

Supporting Information

Hydroboration route to geminal P/B frustrated Lewis pairs with a bulky secondary phosphane component and their reaction with carbon dioxide

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Experimental Procedures

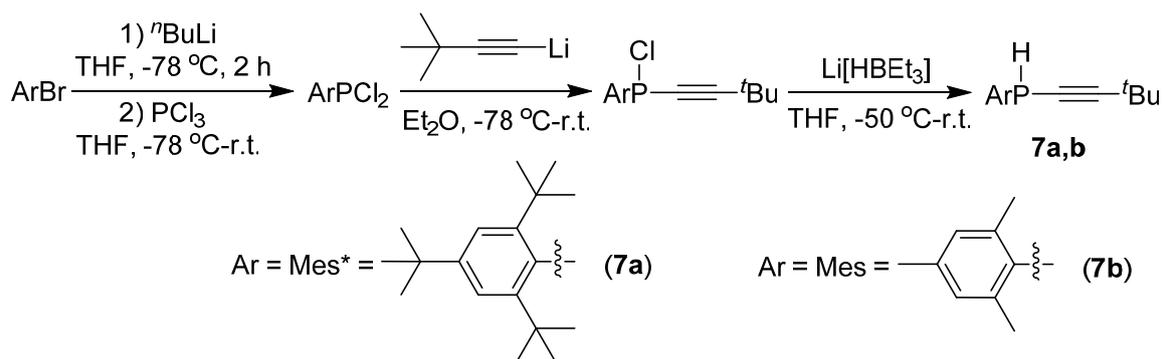
General Information: All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Toluene, CH₂Cl₂, Et₂O, pentane and THF were dried using a Grubbs-type solvent purification system with alumina spheres as the drying agent. All solvents were stored under an argon atmosphere. NMR spectra were recorded on a *Varian* Inova 500 (¹H: 500 MHz, ¹³C: 126 MHz, ³¹P: 202 MHz, ¹⁹F: 470 MHz, ¹¹B: 160 MHz) or a *Varian* Inova 600 (¹H: 600 MHz, ¹³C: 151 MHz, ³¹P: 243 MHz, ¹⁹F: 564 MHz, ¹¹B: 192 MHz). ¹H NMR and ¹³C NMR: chemical shifts δ are given relative to TMS and referenced to the solvent signal. ³¹P NMR: chemical shifts δ are given relative to H₃PO₄ (external reference), ¹⁹F NMR: chemical shifts δ are given relative to CFCl₃ (external reference), ¹¹B NMR: chemical shifts δ are given relative to BF₃·Et₂O (external reference). NMR assignments were supported by additional 1D (NOESY and TOCSY) and 2D (gCOSY, gHSQC and gHMBC) NMR experiments. Elemental analysis data was recorded on Foss-Heraeus CHNO-Rapid. IR spectra were recorded on a Varian 3100 FT-IR (Excalibur Series).

X-Ray diffraction: For compound **16b** data sets were collected with a Nonius Kappa CCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooff, 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) and graphics, XP (BrukerAXS, **2000**). For compounds **9**, **12b**, **13b** and **21** data sets were collected with a Bruker APEX II CCD diffractometer. Data sets for the compounds **10**, **14**, **16a** and **19** were collected with a D8 Venture Dual Source 100 CMOS diffractometer. Programs used: data collection: APEX2 V2014.5-0 (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**) and graphics, XP (Bruker AXS Inc., **2014**). *R*-values are given for observed reflections, and *wR*² values are given for all reflections. *Exceptions and special features:* One *t*Bu group and one half dichloromethane molecule in compound **12b**, one *t*Bu group in compound **13b**, one half dichloromethane molecule in compound **14**, five *t*Bu groups and two C₆F₅ groups in compound **16a**, and one *t*Bu group and one half dichloromethane molecule in compound **21** were found disordered over two positions in the asymmetrical unit. Several restraints (SADI, SAME, ISOR, RIGU and SIMU) were used in order to improve refinement stability. Additionally, for compound **16a** probably two dichloromethane molecules and for compound **16b** one disordered pentane molecule were found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (Spek, A.L. (**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 *hydrogen atom positions at P1 and B1 atoms in 9, at P1 atom in 10, at N1 atom in 12b, at N1 atom in 13b, at N1A and N1B atoms in 14, at P2 atom in 16a and 16b and at P1 atom in 19 were refined freely, but partially with restraint distances (U-fixed value, DFIX or SADI).*

CCDC deposition numbers 1534139 (**9**), 1534140 (**10**), 1534141 (**12b**), 1534142 (**13b**), 1534143 (**14**), 1534144 (**16a**), 1534145 (**16b**), 1534146 (**19**), and 1534147 (**21**) contain the supplementary crystallography data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Materials: Bis(pentafluorophenyl)borane [HB(C₆F₅)₂]^{1,2} was prepared according to the literature procedure. Mes*Br (Mes*- = 2,4,6-*t*Bu₃C₆H₂-) was synthesized by known procedure.³ Compound **7b** (Mes(H)PC≡C*t*Bu; Mes- = mesityl-) was synthesized according to the known procedure.^{4,5} 4,4-dimethyl-1-phenylpent-1-yn-3-one was synthesized according to the known procedure.⁶ All other reagents were commercially available and used as received.

Preparation of compounds 7a and 7b



a) Preparation of compound 7a [see: (a) G. Märkl and S. Reitingner, *Tetrahedron Lett.*, **1988**, 29, 463-466; (b) G. Märkl and R. Hennig, *Liebigs Ann.*, **1996**, 2059-2064]

*1st Step: generation of Mes*PCl₂:*

One equiv. of ⁿBuLi (1.6 M, 6.9 mL, 11.0 mmol) was slowly added to a solution of Mes*Br (3.6 g, 11.0 mmol) in THF (40 mL) at -78 °C. The resulting solution was stirred at -78 °C for 2 h, and then 1.5 equiv. of PCl₃ (1.5 mL, 16.5 mmol) was added at -78 °C. The solution was slowly warmed to room temperature and stirred for further 2 h. Then all volatiles were removed in vacuo to give Mes*PCl₂, which was directly used for the next reaction step without further purification.

2nd Step: generation of Mes(Cl)PC≡C^tBu:*

At -20 °C, one equiv. of ⁿBuLi (1.6 M, 6.9 mL, 11.0 mmol) was slowly added to a solution of 3,3-dimethyl-1-butyne (0.9 g, 11.0 mmol) in Et₂O (20 mL). Then the cooling bath was removed and the mixture was stirred for 2 h at room temperature. After the solution was cooled to -78 °C it was slowly added to a solution of Mes*PCl₂ (see 1st Step) in Et₂O (40 mL) at -78 °C. The resulting solution was slowly warmed to room temperature and stirred for further 12 h. Then all volatiles were removed in vacuo to give Mes*(Cl)PC≡C^tBu, which was directly used for next reaction step without further purification.

3rd Step: preparation of Mes(H)PC≡C^tBu (7a):*

A solution of compound Mes*(Cl)PC≡C^tBu (see 2nd Step) in THF (40 mL) was treated with one equiv. of Li[HBEt₃] (1.0 M in THF, 11.0 mL, 11.0 mmol) at -50 °C. The reaction mixture was slowly warmed to room temperature and stirred for another 2 h. The all volatiles were removed in vacuo to give a sticky yellow oil, which was suspended in pentane (50 mL). The suspension was filtered and the filtrate was concentrated to ca. 5 mL and stored at -35 °C to finally give light yellow crystals of Mes*(H)PC≡C^tBu (7a). Yield: 1.2 g, 30 % (based on Mes*Br).

Elemental analysis: calc. for C₂₄H₃₉P (358.6 g mol⁻¹): C, 80.40; H, 10.96. Found: C, 80.39; H, 11.11.

Melting point: 94 °C.

[Mes*: 2,4,6-tri-*tert*-butylphenyl]

¹H NMR (600 MHz, 299 K, C₆D₆, 7.15 ppm): δ = 7.60 (d, ⁴J_{PH} = 2.6 Hz, 2H, *m*-Mes*), 5.91 (d, ¹J_{PH} = 245.0 Hz, 1H, PH), 1.74 (s, 18H, *o*-C(CH₃)₃-Mes*), 1.22 (s, 9H, *p*-C(CH₃)₃-Mes*), 1.00 (s, 9H, C(CH₃)₃).

¹³C{¹H} NMR (151 MHz, 299 K, C₆D₆, 128.0 ppm): δ = 155.9 (d, ²J_{PC} = 10.6 Hz, *o*-Mes*), 150.7 (*p*-Mes*), 127.8 (d, ¹J_{PC} = 25.3 Hz, *i*-Mes*), 122.9 (d, ³J_{PC} = 4.6 Hz, *m*-Mes*), 112.8 (d, ²J_{PC} = 1.3 Hz, ≡C), 76.4 (d, ¹J_{PC} = 17.7 Hz, PC≡), 38.8 (d, ³J_{PC} = 0.4 Hz, *o*-C(CH₃)₃-Mes*), 35.1 (*p*-C(CH₃)₃-Mes*), 33.9 (d, ⁴J_{PC} = 7.0 Hz, *o*-C(CH₃)₃-Mes*), 31.3 (*p*-C(CH₃)₃-Mes*), 30.6 (d, ⁴J_{PC} = 0.9 Hz, C(CH₃)₃), 28.6 (d, ³J_{PC} = 0.9 Hz, C(CH₃)₃).

³¹P{¹H} NMR (243 MHz, 299 K, C₆D₆): δ = -102.1 (v_{1/2} ~ 1 Hz).

³¹P NMR (243 MHz, 299 K, C₆D₆): δ = -102.1 (dt, ¹J_{PH} = 245.0 Hz, ⁴J_{PH} = 2.6 Hz).

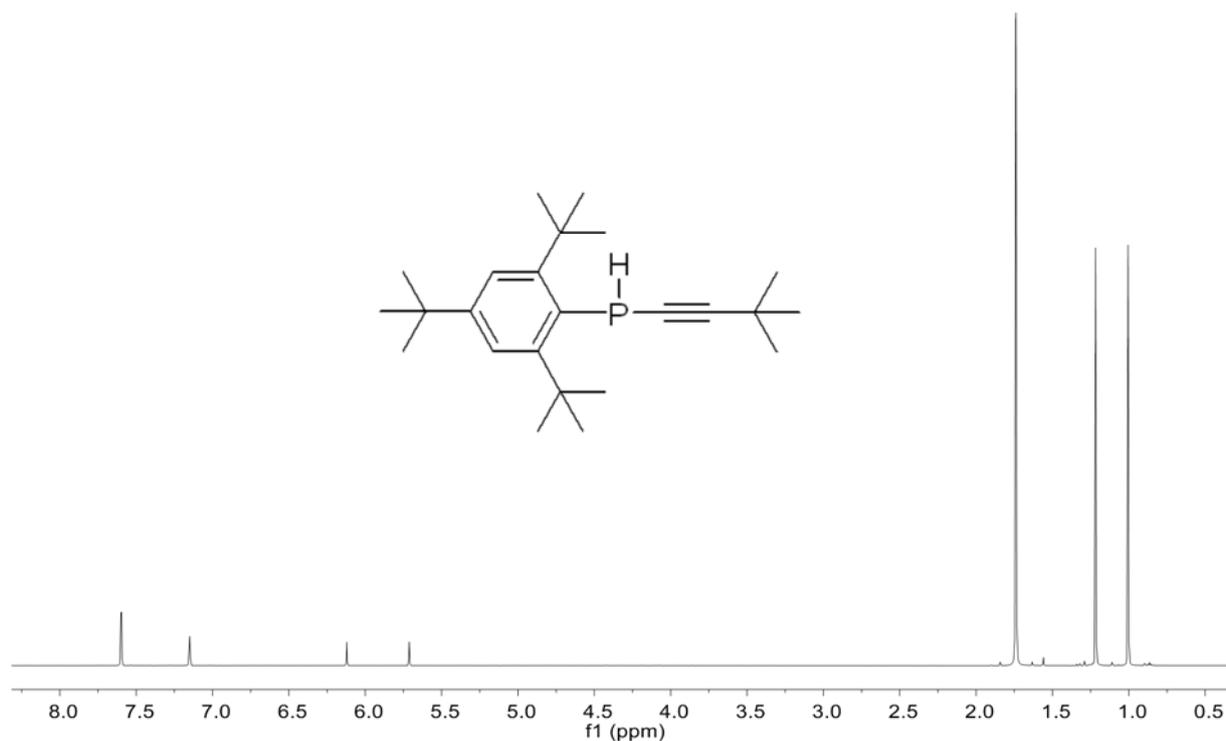


Figure S1. ^1H NMR (600 MHz, 299 K, C_6D_6) spectrum of compound **7a**.

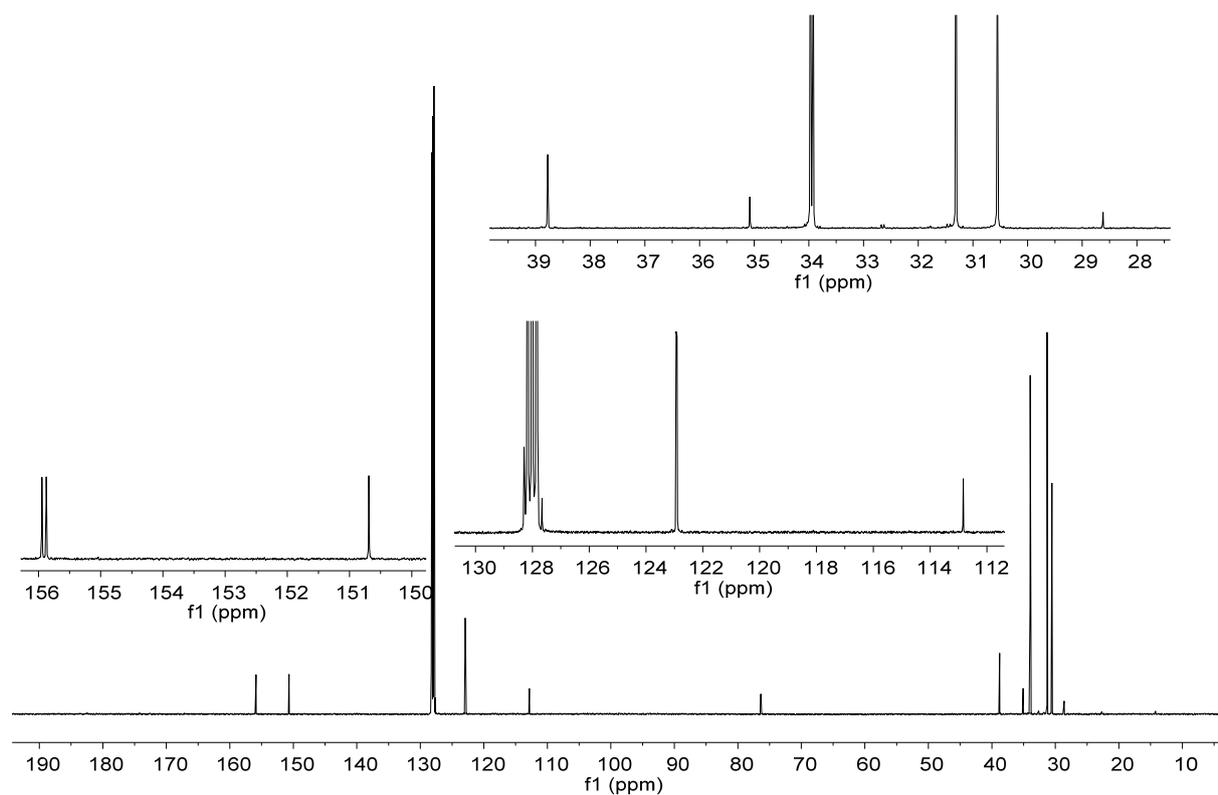


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, C_6D_6) spectrum of compound **7a**.

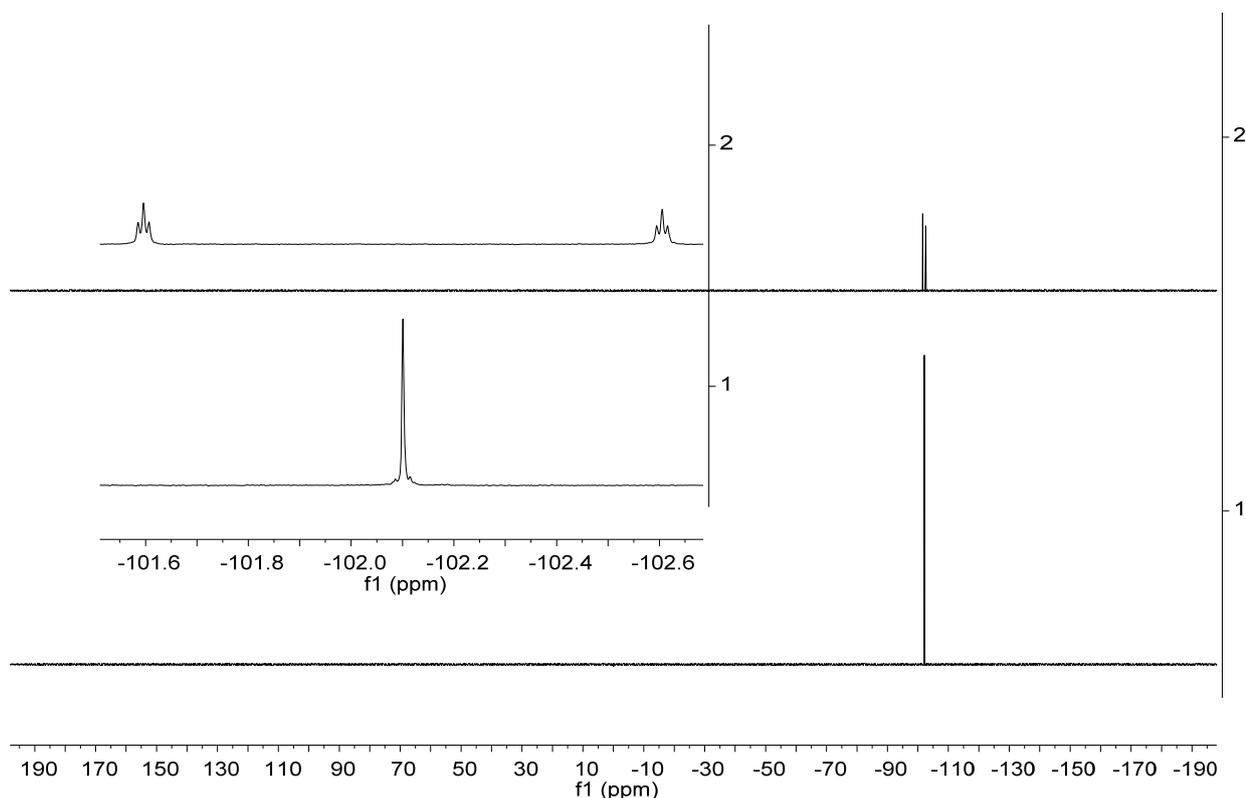


Figure S3. (1) $^{31}\text{P}\{^1\text{H}\}$ and (2) ^{31}P NMR (243 MHz, 299 K, C_6D_6) spectra of compound **7a**.

b) Preparation of compound 7b [see: L. Keweloh, H. Klöcker, E.-U. Würthwein and W. Uhl, *Angew. Chem. Int. Ed.*, **2016**, *55*, 3212-3215]

Compound **7b** was synthesized following the procedure described for the preparation of compound **7a**.

1st Step: generation of MesPCl₂:

The reaction of $^n\text{BuLi}$ (1.6 M, 6.9 mL, 11.0 mmol), MesBr (2.2 g, 11.0 mmol) in THF (40 mL), and PCl_3 (3.0 mL, 33.0 mmol) gave MesPCl₂, which was directly used for the next reaction step without further purification.

2nd Step: generation of Mes(Cl)PC≡C^tBu [see: H. Klöcker, M. Layh, A. Hepp, W. Uhl, *Dalton Trans.* **2016**, *45*, 2031-2043]:

The reaction of $^n\text{BuLi}$ (1.6 M, 6.9 mL, 11.0 mmol), 3,3-dimethyl-1-butyne (0.9 g, 11.0 mmol) in Et₂O (20 mL), and MesPCl₂ (see 1st Step) in Et₂O (40 mL) gave Mes(Cl)PC≡C^tBu, which was directly used for next reaction step without further purification.

3rd Step: preparation of Mes(H)PC≡C^tBu (7b):

The reaction of Mes*(Cl)PC≡C^tBu (see 2nd Step) in THF (40 mL) with Li[HBEt₃] (1.0 M in THF, 11.0 mL, 11.0 mmol) gave colorless crystals of Mes(H)PC≡C^tBu (**7b**). Yield: 0.64 g, 25 % (based on MesBr).

[Mes: 2,4,6-trimethylphenyl]

¹H NMR (600 MHz, 299 K, C_6D_6 , 7.15 ppm): δ = 6.71 (d, $^4J_{\text{PH}}$ = 2.1 Hz, 2H, *m*-Mes), 5.14 (d, $^1J_{\text{PH}}$ = 233.8 Hz, 1H, PH), 2.54 (s, 6H, *o*-CH₃-Mes), 2.02 (s, 3H, *p*-CH₃-Mes), 1.06 (s, 9H, C(CH₃)₃).

³¹P{¹H} NMR (243 MHz, 299 K, C_6D_6): δ = -118.7 ($\nu_{1/2}$ ~ 1 Hz).

³¹P NMR (243 MHz, 299 K, C_6D_6): δ = -118.7 (dm, $^1J_{\text{PH}}$ = 234.0 Hz).

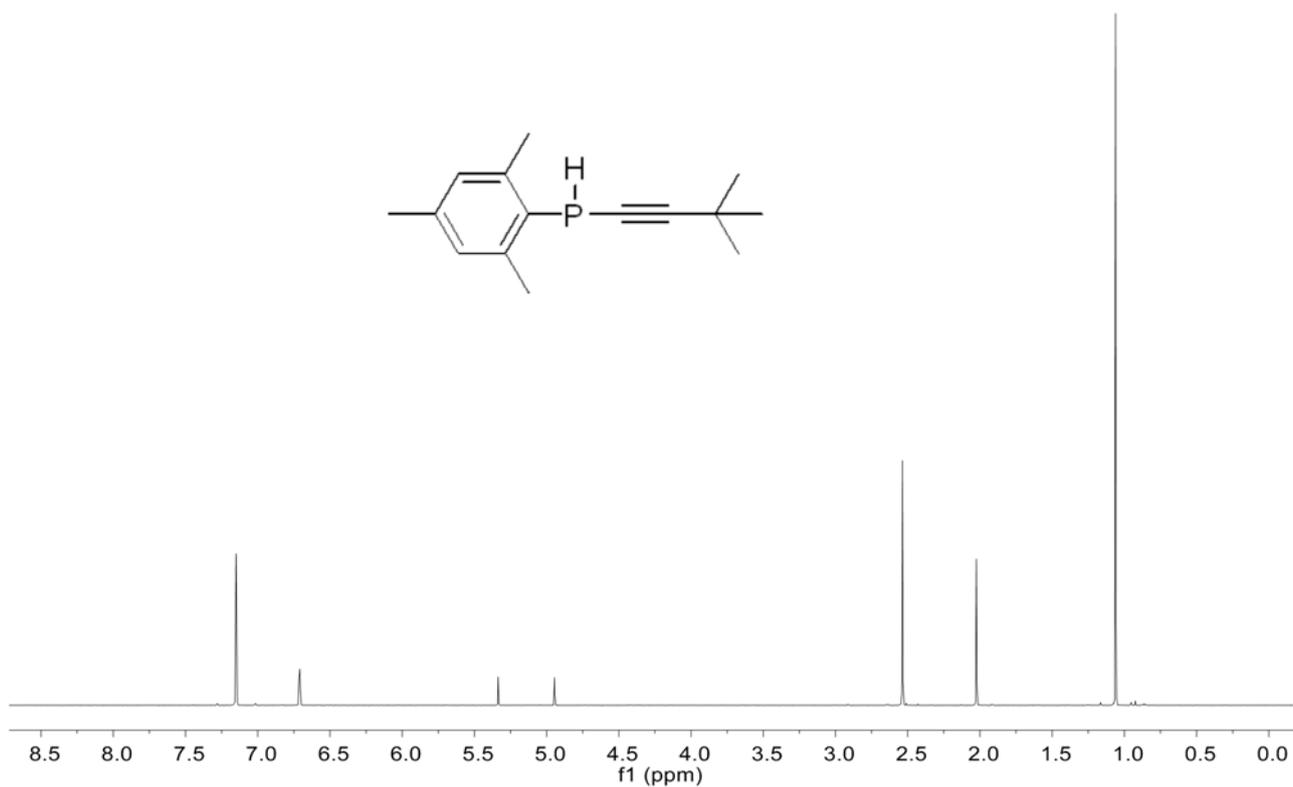


Figure S4. ¹H NMR (600 MHz, 299 K, C₆D₆) spectrum of compound **7b**.

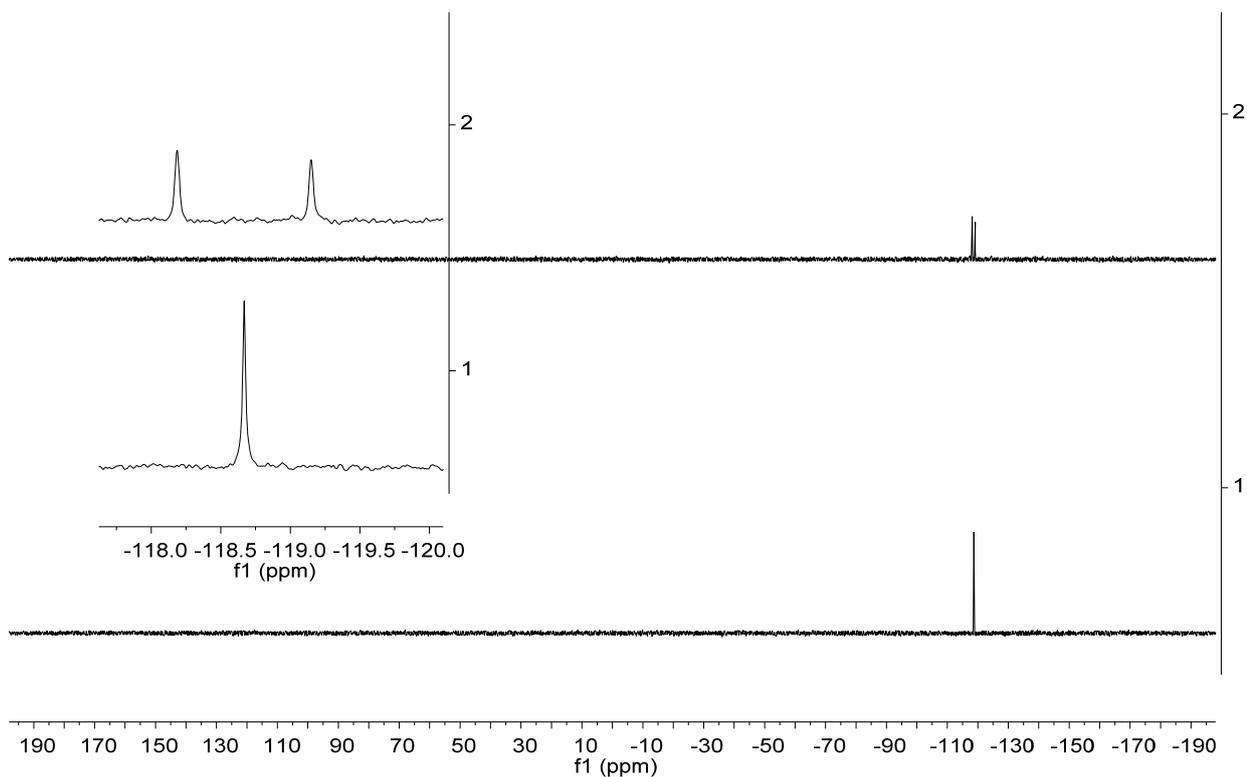
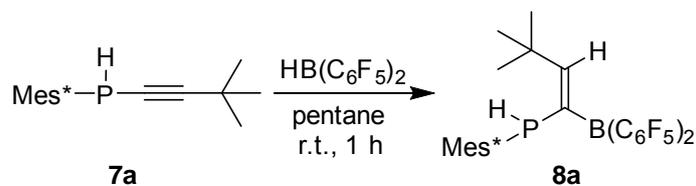


Figure S5. (1) ³¹P{¹H} and (2) ³¹P NMR (243 MHz, 299 K, C₆D₆) spectra of compound **7b**.

Preparation of compound 8a



Scheme S2

After stirring the white suspension of compound **7a** (180 mg, 0.5 mmol) and $\text{HB}(\text{C}_6\text{F}_5)_2$ (173 mg, 0.5 mmol) in pentane (5 mL) at room temperature for 5 min, the formed yellow solution was stirred for 1 h at room temperature to finally give a red solution (with a little bit solid material). The solution was filtered and then all volatiles of the obtained red filtrate were removed in vacuo to give an orange solid. Yield: 318 mg, 90 %.

Elemental analysis: calc. for $\text{C}_{36}\text{H}_{40}\text{PBF}_{10}$ (704.5 g mol⁻¹): C, 61.38; H, 5.72. Found: C, 61.62; H, 5.74.

Decomposition temperature: 108 °C.

[Mes*: 2,4,6-tri-*tert*-butylphenyl]

¹H NMR (600 MHz, 299 K, cyclohexane-*d*₁₂, 1.38 ppm): δ = 7.16 (d, ⁴*J*_{PH} = 2.6 Hz, 2H, *m*-Mes*), 6.60 (dd, ³*J*_{PH} = 25.2 Hz, ⁴*J*_{HH} = 2.6 Hz, 1H, =CH), 5.93 (dd, ¹*J*_{PH} = 234.8 Hz, ⁴*J*_{HH} = 2.6 Hz, 1H, PH), 1.47 (s, 18H, *o*-C(CH₃)₃-Mes*), 1.34 (s, 9H, C(CH₃)₃), 1.24 (s, 9H, *p*-C(CH₃)₃-Mes*).

¹³C{¹H} NMR (151 MHz, 299 K, cyclohexane-*d*₁₂, 26.4 ppm): δ = 170.1 (d, ²*J*_{PC} = 22.0 Hz, =CH), 156.3 (br, *o*-Mes*), 151.9 (br d, ¹*J*_{PC} = 37.8 Hz, BC=), 150.4 (*p*-Mes*), 147.2 (dm, ¹*J*_{FC} ~ 249 Hz, C₆F₅), 143.3 (dm, ¹*J*_{FC} ~ 253 Hz, C₆F₅), 137.8 (dm, ¹*J*_{FC} ~ 252 Hz, C₆F₅), 128.2 (d, ¹*J*_{PC} = 31.2 Hz, *i*-Mes*), 122.9 (*m*-Mes*), 115.7 (br m, *i*-C₆F₅), 39.5 (br s, *o*-C(CH₃)₃-Mes*), 38.2 (C(CH₃)₃), 35.2 (*p*-C(CH₃)₃-Mes*), 34.1 (d, ⁴*J*_{PC} = 7.4 Hz, *o*-C(CH₃)₃-Mes*), 31.4 (*p*-C(CH₃)₃-Mes*), 30.2 (d, ⁴*J*_{PC} = 9.1 Hz, C(CH₃)₃).

³¹P{¹H} NMR (243 MHz, 299 K, cyclohexane-*d*₁₂): δ = -67.2 (*v*_{1/2} ~ 15 Hz).

³¹P NMR (243 MHz, 299 K, cyclohexane-*d*₁₂): δ = -67.2 (dd, ¹*J*_{PH} = 235.0 Hz, ³*J*_{PH} = 25.2 Hz).

¹¹B{¹H} NMR (192 MHz, 299 K, cyclohexane-*d*₁₂): δ = 62.1 (*v*_{1/2} ~ 1500 Hz).

¹⁹F NMR (564 MHz, 299 K, cyclohexane-*d*₁₂): δ = -127.2 (m, 2F, *o*-C₆F₅), -150.4 (t, ³*J*_{FF} = 20.3 Hz, 1F, *p*-C₆F₅), -162.1 (m, 2F, *m*-C₆F₅). [$\Delta\delta^{19}\text{F}_{m,p}$ = 11.7].

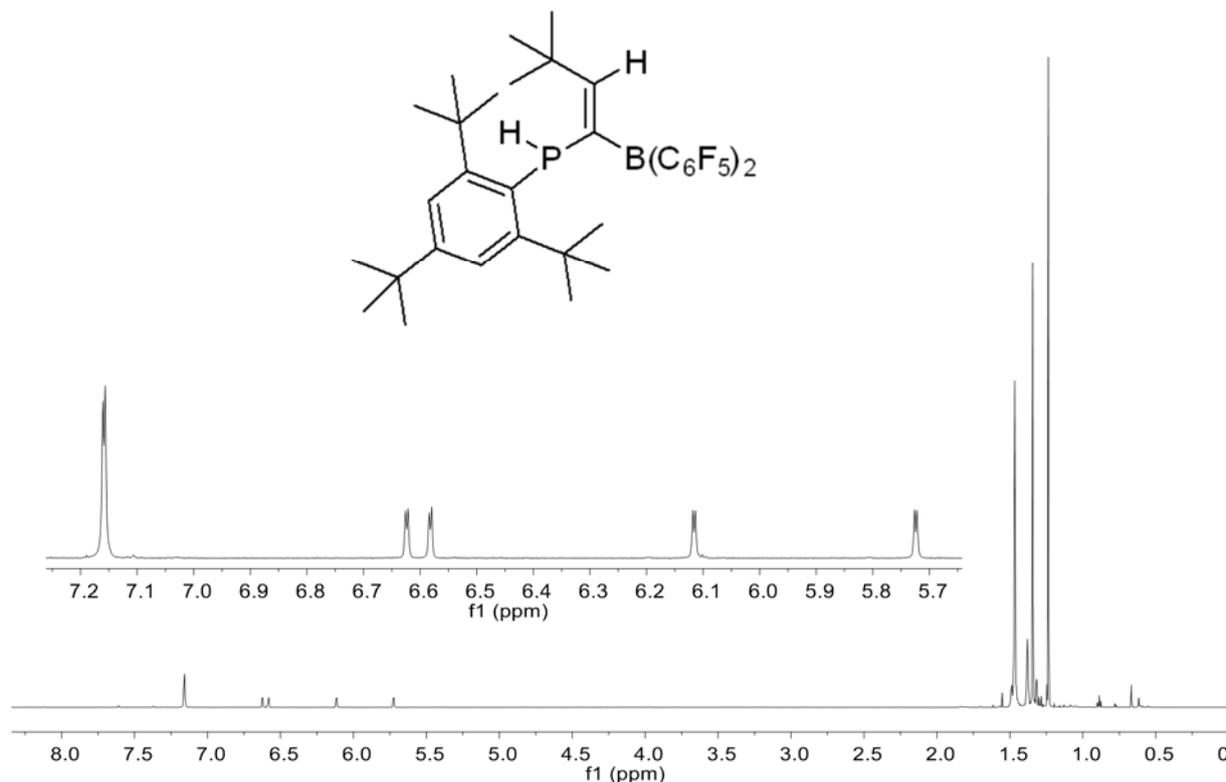


Figure S6. ¹H NMR (600 MHz, 299 K, cyclohexane-*d*₁₂) spectrum of compound **8a**.

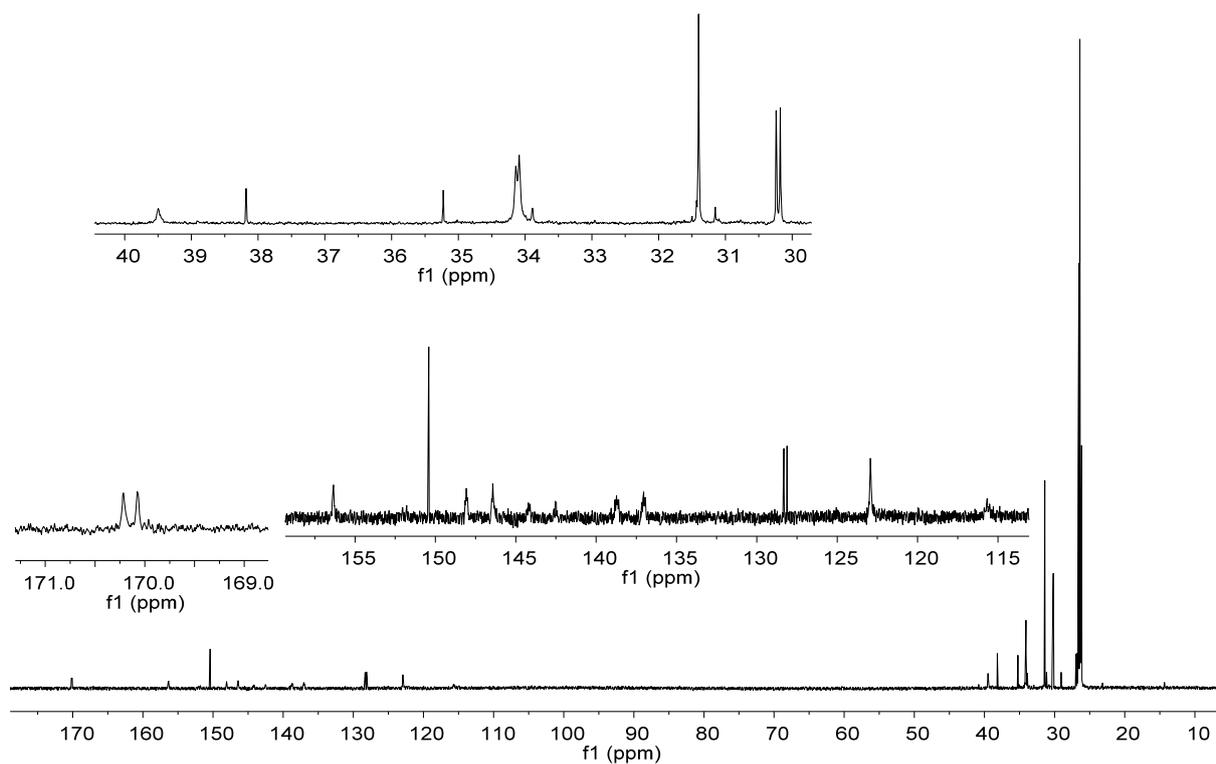


Figure S7. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, cyclohexane- d_{12}) spectrum of compound **8a**.

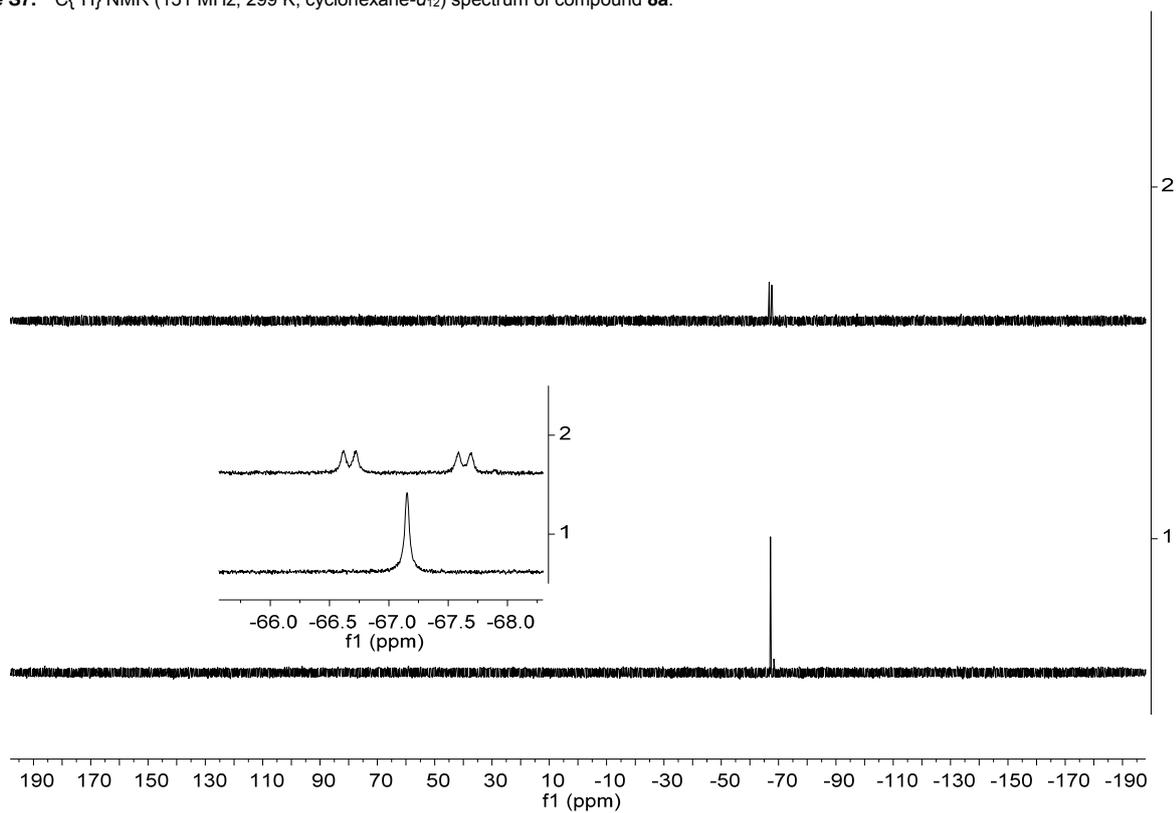


Figure S8. (1) $^{31}\text{P}\{^1\text{H}\}$ and (2) ^{31}P NMR (243 MHz, 299 K, cyclohexane- d_{12}) spectra of compound **8a**.

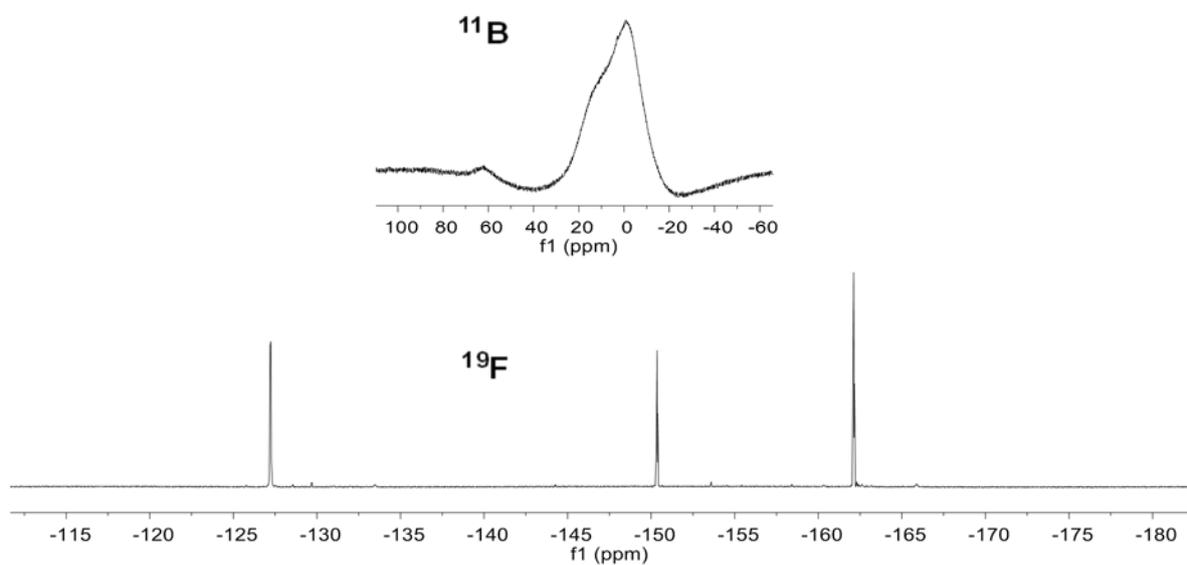
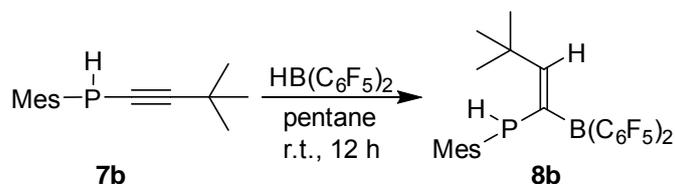


Figure S9. ^{19}F (564 MHz, 299 K, cyclohexane- d_{12}) and $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, cyclohexane- d_{12}) spectra of compound **8a**.

Preparation of compound 8b



Scheme S3

After stirring the white suspension of compound **7b** (116 mg, 0.5 mmol) and $\text{HB(C}_6\text{F}_5)_2$ (173 mg, 0.5 mmol) in pentane (5 mL) at room temperature for 5 min, the formed yellow solution was stirred for 12 h at room temperature to finally give a yellow solution (with a little bit solid material). The solution was filtered and then all volatiles of the obtained yellow filtrate were removed in vacuo to give a yellow solid. Yield: 246 mg, 85 %.

Elemental analysis: calc. for $\text{C}_{27}\text{H}_{22}\text{PBF}_{10}$ (578.2 g mol^{-1}): C, 56.08; H, 3.84. Found: C, 56.38; H, 3.95.

Decomposition temperature: 154 °C.

[Mes: 2,4,6-trimethylphenyl]

$^1\text{H NMR}$ (600 MHz, 299 K, C_6D_6 , 7.15 ppm): $\delta = 6.96$ (dd, $^3J_{\text{PH}} = 23.8 \text{ Hz}$, $^4J_{\text{HH}} = 2.4 \text{ Hz}$, 1H, =CH), 6.50 (d, $^4J_{\text{PH}} = 1.8 \text{ Hz}$, 2H, *m*-Mes), 5.25 (dd, $^1J_{\text{PH}} = 226.4 \text{ Hz}$, $^4J_{\text{HH}} = 2.4 \text{ Hz}$, 1H, PH), 2.24 (s, 6H, *o*- CH_3 -Mes), 2.01 (s, 3H, *p*- CH_3 -Mes), 1.25 (s, 9H, $\text{C(CH}_3)_3$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, C_6D_6 , 128.0 ppm): $\delta = 173.9$ (d, $^2J_{\text{PC}} = 16.6 \text{ Hz}$, =CH), 146.7 (dm, $^1J_{\text{FC}} \sim 248 \text{ Hz}$, C_6F_5), 145.9 (d, $^1J_{\text{PC}} = 38.2 \text{ Hz}$, BC=), 142.5 (d, $^2J_{\text{PC}} = 13.4 \text{ Hz}$, *o*-Mes), 142.8 (dm, $^1J_{\text{FC}} \sim 256 \text{ Hz}$, C_6F_5), 139.2 (*p*-Mes), 137.4 (dm, $^1J_{\text{FC}} \sim 252 \text{ Hz}$, C_6F_5), 129.0 (d, $^3J_{\text{PC}} = 3.2 \text{ Hz}$, *m*-Mes), 128.1 (*i*-Mes), 115.1 (br m, *i*- C_6F_5), 37.5 ($\text{C(CH}_3)_3$), 29.4 (d, $^4J_{\text{PC}} = 8.4 \text{ Hz}$, $\text{C(CH}_3)_3$), 23.0 (d, $^3J_{\text{PC}} = 11.5 \text{ Hz}$, *o*- CH_3 -Mes), 20.7 (*p*- CH_3 -Mes).

$^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, 299 K, C_6D_6): $\delta = -89.8$ (quint, $J_{\text{PF}} = 2.5 \text{ Hz}$).

^{31}P NMR (243 MHz, 299 K, C_6D_6): $\delta = -89.8$ (dd, $^1J_{\text{PH}} = 226.7 \text{ Hz}$, $^3J_{\text{PH}} = 23.8 \text{ Hz}$).

$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, C_6D_6): $\delta = 62.6$ ($\nu_{1/2} \sim 1100 \text{ Hz}$).

^{19}F NMR (564 MHz, 299 K, C_6D_6): $\delta = -129.3$ (m, 2F, *o*- C_6F_5), -149.1 (t, $^3J_{\text{FF}} = 21.0 \text{ Hz}$, 1F, *p*- C_6F_5), -161.5 (m, 2F, *m*- C_6F_5). [$\Delta\delta^{19}\text{F}_{m,p} = 12.4$].

