Supporting Information

Synthesis and Reactivity of a Low-Coordinate Iron(II) Hydride Complex: Applications in Catalytic Hydrodefluorination

Nicholas M. Hein, Fraser S. Pick, and Michael D. Fryzuk*

Department of Chemistry

The University of British Columbia

2036 Main Mall

Vancouver, BC, CANADA

V6T 1Z1

Contents:

X-ray Crystallographic Data and Collection Parameters

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

Identification code	mf1263
Empirical formula	$C_{38.5}H_{59}FeN_2P$
Formula weight	636.69
Temperature	90K
Crystal size	$0.46 \times 0.45 \times 0.11$ mm^3
Radiation	MoKα (λ = 0.71073 Å)
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	a=27.732(3) Å α=90°
	b=14.1554(13) Å β=110.078(2)°
	c=19.4207(18) Å γ=90°
Volume	7160.3(11) Å^3
Z	8
Density (calculated)	1.181 g/cm^3
Absorption Coefficient	0.494 mm^{-1}
F(000)	2760.0
2θ range for data collection	3.128 to 60.202°
Index ranges	$-35 \leq h \leq 39, -19 \leq k \leq 19, -26 \leq l \leq 27$
Reflections collected	76880
Independent reflections	10512 [R_{int} = 0.0243, R_{sigma} = 0.0160]
Data/restraints/parameters	10512/447/455
Completeness to θ	99.8%
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0317, wR_2 = 0.0762
Final R indexes [all data]	R_1 = 0.0393, wR_2 = 0.0814
Largest diff. peak/hole	0.64/-0.42 eÅ^{-3}

Table S2: Crystal data and structure refinement for **3**

Identification code	mf1206
Empirical formula	$C_{39}H_{66}BFeN_2P$
Formula weight	660.56
Temperature	90K
Crystal size	$0.37 \times 0.21 \times 0.16$ mm^3
Radiation	MoKα (λ = 0.71073 Å)
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a=16.9333(7) Å α=90°
	b=11.7516(5) Å β=100.5590(10)°
	c=20.0066(7) Å γ=90°
Volume	3913.8(3) Å^3
Z	4
Density (calculated)	1.121 g/cm^3
Absorption Coefficient	0.453 mm^{-1}
F(000)	1440.0
2θ range for data collection	4.038 to 50.136°
Index ranges	-20 ≤ h ≤17, -12 ≤ k ≤ 14, -23 ≤ l ≤ 22
Reflections collected	29547
Independent reflections	6921 [R_{int} = 0.0605, R_{sigma} = 0.0656]
Data/restraints/parameters	6921/0/419
Completeness to θ	99.7%
Goodness-of-fit on F^2	1.011
Final R indexes [I>=2σ (I)]	R_1 = 0.0501, wR_2 = 0.1034
Final R indexes [all data]	R_1 = 0.0810, wR_2 = 0.1146
Largest diff. peak/hole	0.46/-0.49 eÅ^{-3}

Table S3: Crystal data and structure refinement for **4**

Identification code	mf1296
Empirical formula	$C_{37}H_{56.67}FeN_2P$
Formula weight	616.33
Temperature	90K
Crystal size	$0.75 \times 0.75 \times 0.55$ mm^3
Radiation	MoKα ($\lambda = 0.71073$ Å)
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a=19.4365(19) Å α=90°
	b=17.908(2) Å β=90°
	c=19.954(2) Å γ=90°
Volume	6945.5(13) Å^3
Z	8
Density (calculated)	1.179 g/cm^3
Absorption Coefficient	0.507 mm^{-1}
F(000)	2669.0
2θ range for data collection	3.706 to 59.222°
Index ranges	-27 ≤ h ≤26, -24 ≤ k ≤ 23, -27 ≤ l ≤ 27
Reflections collected	76719
Independent reflections	9766 [R_{int} = 0.0354, R_{sigma} = 0.0205]
Data/restraints/parameters	9766/0/436
Completeness to θ	99.9%
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0309, wR_2 = 0.0840
Final R indexes [all data]	R_1 = 0.0379, wR_2 = 0.0889
Largest diff. peak/hole	0.42/-0.30 eÅ^{-3}

Table S4: Crystal data and structure refinement for **5**

Identification code	mf1307
Empirical formula	$C_{47}H_{65}FeN_4P$
Formula weight	772.85
Temperature	90K
Crystal size	$0.28 \times 0.16 \times 0.16$ mm^3
Radiation	MoKα ($\lambda = 0.71073$ Å)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a=11.4731(10) Å $\quad$ α=90°
	b=19.0046(18) Å $\quad$ β=90°
	c=20.1296(17) Å $\quad$ γ=90°
Volume	4389.1(7) Å^3
Z	4
Density (calculated)	1.170 g/cm^3
Absorption Coefficient	0.416 mm^{-1}
F(000)	1664.0
2θ range for data collection	4.086 to 55.73°
Index ranges	$-14 \leq h \leq 14$, $-24 \leq k \leq 24$, $-26 \leq l \leq 26$
Reflections collected	64774
Independent reflections	10218 [$R_{int} = 0.0931$, $R_{sigma} = 0.0757$]
Data/restraints/parameters	10218/0/490
Completeness to θ	98.1%
Goodness-of-fit on F^2	1.015
Final R indexes [I>=2σ (I)]	$R_1 = 0.0535$, $wR_2 = 0.1355$
Final R indexes [all data]	$R_1 = 0.0643$, $wR_2 = 0.1405$
Largest diff. peak/hole	0.68/-0.32 eÅ^{-3}

Table S5: Crystal data and structure refinement for **6**

Identification code	mf1302
Empirical formula	$C_{41}H_{65}FeN_2P$
Formula weight	672.77
Temperature	90K
Crystal size	$0.42 \times 0.34 \times 0.33$ mm^3
Radiation	MoKα (λ = 0.71073 Å)
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a=10.5433(8) Å α=95.482(4)°
	b=11.8988(9) Å β=100.646(4)°
	c=16.9020(12) Å γ=108.968(4)°
Volume	1942.9(3) Å^3
Z	2
Density (calculated)	1.150 g/cm^3
Absorption Coefficient	0.458 mm^{-1}
F(000)	732.0
2θ range for data collection	3.672 to 55.088°
Index ranges	-13 ≤ h ≤13, -15 ≤ k ≤ 15, -21 ≤ l ≤ 21
Reflections collected	34076
Independent reflections	8917 [R_{int} = 0.0423, R_{sigma} = 0.0403]
Data/restraints/parameters	8917/0/420
Completeness to θ	99.9%
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0443, wR_2 = 0.1188
Final R indexes [all data]	R_1 = 0.0575, wR_2 = 0.1277
Largest diff. peak/hole	0.88/-0.54 eÅ^{-3}

Table S6: Crystal data and structure refinement for **7**

Identification code	mf1214
Empirical formula	$C_{32.33}H_{49.33}Fe_{0.67}N_{3.33}P_{0.67}$
Formula weight	542.63
Temperature	100K
Crystal size	$0.3 \times 0.17 \times 0.07$ mm^3
Radiation	MoKα ($\lambda = 0.71073$ Å)
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a=10.4848(10) Å $\quad$ α=90°
	b=24.631(3) Å $\quad$ β=98.444(4)°
	c=17.7095(19) Å $\quad$ γ=90°
Volume	4523.9(8) Å^3
Z	6
Density (calculated)	1.195 g/cm^3
Absorption Coefficient	0.407 mm^{-1}
F(000)	1764.0
2θ range for data collection	4.26 to 53.61°
Index ranges	-13 ≤ h ≤9, -31 ≤ k ≤ 30, -22 ≤ l ≤ 18
Reflections collected	28699
Independent reflections	9560 [R_{int} = 0.0604, R_{sigma} = 0.0799]
Data/restraints/parameters	9560/0/531
Completeness to θ	98.7%
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0452, wR_2 = 0.1076
Final R indexes [all data]	R_1 = 0.0716, wR_2 = 0.1177
Largest diff. peak/hole	0.48/-0.34 eÅ^{-3}

Table S7: Crystal data and structure refinement for **8**

Identification code	mf1248_sq
Empirical formula	$C_{73.5}H_{112}F_2Fe_2N_4P_2$
Formula weight	1263.30
Temperature	90K
Crystal size	$0.14 \times 0.12 \times 0.06$ mm^3
Radiation	MoKα ($\lambda = 0.71073$ Å)
Crystal system	Monoclinic
Space group	P2$_1$/c
Unit cell dimensions	a=20.445(6) Å α=90°
	b=13.612(4) Å β=92.564(9)°
	c=26.186(9) Å γ=90°
Volume	7280(4) Å^3
Z	4
Density (calculated)	1.153 g/cm^3
Absorption Coefficient	0.489 mm^{-1}
F(000)	2724.0
2θ range for data collection	1.994 to 44.786°
Index ranges	-21 $\leq$ h $\leq$21, 0 $\leq$ k $\leq$ 14, 0$\leq$ l $\leq$ 28
Reflections collected	9266
Independent reflections	9266 [R$_{sigma}$ = 0.1002]
Data/restraints/parameters	9266/735/802
Completeness to θ	97.9%
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R$_1$ = 0.0613, wR$_2$ = 0.1311
Final R indexes [all data]	R$_1$ = 0.0948, wR$_2$ = 0.1454
Largest diff. peak/hole	0.53/-0.48 eÅ^{-3}

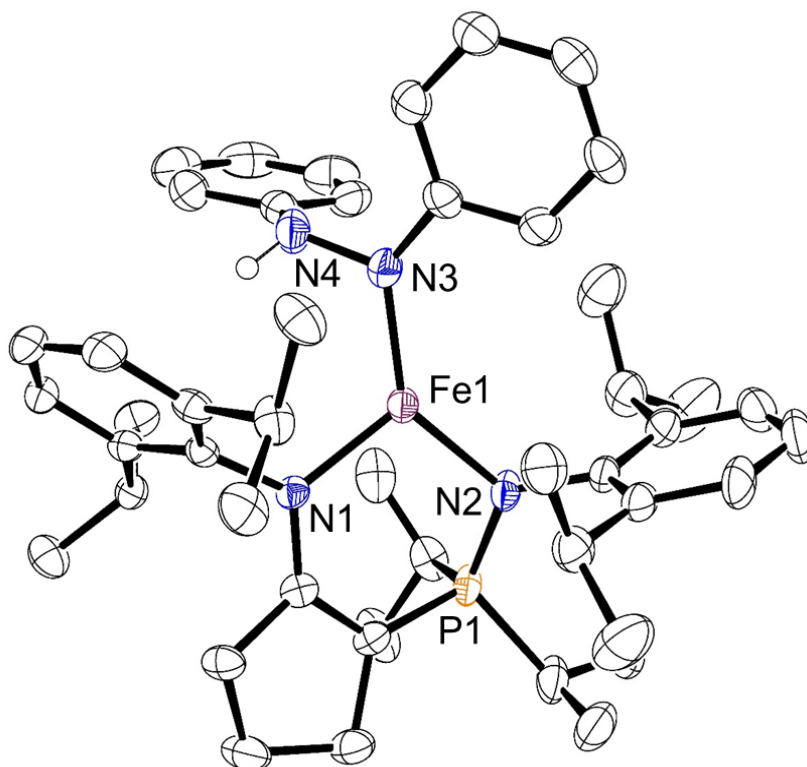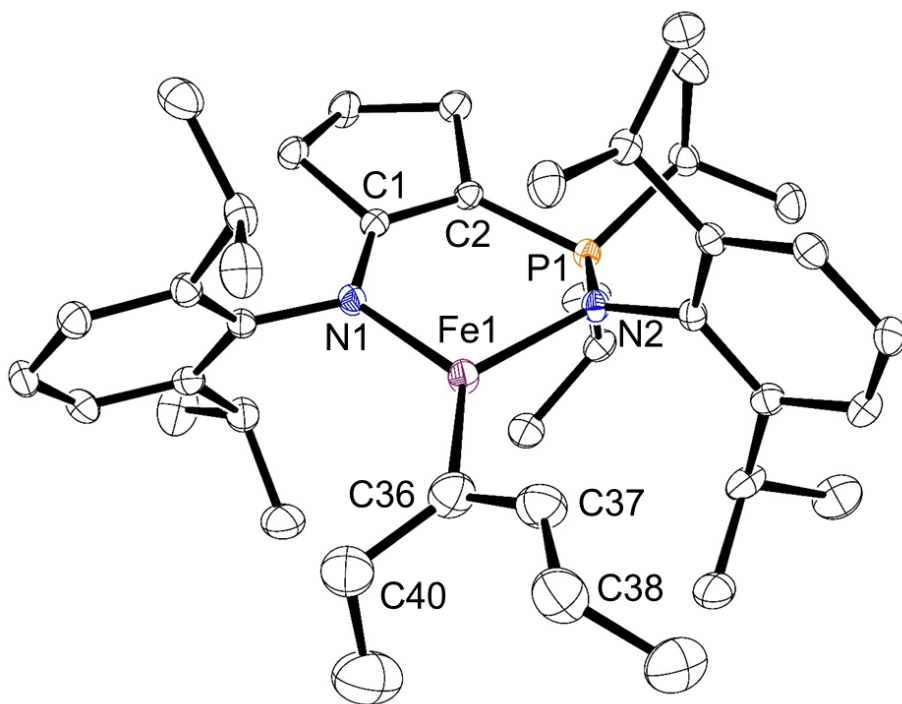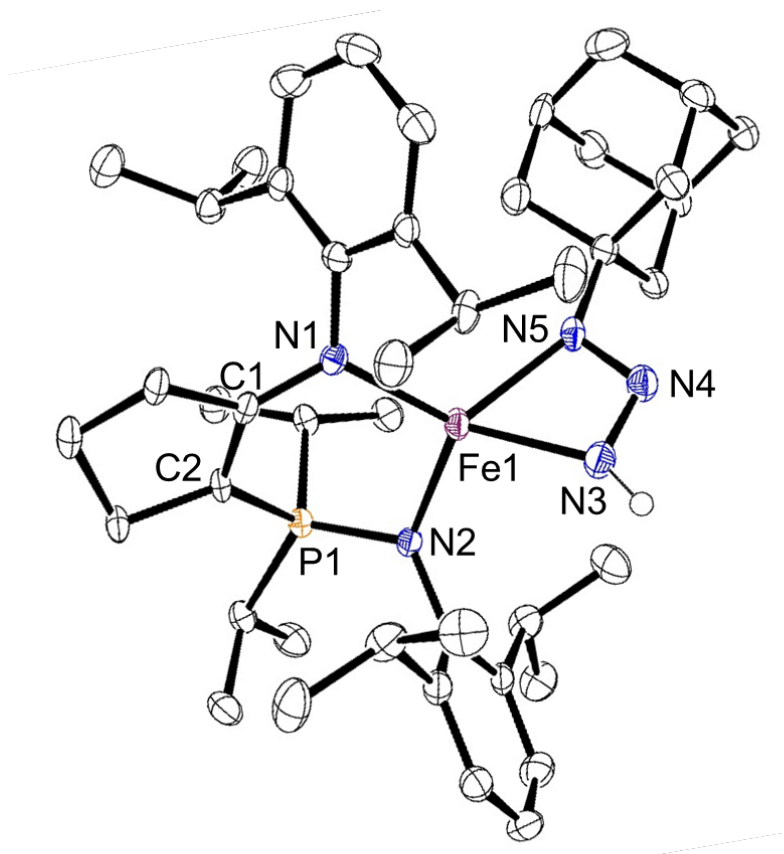**Solid State Molecular Structures**

Figure S1: ORTEP drawing of the solid-state molecular structure of **3** (ellipsoids at 50% probability level). All hydrogen atoms except those bonded to iron have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe1-N1: 1.952(2), Fe1-N2: 1.971(2), P1-N2: 1.632(2), Fe1-H1a: 1.81(3), Fe1-H1b: 1.66(3), N1-Fe1-N2: 105.26(9), and H1a-Fe1-H1b: 59.8(14).

