Supporting information for:

"Carbon-Fluorine Bond Cleavage in Fluoroarenes via a Niobium (III) Imido Complex: From Stoichiometric to Catalytic Hydrodefluorination"

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A. General Considerations

Unless otherwise noted, all reactions were performed either using standard Schlenk line techniques or in an MBraun inert atmosphere glove box under an atmosphere of purified nitrogen (<1 ppm O_2/H_2O). Glassware, cannulae, and Celite were stored in an oven at *ca*. 160 ºC for at least 12 hrs prior to use. Hexanes, Et_2O, THF, DCM and toluene were purified by passage through a column of activated alumina, stored over 3 or 4 Å molecular sieves, and degassed prior to use.[1] Benzyl fluoride, fluorobenzene, 1,2-, 1,3- and 1,4-fluorobenzenes, 1,2,3- and 1,3,5-trifluorobenzenes, 1,2,4,5-tetrafluorobenzene, pentafluorobenzene, and perfluorobenzene were dried and stored over 4 Å molecular sieves. Deuterated solvents (C_6D_6, C_7D_8 and mesitylene-d_{12}) and mesytilene were dried over sodium/benzophenone; and then vacuum transferred to a storage flask containing activated molecular sieves. *N,N'-bis*-(2,6-diisopropylphenyl)-β-diketiminate (BDI),[2] Li(BDI)·Et_2O,[3] (BDI)pyCl_2Nb(N^{t}Bu),[4] (BDI)$(Me)_2$Nb(N^{t}Bu),[4] (BDI)$(\eta^6$-benzene$)_2$Nb(N^{t}Bu),[5] were prepared using literature procedures. All other reagents were acquired from commercial sources and used as received. NMR spectra were recorded on Bruker AV-300, AVQ-400, AVB-400, DRX-500, AV-500, and AV-600 spectrometers. Chemical shifts were measured relative to residual solvent peaks, which were assigned relative to an external TMS standard for $^1H/^{13}C$ and $BF_3.OEt_2$ for ^{19}F set at 0.00 ppm. ^1H and ^{13}C NMR assignments were routinely confirmed by 135/90 DEPT, ^1H-^1H (COSY, NOESY) and ^1H-^{13}C (HSQC and HMBC) experiments. GC/MS analyses were performed using a Agilent 6890 N Network GC system coupled to a 5973 Network mass selective detector. The uncorrected melting points were determined using sealed capillaries prepared under nitrogen on an Optmelt SRS. Elemental analyses were performed at the School of Human Sciences, Science Center, London Metropolitan University. The X-ray structural determinations were performed at CHEXRAY, University of California, Berkeley on Bruker SMART APEX or SMART QUAZAR diffractometers.

B. Synthesis and characterization of compounds 2a-f,h

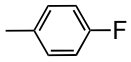
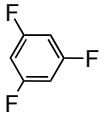
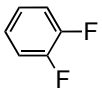
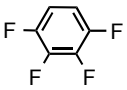
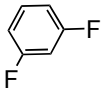
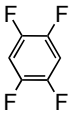
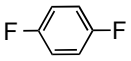
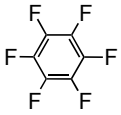
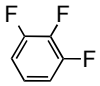
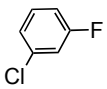
B.1 NMR scale reactions

Method: Complex **1**, (BDI)(η^6-C_6H_6)Nb(N^{t}Bu) (18.5 mg, 0.028 mmol, 0.07 M) was dissolved in 0.4 ml of C_6D_6 containing 2.0 M of fluoroarene and 0.02 M of trimethoxybenzene as internal standard, and the resulting solution was added to a J-Young NMR tube with a Teflon cap. The NMR tube was either stored at room temperature or heated at 60 ^{o}C depending on the condition described in table 1 of the manuscript. The yield of each reaction was calculated by integrating the peak corresponding to the CH of the BDI backbone (*H*C(C(Me)NAr)$_2$) of the new complex, commonly observed in the 5.5-5.0 ppm range, relative to the peak at 6.25 ppm of the internal standard (C_6H_3(OCH_3)$_3$) by ^{1}H NMR. In the case of 1,3,5-trifluorobenzene, the overlap between the substrates and the internal standard forced us to use the signal at 3.42 ppm corresponding to the methoxy group of the internal standard (C_6H_3(OCH_3)$_3$). Due to the strong signals of the substrates, the yields were further confirmed by removing the volatile materials under high vacuum, adding 0.4 mL of fresh C_6D_6 to the J-Young NMR tube, and reanalyzing the solution by NMR.

Competition experiment 1,2- vs 1,3- difluorobenzene: Complex **1** (BDI)(η^6-C_6H_6)Nb(N^{t}Bu) (18.5 mg, 0.028 mmol, 0.07 M) was dissolved in 0.4 ml of C_6D_6 containing 1.0 M of 1,2-difluorobenzene, 1.0 M of 1,3-difluorobenzene and 0.02 M of trimethoxybenzene as internal standard. The resulting solution was added to a J-Young NMR tube with a Teflon cap. The NMR tube was heated at 60 ^{o}C for 30 min. The yield of each complex, **2c and 2d**, was calculated relative to the amount of internal standard by ^{1}H NMR (Figure S.1, left) and further confirmed by integration of the ^{19}F NMR spectrum (Figure S.1, right).

Determination of relative rates: Complex **1** (BDI)(η^6-C_6H_6)Nb(N^tBu) (18 mg, 0.027 mmol, 0.07 M) was dissolved in 0.4 ml of C_6D_6 containing 1.0 M of fluorobenzene (45 μL), 1.0 M of fluoroarene and 0.02 M of trimethoxybenzene as internal standard. The resulting solution was added to a J-Young NMR tube with a Teflon cap. The NMR tube was heated at 60 ^oC and monitored every 30 min. The relative rate between the two complexes, **2a : 2x** (x= b-h), was calculated using the integral ratio of ^{19}F NMR resonance of Nb-F (Table S.1 and Figure S.2, bottom) and further confirmed by the integral ratio of the CH backbond of the BDI ligand in the ^1H spectrum.

Table S.1 Competition experiments and $R_{relative}$ calculation.

Substrate	Integral **2a**	Integral **2x**	$R_{elative}$	Substrate	Integral **2a**	Integral **2x**	$R_{elative}$
	1	0.54	0.54		1	0.44	0.44
	1	16.2	16.2		1	0.36	0.36
	1	11.3	11.3		1	0.04	0.04
	1	1.30	1.30		1	nd	< 0.1[a]
	1	3.95	3.95		nd	1	> 16[a]

nd: not detected by NMR spectroscopy
[a]: Due to the non-detection of one complex, $R_{relative}$ is estimated to be higher or lower than the faster or slower $R_{relative}$ respectively.

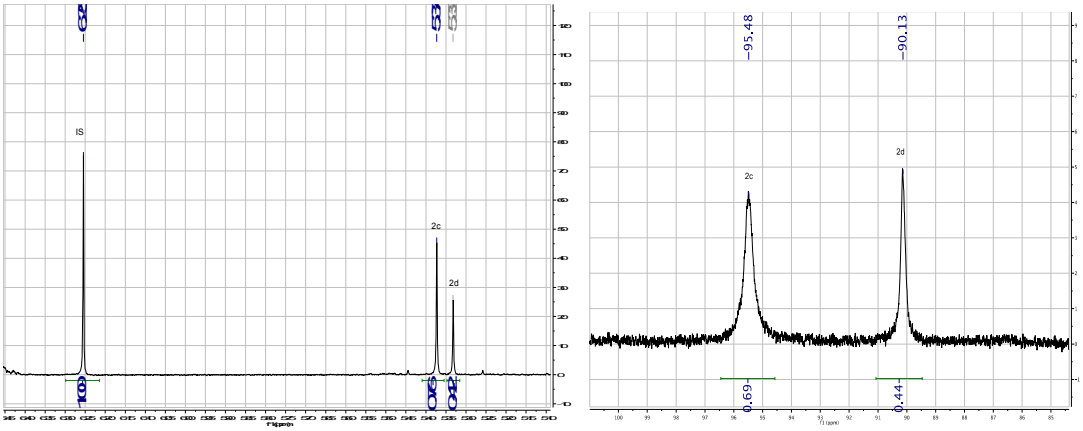


Figure S.1 ^{1}H (left) and ^{19}F (right) NMR spectra of the competition experiment between 1,2- and 1,3-dilfuorobenzenes.

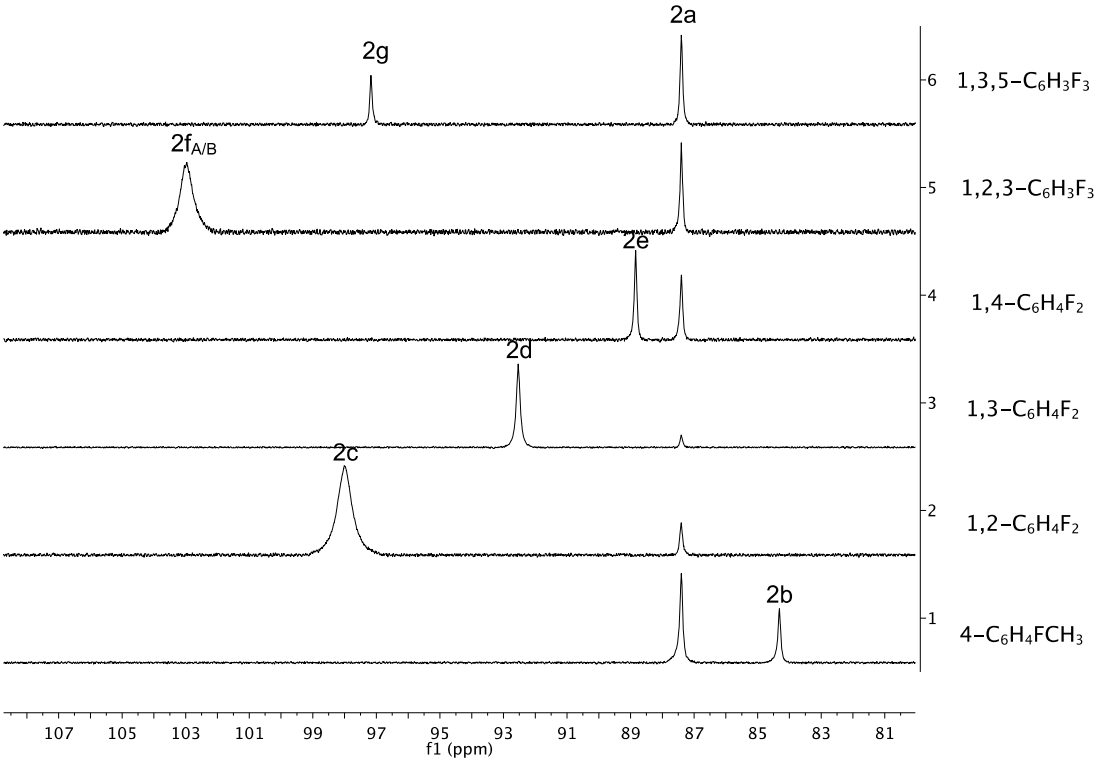


Figure S.2 ^{19}F NMR spectrum of the competition experiment between 1M of fluorobenzene and 1 M of other fluoroarenes.

B.2 Large scale reaction

General method for the synthesis of complexes 2a-f,h. Each fluoroarene (10 mL) was added to a 25-mL Schlenk flask containing (BDI)(η^6-C_6H_6)Nb(N^{t}Bu) (0.120 g, 0.182 mmol, 1.0 equiv.) at room temperature. The dark red solution was heated to 60 °C. The color of the solution turned from dark red to yellow/orange within 15 to 45 min depending on the substrate. After 3 h, the volatile materials were removed under reduced pressure to yield a yellow/orange residue. Trituration with Et_2O (2 × 5 ml), extraction with hexane (20 ml), and storage at -40 °C overnight afforded yellow crystals, which were collected by filtration.

Complex 2a, [(BDI)Nb(N^{t}Bu)(Ph)(F)]: Yield: 97 mg, 0.143 mmol, 79%. X-ray suitable crystals were obtained by recrystallization from hexanes at -40 ^{o}C. ^{1}H NMR (500 MHz, C_7D_8, 293 K): δ (ppm) 8.05 (b, 2 H, *Ph*-Nb), 7.18-6.96 (broad, Ar), 5.39 (s, 1 H, *H*C(C(Me)NAr)$_2$), 2.96 (broad sept, 4 H, C*H*Me$_2$), 1.58 (s, 6 H, HC(C(*Me*)NAr)$_2$), 1.21 (b, 6 H, CH*Me*$_2$), 1.08 (d, 12 H, CH*Me*$_2$, $^3J_{HH}$ = 6.6 Hz), 1.0 (b, 6 H, CH*Me*$_2$), 0.94 (s, 9 H, ^{t}Bu). ^{1}H NMR (500 MHz, C_7D_8, 353 K): δ (ppm) 7.97 (dd, 2 H, *Ph*-Nb), 7.14-6.96 (Ar + C_7D_8), 5.47 (s, 1 H, *H*C(C(Me)NAr)$_2$), 2.96 (sept, 4 H, C*H*Me$_2$, $^3J_{HH}$ = 6.6 Hz), 1.63 (s, 6 H, HC(C(*Me*)NAr)$_2$), 1.08 (b, 12 H, CH*Me*$_2$), 1.04 (d, 12 H, CH*Me*$_2$, $^3J_{HH}$ = 6.6 Hz), 0.91 (s, 9 H, ^{t}Bu). ^{19}F NMR (470 MHz, C_7D_8, 293 K): δ (ppm) 87.4 (s, Nb-*F*). ^{19}F NMR (470 MHz, C_7D_8, 353 K): δ (ppm) 89.4 (s, Nb-*F*). ^{13}C{^{1}H} NMR (125.8 MHz, C_7D_8, 353 K): δ (ppm) 132.5 (CH, *Ph*-Nb), 103.2 (CH, H*C*(C(Me)NAr)$_2$), 30.6 (CH$_3$, Nb=NC(*C*H-$_3$)$_3$), 28.5 (CH, *C*HMe$_2$ of C=NAr), 25.3 (CH$_3$, HC(C(*Me*)NAr)$_2$), 24.8 (CH$_3$, CH*Me*$_2$ of C=NAr), 24.3 (CH$_3$, CH*Me*$_2$ of C=N*Ar*), 23.2 (CH$_3$, CH*Me*$_2$ of C=N*Ar*). Anal. Calcd for $C_{39}H_{55}F_1N_3Nb_1$: C, 69.11; H, 8.18; N, 6.20. Found: C, 68.89; H, 8.35; N, 6.16.

