Electronic Supplementary Information

Reactivity of N-(isocyanoimino)triphenylphosphorane toward group 13 Lewis acids

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General Considerations

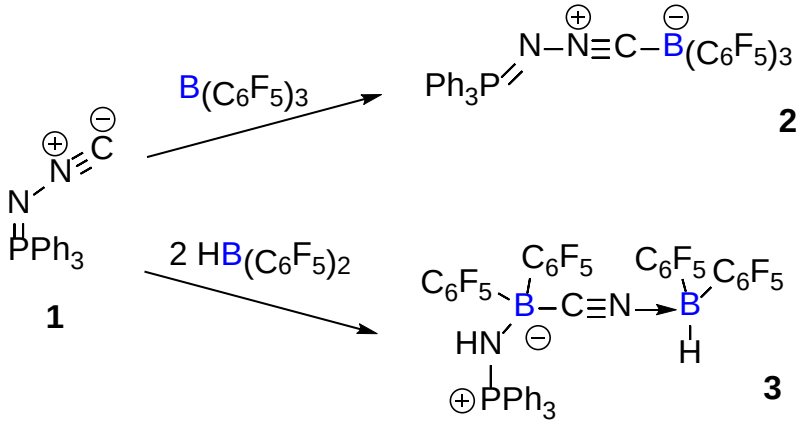
All experiments were carried out under inert gas atmosphere by using Schlenk-type glassware or in an Ar-filled glove box. Toluene, n-hexane, fluorobenzene and deuterated solvents (C_6D_6, CD_2Cl_2, C_6D_5Br, $CDCl_3$, CD_3CN) were stored with 3Å molecular sieves. All solvents were stored under argon atmosphere.

$B(C_6F_5)_3$[S1], $HB(C_6F_5)_2$[S2], $Al(C_6F_5)_3$[S3], $ClAl(C_6F_5)_2$[S4]were synthesized according to the literature methods. NMR spectra were recorded with Bruker Avance 500 (^1H: 500 MHz, ^{13}C: 125 MHz, ^{11}B: 160 MHz, ^{19}F: 470 MHz, ^{31}P: 202 MHz) or 600 (^1H: 600 MHz, ^{13}C: 151 MHz, ^{31}P: 243 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.

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[S5], the structure was solved with the XT[S6] structure solution program using Intrinsic Phasing and refined with the XL[S7] refinement package using Least Squares minimization.

Experimental Procedures

Synthesis of compounds 2 and 3



Scheme S1-1：Synthesis of **2** and **3**

Compound 2

A mixture of **1** (30 mg, 0.1 mmol), $B(C_6F_5)_3$ (51 mg, 0.1 mmol) and toluene (5 mL) was stirred at ambient temperature for 2 h. The resulting brown solution was storing at -30 ℃ overnight to afford colourless crystals of **2**. The crystals were collected, washed with cold n-hexane, and then dried under vacuum for 2 hours (53 mg, 65%). Single crystals (colourless) suitable for X-ray analysis were obtained from the toluene solution at -30 ºC for 1 day.

^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.29 (dd, *J* = 12.7， 7.8 Hz, 6H, *m*-C_6H_5), 7.01 (t, *J* = 7.7 Hz, 3H, *p*-C_6H_5), 6.89 (br, 6H, *o*-C_6H_5).

^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 149.16-147.26 (m, *o*-C_6F_5), 140.86-139.39 (m, *p*-C_6F_5), 138.07-136.12 (m, *m*-C_6F_5), 133.86 (d, *J* = 3.0 Hz, P(C_6H_5)$_3$), 132.37 (d, *J* = 10.1 Hz, P(C_6H_5)$_3$), 129.14 (d, *J* = 12.4 Hz, P(C_6H_5)$_3$), 122.92 (d, *J* = 99.2 Hz, P(C_6H_5)$_3$), 116.98 (br, *i*-C_6F_5),112.24 (br, -*C*N).

$^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6, ppm):δ -21.42.

$^{19}F\{^1H\}$ NMR (470 MHz, C_6D_6, ppm): δ -133.21 (br, *o*-C_6F_5), -157.80 (br, *p*-C_6F_5), -163.80 (br, *m*-C_6F_5).

$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, ppm): δ 33.48.

FT-IR (solid, cm^{-1}): 2247(C≡N), 1645, 1514, 1462, 1439, 1282, 1182, 1093, 979, 890, 725, 673.

Compound 3

A mixture of **1** (30 mg, 0.1 mmol), $HB(C_6F_5)_2$ (69 mg, 0.2 mmol) and toluene (5 mL) was stirred at ambient temperature for 2 h. The resulting yellow solution was storing at -30 ℃ overnight to afford yellow crystals of **3**. The crystals were collected, washed with cold n-hexane, and then dried under vacuum for 2 hours (64 mg, 64%). Single crystals (yellow) suitable for X-ray analysis were obtained from the toluene solution at -30 ºC for 2 days.

^1H NMR (500 MHz, C_6D_6, ppm): δ 7.22-7.17 (m, 6H, $P(C_6H_5)_3$), 6.96 (td, *J* = 7.4, 1.6 Hz, 3H, $P(C_6H_5)_3$), 6.86 (td, *J* = 7.7, 3.5 Hz, 6H, $P(C_6H_5)_3$), 4.10 (br, 1H, B*H*)3.62 (s, 1H, N*H*).

$^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, ppm): δ 149.11-148.38 (m, *o*-C_6F_5),147.01-146.45 (m, *p*-C_6F_5), 138.14-136.17 (m, *m*-C_6F_5), 134.38 (d, *J* = 3.1 Hz, $P(C_6H_5)_3$), 132.44 (d, *J* = 11.1 Hz, $P(C_6H_5)_3$), 129.36 (d, *J* = 13.2 Hz, $P(C_6H_5)_3$), 121.83 (d, *J* = 102.5 Hz, $P(C_6H_5)_3$), 115.81 (br, *i*-C_6F_5),112.89 (br, -*C*N).

$^{31}B\{^1H\}$ NMR (160 MHz, C_6D_6, ppm):δ -13.98, -17.44.

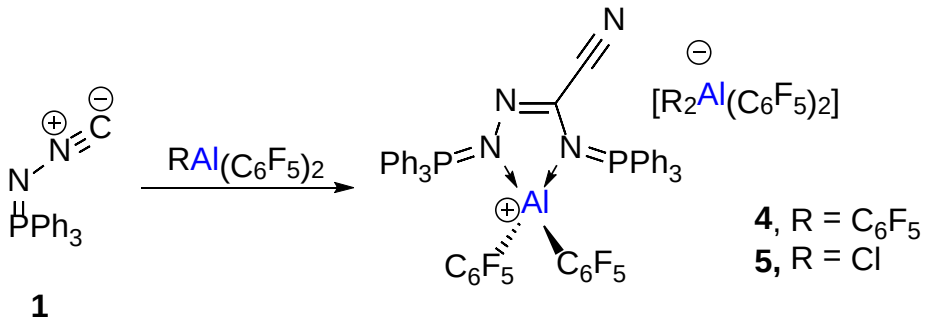
$^{19}F\{^1H\}$ NMR (470 MHz, C_6D_6, ppm): δ -133.64 (br, *o*-C_6F_5), -134.23 (br, *o*-

C_6F_5), -155.06 (br, *p*-C_6F_5), -158.62 (br, *p*-C_6F_5), -162.37 (br, *m*-C_6F_5), -164.41 (br, *m*-C_6F_5).

$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, ppm): δ 35.42.

FT-IR (solid, cm^{-1}): 3397, 2291(C≡N), 1647, 1516, 1464, 1440, 1288, 1096, 971, 751, 724, 690.

Synthesis of compounds 4 and 5



Scheme S1-2: Synthesis of **4** and **5**

Compound 4

A mixture of **1** (30 mg, 0.1 mmol), $Al(C_6F_5)_3$ (57 mg, 0.1 mmol) and toluene (5 mL) was stirred at ambient temperature for 2 h. The resulting yellow solution was storing at -30 ℃ overnight to afford yellow crystals of **4**. The crystals were collected, washed with cold n-hexane, and then dried under vacuum for 2 hours (45 mg, 54%). Single crystals (yellow) suitable for X-ray analysis were obtained from the toluene solution at -30 ºC for 2 days.

^1H NMR (600 MHz, CD_2Cl_2, ppm): δ 7.62-7.49 (m, 12H, $P(C_6H_5)_3$), 7.40-7.27 (m, 12H, $P(C_6H_5)_3$), 7.06-7.00 (m, 6H, $P(C_6H_5)_3$).

$^{13}C\{^1H\}$ NMR (151 MHz, C_6D_5Br, ppm): δ 134.88 (d, *J* = 9.8 Hz, P(*C*$_6$H$_5$)$_3$), 133.83 (d, *J* = 8.6 Hz, P(*C*$_6$H$_5$)$_3$), 133.49 (d, *J* = 10.5 Hz, P(*C*$_6$H$_5$)$_3$), 133.08 (d, *J* = 9.5 Hz, P(*C*$_6$H$_5$)$_3$), 129.47 (d, *J* = 12.7 Hz, P(*C*$_6$H$_5$)$_3$), 129.13 (d, *J* = 12.8 Hz, P(*C*$_6$H$_5$)$_3$), 128.90 (d, *J* = 11.6 Hz, -*C*N), 128.53 (d, *J* = 12.2 Hz, N=*C*), 126.39 (d, *J* = 33.0 Hz, P(*C*$_6$H$_5$)$_3$), 125.71 (d, *J* = 33.5 Hz, P(*C*$_6$H$_5$)$_3$).

$^{19}F\{^1H\}$ NMR (470 MHz, C_6D_5Br, ppm): δ -118.38 (br, *o*-C$_6$*F*$_5$), -137.42 (br, *o*-C$_6$*F*$_5$), -152.74 (br, *p*-C$_6$*F*$_5$), -156.75 (br, *p*-C$_6$*F*$_5$), -160.87 (br, *m*-C$_6$*F*$_5$), -162.26 (br, *m*-C$_6$*F*$_5$).

$^{31}P\{^1H\}$ NMR (243 MHz, C_6D_5Br, ppm): δ 37.36, 24.12.

FT-IR (solid, cm^{-1}): 2252(C≡N), 1559, 1506, 1437, 1111, 1064, 953, 718, 691, 609.

Compound 5

A mixture of **1** (30 mg, 0.1 mmol), ClAl(C_6F_5)$_2$ (40 mg, 0.1 mmol) and toluene (5 mL) was stirred at ambient temperature for 2 h. The resulting yellow solution was storing at -30 ℃ overnight to afford yellow crystals of **5**. The crystals were collected, washed with cold n-hexane, and then dried under vacuum for 2 hours (40 mg, 57%). Single crystals (yellow) suitable for X-ray analysis were obtained from the toluene solution at -30 ºC for 2 days.

^1H NMR (500 MHz, $CDCl_3$, ppm): δ 7.80-7.76 (m, 6H, P(C$_6$*H*$_5$)$_3$), 7.65-7.46 (m, 24H, P(C$_6$*H*$_5$)$_3$).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 136.17 (s, P(*C*$_6$H$_5$)$_3$), 135.58 (s, P(*C*$_6$H$_5$)$_3$), 133.55 (d, *J* = 5.4 Hz, P(*C*$_6$H$_5$)$_3$), 132.64 (d, *J* = 5.8 Hz, P(*C*$_6$H$_5$)$_3$),

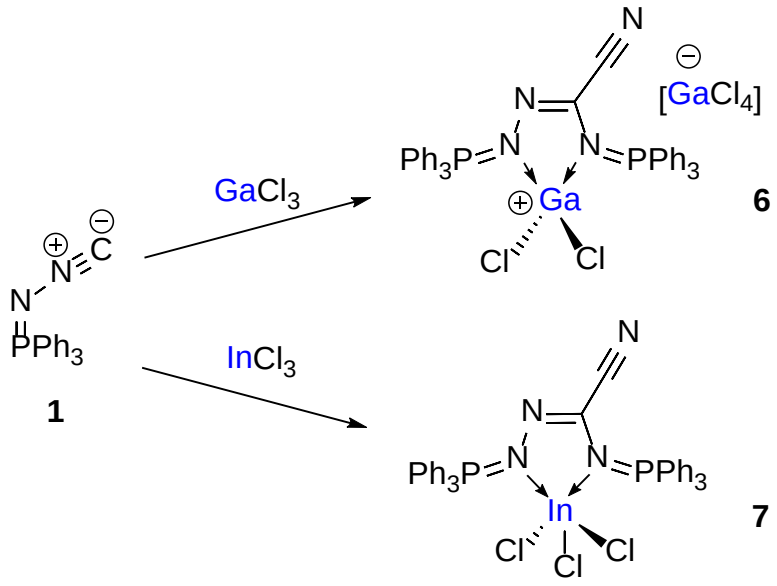
132.64 (d, *J* = 10.5 Hz, -*C*N), 130.44 (d, *J* = 13.5 Hz, P(C_6H_5)$_3$), 130.13 (d, *J* = 13.1 Hz, P(C_6H_5)$_3$), 129.43(d, *J* = 12.9 Hz, N=*C*), 120.38 (d, *J* = 91.7 Hz, P(C_6H_5)$_3$), 119.57 (d, *J* = 91.6 Hz, P(C_6H_5)$_3$).

^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$, ppm): δ -119.47 (br, *o*-C_6F_5), -122.00 (br, *o*-C_6F_5), -148.93 (br, *p*-C_6F_5), -157.13 (br, *p*-C_6F_5), -159.40 (br, *m*-C_6F_5), -163.77 (br, *m*-C_6F_5).

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, ppm): δ 39.84, 36.42.

FT-IR (solid, cm^{-1}): 2922, 2224(C≡N), 1531, 1507, 1436, 1110, 1066, 953, 720, 687.

Synthesis of compounds 6 and 7



Scheme S1-3: Synthesis of **6** and **7**

Compound 6

A mixture of **1** (30 mg, 0.1 mmol), $GaCl_3$ (18 mg, 0.1 mmol) and fluorobenzene

(5 mL) was stirred at ambient temperature for 2 h. The resulting orange solution was storing at -30 ℃ overnight to afford orange crystals of **6**. The crystals were collected, washed with cold n-hexane, and then dried under vacuum for 2 hours (30 mg, 63%). Single crystals (orange) suitable for X-ray analysis were obtained from the fluorobenzene solution at -30 ºC for 1 day.

