

Supporting Information
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Supporting Information

for

Synthesis of Phosphinoboranes via Coordination-Induced Bromine Abstraction of an Isolable Phosphinyl Radical with Bromoboranes

Shintaro Ishida,* Yukihiro Katayama, Fumiya Hirakawa, and Takeaki Iwamoto*

Graduate School Science, Tohoku University, 6-3 Aramaki-aza-aoba, Aoba-Ku, Sendai 980-8578, Japan

ishida@tohoku.ac.jp and takeaki.iwamoto@tohoku.ac.jp

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1. NMR Spectra

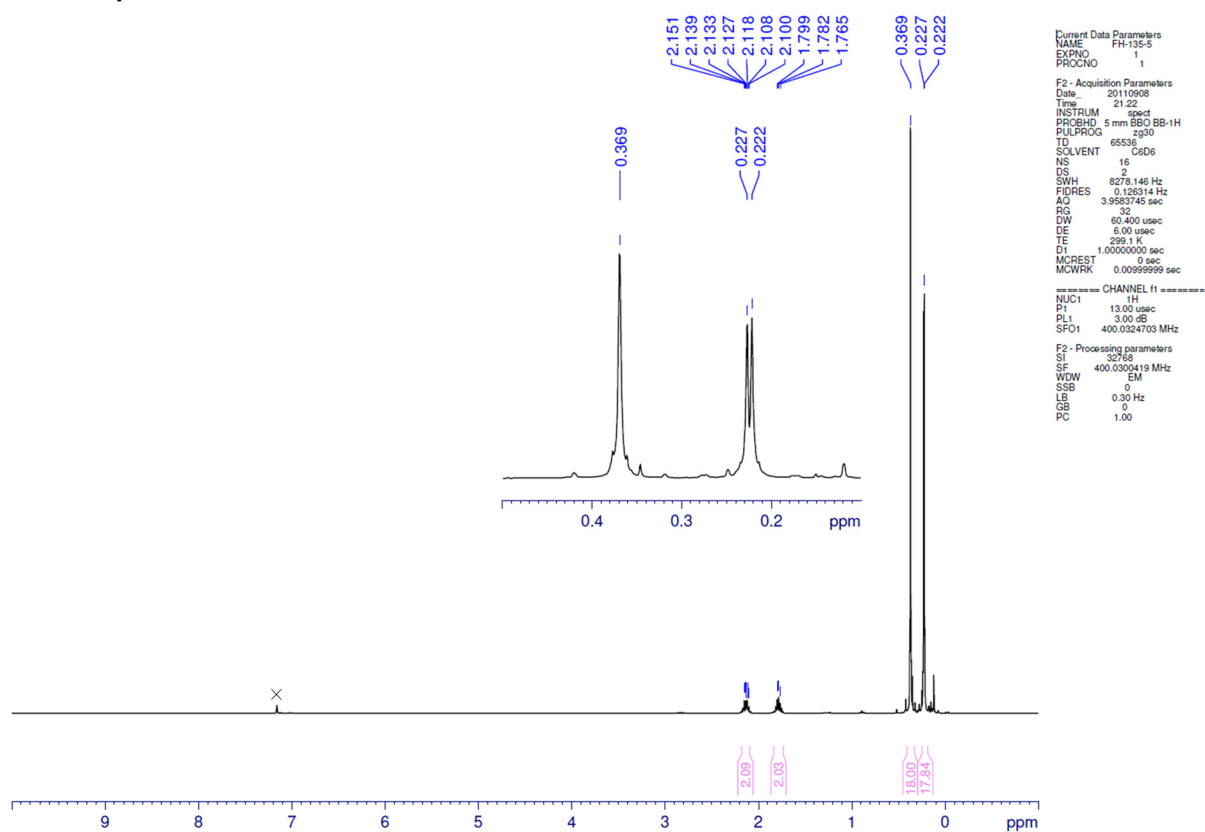


Figure S1. ^1H NMR spectrum of **5** at 299 K in C_6D_6 ($\times = \text{C}_6\text{D}_5\text{H}$).

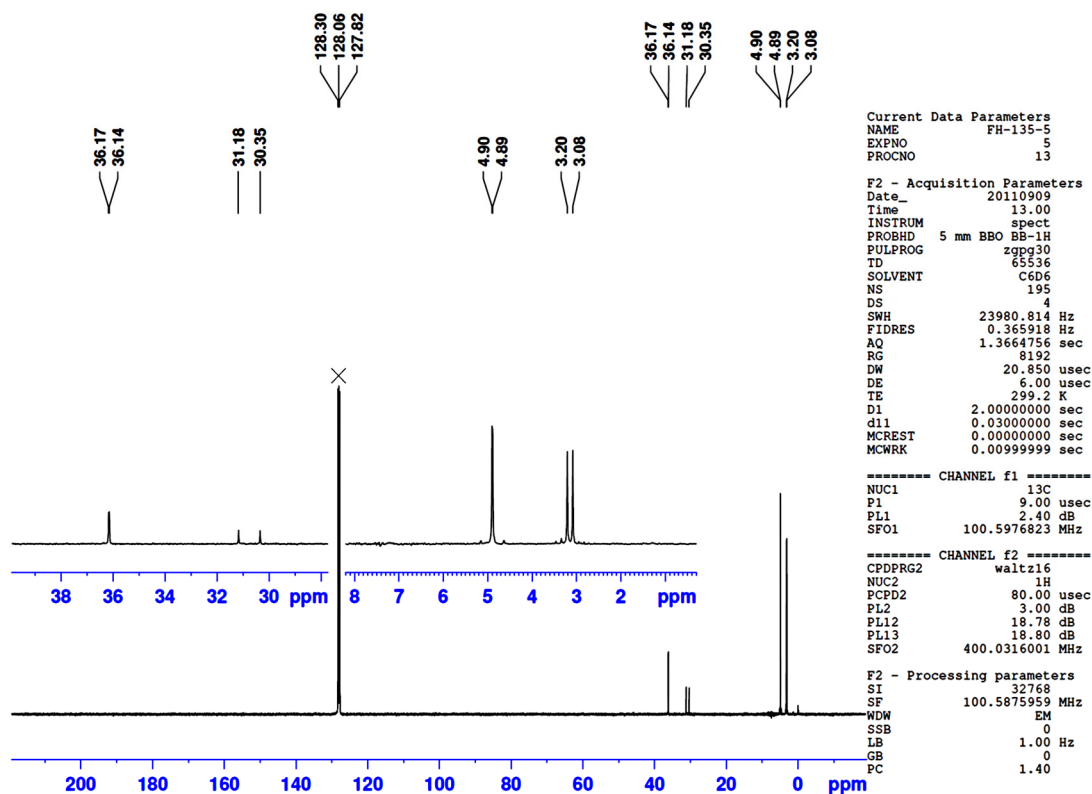
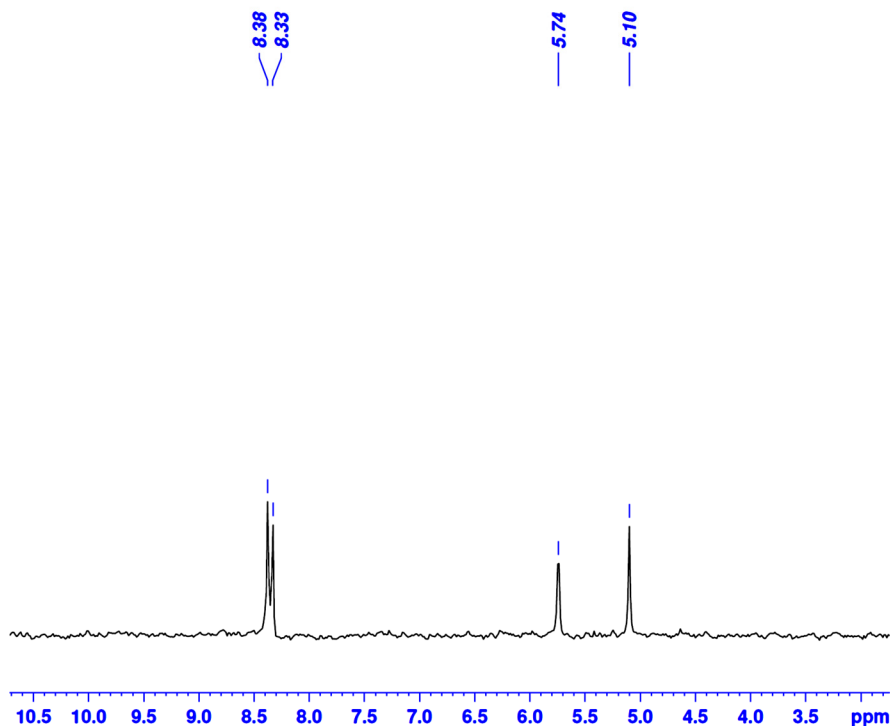


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** at 299 K in C_6D_6 ($\times = \text{C}_6\text{D}_6$).



```

Current Data Parameters
NAME          FH-135-5
EXPNO         4
PROCNO        29

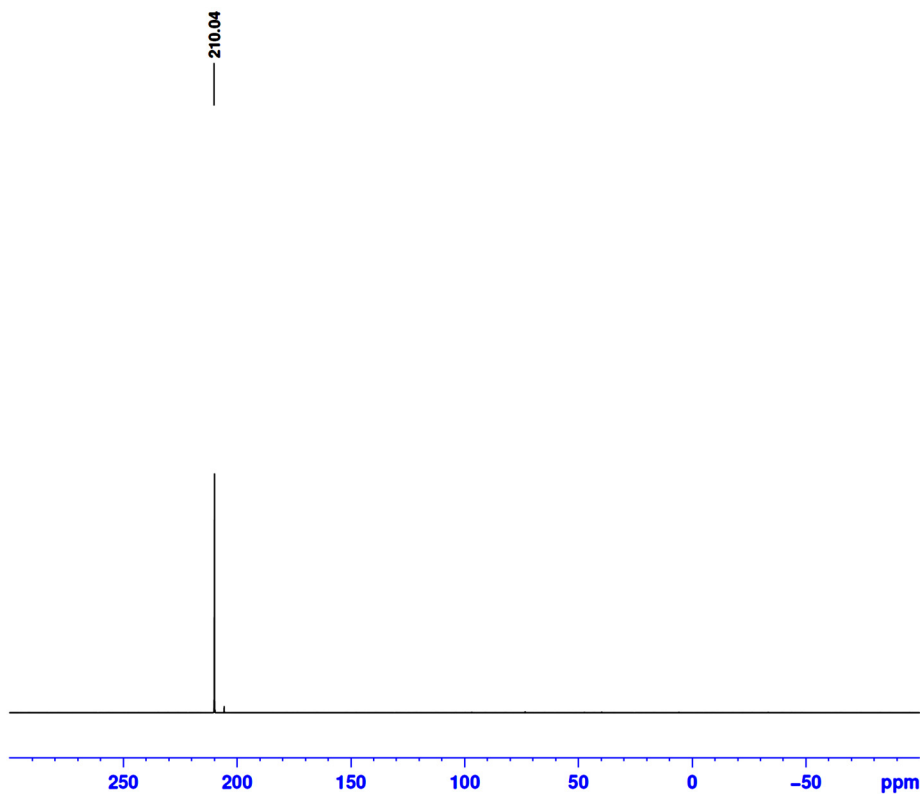
F2 - Acquisition Parameters
Date_         20110909
Time          12.52
INSTRUM       spect
PROBHD        5 mm BBO BB-1H
PULPROG       dept45
TD            65536
SOLVENT       C6D6
NS            37
DS            0
SWH           31847.133 Hz
FIDRES        0.485949 Hz
AQ            1.0289652 sec
RG            18390.4
DW            15.700 usec
DE            6.00 usec
TE            298.7 K
CNST2         60.0000000
D1            3.0000000 sec
d2            0.0083333 sec
d12           0.0002000 sec
DELTA         0.00001324 sec
MCREST        0.0000000 sec
MCWRK         0.00999999 sec

===== CHANNEL f1 =====
NUC1          29Si
P1            10.40 usec
p2            20.80 usec
PL1           0.00 dB
SFO1          79.4747080 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
P3            13.00 usec
p4            26.00 usec
PCPD2         80.00 usec
PL2           3.00 dB
PL12          18.78 dB
SFO2          400.0316001 MHz

F2 - Processing parameters
SI            32768
SF            79.4746818 MHz
WDW           EM
SSB           0
  
