Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis, Spectroscopic Characterisation and Transmetalation of Lithium and Potassium Diaminophosphanide-boranes

Markus Blum,[a] Julian Kappler,[a] Simon H. Schlindwein,[a] Martin Nieger[b] and Dietrich Gudat[a*]

[a] *Institut für Anorganische Chemie, Universität Stuttgart, 70550 Stuttgart, Germany. Fax: +49 711 685 4241; E-mail: gudat@iac.uni-stuttgart.de*

[b] *Department of Chemistry, University of Helsinki, P.O Box 55, 00014 University of Helsinki, Finland.*

Contents: Representation of ^{1}H, ^{31}P, ^{11}B NMR spectra of **2**, **5**, **6**, **8**, **9**, ^{1}H,^{7}Li HOESY and ^{1}H DOSY NMR spectra for **2**, and an ^{1}H NOESY NMR spectrum for **6**; ^{31}P NMR spectra of the thermolysis product of **8**; computed energies and atomic coordinates for $(Et_2N)_2P(BH_3)Li(OEt_2)_n$ (n = 0 – 3).

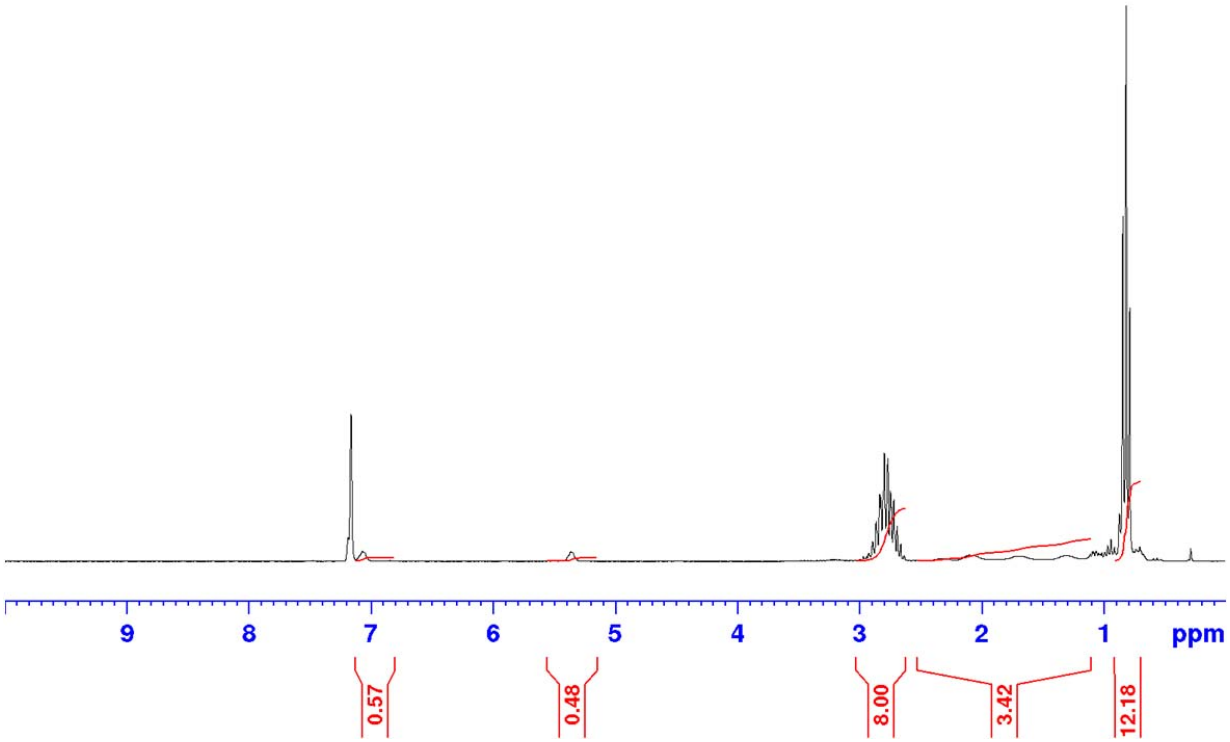

Fig. S1 ^{1}H NMR spectrum of **5** in C_6D_6

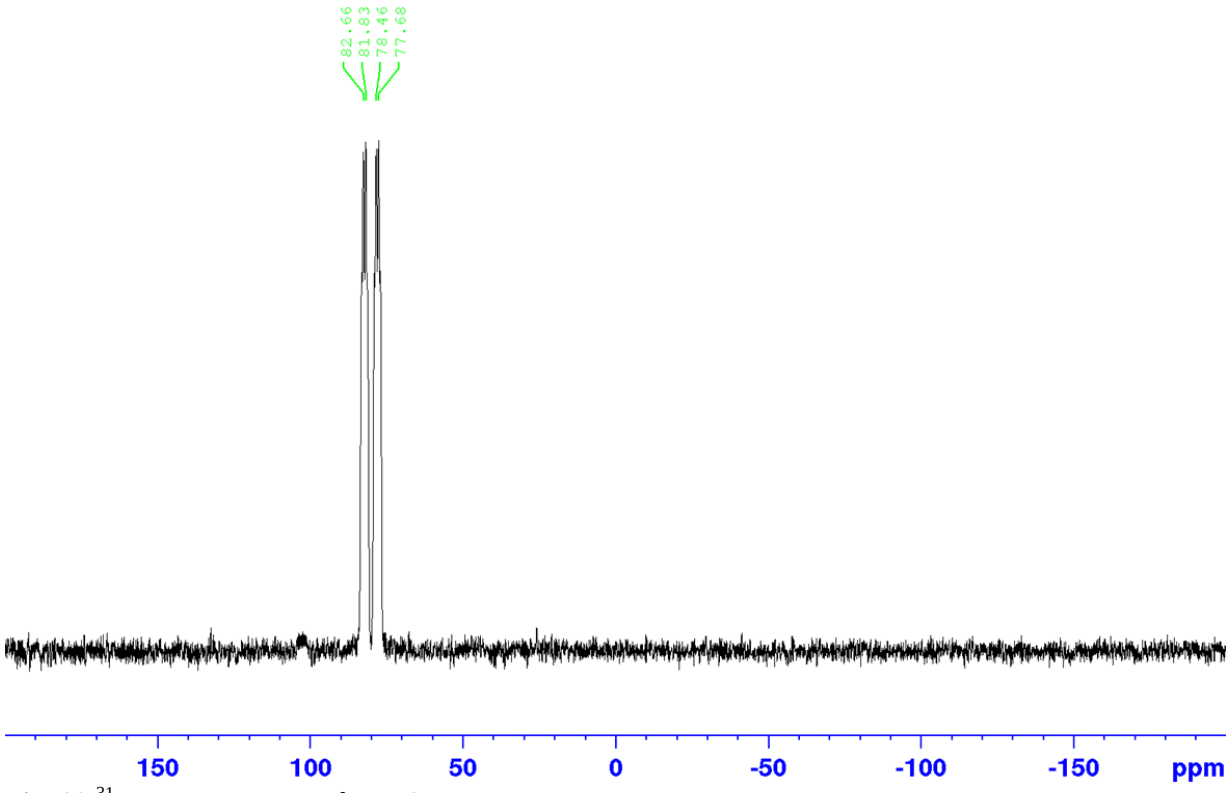

Fig. S2 ^{31}P NMR spectrum of **5** in C_6D_6

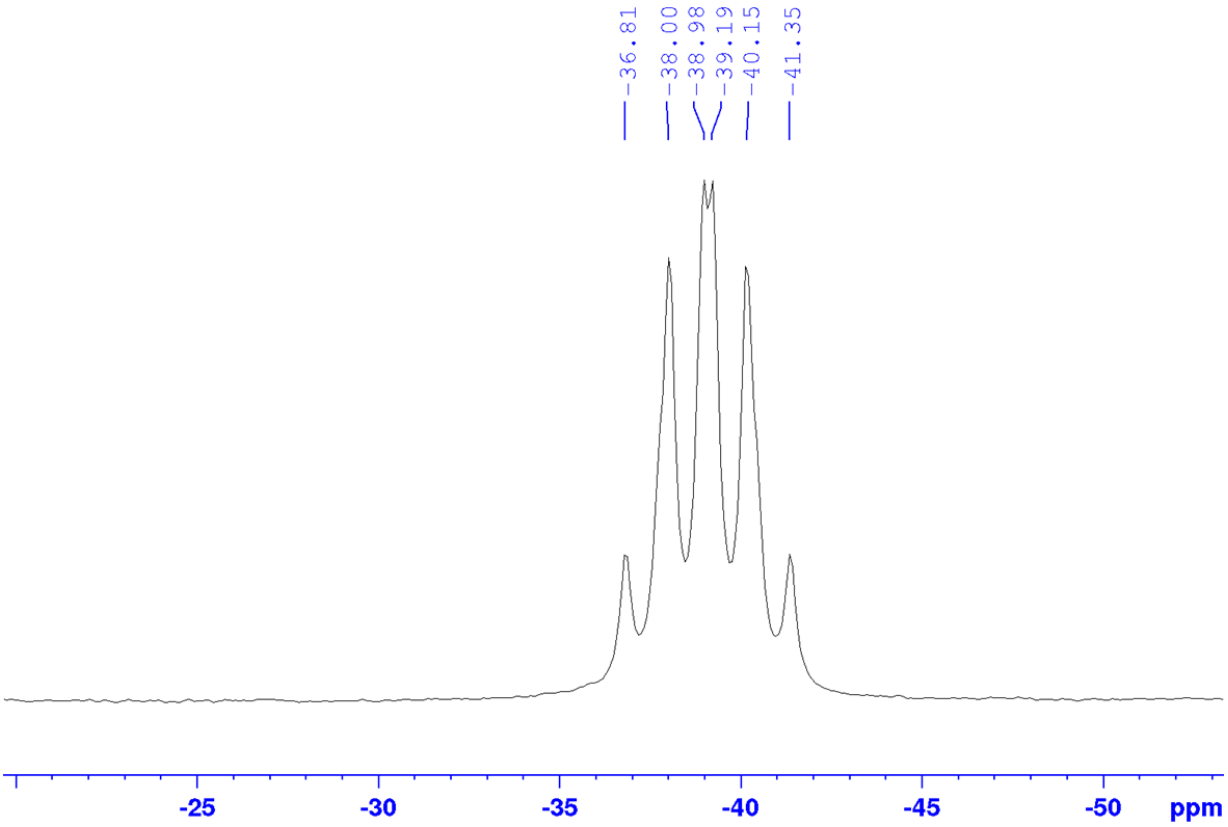

Fig. S3 ^{11}B NMR spectrum of **5** in C_6D_6

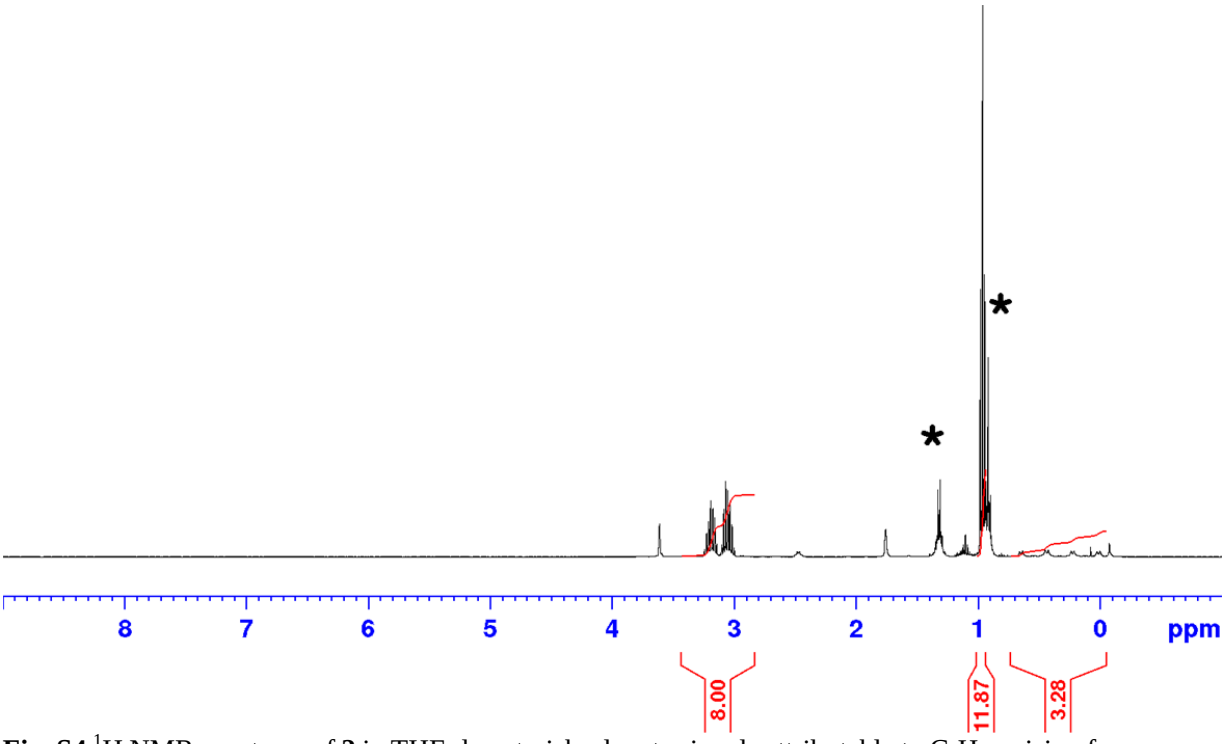

Fig. S4 ^{1}H NMR spectrum of **2** in THF-d_8; asterisks denote signals attributable to C_4H_{10} arising from excess n-BuLi after protonation.

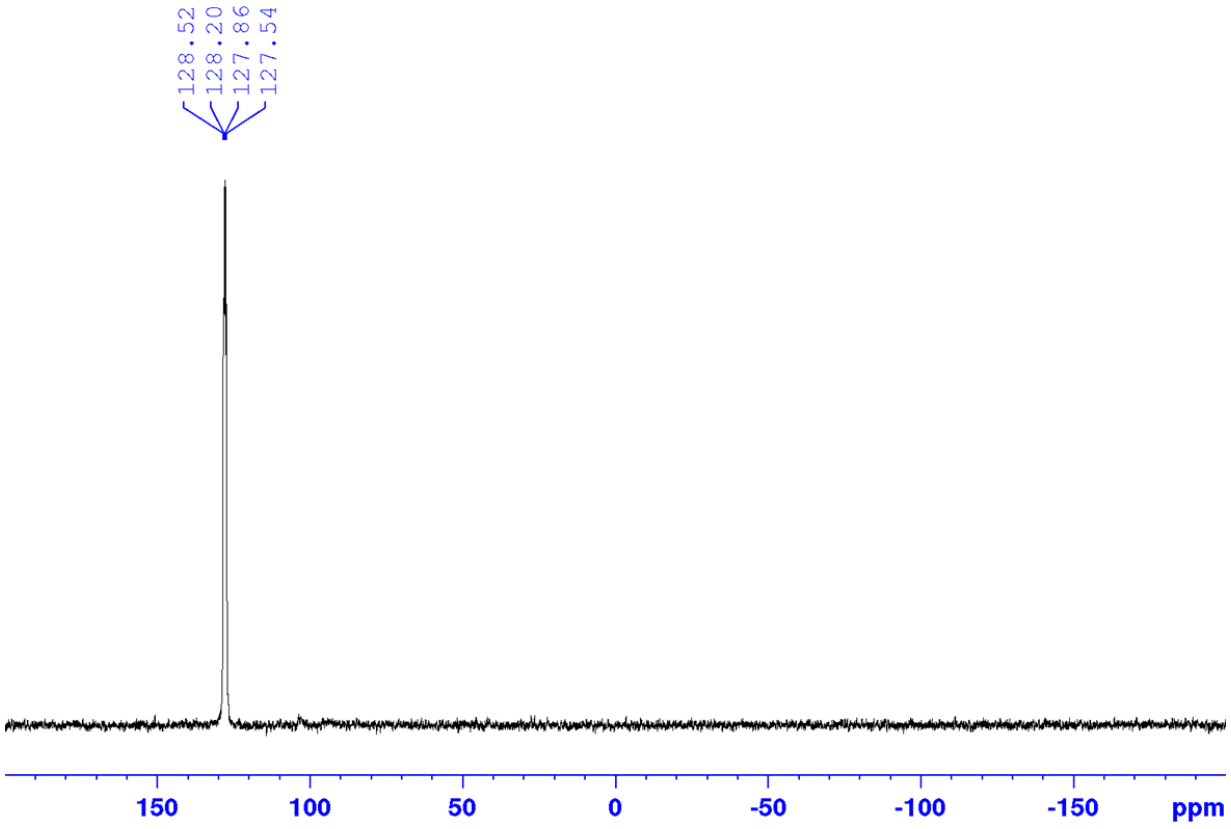

Fig. S5 ^{31}P NMR spectrum of **2** in THF-d_8

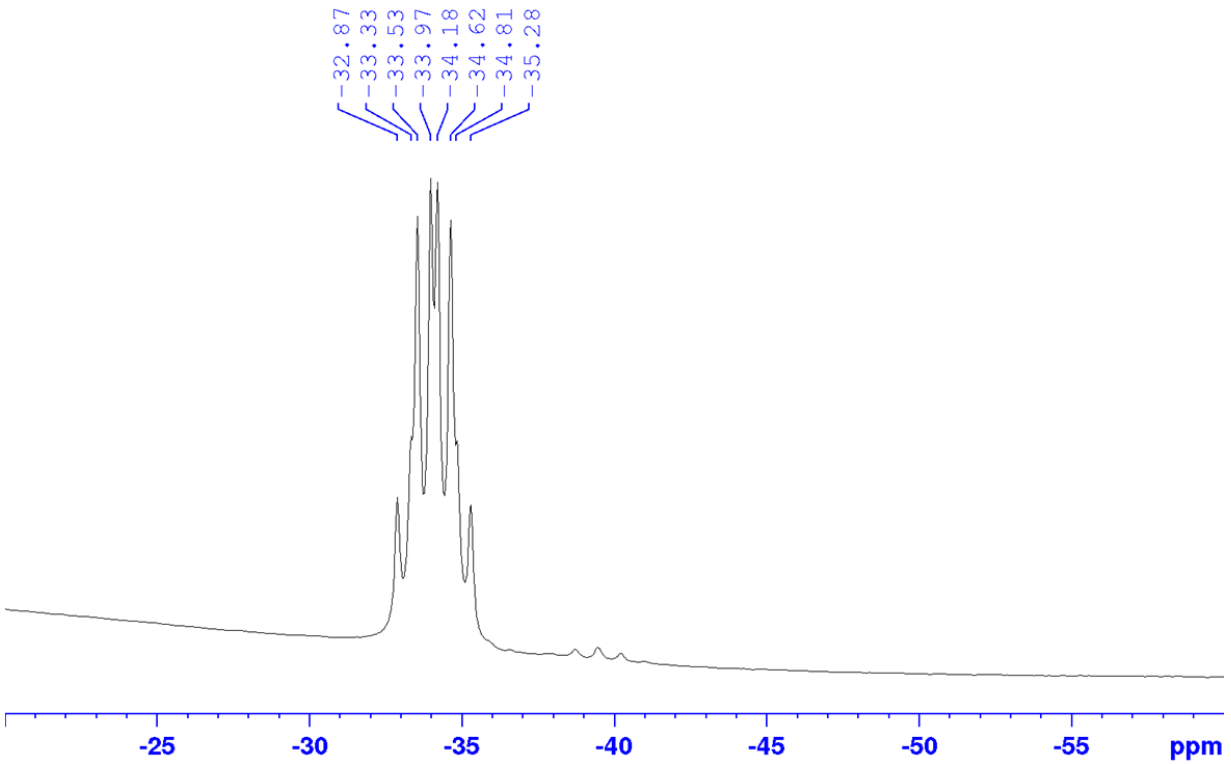

Fig. S6 ^{11}B NMR spectrum of **2** in THF-d_8 (glass background not subtracted)