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.90-7.85 (m, 6H, P(C_6H_5)$_3$), 7.78-7.75 (m, 12H, P(C_6H_5)$_3$), 7.72-7.68 (m, 12H, P(C_6H_5)$_3$).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 136.21 (d, *J* = 3.1 Hz, P(C_6H_5)$_3$), 135.82 (d, *J* = 3.0 Hz, P(C_6H_5)$_3$), 134.27 (d, *J* = 10.7 Hz, P(C_6H_5)$_3$), 134.06 (d, *J* = 11.3 Hz, P(C_6H_5)$_3$), 130.57 (d, *J* = 13.5 Hz, P(C_6H_5)$_3$), 130.28 (d, *J* = 13.1 Hz, P(C_6H_5)$_3$), 129.95(d, *J* = 7.8 Hz, -*C*N), 120.04 (d, *J* = 60.0 Hz, P(C_6H_5)$_3$), 119.23 (d, *J* = 59.5 Hz, P(C_6H_5)$_3$), 115.32 (d, *J* = 20.8 Hz, N=*C*).

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, ppm): δ 41.86, 37.16.

FT-IR (solid, cm^{-1}): 2231(C≡N), 1538, 1436, 1347, 1109,1045, 997, 722, 685, 652, 584.

Compound 7

A mixture of **1** (60 mg, 0.2 mmol), $InCl_3$ (22 mg, 0.1 mmol) and fluorobenzene (5 mL) was stirred at ambient temperature for 2 h. The resulting orange solution was storing at -30 ℃ overnight to afford orange crystals of **7**. The crystals were collected, washed with cold n-hexane, and then dried under vacuum for 2 hours (56 mg, 68%). Single crystals (orange) suitable for X-ray analysis were obtained from the fluorobenzene solution at -30 ºC for 2 days.

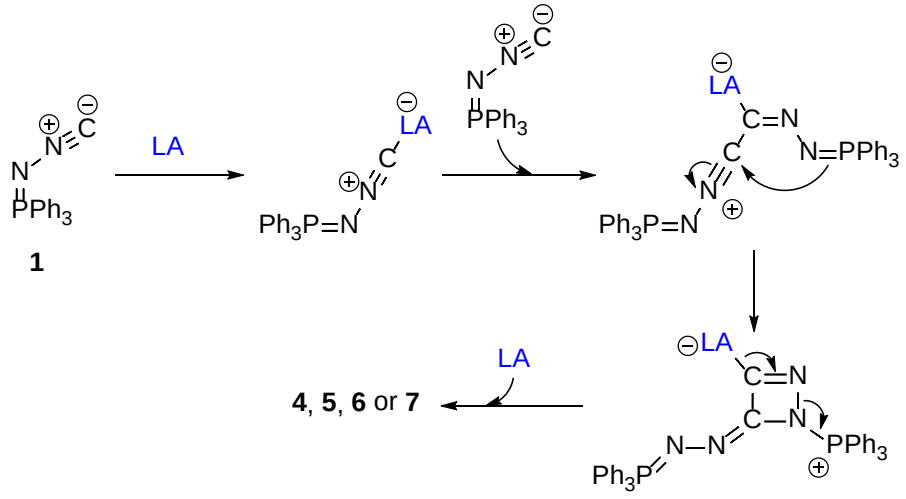
^{1}H NMR (500 MHz, CD_3CN, ppm): δ 7.93-7.72 (m, 24H, P(C_6H_5)$_3$), 7.62-7.59 (m, 6H, P(C_6H_5)$_3$).

^{13}C{^{1}H} NMR (125 MHz, CD_3CN, ppm): δ 136.59 (d, *J* = 3.2 Hz, P(C_6H_5)$_3$), 134.96 (d, *J* = 11.1 Hz, P(C_6H_5)$_3$), 134.58 (d, *J* = 2.9 Hz, P(C_6H_5)$_3$), 133.74(d, *J* = 10.5 Hz, P(C_6H_5)$_3$), 133.57 (d, *J* = 11.2 Hz, -*C*N), 130.97 (d, *J* = 13.4 Hz, P(C_6H_5)$_3$), 130.26 (d, *J* = 12.7 Hz, P(C_6H_5)$_3$), 130.04 (d, *J* = 13.2 Hz, N=*C*), 127.48 (d, *J* = 103.5 Hz, P(C_6H_5)$_3$), 120.62 (d, *J* = 103.8 Hz, P(C_6H_5)$_3$).

^{31}P{^{1}H} NMR (202 MHz, CD_3CN, ppm): δ 37.77, 16.54.

FT-IR (solid, cm^{-1}): 3058, 2218(C≡N), 1530, 1436, 1271, 1106, 1085, 719,686, 571.

