Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary information

An arene-stabilized η^5-pentamethylcyclopentadienyl antimony dication acts as a source of Sb^+ or Sb^{3+} cations

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This PDF file includes:

1. General Information

All manipulations were performed in a MB Unilab glove box produced by MBraun or using standard Schlenk techniques under an inert atmosphere of anhydrous N_2. All glassware was oven-dried and cooled under vacuum before use. Dry, oxygen-free solvents (toluene (tol), dichloromethane, *n*-pentane) were prepared using an Innovative Technologies solvent purification system. 1,2-Difluorobenzene (DFB) was degassed and stored over molecular sieves (4 Å) for at least two days prior to use. Deuterated dichloromethane (CD_2Cl_2) purchased from Cambridge Isotope Laboratories Inc. were degassed and stored over molecular sieves (4 Å) for at least two days prior to use. Commercial reagents were used without further purification unless indicated otherwise. Cp*$SbCl_2$[S1] and bis(diisopropylamino) cyclopropenylidenes (BAC)[S2] were prepared according to literature procedures. NMR spectra were obtained on a Bruker AvanceIII-400 MHz spectrometer, an Agilent DD2 600 MHz spectrometer or an Agilent DD2 500 MHz spectrometer. ^{1}H, $^{13}C\{^{1}H\}$ NMR chemical shifts (δ/ppm) are referenced to the residual solvent resonance of the deuterated solvent. ^{31}P, ^{19}F and $^{11}B\{^{1}H\}$ NMR chemical shifts (δ/ppm) are referenced to H_3PO_4, $CFCl_3$ and $BF_3{\cdot}OEt_2$, respectively. Mass spectroscopy (MS) studies were performed on an Agilent 6538 Q-TOF (ESI) or a JMS-T100LC JOEL (DART). For dicationic compounds **1**, **2** and **5**, and tricationic compound **6**, no targeted cationic peak for the antimony species could be detected by either of the two machines, due to their multiply charged nature. For compound **4**, only the cationic peak of $[(BAC)H]^+$ was detected, due to the vulnerable Sb–C bonds. For compounds **5** and **6**, only cationic peaks of $[bipyH]^+$ (ESI-MS(+) of $[C_{10}H_8N_2]H^+$ calc. 157.08 m/z; found 157.08 m/z) could be observed. Elemental analyses were carried out by staff at ANALEST at the University of Toronto on a Flash 2000 CHNS Analyzer. Satisfactory elemental analyses of compounds **1, 2,** and **5** could also not be obtained due to their significant sensitivity to air and moisture. However, satisfactory elemental analysis of compound **6** was obtained, and is reported herein. We propose that the strong Lewis acidity and significant sensitivity to air and moisture of most of these compounds prevent obtaining the satisfactory MS and EA results. These results are in accordance with what has been recently observed in the literature for an analogous compound, $Cp^*Sb(OTf)_2$, for which microanalyses could also not be obtained due to its high sensitivity.[S3]

2. Preparation and Spectroscopic Data

Generation of 1·tol: Toluene (1 mL) solution of Et_3SiH (56 mg, 0.48 mmol) was added into toluene (3 mL) solution of $[Ph_3C][B(C_6F_5)_4]$ (369 mg, 0.40 mmol), and the mixture was stirred at room temperature for 5 minutes to give colorless solution and pale yellow oil on the bottom. The supernatant was removed, and the oil residue was washed with toluene (4 mL × 3). To the oil residue, toluene (2 mL) was added. Then to the mixture, toluene (1 mL) solution of Cp^*SbCl_2 (66 mg, 0.20 mmol) was added, and the mixture was stirred at room temperature for 30 minutes to give pale yellow precipitate. The supernatant was removed and the yellow solid was washed with toluene (3 mL × 3) and then *n*-pentane (3 mL) and dried under vacuum to give **1**·tol ($[(\eta^5\text{-}Cp^*)Sb(tol)][B(C_6F_5)_4]_2\cdot$tol) as a pale yellow solid (343 mg, 95% yield). Single crystals of **1**·2tol were obtained by layering of *n*-pentane on a toluene/DFB solution at room temperature. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ (ppm) 7.35 (t, $^3J_{H\text{-}H}$ = 7 Hz, 4H, $Ar^{toluene}$-*H*), 7.30 (d, $^3J_{H\text{-}H}$ = 7 Hz, 4H, $Ar^{toluene}$-*H*), 7.25 (t, $^3J_{H\text{-}H}$ = 7 Hz, 2H, $Ar^{toluene}$-*H*), 2.46 (s, 15H, C_5Me_5), 2.39 (s, 6H, $Me^{toluene}$-*H*). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ (ppm) 148.5 (d(m), $^1J_{C\text{-}F}$ = 241 Hz, C_6F_5), 140.7 (m, $Ar^{toluene}$-*C*), 138.7 (d(m), $^1J_{C\text{-}F}$ = 242 Hz, C_6F_5), 136.7 (d(m), $^1J_{C\text{-}F}$ = 240 Hz, C_6F_5), 133.7 (b(m), C_5Me_5), 130.6 (m, $Ar^{toluene}$-*C*), 129.6 (m, $Ar^{toluene}$-*C*), 126.5 (m, $Ar^{toluene}$-*C*), 124.1 (b(m), C_6F_5), 21.6 (s, $Me^{toluene}$-*C*), 10.2 (s, C_5Me_5). **^{19}F NMR** (377 MHz, CD_2Cl_2): δ (ppm) -133.1 (m, C_6F_5), -163.7 (t, $^3J_{F\text{-}F}$ = 20 Hz, C_6F_5), -167.6 (t, $^3J_{F\text{-}F}$ = 18 Hz, C_6F_5). **^{11}B{^{1}H} NMR** (128 MHz, CD_2Cl_2): δ (ppm) -16.7 (s).

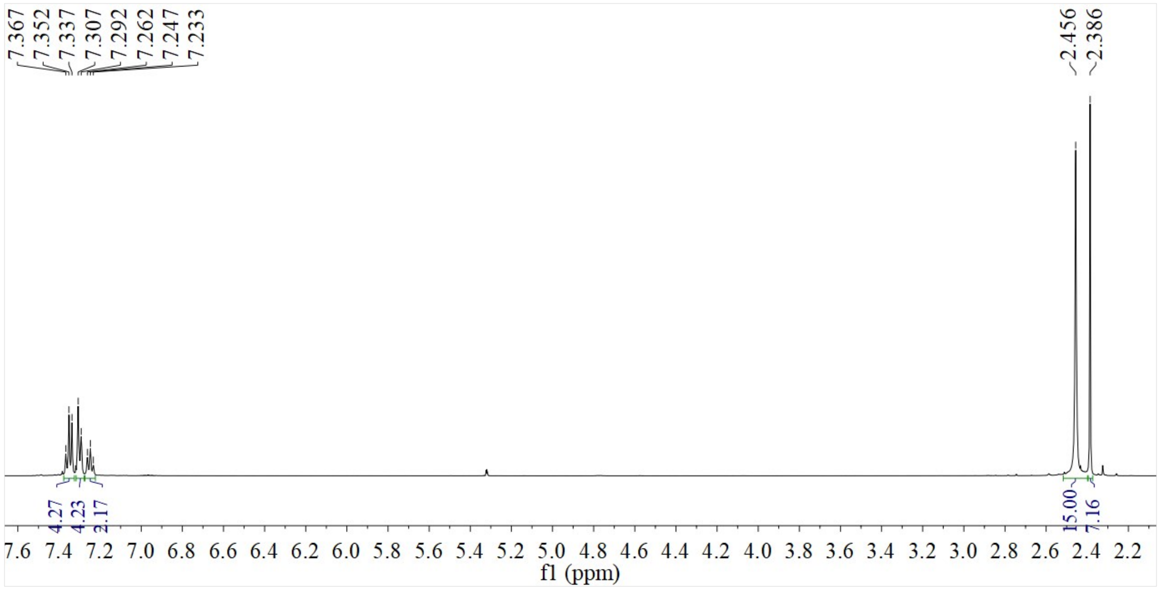

Figure S1. ^{1}H NMR spectrum of **1** (500 MHz, CD_2Cl_2).

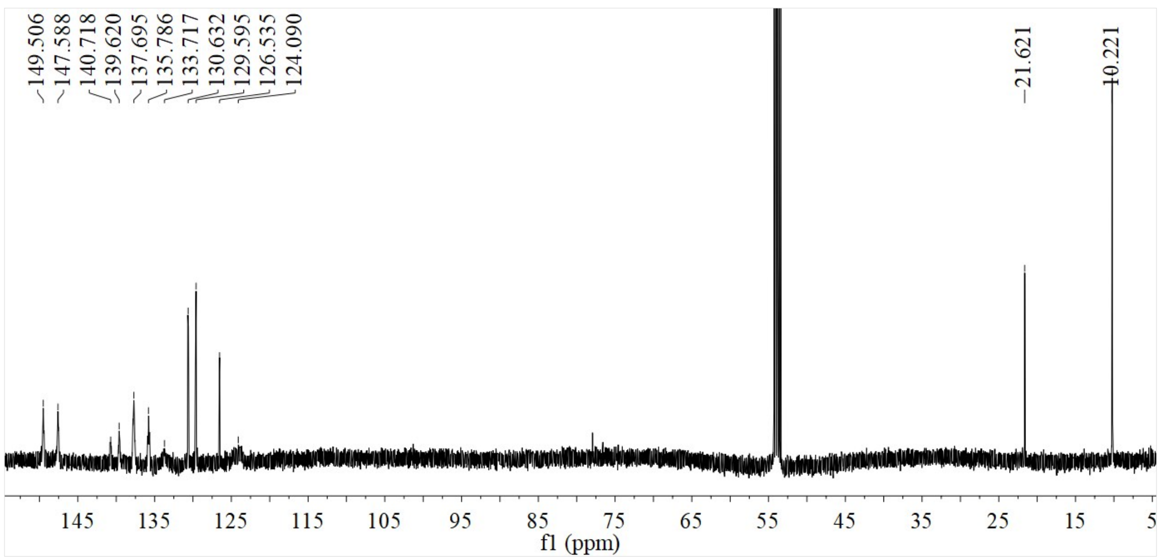

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **1** (126 MHz, CD_2Cl_2).

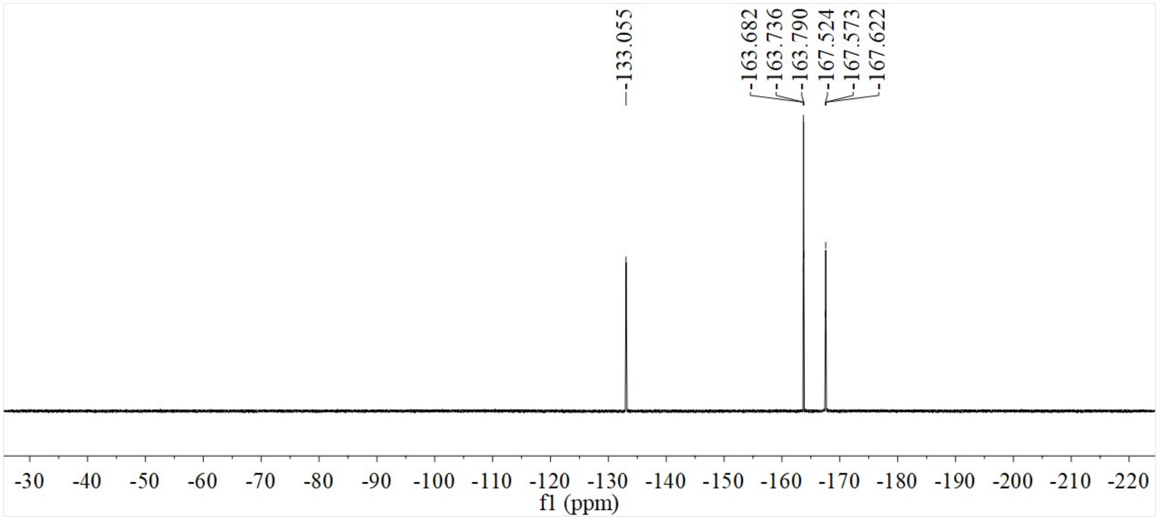

Figure S3. ^{19}F NMR spectrum of **1** (377 MHz, CD_2Cl_2).

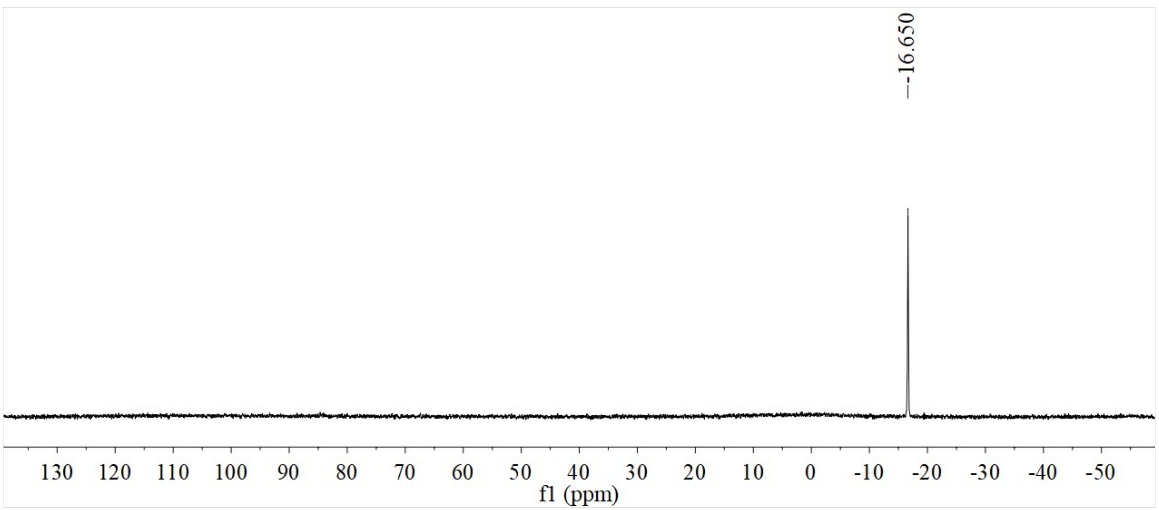

Figure S4. $^{11}B\{^1H\}$ NMR spectrum of **1** (128 MHz, CD_2Cl_2).

Gutmann-Beckett tests: The dicationic compound (0.01 mmol; **1**·tol (18.0 mg), or [(η^5-Cp*)As(tol)][$B(C_6F_5)_4$]$_2$·tol (17.5 mg), or [(η^5-Cp*)P(tol)][$B(C_6F_5)_4$]$_2$·tol (17.1 mg)) and Et_3PO (1.3 mg, 0.01 mmol) were mixed in DFB (0.6 mL) to give a yellow solution. The reaction solution was sealed in an NMR tube and monitored by $^{31}P\{^1H\}$ NMR spectroscopy. **$^{31}P\{^1H\}$ NMR** (162 MHz, DFB): δ (ppm) **1**·tol, 89.0 (s); [(η^5-Cp*)As(tol)][$B(C_6F_5)_4$]$_2$·tol, 99.6 (s); [(η^5-Cp*)P(tol)][$B(C_6F_5)_4$]$_2$·tol, 114.7 (d, $^2J_{P\text{-}P}$ = 42 Hz), -79.1 (d, $^2J_{P\text{-}P}$ = 42 Hz). At the same time, DFB (0.6 mL) solution of

Et$_3$PO (1.3 mg, 0.01 mmol) was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. **^{31}P{^{1}H} NMR** (162 MHz, DFB): δ (ppm) 47.6 (s).