Complex 2b, [(BDI)Nb(N^{t}Bu)(4-CH$_3$Ph)(F)]: Yield: 85 mg, 0.123 mmol, 68%. ^{1}H NMR (500 MHz, C_6D_6, 293 K): δ (ppm) 8.09 (d, 2 H, *pTol*-Nb,), 7.18-6.96 (broad, Ar), 5.49 (s, 1 H, *H*C(C(Me)NAr)$_2$), 3.1 (b, 4 H, C*H*Me$_2$), 1.71 (s, 6 H, HC(C(*Me*)NAr)$_2$), 1.31 (b, 6 H, CH*Me*$_2$), 1.22 (d, 12 H, CH*Me*$_2$, $^3J_{HH}$ = 6.6 Hz), 1.15 (b, 6 H, CH*Me*$_2$), 1.07 (s, 9 H, ^{t}Bu). ^{19}F NMR (470 MHz, C_6D_6, 293 K): δ (ppm) 82.3 (s, Nb-*F*). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 293 K): δ (ppm) 132.5 (CH, *Ph*-Nb), 103.2 (CH, H*C*(C(Me)NAr)$_2$), 30.6 (CH$_3$, Nb=NC(*C*H$_3$)$_3$), 28.5 (CH, *C*HMe$_2$ of C=NAr), 25.3 (CH$_3$, HC(C(*Me*)NAr)$_2$), 24.8 (CH$_3$, CH*Me*$_2$ of C=NAr), 24.3 (CH$_3$, CH*Me*$_2$ of C=N*Ar*), 23.2 (CH$_3$, CH*Me*$_2$ of

C=N*Ar*). Anal. Calcd for $C_{40}H_{58}F_1N_3Nb_1$: C, 69.34; H, 8.44; N, 6.07. Found: C, 69.70; H, 8.77; N, 6.41.

Complex 2c, [(BDI)Nb(N^{t}Bu)(2-C$_6$H$_4$F)(F)]: Yield: 94 mg, 0.134 mmol, 74%. X-ray suitable crystals were obtained by recrystallization from hexanes at -40 ^{o}C. ^{1}H NMR (500 MHz, C_7D_8, 293 K): δ (ppm) 7.85 (b, 2 H, 2-C$_6$*H*$_4$F-Nb), 7.18-6.96 (broad, Ar), 5.39 (s, 1 H, *H*C(C(Me)NAr)$_2$), 2.99 (broad, 4 H, C*H*Me$_2$), 1.59 (s, 6 H, HC(C(*Me*)NAr)$_2$), 1.24 (b, 12 H, CH*Me*$_2$), 1.15 (b, 12 H, CH*Me*$_2$), 1.01 (s, 9 H, ^{t}Bu). ^{1}H NMR (500 MHz, C_7D_8, 353 K): δ (ppm) 7.82 (dd, 2 H, 2-C$_6$*H*$_4$F-Nb), 7.14-6.96 (Ar + C_7D_8), 6.86 (t, 2 H, 2-C$_6$*H*$_4$F-Nb), 6.79 (t, 2 H, *Ar*), 5.46 (s, 1 H, *H*C(C(Me)NAr)$_2$), 2.99 (sept, 4 H, C*H*Me$_2$, $^3J_{HH}$ = 6.6 Hz), 1.63 (s, 6 H, HC(C(*Me*)NAr)$_2$), 1.11 (d, 12 H, CH*Me*$_2$, $^3J_{HH}$ = 6.6 Hz), 1.07 (d, 12 H, CH*Me*$_2$, $^3J_{HH}$ = 6.6 Hz), 0.92 (s, 9 H, ^{t}Bu). ^{19}F NMR (470 MHz, C_7D_8, 293 K): δ (ppm) 98.0 (s, Nb-*F*), -84.2 (b, o-F). ^{19}F NMR (470 MHz, C_7D_8, 353 K): δ (ppm) 99.9 (s, Nb-*F*), -85.2 (s, o-F). ^{13}C{^{1}H} NMR (125.8 MHz, C_7D_8, 353 K): δ (ppm) 131.3 (CH, *Ph*-Nb), 103.9 (CH, H*C*(C(Me)NAr)$_2$), 29.9 (CH$_3$, Nb=NC(*C*H$_3$)$_3$), 28.3 (CH, *C*HMe$_2$ of C=NAr), 25.0 (CH$_3$, HC(C(*Me*)NAr)$_2$), 24.8 (CH$_3$, CH*Me*$_2$ of C=NAr), 24.0 (CH$_3$, CH*Me*$_2$ of C=N*Ar*), 23.9 (CH$_3$, CH*Me*$_2$ of C=N*Ar*). Anal. Calcd for $C_{39}H_{54}F_2N_3Nb_1$: C, 67.32; H, 7.82; N, 6.04. Found: C, 67.49; H, 8.05; N, 6.19.

Complex 2d, [(BDI)Nb(N^{t}Bu)(3-C$_6$H$_4$F)(F)]: Yield: 112 mg, 0.160 mmol, 91%. X-ray suitable crystals were obtained by recrystallization from hexanes at -40 ^{o}C. ^{1}H NMR (500 MHz, C_7D_8, 293 K): δ (ppm) 7.84 (d, 1 H, 3-C$_6$*H*$_4$F-Nb, $^3J_{HH}$ = 6.7 Hz), 7.74 (d, 1 H, 3-F*Ph*-Nb, $^3J_{HH}$ = 6.8 Hz), 7.18-6.96 (broad, Ar), 6.84 (dt, 1 H, 3-C$_6$*H*$_4$FNb, $^3J_{HH}$ = 6.7 Hz, $^4J_{HH}$ = 1.7 Hz), 5.34 (s, 1 H, *H*C(C(Me)NAr)$_2$), 2.91 (sept, 4 H, C*H*Me$_2$, $^3J_{HH}$ = 6.6 Hz), 1.53 (s, 6 H, HC(C(*Me*)NAr)$_2$), 1.20 (b, 6 H, CH*Me*$_2$), 1.06 (d, 12 H, CH*Me*$_2$, $^3J_{HH}$ = 6.6 Hz), 1.02 (b, 6 H, CH*Me*$_2$), 0.89 (s, 9 H, ^{t}Bu). ^{1}H NMR (500 MHz, C_7D_8, 353 K): δ (ppm) 7.80 (dd, 1 H, 3-C$_6$*H*$_4$F-Nb, $^3J_{HH}$ = 6.7 Hz, $^4J_{HH}$ = 1.7 Hz), 7.72 (d, 1 H, 3-C$_6$*H*$_4$F-Nb, $^3J_{HH}$ = 6.8 Hz), 7.18-6.96 (broad, Ar), 6.83 (dt, 1 H, 3-C$_6$*H*$_4$F -Nb, $^3J_{HH}$ = 6.7 Hz, $^4J_{HH}$ = 1.7 Hz), 5.39 (s, 1 H, *H*C(C(Me)NAr)$_2$), 2.91 (sept, 4 H, C*H*Me$_2$, $^3J_{HH}$ = 6.6 Hz), 1.56 (s, 6 H, HC(C(*Me*)NAr)$_2$), 1.09 (d, 12 H, CH*Me*$_2$, $^3J_{HH}$ = 6.8 Hz), 1.06 (d, 12 H, CH*Me*$_2$, $^3J_{HH}$ = 6.6 Hz), 0.88 (s, 9 H, ^{t}Bu). ^{19}F NMR (470 MHz, C_7D_8, 293 K): δ (ppm) 92.1 (s, Nb-*F*), -113.6 (s, m-*F*). ^{19}F NMR (470 MHz, C_7D_8, 353 K): δ (ppm) 94.3 (s, Nb-*F*), -113.9 (s, m-*F*). ^{13}C{^{1}H} NMR (125.8 MHz, C_7D_8, 353 K): δ (ppm) 103.8 (CH,

H*C*(C(Me)NAr)$_2$), 29.7 (CH$_3$, Nb=NC(*C*H$_3$)$_3$), 28.1 (CH, *C*HMe$_2$ of C=NAr), 25.4 (CH$_3$, HC(C(*Me*)NAr)$_2$), 24.6 (CH$_3$, CH*Me$_2$* of C=NAr), 24.1 (CH$_3$, CH*Me*$_2$ of C=N*Ar*), 23.7 (CH$_3$, CH*Me*$_2$ of C=N*Ar*). Anal. Calcd for $C_{39}H_{54}F_2N_3Nb_1$: C, 67.32; H, 7.82; N, 6.04. Found: C, 67.53; H, 8.00; N, 6.21.

Complex 2e, [(BDI)Nb(N^{t}Bu)(4-C$_6$H$_4$F)(F)]: Yield: 100 mg, 0.150 mmol, 87%. ^{1}H NMR (500 MHz, C_7D_8, 293 K): δ (ppm) 8.00 (b, 2 H, 4-C$_6$*H*$_4$F-Nb), 7.18-6.96 (broad, Ar), 5.38 (s, 1 H, *H*C(C(Me)NAr)$_2$), 2.90 (broad, 4 H, C*H*Me$_2$), 1.56 (s, 6 H, HC(C(*Me*)NAr)$_2$), 1.21 (b, 12 H, CH*Me*$_2$), 1.05 (b, 12 H, CH*Me*$_2$), 0.92 (s, 9 H, ^{t}Bu). ^{19}F NMR (470 MHz, C_7D_8, 293 K): δ (ppm) 97.2 (s, 1 F, Nb-*F*), -108.3 (s, 1 F, p-*F*). ^{13}C{^{1}H} NMR (125.8 MHz, C_7D_8, 298 K): δ (ppm) 103.5 (CH, H*C*(C(Me)NAr)$_2$), 29.1 (CH$_3$, Nb=NC(*C*H$_3$)$_3$), 28.6 (CH, *C*HMe$_2$ of C=NAr), 24.9 (CH$_3$, HC(C(*Me*)NAr)$_2$), 24.5 (CH$_3$, CH*Me$_2$* of C=NAr), 23.1 (CH$_3$, CH*Me*$_2$ of C=N*Ar*), 22.6 (CH$_3$, CH*Me*$_2$ of C=N*Ar*). Anal. Calcd for $C_{39}H_{54}F_2N_3Nb_1$: C, 67.32; H, 7.82; N, 6.04. Found: C, 67.10; H, 7.52; N, 6.29.

Complex 2f$_{A/B}$, [(BDI)Nb(N^{t}Bu)(2,x-C$_6$H$_3$F$_2$)(F)], x = 3 or 6: Yield: 83 mg, 0.116 mmol, 65%. Anal. Calcd for $C_{39}H_{53}F_3N_3Nb_1$: C, 65.63; H, 7.48; N, 5.89. Found: C, 65.87; H, 7.81; N, 6.12.

Main resonances for complex **2f$_A$**, [(BDI)Nb(N^{t}Bu)(2,3-C$_6$H$_3$F$_2$)(F)]: (500 MHz, C_7D_8, 293 K): δ (ppm) 5.34 (s, 1 H, *H*C(C(Me)NAr)$_2$), 2.93 (b, 4 H, C*H*Me$_2$, $^3J_{HH}$ = 6.6 Hz), 1.54 (s, 6 H, HC(C(*Me*)NAr)$_2$). ^{1}H NMR (500 MHz, C_7D_8, 353 K): δ (ppm) 5.44 (s, 1 H, *H*C(C(Me)NAr)$_2$), 2.98 (sept, 4 H, C*H*Me$_2$, $^3J_{HH}$ = 6.6 Hz), 1.61 (s, 6 H, HC(C(*Me*)NAr)$_2$). ^{19}F NMR (470 MHz, C_7D_8, 293 K): δ (ppm) 103.2 (b, Nb-*F*). ^{19}F NMR (470 MHz, C_7D_8, 353 K): δ (ppm) 104.4 (s, Nb-*F*).

Main resonances for complex **2f$_B$**, [(BDI)Nb(N^{t}Bu)(2,6-C$_6$H$_3$F$_2$)(F)]: (500 MHz, C_7D_8, 293 K): δ (ppm) 5.32 (s, 1 H, *H*C(C(Me)NAr)$_2$), 3.18 (b, 4 H, C*H*Me$_2$, $^3J_{HH}$ = 6.6 Hz), 1.61 (s, 6 H, HC(C(*Me*)NAr)$_2$). ^{1}H NMR (500 MHz, C_7D_8, 353 K): δ (ppm) 5.39 (s, 1 H, *H*C(C(Me)NAr)$_2$), 3.22 (sept, 4 H, C*H*Me$_2$, $^3J_{HH}$ = 6.6 Hz), 1.66 (s, 6 H, HC(C(*Me*)NAr)$_2$). ^{19}F NMR (470 MHz, C_7D_8, 293 K): δ (ppm) δ (ppm) 103.2 (b, Nb-*F*). ^{19}F NMR (470 MHz, C_7D_8, 353 K): δ (ppm) 109.5 (s, 1 F, Nb-*F*).

Accurate assigment of 2,x-C$_6$H$_4$F$_2$, with x = 3 or 6, was challenging due to the broadness of the signals and the resulting difficulty of integration. Three resonances in a roughly 1:1:1 ratio were observed, consistent with the three inequivalent C-F bonds expected (two

resonances for the non-symmetric 2,3-$C_6H_4F_2$ group of **2f$_A$** and one resonance for the symmetric 2,6-$C_6H_4F_2$ moiety of **2f$_B$**), and the 2:1 ratio between **2f$_A$** and **2f$_B$**. ^{19}F NMR (470 MHz, C_7D_8, 353 K): -80.2 (vb, 2 F, 2,6-$F_2C_6H_4$ of **2f$_B$**), -109.9 (b, 1 F, 2-$F_2C_6H_4$ of **2f$_A$**), -136.1 (d, 1 F, 3-$F_2C_6H_4$ of **2f$_A$**).

Complex 2g, [(BDI)Nb(N^{t}Bu)(3,5-$C_6H_3F_2$)(F)]: Yield: 60 mg, 0.082 mmol, 47%. ^{1}H NMR (500 MHz, C_7D_8, 293 K): δ (ppm) 7.61 (dd, 2 H, 3,5-$C_6H_3F_2$-Nb, $^3J_{HH}$ = 6.7 Hz, $^4J_{HH}$ = 1.6 Hz), 7.18-6.96 (broad, Ar), 6.59 (dt, 1 H, 3,5-$C_6H_3F_2$-Nb, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.5 Hz), 5.32 (s, 1 H, *H*C(C(Me)NAr)$_2$), 2.86 (broad, 4 H, C*H*Me$_2$), 1.51 (s, 6 H, HC(C(*Me*)NAr)$_2$), 1.10 (b, 12 H, CH*Me*$_2$), 1.05 (b, 12 H, CH*Me*$_2$), 0.84 (s, 9 H, ^{t}Bu). ^{19}F NMR (470 MHz, C_7D_8, 293 K): δ (ppm) 97.2 (s, 1 F, Nb-*F*), -111.1 (b, 2 F, m-*F*). ^{13}C{^{1}H} NMR (125.8 MHz, C_7D_8, 298 K): δ (ppm) 103.5 (CH, H*C*(C(Me)NAr)$_2$), 30.3 (CH_3, Nb=NC(*C*H$_3$)$_3$), 28.7 (CH, *C*HMe$_2$ of C=NAr), 25.6 (CH_3, HC(C(*Me*)NAr)$_2$), 24.3 (CH_3, CH*Me*$_2$ of C=NAr), 24.1 (CH_3, CH*Me*$_2$ of C=N*Ar*), 23.8 (CH_3, CH*Me*$_2$ of C=N*Ar*). Anal. Calcd for $C_{39}H_{53}F_3N_3Nb_1$: C, 65.63; H, 7.48; N, 5.89. Found: C, 65.39; H, 7.75; N, 6.01.

