Electronic Supplementary Information

Superacidic Aluminum Azido Species and Reagent-Controlled Self-Assembly of Triazolyl Dimers, Trimers and Tetramers†

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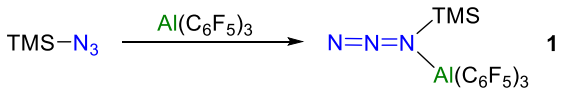
General Considerations

All experiments were carried out under inert gas atmosphere by using Schlenk-type glassware or in an Ar-filled glove box. Toluene, n-Hexane and Deuterated solvents (C_6D_6) were dried with sodium/potassium alloy prior to use and stored with 3Å molecular sieves. All solvents were stored under argon atmosphere. $Al(C_6F_5)_3$[S1], $[HAl(C_6F_5)_2]_2$[S2] and ^{i}Pr-NHC[S3](IPr) were synthesized according to the literature methods. NMR spectra were recorded on a Bruker Advance 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz, ^{19}F: 470 MHz, ^{31}P: 202 MHz) spectrometer at 298 K. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in hertz (Hz), integration. HRMS were recorded on a Thermo Scientific TM Q-Exactive PlusTM mass spectrometer. Single-crystal X-ray diffraction data were collected on a Bruker D8 QUEST diffractometer using Cu (60W, Diamond, μKα = 12.894 mm^{-1}) micro-focus X-ray sources. Using Olex2[S4], the structure was solved with the XT[S5] structure solution program using Intrinsic Phasing and refined with the XL[S6] refinement package using Least Squares minimization.

Experimental Procedures

Synthesis of compound 1



Scheme S1-1: Synthesis of **1**

In the glovebox, a toluene solution (5 mL) of $[Al(C_6F_5)_3]\cdot 0.5$ tol (574 mg, 1 mmol) was added dropwisely into a toluene solution (5 mL) of TMS-N_3 (115 mg, 1 mmol) at room temperature. The reaction mixture was stirred at ambient temperature for 30 min. After removed solvent under vacuum, the resulting solids were washed with n-Hexane (3×2 mL). After evaporation to dryness, **1** was obtained as white solids (578 mg, 90% yield).

Single crystals (colorless) suitable for X-ray analysis were obtained from the toluene solution at -30 °C for 12 hours.

^{1}H NMR (500 MHz, C_6D_6, ppm): δ 0.27 (d, J = 2.4 Hz, 9H, Si(CH_3)$_3$).

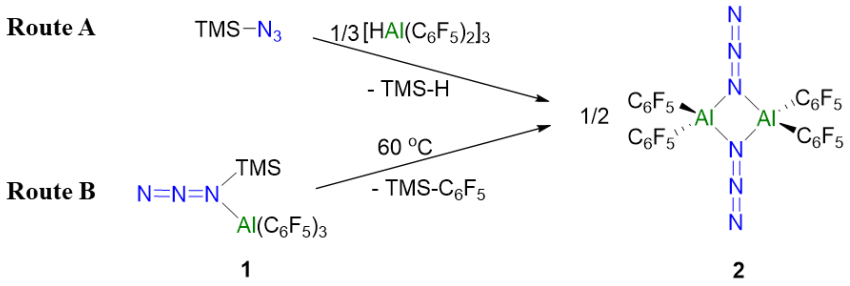
^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 2.38 (s, Si(CH$_3$)$_3$), 111.81 (br, Al-C), 136.47~138.44 (m, m-C_6F_5), 141.64~143.63 (m, p-C_6F_5), 149.51~151.37 (m, o-C_6F_5).

^{19}F{^{1}H} NMR (470 MHz, C_6D_6, ppm): δ -123.0 (br, 4F, o-C$_6F_5$), -150.0 (t, J = 19.9 Hz, 2F, p-C$_6F_5$), -160.1 (br, 4F, m-C$_6F_5$).

HRMS(m/z): $[M+MeCN+H]^+$ calcd. for $C_{23}H_{13}AlF_{15}N_4Si^+$, 685.0480; found: 685.0505.

FT-IR (solid, cm^{-1}): 2170.3 (N≡N stretching), 1643.6, 1510.9, 1442.1, 1358.2 (N=N stretching), 1263.8, 1192.6, 1068.9, 952.5, 835.5.

Synthesis of compound 2



Scheme S1-2: Synthesis of **2**

Route A: In the glovebox, a toluene solution (2 mL) of TMS-N_3 (23mg, 0.2 mmol) was added dropwise into a toluene solution (2 mL) of $[HAl(C_6F_5)_2]_3$ (72.4 mg, 0.07 mmol). After stirring for 30 minutes at room temperature, the resulted solution was dried under vacuum to afford white powders of **2** in 90% yield (72.6 mg). The signal of TMS-H was monitored by NMR in situ.

Route B: In the glovebox, a toluene solution (5 mL) of **1** (128 mg, 0.2 mmol) was heated to 60 ℃ for 12 hours to afford white powders of **2** in 82% yield (66 mg). The signal of TMS-C_6F_5 was monitored by NMR in situ.

Single crystals (colorless) suitable for X-ray analysis were obtained by storing a toluene solution of **2** at -30 ℃ for 12 hours.

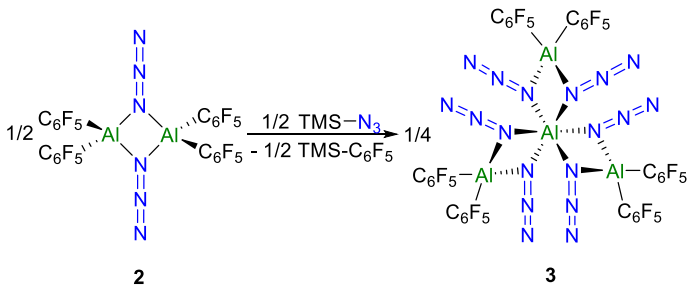
$^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, ppm): δ 105.32 (br, Al-*C*), 134.60~136.31 (m, *m*-C_6F_5), 140.69~142.39 (m, *p*-C_6F_5), 147.08~148.55 (m, *o*-C_6F_5).

$^{19}F\{^1H\}$ NMR (470 MHz, C_6D_6, ppm): δ -124.3 (br, 4F, *o*-C_6F_5), -146.7 (br, 2F, *p*-C_6F_5), -157.7 (br, 4F, *m*-C_6F_5).

HRMS(m/z): $[1/2M+H]^+$ calcd. for $C_{12}HAlF_{10}N_3^+$: 403.9821, found: 403.9835.

FT-IR (solid, cm^{-1}): 2174.0 (N≡N stretching), 1643.6, 1510.2, 1454.6, 1364.8 (N=N stretching), 1261.8, 1071.1, 955.5, 721.8.

Synthesis of compound 3



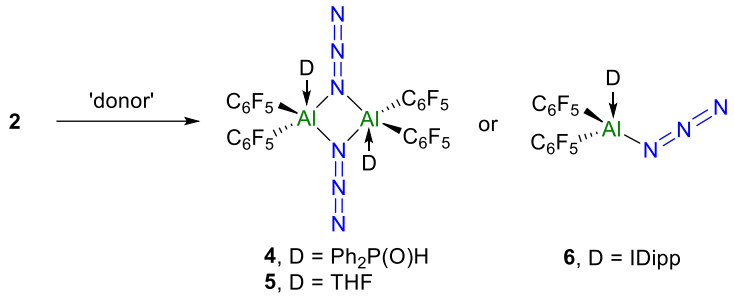
Scheme S1-3: Synthesis of **3**

In the glovebox, a toluene solution (2 mL) of TMS-N_3 (11.5 mg, 0.1 mmol) was added dropwise into a toluene solution (5 mL) of **2** (80.5 mg, 0.1 mmol) and then the reaction mixture was heated at 80 ℃ for 3 days. The precipitate was collected and washed with n-Hexane (3×1.0 mL). After drying under vacuum, white solids of **3** (49.7 mg, 73% yield) were obtained.

Single crystals (colorless) suitable for X-ray analysis were obtained by storing a toluene

solution of **3** at -30 °C for 2 hours.
^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 100.54 (td, *J* = 23.0, 3.6 Hz, Al-*C*), 136.57~138.57 (m, *m*-C_6F_5), 140.64~142.65 (m, *p*-C_6F_5), 145.11~147.08 (m, *o*-C_6F_5).
^{19}F{^{1}H} NMR (470 MHz, C_6D_6, ppm): δ -139.1 (br, 4F, *o*-C_6F_5), -154.1 (t, *J* = 20.8 Hz, 2F, *p*-C_6F_5), -162.3 (br, 4F, *m*-C_6F_5).
HRMS(m/z): $[M-(C_6F_5)_2AlN_3+H]^+$ calcd. for $C_{24}HAl_3F_{20}N_{15}^+$: 959.9660, found: 959.9671.
FT-IR (solid, cm^{-1}): 2168.9 (N≡N stretching), 721.8, 1513.7, 1449.9, 1360.3 (N=N stretching), 1251.8, 1071.4, 952.6, 845.9.

Synthesis of compound 4, 5 and 6



Scheme S1-4: Synthesis of **4, 5** and **6**

In the glovebox, a toluene solution (2 mL) of **D** (for **4**, $Ph_2P(O)H$, 40.4 mg, 0.2 mmol; for **5**, THF, 14.4 mg, 0.2 mmol; for **6**, IDipp, 77.3 mg, 0.2 mmol) was added dropwise into a toluene solution (2 mL) of **2** (80.5 mg, 0.1 mmol). After stirring for 1 hour at room temperature, the resulting solutions were dried under vacuum to afford the corresponding adducts **4**, **5** or **6** as white powders in good yield (**4**, 76%, 91.9 mg; **5**, 83%, 78.8 mg; **6**, 80%, 126.6 mg).
Single crystals (colorless) suitable for X-ray analysis were obtained by storing a toluene solution of **4, 5** and **6** at -30 °C for 12 hours.

4

^{1}H NMR (500 MHz, C_6D_6, ppm): δ 6.83(br, 4H, *o*-C6H_5), 6.95 (t, 2H, *p*-C_6H_5) , 7.13 (d, *J* = 537.8 Hz, 1H, P-*H*), 7.13 (br, 4H, *m*-C_6H_5).
^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): 122.63 (d, *J* = 109.8 Hz, P-*C*), 129.65 (d, *J* = 14.3 Hz, *o*-C_6H_5), 131.58 (d, *J* = 13.6 Hz, *m*-C_6H_5), 135.15 (d, *J* = 3.2 Hz, *p*-C_6H_5), 135.96~138.30 (m, *m*-C_6F_5), 140.74~142.95 (m, *p*-C_6F_5), 149.27~151.38 (m, *o*-C_6F_5).
^{19}F{^{1}H} NMR (470 MHz, C_6D_6, ppm): δ -123.3 (br, 4F, *o*-C_6F_5), 153.3 (t, *J* = 19.8 Hz, 2F, *p*-C_6F_5), -161.5 (br, 4F, *m*-C_6F_5).
^{31}P{^{1}H} NMR (202 MHz, C_6D_6, ppm): δ 34.5 (s, *P*-H).
^{31}P NMR (202 MHz, C_6D_6, ppm): δ 34.5 (d, *J* = 539.7 Hz, *P*-H).
HRMS(m/z):$[1/2M+2CH_3OH+Na]^+$ calcd. for $C_{26}H_{19}AlF_{10}N_3O_3PNa^+$:692.0712, found: 692.0720.
FT-IR (solid, cm^{-1}): 2134.8 (N≡N stretching), 1640.7, 1508.2, 1438.4, 1356.5 (N=N stretching), 1286.0, 1144.8, 1054.9, 950.2.

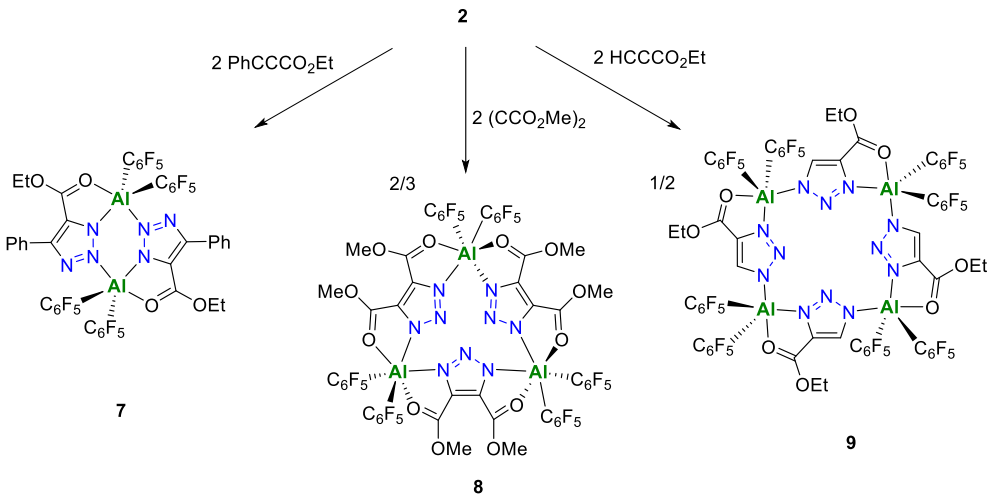
5

^{1}H NMR (500 MHz, Tol-d_6, ppm): δ 0.98 (s, 4H, CH_2(THF)), 3.33(s, 4H, CH_2(THF)).
^{13}C{^{1}H} NMR (125 MHz, Tol-d_6, ppm): 25.86 (s, *C*H$_2$(THF)), 71.56 (s, *C*H$_2$(THF)); Al(C_6F_5)$_2$ not listed.
^{19}F{^{1}H} NMR (470 MHz, Tol-d_6, ppm): δ -123.5 (br, 4F, *o*-C_6F_5), 151.2 (br, 2F, *p*-C_6F_5), -160.4 (br, 4F, *m*-C_6F_5).
HRMS(m/z): [1/2M+2CH$_3$CN+Na]$^+$ calcd. for $C_{20}H_{14}AlF_{10}N_5ONa^+$: 580.0746, found: 580.0750.
FT-IR (solid, cm^{-1}): 2149.6 (N≡N stretching), 1640.9, 1510.7, 1446.0, 1358.7 (N=N stretching), 1270.7, 1068.4, 953.6, 842.4.

6

^{1}H NMR (500 MHz, C_6D_6, ppm): 0.80 (d, *J* = 6.1 Hz, 12H, CH(CH_3)$_2$), 1.17 (d, *J* = 6.7 Hz, 12H, CH(CH_3)$_2$), 2.68 (sept, *J* = 6.7 Hz, 4H, C*H*(CH$_3$)$_2$), 6.39 (s, 2H, N-C*H*-), 6.87 (d, *J* = 7.8 Hz, 4H, Ar-*H*), δ 7.08 (t, *J* = 7.8 Hz, 2H, Ar-*H*).
^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm) δ 21.71, 26.48 (s, CH(*C*H$_3$)$_2$), 28.99 (s, *C*H(CH$_3$)$_2$), 124.24 (s, Ar*C*), 126.14 (s, Ar*C*), 128.35 (s, Ar*C*), 131.59 (s, Ar*C*), 133.23 (s, -N-*C*H-), 137.79~138.87 (m, *m*-C_6F_5), 140.60~142.40 (m, *p*-C_6F_5), 145.68 (s, -N*C*N), 148.09~149.08 (m, *o*-C_6F_5).
^{19}F{^{1}H} NMR (470 MHz, C_6D_6, ppm): δ -120.4 (br, 4F, *o*-C_6F_5), -154.0 (t, *J* = 19.9 Hz, 2F, *p*-C_6F_5), -161.8 (br, 4F, *m*-C_6F_5).
HRMS(m/z): [M+Na]$^+$ calcd. for $C_{39}H_{36}AlF_{10}N_5Na^+$: 814.2519, found: 814.2531.
FT-IR (solid, cm^{-1}): 2151.8 (N≡N stretching), 1637.5, 1509.2, 1441.9, 1387.7 (N=N stretching), 1387.7, 1118.4, 1059.0, 957.1.

Synthesis of compound 7, 8 and 9



Scheme S1-5: Synthesis of **7**, **8** and **9**

A mixture of **2** (40.3 mg, 0.05 mmol), R^{2}C≡CR^1 (for **7**, R^1=Ph, R^2=CO$_2$Et 17.4mg, 0.1mmol; for **8**, R^1=R^2=CO$_2$Et 14.2mg, 0.1mmol; for **9**, R^1=H, R^2=CO$_2$Et 9.8mg, 0.1mmol) and benzene

(2 mL) was stirred under ambient temperature for 1 hour. the resulting solutions were dried under vacuum to afford the Complexes as white powders in good yield (**7**, 85%, 49 mg; **8**, 87%, 47.4 mg; **9**, 76%, 38 mg).

Single crystals (colorless) suitable for X-ray analysis were obtained by storing a solution of Click products (**7, 8** and **9**) in mixed solvent of benzene and n-Hexane at -30 °C for 2 hours.

7

^{1}H NMR (500 MHz, C_6D_6, ppm): δ 0.81 (t, *J* = 7.1 Hz, 3H, C*H*$_3$), 3.94 (q, *J* = 6.7 Hz, 2H, -C*H*$_2$-CH$_3$), 6.81 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 6.89 (t, *J* = 7.6 Hz, 1H, Ar-*H*),7.22 (d, *J* = 7.5 Hz, 2H, Ar-*H*).

^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 13.63 (s, *C*H$_3$), 64.40 (s, -*C*H$_2$-CH$_3$), 80.56 (s, *C*=*C*), 91.06 (s, *C*=*C*), 115.80 (br, Al-*C*), 118.87 (s, Ar-*C*), 128.81, (s, Ar-*C*), 131.44 (s, Ar-*C*), 133.28 (s, Ar-*C*), 136.29~138.33 (m, *m*-*C*$_6$F$_5$), 140.57~142.58 (m, *p*-*C*$_6$F$_5$), 149.11~151.14 (m, *o*-*C*$_6$F$_5$), 156.49 (s, *C*=O).

^{19}F{^{1}H} NMR (470 MHz, C_6D_6, ppm): δ -123.1 (br, 4F, *o*-C$_6$*F*$_5$) -153.6 (t, *J* = 20.1 Hz, 2F, *p*-C$_6$*F*$_5$), -161.5 (br, 4F, *m*-C$_6$*F*$_5$).

HRMS(m/z): [1/2M+H]$^+$calcd. for $C_{23}H_{11}AlF_{10}N_3O_2^+$: 578.0502, found: 578.0516.

FT-IR (solid, cm^{-1}): 1704.8, 1532.9, 1444.2, 1369.1, 1287.4, 1192.1, 1018.5, 948.6.

8

^{1}H NMR (500 MHz, C_6D_6, ppm): δ 3.02 (s, 18H, C*H*$_3$).

^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 52.59 (*C*H$_3$), 75.05 (*C*=*C*), 152.09 (MeO$_2$*C*); Al(*C*$_6$F$_5$)$_2$ not listed.

^{19}F{^{1}H} NMR (470 MHz, C_6D_6, ppm): δ -139.1 (br, 4F, *o*-C$_6$*F*$_5$), -154.0 (t, *J* = 20.1 Hz, 2F, *p*-C$_6$*F*$_5$), -162.3 (br, 4F, *m*-C$_6$*F*$_5$).

HRMS(m/z): [1/3M+CH$_3$CN+Na]$^+$ calcd. for $C_{20}H_9AlF_{10}N_4O_4Na^+$: 609.0172, found: 609.0181.

FT-IR (solid, cm^{-1}): 1614.9, 1509.9, 1434.2, 1380.2, 1263.2, 1133.1, 1066.3, 953.5.

9

^{1}H NMR (500 MHz, C_6D_6, ppm): δ 0.89 (t, *J* = 7.1 Hz, 3H, C*H*$_3$), 3.78, 4.11 (br, 2H, -C*H*$_2$-CH$_3$). 7.86 (s, 1H, *H*C≡CCO$_2$Et).

^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 13.34 (s, *C*H$_3$), 68.18 (s, -*C*H$_2$-CH$_3$), 112.96 (br, Al-*C*), 130.48 (s, HC=*C*CO$_2$Et), 136.23 (s, HC=*C*CO$_2$Et) 136.24~138.39 (m, *m*-*C*$_6$F$_5$), 140.66~143.13 (m, *p*-*C*$_6$F$_5$), 148.74~151.10 (m, *o*-*C*$_6$F$_5$), 167.86 (s, *C*=O).

^{19}F{^{1}H} NMR (470 MHz, C_6D_6, ppm): δ -123.2, 125.34 (br, 4F, *o*-C$_6$*F*$_5$), -151.73, 156.20 (t, *J* = 19.7 Hz, 2F, *p*-C$_6$*F*$_5$), -160.11, 162.92 (br, 4F, *m*-C$_6$*F*$_5$).