Figure S2: ORTEP drawing of the solid-state molecular structure of **4** (ellipsoids at 50% probability level). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe1-N1: 1.9860(10), Fe1-N2: 2.0072(9), C1-N1: 1.3524(14), C1-C2: 1.3853(15), C2-P1: 1.7564(11), P1-N2: 1.6314(9), Fe1-C36: 2.052(5), C36-C37: 1.481(10), N1-Fe1-N2: 103.44(4), and C37-C36-Fe1: 116.9(4).

Figure S3: ORTEP drawing of the solid-state molecular structure of **5** (ellipsoids at 50% probability level). All hydrogen atoms except those bonded to N have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe1-N1: 1.973(3), Fe1-N2: 1.990(3), N3-N4: 1.429(5), Fe1-N3: 1.934(3), P1-N2: 1.644(4), N1-Fe1-N2: 104.46(14), and Fe1-N3-N4: 115.7(3).

Figure S4: ORTEP drawing of the solid-state molecular structure of **6** (ellipsoids at 50% probability level). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe1-N1: 1.9807(16), Fe1-N2: 2.0081(16), Fe1-C36: 2.016(2), C1-C2: 1.387(3), C1-N1: 1.355(2), C2-P1: 1.7605(19), P1-N2: 1.6295(16), C36-C40: 1.526(4), C36-C37: 1.369(4), C37-C38: 1.502(3), N1-Fe1-N2: 102.02(6), C36-Fe1-N1: 130.40(8), C36-Fe1-N2: 127.31(9), and C40-C36-C37: 120.0(2).

Figure S5: ORTEP drawing of the solid-state molecular structure of **7** (ellipsoids at 50% probability level). All hydrogen atoms except those bonded to N have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe1-N1: 2.0170(16), Fe1-N2: 2.0273(17), C1-C2: 1.376(3), C1-N1: 1.369(2), C2-P1: 1.770(2), P1-N2: 1.6263(16), Fe1-N3: 2.1060(17), Fe1-N5: 2.0901(17), N3-N4: 1.321(3), N4-N5: 1.296(2), N1-Fe1-N2: 104.95(7), N3-Fe1-N5: 60.30(7), and N3-N4-N5: 107.26(16).

^{1}H NMR Characterization for Synthesized Complexes

Figure S6: ^{1}H NMR spectrum for [(^{CY5}NpN^{DIPP,DIPP})FeH]$_2$ **2** (400 MHz, d_6-benzene, 25 °C).

Figure S7: ^{1}H NMR spectrum for (^{CY5}NpN^{DIPP,DIPP})FeEt **4** (300 MHz, d_6-benzene, 25 °C).

Figure S8: ^{1}H NMR spectrum for (^CY5^NpN^DIPP,DIPP^)FeN(Ph)NHPh **5** (300 MHz, d_6-benzene, 25 °C).

Figure S9: ^{1}H NMR spectrum for (^{CY5}NpN^{DIPP,DIPP})Fe(3-hexene) **6**
(300 MHz, d_6-benzene, 25 °C).

Figure S10: ^{1}H NMR spectrum for $(^{CY5}NpN^{DIPP,DIPP})Fe(\eta^2\text{-HNNNAd})$ **7** (400 MHz, d_6-benzene, 25 °C).

Figure S11: ^{1}H NMR spectrum for $[(^{CY5}NpN^{DIPP,DIPP})FeF]_2$ **8** (300 MHz, d_6-benzene, 25 °C).

Experimental NMR Spectra

Figure S12: ^{1}H NMR spectra for [(^{CY5}NpN^{DIPP,DIPP})FeH]$_2$ **2** (top), (^{CY5}NpN^{DIPP,DIPP})FeEt **4** (middle), and the product mixture from which single crystals of (^{CY5}NpN^{DIPP,DIPP})FeH$_2$BEt$_2$ **3** where grown (bottom). Red triangles for **2** and blue circles for **4** are used to mark easily discernable signals belonging to their respective compounds in the complicated product mixture shown in the bottom spectrum. All spectra recorded at 300 MHz in d_6-benzene at 25 °C.

Figure S13: ^{1}H NMR spectra for the reaction of **2** with BEt$_3$ at 60 °C for 2h (top spectrum, 300 MHz, d_8-toluene, 25 °C), and for complex **4** (bottom spectrum, 300 MHz, d_6-benzene, 25 °C).

Figure S14: ^{1}H NMR spectra for the stoichiometric reaction of **2** with C_6F_6 at 70 °C in d_8-THF. ^{1}H NMR spectra were collected after 15 minutes, 1 hour, 2 hours, and 1 day. All spectra were collected in d_8-THF at 300 MHz at 25 °C.
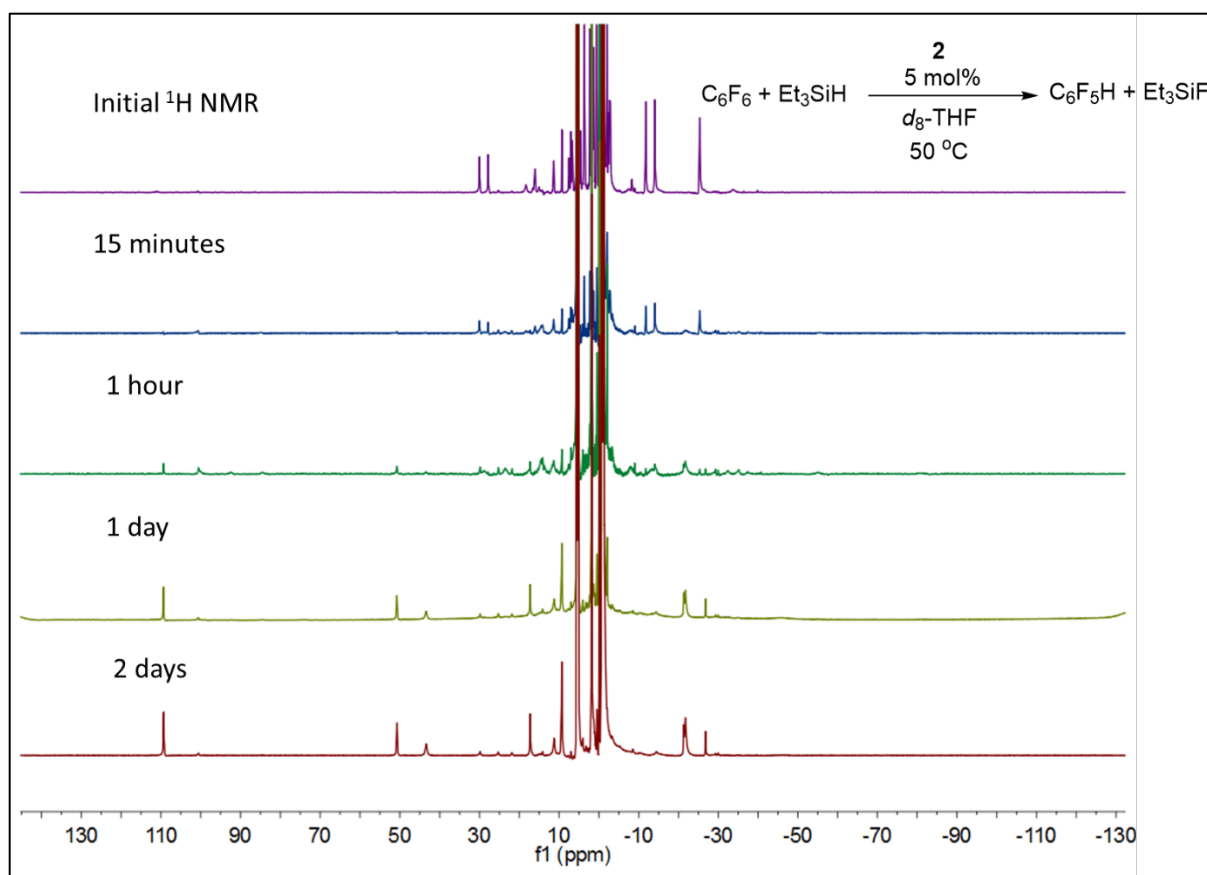
Figure S15: ^{19}F NMR spectra for the stoichiometric reaction of **2** with C_6F_6 at 70 °C in d_8-THF. ^{19}F NMR spectra were collected after 15 minutes, 1 hour, 2 hours, and 1 day. All spectra were collected in d_8-THF at 282 MHz at 25 °C.

Figure S16: Stacked ^{1}H NMR spectra for the catalytic monodefluorination of C_6F_6 in the presence of Et_3SiH using **2** as the catalyst at 50 °C in d_8-THF. It can be seen that the bridging hydride species **2** is completely consumed after allowing the reaction to proceed for 1 hour. A new paramagnetic species is formed, which is the resting state of the catalyst. All spectra collected in d_8-THF at 300 MHz at 25 °C.

Figure S17: Stacked ^{19}F NMR spectra for the catalytic monodefluorination of C_6F_6 in the presence of Et$_3$SiH using **2** as the catalyst at 50 °C in d_8-THF. Fluorobenzene (C_6H_5F) is used as the internal standard. ^{19}F resonances corresponding to pentafluorobenzene (C_6F_5H) at δ - 139.0, - 155.1, and -163.0 and fluorotriethylsilane at δ -175.5 are observed after 1 day of reactivity. All spectra collected in d_8-THF at 282 MHz at 25 °C.