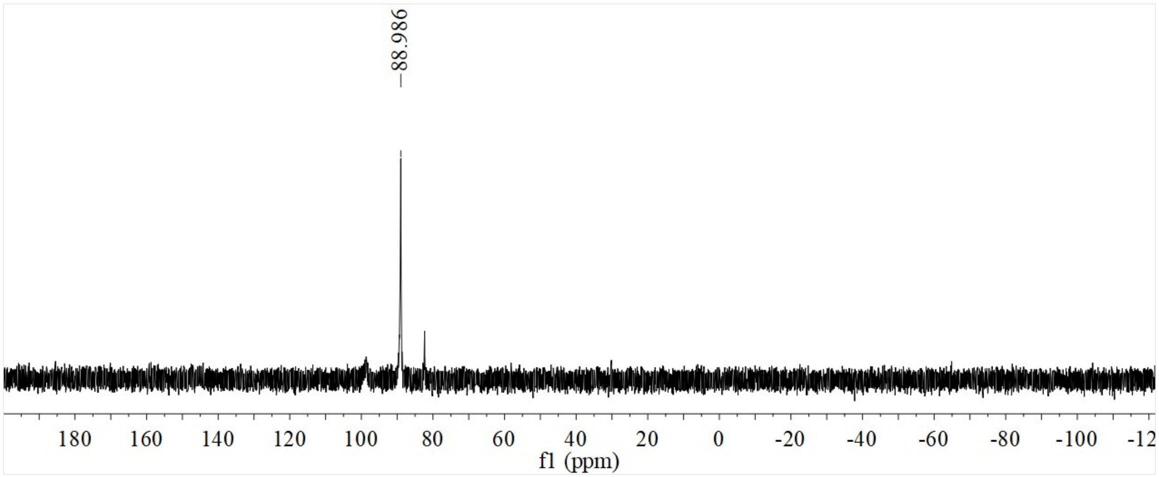

Figure S5. $^{31}P\{^1H\}$ NMR spectrum of reaction solution of **1**·tol and Et$_3$PO (1:1) (162 MHz, DFB).

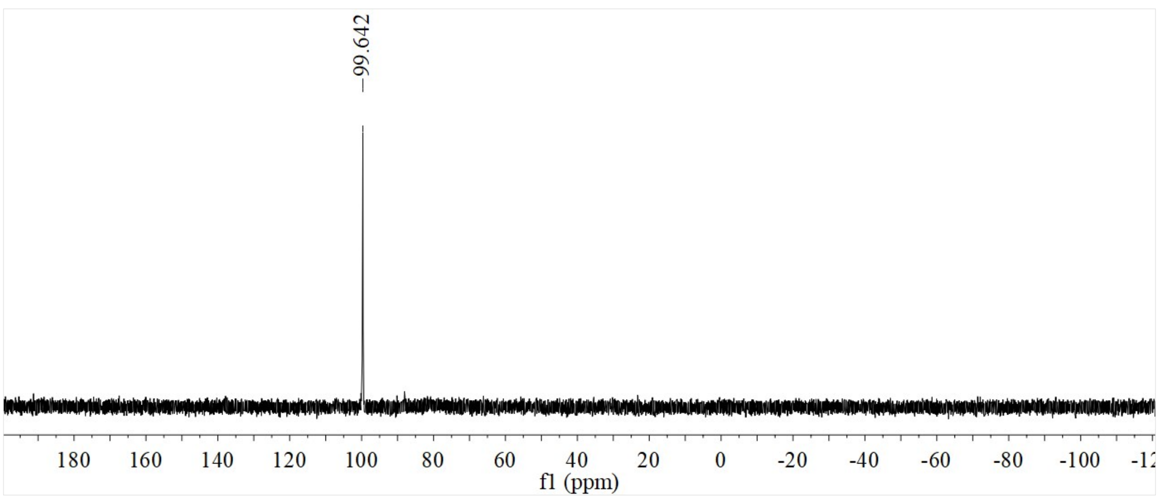

Figure S6. $^{31}P\{^1H\}$ NMR spectrum of reaction solution of [(η^5-Cp*)As(tol)][B(C$_6$F$_5$)$_4$]$_2$·tol and Et$_3$PO (1:1) (162 MHz, DFB).

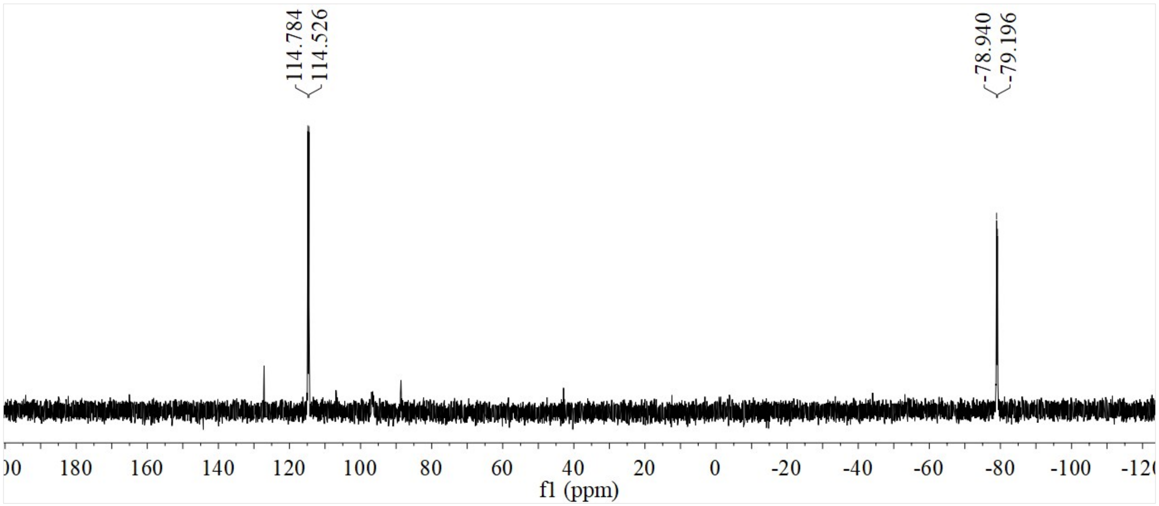

Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of reaction solution of $[(\eta^5\text{-}Cp^*)P(tol)][B(C_6F_5)_4]_2\cdot tol$ and Et_3PO (1:1) (162 MHz, DFB).

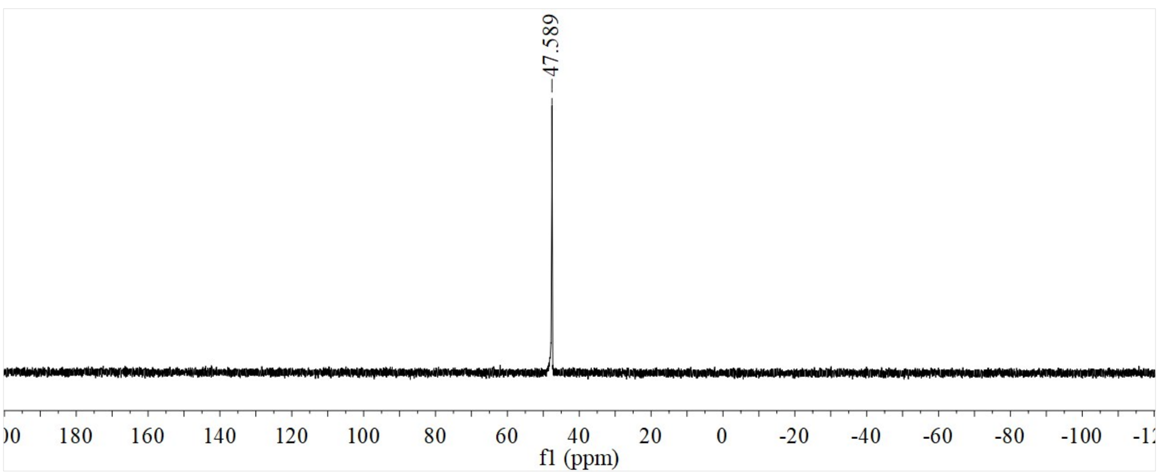

Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum of Et_3PO (162 MHz, DFB).

Generation of 2: 1·tol (36.0 mg, 0.02 mmol) and $[Bu_4N][SbF_6]$ (19.1 mg, 0.04 mmol) were mixed in DFB (1 mL), and the mixture was stirred at room temperature for 2 hours to give a pale yellow turbid solution. The mixture was filtered, and the residue was washed with DFB (0.5 mL) and dried under vacuum to give **2** ($[(Cp^*)Sb][SbF_6]_2$) as a white solid (11.8 mg, 81% yield). **^{1}H NMR** (500 MHz, CD_3CN): δ (ppm) 2.24 (s, 15H, C_5Me_5). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, CD_3CN): δ (ppm) 129.0 (s, C_5Me_5), 10.0 (s, C_5Me_5). **^{19}F NMR** (377 MHz, CD_3CN): δ (ppm) -123.0

(b(m), Sb*F*$_6$).

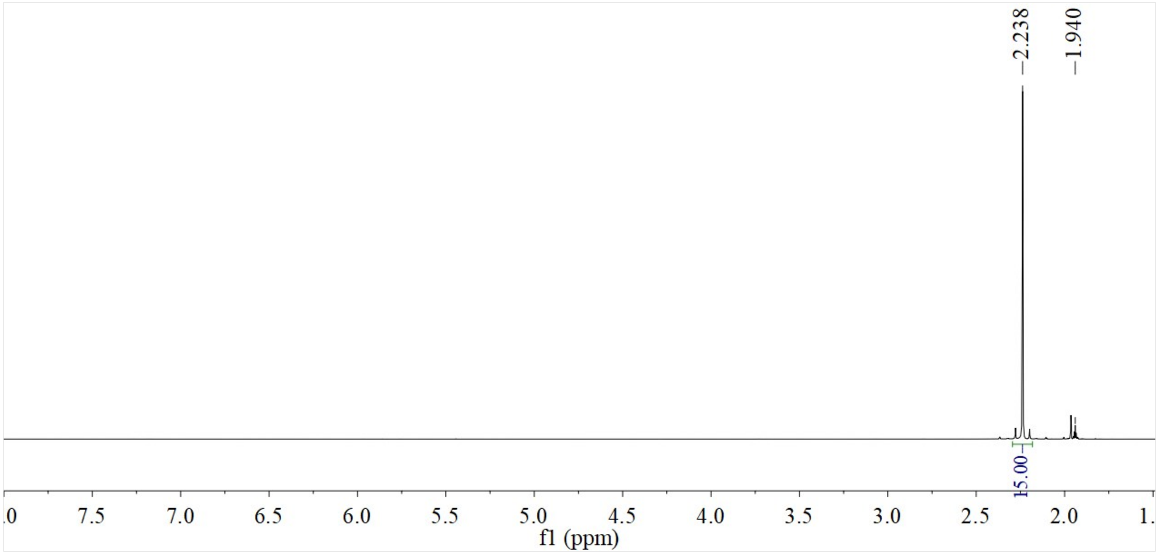

Figure S9. ^{1}H NMR spectrum of **2** (500 MHz, CD_3CN).

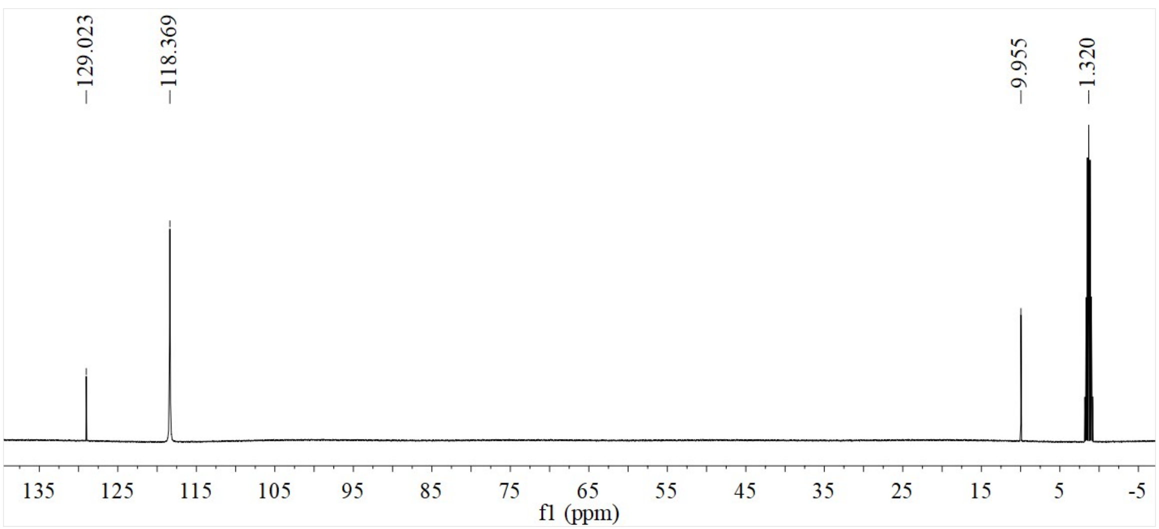

Figure S10. $^{13}C\{^1H\}$ NMR spectrum of **2** (126 MHz, CD_3CN).

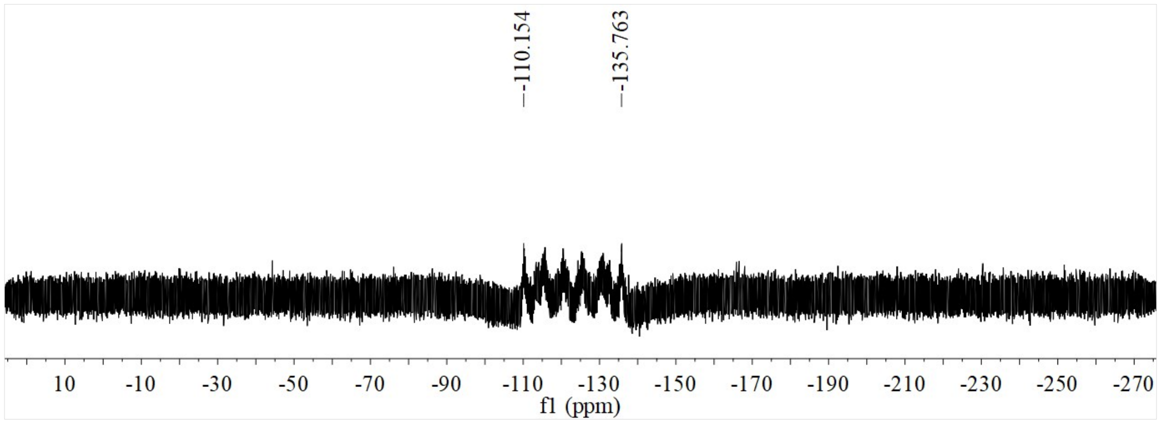

Figure S11. ^{19}F NMR spectrum of **2** (377 MHz, CD_3CN).