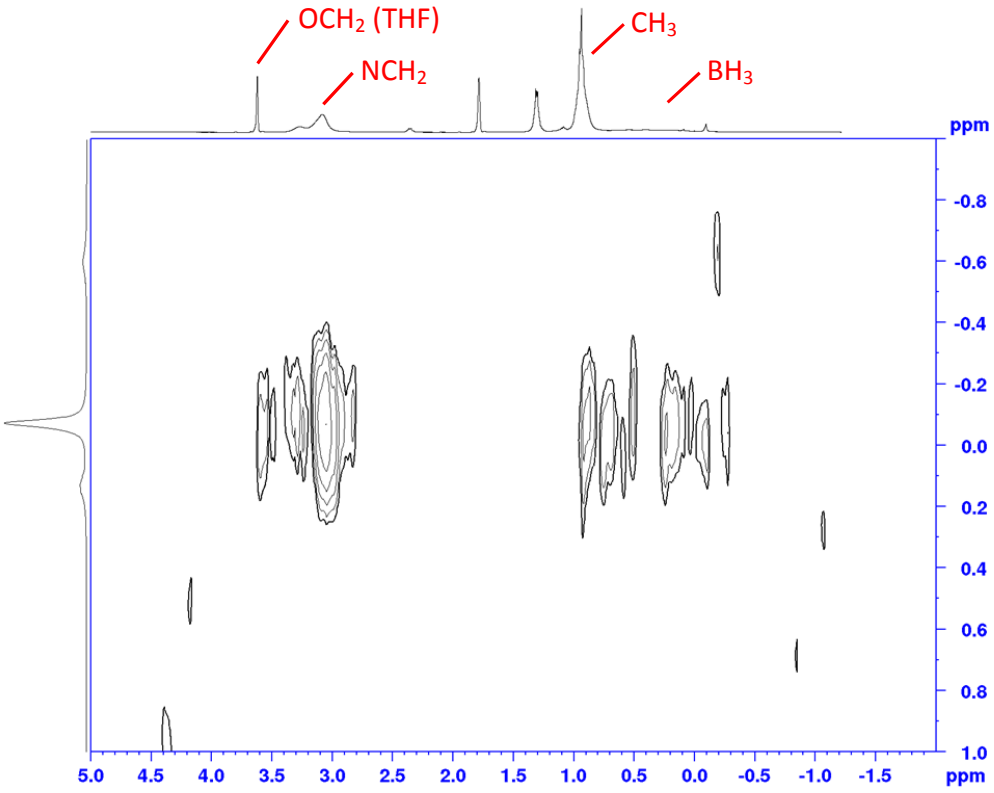

Fig. S7 ^{1}H,^{7}Li-gsHOESY NMR spectrum of **2** in THF-d_8 at -90 °C. The ^{1}H and ^{7}Li spectra are shown as projections on top and on the left side, and peak assignments are marked in the ^{1}H NMR spectrum

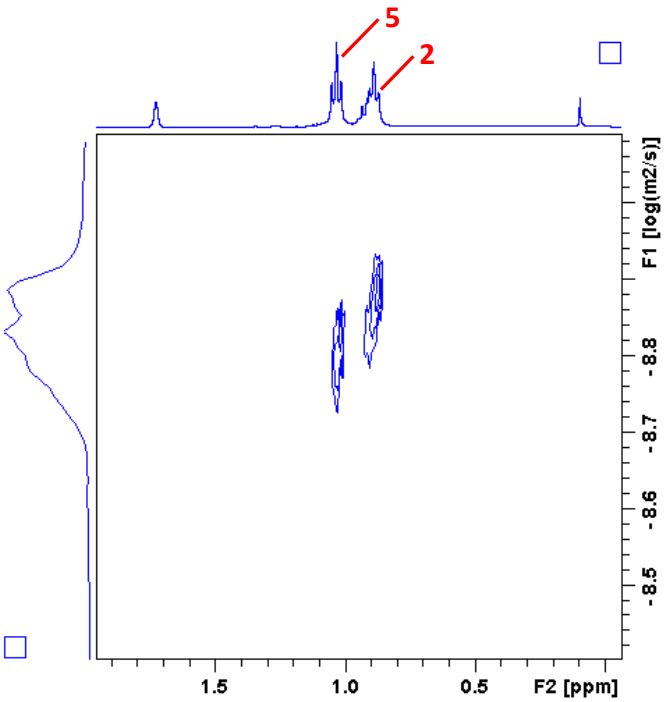

Fig. S8 Expansion of the ^{1}H DOSY NMR spectrum of a mixture of **2** and **5** recorded in THF-d_8 at -50 °C showing the CH3-signals of the diethylamino-groups. The peak assignments are marked in the ^{1}H NMR spectrum shown as projection on top of the pseudo-2D spectrum.

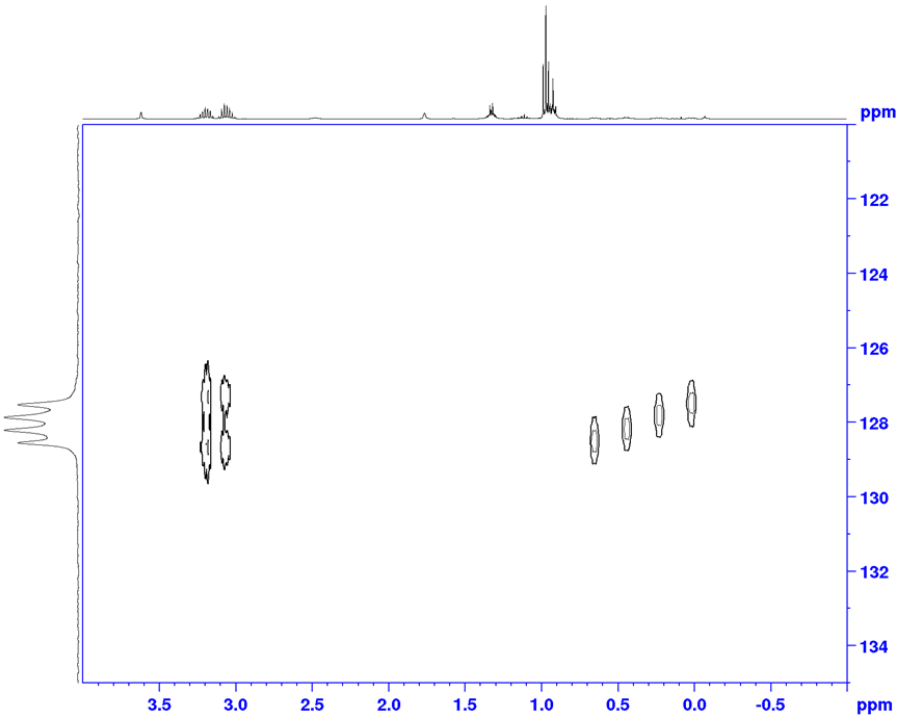

Fig. S9 $^{1}H,^{31}P$-HMQC NMR spectrum of **2** in THF-d_8 showing correlations with the NCH_2 and BH_3 signals.

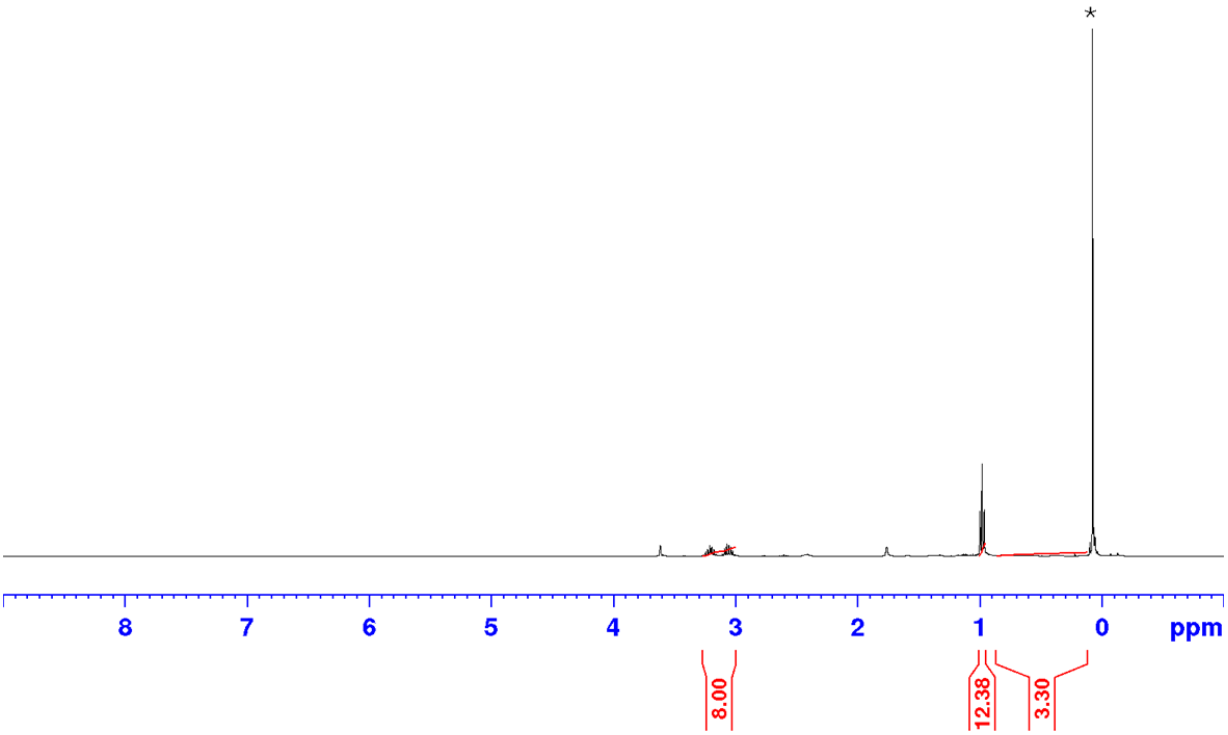

Fig. S10 ^{1}H NMR spectrum of **6** in THF-d_8; the signal marked with an asterisk is due to excess $KN(SiMe_3)_2$.

