Electronic Supplementary Information

Structural characterization and reactivity studies of the aluminum analogue of Piers' borane $[HAl(C_6F_5)_2]_3$

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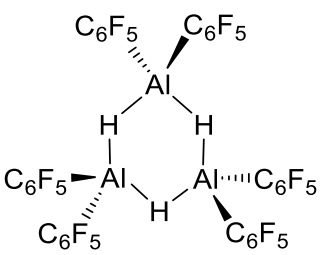
General Information

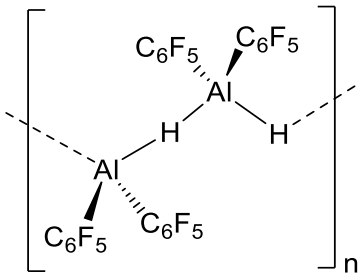
All manipulations were carried out on a Schlenk line or in an argon atmosphere glovebox. Solvents were dried using a MBraun solvent purification system, and stored over 3 Å sieves. Unless otherwise stated, commercial reagents were used without further purification. $[ClAl(C_6F_5)_2]_2$[1] and $[(2,6\text{-}^{i}Pr_2C_6H_3)N{=}C(CH_3)]_2$[2] were synthesized according to the literature methods. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on a Bruker Ascend 500M or a Bruker Ascend 600M spectrometer. 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, $\mu K\alpha = 12.894\ mm^{-1}$) micro-focus X-ray sources. Using Olex2,[3] the structure was solved with the XT[4] structure solution program using Intrinsic Phasing and refined with the XL[5] refinement package using Least Squares minimisation.

Experimental Section

Synthesis of **1** and **1-d**:



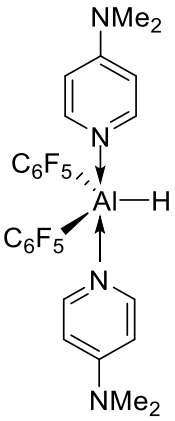
1



1B

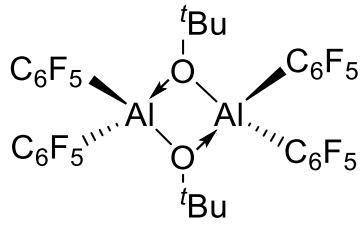
A mixture of $[ClAl(C_6F_5)_2]_2$ (2 mmol, 1586 mg) and $LiAlH_4$ (4 mmol, 151 mg) in 15 mL fluorobenzene was stirred at room temperature until the in situ ^{19}F NMR indicates a completely transformation of starting materials. The mixture was filtrated and the solvent was removed under vacuum. The residues were wash with hexane to give white powders of the product (1015 mg 70 % yield). Colorless crystals were obtained by storage a solution of the product in hexane/toluene (**1**) or chlorobenzene (**1B**). Compound **1-d** was obtained from the analogue reaction of $[ClAl(C_6F_5)_2]_2$ and $LiAlD_4$ with an isolated yield of 63 %. ^1H NMR (500 MHz, C_6D_6, ppm): δ 4.38 (br, 3 H, Al*H*). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, ppm): δ 151.3-149.3 (m, *o*-C_6F_5), 144.0-142.0 (m, *p*-C_6F_5), 138.6-136.2 (m, *m*-C_6F_5), 109.4 (br, *i*-C_6F_5). $^{19}F\{^1H\}$ NMR (470 MHz, C_6D_6, ppm) δ -124.1 (br, 12F, *o*-C_6F_5), -148.6 (br, 6F, *p*-C_6F_5), -159.6 (br, 12F, *m*-C_6F_5). IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1738.8 (Al-H), 1642.7, 1533.8, 1511.4, 1453.7, 1354.5, 1267.9, 1066.2, 950.9. HRMS (*m/z*): $[⅓M + MeCN + Na]^+$ Calcd. for $C_{14}H_4AlF_{10}NNa^+$: 425.9892; Found: 425.9897.

Synthesis of **2**:



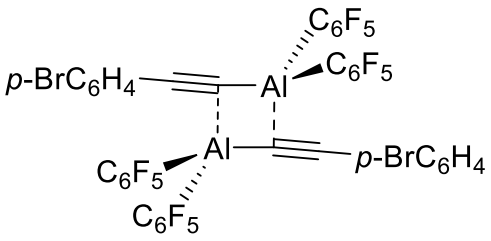
A mixture of **1** (25.9 mg, 0.0715 mmol) and DMAP (17.5 mg, 0.143 mmol) was stirred in 5 mL of toluene for 2 h. The solvent was removed under vacuum, and the resulting white solid was washed with 3 x 2 mL pentane and dried *in vacuo* to yield crude product of **2** (32 mg, 74 % yield). Crystals suitable for X-ray study were grow from a saturate **2** solution in C_6H_5Cl layered with a saturated pentane solution of DMAP at -35 °C overnight. ^{1}H NMR (400 MHz, C_6D_6, 298K): δ 8.37 (s, br, 4H, *o*-NC_5H_4), 5.83 (s, br, 4H, *m*-NC_5H_4), 2.08 (s, 12H, $N(CH_3)_2$). $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298K): δ 154.5 (s, *p*-NC_5H_4), 148.0 (s, *o*-NC_5H_4), 106.4 (s, *p*-NC_5H_4), 38.0 (s, $N(CH_3)_2$). $^{19}F\{^{1}H\}$ NMR (377 MHz, C_6D_6, 298K): δ -121.7 (m, 4F, *o*-C_6F_5), -158.1 (t, J = 20 Hz, 2F, *p*-C_6F_5), -162.7 (p, J = 13 Hz, 4F, *m*-C_6F_5). $^{27}Al\{^{1}H\}$ NMR (104 MHz, C_6D_6, 298K): δ 114.9 (s, br). IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1804.7, 1637.6, 1601.6, 1587.2, 1509.4, 1452.2, 1375.1, 1270.9, 1072.9, 956.5, 772.1. HRMS (*m/z*): $[M + Na]^+$ Calcd. for $C_{26}H_{21}AlF_{10}N_4Na^+$: 629.1314; Found: 629.1325.

Synthesis of **3**:



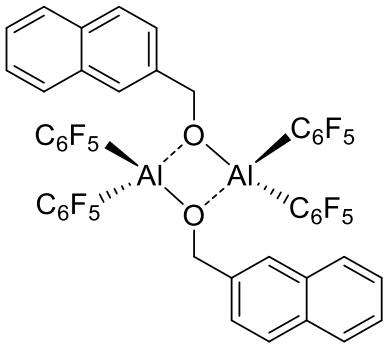
At -30 °C, a solution of **1** (72 mg, 0.067 mmol) in toluene (2 mL) was added slowly to a stirring solution of ^{t}BuOH (15 mg, 0.2 mmol) in toluene (2 mL). Gas evolution was observed immediately. The mixture was stirred for 15 minutes and then concentrated to about 1 mL. Hexane (0.5 mL) was added in and colorless crystals of **3** (118 mg 68% yield) were obtained after storing the mixture at -30°C overnight. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 1.13 (s, 18 H, C*H*$_3$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 150.9-149.0 (m, *o*-*C*$_6$F$_5$), 143.6-141.5 (m, *p*-*C*$_6$F$_5$), 138.3-136.3 (m, *m*-*C*$_6$F$_5$), 112.5 (br, *i*-*C*$_6$F$_5$), 83.3 (*C*Me$_3$), 30.0 (C*Me*$_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$, ppm): δ -119.4 (d, *J* = 14.5 Hz, 8F, *o*-C$_6$*F*$_5$), -149.0 (t, *J* = 20.3 Hz, 4F, *p*-C$_6$*F*$_5$), -160.3 (t, *J* = 17.6 Hz, 8F, *m*-C$_6$*F*$_5$). IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1636.3, 1514.6, 1460.1, 1373.7, 1271.2, 1069.4, 957.3. HRMS (*m/z*): [½M + MeCN + Na]$^{+}$ Calcd. for $C_{18}H_{12}AlF_{10}NNaO^{+}$, 498.0467; Found: 498.0450.

Synthesis of **4**:



At -30 °C, a solution of **1** (72 mg, 0.067 mmol) in toluene (2 mL) was added slowly to a stirring solution of *4*-bromophenylacetylene (43mg, 0.2 mmol) in toluene (2 mL). The reaction mixture became violet after stirring for 2 hours at room temperature. Then the toluene was concentrated to about 1 mL and hexane (0.5 mL) was added. Colorless crystals of **4** (30% yield) were obtained after storing the mixture at -30°C overnight. **4** slowly decomposed to brown oil in vacuum at ambient temperature. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.23 (d, J = 8.4 Hz, 4 H, Ar*H*), 6.82 (d, J = 8.4 Hz, 4 H, Ar*H*). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 151.1-149.3 (m, *o*-C_6F_5), 144.0-141.4 (m, *p*-C_6F_5), 138.4-136.2 (m, *m*-C_6F_5), 136.8, 133.1, 131.7, 115.2 (Ar), 110.9 (br, *i*-C_6F_5), 85.5 (*C*≡CAl), 78.8 (C≡*C*Al). ^{19}F{^{1}H} NMR (470 MHz, C_6D_6, ppm) δ -122.4 (d, J = 17.7 Hz, 8F, *o*-C_6F_5), -149.1 (t, J = 19.5 Hz, 4F, *p*-C_6F_5), -159.8 - -159.9 (m, 8F, *m*-C_6F_5). IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 2724.1, 2164.8, 2061.2, 1642.7, 1581.7, 1460.1, 1370.5, 1275.8, 1072.6, 723.5. HRMS (*m/z*): [½M + Na]$^{+}$ Calcd. for $C_{20}H_4AlBrF_{10}Na^{+}$: 562.9044; Found: 562.9051.

Synthesis of **5**:

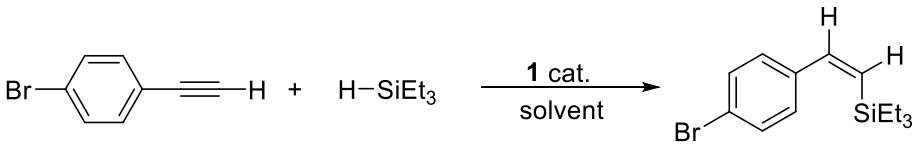


A solution of **1** (72 mg, 0.066 mmol) in in toluene (2 mL) was added slowly into a stirring solution of 2-naphthaldehyde (0.034 g, 0.2 mmol) in toluene (2 mL) at -30 °C. The reaction mixture was warmed to room temperature slowly and the solution became yellow. The resulting reaction mixture was concentrated to 1 mL. The pale-yellow precipitates were isolated and washed with pentane (0.5 mL). Colorless crystals (75 mg, 70.4% yield) were obtained after storing the chlorobenzene solution of **5** at -30 °C overnight. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.54, (s, 1 H, Ar*H*), 7.31-7.28 (m, 2 H, Ar*H*), 7.23 (d, *J* = 8.4 Hz, 1 H, Ar*H*), 7.12-7.07 (m, 3 H, Ar*H*), 4.99 (s, 2 H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 149.7-147.8 (m, *o*-C_6F_5), 142.5-140.5 (m, *p*-C_6F_5), 137.1-134.9 (m, *m*-C_6F_5), 132.9, 132.0, 130.8, 129.0, 128.6, 128.3, 126.5, 126.3, 125.0, 124.6 (Ar), 108.9 (br, *i*-C_6F_5), 68.4 (CH_2). ^{19}F{^{1}H} NMR (470 MHz, C_6D_6, ppm) δ -122.8 (dd, *J* = 26.2, 9.9 Hz, 8F, *o*-C_6F_5), -149.9 (t, *J* = 19.7 Hz, 4F, *o*-C_6F_5), -160.2- -160.3 (m, 8F, *p*-C_6F_5). IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1636.7, 1512.8, 1460.4, 1377.8, 1072.1, 956.4, 719.5. HRMS (*m/z*): [½M + Cl]$^-$ Calcd. for $C_{23}H_9AlClF_{10}O^-$, 553.0003; Found: 553.0007.

General Catalytic Procedures for the Hydrosilylation of Alkynes and Alkenes:

In an argon atmosphere glovebox, alkyne (0.5 mmol), silane (0.55 mmol), solvent (0.6 mL) and catalytical amount of **1** were loaded in a J-Young NMR tube. The tube was sealed securely before being brought outside of the glove box, shaken and monitored by NMR spectroscopy. The solution was filtrated and the products were isolated by removing volatiles under vacuum for more than 6 hours.

Table S1. Optimization of the hydrosilylation conditions[a]



6b **7b**

entry	catalyst loading (mol%)	solvent	time (h)	yield (%)
1	0.5	toluene	40	92
2	0.5	fluorobenzene	40	96
3	0.5	chlorobenzene	40	94
4	0.5	C_6D_6	40	99
5	1	C_6D_6	40	99
6	0.3	C_6D_6	40	90
7	0.5	C_6D_6	0.25	54
8	0.5	C_6D_6	3	76
9	0.5	C_6D_6	8	93
10	0.5	C_6D_6	24	95

[a] Reaction conditions: alkyne or alkene (0.50 mmol), hydrosilane (0.55 mmol), solvent (0.60 mL), room temperature.

Spectral Data for **7a** – **7g**

7a (*Z*)-1-triethylsilyl-2-phenylethene [6] *(CAS: 75645-33-9)*: ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.51 (d, *J* = 15.3 Hz, 1H, C*H*=CHSi), 7.36-7.29 (m, 5H, Ar*H*), 5.82 (d, *J* = 15.2 Hz, 1H, CH=C*H*Si), 0.92 (t, *J* = 7.9 Hz, 9H, $SiCH_2CH_3$), 0.60 (q, *J* = 7.9 Hz, 6H, $SiCH_2CH_3$). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 147.8 (*C*H=CHSi), 140.5, 129.5 (*Ar*), 127.9 (*Ar,* overlapped), 127.9 (*Ar,* overlapped), 127.3 (CH=*C*HSi), 7.5, 4.8 (Si*Et*$_3$). HRMS (*m/z*): $[M+H]^+$ Calcd. for $C_{14}H_{23}Si^+$:219.1564; Found: 219.1561.

7b (*Z*)-1-triethylsilyl-2-(4-bromophenyl)ethene[6] *(CAS: 2243131-75-9)*: ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.35 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.27 (d, *J* = 15.3 Hz, 1H, C*H*=CHSi), 7.06 (d, *J* = 8.4 Hz, 2H, Ar*H*), 5.72 (d, *J* = 15.3 Hz, 1H, CH=C*H*Si), 0.80 (t, *J* = 7.9 Hz, 9H, $SiCH_2CH_3$), 0.47 (q, *J* = 7.9 Hz, 6H, $SiCH_2CH_3$). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 146.3 (*C*H=CHSi), 139.1, 131.0 (*Ar*), 130.5 (CH=*C*HSi), 129.4, 121.3 (*Ar*), 7.4, 4.7 (Si*Et*$_3$). HRMS (*m/z*): $[M+MeCN+H]^+$ Calcd. for $C_{16}H_{25}BrSiN^+$:338.0934; Found: 338.0927.

7c (*Z*)-1-triethylsilyl-2-(2-methylphenyl)ethene *(New Compound)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.45 (d, *J* = 15.1 Hz, 1H, C*H*=CHSi), 7.26 (d, *J* = 7.0 Hz, 1H, Ar*H*)，7.08-7.01 (m, 2H, Ar*H*), 6.98 (d, *J* = 7.5 Hz, 1H, Ar*H*), 5.82 (d, *J* = 15.1 Hz, 1H, CH=C*H*Si), 2.13 (s, 3H, ArCH_3), 0.90 (t, *J* = 8.0 Hz, 9H, $SiCH_2CH_3$), 0.51 (q, *J* = 7.9 Hz,6H, $SiCH_2CH_3$). $^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_6, ppm): δ 148.0 (*C*H=CH), 140.6, 135.7, 129.7, 129.6, 128.7, 128.0 (*Ar*), 125.6 (CH=*C*H), 19.8 (Ar*Me*), 7.7, 5.0 (Si*Et*$_3$). HRMS (*m/z*): $[M+H]^+$ Calcd. for $C_{15}H_{25}Si^+$: 233.1720; Found: 233.1720.

7d (Z)-1-triethylsilyl-2-(2-naphthyl)ethene *(New Compound)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.75 (s, 1H, Ar*H*), 7.60-7.56 (m, 3H, Ar*H* and C*H*=CHSi), 7.42 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.26-7.20 (m, 2H, Ar*H*), 5.88 (d, *J* = 15.2 Hz, CH=C*H*Si), 0.93 (t, *J* = 7.9 Hz, 9H, $SiCH_2CH_3$), 0.64 (q, *J* = 7.9 Hz, 6H, $SiCH_2CH_3$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 148.4 (*C*H=CH), 138.3, 133.7, 133.3, 129.8, 128.3, 128.0, 127.2, 126.5, 126.4, 126.2 (*Ar*), 7.8, 5.3 (Si*Et*$_3$). HRMS (*m/z*): $[M+MeCN+H]^+$ Calcd. for $C_{20}H_{28}SiN^+$: 310.1986; Found: 310.1984.

7e (*Z*)-1-triethylsilyl-1-hexene[6] *(CAS: 62621-38-9)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 6.41 (dt, *J* = 14.4, 7.2 Hz, 1H, CH_2CH=CH), 5.51 (d, *J* = 14.1 Hz, 1H, CH=C*H*Si), 2.11 (q, *J* = 7.0 Hz, 2H, CH_2CH=CH), 1.36-1.26 (m, 4H, $CH_2CH_2CH_3$), 1.02 (t, *J* = 8.0 Hz, 9H, $SiCH_2CH_3$), 0.87 (t, *J* = 7.1 Hz, 3H, $CH_2CH_2CH_3$), 0.67 (q, *J* = 7.9 Hz, 6H, $SiCH_2CH_3$). ^{13}C{^{1}H}NMR (125 MHz, C_6D_6, ppm): δ 150.7, 125.2 (*C*H=*C*H), 34.3, 32.4, 22.9, 14.3 ($CH_2CH_2CH_2CH_3$), 7.9, 5.2 (Si*Et*$_3$).HRMS (*m/z*): $[M+MeCN+H]^+$ Calcd. for $C_{12}H_{26}SiN^+$: 212.1829; Found: 212.1825.

