Supporting Information

A Free Phosphaborene Stable at Room Temperature

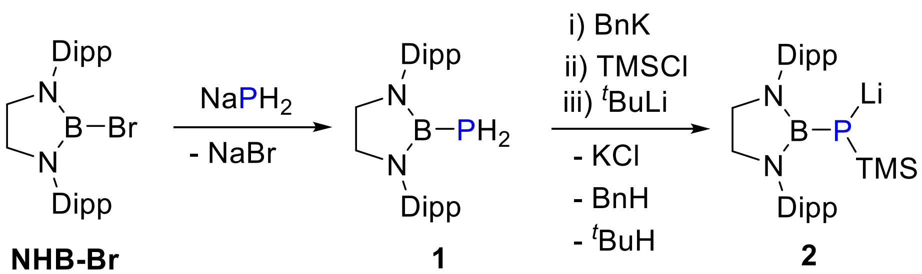
Jiancheng Li, Zhihao Lu, Liu Leo Liu*

Department of Chemistry and Guangdong Provincial Key Laboratory of Catalysis, Southern University of Science and Technology, Shenzhen 518055 (China)

Table of Contents

I. Experimental Section

All manipulations were carried out in a nitrogen-filled glovebox or under an atmosphere of dry nitrogen using standard Schlenk techniques, unless otherwise stated. Toluene, *n*-hexane and tetrahydrofuran (THF) were purified by $LiAlH_4$ and stored over molecular sieves. C_6D_6 was dried by sodium/potassium alloy. NMR spectra were acquired on a Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 101 MHz) or 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz) NMR spectrometer at 298 K. ^{1}H, ^{13}C{^{1}H} spectra were referenced to internal C_6H_6. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept=septet, m = multiplet and/or multiple resonances), coupling constant in hertz (Hz), integration, attribution. High resolution mass spectrometry (HRMS) was performed with a Thermo Fisher Scientific Q-Exactive MS System. Crystal data were collected on a Bruker D8 VENTURE diffractometer with graphite monochromated Cu Kα (λ = 1.54178). Data reduction, scaling and absorption corrections were performed using SAINT (Bruker, V8.38A, 2013). The structure was solved with the XT structure solution program using the Intrinsic Phasing solution method and by using Olex2 as the graphical interface. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multi-scan method (SADABS). The model was refined with the ShelXL program using Least Squares minimization. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions. Commercial reagents were purchased from Energy Chemical, J&K, or TCI Chemical Co. and used as received. **NHB-Br**,[S1] $NaPH_2$,[S2] and **NHC=NSiMe3**[S3] were prepared according to the procedure described in the literature.

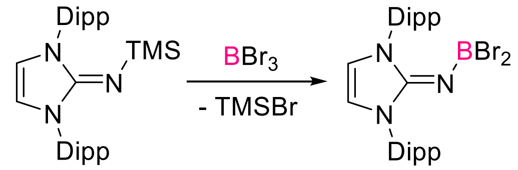


Scheme S1-1. Synthesis of **1** and **2.**

1) **Synthesis of 1** To the solid mixture of **NHB-Br** (2.25g, 4.8 mmol) and $NaPH_2$ (269 mg, 4.8 mmol) at -50 °C pre-cooled THF (20 mL) was added under stirring. The reaction solution was then allowed to warm to room temperature and stirred for further 8 hours. The volatiles were removed through evaporation under vacuum. Then the residues were extracted with *n*-hexane (20 mL), after filtration through a pad of celite, the volatiles were removed to give a colorless solid **1** (1.85 g, 91%). ^{1}H NMR (600 MHz, C_6D_6, 298 K, ppm): δ = 1.28 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH*Me*$_2$), 1.35 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH*Me*$_2$), 1.29 (d, $^1J_{PH}$ = 202.6 Hz, 2 H, P*H*$_2$), 3.51 (s, 4 H, NC*H*$_2$C*H*$_2$N),

3.53 (sept, $^{3}J_{HH}$ = 6.9 Hz, 4 H, C*H*Me$_2$), 7.13-7.21 (m, 6 H, Ar-*H*). ^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6, 298 K, ppm): δ = 25.0, 25.0, 25.2, (CH*Me$_2$*), 28.7 (*C*HMe$_2$), 53.9 (N*C*H$_2$*C*H$_2$N), 124.3 (Ar-*C*), 127.5 (Ar-*C*), 139.6 (Ar-*C*), 147.7 (Ar-*C*). ^{31}P{^{1}H} NMR (243 MHz, 298 K, C_6D_6, ppm): δ = -246.8. ^{31}P NMR (243 MHz, 298 K, C_6D_6, ppm): δ = -246.8 (t, $^{1}J_{PH}$ = 202.6 Hz, *P*H$_2$). ^{11}B{^{1}H} NMR (192.6 MHz, 298 K, C_6D_6, ppm): δ = 35.1 (br). HRMS(m/z): $[M+H]^+$ calcd. for $C_{26}H_{41}N_2BP$: 423.30938, found: 423.30949.

2) **Synthesis of 2** To a solid mixture of **1** (1.85 g, 4.4 mmol) and benzyl potassium (Bnk) (568.9 mg, 4.4 mmol) at -30 °C pre-cooled THF (20 mL) was added under stirring. The red suspension was then allowed to warm to room temperature and stirred for further one hour to give an orange-red clear solution. Then it was cooled to -30 °C again, and to which slightly excess chlorotrimethylsilane (Me_3SiCl) (0.64 mL, 5 mmol) was dropwise added via syringe. The reaction solution was then allowed to warm to room temperature and stirred for further 3 hours. The volatiles were removed through evaporation under vacuum and the residues were then extracted with *n*-hexane (20 mL). After filtration through a pad of celite, the clear colorless solution was cooled to -50 °C and to which tert-butyllithium (*t*BuLi) (1.6 M in *n*-hexane, 2.7 mL, 4.4 mmol) was added drop-by-drop. The reaction solution was then allowed to warm to room temperature and stirred for further 8 hours, resulting in a white suspension. The precipitate was collected by filtration, washed with cold *n*-hexane (5 mL) and dried under vacuum to give **2** as white solid (1.47 g, 67%). ^{1}H NMR (600 MHz, C_6D_6, 298 K, ppm): δ = -0.07 (br, 9 H, Si*Me$_3$*), 1.25 (d, $^{3}J_{HH}$ = 6.9 Hz, 12 H, CH*Me$_2$*), 1.50 (d, $^{3}J_{HH}$ = 6.9 Hz, 12 H, CH*Me$_2$*), 3.61 (s, 4 H, NC*H$_2$*C*H$_2$*N), 3.71 (sept, $^{3}J_{HH}$ = 6.9 Hz, 4 H, C*H*Me$_2$), 7.17-7.23 (m, 6 H, Ar-*H*). ^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6, 298 K, ppm): δ = 6.7 (Si*Me$_3$*), 24.8, 26.3, (CH*Me$_2$*), 28.7 (*C*HMe$_2$), 53.7 (N*C*H$_2$*C*H$_2$N), 124.8 (Ar-*C*), 126.7 (Ar-*C*), 143.6 (Ar-*C*), 148.5 (Ar-*C*). ^{31}P{^{1}H} NMR (243 MHz, 298 K, C_6D_6, ppm): δ = -286.4. ^{11}B{^{1}H} NMR (192.6 MHz, 298 K, C_6D_6, ppm): δ = 38.3 (br). HRMS(m/z): $[M-Li]^-$ calcd. for $C_{29}H_{47}N_2BPSi$: 493.33447, found: 493.33469.

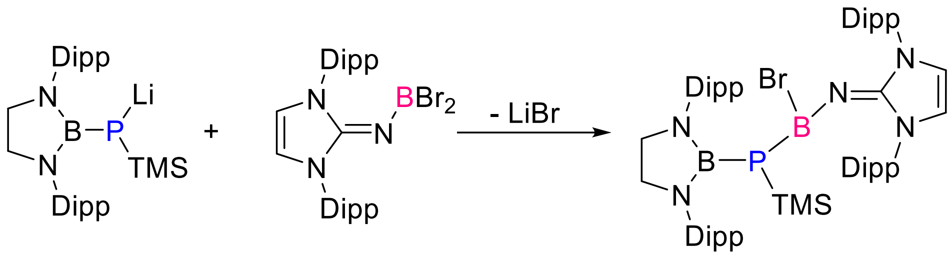


NHC=NSiMe$_3$ **3**

Scheme S1-2. Synthesis of **3**

Synthesis of 3 To a colorless solution of **NHC=NSiMe$_3$** (952 mg, 2 mmol) in toluene (20 mL) at -30 °C boron tribromide (1.0 M in methylene chloride, 2 ml, 2mmol) was added under stirring. The reaction solution was allowed to warm to room temperature and stirred for further 8 hours. After filtration through a pad of celite, the volatiles were removed through evaporation under vacuum. The residues were then washed with *n*-hexane (2 mL) and dried under vacuum to give a colorless solid **3** (974 mg, 85%). ^{1}H NMR (600 MHz, C_6D_6, 298 K, ppm): δ = 1.09 (d, $^{3}J_{HH}$ = 6.9 Hz, 12 H, CH*Me$_2$*), 1.44

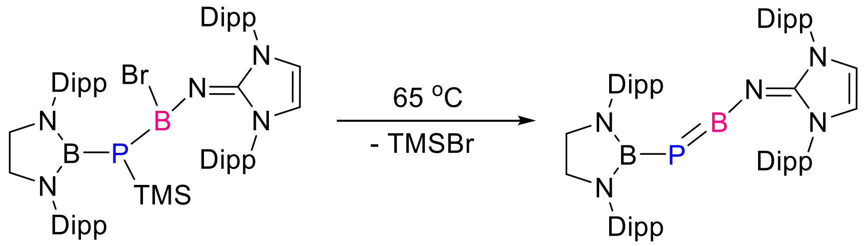
(d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH*Me*$_2$), 2.99 (sept, $^3J_{HH}$ = 6.9 Hz, 4 H, C*H*Me$_2$), 6.01 (s, 2 H, *H*C=C*H*), 7.06-7.19 (m, 6 H, Ar-*H*). ^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6, 298 K, ppm): δ = 23.6, 25.0, (CH*Me*$_2$), 29.2 (*C*HMe$_2$), 116.2 (H*C*=*C*H), 124.5 (Ar-*C*), 130.7 (Ar-*C*), 131.7 (Ar-*C*), 147.2 (Ar-*C*). ^{11}B{^{1}H} NMR (192.6 MHz, 298 K, C_6D_6, ppm): δ = 12.7 (br). HRMS(m/z): $[M+H]^+$ calcd. for $C_{27}H_{37}N_3B^{79}Br_2$: 572.1442, found: 572.1419; $C_{27}H_{37}N_3B^{79}Br^{81}Br$: 574.1421, found: 574.1401; $C_{27}H_{37}N_3B^{81}Br_2$: 576.1401, found: 576.1379.



2 **3** **4**

Scheme S1-3. Synthesis of **4**

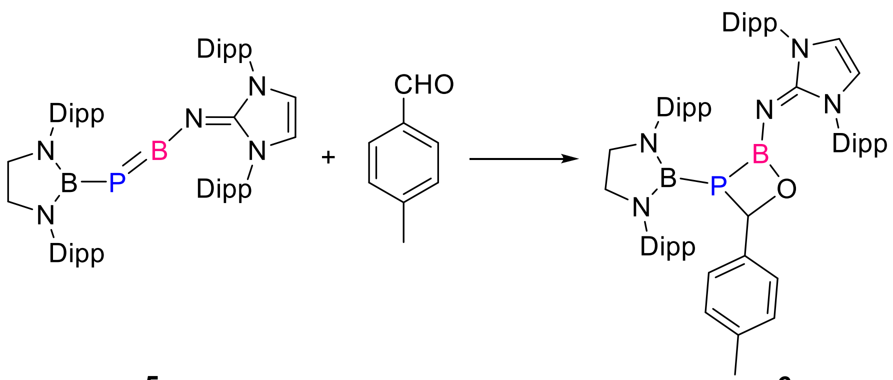
Synthesis of 4 To a solution of **2** (500 mg, 1 mmol) in toluene (5 mL) at -50 °C a pre-cooled (-50 °C) solution of **3** (573 mg, 1 mmol) was added with stirring. The reaction solution was then allowed to warm to room temperature and stirred for further two hours. After filtration through a pad of celite, the volatiles were removed through evaporation under vacuum. The residues were then washed with *n*-hexane (2 mL) and dried under vacuum to give a colorless solid **4** (809 mg, 82%). ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ = -0.07 (d, $^3J_{PH}$ = 5.5 Hz, 9 H, Si*Me*$_3$), 1.05 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 1.33 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 1.34 (d, $^3J_{HH}$ = 6.5 Hz, 12 H, CH*Me*$_2$), 3.10 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 3.59 (s, 4 H, NC*H*$_2$C*H*$_2$N), 3.74 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 6.00 (s, 2 H, *H*C=C*H*), 7.05-7.23 (m, 12 H, Ar-*H*). ^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6, 298 K, ppm): δ = 3.3 (d, $^2J_{PC}$ = 13.0 Hz, Si*Me*$_3$), 23.2, 24.3, 25.9, 27.5, (CH*Me*$_2$), 28.7 (*C*HMe$_2$), 28.8 (*C*HMe$_2$), 54.7 (N*C*H$_2$*C*H$_2$N), 116.3 (H*C*=*C*H), 124.1 (Ar-*C*), 124.3 (Ar-*C*), 126.3 (Ar-*C*), 128.3 (Ar-*C*), 130.1 (Ar-*C*), 133.4 (Ar-*C*), 142.2 (Ar-*C*), 130.1 (Ar-*C*), 147.0 (Ar-*C*), 147.4 (NH*C*=N). ^{31}P{^{1}H} NMR (243 MHz, 298 K, C_6D_6, ppm): δ = -193.7. ^{11}B{^{1}H} NMR (192.6 MHz, 298 K, C_6D_6, ppm): δ = 34.4 (br, NH*B*), 31.0 (br, PSiMe$_3$*B*Br). HRMS(m/z): $[M+H]^+$ calcd. for $C_{56}H_{84}N_5B_2{}^{79}BrPSi$: 986.5598, found: 986.5621; $C_{56}H_{84}N_5B_2{}^{81}BrPSi$: 988.5577, found: 988.5602. X-ray quality single-crystals of **4** were obtained by recrystallization from its saturated solution in *n*-hexane at -35 °C.



4 **5**

Scheme S1-4. Synthesis of **5**

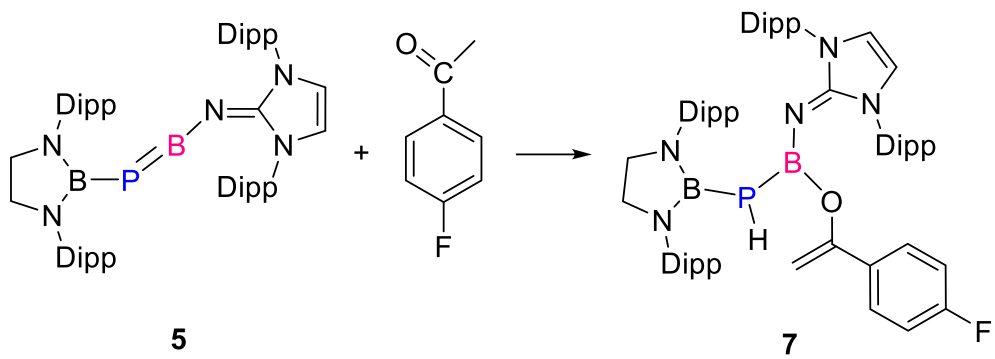
Synthesis of 5 A solution of **4** (49.3 mg, 0.05 mmol) in C_6D_6 (0.5 mL) was heated at 65 °C for 4 hours. The reaction solution was then allowed to cool to room temperature. After filtration through a pad of celite, the volatiles were removed through evaporation under vacuum. The residues were then washed with cold *n*-hexane (0.2 mL) and dried under vacuum to give a colorless solid **5** (36.7 mg, 88%). ^{1}H NMR (600 MHz, C_6D_6, 298 K, ppm): δ = 1.02 (d, $^{3}J_{HH}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 1.31 (d, $^{3}J_{HH}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 1.34 (d, $^{3}J_{HH}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 1.44 (d, $^{3}J_{HH}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 2.59 (sept, $^{3}J_{HH}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 3.53 (s, 4 H, NC*H*$_2$C*H*$_2$N), 3.64 (sept, $^{3}J_{HH}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 5.70 (s, 2 H, *H*C=C*H*), 6.85-7.16 (m, 12 H, Ar-*H*). ^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6, 298 K, ppm): δ = 23.9, 24.2, 25.3, (CH*Me*$_2$), 28.6 (*C*HMe$_2$), 29.1 (*C*HMe$_2$), 53.8 (N*C*H$_2$*C*H$_2$N), 116.1 (H*C*=*C*H), 126.2 (Ar-*C*), 128.3 (Ar-*C*), 130.9 (Ar-*C*), 131.8 (Ar-*C*), 141.5 (Ar-*C*), 142.3 (Ar-*C*), 147.0 (Ar-*C*), 148.0 (NH*C*=N). ^{31}P{^{1}H} NMR (243 MHz, 298 K, C_6D_6, ppm): δ = -291.9. ^{11}B{^{1}H} NMR (192.6 MHz, 298 K, C_6D_6, ppm): δ = 38.6 (br, NH*B*), 53.0 (br, P=*B*). HRMS(m/z): $[M+H]^+$ calcd. for $C_{53}H_{75}N_5B_2P$: 834.5941, found: 834.5928. X-ray quality single-crystals of **5** were obtained by recrystallization from its saturated toluene solution layered with *n*-hexane at -35 °C.



5 **6**

Scheme S1-5. Reactivity of **5** towards aldehyde.

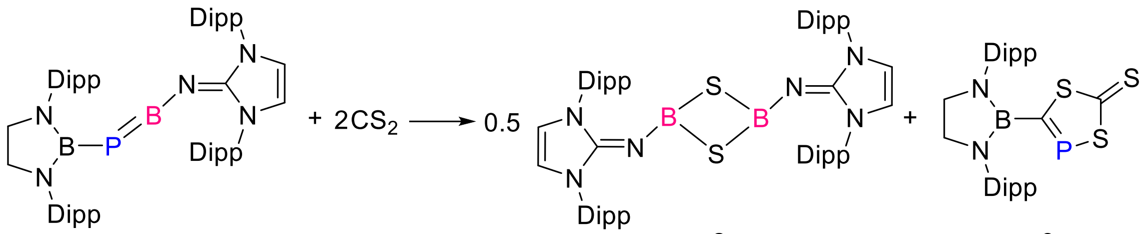
Synthesis of 6 To a solution of **5** (41.7 mg, 0.05 mmol) in toluene (1 mL) at -50 °C a pre-cooled (-50 °C) solution of *p*-methyl benzaldehyde (6 mg, 0.05 mmol) was added in toluene (1 mL) with stirring. The reaction solution was then allowed to warm to room temperature and stirred for further 12 hours. After filtration through a pad of celite, the volatiles were removed through evaporation under vacuum. The residues were then washed with *n*-hexane (0.2 mL) and dried under vacuum to give a colorless solid **6** (42.9 mg, 90%). ^{1}H NMR (600 MHz, C_6D_6, 298 K, ppm): δ = 0.91 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH*Me*$_2$), 1.08 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH*Me*$_2$), 1.12 (d, $^3J_{HH}$ = 6.6 Hz, 6 H, CH*Me*$_2$), 1.12 (d, $^3J_{HH}$ = 6.6 Hz, 6 H, CH*Me*$_2$), 1.23 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH*Me*$_2$), 1.25 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH*Me*$_2$), 1.27 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH*Me*$_2$), 1.37 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH*Me*$_2$), 2.20 (s, 3 H, Ar-*Me*), 2.96 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H, C*H*Me$_2$), 3.01 (sept, $^3J_{HH}$ = 6.9 Hz, 2 H, C*H*Me$_2$), 3.40 (m, 2 H, NCH$_2$C*H*$_2$N), 3.47 (sept, $^3J_{HH}$ = 6.9 Hz, 2 H, C*H*Me$_2$), 3.56 (m, 2 H, NCH$_2$C*H*$_2$N), 3.66 (sept, $^3J_{HH}$ = 6.9 Hz, 4 H, C*H*Me$_2$), 4.84 (d, $^2J_{PH}$ = 3.1 Hz, 1 H, PC*H*O), 5.85 (s, 2 H, *H*C=C*H*), 6.17 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, MeC$_6$*H*$_4$CHO), 6.83 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, MeC$_6$*H*$_4$CHO), 7.04-7.26 (m, 12 H, Ar-*H*). ^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6, 298 K, ppm): δ = 21.9, 24.1, 24.3, 24.6, 24.6, 24.8, 25.3, 25.4, 25.6, (CH*Me*$_2$), 27.2 (Ar-*Me*), 29.1 (*C*HMe$_2$), 29.3 (*C*HMe$_2$), 29.4 (*C*HMe$_2$), 29.5 (*C*HMe$_2$), 55.2 (N*C*H$_2$*C*H$_2$N), 68.9 (d, $^1J_{PC}$=6.3 Hz), 115.7 (H*C*=*C*H), 124.7 (Ar-*C*), 124.9 (Ar-*C*), 125.0 (Ar-*C*), 125.3 (Ar-*C*), 127.3 (Ar-*C*), 128.9 (Ar-*C*), 129.0 (Ar-*C*), 129.1 (Ar-*C*), 130.2 (Ar-*C*), 134.5 (Ar-*C*), 16.2 (Ar-*C*), 141.8 (Ar-*C*), 148.1 (Ar-*C*), 148.1 (Ar-*C*), 148.3 (Ar-*C*), 148.5 (NH*C*=N). ^{31}P{^{1}H} NMR (243 MHz, 298 K, C_6D_6, ppm): δ = -89.6. ^{11}B{^{1}H} NMR (192.6 MHz, 298 K, C_6D_6, ppm): δ = 33.9 (br, NH*B*), P=*B not observed*. HRMS(m/z): [M+H]$^+$ calcd. for $C_{61}H_{83}ON_5B_2P$: 954.6516, found: 954.6529. X-ray quality single-crystals of **6** were obtained by recrystallization from its saturated solution in toluene at -35 °C.



Scheme S1-6. Reactivity of **5** towards ketone.

Synthesis of 7 To a solution of **5** (41.7 mg, 0.05 mmol) in toluene (1 mL) at -50 °C a pre-cooled (-50 °C) solution of *p*-fluoroacetophenone (6.9 mg, 0.05 mmol) was added in toluene (1 mL) with stirring. The reaction solution was then allowed to warm to room temperature and stirred for further four days. After filtration through a pad of celite, the solution was concentrated to 0.3 mL and kept in a refrigerator at -35 °C overnight to obtain colorless crystals of **7** which were collected by filtration and dried under vacuum. (32.9 mg, 68%). ^{1}H NMR (600 MHz, C_6D_6, 298 K, ppm): δ = 0.71 (d, $^1J_{PH}$ = 212.3 Hz, 1 H, P*H*), 1.01 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 1.04 (d, $^3J_{HH}$ = 6.8 Hz, 24 H, CH*Me*$_2$), 1.17 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 3.01 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 3.58 (s, 4 H, NCH$_2$C*H*$_2$N), 3.67 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 4.77 (s, 1 H, C=C*H*$_2$), 4.81

(s, 1 H, C=CH_2), 5.97 (s, 2 H, *H*C=C*H*), 6.82-7.60 (m, 16 H, Ar-*H* and C_6H_4). $^{13}C\{^1H\}$ NMR (150.9 MHz, C_6D_6, 298 K, ppm): δ = 23.0, 24.6, 25.9, 25.9, 28.2, 28.6, (CH*Me*$_2$ and *C*HMe$_2$), 54.4 (N*C*H$_2$*C*H$_2$N), 94.8 (C=*C*H$_2$), 114.7 (d, $^3J_{PC}$ = 21.0 Hz), 115.8 (H*C*=*C*H), 124.1 (Ar-*C*), 124.2 (Ar-*C*), 126.6 (Ar-*C*), 127.6 (Ar-*C*), 129.8 (Ar-*C*), 133.4 (Ar-*C*), 141.4 (Ar-*C*), 147.4 (Ar-*C*), 148.1 (NH*C*=N), 155.1, 162.9 (d, $^1J_{FC}$ = 244.9 Hz, Ar-*C*-F). $^{31}P\{^1H\}$ NMR (243 MHz, 298 K, C_6D_6, ppm): δ = -233.4. ^{31}P NMR (243 MHz, 298 K, C_6D_6, ppm): δ = -233.4 (d, $^1J_{PH}$ = 212.3 Hz). $^{19}F\{^1H\}$ NMR (564.7 MHz, 298 K, C_6D_6, ppm): δ = -115.5. $^{11}B\{^1H\}$ NMR (192.6 MHz, 298 K, C_6D_6, ppm): δ = 37.1 (br, NH*B*), 27.5 (br, P-*B*-O). HRMS(m/z): $[M+H]^+$ calcd. for $C_{61}H_{82}ON_5B_2FP$: 972.6422, found: 972.6416.



Scheme S1-7. Reactivity of **5** towards carbon disulfide.