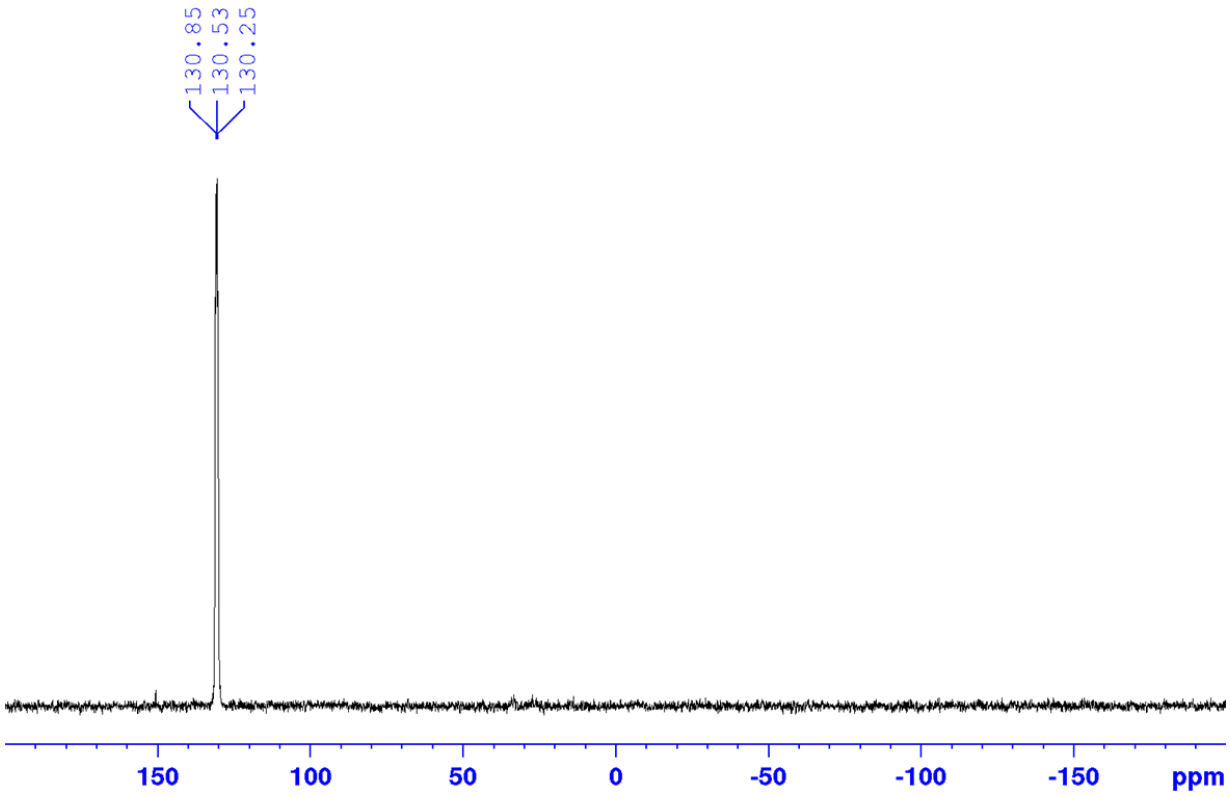

Fig. S11 ^{31}P NMR spectrum of **6** in THF-d_8.

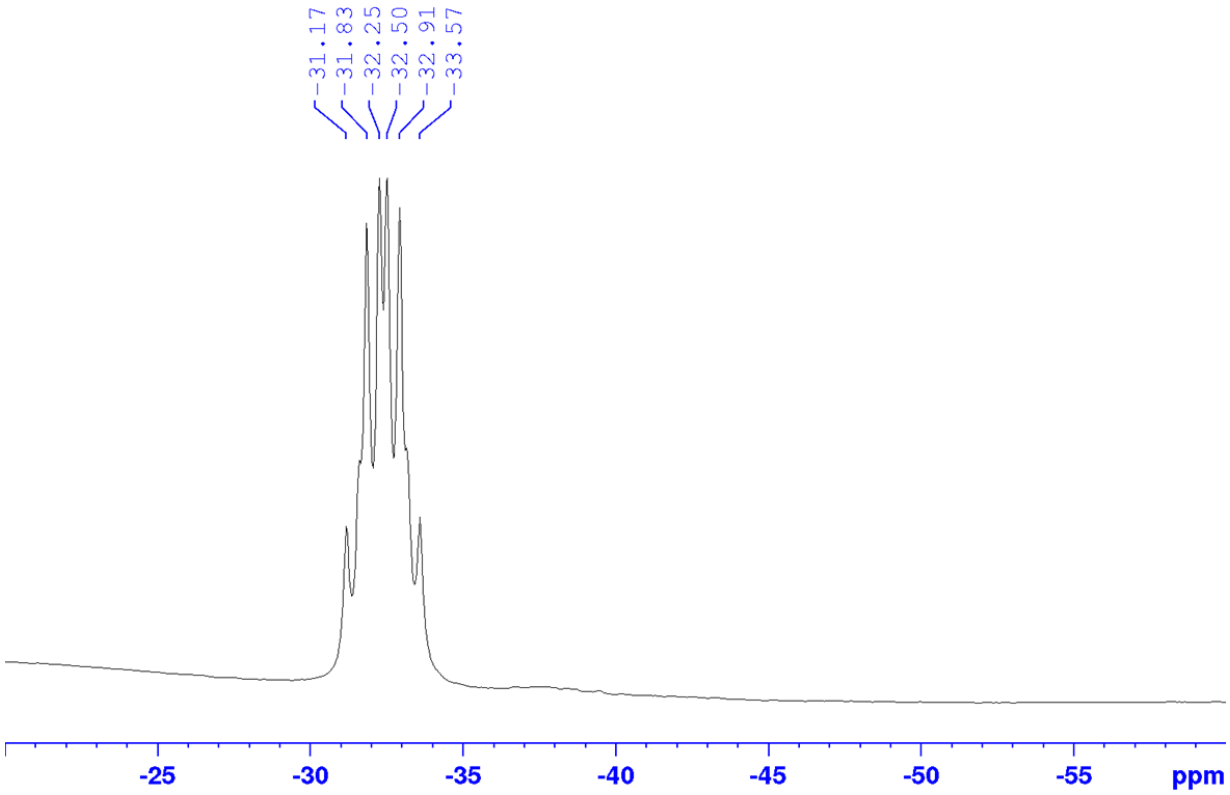

Fig. S12 ^{11}B NMR spectrum of **6** in THF-d_8 (glass background not subtracted).

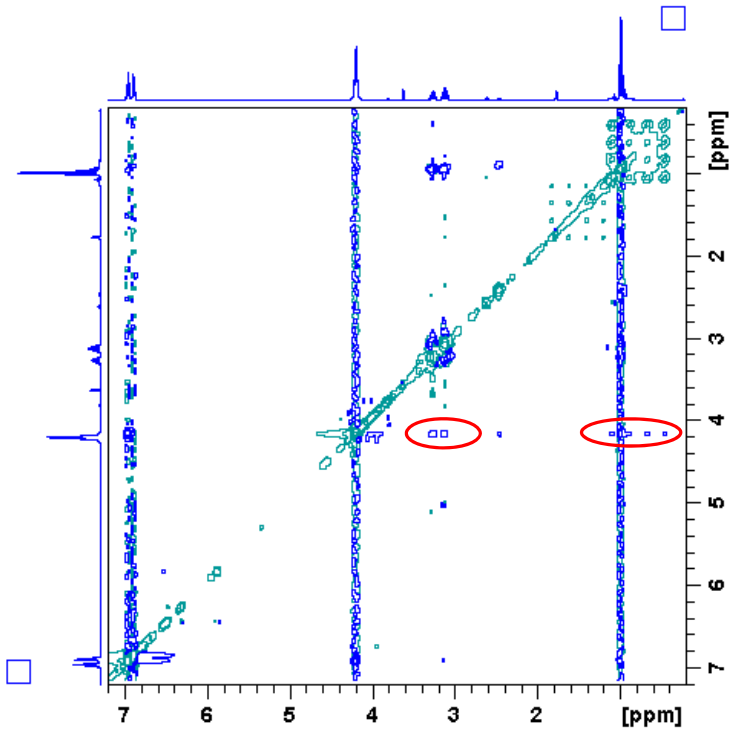

Fig. S13 ^{1}H gsNOESY-NMR spectrum after addition of dibenzo-18-crown-6 to a solution of **6** in THF-d_8. Red ellipses mark cross peaks between the signals of OCH_2 groups in the crown ether and NCH_2 and BH_3 signals in the phosphanide-borane unit (mirror images above the main diagonal are obscured by t_1-noise).

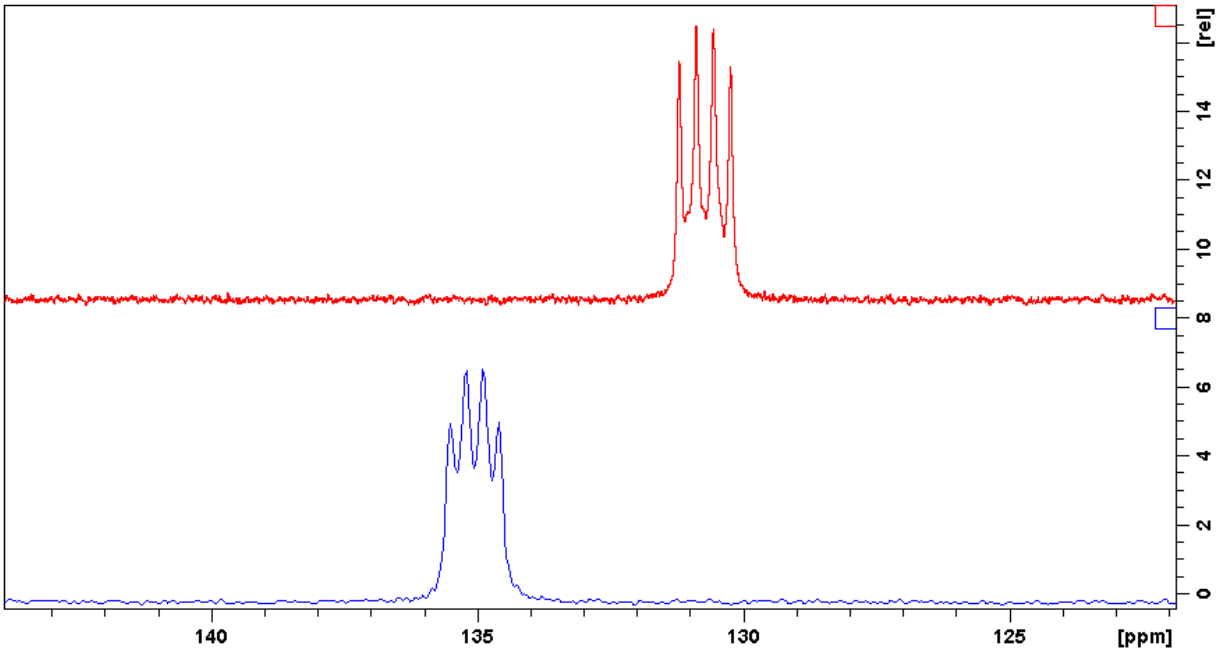

Fig. S14 ^{31}P{^{1}H} NMR spectrum of a solution of **6** in THF-d_8 before (red trace) and after addition of dibenzo-18-crown-6 (blue trace).