7f (*Z*)-1-ethyldimethylsilyl-1,2-diphenylethene *(New Compound)*: ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.46-7.37 (m, 8H, Ar*H* and C*H*=CHSi), 7.32-7.29 (m, 3H, Ar*H*), 0.87 (t, *J* = 7.9 Hz, 3H, $SiCH_2CH_3$), 0.51 (q, *J* = 7.9 Hz, 2H, $SiCH_2CH_3$), 0.01 (s, 6H, $Si(CH_3)_2$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 147.3, 146.5 (*C*=*C*), 145.4, 140.0, 128.5, 127.9, 127.8, 127.2, 127.1, 125.7 (*Ar*), 8.3, 7.3 (Si*Et*), -1.6 (Si*Me*$_2$). HRMS (*m/z*): $[M+MeCN+H]^+$ Calcd. for $C_{20}H_{28}SiN^+$: 310.1986; Found: 310.1984. HRMS (*m/z*): $[M+H]^+$ Calcd. for $C_{20}H_{27}Si^+$:295.1877; Found: 295.1873.

7g triethyl(phenethyl)silane[7] *(CAS: 14355-62-5)*: ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.40 (t, *J* = 7.5 Hz, 2H, Ar*H*), 7.34 (d, *J* = 7.3 Hz, 2H, Ar*H*), 7.29 (t, *J* = 7.2 Hz, 1H, Ar*H*), 2.78-2.74 (m, 2H, CH_2CH_2Si), 1.11 (t, *J* = 8.0 Hz, 9H, $SiCH_2CH_3$), 1.06-1.02 (m, 2H, CH_2CH_2Si),

0.70 (q, *J* = 8.0 Hz, 6H, SiC*H*$_2$CH$_3$). ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$, ppm): δ 145.7, 128.4, 127.8, 125.6 (*Ar*), 30.2 (*C*H$_2$CH$_2$Si), 13.8 (CH$_2$*C*H$_2$Si), 7.5, 3.4 (Si*Et$_3$*). HRMS (*m/z*): [M+MeCN+H]$^+$ Calcd. for $C_{16}H_{28}SiN^+$:262.1986; Found: 262.1984.

7h 2-(triethylsilyl)bicyclo[2.2.1]heptane[8] *(CAS: 164859-22-7)*: ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.21 (br, 1H, norbornane*H*), 2.14 (br, 1H, norbornane*H*), 1.53-1.51 (m, *2*H, norbornane*H*), 1.40-1.31 (m, *2*H, norbornane*H*), 1.21-1.17 (m, 3H, norbornane*H*), 1.10-1.08 (m, 1H, norbornane*H*), 0.96 (t, *J* = 7.9 Hz, 3H, SiCH$_2$C*H$_3$*), 0.52-0.47 (m, 1H, norbornane*H*, overlapped), 0.47 (q, *J* = 7.8 Hz, 2H, SiC*H$_2$*CH$_3$), -0.05 (d, *J* = 10.2 Hz, 6H, Si*Me$_2$*). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 38.3, 38.2, 37.3, 34.6, 32.8, 28.3, 28.2 (norbornane*C*), 7.8, 6.4 (Si*Et*), -4.7, -4.9 (Si*Me$_2$*). HRMS (*m/z*): [M+MeCN+Na]$^+$ Calcd. for $C_{13}H_{25}SiNNa^+$: 246.1648; Found: 246.1642.

X-ray Crystallography

Table S2. Crystal data and structure refinement details for compounds **1-3**

	1	**2**	**3**
CCDC	2164047	2175593	2177643
Empirical formula	$C_{36}H_3Al_3F_{30}$	$C_{26}H_{21}AlF_{10}N_4$	$C_{32}H_{18}Al_2F_{20}O_2$
Formula weight	1086.32	606.45	868.42
Temperature, K	100	150.15	150.0
Crystal system	triclinic	monoclinic	triclinic
Space group	*P*-1	$P2_1/c$	*P*-1
a, Å	10.9346(10)	11.6102(5)	12.0639(4)
b, Å	11.6435(11)	25.9241(10)	18.5498(6)
c, Å	15.7246(14)	11.8202(5)	24.2232(8)
α, deg	94.033(5)	90	84.238(2)
β, deg	104.990(5)	113.3690(2)	76.575(2)
γ, deg	99.074(5)	90	72.095(2)
V, Å^3	1896.7(3)	3265.9(2)	5014.8(3)
Z	2	4	6
D_{calcd}, g/cm^3	1.902	1.233	1.725
μ/mm^{-1}	2.619	0.319	2.141
F(000)	1056.0	1232.0	2592.0
θ range, °	2.929 – 71.641	2.035 – 28.283	3.082 – 68.232
Index ranges	$-13 \le h \le 13$	$-15 \le h \le 15$	$-14 \le h \le 14$
	$-14 \le k \le 14$	$-34 \le k \le 34$	$-22 \le k \le 22$
	$-19 \le l \le 19$	$-15 \le l \le 15$	$-29 \le l \le 29$
Reflections collected	66190	73711	95193
Independent reflections	7317	8095	18346
	R_{int} = 0.0984	R_{int} = 0.1038	R_{int} = 0.0684
	R_{sigma} = 0.0574	R_{sigma} = 0.0669	R_{sigma} = 0.0484
Data/restraints/parameters	7317/0/634	8095/0/373	18346/0/1531
Goodness-of-fit on F^2	1.065	1.004	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0654	R_1 = 0.0595	R_1 = 0.0946
	wR_2 = 0.2023	wR_2 = 0.1546	wR_2 = 0.2705
Final R indexes [all data]	R_1 = 0.0935	R_1 = 0.1146	R_1 = 0.1074
	wR_2 = 0.2196	wR_2 = 0.1810	wR_2 = 0.2814
Largest diff. peak/hole, e/Å^{-3}	0.66/-0.47	0.70/-0.28	1.17/-0.56

Table S3. Crystal data and structure refinement details for compounds **4** and **5**

	4	**5**
CCDC	2164050	2175577
Empirical formula	$C_{40}H_8Al_2Br_2F_{20}$	$C_{29}H_{14}AlClF_{10}O$
Formula weight	1082.24	630.83
Temperature, K	100.00	150.00
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a, Å	10.8687(4)	11.3773(5)
b, Å	11.0798(5)	11.6740(5)
c, Å	11.7308(5)	11.8396(5)
α, deg	86.250(2)	110.793(2)
β, deg	63.214(2)	104.745(2)
γ, deg	61.222(2)	107.462(2)
V, Å^3	1084.39(8)	1282.28(10)
Z	1	2
D_{calcd}, g/cm^3	1.657	1.634
μ/mm^{-1}	3.836	2.552
F(000)	524.0	632.0
θ range, °	4.303 – 70.315	4.368 – 70.132
Index ranges	$-13 \le h \le 13$	$-13 \le h \le 13$
	$-13 \le k \le 13$	$-14 \le k \le 14$
	$-14 \le l \le 14$	$-13 \le l \le 14$
Reflections collected	38344	17723
Independent reflections	4129	4860
	R_{int} = 0.0431	R_{int} = 0.0421
	R_{sigma} = 0.0191	R_{sigma} = 0.0341
Data/restraints/parameters	4129/1/299	4860/1/379
Goodness-of-fit on F^2	1.071	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0298	R_1 = 0.0469
	wR_2 = 0.0839	wR_2 = 0.1376
Final R indexes [all data]	R_1 = 0.0311	R_1 = 0.0496
	wR_2 = 0.0854	wR_2 = 0.1395
Largest diff. peak/hole, e/Å^{-3}	0.41/-0.39	1.18/-0.69

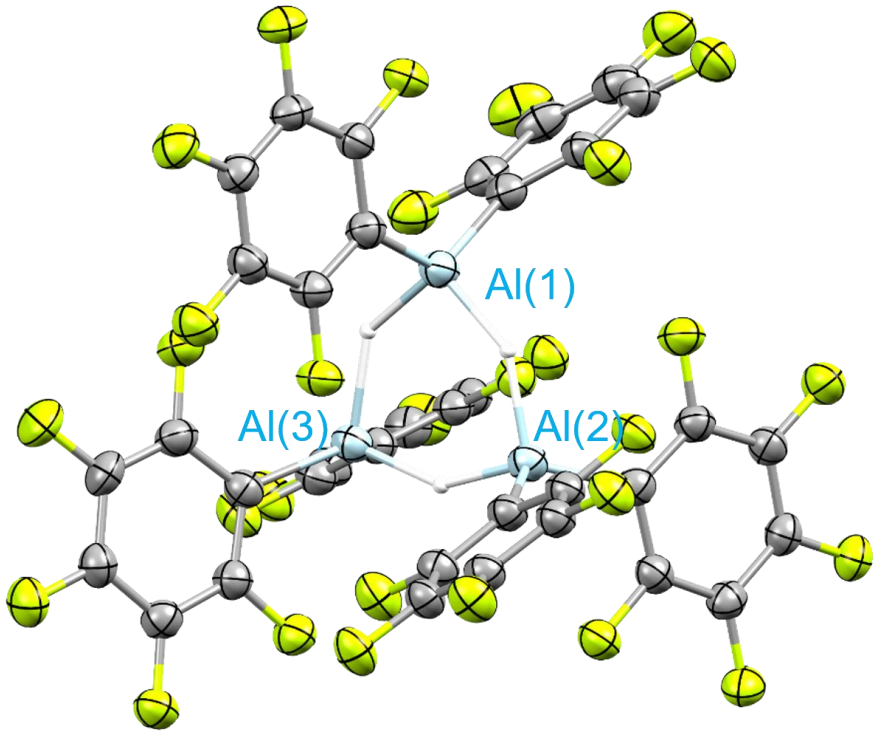


Figure S1. Thermal ellipsoid plot for **1** with the anisotropic displacement parameters depicted at the 30% probability level.

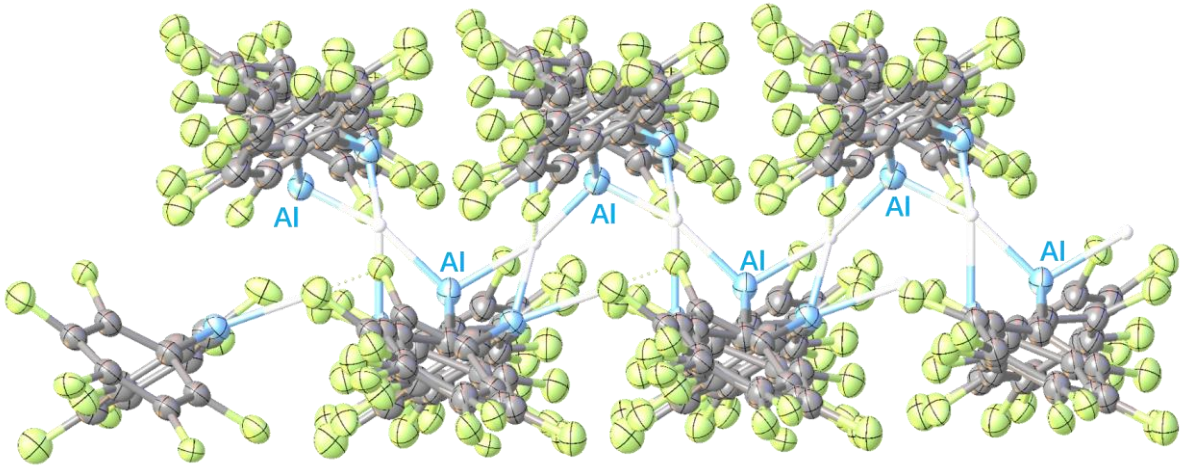


Figure S2. Thermal ellipsoid plot for **1B** with the anisotropic displacement parameters depicted at the 30% probability level.

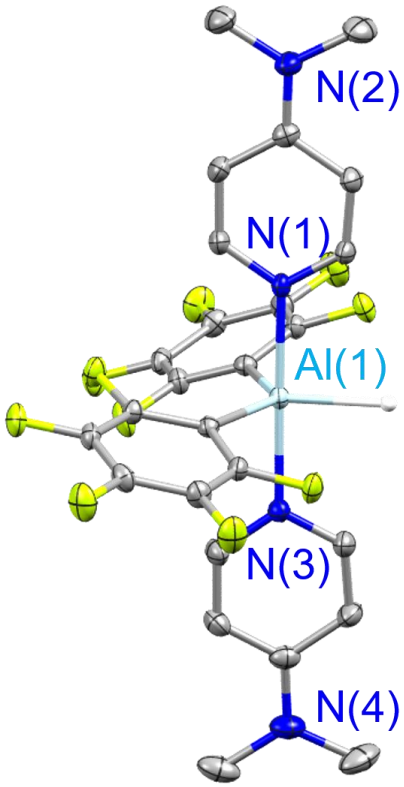


Figure S3. Thermal ellipsoid plot for **2** with the anisotropic displacement parameters depicted at the 30% probability level. Hydrogen atoms except that linked to Al are omitted for clarity.

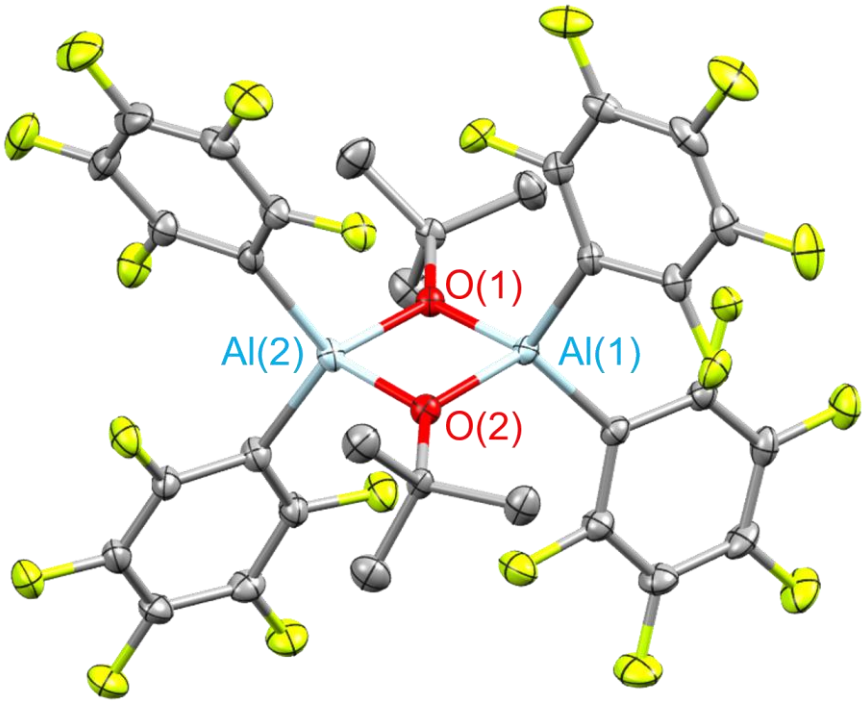


Figure S4. Thermal ellipsoid plot for **3** with the anisotropic displacement parameters depicted at the 30% probability level. Hydrogen atoms are omitted for clarity.

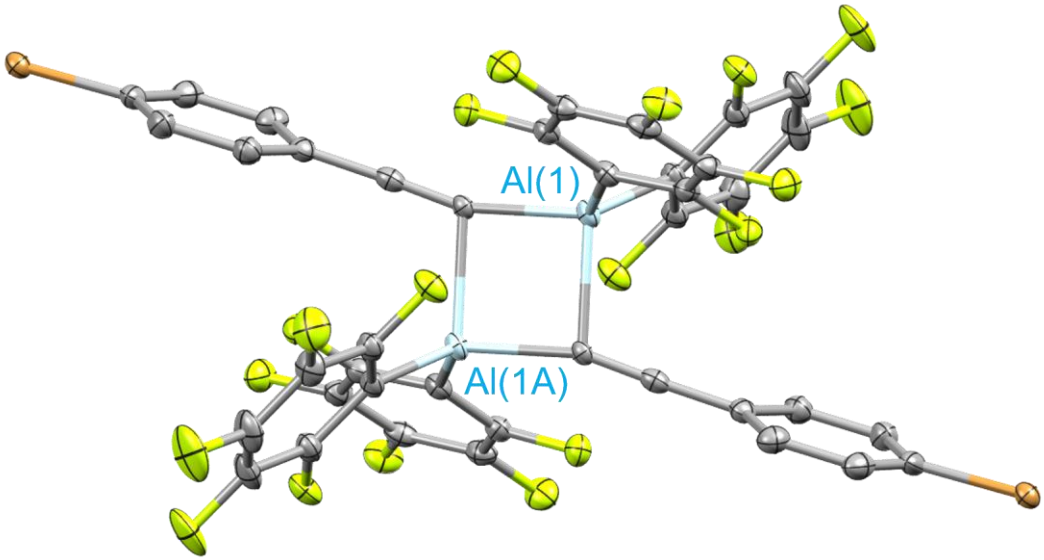


Figure S5. Thermal ellipsoid plot for **4** with the anisotropic displacement parameters depicted at the 30% probability level. Disorders and hydrogen atoms are omitted for clarity.

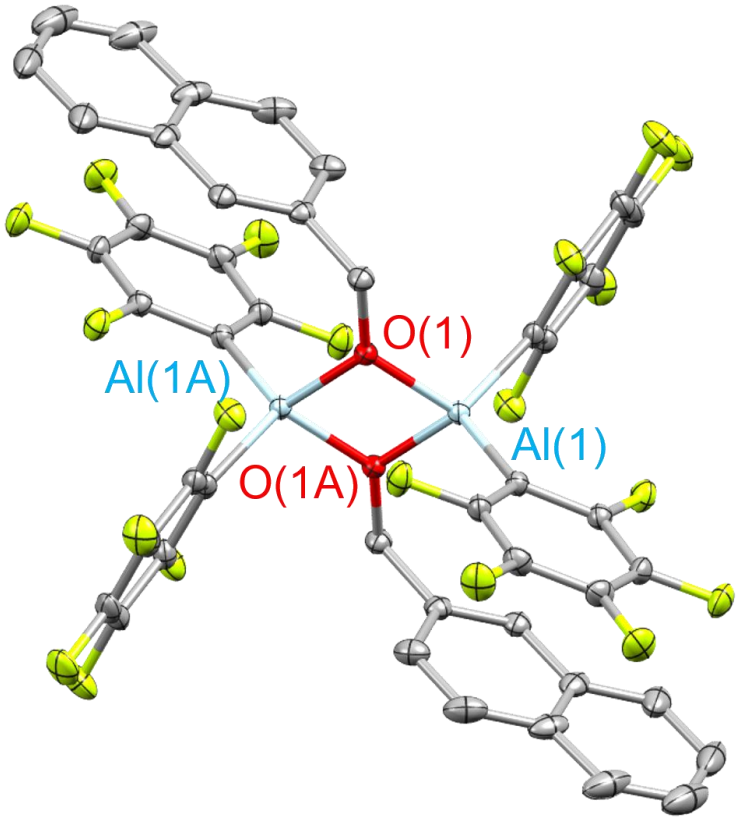


Figure S6. Thermal ellipsoid plot for **5** with the anisotropic displacement parameters depicted at the 30% probability level. Hydrogen atoms are omitted for clarity.