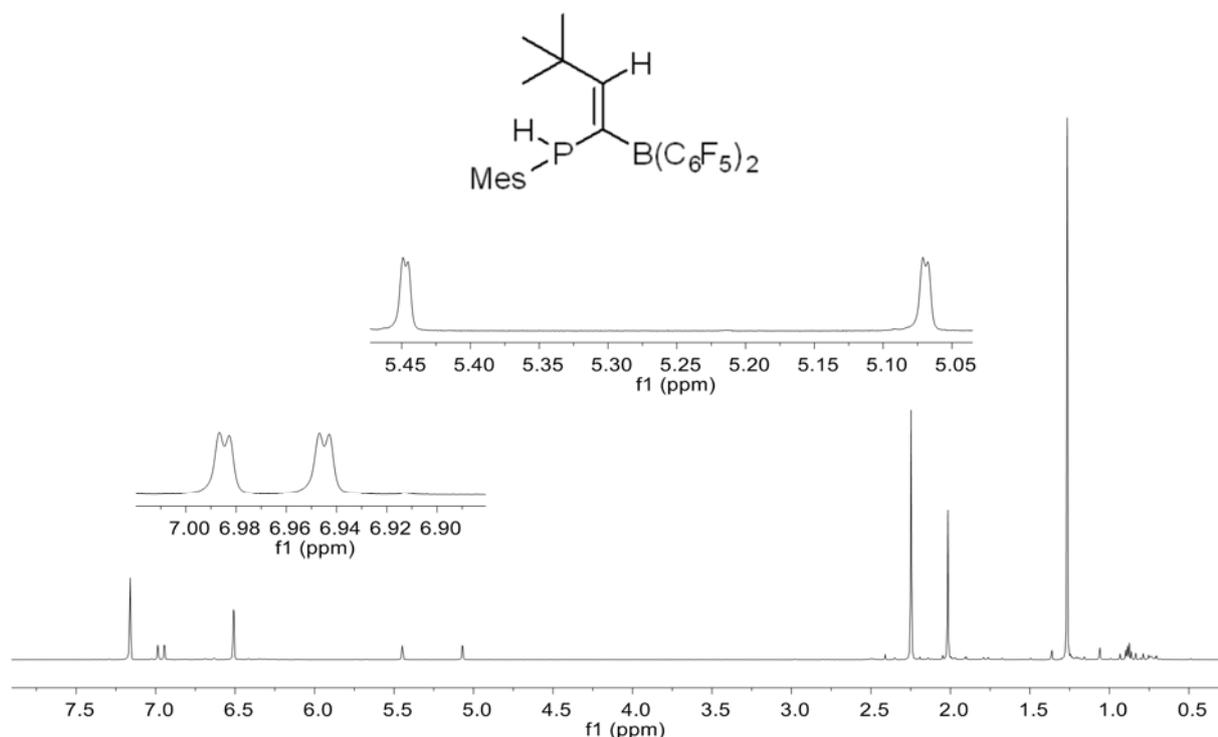


Figure S10. $^1\text{H NMR}$ (600 MHz, 299 K, C_6D_6) spectrum of compound **8b**.

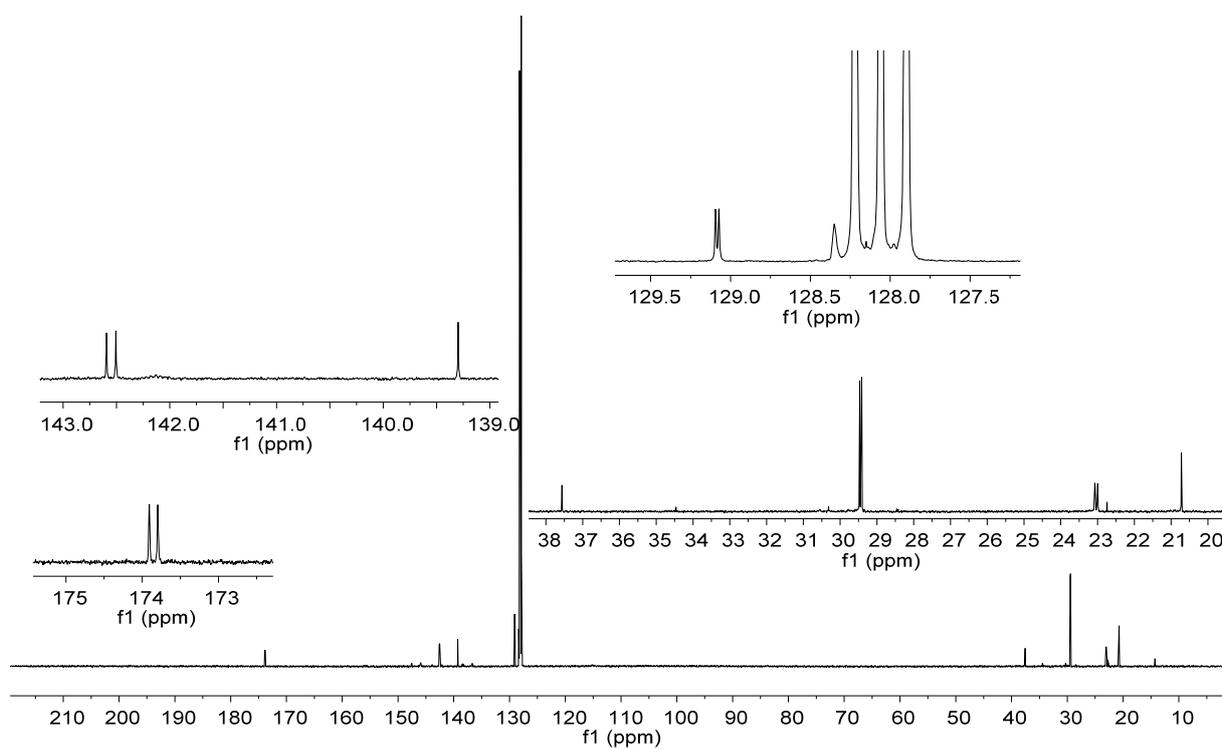


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, C_6D_6) spectrum of compound **8b**.

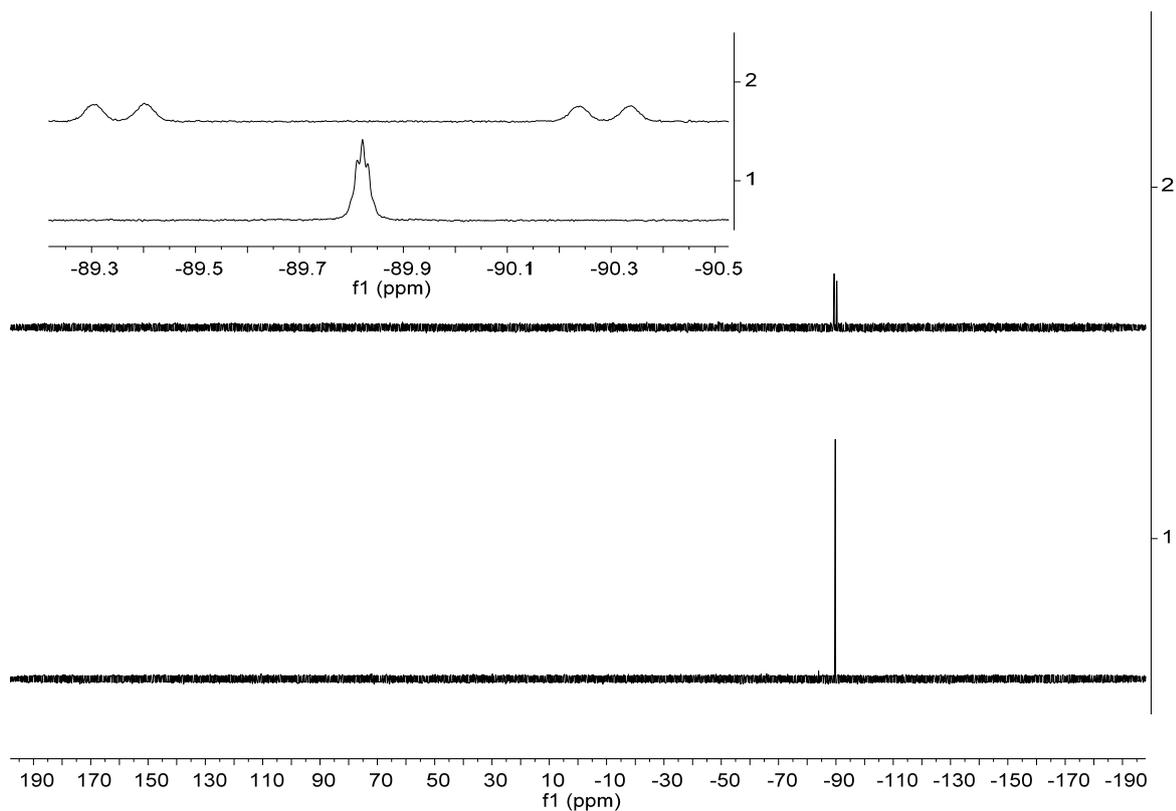


Figure S12. (1) $^{31}\text{P}\{^1\text{H}\}$ and (2) ^{31}P NMR (243 MHz, 299 K, C_6D_6) spectra of compound **8b**.

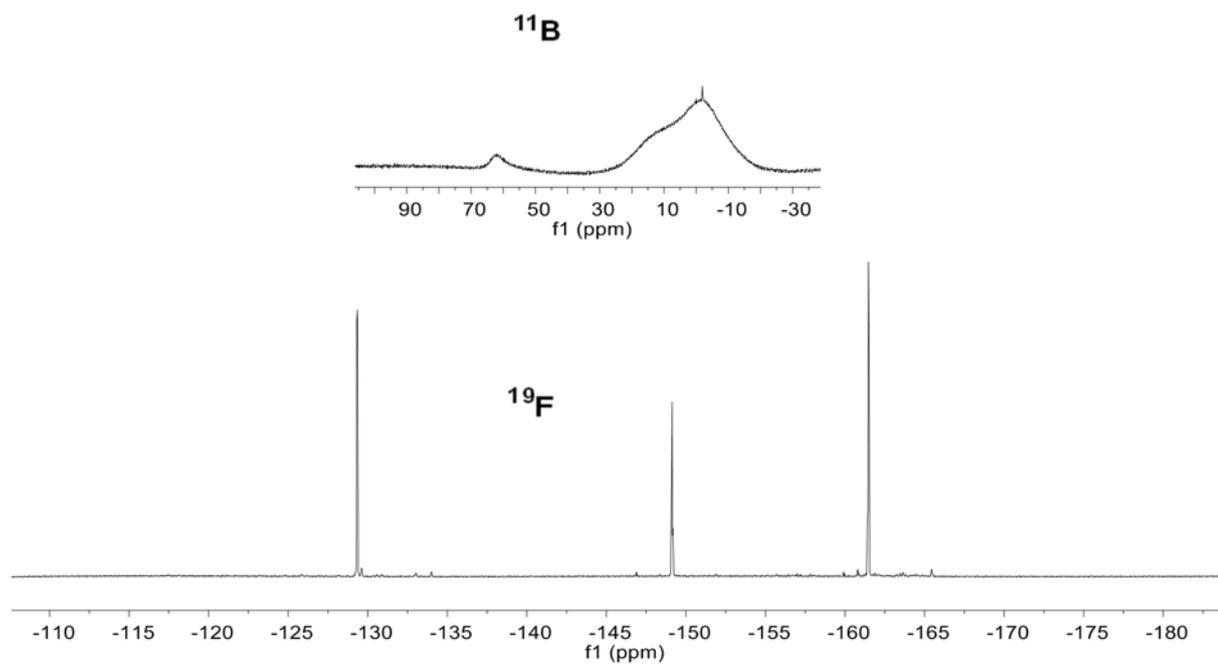
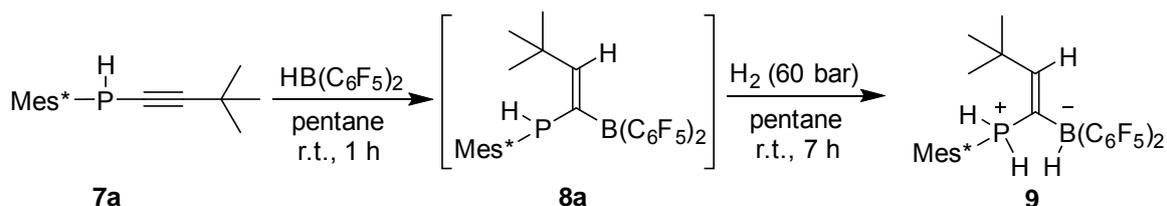


Figure S13. ^{19}F (564 MHz, 299 K, C_6D_6) and $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, C_6D_6) spectra of compound **8b**.

Preparation of compound 9



Scheme S4

After stirring a mixture of compound **7a** (180 mg, 0.5 mmol) and $\text{HB}(\text{C}_6\text{F}_5)_2$ (173 mg, 0.5 mmol) in pentane (5 mL) at room temperature for 1 h, the resulting red mixture was filtered to give a red solution. The solution was transferred to an autoclave and stirred at room temperature for 7 h under a H_2 (60 bar) atmosphere. Then the white solid of the formed suspension was collected by filtration and washed twice with pentane (2×5 mL) to give a white solid. Yield: 290 mg, 82 %.

Elemental analysis: calc. for $\text{C}_{36}\text{H}_{42}\text{PBF}_{10}$ (706.5 g mol⁻¹): C, 61.20; H, 5.99. Found: C, 60.93; H, 5.59.

Decomposition temperature: 173 °C.

[Mes*: 2,4,6-tri-*tert*-butylphenyl]

¹H NMR (600 MHz, 299 K, CD_2Cl_2 , 5.32 ppm): δ = 7.46 (d, $^1J_{\text{PH}} = 489.5$ Hz, 2H, PH_2), 7.59 (d, $^4J_{\text{PH}} = 4.4$ Hz, 2H, *m*-Mes*), 6.52 (d, $^3J_{\text{PH}} = 76.1$ Hz, 1H, =CH), 3.30 (br 1:1:1:1 q, $^1J_{\text{BH}} \sim 90$ Hz, 1H, BH), 1.49 (s, 18H, *o*- $\text{C}(\text{CH}_3)_3$ -Mes*), 1.32 (s, 9H, *p*- $\text{C}(\text{CH}_3)_3$ -Mes*), 0.65 (s, 9H, $\text{C}(\text{CH}_3)_3$).

¹³C{¹H} NMR (151 MHz, 299 K, CD_2Cl_2 , 53.8 ppm): δ = 166.6 (=CH), 157.61 (d, $^4J_{\text{PC}} = 3.2$ Hz, *p*-Mes*), 157.58 (d, $^2J_{\text{PC}} = 6.5$ Hz, *o*-Mes*), 148.8 (dm, $^1J_{\text{FC}} \sim 238$ Hz, C_6F_5), 138.9 (dm, $^1J_{\text{FC}} \sim 250$ Hz, C_6F_5), 137.3 (dm, $^1J_{\text{FC}} \sim 242$ Hz, C_6F_5), 125.0 (d, $^3J_{\text{PC}} = 11.6$ Hz, *m*-Mes*), 122.6 (br m, *i*- C_6F_5), 122.0 (d, $^1J_{\text{PC}} = 25.9$ Hz, BC=), 113.2 (br d, $^1J_{\text{PC}} = 58.1$ Hz, *i*-Mes*), 38.6 (d, $^3J_{\text{PC}} = 2.8$ Hz, *o*- $\text{C}(\text{CH}_3)_3$ -Mes*), 38.4 (d, $^3J_{\text{PC}} = 9.4$ Hz, $\text{C}(\text{CH}_3)_3$), 35.9 (d, $^5J_{\text{PC}} = 0.9$ Hz, *p*- $\text{C}(\text{CH}_3)_3$ -Mes*), 33.8 (d, $^4J_{\text{PC}} = 2.0$ Hz, *o*- $\text{C}(\text{CH}_3)_3$ -Mes*), 30.9 (*p*- $\text{C}(\text{CH}_3)_3$ -Mes*), 28.8 ($\text{C}(\text{CH}_3)_3$).

³¹P{¹H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = -41.4 ($\nu_{1/2} \sim 85$ Hz).

³¹P NMR (243 MHz, 299 K, CD_2Cl_2): δ = -41.4 (br t, $^1J_{\text{PH}} = 486.9$ Hz).

¹¹B{¹H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = -18.7 ($\nu_{1/2} \sim 74$ Hz).

¹¹B NMR (192 MHz, 299 K, CD_2Cl_2): δ = -18.7 (d, $^1J_{\text{BH}} = 85.9$ Hz).

¹⁹F NMR (564 MHz, 299 K, CD_2Cl_2): δ = -132.3 (m, 2F, *o*- C_6F_5), -161.9 (t, $^3J_{\text{FF}} = 20.0$ Hz, 1F, *p*- C_6F_5), -166.2 (m, 2F, *m*- C_6F_5). [$\Delta\delta^{19}\text{F}_{m,p} = 4.3$].

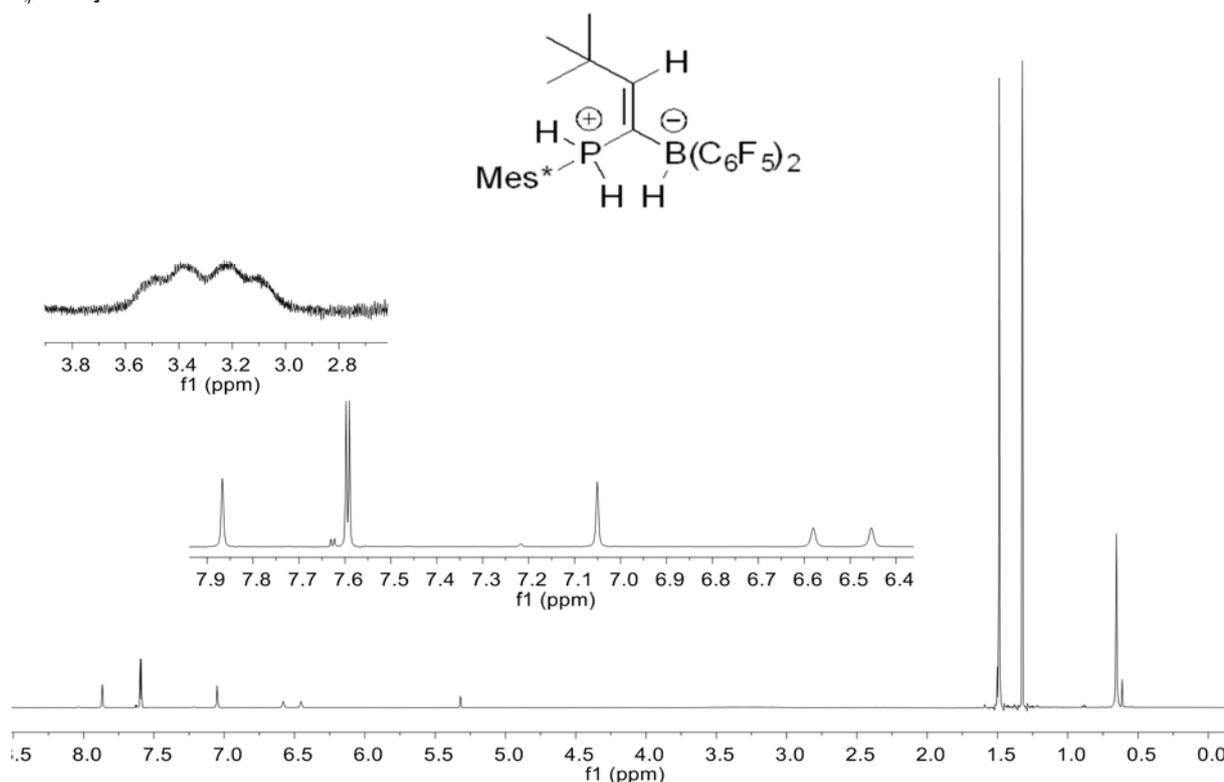


Figure S14. ¹H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound **9**.

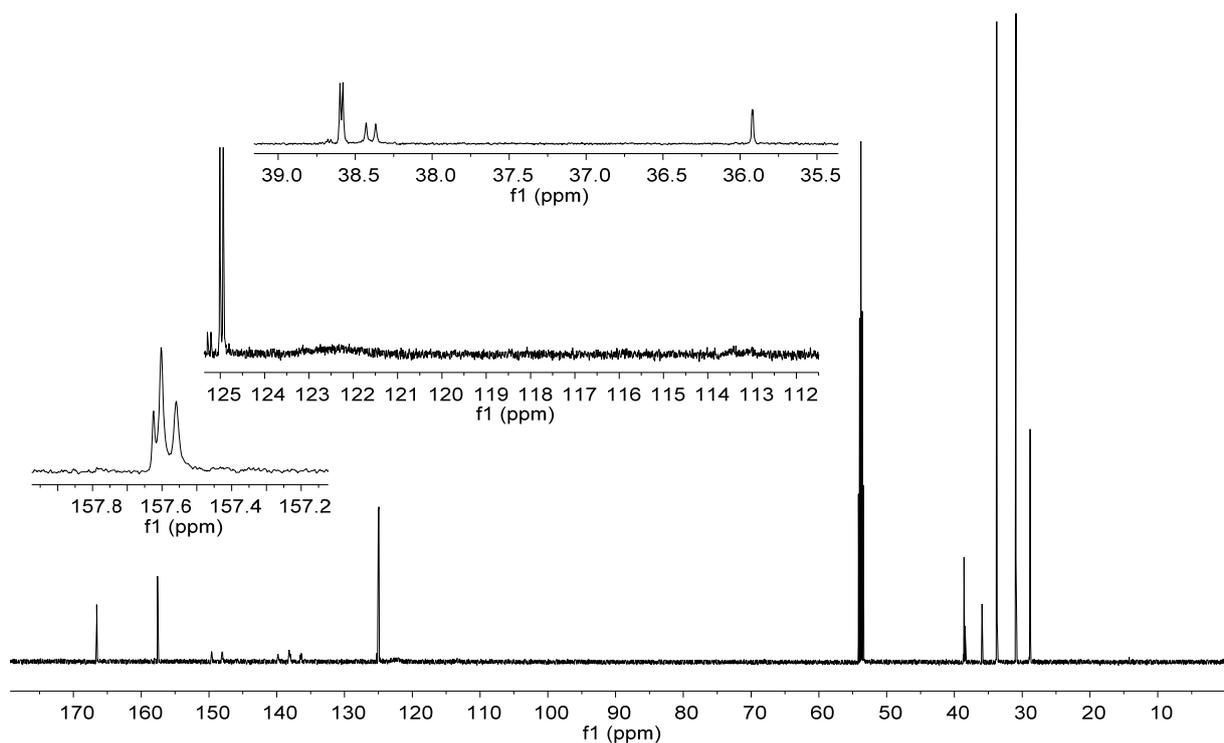


Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound 9.

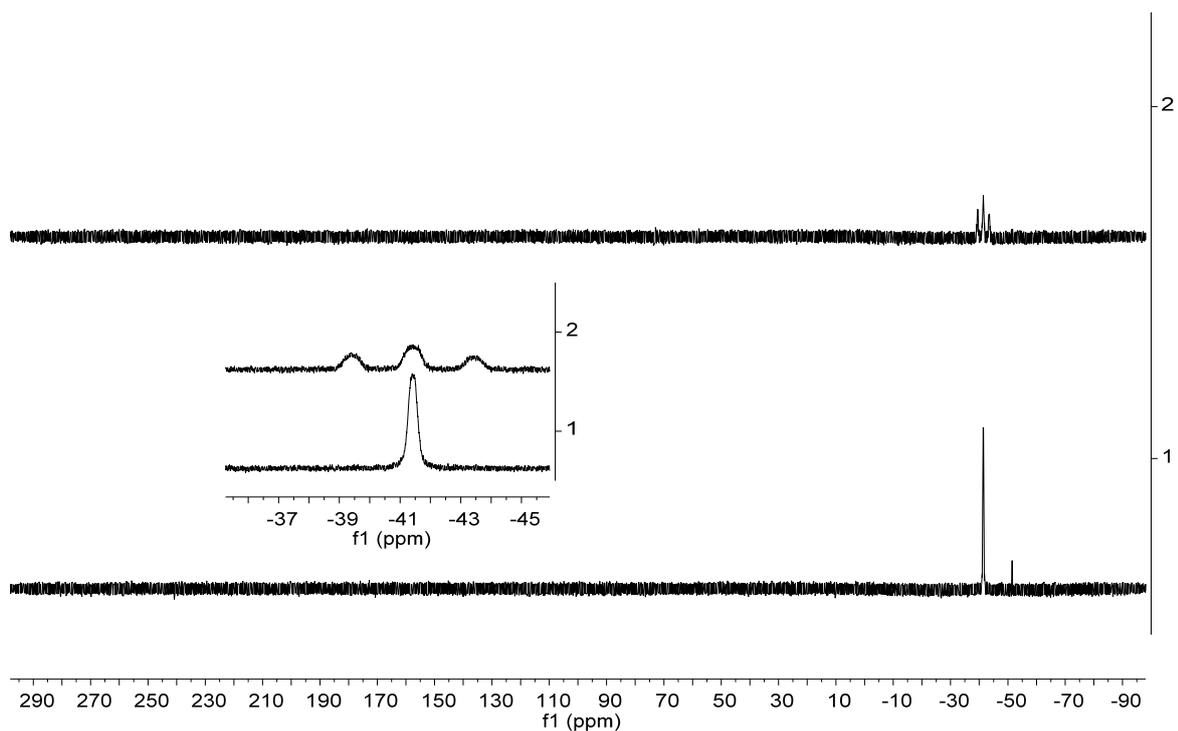


Figure S16. (1) $^{31}\text{P}\{^1\text{H}\}$ and (2) ^{31}P NMR (243 MHz, 299 K, CD_2Cl_2) spectra of compound 9.

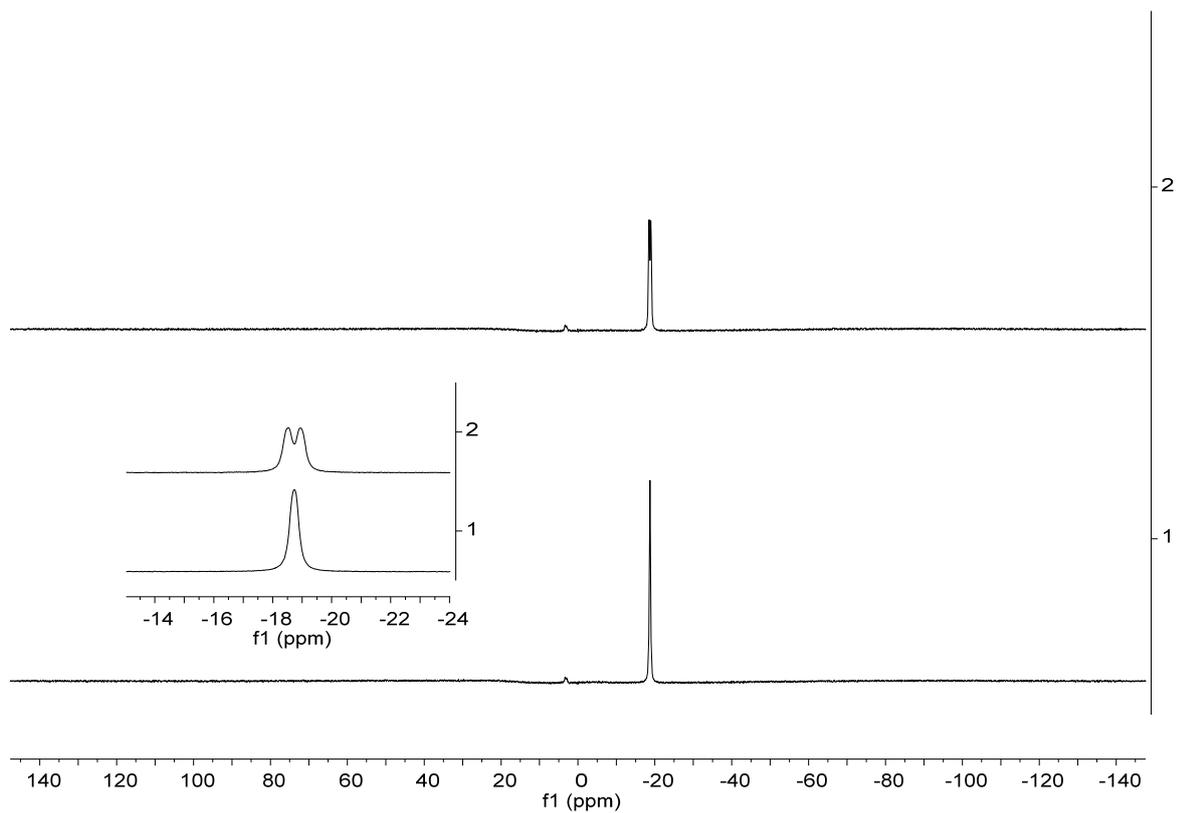


Figure S17. (1) $^{11}\text{B}\{^1\text{H}\}$ and (2) ^{11}B NMR (192 MHz, 299 K, CD_2Cl_2) spectra of compound 9.

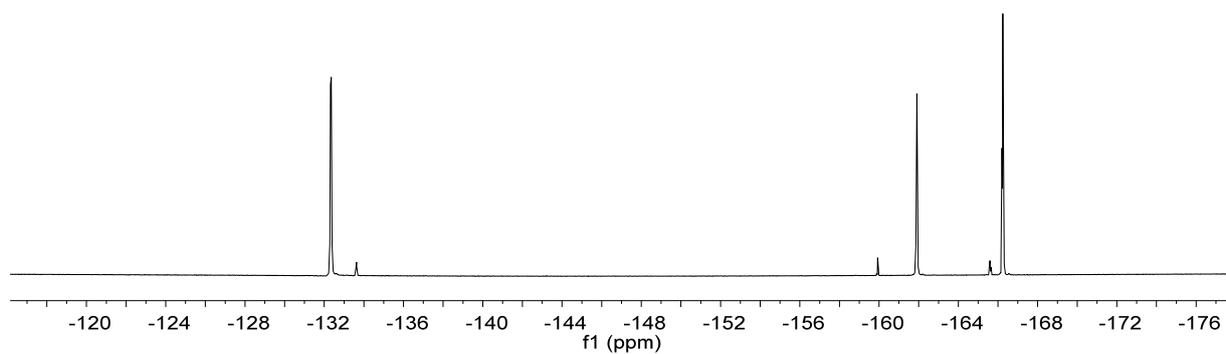


Figure S18. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound 9.

Crystals of compound **9** suitable for the X-ray crystal structure analysis were obtained from a solution of the white solid in CH₂Cl₂ and pentane (1 : 5) at -35 °C.

X-ray crystal structure analysis of compound 9: A colorless prism-like specimen of C₃₆H₄₂BF₁₀P, approximate dimensions 0.200 mm x 0.200 mm x 0.320 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1725 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 monoclinic unit cell yielded a total of 62251 reflections to a maximum θ angle of 66.82° (0.84 Å resolution), of which 6314 were independent (average redundancy 9.859, completeness = 99.5%, $R_{\text{int}} = 4.14\%$, $R_{\text{sig}} = 1.87\%$) and 5783 (91.59%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 12.3185(2)$ Å, $b = 19.8134(4)$ Å, $c = 14.6806(3)$ Å, $\beta = 95.3440(10)^\circ$, volume = 3567.54(12) Å³, are based upon the refinement of the XYZ-centroids of 9848 reflections above $20 \sigma(I)$ with $7.515^\circ < 2\theta < 133.4^\circ$. 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 0.6690 and 0.7720. The final anisotropic full-matrix least-squares refinement on F^2 with 456 variables converged at $R1 = 3.33\%$, for the observed data and $wR2 = 8.68\%$ for all data. The goodness-of-fit was 1.049. The largest peak in the final difference electron density synthesis was 0.476 e⁻/Å³ and the largest hole was -0.335 e⁻/Å³ with an RMS deviation of 0.043 e⁻/Å³. On the basis of the final model, the calculated density was 1.315 g/cm³ and $F(000)$, 1472 e⁻.

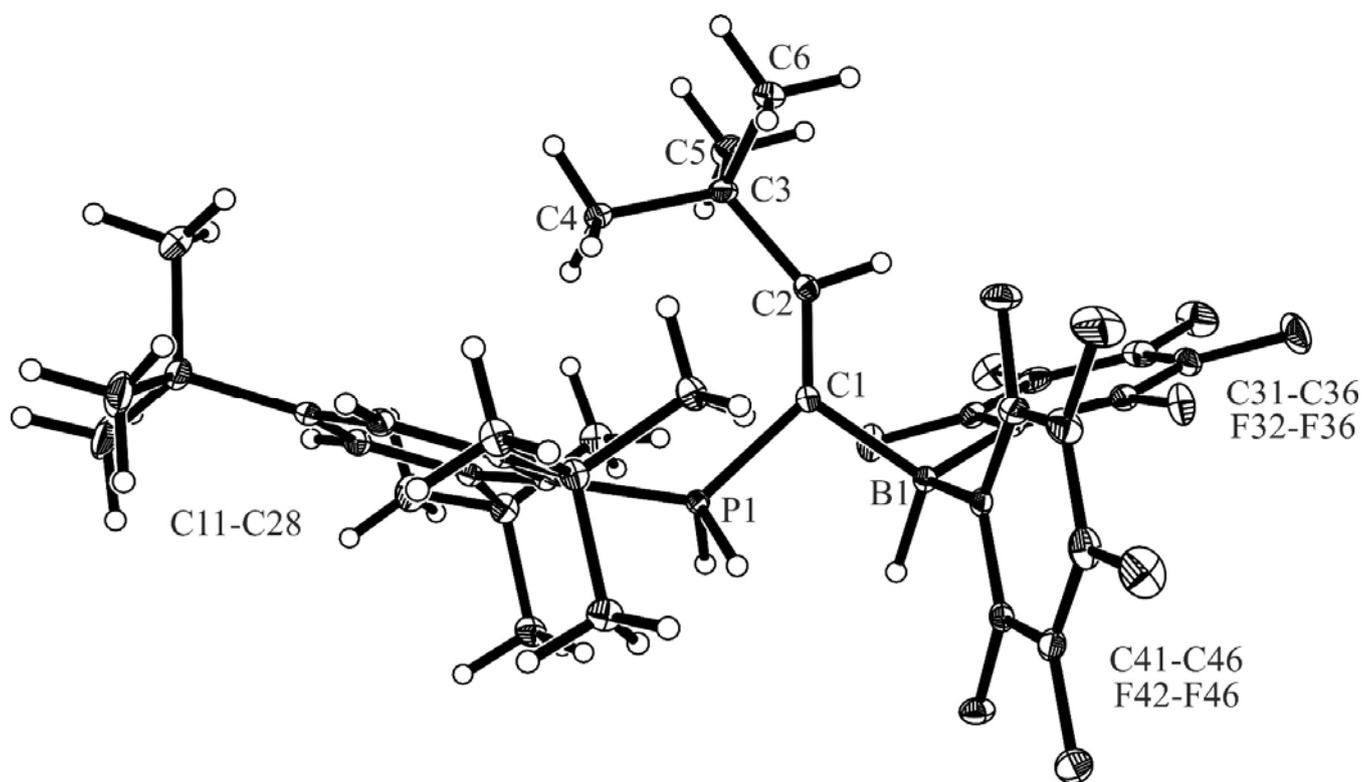
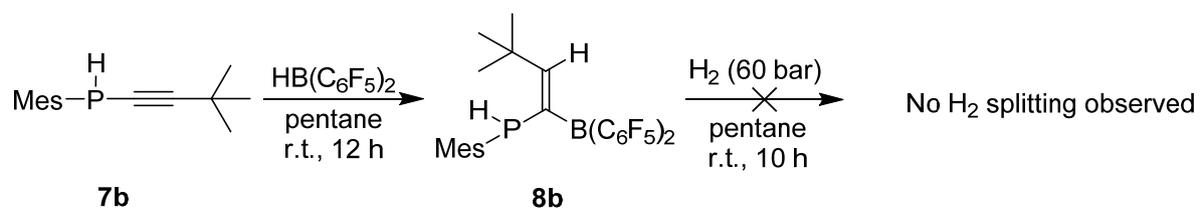


Figure S19. A view of the molecular structure of compound **9**.

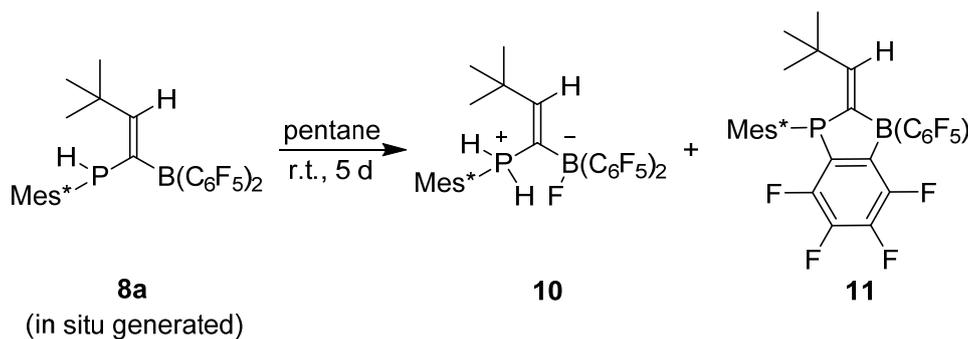
Reaction of compound **8b** with Dihydrogen



Scheme S5

After stirring a mixture of compound **7b** (116 mg, 0.5 mmol) and $\text{HB(C}_6\text{F}_5)_2$ (173 mg, 0.5 mmol) in pentane (5 mL) at room temperature for 12 h, the resulting mixture was filtered to give a yellow solution. The solution was transferred to an autoclave and stirred at room temperature for 10 h under a H_2 (60 bar) atmosphere. The resulting solution was dried in vacuo to give a yellow solid, which was dissolved in CD_2Cl_2 and characterized by NMR experiments: the obtained data were consistent with those of compound **8b**.

Heating of compound 8a: generation of compounds 10 and 11



Scheme S6

a) Generation of compounds 10 and 11 (in situ experiment, NMR scale):

After stirring a mixture of compound **7a** (18.0 mg, 0.05 mmol) and $\text{HB}(\text{C}_6\text{F}_5)_2$ (17.3 mg, 0.05 mmol) in cyclohexane- d_{12} (0.5 mL) at room temperature for 1 h, the resulting red mixture was filtered to give a red solution. The resulting red solution was then characterized by NMR experiments. After ca. 5 days at room temperature, a mixture of mainly compounds **10** and **11** [ratio ca. 54 : 46 (^{31}P , 299 K, cyclohexane- d_{12})] was detected.

[Mes*: 2,4,6-tri-*tert*-butylphenyl]

^1H NMR (500 MHz, 299 K, cyclohexane- d_{12} , 1.38 ppm): δ = 7.72 (d, $^1J_{\text{PH}} = 495.6$ Hz, 2H, PH_2), 7.61 (d, $^4J_{\text{PH}} = 4.3$ Hz, 2H, *m*-Mes*), 6.59 (d, $^3J_{\text{PH}} = 77.0$ Hz, 1H, =CH), 1.48 (s, 18H, *o*-C(CH₃)₃-Mes*), 1.32 (s, 9H, *p*-C(CH₃)₃-Mes*), 0.62 (s, 9H, C(CH₃)₃).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 299 K, cyclohexane- d_{12}): δ = -51.6 (d, $J_{\text{PF}} = 37.8$ Hz).

^{31}P NMR (202 MHz, 299 K, cyclohexane- d_{12}): δ = -51.6 (tdd, $^1J_{\text{PH}} = 496.9$ Hz, $^3J_{\text{PH}} = 78.2$ Hz, $J_{\text{PF}} = 37.8$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, 299 K, cyclohexane- d_{12}): δ = 2.9.

^{19}F NMR (470 MHz, 299 K, cyclohexane- d_{12}): δ = -133.4 (m, 2F, *o*), -160.4 (t, $^3J_{\text{FF}} = 19.8$ Hz, 1F, *p*), -165.9 (m, 2F, *m*)(C₆F₅) [$\Delta\delta^{19}\text{F}_{m,p} = 5.5$], -183.7 (br, 1F, B-F).

NMR data of compound **11** at 299 K in cyclohexane- d_{12} :

^1H NMR (500 MHz, 299 K, cyclohexane- d_{12} , 1.38 ppm): δ = 7.59, 7.51 (each br, each 1H, *m*-Mes*), 7.13 (d, $^3J_{\text{PH}} = 25.5$ Hz, 1H, =CH), 1.80 (br), 1.32 (s), 1.08 (br)(each 9H, C(CH₃)₃-Mes*), 0.67 (s, 9H, C(CH₃)₃).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 299 K, cyclohexane- d_{12}): δ = -15.7 (m).

^{31}P NMR (202 MHz, 299 K, cyclohexane- d_{12}): δ = -15.7 (m).

$^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, 299 K, cyclohexane- d_{12}): δ = 60.2 ($\nu_{1/2} \sim 1800$ Hz).

^{19}F NMR (470 MHz, 299 K, cyclohexane- d_{12}): δ = -125.8, -128.5, -144.3, -158.4 (each m, each 1F, C₆F₄), -131.0, -132.0 (each br, each 1F, *o*), -153.6 (t, $^3J_{\text{FF}} = 19.8$ Hz, 1F, *p*), -162.6 (br m, 2F, *m*)(C₆F₅) [$\Delta\delta^{19}\text{F}_{m,p} = 9.0$].

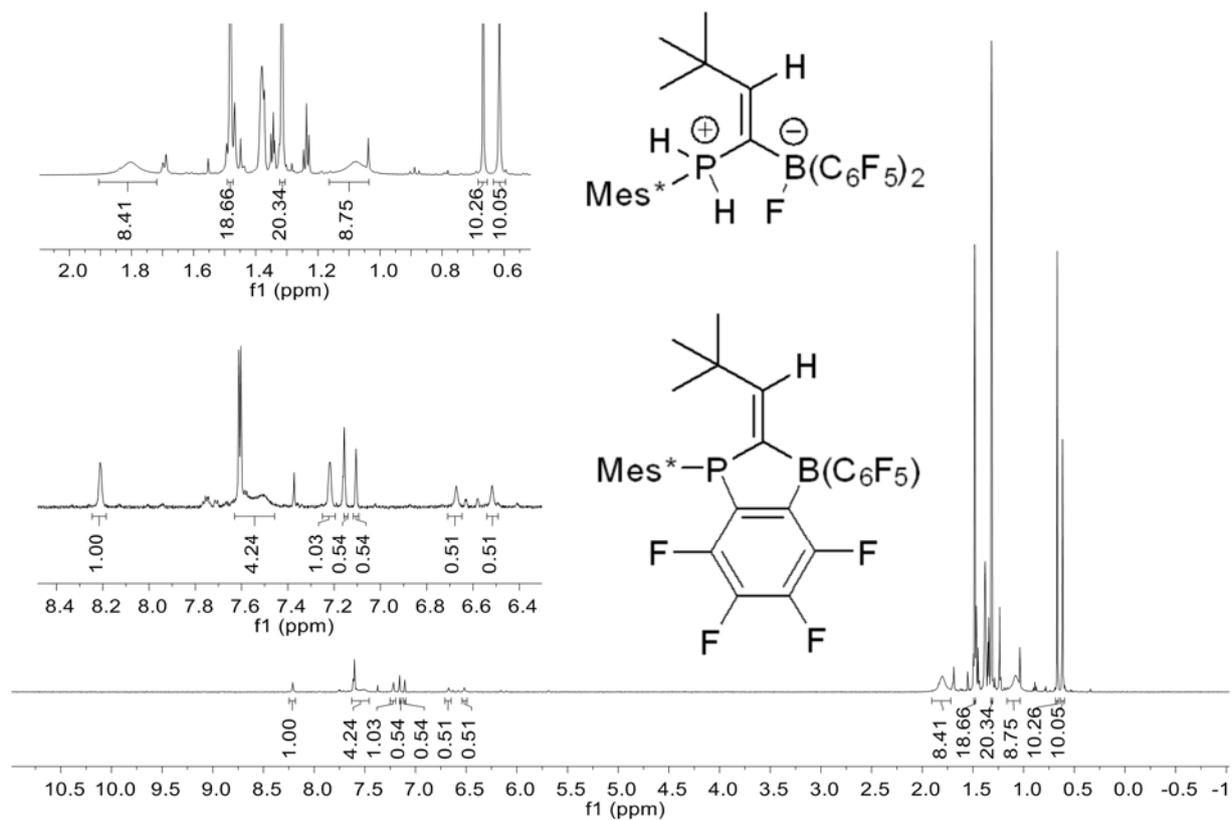


Figure S20. ^1H NMR (500 MHz, 299 K, cyclohexane- d_{12}) spectrum of compounds **10** and **11**.

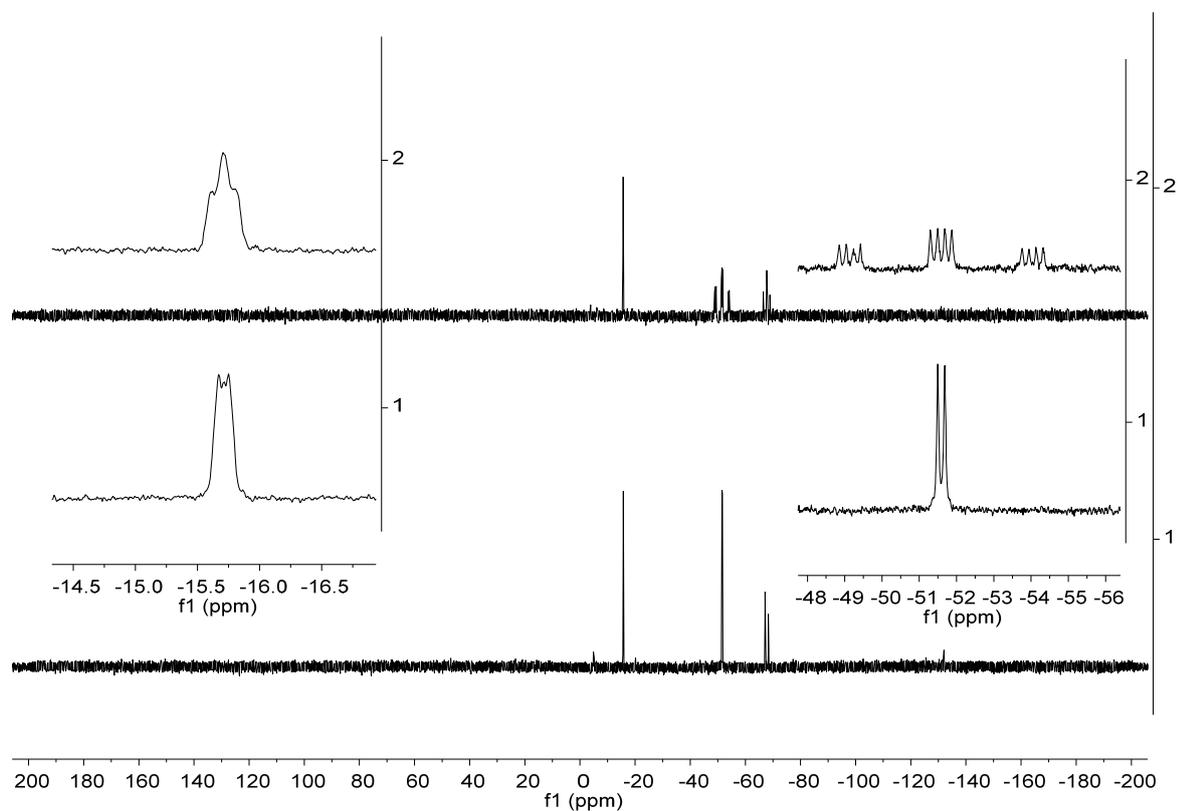


Figure S21. (1) $^{31}\text{P}\{^1\text{H}\}$ and (2) ^{31}P NMR (202 MHz, 299 K, cyclohexane- d_{12}) spectra of compounds **10** and **11**.