Proposed Reaction Mechanism



Scheme S1-4: Proposed reaction mechanism for the formation of **4**-**7**

NMR Spectra of compounds 2-7

Spectra of 2

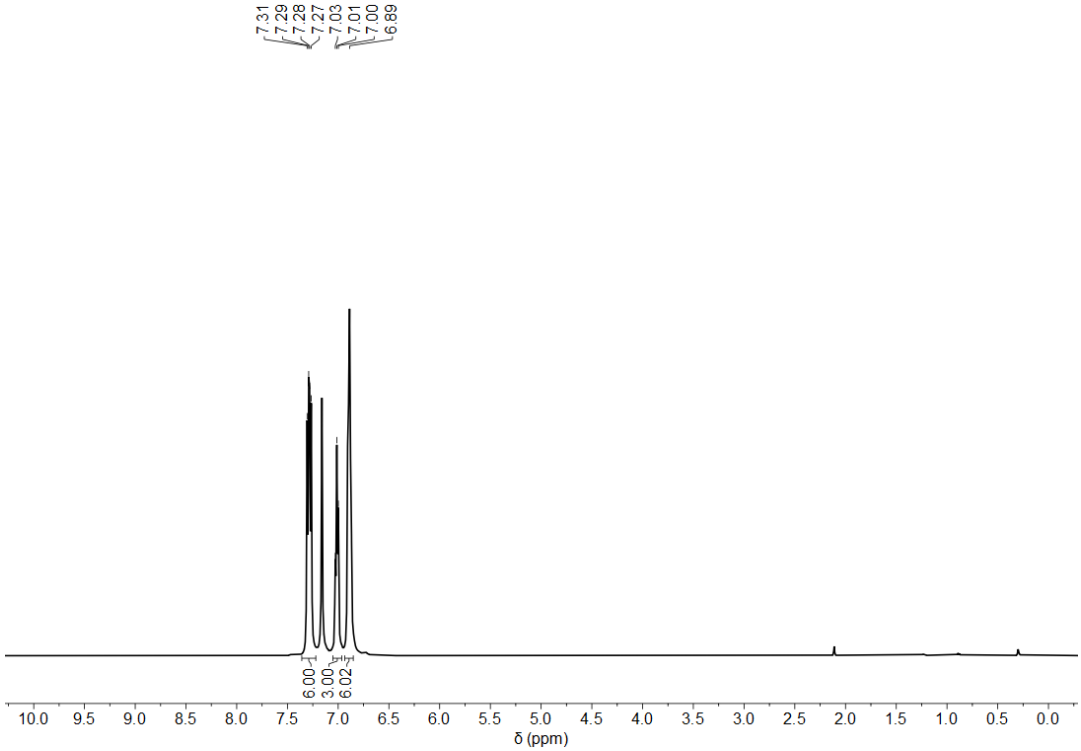


Figure S2-1. ^{1}H NMR spectrum of **2** in C_6D_6

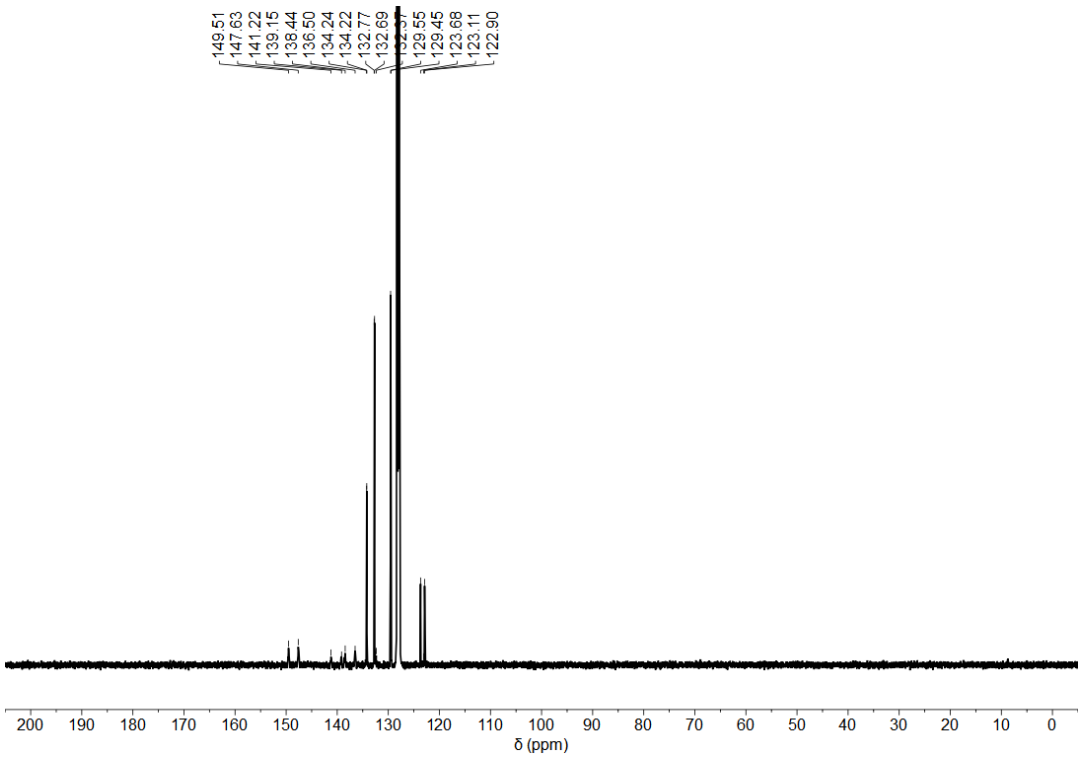


Figure S2-2. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in C_6D_6

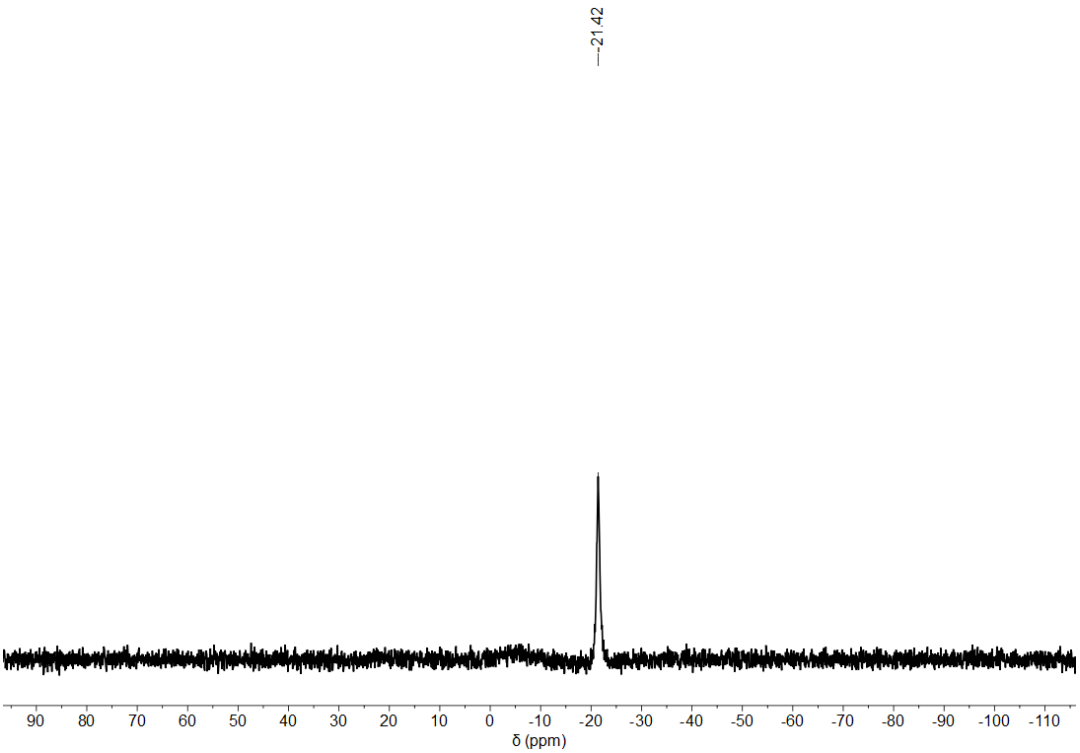


Figure S2-3. $^{11}B\{^{1}H\}$ NMR spectrum of **2** in C_6D_6

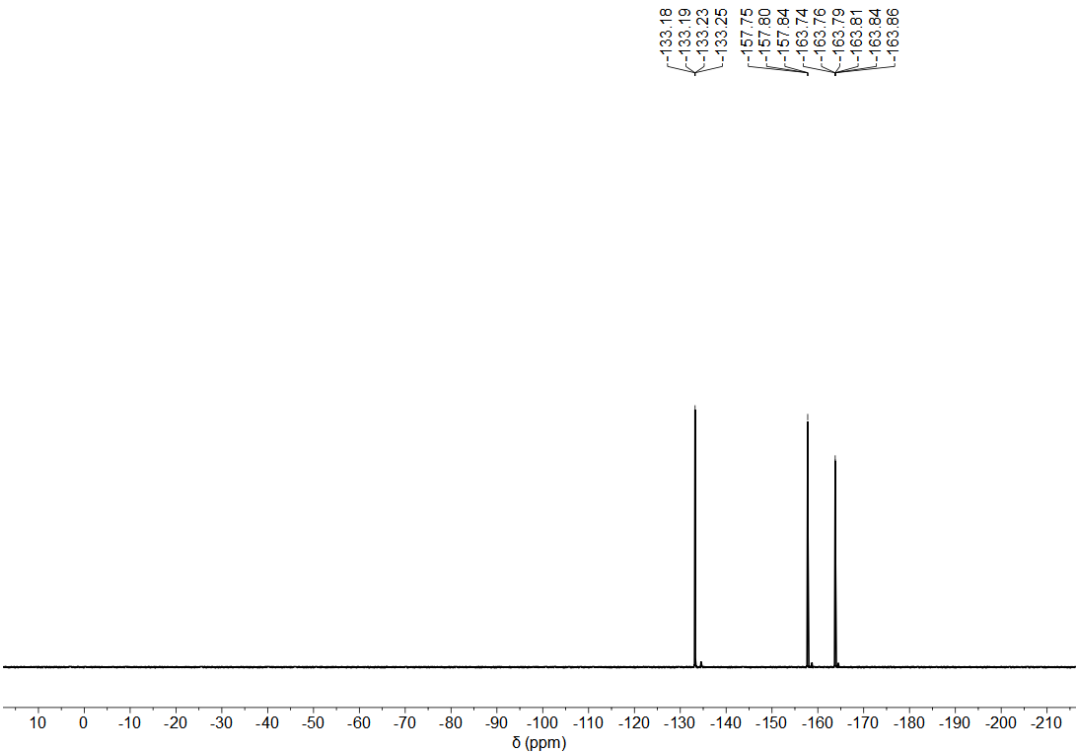


Figure S2-4. $^{19}F\{^{1}H\}$ NMR spectrum of **2** in C_6D_6

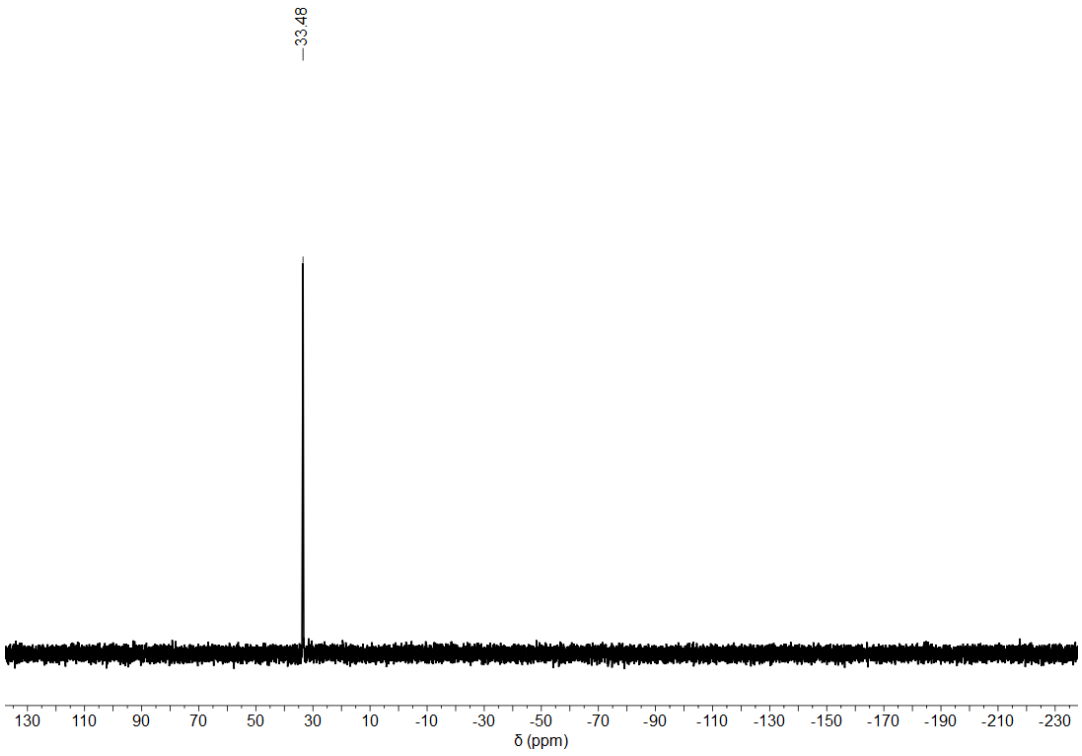


Figure S2-5. $^{31}P\{^{1}H\}$ NMR spectrum of **2** in C_6D_6

Spectra of 3

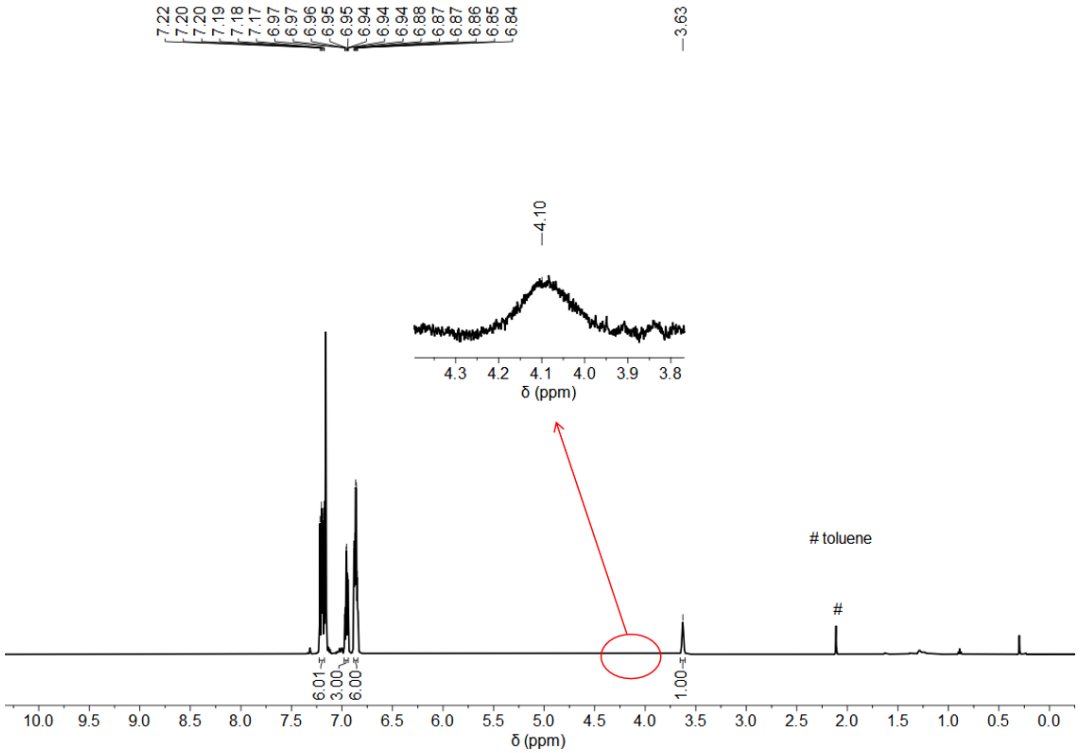


Figure S2-6. ^{1}H NMR spectrum of **3** in C_6D_6 (# toluene)