NMR Spectra

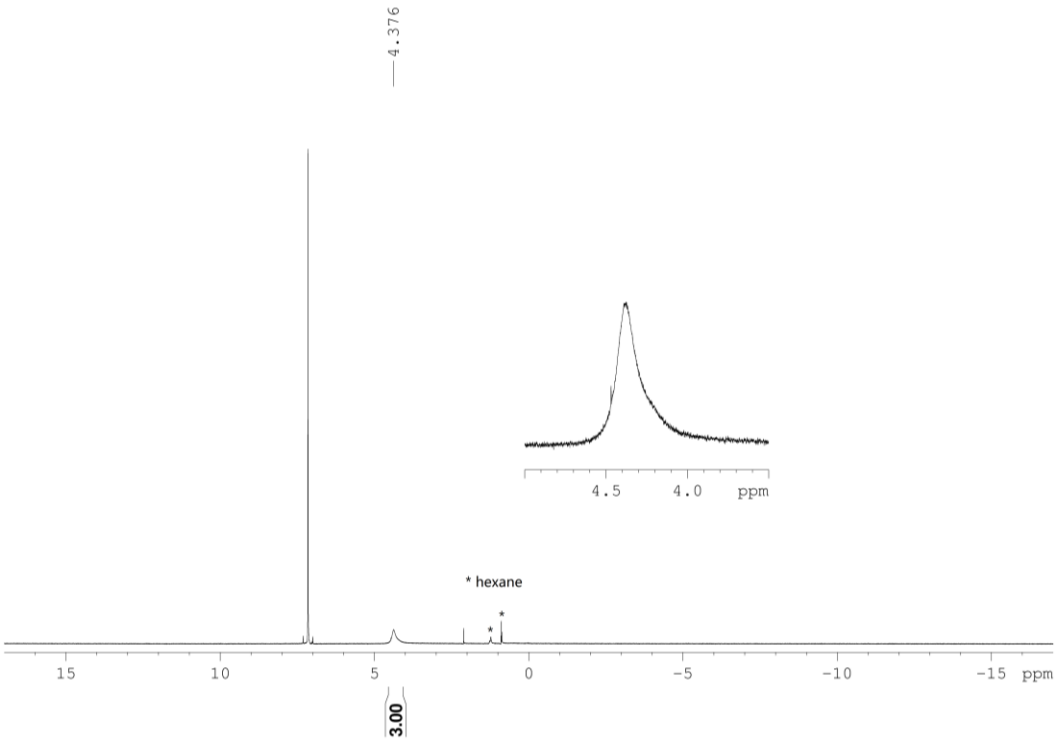


Figure S7. ^{1}H NMR spectrum of **1** in C_6D_6

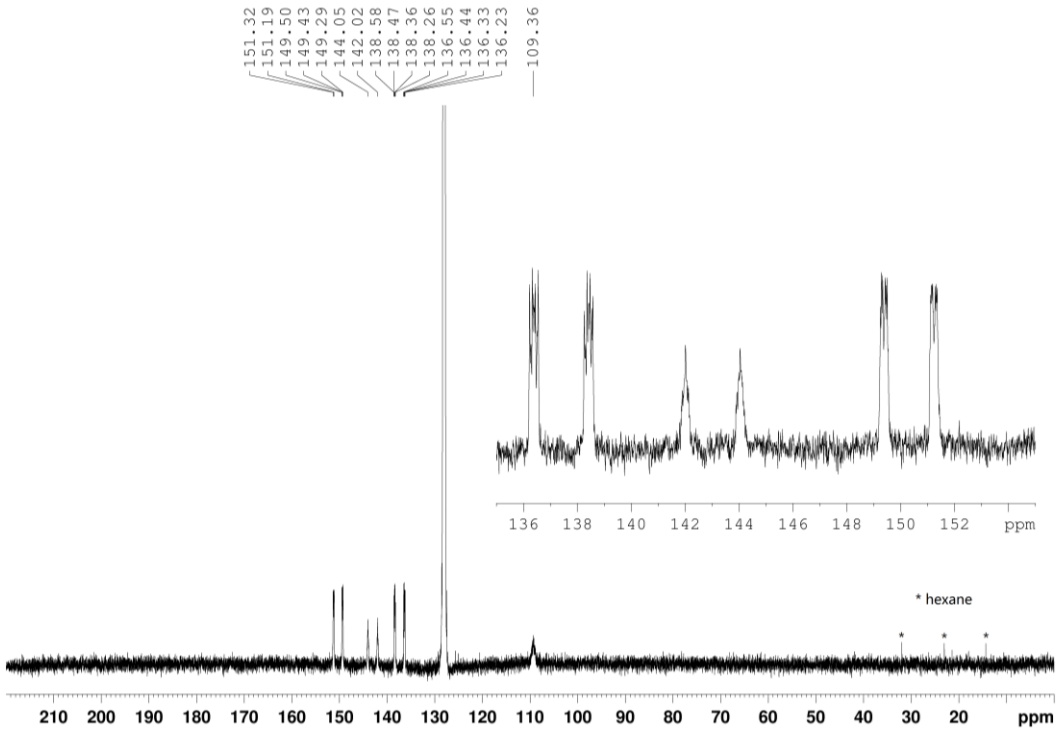


Figure S8. ^{13}C NMR spectrum of **1** in C_6D_6

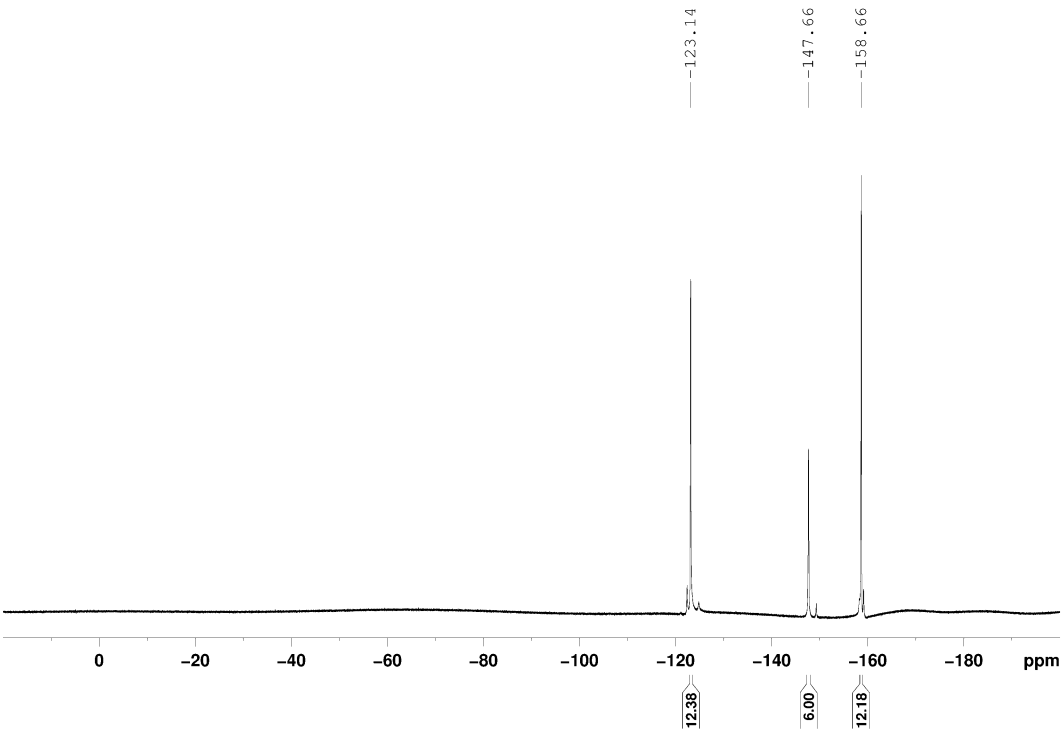


Figure S9. ^{19}F NMR spectrum of **1** in C_6D_6

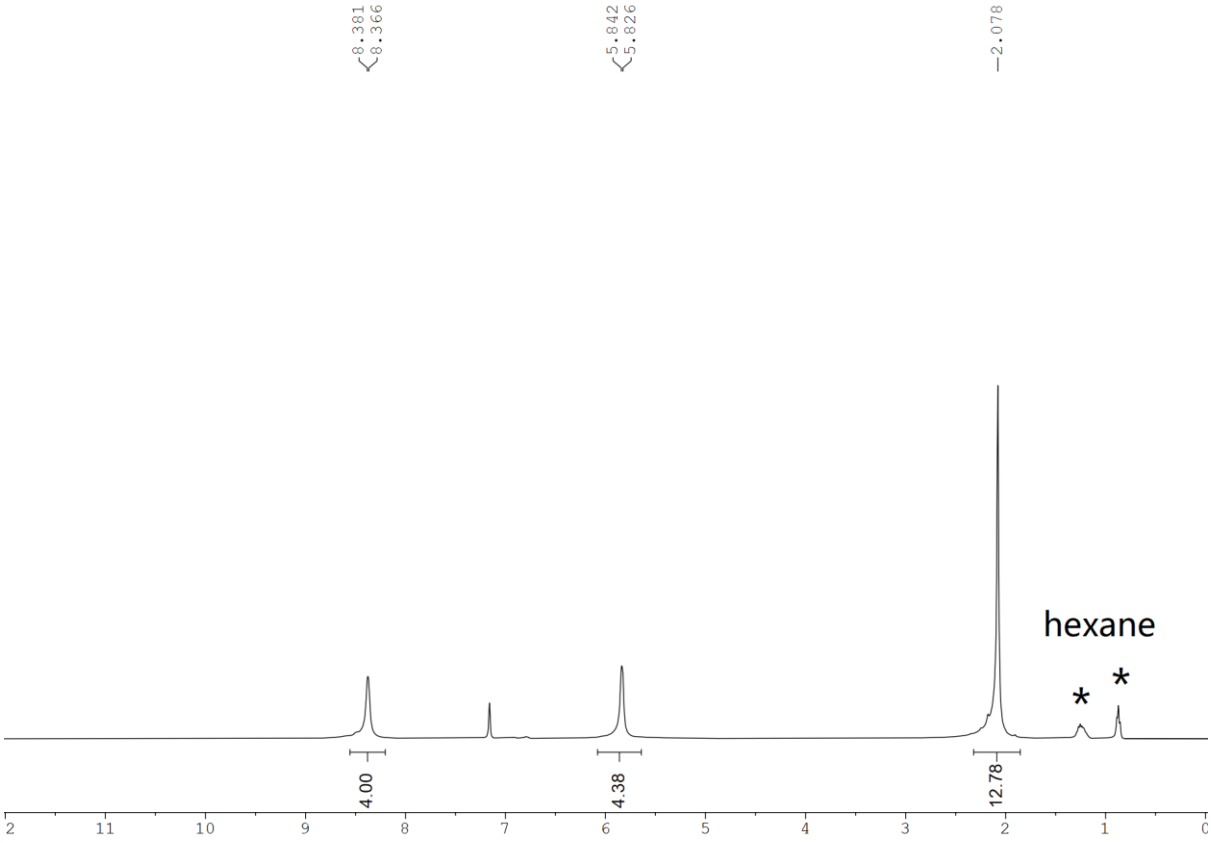


Figure S10. ^{1}H NMR spectrum of **2** in C_6D_6

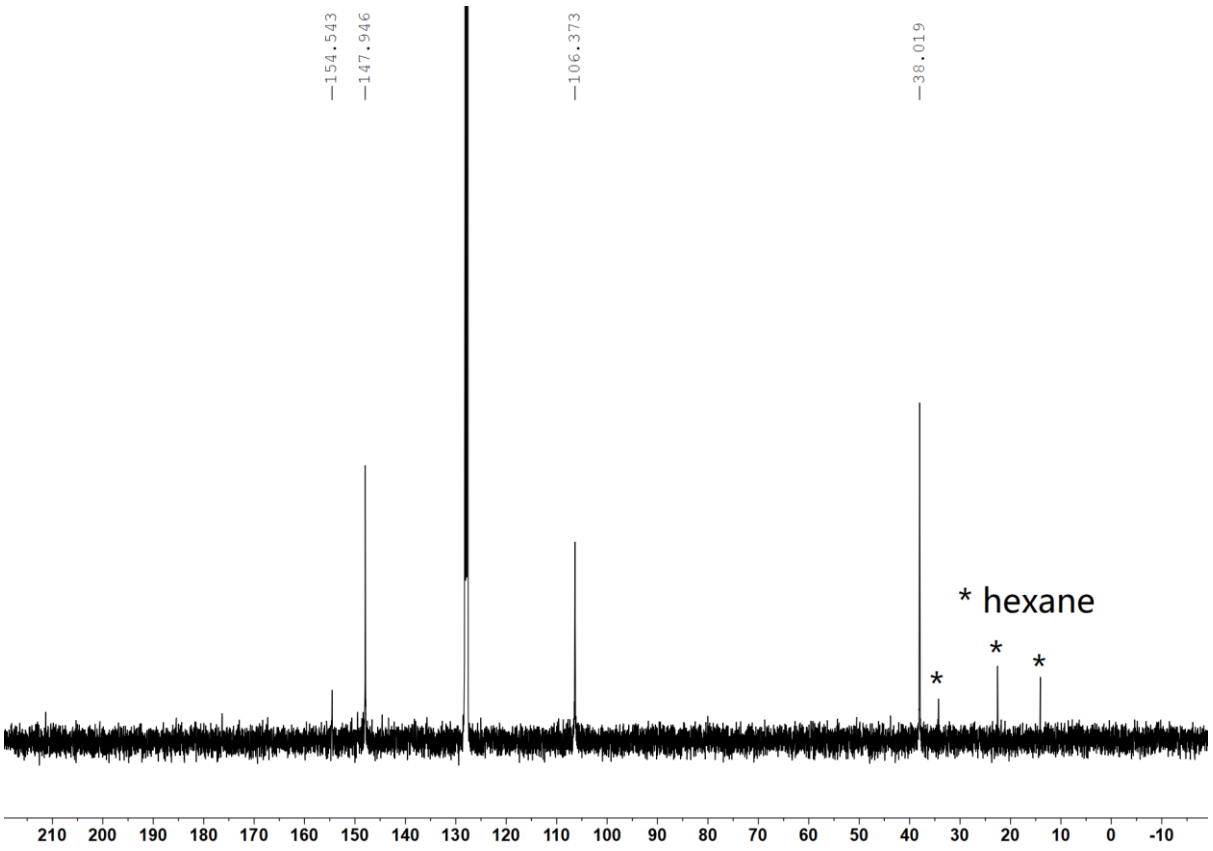


Figure S11. ^{13}C NMR spectrum of **2** in C_6D_6

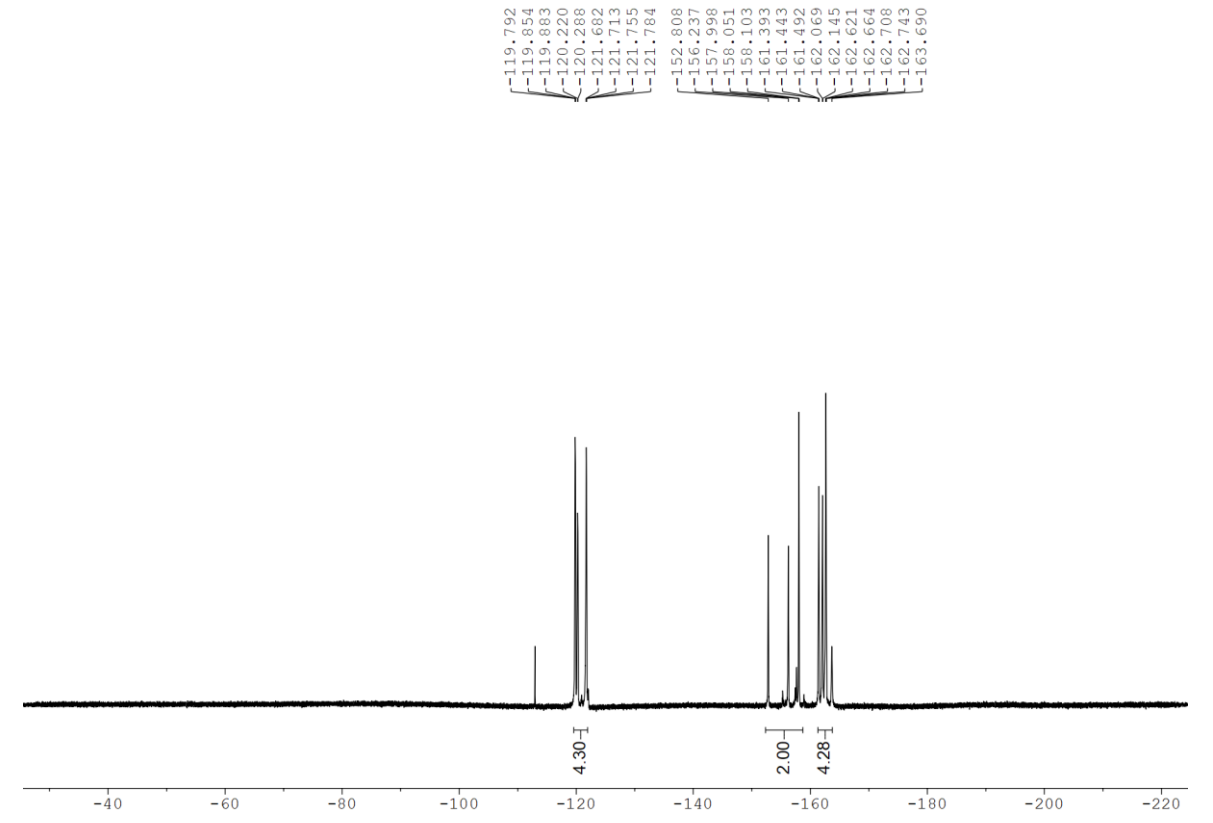


Figure S12. ^{19}F NMR spectrum of **2** in C_6D_6

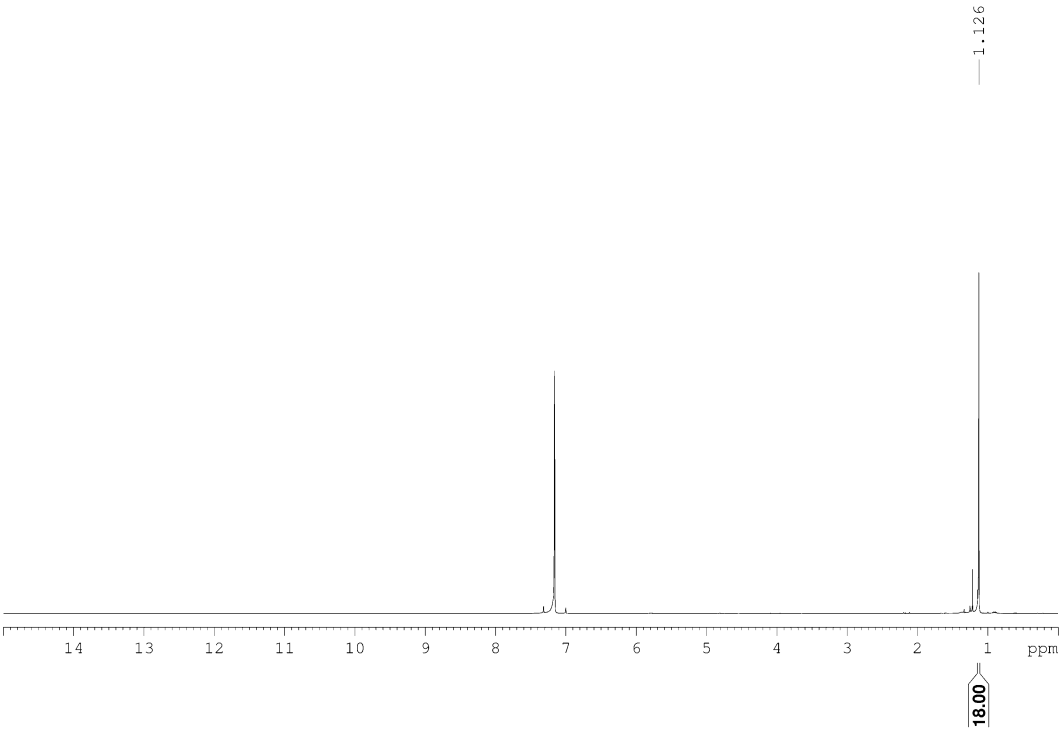


Figure S13. ^{1}H NMR spectrum of **3** in C_6D_6

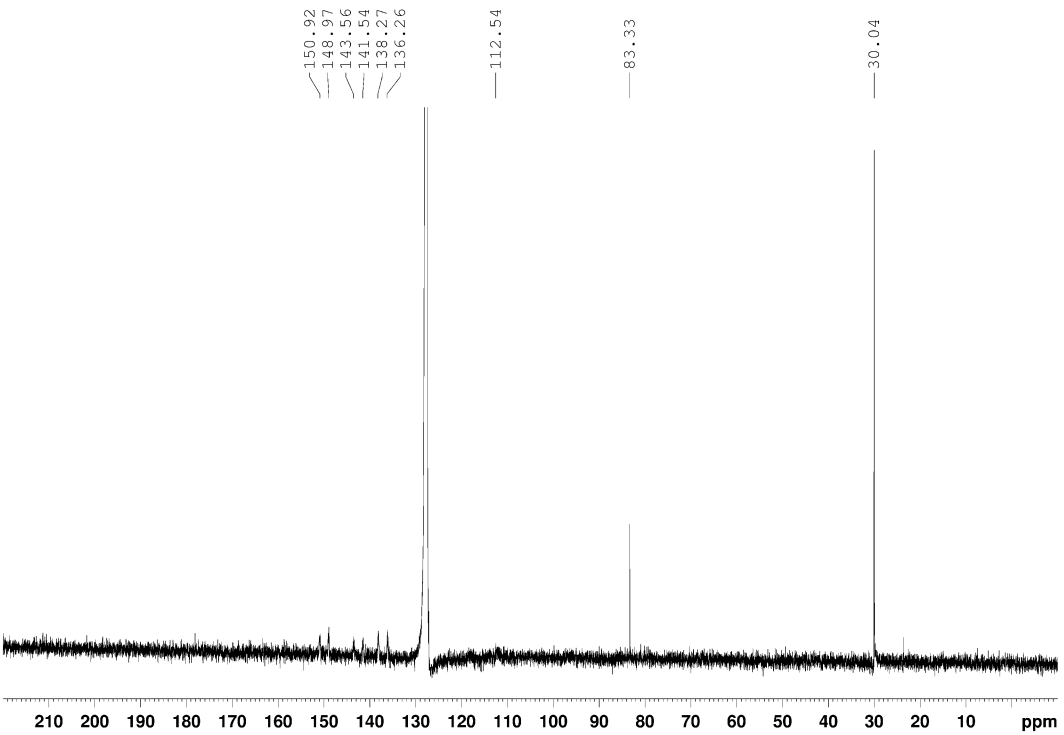


Figure S14. ^{13}C NMR spectrum of **3** in C_6D_6

