

Intramolecular Lewis pairs with two acid sites – reactivity differences between P- and N-based systems

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Supporting Information

N,N-Diallyl-*tert*-butylamine (3)

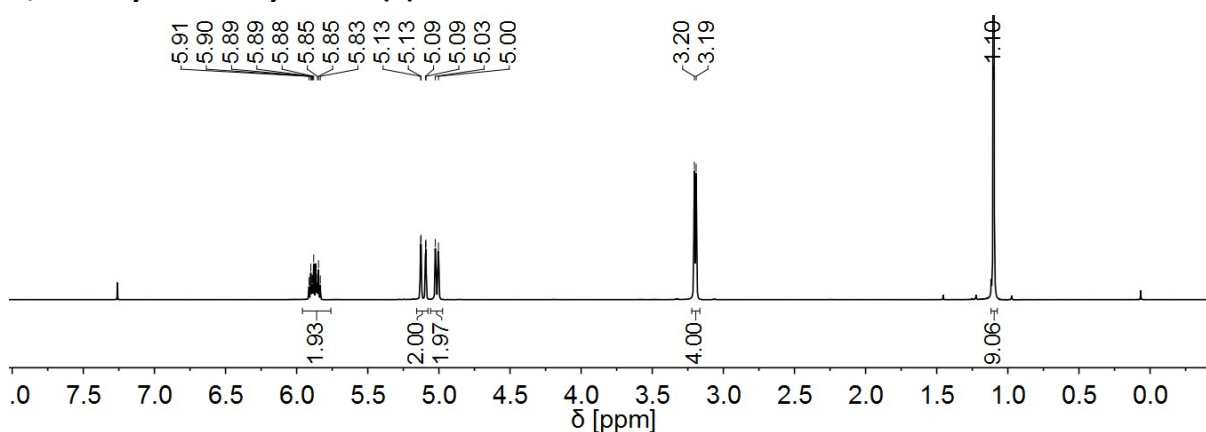


Figure S1. ¹H NMR spectrum (500 MHz, CDCl₃) of *N,N*-Diallyl-*tert*-butylamine (3).

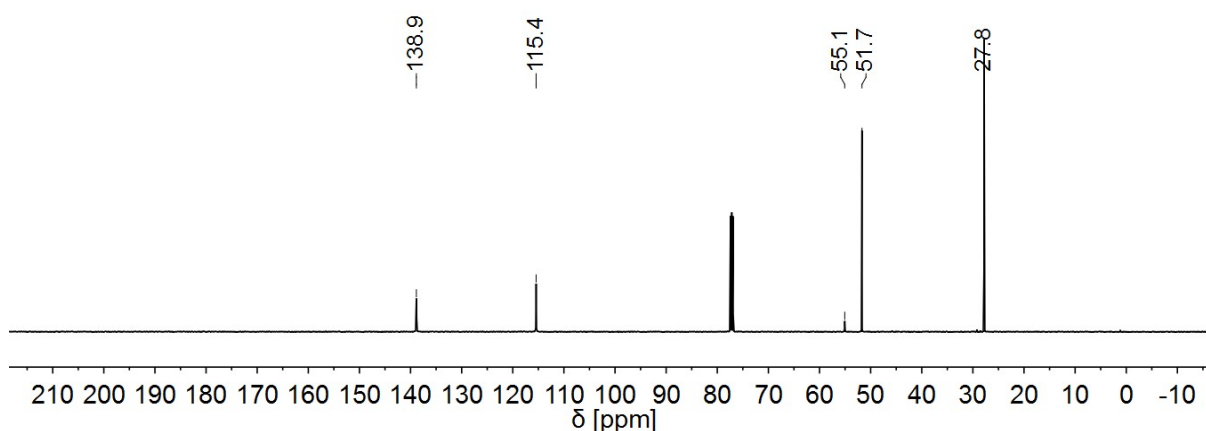


Figure S2. ¹³C NMR spectrum (126 MHz, CDCl₃) of *N,N*-Diallyl-*tert*-butylamine (3).

Cyclic iminium borate 5

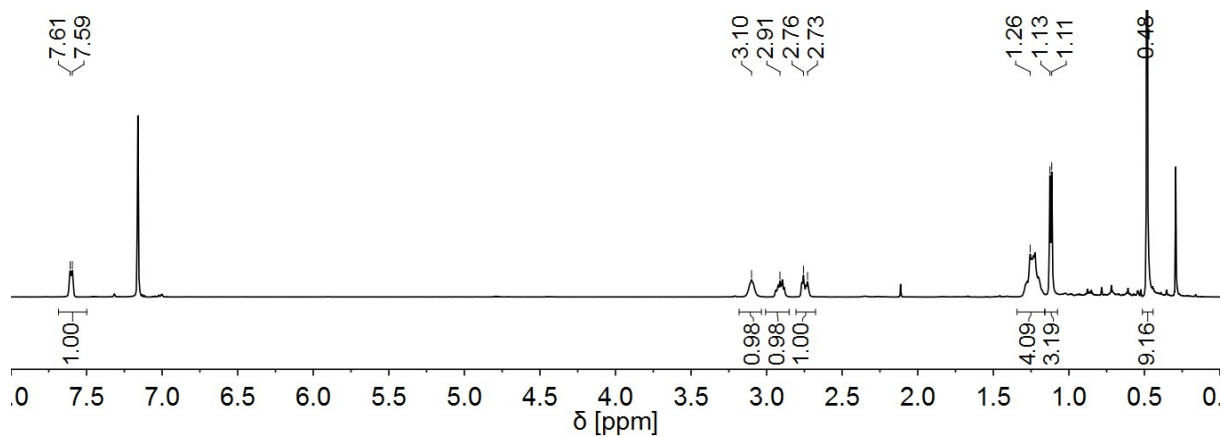


Figure S3. ^1H NMR spectrum (500 MHz, C_6D_6) of the cyclic iminium borate 5.

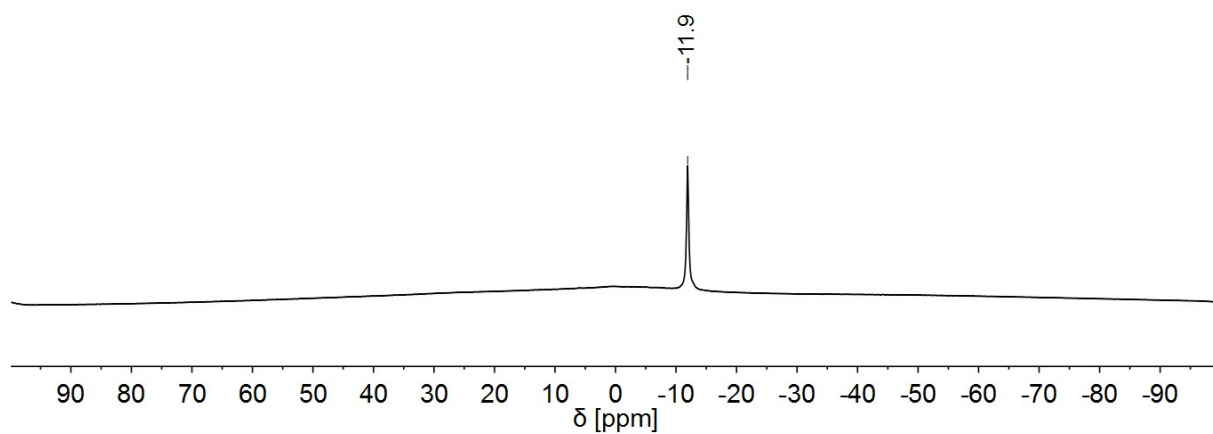


Figure S4. ^{11}B NMR spectrum (160 MHz, C_6D_6) of the cyclic iminium borate 5.

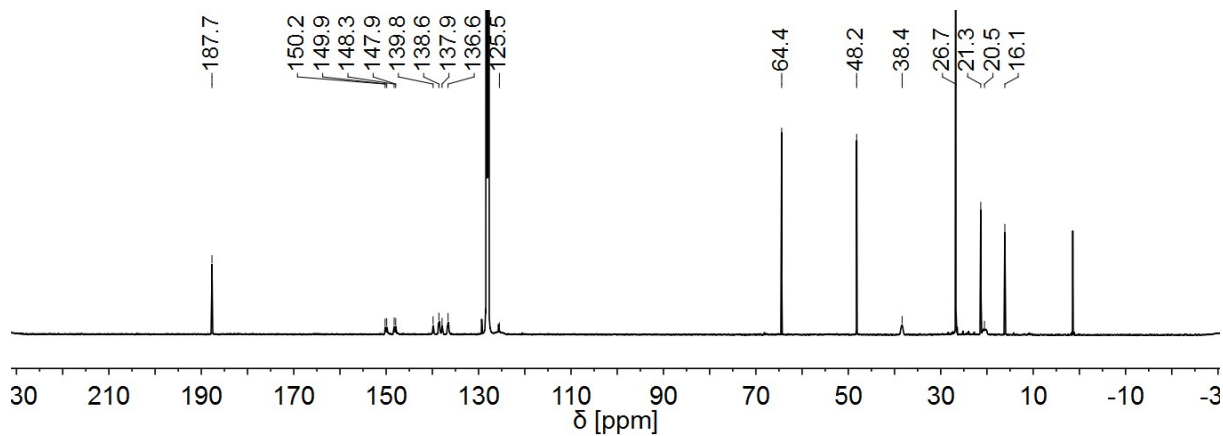


Figure S5. ^{13}C NMR spectrum (126 MHz, C_6D_6) of the cyclic iminium borate 5.

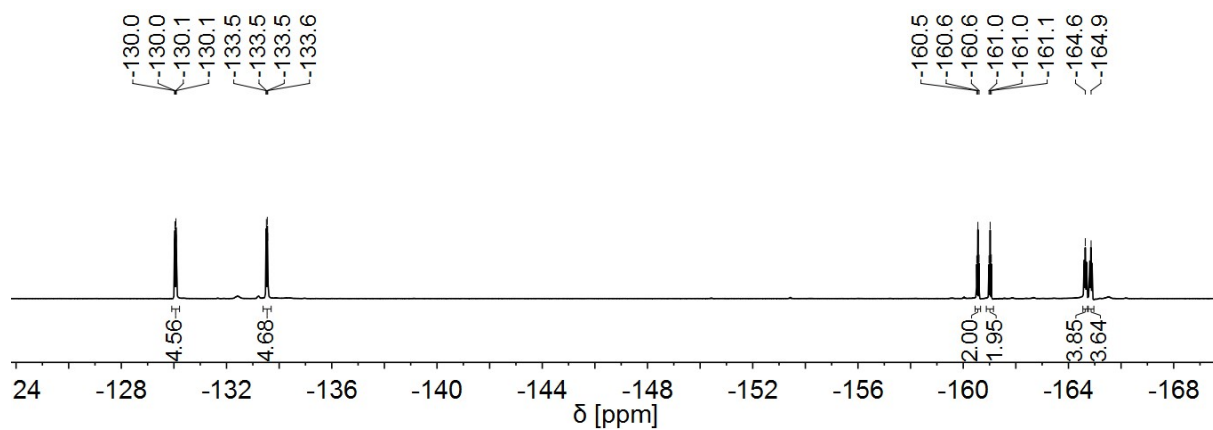


Figure S6. ^{19}F NMR spectrum (470 MHz, C_6D_6) of the cyclic iminium borate **5**.

***tert*-Butyl-*N,N*-dipropargylamine (**8**)**

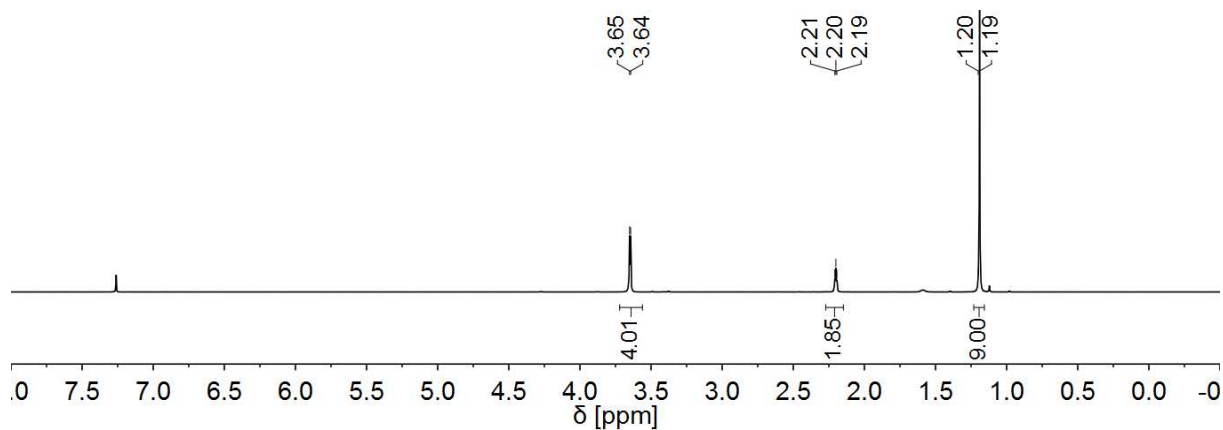


Figure S7. ^1H NMR spectrum (300 MHz, CDCl_3) of *tert*-butyl-*N,N*-dipropargylamine (**8**).

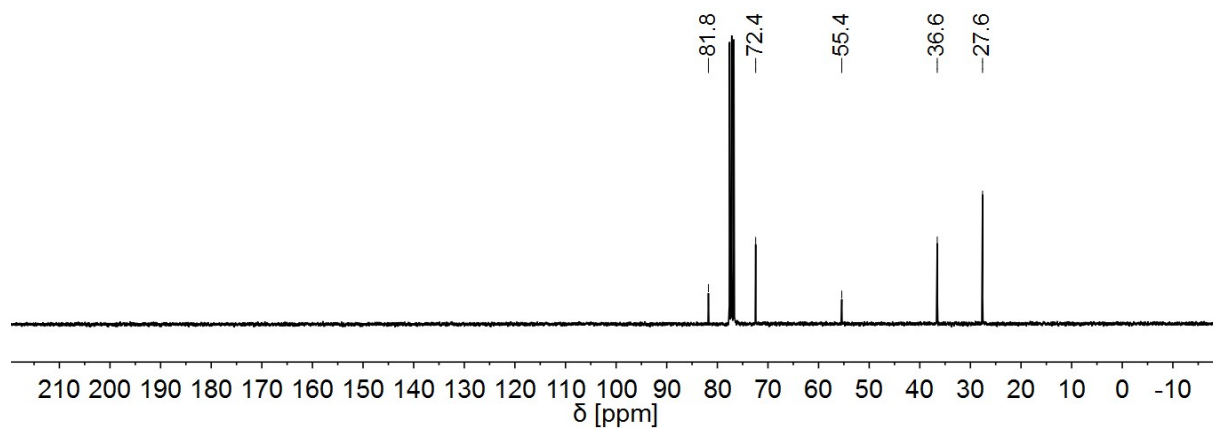


Figure S8. ^{13}C NMR spectrum (76 MHz, CDCl_3) of *tert*-butyl-*N,N*-dipropargylamine (**8**).