Synthesis of 8 and 9 To a solution of **5** (41.7 mg, 0.05 mmol) in toluene (1 mL) at room temperature excess carbon disulfide (10 µL) was added. The reaction solution was stood without disturbance for overnight. After filtration through a pad of celite, the volatiles were removed through evaporation under vacuum. The residues were then extracted with *n*-hexane and then the solution was concentrated to 0.5 mL and kept in a refrigerator at -35 °C overnight to obtain colorless crystals of **8** (16.2 mg, 73%) which were collected by filtration and dried under vacuum. The filtrate was further concentrated to 0.2 mL and kept in a refrigerator at -35 °C overnight toobtain another small amounts of colorless crystals of **8**. The mother solution was vacuumed to give orange residues which was further extracted with *n*-pentane (0.5 mL), and the resulting solution was concentrated to 0.1 mL and kept in a refrigerator at -35 °C 2 days to obtained light yellow crystals of **9** (17.8 mg, 66%). For **8**: ^1H NMR (600 MHz, C_6D_6, 298 K, ppm): δ = 1.15 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CH*Me*$_2$), 1.34 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CH*Me*$_2$), 3.03 (sept, $^3J_{HH}$ = 6.6 Hz, 4 H, C*H*Me$_2$), 5.91 (s, 2 H, *H*C=C*H*), 7.07-7.24 (m, 6 H, Ar-*H*). $^{13}C\{^1H\}$ NMR (150.9 MHz, C_6D_6, 298 K, ppm): δ = 23.9, 24.5, (CH*Me*$_2$), 29.1 (*C*HMe$_2$), 114.8 (H*C*=*C*H), 124.1 (Ar-*C*), 129.9 (Ar-*C*), 133.1 (Ar-*C*), 143.3 (Ar-*C*), 147.7 (NH*C*=N). $^{11}B\{^1H\}$ NMR (192.6 MHz, 298 K, C_6D_6, ppm): δ = 34.9 (br, =N*B*S). HRMS(m/z): $[M+H]^+$ calcd. for $C_{54}H_{73}N_6B_2S_2$: 891.5519, found: 891.5520.; For **9**: ^1H NMR (600 MHz, C_6D_6, 298 K, ppm): δ = 1.19 (d, $^3J_{HH}$ = 7.0 Hz, 12 H, CH*Me*$_2$), 1.21 (d, $^3J_{HH}$ = 7.0 Hz, 12 H, CH*Me*$_2$), 3.41 (sept, $^3J_{HH}$ = 7.0 Hz, 4 H, C*H*Me$_2$), 3.47 (s, 4 H, NC*H*$_2$C*H*$_2$N), 7.06-7.19 (m, 6 H, Ar-*H*). $^{13}C\{^1H\}$ NMR (150.9 MHz, C_6D_6, 298 K, ppm): δ = 24.1, 25.7, (CH*Me*$_2$), 28.7 (*C*HMe$_2$), 53.7 (N*C*H$_2$*C*H$_2$N), 124.8 (Ar-*C*), 128.3 (Ar-*C*), 128.4 (Ar-*C*), 138.8 (Ar-*C*), 147.4 (Ar-*C*), 224.1 (d, $^2J_{PC}$=4.8 Hz, *C*=S). $^{31}P\{^1H\}$ NMR (243 MHz, 298 K, C_6D_6, ppm): δ = 309.9. $^{11}B\{^1H\}$ NMR (192.6

MHz, 298 K, C_6D_6, ppm): δ = 28.0 (br). HRMS(m/z): $[M+H]^+$ calcd. for $C_{28}H_{39}N_2BPS_3$: 541.2101, found: 541.2098.

II. NMR Spectra

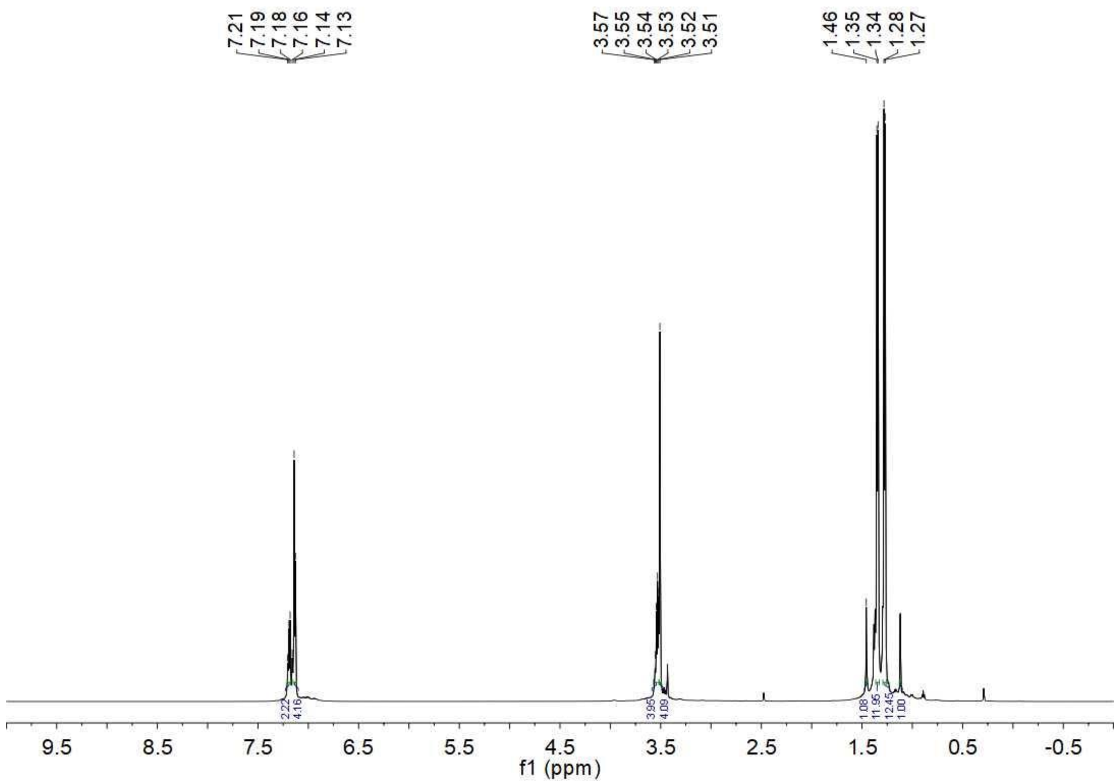


Figure S2-1. ^{1}H NMR Spectrum of **1** (600 MHz, C_6D_6, 298 K).

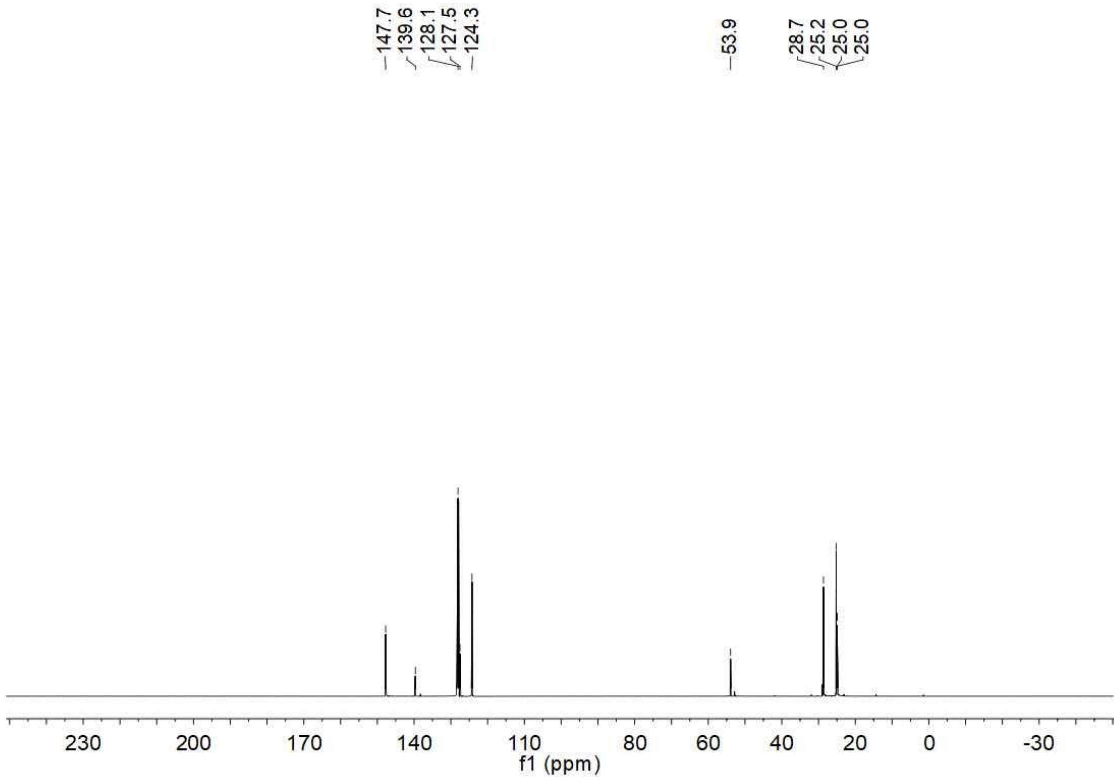


Figure S2-2. $^{13}C\{^{1}H\}$ NMR Spectrum of **1** (150.9 MHz, C_6D_6, 298 K).

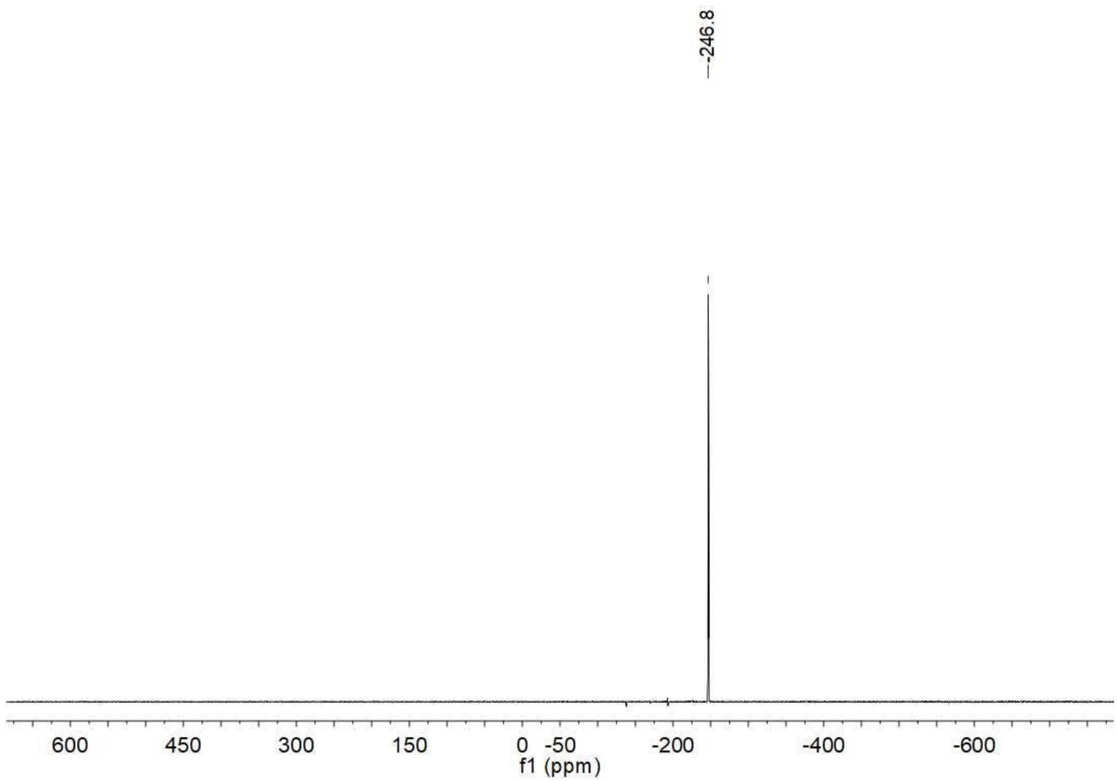


Figure S2-3. $^{31}P\{^{1}H\}$ NMR Spectrum of **1** (243 MHz, C_6D_6, 298 K).

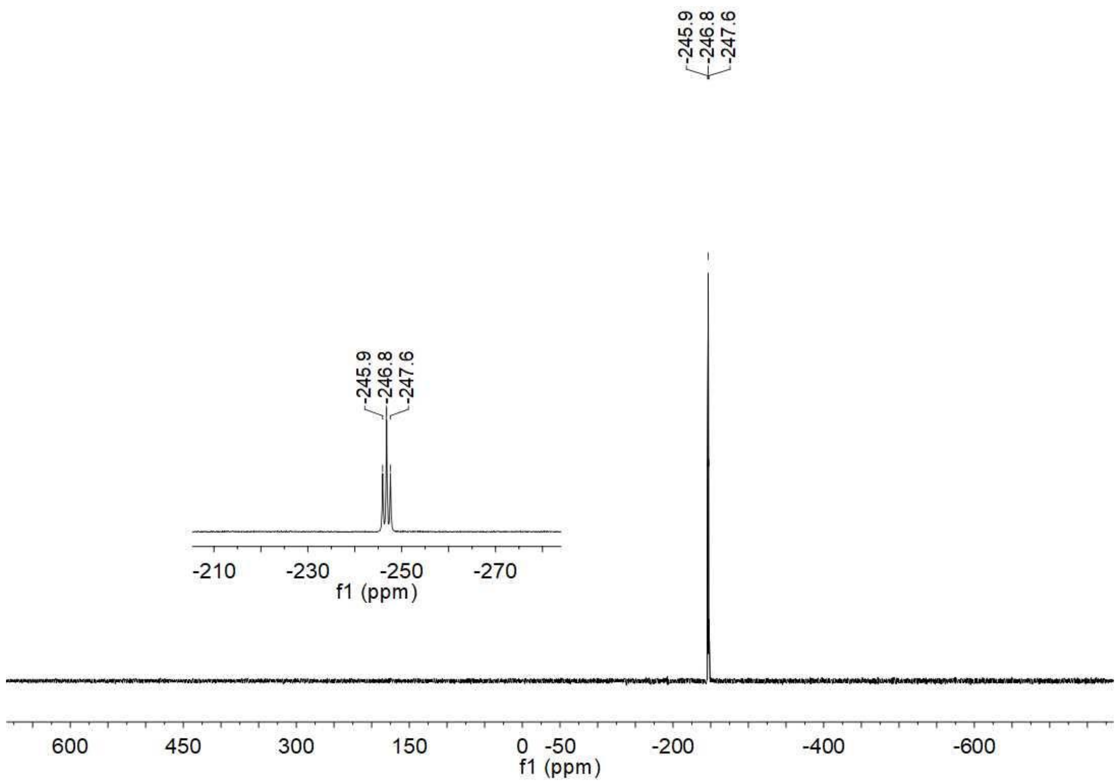


Figure S2-4. ^{31}P NMR Spectrum of **1** (243 MHz, C_6D_6, 298 K).

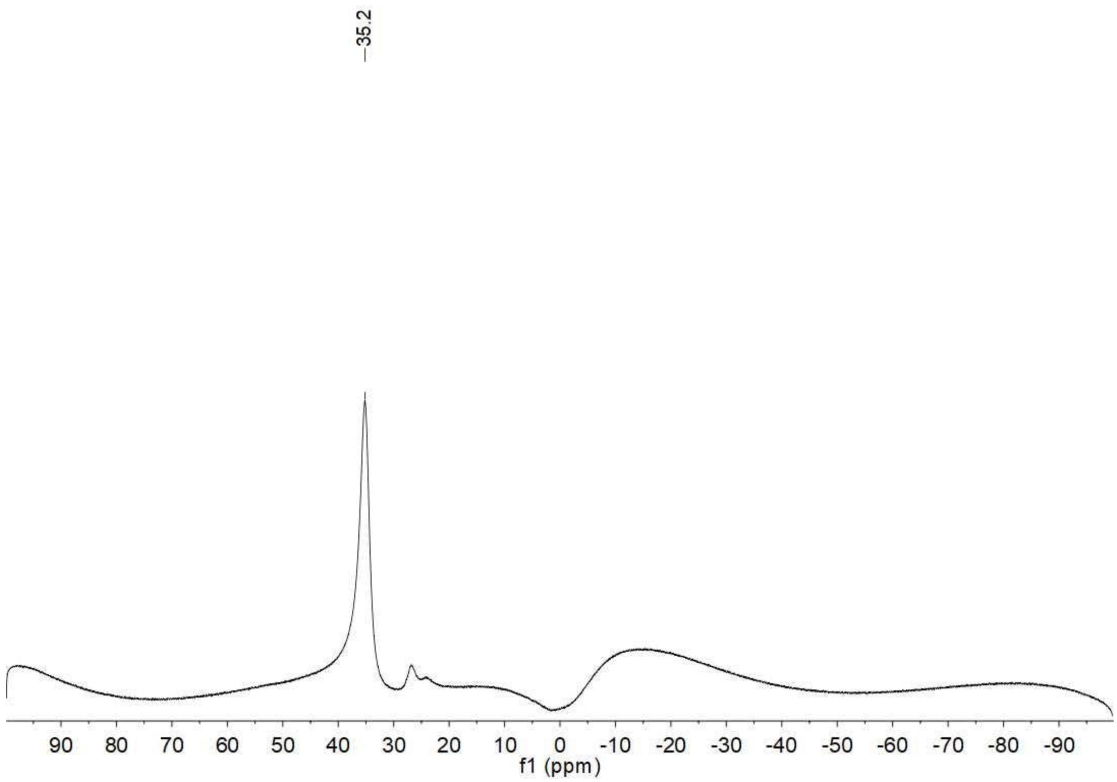


Figure S2-5a. $^{11}B\{^{1}H\}$ NMR Spectrum of **1** (192.6 MHz, C_6D_6, 298 K).

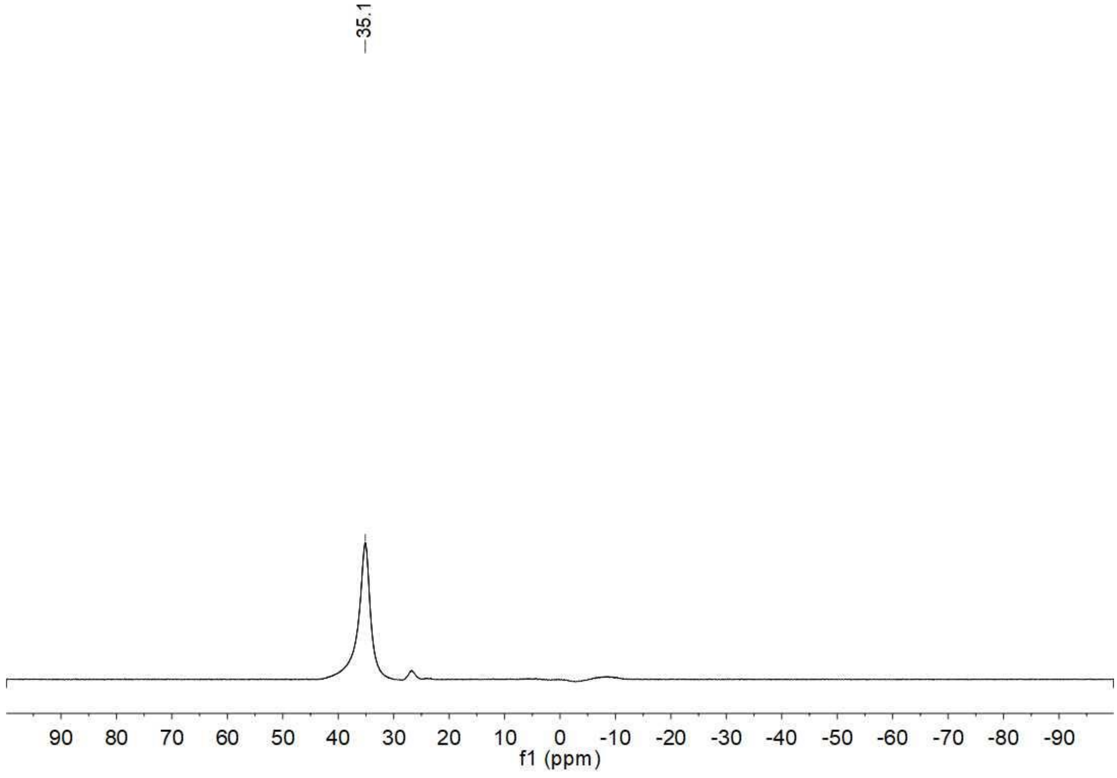


Figure S2-5b. $^{11}B\{^{1}H\}$ NMR Spectrum of **1** (baseline corrected) (192.6 MHz, C_6D_6, 298 K).

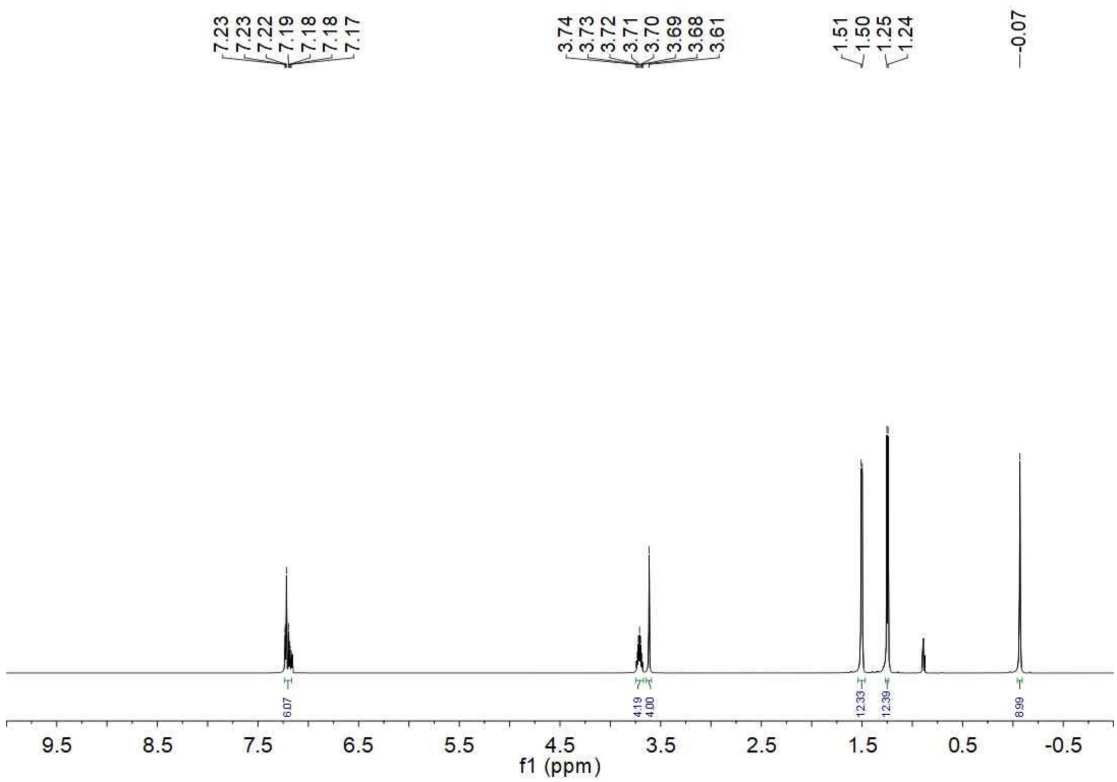


Figure S2-6. ^{1}H NMR Spectrum of **2** (600 MHz, C_6D_6, 298 K).

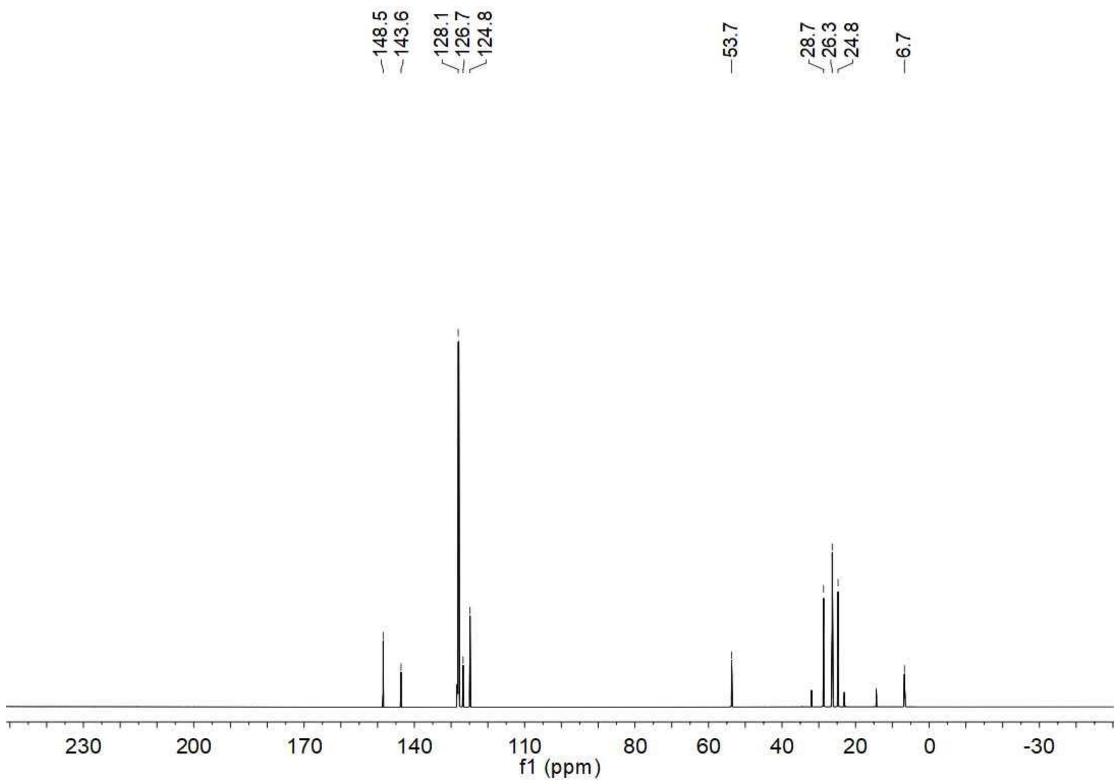


Figure S2-7. $^{13}C\{^{1}H\}$ NMR Spectrum of **2** (150.9 MHz, C_6D_6, 298 K).

