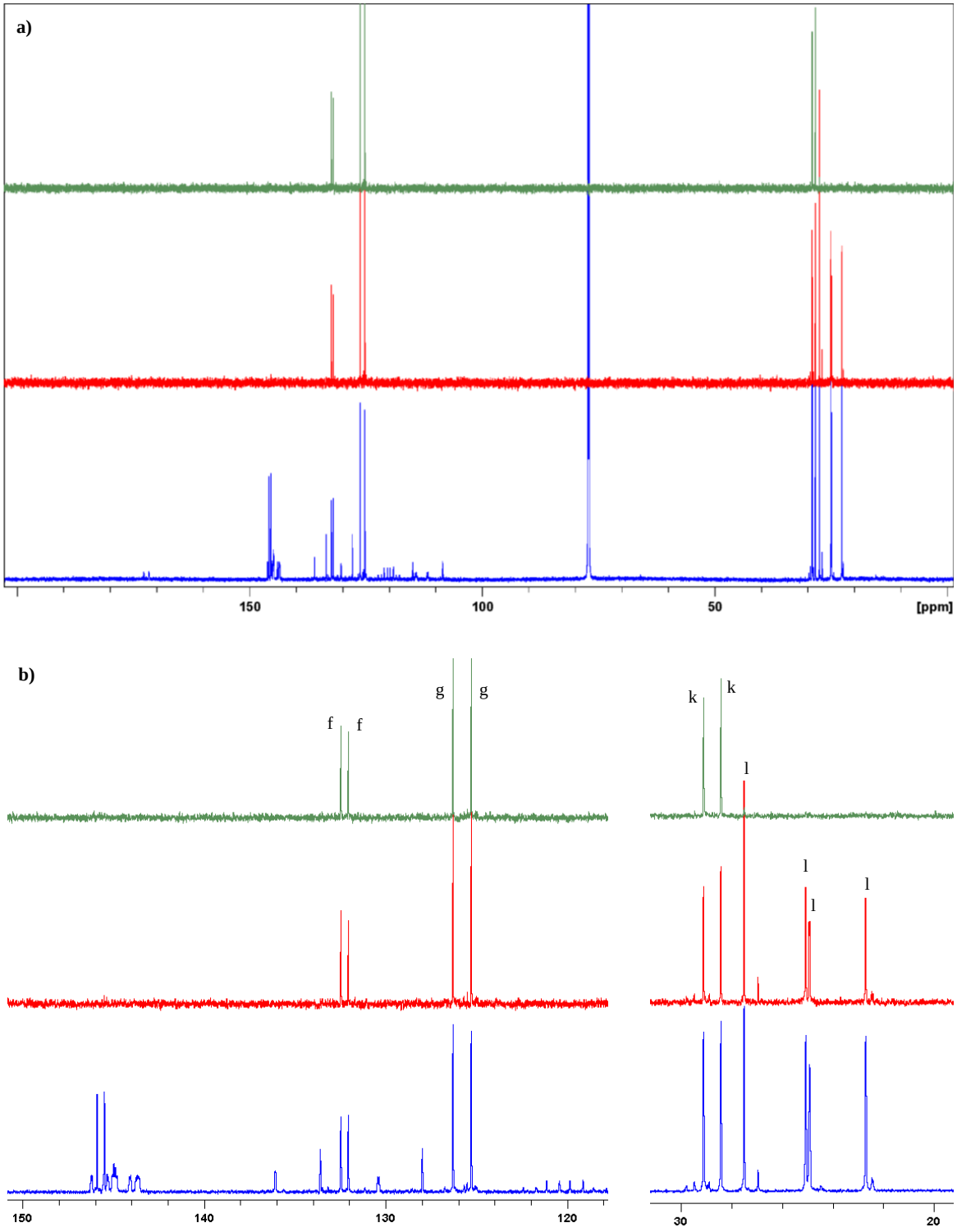



**Figure S11.** a) DEPT90 $^{13}$C NMR (top, green), DEPT45 $^{13}$C NMR (middle, red), and $^{13}$C NMR (bottom, blue) spectra of **4**. b) Expanded spectra with labels.

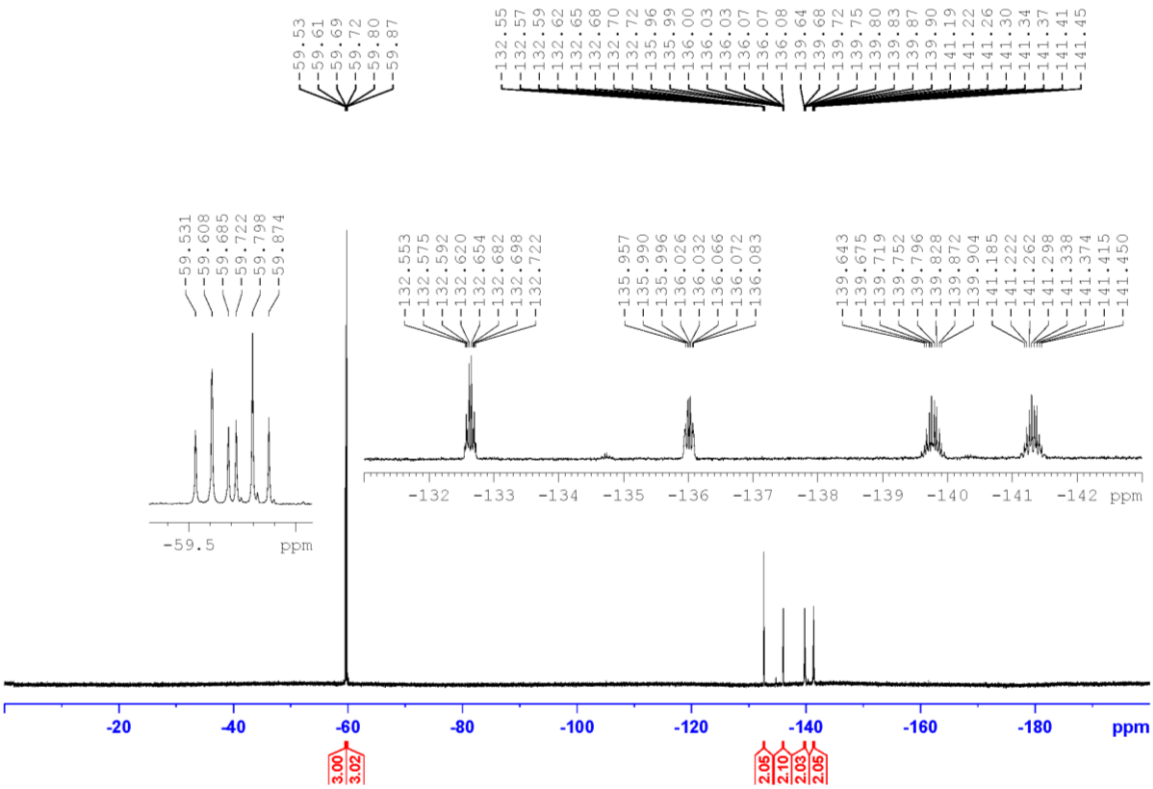



**Figure S12.** Proton decoupled $^{19}F$ NMR spectra ($^{19}F\{^{1}H\}$) of **4**.

**$^{1}$H, $^{13}$C, and $^{19}$F NMR spectra of 6a**

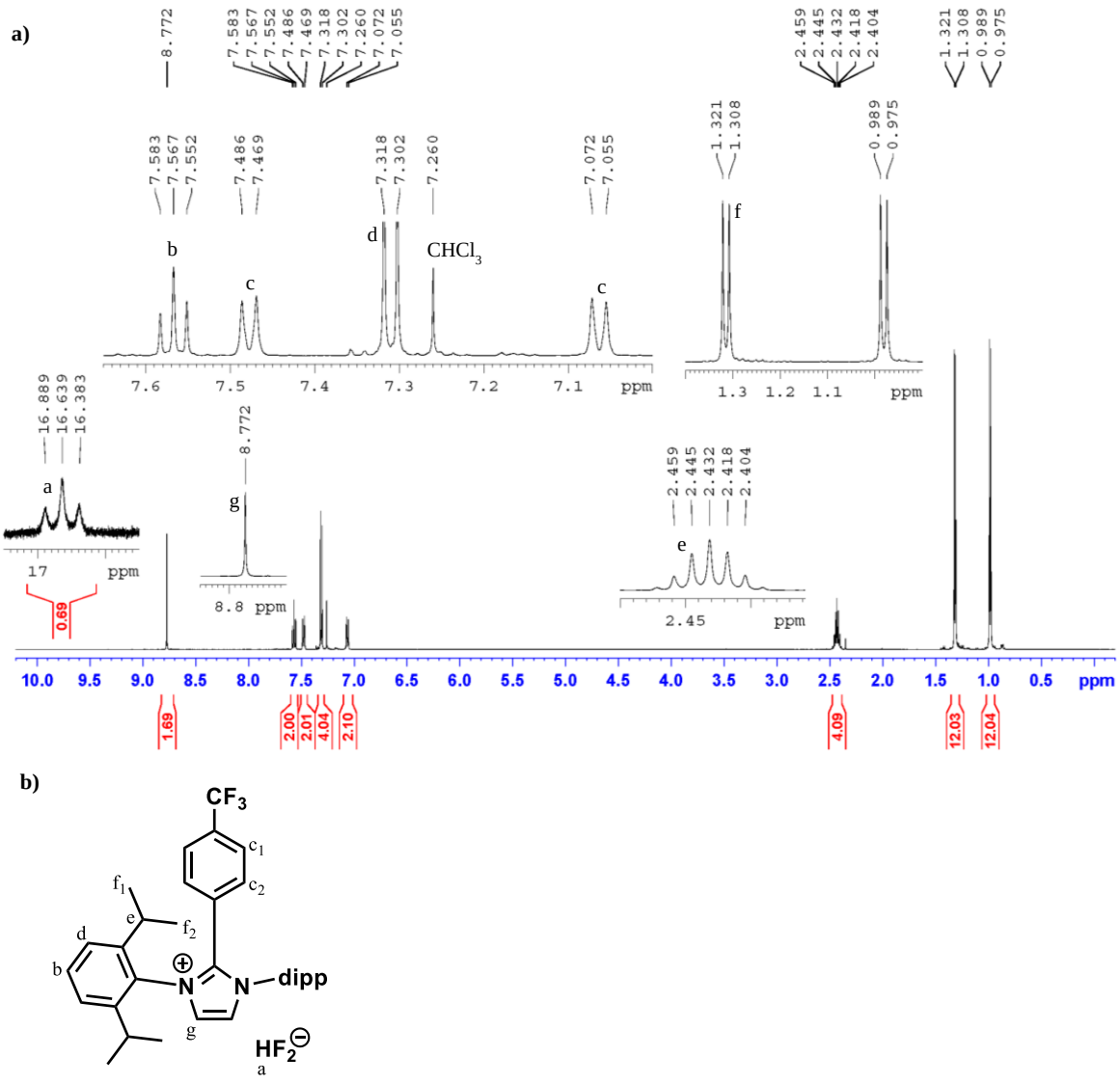



**Figure S13.** a) $^{1}$H NMR spectrum and b) assignment of the signals for the compound **6a**.

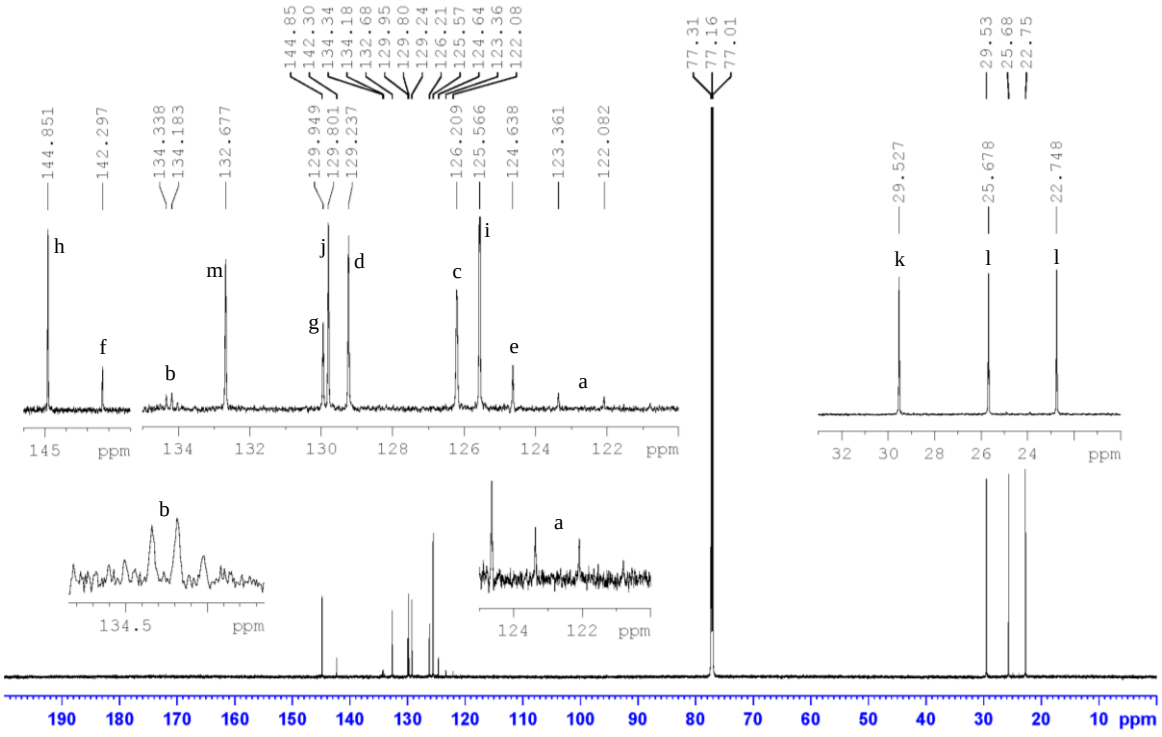



**Figure S14.** Proton decoupled $^{13}C$ NMR spectrum ($^{13}C\{^{1}H\}$) of **6a**.

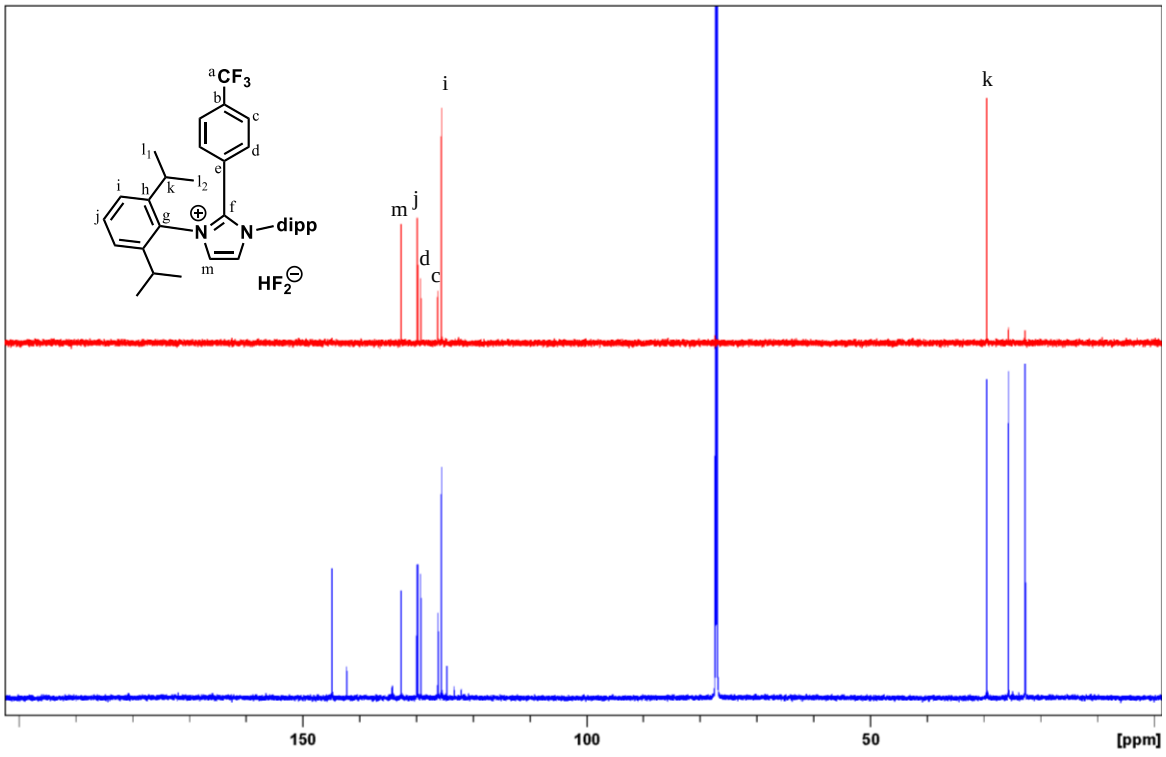



**Figure S15.** DEPT90 $^{13}C$ NMR (top, red) and $^{13}C$ NMR (bottom, blue) spectra of **6a**.

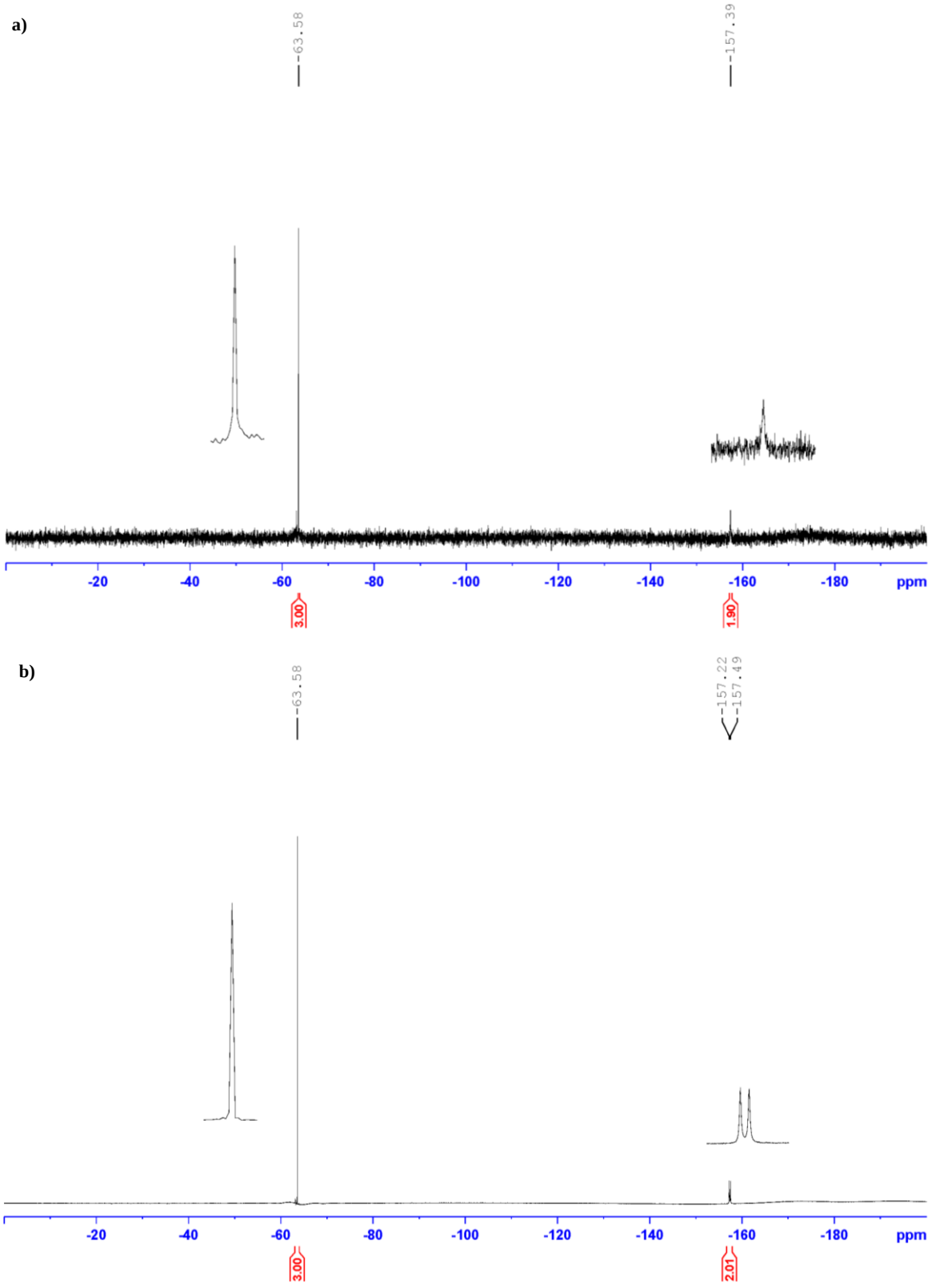



**Figure S16.** a) Proton decoupled $^{19}F$ NMR spectra ($^{19}F\{^{1}H\}$) and b) proton coupled $^{19}F$ NMR spectra ($^{19}F$) for the compound **6a**.