Generation of 3: Toluene (1 mL) solution of Et_3SiH (14 mg, 0.12 mmol) was added into toluene (1 mL) solution of $[Ph_3C][B(C_6F_5)_4]$ (92 mg, 0.10 mmol), and the mixture was stirred at room temperature for 5 minutes to give colorless solution and pale yellow oil on the bottom. The supernatant was removed, and the oil residue was washed with toluene (2 mL × 3). To the oil residue, toluene (1 mL) was added. Then to the mixture, toluene (1 mL) solution of Cp^*SbCl_2 (33 mg, 0.10 mmol) was added, and the mixture was stirred at room temperature for 15 minutes. To the mixture, *n*-pentane (4 mL) was added with rigorous stirring to give pale yellow precipitate. The supernatant was removed, and the pale yellow solid was washed with *n*-pentane (2 mL) and dried under vacuum to give **3** ($[Cp^*Sb(\mu\text{-}Cl)]_2[B(C_6F_5)_4]_2$) as a pale yellow solid (88 mg, 91% yield). Single crystals of **3** were obtained by layering of *n*-pentane on a dichloromethane solution at room temperature. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ (ppm) 2.32 (s, 15H, C_5Me_5). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ (ppm) 148.5 (d(m), $^1J_{C\text{-}F}$ = 240 Hz, C_6F_5), 138.6 (d(m), $^1J_{C\text{-}F}$ = 244 Hz, C_6F_5), 136.7 (d(m), $^1J_{C\text{-}F}$ = 244 Hz, C_6F_5), 131.1 (s, C_5Me_5), 124.3 (b(m), C_6F_5), 10.5 (s, C_5Me_5). **^{19}F NMR** (377 MHz, CD_2Cl_2): δ (ppm) -133.0 (m, C_6F_5), -163.6 (t, $^3J_{F\text{-}F}$ = 20 Hz, C_6F_5), -167.5 (t, $^3J_{F\text{-}F}$ = 18 Hz, C_6F_5). **^{11}B{^{1}H} NMR** (128 MHz, CD_2Cl_2): δ (ppm) -16.6 (s). MS (DART) [M] $C_{10}H_{15}SbCl^+$ calc.

290.99005 m/z; found 290.98937 m/z.

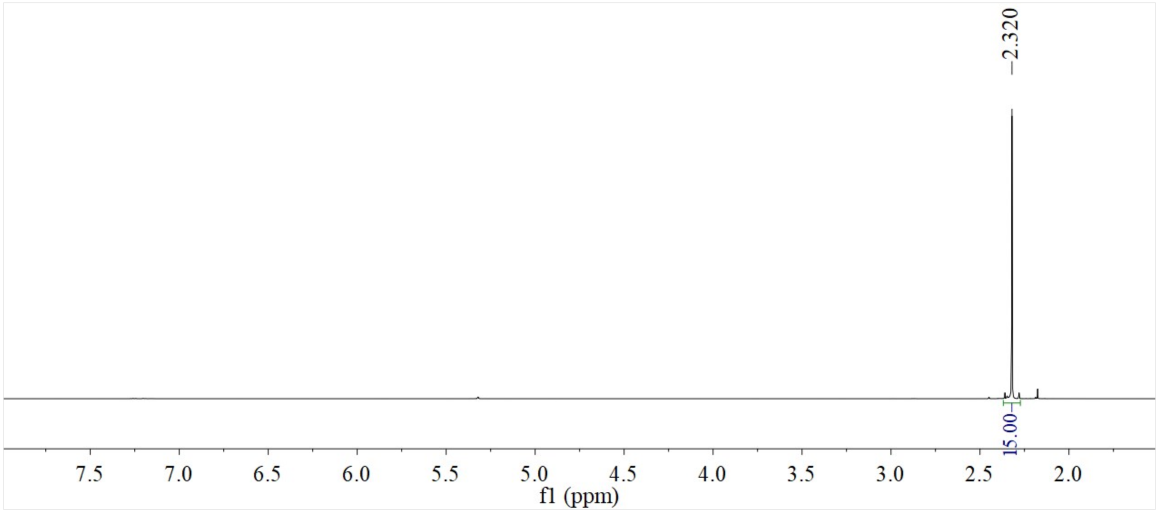

Figure S12. ^{1}H NMR spectrum of **3** (500 MHz, CD_2Cl_2).

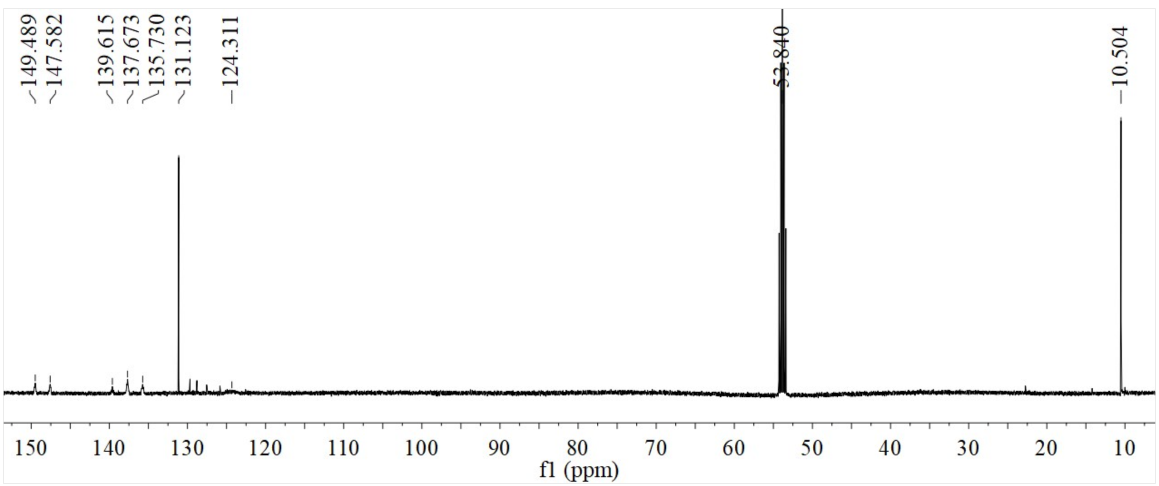

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of **3** (126 MHz, CD_2Cl_2).

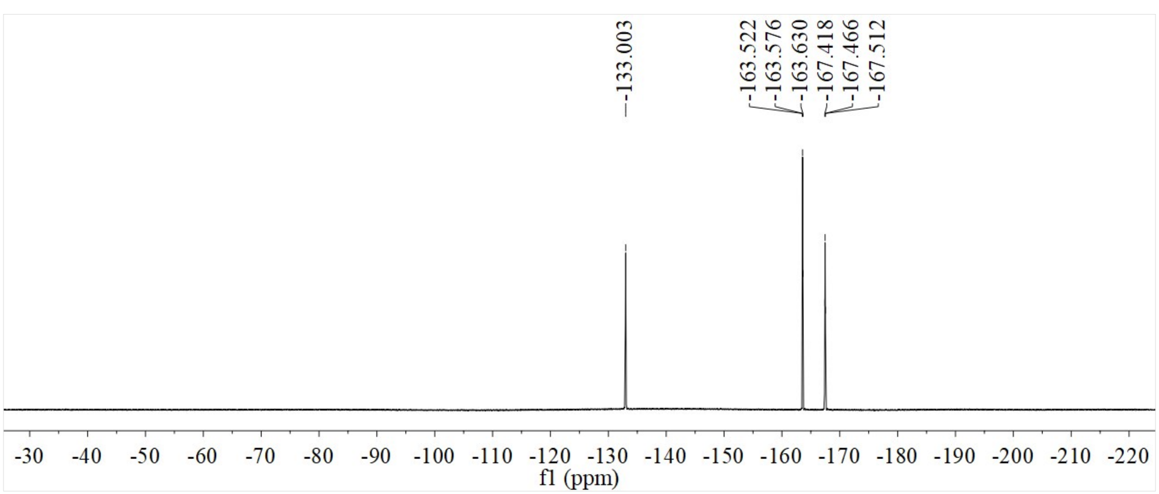

Figure S14. ^{19}F NMR spectrum of **3** (377 MHz, CD_2Cl_2).

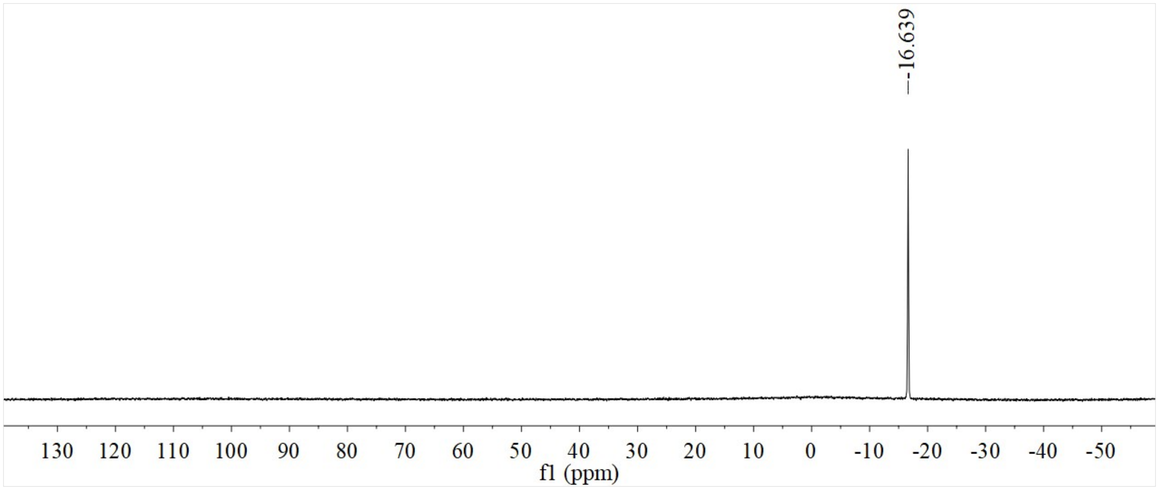

Figure S15. ^{11}B{^{1}H} NMR spectrum of **3** (128 MHz, CD_2Cl_2).

The reaction of 1·tol with Ph_3CCl: 1·tol (18.0 mg, 0.01 mmol) and Ph_3CCl (4.2 mg, 0.015 mmol) were mixed in DFB (1 mL) to give clear yellow solution immediately. To the solution, *n*-pentane (3 mL) was added with rigorous stirring to give yellow precipitate. The supernatant was removed, and the residue was washed with *n*-pentane (2 mL) and dried under vacuum to give a yellow solid (14.5 mg) containing **3** ($[Cp^*Sb(\mu\text{-}Cl)]_2[B(C_6F_5)_4]_2$) and $[Ph_3C][B(C_6F_5)_4]$. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ (ppm) 8.27 (tt, $^3J_{H\text{-}H}$ = 7.5 Hz, $^4J_{H\text{-}H}$ = 1.3 Hz, $[Ph_3C]^+$-*H*), 7.87 (dd, $^3J_{H\text{-}H}$ = 8.4 Hz, $^3J_{H\text{-}H}$ = 7.5 Hz, $[Ph_3C]^+$-*H*), 7.66 (dd, $^3J_{H\text{-}H}$ = 8.4 Hz, $^4J_{H\text{-}H}$ = 1.3 Hz, $[Ph_3C]^+$-*H*), 2.32 (s, 15H, C_5Me_5). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ (ppm) 211.2 (s, $[Ph_3C]^+$), 148.5 (d(m), $^1J_{C\text{-}F}$ = 243 Hz, C_6F_5), 144.0 (s, $[Ph_3C]^+$), 143.0 (s, $[Ph_3C]^+$), 140.3 (s, $[Ph_3C]^+$), 138.6 (d(m), $^1J_{C\text{-}F}$ = 244 Hz, C_6F_5), 136.7 (d(m), $^1J_{C\text{-}F}$ = 244 Hz, C_6F_5), 131.1 (s, C_5Me_5), 131.0 (s, $[Ph_3C]^+$), 124.3 (b(m), C_6F_5), 10.5 (s, C_5Me_5).

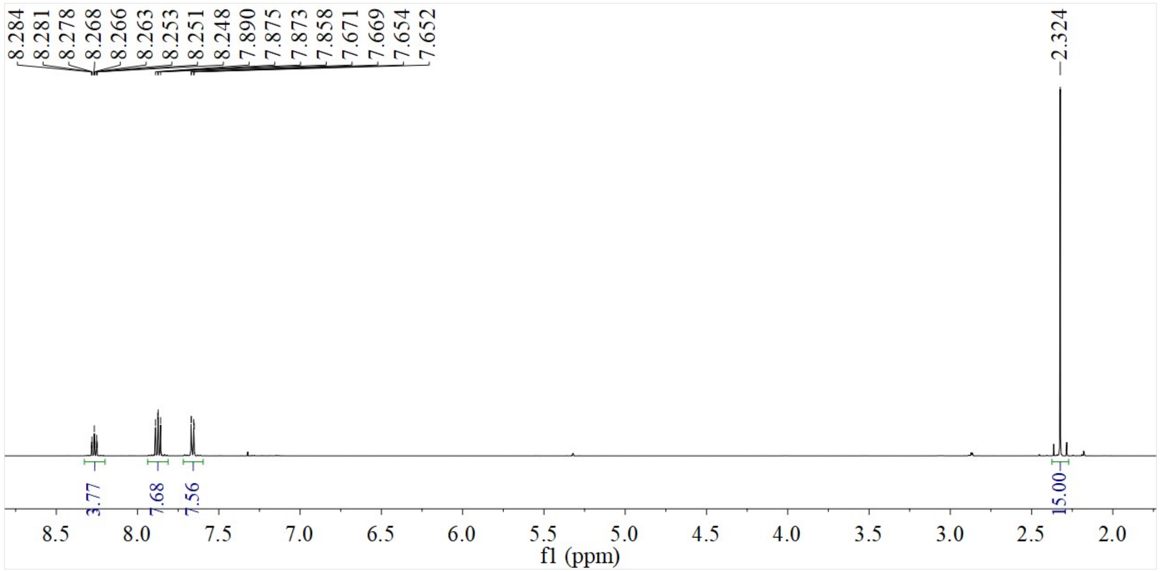

Figure S16. ^{1}H NMR spectrum of crude reaction product of **1**·tol with Ph_3CCl (500 MHz, CD_2Cl_2).

