Supporting Information

Macrocyle Formation by Cooperative Selection at a Double-sited Frustrated Lewis Pair

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# Table of contents

| Section                                                                 | Page |
|------------------------------------------------------------------------|------|
| General information                                                    | S3   |
| Synthesis of compound 2                                                | S4   |
| Synthesis of compound 3                                                | S11  |
| Synthesis of compound 6:                                               |      |
|   Reaction of compound 3 with 2 equiv. of 4-phenylbut-3-yn-2-one (4)   | S17  |
|   Control reaction:                                                    |      |
|   Reaction of compound 3 with 1 equiv. of 4-phenylbut-3-yn-2-one (4)   | S25  |
| Synthesis of compound 11                                               | S28  |
| Synthesis of compound 15a                                              | S39  |
| Synthesis of compound 15b                                              | S50  |
| Synthesis of compound 15c                                              | S59  |
| Synthesis of compound 12d                                              | S68  |
| References                                                             | S76  |
General information

Materials and Methods: All experiments were carried out under a dry argon atmosphere using standard Schlenk-type glassware and/or in a glove box. Solvents were dried and stored under an argon atmosphere. NMR spectra were recorded on a Varian UNITY plus 600 MHz spectrometer ($^1$H 600 MHz, $^{19}$F 564 MHz, $^{31}$P 243 MHz, $^{11}$B 192 MHz, $^{13}$C 151 MHz). $^1$H and $^{13}$C NMR: chemical shifts (δ) are given relative to Me$_4$Si and referenced to the respective solvent signal. $^{19}$F NMR: chemical shifts (δ) are given relative to CFCl$_3$ (external reference, δ = 0). $^{31}$P NMR: chemical shifts (δ) are given relative to H$_3$PO$_4$ (85% in D$_2$O) (external reference, δ = 0). $^{11}$B NMR: chemical shifts (δ) are given relative to BF$_3$·OEt$_2$ (external reference, δ = 0). NMR assignments were supported by addition 2D-NMR experiments. HRMS was recorded on GTC Waters Micromass (Manchester, UK) and melting points were measures on TA-instruments DSC-20. Elemental analyses were performed on a Foss-Heraeus CHNO-Rapid.

Unless otherwise noted, all chemicals were purchased from commercially available sources and used as received. Compounds 1, 2 MesPCl$_2$, and HB(C$_6$F$_5$)$_2$ were prepared according to reported methods.

X-Ray diffraction: For compounds 1, 2 and 11 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). For compound 15b data sets were collected with a Bruker APEX II CCD diffractometer. Data sets for compounds 3, 6, 15a and 15c 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 2 the allyl group, for compound 3 one pentane and one dichloromethane molecules and for compound 15c one pentane molecule 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. For compound 6 three badly disordered dichloromethane molecules, for compound 11 one pentane and two dichloromethane molecules, for compound 15a one dichloromethane molecule, for compound 15b three dichloromethane molecules and for compound 15c one half pentane molecule were found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (Spek, A.L. Acta Crystallogr. 2015, 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. CCDC deposition numbers are 1864103 to 1864109 and 1873800.
Synthesis of compound 2

**1**\textsuperscript{st} Step - Preparation of compound 1\textsuperscript{5}: In a Schlenk flask, \textit{n}-BuLi (24 mL, 38.4 mmol, 2.4 eq., 1.6 M in hexane) was added dropwise to a solution of dimethyl-9\textit{H}-xanthene (3.364 g, 1.6 mmol, 1.0 eq.) and tetramethylethylenediamine (4.8 mL, 32 mmol, 2.0 eq.) in diethyl ether (40 mL), at -78 °C. Then the solution was warmed to 40 °C and stirred at this temperature for 4 h. After cooling this solution to 0 °C, a solution of \textit{I}_2 (8.122 g, 32 mmol, 2.0 eq.) in hexane (50 mL) was added. The mixture was stirred at r.t. for 1 h. After all volatiles were removed in vacuo, the resulting residue was extracted with pentane (100 mL × 3). The combined extracts were concentrated and purified by silica gel chromatography (pentane : dichloromethane = 10 : 1) to give compound \textbf{1} as a white solid (6.211 g, 13.44 mmol, 84 %).

[Xat: dimethyl-9\textit{H}-xanthendiyl]

\textbf{\textit{1}H NMR} (600 MHz, 299 K, CDCl\textsubscript{3}): \(\delta = 7.73, 7.38, 6.86 \text{ (each m, each 1H, Xat)}, 1.61 \text{ (s, 3H, Me}^{\text{Xat}})\).

\textbf{Figure S1} \textbf{\textit{1}H NMR} (600 MHz, 299 K, CDCl\textsubscript{3}) spectrum of compound \textbf{1}
Crystals of compound 1 suitable for the X-ray crystal structure analysis were obtained by slow cooling of a hot solution of compound 1 in heptane.

**X-ray crystal structure analysis of compound 1**: formula C_{15}H_{12}O_2, $M = 462.05$, colorless crystal, 0.14 x 0.10 x 0.03 mm, $a = 9.5054(3)$ Å, $b = 11.5239(3)$ Å, $c = 13.2624(4)$ Å, $V = 1452.8(1)$ Å$^3$, $\rho_{\text{calc}} = 2.113$ g cm$^{-3}$, $\mu = 4.315$ mm$^{-1}$, empirical absorption correction (0.583 $\leq$ T $\leq$ 0.881), Z = 4, orthorhombic, space group *Pnma* (No. 62), $\lambda = 0.71073$ Å, $T = 173(2)$ K, $\omega$ and $\phi$ scans, 9686 reflections collected ($\pm h$, $\pm k$, $\pm l$), 1515 independent ($R_{\text{int}} = 0.047$) and 1354 observed reflections ($I > 2\sigma(I)$), 102 refined parameters, $R = 0.028$, $wR^2 = 0.069$, max. (min.) residual electron density 0.56 (-0.79) e Å$^{-3}$, hydrogen atoms were calculated and refined as riding atoms.

![Figure S2](S5.png)

**Figure S2** Crystal structure of compound 1 (thermal ellipsoids: 30% probability)
2nd Step - Preparation of compound 2: n-BuLi (5 mL, 8 mmol, 2 eq., 1.6 M in hexane) was added dropwise to a solution of compound 1 (1.848 g, 4 mmol, 1 eq.) in diethyl ether (40 mL) at -78 °C. The mixture was stirred at -78 °C for 2 h. Subsequently, a solution of MesPCl₂ (1.769 g, 8 mmol, 2 eq.) in pentane (2 mL) was added. After 2 h stirring at -78 °C, allylmagnesium chloride (8 mL, 8 mmol, 2.0 eq., 1.0 M in hexane) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred at room temperature overnight. After all volatiles were removed in vacuo, the residue was extracted with pentane (50 mL × 3). The combined extracts were concentrated and purified by silica gel chromatography (pentane : dichloromethane = 10 : 1) to give compound 2 as a white solid (0.95 g, 1.6 mmol, 40%).

HRMS: m/z calc. for C₃₉H₄₄OP₂+[Ag⁺] 697.1913, found 697.1918.

Melting point: 211 °C

NMR data of compound 2 from a solution of the obtained white solid in dichloromethane-d₂
[Xat: dimethyl-9H-xanthendiyl; Mes: mesityl]

¹H NMR (600 MHz, 299 K, dichloromethane-d₂) δ = [7.34(d), 6.91(c), 6.75(b)(each m, each 1H, Xat), 6.98 (s, 2H, m-Mes), 5.82 (m, 1H, =CH), [5.22 (br d, 3 JHH = 17.0 Hz, 1H), 4.89 (br d, 3 JHH = 9.7 Hz)](each 1H, =CH₂), [4.37, 3.15](each m, each 1H, PCH₂), 2.48 (s, 6H, o-CH₃Mes), 2.33 (s, 3H, p-CH₃Mes), 1.67 (s, 3H, MeXat).

