Supporting Information

for

Diverse reactivity of carbenes and silylenes towards fluoropyridines

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S1. General experimental information

All manipulations were carried out in an inert atmosphere of argon using standard Schlenk techniques and in argon filled glove box. The solvents, especially tetrahydrofuran, dichloromethane and hexane were purified by MBRAUN solvent purification system MB SPS-800. Chemicals were purchased from Sigma Aldrich and TCI and were used without further purification. The starting material, SIDipp was synthesized by using literature procedure.[S1] ^{1}H, ^{13}C, ^{19}F,^{29}Si and ^{11}B NMR spectra were recorded in C_6D_6 and $CDCl_3$ using a Bruker Avance DPX 200, Bruker Avance DPX 400 or a Bruker Avance DPX 500 spectrometer referenced to external $SiMe_4$. High resolution mass spectra (HRMS) were obtained using a Q Exactive Thermo Scientific. Elemental analyses were performed at the CSIR National Chemical Laboratory, Pune, India. Melting points were measured in a sealed glass tube on a Stuart SMP-30 melting point apparatus and were uncorrected.

S2. Synthetic procedure and characterization of 1

1. Pentafluoropyridine (0.261 g, 1.53 mmol) was added to a solution of IDipp (0.2 g, 0.51 mmol) at 0 °C, in 10 mL of toluene and *n*-hexane mixture. An immediate formation of yellow precipitate was noticed after coming to room temperature. The resulting mixture was stirred for 15 minutes and the precipitate was filtered through a cannula followed by washing with *n*-hexane and diethyl ether. The solution was dried in vacuum and kept for crystallization with the mixture of tetrahydrofuran (5 mL) and toluene (2 mL). Yellow crystals came after keeping this solution at 4 °C for 2-3 days with a yield of 0.468 g (56 %). MP: decomposition at 120 ˚C. ^{1}H NMR (200 MHz, 298 K, $CDCl_3$): δ = 1.26-1.16 (m, 24 H, $CH(CH_3)_2$), 2.41 (sept, J = 6.87 Hz, 4 H, $CH(CH_3)_2$), 7.33 (d, J = 8.39 Hz, 4 H, *meta*-Ar-*H*), 7.58 (t, J = 7.63 Hz, 2 H, *para*-Ar-*H*), 15.05 (br s, 1H, HF_2^-) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ = 15.21 (CH_3, diethyl ether)

22.65, 26.92 (HCMe_2), 29.08 (HCMe_2), 65.84 (CH_2O, diethyl ether), 55.31 (tetrahydrofuran), 125.02 (NCH=CHN) 125.54, 128.13, 132.24 (Ar-C_6H_3), 125.40, 127.67, 128.58, 129.04, 131.59, 131.83 (C_5F_4N), 146.25 (*ipso*-C_6H_3), 157.14 (NCN) ppm; $^{19}F\{^1H\}$ NMR (377 MHz, 298 K, $CDCl_3$): δ = -168.49 (br s, 2 F, HF_2^-), -135.04 (m), -133.77 (m), -123.52 (m), -120.18 (d = 27.62 Hz)), -83.82 (m), -82.48 (d, J = 31.57 Hz) ppm; Elemental analysis calcd (%) for $C_{42}H_{35}F_{12}N_5$ [837.27 $gmol^{-1}$]: C 60.22, H 4.21, N 8.36; found: C 60.47, H 4.01, N 8.21.

NMRs of 1:

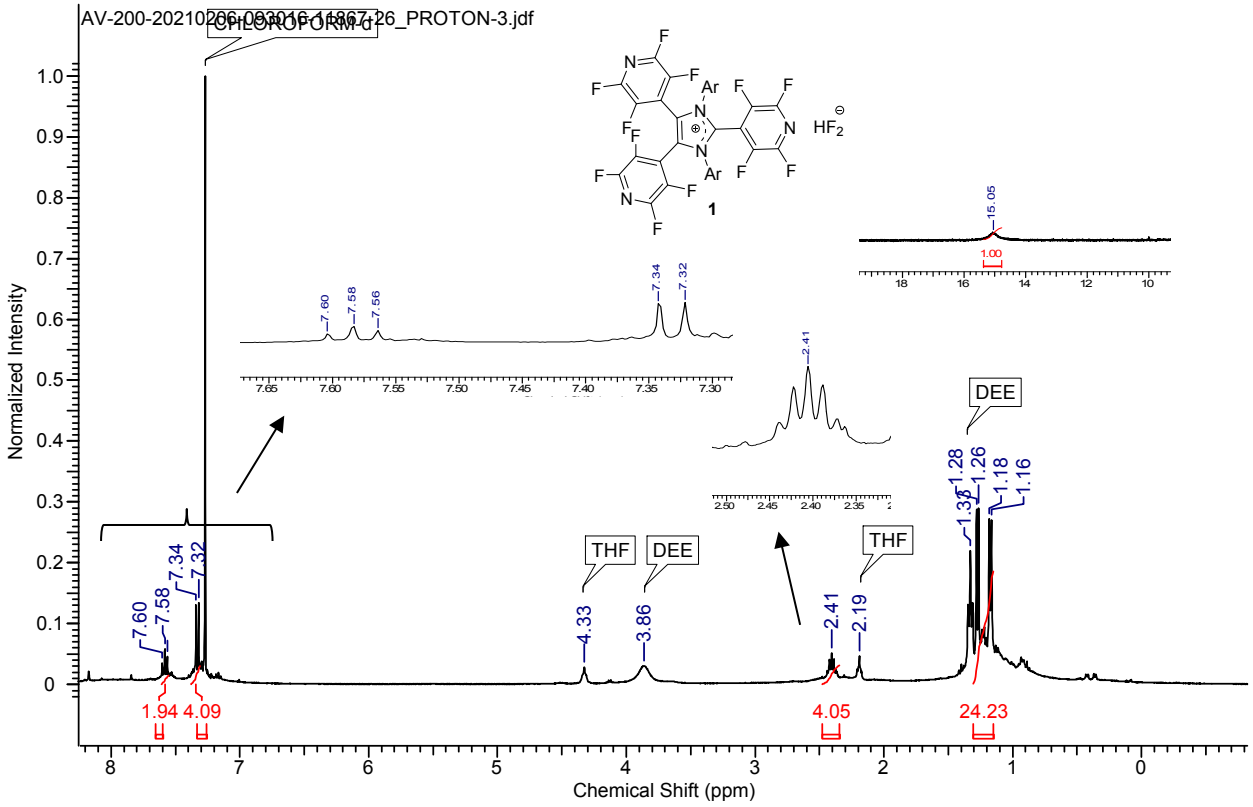


Figure S1.^{1}H NMR spectrum of **1**

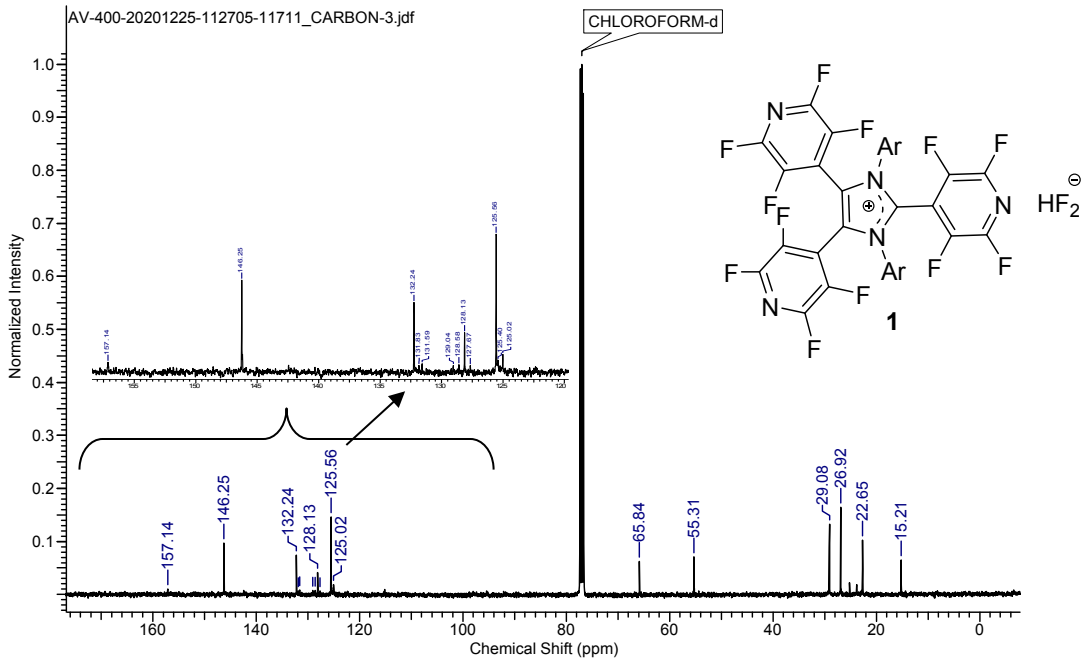


Figure S2.[13]C NMR spectrum of **1**

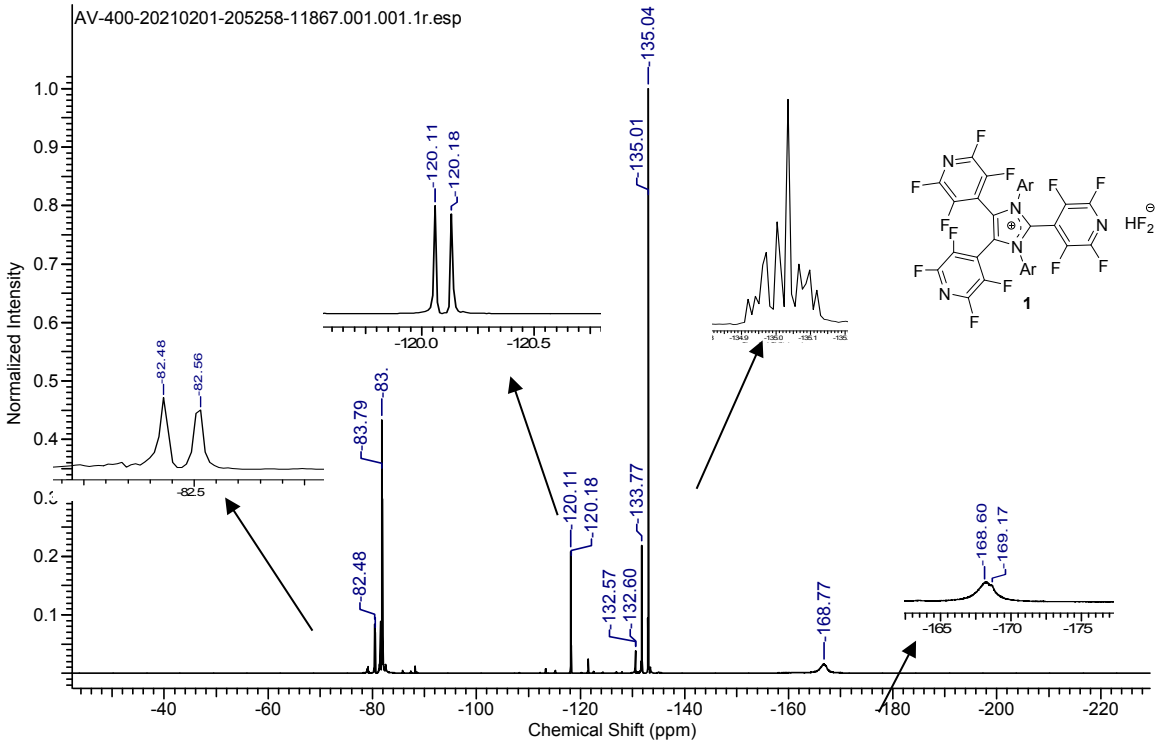


Figure S3. [19]F NMR spectrum of **1**

S3. Synthetic procedure and characterization of 2

2. Pentafluoropyridine (0.17 g, 1.02 mmol) was added to a hexane solution of SIDipp (0.2 g, 0.51 mmol) at 0 °C. An immediate formation of yellow precipitate was noticed after coming to room temperature. The resulting mixture was stirred for 1 hour at that temperature. The precipitate was filtered through a cannula followed by washing with *n*-hexane. The solution was dried in vacuum. Yellow powder of **2** was collected with a yield of 0.350 g (65%). MP: decomposition at 120 ˚C. ^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ = 1.30-1.16 (m, 12 H, $CH(CH_3)_2$),3.00 (sept, J = 6.38 Hz, 4 H, $CH(CH_3)_2$), 4.65 (s, 1H, N-CH_2CH-N),5.00 (s, 2 H, N-CH_2CH-N), 7.19-7.43 (m, 6 H, Ar-*H*) ppm; ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ = 22.65, 23.67 (H*C*Me_2), 26.88, 28.99 (HC*Me*$_2$), 54.42, 56.03 (*C*H_2*C*H), 125.43, 128.37, 132.04 (Ar-*C*$_6H_3$), 124.80, 125.07, 129.77, 130.98, 131.31 (*C*$_5F_4$N), 146.25 (*ipso*-*C*$_6H_3$) ppm; ^{19}F{^{1}H} NMR (377 MHz, 298 K, $CDCl_3$): δ = -132.93 (s, 2 F, *meta*-Ar-C_5F_4N) -83.74 (s, 2 F, *ortho*-Ar-C_5F_4N) ppm; Elemental analysis calcd (%) for $C_{32}H_{37}F_4N_3$ [539.66 gmol^{-1}]: C 71.22, H 6.91, N 7.79; found: C 71.27, H 6.58, N 7.62.