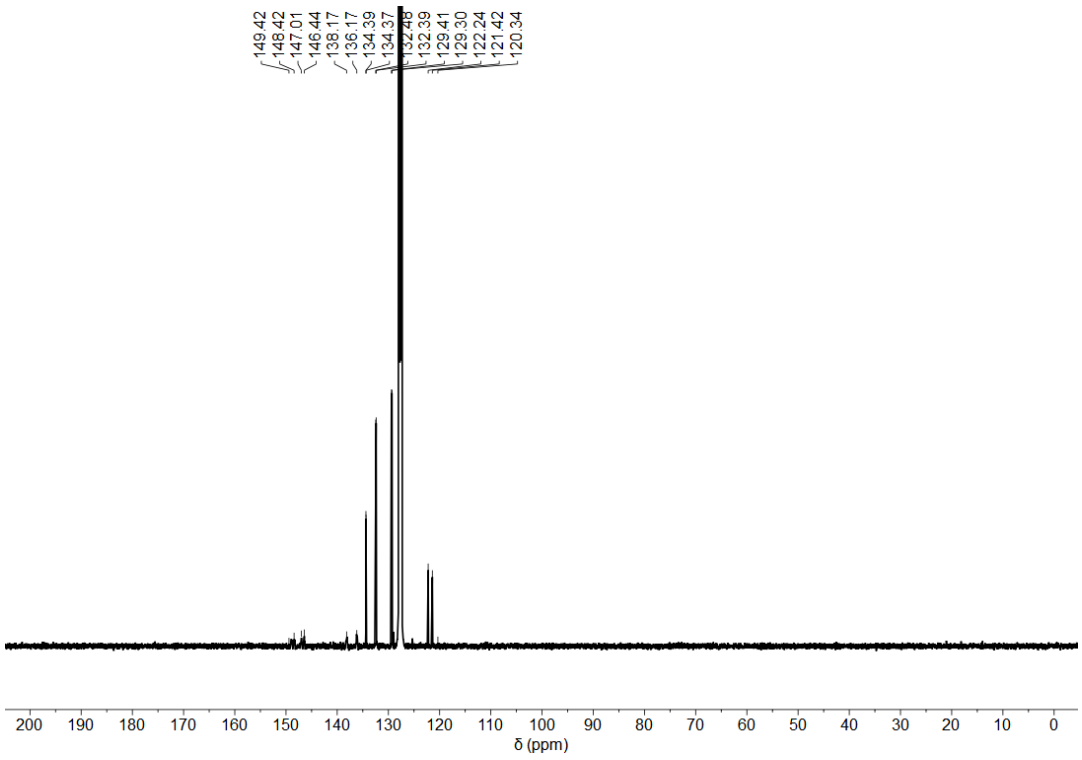


Figure S2-7. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6

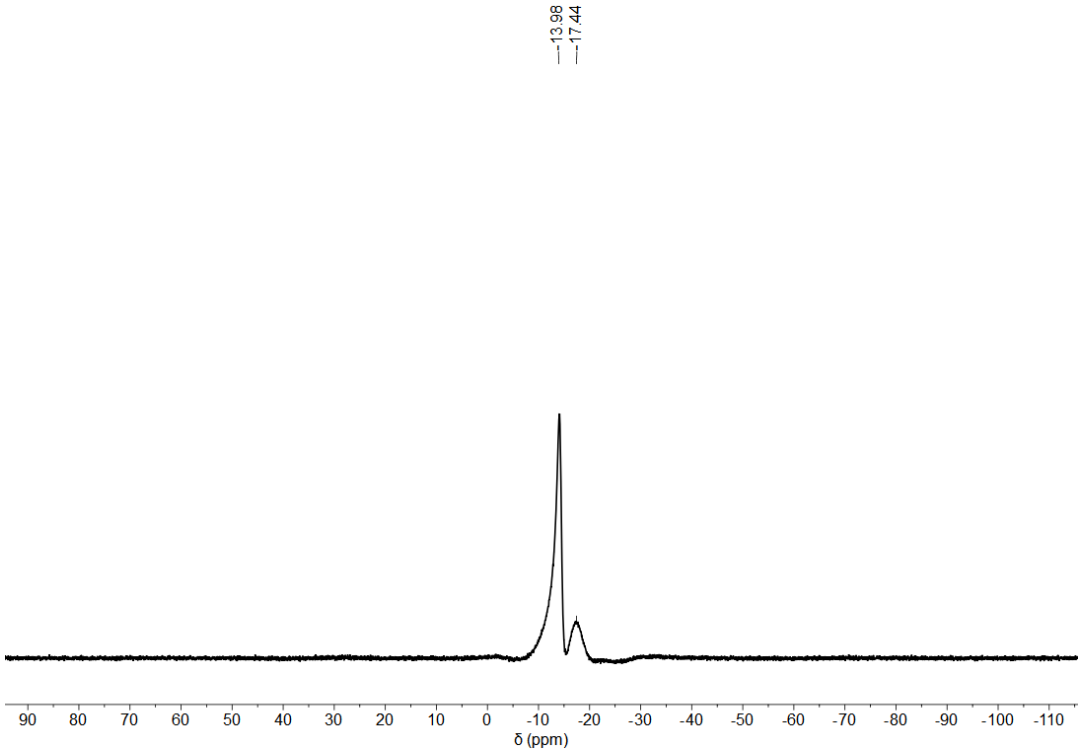


Figure S2-8. $^{11}B\{^{1}H\}$ NMR spectrum of **3** in C_6D_6

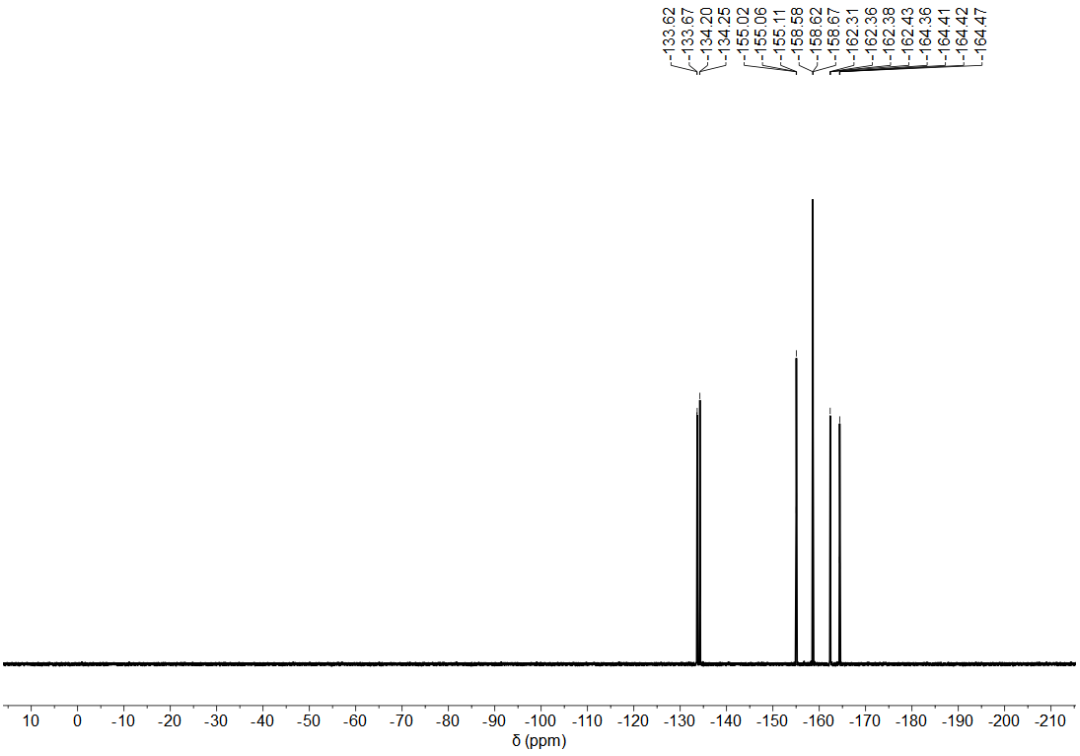


Figure S2-9. $^{19}F\{^{1}H\}$ NMR spectrum of **3** in C_6D_6

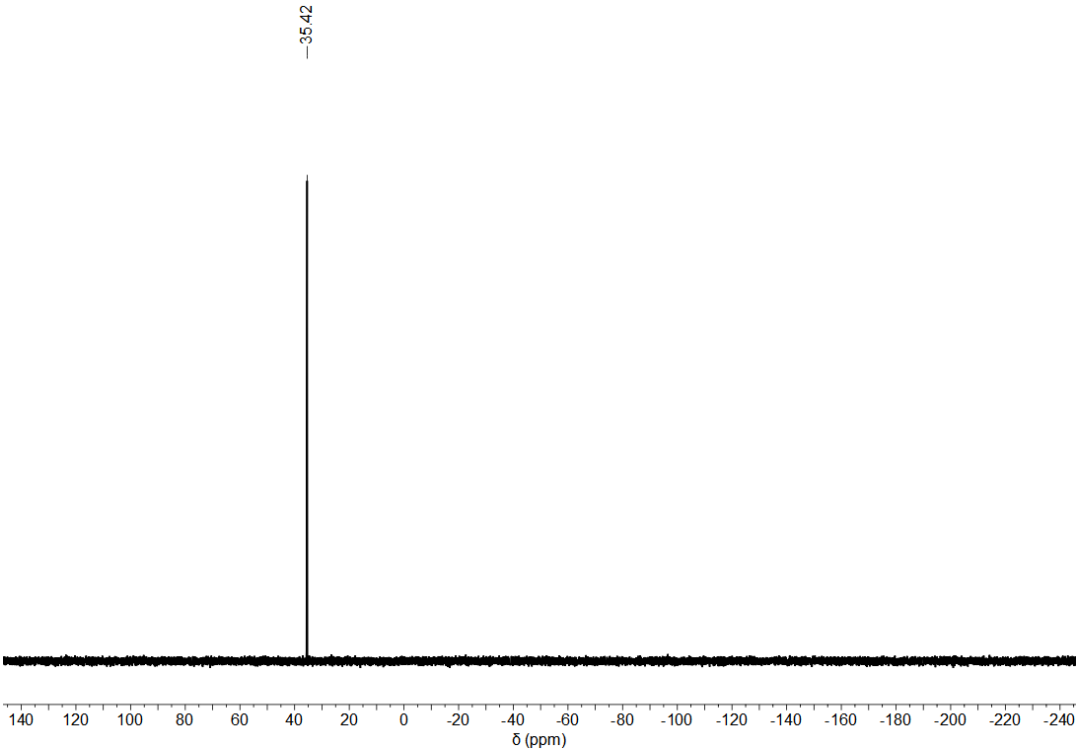


Figure S2-10. $^{31}P\{^{1}H\}$ NMR spectrum of **3** in C_6D_6

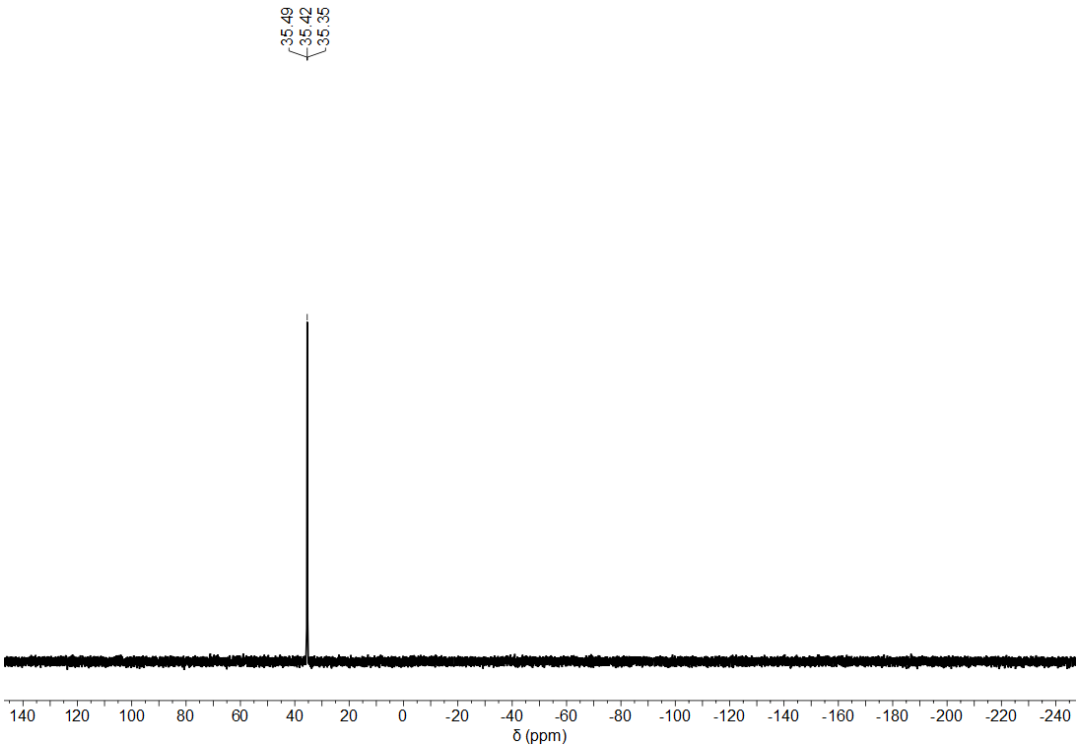


Figure S2-11. ^{31}P NMR spectrum of **3** in C_6D_6

Spectra of 4

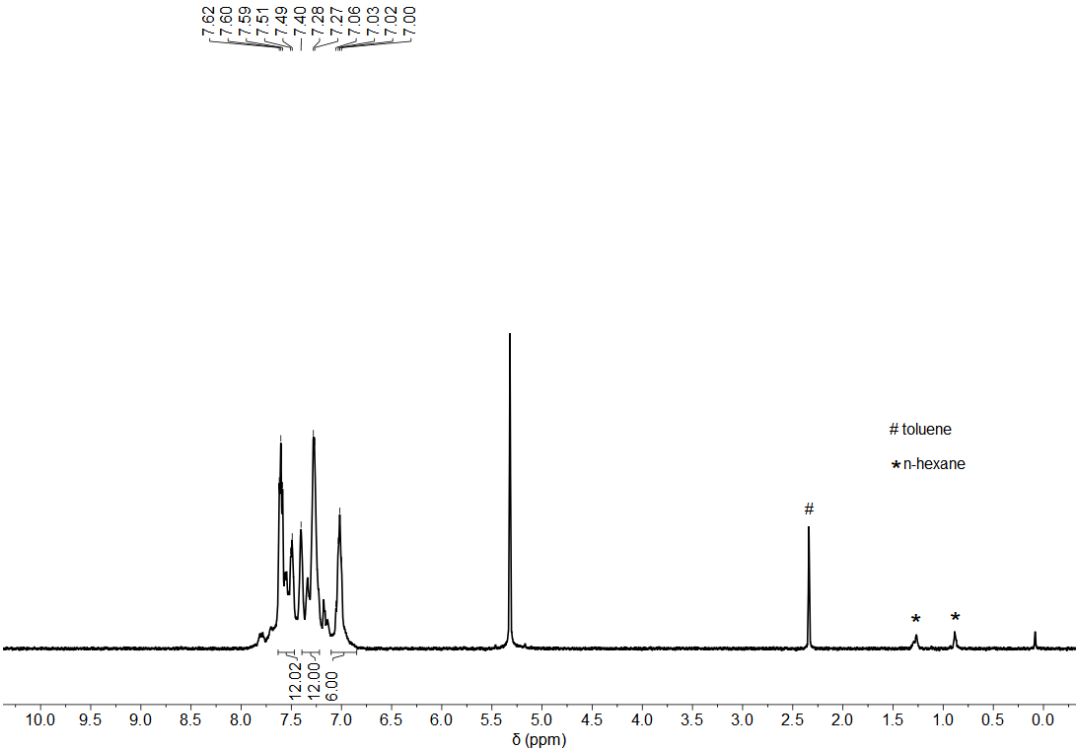


Figure S2-12. ^{1}H NMR spectrum of **4** in CD_2Cl_2 (# toluene * n-hexane)

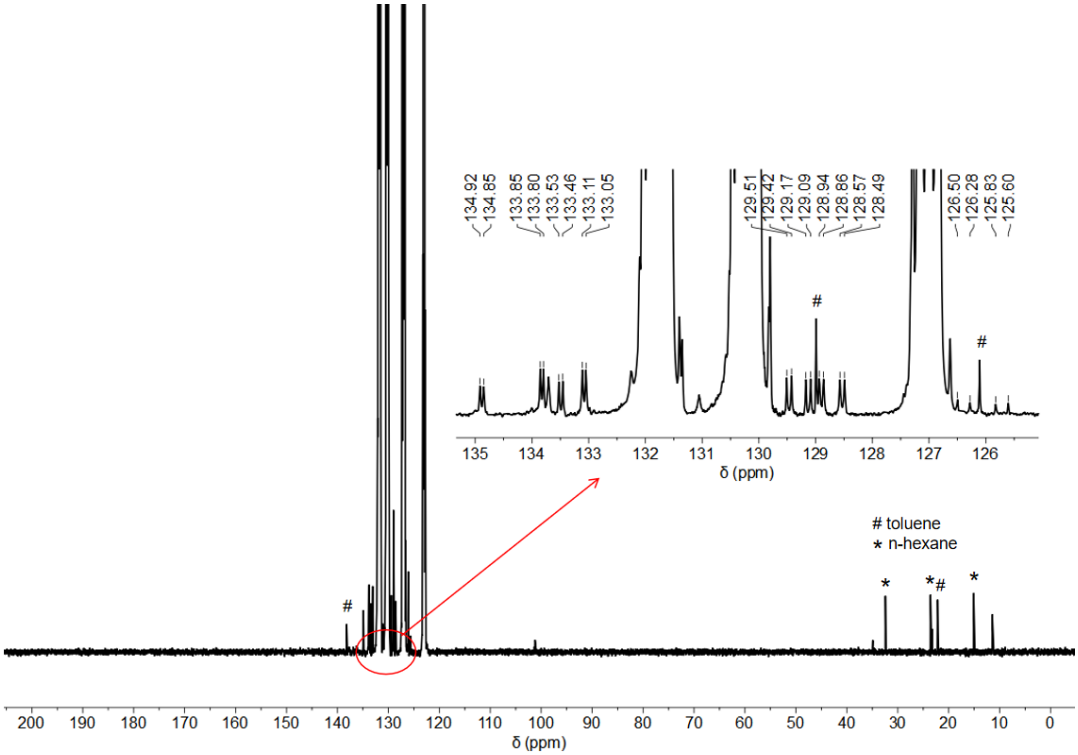


Figure S2-13. ^{13}C NMR spectrum of **4** in C_6D_5Br (# toluene * n-hexane)