¹³C{¹H} NMR (151 MHz, 299 K, dichloromethane-d₂) δ = 150.9 (dd, 2 JPC = 15.7 Hz, 4 JPC = 0.7 Hz, Xat(f)), 146.4 (d, 2 JPC = 16.3 Hz, o-Mes), 140.1 (d, 1 JPC = 1.0 Hz, p-Mes), 134.9 (dd, 2 JPC = 8.7 Hz, JPC = 0.9 Hz, =CH), 130.3 (d, 2 JPC = 1.8 Hz, Xat(b)), 129.7 (Xat(e)), 127.0 (d, 1 JPC = 18.7 Hz, i-Mes), 126.4 (d, 1 JPC = 25.8 Hz, Xat(a)), 126.4 (d, 4 JPC = 1.0 Hz, Xat(d)), 123.1 (Xat(c)), 116.4 (dd, 3 JPC = 10.9 Hz, JPC = 1.3 Hz, =CH₂), 34.4 (t, 4 JPC = 1.4 Hz, C₆Xat), 33.7 (MeXat), 29.5 (dd, JPC = 17.5, 14.7 Hz, PCH₂), 24.0 (d, 3 JPC = 19.1 Hz, o-CH₃Mes), 21.2 (p-CH₃Mes).

³¹P{¹H} NMR (243 MHz, 299 K, dichloromethane-d₂) δ = -31.2 (ν₁/₂ ~ 2 Hz).
Figure S3 $^1$H NMR (600 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 2

Figure S4 $^{31}$P{$^1$H} NMR (243 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 2
Figure S5 $^{13}$C($^1$H) NMR (151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 2

Figure S6 $^{13}$C($^1$H) NMR (151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 2
Figure S7 $^{13}$C{$^1$H, $^{31}$P} NMR (151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 2 (selected resonances)
Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound 2 in pentane at room temperature.

**X-ray crystal structure analysis of compound 2**: formula C_{39}H_{44}OP_{2}, M = 590.68, colorless crystal, 0.20 x 0.13 x 0.10 mm, a = 15.7527(4) Å, b = 15.0017(3) Å, c = 14.2292(4) Å, β = 96.010(1)°, V = 3344.12(14) Å³, ρ_{calc} = 1.173 g cm⁻³, μ = 0.159 mm⁻¹, empirical absorption correction (0.968 ≤ T ≤ 0.984), Z = 4, monoclinic, space group C2/c (No. 15), λ = 0.71073 Å, T = 173(2) K, ω and φ scans, 8679 reflections collected (±h, ±k, ±l), 2906 independent (R_{int} = 0.033) and 2440 observed reflections [I>2σ(I)], 214 refined parameters, R = 0.052, wR² = 0.131, max. (min.) residual electron density 0.22 (-0.20) e Å⁻³, hydrogen atoms were calculated and refined as riding atoms.

**Figure S8** Crystal structure of compound 2 (thermal ellipsoids: 30% probability)
Synthesis of compound 3

![Chemical structure of compounds 2 and 3

Scheme S3

In a Schlenk flask, compound 2 (29.4 mg, 0.05 mmol, 1 eq.) and HB(C₆F₅)₂ (34.6 mg, 0.10 mmol, 2 eq.) were mixed and dichloromethane (1 mL) was added. The mixture was stirred at room temperature for 2 h to give a yellow solution. After all volatiles were removed in vacuo, the resulting yellow solid was washed with cold pentane (1 mL × 3). After drying the resulting solid in vacuo, compound 3 was obtained as a white solid (57.5 mg, 0.045 mmol, 90%).

Elemental analysis (%)
calc. for C₆₃H₄₆B₂F₂₀OP₂: C, 58.99; H, 3.62. Found: C, 58.60; H, 3.61.

HRMS: m/z calc. for C₆₃H₄₆B₂P₂F₂₀+ [H⁺] 1283.2963, found 1283.2996.

Melting point: 211 °C

NMR data of compound 3 from a solution of the obtained white solid in dichloromethane-d₂.

[Xat: dimethyl-9H-xanthendiyl; Mes: mesityl]

¹H NMR (600 MHz, 299 K, dichloromethane-d₂) δ = [7.63 (m, (d)), 7.48 (br, (b)), 6.88 (m, (c))](each 1H, Xat), 6.80 (d, ¹JPH = 3.4 Hz, 2H, m-Mes), [2.36, 1.54](each br, each 1H, PCH₂), 2.26 (s, 3H, p-CH₃Mes), [2.10, 1.27](each br, each 1H, BCH₂), [1.86, 1.68](each br, each 1H, CH₂), 1.82 (br, 6H, o-CH₃Mes), 1.62 (s, 3H, MeXat).

¹³C{¹H} NMR (151 MHz, 299 K, dichloromethane-d₂) δ = 153.1 (d, ²JPC = 3.8 Hz, Xat(f)), 142.8 (br, o-Mes)³, 142.1 (br, p-Mes), 136.1 (br, Xat(b)), 132.7 (d, ³JPC = 2.9 Hz, Xat(e)), 132.6 (br, m-Mes), 130.0 (br, Xat(d)), 123.6 (d, ³JPC = 13.0 Hz, Xat(c)), 122.1 (br, i-Mes), 117.3 (br d, ¹JPC = 46.9 Hz, Xat(a)), 35.1 (C(Xat)), 30.6 (br, MeXat), 27.8 (br d, ¹JPC = 41.0 Hz, PCH₂), 25.9 (br, CH₂), 24.5 (br, o-CH₃Mes), 24.1 (br, BCH₂), 20.8 (p-CH₃Mes), [C₆F₅ not listed; ¹ tentative assignment].

¹¹B{¹H} NMR (192 MHz, 299 K, dichloromethane-d₂) δ = -5.7 (ν1/2 ~ 300 Hz).

¹⁹F NMR (564 MHz, 258 K, dichloromethane-d₂) δ = [-125.4, -134.1](each br, each 1F, o), -158.6 (br t, ³JFF = 21.1 Hz, 1F, p), [-163.7, -165.5](each br m, 1F, m)(C₆F₅)[Δδ¹⁹Fm,p = 5.1, 6.9]; [-125.9, -129.1](each br, each 1F, o), -159.1 (br t, ³JFF = 21.1 Hz, 1F, p), [-164.3, -165.2](each m, each 1F, m)(C₆F₅)[Δδ¹⁹Fm,p = 5.2, 6.1].

³¹P{¹H} NMR (243 MHz, 299 K, dichloromethane-d₂) δ = 26.5 (ν1/2 ~ 100 Hz).

[Comment: the observed NMR data in solution did not strictly exclude different coordination modes]
Figure S9 $^1$H NMR (600 MHz, 299 K, dichloromethane-$d_2$) spectrum of compound 3
Figure S10 $^{13}$C($^1$H) NMR (151 MHz, 299 K, dichloromethane-$d_2$) spectrum of compound 3

Figure S11 $^{13}$C($^1$H) NMR (151 MHz, 299 K, dichloromethane-$d_2$) spectrum of compound 3
Figure S12 $^1$H$^1$B$^1$H NMR (192/600 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 3.

Figure S13 $^{31}$P$^{1}$H NMR (243 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 3.

Figure S14 $^{19}$F NMR (564 MHz, dichloromethane-d$_2$) spectra of compound 3 at (1) 258 K and (2) 299 K.
Crystals of compound 3 suitable for the X-ray crystal structure analysis were obtained from diffusion of pentane to a solution of the white solid in dichloromethane at -36 °C.

**X-ray crystal structure analysis of compound 3:** A colorless needle-like specimen of $\text{C}_{63}\text{H}_{46}\text{B}_{2}\text{F}_{20}\text{OP}_{2} \cdot \text{CH}_{2}\text{Cl}_{2} \cdot \text{C}_{5}\text{H}_{12}$, approximate dimensions 0.042 mm x 0.057 mm x 0.230 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 928 frames were collected. The total exposure time was 21.59 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 71880 reflections to a maximum θ angle of 66.84° (0.84 Å resolution), of which 11114 were independent (average redundancy 6.468, completeness = 96.8%, $R_{\text{int}} = 15.18\%$, $R_{\text{sig}} = 10.10\%$) and 6706 (60.34%) were greater than 2σ($F^2$). The final cell constants of $a = 19.2322(5)$ Å, $b = 12.1403(3)$ Å, $c = 27.9571(7)$ Å, $β = 98.426(2)^\circ$, volume = 6457.1(3) Å$^3$, are based upon the refinement of the XYZ-centroids of 9882 reflections above 20 σ(I) with 6.392° < 2θ < 133.2°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.817. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6220 and 0.9100. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with $Z = 4$ for the formula unit, $\text{C}_{63}\text{H}_{46}\text{B}_{2}\text{F}_{20}\text{OP}_{2} \cdot \text{CH}_{2}\text{Cl}_{2} \cdot \text{C}_{5}\text{H}_{12}$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 948 variables converged at $R_1 = 8.24\%$, for the observed data and $wR_2 = 15.47\%$ for all data. The goodness-of-fit was 1.081. The largest peak in the final difference electron density synthesis was 0.386 e/Å$^3$ and the largest hole was -0.435 e/Å$^3$ with an RMS deviation of 0.077 e/Å$^3$. On the basis of the final model, the calculated density was 1.481 g/cm$^3$ and $F(000) = 2944$ e$^-$. 