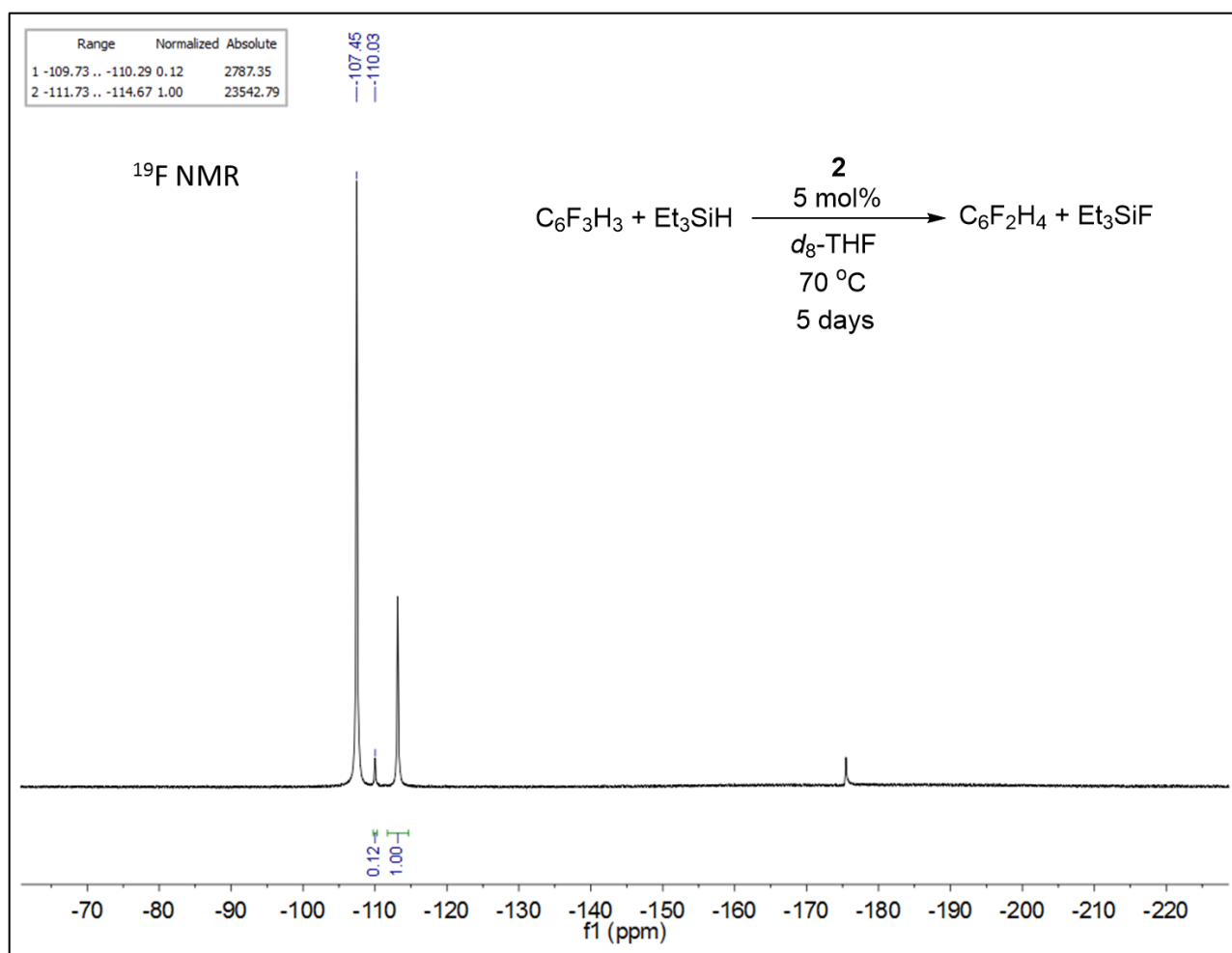**Figure S18:** ^{19}F NMR spectrum for the final time point at 2 days for the catalytic monodefluorination of C_6F_6 in the presence of Et_3SiH using **2** as the catalyst at 50 °C in d_8-THF. A stoichiometric amount of fluorobenzene (C_6H_5F) relative to the initial C_6F_6 and Et_3SiH was used as the internal standard (0.219 M, 0.169 mmol). The ^{19}F resonance corresponding to the *para* position of pentafluorobenzene (C_6F_5H) at δ -155.1 was used for integration purposes (TON=4.2). A relaxation delay of 50 seconds was used between scans in the ^{19}F NMR experiment (282 MHz, d_8-THF, 25 °C).
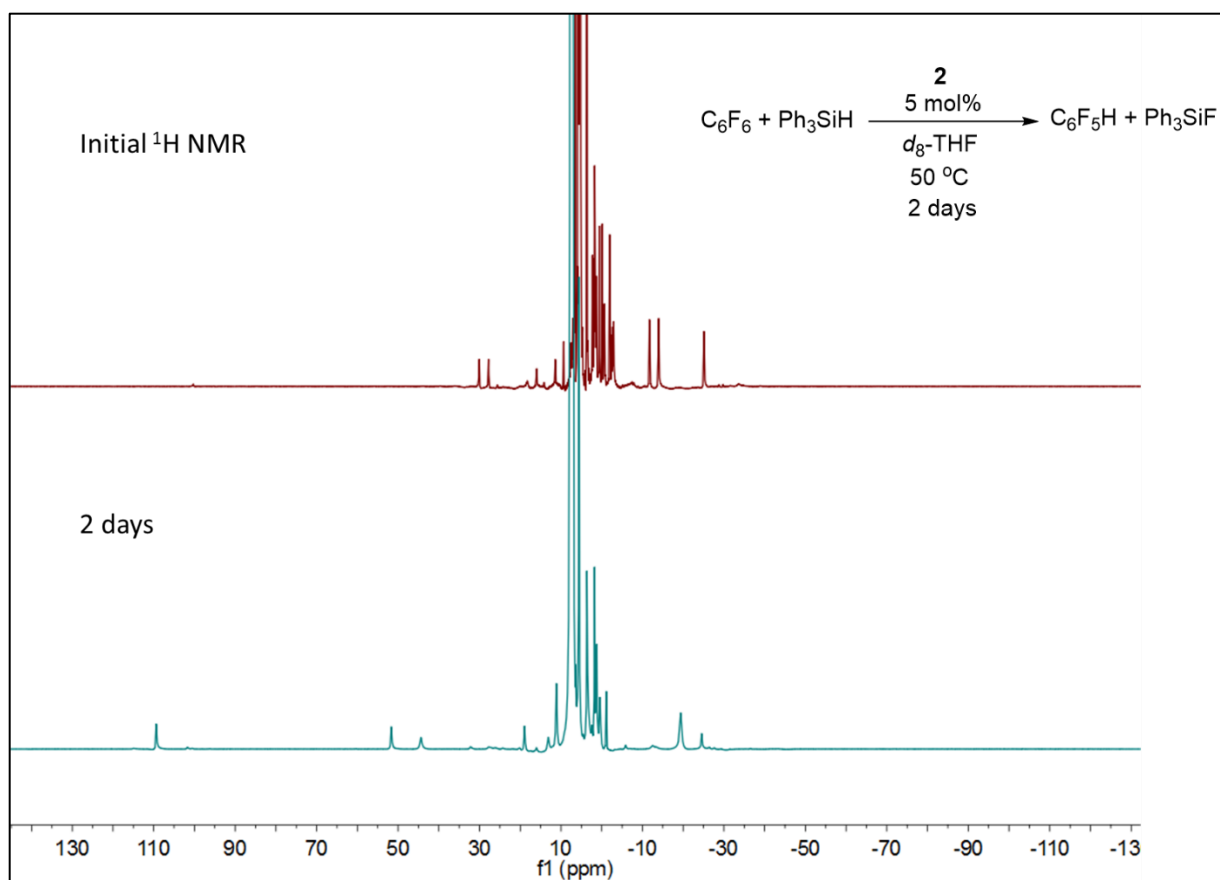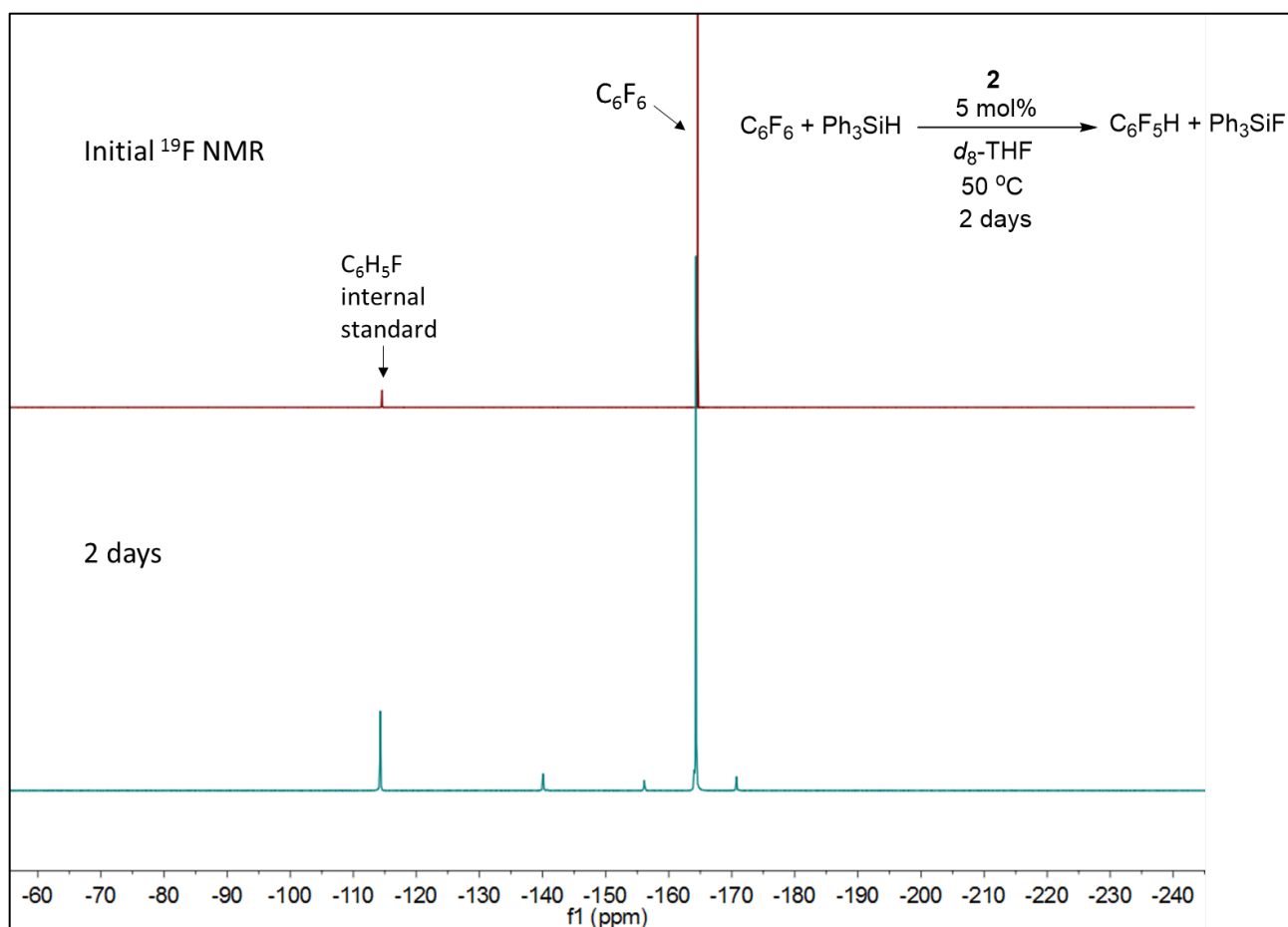
Figure S19: Stacked ^{19}F NMR spectra for the monodefluorination of $C_6F_3H_3$ in the presence of Et$_3$SiH using **2** as the catalyst at 70 °C in d_8-THF. Fluorobenzene (C_6H_5F) is used as the internal standard. The ^{19}F resonances corresponding to 1,3-difluorobenzene ($C_6F_2H_4$) at δ – 110.0 and fluorotriethylsilane at δ -175.5 are first observed after 2 days of reactivity. All spectra collected in d_8-THF at 282 MHz at 25 °C.

Range	Normalized	Absolute
1 -109.73 .. -110.29	0.12	2787.35
2 -111.73 .. -114.67	1.00	23542.79

^{19}F NMR

2
5 mol%

$C_6F_3H_3 + Et_3SiH \xrightarrow{\substack{d_8\text{-THF} \\ 70\,^\circ\text{C} \\ 5\ \text{days}}} C_6F_2H_4 + Et_3SiF$
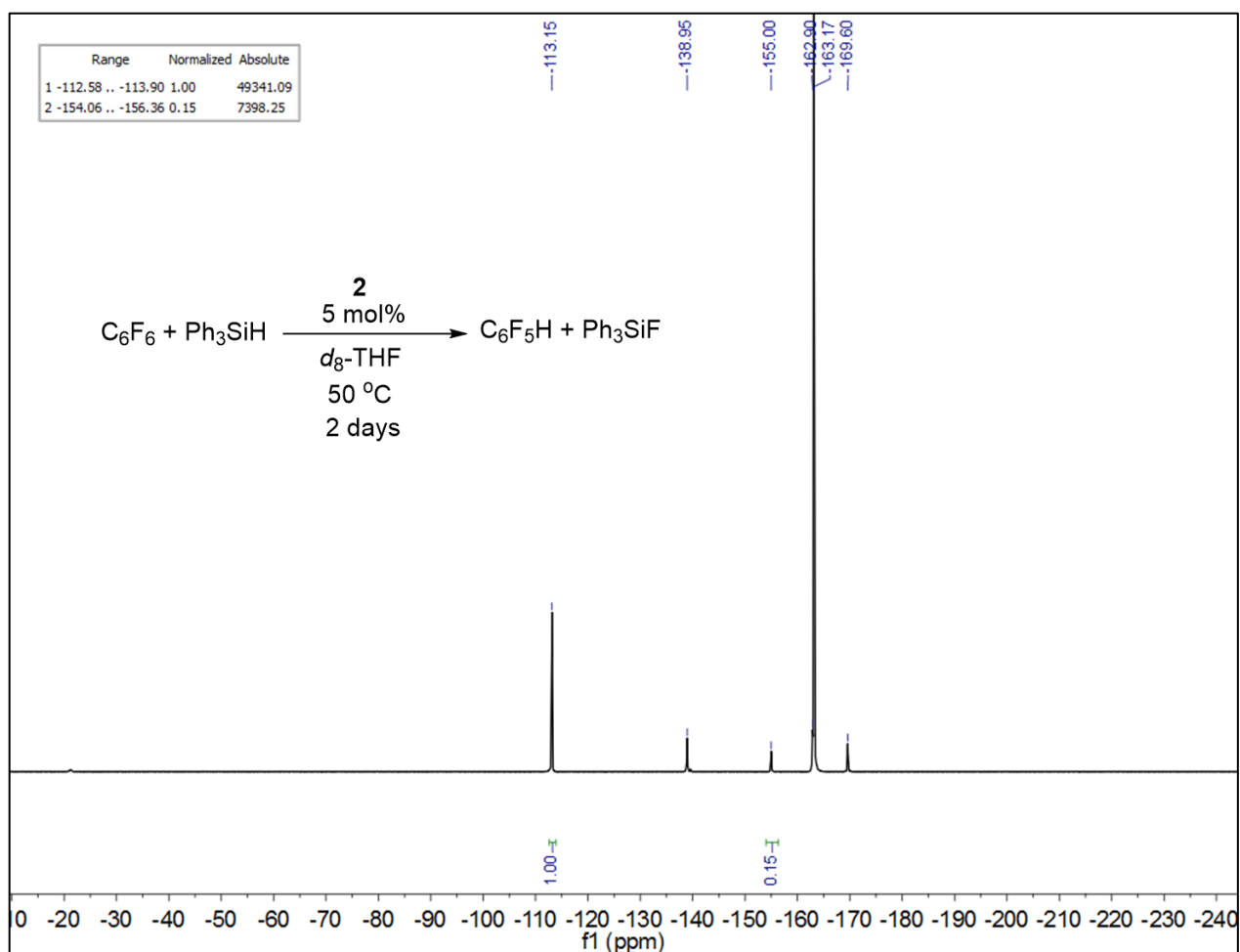
Figure S20: ^{19}F NMR spectrum for the final time point at 5 days for the monodefluorination of $C_6F_3H_3$ in the presence of Et_3SiH using **2** as the catalyst at 70 °C in d_8-THF. A stoichiometric amount of fluorobenzene (C_6H_5F) relative to the initial $C_6F_3H_3$ and Et_3SiH was used as the internal standard (0.546 M, 0.339 mmol). The ^{19}F resonance corresponding to 1,3-difluorobenzene ($C_6F_2H_4$) at δ -110.0 was used for integration purposes (TON=1.2). A relaxation delay of 70 seconds was used between scans in the ^{19}F NMR experiment (282 MHz, d_8-THF, 25 °C).