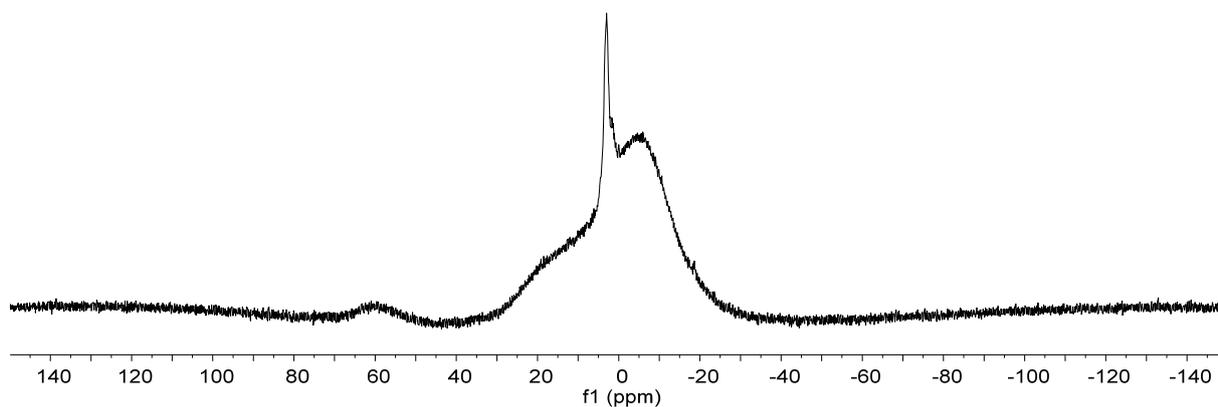


Figure S22. $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, 299 K, cyclohexane- d_{12}) spectrum of compounds **10** and **11**.

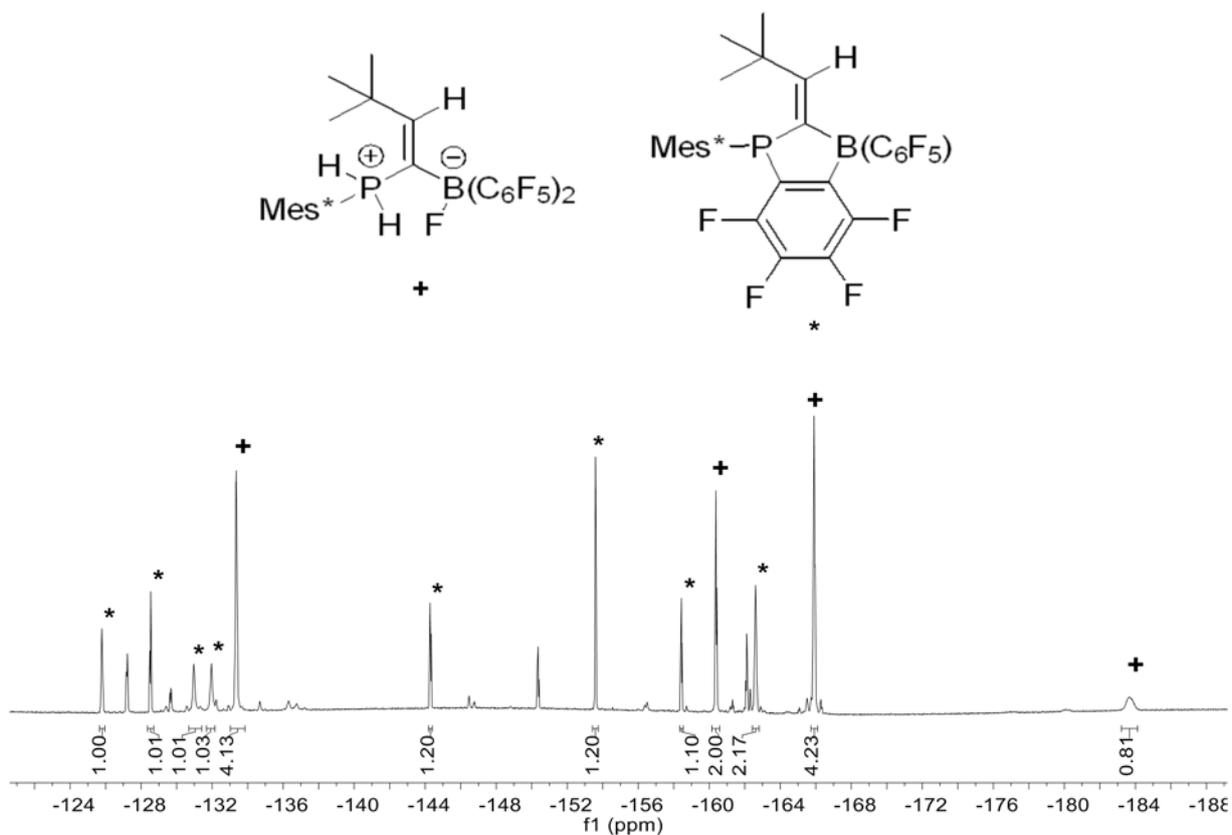


Figure S23. ^{19}F NMR (470 MHz, 299 K, cyclohexane- d_{12}) spectrum of compounds **10** and **11**.

b) Isolation of compound 10 (preparative scale):

After stirring the white suspension of compound **7a** (180 mg, 0.5 mmol) and $\text{HB}(\text{C}_6\text{F}_5)_2$ (173 mg, 0.5 mmol) in pentane (5 mL) at room temperature for 5 min, the formed yellow solution was stirred further for 5 days at room temperature to finally give a red solution (with a little bit solid material). The solution was filtered and then all volatiles of the obtained red filtrate were removed in vacuo to give an orange solid. The orange solid was crystallized twice from pentane (2×5 mL) at $-35\text{ }^\circ\text{C}$ to give colorless crystals of compound **10**, which were suitable for the x-ray crystal structure analysis. Yield: 127 mg, 35 %.

Elemental analysis: calc. for $\text{C}_{36}\text{H}_{41}\text{PBF}_{11}$ (724.5 g mol^{-1}): C, 59.68; H, 5.70. Found: C, 60.10; H, 5.24.

Melting point: $190\text{ }^\circ\text{C}$.

[Mes*: 2,4,6-tri-*tert*-butylphenyl]

^1H NMR (600 MHz, 299 K, CD_2Cl_2 , 5.32 ppm): $\delta = 7.62$ (d, $^1J_{\text{PH}} = 491.4\text{ Hz}$, 2H, PH_2), 7.62 (d, $^4J_{\text{PH}} = 4.6\text{ Hz}$, 2H, *m*-Mes*), 6.51 (d, $^3J_{\text{PH}} = 75.8\text{ Hz}$, 1H, =CH), 1.50 (s, 18H, *o*- $\text{C}(\text{CH}_3)_3$ -Mes*), 1.32 (s, 9H, *p*- $\text{C}(\text{CH}_3)_3$ -Mes*), 0.61 (s, 9H, $\text{C}(\text{CH}_3)_3$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, CD_2Cl_2 , 53.8 ppm): $\delta = 166.0$ (br, =CH), 158.1 (d, $^2J_{\text{PC}} = 6.7\text{ Hz}$, *o*-Mes*), 157.7 (d, $^4J_{\text{PC}} = 3.6\text{ Hz}$, *p*-Mes*), 148.6 (dm, $^1J_{\text{FC}} \sim 242\text{ Hz}$, C_6F_5), 139.8 (dm, $^1J_{\text{FC}} \sim 247\text{ Hz}$, C_6F_5), 137.4 (dm, $^1J_{\text{FC}} \sim 248\text{ Hz}$, C_6F_5), 125.2 (d, $^3J_{\text{PC}} = 12.4\text{ Hz}$, *m*-Mes*), 122.7 (br d, $^1J_{\text{PC}} = 24.8\text{ Hz}$, BC=), 122.4 (br m, *i*- C_6F_5), 110.6 (d, $^1J_{\text{PC}} = 60.0\text{ Hz}$, *i*-Mes*), 38.6 (d, $^3J_{\text{PC}} = 3.0\text{ Hz}$, *o*- $\text{C}(\text{CH}_3)_3$ -Mes*), 38.3 (d, $^3J_{\text{PC}} = 9.7\text{ Hz}$, $\text{C}(\text{CH}_3)_3$), 35.9 (d, $^5J_{\text{PC}} = 1.1\text{ Hz}$, *p*- $\text{C}(\text{CH}_3)_3$ -Mes*), 33.7 (d, $^4J_{\text{PC}} = 1.9\text{ Hz}$, *o*- $\text{C}(\text{CH}_3)_3$ -Mes*), 30.9 (*p*- $\text{C}(\text{CH}_3)_3$ -Mes*), 28.7 (d, $^4J_{\text{PC}} = 1.8\text{ Hz}$, $\text{C}(\text{CH}_3)_3$).

$^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, 299 K, CD_2Cl_2): $\delta = -51.4$ (d, $J_{\text{PF}} = 30.7\text{ Hz}$).

^{31}P NMR (243 MHz, 299 K, CD_2Cl_2): $\delta = -51.4$ (tdd, $^1J_{\text{PH}} = 491.1\text{ Hz}$, $^3J_{\text{PH}} = 75.8\text{ Hz}$, $J_{\text{PF}} = 30.7\text{ Hz}$).

$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, CD_2Cl_2): $\delta = 3.1$ (br d, $^1J_{\text{FB}} = 69.4\text{ Hz}$).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): $\delta = -133.6$ (m, 4F, *o*- C_6F_5), -159.9 (t, $^3J_{\text{FF}} = 20.1\text{ Hz}$, 2F, *p*- C_6F_5), -165.6 (m, 4F, *m*- C_6F_5), -184.6 (br, 1F, B-F), [$\Delta\delta^{19}\text{F}_{m,p} = 5.7$].

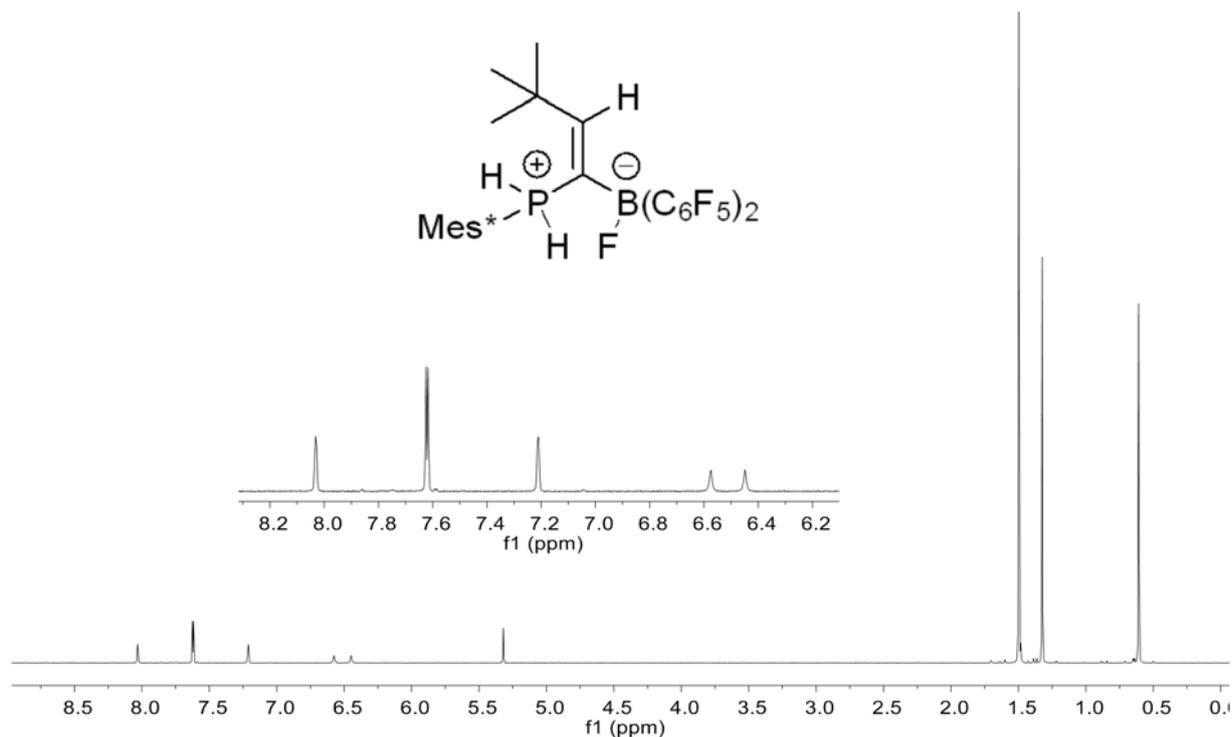


Figure S24. ^1H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound **10**.

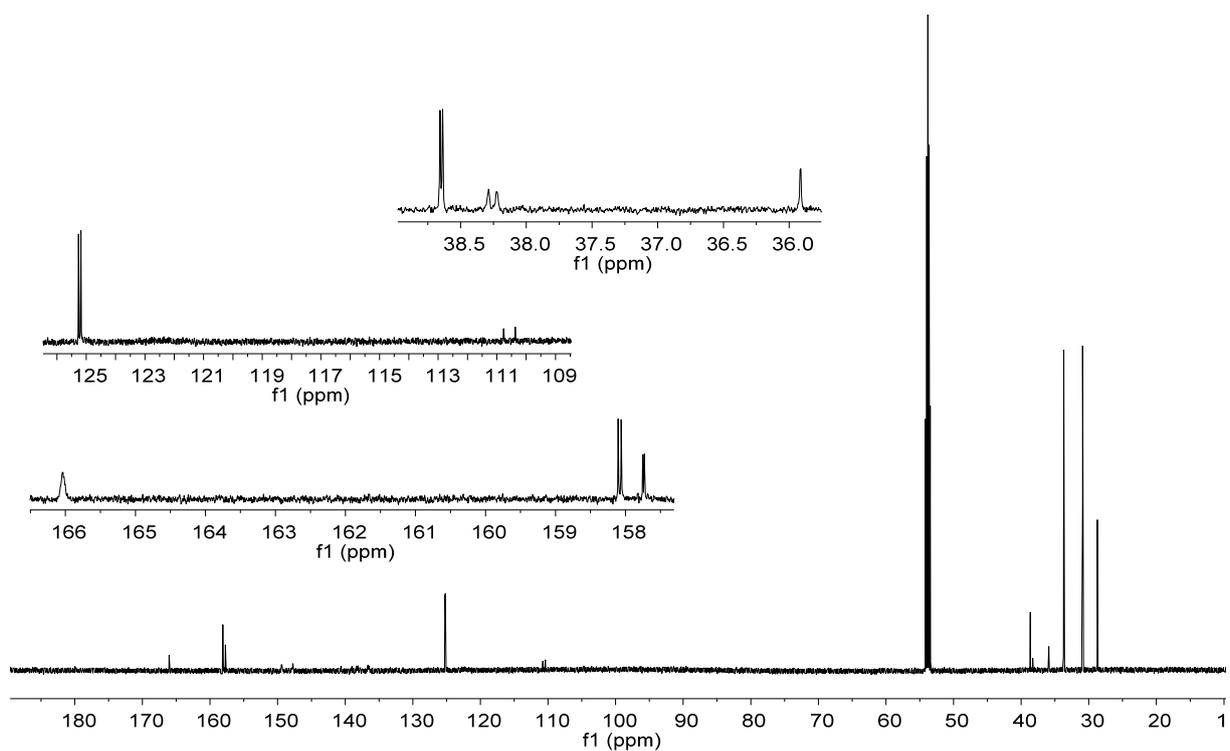


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **10**.

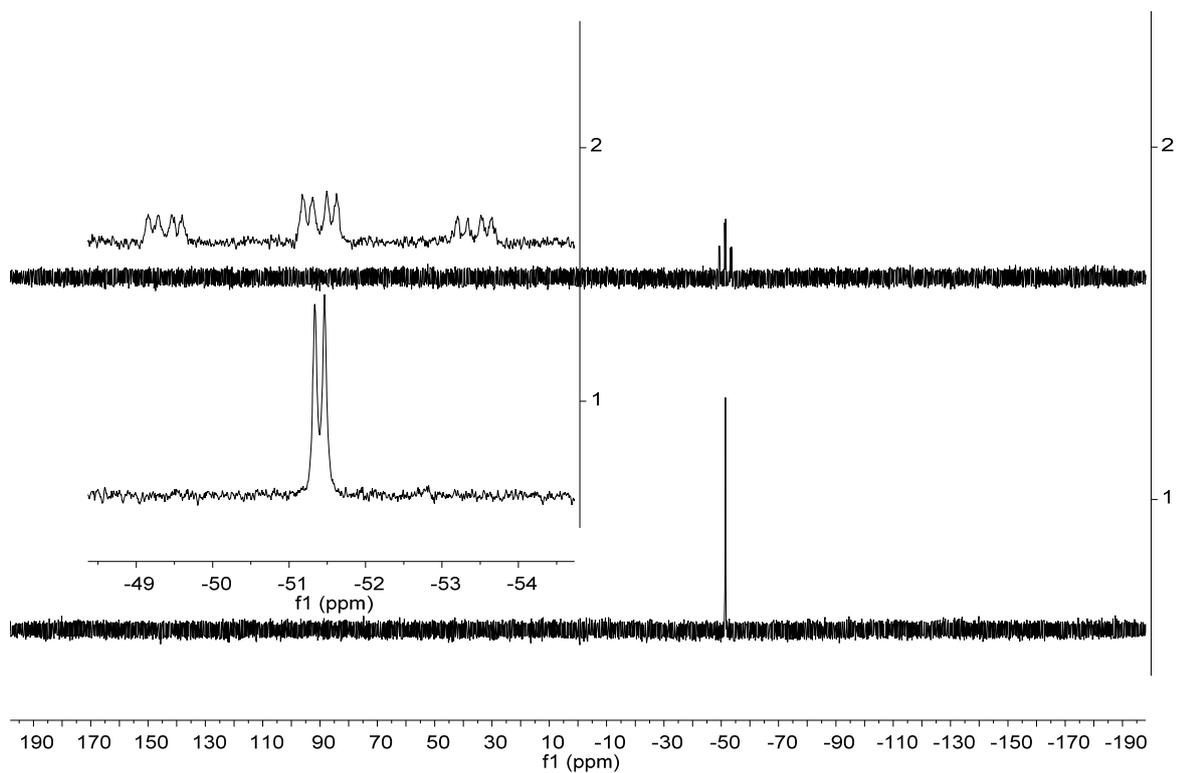


Figure S26. (1) $^{31}\text{P}\{^1\text{H}\}$ and (2) ^{31}P NMR (243 MHz, 299 K, CD_2Cl_2) spectra of compound **10**.

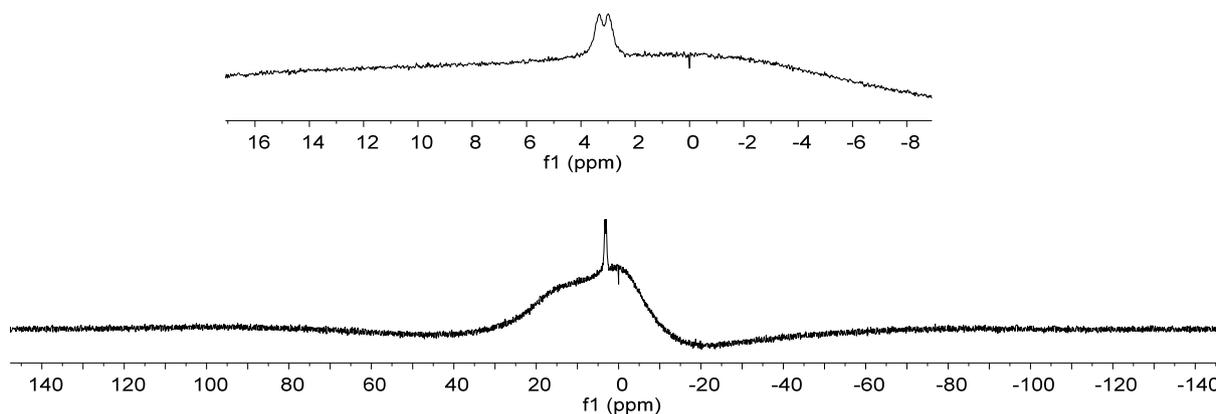


Figure S27. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of compound **10**.

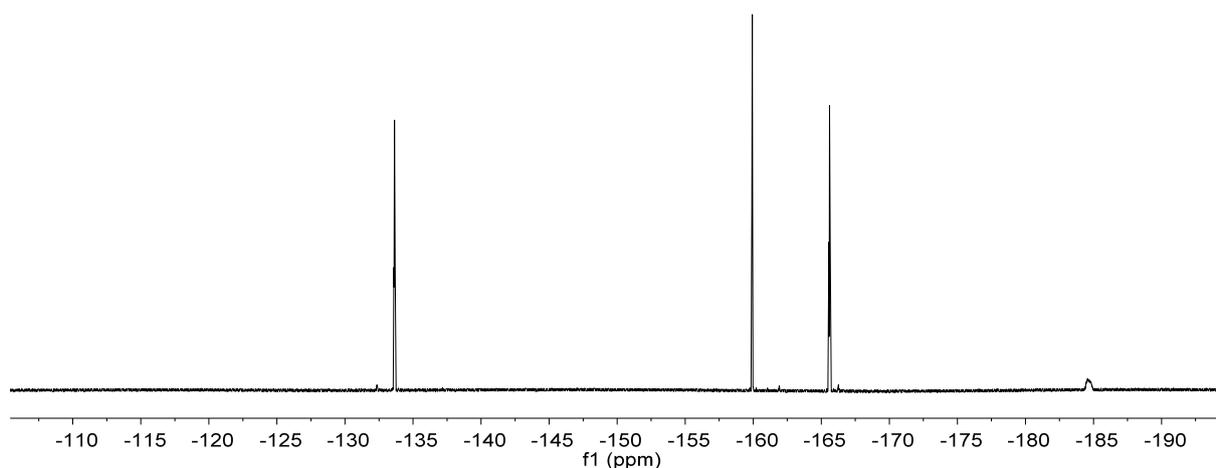


Figure S28. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **10**.

X-ray crystal structure analysis of compound 10: A colorless prism-like specimen of $\text{C}_{36}\text{H}_{41}\text{BF}_{11}\text{P}$, approximate dimensions 0.143 mm x 0.193 mm x 0.252 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 878 frames were collected. The total exposure time was 19.51 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 52190 reflections to a maximum θ angle of 26.43° (0.80 Å resolution), of which 7354 were independent (average redundancy 7.097, completeness = 99.5%, $R_{\text{int}} = 6.63\%$, $R_{\text{sig}} = 3.46\%$) and 5952 (80.94%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 12.3109(8)$ Å, $b = 19.7364(13)$ Å, $c = 14.8469(10)$ Å, $\beta = 95.708(2)^\circ$, volume = $3589.5(4)$ Å³, are based upon the refinement of the XYZ-centroids of 9850 reflections above $20\sigma(I)$ with $4.964^\circ < 2\theta < 52.72^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.878. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9610 and 0.9780. The final anisotropic full-matrix least-squares refinement on F^2 with 462 variables converged at $R1 = 4.41\%$, for the observed data and $wR2 = 10.48\%$ for all data. The goodness-of-fit was 1.034. The largest peak in the final difference electron density synthesis was $0.312 \text{ e}/\text{Å}^3$ and the largest hole was $-0.329 \text{ e}/\text{Å}^3$ with an RMS deviation of $0.054 \text{ e}/\text{Å}^3$. On the basis of the final model, the calculated density was $1.341 \text{ g}/\text{cm}^3$ and $F(000)$, 1504 e⁻.

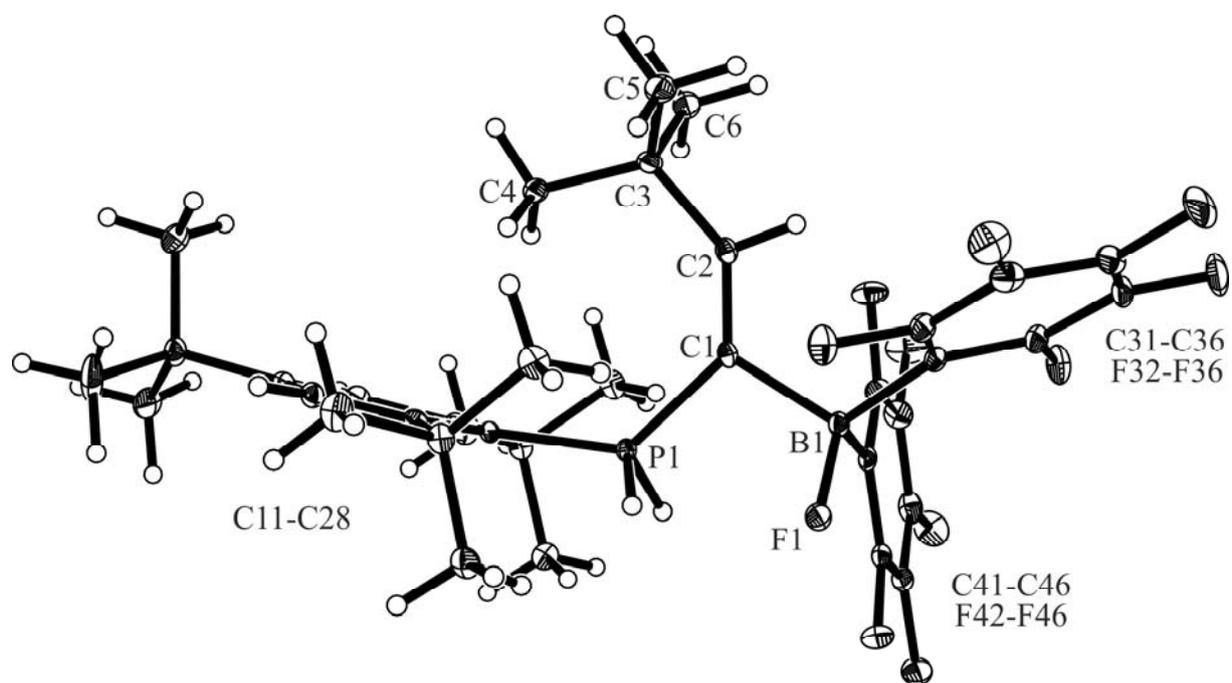
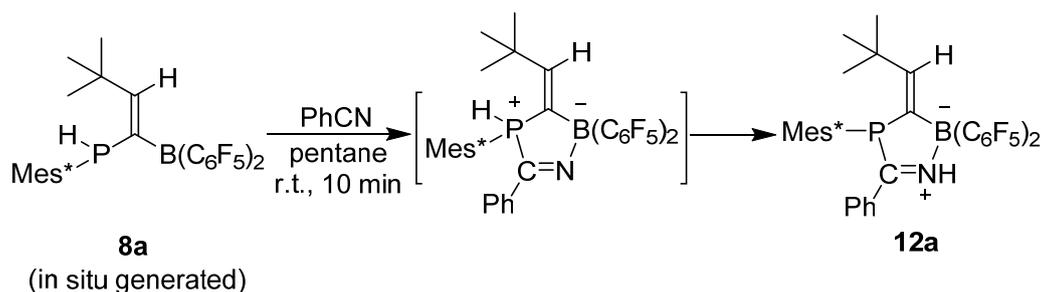


Figure S29. A view of the molecular structure of compound 10.

Preparation of compounds 12a and 12b

a) Preparation of compound 12a



Scheme S7

After stirring a mixture of compound **7a** (180 mg, 0.5 mmol) and $\text{HB}(\text{C}_6\text{F}_5)_2$ (173 mg, 0.5 mmol) in pentane (3 mL) at room temperature for 1 h, the resulting red suspension was filtered to give a clear red solution. Then one equiv. of benzonitrile (52 mg, 0.5 mmol) was added and the clear red solution was stirred for 10 min. Then all volatiles were removed in vacuo to give an orange sticky solid. Yield: 376 mg, 93 %.

Elemental analysis: calc. for $\text{C}_{43}\text{H}_{45}\text{PNBF}_{10}$ (807.6 g mol⁻¹): C, 63.95; H, 5.62; N, 1.73. Found: C, 63.67; H, 5.28; N, 1.70.

Melting point: 198 °C.

[Mes*: 2,4,6-*tert*-butylphenyl]

¹H NMR (600 MHz, 299 K, C_6D_6 , 7.15 ppm): δ = 8.81 (br, 1H, NH), 7.57 (d, ⁴ J_{HH} = 3.1 Hz, 2H, *m*-Mes*), 7.07 (m, 2H, *o*-Ph), 6.82 (m, 1H, *p*-Ph), 6.67 (m, 2H, *m*-Ph), 6.35 (d, ³ J_{PH} = 44.1 Hz, 1H, =CH), 1.49 (s, 18H, *o*-C(CH₃)₃-Mes*), 1.15 (s, 9H, *p*-C(CH₃)₃-Mes*), 0.93 (s, 9H, C(CH₃)₃).

¹³C{¹H} NMR (151 MHz, 299 K, C_6D_6 , 128.0 ppm): δ = 194.3 (d, ¹ J_{PC} = 9.8 Hz, C=NH), 157.6 (d, ² J_{PC} = 13.7 Hz, *o*-Mes*), 153.9 (d, ⁴ J_{PC} = 2.8 Hz, *p*-Mes*), 150.1 (=CH), 148.3 (dm, ¹ J_{FC} ~ 241 Hz, C₆F₅), 139.9 (dm, ¹ J_{FC} ~ 248 Hz, C₆F₅), 139.0 (br d, ¹ J_{PC} = 40.8 Hz, BC=), 137.8 (dm, ¹ J_{FC} ~ 252 Hz, C₆F₅), 133.6 (d, ² J_{PC} = 8.9 Hz, *i*-Ph), 132.7 (*p*-Ph), 129.0 (*m*-Ph), 127.8 (d, ³ J_{PC} = 3.9 Hz, *o*-Ph), 126.3 (d, ³ J_{PC} = 9.7 Hz, *m*-Mes*), 124.8 (d, ¹ J_{PC} = 37.0 Hz, *i*-Mes*), 121.4 (br m, *i*-C₆F₅), 40.5 (d, ³ J_{PC} = 4.1 Hz, *o*-C(CH₃)₃-Mes*), 37.0 (d, ³ J_{PC} = 4.3 Hz, C(CH₃)₃), 35.1 (d, ⁵ J_{PC} = 0.6 Hz, *p*-C(CH₃)₃-Mes*), 34.3 (d, ⁴ J_{PC} = 4.6 Hz, *o*-C(CH₃)₃-Mes*), 30.9 (*p*-C(CH₃)₃-Mes*), 29.8 (d, ⁴ J_{PC} = 1.8 Hz, C(CH₃)₃).

³¹P{¹H} NMR (243 MHz, 299 K, C_6D_6): δ = 6.8 ($\nu_{1/2}$ ~ 35 Hz).

³¹P NMR (243 MHz, 299 K, C_6D_6): δ = 6.8 (br d, ³ J_{PH} = 44.1 Hz).

¹¹B{¹H} NMR (192 MHz, 299 K, C_6D_6): δ = -3.1 ($\nu_{1/2}$ ~ 140 Hz).

¹⁹F NMR (564 MHz, 299 K, C_6D_6): δ = -134.0 (m, 2F, *o*-C₆F₅), -157.8 (t, ³ J_{FF} = 21.0 Hz, 1F, *p*-C₆F₅), -163.4 (m, 2F, *m*-C₆F₅).

[$\Delta\delta^{19}\text{F}_{m,p}$ = 5.6].

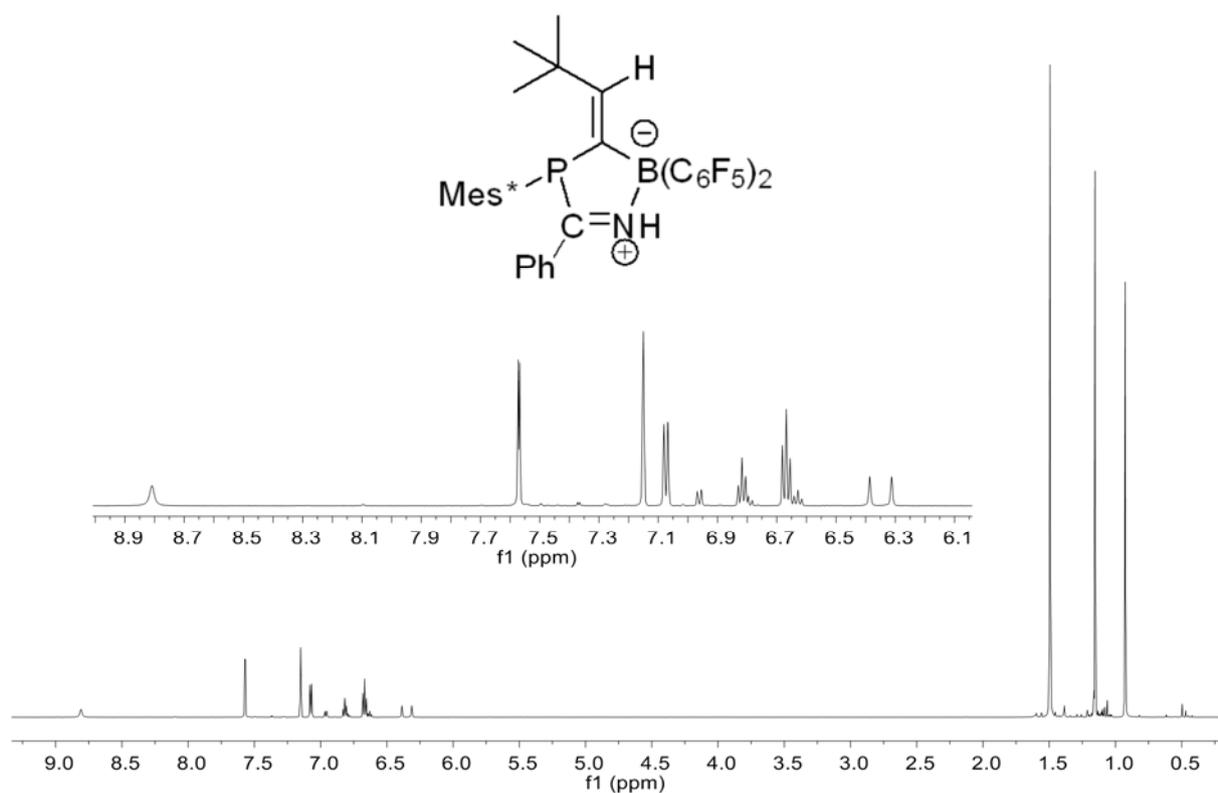


Figure S30. ¹H NMR (600 MHz, 299 K, C₆D₆) spectrum of compound 12a.

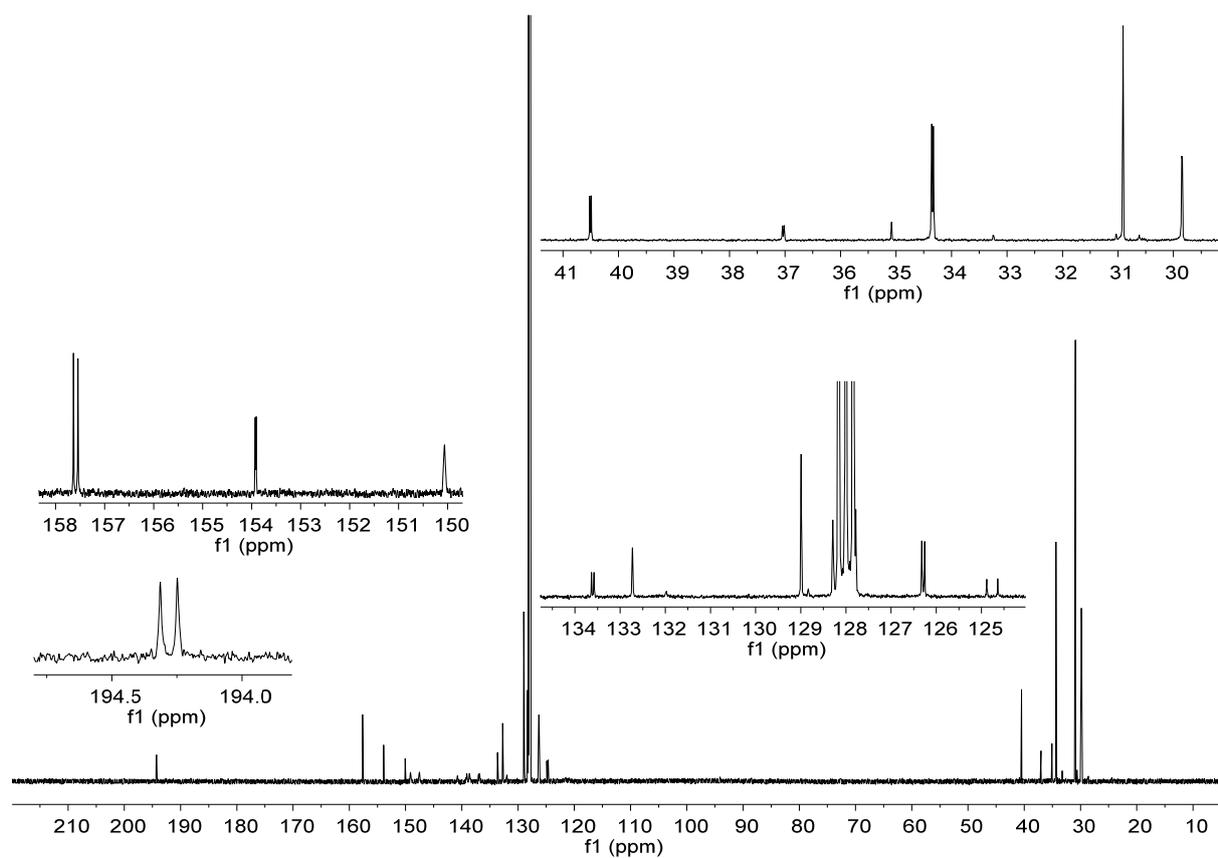


Figure S31. ¹³C{¹H} NMR (151 MHz, 299 K, C₆D₆) spectrum of compound 12a.

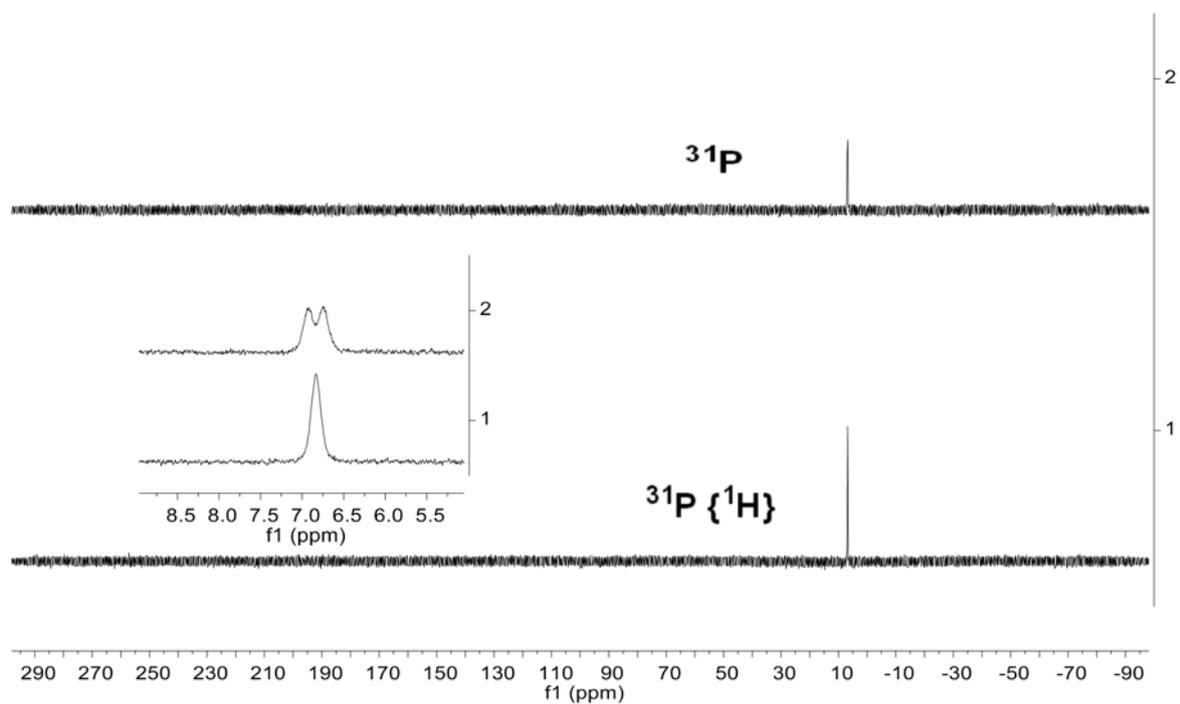


Figure S32. (1) $^{31}\text{P}\{^1\text{H}\}$ and (2) ^{31}P NMR (243 MHz, 299 K, C_6D_6) spectra of compound 12a.

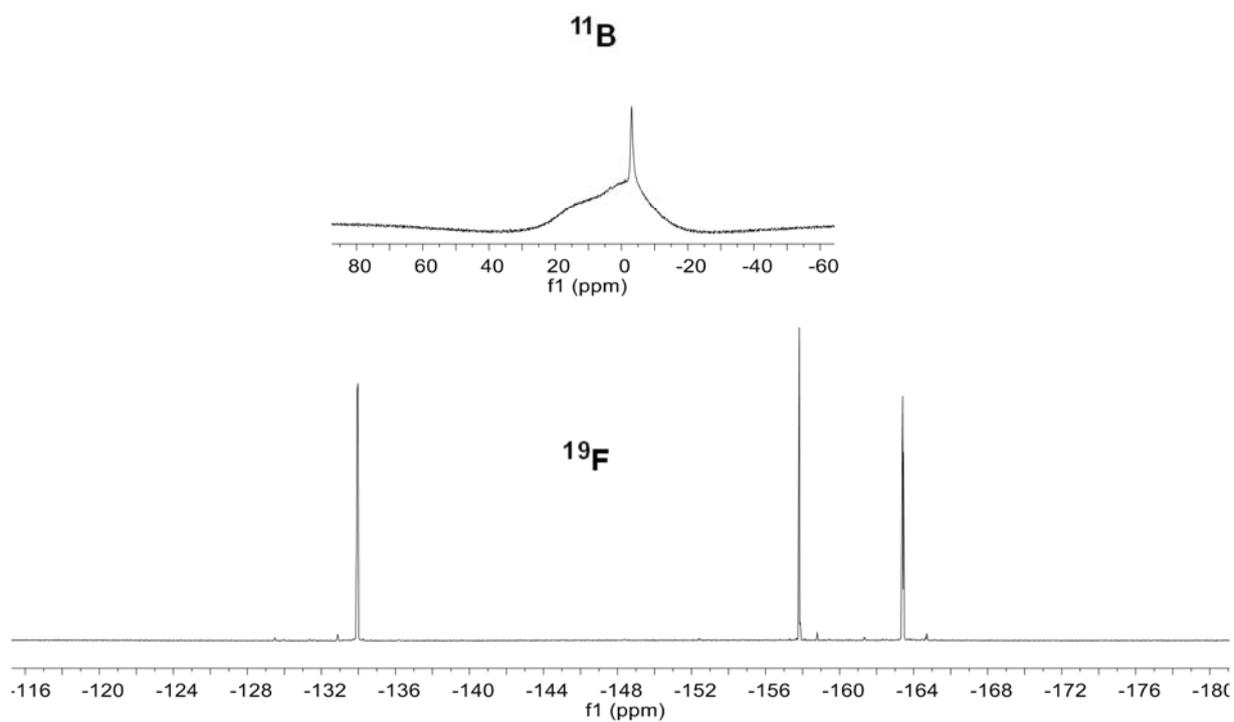
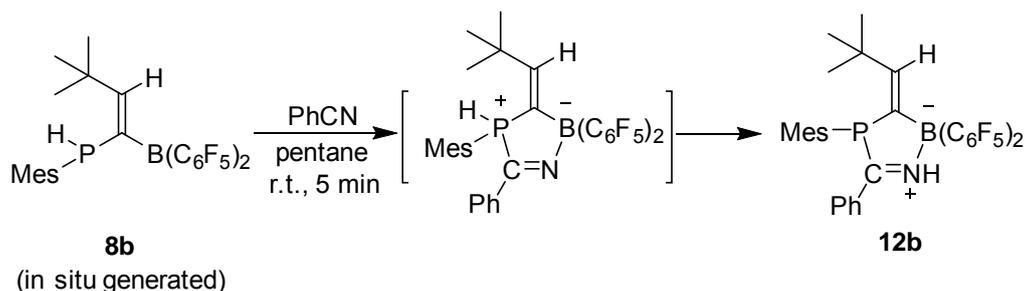


Figure S33. ^{19}F (564 MHz, 299 K, C_6D_6) and $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, C_6D_6) spectra of compound 12a.

b) Preparation of compound 12b



Scheme S8

After stirring a mixture of compound **7b** (116 mg, 0.5 mmol) and $\text{HB}(\text{C}_6\text{F}_5)_2$ (173 mg, 0.5 mmol) in pentane (3 mL) at room temperature for 10 h, the resulting yellow suspension was filtered to give a clear yellow solution. Then one equiv. of benzonitrile (52 mg, 0.5 mmol) was added and after stirring for 5 min a yellow precipitate was formed. The resulting suspension was filtered. The collected solid was washed twice with pentane (2x5 mL) and dried in vacuo to give a yellow solid. Yield: 286 mg, 84 %.

Elemental analysis: calc. for $\text{C}_{34}\text{H}_{27}\text{PBNF}_{10}$ (681.4 g mol^{-1}): C, 59.93; H, 3.99; N, 2.06. Found: C, 59.71; H, 3.81; N, 2.04.

Melting point: 249 °C.

[Mes: 2,4,6-trimethylphenyl]

^1H NMR (600 MHz, 299 K, C_6D_6 , 7.15 ppm): δ = 9.38 (br, 1H, C=NH), 7.21 (m, 2H, *o*-Ph), 6.74 (m, 1H, *p*-Ph), 6.70 (m, 2H, *m*-Ph), 6.62, 6.33 (each br, each 1H, *m*-Mes), 6.51 (d, $^3J_{\text{PH}} = 34.8 \text{ Hz}$, 1H, =CH), 2.81, 2.22 (each br, each 3H, *o*- CH_3 -Mes), 1.73 (s, 3H, *p*- CH_3 -Mes), 0.95 (s, 9H, $\text{C}(\text{CH}_3)_3$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, C_6D_6 , 128.0 ppm): δ = 200.4 (d, $^1J_{\text{PC}} = 17.2 \text{ Hz}$, C=NH), 153.0 (d, $^2J_{\text{PC}} = 6.8 \text{ Hz}$, =CH), 145.3, 145.1 (br)(*o*-Mes), 141.9 (d, $^4J_{\text{PC}} = 1.8 \text{ Hz}$, *p*-Mes), 135.4 (br d, $^1J_{\text{PC}} = 31.1 \text{ Hz}$, BC=), 133.4 (*p*-Ph), 132.9 (d, $^2J_{\text{PC}} = 11.8 \text{ Hz}$, *i*-Ph), 130.4, 130.0 (each br, *m*-Mes), 129.4 (*m*-Ph), 128.0 (d, $^1J_{\text{PC}} = 14.5 \text{ Hz}$, *i*-Mes), 126.8 (d, $^3J_{\text{PC}} = 7.1 \text{ Hz}$, *o*-Ph), 35.2 (d, $^2J_{\text{PC}} = 2.4 \text{ Hz}$, $\text{C}(\text{CH}_3)_3$), 29.2 (d, $^4J_{\text{PC}} = 2.8 \text{ Hz}$, $\text{C}(\text{CH}_3)_3$), 23.8 (br d, $^3J_{\text{PC}} = 27.4 \text{ Hz}$), 22.1 (br)(*o*- CH_3 -Mes), 20.8 (*p*- CH_3 -Mes), [C_6F_5 not listed].