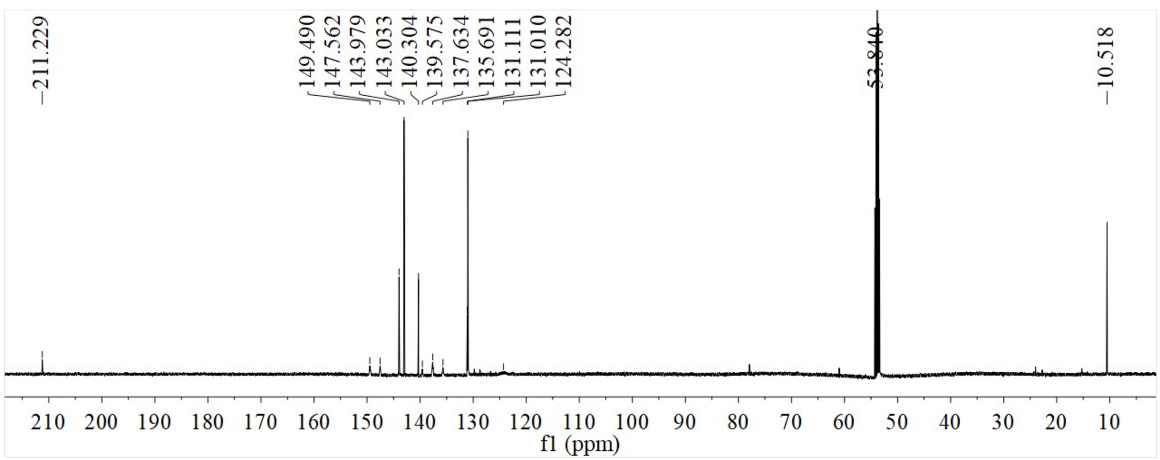

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of crude reaction product of **1**·tol with Ph_3CCl (126 MHz, CD_2Cl_2).

The reaction of 1·tol with 1,2-Bis(diphenylphosphino)ethane (dppe): 1·tol (18.0 mg, 0.01 mmol) and dppe (6.0 mg, 0.015 mmol) were mixed in DFB (0.6 mL) to give a clear pale yellow solution. The reaction solution was sealed in an NMR tube and monitored by ^{31}P NMR spectroscopy. Black precipitate was generated from the reaction solution at room temperature overnight. After 20 hours, the ^{31}P NMR spectra didn't change dramatically. After 2 days, the mixture was filtered, and to the filtrate, *n*-pentane (3 mL) was added with rigorous stirring to give pale yellow precipitate. The supernatant was removed, and the pale yellow solid was washed with *n*-pentane (2 mL) and dried under vacuum to give a pale yellow solid containing $[(Cp^*)_2(dppe)][B(C_6F_5)_4]_2$, $[(Cp^*)(dppe)][B(C_6F_5)_4]$ and $[(dppe)H][B(C_6F_5)_4]$. **$^{31}P\{^1H\}$ NMR** (243 MHz, CD_2Cl_2): δ (ppm) 36.7 (s, $[(Cp^*Sb)($*dppe*$)][B(C_6F_5)_4]_2$ (*proposed*)); 29.9 (s, $[(Cp^*)_2($*dppe*$)][B(C_6F_5)_4]_2$); 31.0, -12.1 (d, $^2J_{P\text{-}P}$ = 42 Hz, $[(Cp^*)($*dppe*$)][B(C_6F_5)_4]$); 10.1, -14.9 (d, $^2J_{P\text{-}P}$ = 45 Hz, $[($*dppe*$)H][B(C_6F_5)_4]$). **^{31}P NMR** (243 MHz, CD_2Cl_2): δ (ppm) 36.7 (m, $[(Cp^*Sb)($*dppe*$)][B(C_6F_5)_4]_2$ (*proposed*)); 29.9 (m, $[(Cp^*)_2($*dppe*$)][B(C_6F_5)_4]_2$); 31.0, -12.1 (m, $[(Cp^*)($*dppe*$)][B(C_6F_5)_4]$); 10.2 (d(m), $^1J_{P\text{-}H}$ = 478 Hz), -14.9 (m) ($[($*dppe*$)H][B(C_6F_5)_4]$). MS (ESI) $[(Cp^*)(dppe)]^+$: [M] $C_{36}H_{39}P_2^+$ calc. 533.2522 m/z; found 533.2516 m/z; $[(dppe)H]^+$: [M] $C_{26}H_{25}P_2^+$ calc. 399.1426 m/z; found 399.1423 m/z.

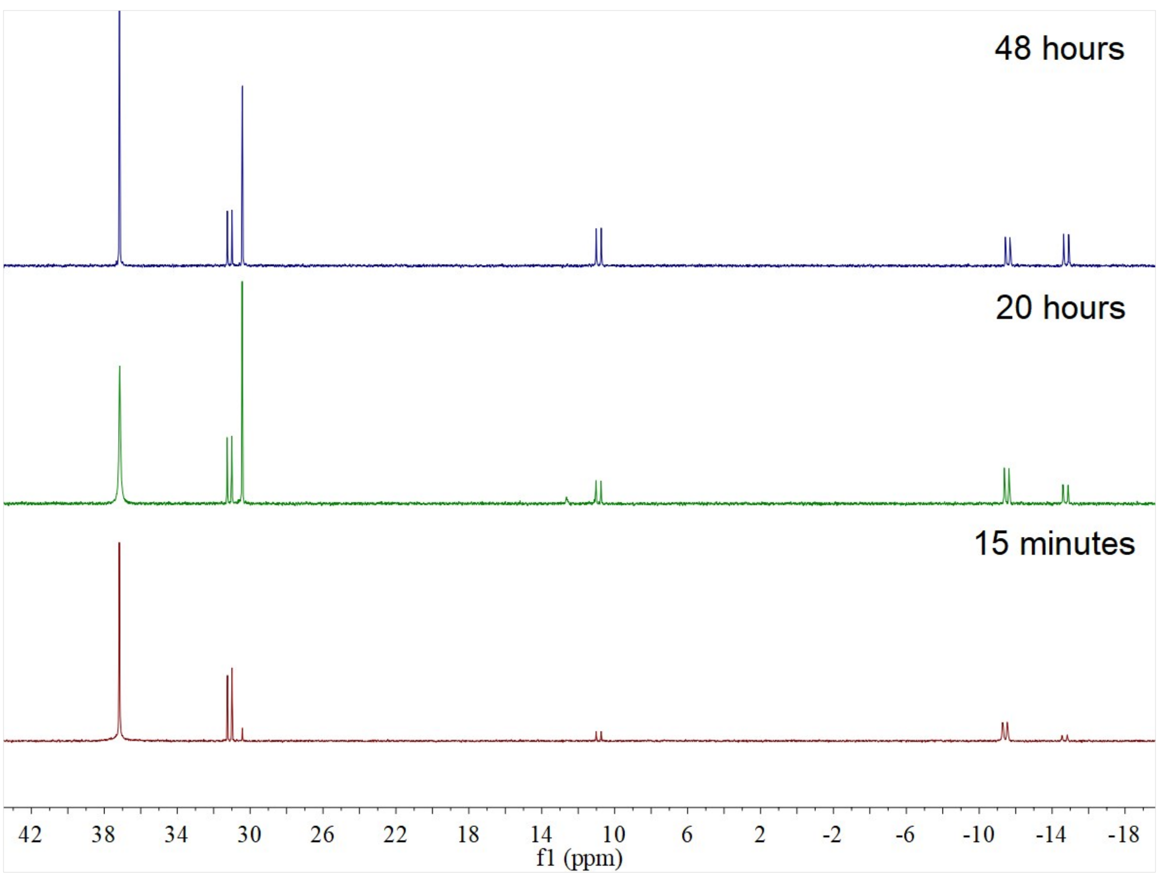

Figure S18. $^{31}P\{^1H\}$ NMR spectra of reaction solution of **1**·tol with dppe (1:1.5) at different time (126 MHz, DFB).

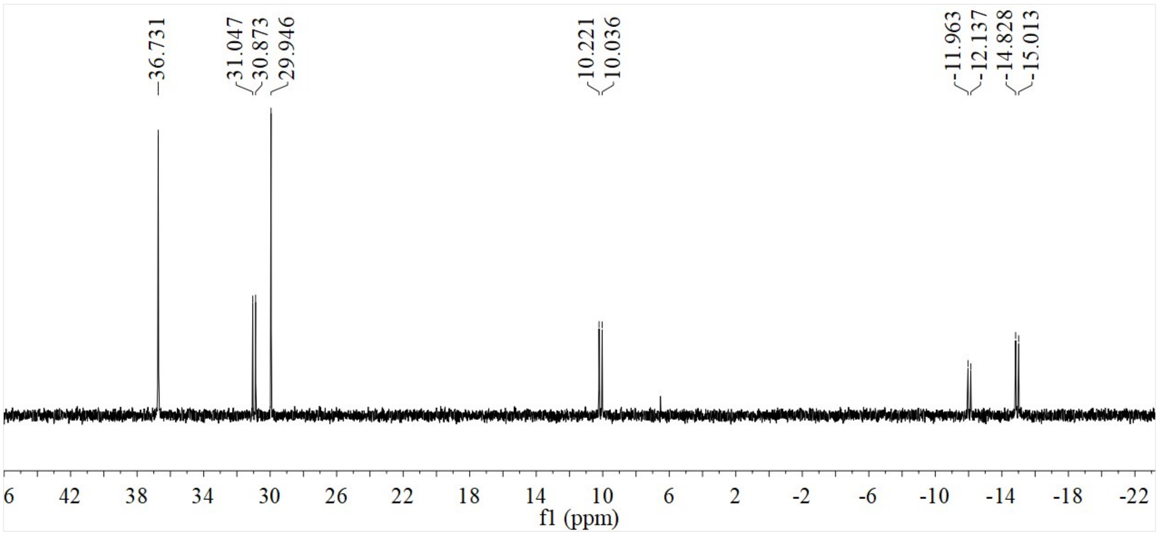

Figure S19. $^{31}P\{^1H\}$ NMR spectrum of crude reaction product of **1**·tol with dppe (1:1.5) (243 MHz, CD_2Cl_2).

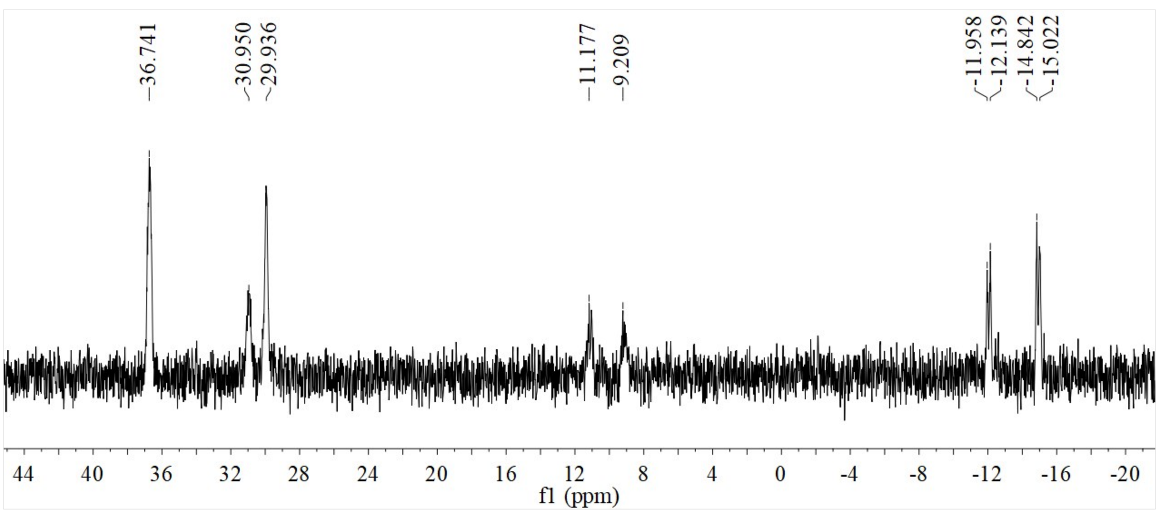

Figure S20. ^{31}P NMR spectrum of crude reaction product of **1**·tol with dppe (1:1.5) (243 MHz, CD_2Cl_2).

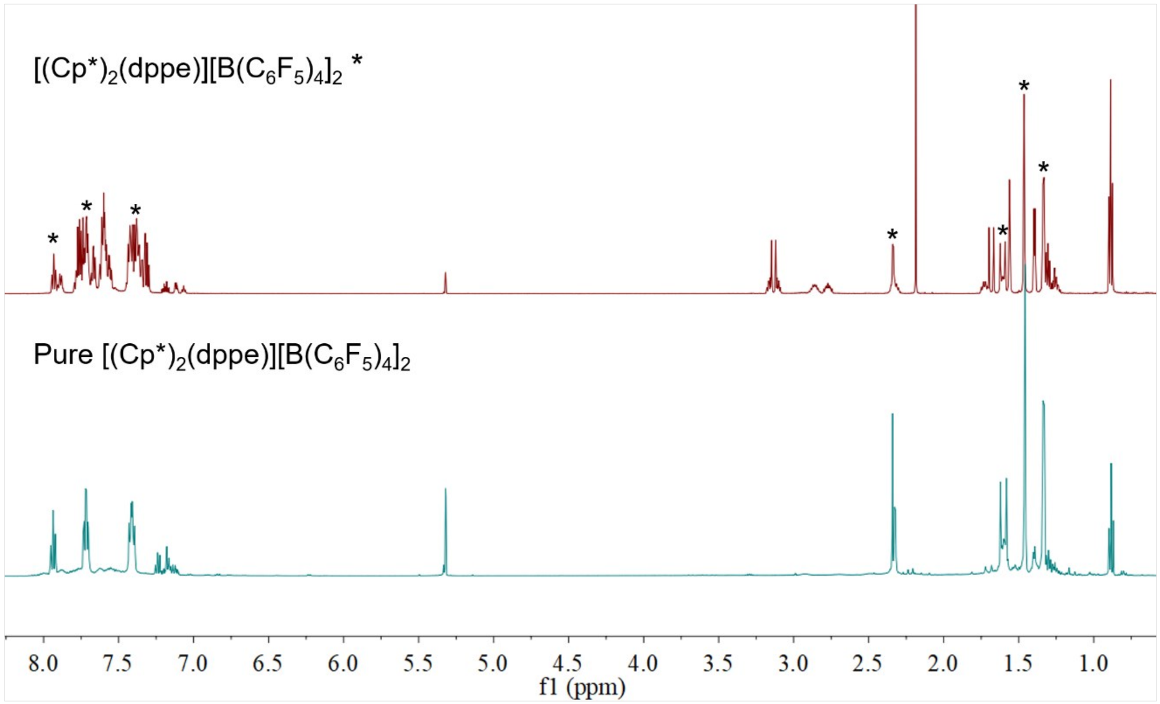

Figure S21. Comparison ^{1}H NMR spectra of crude reaction product of **1**·tol with dppe (1:1.5) and pure [(Cp*)$_2$(dppe)][B(C_6F_5)$_4$]$_2$ (600 MHz, CD_2Cl_2).