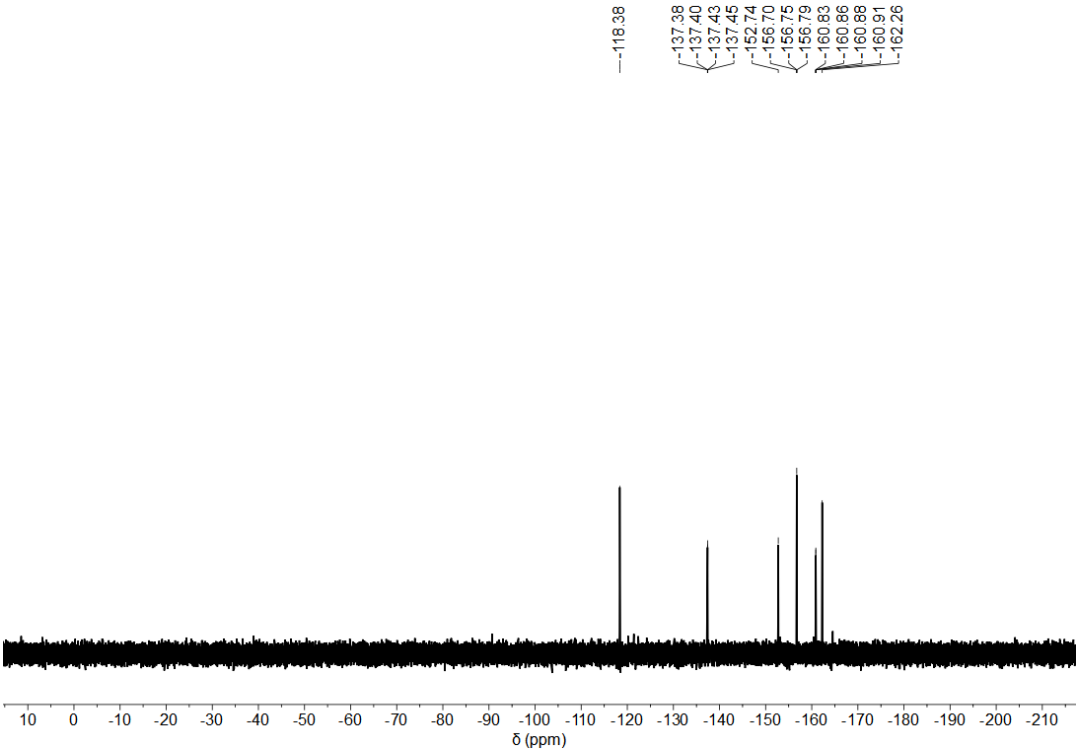


Figure S2-14. $^{19}F\{^{1}H\}$ NMR spectrum of **4** in C_6D_5Br

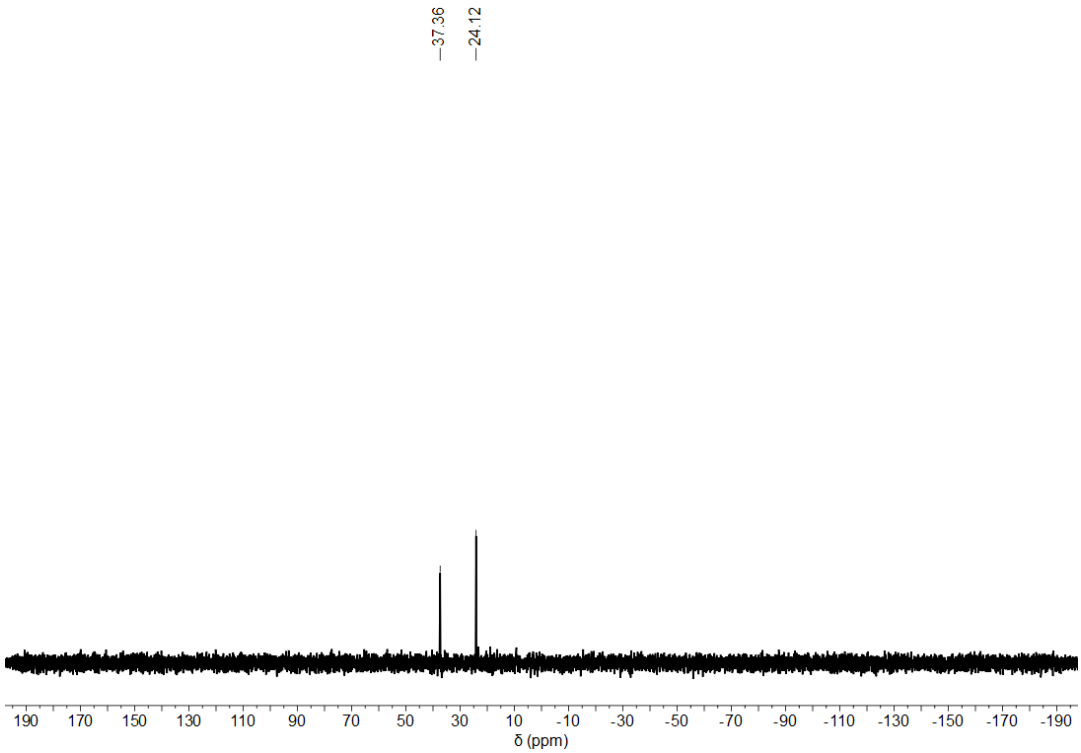


Figure S2-15. $^{31}P\{^{1}H\}$ NMR spectrum of **4** in C_6D_5Br

Spectra of 5

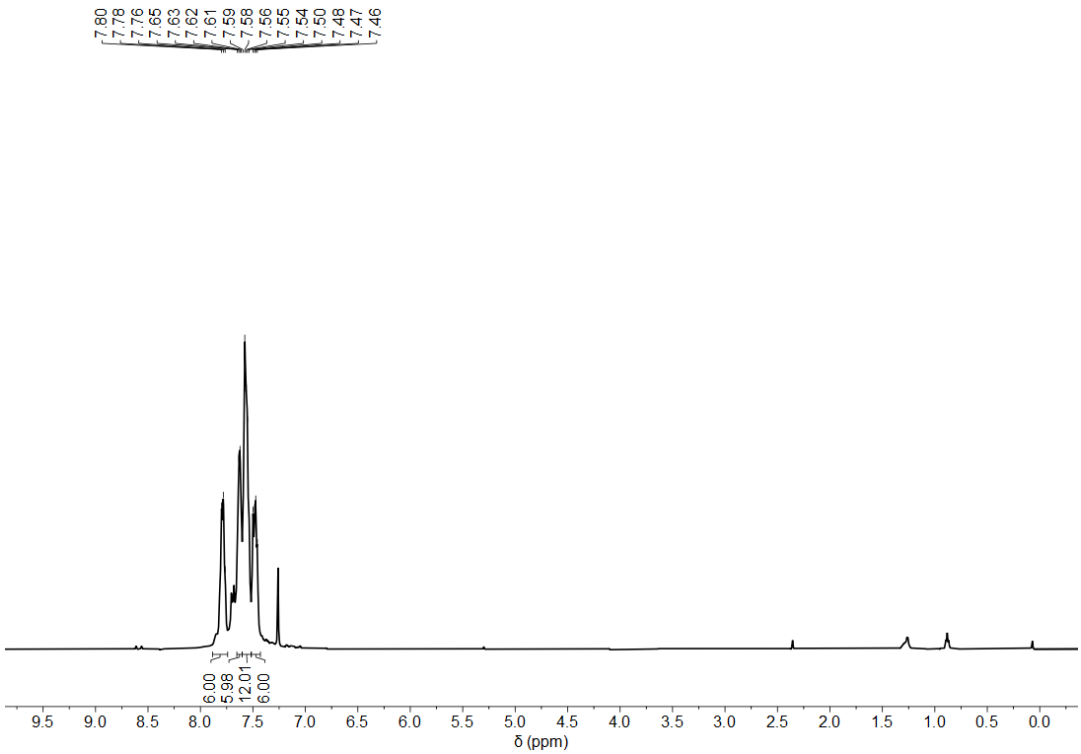


Figure S2-16. ^{1}H NMR spectrum of **5** in $CDCl_3$

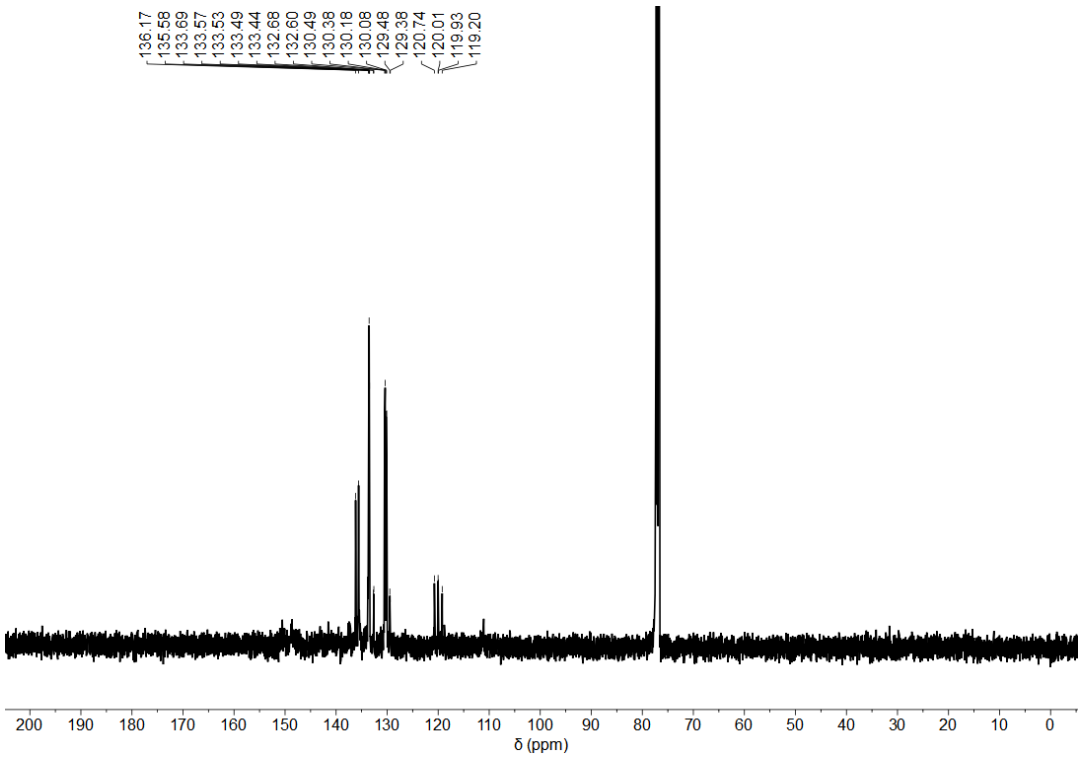


Figure S2-17. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$

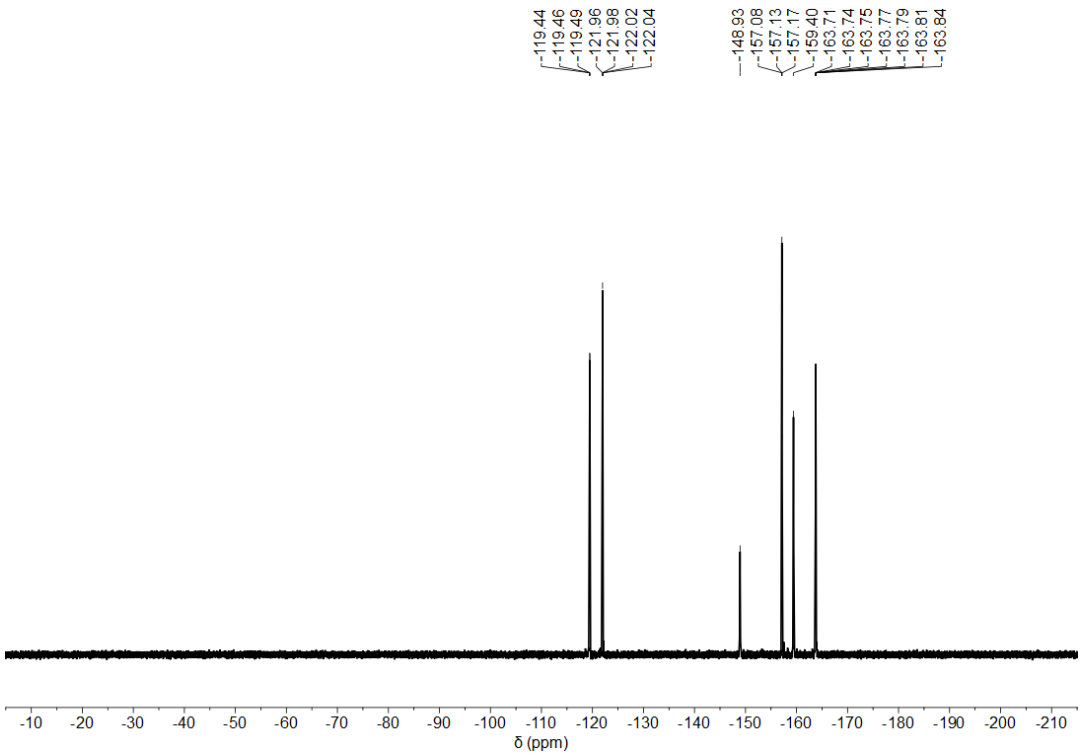


Figure S2-18. $^{19}F\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$

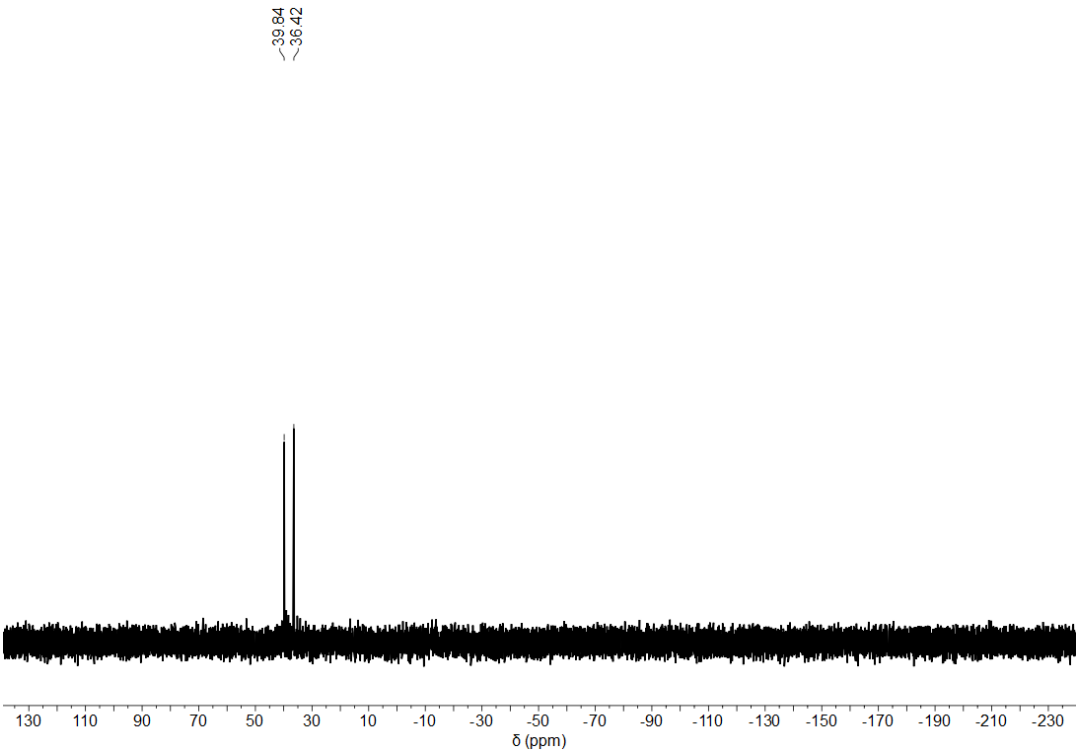


Figure S2-19. $^{31}P\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$

Spectra of 6

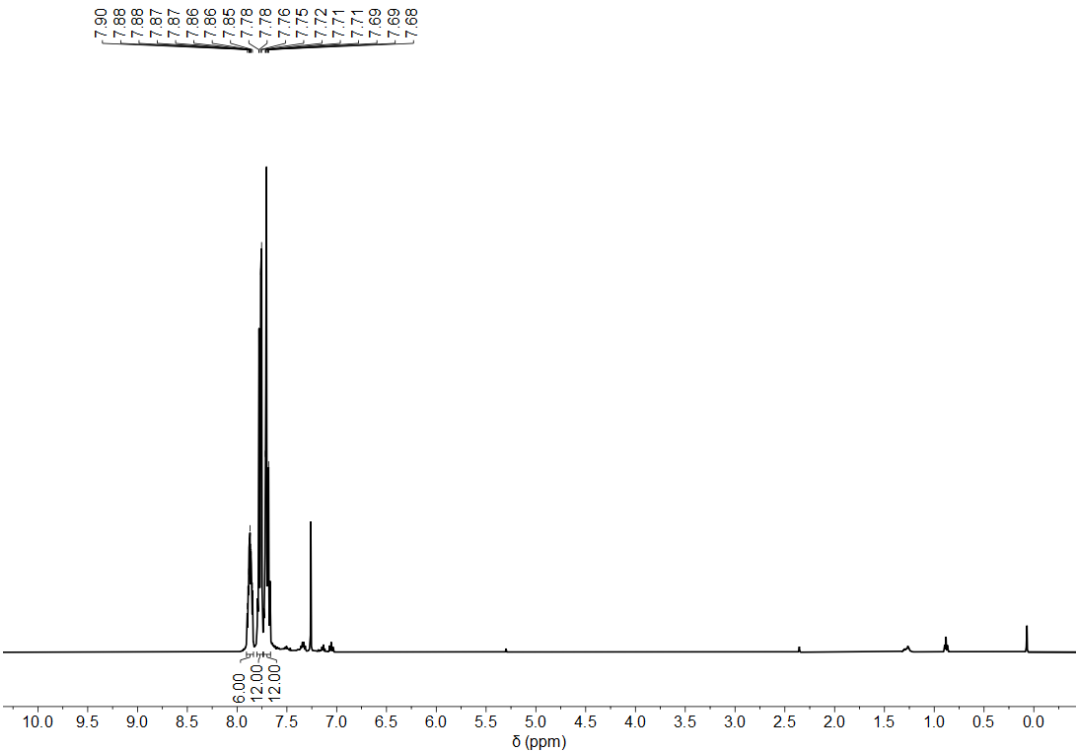