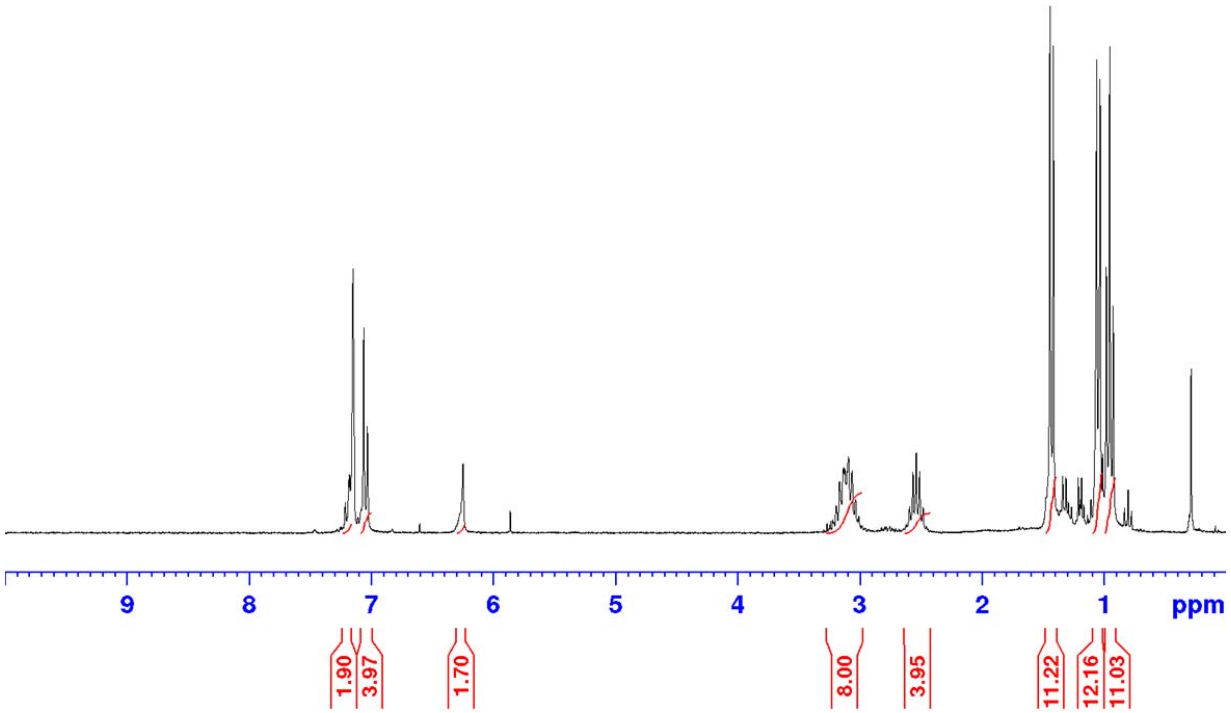

Fig S15. ^{1}H NMR spectrum of a solution of **8** in C_6D_6.

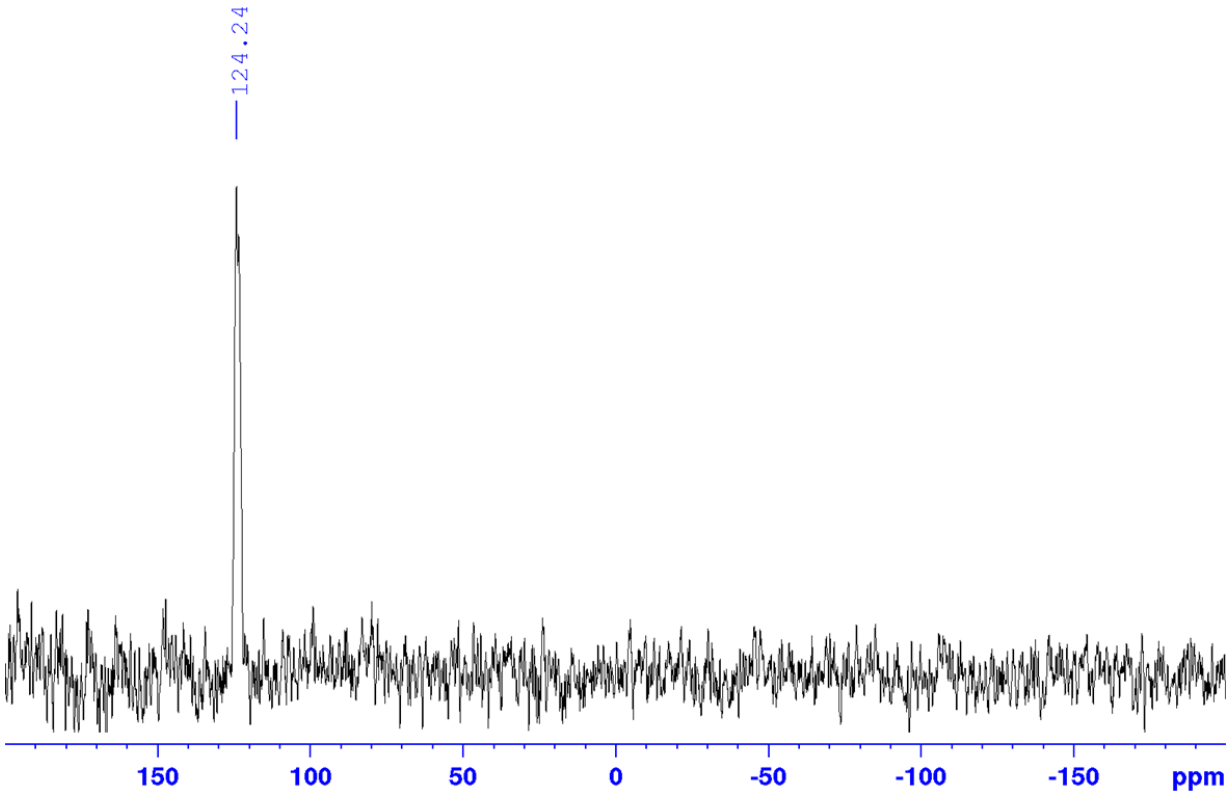

Fig. S16 ^{31}P NMR spectrum of **8** in C_6D_6.

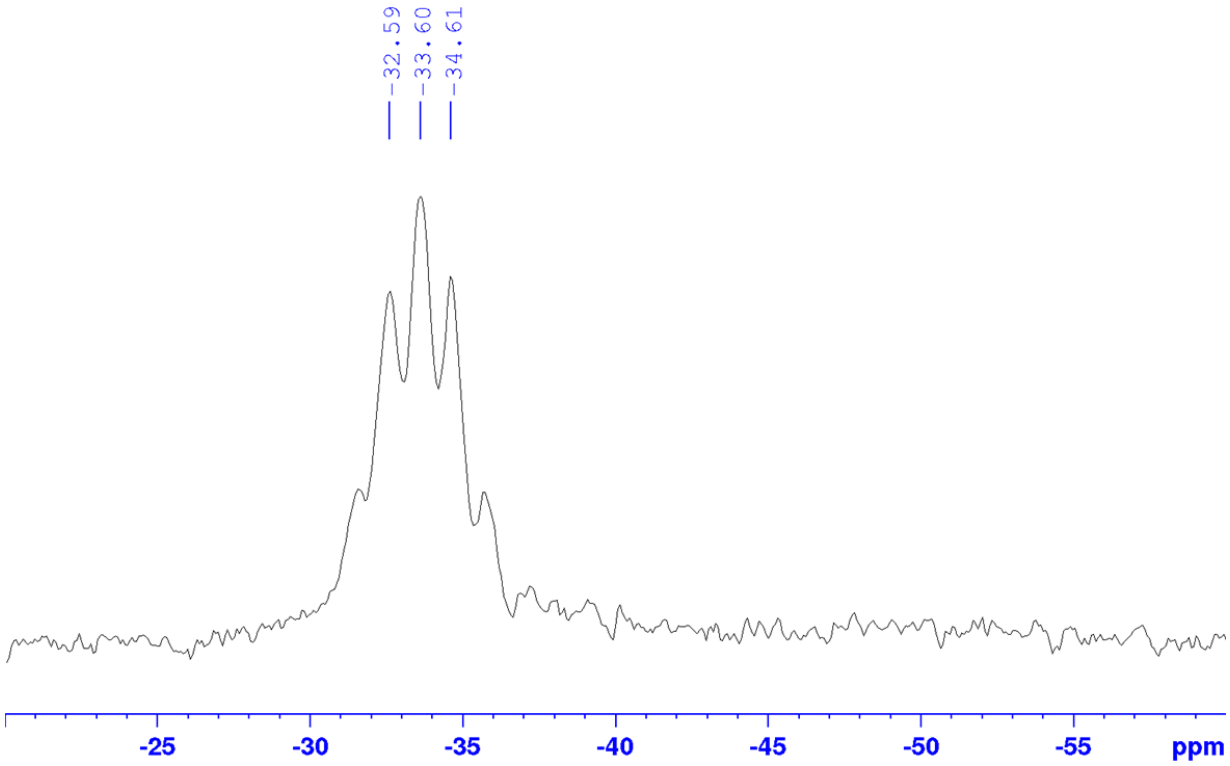

Fig. S17 ^{11}B NMR spectrum of **8** in C_6D_6 (glass background not subtracted).