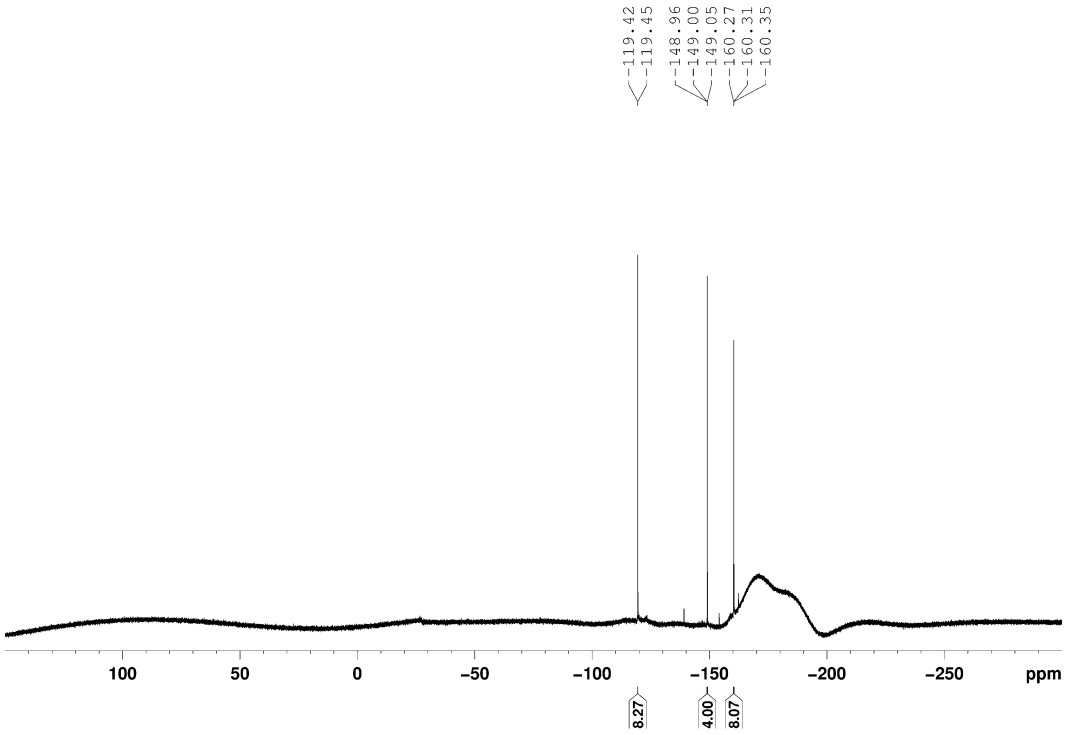


Figure S15. ^{19}F NMR spectrum of **3** in C_6D_6

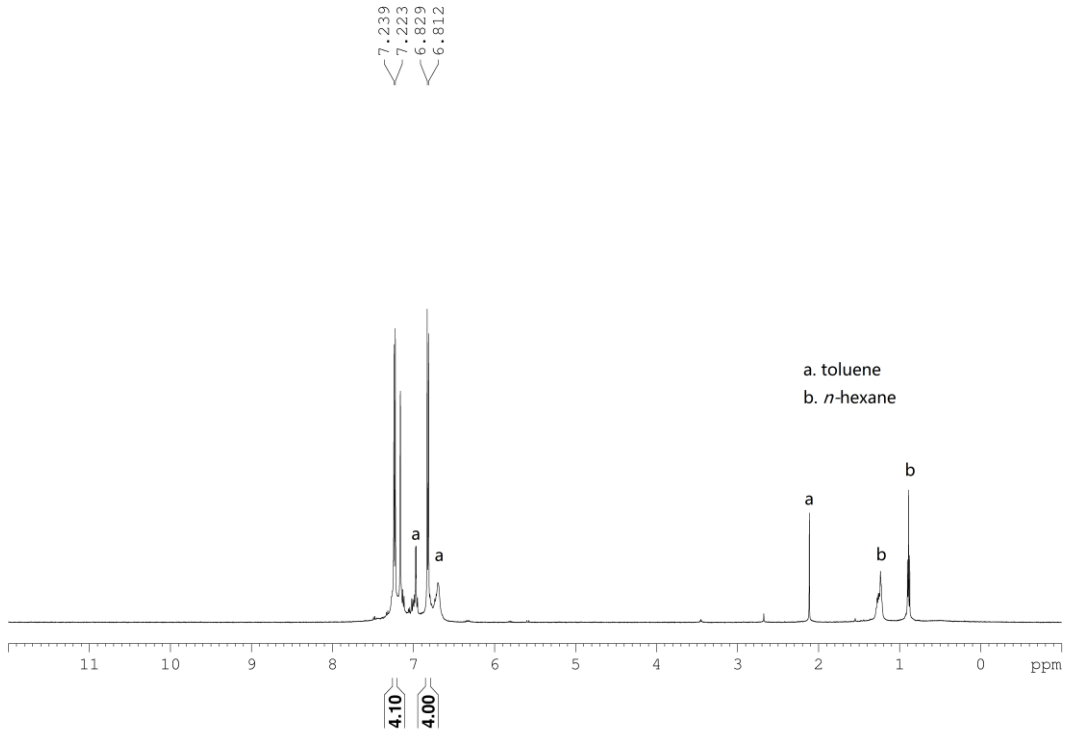


Figure S16. ^{1}H NMR spectrum of **4** in C_6D_6

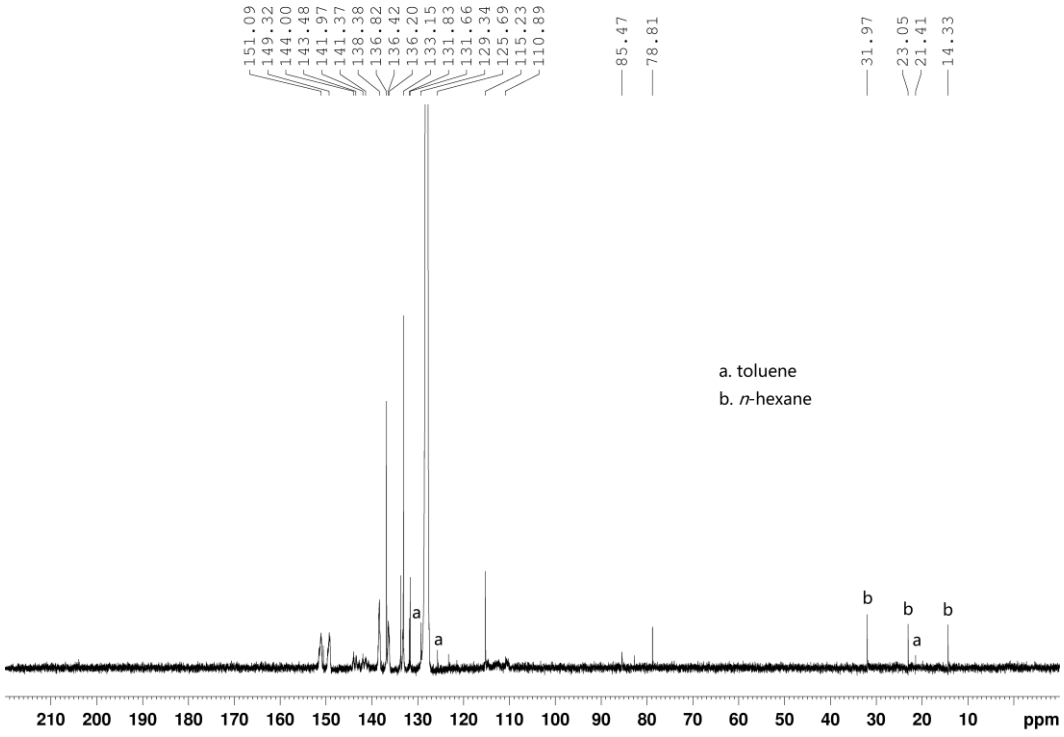


Figure S17. ^{13}C NMR spectrum of **4** in C_6D_6

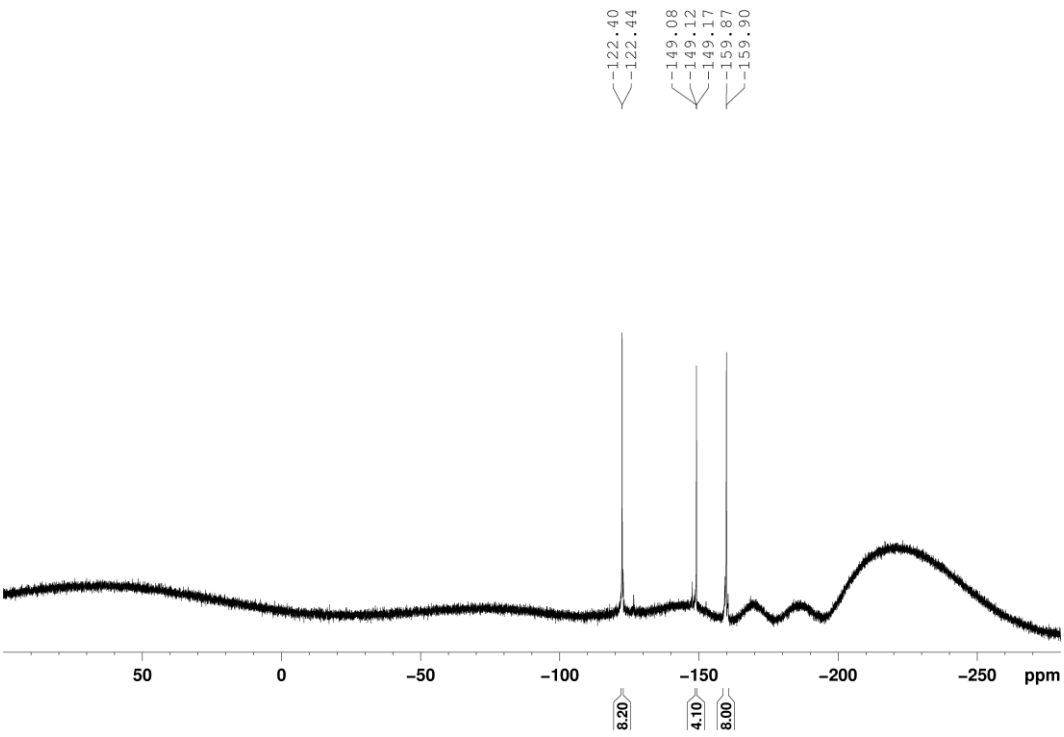


Figure S18. ^{19}F NMR spectrum of **4** in C_6D_6

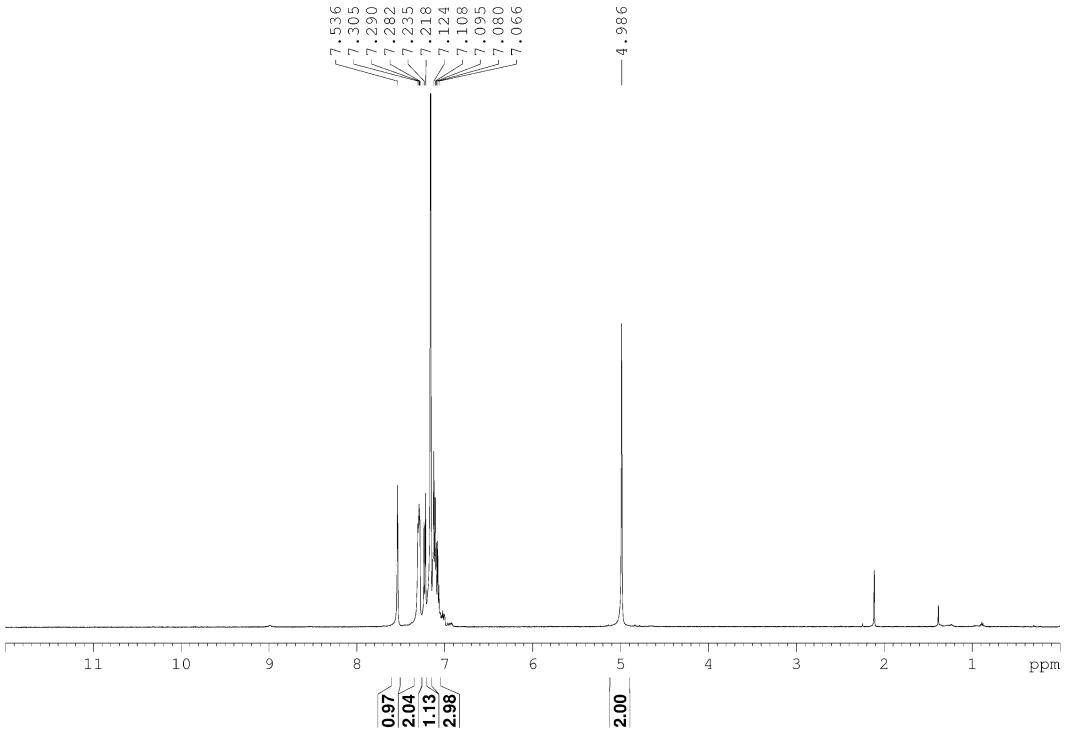


Figure S19. ^{1}H NMR spectrum of **5** in C_6D_6

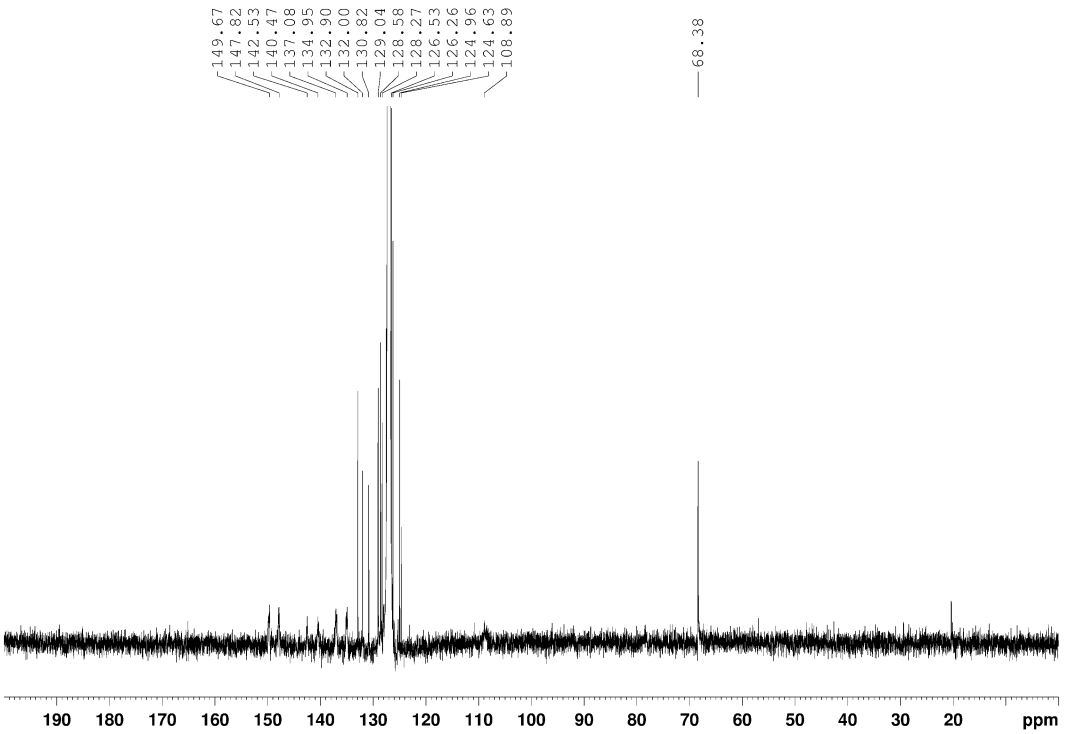


Figure S20. ^{13}C NMR spectrum of **5** in C_6D_6

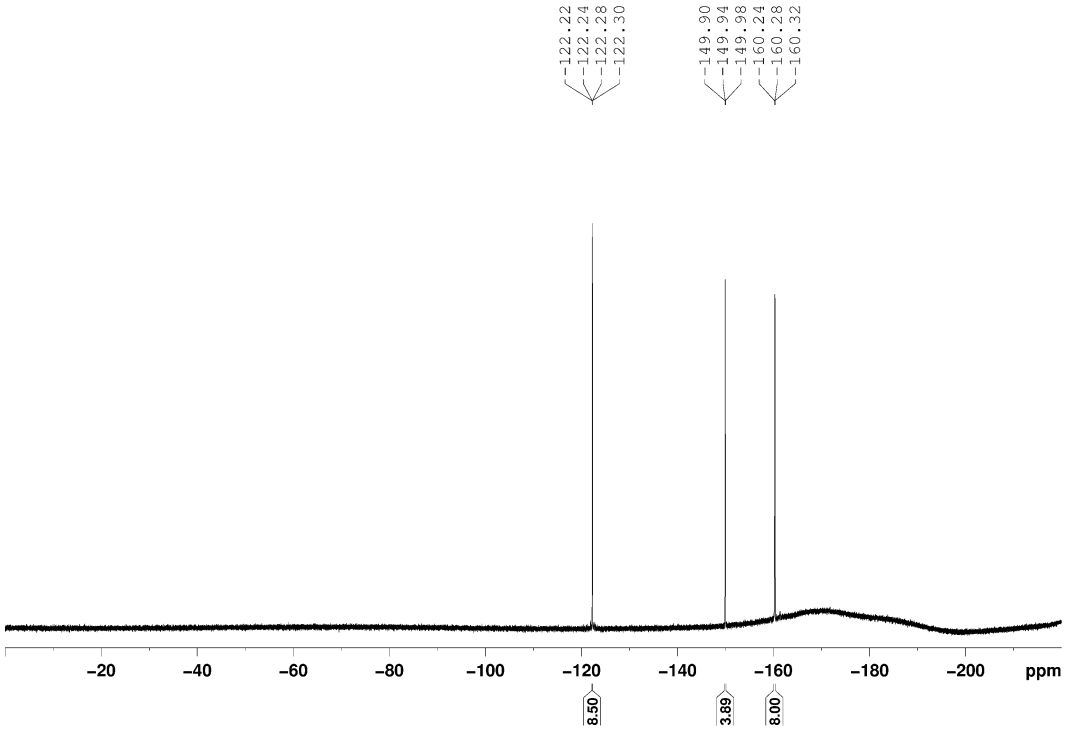


Figure S21. ^{19}F NMR spectrum of **5** in C_6D_6

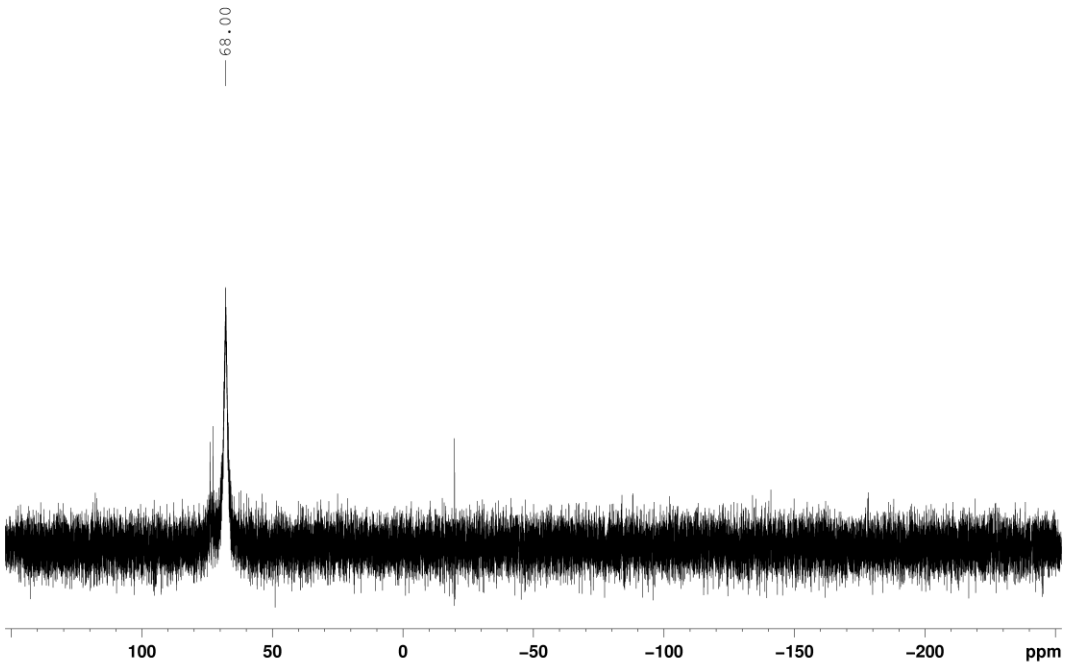


Figure S22. $^{31}P\{^{1}H\}33$ NMR spectrum of the reaction mixture of **1** and Et_3PO in C_6D_6

