Intramolecular Cooperativity in Frustrated Lewis Pairs

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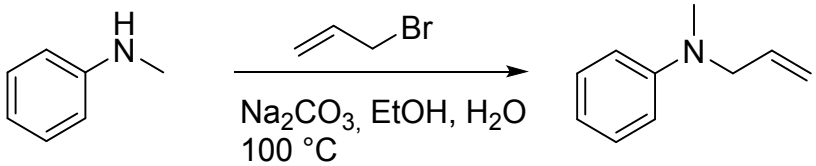
Supporting Information

General procedures

All operations with air and moisture sensitive compounds were performed under conventional Schlenk technique or in a glovebox. Volatile compounds were handled in a vacuum line. Toluene was dried over potassium, *n*-hexane and *n*-pentane over $LiAlH_4$, dichloromethane over P_4O_{10} and distilled prior to use. C_6D_6 and toluene-d8 were dried over Na/K alloy, $CDCl_3$ and CD_2Cl_2 over P_4O_{10}. 1,1-Diphenylethylene (**8**) and allyl bromide were obtained from Sigma Aldrich, *N*-methylaniline from Alfa Aesar, aniline from Merck, hydrogen (5.0) from Linde and deuterium (99.8 atom% D) from Isotec. Bis(pentafluorophenyl)borane (**3**),[1] tris(pentafluorophenyl)borane (**7**),[2] 1-(cyclopent-1-en-1-yl)piperidine (**9**),[3] *N*-benzylidene-*tert*-butylamine (**10**)[4] and (β-styryloxy)trimethylsilane (**11**)[5] were prepared as described in the literature. NMR spectra were recorded using Bruker AV 300, Bruker DRX 500, Bruker Avance III 500 and Bruker AV 600 spectrometers at ambient temperature if not noted otherwise. NMR spectroscopic chemical shifts were referenced to the residual proton or carbon peaks of the used solvents[6] (^{1}H, ^{13}C) or externally (^{11}B: $BF_3{\cdot}OEt_2$; ^{19}F: $CFCl_3$; ^{31}P: 85% H_3PO_4 in H_2O). Elemental analyses were carried out using a EuroEA Elemental Analyzer. EI mass spectra were recorded using an Autospec X magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI source. Samples were introduced by push rod in aluminium crucibles. Ions were accelerated by 8 kV in EI mode. ESI mass spectra were recorded using an Esquire 3000 ion trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a standard ESI source. Samples were introduced by direct infusion with a syringe pump. Nitrogen served both as the nebulizer gas and the dry gas. Only the masses with highest isotopic distribution are listed.

Synthesis of *N*-allyl-*N*-methylaniline (1)



To a solution of *N*-methylaniline (9.72 g, 0.091 mol) in an ethanol water mixture (425 mL, 4:1, v/v) was added allyl bromide (13.6 g, 0.11 mol) and Na_2CO_3 (9.92 g, 0.094 mol). After stirring for 2 hours at ambient temperature the reaction mixture was heated at 100 °C overnight. For workup water (100 mL) was added and the aqueous phase extracted three times with dichloromethane (150 mL each). The combined organic extracts were dried over Na_2SO_4 and the solvent evaporated under reduced pressure. The crude product was stirred over CaH_2 overnight and the dry product **1** (9.91 g, 0.067 mol, 72%) obtained after distillation under reduced pressure (81 °C, 10 mbar).

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.23 (m, 2H, *o*-Ar-**H**), 6.73 (m, 3H, *m*/*p*-Ar-**H**), 5.85 (m, 1H, C**H**=CH_2), 5.12-5.51 (m, 2H, CH=C**H**$_2$), 3.92 (m, 2H, N-C**H**$_2$), 2.94 (s, 3H, N-C**H**$_3$).
^{13}C{^{1}H} NMR (76 MHz, $CDCl_3$): δ [ppm] = 149.6 (*i*-Ar-**C**), 133.9 (**C**H=CH_2), 129.2 (*o*-Ar-**C**), 116.5 (*p*-Ar-**C**), 116.3 (CH=**C**H$_2$), 112.6 (*m*-Ar-**C**), 55.4 (**N**-CH_2), 38.1 (N-**C**H$_3$).
EI-MS (70 eV): *m/z* = 147.1 ($[M]^{+\cdot}$, 66%), 146.1 ($[M-H]^+$, 31%), 132.1 ($[M-CH_3]^+$, 17%), 120.1 ($[M-C_2H_3]^+$, 100%), 106.1 ($[M-C_3H_5]^+$, 10%), 105.1 (15%), 104.1 (17%), 91.1 ($[M-CH_3-C_3H_5]^+$, 13%), 77.0 ($[C_6H_5]^+$, 38%).

CHN analysis: Calcd. for $C_{10}H_{13}N$: C, 81.6; H, 8.9; N, 9.5%. Found: C, 81.5; H, 9.4; N, 9.4%.

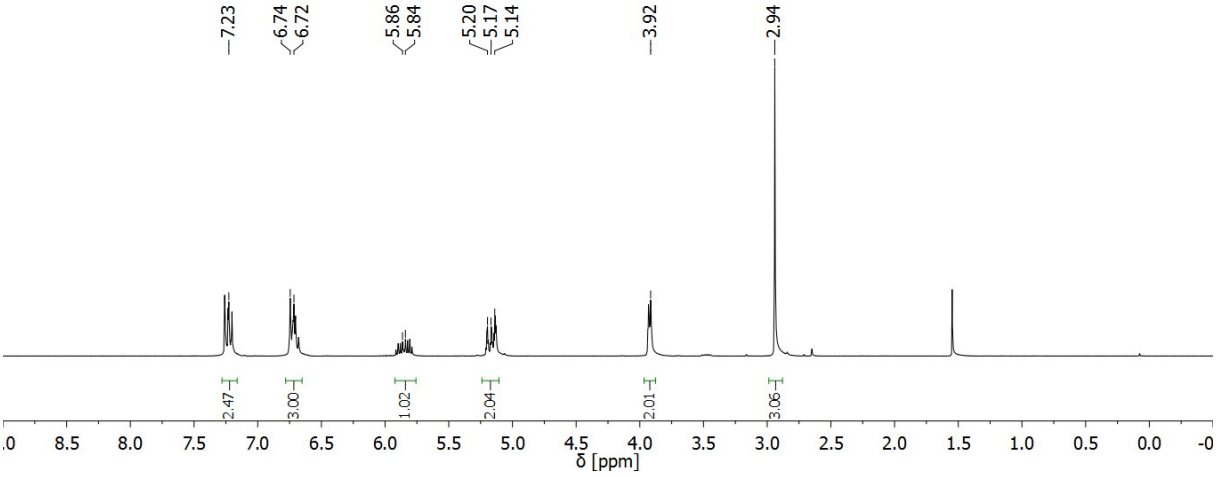


Figure S1. ^{1}H NMR spectrum of *N*-allyl-*N*-methylaniline (**1**) (300 MHz, $CDCl_3$).

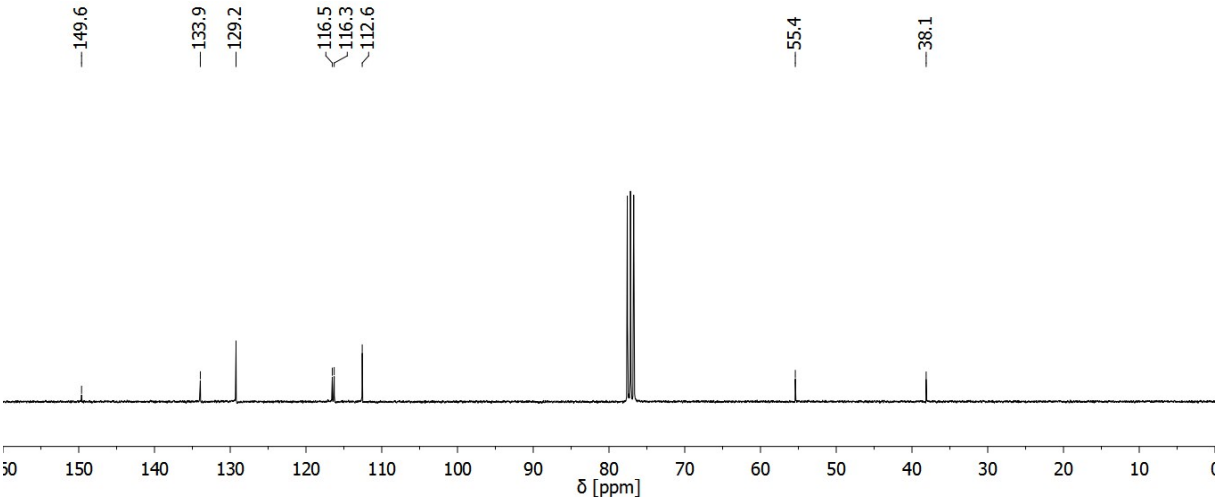
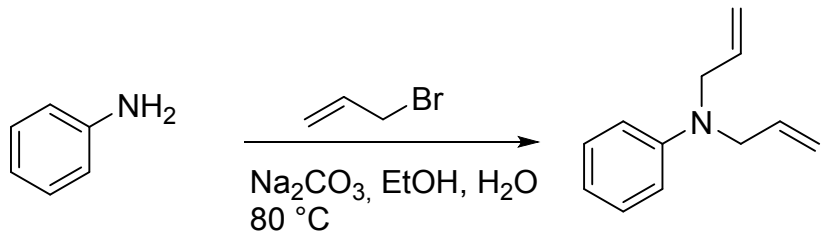


Figure S2. ^{13}C NMR spectrum of *N*-allyl-*N*-methylaniline (**1**) (76 MHz, $CDCl_3$).

Synthesis of *N*,*N*-diallylaniline (2)

Diallylaniline was prepared by an modified procedure described by Schmidt *et al.*[7]



To a solution of aniline (9.88 g, 0.11 mol) in an ethanol water mixture (425 mL, 4:1, v:v) were added Na_2CO_3 (11.3 g, 0.11 mmol) and allyl bromide (30.1 g, 0.25 mmol). After stirring for 30 minutes at ambient temperature the reaction mixture was heated at 80 °C for 1 day. For workup water (100 mL) was added to the red solution and the aqueous phase extracted three times with dichloromethane (150 mL each). The combined organic extracts were dried over Na_2SO_4 and the solvent evaporated under reduced pressure. The crude product was stirred over CaH_2 overnight and the dry product **2** (8.26 g, 47.7 mmol, 45%) obtained after distillation under reduced pressure (99 °C, 7mbar).

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.21 (t, $^3J_{H,H}$ = 8.1 Hz, 2H, *o*-Ar-**H**), 6.71 (m, 3H, *m*/*p*-Ar-**H**), 5.87 (m, 2H, C**H**=CH_2), 5.18 (m, 4H, CH=C**H**$_2$), 3.93 (m, 4H, N-C**H**$_2$).

^{13}C{^{1}H} NMR (76 MHz, $CDCl_3$): δ [ppm] = 148.8 (*i*-Ar-**C**), 143.1 (**C**H=CH_2), 129.2 (*o*-Ar-**C**), 116.4 (*p*-Ar-**C**), 116.1 (CH=**C**H$_2$), 112.5 (*m*-Ar-**C**), 52.9 (N-**C**H$_2$).

ESI-MS (pos. ions, acetonitrile) = 174.0 ([M+H]$^+$).

