Supporting Information for:

Synthesis of Low-Valent Uranium Fluorides by C-F Bond Activation

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General Considerations

All air- and moisture-sensitive manipulations were performed using standard Schlenk techniques or in an MBraun inert atmosphere drybox with an atmosphere of purified nitrogen. The MBraun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen as well as two −35 °C freezers for cooling samples and crystallizations. Solvents for sensitive manipulations were dried and deoxygenated using literature procedures with a Seca solvent purification system.[1] Benzene-d_6 was purchased from Cambridge Isotope Laboratories, dried with molecular sieves and sodium, and degassed by three freeze–pump–thaw cycles. Fluorinated substrates were purchased from Sigma-Aldrich, degassed via three freeze-pump-thaw cycles, and used without further purification. Elemental analyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ. Tp*$_2$UBz (**1-Bz**) was prepared according to a literature procedure.[1]

[1]H spectra were recorded on a Varian Inova 300 spectrometer operating at 299.992 MHz. ^{13}C NMR spectra were recorded on a Bruker AV500HD spectrometer equipped with a 5mm BBFO Z-gradient Cryoprobe Prodigy and operating at 500.130 MHz. ^{11}B NMR spectra were recorded on a Varian Mercury-300 spectrometer operating at a frequency of 96.24 MHz. ^{19}F NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 282.215 MHz. All chemical shifts are reported relative to the peak for SiMe$_4$, using [1]H (residual) chemical shifts of the solvent as a secondary standard. The ^{1}H NMR spectra for paramagnetic molecules were obtained by using an acquisition time of 0.5 s, thus the peak widths reported have an error of ±2 Hz. For paramagnetic molecules, the ^{1}H NMR data are reported with the chemical shift, followed by the peak width at half height in Hertz, the integration value, and where possible, the peak assignment. Electronic absorption spectroscopic measurements were recorded at 294 K in sealed 1 cm quartz cuvettes with a Jasco V-6700 spectrophotometer.

The capillary gas chromatography/mass spectrometry analyses were carried out with an Agilent 5975C (Agilent Laboratories, Santa Clara, CA, USA) mass spectrometer system. Typical electron energy was 70 eV with the ion source temperature maintained at 250 °C. The individual components were separated by using a 30 m HP-5 capillary column (250 μm i.d. × 0.25 μm film thickness). The initial column temperature was set at 100 °C (for 0.1 min) and programmed to reach 320 °C with a ramp of 10.0 °C/min. The flow rate was set at 1 mL/min, and the injector was set at 250 °C.

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Single crystals of **Tp*₂UF (1-F)** suitable for X-ray diffraction were coated with poly(isobutylene) oil in a glovebox and quickly transferred to the goniometer head of a Nonius Kappa CCD equipped with a graphite crystal, incident beam monochromator. Preliminary examination and data collection were performed with a Mo Kα radiation (λ = 0.71073 Å). Single crystals of **Tp*₂UF₂ (1-F₂)** suitable for X-ray diffraction were coated with poly(isobutylene) oil in a glovebox and quickly transferred to the goniometer head of a Rigaku Rapid II image plate diffractometer equipped with a MicroMax002+ high intensity copper X-ray source with confocal optics. Preliminary examination and data collection were performed with Cu Kα radiation (λ = 1.54184 Å). Cell constants for data collection were obtained from least-squares refinement. The space group was identified using the program XPREP.[6] The structures were solved using the structure solution program PATTY in DIRDIFF99. Refinement was performed on a LINUX PC using SHELX-97.[10] The data were collected at a temperature of 150(1) K.

Crystal data for **1-F** (CCDC# - 1406897). $C_{34}H_{45}B_2FN_{12}OU$, M = 1724.87, triclinic, a = 10.4532(3), b = 11.0258(3), c = 18.1147(7) Å, α = 102.1530(10), β = 98.0670(10), γ = 96.7400(10)°, V = 1997.41(11) Å³, T = 200(1) K, space group P-1 (no. 2), Z = 2, 26856 reflections measured, 9438 unique (R_{int} = 0.036) which were used in all calculations. The final w$R(F^2)$ was 0.073 (all data).

Crystal data for **1-F₂** (CCDC# - 1406898). $C_{30}H_{43}B_2F_2N_{12}U$, M = 869.41, monoclinic, a = 11.7840(6), b = 22.3831(10), c = 17.0603(7) Å, β = 93.165(3)°, V = 4493.0(4) Å³, T = 200(1) K, space group P 1 21/n 1 (No. 14), Z = 4, 35248 reflections measured, 7912 unique (R_{int} = 0.115) which were used in all calculations. The final w$R(F^2)$ was 0.173 (all data).

Synthesis of Tp*₂UF (1-F) from 1-Bz. A 20 mL scintillation vial was charged with **1-Bz** (0.250 g, 0.27 mmol) in 14 mL of tetrahydrofuran. While stirring, 1,2,3,4,5-pentafluorotoluene (0.0343 mL, 0.27 mmol) was added via microsyringe resulting in a colour change from green to brown. The volatiles were removed *in vacuo*. The resulting dark brown solid was washed with pentane until the washings ran clear, to give the product Tp*₂UF (216 mg, 0.25 mmol, 94%). Single, X-ray quality crystals were obtained by cooling a tetrahydrofuran/pentane/benzene (10/1/0.5) solution to -35 ºC. Elemental analysis of $C_{30}H_{44}N_{12}B_2FU$: Calculated, C, 41.32; H, 5.21; N, 19.74; Found, C, 41.18; H, 5.32; N, 19.59. ¹H NMR (C_6D_6, 25 ºC) δ (ppm) = -8.54 (27, 18H, *endo*-(CH₃)6), -2.41 (18, 18H, *exo*-(CH₃)6), 6.91 (4, 6H, pyr-CH). ¹³C NMR (THF-d_8, 25 ºC) δ (ppm) = 150.39, 144.87, 74.94, 19.97, -21.55. ¹¹B NMR (THF-d_8, 25 ºC) δ (ppm) = -7.8.

Synthesis of Tp*$_2$UF$_2$ (1-F$_2$) from 1-Bz. A 20 mL scintillation vial was charged with Tp*$_2$UBz **(1-Bz)** (0.250 g, 0.27 mmol) in 14 mL of tetrahydrofuran. With stirring, pentafluorobenzene (30.0 μL, 0.27 mmol) was added via microsyringe resulting in an initial colour change from green to brown, then to blue, which slowly turned to a translucent light brown. The volatiles were removed *in vacuo*. The resulting light brown solid was washed with pentane until the washings ran clear, to give the product Tp*$_2$UF$_2$ (181 mg, 0.21 mmol, 77%). Single, X-ray quality crystals were obtained by slow diffusion of a hexane/pentane (1/0.5) solution into a concentrated tetrahydrofuran solution at -35 °C. Elemental analysis of C$_{30}$H$_{44}$N$_{12}$B$_2$F$_2$U: Calculated, C, 41.40; H, 5.10; N, 19.31; Found, C, 41.4; H, 5.01; N, 19.22. ^{1}H NMR (C$_6$D$_6$, 25 ºC) δ = -7.61 (3, 18H, *endo*-(CH$_3$)6), 6.87 (2, 6H, pyr-CH), 19.31 (4, 18H, *exo*-(CH$_3$)6). ^{13}C NMR (THF-d_8, 25 ºC) δ (ppm) = 147.30, 133.20, 128.98, 33.99, 5.85. ^{11}B NMR (THF-d_8, 25 ºC) δ (ppm) = -63.7.

Alternate synthesis of Tp*$_2$UF$_2$ (1-F$_2$) from 1-Bz. A 20 mL scintillation vial was charged with Tp*$_2$UBz **(1-Bz)** (0.250 g, 0.27 mmol) in 14 mL of tetrahydrofuran. With stirring, perfluorodecalin (65.6 μL, 0.27 mmol) was added via microsyringe resulting in an initial colour change from green to brown, which slowly turned to a translucent light brown. The volatiles were removed *in vacuo*. The resulting light brown solid was washed with pentane until the washings ran clear, to give the product Tp*$_2$UF$_2$ in 68% yield. ^{1}H and ^{13}C analysis showed the material to be **1-F$_2$**.

General reaction of 1-Bz with substrates. A 20 mL scintillation vial was charged with **1-Bz** (0.250 g, 0.27 mmol) in 14 mL of tetrahydrofuran. Substrate (0.27 mmol) was added to the reaction mixture via microsyringe, while stirring at room temperature. The reaction was allowed to stir, between 15 minutes and 24 hours, depending on the substrate. The volatiles were removed *in vacuo*. The resulting solids were washed with pentane until the washings ran clear. Where possible, the organic products were isolated from the pentane washings. The washings were combined, concentrated *in vacuo*, and passed through an alumina column (mobile phase: pentane). The volatiles were removed under reduced pressure to give the organic products. In some instances, the products were submitted for analysis by GC/MS.