```

Figure S3. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **5** at 299 K in C_6D_6 .



```

Current Data Parameters
NAME          FH-135-5
EXPNO         2
PROCNO        31

F2 - Acquisition Parameters
Date_         20110908
Time          21.32
INSTRUM       spect
PROBHD        5 mm BBO BB-1H
PULPROG       zgpg30
TD            65536
SOLVENT       C6D6
NS            86
DS            4
SWH           64935.066 Hz
FIDRES        0.990830 Hz
AQ            0.5046772 sec
RG            10321.3
DW            7.700 usec
DE            6.00 usec
TE            300.0 K
D1            2.0000000 sec
d11           0.0300000 sec
MCREST        0.0000000 sec
MCWRK         0.00999999 sec

===== CHANNEL f1 =====
NUC1          31P
P1            9.60 usec
PL1           5.00 dB
SFO1          161.9512855 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
P3            80.00 usec
PL2           3.00 dB
PL12          18.78 dB
PL13          18.80 dB
SFO2          400.0316001 MHz

F2 - Processing parameters
SI            32768
SF            161.9350268 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
  
```

Figure S4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** at 300 K in C_6D_6 .

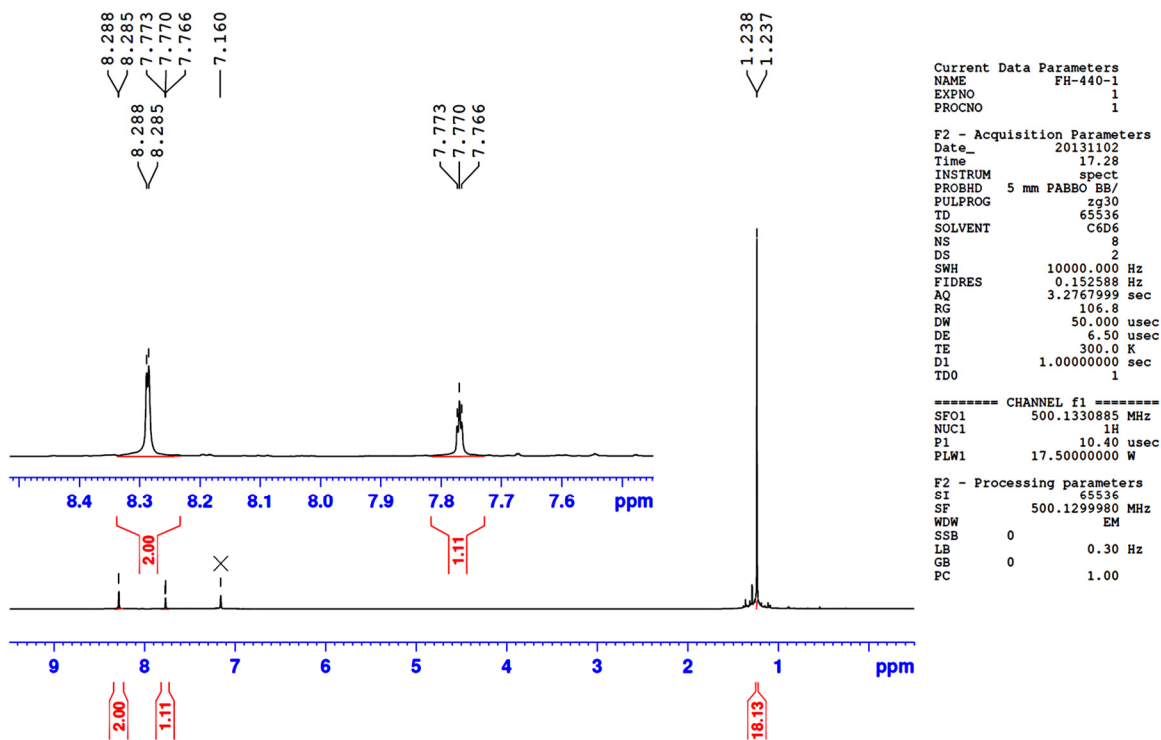


Figure S5. ^1H NMR spectrum of **2b** at 300 K in C_6D_6 ($\times = \text{C}_6\text{D}_5\text{H}$).

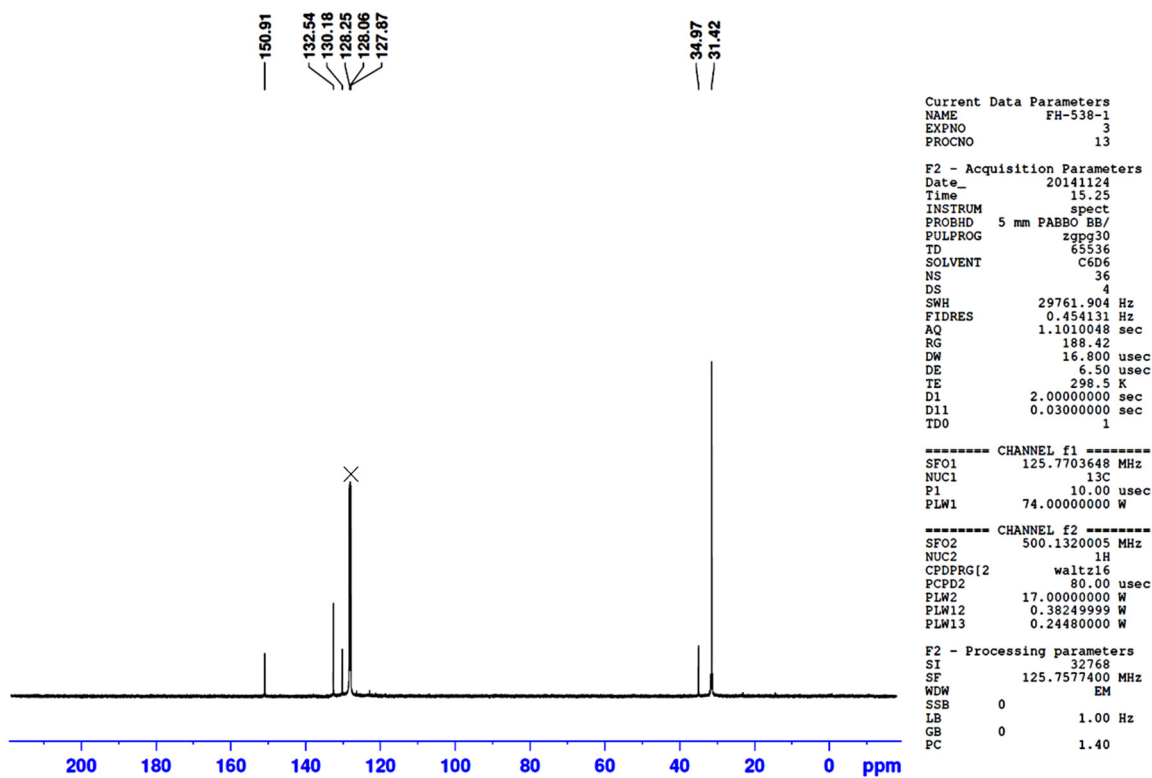
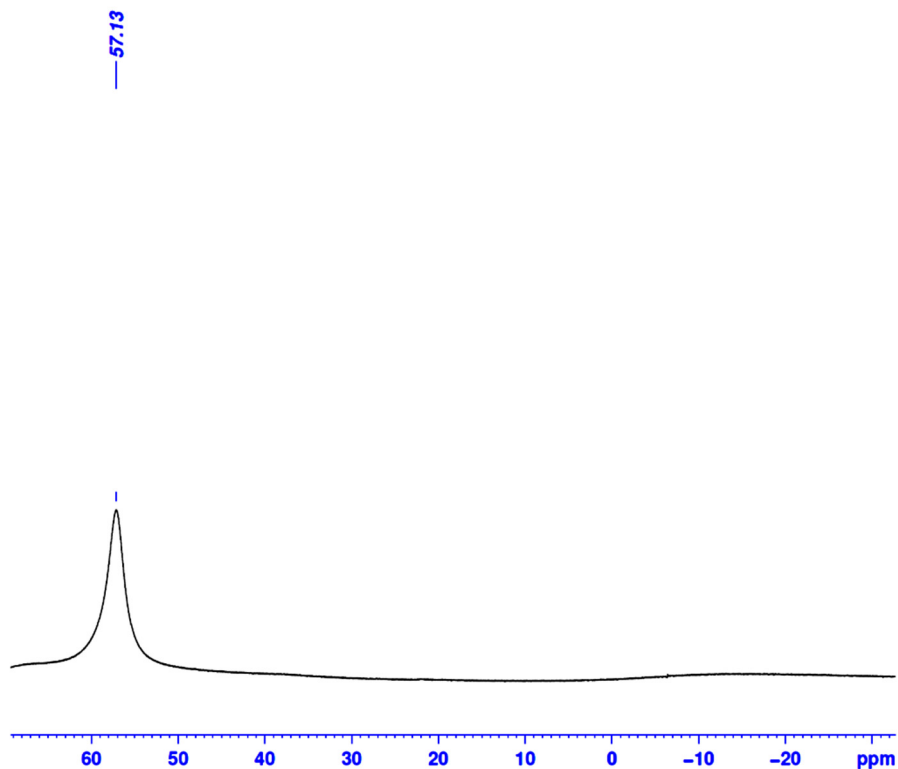