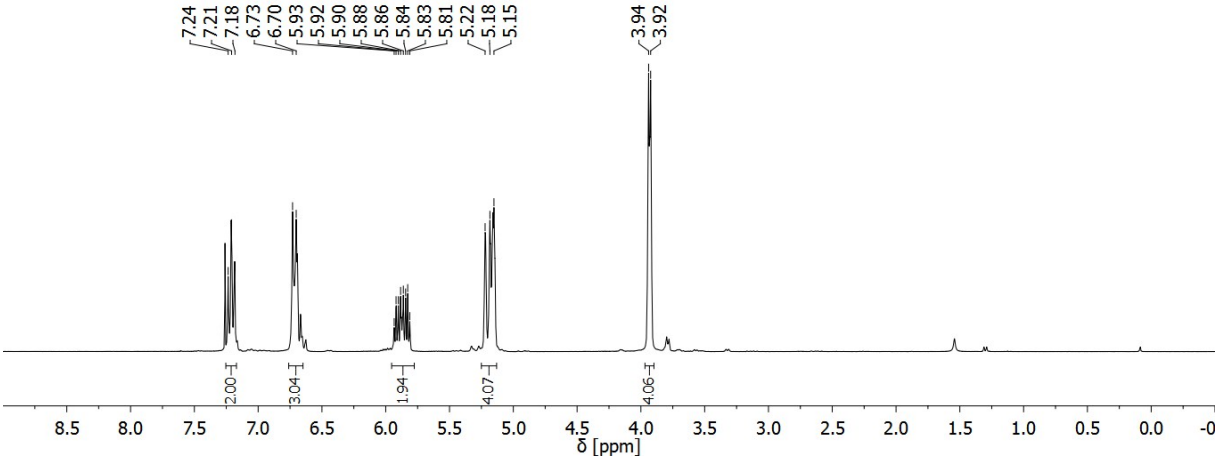


Figure S3. ^{1}H NMR spectrum of *N*,*N*-diallylaniline (**2**) (300 MHz, $CDCl_3$).

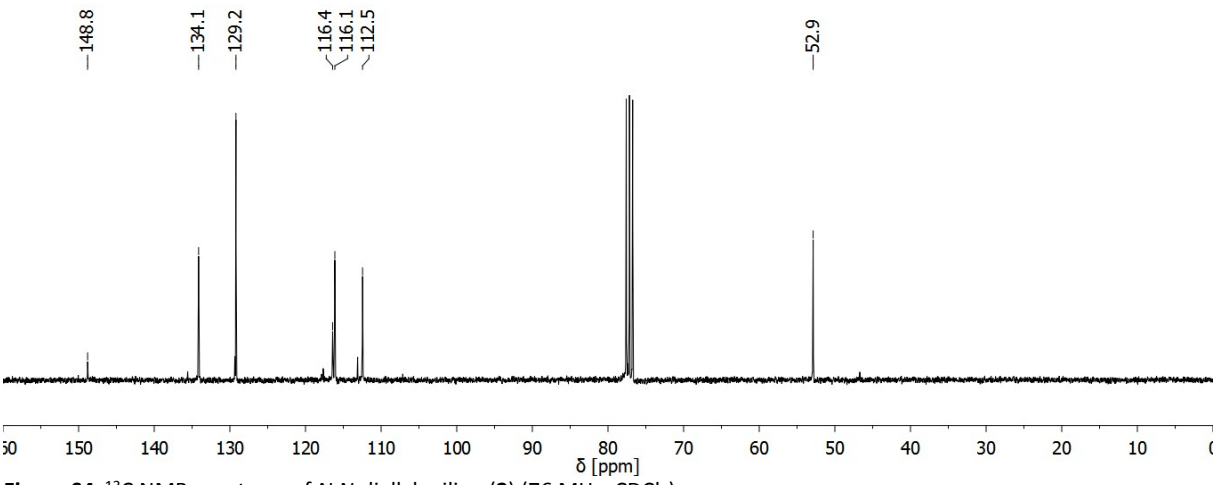
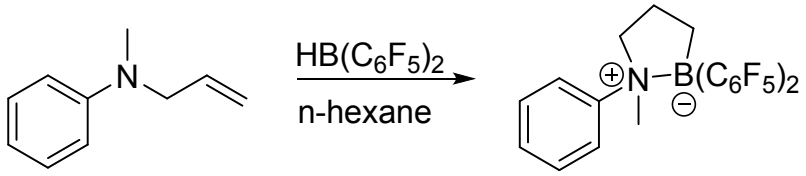


Figure S4. ^{13}C NMR spectrum of *N*,*N*-diallylaniline (**2**) (76 MHz, $CDCl_3$).

Hydroboration of *N*-allyl-*N*-methylaniline 4



To a solution of *N*-allyl-*N*-methylaniline (**1**) (112 mg, 0.76 mmol) in *n*-hexane (5 mL) was added bis(pentafluorophenyl)borane (**3**) (264 mg, 0.76 mmol) and the colorless suspension was stirred at ambient temperature for 4 days. The suspension was filtered through a glass microfiber filter, the solvent evaporated from the resulting yellow solution and dried *in vacuo* to yield the pure hydroboration product **4** (143 mg, 0.29 mmol, 38%).

^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 6.83-6.69 (m, 3H, *o*/*p*-Ar-**H**), 6.78-6.82 (m, 2H, *m*-Ar-**H**), 2.55 (broad, 2H, N-C**H**$_2$), 2.43 (s, 3H, N-C**H**$_3$), 1.81 (broad, 2H, C**H**$_2$-B), 1.61 (broad, 2H, N-CH$_2$-C**H**$_2$).

^{11}B{^{1}H} NMR (160 MHz, C_6D_6): δ [ppm] = 3.7 ($\tau_{1/2}$ = 190 Hz).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ [ppm] = 148.4 (dm, $^1J_{F,C}$ = 240 Hz, *o*-**C**-F), 147.2 (*i*-C$_6$H$_5$), 140.2 ($^1J_{F,C}$ = 250 Hz, p-**C**-F), 137.6 ($^1J_{F,C}$ = 250 Hz, *m*-**C**-F), 128.7 (*o*-**C**-H), 127.9 (p-**C**-H), 121.9 (*m*-**C**-H), 120.6 (broad, *i*-C$_6$F$_5$), 69.2 (N-**C**H$_2$), 45.5 (N-**C**H$_3$), 21.1 (N-CH$_2$-**C**H$_2$), 19.9 (**C**H$_2$-B).

^{19}F NMR (470 MHz, C_6D_6): δ [ppm]= −128.0 (*o*-Ar-**F**), −156.7 (*p*-Ar-**F**), −163.6 (*p*-Ar-**F**).

EI-MS (70 eV): *m/z* = 493.0 ([M]$^{+\cdot}$, 12%), 450.9 (7%), 168 ([C$_6$F$_5$H]$^+$, 32%), 120.0 ([Ph-N(CH$_3$)CH$_2$]$^+$, 100%), 99.0 (15%), 77.0 (C$_6$H$_5$]$^+$, 12%).

Accurate mass: Calcd. for $C_{22}H_{14}BF_{10}N^{+\cdot}$ 493.10542, found 493.10584, dev. 0.85 ppm.

CHN analysis: Calcd. for $C_{22}H_{14}BF_{10}N$: C, 53.6; H, 2.9; N, 2.9%. Found: C, 53.6; H, 3.2; N, 2.8%.

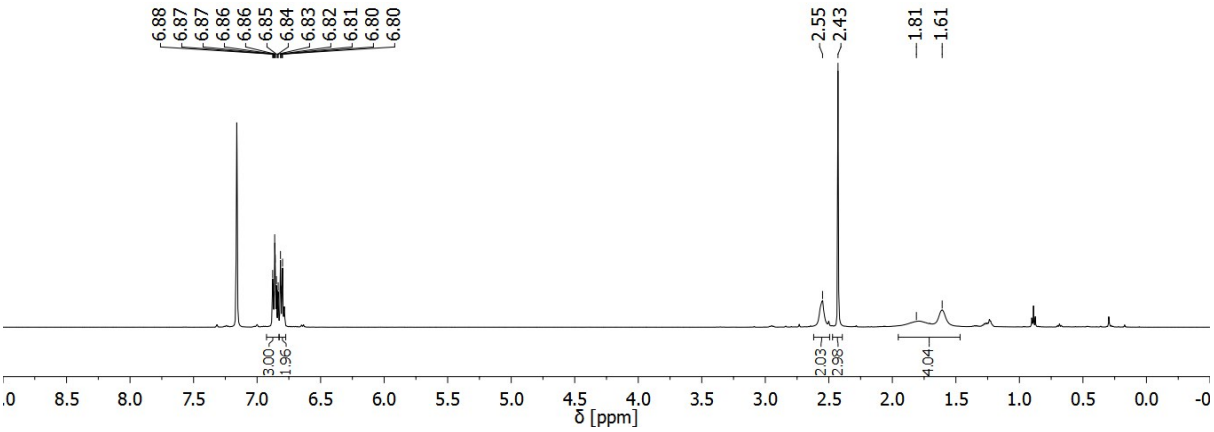


Figure S5. ^{1}H NMR spectrum of the hydroboration product **4** (500 MHz, C_6D_6).

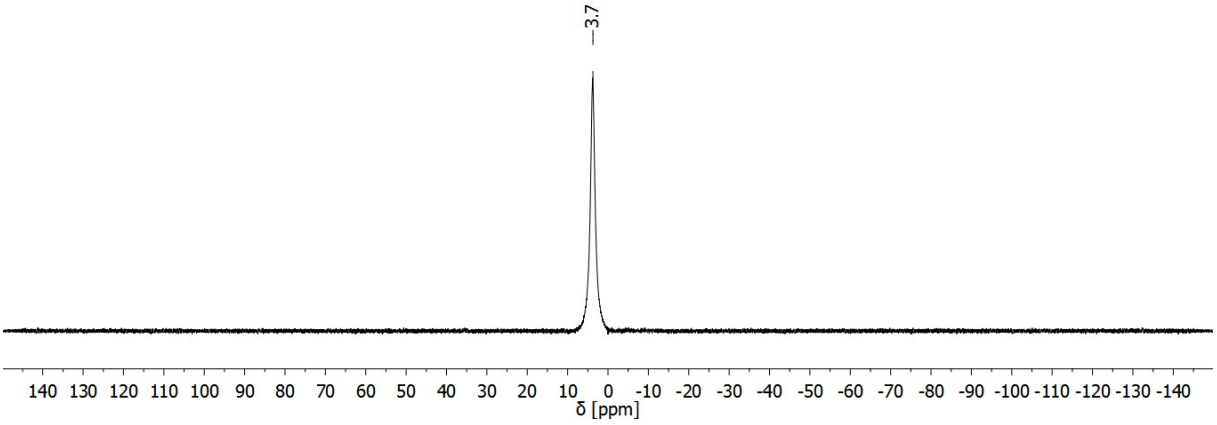


Figure S6. ^{11}B NMR spectrum of the hydroboration product **4** (160 MHz, C_6D_6).

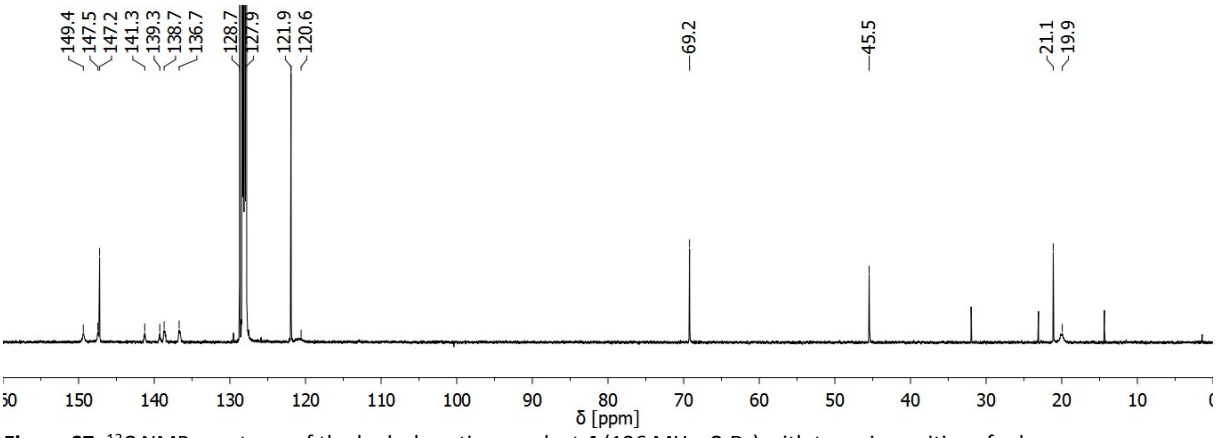


Figure S7. ^{13}C NMR spectrum of the hydroboration product **4** (126 MHz, C_6D_6) with trace impurities of *n*-hexane.