In situ synthesis of $t\text{-Bu-N-}[\text{CH}_2\text{-CH=CH-B}(\text{C}_6\text{F}_5)_2]_2$ **9**

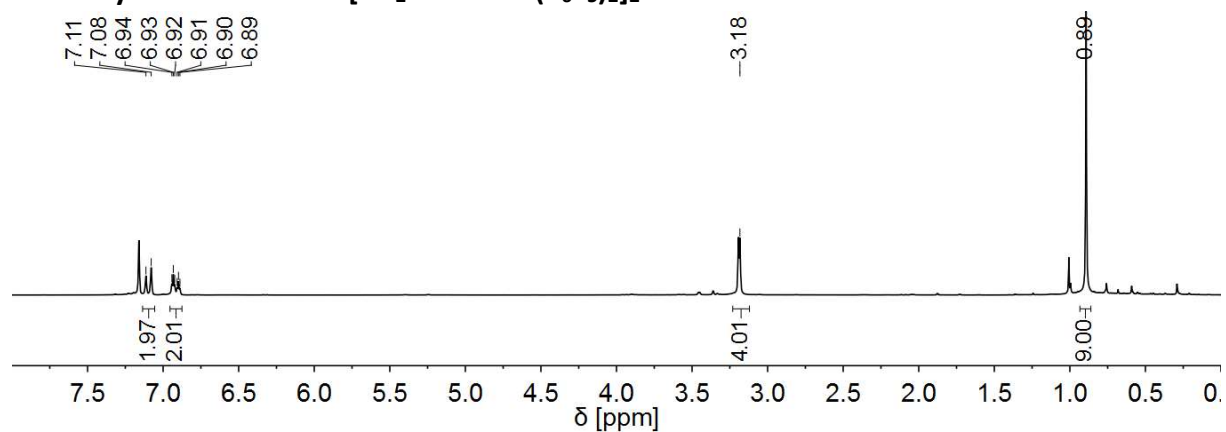


Figure S9. ^1H NMR spectrum (500 MHz, C_6D_6) of the hydroboration product **9** of *tert*-butyl-*N,N*-dipropargylamine (**8**).

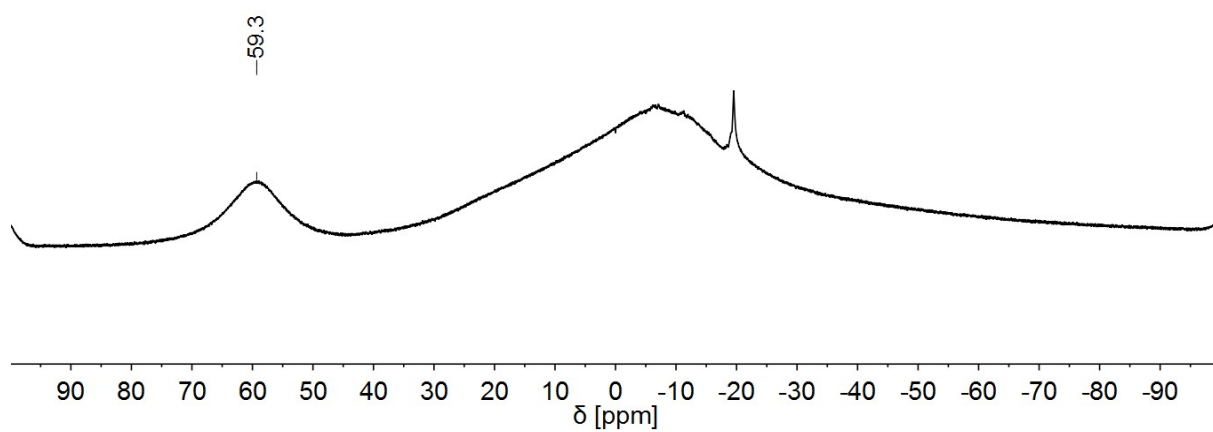


Figure S10. ^{13}B NMR spectrum (160 MHz, C_6D_6) of the hydroboration product **9** of *tert*-butyl-*N,N*-dipropargylamine (**8**) with traces of a decomposition product with a resonance at -19.5 ppm.

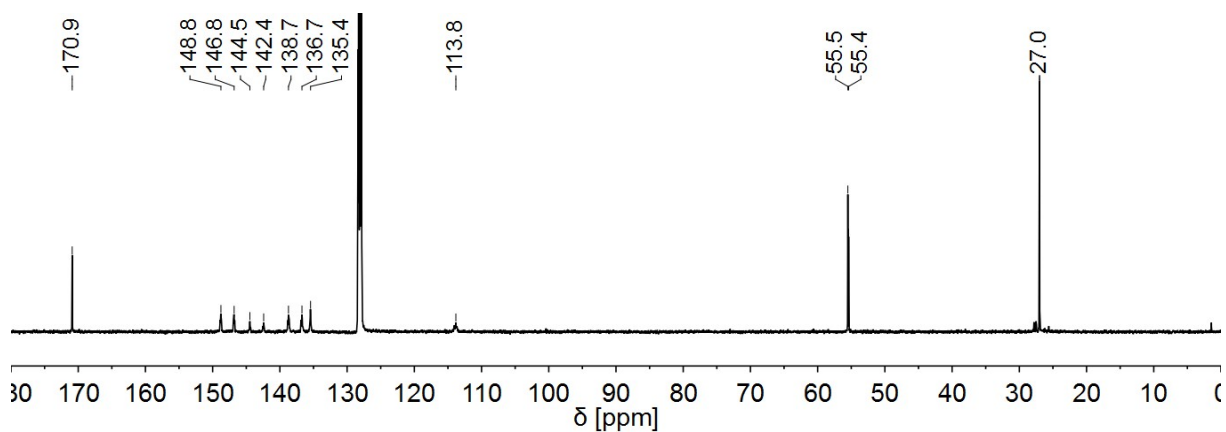


Figure S11. ^{13}C NMR spectrum (126 MHz, C_6D_6) of the hydroboration product **9** of *tert*-butyl-*N,N*-dipropargylamine (**8**).

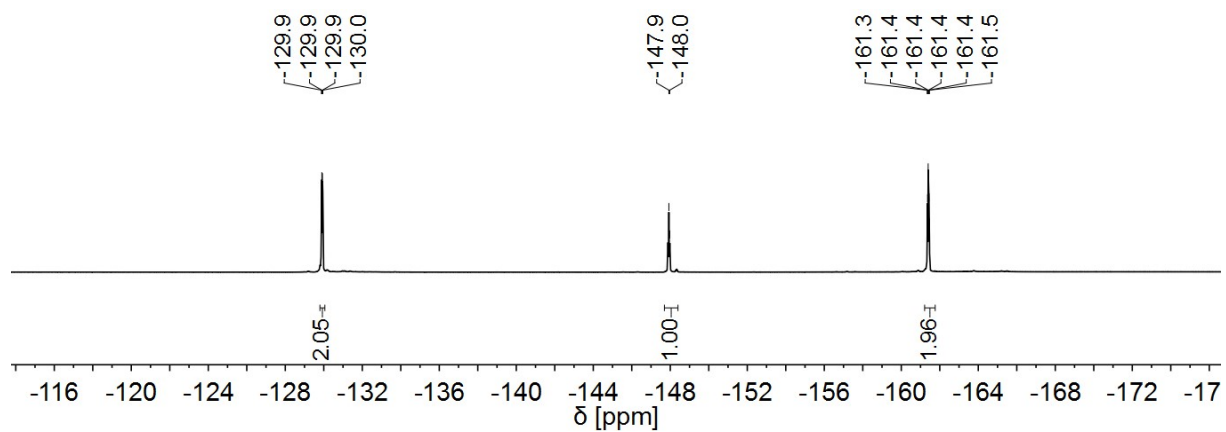


Figure S12. ^{19}F NMR spectrum (470 MHz, C_6D_6) of the hydroboration product 9 of *tert*-butyl-*N,N*-dipropargylamine (8).

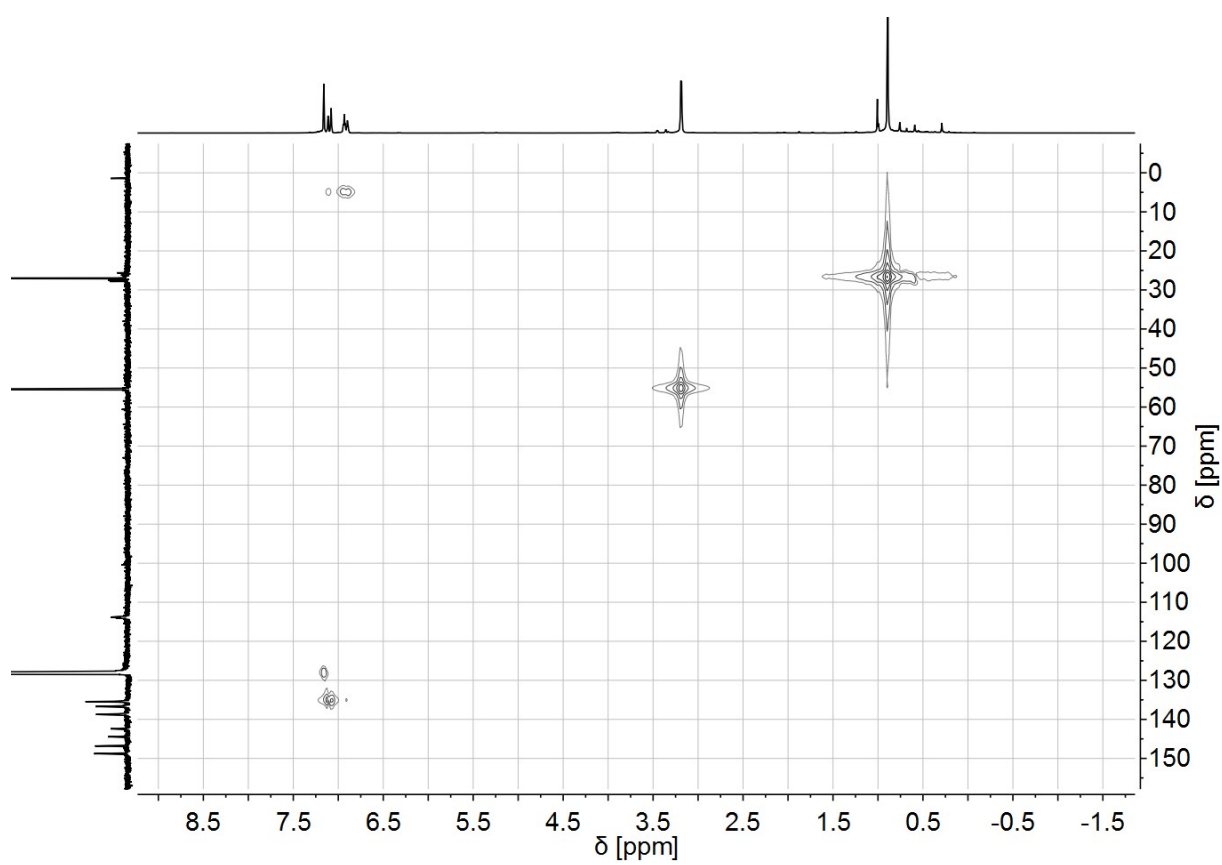


Figure S13. $^1\text{H}^{13}\text{C}$ HMQC NMR spectrum (500 MHz, C_6D_6) of the hydroboration product 9 of *tert*-butyl-*N,N*-dipropargylamine (8).

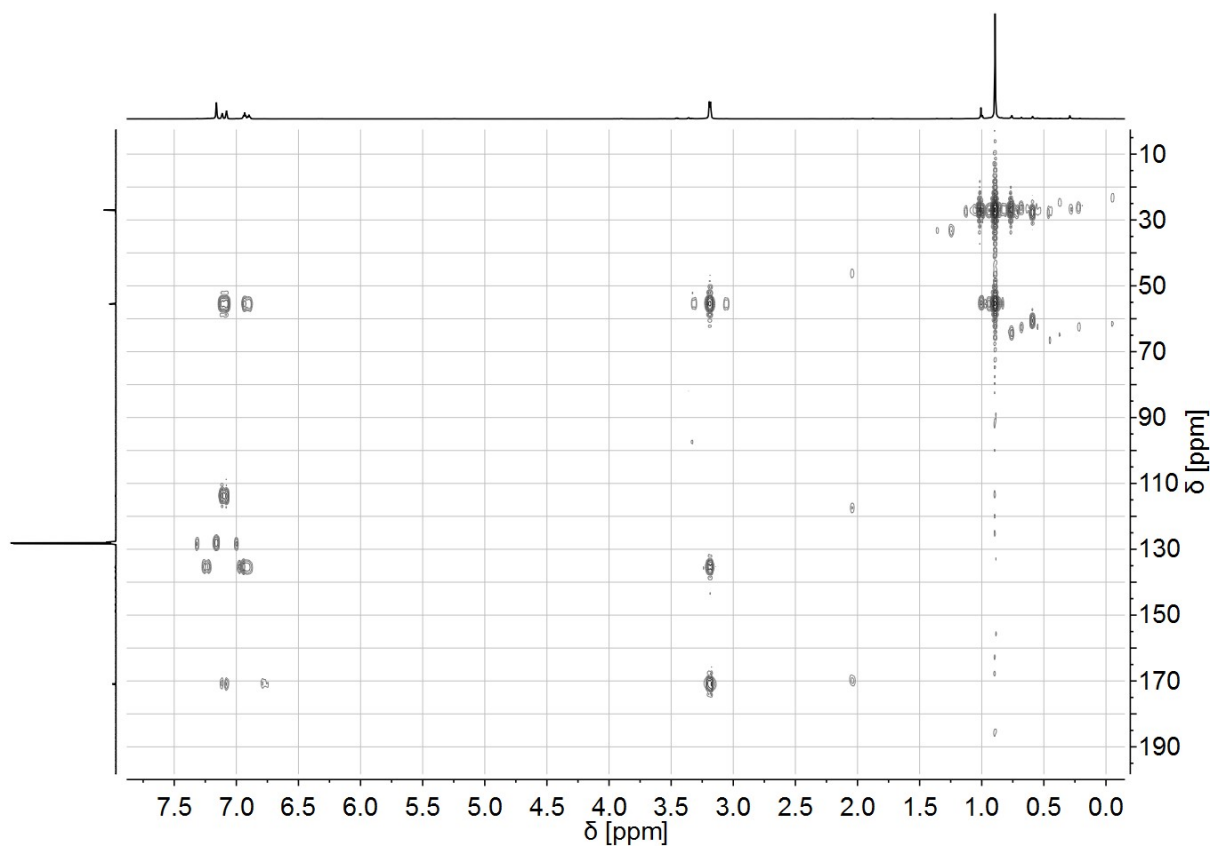


Figure S14. ^{13}C HMBC NMR spectrum (500 MHz, C_6D_6) of the hydroboration product **9** of *tert*-butyl-*N,N*-dipropargylamine (**8**).