Figure S21: Stacked ^{1}H NMR spectra for the catalytic monodefluorination of C_6F_6 in the presence of Ph_3SiH using **2** as the catalyst at 50 °C in d_8-THF. A new paramagnetic species is formed, which is the resting state of the catalyst. All spectra collected in d_8-THF at 300 MHz at 25 °C.
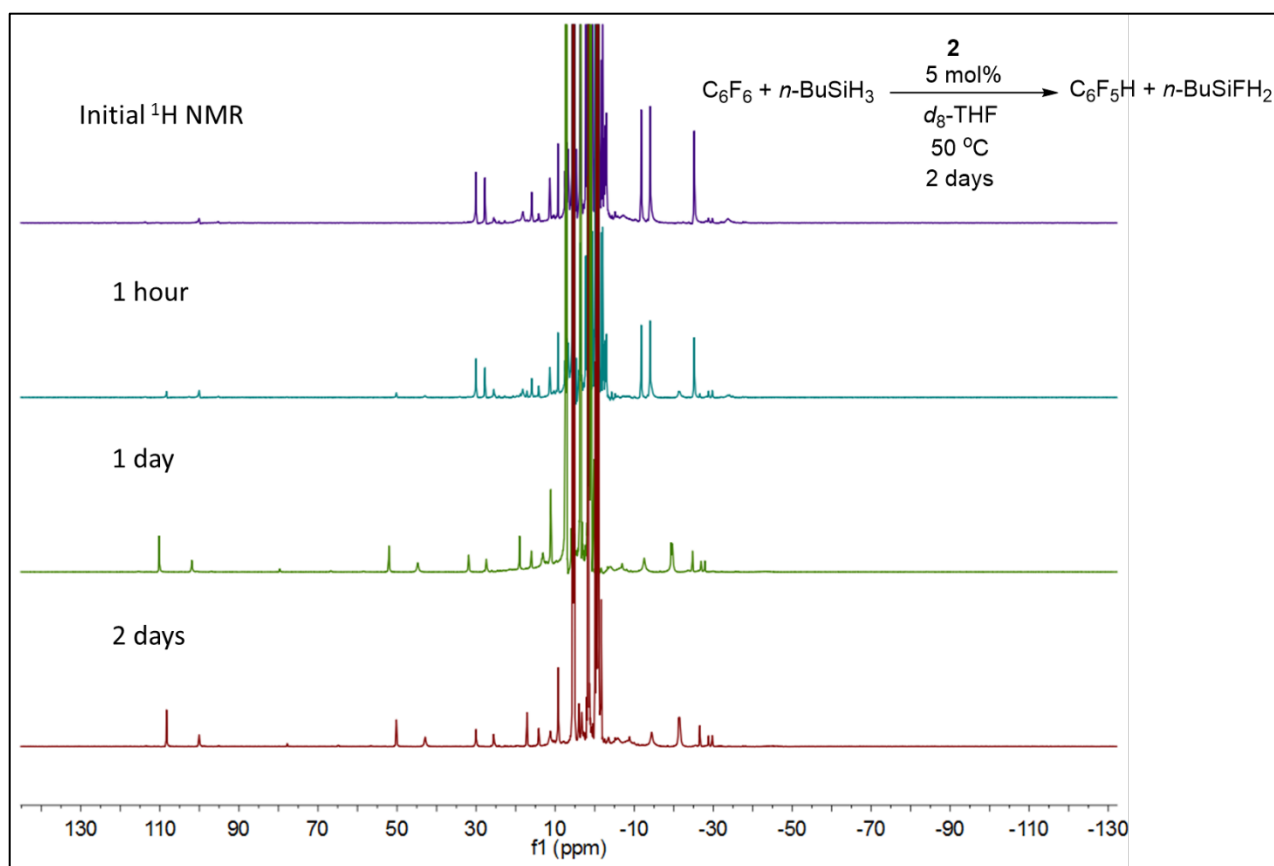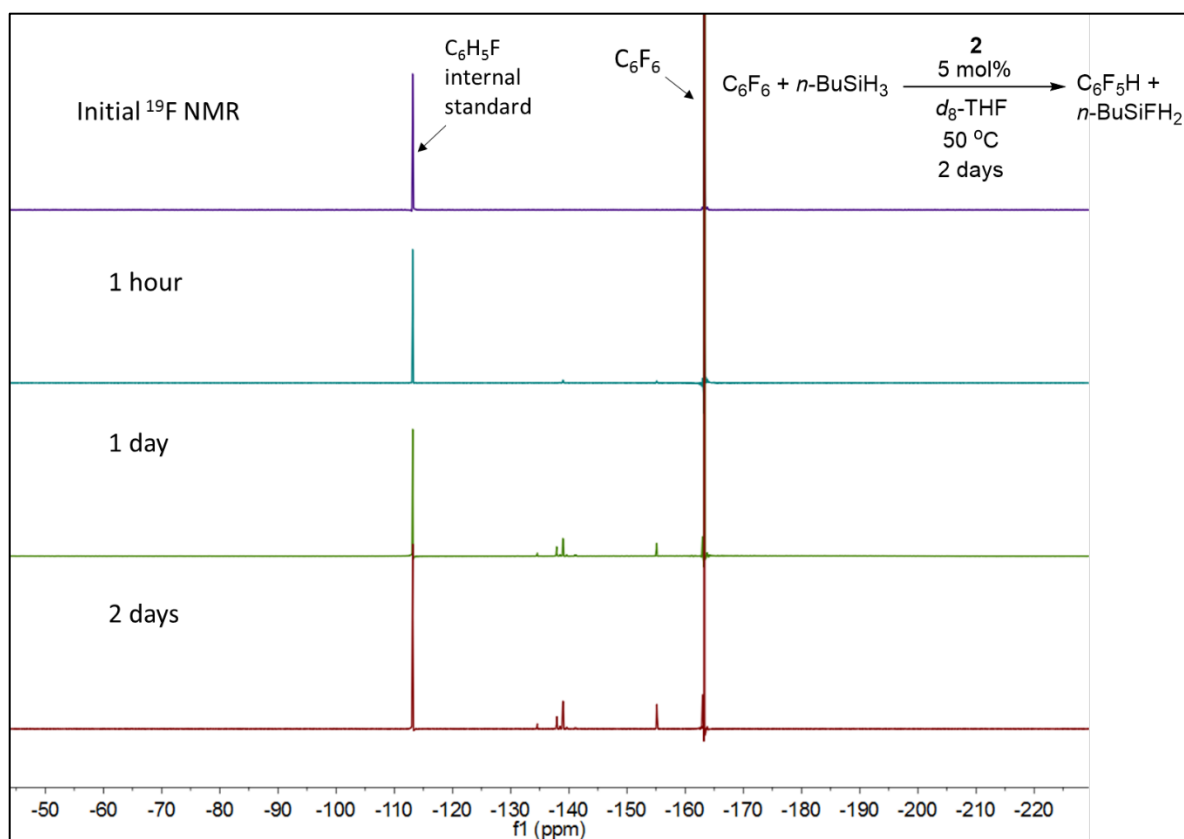
Figure S22: Stacked ^{19}F NMR spectra for the catalytic monodefluorination of C_6F_6 in the presence of Ph_3SiH using **2** as the catalyst at 50 °C in d_8-THF. Fluorobenzene (C_6H_5F) is used as the internal standard. [19]F resonances corresponding to pentafluorobenzene (C_6F_5H) at δ -139.0, -155.0, and -162.9 and fluorotriphenylsilane at δ -169.6 are observed after 2 days of reactivity. All spectra collected in d_8-THF at 282 MHz at 25 °C.
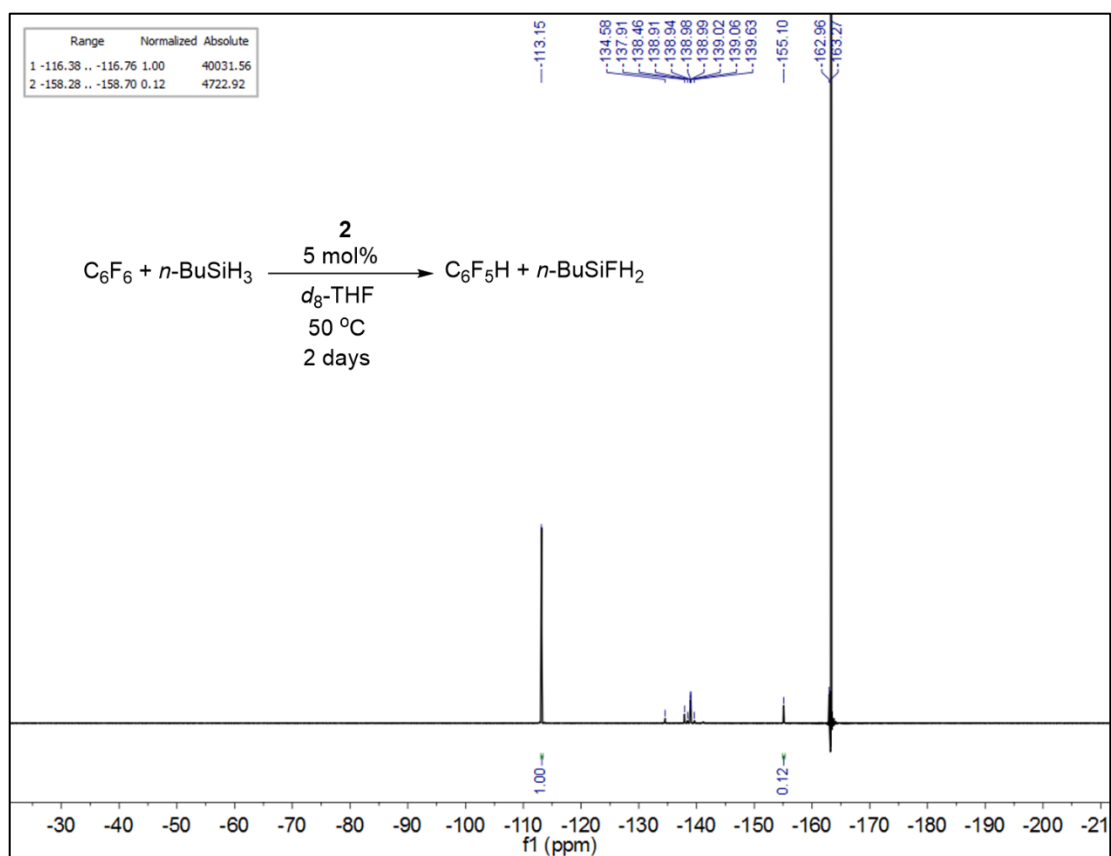
Figure S23: ^{19}F NMR spectrum for the final time point at 2 days for the catalytic monodefluorination of C$_6$F$_6$ in the presence of Ph$_3$SiH using **2** as the catalyst at 50 °C in d_8-THF. A stoichiometric amount of fluorobenzene (C$_6$H$_5$F) relative to the initial C$_6$F$_6$ and Ph$_3$SiH was used as the internal standard (0.796 M, 0.440 mmol). The ^{19}F resonance corresponding to the *para* position of pentafluorobenzene (C$_6$F$_5$H) at δ -155.0 was used for integration purposes (TON=3.0). A relaxation delay of 50 seconds was used between scans in the ^{19}F NMR experiment (282 MHz, d_8-THF, 25 °C).

Figure S24: Stacked ^{1}H NMR spectra for the catalytic monodefluorination of C_6F_6 in the presence of n-BuSiH$_3$ using **2** as the catalyst at 50 °C in d_8-THF. A new paramagnetic species is formed, which is the resting state of the catalyst. All spectra collected in d_8-THF at 300 MHz at 25 °C.

Figure S25: Stacked ^{19}F NMR spectra for the catalytic monodefluorination of C_6F_6 in the presence of n-BuSiH$_3$ using **2** as the catalyst at 50 °C in d_8-THF. Fluorobenzene (C_6H_5F) is used as the internal standard. ^{19}F resonances corresponding to pentafluorobenzene (C_6F_5H) at δ - 138.9, -155.1, and -163.0 are first observed after 1 day of reactivity. All spectra collected in d_8-THF at 282 MHz at 25 °C.

Figure S26: ^{19}F NMR spectrum for the final time point at 2 days for the catalytic monodefluorination of C_6F_6 in the presence of n-BuSiH$_3$ using **2** as the catalyst at 50 °C in d_8-THF. A stoichiometric amount of fluorobenzene (C_6H_5F) relative to the initial C_6F_6 and n-BuSiH$_3$ was used as the internal standard (0.576 M, 0.440 mmol). The ^{19}F resonance corresponding to the *para* position of pentafluorobenzene (C_6F_5H) at δ -155.1 was used for integration purposes (TON=2.4). A relaxation delay of 50 seconds was used between scans in the ^{19}F NMR experiment (282 MHz, d_8-THF, 25 °C).

