Supporting Information

Formation and Reactions of Active Five-membered Phosphane/Borane Frustrated Lewis Pair Ring Systems

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Contents

Part 1: Experimental and Analytical Details

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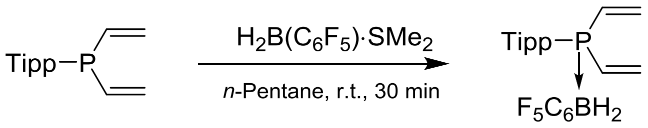
General Information: All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Toluene, CH_2Cl_2, Et_2O, pentane and THF were dried using a Grubbs-type solvent purification system with alumina spheres as the drying agent. All solvents were stored under an argon atmosphere. Elemental analysis data was recorded on Foss-Heraeus CHNO-Rapid. Melting points was recorded on TA-instruments DSC Q-20; NMR spectra were recorded on a *Varian* Inova 500 (^{1}H: 500 MHz, ^{13}C{^{1}H}: 126 MHz, ^{31}P: 202 MHz, ^{19}F: 470 MHz, ^{11}B: 160 MHz) or a *Varian* Inova 600 (^{1}H: 600 MHz, ^{13}C{^{1}H}: 151 MHz, ^{31}P: 243 MHz, ^{19}F: 564 MHz, ^{11}B: 192 MHz). ^{1}H NMR and ^{13}C{^{1}H} NMR: chemical shifts [δ] are given relative to TMS (Trimethylsilane) and referenced to the respective solvent signal. The splitting patterns in the NMR spectra are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, br = broad signal. Coupling constants are given in Hertz (Hz). ^{31}P NMR: chemical shifts δ are given relative to 85% H_3PO_4 in D_2O (external reference, $\delta^{31}P = 0$), ^{19}F NMR: chemical shifts δ are given relative to $CFCl_3$ (external reference, $\delta^{19}F = 0$), ^{11}B NMR: chemical shifts δ are given relative to $BF_3{\cdot}Et_2O$ (external reference, $\delta^{11}B = 0$). Assignments were supported by additional 1D and 2D NMR experiments.

Materials: Bis(pentafluorophenyl)borane $[HB(C_6F_5)_2]$[1] (Piers' borane) and "Lancaster's reagent" $[H_2B(C_6F_5){\cdot}SMe_2]$[2] were prepared according to the literature procedure. 2,4,6-triisopropylphenyl)divinylphosphane $[TippP(CH{=}CH_2)_2]$ (**3a)**, 2,4,6-tri-*tert*-butyl-phenyl)divinylphosphane $[Mes^*P(CH{=}CH_2)_2]$ (**3b**), compound **4a** and **4c** were prepared according to modified literature procedures.[3] All other reagents were commercially available and used as received.

X-Ray diffraction: For compounds **7a**, **9a** and **10b** data sets were collected with a Nonius Kappa CCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, **2008**, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski and W. Minor, *Methods Enzymol.,* 1997, **276**, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski and W. Minor, *Acta Crystallogr*., 2003, **A59**, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*., 1990, **A46**, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*., **2008**, **A64**, 112-122) and graphics, XP (BrukerAXS, **2000**). For compound **8a**, **11a**, **11b**, [**3a**·$H_2B(C_6F_5)$] and **15b** data sets were collected with a Bruker APEX II CCD diffractometer. Data sets for the compounds **8b**, **12a**, **15a** and [**6a**·$H_2B(C_6F_5)\cdot SMe_2$] were collected with a D8 Venture Dual Source 100 CMOS diffractometer. Programs used for compounds **8a**, **8b**, **11a**, **11b**, **12a**, **15a** and **15b**: data collection: APEX3 V2016.1-0 (Bruker AXS Inc., **2016**); cell refinement: SAINT V8.37A (Bruker AXS Inc., **2015**); data reduction: SAINT V8.37A (Bruker AXS Inc., **2015**); absorption correction, SADABS V2014/7 (Bruker AXS Inc., **2014**); structure solution SHELXT-2015 (Sheldrick, **2015**); structure refinement SHELXL-2015 (Sheldrick, **2015**). Programs used for compounds [**3a**·$H_2B(C_6F_5)$] und [**6a**·$H_2B(C_6F_5)\cdot SMe_2$]: data collection: APEX2 V2014.11-0 (Bruker AXS Inc., **2014**); cell refinement: SAINT V8.34A (Bruker AXS Inc., **2013**); data reduction: SAINT V8.34A (Bruker AXS Inc., **2013**); absorption correction, SADABS V2014/2 (Bruker AXS Inc., **2014**); structure solution SHELXT-2014 (Sheldrick, **2014**); structure refinement SHELXL-2014 (Sheldrick, **2014**). *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: For compounds **7a** two isopropyl groups and for compound **8a** one isopropyl group were found disordered over two positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. CCDC deposition numbers are 1812016-1812027.

Synthesis of compound 3a$\cdot H_2B(C_6F_5)$



3a **3a**$\cdot H_2B(C_6F_5)$

Tipp = 2,4,6-triisopropylphenyl

A solution of 2,4,6-triisopropylphenyl)divinylphosphane [TippP(CH=CH$_2$)$_2$]^3 (**3a**) (576.5 mg, 2.00 mmol) in *n*-pentane (5 mL) was added to a solution of [$H_2B(C_6F_5)\cdot SMe_2$]^2 (485.1 mg, 2.00 mmol) in *n*-pentane (15 mL) at room temperature (r.t.). After the reaction mixture was stirred for 30 min., all volatiles were removed *in vacuo* to give compound **3a**$\cdot H_2B(C_6F_5)$ as a white solid (917.5 mg, 98%).

Elemental analysis: calc. for $C_{25}H_{31}BF_5P$ (468.30 g mol^{-1}): C, 64.12; H, 6.67. **Found**: C, 64.40; H, 6.70.

Decomposition: 93 °C

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 7.09 (d, $^4J_{P\text{-}H}$ = 3.5 Hz, 2H, *m*-Tipp), 6.44 (ddd, $^3J_{H\text{-}H}$ = 18.3 Hz, $^2J_{P\text{-}H}$ = 16.6 Hz, $^3J_{H\text{-}H}$ = 12.2 Hz, 2H, =CH), [6.06 (dd, $^3J_{P\text{-}H}$ = 40.4 Hz, $^3J_{H\text{-}H}$ = 12.2 Hz), 6.06 (dd, $^3J_{P\text{-}H}$ = 20.1 Hz, $^3J_{H\text{-}H}$ = 18.3 Hz)](each 2H, =CH$_2$), 3.28 (sept, $^3J_{H\text{-}H}$ = 6.6 Hz, 2H, *o*-^{i}Pr^{CH}), 2.90 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 1H, *p*-^{i}Pr^{CH}), 2.41 (br m, 2H, BH$_2$), 1.25 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 6H, *p*-^{i}Pr^{CH3}), 1.10 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 12H, *o*-^{i}Pr^{CH3}).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 154.9 (d, $^2J_{P\text{-}C}$ = 9.3 Hz, *o*-Tipp), 153.0 (d, $^4J_{P\text{-}C}$ = 2.4 Hz, *p*-Tipp), 148.7 (dm, $^1J_{F\text{-}C}$ = 238.0 Hz, C_6F_5), 139.3 (dm, $^1J_{F\text{-}C}$ = 240.0 Hz, C_6F_5), 137.2 (dm, $^1J_{F\text{-}C}$ = 245.0 Hz, C_6F_5), 131.1 (br, =CH$_2$), 130.9 (d, $^1J_{P\text{-}C}$ = 55.5 Hz, =CH), 124.0 (d, $^3J_{P\text{-}C}$ = 8.9 Hz, *m*-Tipp), 119.5 (d, $^1J_{P\text{-}C}$ = 57.8 Hz, *i*-Tipp), 116.8 (br. *i*-C_6F_5), 34.5 (*p*-^{i}Pr^{CH}), 32.5 (d, $^3J_{PC}$ = 6.0 Hz, *o*-^{i}Pr^{CH}), 24.9 (*o*-^{i}Pr^{CH3}), 23.7 (*p*-^{i}Pr^{CH3}).

^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2): δ = −29.5 ($\nu_{1/2}$ ~ 150 Hz).

^{11}B NMR (160 MHz, 299 K, CD_2Cl_2): δ = −29.5 (br td, $^1J_{B\text{-}H}$ ~ 95 Hz, $^1J_{P\text{-}B}$ ~ 60 Hz).

^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ = −128.7 (m, 2F, *o*-C_6F_5), −160.7 (td, $^3J_{F\text{-}F}$ = 19.9 Hz, $^3J_{F\text{-}F}$ = 5.6 Hz, 1F, *p*-C_6F_5), −165.4 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 4.7].

^{31}P{^{1}H} NMR (202 MHz, 299 K, CD_2Cl_2): δ = 0 (m).

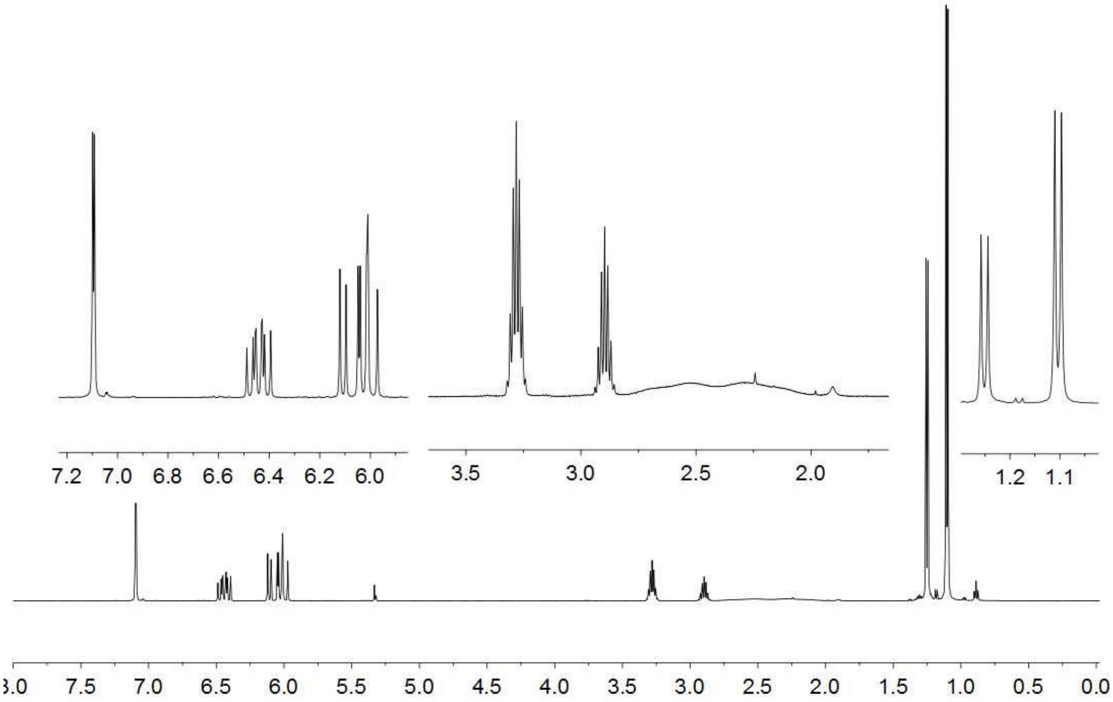


Figure S1 ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of compound **3a**·$H_2B(C_6F_5)$.

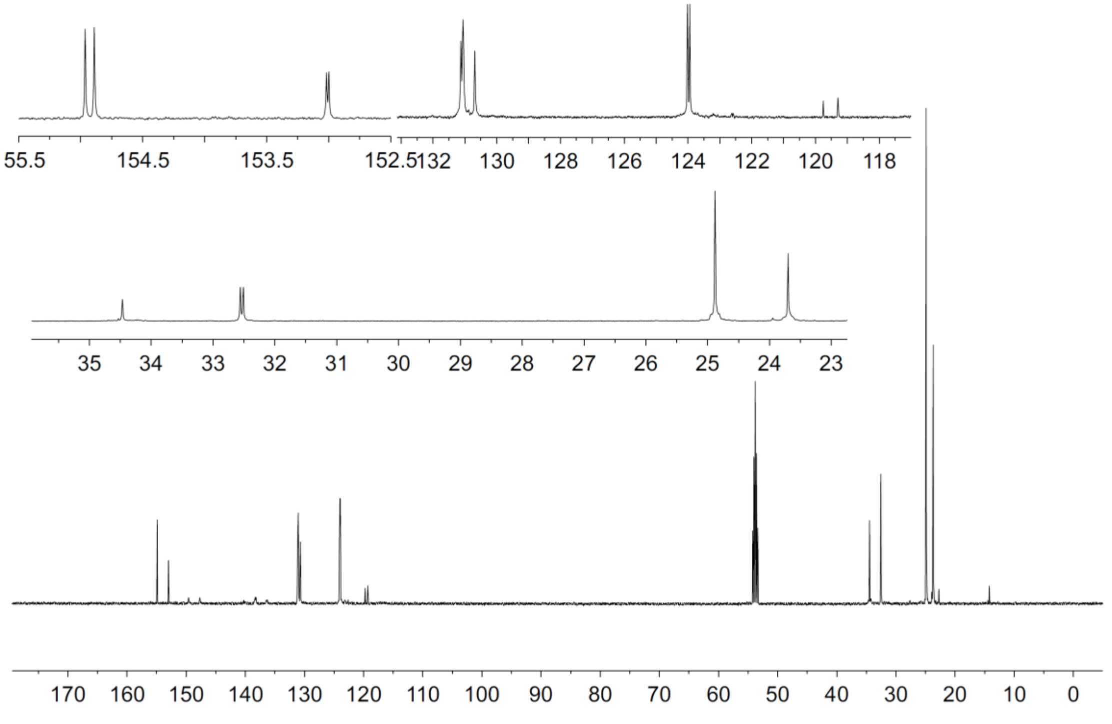


Figure S2 $^{13}C\{^1H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) spectrum of compound **3a**·$H_2B(C_6F_5)$.

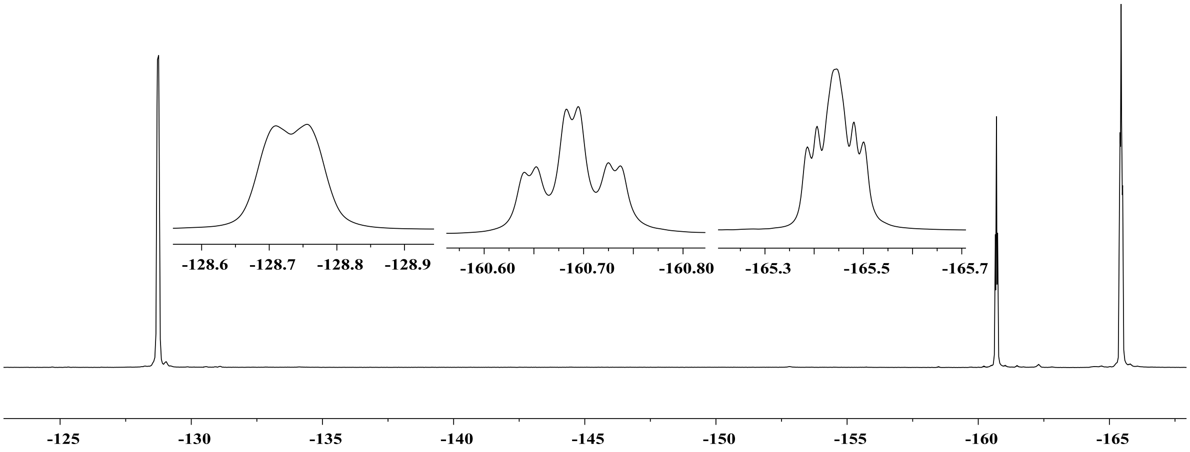


Figure S3 ^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) spectrum of compound **3a**·$[H_2B(C_6F_5)]$.

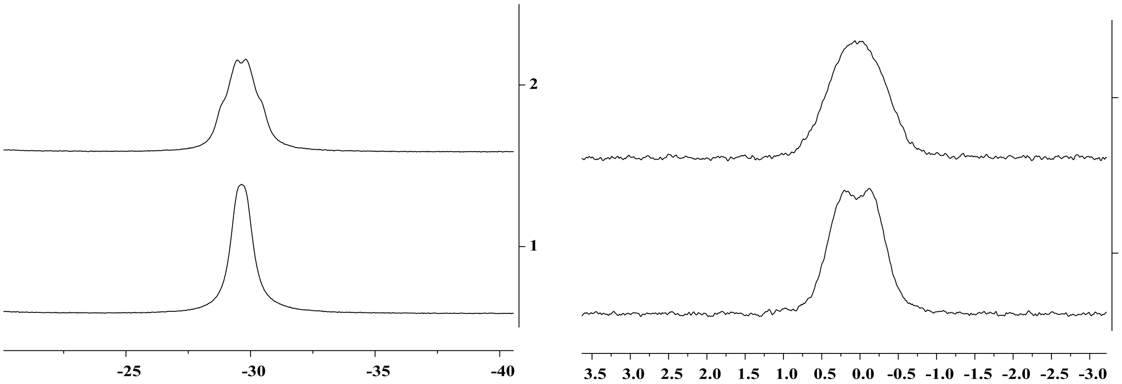


Figure S4 $^{11}B\{^1H\}$ (left, 1) ^{11}B (left, 2) NMR (160 MHz, 299 K, CD_2Cl_2) and $^{31}P\{^1H\}$ (right, 1) ^{31}P (right, 2) NMR (202 MHz, 299 K, CD_2Cl_2) spectra of compound **3a**·$H_2B(C_6F_5)$.

Crystals of compound **3a•**$H_2B(C_6F_5)$ suitable for the X-ray crystal structure analysis were obtained from a solution of the obtained white solid in *n*-pentane at −35 °C.

X-ray crystal structure analysis of compound 3a·$H_2B(C_6F_5)$ (erk8018): A colorless prism-like specimen of $C_{25}H_{31}BF_5P$, approximate dimensions 0.120 mm x 0.120 mm x 0.160 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1919 frames were collected. The total exposure time was 19.67 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 39734 reflections to a maximum θ angle of 66.59° (0.84 Å resolution), of which 4295 were independent (average redundancy 9.251, completeness = 99.9%, R_{int} = 7.14%, R_{sig} = 3.29%) and 3546 (82.56%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.4707(4) Å, b

= 11.7399(4) Å, c = 16.9189(5) Å, β = 100.647(2)°, volume = 2434.36(14) Å^3, are based upon the refinement of the XYZ-centroids of 9224 reflections above 20 σ(I) with 9.221° < 2θ < 135.0°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.912. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8040 and 0.8470. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{25}H_{31}BF_5P$. The final anisotropic full-matrix least-squares refinement on F^2 with 303 variables converged at R1 = 3.80%, for the observed data and wR2 = 10.10% for all data. The goodness-of-fit was 1.050. The largest peak in the final difference electron density synthesis was 0.348 e$^-$/Å^3 and the largest hole was -0.303 e$^-$/Å^3 with an RMS deviation of 0.048 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.278 g/cm^3 and F(000), 984 e$^-$.

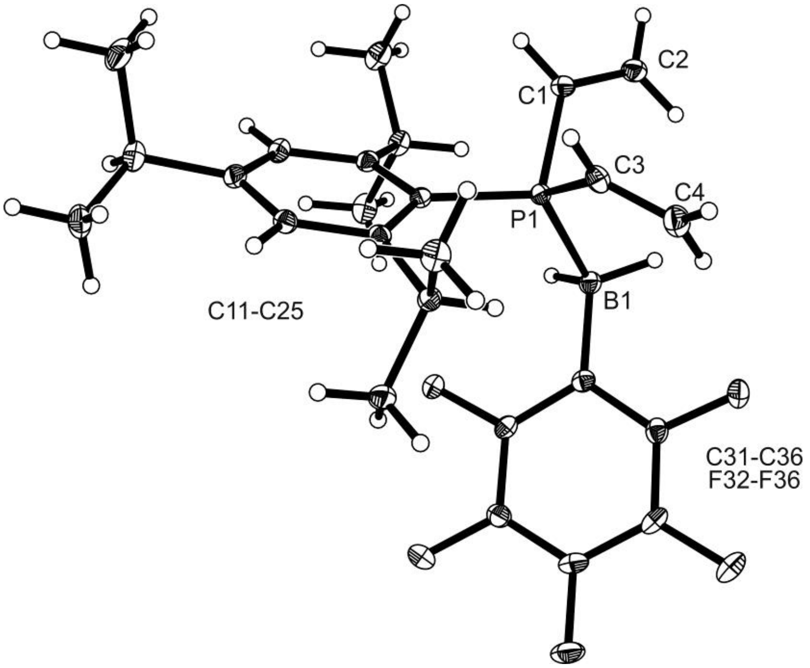
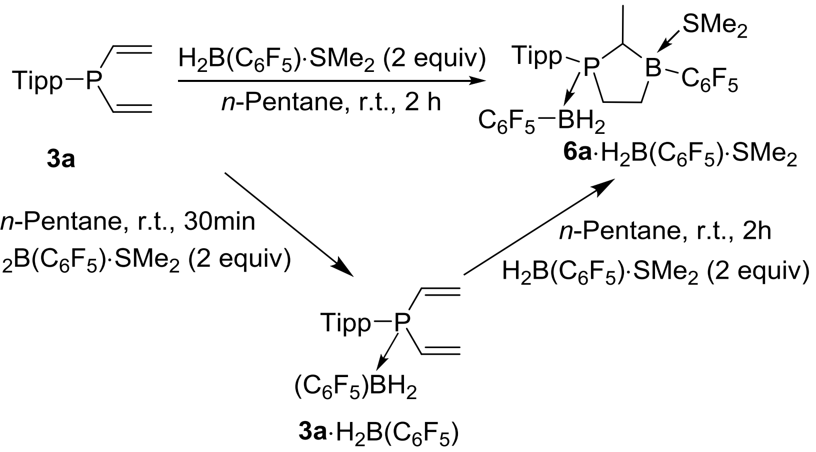


Figure S5 A view of the molecular structure of compound **3a**·$H_2B(C_6F_5)$.

Synthesis of compound 6a·$H_2B(C_6F_5)\cdot SMe_2$



Method A (*starting from compound* **3a**): A solution of TippP(CH=CH$_2$)$_2$ (**3a**) (144.0 mg, 0.50 mmol) in *n*-pentane (5 mL) was added to a solution of $H_2B(C_6F_5)\cdot SMe_2$ (242.5 mg, 1.00 mmol) in *n*-pentane (10 mL) at room temperature. Then the reaction mixture was stirred at room temperature for 2 h. Subsequently the reaction solution was concentrated to about 2 mL *in vacuo* and cooled to −50 °C to give white crystals, which were collected by filtration. After drying *in vacuo*, compound **6a**·$H_2B(C_6F_5)\cdot SMe_2$ was obtained as a white solid (315.5 mg, 89%).

Method B [*starting from compound* **3a**·$H_2B(C_6F_5)$]: compound **3a**·$H_2B(C_6F_5)$ (235.0 mg, 0.50 mmol) and $H_2B(C_6F_5)\cdot SMe_2$ (121.5 mg, 0.50 mmol) were weighed in and dissolved in *n*-pentane (20 mL) to give a colorless solution. Then the reaction mixture was stirred at room temperature for 2 h. Formation of a white precipitate was observed. The solvent was decanted, the remaining residue was washed with cold *n*-pentane (0 °C, 3×2 mL) and dried in vacuo to give compound **6a**·$H_2B(C_6F_5)\cdot SMe_2$ as a white solid (331.5 mg, 93%).

Crystals of compound **6a**·$H_2B(C_6F_5)\cdot SMe_2$ suitable for the X-ray crystal structure analysis were obtained from a solution of the obtained white solid in *n*-pentane at −35 °C.

Elemental analysis: calc. for $C_{33}H_{39}B_2F_{10}PS$: C, 55.80; H, 5.53. **Found**: C, 56.30; H, 5.52.

Melting point: 166 °C

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 7.02 (d, $^4J_{P\text{-}H}$ = 2.9 Hz, 2H, *m*-Tipp), 2.95 (br sept, $^3J_{H\text{-}H}$ = 6.5 Hz, 2H, *o*-^{i}Pr^{CH}), 2.88 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 1H, *p*-^{i}Pr^{CH}), [2.66, 2.32](each m, each 1H, PCH$_2$), 2.15 (br m, 2H, BH$_2$), 2.02 (br m, 1H, PCH), 1.67 (s, 6H, S(CH$_3$)$_2$), [1.54 (br dm, $^3J_{P\text{-}H}$ ~ 35 Hz), 1.41 (m)](each 1H, BCH$_2$), 1.26 (dd, $^3J_{P\text{-}H}$ = 18.3 Hz, $^3J_{H\text{-}H}$ = 7.8 Hz, 3H, Me^{PCH}), [1.23, 1.13](each br d, $^3J_{H\text{-}H}$ = 6.5 Hz, each 6H, *o*-^{i}Pr^{CH3}), [1.23, 1.22](each d, $^3J_{H\text{-}H}$ = 6.9 Hz, each 3H, *p*-^{i}Pr^{CH3}).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD$_2$Cl$_2$): δ = 153.8 (d, $^{2}J_{\text{P-C}}$ = 7.6 Hz, *o*-Tipp), 151.6 (d, $^{4}J_{\text{P-C}}$ = 2.5 Hz, *p*-Tipp), 128.1 (d, $^{1}J_{\text{P-C}}$ = 43.4 Hz, *i*-Tipp), 123.0 (d, $^{3}J_{\text{P-C}}$ = 8.1 Hz, *m*-Tipp), 34.4 (*p*-^{i}Pr$^{\text{CH}}$), 33.9 (d, $^{3}J_{\text{P-C}}$ = 4.4 Hz, *o*-^{i}Pr$^{\text{CH}}$), 28.6 (d, $^{1}J_{\text{P-C}}$ = 36.2 Hz, PCH$_2$), 27.1 (br d, $^{1}J_{\text{P-C}}$ = 32.5 Hz, PCH), [25.5, 24.5](each br, *o*-^{i}Pr$^{\text{CH3}}$), [23.9, 23.8](*p*-^{i}Pr$^{\text{CH3}}$), 18.8 (S(CH$_3$)$_2$), 18.2 (br, BCH$_2$), 14.8 (Me$^{\text{PCH}}$), [C$_6$F$_5$ not listed].

^{11}B{^{1}H} NMR (160 MHz, 299 K, CD$_2$Cl$_2$): δ = 9.4 ($\nu_{1/2}$ ~ 540 Hz), −30.6 ($\nu_{1/2}$ ~ 160 Hz).

^{19}F NMR (470 MHz, 299 K, CD$_2$Cl$_2$): δ = −128.8 (m, 2F, *o*-C$_6$F$_5$), −161.7 (td, $^{3}J_{\text{F-F}}$ = 20.1 Hz, $J_{\text{F-F}}$ = 6.8 Hz, 1F, *p*-C$_6$F$_5$), −165.5 (m, 2F, *m*-C$_6$F$_5$)[$\Delta\delta^{19}\text{F}_{m,p}$ = 3.8], −129.4 (m, 2F, *o*-C$_6$F$_5$), −155.2 (t, $^{3}J_{\text{F-F}}$ = 20.3 Hz, 1F, *p*-C$_6$F$_5$), −162.6 (m, 2F, *m*-C$_6$F$_5$)[$\Delta\delta^{19}\text{F}_{m,p}$ = 7.4].

^{31}P{^{1}H} NMR (202 MHz, 299 K, CD$_2$Cl$_2$): δ = 34.4 ($\nu_{1/2}$ ~160 Hz).

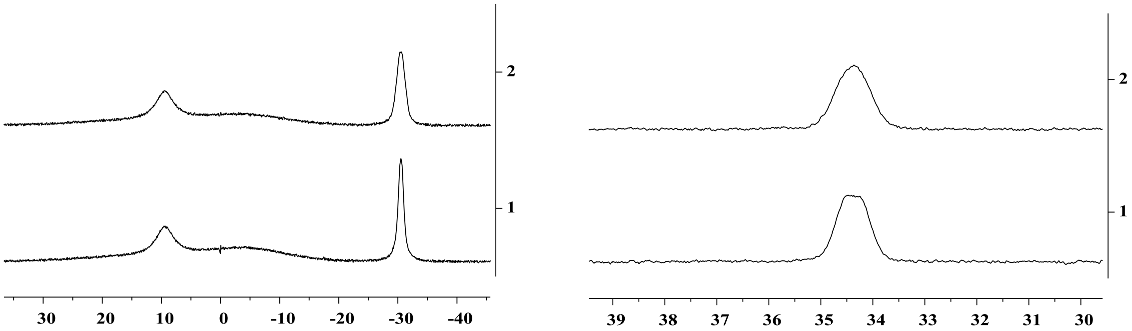


Figure S6 ^{11}B{^{1}H} (left, 1), ^{11}B (left, 2) NMR (160 MHz, 299 K, CD$_2$Cl$_2$) and ^{31}P{^{1}H} (right, 1) ^{12}P (right, 2) NMR (202 MHz, 299 K, CD$_2$Cl$_2$) spectra of compound **6a**·H$_2$B(C$_6$F$_5$)·SMe$_2$.

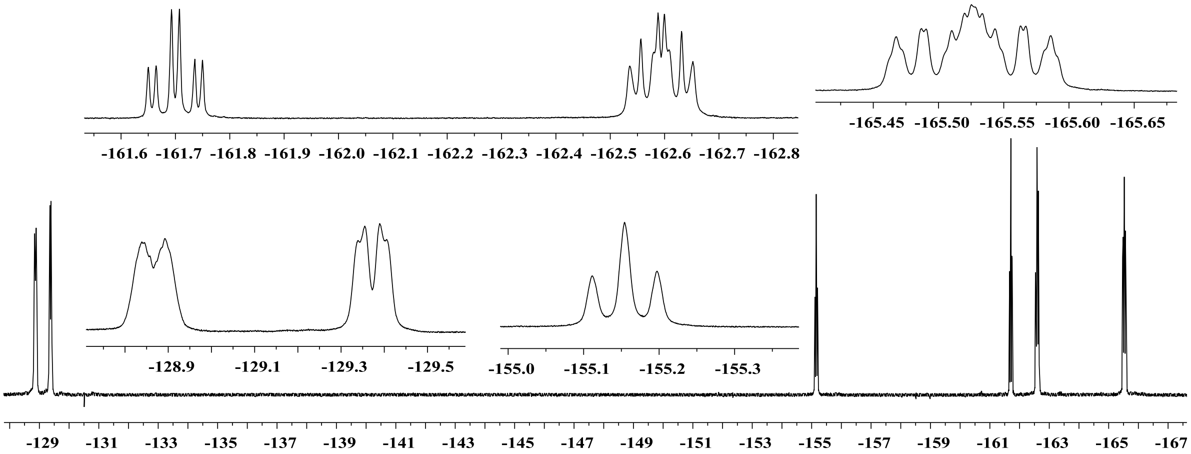


Figure S7 ^{19}F NMR (470 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound **6a**·H$_2$B(C$_6$F$_5$)·SMe$_2$.

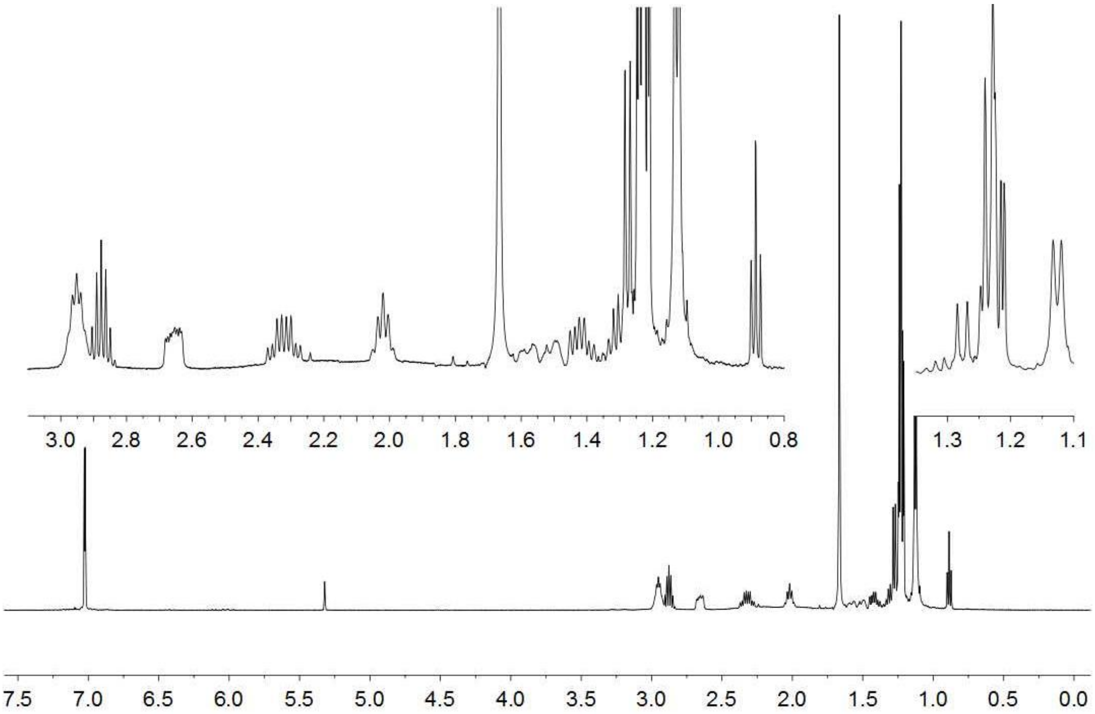


Figure S8 ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of compound **6a**·$H_2B(C_6F_5)\cdot SMe_2$.

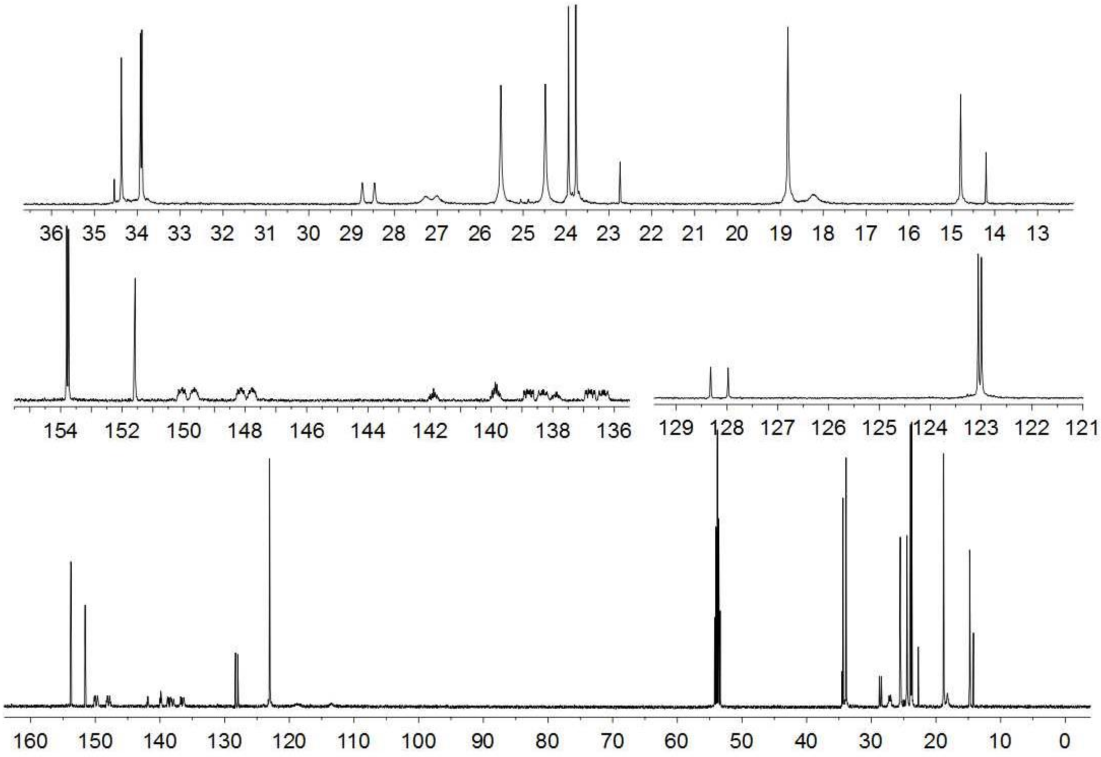


Figure S9 $^{13}C\{^1H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) spectrum of compound **6a**·$H_2B(C_6F_5)\cdot SMe_2$.

X-ray crystal structure analysis of compound 6a·$H_2B(C_6F_5)\cdot SMe_2$ **(erk7948)**: A colorless prism-like specimen of $C_{33}H_{39}B_2F_{10}PS$, approximate dimensions 0.134 mm x 0.169 mm x 0.171 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 445 frames were collected. The total exposure time was 3.73 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 28295 reflections to a maximum θ angle of 25.03° (0.84 Å resolution), of which 5882 were independent (average redundancy 4.810, completeness = 98.2%, R_{int} = 6.26%, R_{sig} = 4.58%) and 4543 (77.24%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.0259(6) Å, b = 24.2046(13) Å, c = 15.7132(10) Å, β = 98.923(2)°, volume = 3391.3(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 9397 reflections above 20 σ(I) with $4.868° < 2\theta < 50.77°$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.933. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9630 and 0.9710. The final anisotropic full-matrix least-squares refinement on F^2 with 441 variables converged at R1 = 5.05%, for the observed data and wR2 = 12.74% for all data. The goodness-of-fit was 1.038. The largest peak in the final difference electron density synthesis was 0.742 $e^-/Å^3$ and the largest hole was -0.339 $e^-/Å^3$ with an RMS deviation of 0.064 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.391 g/cm^3 and F(000), 1472 e^-.

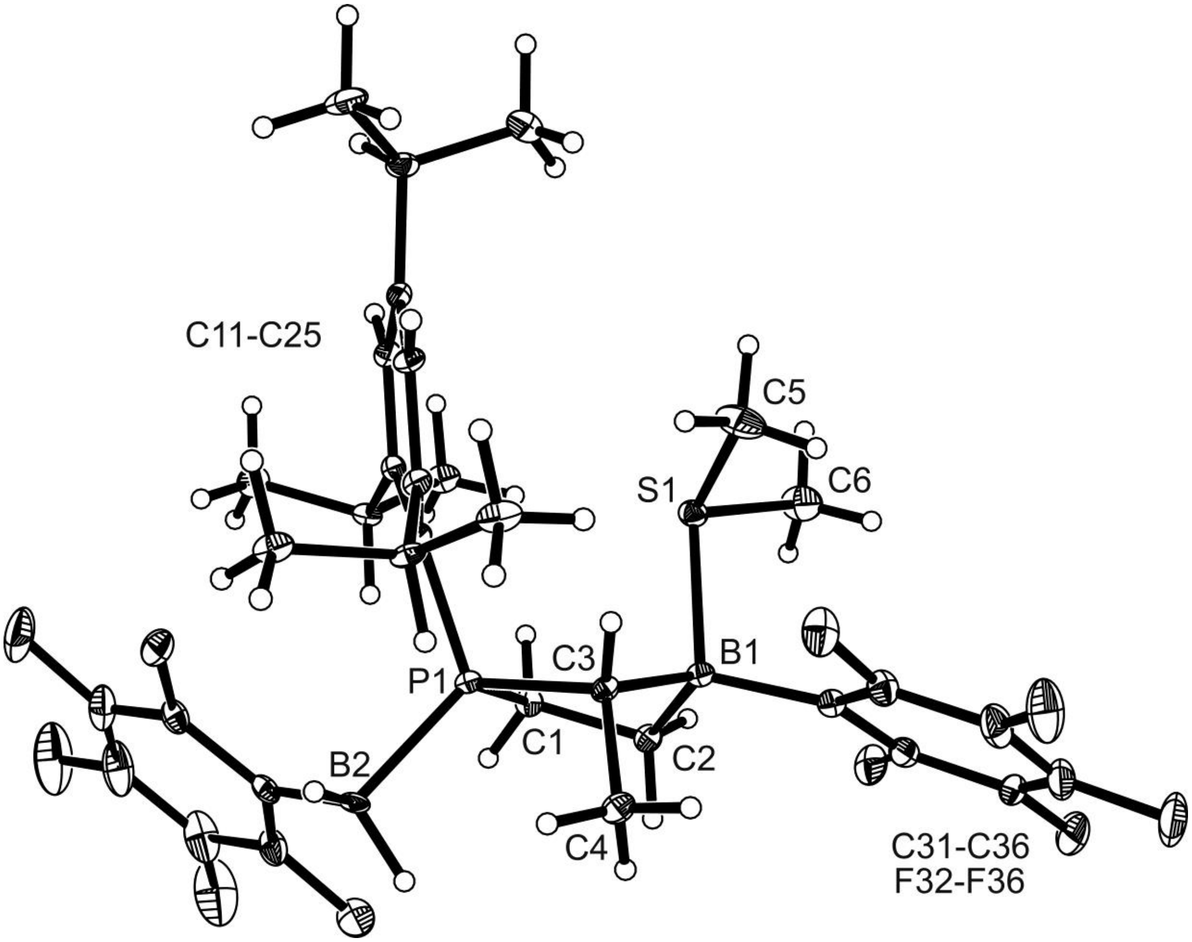
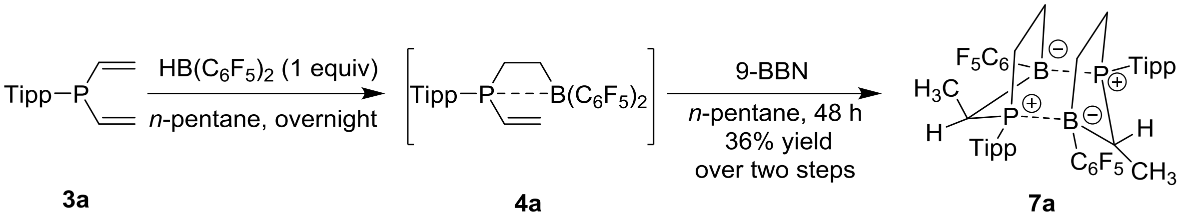


Figure S10 A view of the molecular structure of compound **6a**·$H_2B(C_6F_5)$·SMe_2.