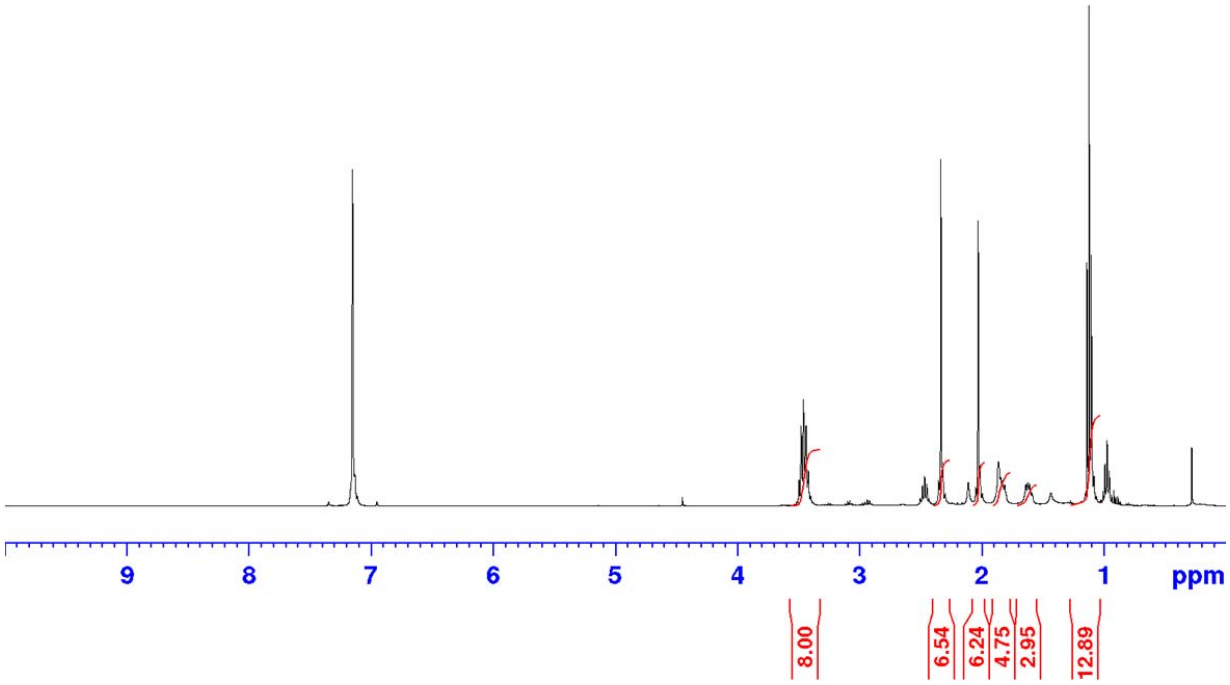

Fig. S18 ^{1}H NMR spectrum of **9** in C_6D_6.

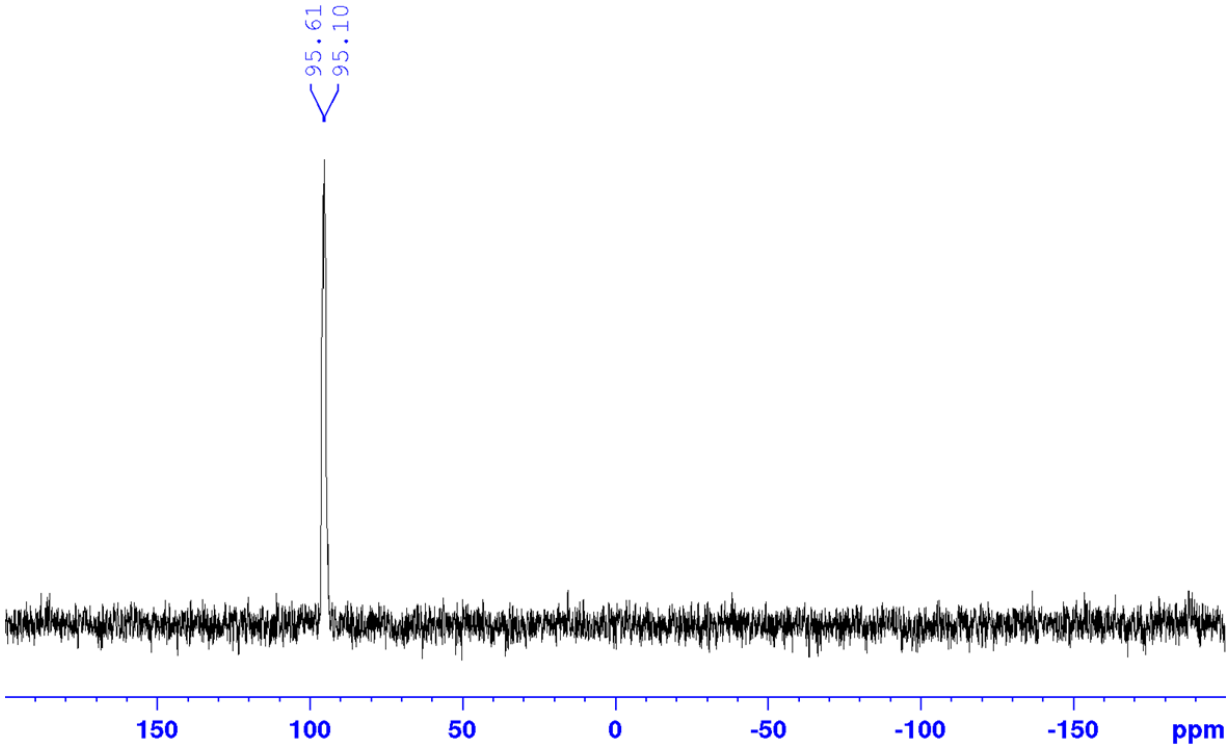

Fig. S19 ^{31}P NMR spectrum of **9** in C_6D_6.

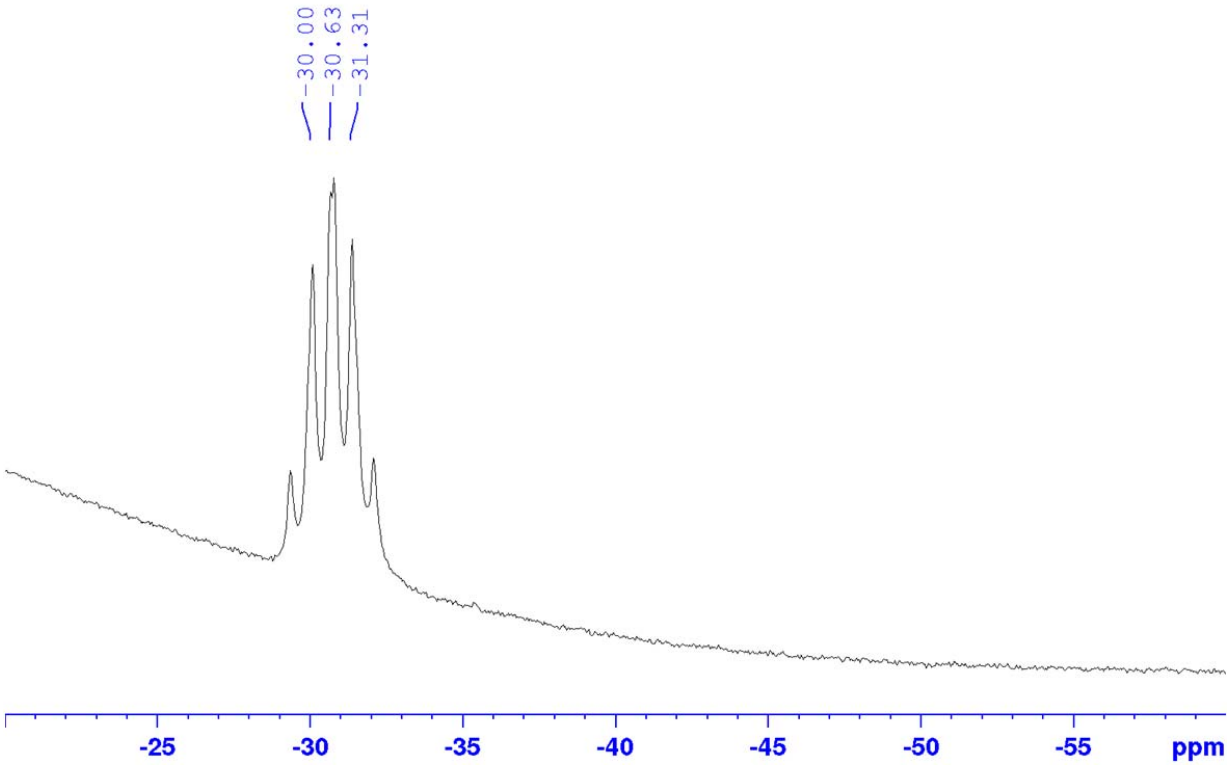

Fig. S20 ^{11}B NMR spectrum of **9** in C_6D_6 (glass background not subtracted).