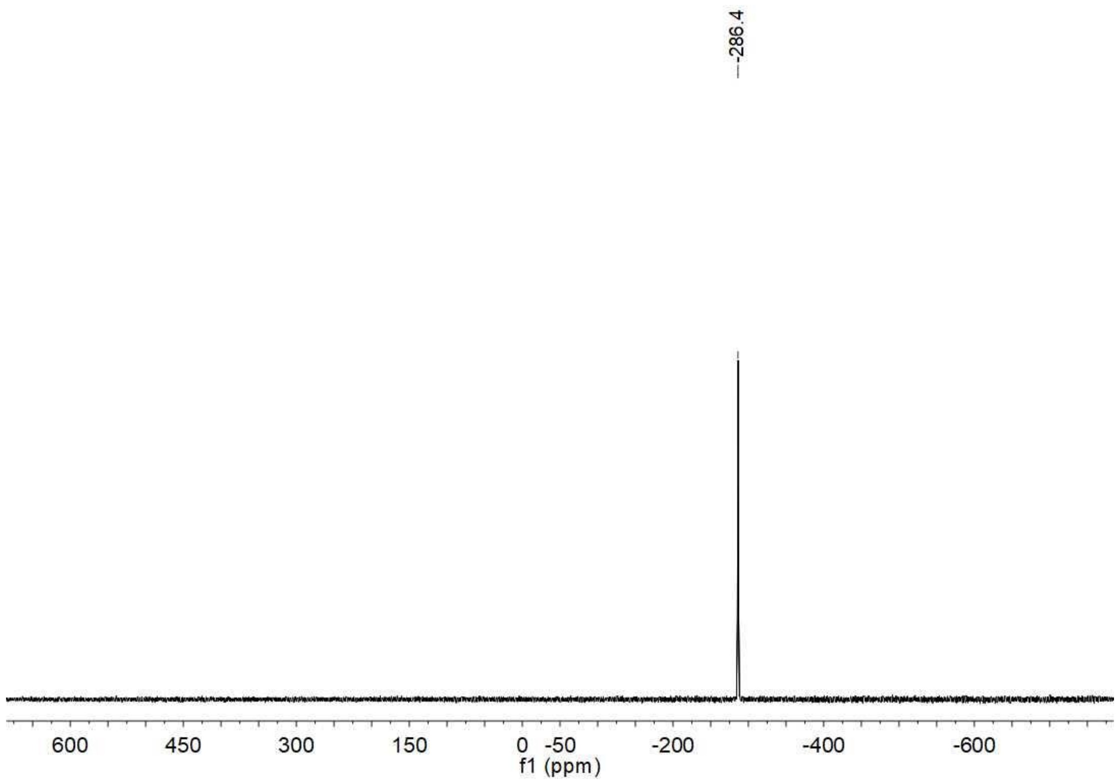


Figure S2-8. $^{31}P\{^{1}H\}$ NMR Spectrum of **2** (243 MHz, C_6D_6, 298 K).

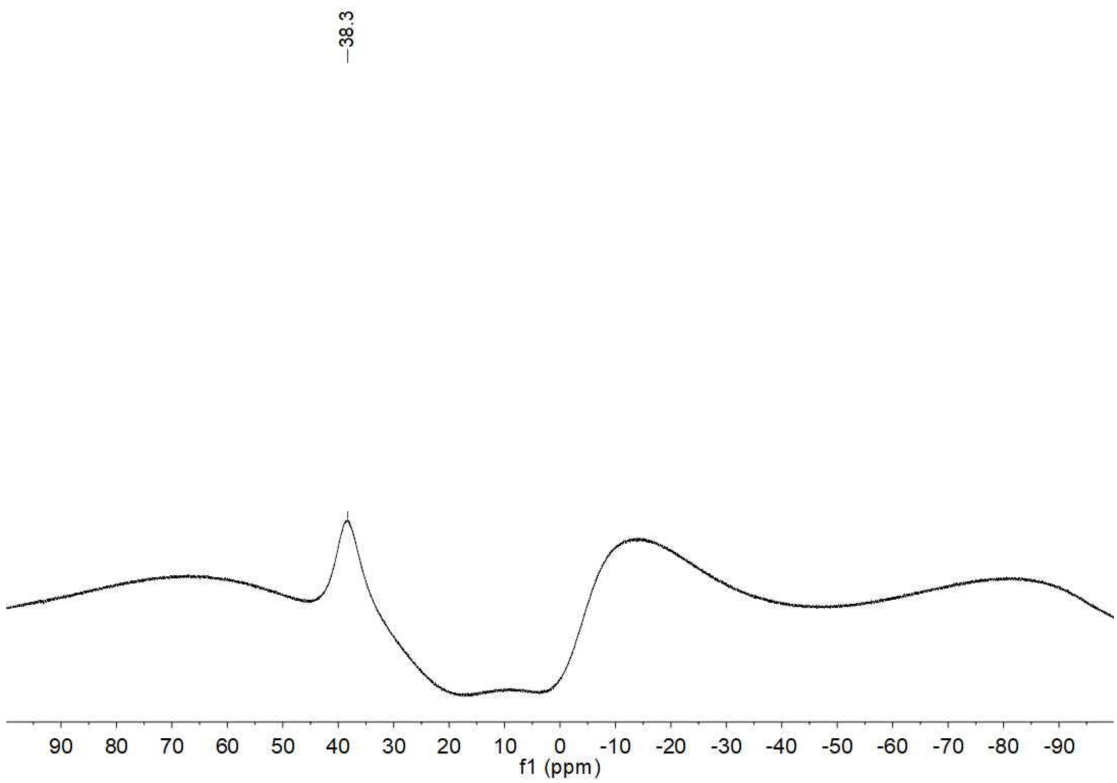


Figure S2-9a. $^{11}B\{^{1}H\}$ NMR Spectrum of **2** (192.6 MHz, C_6D_6, 298 K).

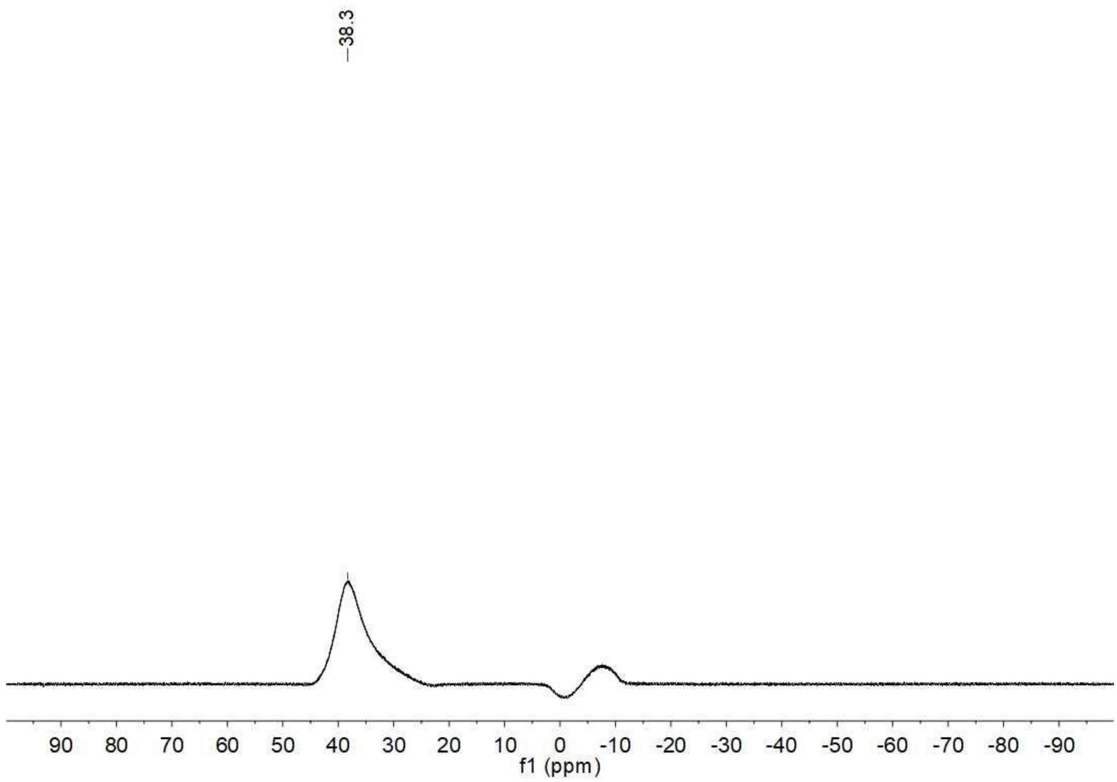


Figure S2-9b. $^{11}B\{^1H\}$ NMR Spectrum of **2** (baseline corrected) (192.6 MHz, C_6D_6, 298 K).

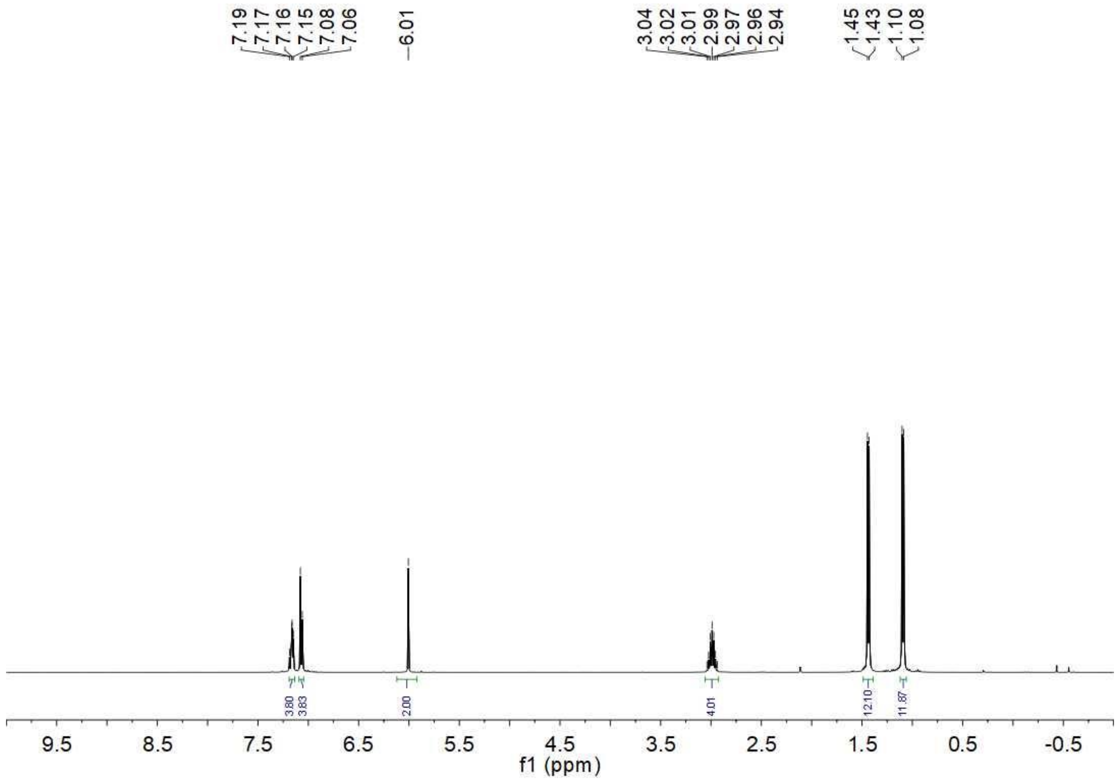


Figure S2-10. ^1H NMR Spectrum of **3** (600 MHz, C_6D_6, 298 K).

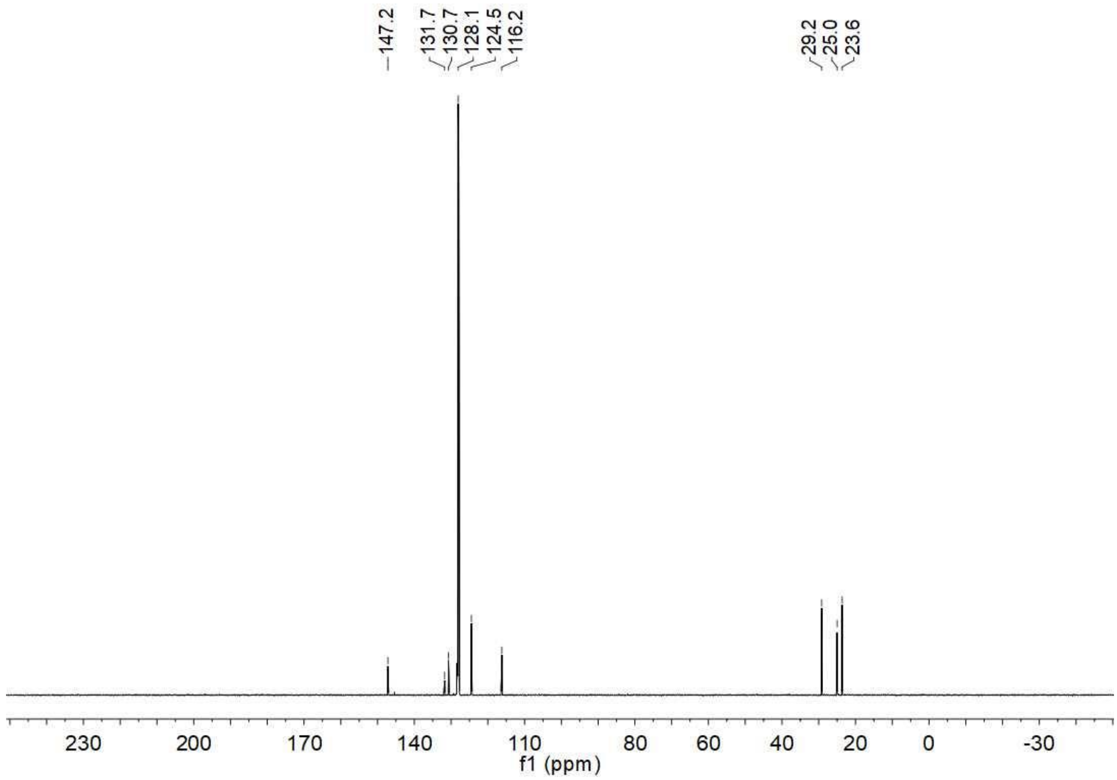


Figure S2-11. $^{13}C\{^{1}H\}$ NMR Spectrum of **3** (150.9 MHz, C_6D_6, 298 K).

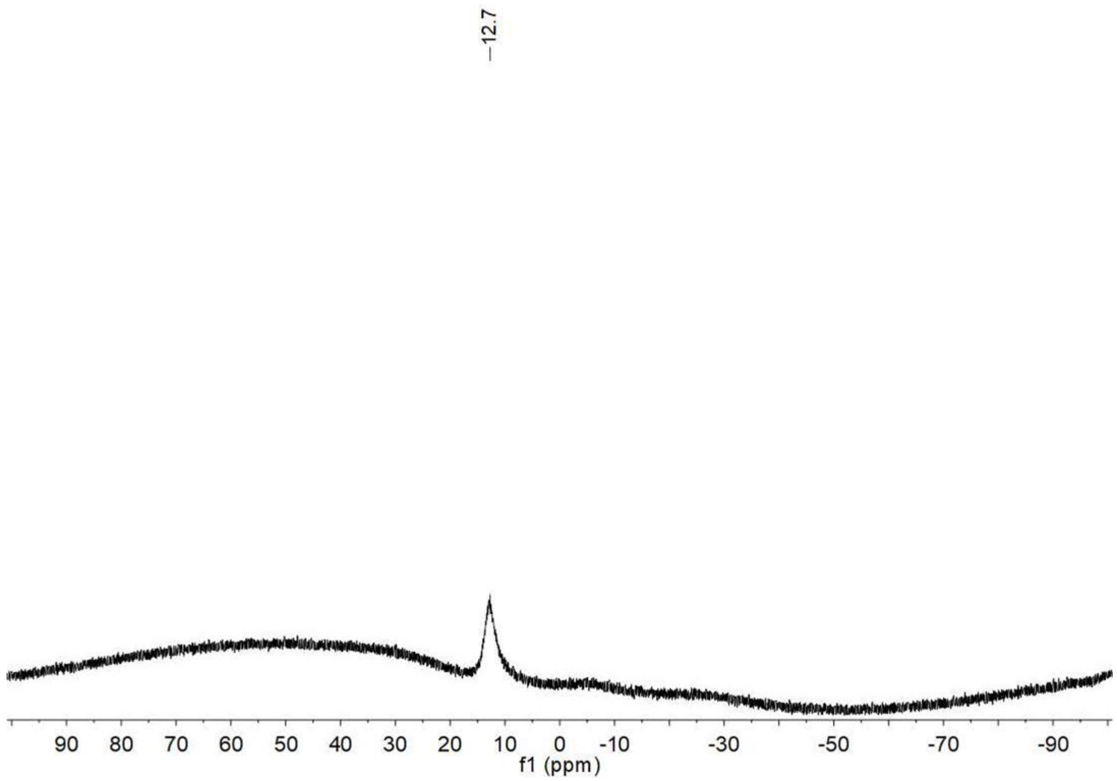


Figure S2-12a. $^{11}B\{^{1}H\}$ NMR Spectrum of **3** (192.6 MHz, C_6D_6, 298 K).

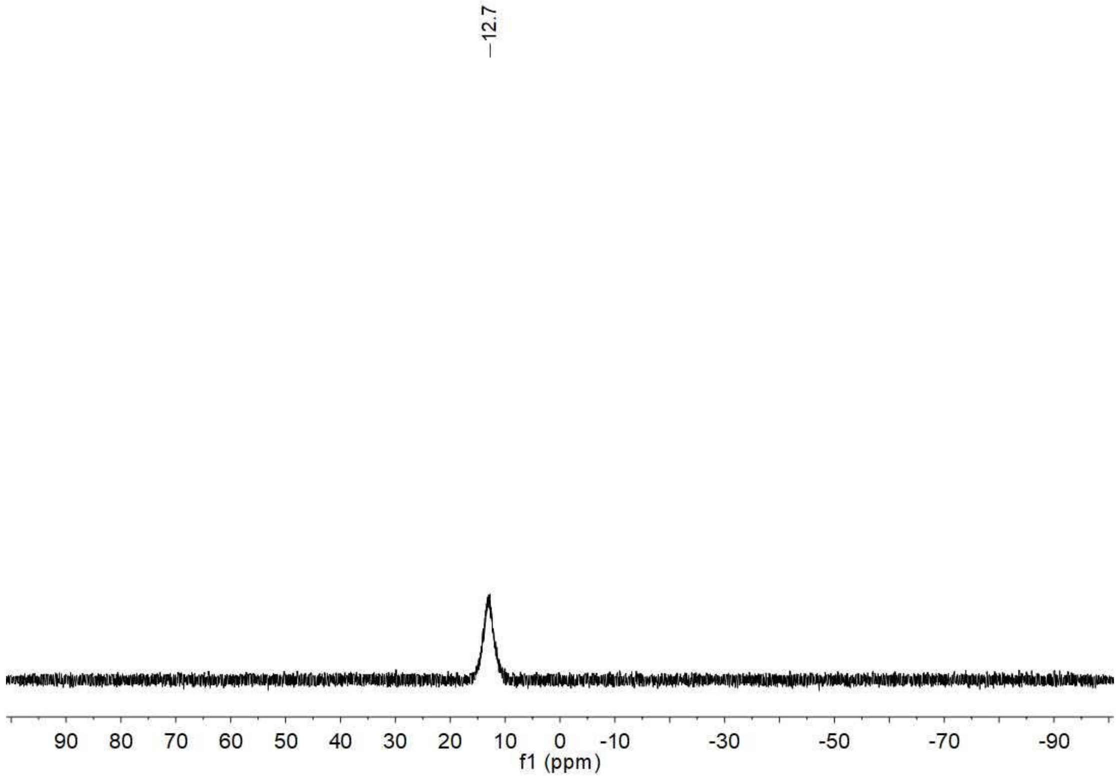


Figure S2-12b. $^{11}B\{^{1}H\}$ NMR Spectrum of **3** (baseline corrected) (192.6 MHz, C_6D_6, 298 K).

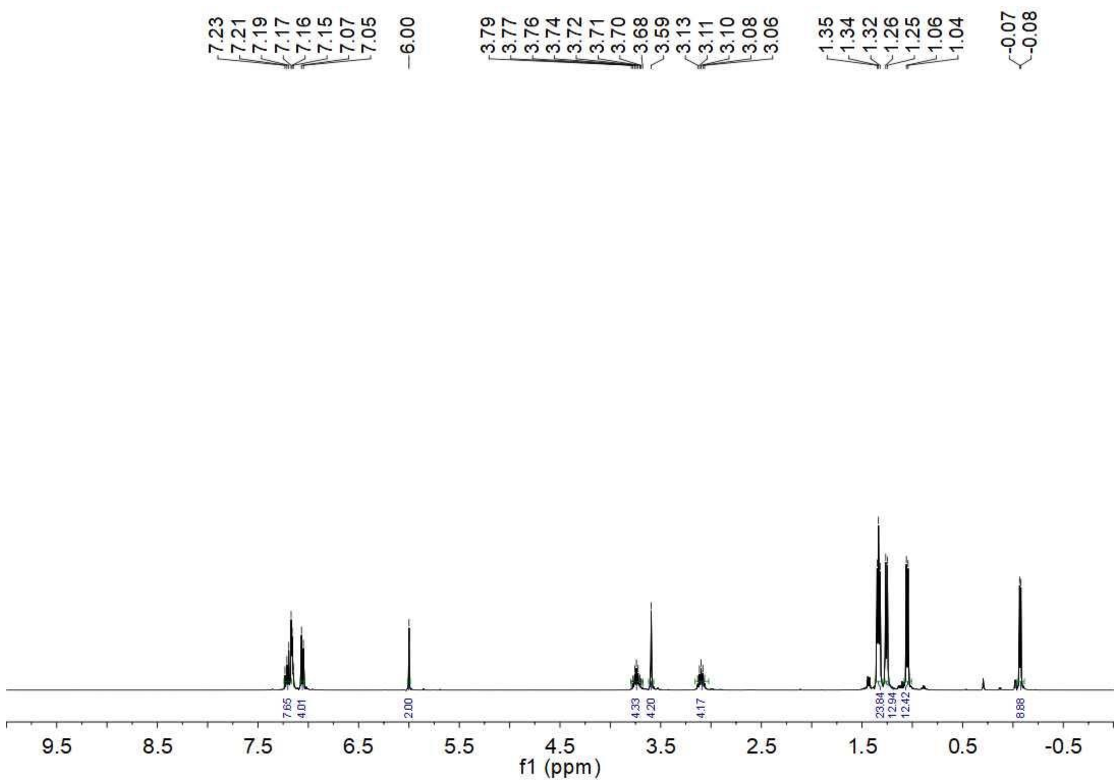


Figure S2-13. ^{1}H NMR Spectrum of **4** (400 MHz, C_6D_6, 298 K).

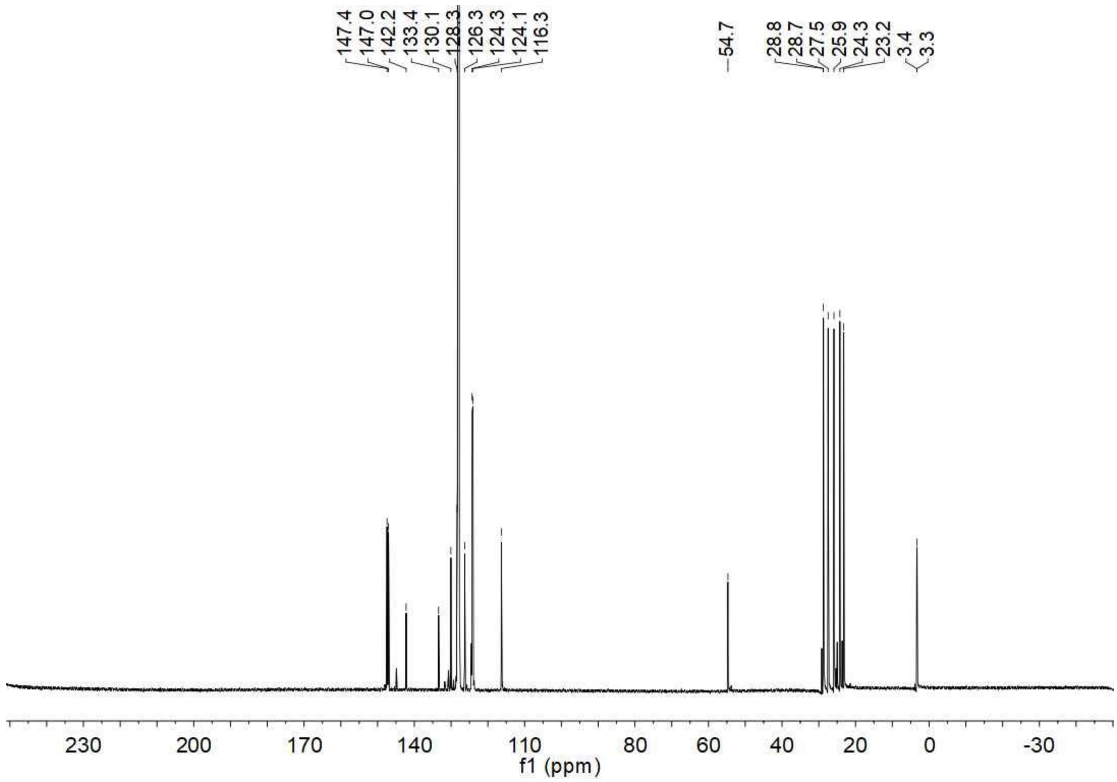


Figure S2-14. $^{13}C\{^1H\}$ NMR Spectrum of **4** (150.9 MHz, C_6D_6, 298 K).

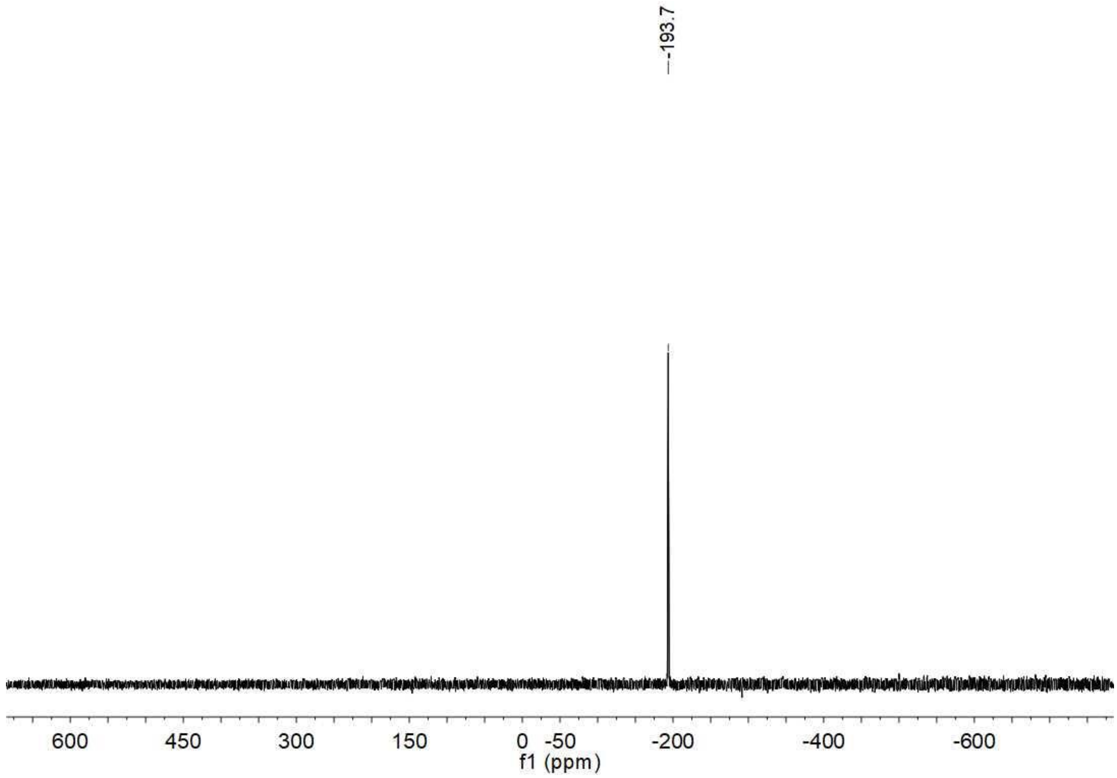


Figure S2-15. $^{31}P\{^1H\}$ NMR Spectrum of **4** (243 MHz, C_6D_6, 298 K).