Synthesis of compound 7a



A solution of bis(pentafluorophenyl)borane (345.9 mg, 1.0 mmol, 1.0 equiv.) in *n*-pentane (5 mL) was added to a solution of [TippP($CH=CH_2$)$_2$] (**3a**) (288.4 mg, 1.0 mmol) in *n*-pentane (5 mL) by cannula under an argon atmosphere. The reaction mixture was stirred at room temperature overnight. After filtration, 9-BBN (122.0 mg, 0.5 mmol, 0.5 equiv.) was added in portions to the filtrate.[4] Then the reaction mixture was stirred at room temperature for 48 hours. The resulting suspension was filtered and washed with cold pentane (0 °C, 3×3 mL). The obtained solid was dried *in vacuo* to give compound **7a** (165 mg, 36%) as a white solid.

Elemental analysis: calc. for $C_{50}H_{62}B_2F_{10}P_2$ (936.60 g mol^{-1}): C, 64.12; H, 6.67. **Found**: C, 64.00; H, 6.90.

Decomposition: 202 °C.

^{1}H NMR (600 MHz, 220 K, CD_2Cl_2): δ (P,B heterocycle a) = 7.06 (s, 1H, *m*-Tipp), 6.81 (s, 1H, *m*'-Tipp), [3.44 (br sept., $^3J_{H\text{-}H}$ = 6.5 Hz, 1H), 1.16, 0.26 (each d, $^3J_{H\text{-}H}$ = 6.5 Hz, each 3H)](*o*'-^{i}Pr), [2.99 (br sept., $^3J_{H\text{-}H}$ = 6.5 Hz, 1H), 1.38, 1.16 (each d, $^3J_{H\text{-}H}$ = 6.5 Hz, each 3H)](*o*-^{i}Pr), [2.79 (sept., $^3J_{H\text{-}H}$ = 6.5 Hz, 1H), 1.14 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 6H)](*p*-^{i}Pr), [2.65, 2.57](each m, each 1H, PCH_2), 2.36 (m, 1H, PCH), [1.94, 1.40](each m, 1H, BCH_2), 0.21 (dd, $^3J_{P\text{-}C}$ = 14.6 Hz, $^3J_{H\text{-}H}$ = 7.0 Hz, 3H, Me^{PCH}); δ (P,B heterocycle b) = 7.01 (s, 1H, *m*-Tipp), 6.84 (s, 1H, *m*'-Tipp), [3.56 (br sept., $^3J_{H\text{-}H}$ = 6.5 Hz, 1H), 1.31, 1.18 (each d, $^3J_{H\text{-}H}$ = 6.5 Hz, each 3H)](*o*-^{i}Pr), [2.80 (br sept., $^3J_{H\text{-}H}$ = 6.5 Hz, 1H), 1.23, 0.67 (each d, $^3J_{H\text{-}H}$ = 6.5 Hz, each 3H)](*o*'-^{i}Pr), [2.75 (sept., $^3J_{H\text{-}H}$ = 6.5 Hz, 1H), 1.12, 1.11 (each d, $^3J_{H\text{-}H}$ = 6.5 Hz, each 3H)](*p*-^{i}Pr), [2.55, 1.66](each m, each 1H, PCH_2), 2.18 (m, 1H, PCH), 2.01 (m, 3H, Me^{PCH}), [1.43, 0.54](each m, each 1H, BCH_2).

^{13}C{^{1}H} NMR (151 MHz, 220 K, CD_2Cl_2): δ (P,B heterocycle a) = 154.0 (d, $^2J_{P\text{-}C}$ = 4.9 Hz, *o*-Tipp), 152.4 (d, $^2J_{P\text{-}C}$ = 9.6 Hz, *o*'-Tipp), 150.1 (d, $^4J_{P\text{-}C}$ = 2.2 Hz, *p*-Tipp), 124.1 (d, $^3J_{P\text{-}C}$ = 7.8 Hz, *m*-Tipp), 123.0 (d, $^1J_{P\text{-}C}$ = 35.0 Hz, *i*-Tipp), 121.2 (d, $^3J_{P\text{-}C}$ = 7.8 Hz, *m*'-Tipp), [33.36, 23.15, 23.11](*p*-^{i}Pr), [33.0 (br), 25.6, 25.36](*o*-^{i}Pr), [32.9 (d, $^3J_{P\text{-}C}$ = 10.1 Hz), 25.2, 21.9](*o*'-^{i}Pr), 21.2 (br d, $^1J_{P\text{-}C}$ = 20.4 Hz, PCH), 20.5 (d, $^1J_{P\text{-}C}$ = 36.9 Hz, PCH_2), 13.2 (dd, $^2J_{P\text{-}C}$ = 12.4 Hz, *J* = 8.5 Hz, Me^{PCH}), 11.8 (br, BCH_2); δ (P,B heterocycle b) = 152.8 (d, $^2J_{P\text{-}C}$ = 11.0 Hz, *o*'-Tipp), 152.2 (d, $^2J_{P\text{-}C}$ = 5.2 Hz, *o*-Tipp), 149.8 (d, $^4J_{P\text{-}C}$ = 2.2 Hz, *p*-Tipp), 128.4 (d, $^1J_{\text{P-C}}$ = 29.9 Hz, *i*-Tipp), 122.6 (d, $^3J_{\text{P-C}}$ = 8.5 Hz, *m*'-Tipp), 122.5 (d, $^3J_{\text{P-C}}$ = 7.2 Hz, *m*-Tipp), [33.39, 23.17, 23.15](*p*-^{i}Pr), [32.5 (d, $^3J_{\text{P-C}}$ = 4.6 Hz), 25.37, 24.8](*o*'-^{i}Pr), [31.4 (br m), 24.7, 24.3](*o*-^{i}Pr), 26.6 (d, $^1J_{\text{P-C}}$ = 44.9 Hz, PCH_2), 23.6 (br, PCH), 15.5 (br, BCH_2), 14.5 (br m, Me$^{\text{PCH}}$), [C_6F_5 not listed].

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = 36.0 ($\nu_{1/2}$ ~ 80 Hz), 29.6 ($\nu_{1/2}$ ~ 100 Hz).

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = −6.6 ($\nu_{1/2}$ ~ 210 Hz), −7.8 ($\nu_{1/2}$ ~ 250 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = −126.6 (m, *o*), −131.2 (m, *o'*), −160.0 (t, $^3J_{\text{F-F}}$ = 20.0 Hz, *p*), −164.9 (m, *m*'), −165.8 (m, *m*)(each 1F, C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 5.8, 4.9]; −128.2 (m, 2F, *o*), −160.6 (t, $^3J_{\text{F-F}}$ = 20.0 Hz, 1F, *p*), −165.2 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 4.6].

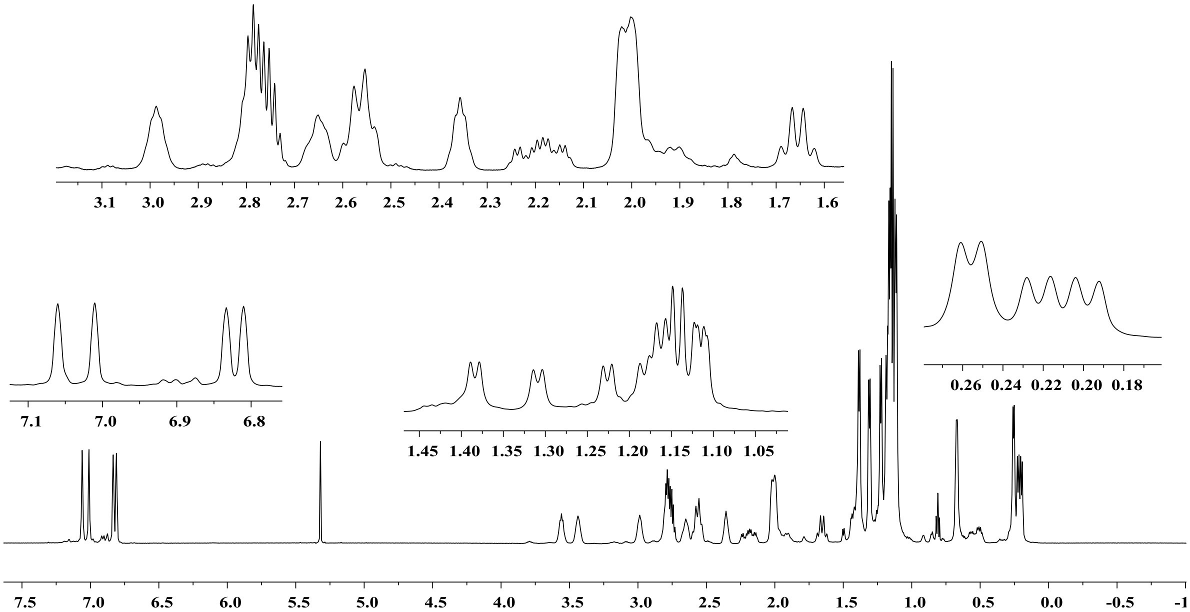


Figure S11 ^{1}H NMR (600 MHz, 220 K, CD_2Cl_2) spectrum of compound **7a**.

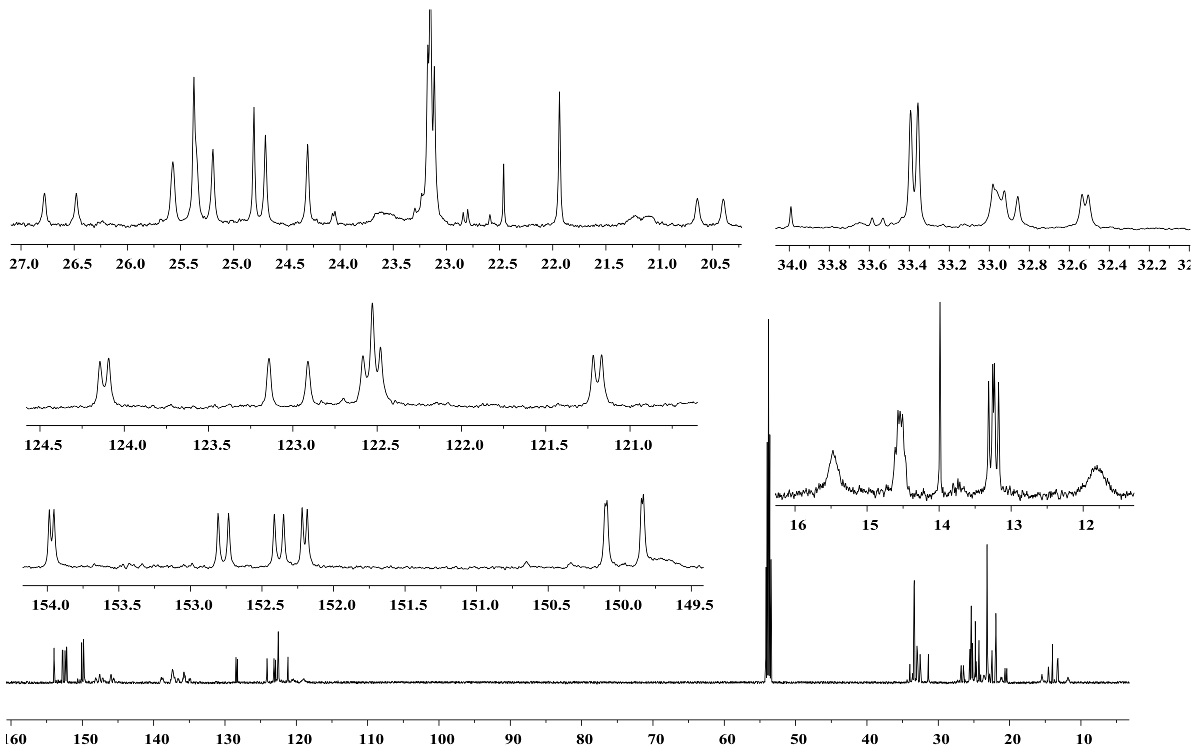


Figure S12 $^{13}C\{^{1}H\}$ NMR (151 MHz, 220 K, CD_2Cl_2) spectrum of compound **7a**.

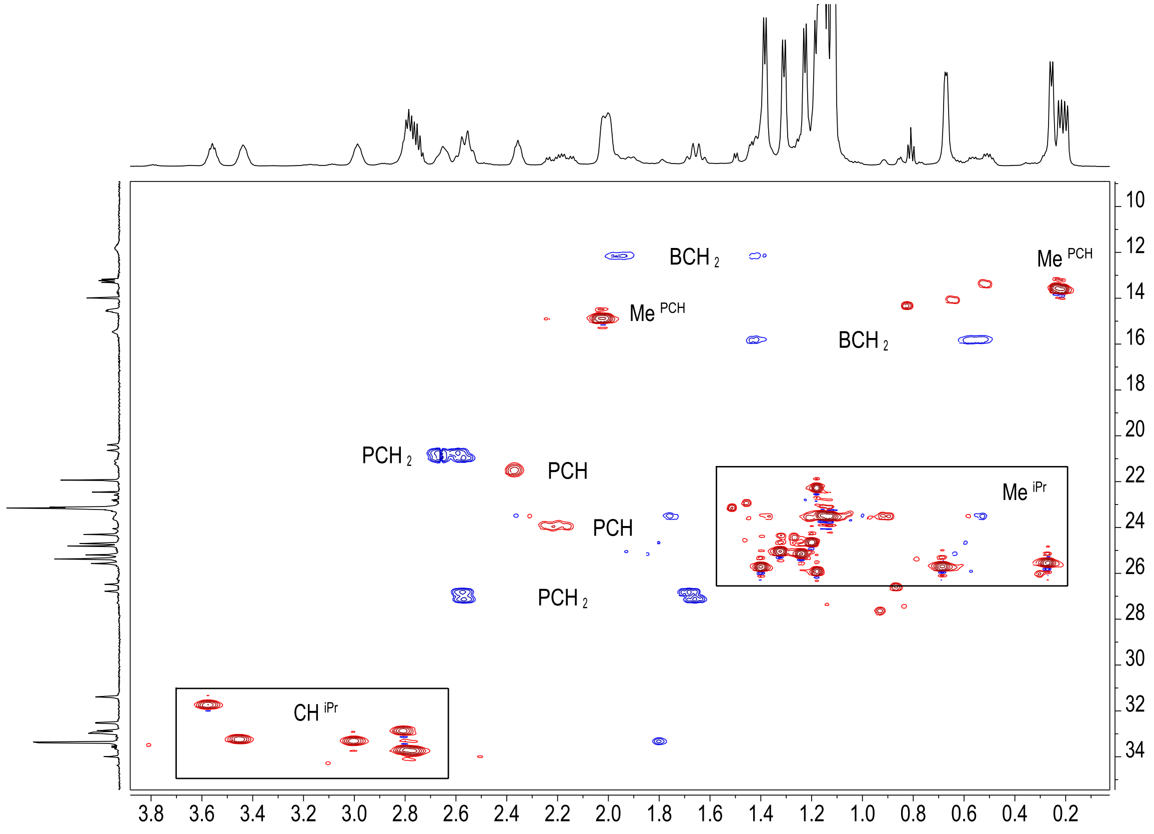


Figure S13 ^{1}H, ^{13}C gHSQC (600 MHz/151 MHz, 220 K, CD_2Cl_2) spectrum of compound **7a**.

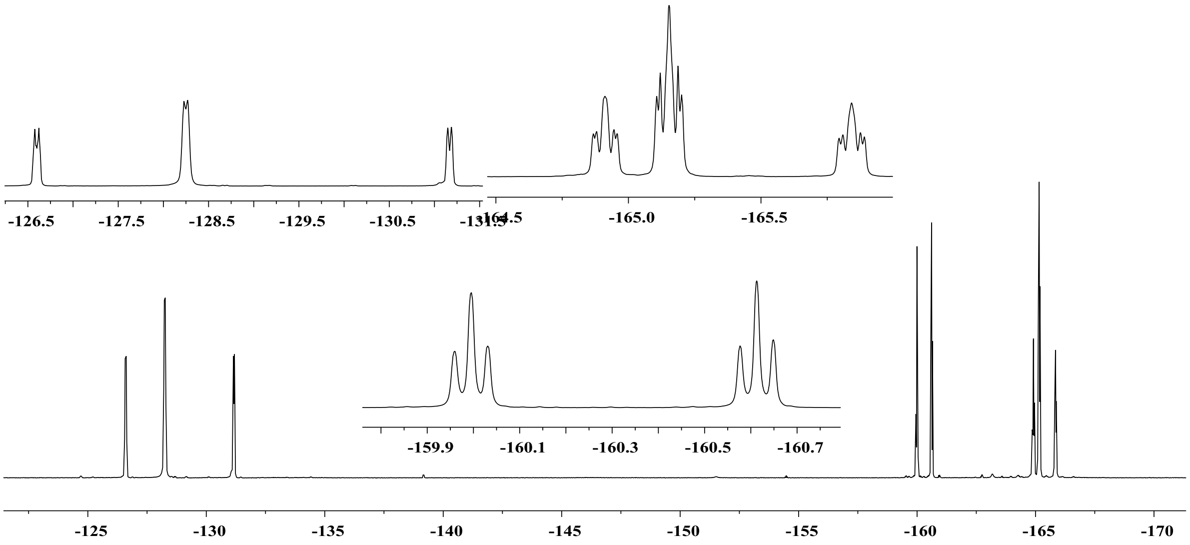


Figure S14 ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **7a**.

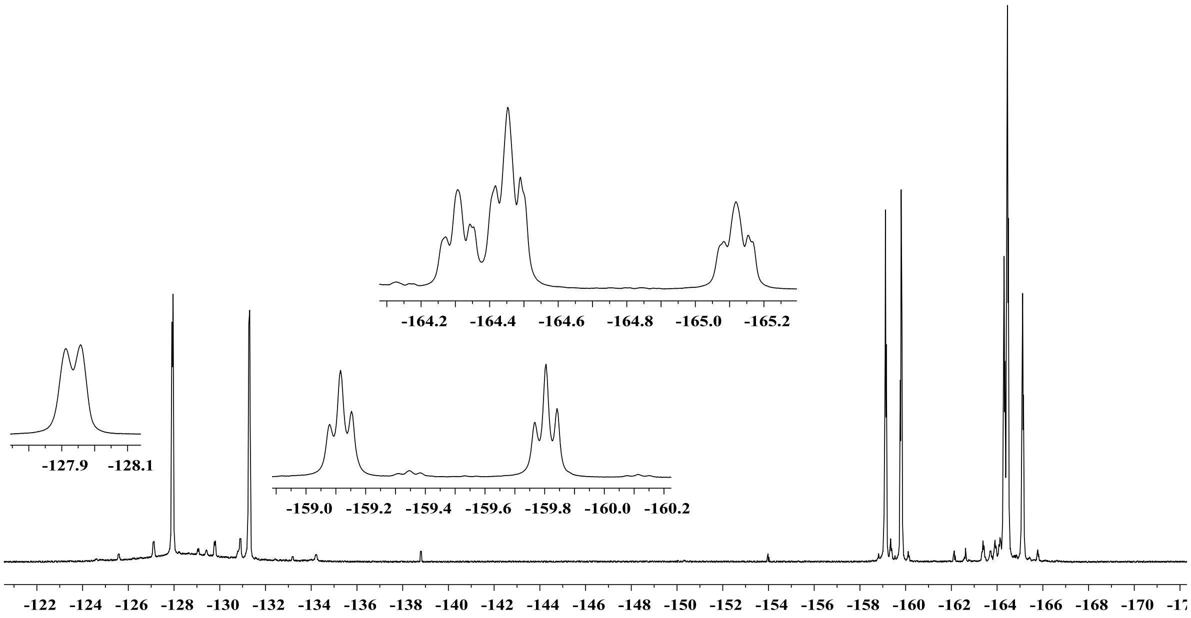


Figure S15 ^{19}F NMR (564 MHz, 220 K, CD_2Cl_2) spectrum of compound **7a**.

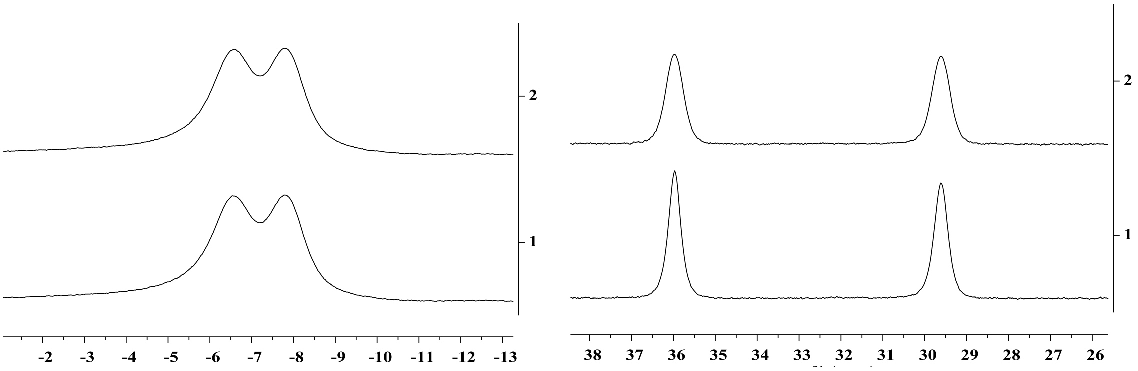


Figure S16 $^{11}B\{^1H\}$ (left,1), ^{11}B (left, 2) NMR (192 MHz, 299 K, CD_2Cl_2) and $^{31}P\{^1H\}$(right, 1), ^{31}P (right, 2) NMR (243 MHz, 299 K, CD_2Cl_2,) spectra of compound **7a**.

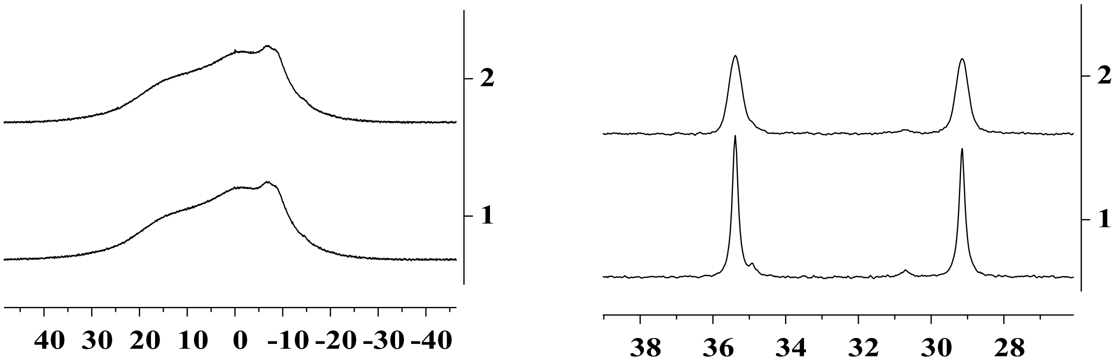


Figure S17 $^{11}B\{^1H\}$ (left,1), ^{11}B (left, 2) NMR (192 MHz, 220 K, CD_2Cl_2) and $^{31}P\{^1H\}$(right, 1), ^{31}P (right, 2) NMR (243 MHz, 220 K, CD_2Cl_2,) spectra of compound **7a**.

Crystals of compound **7a** suitable for the X-ray crystal structure analysis were obtained from a solution of compound **7a** in a mixture of solvents (*n*-pentane: toluene ca. 3:1) at −35 °C.

X-ray crystal structure analysis of compound 7a (erk8526): formula $C_{50}H_{62}B_2F_{10}P_2$, M = 936.56, colourless crystal, 0.16 x 0.06 x 0.02 mm, a = 22.6598(4), b = 11.9386(2), c = 35.4316(7) Å, V = 9585.2(3) Å^3, ρ_{calc} = 1.298 gcm^{-3}, μ = 0.164 mm^{-1}, empirical absorption correction ($0.974 \leq T \leq 0.996$), Z = 8, orthorhombic, space group *P*bca (No. 61), λ = 0.71073 Å, T = 173(2) K, ω and φ scans, 50041 reflections collected ($\pm h$, $\pm k$, $\pm l$), 8402 independent (R_{int} = 0.141) and 5289 observed reflections [I>2σ(I)], 642 refined parameters, R = 0.070, wR^2 = 0.153, max. (min.) residual electron density 0.28 (-0.34) e.Å^{-3}, the hydrogen atoms were calculated and refined as riding atoms.

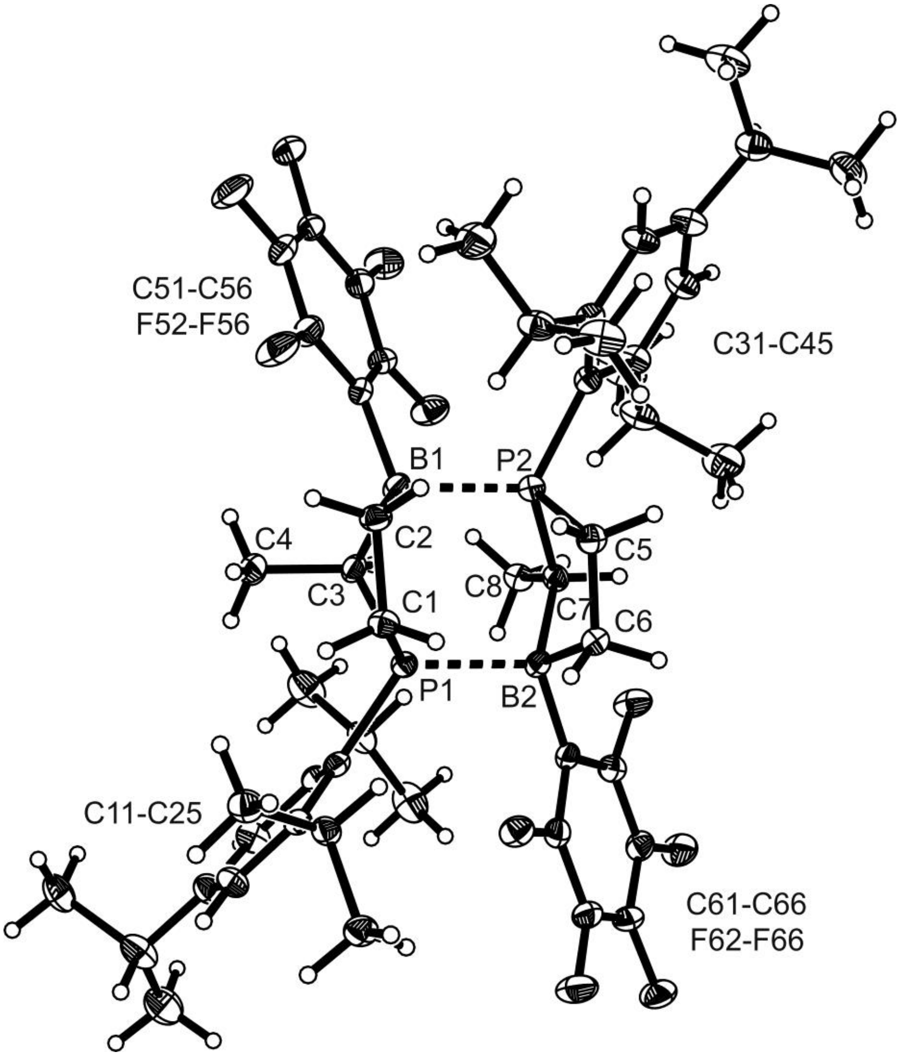
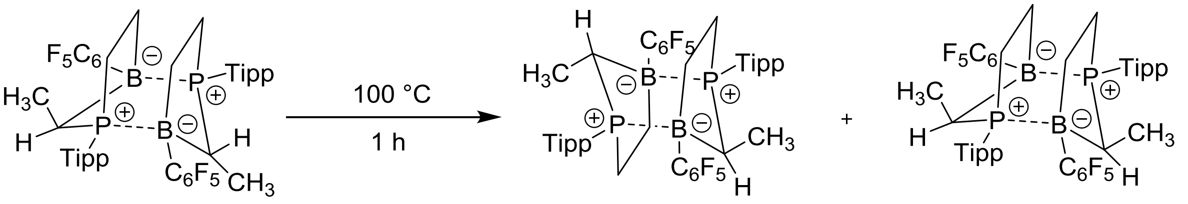


Figure S18 A view of the molecular structure of compound **7a**.

Heating of compound 7a: generation of compounds 8a and 9a



7a **8a** **9a**

1^{st} Experiment:

1^{st} Step: In-situ reaction (NMR scale): compound **7a** (46.8 mg, 0.05 mmol) was dissolved in C_7D_8 (0.5 mL) at room temperature. The NMR tube was sealed and heated at 100 °C for 1 h. Then the solution was characterized by NMR experiments. 1D (^{1}H, ^{31}P, ^{19}F, ^{11}B) NMR spectra showed a mixture of the dimers **8a** and **9a** [ratio ca. 1:1 (^{1}H NMR)].

2^{nd} Step: After cooling the obtained reaction mixture to room temperature, a white powder was isolated by filtration, which was dried *in vacuo* to finally give a white solid (31.2 mg, 0.034 mmol, 67%)

Elemental analysis: calc. for $C_{50}H_{62}B_2F_{10}P_2$ (936.60 g mol^{-1}): C, 64.12; H, 6.67. Found: C, 63.93; H, 6.96.

Melting point: 339 °C.

NMR data obtained from a suspension of the obtained white solid in CD_2Cl_2 revealed the presence of a mixture of compounds **8a** : **9a** [ratio ca. 1:3 (^{1}H NMR)].

[The NMR resonances of compound **9a** were identified by comparison of the respective spectra of the mixture with those obtained from the crystals of compound **9a** (see page S25ff, *2^{nd} Experiment*, *2^{st} Step*).]

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) **9a** (major): δ = 6.98 (m, 1H, *m*-Tipp), 6.95 (m, 1H, *m*'-Tipp), [3.21 (sept, $^3J_{\text{H-H}}$ = 6.5 Hz, 1H), 1.52 (d, $^3J_{\text{H-H}}$ = 6.5 Hz, 3H), 1.00 (dd, $^3J_{\text{H-H}}$ = 6.5 Hz, *J* = 3.5 Hz, 3H)](*o*-^{i}Pr), [2.87 (sept, $^3J_{\text{H-H}}$ = 6.6 Hz, 1H), 1.36, 0.95 (each d, $^3J_{\text{H-H}}$ = 6.6 Hz, each 3H)](*o*'-^{i}Pr), [2.88, 2.10](each m, each 1H, PCH_2), [2.81 (sept, $^3J_{\text{H-H}}$ = 7.0 Hz, 1H), 1.19 (d, $^3J_{\text{H-H}}$ = 7.0 Hz, 6H)](*p*-^{i}Pr), 2.28 (m, 1H, PCH), [1.74, 1.26](each m, each 1H, BCH_2), 0.59 (dd, $^3J_{\text{P-H}}$ = 14.0 Hz, $^3J_{\text{H-H}}$ = 7.2 Hz, 3H, Me$^{\text{PCH}}$); **8a** (minor): δ = 7.10 (m, 1H, *m*-Tipp), 6.92 (m, 1H, *m*'-Tipp), [3.87 (sept, $^3J_{\text{H-H}}$ = 6.6 Hz, 1H), 1.57, 1.21 (each d, $^3J_{\text{H-H}}$ = 6.6 Hz, each 3H)](*o*-^{i}Pr), [3.21, 2.24](each m, each 1H, PCH_2), 2.90 (m, 1H, PCH), [2.83 (sept, $^3J_{\text{H-H}}$ = 6.0 Hz, 1H), 1.203, 1.201 (each d, $^3J_{\text{H-H}}$ = 6.0 Hz, each 3H)](*p*-^{i}Pr), [2.58 (sept, $^3J_{\text{H-H}}$ = 6.5 Hz, 1H), 1.30, 0.40 (each d, $^3J_{\text{H-H}}$ = 6.5 Hz, each 3H)](*o*'-^{i}Pr), [1.98, 1.50](each m, each 1H, BCH_2), 0.70 (dd, $^3J_{\text{P-H}}$ = 15.8 Hz, $^3J_{\text{H-H}}$ = 8.7 Hz, 3H, Me$^{\text{PCH}}$).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2) **9a** (major): δ = 154.8 (d, $^2J_{\text{P-C}}$ = 5.9 Hz, *o'*-Tipp), 154.1 (d, $^2J_{\text{P-C}}$ = 8.5 Hz, *o*-Tipp), 151.4 (d, $^4J_{\text{P-C}}$ = 2.5 Hz, *p*-Tipp), 123.5 (d, $^1J_{\text{P-C}}$

= 35.6 Hz, *i*-Tipp), 123.3 (d, $^{3}J_{\text{P-C}}$ = 7.4 Hz, *m*'-Tipp), 122.6 (d, $^{3}J_{\text{P-C}}$ = 8.0 Hz, *m*-Tipp), [34.5 (d, $^{3}J_{\text{P-C}}$ = 5.8 Hz), 27.9 (d, *J* = 4.5 Hz), 23.5](*o*-^{i}Pr), [34.2, 26.7, 24.9](*o*'-^{i}Pr), [34.2, 23.7](*p*-^{i}Pr), 23.5 (d, $^{1}J_{\text{P-C}}$ = 48.1 Hz, PCH_2), 18.5 (br, PCH), 14.5 (br, BCH_2), 13.6 (br m, Me^{PCH}); **8a** (minor): δ = 154.50 (d, $^{2}J_{\text{P-C}}$ = 9.0 Hz, *o*-Tipp), 154.48 (d, $^{2}J_{\text{P-C}}$ = 6.2 Hz, *o*'-Tipp), 151.6 (d, $^{4}J_{\text{P-C}}$ = 2.1 Hz, *p*-Tipp), 123.5 (d, $^{3}J_{\text{P-C}}$ = 7.7 Hz, *m*'-Tipp), 122.8 (d, $^{3}J_{\text{P-C}}$ = 8.6 Hz, *m*-Tipp), 122.3 (d, $^{1}J_{\text{P-C}}$ = 34.3 Hz, *i*-Tipp), [33.8 (d, $^{3}J_{\text{P-C}}$ = 3.4 Hz), 27.6 (d, *J* = 8.3 Hz), 23.62 (d, *J* = 2.8 Hz)](*o*-^{i}Pr), [34.23 (d, $^{3}J_{\text{P-C}}$ = 3.4 Hz), 26.2, 24.9](*o*'-^{i}Pr), [34.2, 23.6](*p*-^{i}Pr), 26.0 (d, $^{1}J_{\text{P-C}}$ = 40.5 Hz, PCH_2), 26.1 (br, PCH), 15.6 (br, BCH_2), 14.3 (br m, Me^{PCH}), [C_6F_5 not listed].

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2) **9a** (major): δ = 35.7 ($\nu_{1/2}$ ~ 130 Hz), **8a** (minor): *δ* = 31.5 ($\nu_{1/2}$ ~ 150 Hz).

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2) **9a** (major): δ = −11.1 ($\nu_{1/2}$ ~ 210 Hz), **8a** (minor): *δ* = −9.7 ($\nu_{1/2}$ ~ 140 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) **9a** (major): δ = [−127.0, −129.2](each m, each 1F, *o*-C_6F_5), −159.9 (m, 1F, *p*-C_6F_5), [−164.4, −164.6](each m, each 1F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 4.5, 4.7]; **8a** (minor): [−127.8, −130.9](each m, each 1F, *o*-C_6F_5), −160.0 (m, 1F, *p*-C_6F_5), [−164.2, −164.8](each m, each 1F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 4.2, 4.8].

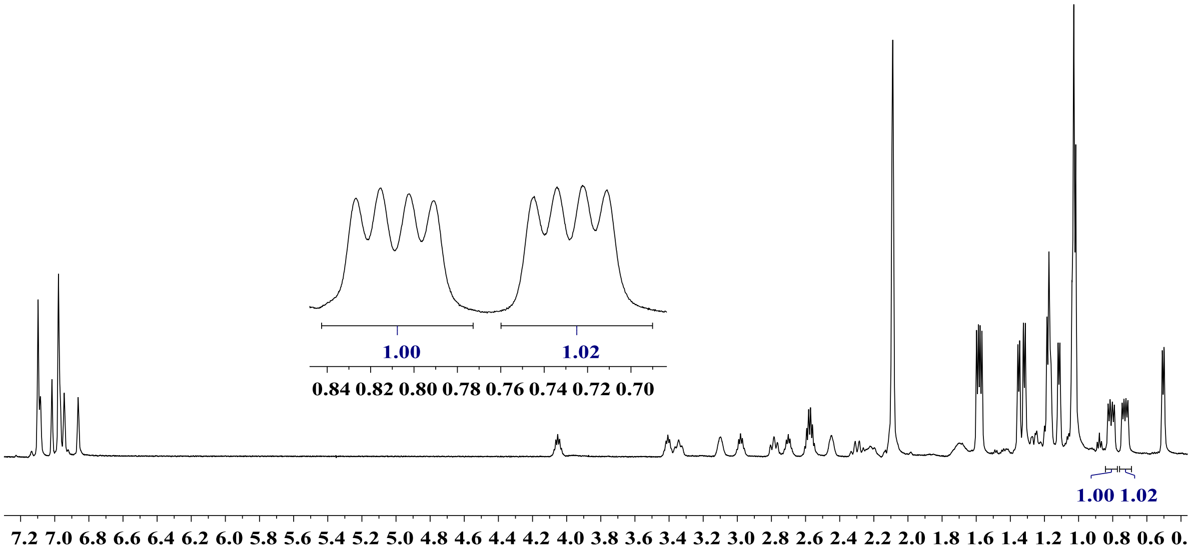


Figure S19 ^{1}H NMR (600 MHz, 299 K, toluene-d_8) spectrum of the mixture of compounds **8a** and **9a** after heating compound **7a** at 100 °C for 1 h (see 1st Step).

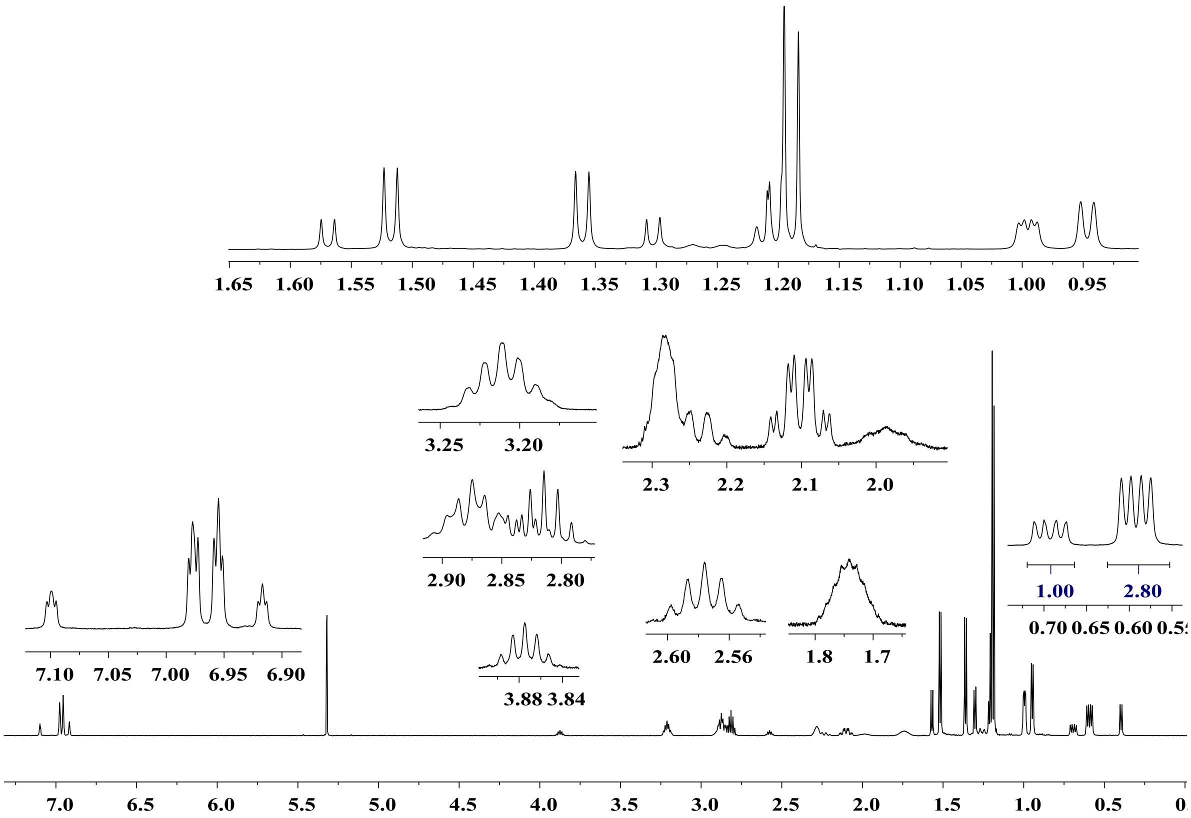


Figure S20 ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of the obtained white solid (see 2nd Step).