2,3,5,6-tetrafluoro-4-benzyl-toluene expected mass: 254.07; observed mass (EI, CI): 254, 255.

1,2,3,4,5-pentafluoro-6-benzyl-benzene expected mass: 258.05; observed mass (EI, CI): 258, 259.

1,2,4,5-tetrafluoro-6-benzyl-3-(trifluoromethyl)benzene expected mass: 308.04; observed mass (EI, CI): 308, 309.

Perfluorodecalin reaction (reaction time/product/yield): 1 hour, Tp*$_2$UF$_2$ (68%)

Perfluorocyclohexene reaction (reaction time/product/yield): 1 hour, Tp*$_2$UF$_2$ (74%)

Tetrafluorotoluene reaction (reaction time/product/yield): 1 hour, Tp*$_2$UF$_2$ (75%)

NMR tube reaction between 1-Bz and pentafluorobenzene. A J-Young tube was charged with **1-Bz** (0.025 g, 0.027 mmol) in approx. 0.7 mL of tetrahydrofuran. Pentafluorobenzene (4.5 mg, 3.00 μL, 0.027 mmol) was added *via* microsyringe, and the tube was capped and inverted multiple times to mix. Continuous mixing was accomplished by attaching the sample to a mechanically rotated spindle. NMR spectra (^{1}H, ^{11}B, and ^{19}F) were recorded at various time points over the course of 48 hrs. During this time, the solution colour changed from green to purple, then blue, and finally light brown.

NMR tube reaction between 1-Bz and 2,3,5,6-tetrafluorotoluene. A J-Young tube was charged with **1-Bz** (0.025 g, 0.027 mmol) in approx. 0.7 mL of tetrahydrofuran. 2,3,5,6-tetrafluorotoluene (4.4 mg, 3.29 μL, 0.027 mmol) was added *via* microsyringe, and the tube was capped and inverted multiple times to mix. Continuous mixing was accomplished by attaching the sample to a mechanically rotated spindle. NMR spectra (^{1}H, ^{11}B, and ^{19}F) were recorded at various time points over the course of 72 hrs. During this time, the solution colour changed from green to purple, then blue, and finally light brown. Note: This reaction is significantly slower than the reaction with pentafluorobenzene and needs vigorous stirring to go to completion.

Benzyne trapping reaction with anthracene. A 20 mL scintillation vial was charged with **1-Bz** (0.250 g, 0.27 mmol) in 14 mL of tetrahydrofuran. Anthracene (144.7 mg, 0.81 mmol) was added to the solution as a solid. Pentafluorobenzene (45.5 mg, 30.0 μL, 0.27 mmol) was added to the reaction mixture via microsyringe, while stirring at room temperature. The reaction was allowed to stir for 24 hours, and the volatiles were removed *in vacuo*. The resulting solids were washed with pentane until the washings ran clear. The pentane washings were concentrated under vacuum and passed through an alumina column (mobile phase: pentane). The volatiles were removed under reduced pressure to give the organic products. The ^{19}F NMR spectra was recorded and the sample was submitted for analysis by GC/MS. 1,2,4,5-tetrafluoro-3-benzyl-benzene expected mass: 240.06; observed mass (EI, CI): 239.95, 241.00. 1,2,3,4-tetrafluorotriptycene expected mass: 326.29; observed mass (EI, CI): 325.95, 326.95.
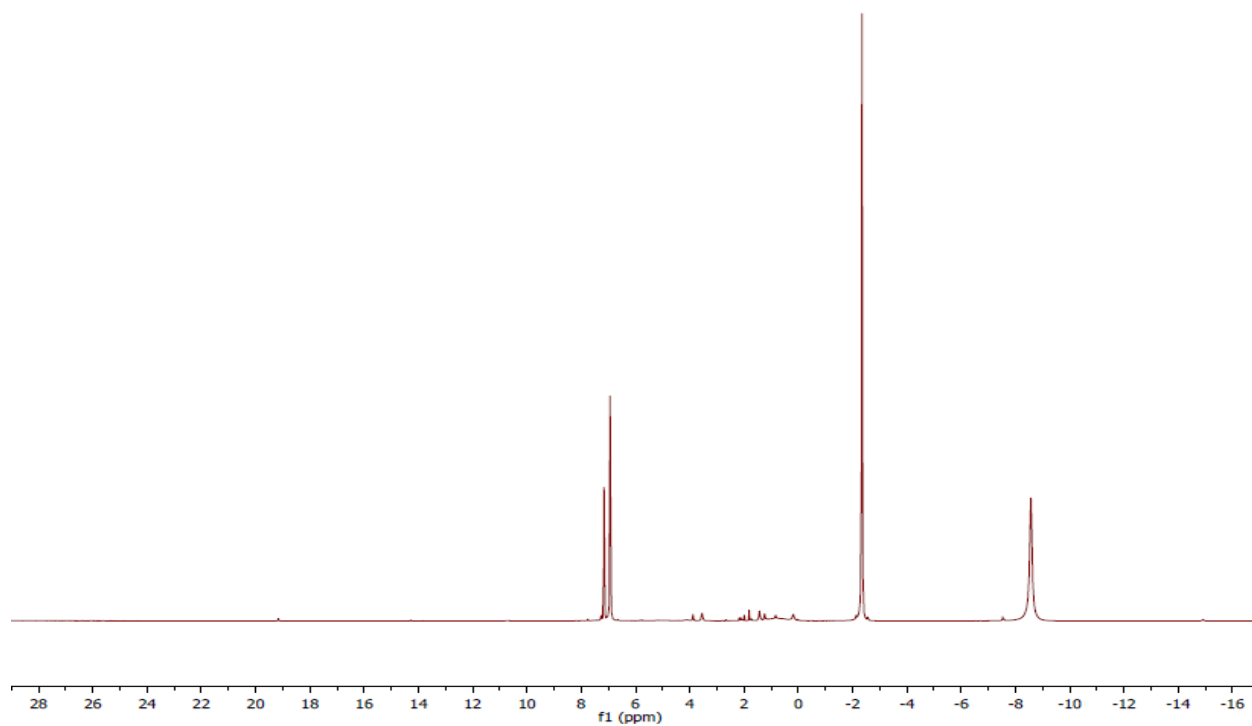
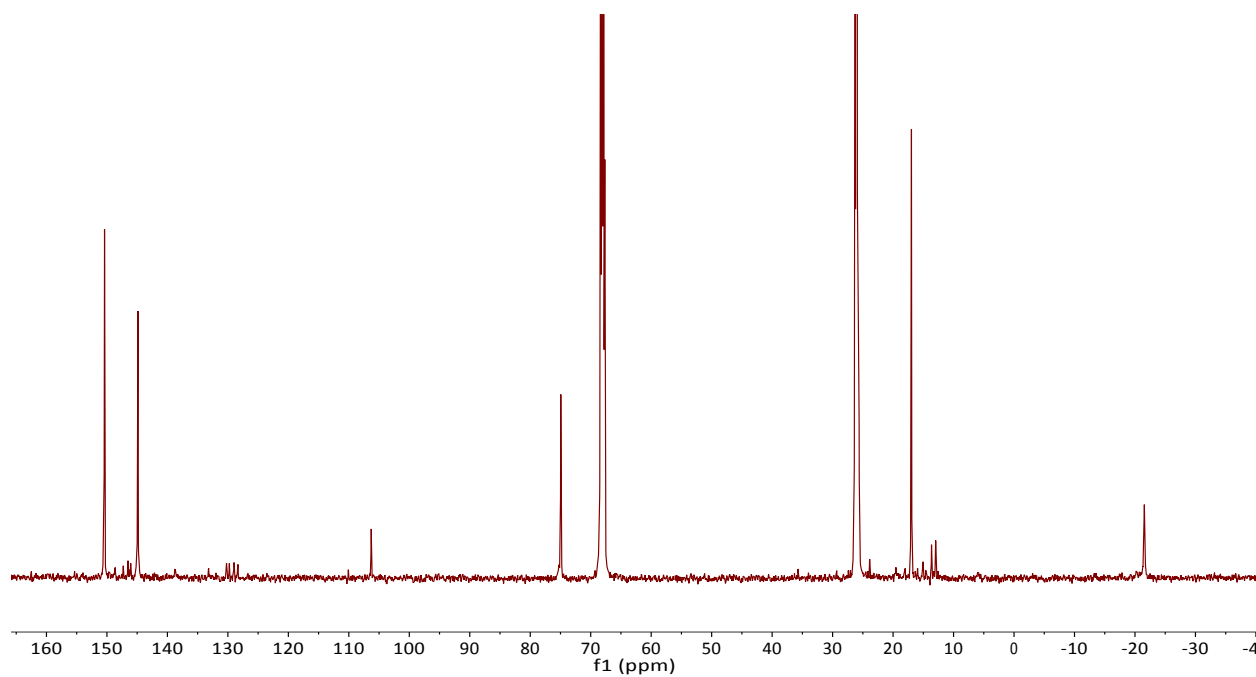**Figure S1.** ^{1}H NMR spectrum of **Tp*$_2$UF** (**1-F**) (C$_6$D$_6$, 23 °C).