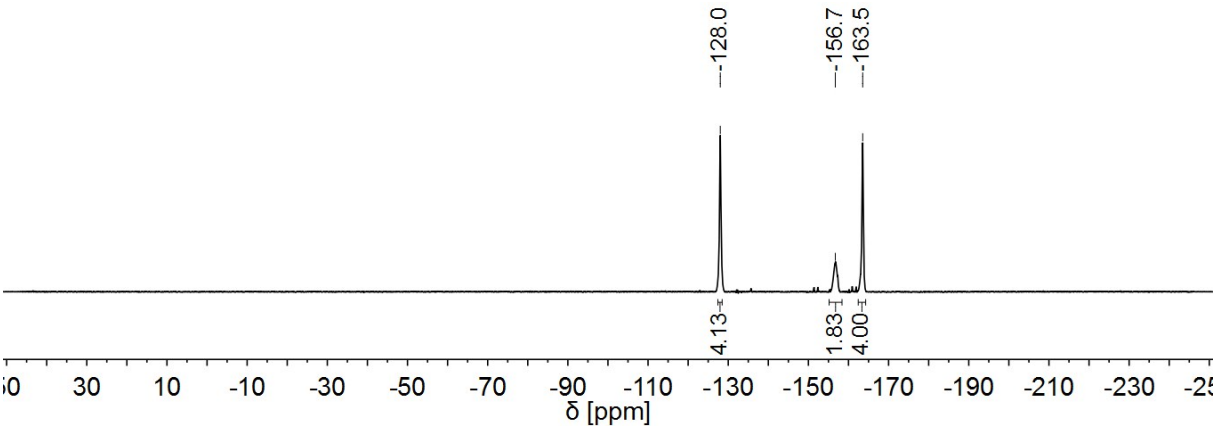


Figure S8. ^{19}F NMR spectrum of the hydroboration product **4** (282 MHz, C_6D_6).

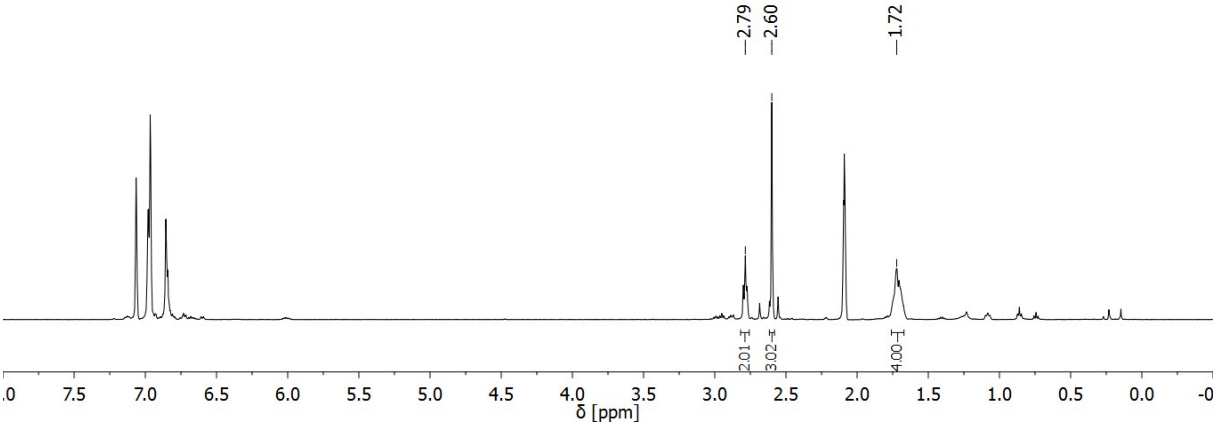


Figure S9. High temperature ^{1}H NMR spectrum of the hydroboration product **4** (500 MHz, Tol-d8, 363 K).

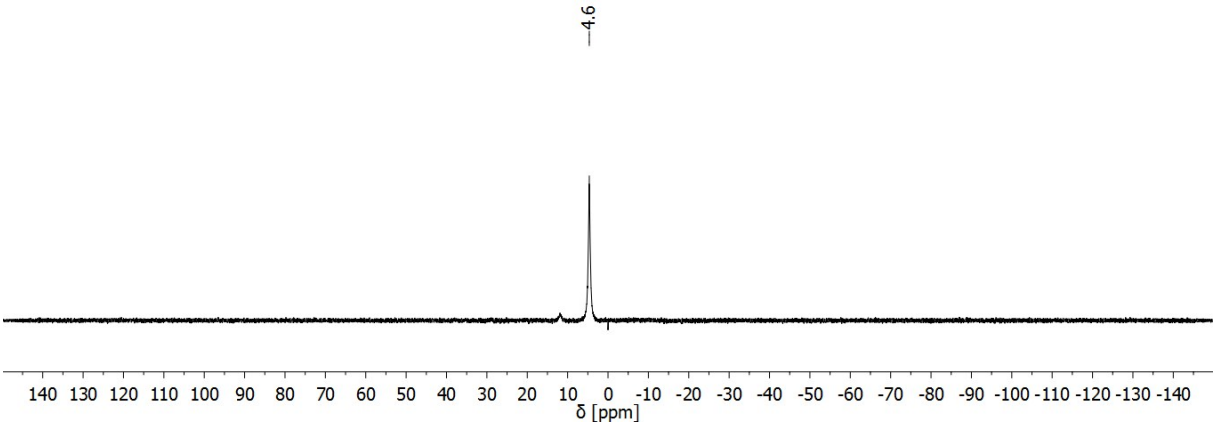


Figure S10. High temperature ^{11}B NMR spectrum of the hydroboration product **4** (160 MHz, Tol-d8, 363 K).

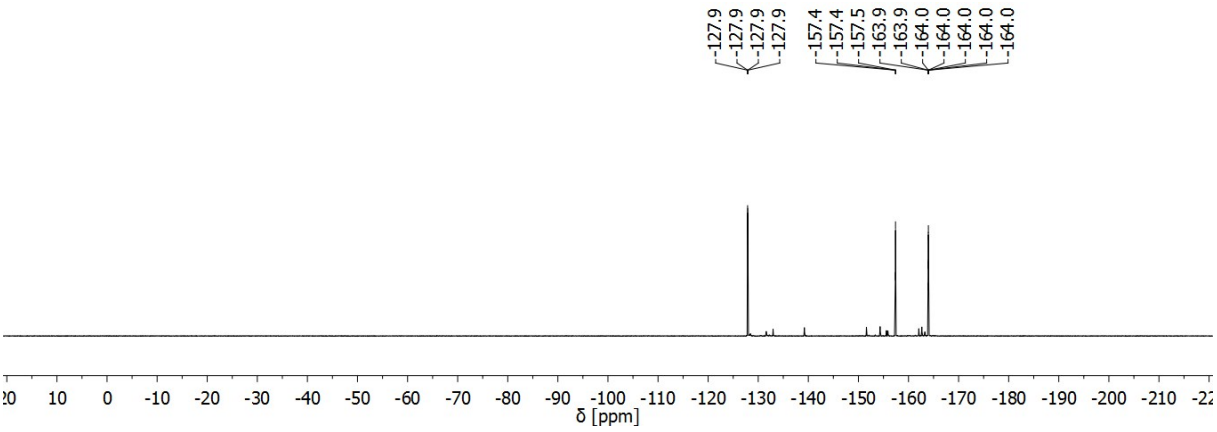
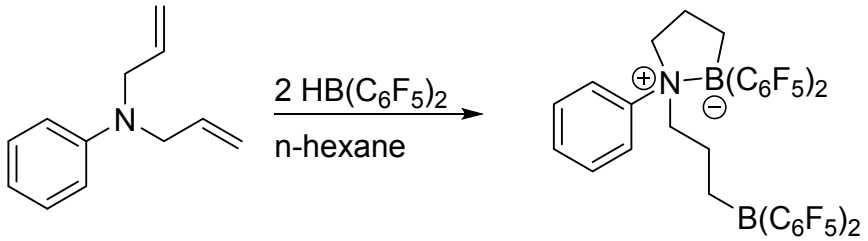


Figure S11. High temperature^{19}F NMR spectrum of the hydroboration product **4** (470 MHz, Tol-d8, 363 K).

Hydroboration of diallylaniline 5



To a colourless solution of *N*,*N*-diallylaniline (**2**) (106 mg, 0.61 mmol) in *n*-hexane (10 mL) was added bis(pentafluorophenyl)borane (**3**) (424 mg, 1.23 mmol). The yellow suspension was stirred at ambient temperature for two days. The solvent was condensed off, the resulting yellow solid dissolved in dichloromethane (5 mL) and the product crystallized at −30 °C. The supernatant was taken off with a syringe, the slightly yellow solid washed with *n*-pentane (2 mL) and dried in *vacuo* to yield the product **5** (251 mg, 47%).

^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 6.77 (m, 3H, *o*/*p*-Ar-**H**), 6.70 (m, 2H, *m*-Ar-**H**), 3.26 (t, $^3J_{H,H}$ = 7.6 Hz, 4H, N-C**H**$_2$), 1.60 (t, $^3J_{H,H}$ = 7.3 Hz, 4H, C**H**$_2$-B), 1.50 (quin, $^3J_{H,H}$ = 7.6 Hz, 4H, N-CH$_2$-C**H**$_2$).

^{11}B{^{1}H} NMR (160 MHz, C_6D_6): δ [ppm] = 40.6 (very broad due to dynamic exchange).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ [ppm] = 147.0 (dm, $^1J_{F,C}$ = 245 Hz, *o*-**C**-F), 144.5 (*i*-C_6H_5), 142.1 (dm, $^1J_{F,C}$ = 250 Hz, *p*-**C**-F), 137.8 (dm, $^1J_{F,C}$ = 250 Hz, *m*-**C**-F), 128.5 (*o*-**C**-H), 127.6 (*p*-**C**-H), 122.5 (*m*-**C**-H), 117.0 (*i*-C_6F_5), 56.8 (N-**C**H$_2$), 23.4 (**C**H$_2$-B), 20.1 (N-CH$_2$-**C**H$_2$).

^{19}F NMR (470 MHz, C_6D_6): δ [ppm] = −128.9 (m, 8F, *o*-Ar-**F**), −150.9 (m, 4F, *p*-Ar-**F**), −161.7 (m, 8F, *m*-Ar-**F**).

EI-MS (70 eV): *m/z* = 865.1 ([M]$^{+\cdot}$, 1%), 705.9 (7%), 521.1([M−B(C_6F_5)$_2$]$^+$, 10%), 511.9(46%), 479.0(64%), 311.0(25%), 276.9(100%), 257.9(37%), 226.9(61%), 216.0(17%).

CHN analysis: Calcd. for $C_{36}H_{17}B_2F_{20}N$: C, 50.0; H, 2.0; N, 1.6%. Found: C, 49.6; H, 2.3; N, 1.6%.

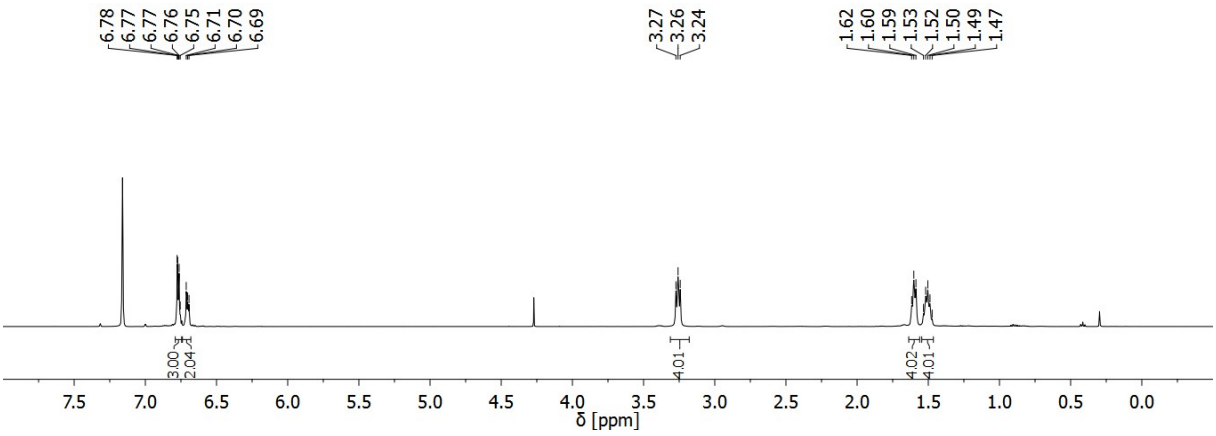


Figure S12. ^{1}H NMR spectrum of the hydroboration product **5** (500 MHz, C_6D_6). Due to dynamic exchange of the two boron units at the central Lewis base only one set of signals is observed for the two 1,3-propandiyl spacers.

