Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

A Convenient Route to Internally Phosphane-stabilized Aryltriborane(7) Compounds

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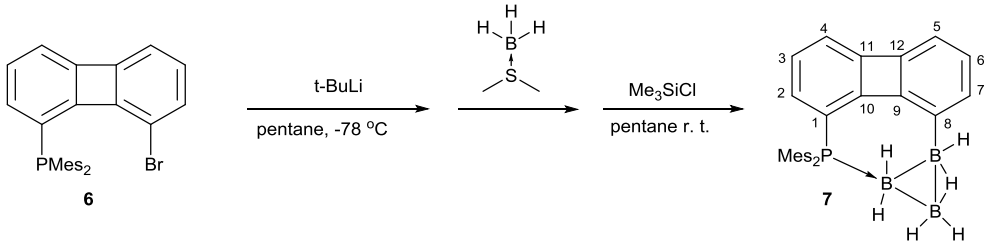
Experimental Procedures

General Information. All reactions involving air- or moisture-sensitive compounds were carried out under an inert gas atmosphere (Argon) by using Schlenk-type glassware or in a glovebox. All solvents were dried and degassed before use, if necessary for the respective reaction. Chemicals: Unless otherwise noted all chemicals were used as purchased. The following instruments were used for physical characterization of the compounds: elemental analyses: Foss–Heraeus CHNO-Rapid; NMR: Varian UNITY plus NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 151 MHz; ^{11}B, 192 MHz; ^{31}P, 243 MHz, ^{19}F, 564 MHz or ^{1}H, 500 MHz; ^{13}C, 126 MHz; ^{11}B, 160 MHz; ^{31}P, 202 MHz, ^{19}F, 470 MHz). NMR chemical shifts are given relative to $SiMe_4$ and referenced to the respective solvent signal (^{1}H and ^{13}C) or an external standard [$\delta(BF_3{\cdot}OEt_2) = 0$ for ^{11}B NMR, δ(85% H_3PO_4 in D_2O) = 0 for ^{31}P NMR, $\delta(CFCl_3) = 0$ for ^{19}F NMR]. Numbering of the compounds for the assignment of NMR signals followed the numbering of the X-ray structure.

Materials: Compound **6**[1], (2-bromophenyl)zinc(II) iodide[2] and bis(pentafluorophenyl)borane[3] were prepared according to procedures reported in the literature.

X-Ray diffraction: For compounds **10**, **12** and **13** 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, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, 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). Data sets for compounds **7** and **11** were collected with a D8 Venture CMOS diffractometer. Programs used: 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**) and graphics, XP (Bruker AXS Inc., **2015**). *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features:* For compound **13** three badly disordered cyclopentane molecules were found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (A. L. Spek (**2015**) Acta Cryst., C71, 9-18) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecules. The structure was refined using the 'HKLF 5' option, whereby the BASF factor was refined to 0.23. CCDC deposition numbers are 1858045 to 1858048 and 1859606.

Preparation of triborane(7) derivative 7



Scheme S1 The synthesis of triborane(7) derivative **7**

At -78 °C, a solution of t-BuLi [1.7 mol/L in hexane; 1.8 mL (3 mmol, 1 eq.)] was added to a solution of (8-bromobiphenylen-1-yl)dimesitylphosphane (**6**) (1.5 g, 3 mmol, 1 eq.) in pentane (100 mL). Then the mixture was warmed to room temperature and stirred for 3 hours. The mixture was cooled to -78 °C and $BH_3{\cdot}SMe_2$ [2 mol/L in THF; 6 mL (12 mmol, 4 eq.)] was added. Then the mixture was warmed to room temperature and stirred overnight. Trimethylsilyl chloride (650 mg, 6.0 mmol, 2 eq.) was added in one portion via syringe and the mixture

was stirred for 1 day at room temperature. The volatiles were removed in vacuum. The residue was dispersed in the combined solvents of pentane (50 mL) and toluene (50 mL). The mixture was filtered, the solvents were removed in vacuum, and the residue was washed with pentane (3 x 5 mL). The pale yellow powder was collected and dried in vacuum to give the product **7** (690 mg, 1.5 mmol, 50% yield).

E. A. for $C_{30}H_{34}B_3P$: calc. C (78.67 %), H (7.48 %), found: C (78.37 %), H (7.48%)

Melting Point (DSC): 129 °C

^{1}H NMR (500 MHz, methylene chloride-d_2, 258 K): δ = 6.95 (d, $^3J_{HH}$ = 8.0 Hz, 1H, 7-CH), 6.92 (d, $^4J_{PH}$ = 3.0 Hz, 1H, *m*-Mes^a), 6.88 (m, 1H, *m*'-Mes^a), 6.86 (d, $^4J_{PH}$ = 3.0 Hz, 1H, *m*-Mes^b), 6.79 (m, 1H, *m*'-Mes^b), 6.79 (dd, $^3J_{HH}$ = 8.0, 7.0 Hz, 1H, 6-CH), 6.66 (d, $^3J_{HH}$ = 7.0 Hz, 1H, 5-CH), 6.65 (m, 1H, 4-CH), 6.63 (m, 1H, 3-CH), 6.56 (m, 1H, 2-CH), 2.67 (s, 3H, *o*-CH_3^{Mesa}), 2.27(s, 3H, *p*-CH_3^{Mesb}), 2.26 (s, 3H, *p*-CH_3^{Mesa}), 2.22 (s, 3H, *o*'-CH_3^{Mesb}), 2.14 (s, 3H, *o*-CH_3^{Mesb}), 1.78 (s, 3H, *o*'-CH_3^{Mesa}), [BH not listed].

^{13}C{^{1}H} NMR (126 MHz, methylene chloride-d_2, 258 K): δ = 159.8 (d, $^2J_{PC}$ = 13.4 Hz, 10-C), 154.0 (d, $^3J_{PC}$ = 2.6 Hz, 9-C), 152.2 (d, $^3J_{PC}$ = 14.7 Hz, 11-C), 150.2 (12-C), 142.9 (d, $^2J_{PC}$ = 14.3 Hz, *o*-Mes^a), 142.2 (d, $^2J_{PC}$ = 3.2 Hz, *o*'-Mes^a), 141.6 (*p*-Mes^a), 141.2 (d, $^2J_{PC}$ = 13.4 Hz, *o*-Mes^b), 140.7 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Mes^b), 140.4 (d, $^2J_{PC}$ = 4.5 Hz, *o*'-Mes^b), 137.9 (br, 8-C), 133.5 (7-CH), 132.2 (d, $^3J_{PC}$ = 8.5 Hz, *m*'-Mes^a), 132.0 (d, $^3J_{PC}$ = 10.9 Hz, *m*-Mes^a), 131.5 (d, $^3J_{PC}$ = 9.5 Hz, *m*'-Mes^b), 130.7 (d, $^3J_{PC}$ = 11.1 Hz, *m*-Mes^b), 130.1 (d, $^2J_{PC}$ = 3.0 Hz, 2-CH), 129.1 (6-CH), 128.4 (d, $^3J_{PC}$ = 6.8 Hz, 3-CH), 126.8 (d, $^1J_{PC}$ = 64.9 Hz, *i*-Mes^b), 123.1 (d, $^1J_{PC}$ = 62.2 Hz, *i*-Mes^a), 118.9 (4-CH), 117.2 (5-CH), 116.9 (d, $^1J_{PC}$ = 57.3 Hz, 1-C), 25.8 (d, $^3J_{PC}$ = 5.4 Hz, *o*-CH_3^{Mesa}), 25.1 (d, $^3J_{PC}$ = 3.5 Hz, *o*'-CH_3^{Mesa}), 24.6 (d, $^3J_{PC}$ = 3.2 Hz, *o*'-CH_3^{Mesb}), 23.3 (d, $^3J_{PC}$ = 5.6 Hz, *o*-CH_3^{Mesb}), 20.9 (d, $^5J_{PC}$ = 1.2 Hz, *p*-CH_3^{Mesb}), 20.8 (d, $^5J_{PC}$ = 1.0 Hz, *p*-CH_3^{Mesa}).

^{11}B{^{1}H} NMR (160 MHz, methylene chloride-d_2, 299 K): δ = 8.4 ($\nu_{1/2}$ ≈ 400 Hz), -23.9 ($\nu_{1/2}$ ≈ 180 Hz), -36.5 (d, $^1J_{PB}$ ≈ 91 Hz).

^{11}B{^{1}H} NMR (160 MHz, methylene chloride-d_2, 258 K): δ = 8.6 ($\nu_{1/2}$ ≈ 750 Hz), -24.1 ($\nu_{1/2}$ ≈ 360 Hz), -36.7 ($\nu_{1/2}$ ≈ 250 Hz).

^{31}P{^{1}H} NMR (202 MHz, methylene chloride-d_2, 258 K): δ = 7.8 (m).

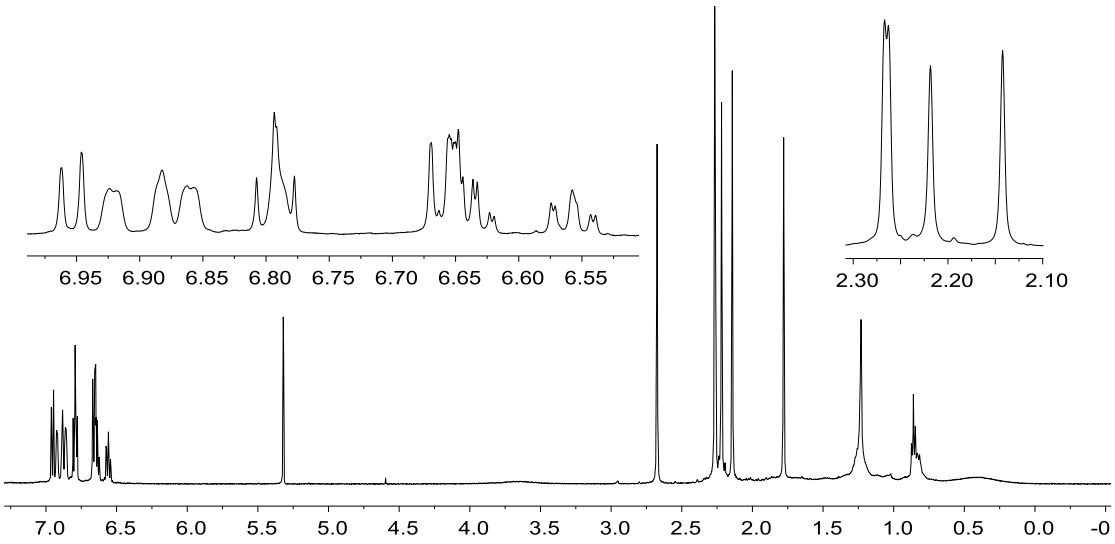


Figure S1 ^{1}H NMR (500 MHz, 258K, methylene chloride-d_2) spectrum of compound **7**.

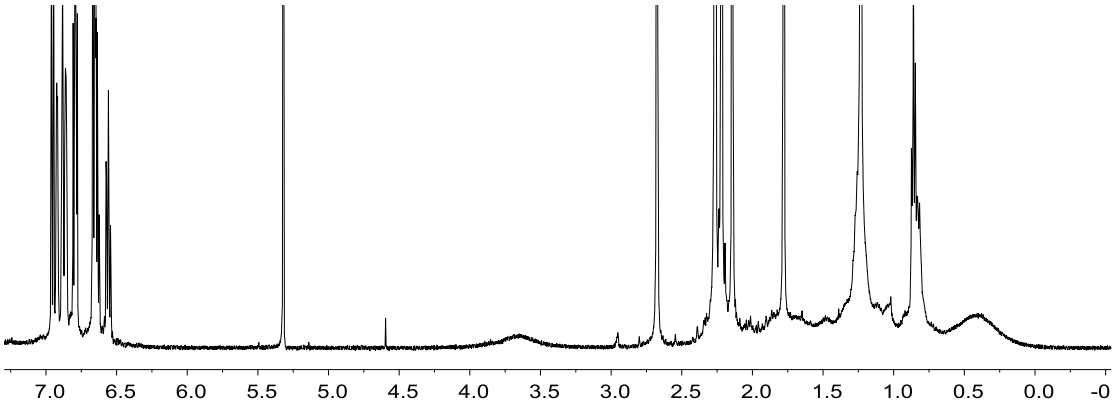


Figure S2 ^{1}H NMR (500 MHz, 258K, methylene chloride-d_2) spectrum of compound **7**.

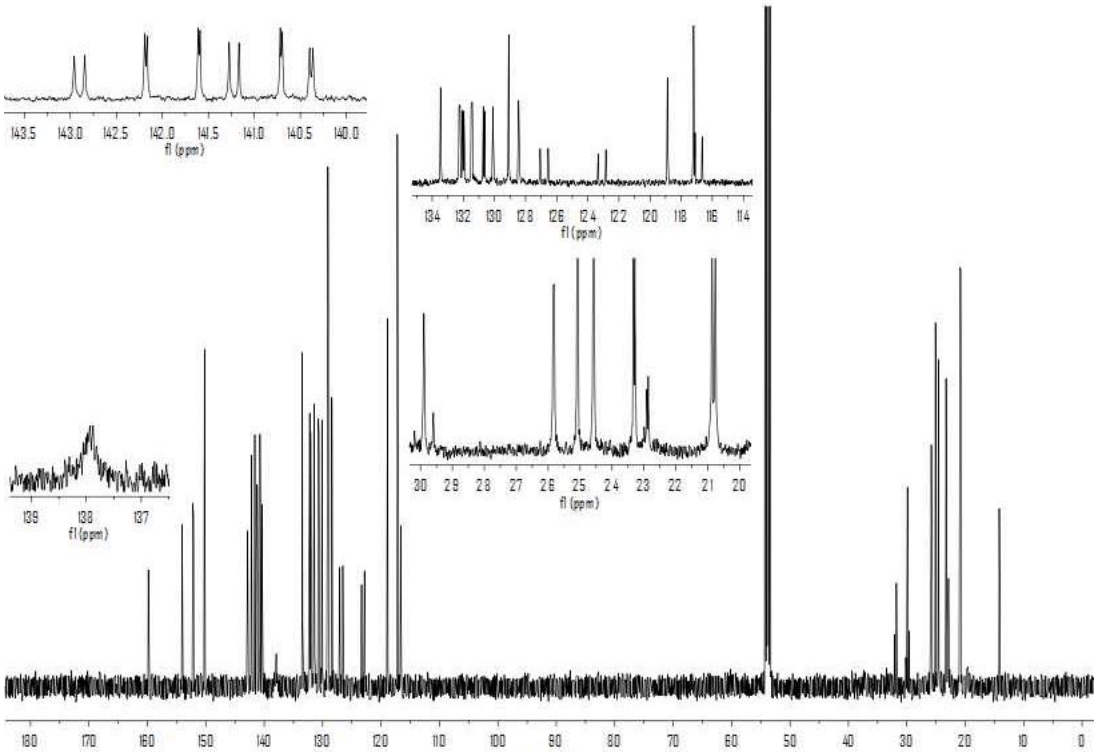


Figure S3 ^{13}C{^{1}H} NMR (126 MHz, 258K, methylene chloride-d_2) spectrum of compound **7**.