Figure S2. ^{13}C NMR spectrum of **Tp*$_2$UF** (**1-F**) (THF-d_8, 23 °C).

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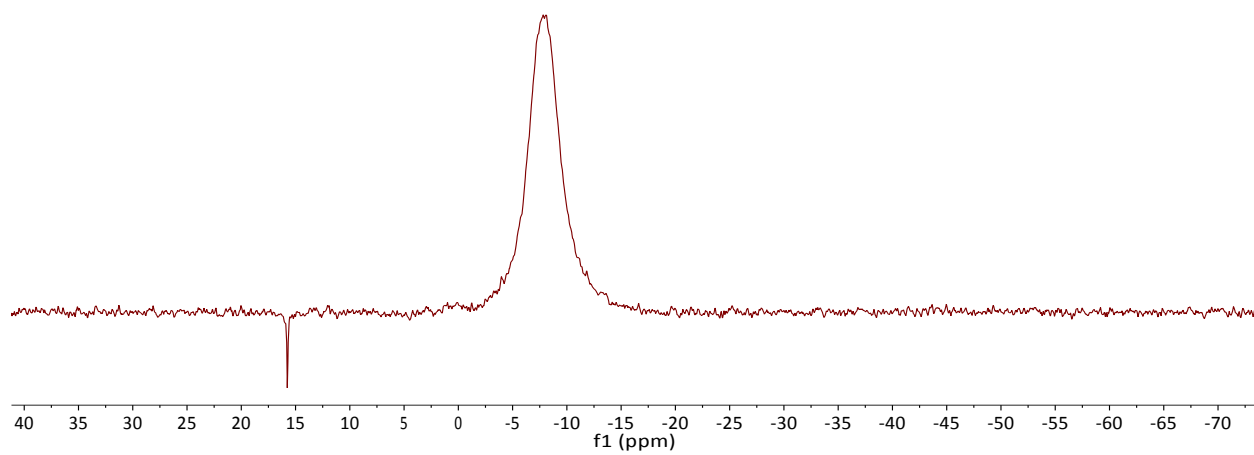
Figure S3. ^{11}B NMR spectrum of **Tp*₂UF (1-F)** (THF-d_8, 23 °C).
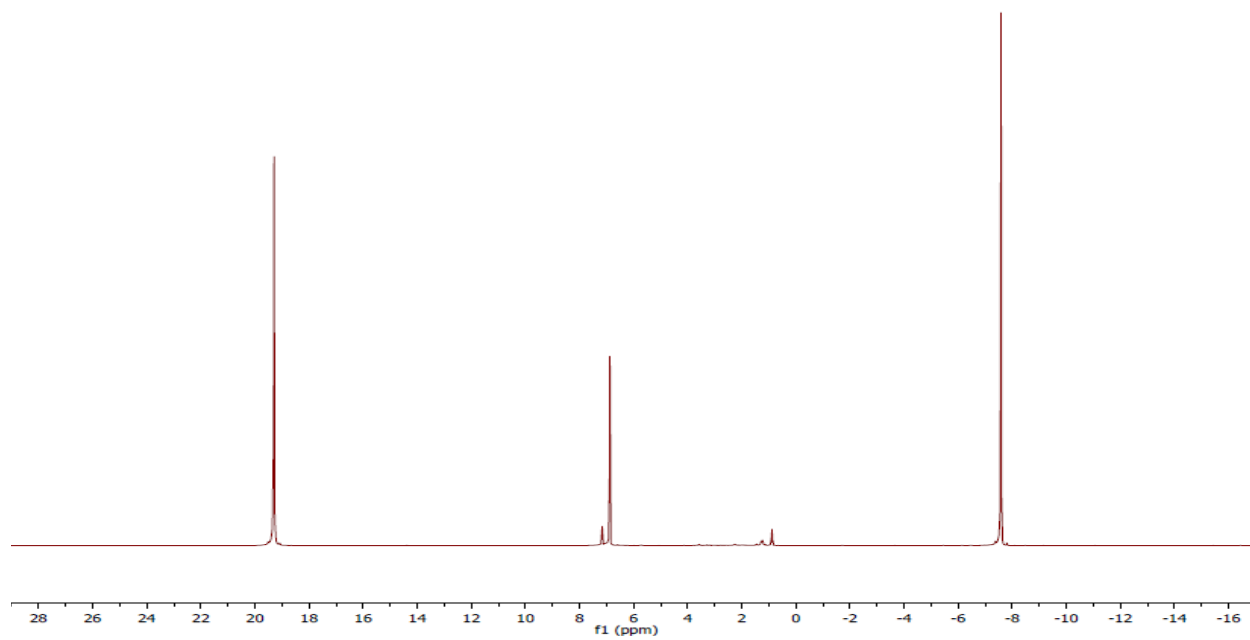
Figure S4. ^1H NMR spectrum of **Tp*₂UF₂ (1-F₂)** (C₆D₆, 23 °C).
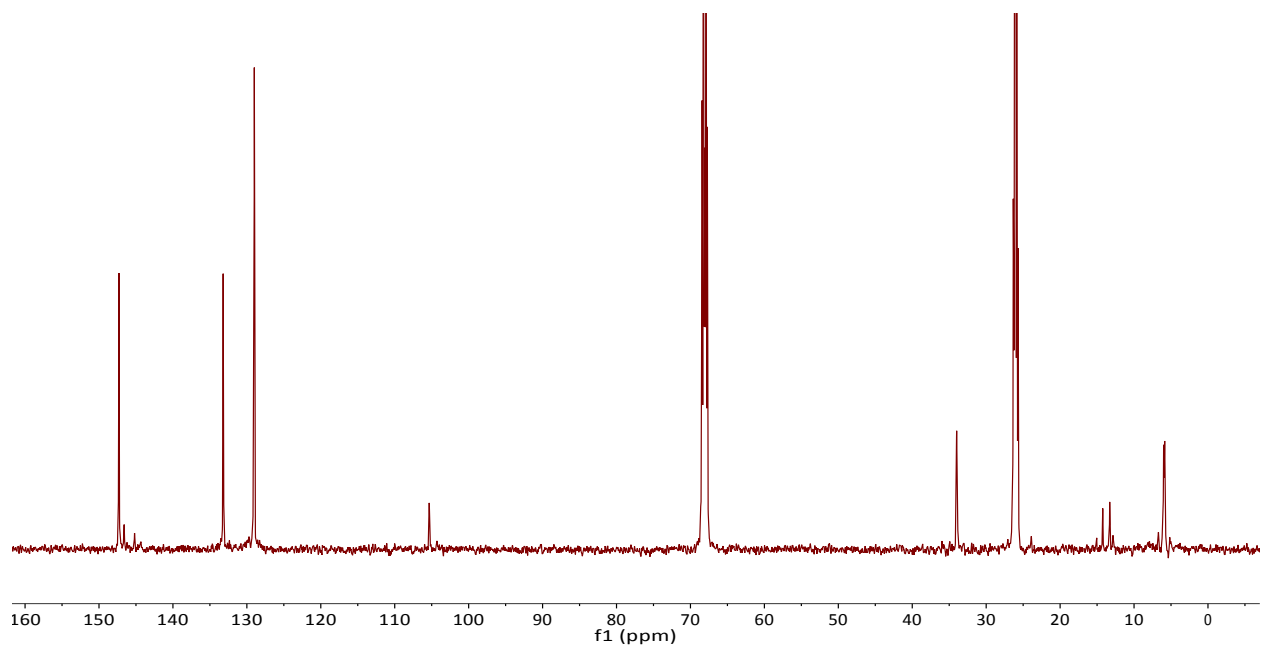
Figure S5. ^{13}C NMR spectrum of **Tp*$_2$UF$_2$ (1-F$_2$)** (THF-d_8, 23 °C).
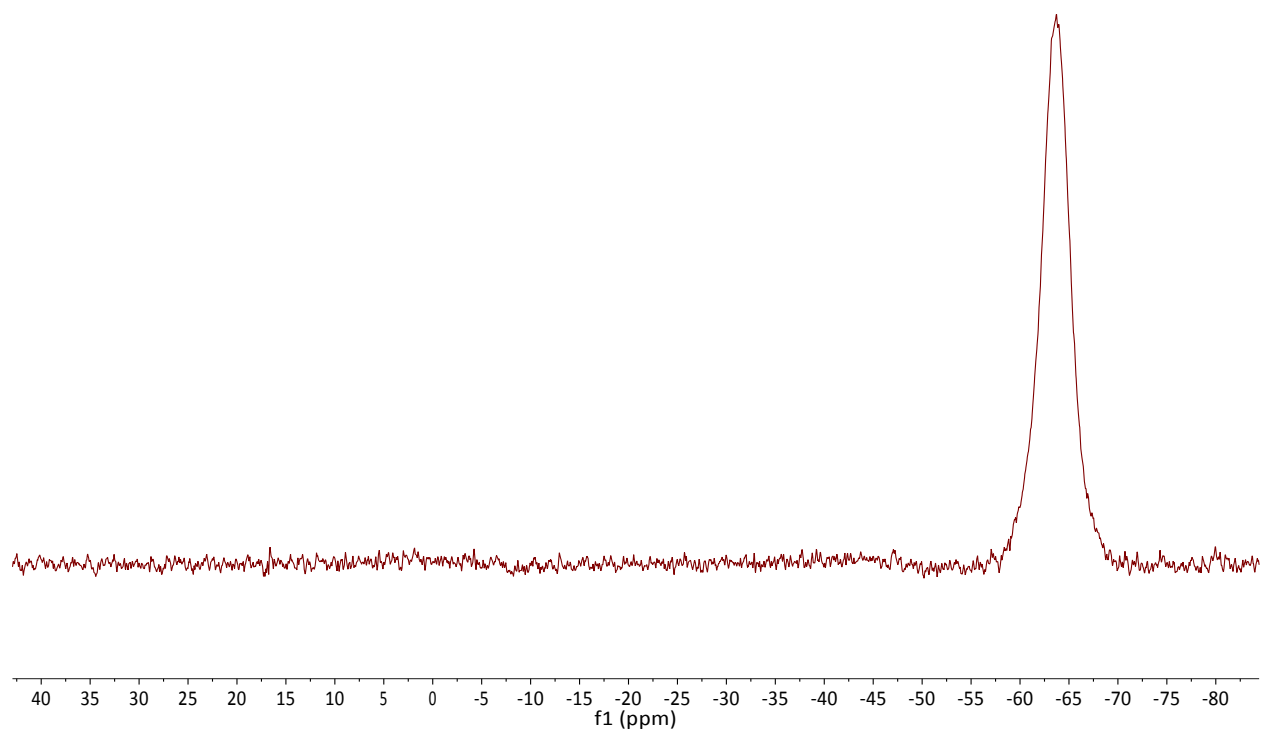
Figure S6. ^{11}B NMR spectrum of **Tp*$_2$UF$_2$ (1-F$_2$)** (THF-d_8, 23 °C).
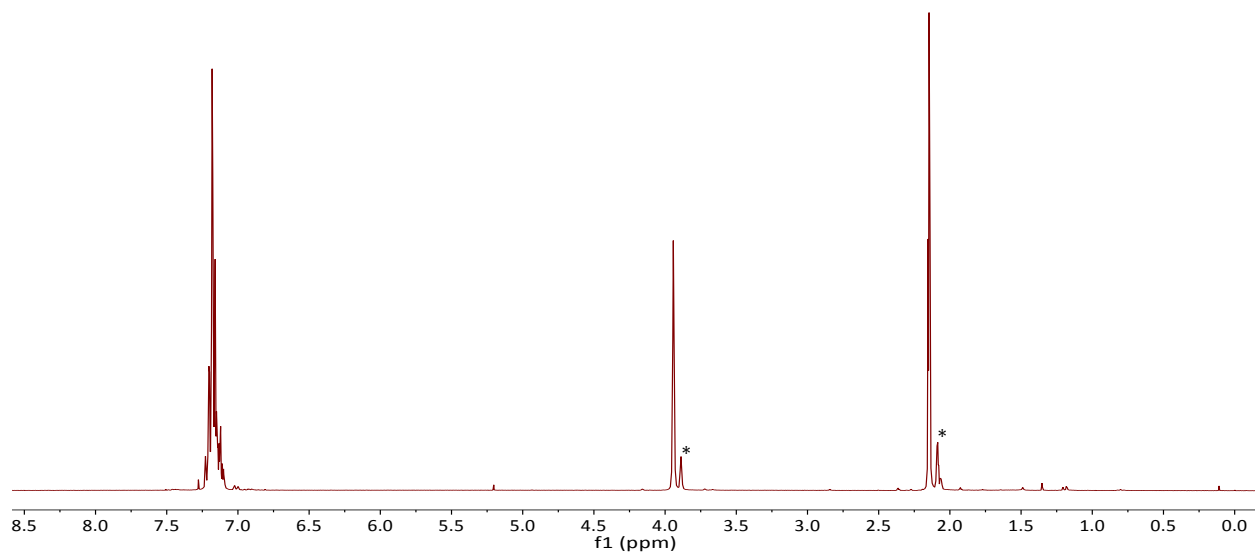
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Figure S7. ^{1}H NMR (CDCl$_3$) of 2,3,5,6-tetrafluoro-4-benzyl-toluene from reaction of **1-Bz** with 1,2,3,4,5-pentafluorotoluene. * 2,4,5,6-tetrafluoro-3-benzyl-toluene isomer (8% by integration).