NMRs of 2:

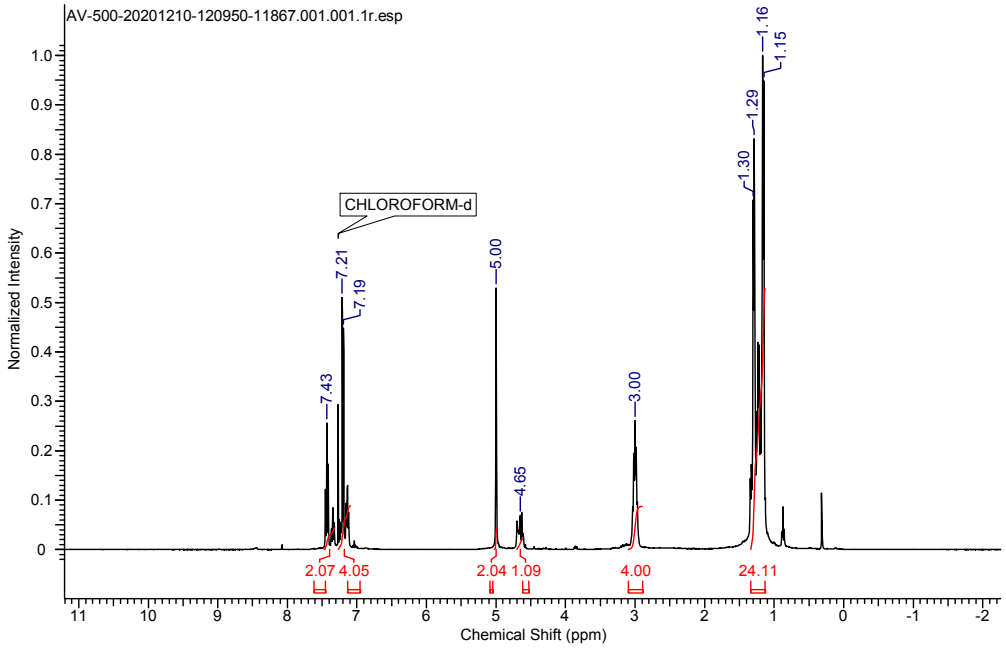


Figure S4. ^{1}H NMR spectrum of **2**

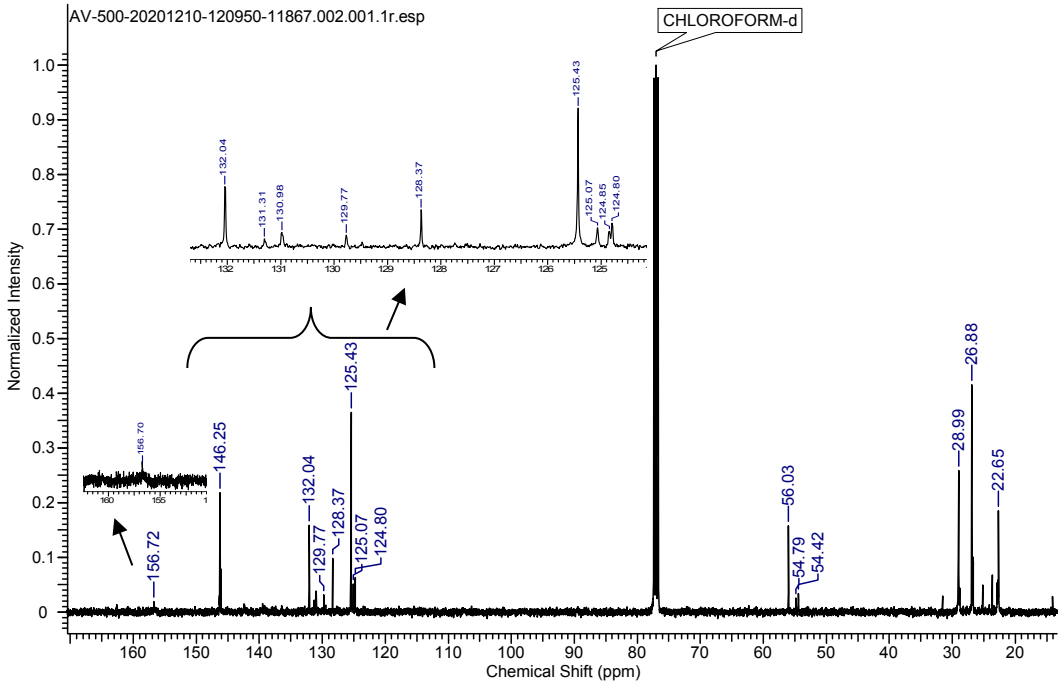


Figure S5. ^{13}C NMR spectrum of **2**

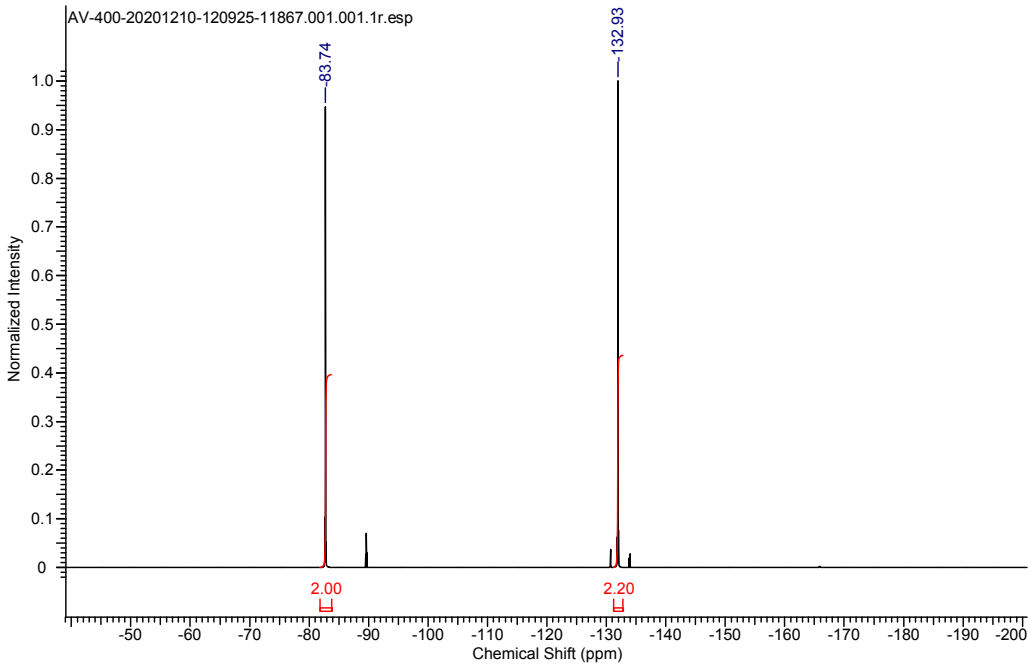


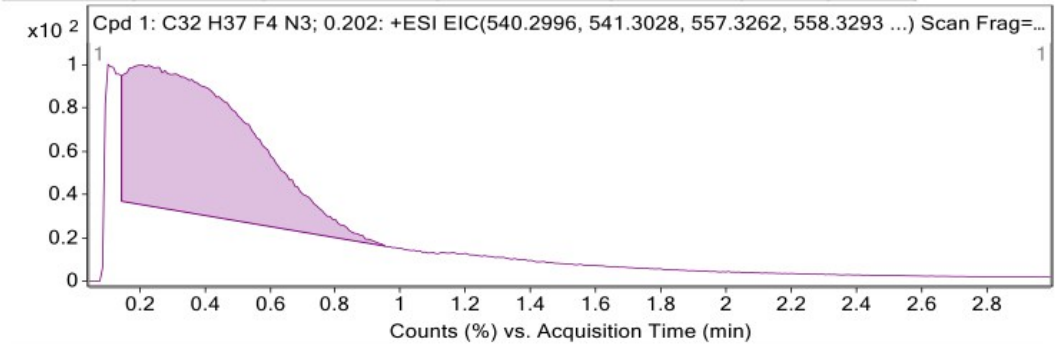
Figure S6. ^{19}F NMR spectrum of **2**

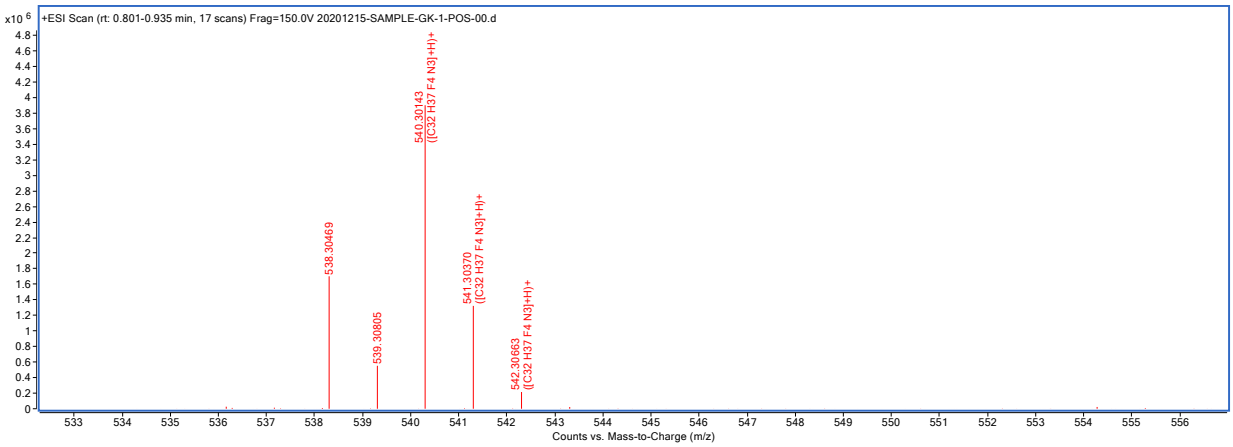
HRMS of 2:

Compound Table

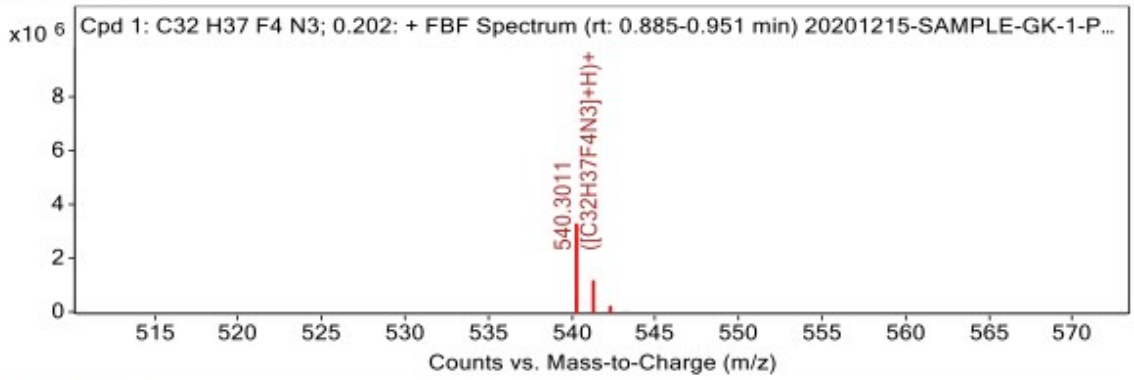
Label	Tgt Score	Mass Error (ppm)	Tgt Formula	Obs. RT	Ref. Mass	Obs. Mass
Cpd 1: C32 H37 F4 N3; 0.202	95.81	2.25	C32 H37 F4 N3	0.202	539.2924	539.2936

Obs. m/z	Obs. RT	Obs. Mass	Tgt Formula	Tgt Mass	Tgt Mass Error	Find Cpds Algorith
540.3011	0.202	539.2936	C32 H37 F4 N3	539.2924	2.25	Find by Formula

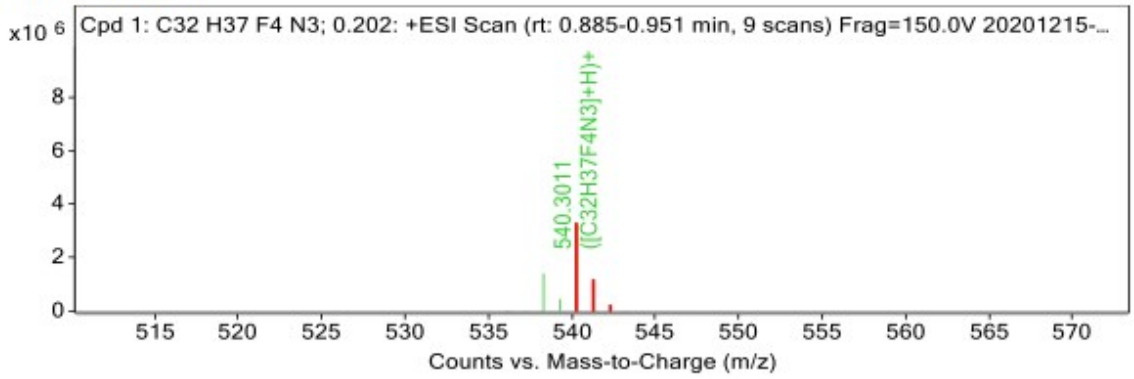




MS Zoomed Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

Obs. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
540.3011	1	3277346.5	C32H37F4N3	(M+H)+	
541.3036	1	1090947.75	C32H37F4N3	(M+H)+	
542.3064	1	177153.86	C32H37F4N3	(M+H)+	
543.3086	1	18434.22	C32H37F4N3	(M+H)+	
540.3011	1	3277346.5	C32H37F4N3	(M+H)+	2.64