Complex 2h, [(BDI)Nb(N^{t}Bu)(2,3,6-$C_6H_2F_3$)(F)]: Yield: 71 mg, 0.100 mmol, 55%. %. ^{1}H NMR (500 MHz, C_7D_8, 293 K): δ (ppm) 7.18-6.96 (broad, Ar), 6.41 (b, 1 H, 2,3,6-$C_6H_2F_3$), 6.15 (b, 1 H, 2,3,6-$C_6H_2F_3$), 5.29 (s, 1 H, *H*C(C(Me)NAr)$_2$), 3.34 (b, 2 H, C*H*Me$_2$), 3.14 (b, 2 H, C*H*Me$_2$), 1.59 (s, 3 H, HC(C(*Me*)NAr)$_2$), 1.58 (s, 3 H, HC(C(*Me*)NAr)$_2$), 1.38 (d, 6 H, CH*Me*$_2$, $^3J_{HH}$ = 6.8 Hz), 1.32 (d, 6 H, CH*Me*$_2$, $^3J_{HH}$ = 6.6 Hz), 1.16 (s, 9 H, ^{t}Bu), 1.10 (d, 12 H, CH*Me*$_2$, $^3J_{HH}$ = 6.6 Hz). ^{1}H NMR (500 MHz, C_7D_8, 353 K): δ (ppm) 7.18-6.96 (broad, Ar), 6.52 (b, 1 H, 2,3,6-$C_6H_2F_3$), 6.23 (b, 1 H, 2,3,6-$C_6H_2F_3$), 5.37 (s, 1 H, *H*C(C(Me)NAr)$_2$), 3.20 (b, 4 H, C*H*Me$_2$), 1.65 (s, 3 H, HC(C(*Me*)NAr)$_2$), 1.21 (d, 12 H, CH*Me*$_2$, $^3J_{HH}$ = 6.8 Hz), 1.19 (d, 12 H, CH*Me*$_2$, $^3J_{HH}$ = 6.6 Hz), 1.07 (s, 9 H, ^{t}Bu). ^{19}F NMR (470 MHz, C_7D_8, 293 K): δ (ppm) 120.3 (s, 1F, Nb-*F*), -90.1 (s, 1F, 6-*F*), -103.7 (s, 1F, 2-*F*), -142.1 (s, 1F, 3-*F*). ^{19}F NMR (470 MHz, C_7D_8, 353 K): δ (ppm) 116.6 (s, 1F, Nb-*F*), -94.3 (s, 1F, 6-*F*), -108.4 (s, 1F, 2-*F*), -144.9 (s, 1F, 3-*F*). Anal. Calcd for $C_{39}H_{52}F_4N_3Nb_1$: C, 64.01; H, 7.16; N, 5.74. Found: C, 64.37; H, 7.02; N, 6.02.

Complex 2j, [(BDI)Nb(N^{t}Bu)(3-C_6H_5F)(Cl)]: Yield: 113 mg, 0.158 mmol, 88%. ^{1}H NMR (500 MHz, C_6D_6, 293 K): δ (ppm) 7.82 (b, 2 H, *Ph*-Nb), 7.18-6.96 (broad, Ar),

5.66 (s, 1 H, *H*C(C(Me)NAr)$_2$), 2.75 (broad, 4 H, C*H*Me$_2$), 1.74 (s, 3 H, HC(C(*Me*)NAr)$_2$), 1.57 (s, 3 H, HC(C(*Me*)NAr)$_2$), 1.35 (b, 6 H, CH*Me*$_2$), 1.05 (d, 12 H, CH*Me*$_2$, $^3J_{HH}$ = 6.7 Hz), 1.01 (s, 9 H, ^{t}Bu), 0.65 (b, 6 H, CH*Me*$_2$),. ^{19}F NMR (470 MHz, C_6D_6, 293 K): δ (ppm) -113.8 (b, 1F, m-*F*-Ar). Anal. Calcd for $C_{39}H_{54}Cl_1F_1N_3Nb_1$: C, 65.77; H, 7.64; N, 5.90. Found: C, 65.45; H, 7.83; N, 6.11.

C. Determination of molecular structures by single-crystal X-ray diffraction

X-ray structural determinations were performed on a Bruker SMART 1000 or SMART APEX diffractometer. Both are 3-circle diffractometers that couple a CCD detector[7] with a sealed-tube source of monochromated Mo Ka radiation (λ = 0.71073 Å). A crystal of appropriate size was coated in Paratone-N oil and mounted on a Kapton® loop. The loop was transferred to the diffractometer, centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrices and cell constants were determined by collection of 60 10 s frames, followed by spot integration and least-squares refinement. The reported cell dimensions were calculated from all reflections with $I > 10\ \sigma$. The data were corrected for Lorentz and polarization effects; no correction for crystal decay was applied. An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.[7] All software used for diffraction data processing and crystal-structure solution and refinement are contained in the APEX2 program suite (Bruker AXS, Madison, WI).[8] Thermal parameters for all non-hydrogen atoms were refined anisotropically. For all structures, $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$; $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$. Thermal ellipsoid plots were created using the ORTEP-3 software package and POV-ray.[9]

Table S. 2 Crystallographic parameters for complexes **2a, 2c**, **2d** and **2h**

Compound	**2a**	**2c**	**2d**	**2h**
Formula	$C_{39}H_{55}FN_3Nb$	$C_{39}H_{54}F_2N_3Nb$	$C_{39}H_{54}F_2N_3Nb$	$C_{39}H_{52}F_4N_3Nb$
Formula weight (amu)	677.77	695.75	695.76	731.74
Space Group	P_{-1}	P_{-1}	P_{-1}	$P2_{1/c}$
a (Å)	10.795(5)	10.8194(10)	10.9151(4)	12.7898(5)
b (Å)	12.323(5)	12.3148(12)	12.3010(4)	11.5223(4)
c (Å)	13.680(5)	13.7249(13)	13.7072(5)	24.9612(9)
α (°)	79.363(5)°	79.695(6)°	79.714(6)°	90°
β (°)	87.377(5)°	87.396(6)°	87.243(6)°	91.2170(10)°
γ (°)	88.428(5)°	88.376(6)°	88.804(6)°	90°
V (Å^3)	1786.3(13)	1797.0(3)	1808.60(11)	3677.7(2)
Z	2	2	2	4
ρ_{calcd} (g/cm^3)	1.260	1.284	1.278	1.322
F_{000}	720	734	736	1536
μ (mm^{-1})	0.372	0.375	0.373	0.378
T_{min}/T_{max}	0.8654/0.8966	0.9458/0.9706	0.9427/0.9708	0.9717/0.9802
No. rflns measured	27323	26452	42043	26888
No. indep. rflns	6588	6544	6684	6733
R_{int}	0.0168	0.0659	0.0493	0.0468
No. obs. ($I >$ 2.00σ(I))	6588	6544	6684	6733
No. variables	410	429	419	437
R_1, wR_2	0.0224/0.0587	0.0445/0.0829	0.0302/0.0702	0.0368/0.0862
R_1 (all data)	0.0240	0.0677	0.0371	0.0522

GoF	1.066	1.036	1.055	1.017
Res. peak/hole (e^{-}/Å^3)	0.349/-0.326	0.756/-0.469	0.469/-0.356	0.963/-0.325

C.1 Ortep view of compounds 2a,c-d

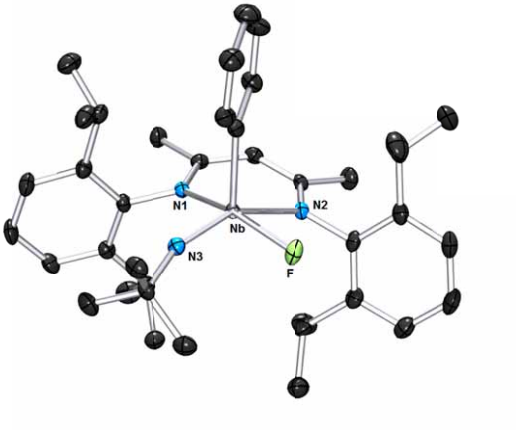


Figure S. 3 Ortep view of compound **2a**

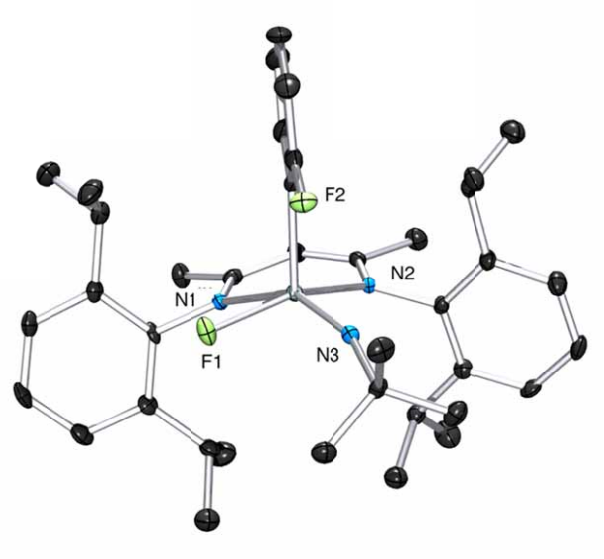


Figure S. 4 Ortep view of compound **2c**

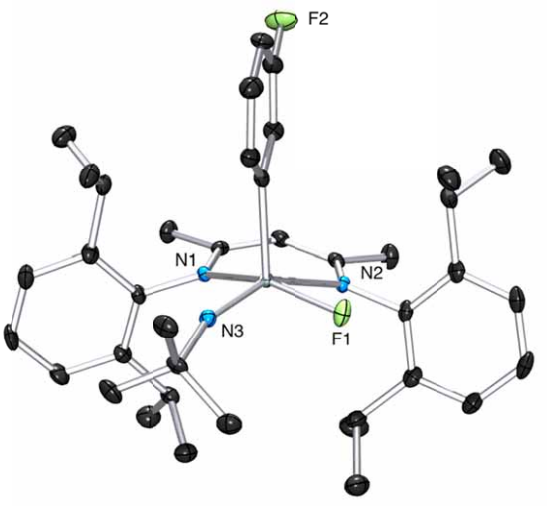


Figure S. 5 Ortep view of compound **2d**

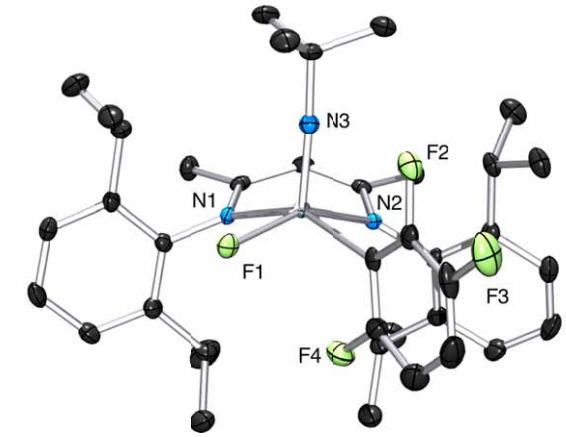


Figure S. 6 Ortep view of compound **2h**

C.2 Selected bond distances and angles of compounds 2a, 2c-d,h

Table S. 3 Selected distances and bond angles for complexes **2a, 2c-d,h**

	2a	**2c**	**2d**	**2h**
Nb-N_1 (BDI)	2.1422(14)	2.134(2)	2.1333(17)	2.194(2)
Nb-N_2 (BDI)	2.2968(14)	2.301(2)	2.3061(16)	2.180(2)
Nb-N_3 (Imido)	1.7659(14)	1.758(2)	1.7631(17)	1.746(3)
Nb-C_1 (Aryl)	2.1580(18)	2.176(3)	2.167(2)	2.246(2)
Nb-F_1	1.93225(11)	1.9336(17)	1.9411(12)	1.946(2)
C-F_2	-	1.246(4)	1.363(3)	1.359(3)
C_1-Nb-F_1	101.27(6)	100.74(9)	100.96(7)	85.33(7)
τ^{11}	0.05	0.07	0.04	0.02

D. NMR analysis of intermediate B

D.1 Method

A solution of C_9D_{12} containing fluorobenzene (10 µl, 0.107 mmol, 2 equiv.) and (BDI)$(Me)_2$Nb(N^{t}Bu) (35 mg, 0.057 mmol, 1 equiv.) was added to a J-Young NMR tube with a Teflon cap. The solution was freeze-pump-thawed three times and then refilled with 1 atm of H_2. The NMR tube with the thawing solution was placed in the spectrometer, with the probe pre-cooled to 263 K, and several ^{1}H NMR spectra were recorded. Between each spectrum, the NMR tube was ejected from the spectrometer and was shaken at room temperature for 1-2 mins before being brought back to 263 K. Figure S.5 shows the quick formation of the intermediate **A,** followed by the formation of **B**, also observed by ^{19}F NMR spectroscopy (Figure S.6). The persistence of these intermediates at 263 K allowed for their complete characterization (Figures S.7 and S.8). The spectrometer probe was then warmed to 313 K in order to observe the further conversion of **B** to the final product **2a** (Figures S.9 and S.10).

Characterization of **B**: ^{1}H NMR (600 MHz, C_9D_{12}, 263 K): δ(ppm) 5.05 (s, 1 H, *H*C(C(Me)NAr)$_2$), 4.50 (m, 2 H, C*H*Me$_2$, $^3J_{HH}$ = 6.9 Hz), 3.67 (t, 1 H, *p-Ph*F, $^3J_{HH}$ = 6.6 Hz), 3.36 (broad, 2 H, *m-Ph*F), 3.29 (t, 2 H, *o-Ph*F, $^3J_{HH}$ = 6.2 Hz), 2.61 (m, 2 H, C*H*Me$_2$, $^3J_{HH}$ = 6.9 Hz), 1.68 (s, 6 H, HC(C(*Me*)NAr)$_2$), 1.34 (s, 9 H, ^{t}Bu), 1.31 (d, 6 H, CH*Me*$_2$, $^3J_{HH}$ = 6.9 Hz), 1.10 (d, 6 H, CH*Me*$_2$, $^3J_{HH}$ = 6.6 Hz), 0.96 (d, 6 H, CH*Me*$_2$, $^3J_{HH}$ = 6.6 Hz), 0.94 (d, 6 H, CH*Me*$_2$, $^3J_{HH}$ = 6.9 Hz). ^{19}F NMR (564 MHz, C_9D_{12}, 263 K): δ(ppm) -113.4 (s, 3 F, Ph*F*). ^{13}C NMR (125 MHz, C_9D_{12}, 263 K): δ(ppm) 116 (CH, *m-Ph*F), 115 (CH, *p-Ph*F), 102 (CH, H*C*(C(Me)NAr)$_2$), 84 (CH, *o-Ph*F).