Synthesis of $^t\text{Bu-N-}[\text{CH}_2\text{-CH=CH-B}(\text{C}_6\text{F}_5)_2]_2 \cdot 2\text{NMe}_3$ (10**)**

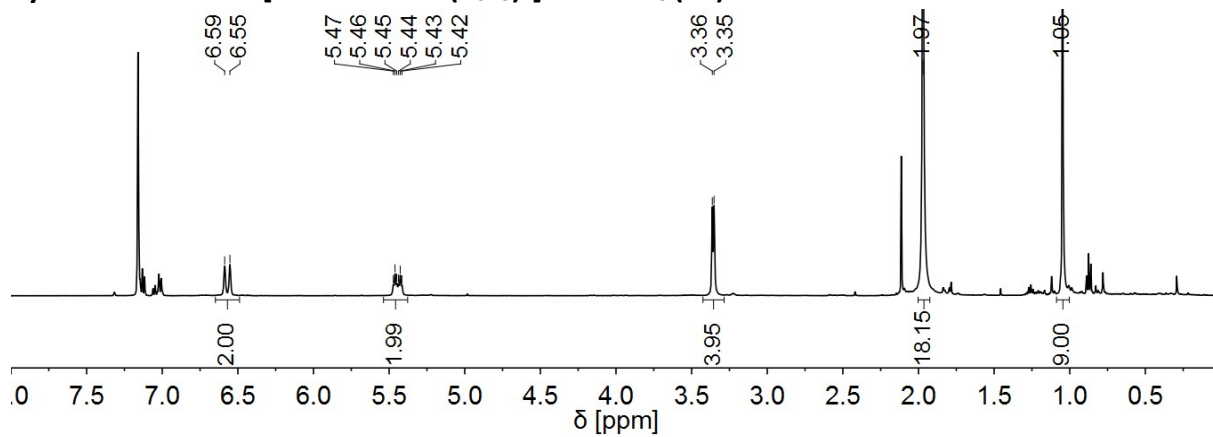


Figure S15. ^1H NMR spectrum (500 MHz, C_6D_6) of amine adduct $^t\text{Bu-N-}[\text{CH}_2\text{-CH=CH-B}(\text{C}_6\text{F}_5)_2]_2 \cdot 2\text{NMe}_3$ (**10**) with trace impurities of toluene.

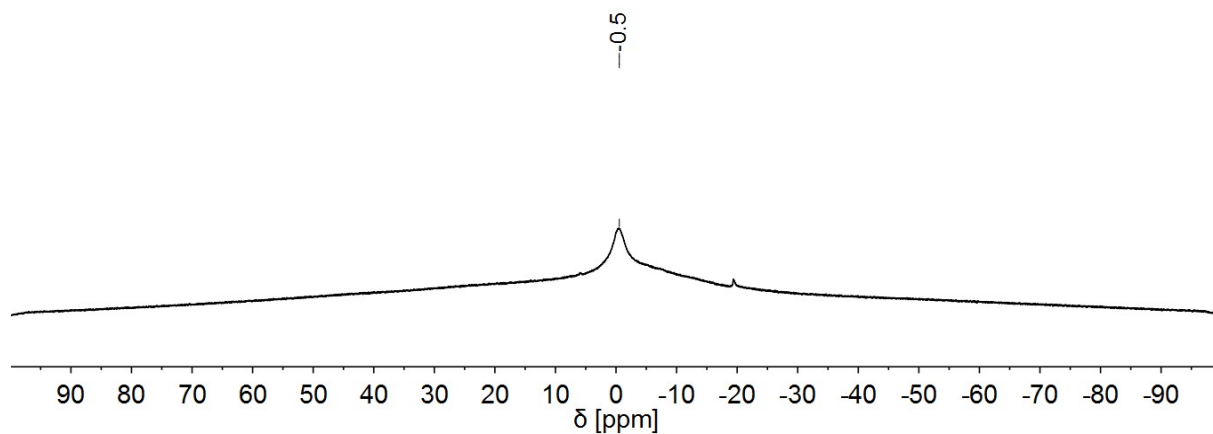


Figure S16. ^{13}B NMR spectrum (160 MHz, C_6D_6) of amine adduct $^t\text{Bu-N}[\text{CH}_2\text{-CH=CH-B}(\text{C}_6\text{F}_5)_2]_2 \cdot 2\text{NMe}_3$ (**10**).

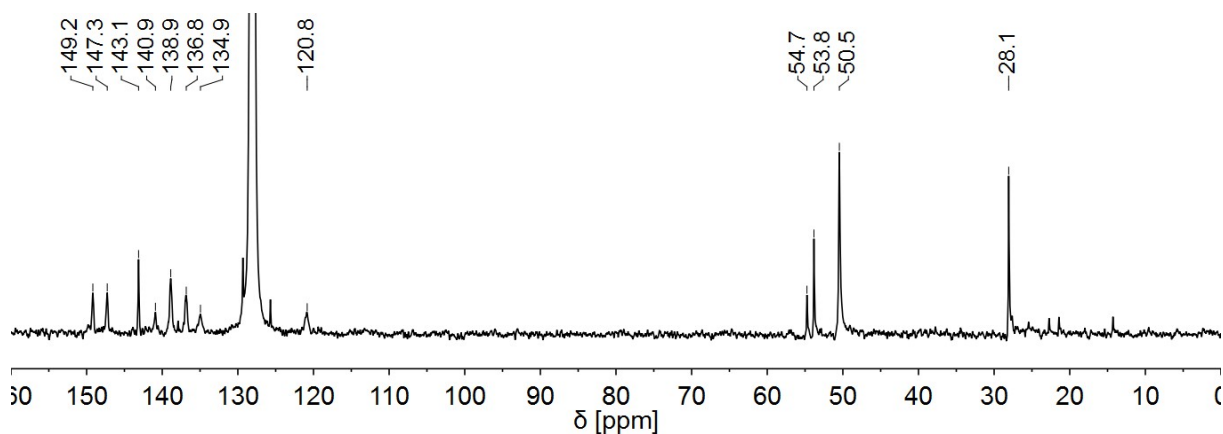


Figure S17. ^{13}C NMR spectrum (126 MHz, C_6D_6) of amine adduct $^t\text{Bu-N}[\text{CH}_2\text{-CH=CH-B}(\text{C}_6\text{F}_5)_2]_2 \cdot 2\text{NMe}_3$ (**10**) with trace impurities of toluene.

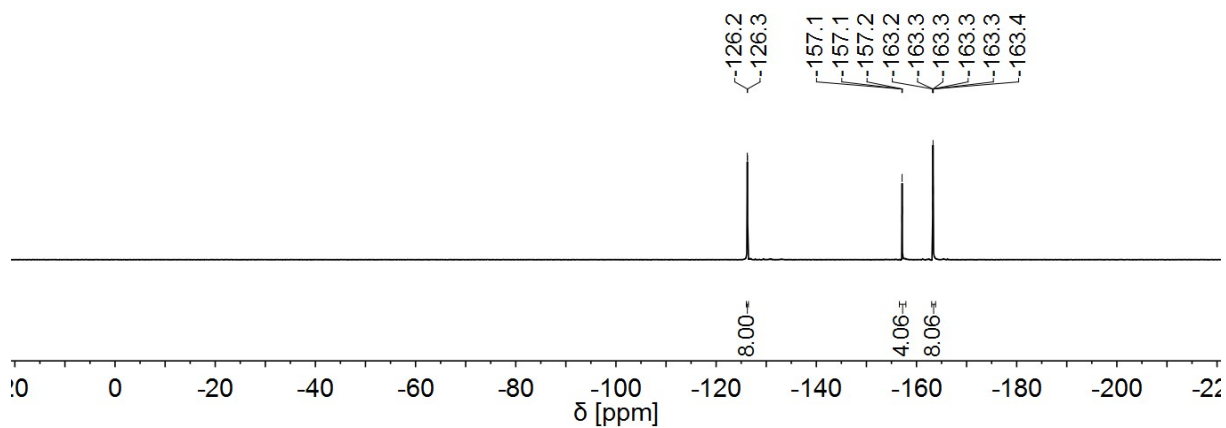


Figure S18. ^{19}F NMR spectrum (470 MHz, C_6D_6) of amine adduct $^t\text{Bu-N}[\text{CH}_2\text{-CH=CH-B}(\text{C}_6\text{F}_5)_2]_2 \cdot 2\text{NMe}_3$ (**10**).

Diallylphenylphosphine 12

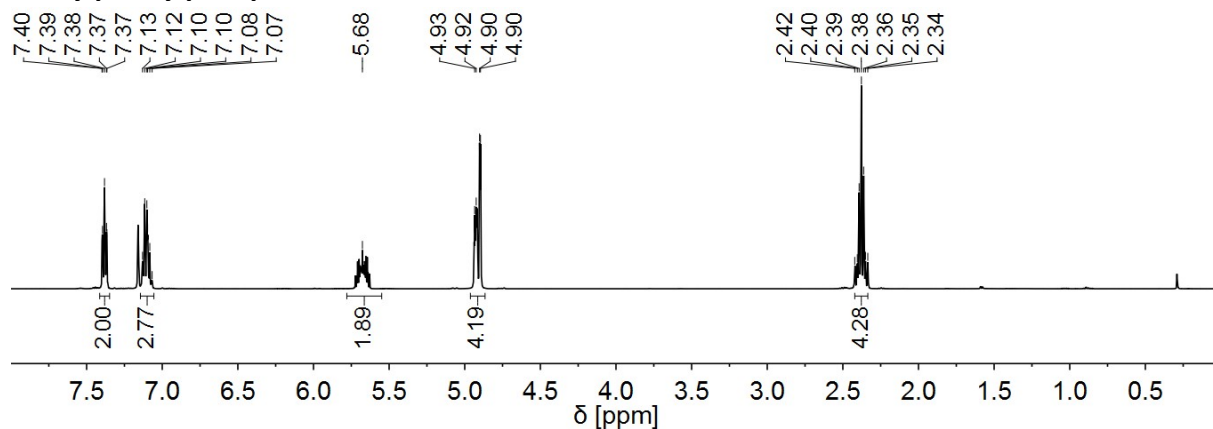


Figure S19. ¹H NMR spectrum (500 MHz, C₆D₆) of diallylphenylphosphine (12).

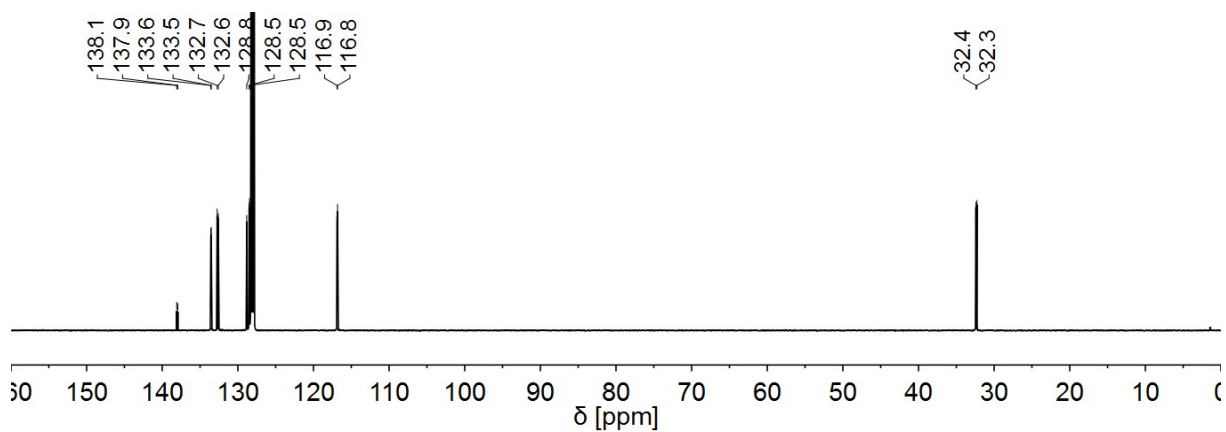


Figure S20. ¹³C NMR spectrum (126 MHz, C₆D₆) of diallylphenylphosphine (12).

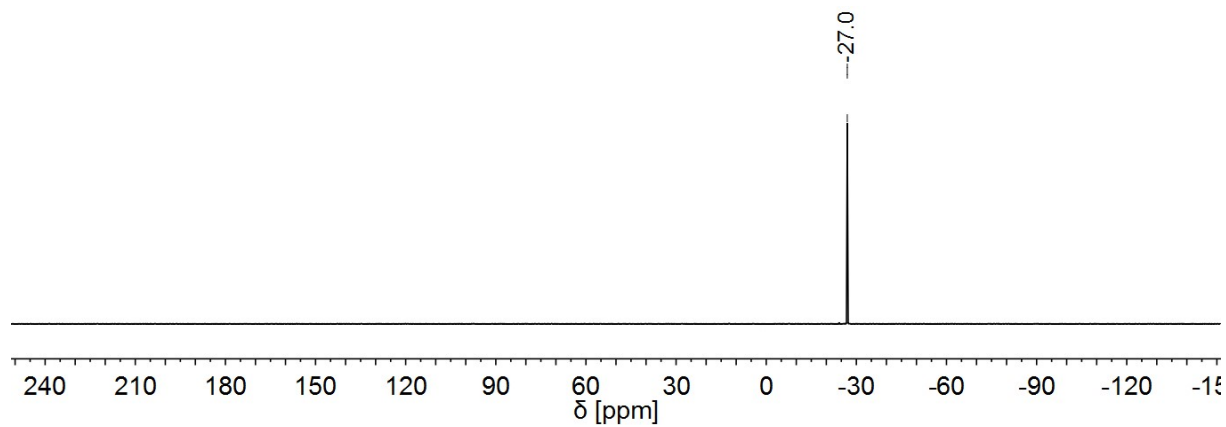


Figure S21. ³¹P NMR spectrum (203 MHz, C₆D₆) of diallylphenylphosphine (12).