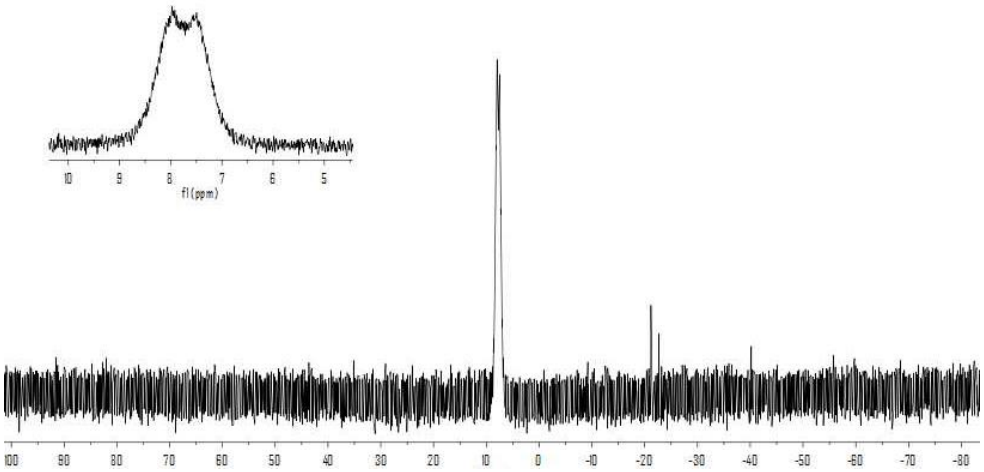


Figure S4 ^{31}P{^{1}H} NMR (202 MHz, 258 K, methylene chloride-d_2,) spectrum of compound **7**.

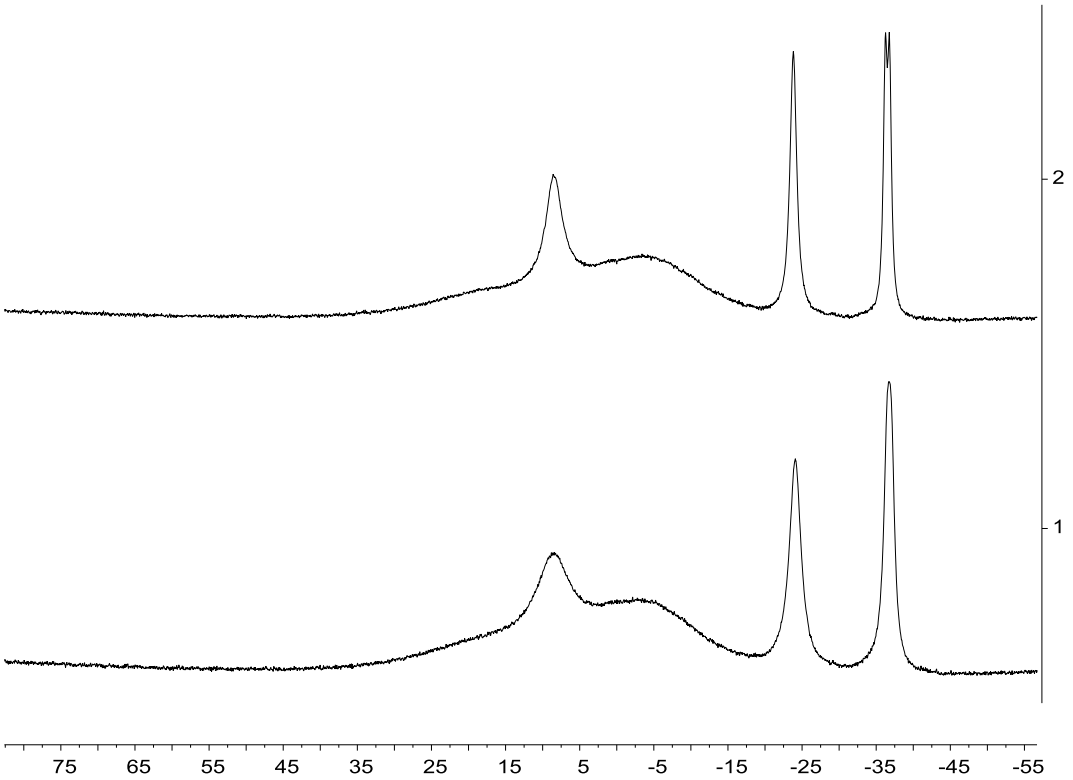


Figure S5 $^{11}B\{^1H\}$ NMR (160 MHz, methylene chloride-d_2) spectra of compound **7**.at (1) 258 K and (2) 299 K.

Crystals suitable for the *X*-ray crystal structure analysis were obtained from a solution of compound **7** in cyclopentane at room temperature.

X-ray crystal structure analysis of compound 7 (erk8660): A pale yellow prism-like specimen of $C_{30}H_{34}B_3P$, approximate dimensions 0.139 mm x 0.215 mm x 0.290 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 634 frames were collected. The total exposure time was 7.27 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 20970 reflections to a maximum θ angle of 68.37° (0.83 Å resolution), of which 4654 were independent (average redundancy 4.506, completeness = 99.1%, R_{int} = 5.24%, R_{sig} = 4.42%) and 3867 (83.09%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.7002(3) Å, b = 17.2942(5) Å, c = 12.6635(4) Å, β = 91.842(2)°, volume = 2561.08(13) Å^3, are based upon the refinement of the XYZ-centroids of 9896 reflections above 20 σ(I) with 8.657° < 2θ < 136.7°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.816. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7500 and 0.8680. 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, $C_{30}H_{34}B_3P$. The final anisotropic full-matrix least-squares refinement on F^2 with 337 variables converged at R1 = 4.90%, for the observed data and wR2 = 12.76% for all data. The goodness-of-fit was 1.055. The largest peak in the final difference electron density synthesis was 0.381 $e^-/Å^3$ and the largest hole was -0.356 $e^-/Å^3$ with an RMS deviation of 0.055 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.188 g/cm^3 and F(000), 976 e^-.

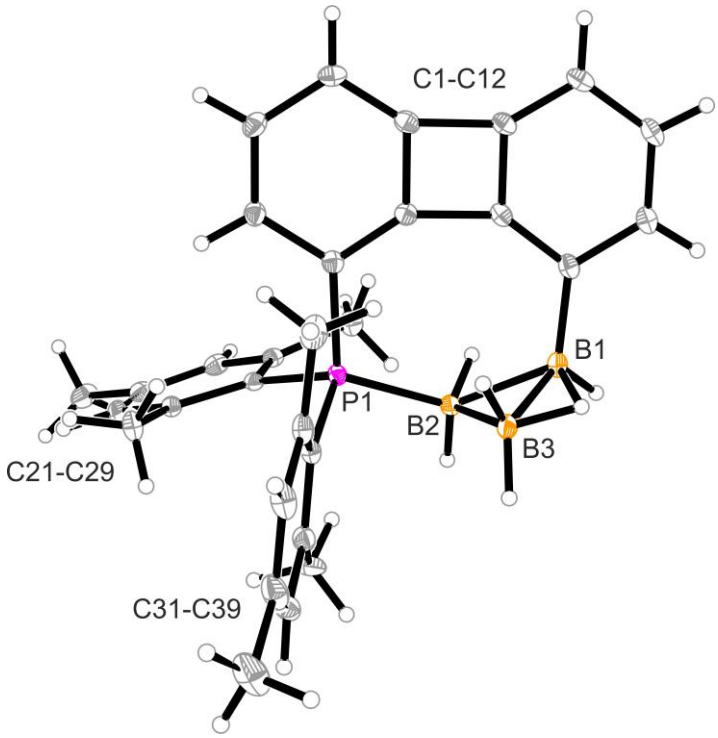
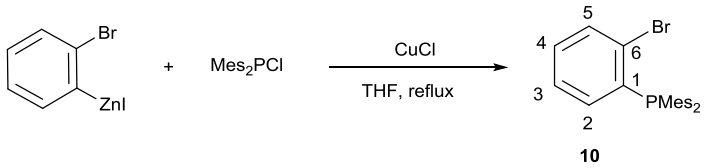


Figure S6 Crystal structure of compound **7**. (Thermal ellipsoids are shown with 30% probability.)

Preparation of phosphane derivative 10



10

Scheme S2. The synthesis of compound **10**

At room temperature, a solution of chlorodimesitylphosphane (6.08 g, 20 mmol, 1 eq.) in THF (20 mL) was added in one portion to a solution of the *in situ* prepared Zinc reagents (20 mmol in 30 mL THF, 1 eq.), followed by addition of CuCl (200 mg, 2 mmol, 10% eq.). Then the mixture was refluxed for 3 days. It was cooled to room temperature and saturated aq. NH_4Cl (100 mL) was added. Then the organic phase was separated and the aqueous phase was extracted with diethyl ether (3 x 50 mL). The combined organic phases were dried over $MgSO_4$ and then all volatiles were removed in vacuum. The residue was purified by column chromatography (silica gel, pentane: methylene chloride ca. 10 : 1) to finally give compound **10** as a white powder (4.3 g, 10 mmol, 50%).

E. A. for $C_{24}H_{26}PBr$: calc. C (67.77 %), H (6.16%), found: C (67.50 %), H (5.95 %).

Melting Point (DSC): 138 °C

^{1}H NMR (600 MHz, benzene-d_6, 299 K): δ = 7.37 (ddm, *J* = 7.9, 4.3 Hz, 1H, 2-CH), 7.20 (dm, $^3J_{HH}$ = 7.6 Hz, 1H, 5-CH), 6.72 (m, 4H, *m*-Mes), 6.72 (m, 1H, 4-CH), 6.66 (m, 1H, 3-CH), 2.26 (s, 12H, *o*-CH_3^{Mes}), 2.07 (s, 6H, *p*-CH_3^{Mes}).

^{13}C{^{1}H} NMR (151 MHz, benzene-d_6, 299 K): δ = 143.5 (d, $^2J_{PC}$ = 16.9 Hz, *o*-Mes), 140.4 (d, $^2J_{PC}$ = 14.2 Hz, 6-C), 138.5 (*p*-Mes), 134.0 (d, $^3J_{PC}$ = 2.2 Hz, 5-CH), 133.2 (d, $^2J_{PC}$ = 2.2 Hz, 2-CH), 131.8 (d, $^1J_{PC}$ = 37.5 Hz, 1-C), 130.6 (d, $^3J_{PC}$ = 3.7 Hz, *m*-Mes), 129.9 (d, $^1J_{PC}$ = 19.4 Hz, *i*-Mes), 129.4 (3-CH), 127.2 (4-CH), 22.9 (d, $^3J_{PC}$ = 16.6 Hz, *o*-CH_3^{Mes}), 20.9 (*p*-CH_3^{Mes}).

^{31}P{^{1}H} NMR (243 MHz, benzene-d_6, 299 K): δ = -20.9 ($\nu_{1/2}$ ≈ 2 Hz).

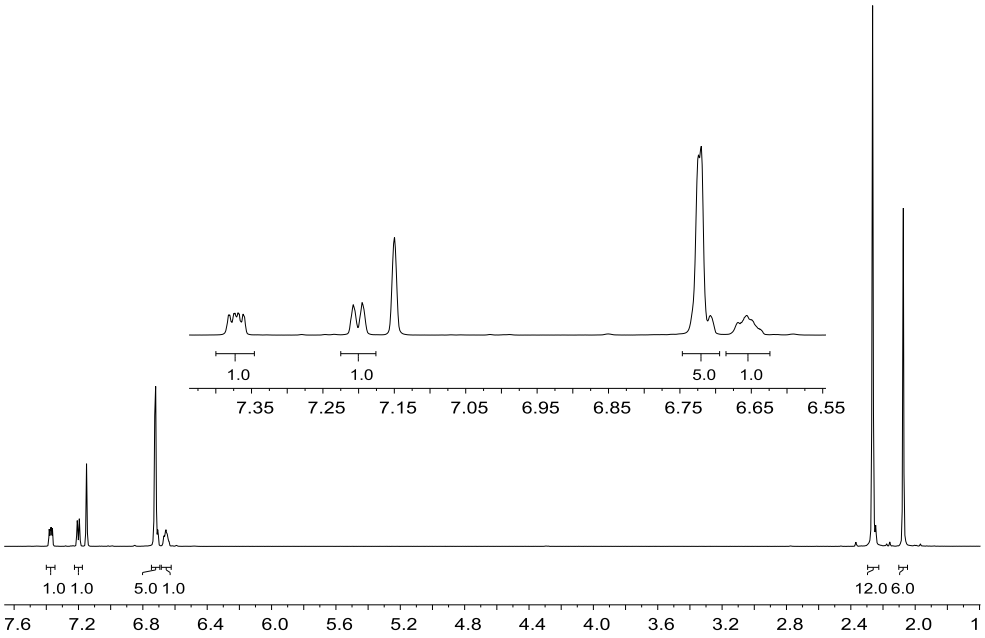


Figure S7. ^{1}H NMR (600 MHz, benzene-d_6, 299 K) spectrum of compound **10**.