**$^{1}$H, $^{13}$C, and $^{19}$F NMR spectra of 6b**

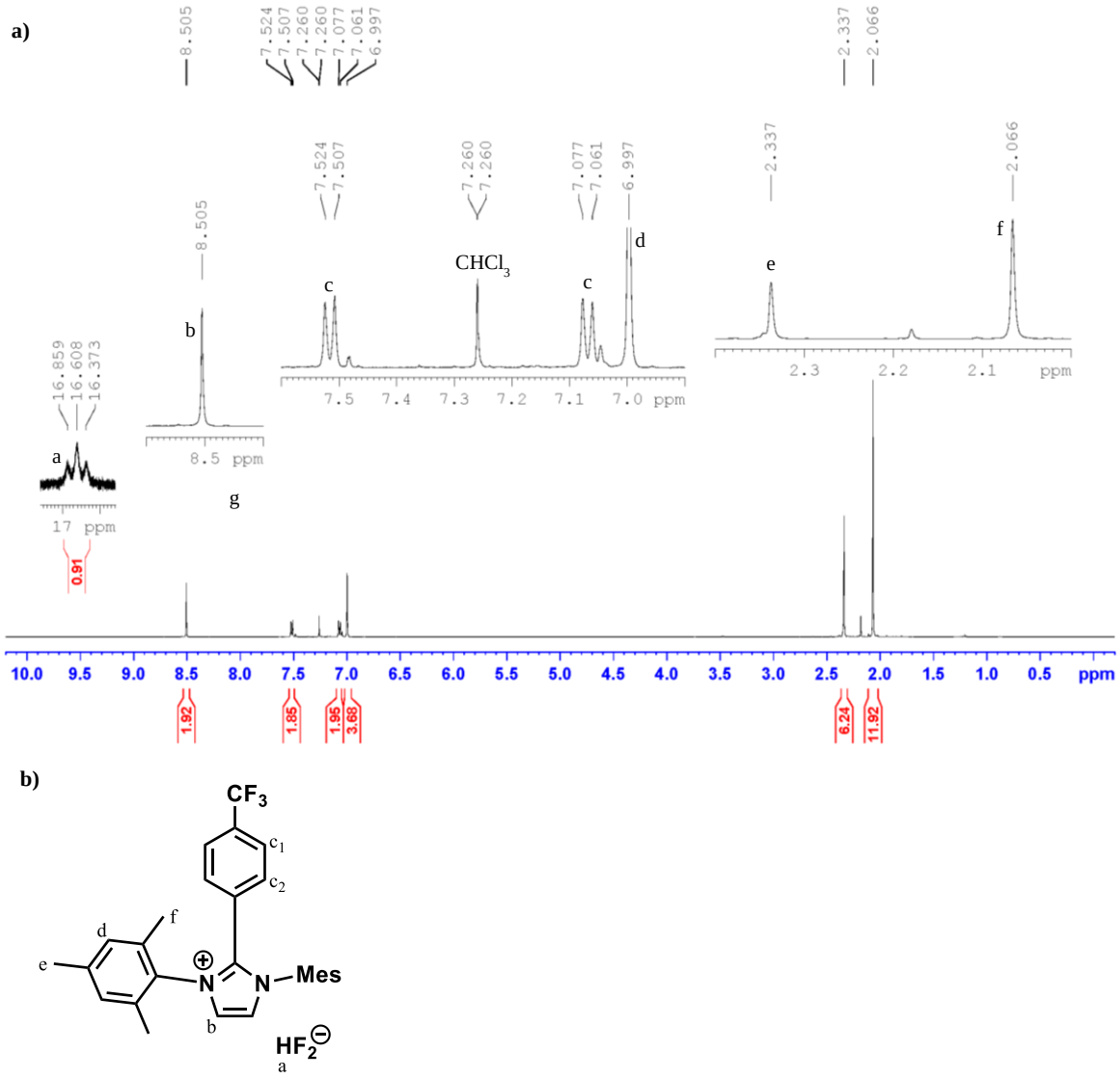



**Figure S17.** a) $^{1}$H NMR spectrum and b) assignment of the signals for the compound **6b**.

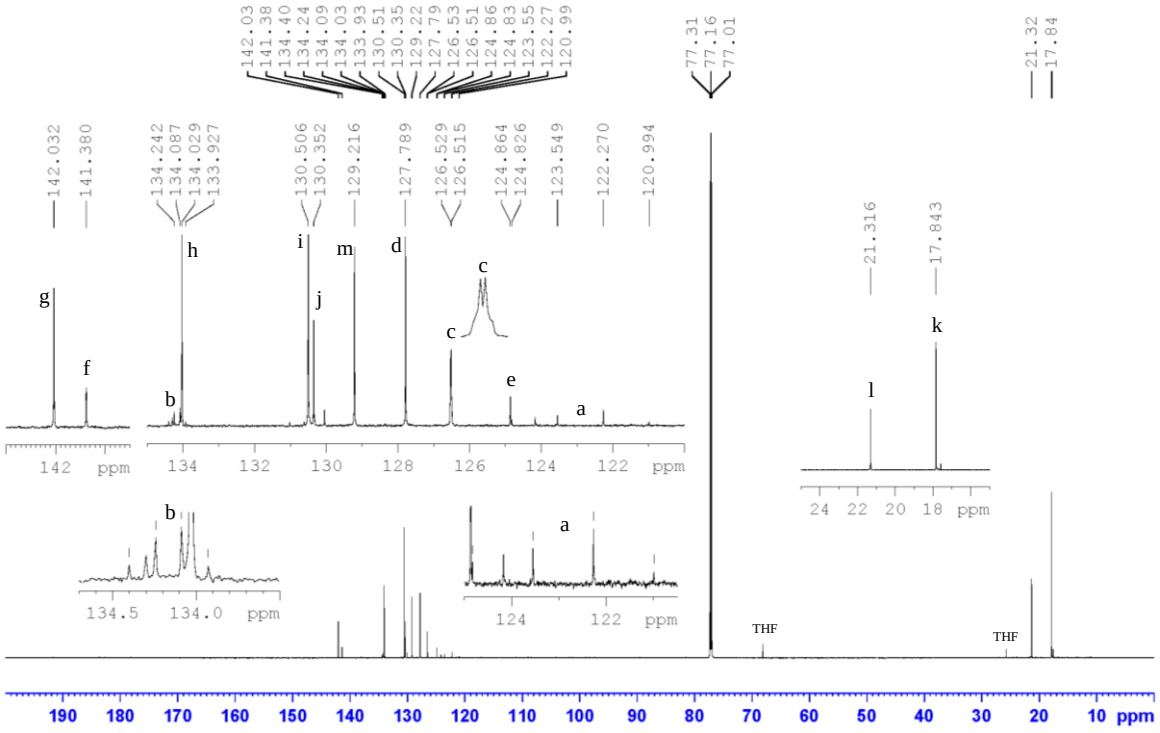



**Figure S18.** Proton decoupled $^{13}C$ NMR spectrum ($^{13}C\{^{1}H\}$) of **6b**.

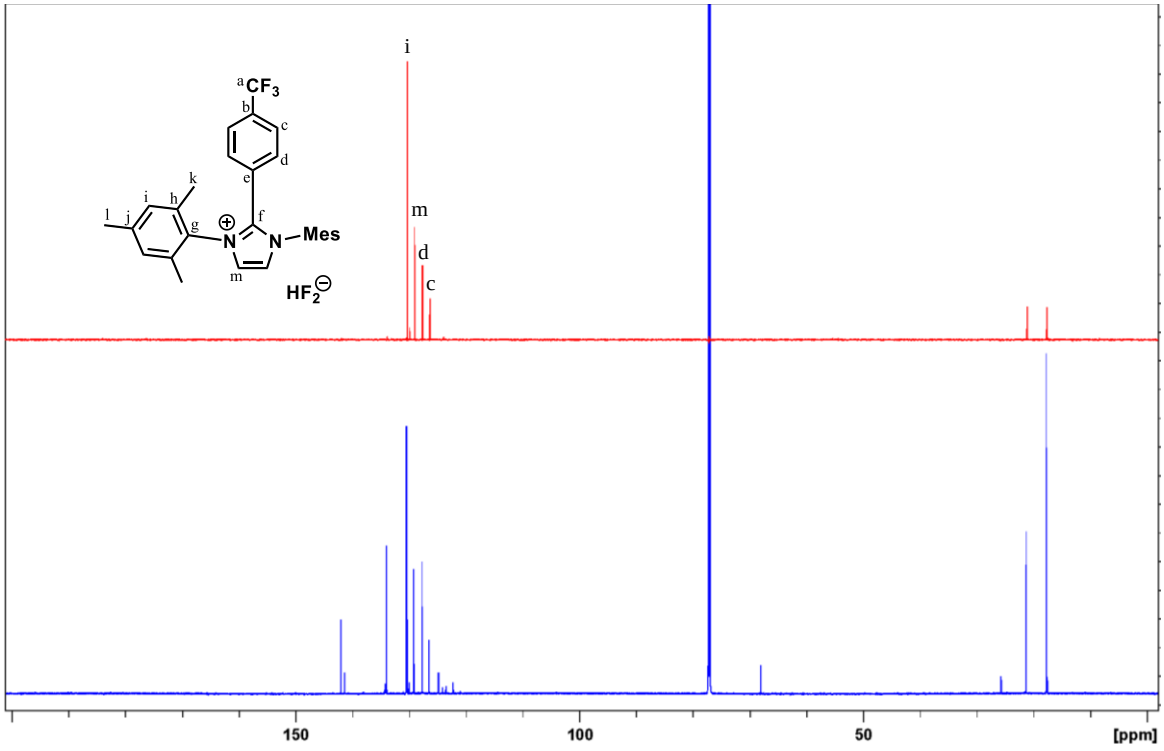



**Figure S19.** DEPT90 $^{13}C$ NMR (top, red) and $^{13}C$ NMR (bottom, blue) spectra of **6b**.

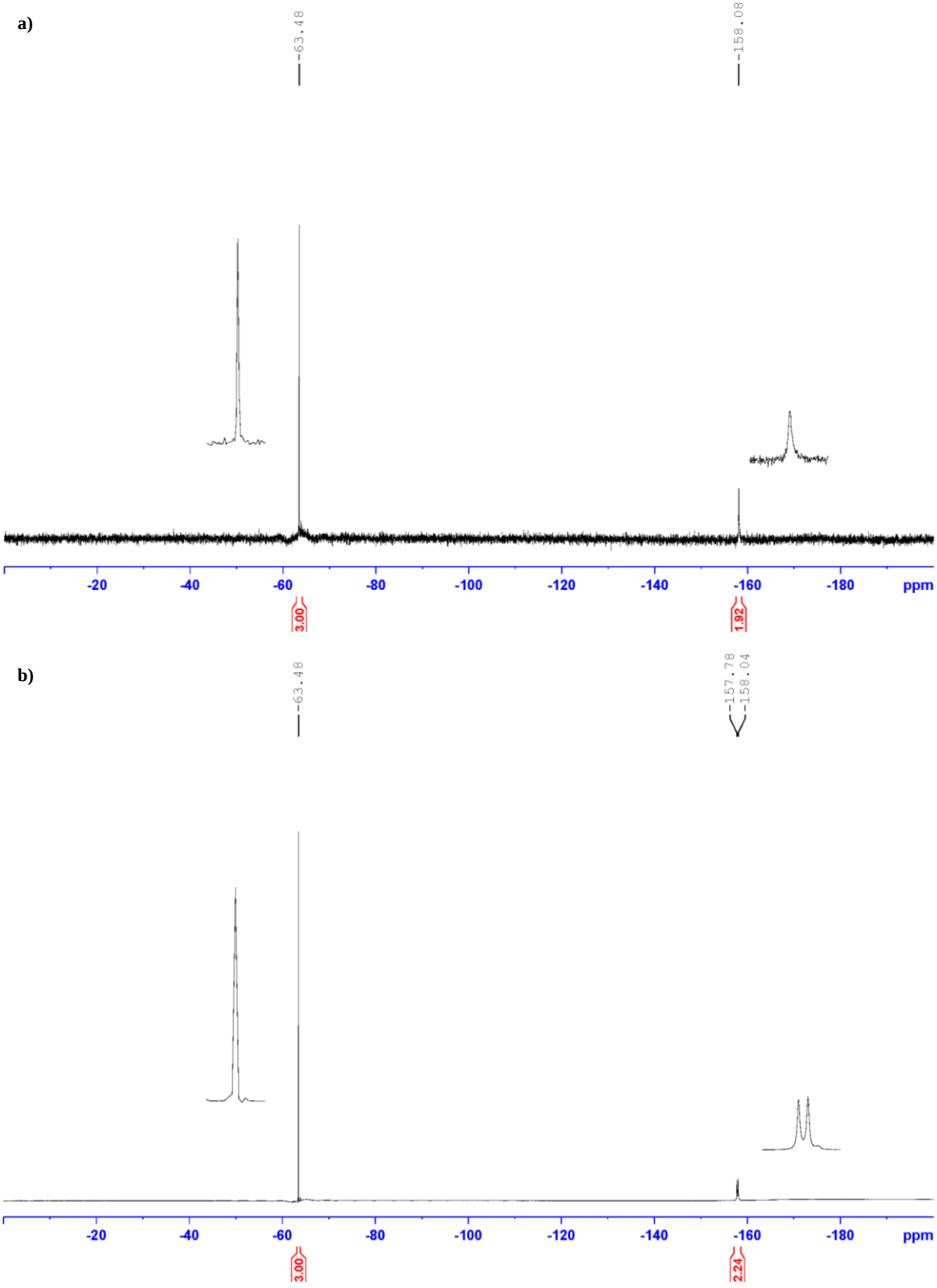



**Figure S20.** a) Proton decoupled $^{19}F$ NMR spectra ($^{19}F\{^{1}H\}$) and b) proton coupled $^{19}F$ NMR spectra ($^{19}F$) for the compound **6b**.

## X-ray Crystallographic Analysis

CCDC 1484680-1484682 contains the supplementary crystallographic data for **2**, **3**, and **6a**, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

**X-ray crystal structure determination of 2**

A green crystal (0.55 × 0.55 × 0.50 $mm^3$) was picked up with paraton oil and mounted on a Bruker Venture CMOS diffractometer equipped with a graphite-monochromated Mo Kα ($\lambda$= 0.71073 Å) radiation source at room temperature. The data were corrected for Lorentz and polarization effects (SAINT), and multi-scan absorption corrections based on equivalent reflections were applied (SADABS). The structure was solved by direct methods and refined by full-matrix least-squares on $F^2$ (SHELXTL). All the non-hydrogen atoms were refined anisotropically and hydrogen atoms were added to their ideal positions. Solvent mask[3] was used to exclude solvent molecules during the refinement (Grid = 0.25 Å, Solvent R = 1.2 Å).

**Table S1. Crystal data and structure refinement for 2.**

| | | |
|---|---|---|
| Identification code | p21c_a | |
| Empirical formula | C41 H36 F16 N2 | |
| Formula weight | 860.72 | |
| Temperature | 100.0 K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/c$ | |
| Unit cell dimensions | $a$ = 12.7034(7) Å | $\alpha$ = 90°. |
| | $b$ = 15.8896(10) Å | $\beta$ = 94.795(2)°. |
| | $c$ = 29.1048(19) Å | $\gamma$ = 90°. |
| Volume | 5854.3(6) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 0.977 Mg/m$^3$ | |
| Absorption coefficient | 0.093 mm$^{-1}$ | |
| F(000) | 1760 | |
| Crystal size | 0.55 x 0.55 x 0.5 mm$^3$ | |
| Theta range for data collection | 2.057 to 25.727°. | |
| Index ranges | -15<=h<=15, -19<=k<=19, -35<=l<=35 | |
| Reflections collected | 89209 | |
| Independent reflections | 11136 [R(int) = 0.0612] | |
| Completeness to theta = 25.242° | 99.7 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7453 and 0.6928 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 11136 / 127 / 589 | |
| Goodness-of-fit on $F^2$ | 1.058 | |
| Final R indices [I>2sigma(I)] | $R_1$ = 0.0890, $wR_2$ = 0.2799 | |
| R indices (all data) | $R_1$ = 0.1075, $wR_2$ = 0.2909 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.472 and -0.572 e.Å$^{-3}$ | |

**Table S2. Atomic coordinates ( × $10^4$) and equivalent isotropic displacement parameters ($Å^2$ × $10^3$) for 2. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| F(1) | 8964(2) | 4438(1) | 6628(1) | 30(1) |
| F(2) | 10556(2) | 3382(2) | 6686(1) | 39(1) |
| F(3) | 6559(2) | 2209(1) | 6343(1) | 33(1) |
| F(4) | 8159(2) | 1130(1) | 6363(1) | 42(1) |
| F(5A) | 10254(3) | 1138(2) | 6140(1) | 64(1) |
| F(5B) | 9967(16) | 734(13) | 6558(9) | 60(5) |
| F(6) | 11243(2) | 1884(2) | 6574(1) | 67(1) |
| F(7A) | 10199(2) | 1030(2) | 6870(1) | 52(1) |
| F(7B) | 10697(15) | 1614(12) | 7072(6) | 53(4) |
| F(8) | 3514(2) | 4758(2) | 6075(1) | 36(1) |
| F(9) | 1740(2) | 5260(2) | 6388(1) | 55(1) |
| F(10) | 5312(2) | 5223(2) | 7536(1) | 36(1) |
| F(11) | 3517(2) | 5711(2) | 7861(1) | 48(1) |
| F(12A) | 1374(3) | 5196(3) | 7712(2) | 68(1) |
| F(12B) | 1181(7) | 6566(6) | 6958(3) | 56(2) |
| F(13A) | 1654(4) | 6499(3) | 7553(2) | 43(1) |
| F(13B) | 866(12) | 5339(9) | 7277(6) | 72(4) |
| F(14A) | 719(3) | 5676(4) | 7086(2) | 65(1) |
| F(14B) | 1642(18) | 6247(13) | 7667(8) | 93(7) |
| F(15) | 3133(3) | 6697(2) | 6145(1) | 76(1) |
| F(16) | 4783(2) | 6589(2) | 5994(1) | 56(1) |
| N(1) | 6102(2) | 4059(2) | 6751(1) | 17(1) |
| N(2) | 6667(2) | 4547(2) | 6115(1) | 19(1) |
| C(1) | 6839(2) | 3972(2) | 6452(1) | 17(1) |
| C(2) | 5441(2) | 4716(2) | 6595(1) | 19(1) |
| C(3) | 5801(3) | 5015(2) | 6202(1) | 21(1) |
| C(4) | 5999(3) | 3512(2) | 7152(1) | 20(1) |
| C(5) | 4287(3) | 2863(2) | 6735(1) | 26(1) |
| C(6) | 5168(3) | 2930(2) | 7130(1) | 23(1) |
| C(7) | 6735(3) | 3591(2) | 7544(1) | 24(1) |
| C(8) | 7618(3) | 4232(3) | 7590(1) | 32(1) |
| C(9) | 5107(3) | 2393(2) | 7507(1) | 35(1) |
| C(10) | 6622(3) | 3045(3) | 7901(1) | 34(1) |
| C(11) | 3234(3) | 3104(3) | 6915(1) | 35(1) |
| C(12) | 4204(3) | 1975(3) | 6531(2) | 38(1) |
| C(13) | 5831(3) | 2447(3) | 7889(1) | 36(1) |
| C(14) | 7507(3) | 4819(3) | 8002(2) | 45(1) |
| C(15) | 8703(3) | 3788(3) | 7668(2) | 46(1) |
| C(16) | 7146(3) | 4530(2) | 5674(1) | 22(1) |
| C(17) | 7923(3) | 5128(2) | 5598(1) | 26(1) |
| C(18) | 8231(3) | 5837(2) | 5929(1) | 28(1) |
| C(19) | 6751(3) | 3947(2) | 5345(1) | 29(1) |
| C(20) | 8348(3) | 5089(3) | 5168(1) | 35(1) |
| C(21) | 5819(3) | 3375(3) | 5415(1) | 36(1) |
| C(22) | 7196(3) | 3959(3) | 4924(1) | 37(1) |
| C(23) | 7677(3) | 6651(2) | 5758(2) | 36(1) |
| C(24) | 7979(3) | 4504(3) | 4840(1) | 41(1) |
| C(25) | 9442(3) | 5974(3) | 5985(2) | 38(1) |
| C(26) | 4812(4) | 3741(4) | 5173(2) | 54(1) |
| C(27) | 6007(5) | 2467(3) | 5250(2) | 62(2) |
| C(28) | 4476(3) | 4977(2) | 6794(1) | 25(1) |
| C(29) | 4428(3) | 5224(2) | 7249(1) | 28(1) |
| C(30) | 3498(3) | 5475(3) | 7420(1) | 37(1) |
| C(31) | 3542(3) | 5008(2) | 6515(1) | 30(1) |

| | | | | |
|---|---|---|---|---|
| C(32) | 2568(3) | 5506(3) | 7135(2) | 41(1) |
| C(33) | 2611(3) | 5269(3) | 6680(2) | 38(1) |
| C(34) | 1551(4) | 5760(4) | 7332(2) | 63(2) |
| C(35) | 7722(3) | 3356(2) | 6478(1) | 21(1) |
| C(36) | 7549(3) | 2507(2) | 6417(1) | 24(1) |
| C(37) | 8762(3) | 3625(2) | 6555(1) | 24(1) |
| C(38) | 9588(3) | 3062(2) | 6580(1) | 29(1) |
| C(39) | 9424(3) | 2214(3) | 6516(1) | 32(1) |
| C(40) | 8381(3) | 1941(2) | 6433(1) | 29(1) |
| C(41) | 10299(3) | 1572(3) | 6541(2) | 43(1) |