D.2 NMR analysis

D.2.1 Evolution of ^{1}H NMR with time

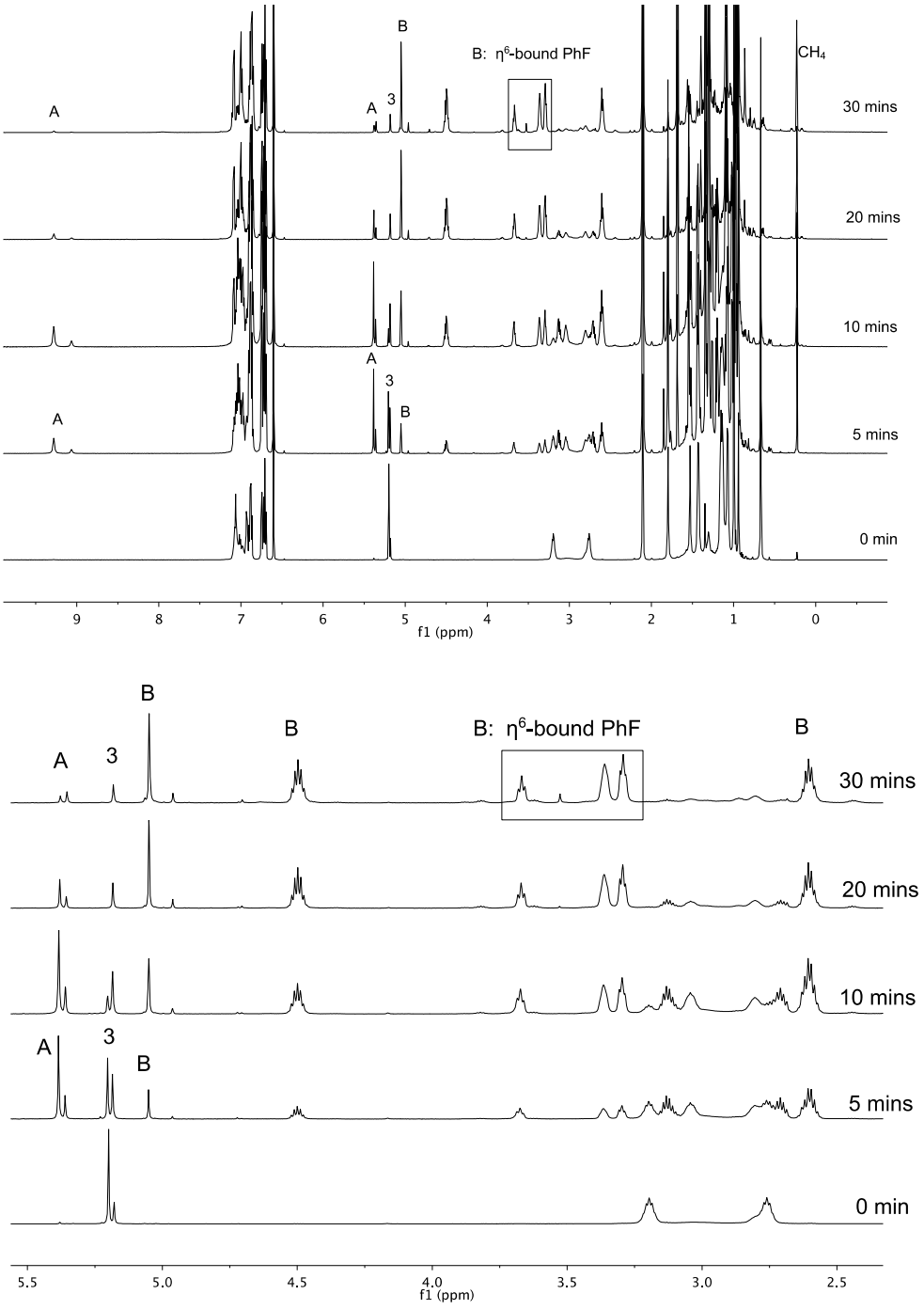


Figure S. 7 Formation of complex **B** with time. Spectra recorded at 263 K, full spectrum (top), expansion of the 5.5-2.4 ppm range (bottom).

D.2.2 Evolution of ^{19}F NMR with time

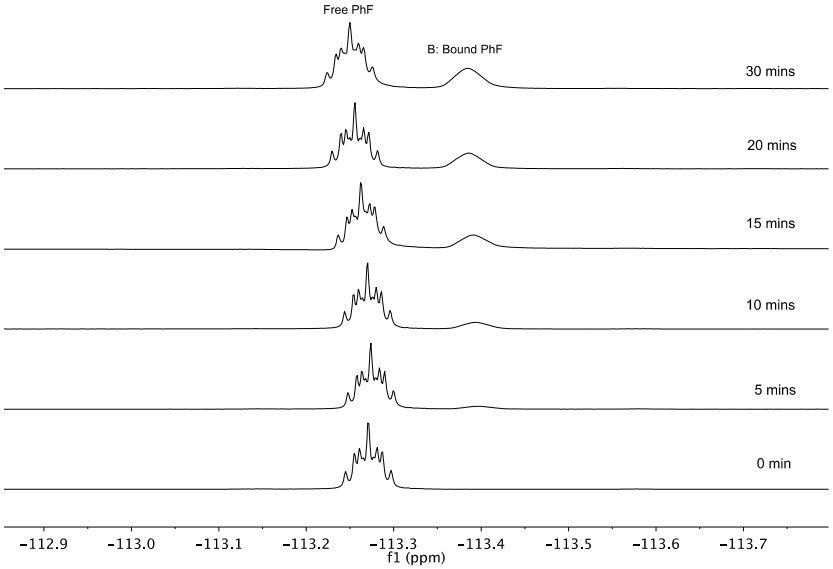


Figure S. 8 Formation of complex **A** with time. ^{19}F NMR spectra recorded at 263 K

D.2.3 Characterization of **B**

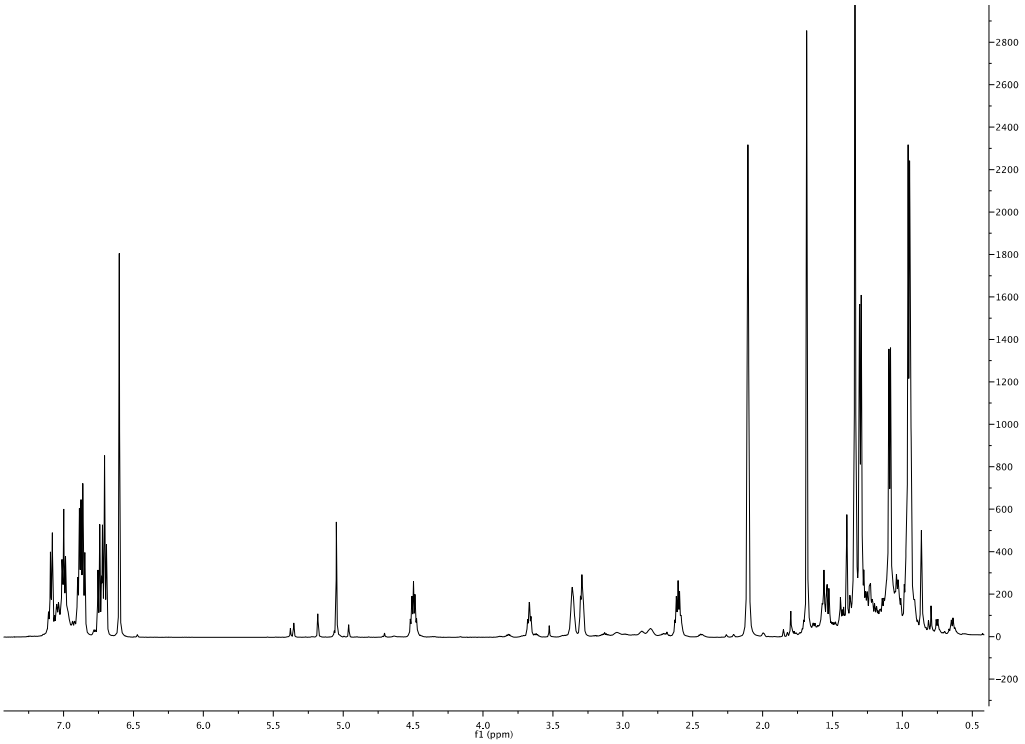


Figure S. 9 ^{1}H NMR of B recorded at 263 K.

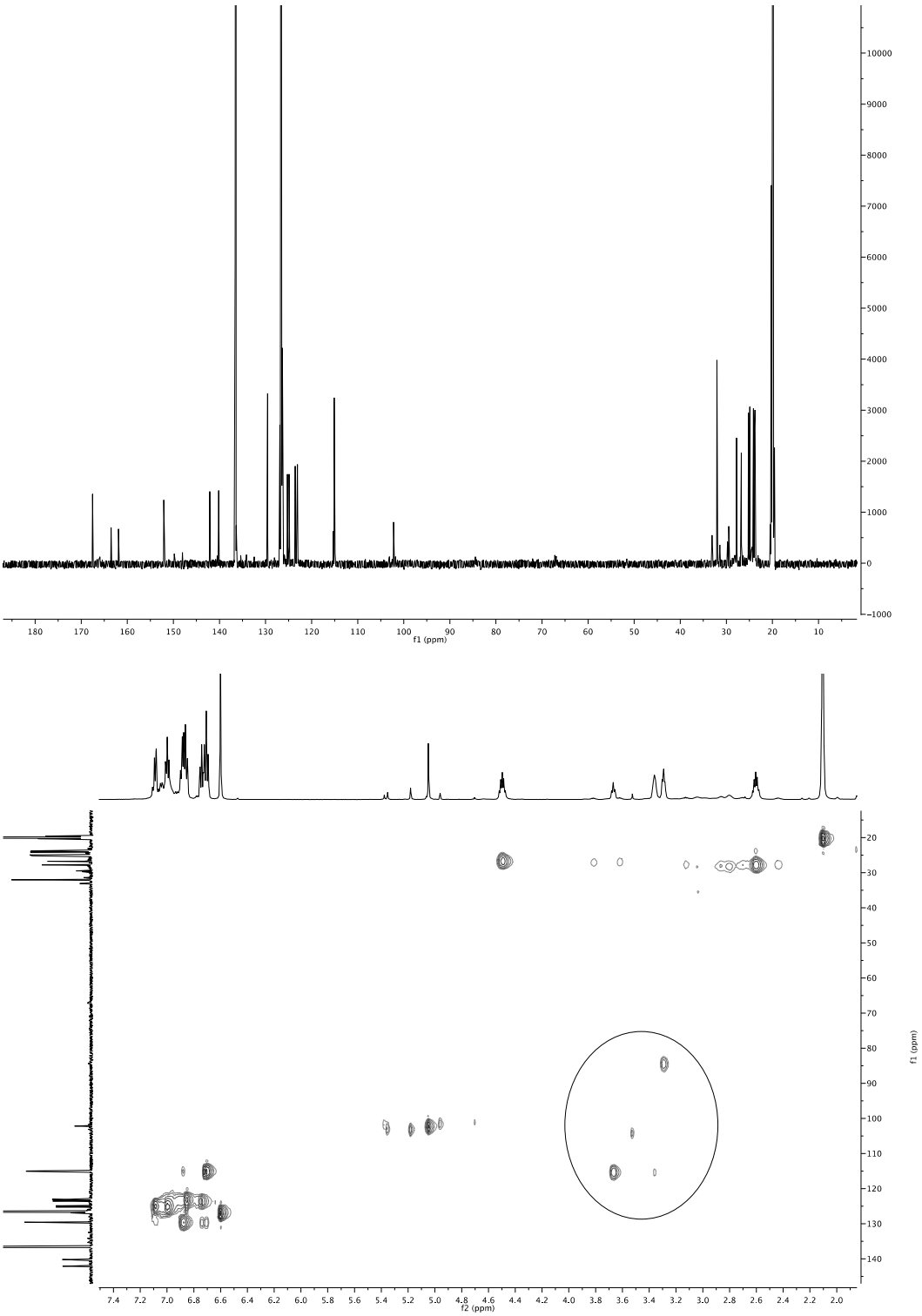


Figure S. 10 ^{13}C NMR (Top) and HSQC spectra (bottom) showing the upfield value of the arene carbon of the bound PhF. Spectra recorded at 263 K.

D.2.4 Conversion of **B** to **2a**

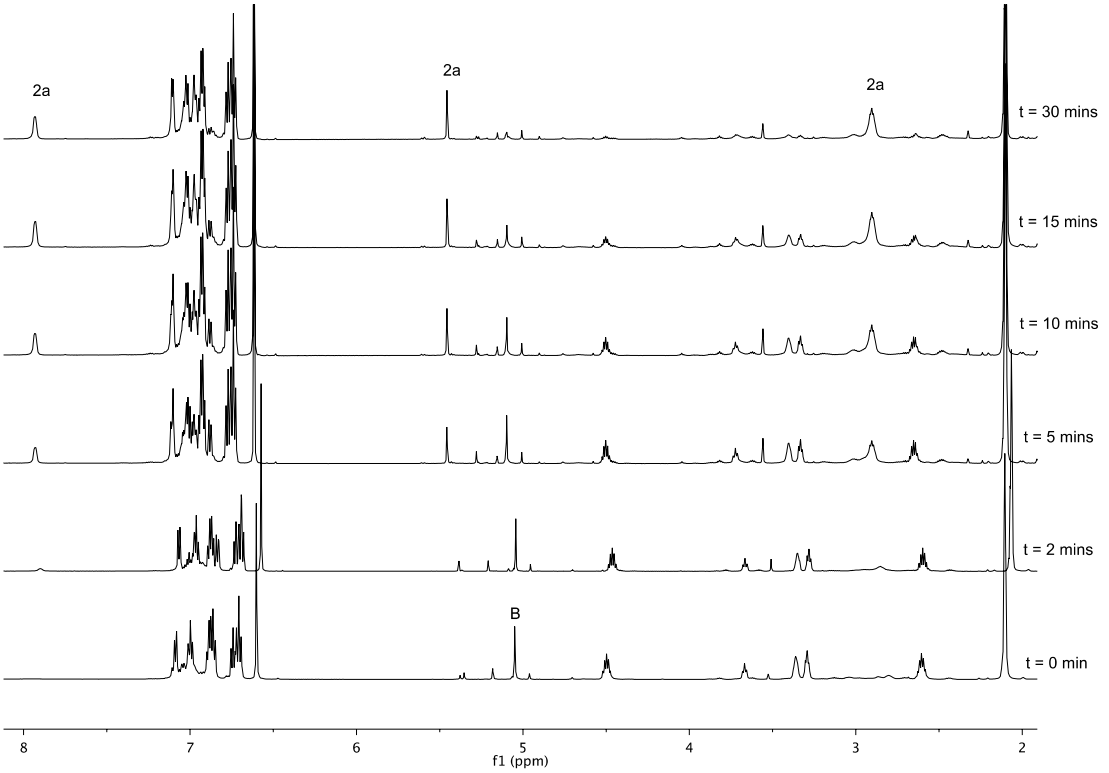


Figure S. 11 Formation of complex **2a** and disapearance of **B** with time. ^{1}H NMR spectra recorded at 313 K.