Figure S7. HRMS spectrum of **2**

S4. Synthetic procedure and characterization of 3

3. Pentafluoropyridine (0.086 g, 0.51 mmol) was added to a solution of SIDipp (0.2 g, 0.51 mmol) at 0 °C, in 10 mL of THF. The resulting mixture was stirred for 30 minutes at room temperature and trifluoroboranediethyletherate (0.065 mL, 0.051 mmol) was added drop wise at -78 °C. The solution became colorless immediately. After stirring the reaction mixture for further 30 minutes at room temperature, the solution was dried in vacuum and extracted through a frit with the mixture of tetrahydrofuran and dichloromethane. Colorless crystals came after keeping this solution mixture at - 36 °C for 4–5 days with a yield of 0.29 g (48 %). MP: decomposition at 72 ˚C. ^{1}H NMR (200 MHz, 298 K, $CDCl_3$): δ = 1.19 (d, J = 6.10 Hz, 12 H, CH(CH_3)$_2$), 1.37 (d, J = 6.87 Hz, 12 H, CH(CH_3)$_2$) 3.01 (sept, J = 6.87 Hz, 4 H, CH(CH$_3$)$_2$, 4.87(bs, 2 H, NH), 7.23(d, J = 8.39 Hz, 4 H, *meta*-Ar-H), 7.47 (t, J = 7.63 Hz, *para*-Ar-H) ppm; ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ = 22.63, 23.72 (HCMe_2), 26.86, 29.08 (HCMe_2), 55.31 (CH$_2$Cl$_2$, dichloromethane) 125.55, 128.16, 132.24 (Ar-C_6H$_3$), 124.44, 136.40, 139.11 (C_5F$_4$N), 146.34 (*ipso*-C_6H$_3$), 157.14 (NCN) ppm; ^{19}F{^{1}H} NMR (377 MHz, 298 K, $CDCl_3$): δ = -153.18 (s, 4 F, 2BF_4^-), –132.86 (s, 2 F, *meta*-Ar-C$_5F_4$N), -83.61 (s, 2 F, *ortho*-Ar-C$_5F_4$N) ppm; ^{11}B{^{1}H} NMR (128 MHz, 298 K, $CDCl_3$): -1.05 (br s, 1 B, BF$_4$) ppm. Elemental analysis calcd (%) for $C_{30}H_{36}F_8BN_3$ [601.43 gmol^{-1}]: C 59.91, H 6.03, N 6.99; found: C 59.11, H 5.61, N 6.12.

NMRs of 3:

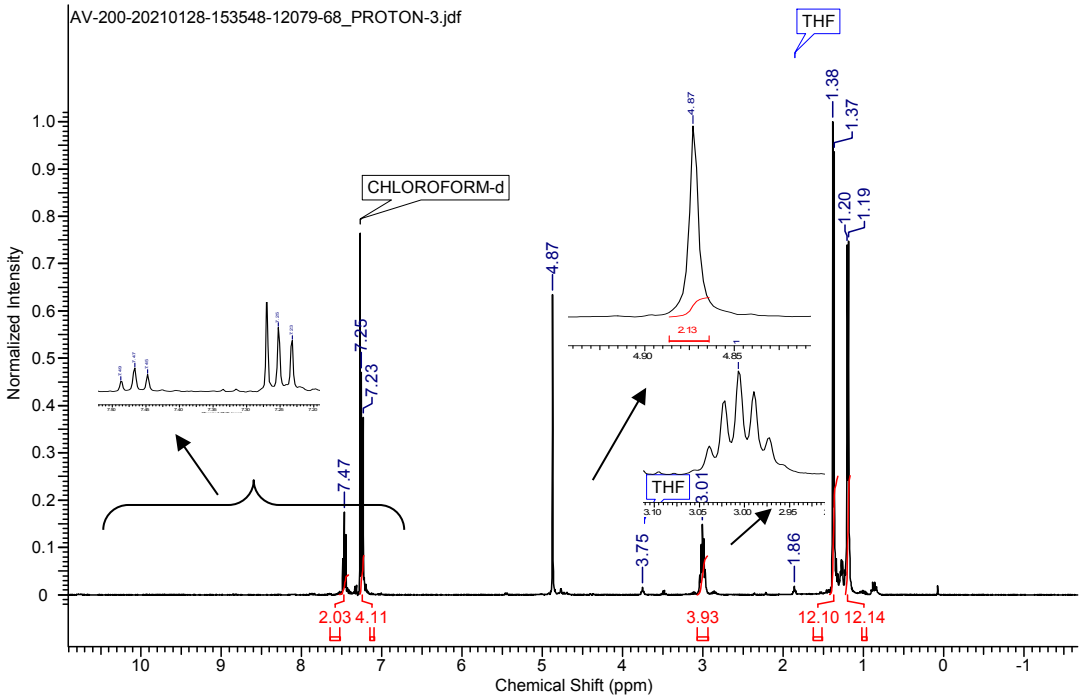


Figure S8. ^{1}H NMR spectrum of **3**

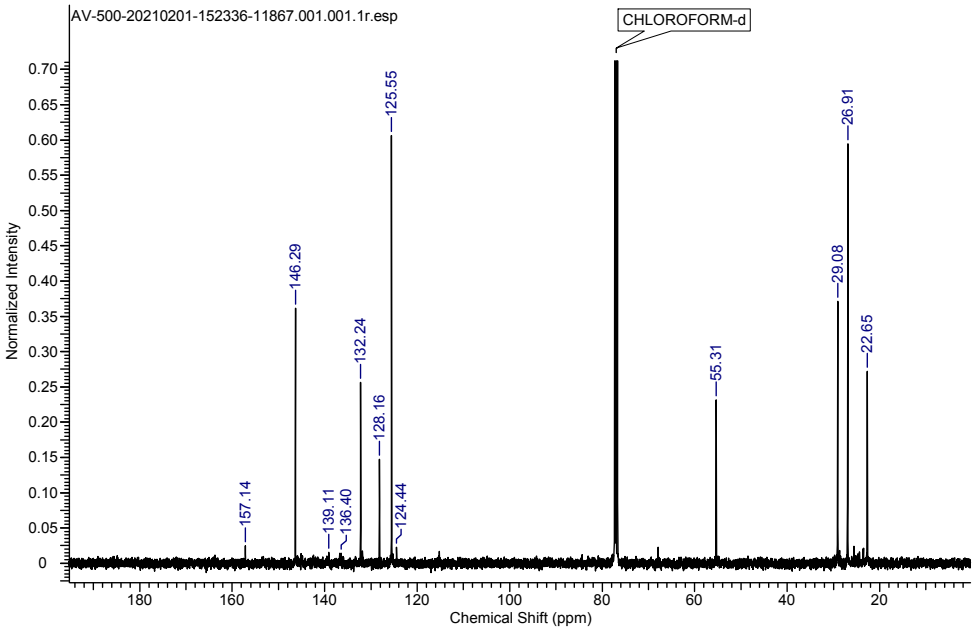


Figure S9. ^{13}C NMR spectrum of **3**

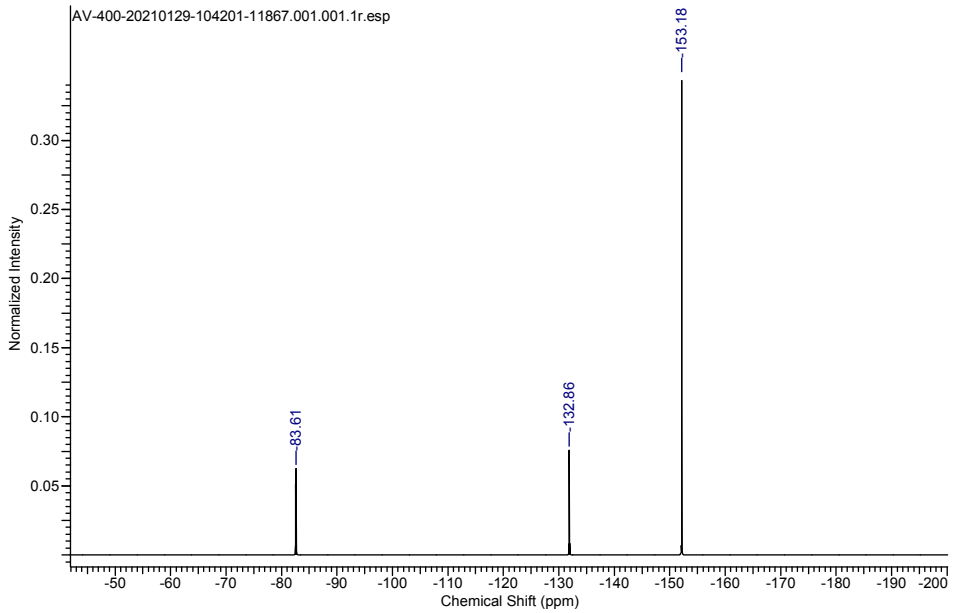


Figure S10. ^{19}F NMR spectrum of **3**

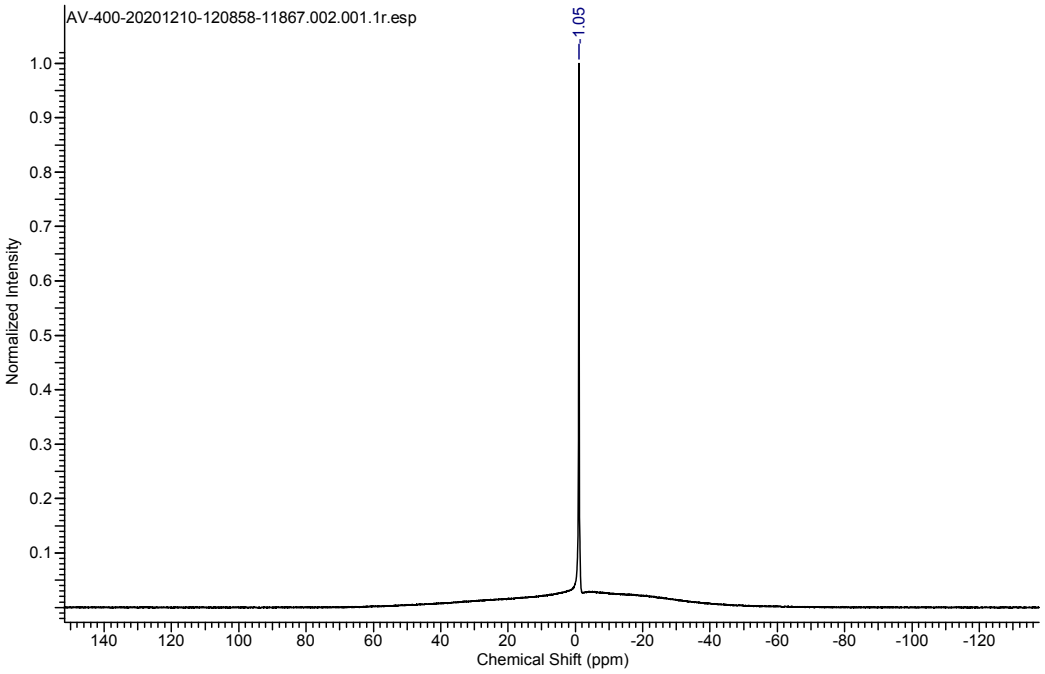
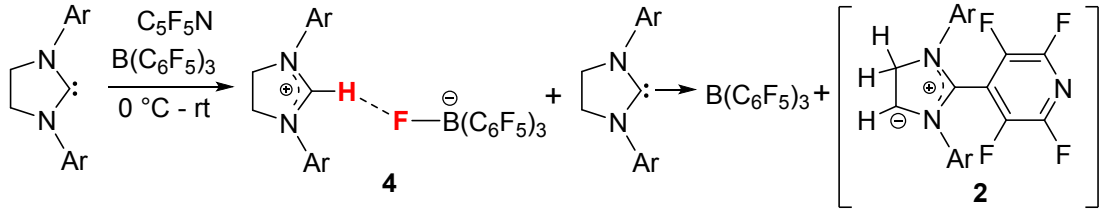


Figure S11. ^{11}B NMR spectrum of **3**

S5. Synthetic procedure and characterization and crystal structure of 4



Scheme S1. Synthesis of **4**

Pentafluoropyridine(0.85 g, 0.51 mmol) and $B(C_6F_5)_3$ (0.52 g, 1.02 mmol) were added to a toluene solution (20 mL) of SIDipp (0.60 g, 1.53 mmol) at 0 °C. The resulting solution was changed to pink color after coming to room temperature. After stirring for further 1 hour at room temperature, we have collected an aliquot of 0.5 mL to monitor the reaction by NMR spectroscopy, which revealed multiple product formation. The solution was subsequently filtered through a frit. Storing the solution at 4 °C for 2-3 days resulted in colorless crystals of **4**. Yield 0.26 g (28 %). ^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ = 1.20-1.35 (m, 12 H, $CH(CH_3)_2$), 2.87 (sept, J = 6.5 Hz, 4 H, $CH(CH_3)_2$), 4.41 (s, 4 H, N-CH_2CH_2-N), 7.31-7.53 (m, 12 H, Ar-*H*), 8.78 (s, 1H, N-C*H*-N) ppm; ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ = 23.84, 24.48 ($HCMe_2$), 28.15, 29.37 ($HCMe_2$), 53.59, 55.19 (CH_2CH_2),122.38, 123.38, 124.90, 129.48, 134.13, 135.41, 137.24, 146.69, 147.47, 148.53 (3*C_6F_5), 125.18, 128.57, 131.95 (Ar-C_6H_3), 145.63 (*ipso*-C_6H_3), 160.06 (N-*C*H-N) ppm; ^{19}F{^{1}H} NMR (377 MHz, 298 K, $CDCl_3$): δ = -109.91, -119.91, -124.85, -127.78, -130.91, -133.50, -135.65, -158.47, -162.62, -164.62, -166.19, -166.99 (15 F, 3*C_6F_5) -135.73 (d, J = 31.21 Hz, 1 F, B-*F*) ppm; ^{11}B{^{1}H} NMR (128 MHz, 298 K, $CDCl_3$): -15.55 (SIDipp-*B*$(C_6F_5)_3$, -4.19 (s, 1 B, F*B*$(C_6F_5)_3$) ppm.