**Table S3. Bond lengths [Å] and angles [°] for 2.**

| | | | |
|---|---|---|---|
| F(1)-C(37) | 1.331(4) | C(11)-H(11A) | 0.9800 |
| F(2)-C(38) | 1.342(4) | C(11)-H(11B) | 0.9800 |
| F(3)-C(36) | 1.344(4) | C(11)-H(11C) | 0.9800 |
| F(4)-C(40) | 1.331(4) | C(12)-H(12A) | 0.9800 |
| F(5A)-F(5B) | 1.45(2) | C(12)-H(12B) | 0.9800 |
| F(5A)-C(41) | 1.354(6) | C(12)-H(12C) | 0.9800 |
| F(5B)-F(7A) | 1.04(2) | C(13)-H(13) | 0.9500 |
| F(5B)-C(41) | 1.40(2) | C(14)-H(14A) | 0.9800 |
| F(6)-F(7B) | 1.71(2) | C(14)-H(14B) | 0.9800 |
| F(6)-C(41) | 1.293(5) | C(14)-H(14C) | 0.9800 |
| F(7A)-F(7B) | 1.24(2) | C(15)-H(15A) | 0.9800 |
| F(7A)-C(41) | 1.302(5) | C(15)-H(15B) | 0.9800 |
| F(7B)-C(41) | 1.587(19) | C(15)-H(15C) | 0.9800 |
| F(8)-C(31) | 1.337(4) | C(16)-C(17) | 1.401(5) |
| F(9)-C(33) | 1.336(4) | C(16)-C(19) | 1.394(5) |
| F(10)-C(29) | 1.344(4) | C(17)-C(18) | 1.510(5) |
| F(11)-C(30) | 1.337(5) | C(17)-C(20) | 1.407(5) |
| F(12A)-F(13B) | 1.391(17) | C(18)-H(18) | 1.0000 |
| F(12A)-F(14B) | 1.71(2) | C(18)-C(23) | 1.535(5) |
| F(12A)-C(34) | 1.456(8) | C(18)-C(25) | 1.549(5) |
| F(12B)-F(14A) | 1.587(13) | C(19)-C(21) | 1.520(5) |
| F(12B)-C(34) | 1.720(13) | C(19)-C(22) | 1.392(5) |
| F(13A)-F(14B) | 0.52(2) | C(20)-H(20) | 0.9500 |
| F(13A)-C(34) | 1.340(8) | C(20)-C(24) | 1.385(6) |
| F(13B)-F(14A) | 0.784(13) | C(21)-H(21) | 1.0000 |
| F(13B)-C(34) | 1.098(15) | C(21)-C(26) | 1.523(6) |
| F(14A)-C(34) | 1.233(7) | C(21)-C(27) | 1.545(7) |
| F(14B)-C(34) | 1.24(2) | C(22)-H(22) | 0.9500 |
| F(15)-H(15) | 1.110(12) | C(22)-C(24) | 1.358(6) |
| F(16)-H(15) | 1.096(12) | C(23)-H(23A) | 0.9800 |
| N(1)-C(1) | 1.336(4) | C(23)-H(23B) | 0.9800 |
| N(1)-C(2) | 1.391(4) | C(23)-H(23C) | 0.9800 |
| N(1)-C(4) | 1.471(4) | C(24)-H(24) | 0.9500 |
| N(2)-C(1) | 1.344(4) | C(25)-H(25A) | 0.9800 |
| N(2)-C(3) | 1.368(4) | C(25)-H(25B) | 0.9800 |
| N(2)-C(16) | 1.468(4) | C(25)-H(25C) | 0.9800 |
| C(1)-C(35) | 1.485(4) | C(26)-H(26A) | 0.9800 |
| C(2)-C(3) | 1.353(5) | C(26)-H(26B) | 0.9800 |
| C(2)-C(28) | 1.460(5) | C(26)-H(26C) | 0.9800 |
| C(3)-H(3) | 0.9500 | C(27)-H(27A) | 0.9800 |
| C(4)-C(6) | 1.401(5) | C(27)-H(27B) | 0.9800 |
| C(4)-C(7) | 1.419(5) | C(27)-H(27C) | 0.9800 |
| C(5)-H(5) | 1.0000 | C(28)-C(29) | 1.387(5) |
| C(5)-C(6) | 1.540(5) | C(28)-C(31) | 1.381(5) |
| C(5)-C(11) | 1.525(5) | C(29)-C(30) | 1.379(5) |
| C(5)-C(12) | 1.530(5) | C(30)-C(32) | 1.385(6) |
| C(6)-C(9) | 1.396(5) | C(31)-C(33) | 1.377(5) |
| C(7)-C(8) | 1.513(5) | C(32)-C(33) | 1.384(6) |
| C(7)-C(10) | 1.371(5) | C(32)-C(34) | 1.510(6) |
| C(8)-H(8) | 1.0000 | C(35)-C(36) | 1.376(5) |
| C(8)-C(14) | 1.535(6) | C(35)-C(37) | 1.389(5) |
| C(8)-C(15) | 1.549(6) | C(36)-C(40) | 1.386(5) |
| C(9)-H(9) | 0.9500 | C(37)-C(38) | 1.376(5) |
| C(9)-C(13) | 1.385(6) | C(38)-C(39) | 1.373(6) |
| C(10)-H(10) | 0.9500 | C(39)-C(40) | 1.395(5) |
| C(10)-C(13) | 1.381(6) | C(39)-C(41) | 1.507(5) |

| | | | |
|---|---|---|---|
| C(41)-F(5A)-F(5B) | 59.7(9) | C(7)-C(8)-C(15) | 110.5(3) |
| F(7A)-F(5B)-F(5A) | 117.3(18) | C(14)-C(8)-H(8) | 109.2 |
| F(7A)-F(5B)-C(41) | 62.5(12) | C(14)-C(8)-C(15) | 107.5(3) |
| C(41)-F(5B)-F(5A) | 56.7(9) | C(15)-C(8)-H(8) | 109.2 |
| C(41)-F(6)-F(7B) | 61.8(7) | C(6)-C(9)-H(9) | 119.5 |
| F(5B)-F(7A)-F(7B) | 147.6(16) | C(13)-C(9)-C(6) | 121.1(4) |
| F(5B)-F(7A)-C(41) | 72.3(13) | C(13)-C(9)-H(9) | 119.5 |
| F(7B)-F(7A)-C(41) | 77.1(9) | C(7)-C(10)-H(10) | 118.7 |
| F(7A)-F(7B)-F(6) | 90.7(11) | C(7)-C(10)-C(13) | 122.6(3) |
| F(7A)-F(7B)-C(41) | 53.1(8) | C(13)-C(10)-H(10) | 118.7 |
| C(41)-F(7B)-F(6) | 45.9(5) | C(5)-C(11)-H(11A) | 109.5 |
| F(13B)-F(12A)-F(14B) | 81.5(10) | C(5)-C(11)-H(11B) | 109.5 |
| F(13B)-F(12A)-C(34) | 45.3(6) | C(5)-C(11)-H(11C) | 109.5 |
| C(34)-F(12A)-F(14B) | 45.4(8) | H(11A)-C(11)-H(11B) | 109.5 |
| F(14A)-F(12B)-C(34) | 43.6(4) | H(11A)-C(11)-H(11C) | 109.5 |
| F(14B)-F(13A)-C(34) | 68(3) | H(11B)-C(11)-H(11C) | 109.5 |
| F(14A)-F(13B)-F(12A) | 145.4(18) | C(5)-C(12)-H(12A) | 109.5 |
| F(14A)-F(13B)-C(34) | 80.0(13) | C(5)-C(12)-H(12B) | 109.5 |
| C(34)-F(13B)-F(12A) | 70.5(10) | C(5)-C(12)-H(12C) | 109.5 |
| F(13B)-F(14A)-F(12B) | 134.7(14) | H(12A)-C(12)-H(12B) | 109.5 |
| F(13B)-F(14A)-C(34) | 61.3(12) | H(12A)-C(12)-H(12C) | 109.5 |
| C(34)-F(14A)-F(12B) | 73.9(6) | H(12B)-C(12)-H(12C) | 109.5 |
| F(13A)-F(14B)-F(12A) | 144(4) | C(9)-C(13)-H(13) | 120.1 |
| F(13A)-F(14B)-C(34) | 89(3) | C(10)-C(13)-C(9) | 119.7(3) |
| C(34)-F(14B)-F(12A) | 56.4(9) | C(10)-C(13)-H(13) | 120.1 |
| C(1)-N(1)-C(2) | 107.6(3) | C(8)-C(14)-H(14A) | 109.5 |
| C(1)-N(1)-C(4) | 124.7(3) | C(8)-C(14)-H(14B) | 109.5 |
| C(2)-N(1)-C(4) | 127.6(3) | C(8)-C(14)-H(14C) | 109.5 |
| C(1)-N(2)-C(3) | 108.6(3) | H(14A)-C(14)-H(14B) | 109.5 |
| C(1)-N(2)-C(16) | 124.9(3) | H(14A)-C(14)-H(14C) | 109.5 |
| C(3)-N(2)-C(16) | 124.7(3) | H(14B)-C(14)-H(14C) | 109.5 |
| N(1)-C(1)-N(2) | 108.9(3) | C(8)-C(15)-H(15A) | 109.5 |
| N(1)-C(1)-C(35) | 127.0(3) | C(8)-C(15)-H(15B) | 109.5 |
| N(2)-C(1)-C(35) | 124.1(3) | C(8)-C(15)-H(15C) | 109.5 |
| N(1)-C(2)-C(28) | 126.0(3) | H(15A)-C(15)-H(15B) | 109.5 |
| C(3)-C(2)-N(1) | 107.6(3) | H(15A)-C(15)-H(15C) | 109.5 |
| C(3)-C(2)-C(28) | 126.1(3) | H(15B)-C(15)-H(15C) | 109.5 |
| N(2)-C(3)-H(3) | 126.3 | C(17)-C(16)-N(2) | 118.3(3) |
| C(2)-C(3)-N(2) | 107.4(3) | C(19)-C(16)-N(2) | 117.4(3) |
| C(2)-C(3)-H(3) | 126.3 | C(19)-C(16)-C(17) | 124.2(3) |
| C(6)-C(4)-N(1) | 118.1(3) | C(16)-C(17)-C(18) | 123.7(3) |
| C(6)-C(4)-C(7) | 122.6(3) | C(16)-C(17)-C(20) | 115.9(3) |
| C(7)-C(4)-N(1) | 119.3(3) | C(20)-C(17)-C(18) | 120.1(3) |
| C(6)-C(5)-H(5) | 108.7 | C(17)-C(18)-H(18) | 108.4 |
| C(11)-C(5)-H(5) | 108.7 | C(17)-C(18)-C(23) | 109.6(3) |
| C(11)-C(5)-C(6) | 109.2(3) | C(17)-C(18)-C(25) | 112.0(3) |
| C(11)-C(5)-C(12) | 109.4(3) | C(23)-C(18)-H(18) | 108.4 |
| C(12)-C(5)-H(5) | 108.7 | C(23)-C(18)-C(25) | 109.8(3) |
| C(12)-C(5)-C(6) | 112.0(3) | C(25)-C(18)-H(18) | 108.4 |
| C(4)-C(6)-C(5) | 125.3(3) | C(16)-C(19)-C(21) | 123.1(3) |
| C(9)-C(6)-C(4) | 117.3(3) | C(22)-C(19)-C(16) | 116.4(4) |
| C(9)-C(6)-C(5) | 117.4(3) | C(22)-C(19)-C(21) | 120.2(3) |
| C(4)-C(7)-C(8) | 124.4(3) | C(17)-C(20)-H(20) | 119.6 |
| C(10)-C(7)-C(4) | 116.7(3) | C(24)-C(20)-C(17) | 120.7(4) |
| C(10)-C(7)-C(8) | 118.9(3) | C(24)-C(20)-H(20) | 119.6 |
| C(7)-C(8)-H(8) | 109.2 | C(19)-C(21)-H(21) | 107.9 |
| C(7)-C(8)-C(14) | 111.3(3) | C(19)-C(21)-C(26) | 110.1(3) |

| | | | |
|---|---|---|---|
| C(19)-C(21)-C(27) | 112.0(4) | F(12A)-C(34)-C(32) | 108.3(5) |
| C(26)-C(21)-H(21) | 107.9 | F(13A)-C(34)-F(12A) | 100.9(5) |
| C(26)-C(21)-C(27) | 111.0(4) | F(13A)-C(34)-F(12B) | 70.2(5) |
| C(27)-C(21)-H(21) | 107.9 | F(13A)-C(34)-C(32) | 111.3(4) |
| C(19)-C(22)-H(22) | 119.1 | F(13B)-C(34)-F(12A) | 64.2(10) |
| C(24)-C(22)-C(19) | 121.8(4) | F(13B)-C(34)-F(12B) | 101.0(10) |
| C(24)-C(22)-H(22) | 119.1 | F(13B)-C(34)-F(13A) | 130.4(9) |
| C(18)-C(23)-H(23A) | 109.5 | F(13B)-C(34)-F(14A) | 38.7(7) |
| C(18)-C(23)-H(23B) | 109.5 | F(13B)-C(34)-F(14B) | 120.9(14) |
| C(18)-C(23)-H(23C) | 109.5 | F(13B)-C(34)-C(32) | 118.3(9) |
| H(23A)-C(23)-H(23B) | 109.5 | F(14A)-C(34)-F(12A) | 101.3(6) |
| H(23A)-C(23)-H(23C) | 109.5 | F(14A)-C(34)-F(12B) | 62.5(5) |
| H(23B)-C(23)-H(23C) | 109.5 | F(14A)-C(34)-F(13A) | 114.8(6) |
| C(20)-C(24)-H(24) | 119.5 | F(14A)-C(34)-F(14B) | 122.9(12) |
| C(22)-C(24)-C(20) | 120.9(4) | F(14A)-C(34)-C(32) | 118.0(5) |
| C(22)-C(24)-H(24) | 119.5 | F(14B)-C(34)-F(12A) | 78.2(10) |
| C(18)-C(25)-H(25A) | 109.5 | F(14B)-C(34)-F(12B) | 92.1(11) |
| C(18)-C(25)-H(25B) | 109.5 | F(14B)-C(34)-F(13A) | 23.0(10) |
| C(18)-C(25)-H(25C) | 109.5 | F(14B)-C(34)-C(32) | 115.9(11) |
| H(25A)-C(25)-H(25B) | 109.5 | C(32)-C(34)-F(12B) | 99.0(5) |
| H(25A)-C(25)-H(25C) | 109.5 | C(36)-C(35)-C(1) | 121.8(3) |
| H(25B)-C(25)-H(25C) | 109.5 | C(36)-C(35)-C(37) | 117.5(3) |
| C(21)-C(26)-H(26A) | 109.5 | C(37)-C(35)-C(1) | 120.7(3) |
| C(21)-C(26)-H(26B) | 109.5 | F(3)-C(36)-C(35) | 120.2(3) |
| C(21)-C(26)-H(26C) | 109.5 | F(3)-C(36)-C(40) | 118.6(3) |
| H(26A)-C(26)-H(26B) | 109.5 | C(35)-C(36)-C(40) | 121.2(3) |
| H(26A)-C(26)-H(26C) | 109.5 | F(1)-C(37)-C(35) | 119.5(3) |
| H(26B)-C(26)-H(26C) | 109.5 | F(1)-C(37)-C(38) | 119.1(3) |
| C(21)-C(27)-H(27A) | 109.5 | C(38)-C(37)-C(35) | 121.3(3) |
| C(21)-C(27)-H(27B) | 109.5 | F(2)-C(38)-C(37) | 116.4(3) |
| C(21)-C(27)-H(27C) | 109.5 | F(2)-C(38)-C(39) | 121.9(3) |
| H(27A)-C(27)-H(27B) | 109.5 | C(39)-C(38)-C(37) | 121.6(3) |
| H(27A)-C(27)-H(27C) | 109.5 | C(38)-C(39)-C(40) | 117.4(3) |
| H(27B)-C(27)-H(27C) | 109.5 | C(38)-C(39)-C(41) | 123.7(4) |
| C(29)-C(28)-C(2) | 124.3(3) | C(40)-C(39)-C(41) | 118.9(4) |
| C(31)-C(28)-C(2) | 119.1(3) | F(4)-C(40)-C(36) | 118.1(3) |
| C(31)-C(28)-C(29) | 116.6(3) | F(4)-C(40)-C(39) | 120.9(3) |
| F(10)-C(29)-C(28) | 119.6(3) | C(36)-C(40)-C(39) | 121.0(3) |
| F(10)-C(29)-C(30) | 118.2(3) | F(5A)-C(41)-F(5B) | 63.5(10) |
| C(30)-C(29)-C(28) | 122.2(3) | F(5A)-C(41)-F(7B) | 148.1(8) |
| F(11)-C(30)-C(29) | 118.7(3) | F(5A)-C(41)-C(39) | 109.0(4) |
| F(11)-C(30)-C(32) | 120.7(3) | F(5B)-C(41)-F(7B) | 94.5(13) |
| C(29)-C(30)-C(32) | 120.6(4) | F(5B)-C(41)-C(39) | 114.9(9) |
| F(8)-C(31)-C(28) | 120.3(3) | F(6)-C(41)-F(5A) | 103.3(4) |
| F(8)-C(31)-C(33) | 117.9(3) | F(6)-C(41)-F(5B) | 130.0(9) |
| C(33)-C(31)-C(28) | 121.7(3) | F(6)-C(41)-F(7A) | 110.3(4) |
| C(30)-C(32)-C(34) | 119.8(4) | F(6)-C(41)-F(7B) | 72.2(8) |
| C(33)-C(32)-C(30) | 117.5(4) | F(6)-C(41)-C(39) | 114.9(4) |
| C(33)-C(32)-C(34) | 122.6(4) | F(7A)-C(41)-F(5A) | 107.3(4) |
| F(9)-C(33)-C(31) | 117.7(4) | F(7A)-C(41)-F(5B) | 45.2(10) |
| F(9)-C(33)-C(32) | 120.9(3) | F(7A)-C(41)-F(7B) | 49.8(7) |
| C(31)-C(33)-C(32) | 121.4(3) | F(7A)-C(41)-C(39) | 111.5(4) |
| F(12A)-C(34)-F(12B) | 152.6(5) | C(39)-C(41)-F(7B) | 101.1(7) |

Symmetry transformations used to generate equivalent atoms:

**Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for 2. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \ldots + 2hka^*b^*U^{12}]$**