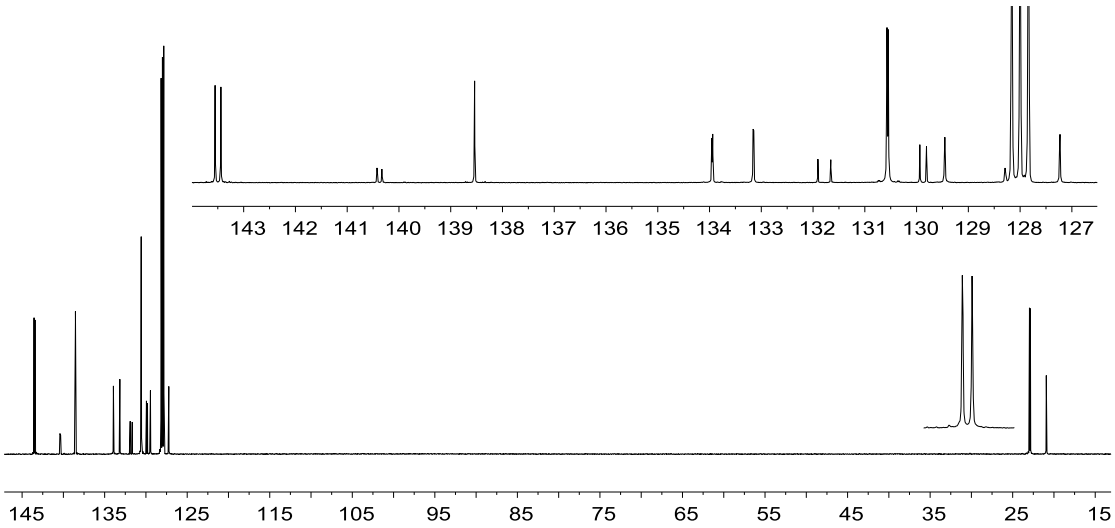


Figure S8. ^{13}C{^{1}H} NMR (151 MHz, benzene-d_6, 299 K) spectrum of compound **10**.

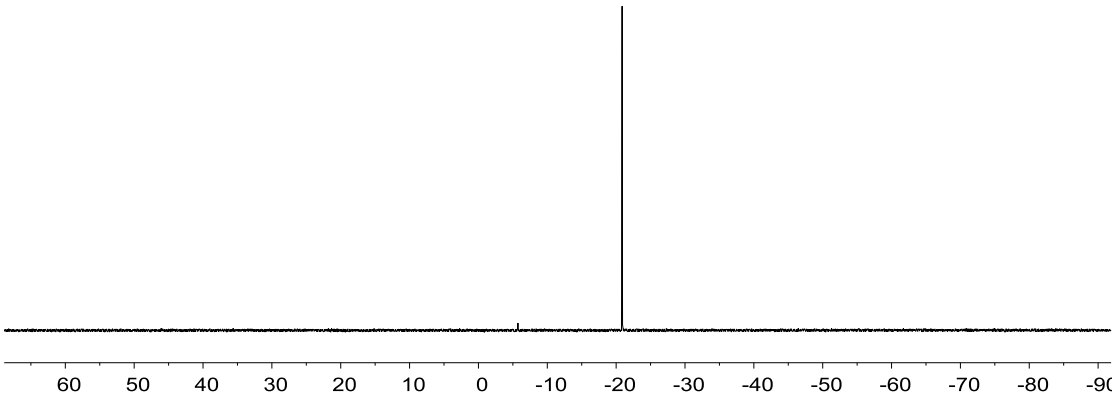


Figure S9. ^{31}P{^{1}H} NMR (243 MHz, benzene-d_6, 299 K) spectrum of compound **10**.

Crystals suitable for the *X*-ray crystal structure analysis were obtained from a solution of compound **10** in benzene at room temperature.

X-ray crystal structure analysis of compound 10 (erk9119): formula $C_{24}H_{26}BrP$, M = 425.33, colourless crystal, 0.32 x 0.04 x 0.03 mm, a = 7.9924(2) Å, b = 15.6376(5) Å, c = 33.0811(13) Å, V = 4134.50(2) Å^3, ρ_{calc} = 1.367 gcm^{-3}, μ = 2.071 mm^{-1}, empirical absorption correction (0.557 ≤ T ≤ 0.941), Z = 8, orthorhombic, space group *P*212121 (No. 19), λ = 0.71073 Å, T = 173(2) K, ω and ϕ scans, 29596 reflections collected (±*h*, ±*k*, ±*l*), 7243 independent (R_{int} = 0.123) and 5853 observed reflections [$I>2\sigma I$)], 481 refined parameters, R = 0.071, wR^2 = 0.146, max. (min.) residual electron density 0.49 (-0.61) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

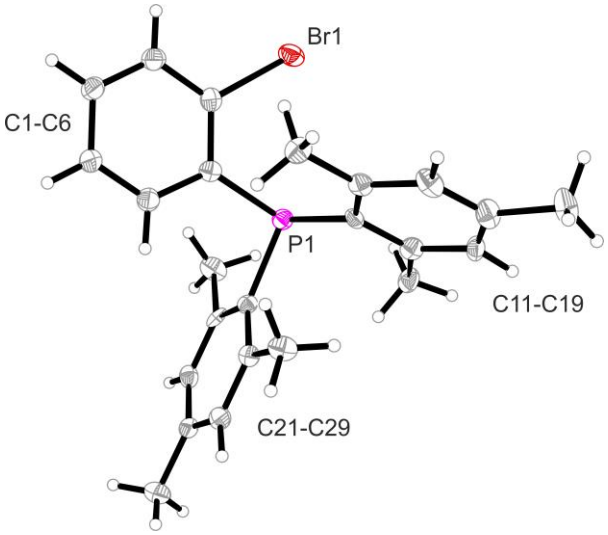
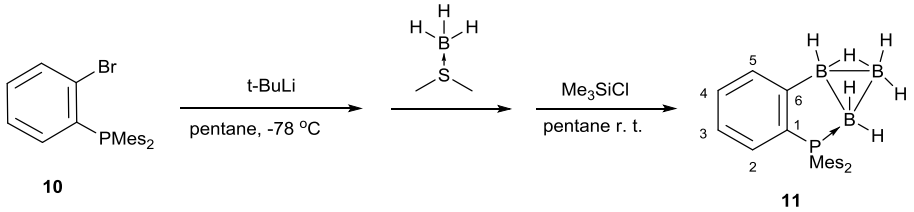


Figure S10. Molecular structure of compound **10**. Only one molecule of two found in the asymmetric unit is shown. (Thermal ellipsoids are shown with 30% probability.)

Preparation of triborane(7) derivative 11



Scheme S3. The synthesis of triborane derivative **11**.

At -78 °C, t-BuLi solution [1.7 mol/L in hexane, 2.4 mL (4.0 mmol, 1 eq.)] was added to a solution of (2-bromophenyl)dimesitylphosphane **10** (1.7 g, 4.0 mmol, 1 eq.) in pentane (120 mL). Then the mixture was warmed to room temperature and stirred for 3 hours. Then the mixture was cooled to -78 °C and BH_3·SMe_2 [2 mol/L in toluene, 8 mL (16 mmol, 4 eq.) was added. The reaction mixture was warmed to room temperature and stirred overnight. Trimethylsilyl chloride (860 mg, 8.0 mmol, 2 eq.) was added in one portion via syringe and the mixture was stirred for 1 day at room temperature. The volatiles were removed in vacuum. The residue was dispersed in the combined solvents of pentane (50 mL) and toluene (50 mL). The mixture was filtered and the solvents were removed in vacuum, and the residue was washed with pentane (3 x 8 mL). The white powder was collected and dried in vacuum to give the product **11** (1.3 g , 3.3 mmol, 83% yield) .

E. A. for $C_{24}H_{32}B_3P$: calc. C (75.08 %), H (8.40 %), found: C (74.95 %), H (8.66 %).

Melting Point (DSC): 150 °C

^{1}H NMR (600 MHz, methylene chloride-d_2, 193 K): δ = 7.63 (d, $^{3}J_{HH}$ = 7.1 Hz, 1H, 5-CH), 7.37 (t, $^{3}J_{HH}$ = 7.1 Hz, 1H, 4-CH), 7.30 (dd, $^{3}J_{PH}$ = 9.3 Hz, $^{3}J_{HH}$ = 7.1 Hz, 1H, 2-CH), 7.17 (tm, $^{3}J_{HH}$ = 7.1 Hz, 1H, 3-CH), 6.87 (br, 1H, *m*-Mes^{b}), 6.86 (br, 1H, *m*-Mes^{a}), 6.82 (br, 1H, *m*'-Mes^{a}), 6.74 (br, 1H, *m*'-Mes^{b}), 2.46 (s, 3H, *o*'-CH_3^{Mesa}), 2.23 (s, 3H, *p*-CH_3^{Mesb}), 2.20 (s, 3H, *p*-CH_3^{Mesa}), 2.05 (s, 3H, *o*-CH_3^{Mesb}), 1.83 (s, 3H, *o*-CH_3^{Mesa}), 1.78 (s, 3H, *o*'-CH_3^{Mesb}), [BH not listed].

^{13}C{^{1}H} NMR (151 MHz, methylene chloride-d_2, 193K): δ = 155.1 (br d, $^{2}J_{PC}$ ~ 43 Hz, 6-C), 142.0 (d, $^{2}J_{PC}$ = 15.3 Hz, *o*'-Mes^{a}), 141.1 (*p*-Mes^{a}), 140.80 (*o*-Mes^{a}), 140.75 (d, $^{2}J_{PC}$ = 4.6 Hz, *o*'-Mes^{b}), 140.3 (*p*-Mes^{b}), 138.8 (d, $^{2}J_{PC}$ = 12.4 Hz, *o*-Mes^{b}), 135.0 (d, $^{1}J_{PC}$ = 66.8 Hz, 1-C), 133.8 (d, $^{3}J_{PC}$ = 18.3 Hz, 5-CH), 131.7 (d, $^{2}J_{PC}$ = 6.2 Hz, 2-CH), 131.2 (d, $^{3}J_{PC}$ = 8.3 Hz, *m*-Mes^{a}), 130.7 (d, $^{3}J_{PC}$ = 11.1 Hz, *m*'-Mes^{a}), 130.4 (4-CH), 130.3 (d, $^{3}J_{PC}$ = 8.7 Hz, *m*'-Mes^{b}), 130.2 (d, $^{3}J_{PC}$ = 9.9 Hz, *m*-Mes^{b}), 127.2 (3-CH), 127.0 (d, $^{1}J_{PC}$ = 51.2 Hz, *i*-Mes^{b}), 122.8 (d, $^{1}J_{PC}$ = 61.1 Hz, *i*-Mes^{a}), 25.6 (d, $^{3}J_{PC}$ = 5.6 Hz, *o*'-CH_3^{Mesa}), 24.5 (d, $^{3}J_{PC}$ = 3.4 Hz, *o*'-CH_3^{Mesb}), 24.4 (d, $^{3}J_{PC}$ = 3.7 Hz, *o*-CH_3^{Mesa}), 22.8 (d, $^{3}J_{PC}$ = 8.7 Hz, *o*-CH_3^{Mesb}), 20.5 (*p*-CH_3^{Mesb}), 20.4 (*p*-CH_3^{Mesa}).·

^{11}B{^{1}H} NMR (192 MHz, methylene chloride-d_2, 299 K): δ = -4.8 ($v_{1/2}$ ≈ 250 Hz), -6.8 ($v_{1/2}$ ≈ 150 Hz), -32.2 (d, $^{1}J_{PB}$ ≈ 94 Hz).

^{31}P{^{1}H} NMR (243 MHz, methylene chloride-d_2, 299 K): δ = 19.5 (m).

^{31}P{^{1}H} NMR (243 MHz, methylene chloride-d_2, 193 K): δ = 18.3 (m).

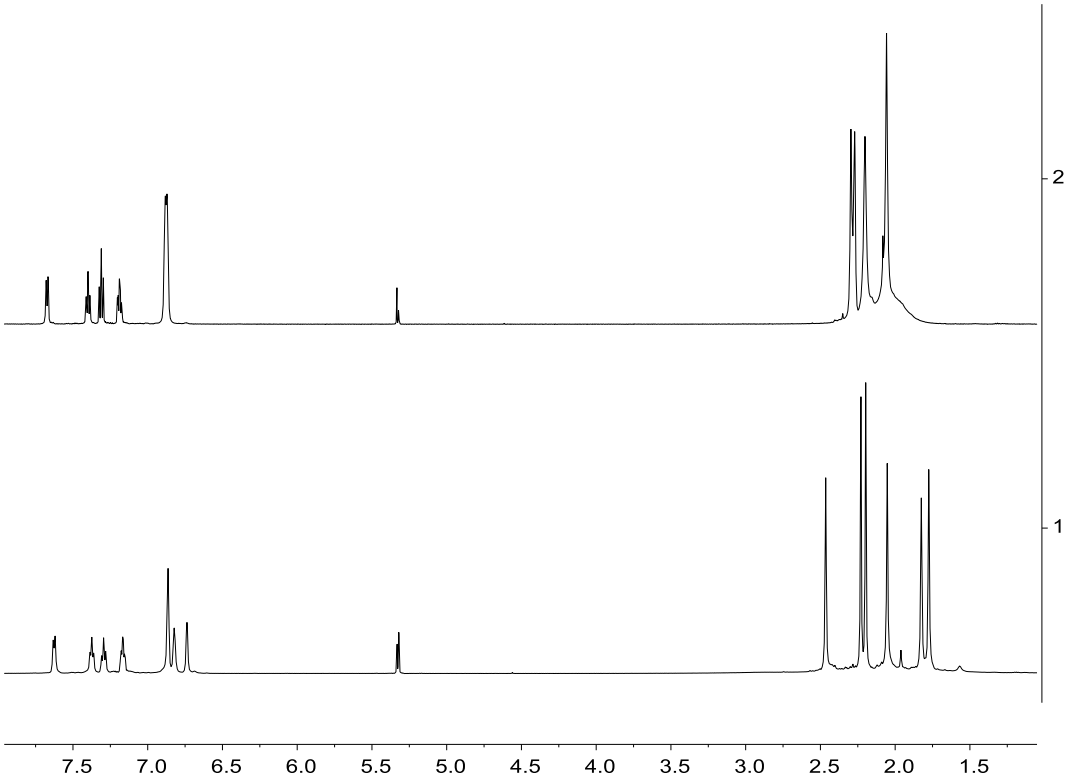


Figure S11. ^{1}H NMR (600 MHz, methylene chloride-d_2) spectra of compound **11** at (1) 193 K and (2) 299 K.