HRMS(m/z): [1/4M+Na]$^+$ calcd. for $C_{17}H_6AlF_{10}N_3O_2Na^+$: 524.0008, found: 524.0021.

FT-IR (solid, cm^{-1}): 1712.8, 1531.1, 1444.8, 1374.1, 1336.4, 1179.2, 1069.1, 953.6.

Gutmann–Beckett methods

Et$_3$PO (13.4 mg, 0.1mmol, 2.0 equiv) was added into a C_6D_6 (0.6 mL) solution of **2** (40 mg, 0.05mmol, 1.0 equiv). The resulting mixtures were transferred to a NMR tube and ^{31}P NMR

spectrum was collected. The relationship AN=$\{(\delta P_{sample} - \delta P_{ref\ (in\ hex)}(Et_3PO)\}$ ×2.215 was used to calculate AN values according to the literature reported [S7].

$^{31}P\{^1H\}$ NMR resonance of Et_3PO: $\delta P_{ref\ (in\ hex)}$ (Et_3PO)= 41

Induced $^{31}P\{^1H\}$ NMR signal shift of $\delta P(Et_3PO)$ - **2** = 78.24, $\Delta\delta$ = 37.24. AN = 82.4

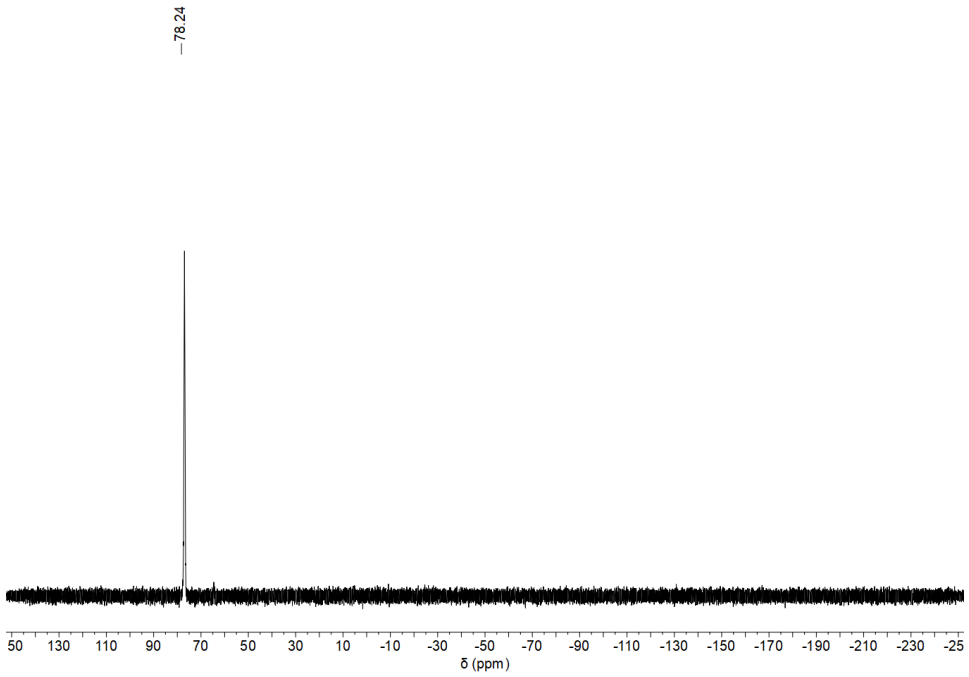


Figure S1-1. $^{31}P\{^1H\}$ NMR spectrum of (Et_3PO)-**2** adduct in C_6D_6

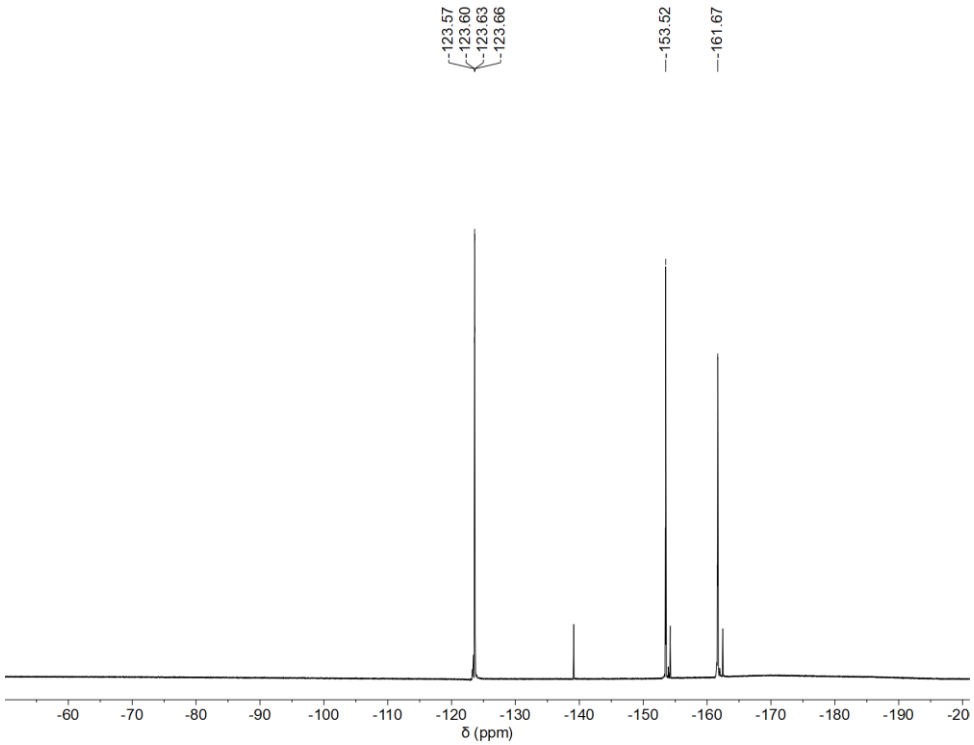


Figure S1-2. $^{19}F\{^1H\}$ NMR spectrum of (Et_3PO)-**2** adduct in C_6D_6

Spectroscopic Data

Spectra of 1

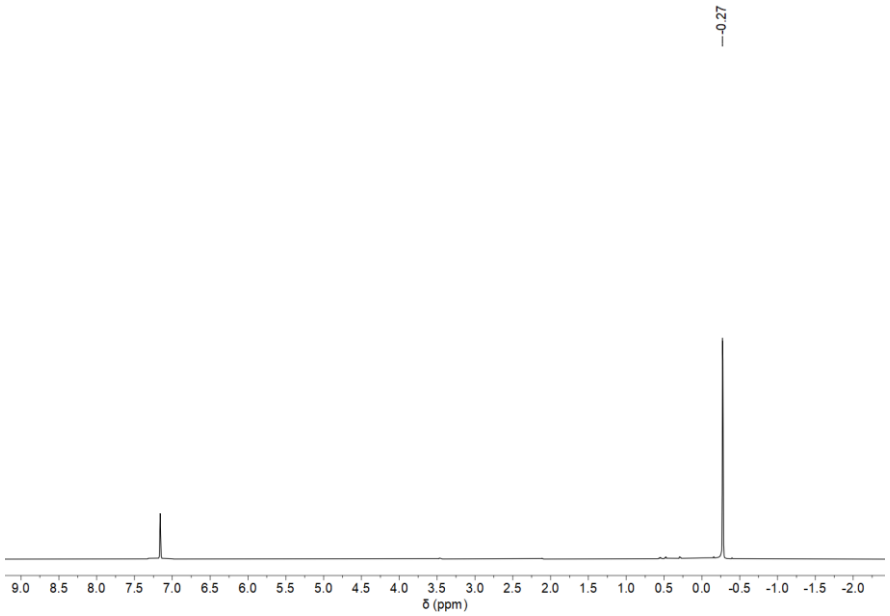


Figure S2-1. ^{1}H NMR spectrum of **1** in C_6D_6

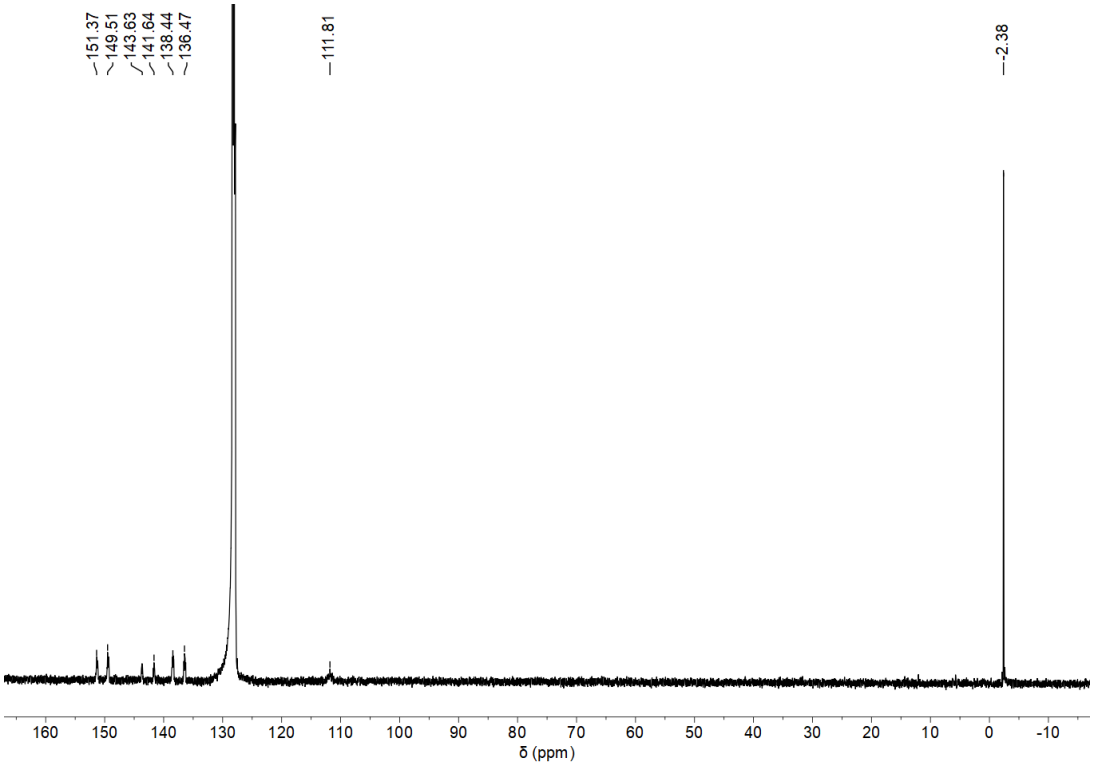