$^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, 299 K, C_6D_6): δ = -2.8 (m).

^{31}P NMR (243 MHz, 299 K, C_6D_6): δ = -2.8 (br d, $^3J_{\text{PH}} = 34.8 \text{ Hz}$).

$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, C_6D_6): δ = -1.8 ($\nu_{1/2} \sim 150 \text{ Hz}$).

^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = -133.3 (m, 2F, *o*), -157.8 (t, $^3J_{\text{FF}} = 20.9 \text{ Hz}$, 1F, *p*), -163.3 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}\text{F}_{m,p} = 5.5$], -135.4 (m, 2F, *o*), -157.0 (t, $^3J_{\text{FF}} = 20.9 \text{ Hz}$, 1F, *p*), -162.8 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}\text{F}_{m,p} = 5.8$].

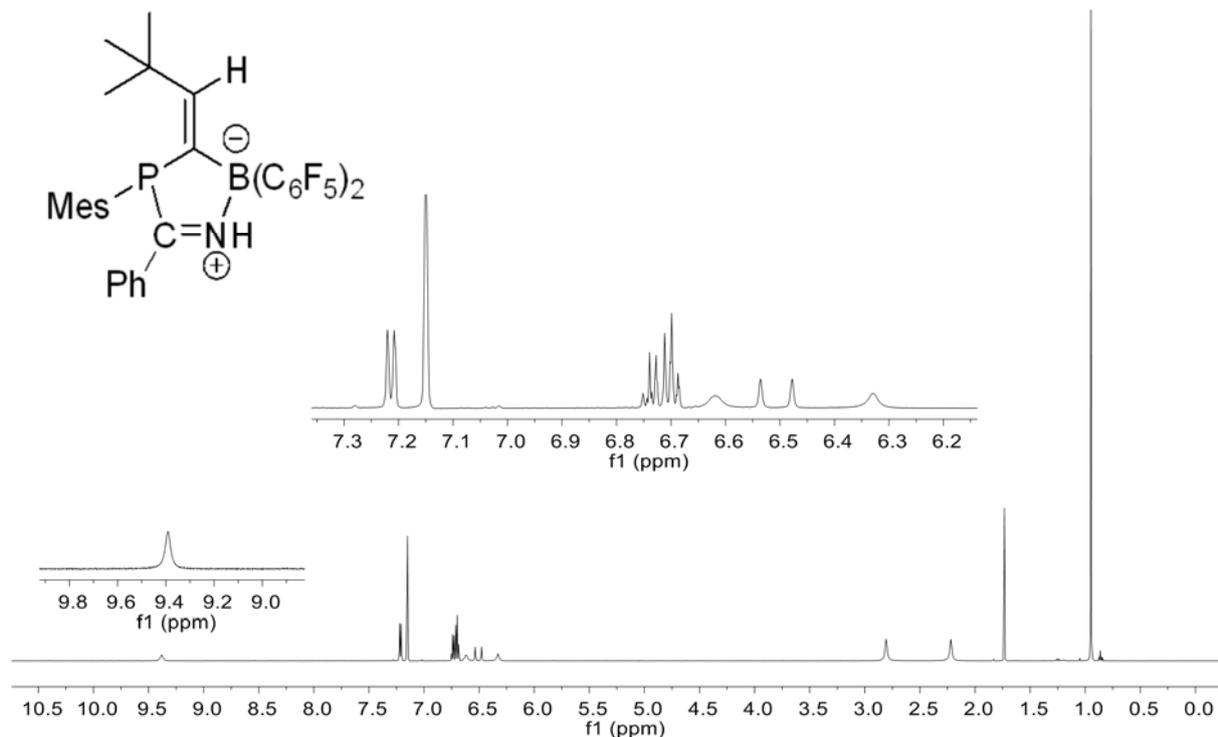


Figure S34. ^1H NMR (600 MHz, 299 K, C_6D_6) spectrum of compound **12b**.

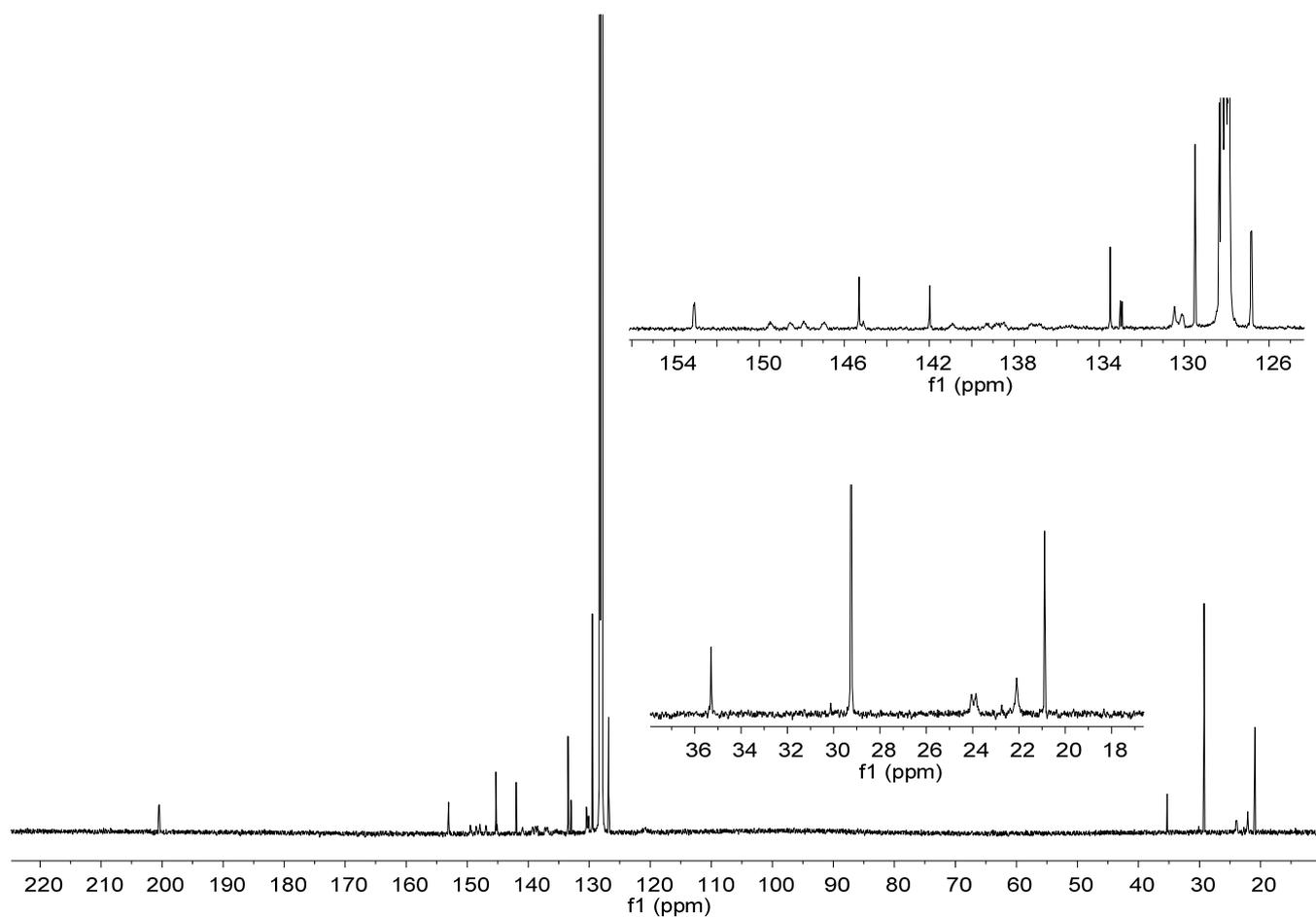


Figure S35. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, C_6D_6) spectrum of compound **12b**.

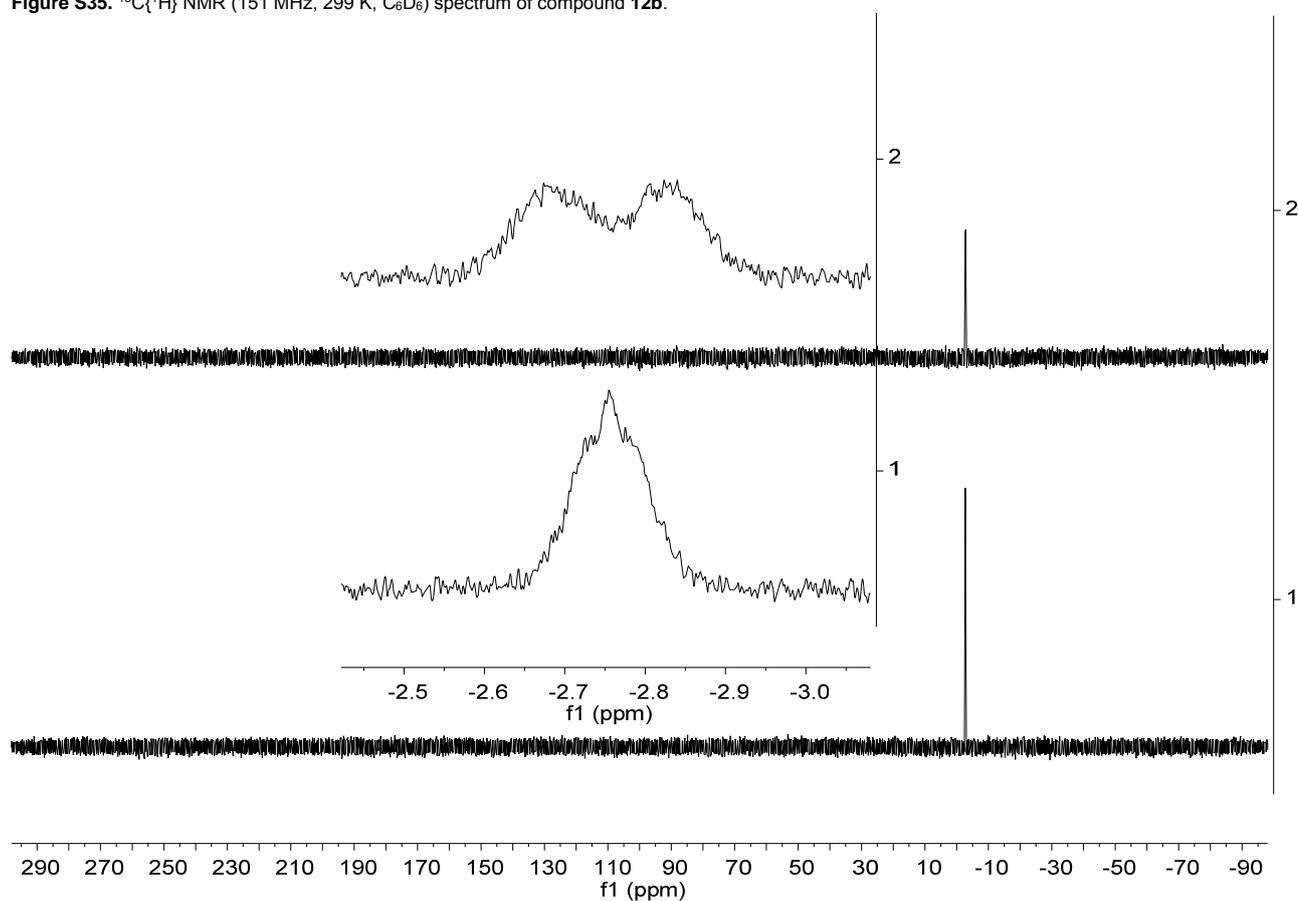


Figure S36. (1) $^{31}\text{P}\{^1\text{H}\}$ and (2) ^{31}P NMR (243 MHz, 299 K, C_6D_6) spectra of compound **12b**.

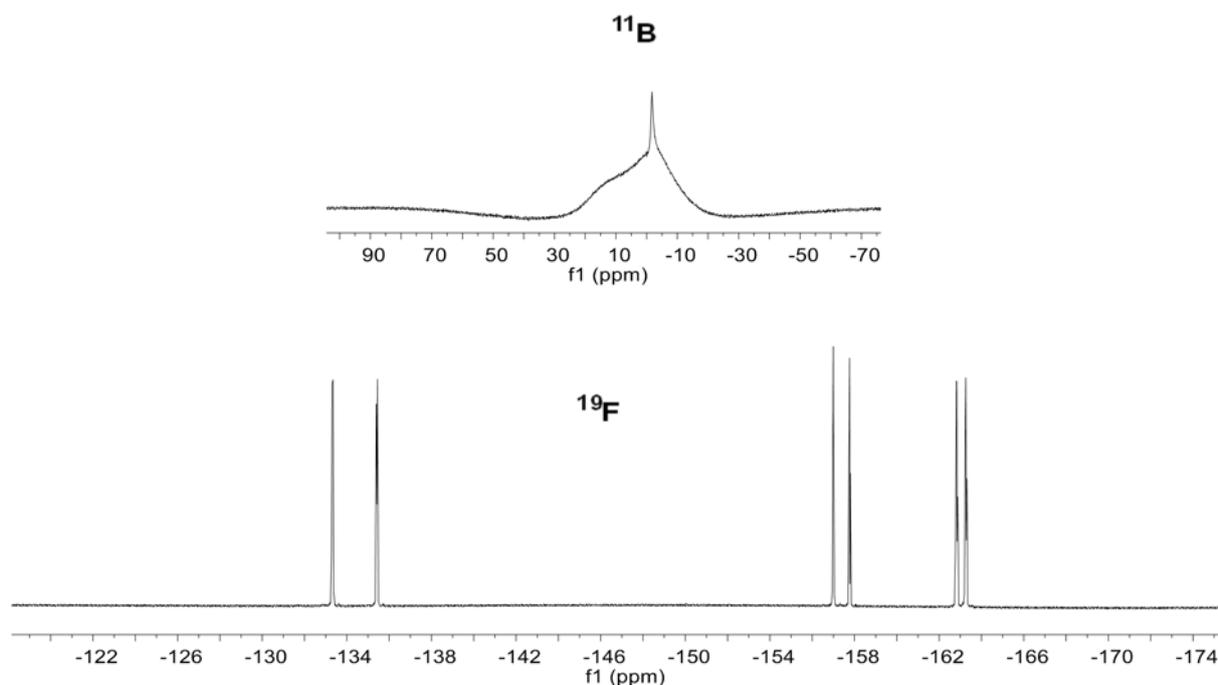


Figure S37. ^{19}F (564 MHz, 299 K, C_6D_6) and $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, C_6D_6) spectra of compound **12b**.

Crystals of compound **12b** suitable for the X-ray crystal structure analysis were obtained from a solution of the yellow solid in CH_2Cl_2 and pentane (ratio ca. 1 : 5) at $-35\text{ }^\circ\text{C}$.

X-ray crystal structure analysis of compound 12b: A specimen of $\text{C}_{34}\text{H}_{27}\text{BF}_{10}\text{NP} \cdot \frac{1}{2} \times \text{CH}_2\text{Cl}_2$, approximate dimensions 0.050 mm x 0.140 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a triclinic unit cell yielded a total of 24961 reflections to a maximum θ angle of 66.65° (0.84 Å resolution), of which 5592 were independent (average redundancy 4.464, completeness = 96.8%, $R_{\text{int}} = 4.40\%$, $R_{\text{sig}} = 3.47\%$) and 4776 (85.41%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 11.2145(3)$ Å, $b = 12.6515(3)$ Å, $c = 12.8136(4)$ Å, $\alpha = 71.1650(10)^\circ$, $\beta = 71.6280(10)^\circ$, $\gamma = 81.5080(10)^\circ$, volume = $1630.81(8)$ Å³, are based upon the refinement of the XYZ-centroids of reflections above $20\sigma(I)$. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6610 and 0.8950. The final anisotropic full-matrix least-squares refinement on F^2 with 492 variables converged at $R1 = 3.76\%$, for the observed data and $wR2 = 9.87\%$ for all data. The goodness-of-fit was 1.044. The largest peak in the final difference electron density synthesis was $0.358\text{ e}/\text{Å}^3$ and the largest hole was $-0.363\text{ e}/\text{Å}^3$ with an RMS deviation of $0.050\text{ e}/\text{Å}^3$. On the basis of the final model, the calculated density was $1.474\text{ g}/\text{cm}^3$ and $F(000)$, 738 e^- .

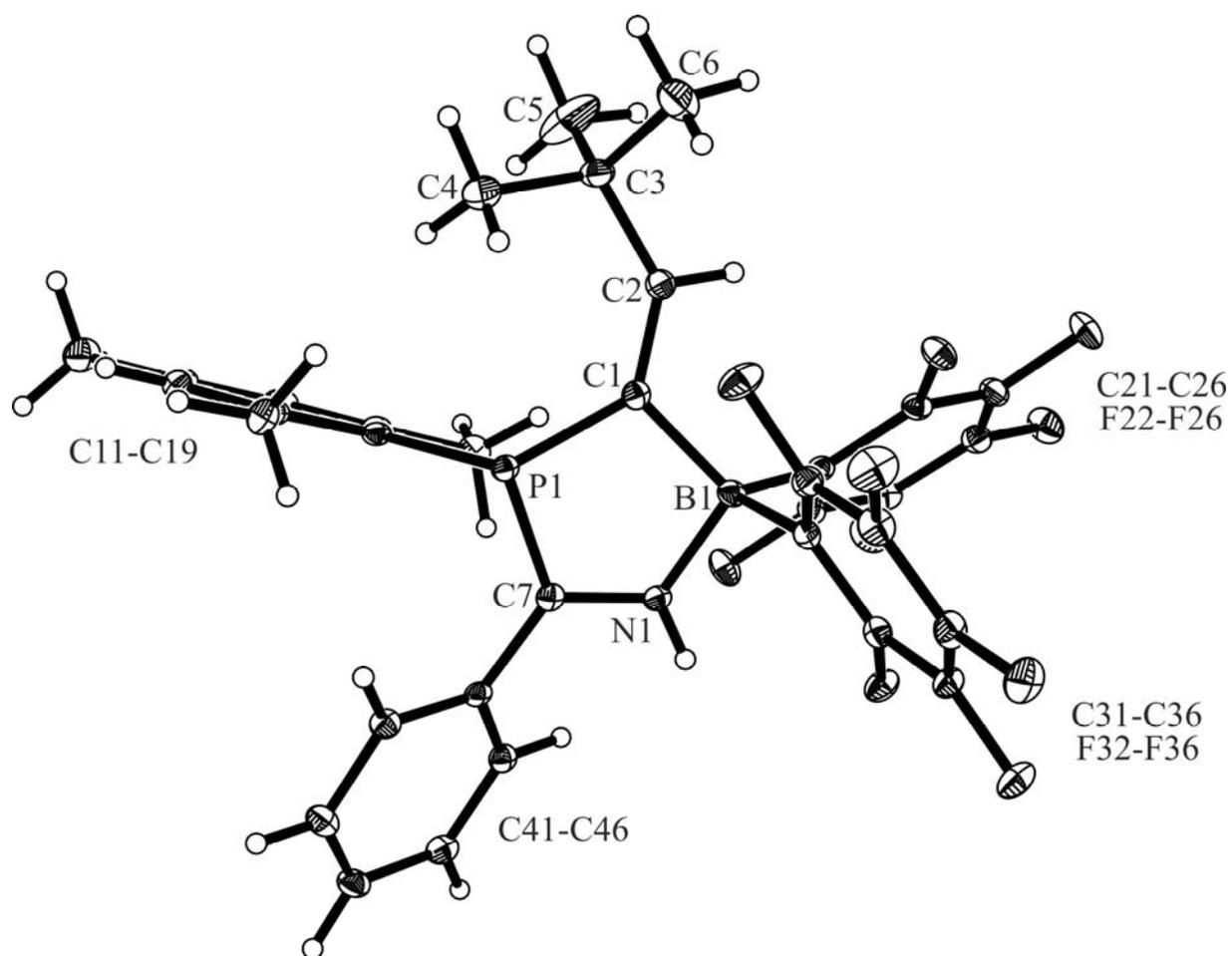
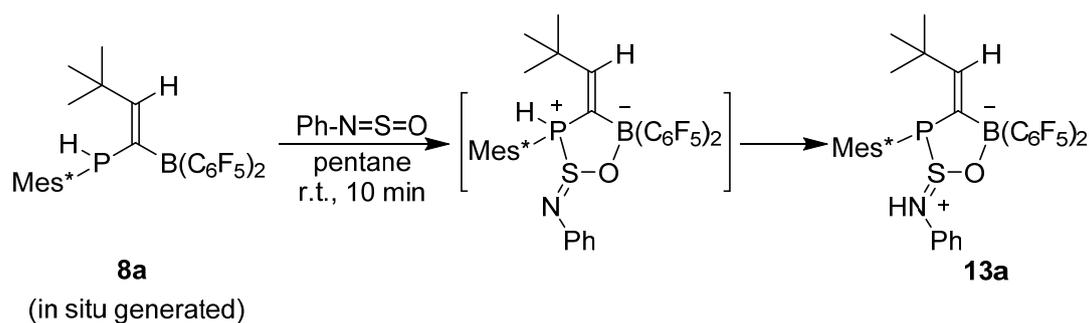


Figure S38. A view of the molecular structure of compound 12b.

Preparation of compounds 13a and 13b

a) Preparation of compound 13a



Scheme S9

After stirring a mixture of compound **7a** (180 mg, 0.5 mmol) and $\text{HB}(\text{C}_6\text{F}_5)_2$ (173 mg, 0.5 mmol) in pentane (3 mL) at room temperature for 1 h, the resulting red suspension was filtered to give a clear red solution. Then one equiv. of *N*-sulfinylaniline (70 mg, 0.5 mmol) was added and after the clear red solution was stirred for 10 min. a white precipitate was formed. The resulting suspension was filtered. The collected solid was washed twice with pentane (2×5 mL) and dried in vacuo to give a white solid. Yield: 329 mg, 78 %.

Elemental analysis: calc. for $\text{C}_{42}\text{H}_{45}\text{PBONSF}_{10}$ (843.7 g mol⁻¹): C, 59.79; H, 5.38; N, 1.66. Found: C, 59.72; H, 5.33; N, 1.90.

Decomposition temperature: 130 °C.

[Mes*: 2,4,6-tri-tert-butylphenyl]

¹H NMR (600 MHz, 299 K, C_6D_6 , 7.15 ppm): δ = 7.50 (d, $^4J_{\text{HH}} = 2.1$ Hz), 7.45 (dd, $^4J_{\text{PH}} = 5.6$ Hz, $^4J_{\text{HH}} = 2.1$ Hz)(each 1H, *m*-Mes*), 6.83 (m, 2H, *m*-Ph), 6.74 (m, 1H, *p*-Ph), 6.51 (m, 2H, *o*-Ph), 6.16 (d, $^3J_{\text{PH}} = 27.0$ Hz, 1H, =CH), 5.78 (s, 1H, NH), 1.58, 1.43 (each s, each 9H, *o*-C(CH₃)₃-Mes*), 1.17 (s, 9H, *p*-C(CH₃)₃-Mes*), 0.61 (s, 9H, C(CH₃)₃).

¹³C{¹H} NMR (151 MHz, 299 K, C_6D_6 , 128.0 ppm): δ = 164.2 (d, $^2J_{\text{PC}} = 39.0$ Hz), 160.5 (d, $^2J_{\text{PC}} = 5.8$ Hz)(*o*-Mes*), 154.9 (d, $^4J_{\text{PC}} = 2.3$ Hz, *p*-Mes*), 154.2 (d, $^2J_{\text{PC}} = 10.2$ Hz, =CH), 139.8 (d, $^1J_{\text{PC}} = 60.3$ Hz, BC=), 139.6 (d, $^3J_{\text{PC}} = 7.0$ Hz, *i*-Ph), 129.9 (*m*-Ph), 127.4 (d, $^3J_{\text{PC}} = 1.8$ Hz), 123.5 (d, $^3J_{\text{PC}} = 14.4$ Hz)(*m*-Mes*), 127.4 (d, $^1J_{\text{PC}} = 67.5$ Hz, *i*-Mes*), 125.7 (*p*-Ph), 118.9 (*o*-Ph), 40.5 (d, $^2J_{\text{PC}} = 1.1$ Hz), 39.2 (d, $^2J_{\text{PC}} = 8.0$ Hz)(*o*-C(CH₃)₃-Mes*), 36.4 (C(CH₃)₃), 35.0 (*p*-C(CH₃)₃-Mes*), 34.3 (d, $^3J_{\text{PC}} = 11.1$ Hz), 33.8 (*o*-C(CH₃)₃-Mes*), 30.8 (*p*-C(CH₃)₃-Mes*), 28.9 (d, $^4J_{\text{PC}} = 4.4$ Hz, C(CH₃)₃), [C₆F₅ not listed].

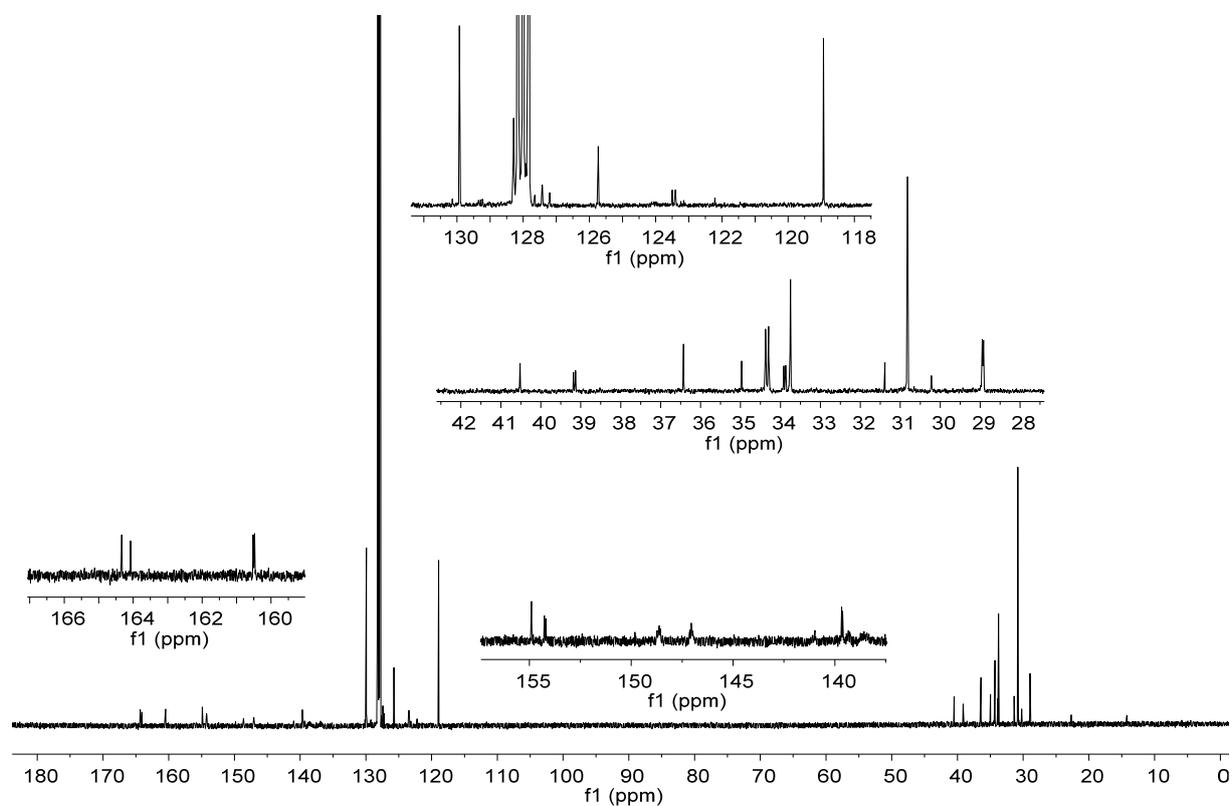
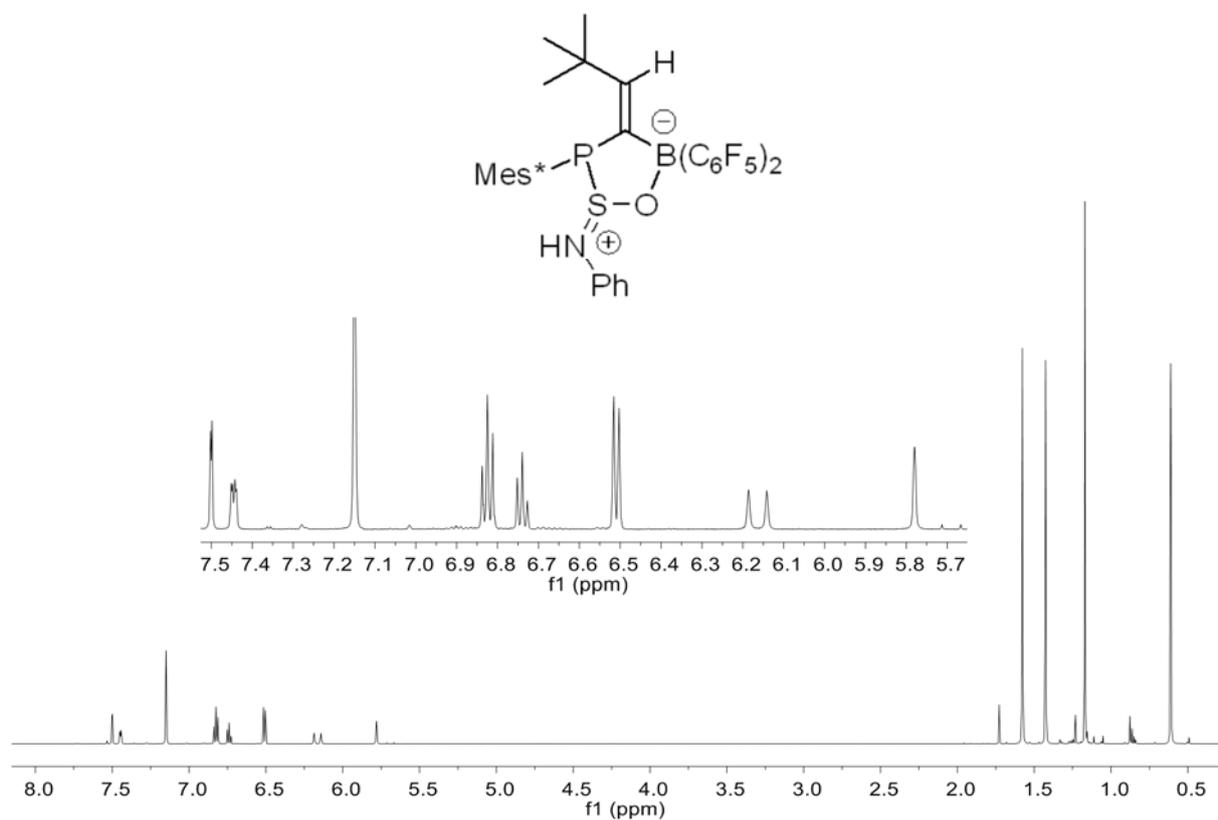
³¹P{¹H, ¹⁹F} NMR (243 MHz, 299 K, C_6D_6): δ = 116.9 ($\nu_{1/2} \sim 7$ Hz).

³¹P{¹H} NMR (243 MHz, 299 K, C_6D_6): δ = 116.9 (t, $J_{\text{PF}} = 24.0$ Hz).

³¹P NMR (243 MHz, 299 K, C_6D_6): δ = 116.9 (br q, $^3J_{\text{PH}} \sim J_{\text{PF}} = 24.0$ Hz).

¹¹B{¹H} NMR (192 MHz, 299 K, C_6D_6): δ = 9.3 ($\nu_{1/2} \sim 300$ Hz).

¹⁹F NMR (564 MHz, 299 K, C_6D_6): δ = -131.8, -131.9 (each m, each 2F, *o*), -156.7, -157.6 (each t, $^3J_{\text{FF}} = 21.0$ Hz, each 1F, *p*), -163.1, -163.9 (each m, each 2F, *m*)(C₆F₅).



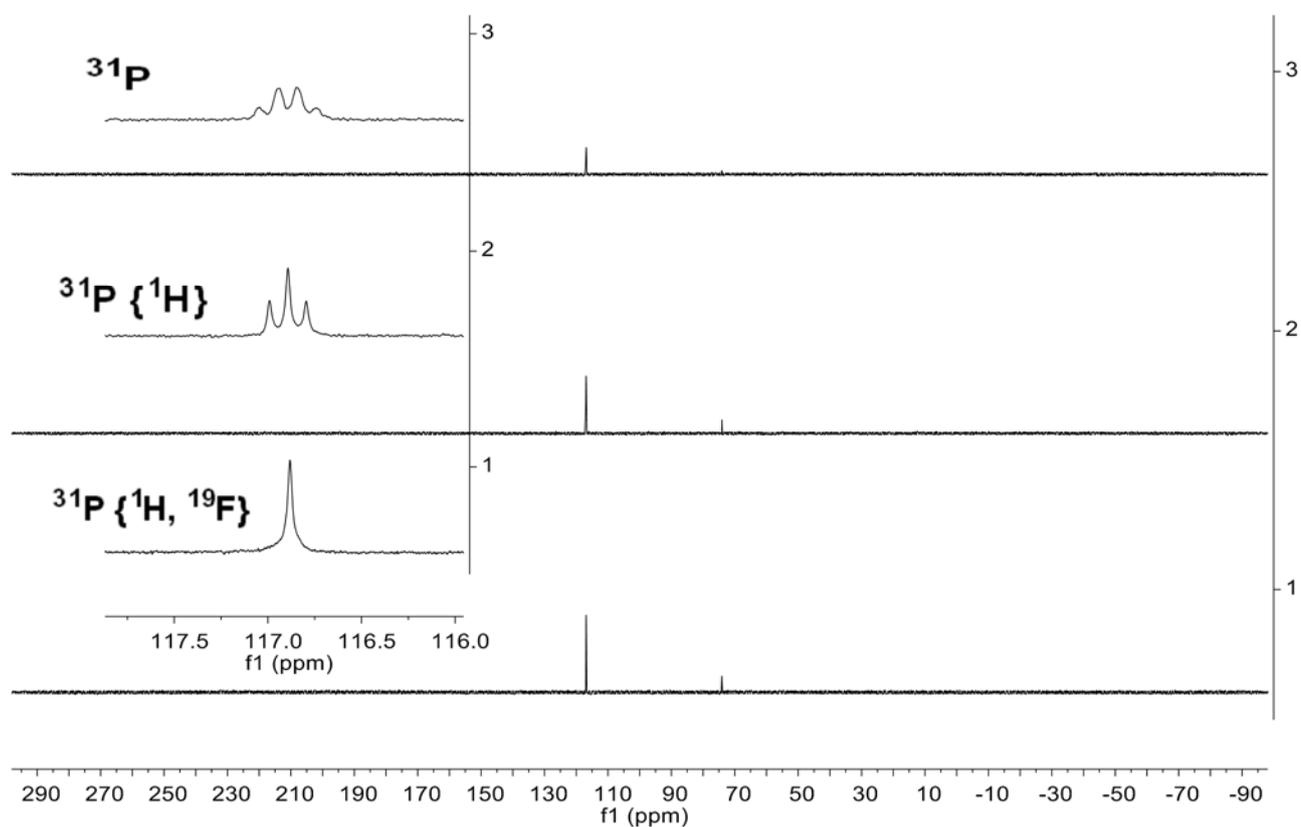


Figure S41. Coupling and decoupling ^{31}P NMR (243 MHz, 299 K, C_6D_6) spectra of compound **13a**.

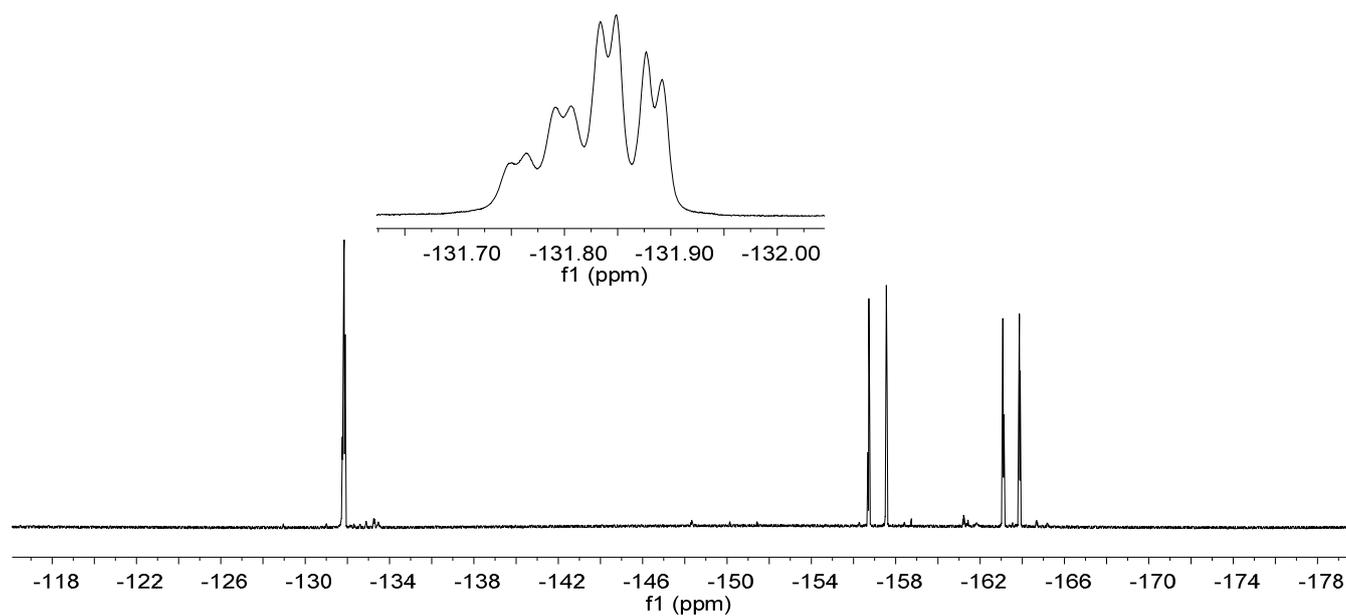


Figure S42. ^{19}F NMR (564 MHz, 299 K, C_6D_6) spectrum of compound **13a**.

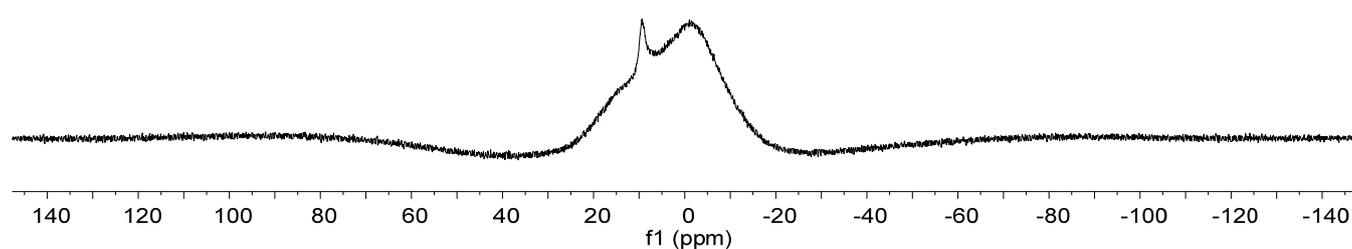
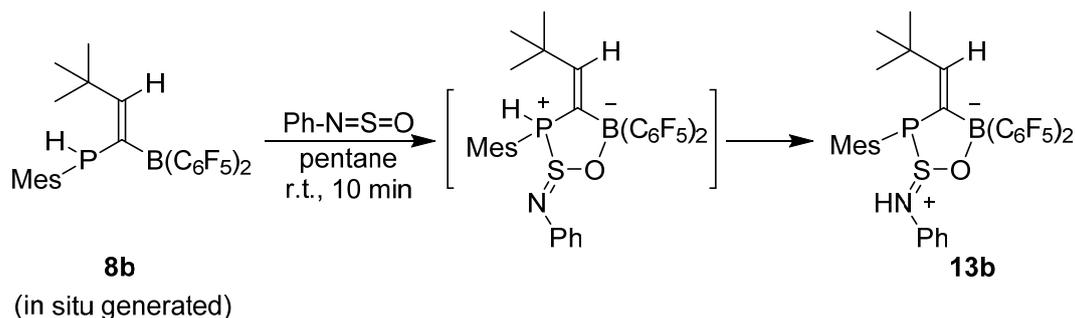


Figure S43. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, C_6D_6) spectrum of compound **13a**.

b) Preparation of compound 13b



Scheme S10

After stirring a mixture of compound **7b** (116 mg, 0.5 mmol) and $\text{HB}(\text{C}_6\text{F}_5)_2$ (173 mg, 0.5 mmol) in pentane (3 mL) at room temperature for 10 h, the resulting yellow suspension was filtered to give a clear yellow solution. Then one equiv. of *N*-sulfanylaniiline (70 mg, 0.5 mmol) was added and after the clear yellow solution was stirred for 10 min. a white precipitate was formed. The resulting suspension was filtered. The collected solid was washed twice with pentane (2×5 mL) and dried in vacuo to give a white solid. Yield: 312 mg, 87 %.

Elemental analysis: calc. for $\text{C}_{33}\text{H}_{27}\text{PBONSF}_{10}$ (717.4 g mol⁻¹): C, 55.25; H, 3.79; N, 1.95. Found: C, 55.17; H, 3.71; N, 1.96.

Melting point: 175 °C.

[Mes: 2,4,6-trimethylphenyl]

¹H NMR (600 MHz, 299 K, C_6D_6 , 7.15 ppm): δ = 6.77 (m, 2H, *m*-Ph), 6.70 (m, 1H, *p*-Ph), 6.64 (d, ⁴ J_{PH} = 2.0 Hz, 2H, *m*-Mes), 6.32 (m, 2H, *o*-Ph), 6.25 (d, ³ J_{PH} = 28.5 Hz, 1H, =CH), 5.65 (s, 1H, NH), 2.58 (s, 6H, *o*-CH₃-Mes), 1.91 (s, 3H, *p*-CH₃-Mes), 0.90 (s, 9H, C(CH₃)₃).

¹³C{¹H} NMR (151 MHz, 299 K, C_6D_6 , 128.0 ppm): δ = 154.1 (d, ² J_{PC} = 9.5 Hz, =CH), 145.8 (br), 145.7 (*o*-Mes), 143.3 (*p*-Mes), 139.2 (d, ³ J_{PC} = 8.5 Hz, *i*-Ph), 138.0 (d, ¹ J_{PC} = 59.1 Hz, BC=), 131.0 (br, *m*-Mes), 129.7 (*m*-Ph), 125.8 (*p*-Ph), 125.3 (d, ¹ J_{PC} = 34.7 Hz, *i*-Mes), 119.0 (*o*-Ph), 35.5 (C(CH₃)₃), 29.3 (d, ⁴ J_{PC} = 4.4 Hz, C(CH₃)₃), 23.7, 23.6 (each br, *o*-CH₃-Mes), 21.0 (*p*-CH₃-Mes), [C₆F₅ not listed].

³¹P{¹H, ¹⁹F} NMR (243 MHz, 299 K, CD_2Cl_2): δ = 95.7 ($\nu_{1/2}$ ~ 10 Hz).

³¹P{¹⁹F} NMR (243 MHz, 299 K, CD_2Cl_2): δ = 95.7 (d, ³ J_{PH} = 28.5 Hz).

³¹P{¹H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = 95.7 (t, J_{PF} = 18.4 Hz).

³¹P NMR (243 MHz, 299 K, CD_2Cl_2): δ = 95.7 (m).

¹¹B{¹H} NMR (192 MHz, 299 K, C_6D_6): δ = 10.0 ($\nu_{1/2}$ ~ 300 Hz).

¹⁹F NMR (564 MHz, 299 K, C_6D_6): δ = -131.1 (m, 2F, *o*), -157.3 (t, ³ J_{FF} = 21.2 Hz, 1F, *p*), -163.3 (m, 2F, *m*)(C₆F₅)[$\Delta\delta^{19}\text{F}_{m,p}$ = 6.0], -133.4 (m, 2F, *o*), -156.8 (t, ³ J_{FF} = 21.2 Hz, 1F, *p*), -163.6 (m, 2F, *m*)(C₆F₅)[$\Delta\delta^{19}\text{F}_{m,p}$ = 6.8].

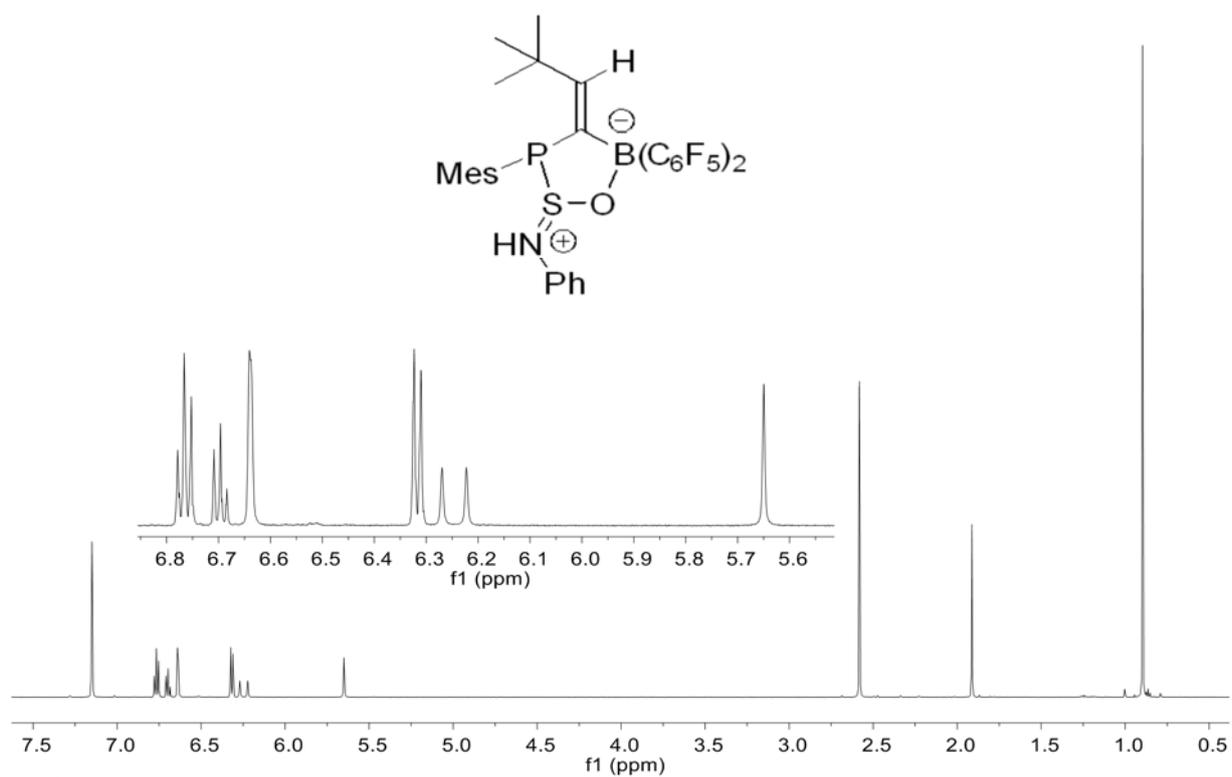


Figure S44. ¹H NMR (600 MHz, 299 K, C₆D₆) spectrum of compound 13b.