Figure S27: Stacked ^{1}H NMR spectra for the catalytic monodefluorination of C_5F_5N in the presence of Et_3SiH using **2** as the catalyst at 50 °C in d_8-THF. A new paramagnetic species is immediately formed from **2** at time point zero. This species is different from the resting state produced during catalysis, as observed at the 18h and 3 day time points. All spectra collected in d_8-THF at 300 MHz at 25 °C.
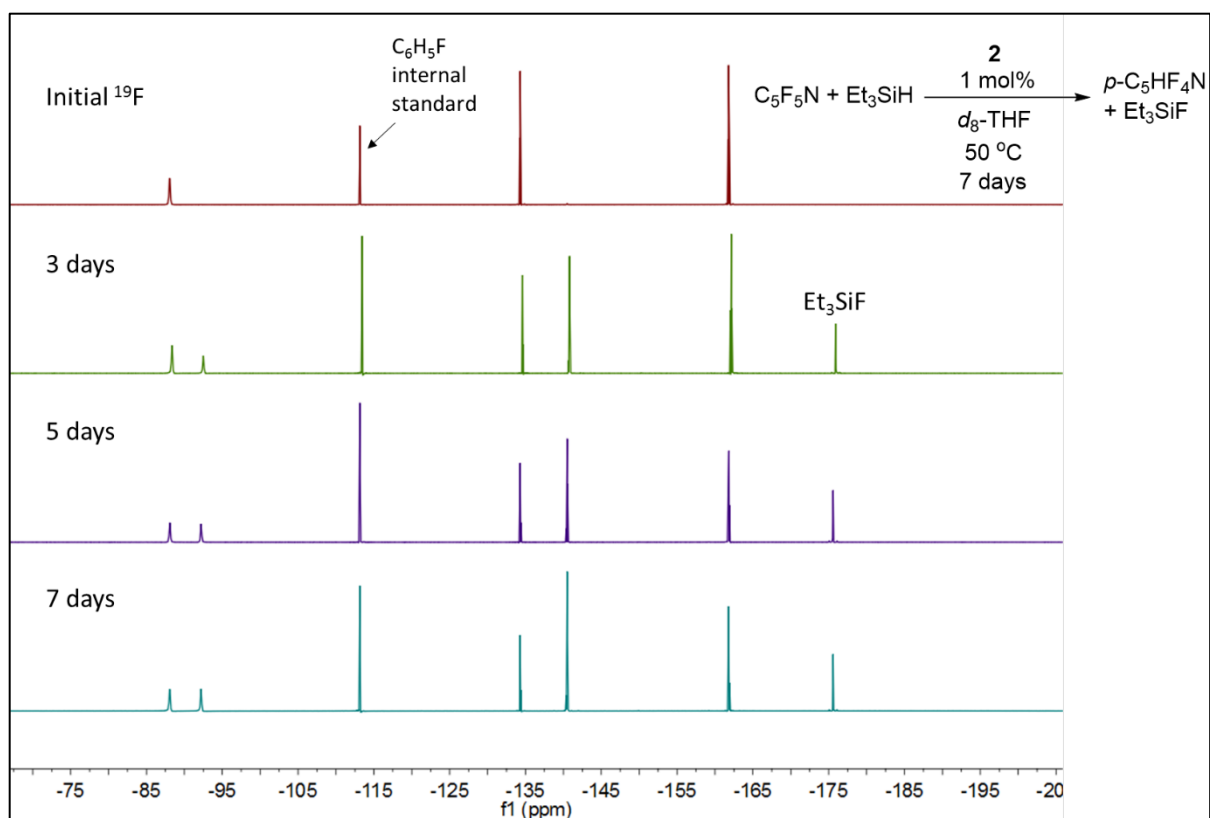
Figure S28: Stacked ^{19}F NMR spectra for the monodefluorination of C_5F_5N in the presence of Et_3SiH using 1 mol% **2** as the catalyst at 50 °C in d_8-THF. Fluorobenzene (C_6H_5F) is used as the internal standard. After a week of reactivity, 50% conversion is obtained as determined by quantitative integration of the Et_3SiF resonance at δ -175.6. All spectra collected in d_8-THF at 282 MHz at 25 °C.
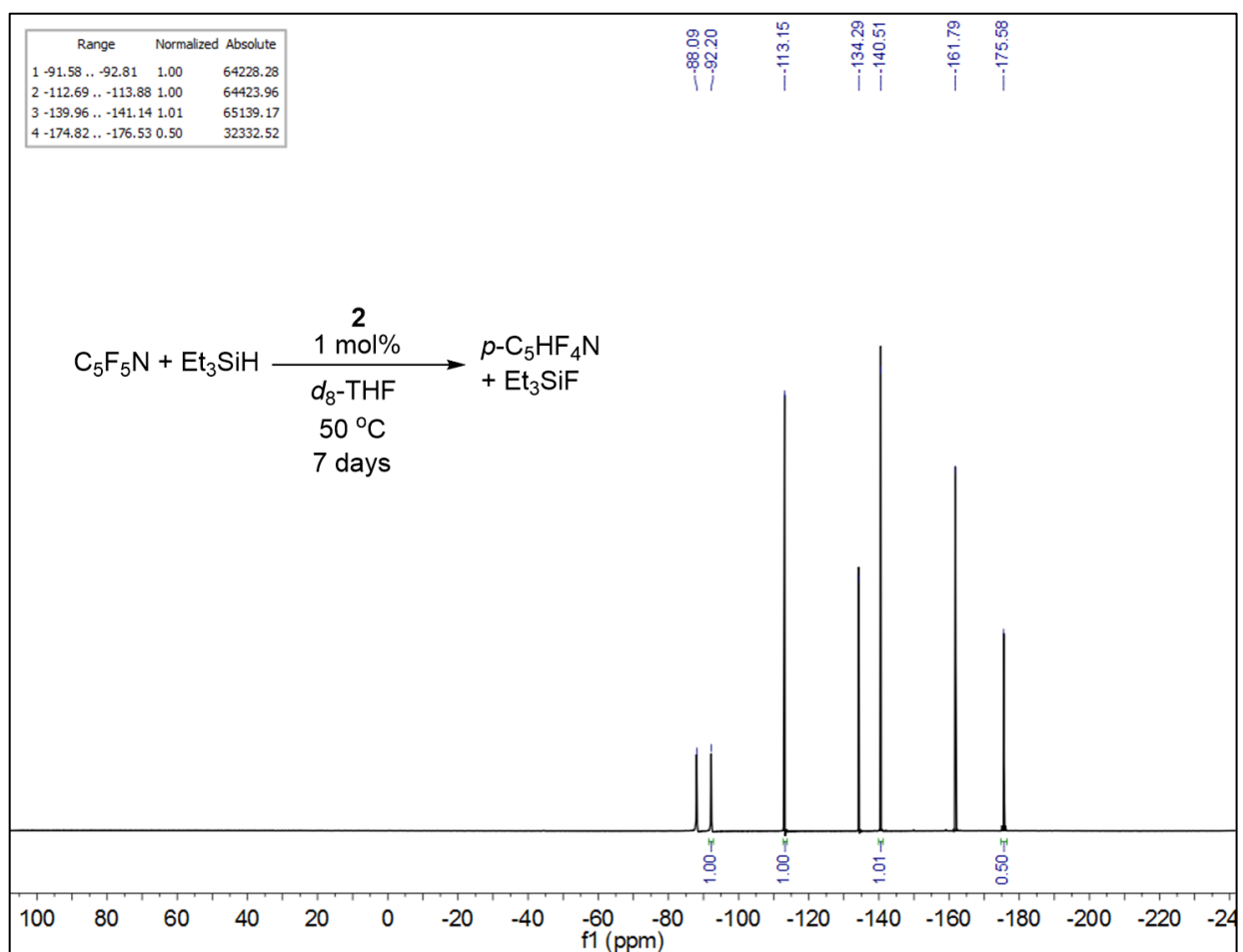
Figure S29: ^{19}F NMR spectrum for the final time point of 7 days in the monodefluorination of C$_5$F$_5$N in the presence of Et$_3$SiH using 1 mol% **2** as the catalyst at 50 °C in d_8-THF. Fluorobenzene (C$_6$H$_5$F) at δ -113.2 is used as the internal standard (1.083 M, 0.678 mmol). Integration of the Et$_3$SiF resonance at δ -175.6 relative to C$_6$H$_5$F shows 50% conversion (TON=50). A relaxation delay of 70 seconds was used between each scan in the ^{19}F NMR experiment (282 MHz, d_8-THF, 25 °C).