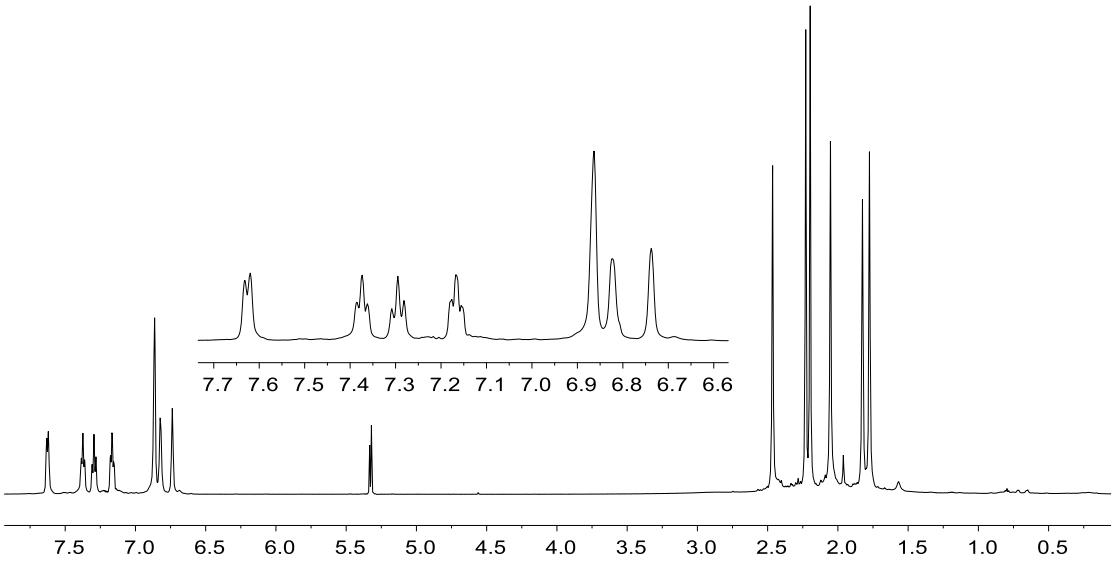


Figure S12. ^{1}H NMR (600 MHz, methylene chloride-d_2, 193 K) spectrum of compound **11**

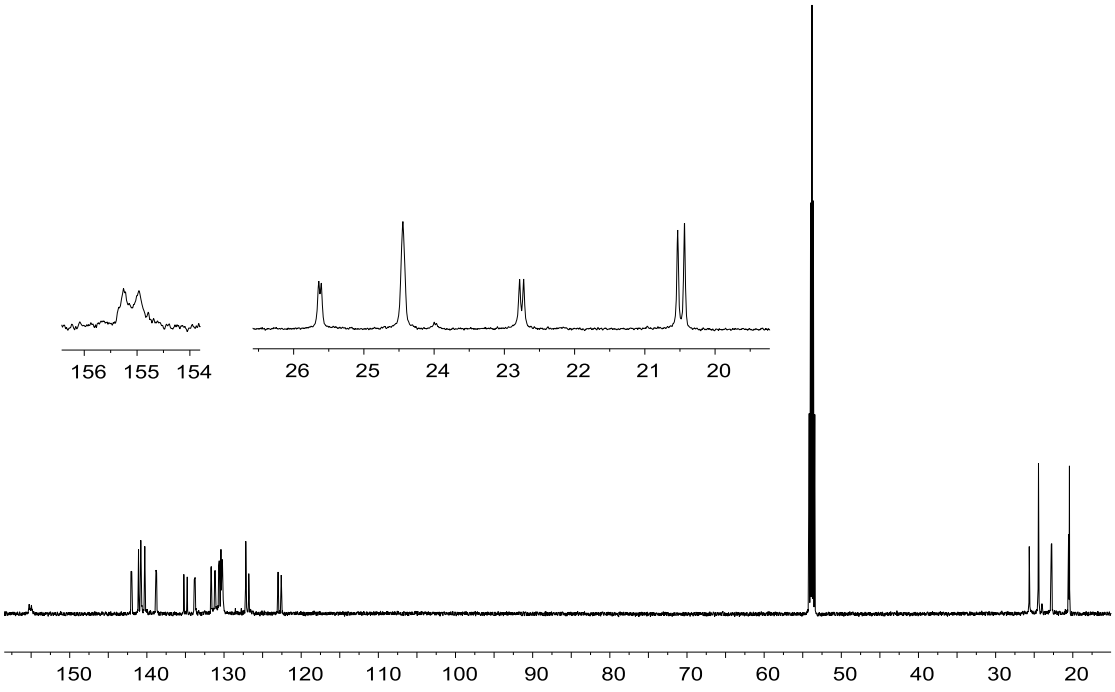


Figure S13. ^{13}C{^{1}H} NMR (151 MHz, methylene chloride- d_2, 193K) spectrum of compound **11**

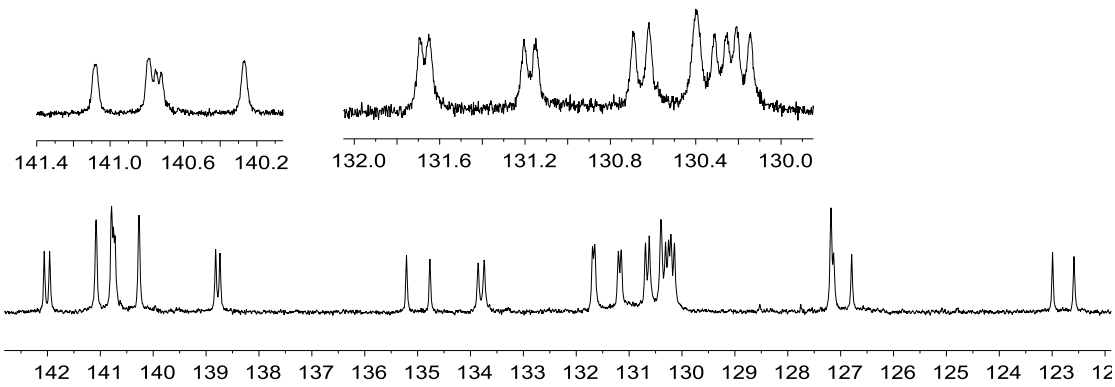


Figure S14. ^{13}C{^{1}H} NMR (151 MHz, methylene chloride- d_2, 193K) spectrum of compound **11**

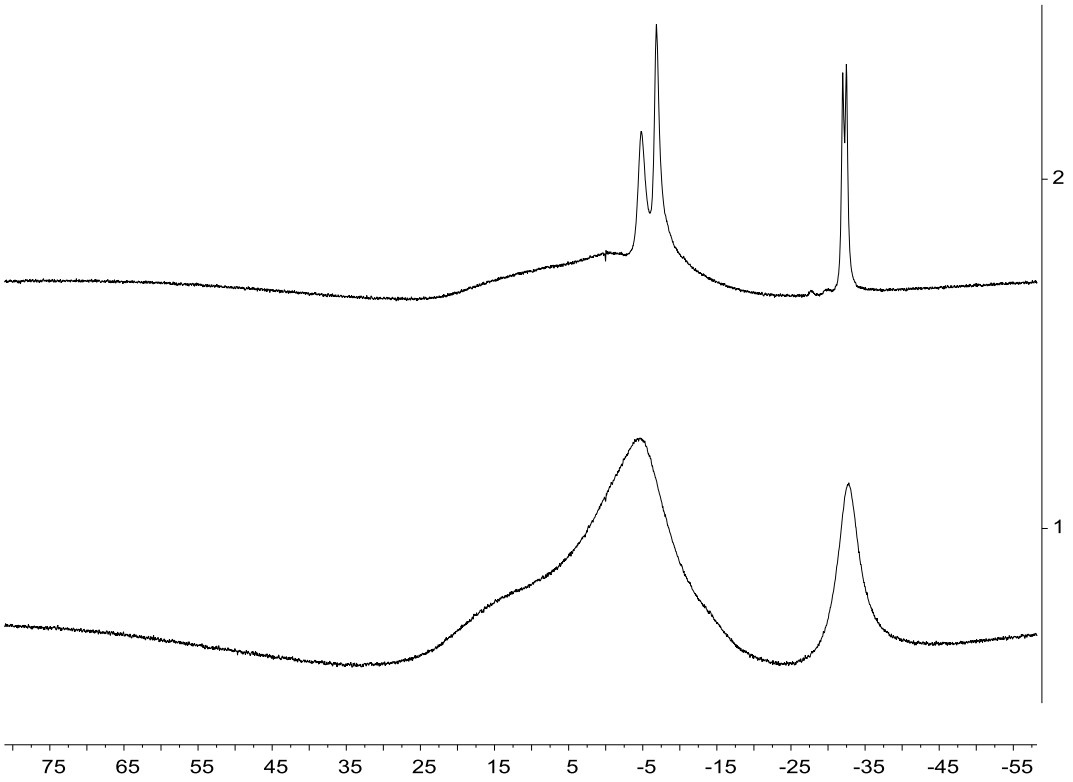


Figure S15. $^{11}B\{^1H\}$ NMR (192 MHz, methylene chloride- d_2) spectra of compound **11** at (1) 193 K and (2) 299 K.

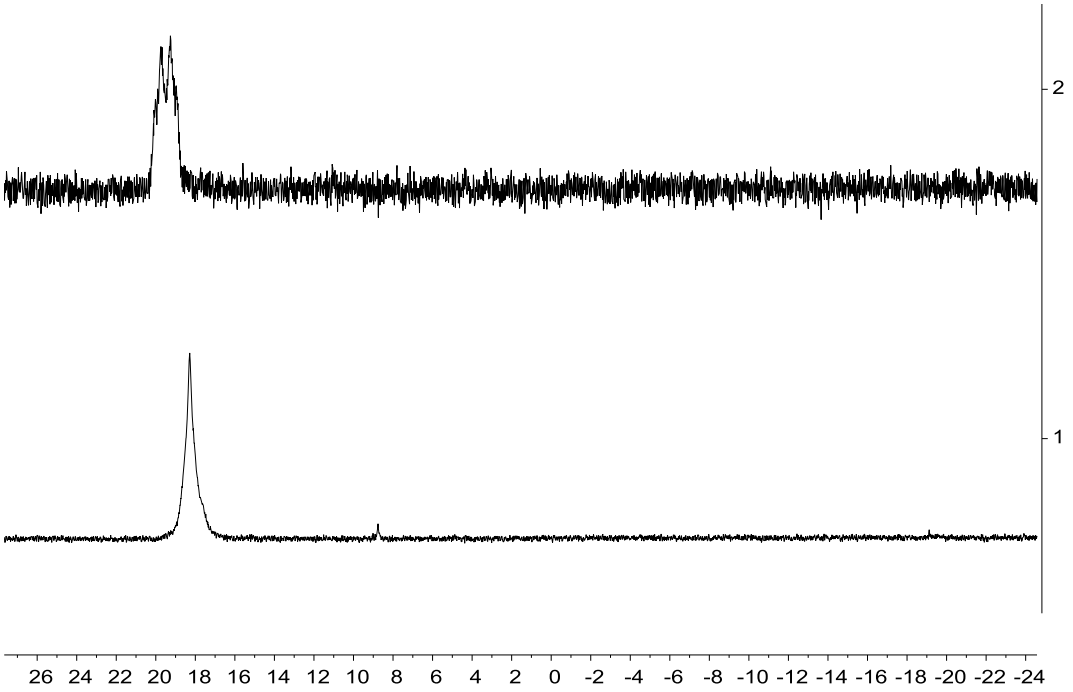


Figure S16. $^{31}P\ \{^1H\}$ NMR (243 MHz, methylene chloride-d_2) spectra of compound **11** at (1) 193 K and (2) 299 K.

Crystals suitable for the *X*-ray crystal structure analysis were obtained from a solution of compound **11** in a mixed solvent (cyclopentane: methylene chloride ca. 1:1 ratio) at room temperature.