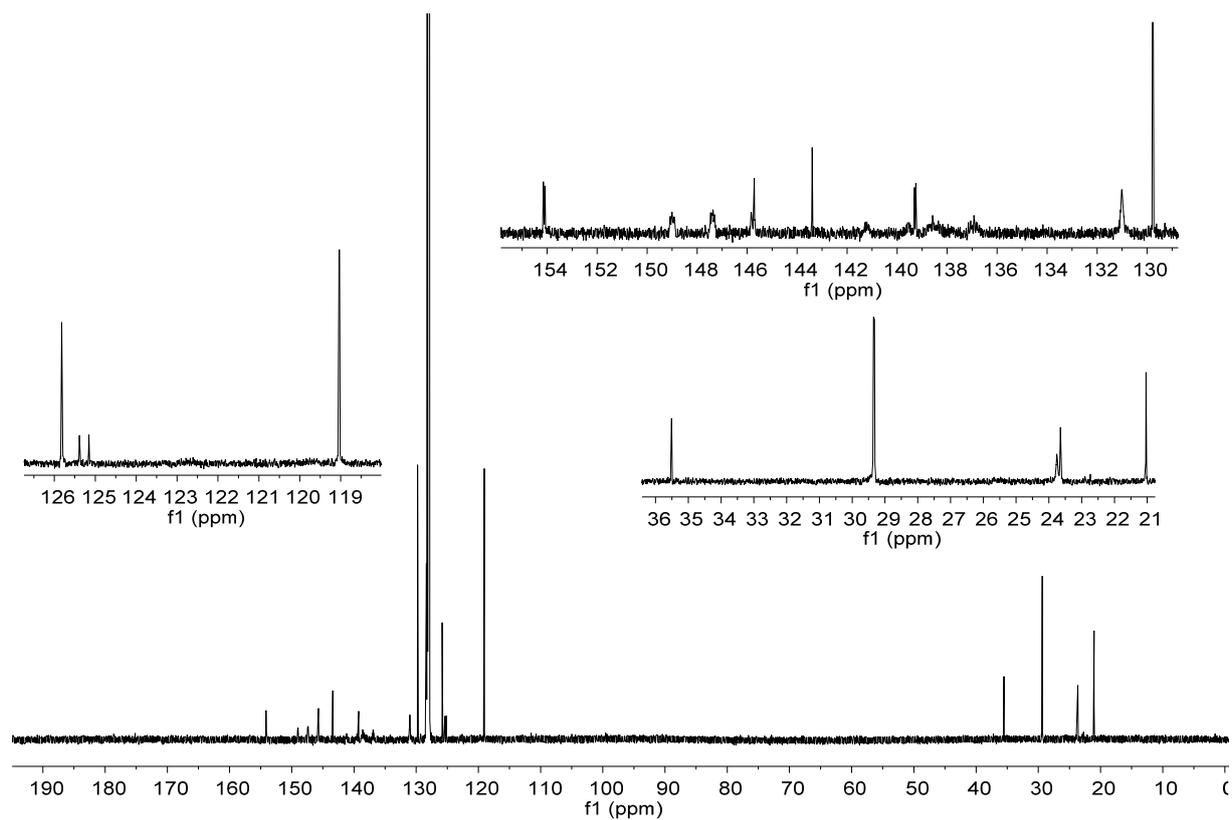


Figure S45. ¹³C{¹H} NMR (151 MHz, 299 K, C₆D₆) spectrum of compound 13b.

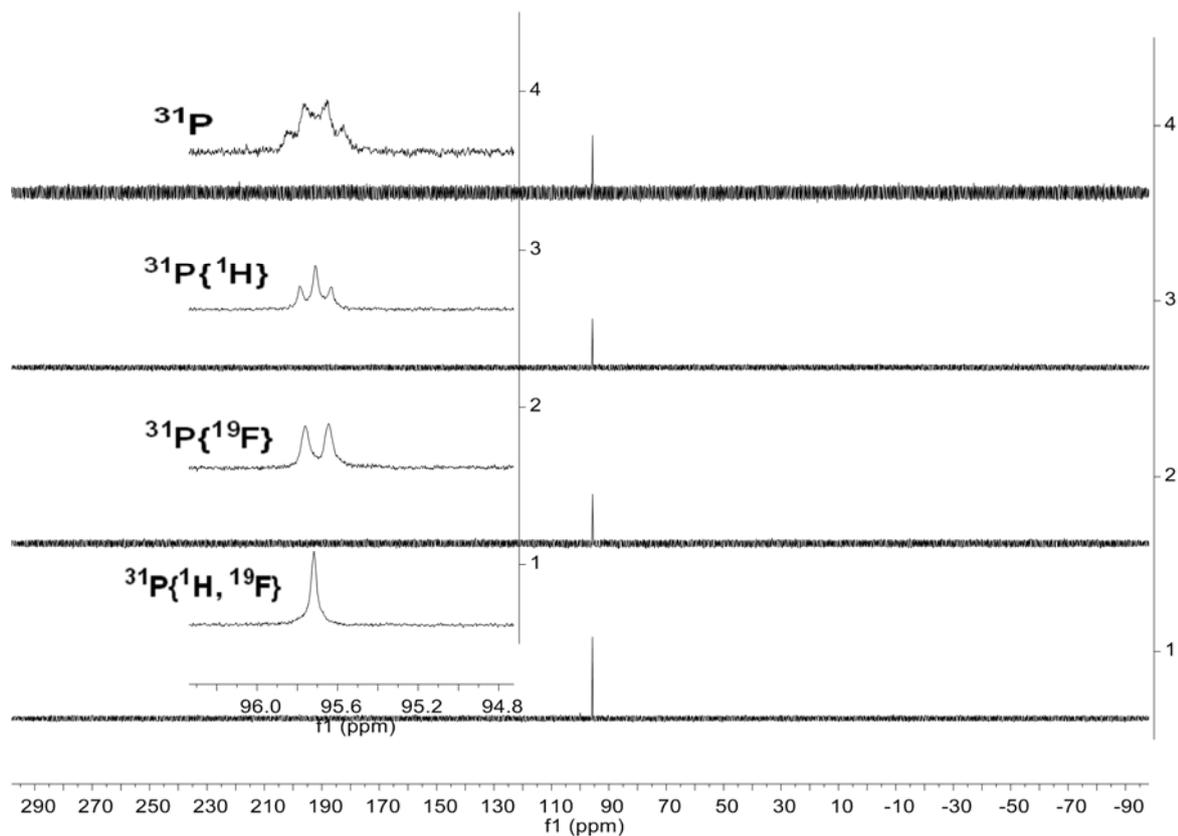


Figure S46. Coupled and decoupled ^{31}P NMR (243 MHz, 299 K, C_6D_6) spectra of compound **13b**.

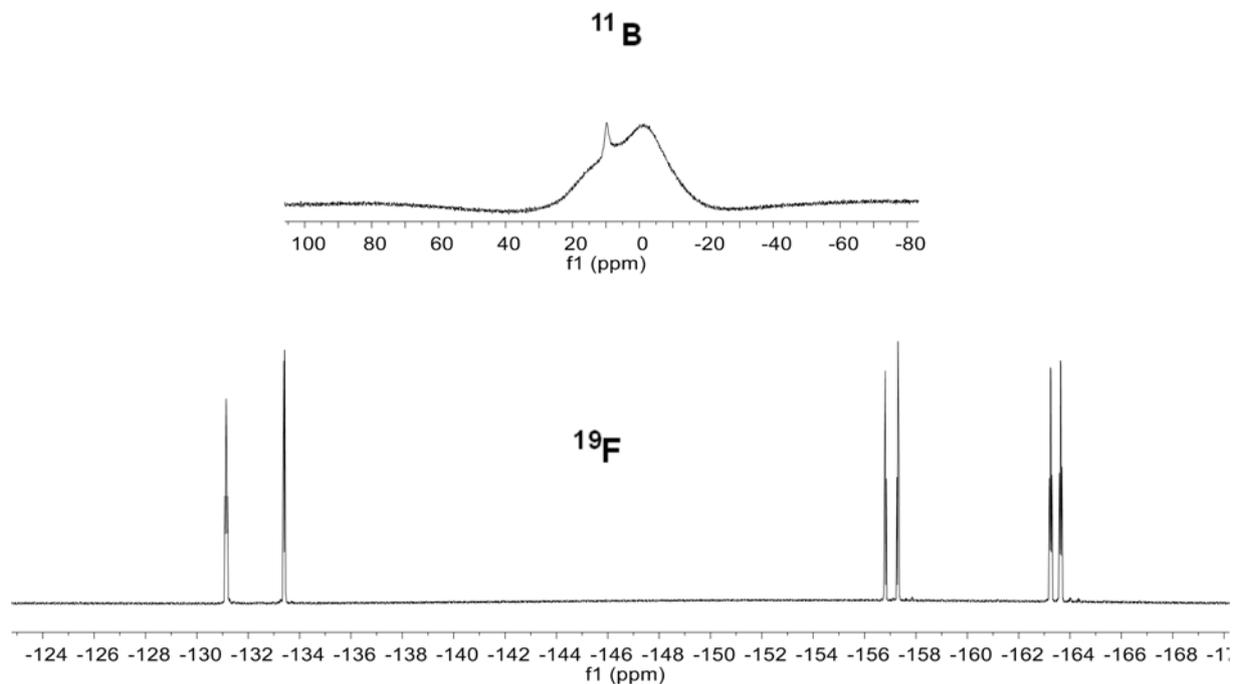


Figure S47. ^{19}F (564 MHz, 299 K, C_6D_6) and $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, C_6D_6) spectra of compound **13b**.

Crystals of compound **13b** suitable for the X-ray crystal structure analysis were obtained from a solution of the white solid in toluene and pentane (ratio ca. 1 : 5) at $-35\text{ }^{\circ}\text{C}$.

X-ray crystal structure analysis of compound 13b: A colorless plate-like specimen of $\text{C}_{33}\text{H}_{27}\text{BF}_{10}\text{NOPS}$, approximate dimensions $0.050\text{ mm} \times 0.160\text{ mm} \times 0.180\text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 2074 frames were collected. The total exposure time was 22.89 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 55525 reflections to a maximum θ angle of 68.19° (0.83 \AA resolution), of which 5799 were independent (average redundancy 9.575, completeness = 98.4%, $R_{\text{int}} = 6.26\%$, $R_{\text{sig}} = 3.39\%$) and 5030 (86.74%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 16.5186(4)\text{ \AA}$, $b = 11.2948(3)\text{ \AA}$, $c = 17.6854(5)\text{ \AA}$, $\beta = 102.2340(10)^{\circ}$, volume = $3224.71(15)\text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9908 reflections above $20\sigma(I)$ with $9.353^{\circ} < 2\theta < 135.3^{\circ}$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.850. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6980 and 0.9000. The final anisotropic full-matrix least-squares refinement on F^2 with 474 variables converged at $R1 = 7.46\%$, for the observed data and $wR2 = 16.34\%$ for all data. The goodness-of-fit was 1.179. The largest peak in the final difference electron density synthesis was $0.690\text{ e}^{-}/\text{\AA}^3$ and the largest hole was $-0.622\text{ e}^{-}/\text{\AA}^3$ with an RMS deviation of $0.090\text{ e}^{-}/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.478 g/cm^3 and $F(000)$, 1464 e^{-} .

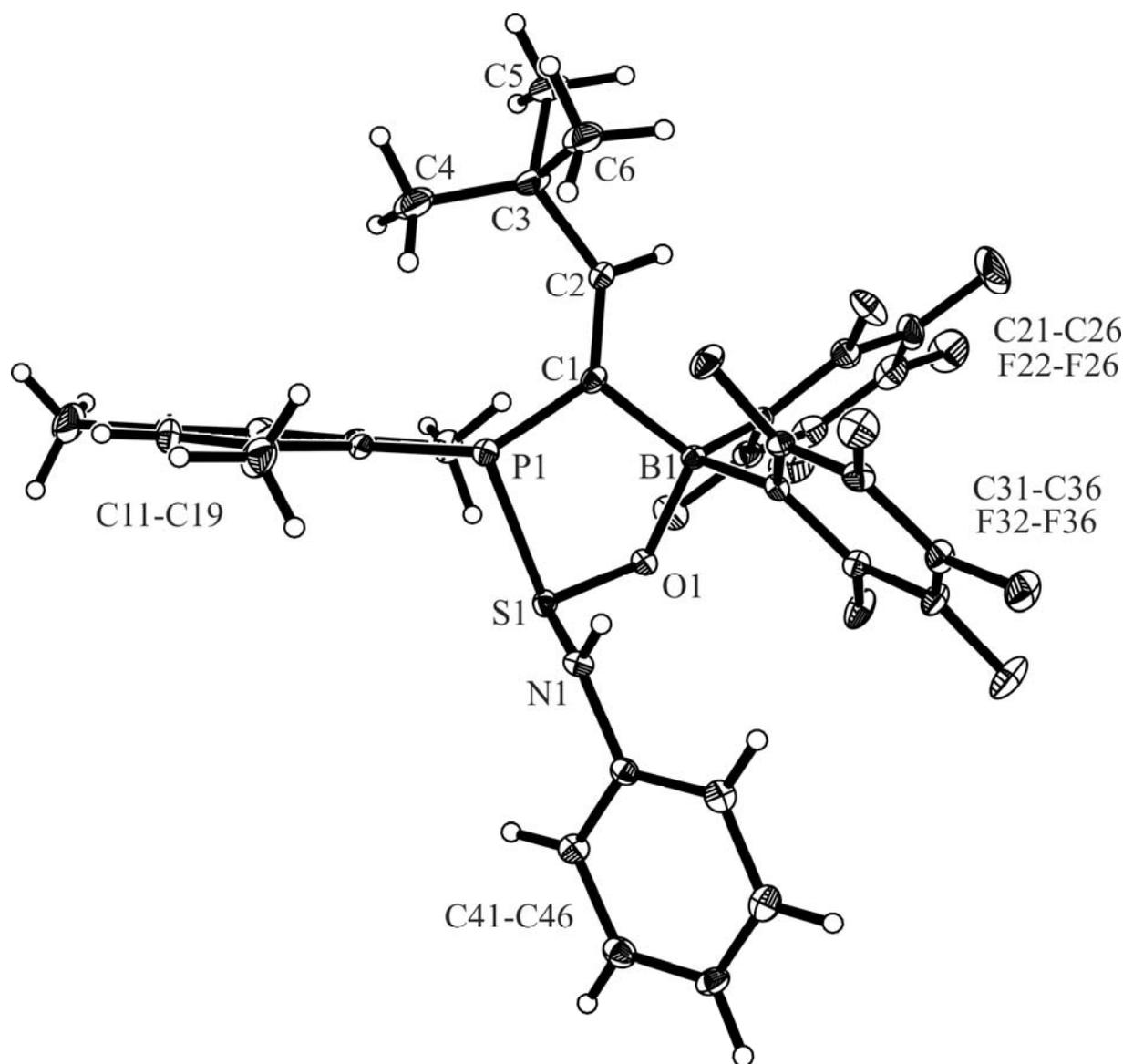
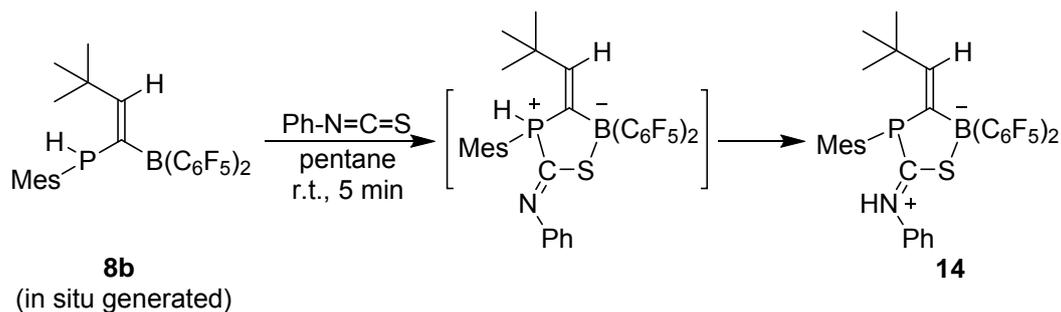


Figure S48. A view of the molecular structure of compound **13b**.

Preparation of compound 14



Scheme S11

After stirring a mixture of compound **7b** (116 mg, 0.5 mmol) and $\text{HB}(\text{C}_6\text{F}_5)_2$ (173 mg, 0.5 mmol) in pentane (3 mL) at room temperature for 10 h, the resulting yellow suspension was filtered to give a clear yellow solution. Then one equiv. of phenyl isothiocyanate (68 mg, 0.5 mmol) was added and after the clear yellow solution was stirred for 5 min. a white precipitate was formed. The resulting suspension was filtered. The collected solid was washed twice with pentane (2×5 mL) and dried in vacuo to give a white solid. Yield: 292 mg, 82 %.

Elemental analysis: calc. for $\text{C}_{34}\text{H}_{27}\text{PBNSF}_{10}$ (713.4 g mol⁻¹): C, 57.24; H, 3.81; N, 1.96. Found: C, 56.93; H, 3.46; N, 2.15.

Decomposed temperature: 175 °C.

[Mes: 2,4,6-trimethylphenyl]

¹H NMR (600 MHz, 273 K, CD_2Cl_2 , 5.32 ppm): δ = 8.20 (s, 1H, NH), 7.44 (m, 2H, *m*-Ph), 7.36 (m, 1H, *p*-Ph), 7.26 (m, 2H, *o*-Ph), 7.06 (m, 2H, *m*-Mes), 5.71 (d, ³*J*_{PH} = 34.0 Hz, 1H, =CH), 2.77, 2.37 (each br, each 3H, *o*-CH₃-Mes), 2.32 (s, 3H, *p*-CH₃-Mes), 0.78 (s, 9H, C(CH₃)₃).

¹³C{¹H} NMR (151 MHz, 273 K, CD_2Cl_2 , 53.8 ppm): δ = 216.5 (d, ¹*J*_{PC} = 29.6 Hz, C=NH), 152.0 (d, ²*J*_{PC} = 7.0 Hz, =CH), 147.2 (br d, ²*J*_{PC} = 34.2 Hz), 145.0 (br)(*o*-Mes), 143.5 (d, ⁴*J*_{PC} = 1.7 Hz, *p*-Mes), 137.7 (*i*-Ph), 136.3 (br d, ¹*J*_{PC} = 28.2 Hz, BC=), 131.3 (br), 130.2 (br d, ³*J*_{PC} = 8.2 Hz)(*m*-Mes), 129.9 (*m*-Ph), 129.4 (d, ¹*J*_{PC} = 21.2 Hz, *i*-Mes), 129.0 (*p*-Ph), 124.0 (d, ⁴*J*_{PC} = 2.4 Hz, *o*-Ph), 35.1 (d, ³*J*_{PC} = 1.5 Hz, C(CH₃)₃), 29.4 (d, ⁴*J*_{PC} = 2.1 Hz, C(CH₃)₃), 24.0 (br d, ³*J*_{PC} = 27.4 Hz), 22.6 (br)(*o*-CH₃-Mes), 21.3 (*p*-CH₃-Mes), [C₆F₅ not listed].

³¹P{¹H, ¹⁹F} NMR (243 MHz, 299 K, CD_2Cl_2): δ = 21.3 (*v*_{1/2} ~ 13 Hz).

³¹P{¹⁹F} NMR (243 MHz, 299 K, CD_2Cl_2): δ = 21.3 (d, ³*J*_{PH} = 34.2 Hz).

³¹P{¹H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = 21.3 (quint, *J*_{PF} = 17.4 Hz).

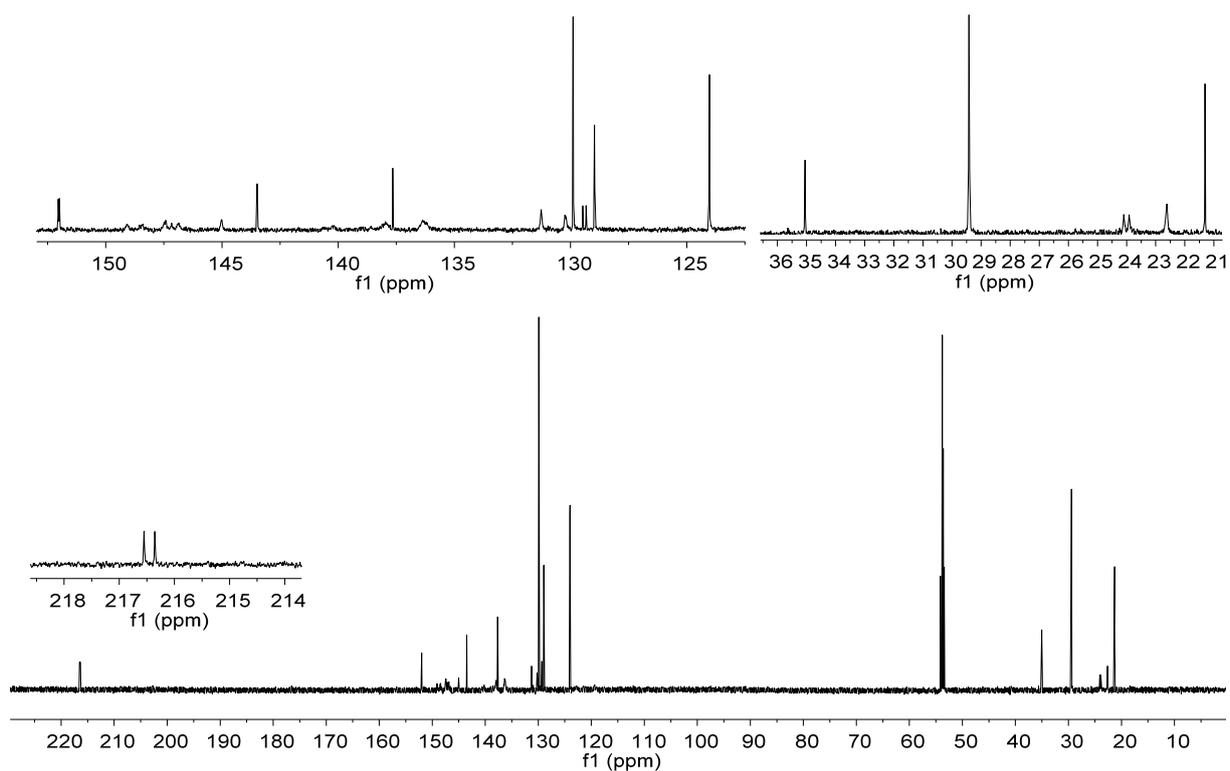
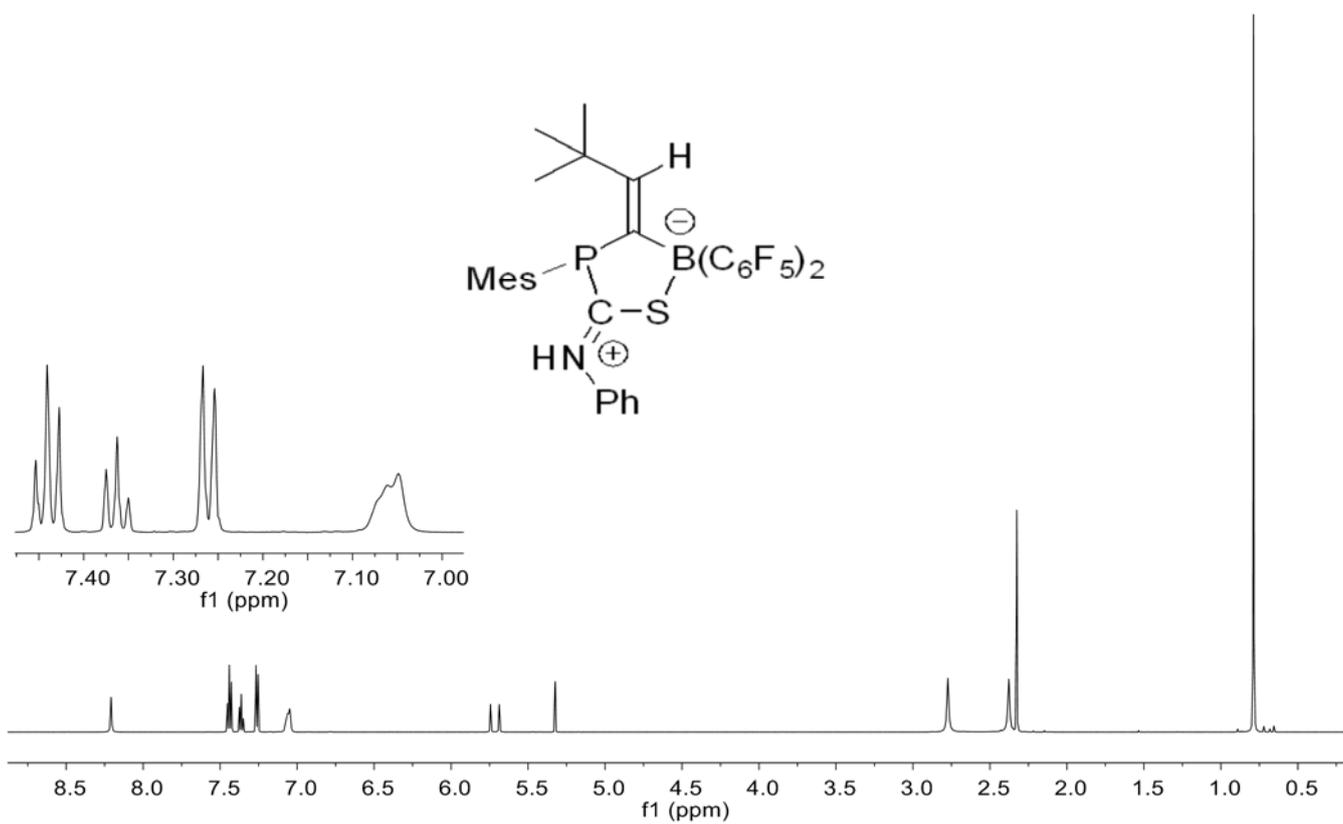
³¹P NMR (243 MHz, 299 K, CD_2Cl_2): δ = 21.3 (d quint, ³*J*_{PH} = 34.2 Hz, *J*_{PF} = 17.4 Hz).

³¹P{¹H} NMR (243 MHz, 273 K, CD_2Cl_2): δ = 20.7 (m).

³¹P NMR (243 MHz, 273 K, CD_2Cl_2): δ = 20.7 (m).

¹¹B{¹H} NMR (192 MHz, 273 K, CD_2Cl_2): δ = -4.2 (*v*_{1/2} ~ 400 Hz).

¹⁹F NMR (564 MHz, 273 K, CD_2Cl_2): δ = -130.9 (m, 2F, *o*), -158.6 (t, ³*J*_{FF} = 20.6 Hz, 1F, *p*), -164.9 (m, 2F, *m*)(C₆F₅)[$\Delta\delta^{19}\text{F}_{m,p}$ = 6.3], -131.8 (m, 2F, *o*), -160.3 (t, ³*J*_{FF} = 20.6 Hz, 1F, *p*), -165.3 (m, 2F, *m*)(C₆F₅)[$\Delta\delta^{19}\text{F}_{m,p}$ = 5.0].



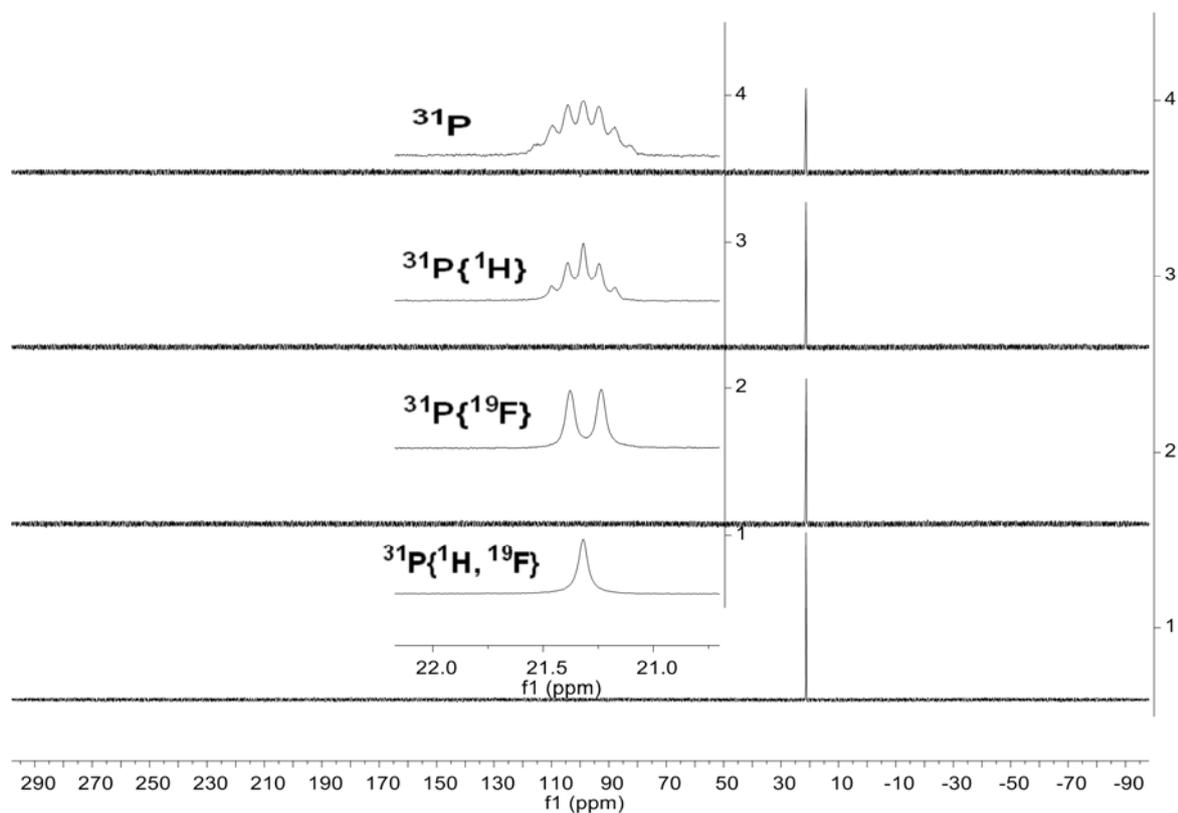


Figure S51. Coupled and decoupled ^{31}P NMR (243 MHz, 299 K, CD_2Cl_2) spectra of compound 14.

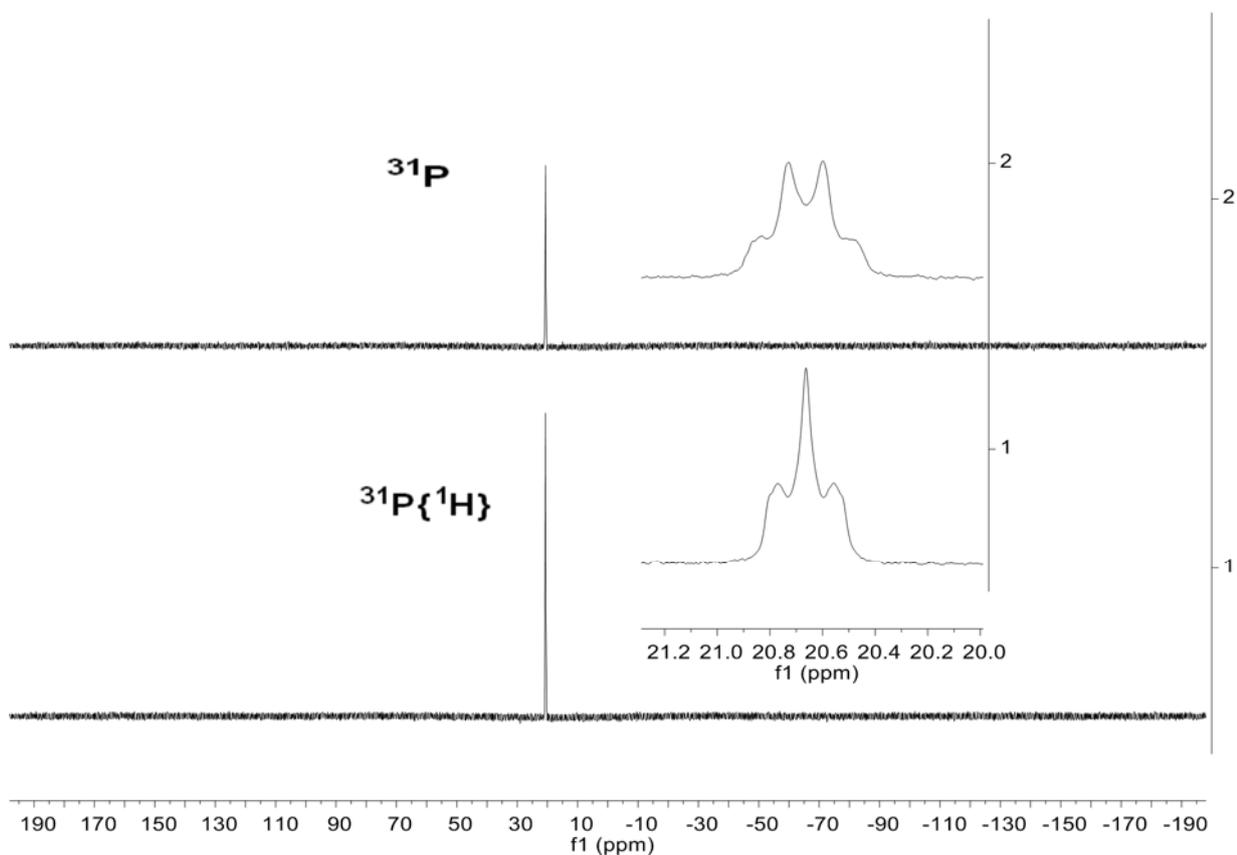


Figure S52. Coupled and decoupled ^{31}P NMR (243 MHz, 273 K, CD_2Cl_2) spectra of compound 14.

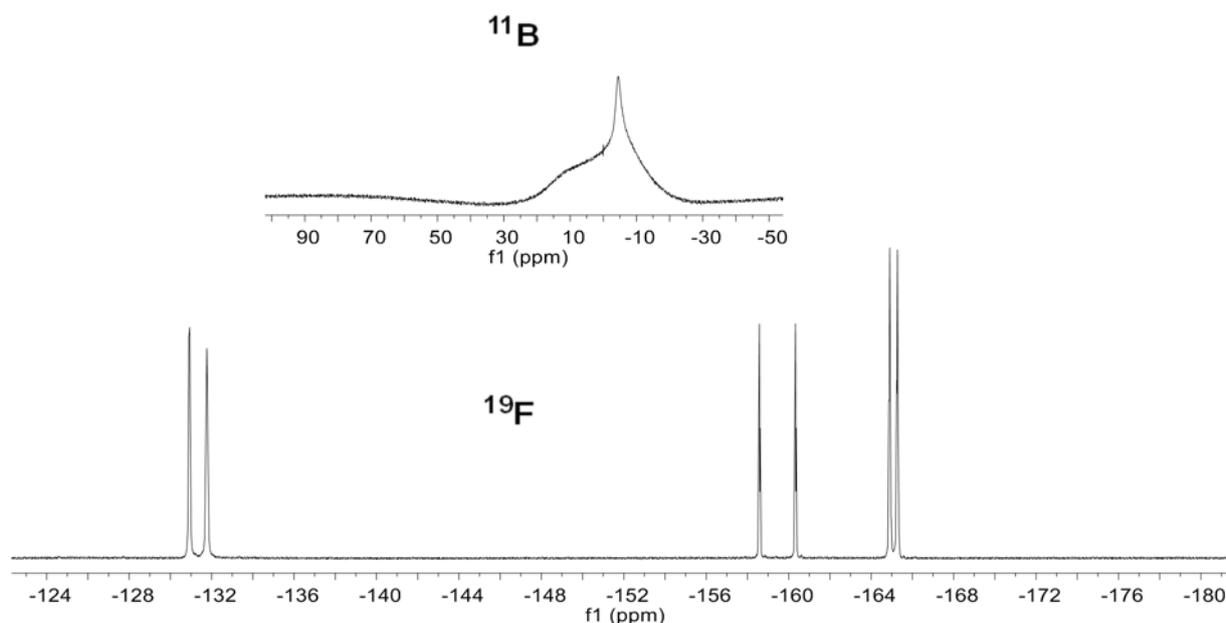


Figure S53. ^{19}F (564 MHz, 273 K, CD_2Cl_2) and $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 273 K, CD_2Cl_2) spectra of compound **14**.

Crystals of compound **14** suitable for the X-ray crystal structure analysis were obtained from a solution of the white solid in benzene and pentane (ratio ca. 1 : 10) at room temperature.

X-ray crystal structure analysis of compound 14: A specimen of $\text{C}_{34}\text{H}_{27}\text{BF}_{10}\text{NPS} \cdot \frac{1}{2} \times \text{CH}_2\text{Cl}_2$, approximate dimensions 0.091 mm x 0.113 mm x 0.454 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a monoclinic unit cell yielded a total of 149315 reflections to a maximum θ angle of 24.71° (0.85 Å resolution), of which 11370 were independent (average redundancy 13.132, completeness = 99.9%, $R_{\text{int}} = 13.01\%$, $R_{\text{sig}} = 5.66\%$) and 8661 (76.17%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a} = 25.031(2)$ Å, $\underline{b} = 12.0655(13)$ Å, $\underline{c} = 24.693(2)$ Å, $\beta = 116.480(2)^\circ$, volume = $6675.2(12)$ Å³, are based upon the refinement of the XYZ-centroids of reflections above $20\sigma(I)$. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8730 and 0.9720. The final anisotropic full-matrix least-squares refinement on F^2 with 918 variables converged at $R1 = 7.32\%$, for the observed data and $wR2 = 18.37\%$ for all data. The goodness-of-fit was 1.090. The largest peak in the final difference electron density synthesis was $0.528 \text{ e}/\text{Å}^3$ and the largest hole was $-1.747 \text{ e}/\text{Å}^3$ with an RMS deviation of $0.106 \text{ e}/\text{Å}^3$. On the basis of the final model, the calculated density was $1.504 \text{ g}/\text{cm}^3$ and $F(000)$, 3080 e⁻.

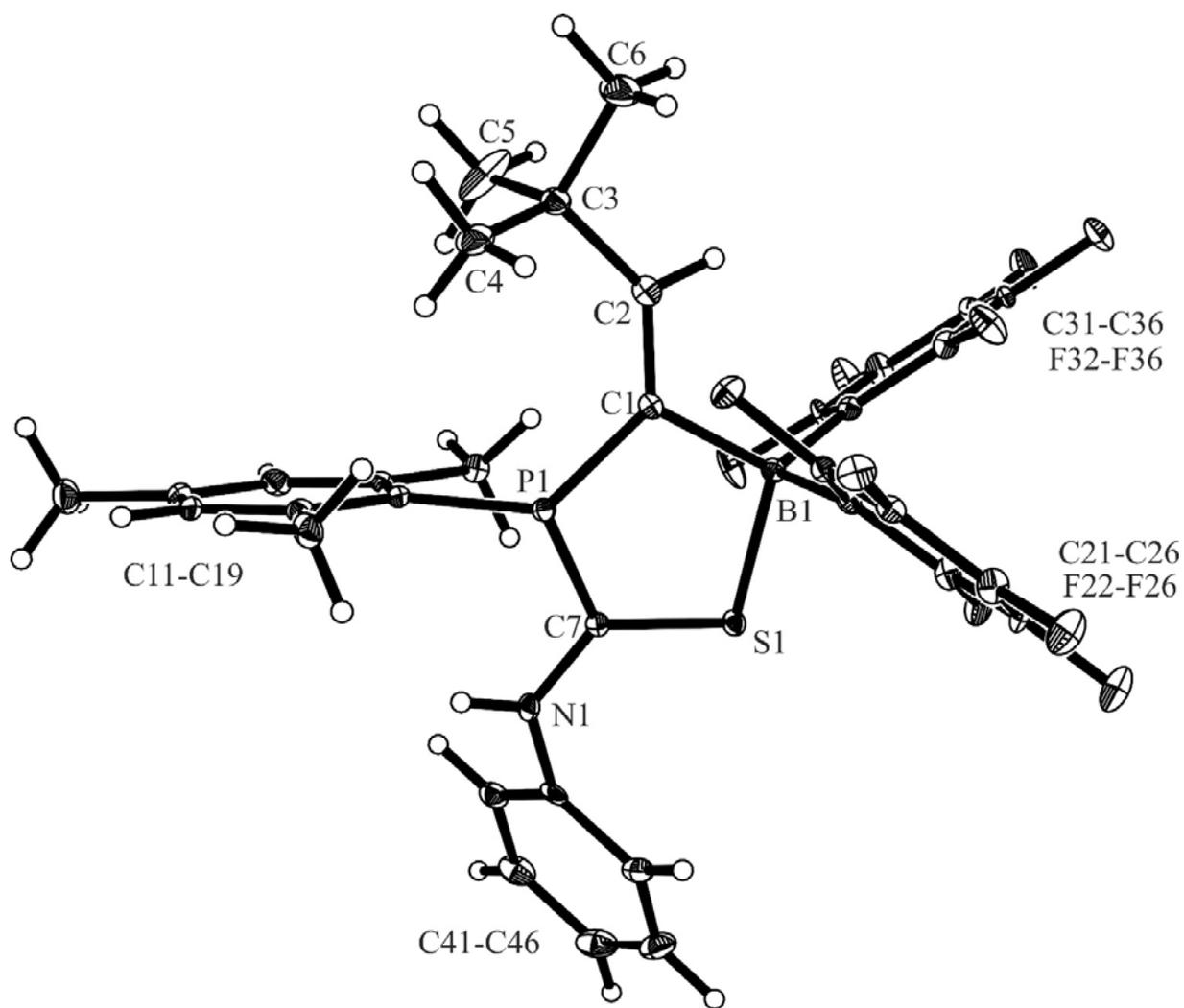
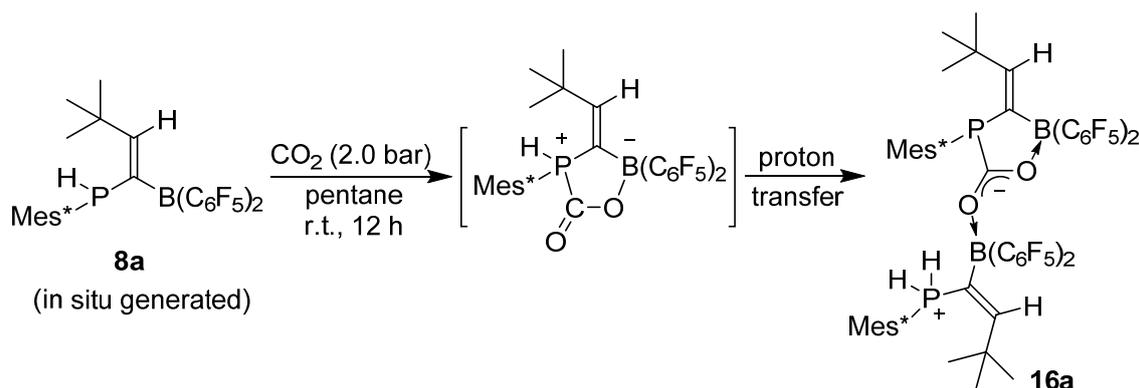


Figure S54. A view of the molecular structure of compound 14.

Preparation of compounds 16a and 16b and 17

a) Preparation of compound 16a



Scheme S12

After stirring a mixture of compound **7a** (180 mg, 0.5 mmol) and $\text{HB}(\text{C}_6\text{F}_5)_2$ (173 mg, 0.5 mmol) in pentane (3 mL) at room temperature for 1 h, the resulting red suspension was filtered to give a clear red solution which was exposed to CO_2 gas (2.0 bar). After the reaction mixture was stirred at room temperature for 12 h a white precipitate was formed. The resulting suspension was filtered. The collected solid was washed twice with pentane (2×5 mL) and dried in vacuo to give a white solid. Yield: 218 mg, 60 %.

Elemental analysis: calc. for $\text{C}_{73}\text{H}_{80}\text{P}_2\text{B}_2\text{O}_2\text{F}_{20}$ (1453.0 g mol⁻¹): C, 60.35; H, 5.55. Found: C, 60.28; H, 5.48.

Decomposition temperature: 195 °C.

[Mes*: 2,4,6-tri-tert-butylphenyl]

¹H NMR (500 MHz, 299 K, CD_2Cl_2 , 5.32 ppm): δ = 7.60 (br d, $^4J_{\text{PH}} = 2.5$ Hz), 7.57 (d, $^4J_{\text{PH}} = 4.8$ Hz)(each 2H, *m*-Mes*), 7.43 (br d, $^1J_{\text{PH}} = 491.0$ Hz, 2H, PH_2), 6.71 (d, $^3J_{\text{PH}} = 74.0$ Hz), 5.48 (d, $^3J_{\text{PH}} = 40.0$ Hz)(each 1H, =CH), 1.55 (br), 1.15 (s)(each 18H, *o*- $\text{C}(\text{CH}_3)_3$ -Mes*), 1.32, 1.28 (each s, each 9H, *p*- $\text{C}(\text{CH}_3)_3$ -Mes*), 0.58, 0.54 (each s, each 9H, $\text{C}(\text{CH}_3)_3$).

¹H NMR (600 MHz, 233 K, CD_2Cl_2 , 5.32 ppm): δ = 7.64 (s, 1H), 7.48 (s, 2H), 7.38 (d, $^4J_{\text{PH}} = 5.8$ Hz, 1H)(*m*-Mes*), 7.61 (dd, $^1J_{\text{PH}} = 504.8$ Hz, $J = 5.8$ Hz), 7.10 (dd, $^1J_{\text{PH}} = 477.9$ Hz, $J = 5.8$ Hz)(each 1H, PH_2), 6.61 (dd, $^3J_{\text{PH}} = 72.9$ Hz, $J = 3.0$ Hz), 5.38 (d, $^3J_{\text{PH}} = 39.4$ Hz)(each 1H, =CH), 1.62 (o), 1.33 (o), 1.26 (p), 1.21 (p), 1.10 (o), 1.02 (o) (each s, each 9H, $\text{C}(\text{CH}_3)_3$ -Mes*), 0.51, 0.44 (each s, each 9H, $\text{C}(\text{CH}_3)_3$).

¹³C{¹H} NMR (126 MHz, 299 K, CD_2Cl_2 , 53.8 ppm): δ = 201.0 (C=O), 165.7 (br), 147.4 (d, $^2J_{\text{PC}} = 4.1$ Hz)(=CH), 158.7 (d, $^4J_{\text{PC}} = 3.3$ Hz), 153.9 (d, $^4J_{\text{PC}} = 2.8$ Hz)(*p*-Mes*), 158.6 (br d, $^2J_{\text{PC}} = 15.5$ Hz), 157.6 (d, $^2J_{\text{PC}} = 7.3$ Hz)(*o*-Mes*), 137.6 (br d, $^1J_{\text{PC}} = 32.7$ Hz), 119.1 (br d, $^1J_{\text{PC}} = 32.5$ Hz)(BC=), 126.2 (br), 125.2 (d, $^3J_{\text{PC}} = 12.5$ Hz)(*m*-Mes*), 121.8 (d, $^1J_{\text{PC}} = 36.3$ Hz), 109.5 (d, $^1J_{\text{PC}} = 57.6$ Hz)(*i*-Mes*), 40.3 (br), 38.1 (d, $^3J_{\text{PC}} = 3.0$ Hz)(*o*- $\text{C}(\text{CH}_3)_3$ -Mes*), 38.9 (d, $^3J_{\text{PC}} = 9.0$ Hz), 36.3 (d, $^3J_{\text{PC}} = 3.9$ Hz)($\text{C}(\text{CH}_3)_3$), 36.1, 35.4 (d, $^5J_{\text{PC}} = 0.8$ Hz)(*p*- $\text{C}(\text{CH}_3)_3$ -Mes*), 34.7 (d, $^4J_{\text{PC}} = 5.4$ Hz), 33.2 (*o*- $\text{C}(\text{CH}_3)_3$ -Mes*), 31.1, 30.8 (*p*- $\text{C}(\text{CH}_3)_3$ -Mes*), 29.3 (d, $^4J_{\text{PC}} = 2.1$ Hz), 28.5 (d, $^4J_{\text{PC}} = 1.2$ Hz)($\text{C}(\text{CH}_3)_3$), [C_6F_5 not listed].

³¹P{¹H} NMR (202 MHz, 299 K, CD_2Cl_2): δ = -4.5 (m, 1P), -48.3 ($\nu_{1/2} \sim 5$ Hz, 1P).

³¹P NMR (202 MHz, 299 K, CD_2Cl_2): δ = -4.5 (br d, $^3J_{\text{PH}} \sim 40.0$ Hz, 1P), -48.3 (td, $^1J_{\text{PH}} = 491.4$ Hz, $^3J_{\text{PH}} = 73.8$ Hz, 1P).