NMRs of 4:

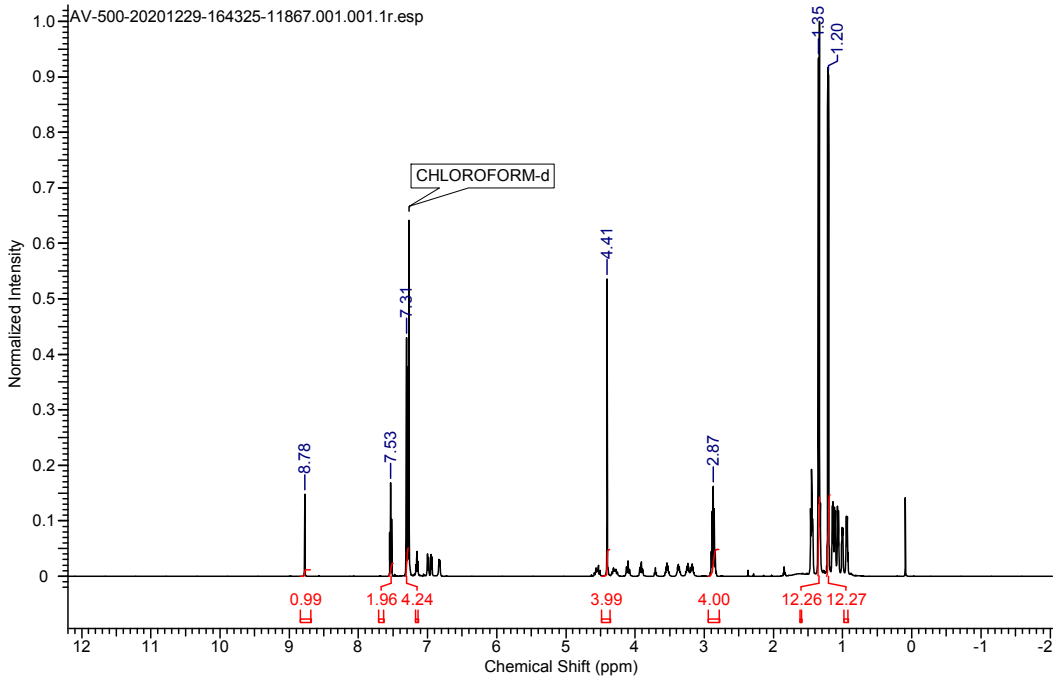


Figure S12. ^{1}H NMR spectrum of **4**

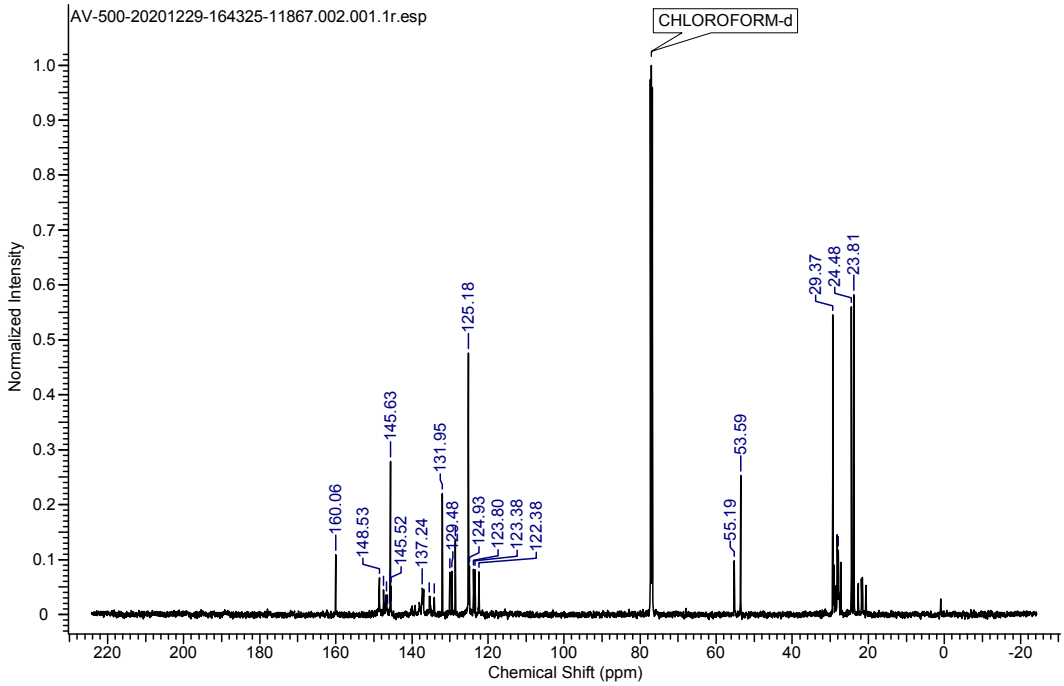


Figure S13. ^{13}C NMR spectrum of **4**

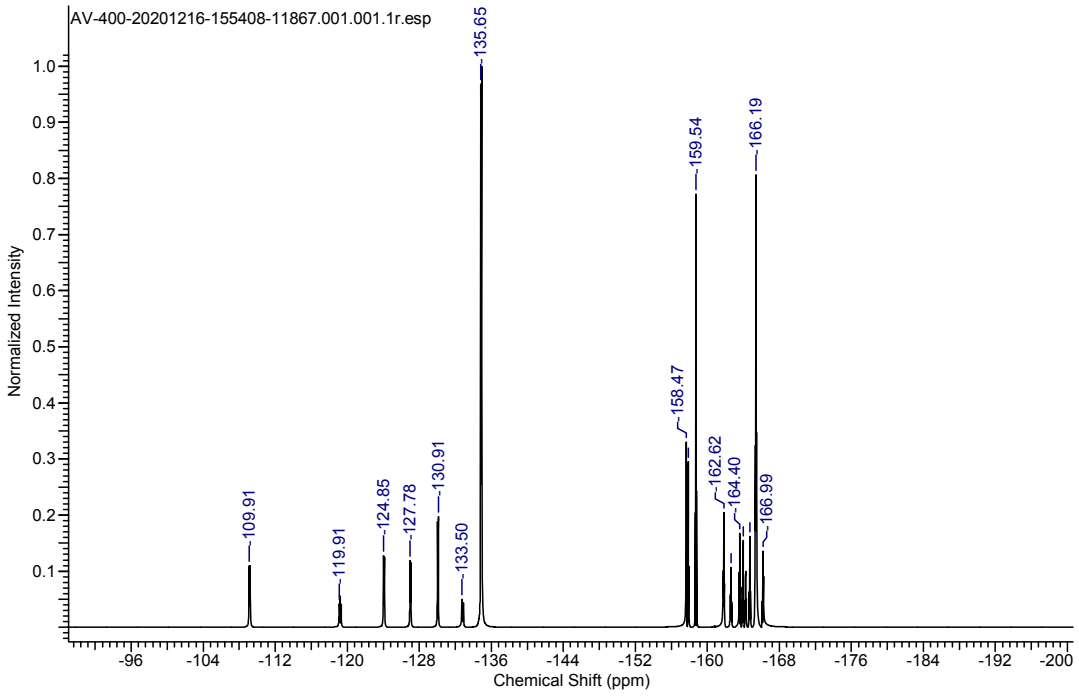


Figure S14. ^{19}F NMR spectrum of **4**

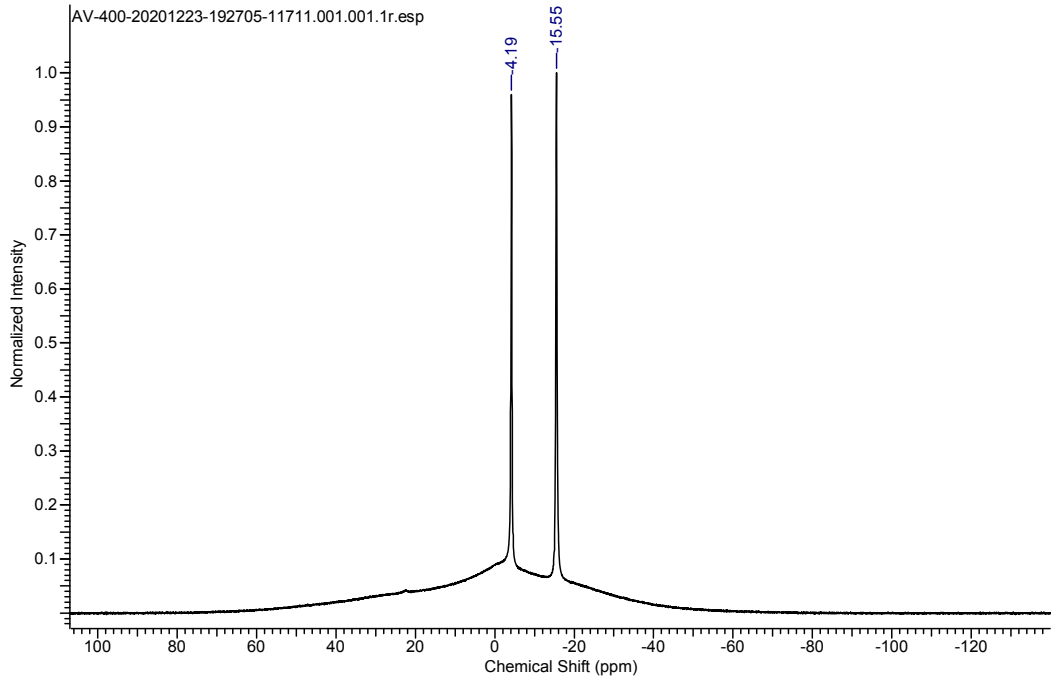


Figure S15. ^{11}B NMR spectrum of **4**

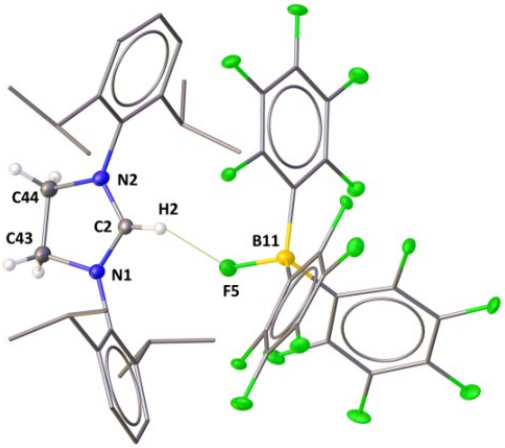


Figure S16. The molecular structure of **4**. Hydrogen atoms (apart from those bound to imidazolium ring) are not shown for clarity. Selected bond lengths (Å) and bond angles (°): N1–C2 1.315(3), N2–C2 1.315(3), C43–C44 1.544(3), C2–H2 0.9500, B11-F5 1.473(3); N1–C2–N2 113.1(2), C43– N1–C2 110.70(18), C44–N2–C2 110.34(19).

S6. Synthetic procedure and characterization of 5a and 5b

5a&5b. Tetrafluoropyridine (0.038 g, 0.255 mmol) was added to a solution of IDipp (0.2 g, 0.51 mmol) at 0 °C, in 10 mL of toluene and hexane mixture. An immediate formation of yellow precipitate was noticed after coming to room temperature. The resulting mixture was stirred for 15 minutes at that temperature. The precipitate was filtered through a cannula followed by washing with pentane. The saturated dichloromethane solution (5 mL) was kept for crystallization at 4 °C. Yellow crystals of **5b** along with few crystals of **5a** came after 2-3 days. ^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ = 1.24-1.02 (m, 48 H, $CH(CH_3)_2$), 2.44 (m, 8 H, $CH(CH_3)_2$), 7.59 (m, 1 H, C_5F_2HN), 8.49-9.06(s, 4 H, 2*C*H*=C*H*) ppm; 7.43-7.16 (m,12 H, Ar-*H*) ppm; ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ = 22.37, 25.49 ($HCMe_2$), 29.23 ($HCMe_2$), 124.42, 124.78 (N*C*H=*C*HN), 128.18, 128.99, 132.05, 132.37 (Ar-C_6H_3), 125.25, 128.01, 127.67, 128.85, 130.35, 131.37 (C_5F_2HN), 146.23 (*ipso*-C_6H_3); ^{19}F{^{1}H} NMR (377 MHz, 298 K,

$CDCl_3$): δ = -130.14 (br s, 6 F, SiF_6^{2-}), -124.07 (d, J = 27.62 Hz, 1 F), -84.60 (d, J = 27.62 Hz, 1 F) ppm.