X-ray crystal structure analysis of compound 11 (erk9105): A pale yellow plate-like specimen of $C_{24}H_{32}B_3P$, approximate dimensions 0.077 mm x 0.133 mm x 0.214 mm, was used for the X-ray crystallographic analysis. The

X-ray intensity data were measured. A total of 952 frames were collected. The total exposure time was 22.14 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 30888 reflections to a maximum θ angle of 66.85° (0.84 Å resolution), of which 3869 were independent (average redundancy 7.983, completeness = 99.9%, R_{int} = 13.33%, R_{sig} = 5.14%) and 3054 (78.94%) were greater than 2σ(F^2). The final cell constants of a = 10.0213(3) Å, b = 12.6524(4) Å, c = 17.7395(6) Å, β = 103.7880(10)°, volume = 2184.44(12) $Å^3$, are based upon the refinement of the XYZ-centroids of 9920 reflections above 20 σ(I) with 5.129° < 2θ < 133.2°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.813. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7940 and 0.9180. 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, $C_{24}H_{32}B_3P$. The final anisotropic full-matrix least-squares refinement on F^2 with 283 variables converged at R1 = 7.46%, for the observed data and wR2 = 15.25% for all data. The goodness-of-fit was 1.154. The largest peak in the final difference electron density synthesis was 0.195 $e^-/Å^3$ and the largest hole was -0.336 $e^-/Å^3$ with an RMS deviation of 0.053 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.167 g/cm^3 and F(000), 824 e^-.

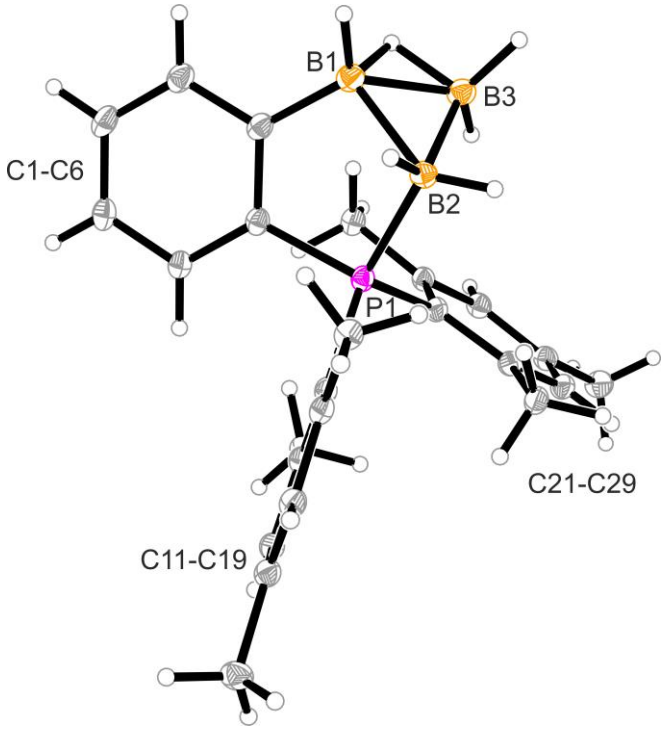
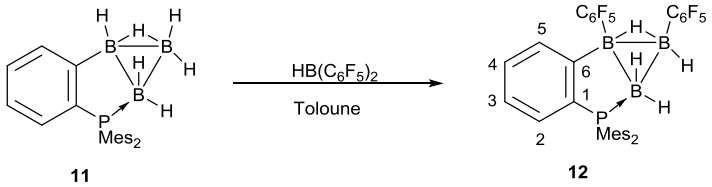


Figure S17. Molecular structure of compound **11**. (Thermal ellipsoids are shown with 15% probability.)

Preparation of triborane(7) derivative 12



11 **12**

Scheme S4. The reaction of triborane(7) derivative **11** with $HB(C_6F_5)_2$.

A solution of compound **11** (38.4 mg, 0.1 mmol) in toluene (2 mL) was added to a suspension of $HB(C_6F_5)_2$ (69.2 mg, 0.2 mmol) in toluene (2 mL). The mixture was stirred at room temperature for 3 days to give a colorless

solution with a white precipitate. All volatiles were removed in vacuo and the residue was dispersed in pentane (15 mL). The white solid was filtrated off and the clear solution was stored at -35 °C for 4 days to give colorless crystalline solid. The crystalline solids were collected and dried in vacuum to give the product **12** (34 mg, 0.047 mmol, 47% yield).

E. A. for $C_{36}H_{30}B_3F_{10}P$: calc. C (60.39 %), H (4.22 %), found: C (60.93 %), H (4.47 %).

Melting Point (DSC): 157 °C

^{1}H NMR (600 MHz, toluene-d_8, 228 K): δ = 7.37 (m, 1H, 2-CH), 7.05 (br d, $^{3}J_{HH}$ = 7.6 Hz, 1H, 5-CH), 6.93 (m, 1H, 4-CH), 6.74 (m, 1H, 3-CH), 6.40 (br, 1H, *m*-Mes^{a}), 6.36 (br, 1H, *m*-Mes^{b}), 6.33 (br, 1H, *m*'-Mes^{a}), 6.28 (br, 1H, *m*'-Mes^{b}), 2.78 (s, 3H, *o*'-CH_3^{Mesa}), 2.03 (s, 3H, *o*'-CH_3^{Mesb}), 1.89 (s, 3H, *p*-CH_3^{Mesb}), 1.88 (s, 3H, *p*-CH_3^{Mesa}), 1.86 (s, 3H, *o*-CH_3^{Mesb}), 1.75 (s, 3H, *o*-CH_3^{Mesa}), [BH not listed].

^{13}C{^{1}H} NMR (151 MHz, toluene-d_8, 228 K): δ = 154.0 (br d, $^{2}J_{PC}$ ~ 40 Hz, 6-C), 143.4 (d, $^{2}J_{PC}$ = 14.8 Hz, *o*'-Mes^{a}), 142.4 (d, $^{2}J_{PC}$ = 3.2 Hz, *o*-Mes^{b}), 141.7 (*p*-Mes^{a}), 141.1 (*o*-Mes^{a}), 140.9 (*p*-Mes^{b}), 138.9 (d, $^{2}J_{PC}$ = 12.7 Hz, *o*'-Mes^{b}), 134.5 (d, $^{3}J_{PC}$ = 5.5 Hz, 5-CH), 134.2 (d, $^{1}J_{PC}$ = 52.5 Hz, 1-C), 132.4 (d, $^{2}J_{PC}$ = 6.1 Hz, 2-CH), 132.1 (d, $^{3}J_{PC}$ = 8.5 Hz, *m*-Mes^{a}), 131.9 (4-CH), 131.8 (d, $^{3}J_{PC}$ = 11.3 Hz, *m*'-Mes^{a}), 131.4 (d, $^{3}J_{PC}$ = 9.9 Hz, *m*'-Mes^{b}), 131.2 (d, $^{3}J_{PC}$ = 8.7 Hz, *m*-Mes^{b}), 128.8 (3-CH), 127.3 (d, $^{1}J_{PC}$ = 61.6 Hz, *i*-Mes^{b}), 123.9 (d, $^{1}J_{PC}$ = 63.3 Hz, *i*-Mes^{a}), 26.4 (*o*'-CH_3^{Mesa}), 24.8 (d, $^{3}J_{PC}$ = 2.9 Hz, *o*-CH_3^{Mesa}), 24.7 (d, $^{3}J_{PC}$ = 2.6 Hz, *o*-CH_3^{Mesb}), 23.1 (d, $^{3}J_{PC}$ = 8.9 Hz, *o*'-CH_3^{Mesb}), 20.67 (*p*-CH_3^{Mesb}), 20.59 (*p*-CH_3^{Mesa}), [C_6F_5 not listed].

^{11}B{^{1}H} NMR (192 MHz, toluene-d_8, 299 K): δ = 1.6 ($v_{1/2}$ ≈ 300 Hz), -3.2 ($v_{1/2}$ ≈ 400 Hz), -28.9 ($v_{1/2}$ ≈ 350 Hz).

^{31}P{^{1}H} NMR (243 MHz, toluene-d_8, 299 K): δ = 18.2 (m).

^{31}P{^{1}H} NMR (243 MHz, toluene-d_8, 228 K): δ = 17.5 (m).

^{19}F NMR (564 MHz, toluene-d_8, 208 K): δ = [-128.2 (*o*), -134.6 (*o*'), -154.8 (*p*), -162.1 (*m*), -162.3 (*m*')](each br, each 1F, C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 7.5, 7.3]; [-131.8 (2F, *o*), -155.7 (1F, *p*), -163.4 (2F, *m*)](each br, C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 7.7].

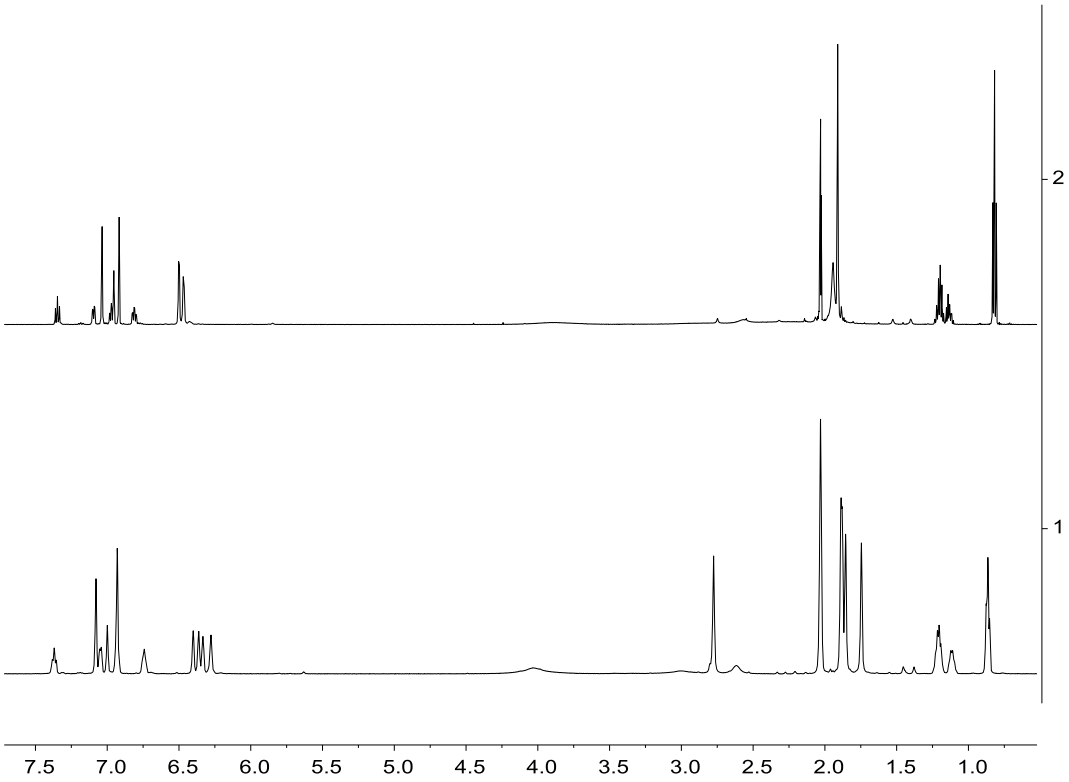


Figure S18. ^{1}H NMR (600 MHz, toluene-d_8) spectra of compound **12** (admixed with pentane) at (1) 208 K and (2) 299 K.

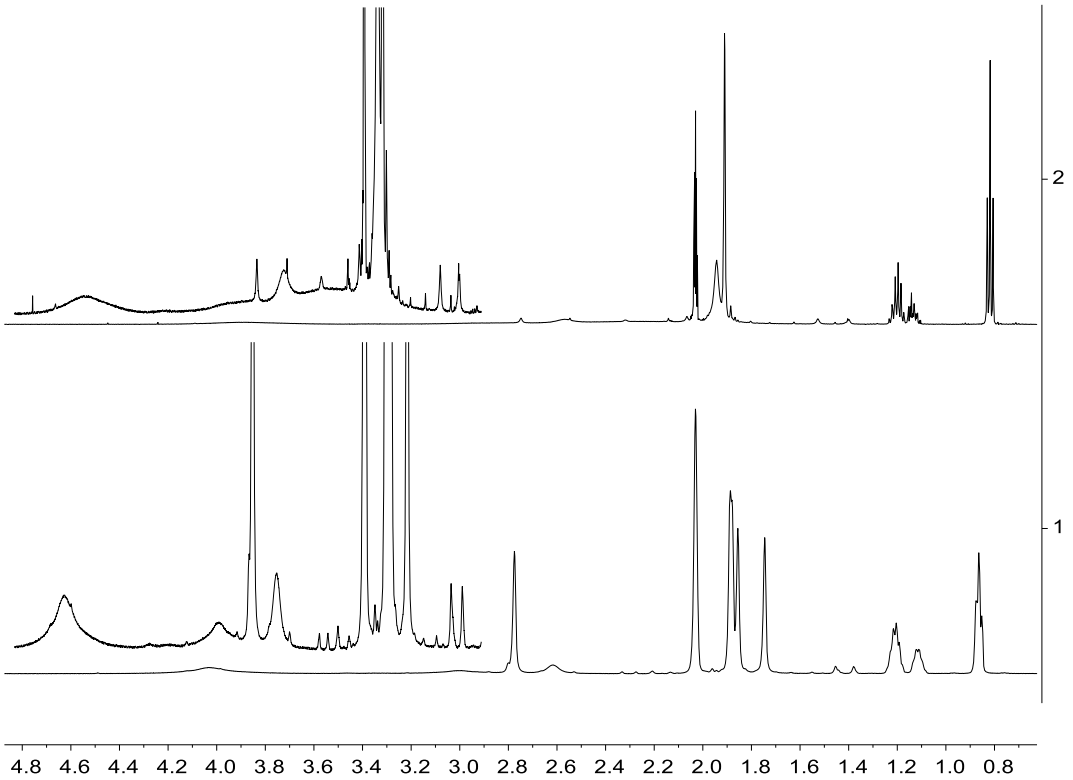


Figure S19. ^{1}H NMR (600 MHz, toluene-d_8) spectra of compound **12** (admixed with pentane) at (1) 208 K and (2) 299 K.