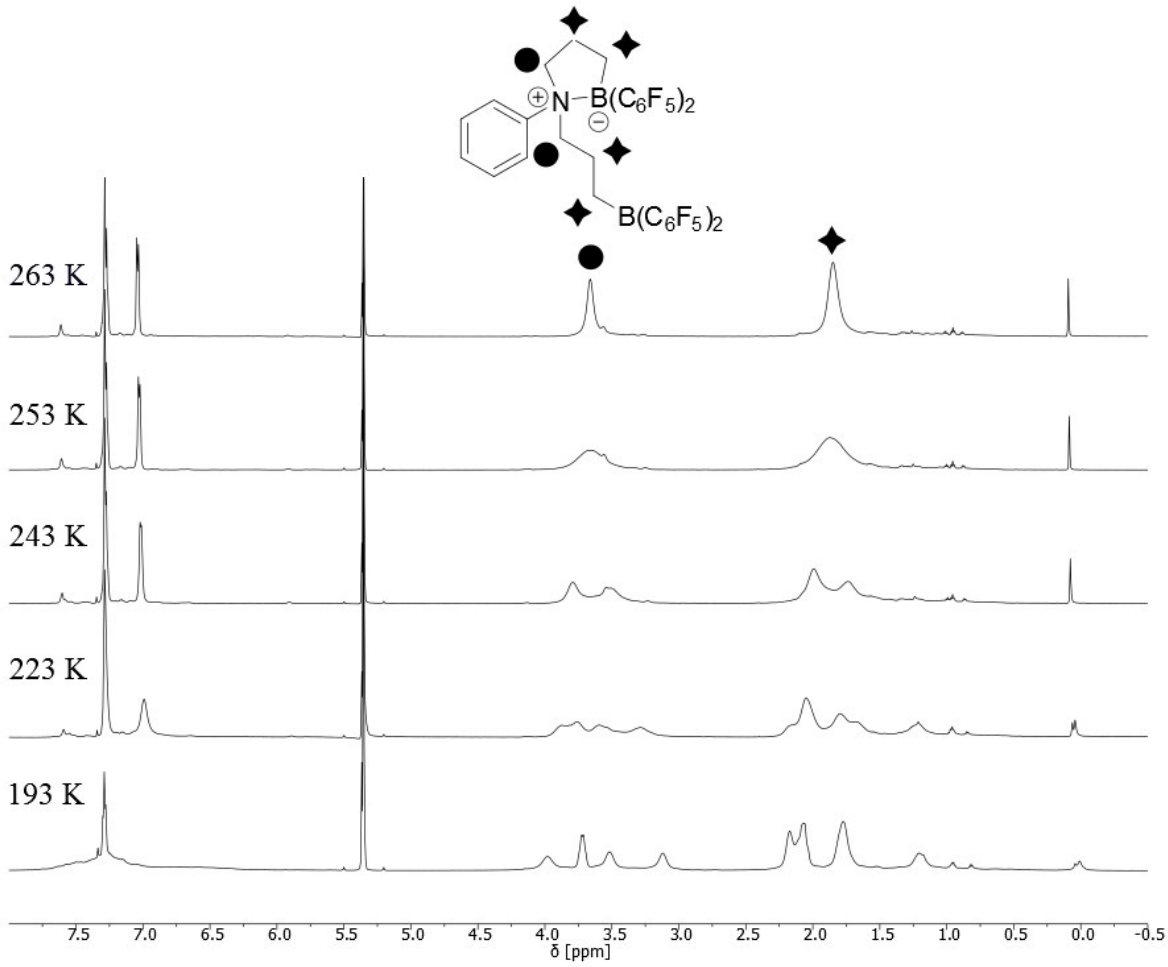


Figure S13. Excerpt of the variable temperature ^{1}H NMR spectrum (600 MHz, CD_2Cl_2) measurements between 193 K and 283 K of compound **5**.

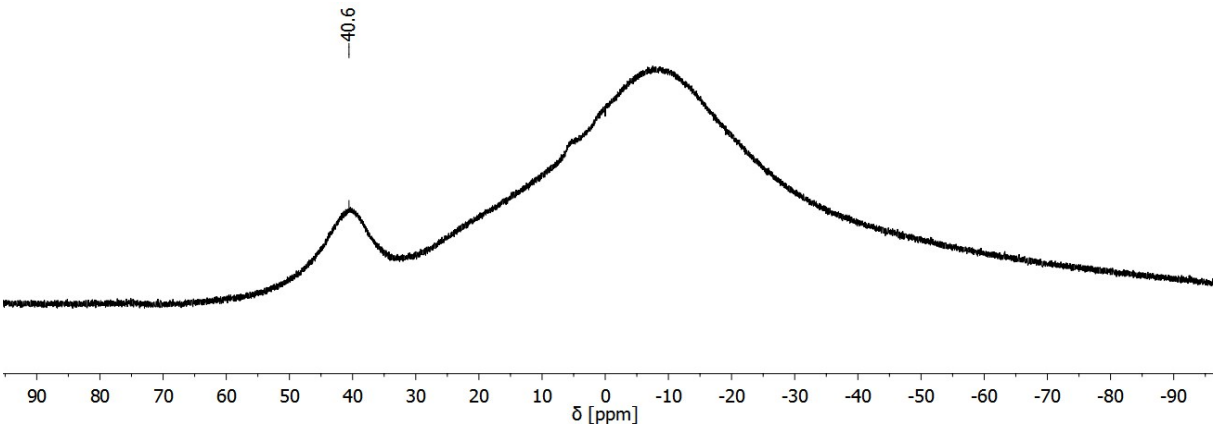


Figure S14. ^{11}B NMR spectrum of the hydroboration product **5** (160 MHz, C_6D_6). Due to dynamic exchange of the two boron units at the central Lewis base only one boron coalescence resonance is observed at averaged chemical shift.

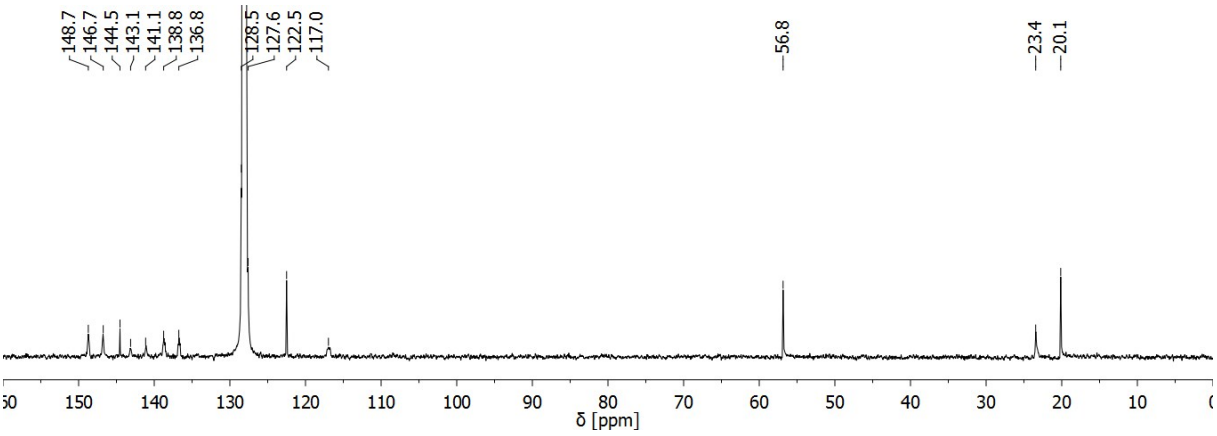


Figure S15. ^{13}C NMR spectrum of the hydroboration product **5** (126 MHz, C_6D_6). Due to dynamic exchange of the two boron units at the central Lewis base only set of signals is observed for the C_6F_5 rings as well as the propyl spacer.

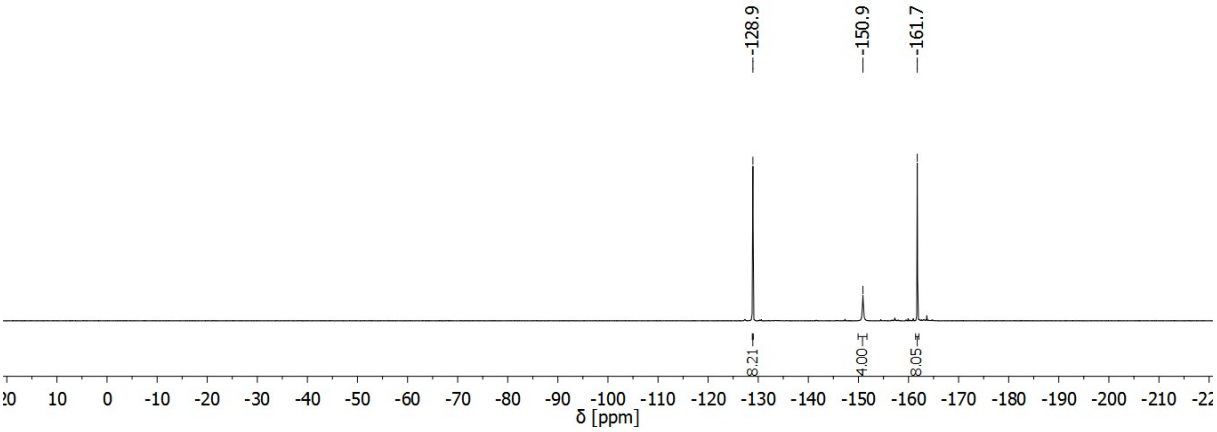
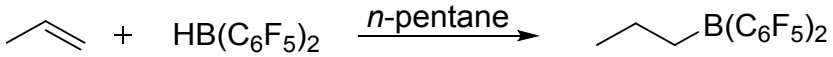


Figure S16. ^{19}F NMR spectrum of the hydroboration product **5** (470 MHz, C_6D_6). Due to dynamic exchange of the two boron units at the central Lewis base only set of signals is observed for the C_6F_5 rings.

Bis(pentafluorophenyl)propylborane (6)



Bis(pentafluorophenyl)borane (**3**) (255 mg, 0.74 mmol) was suspended in *n*-pentane (5 mL). The suspension was frozen in liquid nitrogen, evacuated and propene (7.4mmol) was condensed onto the frozen suspension at −196 °C. The reaction flask was backfilled with nitrogen, connected to a bubbles counter and warmed to ambient temperature. The colorless suspension was stirred overnight, filtrated over a glass microfiber filter and the solvent evaporated from the filtrate to yield bis(pentafluorophenyl)propylborane (**9**) (261 mg, 0.67 mmol, 91%) as a colorless liquid.

^{1}H NMR (300 MHz, C_6D_6): δ [ppm] = 1.83 (t, $^3J_{H,H}$ = 7.4 Hz, 2H, C**H**$_2$-B), 1.40 (sext, $^3J_{H,H}$ = 7.4 Hz, 2H, CH$_3$-C**H**$_2$-CH$_2$-B), 0.91 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, **C**H$_3$).

^{11}B NMR (96 MHz, C_6D_6): δ [ppm] = 75.0.

^{13}C NMR (76 MHz, C_6D_6): δ [ppm] = 147.1 (dm, $^1J_{F,C}$ = 250 Hz, *o*-**C**-F), 143.5 (dm, $^1J_{F,C}$ = 260 Hz, *p*-**C**-F), 137.6 (dm, $^1J_{F,C}$ = 155Hz, *m*-**C**-F), 114.0 (br, *i*-C_6F_5), 34.6 (br, **C**H$_2$-B), 18.9 (CH$_3$-**C**H$_2$-CH$_2$-B), 17.5 (**C**H$_3$).