NMRs of 5b

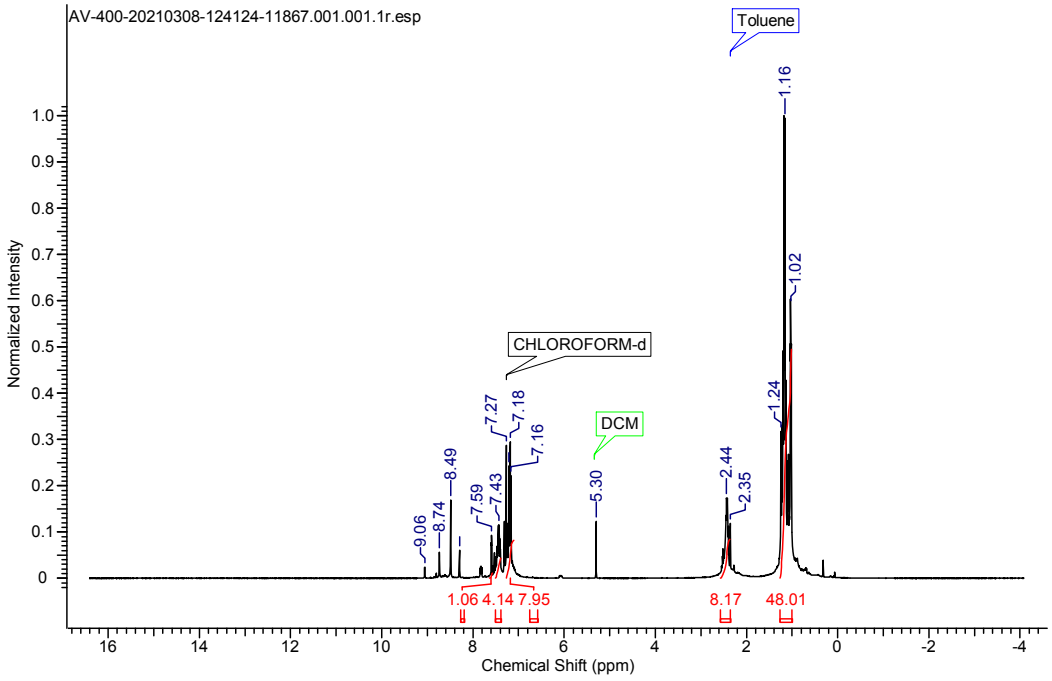


Figure S17. ^{1}H NMR spectrum of **5b**

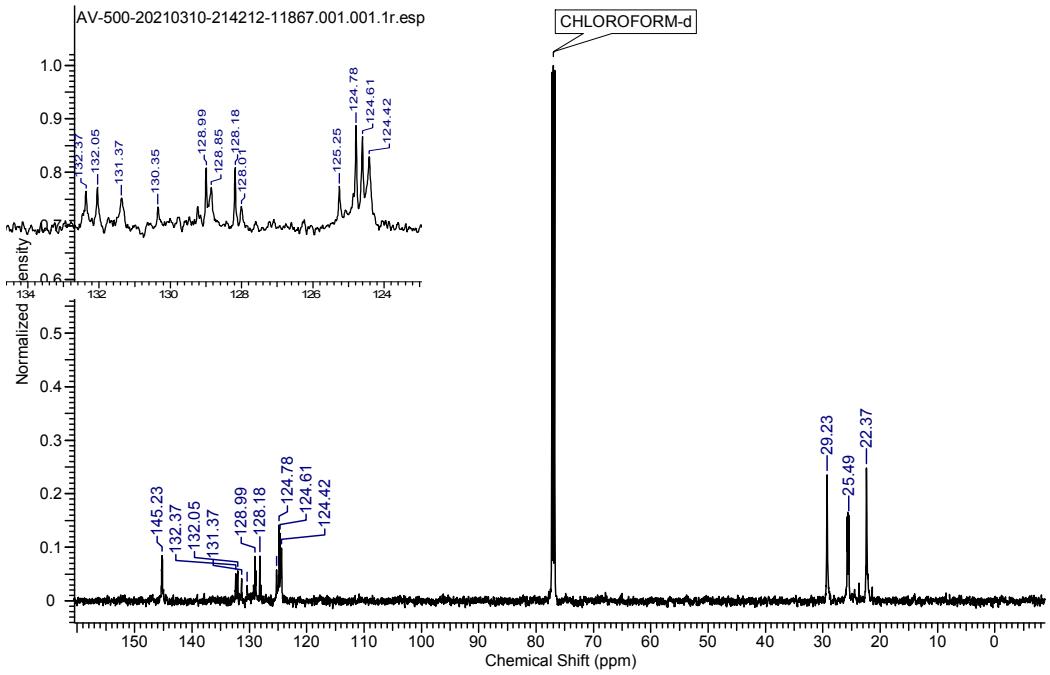


Figure S18. ^{13}C NMR spectrum of **5b**

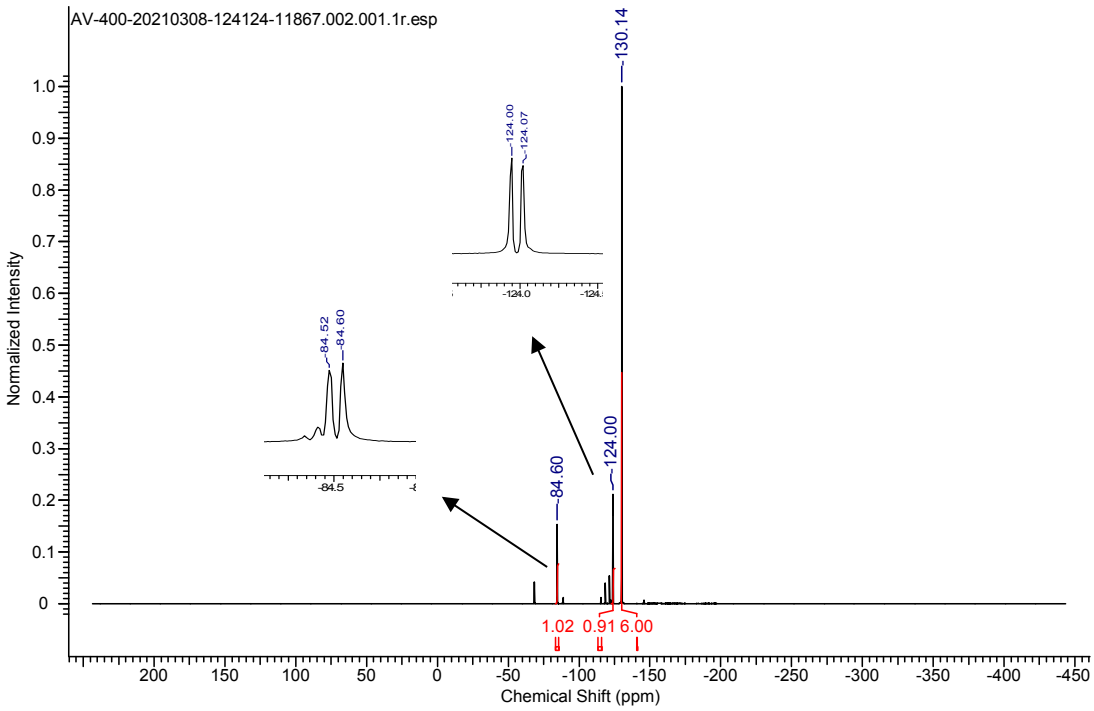


Figure S19. ^{19}F NMR spectrum of **5b**

S7. Synthetic procedure and characterization of 6

6. Pentafluoropyridine (0.09 g, 0.51 mmol) was added to a toluene solution of [PhC(N*t*Bu)$_2$]SiSi(Si(CH$_3$)$_3$) (0.26 g, 0.51 mmol) at -30 °C. An immediate change from yellow to colorless was observed after coming at room temperature. The resulting mixture was stirred for 1 hour at room temperature. The solution was dried in vacuum and kept for crystallization with concentrated toluene solution (5 mL). Colorless crystals came after keeping this solution at -4 °C for 1 day with a yield of 0.405 g (60 %). MP: 98˚C. ^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 0.52 (s, 27H, SiMe$_3$), 0.97 (s, 18H, *t*Bu), 6.92 (m, 5 H, Ph) ppm; ^{13}C{^{1}H} NMR (101 MHz, 298 K, C_6D_6): δ = 5.05 (Si(Si*Me*$_3$)$_3$), 32.72 (C*Me*$_3$), 55.47(*C*Me$_3$), 130.44,133.74 (Ph), 172.05 (N*C*N) ppm;Si(*C*$_5$F$_4$N) were not detected due to signal broadness (^{19}F coupling); ^{19}F{^{1}H} NMR (377 MHz, 298K, C_6D_6): δ = -157.18 (s, 2 F, *meta*-Ar-C$_5$*F*$_4$N), -140.08 (s, 2 F, *ortho*-Ar-C$_5$*F*$_4$N), -50.41 (s, 1 F, Si-*F*) ppm; ^{29}Si{^{1}H} NMR (99.36 MHz, 298 K, C_6D_6): δ = -8.35 (s, 3Si, SiSi(*Si*Me$_3$)$_3$), -77.09, -73.82 (d, *J* = 333.06 Hz) *Si*Si(SiMe$_3$)$_3$), -115.94 (s, 1Si, Si*Si*(SiMe$_3$)$_3$) ppm. Elemental analysis calcd (%) for $C_{29}H_{50}F_5N_3Si_5$ [676.73 gmol^{-1}]: C 51.51, H 7.45, N 6.21; found: C 51.27, H 7.38, N 6.51.

NMRs of 6:

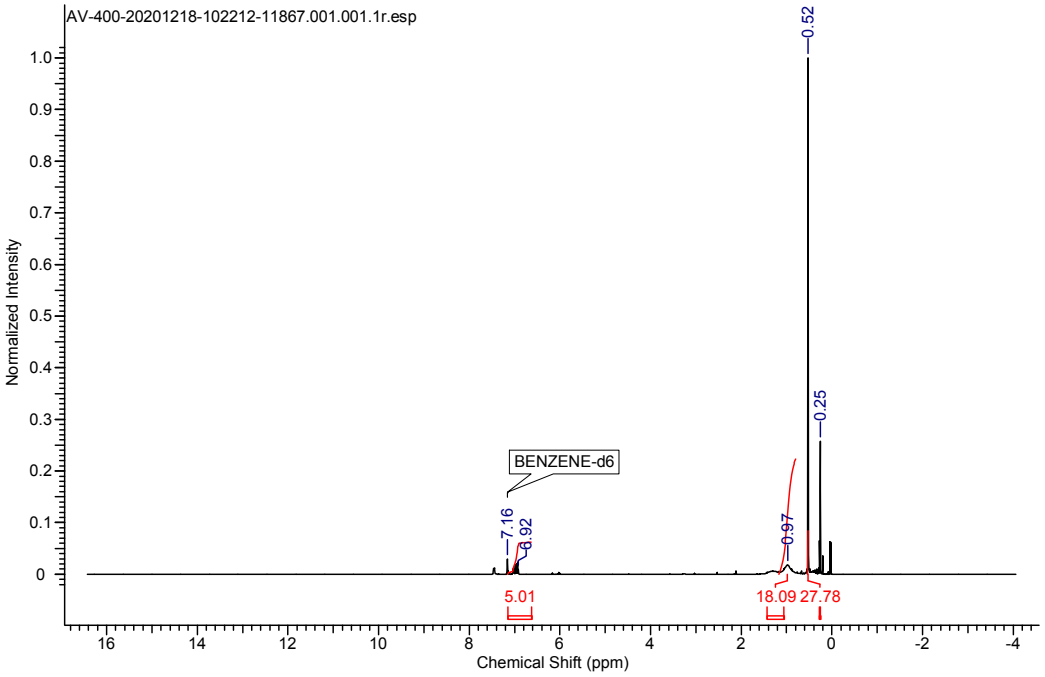


Figure S20. ^{1}H NMR spectrum of **6**

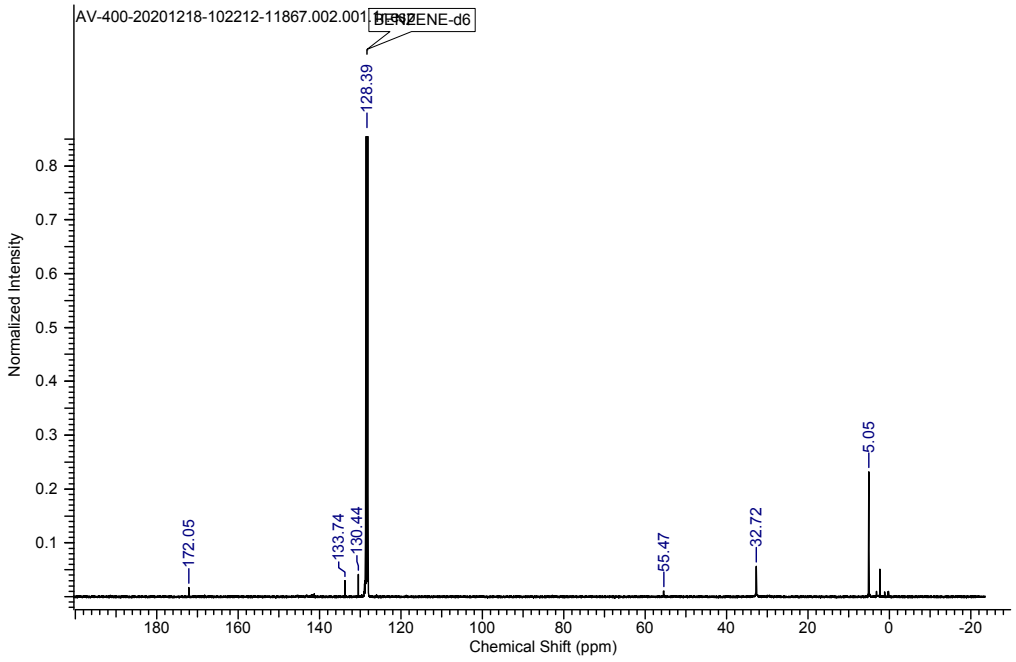


Figure S21. ^{13}C NMR spectrum of**6**

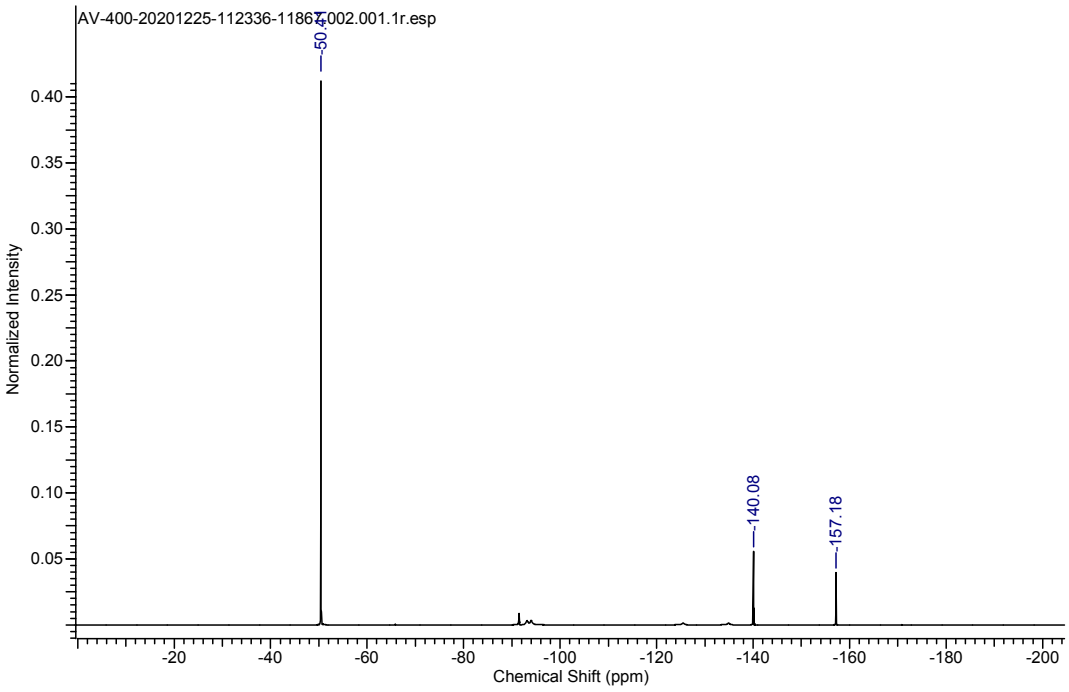


Figure S22. ^{19}F NMR spectrum of **6**

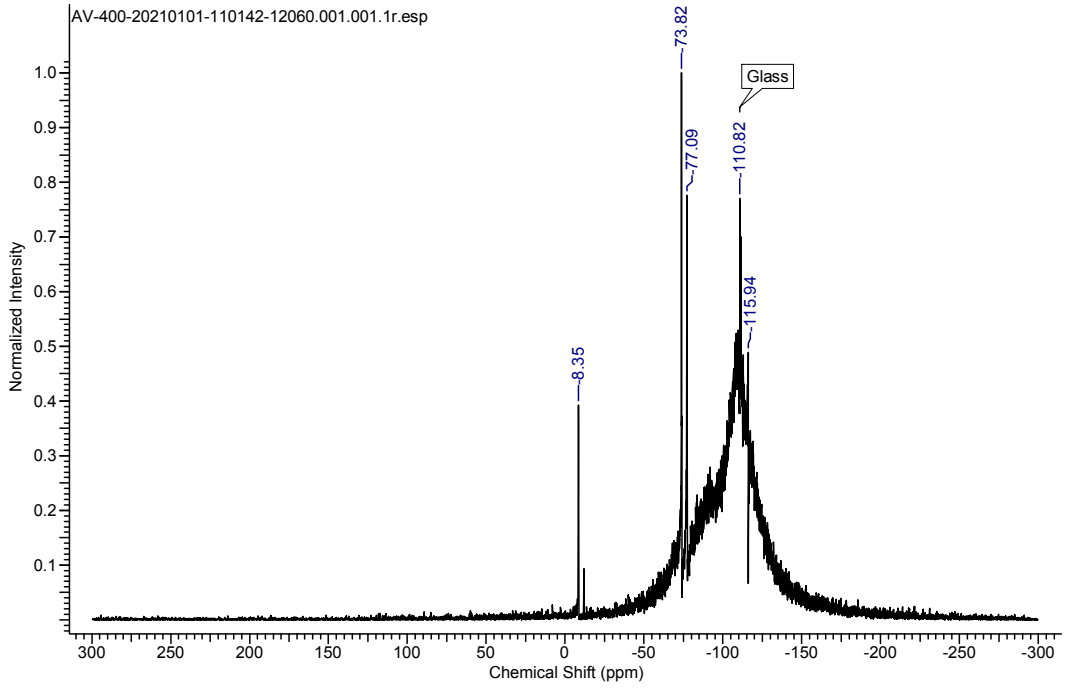


Figure S23. ^{29}Si NMR spectrum of **6**

S8. The spectroscopic data for the reaction of Denk's silylene with C_5F_5N

Pentafluoropyridine (0.08 g, 0.50 mmol) was added to a toluene solution of Denk's dipp-silylene (0.21 g, 0.50 mmol) at -30 °C. An immediate color change from brownish yellow to pale yellow was observed after coming at room temperature. The resulting mixture was stirred for 1 hour at room temperature. The solution was dried in vacuum and a yellow powder was obtained with a yield of 0.355 g (62 %). MP: 78 ˚C.

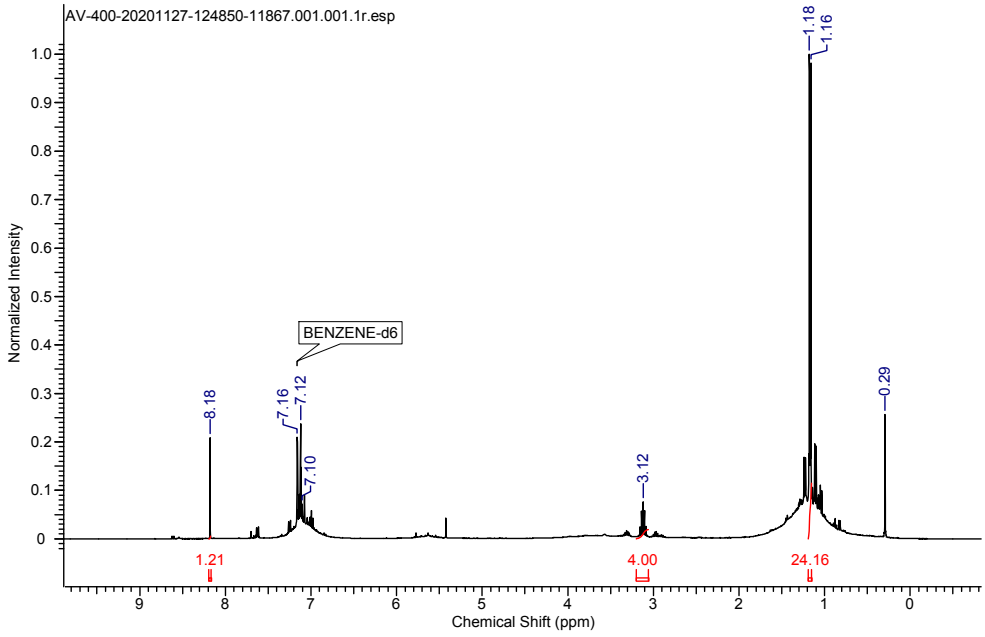


Figure S24. ^{1}H NMR spectrum

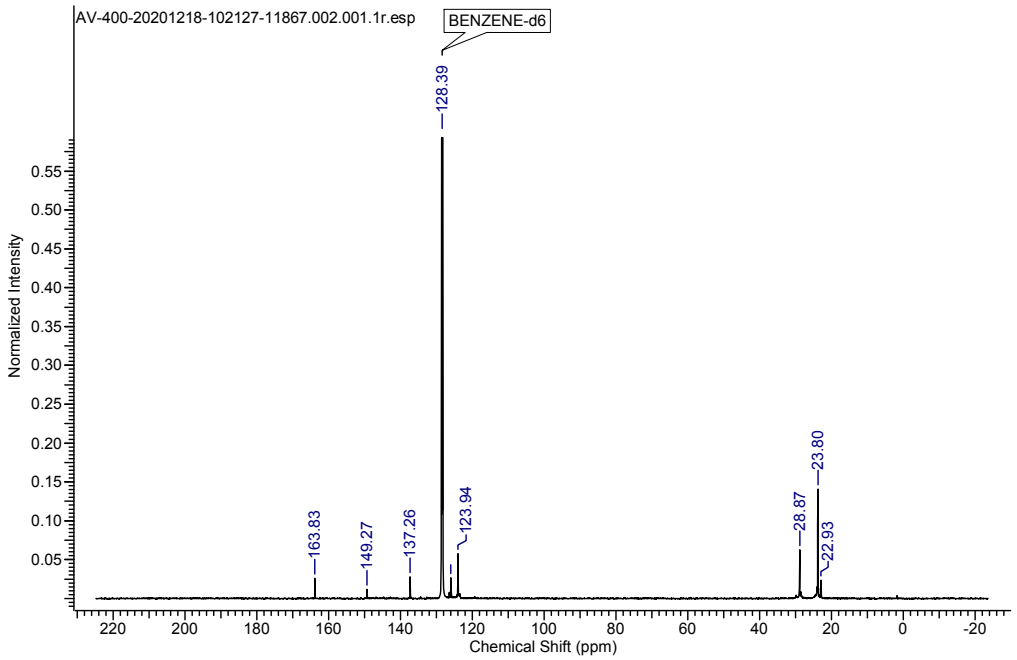


Figure S25. ^{13}C NMR spectrum

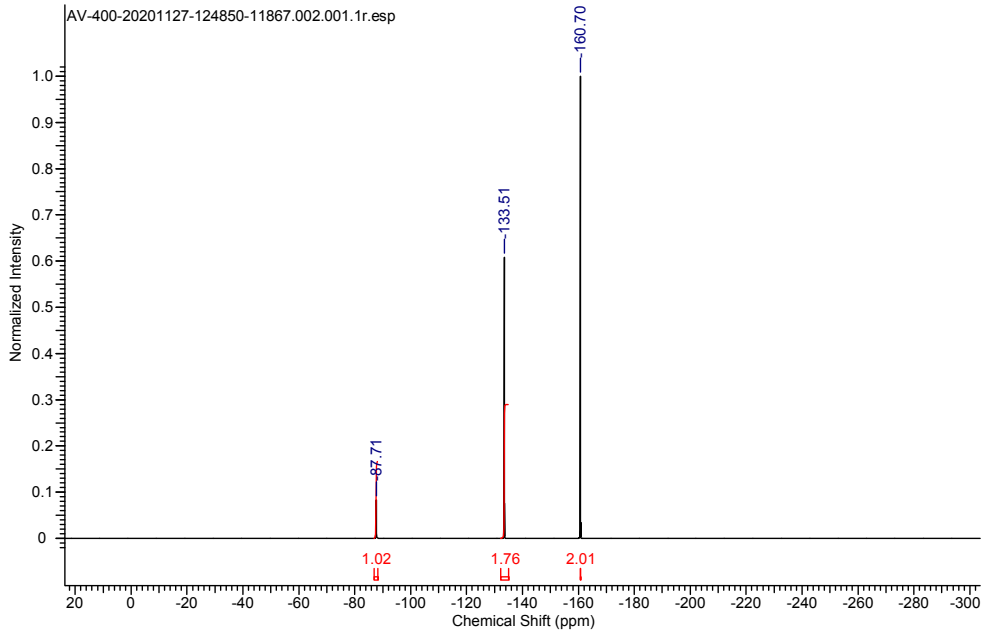


Figure S26. ^{19}F NMR spectrum

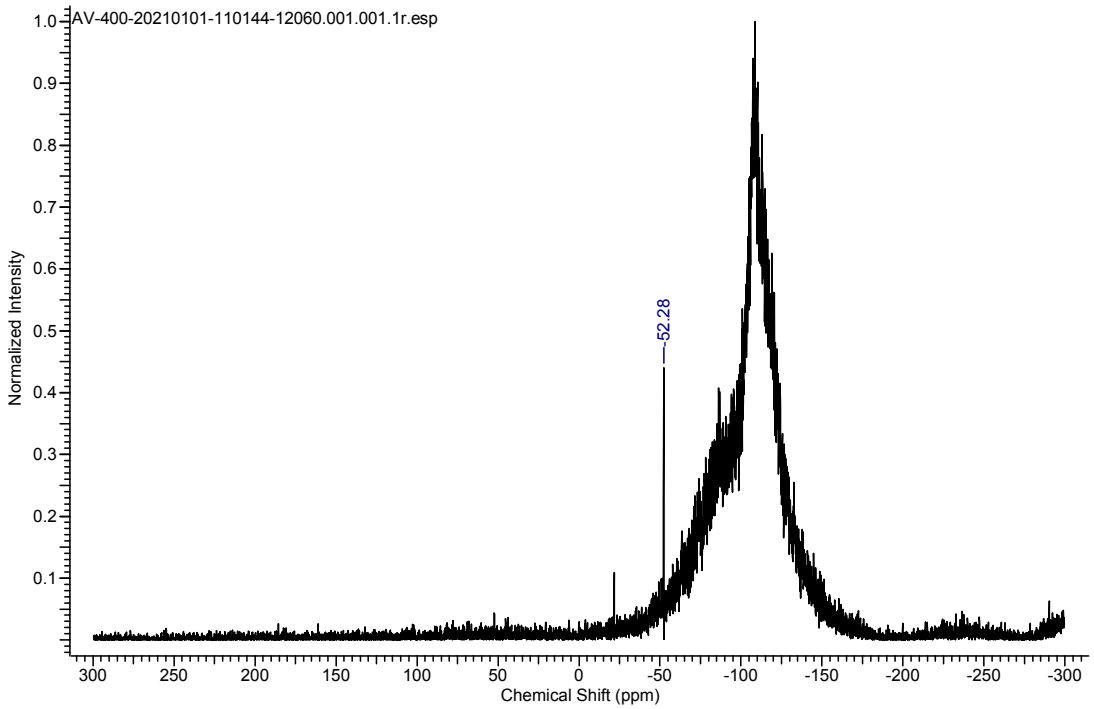


Figure S27. ^{29}Si NMR spectrum

S9. Crystallographic data for the structural analyses of 1, 3, 4, 5b and 6

Single crystals of **1**, **3**, **4, 5b** and **6** were mounted on a Bruker SMART APEX II single crystal X-ray CCD diffractometer having graphite monochromatised (Mo-Kα = 0.71073 Å) radiation at low temperature, 100 K. The X-ray generator was operated at 50 kV and 30 mA. The X-ray data acquisition was monitored by APEX2 program suit. The data were corrected for Lorentz-polarization and absorption effects using SAINT and SADABS programs which are an integral part of APEX2 package.[S2] The structures were solved by direct methods and refined by full matrix least squares, based on F^2, using SHELXL Crystal structures were refined using Olex2-1.0 software. Anisotropic refinement was performed for all non-H atom. The C-H hydrogen atoms were calculated using the riding model.[S3] The structures were examined using the ADSYM subroutine of PLATON to assure that no additional symmetry could be applied to the models. The molecular weight of each structure mentioned herein has been calculated

considering the solvent molecules trapped in the crystal. Mercury software was used to prepare packing diagrams and molecular interactions.Crystallographic information (CCDC Nos. 2055788 (**1**), 2055789 (**3**), 2055790 (**4**), 2070006 (**5b**) and 2055791 (**6**)) is available at www.ccdc.cam.ac.uk/data or as part of Supporting Information.