The reaction of 1·tol with BAC: DFB (0.5 mL) solution of **1**·tol (18.0 mg, 0.01 mmol) and toluene (0.5 mL) solution of BAC (7.1 mg, 0.03 mmol) were mixed at room temperature. The reaction solution was layered by 3 mL of pentane and stood at -35 ^{o}C overnight to give yellow crystals in red oil. The supernatant was removed. It was difficult to sperate clean crystals from the oil. The residue was washed with *n*-pentane (2 mL) and dried under vacuum to give a yellow solid containing **4** ([(BAC)$_2$Sb][B(C_6F_5)$_4$]), [(BAC)H][B(C_6F_5)$_4$] and some unidentified byproducts. Attempts to isolate pure **4** failed, and more work-up led to more decompostion of **4** to [(BAC)H][B(C_6F_5)$_4$]. **^{1}H NMR** (500 MHz, CD_3CN): δ (ppm) [(BAC)H][B(C_6F_5)$_4$]: 7.23 (s, (BAC)*H*), 3.99 (sept, $^3J_{H\text{-}H}$ = 8 Hz, C*H*Me$_2$), 3.89 (sept, $^3J_{H\text{-}H}$ = 8 Hz, C*H*Me$_2$), 1.31 (d, $^3J_{H\text{-}H}$ = 8 Hz, CH*Me*$_2$), 1.30 (d, $^3J_{H\text{-}H}$ = 8 Hz, CH*Me*$_2$); **4** (maybe overlapped with some byproducts): 4.21 (sept, $^3J_{H\text{-}H}$ = 8 Hz, C*H*Me$_2$), 4.09 (sept, $^3J_{H\text{-}H}$ = 8 Hz, C*H*Me$_2$), 1.41-1.23 (m, CH*Me*$_2$). **^{13}C{^{1}H} NMR** (126 MHz,

CD_3CN): δ (ppm) [B(C_6F_5)$_4$]: 149.1 (d(m), $^1J_{C\text{-}F}$ = 239 Hz), 139.3 (d(m), $^1J_{C\text{-}F}$ = 246 Hz), 137.3 (d(m), $^1J_{C\text{-}F}$ = 242 Hz, C_6F_5), 126.2 (t, $^2J_{F\text{-}C}$ = 5 Hz); toluene-*C*: 138.9, 129.9, 129.2, 126.3, 12.8; [(BAC)H]$^+$-*C*: 135.2, 58.5, 49.1, 20.9, 20.6; **4**$^+$-*C*: 145.0, 109.7, 53.4 (br), 21.8, 21.6. MS (ESI) [(BAC)H]$^+$: [M] $C_{15}H_{29}N_2^+$ calc. 237.2325 m/z; found 237.2334 m/z.

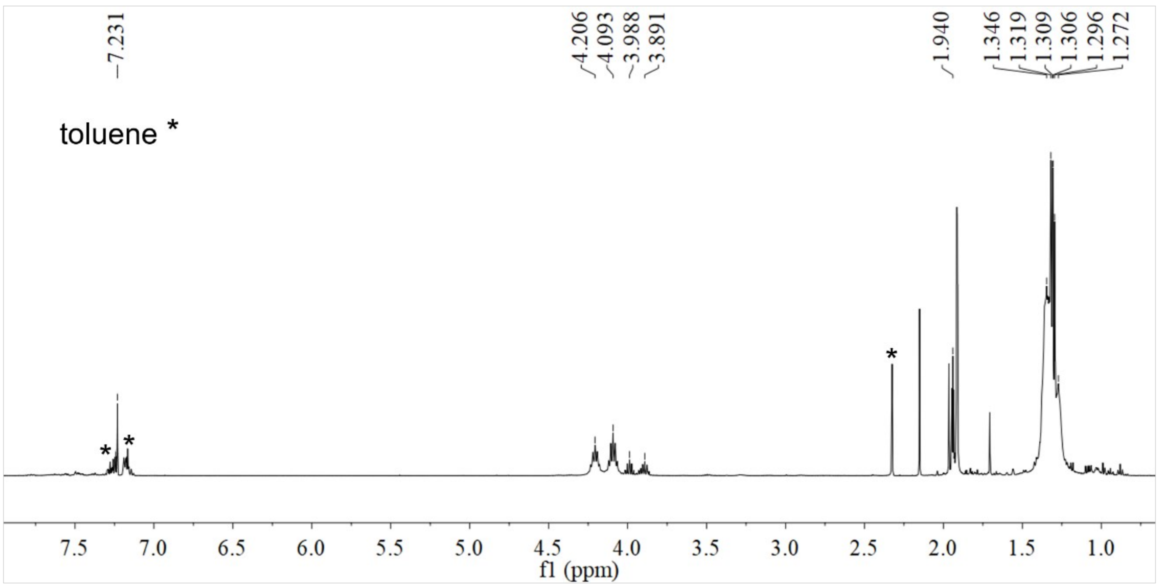

Figure S22. ^{1}H NMR spectrum of crude product of the reaction of **1**·tol with BAC (500 MHz, CD_3CN).

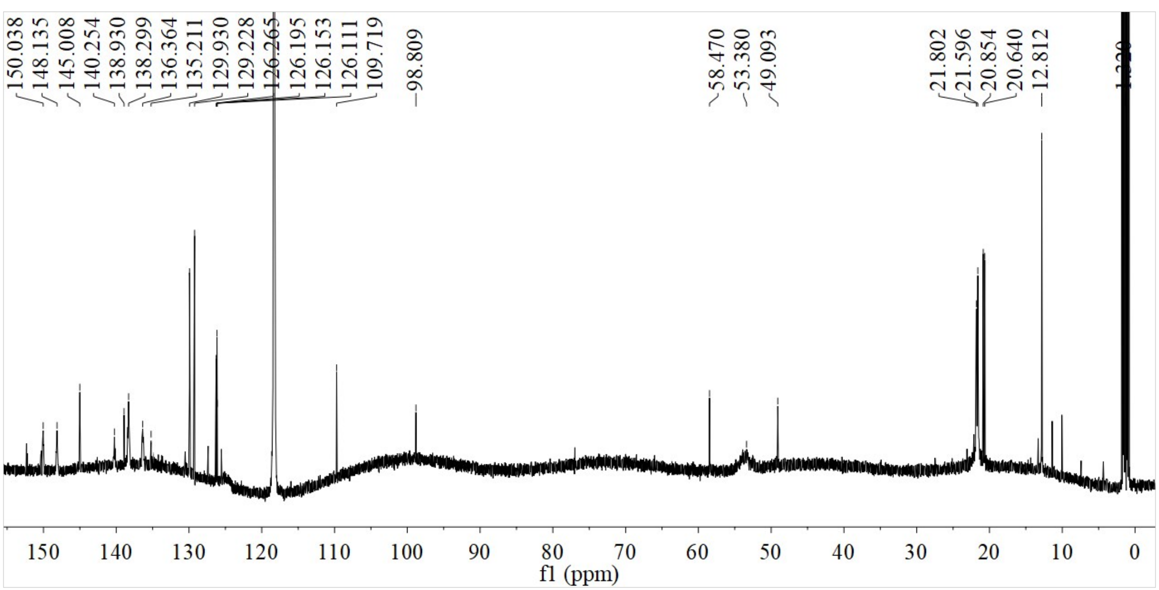

Figure S23. $^{13}C\{^1H\}$ NMR spectrum of crude product of the reaction of **1**·tol with BAC (500 MHz, CD_3CN).

Generation of 5: DFB (0.5 mL) solution of **1**·tol (36.0 mg, 0.02 mmol) was added into toluene (0.5 mL) solution of bipy (6.2 mg, 0.04 mmol) at room temperature, and the mixture was stirred for 3 hours. To the reaction solution, *n*-pentane (4 mL) was added with rigorous stirring to give a pale yellow precipitate. The supernatant was removed, and the residue was washed with *n*-pentane (2 mL × 2) and dried under vacuum to give **5** as a pale yellow solid (35.8 mg, 93%). **^{1}H NMR** (500 MHz, CD_3CN): δ (ppm) 8.68 (d(m), $^3J_{H\text{-}H}$ = 5 Hz, 4H, bipy-*H*), 8.51 (d(m), $^3J_{H\text{-}H}$ = 8 Hz, 4H, bipy-*H*), 8.26 (td, $^3J_{H\text{-}H}$ = 8 Hz, $^4J_{H\text{-}H}$ = 2 Hz, 4H, bipy-*H*), 7.77 (ddd, $^3J_{H\text{-}H}$ = 8 Hz, $^3J_{H\text{-}H}$ = 5 Hz, $^4J_{H\text{-}H}$ = 1 Hz, 4H, bipy-*H*), 2.20-1.97 (br, 15H, C_5Me_5). **$^{13}C\{^1H\}$ NMR** (126 MHz, CD_3CN): δ (ppm) 152.0 (s, bipy-*C*), 149.1 (d(m), $^1J_{C\text{-}F}$ = 239 Hz, C_6F_5), 148.4 (s, bipy-*C*), 142.7 (s, bipy-*C*), 139.3 (d(m), $^1J_{C\text{-}F}$ = 244 Hz, C_6F_5), 137.3 (d(m), $^1J_{C\text{-}F}$ = 245 Hz, C_6F_5), 128.3 (s, bipy-*C*), 127.6 (s, C_5Me_5), 127.4 (s, C_5Me_5), 126.1 (t, $^2J_{F\text{-}C}$ = 5 Hz, C_6F_5), 124.4 (s, bipy-*C*), 10.7 (s, C_5Me_5), 10.1 (s, C_5Me_5), 34.9, 23.1, 14.3 (pentane-*C*). **^{19}F NMR** (377 MHz, CD_3CN): δ (ppm) -133.8 (m, C_6F_5), -163.9 (t, $^3J_{F\text{-}F}$ = 20 Hz, C_6F_5), -168.3 (t, $^3J_{F\text{-}F}$ = 17 Hz, C_6F_5). **$^{11}B\{^1H\}$ NMR** (128 MHz, CD_3CN): δ (ppm) -16.8 (s).

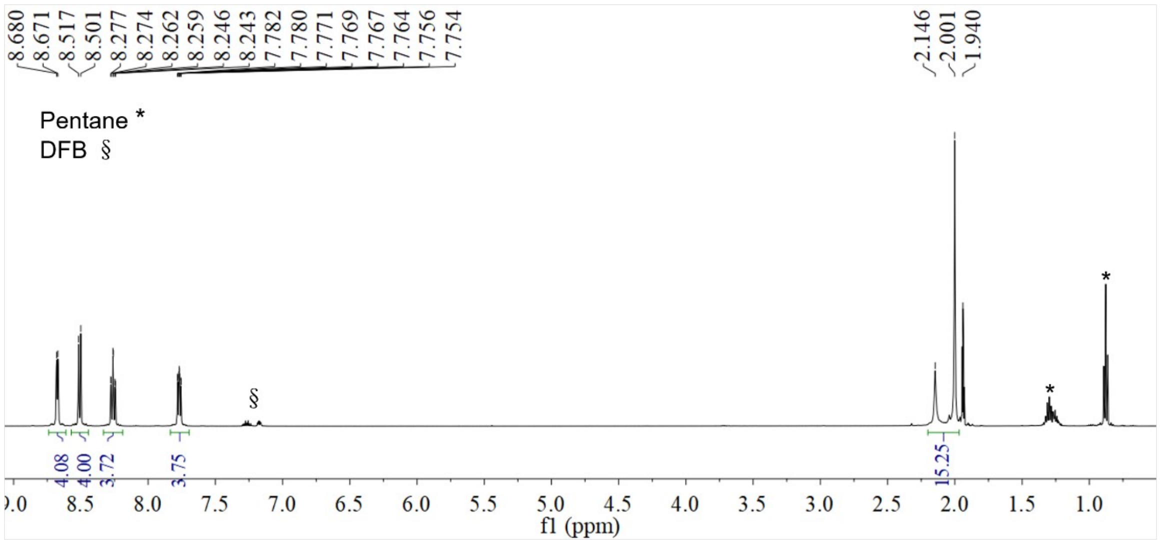

Figure S24. ^1H NMR spectrum of **5** (500 MHz, CD_3CN).

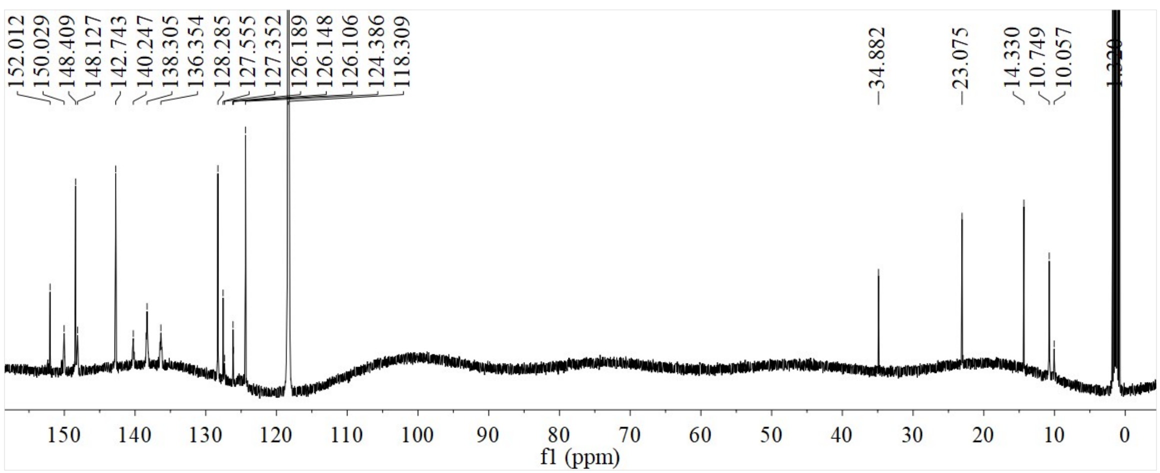

Figure S25. $^{13}C\{^1H\}$ NMR spectrum of **5** (128 MHz, CD_3CN).

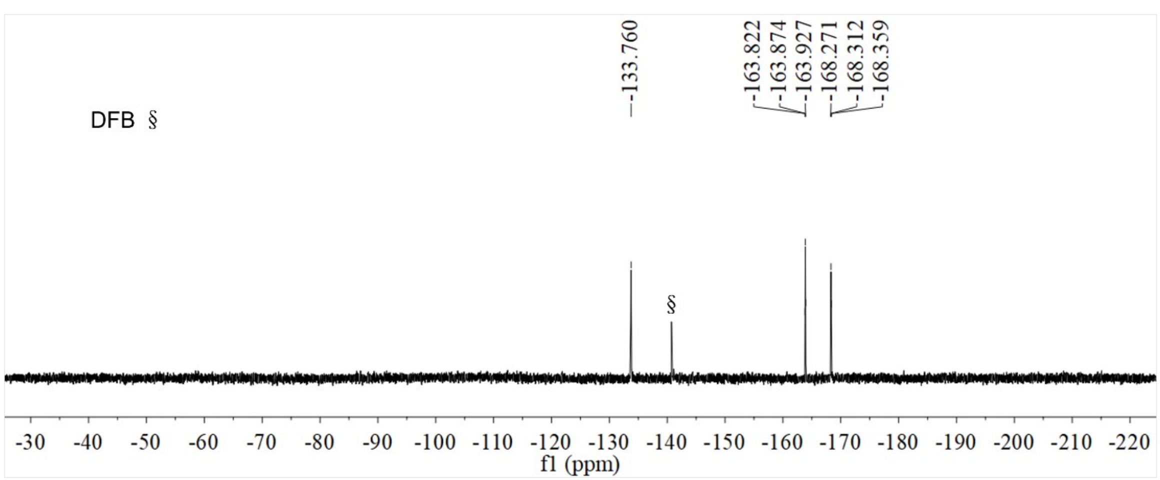

Figure S26. ^{19}F NMR spectrum of **5** (377 MHz, CD_3CN).