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2b** at 299 K in C_6D_6 ($\times = \text{C}_6\text{D}_6$).



```

Current Data Parameters
NAME      FH-538-1
EXPNO    2
PROCNO   11

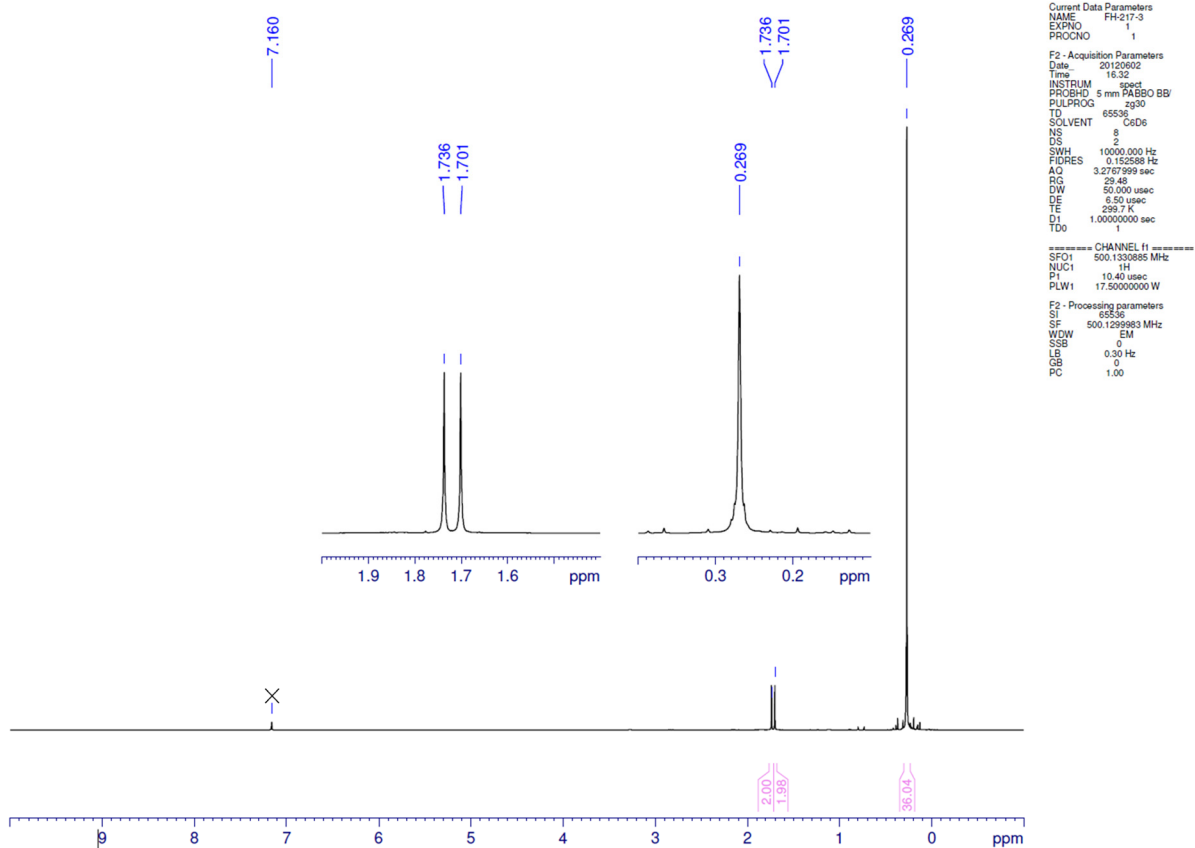
F2 - Acquisition Parameters
Date_    20141124
Time     15.23
INSTRUM spect
PROBHD   5 mm PABBO BB/
PULPROG zg
TD       65536
SOLVENT  C6D6
NS       128
DS       4
SWH      32467.533 Hz
FIDRES   0.495415 Hz
AQ       1.0092545 sec
RG       188.42
DW       15.400 usec
DE       7.24 usec
TE       298.2 K
D1       0 sec
TD0      1

===== CHANNEL f1 =====
SFO1    160.4566109 MHz
NUC1    11B
P1      17.70 usec
PLW1    46.00000000 W

F2 - Processing parameters
SI      32768
SF      160.4616516 MHz
WDW     EM
SSB     0
LB      1.00 Hz
GB      0
PC      1.40

```

Figure S7. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **2b** at 298 K in C_6D_6 .



```

Current Data Parameters
NAME      FH-217-3
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20120602
Time     16.32
INSTRUM spect
PROBHD   5 mm PABBO BB/
PULPROG zg30
TD       65536
SOLVENT  C6D6
NS       8
DS       2
SWH      100000.000 Hz
FIDRES   0.152598 Hz
AQ       3.2767899 sec
RG       29.48
DW       50.000 usec
DE       6.50 usec
TE       299.7 K
D1       1.00000000 sec
TD0      1

===== CHANNEL f1 =====
SFO1    500.1330885 MHz
NUC1    1H
P1      10.40 usec
PLW1    17.50000000 W

F2 - Processing parameters
SI      85536
SF      500.1299983 MHz
WDW     EM
SSB     0
LB      0.30 Hz
GB      0
PC      1.00

```

Figure S8. ^1H NMR spectrum of **3a** at 300 K in C_6D_6 ($\times = \text{C}_6\text{D}_5\text{H}$).

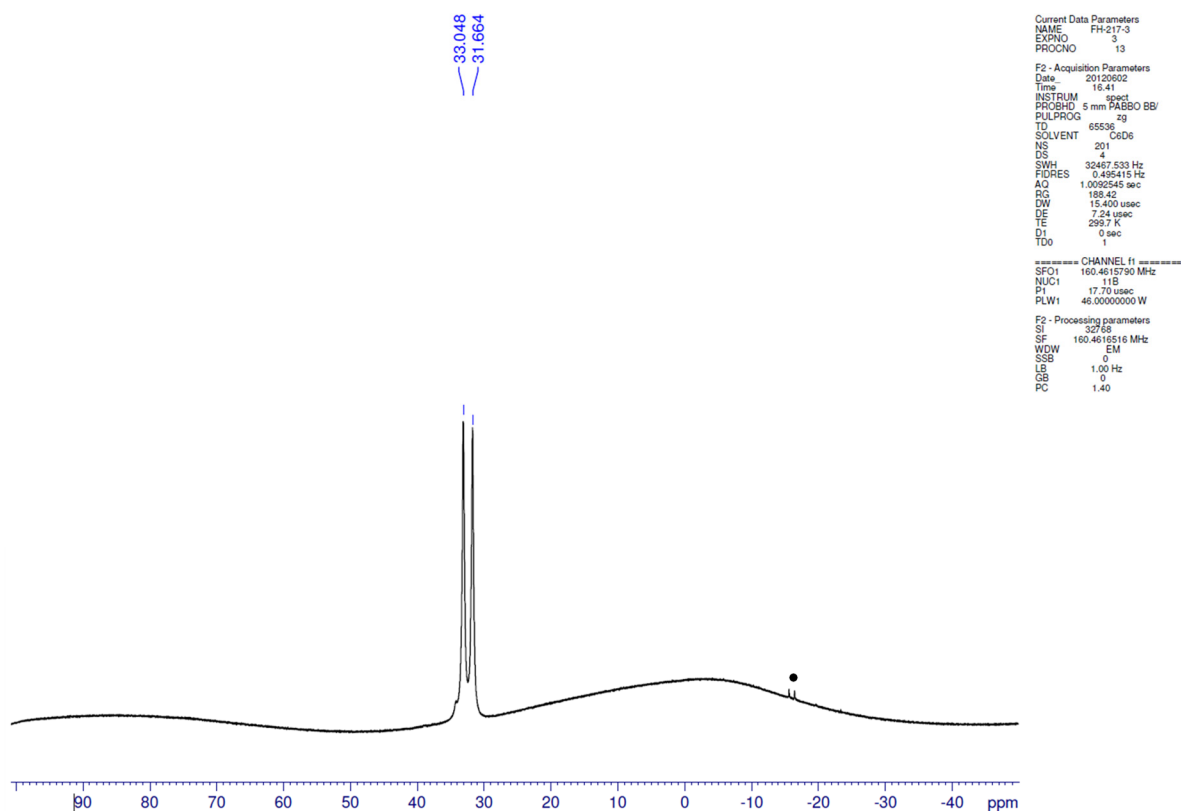


Figure S9. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **3a** at 300 K in C_6D_6 (• = impurity).

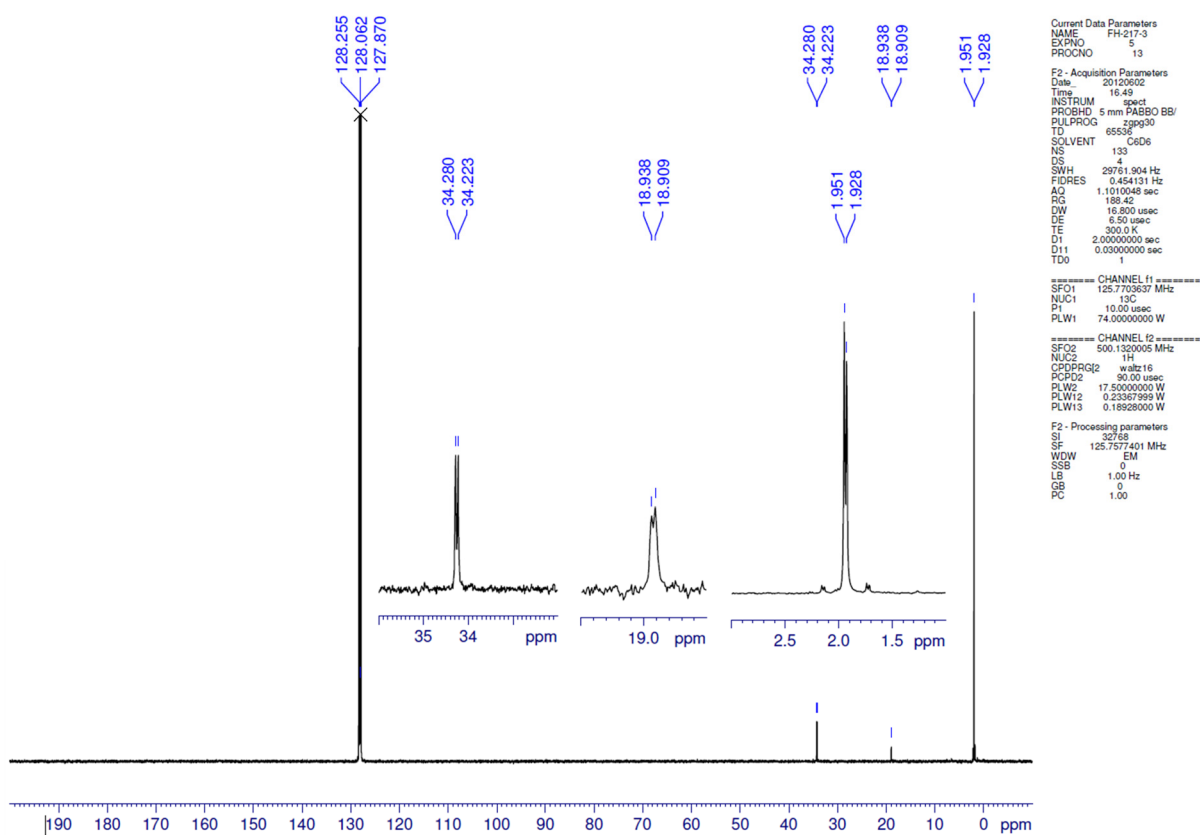


Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3a** at 296 K in C_6D_6 (x = C_6D_6).