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| F(1) | 27(1) | 25(1) | 39(1) | 5(1) | -2(1) | -3(1) |
| F(2) | 19(1) | 49(1) | 50(1) | 6(1) | 2(1) | 0(1) |
| F(3) | 32(1) | 23(1) | 44(1) | -1(1) | 0(1) | -3(1) |
| F(4) | 55(2) | 21(1) | 51(2) | -1(1) | 6(1) | 7(1) |
| F(5A) | 72(2) | 60(2) | 63(2) | -12(2) | 16(2) | 36(2) |
| F(5B) | 60(7) | 54(7) | 68(7) | -6(6) | 7(6) | 11(6) |
| F(6) | 38(1) | 56(2) | 111(2) | 27(2) | 26(2) | 16(1) |
| F(7A) | 44(2) | 51(2) | 63(2) | 34(2) | 19(2) | 21(2) |
| F(7B) | 59(7) | 51(6) | 49(6) | 13(5) | -4(5) | 11(6) |
| F(8) | 29(1) | 51(1) | 28(1) | -9(1) | -6(1) | 9(1) |
| F(9) | 24(1) | 94(2) | 44(2) | -26(1) | -9(1) | 14(1) |
| F(10) | 29(1) | 49(1) | 31(1) | -8(1) | -6(1) | 6(1) |
| F(11) | 38(1) | 74(2) | 32(1) | -21(1) | 4(1) | 7(1) |
| F(12A) | 59(2) | 69(3) | 81(3) | 8(2) | 39(2) | 8(2) |
| F(12B) | 45(4) | 72(5) | 53(4) | -22(4) | 7(3) | 24(4) |
| F(13A) | 40(2) | 38(2) | 55(3) | -9(2) | 21(2) | 11(2) |
| F(13B) | 60(6) | 75(6) | 83(6) | 4(5) | 20(5) | -8(5) |
| F(14A) | 31(2) | 104(4) | 60(3) | -26(3) | 4(2) | 16(2) |
| F(14B) | 85(8) | 101(9) | 95(9) | -7(6) | 12(6) | 8(6) |
| F(15) | 66(2) | 105(3) | 54(2) | -29(2) | -4(2) | 14(2) |
| F(16) | 73(2) | 32(1) | 61(2) | -2(1) | -2(1) | 2(1) |
| N(1) | 17(1) | 18(1) | 16(1) | 1(1) | -1(1) | -1(1) |
| N(2) | 20(1) | 22(1) | 15(1) | 0(1) | 4(1) | -1(1) |
| C(1) | 17(1) | 18(2) | 16(2) | -2(1) | -2(1) | -3(1) |
| C(2) | 17(2) | 21(2) | 19(2) | 2(1) | -3(1) | -2(1) |
| C(3) | 23(2) | 18(2) | 21(2) | 3(1) | -5(1) | 2(1) |
| C(4) | 25(2) | 21(2) | 14(2) | 2(1) | 3(1) | 4(1) |
| C(5) | 24(2) | 32(2) | 21(2) | 2(1) | 1(1) | -6(1) |
| C(6) | 22(2) | 26(2) | 21(2) | 4(1) | 2(1) | 1(1) |
| C(7) | 22(2) | 34(2) | 17(2) | 1(1) | -1(1) | 5(1) |
| C(8) | 29(2) | 42(2) | 22(2) | -2(2) | -5(1) | -6(2) |
| C(9) | 37(2) | 30(2) | 38(2) | 14(2) | 3(2) | -6(2) |
| C(10) | 36(2) | 45(2) | 20(2) | 1(2) | -3(2) | 6(2) |
| C(11) | 22(2) | 44(2) | 38(2) | 5(2) | 2(2) | -5(2) |
| C(12) | 31(2) | 35(2) | 47(2) | -4(2) | -3(2) | -10(2) |
| C(13) | 46(2) | 39(2) | 21(2) | 13(2) | 2(2) | -1(2) |
| C(14) | 39(2) | 53(3) | 41(2) | -9(2) | -13(2) | -4(2) |
| C(15) | 25(2) | 81(3) | 32(2) | 9(2) | -7(2) | -3(2) |
| C(16) | 26(2) | 26(2) | 13(2) | 7(1) | 1(1) | 1(1) |
| C(17) | 23(2) | 31(2) | 22(2) | 8(1) | 2(1) | -2(1) |
| C(18) | 26(2) | 29(2) | 28(2) | 8(2) | 1(1) | -5(1) |
| C(19) | 35(2) | 33(2) | 19(2) | -1(1) | -5(1) | 1(2) |
| C(20) | 33(2) | 41(2) | 32(2) | 11(2) | 10(2) | -6(2) |
| C(21) | 47(2) | 39(2) | 22(2) | -1(2) | -2(2) | -17(2) |
| C(22) | 46(2) | 46(2) | 17(2) | -3(2) | 0(2) | -1(2) |
| C(23) | 40(2) | 30(2) | 40(2) | 7(2) | 2(2) | -2(2) |
| C(24) | 47(2) | 60(3) | 17(2) | 3(2) | 6(2) | 2(2) |
| C(25) | 35(2) | 40(2) | 38(2) | 7(2) | 1(2) | -10(2) |
| C(26) | 42(2) | 74(3) | 43(3) | 9(2) | -8(2) | -19(2) |
| C(27) | 101(4) | 37(2) | 49(3) | -13(2) | 7(3) | -26(3) |
| C(28) | 25(2) | 23(2) | 26(2) | 0(1) | 1(1) | 0(1) |
| C(29) | 25(2) | 34(2) | 26(2) | -3(2) | -4(1) | 1(2) |
| C(30) | 32(2) | 46(2) | 32(2) | -14(2) | 2(2) | 4(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(31) | 30(2) | 33(2) | 26(2) | -9(2) | -1(2) | 2(2) |
| C(32) | 28(2) | 47(2) | 47(2) | -20(2) | -1(2) | 5(2) |
| C(33) | 21(2) | 44(2) | 46(2) | -14(2) | -6(2) | 10(2) |
| C(34) | 31(2) | 91(4) | 66(3) | -46(3) | 2(2) | -3(3) |
| C(35) | 23(2) | 21(2) | 18(2) | 4(1) | 3(1) | 1(1) |
| C(36) | 23(2) | 28(2) | 23(2) | 1(1) | 4(1) | -3(1) |
| C(37) | 24(2) | 26(2) | 20(2) | 5(1) | -1(1) | 2(1) |
| C(38) | 24(2) | 39(2) | 25(2) | 6(2) | 4(1) | 5(2) |
| C(39) | 27(2) | 39(2) | 30(2) | 10(2) | 6(2) | 9(2) |
| C(40) | 38(2) | 26(2) | 25(2) | 2(1) | 6(2) | 6(2) |
| C(41) | 40(2) | 36(2) | 54(3) | 14(2) | 8(2) | 9(2) |

**X-ray crystal structure determination of 3**

A colorless crystal (0.10 × 0.09 × 0.09 $mm^3$) was picked up with paraton oil and mounted on a Bruker Venture CMOS diffractometer equipped with a graphite-monochromated Mo Kα ($\lambda$= 0.71073 Å) radiation source at room temperature. The data were corrected for Lorentz and polarization effects (SAINT), and multi-scan absorption corrections based on equivalent reflections were applied (SADABS). The structure was solved by direct methods and refined by full-matrix least-squares on $F^2$ (SHELXTL). All the non-hydrogen atoms were refined anisotropically and hydrogen atoms were added to their ideal positions.

**Table S5. Crystal data and structure refinement for 3.**

| | | |
|---|---|---|
| Identification code | p21c_a | |
| Empirical formula | C45 H42 Au Cl F14 N2 O | |
| Formula weight | 1125.22 | |
| Temperature | 100 K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/c$ | |
| Unit cell dimensions | $a$ = 15.0816(11) Å | $\alpha$ = 90°. |
| | $b$ = 14.3924(11) Å | $\beta$ = 96.525(3)°. |
| | $c$ = 20.4104(17) Å | $\gamma$ = 90°. |
| Volume | 4401.6(6) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.698 $Mg/m^3$ | |
| Absorption coefficient | 3.500 $mm^{-1}$ | |
| F(000) | 2224 | |
| Crystal size | 0.10 x 0.09 x 0.09 $mm^3$ | |
| Theta range for data collection | 2.133 to 26.754°. | |
| Index ranges | -19<=h<=19, -18<=k<=18, -25<=l<=25 | |
| Reflections collected | 66030 | |
| Independent reflections | 9353 [R(int) = 0.1189] | |
| Completeness to theta = 25.242° | 99.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7454 and 0.6714 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 9353 / 142 / 639 | |
| Goodness-of-fit on $F^2$ | 1.096 | |
| Final R indices [I>2sigma(I)] | $R_1$ = 0.0527, $wR_2$ = 0.0760 | |
| R indices (all data) | $R_1$ = 0.0912, $wR_2$ = 0.0850 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 1.662 and -1.881 e.$Å^{-3}$ | |

**Table S6. Atomic coordinates ( × $10^4$) and equivalent isotropic displacement parameters (Å$^2$ × $10^3$) for 3. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Au(1) | 3148(1) | 3537(1) | 8283(1) | 18(1) |
| Cl(1) | 3186(1) | 4036(1) | 9344(1) | 30(1) |
| N(1) | 3600(3) | 2596(3) | 6399(2) | 15(1) |
| N(2) | 2445(3) | 2962(3) | 6892(2) | 16(1) |
| F(1) | 4584(2) | 1706(2) | 8052(2) | 28(1) |
| F(2) | 6217(3) | 1805(3) | 8657(2) | 43(1) |
| F(3) | 5204(3) | 4158(3) | 6650(2) | 42(1) |
| F(4) | 6831(3) | 4288(3) | 7272(2) | 62(1) |
| F(5) | 8087(3) | 2727(4) | 8082(3) | 80(2) |
| F(6A) | 7648(6) | 3945(7) | 8599(6) | 48(2) |
| F(6B) | 7894(6) | 4034(7) | 8189(6) | 56(3) |
| F(7A) | 7465(7) | 3279(9) | 8959(5) | 65(3) |
| F(7B) | 7635(5) | 2556(7) | 8923(4) | 47(2) |
| F(8) | 2692(2) | 753(2) | 6090(2) | 26(1) |
| F(9) | 1689(2) | -93(3) | 5136(2) | 39(1) |
| F(10) | 374(3) | 2798(3) | 4486(2) | 50(1) |
| F(11) | 1400(2) | 3624(3) | 5445(2) | 34(1) |
| F(12A) | 697(10) | 1210(8) | 3633(6) | 46(3) |
| F(12B) | 821(9) | 757(9) | 3696(7) | 51(3) |
| F(13A) | -269(14) | 1465(16) | 3936(10) | 68(5) |
| F(13B) | -385(5) | 1059(7) | 4184(4) | 62(2) |
| F(14A) | 538(7) | -87(6) | 4196(5) | 69(3) |
| F(14B) | 52(9) | 134(11) | 4395(6) | 58(4) |
| C(1) | 2699(4) | 2622(4) | 6327(3) | 17(1) |
| C(2) | 3174(4) | 3121(4) | 7360(3) | 17(1) |
| C(3) | 3896(4) | 2901(4) | 7034(3) | 15(1) |
| C(4) | 1513(4) | 3129(4) | 6993(3) | 21(1) |
| C(5) | 1421(4) | 1449(5) | 7363(3) | 34(2) |
| C(6) | 1510(5) | 1284(5) | 8106(3) | 42(2) |
| C(7) | 1028(4) | 2391(5) | 7200(3) | 24(2) |
| C(8) | 1174(4) | 4017(5) | 6872(3) | 30(2) |
| C(9) | 1984(5) | 5418(5) | 7324(4) | 46(2) |
| C(10) | 1724(5) | 4839(5) | 6704(4) | 43(2) |
| C(11) | 130(5) | 2570(6) | 7274(3) | 42(2) |
| C(12) | -234(5) | 3431(7) | 7136(4) | 53(2) |
| C(13) | 877(6) | 683(6) | 6994(4) | 55(2) |
| C(14) | 267(5) | 4141(6) | 6944(3) | 43(2) |
| C(15) | 1250(7) | 5467(5) | 6167(4) | 71(3) |
| C(16) | 5324(4) | 2231(5) | 4937(3) | 30(2) |
| C(17) | 4169(4) | 2431(4) | 5871(3) | 18(1) |
| C(18) | 4742(4) | 1668(4) | 5915(3) | 16(1) |
| C(19) | 5320(4) | 1578(4) | 5430(3) | 24(1) |
| C(20) | 4786(4) | 912(4) | 6439(3) | 22(1) |
| C(21) | 4741(4) | 2965(5) | 4902(3) | 29(2) |
| C(22) | 4140(4) | 3098(4) | 5365(3) | 21(1) |
| C(23) | 3481(4) | 3903(4) | 5275(3) | 26(1) |
| C(24) | 5730(4) | 864(5) | 6814(3) | 28(2) |
| C(25) | 4550(4) | -38(4) | 6125(3) | 28(2) |
| C(26) | 2938(5) | 3846(6) | 4595(3) | 46(2) |
| C(27) | 3912(5) | 4859(5) | 5366(4) | 49(2) |
| C(28) | 5448(4) | 3571(5) | 7142(3) | 27(1) |
| C(29) | 6304(4) | 3624(6) | 7465(4) | 39(2) |
| C(30) | 5984(4) | 2416(5) | 8173(3) | 30(2) |

| | | | | |
|---|---|---|---|---|
| C(31) | 6581(4) | 3059(5) | 7989(3) | 32(2) |
| C(32) | 4833(4) | 2930(4) | 7331(3) | 17(1) |
| C(33) | 5122(4) | 2362(4) | 7857(3) | 22(1) |
| C(34) | 7503(5) | 3161(6) | 8352(4) | 45(2) |
| C(35) | 2135(4) | 1263(4) | 5686(3) | 18(1) |
| C(36) | 2107(4) | 2210(4) | 5783(3) | 18(1) |
| C(37) | 944(4) | 2264(5) | 4876(3) | 28(2) |
| C(38) | 1594(4) | 820(5) | 5191(3) | 27(2) |
| C(39) | 1483(4) | 2696(4) | 5374(3) | 24(1) |
| C(40) | 990(4) | 1316(5) | 4772(3) | 32(2) |
| C(41) | 426(5) | 862(6) | 4203(4) | 46(2) |
| C(42) | 7935(7) | 1894(7) | 6090(6) | 88(4) |
| C(43B) | 7893(14) | 3192(14) | 5422(9) | 54(5) |
| C(44) | 8502(9) | 2300(9) | 5623(5) | 95(4) |
| C(45) | 7465(9) | 3395(8) | 5955(5) | 99(4) |
| O(1) | 7568(5) | 2665(6) | 6419(4) | 92(2) |
| C(43A) | 8450(20) | 3280(20) | 5550(14) | 98(9) |

**Table S7. Bond lengths [Å] and angles [°] for 3.**

| | | | |
|---|---|---|---|
| Au(1)-Cl(1) | 2.2762(15) | C(11)-H(11) | 0.9500 |
| Au(1)-C(2) | 1.981(6) | C(11)-C(12) | 1.372(11) |
| N(1)-C(1) | 1.350(7) | C(12)-H(12) | 0.9500 |
| N(1)-C(3) | 1.392(7) | C(12)-C(14) | 1.354(11) |
| N(1)-C(17) | 1.472(7) | C(13)-H(13A) | 0.9800 |
| N(2)-C(1) | 1.349(7) | C(13)-H(13B) | 0.9800 |
| N(2)-C(2) | 1.391(7) | C(13)-H(13C) | 0.9800 |
| N(2)-C(4) | 1.463(7) | C(14)-H(14) | 0.9500 |
| F(1)-C(33) | 1.335(7) | C(15)-H(15A) | 0.9800 |
| F(2)-C(30) | 1.340(8) | C(15)-H(15B) | 0.9800 |
| F(3)-C(28) | 1.331(7) | C(15)-H(15C) | 0.9800 |
| F(4)-C(29) | 1.331(8) | C(16)-H(16) | 0.9500 |
| F(5)-C(34) | 1.257(8) | C(16)-C(19) | 1.378(8) |
| F(6A)-F(6B) | 0.963(12) | C(16)-C(21) | 1.371(9) |
| F(6A)-F(7A) | 1.257(15) | C(17)-C(18) | 1.393(8) |
| F(6A)-C(34) | 1.245(11) | C(17)-C(22) | 1.406(8) |
| F(6B)-C(34) | 1.442(13) | C(18)-C(19) | 1.396(7) |
| F(7A)-F(7B) | 1.077(12) | C(18)-C(20) | 1.523(8) |
| F(7A)-C(34) | 1.259(12) | C(19)-H(19) | 0.9500 |
| F(7B)-C(34) | 1.451(12) | C(20)-H(20) | 1.0000 |
| F(8)-C(35) | 1.328(6) | C(20)-C(24) | 1.540(8) |
| F(9)-C(38) | 1.329(7) | C(20)-C(25) | 1.534(8) |
| F(10)-C(37) | 1.344(7) | C(21)-H(21) | 0.9500 |
| F(11)-C(39) | 1.352(7) | C(21)-C(22) | 1.396(8) |
| F(12A)-F(12B) | 0.686(15) | C(22)-C(23) | 1.524(8) |
| F(12A)-F(13A) | 1.69(3) | C(23)-H(23) | 1.0000 |
| F(12A)-C(41) | 1.371(15) | C(23)-C(26) | 1.532(9) |
| F(12B)-F(14A) | 1.673(17) | C(23)-C(27) | 1.525(9) |
| F(12B)-C(41) | 1.261(15) | C(24)-H(24A) | 0.9800 |
| F(13A)-F(13B) | 0.80(2) | C(24)-H(24B) | 0.9800 |
| F(13A)-C(41) | 1.42(2) | C(24)-H(24C) | 0.9800 |
| F(13B)-F(14B) | 1.526(18) | C(25)-H(25A) | 0.9800 |
| F(13B)-C(41) | 1.252(11) | C(25)-H(25B) | 0.9800 |
| F(14A)-F(14B) | 0.933(14) | C(25)-H(25C) | 0.9800 |
| F(14A)-C(41) | 1.376(12) | C(26)-H(26A) | 0.9800 |
| F(14B)-C(41) | 1.272(15) | C(26)-H(26B) | 0.9800 |
| C(1)-C(36) | 1.468(8) | C(26)-H(26C) | 0.9800 |
| C(2)-C(3) | 1.376(7) | C(27)-H(27A) | 0.9800 |
| C(3)-C(32) | 1.474(7) | C(27)-H(27B) | 0.9800 |
| C(4)-C(7) | 1.382(8) | C(27)-H(27C) | 0.9800 |
| C(4)-C(8) | 1.388(9) | C(28)-C(29) | 1.383(9) |
| C(5)-H(5) | 1.0000 | C(28)-C(32) | 1.394(8) |
| C(5)-C(6) | 1.526(8) | C(29)-C(31) | 1.370(10) |
| C(5)-C(7) | 1.503(10) | C(30)-C(31) | 1.372(9) |
| C(5)-C(13) | 1.522(9) | C(30)-C(33) | 1.386(8) |
| C(6)-H(6A) | 0.9800 | C(31)-C(34) | 1.506(9) |
| C(6)-H(6B) | 0.9800 | C(32)-C(33) | 1.379(8) |
| C(6)-H(6C) | 0.9800 | C(35)-C(36) | 1.379(8) |
| C(7)-C(11) | 1.404(9) | C(35)-C(38) | 1.380(8) |
| C(8)-C(10) | 1.508(10) | C(36)-C(39) | 1.377(8) |
| C(8)-C(14) | 1.403(9) | C(37)-C(39) | 1.375(8) |
| C(9)-H(9A) | 0.9800 | C(37)-C(40) | 1.384(10) |
| C(9)-H(9B) | 0.9800 | C(38)-C(40) | 1.376(9) |
| C(9)-H(9C) | 0.9800 | C(40)-C(41) | 1.509(9) |
| C(9)-C(10) | 1.529(10) | C(42)-H(42A) | 0.9900 |
| C(10)-H(10) | 1.0000 | C(42)-H(42B) | 0.9900 |
| C(10)-C(15) | 1.534(10) | C(42)-C(44) | 1.473(14) |

| | | | |
|---|---|---|---|
| C(42)-O(1) | 1.439(12) | C(44)-H(44A) | 0.9900 |
| C(43B)-H(43A) | 0.9900 | C(44)-H(44B) | 0.9900 |
| C(43B)-H(43B) | 0.9900 | C(45)-H(45A) | 0.9900 |
| C(43B)-C(44) | 1.60(2) | C(45)-H(45B) | 0.9900 |
| C(43B)-C(45) | 1.357(19) | C(45)-O(1) | 1.411(11) |