Figure S2-2. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in C_6D_6

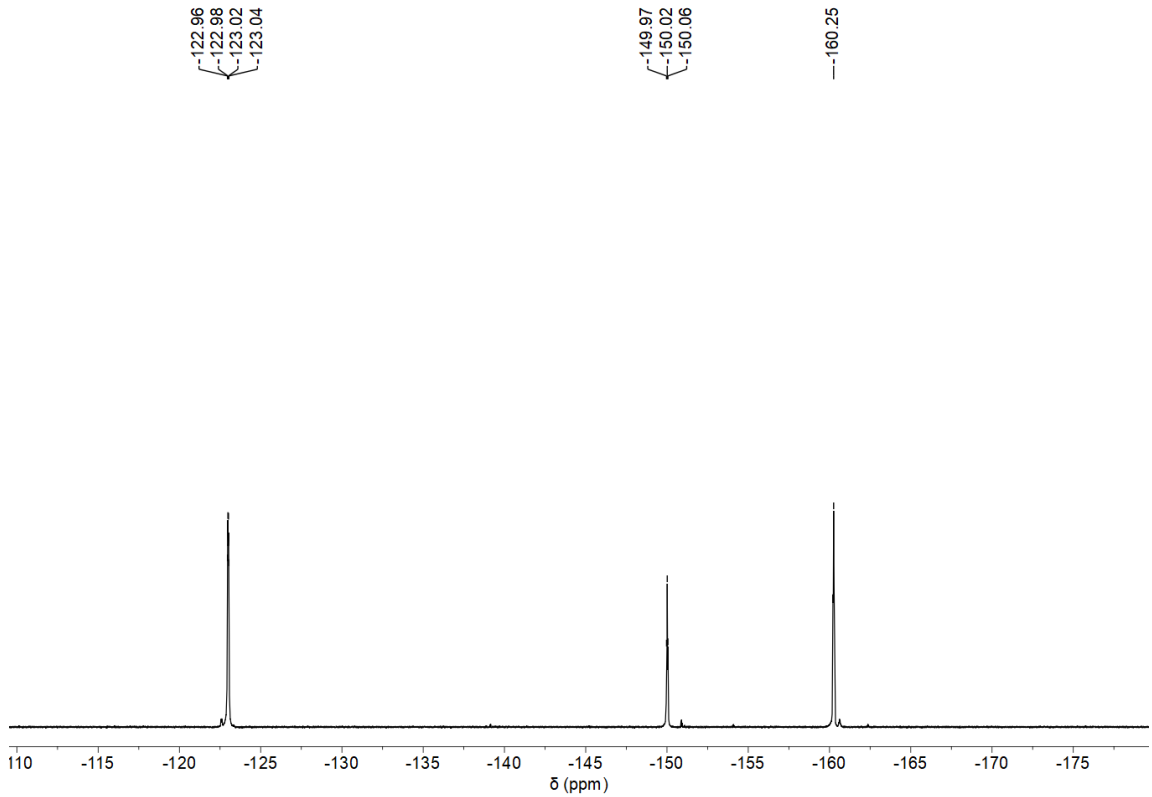


Figure S2-3. $^{19}F\{^{1}H\}$ NMR spectrum of **1** in C_6D_6

Spectra of 2

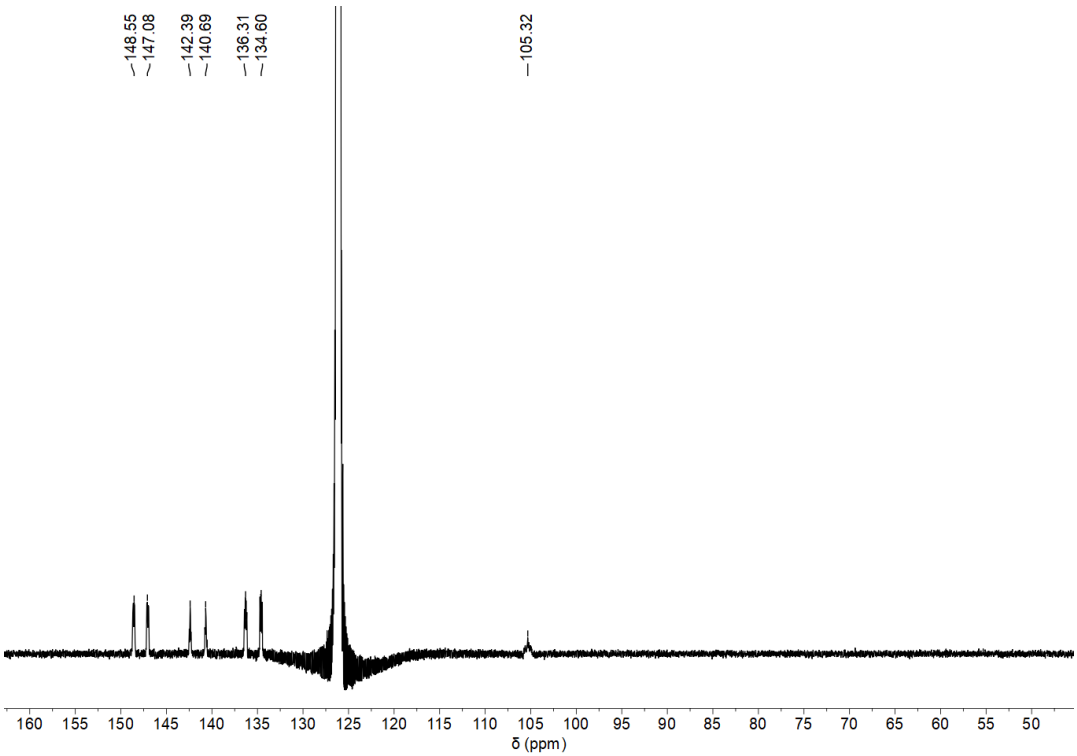


Figure S2-4. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in C_6D_6

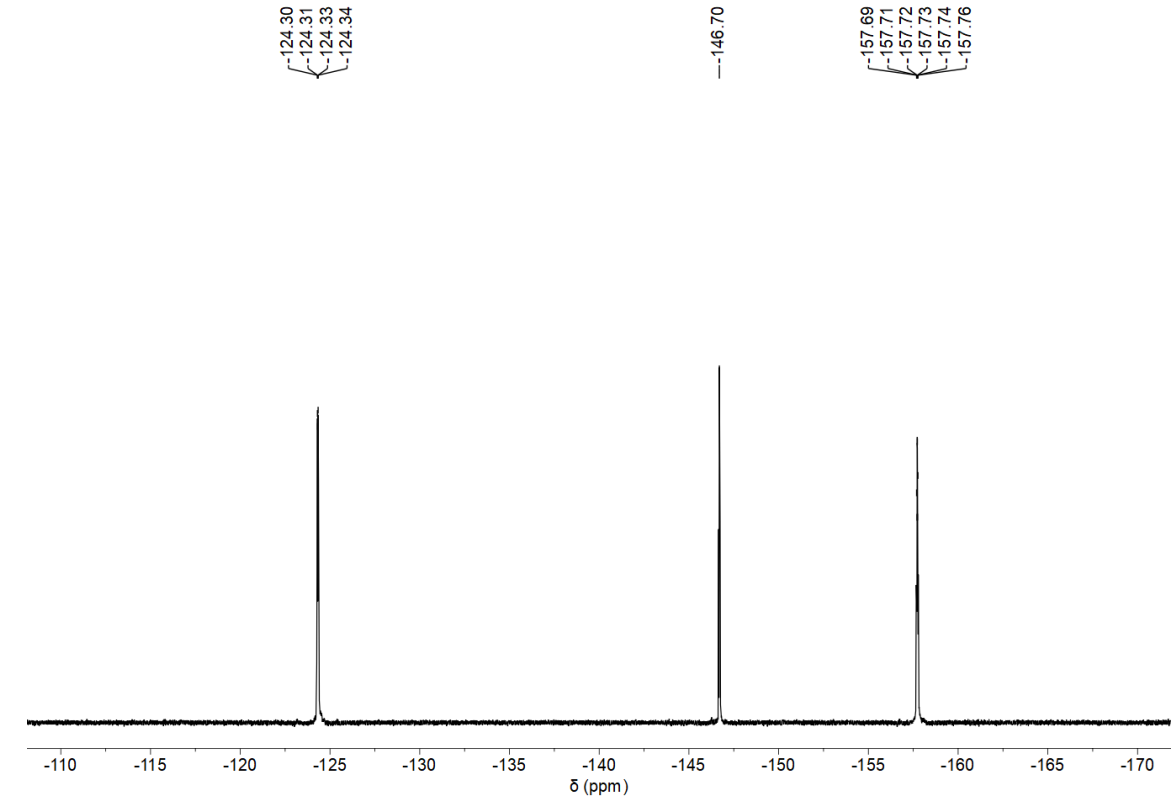


Figure S2-5. $^{19}F\{^{1}H\}$ NMR spectrum of **2** in C_6D_6

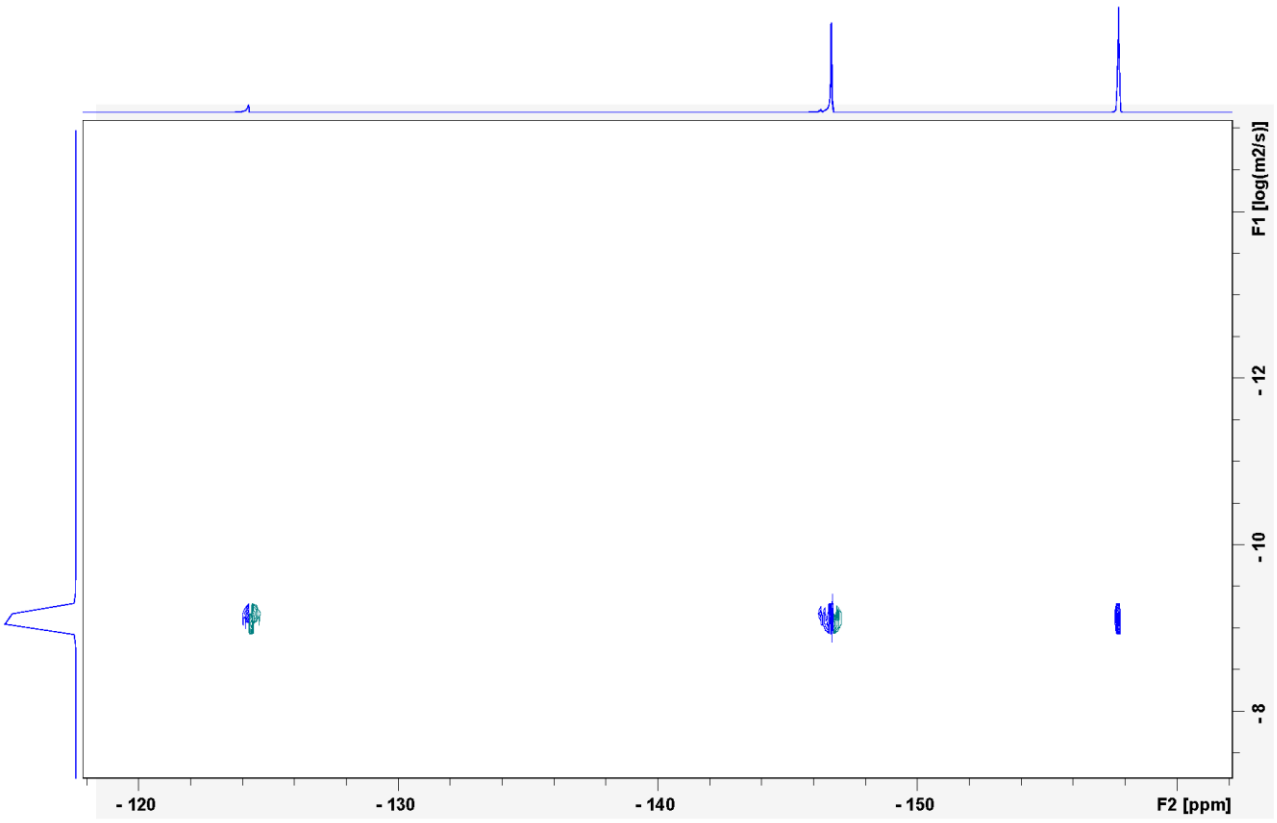


Figure S2-6. ^{19}F-^{19}F DOSY NMR spectrum of **2** in C_6D_6

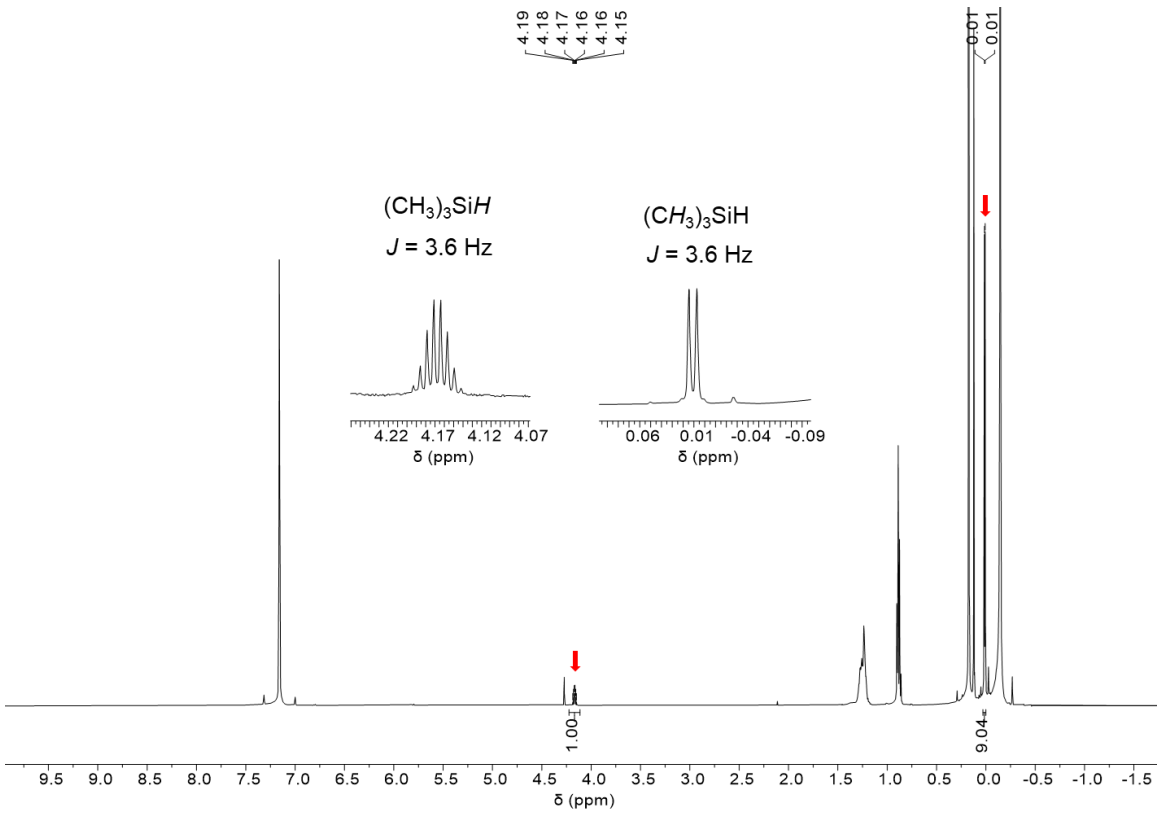


Figure S2-7. In-situ ^{1}H NMR spectrum of **route A** in C_6D_6

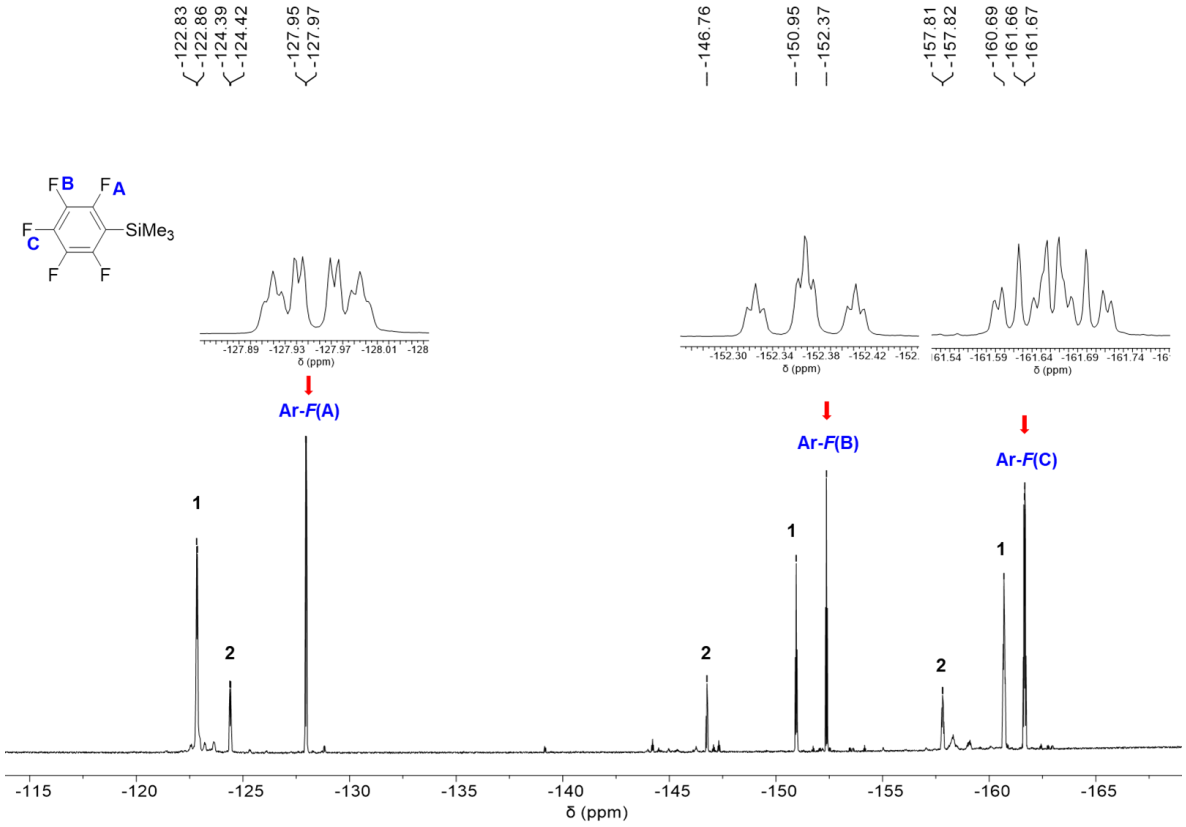


Figure S2-8. In-situ $^{19}F\{^{1}H\}$ NMR spectrum of **route B** in C_6D_6

Spectra of 3

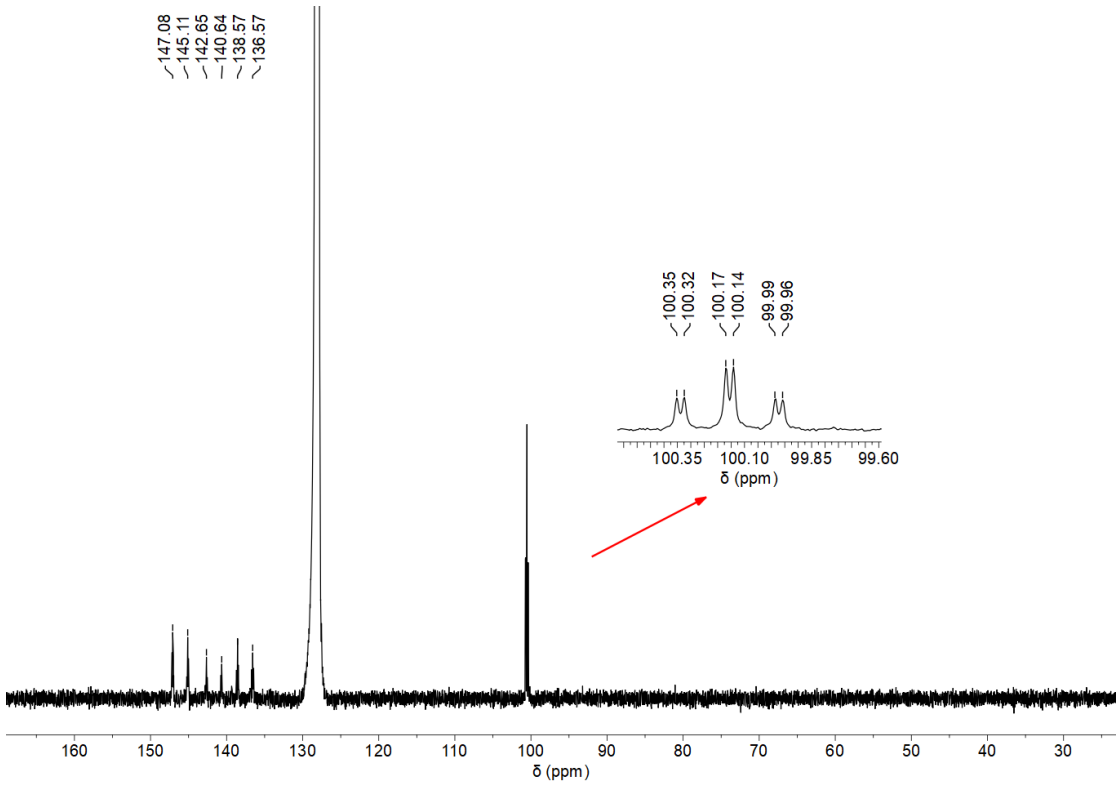


Figure S2-9. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6

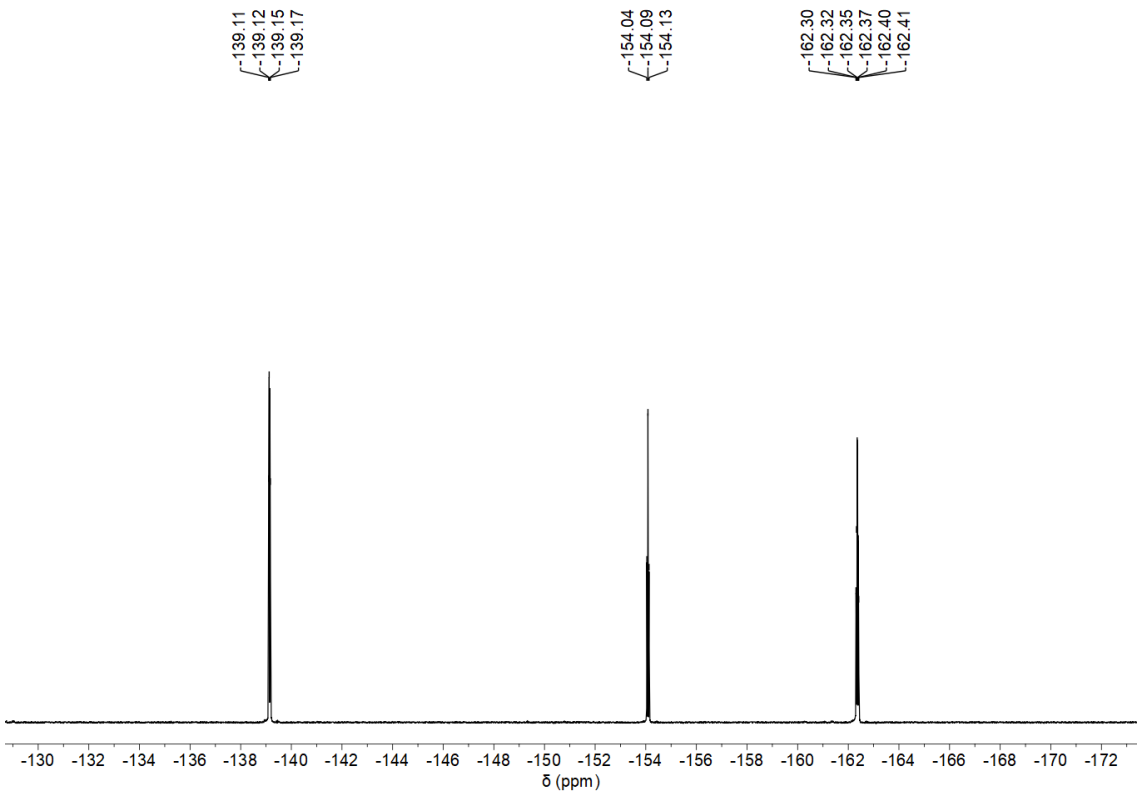


Figure S2-10. $^{19}F\{^{1}H\}$ NMR spectrum of **3** in C_6D_6

Spectra of 4

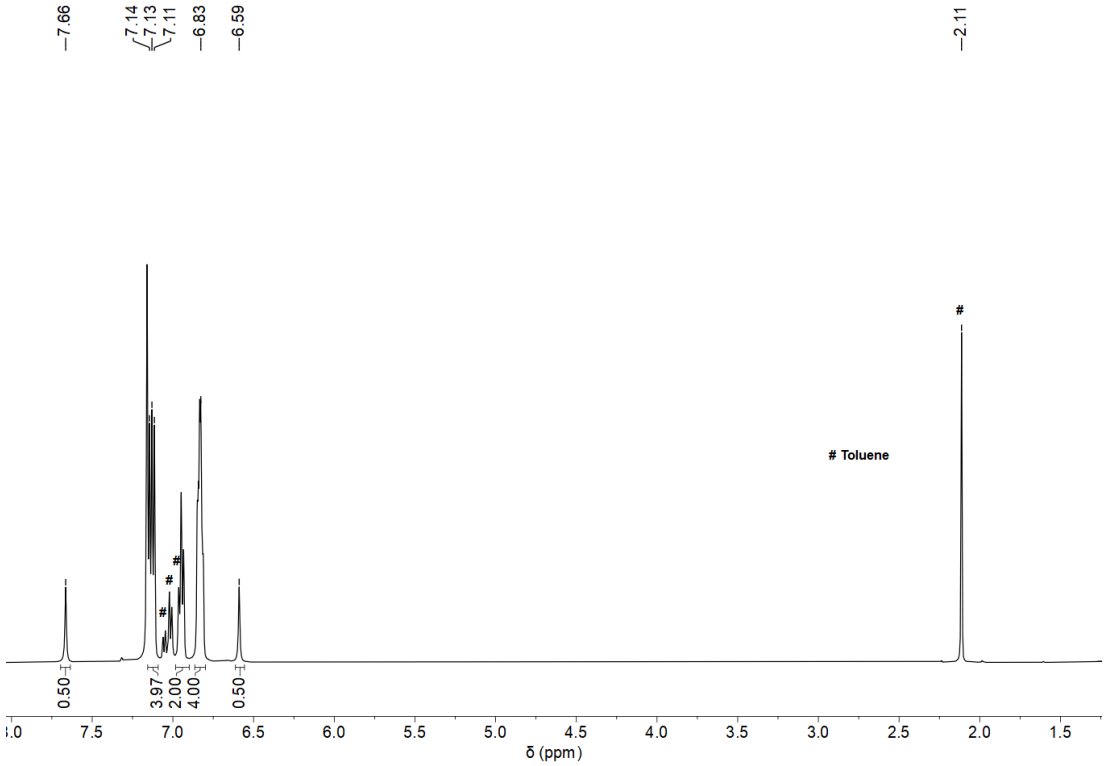


Figure S2-11 ^{1}H NMR spectrum of **4** in C_6D_6 (# = Toluene)

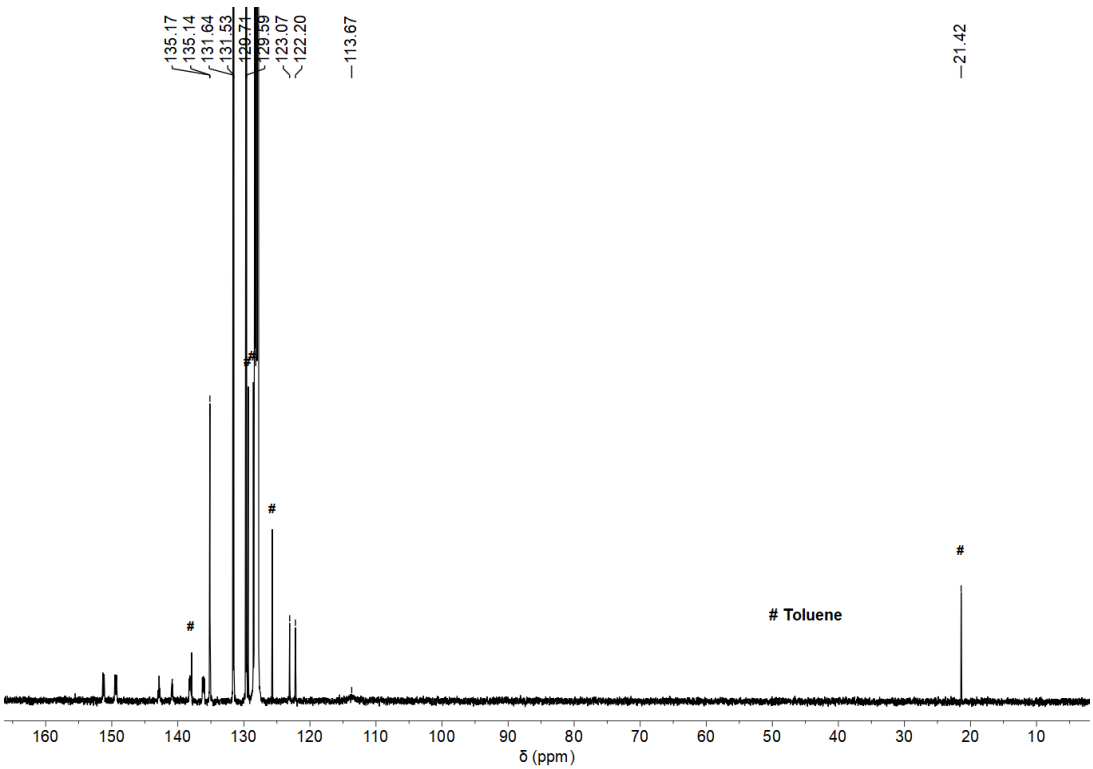


Figure S2-12 ^{13}C{^{1}H} NMR spectrum of **4** in C_6D_6 (# = Toluene)