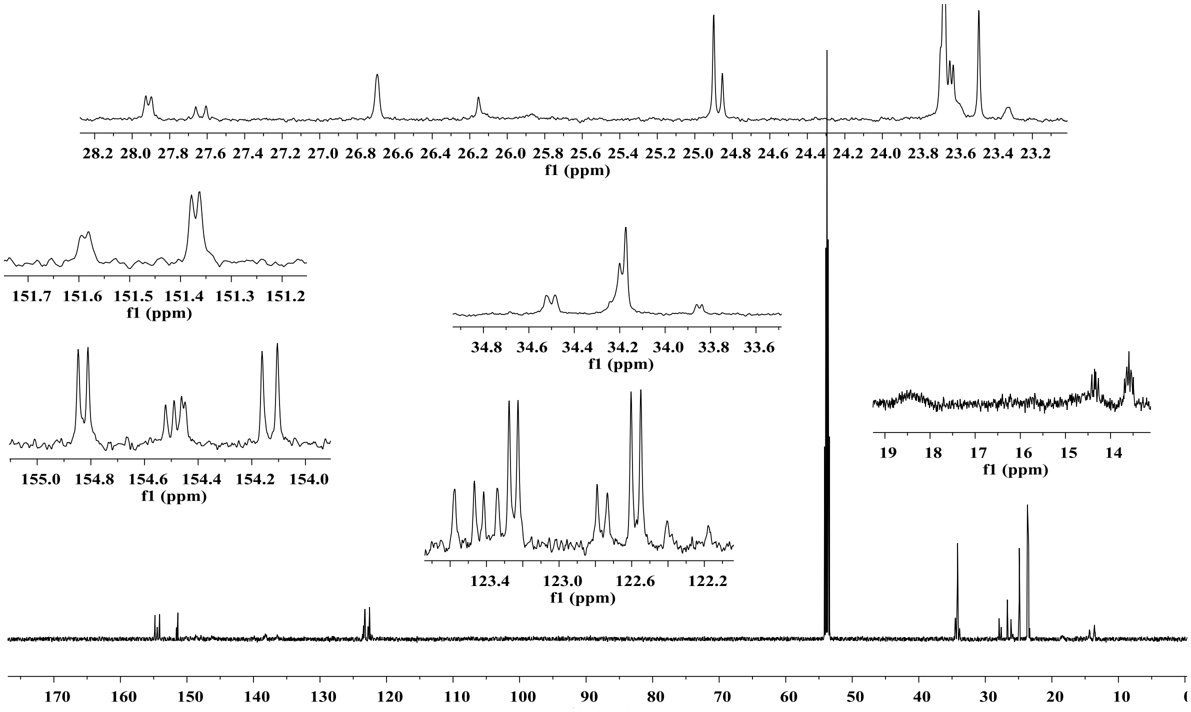


Figure S21 $^{13}C\{^{1}H\}$NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of the obtained white solid (see 2nd Step).

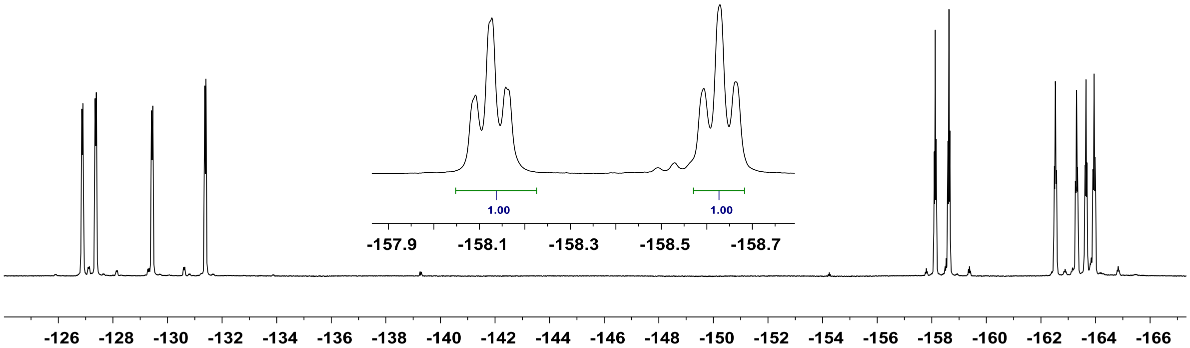


Figure S22 ^{19}F NMR (top) (564 MHz, 299 K, toluene-*d*$_8$) spectrum of the mixture of compounds **8a** and **9a** after heating compound **7a** at 100 °C for 1 h (see 1st Step).

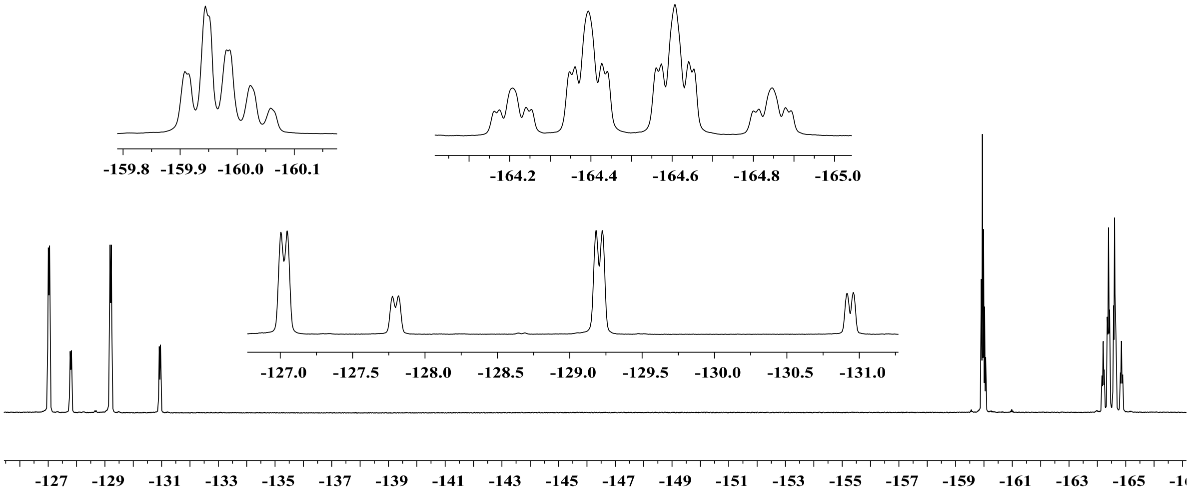


Figure S23 ^{19}F NMR (bottom) (564 MHz, 299 K, CD$_2$Cl$_2$) spectrum of the obtained white solid (see 2nd Step).

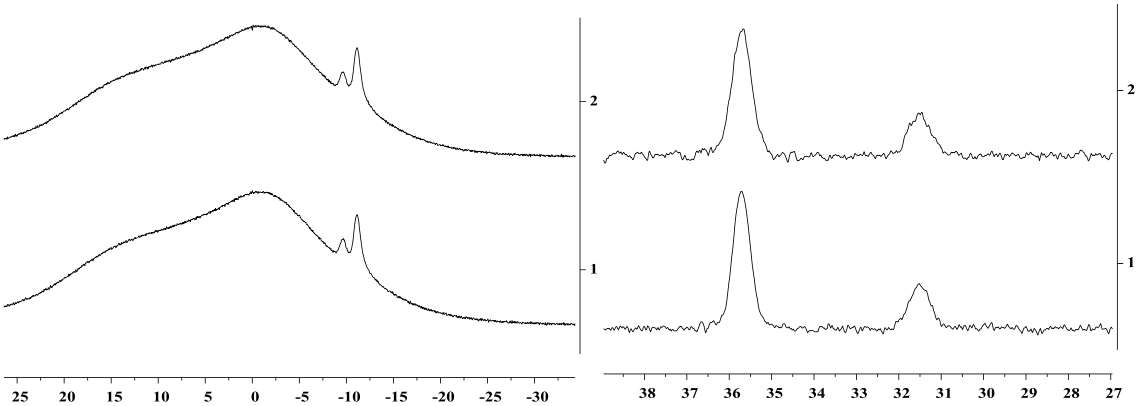


Figure S24 ^{11}B{^{1}H} (left, 1), ^{11}B (left, 2) NMR (192 MHz, 299 K, CD$_2$Cl$_2$) and ^{31}P{^{1}H} (right, 1), ^{31}P (right, 2) NMR (243 MHz, 299 K, CD$_2$Cl$_2$) spectra of the obtained white solid (see 2nd step).

2nd Experiment:

1st Step: Compound **7a** (187.2 mg, 0.20 mmol) was dissolved in C_7H_8 (5 mL) at room temperature. The solution was heated at 100 °C for 1 h. Then the solution was carefully cooled to room temperature without stirring. The formed crystalline material was collected. The obtained crystals were suitable for the X-ray crystal structure analysis of compound **8a**.

X-ray crystal structure analysis of compound 8a (erk8594): A colorless plate-like specimen of $C_{50}H_{62}B_2F_{10}P_2 \cdot 2\times C_7H_8$, approximate dimensions 0.040 mm x 0.100 mm x 0.180 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 997 frames were collected. The total exposure time was 19.83 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 13797 reflections to a maximum θ angle of 66.67° (0.84 Å resolution), of which 4986 were independent (average redundancy 2.767, completeness = 96.3%, R_{int} = 3.61%, R_{sig} = 4.11%) and 4328 (86.80%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 10.8445(3) Å, $\underline{b}$ = 11.9200(3) Å, $\underline{c}$ = 13.1484(3) Å, α = 86.0520(10)°, β = 70.2850(10)°, γ = 66.5020(10)°, volume = 1463.09(7) Å^3, are based upon the refinement of the XYZ-centroids of 6826 reflections above 20 σ(I) with 7.162° < 2θ < 133.2°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.828. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8030 and 0.9510. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 1 for the formula unit, $C_{50}H_{62}B_2F_{10}P_2 \cdot 2\times C_7H_8$. The final anisotropic full-matrix least-squares refinement on F^2 with 381 variables converged at R1 = 3.80%, for the observed data and wR2 = 10.22% for all data. The goodness-of-fit was 1.044. The largest peak in the final difference electron density synthesis was 0.366 $e^-/Å^3$ and the largest hole was -0.285 $e^-/Å^3$ with an RMS deviation of 0.048 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.272 g/cm^3 and F(000), 592 e^-.

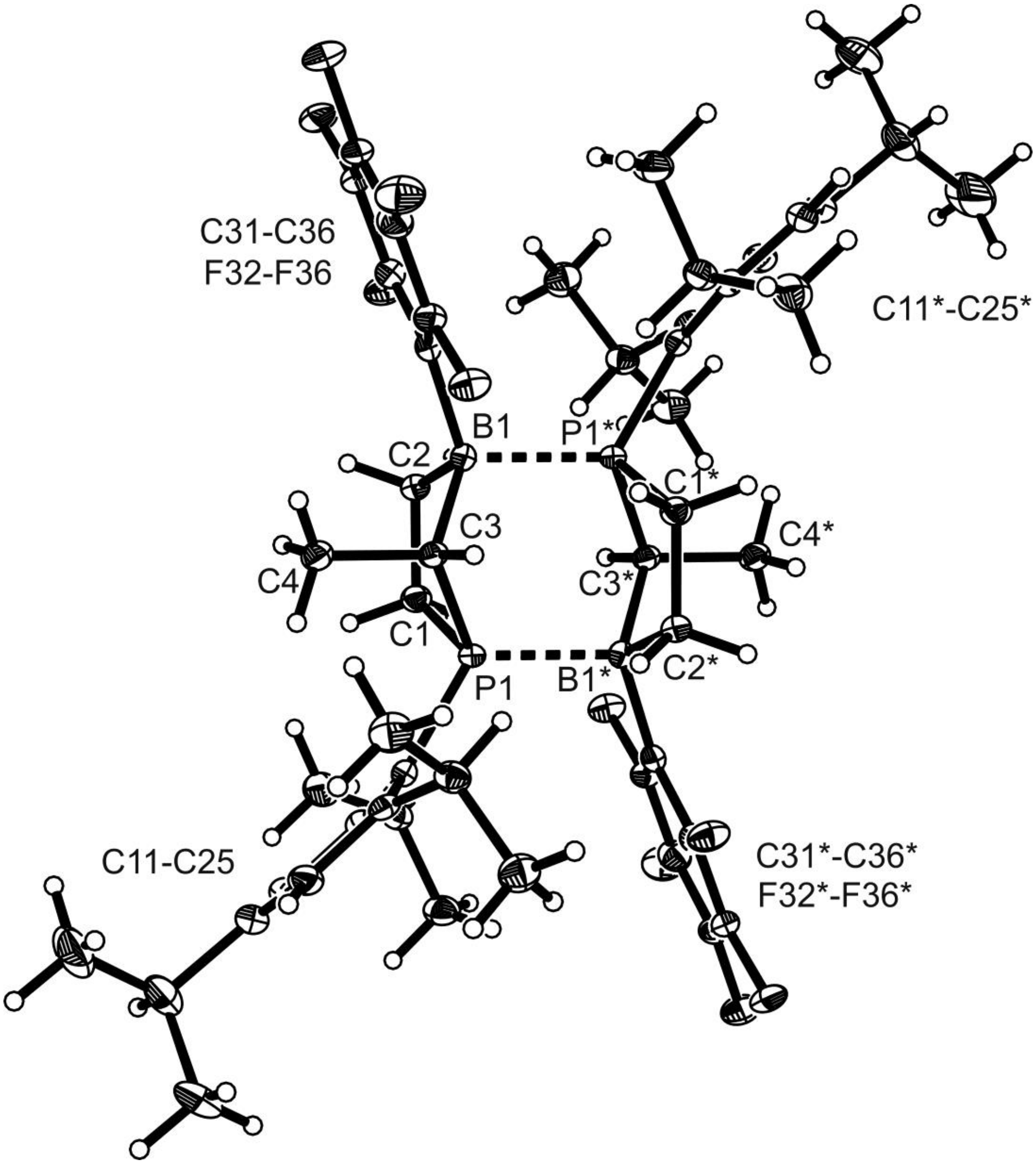


Figure S25 A view of the molecular structure of compound **8a**.

2nd Step: After storing the mother liquid at room temperature for ca. 2 days, crystals suitable for the X-ray crystal structure analysis of compound **9a** were obtained.

X-ray crystal structure analysis of compound 9a (erk8916): formula $C_{50}H_{62}B_2F_{10}P_2 \cdot 2 \times C_7H_8$, M = 1120.82, colourless crystal, 0.22 x 0.14 x 0.06 mm, a = 24.3500(3), b = 15.0736(3), c = 17.1713(3) Å, β = 113.773(1)°, V = 5767.8(2) Å^3, ρ_{calc} =

1.291 gcm^{-3}, μ = 0.148 mm^{-1}, empirical absorption correction (0.968 ≤ T ≤ 0.991), Z = 4, monoclinic, space group $C2/c$ (No. 15), λ = 0.71073 Å, T = 173(2) K, ω and φ scans, 15985 reflections collected ($\pm h$, $\pm k$, $\pm l$), 4974 independent (R_{int} = 0.037) and 4266 observed reflections [I>2σ(I)], 360 refined parameters, R = 0.048, wR^2 = 0.122, max. (min.) residual electron density 0.61 (-0.26) e.Å^{-3}, the hydrogen atoms were calculated and refined as riding atoms.

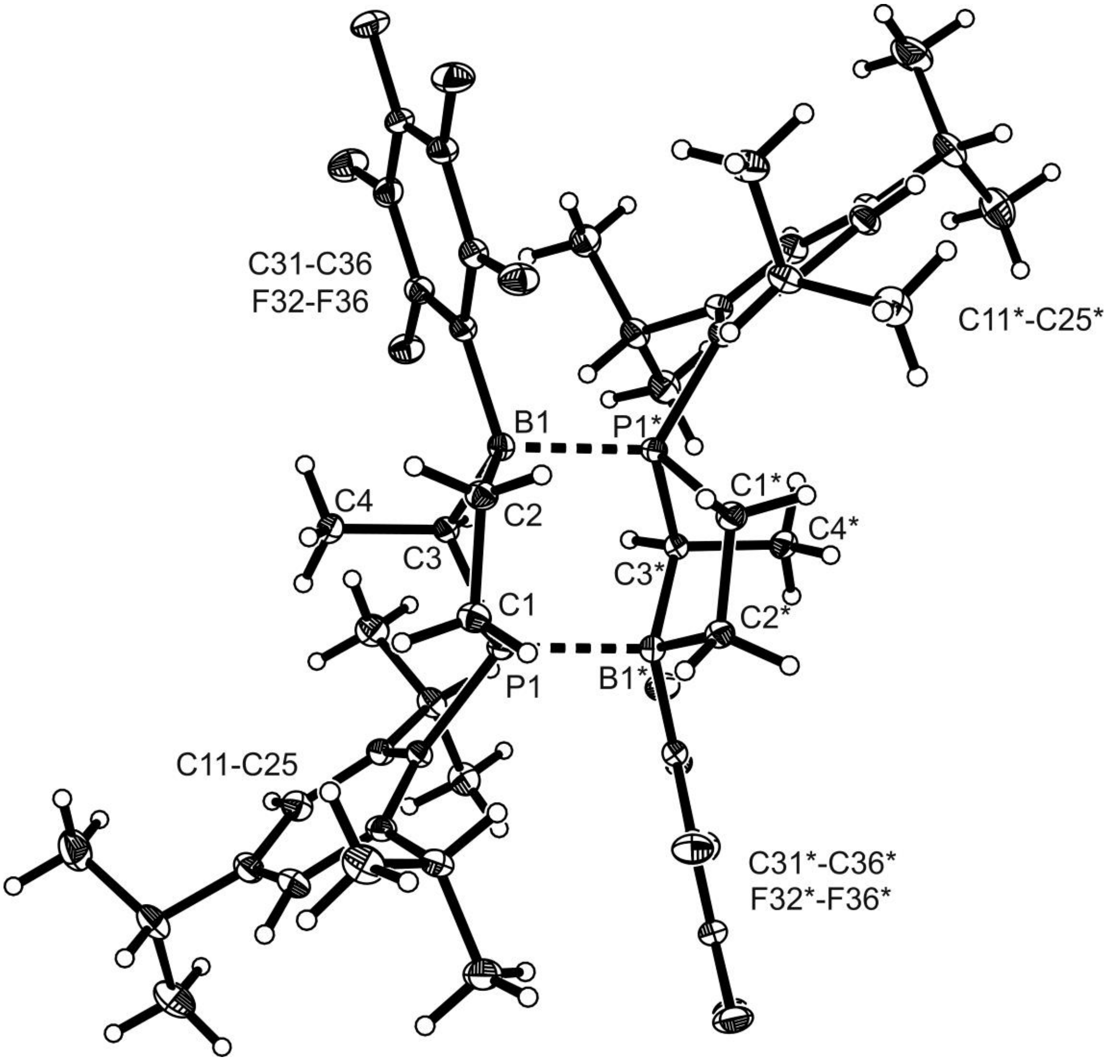


Figure S26 A view of the molecular structure of compound **9a**.

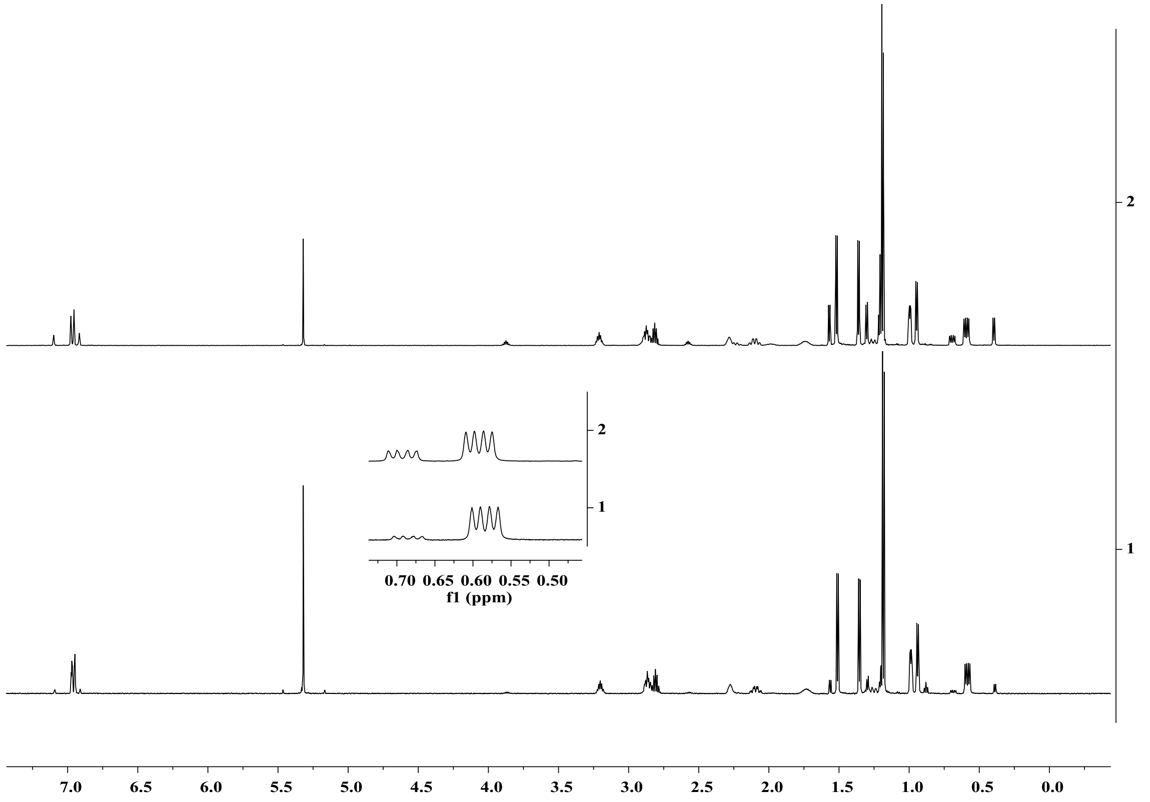


Figure S27 ^{1}H NMR (600 MHz, 299 K, CD$_2$Cl$_2$) spectrum of (1) crystals of compound **9a** (see *2nd Experiment*, *2st Step*) and (2) of the obtained white solid (see *1st Experiment*, *2st Step*).

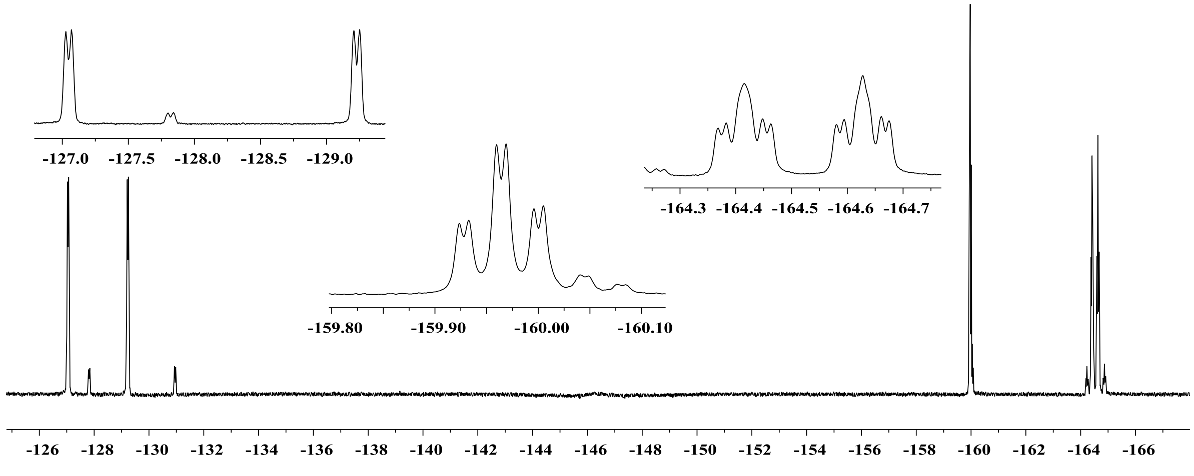
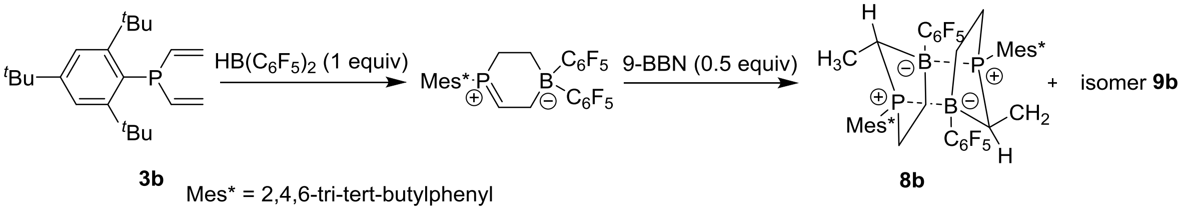


Figure S28 ^{19}F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectrum of crystals of compound **9a** (see *2nd Experiment*, *2st Step*).

Synthesis of compounds 8b and 9b



A solution of bis(pentafluorophenyl)borane (345.9 mg, 1.0 mmol, 1.0 equiv.) in *n*-pentane (10 mL) was added to a pentane solution (5 mL) of 2,4,6-tri-tert-butylphenyl)divinylphosphane [Mes*P(CH=CH$_2$)$_2$] (**3b**, 330.5 mg, 1.0 mmol) by cannula under an argon atmosphere. The reaction mixture was stirred at room temperature overnight. The resulting precipitate was collected by filtration, washed with pentane (3×3 mL) and dried *in vacuo*. After the obtained solid was dissolved in dichloromethane, 9-BBN (122.0 mg, 0.5 mmol, 0.5 equiv.) was added in portions. The reaction mixture was stirred at room temperature for 48 hours. Then all volatiles were removed *in vacuo* and the resulting solid was washed with *n*-pentane (3×3 mL) to finally give a white solid (357.3 mg, 70%).

Elemental analysis: calc. for $C_{56}H_{74}B_2F_{10}P_2$ (1020.76 g mol^{-1}): C, 65.89; H, 7.31 Found: C, C, 65.33; H, 7.08.

Decomposition: 220 °C.

The NMR data of a suspension of the obtained white solid in toluene-d_8 showed a mixture of two main compounds [tentatively assigned as major (**9b**) : minor (**8b**) and traces of **6b** (ratio ca. 63 : 33 : 4, ^{19}F NMR)], but the respective solid state NMR spectra show only compound **8b** (see solid state NMR, page S73ff).

^{1}H NMR (600 MHz, 299 K, toluene-d_8) (major): δ = [7.23, 7.19](each m, each 1H, *m*-Mes*), [3.31, 2.29](each m, each 1H, PCH$_2$), 2.92 (br, 1H, PCH), [2.40, 1.64](each br m, each 1H, BCH$_2$), [1.55, 1.16, 1.03](each s, each 9H, ^{t}Bu), 0.06 (3H, Me^{PCH}); (minor): δ = [7.27, 7.23](each m, each 1H, *m*-Mes*), [2.66, 1.65, 1.49, 1.24](each m, each 1H, CH$_2$), 2.57 (br, 1H, PCH), [1.51, 1.29, 1.19](each s, each 9H, ^{t}Bu), 0.04 (3H, Me^{PCH}).

^{19}F NMR (564 MHz, 299 K, toluene-d_8) (major): δ = [−123.1, −126.0](each m, each 1F, *o*-C$_6$F$_5$), −158.5 (t, $^3J_{F\text{-}F}$ = 20.8 Hz, 1F, *p*-C$_6$F$_5$), [−162.9, −165.0](each m, each 1F, *m*-C$_6$F$_5$) [$\Delta\delta^{19}F_{m,p}$ = 4.4, 6.5]; (minor): δ = [−119.9, −120.5](each m, *o*-C$_6$F$_5$), −158.0 (t, $^3J_{F\text{-}F}$ = 20.9 Hz, *p*-C$_6$F$_5$), [−164.2, −164.8](each m, each 1F, *m*-C$_6$F$_5$)[$\Delta\delta^{19}F_{m,p}$ = 6.2, 6.8].

^{31}P{^{1}H} NMR (243 MHz, 299 K, toluene-d_8): δ = 50.8 ($\nu_{1/2}$ ~ 30 Hz, minor), 50.3 ($\nu_{1/2}$ ~ 40 Hz, major).

^{11}B{^{1}H} NMR (192 MHz, 299 K, toluene-d_8): δ = −2.5 ($\nu_{1/2}$ ~ 500 Hz).

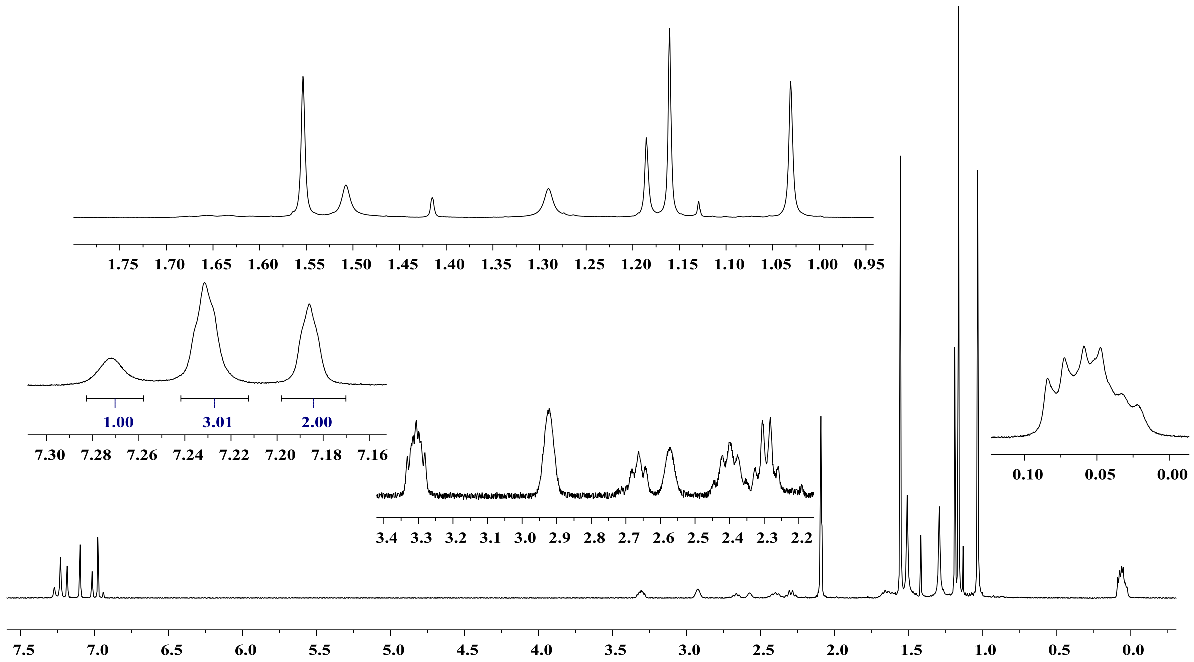


Figure S29 ^{1}H NMR (600 MHz, 299 K, toluene-d_8) spectrum of a suspension of the obtained white solid.

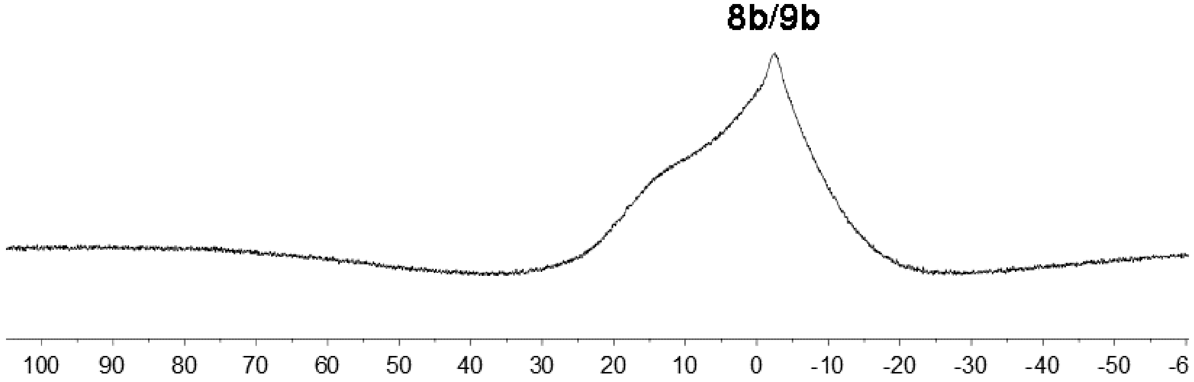


Figure S30 ^{1}B{^{1}H} NMR (192 MHz, 299 K, toluene-d_8) spectrum of a suspension of the obtained white solid.

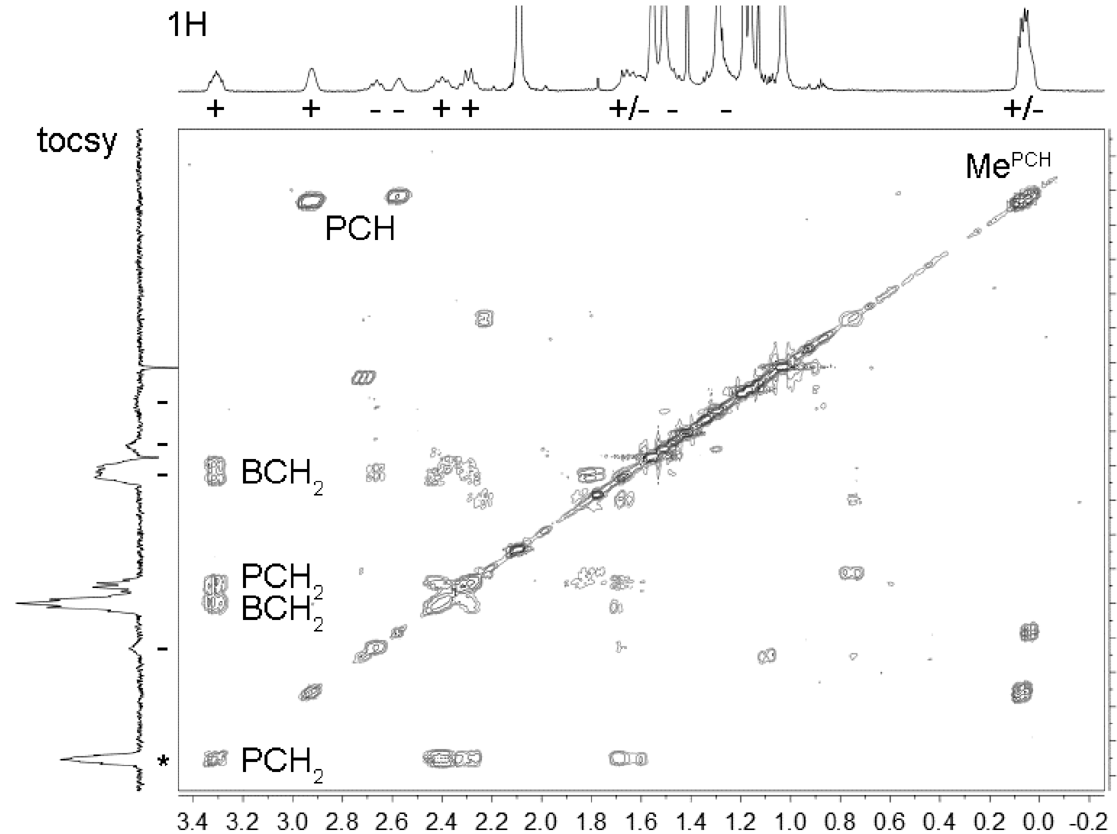


Figure S31 ^{1}H,^{1}H gcosy (600 MHz, 299 K, toluene-d_8) spectrum of a suspension of the obtained white solid. (+) Major and (-) minor component. Projections: (f1) ^{1}H and (f2) ^{1}H{^{1}H} tocsy (600 MHz, 299 K, toluene-d_8) spectra [* δ^1H_{irr} = 3.31 (PCH$_2$, major)].

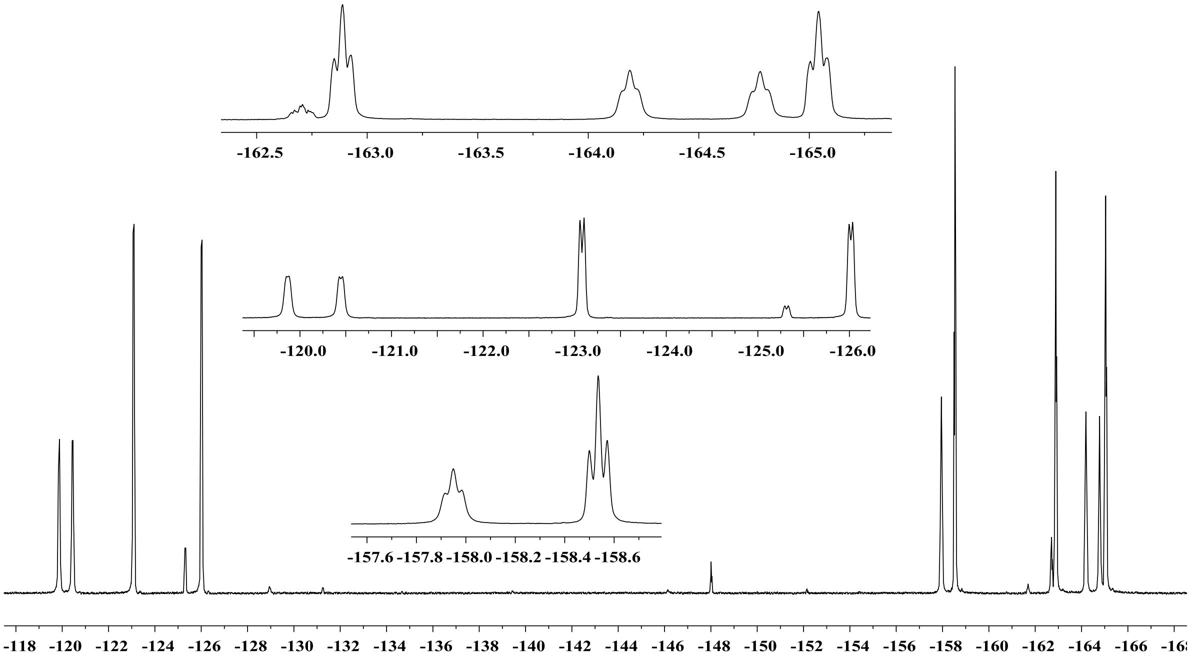


Figure S32 ^{19}F NMR (564 MHz, 299 K, toluene-d_8) spectrum of a suspension of the obtained white solid.

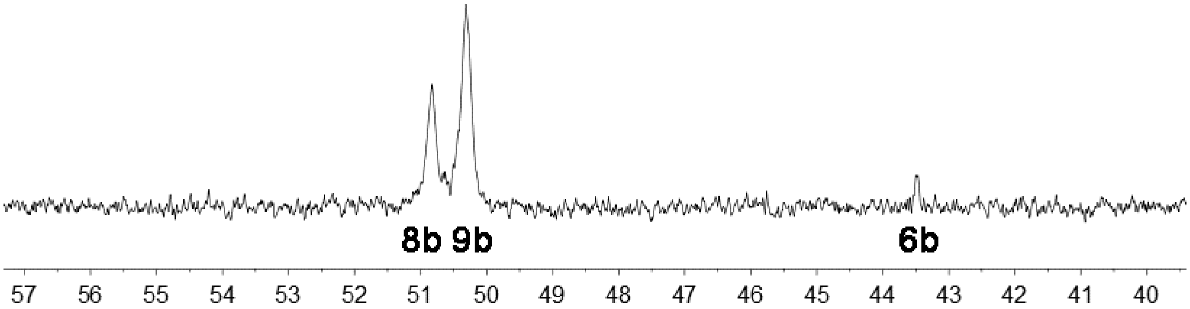


Figure S33 $^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, toluene-d_8) spectra of a suspension the obtained white solid.

2nd Experiment: Crystals of compound **8b** suitable for the X-ray crystal structure analysis were obtained from a solution of compound **4c** (33.8 mg) and 9-BBN (6.1 mg) in a mixture of solvents (ca. 5mL, dichloromethane : toluene ca. 1:4) at room temperature.