¹¹B{¹H} NMR (160 MHz, 299 K, CD_2Cl_2): δ = 4.2, 1.8.

¹⁹F NMR (564 MHz, 233 K, CD_2Cl_2): δ = -124.0, -129.2, -129.5, -131.8, -133.0, -133.9, -134.0, -141.0 (each m, each 1F, *o*- C_6F_5), -158.5, -158.6, -159.1, -160.4 (each t, $^3J_{\text{FF}} = 21.2$ Hz, each 1F, *p*- C_6F_5), -163.6, -164.9, -165.0, -165.6, -166.0, -166.3, -166.4, -166.7 (each m, each 1F, *m*- C_6F_5).

[Comment: although both the *o*-¹⁹F resonances at -129.5 (dm, $^{\text{TS}}J_{\text{FF}} = 71.2$ Hz) and -131.8 (dm, $^{\text{TS}}J_{\text{FF}} = 71.2$ Hz) belong to different C_6F_5 substituents (supported by ¹⁹F, ¹⁹F gcosy NMR experiment), each signal showed an ABX-like pattern at 233 K (CD_2Cl_2), which could be explained by a ¹⁹F, ¹⁹F-“through-space” (TS) coupling at low temperature (see reference 17 in the manuscript)]

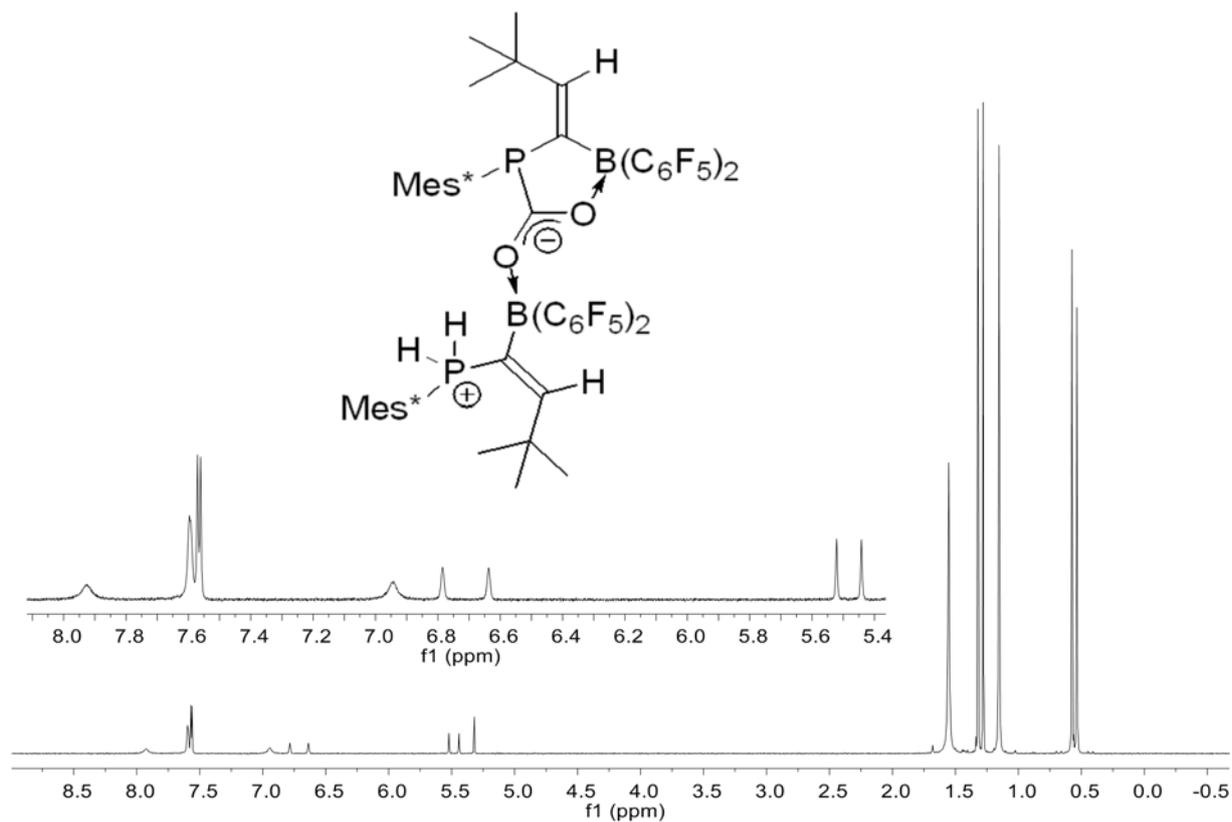


Figure S55. ¹H NMR (500 MHz, 299 K, CD₂Cl₂) spectrum of compound 16a.

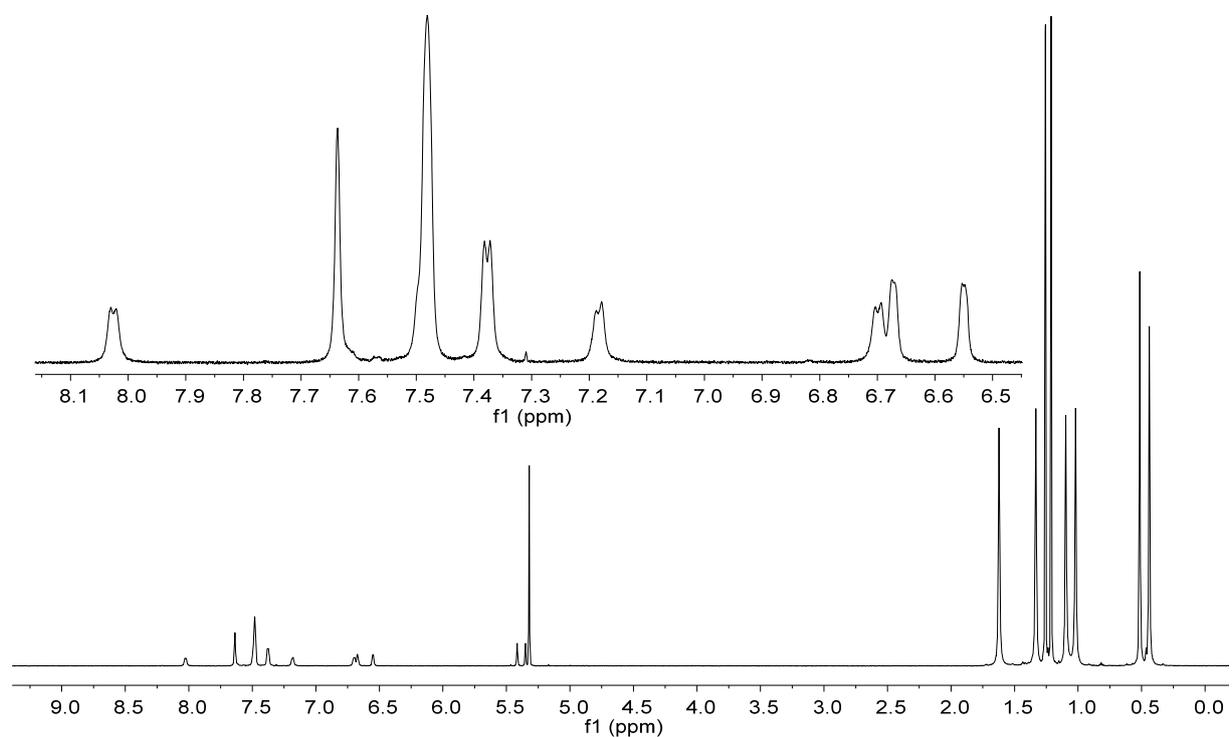


Figure S56. ¹H NMR (600 MHz, 233 K, CD₂Cl₂) spectrum of compound 16a.

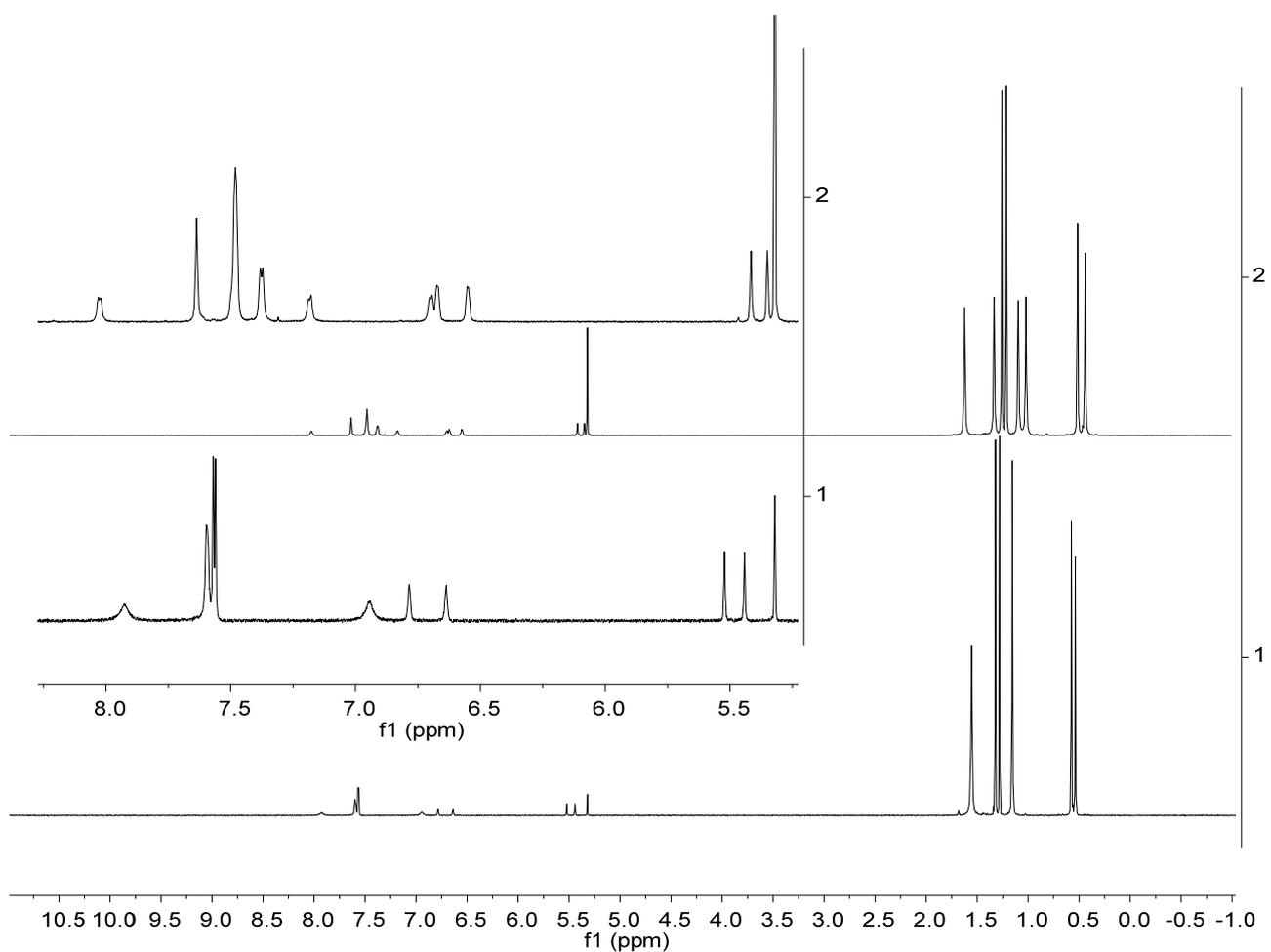


Figure S57. (1) ^1H NMR (500 MHz, 299 K, CD_2Cl_2), (2) ^1H NMR (600 MHz, 233 K, CD_2Cl_2) spectra of compound **16a**.

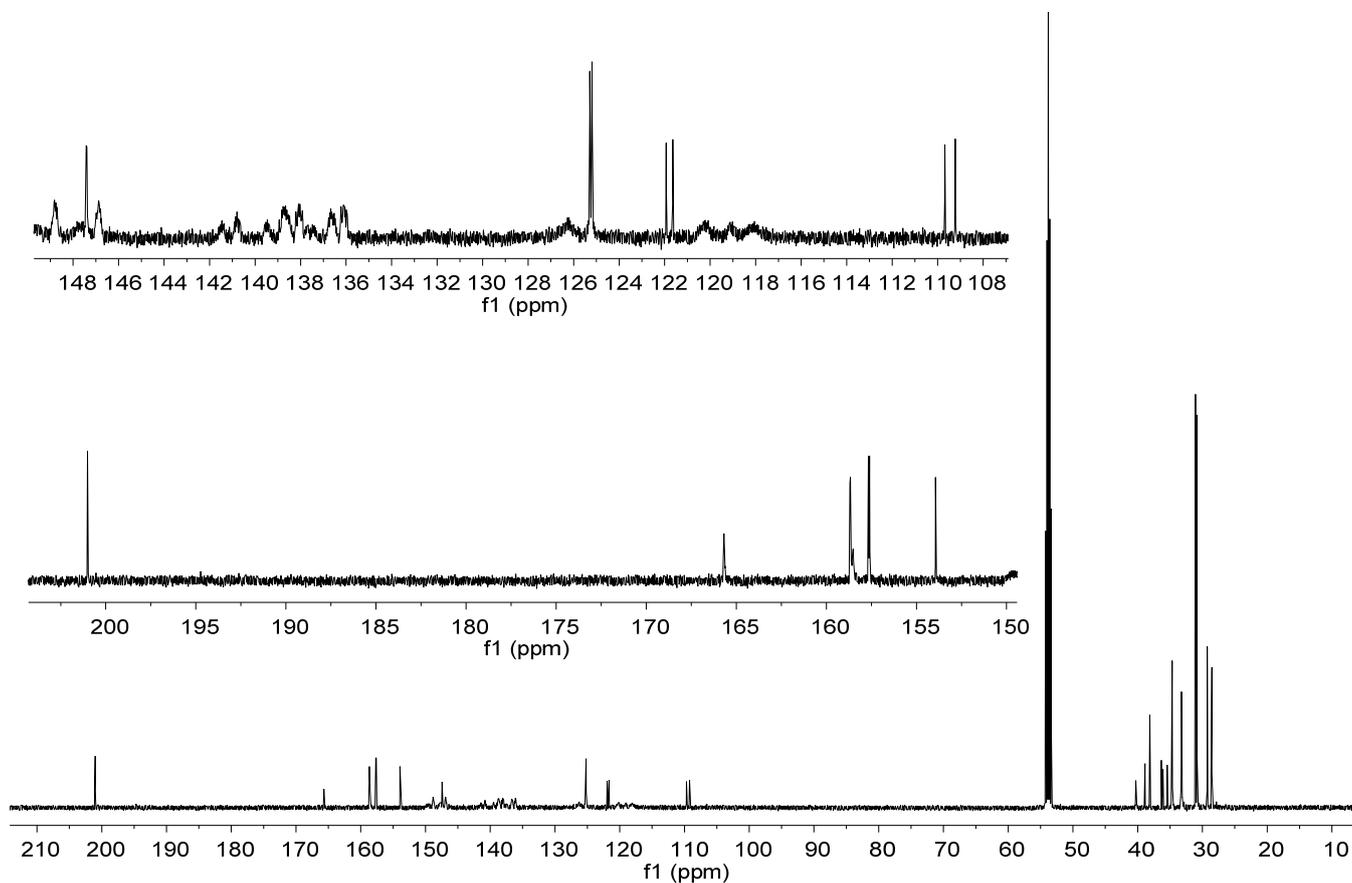


Figure S58. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 299 K, CD_2Cl_2) spectrum of compound **16a**.

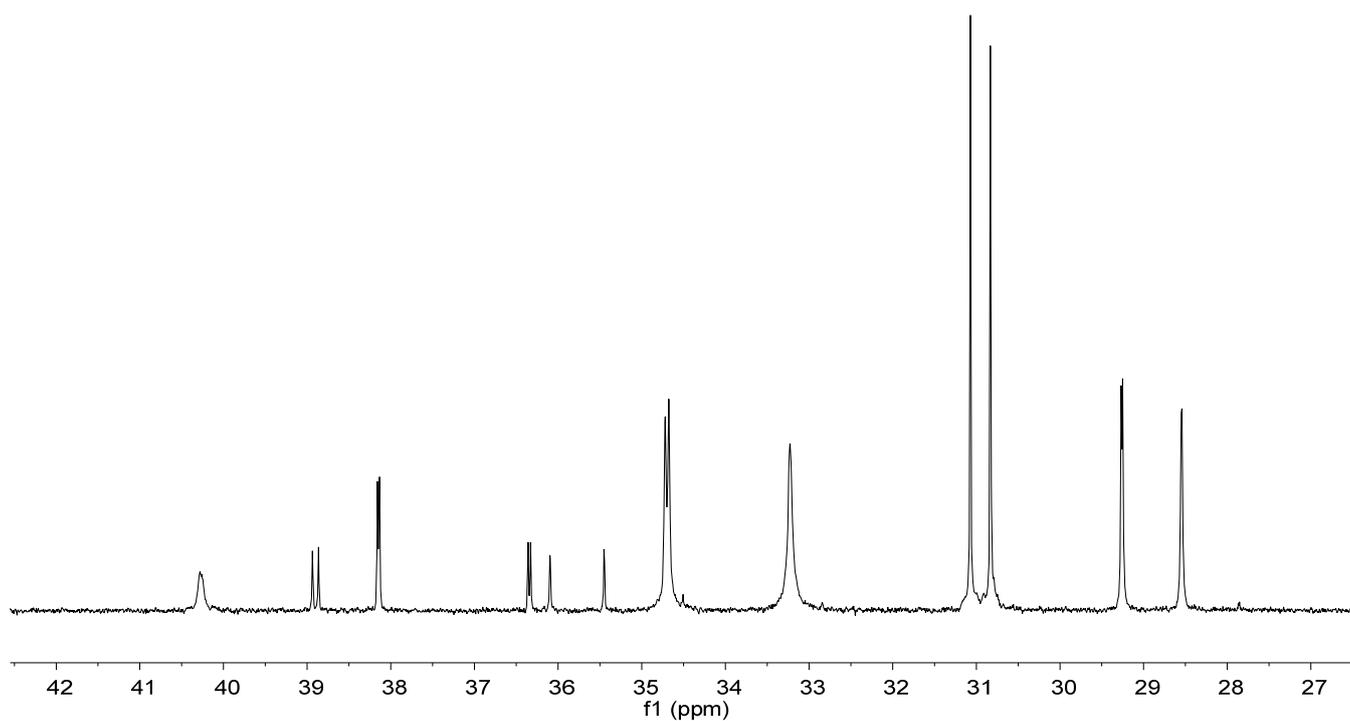


Figure S59. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 299 K, CD_2Cl_2) spectrum (42 ppm-27 ppm) of compound **16a**.

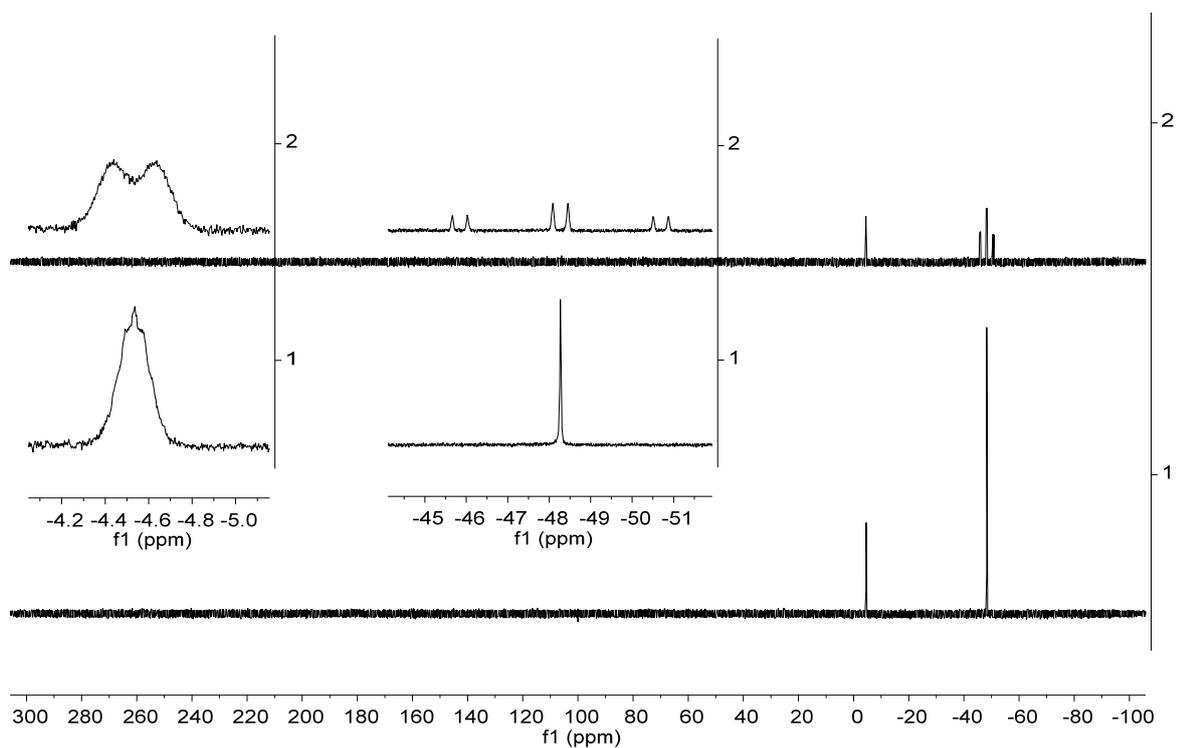


Figure S60. (1) $^{31}\text{P}\{^1\text{H}\}$ and (2) ^{31}P NMR (202 MHz, 299 K, CD_2Cl_2) spectra of compound **16a**.

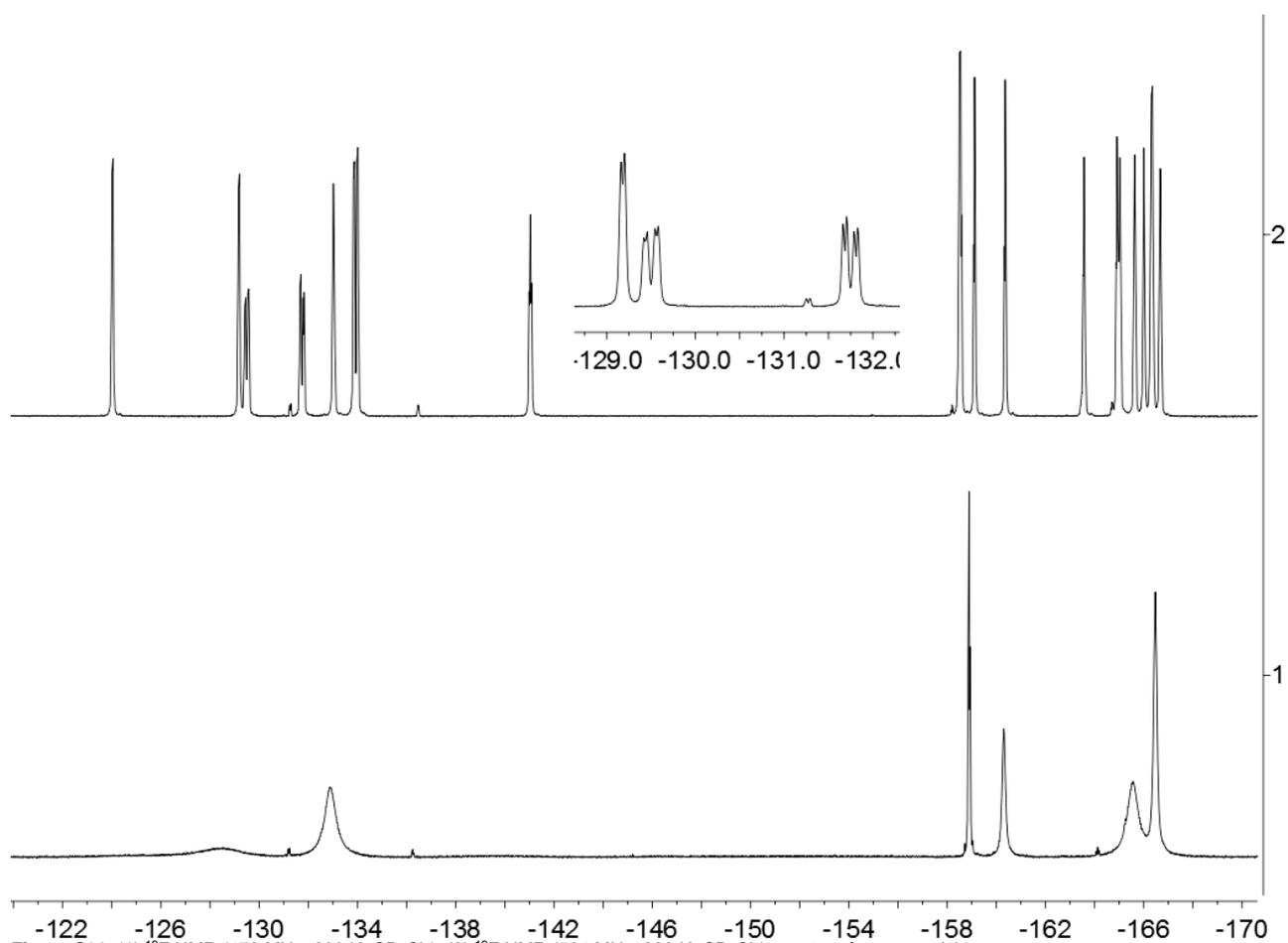


Figure S61. (1) ^{19}F NMR (470 MHz, 299 K, CD_2Cl_2), (2) ^{19}F NMR (564 MHz, 233 K, CD_2Cl_2) spectra of compound **16a**.

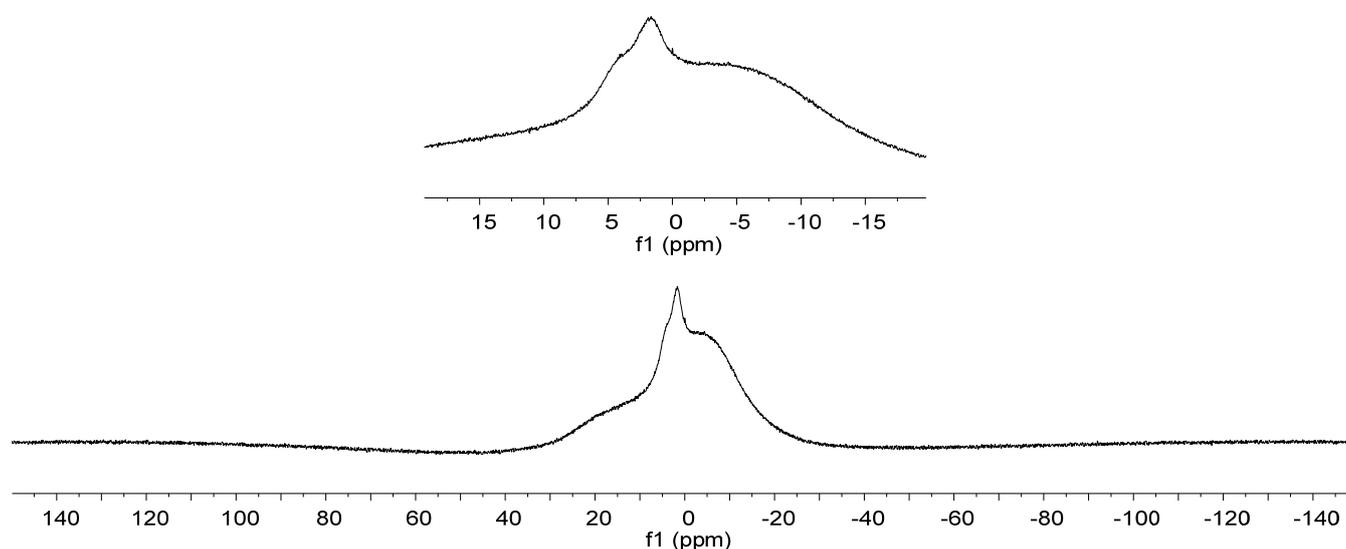


Figure S62. $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, 299 K, CD_2Cl_2) spectrum of compound **16a**.

Crystals of compound **16a** suitable for the X-ray crystal structure analysis were obtained from a solution of the white solid in benzene and pentane (ratio ca. 1 : 10) at room temperature.

X-ray crystal structure analysis of compound 16a: A colorless plate-like specimen of $\text{C}_{33}\text{H}_{27}\text{BF}_{10}\text{NOPS}$, approximate dimensions 0.050 mm x 0.160 mm x 0.180 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 2074 frames were collected. The total exposure time was 22.89 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 55525 reflections to a maximum θ angle of 68.19° (0.83 Å resolution), of which 5799 were independent (average redundancy 9.575, completeness = 98.4%,

$R_{\text{int}} = 6.26\%$, $R_{\text{sig}} = 3.39\%$) and 5030 (86.74%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 16.5186(4)$ Å, $b = 11.2948(3)$ Å, $c = 17.6854(5)$ Å, $\beta = 102.2340(10)^\circ$, volume = 3224.71(15) Å³, are based upon the refinement of the XYZ-centroids of 9908 reflections above $20 \sigma(I)$ with $9.353^\circ < 2\theta < 135.3^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.850. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6980 and 0.9000. The final anisotropic full-matrix least-squares refinement on F^2 with 474 variables converged at $R1 = 7.46\%$, for the observed data and $wR2 = 16.34\%$ for all data. The goodness-of-fit was 1.179. The largest peak in the final difference electron density synthesis was $0.690 \text{ e}/\text{Å}^3$ and the largest hole was $-0.622 \text{ e}/\text{Å}^3$ with an RMS deviation of $0.090 \text{ e}/\text{Å}^3$. On the basis of the final model, the calculated density was $1.478 \text{ g}/\text{cm}^3$ and $F(000)$, 1464 e⁻.

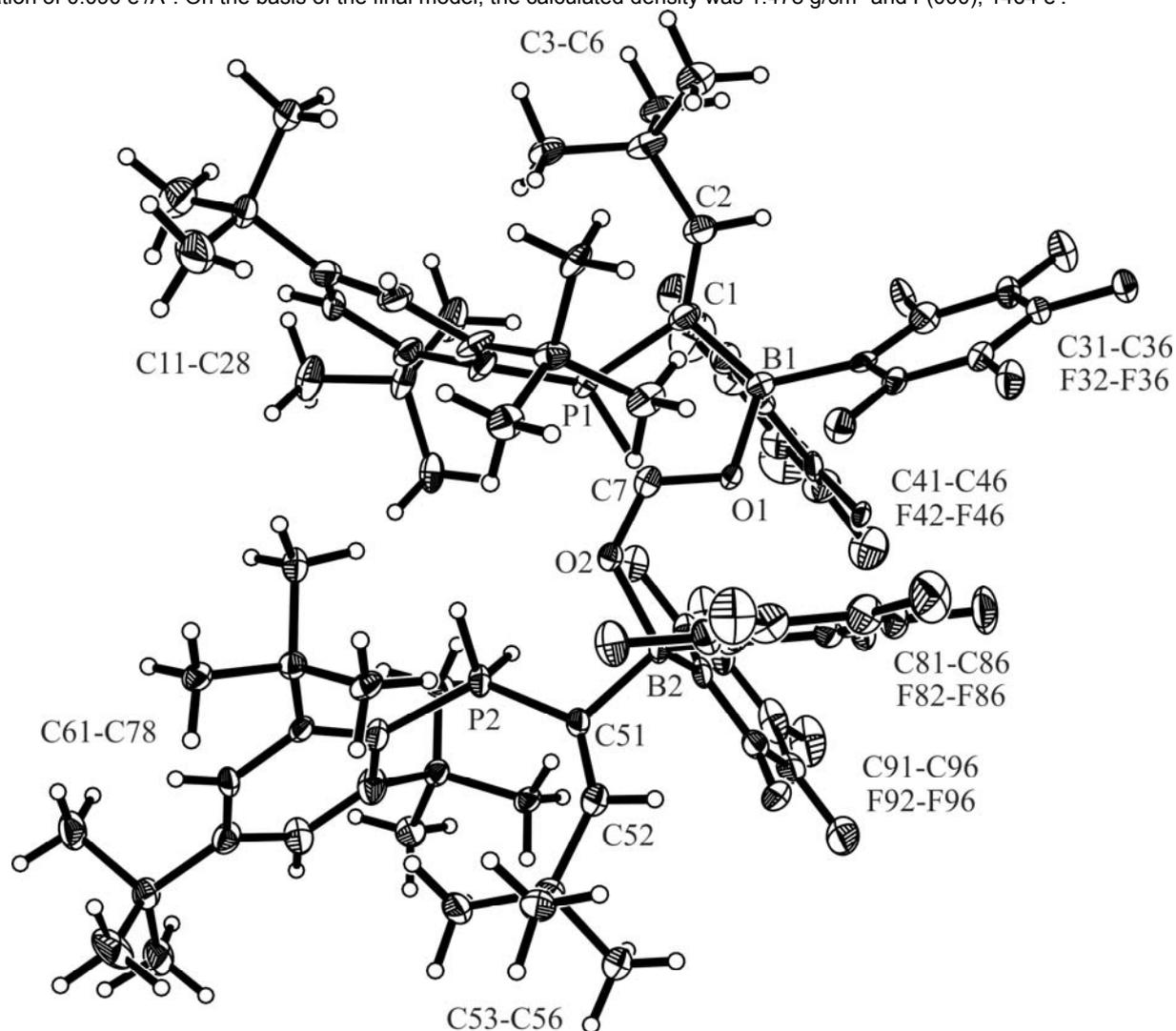
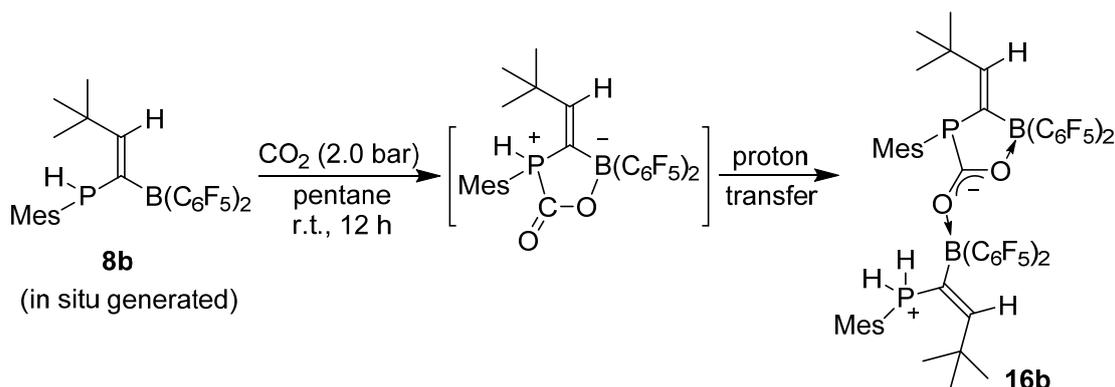


Figure S63. A view of the molecular structure of compound 16a.

b) Preparation of compound 16b



Scheme S13

After stirring a mixture of compound **7b** (116 mg, 0.5 mmol) and $\text{HB}(\text{C}_6\text{F}_5)_2$ (173 mg, 0.5 mmol) in pentane (5 mL) at room temperature for 12 h, the resulting yellow suspension was filtered to give a clear yellow solution which was exposed to CO_2 gas (2.0 bar). After the reaction mixture stirred at room temperature for 12 h a white precipitate was formed. The resulting suspension was filtered. The collected solid was washed twice with pentane (2x5 mL) and dried in vacuo to give a white solid. Yield: 195 mg, 65 %.

Elemental analysis: calc. for $\text{C}_{55}\text{H}_{44}\text{P}_2\text{B}_2\text{O}_2\text{F}_{20}$ (1200.5 g mol⁻¹): C, 55.03; H, 3.69. Found: C, 55.48; H, 4.06.

Melting point: 144 °C.

[Mes: 2,4,6-trimethylphenyl]

¹H NMR (600 MHz, 288 K, CD_2Cl_2 , 5.32 ppm): δ = 6.61 (d, $^1J_{\text{PH}} = 479.7$ Hz), 6.40 (d, $^1J_{\text{PH}} = 486.8$ Hz)(each 1H, PH_2), 6.98 (s, 1H), 6.96 (d, $^4J_{\text{PH}} = 5.0$ Hz, 2H), 6.70 (d, $^4J_{\text{PH}} = 5.7$ Hz, 1H)(*m*-Mes), 6.66 (d, $^3J_{\text{PH}} = 68.8$ Hz), 5.66 (d, $^3J_{\text{PH}} = 32.6$ Hz)(each 1H, =CH), 2.37, 2.327 (each s, each 3H, *p*- CH_3 -Mes), 2.332/2.03 (each 3H), 2.10 (6H)(each s, *o*- CH_3 -Mes), 0.84, 0.72 (each s, each 9H, $\text{C}(\text{CH}_3)_3$).

¹³C{¹H} NMR (151 MHz, 288 K, CD_2Cl_2 , 53.8 ppm): δ = 205.2 (d, $^1J_{\text{PC}} = 5.6$ Hz, C=O), 169.5 (br), 150.1 (d, $^3J_{\text{PC}} = 6.0$ Hz)(=CH), 146.4 (br d, $^2J_{\text{PC}} = 37.2$ Hz)/145.3 (br d, $^2J_{\text{PC}} = 4.4$ Hz), 143.3 (br d, $^2J_{\text{PC}} = 9.8$ Hz)(*o*-Mes), 146.2 (d, $^4J_{\text{PC}} = 3.1$ Hz), 142.1 (d, $^2J_{\text{PC}} = 1.7$ Hz)(*p*-Mes), 135.4 (br d, $^1J_{\text{PC}} = 26.5$ Hz), 114.0 (br d, $^1J_{\text{PC}} = 29.9$ Hz)(BC=), 131.5 (d, $^3J_{\text{PC}} = 11.3$ Hz, 2C), 130.3 (br), 129.8 (br d, $^3J_{\text{PC}} = 9.1$ Hz)(*m*-Mes), 127.6 (d, $^1J_{\text{PC}} = 16.8$ Hz), 110.3 (d, $^1J_{\text{PC}} = 79.5$ Hz)(*i*-Mes), 37.8 (d, $^3J_{\text{PC}} = 9.5$ Hz), 34.9 (d, $^3J_{\text{PC}} = 2.0$ Hz)($\text{C}(\text{CH}_3)_3$), 28.97, 28.96 (d, $^4J_{\text{PC}} = 2.1$ Hz)($\text{C}(\text{CH}_3)_3$), 23.8 (br d, $^3J_{\text{PC}} = 30.0$ Hz)/22.7 (br), 22.2 (d, $^3J_{\text{PC}} = 9.4$ Hz)(*o*- CH_3 -Mes), 21.5 (d, $^5J_{\text{PC}} = 1.0$ Hz), 21.3 (*p*- CH_3 -Mes), [C_6F_5 not listed].

³¹P{¹H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = -17.7 (m, 1P), -60.3 (m, 1P).

³¹P NMR (243 MHz, 299 K, CD_2Cl_2): δ = -17.7 (m, 1P), -60.3 (td, $^1J_{\text{PH}} = 482.9$ Hz, $^3J_{\text{PH}} = 70.5$ Hz, 1P).

¹¹B{¹H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 7.2, 1.9

¹⁹F NMR (564 MHz, 299 K, CD_2Cl_2): δ = -127.6, -130.9, -132.5, -133.5 (each br m, each 2F, *o*- C_6F_5), -156.4, -156.6, -157.9, -158.5 (each br t, $^3J_{\text{FF}} = 19.2$ Hz, each 1F, *p*- C_6F_5), -162.6, -163.9, -164.2, -164.5 (each br m, each 2F, *m*- C_6F_5).

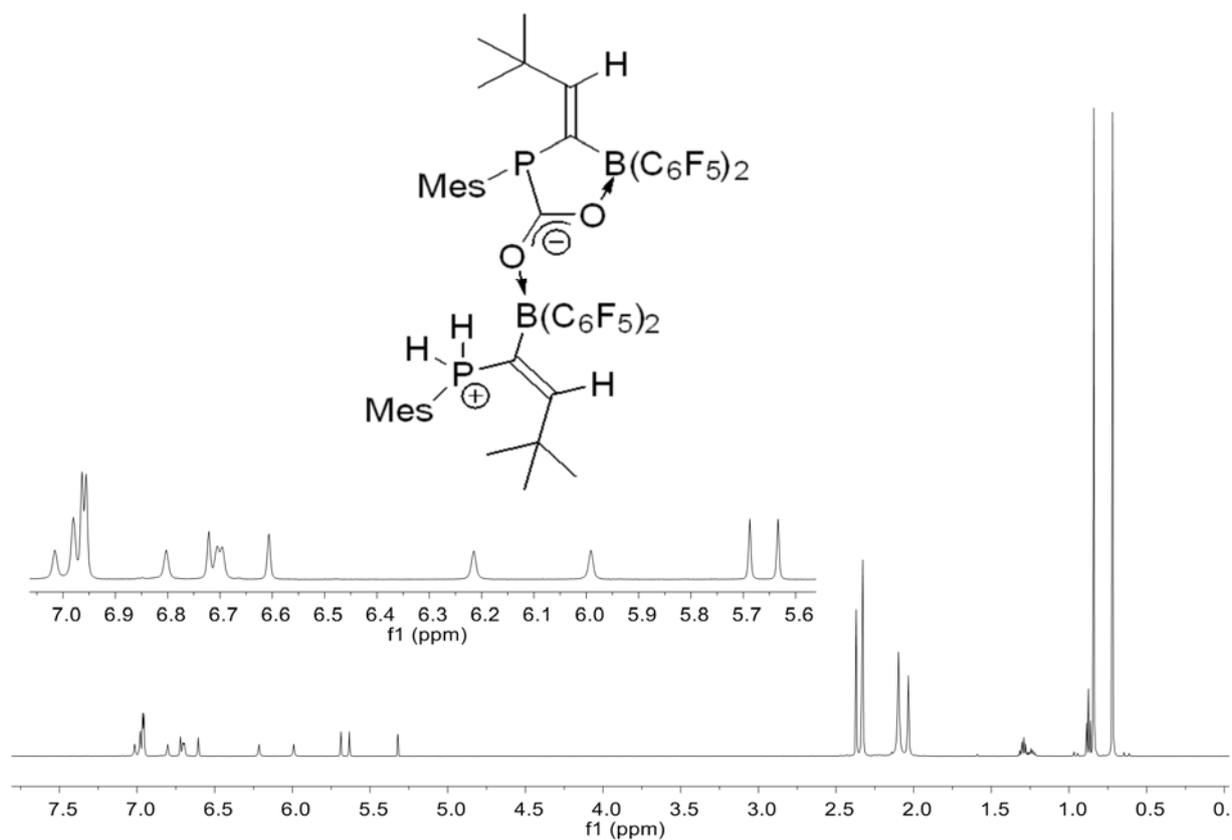


Figure S64. ^1H NMR (600 MHz, 288 K, CD_2Cl_2) spectrum of compound **16b**.

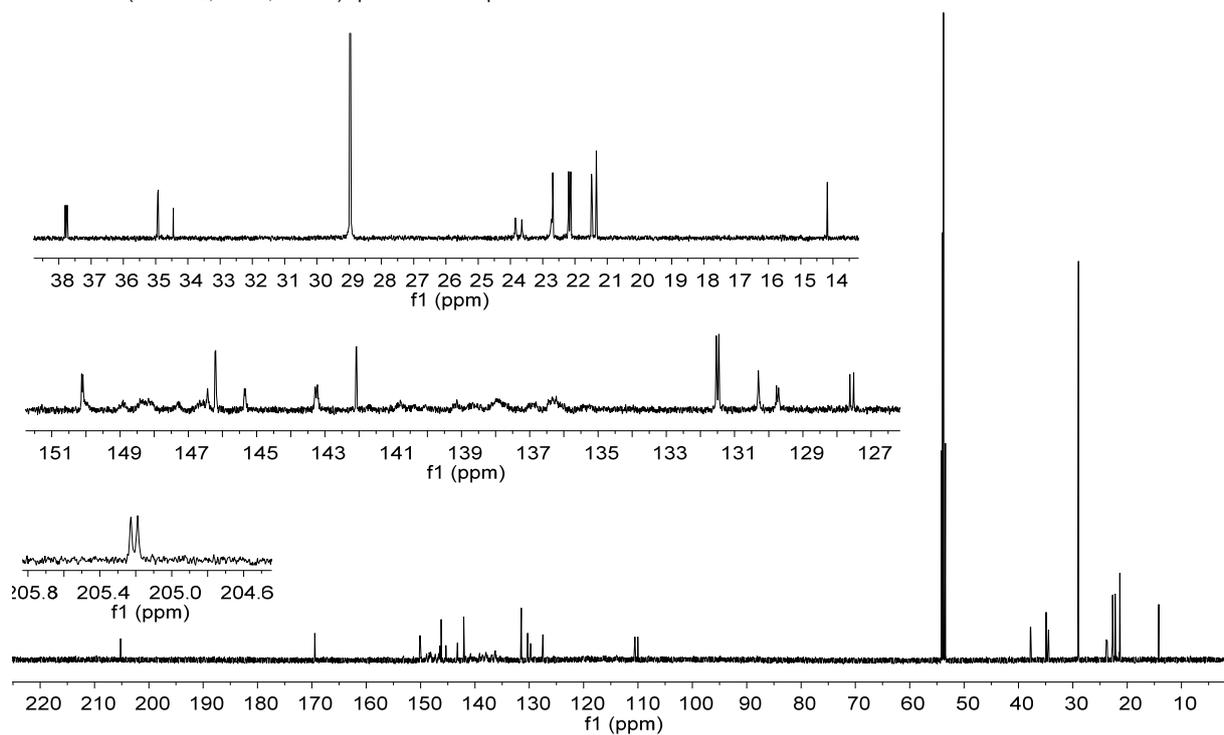


Figure S65. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 288 K, CD_2Cl_2) spectrum of compound **16b**.

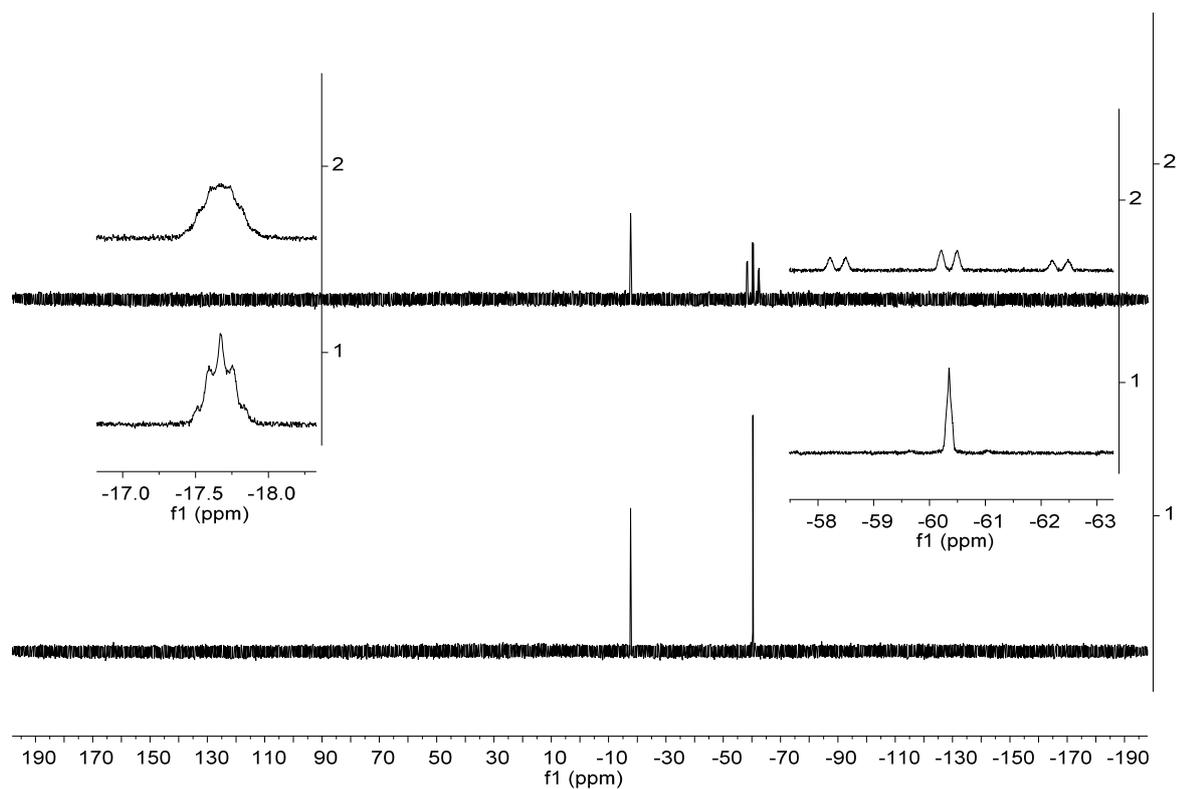


Figure S66. (1) $^{31}\text{P}\{^1\text{H}\}$ and (2) ^{31}P NMR (243 MHz, 299 K, CD_2Cl_2) spectra of compound **16b**.