Figure S2-20. ^{1}H NMR spectrum of **6** in $CDCl_3$

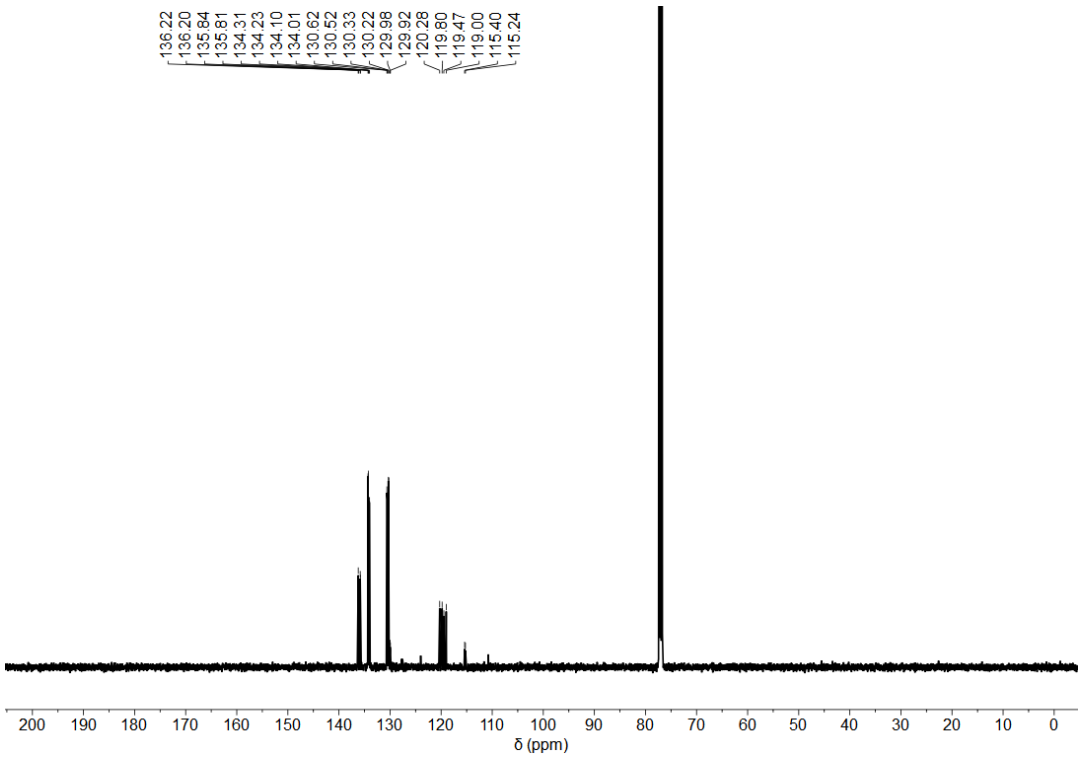


Figure S2-21. $^{13}C\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$

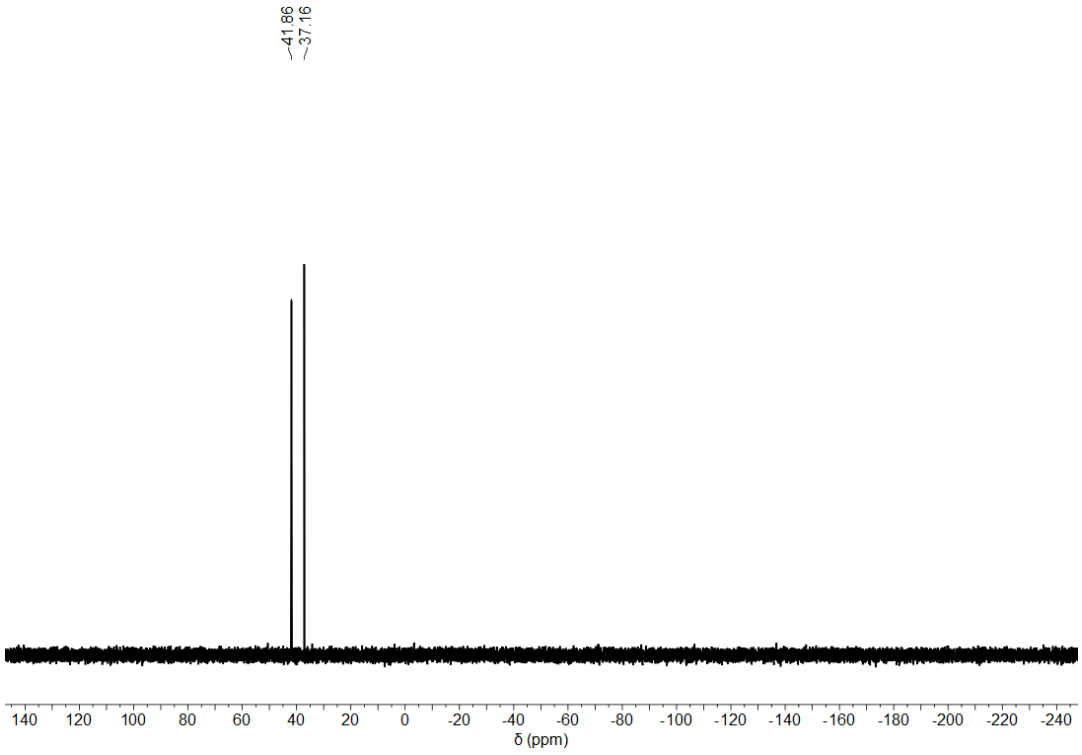


Figure S2-22. $^{31}P\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$

Spectra of 7

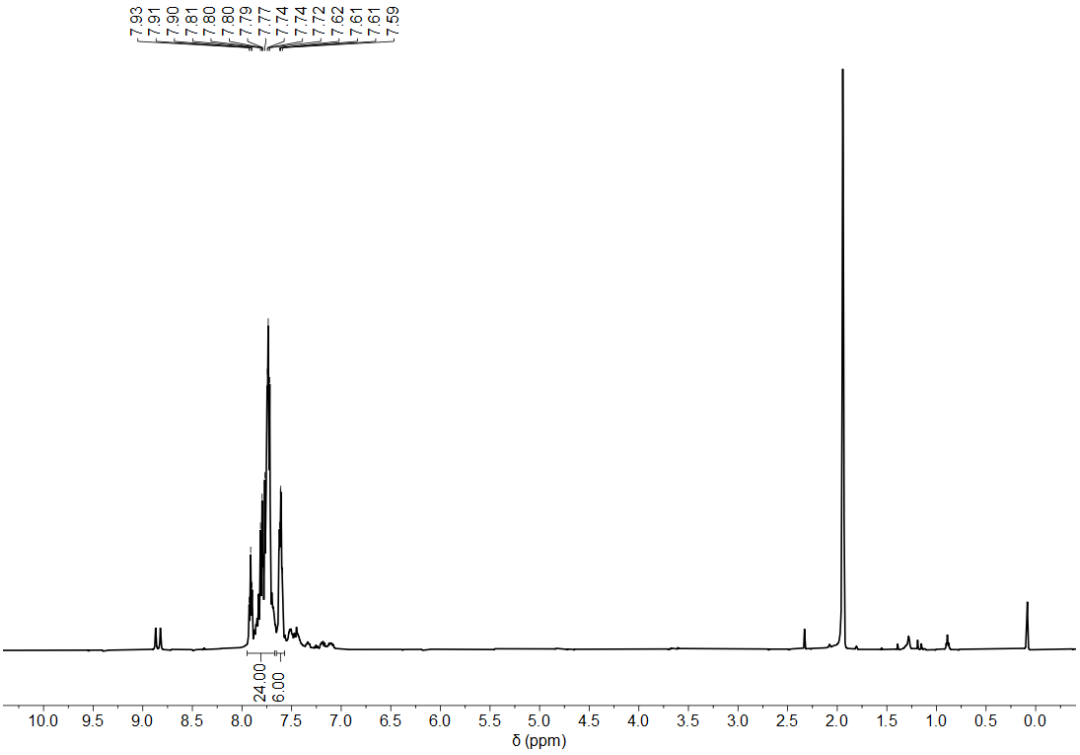


Figure S2-23. ^{1}H NMR spectrum of **7** in CD_3CN

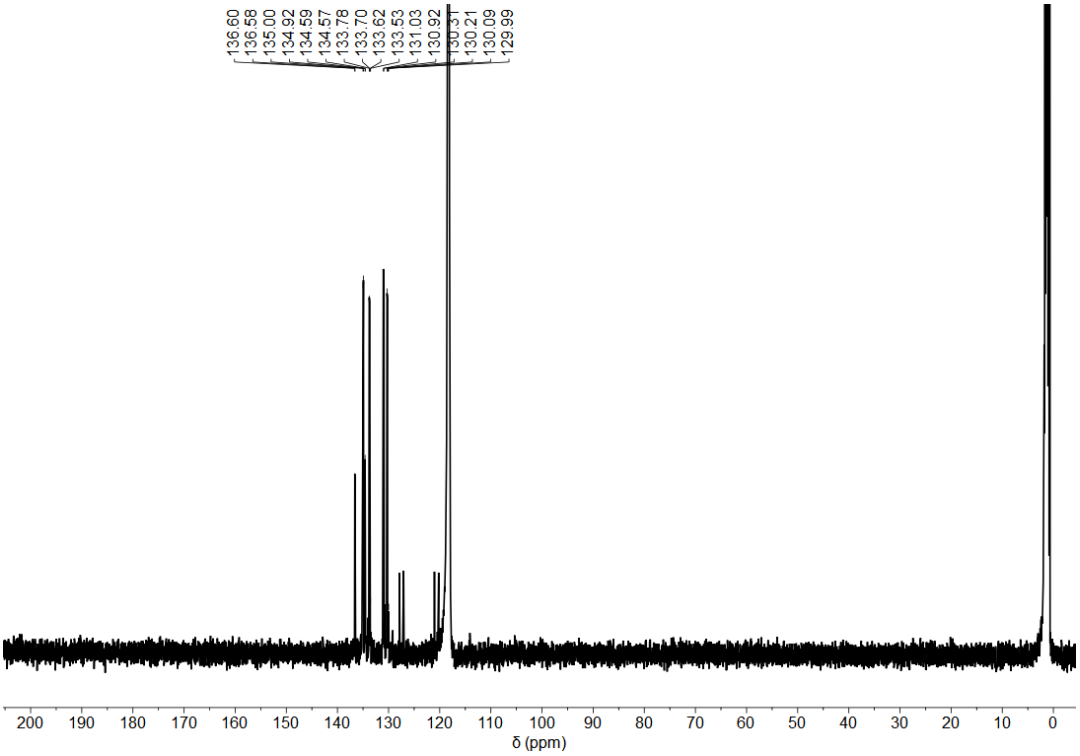


Figure S2-24. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in CD_3CN

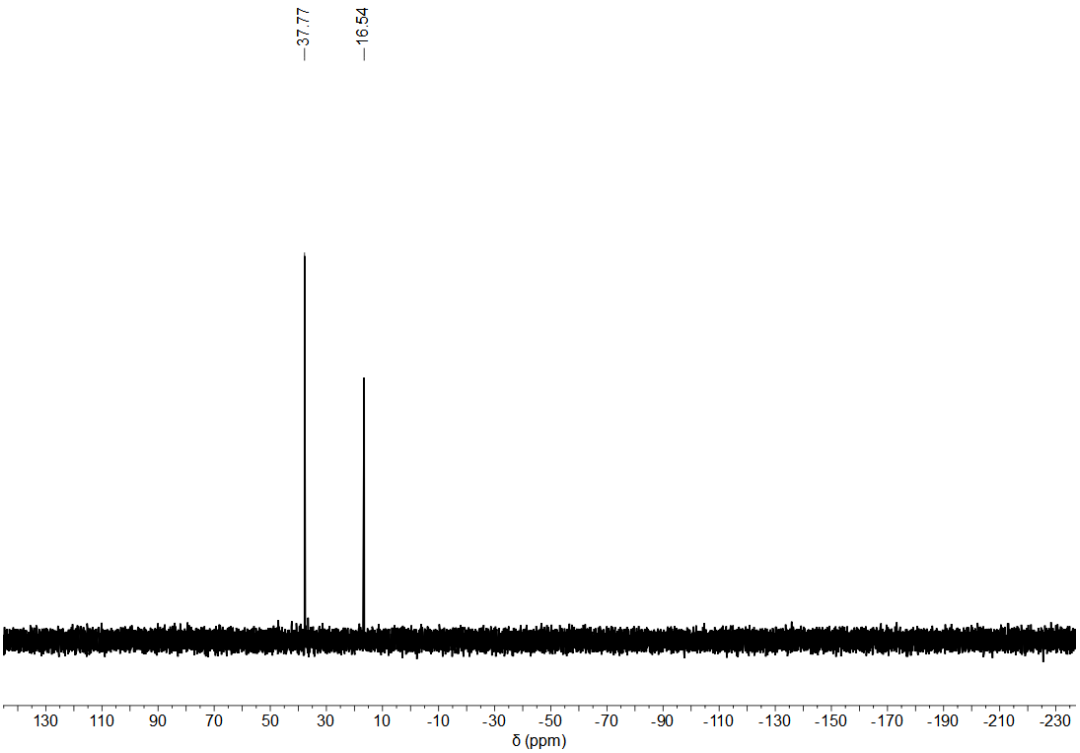


Figure S2-25. $^{31}P\{^{1}H\}$ NMR spectrum of **7** in CD_3CN

X-ray Crystallographic Data

Table S3-1. Crystal data and structure refinement details for compounds **2, 3** and **4**.