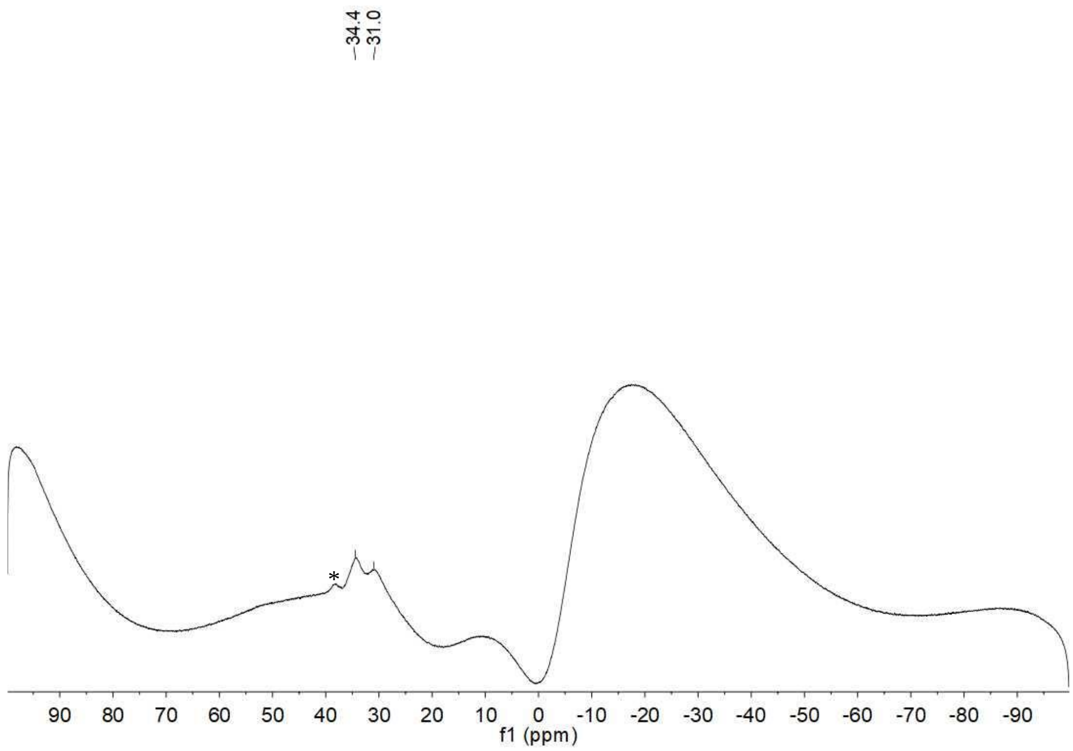


Figure S2-16a. $^{11}B\{^{1}H\}$ NMR Spectrum of **4** (192.6 MHz, *n*-hexane, 298 K) (* marks signals attributed to the N-heteroboryl of **5** generated from spontaneous $ClSiMe_3$-elimination of **4** during the data collection).

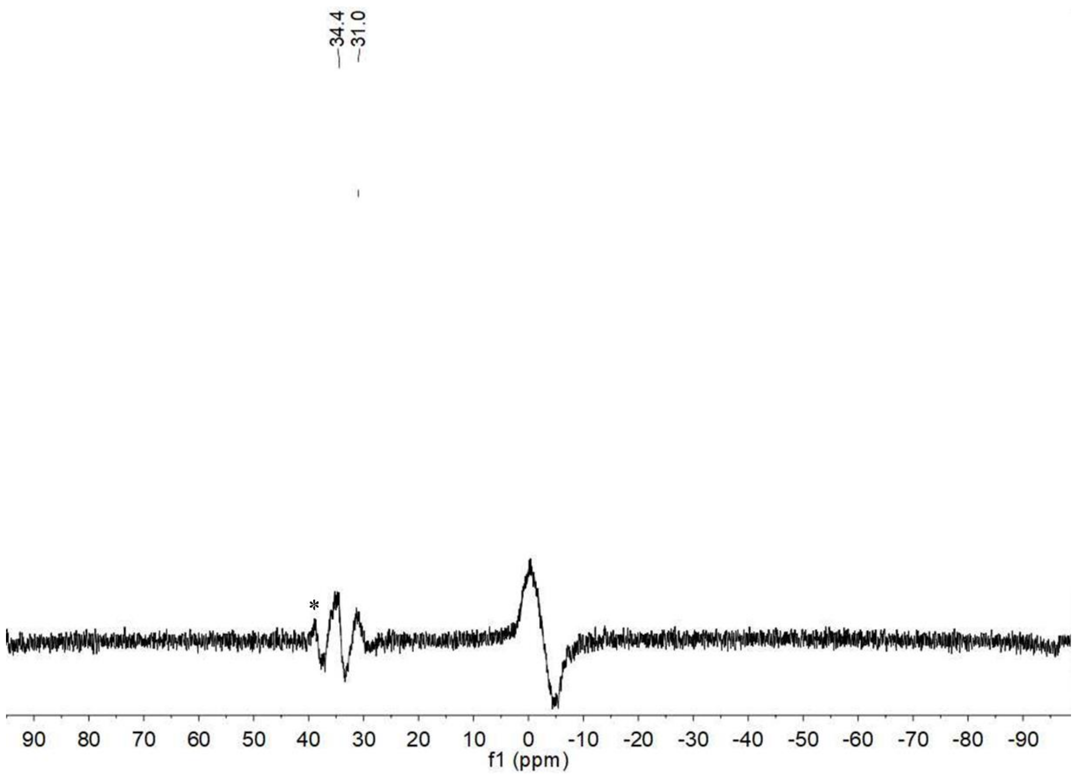


Figure S2-16b. $^{11}B\{^{1}H\}$ NMR Spectrum of **4** (baseline corrected) (192.6 MHz, *n*-hexane, 298 K) (* marks signals attributed to the N-heteroboryl of **5** generated from spontaneous $ClSiMe_3$-elimination of **4** during the data collection).

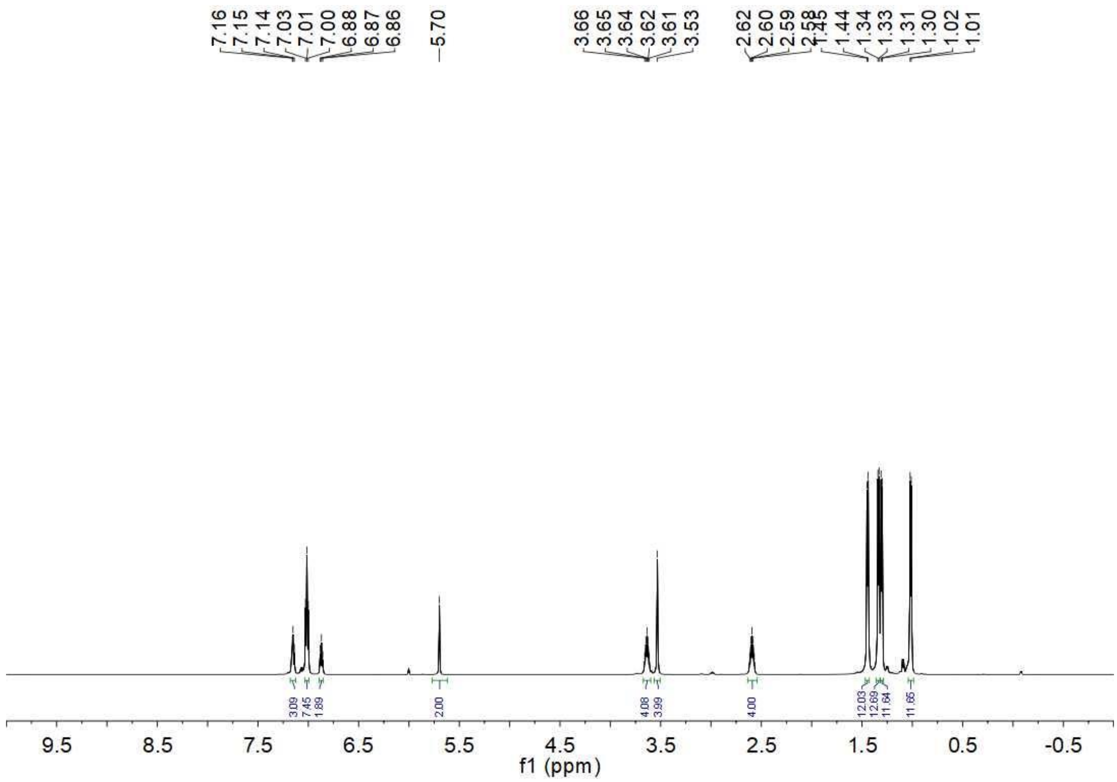


Figure S2-17. ^{1}H NMR Spectrum of **5** (600 MHz, C_6D_6, 298 K).

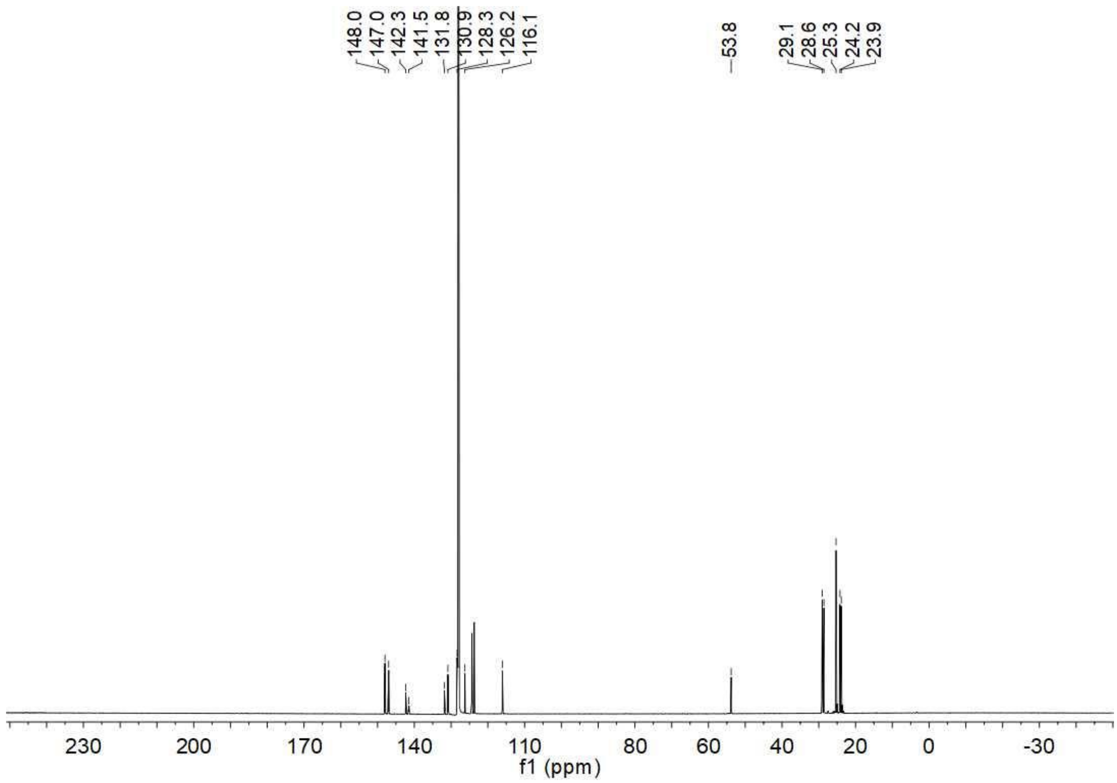


Figure S2-18. $^{13}C\{^{1}H\}$ NMR Spectrum of **5** (150.9 MHz, C_6D_6, 298 K).

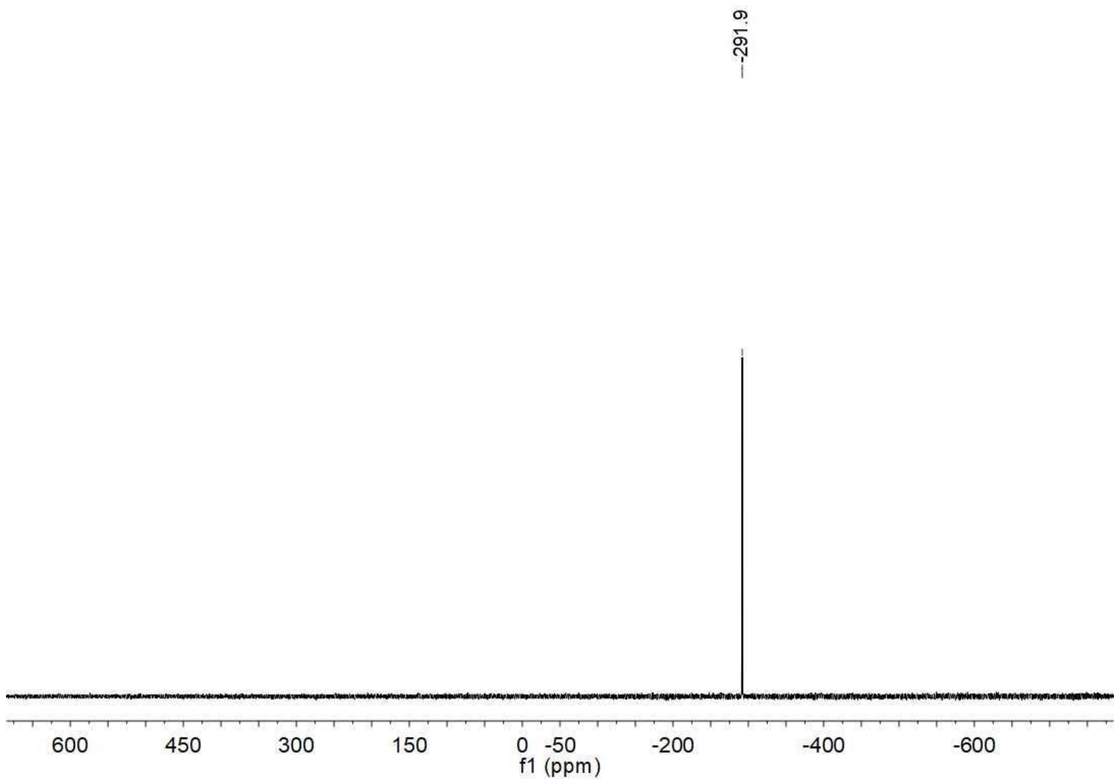


Figure S2-19. $^{31}P\{^{1}H\}$ NMR Spectrum of **5** (243 MHz, C_6D_6, 298 K).

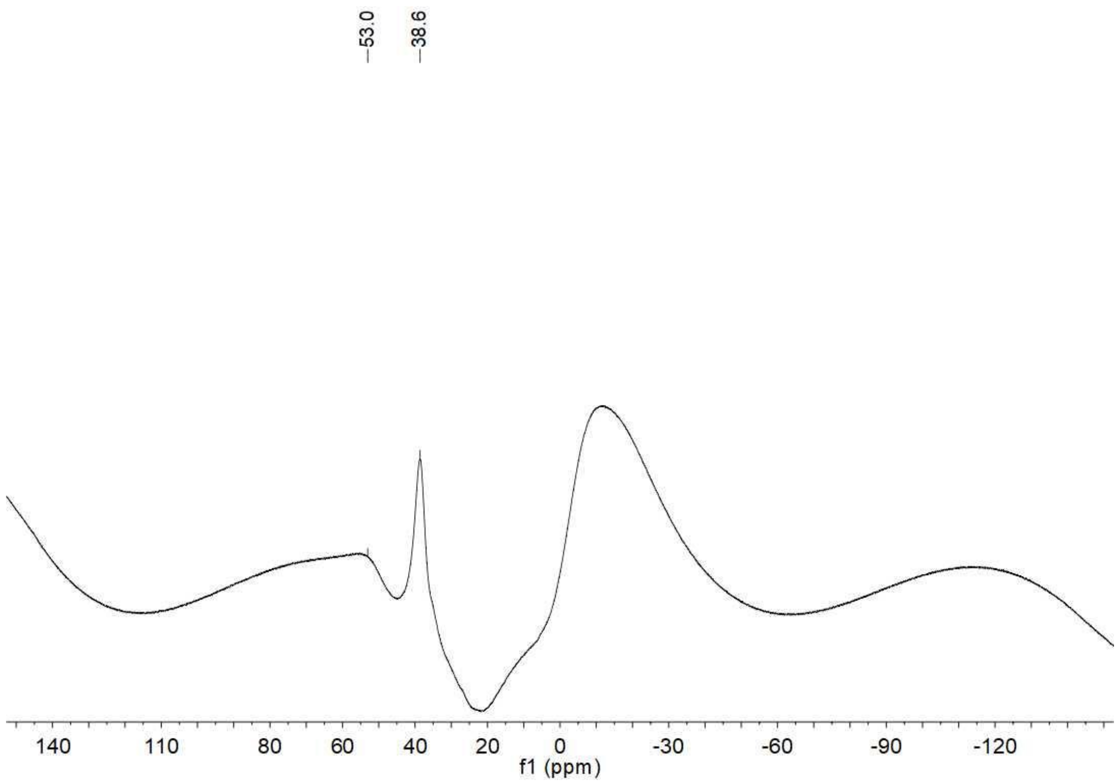


Figure S2-20a. $^{11}B\{^{1}H\}$ NMR Spectrum of **5** (192.6 MHz, C_6D_6, 298 K).

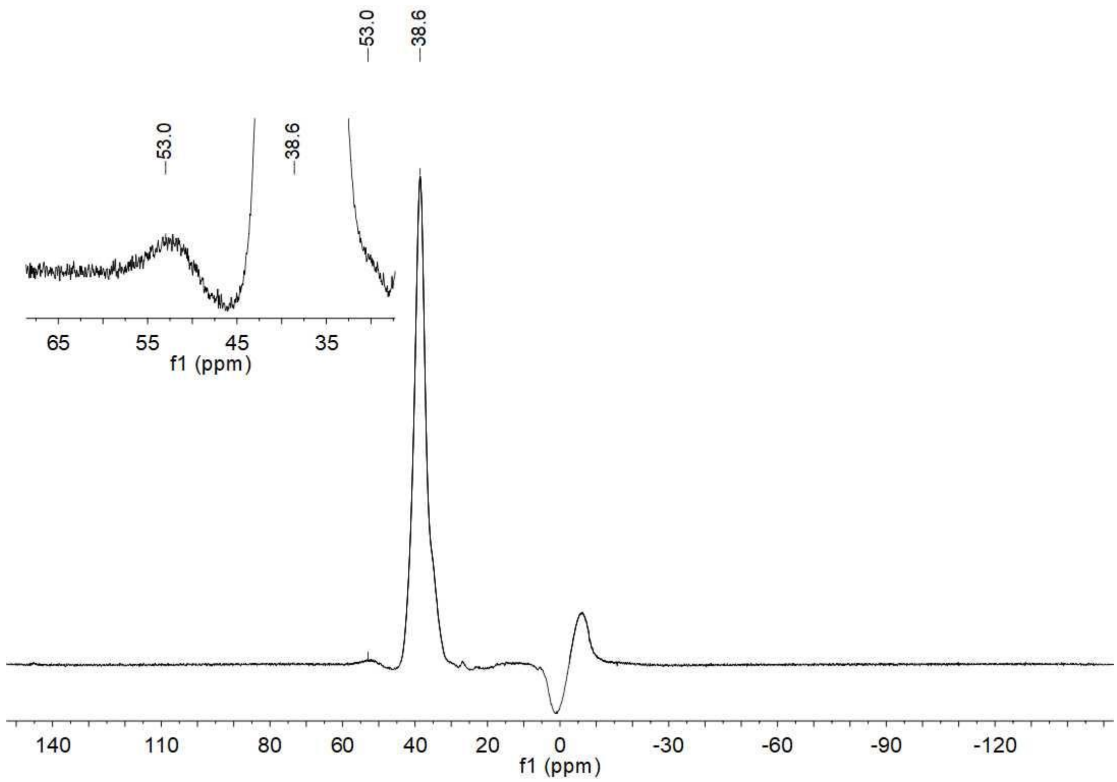


Figure S2-20b. $^{11}B\{^1H\}$ NMR Spectrum of **5** (baseline corrected) (192.6 MHz, C_6D_6, 298 K).

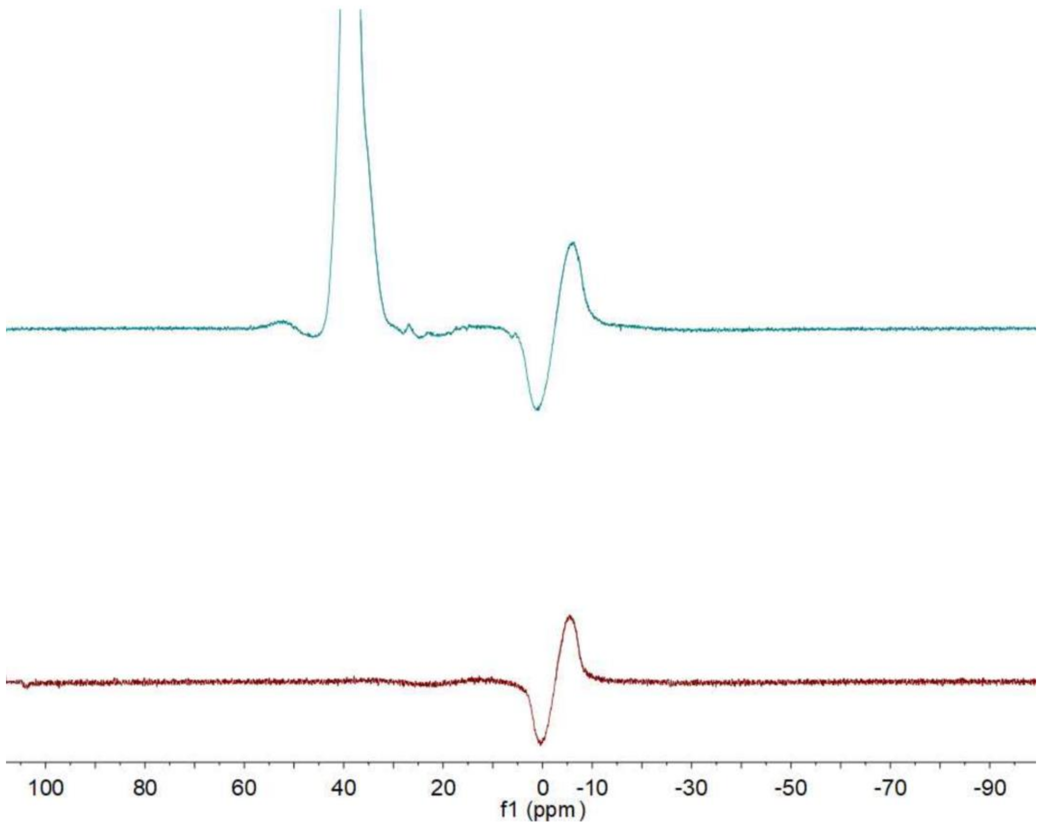


Figure S2-20c. Overlay $^{11}B\{^1H\}$ NMR Spectra of **5** (C_6D_6, in blue-green) and blank sample (pure C_6D_6, in red) (baseline corrected) (192.6 MHz, 298 K).

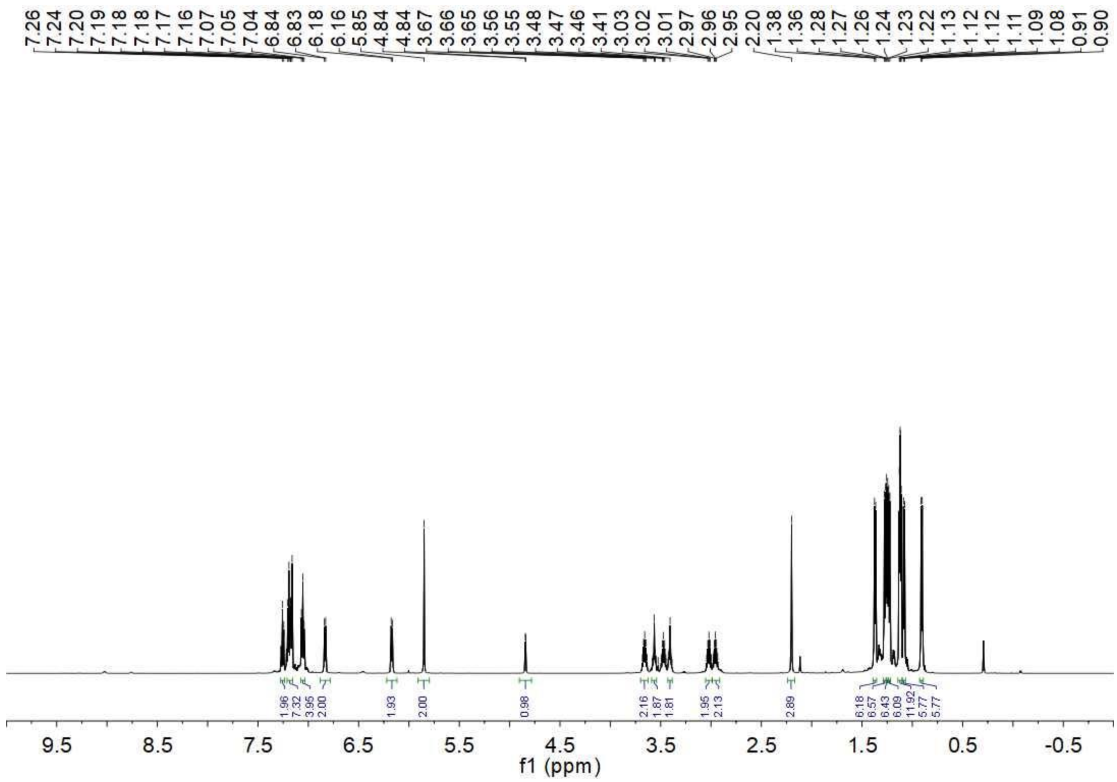


Figure S2-21. ^{1}H NMR Spectrum of **6** (600 MHz, C_6D_6, 298 K).