S15
**Figure S15** Crystal structure of compound 3 (thermal ellipsoids: 30% probability)

**Figure S16** Crystal structure of compound 3 (thermal ellipsoids: 30% probability, substituents at P1/2 and B1/2 are omitted for clarity except their ipso-carbon atoms)
Synthesis of compound 6: reaction of compound 3 with 2 equiv. of 4-phenylbut-3-yn-2-one (4)

A solution of compound 2 (29.4 mg, 0.05 mmol, 1 eq.) in dichloromethane (1 mL) was added to a suspension of HB(C₆F₅)₂ (34.6 mg, 0.1 mmol, 2 eq.) in dichloromethane (1 mL). After the resulting mixture was stirred at room temperature for 30 min, a solution of 4-phenylbut-3-yn-2-one (14.4 mg, 0.1 mmol, 2 eq.) in dichloromethane (1 mL) was added. After stirring for 15 min at room temperature, the resulting green solution was kept at -35 °C for 24 h to give colorless crystals (suitable for the X-ray crystal structure analysis). The crystals were collected and dried in vacuo to give compound 6 as white solid (39.3 mg, 0.025 mmol, 50%).

HRMS: m/z calc. for C₈₃H₆₂O₃P₂B₂F₂0+Na⁺ 1593.3933, found 1593.3957.

Decomp.: 219 °C

NMR data from a solution of the obtained white solid in dichloromethane-d₂.
[Xat: dimethyl-9H-xanthendiyl; Mes: mesityl; Ph: phenyl]

¹H NMR (600 MHz, 299 K, dichloromethane-d₂) δ = [8.21 (dd, ³JPH = 17.9 Hz, ³JHH = 7.5 Hz, (b)), 7.91 (d, ³JHH = 7.5 Hz, (d)), 7.55 (t, ³JHH = 7.5 Hz, (c))](each 1H, Xat), [7.07, 6.51](each br, each 1H, m-Mes), 7.04 (m, 1H, p-Ph), 7.03 (d, ³JPH = 40.8, 1H, =CH), 6.92 (m, 2H, m-Ph), 6.74 (br, 2H, o-Ph), [4.20, 4.02](each br s, each 1H, =CH₂), [2.62(br)/1.46(br), 1.28 (m)/0.85(m), 0.81(m)/0.52(br)](each 1H, CH₂), [2.35 (br), 1.44 (s)](each 3H, o-CH₃ Mes), 2.23 (s, 3H, p-CH₃ Mes), 1.61 (s, 3H, MeXat), [¹ from the ¹H,¹³C ghsqc experiment].

¹³C{¹H} NMR (151 MHz, 299 K, dichloromethane-d₂) δ = 158.4 (m, =CH), 156.6 (m, =CO), 151.1 (Xat(f)), 145.0 (d, ¹JPC = 2.9 Hz, p-Mes), [143.7 (d, ²JPC = 6.1 Hz), 142.3 (d, ²JPC = 11.0 Hz)](o-Mes), 139.7 (d, ²JPC = 11.1 Hz, i-Ph), 136.0 (d, ²JPC = 7.9 Hz, Xat(b)), 134.6 (Xat(d)), [134.2 (d, ³JPC = 10.6 Hz), 133.2 (d, ³JPC = 12.0 Hz)](m-Mes), 131.8 (d, ³JPC = 6.7 Hz, Xat(c)), 129.8 (br m, o-Ph),
128.2 (m, p-Ph), 127.9 (m-Ph), 125.9 (d, \(3^J_{PC} = 13.2\) Hz, Xat(c)), 120.1 (d, \(1^J_{PC} = 82.4\) Hz, i-Mes), n.o. (=CP), 111.7 (Xat(a))\(^1\), 101.2 (=CH\(_2\))^2, 34.5 (Me\(^{Xa}\)), 34.5 (C\(^{Xa}\)), [33.4, 26.9, 22.7](CH\(_2\))^2, [25.3 (d, \(3^J_{PC} = 4.9\) Hz), 25.0 (m)](o-CH\(_3\)Me\(_c\)), 20.8 (p-CH\(_3\)Me\(_c\)), [C\(_6\)F\(_5\) not listed; \(^1\) from the \(^1\)H,\(^13\)C ghmbc experiment; \(^2\) from the \(^1\)H,\(^13\)C ghsqc experiment].

\(^{11}\)B\{\(^1\)H\} NMR (192 MHz, 299 K, dichloromethane-d\(_2\)) \(\delta = -2.3\).

\(^{19}\)F NMR (564 MHz, 299 K, dichloromethane-d\(_2\)) \(\delta = [-133.4, -134.4]\) (each br, each 2F, o-C\(_6\)F\(_5\)), [-162.1 (t, \(3^J_{FF} = 20.2\) Hz), -163.7 (t, \(3^J_{FF} = 20.3\) Hz)] (each 1F, p-C\(_6\)F\(_5\)), [-166.5 (br m), -167.2 (br)] (each 2F, m-C\(_6\)F\(_5\)).

\(^{31}\)P\{\(^1\)H\} NMR (243 MHz, 299 K, dichloromethane-d\(_2\)) \(\delta = 35.0\) (\(\nu/2 \sim 20\) Hz).

Figure S17 \(^1\)H NMR (600 MHz, 299 K, dichloromethane-d\(_2\)) spectrum of compound 6
Figure S18 $^{13}$C$^1$H NMR (151 MHz, 299 K, dichloromethane-$d_2$) spectrum of compound 6

Figure S19 $^1$H,$^{13}$C ghsqC (600/151 MHz, 299 K, dichloromethane-$d_2$) spectrum of compound 6
Figure S20 $^1$H,$^{13}$C ghsqc (600/151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 6
Figure S1 $^1$H, $^{13}$C ghsqc (600/151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 6

Figure S2 $^{11}$B{$^1$H} NMR (192 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 6
Figure S23 $^{19}$F NMR (564 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 6

Figure S24 $^{31}$P($^1$H) NMR (243 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 6
X-ray crystal structure analysis of compound 6: A colorless prism-like specimen of C₈₃H₆₂B₂F₂₀O₃P₂, approximate dimensions 0.173 mm x 0.212 mm x 0.360 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1080 frames were collected. The total exposure time was 22.50 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 70540 reflections to a maximum θ angle of 25.48° (0.83 Å resolution), of which 8037 were independent (average redundancy 8.777, completeness = 99.3%, R_int = 13.26%, R_sig = 7.90%) and 5818 (72.39%) were greater than 2σ(F²). The final cell constants of a = 17.9825(16) Å, b = 18.4942(16) Å, c = 27.106(2) Å, β = 105.019(3)°, volume = 8706.8(13) Å³, are based upon the refinement of the XYZ-centroids of 9848 reflections above 20σ(I) with 4.671° < 2θ < 50.87°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.683. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9530 and 0.9770. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group C2/c, with Z = 4 for the formula unit, C₈₃H₆₂B₂F₂₀O₃P₂. The final anisotropic full-matrix least-squares refinement on F² with 501 variables converged at R1 = 9.49%, for the observed data and wR2 = 21.14% for all data. The goodness-of-fit was 1.060. The largest peak in the final difference electron density synthesis was 0.561 e/Å³ and the largest hole was -0.462 e/Å³ with an RMS deviation of 0.089 e/Å³. On the basis of the final model, the calculated density was 1.198 g/cm³ and F(000), 3216 e⁻.
Figure S25 Crystal structure of compound 6 (thermals ellipsoid: 30% probability)

Figure S26 Crystal structure of compound 6 (thermals ellipsoid: 30% probability, substituents at P1/2 and B1/2 are omitted for clarity except their ipso-carbon atoms)
Control reaction: reaction of compound 3 with 1 equiv. of 4-phenylbut-3-yn-2-one (4)

Scheme S5

A solution of compound 2 (29.5 mg, 0.05 mmol, 1 eq.) and HB(C₆F₅)₂ (34.6 mg, 0.10 mmol, 2 eq.) in dichloromethane (ca. 2.0 mL) was stirred for 60 min at r.t. Then a solution of compound 4 (7.2 mg, 0.05 mmol, 1 eq.) in dichloromethane (ca. 1 mL) was added dropwise. After the mixture was stirred at r.t. for 20 hours, all volatiles were removed in vacuo and the obtained residue was characterized by NMR experiments (CD₂Cl₂).