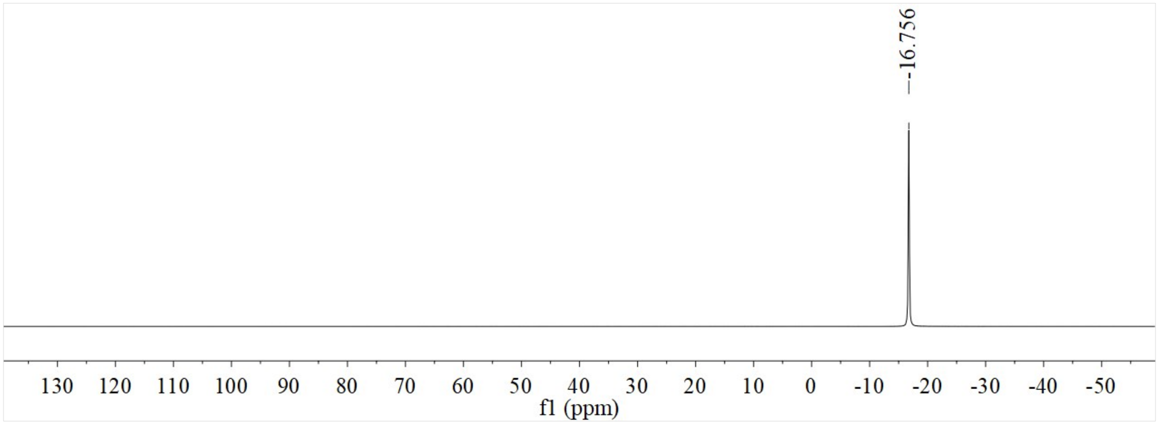

Figure S27. $^{11}B\{^1H\}$ NMR spectrum of **5** (128 MHz, CD_3CN).

The synthesis of 6: DFB (0.5 mL) solution of **1**·tol (36.0 mg, 0.02 mmol) was added into DFB (0.5 mL) solution of bipy (6.9 mg, 0.044 mmol) at room temperature, and the mixture was stirred for 10 minutes. To the reaction solution, DFB (1 mL) solution of $[Bu_4N][OTf]$ (23.5 mg, 0.06 mmol) was added at room temperature, and the mixture was stirred for 2 hours to give a pale yellow turbid solution. The mixture was filtered, and the residue was washed with DFB (0.5 mL) and dried under vacuum to give **6** ($[(bipy)_2Sb][OTf]_3$) as a white solid (9.8 mg, 56% yield). Single crystals of **6** were obtained by slow diffusion of diethyl ether into a acetonitrile solution at room temperature. **^{1}H NMR** (500 MHz, CD_3CN): δ (ppm) 8.85 (m, 4H, bipy-*H*), 8.75 (m, 4H, bipy-*H*), 8.59 (t, $^3J_{H\text{-}H}$ = 7 Hz, 4H, bipy-*H*), 8.03 (m, 4H, bipy-*H*). **^{13}C{^{1}H} NMR** (126 MHz, CD_3CN): δ (ppm) 149.3 (br, bipy-*C*), 149.1 (m, bipy-*C*), 146.9 (m, bipy-*C*), 131.2 (m, bipy-*C*), 126.9 (m, bipy-*C*), 121.2 (q, $^1J_{F\text{-}C}$ = 320 Hz, $\mathit{C}F_3SO_3$). **^{19}F NMR** (377 MHz, CD_3CN): δ (ppm) -79.3 (s, $C\mathit{F}_3SO_3$). Elem. Anal. Found (Calc'd) for $C_{23}H_{16}N_4O_9F_9S_3Sb$: C 31.19 (31.34), H 1.81 (1.83), N 6.34 (6.36).

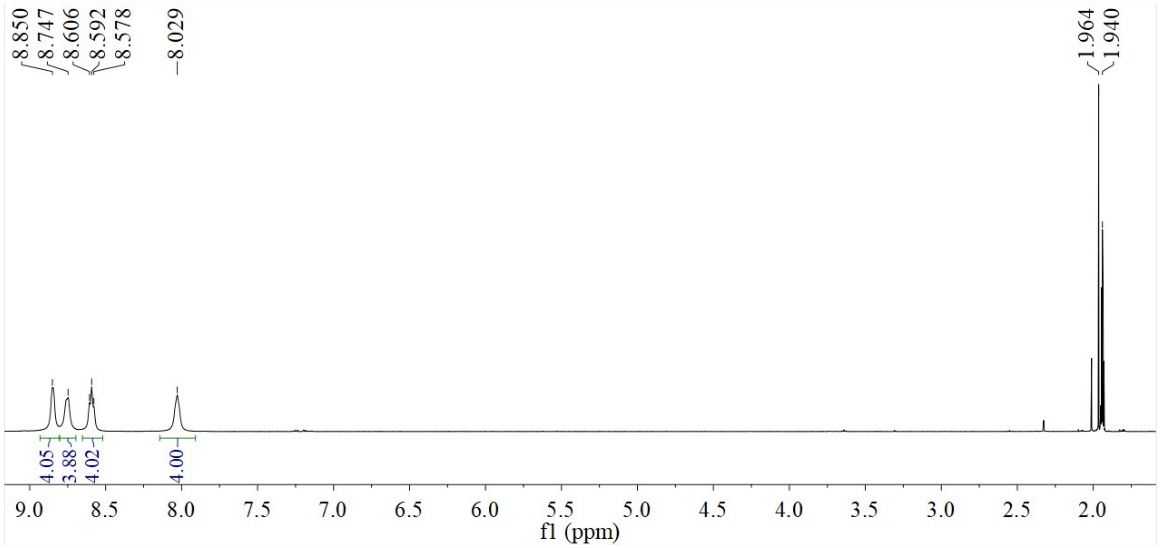

Figure S28. ^{1}H NMR spectrum of **6** (500 MHz, CD_3CN).

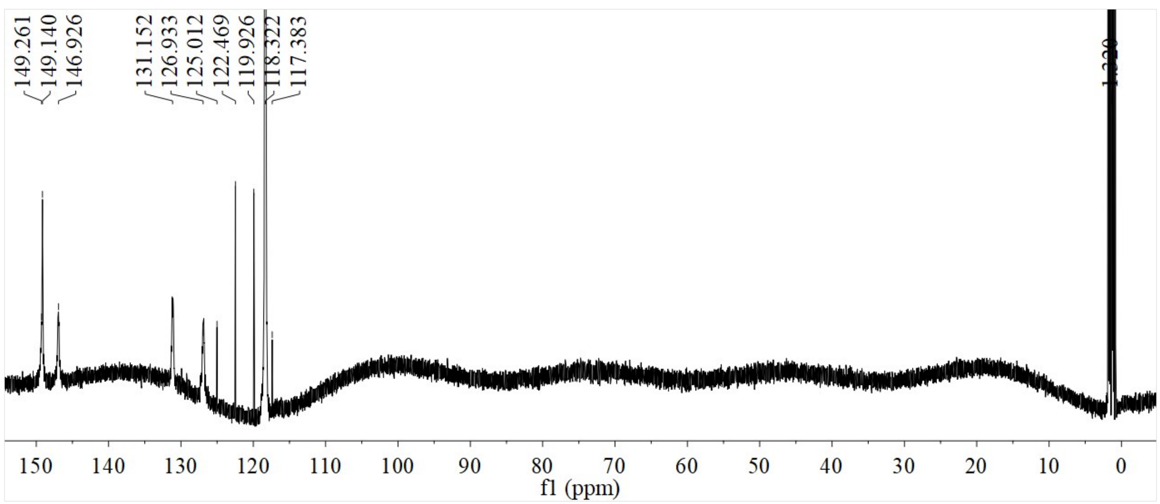

Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **6** (128 MHz, CD_3CN).

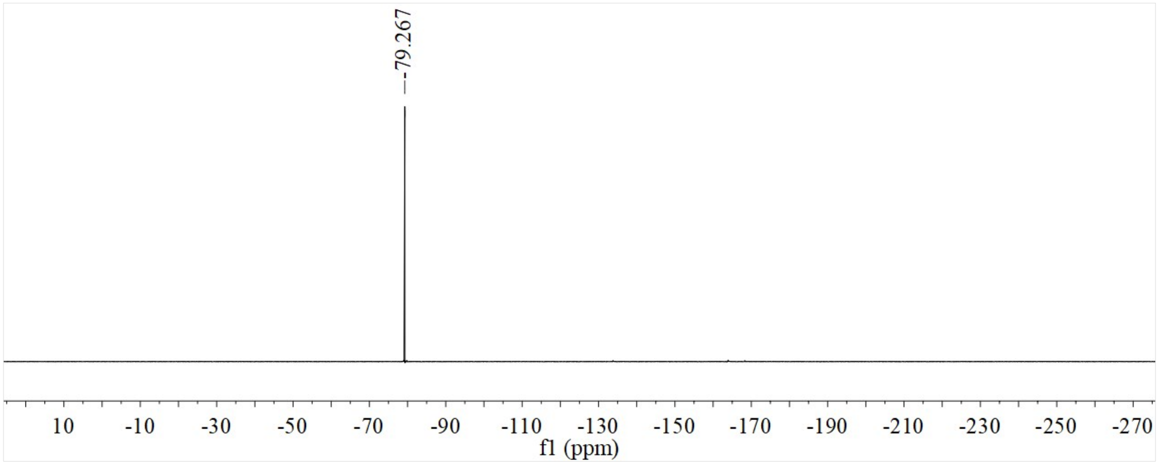

Figure S30. ^{19}F NMR spectrum of **6** (377 MHz, CD_3CN).

3. Crystallographic Details

Single crystals were coated with Paratone-N oil, mounted using a glass fibre pin and frozen in the cold nitrogen stream of the goniometer. Data sets were collected on a Siemens Smart System CCD diffractometer which was equipped with a rotation anode using graphite-monochromated MoKα radiation (λ = 0.71073 Å). Data reduction was performed using the Bruker SMART software package. Data sets were corrected for absorption effects using SADABS routine (empirical multi-scan method). The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with anisotropic thermal parameters for nonhydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation. Calculations were carried out using the SHELXL-97, SHELXL-2014 or Olex2 program.[S4] CCDC deposition numbers for **1**, **4** and **6** are CCDC 1993358-1993360. The crystallography data of **3** is consistent with literature.[S4] For the crystallography data of **6**, a level B alert was flagged by checkCIF for short distance of O4 and N1. We contribute this alert were caused from the electrostatic interaction between the triflate anion and the cation.

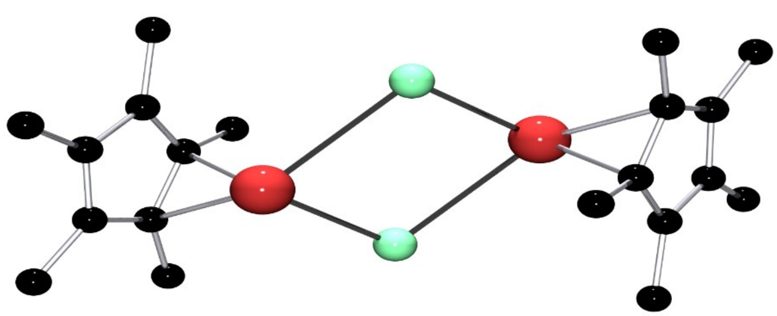

Figure S31. POV-ray depictions of the cation of **3**; C: black; Sb: brown; Cl: aquamarine. All H atoms and the $[B(C_6F_5)_4]^-$ anions are omitted for clarity.

Table S1 Crystallographic data and refinement parameters for **1**, **3**, **4** and **6**.

	1·2toluene	0.5**3**
formula	$C_{79}H_{39}B_2F_{40}Sb$	$C_{34}H_{15}BF_{20}SbCl$
formula Mass	1891.47	971.47
color	yellow	yellow
cryst system	Monoclinic	Triclinic
space group	$P2_1/c$	$P\bar{1}$
a, Å	16.5682(4)	10.6109(7)
b, Å	15.2566(4)	12.6652(9)
c, Å	28.2917(7)	12.8705(8)
α, deg	90	90.720(3)
β, deg	90.0060(10)	96.504(2)
γ, deg	90	104.570(2)
V, Å^3	7151.4(3)	1661.74(19)
Z	4	2
D_{calcd}, (mg/m^3)	1.757	1.942
F(000)	3736	944
T(K)	150(2)	150(2)
θ range, deg	2.316 to 26.737	3.163 to 30.678
no. of independent reflns	15155	10203
No. of params	1095	519
final R_1, wR (I > 2σ(I))	0.0484, 0.0992	0.0341, 0.0740
goodness of fit on F^2	1.022	1.022
$\Delta\rho_{max, min}$, eÅ^{-3}	1.012, -1.242	0.873, -1.076

	4·toluene	**6**·0.5Et_2O
formula	$C_{61}H_{64}BF_{20}N_4Sb$	$C_{25}H_{21}S_3F_9N_4O_{9.5}Sb$
formula Mass	1365.72	918.39
color	yellow	colorless
cryst system	Monoclinic	Triclinic
space group	$P2/n$	$P\bar{1}$
a, Å	19.218(3)	9.1010(4)
b, Å	8.3161(12)	13.2750(6)
c, Å	20.922(3)	13.8328(6)
α, deg	90	81.615(2)
β, deg	111.897(4)	86.390(2)
γ, deg	90	84.352(2)
V, Å^3	3102.5(7)	1643.32(13)
Z	2	2
D_{calcd}, (mg/m^3)	1.462	1.856
F(000)	1388	910
T(K)	150(2)	150(2)
θ range, deg	1.816 to 26.371	2.619 to 27.103
no. of independent reflns	6332	7241
No. of params	422	485
final R_1, wR ($I > 2\sigma(I)$)	0.0385, 0.0944	0.0325, 0.0900
goodness of fit on F^2	1.086	1.029
$\Delta\rho_{max, min}$, eÅ^{-3}	0.468, -0.725	2.212, -1.143

4. Computational Details

All geometry optimizations were performed using the Gaussian 09 package[S5] with the functional M06-2X with the basis set of def2-SVP.[S5] Frequency calculations at the same level of theory were performed to identify the number of imaginary frequencies (zero for local minimum and one for transition states) and provide the thermal corrections of Gibbs free energy. Transition states were submitted to intrinsic reaction coordinate (IRC) calculations to determine two corresponding minima. The single-point energy calculations were performed at the M06-2X/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, while Bondi radii[S7] 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 single-point energies to obtain the Gibbs free energy or enthalpy in solution, respectively. All the energies reported in the paper correspond to the reference state of 1 mol/L, 298K.

Intrinsic bond orbitals (IBOs) were carried out using ORCA program at the PBE/def2-TZVP level.[S8] The EDA-NOCV and dual descriptor calculations were carried out with the M06-2X/TZP level using ADF/2019.103 on Graham.[S9] The relativistic scalar effect was included by using the zeroth-order regular approximation (ZORA) and the integration grid of Becke Good was employed. NBO calculations were carried out using NBO 6.0 program[S10] at the M06-2X/def2-TZVP level of theory. Optimized structures with orbitals were visualized by the Chemcraft[S11] or IBOview program.[S12]

A relaxed potential energy surface scan was performed with a step size of 0.1 angstroms for the dissociation of a BAC molecule from **IN1** or **IN2**. The energies increase continually, suggesting the dissociation/approach of the BAC ligand with $[(\eta^5\text{-Cp*})Sb(tol)]^{2+}$ or **IN1** has no transition state.