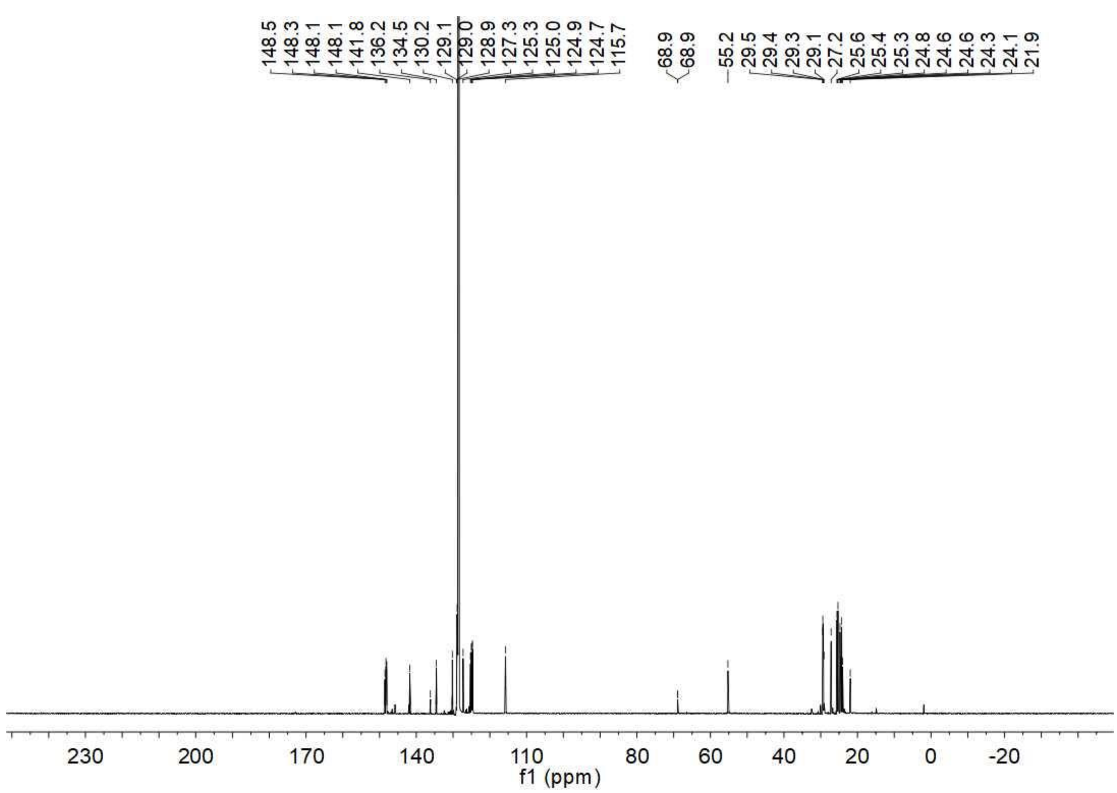


Figure S2-22. $^{13}C\{^{1}H\}$ NMR Spectrum of **6** (150.9 MHz, C_6D_6, 298 K).

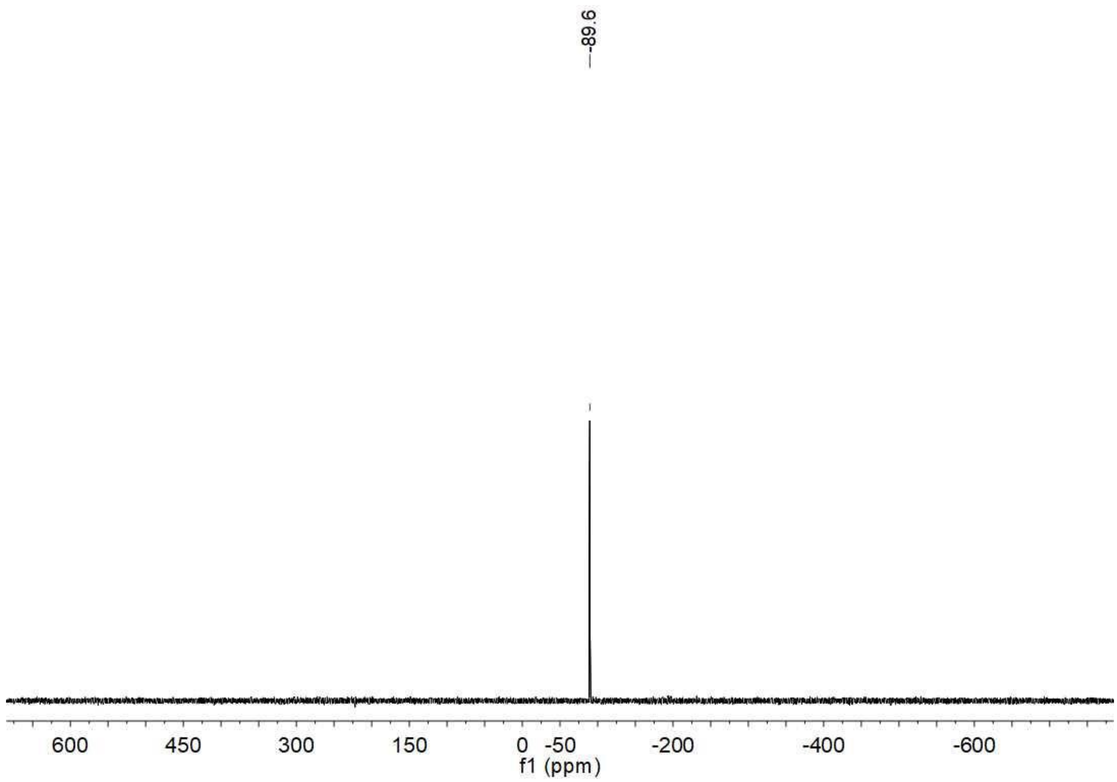


Figure S2-23. $^{31}P\{^{1}H\}$ NMR Spectrum of **6** (243 MHz, C_6D_6, 298 K).

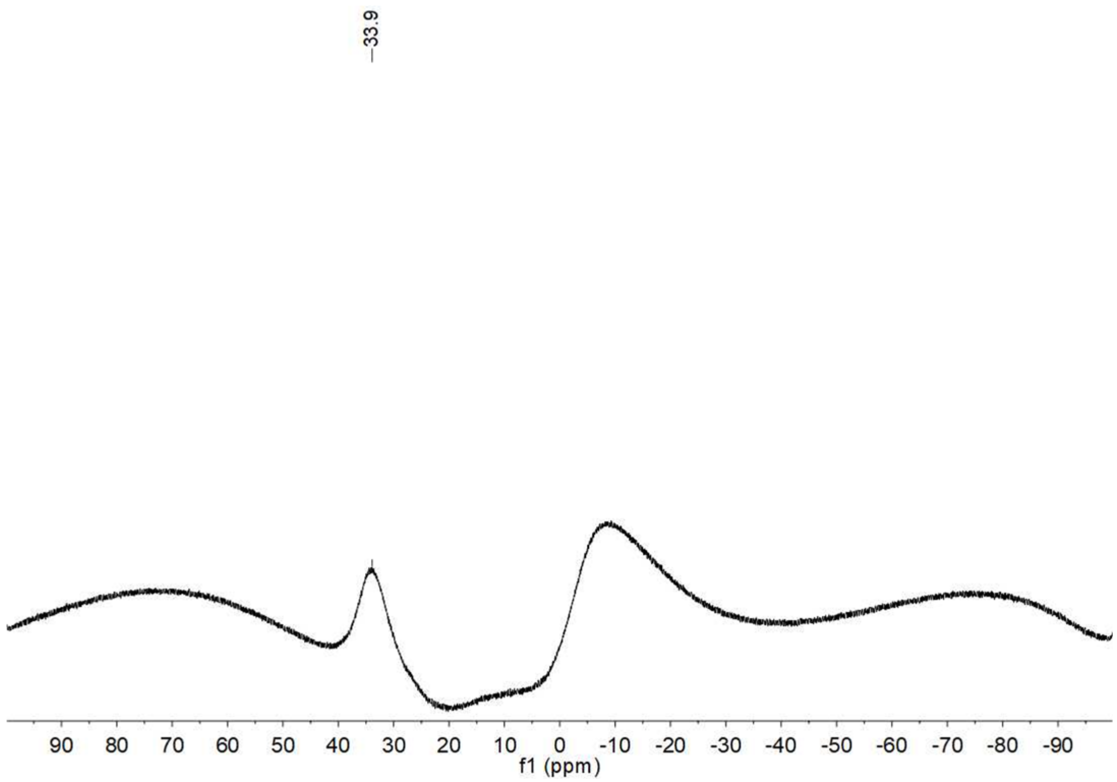


Figure S2-24a. $^{11}B\{^{1}H\}$ NMR Spectrum of **6** (192.6 MHz, C_6D_6, 298 K).

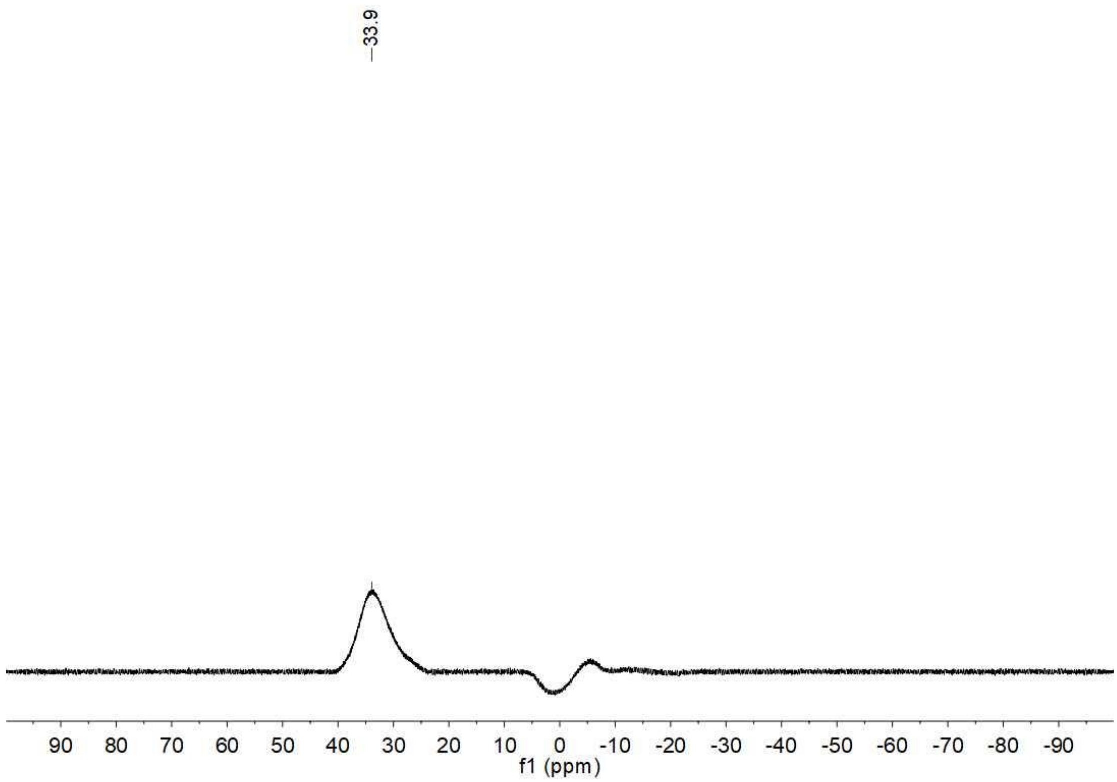


Figure S2-24b. $^{11}B\{^1H\}$ NMR Spectrum of **6** (baseline corrected) (192.6 MHz, C_6D_6, 298 K).

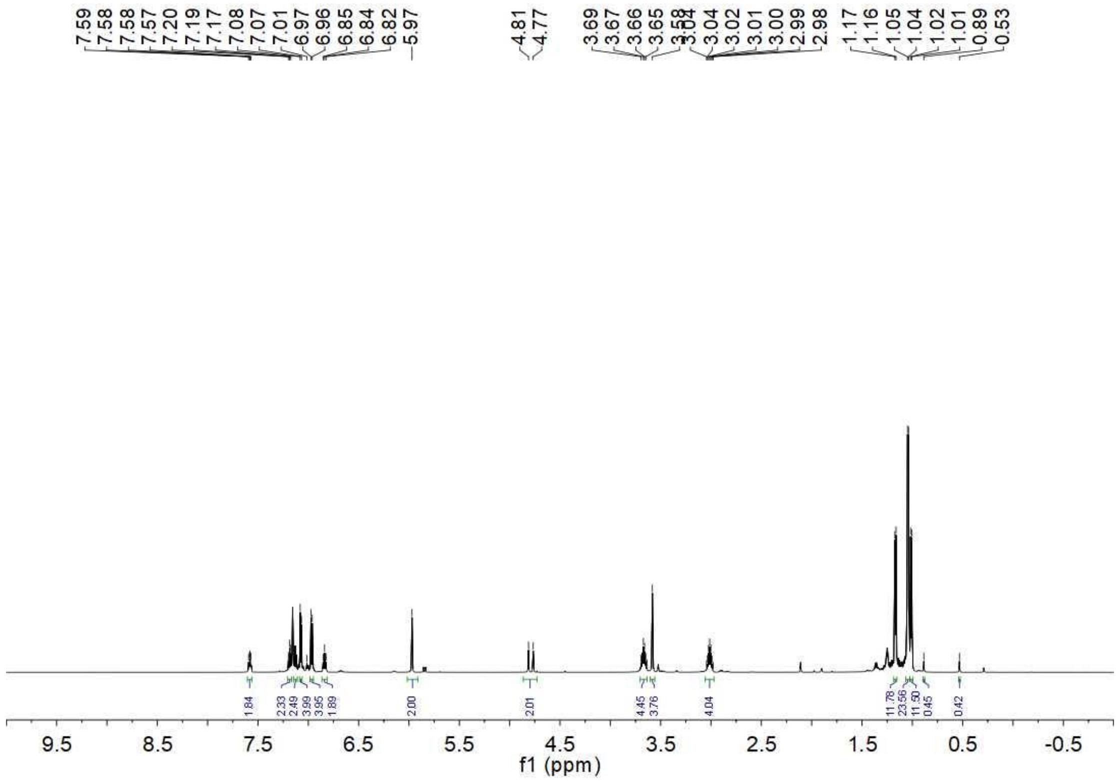


Figure S2-25. ^1H NMR Spectrum of **7** (600 MHz, C_6D_6, 298 K).

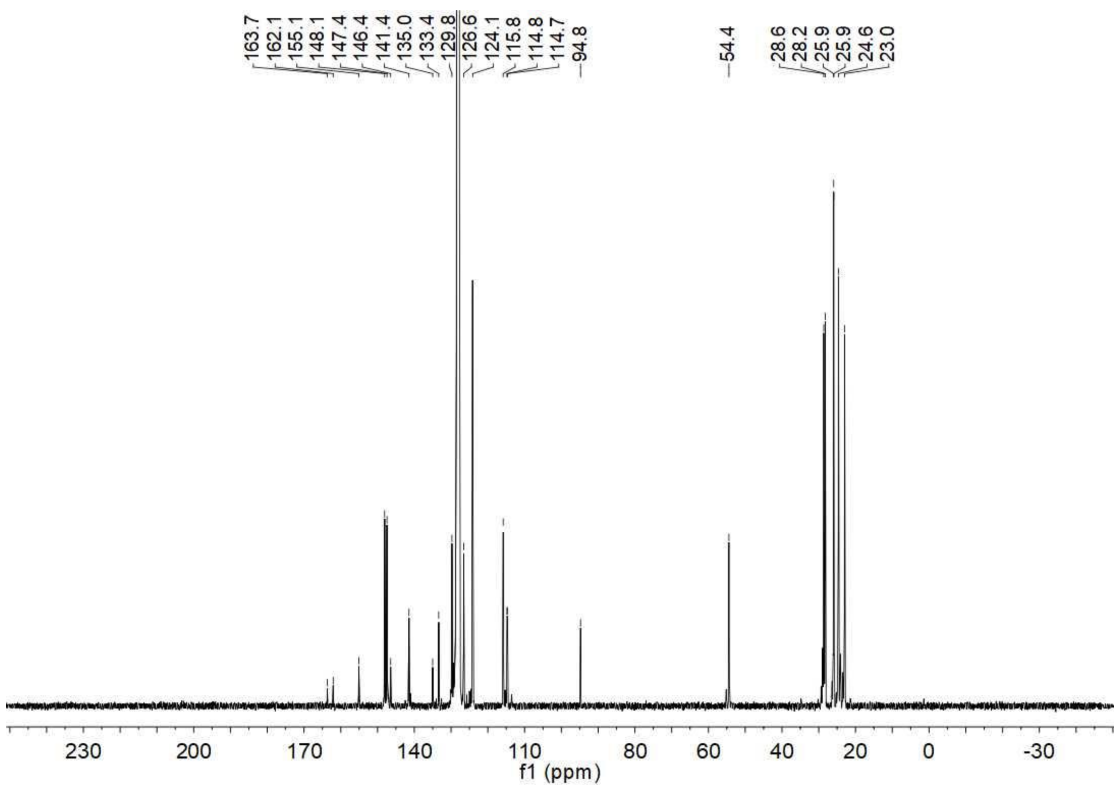


Figure S2-26. $^{13}C\{^{1}H\}$ NMR Spectrum of **7** (150.9 MHz, C_6D_6, 298 K).

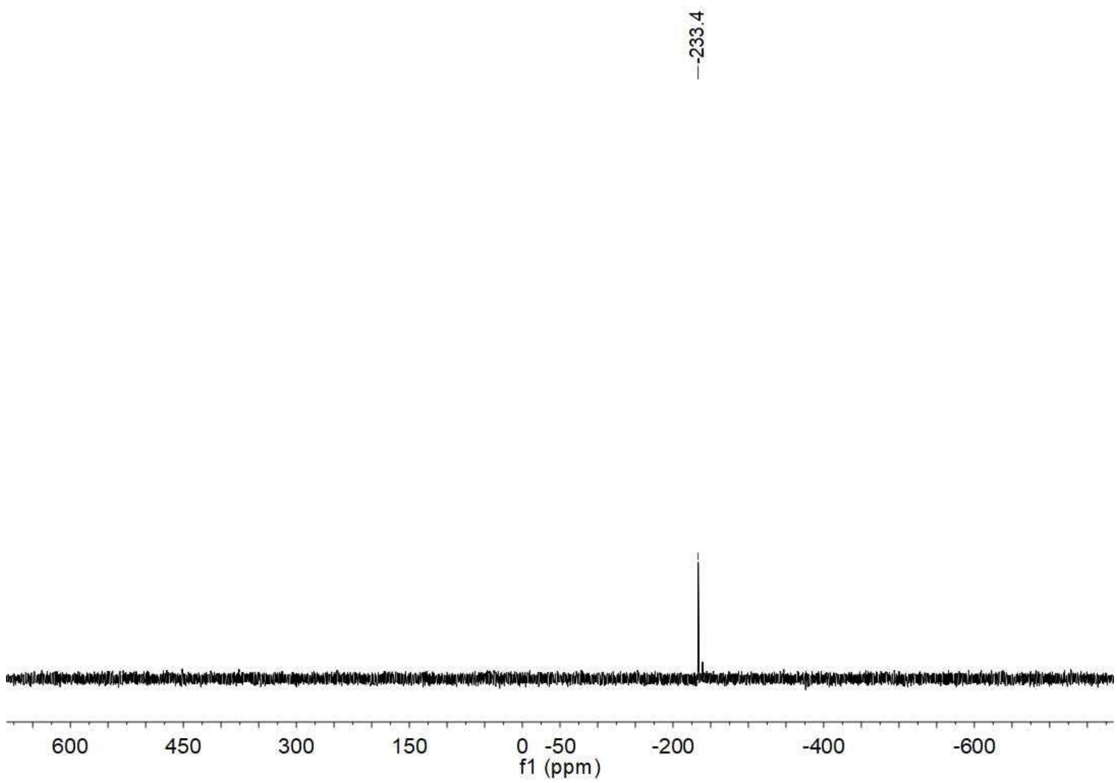


Figure S2-27. $^{31}P\{^{1}H\}$ NMR Spectrum of **7** (243 MHz, C_6D_6, 298 K).

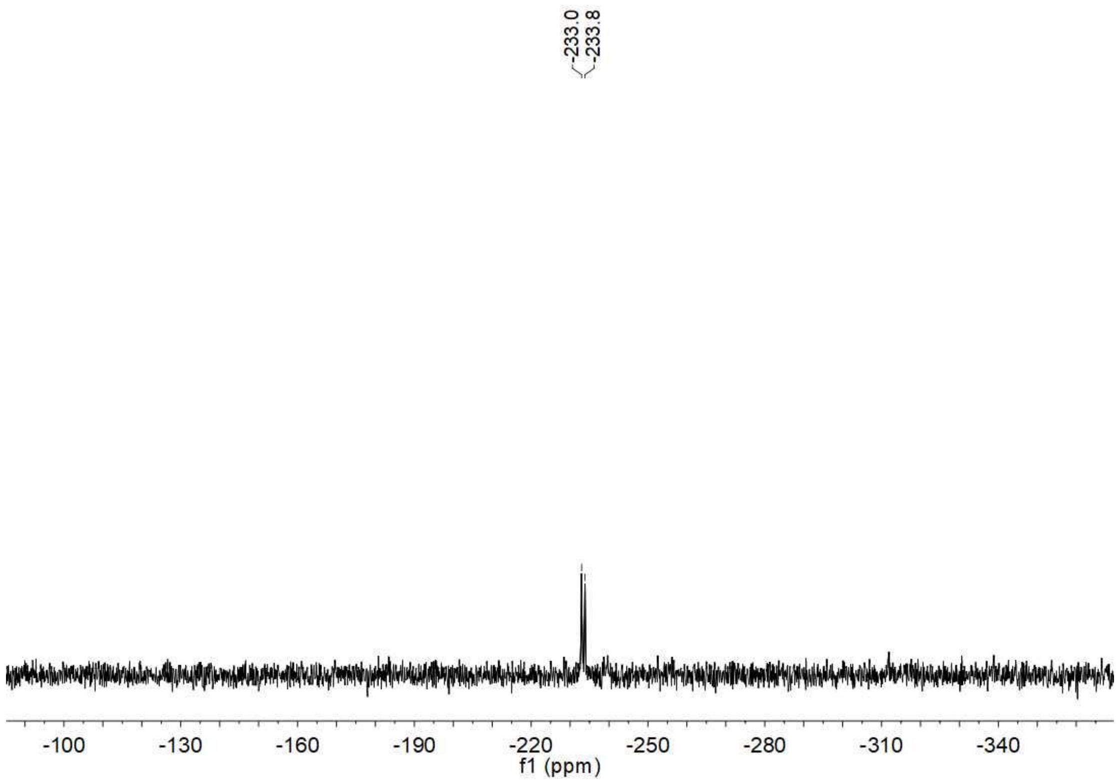


Figure S2-28. ^{31}P NMR Spectrum of **7** (243 MHz, C_6D_6, 298 K).

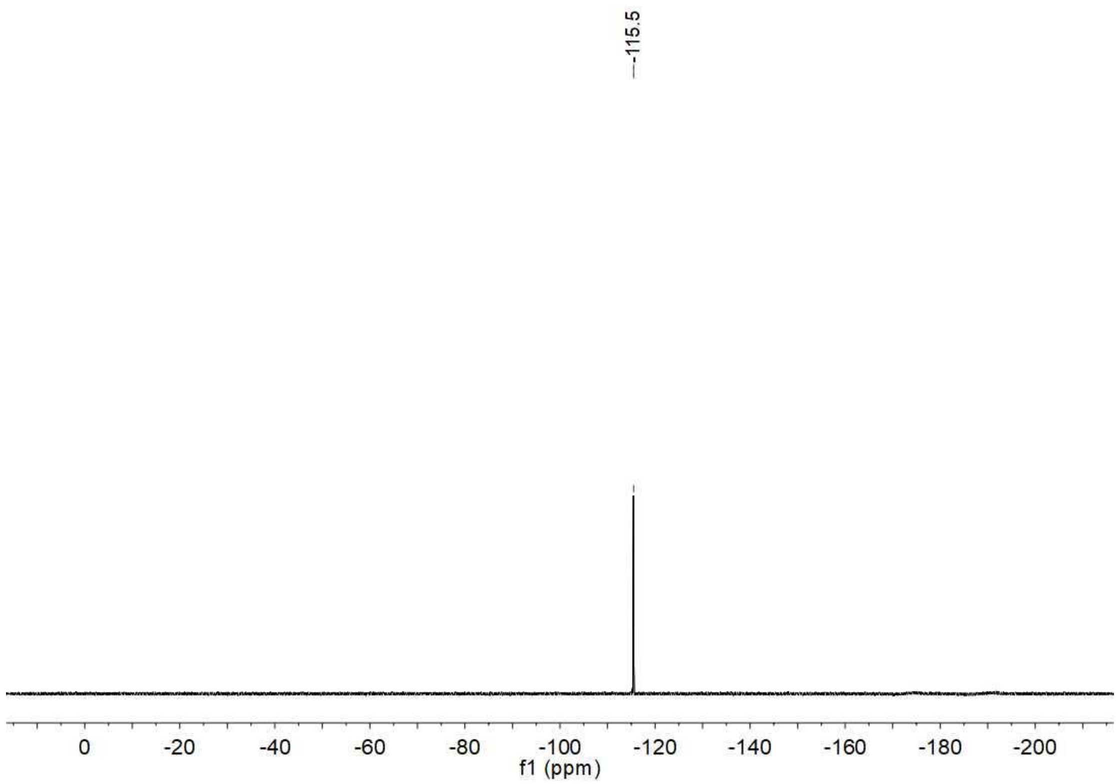


Figure S2-29. $^{19}F\{^1H\}$ NMR Spectrum of **7** (192.6 MHz, C_6D_6, 298 K).