Figure S30: Stacked ^{1}H NMR spectra for the catalytic monodefluorination of C_5F_5N in the presence of Et_3SiH using **2** as the catalyst at 50 °C in d_6-benzene. A new paramagnetic species is formed from **2** after 1 day of allowing catalysis to proceed. All spectra collected in d_8-THF at 300 MHz at 25 °C.
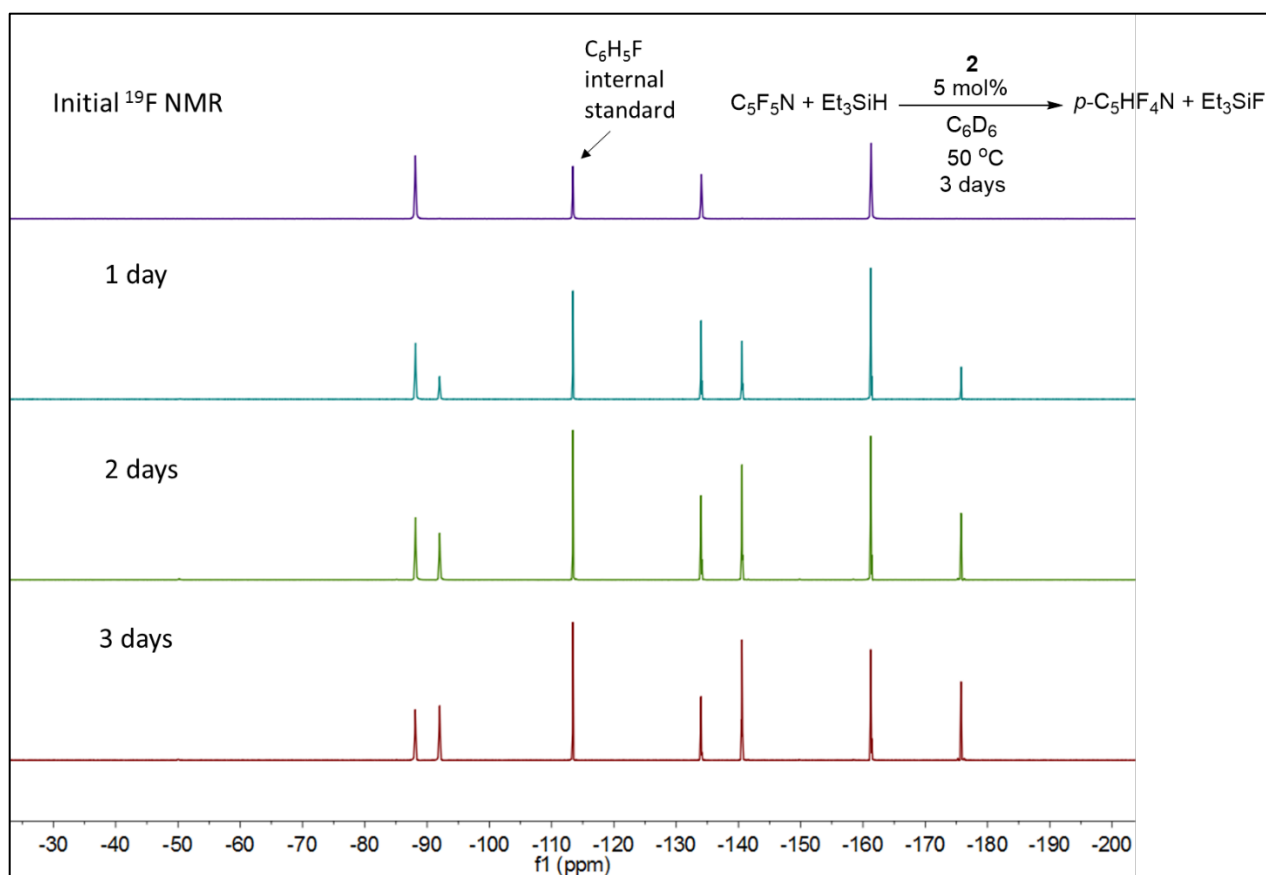
Figure S31: Stacked ^{19}F NMR spectra for the monodefluorination of C_5F_5N in the presence of Et_3SiH using 5 mol% **2** as the catalyst at 50 °C in d_6-benzene. Fluorobenzene (C_6H_5F) is used as the internal standard. Conversion is lower compared to when catalysis is performed in d_8-THF (**Figure S28**). A relaxation delay of 70 seconds was used between each scan in the ^{19}F NMR experiment. All spectra collected in d_6-benzene at 282 MHz at 25 °C.
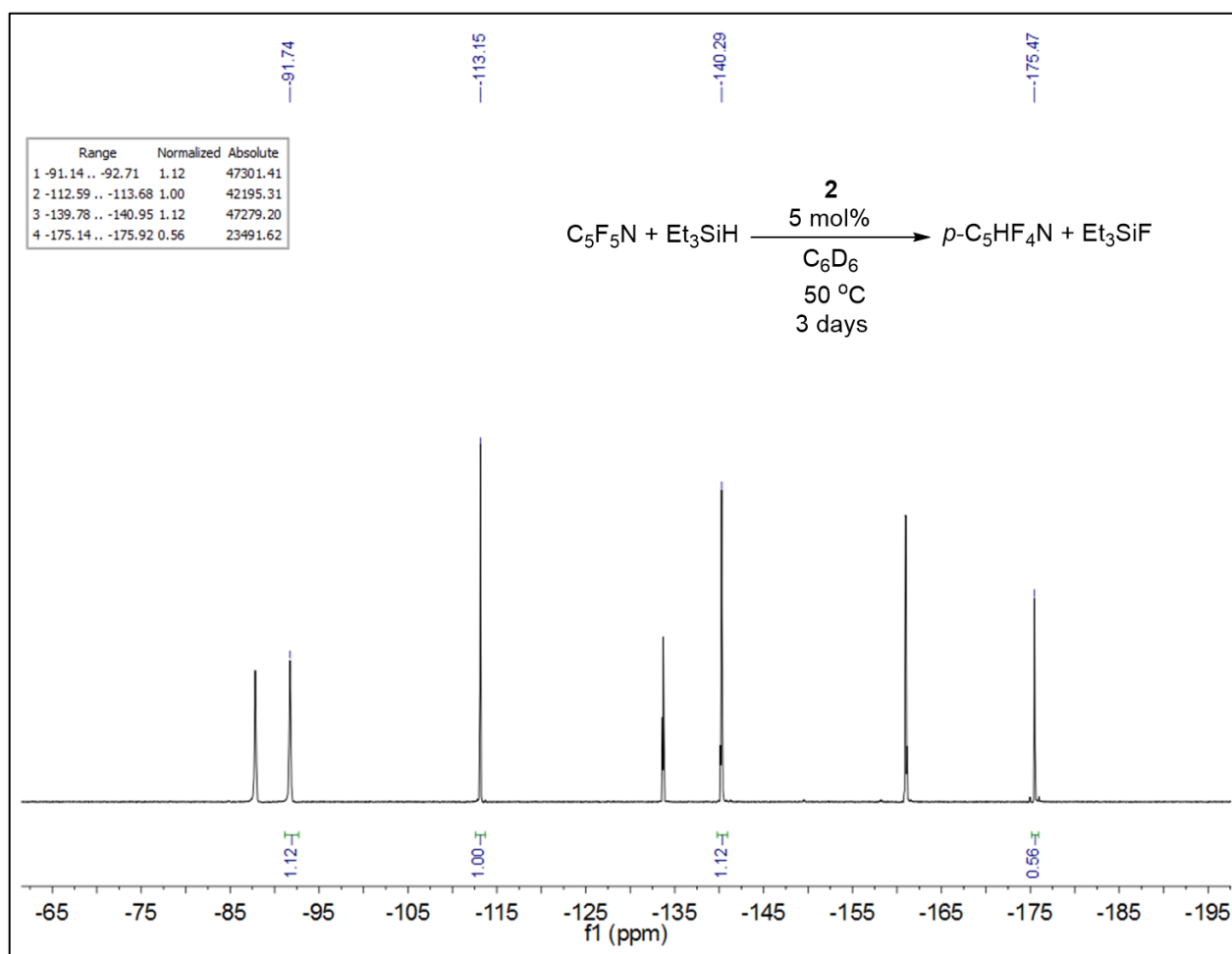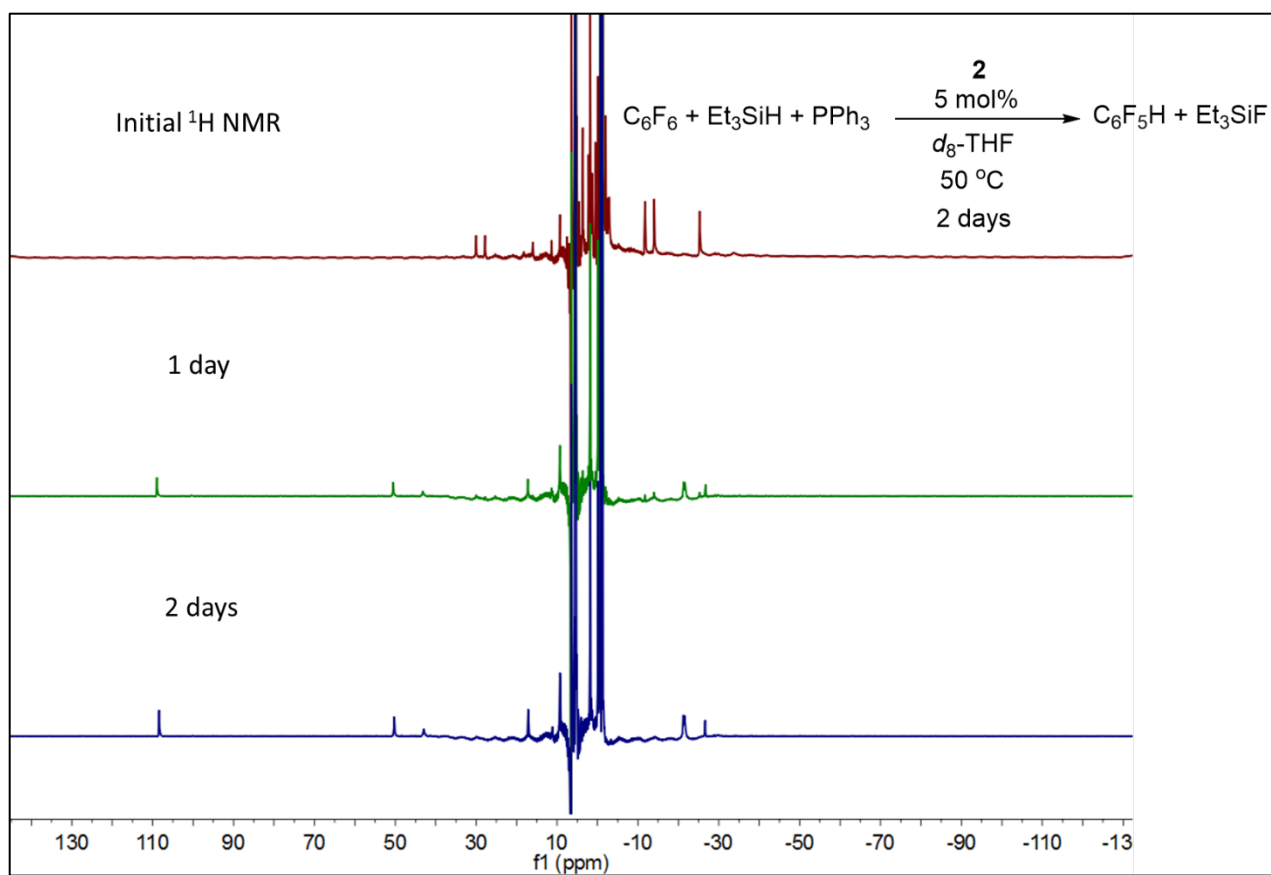
Figure S32: ^{19}F NMR spectrum for the final time point after 3 days for the monodefluorination of C_5F_5N in the presence of Et_3SiH using 5 mol% **2** as the catalyst at 50 °C in d_6-benzene. Fluorobenzene (C_6H_5F) at δ -113.2 is used as the internal standard (0.703 M, 0.372 mmol). Integration of the Et_3SiF resonance at δ -175.6 relative to C_6H_5F shows 56% conversion (TON=11.2). A relaxation delay of 70 seconds was used between each scan in the ^{19}F NMR experiment (282 MHz, d_8-THF, 25 °C).