Figure S8. ^{19}F NMR (CDCl$_3$) of 2,3,5,6-tetrafluoro-4-benzyl-toluene from reaction of **1-Bz** with 2,3,4,5,6-pentafluorotoluene. * 2,4,5,6-tetrafluoro-3-benzyl-toluene isomer (8% by integration).
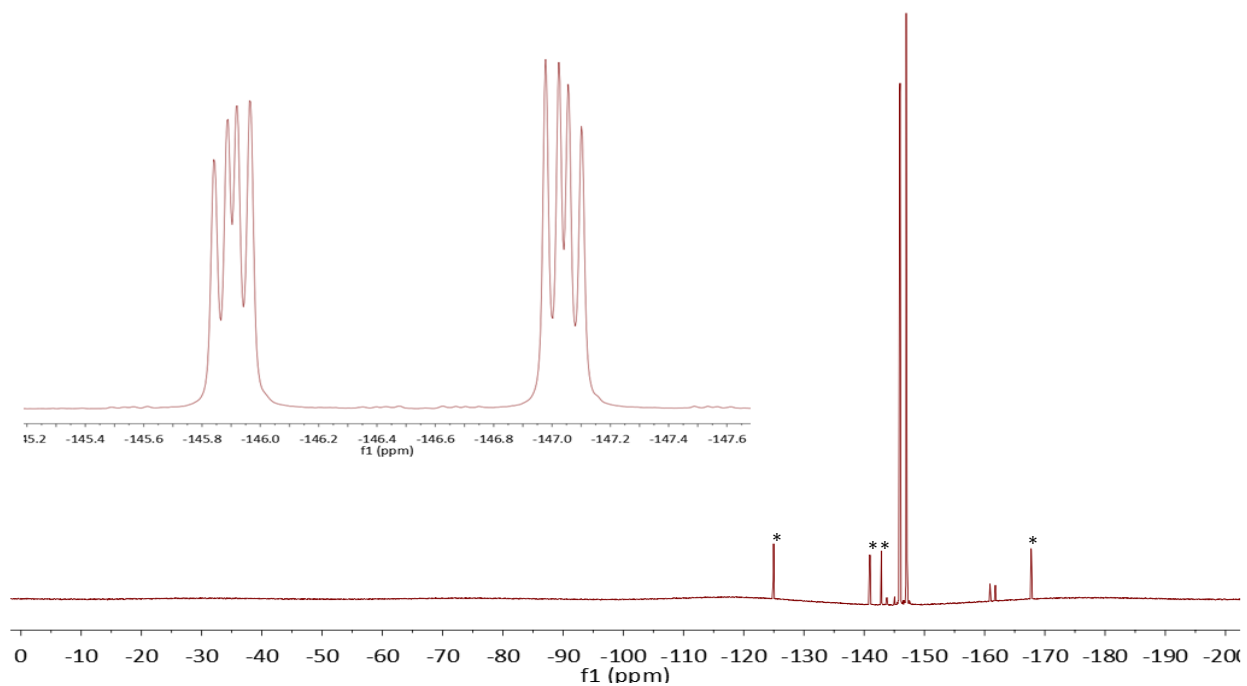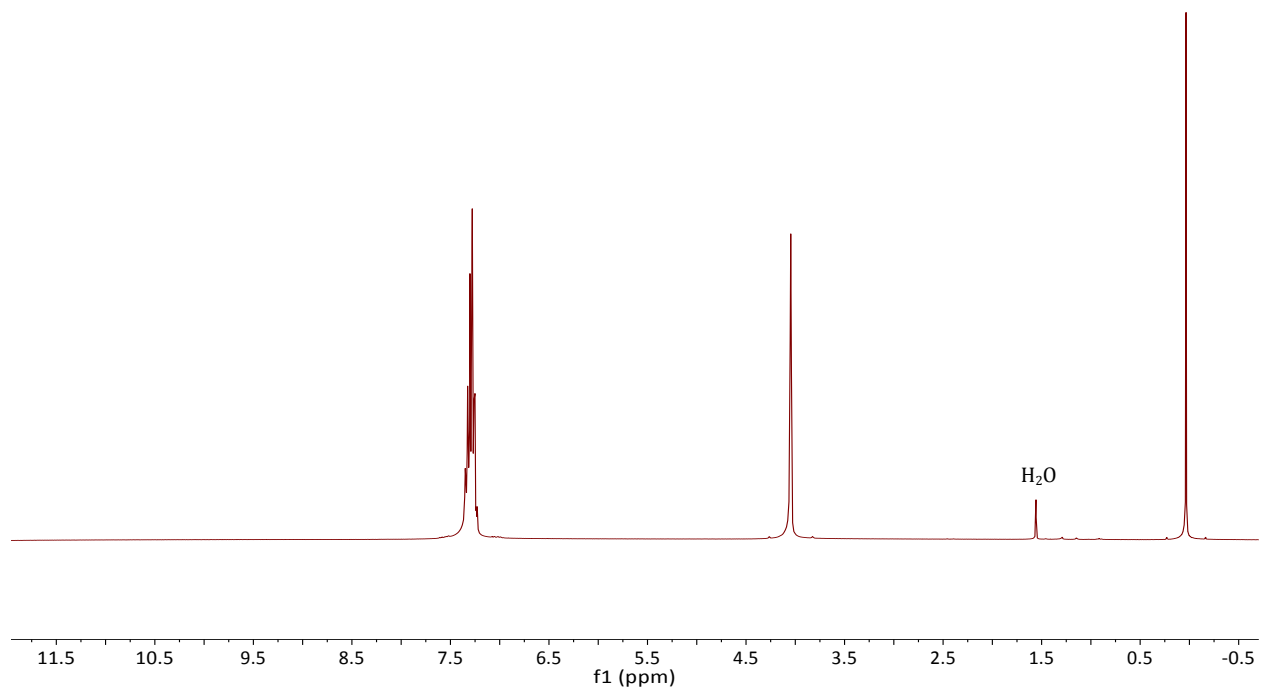
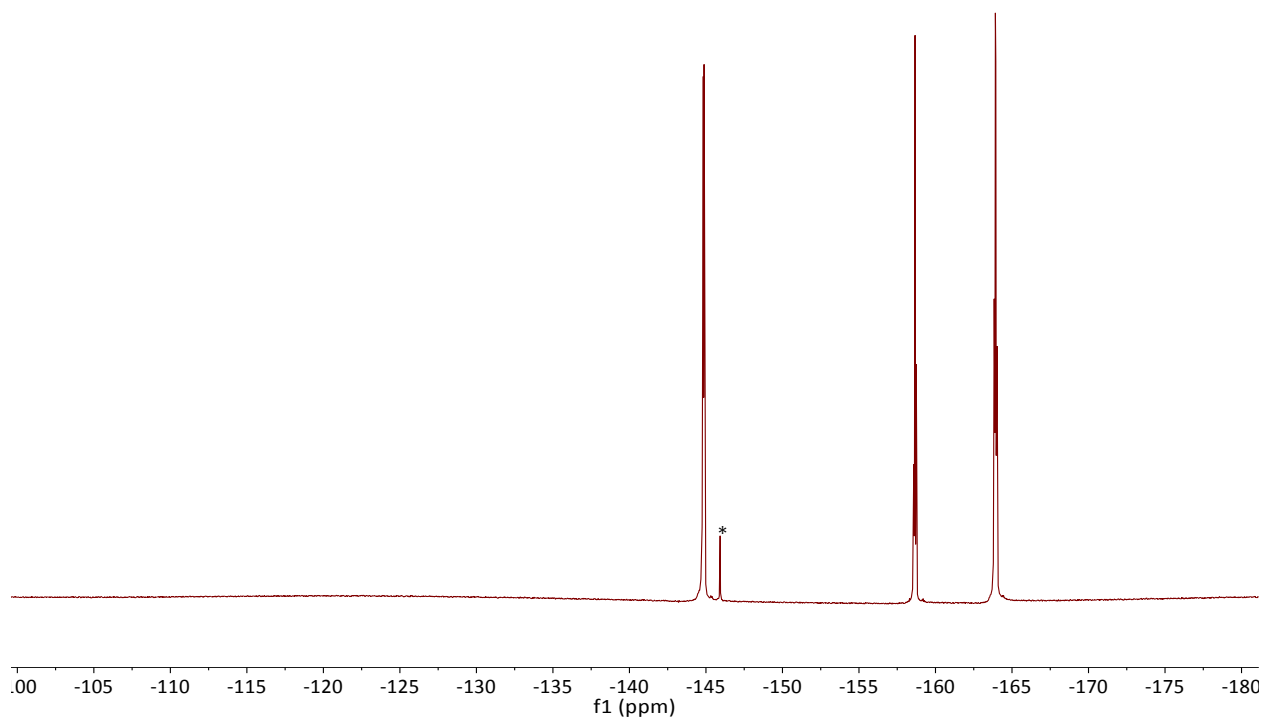**Figure S9.** ^{1}H NMR (CDCl$_3$, 1% v/v TMS) spectrum of 1,2,3,4,5-pentafluoro-6-benzyl-benzene