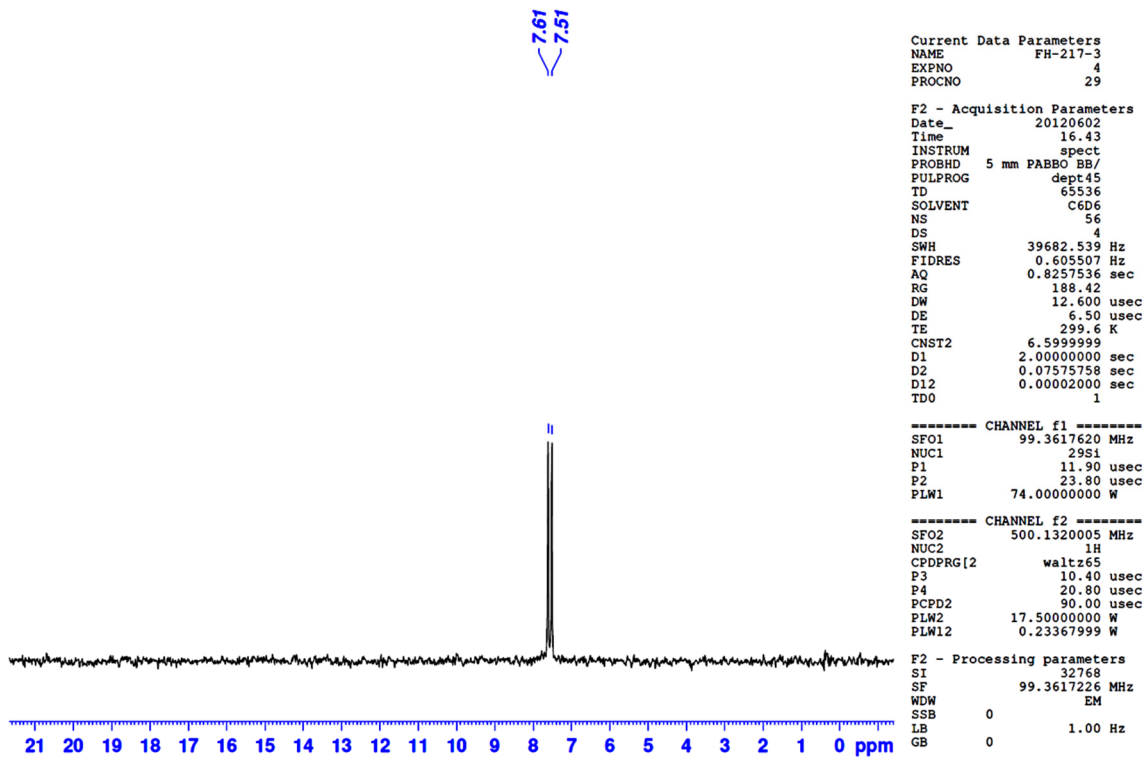


Figure S11. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **3a** at 300 K in C_6D_6 .

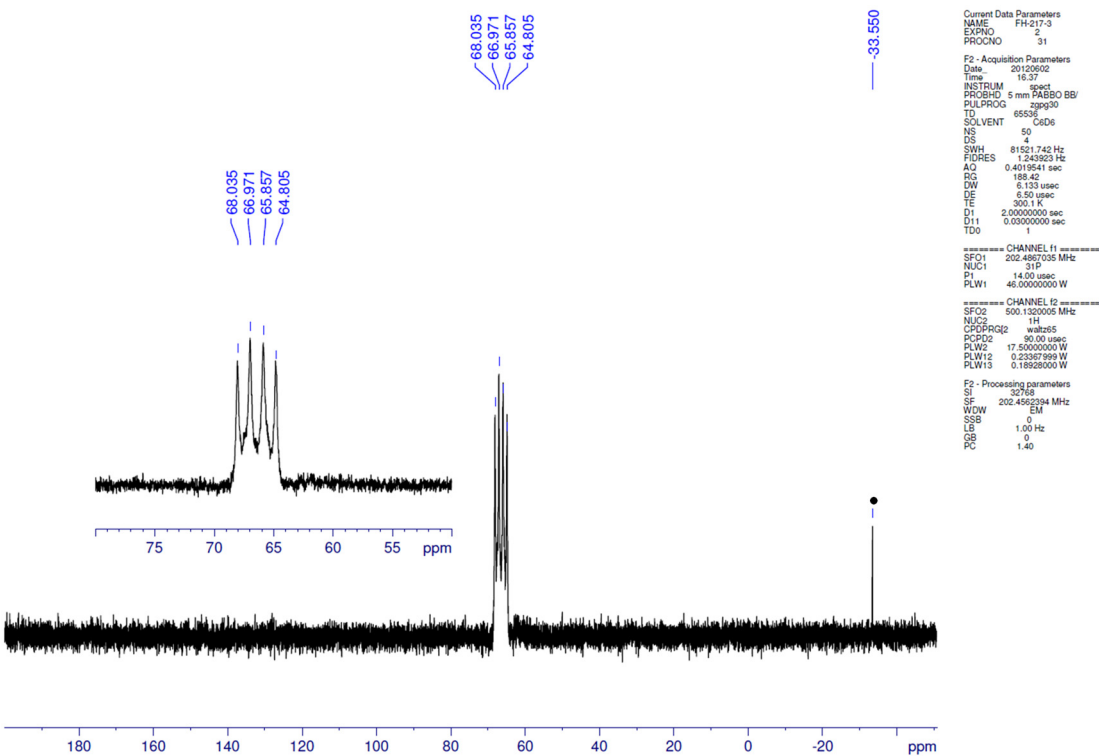


Figure S12. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3a** at 300 K in C_6D_6 . (● = impurity).

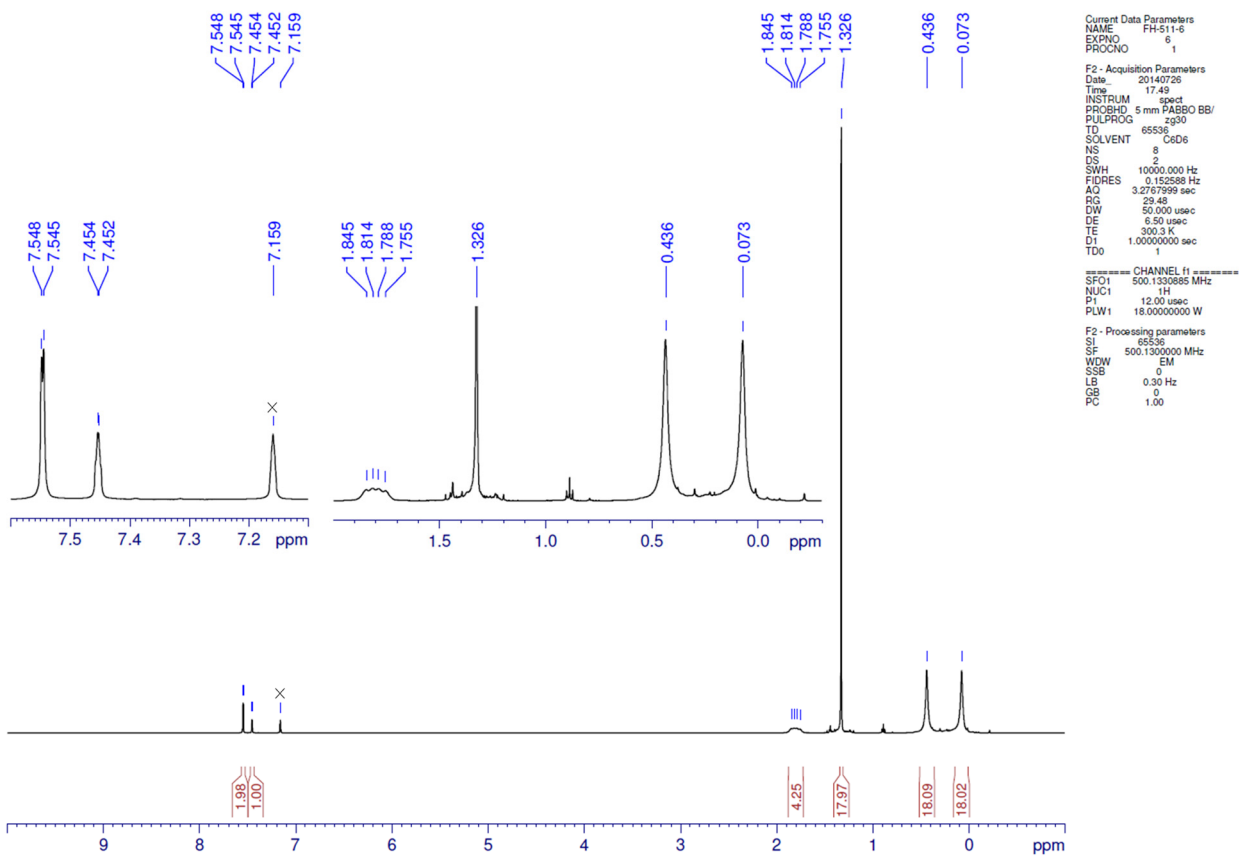


Figure S13. ^1H NMR spectrum of **3b** at 300 K in C_6D_6 ($\times = \text{C}_6\text{D}_5\text{H}$).