^{19}F NMR (282 MHz, C_6D_6): δ [ppm] = −130.7 (m, 4F, *o*-Ar-**F**), −147.4 (m, 2F, *p*-Ar-**F**), −161.0 (m, 4F, *m*-Ar-**F**).

EI-MS (70 eV): *m/z* = 388.0 ([M]$^{+\cdot}$, 24%), 346 ([M−C_3H_6]$^+$, 91%), 295.0 (22%), 277.0 (97%), 254.0 (42%), 227.0 (61%), 181.0 (42%), 129.0 (51%), 117.0 (22%), 43.1([C_3H_7]$^+$, 100%), 42.1 ([C_3H_6]$^+$, 89%).

Accurate mass: Calcd. for $C_{15}H_7BF_{10}^{+\cdot}$ 388.04757, found 388.04563, dev. 5.00 ppm.

CHN analysis: Calcd. for $C_{15}H_7BF_{10}$: C, 46.4; H, 1.8%. Found: C, 44.7; H, 1.8%.

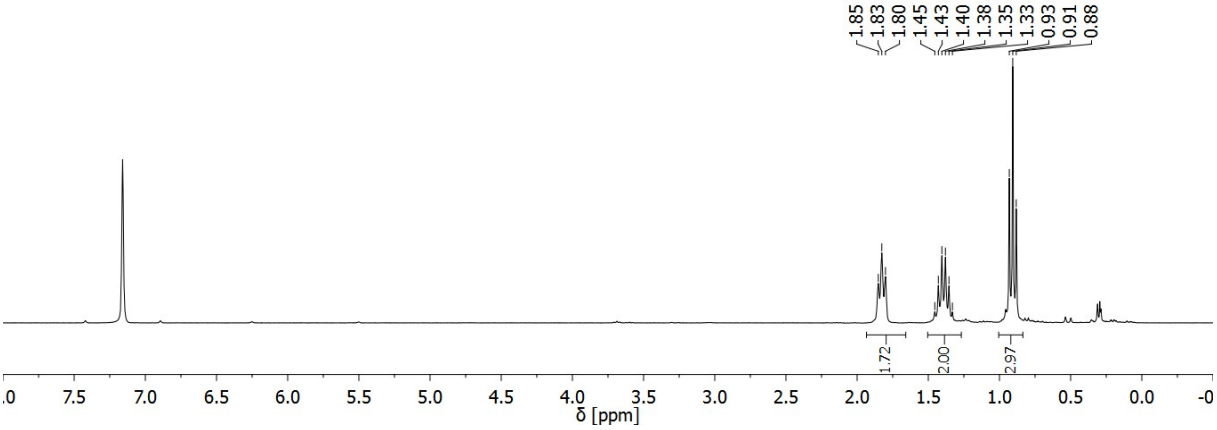


Figure S17. ^{1}H NMR spectrum of bis(pentafluorophenyl)propylborane (**9**) (300 MHz, C_6D_6).

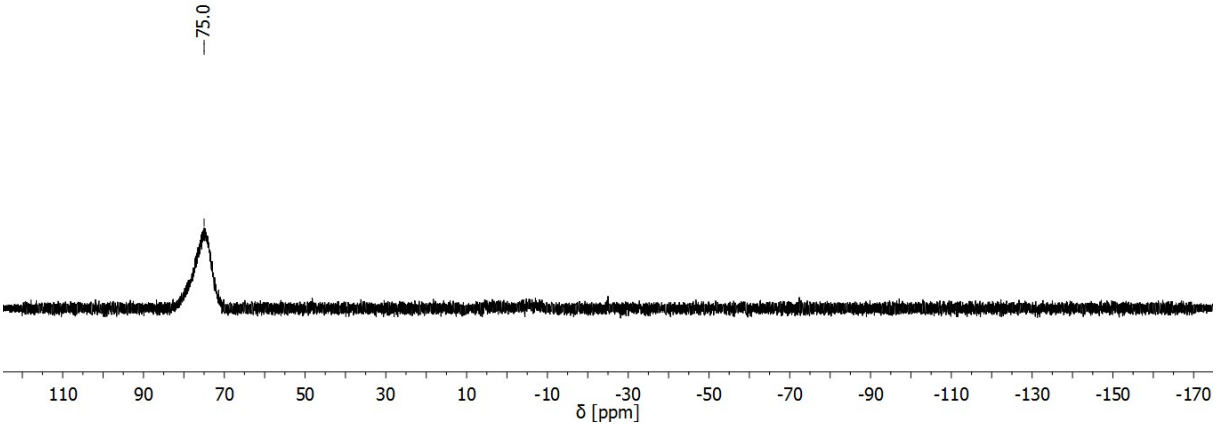


Figure S18. ^{11}B NMR spectrum of bis(pentafluorophenyl)propylborane (**9**) (96 MHz, C_6D_6).

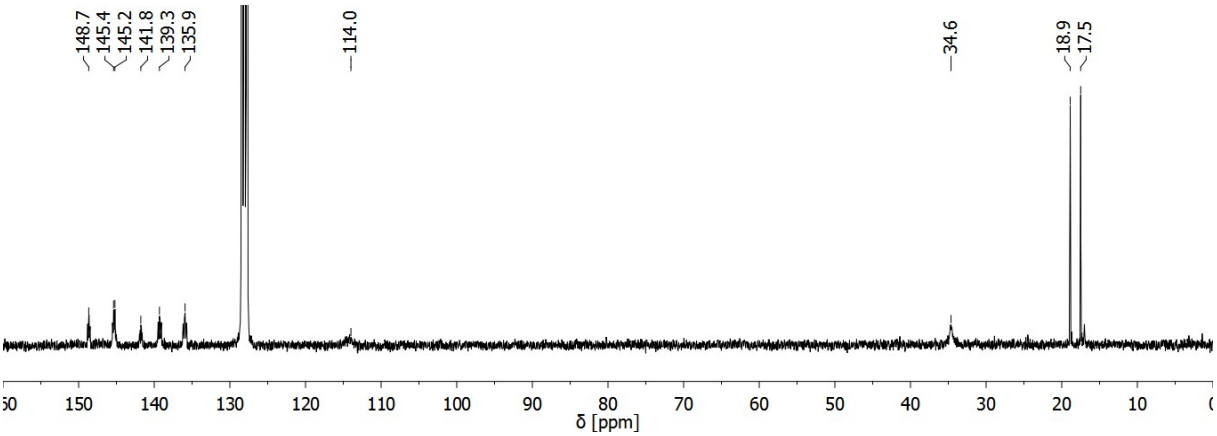


Figure S19. ^{13}C NMR spectrum of bis(pentafluorophenyl)propylborane (**9**) (76 MHz, C_6D_6).

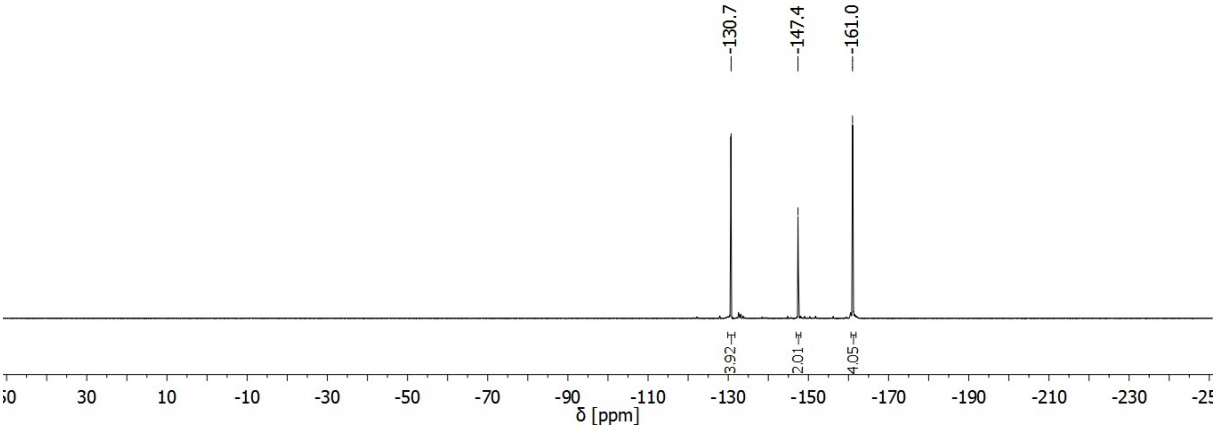


Figure S20. ^{19}F NMR spectrum of bis(pentafluorophenyl)propylborane (**9**) (282 MHz, C_6D_6).

H/D-scrambling experiments

A young NMR tube was charged with 0.019 mmol catalyst and 0.5 mL CD_2Cl_2. The solution was degassed two times by freeze-pump-thaw procedure and backfilled with one atmosphere of a 1:1 mixture of hydrogen and deuterium, premixed in a special 60 mL glass tube.[8] The NMR tube was kept at ambient temperature. The formation of HD was observed by ^{1}H NMR spectroscopy showing a 1:1:1 triplet at 4.57 ppm with a $^1J_{D,H}$ = 42.7 Hz coupling constant.

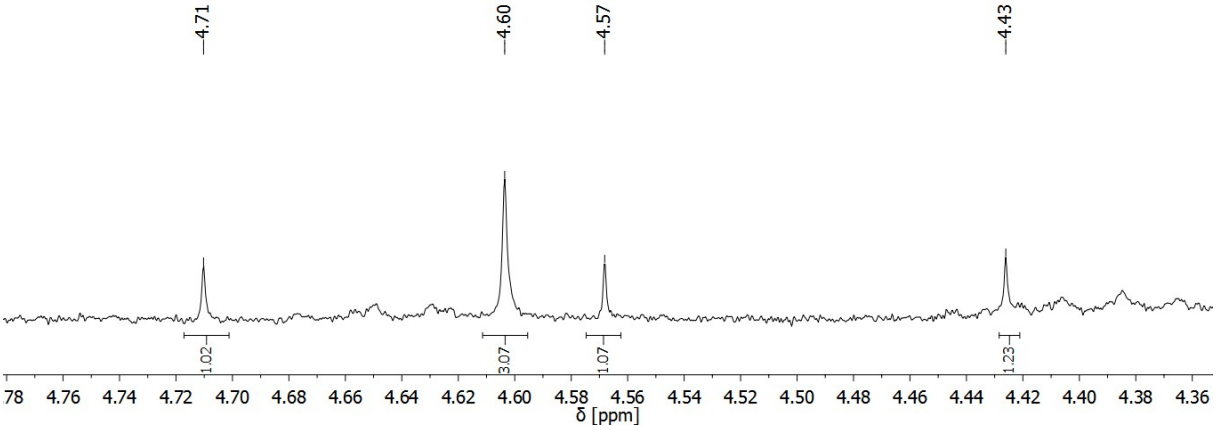


Figure S21. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of a 1:1 mixture of H_2/D_2 in the presence of the hydroborated diallylaniline **5** after 18 hours.

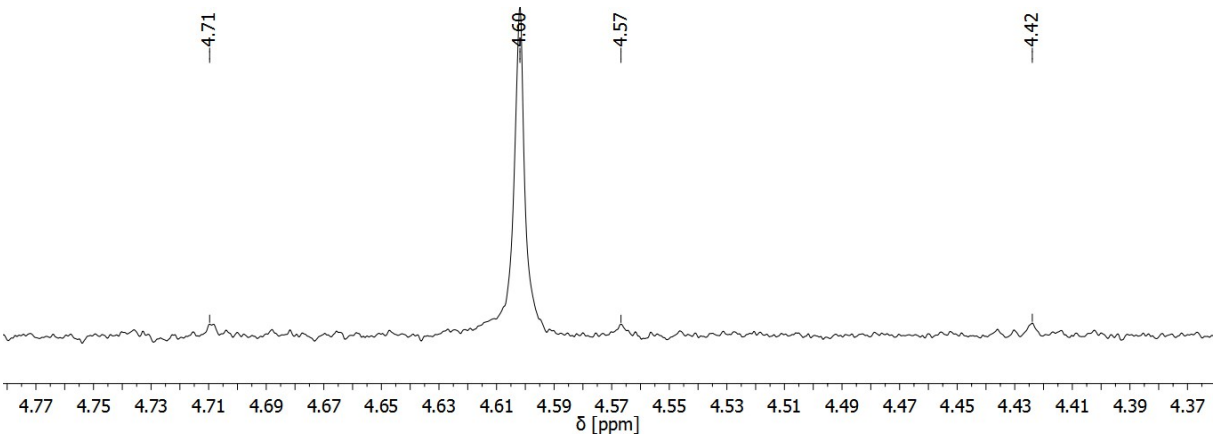


Figure S22. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of a 1:1 mixture of H_2/D_2 in the presence of the hydroborated allyl-*N*-methylaniline **4** after 15 days.