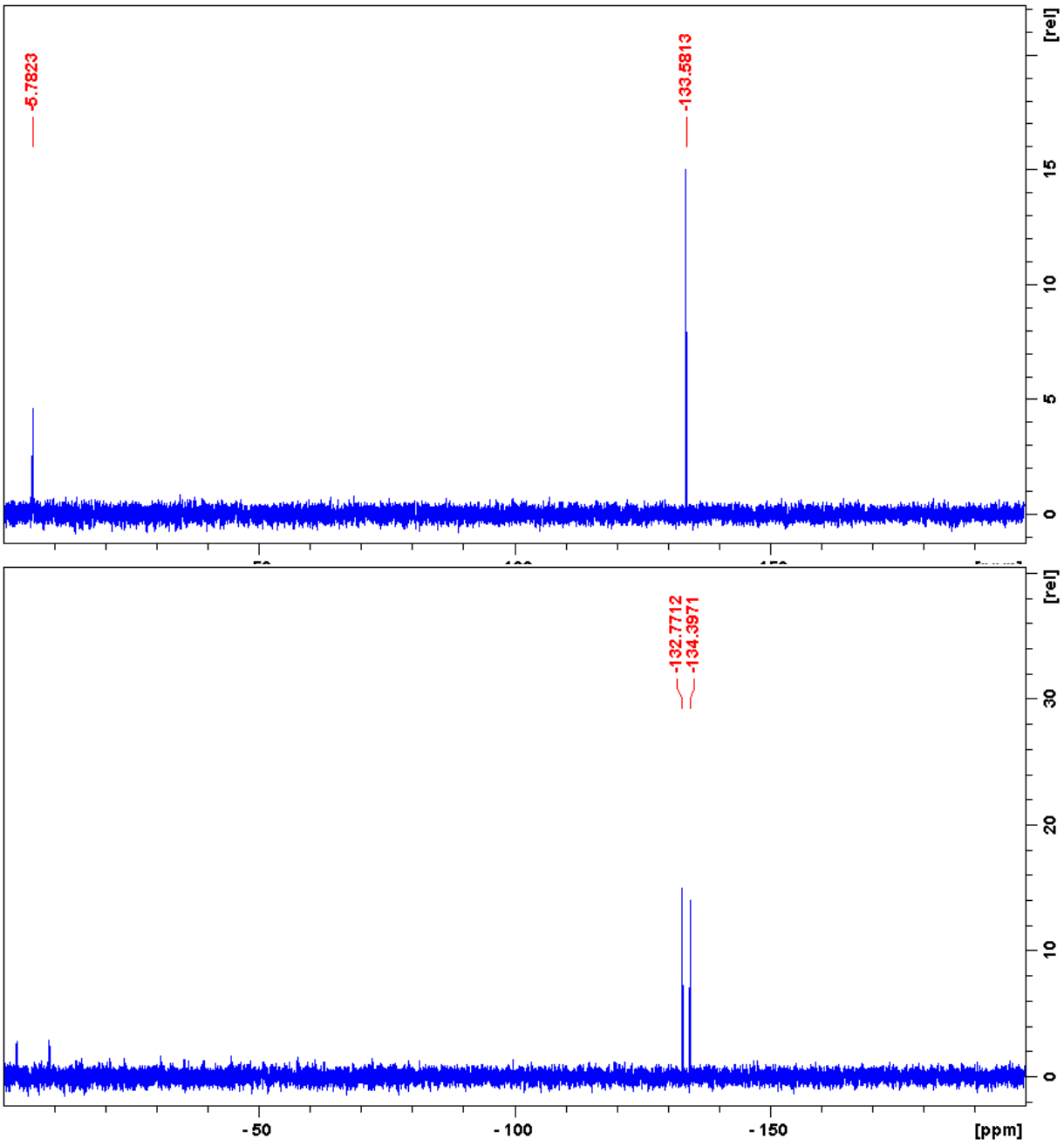

Fig. S21 $^{31}P\{^{1}H\}$ (top) and ^{31}P (bottom) NMR spectra of a solution of **8** in C_7D_8 after thermolysis at 95 °C.

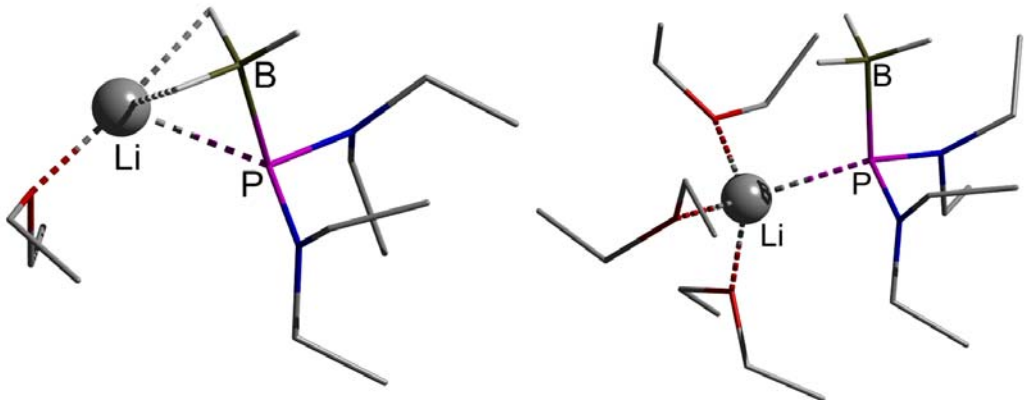

Fig. S22 Molecular structures of $(Et_2N)_2P(BH_3)Li(OEt_2)_n$ (n = 1, 3) computed at the COSMO-RI-BP86-D3BJ/def2-tzvp level of theory.

Table S1: Electronic energies (E + OC) and standard Gibbs free energies (DG^0) of $(Et_2N)_2P(BH_3)Li(OEt_2)_n$ (n = 0 - 3) and of $(Et_2N)_2P\text{-}BH_3\cdots Li(OEt_2)_n$ (n = 0, 2) computed at the COSMO-RI-BP86-D3BJ/def2-tzvp level of theory.

$(Et_2N)_2P(BH_3)Li$

E + OC	-2106364.996 kJ/mol		
ΔG	-2105697.71 kJ/mol		
P	-1.404903	1.676425	-0.505850
B	-0.873425	2.986181	0.860358
H	-1.790410	3.821405	0.846736
H	-0.679524	2.599669	1.993683
H	0.141780	3.533019	0.404513
N	-2.835653	0.966642	0.101402
N	-0.095762	0.577968	-0.633360
C	-3.872543	0.526978	-0.833866
C	-2.980084	0.526569	1.486106
C	-4.826772	1.645517	-1.257861
H	-5.345886	2.072361	-0.389107
H	-5.580116	1.274269	-1.970376
H	-4.260910	2.452858	-1.746382
H	-4.439707	-0.294483	-0.364527
H	-3.403780	0.098398	-1.735700
C	-4.161768	1.168860	2.215870
H	-5.119026	0.912525	1.738806
H	-4.058141	2.262842	2.214651
H	-4.204574	0.821057	3.259247
H	-3.078910	-0.576881	1.525288
H	-2.051933	0.780866	2.014692
C	0.176710	-0.062559	-1.919548
C	0.648653	0.085729	0.524313
C	-0.696773	-1.270561	-2.279052
H	-1.754490	-0.976018	-2.333097
H	-0.609010	-2.076459	-1.538935
H	-0.406038	-1.672618	-3.262002
H	1.239359	-0.362760	-1.924085
H	0.056841	0.698535	-2.708701
C	0.248823	-1.299181	1.048643
H	0.495631	-2.094205	0.331849
H	-0.830277	-1.343342	1.251091
H	0.784117	-1.516961	1.985836
H	1.724694	0.074478	0.268260
H	0.521570	0.826145	1.326706
Li	-1.172624	4.013019	-1.003160

$(Et_2N)_2P(BH_3)Li(OEt_2)$

E + OC	-2720206.182 kJ/mol		
ΔG	-2719210.22 kJ/mol		
P	-1.109346	1.367482	-1.612481

B	-0.555997	3.245184	-1.440362
H	-1.275292	3.878956	-2.225649
H	-0.586438	3.762633	-0.342739
H	0.595399	3.251168	-1.896281
N	-2.758364	1.372105	-1.128699
N	-0.086587	0.473489	-0.570674
C	-3.363523	2.402868	-0.287066
C	-3.634995	0.291055	-1.559795
C	-3.140712	2.257126	1.220618
H	-3.504024	1.291083	1.595874
H	-3.665958	3.059086	1.762555
H	-2.071568	2.334877	1.455446
H	-4.446803	2.409434	-0.502117
H	-2.974135	3.383873	-0.601232
C	-4.098300	-0.657022	-0.448721
H	-4.733422	-0.135871	0.281519
H	-3.235884	-1.076674	0.086112
H	-4.686926	-1.486592	-0.870456
H	-4.528078	0.717875	-2.058914
H	-3.085292	-0.278548	-2.325741
C	0.404650	-0.827457	-1.027374
C	0.322866	0.895031	0.764760
C	-0.577624	-1.994186	-0.885459
H	-1.475300	-1.806701	-1.491485
H	-0.894583	-2.132437	0.156612
H	-0.119180	-2.931756	-1.237200
H	1.332155	-1.050591	-0.471622
H	0.688982	-0.741153	-2.089438
C	-0.244085	0.049440	1.910320
H	0.141125	-0.979533	1.878271
H	-1.339981	0.007332	1.854126
H	0.038855	0.480975	2.882948
H	1.429078	0.887534	0.828725
H	0.012908	1.942162	0.884091
Li	-0.439081	2.655686	-3.535355
O	-1.604350	2.512926	-5.044570
C	-2.738799	3.415426	-5.079944
C	-1.909886	1.173568	-5.497341
C	-3.855281	3.028375	-4.123464
C	-0.620253	0.382789	-5.564370
H	-0.824377	-0.625076	-5.951250
H	-0.189172	0.271017	-4.557344
H	0.109954	0.867425	-6.227501
H	-2.395467	1.245986	-6.485595
H	-2.612465	0.701895	-4.791765
H	-4.384550	2.123779	-4.451114
H	-4.588904	3.845735	-4.076201
H	-3.100131	3.469139	-6.121020

H	-2.319563	4.394754	-4.811939
H	-3.457441	2.853256	-3.113899

$(Et_2N)_2P(BH_3)Li(OEt_2)_2$

E + OC	-3334027.634 kJ/mol		
ΔG	-3332716.99 kJ/mol		
P	-0.881942	0.298069	-1.578300
B	-0.139378	2.089073	-1.779926
H	-0.868168	2.686820	-2.567682
H	-0.048360	2.712170	-0.728972
H	0.969211	1.909205	-2.278950
N	-2.460239	0.532387	-0.918472
N	0.162052	-0.548287	-0.496904
C	-2.877871	1.768236	-0.259194
C	-3.436274	-0.545353	-0.946968
C	-2.453759	1.923134	1.204535
H	-2.830981	1.104494	1.831616
H	-2.832086	2.873899	1.611912
H	-1.358564	1.935928	1.278605
H	-3.978506	1.829611	-0.336520
H	-2.470916	2.616909	-0.829161
C	-3.775848	-1.167654	0.412814
H	-4.293459	-0.446897	1.061200
H	-2.863642	-1.497306	0.927096
H	-4.439827	-2.036504	0.283421
H	-4.377407	-0.185205	-1.412043
H	-3.035351	-1.325049	-1.615833
C	0.441338	-1.964870	-0.717925
C	0.815977	0.068657	0.650289
C	-0.596972	-2.954359	-0.176822
H	-1.565940	-2.799247	-0.671880
H	-0.747758	-2.837851	0.904234
H	-0.278209	-3.990586	-0.372580
H	1.427127	-2.186993	-0.271546
H	0.549035	-2.141630	-1.800790
C	0.340470	-0.438638	2.017196
H	0.599863	-1.496454	2.169502
H	-0.749510	-0.336496	2.108565
H	0.813261	0.139573	2.826174
H	1.911913	-0.082483	0.575052
H	0.645948	1.151382	0.575076
Li	-0.962191	-0.868397	-3.711064
O	-2.034403	-0.082455	-5.054535
C	-2.393016	1.321054	-4.920752
C	-2.406193	-0.679609	-6.312636
C	-3.717551	1.481275	-4.200519
C	-1.393963	-0.380997	-7.407401
H	-1.687656	-0.886280	-8.338895