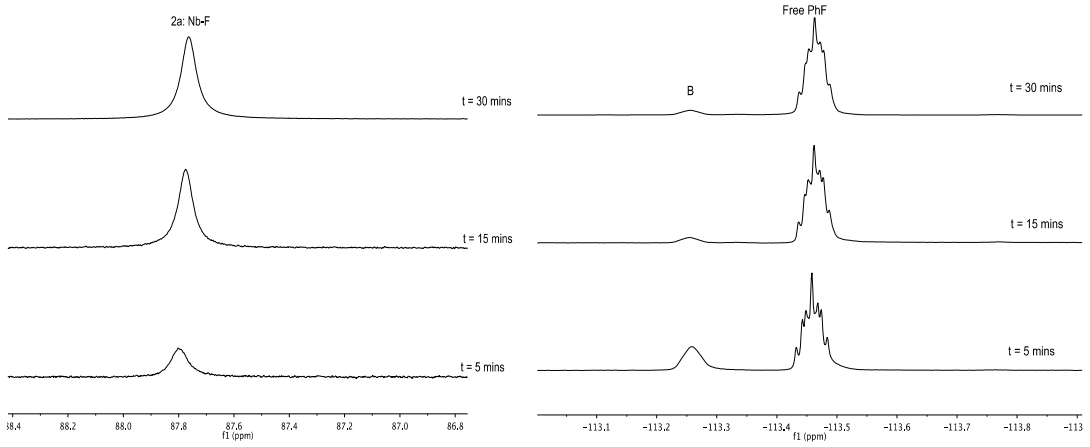
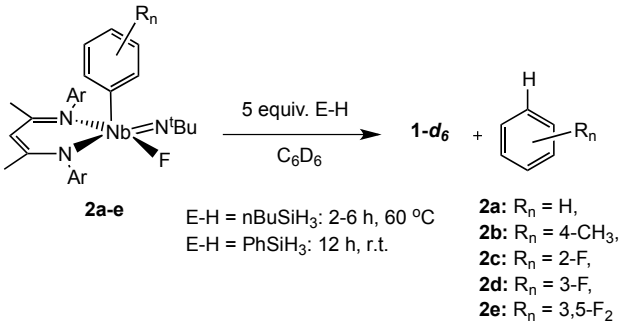


Figure S. 12 Formation of complex **2a** and disapearance of **B** with time. ^{19}F NMR spectra recorded at 313 K

E. Stoichiometric hydrodefluorination



A solution of C_6D_6 containing each complex **2a-e** (10-15 mg, 0.107 mmol, 1 equiv.) and $RSiH_3$ (R = $nBuSiH_3$: 35 µL, 0.057 mmol, 5 equiv., R = Ph: 35 µL, 0.057 mmol, 5 equiv.) was added to a J-Young NMR tube with a Teflon cap. The solution was either stored at room temperature (R = Ph) or heated to 60 °C (R = nBu) for several hours. The yellow-orange solution slowly turned dark red, the color characteristic of the arene bound complex. ^{1}H NMR spectra were then recorded, revealing the presence of complex **1-*d*$_6$** as the only organometallic species (example for complex **2a** and $nBuSiH_3$, Figure S.11). After completion, the volatile materials were vacuum-tranfered away from the organometallic compound and analyzed by ^{1}H, ^{19}F NMR in C_6D_6 and further analyzed by GC-MS showing the presence of the mono-hydrodefluorinated arene and $RSiF_3$.

- <u>$nBuSiF_3$:</u> ^{1}H NMR (600 MHz, C_6D_6, 293 K): δ(ppm) 1.13 (m, 2 H, $CH_3(CH_2)_2CH_2SiF_3$), 1.06 (m, 2 H, $CH_3(CH_2)_2CH_2SiF_3$), 0.76 (t, 3 H, $CH_3(CH_2)_2CH_2SiF_3$, $^3J_{HH}$ = 8.2 Hz), 0.40 (m, 2 H, $CH_3(CH_2)_2CH_2SiF_3$. ^{19}F NMR (564 MHz, C_6D_6, 293 K): δ(ppm) -136.2 (s, 3F, nBuSi*F*$_3$).
- <u>$PhSiF_3$:</u> ^{19}F NMR (564 MHz, C_6D_6, 293 K): δ(ppm) -141.8 (s, 3F, PhSi*F*$_3$).

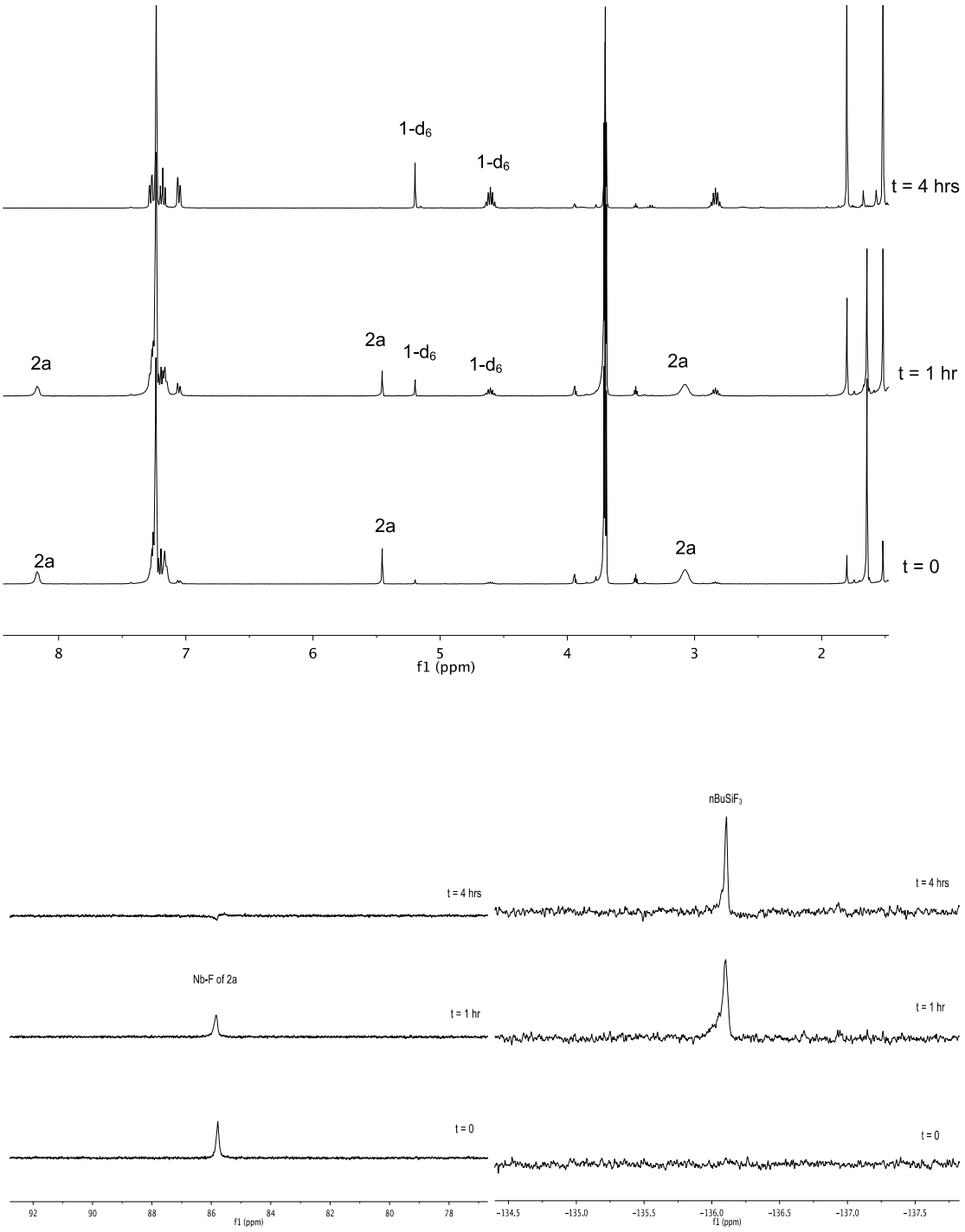
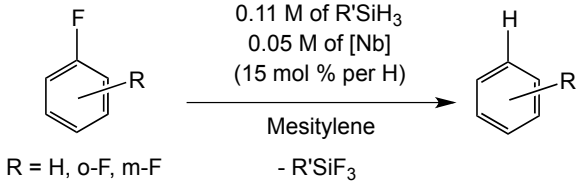


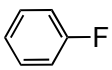
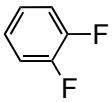
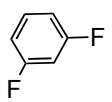
Figure S. 13 Example of ^{1}H (top) and ^{19}F NMR (bottom) monitoring of stoichiometric hydrodefluorination of fluorobenzene with $nBuSiH_3$.

F. Catalytic hydrodefluorination



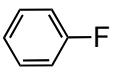
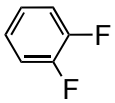
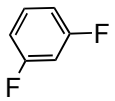
Complex 1 as a catalyst: Asolution of 0.4 ml mesitylene containing complex **1** (13.5 mg, 0.020 mmol, 0.05 M), fluoroarene and silane, as well as a solution of mesitylene containing C_6F_6 as internal standard (0.10 M), was added to a J-Young NMR tube with a Teflon cap (see Table S.3). The reaction mixture was heated in an oil bath for several hours (70 ^oC for $nBuSiH_3$ and 40 ^oC $nBuSiH_3$) and the conversion was frequently monitored by ^{19}F NMR spectroscopy, performing 2 scans with a delay time d_1 of 20 s.

Table S. 4

Entry	ArF	[ArF] (M)	V (μL)	[$nBuSiH_3$] (M)	V (μL)	mol % of **1**[a]	C_9H_{12} (μL)	[C_6F_6] (M)	Time	T (^oC)	Yield (%)
1		3.0	113	0.11	5.7	15	281	0.070	12 h	70	7(2)
2		3.0	113	0.11	5.7	15	281	0.070	24 h	70	9(2)
3		3.0	113	0.11	5.7	15	281	0.070	12 h	90	<1
4		3.0	113	0.33	17.1	5	270	0.068	12 h	70	<1
5		neat	0.390	0.11	5.7	15	-	0.110 (5 μL)	12 h	70	63(2)
6		3.0	118	0.11	5.7	15	276	0.069	12 h	70	42(3)
7		3.0	118	0.33	17.1	5	255	0.064	12 h	70	24(2)
8		3.0	118	0.11	5.7	15	276	0.069	12 h	70	34(4)
9		3.0	118	0.33	17.1	5	255	0.064	12 h	70	19(2)

Complex 1 as a precatalyst: A solution of 0.4 ml containing complex **1** (13.5 mg, 0.020 mmol, 0.05 M), fluoroarene, as well as a solution of mesitylene containing C_6F_6 as internal standard (0.10 M) (see Table S.4), was added to a J-Young NMR tube with a Teflon cap. For the run involving 1,2- and 1,3-difluorobenzene, a capillary tube containing 0.1 M of fluorobiphenyl in mesitylene was added and used as a 2nd internal standard (see calibration). The reaction mixture was heated at 50 °C in an oil bath for 30 min, which resulted in a color change from red to yellow, characteristic of the Nb(V) aryl fluoride complex. A 0.11 M solution of silane (corresponding to 15 mol% catalyst loading per H, see Table S.4) was then added and the NMR tube, which was heated in an oil bath for several hours (70 °C for $nBuSiH_3$ and 40 °C $PhSiH_3$). The conversion was frequently monitored by ^{19}F NMR spectroscopy and the yield calculated using the internal standard peak (see example of monitored conversion for fluorobenzene, Figure S.12, and 1,3-difluorbenzene, Figure S.13). Each of the following experiments has been repeated twice, affording very similar yields; the yields presented are an average of the two runs.

Table S. 5

Entry	ArF (3.0 M)	V (µL)	E-H (0.11 M	V (µL)	C_9H_{12} (µL)	$[C_6F_6]$ (M)	Time	T (°C)	Yield (%)
1		113	$nBuSiH_3$	5.7	281	0.070	16 h	70	71(4)
2		113	$PhSiH_3$	5.4	281	0.070	12 h	40	12(4)
3		118	$nBuSiH_3$	17.1	255	0.069	16 h	70	90(4)
4		118	$PhSiH_3$	16.9	254	0.069	16 h	40	82(4)
5		118	$nBuSiH_3$	17.1	255	0.069	16 h	70	97(4)
6		118	$PhSiH_3$	16.9	254	0.069	16 h	40	85(4)

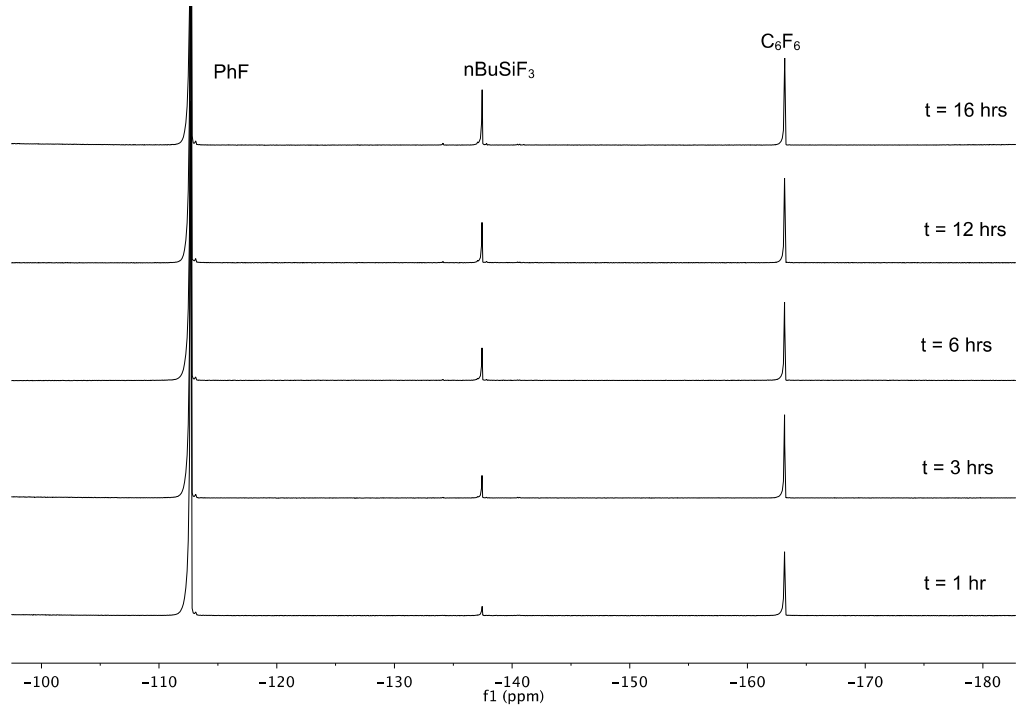


Figure S. 14. Example of ^{19}F NMR monitoring of catalytic hydrodefluorination of fluorobenzene with $nBuSiH_3$ using C_6F_6 as internal standard