Catalysis study

In high pressure NMR tubes

A Wilmad high pressure NMR tube was filled with a solution of 0.1 mmol unsaturated reactant **8–11** and 6 Mol% catalyst in 0.5 mL CD_2Cl_2 and filled with 6 bar pressure hydrogen. The catalytic reaction was monitored by ^{1}H NMR spectroscopy.

In a steel autoclave

Four glass tubes in a steel autoclave were charged with a magnetic stir bar and 6 Mol-% of following catalyst systems: a) compound **4**, b) compound **5**, c) compound **4** and **6**, d) compound **6**. The tubes were filled with 3 mL of the same solution of imine **10** (0.31 M, 0.93 mmol) or silylenol ether **11** (0.25 M, 0.75 mmol), respectively. The autoclave was sealed, purged three times with hydrogen and then pressurized to 6 bar with hydrogen. The mixtures were stirred for 4 or 18.5 h, the autoclave opened inside a glovebox, the reaction solutions transferred into flasks and dichloromethane was condensed off. The conversion was determined by the ^{1}H NMR spectra of the raw products.

Crystallographic data

The crystal structure was determined at 100.0(1) K by X-ray diffraction using Cu-Kα radiation (λ = 1.5418 Å) on a Agilent SuperNova diffractometer. Using Olex2[9], the structure was solved with the SHELXS[11] structure solution program using direct Methods and refined with the SHELXL[10] refinement package using least squares minimization. Data are listed in Table S1. CCDC 1449801 contains the supplementary crystallographic data for this paper. These data can be obtained via www.ccdc.cam.ac.uk/dara_request/cif free of charge from The Cambridge Crystallographic Data Center.

Table S1. Crystallographic data of compounds **5**.

Empirical formula	$C_{36}H_{17}B_2F_{20}N$
M_r	865.12
$F(000)$	1720.0
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	14.9491(3)
b [Å]	11.0572(3)
c [Å]	20.4604(4)
β [°]	102.897(2)
V [Å^3]	3296.71(12)
Z	4
$\rho_{calcd.}$ [g cm^{-3}]	1.743
μ [mm^{-1}]	1.634
$2\Theta_{max}$ [°]	143.984
Index range h	$-18 \leq h \leq 18$
Index range k	$-13 \leq k \leq 13$
Index range l	$-18 \leq l \leq 25$
Refl. collect.	28032
Indep. refl.	6470
R_{int}	0.0431
Observed refl., $I>2\sigma(I)$	5258
Parameters	532
R_1, $I>2\sigma(I)$	0.0352
wR_2, $I>2\sigma(I)$	0.0830
R_1 (all data)	0.0478
wR_2 (all data)	0.0902
GoF	1.030
$\rho_{max/min}$ [e Å^{-3}]	0.38/−0.25
CCDC-No.	1449801

Computational details

Density functional theory (DFT) calculations were performed using the Turbomole 7.0[11,12] software package. Structures were optimized at PBEh-3c level of theory.[13] Stationary points were proven to be minima on the potential energy surface by harmonic frequency analyses. Here, two geometries (**open-5** and **5-H_2**) exhibited very small (< 2 cm^{-1}) imaginary frequencies, which we think can be ascribed to numerical artefacts.

Corrections to Gibbs free energies ($\delta_{solvation}$) were calculated at standard conditions. In addition, single-point energies at PW6B95-D3BJ(abc)/def2-TZVP[14–18] level of theory were calculated, both, applying the COSMO approach[19] (CH_2Cl_2, ε = 8.93) to include solvation effects, and in the gas phase. To accelerate the geometry optimizations and frequency calculations the density-fitting RI-J approach was used.[20] The absolute values for Gibbs free energy are provided in Table S2, cartesian coordinates for all compounds in Tables S3–S9 and optimized structures in Figures S23–S29. In the latter, fluorine and hydrogen atoms, apart from those resulting from hydrogen splitting, are only adumbrated for clarity reasons.

Table S2. Calculated electronic energies (ΔE, PW6B95-D3BJ(abc)/def2-TZVP), solvation free energies ($\delta_{solvation}$, PW6B95-D3BJ(abc)/def2-TZVP/COSMO(CH_2Cl_2)) and thermodynamic contributions (δ_{thermo}, PBEh-3c) as well as resulting Gibbs free energies (ΔG) of the compounds depicted in Figures S23–S29. All parameters are given in kJ mol^{-1}.

	ΔE	δ_{thermo}	$\delta_{solvation}$	ΔG
closed-4	−5061488.94	691.38	−33.27	−5060830.82
open-4	−5061449.86	665.91	−26.36	−5060810.31
4-H_2	−5064497.96	730.30	−90.72	−5063858.38
closed-5	−9159824.30	1010.18	−44.40	−9158858.52
open-5	−9159778.82	978.14	−36.70	−9158837.38
5-H_2	−9162835.48	1053.09	−104.00	−9161886.39
bridged-5-H_2	−9162907.45	1063.97	−74.58	−9161918.06
H_2	−3084.75	−6.46	−0.79	−3092.00

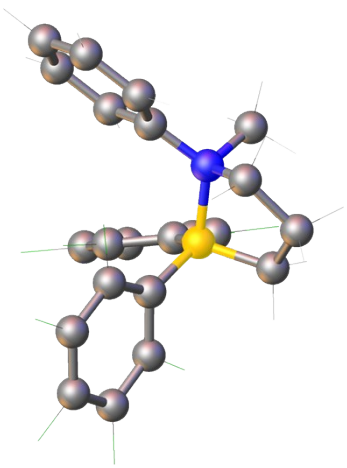


Figure S23. Optimized molecular structure of the 5-membered ring conformer of **4** (**closed-4**).

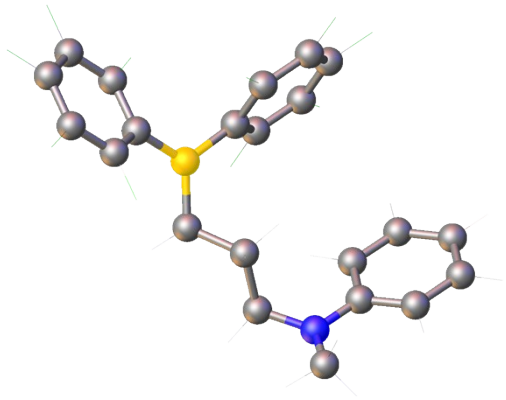
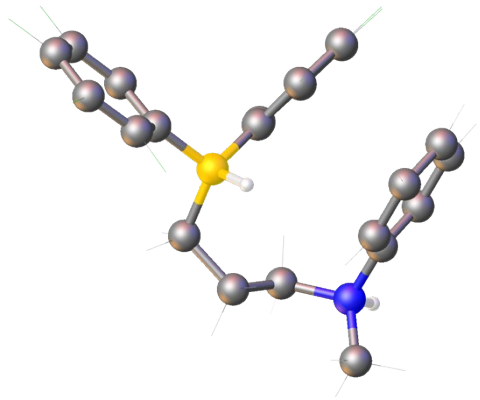


Figure S24. Optimized molecular structure of the open-chain conformer of **4** (**open-4**).



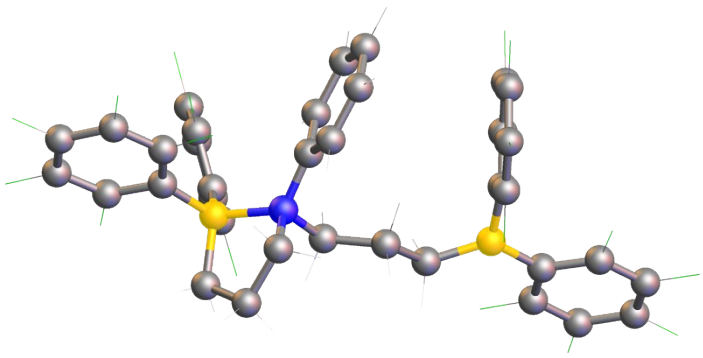


Figure S25. Optimized molecular structure of the hydrogen splitting product of **4** (**4-H_2**).
Figure S26. Optimized molecular structure of the 5-membered-ring conformer of **5** (**closed-5**).

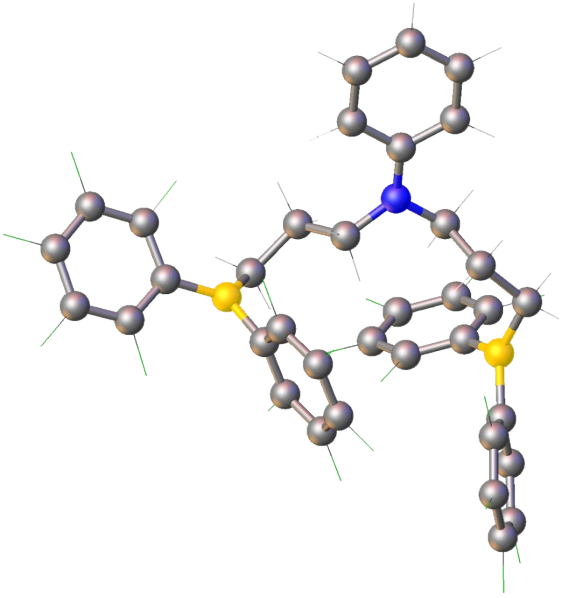


Figure S27. Optimized molecular structure of the open-chain conformer of **5** (**open-5**).

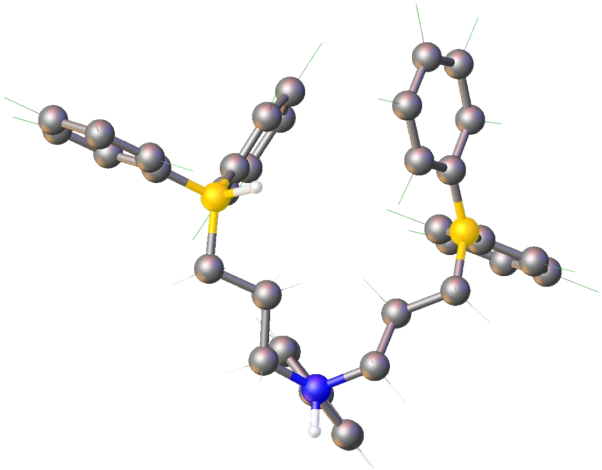


Figure S28. Optimized molecular structure of the open-chain conformer of the hydrogen splitting product of **5** (**5-H_2**).

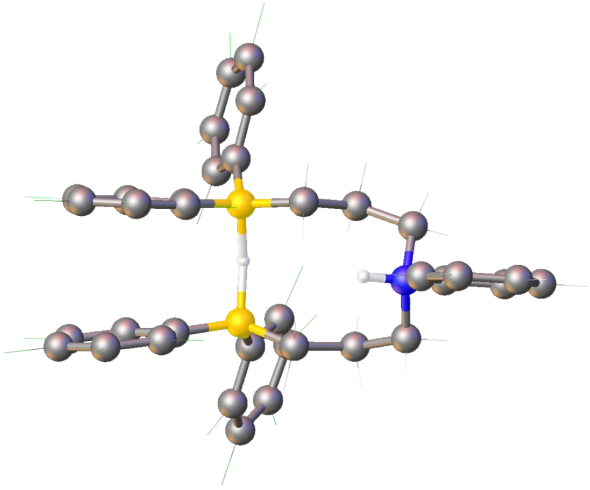


Figure S29. Optimized molecular structure of the 10-membered-ring conformer of the hydrogen splitting product of **5** (**bridged-5-H_2**).

Table S3. Cartesian coordinates of the optimized structure of **closed-4**.