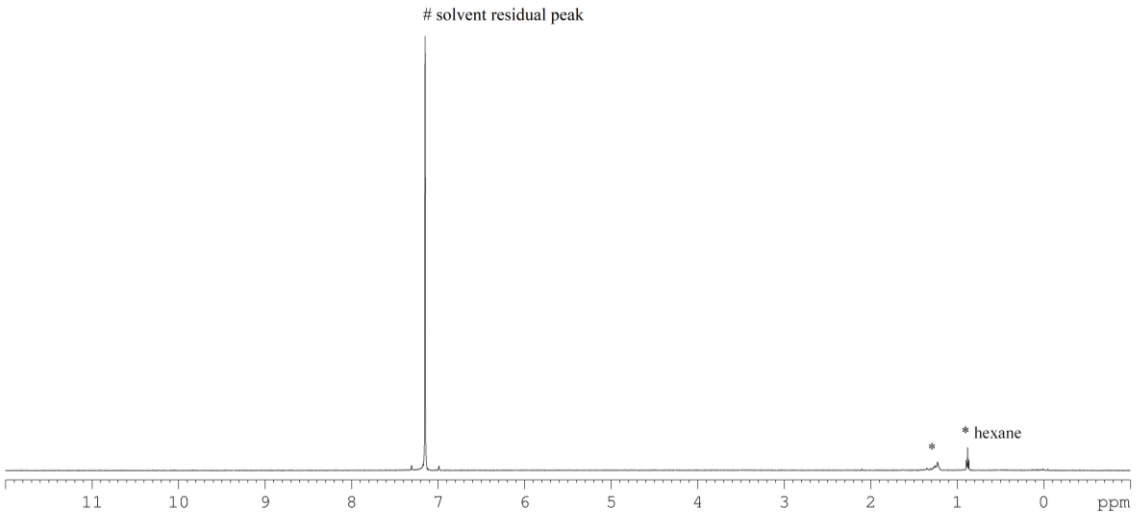


Figure S23 ^{1}H NMR spectrum of **1-d** in C_6D_6

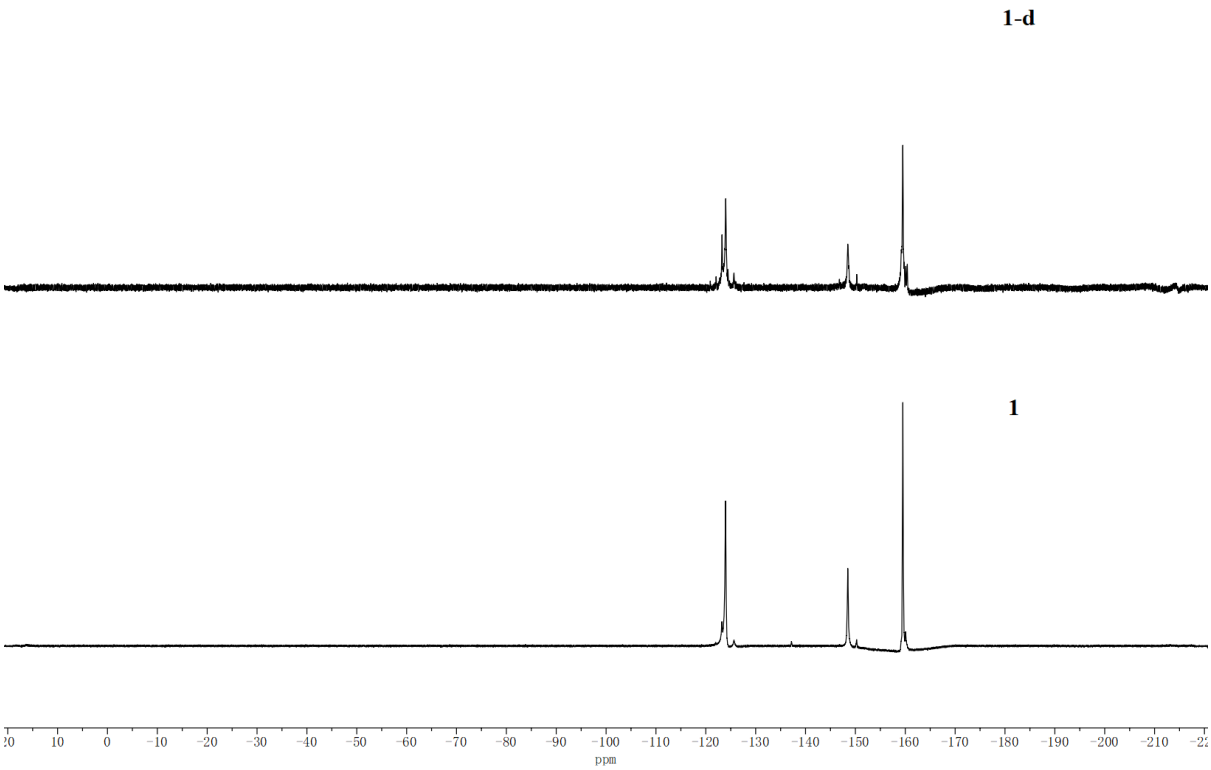


Figure S24 ^{19}F NMR spectra of **1-d** (top) and **1** (bottom) in C_6D_6

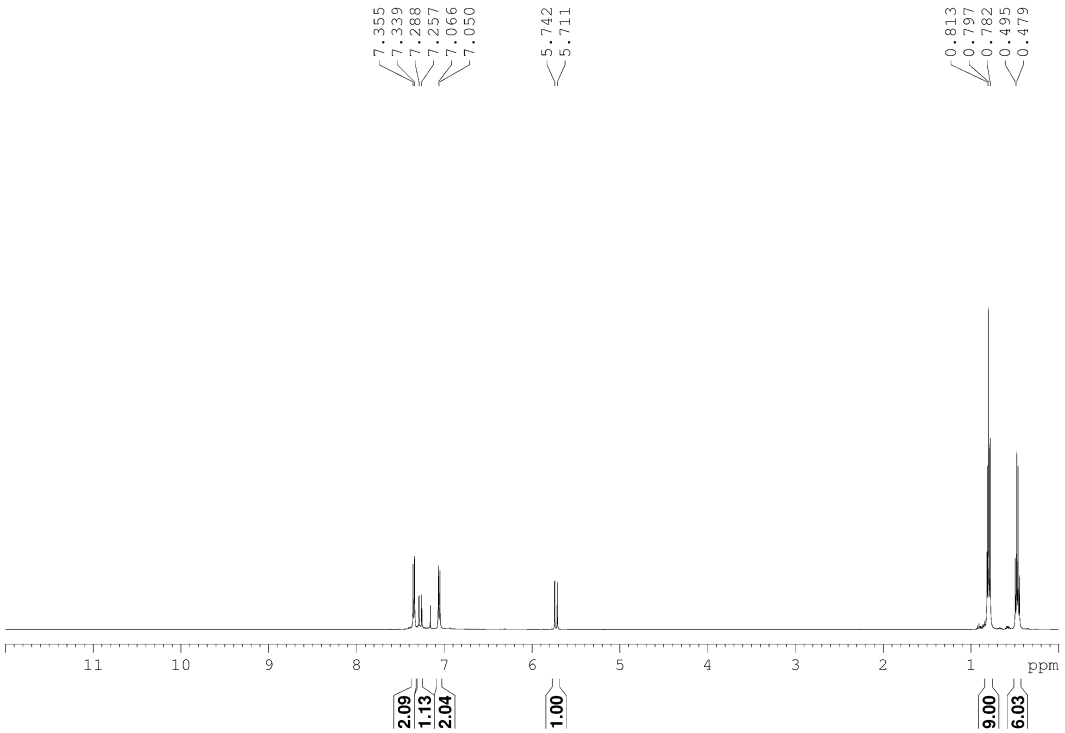


Figure S25 ^{1}H NMR spectrum of **7a** in $CDCl_3$

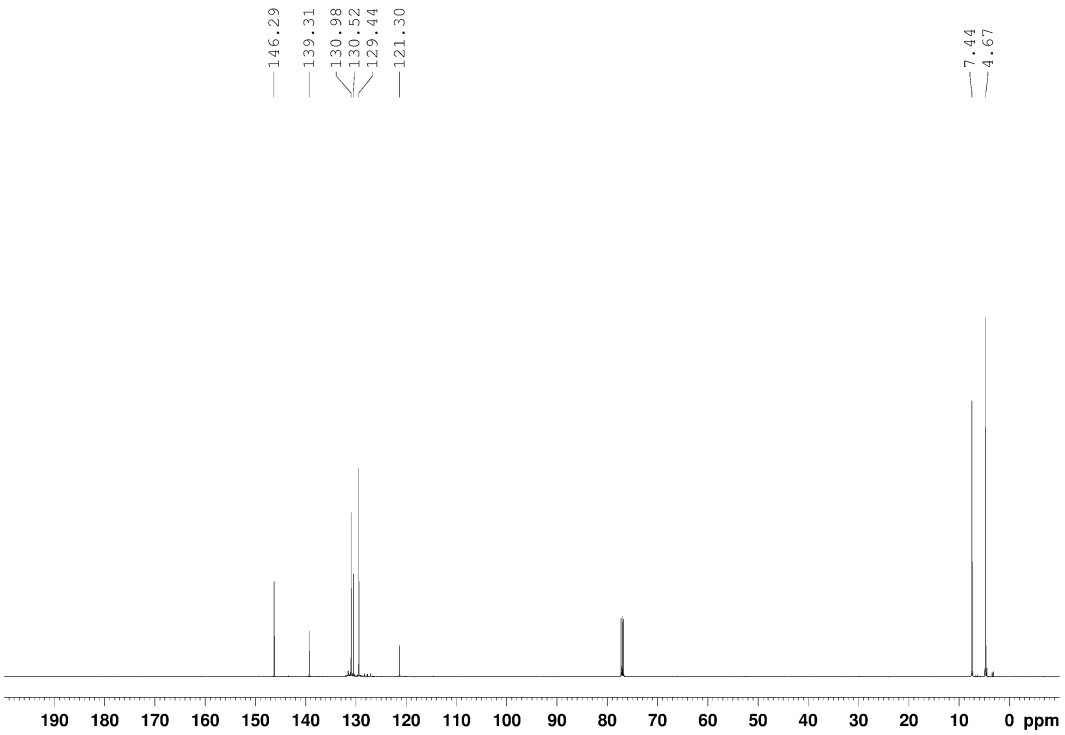


Figure S26 ^{13}C NMR spectrum of **7a** in $CDCl_3$

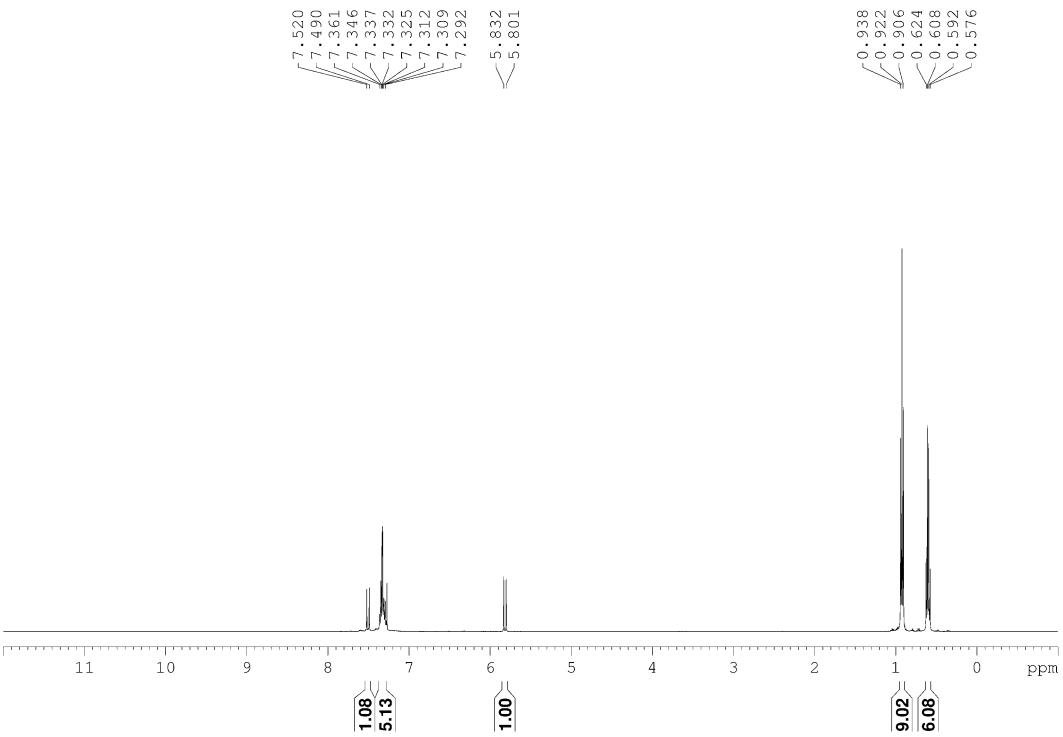


Figure S27 ^{1}H NMR spectrum of **7b** in $CDCl_3$

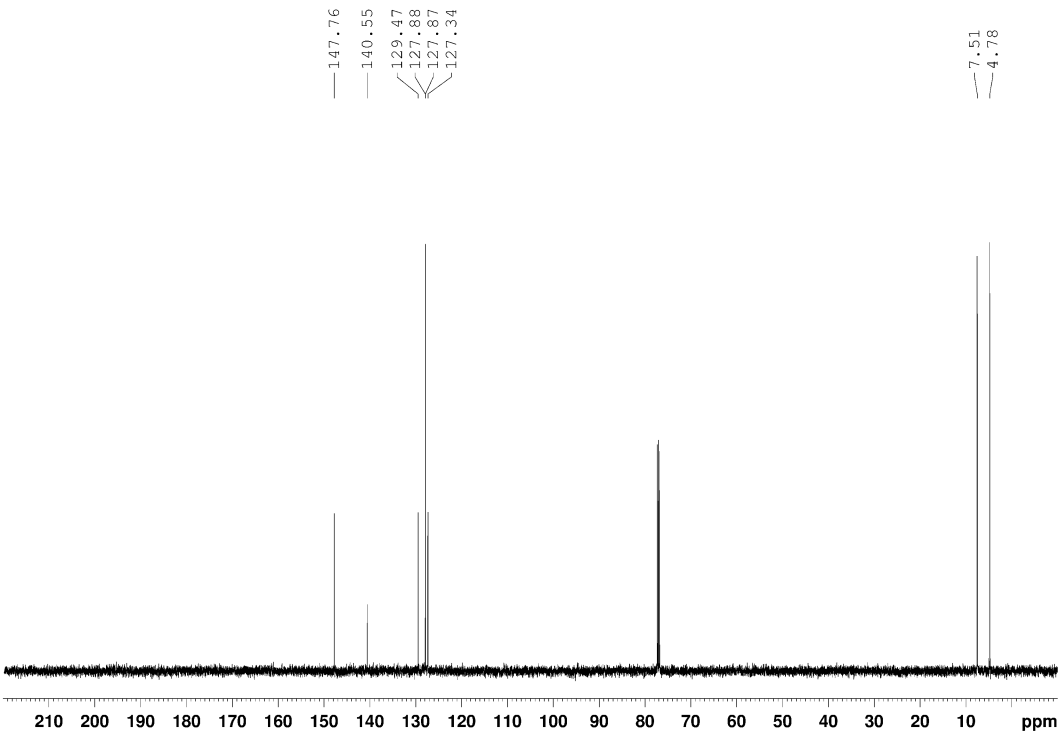


Figure S28 ^{13}C NMR spectrum of **7b** in $CDCl_3$

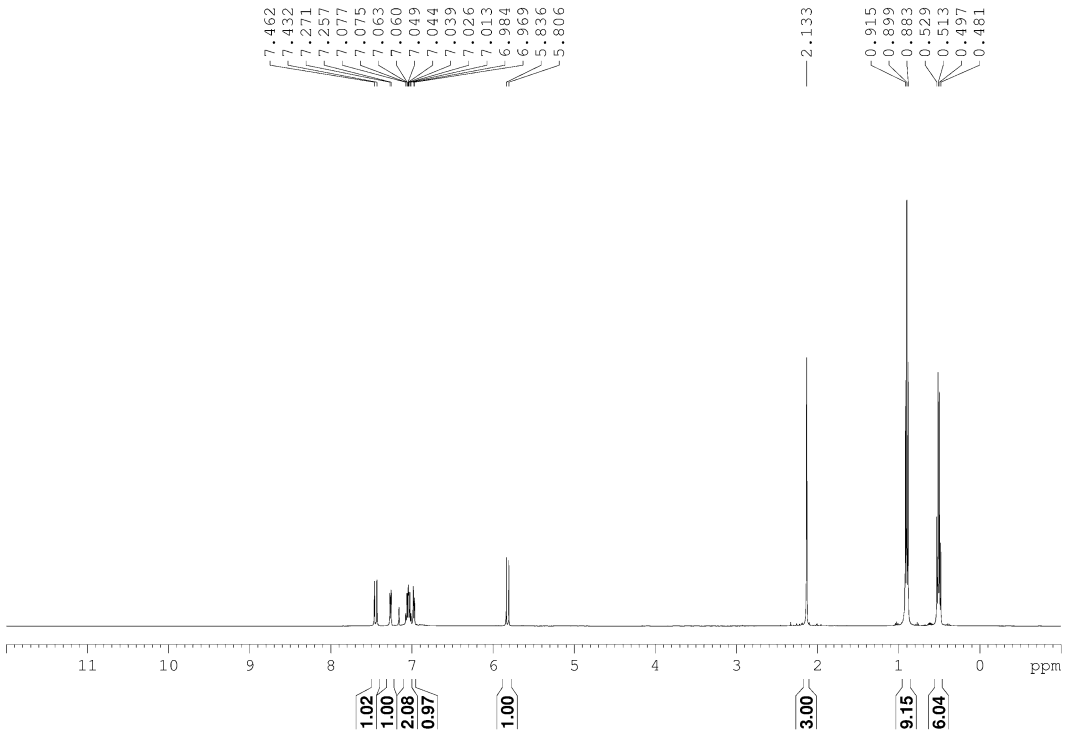


Figure S29 ^{1}H NMR spectrum of **7c** in C_6D_6

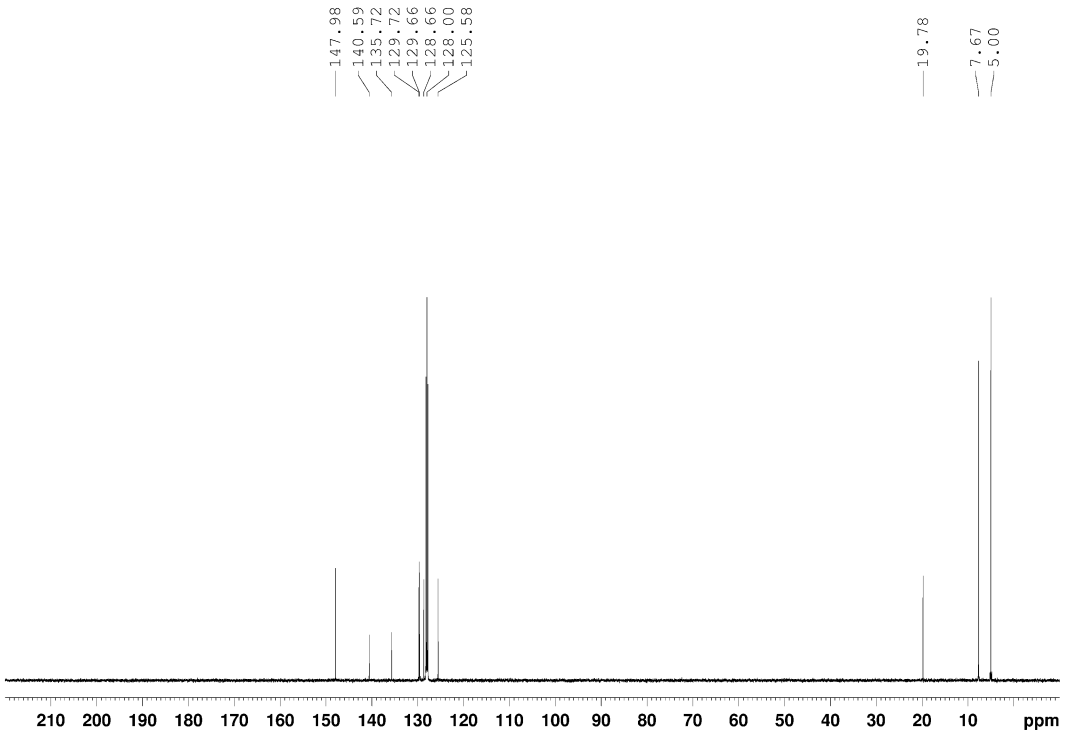


Figure S30 ^{13}C NMR spectrum of 7**c** in C_6D_6

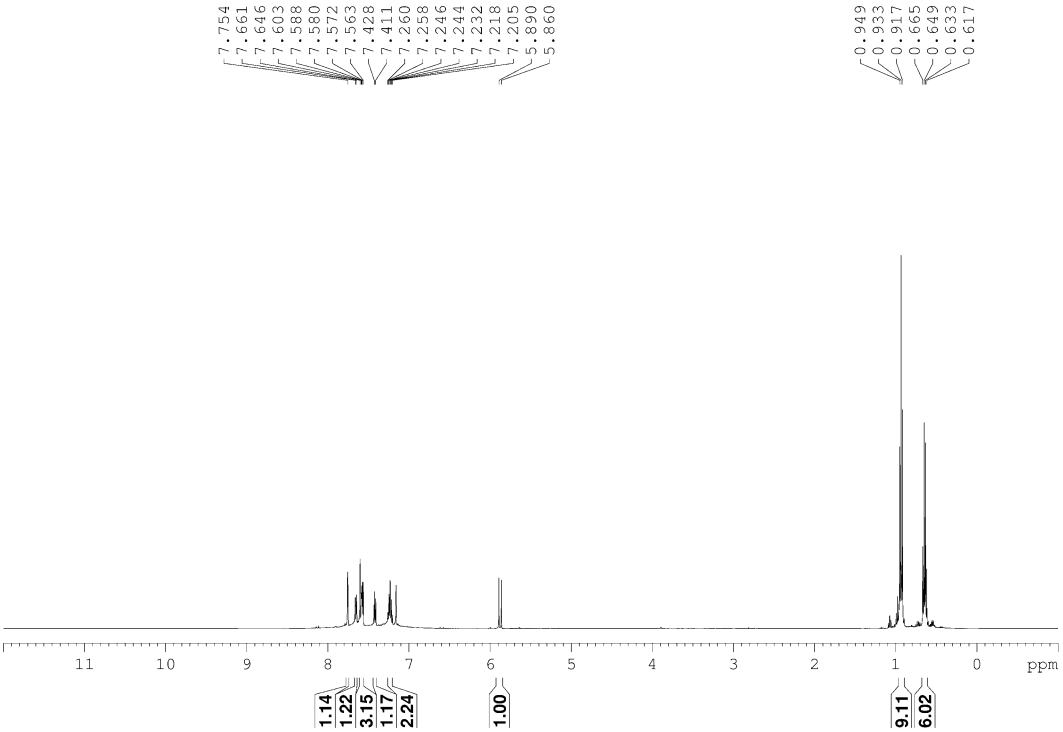


Figure S31. ^{1}H NMR spectrum of **7d** in C_6D_6

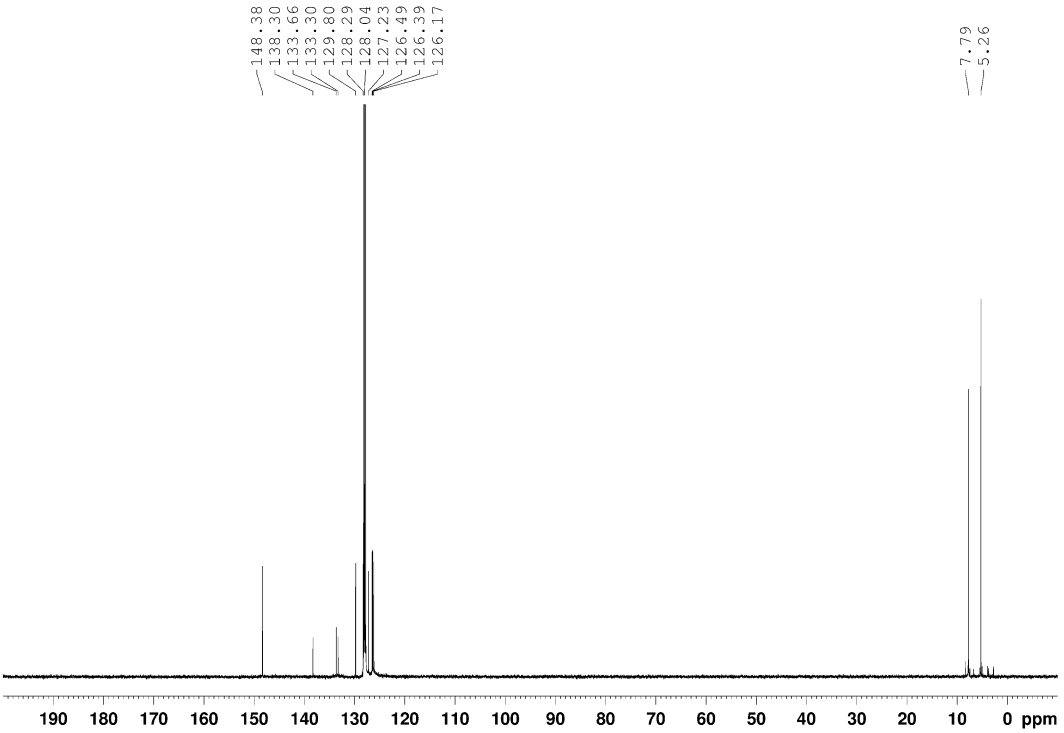


Figure S32. ^{13}C NMR spectrum of **7d** in C_6D_6