Figure S10. ^{19}F NMR (CDCl$_3$, 1% v/v TMS) spectrum of 1,2,3,4,5-pentafluoro-6-benzyl-benzene. * Unreacted C$_6$F$_6$ (< 1% by integration).
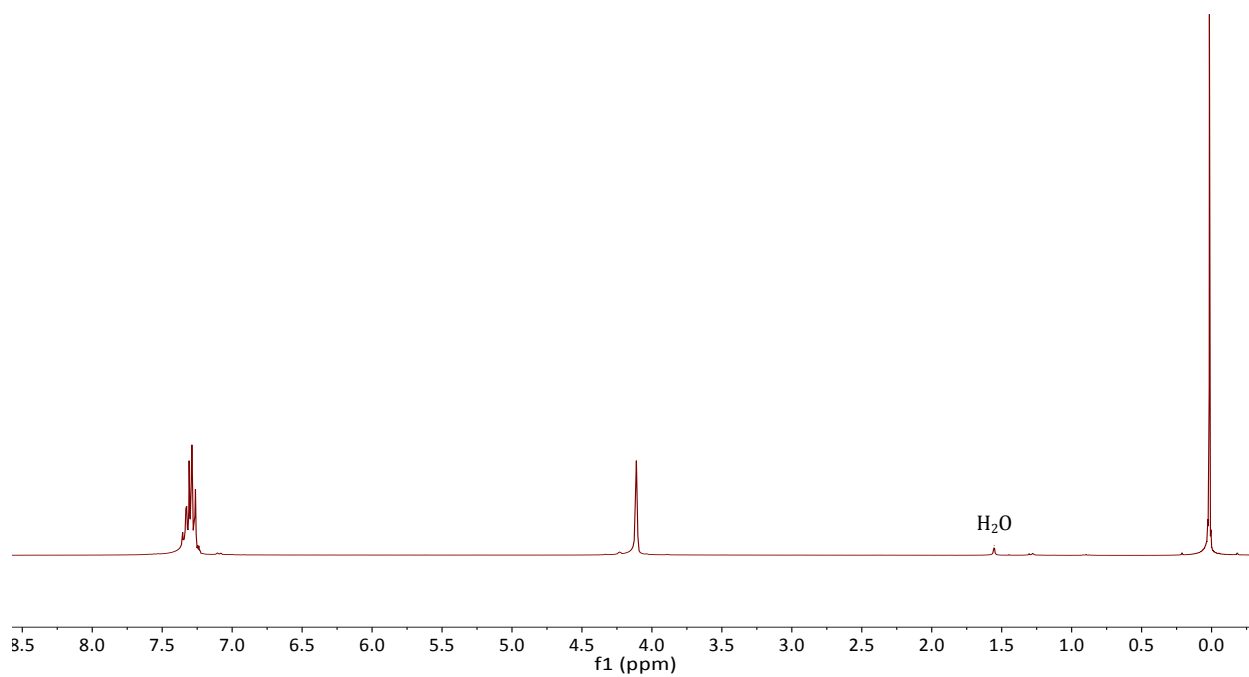
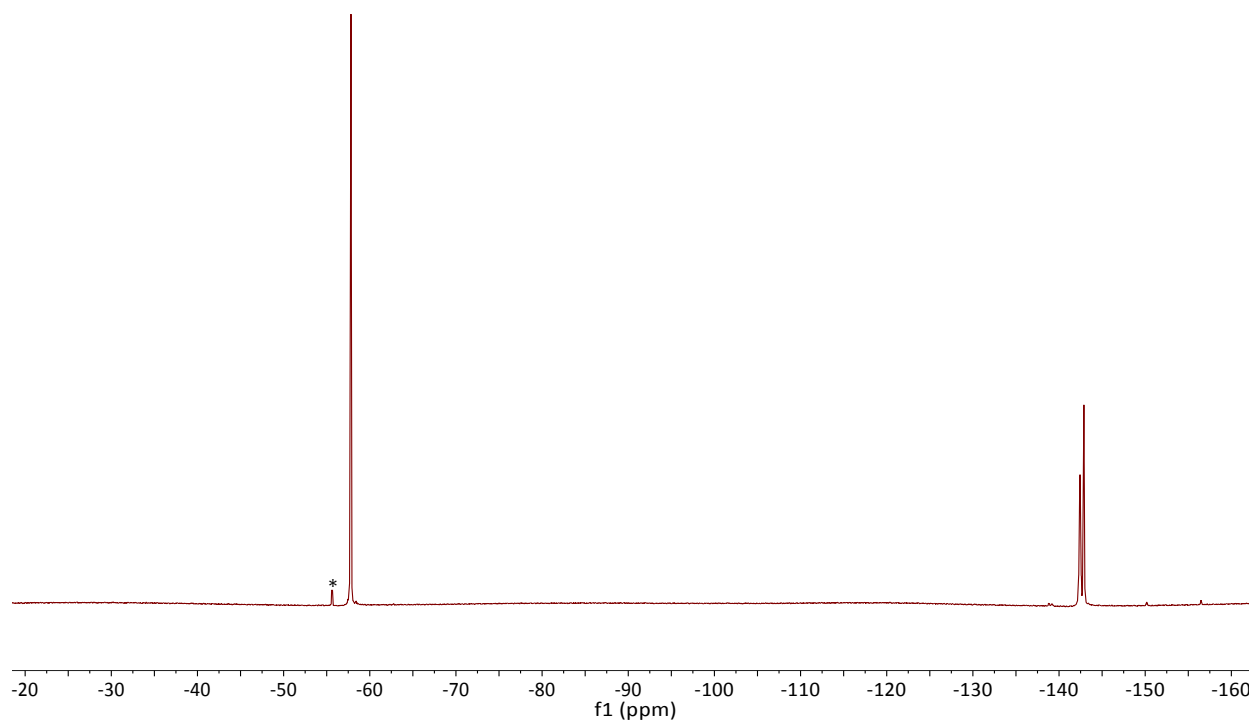**Figure S11**. ^{1}H NMR (CDCl$_3$, 1% v/v TMS) spectrum of 1,2,4,5-tetrafluoro-6-benzyl-3-(trifluoromethyl)benzene