Figure S33: Stacked ^{1}H NMR spectra for the catalytic monodefluorination of C_6F_6 in the presence of Et_3SiH and PPh_3 using **2** as the catalyst at 50 °C in d_8-THF. A new paramagnetic species is formed from **2** after 1 day of allowing catalysis to proceed, though this species has the same chemical shifts as the iron containing resting state when catalysis is performed in the absence of PPh_3. All spectra collected in d_8-THF at 300 MHz at 25 °C.
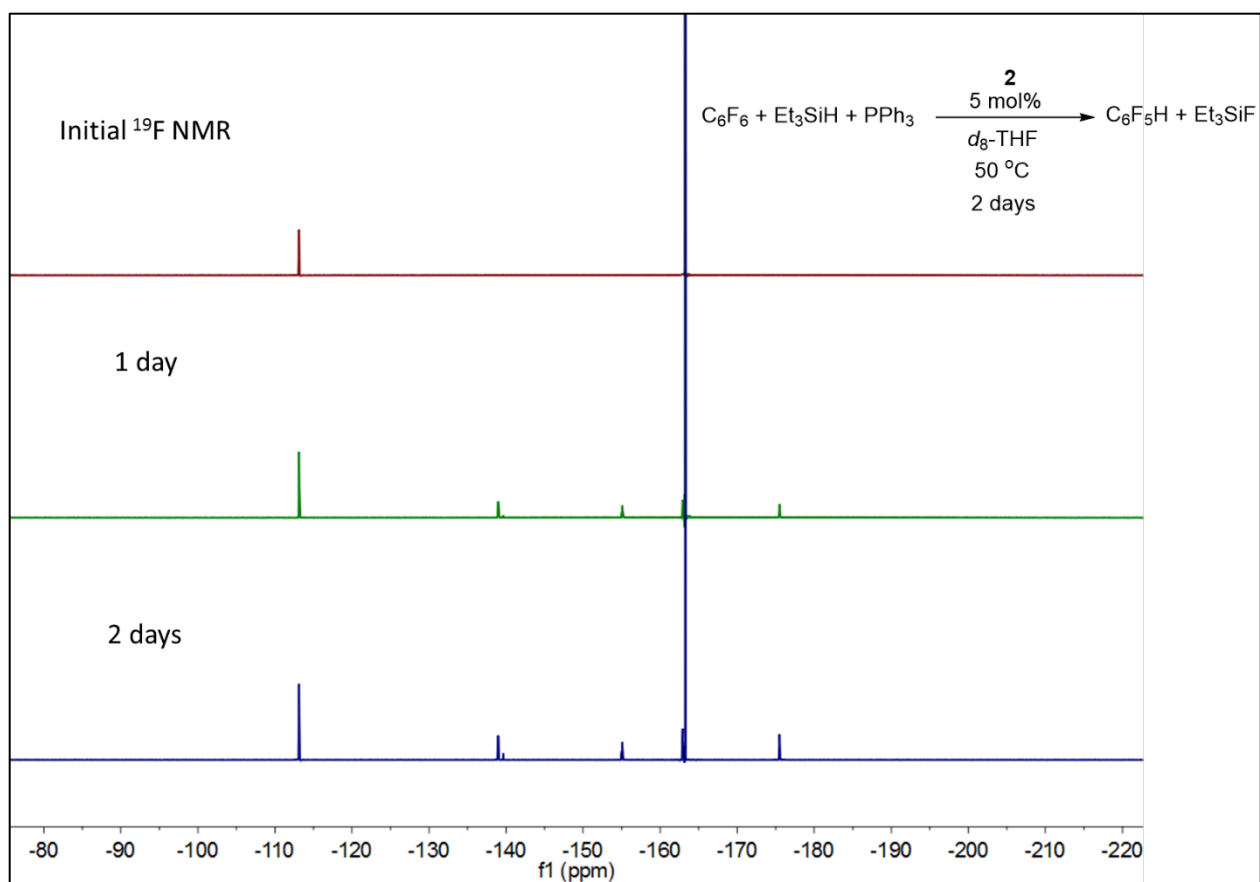
Figure S34: Stacked ^{19}F NMR spectra for the monodefluorination of C_6F_6 in the presence of Et_3SiH and PPh_3 using 5 mol% **2** as the catalyst at 50 °C in d_8-THF. Fluorobenzene (C_6H_5F) is used as the internal standard. All spectra collected in d_6-benzene at 282 MHz at 25 °C.
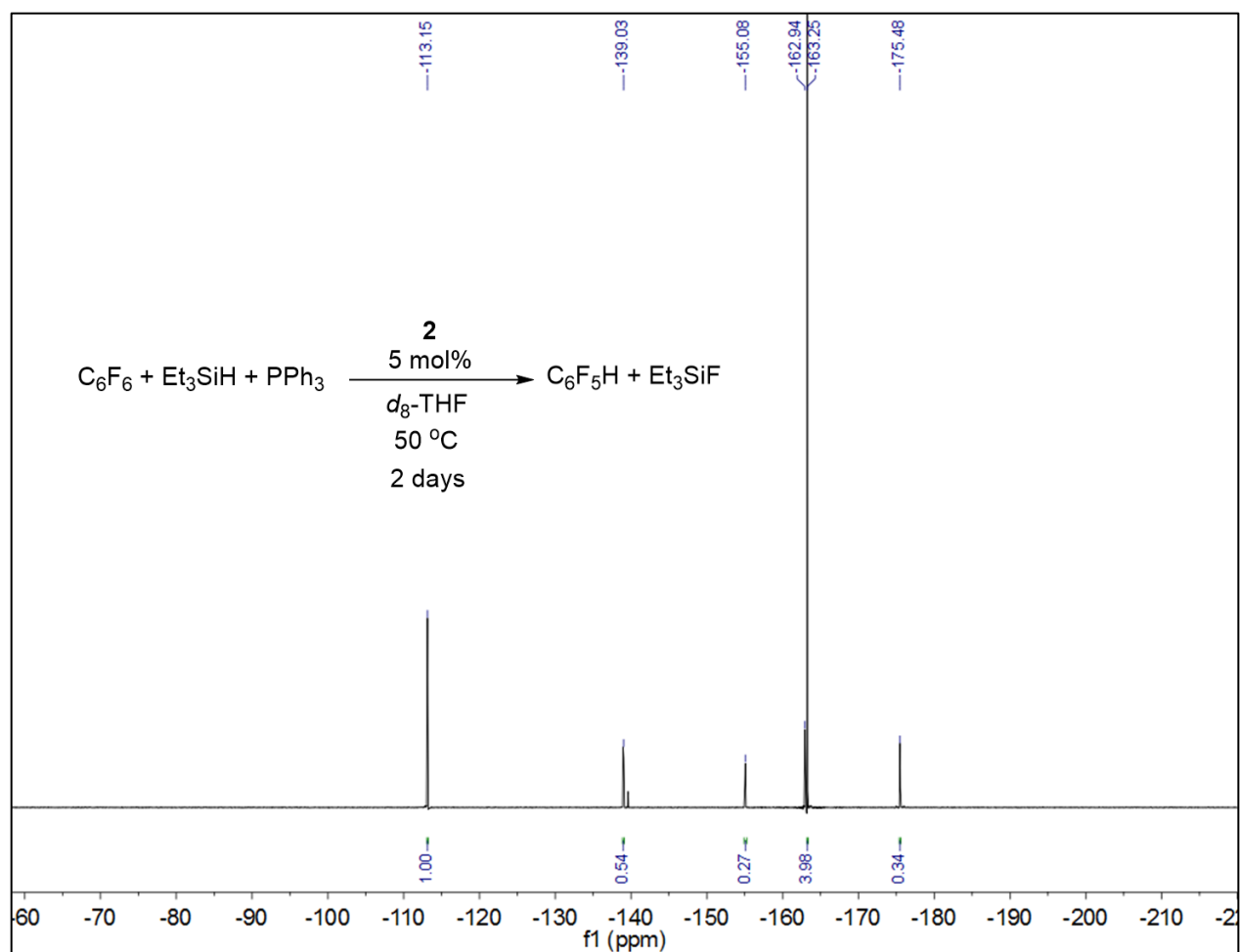
Figure S35: ^{19}F NMR spectrum for the final time point after 2 days for the monodefluorination of C_6F_6 in the presence of Et_3SiH and PPh_3 using 5 mol% **2** as the catalyst at 50 °C in d_8-THF. Fluorobenzene (C_6H_5F) at δ -113.2 is used as the internal standard (0.469 M, 0.203 mmol). The ^{19}F resonance corresponding to the *para* position of pentafluorobenzene (C_6F_5H) at δ -155.1 was used for integration purposes (TON=5.4). A relaxation delay of 50 seconds was used between scans in the ^{19}F NMR experiment (282 MHz, d_8-THF, 25 °C).
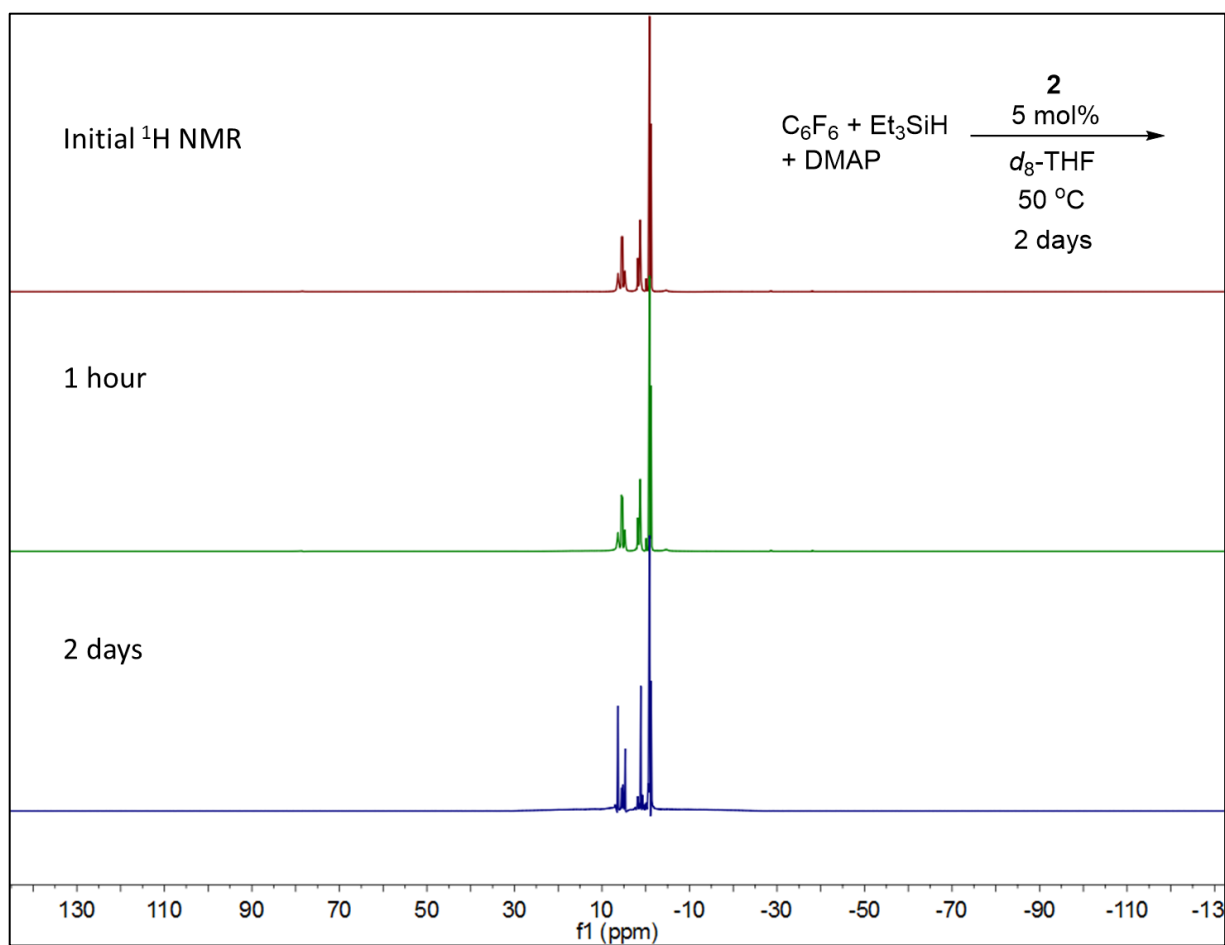
Figure S36: Stacked ^{1}H NMR spectra for the attempted monodefluorination of C_6F_6 in the presence of Et_3SiH and 4-(dimethylamino)pyridine (DMAP) using 5 mol% **2** at 50 °C in d_8-THF. A new species is immediately formed from the coordination of DMAP to **2**. All spectra collected in d_8-THF at 300 MHz at 25 °C.
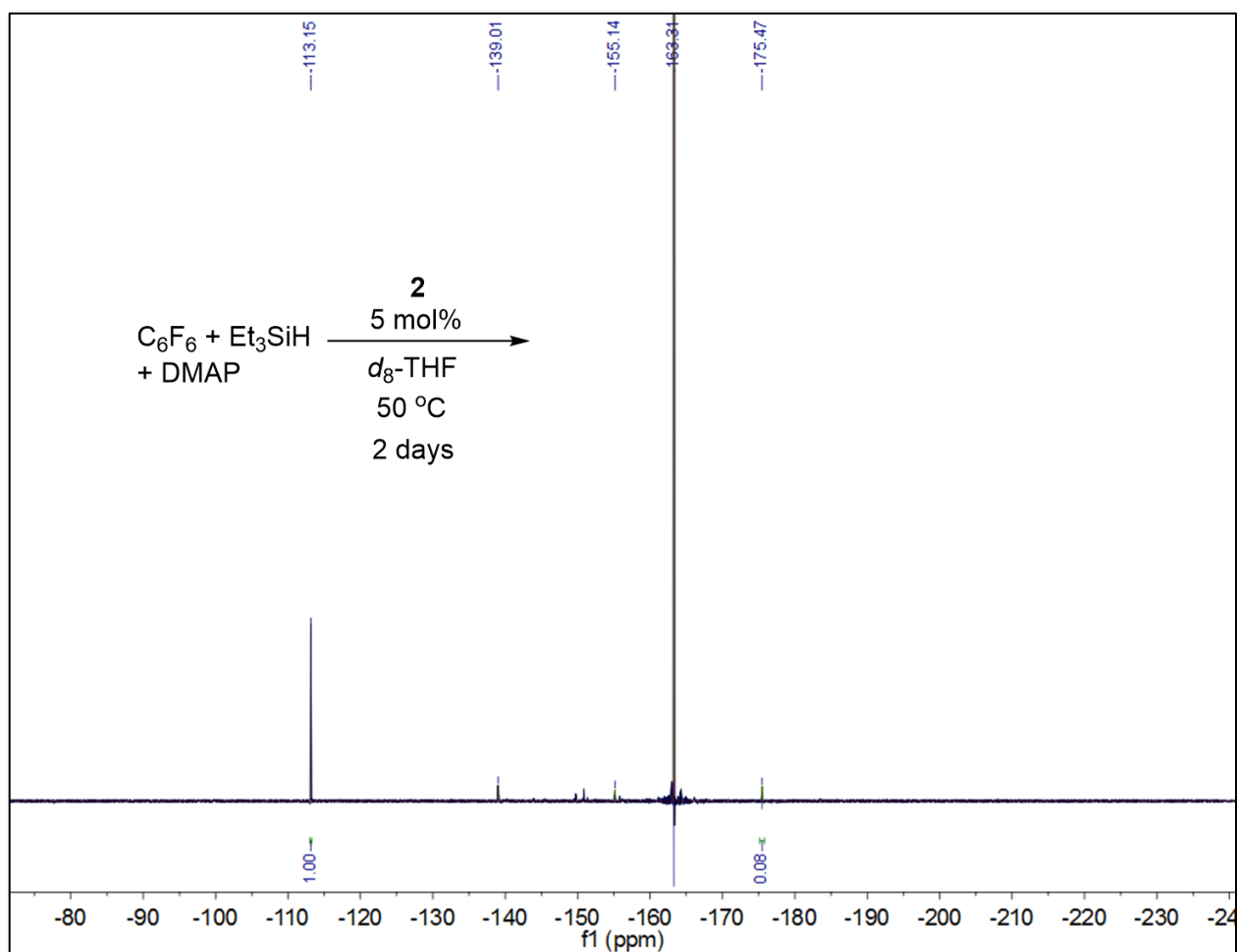
Figure S37: ^{19}F NMR spectrum for the final time point after 2 days for the attempted monodefluorination of C_6F_6 in the presence of Et_3SiH and 4-(dimethylamino)pyridine using 5 mol% **2** at 50 °C in d_8-THF. Fluorobenzene (C_6H_5F) at δ -113.2 is used as the internal standard (0.462 M, 0.237 mmol). Negligible amounts of the defluorinated product C_6F_5H were formed (282 MHz, d_8-THF, 25 °C).