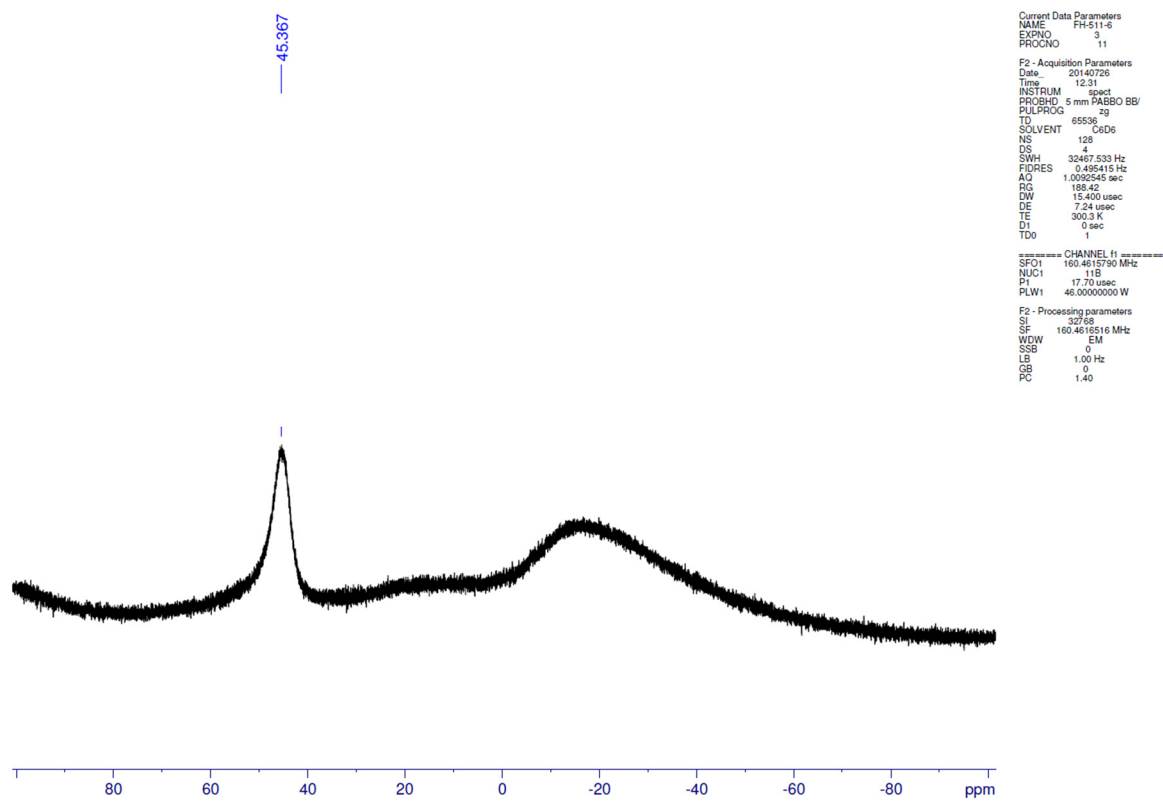


Figure S14. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **3b** at 300 K in C_6D_6 .

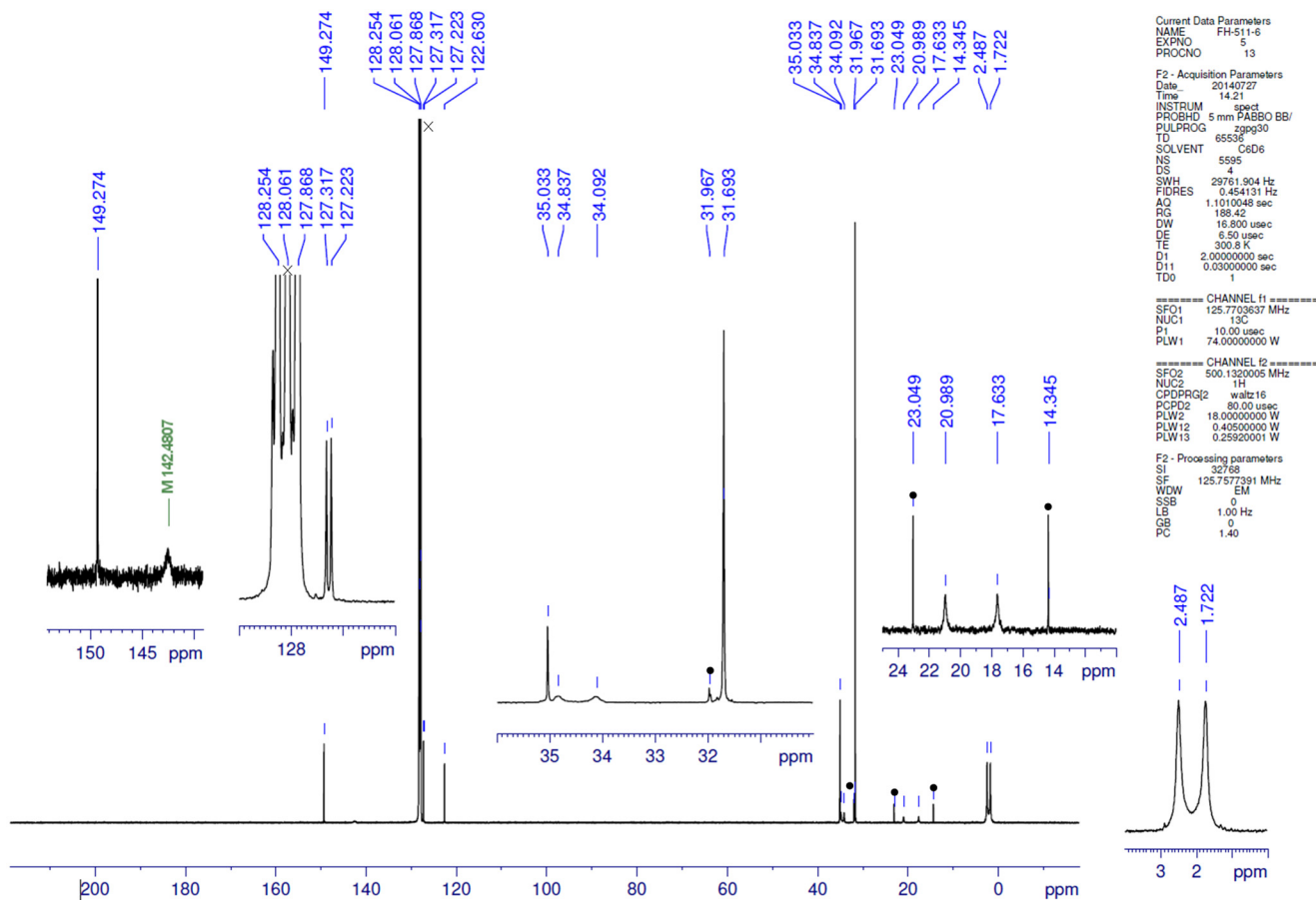


Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3b** at 301 K in C_6D_6 (x = C_6D_6 , • = hexane).

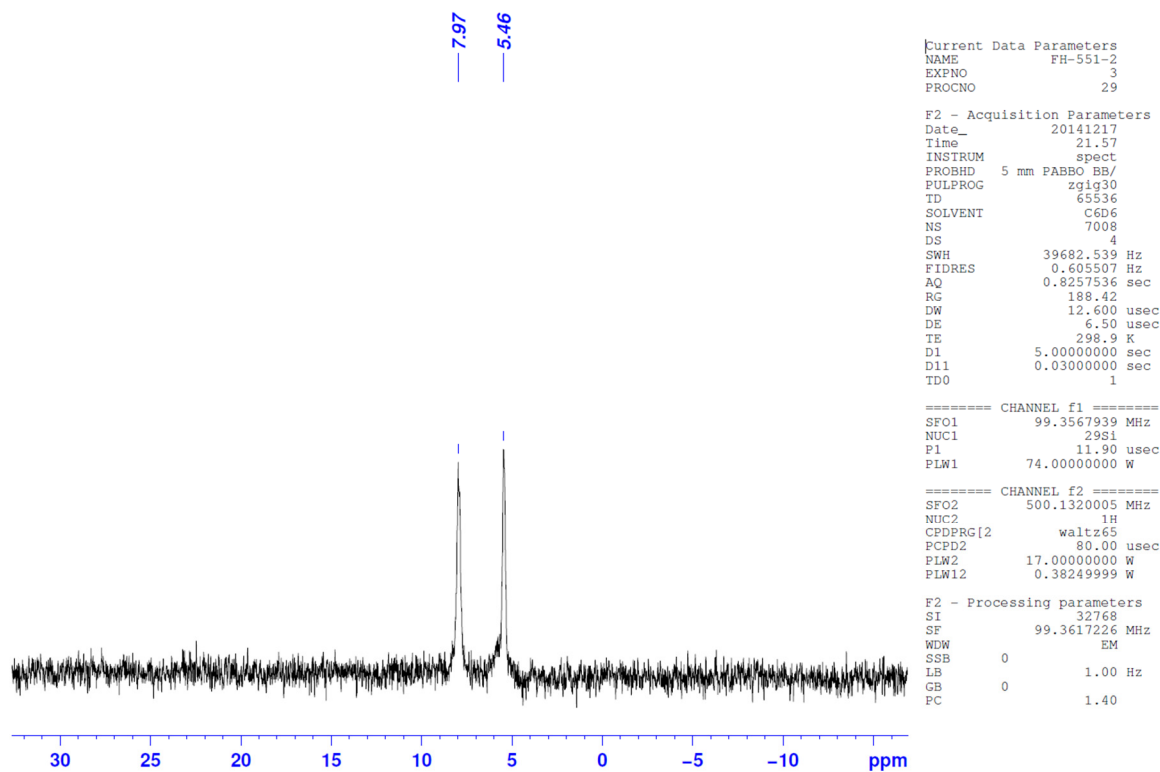


Figure S16. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **3b** at 299 K in C_6D_6 .

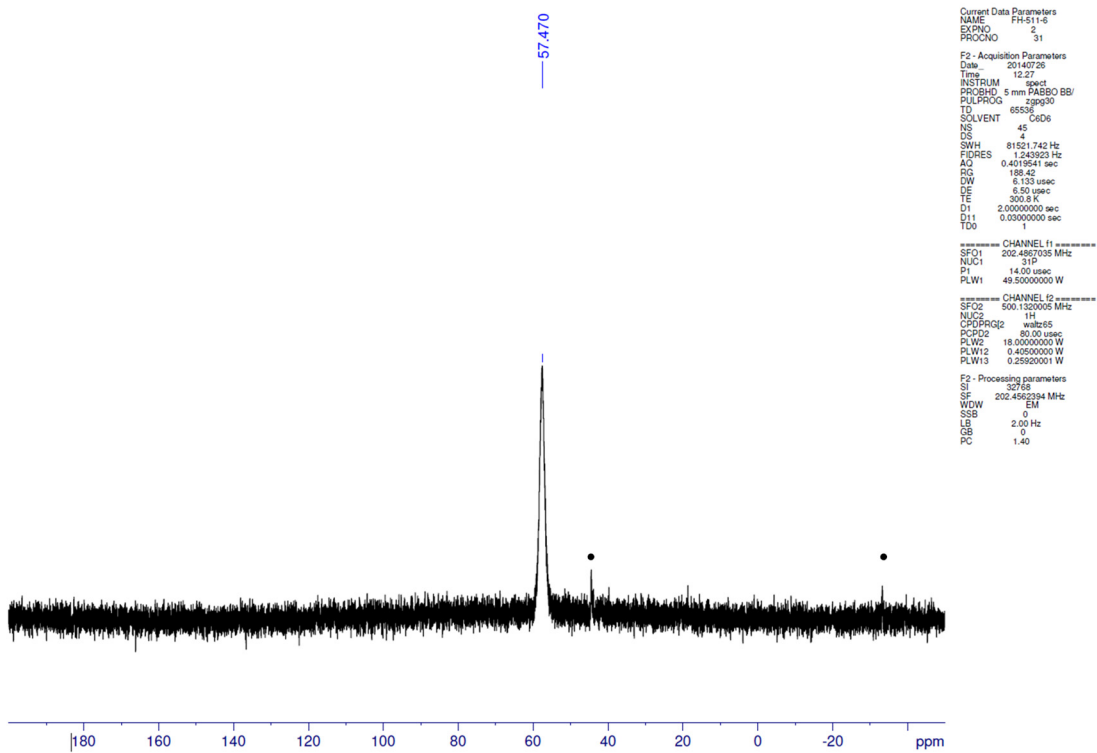


Figure S17. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3b** at 301 K in C_6D_6 (• = impurity).