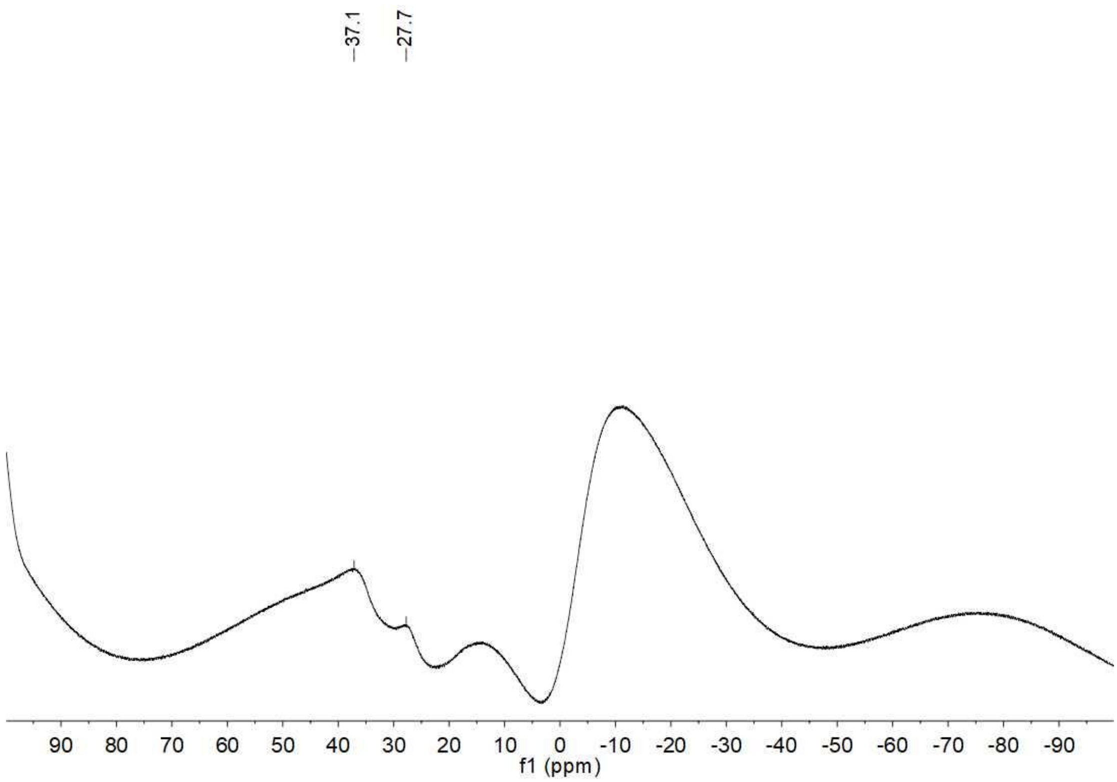


Figure S2-30a. $^{11}B\{^{1}H\}$ NMR Spectrum of **7** (192.6 MHz, C_6D_6, 298 K).

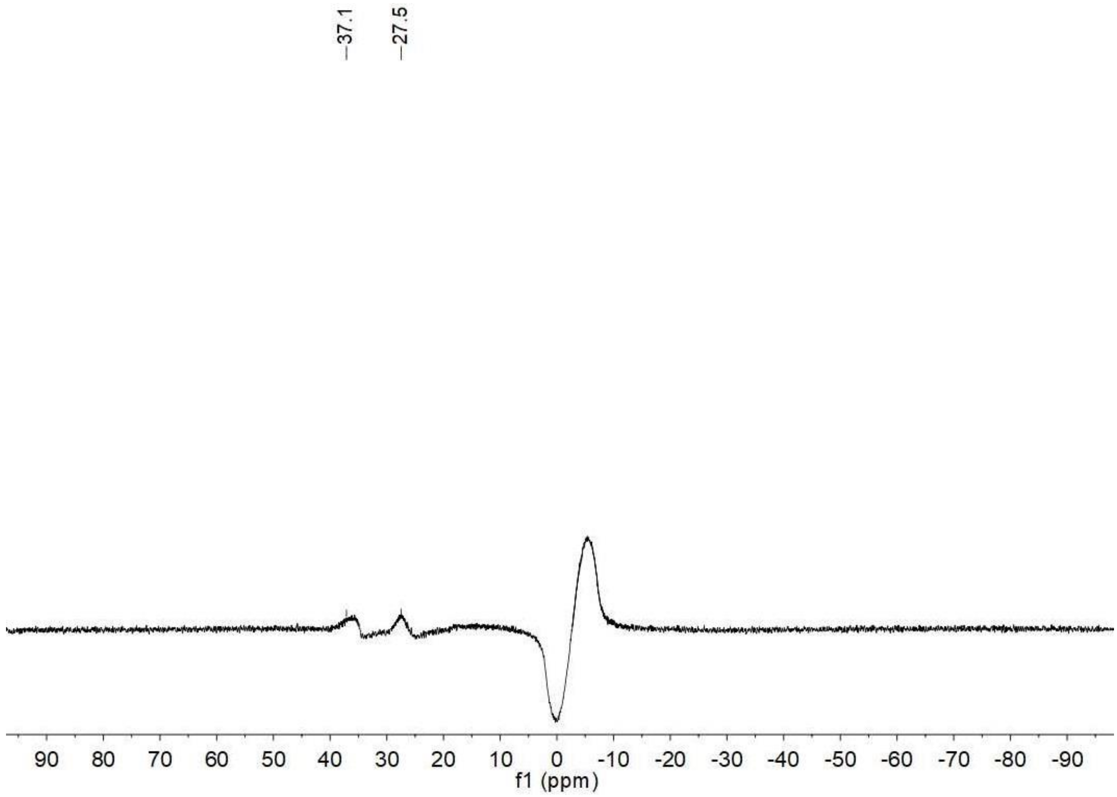


Figure S2-30b. $^{11}B\{^{1}H\}$ NMR Spectrum of **7** (baseline corrected) (192.6 MHz, C_6D_6, 298 K).

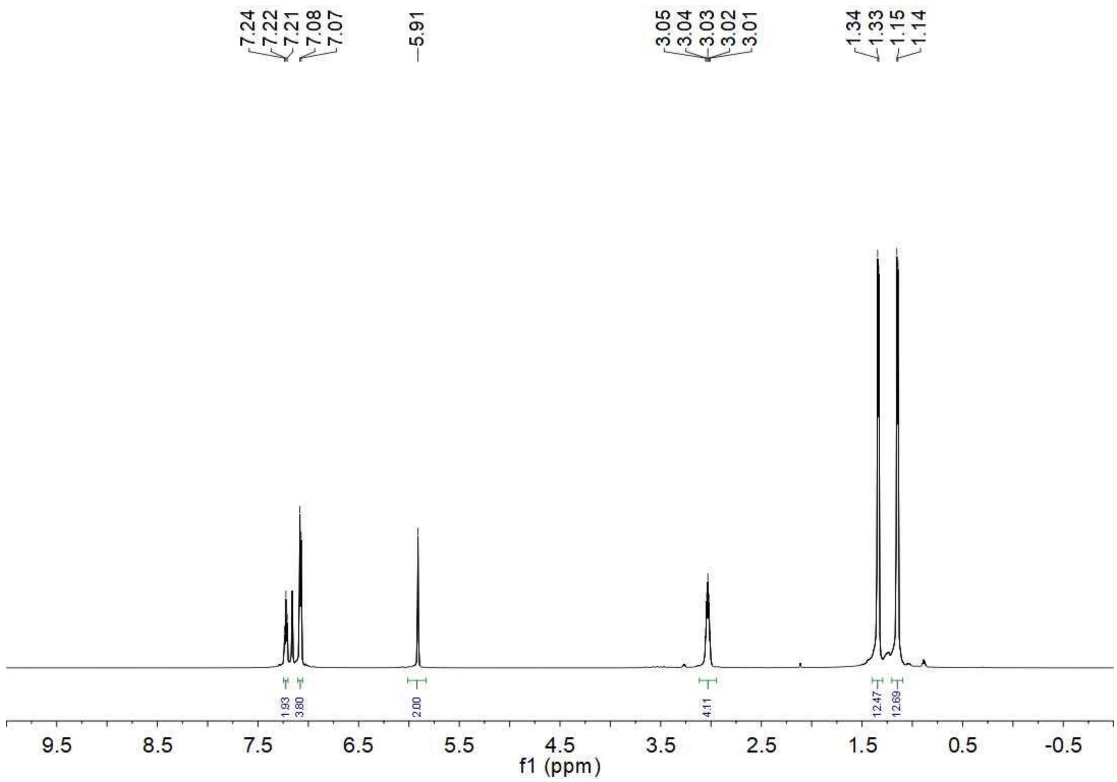


Figure S2-31. ^{1}H NMR Spectrum of **8** (600 MHz, C_6D_6, 298 K).

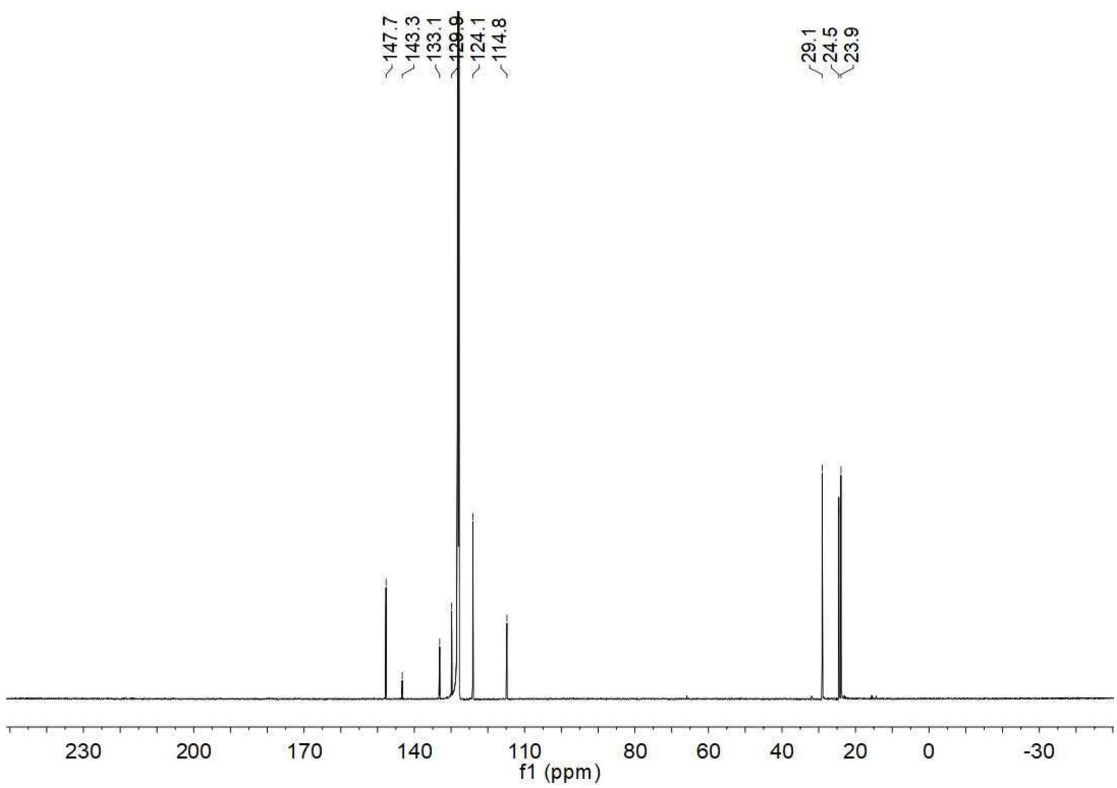


Figure S2-32. $^{13}C\{^{1}H\}$ NMR Spectrum of **8** (150.9 MHz, C_6D_6, 298 K).

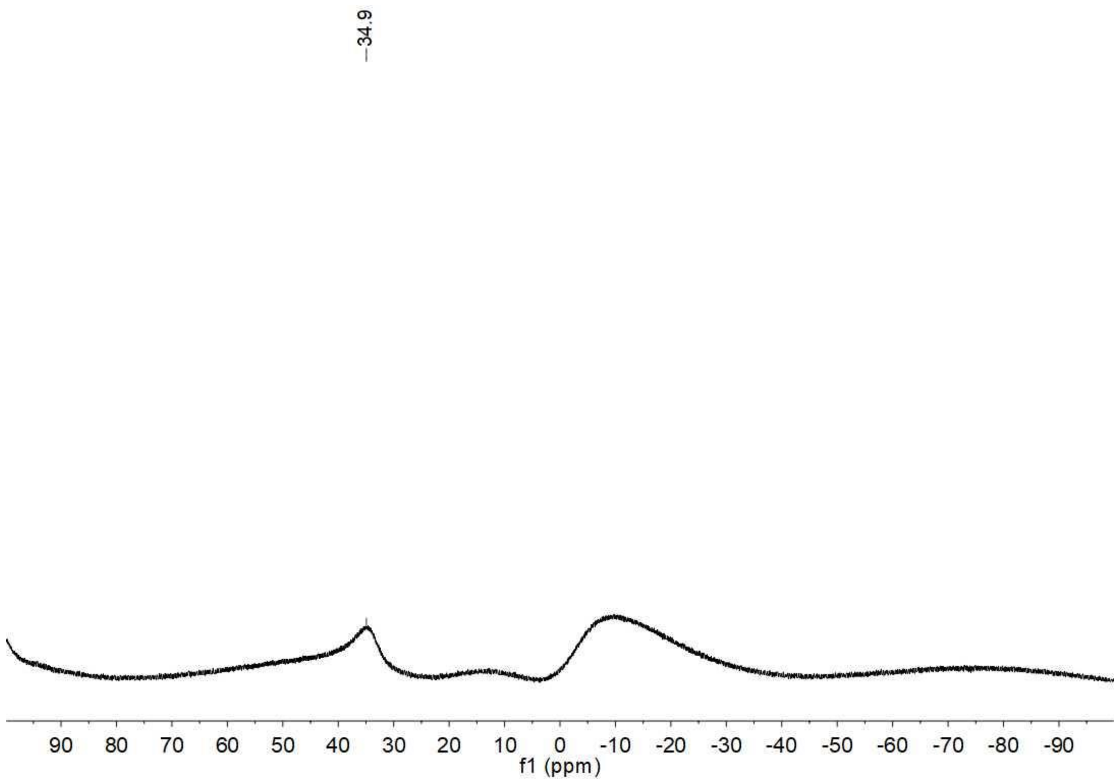


Figure S2-33a. $^{11}B\{^1H\}$ NMR Spectrum of **8** (192.6 MHz, C_6D_6, 298 K).

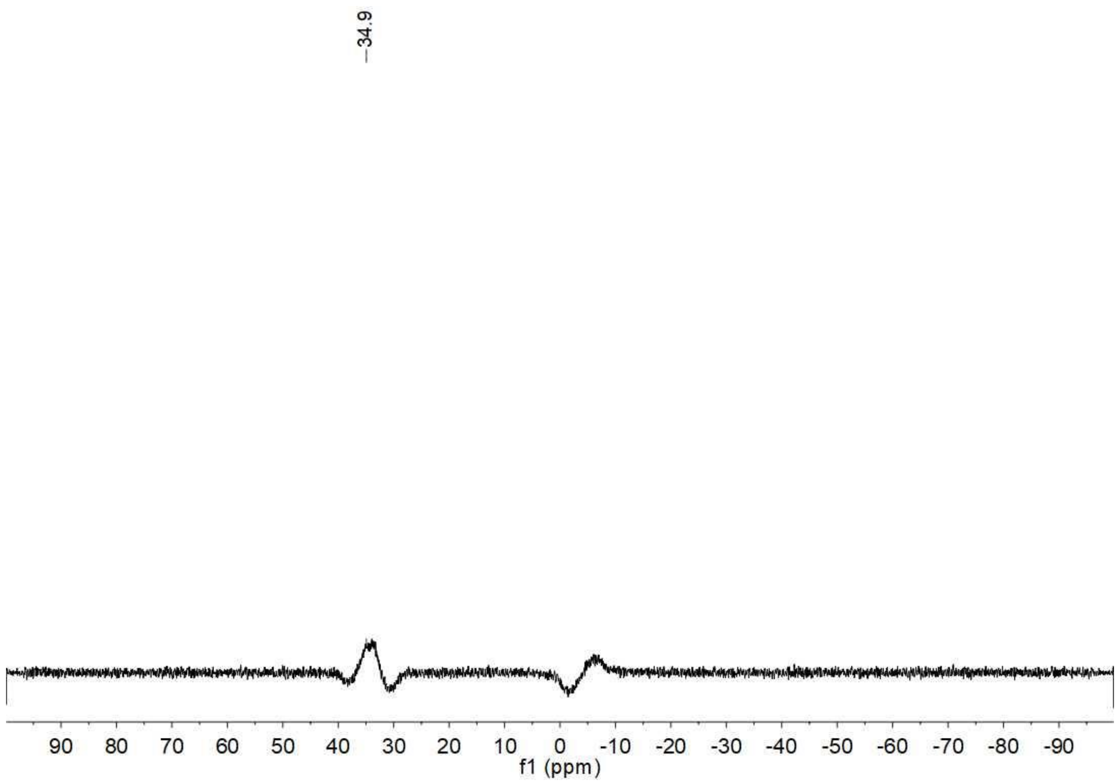


Figure S2-33b. $^{11}B\{^1H\}$ NMR Spectrum of **8** (baseline corrected) (192.6 MHz, C_6D_6, 298 K).

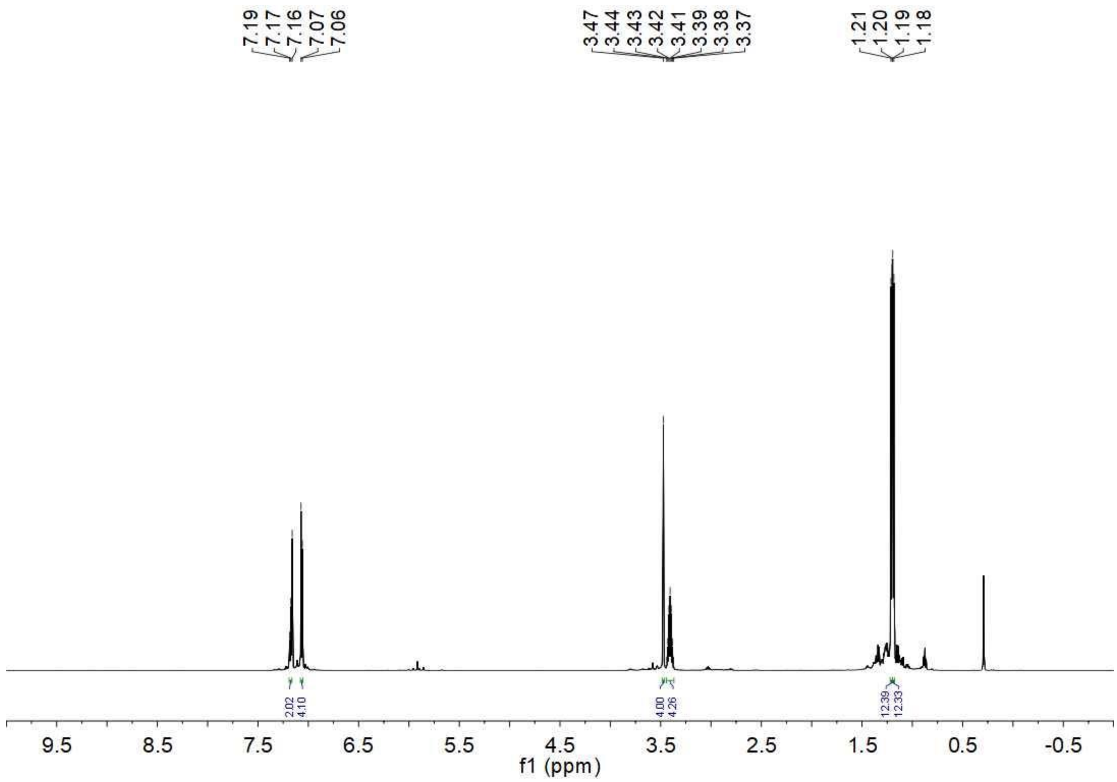


Figure S2-34. ^{1}H NMR Spectrum of **9** (600 MHz, C_6D_6, 298 K).

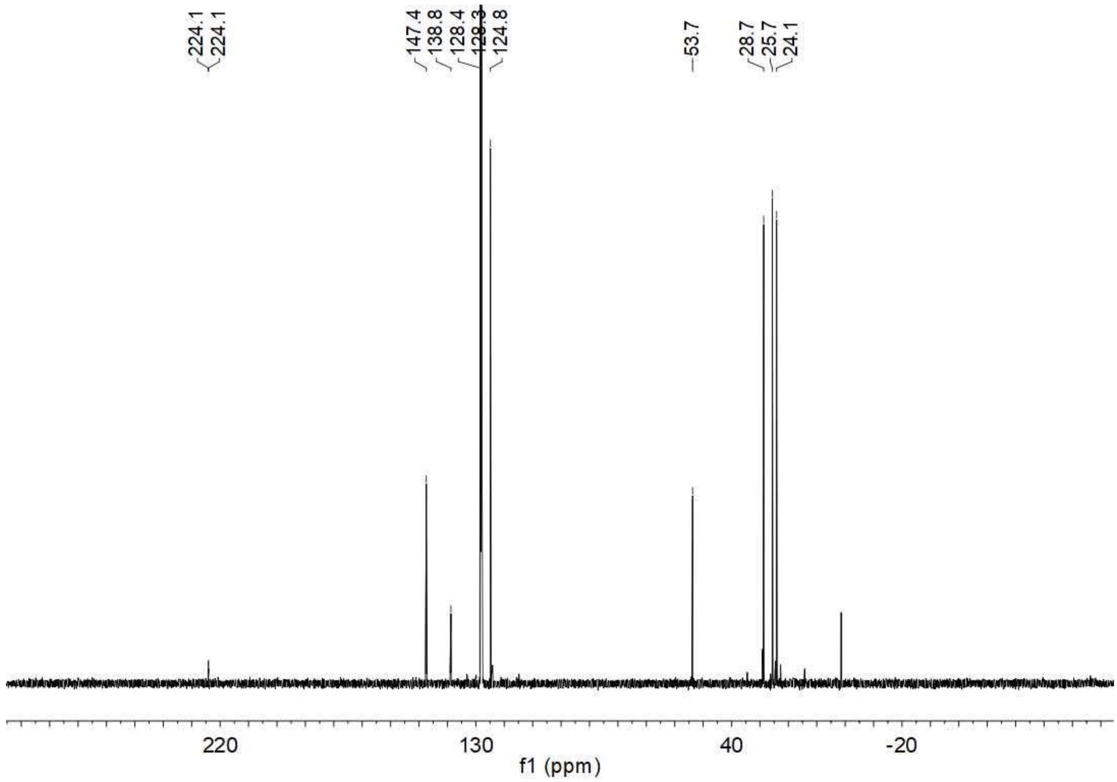


Figure S2-35. $^{13}C\{^{1}H\}$ NMR Spectrum of **9** (150.9 MHz, C_6D_6, 298 K).

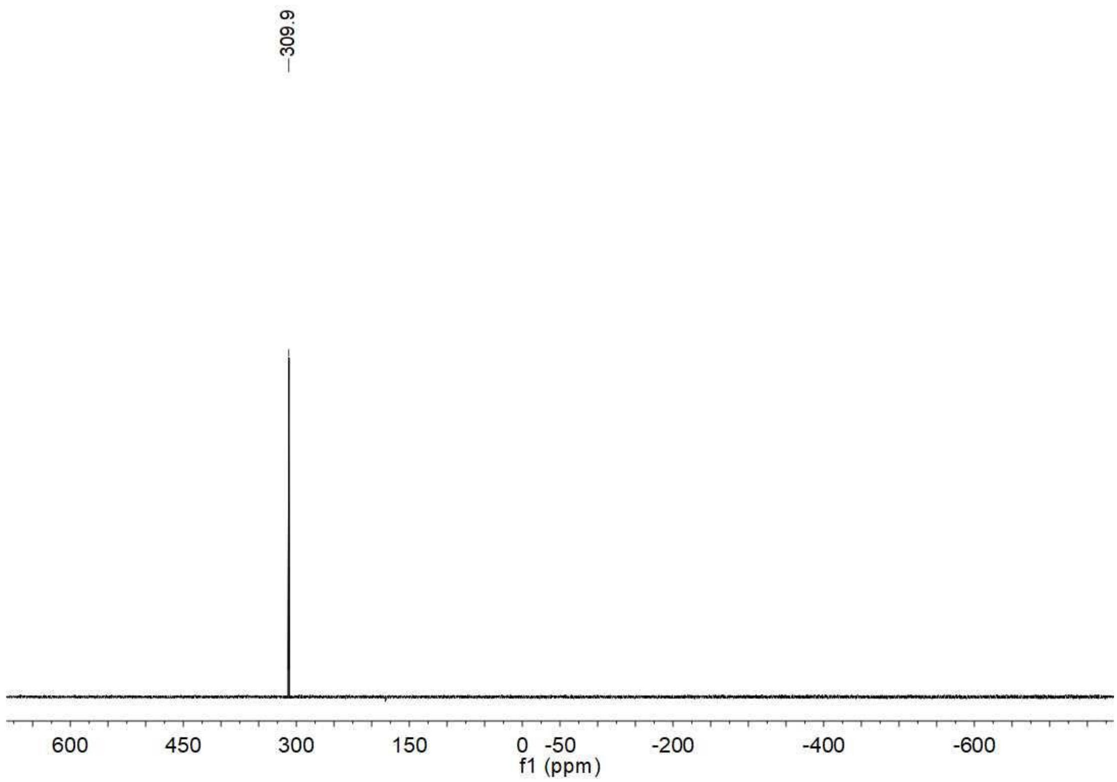


Figure S2-36. $^{31}P\{^{1}H\}$ NMR Spectrum of **9** (243 MHz, C_6D_6, 298 K).