Figure S12. ^{19}F NMR (CDCl$_3$, 1% v/v TMS) spectrum of 1,2,4,5-tetrafluoro-6-benzyl-3-(trifluoromethyl)benzene.
* Unreacted C$_6$F$_5$CF$_3$ (< 2% by integration).

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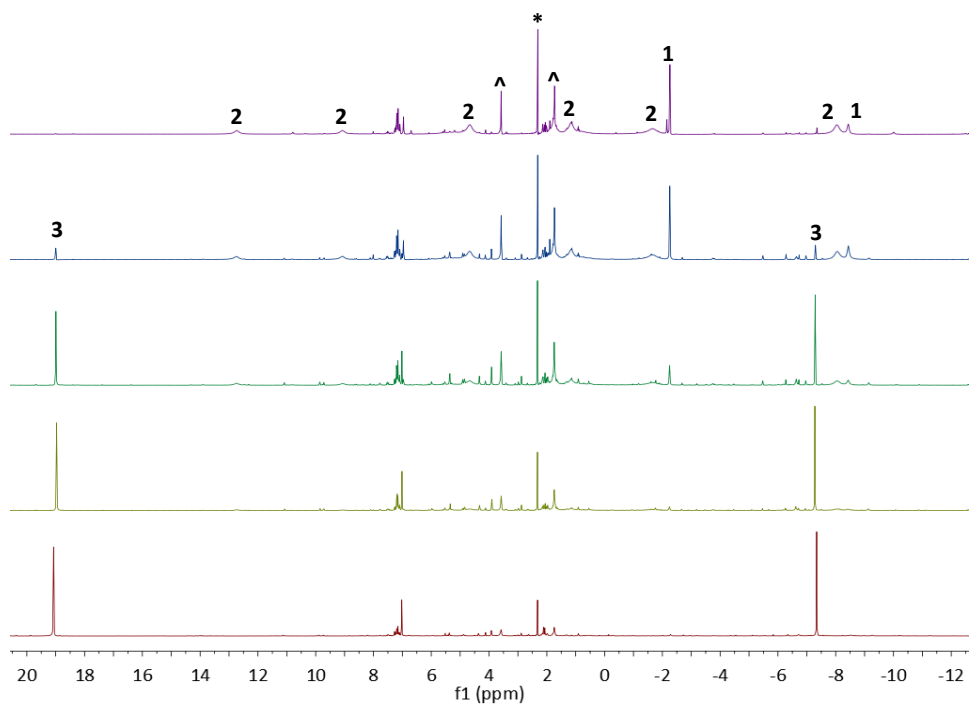
Figure S13. ^{1}H NMR (THF-d_8) spectrum of NMR tube reaction between **1-Bz** and pentaflurobenzene.
[1] **1-F**. [2] **1-F*** (another broad peak is not shown at -32.13 ppm). [3] **1-F$_2$**. ^ Residual THF. * Toluene produced during the reaction. Time points from top to bottom: 5 min., 40 min., 90 min., 190min., 28.5 hrs.
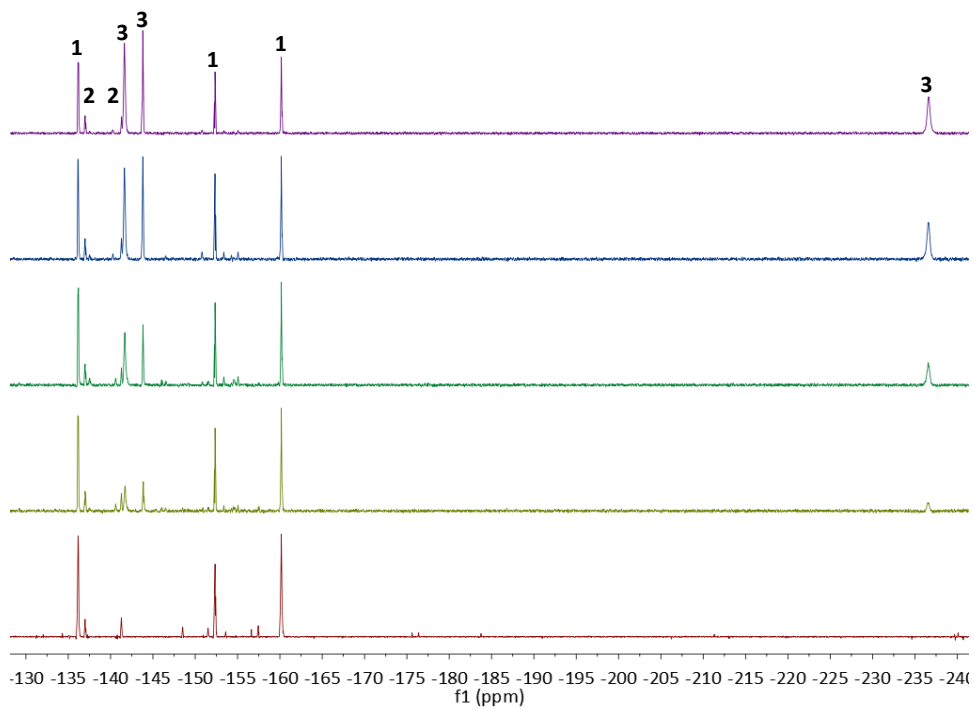
Figure S14. ^{19}F NMR (THF-d_8) spectrum of NMR tube reaction between **1-Bz** and pentafluorobenzene
[1] Unreacted pentafluorobenzene. [2] 1,2,4,5-tetrafluoro-3-benzyl-benzene. [3] **1-F***. Time points from top to bottom: 5 min., 40 min., 90 min., 190min., 28.5 hrs.