Figure S27³¹P{¹H} NMR (243 MHz, 299 K, dichloromethane-d₂) spectra of (4) compound 2, (3) compound 3; (2) compound 6, and (1) the obtained mixture.
Figure S28 $^{31}$P{$^1$H} NMR (243 MHz, 299 K, dichloromethane-d$_2$) spectra of (3) compound 3; (2) compound 6, and (1) the obtained mixture.

Figure S29 (1) $^{31}$P{$^1$H} and (2) $^{31}$P NMR (243 MHz, 299 K, dichloromethane-d$_2$) spectra of the obtained mixture.
Figure S30 (1) $^1$B$^1$H and (2) $^1$B NMR (192 MHz, 299 K, dichloromethane-d$_2$) spectra of the obtained mixture.
Synthesis of compound 11

A solution of diphosphine 2 (29.5 mg, 0.05 mmol, 1.0 eq.) in dichloromethane (1 mL) was added to a suspension of HB(C₆F₅)₂ (34.6 mg, 0.1 mmol, 2.0 eq.) in dichloromethane (1 mL). The resulting yellow solution was stirred for 60 min at r.t. and then a solution of resorcinol (5.5 mg, 0.05 mmol, 1.0 eq.) in toluene (1 mL) was added. The yellow color of the solution faded immediately. The colorless solution was stirred at r.t. for 3 hours. After removal of all volatiles in vacuo, the resulting white solid was washed with pentane (2 mL × 2). The obtained solid was dissolved with dichloromethane (1 mL) and layered with pentane (3 ml). After storing the two layer system at -35°C, colorless crystals were obtained, which were suitable for the X-ray crystal structure analysis. The colorless crystals were collected and dried in vacuo to give compound 11 as a white crystalline solid (48.2 mg, 0.0346 mmol, 69%)

**Elemental analysis (%)** calc. for C₆₉H₅₂B₂F₂₀O₃P₂: C, 59.50; H, 3.76. Found: C, 59.19; H, 3.52.

**Melting point**: 201 °C

NMR data from a solution of the obtained white crystalline solid in dichloromethane-d₂:
mixture of two compounds [major : minor ~ 63 : 37 (³¹P), 64 : 36 (¹H), 63 : 37 (¹⁹F)]
[Xat: dimethyl-9H-xanthendiyl; Mes: mesityl]

**¹H NMR** (600 MHz, 299 K, dichloromethane-d₂) δ = major: 8.24 (dm, ¹JₚH = 487.4 Hz, PH), [7.85/7.38 (d), 7.02/6.82 (b), 7.23/7.00 (c)](each m, each 1H, Xat), [7.27 (d, ¹JₚH = 4.3 Hz), 6.93 (d, ¹JₚH = 2.2 Hz)](each 2H, m-Mes), 6.70 (dt, ³JₚH = 9.7 Hz, 3.4 Hz, 1H, HC(6)), 6.43 (dm, ³JₚH = 9.8 Hz, 1H, HC(5)), 5.51 (d, ³JₚH = 1.7 Hz, 1H, HC(9)), [4.60 (1H)/2.71 (1H), 1.85 (2H), 1.34 (2H)](each m, CH₂), [3.19, 2.37][each dm, ²JₚH = 26.4, each 1H, H₂C(7)], [2.71/2.20, 1.63/1.35, 1.29/0.96][each m, each 2H, CH₂], [2.58, 2.35](each s, each 6H, o-MeMes), [2.50, 2.34](each s, each 3H, p-MeMes), [1.799, 1.57](each s, each 3H, MeXat); minor: 8.22 (dm, ¹JₚH = 486.7 Hz, PH), [7.85/7.38 (d), 6.99/6.82 (b), 7.23/7.00 (c)](each m, each 1H, Xat), [7.25 (d, ¹JₚH = 4.6 Hz), 6.91 (d, ¹JₚH = 2.2 Hz)](each 2H, m-Mes), 6.64 (dt, ³JₚH = 9.8 Hz, 3.4 Hz, 1H, HC(6)), 6.09 (dm, ³JₚH = 9.9 Hz, 1H, HC(5)), 5.55 (d, ³JₚH = 1.5 Hz, 1H, HC(9)), [4.60 (1H)/2.71 (1H), 1.85 (2H), 1.34
(2H) (each m, CH₂), [3.37, 3.30] (each dm, 2J_HH = 26.4 Hz, each 1H, H₂C(7)), [2.71/2.20, 1.63/1.35, 1.29/0.96] (each m, each 2H, CH₂), [2.56, 2.36] (each s, each 6H, o-MeⁿMes), [2.49, 2.33] (each s, each 3H, p-MeⁿMes), [1.797, 1.56] (each s, each 3H, Me²Xₐ).

¹³C{¹H} NMR (151 MHz, 299 K, dichloromethane-d₂) δ = major: 191.7 (C(8)), 185.4 (C(4)), [153.3, 150.2] (Xat(f)), [147.7 (d, 4J_PC = 2.6 Hz), 140.1] (p-Mes), [146.3 (d, 4J_PC = 15.6 Hz), 144.6 (d, 4J_PC = 7.9 Hz)] (o-Mes), 143.8 (HC(6)), [134.8, 126.4] (Xat(d)), [133.75, 126.3] (Xat(e)), [133.5 (m), 125.2 (m)] (m-Mes), 127.7 (HC(5)), [127.4 (m)², 103.2 (d, 4J_PC = 80.1 Hz)] (Xat(a)), [125.2, 22.12] (each 1F, 106.6 (d, 4J_PC = 87.6 Hz)] (i-Mes), [125.2 (m), 125.1 (m)] (Xat(c)), 102.76 (HC(9)), 37.8 (H₂C(7)), [35.3, 30.0] (Me²Xₐ), 34.8 (C²Xₐ), [29.2, 24.1, 22.2] (each m, CH₂)¹, [25.0, 24.6, 22.0] (each m, CH₂)¹, [23.8 (d, 4J_PC = 18.4 Hz), 22.6 (br d, 4J_PC = 7.5 Hz)] (o-MeⁿMes), [21.6, 21.11] (p-MeⁿMes); minor: 190.9 (C(8)), 185.9 (C(4)), [153.4, 150.1] (Xat(f)), [147.6 (d, 4J_PC = 1.8 Hz), 140.2] (p-Mes), [145.9 (d, 4J_PC = 15.6 Hz), 144.5 (d, 4J_PC = 7.2 Hz)] (o-Mes), 143.3 (HC(6)), [134.7, 126.3] (Xat(d)), [133.5 (m), 129.3] (Xat(e)), [132.6 (m), 131.3] (Xat(b)), [132.0 (d, 3J_PC = 11.2 Hz), 130.4 (d, 3J_PC = 3.8 Hz)] (m-Mes), 127.4 (m, HC(5))¹, [127.4 (m)², 103.2 (d, 4J_PC = 79.6 Hz) (Xat(a)), [125.4, 22.12] (each 1F, 22.6 (br d, 4J_PC = 7.5 Hz)] (o-MeⁿMes), [21.6, 22.12] (p-MeⁿMes), [CaF₅ not listed,¹ from the ghsqc experiment,² from the hmbc experiment).

¹¹B{¹H} NMR (192 MHz, 299 K, dichloromethane-d₂) δ = 0.8 (ν_H/2 ~ 400 Hz)

¹⁹F NMR (564 MHz, 299K, dichloromethane-d₂) δ = major: [-133.75, -134.5, -135.3, -135.9] (each m, each 2F, o-C₆F₅), [-160.1 (m), -160.6 (m), -161.8 (t, 3J_FF = 20.5 Hz), -162.5 (t, 3J_FF = 20.5 Hz)] (each 1F, p-C₆F₅), [-165.4, -165.9, -166.0, -166.6] (each m, each 2F, m-C₆F₅); minor: [-133.81, -134.6, -135.4, -135.6] (each m, each 2F, o-C₆F₅), [-160.4 (m), -160.5 (m), -162.0 (t, 3J_FF = 20.5 Hz), -162.2 (t, 3J_FF = 20.5 Hz)] (each 1F, p-C₆F₅), [-165.4, -165.9, -166.0, -166.6] (each m, each 2F, m-C₆F₅).