| | | | |
|---|---|---|---|
| C(2)-Au(1)-Cl(1) | 177.31(17) | C(5)-C(6)-H(6C) | 109.5 |
| C(1)-N(1)-C(3) | 107.8(4) | H(6A)-C(6)-H(6B) | 109.5 |
| C(1)-N(1)-C(17) | 126.0(5) | H(6A)-C(6)-H(6C) | 109.5 |
| C(3)-N(1)-C(17) | 125.4(4) | H(6B)-C(6)-H(6C) | 109.5 |
| C(1)-N(2)-C(2) | 111.5(5) | C(4)-C(7)-C(5) | 123.5(6) |
| C(1)-N(2)-C(4) | 123.5(5) | C(4)-C(7)-C(11) | 116.3(7) |
| C(2)-N(2)-C(4) | 125.0(5) | C(11)-C(7)-C(5) | 120.2(6) |
| F(6B)-F(6A)-F(7A) | 137.8(14) | C(4)-C(8)-C(10) | 124.2(6) |
| F(6B)-F(6A)-C(34) | 80.4(10) | C(4)-C(8)-C(14) | 116.3(7) |
| C(34)-F(6A)-F(7A) | 60.4(8) | C(14)-C(8)-C(10) | 119.5(7) |
| F(6A)-F(6B)-C(34) | 58.4(9) | H(9A)-C(9)-H(9B) | 109.5 |
| F(6A)-F(7A)-C(34) | 59.3(8) | H(9A)-C(9)-H(9C) | 109.5 |
| F(7B)-F(7A)-F(6A) | 128.8(12) | H(9B)-C(9)-H(9C) | 109.5 |
| F(7B)-F(7A)-C(34) | 76.3(9) | C(10)-C(9)-H(9A) | 109.5 |
| F(7A)-F(7B)-C(34) | 57.5(8) | C(10)-C(9)-H(9B) | 109.5 |
| F(12B)-F(12A)-F(13A) | 111(2) | C(10)-C(9)-H(9C) | 109.5 |
| F(12B)-F(12A)-C(41) | 66(2) | C(8)-C(10)-C(9) | 109.6(6) |
| C(41)-F(12A)-F(13A) | 54.2(9) | C(8)-C(10)-H(10) | 108.1 |
| F(12A)-F(12B)-F(14A) | 136(3) | C(8)-C(10)-C(15) | 113.6(7) |
| F(12A)-F(12B)-C(41) | 84(2) | C(9)-C(10)-H(10) | 108.1 |
| C(41)-F(12B)-F(14A) | 53.8(7) | C(9)-C(10)-C(15) | 109.0(6) |
| F(13B)-F(13A)-F(12A) | 109(2) | C(15)-C(10)-H(10) | 108.1 |
| F(13B)-F(13A)-C(41) | 61.3(17) | C(7)-C(11)-H(11) | 119.6 |
| C(41)-F(13A)-F(12A) | 51.5(9) | C(12)-C(11)-C(7) | 120.8(7) |
| F(13A)-F(13B)-F(14B) | 134(2) | C(12)-C(11)-H(11) | 119.6 |
| F(13A)-F(13B)-C(41) | 84.4(19) | C(11)-C(12)-H(12) | 119.4 |
| C(41)-F(13B)-F(14B) | 53.4(7) | C(14)-C(12)-C(11) | 121.2(7) |
| F(14B)-F(14A)-F(12B) | 106.6(14) | C(14)-C(12)-H(12) | 119.4 |
| F(14B)-F(14A)-C(41) | 63.5(11) | C(5)-C(13)-H(13A) | 109.5 |
| C(41)-F(14A)-F(12B) | 47.7(6) | C(5)-C(13)-H(13B) | 109.5 |
| F(14A)-F(14B)-F(13B) | 120.7(16) | C(5)-C(13)-H(13C) | 109.5 |
| F(14A)-F(14B)-C(41) | 75.5(12) | H(13A)-C(13)-H(13B) | 109.5 |
| C(41)-F(14B)-F(13B) | 52.2(8) | H(13A)-C(13)-H(13C) | 109.5 |
| N(1)-C(1)-C(36) | 126.1(5) | H(13B)-C(13)-H(13C) | 109.5 |
| N(2)-C(1)-N(1) | 107.3(5) | C(8)-C(14)-H(14) | 119.5 |
| N(2)-C(1)-C(36) | 125.8(5) | C(12)-C(14)-C(8) | 121.1(7) |
| N(2)-C(2)-Au(1) | 127.0(4) | C(12)-C(14)-H(14) | 119.5 |
| C(3)-C(2)-Au(1) | 129.2(4) | C(10)-C(15)-H(15A) | 109.5 |
| C(3)-C(2)-N(2) | 103.8(5) | C(10)-C(15)-H(15B) | 109.5 |
| N(1)-C(3)-C(32) | 125.7(5) | C(10)-C(15)-H(15C) | 109.5 |
| C(2)-C(3)-N(1) | 109.5(5) | H(15A)-C(15)-H(15B) | 109.5 |
| C(2)-C(3)-C(32) | 124.7(5) | H(15A)-C(15)-H(15C) | 109.5 |
| C(7)-C(4)-N(2) | 117.8(6) | H(15B)-C(15)-H(15C) | 109.5 |
| C(7)-C(4)-C(8) | 124.4(6) | C(19)-C(16)-H(16) | 119.8 |
| C(8)-C(4)-N(2) | 117.8(5) | C(21)-C(16)-H(16) | 119.8 |
| C(6)-C(5)-H(5) | 107.9 | C(21)-C(16)-C(19) | 120.5(6) |
| C(7)-C(5)-H(5) | 107.9 | C(18)-C(17)-N(1) | 119.3(5) |
| C(7)-C(5)-C(6) | 110.4(6) | C(18)-C(17)-C(22) | 123.5(5) |
| C(7)-C(5)-C(13) | 111.6(6) | C(22)-C(17)-N(1) | 117.1(5) |
| C(13)-C(5)-H(5) | 107.9 | C(17)-C(18)-C(19) | 117.4(5) |
| C(13)-C(5)-C(6) | 111.2(6) | C(17)-C(18)-C(20) | 125.8(5) |
| C(5)-C(6)-H(6A) | 109.5 | C(19)-C(18)-C(20) | 116.8(5) |
| C(5)-C(6)-H(6B) | 109.5 | C(16)-C(19)-C(18) | 120.7(6) |

| | | | |
|---|---|---|---|
| C(16)-C(19)-H(19) | 119.7 | F(1)-C(33)-C(30) | 118.0(6) |
| C(18)-C(19)-H(19) | 119.7 | F(1)-C(33)-C(32) | 120.2(5) |
| C(18)-C(20)-H(20) | 109.0 | C(32)-C(33)-C(30) | 121.7(6) |
| C(18)-C(20)-C(24) | 110.2(5) | F(5)-C(34)-F(6B) | 90.3(7) |
| C(18)-C(20)-C(25) | 110.7(5) | F(5)-C(34)-F(7A) | 127.6(9) |
| C(24)-C(20)-H(20) | 109.0 | F(5)-C(34)-F(7B) | 90.8(7) |
| C(25)-C(20)-H(20) | 109.0 | F(5)-C(34)-C(31) | 113.0(6) |
| C(25)-C(20)-C(24) | 109.0(5) | F(6A)-C(34)-F(5) | 121.9(9) |
| C(16)-C(21)-H(21) | 118.9 | F(6A)-C(34)-F(6B) | 41.2(6) |
| C(16)-C(21)-C(22) | 122.2(6) | F(6A)-C(34)-F(7A) | 60.3(8) |
| C(22)-C(21)-H(21) | 118.9 | F(6A)-C(34)-F(7B) | 102.5(9) |
| C(17)-C(22)-C(23) | 125.0(5) | F(6A)-C(34)-C(31) | 113.4(7) |
| C(21)-C(22)-C(17) | 115.8(6) | F(6B)-C(34)-F(7B) | 133.3(8) |
| C(21)-C(22)-C(23) | 119.1(6) | F(6B)-C(34)-C(31) | 110.5(8) |
| C(22)-C(23)-H(23) | 107.6 | F(7A)-C(34)-F(6B) | 100.1(9) |
| C(22)-C(23)-C(26) | 110.1(5) | F(7A)-C(34)-F(7B) | 46.2(7) |
| C(22)-C(23)-C(27) | 114.1(5) | F(7A)-C(34)-C(31) | 110.7(7) |
| C(26)-C(23)-H(23) | 107.6 | F(7B)-C(34)-C(31) | 111.8(7) |
| C(27)-C(23)-H(23) | 107.6 | F(8)-C(35)-C(36) | 119.0(5) |
| C(27)-C(23)-C(26) | 109.6(6) | F(8)-C(35)-C(38) | 118.6(5) |
| C(20)-C(24)-H(24A) | 109.5 | C(36)-C(35)-C(38) | 122.4(6) |
| C(20)-C(24)-H(24B) | 109.5 | C(35)-C(36)-C(1) | 118.8(5) |
| C(20)-C(24)-H(24C) | 109.5 | C(39)-C(36)-C(1) | 124.7(6) |
| H(24A)-C(24)-H(24B) | 109.5 | C(39)-C(36)-C(35) | 116.4(5) |
| H(24A)-C(24)-H(24C) | 109.5 | F(10)-C(37)-C(39) | 117.6(6) |
| H(24B)-C(24)-H(24C) | 109.5 | F(10)-C(37)-C(40) | 120.9(6) |
| C(20)-C(25)-H(25A) | 109.5 | C(39)-C(37)-C(40) | 121.5(6) |
| C(20)-C(25)-H(25B) | 109.5 | F(9)-C(38)-C(35) | 117.3(6) |
| C(20)-C(25)-H(25C) | 109.5 | F(9)-C(38)-C(40) | 122.0(6) |
| H(25A)-C(25)-H(25B) | 109.5 | C(40)-C(38)-C(35) | 120.7(6) |
| H(25A)-C(25)-H(25C) | 109.5 | F(11)-C(39)-C(36) | 120.1(5) |
| H(25B)-C(25)-H(25C) | 109.5 | F(11)-C(39)-C(37) | 118.2(6) |
| C(23)-C(26)-H(26A) | 109.5 | C(37)-C(39)-C(36) | 121.7(6) |
| C(23)-C(26)-H(26B) | 109.5 | C(37)-C(40)-C(41) | 120.7(7) |
| C(23)-C(26)-H(26C) | 109.5 | C(38)-C(40)-C(37) | 117.2(6) |
| H(26A)-C(26)-H(26B) | 109.5 | C(38)-C(40)-C(41) | 122.0(7) |
| H(26A)-C(26)-H(26C) | 109.5 | F(12A)-C(41)-F(13A) | 74.3(11) |
| H(26B)-C(26)-H(26C) | 109.5 | F(12A)-C(41)-F(14A) | 107.7(9) |
| C(23)-C(27)-H(27A) | 109.5 | F(12A)-C(41)-C(40) | 107.3(8) |
| C(23)-C(27)-H(27B) | 109.5 | F(12B)-C(41)-F(12A) | 29.9(7) |
| C(23)-C(27)-H(27C) | 109.5 | F(12B)-C(41)-F(13A) | 98.9(12) |
| H(27A)-C(27)-H(27B) | 109.5 | F(12B)-C(41)-F(14A) | 78.6(9) |
| H(27A)-C(27)-H(27C) | 109.5 | F(12B)-C(41)-F(14B) | 114.9(11) |
| H(27B)-C(27)-H(27C) | 109.5 | F(12B)-C(41)-C(40) | 114.0(8) |
| F(3)-C(28)-C(29) | 119.2(6) | F(13A)-C(41)-C(40) | 110.9(11) |
| F(3)-C(28)-C(32) | 119.6(5) | F(13B)-C(41)-F(12A) | 106.0(9) |
| C(29)-C(28)-C(32) | 121.2(6) | F(13B)-C(41)-F(12B) | 123.5(10) |
| F(4)-C(29)-C(28) | 117.0(7) | F(13B)-C(41)-F(13A) | 34.3(9) |
| F(4)-C(29)-C(31) | 121.2(6) | F(13B)-C(41)-F(14A) | 110.2(9) |
| C(31)-C(29)-C(28) | 121.6(6) | F(13B)-C(41)-F(14B) | 74.4(9) |
| F(2)-C(30)-C(31) | 121.2(6) | F(13B)-C(41)-C(40) | 113.0(7) |
| F(2)-C(30)-C(33) | 117.4(6) | F(14A)-C(41)-F(13A) | 133.5(11) |
| C(31)-C(30)-C(33) | 121.4(7) | F(14A)-C(41)-C(40) | 112.2(7) |
| C(29)-C(31)-C(30) | 117.5(6) | F(14B)-C(41)-F(12A) | 138.4(10) |
| C(29)-C(31)-C(34) | 120.5(7) | F(14B)-C(41)-F(13A) | 106.7(13) |
| C(30)-C(31)-C(34) | 122.0(7) | F(14B)-C(41)-F(14A) | 41.0(7) |
| C(28)-C(32)-C(3) | 122.8(5) | F(14B)-C(41)-C(40) | 110.5(8) |
| C(33)-C(32)-C(3) | 120.5(5) | H(42A)-C(42)-H(42B) | 108.7 |
| C(33)-C(32)-C(28) | 116.5(5) | C(44)-C(42)-H(42A) | 110.5 |

| | | | |
|---|---|---|---|
| C(44)-C(42)-H(42B) | 110.5 | C(42)-C(44)-H(44B) | 112.3 |
| O(1)-C(42)-H(42A) | 110.5 | C(43B)-C(44)-H(44A) | 112.3 |
| O(1)-C(42)-H(42B) | 110.5 | C(43B)-C(44)-H(44B) | 112.3 |
| O(1)-C(42)-C(44) | 106.1(9) | H(44A)-C(44)-H(44B) | 109.9 |
| H(43A)-C(43B)-H(43B) | 108.7 | C(43B)-C(45)-H(45A) | 109.5 |
| C(44)-C(43B)-H(43A) | 110.5 | C(43B)-C(45)-H(45B) | 109.5 |
| C(44)-C(43B)-H(43B) | 110.5 | C(43B)-C(45)-O(1) | 110.6(12) |
| C(45)-C(43B)-H(43A) | 110.5 | H(45A)-C(45)-H(45B) | 108.1 |
| C(45)-C(43B)-H(43B) | 110.5 | O(1)-C(45)-H(45A) | 109.5 |
| C(45)-C(43B)-C(44) | 106.1(13) | O(1)-C(45)-H(45B) | 109.5 |
| C(42)-C(44)-C(43B) | 97.2(11) | C(45)-O(1)-C(42) | 106.3(8) |
| C(42)-C(44)-H(44A) | 112.3 | | |

Symmetry transformations used to generate equivalent atoms:

**Table S8. Anisotropic displacement parameters ($Å^2 \times 10^3$) for 3. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \ldots + 2hka^*b^*U^{12}]$**

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Au(1) | 19(1) | 22(1) | 15(1) | -3(1) | 7(1) | -3(1) |
| Cl(1) | 32(1) | 43(1) | 17(1) | -5(1) | 10(1) | -3(1) |
| N(1) | 18(2) | 16(3) | 11(2) | -4(2) | 5(2) | -4(2) |
| N(2) | 15(2) | 19(3) | 15(3) | -2(2) | 4(2) | -2(2) |
| F(1) | 28(2) | 29(2) | 26(2) | 4(2) | 4(2) | -3(2) |
| F(2) | 42(2) | 53(3) | 31(2) | -7(2) | -9(2) | 19(2) |
| F(3) | 46(2) | 43(3) | 38(2) | 6(2) | 6(2) | -22(2) |
| F(4) | 46(3) | 81(4) | 61(3) | -7(3) | 20(2) | -41(3) |
| F(5) | 37(3) | 93(4) | 105(4) | -57(3) | -15(3) | 19(3) |
| F(6A) | 35(5) | 37(4) | 65(6) | -25(4) | -20(4) | 2(4) |
| F(6B) | 38(5) | 47(5) | 77(6) | -6(5) | -16(5) | -14(4) |
| F(7A) | 50(5) | 86(6) | 57(5) | -14(5) | -8(4) | -14(5) |
| F(7B) | 29(4) | 59(5) | 47(5) | 12(4) | -18(4) | -7(4) |
| F(8) | 25(2) | 17(2) | 36(2) | -3(2) | 3(2) | -2(2) |
| F(9) | 44(2) | 31(2) | 42(2) | -20(2) | 11(2) | -19(2) |
| F(10) | 37(2) | 77(3) | 34(2) | 9(2) | -15(2) | 1(2) |
| F(11) | 31(2) | 37(2) | 32(2) | 2(2) | -3(2) | 8(2) |
| F(12A) | 66(6) | 58(7) | 13(4) | -1(5) | 0(4) | -9(6) |
| F(12B) | 50(5) | 73(7) | 31(6) | -17(6) | 6(4) | -22(6) |
| F(13A) | 56(7) | 78(9) | 65(9) | -10(7) | -17(6) | 2(7) |
| F(13B) | 27(4) | 94(6) | 61(5) | -20(4) | -10(3) | -21(4) |
| F(14A) | 85(6) | 48(5) | 65(6) | -22(4) | -36(5) | 0(5) |
| F(14B) | 56(7) | 71(8) | 45(6) | -3(6) | -9(6) | -42(7) |
| C(1) | 21(3) | 12(3) | 18(3) | 2(2) | 6(2) | -5(3) |
| C(2) | 20(3) | 7(3) | 25(3) | -4(2) | 5(2) | -3(2) |
| C(3) | 17(3) | 16(3) | 13(3) | -3(2) | 3(2) | -2(3) |
| C(4) | 16(3) | 30(4) | 16(3) | -5(3) | 1(2) | 2(3) |
| C(5) | 46(4) | 36(4) | 21(3) | -6(3) | 11(3) | -19(4) |
| C(6) | 62(5) | 37(5) | 26(4) | 1(3) | 0(3) | -21(4) |
| C(7) | 21(3) | 42(4) | 11(3) | -9(3) | 3(2) | -13(3) |
| C(8) | 33(4) | 32(4) | 25(4) | -10(3) | 10(3) | 8(3) |
| C(9) | 47(5) | 32(4) | 57(5) | -2(4) | 1(4) | 3(4) |
| C(10) | 58(5) | 26(4) | 47(4) | -1(4) | 16(4) | 13(4) |
| C(11) | 30(4) | 73(6) | 26(4) | -11(4) | 13(3) | -22(4) |
| C(12) | 23(4) | 93(7) | 43(5) | -24(5) | 5(3) | 7(5) |
| C(13) | 88(6) | 51(5) | 29(4) | -7(4) | 17(4) | -38(5) |
| C(14) | 29(4) | 66(6) | 33(4) | -13(4) | 7(3) | 21(4) |
| C(15) | 134(9) | 27(5) | 49(5) | 1(4) | -5(6) | 16(5) |
| C(16) | 30(4) | 41(4) | 23(4) | -3(3) | 16(3) | -4(3) |
| C(17) | 19(3) | 21(3) | 16(3) | -5(3) | 7(2) | -5(3) |
| C(18) | 17(3) | 14(3) | 16(3) | -3(2) | 0(2) | -4(2) |
| C(19) | 27(3) | 24(4) | 25(3) | -2(3) | 12(3) | 0(3) |
| C(20) | 26(3) | 21(3) | 20(3) | -1(3) | 11(3) | 3(3) |
| C(21) | 39(4) | 31(4) | 18(3) | 3(3) | 7(3) | -10(3) |
| C(22) | 23(3) | 20(3) | 21(3) | -5(3) | 4(3) | -5(3) |
| C(23) | 31(4) | 24(3) | 22(3) | 2(3) | 6(3) | -3(3) |
| C(24) | 32(4) | 34(4) | 20(3) | -1(3) | 4(3) | 8(3) |
| C(25) | 28(4) | 23(4) | 34(4) | -3(3) | 9(3) | 4(3) |
| C(26) | 52(5) | 54(5) | 32(4) | 10(4) | 1(4) | 13(4) |
| C(27) | 43(5) | 29(4) | 75(6) | -2(4) | 8(4) | -3(4) |
| C(28) | 28(3) | 28(3) | 26(3) | -8(3) | 5(3) | 0(3) |
| C(29) | 27(4) | 48(5) | 44(4) | -18(4) | 20(3) | -20(4) |
| C(30) | 26(4) | 40(4) | 23(4) | -19(3) | 0(3) | 8(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(31) | 20(3) | 42(4) | 33(4) | -26(3) | 1(3) | 3(3) |
| C(32) | 19(3) | 17(3) | 17(3) | -9(2) | 6(2) | -4(3) |
| C(33) | 19(3) | 25(4) | 23(3) | -10(3) | 5(3) | 0(3) |
| C(34) | 29(4) | 58(5) | 48(5) | -31(4) | 9(4) | 0(4) |
| C(35) | 19(3) | 17(4) | 18(3) | 0(2) | 6(2) | -3(3) |
| C(36) | 14(3) | 26(4) | 13(3) | -3(3) | 4(2) | -2(3) |
| C(37) | 17(3) | 44(4) | 23(3) | -1(3) | -2(3) | -2(3) |
| C(38) | 26(4) | 30(4) | 29(4) | -12(3) | 16(3) | -15(3) |
| C(39) | 24(3) | 24(4) | 23(3) | 2(3) | 6(3) | -1(3) |
| C(40) | 25(3) | 53(5) | 19(3) | -8(3) | 4(3) | -16(4) |
| C(41) | 41(5) | 73(6) | 24(4) | -14(4) | -3(3) | -22(5) |
| C(42) | 65(7) | 57(7) | 141(11) | 17(7) | 11(7) | -9(6) |
| C(43B) | 81(13) | 50(10) | 33(10) | 20(8) | 18(10) | 30(11) |
| C(44) | 136(11) | 103(10) | 50(7) | -3(6) | 20(7) | -3(9) |
| C(45) | 151(11) | 78(9) | 69(8) | 17(7) | 12(8) | 23(8) |
| O(1) | 99(6) | 100(6) | 76(5) | 21(5) | 8(4) | -16(5) |
| C(43A) | 138(17) | 79(14) | 72(13) | 24(11) | -1(13) | 8(15) |

**X-ray crystal structure determination of 6a**

A colorless crystal (0.35 × 0.30 × 0.05 $mm^3$) was picked up with paraton oil and mounted on a Bruker Venture CMOS diffractometer equipped with a graphite-monochromated Mo Kα ($\lambda$= 0.71073 Å) radiation source at room temperature. The data were corrected for Lorentz and polarization effects (SAINT), and multi-scan absorption corrections based on equivalent reflections were applied (SADABS). The structure was solved by direct methods and refined by full-matrix least-squares on $F^2$ (SHELXTL). All the non-hydrogen atoms were refined anisotropically and hydrogen atoms were added to their ideal positions.