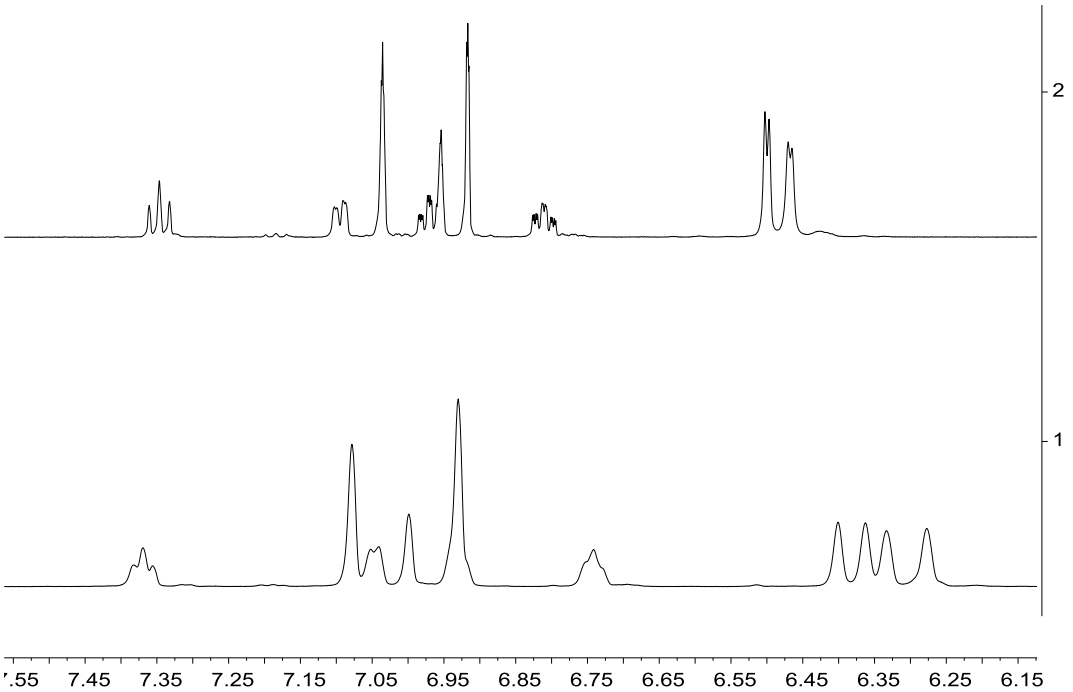


Figure S20. ^{1}H NMR (600 MHz, toluene-d_8) spectra of compound **12** (admixed with pentane) at (1) 208 K and (2) 299 K.

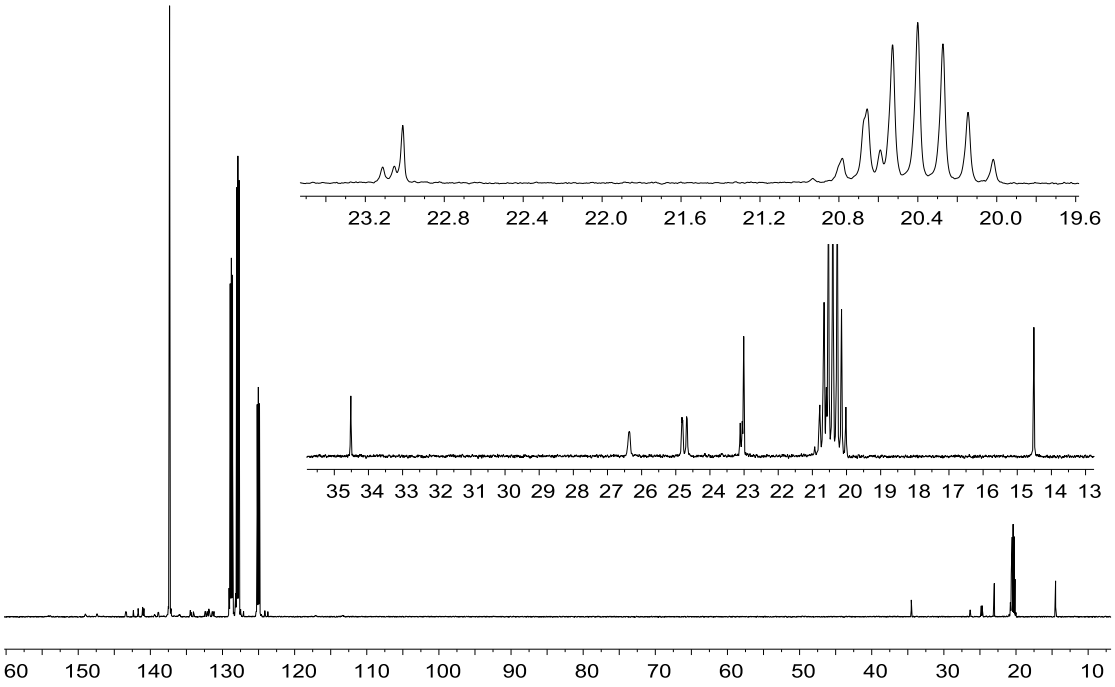


Figure S21. $^{13}C\{^{1}H\}$ NMR (151 MHz, toluene-d_8, 228 K) spectrum of compound **12**

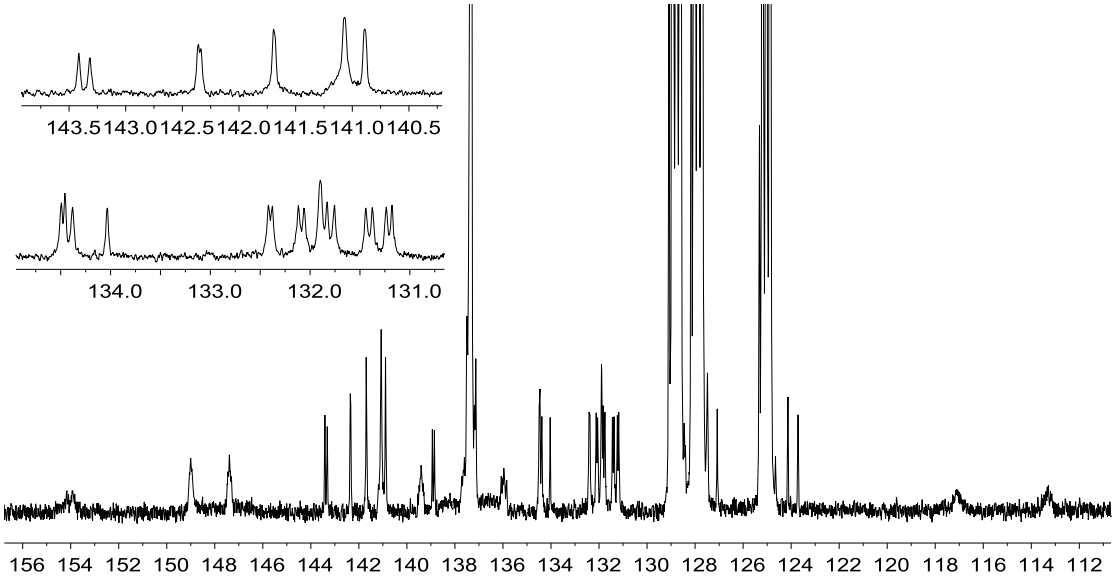


Figure S22. $^{13}C\{^{1}H\}$ NMR (151 MHz, toluene-d_8, 228 K) spectrum of compound **12**

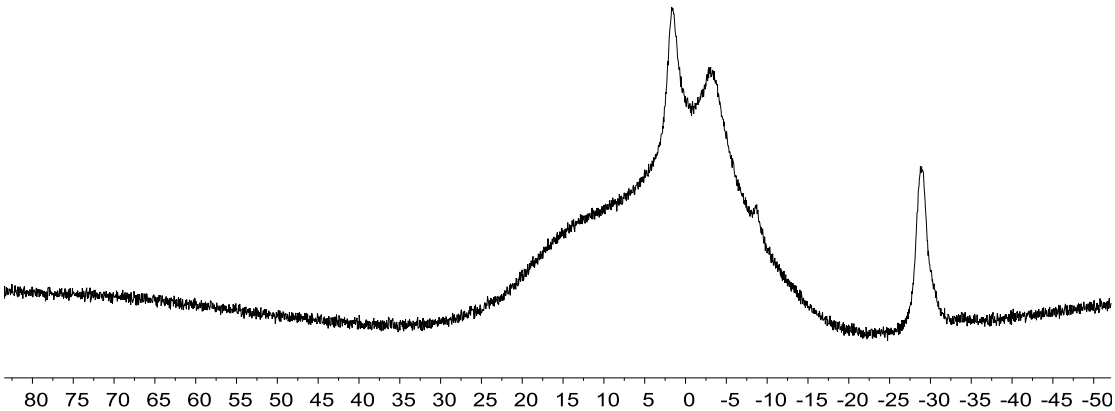


Figure S23. $^{11}B\{^{1}H\}$ NMR (192 MHz, toluene-d_8, 299 K) spectrum of compound **12**.

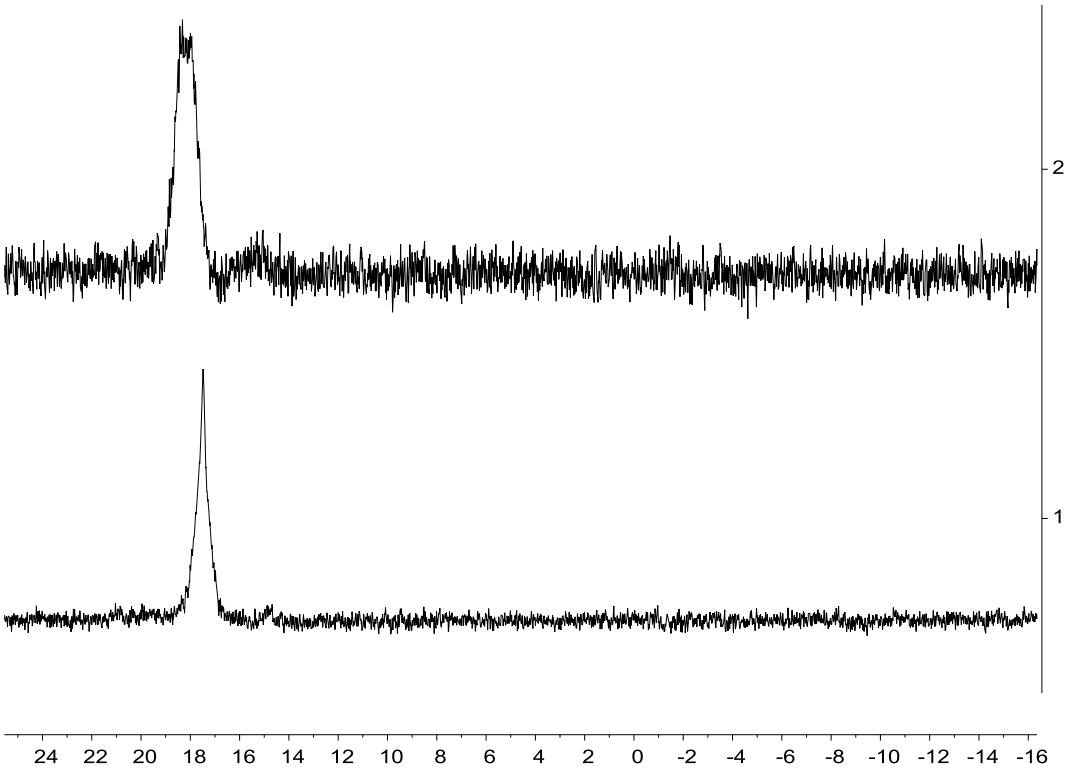


Figure S24. $^{31}P\{^{1}H\}$ NMR (243 MHz, toluene-d_8, 299 K) spectra of compound **12** at (1) 228 K and (2) 299 K.

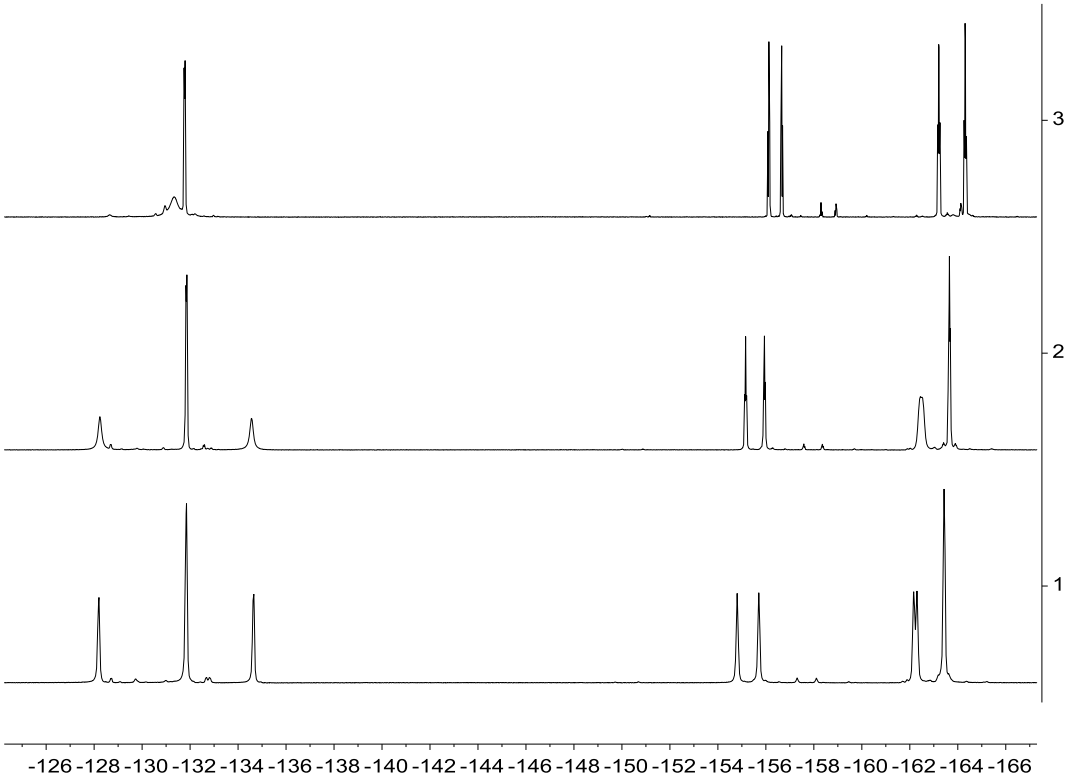


Figure S25. ^{19}F NMR (564 MHz, toluene-d_8, 208 K) spectra of compound **12** at (1) 208 K, (2) 228 K, and (3) 299 K.