³¹P{¹H} NMR (243 MHz, 299 K, dichloromethane-d₂) δ = major: -14.1 (ν_H/2 ~ 10 Hz), -37.5 (ν_H/2 ~ 10 Hz); minor: -13.9 (ν_H/2 ~ 10 Hz), -37.0 (ν_H/2 ~ 10 Hz).

³¹P NMR (243 MHz, 299 K, dichloromethane-d₂) δ = major: -14.1 (br dm, 1J_PP ~ 490 Hz, 1P, PH), -37.5 (m, 1P, P); minor: -13.9 (br dm, 1J_PP ~ 490 Hz, 1P, PH), -37.0 (m, 1P, P).

S29
Figure S3 $^1$H NMR (600 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 11

Figure S3 $^1$H NMR (600 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 11

S30
Figure S3 \( ^1H \) NMR (600 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 11
Figure S34 $^{13}$C{$^1$H} NMR (151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 11

Figure S35 $^{13}$C{$^1$H} NMR (151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 11
Figure S36 (1) $^1$H NMR and (2,3) $^1$H$^*$ $^1$H tocsy (600 MHz, 299 K, dichloromethane-d$_2$) spectra of compound 11: (2) $\delta^1$H$_{irr}(*) = 0.96$ (CH$_2$); (3) $\delta^1$H$_{irr}(*) = 4.60$ (CH$_2$).
Figure S37 $^1$H, $^{13}$C ghsqc (600/151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 11: projections (f1) $^{13}$C($^1$H) NMR (151 MHz, 299 K, dichloromethane-d$_2$) spectrum and (f2) (bottom) $^1$H NMR and (middle, top) $^1$H($^1$H) tocsy (600 MHz, 299 K, dichloromethane-d$_2$) spectra: δ$^1$H$_{irr}$(*) = 0.96 (CH$_2$), δ$^1$H$_{irr}$(*) = 4.60 (CH$_2$).
Figure S38 $^1$H,$^{13}$C ghsqc (600/151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 11

Figure S39 $^{11}$B($^1$H) NMR (192 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 11
Figure S4 $^1$H NMR (564 MHz, dichloromethane-$d_2$) spectrum of compound 11

Figure S4 $^1$H NMR (564 MHz, dichloromethane-$d_2$) spectrum of compound 11

Figure S4 $^1$H NMR (564 MHz, dichloromethane-$d_2$) spectrum of compound 11

Figure S4 $^1$H NMR (564 MHz, dichloromethane-$d_2$) spectrum of compound 11
Figure S42 (1) $^{31}$P{¹H} and (2) $^{31}$P NMR (243 MHz, 299 K, dichloromethane-d$_2$) spectra of compound II.
Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound 11 in dichloromethane at room temperature.

**X-ray crystal structure analysis of compound 11 (erk9064):** formula C_{69}H_{52}B_{2}F_{20}O_{3}P_{2}, M = 1392.67, colorless crystal, 0.13 x 0.05 x 0.03 mm, a = 27.6945(7) Å, b = 19.6666(5) Å, c = 29.9455(9) Å, β = 113.359(1°), V = 14973.2(7) Å³, ρ_{calc} = 1.236 gcm⁻³, μ = 0.149 mm⁻¹, empirical absorption correction (0.980 ≤ T ≤ 0.995), Z = 8, monoclinic, space group C2/c (No. 15), λ = 0.71073 Å, T = 173(2) K, ω and φ scans, 67824 reflections collected (±h, ±k, ±l), 13139 independent (R_{int} = 0.124) and 6186 observed reflections [I>2σ(I)], 877 refined parameters, R = 0.100, wR² = 0.235, max. (min.) residual electron density 0.29 (-0.29) e.Å⁻³, the hydrogen atom at P1 was refined freely; others were calculated and refined as riding atoms.

*Figure S43* Crystal structure of compound 11 (thermal ellipsoids: 15% probability)
Figure S44 Crystal structure of compound 11 (thermal ellipsoids: 15% probability, substituents at P1/2 and B1/2 are omitted for clarity except their ipso-carbon atoms)
Synthesis of compound 15a

In a Schlenk flask, a mixture of compound 2 (118.1 mg, 0.20 mmol, 1.0 eq.) and HB(C₆F₅)₂ (138.4 mg, 0.40 mmol, 2.0 eq.) in toluene (4 mL) was stirred for 15 min at room temperature to give a pale yellow solution. Then the solution was mixed with phenylacetylene (40.8 mg, 0.40 mmol, 2.0 eq.) and stirred at room temperature for 3 days. Then all volatiles were removed in vacuo to give a crude yellow solid, which was washed with benzene (1 mL) and pentane (1 mL × 2) and dried in vacuo to give compound 15a as a white solid (211.0 mg, 0.142 mmol, 71%).

HRMS of compound 15a: m/z calc. for C₇₉H₅₈B₂F₂₀OP₂[OH⁻] 1503.3863; found 1503.3885.

Melting point: 136 °C

NMR data from a solution of the obtained white solid in dichloromethane-d₂:

[1H NMR (600 MHz, 299 K, dichloromethane-d₂)[selected resonances] δ = 8.02 (br d, 1JPH = 479.6 Hz, 1H, PH), 6.14 (t, 3JHH = 7.1 Hz, 1H, HC(7)), [2.67/2.52, 2.53/2.38], 2.02/1.91 (each br m, each 1H, H₂C(8,9,10)), [4.94/2.69, 2.18/1.10, 1.91/1.24] (each br m, each 1H, H₂C(1,2,3)), [1.75, 1.55](each s, each 3H, MeXat), [tentative assignment, 1 from the ghsqc experiment].

[13C{1H} NMR (151 MHz, 299 K, dichloromethane-d₂)[selected resonances] δ = 130.8 (HC(7)), [35.1, 30.6](MeXat), 34.7 (CXat), [30.8 (br), 28.7 (br d, J = 21.3 Hz), 26.4 (br d, J = 14.0 Hz))(H₂C(8,9,10)), [27.1, 24.5, 23.9 (d, 17.4 Hz))(H₂C(1,2,3)), [tentative assignment, 1 from the ghsqc experiment].

[11B{1H} NMR (192 MHz, 299 K, dichloromethane-d₂) δ = 61.0 (very broad), -9.7 (ν₁/₂ ~ 150 Hz).

[31P{1H} NMR (243 MHz, 299 K, dichloromethane-d₂) δ = -12.3 (ν₁/₂ ~ 5 Hz, 1P), -32.3 (ν₁/₂ ~ 15 Hz,1P).

[31P NMR (243 MHz, 299 K, dichloromethane-d₂) δ = -12.3 (br dm, 1JPH ~ 480 Hz, 1P), -32.3 (1P).
Figure S45 $^1$H NMR (600 MHz, 299 K, dichloromethane-$d_2$) spectrum of compound 15a

Figure S46 $^1$H NMR (600 MHz, 299 K, dichloromethane-$d_2$) spectrum of compound 15a
Figure S47 $^1$H NMR (600 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 15a

Figure S48 $^{13}$C($^1$H) NMR (151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 15a
Figure S49 $^{13}$C-$^1$H NMR (151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 15a

Figure S50 $^1$H, $^{13}$C ghsqc (600/151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 15a
Figure S5 $^1$H,$^{13}$C ghsqc (600/151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 15a. Projections (f1) $^{13}$C($^1$H) NMR (151 MHz, 299 K, dichloromethane-d$_2$) spectrum, (f2) $^1$H NMR (600 MHz, 299 K, dichloromethane-d$_2$) spectrum and $^1$H($^1$H) tocsy spectra [δ $^1$H$_{irr}$(*): 6.14 (=C(7)H) and 2.68 (CH$_2$)]
Figure S52 $^{11}$B{$^1$H} NMR (192 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 15a

Figure S53 (1) $^{31}$P{$^1$H} NMR and (2) $^{31}$P NMR (243 MHz, 299 K, dichloromethane-d$_2$) spectra of compound 15a
Figure S54 $^{19}$F NMR (564 MHz, dichloromethane-d$_2$) spectra of compound 15a at (2) 299K and (1) 213K

Figure S55 (1,3) $^{31}$P{$_1^1$H} NMR and (2,4) $^{31}$P NMR (243 MHz, dichloromethane-d$_2$) spectra of compound 15a at (3,4) 299K and (1,2) 213K
Crystals of compound 15a suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of the obtained white solid in dichloromethane at room temperature.