**Table S9. Crystal data and structure refinement for 6a.**

| | | |
|---|---|---|
| Identification code | c2c_a | |
| Empirical formula | C34 H41 F5 N2 | |
| Formula weight | 572.69 | |
| Temperature | 100 K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | C2/c | |
| Unit cell dimensions | $a$ = 18.227(7) Å | $\alpha$ = 90°. |
| | $b$ = 17.040(6) Å | $\beta$ = 101.779(13)°. |
| | $c$ = 20.143(8) Å | $\gamma$ = 90°. |
| Volume | 6125(4) Å$^3$ | |
| Z | 8 | |
| Density (calculated) | 1.242 Mg/m$^3$ | |
| Absorption coefficient | 0.093 mm$^{-1}$ | |
| F(000) | 2432 | |
| Crystal size | 0.35 x 0.30 x 0.05 mm$^3$ | |
| Theta range for data collection | 2.066 to 26.833°. | |
| Index ranges | -22<=h<=22, -21<=k<=21, -25<=l<=25 | |
| Reflections collected | 38920 | |
| Independent reflections | 6502 [R(int) = 0.0985] | |
| Completeness to theta = 25.242° | 99.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7454 and 0.6675 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 6502 / 73 / 408 | |
| Goodness-of-fit on F$^2$ | 1.020 | |
| Final R indices [I>2sigma(I)] | $R_1$ = 0.0734, $wR_2$ = 0.1592 | |
| R indices (all data) | $R_1$ = 0.1191, $wR_2$ = 0.1826 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 1.457 and -0.372 e.Å$^{-3}$ | |

**Table S10. Atomic coordinates ( × $10^4$) and equivalent isotropic displacement parameters ($Å^2$ × $10^3$) for 6a. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| F(1) | 4348(2) | 3920(2) | 6761(2) | 37(1) |
| F(2) | 3712(2) | 4849(2) | 7105(1) | 48(1) |
| F(3) | 4741(2) | 5095(2) | 6772(2) | 54(1) |
| F(4) | 1383(1) | 5497(1) | 1330(1) | 55(1) |
| F(5) | 1490(2) | 4205(1) | 1327(1) | 75(1) |
| F(6) | 4058(6) | 4003(7) | 6861(6) | 58(3) |
| F(7) | 3967(5) | 5226(5) | 7026(4) | 57(2) |
| F(8) | 4920(6) | 4797(5) | 6666(5) | 47(3) |
| N(1) | 2470(1) | 4345(1) | 3427(1) | 20(1) |
| N(2) | 2282(1) | 5591(1) | 3514(1) | 20(1) |
| C(1) | 2550(1) | 4949(2) | 3866(1) | 18(1) |
| C(2) | 2146(1) | 4617(2) | 2786(1) | 22(1) |
| C(3) | 2034(1) | 5388(2) | 2837(1) | 22(1) |
| C(4) | 2930(1) | 4910(1) | 4588(1) | 20(1) |
| C(5) | 2570(2) | 5073(2) | 5116(1) | 24(1) |
| C(6) | 2961(2) | 5011(2) | 5781(1) | 26(1) |
| C(7) | 3702(2) | 4782(2) | 5918(1) | 26(1) |
| C(8) | 4127(2) | 4676(2) | 6639(2) | 34(1) |
| C(9) | 3684(2) | 4686(2) | 4729(1) | 34(1) |
| C(10) | 4068(2) | 4621(2) | 5393(2) | 37(1) |
| C(11) | 2540(2) | 3521(2) | 3619(1) | 25(1) |
| C(12) | 3178(2) | 3106(2) | 3544(2) | 31(1) |
| C(13) | 3821(2) | 3464(2) | 3267(2) | 32(1) |
| C(14) | 1927(2) | 3192(2) | 3852(1) | 35(1) |
| C(15) | 1212(2) | 3640(2) | 3875(2) | 43(1) |
| C(16) | 3198(2) | 2314(2) | 3715(2) | 46(1) |
| C(17) | 4591(2) | 3276(2) | 3723(2) | 54(1) |
| C(18) | 1988(2) | 2406(2) | 4023(2) | 51(1) |
| C(19) | 3798(2) | 3182(2) | 2540(2) | 56(1) |
| C(20) | 591(2) | 3420(3) | 3290(2) | 58(1) |
| C(21) | 2604(2) | 1977(2) | 3953(2) | 59(1) |
| C(22) | 933(3) | 3575(3) | 4536(2) | 82(2) |
| C(23) | 2209(2) | 6369(2) | 3792(1) | 22(1) |
| C(24) | 2780(2) | 6914(2) | 3783(1) | 24(1) |
| C(25) | 1549(2) | 6532(2) | 4026(1) | 24(1) |
| C(26) | 3501(2) | 6725(2) | 3540(1) | 28(1) |
| C(27) | 2670(2) | 7669(2) | 4016(1) | 28(1) |
| C(28) | 923(2) | 5937(2) | 4007(1) | 29(1) |
| C(29) | 1475(2) | 7293(2) | 4258(1) | 30(1) |
| C(30) | 2024(2) | 7848(2) | 4250(1) | 32(1) |
| C(31) | 361(2) | 5981(2) | 3327(2) | 38(1) |
| C(32) | 3578(2) | 7236(2) | 2932(2) | 39(1) |
| C(33) | 503(2) | 6018(2) | 4594(2) | 40(1) |
| C(34) | 4190(2) | 6829(2) | 4114(2) | 41(1) |

**Table S11. Bond lengths [Å] and angles [°] for 6a.**

| | | | |
|---|---|---|---|
| F(1)-F(6) | 0.618(11) | C(16)-H(16) | 0.9500 |
| F(1)-C(8) | 1.358(5) | C(16)-C(21) | 1.395(5) |
| F(2)-F(6) | 1.687(12) | C(17)-H(17A) | 0.9800 |
| F(2)-F(7) | 0.827(8) | C(17)-H(17B) | 0.9800 |
| F(2)-C(8) | 1.352(5) | C(17)-H(17C) | 0.9800 |
| F(3)-F(7) | 1.610(11) | C(18)-H(18) | 0.9500 |
| F(3)-F(8) | 0.662(8) | C(18)-C(21) | 1.370(6) |
| F(3)-C(8) | 1.308(5) | C(19)-H(19A) | 0.9800 |
| F(4)-H(4) | 1.161(13) | C(19)-H(19B) | 0.9800 |
| F(5)-H(4) | 1.098(13) | C(19)-H(19C) | 0.9800 |
| F(6)-C(8) | 1.247(12) | C(20)-H(20A) | 0.9800 |
| F(7)-C(8) | 1.288(9) | C(20)-H(20B) | 0.9800 |
| F(8)-C(8) | 1.451(11) | C(20)-H(20C) | 0.9800 |
| N(1)-C(1) | 1.345(3) | C(21)-H(21) | 0.9500 |
| N(1)-C(2) | 1.384(3) | C(22)-H(22A) | 0.9800 |
| N(1)-C(11) | 1.455(3) | C(22)-H(22B) | 0.9800 |
| N(2)-C(1) | 1.340(3) | C(22)-H(22C) | 0.9800 |
| N(2)-C(3) | 1.390(3) | C(23)-C(24) | 1.397(4) |
| N(2)-C(23) | 1.456(3) | C(23)-C(25) | 1.408(4) |
| C(1)-C(4) | 1.480(3) | C(24)-C(26) | 1.528(4) |
| C(2)-H(2) | 0.9500 | C(24)-C(27) | 1.399(4) |
| C(2)-C(3) | 1.337(4) | C(25)-C(28) | 1.521(4) |
| C(3)-H(3) | 0.9500 | C(25)-C(29) | 1.393(4) |
| C(4)-C(5) | 1.386(4) | C(26)-H(26) | 1.0000 |
| C(4)-C(9) | 1.399(4) | C(26)-C(32) | 1.533(4) |
| C(5)-H(5) | 0.9500 | C(26)-C(34) | 1.534(4) |
| C(5)-C(6) | 1.389(4) | C(27)-H(27) | 0.9500 |
| C(6)-H(6) | 0.9500 | C(27)-C(30) | 1.388(4) |
| C(6)-C(7) | 1.379(4) | C(28)-H(28) | 1.0000 |
| C(7)-C(8) | 1.511(4) | C(28)-C(31) | 1.536(4) |
| C(7)-C(10) | 1.388(4) | C(28)-C(33) | 1.541(4) |
| C(9)-H(9) | 0.9500 | C(29)-H(29) | 0.9500 |
| C(9)-C(10) | 1.381(4) | C(29)-C(30) | 1.380(4) |
| C(10)-H(10) | 0.9500 | C(30)-H(30) | 0.9500 |
| C(11)-C(12) | 1.394(4) | C(31)-H(31A) | 0.9800 |
| C(11)-C(14) | 1.415(4) | C(31)-H(31B) | 0.9800 |
| C(12)-C(13) | 1.525(4) | C(31)-H(31C) | 0.9800 |
| C(12)-C(16) | 1.392(4) | C(32)-H(32A) | 0.9800 |
| C(13)-H(13) | 1.0000 | C(32)-H(32B) | 0.9800 |
| C(13)-C(17) | 1.546(4) | C(32)-H(32C) | 0.9800 |
| C(13)-C(19) | 1.534(5) | C(33)-H(33A) | 0.9800 |
| C(14)-C(15) | 1.520(5) | C(33)-H(33B) | 0.9800 |
| C(14)-C(18) | 1.381(5) | C(33)-H(33C) | 0.9800 |
| C(15)-H(15) | 1.0000 | C(34)-H(34A) | 0.9800 |
| C(15)-C(20) | 1.506(5) | C(34)-H(34B) | 0.9800 |
| C(15)-C(22) | 1.522(5) | C(34)-H(34C) | 0.9800 |
| | | | |
| F(6)-F(1)-C(8) | 66.4(13) | F(2)-F(7)-F(3) | 121.2(10) |
| F(7)-F(2)-F(6) | 110.4(9) | F(2)-F(7)-C(8) | 76.0(7) |
| F(7)-F(2)-C(8) | 67.6(7) | C(8)-F(7)-F(3) | 52.2(4) |
| C(8)-F(2)-F(6) | 46.9(4) | F(3)-F(8)-C(8) | 64.3(11) |
| F(8)-F(3)-F(7) | 136.9(14) | C(1)-N(1)-C(2) | 109.0(2) |
| F(8)-F(3)-C(8) | 88.5(12) | C(1)-N(1)-C(11) | 124.8(2) |
| C(8)-F(3)-F(7) | 51.1(4) | C(2)-N(1)-C(11) | 124.7(2) |
| F(1)-F(6)-F(2) | 133.3(16) | C(1)-N(2)-C(3) | 109.1(2) |
| F(1)-F(6)-C(8) | 86.6(14) | C(1)-N(2)-C(23) | 126.2(2) |
| C(8)-F(6)-F(2) | 52.3(5) | C(3)-N(2)-C(23) | 124.5(2) |

| | | | |
|---|---|---|---|
| N(1)-C(1)-C(4) | 125.4(2) | C(19)-C(13)-C(17) | 110.3(3) |
| N(2)-C(1)-N(1) | 107.2(2) | C(11)-C(14)-C(15) | 123.5(3) |
| N(2)-C(1)-C(4) | 127.2(2) | C(18)-C(14)-C(11) | 115.9(3) |
| N(1)-C(2)-H(2) | 126.2 | C(18)-C(14)-C(15) | 120.5(3) |
| C(3)-C(2)-N(1) | 107.5(2) | C(14)-C(15)-H(15) | 106.7 |
| C(3)-C(2)-H(2) | 126.2 | C(14)-C(15)-C(22) | 115.5(3) |
| N(2)-C(3)-H(3) | 126.4 | C(20)-C(15)-C(14) | 111.2(3) |
| C(2)-C(3)-N(2) | 107.1(2) | C(20)-C(15)-H(15) | 106.7 |
| C(2)-C(3)-H(3) | 126.4 | C(20)-C(15)-C(22) | 109.6(3) |
| C(5)-C(4)-C(1) | 123.0(2) | C(22)-C(15)-H(15) | 106.7 |
| C(5)-C(4)-C(9) | 119.9(2) | C(12)-C(16)-H(16) | 120.0 |
| C(9)-C(4)-C(1) | 117.1(2) | C(12)-C(16)-C(21) | 120.0(3) |
| C(4)-C(5)-H(5) | 120.2 | C(21)-C(16)-H(16) | 120.0 |
| C(4)-C(5)-C(6) | 119.7(3) | C(13)-C(17)-H(17A) | 109.5 |
| C(6)-C(5)-H(5) | 120.2 | C(13)-C(17)-H(17B) | 109.5 |
| C(5)-C(6)-H(6) | 119.9 | C(13)-C(17)-H(17C) | 109.5 |
| C(7)-C(6)-C(5) | 120.2(3) | H(17A)-C(17)-H(17B) | 109.5 |
| C(7)-C(6)-H(6) | 119.9 | H(17A)-C(17)-H(17C) | 109.5 |
| C(6)-C(7)-C(8) | 120.9(3) | H(17B)-C(17)-H(17C) | 109.5 |
| C(6)-C(7)-C(10) | 120.5(3) | C(14)-C(18)-H(18) | 119.4 |
| C(10)-C(7)-C(8) | 118.6(3) | C(21)-C(18)-C(14) | 121.2(3) |
| F(1)-C(8)-F(8) | 82.6(4) | C(21)-C(18)-H(18) | 119.4 |
| F(1)-C(8)-C(7) | 111.3(3) | C(13)-C(19)-H(19A) | 109.5 |
| F(2)-C(8)-F(1) | 105.6(3) | C(13)-C(19)-H(19B) | 109.5 |
| F(2)-C(8)-F(8) | 129.6(5) | C(13)-C(19)-H(19C) | 109.5 |
| F(2)-C(8)-C(7) | 113.1(3) | H(19A)-C(19)-H(19B) | 109.5 |
| F(3)-C(8)-F(1) | 105.7(3) | H(19A)-C(19)-H(19C) | 109.5 |
| F(3)-C(8)-F(2) | 108.4(3) | H(19B)-C(19)-H(19C) | 109.5 |
| F(3)-C(8)-F(8) | 27.1(3) | C(15)-C(20)-H(20A) | 109.5 |
| F(3)-C(8)-C(7) | 112.4(3) | C(15)-C(20)-H(20B) | 109.5 |
| F(6)-C(8)-F(1) | 27.0(5) | C(15)-C(20)-H(20C) | 109.5 |
| F(6)-C(8)-F(2) | 80.8(6) | H(20A)-C(20)-H(20B) | 109.5 |
| F(6)-C(8)-F(3) | 124.9(6) | H(20A)-C(20)-H(20C) | 109.5 |
| F(6)-C(8)-F(7) | 113.6(7) | H(20B)-C(20)-H(20C) | 109.5 |
| F(6)-C(8)-F(8) | 106.7(6) | C(16)-C(21)-H(21) | 119.1 |
| F(6)-C(8)-C(7) | 112.7(5) | C(18)-C(21)-C(16) | 121.7(3) |
| F(7)-C(8)-F(1) | 132.5(5) | C(18)-C(21)-H(21) | 119.1 |
| F(7)-C(8)-F(2) | 36.4(4) | C(15)-C(22)-H(22A) | 109.5 |
| F(7)-C(8)-F(3) | 76.6(5) | C(15)-C(22)-H(22B) | 109.5 |
| F(7)-C(8)-F(8) | 102.7(6) | C(15)-C(22)-H(22C) | 109.5 |
| F(7)-C(8)-C(7) | 111.1(4) | H(22A)-C(22)-H(22B) | 109.5 |
| F(8)-C(8)-C(7) | 109.3(5) | H(22A)-C(22)-H(22C) | 109.5 |
| C(4)-C(9)-H(9) | 120.0 | H(22B)-C(22)-H(22C) | 109.5 |
| C(10)-C(9)-C(4) | 120.0(3) | C(24)-C(23)-N(2) | 118.2(2) |
| C(10)-C(9)-H(9) | 120.0 | C(24)-C(23)-C(25) | 124.2(2) |
| C(7)-C(10)-H(10) | 120.2 | C(25)-C(23)-N(2) | 117.5(2) |
| C(9)-C(10)-C(7) | 119.7(3) | C(23)-C(24)-C(26) | 123.7(2) |
| C(9)-C(10)-H(10) | 120.2 | C(23)-C(24)-C(27) | 116.7(3) |
| C(12)-C(11)-N(1) | 119.4(2) | C(27)-C(24)-C(26) | 119.5(3) |
| C(12)-C(11)-C(14) | 124.6(3) | C(23)-C(25)-C(28) | 123.2(2) |
| C(14)-C(11)-N(1) | 116.0(3) | C(29)-C(25)-C(23) | 116.4(3) |
| C(11)-C(12)-C(13) | 123.8(2) | C(29)-C(25)-C(28) | 120.4(3) |
| C(16)-C(12)-C(11) | 116.5(3) | C(24)-C(26)-H(26) | 108.2 |
| C(16)-C(12)-C(13) | 119.6(3) | C(24)-C(26)-C(32) | 111.2(2) |
| C(12)-C(13)-H(13) | 108.0 | C(24)-C(26)-C(34) | 111.0(2) |
| C(12)-C(13)-C(17) | 111.9(3) | C(32)-C(26)-H(26) | 108.2 |
| C(12)-C(13)-C(19) | 110.5(3) | C(32)-C(26)-C(34) | 110.1(3) |
| C(17)-C(13)-H(13) | 108.0 | C(34)-C(26)-H(26) | 108.2 |
| C(19)-C(13)-H(13) | 108.0 | C(24)-C(27)-H(27) | 119.8 |

| | | | |
|---|---|---|---|
| C(30)-C(27)-C(24) | 120.3(3) | H(31B)-C(31)-H(31C) | 109.5 |
| C(30)-C(27)-H(27) | 119.8 | C(26)-C(32)-H(32A) | 109.5 |
| C(25)-C(28)-H(28) | 107.5 | C(26)-C(32)-H(32B) | 109.5 |
| C(25)-C(28)-C(31) | 110.5(2) | C(26)-C(32)-H(32C) | 109.5 |
| C(25)-C(28)-C(33) | 114.1(2) | H(32A)-C(32)-H(32B) | 109.5 |
| C(31)-C(28)-H(28) | 107.5 | H(32A)-C(32)-H(32C) | 109.5 |
| C(31)-C(28)-C(33) | 109.5(2) | H(32B)-C(32)-H(32C) | 109.5 |
| C(33)-C(28)-H(28) | 107.5 | C(28)-C(33)-H(33A) | 109.5 |
| C(25)-C(29)-H(29) | 119.6 | C(28)-C(33)-H(33B) | 109.5 |
| C(30)-C(29)-C(25) | 120.9(3) | C(28)-C(33)-H(33C) | 109.5 |
| C(30)-C(29)-H(29) | 119.6 | H(33A)-C(33)-H(33B) | 109.5 |
| C(27)-C(30)-H(30) | 119.3 | H(33A)-C(33)-H(33C) | 109.5 |
| C(29)-C(30)-C(27) | 121.4(3) | H(33B)-C(33)-H(33C) | 109.5 |
| C(29)-C(30)-H(30) | 119.3 | C(26)-C(34)-H(34A) | 109.5 |
| C(28)-C(31)-H(31A) | 109.5 | C(26)-C(34)-H(34B) | 109.5 |
| C(28)-C(31)-H(31B) | 109.5 | C(26)-C(34)-H(34C) | 109.5 |
| C(28)-C(31)-H(31C) | 109.5 | H(34A)-C(34)-H(34B) | 109.5 |
| H(31A)-C(31)-H(31B) | 109.5 | H(34A)-C(34)-H(34C) | 109.5 |
| H(31A)-C(31)-H(31C) | 109.5 | H(34B)-C(34)-H(34C) | 109.5 |

Symmetry transformations used to generate equivalent atoms:

**Table S12. Anisotropic displacement parameters ($Å^2 \times 10^3$) for 6a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \ldots + 2hka^*b^*U^{12}]$**