2. Computational Study

Cartesian coordinates of the optimized structures with electron and Gibbs energies calculated at the (U)B3PW91-D3/6-31G(d) level of theory.

Table S1. Phosphinoborane **3a**, Enthalpie (0K) = -7300.689911786460, Gibbs Energy = -7300.756540114166 (298.150 K, 1.000 Atm)

P	0.036696044036	-0.119316748977	-0.304629443514
C	-1.366467657132	-1.291749793439	-0.036382759372
H	-0.624739996601	-2.610518575766	-0.419195840983
H	-1.169009390805	-3.487460262295	-0.046462610177
H	-0.581008607182	-2.715424538985	-1.509577032794
C	0.811440768009	-2.601464072377	0.141836140857
H	1.393892985452	-3.410809953698	-0.316264746836
H	0.767932402010	-2.834110041265	1.206620854599
C	1.511489336863	-1.216690851654	-0.084523781811
Si	-2.032826947769	-1.385296382586	1.774349524734
C	-0.992584423714	-2.482682543814	2.920262722476
H	0.025917313896	-2.134719302554	3.106364506738
H	-0.941461285342	-3.515052071134	2.554730722424
H	-1.509148824631	-2.510903653691	3.888473127877
C	-2.196780155502	0.302343606956	2.592899525725
H	-2.907119136752	0.959834616532	2.087012467361
H	-1.238059458637	0.829805812996	2.624836305480
H	-2.538281889712	0.156650414327	3.625158247635
C	-3.703653692731	-2.281500673022	1.804295198174
H	-4.040159834215	-2.333851878955	2.847610338555
H	-3.596904277106	-3.313181210140	1.449026271924
H	-4.496908577504	-1.802283469885	1.225833944415
Si	-2.805113877113	-0.993399955338	-1.302694565163
C	-4.241374999380	0.072686068394	-0.667731722723
H	-4.345043486215	0.955219999028	-1.307684161141
H	-4.123613260784	0.430947890712	0.356810605158
H	-5.177987229049	-0.495052767956	-0.721040910037
C	-3.517977975539	-2.684697911845	-1.769134499168
H	-4.346446886027	-2.534972407720	-2.472788556978
H	-3.914165488848	-3.227026211637	-0.904504102643
H	-2.780169605944	-2.780169605944	-2.263557067217
C	-2.177846859321	-0.184936370365	-2.885454408862
H	-1.384088546343	-0.757556897292	-3.373460172973
H	-1.807928344183	0.827112114437	-2.691375129130
H	-3.016154178240	-0.110049503845	-3.590371247155
Si	2.651112269114	-0.767586198993	1.409184722792
C	3.300660634897	-2.388059843792	2.142368158408
H	4.108122043870	-2.465055188845	2.85047073104
C	3.706682882071	-3.053351174242	1.372860230227
H	2.527558083766	-2.938644872744	2.689806773180
C	4.147105635436	0.282749798178	0.938670601494
H	3.840899405322	1.215726585298	0.459919470323
H	4.860737064158	-0.227063153375	0.284868992718
H	4.674457735726	0.542888125452	1.865348262070
C	1.754467126524	0.185268129289	2.768326676276
C	2.387575613415	0.192791690128	3.664766137852
H	0.790373131999	-0.246657134246	3.044130432535
H	1.584047612025	1.222724997173	2.467727182774
Si	2.501409783446	-1.284899716849	-1.734351034120
H	1.443430857856	-1.98602537975	-3.132747036438
H	0.568634843275	-1.360743562962	-3.331458124502
H	1.106242448292	-3.009581586724	-2.936918153623
C	2.049002356560	-2.010385548782	-4.047454888739
C	3.943346829373	-2.498033000590	-1.537344993799
H	3.592023924864	-3.499677724319	-1.262397741046
H	4.679117194399	-2.185994416915	-0.790014318821
H	4.465918352835	-2.589392369206	-2.497685389367
C	3.141615229249	0.405511033130	-2.278272504441
H	3.117014931164	0.474219746954	-3.371986263172
H	4.174902572081	0.566510858518	-1.954871063031
H	2.541446444225	1.226618960800	-1.876805187853
B	-0.079730491996	1.655486979401	-0.020049662507
Br	-1.820110144857	2.468408366212	-0.165801853833
Br	1.479021872071	2.774685604799	0.129802083509

Table S2. Phosphinoborane **3b**, Enthalpie (0K) = -5274.658585207984, Gibbs Energy = -5274.739646212006 (298.150 K, 1.000 Atm)

Br	-0.641568495351	-2.773152774838	-1.131293682569
P	-1.142676931839	0.141119744456	0.190299003535
Si	-3.804533965927	-0.561135751022	-1.405421367621
Si	-0.657084757450	2.981672717728	-1.134162266679
Si	-3.569206982515	-1.017435771047	1.750085686565
H	0.573009800771	2.317877589637	1.728169444039
C	5.791577260698	-0.912984732864	-2.659286251824
H	6.430836635787	-0.569783335757	-3.482071663320
H	5.396988972681	-1.901178039775	-2.921041121350
H	6.425786116661	-1.029688786715	-1.774214512927
H	4.325180975339	-0.648331188926	-0.013057009769
H	5.394918216286	-0.502682674513	-0.111609923932
C	3.758338209261	-0.403084079475	-1.269687876406
C	-2.994558195109	0.039861330172	0.039861330172
C	2.378730820735	-0.575714728649	-1.403841528948
H	1.902245394846	-0.413424199987	-2.3629295631881
C	-2.211710203119	2.300101609940	2.300101609940
C	-2.155862857666	2.037761974390	2.257314824317
C	-2.411354774113	3.379200177836	1.153132270384
C	1.577116769366	-0.934151855751	-0.313351156618
C	-0.865853636270	1.957000675572	0.490044030555
C	3.574189694330	-1.071235480787	1.088664998141
C	-2.288714363057	3.340281447978	-2.028977881947
H	-2.951282584143	3.956543424836	-1.409635672308

H	-2.845611114326	2.460572687214	-2.356126201150
H	-2.047670961266	3.927346163318	-2.924620989087
C	-2.690188368510	-0.332950290408	-2.913005123738
H	-2.226632420388	0.653729468180	-2.978754504887
H	-3.293707701242	-0.482757451176	-3.817541857502
H	-1.889353909718	-1.077157048326	-2.911194057783
C	4.268156923319	-1.326781765396	2.431105165798
C	2.267159626325	2.367706039672	0.906221778908
H	3.038939362520	2.532638289612	1.675710669494
H	2.357755338478	3.179069925863	0.177480077281
H	2.508656319425	1.430874523092	0.400745122564
C	-3.375165448094	1.531588429007	0.538504480437
H	-3.648179417274	2.0452456822494	-0.385350263361
C	-4.262585437622	1.589469376335	1.180852718736
H	0.576258345975	1.059650883446	3.136155393238
H	0.455249781813	0.033008800282	2.783822695133
H	-0.224542678421	1.274168874920	3.852188423414
H	1.528672593875	1.126012058720	3.675923870800
C	4.644833584005	0.086259851108	-2.419775734528
C	4.828939317984	0.006616444141	0.006616444141
H	5.340728009909	-0.143657675218	3.919459395934
H	4.020708674250	0.730775927549	3.112696116618
H	5.546080549115	0.450355116598	2.261340880919
C	0.263937244477	3.980168802588	2.581591029187
H	0.988901314741	4.081540206126	3.399372676467
H	-0.735795136400	4.024243872457	3.028532022759
H	0.383514135366	4.846564867800	1.927037914640
C	-0.031183519885	4.733208480407	-0.766898611431
H	0.977639705833	4.781446208833	-0.349046297874
H	-0.707771197360	5.262159701934	-0.086036777456
H	-0.023579172417	5.288852850710	-1.713220276449
C	3.309672521943	-1.899895989342	3.483651317631
H	2.868121767453	-2.847123971974	3.153043895916
H	2.496136495663	-1.205450700922	3.719293421530
H	3.856382808791	-2.09359446345	4.413659446345
C	2.194029200742	-1.201967922238	0.915919706748
H	1.570874811406	-1.522210510713	1.742827407092
C	-4.305988887127	-2.380883361306	-1.398196257694
H	-4.683317982804	-2.626384473765	-2.399120588581
H	-5.096405679879	-2.616412073527	-0.679751340459
H	-3.448295133678	-3.027177739987	-1.199145640563
C	-5.387181848408	0.646958073180	-1.673596915698
H	-5.181654263248	1.481387402522	-1.970431052006
H	-6.014644108802	0.472565681526	-0.775795247
H	-5.973872310471	-0.014084380209	-2.477609757637
C	0.530823641317	2.142577696705	-2.322857284027
H	0.671013207291	2.764894657664	-3.214967509397
H	0.147124360952	1.167819561818	-2.640193550181
H	1.508088563525	1.979815229917	-1.859529411677
H	5.419650665676	-2.331695963737	2.241069346147
C	5.918807150769	-2.523395287908	3.198878982414
H	6.177709405558	-1.963014975144	1.542309017602
H	5.042924883168	-3.285099653337	1.853996412875
C	-2.199027260257	-2.8114902453980	1.700074634025
H	-2.841129267794	-3.173837795685	2.723902831242
H	-2.050731341939	-2.928865978656	1.72526343748
H	-3.730016503554	-3.458665669671	1.218685598605
C	-2.967152657053	-0.274588298673	3.379059477341
H	-3.341870185818	0.050923398762	3.547016560606
H	-1.875927455092	-0.259069068174	3.44408595429
H	-3.340618463098	-0.899731513580	4.000144746805
C	-5.462751819771	-0.968909312949	1.841412323569
H	-5.787401074758	-1.551724170700	2.12569073561
H	-5.951903881374	-1.394616655141	0.960163196450
H	-5.842578088374	0.050923398762	1.973975078855
C	5.226188470239	1.461422423710	-2.037993560774
H	5.838040062223	1.405194295143	-1.131259078247
H	4.421812278043	2.18247778500	-1.851652439559
H	5.857503731192	1.850274133385	-2.846711381406
B	0.026805381735	-1.076154662454	-0.444150115496
C	3.864958051787	0.242590259869	-3.732179505783
H	3.061612496404	0.982774755104	-3.644422853259
H	3.423400946881	-0.707037497465	-4.055741254152
H	4.541724773523	0.582082188863	-4.524699729915