X-ray crystal structure analysis of compound 8b (erk8928): A prism-like specimen of $C_{56}H_{74}B_2F_{10}P_2$, approximate dimensions 0.060 mm x 0.148 mm x 0.250 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 856 frames were collected. The total exposure time was 22.57 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 13412 reflections to a maximum θ angle of 68.55° (0.83 Å resolution), of which 4634 were independent (average redundancy 2.894, completeness = 95.6%, R_{int} = 4.52%, R_{sig} = 4.98%) and 3917 (84.53%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 10.6253(5) Å, $\underline{b}$ = 10.6747(5) Å, $\underline{c}$ = 12.3972(6) Å, α = 103.882(2)°, β = 97.692(2)°, γ = 100.679(2)°, volume = 1317.76(11) $Å^3$, are based upon the refinement of the XYZ-centroids of 9306 reflections above 20 σ(I) with $8.620° < 2\theta < 137.1°$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.867. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7280 and 0.9230. The final anisotropic full-matrix least-squares refinement on F^2 with 326 variables converged at R1 = 6.43%, for the observed data and wR2 = 17.09% for all data. The goodness-of-fit was 1.048. The largest peak in the final difference electron density synthesis was 0.935 $e^-/Å^3$ and the largest hole was -0.366 $e^-/Å^3$ with an RMS deviation of 0.073 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.286 g/cm^3 and F(000), 540 e^-.

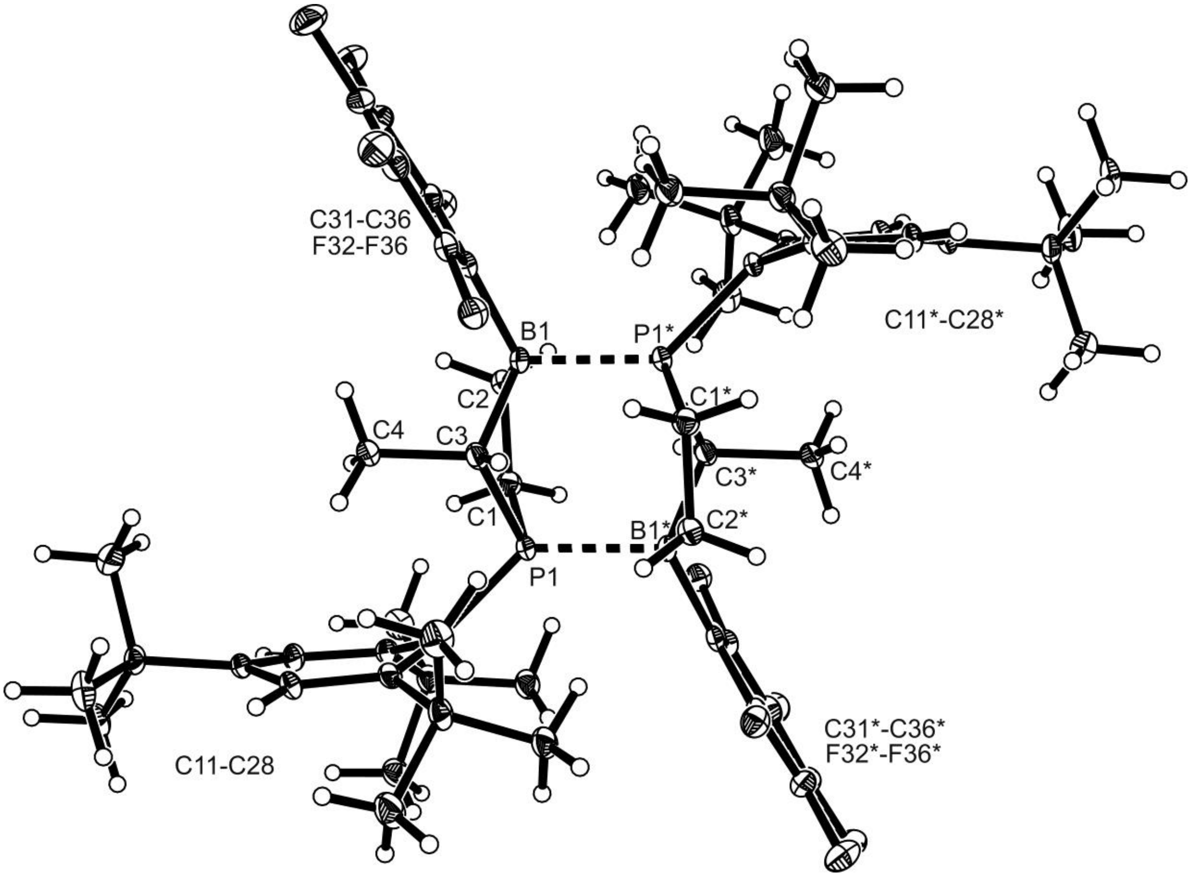
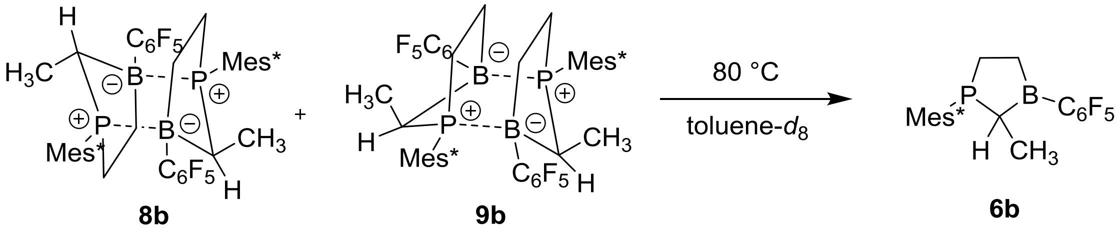


Figure S 34 A view of the molecular structure of compound **8b**.

Heating of dimers 8b/9b: generation of compound 6b



In-situ reaction (NMR scale): After the obtained solid (**8b**/**9b**) (17.4 mg, 0.016 mmol) was suspended in C_7D_8 (0.5 mL) at room temperature, the used NMR tube was sealed and subsequently heated to 80°C by direct monitoring with NMR spectroscopy [**8b**/**9b** : **6b** ca. 1 : 2.5 (^{31}P NMR)].

^{1}H NMR (500 MHz, 353 K, toluene-d_8) δ = 6.98 (m, 2H, *m*-Mes*), 2.66 (br m, 1H, PCH), [2.24 (br dd, $^{2}J_{\text{P-H}}$ = 14.5 Hz, $^{3}J_{\text{H-H}}$ = 8.0 Hz, 1H), 1.82 (m, 1H)](PCH$_2$), [1.68, 0.87](each m, each 1H, BCH$_2$), 1.42 (s, 18H, *o*-^{t}Bu), 1.14 (s, 9H, *p*-^{t}Bu), 1.07 (dd, $^{3}J_{\text{P-H}}$ = 17.1, $^{3}J_{\text{H-H}}$ = 7.9 Hz, 3H, Me$^{\text{PCH}}$).

^{13}C{^{1}H} NMR (126 MHz, 353 K, toluene-d_8) δ = 157.3 (d, $^{2}J_{\text{P-C}}$ = 4.2 Hz, *o*-Mes*), 148.1 (*p*-Mes*), 136.0 (d, $^{1}J_{\text{P-C}}$ = 51.3 Hz, *i*-Mes*), 121.6 (*m*-Mes*), [40.0 (d, $^{3}J_{\text{P-C}}$ = 2.1 Hz), 33.8 (d, J = 8.1 Hz)](*o*-^{t}Bu), 39.1 (br, PCH), [34.3, 31.3](*p*-^{t}Bu), 28.9 (d, $^{1}J_{\text{P-C}}$ = 18.7 Hz, PCH$_2$), 27.9 (br, BCH$_2$), 10.0 (d, $^{3}J_{\text{P-C}}$ = 28.3 Hz, Me$^{\text{PCH}}$), [C$_6$F$_5$ not listed].

^{19}F NMR (470 MHz, 353 K, toluene-d_8): δ = −125.6 (m, 2F, *o*-C$_6$F$_5$), −148.6 (t, $^{3}J_{\text{F-F}}$ = 20.1 Hz, 1F, *p*-C$_6$F$_5$), −162.7 (m, 2F, *m*-C$_6$F$_5$)[Δδ^{19}F$_{m,p}$ = 14.1].

^{31}P{^{1}H} NMR (202 MHz, 353 K, toluene-d_8): δ = 50.9 ($\nu_{1/2}$ ~ 180 Hz, **8b**/**9b**), 42.0 ($\nu_{1/2}$ ~ 20 Hz, **6b**).

^{11}B{^{1}H} NMR (160 MHz, 353 K, toluene-d_8): δ = 79.0 ($\nu_{1/2}$ ~ 500 Hz, **6b**), -2.0 ($\nu_{1/2}$ ~ 200 Hz, **8b**/**9b**).

^{10}B{^{1}H} NMR (54 MHz, 353 K, toluene-d_8): δ = 79.0 ($\nu_{1/2}$ ~ 400 Hz, **6b**), -2.0 ($\nu_{1/2}$ ~ 300 Hz, **8b**/**9b**).

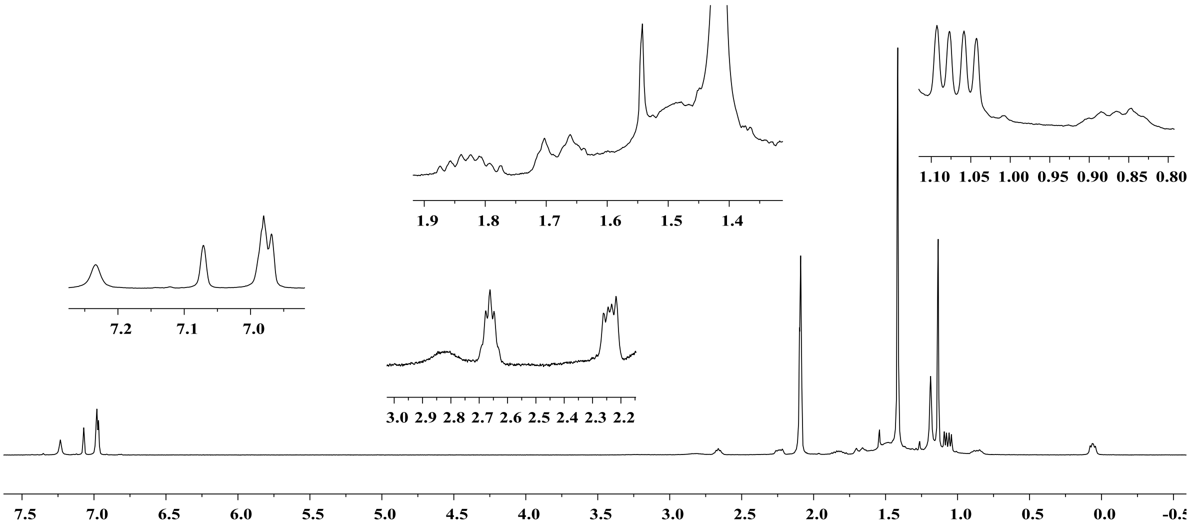


Figure S35 ^{1}H NMR (500 MHz, 353 K, toluene-d_8) spectrum of compound **6b**.

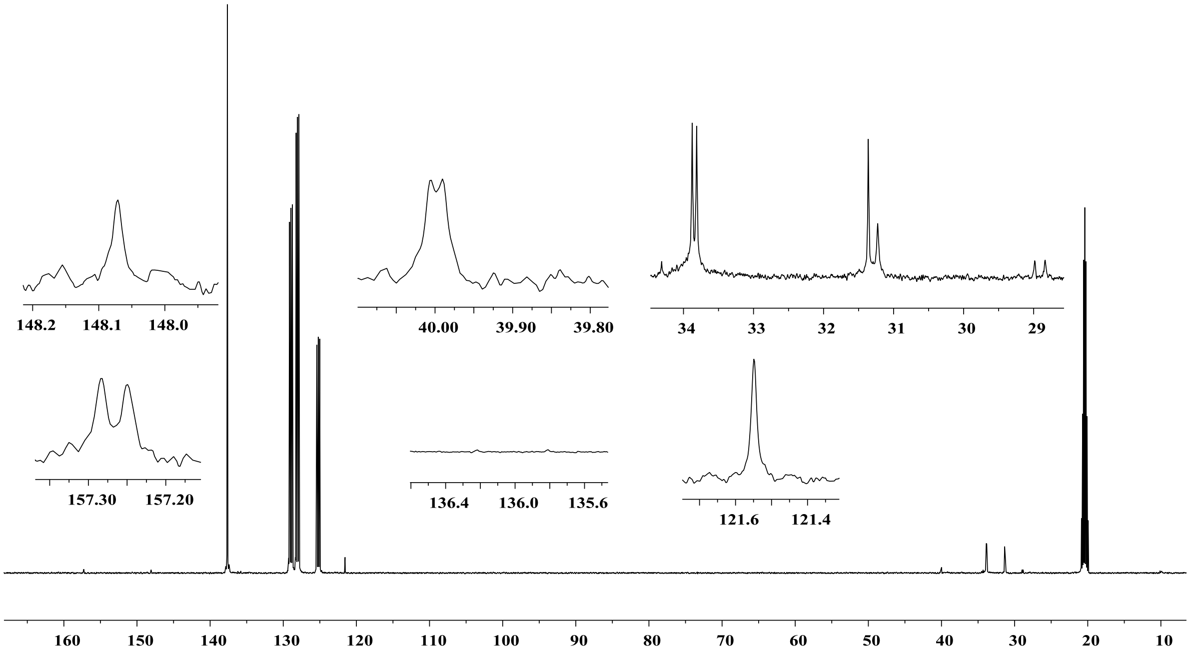


Figure S36 ^{13}C{^{1}H} NMR (126 MHz, 353 K, toluene-d_8) spectrum of compound **6b**.

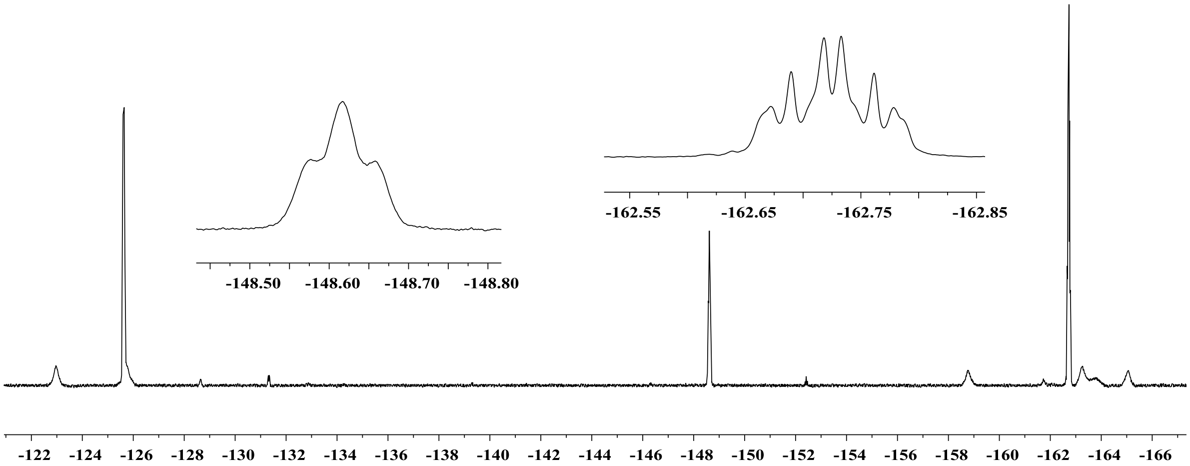


Figure S37 ^{19}F NMR (470 MHz, 353 K, toluene-d_8) NMR spectrum of compound **6b**.

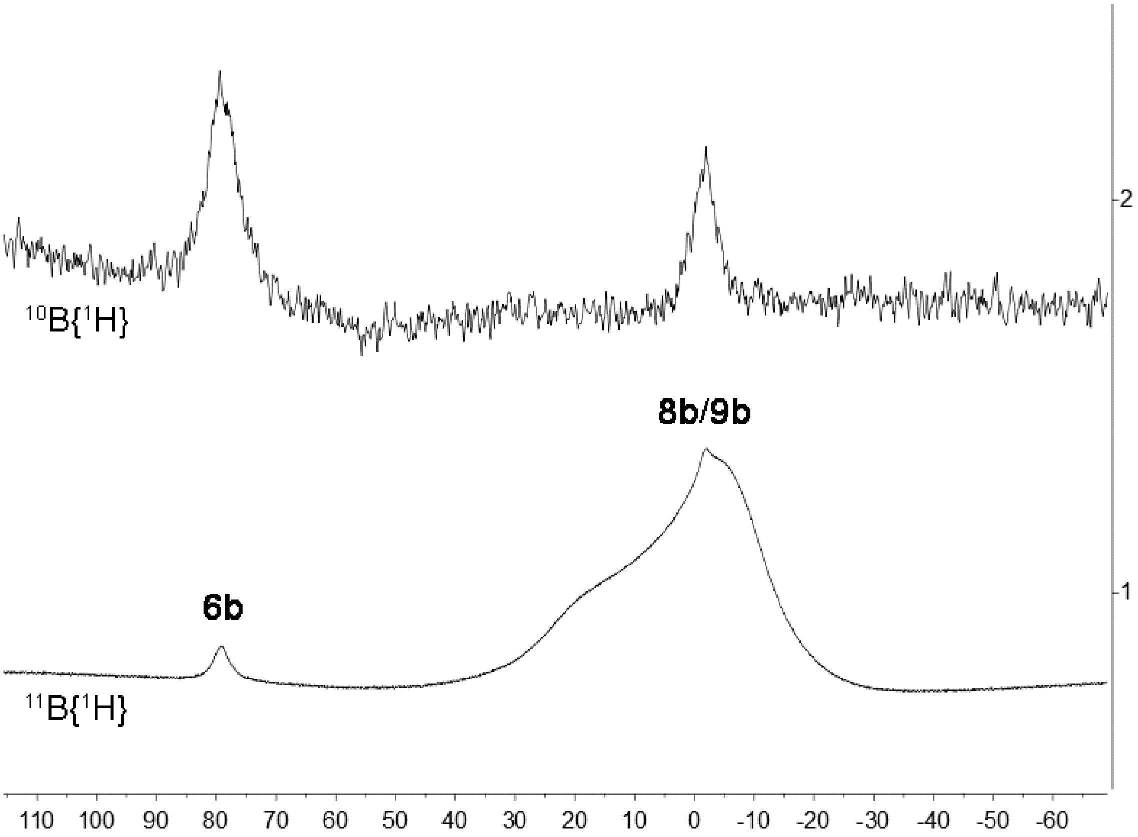


Figure S38 (1) ^{11}B{^{1}H} NMR (160 MHz) and (2) ^{10}B{^{1}H} NMR (54 MHz, 353 K, toluene-d_8) spectra of compound **6b**.

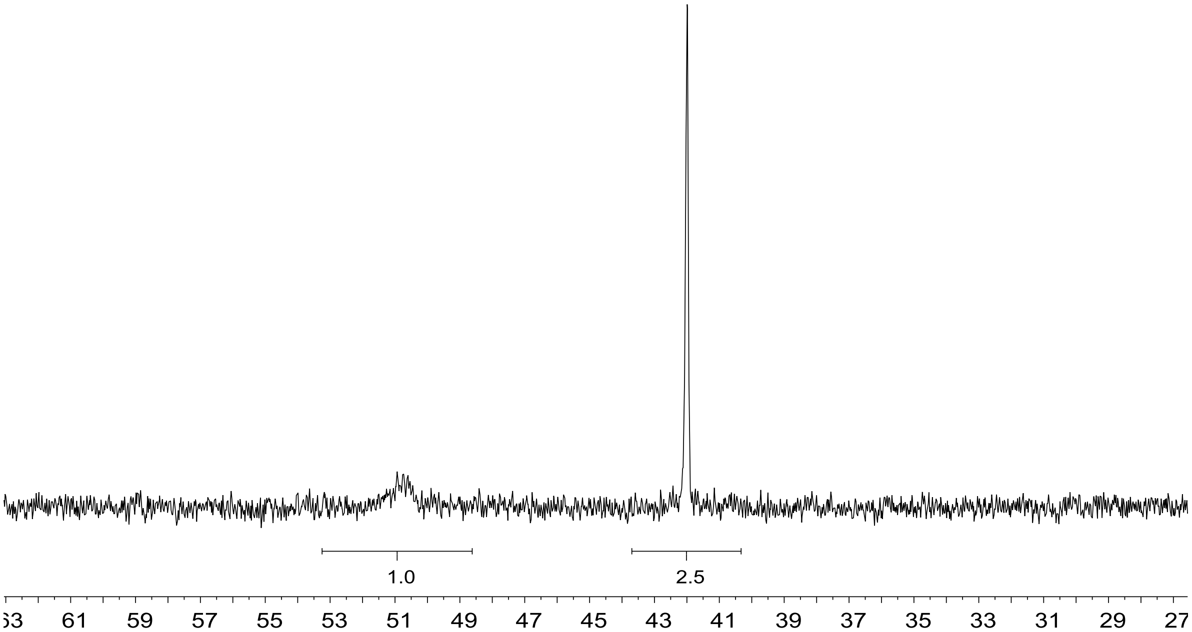
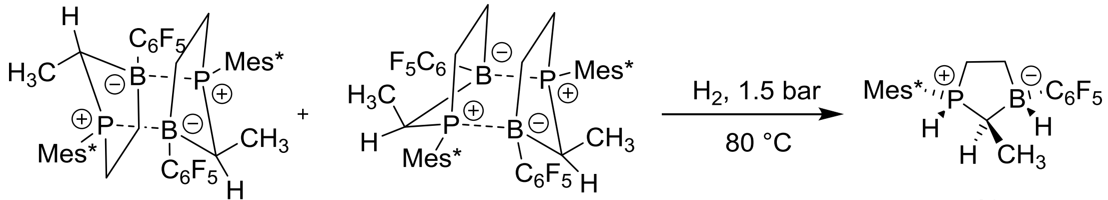


Figure S39 ^{31}P{^{1}H} NMR (202 MHz, 353 K, toluene-d_8) spectra of compound **6b**.

Reaction of dimers 8b/9b with dihydrogen: synthesis of compound 10b



8b **9b** **10b**

1st Experiment (in-situ reaction, NMR scale): After the obtained solid (**8b**/**9b**) (30.7 mg, 0.03 mmol) was suspended in C_7D_8 (0.6 mL) at room temperature the mixture was transferred into a J. Young valve NMR tube, which was subsequently degassed. Then the mixture was exposed to an H_2 atmosphere (1.5 bar) and heated to 80 °C for 48 h.

^{1}H NMR (600 MHz, 263 K, toluene-d_8): δ = 7.40 (s, 1H, *m*-Mes*), 7.36 (s, 1H, *m*’-Mes*), 6.24 (dm, $^1J_{\text{P-H}}$ = 448.8 Hz, 1H, PH), [2.54, 2.18](each m, each 1H, PCH_2), 2.49 (br, 1H, BH), 2.43 (m, 1H, PCH), [1.53, 1.39](each m, each 1H, BCH_2), 1.30 (s, 9H, *o*-^{t}Bu), 1.19 (s, 9H, *o’*-^{t}Bu), 1.11 (s, 9H, *p*-^{t}Bu), 1.00 (dd, $^3J_{\text{P-H}}$ = 23.6 Hz, $^3J_{\text{H-H}}$ = 17.5 Hz, 3H, Me$^{\text{PCH}}$).

^{13}C{^{1}H} NMR (151 MHz, 263 K, toluene-d_8): δ = 158.7 (d, $^2J_{\text{P-C}}$ = 4.3 Hz, *o’*-Mes*), 158.5 (d, $^2J_{\text{P-C}}$ = 8.8 Hz, *o*-Mes*), 154.1 (d, $^4J_{\text{P-C}}$ = 3.4 Hz, *p*-Mes*), 149.0 (dm, $^1J_{\text{F-C}}$ ~ 234 Hz, C_6F_5), 138.3 (dm, $^1J_{\text{F-C}}$ ~ 245 Hz, C_6F_5), 137.2 (dm, $^1J_{\text{F-C}}$ ~ 245 Hz, C_6F_5), n.o. (i-C_6F_5), 125.3 (d, $^3J_{\text{P-C}}$ = 11.6 Hz, *m*-Mes*), 123.8 (d, $^3J_{\text{P-C}}$ = 9.7 Hz, *m*’-Mes*), 115.0 (d, $^1J_{\text{P-C}}$ = 49.5 Hz, *i*-Mes*), [38.7 (d, $^3J_{\text{P-C}}$ = 2.7 Hz), 32.5](*o*-^{t}Bu), [38.0 (d, $^3J_{\text{P-C}}$ = 3.0 Hz), 33.7](*o’*-^{t}Bu), [34.9, 30.6](*p*-^{t}Bu), 27.9 (br, PCH), 27.1 (d, $^1J_{\text{P-C}}$ = 53.1 Hz, PCH_2), 16.5 (br, BCH_2), 13.9 (d, $^2J_{\text{P-C}}$ = 1.2 Hz, Me$^{\text{PCH}}$).

^{31}P{^{1}H} NMR (243 MHz, 263 K, toluene-d_8): δ = 32.0 ($\nu_{1/2}$ ~ 35 Hz).

^{31}P NMR (243 MHz, 263 K, toluene-d_8): δ = 32.0 (d, $^1J_{\text{P-H}}$ ~ 449 Hz).

^{11}B{^{1}H} NMR (192 MHz, 263 K, toluene-d_8): δ = −15.0 ($\nu_{1/2}$ ~ 100 Hz).

^{11}B NMR (192 MHz, 263 K, toluene-d_8): δ = −15.0 (d, $^1J_{\text{B-H}}$ ~ 83 Hz).

^{19}F NMR (564 MHz, 263 K, toluene-d_8): δ = −133.7 (m, 2F, *o*-C_6F_5), −162.2 (t, $^3J_{\text{F-F}}$ = 20.1 Hz, 1F, *p*-C_6F_5), −165.2 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}\text{F}_{m,p}$ = 3.0].

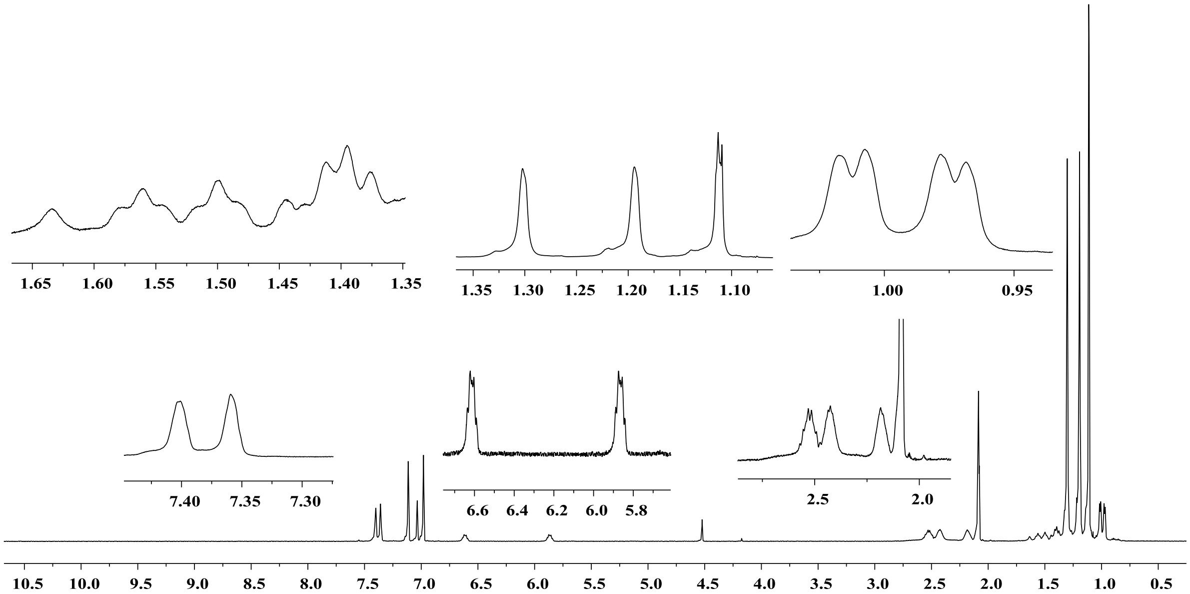


Figure S40 ^{1}H NMR (600 MHz, 263 K, toluene-d_8) spectrum of compound **10b**.

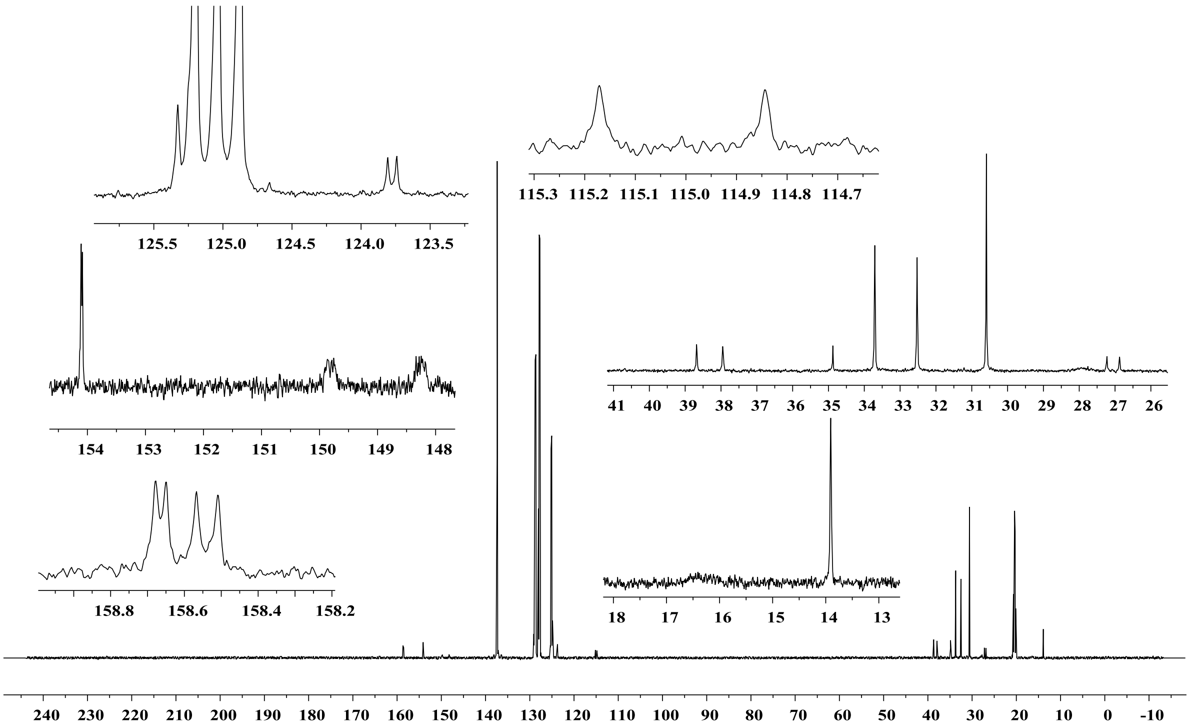


Figure S41 ^{13}C{^{1}H} NMR (151 MHz, 263 K, toluene-d_8) spectrum of compound **10b**.

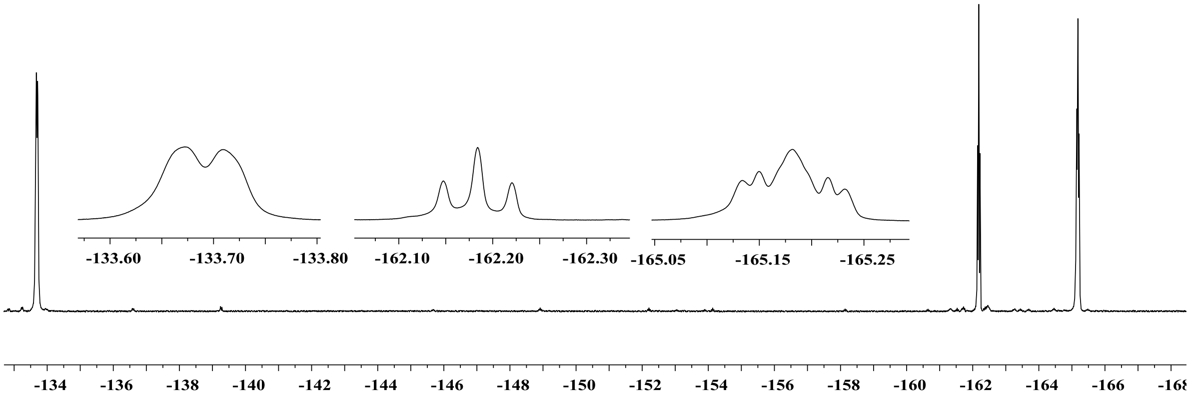


Figure S42 ^{19}F NMR (564 MHz, 263 K, toluene-*d*$_8$) spectrum of compound **10b**.

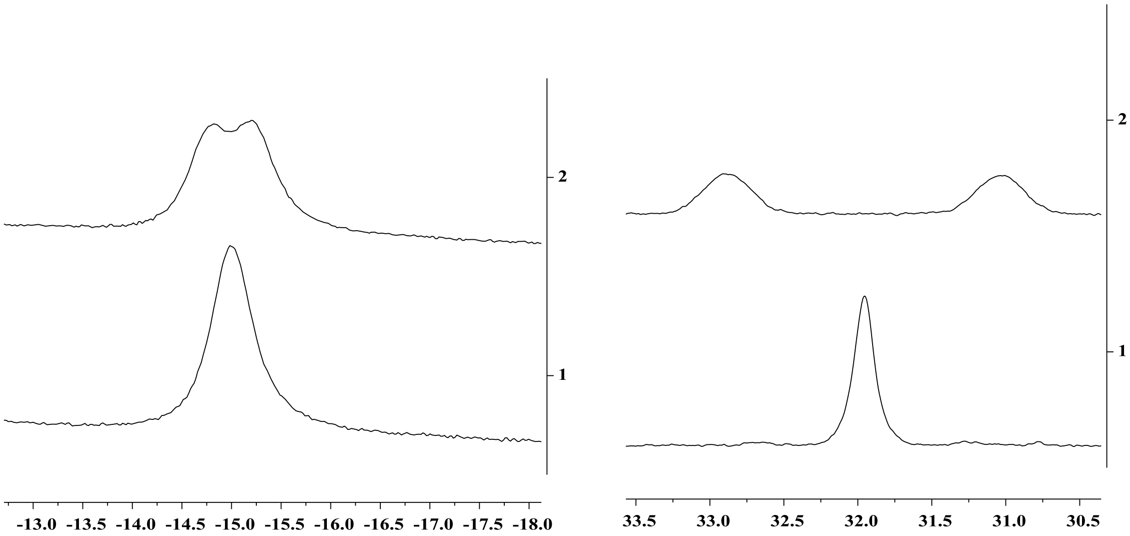


Figure S43 ^{11}B{^{1}H} (left, 1), ^{11}B (left, 2) NMR (192 MHz, 263 K, toluene-*d*$_8$) and ^{31}P{^{1}H} (right, 1), ^{31}P (right, 2) NMR (243 MHz, 263 K, toluene-*d*$_8$) spectra of compound **10b**.

2nd Experiment: After the obtained solid (**8b**/**9b**) (153.5 mg, 0.15 mmol) was suspended in C_7D_8 (0.5 mL) at room temperature, the mixture was degassed by freeze-pump-thaw cycles (×2). Then the mixture was exposed to an H_2 atmosphere (1.5 bar) and heated to 80 °C for 48 h. Then all volatiles were removed *in vacuo*. The obtained residue was suspended in *n*-pentane (4 mL) and filtered. The filtrate was stored in the fridge at –35 °C for 48 h. The formed crystals of compound **10b**, suitable for the X-ray crystal structure analysis, were collected by filtration. After drying *in vacuo* compound **10b** (76.8 mg, 50%) was obtained as a white solid.

Elemental analysis: calc. for $C_{28}H_{39}BF_5P$ (512.2803 g mol^{-1}): C, 65.63; H, 7.67; Found: C, 65.04; H, 7.81.
Melting point: 122 °C

X-ray crystal structure analysis of 10b (erk8900): formula $C_{28}H_{39}BF_5P$, M = 512.37, colourless crystal, 0.10 x 0.10 x 0.02 mm, a = 10.2009(3), b = 13.8694(6), c = 20.6471(9) Å, α = 104.008(4), β = 97.438(3), γ = 91.575(2)°, V = 2805.2(2) Å^3, ρ_{calc} = 1.213 gcm^{-3}, μ = 0.146 mm^{-1}, empirical absorption correction (0.985 ≤ T ≤ 0.997), Z = 4, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 173(2) K, ω and φ scans, 24376 reflections collected (±h, ±k, ±l), 9446 independent (R_{int} = 0.066) and 6481 observed reflections [$I>2\sigma(I)$], 667 refined parameters, R = 0.084, wR^2 = 0.179, max. (min.) residual electron density 0.84 (-0.44) e.Å^{-3}, the position of the hydrogen atoms at P1, P1A, B1 and B1A were refined freely; others hydrogen atoms were calculated and refined as riding atoms.

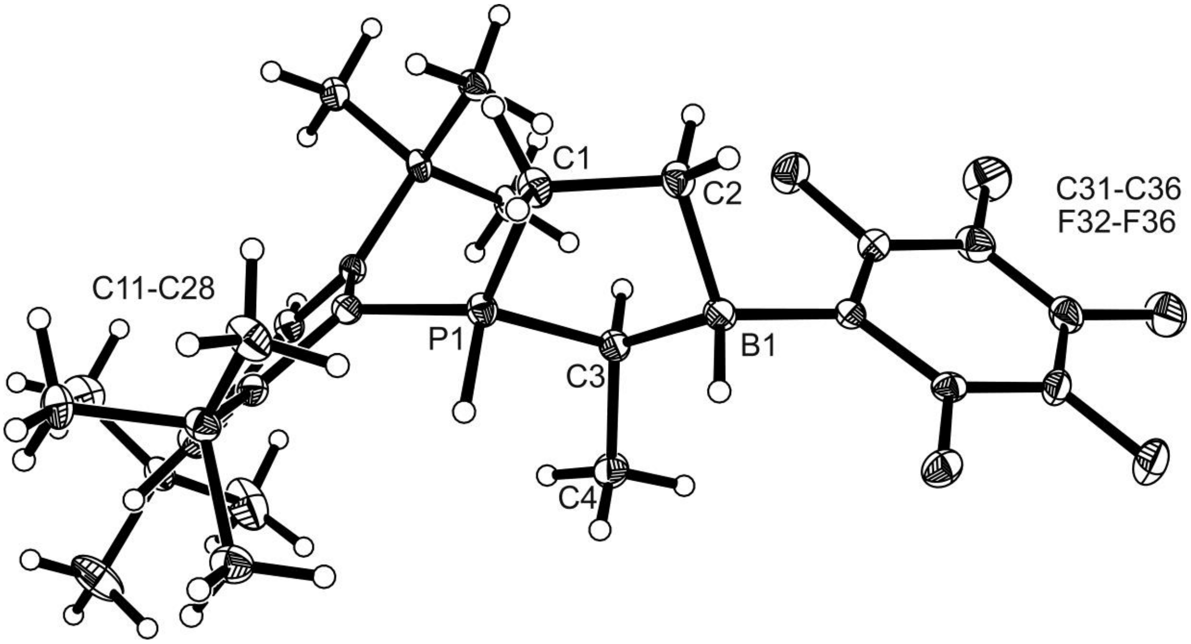
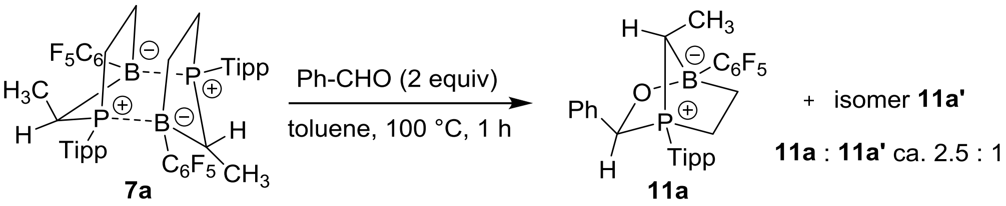


Figure S44 A view of the molecular structure of compound **10b**.

Reaction of compound 7a with benzaldehyde: synthesis of compound 11a



1^st^ Step: Benzaldehyde (21.2 mg, 0.2 mmol, 2.0 equiv.) was added to a toluene solution (4 mL) of dimer **7a** (93.6 mg, 0.1 mmol) by cannula under an argon atmosphere. The reaction mixture was stirred at 100 °C for 1 h and then all volatiles were removed *in vacuo*. The obtained residue was washed with cold pentane (0 °C, 3×2 mL). After drying *in vacuo* a white solid (A) was obtained (74.7 mg, 65%). [major (**11a**) : minor ca. 72 : 28 (^{19}F)]
Elemental analysis: calc. for $C_{32}H_{37}BF_5OP$ (574.42 g mol^{-1}): C, 66.91; H, 6.49. Found: C, 66.64; H, 6.39.
Melting point: 182 °C.