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| F(1) | 45(2) | 38(2) | 24(2) | 10(1) | -1(2) | 14(2) |
| F(2) | 57(2) | 68(2) | 16(1) | 1(1) | 3(1) | 16(2) |
| F(3) | 57(2) | 62(2) | 32(2) | 11(2) | -17(2) | -28(2) |
| F(4) | 62(1) | 51(1) | 49(1) | 6(1) | 0(1) | 0(1) |
| F(5) | 123(2) | 58(1) | 34(1) | -13(1) | -6(1) | 7(1) |
| F(6) | 68(5) | 53(4) | 45(4) | 16(3) | -9(4) | -16(4) |
| F(7) | 64(4) | 71(4) | 33(3) | -12(3) | -1(3) | 4(3) |
| F(8) | 44(4) | 49(4) | 41(4) | -7(3) | -11(3) | 6(3) |
| N(1) | 20(1) | 24(1) | 15(1) | -1(1) | 4(1) | -2(1) |
| N(2) | 20(1) | 25(1) | 14(1) | 1(1) | 3(1) | 2(1) |
| C(1) | 16(1) | 25(1) | 15(1) | 2(1) | 6(1) | -1(1) |
| C(2) | 19(1) | 32(2) | 15(1) | -2(1) | 4(1) | -1(1) |
| C(3) | 19(1) | 33(2) | 14(1) | 2(1) | 2(1) | 2(1) |
| C(4) | 22(1) | 18(1) | 18(1) | 1(1) | 1(1) | -2(1) |
| C(5) | 25(1) | 28(1) | 19(1) | 1(1) | 5(1) | 2(1) |
| C(6) | 34(2) | 25(1) | 18(1) | 1(1) | 4(1) | 0(1) |
| C(7) | 34(2) | 21(1) | 19(1) | 2(1) | -2(1) | -4(1) |
| C(8) | 46(2) | 28(2) | 23(2) | 3(1) | -6(1) | -4(1) |
| C(9) | 25(2) | 57(2) | 20(2) | -3(1) | 2(1) | 6(1) |
| C(10) | 26(2) | 54(2) | 28(2) | 0(1) | -2(1) | 6(1) |
| C(11) | 30(2) | 22(1) | 21(1) | 0(1) | 1(1) | -9(1) |
| C(12) | 33(2) | 21(1) | 34(2) | -1(1) | -6(1) | -5(1) |
| C(13) | 26(2) | 24(1) | 45(2) | -7(1) | 4(1) | 2(1) |
| C(14) | 45(2) | 40(2) | 19(1) | -5(1) | 5(1) | -23(2) |
| C(15) | 39(2) | 55(2) | 40(2) | -22(2) | 23(2) | -25(2) |
| C(16) | 50(2) | 21(2) | 57(2) | 3(1) | -14(2) | -2(1) |
| C(17) | 29(2) | 33(2) | 93(3) | -7(2) | -7(2) | 9(1) |
| C(18) | 65(3) | 44(2) | 41(2) | 6(2) | 2(2) | -32(2) |
| C(19) | 47(2) | 59(2) | 65(3) | -29(2) | 21(2) | -4(2) |
| C(20) | 41(2) | 78(3) | 54(2) | -23(2) | 12(2) | 2(2) |
| C(21) | 81(3) | 24(2) | 61(2) | 15(2) | -13(2) | -21(2) |
| C(22) | 74(3) | 132(4) | 50(3) | -14(3) | 35(2) | -21(3) |
| C(23) | 24(1) | 26(1) | 12(1) | 3(1) | -1(1) | 5(1) |
| C(24) | 30(2) | 26(1) | 16(1) | 2(1) | 4(1) | 4(1) |
| C(25) | 26(2) | 33(2) | 13(1) | 4(1) | 0(1) | 8(1) |
| C(26) | 29(2) | 26(1) | 29(2) | -1(1) | 9(1) | -2(1) |
| C(27) | 37(2) | 24(1) | 22(1) | 1(1) | 2(1) | 3(1) |
| C(28) | 23(1) | 40(2) | 25(2) | 1(1) | 4(1) | 9(1) |
| C(29) | 32(2) | 37(2) | 21(1) | 1(1) | 3(1) | 17(1) |
| C(30) | 44(2) | 27(2) | 25(2) | -2(1) | 4(1) | 12(1) |
| C(31) | 24(2) | 59(2) | 30(2) | -2(2) | 5(1) | 4(1) |
| C(32) | 49(2) | 40(2) | 33(2) | 4(1) | 18(2) | -3(2) |
| C(33) | 34(2) | 59(2) | 30(2) | 5(2) | 13(1) | 3(2) |
| C(34) | 33(2) | 50(2) | 39(2) | -3(2) | 6(2) | 0(2) |

**X-ray crystal structures and additional informations**

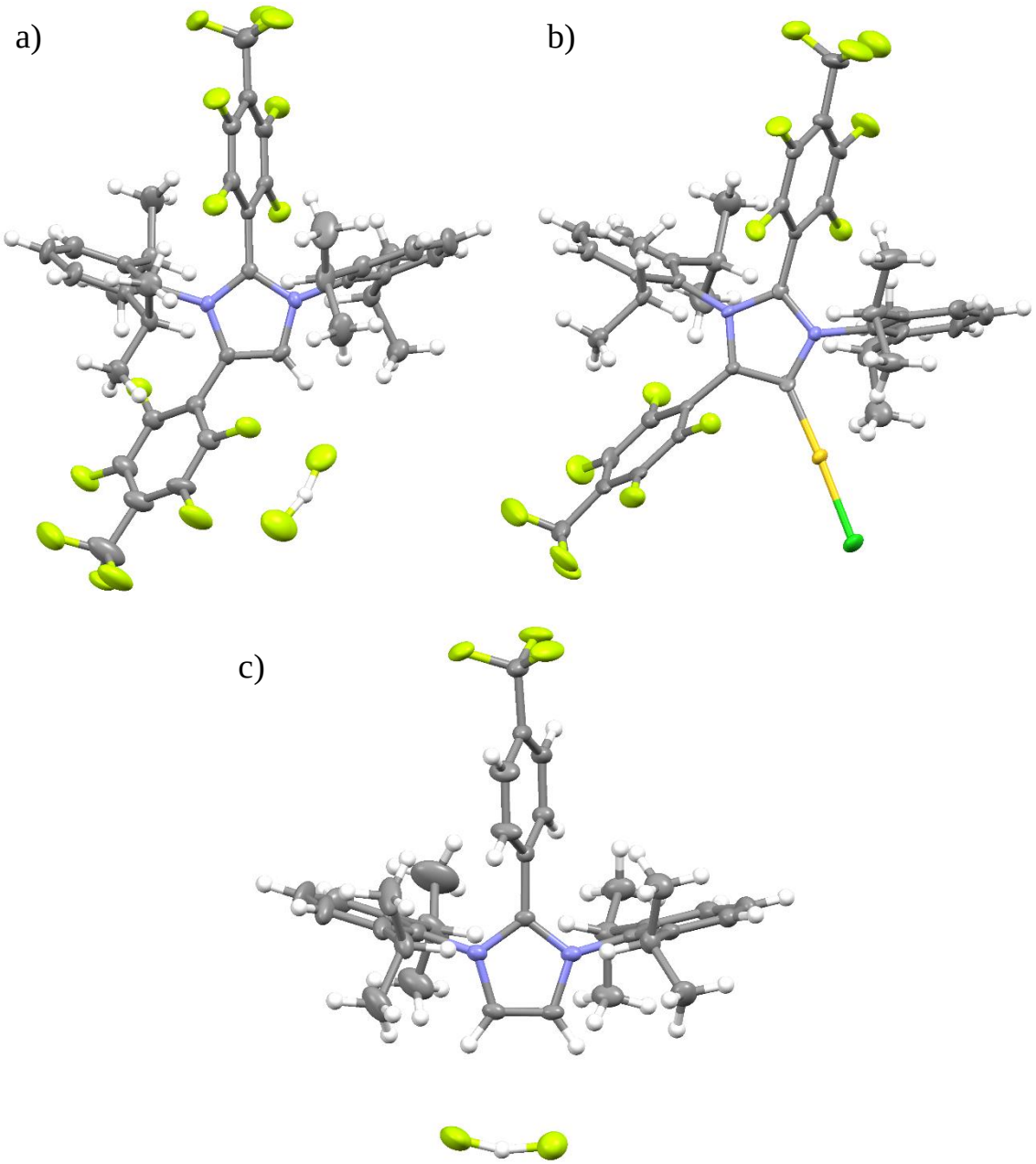
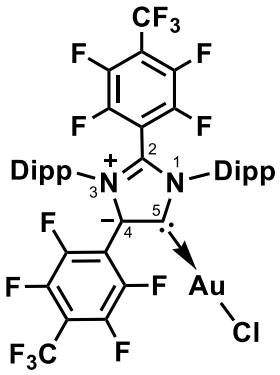
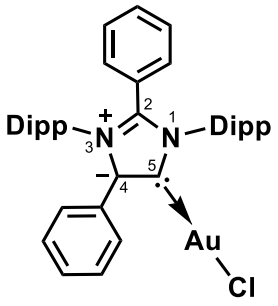



**Figure S21. Structure of a) 2, b) 3, and c) 6a. The thermal ellipsoids for nonhydrogen atoms are set at a 50% probability level.**

**Table S13. Metric comparison between 3 (CCDC 1484681) and similar gold(I) chloride complex bearing nonfluorinated *a*NHC ligand (CCDC 744123).**




**3 (CCDC 1484681)**




**CCDC 744123**

Bond length (Å) and angle (˚)

| **Structure** | C5–Au | Au–Cl | N1–C5 | C4–C5 | C5–Au–Cl |
|---|---|---|---|---|---|
| **3** (CCDC 1484681) | 1.981(6) | 2.276(2) | 1.391(7) | 1.376(9) | 177.3(2) |
| CCDC 744123 | 1.981(5) | 2.271(2) | 1.392(7) | 1.375(8) | 177.5(2) |

# DFT Calculation

### General information

Density functional theory (DFT) calculations were performed using Gaussian09 with following input files.[4]

· *For optimization and frequency calculations:*

```
# M06/gen gfinput scf=tight nosymm 6d 10f opt freq=noraman
```

· *For optimization and frequency calculation of transition states:*

```
# M06/gen gfinput scf=tight nosymm 6d 10f opt=(ts,noeigentest,modredundant) freq=noraman
```

· *For solvation free energy calculations:*

```
# M06/gen gfinput scf=tight nosymm 6d 10f scrf=(smd, solvent= TetraHydroFuran)
```

· *For intrinsic reaction coordinate (IRC) calculations:*

```
# M06/gen geom=checkpoint guess=read scf=tight nosymm 6d 10f IRC=(rcfc,maxpoint=300,maxcyc=2000)
```

The nature of all stationary points calculated from full optimizations was confirmed *via* frequency analysis, which revealed zero and one imaginary frequency for ground and transition state (TS), respectively. TS was analyzed further with IRC calculations. All calculations were performed using the M06 functional with 6-31G(d,p) basis set.[5] Solvation free energies were computed by single point calculation on gas phase-optimized geometries using SMD model of Cramer and Truhlar.[6]

### Energy diagram

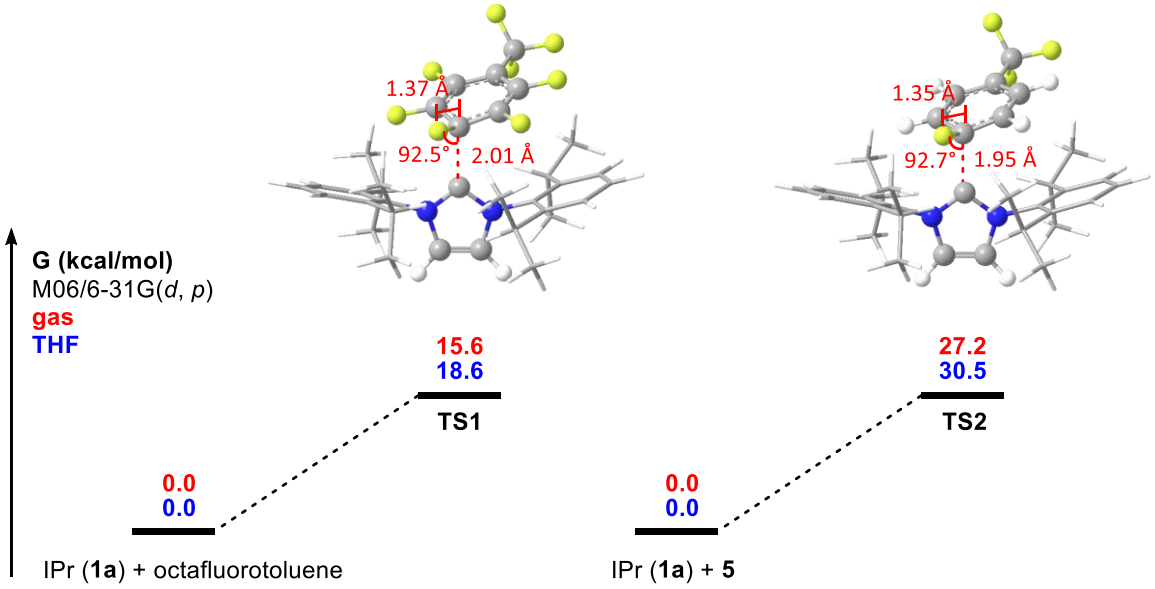



**Figure S22.** Calculated activation energy of the reaction between *I*Pr and fluoroarenes.

**IRC calculation result**

· *I*Pr(**1a**) + octafluorotoluene

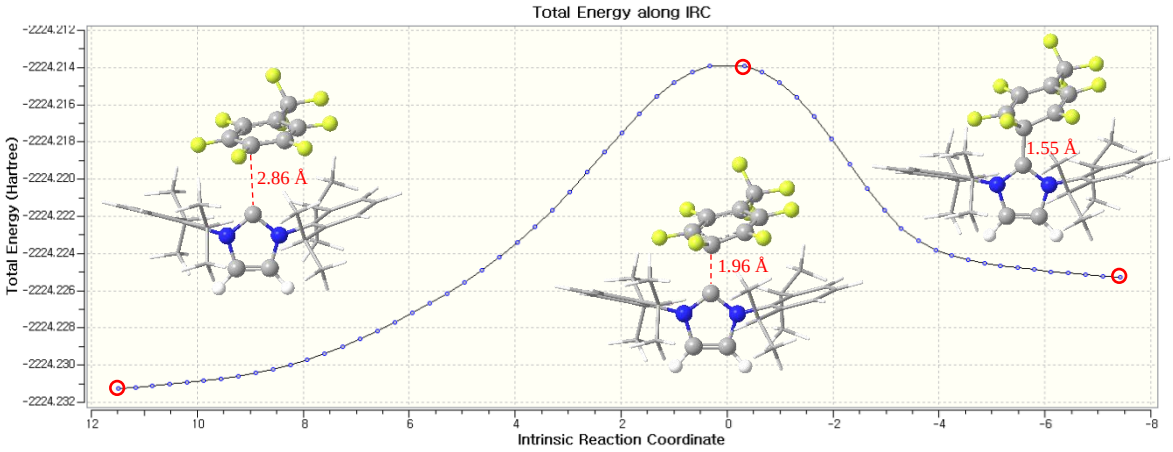



**Figure S23.** IRC analysis of the TS between *I*Pr(**1a**) and octafluorotoluene.

| **IRC** | **Energy (Hartree)** | -1.32064 | -2224.21560263 | 5.61191 | -2224.22668749 |
|---|---|---|---|---|---|
| -7.42586 | -2224.22526731 | -0.99048 | -2224.21481217 | 5.94197 | -2224.22720300 |
| -7.09626 | -2224.22520360 | -0.66034 | -2224.21425584 | 6.27203 | -2224.22768888 |
| -6.76699 | -2224.22513448 | -0.33022 | -2224.21392528 | 6.60209 | -2224.22815110 |
| -6.43902 | -2224.22505901 | 0.33022 | -2224.21392639 | 6.93217 | -2224.22859096 |
| -6.11887 | -2224.22497097 | 0.66034 | -2224.21426086 | 7.26224 | -2224.22900476 |
| -5.79156 | -2224.22486185 | 0.99048 | -2224.21481412 | 7.59201 | -2224.22938387 |
| -5.48044 | -2224.22475715 | 1.32066 | -2224.21556590 | 7.92044 | -2224.22971353 |
| -5.16404 | -2224.22464656 | 1.65085 | -2224.21647696 | 8.24602 | -2224.22998793 |
| -4.86165 | -2224.22451026 | 1.98103 | -2224.21749460 | 8.57265 | -2224.23021782 |
| -4.54626 | -2224.22432930 | 2.31120 | -2224.21856410 | 8.90042 | -2224.23041257 |
| -4.24423 | -2224.22410715 | 2.64135 | -2224.21963709 | 9.22496 | -2224.23057759 |
| -3.94679 | -2224.22380570 | 2.97147 | -2224.22067524 | 9.55232 | -2224.23072096 |
| -3.62171 | -2224.22332768 | 3.30159 | -2224.22165646 | 9.87815 | -2224.23084232 |
| -3.29552 | -2224.22263244 | 3.63168 | -2224.22257303 | 10.19517 | -2224.23094197 |
| -2.96931 | -2224.22169424 | 3.96176 | -2224.22342007 | 10.51770 | -2224.23103011 |
| -2.64071 | -2224.22052716 | 4.29181 | -2224.22419377 | 10.84363 | -2224.23111120 |
| -2.31103 | -2224.21920491 | 4.62185 | -2224.22489805 | 11.16904 | -2224.23118694 |
| -1.98096 | -2224.21786041 | 4.95189 | -2224.22554242 | 11.49243 | -2224.23125820 |
| -1.65081 | -2224.21662871 | 5.28192 | -2224.22613613 | | |

· *I*Pr(**1a**) + **5**

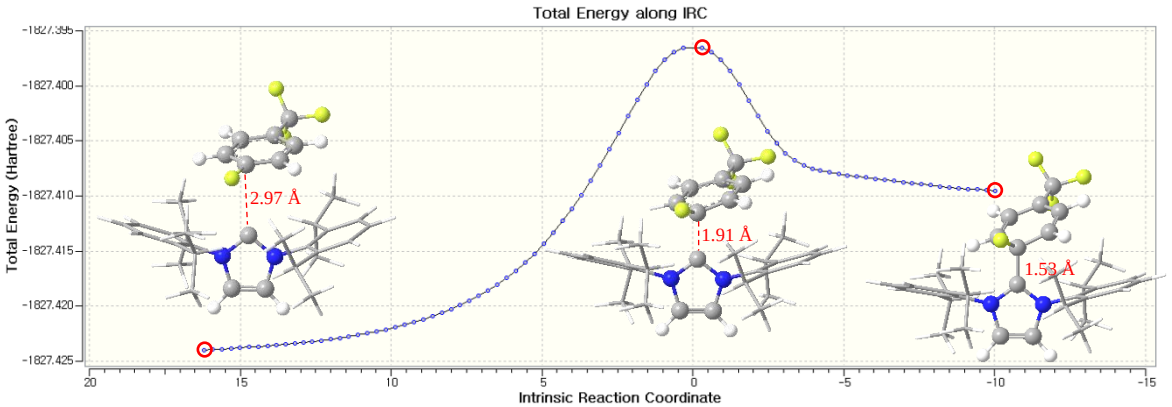



**Figure S24.** IRC analysis of the TS between *I*Pr(**1a**) and **5**.

| IRC | Energy (Hartree) | -1.54239 | -1827.39989133 | 7.70957 | -1827.41989879 |
|---|---|---|---|---|---|
| -10.02924 | -1827.40953016 | -1.23393 | -1827.39864139 | 8.01779 | -1827.42026455 |
| -9.72131 | -1827.40947514 | -0.92545 | -1827.39765038 | 8.32589 | -1827.42060148 |
| -9.41333 | -1827.40941546 | -0.61700 | -1827.39694547 | 8.63417 | -1827.42091251 |
| -9.10672 | -1827.40935106 | -0.30851 | -1827.39652573 | 8.94246 | -1827.42119947 |
| -8.80207 | -1827.40928036 | 0.30817 | -1827.39651812 | 9.25067 | -1827.42146314 |
| -8.49507 | -1827.40920140 | 0.61661 | -1827.39693498 | 9.55874 | -1827.42170423 |
| -8.18887 | -1827.40911477 | 0.92507 | -1827.39764046 | 9.86669 | -1827.42192390 |
| -7.88169 | -1827.40901992 | 1.23355 | -1827.39862367 | 10.17476 | -1827.42212372 |
| -7.57437 | -1827.40892065 | 1.54204 | -1827.39984441 | 10.48265 | -1827.42230493 |
| -7.26773 | -1827.40882160 | 1.85051 | -1827.40123621 | 10.78955 | -1827.42246819 |
| -6.96183 | -1827.40872510 | 2.15898 | -1827.40272760 | 11.09434 | -1827.42261523 |
| -6.65401 | -1827.40862954 | 2.46744 | -1827.40425552 | 11.39858 | -1827.42275092 |
| -6.34750 | -1827.40853427 | 2.77588 | -1827.40576924 | 11.70555 | -1827.42287956 |
| -6.04202 | -1827.40843728 | 3.08430 | -1827.40722974 | 12.00775 | -1827.42299930 |
| -5.73469 | -1827.40833626 | 3.39271 | -1827.40861394 | 12.31037 | -1827.42311290 |
| -5.43488 | -1827.40823292 | 3.70112 | -1827.40991603 | 12.60915 | -1827.42321396 |
| -5.12982 | -1827.40812078 | 4.00953 | -1827.41113627 | 12.90661 | -1827.42330140 |
| -4.82562 | -1827.40799921 | 4.31794 | -1827.41227551 | 13.19400 | -1827.42337571 |
| -4.52429 | -1827.40786220 | 4.62634 | -1827.41333692 | 13.48867 | -1827.42344565 |
| -4.22914 | -1827.40770007 | 4.93476 | -1827.41432181 | 13.79647 | -1827.42351588 |
| -3.94895 | -1827.40749698 | 5.24316 | -1827.41522875 | 14.09925 | -1827.42358432 |
| -3.67891 | -1827.40722244 | 5.55154 | -1827.41605421 | 14.40326 | -1827.42365153 |
| -3.37979 | -1827.40677607 | 5.85994 | -1827.41679714 | 14.70603 | -1827.42371812 |
| -3.07421 | -1827.40612010 | 6.16831 | -1827.41746118 | 15.00670 | -1827.42378172 |
| -2.77197 | -1827.40523332 | 6.47665 | -1827.41805435 | 15.30229 | -1827.42383769 |
| -2.46604 | -1827.40409909 | 6.78500 | -1827.41858602 | 15.60277 | -1827.42388733 |
| -2.15886 | -1827.40276106 | 7.09328 | -1827.41906523 | 15.90448 | -1827.42393165 |
| -1.85077 | -1827.40131070 | 7.40139 | -1827.41950060 | 16.19837 | -1827.42397129 |

## Coordinates of optimized structures

The optimized geometries were displayed in Cartesian coordinates (atomic unit). E° represents 'total electronic energy' and G° represents 'standard Gibbs free energy' in Hartree unit. $E°_{(THF)}$ represent 'total electronic energy' in THF. For transition states, *v* represents the first and only negative imaginary frequency in $cm^{-1}$ unit.