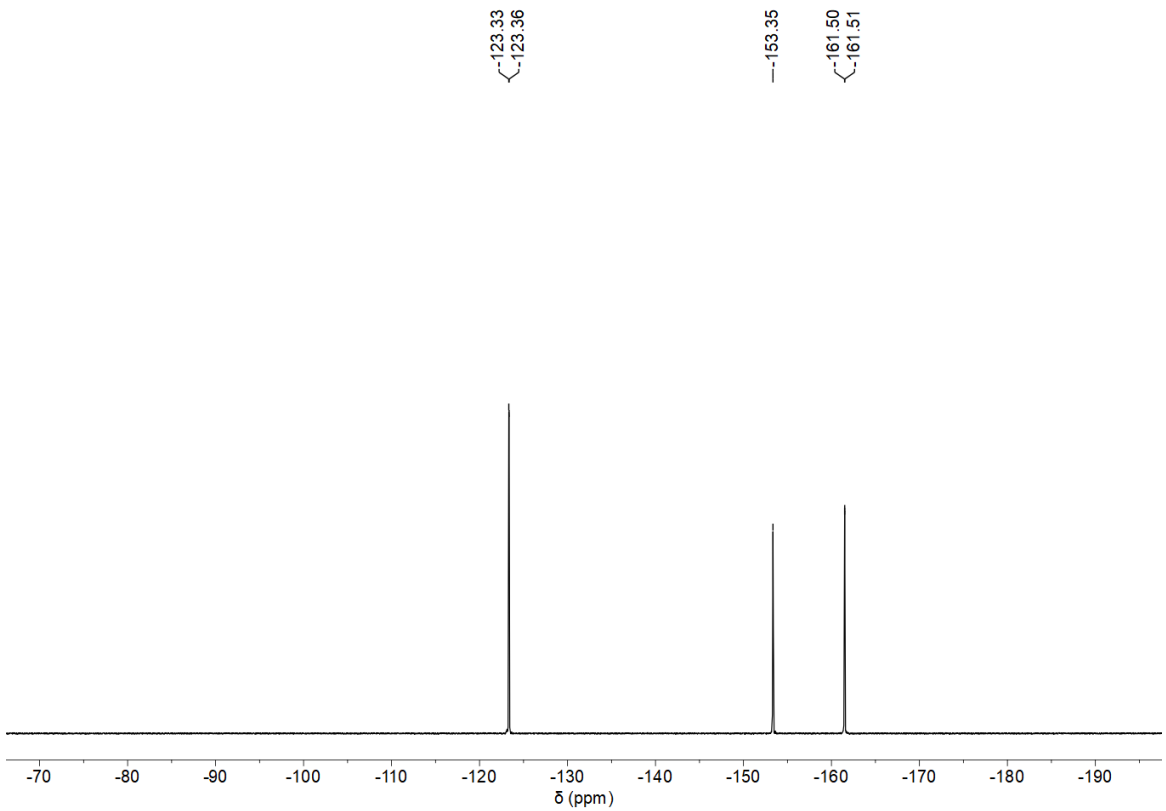


Figure S2-13 $^{19}F\{^{1}H\}$ NMR spectrum of **4** in C_6D_6

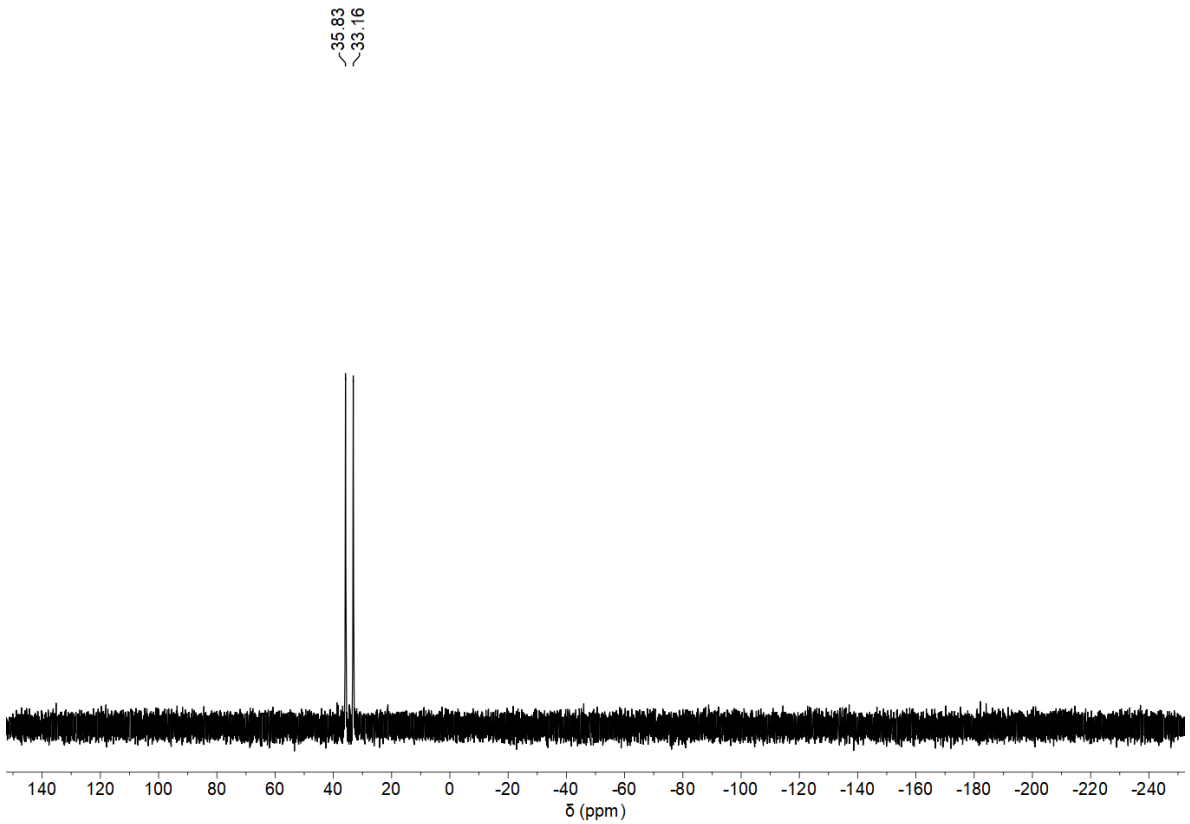


Figure S2-14 ^{31}P NMR spectrum of **4** in C_6D_6

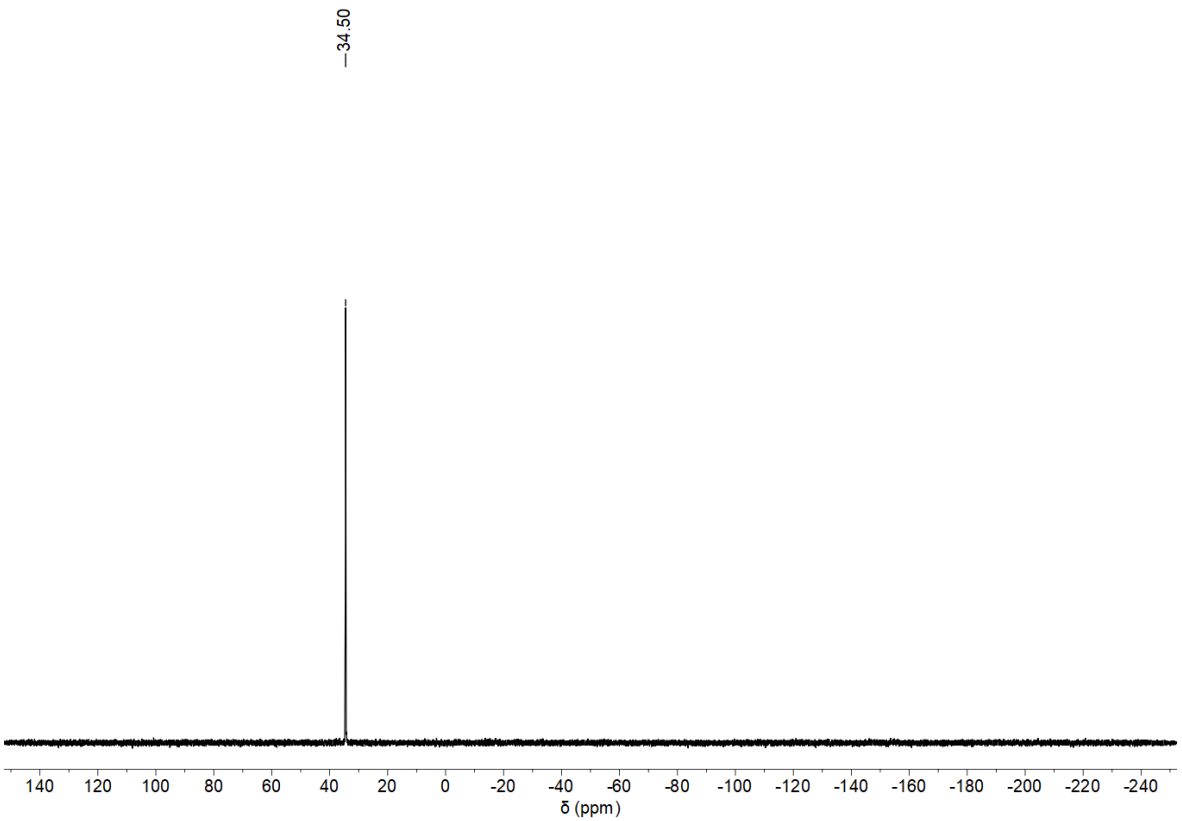


Figure S2-15 $^{31}P\{^{1}H\}$ NMR spectrum of **4** in C_6D_6

Spectra of 5

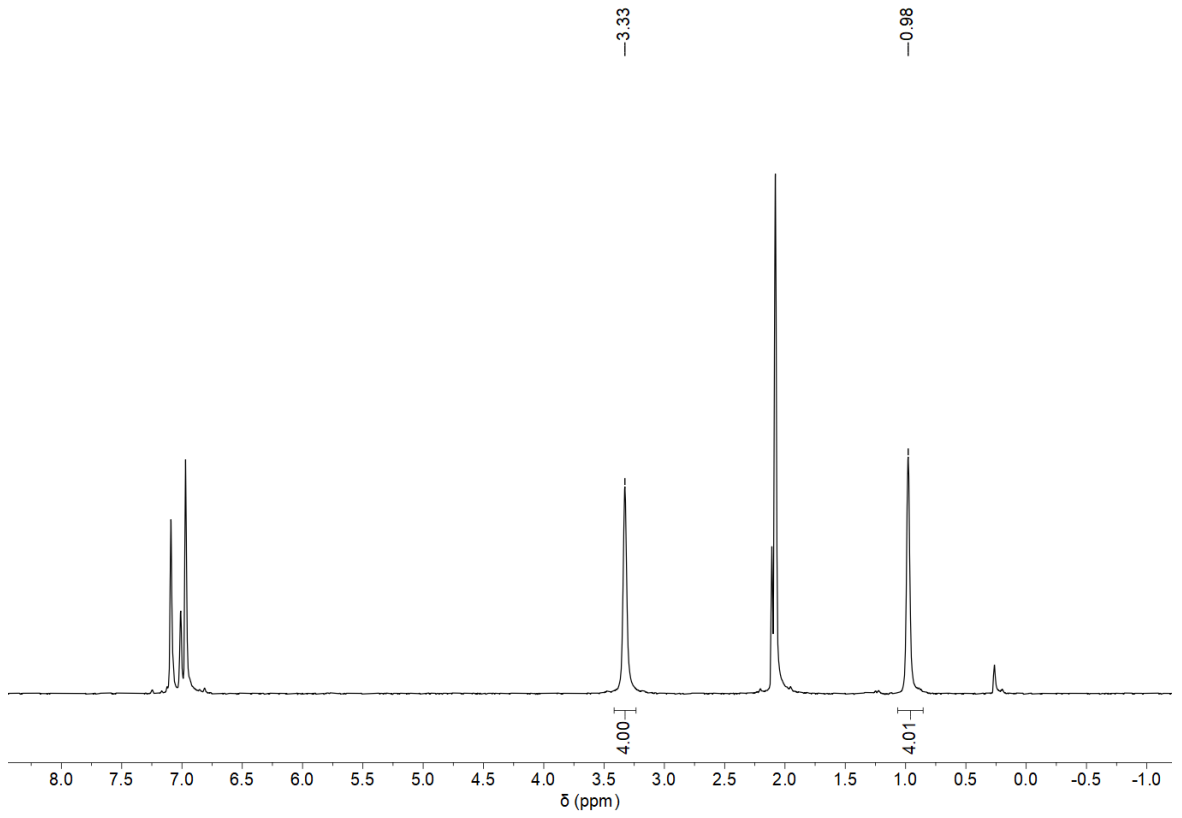


Figure S2-16 ^{1}H NMR spectrum of **5** in Toluene-d_8

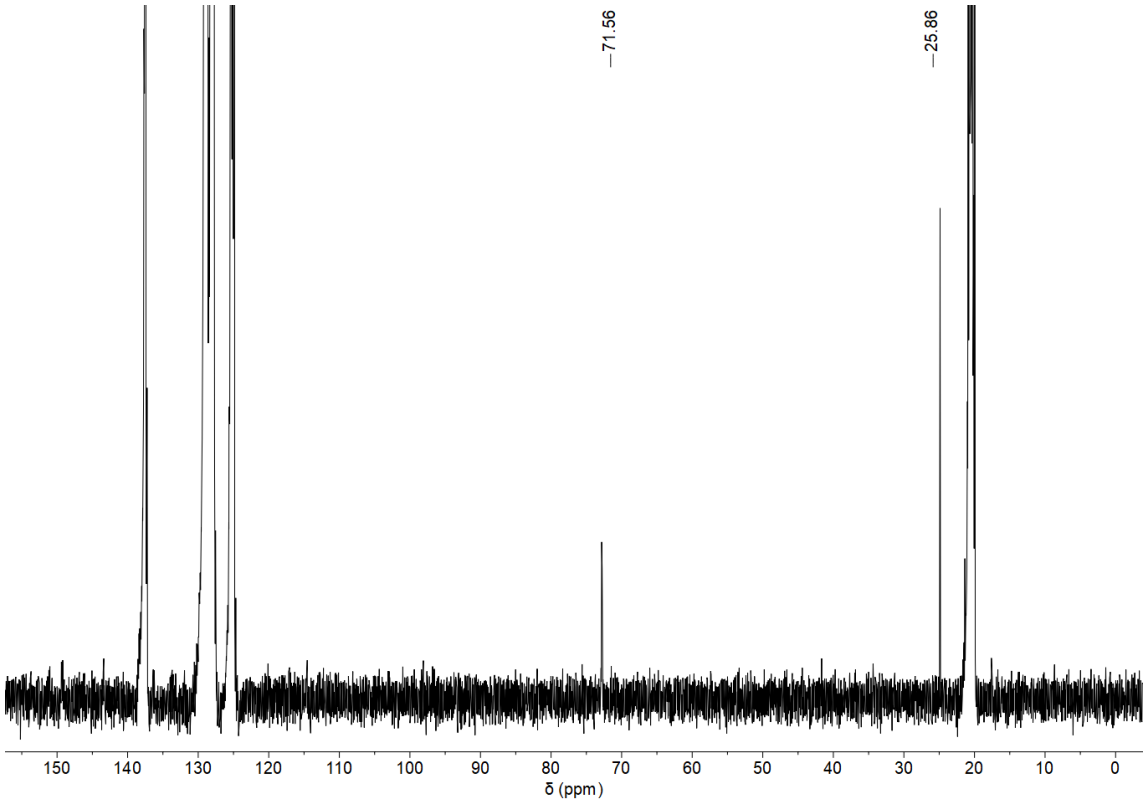


Figure S2-17 $^{13}C\{^{1}H\}$ NMR spectrum of **5** in Toluene-d_8

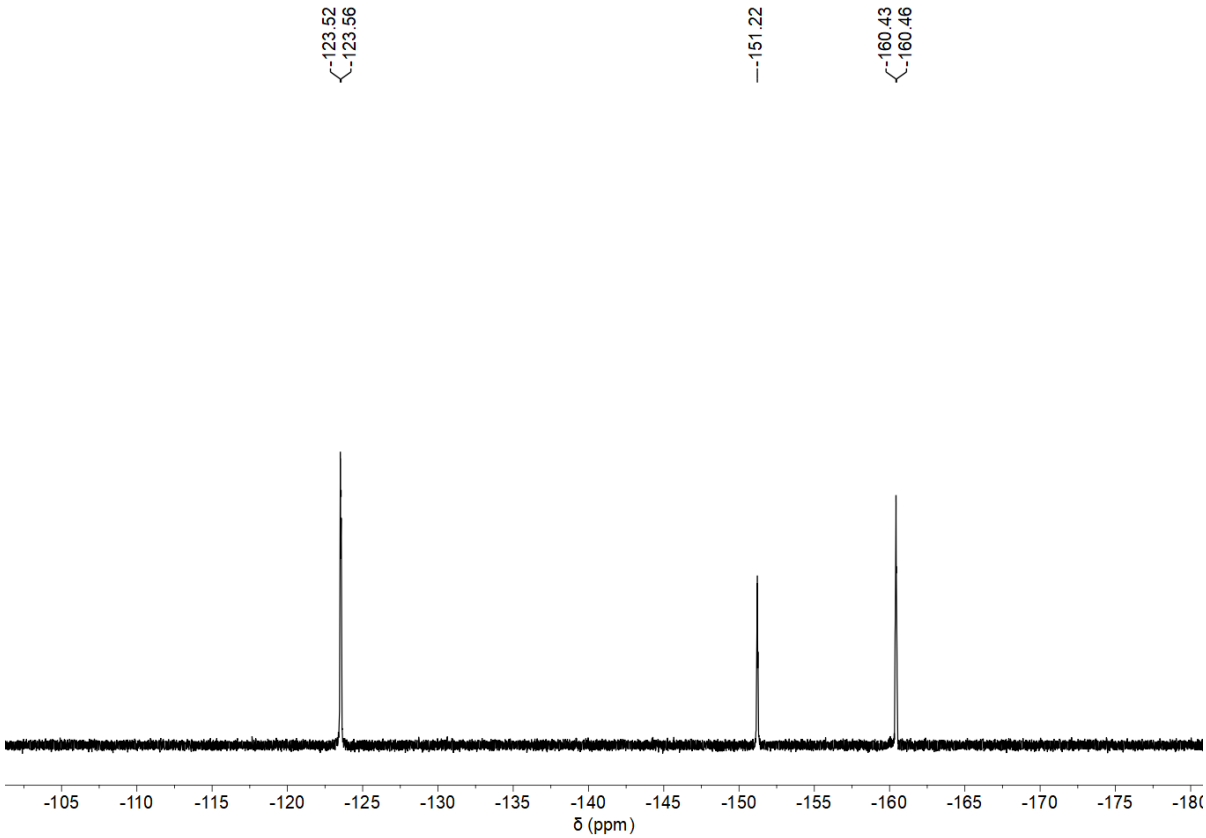


Figure S2-18 $^{19}F\{^{1}H\}$ NMR spectrum of **5** in Toluene-d_8

Spectra of 6

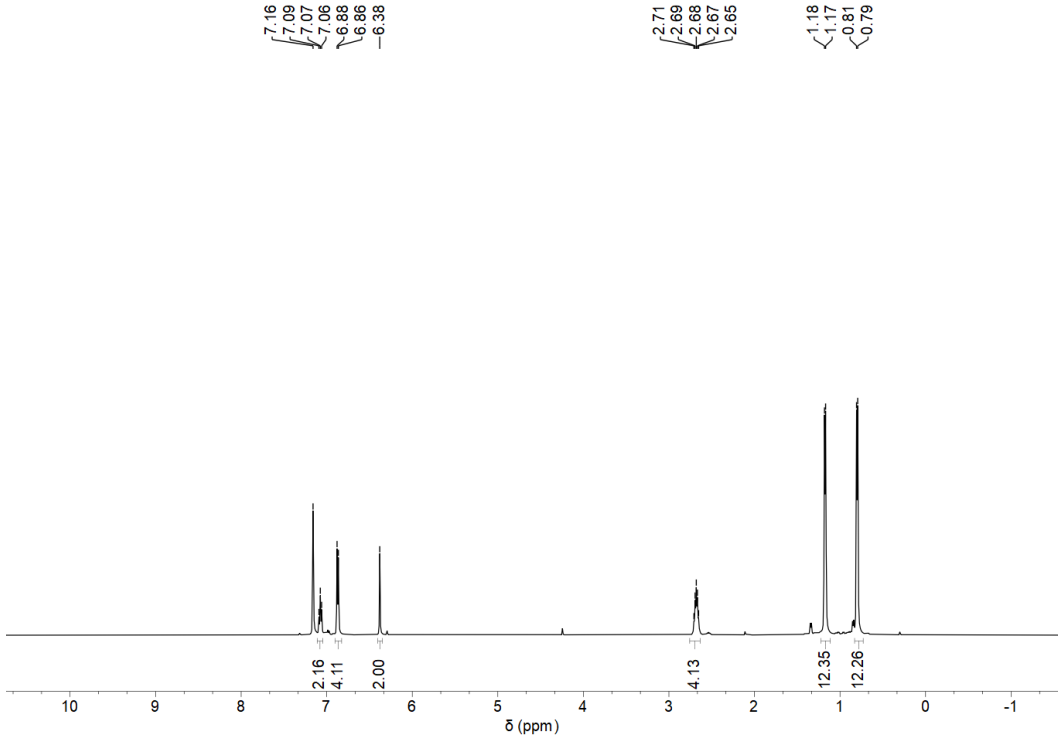


Figure S2-19 ^{1}H NMR spectrum of **6** in C_6D_6