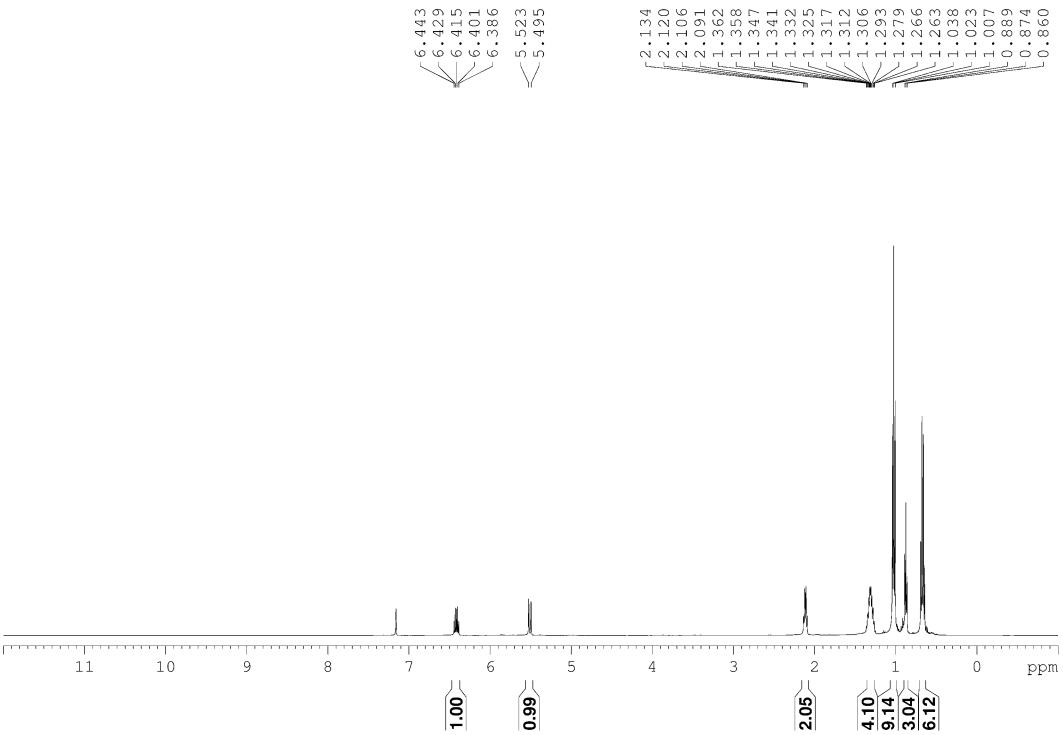


Figure S33. ^{1}H NMR spectrum of **7e** in C_6D_6

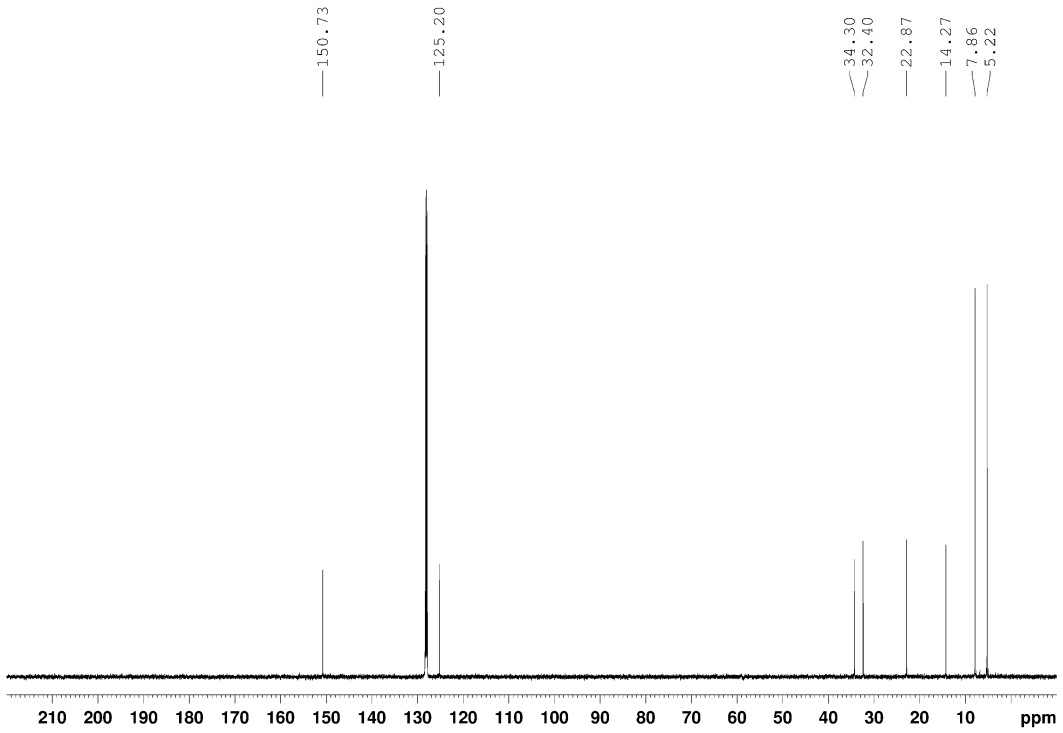


Figure S34. ^{13}C NMR spectrum of **7e** in C_6D_6

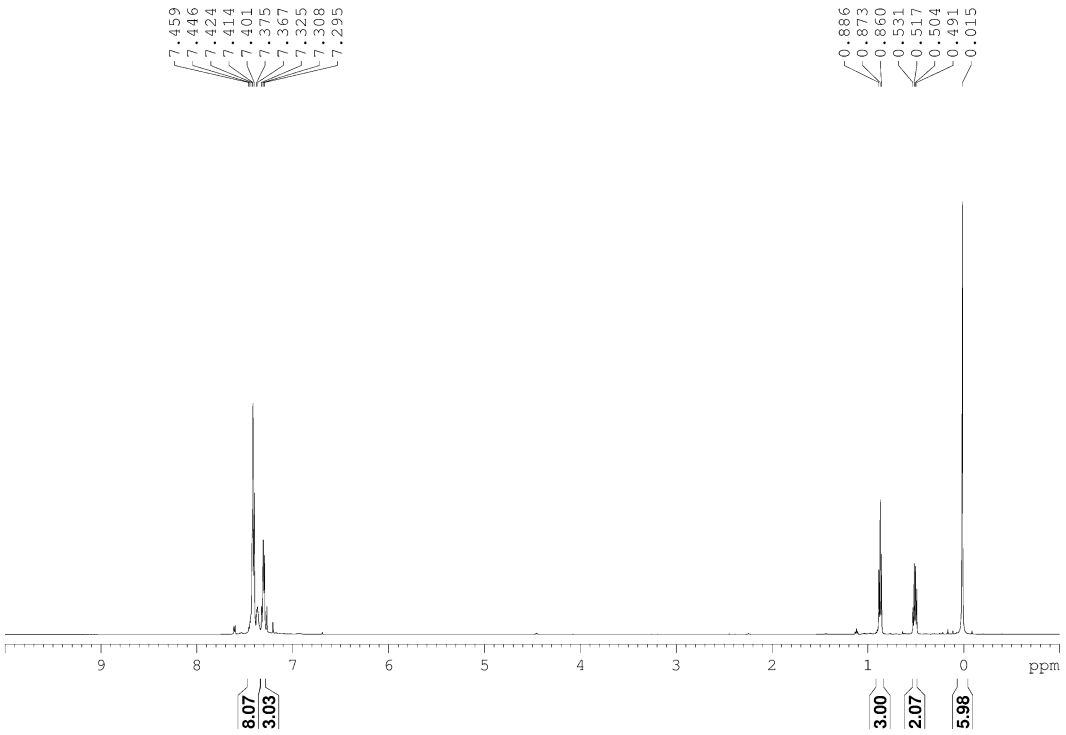


Figure S35. ^{1}H NMR spectrum of **7f** in C_6D_6

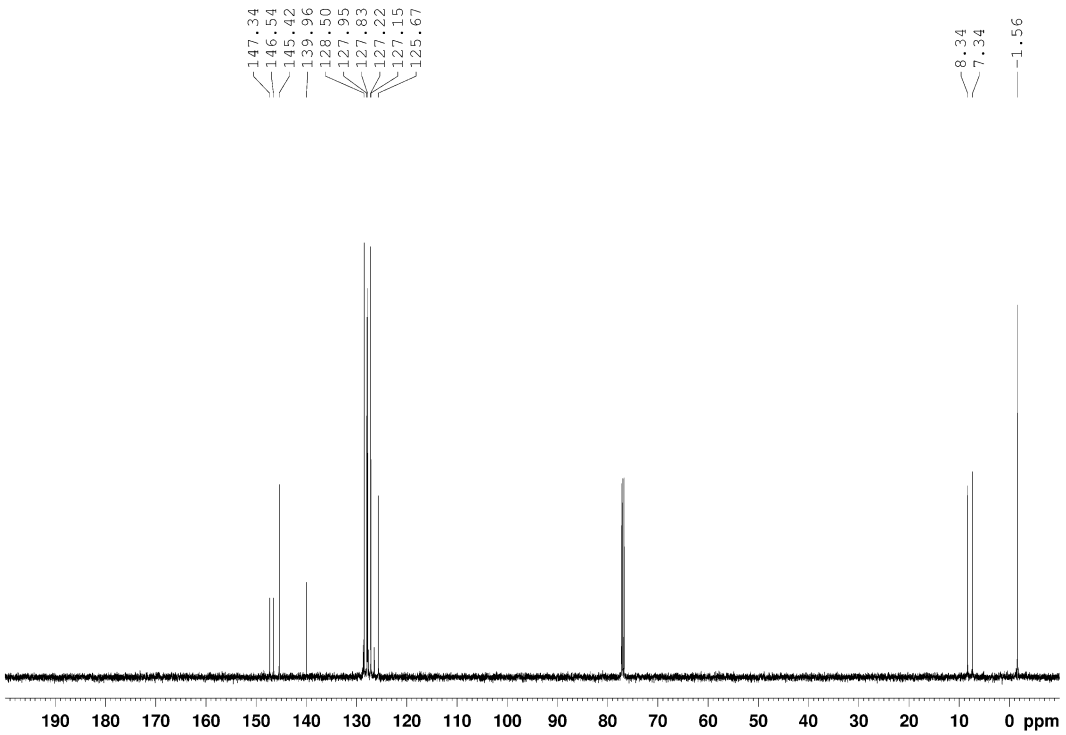


Figure S36. ^{13}C NMR spectrum of **7f** in C_6D_6

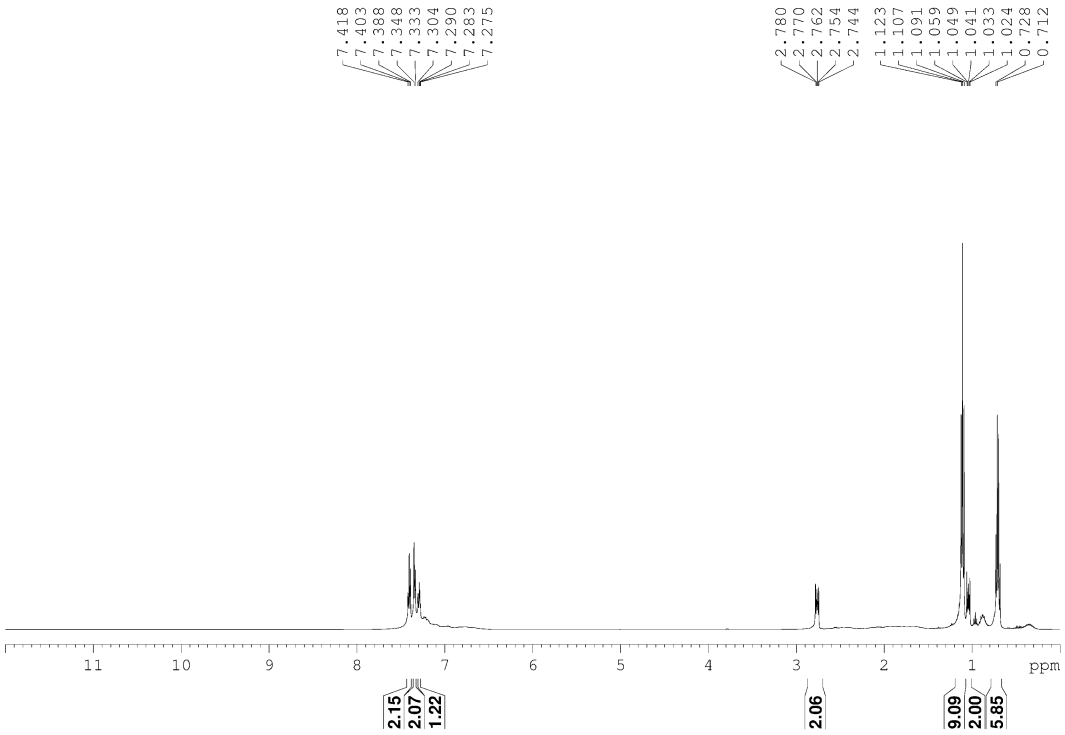


Figure S37. ^{1}H NMR spectrum of **7g** in C_6D_6

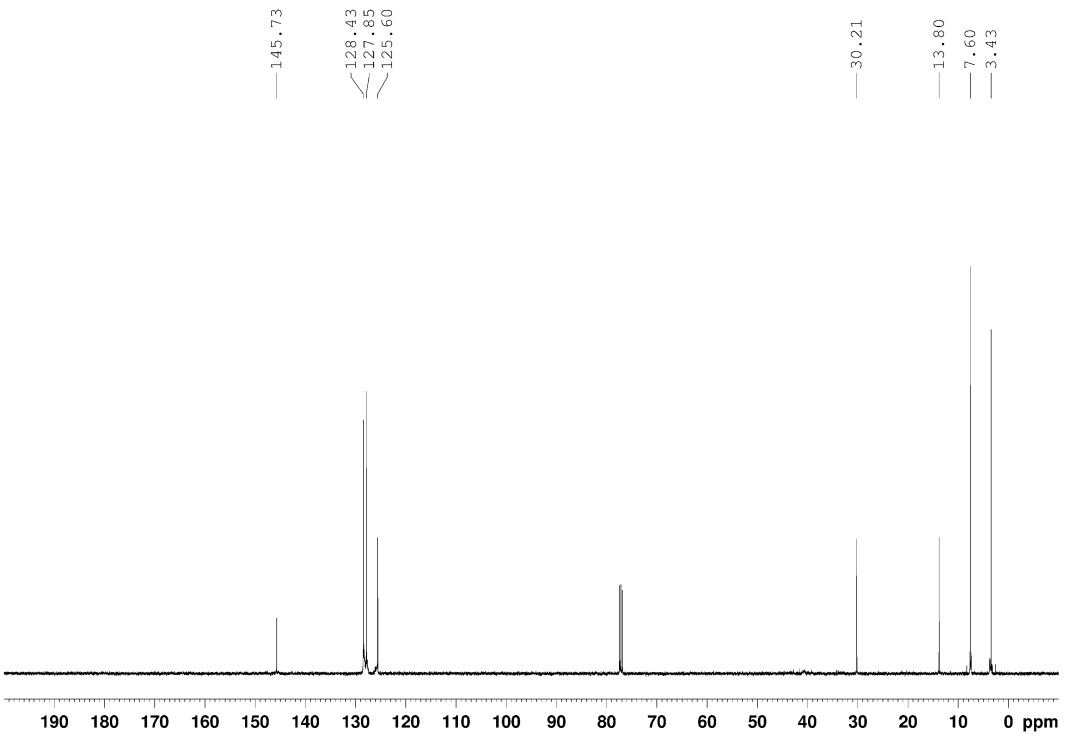


Figure S38. ^{13}C NMR spectrum of **8g** in C_6D_6

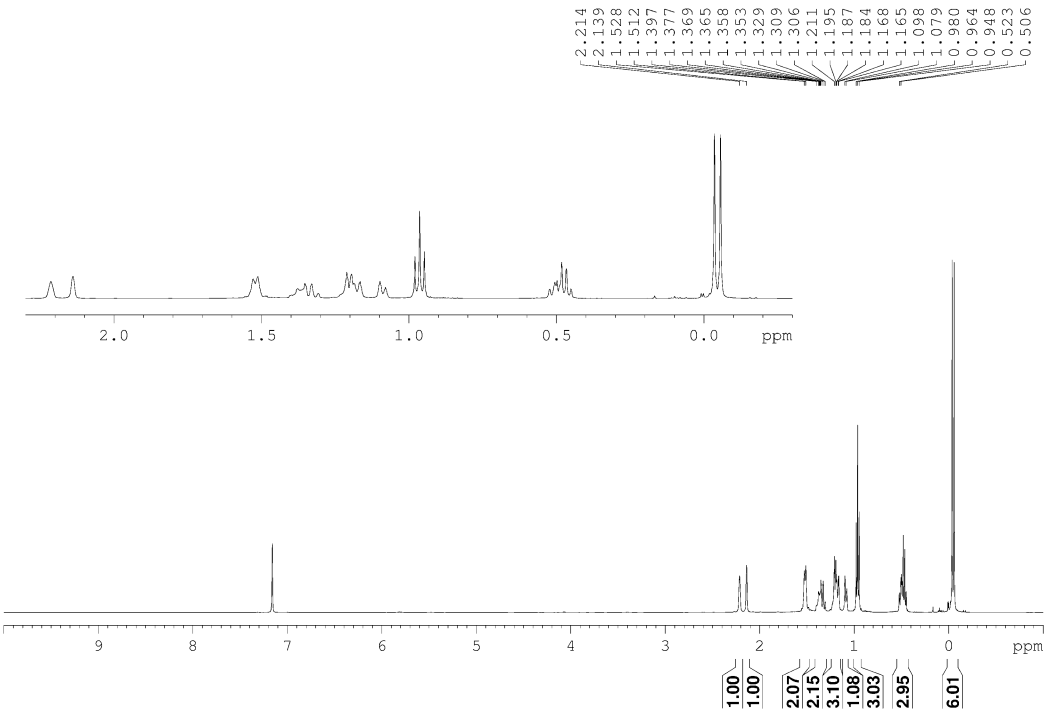


Figure S39. ^{1}H NMR spectrum of **7h** in C_6D_6

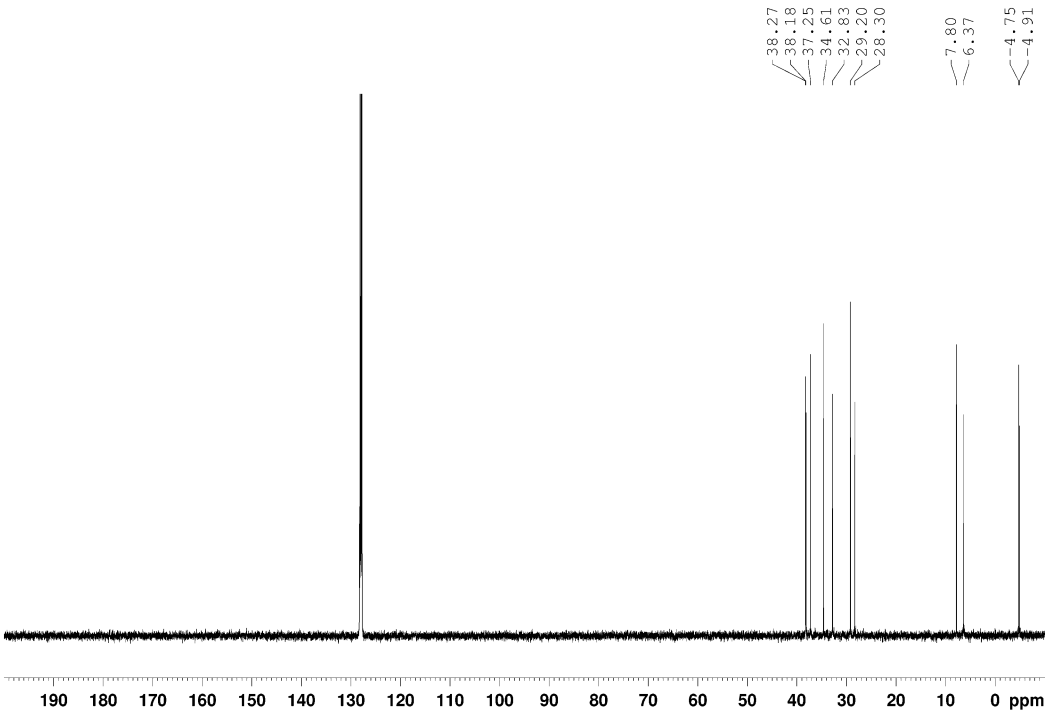


Figure S40. ^{13}C NMR spectrum of **7h** in C_6D_6

Computational Details

Density functional theory (DFT) calculations were carried out using the Gaussian 16 package[9]. Geometry optimizations were performed with the hybrid B3LYP density functional augmented with the D3BJ version of Grimme's empirical dispersion correction[10]. The Def2-SVP basis set was employed for all the atoms[11]. Frequency calculations at the same level of theory were performed to identify the number of imaginary frequencies (zero for local minimum) and provide the thermal corrections of Gibbs free energy. The single-point energy calculations were performed at the B3LYP(D3BJ)/def2-TZVP level of theory for solution-phase (fluorobenzene). The gas-phase geometry was used for all the solution phase calculations. The SMD method was used with the corresponding solvent[12], while Bondi radii[13] were chosen as the atomic radii to define the molecular cavity. The corrections of Gibbs free energy or enthalpy from frequency calculations were added to the singlepoint energies to obtain the Gibbs free energy or enthalpy in solution, respectively. The FIA calculations were performed at the B3LYP/def2-TZVP level of theory.