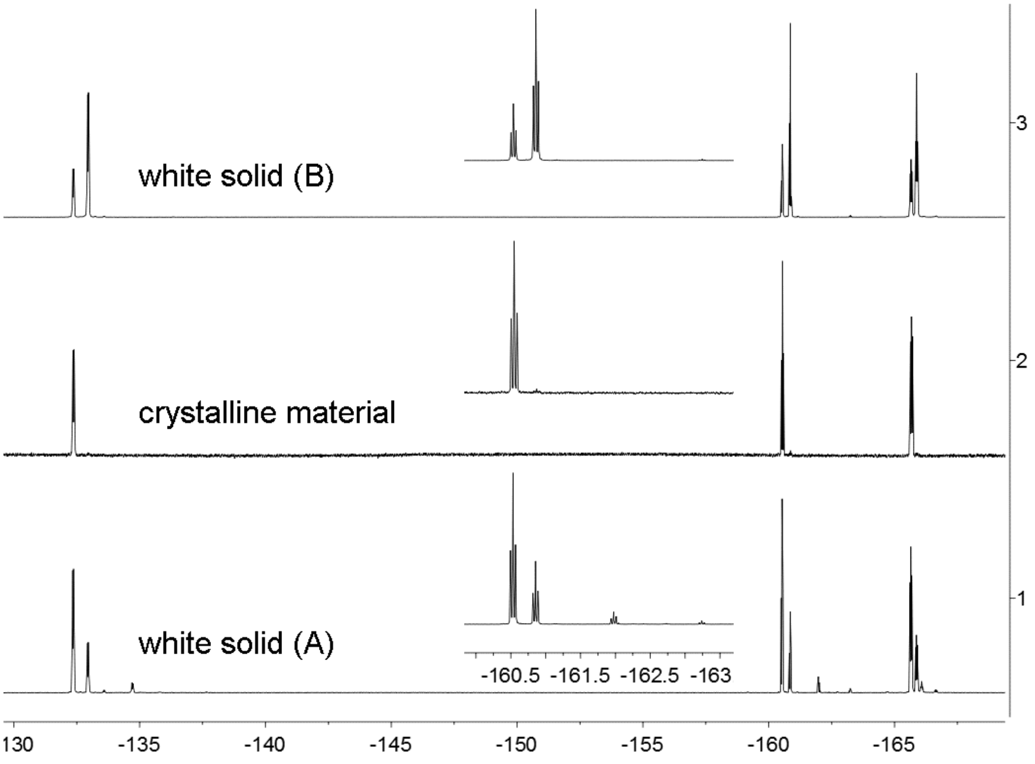


Figure S45 (1) ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of the isolated white solid (A) (see page S40ff), (2) ^{19}F NMR (470 MHz) spectrum of compound **11a** (crystalline material, see page S41ff) and (3) ^{19}F NMR (564 MHz) spectrum of the isolated white solid (B) (see page S44ff).

2^{nd} *Step:* Crystals of compound **11a** suitable for the X-ray crystal structure analysis were obtained from a solution of the isolated white solid (A) in a mixture of solvents (*n*-pentane: dichloromethane ca. 10 : 1) at −35 °C, which were collected by filtration.

X-ray crystal structure analysis of compound 11a (erk8743): A colorless prism-like specimen of $C_{32}H_{37}BF_5OP$, approximate dimensions 0.190 mm x 0.240 mm x 0.260 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1704 frames were collected. The total exposure time was 18.06 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 52626 reflections to a maximum θ angle of 66.74° (0.84 Å resolution), of which 10304 were independent (average redundancy 5.107, completeness = 99.4%, R_{int} = 4.85%, R_{sig} = 3.32%) and 8549 (82.97%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 12.1408(3) Å, $\underline{b}$ = 15.4506(4) Å, $\underline{c}$ = 16.6403(5) Å, α = 77.2090(10)°, β = 76.7190(10)°, γ = 77.9290(10)°, volume = 2921.08(14) Å^3, are based upon the refinement of the XYZ-centroids of 9848 reflections above 20 σ(I) with 7.361° < 2θ < 133.3°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.864. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7260 and 0.7880. The final anisotropic full-matrix least-squares refinement on F^2 with 735 variables converged at R1 = 4.54%, for the observed data and wR2 = 12.43% for all data. The goodness-of-fit was 1.054. The largest peak in the final difference electron density synthesis was 0.573 e^-/Å^3 and the largest hole was -0.336 e^-/Å^3 with an RMS deviation of 0.051 e^-/Å^3. On the basis of the final model, the calculated density was 1.306 g/cm^3 and F(000), 1208 e^-.

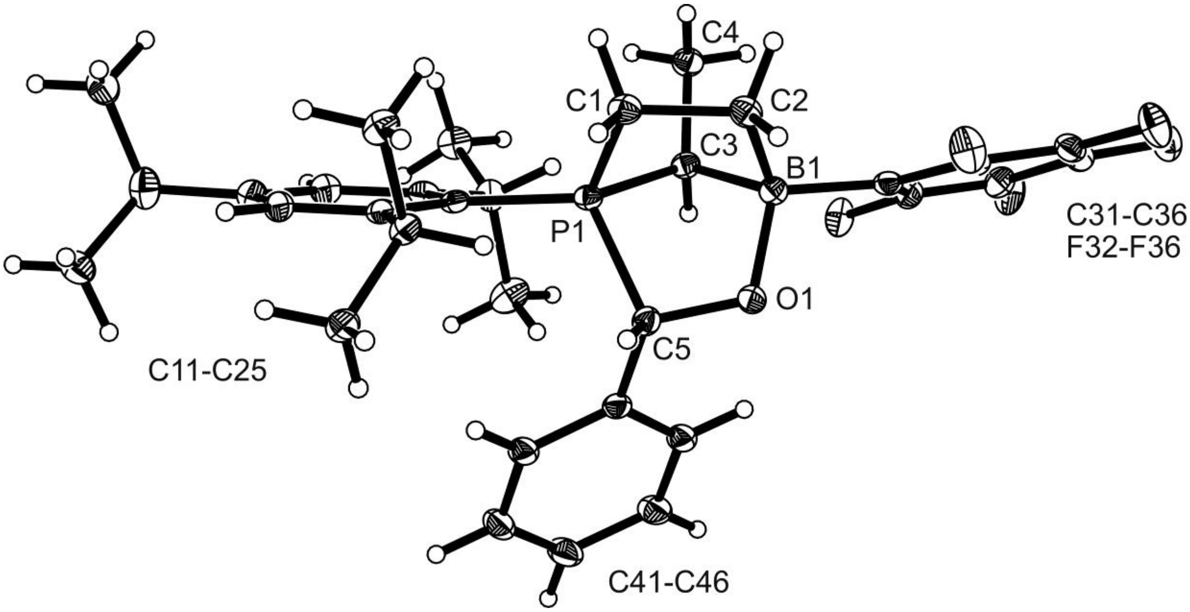


Figure S46 A view of the molecular structure of compound **11a**.

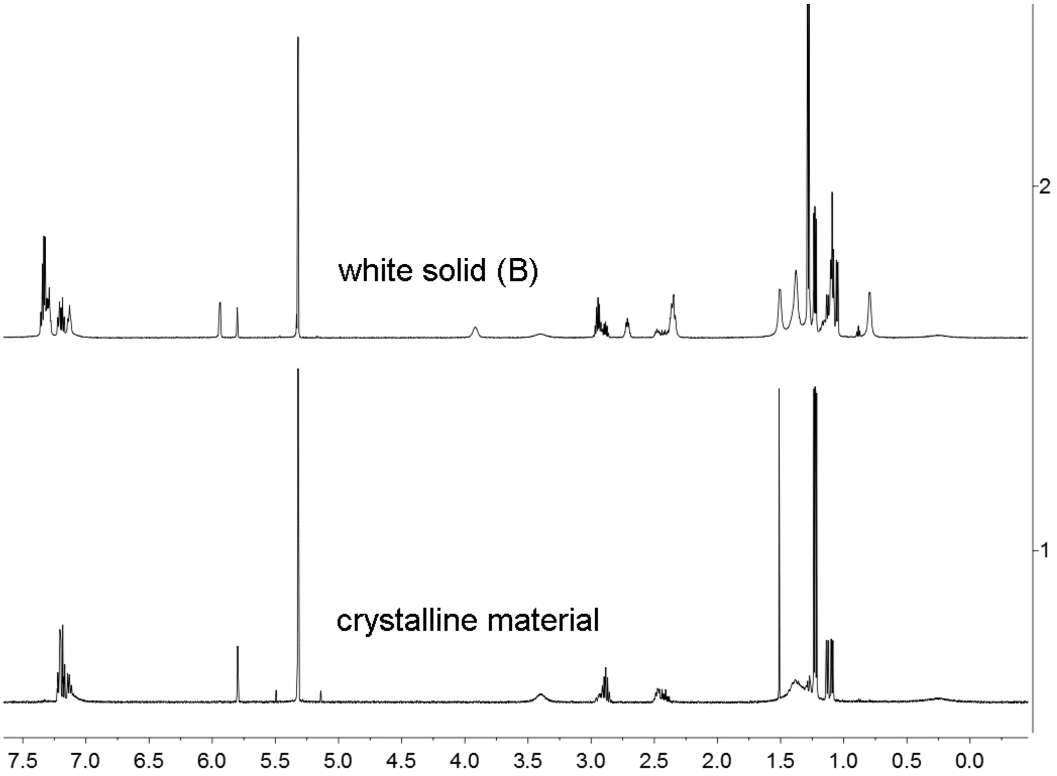


Figure S47 (1) ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of compound **11a** (crystalline material, see above) and (2) ^{1}H NMR (600 MHz) spectrum of the isolated white solid (B) (see page S44ff).

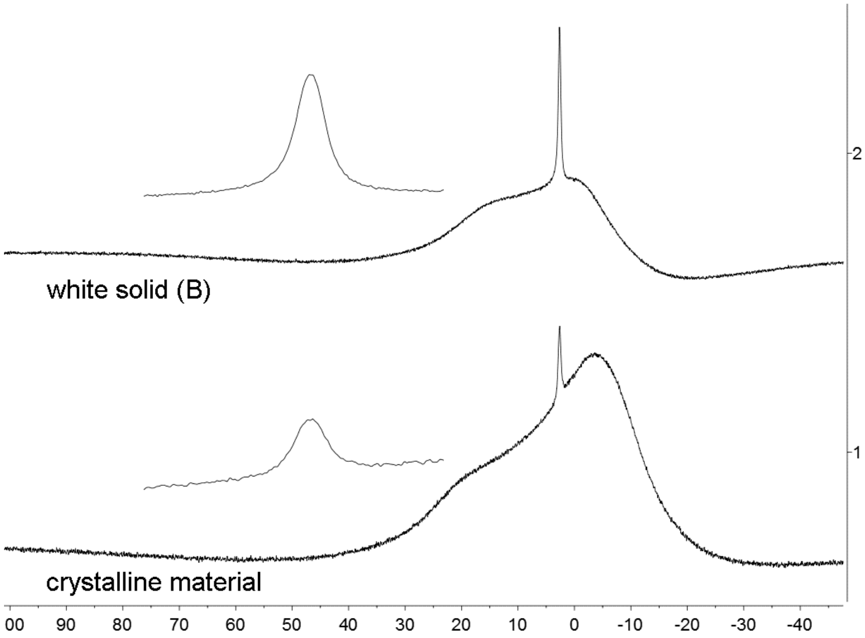


Figure S48 (1) $^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, CD_2Cl_2) spectrum of compound **11a** (crystalline material, see above) and (2) $^{11}B\{^{1}H\}$ NMR (192 MHz) spectrum of the isolated white solid (B) (see page S44ff).

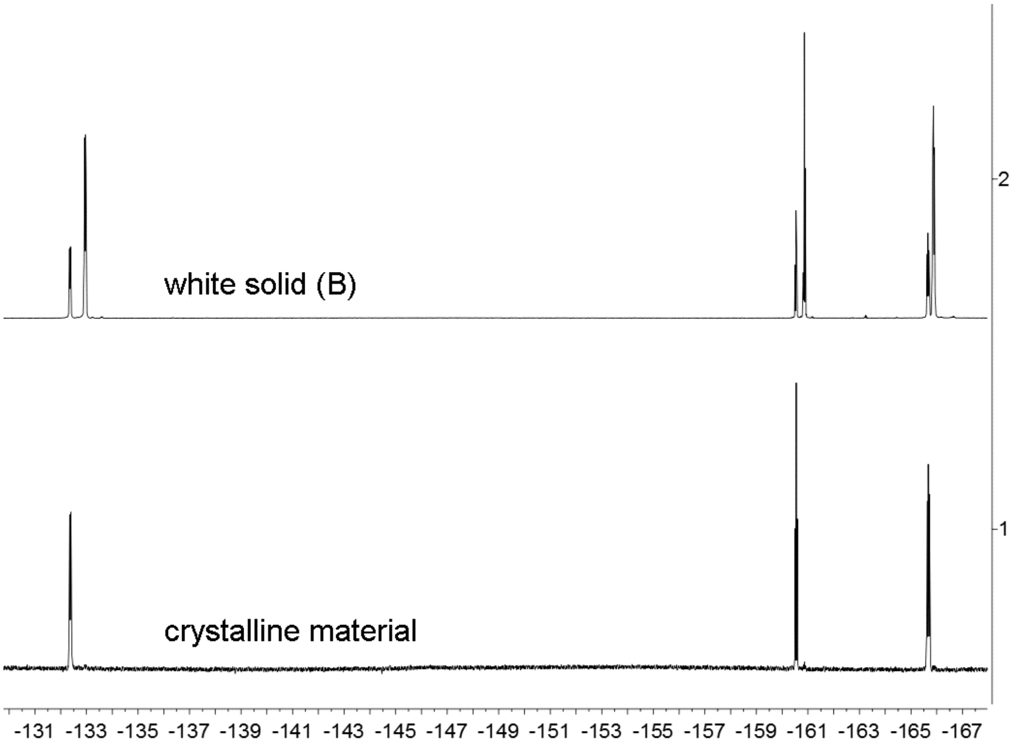


Figure S49 (1) ^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) spectrum of compound **11a** (crystalline material, see above) and (2) ^{19}F NMR (564 MHz) spectrum of the isolated white solid (B) (see page S44ff).

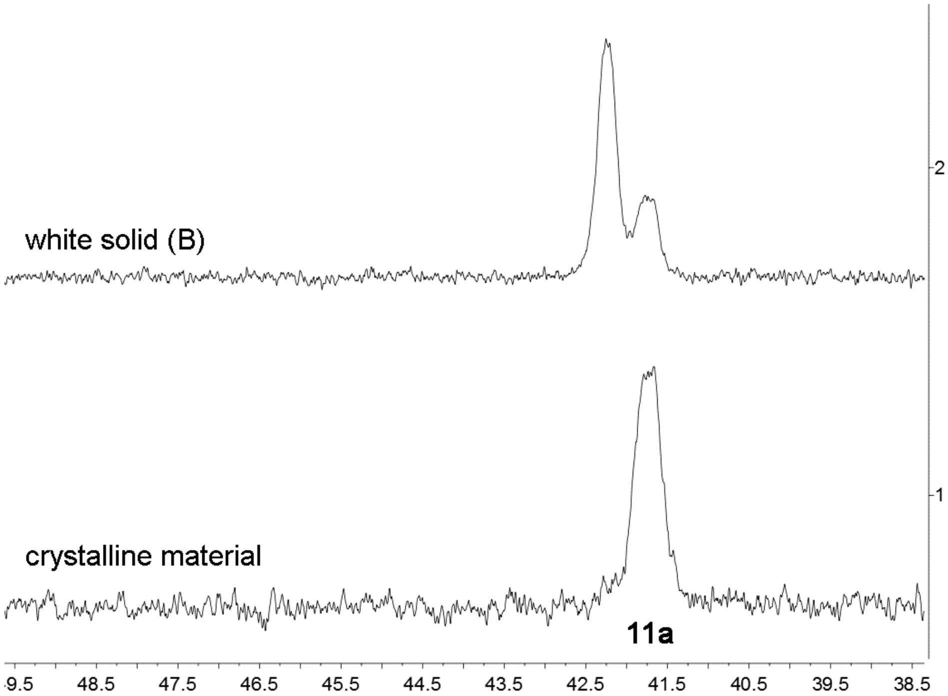


Figure S50 (1) $^{31}P\{^1H\}$ NMR (202 MHz, 299 K, CD_2Cl_2) spectrum of compound **11a** (crystalline material, see above) and (2) $^{31}P\{^1H\}$ NMR (243 MHz) spectrum of the isolated white solid (B) (see page S44ff).

3rd Step: The obtained filtrate (see *2nd Step*) was concentrated and stored at −35 °C. The formed precipitate was collected by filtration [white solid (B)] and used for NMR characterization. The respective NMR data in CD_2Cl_2 revealed the presence of a mixture of two isomers **11a'** and **11a** [major : minor ca. 70 : 30 (^1H NMR)].

[The NMR resonances of the minor component were identified by comparison of the respective spectra of the mixture with those obtained from the crystals of compound **11a** (see page 41ff)]

^{1}H NMR (600 MHz, 223 K, CD_2Cl_2) **11a** (minor): δ = 7.18 (m, 2H, *m*-Ph), 7.16 (br. 1H, *m*-Tipp), 7.15 (m, 2H, *o*-Ph), 7.12 (m. 1H, *p*-Ph), 6.97 (br. 1H, *m*'-Tipp), 5.80 (m, 1H, PCHO), [3.41 (sept, $^3J_{H\text{-}H}$ = 6.7 Hz, 1H), 1.42, 1.36 (each d, $^3J_{H\text{-}H}$ = 6.7 Hz, each 3H)](*o*-^{i}Pr), [3.25 (sept, $^3J_{H\text{-}H}$ = 6.5 Hz, 1H), 1.17, 0.06 (each d, $^3J_{H\text{-}H}$ = 6.5 Hz, each 3H)](*o*'-^{i}Pr), [2.89, 2.39](each m, each 1H, PCH_2), [2.83 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 1H), 1.16, 1.14 (each d, $^3J_{H\text{-}H}$ = 6.9 Hz, 3H)](*p*-^{i}Pr), 2.48 (m, 1H, PCH), [1.30, 1.13](each m, each 1H, BCH_2), 1.03 (dd, 3H, $^3J_{P\text{-}H}$ = 20.2 Hz, $^3J_{H\text{-}H}$ = 7.1 Hz, 3H, Me^{PCH}); **11a'** (major): δ = 7.33 (m, 2H, *m*-Ph), 7.27 (m, 3H, *o,p*-Ph), 7.23 (br. 1H, *m*-Tipp), 7.07 (br. 1H, *m*'-Tipp), 5.89 (m, 1H, PCHO), [3.78 (sept,

$^{3}J_{\text{H-H}}$ = 6.5 Hz, 1H), 1.43, 1.29 (each d, $^{3}J_{\text{H-H}}$ = 6.5 Hz, each 3H)](*o*-^{i}Pr), [2.88 (sept, $^{3}J_{\text{H-H}}$ = 7.0 Hz, 1H), 1.20 (d, $^{3}J_{\text{H-H}}$ = 7.0 Hz, 6H)](*p*-^{i}Pr), 2.66 (m, 1H, PCH), 2.26 (m, 2H, PCH_2), [2.17 (sept, $^{3}J_{\text{H-H}}$ = 6.5 Hz, 1H), 1.01, 0.74 (each d, $^{3}J_{\text{H-H}}$ = 6.5 Hz, each 3H)](*o*'-^{i}Pr), [1.30, 1.03](each m, each 1H, BCH_2), 0.98 (dd, $^{3}J_{\text{P-H}}$ = 20.2 Hz, $^{3}J_{\text{H-H}}$ = 7.1 Hz, 3H, Me^{PCH}).

^{13}C{^{1}H} NMR (151 MHz, 223 K, CD_2Cl_2) **11a (**minor**)**: δ = 155.7 (d, $^{2}J_{\text{P-C}}$ = 10.2 Hz, *o*'-Tipp), 155.13 (d, $^{2}J_{\text{P-C}}$ = 9.4 Hz, *o*-Tipp), 154.09 (*p*-Tipp), 138.6 (d, $^{2}J_{\text{P-C}}$ = 3.6 Hz, *i*-Ph), 128.0 (*m*-Ph), 127.46 (m, *p*-Ph), 125.8 (m, *o*-Ph), 123.5 (d, $^{3}J_{\text{P-C}}$ = 10.4 Hz, *m*-Tipp), 123.4 (d, $^{3}J_{\text{P-C}}$ = 10.7 Hz, *m*'-Tipp), 112.2 (d, $^{1}J_{\text{P-C}}$ = 50.2 Hz, *i*-Tipp), 77.0 (d, $^{1}J_{\text{P-C}}$ = 46.6 Hz, PCHO), [33.9, 23.1, 23.0](*p*-^{i}Pr), [33.6 (d, $^{3}J_{\text{P-C}}$ = 3.9 Hz), 25.53, 24.2](*o*-^{i}Pr), [30.2 (d, $^{3}J_{\text{P-C}}$ = 4.7 Hz), 24.7, 23.6](*o*'-^{i}Pr), 24.5 (br m, PCH), 21.9 (d, $^{1}J_{\text{P-C}}$ = 51.1 Hz, PCH_2), 13.4 (br, BCH_2), 7.4 (d, $^{2}J_{\text{P-C}}$ = 5.1 Hz, Me^{PCH}); **11a'** (major): δ = 155.8 (d, $^{2}J_{\text{P-C}}$ = 8.9 Hz, *o*'-Tipp), 155.1 (d, $^{2}J_{\text{P-C}}$ = 11.9 Hz, *o*-Tipp), 154.4 (d, $^{4}J_{\text{P-C}}$ = 2.5 Hz, *p*-Tipp), 138.4 (d, $^{2}J_{\text{P-C}}$ = 1.8 Hz, *i*-Ph), 128.4 (*m*-Ph), 127.50 (m, *p*-Ph), 124.6 (m, *o*-Ph), 124.0 (d, $^{3}J_{\text{P-C}}$ = 10.0 Hz, *m*'-Tipp), 123.7 (d, $^{3}J_{\text{P-C}}$ = 10.6 Hz, *m*-Tipp), 111.1 (d, $^{1}J_{\text{P-C}}$ = 47.4 Hz, *i*-Tipp), 77.5 (d, $^{1}J_{\text{P-C}}$ = 48.0 Hz, PCHO), [34.0, 23.1](*p*-^{i}Pr), [32.7 (d, $^{3}J_{\text{P-C}}$ = 5.6 Hz), 25.46, 23.7](*o*-^{i}Pr), [31.7 (d, $^{3}J_{\text{P-C}}$ = 2.4 Hz), 25.1, 23.7](*o*'-^{i}Pr), 29.4 (br m, PCH), 19.0 (d, $^{1}J_{\text{P-C}}$ = 51.0 Hz, PCH_2), 14.6 (br, BCH_2), 8.8 (d, $^{2}J_{\text{P-C}}$ = 4.5 Hz, Me^{PCH}), [C_6F_5 not listed].

^{31}P{^{1}H} NMR (243 MHz, 223 K, CD_2Cl_2): δ = 42.1 ($\nu_{1/2}$ ~ 20 Hz, major **11a'**), δ = 40.8 ($\nu_{1/2}$ ~ 30 Hz, minor **11a**).

^{11}B{^{1}H} NMR (192 MHz, 223 K, CD_2Cl_2): δ = 2.4 ($\nu_{1/2}$ ~ 400 Hz).

^{19}F NMR (564 MHz, 223 K, CD_2Cl_2) **11a** (minor): δ = −132.2 (m, 2F, *o*-C_6F_5), −159.6 (t, $^{3}J_{\text{F-F}}$ = 20.9 Hz, 1F, *p*-C_6F_5), −164.9 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 5.3]; **11a'** (major): δ = −132.7 (m, 2F, *o*-C_6F_5), −159.9 (t, $^{3}J_{\text{F-F}}$ = 20.9 Hz, 1F, *p*-C_6F_5), −165.1 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 5.2].

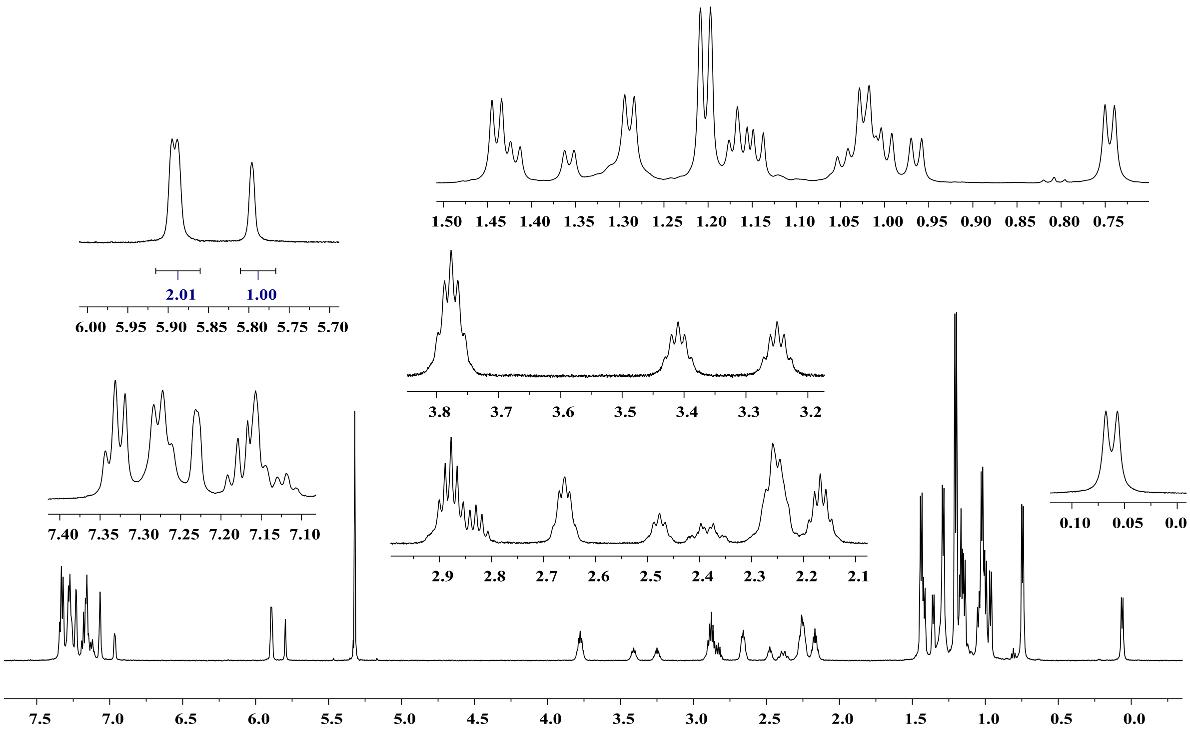


Figure S51 ^{1}H NMR (600 MHz, 223 K, CD_2Cl_2) spectrum of compound **11a** and **11a'**.

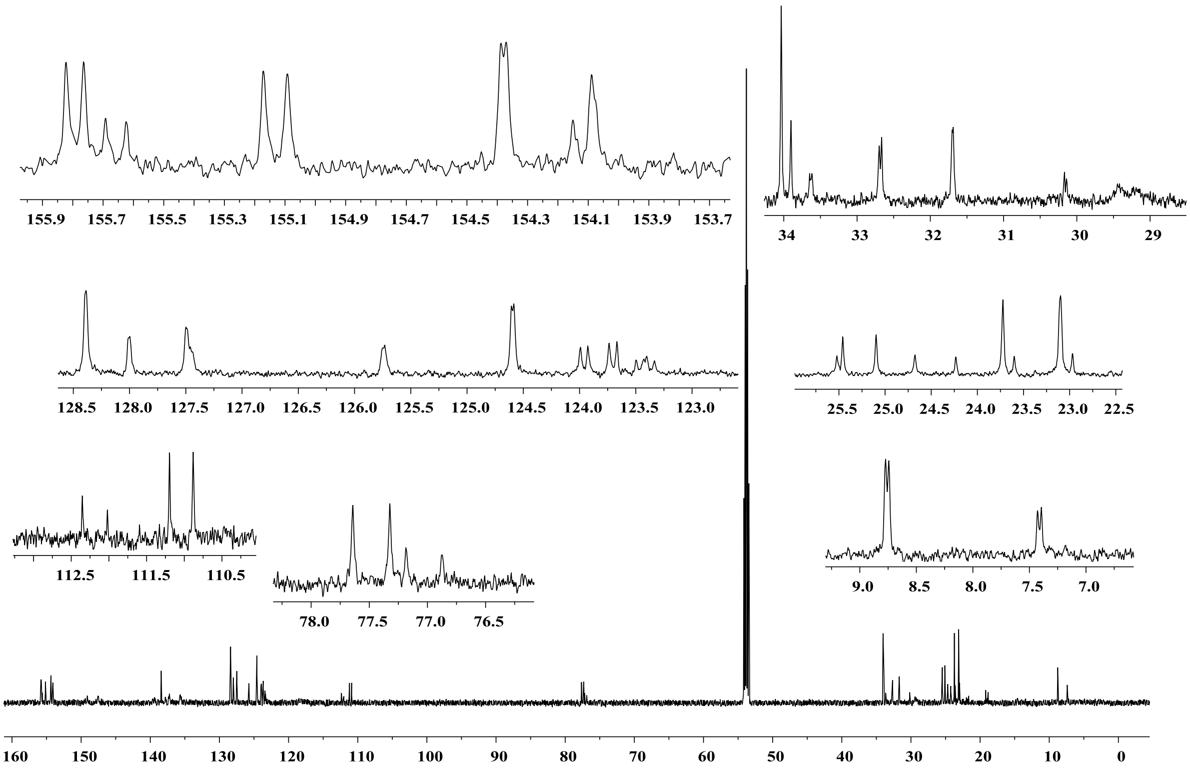


Figure S52 $^{13}C\{^{1}H\}$ NMR (151 MHz, 223 K, CD_2Cl_2) spectrum of compound **11a** and **11a'**.

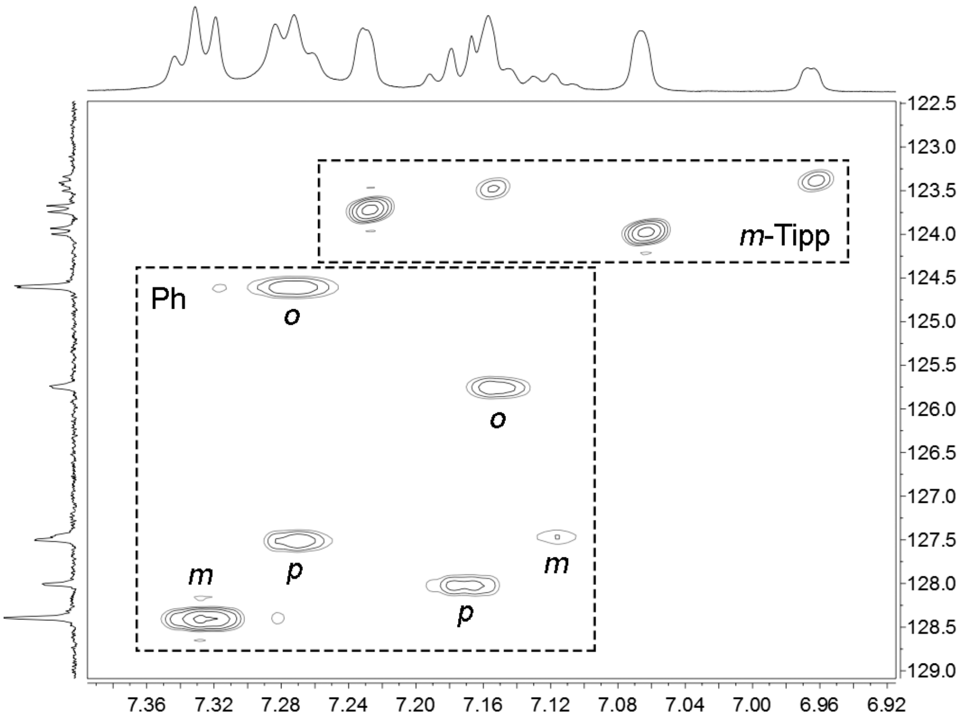


Figure S53 ^{1}H,^{13}C ghsqc (600/151 MHz, 233 K, CD$_2$Cl$_2$) spectrum of compound **11a** and **11a'**.

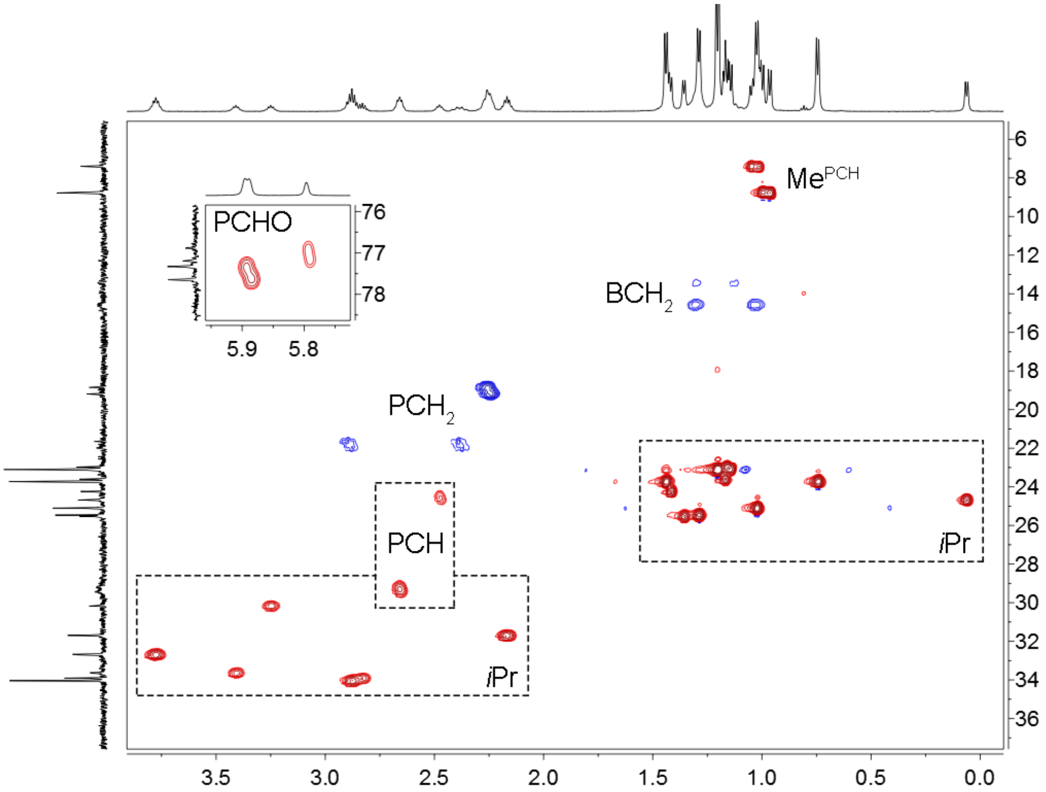


Figure S54 ^{1}H,^{13}C ghsqc (600/151 MHz, 233 K, CD$_2$Cl$_2$) spectrum of compound **11a** and **11a'**.

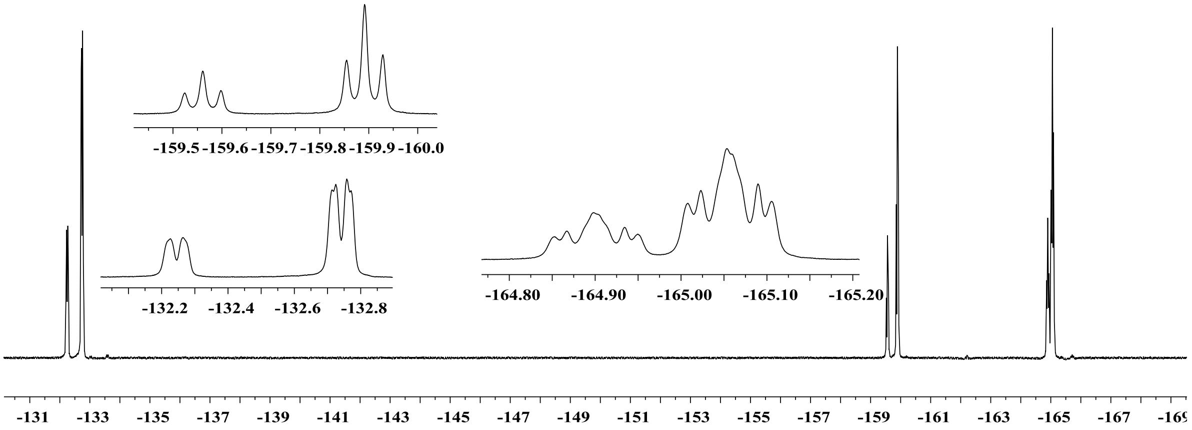


Figure S55 ^{19}F NMR (564 MHz, 223 K, CD_2Cl_2) spectra of compound **11a** and **11a'**.

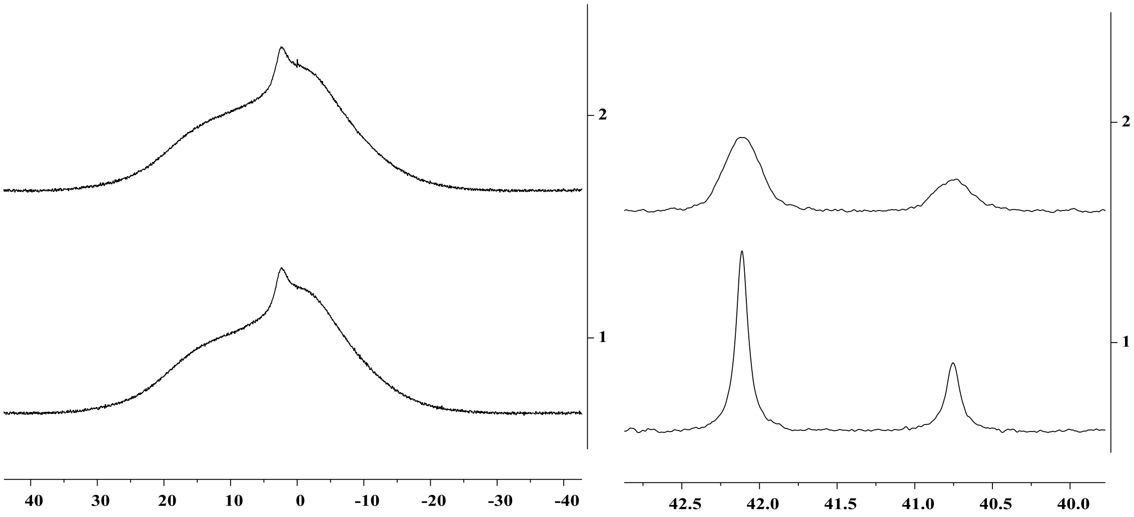
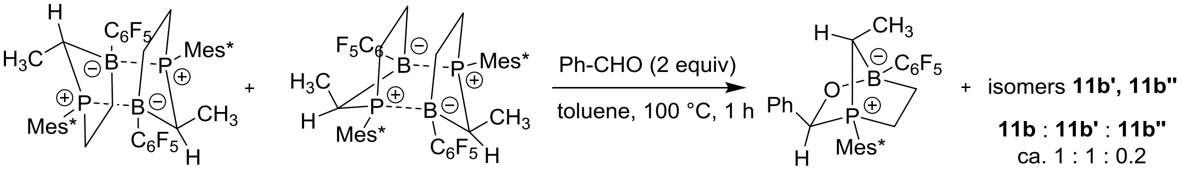


Figure S56 ^{11}B{^{1}H} (left, 1), ^{11}B (left, 2) NMR (192 MHz, 223 K, CD_2Cl_2) and ^{31}P{^{1}H} (right, 1), ^{31}P (right, 2) NMR (243 MHz, 223 K, CD_2Cl_2) spectra of compound **11a** and **11a'**.

Reaction of the dimers 8a/9a with benzaldehyde:

There was no reaction of the dimer mixture **8a/9a** with benzaldehyde observed at 100 °C for four hours.

Reaction of the dimers 8b/9b with benzaldehyde: synthesis of compounds 11b



8b **9b** **11b**

Benzaldehyde (21.2 mg, 0.2 mmol, 2.0 equiv.) was added to a toluene solution (4 mL) of **8b**/**9b** isomers (102.0 mg, 0.10 mmol) by cannula under an argon atmosphere. The reaction mixture was stirred at 100 °C for 1 h and then all volatiles were removed *in vacuo*. The obtained residue was washed three times with cold pentane (0 °C, 3×2 mL). After drying *in vacuo*, a white solid was obtained (86.0 mg, 70 %).

Elemental analysis: calc. for $C_{35}H_{43}BF_5OP$ (616.30 g mol^{-1}): C, 68.19; H, 7.03. Found: C, 68.16; H, 7.23.

Melting point: 170 °C.

NMR data obtained from a solution of the obtained white solid in CD_2Cl_2 revealed the presence of a mixture of three isomers of compound **11b** [ca. 1 : 1 : 0.2 (^{1}H NMR)].