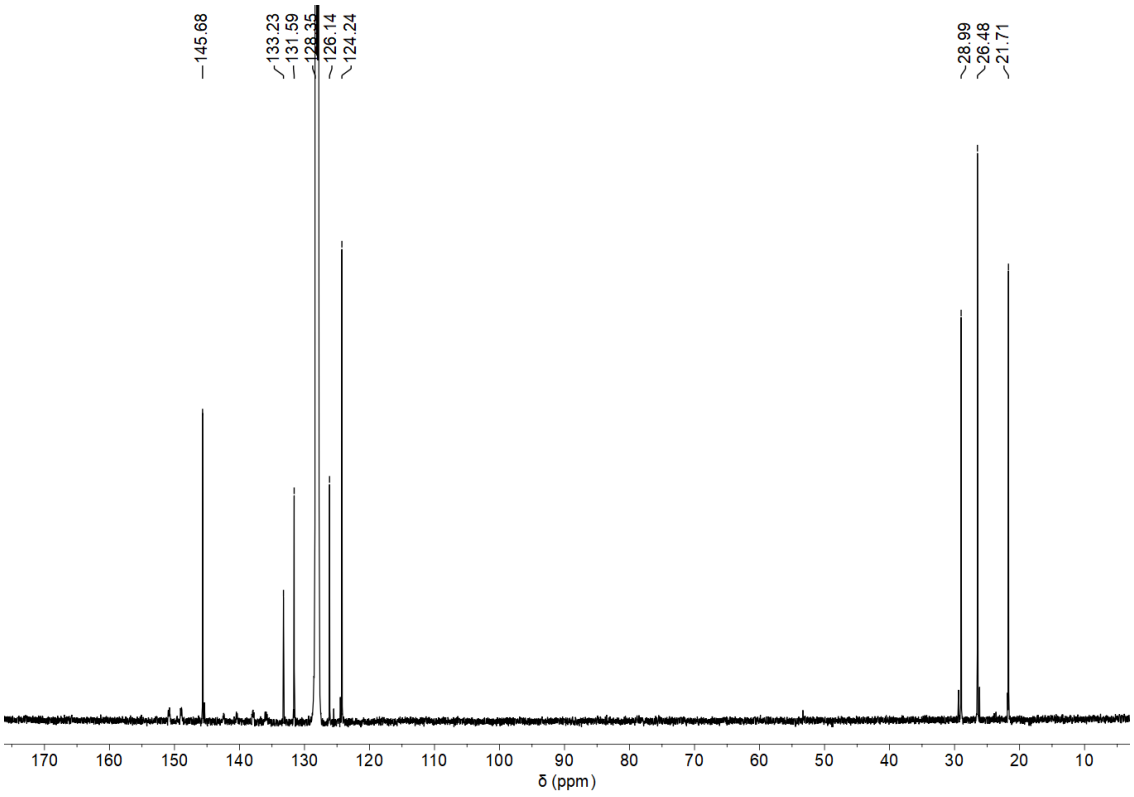


Figure S2-20 $^{13}C\{^{1}H\}$ NMR spectrum of **6** in C_6D_6

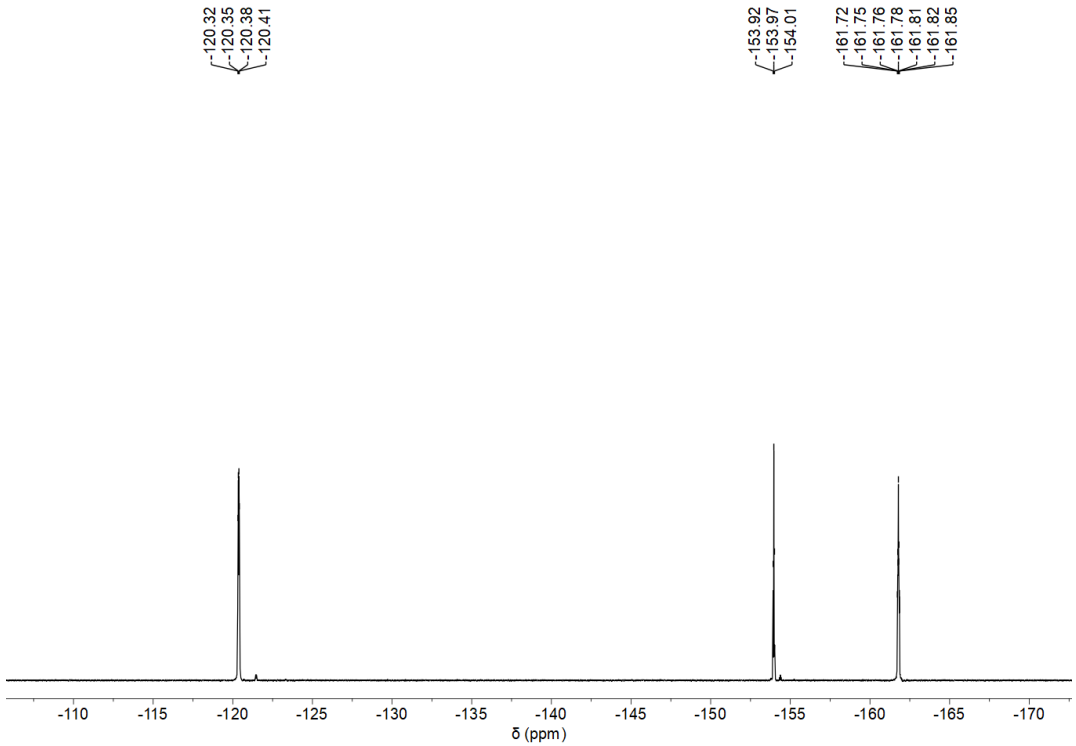


Figure S2-21 $^{19}F\{^{1}H\}$ NMR spectrum of **6** in C_6D_6

Spectra of 7

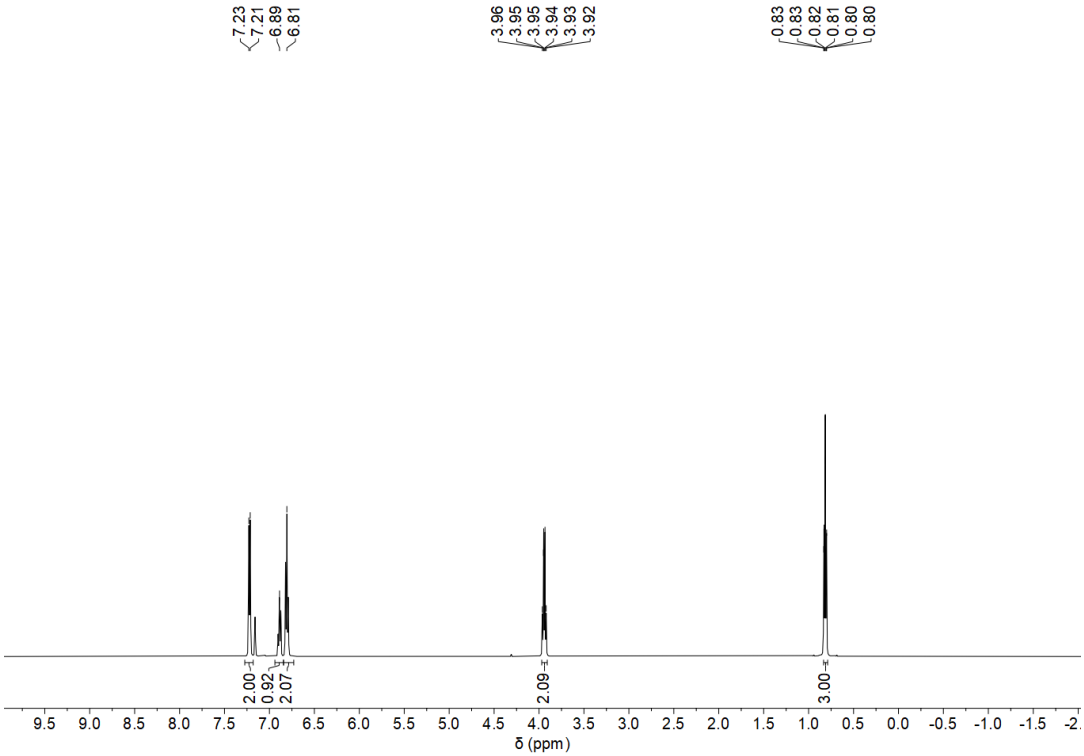


Figure S2-22 ^{1}H NMR spectrum of **7** in C_6D_6

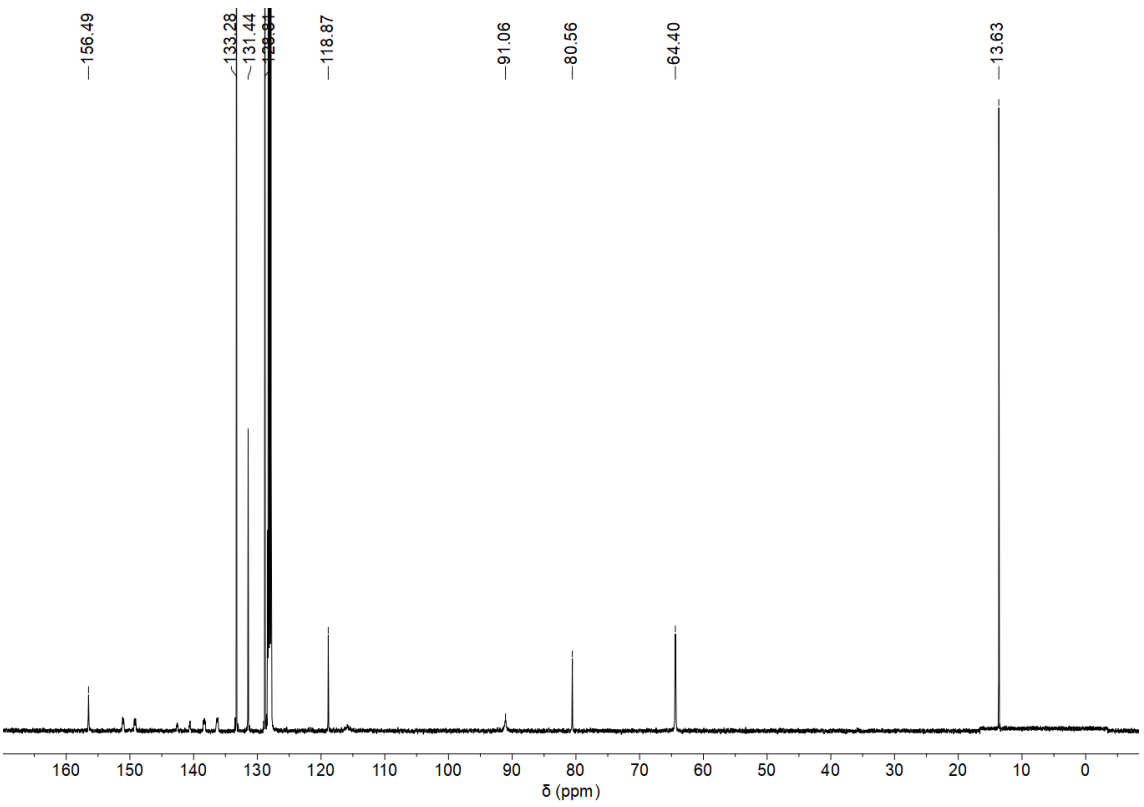


Figure S2-23 $^{13}C\{^{1}H\}$ NMR spectrum of **7** in C_6D_6

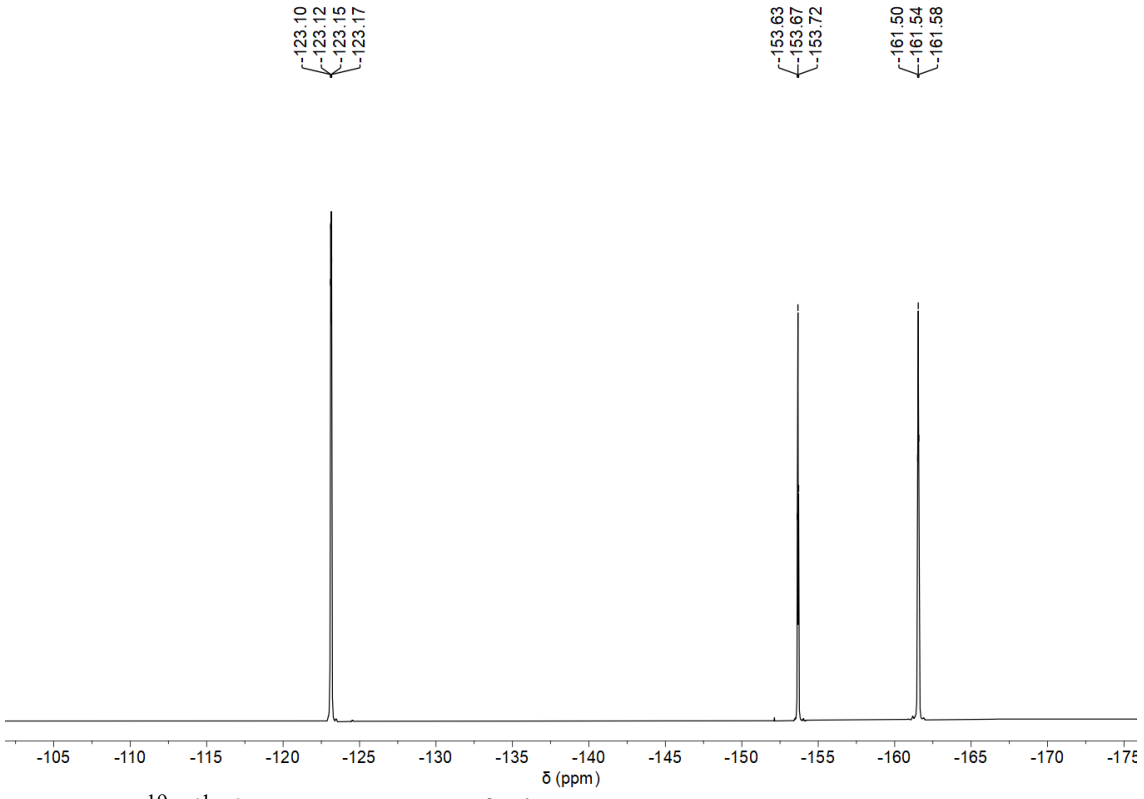


Figure S2-24 $^{19}F\{^{1}H\}$ NMR spectrum of **7** in C_6D_6

Spectra of 8

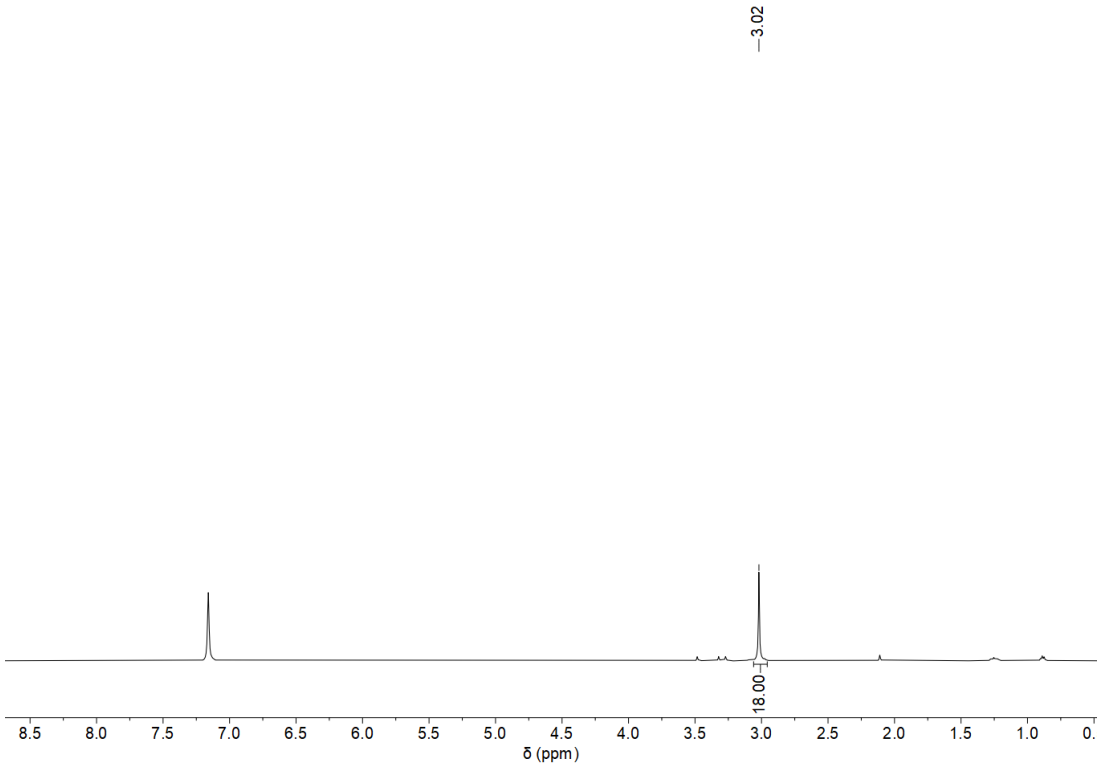


Figure S2-25 ^{1}H NMR spectrum of **8** in C_6D_6.

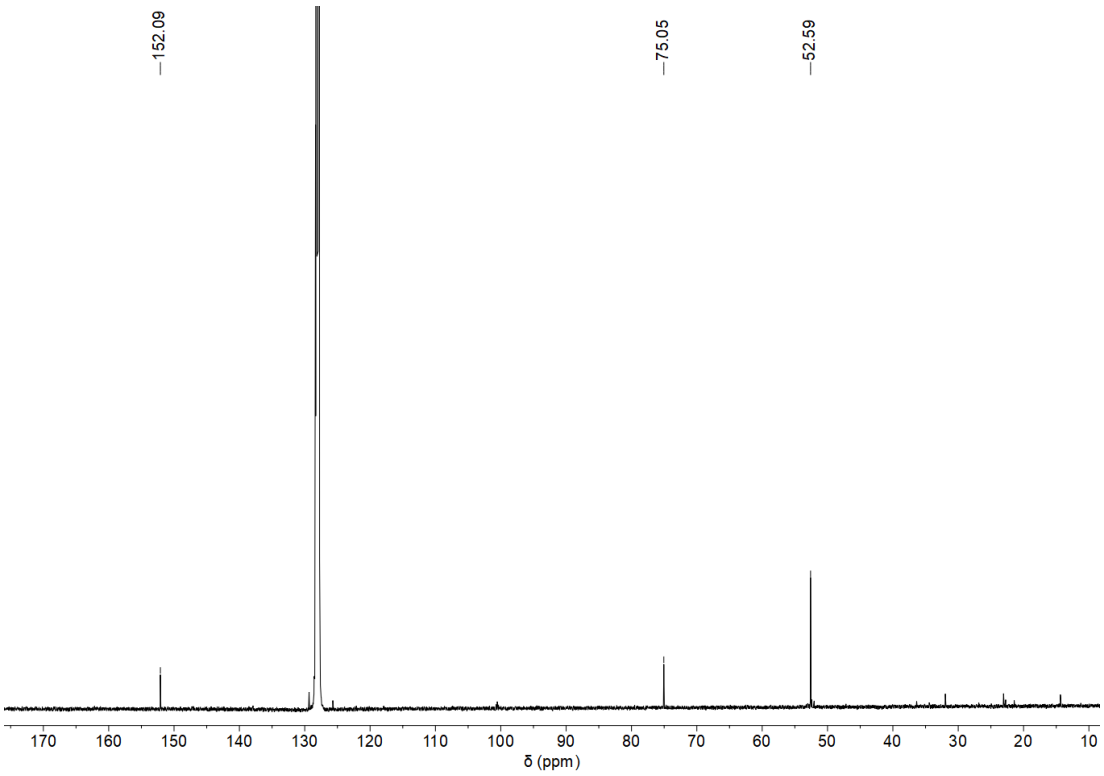


Figure S2-26 ^{13}C{^{1}H} NMR spectrum of **8** in C_6D_6.