Compounds	**2**	**3**	**4**
CCDC	2379880	2379881	2379882
Empirical formula	$C_{37}H_{15}BF_{15}N_2P$	$C_{50}H_{25}B_2F_{20}N_2P$	$C_{81}H_{38}Al_2F_{30}N_4P_2$
Formula weight	814.29	1086.31	1753.05
Temperature, K	150.00	150.00	150.00
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	P-1	P-1
a, Å	11.6295(3)	11.9853(9)	11.2784(2)
b, Å	11.5884(3)	12.0437(9)	17.5791(4)
c, Å	24.2727(6)	18.3470(14)	20.1614(5)
α, deg	90	93.329(4)	94.3340(10)
β, deg	98.2250(10)	104.396(4)	99.0020(10)
γ, deg	90	115.728(4)	100.3890(10)
V, $Å^3$	3237.52(14)	2268.7(3)	3861.10(15)
Z	4	2	2
D_{calcd}, g/cm^3	1.671	1.590	1.508
μ/mm^{-1}	1.862	1.656	1.820
F(000)	1624.0	1088.0	1756.0
2θ range, °	8.028-137.49	5.066-133.162	4.462-136.692
Index ranges	$-14 \le h \le 13$	$-14 \le h \le 14$	$-13 \le h \le 13$
	$-13 \le k \le 13$	$-14 \le k \le 13$	$-21 \le k \le 21$
	$-28 \le l \le 29$	$-21 \le l \le 21$	$-24 \le l \le 24$
Reflections collected	37185	41072	50107
Independent reflections	5926	7987	14089
	$R_{int} = 0.0516$	$R_{int} = 0.0675$	$R_{int} = 0.0751$
	$R_{sigma} = 0.0290$	$R_{sigma} = 0.0469$	$R_{sigma} = 0.0682$
Data/restraints/parameters	5926/0/505	7987/186/754	14089/0/1073
Goodness-of-fit on F^2	1.059	1.083	1.012
Final R indexes [I>=2σ (I)]	$R_1 = 0.0315$	$R_1 = 0.0578$	$R_1 = 0.0526$
	$wR_2 = 0.0823$	$wR_2 = 0.1596$	$wR_2 = 0.1299$
Final R indexes [all data]	$R_1 = 0.0350$	$R_1 = 0.0747$	$R_1 = 0.0799$
	$wR_2 = 0.0848$	$wR_2 = 0.1731$	$wR_2 = 0.1439$
Largest diff. peak/hole, $e/Å^{-3}$	0.43/-0.33	0.63/-0.66	0.45/-0.44

Table S3-2. Crystal data and structure refinement details for compounds **5, 6** and **7**.

Compounds	**5**	**6**	**7**
CCDC	2379885	2379884	2379883
Empirical formula	$C_{81.3}H_{50.2}Al_2Cl_2F_{21}N_4P_2$	$C_{82}H_{65}Cl_{12}FGa_4N_8P_4$	$C_{62}H_{50}Cl_3F_4InN_4P_2$
Formula weight	1668.85	2009.58	1210.17
Temperature, K	150.00	150.00	150.00
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	P-1	Cc
a, Å	15.3044(6)	17.4641(12)	24.0532(5)
b, Å	25.9421(11)	17.7994(11)	20.9341(4)
c, Å	19.9557(8)	17.8166(10)	11.6059(2)
α, deg	90	79.202(4)	90
β, deg	109.490(2)	62.982(4)	102.4310(10)
γ, deg	90	61.288(4)	90
V, Å^3	7469.0(5)	4323.8(5)	5706.94(19)
Z	4	2	4
D_{calcd}, g/cm^3	1.484	1.544	1.408
μ/mm^{-1}	2.312	5.942	5.591
F(000)	3380.0	2020.0	2464.0
2θ range, °	5.802-137.176	5.572-133.19	5.654-133
Index ranges	$-18 \le h \le 18$	$-20 \le h \le 20$	$-28 \le h \le 28$
	$-31 \le k \le 31$	$-21 \le k \le 21$	$-24 \le k \le 24$
	$-24 \le l \le 24$	$-21 \le l \le 21$	$-12 \le l \le 13$
Reflections collected	318927	143281	44823
Independent reflections	13718	15249	9390
	R_{int} = 0.0732	R_{int} = 0.1602	R_{int} = 0.0555
	R_{sigma} = 0.0211	R_{sigma} = 0.0757	R_{sigma} = 0.0502
Data/restraints/parameters	13718/270/1150	15249/42/988	9390/221/766
Goodness-of-fit on F^2	1.097	1.066	1.090
Final R indexes [I>=2σ (I)]	R_1 = 0.0445	R_1 = 0.0662	R_1 = 0.0304
	wR_2 = 0.1163	wR_2 = 0.1763	wR_2 = 0.0675
Final R indexes [all data]	R_1 = 0.0503	R_1 = 0.1028	R_1 = 0.0321
	wR_2 = 0.1196	wR_2 = 0.1983	wR_2 = 0.0682
Largest diff. peak/hole, e/Å^{-3}	0.54/-0.42	1.07/-0.96	0.61/-0.73

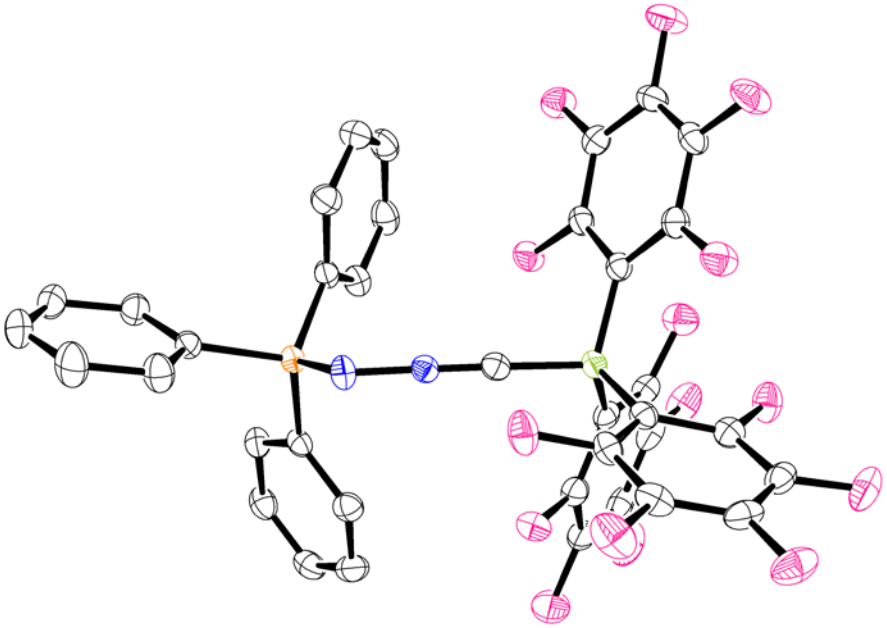


Figure S3-1. Solid-state structures of **2**. Hydrogen atoms omitted for clarity. Thermal ellipsoids are set at the 50% probability level.

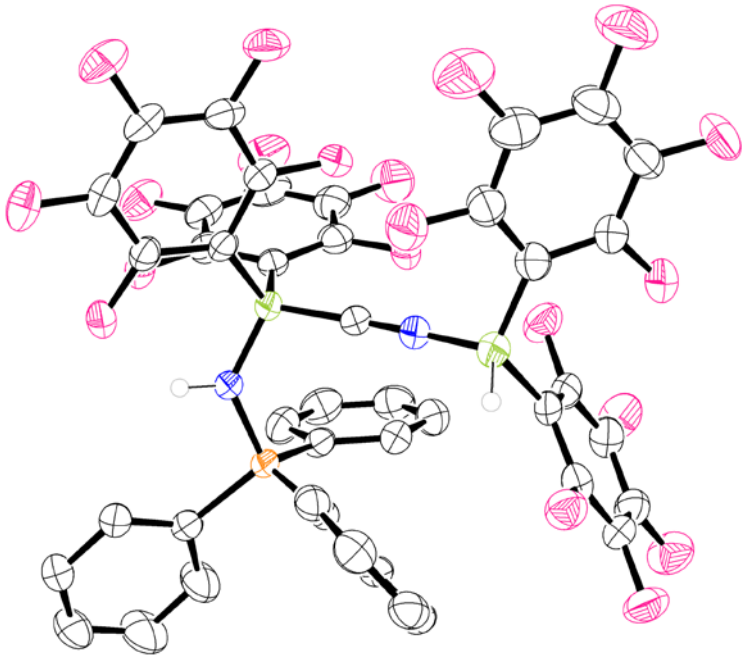


Figure S3-2. Solid-state structures of **3**. Hydrogen atoms (except those linked to N or B atoms) omitted for clarity. Thermal ellipsoids are set at the 50% probability level.

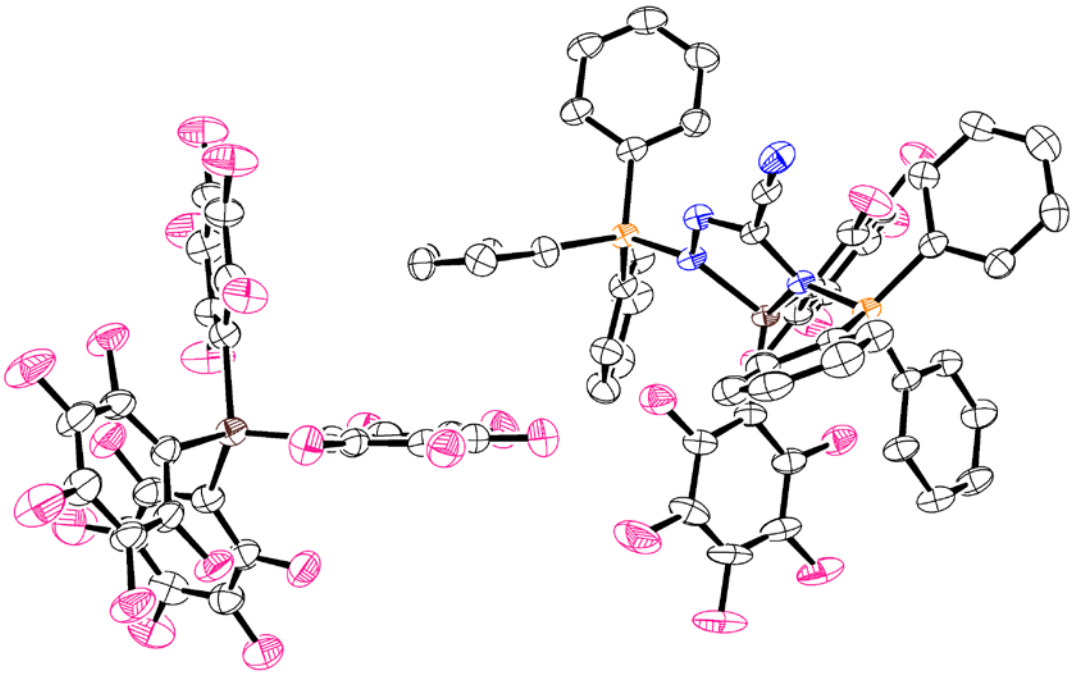


Figure S3-3. Solid-state structures of **4**. Hydrogen atoms omitted for clarity. Thermal ellipsoids are set at the 50% probability level.

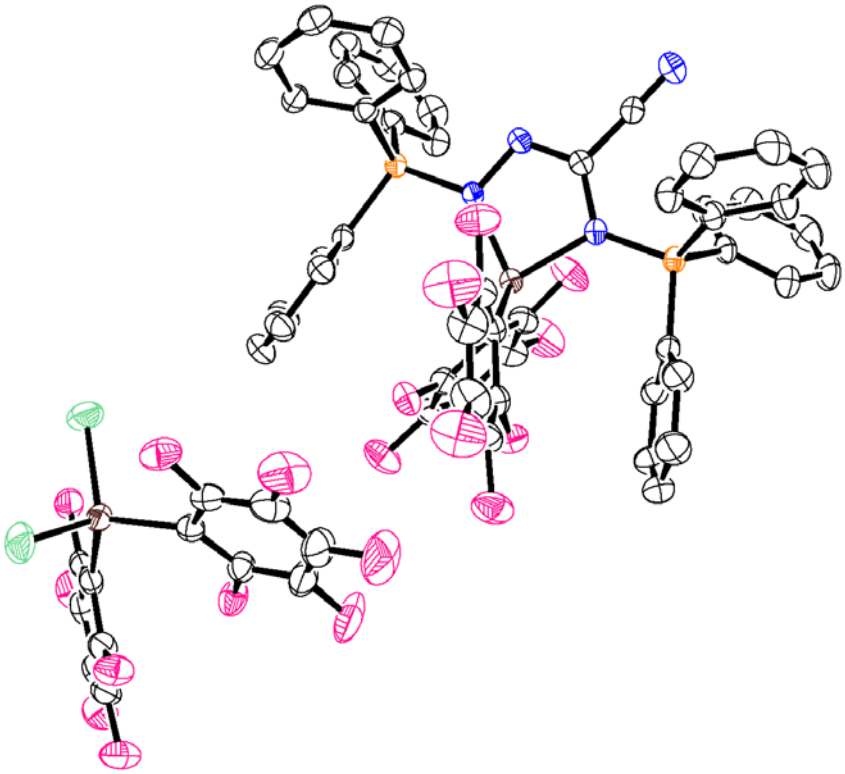


Figure S3-4. Solid-state structures of **5**. Hydrogen atoms omitted for clarity. Thermal ellipsoids are set at the 50% probability level.