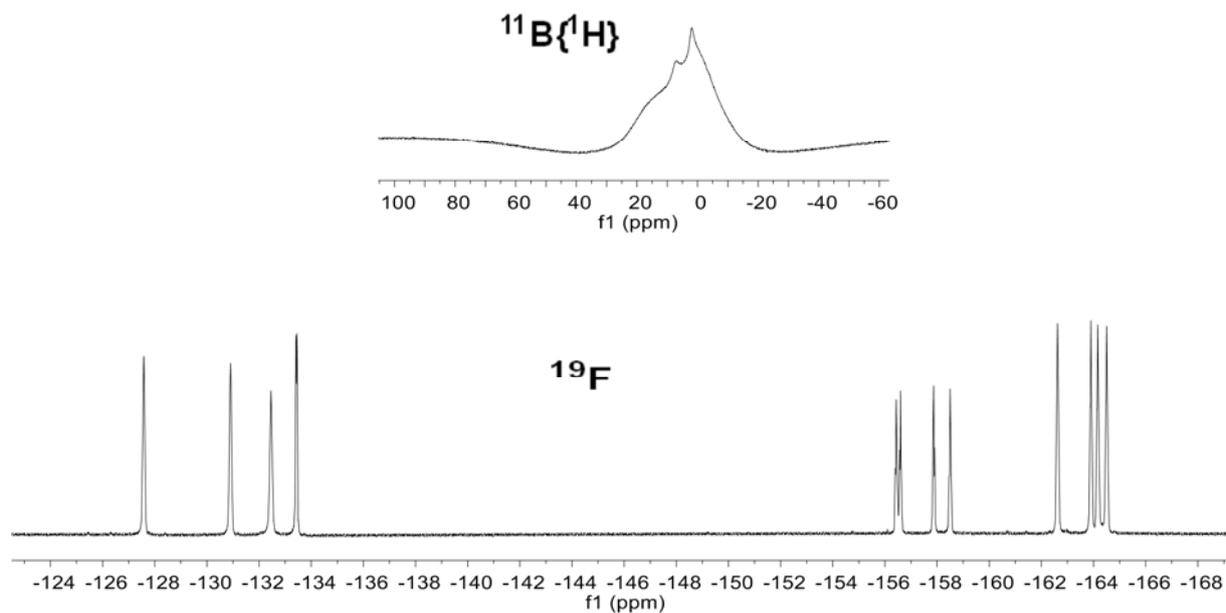


Figure S67. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) and $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectra of compound **16b**.

Crystals of compound **16b** suitable for the X-ray crystal structure analysis were obtained from a solution of the white solid in benzene and pentane (ratio ca. 1 : 10) at room temperature.

X-ray crystal structure analysis of compound 16b: formula $C_{55}H_{44}B_2F_{20}O_2P_2$, $M = 1200.46$, colourless crystal, $0.12 \times 0.07 \times 0.01$ mm, $a = 15.8307(4)$, $b = 16.0409(5)$, $c = 24.4074(8)$ Å, $\beta = 93.073(3)^\circ$, $V = 6189.1(3)$ Å³, $\rho_{\text{calc}} = 1.288$ gcm⁻³, $\mu = 0.167$ mm⁻¹, empirical absorption correction ($0.980 \leq T \leq 0.998$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, $T = 173(2)$ K, ω and ϕ scans, 53014 reflections collected ($\pm h, \pm k, \pm l$), 10750 independent ($R_{\text{int}} = 0.130$) and 5926 observed reflections [$I > 2\sigma(I)$], 748 refined parameters, $R = 0.089$, $wR^2 = 0.211$, max. (min.) residual electron density 0.41 (-0.31) e.Å⁻³, the hydrogen atom positions at P2 atom were refined freely, but with fixed U-value, others were calculated and refined as riding atoms.

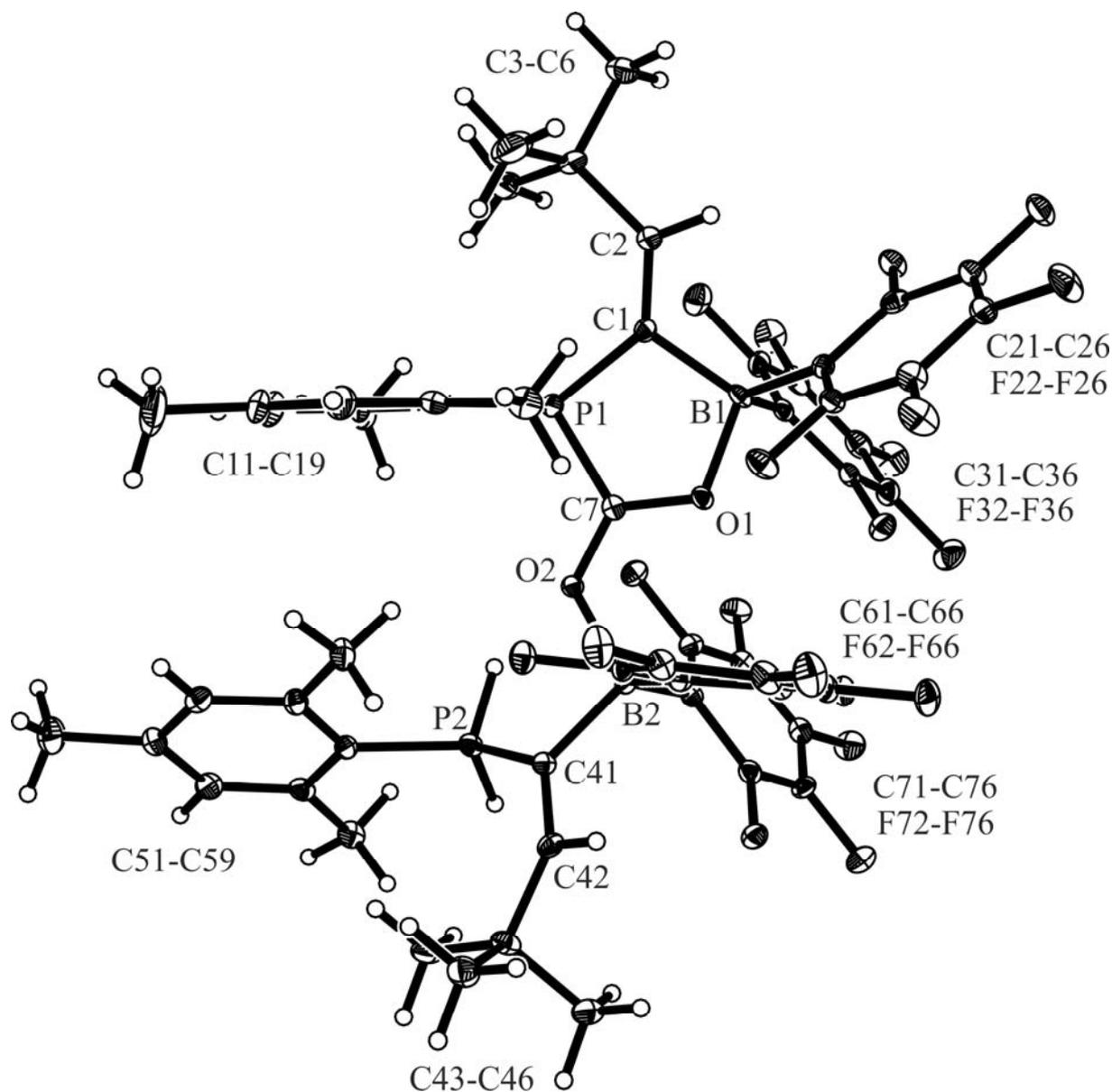
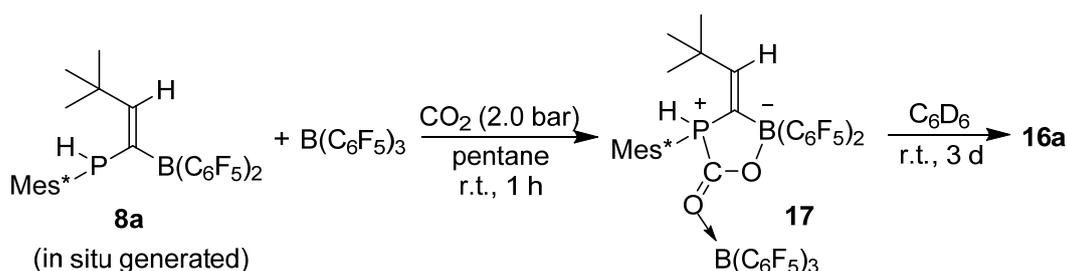


Figure S68. A view of the molecular structure of compound **16b**.

c) Preparation of compound 17 and rearrangement to compound 16a



Preparation of compound 17:

After stirring a mixture of compound **7a** (180 mg, 0.5 mmol) and $\text{HB}(\text{C}_6\text{F}_5)_2$ (173 mg, 0.5 mmol) in pentane (5 mL) at room temperature for 1 h, the resulting red suspension was filtered to give a clear red solution. $\text{B}(\text{C}_6\text{F}_5)_3$ (256 mg, 0.5 mmol) was added and then the reaction mixture was exposed to CO_2 gas (2.0 bar). After the reaction mixture was stirred at room temperature for 1 h a white precipitate was formed. The resulting suspension was filtered. The collected solid was washed twice with pentane (2×5 mL) and dried in vacuo to give a white solid. Yield: 447 mg, 71 %.

Elemental analysis: calc. for $\text{C}_{55}\text{H}_{40}\text{PB}_2\text{O}_2\text{F}_{25}$ (1260.5 g mol⁻¹): C, 52.41; H, 3.20. Found: C, 53.43; H, 3.30.

Melting point: 150 °C.

[Mes*: 2,4,6-tri-*tert*-butylphenyl]

¹H NMR (600 MHz, 299 K, CD_2Cl_2 , 5.32 ppm): δ = 8.24 (d, $^1J_{\text{PH}}$ = 484.3 Hz, 1H, PH), 7.76 (dm, $^4J_{\text{PH}}$ = 6.2 Hz), 7.73 (dm, $^4J_{\text{PH}}$ = 5.8 Hz)(each 1H, *m*-Mes*), 6.78 (d, $^3J_{\text{PH}}$ = 68.6 Hz, 1H, =CH), 1.61, 1.358 (s, 9H, *o*- $\text{C}(\text{CH}_3)_3$ -Mes*), 1.355 (s, 18H, *p*- $\text{C}(\text{CH}_3)_3$ -Mes*), 0.58 (s, 9H, $\text{C}(\text{CH}_3)_3$).

¹³C{¹H} NMR (151 MHz, 299 K, CD_2Cl_2 , 53.8 ppm): δ = 175.9 (d, $^1J_{\text{PC}}$ = 117.6 Hz, C=O), 173.3 (=CH), 161.9 (d, $^2J_{\text{PC}}$ = 10.2 Hz), 161.8 (d, $^2J_{\text{PC}}$ = 9.4 Hz)(*o*-Mes*), 160.6 (d, $^4J_{\text{PC}}$ = 4.3 Hz, *p*-Mes*), 128.5 (d, $^3J_{\text{PC}}$ = 14.7 Hz), 127.4 (d, $^3J_{\text{PC}}$ = 14.5 Hz)(*m*-Mes*), 117.9 (br d, $^1J_{\text{PC}}$ = 43.2 Hz, BC=), 105.5 (d, $^1J_{\text{PC}}$ = 69.7 Hz, *i*-Mes*), 39.8 (d, $^3J_{\text{PC}}$ = 2.8 Hz), 39.1 (d, $^3J_{\text{PC}}$ = 4.2 Hz)(*o*- $\text{C}(\text{CH}_3)_3$ -Mes*), 38.2 (d, $^3J_{\text{PC}}$ = 8.2 Hz, $\text{C}(\text{CH}_3)_3$), 36.0 (d, $^5J_{\text{PC}}$ = 1.4 Hz, *p*- $\text{C}(\text{CH}_3)_3$ -Mes*), 34.5, 32.8 (*o*- $\text{C}(\text{CH}_3)_3$ -Mes*), 30.7 (*p*- $\text{C}(\text{CH}_3)_3$ -Mes*), 27.8 (d, $^4J_{\text{PC}}$ = 1.5 Hz, $\text{C}(\text{CH}_3)_3$), [C_6F_5 not listed].

³¹P{¹H} NMR (202 MHz, 299 K, CD_2Cl_2): δ = -26.8 ($\nu_{1/2}$ ~ 50 Hz).

³¹P NMR (202 MHz, 299 K, CD_2Cl_2): δ = -26.8 (br dd, $^1J_{\text{PH}}$ = 484.3 Hz, $^3J_{\text{PH}}$ = 68.6 Hz).

¹¹B{¹H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 12.1 ($\nu_{1/2}$ ~ 550 Hz), 4.9 ($\nu_{1/2}$ ~ 450 Hz).

¹⁹F NMR (564 MHz, 299 K, CD_2Cl_2): δ = -132.0 (m, 2F, *o*), -156.5 (t, $^3J_{\text{FF}}$ = 19.2 Hz, 1F, *p*), -164.4 (m, 2F, *m*)($\text{B}(\text{C}_6\text{F}_5)_2$)[$\Delta\delta^{19}\text{F}_{m,p}$ = 7.9], -135.9 (m, 2F, *o*), -156.0 (t, $^3J_{\text{FF}}$ = 19.2 Hz, 1F, *p*), -163.2 (m, 2F, *m*)($\text{B}(\text{C}_6\text{F}_5)_2$)[$\Delta\delta^{19}\text{F}_{m,p}$ = 7.2], -132.7 (br, 6F, *o*), -155.9 (br, 3F, *p*), -164.7 (br s, 6F, *m*)($\text{B}(\text{C}_6\text{F}_5)_3$)[$\Delta\delta^{19}\text{F}_{m,p}$ = 8.8].

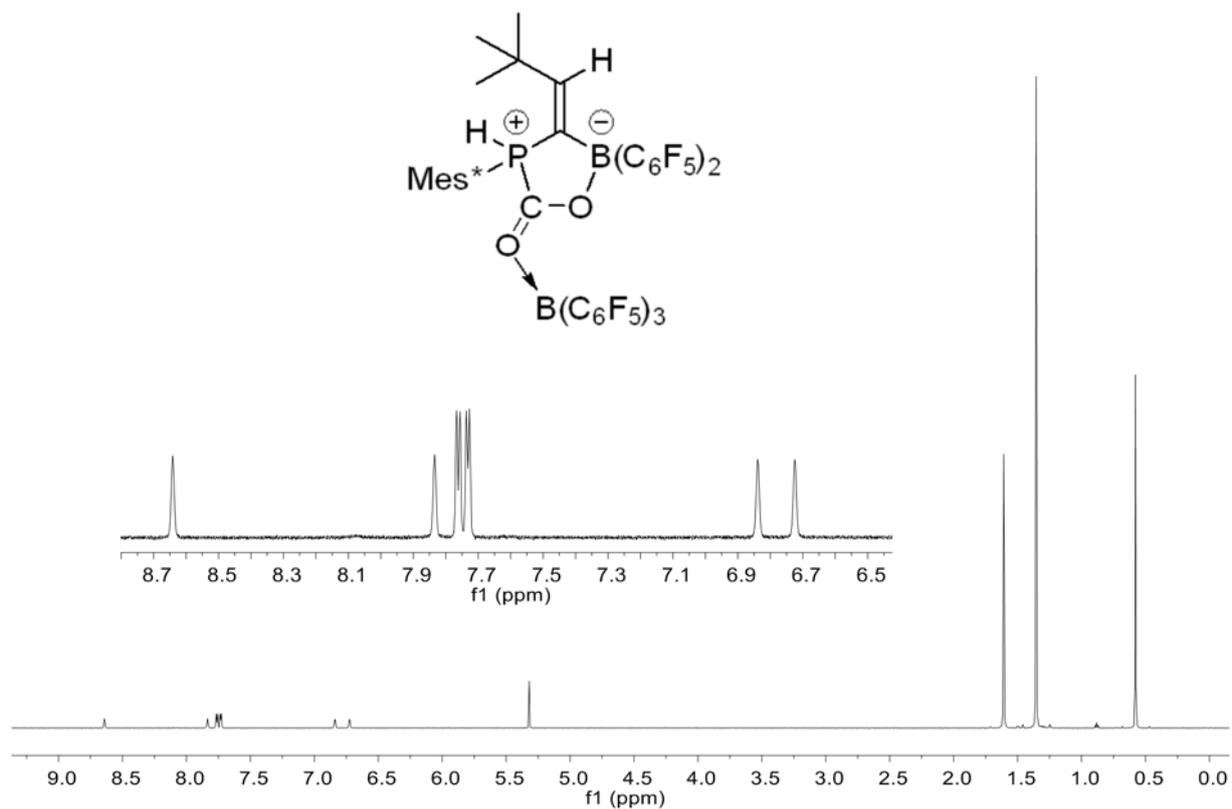


Figure S69. ^1H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound 17.

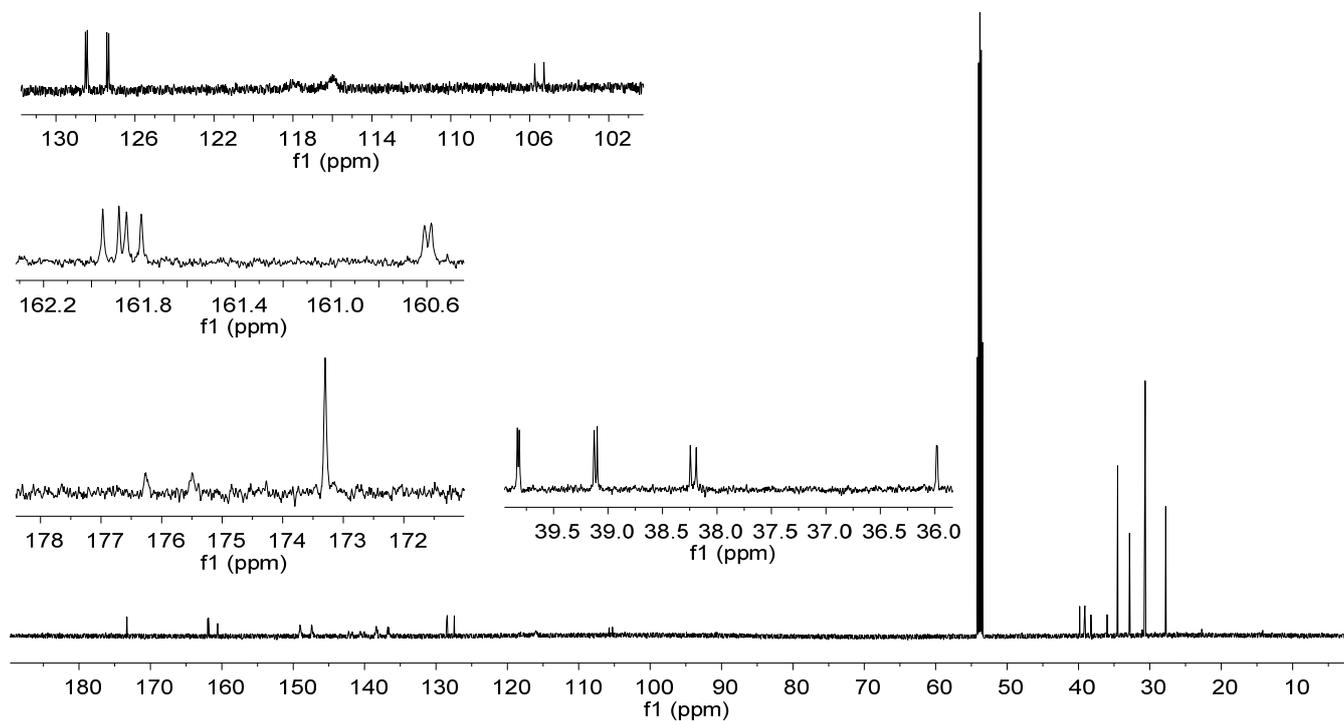


Figure S70. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound 17.

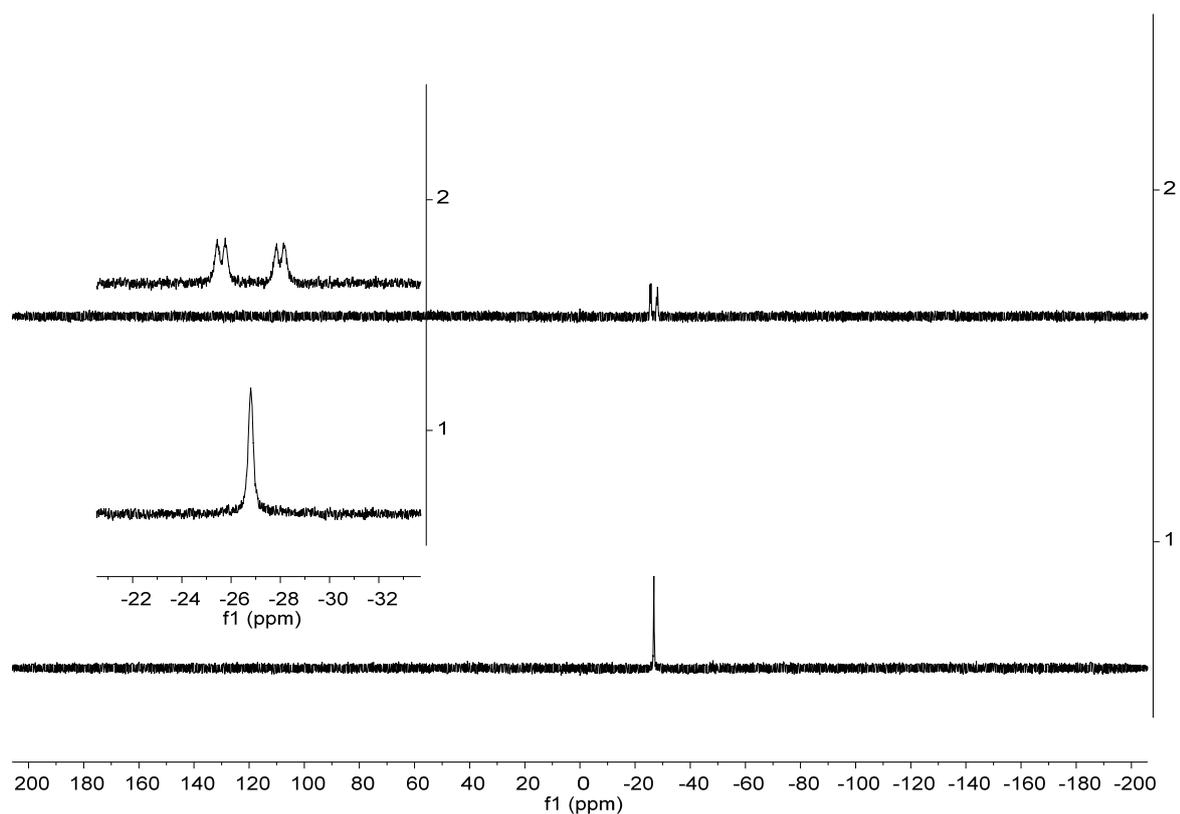


Figure S71. (1) $^{31}\text{P}\{^1\text{H}\}$ and (2) ^{31}P NMR (202 MHz, 299 K, CD_2Cl_2) spectra of compound 17.

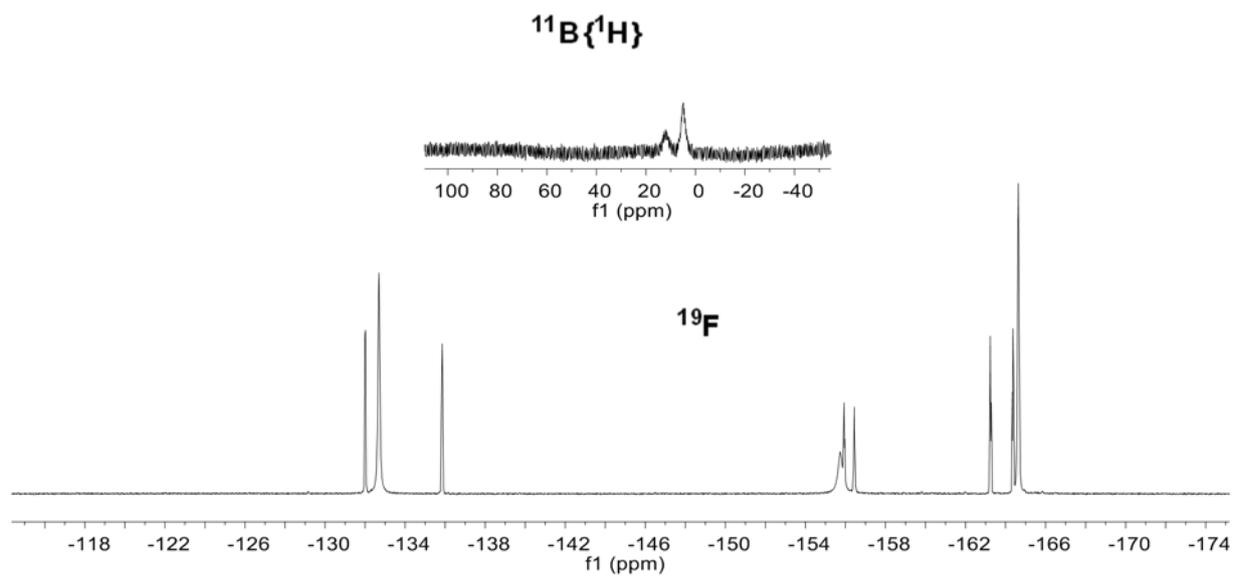


Figure S72. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) and $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectra of compound 17.

Rearrangement of compound **17** to compound **16a**

In solution (C_6D_6) compound **17** slowly converted to compound **16a**.

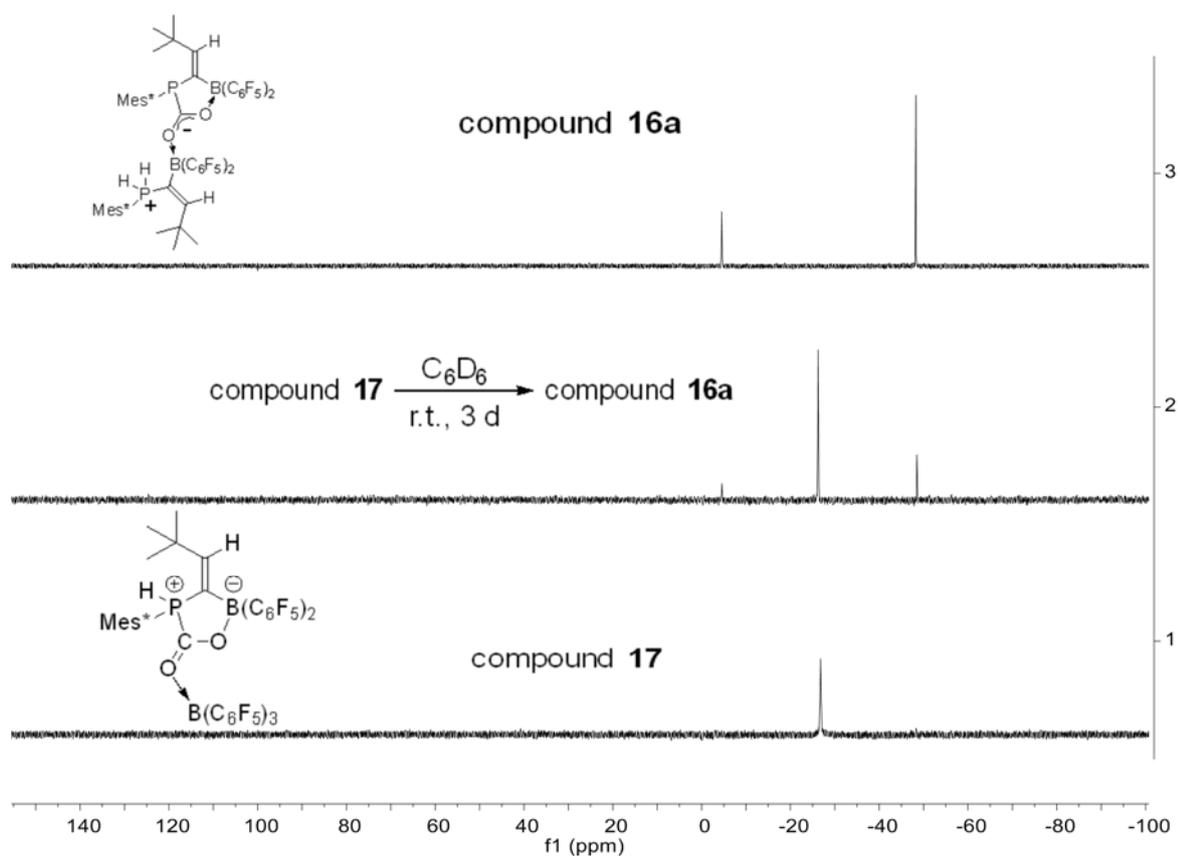
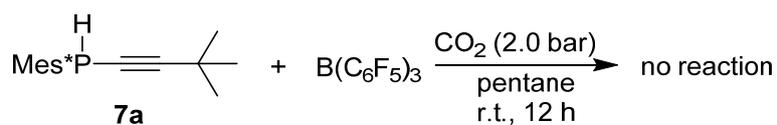


Figure S73. Comparative $^{31}P\{^1H\}$ NMR spectra of the conversion of compound **17** to compound **16a** at room temperature.

d) Control reaction of compound **7a** with $B(C_6F_5)_3$ and CO_2



Scheme S5

A yellow solution of compound **7a** (180 mg, 0.5 mmol) and $B(C_6F_5)_3$ (256 mg, 0.5 mmol) in pentane (5 mL) was exposed to CO_2 gas (2.0 bar) at room temperature and stirred at room temperature for 12 h. No solid was precipitated from the pentane solution, thus the solvent was removed in vacuo to afford light yellow solids, which are the starting materials **7a** and $B(C_6F_5)_3$ confirmed by NMR spectroscopy.

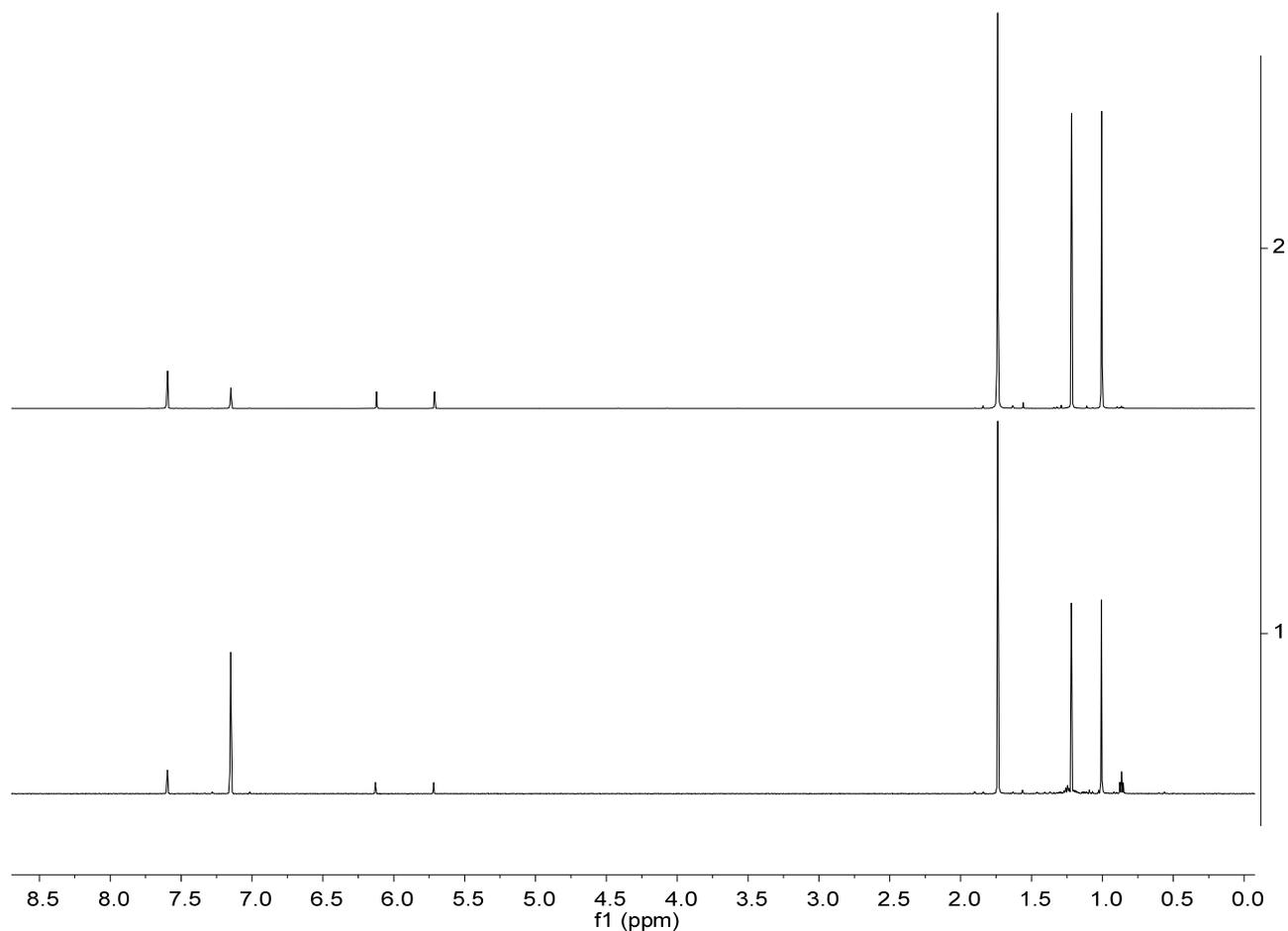
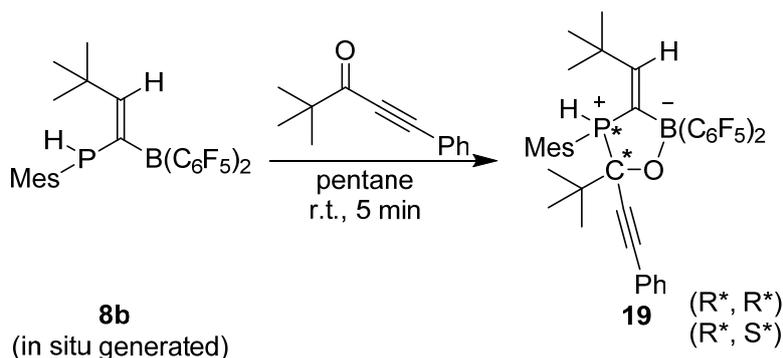


Figure S74. (1) 1H NMR (600 MHz, 299 K, C_6D_6) spectrum of light yellow solids, (2) 1H NMR (600 MHz, 299 K, C_6D_6) spectrum of compound **7a**.

Preparation of compounds 19 and 21

a) Preparation of compound 19



Scheme S16

After stirring a mixture of compound **7b** (116 mg, 0.5 mmol) and $\text{HB}(\text{C}_6\text{F}_5)_2$ (173 mg, 0.5 mmol) in pentane (3 mL) at room temperature for 10 h, the resulting yellow suspension was filtered to give a clear yellow solution. Then one equiv. of 4,4-dimethyl-1-phenylpent-1-yn-3-one (93 mg, 0.5 mmol) was added and after stirring for 5 min a white precipitate was formed. The resulting suspension was filtered. The collected solid was washed twice with pentane (2×5 mL) and dried in vacuo to give a white solid. Yield: 321 mg, 84 %.

Crystals of compound **19** suitable for the X-ray crystal structure analysis were obtained from a solution of the white solid in CH_2Cl_2 and pentane (ratio ca. 1 : 5) at -35°C .

X-ray crystal structure analysis of compounds (R*,R*)-19: A colorless prism-like specimen of $\text{C}_{40}\text{H}_{36}\text{BF}_{10}\text{OP}$, approximate dimensions 0.067 mm x 0.172 mm x 0.232 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 476 frames were collected. The total exposure time was 3.81 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 54957 reflections to a maximum θ angle of 25.03° (0.84 Å resolution), of which 12926 were independent (average redundancy 4.252, completeness = 99.9%, $R_{\text{int}} = 11.76\%$, $R_{\text{sig}} = 9.43\%$) and 8251 (63.83%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 11.3099(6)$ Å, $b = 16.9914(9)$ Å, $c = 19.1256(9)$ Å, $\alpha = 87.067(2)^\circ$, $\beta = 89.422(2)^\circ$, $\gamma = 85.654(2)^\circ$, volume = $3659.9(3)$ Å³, are based upon the refinement of the XYZ-centroids of 8316 reflections above $20\sigma(I)$ with $4.927^\circ < 2\theta < 54.46^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.949. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9640 and 0.9890. The final anisotropic full-matrix least-squares refinement on F^2 with 981 variables converged at $R1 = 5.39\%$, for the observed data and $wR2 = 10.66\%$ for all data. The goodness-of-fit was 1.022. The largest peak in the final difference electron density synthesis was $0.391 \text{ e}/\text{Å}^3$ and the largest hole was $-0.413 \text{ e}/\text{Å}^3$ with an RMS deviation of $0.068 \text{ e}/\text{Å}^3$. On the basis of the final model, the calculated density was $1.387 \text{ g}/\text{cm}^3$ and $F(000)$, 1576 e.

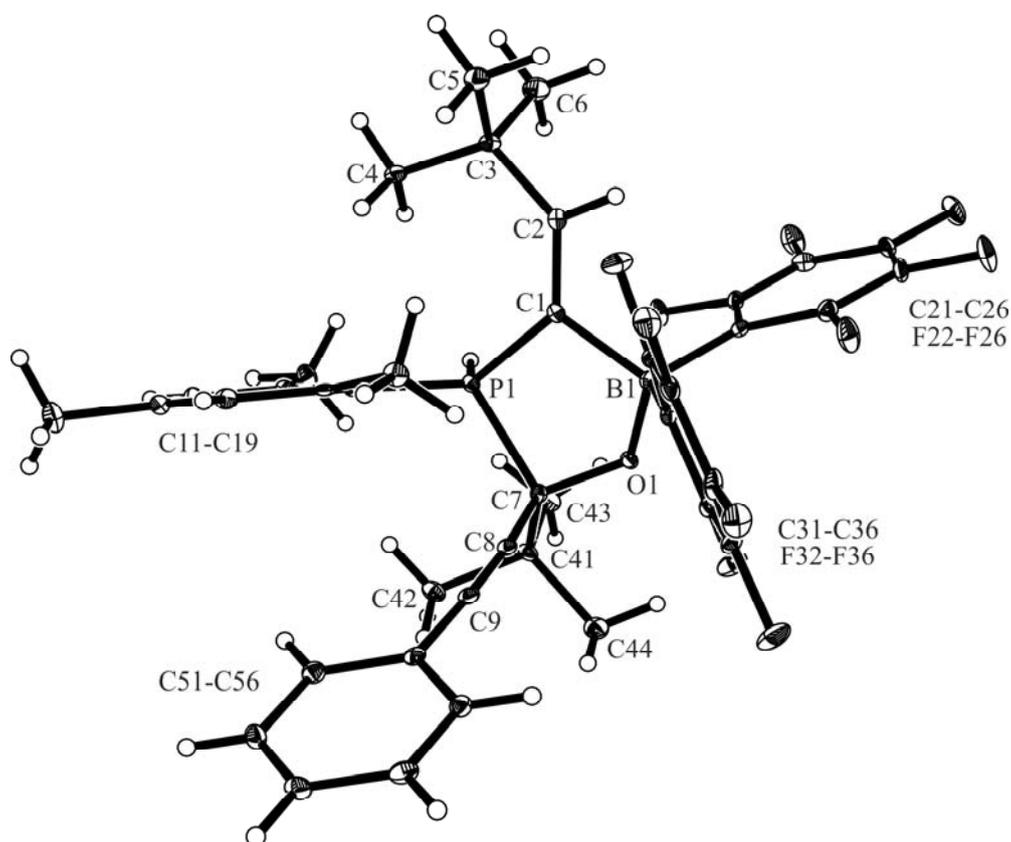


Figure S75. A view of the molecular structure of compounds (R^* , R^*)-**19**.

Comment: due to the presence of two chiral atoms (P and C) compound **19** shows two sets of NMR signals, namely (R^* , R^*)-**19**, and (R^* , S^*)-**19**. In the crystalline state, only (R^* , R^*)-**19** was observed which was confirmed by X-ray diffraction and NMR spectroscopy; however, in the solution state, (R^* , R^*)-**19** isomerized slowly to (R^* , S^*)-**19** finally after 14 h in a ca. 4:1 ratio.

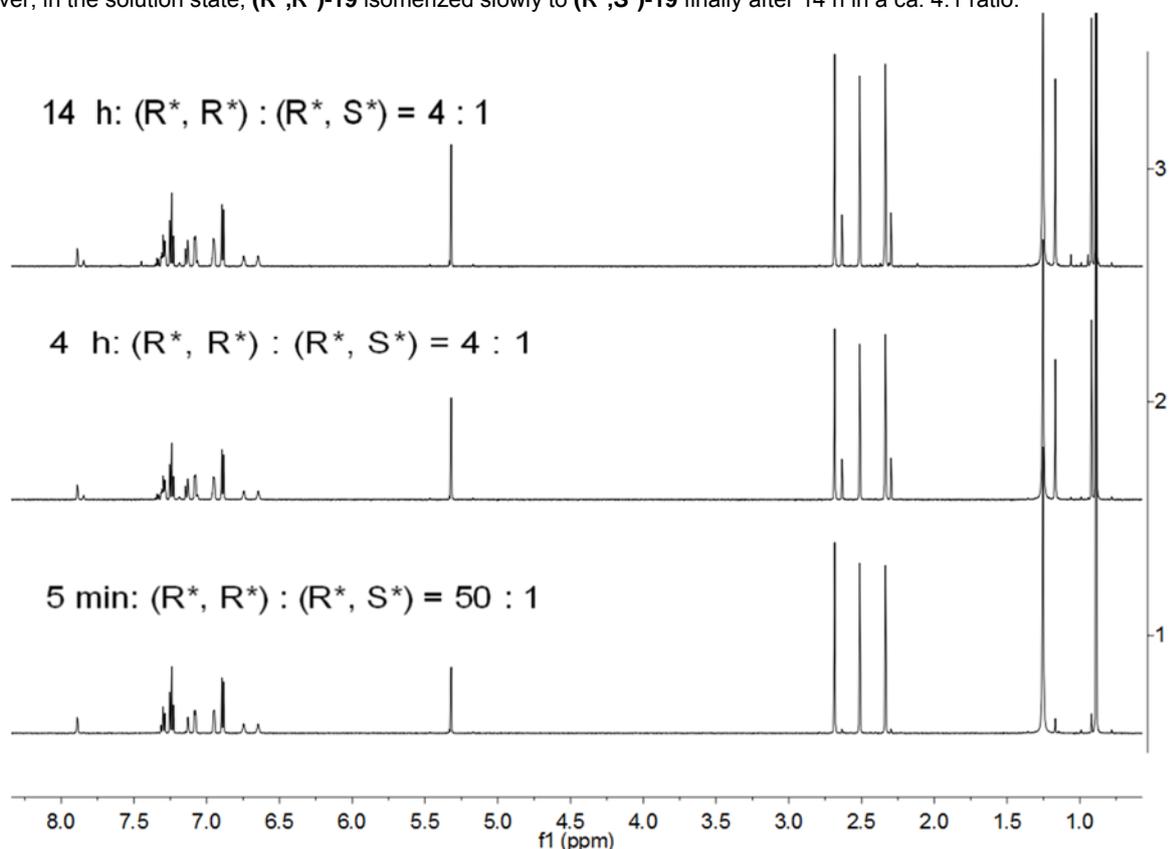
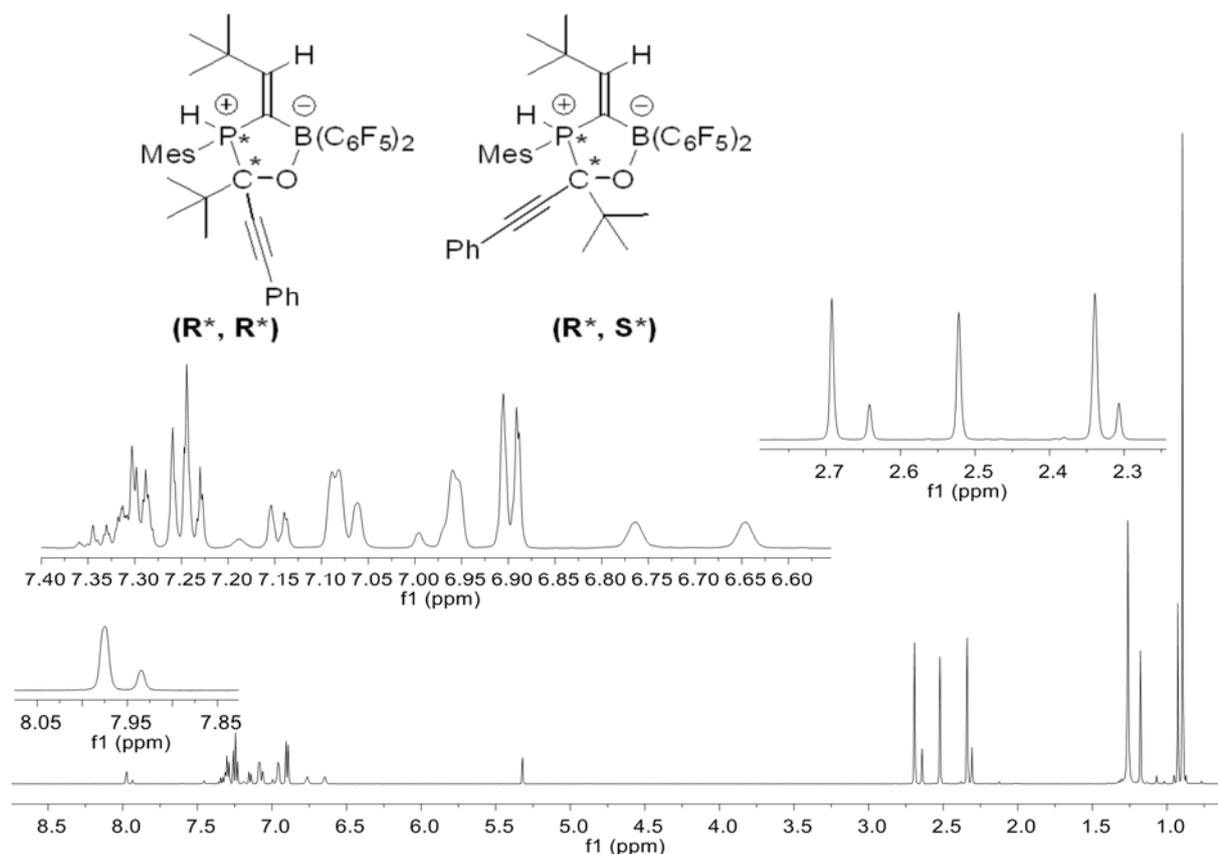


Figure S76. ^1H NMR (600 MHz, 299 K, CD_2Cl_2) spectra of the isomerization of the crystals of compound **19** in solution.