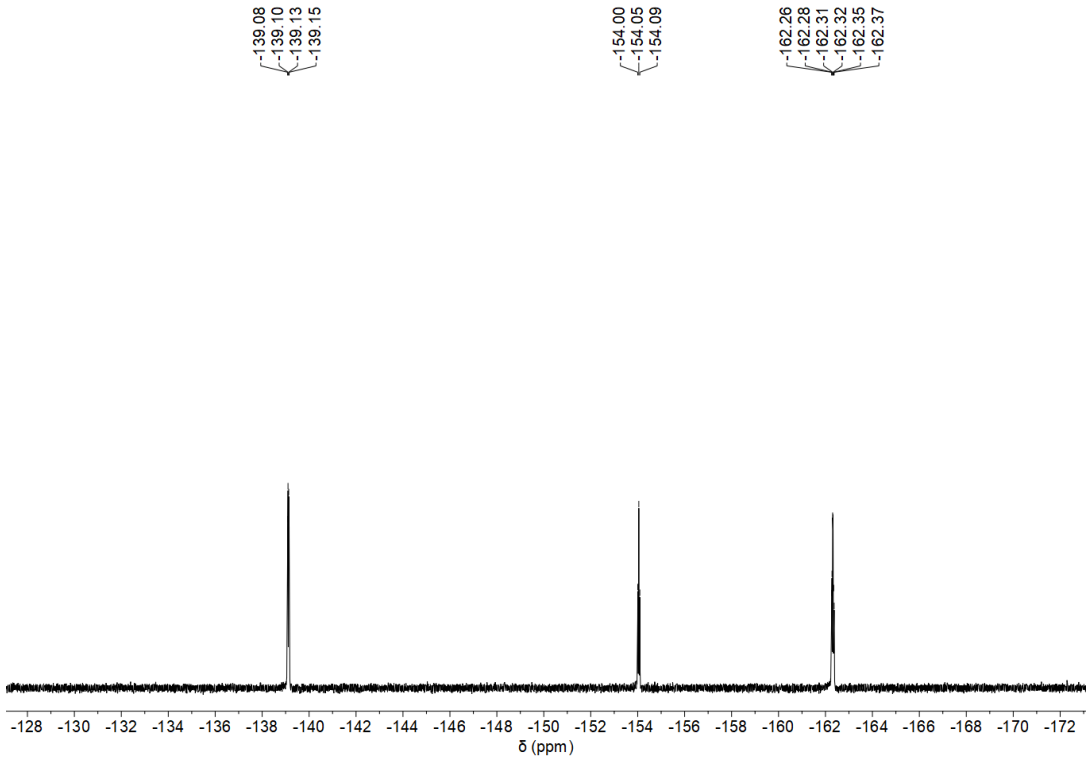


Figure S2-27 $^{19}F\{^{1}H\}$ NMR spectrum of **8** in C_6D_6

Spectra of 9

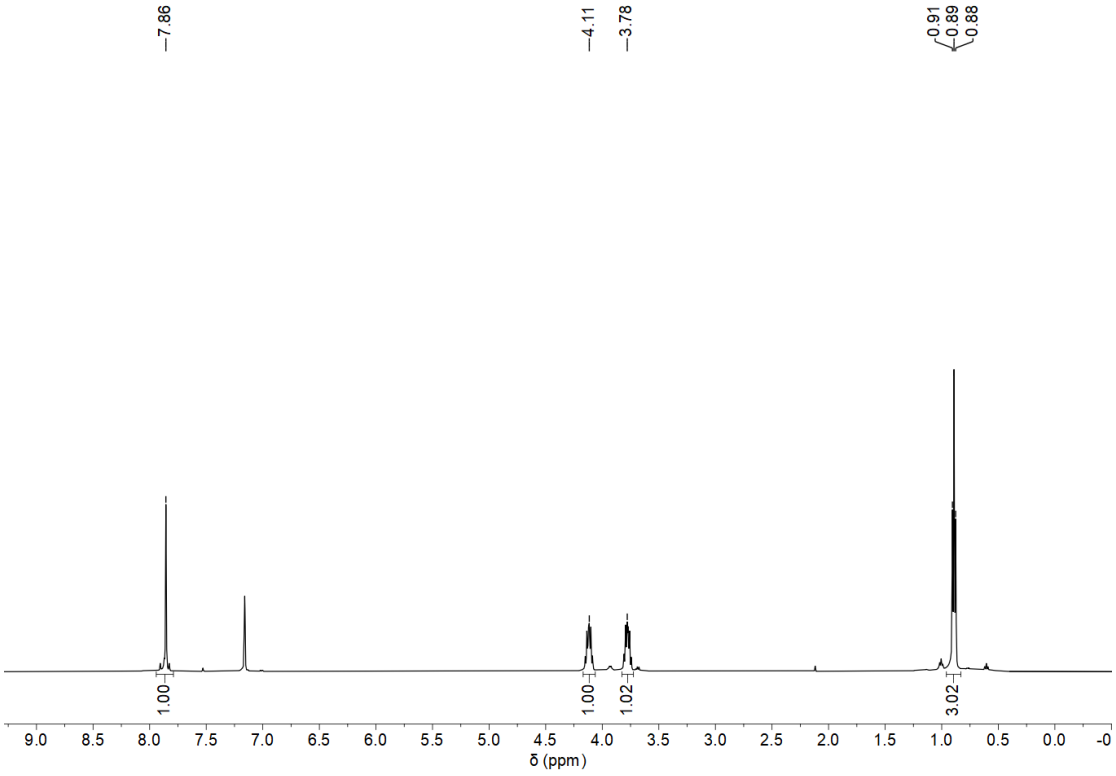


Figure S2-28 ^{1}H NMR spectrum of **9** in C_6D_6

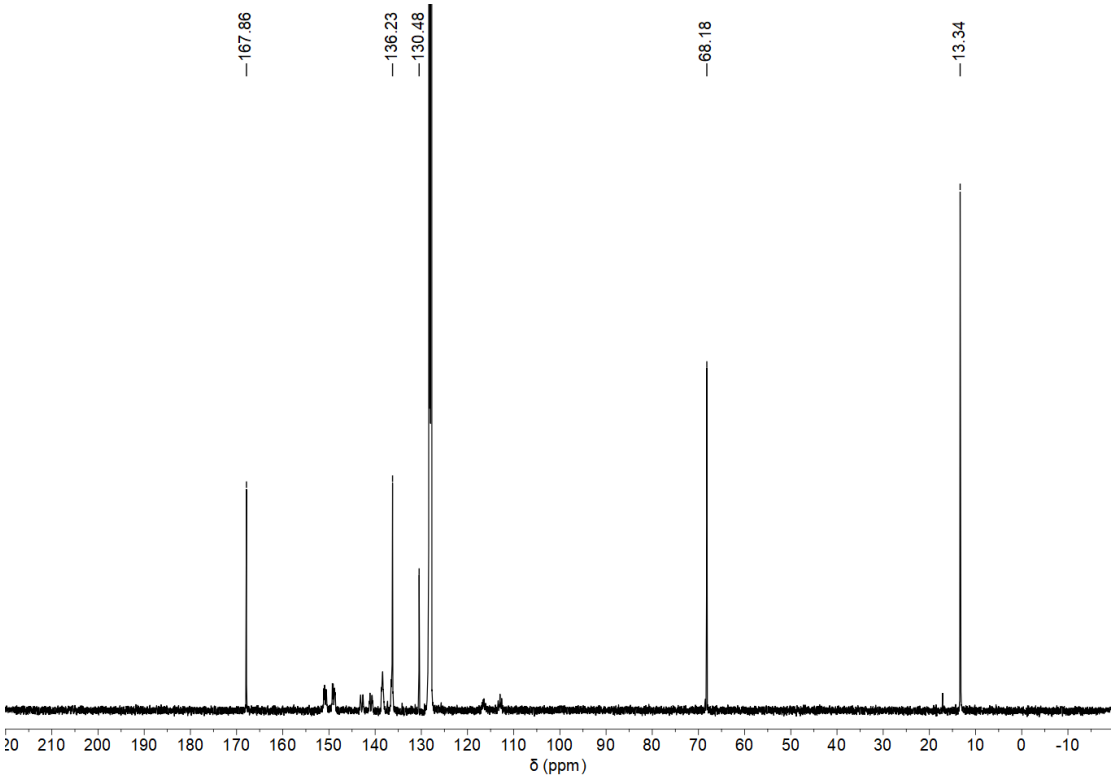


Figure S2-29 $^{13}C\{^{1}H\}$ NMR spectrum of **9** in C_6D_6

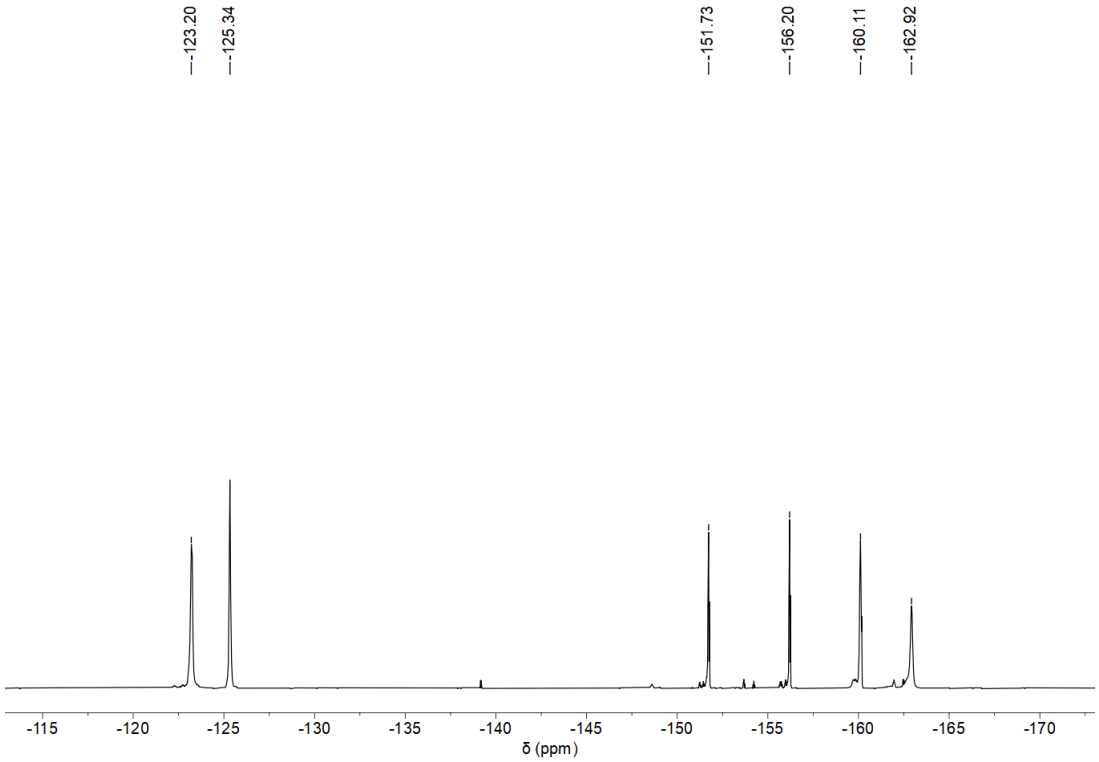


Figure S2-30 $^{19}F\{^{1}H\}$ NMR spectrum of **9** in C_6D_6

X-ray Crystallographic Data

Table S3-1. Crystal data and structure refinement details for compounds **1**, **2** and **3**.

Compounds	**1**	**2**	**3**
CCDC	2329988	2164107	2329987
Empirical formula	$C_{21}H_9AlF_{15}N_3Si$	$C_{43}H_8Al_3F_{30}N_9$	$Al_4C_{36}F_{30}N_{18}$
Formula weight	643.38	1301.52	1362.46
Temperature, K	157.00	100.00	150.00
Crystal system	triclinic	triclinic	monoclinic
Space group	*P*-1	*P*-1	*C*2/c
a, Å	10.2671(4)	10.2372(8)	16.9325(12)
b, Å	10.9361(4)	13.6057(11)	15.4312(11)
c, Å	11.5321(5)	19.0058(15)	18.9284(15)
α, deg	73.646(2)	105.775(3)	90
β, deg	81.9810(10)	93.636(4)	98.544(4)
γ, deg	83.748(2)	97.319(4)	90
V, Å^3	1227.00(9)	2513.4(3)	4890.9(6)
Z	2	2	4
D_{calcd}, g/cm^3	1.741	1.720	1.850
μ/mm^{-1}	2.457	2.151	2.467
F(000)	636.0	1276.0	2656.0
2θ range, °	8.042-136.676	4.856-142.432	7.79-149.466
Index ranges	$-12 \le h \le 12$	$-12 \le h \le 12$	$-21 \le h \le 21$
	$-13 \le k \le 13$	$-16 \le k \le 16$	$-17 \le k \le 19$
	$-13 \le l \le 13$	$-23 \le l \le 23$	$-23 \le l \le 21$
Reflections collected	38117	89652	32773
Independent reflections	4490	9605	4980
	R_{int} = 0.0494	R_{int} = 0.0842	R_{int} = 0.0583
	R_{sigma} = 0.0262	R_{sigma} = 0.0407	R_{sigma} = 0.0336
Data/restraints/parameters	4490/0/373	9605/0/776	4980/0/398
Goodness-of-fit on F^2	1.053	1.064	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0348	R_1 = 0.0582	R_1 = 0.0417
	wR_2 = 0.0940	wR_2 = 0.1674	wR_2 = 0.1103
Final R indexes [all data]	R_1 = 0.0356	R_1 = 0.0636	R_1 = 0.0554
	wR_2 = 0.0947	wR_2 = 0.1731	wR_2 = 0.1193
Largest diff. peak/hole, e/Å^{-3}	0.32/-0.25	0.69/-0.28	0.38/-0.30

Table S3-2. Crystal data and structure refinement details for compounds **4**, **5** and **6**.

Compounds	**4**	**5**	**6**
CCDC	2329992	2329990	2329991
Empirical formula	$C_{48}H_{22}Al_2F_{20}N_6O_2P_2$	$C_{32}H_{16}Al_2F_{20}N_6O_2$	$C_{39}H_{36}AlF_{10}N_5$
Formula weight	1210.61	950.47	791.71
Temperature, K	300.00	150.00	150.00
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	P-1	$P2_1/n$
a, Å	10.9682(6)	9.2131(3)	19.2920(6)
b, Å	17.7358(10)	10.4091(3)	9.3783(3)
c, Å	14.8935(9)	11.8882(4)	22.1910(6)
α, deg	90	67.1200(1)	90
β, deg	107.531(4)	84.917(2)	108.446(2)
γ, deg	90	82.702(2)	90
V, Å^3	2762.7(3)	1040.91(6)	3808.7(2)
Z	2	1	4
D_{calcd}, g/cm^3	1.455	1.516	1.381
μ/mm^{-1}	2.037	1.819	1.218
F(000)	1208.0	472.0	1632.0
2θ range, °	8.454-133.89	9.268-136.658	5.302-133.174
Index ranges	$-13 \le h \le 13$	$-11 \le h \le 10$	$-22 \le h \le 22$
	$-21 \le k \le 21$	$-12 \le k \le 12$	$-11 \le k \le 11$
	$-17 \le l \le 17$	$-14 \le l \le 14$	$-26 \le l \le 26$
Reflections collected	47777	17341	69159
Independent reflections	4894	3770	6671
	R_{int} = 0.0997	R_{int} = 0.0403	R_{int} = 0.0626
	R_{sigma} = 0.0435	R_{sigma} = 0.0276	R_{sigma} = 0.0273
Data/restraints/parameters	4894/0/365	3770/5/290	6671/18/534
Goodness-of-fit on F^2	1.027	1.170	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0434	R_1 = 0.0461	R_1 = 0.0381
	wR_2 = 0.1090	wR_2 = 0.1642	wR_2 = 0.0963
Final R indexes [all data]	R_1 = 0.0656	R_1 = 0.0491	R_1 = 0.0443
	wR_2 = 0.1214	wR_2 = 0.1672	wR_2 = 0.1005
Largest diff. peak/hole, e/Å^{-3}	0.15/-0.24	0.33/-0.32	0.28/-0.25

Table S3-3. Crystal data and structure refinement details for compounds **7**, **8** and **9**

	7·C_6H_6	**8**	**9** (monomer)
CCDC	2356544	2329989	2359713
Empirical formula	$C_{52}H_{26}Al_2F_{20}N_6O_4$	$C_{66}H_{28}Al_3F_{32}N_9O_{12}$	$C_{17}H_6AlF_{10}N_3O_2$
Formula weight	1232.75	1827.91	501.23
Temperature, K	150.00	150.00	150.00
Crystal system	triclinic	orthorhombic	tetragonal
Space group	*P*-1	*P*cca	*P4/ncc*
a, Å	9.6882(2)	18.8878(6)	21.4449(5)
b, Å	11.7436(3)	20.7586(7)	21.4449(5)
c, Å	12.2421(3)	19.2371(6)	20.4556(8)
α, deg	70.2630(10)	90	90
β, deg	81.3600(10)	90	90
γ, deg	76.2790(10)	90	90
V, $Å^3$	1269.85(5)	7542.6(4)	9407.2(6)
Z	1	4	16
D_{calcd}, g/cm^3	1.612	1.610	1.416
μ/mm^{-1}	1.681	1.790	1.677
F(000)	618.0	3640.0	3968.0
2θ range, °	8.164 - 136.664	4.256-136.92	8.12 - 133.18
Index ranges	$-11 \le h \le 11$	$-22 \le h \le 19$	$-25 \le h \le 25$
	$-14 \le k \le 14$	$-21 \le k \le 25$	$-23 \le k \le 20$
	$-14 \le l \le 14$	$-17 \le l \le 23$	$-24 \le l \le 24$
Reflections collected	35775	48037	67395
Independent reflections	4558	6916	4336
	R_{int} = 0.0423	R_{int} = 0.0905	R_{int} = 0.1320
	R_{sigma} = 0.0241	R_{sigma} = 0.0534	R_{sigma} = 0.0320
Data/restraints/parameters	4558/0/380	6916/0/554	4336/0/299
Goodness-of-fit on F^2	1.065	1.027	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0392	R_1 = 0.0498	R_1 = 0.0618
	wR_2 = 0.1066	wR_2 = 0.1307	wR_2 = 0.1697
Final R indexes [all data]	R_1 = 0.0403	R_1 = 0.0724	R_1 = 0.0817
	wR_2 = 0.1074	wR_2 = 0.1446	wR_2 = 0.1928
Largest diff. peak/hole, $e/Å^{-3}$	0.32/-0.32	0.36/-0.41	0.39/-0.36

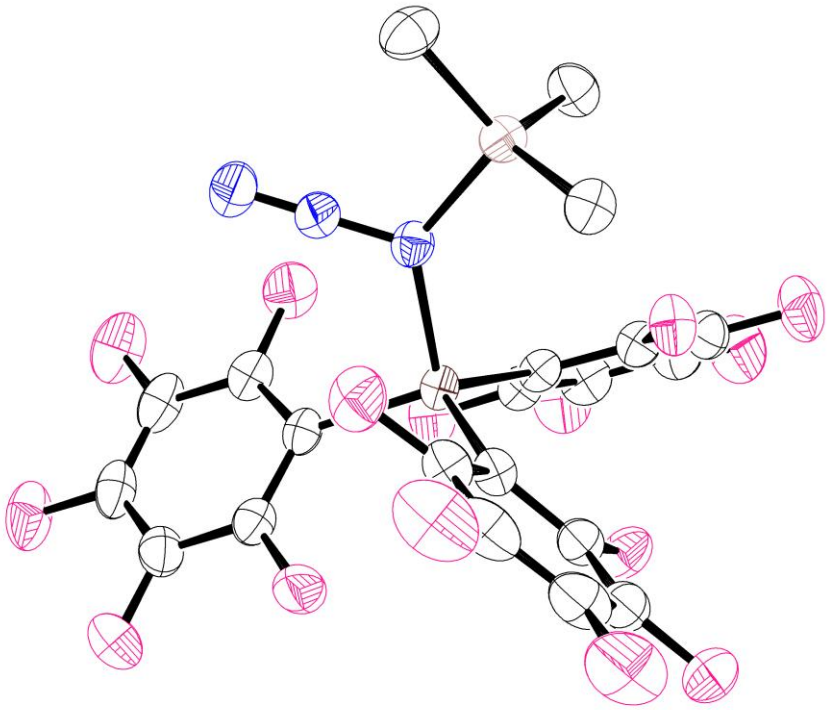


Figure S3-1. Solid-state structures of **1**. Hydrogen atoms omitted for clarity. Thermal ellipsoids are set at the 50% probability level.