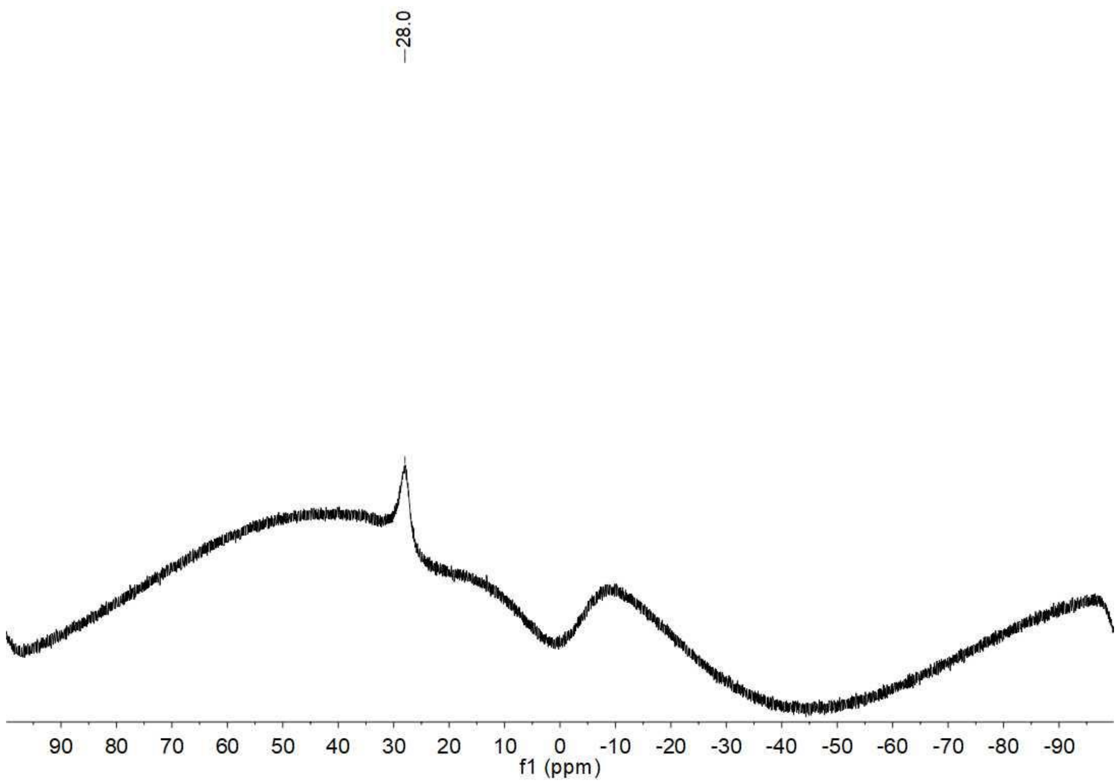


Figure S2-37a. $^{11}B\{^{1}H\}$ NMR Spectrum of **9** (192.6 MHz, C_6D_6, 298 K).

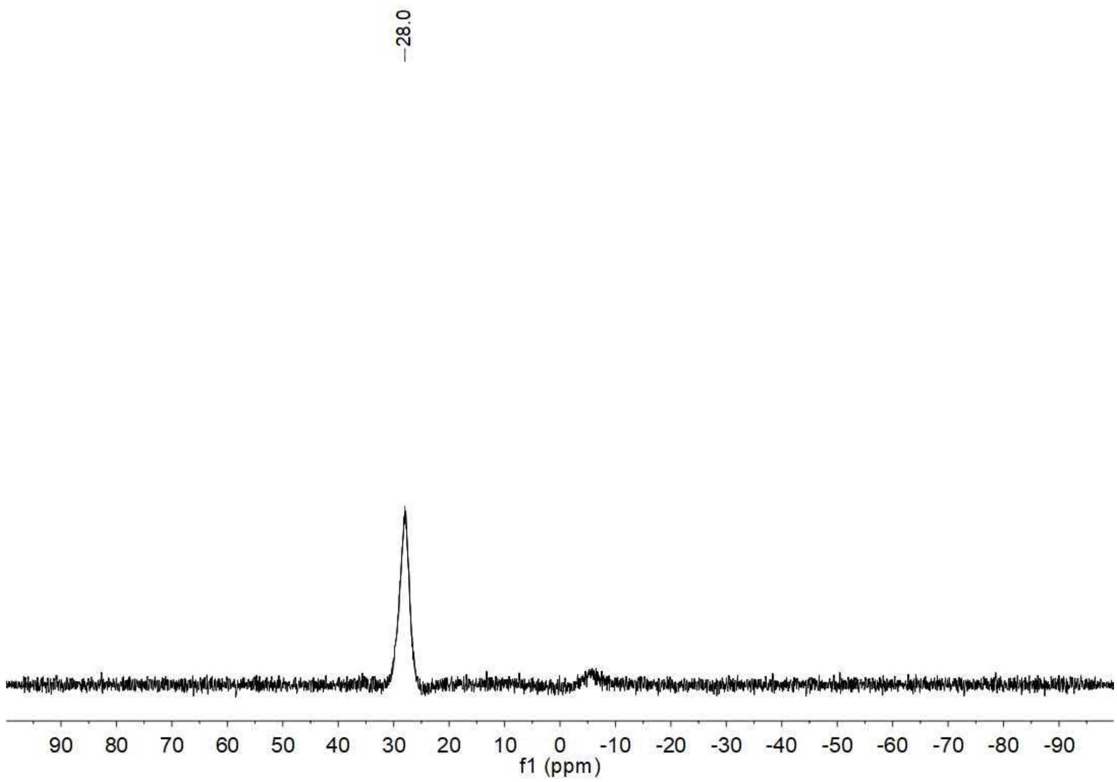


Figure S2-37b. $^{11}B\{^{1}H\}$ NMR Spectrum of **9** (baseline corrected) (192.6 MHz, C_6D_6, 298 K).

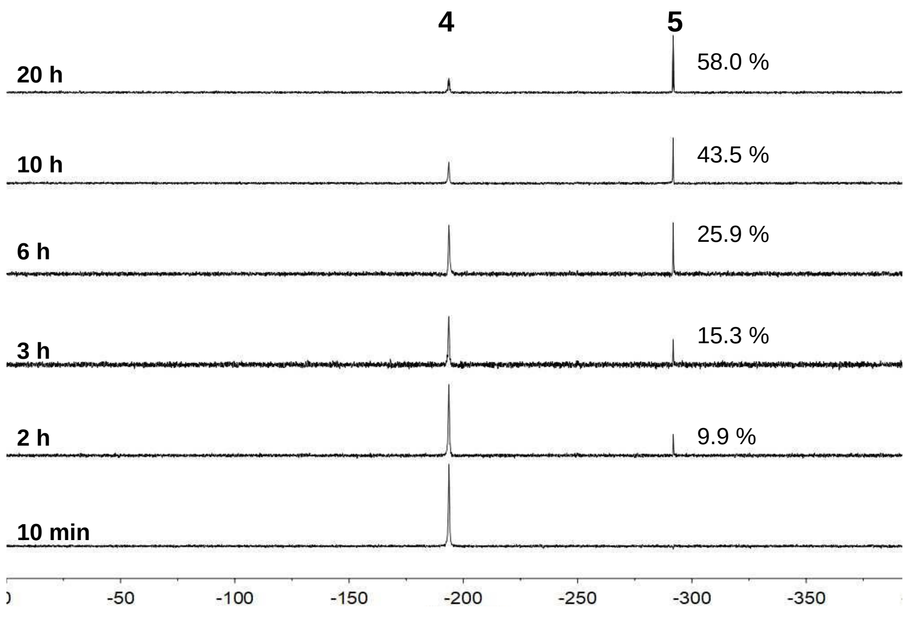


Figure S2-38. Monitoring ^{31}P NMR spectrum of the spontaneous transformation of **4** to **5** at room temperature. The conversion was determined by the relative integral area.

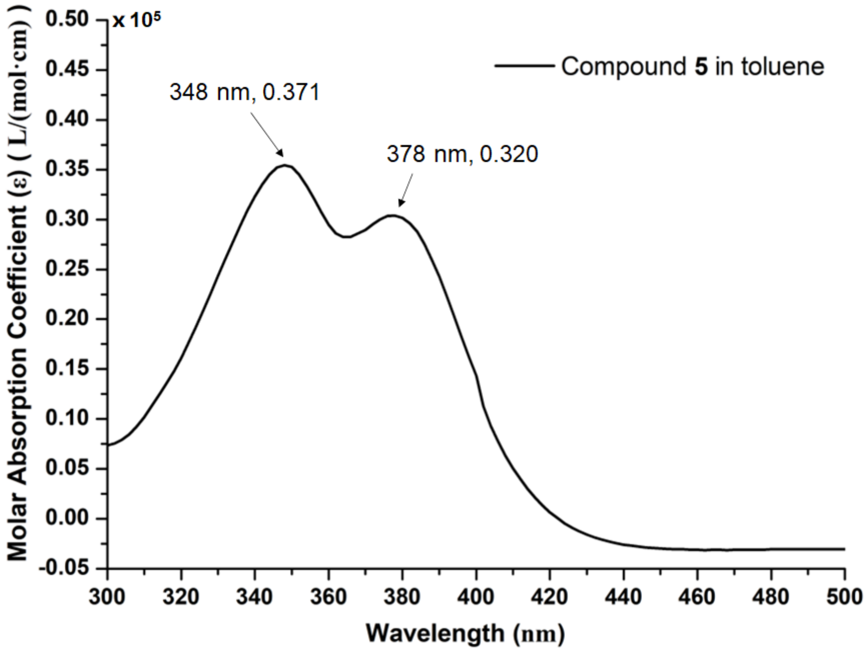


Figure S2-39. UV-Vis spectrum of **5** in toluene (10^{-5} mol/L).

III. X-ray crystallographic data

	4	**5**	**6**
Empirical formula	$C_{56}H_{83}B2BrN_5PSi$	$C_{53}H_{74}B_2N_5P$	$C_{62}H_{82}BN_5OP$
formula weight	986.86	833.76	955.10
crystal system	Monoclinic	Triclinic	Monoclinic
space group	P 1 21/n 1	P-1	P 1 21/c 1
a/Å	11.3609(4)	11.6492(4)	18.0357(6)
b/Å	29.6600(12)	12.9718(4)	16.6539(6)
c/Å	17.1112(6)	18.7856(7)	18.7110(6)
α/deg	90	94.196(2)	90
β/deg	100.873(2)	94.871(2)	90.877(2)
γ/deg	90	115.345(2)	90
V/Å^3	5662.4(4)	2537.23(16)	5619.5(3)
Z	4	2	4
ρ_{calcd}/g·cm^{-3}	1.158	1.091	1.129
μ/mm^{-1}	1.744	0.760	0.763
F(000)	2112.0	904.0	2068
crystal size/mm^3	0.26 x 0.18 x 0.15	0.25 x 0.18 x 0.15	0.24 x 0.18 x 0.15
θ range/deg	2.980 – 68.403	2.378 – 72.078	2.450 – 68.465
index ranges	-13<=h<=13	-14<=h<=14	-21<=h<=20
	-28<=k<=35	-15<=k<=15	-16<=k<=19
	-18<=l<=20	-23<=l<=23	-21<=l<=22
collected data	53573	41106	70495
unique data	10358 R_{int} = 0.0622	9695 R_{int} = 0.0325	10292 R_{int} = 0. 1100
completeness to θ	99.8 %	98.2 %	99.9 %
data/restraints/parameters	10364 / 0 / 614	9695 / 14 / 560	10292/0/ 648
GOF on F^2	1.046	1.085	1.055
final R indices [$I > 2 \ (I)$]	R_1 = 0.0364 wR_2 = 0.0780	R_1 = 0.0408 wR2 = 0.1013	R_1 = 0.0688 wR_2 = 0.1599
R indices (all data)	R_1 = 0.0465 wR_2 = 0.0819	R_1 = 0.0449 wR_2 = 0.1041	R_1 = 0.0928 wR_2 = 0.1724
Largest diff peak/hole (e·Å^{-3})	0.345 / -0.402	0.435 / -0.495	0.470/ -0.464

[a] $R_1 = \sum(||F_o|-|F_c||)/\sum|F_o|$, $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)]^{1/2}$, GOF = $[\sum w(F_o^2-F_c^2)^2/(N_o-N_p)]^{1/2}$.

(continued)

	7	**8**	**9**
Empirical formula	$C_{67}H_{95}B_2FN_5OP_2$	$C_{45}H_{72}B_2N_6S_2$	$C_{28}H_{38}BN_2PS_3$
formula weight	1058.06	890.91	540.56
crystal system	Orthorhombic	Triclinic	Monoclinic
space group	*P2(1)2(1)2(1)*	*P-1*	*P 1 21/c 1*
a/Å	12.9560(6)	10.3831(5)	26.3039(11)
b/Å	21.9701(9)	10.7408(5)	11.7737(5)
c/Å	22.1424(10)	24.9975(11)	20.0625(9)
α/deg	90	84.124(3)	90
β/deg	90	85.546(3)	108.695(2)
γ/deg	90	72.073(3)	90
V/Å^3	6302.7(5)	2635.4(2)	5885.4(4)
Z	4	2	8
ρ_{calcd}/g·cm^{-3}	1.115	1.123	1.220
μ/mm^{-1}	0.744	1.211	1.945
F(000)	2296	960	2304
crystal size/mm^3	0.11 x 0.10 x 0.09	0.20 x 0.20 x 0.10	0.23 x 0.15 x 0.06
2θ range/deg	2.833 – 69.080	3.559 – 68.375	1.542 – 53.960
index ranges	-15<=h<=15 -26<=k<=26 -26<=l<=26	-11<=h<=11 -12<=k<=12 -30<=l<=30	-31<=h<=31 -14<=k<=13 -24<=l<=24
collected data	104625	56539	62894
unique data	11717 R_{int} = 0.1174	9364 R_{int} = 0.0853	10769 R_{int} = 0.0762
completeness to θ	100 %	97.2 %	99.9 %
data/restraints/parameters	11717 / 198 / 712	9364 / 0 / 593	10769 / 0 / 647
GOF on F^2	1.050	1.038	1.042
final R indices [I > 2 (I)]	R_1 = 0.0721 wR2 = 0.1891	R_1 = 0.0549 wR2 = 0.1270	R_1 = 0.0422 wR2 = 0.0887
R indices (all data)	R_1 = 0.0878 wR$_2$ = 0.2046	R_1 = 0.0735 wR$_2$ = 0.1352	R_1 = 0.0655 wR$_2$ = 0.0968
Largest diff peak/hole (e·Å^{-3})	0.610 / -0.465	0.673 / -0.437	0.260 / -0.351

[a] $R_1 = \sum(||F_o|-|F_c||)/\sum|F_o|$, $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)]^{1/2}$, GOF = $[\sum w(F_o^2-F_c^2)^2/(N_o-N_p)]^{1/2}$.

IV. Computational details

Geometry optimizations were carried out with the Gaussian 16 package[S4] with the M06-2X functional.[S5] The def2-SVP basis set was used for all the atoms. Frequency calculations at the same level of theory were performed to identify the number of imaginary frequencies (zero for local minimum) and provide the Gibbs free energies. All the energies reported in the paper correspond to the reference state of 1 mol/L, 298K. Natural bond orbital (NBO) and natural resonance theory (NRT) calculations were carried out using NBO 7.0 program[S6] at the M06-2X/def2-SVP level of theory. These NRT calculations were done for a model of **5** in which Dipp groups were replaced by hydrogen atoms, but at the geometry corresponding to **5**. Optimized structures were visualized by the CYLview,[S7] Chemcraft[S8] or IBOview program.[S9] EDA-NOCV and ELF calculations were carried out using Amsterdam Modeling Suite (ADF/2019.304)[S10] at the BP86/TZP level of theory. Intrinsic bond orbitals (IBOs) were carried out using ORCA program at the M06-2X/def2-SVP level of theory.[S9]

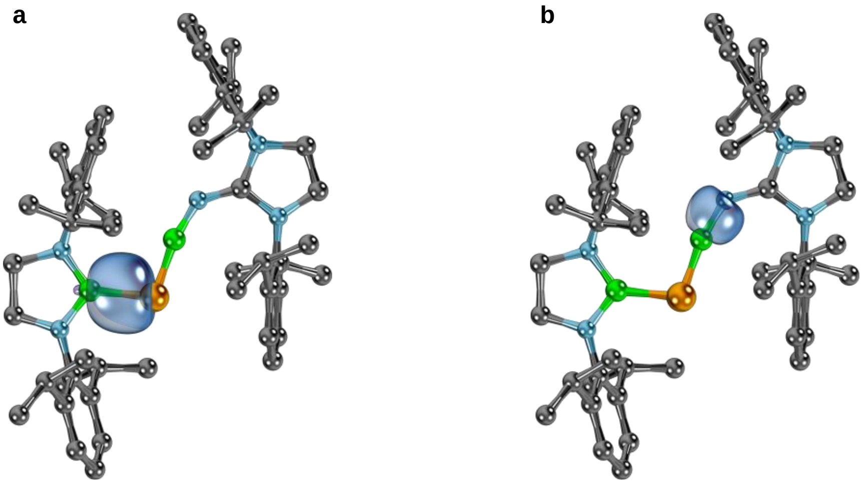


Figure S4-1. Depiction of selected IBOs of **5**. (a) P−B(1) σ-bonding orbital. (b) N−B(2) σ-bonding orbital.

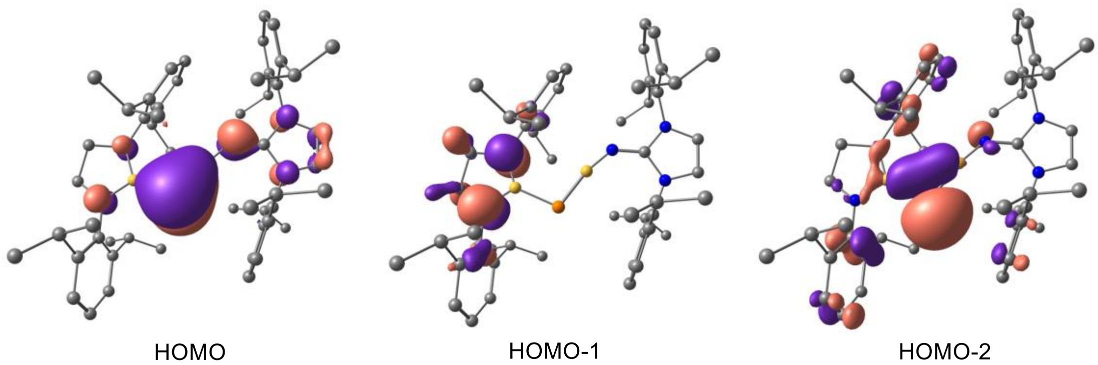


Figure S4-2. Frontier molecular orbitals of **5**.

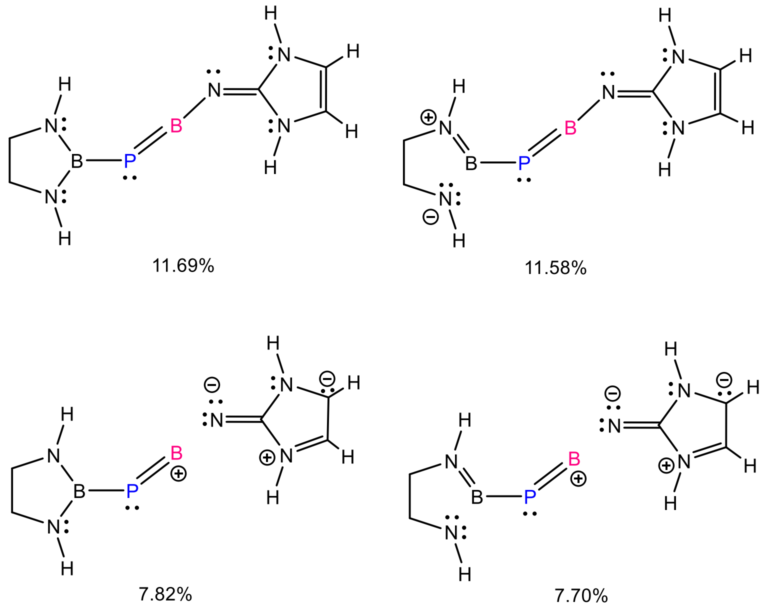


Figure S4-3. Four predominant resonance structures (weight > 7.0%) and their weights for the simplified model of **5** (Dipp groups were replaced with H).

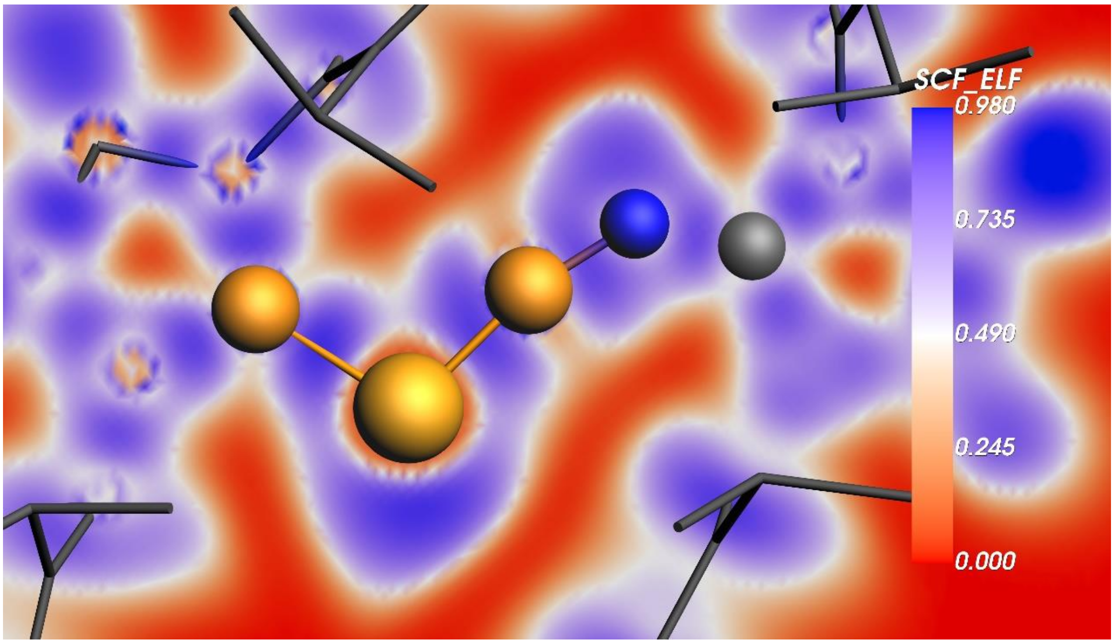


Figure S4-4. ELF plot of **5** in the P(1)–B(2)–N(1) plane.

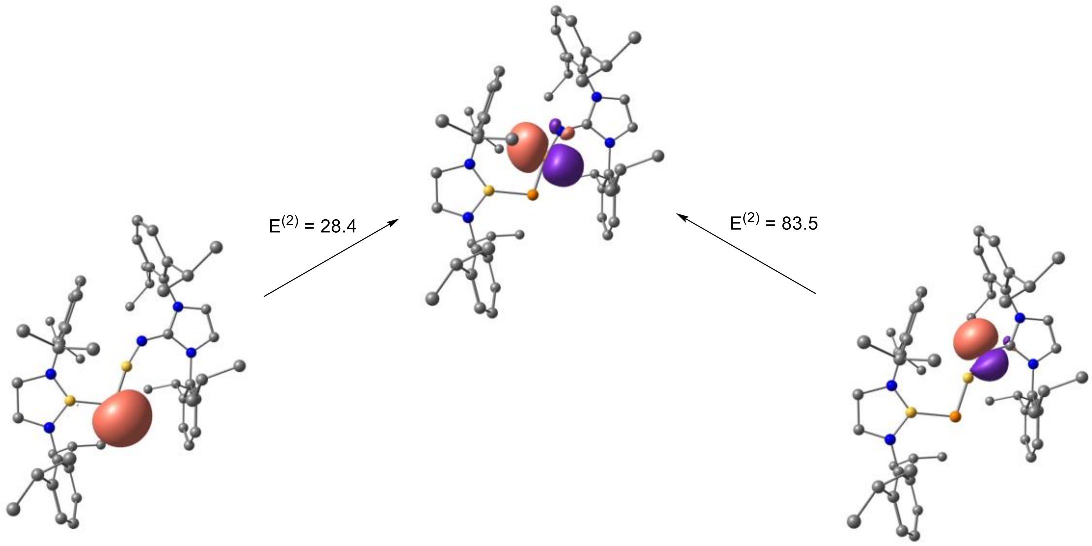


Figure S4-5. Selected NBOs of **5** for the second-order perturbation theory analysis. Energies are given in kcal/mol.

	hartree	eV	kcal/mol	kJ/mol
Pauli Repulsion				
Kinetic (Delta T^0):	2.424835050982034	65.9831	1521.61	6366.40
Delta V^Pauli Coulomb:	-1.291142187406291	-35.1338	-810.20	-3389.89
Delta V^Pauli LDA-XC:	-0.433146490493037	-11.7865	-271.80	-1137.23
Delta V^Pauli GGA-Exchange:	0.084641153462208	2.3032	53.11	222.23
Delta V^Pauli GGA-Correlation:	-0.034246638756601	-0.9319	-21.49	-89.91
Total Pauli Repulsion:	0.750940887788314	20.4341	471.22	1971.60
(Total Pauli Repulsion = Delta E^Pauli in BB paper)				
Steric Interaction				
Pauli Repulsion (Delta E^Pauli):	0.750940887788314	20.4341	471.22	1971.60
Electrostatic Interaction:	-0.391164927472801	-10.6441	-245.46	-1027.00
(Electrostatic Interaction = Delta V_elstat in the BB paper)				
Total Steric Interaction:	0.359775960315513	9.7900	225.76	944.59
(Total Steric Interaction = Delta E^0 in the BB paper)				
Orbital Interactions				
A:	-0.499995271932126	-13.6056	-313.75	-1312.74
Total Orbital Interactions:	-0.499995271932127	-13.6056	-313.75	-1312.74
Alternative Decomposition Orb.Int.				
Kinetic:	-2.226265057546718	-60.5798	-1397.00	-5845.06
Coulomb:	1.533497027922097	41.7286	962.28	4026.20
XC:	0.192772757692494	5.2456	120.97	506.12
Total Orbital Interactions:	-0.499995271932127	-13.6056	-313.75	-1312.74
Residu (E=Steric+OrbInt+Res):	0.000000067616392	0.0000	0.00	0.00
Total Bonding Energy:	-0.140219244000222	-3.8156	-87.99	-368.15

Figure S4-6. EDA-NOCV results of **5** ([**NHB**-P:](singlet) + [NHC=NB:](singlet)).

```
                              hartree         eV      kcal/mol      kJ/mol
                        --------------------  -----------  ----------  -----------

Pauli Repulsion
 Kinetic (Delta T^0):             1.299904225183337      35.3722       815.70       3412.90
 Delta V^Pauli Coulomb:           -0.688611415550979      -18.7381       -432.11       -1807.95
 Delta V^Pauli LDA-XC:            -0.321111221214903      -8.7379       -201.50       -843.08
 Delta V^Pauli GGA-Exchange:        0.078225528640964       2.1286        49.09        205.38
 Delta V^Pauli GGA-Correlation:    -0.032354721909607      -0.8804       -20.30        -84.95
                        --------------------  -----------  ----------  -----------
 Total Pauli Repulsion:           0.336052395148811       9.1445       210.88        882.31
(Total Pauli Repulsion =
 Delta E^Pauli in BB paper)

Steric Interaction
 Pauli Repulsion (Delta E^Pauli):    0.336052395148811       9.1445       210.88        882.31
 Electrostatic Interaction:      -0.229882393447951       -6.2554       -144.25       -603.56
(Electrostatic Interaction =
 Delta V_elstat in the BB paper)
                        --------------------  -----------  ----------  -----------
 Total Steric Interaction:        0.106170001700859       2.8890        66.62        278.75
(Total Steric Interaction =
 Delta E^0 in the BB paper)

Orbital Interactions
 A:                        -0.312558187183628      -8.5051       -196.13       -820.62
                        --------------------  -----------  ----------  -----------
 Total Orbital Interactions:       -0.312558187183629      -8.5051       -196.13       -820.62

Alternative Decomposition Orb.Int.
 Kinetic:                  -1.090626866322229      -29.6775       -684.38       -2863.44
 Coulomb:                   0.629588860293185       17.1320       395.07       1652.99
 XC:                        0.148479818845416       4.0403        93.17        389.83
                        --------------------  -----------  ----------  -----------
 Total Orbital Interactions:       -0.312558187183629      -8.5051       -196.13       -820.62

 Residu (E=Steric+OrbInt+Res):      -0.000001034824439       0.0000        0.00         0.00

Total Bonding Energy:              -0.206389220307209      -5.6161       -129.51       -541.87
```

Figure S4-7. EDA-NOCV results of **5** ([**NHB**-P](triplet) + [NHC=NB](triplet)).