Hydroboration of Diallylphenylphosphine to 13

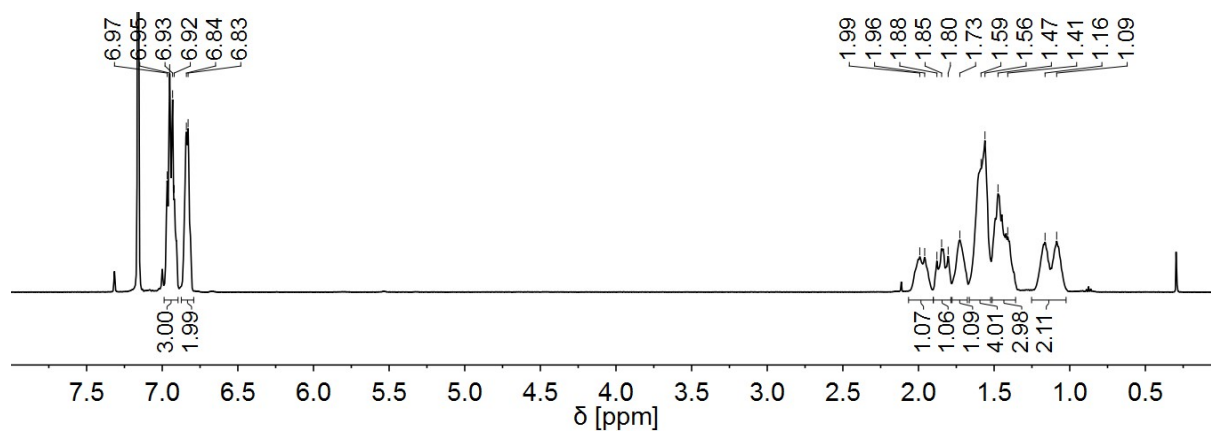


Figure S22. ¹H NMR spectrum (500 MHz, C₆D₆) of the doubly hydroboration product **13** of diallylphenylphosphine (**12**).

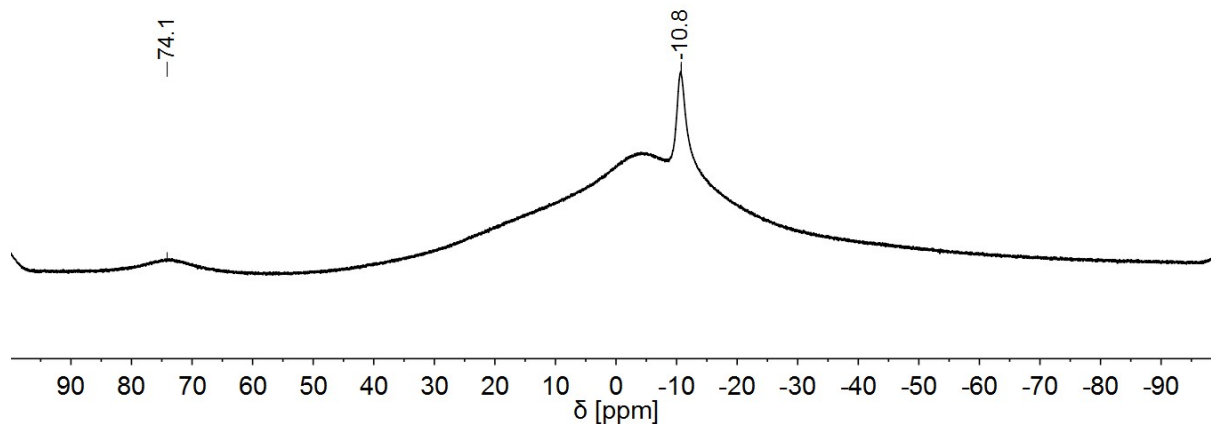


Figure S23. ¹³B NMR spectrum (160 MHz, C₆D₆) of the doubly hydroboration product **13** of diallylphenylphosphine (**12**).

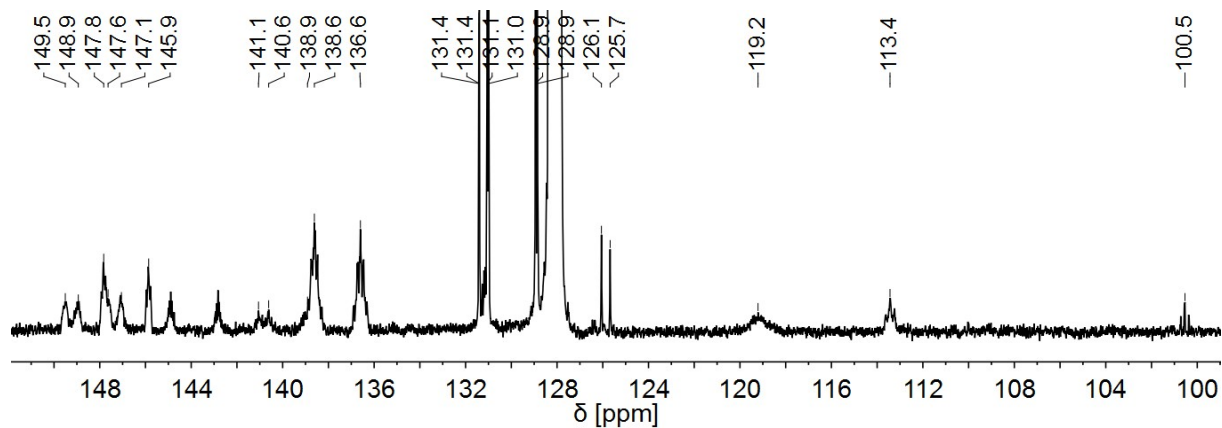


Figure S24. Excerpt of ¹³C NMR spectrum (126 MHz, C₆D₆) of the doubly hydroboration product **13** of diallylphenylphosphine (**12**).

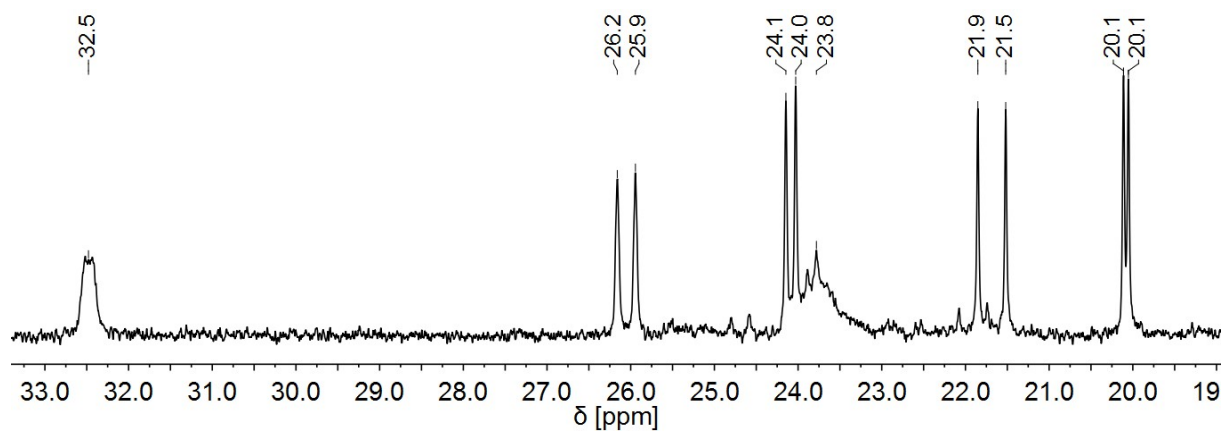


Figure S25. Excerpt of ^{13}C NMR spectrum (126 MHz, C_6D_6) of the doubly hydroboration product **13** of diallylphenylphosphine (**12**).

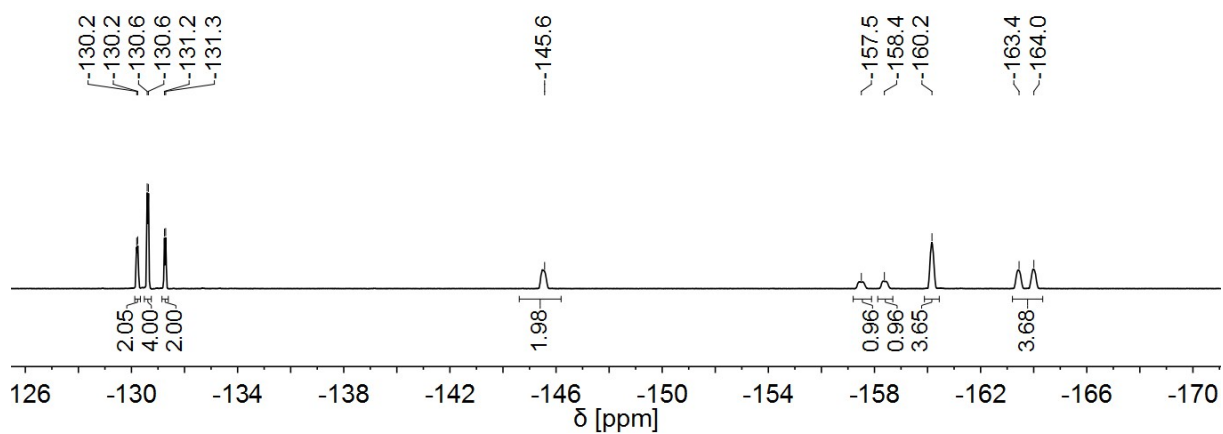


Figure S26. ^{19}F NMR spectrum (470 MHz, C_6D_6) of the doubly hydroboration product **13** of diallylphenylphosphine (**12**).

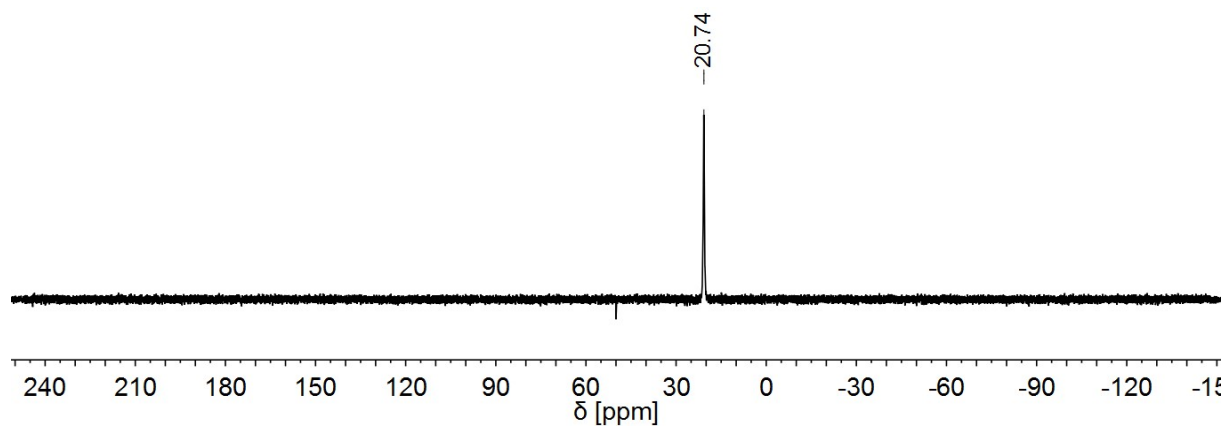


Figure S27. ^{31}P NMR spectrum (203 MHz, C_6D_6) of the doubly hydroboration product **13** of diallylphenylphosphine (**12**).

Diallyl-*tert*-butylphosphine 15

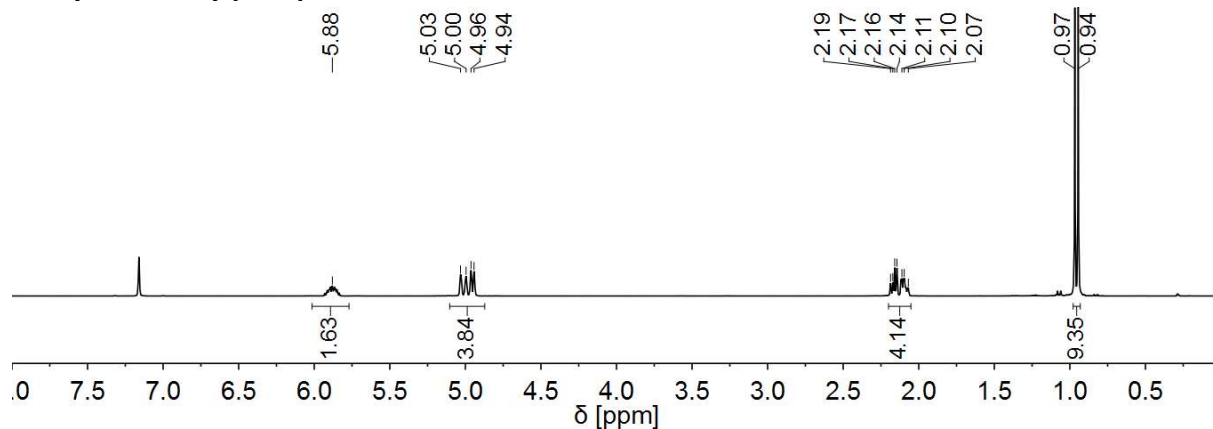


Figure S28. ¹H NMR spectrum (500 MHz, C₆D₆) of diallyl-*tert*-butylphosphine (15).

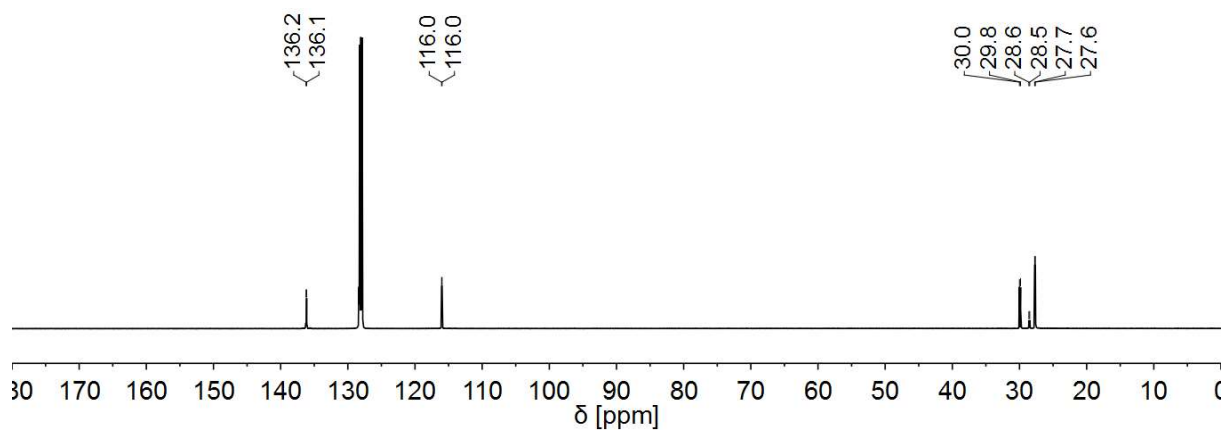


Figure S29. ¹³C NMR spectrum (126 MHz, C₆D₆) of diallyl-*tert*-butylphosphine (15).