**X-ray crystal structure analysis of compound 15a (erk9150):** A colorless plate-like specimen of C_{79}H_{58}B_{2}F_{20}OP_{2}, approximate dimensions 0.052 mm x 0.099 mm x 0.270 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1920 frames were collected. The total exposure time was 40.42 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 61768 reflections to a maximum θ angle of 67.01° (0.84 Å resolution), of which 13232 were independent (average redundancy 4.668, completeness = 95.7%, R_{int} = 11.65%, R_{sig} = 8.21%) and 9139 (69.07%) were greater than 2σ(F^2). The final cell constants of a = 14.3326(4) Å, b = 17.0503(5) Å, c = 18.1476(5) Å, α = 89.054(2)°, β = 70.5210(10)°, γ = 69.128(2)°, volume = 3880.2(2) Å^3, are based upon the refinement of the XYZ-centroids of 9968 reflections above 20 σ(I) with 5.200° < 2θ < 134.0°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.889. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7200 and 0.9350. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P-1, with Z = 2 for the formula unit, C_{79}H_{58}B_{2}F_{20}OP_{2}. The final anisotropic full-matrix least-squares refinement on F^2 with 949 variables converged at R1 = 7.59%, for the observed data and wR2 = 18.80% for all data. The goodness-of-fit was 1.039. The largest peak in the final difference electron density synthesis was 0.441 e/Å^3 and the largest hole was -0.363 e/Å^3 with an RMS deviation of 0.074 e/Å^3. On the basis of the final model, the calculated density was 1.273 g/cm^3 and F(000), 1520 e^-.
Figure S56 Crystal structure of compound 15a (thermal ellipsoids: 30% probability)
Figure S57 Crystal structure of compound 15a (thermal ellipsoids: 30% probability, substituents at P1/2 and B1/2 are omitted for clarity except their ipso-carbon atoms).
Synthesis of compound 15b

In a Schlenk flask, a mixture of compound 2 (118.1 mg, 0.20 mmol, 1.0 eq.) and HB(C₆F₅)₂ (138.4 mg, 0.40 mmol, 2.0 eq.) in dichloromethane (2 mL) was stirred for 15 min at room temperature to give a pale yellow solution. Then the solution was mixed with 4-methylphenylacetylene (46.5 mg, 0.40 mmol, 2.0 eq.) and stirred at room temperature for 24 hours. Then all volatiles were removed in vacuo to give a crude yellow solid, which was crystallized from dichloromethane/pentane at room temperature to give white crystals, which were suitable for the X-ray crystal structure analysis. After filtration, the collected white crystals were dried in vacuo to give compound 7b as a white solid (200.0 mg, 0.132 mmol, 66%).

Elemental analysis (%) calcd. for C₈₁H₆₂B₂F₂₀OP₂: C 64.22, H 4.13; Found: C 64.22, H 4.36

Melting point: 126 °C

NMR data from a solution of the obtained white solid in dichloromethane-d₂.

[Xat: dimethyl-9H-xanthendiyl; Mes: mesityl; Tol: p-methylphenyl]

⁵¹H NMR (600 MHz, 299 K, dichloromethane-d₂)[selected resonances] δ = 8.04 (br d, ⁱJₚH = 479.6 Hz, 1H, PH), 6.05 (t, ³J_HH = 7.0 Hz, 1H, HC(7)), [2.66/2.52, 2.50/n.o., 2.00/1.90](each br m, each 1H, H₂C(8,9,10)), [4.91/2.69, n.o./1.07, 1.92/1.22] (each br m, each 1H, H₂C(1,2,3)), [2.34, 2.02](each s, each 3H, Tol), [1.75, 1.55](each s, each 3H, Me⁹år).

¹³C{¹H} NMR (151 MHz, 299 K, dichloromethane-d₂)[selected resonances] δ = 130.0 (HC(7)), [35.1, 30.6](Me⁹år), 34.7 (C⁹år), [30.8 (br), 28.8 (br d, J = 14.8 Hz)](H₂C(8,9,10)), [n.o., 24.6¹, 24.0¹](H₂C(1,2,3)), [21.1, 20.5](Tol), [¹ from the ghsqc experiment].

¹¹B{¹H} NMR (192 MHz, 299 K, dichloromethane-d₂) δ = 61.0 (very broad), -9.8 (ν₁/₂ ~ 150 Hz).

³¹P{¹H} NMR (243 MHz, 299 K, dichloromethane-d₂) δ = -12.2 (ν₁/₂ ~ 5 Hz, 1P), -32.2 (ν₁/₂ ~ 20 Hz,1P).

³¹P NMR (243 MHz, 299 K, dichloromethane-d₂) δ = -12.2 (br dm, ¹JₚH ~ 480 Hz, 1P), -32.2 (1P).
Figure S58 $^1$H NMR (600 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 15b

Figure S59 $^1$H NMR (600 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 15b
Figure S60 (3) $^1$H NMR (600 MHz, 299 K, dichloromethane-$d_2$) and (1,2) $^1$H$^1$H tocsy $[\delta^1\text{H}_m(\ast) = 6.05 (=\text{C}(7)\text{H}, (1)), 2.68 (\text{CH}_2, (2))]$ spectra of compound 15b
Figure S61 $^{13}$C-$^1$H NMR (151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 15b

Figure S62 $^{13}$C-$^1$H NMR (151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 15b
Figure S63 $^1$H NMR (192 MHz, 299 K, dichloromethane-$d_2$) spectrum of compound 15b

Figure S64 $^{19}$F NMR (564 MHz, dichloromethane-$d_2$) spectra of compound 15b at (2) 299K and (1) 213K
Figure S65 (1,3) $^{31}$P{'H} NMR and (2,4) $^{31}$P NMR (243 MHz, dichloromethane-d$_2$) spectra of compound 15b at (3,4) 299K and (1,2) 213K
X-ray crystal structure analysis of compound 15b (erk9055): A colorless prism-like specimen of C_{81}H_{62}B_{2}F_{20}OP_{2}, approximate dimensions 0.020 mm x 0.080 mm x 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1785 frames were collected. The total exposure time was 51.50 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 66703 reflections to a maximum θ angle of 66.75° (0.84 Å resolution), of which 13850 were independent (average redundancy 4.816, completeness = 99.2%, R_{int} = 19.34%, R_{sig} = 14.97%) and 6605 (47.69%) were greater than 2σ(F^{2}). The final cell constants of a = 14.5457(6) Å, b = 16.7702(6) Å, c = 18.6337(8) Å, α = 89.164(3)°, β = 69.100(3)°, γ = 69.249(3)°, volume = 3938.2 Å^3, are based upon the refinement of the XYZ-centroids of 4053 reflections above 20 σ(I) with 6.956° < 2θ < 123.7°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.798. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8600 and 0.9750. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P-1, with Z = 2 for the formula unit, C_{81}H_{62}B_{2}F_{20}OP_{2}. The final anisotropic full-matrix least-squares refinement on F^{2} with 969 variables converged at R1 = 8.01%, for the observed data and wR2 = 23.45% for all data. The goodness-of-fit was 0.939. The largest peak in the final difference electron density synthesis was 0.455 e/Å^{3} and the largest hole was -0.325 e/Å^{3} with an RMS deviation of 0.068 e/Å^{3}. On the basis of the final model, the calculated density was 1.277 g/cm^{3} and F(000), 1552 e^{.}
Figure S66 Crystal structure of compound 15b (thermal ellipsoids: 15% probability)
Figure S67 Crystal structure of compound 15b (thermal ellipsoids: 15% probability, substituents at P1/2 and B1/2 are omitted for clarity except their ipso-carbon atoms).
Synthesis of compound 15c

In a Schlenk flask, a mixture of compound 2 (118.1 mg, 0.20 mmol, 1.0 eq.) and HB(C₆F₅)₂ (138.4 mg, 0.4 mmol, 2.0 eq.) in dichloromethane (2 mL) was stirred for 15 min at room temperature to give a pale yellow solution. Then the solution was mixed with 4-methoxyphenylacetylene (52.9 mg, 0.40 mmol, 2.0 eq.) and stirred at room temperature for 24 hours. Then all volatiles were removed in vacuo to give a crude yellow solid, which was crystallized from dichloromethane/pentane at room temperature to give colorless crystals, which were suitable for the X-ray crystal structure analysis. After filtration, the collected colorless crystals were dried in vacuo to give compound 15c as a white solid (219.6 mg, 0.142 mmol, 71%).