H	-0.396056	-0.736906	-7.117089
H	-1.329387	0.696326	-7.612741
H	-3.414993	-0.334636	-6.591487
H	-2.468885	-1.761010	-6.122041
H	-4.533427	0.970740	-4.732212
H	-3.971314	2.548735	-4.126426
H	-2.407850	1.777984	-5.921703
H	-1.585915	1.789118	-4.339732
O	0.719142	-1.565609	-4.266745
C	1.009755	-2.618909	-5.207427
C	1.853927	-0.720721	-3.933108
C	1.589117	-3.845498	-4.521501
H	1.779340	-4.634141	-5.263616
H	0.887923	-4.234571	-3.770723
H	2.540418	-3.614688	-4.022587
H	1.688266	-2.234897	-5.986611
H	0.052521	-2.861299	-5.691488
C	1.999126	0.427243	-4.914336
H	2.156532	0.068263	-5.941756
H	2.863005	1.046629	-4.634011
H	1.105739	1.065082	-4.890463
H	2.760660	-1.343318	-3.891270
H	1.647791	-0.341530	-2.921758
H	-3.634006	1.078904	-3.182095

$(Et_2N)_2P(BH_3)Li(OEt_2)_3$ (P…Li isomer)

E + OC	-3947860.642 kJ/mol		
ΔG	-3946219.87 kJ/mol		
P	-2.710321	0.878431	-0.686574
B	-3.951149	2.095420	0.194583
H	-3.309405	3.113621	0.425809
H	-4.845417	2.340353	-0.612505
H	-4.420147	1.627761	1.227064
N	-3.649972	-0.545768	-1.017274
N	-1.495629	0.546374	0.509038
C	-4.978505	-0.808322	-0.471952
C	-3.107464	-1.548597	-1.917594
C	-5.045035	-1.610283	0.833697
H	-4.576536	-2.599029	0.739446
H	-6.095287	-1.756545	1.132691
H	-4.537354	-1.068518	1.642727
H	-5.558033	-1.338796	-1.250916
H	-5.472449	0.159681	-0.309030
C	-2.534986	-2.817201	-1.270686
H	-3.319369	-3.414915	-0.787359
H	-1.784666	-2.560991	-0.509568
H	-2.053477	-3.449923	-2.032759
H	-3.887613	-1.851601	-2.644785

H	-2.310255	-1.055440	-2.495751
C	-1.853190	0.271948	1.904617
C	-0.264661	-0.088696	0.055594
C	-1.547843	1.432671	2.852845
H	-2.110028	2.320956	2.535334
H	-0.478485	1.684448	2.853904
H	-1.846781	1.180902	3.882765
H	-1.332677	-0.643956	2.240662
H	-2.929310	0.056023	1.958193
C	0.994752	0.350115	0.804271
H	0.956801	0.061837	1.864051
H	1.124705	1.439763	0.756147
H	1.881088	-0.129150	0.361595
H	-0.333819	-1.197543	0.122633
H	-0.158145	0.149965	-1.014217
Li	-1.663597	1.853392	-2.748058
O	-3.061656	1.958999	-4.112267
C	-2.825005	2.117505	-5.524446
C	-4.454864	2.070160	-3.727586
C	-2.699906	3.577873	-5.930258
C	-5.220569	0.781175	-3.963434
H	-6.262312	0.911231	-3.636804
H	-4.774487	-0.026527	-3.370742
H	-5.233263	0.491403	-5.023710
H	-4.910361	2.917712	-4.265966
H	-4.443943	2.310015	-2.655435
H	-2.522093	3.651229	-7.013081
H	-1.857620	4.053744	-5.410375
H	-3.628570	1.616315	-6.086845
H	-1.890504	1.579020	-5.730962
O	-0.177949	0.996490	-3.781034
C	-0.345633	-0.312525	-4.370661
C	0.859668	1.807747	-4.368383
C	0.321771	-1.420630	-3.572487
H	0.086421	-2.391716	-4.032372
H	-0.052663	-1.434293	-2.541453
H	1.412169	-1.307388	-3.543876
H	0.030512	-0.283672	-5.406730
H	-1.432540	-0.481626	-4.416031
C	2.265971	1.399510	-3.956447
H	2.349927	1.352816	-2.861888
H	2.984667	2.145529	-4.325974
H	2.551617	0.424242	-4.372027
H	0.638317	2.826613	-4.025804
H	0.748654	1.783103	-5.466699
O	-0.821436	3.579331	-2.265833
C	-1.289758	4.917629	-2.549882
C	0.230636	3.511243	-1.278052

C	-0.232298	3.889602	0.116457
H	-0.579741	4.931245	0.161407
H	0.607331	3.789267	0.819965
H	-1.041228	3.222953	0.440087
H	1.072722	4.141872	-1.614476
H	0.564698	2.464549	-1.298585
C	-2.770149	5.048385	-2.248609
H	-2.984026	4.771581	-1.207975
H	-3.357445	4.387950	-2.898024
H	-3.098102	6.083184	-2.425583
H	-1.079959	5.120332	-3.613206
H	-0.701824	5.633729	-1.957469
H	-3.614333	4.141832	-5.700330

$(Et_2N)_2P\text{-}BH_3\cdots Li$

E + OC -2106332.290 kJ/mol

ΔG -2105667.17 kJ/mol

P	-5.989381	1.831156	1.591598
N	-6.269375	3.349024	0.842878
N	-6.738378	0.755120	0.397140
C	-5.765414	3.672047	-0.485018
C	-6.798549	4.447527	1.649484
C	-8.328112	4.517218	1.703503
H	-8.760295	4.617524	0.698312
H	-8.659368	5.373086	2.312693
H	-8.730482	3.599794	2.157230
H	-6.394070	5.391922	1.246374
H	-6.413457	4.363832	2.679349
C	-6.842237	4.156619	-1.459587
H	-6.405306	4.340866	-2.453245
H	-7.306032	5.094314	-1.120759
H	-7.633364	3.400555	-1.561241
H	-5.309349	2.757263	-0.886372
H	-4.963154	4.436649	-0.419482
C	-8.195500	0.871760	0.340325
C	-6.254959	-0.632978	0.403739
C	-8.765227	0.451159	-1.013728
H	-9.856651	0.591674	-1.032949
H	-8.561482	-0.607917	-1.229578
H	-8.318316	1.052111	-1.818879
H	-8.442723	1.927938	0.518666
H	-8.686106	0.286026	1.149058
C	-5.457297	-0.987013	-0.851552
H	-6.069449	-0.845279	-1.753323
H	-5.116355	-2.034751	-0.820547
H	-4.578505	-0.333934	-0.931731
H	-7.119180	-1.313007	0.498777
H	-5.629989	-0.822672	1.293846

B	-4.093788	1.480136	1.318691
H	-3.696636	1.542137	0.147757
H	-3.750741	0.383983	1.776215
H	-3.488602	2.342974	1.969958
Li	-2.072737	1.213248	1.181202

$(Et_2N)_2P\text{-}BH_3\cdots Li(OEt_2)_2$

E + OC -3334012.997 kJ/mol

ΔG -3332712.11 kJ/mol

P	-3.985029	1.984149	0.286823
N	-4.664843	3.538273	0.641251
N	-4.964754	1.149455	-0.870288
C	-4.553419	4.718449	-0.205202
C	-5.589643	3.632265	1.767477
C	-7.024145	3.150415	1.504265
H	-7.505385	3.717443	0.696621
H	-7.637398	3.254154	2.413316
H	-7.020581	2.090629	1.213706
H	-5.611000	4.684018	2.106728
H	-5.174449	3.035939	2.597809
C	-5.782775	5.078324	-1.051923
H	-5.544635	5.913442	-1.729764
H	-6.630687	5.390233	-0.426309
H	-6.103381	4.220950	-1.659404
H	-3.696484	4.554792	-0.872250
H	-4.300734	5.590121	0.430701
C	-5.123040	1.560975	-2.256206
C	-5.767249	0.017968	-0.422150
C	-4.448278	0.642688	-3.282469
H	-4.540001	1.061296	-4.297697
H	-4.900434	-0.359031	-3.288844
H	-3.381727	0.538825	-3.039067
H	-4.695515	2.567694	-2.358756
H	-6.201507	1.650245	-2.497314
C	-5.020112	-1.321783	-0.404696
H	-4.658561	-1.592593	-1.406132
H	-5.671416	-2.131815	-0.038858
H	-4.148183	-1.249846	0.261892
H	-6.661891	-0.059634	-1.066337
H	-6.134529	0.220198	0.598977
B	-2.406986	2.412012	-0.750675
Li	-0.717354	3.000813	-1.851328
O	-0.270888	4.730691	-2.492657
O	0.473138	1.711425	-2.677502
C	-1.130227	5.867162	-2.219264
C	0.929436	5.017692	-3.239752
C	-1.054077	6.302890	-0.766502
H	-1.772453	7.116344	-0.588430

H	-0.050929	6.661245	-0.501692
H	-1.317837	5.467028	-0.104388
H	-2.151175	5.540373	-2.467595
H	-0.859351	6.683619	-2.906533
C	1.970516	5.787296	-2.442804
H	2.222542	5.256094	-1.514385
H	1.624034	6.797131	-2.184945
H	2.886422	5.889687	-3.042676
H	0.650171	5.562134	-4.157625
H	1.315098	4.031116	-3.530647
C	1.187566	0.877756	-1.737330
C	1.678084	1.753817	-0.602664
H	0.838562	2.195360	-0.044400
H	2.323823	2.559438	-0.979187
H	2.262263	1.151149	0.105437
H	2.031100	0.390228	-2.249817
H	0.501042	0.095440	-1.368830
C	-0.190796	0.970367	-3.727927
C	0.770607	0.409305	-4.761686
H	1.385314	1.209600	-5.196318
H	0.196742	-0.063472	-5.571294
H	1.434773	-0.354497	-4.335610
H	-0.878473	1.690972	-4.193454
H	-0.798252	0.173705	-3.265558
H	-2.629370	2.974147	-1.832451
H	-1.823629	1.358168	-0.991163
H	-1.651448	3.140177	-0.097362