1. Sum formula:($C_{49}H_{44}F_{15}N_5$), yellow, 0.2 × 0.12 × 0.1 mm^3, monoclinic, space group '$P2_1/n$', a = 12.4788(17) Å, b = 19.2697(19)Å, c = 18.877(3)Å, $\alpha = \gamma = 90°$, β =90.694(8), V = 4538.9(11) $Å^3$, Z = 4, T = 100(2) K, $2\theta_{max}$ = 144.74°, D_{calc} (g cm^{-3}) = 1.446, $F(000)$ = 2032, μ (mm^{-1}) = 1.125, 201625 reflections collected, 7877 unique reflections (R_{int} = 0.16), 8937 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.6293, T_{max} = 0.7536, 649 refined parameters, S = 1.099, $R1$ = 0.0638, $wR2$ = 0.1272 (all data R = 0.0740, $wR2$ = 0.1394), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.45, $\Delta\rho_{min}$= -0.37 ($eÅ^{-3}$).

3. Sum formula: ($C_{31}H_{35}BCl_2F_8N_3$), Colorless, 0.35 × 0.32 × 0.27 mm^3, monoclinic, space group '$P2_1/n$', a = 10.7352(3) Å, b = 17.7450(5) Å, c = 18.4206(5) Å, $\alpha = \gamma = 90°$, β =100.624(2), V = 3448.90(17) $Å^3$, Z = 4, T = 100(2) K, $2\theta_{max}$ = 56.68 °, D_{calc} (g cm^{-3}) = 1.321, $F(000)$ = 1412, μ (mm^{-1}) = 0.257, 59318 reflections collected, 8556 unique reflections (R_{int} = 0.042), 6946 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.5546, T_{max} = 0.7457, 439 refined parameters, S = 0.978, $R1$ = 0.0623, $wR2$ = 0.1771 (all data R = 0.0748, $wR2$ = 0.1895), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.88, $\Delta\rho_{min}$= -0.72 ($eÅ^{-3}$).

4. ($C_{57}H_{51}BF_{16}N_2$), Colorless, 0.22 × 0.12 × 0.1 mm^3, triclinic, space group 'P-1', a = 10.350(2) Å, b = 11.9292(18) Å, c = 22.376(12) Å, α =83.095(18)°,β = 83.19(2)°, γ = 70.263(12)°, V = 2572.5(15) $Å^3$, Z = 2, T = 100(2) K, $2\theta_{max}$ = 52.08 °, D_{calc} (g cm^{-3}) = 1.393, $F(000)$ = 1112, μ (mm^{-1}) = 0.121, 36581 reflections collected, 10656 unique reflections (R_{int} = 0.032), 8721 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.6846, T_{max} = 0.7454,

693 refined parameters, S = 1.097, $R1$ = 0.0622, $wR2$ = 0.1492 (all data R = 0.0783, $wR2$ = 0.1573), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.48, $\Delta\rho_{min}$= -0.52 (eÅ^{-3}).

5b. ($C_{59}H_{73}F_2N_5F_6Si\cdot 6(CH_2Cl_2)$), Yellow, 0.12 × 0.09 × 0.08 mm^3, monoclinic, space group "$P2_1/n$", a = 15.6778(15)Å, b = 19.214(2) Å, c = 26.770(3)Å, $\alpha = \gamma = 90$ °, β =105.888(3) °, V = 7755.9(14) Å^3, Z = 4, T = 100(2) K, $2\theta_{max}$ = 49.32 °, D_{calc} (g cm^{-3}) = 1.32, $F(000)$ = 3200, μ (mm^{-1}) = 0.503, 309048 reflections collected, 13648 unique reflections (R_{int} = 0.16), 9882observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.6324, T_{max} = 0.961, 854 refined parameters, S = 1.058, $R1$ = 0.0861, $wR2$ = 0.2161 (all data R = 0.1100, $wR2$ = 0.2342), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.097, $\Delta\rho_{min}$= -0.903 (eÅ^{-3}).

6. ($C_{29}H_{50}F_5N_3Si_5$), Colorless, 0.18 × 0.12 × 0.06 mm^3, orthorhombic, space group '*Pbca*', a = 24.4829(10) Å, b = 13.9216(7) Å, c = 42.4462(19) Å, $\alpha = \beta = \gamma = 90$ °, V = 14467.4(11) Å^3, Z = 16, T = 100(2) K, $2\theta_{max}$ = 56.46 °, D_{calc} (g cm^{-3}) = 1.242, $F(000)$ = 5760, μ (mm^{-1}) = 0.247, 618560 reflections collected, 14208 unique reflections (R_{int} = 0.11), 12709 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.5322, T_{max} = 0.7457, 787 refined parameters, S = 1.226, $R1$ = 0.0388, $wR2$ = 0.1081 (all data R = 0.0470, $wR2$ = 0.1201), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.50, $\Delta\rho_{min}$= -0.841(eÅ^{-3}).

S10. Details of the theoretical calculations

All the calculations in this study have been performed with density functional theory (DFT), with the aid of the Turbomole 7.1 suite of programs,[S4] using the PBE functional.[S5] The TZVP[S6] basis set has been employed. The resolution of identity (RI),[S7] along with the multipole accelerated resolution of identity (marij)[S8] approximations have been employed for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations. Solvent correction were incorporated with optimization calculations using the COSMO model,[S9] with a

hexane-toluene mixture (ε = 2.99) as the solvent. The values reported are ΔG values, with zero point energy corrections, internal energy and entropic contributions included through frequency calculations on the optimized minima, with the temperature taken to be 298.15 K. Harmonic frequency calculations were performed for all stationary points to confirm them as local minima or transition state structures.

Care was taken to ensure that the obtained transition state structures possessed only one imaginary frequency corresponding to the correct normal mode. The validity of the obtained transition states was further confirmed by doing IRC[S10, S11] calculations: the correct reactant and product structures were obtained for every transition state obtained. To do the IRC calculations, Turbomole 7.1 was employed.

Details of minima and TS search. Stationary points are places on the potential energy surface (PES) with a zero gradient, i.e. zero first derivatives of the energy with respect to atomic coordinates. Two types of stationary points are of special importance to chemists. These are minima (reactants, products, intermediates) and first-order saddle points (transition states). These two types of stationary points can be characterized by the curvature of the PES. At a minimum the Hessian matrix (second derivatives of energy with respect to atomic coordinates) is positive, that is the curvature is positive in all directions. If there is only one negative curvature, the stationary point is a transition state (TS). Because vibrational frequencies are basically the square roots of the curvatures, a minima has all real frequencies, and a saddle point has one imaginary vibrational "frequency". Structure optimizations are most efficiently done by so-called quasi-Newton–Raphson methods.[S12]For TS optimizations the TRIM (Trust Radius Image Minimization) method implemented in Turbomole 7.1 software packages, tries to maximize the energy along one of the Hessian eigenvectors, while minimizing it in all other directions. Thus,

one “follows” one particular eigenvector, hereafter called the “transition” vector. After computing the Hessian for the guess structure one have to identify which vector to follow. For a good TS guess this is the eigenvector with negative eigen value, or imaginary frequency.

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PBE/TZVP optimized geometries for all the compounds and transition states

C_5F_5N

E = -466865.02 kcal/mol

C	3.6827612	-1.7380845	-0.4283367
C	3.1323158	-2.9328869	-0.9026663
C	5.0604937	-1.5247532	-0.5380680
C	4.0089825	-3.8583357	-1.4697966
C	5.8183189	-2.5372477	-1.1275061
N	5.3067901	-3.6640595	-1.5770507
F	5.6097829	-0.3869599	-0.0914841
F	7.1435527	-2.3666628	-1.2505115
F	1.8148858	-3.1590320	-0.8089977
F	3.5158826	-5.0151349	-1.9369241
F	2.8999339	-0.8099429	0.1225416

NHC

E = -431491.21 kcal/mol

C	1.8157165	-0.2181657	-0.8847948
C	2.7676629	-0.2438297	0.0820763
C	1.9065340	1.9038570	0.0338471
H	3.3675430	-1.0684771	0.4481114
H	1.4347293	-1.0150373	-1.5125116
N	1.3094426	1.0872103	-0.8978979
N	2.8080476	1.0472190	0.6232711
C	3.6850519	1.4542366	1.6731255
C	4.8871971	0.7740460	1.9028946
C	3.3334966	2.5473840	2.4753407
C	5.7252003	1.1783018	2.9448582
H	5.1863223	-0.0534878	1.2582770
C	4.1832307	2.9489070	3.5046771
H	2.3992891	3.0673793	2.2632570
C	5.3788495	2.2651170	3.7500440
H	6.6609059	0.6430870	3.1167271
H	3.9031046	3.8010731	4.1269086
H	6.0376319	2.5793591	4.5613212
C	0.2822068	1.5419252	-1.7776262
C	-0.5441499	2.5996622	-1.3787137
C	0.0992452	0.9407428	-3.0286931
C	-1.5531016	3.0449446	-2.2310820
H	-0.3690375	3.0580053	-0.4054685
C	-0.9216478	1.3885310	-3.8704585
H	0.7664998	0.1431095	-3.3585727
C	-1.7519887	2.4400352	-3.4766179
H	-2.1960665	3.8682825	-1.9140908
H	-1.0571792	0.9173020	-4.8456647
H	-2.5473408	2.7891830	-4.1373645

TS1

E = -696602746070.29 kcal/mol

Imaginary frequency = -209.97

C	3.2235153	3.4820804	0.3983292
C	2.3785073	3.6990790	-0.6931918
C	1.8837275	4.9743998	-0.9776346
C	2.2341256	6.0434706	-0.1505161
C	3.0799060	5.8391345	0.9427861
C	3.5766992	4.5592374	1.2098962
N	1.9977358	2.5924782	-1.5194643
C	0.6888145	2.3637225	-1.9425135
C	0.7009817	1.1837618	-2.6196389
N	2.0139184	0.7248284	-2.5879054
C	2.8335342	1.5852307	-1.9145098
C	2.4559120	-0.4970836	-3.1876980
C	2.0932421	-0.7917186	-4.5062437
C	2.5312958	-1.9848281	-5.0809002
C	3.3280780	-2.8684256	-4.3463719
C	3.6840770	-2.5629567	-3.0306227
C	3.2450464	-1.3762836	-2.4415820
C	4.7015867	1.8688733	-2.6809434
C	5.6007276	0.8586662	-2.2322699
C	6.0996531	-0.0705458	-3.1242119
N	5.8613548	-0.0766653	-4.4260410
C	5.0629180	0.8751178	-4.8731197
C	4.5096071	1.8762648	-4.0925216
F	5.8335608	0.7662878	-0.8976542
F	4.8091701	3.1102536	-2.0663862
F	3.6611709	2.8006701	-4.6188281
F	4.7839653	0.8663788	-6.1974987
F	6.8894290	-1.0622078	-2.6483156
H	1.2573465	5.1342634	-1.8568289
H	3.6064167	2.4787170	0.5873396

H	1.8561914	7.0424978	-0.3736246
H	4.2415834	4.3951125	2.0593590
H	3.3565780	6.6777947	1.5837831
H	1.5140337	-0.0708357	-5.0857997
H	3.5078166	-1.1207272	-1.4139960
H	2.2707761	-2.2110254	-6.1157438
H	4.3164387	-3.2441483	-2.4597980
H	3.6824104	-3.7922430	-4.8057554
H	-0.0995851	0.6125120	-3.0746647
H	-0.1283100	3.0264400	-1.6835134