C	−0.2598806	−0.4487361	−0.8804871
C	−1.1878198	−2.4009255	0.1600779
C	−1.6436744	−3.0022598	−1.1637546
C	−2.6073559	−2.0042324	−1.8323645
B	−2.8435515	−0.7881602	−0.7593633
H	−0.1556514	−2.6560076	0.4088635
H	−1.8200529	−2.7401632	0.9742782
H	−0.3463941	0.6194511	−1.0473915
H	−0.3300791	−0.9578208	−1.8349416
H	−2.1203927	−3.9617187	−0.9645365
H	−0.7861941	−3.2220633	−1.8016694
H	−3.5406935	−2.5063300	−2.0766566
H	−2.2034047	−1.6921341	−2.7909273
N	−1.3291125	−0.9178176	0.0508832
C	−1.0868005	−0.2108487	1.3165334
C	−1.2329618	1.1692023	1.3575771
C	−0.6170742	−0.8705069	2.4441982
C	−0.9661712	1.8702213	2.5211189
H	−1.5358737	1.7185312	0.4800013
C	−0.3469034	−0.1632712	3.6057496
H	−0.4669997	−1.9390730	2.4550819
C	−0.5281019	1.2075521	3.6557324
H	−1.1019173	2.9430797	2.5323541
H	0.0048178	−0.6987976	4.4771827
H	−0.3224099	1.7548642	4.5654129
C	−4.1683908	−1.2047541	0.1242873
C	−4.3330243	−1.5676702	1.4486680
C	−5.3565644	−1.2089259	−0.6059324
C	−5.5490243	−1.9223035	2.0126867
C	−6.5913034	−1.5468017	−0.0874777
C	−6.6905893	−1.9126598	1.2414508
C	−3.0591505	0.7384234	−1.3245664
C	−2.6567144	1.1907908	−2.5768446
C	−3.7957671	1.6753484	−0.5997669
C	−2.9645990	2.4432520	−3.0837456
C	−4.1268471	2.9341507	−1.0679089
C	−3.7117111	3.3214480	−2.3268973
F	−3.2944350	−1.5932840	2.2920237
F	−5.6170865	−2.2672860	3.2944815
F	−7.8627175	−2.2481497	1.7625339
F	−7.6774197	−1.5256135	−0.8509636
F	−4.2045542	1.4042491	0.6403757
F	−4.8296990	3.7735068	−0.3168430
F	−4.0124293	4.5236190	−2.7932211
F	−2.5425440	2.8051925	−4.2899530
F	−1.9127415	0.4305400	−3.3855022
F	−5.3434241	−0.8514390	−1.8949620
H	0.7120827	−0.6529045	−0.4319768

Table S4. Cartesian coordinates of the optimized structure of **open-4**.

C	1.7112605	−1.4015002	2.9527759
C	0.7225734	−0.5474482	2.1575534
C	−0.3870339	−1.3741394	1.4896067
H	2.0221292	−2.2582040	2.3478779
H	1.2211122	−1.8329383	3.8276430
H	1.2863425	0.0088446	1.4058216
H	0.2755884	0.2050478	2.8129348
H	−1.1289775	−1.6929659	2.2211685
H	0.0546304	−2.3019532	1.1026520
N	2.8739399	−0.6725801	3.4025972
C	3.7727167	−0.1917531	2.4661925
C	4.6539467	0.8562375	2.7705913
C	3.8461102	−0.7340518	1.1714539
C	5.5603655	1.3236702	1.8327406
H	4.6361900	1.3271460	3.7428407
C	4.7535990	−0.2533441	0.2448132
H	3.1967227	−1.5447864	0.8728322
C	5.6220097	0.7808708	0.5602599
H	6.2215309	2.1357037	2.1074244
H	4.7761387	−0.6988867	−0.7414879
H	6.3259886	1.1554131	−0.1697578
B	−1.0044384	−0.6463401	0.2476178
C	−0.0343831	−0.0887295	−0.8603581
C	1.0116275	−0.8236585	−1.3990788
C	−0.1474154	1.2242977	−1.2931699
C	1.8957634	−0.2975868	−2.3193524
C	0.7269266	1.7914715	−2.2011251
C	1.7540167	1.0204863	−2.7156801
C	−2.5439005	−0.4345511	0.0705979
C	−3.3600958	−0.0538137	1.1273838
C	−3.1667752	−0.6168035	−1.1574713
C	−4.7204369	0.1396800	0.9843037
C	−4.5263340	−0.4489320	−1.3349011
C	−5.3025575	−0.0647923	−0.2548570
F	−5.0919092	−0.6473861	−2.5164132
F	−6.6027980	0.1084156	−0.4078584
F	−5.4677793	0.5190171	2.0106972
F	−2.8270770	0.1834454	2.3223888
F	−2.4487821	−0.9995923	−2.2086877
F	−1.1108264	1.9973552	−0.7945494
F	2.5999818	1.5411142	−3.5863262
F	2.8783155	−1.0360751	−2.8182326
F	1.1780904	−2.1000247	−1.0526292
F	0.5967915	3.0556252	−2.5759712
C	2.7774995	−0.0098438	4.6776245
H	2.0744168	−0.5505126	5.3081793
H	3.7379377	−0.0144844	5.1956667
H	2.4362977	1.0307536	4.6110294

Table S5. Cartesian coordinates of the optimized structure of **4-H$_2$**.

C	−2.1267641	2.8545190	−0.7572617
C	−0.9085282	3.2633541	0.0570315
C	0.3611599	2.5309413	−0.3901380
H	−1.9851271	1.8983939	−1.2452654
H	−2.3597138	3.5935175	−1.5256165
H	−1.0418005	3.0159717	1.1121740
H	−0.8040212	4.3516333	0.0039754
H	1.1912153	3.0598960	0.0862703
H	0.5224492	2.6660512	−1.4630725
N	−3.4145588	2.6849758	0.0438728
C	−3.4953754	1.3850588	0.7294424
C	−4.1729775	0.3708111	0.0732026
C	−2.8870179	1.1739514	1.9519108
C	−4.2520347	−0.8804507	0.6595881
H	−4.6277416	0.5371024	−0.8976328
C	−2.9698918	−0.0850949	2.5261609
H	−2.3297598	1.9483529	2.4574626
C	−3.6515417	−1.1077425	1.8887138
H	−4.7728796	−1.6784838	0.1491315
H	−2.4751178	−0.2656385	3.4693861
H	−3.6993754	−2.0887482	2.3396620
B	0.4205178	0.9818548	0.1628076
C	−0.4457636	−0.1817504	−0.6131026
C	−0.8699847	−0.1853286	−1.9325404
C	−0.8034364	−1.3215568	0.0966294
C	−1.6341436	−1.1910848	−2.5025236
C	−1.5526933	−2.3575694	−0.4317171
C	−1.9816203	−2.2893405	−1.7423737
C	1.9723849	0.4966088	0.2996148
C	2.6850613	0.6739408	1.4758292
C	2.6876788	−0.0906371	−0.7305541
C	4.0028001	0.2817760	1.6371311
C	4.0037570	−0.5042107	−0.6141635
C	4.6661195	−0.3167951	0.5831392
F	4.6380181	−1.0724143	−1.6384436
F	5.9326795	−0.7007820	0.7177034
F	4.6385068	0.4736159	2.7928219
F	2.1110778	1.2598991	2.5325446
F	2.1123915	−0.2730392	−1.9245421
F	−0.4290239	−1.4649000	1.3702214
F	−2.7285159	−3.2623081	−2.2603065
F	−2.0381483	−1.1099990	−3.7707644
F	−0.5716891	0.8401771	−2.7472268
F	−1.8957220	−3.4061480	0.3181282
H	−0.0549018	1.0287460	1.2847171
H	−4.1530809	2.6550028	−0.6579907
C	−3.7238841	3.8530413	0.9060551
H	−3.7494020	4.7455826	0.2856126
H	−4.6868757	3.6976274	1.3846078
H	−2.9540410	3.9711508	1.6596210

Table S6. Cartesian coordinates of the optimized structure of **closed-5**.

C	−0.3990415	0.2947461	1.4179860
C	−2.3108178	1.2422126	2.5980113
C	−2.3770521	0.0356289	3.5194674
C	−2.6720041	−1.1995502	2.6474194
B	−2.8000636	−0.6676073	1.0984073
C	0.5848210	1.4084645	1.7412807
C	2.0334775	0.9406548	1.5935553
H	−1.6633303	2.0334600	2.9758792
H	−3.2989124	1.6690780	2.4571987
H	−0.1170409	−0.1676414	0.4749221
H	−0.3631646	−0.4875645	2.1708405
H	−3.1482491	0.2091402	4.2697818
H	−1.4430733	−0.0751029	4.0740449
H	−3.5987692	−1.6625818	2.9796036
H	−1.9107428	−1.9566227	2.8116911
H	0.4357833	1.7817071	2.7565435
H	0.3956102	2.2444411	1.0708590
H	2.1082011	0.2682130	0.7209999
H	2.3298960	0.3168584	2.4378674
B	3.0876443	2.0492644	1.2355234
N	−1.8319803	0.7530600	1.2703702
C	−1.8302709	1.7867896	0.2262593
C	−1.3953939	1.4575231	−1.0513244
C	−2.1242383	3.1148902	0.5085759
C	−1.2860344	2.4288896	−2.0325853
H	−1.1072679	0.4466123	−1.2948417
C	−2.0114490	4.0848740	−0.4759400
H	−2.4442051	3.4260285	1.4910041
C	−1.5955745	3.7496725	−1.7530520
H	−0.9519407	2.1439245	−3.0210193
H	−2.2528282	5.1111806	−0.2331886
H	−1.5086445	4.5079759	−2.5192176
C	4.6260408	1.8805749	1.4269723
C	5.2366584	0.6356308	1.5793399
C	5.4875089	2.9792233	1.4293688
C	6.6013644	0.4796702	1.7198917
C	6.8551646	2.8602612	1.5813191
C	7.4118819	1.6014975	1.7232515
C	2.5274836	3.3345154	0.5115160
C	1.9097059	4.3637790	1.1914771
C	2.5082285	3.3850707	−0.8656491
C	1.2853315	5.4074151	0.5388657
C	1.8876073	4.4072632	−1.5594830
C	1.2755617	5.4208006	−0.8459231
C	−4.4072567	−0.4301459	0.8275512
C	−5.1706857	0.7050310	0.6243788
C	−5.1498646	−1.6106813	0.8112653
C	−6.5439940	0.6946428	0.4342294
C	−6.5158206	−1.6727502	0.6170560
C	−7.2259971	−0.5024192	0.4284499
C	−2.2194613	−1.5921316	−0.1276839
C	−1.2897296	−2.6170029	0.0100334
C	−2.7380229	−1.4725463	−1.4168517
C	−0.9097812	−3.4605325	−1.0214169
C	−2.3891511	−2.2942364	−2.4735317
C	−1.4678672	−3.3031714	−2.2730369
F	−4.6094713	1.9195729	0.5932146
F	−7.2029768	1.8345581	0.2530296
F	−8.5387183	−0.5326501	0.2461046
F	−7.1492736	−2.8399119	0.6126557
F	−3.6052995	−0.5033019	−1.7111252
F	−2.9224663	−2.1167343	−3.6760565
F	−1.1138930	−4.0968866	−3.2717623
F	−0.0095557	−4.4149196	−0.8153757
F	−0.6748560	−2.8461729	1.1741059
F	−4.5306174	−2.7849631	0.9773418
F	5.0078555	4.2088932	1.3098653
F	7.6334485	3.9309121	1.5926010
F	8.7156485	1.4702260	1.8624382

F	7.1393182	−0.7231292	1.8483165
F	4.5095900	−0.4736942	1.5619301
F	3.0753677	2.3874702	−1.5496819
F	1.8523589	4.4136246	−2.8843123
F	0.6542292	6.3979453	−1.4884137
F	0.6783044	6.3746705	1.2123233
F	1.8935178	4.3282182	2.5265171

Table S7. Cartesian coordinates of the optimized structure of **open-5**.