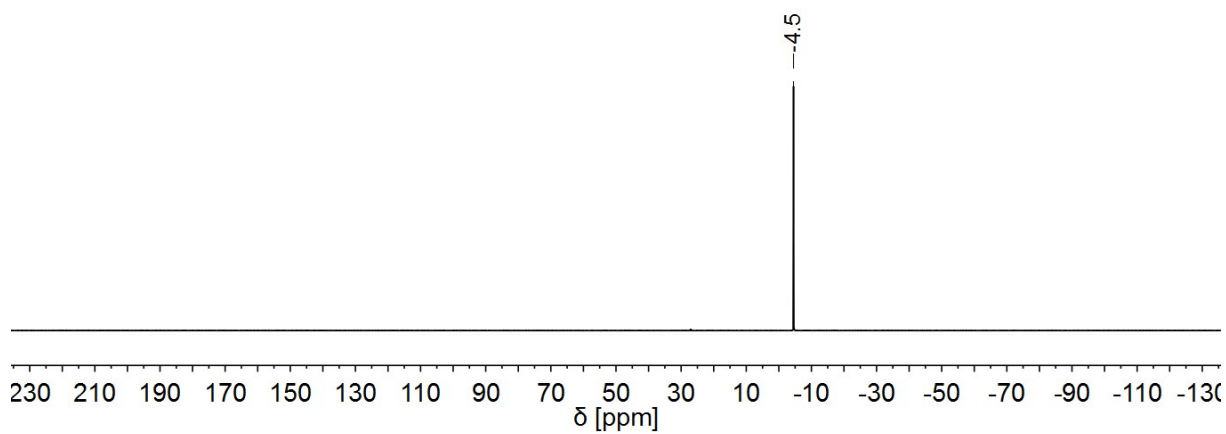


Figure S30. ³¹P NMR spectrum (203 MHz, C₆D₆) of diallyl-*tert*-butylphosphine (15).

Hydroboration of *tert*-butyldiallylphosphine to **16**

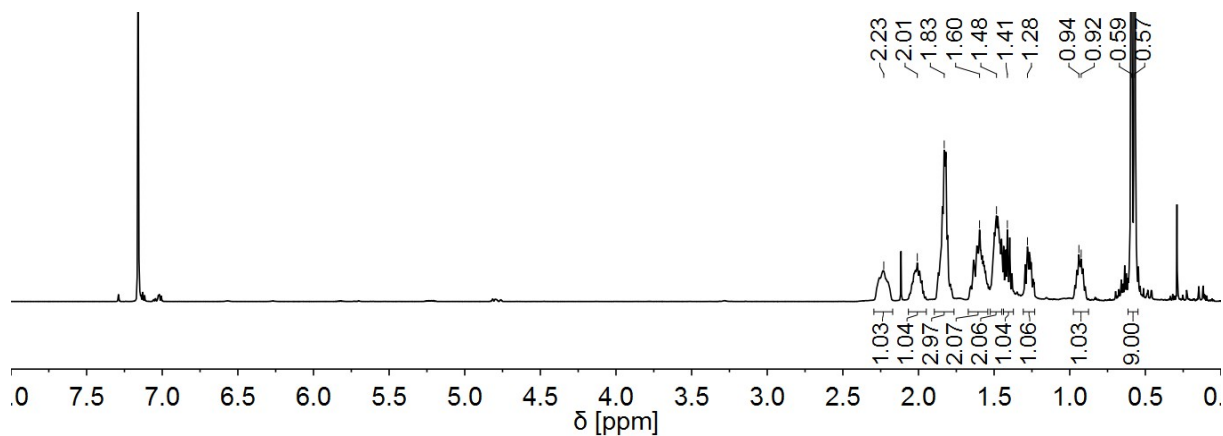


Figure S31. ¹H NMR spectrum (600 MHz, C₆D₆) of the doubly hydroboration product **16** of *tert*-butyldiallylphosphine (**15**).

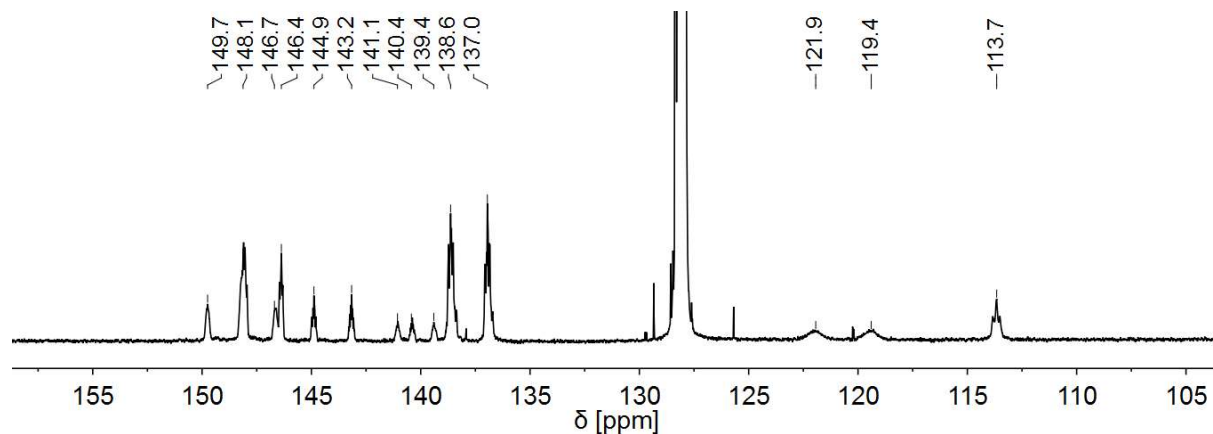


Figure S32. Excerpt of ¹³C NMR spectrum (151 MHz, C₆D₆) of the doubly hydroboration product **16** of *tert*-butyldiallylphosphine (**15**).

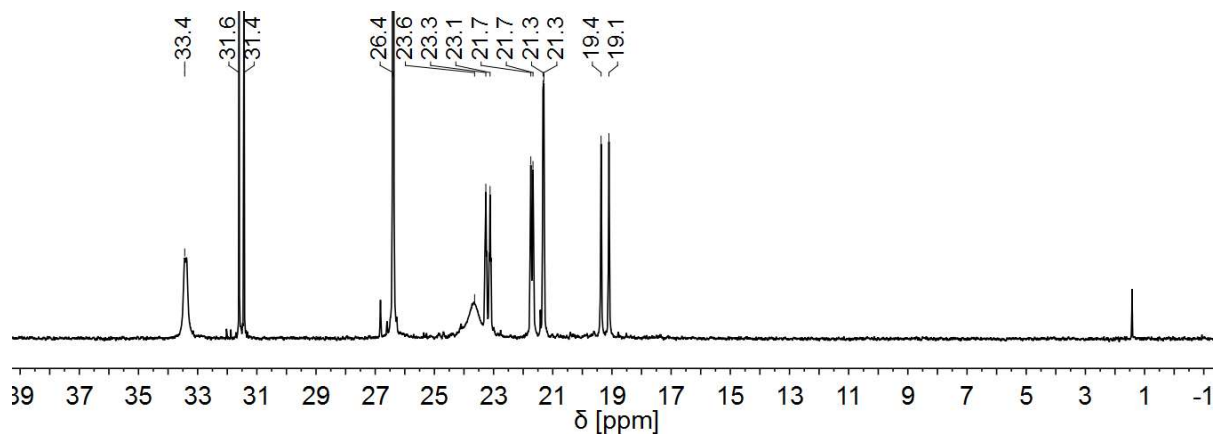


Figure S33. Excerpt of ¹³C NMR spectrum (151 MHz, C₆D₆) of the doubly hydroboration product **16** of *tert*-butyldiallylphosphine (**15**).

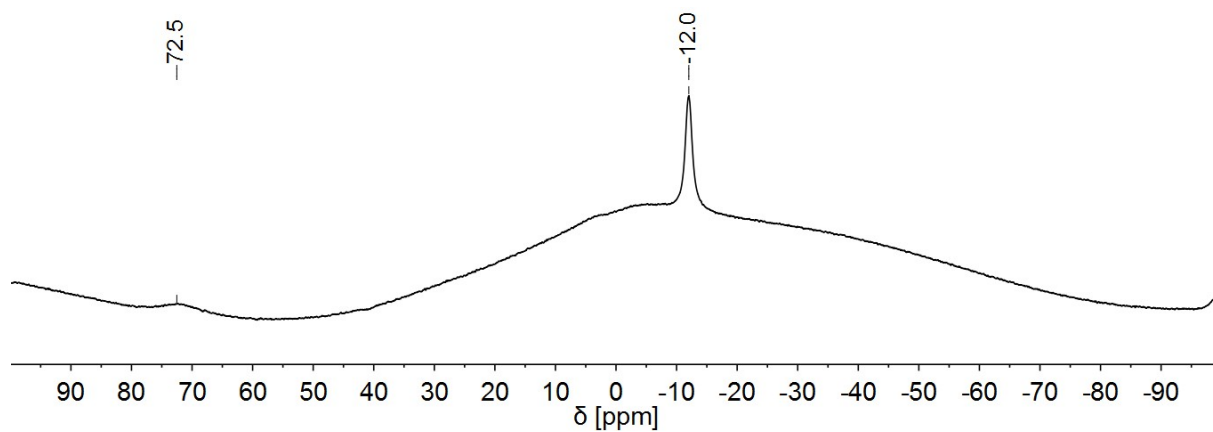


Figure S34. ^{11}B NMR spectrum (160 MHz, C_6D_6) of the doubly hydroboration product **16** of *tert*-butylidiallylphosphine (**15**).

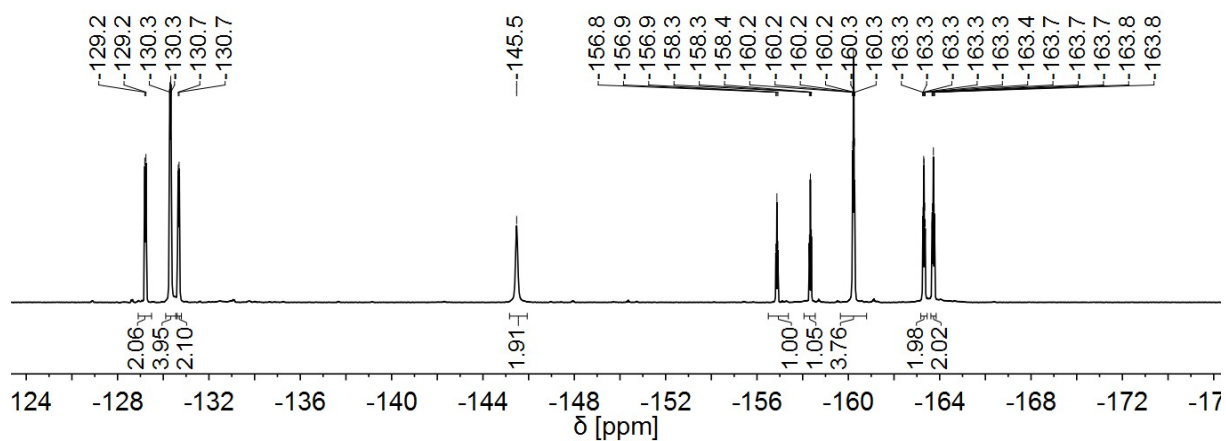


Figure S35. ^{19}F NMR spectrum (470 MHz, C_6D_6) of the doubly hydroboration product **16** of *tert*-butylidiallylphosphine (**15**).

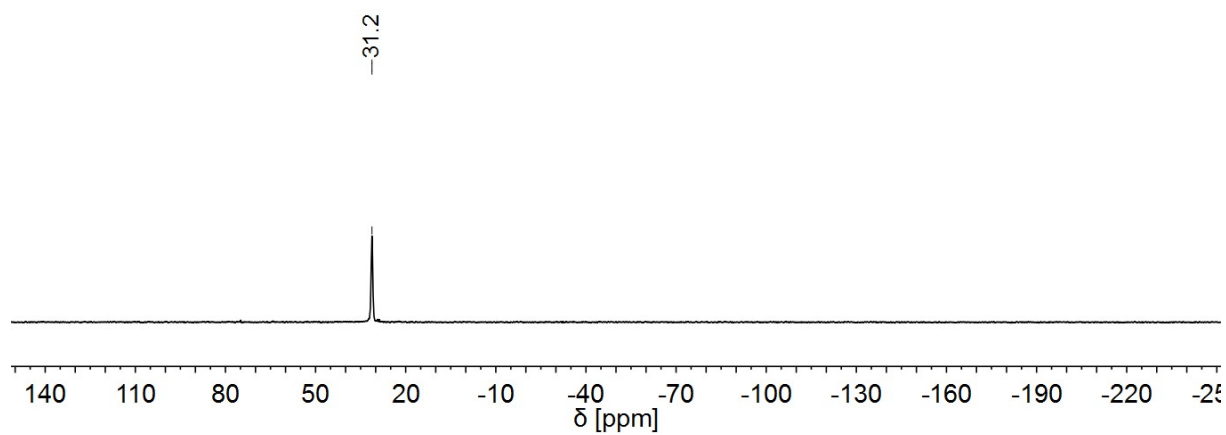


Figure S36. ^{31}P NMR spectrum (203 MHz, C_6D_6) of the doubly hydroboration product **16** of *tert*-butylidiallylphosphine (**15**).

Computational details

Table S1. Calculated electronic energies (ΔE , PW6B95-D3BJ(abc)/def2-TZVP), solvation free energies ($\delta_{\text{solvation}}$, PW6B95-D3BJ(abc)/def2-TZVP/COSMO(CH₂Cl₂)) and thermodynamic contributions (δ_{thermo} , PBEh-3c) as well as resulting Gibbs free energies (ΔG) of the compounds depicted in Figures S37–S44. All parameters are given in kJ mol⁻¹.

	ΔE	δ_{thermo}	$\delta_{\text{solvation}}$	ΔG
closed-13	-9912966.34	971.52	-44.71	-9912039.53
open-13	-9912870.55	961.75	-34.96	-9911943.75
13-H₂	-9915957.14	1012.42	-94.40	-9915039.12
bridged-13-H₂	-9916003.17	1031.99	-86.27	-9915057.45
closed-16	-9718838.02	1055.64	-39.85	-9717822.24
open-16	-9718750.34	1045.24	-32.16	-9717737.26
16-H₂	-9721851.47	1096.15	-95.52	-9720850.84
bridged-16-H₂	-9721904.73	1114.81	-83.37	-9720873.29
H ₂	-3084.75	-6.46	-0.79	-3092.00

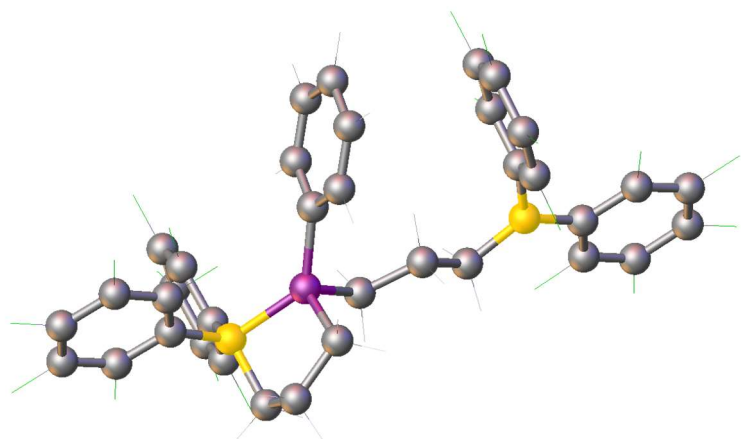


Figure S37. Optimized molecular structure of the 5-membered ring conformer of **13** (**closed-13**).