Crystals suitable for the *X*-ray crystal structure analysis were obtained from a solution of compound **12** in cyclopentane at room temperature.

X-ray crystal structure analysis of compound 12 (erk9206): formula $C_{36}H_{30}B_3F_{10}P$, *M* = 716.00, colorless crystal, 0.18 x 0.14 x 0.10 mm, *a* = 13.6837(2) Å, *b* = 13.2326(2) Å, *c* = 19.2001(4) Å, □ = 102.622(1)°, *V* = 3392.56(10) Å^3, ρ_{calc} = 1.402 gcm^{-3}, μ = 0.162 mm^{-1}, empirical absorption correction (0.971 ≤ T ≤ 0.984), *Z* = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, *T* = 173(2) K, ω and ϕ scans, 18717 reflections collected (±*h*, ±*k*, ±*l*), 5865 independent (R_{int} = 0.039) and 4828 observed reflections [*I*>2σ*I*)], 473 refined parameters, *R* = 0.050, wR^2 = 0.108, max. (min.) residual electron density 0.32 (-0.25) e.Å^{-3}, the hydrogen atoms at B1, B2 and B3 were refined freely; others hydrogen atoms were calculated and refined as riding atoms.

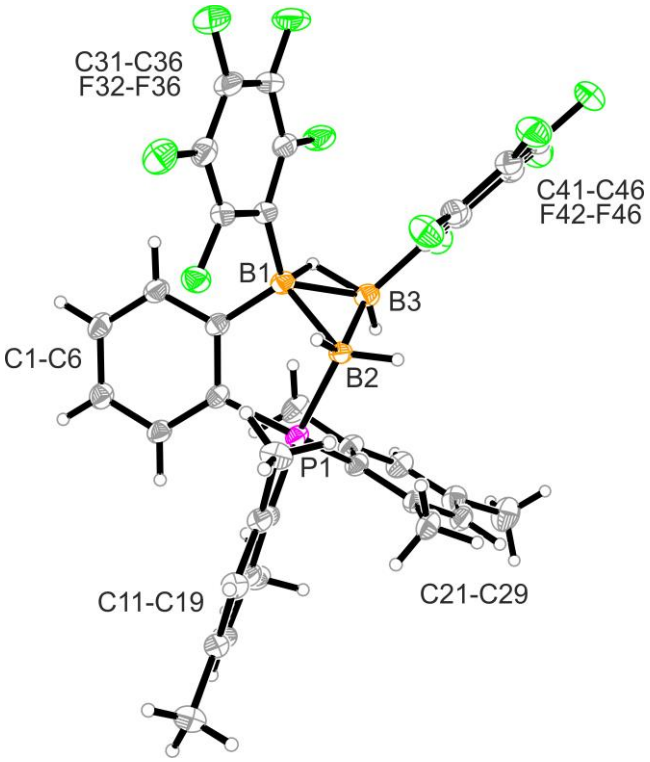
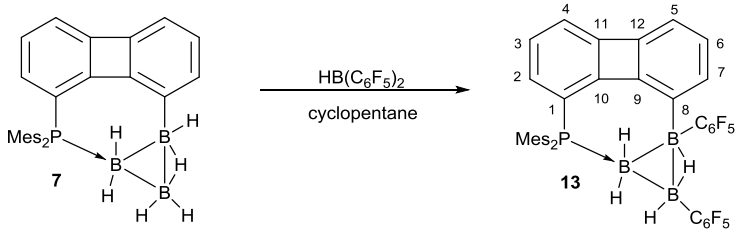


Figure S26. Molecular structure of compound **12**. (Thermal ellipsoids are shown with 30% probability.)

Preparation of triborane(7) derivative 13



Scheme S5. The reaction of triborane(7) derivative **7** with $HB(C_6F_5)_2$

A solution of compound **7** (45.8 mg, 0.1 mmol) in cyclopentane (5 mL) was added to a suspension of $HB(C_6F_5)_2$ (69.2 mg, 0.2 mmol) in cyclopentane (5 mL). The mixture was stirred at room temperature for 3 days to give a yellow solution with a bright yellow precipitate. All volatiles were removed in vacuum and the residue was dispersed in pentane (30 mL). The yellow solid was filtered off and the clear solution was stored at -35 °C for 1 day to give a light yellow powder. The solid was collected and dried in vacuum to give the product **13** (33 mg, 0.041 mmol, 41% yield).

E. A. for $C_{42}H_{32}B_3F_{10}P$: calc. C (63.65 %), H (4.08 %), found: C (64.64 %), H (4.50 %).

Melting Point (DSC): 131 °C

^{1}H NMR (500 MHz, methylene chloride-d_2, 299 K): δ = 6.95 (br d, $^{4}J_{PH}$ = 3.7 Hz, 1H, *m*-Mes^{a}), 6.88 (br m, 1H, *m*'-Mes^{a}), 6.85 (br m, 1H, *m*-Mes^{b}), 6.77 (m, 1H, 6-CH), 6.73 (m, 1H, 5-CH), 6.73 (m, 1H, 3-CH)^{t}, 6.72 (m, 1H, 4-CH)^{t}, 6.70 (m, 1H, 2-CH)^{t}, 6.49 (d, $^{3}J_{HH}$ = 7.9 Hz, 1H, 7-CH), 6.34 (br d, $^{4}J_{PH}$ = 3.6 Hz, 1H, *m*'-Mes^{b}), 2.78 (s, 3H, *o*-CH_3^{Mesa}), 2.44 (s, 3H, *o*-CH_3^{Mesb}), 2.27 (s, 3H, *p*-CH_3^{Mesa}), 2.18 (s, 3H, *p*-CH_3^{Mesb}), 1.82 (s, 3H, *o*'-CH_3^{Mesa}), 1.73 (s, 3H, *o*'-CH_3^{Mesb}), [BH not listed, ^{t} tentative assignment].

^{13}C{^{1}H} NMR (126 MHz, methylene chloride-d_2, 299 K): δ = 159.4 (d, $^{2}J_{PC}$ = 13.1 Hz, 10-C), 153.5 (d, $^{3}J_{PC}$ = 3.9 Hz, 9-C), 152.4 (d, $^{3}J_{PC}$ = 14.7 Hz,11-C), 150.7 (12-C), 142.8 (d, $^{2}J_{PC}$ = 13.7 Hz, *o*-Mes^{a}), 142.34 (d, $^{4}J_{PC}$ = 2.6 Hz, *p*-Mes^{a}), 142.28 (d, $^{2}J_{PC}$ = 3.9 Hz, *o*'-Mes^{a}), 141.5 (d, $^{4}J_{PC}$ = 2.6 Hz, *p*-Mes^{b}), 141.2 (d, $^{2}J_{PC}$ = 5.2 Hz, *o*-Mes^{b}), 140.8 (d, $^{2}J_{PC}$ = 13.1 Hz, *o*'-Mes^{b}), 136.3 (br, 8-C), 132.7 (d, $^{3}J_{PC}$ = 9.0 Hz, *m*'-Mes^{a}), 132.5 (7-CH), 132.44 (d, $^{3}J_{PC}$ = 10.8 Hz, *m*-Mes^{a}), 132.42 (br d, $^{3}J_{PC}$ = 9.5 Hz, *m*-Mes^{b}), 130.6 (d, $^{2}J_{PC}$ = 3.3 Hz, 2-CH)^{t}, 130.2 (d, $^{3}J_{PC}$ = 10.8 Hz, *m*'-Mes^{b}), 130.1 (6-CH), 129.5 (d, $^{3}J_{PC}$ = 7.0 Hz, 3-CH)^{t}, 125.0 (d, $^{1}J_{PC}$ = 65.2 Hz, *i*-Mes^{b}), 123.1 (d, $^{1}J_{PC}$ = 64.2 Hz, *i*-Mes^{a}), 119.5 (d, $^{4}J_{PC}$ = 2.3 Hz, 4-CH), 118.4 (5-CH), 117.1 (d, $^{1}J_{PC}$ = 59.3 Hz, 1-C), 25.4 (dd, *J* = 6.2, 3.3 Hz, *o*-CH_3^{Mesa}), 25.1 (d, $^{3}J_{PC}$ = 3.9 Hz, *o*'-CH_3^{Mesa}), 24.9 (d, $^{3}J_{PC}$ = 3.4 Hz, *o*-CH_3^{Mesb}), 23.1 (d, $^{3}J_{PC}$ = 4.9 Hz, *o*'-CH_3^{Mesb}), 20.9 (d, $^{5}J_{PC}$ = 1.3 Hz, *p*-CH_3^{Mesa}), 20.6 (*p*-CH_3^{Mesb}), [C_6F_5 not listed, , ^{t} tentative assignment].

^{11}B{^{1}H} NMR (160 MHz, methylene chloride-d_2, 299 K): δ = 8.0 ($v_{1/2}$ ≈ 530 Hz), -22.4 ($v_{1/2}$ ≈ 220 Hz), -35.6 (d, $^{1}J_{PB}$ ≈ 96 Hz).

^{31}P{^{1}H} NMR (202 MHz, methylene chloride-d_2, 299 K): δ = 5.4 (m).

^{19}F NMR (470 MHz, methylene chloride-d_2, 238 K): δ = [-127.0 (m, *o*), -128.1 (m, *o*'), -160.5 (t, $^{3}J_{FF}$ = 20.7 Hz, *p*), -165.7 (m, *m*), -166.6 (m, *m*')](each 1F, C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 6.1, 5.2]; [-130.3 (m, *o*), -134.1 (m, *o'*), -156.1 (t, $^{3}J_{FF}$ = 20.8 Hz, *p*), -163.5 (m, *m'*), -163.6 (m, *m*)](each 1F, C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 7.5, 7.4].

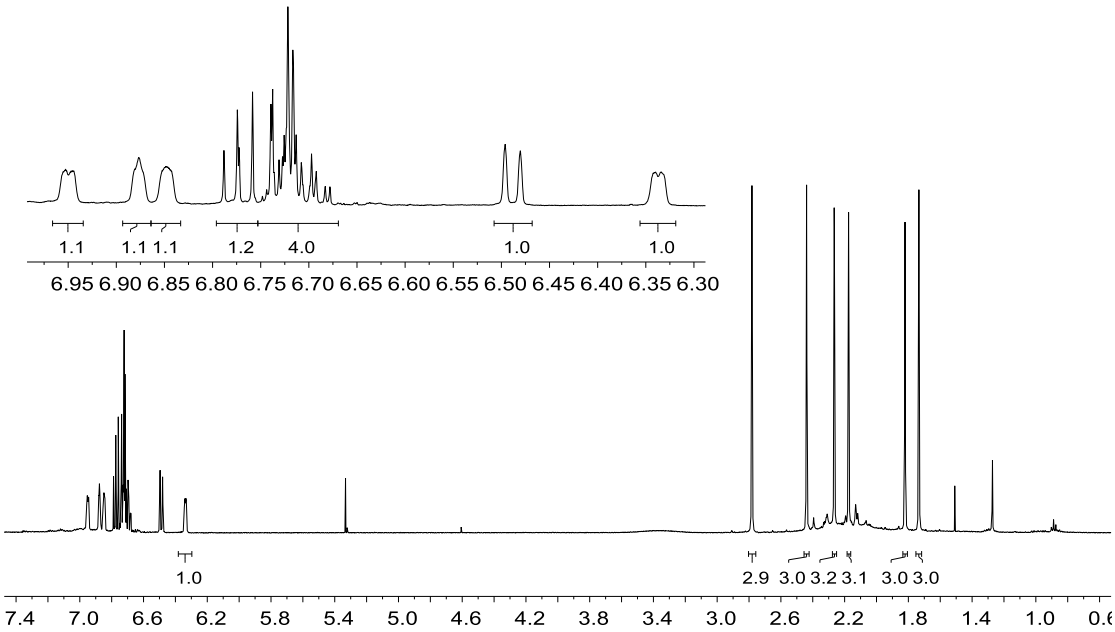


Figure S27. ^{1}H NMR (500 MHz, methylene chloride-d_2, 299 K) spectrum of compound **13**