Table S3. Phosphinyl Radical-Borane Complex **6b**, Enthalpie (0K) = -7846.397476188886, Gibbs Energy = -7846.479885905918 (298.150 K, 1.000 Atm)

Br	0.633181709471	-1.700772311821	-2.187677336570
Br	0.268110570294	-2.674063393260	0.951365760105
P	1.078093663297	0.396882309077	0.112596392017
Si	0.467186466409	3.411546836875	0.370136346758
Si	3.722425339341	-1.317838404758	0.89537530109
Si	3.632281527657	0.565297273434	-1.676855667032
Si	0.551996568751	1.489428180852	2.682217078582
C	0.819432286986	1.758172376915	1.337557293113
C	2.911873697815	0.276575618014	0.121802146491
C	2.202514027362	1.066084353621	2.046003540883
H	2.379328878396	2.791060481910	2.498278549722
H	2.221267032065	1.079887614407	2.864876015033
C	-1.648869658350	-0.786976287207	-

H	1.722434254890	5.152173436469	-0.810457145905				
H	2.598949480413	3.638535391975	-1.027432480009	P	-0.003698694266	-0.047915808287	-1.047985750753
H	2.716027018586	4.524463110390	0.504204777318	C	-1.383914319965	-0.069345216158	0.220985331581
C	-2.58965566468	-1.254353835099	0.477978154647	C	-0.694802399863	-0.369527275549	1.580086141570
H	-2.250418855286	-1.912212069990	1.267811477100	H	-1.291622776257	-0.016152081823	2.432194703399
C	-3.942328151277	-0.910766130639	0.399354740474	H	-0.582413667619	-1.45246752633	1.782665752633
C	3.455933726540	-2.928769478366	-0.048370120481	C	0.695557304287	0.282066187306	1.584671665074
H	3.257456306314	-3.734753454071	0.666098979359	H	1.302269986810	-0.093122811398	2.421103960323
H	4.359376812725	-3.183696071293	-0.612411553165	H	0.577151768666	1.762221757523	1.762221757523
C	2.612914804532	-2.893135342844	-0.739278322172	C	1.379649297275	0.030400151830	0.210044848476
C	-3.447971148448	0.384896614059	-1.624709311343	Si	-2.329474038008	1.614005307671	1.242266052092
C	-4.980453991825	-1.429270210742	1.4005046094969	C	-1.610484020377	2.826433142716	1.507170992977
C	-2.106051376282	0.021922632430	-1.499321257206	H	-0.601333124482	3.178119417214	1.280237665388
H	-1.389416651440	0.343858512992	-2.246784584617	H	-1.599105378448	2.396985913399	2.515814726784
C	-4.342328126741	-0.087069506419	-0.655323579829	C	-2.264560167701	3.707155906401	1.537404765207
H	-5.391644942687	0.182843401915	-0.740089245036	H	-0.340650275584	2.425820220321	-1.459550073302
C	-2.284329565479	1.793640286417	2.015325054269	H	-2.681990717712	1.739193413415	-2.241191065960
H	-2.463545697273	1.274060092103	1.072370561839	H	-1.342952411719	2.776937599063	-1.740200388459
H	-2.501557252167	2.855983164679	1.870340582494	H	-3.016317549566	3.290146044371	-1.450590591536
H	-3.008262754767	1.403875755369	2.740193409664	C	-4.127426236593	1.440880128026	0.819661362026
C	2.402202165025	1.400113061892	-2.841410051288	H	-4.47561551401098	2.44781686108	0.861540675726
H	2.914950280862	1.604325604735	-3.790257082267	H	-4.190688556457	1.0154400589872	1.827510345814
H	2.009575803105	2.349057545793	-2.467993693400	H	-4.756114706068	0.840088042175	0.156124289039
H	1.558636809376	0.735829267796	-3.048617903017	Si	-2.563850513502	-1.497045644017	-0.288359198358
C	-0.222697084934	4.776372580613	1.483022315807	C	-3.490350521711	-1.074220569295	-1.880240143448
H	0.472721944324	5.025455036071	2.291805100805	H	-2.782764304689	-0.864521780148	-2.691160679982
H	-1.200942735675	4.566151596741	1.920427645063	H	-4.154497481205	-0.209915331491	-1.782002785252
H	0.326152193308	5.671820896948	0.856758294684	H	-4.102808005698	-1.930801251882	-2.186942448252
H	5.134979337241	1.709187517097	-1.508903971882	C	-3.763150281040	-1.922680191029	1.113965037833
H	5.694443478191	1.679012512118	-2.451999628332	H	-4.200581261294	-2.910213683518	0.920691078432
H	5.813545214013	1.395348401204	-0.709222391470	H	-4.583291114080	-1.211077521084	1.232353794301
C	4.859219926601	2.753625289293	-1.327264828617	H	-3.228230487750	-1.984285586172	2.069667430166
C	-0.723811240800	3.111210687902	-1.050248810138	C	-1.628651846886	-3.110261378200	-0.609036562696
H	-1.644418701141	2.619872112276	-0.723338362898	H	-1.329424821666	-3.590326814364	0.328895936705
H	-0.271496988809	2.475997319265	-1.818103507827	H	-0.739326565263	-2.980579346545	-1.233439239991
H	-0.991276391798	4.067736163893	-1.515556874880	H	-2.302694229794	-3.806705176423	-1.124899363324
C	-3.975574537973	1.245096080877	-2.778798808358	Si	2.503895958455	1.511783593750	-0.281205925649
C	5.598052781303	-1.028981406713	0.922078305303	C	3.490103850708	2.094551436307	1.224491834888
H	5.906277700044	-0.155081815074	1.505896618115	H	4.092035261722	2.969436676665	0.949905253803
H	6.030997034119	-0.937784950140	-0.078926776266	H	4.167194313952	1.332317465550	1.619037691560
H	6.053322508853	-1.908983294112	1.393016553527	H	2.818858130685	2.399874612418	2.035664252930
C	-0.417665200325	-0.212853463510	3.466363672414	C	3.662524282590	1.103719930509	1.174397654117
H	-1.274249719587	-0.355082444075	4.137301449263	H	3.085534184524	0.783203152108	-2.592975875576
H	0.490192189786	-0.285409249957	4.076682153944	H	4.400191084914	0.327206264839	-1.494059978270
H	-0.404096390482	-1.037449789036	2.753170904851	H	4.208942128948	2.012110700806	-1.998314043278
C	-4.329464987283	-2.178865574472	2.571053838438	C	1.503807267521	3.002098950444	-0.877656591458
C	-3.616317554645	1.543341209649	3.109257088600	H	2.162381412732	3.878767323235	-0.926169772213
H	-3.799625683367	-3.077966181866	2.237840892045	H	0.667132773910	3.253085982979	-0.221295868224
H	-5.101148627702	-2.496349473731	3.281910345278	H	1.099766472074	2.828650436149	-1.880550453765
C	3.202071982628	-1.481868506555	2.701125742156	Si	2.397409986465	-1.602606526394	0.22594955427
C	3.651761171764	-2.394160519409	3.112731434298	H	1.587239515800	-2.934272562820	1.295932888284
C	2.118320066974	-1.577817977482	2.796457519802	C	0.640258297965	-3.288509656353	0.884827114080
C	3.549178844839	-0.641099079664	3.311574062936	H	1.415779572640	-2.592504570367	2.32922307860
B	-0.108782720383	-1.181951619994	-0.358852869691	H	2.267506417835	-3.793912193870	1.347227172707
H	-0.210333317587	2.665583689229	4.127912953958	C	4.094570466106	-1.363489192018	1.036197706268
H	-0.412548042245	3.719944714021	3.929193587260	C	3.989054509652	-0.996726006632	2.064207234471
H	0.823504531236	2.574327429345	4.480411294048	H	4.761922738398	-0.861603590220	0.501721317579
H	-0.859453960734	2.355718561523	4.957131955341	H	4.591698797021	-2.340418405106	1.088404203430
H	-5.790014791337	-0.254375536182	1.980149007231	H	2.621961872610	-2.319371483748	-1.505276916632
H	-6.522142460624	-0.621656181700	2.709717097725	H	3.245368463141	-3.220318625916	-1.448175667888
H	-6.342015873415	0.289129984459	1.206339599651	H	3.102404095015	-1.622035001446	-2.197564113847
H	-5.133365408753	0.461822835164	2.485634006450	H	1.656748529422	-2.604833856154	-1.938011997411
C	4.234716246875	-0.981611424065	-2.568006123208				
H	3.443318916875	-1.725363416401	-2.678291113339				
H	5.099288636780	-1.455219993506	-2.0944485805749				
H	4.541178964007	-0.666455758788	-3.573994441886				
C	-2.877528646712	1.613681759645	-3.785674143175				
H	-3.308918711594	2.208345666863	-4.599232434993	P	0.019552776025	-0.511945327615	-0.673270030746
H	-2.420491191209	0.724249686998	-4.230534078885	C	-1.420505228621	-0.409245040922	0.531912872958
C	-2.086041486120	2.21292794456	-3.324372000979	C	-0.742798514565	-1.152422096240	1.723713835452
H	-4.572028200195	-2.547497080387	-2.212395595686	H	-1.351752660910	-1.078279463659	2.634185113998
H	-3.809087755386	3.126006262486	-1.679641130583	H	-0.652753855896	-2.226800344438	1.510215295477
H	-5.390519536355	2.348395731435	-1.512170015167	C	0.664266119310	-0.570430643816	1.958820480924
H	-4.968773490498	3.17611055435	-3.022941255777	H	1.243128420105	-1.232495203860	2.617052568017
H	-5.934150781187	-2.393815362034	0.670456379153	C	0.563173128590	0.373714238470	2.500540380882
H	-6.691584859571	-2.784830066391	1.361551051335	C	1.390816394467	-0.343256835560	0.596979110431
H	-5.380857298527	-3.241333655570	0.250682679091	Si	-2.227494135111	1.241531127956	1.142005095762
H	-6.454178980896	-1.892975736367	-0.153623839699	C	-1.415510704543	1.949509154697	2.705540331500
C	-5.069319238641	0.466865638647	-3.535576257411	H	-0.388141367058	2.302859013675	2.600588685311
H	-5.451059057177	1.062976654501	-4.373736224961	H	-1.445372725253	1.223573961825	3.526927305036
H	-5.919088281741	0.220327922504	-2.890329414484	H	-2.024557799868	2.808165100734	3.016458316945
H	-4.669639338907	-0.471656090292	-3.935634283206	H	-2.398369460690	2.600563395820	-0.154096645721
				H	-2.790431083689	2.212400713653	-1.098771238910
				H	-1.464716385095	3.119851568729	-0.377547358887
				H	-3.116700129450	3.333296248284	0.235505290793
				H	-3.994834077633	0.932166934009	1.75848522017
				H	-4.334562644552	1.863193963134	2.227518965610
				H	-4.056552769682	0.140489556668	2.509275528978
				H	-4.700683651365	0.699206079286	0.953162862836
				Si	-2.742172037053	-1.540238494655	-0.316610699681
				H	-3.515033483220	-0.572090503038	-1.741129041246
				H	-4.075584295075	-1.241861078332	-2.403538219140
				H	-2.731456469802	-0.085338583071	-2.335465889519
				H	-4.202241357691	0.207639723950	-1.394913734188
				H	-4.037066806479	-2.195782343764	0.904098826515
				H	-4.01851119790	-3.162613559244	0.536941897553
				H	-4.902233220535	-1.541651477237	1.031723998885
				H	-3.597976772811	-2.369760590496	1.893715871040
				H	-1.976243987974	-3.121936039382	-1.022470207283
				H	-1.518656709443	-3.735767510325	-0.237954272458
				H	-1.226659143213	-2.937495167243	-1.795995989753
				H	-2.786958083732	-3.717184086932	-1.462966945772
				Si	2.439374269467	1.268765290491	0.663296561741