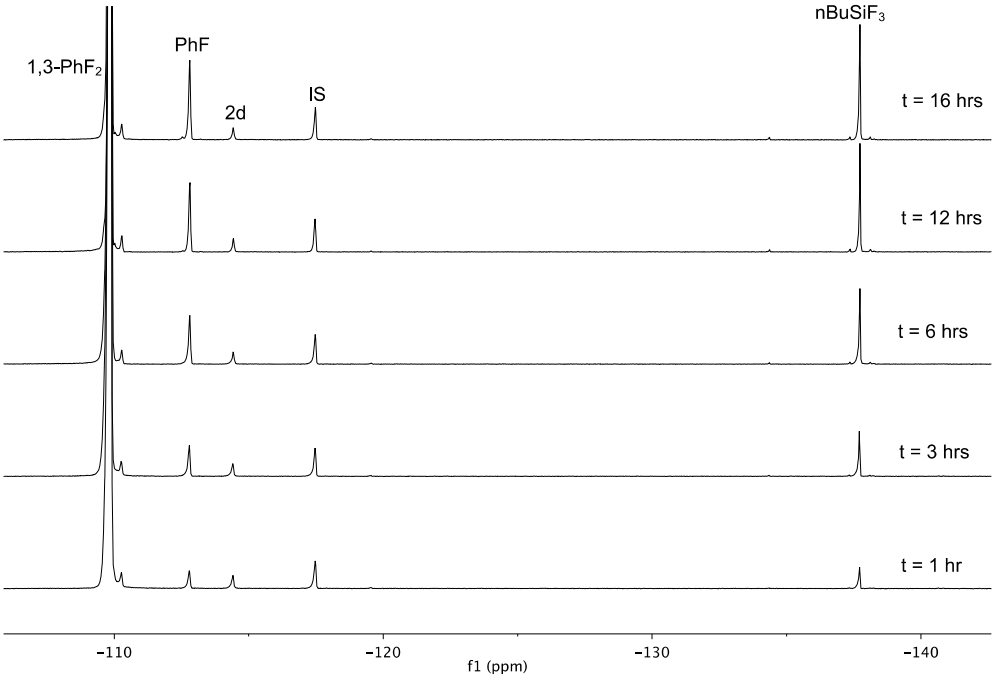
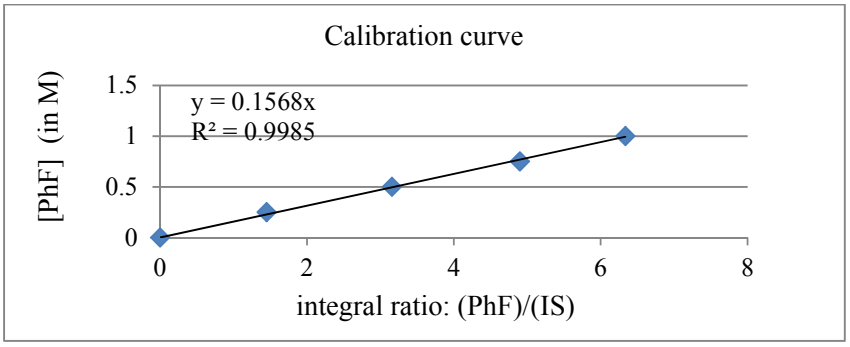


Figure S. 15. Example of ^{19}F NMR monitoring of catalytic hydrodefluorination of 1,3-difluorobenzene with $nBuSiH_3$

Calibration curve: A capillary tube containing 1.0 M of fluorobiphenyl in mesitylene was added to an NMR tube containing 0.25, 0.5, 0.75 and 1.0 M of fluorobenzene in mesitylene. ^{19}F NMR spectra were recorded by performing 2 scans with a delay time d_1 of 20 s. The ratio of fluorobenzene/fluorobiphenyl peaks were then plotted as a function of fluorobenzene concentration.

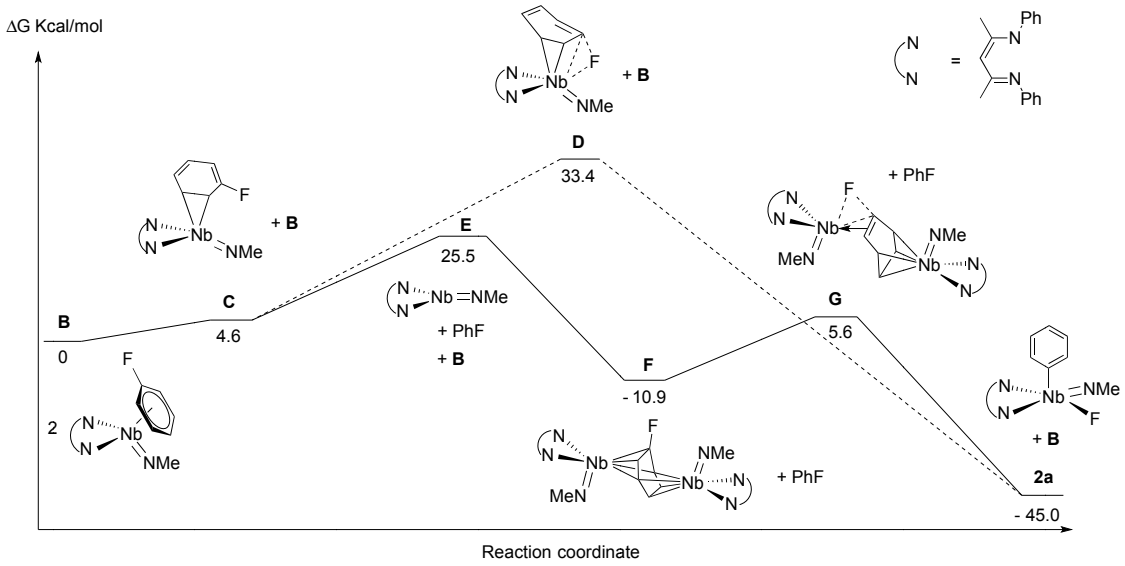


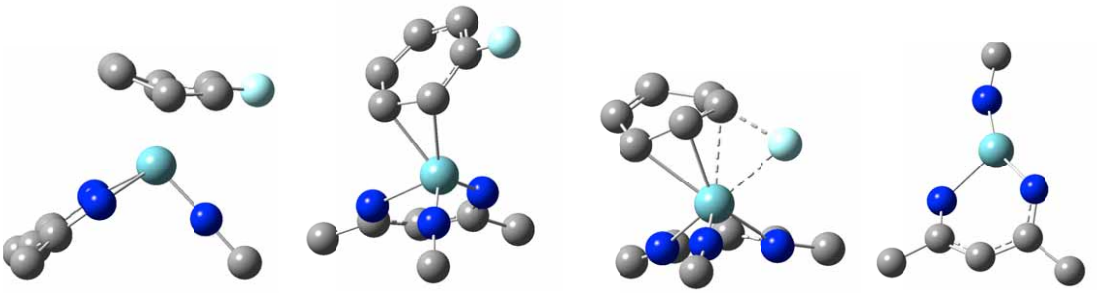
G. DFT calculations

All structures and energies were calculated using the Gaussian09 suite of programs.[10] Self-consistent field computations were performed with tight convergence criteria on ultrafine grids, while geometry optimizations were converged to tight geometric convergence criteria for all compounds. Spin expectation values $<S>^2$ indicated that spin contamination was not significant in any result. Frequencies were calculated analytically at 298.15 K and 1 atm. Structures were considered true minima if they did not exhibit imaginary vibration modes and were considered as transition states when only one imaginary vibration mode was found. Intrinsic Reaction Coordinates (IRC) calculations were performed to ensure the transition state geometries connected the reactants and the products. Optimized geometries were compared using the sum of their electronic and zero-point energies. In order to reduce the computational time, the system was structurally simplified by replacing 2,6-diisopropylphenyl groups by phenyl groups and the N^{t}Bu imido group by a NMe imido group. The PBE1PBE hybrid functional was used throughout this computational study.[11] For geometry optimizations and frequency calculations, the light atoms (H, C, N and F) were treated with the 6-311G(d,p) basis,[12] while the niobium atom was treated with a Stuttgart/Dresden ECPs pseudopotential (SDD).[13,14]

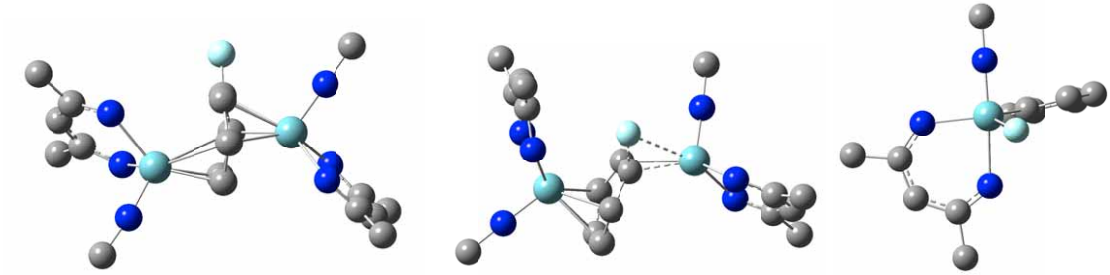
G.1 Optimized structures

G.1.1 C-F bond activation



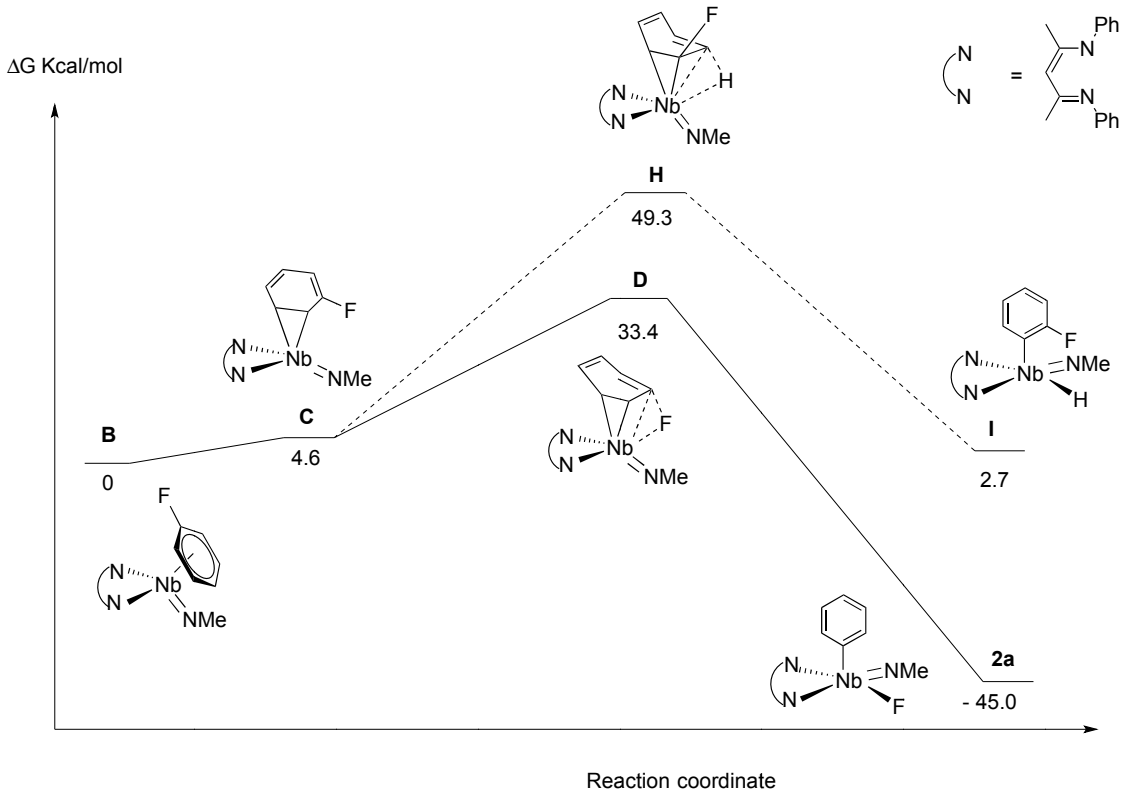


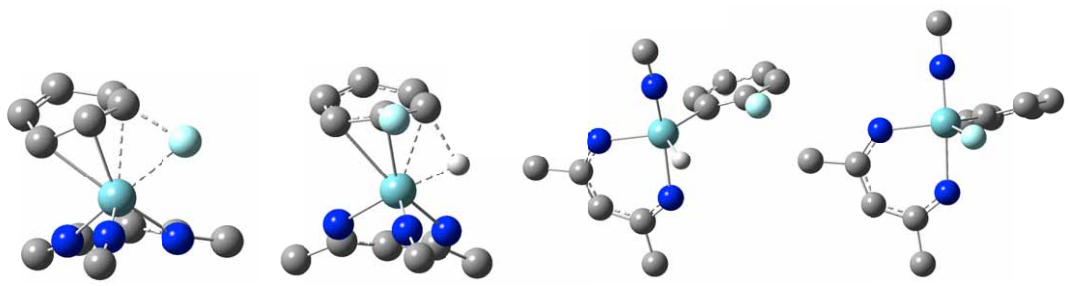
B **C** **D** **E**



F **G** **2a**

G.1.2 C-F vs C-H bond activation





D **H** **I** **2a**

G.2 Atoms coordinates

C_6H_5F:

G (a.u.) = -331.11256

C	-0.46558400	0.12875300	0.00006100
C	0.93373500	0.11948100	0.00052800
C	1.60760500	1.33991400	-0.00006200
C	0.93384100	2.56041500	-0.00104600
C	-0.46546200	2.55129400	-0.00148100
C	-1.16771200	1.34004800	-0.00095900
H	-1.00728100	-0.81966300	0.00049600
H	1.50519700	-0.80997400	0.00130800
H	1.50543800	3.48978900	-0.00145600
H	-1.00709700	3.49974200	-0.00225700
H	-2.25930200	1.34011600	-0.00132300
F	2.96580100	1.33987600	0.00042300

Intermediate B:

G (a.u.) = -1249.208739

Nb	-1.43098600	2.08250300	0.51325800
N	-1.68586800	0.45042500	-0.21688900
N	0.27715800	2.81034500	-0.75078900
N	-2.65462500	3.30106500	-0.90812000
C	-1.87623200	-0.82020000	-0.82846100
C	1.55706300	2.36546300	-0.28714500
C	2.48974400	3.27496400	0.24612400
C	3.72080500	2.82431000	0.73595100
H	4.43032500	3.54275100	1.15460500
C	4.04275800	1.46311700	0.69562300
H	5.00260900	1.11211100	1.08063200
C	3.12018100	0.55459000	0.15944000
H	3.36026200	-0.51095400	0.12327600
C	1.88732900	0.99851500	-0.32601300
C	1.51398200	3.72632800	-2.69333300
H	2.10441500	2.80091700	-2.76883200
H	2.16156100	4.47294100	-2.20854800
H	1.27885100	4.08307300	-3.70401300
C	0.23691200	3.49580600	-1.90370400
C	-0.94033400	4.00455200	-2.48233500
H	-0.80349000	4.51735700	-3.43396000
C	-2.27086900	3.92337100	-2.03432900
C	-3.31301100	4.55835200	-2.93859400
H	-3.74072600	5.46719200	-2.48813500
H	-4.15411600	3.87114700	-3.11543800
H	-2.86707300	4.83154500	-3.90313300
C	-4.05239100	3.29986800	-0.59498500
C	-4.68858100	4.46097300	-0.11691100
C	-6.04750400	4.44046200	0.21664100
H	-6.52399900	5.34928200	0.59328600
C	-6.79407900	3.26577500	0.07233000
H	-7.85438000	3.25071300	0.33370800
C	-6.16701000	2.10882400	-0.41028500
H	-6.74057300	1.18620600	-0.53060800
C	-4.80899800	2.12245400	-0.73968900
C	-2.28745300	1.55858800	2.69479400
C	-0.91014800	1.42037500	2.81963100
C	0.00203800	2.42041600	2.36138800
C	-0.58229400	3.76820400	2.29547000
C	-1.94757500	3.94985900	2.23267100
C	-2.85142100	2.80436800	2.19809500
H	-2.92631800	0.69557500	2.88566100
H	1.07217400	2.28154600	2.50194800
H	0.09198700	4.62119900	2.20453400
H	-2.35656800	4.95239600	2.09545300
H	-3.92928100	2.95145900	2.21835900
F	-0.40277000	0.22079600	3.19607600
H	-4.30665100	1.22148600	-1.09719300
H	-0.98851500	-1.12372400	-1.41751300
H	-2.05966300	-1.61188000	-0.07686200
H	-2.74101500	-0.81410600	-1.52101400
H	1.15286500	0.29578800	-0.72448900
H	2.23218000	4.33643700	0.28879900
H	-4.10295600	5.37599000	0.00385800

Intermediate C:

G (a.u.) = -1249.201423

C	8.16263300	-7.49030700	-2.91696900
H	7.75912000	-8.40668800	-3.36837600
H	9.17016200	-7.72537600	-2.53537300
H	8.28065900	-6.72749800	-3.70133600
C	7.25325900	-6.99855100	-1.81758600
C	6.35058400	-7.86737500	-1.20388600
H	6.29173400	-8.87486100	-1.61699900
C	5.57402300	-7.63437500	-0.03686600
C	4.78826700	-8.82593700	0.47960000
H	5.11623100	-9.11055100	1.49136000
H	4.91433000	-9.68994900	-0.18458600
H	3.71394300	-8.59695800	0.55509900
C	4.91103100	-6.50987500	1.94278100
C	3.52987400	-6.29974100	2.09760900
C	2.94809600	-6.33000500	3.37024400
H	1.87328100	-6.16133700	3.47319100
C	3.73120100	-6.57556900	4.50290800
H	3.27435700	-6.59754900	5.49461300
C	5.10633000	-6.79626900	4.35229500
H	5.72788600	-6.99705900	5.22866500
C	5.69274300	-6.76404200	3.08448400
C	8.24310300	-4.71505500	-1.65882500
C	7.73671700	-3.40181200	-1.90565200
C	8.61248500	-2.29418700	-1.87228500
H	8.20377400	-1.29716600	-2.04716500
C	9.97300700	-2.47888900	-1.66180900
H	10.65005900	-1.62269500	-1.64790300
C	10.48455200	-3.78605400	-1.48662000
H	11.55848400	-3.92825100	-1.33985000
C	9.64671800	-4.88901600	-1.47006700
C	8.27292800	-4.28934900	2.80768600
C	3.64802300	-4.00784400	-0.71627800
H	2.98631600	-4.87118900	-0.61035900
C	3.67766700	-3.33614100	-1.91816100
H	3.07751600	-3.70030500	-2.75544600
C	4.42187900	-2.11528800	-2.07978300
H	4.35752500	-1.51374300	-2.98644800
C	5.19226500	-1.71372600	-1.02318900

C	5.36275900	-2.47074800	0.17868800
H	5.79627000	-1.93731400	1.02749900
C	4.44023400	-3.59236200	0.42304500
H	4.06548400	-3.79535600	1.43070500
N	5.54179900	-6.47553200	0.65096900
N	7.27460100	-5.70440100	-1.45003600
N	7.41449100	-4.31812400	1.66919600
Nb	6.50326600	-4.53765800	0.14061400
H	8.44725300	-3.24972500	3.14234600
H	7.81533400	-4.83316900	3.65656000
H	9.25920300	-4.74670400	2.60188600
H	6.76393800	-6.93255000	2.95801000
H	2.91267300	-6.11811200	1.21570500
H	6.71851400	-3.27679000	-2.28881700
H	10.04322900	-5.88845400	-1.28225900
F	5.89587400	-0.54557700	-1.10942200

Transition state D:

G (a.u.) = -1249.155525

ν = - 271.57 cm^{-1}

C	7.97157700	-6.41591100	-3.19615700
H	8.43750500	-5.52158100	-3.63383000
H	7.35607300	-6.91500000	-3.95735600
H	8.78207300	-7.10758800	-2.91839000
C	7.11622800	-6.05404500	-1.99906500
C	5.97697100	-6.84872900	-1.75045000
H	5.74074100	-7.59650600	-2.50807800
C	5.34705200	-7.01634900	-0.48907500
C	4.64431200	-8.33287700	-0.23374200
H	5.08191500	-8.83959900	0.64061800
H	4.73624700	-8.99539900	-1.10312000
H	3.57615900	-8.18491900	-0.01321300
C	5.11602800	-6.43179700	1.83210200
C	3.79180000	-6.55750600	2.28170400
C	3.52978900	-6.87123600	3.61958800
H	2.49482900	-6.96892600	3.95668500
C	4.58188500	-7.05505900	4.52390500
H	4.37358300	-7.29751200	5.56827700
C	5.90297700	-6.92313000	4.07972000
H	6.73248000	-7.06499200	4.77694700
C	6.17114700	-6.61094300	2.74307400
C	8.81666900	-4.56708900	-1.18139100
C	9.13121300	-3.23519500	-1.50858500
C	10.45406500	-2.78894700	-1.42497200
H	10.68599200	-1.75362000	-1.68694600
C	11.47680200	-3.65433500	-1.01926500
H	12.50807800	-3.29940400	-0.95872500
C	11.16631500	-4.97873700	-0.68814800
H	11.95407600	-5.66157400	-0.35990300
C	9.84664300	-5.43210300	-0.76315400
C	7.21026200	-2.92422300	2.63431300
C	2.57447200	-4.23242300	-0.13828500
H	1.78145300	-4.75648200	0.40778000
C	2.59090100	-4.28151600	-1.51246600
H	1.80278700	-4.75887300	-2.09685700
C	3.80711000	-3.76168300	-2.13985100
H	4.26915000	-4.22098000	-3.01861400
C	4.37182500	-2.75250500	-1.43500800
C	4.23590700	-2.40481600	-0.08987300
H	4.39866400	-1.39517400	0.29508400
C	3.60035300	-3.52552700	0.61409700
H	3.53233200	-3.48685300	1.70344500
N	5.43002700	-6.09161500	0.47576100
N	7.46852700	-5.03226300	-1.20072700
N	6.68112900	-3.45904100	1.42395300
Nb	5.87830000	-4.01834500	-0.05770900
H	7.08493400	-3.64561800	3.46316900
H	8.28755400	-2.70284500	2.52874200
H	6.69583000	-1.98754300	2.91723400
H	7.19675900	-6.49515700	2.38610900
H	2.97228800	-6.40088200	1.57860900
H	8.32751600	-2.57284200	-1.83707300
H	9.59568300	-6.45712100	-0.47821600
F	6.18574700	-2.65768900	-1.86446200

Intermediate E:

G (a.u.) = -918.055493

Nb	-0.52938700	1.97510000	-0.73343100
N	-0.81302100	1.11677800	0.84165100
N	0.64119000	2.51984300	-2.47426700
N	-2.14254500	3.09778800	-1.36601900
C	-0.55362800	0.30005200	1.98560800
C	1.54268000	2.41391300	-1.39962800
C	1.48170300	3.38182700	-0.30101900
C	2.19304700	3.07905600	0.89409500
H	2.22471600	3.83661900	1.68208400
C	2.85233300	1.87360700	1.07514700
H	3.38695600	1.67209200	2.00502700
C	2.84715000	0.90759200	0.03491600
H	3.36904400	-0.04224100	0.17459000
C	2.20357000	1.15647800	-1.16852300
C	1.43655400	4.68243300	-3.38371700
H	2.35283600	4.14479200	-3.67240400
H	1.69526800	5.33377600	-2.52842300
H	1.12836700	5.34422200	-4.20685700
C	0.33028900	3.72042800	-3.03263600
C	-1.01421800	4.03901900	-3.34182200
H	-1.17851200	4.71684500	-4.18524700
C	-2.16666900	3.67977000	-2.63161800
C	-3.51221600	4.02422500	-3.23045300
H	-4.13146000	3.12126500	-3.35596000
H	-3.38295500	4.48799500	-4.21658000
H	-4.08724000	4.70940900	-2.58738200
C	-3.35391700	3.11642000	-0.59195900
C	-3.69003300	4.26664800	0.14151200
C	-4.84698400	4.28733500	0.92599200
H	-5.09450900	5.18407800	1.49936800
C	-5.67942100	3.16325100	0.98722900
H	-6.58040000	3.17963600	1.60443500
C	-5.34636900	2.01631400	0.25781500
H	-5.98703500	1.13236800	0.30339500
C	-4.19141000	1.99150700	-0.53025100
H	1.17818400	4.41329100	-0.48209100
H	2.22949900	0.43193300	-1.98445400
H	-0.76494100	-0.76618600	1.78049600
H	0.50484400	0.37584600	2.30725700
H	-1.18645800	0.60441600	2.84013800
H	-3.92240800	1.09572800	-1.09529700

H	-3.02589500	5.13291000	0.09792600

Intermediate F:

G (a.u.) = -2167.322205

C	0.69343600	0.23054800	-0.26667200
C	0.57587200	0.06877800	-1.65822500
H	-0.11090900	0.76709900	-2.13676500
C	1.22694400	-0.81205800	-2.55040600
C	-0.12541600	1.34633600	0.35490900
H	-0.58781400	1.01892200	1.29816700
H	-0.91324400	1.67278000	-0.33591800
H	0.49870200	2.22145300	0.59351200
C	0.91368600	-0.59814700	-4.02124800
H	1.76567700	-0.14639000	-4.55229900
H	0.04991400	0.06881800	-4.13502800
H	0.70014200	-1.55270700	-4.52459800
C	1.61556200	-0.22703400	1.89749500
C	2.32327500	0.91979400	2.30623000
C	2.52857100	1.17477300	3.66523800
H	3.08782000	2.06360500	3.96801000
C	2.03534300	0.29269200	4.63558800
H	2.20261500	0.49291100	5.69609100
C	1.33081100	-0.84895900	4.23566300
H	0.94253700	-1.54402900	4.98398200
C	1.12123300	-1.10928600	2.87723000
C	2.66058700	-2.58135600	-3.22733600
C	2.23230500	-3.90042700	-3.46523200
C	2.80859100	-4.65658200	-4.48897400
H	2.46108100	-5.67797000	-4.66417800
C	3.82198900	-4.11261100	-5.29075300
H	4.26804600	-4.70458600	-6.09313900
C	4.25733200	-2.80504300	-5.05072300
H	5.05126500	-2.36934500	-5.66204500
C	3.68567100	-2.04333700	-4.02521200
C	-0.24806800	-4.43175600	-0.27563400
C	9.03397000	-6.01275600	-1.41866700
H	8.49338500	-6.20711600	-2.35753500
H	9.48983200	-6.95246100	-1.08278100
H	9.83263200	-5.29528700	-1.66106700
C	8.11036100	-5.45676800	-0.34802400
C	7.87850200	-6.30243500	0.75488000
H	8.38083300	-7.26816600	0.70569900
C	7.14357600	-6.07671300	1.93218900
C	7.18370700	-7.19410200	2.96086800
H	7.40736500	-6.79863400	3.96328700
H	7.94733000	-7.93470000	2.69205800
H	6.21554300	-7.71236800	3.03689100
C	5.76774500	-4.86351800	3.44346600
C	4.58471000	-5.59325400	3.66990200
C	3.88637600	-5.45898000	4.87512500
H	2.96537100	-6.02704300	5.02976900
C	4.35912300	-4.60275800	5.87617700
H	3.81286300	-4.49908500	6.81632000
C	5.54063200	-3.88051500	5.66023900
H	5.92165500	-3.21097300	6.43561800
C	6.23852300	-4.00614100	4.45607800
C	8.00402600	-3.46456000	-1.62904900
C	7.46715500	-3.73574800	-2.90087400
C	7.86504600	-2.98340800	-4.01126800
H	7.43711900	-3.20890900	-4.99108700
C	8.79777000	-1.94943900	-3.87235500
H	9.10569000	-1.36335200	-4.74119600
C	9.32895300	-1.67105300	-2.60651200
H	10.05456000	-0.86311100	-2.48276500
C	8.93702700	-2.42019000	-1.49370100
C	8.76153300	-1.41159000	2.41086400
C	3.91244100	-3.73808000	0.65703400
H	3.69161800	-4.77813500	0.89493200
C	4.33563500	-3.36672500	-0.71930600
H	4.48401400	-4.17884600	-1.43306700
C	5.25566000	-2.18793000	-0.86955900
H	5.60717900	-1.90667100	-1.86137500
C	5.11507300	-1.18217900	0.12540600
C	4.64333300	-1.46687900	1.42844900
H	4.72303900	-0.70037400	2.19806400
C	4.19097900	-2.80013200	1.77605900
H	3.78835800	-2.98746700	2.77027000
N	1.46143800	-0.55101400	0.51643100
N	2.05662600	-1.80615000	-2.18513600
N	0.93300400	-3.64425800	-0.14264700
N	6.46438500	-4.94913800	2.19747700
N	7.60851500	-4.21959500	-0.47673500
N	7.71137200	-2.13030100	1.77541800
Nb	2.30446600	-2.49373200	-0.10596500
Nb	6.36986000	-3.04806500	0.99361900
H	9.03510900	-1.86295100	3.38516800
H	9.67895300	-1.39700300	1.78949600
H	8.47743000	-0.35868100	2.60079800
H	7.14873300	-3.43260200	4.26977300
H	4.20843200	-6.25436600	2.88537500
H	6.72260800	-4.52805600	-3.01019800
H	9.33609500	-2.20364800	-0.50119900
H	2.73741200	1.58783500	1.54724500
H	0.57020800	-1.99669900	2.55328200
H	-1.07238500	-4.04048500	0.35036900
H	-0.60916000	-4.43906000	-1.32272200
H	-0.07168700	-5.48296400	0.02209900
H	1.45226700	-4.31896600	-2.82631100
H	4.03423600	-1.02625100	-3.83066400
F	5.65735000	0.05201800	-0.09405700