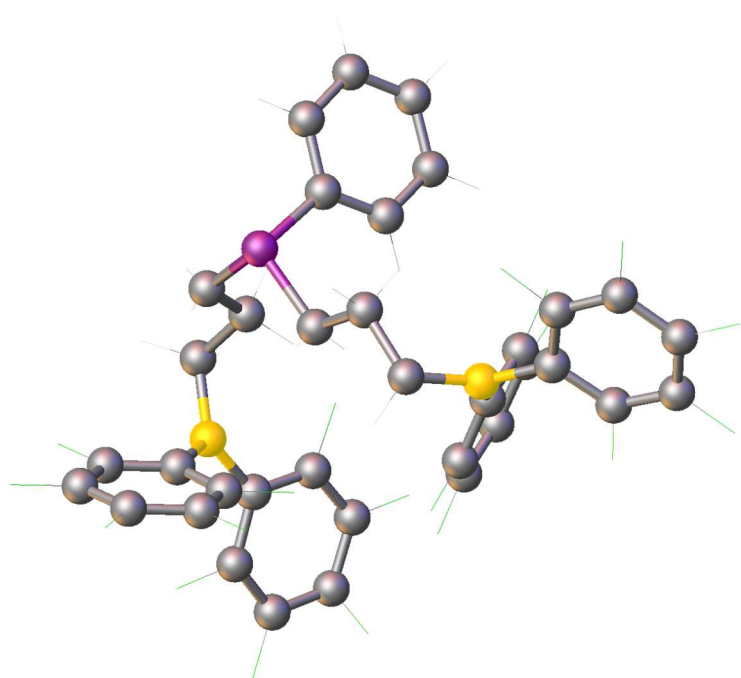


Figure S38. Optimized molecular structure of the open conformer of **13** (**open-13**).

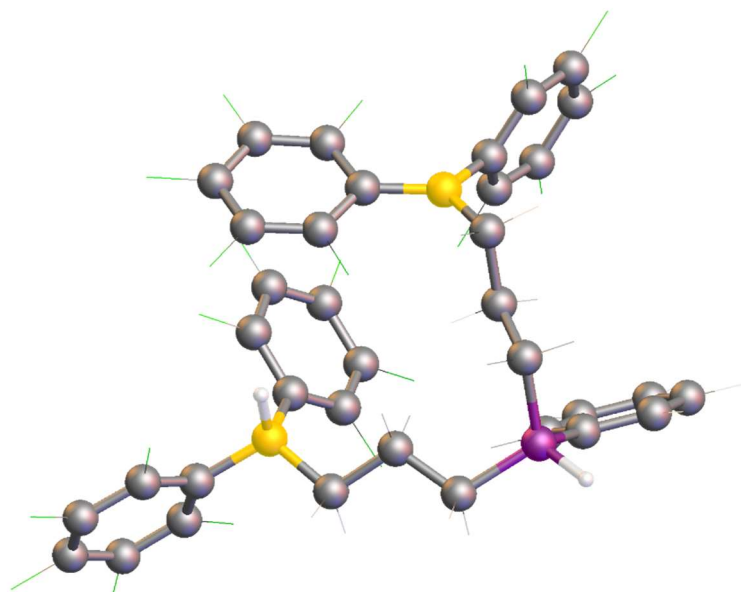


Figure S39. Optimized molecular structure of the hydrogen splitting product of **13** (**13-H₂**).

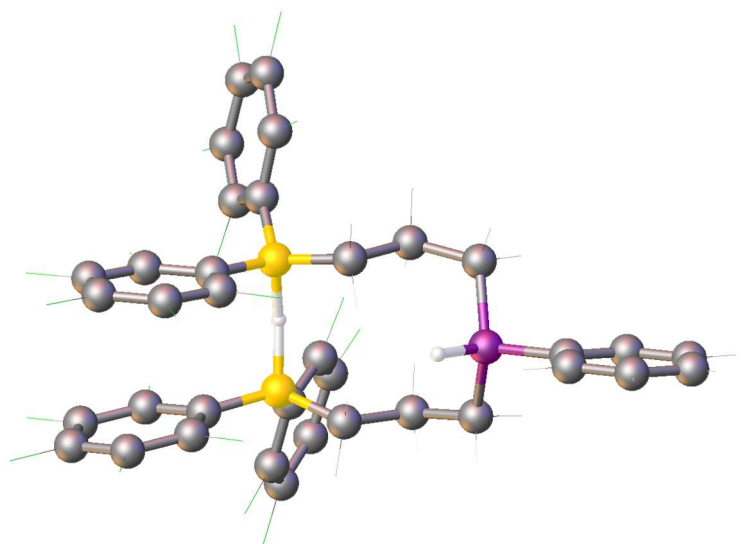


Figure S40. Optimized molecular structure of the 10-membered ring conformer of the hydrogen splitting product of **13** (**bridged-5-H₂**).

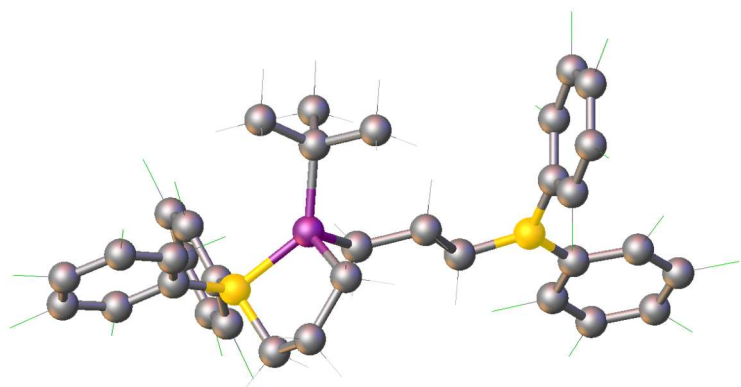


Figure S41. Optimized molecular structure of the 5-membered ring conformer of **16** (**closed-16**).

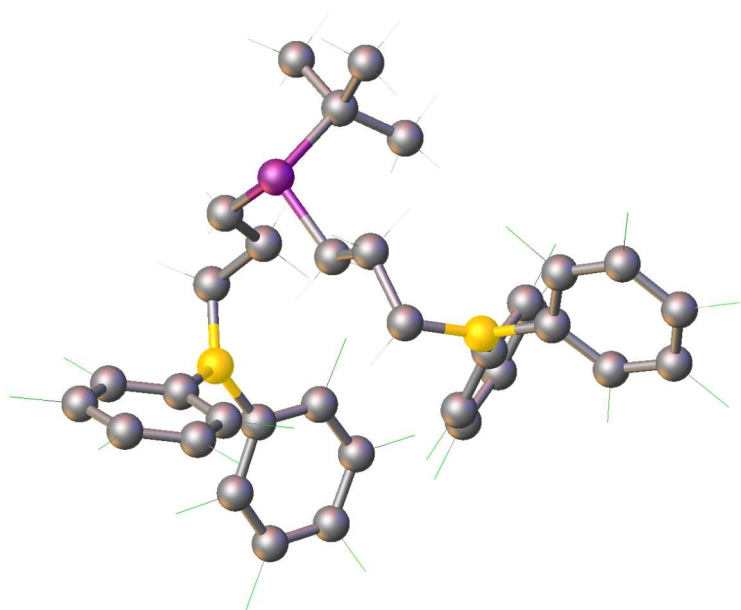


Figure S42. Optimized molecular structure of the open conformer of **16** (**open-16**).

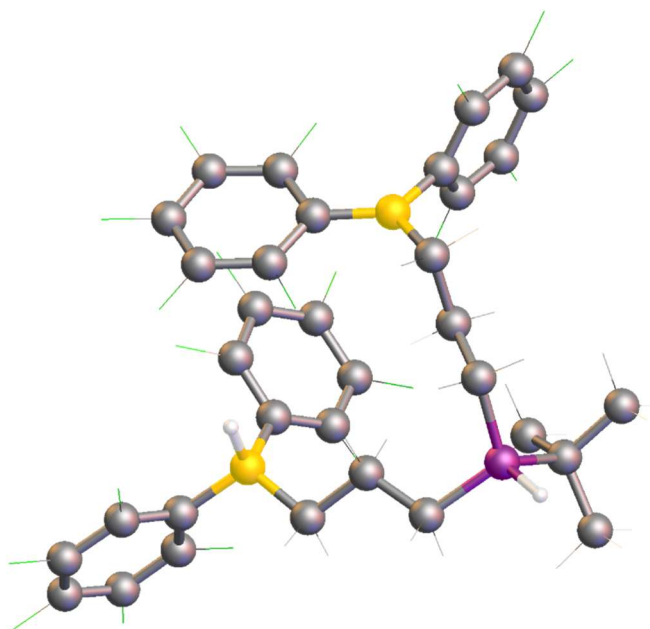


Figure S43. Optimized molecular structure of the open chain conformer of the hydrogen splitting product of **16** (**16-H₂**).

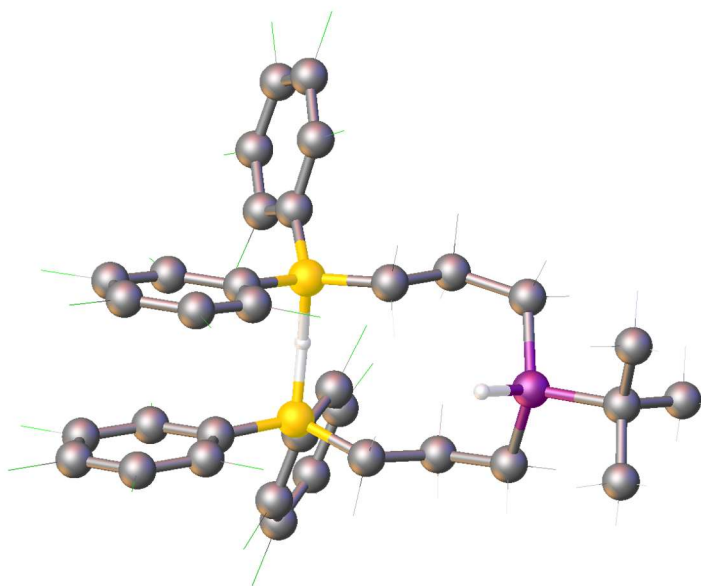


Figure S44. Optimized molecular structure of the 10-membered ring conformer of the hydrogen splitting product of **16** (bridged-16-H₂).

Table S2. Cartesian coordinates of the optimized structure of **closed-13**.

C	-0.1894970	0.1793937	1.1567805
C	-2.3185495	1.2717538	2.8463079
C	-3.1553394	0.1314444	3.4595501
C	-2.8353018	-1.1841391	2.7457823
B	-3.0488104	-0.9591364	1.1306519
C	0.7864966	1.3380065	1.3106198
C	2.2516969	0.9084569	1.2787412
H	-1.3783976	1.4175691	3.3809010
H	-2.8474083	2.2227985	2.8640403
H	-0.0031403	-0.3508180	0.2184142
H	-0.0753562	-0.5609629	1.9516032
H	-4.2150694	0.3672957	3.3477550
H	-2.9671665	0.0713475	4.5329532
H	-3.4898548	-1.9811406	3.1054194
H	-1.8244628	-1.4944093	3.0202415
H	0.5851519	1.8759989	2.2416566
H	0.5971461	2.0506294	0.5089568
H	2.4075849	0.2310578	0.4240899
H	2.4938327	0.2979561	2.1517383
B	3.2868243	2.0718117	1.0537085
P	-1.9501224	0.7145337	1.1354514
C	-1.8907421	2.1105010	-0.0249112
C	-1.4977615	1.8651949	-1.3397747
C	-2.1126088	3.4226635	0.3803770
C	-1.3257206	2.9143217	-2.2278677
H	-1.3053946	0.8564988	-1.6793428
C	-1.9407148	4.4715390	-0.5108300
H	-2.4086454	3.6455707	1.3959812
C	-1.5466177	4.2206649	-1.8158780
H	-1.0201938	2.7095177	-3.2450178
H	-2.1158220	5.4870676	-0.1815061
H	-1.4118186	5.0392144	-2.5100816
C	4.8254134	1.9249634	1.2619254
C	5.4495933	0.6876006	1.4378349
C	5.6770812	3.0336189	1.2763356
C	6.8118351	0.5490472	1.6166005
C	7.0422158	2.9311083	1.4623975
C	7.6093676	1.6803241	1.6315668
C	2.6855646	3.4268464	0.5089558
C	2.1272396	4.3651822	1.3509752
C	2.5549233	3.6353622	-0.8470979
C	1.4579444	5.4763065	0.8770859
C	1.8868884	4.7296255	-1.3648400
C	1.3391818	5.6520537	-0.4916094
C	-4.6279863	-0.7529369	0.8304180
C	-5.2892140	0.4495341	0.6723136
C	-5.4357192	-1.8791075	0.7589345
C	-6.6478226	0.5542516	0.4324415
C	-6.7975728	-1.8266199	0.5229574
C	-7.4075976	-0.5968356	0.3536518
C	-2.3882054	-1.9930259	0.0719008
C	-1.6329588	-3.1117097	0.3876589
C	-2.6030185	-1.7974384	-1.2860529
C	-1.1249748	-3.9770646	-0.5685535
C	-2.1160140	-2.6332162	-2.2732688
C	-1.3692124	-3.7379891	-1.9069194
F	-4.6067797	1.6024173	0.7587162
F	-7.2236366	1.7425955	0.2840302
F	-8.7121475	-0.5229623	0.1274770
F	-7.5228588	-2.9373046	0.4641313
F	-3.3084239	-0.7348921	-1.6900669
F	-2.3504919	-2.3850391	-3.5572008
F	-0.8882429	-4.5565958	-2.8319210
F	-0.4063279	-5.0349731	-0.2094006
F	-1.3599342	-3.4179649	1.6569007
F	-4.8970719	-3.0884972	0.9320005
F	5.1948298	4.2585069	1.1269862
F	7.8085768	4.0106920	1.4807488
F	8.9102179	1.5655678	1.8065146
F	7.3597576	-0.6464591	1.7714075
F	4.7402541	-0.4325681	1.4173644

F	3.0595938	2.7255245	-1.6857227
F	1.7483835	4.8920980	-2.6733176
F	0.6794127	6.6988042	-0.9664341
F	0.9169127	6.3577034	1.7070831
F	2.2175675	4.1733686	2.6706086

Table S3. Cartesian coordinates of the optimized structure of **open-13**.