^{1}H NMR (600 MHz, 213 K, CD_2Cl_2)[selected resonances] first isomer (45 mol%): δ = 6.46 (s, 1H, PCHO), [2.62, 1.65](each m, each 1H, PCH_2), 2.28 (sept, $^2J_{P\text{-}H} \sim {}^3J_{H\text{-}H}$ = 6.6 Hz, 1H, PCH), [1.36, 1.04](each m, 1H, BCH_2), 0.24 (dd, $^3J_{P\text{-}H}$ = 19.1 Hz, $^3J_{H\text{-}H}$ = 7.1 Hz, 3H, Me^{PCH}); second isomer (45 mol%): δ = 5.96 (d, $^2J_{\text{P-H}}$ = 6.1 Hz, 1H, PCHO), [2.76, 1.62] (each m, each 1H, PCH_2), 2.03 (sept, $^2J_{P\text{-}H} \sim {}^3J_{H\text{-}H}$ = 6.8 Hz, 1H, PCH), [1.10, 1.05](each m, each 1H, BCH_2), 0.30 (dd, $^3J_{P\text{-}C}$ = 18.2 Hz, $^3J_{H\text{-}H}$ = 7.0 Hz, 3H, Me^{PCH}); third isomer (10 mol%): δ = 5.49 (d, $^2J_{\text{P-H}}$ = 5.9 Hz, 1H, PCHO), [2.47, 1.30](each m, each 1H, PCH_2), 2.94 (sept, $^2J_{P\text{-}H} \sim {}^3J_{H\text{-}H}$ = 6.8 Hz, 1H, PCH), [1.06, 1.00](each m, each 1H, BCH_2), 1.18 (m, 3H, Me^{PCH}).

^{13}C{^{1}H} NMR (151 MHz, 213 K, CD_2Cl_2)[selected resonances] first isomer (45 mol%): δ = 139.6 (d, $^2J_{\text{P-C}}$ = 2.1 Hz, *i*-Ph), 80.8 (d, $^1J_{\text{P-C}}$ = 29.4 Hz, PCHO), 30.2 (br d, $^1J_{\text{P-C}}$ ~ 40 Hz, PCH), 24.0 (d, $^1J_{\text{P-C}}$ = 52.8 Hz, PCH_2), 17.8 (br, BCH_2), 8.1 (d, $^3J_{\text{P-C}}$ = 5.9 Hz, Me^{PCH}); second isomer (45 mol%): δ = 139.7 (d, $^2J_{\text{P-C}}$ = 4.3 Hz, *i*-Ph), 82.0 (d, $^1J_{\text{P-C}}$ = 26.4 Hz, PCHO), 29.0 (d, $^1J_{\text{P-C}}$ = 54.6 Hz, PCH_2), 26.2 (br d, $^1J_{\text{P-C}}$ ~ 45 Hz, PCH), 13.7 (br, BCH_2), 8.3 (d, $^3J_{\text{P-C}}$ = 5.9 Hz, Me^{PCH}); third isomer (10 mol%): 139.8 (d, $^2J_{\text{P-C}}$ = 4.6 Hz, *i*-Ph), 79.7 (d, $^1J_{\text{P-C}}$ = 58.2 Hz, PCHO), 23.4 (d, $^1J_{\text{P-C}}$ = 51.1 Hz, PCH_2), 30.0 (br d, $^1J_{\text{P-C}}$ ~ 25 Hz, PCH), 13.3 (br, BCH_2), 10.8 (br m, Me^{PCH}).

^{31}P NMR (243 MHz, 213 K, CD_2Cl_2) δ = 56.9 ($\nu_{1/2}$ ~ 20 Hz, 45 mol%), 48.3 ($\nu_{1/2}$ ~ 20 Hz, 45 mol%), 46.7 ($\nu_{1/2}$ ~ 20 Hz, 10 mol%).

^{31}P NMR (243 MHz, 299 K, CD_2Cl_2) δ = 57.4 ($\nu_{1/2}$ ~ 70 Hz, 45 mol%), 48.4 ($\nu_{1/2}$ ~ 130 Hz, 55 mol%).

^{11}B{^{1}H} NMR (192 MHz, 213 K, CD_2Cl_2): δ = 1.4 ($\nu_{1/2}$ ~ 450 Hz).

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 1.8 ($\nu_{1/2}$ ~ 100 Hz).

^{19}F NMR (564 MHz, 213 K, CD_2Cl_2) δ = (45 mol%): −132.4 (m, 2F, *o*-C_6F_5), −159.9 (t, $^{3}J_{F\text{-}F}$ = 20.8 Hz, 1F, *p*-C_6F_5), −165.2 (m, 2F, *m*-C_6F_5). [$\Delta\delta^{19}F_{m,p}$ = 5.3]; (45 mol%): −133.1 (m, 2F, *o*-C_6F_5), −160.2 (t, $^{3}J_{F\text{-}F}$ = 20.9 Hz, 1F, *p*-C_6F_5), −165.3 (m, 2F, *m*-C_6F_5). [$\Delta\delta^{19}F_{m,p}$ = 5.1]; (10 mol%): −133.0 (m, 2F, *o*-C_6F_5), −159.7 (t, $^{3}J_{F\text{-}F}$ = 20.9 Hz, 1F, *p*-C_6F_5), −165.0 (m, 2F, *m*-C_6F_5). [$\Delta\delta^{19}F_{m,p}$ = 5.3].

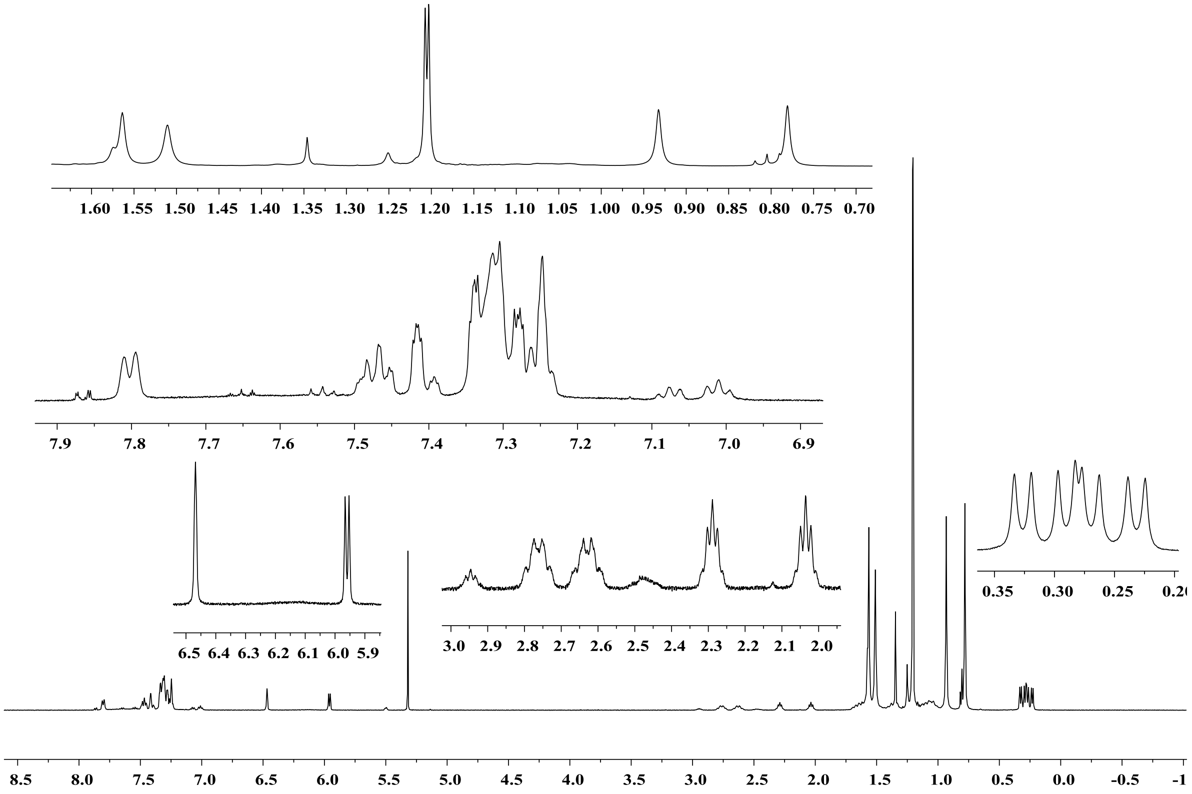


Figure S57 ^{1}H NMR (600 MHz, 213 K, CD_2Cl_2) spectrum of obtained white solid.

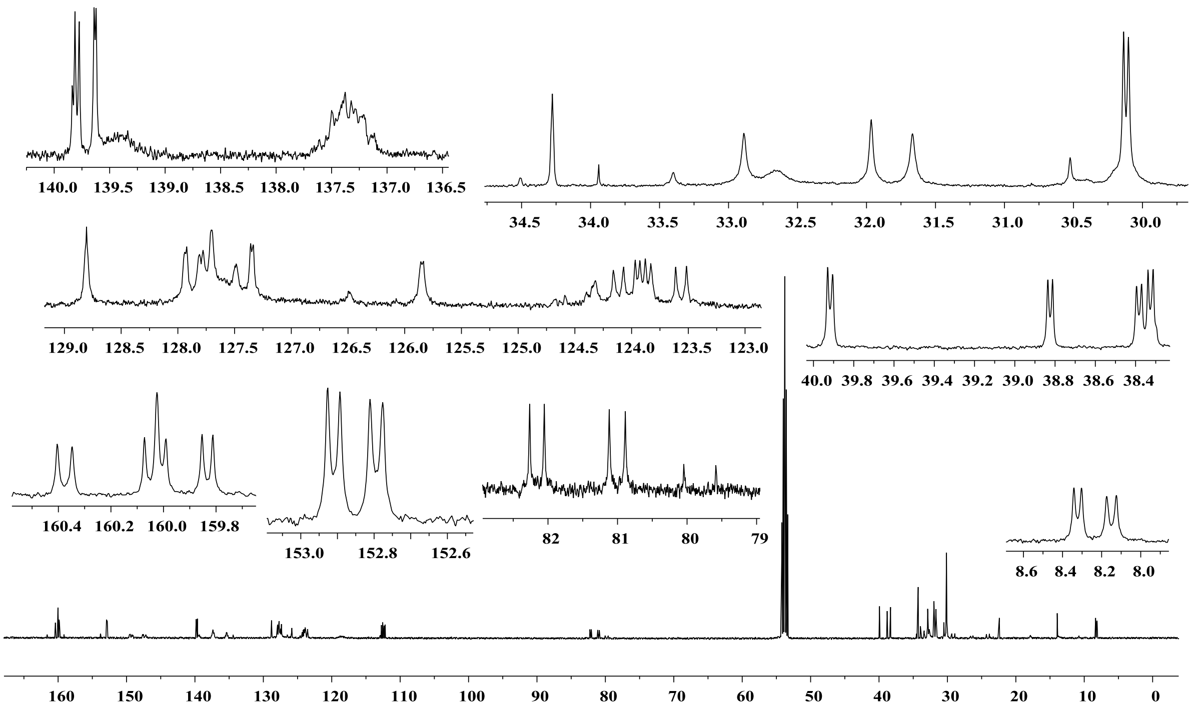


Figure S58 $^{13}C\{^1H\}$ NMR (151 MHz, 213 K, CD_2Cl_2) spectrum of obtained white solid.

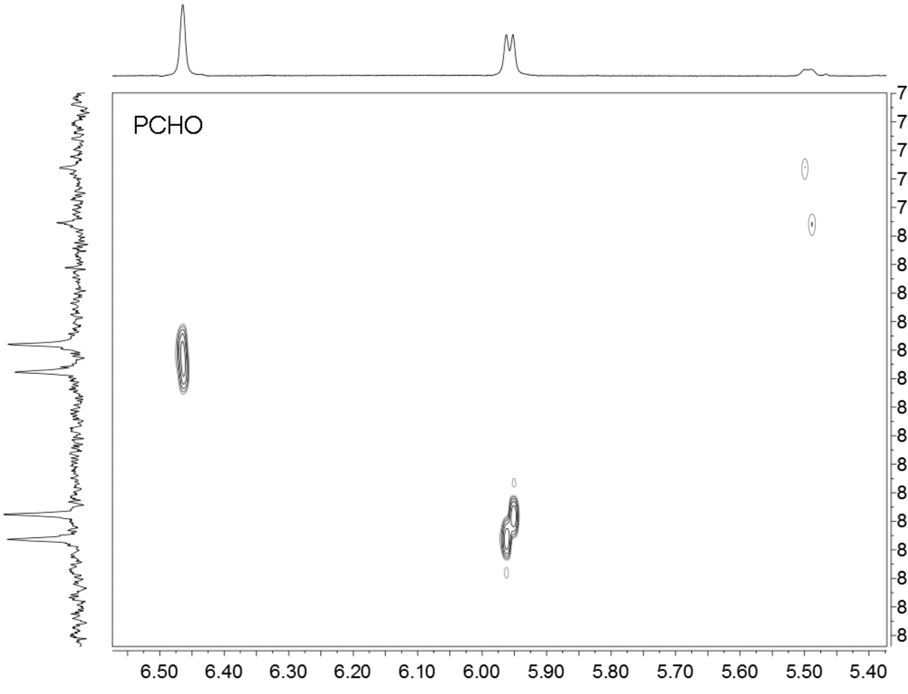


Figure S59 $^1H,^{13}C$ ghsqc (600/151 MHz, 233 K, CD_2Cl_2) spectrum of obtained white solid.

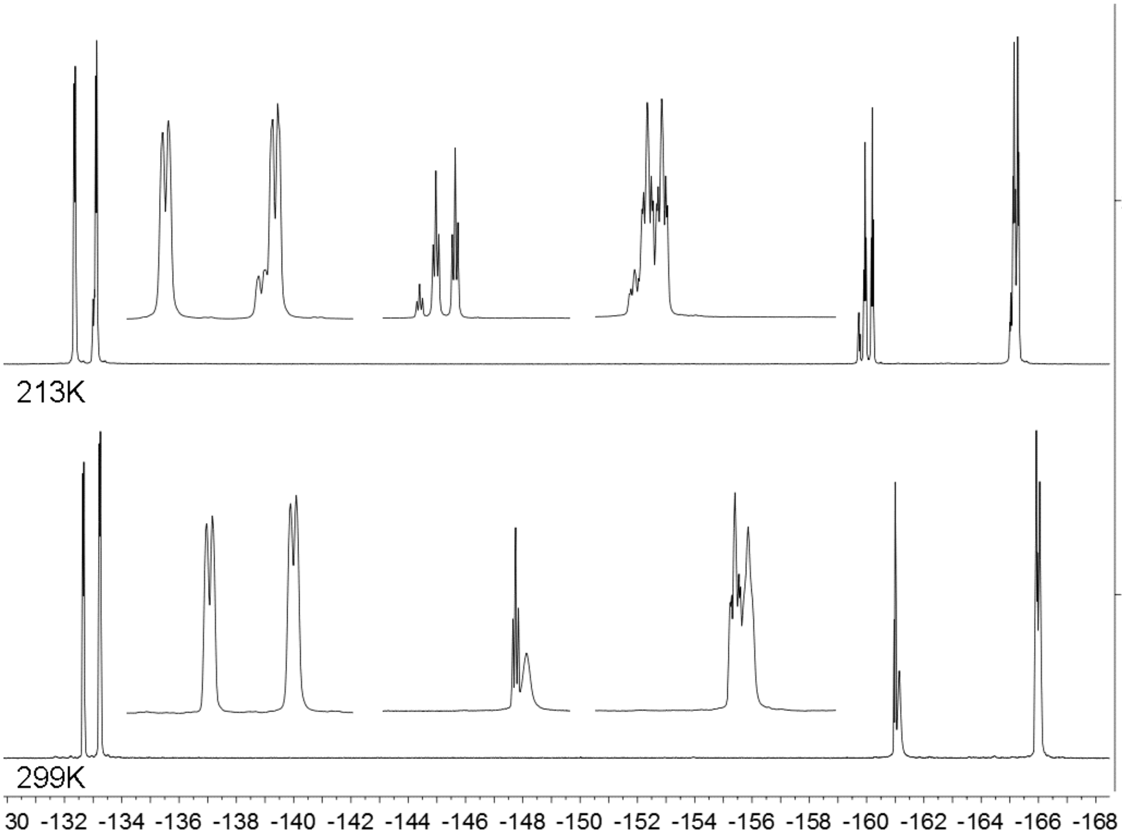


Figure S60 (1) ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) and (2) ^{19}F NMR (213 K) spectra of the obtained white solid.

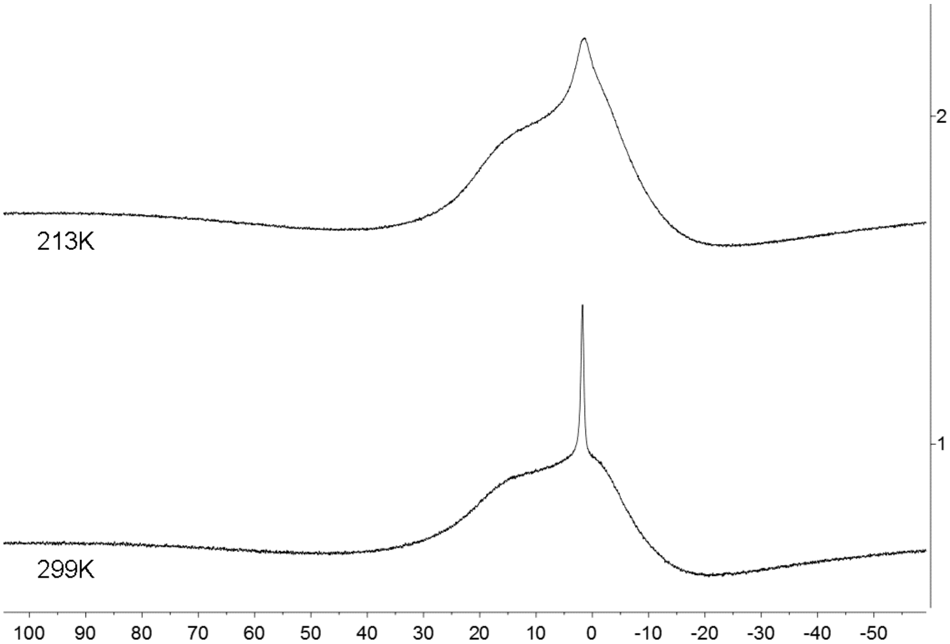


Figure S61 (1) ^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2) and (2) ^{11}B{^{1}H} NMR (213 K) spectra of the obtained white solid.

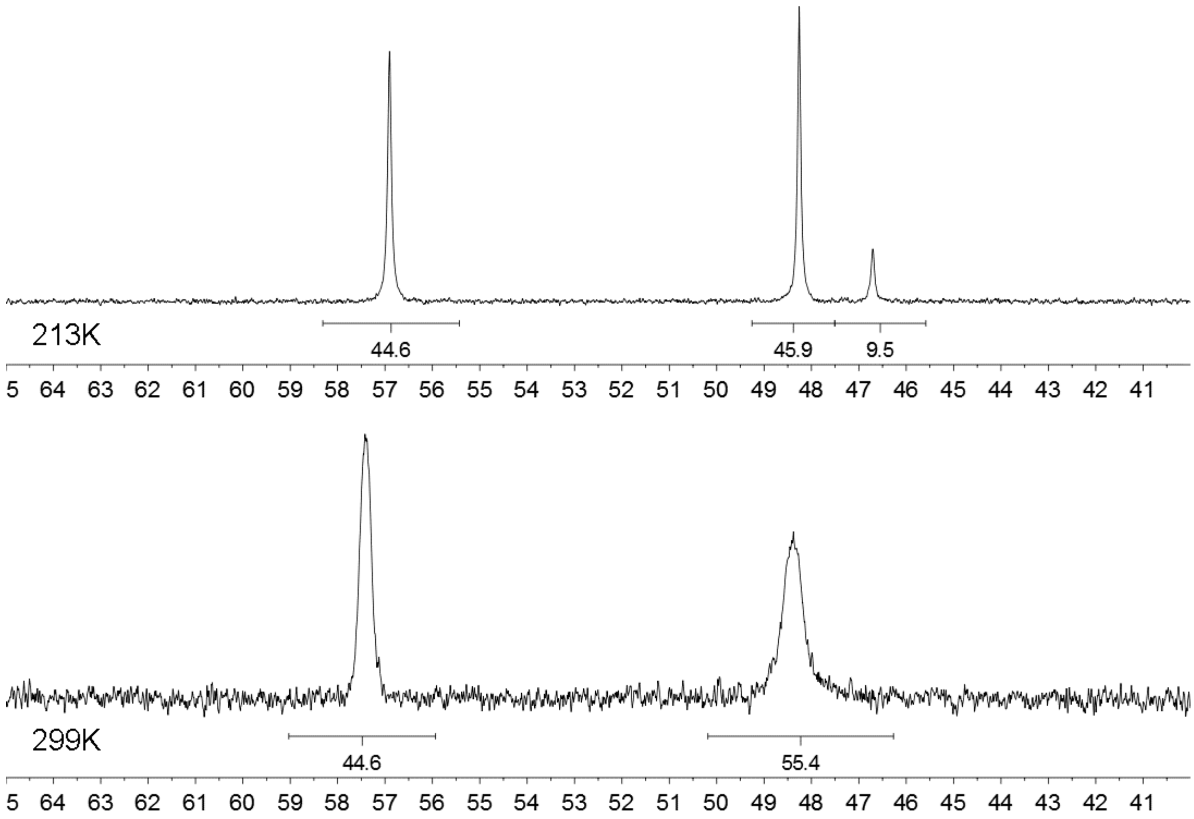


Figure S62 (bottom) $^{31}P\{^1H\}$ NMR (243 MHz, 299 K, CD_2Cl_2) and (top) $^{31}P\{^1H\}$ NMR (213 K) spectra of the obtained white solid.

Crystals of compound **11b** suitable for the X-ray crystal structure analysis were obtained from a solution of the isolated white solid in a mixture of solvents (*n*-pentane: dichloromethane ca. 10 : 1) at −35 °C.

X-ray crystal structure analysis of compound 11b (erk8815): A colorless prism-like specimen of $C_{35}H_{43}BF_5OP$, approximate dimensions 0.180 mm x 0.200 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1461 frames were collected. The total exposure time was 20.29 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 19554 reflections to a maximum θ angle of 66.69° (0.84 Å resolution), of which 5527 were independent (average redundancy 3.538, completeness = 98.9%, R_{int} = 5.25%, R_{sig} = 4.71%) and 4813 (87.08%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 9.8784(7) Å, $\underline{b}$ = 12.2893(9) Å, $\underline{c}$ = 14.1512(11) Å, α = 71.507(4)°, β = 75.714(3)°, γ = 88.224(4)°, volume = 1576.8(2) Å^3, are based upon the refinement of the XYZ-centroids of 8192 reflections above 20 σ(I) with 7.595° < 2θ < 133.1°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.901. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7870 and 0.8060. The final anisotropic full-matrix least-squares refinement on F^2 with 398 variables converged at R1 = 3.78%, for the observed data and wR2 = 9.48% for all data. The goodness-of-fit was 1.052. The largest peak in the final difference electron density synthesis was 0.279 $e^-/Å^3$ and the largest hole was -0.300 $e^-/Å^3$ with an RMS deviation of 0.053 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.298 g/cm^3 and F(000), 652 e^-.

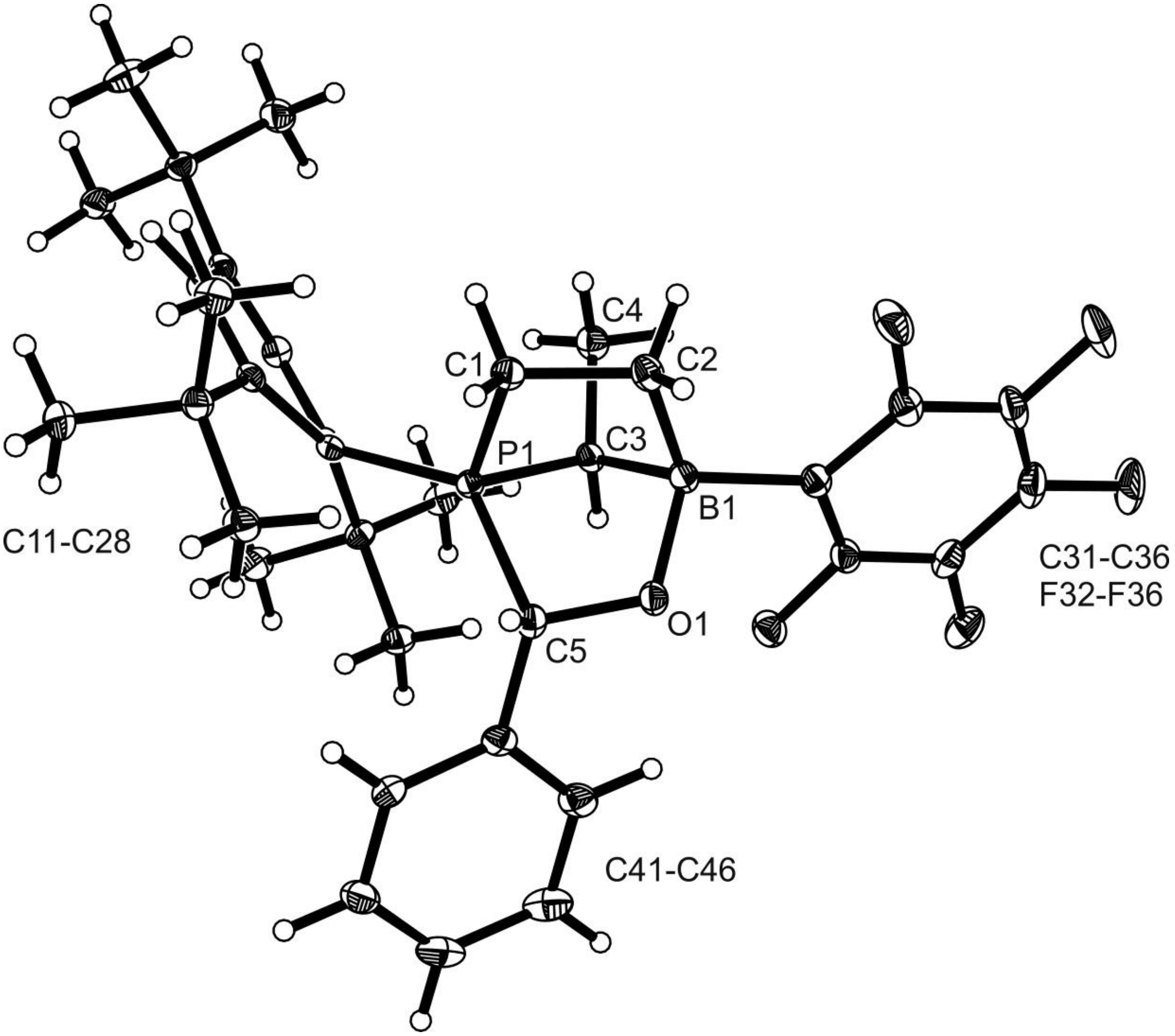
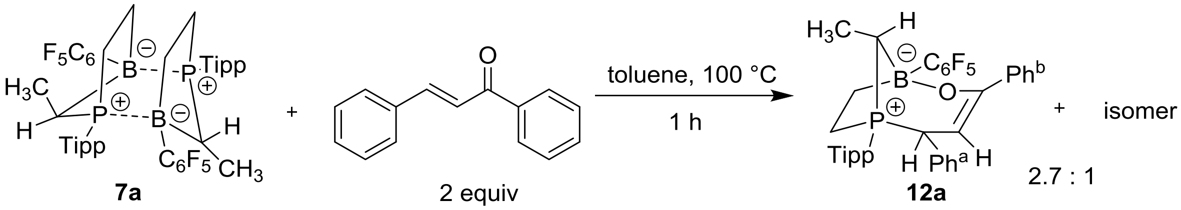


Figure S63 A view of the molecular structure of compound **11b**.

Reaction of dimer 7a with chalcone: synthesis of compounds 12



After (*E*)-chalcone (41.6 mg, 0.2 mmol, 2.0 equiv.) was added to a toluene solution (4 mL) of dimer **7a** (93.6 mg, 0.1 mmol), the reaction mixture was stirred at 100 °C for 1 h. Then all volatiles were removed *in vacuo*. The obtained residue was washed with cold pentane (0 °C, 3×2 mL) and dried *in vacuo,* to finally give a white solid (79.8 mg, 59 %).

Elemental analysis: calc. for $C_{50}H_{62}B_2F_{10}P_2$ (676.56 g mol^{-1}): C, 71.01; H, 6.41. Found: C, 71.61; H, 5.82.

Melting point: 199 °C.

NMR data obtained from a solution of the obtained white solid in CD_2Cl_2 revealed the presence of a mixture of two main isomers of compound **12a** [ca. 73 : 27 (^{1}H NMR) and traces of a component tentatively assigned as a third isomer ca. 1 mol%].

[The NMR resonances of the major component was identified by comparison of the respective spectra of the mixture with those obtained from the crystals of compound **12a** (see page 59ff).]

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2)[selected resonances] (major, **12a**): δ = 5.70 (dd, $^3J_{P\text{-}H}$ =18.4 Hz, $^3J_{H\text{-}H}$ =5.8 Hz, 1H, =CH), 4.52 (dd, $^2J_{P\text{-}H}$ = 15.6 Hz, $^3J_{H\text{-}H}$ = 5.8 Hz, 1H, PhCH), 2.60 (m, 1H, PCH), [2.57, 2.48](each m, each 1H, PCH_2), [1.35, 1.29](each m, each 1H, BCH_2), 0.57 (dd, $^2J_{P\text{-}H}$ =20.4 Hz, $^3J_{H\text{-}H}$ = 7.5 Hz, 3H, Me^{PCH}); (minor): δ = 5.69 (dd, $^3J_{P\text{-}H}$ =23.8 Hz, $^3J_{H\text{-}H}$ =8.7 Hz, 1H, =CH), 4.65 (ddm, $^2J_{P\text{-}H}$ = 19.1 Hz, $^3J_{H\text{-}H}$ = 8.7 Hz, 1H, PhCH), 2.10 (m, 1H, PCH), [3.15, 2.40](each m, each 1H, PCH_2), [1.15, 0.93](each m, each 1H, BCH_2), 0.89 (dd, $^2J_{P\text{-}H}$ =17.2 Hz, $^3J_{H\text{-}H}$ = 6.8 Hz, 3H, Me^{PCH}); (third isomer): δ = 5.88 (dd, $^3J_{P\text{-}H}$ =19.3 Hz, $^3J_{H\text{-}H}$ = 8.5 Hz, 1H, =CH), 4.52 (dd, $^2J_{P\text{-}H}$ = 18.5 Hz, $^3J_{H\text{-}H}$ = 8.5 Hz, 1H, PhCH), 2.82 (m, 1H, PCH), 0.74 (dd, $^2J_{P\text{-}H}$ =20.0 Hz, $^2J_{H\text{-}H}$ = 7.3 Hz, 3H, Me^{PCH}).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2)[selected resonances] (major, **12a**): δ = 159.5 (d, $^3J_{P\text{-}C}$ = 5.5 Hz, =CPh), 139.3 (d, $^4J_{P\text{-}C}$ = 2.1 Hz, i-Ph^b), 137.8 (d, $^2J_{P\text{-}C}$ = 5.9 Hz, i-Ph^a), 118.1 (d, $^1J_{P\text{-}C}$ = 57.4 Hz, *i*-Tipp), 101.0 (d, $^2J_{P\text{-}C}$ = 5.3 Hz, =CH), 45.4 (d, $^1J_{P\text{-}C}$ = 36.0 Hz, PhCH), 28.5 (br, PCH), 24.0 (d, $^1J_{P\text{-}C}$ = 51.0 Hz, PCH_2), 17.1 (br, BCH_2), 13.0 (d, $^2J_{P\text{-}C}$ = 5.8 Hz, Me^{PCH}); (minor): δ = 162.9 (d, $^3J_{P\text{-}C}$ = 3.4 Hz, =CPh), 141.7 (d, $^4J_{P\text{-}C}$ = 1.6 Hz, i-Ph^b), 135.6 (d, $^2J_{P\text{-}C}$ = 3.8 Hz, i-Ph^A), 121.9 (d, $^1J_{P\text{-}C}$ = 53.2 Hz, *i*-Tipp), 95.8 (d, $^2J_{P\text{-}C}$ = 4.4 Hz, =CH), 43.6 (d, $^1J_{P\text{-}C}$ = 37.5 Hz, PhCH), 31.4 (br, PCH), 32.8 (d, $^1J_{P\text{-}C}$ = 61.4 Hz, PCH_2), 15.6 (br, BCH_2), 10.4 (d, $^2J_{P\text{-}C}$ = 4.3 Hz, Me^{PCH}), [C_6F_5 not listed].

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = 59.8 ($\nu_{1/2}$ ~ 15 Hz, 73 mol%, **12a**); 47.0 ($\nu_{1/2}$ ~ 10 Hz, 27 mol%).

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 5.3 ($\nu_{1/2}$ ~ 130 Hz, minor); 3.9 ($\nu_{1/2}$ ~ 130 Hz, **12a**).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = (73 mol%, 12a): −132.5 (br m, 2F, *o*-C_6F_5), −161.7 (t, $^3J_{F\text{-}F}$ = 20.2 Hz, 1F, *p*-C_6F_5), −165.7 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 4.0]; (27 mol%): −134.8 (m, 2F, *o*-C_6F_5), −162.6 (t, 1F, $^3J_{F\text{-}F}$ = 20.3 Hz, *p*-C_6F_5), −166.2 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 3.6].

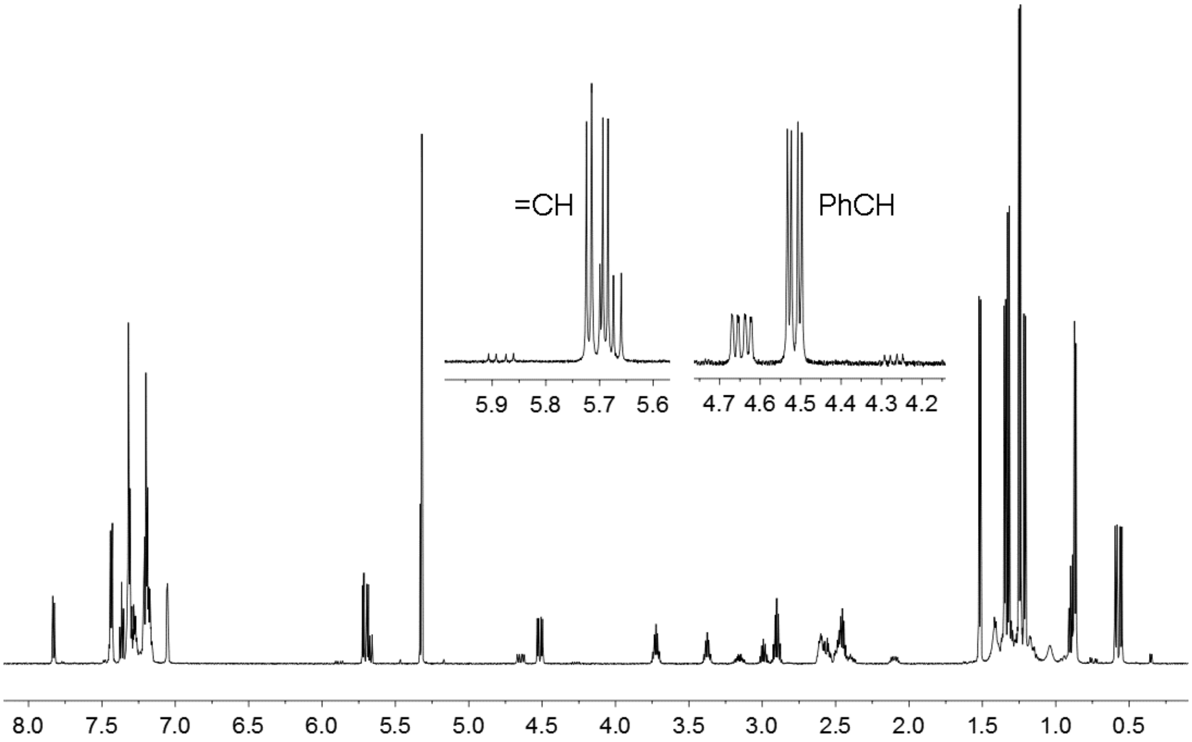


Figure S64 ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of the obtained white solid.

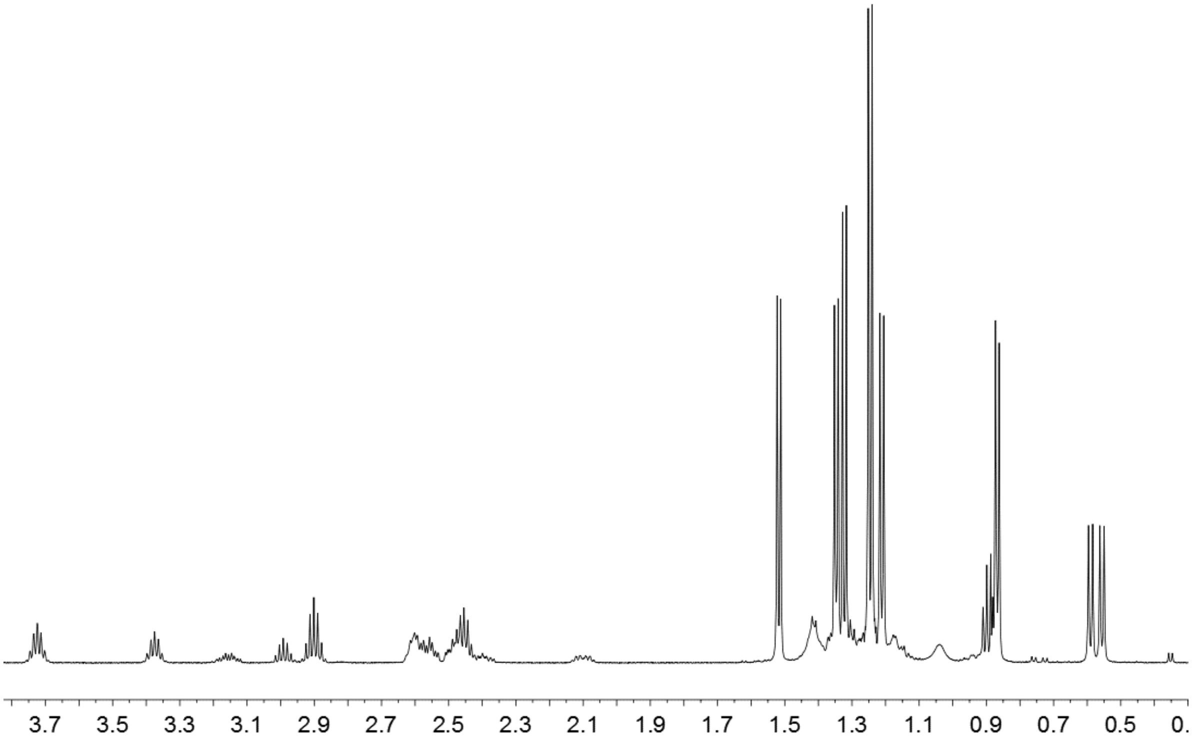


Figure S65 ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of the obtained white solid.

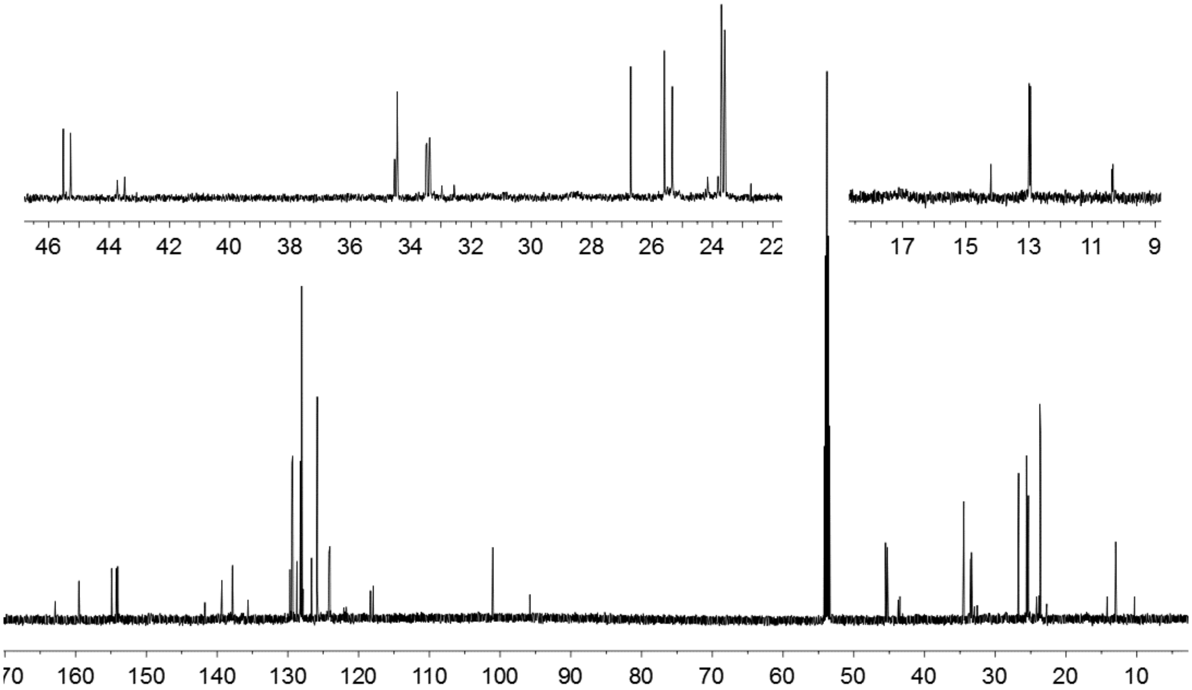


Figure S66 $^{13}C\{^1H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of the obtained white solid.