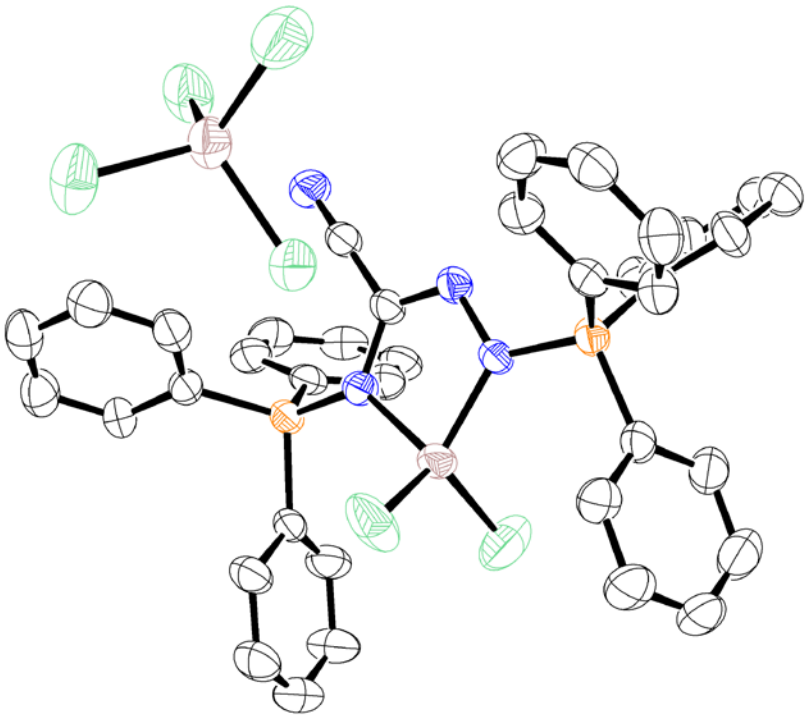


Figure S3-5. Solid-state structures of **6**. Hydrogen atoms omitted for clarity. Thermal ellipsoids are set at the 50% probability level.

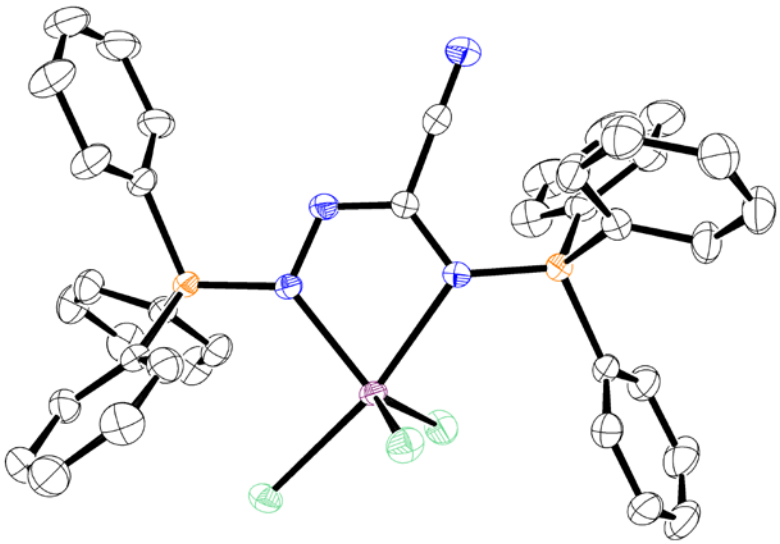


Figure S3-6. Solid-state structures of **7**. Hydrogen atoms omitted for clarity. Thermal ellipsoids are set at the 50% probability level.

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 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 Chemcraft[S9] program.

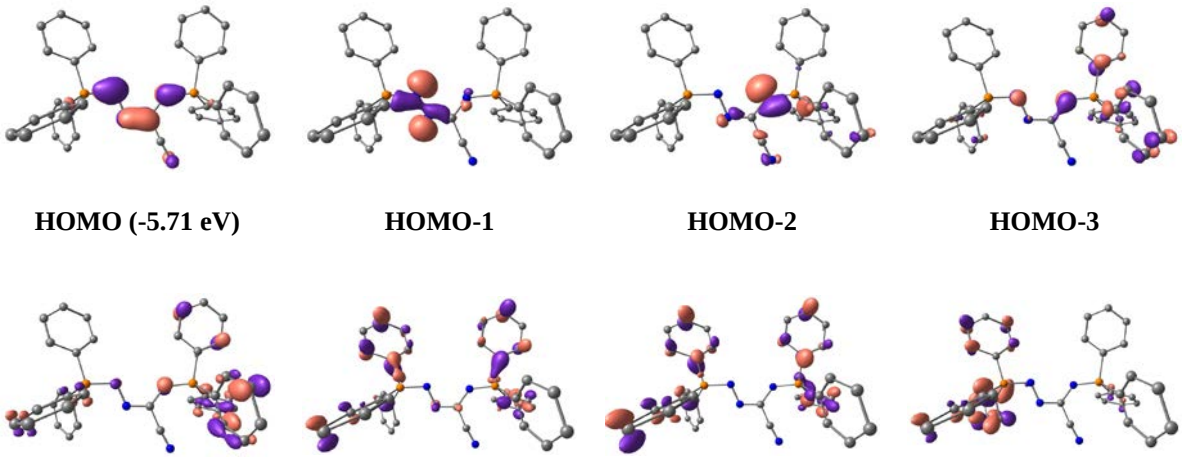


Figure S4-1. Selected molecular orbitals for **A** at M06-2X/def2-TZVP level. Isovalue = 0.05.

Reference

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[S2] D. J. Parks, H.Von, R. E. Spence, W. E. Piers, *Angew. Chem. Int. Ed.*, 1995, **34**, 809-811.

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[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, D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

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Cartesian Coordinates of the Optimized Geometries

A (M06-2X/def2-SVP)

SCF Done: E(RM062X) = -2365.57592578 A.U.

P	-2.85367200	-0.10014100	-0.13380100
P	2.94632200	-0.00910300	-0.09236900
N	0.77965200	1.17330500	-0.28507800
N	-1.31564400	0.08909400	-0.41820600
C	-3.13656800	-1.89066400	-0.20970400
C	2.72657500	-2.58289000	-1.06431000
H	1.77183800	-2.22080600	-1.45018800
C	-4.42661700	-2.42984700	-0.23540200
H	-5.29996000	-1.77316700	-0.24092000
N	-1.66785900	3.53183400	-0.38487000
C	4.74111100	-2.13922800	0.21450100
H	5.35096000	-1.45933300	0.81437900
C	4.70329800	1.11552000	1.84241400
H	5.41577500	1.28665800	1.03133900
C	-2.01695700	-2.72805400	-0.21531400
H	-1.02470800	-2.26876400	-0.20192600
C	5.17224700	-3.44501300	-0.01334700
H	6.12265800	-3.78347000	0.40143500
C	3.45791800	0.53817400	1.57186600
N	1.35103500	-0.06661800	-0.29776300
C	-0.51024900	1.19055700	-0.33814600
C	3.59175400	2.42518300	-1.23672900
H	2.81669600	2.80957200	-0.57063000
C	3.52135300	-1.70745300	-0.31608200
C	-3.48973000	0.44822600	1.49003600
C	3.89852300	1.05569700	-1.22452300
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H	2.54547800	-4.57442100	-1.86625900
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H	-3.32213500	-1.50610000	2.40407400

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H	2.12715900	0.60198800	4.70488200
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H	-3.61842500	-5.73443600	-0.28374600
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C	-4.18115600	2.23964100	2.96255900
H	-4.41358900	3.29378700	3.11909400
C	4.25585600	3.27387300	-2.11863100
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C	4.86068900	0.54726600	-2.10333200
H	5.09189000	-0.51999400	-2.10800000

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H	-6.17277900	2.28138500	-4.11425700
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H	4.35262500	1.59769400	5.19316300
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H	5.74530100	3.43609900	-3.67292800
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A (M06-2X/def2-TZVP)

SCF Done: E(RM062X) = -2367.67230577 A.U.

P	2.85367200	0.10014100	-0.13380100
P	-2.94632200	0.00910300	-0.09236900
N	-0.77965200	-1.17330500	-0.28507800
N	1.31564400	-0.08909400	-0.41820600
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C	-2.72657500	2.58289000	-1.06431000
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C	4.42661700	2.42984700	-0.23540200
H	5.29996000	1.77316700	-0.24092000
N	1.66785900	-3.53183400	-0.38487000
C	-4.74111100	2.13922800	0.21450100
H	-5.35096000	1.45933300	0.81437900
C	-4.70329800	-1.11552000	1.84241400
H	-5.41577500	-1.28665800	1.03133900
C	2.01695700	2.72805400	-0.21531400
H	1.02470800	2.26876400	-0.20192600
C	-5.17224700	3.44501300	-0.01334700
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N	-1.35103500	0.06661800	-0.29776300
C	0.51024900	-1.19055700	-0.33814600
C	-3.59175400	-2.42518300	-1.23672900
H	-2.81669600	-2.80957200	-0.57063000
C	-3.52135300	1.70745300	-0.31608200
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C	2.19719800	4.11112900	-0.24070200
H	1.32699000	4.76949800	-0.24393700
C	4.20102800	-1.58468500	-3.58437600
H	3.76268900	-1.84668000	-4.54818500
C	3.40556700	-1.01161900	-2.59403800
H	2.34416000	-0.82005500	-2.76788500
C	-5.02538700	-1.48839100	3.14667100
H	-5.99598000	-1.93876900	3.35969400
C	5.31619900	-0.94051000	-1.10582800
H	5.74927200	-0.71403100	-0.12841500
C	1.10377300	-2.52186800	-0.36130800
C	-4.38374000	4.31794600	-0.76335100
H	-4.72155900	5.34068200	-0.93860200
C	-2.85336700	-0.73668100	3.90202500
H	-2.12715900	-0.60198800	4.70488200
C	4.26577800	-1.33663100	4.02251700
H	4.57156500	-1.68339200	5.01095900
C	3.95692900	0.00811600	3.82099800
H	4.02041400	0.71548600	4.64910400
C	-2.52859700	-0.35600000	2.60157400
H	-1.55195300	0.07166300	2.36217800
C	3.79424400	-1.80114900	1.69781500
H	3.71845600	-2.51631900	0.87528300
C	4.59771400	3.81202000	-0.26116300
H	5.60282300	4.23533700	-0.28388000
C	3.48247500	4.65184900	-0.26260900
H	3.61842500	5.73443600	-0.28374600
C	6.10915600	-1.50820900	-2.10126100
H	7.16336900	-1.71029000	-1.90653700

C	4.18115600	-2.23964100	2.96255900
H	4.41358900	-3.29378700	3.11909400
C	-4.25585600	-3.27387300	-2.11863100
H	-4.01217000	-4.33712600	-2.13145600
C	-4.86068900	-0.54726600	-2.10333200
H	-5.09189000	0.51999400	-2.10800000
C	5.55161600	-1.82946700	-3.33933200
H	6.17277900	-2.28138500	-4.11425700
C	-4.10134000	-1.29770300	4.17449900
H	-4.35262500	-1.59769400	5.19316300
C	-5.22530900	-2.76672900	-2.98566200
H	-5.74530100	-3.43609900	-3.67292800
C	-5.52605000	-1.40590000	-2.97899600
H	-6.27962000	-1.00754100	-3.65993200

A (M06-2X/def2-TZVP; SMD, toluene)

SCF Done: E(RM062X) = -2367.71648623 A.U.

P	2.85367200	0.10014100	-0.13380100
P	-2.94632200	0.00910300	-0.09236900
N	-0.77965200	-1.17330500	-0.28507800
N	1.31564400	-0.08909400	-0.41820600
C	3.13656800	1.89066400	-0.20970400
C	-2.72657500	2.58289000	-1.06431000
H	-1.77183800	2.22080600	-1.45018800
C	4.42661700	2.42984700	-0.23540200
H	5.29996000	1.77316700	-0.24092000
N	1.66785900	-3.53183400	-0.38487000
C	-4.74111100	2.13922800	0.21450100
H	-5.35096000	1.45933300	0.81437900
C	-4.70329800	-1.11552000	1.84241400
H	-5.41577500	-1.28665800	1.03133900
C	2.01695700	2.72805400	-0.21531400
H	1.02470800	2.26876400	-0.20192600
C	-5.17224700	3.44501300	-0.01334700
H	-6.12265800	3.78347000	0.40143500
C	-3.45791800	-0.53817400	1.57186600

N	-1.35103500	0.06661800	-0.29776300
C	0.51024900	-1.19055700	-0.33814600
C	-3.59175400	-2.42518300	-1.23672900
H	-2.81669600	-2.80957200	-0.57063000
C	-3.52135300	1.70745300	-0.31608200
C	3.48973000	-0.44822600	1.49003600
C	-3.89852300	-1.05569700	-1.22452300
C	3.96223300	-0.68509600	-1.35360100
C	-3.16284600	3.88826300	-1.28443800
H	-2.54547800	4.57442100	-1.86625900
C	3.56583700	0.45278400	2.55905400
H	3.32213500	1.50610000	2.40407400
C	2.19719800	4.11112900	-0.24070200
H	1.32699000	4.76949800	-0.24393700
C	4.20102800	-1.58468500	-3.58437600
H	3.76268900	-1.84668000	-4.54818500
C	3.40556700	-1.01161900	-2.59403800
H	2.34416000	-0.82005500	-2.76788500
C	-5.02538700	-1.48839100	3.14667100
H	-5.99598000	-1.93876900	3.35969400
C	5.31619900	-0.94051000	-1.10582800
H	5.74927200	-0.71403100	-0.12841500
C	1.10377300	-2.52186800	-0.36130800
C	-4.38374000	4.31794600	-0.76335100
H	-4.72155900	5.34068200	-0.93860200
C	-2.85336700	-0.73668100	3.90202500
H	-2.12715900	-0.60198800	4.70488200
C	4.26577800	-1.33663100	4.02251700
H	4.57156500	-1.68339200	5.01095900
C	3.95692900	0.00811600	3.82099800
H	4.02041400	0.71548600	4.64910400
C	-2.52859700	-0.35600000	2.60157400
H	-1.55195300	0.07166300	2.36217800
C	3.79424400	-1.80114900	1.69781500
H	3.71845600	-2.51631900	0.87528300

C	4.59771400	3.81202000	-0.26116300
H	5.60282300	4.23533700	-0.28388000
C	3.48247500	4.65184900	-0.26260900
H	3.61842500	5.73443600	-0.28374600
C	6.10915600	-1.50820900	-2.10126100
H	7.16336900	-1.71029000	-1.90653700
C	4.18115600	-2.23964100	2.96255900
H	4.41358900	-3.29378700	3.11909400
C	-4.25585600	-3.27387300	-2.11863100
H	-4.01217000	-4.33712600	-2.13145600
C	-4.86068900	-0.54726600	-2.10333200
H	-5.09189000	0.51999400	-2.10800000
C	5.55161600	-1.82946700	-3.33933200
H	6.17277900	-2.28138500	-4.11425700
C	-4.10134000	-1.29770300	4.17449900
H	-4.35262500	-1.59769400	5.19316300
C	-5.22530900	-2.76672900	-2.98566200
H	-5.74530100	-3.43609900	-3.67292800
C	-5.52605000	-1.40590000	-2.97899600
H	-6.27962000	-1.00754100	-3.65993200