Elemental analysis (%) calcd. for C₈₁H₆₂B₂F₂₀O₃P₂: C 62.89, H 4.04; Found: C 62.89, H 4.04

Decomp.: 230 °C

NMR data from a solution of the obtained white solid in dichloromethane-d₂.
[Xat: dimethyl-9H-xanthendiyl; Mes: mesityl; An: p-anisyl]

¹H NMR (600 MHz, 299 K, dichloromethane-d₂)[selected resonances] δ = 8.06 (br d, ¹JPH = 478.4 Hz, 1H, PH), 5.99 (br t, ³JHH = 6.7 Hz, 1H, HC(7)), [2.66/2.52, 2.50/2.47, 2.00/1.90](each br m, each 1H, H₂C(8,9,10)), [4.90/2.69, n.o./1.02, 1.93/1.20] (each br m, each 1H, H₂C(1,2,3)), [3.82, 3.57](each s, each 3H, OMe), [1.75, 1.56](each s, each 3H, MeXat).

¹³C[¹H] NMR (151 MHz, 299 K, dichloromethane-d₂)[selected resonances] δ = 129.4 (HC(7)), [35.1, 30.7 (br)](MeXat), 34.7 (CXat), [30.8 (br), 28.9 (br)¹], 26.4 (br d, J = 14.6 Hz)](H₂C(8,9,10)), [n.o., 24.6¹], 24.1¹](H₂C(1,2,3)), [55.7, 55.3](OMe), [¹ from the ghsc experiment].

¹¹B[¹H] NMR (192 MHz, 299 K, dichloromethane-d₂) δ = 60.0 (very broad), -9.9 (ν₁/₂ = 150 Hz).

³¹P[¹H] NMR (243 MHz, 299 K, dichloromethane-d₂) δ = -12.2 (ν₁/₂ ~ 5 Hz, 1P), -32.1 (ν₁/₂ ~ 30 Hz,1P).

³¹P NMR (243 MHz, 299 K, dichloromethane-d₂) δ = -12.2 (br dm, ¹JPH ~ 480 Hz, 1P), -32.1 (1P).
Figure S68\textsuperscript{1}H NMR (600 MHz, 299 K, dichloromethane-d\textsubscript{2}) spectrum of compound 15c

Figure S69\textsuperscript{1}H NMR (600 MHz, 299 K, dichloromethane-d\textsubscript{2}) spectrum of compound 15c
Figure S70 $^1$H NMR (600 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 15c

Figure S71 $^{13}$C($^1$H) NMR (151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 15c
Figure S72 $^{13}$C{H} NMR (151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 15c

Figure S73 $^1$B{H} NMR (243 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 15c
Figure S74 $^{19}$F NMR (564 MHz, dichloromethane-d$_2$) spectra of compound 15c at (2) 299K and (1) 213K
Figure S75 (1,3) $^{31}$P($^1$H) NMR and (2,4) $^{31}$P NMR (243 MHz, dichloromethane-d$_2$) spectra of compound 15c at (3,4) 299K and (1,2) 213K.
X-ray crystal structure analysis of compound 15c (erk9138): A pale yellow prism-like specimen of C_{86}H_{74}B_{2}F_{20}O_{3}P_{2}, approximate dimensions 0.115 mm x 0.120 mm x 0.199 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1288 frames were collected. The total exposure time was 22.79 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 132421 reflections to a maximum θ angle of 66.92° (0.84 Å resolution), of which 13505 were independent (average redundancy 9.805, completeness = 96.6%, R_{int} = 14.13%, R_{sig} = 6.35%) and 9363 (69.33%) were greater than 2σ(F^2). The final cell constants of \( a = 15.5786(4) \ \text{Å}, \ b = 28.6341(8) \ \text{Å}, \ c = 18.1493(5) \ \text{Å}, \ \beta = 104.093(2)^\circ, \ \text{volume} = 7852.3(4) \ \text{Å}^3, \) are based upon the refinement of the XYZ-centroids of 9825 reflections above 2σ(I) with 5.849° < 2θ < 133.5°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.922. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7750 and 0.8600. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group \( P2_1/c, \) with \( Z = 4 \) for the formula unit, C_{86}H_{74}B_{2}F_{20}O_{3}P_{2}. The final anisotropic full-matrix least-squares refinement on F^2 with 1078 variables converged at R1 = 6.47%, for the observed data and wR2 = 12.96% for all data. The goodness-of-fit was 1.089. The largest peak in the final difference electron density synthesis was 0.301 e/Å^3 and the largest hole was -0.315 e/Å^3 with an RMS deviation of 0.066 e/Å^3. On the basis of the final model, the calculated density was 1.369 g/cm^3 and F(000), 3336 e^-.
Figure S76 Crystal structure of compound 15c (thermal ellipsoids: 30% probability)
Figure S77 Crystal structure of compound 15c (thermal ellipsoids: 30% probability, substituents at P1/2 and B1/2 are omitted for clarity except their ipso-carbon atoms).
Synthesis of compound 12d

In a Schlenk flask, the solutions of compound 2 (59.0 mg, 0.1 mmol, 1.0 eq.) in dichloromethane (2 mL) and HB(C₆F₅)₂ (69.2 mg, 0.2 mmol, 2.0 eq.) in dichloromethane (3 mL) were combined and then stirred for 30 min at room temperature to give a pale yellow solution. Then the reaction mixture was mixed with a solution of 2-tolylacetylene (23.2 mg, 0.2 mmol, 2.0 eq.) in dichloromethane (2 mL) and the resulting solution was stirred at room temperature for 20 hours. Then all volatiles were removed in vacuo and the obtained orange solid was washed with pentane (3x 2 mL). The off-white residue was dissolved in dichloromethane (ca. 2 mL) and the solution was covered with pentane (5mL). After three days the white crystalline precipitate was isolated by decantation, washed with pentane and drying in vacuo to finally give compound 12d as a white solid (56.2 mg, 0.0402 mmol, 40%).

HRMS of compound 12d: m/z calc. for C₇₂H₅₄B₂F₂₀OP₂+[Na⁻] 1421.3431; found 1421.3434.

NMR data from a solution of the obtained white solid in dichloromethane-d₂:

[1H NMR (600 MHz, 299 K, dichloromethane-d₂) δ = [7.86 (dm, 3JHH = 7.7 Hz, d), 7.22 (td, 3JHH ~ 3JHH = 7.7 Hz, 4JPH = 1.7 Hz, c), 6.87 (dm, 3JPH = 16.3 Hz, 3JHH = 7.7 Hz, b)(each 1H, XatA), 7.71 (dm, 3JHH = 7.8 Hz, d), 7.53 (dd, 3JPH = 14.2 Hz, 3JHH = 7.8 Hz, b), 7.13 (td, 3JHH ~ 3JHH = 7.8 Hz, 4JPH = 2.1 Hz, c)(each 1H, XatB), [7.11 (m), 7.07 (o’), 7.06 (p), 7.00 (m’)](each m, each 1H, o-Tol), 6.97 (d, 4JPH = 4.4 Hz, 2H, m-MesA), 6.80 (br, 2H, m-MesB), 6.36 (br dd, 1JPH = 484.9 Hz, 3JHH = 10.0 Hz, 1H, PH), [2.98/2.65 (each m, each 1H, H₂C(4)), 2.38/2.26 (each m, each 1H, H₂C(5)), 2.38/1.38 (each m, each 1H, H₂C(6))), [2.91/2.58 (each m, each 1H, H₂C(1)), 1.58/1.45 (each m, each 1H, H₂C(2)), 1.28/1.11 (each m, each 1H, H₂C(3))], 2.35 (s, 3H, p-MeMesA), 2.22 (s, 3H, Meo-Tol), 2.18 (s, 3H, p-MeMesB), 2.09 (s, 6H, o-MeMesA), 1.96 (br, 6H, o-MeMesB), [1.78, 1.60](each s, each 3H, MeXat).