Table S4. Dibromoboryl Radical **7a**, Enthalpie (0K) = -5168.211579188337, Gibbs Energy = -5168.239594074004 (298.150 K, 1.000 Atm)

Br	-1.679217168708	-0.055125449096	0.000000000000
Br	1.679212594406	-0.055127752184	0.000000000000</

C	3.321043662337	1.308830508439	2.338835460496	H	-4.522268231785	0.238921981848	1.272942540285
H	3.989709575960	2.178649513239	2.363418511055	H	-3.170931318078	1.098671241146	0.512811051941
H	3.920542762099	0.420489233553	2.552392857067	C	4.237677717764	0.632455790866	0.243499277320
H	2.600316178515	1.432038788559	3.156002172840	H	4.182202312261	1.71585628951	0.389525276758
C	3.702098160652	1.363131425947	-0.734167302159	H	4.083660407778	0.445863097551	-0.822205339837
H	3.196022537188	1.309416847245	-1.704002639931	H	5.258907907280	0.303842481584	0.504455979228
H	4.465651019771	0.580933636662	-0.698803803334	C	-1.451421865736	-1.904981499218	-2.706321485456
H	4.212474662369	2.332669776388	-0.676809428637	H	-2.125697019171	-2.271487970818	-3.491111235442
C	1.435929918265	2.874633990525	0.591540533984	H	-0.514207374203	-2.459139392658	-2.793330770279
H	1.799623027074	3.564484112341	1.363048285384	H	-1.248674268414	-0.848297028290	-2.904035623768
H	0.369513835848	0.721867016363	0.752419335612	C	4.203263809584	-2.679874356529	-0.726147339602
H	1.548376888258	3.355050907619	-0.384517367030	H	4.262836053840	-3.437592788767	0.062687682270
Si	2.506967155497	-1.839789867564	0.114500295020	H	4.885053374808	-1.864549826263	-0.475692212347
C	1.605563502520	-3.470662272627	0.434574113559	H	4.571402540937	-3.147259134210	-1.648812899033
H	0.727052321633	-3.586663782257	-0.206070893572	C	-2.646193898053	-3.978956713540	-0.793259120953
H	1.291553896852	1.479495503176	1.479495503176	H	-3.439159179081	-4.287966155832	-1.485230740040
H	2.289870585456	-4.299594289538	0.213847298818	H	-2.982498895082	-4.207641435509	0.223088632521
C	4.078144612404	-1.929905927180	1.165407588121	H	-1.92768301008807	-4.598391452595	-1.005551879717
H	3.844777058594	-1.963429369168	2.235968158491	C	2.331143464596	-1.084813862618	-2.597102844648
H	4.765208239226	-1.095730026003	0.991912751226	H	2.300749350334	-0.016193222853	-2.365967037507
H	4.611854815780	-2.856043834445	0.917313991390	H	1.433222838948	-1.304764934199	-3.183908312784
C	2.980889351226	-1.754513973985	-1.719143215169	H	3.203024821990	-1.275609216243	-3.234076548233
H	2.850066241092	-2.739871999948	-2.181101804762	C	-3.517671375576	-2.3088029296393	2.381250509250
H	4.028002001194	-1.460374838444	-1.846446504346	H	-2.974924423514	-3.198843771433	2.715387988892
H	2.364646286024	-1.046776660499	-2.284224922687	H	-4.202889146500	-2.608456650323	1.582340828910
Br	0.063395305294	1.317012912568	-2.014010095321	H	-4.131293370466	-1.966869900992	3.224910963091

Table S8. Phosphinyl Radical Borane Complex **6a**,
Enthalpie (0K) = -9872.420553797187,
Gibbs Energy = -9872.487714435456 (298.150 K, 1.000 Atm)

Br	-1.669709320577	1.647004500600	-1.732773272581
Br	-0.704667566871	2.474493279216	1.305963077229
P	0.096074884969	-0.411388902110	-0.117311939619
Si	2.412313075032	-2.167684720376	-1.056618411792
Si	-2.384503306961	-0.871666383708	1.885900435146
Si	-2.315954373593	-2.131189219717	-1.044912718745
Si	2.981757207117	-0.211698529338	1.382035056195
C	1.609085527775	-1.257832618328	0.475955199356
C	-1.224149357755	-1.5282641099531	0.467237558989
C	0.999654806289	-2.259438180773	1.502569155309
H	1.658938510009	-3.124048322602	1.649835013932
H	0.907998128552	-1.769185016297	2.479502668223
C	-0.388422654045	-2.726287675159	1.040743813086
H	-0.915606197243	-3.206378796081	1.872659534695
H	-0.265454632114	-3.503386142791	0.284896200621
C	1.589318472284	-3.835730930580	-1.409892955382
H	2.130021757442	-4.290370079343	-2.250154409797
H	0.536305300468	-3.782034194421	-1.693481408438
H	1.682740763643	-4.520676828429	-0.559139977195
C	-3.492174561817	0.580907320139	1.417838295353
H	-3.483746587009	1.315494683690	2.229592470554

H	-4.522268231785	0.238921981848	1.272942540285
H	-3.170931318078	1.098671241146	0.512811051941
C	4.237677717764	0.632455790866	0.243499277320
H	4.182202312261	1.71585628951	0.389525276758
H	4.083660407778	0.445863097551	-0.822205339837
H	5.258907907280	0.303842481584	0.504455979228
C	-1.451421865736	-1.904981499218	-2.706321485456
H	-2.125697019171	-2.271487970818	-3.491111235442
H	-0.514207374203	-2.459139392658	-2.793330770279
H	-1.248674268414	-0.848297028290	-2.904035623768
C	4.203263809584	-2.679874356529	-0.726147339602
H	4.262836053840	-3.437592788767	0.062687682270
H	4.885053374808	-1.864549826263	-0.475692212347
H	4.571402540937	-3.147259134210	-1.648812899033
C	-2.646193898053	-3.978956713540	-0.793259120953
H	-3.439159179081	-4.287966155832	-1.485230740040
H	-2.982498895082	-4.207641435509	0.223088632521
H	-1.92768301008807	-4.598391452595	-1.005551879717
C	2.331143464596	-1.084813862618	-2.597102844648
H	2.300749350334	-0.016193222853	-2.365967037507
H	1.433222838948	-1.304764934199	-3.183908312784
H	3.203024821990	-1.275609216243	-3.234076548233
C	-3.517671375576	-2.3088029296393	2.381250509250
H	-2.974924423514	-3.198843771433	2.715387988892
H	-4.202889146500	-2.608456650323	1.582340828910
H	-4.131293370466	-1.966869900992	3.224910963091
C	2.260091793066	1.063919451898	2.552460730458
H	3.082338249288	1.452357581187	3.167241949163
H	1.512580711725	0.638532739448	3.229722626982
H	1.804961137773	1.901701470879	2.022567902940
C	-1.360393986267	-0.448646510852	3.411143728913
H	-2.040318054210	-0.108204111960	4.202271800174
H	-0.669173897563	0.370615093087	3.198654950210
H	-0.802728698459	-1.305330375289	3.804369682993
B	-0.182288068705	1.534650752243	-0.381757789234
C	3.906901545805	-1.435008729407	2.493624038907
H	4.365679751863	-2.270450589013	1.959431814829
H	3.256783891937	-1.843374326289	3.274968358805
H	4.711355538572	-0.884345403295	2.997781285775
C	-3.987352114529	-1.278731539380	-1.211071347353
H	-3.881430993027	-0.201411816064	-1.358362387865
H	-4.663214540529	-1.452947528618	-0.369520206866
H	-4.464693583426	-1.692972903071	-2.108663716909
Br	1.553008255101	2.242918144429	-1.075210056579

Table S9. Bromine Atom Br, Enthalpie (0K) = -2571.638975,
Gibbs Energy = -2571.655805 (298.150 K, 1.000 Atm)

Br	0	0	0
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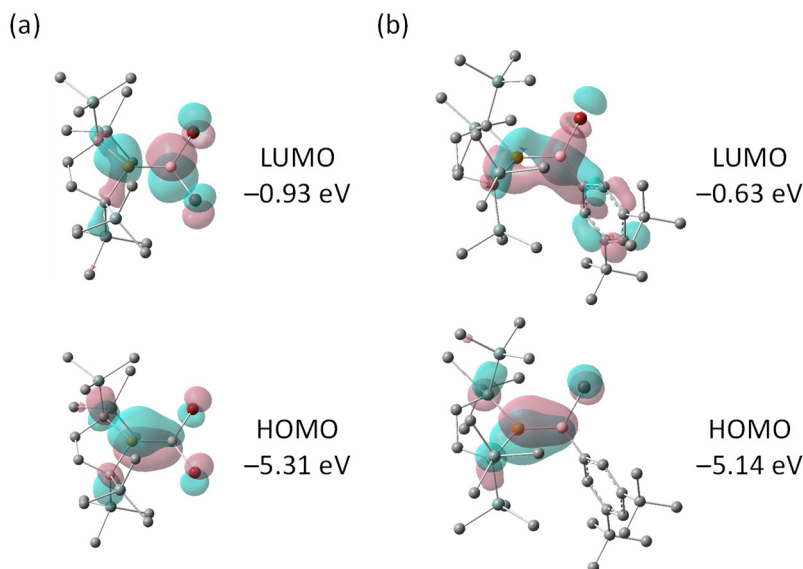


Figure S18. Frontier orbitals of (a) **3a** and (b) **3b** calculated at the B3PW91-D3/6-31G(d) level of theory (isosurface value: $0.04 e^- au^{-3}$).