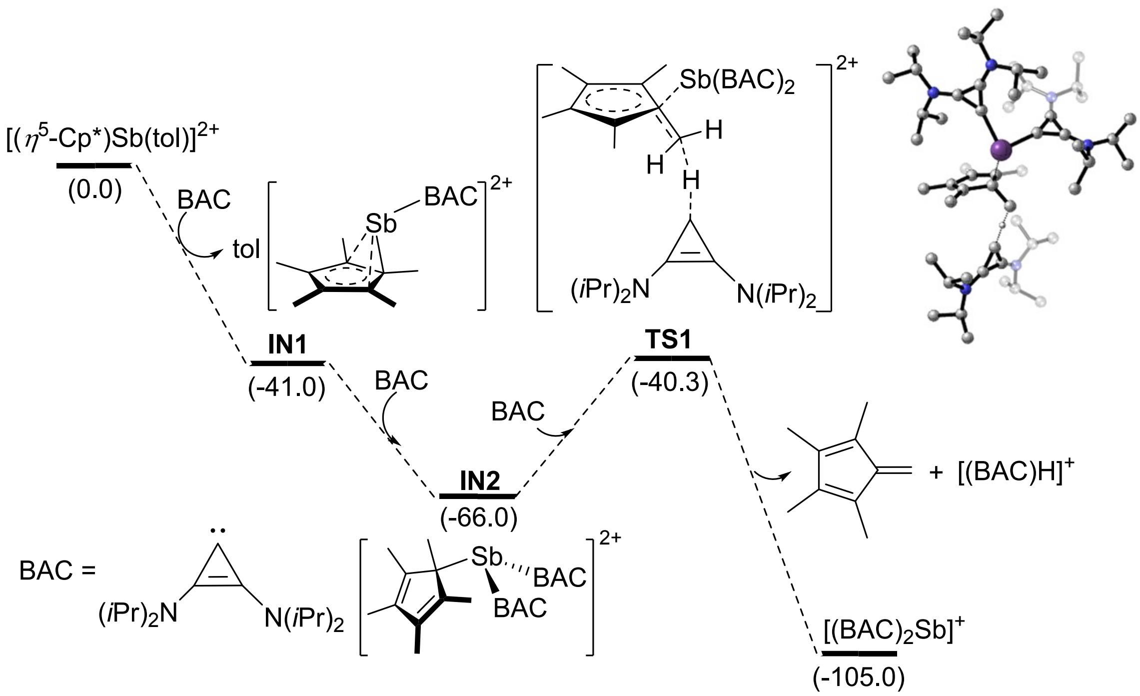

Figure S32. Free energy profile (kcal mol^{-1}) for the formation of **4**.

Table S2. Energies of Intermediates and Transition States.

Species	Thermal Corrections of Gibbs Free Energies (Hartree)	Solvation Energies (Hartree)
[(η^5-Cp*)Sb(tol)]$^{2+}$	0.300628	-901.4079561
BAC	0.359036	-697.8068152
tol	0.09867	-271.5440405
IN1	0.562965	-1327.738085
IN2	0.955728	-2025.618476
TS1	1.329665	-2723.399282
[(BAC)$_2$Sb]$^+$	0.738876	-1635.735192
[(BAC)H]$^+$	0.372694	-698.2948355
tetramethylfulvene	0.17261	-389.4269247

Cartesian Coordinates:

[(η^5-Cp*)Sb(tol)]$^{2+}$:

51	-3.394018	-2.959029	-1.823535
6	-2.805591	-4.694484	-0.193434

6	-2.209192	-5.103971	-1.436244
6	-1.247341	-4.102390	-1.828664
6	-1.246474	-3.058084	-0.818120
6	-2.216059	-3.425519	0.195640
6	-3.751995	-5.501852	0.632658
1	-4.385493	-4.875092	1.271909
1	-3.161418	-6.157692	1.293514
1	-4.390537	-6.146363	0.016517
6	-2.450401	-6.400870	-2.138051
1	-3.462747	-6.783661	-1.961058
1	-1.741160	-7.149071	-1.748312
1	-2.284171	-6.322372	-3.219195
6	-0.299960	-4.203983	-2.978154
1	-0.732020	-4.758671	-3.819810
1	0.592169	-4.757781	-2.641835
1	0.035927	-3.221200	-3.329886
6	-0.289809	-1.912926	-0.739887
1	0.038109	-1.579667	-1.732127
1	0.606434	-2.244794	-0.190551
1	-0.710526	-1.059902	-0.192957
6	-2.432690	-2.717463	1.493547
1	-2.262158	-1.637173	1.406456
1	-1.708956	-3.106648	2.228275
1	-3.437690	-2.892829	1.896269
6	-5.261202	-0.602146	-1.211113
6	-3.946061	-0.131039	-1.416843
1	-3.400018	0.309956	-0.578092

6	-3.363333	-0.140776	-2.697647
1	-2.365537	0.280238	-2.842268
6	-4.079766	-0.643410	-3.792470
1	-3.643133	-0.623916	-4.792675
6	-5.379313	-1.132131	-3.597473
1	-5.953247	-1.506477	-4.447578
6	-5.957214	-1.116950	-2.324522
1	-6.980273	-1.478087	-2.193591
6	-5.927065	-0.486255	0.129268
1	-6.621779	-1.315674	0.315200
1	-6.521181	0.441305	0.154372
1	-5.198414	-0.424762	0.947639

BAC:

6	5.226360	0.750853	17.644298
1	5.080184	0.223550	18.599698
6	6.716774	2.480174	16.861324
6	7.484748	3.448127	16.288736
6	8.712868	5.116796	15.050921
1	9.538580	5.806609	15.283643
6	5.598881	-0.277650	16.579454
1	4.788010	-1.009469	16.452981
1	6.514501	-0.816985	16.862478
1	5.771041	0.226104	15.617576
6	3.934070	1.487680	17.300166
1	4.058696	2.040414	16.358160
1	3.670328	2.201026	18.094316

1	3.106587	0.773277	17.182536
6	10.728427	4.314582	17.267961
1	11.173757	4.960488	16.495912
1	10.844480	3.268809	16.950868
1	11.297635	4.465114	18.196544
6	6.964947	1.760173	19.191069
1	7.741811	2.531945	19.097325
6	5.983470	2.210701	20.271885
1	5.176272	1.474893	20.408052
1	5.529291	3.174887	20.004149
1	6.498099	2.321318	21.237173
6	7.495675	5.943675	14.643030
1	7.719572	6.536314	13.744295
1	7.204192	6.630180	15.450968
1	6.648041	5.278752	14.424314
6	9.253634	4.650181	17.485161
1	8.863097	3.972299	18.256968
6	9.056765	6.083357	17.977198
1	9.606363	6.246692	18.915357
1	7.991815	6.287846	18.155215
1	9.430278	6.812442	17.242073
6	7.652755	0.443976	19.550507
1	8.179848	0.535305	20.511046
1	8.380707	0.164460	18.776208
1	6.921919	-0.373230	19.648369
6	9.168985	4.180732	13.934165
1	8.368252	3.466366	13.695641

1	10.062718	3.617050	14.239039
1	9.410342	4.754756	13.027944
6	6.495970	2.818973	15.517814
7	6.330113	1.696819	17.875851
7	8.454011	4.371547	16.293683

tol:

6	-0.294043	0.343601	-0.015159
6	1.105514	0.364481	-0.000695
6	1.804917	1.569656	0.012079
6	1.114458	2.781053	0.008663
6	-0.279278	2.774938	-0.008957
6	-0.974006	1.566292	-0.021670
1	1.654998	-0.580043	-0.001986
1	2.896198	1.562527	0.021199
1	1.661095	3.725232	0.015920
1	-0.831049	3.716554	-0.016475
1	-2.066413	1.570100	-0.039594
6	-1.046276	-0.961769	0.002348
1	-0.508658	-1.739150	-0.557410
1	-1.173059	-1.326349	1.033618
1	-2.047382	-0.850859	-0.435284

IN1:

51	-3.032036	-1.527381	-1.398180
6	-2.774970	-4.263516	-0.474475
6	-2.106768	-4.139829	-1.688389

6	-1.185734	-2.997325	-1.612216
6	-1.269584	-2.468842	-0.257851
6	-2.308014	-3.227433	0.412483
6	-3.827624	-5.256474	-0.095595
1	-4.778168	-4.761030	0.152086
1	-3.515252	-5.829052	0.790076
1	-4.018591	-5.971457	-0.903368
6	-2.234325	-5.000324	-2.900327
1	-3.123294	-5.639067	-2.857559
1	-1.352231	-5.655839	-2.982571
1	-2.280284	-4.403046	-3.821331
6	-0.054352	-2.782358	-2.570847
1	-0.374867	-2.910214	-3.612823
1	0.721340	-3.538564	-2.368177
1	0.406419	-1.793905	-2.460768
6	-0.269510	-1.566173	0.400893
1	0.159181	-0.846713	-0.308934
1	0.554391	-2.176437	0.802403
1	-0.712603	-1.008171	1.235827
6	-2.675225	-3.126921	1.853135
1	-2.388520	-2.167704	2.299829
1	-2.137319	-3.921478	2.398087
1	-3.747464	-3.301418	2.011725
7	-1.187737	2.238460	-2.958886
7	-3.198255	2.497098	0.135835
6	-1.841008	1.689074	-1.973642
6	-2.615397	1.794984	-0.795318

6	-2.343131	0.548789	-1.353363
6	-1.197710	3.711974	-3.174292
1	-1.816985	4.109114	-2.359564
6	-2.981447	3.964432	0.264217
1	-2.204538	4.198668	-0.475338
6	-4.116224	1.826660	1.092487
1	-4.461236	2.625579	1.761007
6	-3.378214	0.792300	1.932596
1	-3.020466	-0.044633	1.309122
1	-4.054762	0.376531	2.691329
1	-2.513467	1.236638	2.444420
6	-4.252940	4.728128	-0.080804
1	-4.602600	4.487211	-1.094838
1	-4.061189	5.808268	-0.029856
1	-5.061487	4.506750	0.631771
6	-1.887035	4.053912	-4.491273
1	-1.301060	3.727469	-5.362312
1	-1.996025	5.144127	-4.567858
1	-2.888561	3.605730	-4.548803
6	0.203282	4.297370	-3.066843
1	0.668216	4.060601	-2.099575
1	0.149170	5.390005	-3.163513
1	0.856160	3.932982	-3.873700
6	-5.332717	1.258878	0.372651
1	-5.849404	2.033179	-0.209909
1	-6.042712	0.845170	1.101066
1	-5.052512	0.444513	-0.316204

6	-2.425568	4.313692	1.640328
1	-3.161276	4.149768	2.440372
1	-2.163835	5.380131	1.659288
1	-1.517659	3.737552	1.865867
6	-0.416732	1.387616	-3.900492
1	-0.150721	2.052873	-4.732073
6	0.862721	0.900781	-3.229858
1	1.515156	1.737932	-2.950796
1	1.423085	0.240406	-3.906044
1	0.621923	0.339328	-2.313105
6	-1.262076	0.252917	-4.465765
1	-1.430943	-0.533318	-3.711233
1	-0.730960	-0.217368	-5.304260
1	-2.231273	0.616061	-4.835707

IN2:

6	6.364164	-0.818767	-1.642978
6	5.991786	-1.253590	-2.874048
6	6.752211	-0.517078	-3.903946
6	7.619348	0.339754	-3.306215
6	7.460493	0.197195	-1.818312
6	5.963528	-1.346055	-0.298884
1	5.641949	-0.549134	0.396790
1	6.796736	-1.875110	0.191182
1	5.131478	-2.056638	-0.378110
6	5.077238	-2.385783	-3.220860
1	4.581611	-2.808490	-2.338716

1	5.649418	-3.196592	-3.698365
1	4.305864	-2.083045	-3.945289
6	6.588863	-0.772796	-5.368067
1	5.563677	-0.537686	-5.697211
1	6.761672	-1.833162	-5.606615
1	7.281309	-0.170700	-5.969856
6	8.714676	1.125977	-3.967808
1	8.369798	2.086175	-4.381611
1	9.154402	0.556128	-4.798383
1	9.529013	1.351819	-3.262699
6	8.755891	-0.275626	-1.137142
1	9.608904	0.379268	-1.358000
1	8.994287	-1.276604	-1.529710
1	8.657874	-0.356893	-0.043623
7	3.894072	4.948014	-0.164138
7	10.309067	4.439229	-1.785274
7	7.545038	4.937278	-4.140046
7	2.428128	2.072733	-1.819244
6	4.067036	3.767821	-0.713619
6	3.510018	2.656264	-1.372489
6	4.876873	2.702947	-1.099548
6	7.880421	3.505764	-1.974534
6	9.085526	4.166124	-2.167724
6	2.617142	5.686202	-0.344956
1	2.099528	5.163610	-1.160135
6	10.752859	4.121134	-0.404788
1	11.753528	4.565129	-0.325995

6	8.021558	4.347525	-3.071180
6	1.092195	2.681300	-1.583031
1	1.263011	3.467512	-0.837684
6	6.173118	4.649286	-4.620692
1	6.106723	5.139390	-5.600946
6	2.487651	0.790884	-2.562073
1	1.485469	0.674290	-2.995652
6	8.359480	5.941040	-4.873937
1	9.212105	6.150396	-4.215520
6	11.248389	5.154927	-2.685622
1	10.759600	5.144748	-3.669081
6	12.556871	4.385465	-2.834287
1	13.141552	4.368189	-1.903759
1	13.176913	4.876547	-3.596162
1	12.374526	3.351560	-3.158484
6	2.748202	-0.367848	-1.610667
1	3.741436	-0.269689	-1.150465
1	2.720950	-1.317206	-2.161596
1	1.989958	-0.411182	-0.818207
6	10.874006	2.622790	-0.175408
1	9.881227	2.148604	-0.155007
1	11.341620	2.429539	0.799440
1	11.483551	2.141597	-0.952858
6	0.560234	3.306244	-2.866741
1	1.263641	4.051286	-3.267926
1	-0.400464	3.803513	-2.675813
1	0.388719	2.543302	-3.640802

6	2.868570	7.111079	-0.828451
1	3.355276	7.735072	-0.065618
1	1.905417	7.583444	-1.064074
1	3.483232	7.118042	-1.739617
6	1.768197	5.627687	0.918702
1	1.572166	4.588448	1.221795
1	0.804493	6.127358	0.749958
1	2.263265	6.141284	1.756380
6	5.147476	5.282161	-3.685066
1	5.294104	4.915345	-2.658510
1	4.127231	5.025356	-4.006046
1	5.240176	6.376792	-3.677051
6	9.853224	4.799795	0.621774
1	9.792424	5.881681	0.438297
1	10.255517	4.642457	1.631558
1	8.834997	4.379286	0.599110
6	7.609856	7.255527	-5.060388
1	6.751131	7.157116	-5.739188
1	8.291441	7.991273	-5.507912
1	7.262331	7.657862	-4.098785
6	5.948953	3.160471	-4.833477
1	6.672153	2.750759	-5.552221
1	4.942980	2.999503	-5.242270
1	6.028950	2.593153	-3.892827
6	3.481994	0.881373	-3.707848
1	3.234446	1.730226	-4.360788
1	3.437872	-0.036578	-4.309402