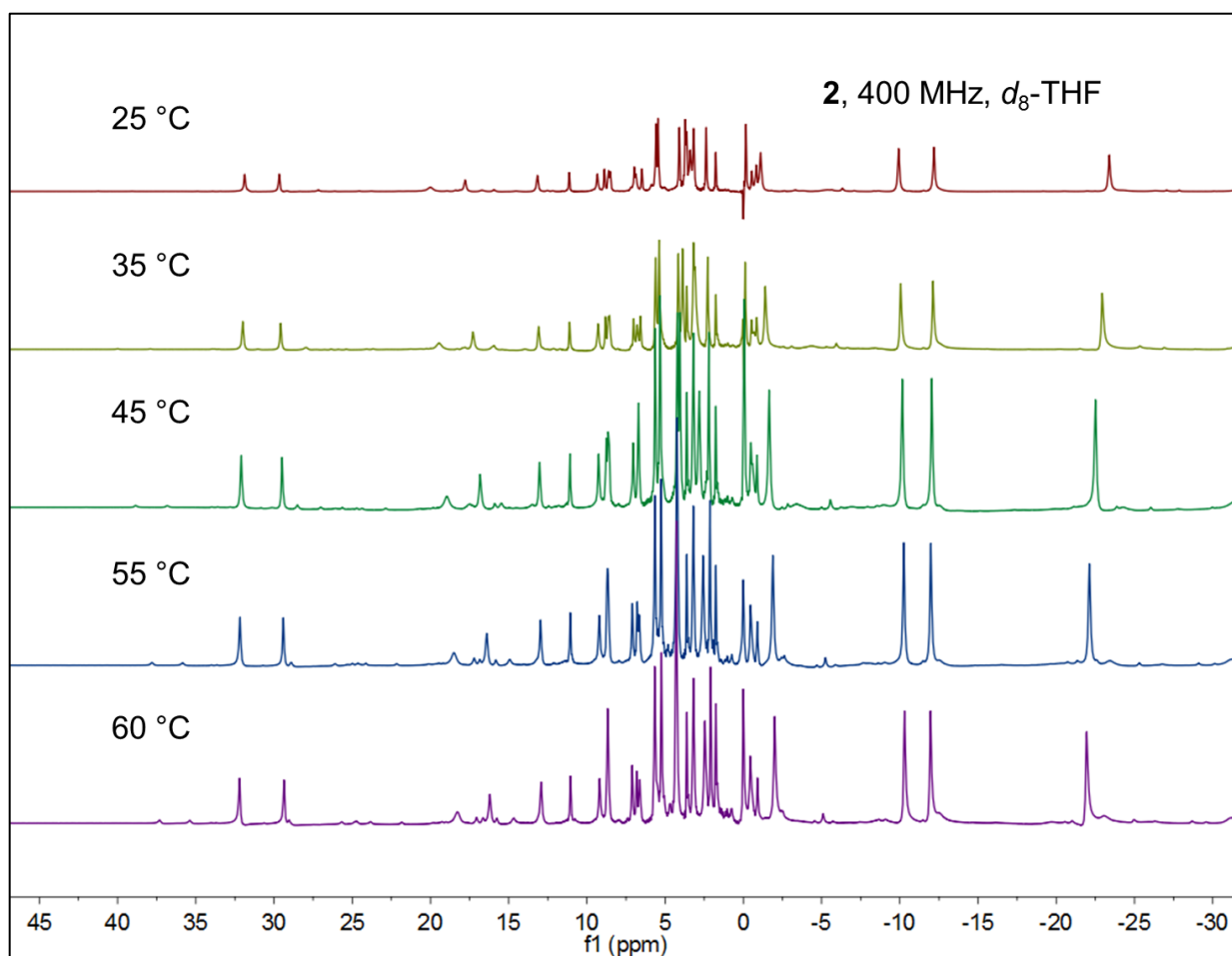
Figure S38: Stacked variable temperature for a d_8-THF solution of the dimeric iron hydride **2**. There is not an appreciable difference in the spectra across the various temperatures recorded (see **Figure S39** for a more detailed perspective).
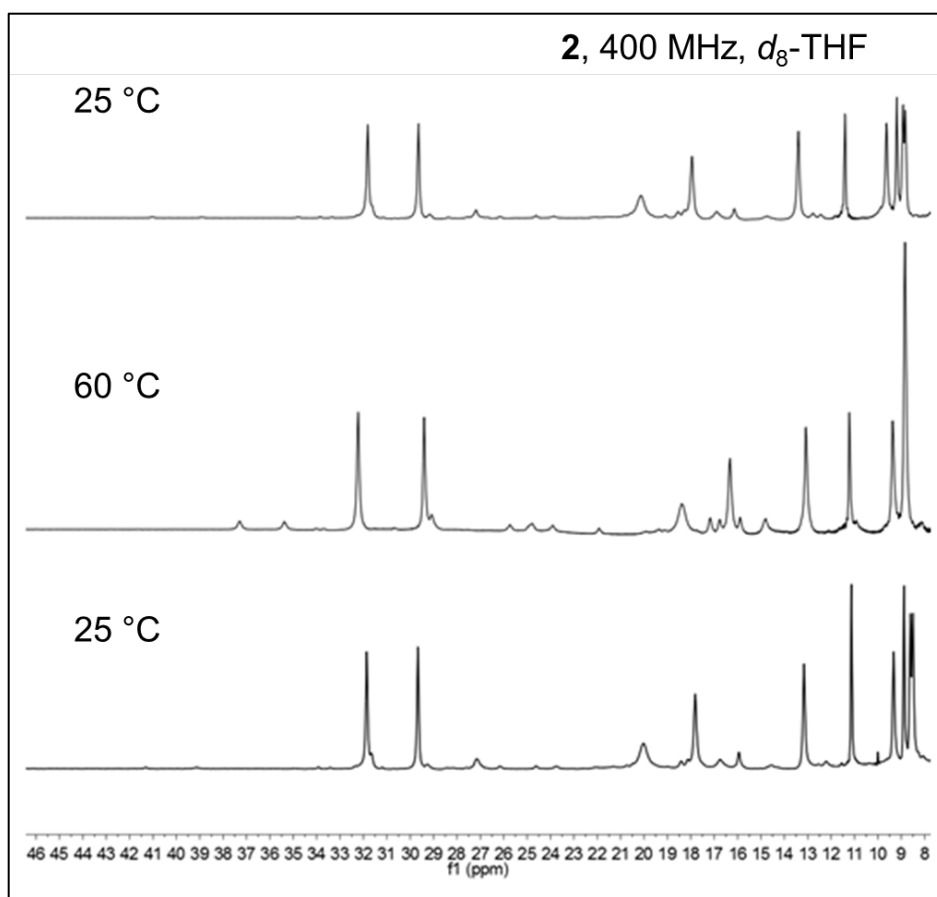
Figure S39: Stacked variable temperature for a d_8-THF solution of the dimeric iron hydride **2**. This zoomed-in region shows a new set of resonances that appear at δ 37.3 and 35.4 at 60 °C. These same signals disappear upon cooling the NMR sample to 25 °C. The reversibility of signal appearance/disappearance gives support to the hypothesis that increased temperatures cause a shift in the dimer/monomer equilibrium of **2** to shift to slight monomer production at elevated temperature.
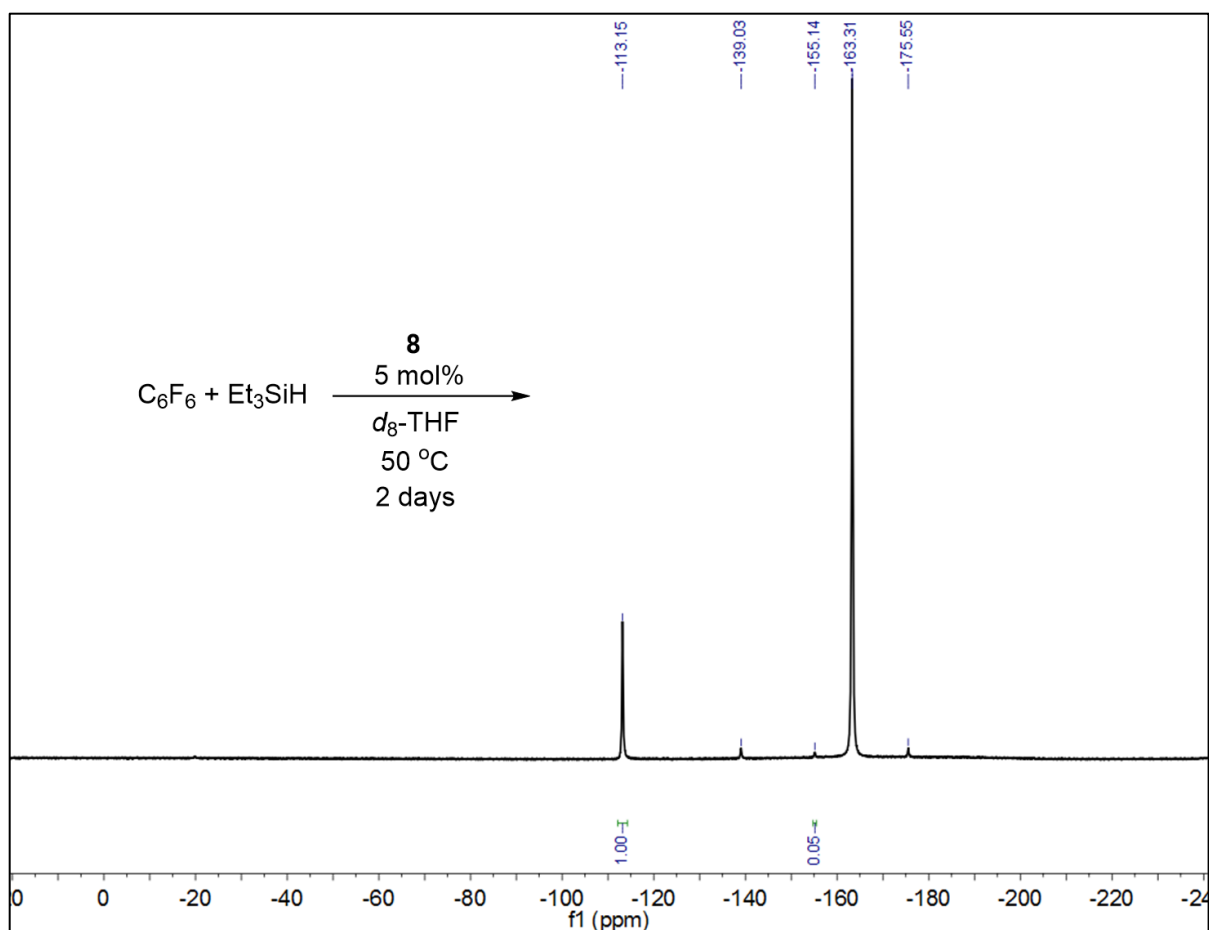
Figure S40: ^{19}F NMR spectrum for the final time point after 2 days for the attempted monodefluorination of C_6F_6 in the presence of Et_3SiH using 5 mol% **8** at 50 °C in d_8-THF. Fluorobenzene (C_6H_5F) at δ -113.2 is used as the internal standard (0.462 M, 0.295 mmol). The ^{19}F resonance corresponding to the *para* position of pentafluorobenzene (C_6F_5H) at δ -155.1 was used for integration purposes (TON=0.8). A relaxation delay of 50 seconds was used between scans in the ^{19}F NMR experiment (282 MHz, d_8-THF, 25 °C).
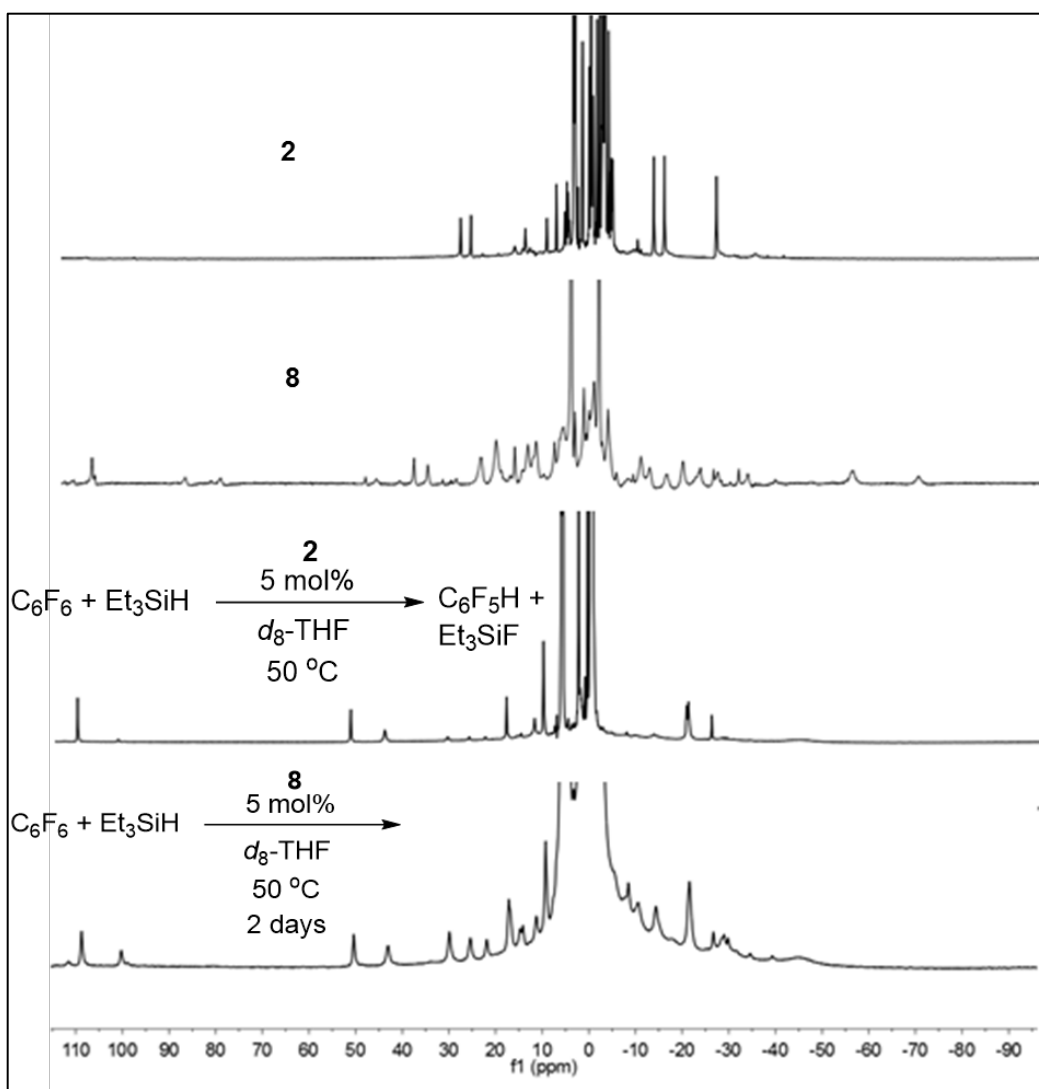
Figure S41: A comparison of the ^1H NMR spectra for **2**, **8**, and the final time points for the HDF catalytic runs using **2** and **8** as precatalysts. The resting state during catalysis is not the hydride species **2** or the fluoride species **8**. All spectra collected in d_8-THF at 300 MHz at 25 °C.
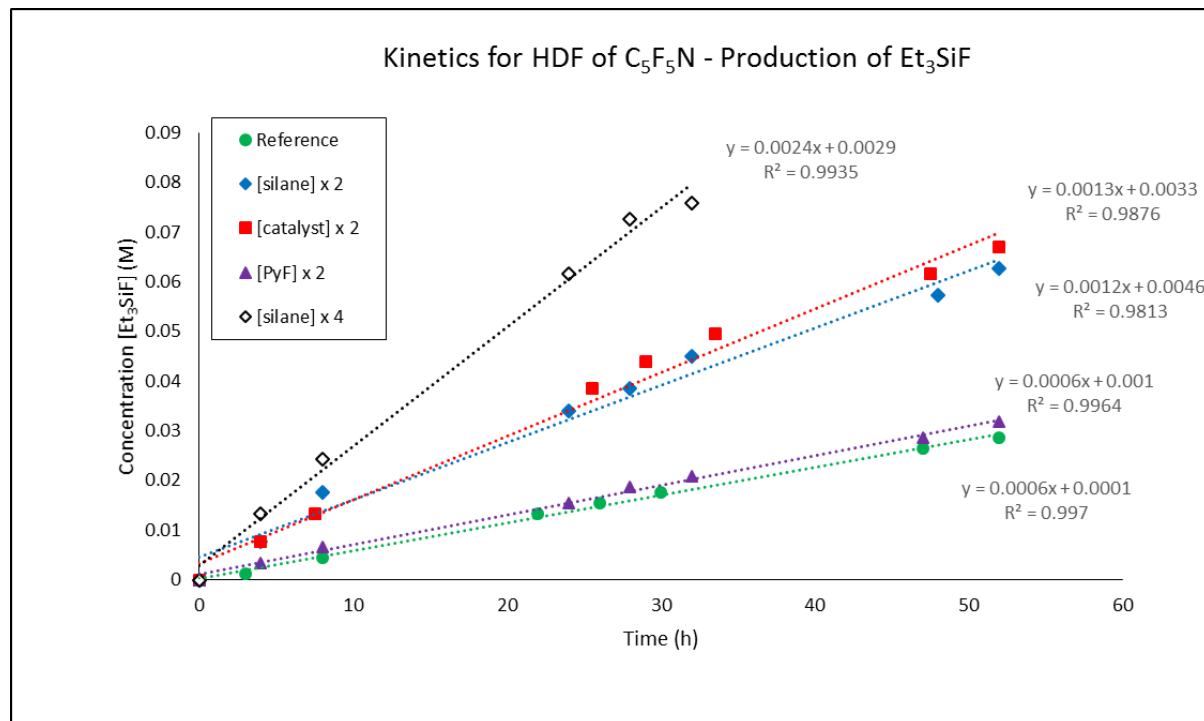
Figure S42: Kinetic evaluation for the production of Et_3SiF during the hydrodefluorination of pentafluoropyridine. The trials shown in the above figure are from the same conditions outlined in the main text (reference: [silane]=[PyF]=0.11 M, [Fe]=5.5 x 10^{-3} M using d_8-THF at 50 °C).