Table S4-1. Results of EDA analysis of compound **5** using different electronic states as interacting fragments**.**

	5	
Energy Term	[**NHB**-P:](S) + [NHC=NB:](S)	[**NHB**-P:](T)+ [NHC=NB:](T)
ΔE_{int} (kcal/mol)	-87.99	-129.51
ΔE_{Pauli} (kcal/mol)	471.22	210.88
ΔE_{elstat}[a] (kcal/mol)	-245.46(43.9%)	-144.25 (42.4%)
ΔE_{orb}[a] (kcal/mol)	-313.75 (56.1%)	-196.13 (57.6%)

[a]The values in parentheses are the percentage contributions to the total attractive interactions ($\Delta E_{elstat} + \Delta E_{orb}$).

Cartesian Coordinates:

Compound **5**:

P	-2.71205000	5.19015400	14.03214300
N	-4.92736000	8.86168300	14.54148100
N	-3.58555700	10.50251100	14.01944800
N	-2.71817800	8.28178700	13.83389900
N	-0.57566600	3.19274900	13.91955000
N	0.32022300	5.30302300	13.65945900
C	-5.42064200	7.54594100	14.82142100
C	0.42733100	6.64036600	13.20313300
C	-3.65419400	9.13505700	14.10678600
C	-1.40720100	2.11284500	14.31408400
C	-5.84942700	6.74435500	13.74643700
C	0.90270600	7.62604000	14.09529200
C	-2.55160000	11.23956500	13.35664300
C	0.05810800	6.96759900	11.88091300
C	-5.41269700	7.10178400	16.15124500
C	1.33162800	7.22105700	15.49836800
H	1.82108400	6.23935700	15.40445400
C	-1.60257600	11.92816200	14.13268100
C	-1.83263100	1.19288200	13.33010900
C	0.12601700	8.30771500	11.48538000
H	-0.15813300	8.58218400	10.46646200
C	-2.59169900	11.30654400	11.95569800
C	-4.80037300	11.06032300	14.40619500
H	-4.95464100	12.13418400	14.39106300
C	0.87546700	3.04337100	13.98794900
H	1.22732500	2.15541300	13.43884100
H	1.20509900	2.93711000	15.04057100
C	-5.62659900	10.04392300	14.73833700
H	-6.65043500	10.03991600	15.09826700
C	-6.35391800	5.48099900	14.05549700
H	-6.68164700	4.81965600	13.25420200
C	0.95773700	8.95043900	13.65582400
H	1.33107100	9.73177800	14.31930100
C	-1.78956700	1.96007100	15.66128700
C	-1.66423700	11.86154500	15.65075400
H	-2.72994100	11.91361800	15.92731000
C	1.39433900	4.35165400	13.38207600
H	2.35459000	4.66687400	13.82028600
H	1.54643200	4.24256200	12.29011200
C	0.55733600	9.29307300	12.36591500
H	0.59873200	10.33438500	12.04390500
C	-0.35128000	5.90051200	10.87586900
H	-0.44604500	4.94592700	11.41382600
C	-4.79683000	7.91881700	17.27361700
H	-4.46828400	8.88339800	16.85813800
C	-1.44273100	1.40698700	11.87609200
H	-0.44215300	1.86564700	11.87470100
C	-2.61408400	0.88156500	16.00335400
H	-2.92059100	0.75123200	17.04403000
C	-5.92459200	5.82606000	16.40777400
H	-5.92317000	5.44181300	17.42994900
C	2.33721900	8.18596800	16.12478200
H	3.19045600	8.37613700	15.45757300
H	2.72132700	7.76988000	17.06736200
H	1.87064100	9.15378100	16.36550100
C	-2.64994500	0.12851800	13.71478100
H	-2.98888100	-0.59216600	12.96929100
C	-1.59556700	12.05548300	11.31892100
H	-1.58775300	12.12392000	10.22954300
C	-0.63434200	12.66963100	13.45201300
H	0.11810900	13.22317800	14.01374400
C	-6.40211300	5.03117700	15.37297400
H	-6.78553400	4.03290100	15.58831800
C	-3.67628200	10.60846000	11.15063300
H	-4.47066600	10.29691300	11.84718700
C	-0.62759700	12.72591000	12.05851400
H	0.13830100	13.31004900	11.54554700
C	-5.71475500	7.22626900	12.30895500
H	-4.76050200	7.77441500	12.24385900
C	-4.32107000	11.54223400	10.12371500
H	-3.60762100	11.83186200	9.33785800
H	-4.69977000	12.46027200	10.59557500

H	-5.16297600	11.03442800	9.63107300
C	-3.04193400	-0.02670100	15.04319000
H	-3.68210100	-0.86339100	15.32840200
C	-1.12394000	10.52241200	16.16403300
H	-0.03820800	10.46433000	15.99618400
H	-1.57586700	9.66684900	15.64250900
H	-1.30731900	10.41832100	17.24437100
C	-1.70896000	6.18348500	10.22982700
H	-1.68189800	7.10224800	9.62308700
H	-2.49065300	6.28808600	10.99690700
H	-1.99194500	5.35357600	9.56460800
C	-1.31277000	2.91025200	16.74790600
H	-0.73956200	3.71486300	16.26429300
C	-5.80608600	8.21364800	18.38588100
H	-6.16141200	7.28324200	18.85394800
H	-6.68368900	8.75224900	17.99935100
H	-5.34285600	8.82717900	19.17238500
C	-1.36669000	0.11156200	11.06887700
H	-2.36412900	-0.32723700	10.91370900
H	-0.73699400	-0.64075400	11.56586400
H	-0.94432100	0.31249100	10.07357800
C	0.73290200	5.73307200	9.80398100
H	0.47364500	4.91475200	9.11511800
H	1.71206700	5.51217100	10.25330100
H	0.83946400	6.65470400	9.21052000
B	-0.91236700	4.58754100	13.85503200
C	-0.95516000	13.02642800	16.33757700
H	-1.13881600	12.98796200	17.42047400
H	-1.30607700	13.99877300	15.96279600
H	0.13418600	12.97389300	16.19106200
C	-3.55252400	7.20504600	17.81383500
H	-3.03023900	7.83889100	18.54638200
H	-2.85659700	6.95446200	16.99859400
H	-3.82909100	6.26422600	18.31387500
C	0.12295500	7.02964900	16.42260900
H	-0.40969700	7.98284200	16.55783300
H	0.44684600	6.67608800	17.41423100
H	-0.58594000	6.30021300	16.00642800
B	-2.55453500	6.95652700	13.89416200
C	-2.39826400	2.40429100	11.20857200
H	-2.08670800	2.60373000	10.17102200
H	-2.42972100	3.35794600	11.75604000
H	-3.42042800	1.99430900	11.18829500
C	-3.12800100	9.34173100	10.49068900
H	-3.93115600	8.79445500	9.97220900
H	-2.67415500	8.67685000	11.23859500
H	-2.35590900	9.59683700	9.74643700
C	-5.62426100	6.07652900	11.30615300
H	-4.85977700	5.34760500	11.61426800
H	-5.35131300	6.46814000	10.31520900
H	-6.58842300	5.55590100	11.19868700
C	-2.48225500	3.56799000	17.48646500
H	-3.08652900	2.81891600	18.02270600
H	-3.13166400	4.10852300	16.78154700
H	-2.10283400	4.28617900	18.23008800
C	-6.84215900	8.19406600	11.92946100
H	-7.81681700	7.68492300	11.97995300
H	-6.70155000	8.56065700	10.90083100
H	-6.87866000	9.06662800	12.59773200
C	-0.37972000	2.19055400	17.72858300
H	0.01144500	2.89462300	18.47857600
H	0.47233100	1.73106200	17.20657400
H	-0.91433100	1.39017500	18.26373700

Compound $\mathbf{5_2}$ dimer:

P	0.00323800	-1.31100300	-0.41907400
N	-0.62995500	-4.23373100	-1.12599900
N	-5.10596800	0.59981200	0.36765300
N	0.51632600	-4.09080200	0.92518100
N	-4.17559600	0.33813100	2.37099500
N	-2.71628000	0.07710900	0.46266600

C	-3.84983400	0.31043600	0.99054700
C	-1.88561600	-4.58086200	-3.27262700
C	-0.70381300	-4.24266300	-2.55827900
C	1.45178800	-4.03446100	2.01941700
C	-3.10236100	-5.25423000	-2.64361600
H	-3.19488600	-4.90065900	-1.60450300
C	-5.54968400	0.63070700	-0.99460000
C	-4.04235400	-1.83097000	3.47536500
C	-6.09788900	0.73159300	1.33837500
H	-7.12991600	0.88794900	1.06028100
C	3.32393800	-4.37892300	0.36047000
H	2.54572200	-4.84279400	-0.25667000
C	0.48277800	-4.02743300	-3.31807400
C	-3.68548400	-0.46327300	3.46558900
C	-5.26288900	-0.45178000	-1.83667500
C	-6.35849100	1.70678900	-1.45102200
C	2.80097400	-4.39005000	1.77789500
C	-3.21441000	0.18980100	4.61969900
C	-0.89954200	-5.47729400	-0.39513800
H	-0.76101200	-6.35301700	-1.03734100
H	-1.93292500	-5.50322100	-0.00871800
C	-5.54313900	0.59033800	2.54006200
H	-5.98803600	0.58480800	3.52831300
C	-0.44533400	-3.58592300	3.62448800
H	-1.02066300	-3.81558500	2.71917100
C	-3.93141300	-2.53032100	4.67689300
H	-4.23286800	-3.57752100	4.71660900
C	3.62100700	-4.73411500	2.85313700
H	4.64277400	-5.06277200	2.66496100
C	-1.91375600	-4.39124200	-4.66190800
H	-2.83398100	-4.59856400	-5.20696600
C	0.09945800	-5.48940200	0.75453600
H	-0.35158700	-5.86616100	1.68672100
H	0.97991400	-6.12451400	0.54360100
C	1.84684200	-4.27820900	4.39972300
H	1.47229500	-4.23262500	5.42361700
C	-3.46177900	-1.90723300	5.82858100
H	-3.38175100	-2.47023700	6.76002300
C	-5.68997100	-0.41276000	-3.16825600
H	-5.43305900	-1.24423400	-3.82831300
C	-2.89568900	1.67991900	4.63756300
H	-2.38935200	1.91364400	3.68820300
C	0.98136800	-3.97558000	3.34161700
C	-4.41905600	-4.97303900	-3.37908300
H	-4.56340400	-3.90945800	-3.59739600
H	-5.26816900	-5.32044700	-2.77429800
H	-4.45733900	-5.52537300	-4.32910400
C	-6.78301800	2.91086200	-0.61155200
H	-6.17234700	2.93435800	0.30303200
C	-6.45458600	0.64160400	-3.64256100
H	-6.79380200	0.65906500	-4.67954800
C	-6.80228700	1.67212100	-2.77379300
H	-7.41913400	2.49209900	-3.14516900
C	-3.09258800	-0.56913900	5.79224500
H	-2.72324500	-0.09834500	6.70218400
C	3.15048900	-4.68553000	4.16180900
H	3.80213700	-4.96813200	4.99116600
C	1.84380100	-4.31179500	-2.70343500
H	1.94164500	-3.74044400	-1.77375000
C	0.40071000	-3.81733800	-4.69550100
H	1.30571900	-3.59145600	-5.25966900
C	-1.04521400	-4.36946700	4.79281500
H	-0.80895500	-5.44151800	4.71548700
H	-2.13512000	-4.25801700	4.81158700
H	-0.66911100	-4.00707600	5.76255100
C	-0.80831600	-3.94278600	-5.36779200
H	-0.87106300	-3.76170900	-6.44207600
C	-4.55781600	-1.69130800	-1.34709200
H	-4.23175600	-1.52908400	-0.32167300

C	-4.52876000	-2.54386400	2.22439400
H	-4.95553500	-1.79030000	1.54764600
B	0.02944300	-3.29811500	-0.18084000
C	-0.50546900	-2.07060700	3.83053900
H	0.04080200	-1.79206500	4.74532200
H	-1.53811800	-1.72491200	3.92782300
H	-0.03834800	-1.54428100	2.98256000
C	-3.34401800	-3.21499800	1.51314000
H	-2.52446400	-2.50303100	1.32291700
H	-3.65720400	-3.64218000	0.54854000
H	-2.95708400	-4.03583700	2.13766200
C	3.46875400	-2.92308800	-0.09274300
H	2.52252200	-2.37670300	0.00878400
H	3.79097500	-2.85310700	-1.14088800
H	4.19819300	-2.38728700	0.53156600
C	-2.93396200	-6.78588500	-2.65200400
H	-2.88049500	-7.13602400	-3.69397400
H	-3.80227300	-7.26800500	-2.17744000
H	-2.02931000	-7.13646300	-2.14686300
C	-6.57811400	4.24893400	-1.33691300
H	-5.57318600	4.34347100	-1.76483600
H	-6.73530900	5.08048600	-0.63438700
H	-7.30216700	4.37499100	-2.15507600
C	-1.96766700	2.06057000	5.79202400
H	-2.50262700	2.03362000	6.75410800
H	-1.60039100	3.08585500	5.64721000
H	-1.09985500	1.39062400	5.86152300
B	-1.36542400	0.01447100	0.12871400
C	1.90512100	-5.81995600	-2.39952500
H	1.14987500	-6.12972300	-1.66933900
H	2.89425100	-6.10459100	-2.01062200
H	1.72910500	-6.38412300	-3.32831000
C	-4.15653700	2.55322400	4.72881800
H	-4.76819100	2.51101200	3.82035900
H	-3.86580300	3.60369900	4.88282100
H	-4.77488100	2.24659800	5.58775400
C	-5.64016100	-3.55814100	2.49975200
H	-5.27384000	-4.42184300	3.07429400
H	-6.03186100	-3.94545800	1.54835600
H	-6.47157500	-3.10091100	3.05548500
C	4.60750700	-5.17422000	0.13624200
H	5.47520000	-4.71634600	0.63561200
H	4.83750100	-5.21132300	-0.93954500
H	4.51281200	-6.20879100	0.49825900
C	-8.26901200	2.82207400	-0.22427200
H	-8.89056200	2.88185400	-1.13058800
H	-8.54679400	3.66146600	0.43007700
H	-8.54105700	1.88783600	0.28393200
C	3.04578500	-3.98939700	-3.58638600
H	3.04100000	-4.60198800	-4.50081100
H	3.96618600	-4.23896200	-3.03880900
H	3.09558500	-2.93334000	-3.87311700
C	-5.57410500	-2.83865300	-1.29729300
H	-6.36333200	-2.60111000	-0.56598900
H	-5.10076900	-3.78521300	-0.99759900
H	-6.06504400	-2.99884300	-2.26675700
C	-3.28064500	-1.94438400	-2.14478800
H	-3.46596800	-2.23172000	-3.18975900
H	-2.67895700	-2.73150000	-1.66919600
H	-2.66099900	-1.03478500	-2.16559900
P	-0.01667400	1.47287200	0.24739200
N	-0.07453000	2.86501000	-2.54535100
N	4.83221100	1.42177800	-0.45754000
N	0.25142000	4.26824700	-0.72954100
N	4.09032600	1.15239300	1.60180400
N	2.72788600	0.24591100	-0.17296800
C	3.75598600	0.86808200	0.26344500
C	0.22054500	0.75475600	-3.79817800
C	-0.57701700	1.84283500	-3.40365700

C	0.14321900	4.90037800	0.54301200
C	1.70758000	0.73919000	-3.51704100
H	1.89083200	1.24774200	-2.55846600
C	5.19672000	1.37143300	-1.84507900
C	2.51745400	0.88327900	3.46026600
C	5.70509000	2.07983100	0.41231400
H	6.56495700	2.61982500	0.02954500
C	-2.38925000	4.49677600	0.54515000
H	-2.12689200	4.06390300	-0.42777900
C	-1.90330800	1.96276400	-3.86650200
C	3.63226600	0.41773300	2.74611300
C	5.21526800	2.56946700	-2.57958700
C	5.76695500	0.19186300	-2.36927100
C	-1.11171600	5.00122000	1.18539800
C	4.39255600	-0.69087600	3.18046100
C	0.15360100	4.20098700	-3.10815000
H	-0.60226400	4.46049100	-3.86236600
H	1.12343600	4.25059600	-3.62298000
C	5.25241700	1.91394100	1.66246700
H	5.63537500	2.28373000	2.60627200
C	2.59887700	5.59263000	0.38652800
H	2.49974200	4.96317600	-0.50642100
C	2.08466300	0.13236300	4.55730700
H	1.20569400	0.45870300	5.11495800
C	-1.19360600	5.63692400	2.42858200
H	-2.16144700	5.69788800	2.93231900
C	-0.35892900	-0.25139700	-4.58005900
H	0.23005900	-1.12648100	-4.85408700
C	0.10878900	5.14293200	-1.89593800
H	0.90587800	5.90345700	-1.93466500
H	-0.85476500	5.68642500	-1.83752800
C	1.14422200	6.16507200	2.35427400
H	2.01903000	6.64712500	2.79777400
C	2.76507400	-1.01400000	4.94975100
H	2.40685100	-1.59972600	5.79845800
C	5.74553400	2.55176600	-3.87541000
H	5.75744400	3.47491700	-4.45821000
C	5.75986800	-1.01431700	2.59028400
H	5.78712200	-0.62730700	1.55971900
C	1.27182200	5.52464900	1.11762100
C	2.29558700	-0.66394100	-3.43300800
H	1.69410200	-1.31333000	-2.77839200
H	3.32130300	-0.62140300	-3.03620300
H	2.33979900	-1.11966000	-4.43528700
C	5.99364700	-1.01757500	-1.48540600
H	5.13859500	-1.08784400	-0.79874000
C	6.23445000	1.38067700	-4.43447000
H	6.62651600	1.37975900	-5.45258500
C	6.24286300	0.20929700	-3.68201800
H	6.66255900	-0.69952200	-4.11285300
C	3.92316600	-1.40405700	4.28513000
H	4.47296800	-2.27668200	4.63710700
C	-0.07435600	6.20855900	3.02193900
H	-0.15502800	6.70417500	3.99076600
C	-2.79941500	3.05363500	-3.31340100
H	-2.20455100	3.93905600	-3.06476600
C	-2.43444800	0.96238600	-4.68419300
H	-3.46777800	1.03649800	-5.02739900
C	2.88734400	7.03268200	-0.05458100
H	2.05958500	7.44789400	-0.64804400
H	3.80557500	7.08243100	-0.65955100
H	3.02817900	7.68688900	0.81998000
C	-1.67273100	-0.15319300	-5.02129900
H	-2.10262000	-0.95319100	-5.62785800
C	4.70353800	3.88347700	-2.02366000
H	4.39892100	3.72250700	-0.98155500
C	1.93316300	2.25278000	3.17933500
H	2.00241500	2.44844800	2.09859000
B	0.03029800	2.89231100	-1.11266200

C	3.75254600	5.03332700	1.21673900
H	3.86112300	5.56410700	2.17517200
H	4.70612400	5.13156700	0.67500100
H	3.59183400	3.96770200	1.43127800
C	0.47366200	2.39213700	3.59246500
H	-0.12463100	1.53069100	3.26147200
H	0.04203600	3.29586900	3.13616500
H	0.39627600	2.49189900	4.68421900
C	-3.04388400	3.39892500	1.38299500
H	-2.34939900	2.55858500	1.53106400
H	-3.94807100	3.01352700	0.88354300
H	-3.34282500	3.78546300	2.37012700
C	2.40430200	1.52581300	-4.63540600
H	2.20824000	1.04215500	-5.60550600
H	3.49027900	1.55323600	-4.47498000
H	2.02879600	2.55741300	-4.69854200
C	6.08607000	-2.32654300	-2.26401800
H	5.24571200	-2.43906300	-2.96229700
H	6.07310500	-3.17750100	-1.56727500
H	7.02332000	-2.38789900	-2.83778500
C	6.08878600	-2.50409900	2.53965500
H	6.15409300	-2.93833300	3.54882200
H	7.06790900	-2.65466100	2.06007900
H	5.33455100	-3.06630900	1.98399900
B	1.34209900	0.08862200	-0.10919600
C	-3.90899900	3.49808900	-4.26379800
H	-3.50409100	3.78979400	-5.24435300
H	-4.44468000	4.36302800	-3.84433000
H	-4.65115600	2.70144400	-4.41886700
C	6.86219700	-0.31887800	3.40647300
H	6.68434400	0.75376200	3.53946900
H	7.83993300	-0.44887300	2.91767100
H	6.91761000	-0.77087300	4.40896500
C	2.77541100	3.28918400	3.93943600
H	2.74490500	3.07290700	5.01885200
H	2.37399400	4.29921500	3.77479500
H	3.82840100	3.28040800	3.62402100
C	-3.36500500	5.64988700	0.29015400
H	-3.69537500	6.10843500	1.23514600
H	-4.26050300	5.28357400	-0.23278500
H	-2.90432200	6.43902100	-0.32226600
C	7.27476400	-0.82108900	-0.66063400
H	8.14400000	-0.73846300	-1.33119200
H	7.43440500	-1.68411300	0.00352300
H	7.23547400	0.08459400	-0.03958700
C	-3.35624300	2.48146100	-2.01706600
H	-3.91881300	1.58415300	-2.27788600
H	-4.01448700	3.18216800	-1.48398300
H	-2.55190200	2.17123000	-1.33448300
C	5.78805500	4.96351900	-2.03781000
H	6.68482700	4.64438000	-1.48594000
H	5.41212800	5.88717000	-1.57413900
H	6.09715700	5.21070900	-3.06449600
C	3.45797100	4.31084200	-2.79449400
H	3.64742600	4.35326000	-3.87848800
H	3.11252600	5.30457900	-2.47162500
H	2.65603900	3.58096600	-2.61468900

VI. References

[S1] Segawa, Y.; Suzuki, Y.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc.* **2008**, *130*, 16069–16079.

[S2] Schreiber, R. E.; Goicoechea, J. M. *Angew.Chem., Int.Ed.* **2021**, *60*, 3759–3767.

[S3] a) Tamm, M.; Randoll, S.; Herdtweck, E.; Kieigrewe, N.; Kehr, G.; Erker, G.; Rieger, B. *Dalton. Trans.* **2006**, *3*, 459-467. b) Liu, B.-C.; Ge, N.; Zhai, Y.-Q.; Zhang, T.; Ding, Y.-S.; Zheng, Y.-Z. *Chem. Commun.* **2019**, *55*, 9355-9358.

[S4] Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2016**.

[S5] Zhao, Y.; Truhlar, D. G.; *Theor. Chem. Acc.* **2008**, *120*, 215-241.

[S6] Glendening, E. D; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Karafiloglou, P.; Landis, C. R.; Weinhold, F. NBO 7.0, University of Wisconsin: Madison, WI, **2018**.

[S7] Legault, C. Y. CYLview, 1.0b; Université de Sherbrooke: Sherbrooke, Quebec, Canada, **2009**; www.cylview.org.

[S8] Andrienko, G. A. ChemCraft, http://www.chemcraftprog.com.

[S9] Knizia, G. *J. Chem. Theory Comput.* **2013**, *9*, 4834-4843.

[S10] te Velde, G.; Bickelhaupt,F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.;Ziegler, T.; *J. Comput. Chem.* **2001**, *22*, 931-967. ADF 2019.304, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com