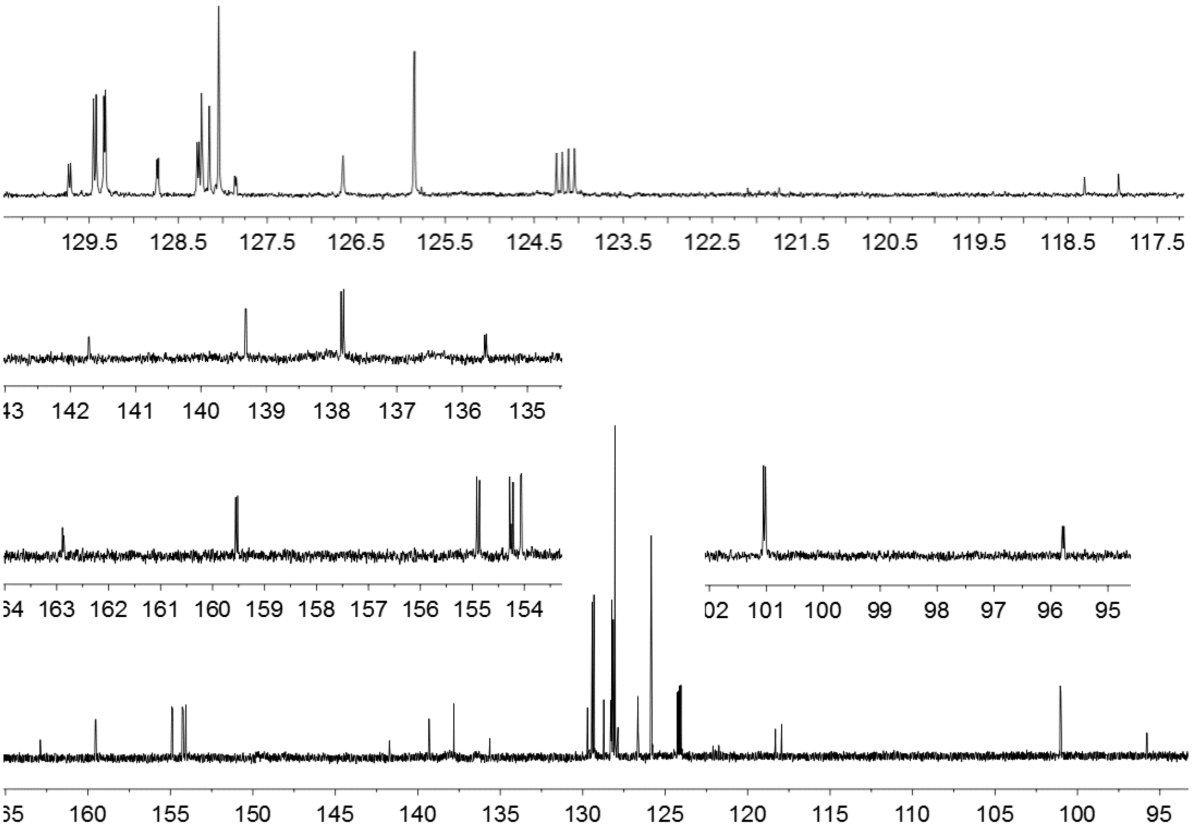


Figure S67 $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of the obtained white solid.

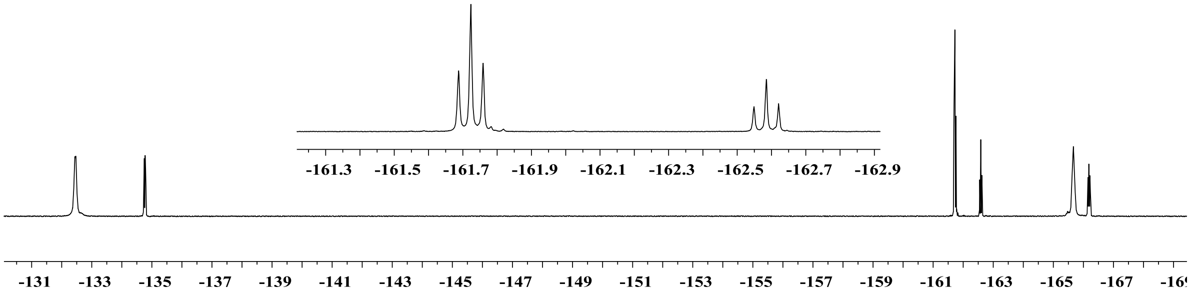


Figure S68 ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of obtained white solid.

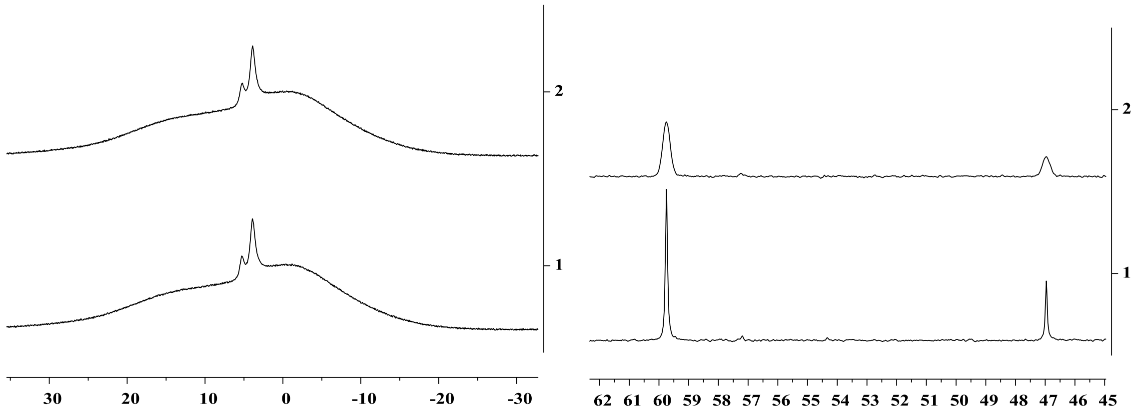


Figure S69 $^{11}B\{^{1}H\}$ (left, 1), ^{11}B (left, 2) NMR (192 MHz, 299 K, CD_2Cl_2) and $^{31}P\{^{1}H\}$ (right, 1), ^{31}P (right, 2) NMR (243 MHz, 299 K, CD_2Cl_2) spectra of obtained white solid.

Crystals of compound **12a** suitable for the X-ray crystal structure analysis were obtained from a solution of the isolated white solid in a mixture of solvents (pentane and dichloromethane ca. 10 : 1) at −35 °C.

X-ray crystal structure analysis of compound 12a (erk8718): A colorless plate-like specimen of $C_{40}H_{43}BF_5OP$, approximate dimensions 0.076 mm x 0.214 mm x 0.254 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 468 frames were collected. The total exposure time was 7.80 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 23118 reflections to a maximum θ angle of 25.42° (0.83 Å resolution), of which 6310 were independent (average redundancy 3.664, completeness = 99.0%, R_{int} = 9.99%, R_{sig} = 8.72%) and 4168 (66.05%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.3401(14) Å, b = 12.3804(15) Å, c = 13.2251(16) Å, α = 80.247(4)°, β = 71.021(4)°, γ = 87.949(4)°, volume = 1730.1(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 4017 reflections above 20 σ(I) with 5.006° < 2θ < 49.40°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.902. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9660 and 0.9900. The final anisotropic full-matrix least-squares refinement on F^2 with 440 variables converged at R1 = 5.32%, for the observed data and wR2 = 10.91% for all data. The goodness-of-fit was 1.007. The largest peak in the final difference electron density synthesis was 0.474 e^{-}/Å^{3} and the largest hole was -0.349 e^{-}/Å^{3} with an RMS deviation of 0.060 e^{-}/Å^{3}. On the basis of the final model, the calculated density was 1.299 g/cm^{3} and F(000), 712 e^{-}.

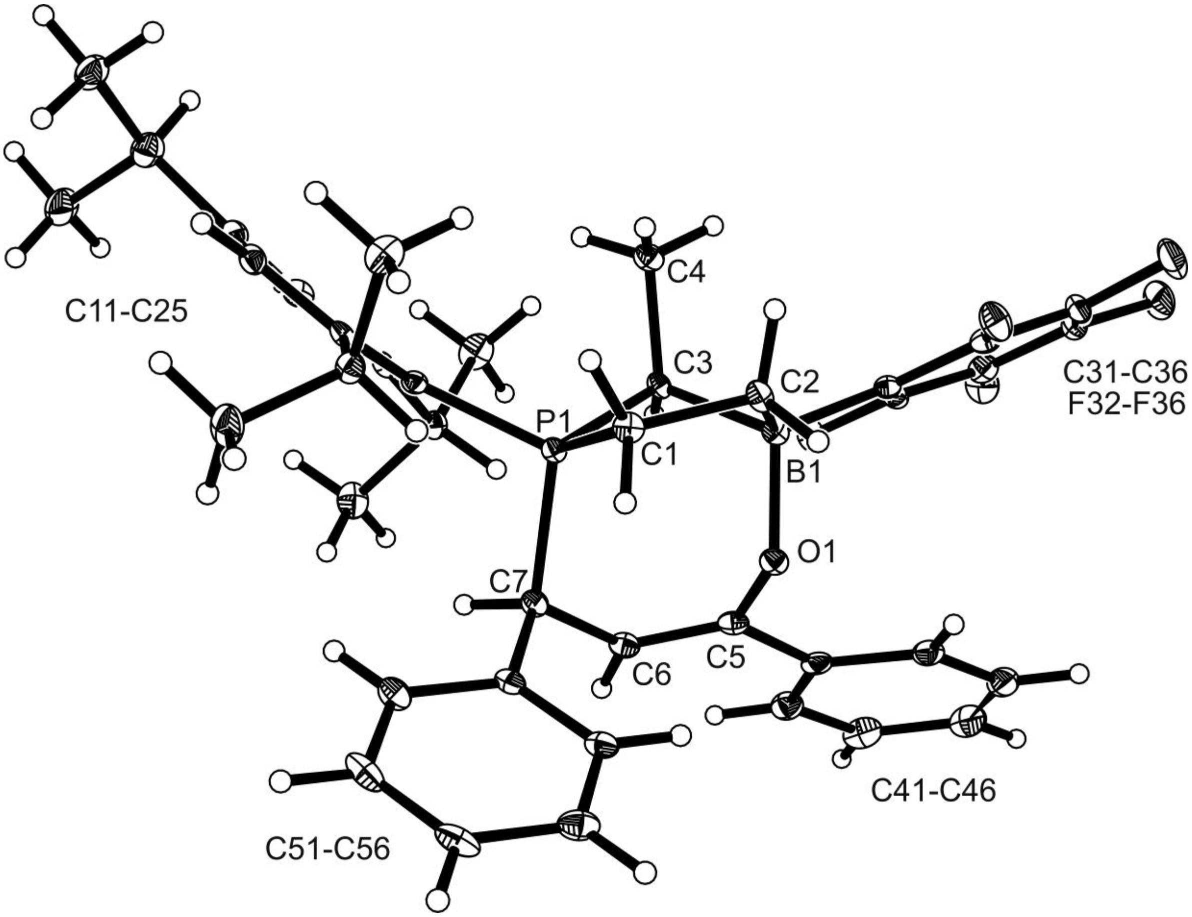


Figure S70 A view of the molecular structure of compound **12a**.

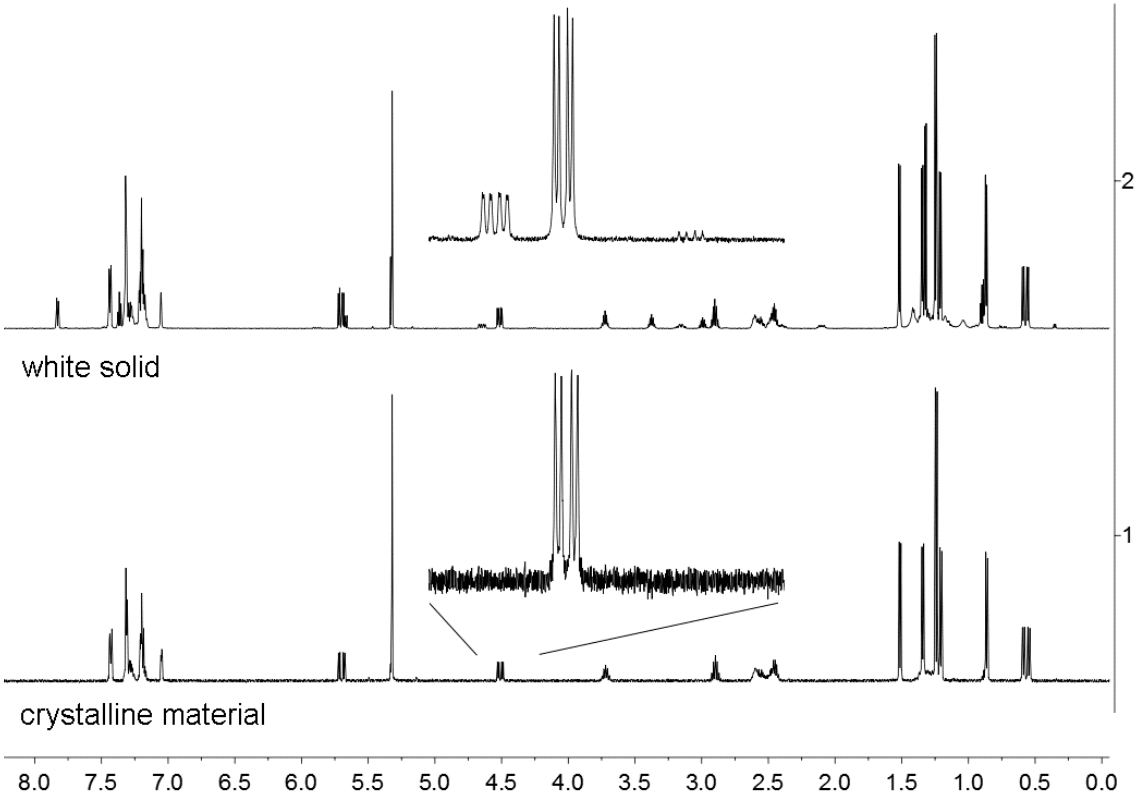


Figure S71 (1) ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of compound **12a** (crystalline material, see above) and (2) ^{1}H NMR (600 MHz) spectrum of the isolated white solid (see page 55ff).

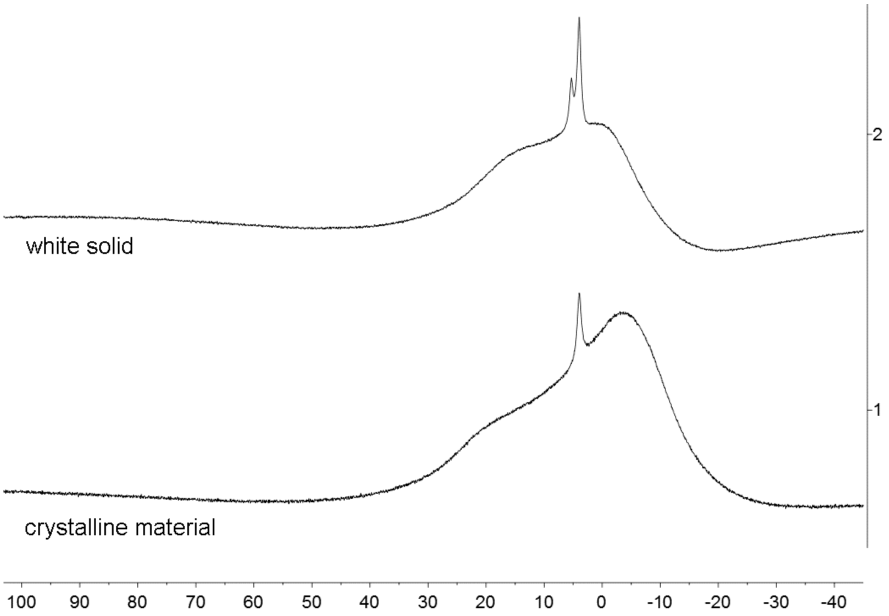


Figure S72 (1) $^{11}B\{^1H\}$ NMR (160 MHz, 299 K, CD_2Cl_2) spectrum of compound **12a** (crystalline material, see above) and (2) $^{11}B\{^1H\}$ NMR (192 MHz) spectrum of the isolated white solid (see page 55ff).

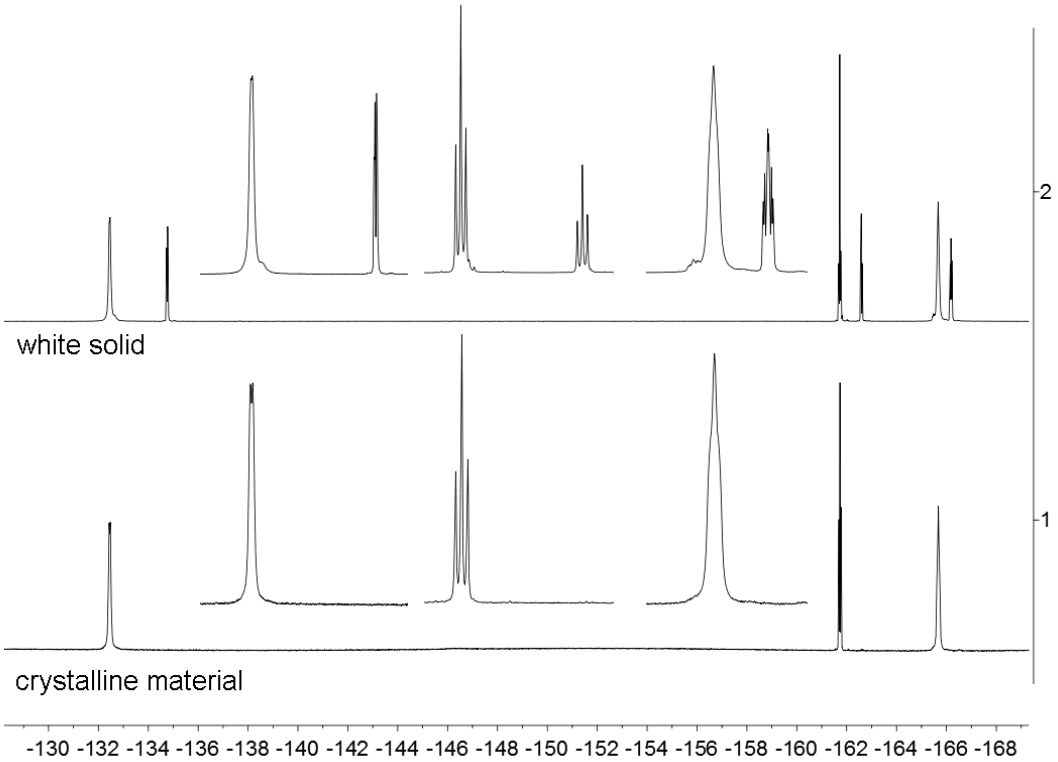


Figure S73 (1) ^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) spectrum of compound **12a** (crystalline material, see above) and (2) ^{31}P{^{1}H} NMR (564 MHz) spectrum of the isolated white solid (see page 55ff).

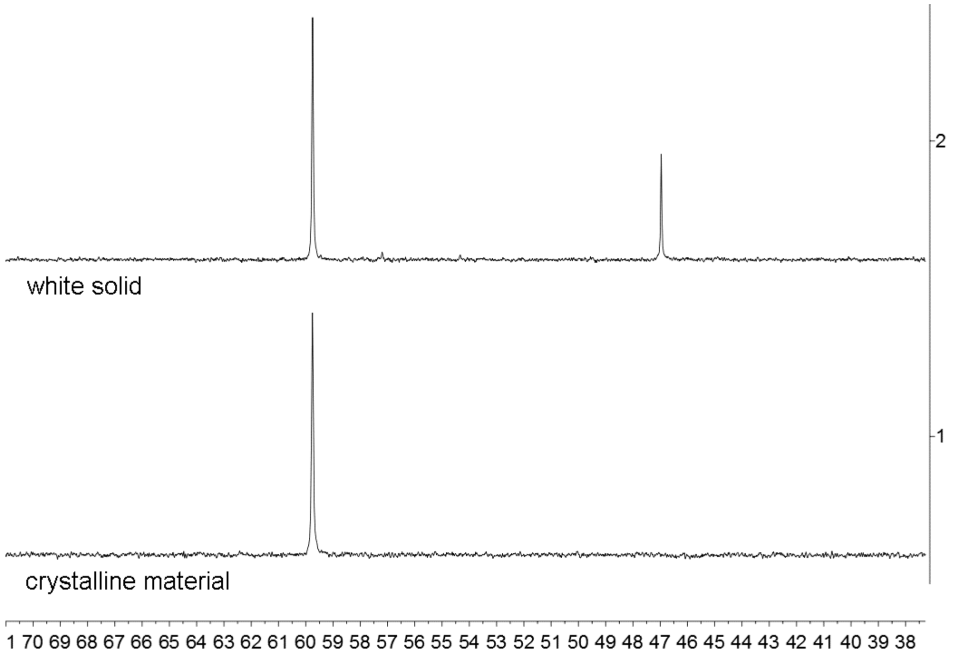
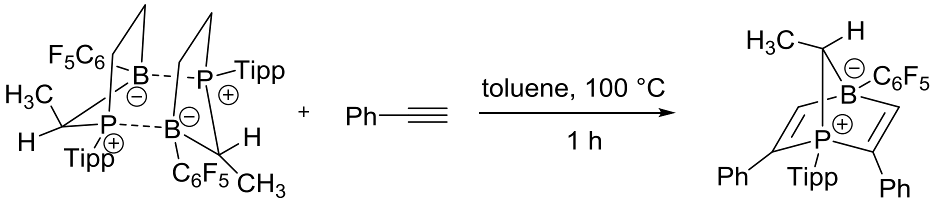


Figure S74 (1) ^{31}P{^{1}H} NMR (202 MHz, 299 K, CD_2Cl_2) spectrum of compound **12a** (crystalline material, see above) and (2) ^{31}P{^{1}H} NMR (243 MHz) spectrum of the isolated white solid (see page 55ff).

Reaction of dimer 7a with phenylacetylene: synthesis of compound 15a.



7a **15a**

Phenylacetylene (408.4 mg, 4 mmol, 40.0 equiv.) was added to a toluene solution (4 mL) of dimer **7a** (93.6 mg, 0.1 mmol) by cannula under an argon atmosphere. The reaction mixture was stirred at 100 °C for 1 h and then all volatiles were removed *in vacuo*. The obtained residue was dissolved in pentane and stored at –35 °C for 48 hours to give colorless crystals, which were collected by filtration (22.9 mg, 20%).

Elemental analysis: calc. for $C_{39}H_{39}BF_5P$ (644.28 g mol^{-1}): C, 72.68; H, 6.10; Found: C, 72.05; H, 6.23.

Melting point: 227 °C.

^{1}H NMR (500 MHz, 288 K, toluene-d_8)[selected resonances]: δ = [8.79 (d, $^3J_{P\text{-}H}$ = 48.4 Hz, 1H), 8.61 (d, $^3J_{P\text{-}H}$ = 43.5 Hz, 1H)](=CH), [7.17, 6.91](each br m, each 1H, *m*-Tipp), [3.91 (br m, 1H), 1.22, 1.06 (each d, $^3J_{H\text{-}H}$ = 6.5 Hz, each 3H)](*o*-^{i}Pr), 3.35 (m, 1H, PCH), [2.81 (br m, 1H), 0.32, 0.16 (each d, $^3J_{H\text{-}H}$ = 6.4 Hz, each 3H)](*o*-^{i}Pr), [2.59 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 1H), 1.061, 1.059 (each d, $^3J_{H\text{-}H}$ = 6.9 Hz, each 3H)](*p*-^{i}Pr), 1.39 (dd, $^3J_{P\text{-}H}$ = 21.5 Hz, $^3J_{P\text{-}H}$ = 14.9 Hz, Me^{PCH}).

^{13}C{^{1}H} NMR (126 MHz, 288 K, toluene-d_8)[selected resonances]: δ = 177.4 (br, =CH), [155.9 (d, $^2J_{P\text{-}C}$ = 7.2 Hz), 155.0 (d, $^2J_{P\text{-}C}$ = 11.1 Hz)](*o*-Tipp), 154.5 (d, $^4J_{P\text{-}C}$ = 2.9 Hz, *p*-Tipp), [141.6 (d, $^1J_{P\text{-}C}$ = 73.3 Hz), 138.7 (d, $^1J_{P\text{-}C}$ = 70.3 Hz)](PC=), [139.8, 138.1](each d, $^2J_{P\text{-}C}$ =15.0 Hz, *i*-Ph), [124.1 (d, $^3J_{P\text{-}C}$ = 10.5 Hz), 123.1 (d, $^3J_{P\text{-}C}$ = 10.0 Hz)](*m*-Tipp), 115.6 (d, $^3J_{P\text{-}C}$ = 52.8 Hz, *i*-Tipp), 76.8 (br, PCH), [34.4, 23.52, 23.50](*p*-^{i}Pr), [34.0, 25.8, 23.7](*o*-^{i}Pr), [31.9, 26.0, 24.0](*o*-^{i}Pr), 12.4 (d, $^2J_{P\text{-}C}$ = 3.1 Hz, Me^{PCH}).

^{31}P{^{1}H} NMR (202 MHz, 288 K, toluene-d_8): δ = 29.7 (partially relaxed 1:1:1:1 q, $J_{P\text{-}B}$ ~ 20 Hz).

^{11}B{^{1}H} NMR (160 MHz, 288 K, toluene-d_8): δ = –7.5 (d, $J_{P\text{-}B}$ ~ 20 Hz).

^{19}F NMR (470 MHz, 288 K, toluene-d_8): δ = −133.8 (m, 2F, *o*-C_6F_5), −159.8 (t, $^3J_{F\text{-}F}$ = 20.4 Hz, 1F, *p*-C_6F_5), −164.5 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 4.7].

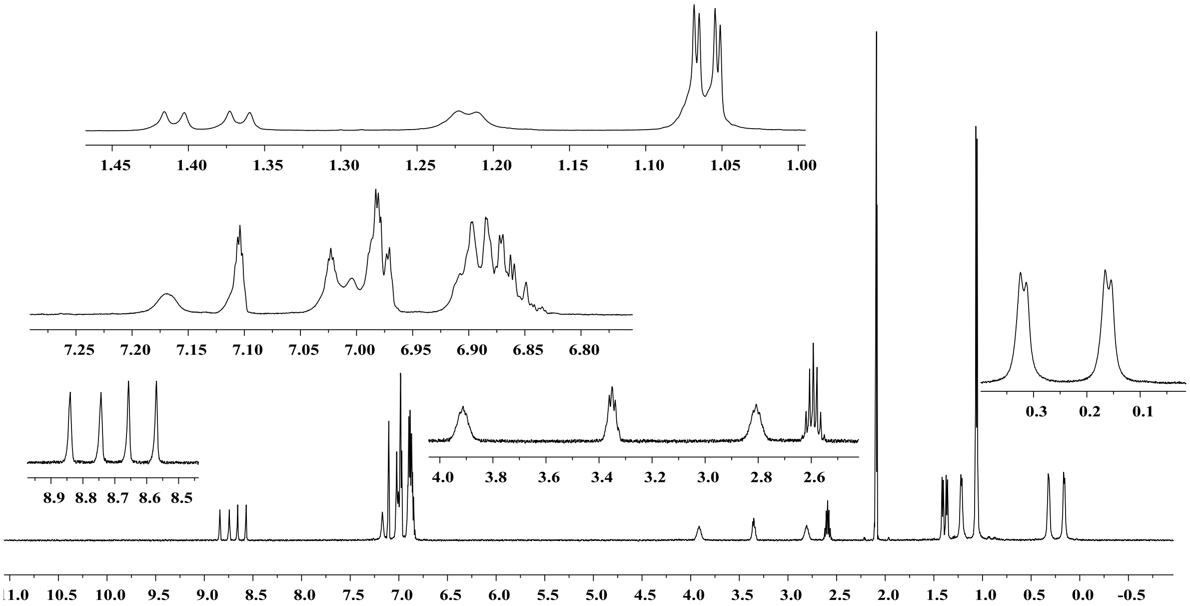


Figure S75 ^{1}H NMR (500 MHz, 288 K, toluene-d_8) spectrum of compound **15a**.

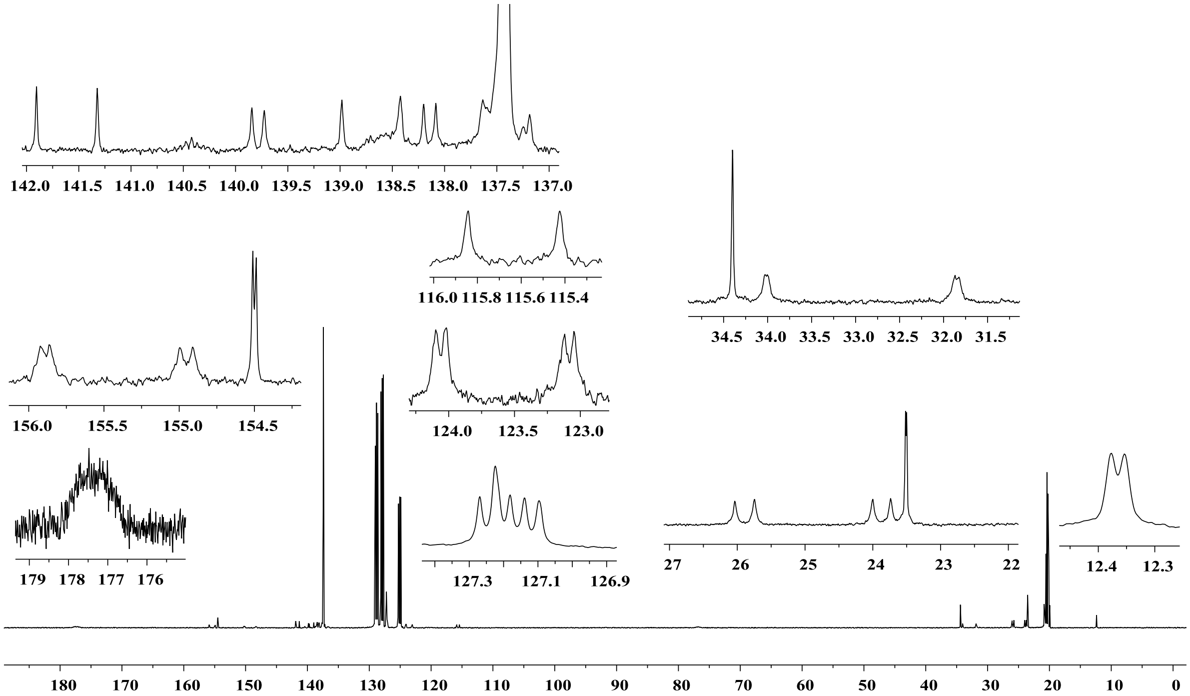


Figure S76 ^{13}C{^{1}H} NMR (126 MHz, 288 K, toluene-d_8) spectrum of compound **15a**.

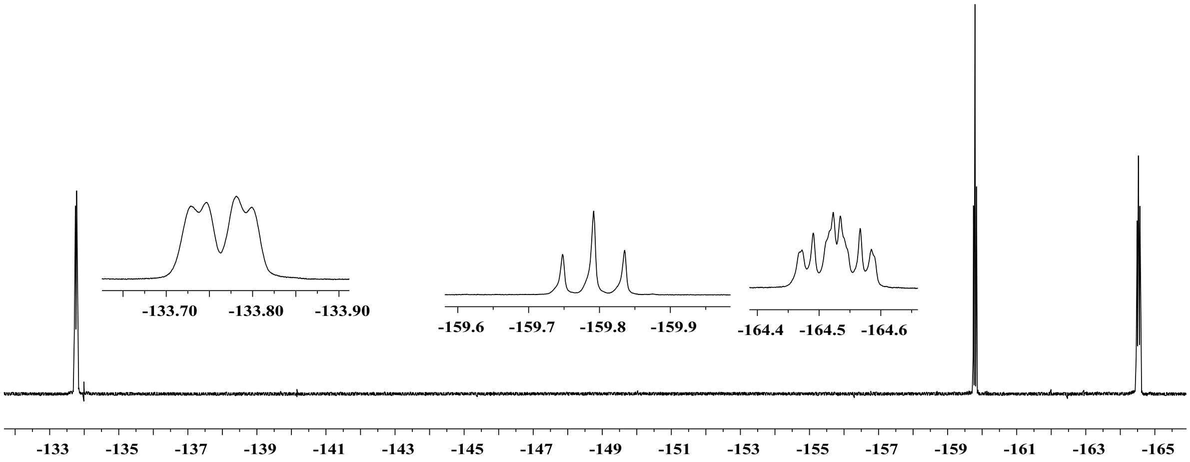


Figure S77 ^{19}F NMR (470 MHz, 288 K, toluene-*d*$_8$) spectrum of compound **15a**.

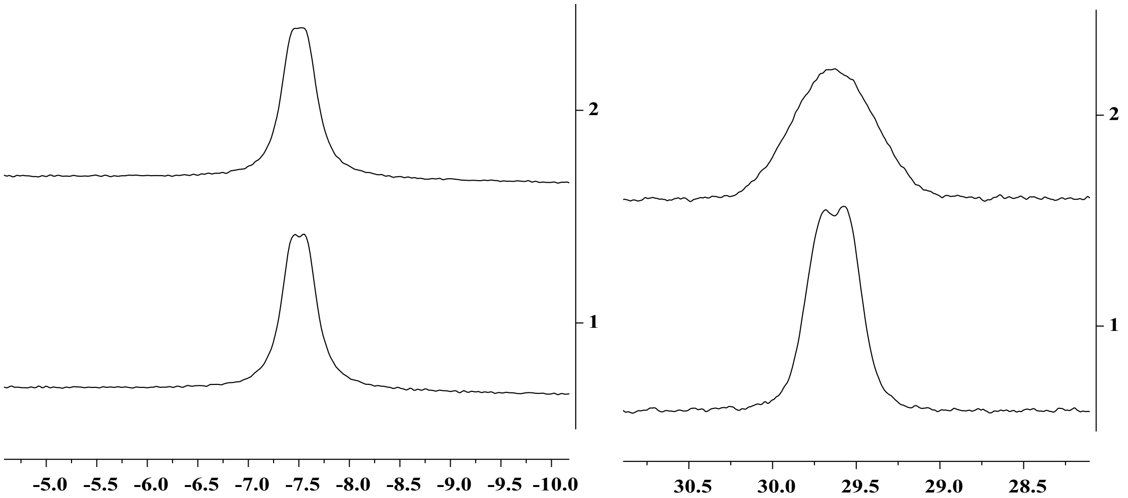


Figure S78 ^{11}B{^{1}H} (left, 1), ^{11}B (left, 2) NMR (160 MHz, 288 K, toluene-*d*$_8$) and ^{31}P{^{1}H} (right, 1), ^{31}P (right, 2) NMR (202 MHz, 288 K, toluene-*d*$_8$) spectra of compound **15a**.

Crystals of compound **15a** suitable for the X-ray crystal structure analysis were obtained from a solution of compound **15a** in a mixture of solvents (*n*-pentane : dichloromethane ca. 15 : 1) at −35 °C.

X-ray crystal structure analysis of compound 15a (erk8643): A colorless prism-like specimen of $C_{39}H_{39}BF_5P$, approximate dimensions 0.107 mm x 0.116 mm x 0.174 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 505 frames were collected. The total exposure time was 11.22 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 27053 reflections to a maximum θ angle of 25.36° (0.83 Å resolution), of which 6033 were independent (average redundancy 4.484, completeness = 99.7%, R_{int} = 8.82%, R_{sig} = 6.75%) and 4440 (73.60%) were greater than 2σ(F^2). The final cell constants of <u>a</u> = 10.1084(8) Å, <u>b</u> = 12.6426(9) Å, <u>c</u> = 13.2320(11) Å, α = 94.185(3)°, β = 92.423(3)°, γ = 101.427(3)°, volume = 1650.3(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 6380 reflections above 20 σ(I) with 5.004° < 2θ < 50.61°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.778. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9760 and 0.9850. The final anisotropic full-matrix least-squares refinement on F^2 with 422 variables converged at R1 = 4.85%, for the observed data and wR2 = 11.41% for all data. The goodness-of-fit was 1.020. The largest peak in the final difference electron density synthesis was 0.403 $e^-/Å^3$ and the largest hole was -0.357 $e^-/Å^3$ with an RMS deviation of 0.058 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.297 g/cm^3 and F(000), 676 e^-.

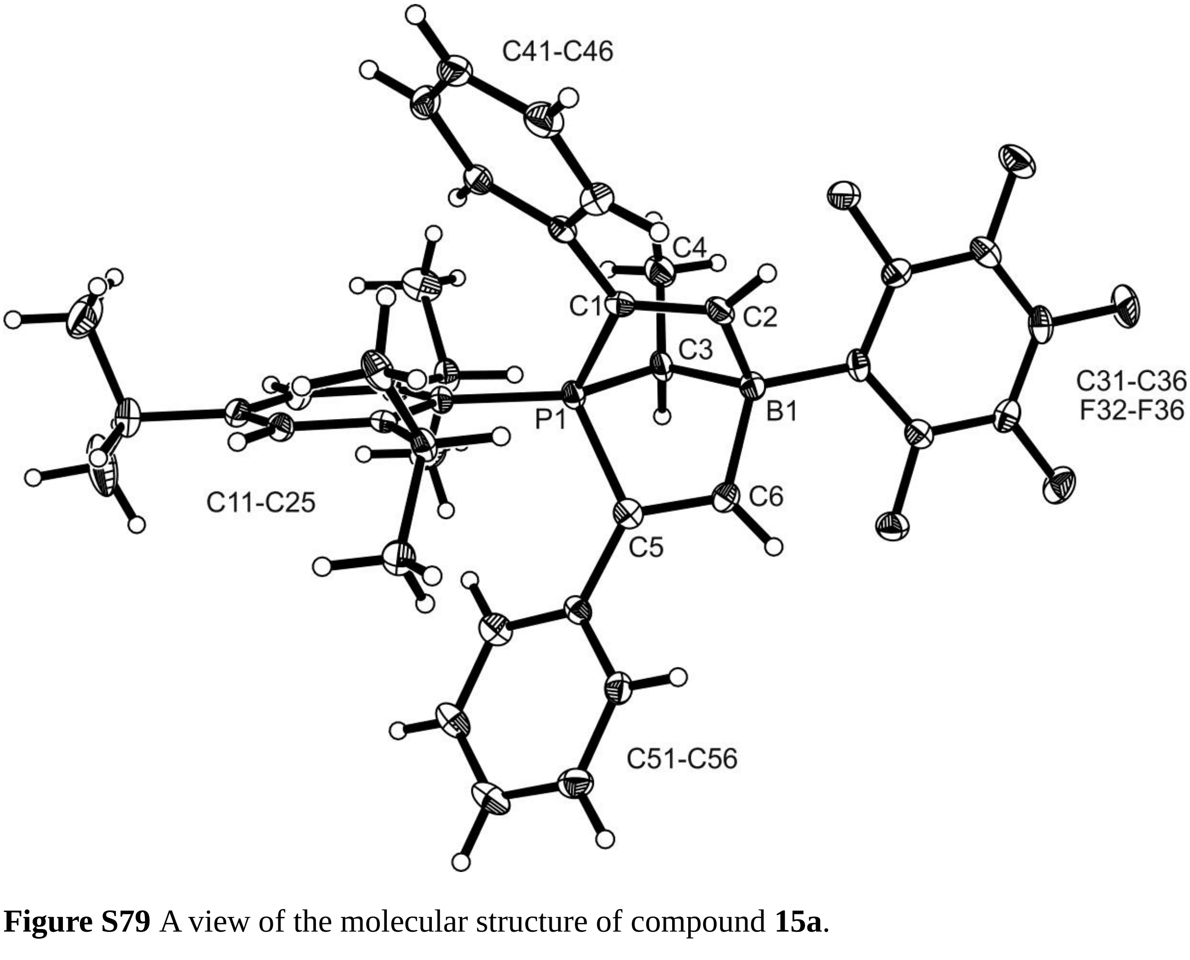
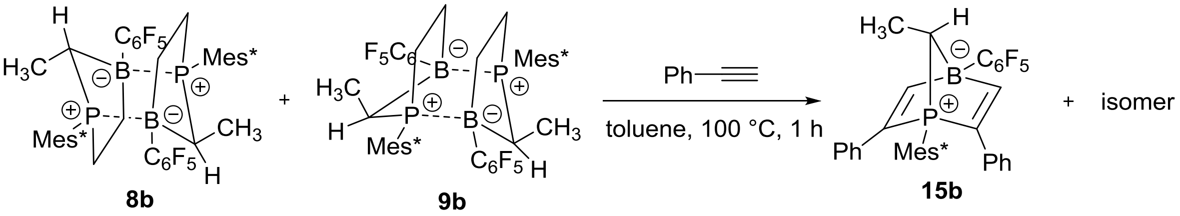


Figure S79 A view of the molecular structure of compound **15a**.