Int1

E = -1365267.78 kcal/mol

C	2.2115542	3.8294905	0.8857157
C	2.1762498	3.7180432	-0.5139299
C	2.6398357	4.7784109	-1.3110771
C	3.1566036	5.9247626	-0.7046485
C	3.1857451	6.0431304	0.6887478
C	2.7037339	4.9935693	1.4779598
N	1.6768406	2.5387534	-1.1118696
C	0.7338283	1.6643677	-0.5390080
C	0.7570397	0.5043910	-1.2242474
N	1.7150665	0.6118402	-2.2497795
C	2.2412525	1.9348936	-2.2714723
C	2.2699814	-0.4669896	-2.9746535
C	2.7609216	-0.2705340	-4.2765762
C	3.3375770	-1.3382870	-4.9663809
C	3.3999125	-2.6103060	-4.3883040
C	2.8897419	-2.8059734	-3.1007393
C	2.3371142	-1.7410462	-2.3877596
C	3.7701905	2.0041728	-2.3382938
C	4.4836861	1.3787188	-1.3020810
C	5.8768796	1.3977180	-1.3041580
N	6.5879779	1.9873239	-2.2410251
C	5.9419591	2.5827559	-3.2177927
C	4.5461481	2.6273910	-3.3258622
F	3.8365239	0.7558180	-0.3020533
F	1.7355080	2.6409530	-3.4874035
F	4.0209357	3.2698105	-4.3782296
F	6.6791080	3.1823960	-4.1678852
F	6.5420371	0.7887846	-0.3094682
H	2.5708200	4.7112625	-2.3973016
H	1.8788519	2.9949717	1.5049783
H	3.5194992	6.7414009	-1.3315999
H	2.7278120	5.0703408	2.5666995
H	3.5798144	6.9469302	1.1562876
H	2.6682436	0.7078596	-4.7497671
H	1.9830319	-1.8869599	-1.3661246
H	3.7216213	-1.1756191	-5.9752270
H	2.9395170	-3.7922473	-2.6351341
H	3.8419273	-3.4433099	-4.9372839
H	0.1188510	-0.3674728	-1.1464402
H	0.0710521	1.9982665	0.2501862

TS2

E = -1365244.22 kcal/mol

Imaginary frequency = -249.43

C	-0.7930143	-0.8183938	10.1149922
C	-0.4871000	-1.5519000	8.9294000
C	0.8523976	-2.0451341	8.9042185
C	1.7609867	-1.6437399	9.8618407
N	1.4712051	-0.8856080	10.9100986
C	0.2116318	-0.4916877	11.0058471
C	-0.6613000	-0.2616000	7.3824000
N	-1.8439746	0.3710859	6.9845501
C	-1.5891607	1.6172033	6.5051330
N	-0.2493891	1.8123616	6.5923688
C	0.3233580	0.6731560	7.1334855
C	-3.1793023	-0.1704958	7.0969442
C	-3.5285734	-1.2963032	6.3505677
C	-4.8288365	-1.7922785	6.4580566
C	-5.7582945	-1.1672179	7.2959951
C	-5.3891348	-0.0421540	8.0394058
C	-4.0905913	0.4619387	7.9455770
C	-2.5720542	2.5683904	5.9874005
C	-3.3714611	2.2560109	4.8771123
C	-4.3041197	3.1959528	4.4349221
N	-4.4653789	4.3726729	5.0015878
C	-3.7191759	4.6864430	6.0390893
C	-2.7617027	3.8259886	6.5782683
C	0.4588234	2.9929670	6.1742753
C	0.3049269	3.4677798	4.8691270
C	0.9904224	4.6224883	4.4863792
C	1.8290632	5.2759080	5.3948231
C	1.9850391	4.7770181	6.6922278
C	1.2953338	3.6317213	7.0929599
F	-3.2209443	1.0889132	4.2370055

F	-5.0687277	2.9057948	3.3745467
F	-3.9048371	5.8897056	6.5973051
F	-2.0454652	4.1830476	7.6546188
F	1.2270644	-2.7800655	7.8240567
F	3.0470518	-2.0541522	9.7510413
F	-0.1022147	0.2772639	12.0760969
F	-2.0526264	-0.3273062	10.2627095
F	-1.4752000	-2.4035000	8.4600000
F	-0.5492000	-2.1531000	5.2601000
H	-0.4043000	-1.7678000	6.1233000
H	-3.7770104	1.3166681	8.5469336
H	-6.7726669	-1.5620575	7.3742152
H	-6.1066080	0.4386314	8.7058649
H	-2.7945882	-1.7665387	5.6957270
H	-0.3249024	2.9306209	4.1583540
H	0.8771740	5.0025503	3.4700795
H	2.3662551	6.1753223	5.0896949
H	2.6384006	5.2863286	7.4019406
H	1.3870759	3.2477952	8.1099160
H	-5.1154142	-2.6721094	5.8799592
H	1.3960793	0.6165348	7.2865094

Int2

E = -1769145.2724841526 kcal/mol

C	3.2081778	3.5850808	0.6161585
C	2.1984416	3.5331528	-0.3481387
C	1.5121469	4.6696676	-0.7788851
C	1.8527510	5.8968964	-0.2047535
C	2.8637351	5.9763389	0.7581609
C	3.5456663	4.8237202	1.1638326
N	1.8592238	2.2515584	-0.9244565
C	0.6159183	1.6140057	-0.8937663
C	0.7759775	0.4182978	-1.5469711
N	2.0826224	0.3343937	-1.9602184
C	2.7288090	1.4712948	-1.6076865
C	2.6089672	-0.7142620	-2.7998535
C	3.0465247	-0.3896785	-4.0854164
C	3.5648844	-1.4130493	-4.8834253
C	3.6227305	-2.7256163	-4.4024419
C	3.1573456	-3.0288319	-3.1177708
C	2.6481836	-2.0170400	-2.3016514
C	4.1298412	1.7779477	-1.8955862
C	5.1421894	0.8697582	-1.5406287
C	6.4645201	1.1588226	-1.8734619
N	6.8234809	2.2643017	-2.4892555
C	5.8947517	3.1397683	-2.8083564
C	4.5317093	2.9604185	-2.5438070
F	4.8428658	-0.2511574	-0.8625695
F	1.6191384	2.2582192	-4.0024178
F	3.6612150	3.8994361	-2.9001583
F	6.2891156	4.2612138	-3.4251376
F	7.4297152	0.2869082	-1.5446248
H	0.7706787	4.5677819	-1.5810218
H	3.7039991	2.6711709	0.9474857
H	1.3312214	6.7993999	-0.5283490
H	4.3316287	4.8836111	1.9178979
H	3.1258785	6.9419735	1.1936505
H	2.9200457	0.6347824	-4.4432119
H	2.3064648	-2.2288224	-1.2872353
H	3.9106923	-1.1823504	-5.8924557
H	3.1999709	-4.0530595	-2.7438846
H	4.0265372	-3.5187287	-5.0340141
H	0.0585104	-0.3581302	-1.7775821
C	-0.6079533	2.1883661	-0.3406505
C	-1.7995644	2.1476178	-1.0857357
C	-2.9361920	2.7723636	-0.5688508
N	-2.9655198	3.3833591	0.5966587
C	-1.8691785	3.3992266	1.3233309
C	-0.6740061	2.8053929	0.9181344
F	-1.8631119	1.5109640	-2.2581302
F	-0.0335885	3.5838968	-3.0947475
F	0.3909136	2.8072875	1.7398693
F	-1.9266279	4.0065094	2.5206756
F	-4.0692585	2.7556319	-1.2862642
H	0.7784912	2.9367369	-3.5694536

TS3

E =-1769121.75 kcal/mol

Imaginary frequency = -254.86

C	0.8024505	3.5017577	5.2180950
C	0.3831611	3.3724427	6.5445453
C	0.5946970	4.3773763	7.4898324
C	1.2396762	5.5491534	7.0868705
C	1.6646593	5.6985551	5.7630424
C	1.4477501	4.6780529	4.8310759
N	-0.2680214	2.1433139	6.9426669
C	0.3645296	0.9418148	7.2643874
C	-0.5966896	-0.0446629	7.4514636

N	-1.8096437	0.6227315	7.2256437
C	-1.6005155	1.9281885	6.9171042
C	1.8269500	0.8727585	7.3824923
C	2.6037181	0.1686705	6.4525638
C	3.9917570	0.1385625	6.6190471
N	4.6118354	0.7490021	7.6051132
C	3.8999951	1.4178749	8.4876510
C	2.5094294	1.5123715	8.4270800
C	-2.6062557	2.9008049	6.4801696
C	-2.9740681	3.9999576	7.2654055
C	-3.9267826	4.8913607	6.7672425
N	-4.5042317	4.7414685	5.5946712
C	-4.1763105	3.7107545	4.8452277
C	-3.2302528	2.7588323	5.2327581
C	-3.1373196	0.0529169	7.2840872
C	-3.4696477	-1.0054265	6.4378002
C	-4.7695775	-1.5129156	6.4831282
C	-5.7158392	-0.9633880	7.3538426
C	-5.3637313	0.0964145	8.1952705
C	-4.0660132	0.6087530	8.1677476
F	2.0289900	-0.4413939	5.4087629
F	4.7415520	-0.5266950	5.7300211
F	4.5564012	2.0313447	9.4810164
F	1.8279304	2.1889072	9.3677700
F	-2.4372172	4.1735194	8.4827563
F	-4.2822531	5.9491089	7.5061411
F	-4.7775307	3.5878798	3.6566495
F	-2.9100847	1.7362185	4.4295442
C	-0.4019947	-1.3722013	8.9413849
C	-0.7514745	-0.6818331	10.1423700
C	0.2273257	-0.3372219	11.0569703
N	1.5004471	-0.6838803	10.9690607
C	1.8308758	-1.4102114	9.9121455
C	0.9530704	-1.8255273	8.9310753
F	-2.0329979	-0.2566313	10.2930861
F	-1.3542165	-2.2526802	8.4477922
F	1.3750421	-2.5222582	7.8470681
F	3.1362024	-1.7520731	9.7988602
F	-0.1298768	0.3933245	12.1364309
F	-0.5537862	-1.9689482	5.4048383
H	-0.4456206	-1.4752817	6.2254832
H	-3.7660465	1.4060331	8.8492886
H	-6.7295605	-1.3664644	7.3815876
H	-6.0943408	0.5179231	8.8870886
H	-2.7253902	-1.4198196	5.7574340
H	0.6256214	2.6930732	4.5066049
H	1.7812545	4.7949331	3.7991063
H	2.1708489	6.6150398	5.4559187
H	1.4136826	6.3435011	7.8138853
H	0.2676946	4.2389410	8.5201447
H	-5.0415431	-2.3420008	5.8282345

Pdt

E = -1769187.36 kcal/mol

C	1.5089255	-0.0406778	-1.4868727
C	2.5714899	-0.2666586	-0.6389239
C	1.9802193	1.8788092	-0.4613434
N	1.1717576	1.3012752	-1.3778699
N	2.8622408	0.9499868	-0.0267560
C	3.9160932	1.2155973	0.9292251
C	4.8911246	2.1613099	0.6001732
C	3.9117384	0.5324253	2.1458195
C	5.8932481	2.4377682	1.5312592
H	4.8779008	2.6540040	-0.3732079
C	4.9327780	0.8130326	3.0576469
H	3.0868897	-0.1566418	2.3628193
C	5.9159943	1.7612014	2.7562488
H	6.6624776	3.1735504	1.2927101
H	4.9458417	0.2962620	4.0185054
H	6.7037785	1.9774667	3.4798758
C	0.0468642	1.9349607	-2.0276705
C	-1.0180657	2.3757382	-1.2400248
C	0.0532727	2.0531064	-3.4192089
C	-2.1069128	2.9703074	-1.8814462
H	-0.9867892	2.1899118	-0.1633602
C	-1.0493779	2.6400295	-4.0422364
H	0.9106319	1.7088487	-3.9997189
C	-2.1243427	3.1013081	-3.2741623
H	-2.9540731	3.3161402	-1.2871691
H	-1.0633867	2.7432254	-5.1280638
H	-2.9836624	3.5603716	-3.7661689
C	3.2865080	-1.5170941	-0.3860683
C	2.5953229	-2.7035212	-0.0839754
C	4.6857793	-1.6051294	-0.4644763
C	3.3336909	-3.8648041	0.1620783
C	5.3088202	-2.8220936	-0.1916776
C	0.8210812	-0.9753572	-2.3812198
C	-0.5417590	-1.2793277	-2.2391437
C	1.5178565	-1.6291764	-3.4080166
C	-1.1222813	-2.1849365	-3.1313915

C	0.8296612	-2.5225061	-4.2309554
C	1.9552764	3.2903695	-0.0736965
C	1.8396481	3.7141624	1.2622389
C	2.0681258	4.2897823	-1.0552594
C	1.8132624	5.0908003	1.5182873
C	2.0270919	5.6286129	-0.6700226
N	-0.4520155	-2.7834677	-4.0929869
N	4.6473545	-3.9168979	0.1150392
N	1.8990826	6.0106190	0.5822124
F	5.4183084	-0.5396716	-0.8297532
F	6.6468212	-2.9009739	-0.2586958
F	1.2616171	-2.7478340	-0.0515999
F	2.6795017	-4.9957632	0.4603110
F	1.6986266	5.5074363	2.7852615
F	1.7764256	2.8542905	2.2724343
F	1.4880420	-3.1438043	-5.2192953
F	2.8248716	-1.3845412	-3.6088361
F	-2.4244001	-2.4744738	-3.0112332
F	-1.2668887	-0.7299267	-1.2628622
F	2.1409996	6.5823325	-1.6049501
F	2.2561758	3.9605344	-2.3442433
F	1.2602697	-0.8071768	1.9985179
H	0.6349380	0.0596338	1.6186791
F	0.0398172	0.9696187	1.1853509