1	4.513722	0.990803	-3.341804
6	0.119145	1.687667	-0.956946
1	-0.131928	0.860030	-1.634744
1	-0.817302	2.211969	-0.723563
1	0.517573	1.272947	-0.021092
6	11.449209	6.595266	-2.233047
1	10.491625	7.133785	-2.174703
1	12.101628	7.124532	-2.940741
1	11.932199	6.640212	-1.245404
6	4.918120	5.539713	0.731095
1	4.431907	6.425591	1.158910
6	8.867350	5.350643	-6.183370
1	9.452945	4.436994	-6.003702
1	9.507267	6.076293	-6.703371
1	8.034585	5.101128	-6.858250
6	5.252209	4.601619	1.884054
1	4.344918	4.318402	2.435283
1	5.934886	5.101117	2.584761
1	5.747618	3.683030	1.535605
6	6.141412	6.002949	-0.047723
1	6.651762	5.151587	-0.522954
1	6.856581	6.488265	0.630591
1	5.862909	6.720907	-0.831625
51	6.920613	2.040179	-0.680574

TS1:

6	6.615632	-0.897555	-1.489105

6	6.252530	-1.315232	-2.729632
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6	7.860998	0.312331	-3.126597
6	7.708394	0.104768	-1.660698
6	6.191563	-1.412132	-0.150417
1	5.874494	-0.602266	0.528746
1	7.018321	-1.937730	0.352985
1	5.354465	-2.117208	-0.235548
6	5.314329	-2.420903	-3.098991
1	4.845105	-2.877922	-2.218026
1	5.854823	-3.216985	-3.635315
1	4.516490	-2.076571	-3.777012
6	6.862609	-0.805955	-5.213614
1	5.824241	-0.629910	-5.538639
1	7.095833	-1.853905	-5.458828
1	7.518286	-0.165035	-5.816429
6	8.957103	1.140073	-3.717668
1	8.903179	2.192560	-3.403309
1	8.933373	1.111912	-4.814651
1	9.941190	0.757676	-3.402206
6	8.912649	-0.064199	-0.878244
1	9.729171	0.638652	-1.089478
1	9.328694	-1.236023	-1.384013
1	8.785696	-0.255060	0.196368
7	3.683895	5.383573	-0.299420
7	10.135536	4.770142	-0.845228
7	7.817897	5.181184	-3.658378

7	2.490618	2.262280	-1.848841
6	3.916766	4.165517	-0.736220
6	3.455951	2.986791	-1.334709
6	4.788376	3.106410	-0.963028
6	7.861669	3.673622	-1.511192
6	9.029482	4.423535	-1.465019
6	2.382183	6.039910	-0.561405
1	1.898780	5.413284	-1.323474
6	10.336334	4.408408	0.579355
1	11.246363	4.945781	0.877079
6	8.137060	4.572487	-2.537403
6	1.088152	2.735310	-1.857698
1	1.085293	3.633316	-1.225030
6	6.616190	4.790713	-4.432723
1	6.736237	5.284908	-5.406481
6	2.813302	0.935309	-2.421913
1	1.893444	0.611525	-2.927605
6	8.665952	6.280837	-4.178409
1	9.343293	6.532782	-3.352553
6	11.140354	5.629064	-1.512620
1	10.864423	5.616835	-2.575984
6	12.539295	5.029109	-1.412818
1	12.923340	5.034986	-0.383125
1	13.231279	5.627201	-2.020873
1	12.554818	3.997464	-1.790054
6	3.149516	-0.058154	-1.317493
1	4.036984	0.276266	-0.757472

1	3.384838	-1.039367	-1.751650
1	2.314010	-0.175295	-0.614643
6	10.577752	2.915919	0.751186
1	9.681573	2.338047	0.481849
1	10.812353	2.692521	1.800672
1	11.415369	2.573488	0.127839
6	0.659291	3.119301	-3.269124
1	1.326761	3.885997	-3.689070
1	-0.364379	3.517473	-3.259342
1	0.668438	2.246693	-3.939620
6	2.573451	7.422613	-1.176026
1	3.024200	8.133464	-0.469030
1	1.594480	7.829106	-1.463777
1	3.200581	7.371375	-2.077175
6	1.517771	6.059927	0.693459
1	1.365923	5.043758	1.085834
1	0.534827	6.497132	0.470970
1	1.978701	6.669759	1.484984
6	5.353427	5.324305	-3.766290
1	5.274202	4.926971	-2.745060
1	4.463702	5.012673	-4.332590
1	5.363540	6.421353	-3.714888
6	9.185564	4.924311	1.436765
1	9.051196	6.006924	1.300437
1	9.396635	4.732832	2.497538
1	8.242293	4.413773	1.187306
6	7.852749	7.535069	-4.481496

1	7.149814	7.387986	-5.313813
1	8.537171	8.342718	-4.773643
1	7.291646	7.868028	-3.597117
6	6.568137	3.290522	-4.680731
1	7.472239	2.955570	-5.206124
1	5.699000	3.049108	-5.307841
1	6.478877	2.720542	-3.742757
6	3.915885	1.045437	-3.467380
1	3.683455	1.833510	-4.198306
1	4.009819	0.092045	-4.004642
1	4.893413	1.254631	-3.003916
6	0.151120	1.723132	-1.206855
1	0.076412	0.793326	-1.788851
1	-0.858312	2.151868	-1.147669
1	0.477851	1.477542	-0.187252
6	11.068911	7.058520	-0.988626
1	10.059217	7.477919	-1.114338
1	11.780458	7.698067	-1.528642
1	11.328911	7.102820	0.079804
6	4.681002	6.079706	0.546270
1	4.165461	6.980338	0.905350
6	9.487769	5.802444	-5.369382
1	10.098317	4.927912	-5.100073
1	10.157584	6.601516	-5.715250
1	8.840745	5.524058	-6.214725
6	5.058326	5.239502	1.760771
1	4.165776	4.951614	2.333583

1	5.718165	5.817893	2.421925
1	5.595040	4.324080	1.466598
6	5.892639	6.508556	-0.271806
1	6.419875	5.623833	-0.659122
1	6.591156	7.075274	0.359591
1	5.595127	7.141723	-1.119199
51	6.712727	2.116626	-0.510955
6	8.641238	-4.906098	-0.043884
1	8.560079	-5.901260	0.414948
6	10.098163	-3.916255	-1.679246
6	10.840277	-3.238419	-2.630323
6	11.945797	-1.881130	-4.275456
1	12.775276	-2.040667	-4.978664
6	7.338952	-4.612342	-0.784370
1	6.498006	-4.568686	-0.077499
1	7.129712	-5.399418	-1.522783
1	7.404718	-3.648113	-1.312685
6	8.943799	-3.899512	1.061422
1	9.087867	-2.892533	0.641818
1	9.857672	-4.179432	1.603813
1	8.113488	-3.863920	1.780795
6	12.342067	-4.724197	-5.407306
1	12.657401	-3.934902	-6.106300
1	11.277246	-4.936172	-5.577299
1	12.917680	-5.627317	-5.652174
6	10.438385	-6.294475	-1.193210
1	11.207813	-6.104250	-1.953428

6	11.137599	-6.750276	0.083967
1	10.414771	-6.957855	0.887183
1	11.843061	-5.986774	0.439752
1	11.695235	-7.678077	-0.103298
6	12.354378	-0.774894	-3.307174
1	12.516010	0.166053	-3.852499
1	13.286179	-1.038397	-2.787361
1	11.572766	-0.613046	-2.549345
6	12.595440	-4.320674	-3.957856
1	12.258976	-5.141402	-3.310371
6	14.072326	-4.065957	-3.671128
1	14.661327	-4.964617	-3.900028
1	14.228493	-3.808748	-2.614401
1	14.467524	-3.247959	-4.291933
6	9.478414	-7.345934	-1.742819
1	10.021450	-8.278329	-1.949134
1	9.012489	-7.002953	-2.677222
1	8.682470	-7.582433	-1.020960
6	10.694729	-1.540646	-5.082335
1	9.820805	-1.440336	-4.419516
1	10.484235	-2.330496	-5.817129
1	10.835006	-0.594260	-5.624283
6	9.860649	-2.563377	-1.908886
7	9.764978	-4.999563	-0.996318
7	11.771790	-3.163674	-3.568748

$[(BAC)_2Sb]^+$:

7	5.675661	3.629654	14.746880
7	7.959146	3.443065	8.616253
7	6.049014	0.803022	10.338207
7	8.218839	1.744795	16.639567
6	6.836543	2.993138	14.793027
6	7.785262	2.284874	15.515832
6	8.002937	2.560675	14.166554
6	8.043716	2.370816	10.998104
6	7.723400	2.707962	9.685348
6	4.744530	3.546635	15.887500
1	5.100534	2.695253	16.485785
6	8.902569	4.579275	8.707059
1	8.831389	5.088151	7.735613
6	7.010390	1.710525	10.340426
6	7.520379	1.981789	17.916155
1	6.735776	2.715519	17.683562
6	6.038765	-0.272292	11.354438
1	5.295886	-0.996405	10.991064
6	9.431360	0.898212	16.619720
1	9.518159	0.499704	17.640402
6	5.070357	0.763012	9.235379
1	5.194856	1.720551	8.708986
6	7.270494	3.167317	7.341648
1	6.751103	2.211055	7.497468
6	8.262439	2.962548	6.200528
1	8.812962	3.884435	5.964309
1	7.720208	2.663200	5.293182

1	8.987112	2.174001	6.445107
6	10.678156	1.724784	16.322401
1	10.628387	2.169547	15.316875
1	11.572584	1.088294	16.357893
1	10.797688	2.535805	17.053453
6	10.335000	4.091383	8.893578
1	10.444910	3.558692	9.850360
1	11.026663	4.944444	8.908913
1	10.633094	3.415748	8.080577
6	6.860336	0.704797	18.425386
1	6.164173	0.297699	17.677841
1	6.301078	0.907697	19.349149
1	7.610352	-0.067316	18.653688
6	3.329572	3.209253	15.428126
1	2.884881	4.020363	14.833397
1	2.685677	3.055844	16.304840
1	3.321731	2.287756	14.829397
6	4.802682	4.809648	16.741215
1	5.828841	5.003310	17.087291
1	4.151248	4.709592	17.620450
1	4.462581	5.688742	16.173243
6	5.584650	0.247038	12.713352
1	6.298835	0.992931	13.091414
1	5.540879	-0.579884	13.436267
1	4.589666	0.709084	12.647843
6	8.469030	5.561010	9.790524
1	7.429252	5.882560	9.632067

1	9.114421	6.449878	9.769605
1	8.556064	5.106722	10.789465
6	3.640533	0.725447	9.766394
1	3.423804	-0.212483	10.297766
1	2.933964	0.798364	8.928502
1	3.455430	1.566646	10.448889
6	7.390944	-0.974074	11.421443
1	7.693760	-1.334268	10.427888
1	7.330216	-1.838064	12.097568
1	8.170362	-0.296545	11.803624
6	9.256846	-0.278984	15.665769
1	8.353778	-0.853073	15.918900
1	10.124482	-0.949429	15.735080
1	9.180851	0.065692	14.622920
6	8.447233	2.620010	18.946815
1	9.262151	1.942408	19.239965
1	7.878592	2.863223	19.854853
1	8.887874	3.547815	18.556325
6	6.236051	4.245834	7.037231
1	5.506983	4.333681	7.856157
1	5.693868	4.005947	6.112124
1	6.715519	5.226447	6.897481
6	5.380361	4.561496	13.638703
1	4.514067	5.145551	13.980770
6	5.371540	-0.376796	8.267801
1	6.395299	-0.297874	7.873270
1	4.669957	-0.357686	7.422266

1	5.270356	-1.354527	8.762436
6	6.537964	5.527394	13.409751
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1	6.256513	6.275921	12.656089
1	7.434232	4.997546	13.051564
6	4.985394	3.808177	12.374059
1	5.810212	3.157252	12.053405
1	4.767761	4.515925	11.560871
1	4.094471	3.188488	12.547632
51	9.482410	2.562675	12.600904

$[(BAC)H]^+$:

6	5.212675	0.729891	17.655277
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6	6.681552	2.454577	16.842919
6	7.485247	3.464292	16.244425
6	8.725710	5.138891	15.040583
1	9.553556	5.803775	15.318793
6	5.591997	-0.328742	16.627368
1	4.793826	-1.079371	16.554791
1	6.522034	-0.840428	16.910339
1	5.725094	0.111288	15.627937
6	3.909124	1.447665	17.327831
1	3.965102	1.960566	16.356461
1	3.660538	2.187870	18.100584
1	3.089320	0.719418	17.270881
6	10.705682	4.274487	17.259903

1	11.163635	4.939337	16.513067
1	10.823915	3.235207	16.923711
1	11.264406	4.400353	18.197044
6	6.976527	1.790583	19.173167
1	7.746831	2.564695	19.059918
6	5.988129	2.250681	20.238831
1	5.194019	1.507620	20.402748
1	5.522485	3.206893	19.963310
1	6.512898	2.384547	21.194279
6	7.530071	5.998449	14.648891
1	7.791547	6.626866	13.787177
1	7.226935	6.654909	15.475809
1	6.667899	5.379651	14.359370
6	9.238201	4.616677	17.491711
1	8.838843	3.927487	18.247244
6	9.031125	6.043230	17.988243
1	9.570585	6.185250	18.934310
1	7.966882	6.252880	18.163112
1	9.422107	6.782385	17.273909
6	7.665773	0.477623	19.526858
1	8.202658	0.588945	20.478439
1	8.389863	0.187231	18.753291
1	6.940228	-0.339196	19.653385
6	9.202864	4.225471	13.918178
1	8.407589	3.538356	13.593929
1	10.071921	3.631271	14.232301
1	9.494004	4.828548	13.047878

6	6.503816	2.820928	15.531350
7	6.321405	1.702641	17.848444
7	8.436925	4.358639	16.273932
1	5.968514	2.693082	14.595198

tetramethylfulvene:

6	6.774875	3.689332	3.550615
6	6.042167	4.316972	2.600167
6	6.878331	5.368339	1.948846
6	8.111008	5.369905	2.509847
6	8.119307	4.313921	3.549918
6	6.389453	2.574405	4.468418
1	6.494336	2.872244	5.523644
1	7.030711	1.691994	4.315202
1	5.349102	2.262776	4.311034
6	4.624049	4.067492	2.198112
1	4.168631	3.258683	2.783143
1	4.557243	3.794876	1.132774
1	4.009926	4.971887	2.333810
6	6.350445	6.237684	0.853114
1	5.478843	6.819109	1.193594
1	6.013520	5.632053	-0.003172
1	7.107136	6.944314	0.489939
6	9.293433	6.231779	2.205101
1	9.077442	6.941619	1.396603
1	10.160503	5.626375	1.896900
1	9.601380	6.813697	3.088324

6	9.149443	3.984230	4.340699
1	10.108741	4.501989	4.268427
1	9.062169	3.187536	5.083192

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