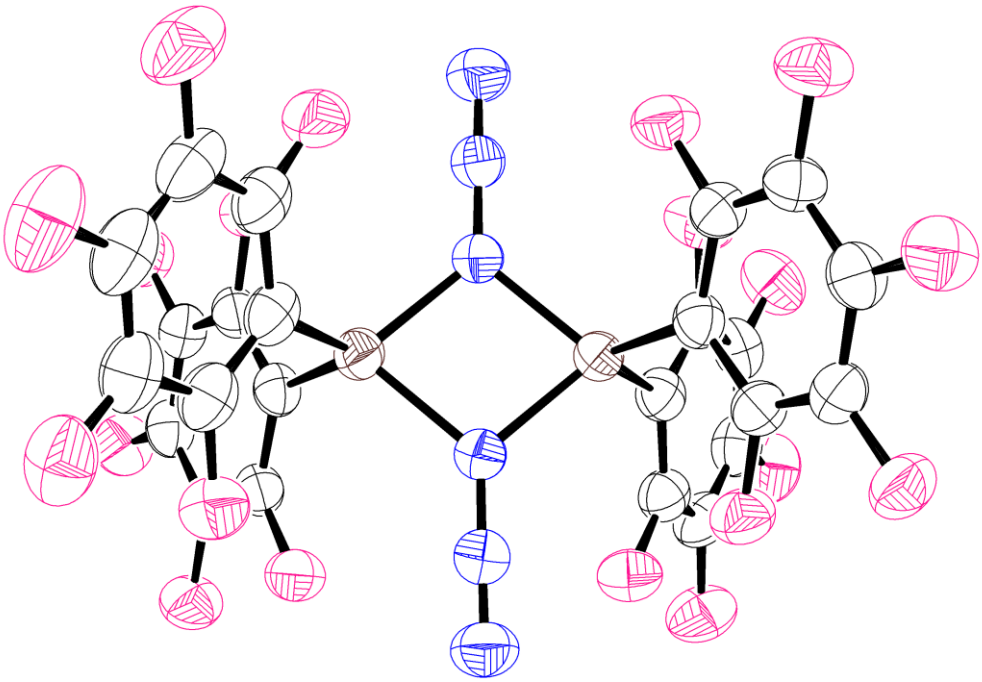


Figure S3-2. Solid-state structures of **2**. Thermal ellipsoids are set at the 50% probability level.

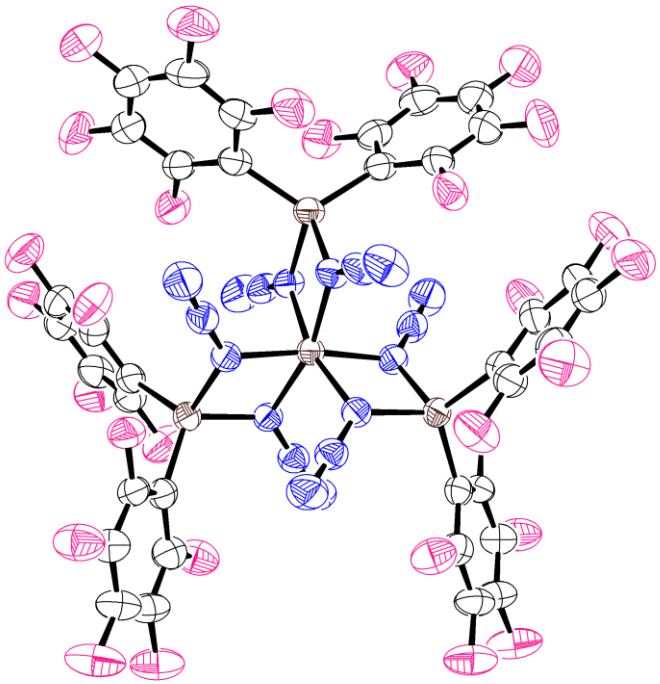


Figure S3-3. Solid-state structures of **3**. Thermal ellipsoids are set at the 50% probability level.

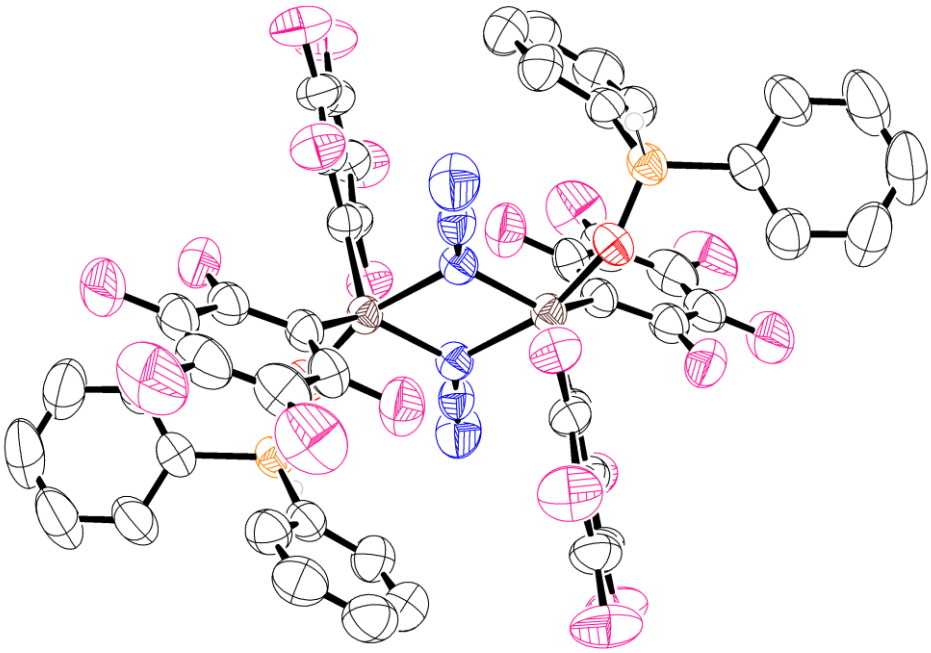


Figure S3-4. Solid-state structures of **4**. Hydrogen atoms except those on P atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level.

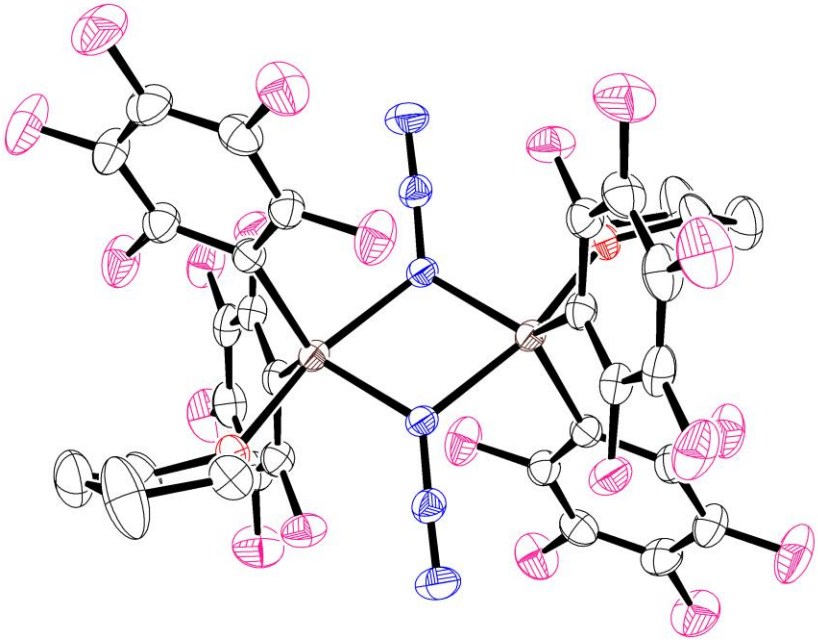


Figure S3-5. Solid-state structures of **5**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level.

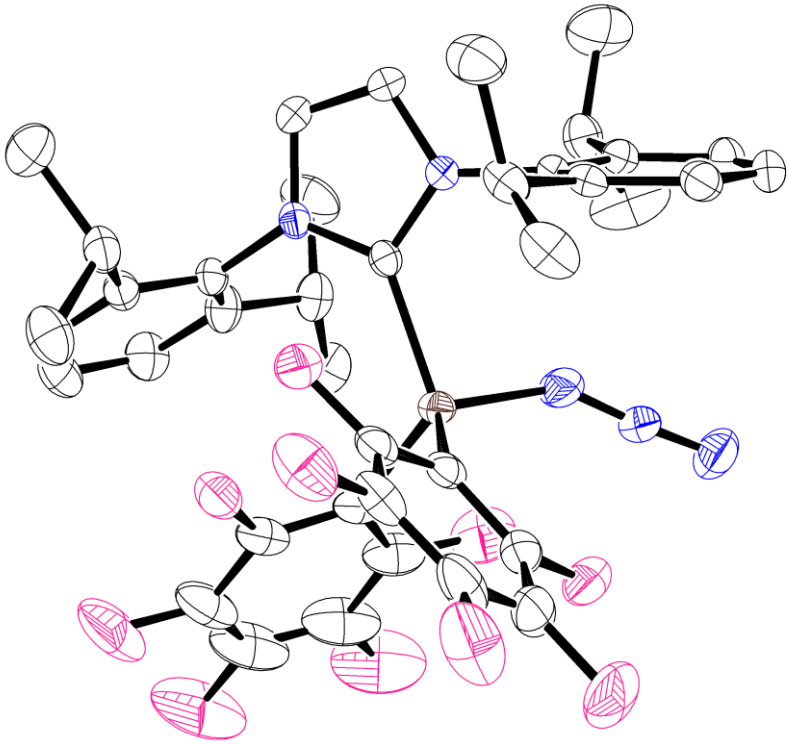


Figure S3-6. Solid-state structures of **6**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level.

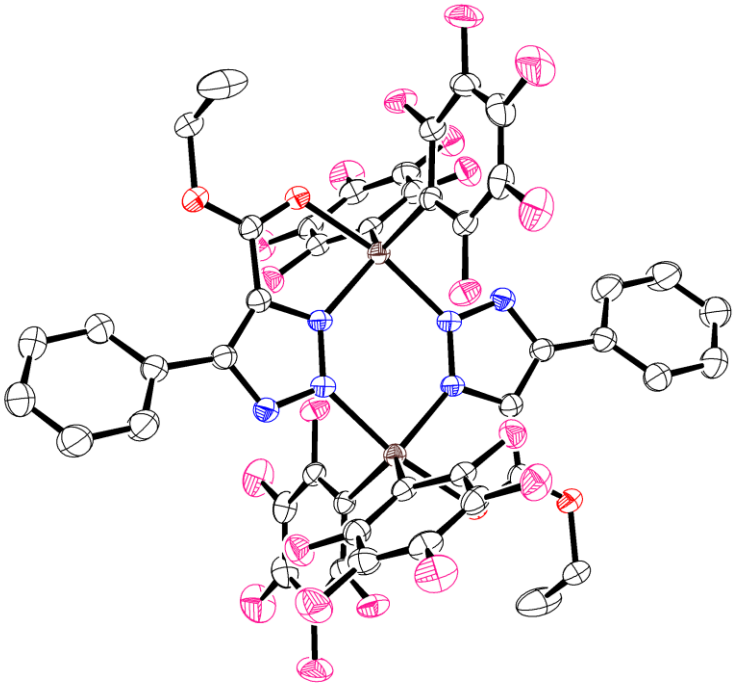


Figure S3-7. Solid-state structures of **7**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level.

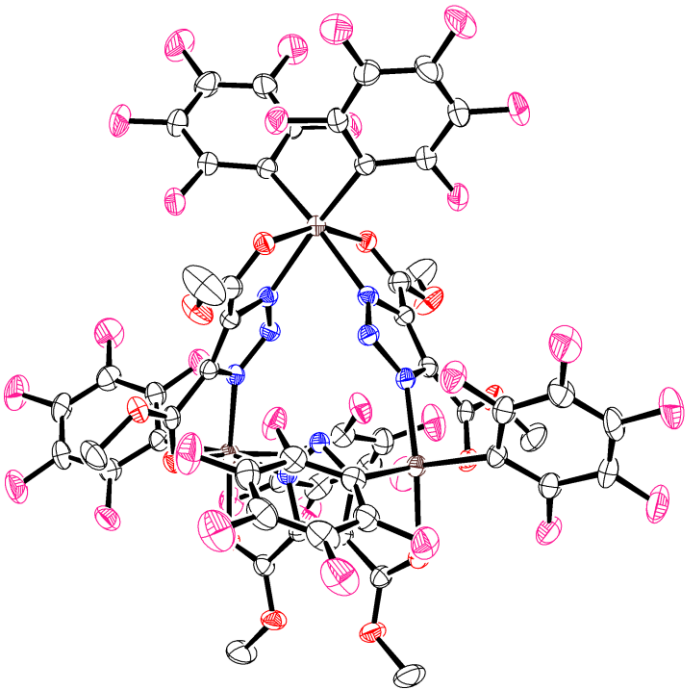


Figure S3-8. Solid-state structures of **8**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level.

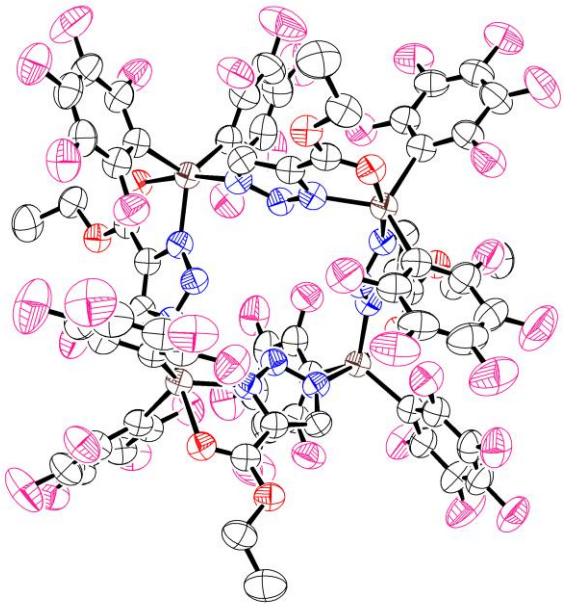


Figure S3-9. Solid-state structures of **9**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level.

Computational Details

Geometry optimizations were carried out with the Gaussian 16 package[S8] with the M06-2X functional and the def2-SVP basis set. The single-point energy calculations were performed at the M06-2X/def2-TZVP level of theory for solution-phase (toluene).

The gas-phase geometry was used for all the solution phase calculations. The SMD method was used with the corresponding solvent. The corrections of Gibbs free energy from frequency calculations were added to the single-point energies to obtain the Gibbs free energy in solution, respectively. Optimized structures were visualized by the Multiwfn[9] program.

For gas phase FIA and HIA calculation, geometries and final electronic energies were obtained at the BP86-D3/def2-SVP level of theory. The FIA reaction enthalpies were calculated according to the scheme proposed by Krossing[S10] using the given G3 anchor points and isodesmic reactions. For solvent corrected (toluene) FIA (FIA_{solv}) and HIA (HIA_{solv}), the PCM method was used on the BP86-D3/def2-SVP-level.

Table S4-1. Energy of Intermediates for the trimerization of **2**(monomer) and **2**(dimer).

Species	Thermal Corrections of Gibbs Free Energies (Hartree)	Single Point Energy (Hartree) SMD (toluene)	Solvation Energies (Hartree) SMD (toluene)
2(monomer)	0.060307	-1862.42849468	-1862.368188
2(dimer)	0.143495	-3724.95521187	-3724.811717

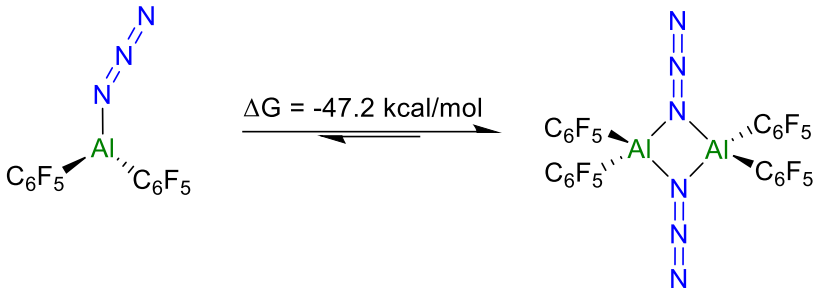


Figure S4-1. The trimerization of the monomers **2**(monomer) and **2**(dimer).

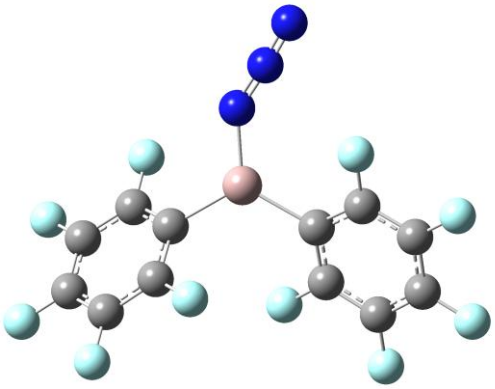
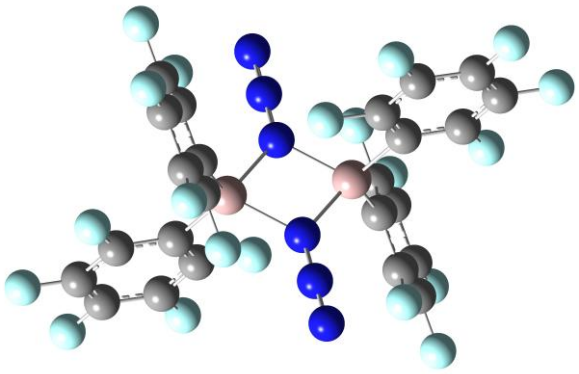
Table S4-2. Computed energies of FIAs and HIAs.

	G (a.u.)	G_{solv} (a.u.)	ΔG_{solv} (kJ/mol)	FIA (kJ/mol)	FIA_{solv} (kJ/mol)	HIA (kJ/mol)	HIA_{solv} (kJ/mol)
SbF_5	-739.254323	-739.257384	-8.0366555	**483.23**	**383.48**		
SbF_6-	-839.181431	-839.233795	-137.481682				
$B(C_6F_5)_3$	-2206.624189	-2206.625571	-3.628441	**458.29**	**272.65**	**488.09**	**286.43**
$B(C_6F_5)_3$-F	-2306.575458	-2306.588818	-35.07668				
$B(C_6F_5)_3$-H	-2207.346414	-2207.359579	-34.5647075				
2(monomer)	-1861.055953	-1861.058681	-7.162364	**544.31**	**405.04**	**487.96**	**330.66**
2-F	-1961.01058	-1961.042945	-84.9743075				
2-H	-1861.750005	-1861.781413	-82.461704				
2(dimer)	-3722.189903	-3722.189903	-13.458313	**545.1**	**387.62**	**487.66**	**324.49**
2-F	-3822.139918	-3822.139918	-73.0702905				
2-H	-3722.879106	-3722.879106	-67.3782065				
F-	-99.698735	-99.781419	-217.086842				
H-	-0.498737	-0.58733	-232.6009215				

G values are calculated at BP86-D3/def2-SVP level;

G_{solv} values are calculated at PCMBP86-D3/def2-SVP level.

Table S4-3. The Optimized structures of **2**(monomer) and **2**(dimer) and **3**.

2(monomer)	
2(dimer)	

Reference

[S1] G. S. Hair, A. H. Cowley, R. A. Jones, B. G. McBurnett, A. Voigt, *J. Am. Chem. Soc.* 1999, **121**, 4922-4923.

[S2] J. Tan, C. Hu, X. Yang, S. Ju, L. Cao, Y. Wu, L. L. Liu and D. W. Stephan, *Chem. Commun.*, 2023,**59**, 282-285.

[S3] F. E. Hahn and M. C. Jahnke, *Angew. Chem. Int. Ed.* 2008, 47, 3122-3172.

[S4] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42,** 339-341.

[S5] G. Sheldrick, *Acta Crystallogr. Sect. A.*, 2015, **71**, 3-8.

[S6] G. Sheldrick, *Acta Crystallogr. Sect. A.*, 2008, **64**, 112-122.

[S7] V. Gutmann, Coord. *Chem. Rev.*, 1976, **18**, 225-255.