C	0.9984359	2.5866448	1.7460144
C	−1.0175300	1.4938890	0.9331498
C	−1.6222512	2.1107048	−0.3241005
C	−1.9524972	1.0800086	−1.4301679
C	1.7553255	1.4695443	2.4670673
C	3.2758447	1.4370784	2.1835684
H	−0.2383502	0.7831260	0.6405111
H	−1.7649721	0.9005518	1.4657715
H	1.3119638	3.5636183	2.1182232
H	1.2532149	2.5976608	0.6845949
H	−0.9168569	2.8377547	−0.7347996
H	−2.5130753	2.6798128	−0.0606212
H	−1.0056564	0.7990742	−1.9007732
H	−2.5335194	1.5864941	−2.2030791
H	1.2995829	0.5106575	2.2106109
H	1.6044032	1.5770676	3.5434381
H	3.7637814	0.8487571	2.9616115
H	3.6643558	2.4560215	2.2833186
B	3.6103860	0.8801335	0.7553261
N	−0.4334593	2.4517296	1.8408089
C	−1.1504949	2.9661053	2.9017591
C	−2.5512316	2.8795196	2.9392446
C	−0.5190894	3.6052555	3.9795133
C	−3.2702745	3.3991089	4.0011292
H	−3.0991362	2.4216837	2.1270368
C	−1.2537835	4.1288473	5.0293009
H	0.5578697	3.6899799	4.0192820
C	−2.6355874	4.0315510	5.0585765
H	−4.3492378	3.3130723	3.9904485
H	−0.7274674	4.6122490	5.8425464
H	−3.2031809	4.4388915	5.8835250
C	3.3234676	1.7563811	−0.5210820
C	2.4487806	1.2925501	−1.4883683
C	3.8624513	3.0150585	−0.7215566
C	2.0957247	2.0384510	−2.5955319
C	3.5532804	3.7841546	−1.8276523
C	2.6581709	3.2923497	−2.7631819
C	4.1668429	−0.5632820	0.5090678
C	3.7178049	−1.6769871	1.2076056
C	5.1385738	−0.7971123	−0.4579517
C	4.1802605	−2.9541470	0.9561185
C	5.6436619	−2.0554470	−0.7201895
C	5.1541600	−3.1381984	−0.0100296
F	4.7325415	3.5030652	0.1591284
F	4.0969194	4.9791510	−2.0004891
F	2.3409536	4.0207998	−3.8187773
F	1.2298490	1.5743796	−3.4853680
F	1.8789013	0.0968630	−1.3249802
F	5.6444071	0.2229616	−1.1448969
F	6.5845067	−2.2356888	−1.6345689
F	5.6204328	−4.3488313	−0.2522943
F	3.7150586	−3.9937667	1.6302135
F	2.7723608	−1.5414236	2.1332786
B	−2.6553424	−0.2535021	−0.9777895
C	−4.1834383	−0.5199470	−1.1854648
C	−5.1436433	0.4681376	−1.0078753
C	−4.6530444	−1.7690944	−1.5775360
C	−6.4931171	0.2411465	−1.1936732
C	−5.9927999	−2.0275860	−1.7952898
C	−6.9147167	−1.0149602	−1.5950728
C	−1.7986601	−1.3921572	−0.3016898
C	−0.6740828	−1.9468191	−0.8900399
C	−2.1196805	−1.8418507	0.9682757
C	0.1186304	−2.8755950	−0.2418442
C	−1.3481413	−2.7606398	1.6533365
C	−0.2193018	−3.2763651	1.0395150
F	−1.6712279	−3.1464245	2.8785366
F	0.5279451	−4.1640359	1.6714225
F	1.1903035	−3.3904730	−0.8309029

F	−0.3568673	−1.6153562	−2.1392311
F	−3.1888766	−1.3346263	1.5836921
F	−3.7958698	−2.7598604	−1.7975081
F	−8.1997004	−1.2466239	−1.7883440
F	−7.3823752	1.2022377	−0.9929201
F	−4.7767680	1.6802413	−0.6034945
F	−6.4020059	−3.2234357	−2.1915442

Table S8. Cartesian coordinates of the optimized structure of **5-H$_2$**.

C	1.4460729	−2.2981781	3.0735438
C	−0.7488657	−3.3232676	2.2574102
C	−1.1968840	−1.9795887	1.7204311
C	−2.6704908	−1.9564021	1.3339843
C	1.9231086	−1.2777593	2.0596972
C	2.5963993	−0.0628703	2.7243756
H	−1.0646201	−4.1403455	1.6091184
H	−1.1797626	−3.4970881	3.2447686
H	2.2928994	−2.6881577	3.6401870
H	0.7345606	−1.8688877	3.7787435
H	−0.6036427	−1.7058411	0.8500041
H	−1.0239351	−1.1940927	2.4594589
H	−3.2810257	−2.0546653	2.2373234
H	−2.9143010	−2.8179128	0.7054925
H	1.0838398	−0.9535326	1.4484349
H	2.6391490	−1.7482370	1.3854809
H	3.5562583	−0.3736757	3.1450669
H	1.9926303	0.3268782	3.5413472
B	2.8110628	0.9452903	1.5269910
N	0.7599289	−3.5025221	2.4420482
C	1.5018733	−3.9859209	1.2638612
C	2.7032764	−4.6374704	1.4986582
C	1.0576029	−3.7416405	−0.0217596
C	3.4832956	−5.0300281	0.4237286
H	3.0454727	−4.8353455	2.5085385
C	1.8526796	−4.1310110	−1.0909923
H	0.1155477	−3.2575475	−0.2236029
C	3.0642335	−4.7656546	−0.8727164
H	4.4204722	−5.5387939	0.6019429
H	1.5122919	−3.9185610	−2.0948553
H	3.6807187	−5.0590776	−1.7111356
C	1.8850266	2.1429920	1.1999058
C	0.6218200	2.3177586	1.7734554
C	2.2682548	3.1261921	0.2815021
C	−0.2019788	3.3837641	1.4756011
C	1.4679720	4.1999458	−0.0452099
C	0.2251378	4.3235828	0.5526975
C	3.9576638	0.5282977	0.5255425
C	3.6463530	0.0131714	−0.7192626
C	5.2935835	0.5682976	0.8728122
C	4.6109973	−0.4562479	−1.5899107
C	6.2917922	0.1292859	0.0231730
C	5.9415853	−0.3898201	−1.2121232
F	3.4635014	3.0753080	−0.2927785
F	1.8794405	5.1154744	−0.9073479
F	−0.5401747	5.3513899	0.2602463
F	−1.3713140	3.5258072	2.0683595
F	0.1496699	1.4277869	2.6388597
F	5.6377091	1.0638758	2.0630672
F	7.5674153	0.1893389	0.3781390
F	6.8815074	−0.8319291	−2.0315940
F	4.2806537	−0.9708003	−2.7647623
F	2.3654070	−0.0682547	−1.0811107
B	−3.0186648	−0.5052673	0.6447374
C	−2.0880911	−0.1465858	−0.6667071
C	−1.4619499	−1.0472524	−1.5125248
C	−1.8071614	1.1812372	−0.9622702
C	−0.5747638	−0.6953976	−2.5151333
C	−0.9366156	1.5860912	−1.9602636
C	−0.3068458	0.6386757	−2.7444125
C	−4.6089827	−0.4026409	0.3189696
C	−5.5056186	0.1088858	1.2453489
C	−5.1832022	−0.8573519	−0.8564749
C	−6.8709907	0.1814572	1.0264777
C	−6.5408655	−0.8016252	−1.1206355
C	−7.3919968	−0.2750000	−0.1690682
F	−7.0351496	−1.2564410	−2.2713291
F	−8.7014735	−0.2166244	−0.3969096
F	−7.6894381	0.6800516	1.9525240

F	−5.0729173	0.5512117	2.4294271
F	−4.4173391	−1.4037158	−1.8085383
F	−2.3826715	2.1596582	−0.2596572
F	0.5374884	1.0063463	−3.7027411
F	0.0223730	−1.6337003	−3.2558494
F	−1.6679454	−2.3718344	−1.3768971
F	−0.6913973	2.8812563	−2.1696042
H	−2.7279659	0.3317568	1.4761460
H	0.8385509	−4.2486050	3.1315311

Table S9. Cartesian coordinates of the optimized structure of **bridged-5-H_2**.

C	1.0312221	−2.0721121	0.9239339
H	1.9466097	−1.4848041	0.8298294
H	1.0811527	−2.4622797	1.9445934
C	1.0367937	−3.2732969	−0.0375102
H	0.4201699	−3.1156498	−0.9179792
H	0.5876947	−4.1387704	0.4548897
C	2.4149796	−3.7328015	−0.4760903
H	2.3641280	−4.6062881	−1.1265939
H	3.0315853	−3.9876261	0.3865997
C	2.6349202	−2.2672301	−2.5753639
H	3.4814653	−1.8500006	−3.1188974
H	2.3182853	−3.1784846	−3.0838812
C	1.5155930	−1.2356920	−2.4825931
H	0.5830085	−1.7085894	−2.1987144
H	1.3565956	−0.8895157	−3.5064959
C	1.8289394	−0.0449695	−1.5831673
C	4.6140095	−3.0040608	−1.2975589
C	5.0329220	−4.1021583	−2.0297728
C	5.5130797	−2.1910919	−0.6319405
C	6.3872209	−4.3872188	−2.0907061
H	4.3242016	−4.7302656	−2.5540482
C	6.8665534	−2.4874877	−0.6996607
H	5.1733249	−1.3283066	−0.0697156
C	7.3031141	−3.5831145	−1.4269237
H	6.7265338	−5.2403960	−2.6615167
H	7.5763667	−1.8559703	−0.1839439
H	8.3587431	−3.8107742	−1.4799140
C	−1.5841002	−2.0466466	0.6037470
C	−2.1501752	−2.4249451	−0.6006496
C	−2.1474840	−2.6534968	1.7193449
C	−3.2314647	−3.2838867	−0.7041833
C	−3.2261757	−3.5154312	1.6661933
C	−3.7813296	−3.8265788	0.4393652
C	−0.4616173	−0.0096027	2.0143086
C	−1.6956077	0.5623899	2.3060983
C	0.5887441	0.4770115	2.7803538
C	−1.8822631	1.5320858	3.2756014
C	0.4475682	1.4450098	3.7577089
C	−0.8009453	1.9775114	4.0098598
F	−1.6297291	−2.4227082	2.9302844
F	−3.7253893	−4.0504561	2.7744838
F	−4.8141415	−4.6546362	0.3611071
F	−3.7281949	−3.6043829	−1.8946202
F	−1.6389051	−2.0020660	−1.7651807
F	−0.9569621	2.9085411	4.9384848
F	1.5036044	1.8743044	4.4426512
F	1.8394770	0.0364915	2.5885872
F	−2.7874828	0.1950543	1.6410767
F	−3.0879204	2.0363750	3.5047481
B	−0.2794373	−1.1071195	0.8407459
C	0.8199076	1.9739070	−0.0237455
C	−0.2090741	2.8019277	0.4173177
C	2.0720952	2.3169875	0.4746533
C	−0.0316080	3.8634056	1.2850004
F	−1.4613477	2.5819100	0.0273738
C	2.2956659	3.3750113	1.3390303
F	3.1715635	1.6297501	0.1402414
C	1.2350217	4.1536369	1.7534176
F	−1.0659243	4.5956882	1.6783009
F	3.5235151	3.6445146	1.7697516
F	1.4280140	5.1623311	2.5877526
C	−0.5289732	1.1362013	−2.2171335
C	−0.0453303	1.7907244	−3.3418209
C	−1.8978641	0.9128091	−2.2217676
C	−0.8293003	2.1536625	−4.4214723
F	1.2495735	2.1253366	−3.4146686
C	−2.7189226	1.2515049	−3.2840775
F	−2.5037104	0.3771654	−1.1681943
C	−2.1803685	1.8699972	−4.3954338

F	−0.2964636	2.7681791	−5.4733981
F	−4.0215281	0.9985169	−3.2388380
F	−2.9529998	2.2009920	−5.4206877
H	2.5257978	0.6214679	−2.0915540
H	2.3583952	−0.3530909	−0.6793577
B	0.5271386	0.7541094	−1.0474046
N	3.1922843	−2.6768460	−1.2262384
H	−0.1067594	−0.2725196	−0.2799740
H	3.1163952	−1.8297697	−0.6551242

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