[13C{1H} NMR (151 MHz, 299 K, dichloromethane-d₂) δ = [152.5 (d, 2JPC = 1.7 Hz, f), 135.2 (d, 4JPC = 2.3 Hz, d), 133.0 (d, 2JPC = 8.3 Hz, b), 133.0 (d, 3JPC = 6.6 Hz, e), 126.1 (d, 3JPC = 13.4 Hz, c), 102.7 (d, 1JPC = 78.6 Hz, a)(XatA), [150.6 (d, 2JPC = 4.6 Hz, f), 132.7 (d, 2JPC = 13.4 Hz, b), 131.6 (d, S68]
$^{3}J_{PC} = 3.4$ Hz, e), 131.4 (br d, $^{4}J_{PC} = 1.9$ Hz, d), 125.4 (d, $^{2}J_{PC} = 13.1$ Hz, c), 120.0 (d, $^{1}J_{PC} = 44.3$ Hz, a))([Xar]), [139.8 (o), 131.3 (o'), 129.3 (m), 127.6 (i), 126.0 (p), 125.3 (m')](o-Tol), [147.7 (d, $^{4}J_{PC} = 2.6$ Hz, p), 144.3 (d, $^{2}J_{PC} = 9.8$ Hz, o), 132.3 (d, $^{3}J_{PC} = 11.2$ Hz, m), 106.6 (d, $^{1}J_{PC} = 88.7$ Hz, i)](Mes), [143.4 (br, o), 142.7 (d, $^{4}J_{PC} = 2.8$ Hz, p), 132.6 (br d, $^{3}J_{PC} = 8.1$ Hz, m), 120.9 (br d, $^{1}J_{PC} = 40.2$ Hz, i)](Mes), 116.2 (br, ≡C), 93.7 (br, ≡C-oTol), 34.9 (d, $^{4}J_{PC} = 0.8$ Hz, C), [34.8, 31.2](Me), [31.6 (d, $^{1}J_{PC} = 41.6$ Hz, H2C(4)), 24.1 (d, $^{3}J_{PC} = 13.5$ Hz, H2C(5)), 22.3 (br, H2C(6))], [27.9 (br, H2C(3)), 25.5 (d, $^{1}J_{PC} = 41.8$ Hz, H2C(1)), 23.5 (d, $^{3}J_{PC} = 4.0$ Hz, H2C(2))] 23.6 (br, o-MeMes), 22.6 (d, $^{3}J_{PC} = 7.7$ Hz, o-MeMes), 21.5 (d, $^{5}J_{PC} = 1.2$ Hz, p-MeMes), 20.9 (d, $^{5}J_{PC} = 1.5$ Hz, p-MeMes), 20.7 (Me-Tol), [C6F5 not listed].

$^{11}B$-$^{1}H$ NMR (192 MHz, 299 K, dichloromethane-d2) δ = -5.2 ($\nu_{1/2} \sim 300$ Hz), -18.3 ($\nu_{1/2} \sim 80$ Hz).

$^{19}F$ NMR (564 MHz, 299K, dichloromethane-d2) δ = [-128.3 (4F, o), -158.4 (2F, p), -164.2 (br, 4F, m)](each br, PB(C6F5)2) [Δ$\delta^{19}Fm,p$ = 5.8]; [-132.5/-132.7 (each m, each 2F, o), -164.31/-164.34 (each t, $^{3}J_{FF} = 20.0$ Hz, each 1F, p), -167.0 (m, 4F, m)] (=C-B(C6F5)2)[Δ$\delta^{19}Fm,p$ = 2.7].

$^{31}P$-$^{1}H$ NMR (243 MHz, 299 K, dichloromethane-d2) δ = 15.5 ($\nu_{1/2} \sim 50$ Hz, 1P, PB), -14.1 ($\nu_{1/2} \sim 2$ Hz, 1P, PH).

$^{31}P$ NMR (243 MHz, 299 K, dichloromethane-d2) δ = 15.5 ($\nu_{1/2} \sim 100$ Hz, 1P, PB), -14.1 (br dm, $^{1}J_{PH}$ ~ 485 Hz, 1P, PH).

Figure S78 $^{1}H$ NMR (600 MHz, 299 K, dichloromethane-d2) spectrum of compound 12d.
Figure S79 (4) $^1$H NMR and (1,2,3) $^1$H($^1$H) tocsy (600 MHz, 299 K, dichloromethane-d$_2$) spectra of compound 12d: $\delta^1$H$_{irr}$ (*) = (1) 7.71 [Xat$^B$(d)], (2) 7.86 [Xat$^A$(d)], (3) 7.07 [o-Tol(o')].
**Figure S80** (3) $^1$H NMR and (1,2) $^1$H($^1$H) tocsy (600 MHz, 299 K, dichloromethane-d$_2$) spectra of compound 12d: $\delta^1$H$_{irr}$ (*) = (1) 2.98 [H$_2$C(4)], (2) 2.91 [H$_2$C(1)].

**Figure S81** (2) $^1$H NMR (inverted phase) and (1) $^1$H($^1$H) noedif (600 MHz, 299 K, dichloromethane-d$_2$) spectra of compound 12d: $\delta^1$H$_{irr}$ (*) = (1) 6.87 [Xat$^a$(b)].
Figure S82 $^1$H $^1$H NMR (151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 12d

Figure S83 $^1$H $^1$H NMR (151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 12d
Figure S84 $^1$H, $^{13}$C ghsqc (600/151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 12d

Figure S85 $^1$H, $^{13}$C ghsqc (600/151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 12d
Figure S86 $^{11}$B/$^1$H NMR (192 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 12d

Figure S87 $^{19}$F NMR (564 MHz, dichloromethane-d$_2$) spectrum of compound 12d
Figure S8 (1) $^{31}\text{P}^{(1}\text{H})$ and (2) $^{31}\text{P}$ NMR (243 MHz, 299 K, Dichloromethane-d$_2$) spectra of compound 12d
References
(1) McWilliams, K.; Kelly, J.W. Synthesis and conformational preferences of potential β-sheet nucleator based on the 9,9-dimethylxanthene skeleton. J. Org. Chem. 1996, 61, 7408-7114.

(2) Bronger, R.P.J.; Kramer, P.C.J.; van Leeuwen P.W.N.M. Influence of the bite angle on the hydroformylation of internal olefins to linear aldehydes. Organometallics 2003, 22, 5358-5369.

(3) Raebiger, J. W.; Miedaner, A.; Curtis, C.J.; Miller, S.M.; Anderson, O.P.; DuBois, D.L. Using ligand bite angles to control the hydricity of palladium diphosphine complexes. J. Am. Chem. Soc. 2004, 126, 5502-5514.

(4) Wang, H.; Gabbaï, F.P. Synthesis, structure, and cyclic voltametry of 4,6-bis(dimesitylboryl)dibenzofuran: isolation of 4,6-dilithiobenzofuran and 4,5-dilithio-9,9-dimethylxanthene as tmeda adducts. Organometallics 2005, 24, 2898-2902.

(5) Parks, D.J.; von H. Spence, R.E.; Piers, W.E. Bis(pentafluorophenyl)borane: synthesis, properties, and hydroboration chemistry of a highly electrophilic borane reagent. Angew. Chem. Int. Ed. 1995, 34, 809-811, Angew. Chem. 1995, 107, 895-897.

(6) Parks, D.J.; Piers, W.E.; Yap, G.P.A. Synthesis, properties, and hydroboration activity of the highly electrophilic borane bis(pentafluorophenyl)borane, HB(C₆F₅)₂. Organometallics 1998, 17, 5492-5503.

(7) Goldwhite, H.; Kaminski, J.; Millhauser, G; Ortiz, J.; Vargas, M.; Vertal, L. Phosphorus-phosphorus single or double bond formation from PCl₃ₙRₙ (n = 1 or 2) and bis-imidazolidine reducing agent. J. Organomet. Chem. 1986, 310, 21-25.

(8) Wang, Y.; Zhang, P.; Di, X.; Dai, Q.; Zhang, Z-M.; Zhang, J. Gold-catalyzed asymmetric intramolecular cyclization of N-allenamides for the synthesis of chiral tetrahydrocarbolines. Angew. Chem. Int. Ed. 2017, 56, 15905-15909, Angew. Chem. 2017, 129, 16121-16125.