C	1.5036979	3.2792952	1.5622894
C	-0.6784055	2.3177276	-0.0042981
C	-2.1310386	2.3653387	-0.4611490
C	-2.4341676	1.3849473	-1.6293126
C	1.9072821	1.9305684	2.1426476
C	3.4456323	1.6895064	2.0940918
H	-0.0330605	2.5550244	-0.8556663
H	-0.3995837	1.3103246	0.3142931
H	1.8737389	4.0777958	2.2106682
H	1.9794025	3.4512649	0.5922111
H	-2.3626085	3.3794609	-0.7923162
H	-2.7907073	2.1895127	0.3940574
H	-1.5103837	1.2273226	-2.1936510
H	-3.1365327	1.8462395	-2.3230411
H	1.3697286	1.1231709	1.6351852
H	1.5758535	1.8733016	3.1800121
H	3.7698793	1.1544319	2.9853765
H	3.9487460	2.6596300	2.1136225
B	3.7532176	0.9141992	0.7726536
P	-0.3058682	3.6120235	1.2720234
C	-1.0601512	2.9292365	2.7989935
C	-1.3304219	1.5798590	3.0144422
C	-1.3777201	3.8368675	3.8081277
C	-1.8957092	1.1455959	4.2035248
H	-1.0867676	0.8513167	2.2525126
C	-1.9276592	3.4060865	5.0064651
H	-1.1983441	4.8939309	3.6497837
C	-2.1904552	2.0590101	5.2050632
H	-2.1014251	0.0935096	4.3487458
H	-2.1620472	4.1248395	5.7806787
H	-2.6291676	1.7216560	6.1348356
C	3.5854932	1.6679575	-0.6000820
C	2.6092311	1.2594951	-1.4898902
C	4.3201535	2.7875069	-0.9484306
C	2.3370913	1.9377314	-2.6624201
C	4.1004010	3.4772931	-2.1262460
C	3.0953412	3.0516141	-2.9802108
C	4.0932503	-0.6128182	0.7385290
C	3.5671957	-1.5233899	1.6490801
C	4.9663025	-1.1324244	-0.2124451
C	3.8825209	-2.8679320	1.6277532
C	5.3160165	-2.4682595	-0.2552755
C	4.7656448	-3.3372212	0.6705742
F	5.2897251	3.2093053	-0.1394187
F	4.8290310	4.5373847	-2.4435855
F	2.8594718	3.7117108	-4.1012323
F	1.3620077	1.5437517	-3.4706798
F	1.8659721	0.1935416	-1.1885013
F	5.5332803	-0.3246057	-1.1028230
F	6.1692255	-2.9220463	-1.1616135
F	5.0870553	-4.6172148	0.6440114
F	3.3655646	-3.7066264	2.5122133
F	2.6952964	-1.1169621	2.5673536
B	-2.9788075	0.0285109	-1.0717093
C	-4.4801256	-0.3910762	-1.2275917
C	-5.5229849	0.5194295	-1.1108715
C	-4.8374617	-1.7060057	-1.5009945
C	-6.8488828	0.1537061	-1.2423103
C	-6.1506413	-2.1038911	-1.6634685
C	-7.1591850	-1.1654433	-1.5261257
C	-2.0355623	-0.9294752	-0.2528643
C	-0.8575177	-1.4463248	-0.7664555
C	-2.3549502	-1.2736814	1.0500063
C	-0.0168532	-2.2508678	-0.0197607
C	-1.5344723	-2.0656359	1.8308118
C	-0.3582033	-2.5526871	1.2881182
F	-1.8554555	-2.3546922	3.0857070
F	0.4336474	-3.3215453	2.0147680
F	1.1024054	-2.7428654	-0.5347335
F	-0.5385806	-1.2033054	-2.0339948
F	-3.4739342	-0.7989206	1.5954006

F	-3.8916261	-2.6284061	-1.6542910
F	-8.4209297	-1.5292503	-1.6670349
F	-7.8194261	1.0444966	-1.0997793
F	-5.2638101	1.7900210	-0.8196950
F	-6.4530266	-3.3625912	-1.9467745

Table S4. Cartesian coordinates of the optimized structure of **13-H₂**.

C	1.6302930	-2.2812094	3.3554074
C	-1.0005130	-3.4521776	2.4267831
C	-1.2863634	-2.0672834	1.8282094
C	-2.7184672	-1.8862679	1.3512124
C	2.0242276	-1.3186175	2.2342959
C	2.7669960	-0.0713400	2.7487669
H	-1.3566152	-4.2499318	1.7694939
H	-1.5125239	-3.5759080	3.3843755
H	2.5126715	-2.6303341	3.8973435
H	0.9713100	-1.7970876	4.0801906
H	-0.6050287	-1.8827263	0.9959478
H	-1.0626266	-1.2968739	2.5697778
H	-3.3819098	-1.8949809	2.2224997
H	-3.0225162	-2.7344276	0.7313052
H	1.1262143	-1.0289540	1.6889766
H	2.6591333	-1.8413261	1.5170925
H	3.7881692	-0.3540990	3.0147329
H	2.2933458	0.3174785	3.6480796
B	2.7487549	0.9279020	1.5266492
P	0.7644003	-3.7524842	2.7077097
C	1.6202827	-4.3298024	1.2464061
C	2.8436711	-4.9829931	1.3972706
C	1.1303703	-4.0323505	-0.0220476
C	3.5729408	-5.3333084	0.2748083
H	3.2291172	-5.2238922	2.3812270
C	1.8749516	-4.3757978	-1.1399371
H	0.1804133	-3.5368971	-0.1595368
C	3.0918707	-5.0224514	-0.9912356
H	4.5178682	-5.8470145	0.3867386
H	1.4984533	-4.1242413	-2.1214376
H	3.6705123	-5.2876913	-1.8658139
C	1.6398340	1.9824618	1.2857581
C	0.4612883	2.0420617	2.0393115
C	1.7641580	2.9628946	0.2946648
C	-0.5136285	2.9959906	1.8456873
C	0.8098167	3.9350755	0.0756972
C	-0.3333256	3.9478631	0.8556984
C	3.8730691	0.6741702	0.4494639
C	3.6016117	0.0224390	-0.7374366
C	5.1845431	1.0341403	0.6861838
C	4.5864433	-0.2703473	-1.6621212
C	6.1968918	0.7778663	-0.2191750
C	5.8894016	0.1186710	-1.3982927
F	2.8510896	3.0161006	-0.4642036
F	0.9845090	4.8599247	-0.8536048
F	-1.2440319	4.8758325	0.6656075
F	-1.6015175	3.0179224	2.5918814
F	0.2270347	1.1451785	2.9941378
F	5.4791229	1.6697538	1.8227199
F	7.4463138	1.1453211	0.0281777
F	6.8466317	-0.1469192	-2.2730867
F	4.3024506	-0.9175048	-2.7829267
F	2.3480735	-0.3605139	-0.9902885
B	-2.8703925	-0.4302410	0.6135443
C	-1.9247147	-0.2222163	-0.7187800
C	-1.3253753	-1.2009120	-1.4928693
C	-1.6360088	1.0713353	-1.1343174
C	-0.4544985	-0.9451560	-2.5385546
C	-0.7803442	1.3813867	-2.1767813
C	-0.1736924	0.3604460	-2.8846183
C	-4.4267969	-0.1237643	0.2520028
C	-5.2398123	0.6570652	1.0587860
C	-5.0444624	-0.6429461	-0.8741173
C	-6.5660301	0.9289860	0.7647263
C	-6.3642044	-0.3962853	-1.2095014
C	-7.1303411	0.4013001	-0.3811001
F	-6.9038093	-0.9192316	-2.3101767
F	-8.4026099	0.6517775	-0.6795442
F	-7.3051153	1.6901946	1.5713036
F	-4.7634851	1.1862942	2.1887671
F	-4.3581028	-1.4415844	-1.7014920

F	-2.2047736	2.1099053	-0.5121286
F	0.6593841	0.6320780	-3.8841624
F	0.1129214	-1.9500387	-3.2135352
F	-1.5537503	-2.5074667	-1.2503823
F	-0.5298339	2.6495336	-2.5031476
H	-2.4700644	0.3950287	1.4149003
H	0.9149646	-4.7588868	3.6730151

Table S5. Cartesian coordinates of the optimized structure of **bridged-13-H₂**.

C	1.0268798	-1.8441787	1.0841743
H	1.9038089	-1.2052787	0.9728576
H	1.0859792	-2.2059813	2.1155031
C	1.1221056	-3.0581689	0.1557361
H	0.6412096	-2.8811485	-0.8029950
H	0.5751719	-3.8962811	0.5920768
C	2.5423328	-3.5632078	-0.1086674
H	2.5258766	-4.5053268	-0.6655329
H	3.0839757	-3.7589391	0.8211583
C	2.8886278	-1.8453510	-2.6339307
H	3.6997782	-1.2728324	-3.0937931
H	2.7290063	-2.7238601	-3.2663627
C	1.6206432	-0.9887602	-2.5046391
H	0.7693633	-1.6255898	-2.2857287
H	1.4264622	-0.5787638	-3.4978255
C	1.7652634	0.1314829	-1.4853601
C	5.1525358	-3.2829148	-1.4231865
C	5.1584851	-4.4415569	-2.1985469
C	6.3463597	-2.7707592	-0.9225920
C	6.3553525	-5.0818298	-2.4680018
H	4.2369178	-4.8505983	-2.5958751
C	7.5412433	-3.4175826	-1.1964696
H	6.3518816	-1.8707415	-0.3202635
C	7.5449693	-4.5699920	-1.9669464
H	6.3607748	-5.9805258	-3.0691534
H	8.4679185	-3.0193957	-0.8069328
H	8.4786214	-5.0729521	-2.1791842
C	-1.5705406	-2.0138518	0.6430951
C	-2.0315023	-2.4408408	-0.5895985
C	-2.1565765	-2.6488988	1.7303683
C	-3.0372589	-3.3793749	-0.7484610
C	-3.1615170	-3.5917227	1.6214708
C	-3.6135211	-3.9541564	0.3664550
C	-0.6598839	0.1162044	2.0759291
C	-1.9414559	0.6070522	2.3045428
C	0.3195751	0.6787921	2.8836988
C	-2.2361871	1.5740183	3.2500939
C	0.0699155	1.6501418	3.8361705
C	-1.2211243	2.1020817	4.0233286
F	-1.7351256	-2.3661048	2.9672936
F	-3.6879178	-4.1554766	2.7032661
F	-4.5741506	-4.8597453	0.2348487
F	-3.4370538	-3.7442495	-1.9629459
F	-1.4828572	-1.9852594	-1.7245373
F	-1.4805565	3.0322049	4.9301825
F	1.0628166	2.1584735	4.5609684
F	1.6022397	0.3137704	2.7632749
F	-2.9768879	0.1539623	1.6026166
F	-3.4830382	1.9953985	3.4219342
B	-0.3477550	-0.9844596	0.9330288
C	0.6240267	2.0948822	0.0391536
C	-0.4446081	2.8998356	0.4262756
C	1.8421883	2.4697941	0.5962774
C	-0.3331864	3.9742548	1.2896052
F	-1.6737780	2.6428027	-0.0134657
C	1.9998400	3.5430266	1.4568509
F	2.9704452	1.7979411	0.3344123
C	0.9038011	4.3027557	1.8092411
F	-1.4025181	4.6829740	1.6311846
F	3.1989835	3.8437418	1.9453152
F	1.0347235	5.3283487	2.6358357
C	-0.6409748	1.1798348	-2.1778142
C	-0.1665204	1.8505184	-3.2966277
C	-1.9966302	0.8889181	-2.2102135
C	-0.9457327	2.1730766	-4.3930378
F	1.1147836	2.2394324	-3.3484048
C	-2.8121608	1.1852017	-3.2892338
F	-2.5963790	0.3251378	-1.1675199
C	-2.2824659	1.8268262	-4.3918573
F	-0.4222285	2.8082980	-5.4380496
F	-4.1022169	0.8701507	-3.2687436

F	-3.0510424	2.1183656	-5.4328521
H	2.4737266	0.8647383	-1.8740161
H	2.2362522	-0.2583403	-0.5855452
B	0.4087927	0.8548709	-0.9840932
P	3.6046065	-2.4492360	-1.0729190
H	-0.1904536	-0.1745609	-0.2053646
H	3.9720193	-1.3591418	-0.2820130

Table S6. Cartesian coordinates of the optimized structure of **closed-16**.