Transition state G:

G (a.u.) = -2167.296004

ν = - 234.12 cm^{-1}

C	2.09269700	0.13924400	0.93434300
C	2.47658500	0.86680800	-0.21069100
H	2.64550000	1.93173300	-0.05457100
C	2.51179900	0.43578400	-1.54701600
C	1.91873400	0.93616500	2.21192600
H	0.91464700	0.78912500	2.63855500
H	2.07167500	2.00652400	2.02574900
H	2.64023900	0.60420900	2.97423700
C	2.64884200	1.52429100	-2.59687600
H	3.59236900	1.43802300	-3.15698300
H	2.61353800	2.51532300	-2.12781800
H	1.83774300	1.45532400	-3.33844900
C	1.24328200	-1.74853500	2.10457800
C	2.01255500	-2.08796500	3.23220000

C	1.39595300	-2.64727500	4.35609200
H	2.00675600	-2.90524300	5.22515600
C	0.01441600	-2.87799800	4.37264500
H	-0.46141200	-3.31647300	5.25313600
C	-0.75216500	-2.54128600	3.25087900
H	-1.83171900	-2.71379700	3.25252100
C	-0.14341900	-1.98055000	2.12308300
C	2.30042100	-1.13454400	-3.32615500
C	1.06579900	-1.50984800	-3.88618100
C	0.96444800	-1.81154800	-5.24777100
H	-0.00433400	-2.09785300	-5.66538900
C	2.09262800	-1.74844800	-6.07447400
H	2.01237600	-1.98659900	-7.13749200
C	3.32567000	-1.37724300	-5.52455800
H	4.21485800	-1.32622500	-6.15840100
C	3.43086600	-1.07253400	-4.16404600
C	-0.68407100	-3.74820600	-1.21755000
C	9.46632400	-6.70484600	-0.11195800
H	8.79188400	-7.46310500	-0.54010500
H	10.21590000	-7.21425300	0.50582400
H	9.97090200	-6.22268700	-0.96322900
C	8.69067100	-5.69406000	0.70636700
C	8.98089500	-5.63451800	2.08706300
H	9.79625500	-6.28016000	2.41370900
C	8.33858400	-4.92202600	3.11463800
C	8.84096600	-5.13673700	4.52698700
H	8.90828500	-4.18130100	5.06902400
H	9.82996400	-5.61226900	4.51411100
H	8.16147100	-5.78194300	5.10558800
C	6.57500400	-3.53214800	3.99647700
C	5.74200800	-4.35441900	4.77963200
C	4.98902100	-3.80450800	5.81955500
H	4.34627400	-4.45208300	6.42097000
C	5.04426300	-2.42902100	6.08264900
H	4.44965900	-2.00084300	6.89262400
C	5.85521700	-1.60583200	5.29417600
H	5.89481700	-0.53082500	5.48381100
C	6.61889700	-2.15075600	4.25697000
C	7.56400300	-5.08531100	-1.31838000
C	6.64932700	-6.03686200	-1.79864700
C	6.45030700	-6.18593800	-3.17542700
H	5.73240500	-6.92551200	-3.53842000
C	7.15685300	-5.39024200	-4.08354700
H	6.99666400	-5.50721100	-5.15755300
C	8.06507100	-4.43612400	-3.60507800
H	8.61830400	-3.80683500	-4.30680600
C	8.26932500	-4.28149600	-2.23184900
C	8.28648000	-0.60148000	0.07594200
C	3.48521900	-4.62351300	-1.46268400
H	3.04114900	-5.30768300	-2.18765800
C	4.12581500	-3.42788400	-1.91435600
H	4.33245800	-3.29004100	-2.97467400
C	4.92720700	-2.69318800	-0.92279500
H	5.56201800	-1.87089500	-1.25222600
C	4.73196400	-2.92485300	0.47160000
C	3.64588800	-3.82784300	0.89626500
H	3.50954100	-4.03745400	1.95749600
C	3.24018500	-4.80988000	-0.09257900
H	2.61731200	-5.64498000	0.23468300
N	1.83956300	-1.17379700	0.93267300
N	2.38442100	-0.84729600	-1.92680900
N	0.62346800	-3.25813800	-0.95634500
N	7.31336300	-4.06987900	2.89470300
N	7.77474000	-4.91926300	0.09425700
N	7.61926700	-1.80448600	0.44207100
Nb	2.29797400	-2.67902600	-0.63251400
Nb	6.71326800	-3.25332400	0.98036100
H	7.90452600	0.25556200	0.66192000
H	9.37907000	-0.66593500	0.24148500
H	8.12293200	-0.36652300	-0.99368600
H	7.25176200	-1.51589000	3.63215400
H	5.68114400	-5.42169000	4.55276600
H	6.08803500	-6.64349000	-1.08437700
H	8.96259900	-3.53075400	-1.84607800
H	3.09106600	-1.91767200	3.19926200
H	-0.72956000	-1.71548700	1.24060900
H	-1.36267400	-3.55675500	-0.36312800
H	-1.13087700	-3.26890600	-2.11156900
H	-0.68418100	-4.84133000	-1.39804600
H	0.19436300	-1.56463700	-3.23105100
H	4.39623800	-0.79442700	-3.73393500
F	4.79964700	-1.65177200	1.62797900

Transition state H:

G (a.u.) = - 1249.130173

ν = -271.59 cm^{-1}

C	8.24527300	-6.76699200	-2.95496100
H	8.37070400	-5.93688500	-3.66554300
H	7.87932900	-7.64979300	-3.49451400
H	9.24751500	-6.99491500	-2.55928200
C	7.29174400	-6.39779600	-1.83406300
C	6.32255300	-7.36785200	-1.49471600
H	6.32305400	-8.26685600	-2.11033100
C	5.53051700	-7.41893700	-0.33923100
C	4.91428000	-8.76492000	-0.00809700
H	5.11770700	-9.03932800	1.03833000
H	5.32469500	-9.54315200	-0.66307000
H	3.82001400	-8.76005900	-0.12536700
C	4.66909700	-6.55998200	1.72592900
C	3.29304600	-6.85685500	1.77266600
C	2.63499900	-6.98931400	2.99888800
H	1.56638800	-7.21815600	3.01508000
C	3.33523600	-6.82508400	4.20026500
H	2.81813300	-6.92456100	5.15701000
C	4.70273400	-6.52989600	4.16226400
H	5.26110700	-6.40109500	5.09270000
C	5.36511000	-6.39528400	2.93788000
C	8.65890700	-4.50798700	-1.43593900
C	8.73264700	-3.49074100	-2.40117400
C	9.93519300	-2.81197500	-2.61634800
H	9.97967600	-2.02241200	-3.37030200
C	11.07434600	-3.13172900	-1.86659000
H	12.01029000	-2.59369900	-2.03223500
C	11.00209100	-4.14027000	-0.90011500
H	11.88369100	-4.39544200	-0.30662100
C	9.80116400	-4.82713600	-0.68502900

C	8.12620700	-3.39785900	2.47171400
C	2.90660800	-3.92193400	0.17054900
H	2.12546500	-4.61507300	0.48951500
C	3.13097500	-3.70122800	-1.19567300
H	2.47153000	-4.15005900	-1.94260200
C	4.32217900	-3.02345400	-1.56447000
H	4.72648500	-3.15632100	-2.57633000
C	5.03351600	-2.24309400	-0.62987400
C	4.60909100	-2.30868800	0.69395000
C	3.72243800	-3.31502800	1.15611000
H	3.60124700	-3.53622700	2.21927800
N	5.36006800	-6.36598200	0.48579900
N	7.43845600	-5.23084000	-1.19349600
N	7.18218500	-3.85943400	1.51138100
Nb	6.02342600	-4.24208200	0.21873600
H	8.12109600	-4.02840900	3.38111800
H	9.14637200	-3.41743300	2.04583100
H	7.90210000	-2.35841400	2.77223500
H	6.42866100	-6.15251600	2.89837800
H	2.73889200	-6.97009800	0.83850800
H	7.83753000	-3.22990100	-2.96988800
H	9.73212100	-5.61161100	0.07242400
F	5.06561800	-1.38040300	1.59835800
H	6.65554500	-3.01972400	-0.91019000

Intermediate I:

G (a.u.) = -1249.204473

Nb	-1.15853300	2.77605900	0.70430100
N	0.01382400	2.55837500	2.05262200
N	0.33377700	3.02816500	-0.80855500
N	-2.58430500	3.43141400	-0.95780500
C	0.96875500	2.50849100	3.10568600
C	1.68967600	2.84876400	-0.34221600
C	2.44994200	3.96021000	0.05410200
C	3.76472700	3.78954700	0.50223600
H	4.34573100	4.66184300	0.81141600
C	4.33210800	2.51117200	0.55962600
H	5.35801400	2.37962500	0.91020000
C	3.57003000	1.40111100	0.17589000
H	3.99854100	0.39738400	0.22870700
C	2.25600200	1.56628900	-0.27438600
C	1.42437400	3.32725300	-3.01281100
H	1.97032400	2.37346800	-2.94940800
H	2.12944600	4.10869300	-2.69014600
H	1.15310600	3.51084700	-4.05942500
C	0.18530500	3.30908600	-2.13922400
C	-1.02341500	3.58977800	-2.77789300
H	-0.94507800	3.79710800	-3.84492800
C	-2.33256600	3.67295100	-2.24047500
C	-3.44843800	4.06115000	-3.18762500
H	-4.14563000	3.22210700	-3.33787200
H	-3.05029100	4.36266100	-4.16452200
H	-4.04220800	4.88881500	-2.77063000
C	-3.93852100	3.50828000	-0.49042200
C	-4.39509500	4.65870200	0.17668800
C	-5.70838300	4.71742400	0.65308500
H	-6.05301100	5.61587600	1.17056000
C	-6.57311700	3.63053200	0.48139200
H	-7.59566700	3.67675800	0.86258000
C	-6.11531100	2.47801400	-0.16759000
H	-6.77684500	1.61707900	-0.28962000
C	-4.80506200	2.41199900	-0.65052400
H	1.99703700	4.95384000	0.01608600
H	1.65412100	0.70216700	-0.56537900
H	1.98910400	2.68818600	2.71727100
H	0.75420000	3.27373300	3.87374700
H	0.96032700	1.51853000	3.59815500
H	-4.43277600	1.50548900	-1.13261900
H	-3.70587000	5.49218100	0.32234200
C	-3.51512700	-1.66713500	1.06287100
C	-2.63240000	-1.45490000	-0.00340800
C	-1.95773400	-0.23038400	-0.12103700
C	-2.14237600	0.80906100	0.81344400
C	-3.03296900	0.53981900	1.85103700
C	-3.72565300	-0.65678300	2.01011100
H	-4.04421900	-2.61794100	1.16045700
H	-2.46784800	-2.24335200	-0.74221700
H	-1.27454100	-0.08571500	-0.96551000
H	-4.40865800	-0.78657500	2.85219900
H	-1.83206900	4.23262800	1.46628700
F	-3.24901900	1.54147600	2.77278200

Intermediate 2a:

G (a.u.) = -1249.280496

Nb	-1.11165400	3.09531500	0.78384700
N	0.08707900	2.59711200	2.02828100
N	0.35485700	3.14960500	-0.78633300
N	-2.59270400	3.41142500	-0.97777100
C	1.01583100	2.02225100	2.93648900
C	1.70767300	2.88537100	-0.34885200
C	2.50298500	3.91870600	0.17097500
C	3.81462700	3.65803000	0.58098500
H	4.42291700	4.46976700	0.98710300
C	4.34688800	2.36719600	0.47424400
H	5.37172400	2.16646600	0.79371400
C	3.55109300	1.33376800	-0.03332200
H	3.95106000	0.31971700	-0.10873900
C	2.23716600	1.58920100	-0.44314200
C	1.45811300	3.56983500	-2.96675700
H	1.99925900	2.61177200	-2.99851200
H	2.16377700	4.30930100	-2.55805500
H	1.19679700	3.85932700	-3.99165600
C	0.21087000	3.46998500	-2.11090700
C	-0.99822100	3.71310700	-2.75741800
H	-0.91458900	3.95996800	-3.81542300
C	-2.32435700	3.67161300	-2.25139200
C	-3.43837400	3.94937000	-3.24015800
H	-4.02589200	3.03888800	-3.43534300
H	-3.03531300	4.31309800	-4.19362500
H	-4.14125000	4.69384500	-2.83743200
C	-3.97135500	3.37057100	-0.57274700
C	-4.53166100	4.46770900	0.10287900
C	-5.86875500	4.42693800	0.51339900
H	-6.29506700	5.28552700	1.03792800
C	-6.65313800	3.29576900	0.26373600

H	-7.69489100	3.26573100	0.59105500	C	-3.52051800	-1.27390400	1.36613200
C	-6.08992900	2.19632400	-0.39532000	C	-2.67246800	-1.06920000	0.27157900
H	-6.68783800	1.30024000	-0.57793100	C	-2.01628700	0.15966900	0.11211900
C	-4.75635500	2.22892600	-0.81088400	C	-2.17913100	1.20276000	1.04677800
H	2.08103700	4.92283800	0.25767800	C	-3.02334600	0.96987500	2.15037900
H	1.60812900	0.78439300	-0.83109700	C	-3.69612800	-0.24926400	2.30407600
H	1.99903400	1.87164400	2.45281000	H	-4.03953800	-2.22779900	1.48927600
H	1.16195000	2.66454300	3.82428500	H	-2.52566200	-1.86509500	-0.46449800
H	0.65281600	1.03524000	3.28136300	H	-1.37205900	0.29935900	-0.76374100
H	-4.30438900	1.36233500	-1.29740000	H	-3.17202200	1.75140200	2.90313700
H	-3.90317100	5.33179900	0.32274800	H	-4.35586300	-0.40109000	3.16301100
F	-1.88451300	4.68776000	1.58913900				

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