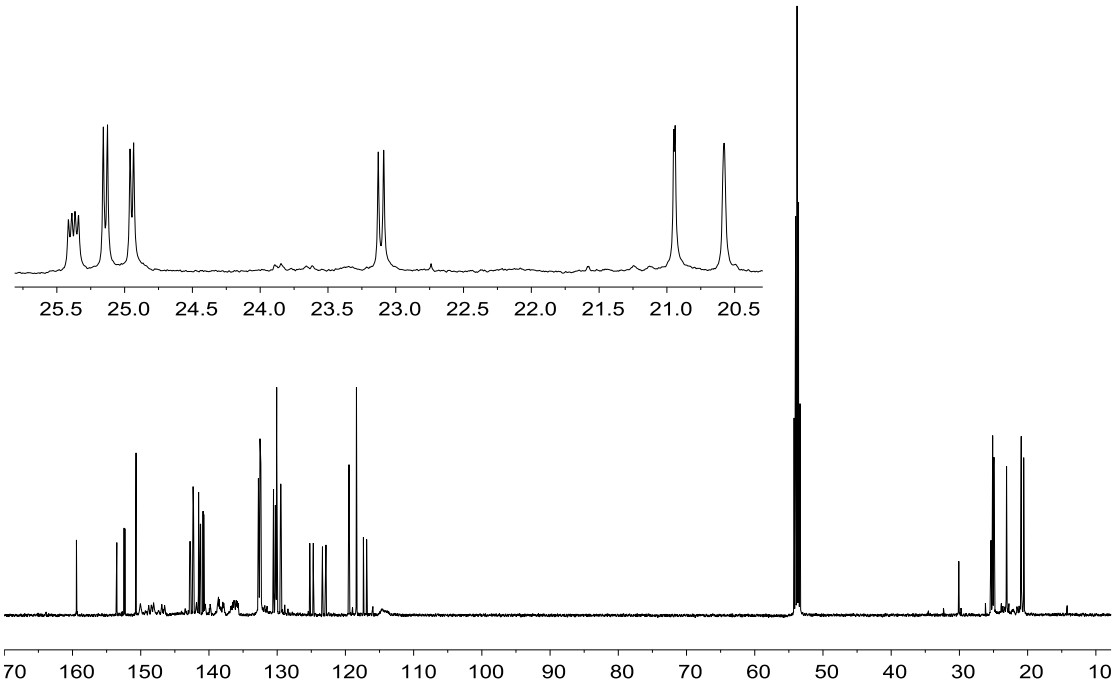


Figure S28. $^{13}C\{^{1}H\}$ NMR (126 MHz, methylene chloride-d_2, 299 K) spectrum of compound **13**

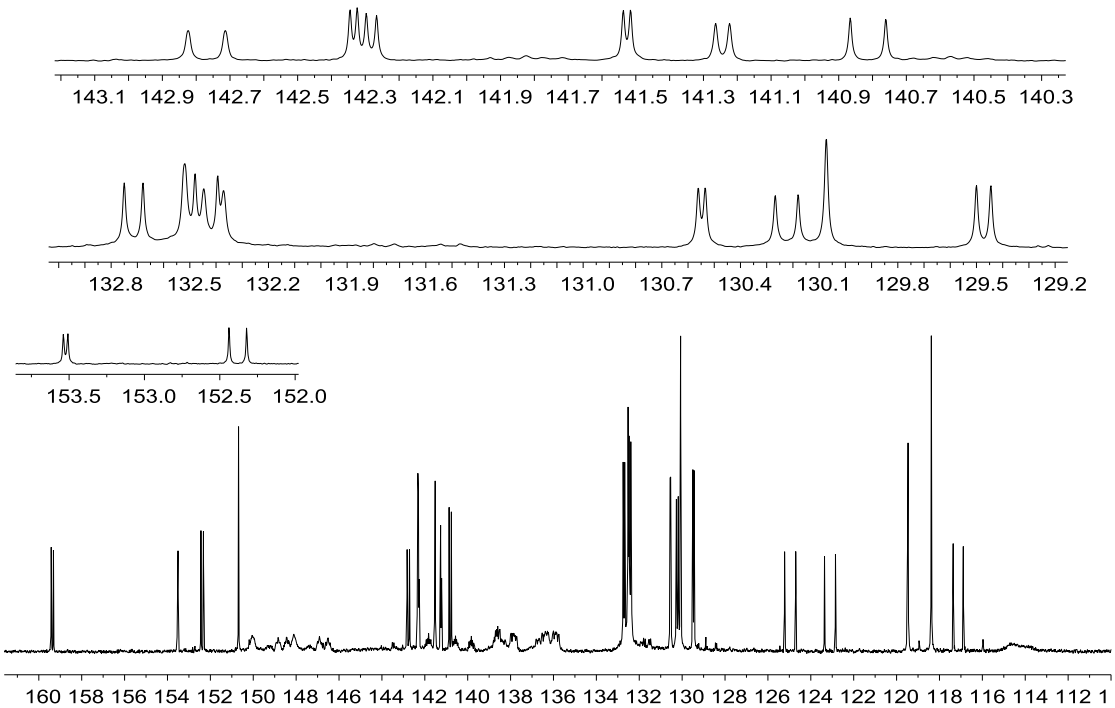


Figure S29. $^{13}C\{^{1}H\}$ NMR (126 MHz, methylene chloride-d_2, 299 K) spectrum of compound **13**

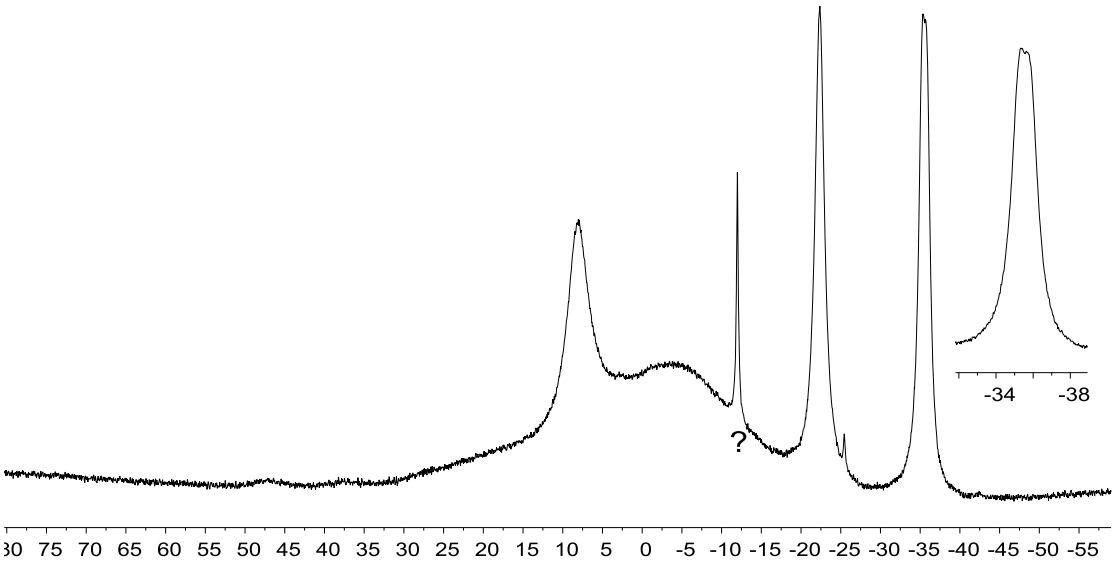


Figure S30. $^{11}B\{^1H\}$ NMR 160 MHz, methylene chloride-d_2, 299 K) spectrum (of compound **13** (? B impurity)

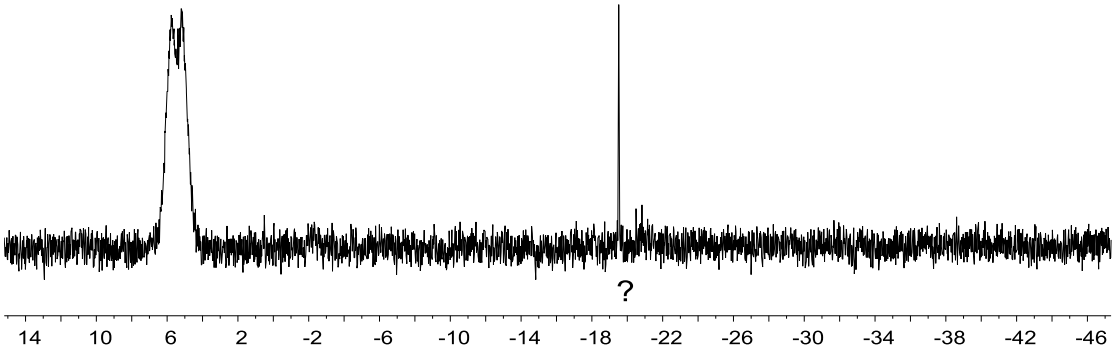


Figure S31. $^{31}P\{^1H\}$ NMR (202 MHz, methylene chloride-d_2, 299 K) spectrum of compound **13** (? PH impurity)

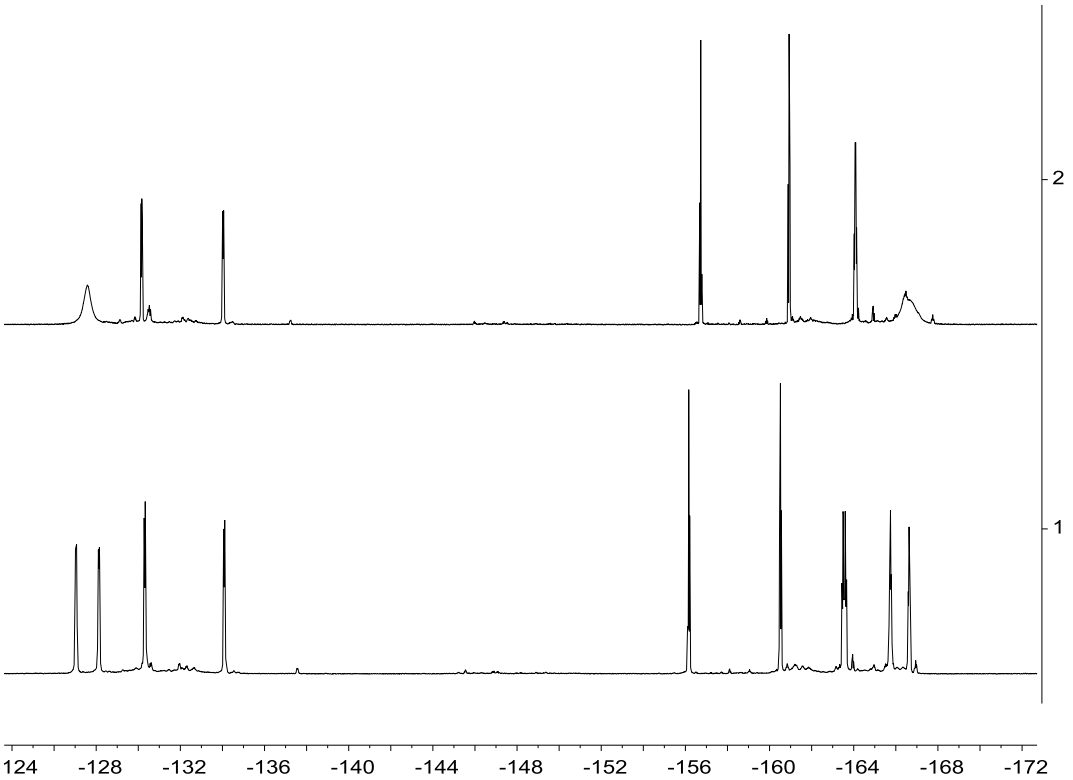


Figure S32. ^{19}F NMR (470 MHz, methylene chloride-d_2, 238 K) spectra of compound **13** at (1) 238 K and (2) 299 K.

Crystals suitable for the *X*-ray crystal structure analysis were obtained from a solution of compound **13** in cyclopentane at room temperature.

X-ray crystal structure analysis of compound 13 (erk9220): formula $C_{42}H_{32}B_3F_{10}P$, M = 790.08, colourless crystal, 0.10 x 0.07 x 0.03 mm, a = 15.0735(4) Å, b = 15.1214(4) Å, c = 19.5400(6) Å, α = 84.907(2)°, β = 81.768(2)°, γ = 86.110(1)°, V = 4383.60(2) Å^3, ρ_{calc} = 1.197 gcm^{-3}, μ = 0.132 mm^{-1}, empirical absorption correction (0.987 ≤ T ≤ 0.996), Z = 4, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 173(2) K, ω and ϕ scans, 44882 reflections collected (±h, ±k, ±l), 15315 independent (R_{int} = 0.091) and 8989 observed reflections [I>2σI)], 1054 refined parameters, R = 0.083, wR^2 = 0.237, max. (min.) residual electron density 0.53 (-0.38) e.Å^{-3}, the hydrogen atoms at B1, B2 and B3 were refined freely; others hydrogen atoms were calculated and refined as riding atoms.

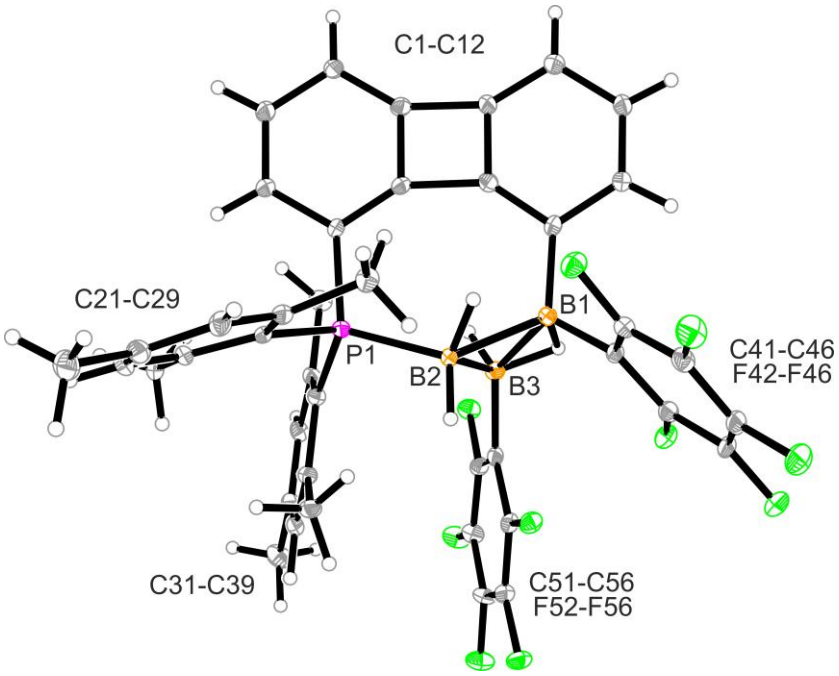


Figure S33. Molecular structure of compound **13**. (Thermal ellipsoids are shown with 15% probability.)

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