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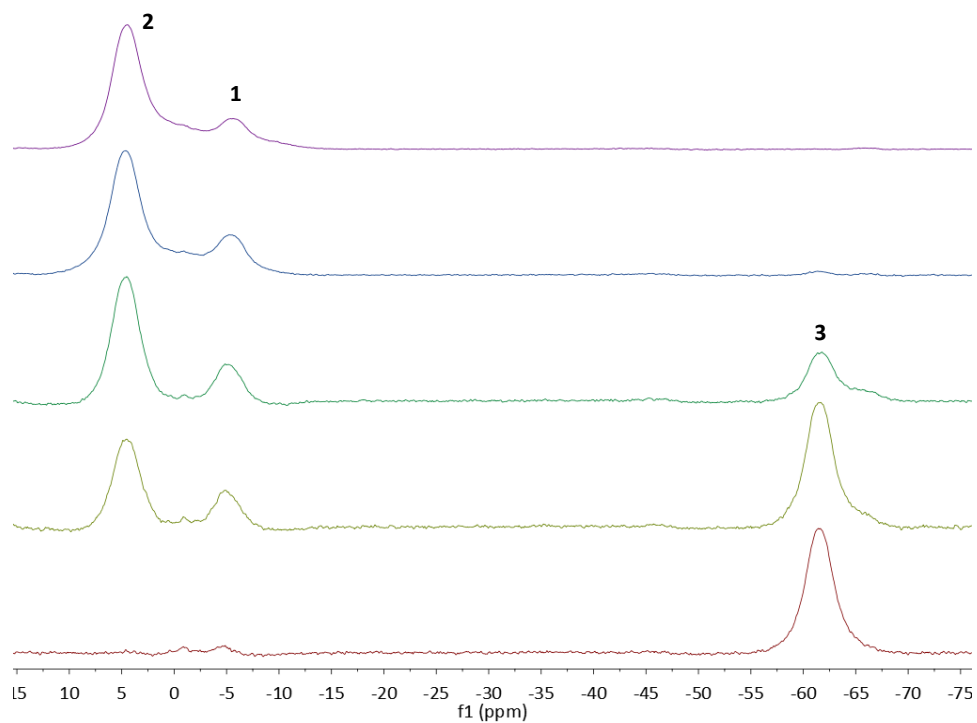
Figure S15. ^{11}B NMR (THF-d_8) spectrum of NMR tube reaction between **1-Bz** and pentaflurobenzene [1] **1-F**. [2] **1-F***. [3] **1-F$_2$**. Time points from top to bottom: 5 min., 40 min., 90 min., 190min., 28.5 hrs.
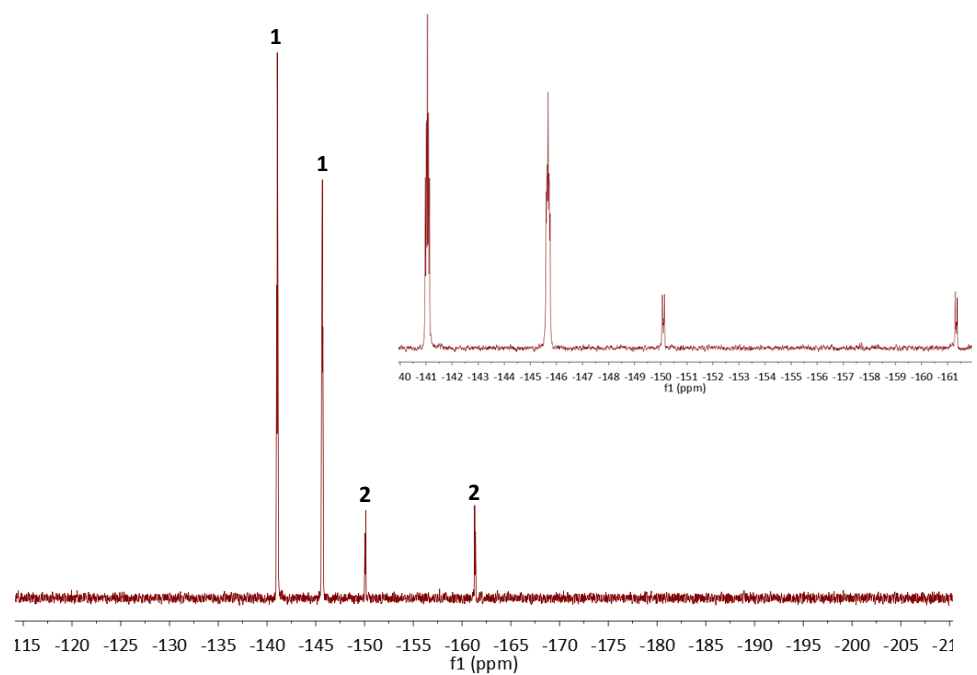
Figure S16. ^{19}F NMR (CDCl$_3$) spectrum of benzyne trapping experiment with anthracene. [1] 1,2,4,5-tetrafluoro-3-benzyl-benzene. [2] 1,2,3,4-tetrafluorotriptycene.

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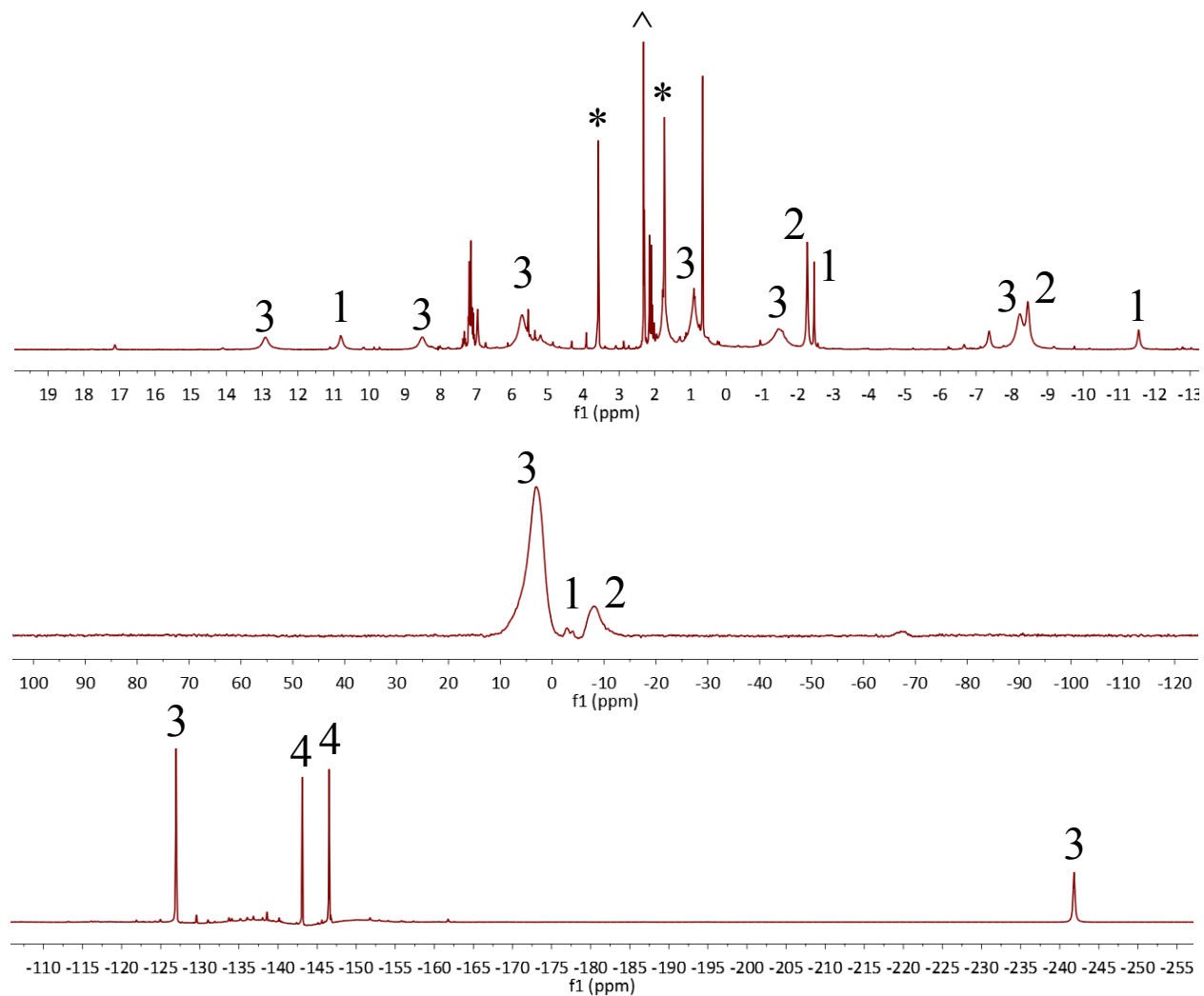
Figure S17. ¹H (top), ¹¹B (middle), and ¹⁹F (bottom) NMR (THF-d_8) spectrum of NMR tube reaction between **1-Bz** and 2,3,5,6-tetrafluorotoluene at the 60 minute timepoint. ¹ **1-F**. ² **1-Bz**. ³ 1-F*-analogue, ⁴ C₆F₄HMe, * Residual THF, ^ Toluene. Note: the signals for **1-Bz** and **1-F** in the ¹¹B NMR are not resolved.