Natural bond orbital (NBO) calculations were carried out using NBO 7.0 program at the B3LYP/def2-TZVP level of theory[14]. Quantum theory of atoms in molecules (QTAIM) analysis[15] was carried out using Amsterdam Modeling Suite (ADF/2019.304)[16] at the B3LYP/TZP level of theory using the B3LYP/def2-TZVP optimized geometries. Optimized structures were visualized by IBOview program.[17] Intrinsic bond orbitals (IBOs) were carried out using ORCA program at the B3LYP/def2-SVP level of theory.[18]

Table S4. Energy of Intermediates for the trimerization of $HAl(C_6F_5)_2$ and $HB(C_6F_5)_2$.

Species	Thermal Corrections of Gibbs Free Energies (Hartree)	Solvation Energies (Hartree) SMD (fluorobenzene)
$HAl(C_6F_5)_2$	0.054944	-1699.300517
1	0.218765	-5097.953121
$HB(C_6F_5)_2$	0.064859	-1481.680492
1-B-trimer	0.245402	-4445.005072
1-Al-dimer	0.136728	-3398.63002
1-B-dimer	0.154919	-2963.373925

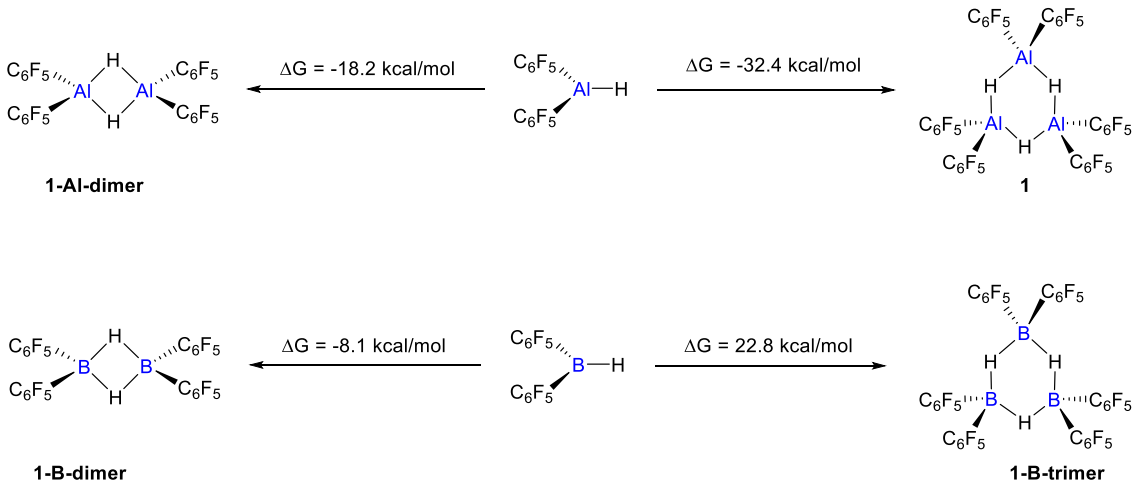


Figure S41. The energies for di- and trimerization of the monomers $HAl(C_6F_5)_2$ and $HB(C_6F_5)_2$.

Table S5. Enthalpy of Intermediates for the FIA of $HAl(C_6F_5)_2$ and $HB(C_6F_5)_2$.

Species	Sum of electronic and thermal Enthalpies (Hartree)	△H (H: Enthalpy, kJ/mol)	△H for the TMS-system (CCDC(T)/CBS, kJ/mol)	The isodesmic FIA value
$HB(C_6F_5)_2$	-1481.553765			
$HAl(C_6F_5)_2$	-1699.167165			
$HAl(C_6F_5)_2F^-$	-1799.242686	445.2	952.5	**507.3**
$HB(C_6F_5)_2F^-$	-1581.591727	543.8	952.2	**408.7**
Me_3SiF	-509.189459			
Me_3Si^+	-408.944369			

Table S6. The selected NBO charges of $HAl(C_6F_5)_2$

Atom	No	Charge	Core	Valence	Rydberg	Total
Al	1	**1.549910**	9.999940	1.434850	0.015300	11.450090
H	24	**-0.375410**	0.000000	1.371620	0.003790	1.375410

Table S7. The selected NBO charges of $HB(C_6F_5)_2$

Atom	No	Charge	Core	Valence	Rydberg	Total
H	23	**-0.03482**	0.00000	1.03253	0.00229	1.03482
B	24	**0.57015**	1.99997	2.41841	0.01147	4.42985

Cartesian coordinates

1:

Al	-0.15293600	1.60866500	-0.98487200
Al	0.00004300	-0.00129400	1.80654700
Al	0.15254100	-1.60693000	-0.98747700
F	-2.75842200	-0.84124900	-0.31652700
F	-3.35791300	-2.79779600	4.73394600
F	2.75819700	0.84190900	-0.31587100
F	-2.50414600	1.95318400	2.22866400
F	4.79500900	-1.55140100	3.59323300
F	0.45960900	4.30519900	-2.55549200
F	2.80779600	5.50119700	-3.10766800
F	1.05815600	2.38639500	3.35799500
F	5.22818100	0.81775400	4.84688000
F	-5.22603500	-0.82623500	4.84884600
F	4.05356700	-5.08757700	-0.49183200
F	2.50196900	-1.95830500	2.22758800
F	-4.79613300	1.54349000	3.59514200
F	-1.05476300	-2.38988900	3.35821000
F	1.61970700	-4.03073300	0.07912800
F	-5.11194000	-2.04557600	-0.87957000
F	5.13631800	4.38189400	-2.27473200
F	3.36233900	2.79151700	4.73280400
F	5.11156400	2.04718700	-0.87744000
F	-1.62052500	4.03057500	0.08574000
F	-2.37179700	0.60850200	-3.07030000
F	5.63636800	-3.89468600	-2.35122500
F	2.37161800	-0.60360300	-3.07125800
F	-0.46042700	-4.30056600	-2.56288100
F	-4.05449800	5.08796400	-0.48354500
F	-2.80873500	-5.49561600	-3.11651800
F	-5.13705400	-4.37780500	-2.28095200
F	-5.63707500	3.89789800	-2.34495000
F	-4.79367300	1.66049500	-3.63355300
F	4.79335000	-1.65504500	-3.63616800
C	1.70806800	0.20470400	2.75168800
C	4.09855000	0.62218000	4.17497600
C	2.74592800	2.00475100	-1.01023200
C	-1.70745800	-0.20893100	2.75230300
C	-1.52842700	-2.52999500	-1.41352700

C	-3.87414200	0.58274700	3.53421500
C	-1.92637500	2.28588300	-1.46419900
C	-2.68858100	0.76711900	2.83907400
C	-2.39869100	3.42856500	-0.83580000
C	-2.74634100	-2.00287900	-1.01291700
C	3.63458800	-3.98759400	-1.11583200
C	3.87411700	-0.58958300	3.53271700
C	-3.14037800	-1.63602100	4.11730900
C	2.68806800	-0.77251400	2.83803900
C	-4.09690400	-0.62930000	4.17651100
C	-1.97335700	-1.40087000	3.40909600
C	1.97561400	1.39629600	3.40842700
C	1.52791100	2.53257500	-1.40958300
C	1.59097700	3.72353400	-2.12202900
C	3.14319300	1.63003100	4.11619500
C	1.92591300	-2.28354000	-1.46791500
C	4.44523700	-3.37884300	-2.06683700
C	-3.96695400	-2.59436500	-1.28633000
C	2.78733600	4.35918200	-2.42162400
C	-1.59166600	-3.71968200	-2.12806700
C	-2.76549200	1.71737200	-2.40906600
C	3.96648000	2.59670900	-1.28293500
C	2.39802900	-3.42733500	-0.84139000
C	-4.44587800	3.38178100	-2.06138500
C	3.98100800	3.78888400	-1.99724900
C	-3.98167000	-3.78528800	-2.00274500
C	-2.78811200	-4.35481300	-2.42845300
C	-4.01217700	2.23715400	-2.71941200
C	2.76512700	-1.71359300	-2.41182700
C	-3.63533700	3.98907100	-1.10936700
C	4.01174200	-2.23307300	-2.72299300
H	0.13992000	-1.25248900	0.67346700
H	-0.14047700	1.25180400	0.67562000
H	-0.00004700	0.00132000	-1.50590600

1-B:

F	2.64959800	-1.12407100	-0.64075700
F	4.78441900	2.33083100	-2.12155900
F	-2.64741100	0.91476700	0.66153300
F	1.98731500	1.80955200	2.48934700
F	-1.23439300	5.76865600	-1.50662300
F	-1.15378800	-3.25948600	2.35351100

F	-3.60537700	-3.77856800	3.17916700
F	-1.05878800	2.17322100	2.55577700
F	-2.44903400	6.31096000	0.86823900
F	6.01273100	2.71711300	0.27611600
F	-4.43838400	1.21385900	-3.26069400
F	0.08182800	3.45348500	-1.84608700
F	4.58996500	2.44310500	2.58334600
F	2.20548700	1.66823000	-2.22855300
F	-1.90012900	1.58951500	-2.47620300
F	4.47843100	-2.12796900	-2.28452500
F	-5.61468000	-1.98780400	2.78465000
F	-2.34032300	4.49729900	2.89228300
F	-5.09218800	0.36244400	1.50942100
F	0.48182100	-0.03185900	3.73429700
F	1.34694400	-3.19959600	0.35119100
F	-5.59223700	-1.23782400	-3.02987300
F	-1.62693100	-2.94359200	-1.19946700
F	-0.45733900	-1.00347000	-4.22446500
F	2.38747200	-1.15139800	5.26665000
F	1.39159600	-1.98674800	-5.83489200
F	3.87836700	-2.57138800	-4.90380600
F	3.78895400	-3.29345900	4.34359800
F	3.25055600	-4.30872000	1.87914500
F	-4.17234600	-3.31601300	-1.99177300
C	-0.46651600	2.70177800	0.32434100
C	-1.81152200	5.15818400	0.69448300
C	-2.82181400	-0.24715400	1.30505400
C	1.99399000	1.65278400	0.13501000
C	0.98049400	-1.05485200	-2.32010400
C	4.00194800	2.23868400	1.40539700
C	0.92864900	-1.49360700	1.93588700
C	2.66158800	1.89330400	1.33381400
C	1.19678800	-1.04385300	3.22712100
C	2.28112200	-1.35501800	-1.90931800
C	-3.74797700	0.19840200	-2.74507200
C	-1.19426600	4.87776100	-0.51644000
C	4.09828000	2.18536400	-0.98807700
C	-0.53098400	3.67139600	-0.67473800
C	4.72795700	2.38345100	0.23204300
C	2.75725100	1.83416800	-1.01704700
C	-1.08655300	3.03214600	1.52747700
C	-1.74134500	-1.10871200	1.50280000
C	-2.07455900	-2.31261300	2.14253300
C	-1.75385100	4.23084100	1.72526200

C	-1.67897200	-0.65452200	-1.77794600
C	-4.33881000	-1.05298700	-2.63133600
C	3.25696000	-1.86505400	-2.74618400
C	-3.35604200	-2.61773600	2.57698200
C	0.73330400	-1.28213300	-3.68063000
C	1.63227200	-2.62351000	1.52862400
C	-4.11291100	-0.51402200	1.72975500
C	-2.43914200	0.37304700	-2.32409500
C	2.86783500	-2.72049700	3.57659400
C	-4.38436600	-1.71016400	2.37578900
C	2.95661200	-2.08793500	-4.08243700
C	1.68711500	-1.78958500	-4.55143100
C	2.59722700	-3.23144300	2.31402700
C	-2.30666400	-1.89451500	-1.69323500
C	2.15673900	-1.62366400	4.04252900
C	-3.61271000	-2.11120100	-2.10202100
H	0.08336300	0.77835100	-1.01891400
H	0.02669400	0.51205100	1.05774100
H	-0.00183800	-1.16509800	-0.19040300
B	0.42370800	1.40265300	0.12135700
B	-0.16041800	-0.52373200	-1.35553300
B	-0.23132500	-0.82375100	1.09180300

$HAl(C_6F_5)_2$:

Al	0.00174100	-1.71025100	-0.00270900
F	2.68265100	-2.08017400	1.51336800
F	-3.19448700	2.07337900	1.94759700
F	-0.85193900	0.72679600	1.80120200
F	5.02616600	-0.73133600	1.36027200
F	-5.27159700	1.35297000	0.35361500
F	-2.66462900	-2.05506800	-1.54950100
F	0.83730200	0.76181900	-1.76898300
F	3.17677000	2.11295500	-1.91103400
F	5.26879900	1.36518600	-0.34951900
F	-5.01137800	-0.71120800	-1.39267300
C	1.68648400	-0.70308800	-0.12292900
C	2.78526500	-1.04926100	0.65042500
C	-3.05545600	1.06007000	1.09160000
C	-1.68539000	-0.70743000	0.12084200
C	-4.12095700	0.69150400	0.27872100
C	3.99398000	-0.37376600	0.59524800
C	1.85831100	0.37676500	-0.97686800
C	-1.86587200	0.35600400	0.99315200

C	4.11949400	0.70125900	-0.27662800
C	3.04637200	1.08376500	-1.07284100
C	-2.77659100	-1.04021200	-0.66860900
C	-3.98651000	-0.36699800	-0.61186300
H	0.00364800	-3.27628800	-0.00537200

$HAl(C_6F_5)_2F^-$:

F	2.74959700	-2.36222200	0.36170100
F	-2.88916200	0.25224700	2.95107200
F	-0.74821600	-0.87606500	1.77687400
F	4.86891200	-0.91284700	1.13416000
F	-4.96521400	1.15238600	1.43436300
F	-2.75308300	-0.21413900	-2.46698100
F	0.75507000	1.54273700	-1.43418200
F	2.89226300	2.98104900	-0.65062400
F	4.96202800	1.76160500	0.63828600
F	-4.87729200	0.90942600	-1.27595000
C	1.64490300	-0.47502700	-0.56678500
C	2.72637000	-1.04124300	0.08930200
C	-2.83784700	0.12948400	1.61136500
C	-1.64479300	-0.59696200	-0.40019400
C	-3.89697100	0.58976800	0.84494000
C	3.84015700	-0.31847500	0.50008800
C	1.75359600	0.88678200	-0.79368100
C	-1.74884600	-0.44814700	0.97334300
C	3.89458000	1.04337200	0.25047400
C	2.83977700	1.65807300	-0.40548600
C	-2.72960700	-0.12182100	-1.11866100
C	-3.84555700	0.46389400	-0.53378700
H	-0.02385000	-1.44352100	-2.84005700
Al	-0.00287000	-1.50035000	-1.24561500
F	0.01471700	-3.08641200	-0.65454900

$HB(C_6F_5)_2$:

F	-2.36679900	2.46174200	1.08520400
F	3.10089200	-2.33067400	1.35514100
F	0.63873100	-1.29016900	1.23313500
F	-4.82318000	1.39278700	0.95632400
F	5.19806500	-1.00405500	0.26039200
F	2.36688700	2.46176100	-1.08516400
F	-0.63874600	-1.29026900	-1.23304700
F	-3.10087300	-2.33065800	-1.35518400

F	-5.19810500	-1.00397000	-0.26048700
F	4.82312700	1.39281500	-0.95639200
C	-1.38523200	0.62284700	-0.04294000
C	-2.50791600	1.27936200	0.47854900
C	2.90211600	-1.16186800	0.74586100
C	1.38521900	0.62289100	0.04305100
C	3.98026400	-0.48145200	0.19311400
C	-3.78504000	0.74650800	0.42588800
C	-1.63574100	-0.60955200	-0.65745700
C	1.63576300	-0.60954100	0.65757000
C	-3.98025700	-0.48145900	-0.19314900
C	-2.90212600	-1.16187000	-0.74585400
C	2.50791000	1.27939200	-0.47848700
C	3.78505600	0.74650700	-0.42589300
H	-0.00005300	2.50724700	-0.00042000
B	-0.00000600	1.32167500	-0.00008000

$HB(C_6F_5)_2F^-$:

F	2.79348300	-2.45048000	0.37681500
F	-3.59210000	1.26073600	2.18073500
F	-1.14491600	0.17431400	2.23947000
F	5.06227100	-1.05760400	0.15133500
F	-5.16012500	1.00486100	-0.03542600
F	-1.80408900	-1.48395600	-2.15887800
F	0.31222800	1.51607000	-0.45479200
F	2.58840000	2.86861600	-0.68989700
F	4.99377300	1.61540900	-0.38870400
F	-4.23180400	-0.37472600	-2.19777900
C	1.42267500	-0.54676200	-0.00010800
C	2.68113900	-1.13183200	0.13322200
C	-3.13745000	0.56630900	1.11953200
C	-1.35804600	-0.74201900	0.05977200
C	-3.93736000	0.44460700	-0.00554900
C	3.87520500	-0.43586000	0.01232700
C	1.45433600	0.81209300	-0.28377700
C	-1.87927200	-0.01817600	1.12703600
C	3.84816900	0.92144600	-0.26537700
C	2.62579700	1.54978700	-0.41776700
C	-2.19388800	-0.82717600	-1.04566600
C	-3.46005500	-0.25578700	-1.09921300
H	0.15037300	-2.33644200	-0.75523500
F	0.15486800	-2.18822000	1.42019200
B	0.09084100	-1.52970500	0.15220300

$SiMe_3F$:

Si	0.000019	-0.000013	0.025181
C	0.375703	1.746070	-0.522899
H	0.392067	1.821151	-1.613304
H	-0.376823	2.445576	-0.152054
H	1.349143	2.074357	-0.151722
C	-1.700069	-0.547623	-0.522812
H	-1.773447	-0.570881	-1.613215
H	-1.929596	-1.549119	-0.152059
H	-2.471035	0.131243	-0.151485
C	1.324255	-1.198422	-0.522962
H	2.306388	-0.896395	-0.152381
H	1.121926	-2.205541	-0.151607
H	1.380822	-1.250253	-1.613372
F	0.000107	-0.000010	1.645633

$SiMe_3^+$:

Si	-0.000043	-0.000073	0.000051
C	1.414981	-1.159797	0.000510
H	2.058091	-0.955040	0.864157
H	1.109937	-2.205368	0.017681
H	2.033857	-0.979348	-0.886480
C	-1.712000	-0.645336	-0.000338
H	-1.864204	-1.277022	0.882786
H	-2.464668	0.142025	-0.012158
H	-1.857725	-1.299120	-0.868048
C	0.297069	1.805201	-0.000210
H	1.355325	2.063379	-0.004122
H	-0.189254	2.256894	-0.872627
H	-0.181057	2.254207	0.878329

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