**_i_Pr (1a) [E° = -1159.1938922; G° = -1158.681645; $E°_{(THF)}$ = -1159.2208002]**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 1.4466666365 | -0.3398648694 | -0.050772407 | C | -3.9245887628 | 0.8275442157 | 1.4870169239 |
| C | 0.3585629508 | 0.4605189221 | -0.0493573078 | C | -4.6496244554 | 1.092343601 | 0.3357621402 |
| H | 2.5035215163 | -0.1203062971 | -0.1203145109 | H | -4.6758398114 | 1.052307449 | -1.8088262821 |
| H | 0.2547907972 | 1.5353510353 | -0.1105459791 | H | -4.372244189 | 1.0149824047 | 2.4619939884 |
| N | -0.7408907785 | -0.3884403218 | 0.0487295093 | H | -5.6601360799 | 1.4880705495 | 0.4097337564 |
| N | 0.9642638395 | -1.6409342598 | 0.0629814351 | C | -1.8523444629 | 0.0329736025 | 2.685239694 |
| C | -0.4022223936 | -1.7137806591 | 0.1225474314 | C | -2.5792301778 | -0.9962836119 | 3.5462929215 |
| C | 1.8195512094 | -2.7878081188 | 0.0411054811 | C | -1.5785802176 | 1.316507792 | 3.464848987 |
| C | 2.3670921139 | -3.246677183 | 1.2489838387 | H | -0.8841358366 | -0.4061352566 | 2.4049577493 |
| C | 2.0871739681 | -3.3980463884 | -1.1885346013 | H | -2.7422666704 | -1.9258070433 | 2.9888676134 |
| C | 3.2107868997 | -4.3542347614 | 1.1957541986 | H | -1.9925476588 | -1.2327135337 | 4.4423881823 |
| C | 2.9401942693 | -4.503663238 | -1.1915223752 | H | -3.5563971379 | -0.6248888265 | 3.8808976397 |
| C | 3.4974781807 | -4.9760787083 | -0.013736683 | H | -1.0296375661 | 2.044574331 | 2.8555959335 |
| H | 3.6495106974 | -4.7403030885 | 2.113115834 | H | -2.5133841462 | 1.7920578843 | 3.7892609688 |
| H | 3.1671696448 | -5.0018572765 | -2.1330015927 | H | -0.9844519419 | 1.1058330889 | 4.3622253641 |
| H | 4.159173058 | -5.839153944 | -0.0342278388 | C | -2.2086182675 | -0.0032245988 | -2.3844276997 |
| C | -2.0836984548 | 0.0956195918 | 0.1459545847 | C | -2.719309438 | 0.8710483436 | -3.5225310607 |
| C | -2.7985358246 | 0.3463255829 | -1.0351343783 | C | -2.4733192353 | -1.4809214054 | -2.6811777201 |
| C | -2.6250841858 | 0.3209424281 | 1.416085359 | H | -1.1187623104 | 0.1349470415 | -2.3197614341 |
| C | -4.0921840149 | 0.8486415149 | -0.9138599897 | H | -2.6204848362 | 1.9394270434 | -3.2985469036 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -2.1547473983 | 0.6604408974 | -4.4379437587 | H | 3.2001725443 | -3.2908089829 | -3.760585096 |
| H | -3.774426095 | 0.6684914346 | -3.7476119403 | H | 2.0919357953 | -2.0600684758 | -4.3838952158 |
| H | -2.0437305369 | -2.1229404402 | -1.9015994357 | C | 1.9830878196 | -2.604218274 | 2.5648629058 |
| H | -3.5549185349 | -1.6678940871 | -2.722006837 | C | 3.055313696 | -2.7250590681 | 3.64006839 |
| H | -2.0446482613 | -1.7651528454 | -3.6507695739 | C | 0.6612453637 | -3.1991213431 | 3.0559026072 |
| C | 1.4749640311 | -2.9077221595 | -2.4829114013 | H | 1.817076755 | -1.5322854304 | 2.3786268559 |
| C | 0.5719607039 | -3.9779329637 | -3.0898705125 | H | 4.0326514632 | -2.3741300322 | 3.2890059447 |
| C | 2.5484635097 | -2.4570474791 | -3.4693551156 | H | 2.7746793885 | -2.1306929301 | 4.5170611304 |
| H | 0.8435721288 | -2.0373503416 | -2.253976885 | H | 3.1708740987 | -3.7614526993 | 3.983218251 |
| H | -0.2177705517 | -4.2648866593 | -2.3864614823 | H | -0.1347642225 | -3.061824282 | 2.3124374661 |
| H | 0.1000690324 | -3.6114347928 | -4.0096274567 | H | 0.7777586239 | -4.2765588981 | 3.2354924422 |
| H | 1.1405559517 | -4.881056984 | -3.347273939 | H | 0.3533862435 | -2.7312538676 | 3.9999742854 |
| H | 3.1832482641 | -1.6741684478 | -3.0370189784 | | | | |

**Octafluorotoluene [$E^\circ$ = -1065.0137827; $G^\circ$ = -1064.986319; $E^\circ_{(THF)}$ = -1065.015400]**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.8395114622 | 0.4487508886 | -0.1174748272 | F | -0.0356769449 | 1.4645387483 | -0.387687772 |
| C | -0.2742616396 | -0.7734011257 | 0.209671389 | F | -4.3549552558 | -0.3811670278 | 0.0992734334 |
| C | -1.104309476 | -1.8514969637 | 0.494490485 | F | -3.2676212533 | -2.7275467074 | 0.7233767665 |
| C | -2.4826166037 | -1.6987128145 | 0.4507898751 | C | -2.736084132 | 1.9933118779 | -0.533415288 |
| C | -3.036246006 | -0.4652433171 | 0.1219501597 | F | -4.0624938253 | 2.0520476629 | -0.5481419867 |
| C | -2.2222385053 | 0.6265681292 | -0.1683879371 | F | -2.298221475 | 2.3505523422 | -1.7423357657 |
| F | -0.5798134402 | -3.0205282073 | 0.8070927635 | F | -2.2939169362 | 2.9022519632 | 0.3382009106 |
| F | 1.0391129557 | -0.919926449 | 0.2525957936 | | | | |

**1-fluoro-4-trifluoromethylbenzene (5) [$E^\circ$ = -668.2158685; $G^\circ$ = -668.154647; $E^\circ_{(THF)}$ = -668.2218556]**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 1.0832694923 | 0.4814446923 | -0.1002208628 | F | -2.2052479799 | 1.9749122529 | -0.4310973569 |
| C | 1.6572271558 | -0.7386932156 | 0.2186471118 | F | -0.3916813298 | 2.9141947242 | 0.270970681 |
| C | 0.8208202162 | -1.8146670639 | 0.4812584639 | F | -0.5458204349 | 2.2841625077 | -1.7755715156 |
| C | -0.5594292014 | -1.7087355744 | 0.4333960301 | H | 1.7110448131 | 1.3441816916 | -0.3108271108 |
| C | -1.1227119133 | -0.4800969444 | 0.1118641815 | H | 2.7332321277 | -0.8733420945 | 0.2691889085 |
| C | -0.3040458418 | 0.6119829047 | -0.152259462 | H | -1.1689461005 | -2.5810487433 | 0.6478833781 |
| F | 1.366727911 | -2.9908721159 | 0.7905444765 | H | -2.2018935124 | -0.3694729827 | 0.066805422 |
| C | -0.8725454019 | 1.946050961 | -0.5205813452 | | | | |

**TS1 [$E^\circ$ = -2224.2138581; $G^\circ$ = -2223.6431; $E^\circ_{(THF)}$ = -2224.2375395; $\nu$ = -232.92]**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.1066729102 | -0.0966664096 | -1.7489550482 | C | -3.4635378398 | 3.1649644283 | -0.7840414448 |
| C | 1.7623205895 | -0.2294816488 | -2.0175966334 | C | -2.8197586744 | 1.9465926718 | -0.5707109332 |
| C | 0.7964936723 | 0.7212677654 | -1.5934242211 | C | 2.0071880019 | -2.4761970211 | 0.4265681757 |
| C | 1.3710708917 | 1.9555383139 | -1.1828475773 | C | 2.6528540506 | -3.5822232667 | -0.1221659434 |
| C | 2.7091724821 | 2.0795553823 | -0.9014174262 | C | 1.9783071782 | -4.464534401 | -0.9574230555 |
| C | 3.6349427531 | 1.0622321765 | -1.1664082444 | C | 0.6391849761 | -4.2677122074 | -1.2571679666 |
| F | -0.3027865638 | 0.8322108573 | -2.3979646776 | C | -0.0546711501 | -3.1733680273 | -0.7411609463 |
| C | -1.5380946981 | -0.0848163144 | 1.8146835884 | C | -0.277811206 | 3.0073038452 | 2.1334113854 |
| C | -0.8303661781 | -1.2321314403 | 1.7548916473 | C | 0.6910189009 | 4.1786232975 | 1.9916204419 |
| N | -0.0536479131 | -1.1588493268 | 0.605266943 | C | -0.8339245866 | 2.9594638163 | 3.5569329781 |
| C | -0.2839871341 | -0.0066501443 | -0.0692745764 | C | -3.2404515974 | 0.7033353988 | -1.3267466918 |
| N | -1.1821392495 | 0.6606775858 | 0.6968834353 | C | -4.4394833756 | 0.0435561648 | -0.6474423666 |
| C | -1.808898275 | 1.9210193817 | 0.3992688748 | C | -3.5250758616 | 0.9771775718 | -2.7980961774 |
| C | 0.6586650988 | -2.297409856 | 0.0859453025 | C | -1.5083576385 | -2.9433443733 | -1.1064520979 |
| C | -1.4074704398 | 3.0503220389 | 1.1234596105 | C | -1.6512208852 | -2.4582316798 | -2.5495439274 |
| C | -2.0916014389 | 4.2395168917 | 0.877999713 | C | -2.3589641006 | -4.1872913439 | -0.8628499857 |
| C | -3.1110929565 | 4.2963534268 | -0.0617970044 | C | 2.7199163243 | -1.5377361921 | 1.380926093 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 2.396810064 | -1.9028473668 | 2.8319932507 | H | -1.4919486507 | 2.0973919377 | 3.7165546384 |
| C | 4.2341818959 | -1.520373805 | 1.2028045845 | H | -1.4182251005 | 3.8640519306 | 3.7707604542 |
| C | 5.0677987654 | 1.2936558561 | -0.8417584395 | H | -2.4061912739 | -0.0091290688 | -1.2977549044 |
| F | 5.5732890437 | 2.3360960916 | -1.5141089091 | H | -4.7119917037 | -0.8853705093 | -1.1657618538 |
| F | 5.2362324539 | 1.5735079527 | 0.4641719555 | H | -4.2261318339 | -0.2039517918 | 0.4001575174 |
| F | 5.8341259726 | 0.2346691518 | -1.1162914099 | H | -5.3129566142 | 0.7090498935 | -0.6629470636 |
| F | 3.8929748929 | -1.114246494 | -2.095502797 | H | -3.7079417358 | 0.0329908014 | -3.3249270539 |
| F | 1.3115289545 | -1.3465440307 | -2.6052266685 | H | -2.6746916463 | 1.4746402791 | -3.2760271991 |
| F | 0.5370950475 | 2.9806303396 | -0.9553109719 | H | -4.4171340093 | 1.6010811504 | -2.9379501388 |
| F | 3.1446687009 | 3.2384095298 | -0.4064101847 | H | -1.910112925 | -2.1515040094 | -0.4564418156 |
| H | -2.2679144692 | 0.2758020387 | 2.5257681374 | H | -2.7122106832 | -2.3080334071 | -2.7920036324 |
| H | -0.8192885459 | -2.1071967024 | 2.3892095672 | H | -1.119572719 | -1.5153290184 | -2.7182258414 |
| H | -1.8091810913 | 5.1380224462 | 1.4229417581 | H | -1.2483807894 | -3.1979997195 | -3.2536618471 |
| H | -3.6287014507 | 5.2357667216 | -0.2414686732 | H | -3.4185901827 | -3.9590521617 | -1.0294529793 |
| H | -4.2556209542 | 3.2255825019 | -1.5272045393 | H | -2.2467778545 | -4.5587399741 | 0.1624644031 |
| H | 3.703437016 | -3.7514977644 | 0.0992168886 | H | -2.0921519351 | -5.0034567245 | -1.5456371663 |
| H | 2.5072229146 | -5.3155417054 | -1.3799224839 | H | 2.3444259851 | -0.5183486431 | 1.1919697739 |
| H | 0.1249526827 | -4.9644590369 | -1.9162802779 | H | 2.9430101703 | -1.2482148546 | 3.5211757645 |
| H | 0.2998132106 | 2.085866444 | 1.9595771008 | H | 1.3298208098 | -1.8142197558 | 3.0613560928 |
| H | 0.2096964852 | 5.1337366054 | 2.2369907857 | H | 2.7027184004 | -2.9374738789 | 3.0357461364 |
| H | 1.5273963699 | 4.0528767885 | 2.6886801992 | H | 4.6639137682 | -0.6774436165 | 1.7542172759 |
| H | 1.0984054545 | 4.2481320824 | 0.9794801821 | H | 4.5370679211 | -1.4211499212 | 0.1566996617 |
| H | -0.0210449348 | 2.9044535957 | 4.2904247126 | H | 4.6886820563 | -2.4374085403 | 1.6009697661 |

**TS2 [$E^{\circ}$ = -1827.3963841; $G^{\circ}$ = -1826.792918; $E^{\circ}_{(THF)}$ = -1827.4239796; $\nu$ = -278.04]**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.0668392057 | -0.0501868355 | -1.7240385393 | C | -3.2349814672 | 0.6758873589 | -1.3407747868 |
| C | 1.72698299 | -0.2443647808 | -1.9741761392 | C | -4.4129610159 | 0.0197262385 | -0.6229140623 |
| C | 0.7536507468 | 0.7004285391 | -1.5291135831 | C | -3.5572591098 | 0.9286371335 | -2.8078818326 |
| C | 1.2589505807 | 1.9417841399 | -1.0299088305 | C | -1.492021326 | -2.9448907679 | -1.1419995332 |
| C | 2.6007568275 | 2.0998687416 | -0.7650649069 | C | -1.6215696586 | -2.4265960027 | -2.574432747 |
| C | 3.5296739277 | 1.0999088155 | -1.0762255967 | C | -2.3308261224 | -4.206200032 | -0.9470351175 |
| F | -0.3453803996 | 0.824566539 | -2.368404043 | C | 2.6805846271 | -1.5847284558 | 1.4646026481 |
| C | -1.4949619107 | -0.0475148169 | 1.8529176041 | C | 2.3970775355 | -1.9969737082 | 2.9113774026 |
| C | -0.7984568059 | -1.2024536132 | 1.8092301209 | C | 4.190161205 | -1.5178135494 | 1.2611775218 |
| N | -0.067050729 | -1.1784207504 | 0.626109267 | C | 4.9628698421 | 1.3305420703 | -0.790104164 |
| C | -0.3178612118 | -0.0536403349 | -0.0848407328 | F | 5.4652248025 | 2.3919573883 | -1.4483280934 |
| N | -1.1794985475 | 0.6509263069 | 0.6919933997 | F | 5.1882373803 | 1.5880767231 | 0.5183960542 |
| C | -1.7874788764 | 1.9100880957 | 0.3589454164 | F | 5.7291837597 | 0.2743167281 | -1.1120151152 |
| C | 0.644740369 | -2.3187073598 | 0.1156998217 | H | 3.7790581834 | -0.8014613514 | -2.0597557904 |
| C | -1.3709008387 | 3.0557745866 | 1.0516189367 | H | 1.3856957047 | -1.1373260032 | -2.4944494447 |
| C | -2.0412993204 | 4.2486381052 | 0.7788942941 | H | 0.5480073328 | 2.7442998853 | -0.8428504947 |
| C | -3.0656829153 | 4.2950359534 | -0.1549644681 | H | 2.9552660521 | 3.0410347512 | -0.3439445652 |
| C | -3.4325334662 | 3.1497944859 | -0.8482361726 | H | -2.1980956448 | 0.3414372221 | 2.5758412693 |
| C | -2.8008237105 | 1.9298865707 | -0.611291241 | H | -0.7699108104 | -2.0508159104 | 2.4777780519 |
| C | 1.9797946802 | -2.5173727494 | 0.4972587427 | H | -1.7457358668 | 5.1559590556 | 1.3019524381 |
| C | 2.6357089843 | -3.6190430867 | -0.0473678707 | H | -3.5752347256 | 5.2350126761 | -0.3536352042 |
| C | 1.9918146166 | -4.4691903211 | -0.9385945058 | H | -4.227338009 | 3.2021871575 | -1.5888680744 |
| C | 0.6677732967 | -4.2493916968 | -1.2882504105 | H | 3.6750163733 | -3.8029836477 | 0.2140997698 |
| C | -0.04230913 | -3.1708206616 | -0.7580626775 | H | 2.530310006 | -5.3129750306 | -1.3638285584 |
| C | -0.2335468697 | 3.033106533 | 2.0534392696 | H | 0.1744001436 | -4.9246785525 | -1.984871996 |
| C | 0.7291484655 | 4.2020774559 | 1.8549844967 | H | 0.3402163863 | 2.1079476359 | 1.8938141695 |
| C | -0.760995814 | 3.0358924005 | 3.4881824547 | H | 1.6263588832 | 4.0593984012 | 2.4677687464 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 1.04294395 | 4.2979307189 | 0.8097296481 | H | -2.6819272997 | -2.3104951989 | -2.8372393181 |
| H | 0.2768547662 | 5.1550599636 | 2.1577154848 | H | -1.1350270382 | -1.4523923189 | -2.7069783824 |
| H | 0.0683503224 | 3.0225710235 | 4.2051179081 | H | -1.1789605553 | -3.1321730893 | -3.2898114309 |
| H | -1.4003602459 | 2.1710852978 | 3.6986925588 | H | -3.3920625782 | -3.9828117013 | -1.1099375563 |
| H | -1.3545186209 | 3.9397927718 | 3.6780790543 | H | -2.2190875552 | -4.6148969771 | 0.0637042364 |
| H | -2.391205982 | -0.0244030369 | -1.3233283004 | H | -2.0525372592 | -4.9933039227 | -1.6589657921 |
| H | -4.6933127108 | -0.9173246036 | -1.122270674 | H | 2.2760411593 | -0.5729565937 | 1.3011325588 |
| H | -4.1729517387 | -0.2134449214 | 0.422195046 | H | 2.9270864935 | -1.3362911029 | 3.6074577057 |
| H | -5.2908748709 | 0.6797785614 | -0.6260009425 | H | 1.3321815133 | -1.9620852242 | 3.1630471826 |
| H | -3.7524948925 | -0.0232861429 | -3.3160296042 | H | 2.7507190651 | -3.0220124145 | 3.0856088116 |
| H | -2.71822245 | 1.4179010095 | -3.313412822 | H | 4.6025123412 | -0.6680101981 | 1.8153596204 |
| H | -4.4543418076 | 1.5480679358 | -2.9358055204 | H | 4.4651882748 | -1.3816397973 | 0.211763805 |
| H | -1.910191894 | -2.1751803013 | -0.4756061746 | H | 4.684388007 | -2.425178413 | 1.6333582993 |

## References

[1] X. Bantreil, S. P. Nolan, *Nat. Protoc.* **2011**, *6*, 69.

[2] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176.

[3] B. Rees, L. Jennera, M. Yusupova, *Acta Cryst. D*, **2005**, *61*, 1299.

[4] M. J. Frisch *et al.*, Gaussian 09, Revision A.02 (Gaussian, Inc., Wallingford CT, 2009).

[5]. P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213.

[6] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378.