1F - C$_{30}$H$_{37}$B$_2$FN$_{12}$U,C$_4$H$_8$O (CCDC# - 1406897)
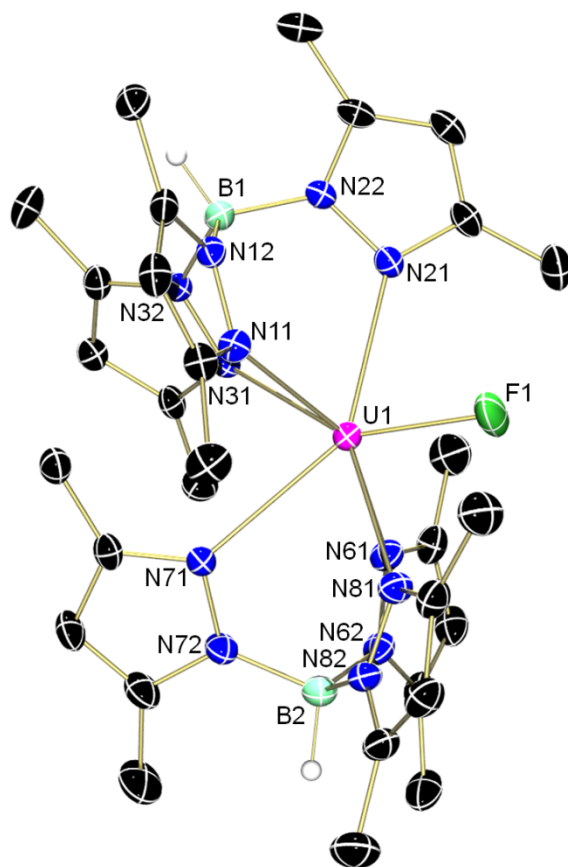
Table S1. Select Bond distances for **1-F**.

Bond	Bond Length (Å)	Bond	Bond Length (Å)
U1 – F1	2.156(3)	U1 – N61	2.542(4)
U1 – N11	2.552(3)	U1 – N71	2.739(3)
U1 – N21	2.640(4)	U1 – N81	2.604(4)
U1 – N31	2.644(3)		

DATA COLLECTION

A brown plate of C$_{30}$H$_{37}$B$_2$FN$_{12}$U,C$_4$H$_8$O having approximate dimensions of 0.25 x 0.25 x 0.12 mm was mounted on a nylon loop in a random orientation. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.71073 Å) on a Nonius Kappa CCD equipped with a graphite crystal, incident beam monochromator.

Cell constants for data collection were obtained from least-squares refinement, using the setting angles of 26856 reflections in the range 1 < θ < 27°. The triclinic cell parameters and calculated volume are: a = 10.4532(3) Å, b = 11.0258(3) Å, c = 18.1147(7) Å, α = 102.1530(10)°, β =98.0670(10)°, γ = 96.7400(10)°, V = 1997.41(11) Å^3. For Z = 2 and F.W. = 916.47 g/mol, the calculated density is 1.52 g/cm^3. The refined mosaicity from DENZO/SCALEPACK[2] was 0.57° indicating moderate crystal quality. The space group was determined by the program ABSEN.[3] There were no systematic absences; the space group was determined to be P-1 (#2).

The data were collected at a temperature of 200(1) K. Data were collected to a maximum 2θ of 55.7°.

DATA REDUCTION

A total of 26856 reflections were collected, of which 9438 were unique. Frames were integrated with HKL3000.[2]

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 41.1/mm for Mo Kα radiation. An empirical absorption correction using SCALEPACK[2] was applied. Transmission coefficients ranged from 0.216 to 0.611. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 4.3% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by direct methods using SIR2004[4]. The remaining atoms were located in succeeding difference Fourier syntheses. Some hydrogen atoms were constrained while others were independent. See cif file for more details. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$ and the weight w is defined as $w = 1/[\sigma^2(F_o^2)+(0.0378P)^2]$ where $P=(F_o^2+2 F_c^2)/3$. Scattering factors were taken from the "International Tables for Crystallography".[5] 9438 reflections were used in the refinements. However, only the 7259 reflections with $F_o^2 > 2\sigma(F_o^2)$ were used in, calculating R1. The final cycle of refinement included 469 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted agreement factors of:

$R1 = \Sigma |F_o - F_c| / \Sigma F_o = 0.036$
$R2 = SQRT (\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2) = 0.073$

The goodness-of-fit parameter was 0.97. The highest peak in the final difference Fourier had a height of 1.00 e/A^3. The minimum negative peak had a height of -1.39 e/A^3.

Refinement was performed on a LINUX PC using SHELX 2013[6]. Crystallographic drawings were done using programs ORTEP[7],and PLUTON[8].

1-F$_2$ - **C$_{30}$H$_{43}$B$_2$F$_2$N$_{12}$U** (CCDC# - 1406898)
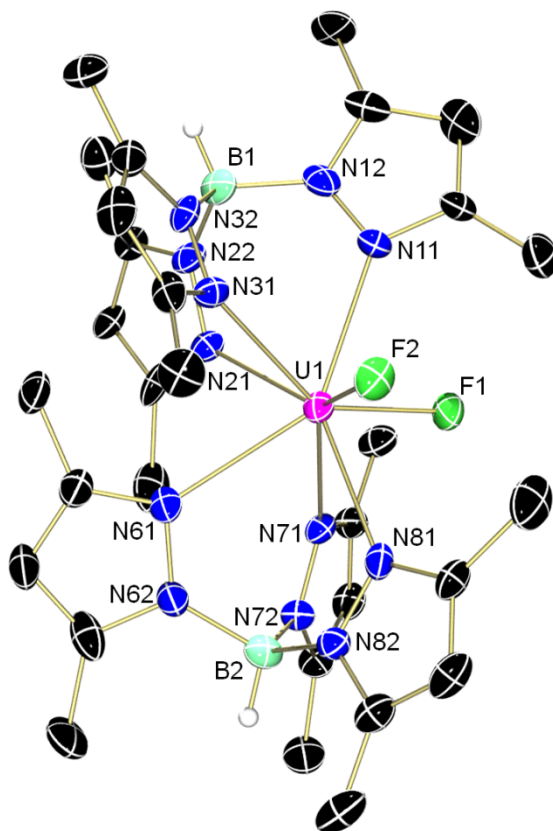
Table S2. Select Bond distances for **1-F$_2$**.

Bond	Bond Length (Å)	Bond	Bond Length (Å)
U1 – F1	2.090(6)	U1 – N31	2.545(9)
U1 – F2	2.086(6)	U1 – N61	2.677(9)
U1 – N11	2.596(10)	U1 – N71	2.582(9)
U1 – N21	2.678(9)	U1 – N81	2.615(10)

DATA COLLECTION

A yellow plate of C$_{30}$H$_{43}$B$_2$F$_2$N$_{12}$U having approximate dimensions of 0.20 x 0.20 x 0.10 mm was mounted on a nylon loop in a random orientation. Preliminary examination and data collection were performed with Cu Kα radiation (λ = 1.54184 Å) on a Rigaku Rapid II equipped with confocal optics.

Cell constants for data collection were obtained from least-squares refinement, using the setting angles of 35248 reflections in the range 2 < θ < 72°. The monoclinic cell parameters and calculated volume are: a = 11.7840(6) Å, b = 22.3831(10) Å, c = 17.0603(7) Å, β = 93.165(3)°, V = 4493.0(4) Å^3. For Z = 4 and F.W. = 869.41 g/mol, the calculated density is 1.29 g/cm^3. The refined mosaicity from DENZO/SCALEPACK was (ref. 1) was 0.05° indicating good crystal quality. The space group was determined by the program XPREP(ref 2). From the systematic presences of:

h0l   h+l=2n
0k0   k=2n

and from subsequent least-squares refinement, the space group was determined to be P121/n1 (# 14).

The data were collected at a temperature of 200(1) K. Data were collected to a maximum 2θ of 145.3°.

DATA REDUCTION

A total of 35248 reflections were collected, of which 7912 were unique. Frames were integrated with HKL3000[2].

     Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 104.9/mm for Cu Kα radiation. An empirical absorption correction using SCALEPACK[2] was applied. Transmission coefficients ranged from 0.043 to 0.350. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 0.0% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

     The structure was solved by direct methods using SHELXT[9]. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w(|F_o|^2-|F_c|^2)^2$ and the weight w is defined as $w=1/[\sigma]$. Scattering factors were taken from the "International Tables for Crystallography".[5] 7912 reflections were used in the refinements. However, only the 4733 reflections with $F_o{}^2>2\sigma(F_o{}^2)$ were used in calculating R1. The final cycle of refinement included 435 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted agreement factors of:

$$R1 = \Sigma\ |F_o - F_c| / \Sigma\ F_o =\ 0.063$$
$$R2 = SQRT\ (\ \Sigma\ w\ (\ F_o{}^2 - F_c{}^2\ )^2 / \Sigma\ w\ (F_o{}^2)^2\ ) =\ 0.173$$

The goodness-of-fit parameter was 0.98. The highest peak in the final difference Fourier had a height of 1.65 e/A^3. The minimum negative peak had a height of -1.81 e/A^3.

Refinement was performed on a LINUX PC using SHELX2013[6]. Crystallographic drawings were done using programs ORTEP[7], and PLUTON[8].

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