Colorless crystals from crystallization of the white solid:**Elemental analysis:** calc. for C₄₀H₃₆PBOF₁₀ (764.5 g mol⁻¹): C, 62.84; H, 4.75. Found: C, 62.76; H, 4.49.**Decomposed temperature:** 180 °C.**Compound 19 [colorless crystals in CD₂Cl₂ after 4 hours: ratio (R*,R*)-19 : (R*,S*)-19 ca. 78 : 22 (1H)]**

[Mes: 2,4,6-trimethylphenyl]

¹H NMR (500 MHz, 299 K, CD₂Cl₂, 5.32 ppm): (R*,R*)-19 δ = 7.52 (d, ¹J_{PH} = 456.6 Hz, 1H, PH), 7.30 (m, 1H, *p*-Ph), 7.24 (m, 2H, *m*-Ph), 7.08 (d, ⁴J_{PH} = 3.0 Hz), 6.96 (d, ⁴J_{PH} = 3.5 Hz)(each 1H, *m*-Mes), 6.90 (m, 2H, *o*-Ph), 6.70 (d, ³J_{PH} = 59.0 Hz, 1H, =CH), 2.69, 2.52 (each s, each 3H, *o*-CH₃-Mes), 2.34 (s, 3H, *p*-CH₃-Mes), 1.26 (s, 9H, ^oC(CH₃)₃), 0.90 (s, 9H, C(CH₃)₃).(R*,S*)-19 δ = 7.46 (d, ¹J_{PH} = 470.2 Hz, 1H, PH), 7.34 (m, 1H, *p*-Ph), 7.30 (m, 2H, *m*-Ph), 7.25 (d, ³J_{PH} = 59.4 Hz, 1H, =CH), 7.15 (m, 2H, *o*-Ph), 7.08 (d, ⁴J_{PH} = 3.0 Hz), 6.97 (d, ⁴J_{PH} = 3.5 Hz)(each 1H, *m*-Mes), 2.64, 2.13 (each s, each 3H, *o*-CH₃-Mes), 2.34 (s, 3H, *p*-CH₃-Mes), 1.18 (s, 9H, ^oC(CH₃)₃), 0.93 (s, 9H, C(CH₃)₃).**¹³C{¹H} NMR** (126 MHz, 299 K, CD₂Cl₂, 53.8 ppm): (R*,R*)-19 δ = 167.4 (m, =CH), 145.7 (d, ²J_{PC} = 10.0 Hz), 141.5 (d, ²J_{PC} = 7.9 Hz)(*o*-Mes), 145.3 (d, ⁴J_{PC} = 3.2 Hz, *p*-Mes), 131.99 (d, ³J_{PC} = 11.5 Hz), 131.95 (d, ³J_{PC} = 10.0 Hz)(*m*-Mes), 131.2 (d, ⁵J_{PC} = 2.4 Hz, *o*-Ph), 129.2 (*p*-Ph), 128.7 (*m*-Ph), 122.4 (br d, ¹J_{PC} = 53.9 Hz, BC=), 122.0 (d, ⁴J_{PC} = 3.0 Hz, *i*-Ph), 117.4 (d, ¹J_{PC} = 65.5 Hz, *i*-Mes), 91.2 (d, ³J_{PC} = 9.5 Hz, ≡CPh), 89.55 (d, ¹J_{PC} = 62.1 Hz, OC), 87.7 (d, ²J_{PC} = 9.6 Hz, C≡), 41.7 (d, ²J_{PC} = 2.3 Hz, ^oC(CH₃)₃), 37.8 (d, ³J_{PC} = 7.2 Hz, C(CH₃)₃), 28.6 (d, ⁴J_{PC} = 1.2 Hz, C(CH₃)₃), 26.1 (br, ^oC(CH₃)₃), 24.8 (br d, ³J_{PC} = 5.2 Hz), 23.4 (d, ³J_{PC} = 7.7 Hz)(*o*-CH₃-Mes), 21.46 (d, ⁵J_{PC} = 1.4 Hz, *p*-CH₃-Mes), [C₆F₅ are listed].(R*,S*)-19 δ = 168.0 (m, =CH), 145.8 (d, ⁴J_{PC} = 3.5 Hz, *p*-Mes), 145.0 (d, ²J_{PC} = 10.8 Hz), 141.9 (d, ²J_{PC} = 8.4 Hz)(*o*-Mes), 132.04 (d, ³J_{PC} = 11.5 Hz), 131.88 (d, ³J_{PC} = 9.0 Hz)(*m*-Mes), 131.6 (d, ⁵J_{PC} = 3.6 Hz, *o*-Ph), 129.4 (*p*-Ph), 128.6 (*m*-Ph), 122.5 (br d, ¹J_{PC} = 54.2 Hz, BC=), 121.7 (d, ⁴J_{PC} = 4.0 Hz, *i*-Ph), 120.0 (d, ¹J_{PC} = 53.4 Hz, *i*-Mes), 91.5 (d, ³J_{PC} = 10.0 Hz, ≡CPh), 91.0 (d, ¹J_{PC} = 59.1 Hz, OC), 89.6 (d, ²J_{PC} = 12.4 Hz, C≡), 41.0 (d, ²J_{PC} = 2.6 Hz, ^oC(CH₃)₃), 37.8 (d, ³J_{PC} = 7.2 Hz, C(CH₃)₃), 28.8 (d, ⁴J_{PC} = 1.1 Hz, C(CH₃)₃), 25.9 (br, ^oC(CH₃)₃), 25.5 (br d, ³J_{PC} = 6.1 Hz), 23.2 (d, ³J_{PC} = 8.5 Hz)(*o*-CH₃-Mes), 21.52 (d, ⁵J_{PC} = 1.4 Hz, *p*-CH₃-Mes), [C₆F₅ are listed].**³¹P{¹H} NMR** (243 MHz, 299 K, CD₂Cl₂): (R*,R*)-19 δ = -23.4 (v_{1/2} ~ 37 Hz). (R*,S*)-19 δ = -3.1 (v_{1/2} ~ 33 Hz).**³¹P NMR** (243 MHz, 299 K, CD₂Cl₂): (R*,R*)-19 δ = -23.4 (dd, ¹J_{PH} = 456.6 Hz, ³J_{PH} = 58.3 Hz). (R*,S*)-19 δ = -3.1 (dd, ¹J_{PH} = 470.7 Hz, ³J_{PH} = 58.2 Hz).**¹¹B{¹H} NMR** (192 MHz, 299 K, CD₂Cl₂): (R*,R*), (R*,S*)-19 δ = 1.9 (v_{1/2} ~ 70 Hz).**¹⁹F NMR** (470 MHz, 299 K, CD₂Cl₂): (R*,R*)-19 δ = -132.3 (m, 2F, *o*), -162.0 (t, ³J_{FF} = 20.0 Hz, 1F, *p*), -167.2 (m, 2F, *m*)(C₆F₅)[Δδ¹⁹F_{*m,p*} = 5.2], -133.4 (m, 2F, *o*), -160.2 (t, ³J_{FF} = 20.2 Hz, 1F, *p*), -165.9 (m, 2F, *m*)(C₆F₅)[Δδ¹⁹F_{*m,p*} = 5.7]. (R*,S*)-19 δ = -131.9 (m, 2F, *o*), -161.6 (t, ³J_{FF} = 20.0 Hz, 1F, *p*), -165.7 (m, 2F, *m*)(C₆F₅)[Δδ¹⁹F_{*m,p*} = 4.1], -133.0 (m, 2F, *o*), -162.8 (t, ³J_{FF} = 20.0 Hz, 1F, *p*), -167.3 (m, 2F, *m*)(C₆F₅)[Δδ¹⁹F_{*m,p*} = 4.5].**Figure S77.** ¹H NMR (500 MHz, 299 K, CD₂Cl₂) spectrum of compound 19.

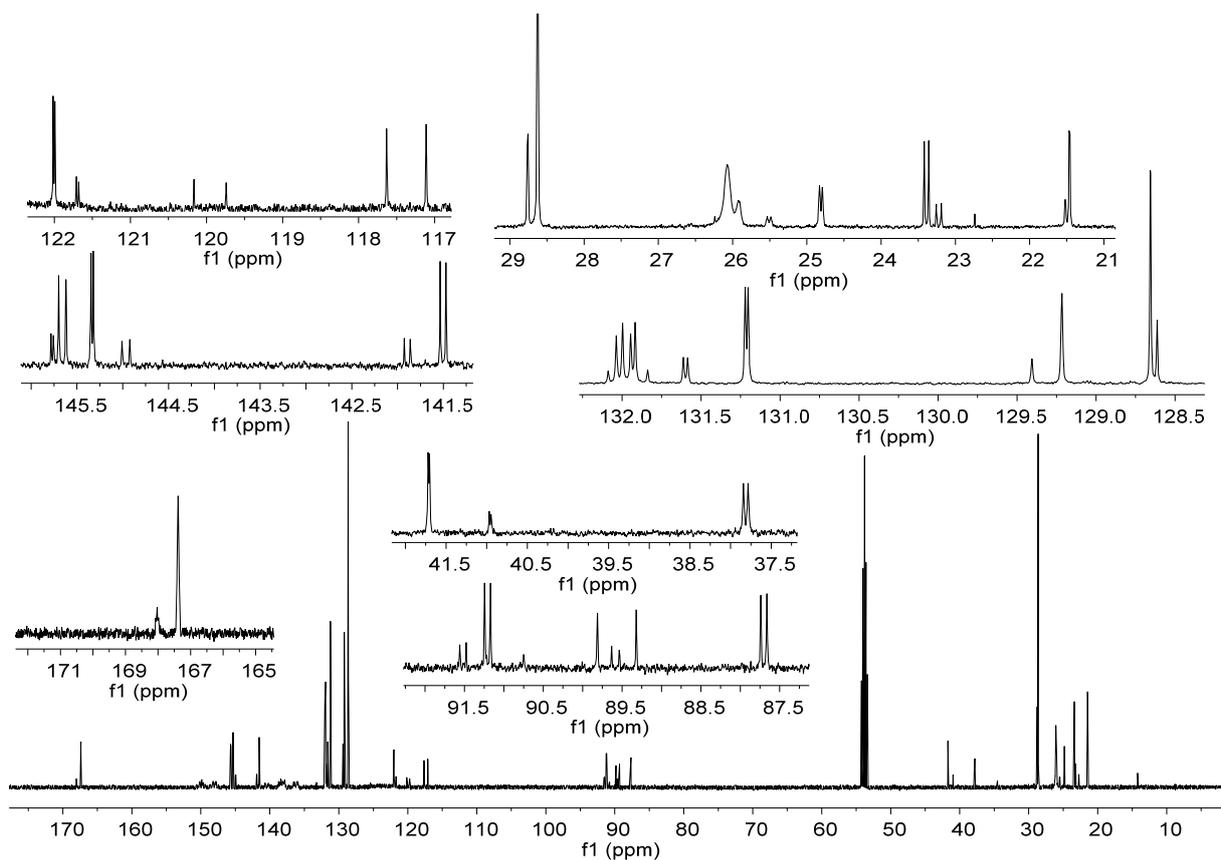


Figure S78. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 299 K, CD_2Cl_2) spectrum of compound 19.

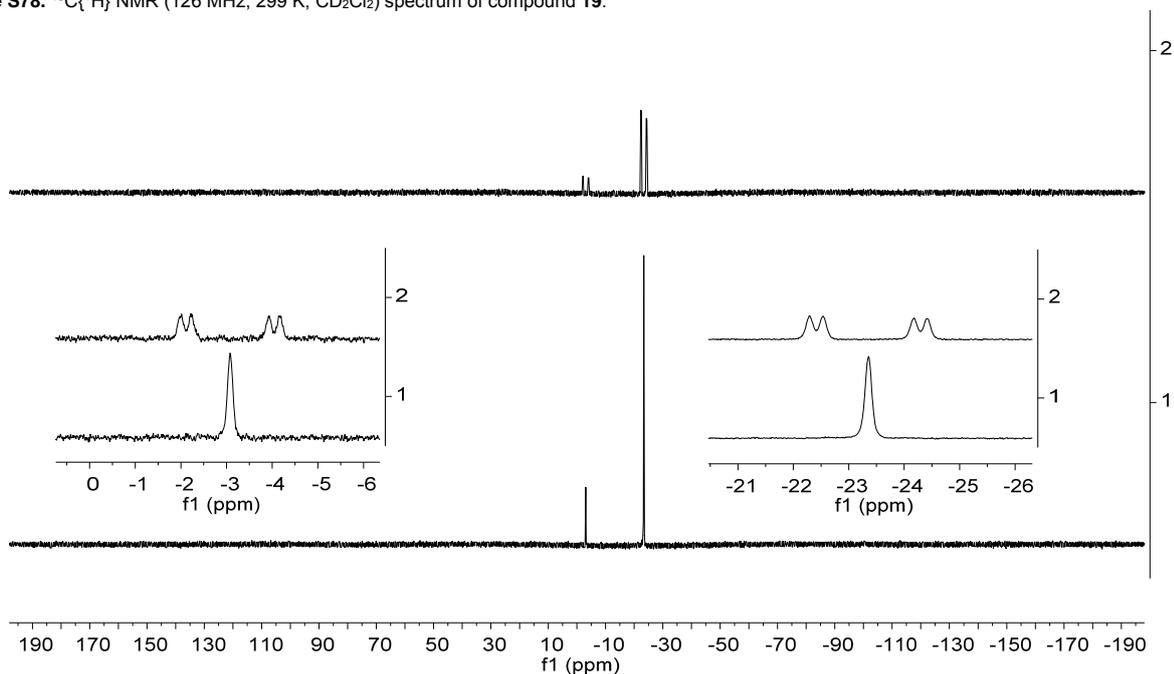


Figure S79. (1) $^{31}\text{P}\{^1\text{H}\}$ and (2) ^{31}P NMR (243 MHz, 299 K, CD_2Cl_2) spectra of compound 19.

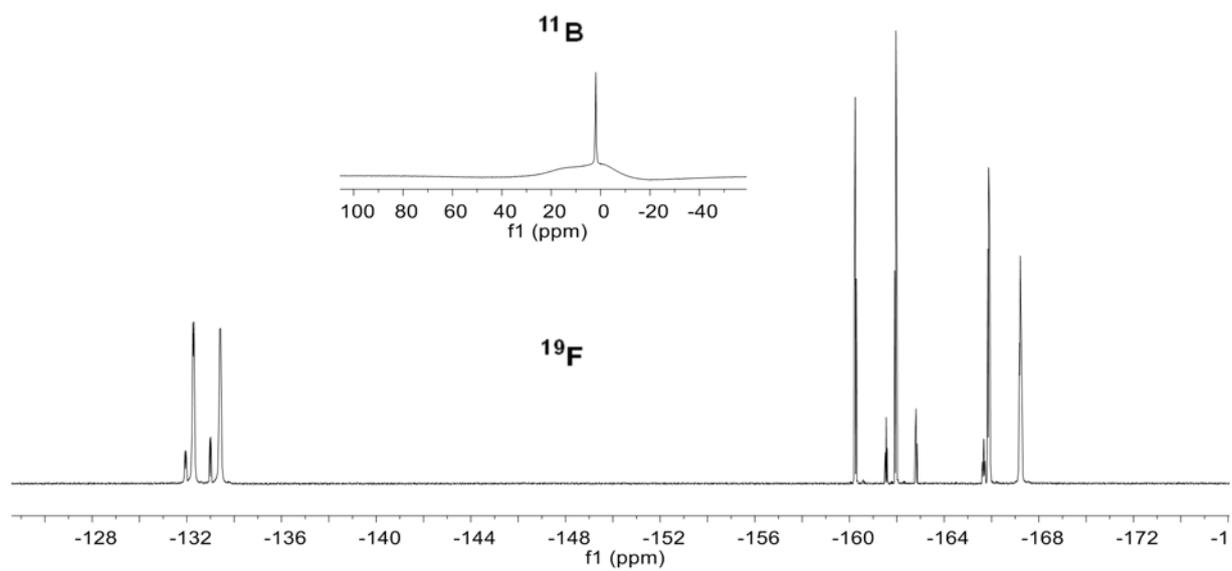
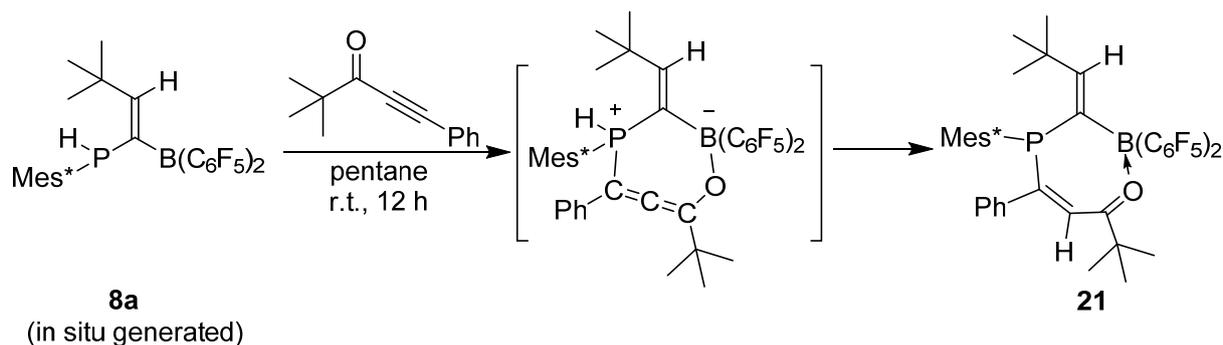


Figure S80. ^{19}F (470 MHz, 299 K, CD_2Cl_2), and $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectra of compound **19**.

b) Preparation of compound 21



Scheme S17

After stirring a mixture of compound **7a** (180 mg, 0.5 mmol) and $\text{HB}(\text{C}_6\text{F}_5)_2$ (173 mg, 0.5 mmol) in pentane (3 mL) at room temperature for 1 h, the resulting red suspension was filtered to give a clear red solution. Then one equiv. of 4,4-dimethyl-1-phenylpent-1-yn-3-one (93 mg, 0.5 mmol) was added and after stirring for 12 h a dark purple suspension was formed which was filtered. The filtrate was stored at -35°C to give dark red crystal. Yield: 339 mg, 76 %.

Elemental analysis: calc. for $\text{C}_{49}\text{H}_{54}\text{PBOF}_{10}$ (0.5 CH_2Cl_2): C, 63.71; H, 5.94. Found: C, 63.98; H, 5.90.

Melting point: 183°C .

[Mes*: 2,4,6-tri-*tert*-butylphenyl]

^1H NMR (600 MHz, 299 K, CD_2Cl_2 , 5.32 ppm): δ = 7.44 (d, $^4J_{\text{PH}} = 4.1$ Hz, 2H, *m*-Mes*), 6.99 (m, 1H, *p*-Ph), 6.83 (m, 2H, *m*-Ph), 6.07 (d, $^3J_{\text{PH}} = 30.3$ Hz, 1H, $^{\text{CO}}\text{=CH}$), 5.97 (m, 2H, *o*-Ph), 5.77 (d, $^3J_{\text{PH}} = 72.2$ Hz, 1H, $^{\text{=CH}}$), 1.39 (s, 18H, *o*- $\text{C}(\text{CH}_3)_3$ -Mes*), 1.31 (s, 9H, *p*- $\text{C}(\text{CH}_3)_3$ -Mes*), 1.20 (s, 9H, $^{\text{CO}}\text{C}(\text{CH}_3)_3$), 0.89 (s, 9H, $\text{C}(\text{CH}_3)_3$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, CD_2Cl_2 , 53.8 ppm): δ = 199.3 (d, $^3J_{\text{PC}} = 13.3$ Hz, $\text{C}=\text{O}$), 168.4 (d, $^1J_{\text{PC}} = 63.9$ Hz, $\text{PC}=\text{C}$), 157.6 (d, $^2J_{\text{PC}} = 6.2$ Hz, *o*-Mes*), 154.9 (d, $^4J_{\text{PC}} = 3.2$ Hz, *p*-Mes*), 152.5 (d, $^2J_{\text{PC}} = 12.0$ Hz, $^{\text{=CH}}$), 148.5 (dm, $^1J_{\text{FC}} \sim 244$ Hz, C_6F_5), 143.1 (d, $^2J_{\text{PC}} = 2.9$ Hz, *i*-Ph), 139.7 (dm, $^1J_{\text{FC}} \sim 250$ Hz, C_6F_5), 137.3 (dm, $^1J_{\text{FC}} \sim 248$ Hz, C_6F_5), 129.8 (br, $\text{BC}=\text{C}$), 128.3 (d, $^3J_{\text{PC}} = 12.6$ Hz, *o*-Ph), 127.9 (d, $^5J_{\text{PC}} = 3.5$ Hz, *p*-Ph), 127.8 (d, $^4J_{\text{PC}} = 1.8$ Hz, *m*-Ph), 126.1 (d, $^3J_{\text{PC}} = 12.0$ Hz, *m*-Mes*), 121.5 (br m, *i*- C_6F_5), 120.8 (d, $^1J_{\text{PC}} = 41.7$ Hz, *i*-Mes*), 116.3 (d, $^2J_{\text{PC}} = 5.5$ Hz, $^{\text{CO}}\text{=CH}$), 42.0 (d, $^4J_{\text{PC}} = 5.9$ Hz, $^{\text{CO}}\text{C}(\text{CH}_3)_3$), 40.2 (d, $^3J_{\text{PC}} = 2.9$ Hz, *o*- $\text{C}(\text{CH}_3)_3$ -Mes*), 38.7 (d, $^3J_{\text{PC}} = 9.4$ Hz, $\text{C}(\text{CH}_3)_3$), 35.4 (d, $^5J_{\text{PC}} = 0.5$ Hz, *p*- $\text{C}(\text{CH}_3)_3$ -Mes*), 34.3 (*o*- $\text{C}(\text{CH}_3)_3$ -Mes*), 31.1 (*p*- $\text{C}(\text{CH}_3)_3$ -Mes*), 30.8 (d, $^4J_{\text{PC}} = 3.1$ Hz, $\text{C}(\text{CH}_3)_3$), 28.9 (d, $^5J_{\text{PC}} = 6.0$ Hz, $^{\text{CO}}\text{C}(\text{CH}_3)_3$).

$^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, 299 K, CD_2Cl_2): δ = 60.2 ($\nu_{1/2} \sim 22$ Hz).

^{31}P NMR (243 MHz, 299 K, CD_2Cl_2): δ = 60.2 (br dd, $^3J_{\text{PH}} = 72.2$ Hz, $^3J_{\text{PH}} = 30.3$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, CD_2Cl_2): δ = 3.9 ($\nu_{1/2} \sim 190$ Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = -131.7 (m, 2F, *o*- C_6F_5), -159.7 (t, $^3J_{\text{FF}} = 20.4$ Hz, 1F, *p*- C_6F_5), -165.7 (m, 2F, *m*- C_6F_5). [$\Delta\delta^{19}\text{F}_{m,p} = 6.0$].

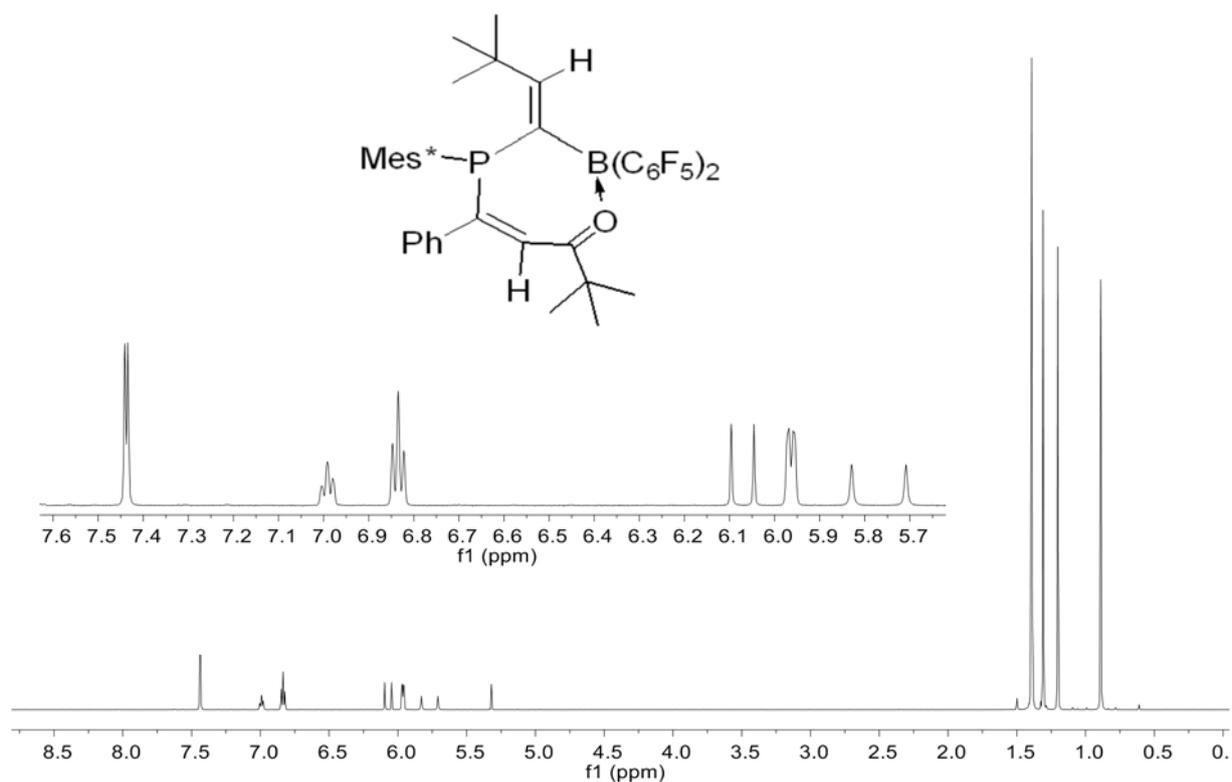


Figure S81. ^1H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound 21.

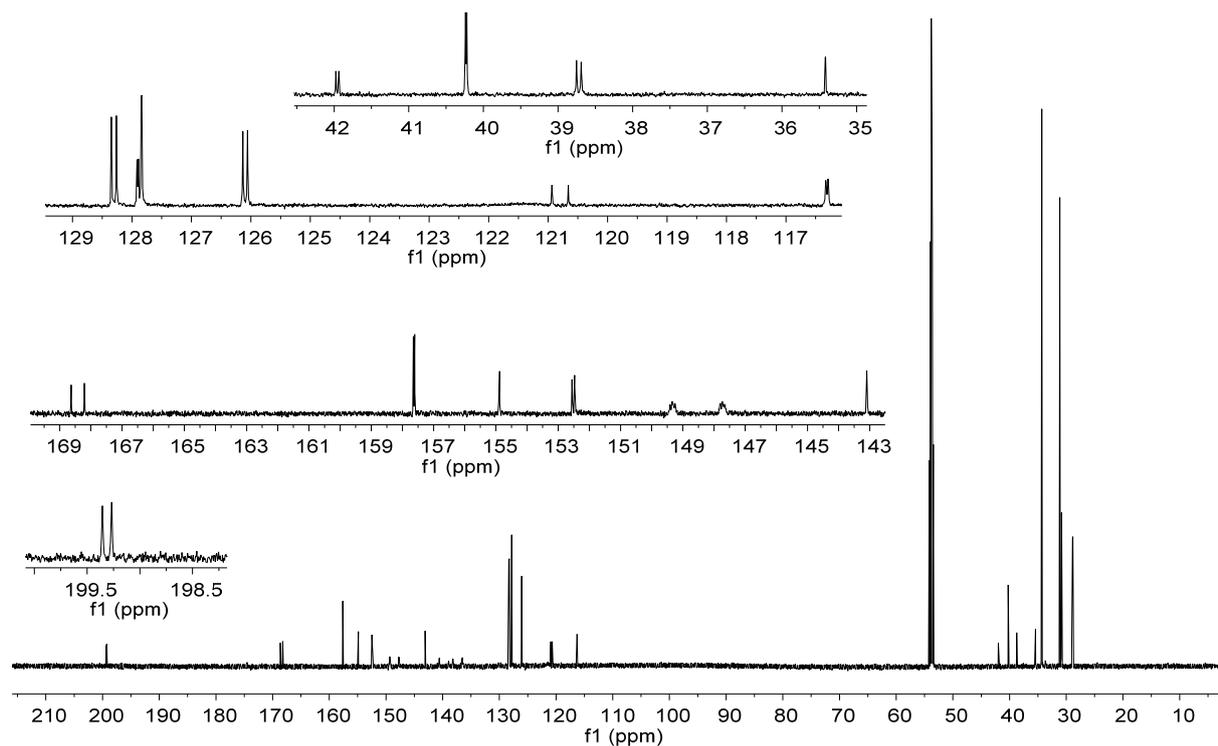


Figure S82. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound 21.

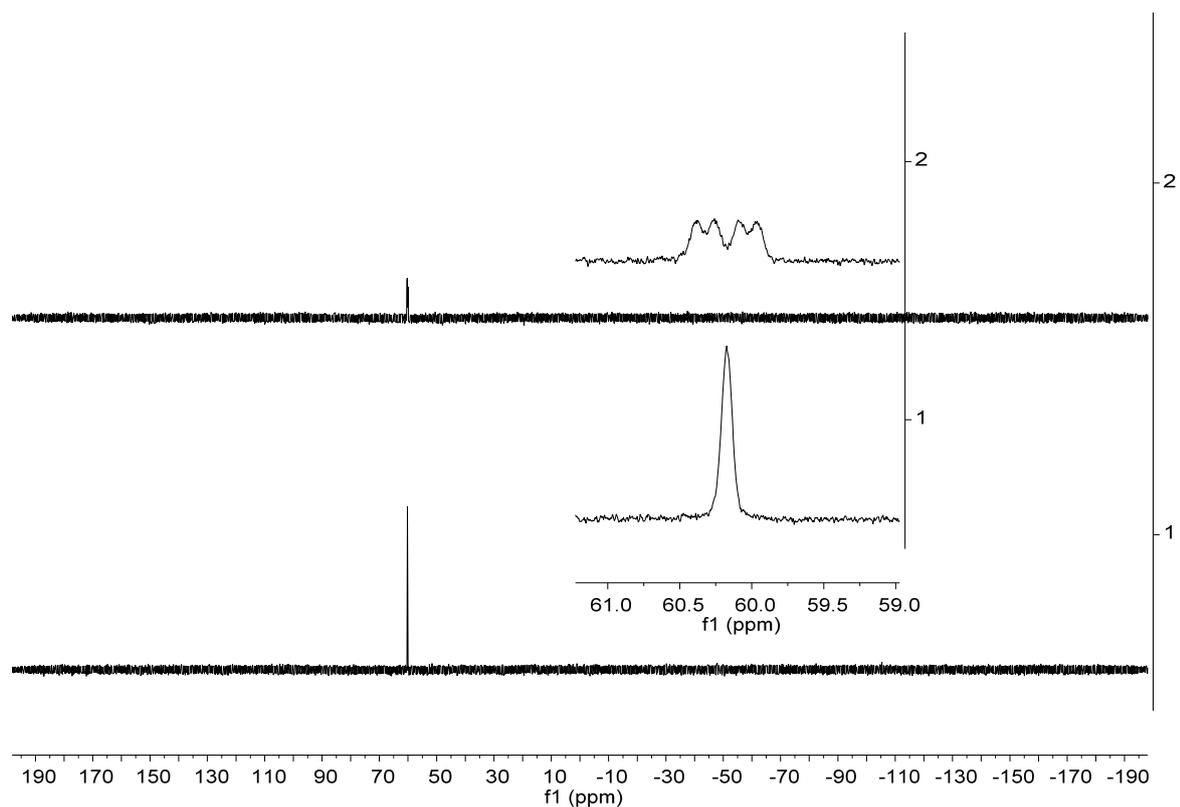


Figure S83. (1) $^{31}\text{P}\{^1\text{H}\}$ and (2) ^{31}P NMR (243 MHz, 299 K, CD_2Cl_2) spectra of compound 21.

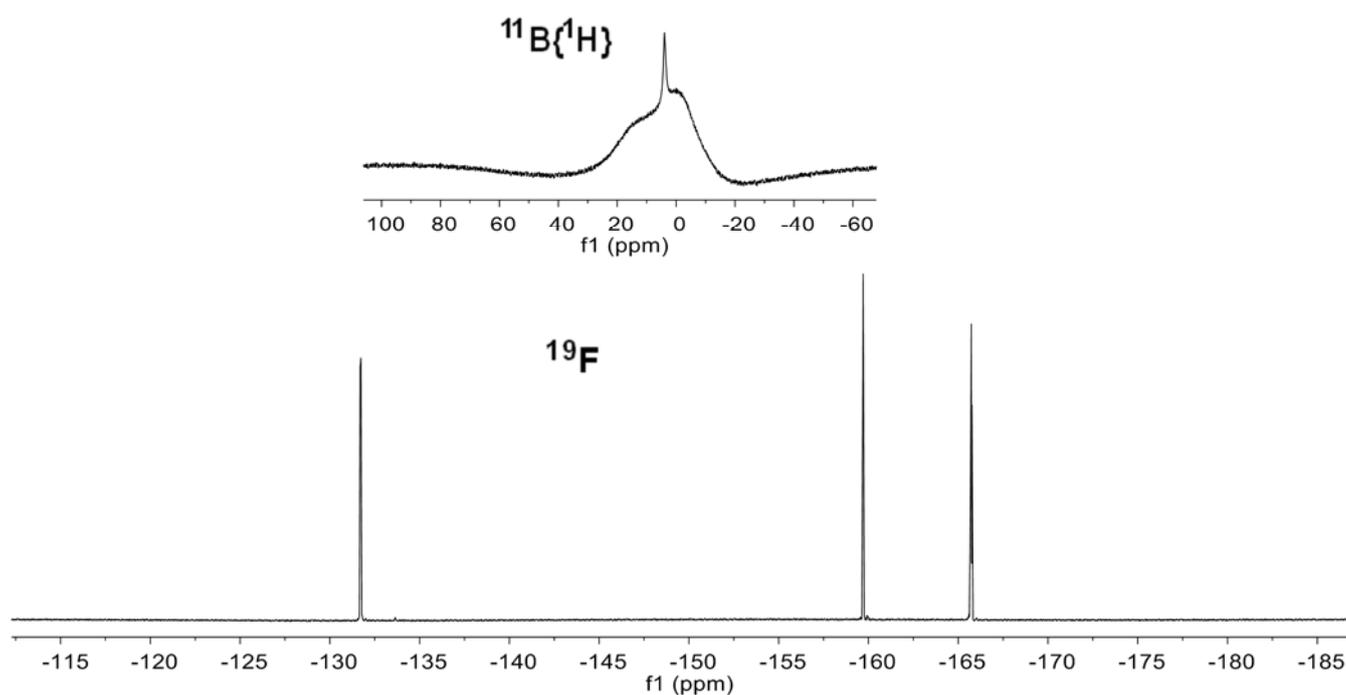


Figure S84. ^{19}F (564 MHz, 299 K, CD_2Cl_2) and $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectra of compound 21.

Crystals of compound **21** suitable for the X-ray crystal structure analysis were obtained from a solution of the purple solid in CH₂Cl₂ and pentane (ratio ca. 1 : 5) at -35 °C.

X-ray crystal structure analysis of compound 21: A specimen of C₄₉H₅₄BF₁₀OP · ½ x CH₂Cl₂, approximate dimensions 0.030 mm x 0.100 mm x 0.140 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a triclinic unit cell yielded a total of 34235 reflections to a maximum θ angle of 66.76° (0.84 Å resolution), of which 8071 were independent (average redundancy 4.242, completeness = 97.5%, $R_{\text{int}} = 6.08\%$, $R_{\text{sig}} = 5.32\%$) and 6105 (75.64%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 11.1681(4)$ Å, $b = 11.2709(4)$ Å, $c = 19.6602(8)$ Å, $\alpha = 76.834(2)^\circ$, $\beta = 75.265(2)^\circ$, $\gamma = 84.210(2)^\circ$, volume = 2328.00(15) Å³, are based upon the refinement of the XYZ-centroids of reflections above 20 $\sigma(I)$. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7960 and 0.9500. The final anisotropic full-matrix least-squares refinement on F^2 with 623 variables converged at $R1 = 5.41\%$, for the observed data and $wR2 = 15.21\%$ for all data. The goodness-of-fit was 1.056. The largest peak in the final difference electron density synthesis was 0.732 e/Å³ and the largest hole was -1.022 e/Å³ with an RMS deviation of 0.064 e/Å³. On the basis of the final model, the calculated density was 1.331 g/cm³ and $F(000)$, 974 e⁻.

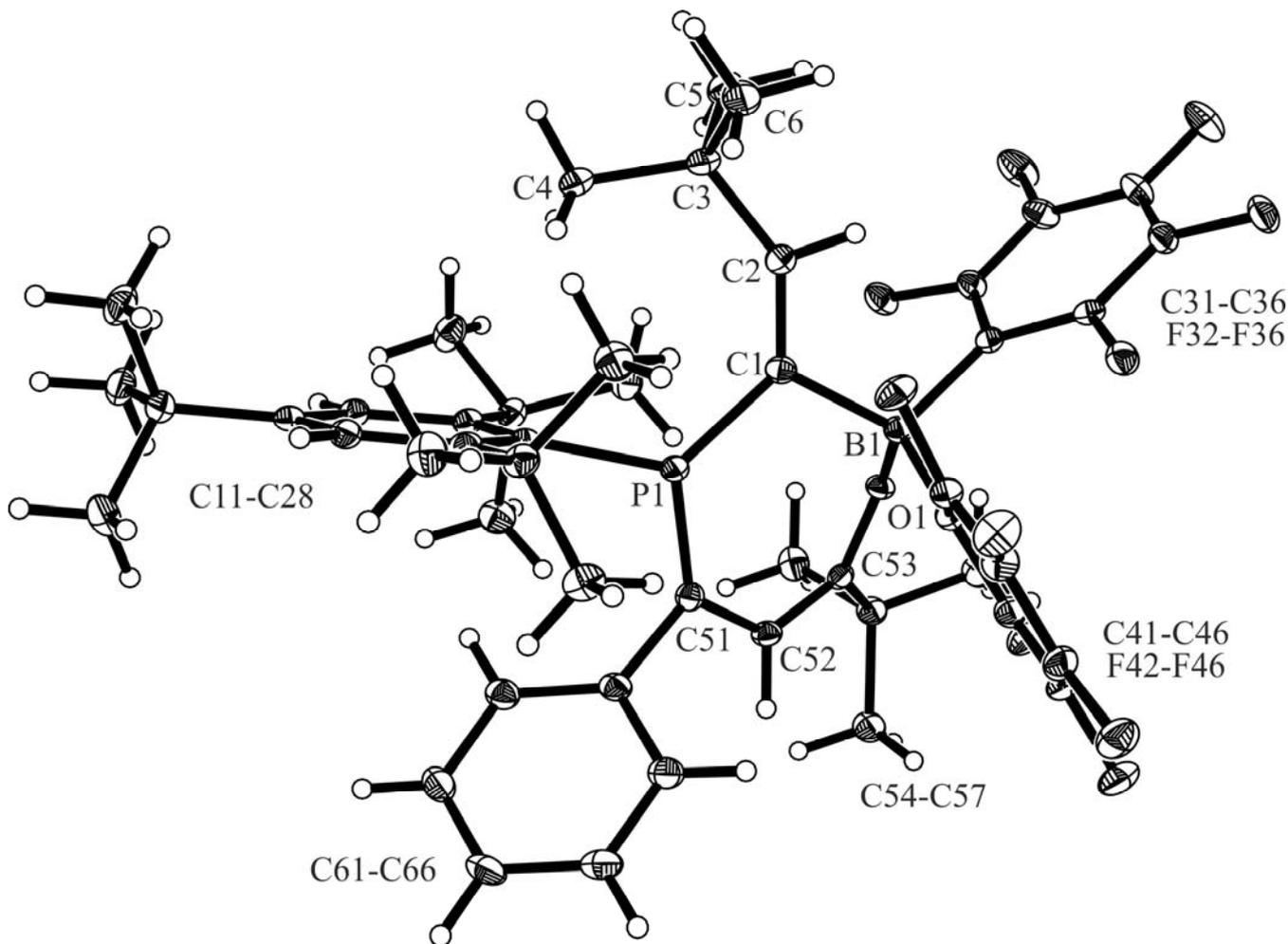
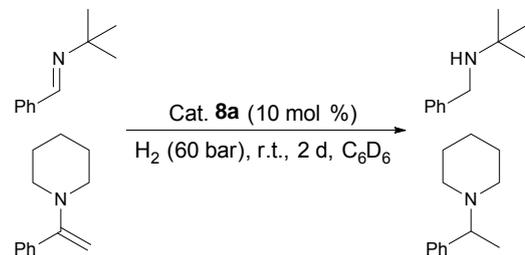


Figure S85. A view of the molecular structure of compound 21.

Procedure for catalytic hydrogenation of imine or enamine using compounds **8a** or **8b**

In an Argon glovebox, compound **8a** (14.1 mg, 0.02 mmol) or **8b** (11.6 mg, 0.02 mmol) and *N*-benzylidene-*tert*-butylamine (32.2 mg, 0.2 mmol) or 1-(1-phenylethenyl)piperidine (37.4 mg, 0.2 mmol) was dissolved in 0.5 mL of C₆D₆, which was then transferred to autoclave. The catalytic reaction was stirred at room temperature for 2 days under H₂ (60 bar) atmosphere. Product conversion was estimated by ¹H NMR spectroscopy (integration of a suitable signal vs remaining starting material).

Table S1. Catalytic Hydrogenation Results.



Entry	Catalyst	Substrate	Conversion (%)
1	8a	PhCH=N ^t Bu	46
2	8a	Ph(C ₅ H ₁₀ N)C=CH ₂	52
3	8b	PhCH=N ^t Bu	0
4	8b	Ph(C ₅ H ₁₀ N)C=CH ₂	0

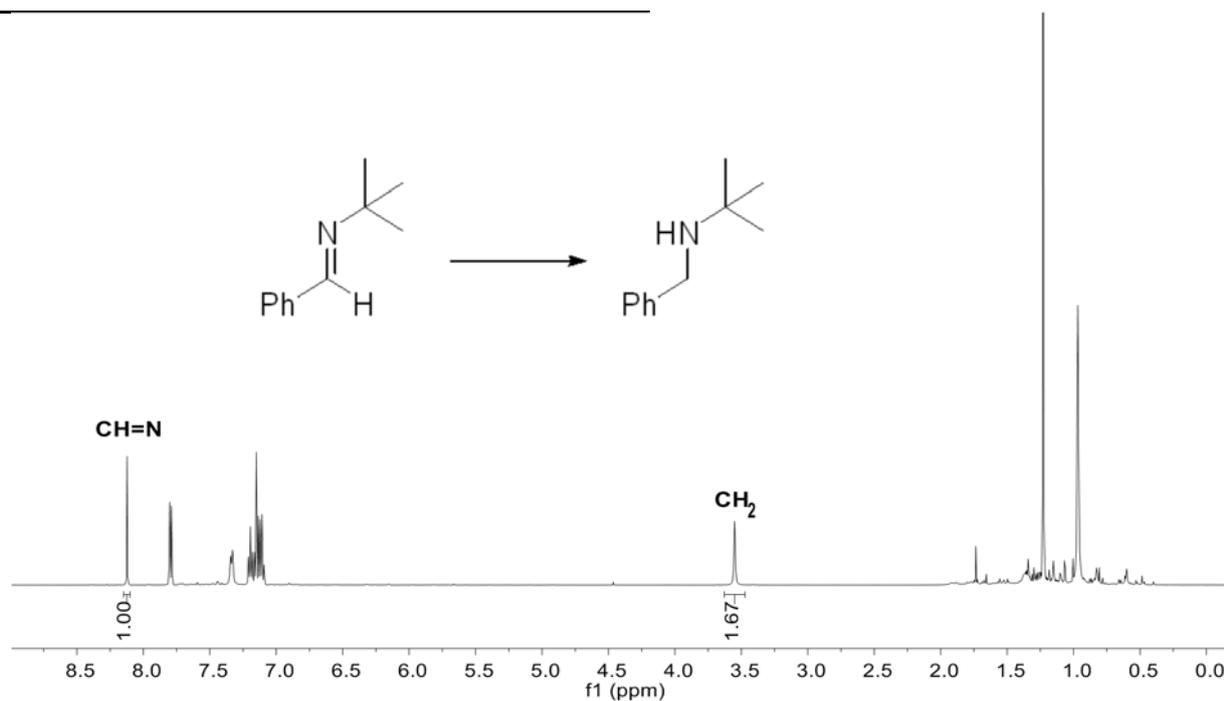


Figure S86. ¹H NMR (500 MHz, 299 K, C₆D₆) spectrum of entry 1.

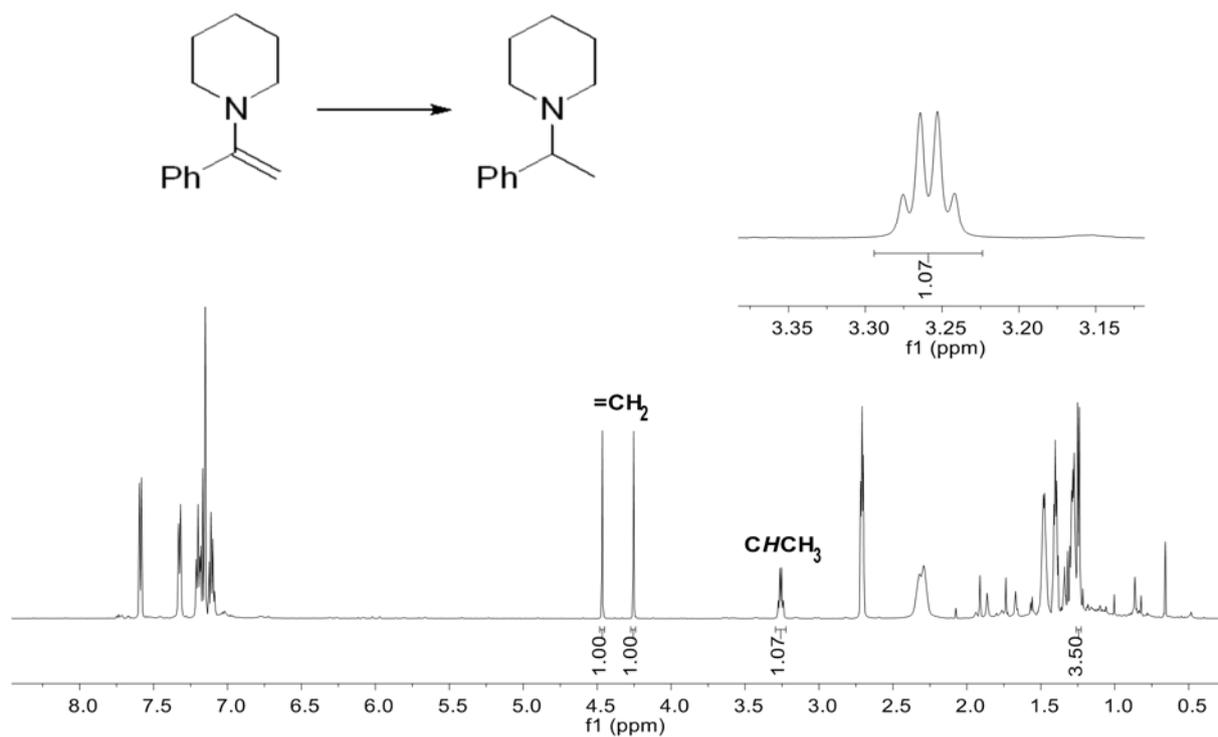


Figure S87. ¹H NMR (500 MHz, 299 K, C₆D₆) spectrum of entry 2.

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