C	-0.3663461	0.5147181	0.7215041
C	-2.3832435	1.6730322	2.4734749
C	-2.9045545	0.5245813	3.3628490
C	-2.5645677	-0.8360984	2.7439043
B	-2.9952359	-0.8708588	1.1569636
C	0.6749069	1.6097801	0.9197115
C	2.0824855	1.0251156	1.0281446
H	-1.4246686	2.0540745	2.8279120
H	-3.0649181	2.5216743	2.4523585
H	-0.1971608	0.0023377	-0.2285571
H	-0.2322190	-0.2500687	1.4887066
H	-3.9817309	0.6252467	3.4862850
H	-2.4809530	0.6162707	4.3646910
H	-3.0882427	-1.6302515	3.2819258
H	-1.5044978	-1.0324746	2.9111154
H	0.4488262	2.1878260	1.8186672
H	0.6423449	2.3148660	0.0888429
H	2.2687075	0.3821599	0.1553740
H	2.1380000	0.3365601	1.8770313
B	3.2667182	2.0571867	1.0642623
P	-2.1591979	0.9535724	0.7935223
C	4.7470517	1.6580155	1.3614547
C	5.1828734	0.3302414	1.3898593
C	5.7353509	2.6153143	1.6125289
C	6.4923825	-0.0298092	1.6400663
C	7.0517284	2.2891366	1.8754836
C	7.4296679	0.9580837	1.8863265
C	2.9200681	3.5587603	0.7212336
C	2.3626297	4.4103926	1.6518693
C	3.0989458	4.0474428	-0.5553720
C	1.9963951	5.7062823	1.3419038
C	2.7427195	5.3355739	-0.9112917
C	2.1900032	6.1662240	0.0490472
C	-4.6116432	-1.0111954	1.0371500
C	-5.5252979	0.0171138	1.1820573
C	-5.1905091	-2.2659503	0.8796173
C	-6.8979230	-0.1413120	1.1170151
C	-6.5566519	-2.4773023	0.8097627
C	-7.4200136	-1.4041296	0.9208727
C	-2.2386508	-1.9104070	0.1600967
C	-1.3234019	-2.8835583	0.5320300
C	-2.5200455	-1.8740713	-1.1978238
C	-0.7144261	-3.7394405	-0.3721916
C	-1.9372986	-2.7033141	-2.1366105
C	-1.0203972	-3.6485838	-1.7159351
F	-5.0930349	1.2660245	1.4161610
F	-7.7091324	0.9028555	1.2507194
F	-8.7313422	-1.5867772	0.8564094
F	-7.0444924	-3.7012660	0.6475589
F	-3.4089636	-0.9824039	-1.6573578
F	-2.2444596	-2.6005162	-3.4250756
F	-0.4429750	-4.4584807	-2.5922009
F	0.1606238	-4.6487379	0.0430252
F	-0.9847691	-3.0570184	1.8112906
F	-4.4265199	-3.3578942	0.8124429
F	5.4380183	3.9067783	1.6274226
F	7.9501900	3.2311724	2.1169332
F	8.6817051	0.6309756	2.1322484
F	6.8579967	-1.3022062	1.6469670
F	4.3366865	-0.6623369	1.1527900
F	3.6233485	3.2399268	-1.4811544
F	2.9199969	5.7776392	-2.1474988
F	1.8425708	7.4028763	-0.2691254
F	1.4666017	6.5055876	2.2565149
F	2.1780865	3.9648315	2.8980815
C	-2.4196310	2.2414356	-0.5603792
C	-1.5883386	1.8455119	-1.7862366
H	-1.7636699	2.5778834	-2.5769364
H	-0.5162573	1.8379131	-1.5969759
H	-1.8733659	0.8738601	-2.1850579
C	-1.9733719	3.6186926	-0.0567198

H	-0.9341922	3.6493085	0.2663220
H	-2.0804232	4.3431648	-0.8677311
H	-2.5905418	3.9713416	0.7692385
C	-3.8836237	2.3417243	-0.9935102
H	-4.3004738	1.3808631	-1.2873908
H	-4.5177090	2.7772242	-0.2271968
H	-3.9385425	2.9999873	-1.8633963

Table S7. Cartesian coordinates of the optimized structure of **open-16**.

C	1.4843986	3.1607227	1.6388795
C	-0.7456651	2.1431865	0.2076127
C	-2.0991833	2.3211379	-0.4714716
C	-2.3534714	1.3324759	-1.6416251
C	1.9345302	1.7988309	2.1554875
C	3.4771614	1.6025791	2.0457593
H	0.0317976	2.1649107	-0.5622273
H	-0.6664981	1.1681100	0.6921646
H	1.8811904	3.9443802	2.2899306
H	1.9384447	3.3578303	0.6625212
H	-2.1582608	3.3365473	-0.8690983
H	-2.9003086	2.2582037	0.2691419
H	-1.4080019	1.1915305	-2.1747268
H	-3.0382202	1.7924080	-2.3545319
H	1.3952191	1.0008088	1.6360904
H	1.6544730	1.6904234	3.2038420
H	3.8509042	1.0645288	2.9156315
H	3.9504108	2.5872823	2.0625811
B	3.7598007	0.8553561	0.7027933
P	-0.3150247	3.5423122	1.3574262
C	3.5618425	1.6331328	-0.6521247
C	2.5922100	1.2187601	-1.5470753
C	4.2720712	2.7732031	-0.9855737
C	2.3044384	1.9075179	-2.7094337
C	4.0371272	3.4743572	-2.1539544
C	3.0399309	3.0406424	-3.0128020
C	4.1108218	-0.6683671	0.6381766
C	3.6299077	-1.5936023	1.5595533
C	4.9531005	-1.1707724	-0.3495531
C	3.9560996	-2.9348237	1.5125185
C	5.3139016	-2.5025416	-0.4185535
C	4.8065095	-3.3862212	0.5179215
F	5.2368040	3.2028156	-0.1748199
F	4.7455869	4.5518667	-2.4580720
F	2.7904451	3.7103538	-4.1249688
F	1.3378057	1.5036526	-3.5228214
F	1.8718011	0.1334179	-1.2611035
F	5.4803958	-0.3498983	-1.2522815
F	6.1377395	-2.9385155	-1.3601161
F	5.1388228	-4.6626026	0.4664571
F	3.4814343	-3.7868333	2.4077993
F	2.7931180	-1.2056018	2.5178041
B	-2.8968111	-0.0431355	-1.1282132
C	-4.3912502	-0.4768236	-1.3111653
C	-5.4480692	0.4207607	-1.2134554
C	-4.7310828	-1.7979638	-1.5820829
C	-6.7678576	0.0382969	-1.3576994
C	-6.0376019	-2.2125796	-1.7567306
C	-7.0592065	-1.2861026	-1.6363994
C	-1.9482131	-1.0074960	-0.3244493
C	-0.7751813	-1.5224772	-0.8481519
C	-2.2453455	-1.3303141	0.9876779
C	0.0819820	-2.3072088	-0.0997460
C	-1.4047384	-2.0931162	1.7753244
C	-0.2359882	-2.5845903	1.2195508
F	-1.7023702	-2.3578734	3.0391746
F	0.5732284	-3.3363118	1.9467381
F	1.1964507	-2.8026714	-0.6227279
F	-0.4784144	-1.2935779	-2.1243425
F	-3.3664839	-0.8554110	1.5346397
F	-3.7752753	-2.7112630	-1.7201899
F	-8.3146005	-1.6660846	-1.7886601
F	-7.7503818	0.9185484	-1.2315285
F	-5.2122543	1.6974912	-0.9280386
F	-6.3214876	-3.4764939	-2.0351778
C	-1.1875636	3.1394150	2.9820280
C	-2.5612848	3.8164296	2.9121129
H	-3.1818988	3.4099728	2.1120747
H	-3.1043907	3.6661635	3.8490825
H	-2.4722545	4.8899950	2.7434711
C	-1.3848476	1.6552385	3.2746559

H	-1.8549232	1.5249988	4.2533772
H	-2.0455008	1.1847600	2.5467325
H	-0.4501518	1.0957965	3.2890983
C	-0.3888829	3.7968436	4.1093265
H	-0.1889856	4.8509526	3.9046205
H	-0.9533776	3.7490553	5.0439373
H	0.5675358	3.3033614	4.2858603

Table S8. Cartesian coordinates of the optimized structure of **16-H₂**.

C	1.6944143	-2.2866594	3.2117019
C	-0.9853177	-3.4318598	2.4119457
C	-1.2467667	-2.0706473	1.7555125
C	-2.6844469	-1.8699307	1.3062245
C	2.0365291	-1.2708706	2.1215630
C	2.7536263	-0.0306522	2.6855724
H	-1.3869276	-4.2414632	1.7968290
H	-1.4781768	-3.5006424	3.3846979
H	2.6007572	-2.6387864	3.7103933
H	1.0711432	-1.8221644	3.9810357
H	-0.5815974	-1.9531513	0.8987451
H	-0.9852999	-1.2741314	2.4561064
H	-3.3320282	-1.8795524	2.1898181
H	-3.0063593	-2.7109446	0.6851251
H	1.1249667	-0.9822763	1.6003622
H	2.6820015	-1.7363630	1.3758070
H	3.7765873	-0.3060859	2.9533310
H	2.2636852	0.3124013	3.5948716
B	2.7393411	1.0246919	1.5105446
P	0.7818191	-3.7660600	2.6570460
C	1.6192674	2.0709122	1.2940215
C	0.4394975	2.0998477	2.0486025
C	1.7325147	3.0776292	0.3271305
C	-0.5441153	3.0493033	1.8799244
C	0.7668964	4.0429705	0.1304282
C	-0.3752884	4.0253207	0.9115258
C	3.8982652	0.8533935	0.4537988
C	3.6830334	0.2546266	-0.7715010
C	5.1859265	1.2591364	0.7404638
C	4.6974057	0.0654271	-1.6911411
C	6.2275364	1.1016652	-0.1543487
C	5.9749909	0.4994099	-1.3761295
F	2.8177384	3.1634865	-0.4307362
F	0.9299710	4.9896871	-0.7785556
F	-1.2963842	4.9468216	0.7427126
F	-1.6305004	3.0442334	2.6283062
F	0.2153937	1.1783199	2.9817236
F	5.4255049	1.8448423	1.9162752
F	7.4525379	1.5114730	0.1421867
F	6.9601829	0.3308561	-2.2432656
F	4.4666356	-0.5244818	-2.8539548
F	2.4536321	-0.1752868	-1.0701043
B	-2.8412680	-0.4052815	0.5870101
C	-1.8996984	-0.1793279	-0.7436544
C	-1.2988122	-1.1503773	-1.5272036
C	-1.6049442	1.1193036	-1.1375969
C	-0.4146134	-0.8810923	-2.5591948
C	-0.7395109	1.4422823	-2.1676173
C	-0.1285882	0.4294770	-2.8832219
C	-4.4017931	-0.0992365	0.2429559
C	-5.2088656	0.6749422	1.0619344
C	-5.0312146	-0.6199908	-0.8759072
C	-6.5411120	0.9377098	0.7871903
C	-6.3579562	-0.3841484	-1.1909759
C	-7.1181965	0.4064844	-0.3504540
F	-6.9102730	-0.9111426	-2.2835376
F	-8.3968924	0.6469854	-0.6296144
F	-7.2740838	1.6927959	1.6053202
F	-4.7213232	1.2057689	2.1865137
F	-4.3500839	-1.4105760	-1.7148313
F	-2.1759631	2.1503842	-0.5036188
F	0.7153389	0.7140613	-3.8704400
F	0.1613827	-1.8754556	-3.2380709
F	-1.5397236	-2.4566239	-1.3088713
F	-0.4821318	2.7148998	-2.4733238
H	-2.4379301	0.4087373	1.3989946
H	0.9138982	-4.6701351	3.7231440
C	1.5607543	-4.6474701	1.2380274
C	1.2816823	-3.9310093	-0.0848354
H	0.2196182	-3.8636828	-0.3111667
H	1.6959620	-2.9254533	-0.1313545

H	1.7439197	-4.5030798	-0.8911146
C	3.0630856	-4.7489142	1.5111244
H	3.2843685	-5.2469831	2.4572570
H	3.5274464	-5.3401618	0.7205271
H	3.5552745	-3.7764256	1.5121818
C	0.9421509	-6.0501462	1.2033689
H	1.3888542	-6.6095067	0.3801327
H	1.1285395	-6.6141653	2.1186902
H	-0.1330904	-6.0297365	1.0235481

Table S9. Cartesian coordinates of the optimized structure of **bridged-16-H₂**.

C	1.0149703	-1.8491813	1.0774096
H	1.8936790	-1.2140148	0.9625524
H	1.0750839	-2.2093669	2.1094003
C	1.1061404	-3.0669182	0.1531561
H	0.6253471	-2.8955868	-0.8061533
H	0.5580206	-3.9017820	0.5943934
C	2.5276740	-3.5788598	-0.1047767
H	2.5014451	-4.5336240	-0.6382881
H	3.0522412	-3.7523156	0.8383005
C	2.8372892	-1.8836055	-2.6370432
H	3.6287852	-1.3159459	-3.1337824
H	2.6386678	-2.7628025	-3.2563944
C	1.5836512	-1.0063203	-2.4876736
H	0.7290330	-1.6300747	-2.2485924
H	1.3759030	-0.6043329	-3.4815557
C	1.7538362	0.1224660	-1.4832995
C	-1.5850501	-2.0084153	0.6466675
C	-2.0473402	-2.4397184	-0.5841347
C	-2.1696070	-2.6407618	1.7366023
C	-3.0484474	-3.3838464	-0.7390846
C	-3.1711971	-3.5878752	1.6314216
C	-3.6213586	-3.9578809	0.3778839
C	-0.6586701	0.1180141	2.0762310
C	-1.9356023	0.6212662	2.3036505
C	0.3256723	0.6709244	2.8846537
C	-2.2218382	1.5915264	3.2485767
C	0.0843640	1.6438619	3.8377435
C	-1.2022890	2.1086984	4.0235934
F	-1.7480112	-2.3532923	2.9724847
F	-3.6949128	-4.1496016	2.7156389
F	-4.5765089	-4.8698050	0.2493444
F	-3.4460145	-3.7554381	-1.9522703
F	-1.5032032	-1.9853327	-1.7216095
F	-1.4526983	3.0417813	4.9300248
F	1.0814959	2.1423588	4.5635680
F	1.6053209	0.2952106	2.7641090
F	-2.9735830	0.1785887	1.5986872
F	-3.4642210	2.0270937	3.4175797
B	-0.3570062	-0.9833509	0.9309490
C	0.6192678	2.0947283	0.0389730
C	-0.4493829	2.8984434	0.4283685
C	1.8386179	2.4693444	0.5932084
C	-0.3371081	3.9711731	1.2935064
F	-1.6788287	2.6413130	-0.0109413
C	1.9969207	3.5405261	1.4563289
F	2.9665501	1.8001629	0.3243061
C	0.9004082	4.2976588	1.8135490
F	-1.4061729	4.6790799	1.6377060
F	3.1967848	3.8413774	1.9430733
F	1.0312101	5.3195566	2.6447997
C	-0.6420676	1.1863411	-2.1795111
C	-0.1592684	1.8620428	-3.2918740
C	-1.9978856	0.8974794	-2.2217374
C	-0.9305240	2.1906724	-4.3919694
F	1.1228508	2.2501597	-3.3334001
C	-2.8057972	1.2005789	-3.3048891
F	-2.6052594	0.3299408	-1.1853732
C	-2.2680843	1.8473623	-4.4007505
F	-0.3983395	2.8288639	-5.4309748
F	-4.0964223	0.8871079	-3.2944841
F	-3.0296912	2.1468247	-5.4447725
H	2.4625429	0.8470945	-1.8876364
H	2.2312885	-0.2614603	-0.5852424
B	0.4026618	0.8552244	-0.9829029
P	3.5913386	-2.4830944	-1.0916452
H	-0.2025725	-0.1726736	-0.2060037
H	3.9416626	-1.3811229	-0.3060421
C	5.2028853	-3.3073163	-1.4466896
C	4.9836528	-4.5118444	-2.3627848
H	5.9429601	-4.9951289	-2.5541739
H	4.3314920	-5.2643548	-1.9180026

H	4.5692815	-4.2293233	-3.3310389
C	5.8090210	-3.7503677	-0.1119932
H	5.2165795	-4.5204462	0.3818097
H	6.7981443	-4.1740564	-0.2925459
H	5.9370608	-2.9185507	0.5829792
C	6.1244049	-2.2853535	-2.1190495
H	5.7643236	-1.9753961	-3.0998709
H	6.2691452	-1.3913011	-1.5104899
H	7.1065671	-2.7362781	-2.2689495