Reaction of dimers 8b/9b with phenylacetylene: synthesis of compounds 15b.



Phenylacetylene (408.4 mg, 4 mmol, 40.0 equiv.) was added to a toluene solution (4 mL) of the dimers **8b**/**9b** (102.0 mg, 0.1 mmol) by cannula under an argon atmosphere. The reaction mixture was stirred at 100 °C for 1 h and then all volatiles were removed *in vacuo*. The obtained residue was dissolved in pentane and stored at –35 °C for 48 hours to give colorless crystals, which was collected by filtration (49.4 mg, 40%)

Elemental analysis: calc. for $C_{42}H_{45}BF_5P$ (686.33 g mol^{-1}): C, 73.47; H, 6.61; Found: C, 73.65; H, 6.61.

Melting point: 194 °C.

NMR data obtained from a solution of the obtained crystalline material in CD_2Cl_2 revealed the presence of a mixture of two main isomers of compound **15b** [ca. 78 : 22 (^{1}H NMR)].

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2)[selected resonances] δ = (78 mol%) [8.80 (d, $^{3}J_{\text{P-H}}$ = 44.6 Hz, 1H), 8.11 (d, $^{3}J_{\text{P-H}}$ = 49.4 Hz, 1H)](=CH), [7.76, 7.32](each m, each 1H, *m*-Mes*), 3.38 (m, 1H, PCH), [1.65, 0.72](each s, each 9H, *o*-^{t}Bu), 1.41 (s, 9H, *p*-^{t}Bu), 0.93 (dd, $^{3}J_{\text{P-H}}$ = 21.2 Hz, $^{3}J_{\text{H-H}}$ = 6.2 Hz, 3H, Me$^{\text{PCH}}$); (22 mol%) [8.35 (d, $^{3}J_{\text{P-H}}$ = 45.7 Hz, 1H), 8.32 (d, $^{3}J_{\text{P-H}}$ = 51.4 Hz, 1H)](=CH), [7.40, 7.27](each m, each 1H, *m*-Mes*), 3.52 (br, 1H, PCH), 1.35 (dd, $^{3}J_{\text{P-H}}$ = 20.4 Hz, $^{3}J_{\text{H-H}}$ = 6.5 Hz, 3H, Me$^{\text{PCH}}$), 1.43 (s, 9H, *p*-^{t}Bu), [1.05, 0.88](each s, each 9H, *o*-^{t}Bu).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2)[selected resonances]: δ = (78 mol%) [177.0 (br), 174.6 (br)](=CH), [161.2 (d, $^{2}J_{\text{P-C}}$ = 7.1 Hz), 160.0 (d, $^{2}J_{\text{P-C}}$ = 4.6 Hz)](*o*-Mes*), 154.6 (d, $^{4}J_{\text{P-C}}$ = 4.0 Hz, *p*-Mes*), [143.5 (d, $^{1}J_{\text{P-C}}$ = 74.1 Hz), 138.0 (d, $^{1}J_{\text{P-C'}}$ = 68.7 Hz)](PC=), [126.5 (d, $^{3}J_{\text{P-C}}$ = 11.7 Hz), 125.5 (d, $^{3}J_{\text{P-C}}$ = 11.1 Hz)](*m*-Mes*), [140.5 (d, $^{2}J_{\text{P-C}}$ = 13.9 Hz), 137.9 (d, $^{2}J_{\text{P-C}}$ = 12.0 Hz)](*i*-Ph), 109.4 (d, $^{1}J_{\text{P-C}}$ = 53.2 Hz, *i*-Mes*), 75.8 (br, PCH), [41.3 (d, $^{3}J_{\text{P-C}}$ = 3.0 Hz), 34.5](*o*-^{t}Bu), [41.6 (d, $^{3}J_{\text{P-C}}$ = 2.0 Hz), 31.9](*o*-^{t}Bu), [35.2 (d, $^{3}J_{\text{P-C}}$ = 1.3 Hz), 31.1](*p*-^{t}Bu), 13.2 (d, $^{2}J_{\text{P-C}}$ = 1.3 Hz, Me$^{\text{PCH}}$); (22 mol%) [178.2 (br), 177.4 (br)](=CH), [164.44, 164.37](each d, $^{2}J_{\text{P-C}}$ = 4.4 Hz, *o*-Mes*), 154.7 (d, $^{4}J_{\text{P-C}}$ = 4.4 Hz, *p*-Mes*), [141.6 (d, $^{1}J_{\text{P-C}}$ = 70.0 Hz), 147.2 (d, $^{1}J_{\text{P-C'}}$ = 73.9 Hz)](PC=), [138.6 (d, $^{2}J_{\text{P-C}}$ = 14.4 Hz), 137.3 (d, $^{2}J_{\text{P-C}}$ = 13.4 Hz)](*i*-Ph), [124.7 (d, $^{3}J_{\text{P-C}}$ = 11.6 Hz), 125.1 (d, $^{3}J_{\text{P-C}}$ = 11.1 Hz)](*m*-Mes*), 105.0 (d, $^{1}J_{\text{P-C}}$ = 54.1 Hz, *i*-Mes*), 66.2 (br, PCH), [42.7 (d, $^{3}J_{\text{P-C}}$ = 2.5 Hz), 32.0](*o*-^{t}Bu), [42.5 (d, $^3J_{P\text{-}C}$ = 2.4 Hz), 33.5](*o*-^{t}Bu), [35.2 (d, *J* = 1.3 Hz), 31.2](*p*-^{t}Bu), 15.4 (d, $^2J_{P\text{-}C}$ = 4.2 Hz, Me^{PCH}).

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = 40.8 (partially relaxed 1:1:1:1 q, $J_{P\text{-}B}$ ~ 30 Hz, 23 mol%); 39.2 (partially relaxed 1:1:1:1 q, $J_{P\text{-}B}$ ~ 30 Hz, 77 mol%).

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = −8.8 (d, $J_{P\text{-}B}$ ~ 30, major), −9.9 (d, $J_{P\text{-}B}$ ~ 30 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = (23 mol%) −134.4 (m, 2F, *o*-C_6F_5), −161.1 (t, $^3J_{F\text{-}F}$ = 20.6 Hz, 1F, *p*-C_6F_5), −166.0 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 4.9]; (77 mol%) −134.6 (m, 2F, *o*-C_6F_5), −161.1 (t, $^3J_{F\text{-}F}$ = 20.6 Hz, 1F, *p*-C_6F_5), −165.9 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 4.8].

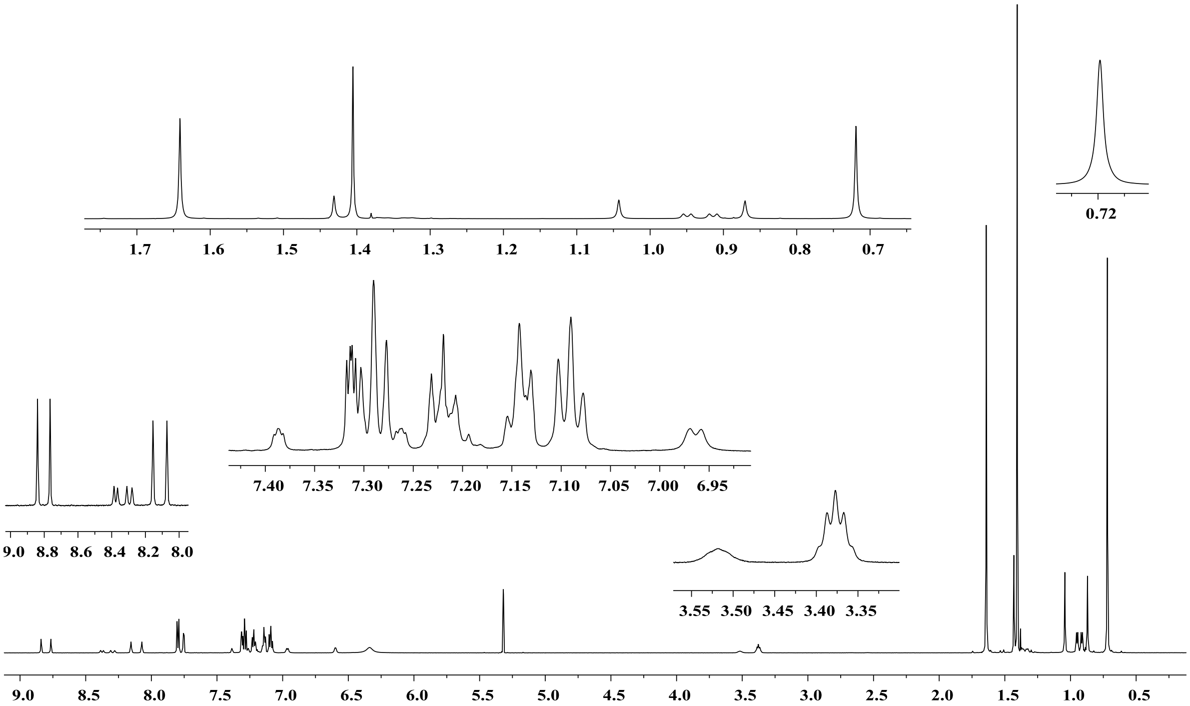


Figure S80 ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of the cystalline material.

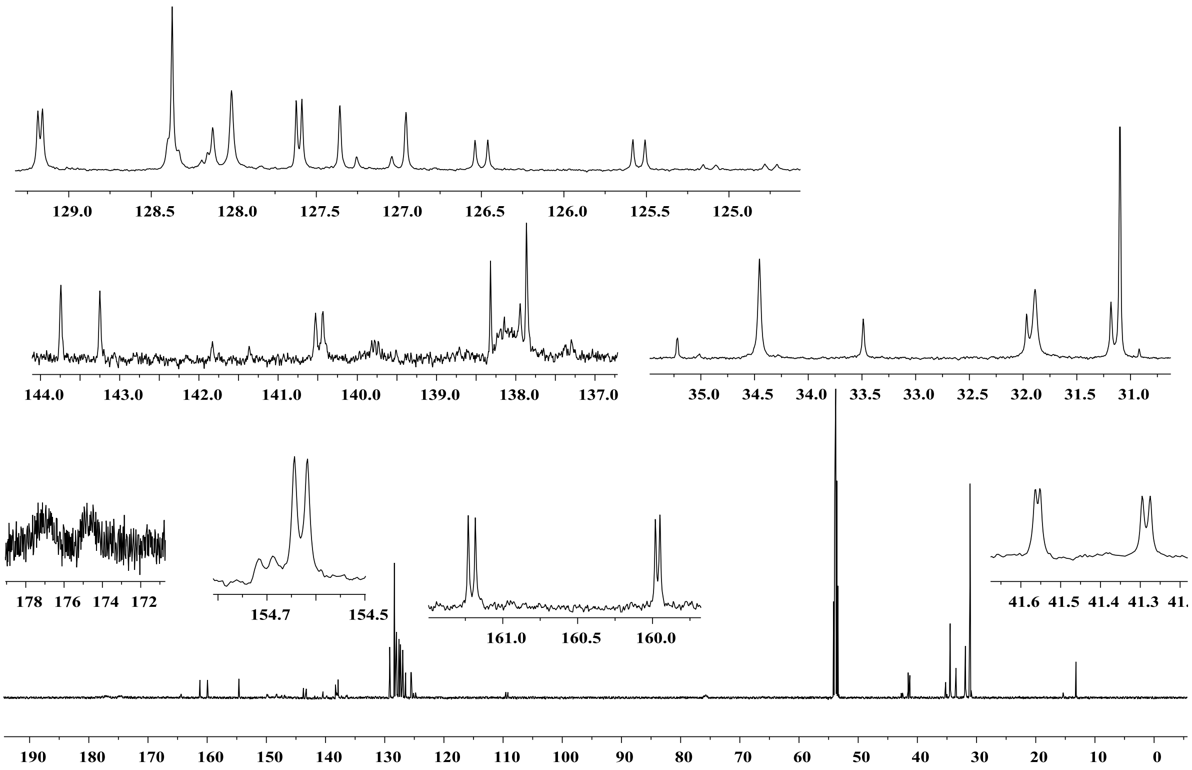


Figure S81 $^{13}C\{^1H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of the cystalline material.

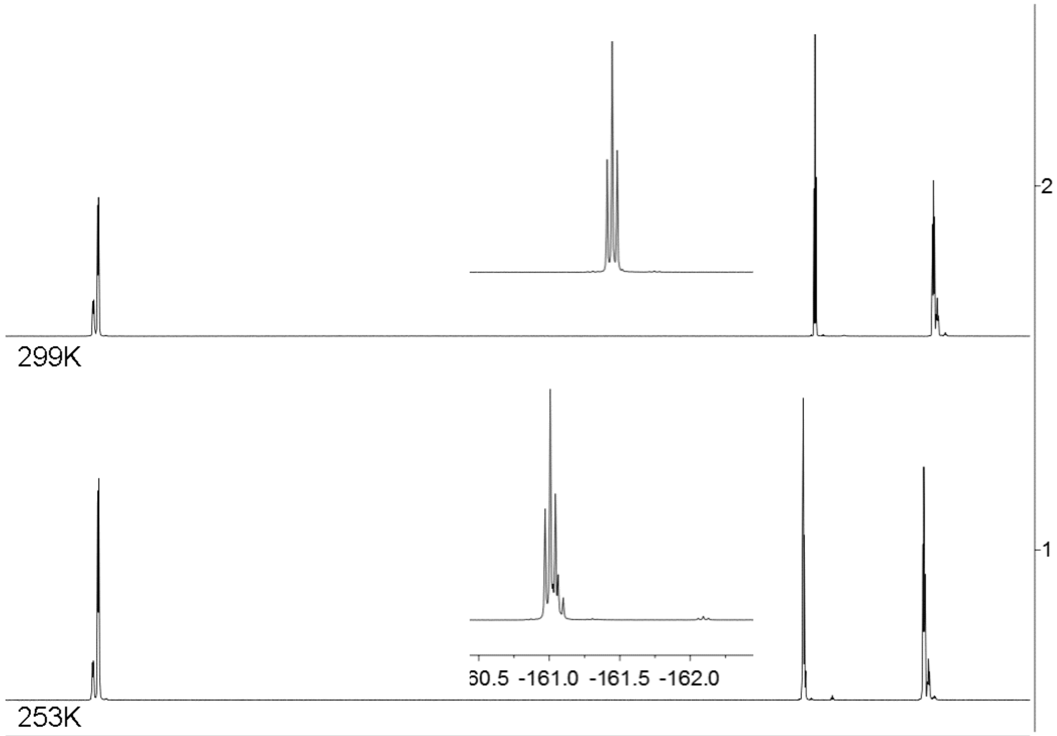


Figure S82 ^{19}F NMR (564 MHz, CD_2Cl_2) spectrum of the cystalline material at (1) 253K and (2) 299K.

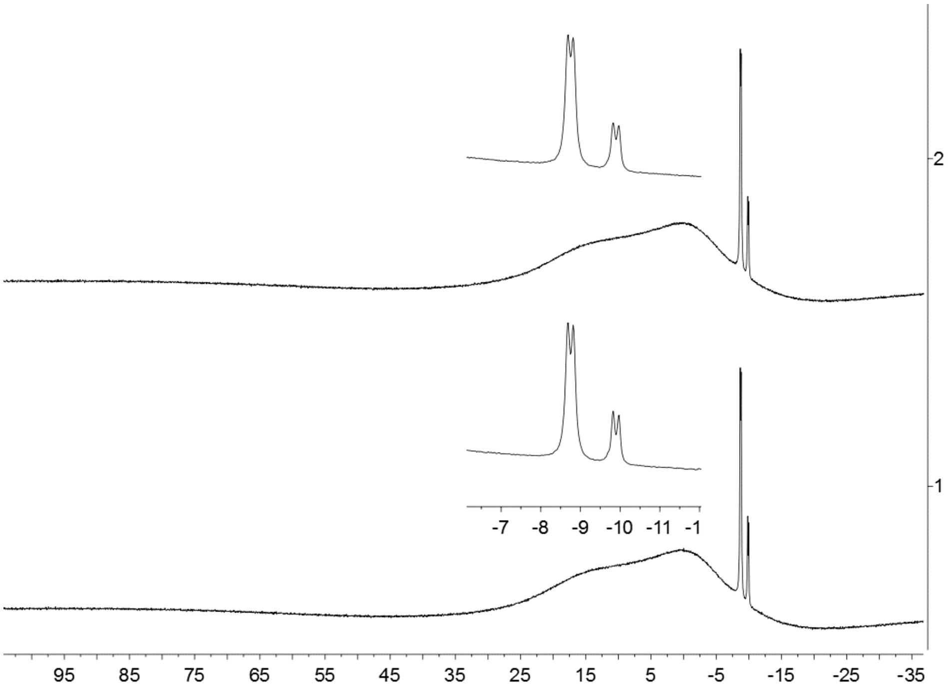


Figure S83 (1) $^{11}B\{^1H\}$ and (2) ^{11}B NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of the cystalline material.

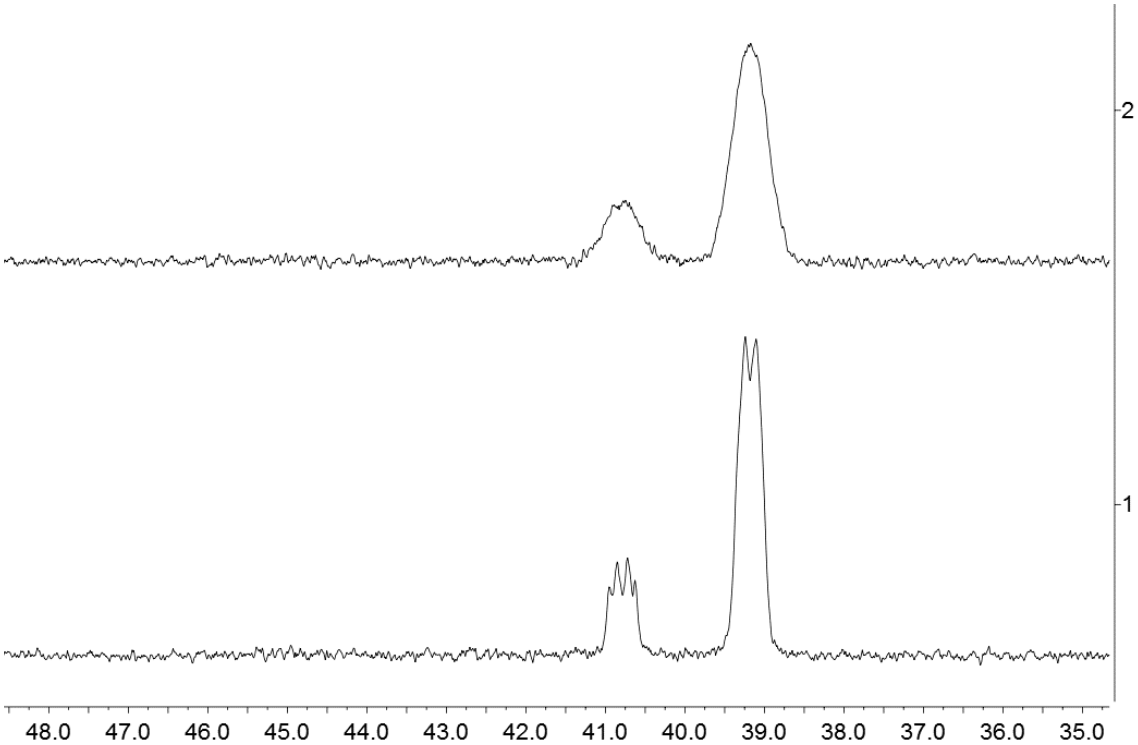


Figure S84 (1) $^{31}P\{^1H\}$ and (2) ^{31}P NMR (243 MHz, 299 K, CD_2Cl_2) spectra of the cystalline material.

Crystals of compound **15b** suitable for the X-ray crystal structure analysis were obtained from a solution of the isolated crystalline material in a mixture solvent (*n*-pentane : dichloromethane ca. 15 : 1) at −35 °C.

X-ray crystal structure analysis of compound 15b (erk8872): A colorless prism-like specimen of $C_{42}H_{45}BF_5P$, approximate dimensions 0.050 mm x 0.180 mm x 0.220 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1753 frames were collected. The total exposure time was 19.44 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 31225 reflections to a maximum θ angle of 66.97° (0.84 Å resolution), of which 6274 were independent (average redundancy 4.977, completeness = 98.9%, R_{int} = 4.69%, R_{sig} = 3.34%) and 5350 (85.27%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 11.1225(6) Å, $\underline{b}$ = 11.7795(6) Å, $\underline{c}$ = 14.5374(8) Å, α = 74.415(3)°, β = 78.609(3)°, γ = 79.231(3)°, volume = 1780.34(17) Å^3, are based upon the refinement of the XYZ-centroids of 9889 reflections above 20 σ(I) with 6.39° < 2θ < 133.6°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.881. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7860 and 0.9450. The final anisotropic full-matrix least-squares refinement on F^2 with 452 variables converged at R1 = 3.76%, for the observed data and wR2 = 9.71% for all data. The goodness-of-fit was 1.064. The largest peak in the final difference electron density synthesis was 0.340 $e^-/Å^3$ and the largest hole was -0.299 $e^-/Å^3$ with an RMS deviation of 0.045 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.281 g/cm^3 and F(000), 724 e^-.

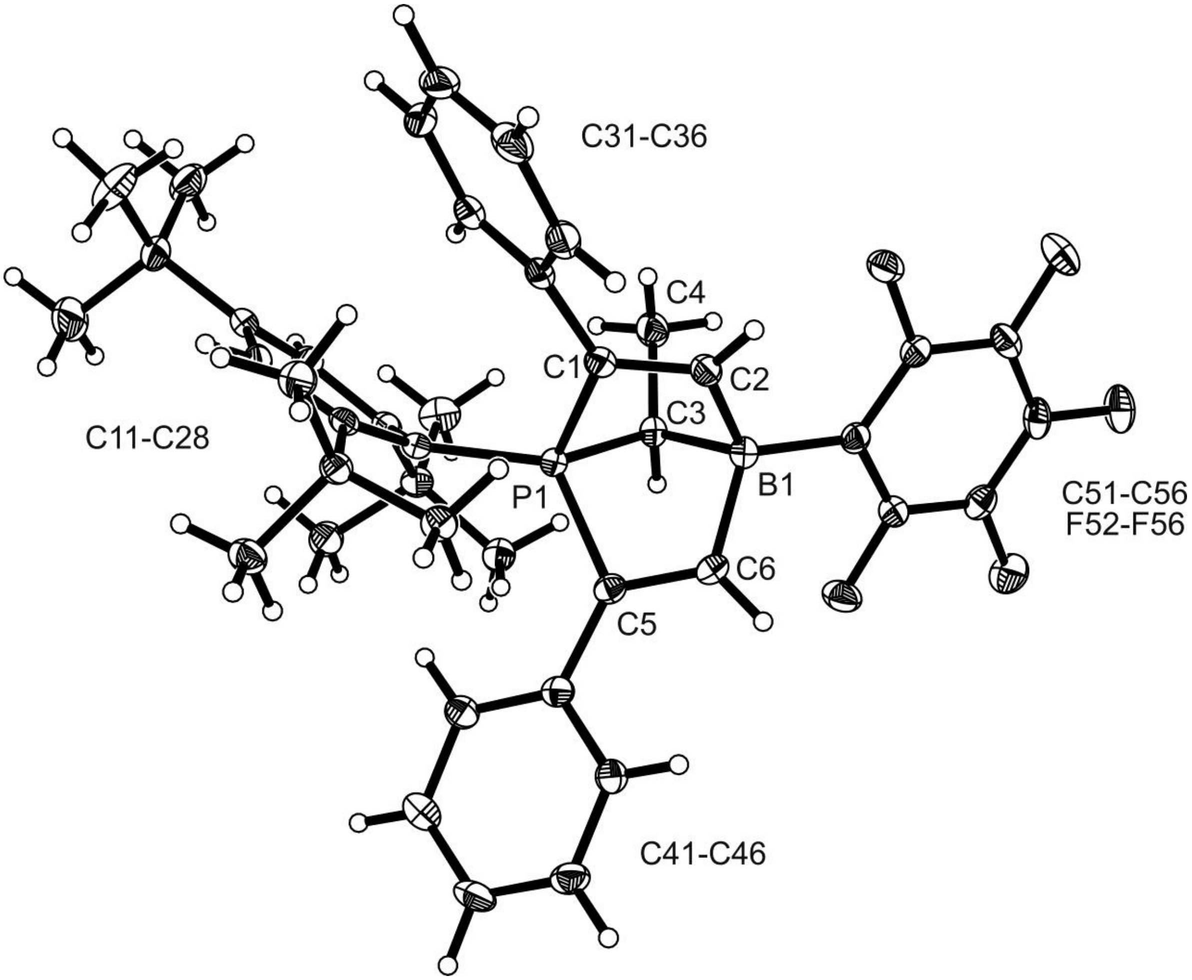


Figure S85 A view of the molecular structure of compound **15b**.

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Part 2. Solid State NMR Experiments

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^{11}B{^{1}H} MAS and ^{31}P{^{1}H} CPMAS NMR spectra of compound **8b** and corresponding line shape simulations (Figure S1) are consistent with the existence of single boron and phosphorus sites each in the symmetric FLP dimer. The ^{11}B{^{31}P} heteronuclear *J*-resolved MAS NMR experiment (Figure S2) results in $^{1}J_{\mathrm{BP}}$ = 49 Hz verifying the direct B-P bonding interactions in the dimer. The smaller intramolecular indirect spin-spin couplings, ^{2}J and ^{3}J cannot be resolved. The quantum chemical calculations and experimental data are in adequate agreement (Table S1). ^{11}B{^{31}P} REDOR and ^{31}P{^{11}B} CP-REAPDOR experiments (Figure S3 and Figure S4, respectively) evidence the spin cluster character of **8b**. The REDOR curve can be simulated with a good approximation by a three-spin system, based on the two closest B···P distances of 208 and 275 pm, respectively. The simulation of the REAPDOR data is a superposition of the corresponding REAPDOR curves of three isotopologues weighted by their natural abundances: a dominant contribution from a ^{31}P(^{11}B)$_2$ (three-spin curve), and two minor contributions from the two different possible isotopologues ^{31}P(^{11}B^{10}B), whose predicted REAPDOR curves arise from two-spin simulations. The sum of these distinct contributions is compared to the experimental data in Figure S89.

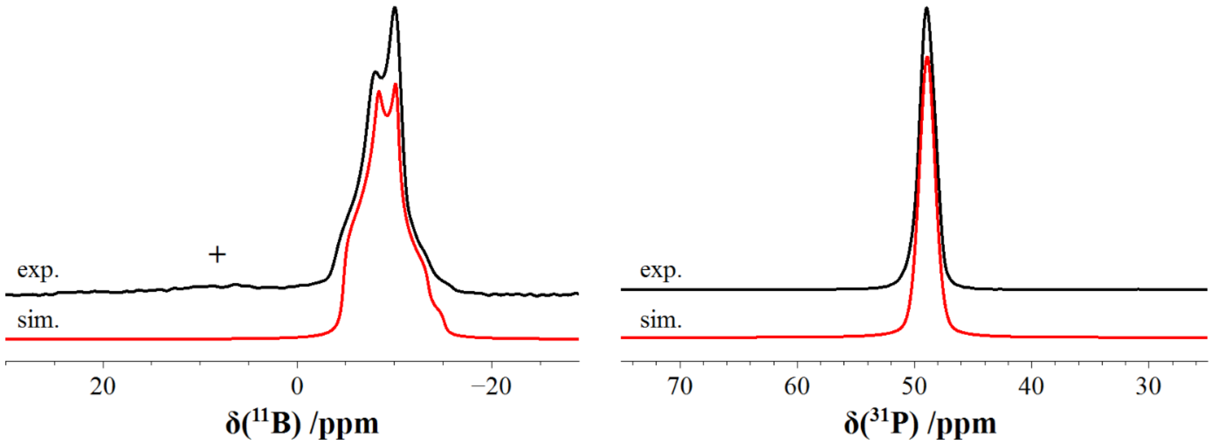

Figure S86 ^{11}B{^{1}H} MAS (left, top) and ^{31}P{^{1}H} CPMAS NMR spectra (right, top) of **8b** measured at 7.05 T with a MAS frequency of 12.0 kHz. Line shape simulations (lower traces) result in δ_{iso}(^{11}B) = -4.6 ppm, C_Q = 1.21 MHz, η_Q = 0.63 and δ_{iso}(^{31}P) = 48.9 ppm. Minor side products are labelled by +.

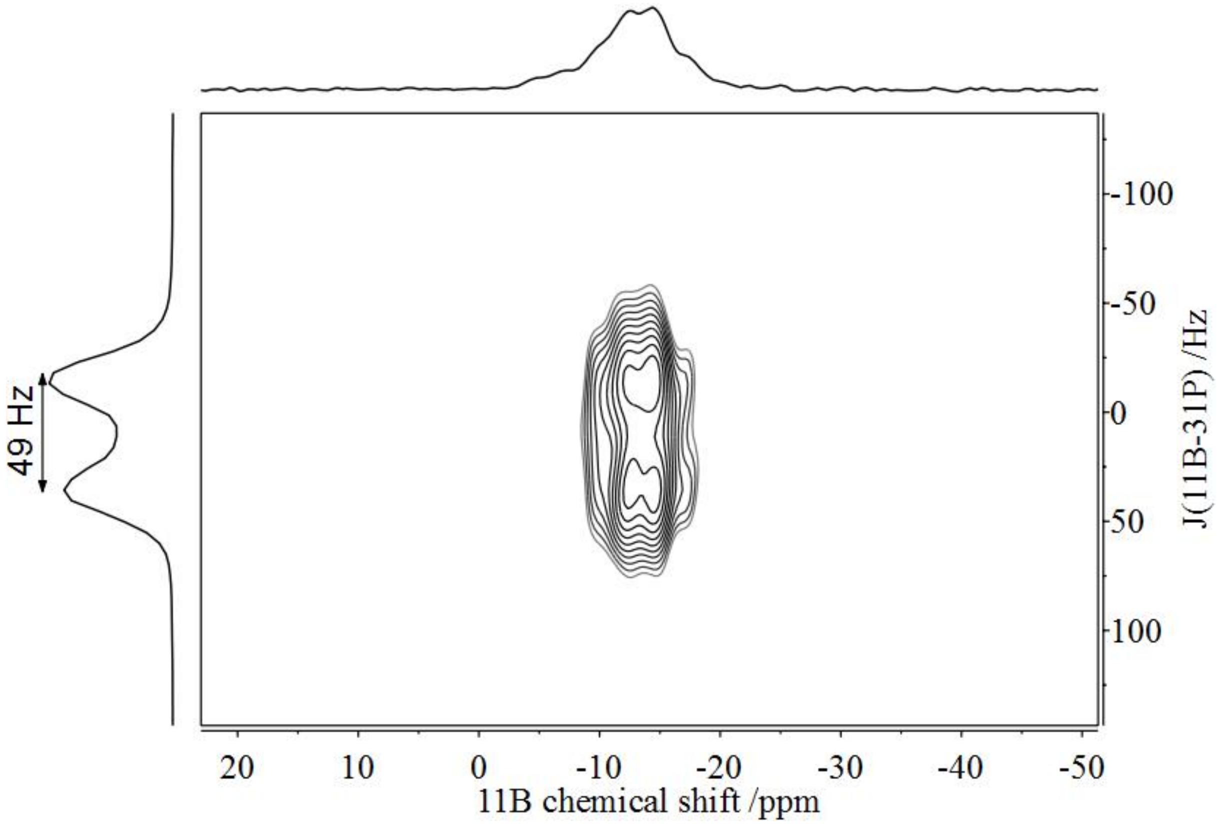

Figure S87 ^{11}B{^{31}P} heteronuclear *J*-resolved MAS NMR spectrum of compound **8b**, acquired at 7.05 T with a MAS frequency of 10.0 kHz.

Table S1: Experimental and DFT calculated ^{11}B and ^{31}P isotropic chemical shifts, ^{11}B nuclear electric quadrupolar coupling parameters C_Q and η_Q, ^{31}P chemical shift anisotropy parameters $\Delta\sigma$ and η_σ, and $J(^{11}\text{B}-^{31}\text{P})$ spin-spin coupling constants of compound **8b**

	experimental (8b)	**DFT (8b)**
$\delta(^{11}\text{B})$ /ppm	-4.6 ± 0.5	0.6
$\delta(^{31}\text{P})$ /ppm	48.9 ± 0.5	62.9
$C_Q(^{11}\text{B})$ /MHz	1.21 ± 3 %	1.34
$\eta_Q(^{11}\text{B})$	0.63 ± 0.1	0.62
$\Delta\sigma(^{31}\text{P})$ /ppm	93.8 ± 10	120.1
$\eta_\sigma(^{31}\text{P})$	0.83 ± 0.2	0.74
$^1J(^{11}\text{B}-^{31}\text{P})$ /Hz	49 ± 2	41
$^2J(^{11}\text{B}-^{31}\text{P})$ /Hz	-	22

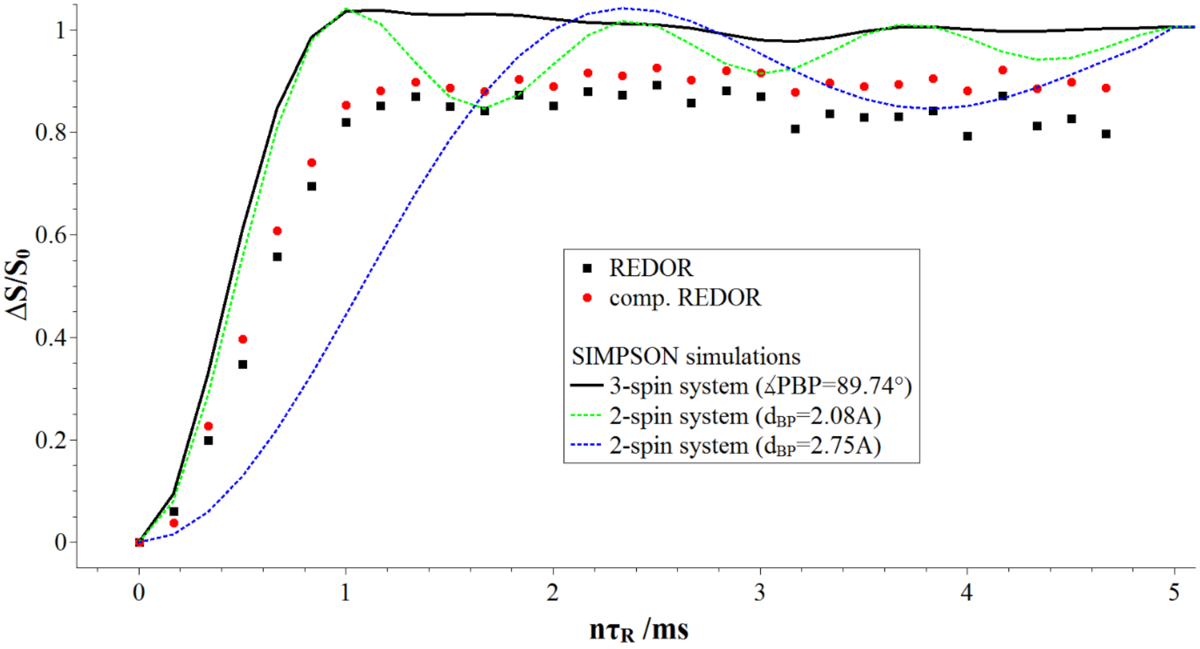

Figure S88 ^{11}B{^{31}P} REDOR curve (squares) and compensated REDOR curve (circles) of **8b**, acquired at 7.05 T with a MAS frequency of 12.5 kHz. SIMPSON simulations are included for the two different 2-spin systems (dotted lines) and the 3-spin system (solid line).

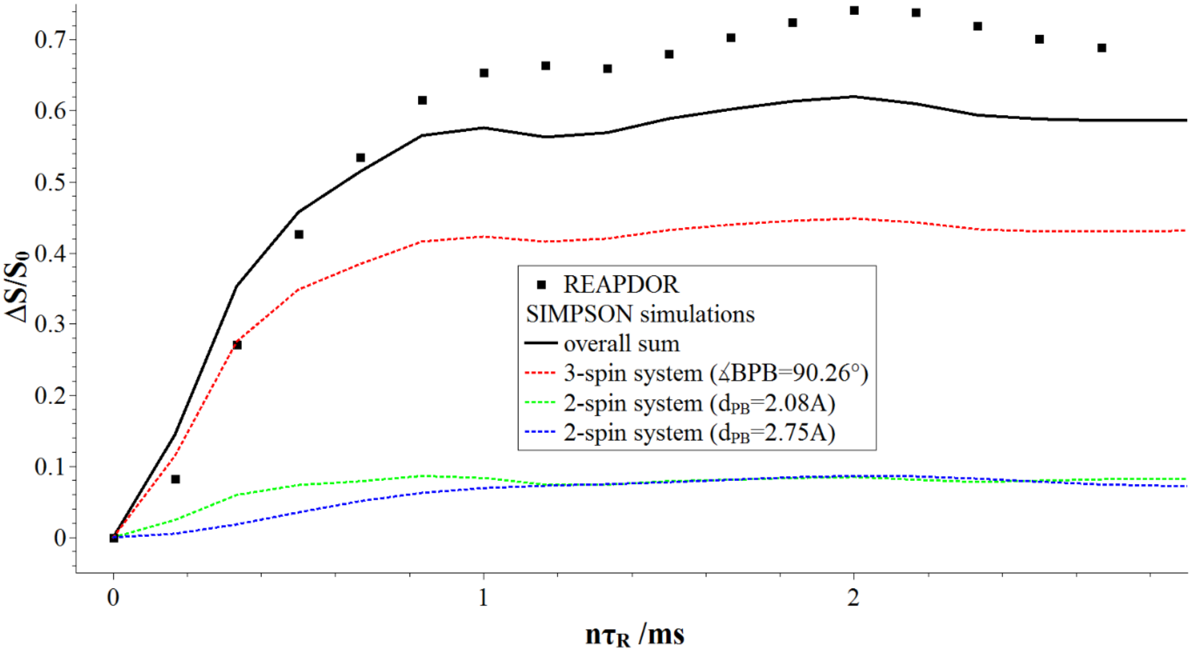

Figure S89 $^{1}H \rightarrow {}^{31}P\{^{11}B\}$ CP-REAPDOR curve (squares) of **8b**, acquired at 7.05 T with a MAS frequency of 10.0 kHz. SIMPSON simulations for the three dominant isotopologues are shown. They are scaled in accordance with their expected abundances of the 2- and 3-spin-systems as arising from the natural $^{10}B/^{11}B$ isotope distribution (dotted lines). The overall sum of the individual components is shown as a solid curve.

Details of the Solid-State NMR Experiments

All solid-state NMR spectra were recorded at 7.05 T using a Bruker Avance III 300 spectrometer and a 4 mm MAS-NMR probe. The $^{11}B\{^{31}P\}$ heteronuclear *J*-resolved MAS-NMR spectrum was acquired at 10.0 kHz spinning frequency with centered π-pulses of 10.1 and 11.5 μs length, respectively, and a z-filter. The evolution time was incremented in 56 steps of 800 μs. $^{11}B\{^{31}P\}$ rotational echo double resonance (REDOR) curves were conducted with the standard sequence of Schaefer and Gullion,[2] at the spinning frequency of 12.5 kHz, using 180° recoupling pulses of 10.1 μs length. $^{31}P\{^{11}B\}\{^{1}H\}$ Cross-polarization (CP) rotational echo adiabatic passage double resonance (REAPDOR) data were measured at a spinning frequency of 10.0 kHz, using a radio frequency power level corresponding to an ^{11}B nutation frequency of 33.7 kHz and a recoupling time of 1/3 of the rotor cycle. The $^{1}H \rightarrow {}^{31}P$ CP contact time was 2.0 ms. The simulations of the REDOR and REAPDOR curves were carried out with the SIMPSON program (version 4.1.1).[3]

Quantum chemical calculations were performed using the TURBOMOLE program package (version 7.1)[4,5] and the GAUSSIAN09 program package (revision D.01)[6] as previously reported.[7] Geometry optimizations were carried out with the crystal structure as input data only optimizing hydrogen atoms on meta-GGA-DFT-level (TPSS/def2-TZVP). Magnetic shieldings were calculated on hybrid-DFT-level (B3LYP/def2-TZVP). The nuclear electric field gradient (EFG) was calculated on GGA-DFT-level (B97-D/def2-TZVP(mod.)). *J*-coupling constants and chemical shift anisotropy parameters were calculated on hybrid-DFT-level (B3LYP/TZVP).

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