[S8] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,; M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone,; G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich,; J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian,; J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young,; F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone,; T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega,;

G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda,; J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai,; T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta,; F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin,; V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand,; K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar,; J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi,; J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas,; J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

[S9] T. Lu, F. Chen, *J. Comput. Chem*., 33, 580-592 (2012)

[S10] **a**) H. Böhrer, N. Trapp, D. Himmel, M. Schleep and I. Krossing, *Dalton Trans*., 2015, **44**, 7489-7499; **b**) P. Erdmann, J. Leitner, J. Schwarz and L. Greb, *Chem, Phys, Chem*.,2020,**21**, 987-994.

Cartesian Coordinates of the Optimized Geometries

2(monomer) (BP86-D3/Def2-SVP)

SCF Done: E(RB-P86) = -1861.10658482 A.U.

Al	-0.02476100	1.24427000	-0.04418200
F	0.95708000	-1.10495400	-1.73232600
F	-3.02559100	1.84281500	-0.82974200
F	3.38702800	-2.37441600	-1.83522900
F	5.44320600	-1.48632700	-0.26200900
F	2.66433100	1.89547500	1.53528600
F	5.09343100	0.64434400	1.41629100
F	-5.03480200	-2.25963900	0.38277500
F	-0.40290800	-1.64134100	1.08905000
F	-2.62232700	-3.21669200	1.24689000
C	-1.63974400	0.15250500	0.12070400
C	1.74802700	0.43444500	-0.10383300
C	-2.89961200	0.60575200	-0.30815200
C	1.96667900	-0.66632500	-0.94617200
C	4.25985700	-0.87313100	-0.21089600
C	-3.95028300	-1.48930100	0.29858900
C	-4.05627500	-0.18814700	-0.23127500
C	3.20031700	-1.33179500	-1.01945500
C	2.82496300	0.85937500	0.68868400
C	-1.57848000	-1.15132200	0.64458400
C	4.08000000	0.22734700	0.65043100
C	-2.70673200	-1.98218500	0.74138500
F	-5.24166800	0.26477300	-0.65030300

N	-0.11654400	3.02621200	-0.17634700
N	-0.89647100	3.96290600	-0.21836700
N	-1.57704500	4.89157400	-0.26519400

2(monomer)-F (BP86-D3/Def2-SVP)

SCF Done: E(RB-P86) = -1961.06173833 A.U.

Al	0.01170900	1.44407700	-0.55310300
F	-0.58795200	-0.73676000	1.64315400
F	3.06215000	1.87240700	0.40219800
F	-2.82066300	-2.15712200	2.26584600
F	-5.14301500	-1.74775300	0.85889700
F	-2.99903900	1.51670500	-1.80523200
F	-5.21863500	0.09271800	-1.17473700
F	4.79683200	-2.50676900	-0.03624400
F	0.30450100	-1.65366700	-1.25276700
F	2.37983600	-3.39105400	-0.98967700
C	1.58826200	0.17793900	-0.41235500
C	-1.69036400	0.44080500	-0.11787600
C	2.84280200	0.58169800	0.05920600
C	-1.70865300	-0.50453300	0.91503000
C	-4.03622100	-1.04701500	0.54633400
C	3.76814800	-1.64618000	-0.15698600
C	3.93404300	-0.29677900	0.19931200
C	-2.84560400	-1.25435500	1.26441700
C	-2.89966000	0.61677900	-0.80121800
C	1.47488800	-1.17212200	-0.76411700
C	-4.07021800	-0.10427100	-0.49476900
C	2.52821300	-2.09603500	-0.64339300
F	5.12928100	0.12640000	0.65777000
N	0.11605600	2.76520500	0.75668300
N	0.80965400	3.69072600	1.11132600
N	1.42983800	4.59196000	1.50631100
F	-0.00939200	2.10891400	-2.12380800

2(monomer)-H (BP86-D3/Def2-SVP)

SCF Done: E(RB-P86) = -1861.80639092 A.U.

Al	0.01438400	1.50610300	-0.77825000
F	-0.58868000	-0.50504400	1.61880000

F	3.06933100	1.97595600	0.12446300
F	-2.81910700	-1.87451200	2.34603400
F	-5.13205700	-1.60285500	0.89291100
F	-2.98150700	1.42509200	-2.03503500
F	-5.20096400	0.05031000	-1.29743200
F	4.79176500	-2.43073100	0.06872700
F	0.29373500	-1.67773600	-1.19260100
F	2.36528400	-3.38846700	-0.78760400
C	1.58287000	0.22057400	-0.52156800
C	-1.68139200	0.51037700	-0.24780700
C	2.84307200	0.65876200	-0.09804500
C	-1.70272500	-0.34069700	0.86423700
C	-4.02625600	-0.92576800	0.52765800
C	3.76349400	-1.58107500	-0.12049000
C	3.93402800	-0.20569800	0.11279300
C	-2.83976300	-1.06245000	1.26919800
C	-2.88692600	0.61814500	-0.95108600
C	1.46719900	-1.15496800	-0.75228700
C	-4.05690100	-0.07954200	-0.59332700
C	2.51925800	-2.06779200	-0.55757600
F	5.13382100	0.25428600	0.52314400
N	0.12528200	2.87492500	0.50263400
N	0.78123100	3.85546300	0.76879000
N	1.36980200	4.81040000	1.08109600
H	-0.00154800	2.05924000	-2.29324800

2(dimer) (BP86-D3/Def2-SVP)

SCF Done: E(RB-P86) = -3722.31636893 A.U.

Al	0.81469100	-1.24265400	0.00002500
F	1.93950600	-4.21004400	0.00132900
F	2.82534500	-1.08238900	2.37373800
F	0.62591800	-6.59357800	0.00130700
F	-2.10996000	-6.64586000	0.00007100
F	-2.24016700	-1.91997800	-0.00118600
F	-3.54393300	-4.31147900	-0.00119600
F	6.90040200	-0.58486600	-0.00075100
F	2.82474800	-1.08272000	-2.37414100

F	5.55387500	-0.74877300	-2.37839900
N	-0.00007800	-0.00006300	-1.27568800
N	-0.00062400	-0.00056000	-2.51228000
N	-0.00109200	-0.00102000	-3.65563300
C	2.76615900	-1.09325100	-0.00019000
C	-0.10389000	-2.98051800	0.00001700
C	3.48935200	-1.00416100	1.19245600
C	0.59133400	-4.20165800	0.00068000
C	-1.47003900	-5.47571900	0.00006000
C	5.57549800	-0.74716700	-0.00056700
C	4.88239900	-0.83210200	1.22388800
C	-0.06204500	-5.44707700	0.00068300
C	-1.50622100	-3.05816500	-0.00058200
C	3.48905000	-1.00432400	-1.19303800
C	-2.20698600	-4.27483600	-0.00060500
C	4.88209000	-0.83227600	-1.22483800
F	5.55446400	-0.74842800	2.37727200
Al	-0.81469100	1.24265500	-0.00002600
F	-1.93950600	4.21004500	-0.00131800
F	-2.82534600	1.08238900	-2.37373800
F	-0.62591800	6.59357900	-0.00129600
F	2.10996000	6.64586000	-0.00007100
F	2.24016600	1.91997800	0.00117500
F	3.54393300	4.31147900	0.00118600
F	-6.90040200	0.58486600	0.00075200
F	-2.82474700	1.08271900	2.37414100
F	-5.55387500	0.74877200	2.37840000
N	0.00007800	0.00006500	1.27568700
N	0.00062600	0.00056100	2.51227800
N	0.00109000	0.00101600	3.65563100
C	-2.76615900	1.09325100	0.00019000
C	0.10389000	2.98051800	-0.00001700
C	-3.48935300	1.00416100	-1.19245600
C	-0.59133400	4.20165800	-0.00067500
C	1.47004000	5.47571900	-0.00005900

C	-5.57549800	0.74716700	0.00056800
C	-4.88240000	0.83210200	-1.22388700
C	0.06204500	5.44707800	-0.00067700
C	1.50622000	3.05816500	0.00057700
C	-3.48904900	1.00432400	1.19303800
C	2.20698600	4.27483600	0.00060000
C	-4.88208900	0.83227500	1.22483900
F	-5.55446500	0.74842900	-2.37727200

2(dimer)-F (BP86-D3/Def2-SVP)

SCF Done: E(RB-P86) = -3822.27203550 A.U.

Al	1.10025600	-1.52318400	-1.61463500
F	2.64123100	-3.97370600	-0.58648300
F	-1.82252200	-1.70644900	-2.55384700
F	5.01613900	-4.23956900	0.74465000
F	6.54852300	-2.02181300	1.25028300
F	3.33557900	0.73270200	-0.86179900
F	5.70044100	0.45838300	0.44605900
F	-3.97838000	-3.75062900	1.11747100
F	0.68257500	-3.00306300	1.29072000
F	-1.58982500	-3.91103200	2.45706700
N	0.90468300	-0.03664600	1.07679600
N	1.76714000	-0.17477200	1.91084000
N	2.59724600	-0.36752600	2.69620800
C	-0.46949300	-2.35708300	-0.69896200
C	2.89156900	-1.61341900	-0.75073000
C	-1.71788500	-2.28684000	-1.33383000
C	3.37171600	-2.85967300	-0.33299800
C	5.37785600	-1.89190000	0.60513700
C	-2.85265600	-3.30982000	0.53605400
C	-2.90436200	-2.76415200	-0.75765100
C	4.58769400	-3.02677500	0.35043100
C	3.71486000	-0.51310900	-0.48616700
C	-0.46437900	-2.91195200	0.58803700
C	4.94024200	-0.62078600	0.19447800
C	-1.62703900	-3.39173200	1.21891800
F	-4.08797500	-2.67180100	-1.39403200

Al	-0.12943200	1.03841000	0.02471900
F	-2.44949500	1.48801900	-1.96299700
F	-0.99345500	2.93389600	2.24176500
F	-5.08277900	0.74270800	-1.91609000
F	-6.09400500	-0.53576900	0.29021200
F	-1.85722100	-0.38992900	2.37521200
F	-4.47144400	-1.09505200	2.42796800
F	0.75560700	7.10444500	0.84078200
F	1.46546200	3.26685800	-1.82635900
F	1.81006000	5.92555500	-1.39623100
N	0.45430900	0.35843300	-1.70807500
N	0.28202600	0.89324200	-2.80909600
N	0.13285700	1.38396500	-3.83288400
C	0.21334200	2.99984800	0.19026700
C	-2.05615600	0.56773200	0.19461300
C	-0.30376600	3.64871600	1.31997200
C	-2.92551200	0.83992500	-0.86710200
C	-4.80246900	-0.17651300	0.26046900
C	0.58123700	5.78998700	0.63385800
C	-0.14124600	5.02273900	1.56578400
C	-4.28133700	0.47637500	-0.87166900
C	-2.61586600	-0.08113900	1.30148500
C	0.92719000	3.80224500	-0.70867000
C	-3.96877100	-0.46145300	1.35546100
C	1.12185000	5.18222100	-0.51338300
F	-0.65225500	5.61065900	2.66106800
F	1.21615600	-1.90613100	-3.27102300

2(dimer)-H (BP86-D3/Def2-SVP)

SCF Done: E(RB-P86) = -3723.01635461 A.U.

Al	-1.28710100	-1.37834800	1.82037900
F	-3.06018400	-3.68228400	0.86425200
F	1.61017700	-1.92424800	2.65922400
F	-5.43748300	-3.77843600	-0.48567100
F	-6.73082200	-1.44670000	-1.13271800
F	-3.27479700	1.07891700	0.87748100
F	-5.64020700	0.97445500	-0.44640400

F	3.40675400	-4.23641000	-1.04760700
F	-1.11879100	-2.89413400	-1.13248500
F	0.99032500	-4.08612000	-2.33645100
N	-0.93865100	0.07150600	-1.13458100
N	-1.87173300	-0.01649200	-1.89332600
N	-2.76518800	-0.15432700	-2.61952000
C	0.14698000	-2.38827300	0.83218500
C	-3.06584300	-1.30323300	0.89666100
C	1.40725900	-2.48397100	1.43970200
C	-3.67071500	-2.51333300	0.53867200
C	-5.55875000	-1.40120400	-0.47810900
C	2.36085000	-3.64999900	-0.44572500
C	2.50968700	-3.11376400	0.84441600
C	-4.89104200	-2.59490200	-0.15102400
C	-3.77223500	-0.14247100	0.56241000
C	0.04318800	-2.94313200	-0.45130500
C	-4.99738800	-0.16169400	-0.12758900
C	1.12105000	-3.57206900	-1.10240400
F	3.70706000	-3.17785700	1.45863500
Al	0.19249000	0.98014400	-0.03843900
F	2.52385800	1.15938700	1.99485400
F	1.60899400	2.78843800	-2.07286000
F	5.05119700	0.12110000	1.98850400
F	5.94136900	-1.28258300	-0.19447500
F	1.77601200	-0.67757400	-2.33875400
F	4.29331300	-1.67219300	-2.35100500
F	0.19419600	7.12476700	-0.81550400
F	-1.38302100	3.37712000	1.59249900
F	-1.32602200	6.06033100	1.20139100
N	-0.46296800	0.44953000	1.73120700
N	-0.26067800	1.08115200	2.77359600
N	-0.08141000	1.65782000	3.74809300
C	0.12969800	2.97446700	-0.21230600
C	2.04940000	0.26732100	-0.16067200
C	0.88391600	3.56769800	-1.23505400

C	2.93159200	0.44901000	0.91026500
C	4.69755900	-0.78089700	-0.18460300
C	0.17374800	5.79643500	-0.62379800
C	0.92982500	4.95458200	-1.45916400
C	4.23824700	-0.06379600	0.93496000
C	2.54850300	-0.44945300	-1.25480400
C	-0.61231700	3.85193400	0.58952500
C	3.85096400	-0.97904200	-1.28857000
C	-0.60471800	5.24770600	0.41052100
F	1.66699200	5.48563400	-2.45013500
H	-1.39267400	-1.65968500	3.39643200

SbF_5 (BP86-D3/Def2-SVP)

SCF Done: E(RB-P86) = -739.231044542 A.U.

Sb	0.00000200	0.00013600	0.00000000
F	0.00000200	0.00340300	1.92298800
F	0.00753400	1.91467900	0.00000000
F	0.00000200	0.00340300	-1.92298800
F	1.65161100	-0.96762500	0.00000000
F	-1.65916100	-0.95463100	0.00000000

SbF_6^- (BP86-D3/Def2-SVP)

BP86-D3/Def2-SVP

SCF Done: E(RB-P86) = -839.163326436 A.U.

Sb	0.00000000	0.00000000	0.00000000
F	0.00000000	0.00000000	1.95131100
F	0.00000000	0.00000000	-1.95131100
F	0.00000000	1.95131100	0.00000000
F	-1.95131100	0.00000000	0.00000000
F	0.00000000	-1.95131100	0.00000000
F	1.95131100	0.00000000	0.00000000

$B(C_6F_5)_3$ (BP86-D3/Def2-SVP)

SCF Done: E(RB-P86) = -2206.70915384 A.U.

B	-0.00016400	0.00084300	0.00000800
C	1.31541200	0.85374600	0.00000100
C	2.45984600	0.46155500	-0.73047600
C	1.42556600	2.05828500	0.73087000
C	3.64318400	1.21537100	-0.75114100

C	2.59736100	2.82994400	0.75150600
C	3.70931300	2.40426600	0.00010200
C	0.08096500	-1.56491700	0.00018800
C	-0.83000900	-2.36047100	-0.73081600
C	1.06953000	-2.26192000	0.73095300
C	-0.76797900	-3.76213900	-0.75144800
C	1.15273500	-3.66250700	0.75169300
C	0.22865500	-4.41324200	0.00021700
C	-1.39684300	0.71318600	0.00020100
C	-2.49454900	0.20514100	0.73095000
C	-1.63082000	1.89961000	-0.73108900
C	-3.74943500	0.83270400	0.75140400
C	-2.87605000	2.54609300	-0.75196900
C	-3.93805600	2.00811100	-0.00031900
F	-1.63559100	-4.48104200	-1.47026300
F	0.29768100	-5.74378800	0.00016900
F	2.09035600	-4.28781800	1.47009900
F	1.96384600	-1.58809900	1.47367300
F	-1.78860400	-1.78284400	-1.47438000
F	2.43852400	-0.65814100	-1.47296100
F	0.39558900	2.49617100	1.47438600
F	2.67088200	3.95441500	1.47013400
F	4.82760600	3.12850700	0.00022000
F	4.69962200	0.82235400	-1.46928000
F	-2.35765000	-0.90616900	1.47374000
F	-0.65135000	2.44136100	-1.47446700
F	-3.06530400	3.65676200	-1.47090200
F	-5.12515300	2.61301300	-0.00055500
F	-4.75958000	0.33297500	1.46983100

$B(C_6F_5)_3$-F (BP86-D3/Def2-SVP)

BP86-D3/Def2-SVP

SCF Done: E(RB-P86) = -2306.63094768 A.U.

B	-0.09818500	-0.05987500	-0.93680500
C	0.39594200	1.42673700	-0.36800000
C	-0.18350800	2.16971800	0.67219100
C	1.55101900	1.99503800	-0.93542500

C	0.31014800	3.41571200	1.10285900
C	2.08110200	3.23749000	-0.54120300
C	1.45381600	3.95209200	0.49172400
C	-1.64324200	-0.44943800	-0.48245700
C	-2.05746400	-1.65502400	0.10245400
C	-2.68138300	0.44365300	-0.80398900
C	-3.40498300	-1.95472000	0.38860200
C	-4.03786900	0.19103400	-0.54206300
C	-4.40188100	-1.02512300	0.06009400
C	1.04008800	-1.12251400	-0.36859000
C	1.85159900	-1.92721900	-1.18482000
C	1.30680500	-1.20474600	1.00807100
C	2.87204600	-2.75402300	-0.67064400
C	2.30718500	-2.01533400	1.56742700
C	3.10325900	-2.79561000	0.71222100
F	-3.74895200	-3.12909000	0.95634300
F	-5.69660600	-1.29487400	0.31773000
F	-4.99247600	1.08941700	-0.85942500
F	-2.40003000	1.63153000	-1.38188900
F	-1.17261100	-2.62551300	0.42864100
F	-1.27336000	1.72005800	1.33373400
F	2.22951300	1.34427200	-1.90336000
F	3.18872500	3.74113300	-1.12397900
F	1.94420600	5.14221300	0.89090500
F	-0.29230900	4.09556600	2.10020100
F	1.69330300	-1.96605500	-2.52181000
F	0.55539600	-0.49198600	1.88076800
F	2.51369500	-2.05893200	2.89974400
F	4.07371600	-3.58299700	1.21746400
F	3.62936300	-3.51002900	-1.49288000
F	-0.10547800	-0.02326300	-2.36070800

$B(C_6F_5)_3$-H (BP86-D3/Def2-SVP)

SCF Done: E(RB-P86) = -2207.41087896 A.U.

B	-0.05536000	-0.06917000	-0.87572900
C	1.20972700	-0.97477200	-0.36630600
C	1.63944400	-0.98391000	0.97104500

C	1.97987700	-1.74795300	-1.24992300
C	2.75959000	-1.70077500	1.42445400
C	3.11187300	-2.48205200	-0.84541500
C	3.50503800	-2.45403500	0.50173000
C	0.19459400	1.47332600	-0.37493200
C	-0.47342200	2.12520300	0.67473400
C	1.18716800	2.23870400	-1.01414700
C	-0.20875100	3.45420100	1.05556800
C	1.49218200	3.56714000	-0.66723000
C	0.78636600	4.17922100	0.38148900
C	-1.53022000	-0.65762900	-0.48694500
C	-2.67587400	0.05178100	-0.89654900
C	-1.79776500	-1.86892500	0.17239600
C	-3.99211800	-0.38182100	-0.67087700
C	-3.09929700	-2.34884300	0.42159700
C	-4.20601600	-1.59836900	-0.00096000
F	-0.88501000	4.03607900	2.06805200
F	1.06062400	5.45141400	0.73516300
F	2.45147600	4.25801100	-1.31886200
F	1.91041600	1.70505800	-2.02365300
F	-1.42869900	1.48971000	1.38953600
F	0.94585800	-0.29758400	1.90749100
F	1.65769000	-1.83159500	-2.55839800
F	3.82404200	-3.21068900	-1.73099900
F	4.58515800	-3.15068600	0.90934700
F	3.12796300	-1.68218100	2.72239900
F	-2.53875400	1.22920100	-1.54876600
F	-0.79525300	-2.66620000	0.61221400
F	-3.29398100	-3.52086000	1.06187300
F	-5.45974800	-2.04010900	0.22725500
F	-5.04984900	0.34677100	-1.08515800
H	-0.02498300	-0.04416700	-2.10716200