Phosphole Formation by 1,1-Carboboration - Reactions of Bis-alkynyl Phosphanes with a Frustrated P/B Lewis Pair

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[†] X-ray single crystal structure analysis

Supporting Information

General Procedures. 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. Solvents were dried and stored under an argon atmosphere. The following instruments were used for physical characterization of the compounds: NMR spectra: *Varian* Inova 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{19}F: 470 MHz, ^{11}B: 160 MHz, ^{31}P: 202 MHz), *Varian* UnityPlus 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{19}F: 564 MHz, ^{11}B: 192 MHz, ^{31}P: 243 MHz). ^{1}H NMR and ^{13}C NMR: chemical shift δ is given relative to TMS and referenced to the solvent signal. ^{19}F NMT: chemical shift δ is given relative to $CFCl_3$ (external reference); ^{11}B NMR: chemical shift δ is given relative to $BF_3{\cdot}Et_2O$ (external reference). NMR assignments are supported by additional 2D NMR experiments. Elemental analyses were performed on a *Elementar Vario El III*. IR spectra were recorded on a *Varian* 2100 FT-IR (Excalibur Series). Melting points were obtained with a DSC Q20 (*TA Instruments*).

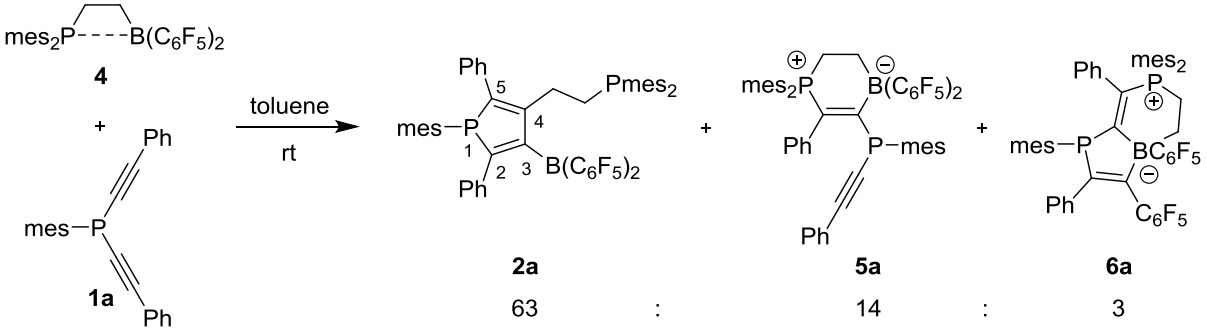
X-Ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (Nonius B.V., 1998); data reduction Denzo-SMN (Z. Otwinowski and W. Minor, *Methods Enzymol.* 1997, **276**, 307.); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski and W. Minor, *Acta Crystallogr*. 2003, **A59**, 228.); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*. 1990, **A46**, 467.); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. 2008, **A64**, 112.) and graphics, XP (BrukerAXS, 2000). Thermals ellipsoids are shown with 30% probability, *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: For the compound **5a** one badly disordered benzene molecule was found in the asymmetric unit. The program SQUEEZE (A. L. Spek, *J. Appl. Cryst*., 2003, **36**, 7.) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecule. For compound **6b** one ^{i}Pr group was found disordered over two positions. Compound **9a** presents ^{t}Bu group disordered over

two positions and one dichloromethane molecule in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability.

The CCDC (Cambridge Crystallographic Data Centre) deposition numbers are 1416705 to 1416707.

Materials. Bis(pentafluorophenyl)borane[1], bis(phenylethynyl)mesitylphosphane[2] (**1a**), bis(pentynyl)-mesitylphosphane[2] (**1c**), bis(phenylethynyl)(2,4,6-triisopropylphenyl)phosphane[2] (**1b**), bis(pentynyl)(2,4,6-triisopropylphenyl)phosphane[2] (**1d**), dimesitylvinylphosphane[3] and {2-[bis(pentafluorophenyl)boryl]ethyl}dimesitylphosphane[3] (**4**) were prepared according to modified literature procedures.

Reaction of P/B-system 4 with bis(phenylethynyl)mesitylphosphane (1a)



The in situ reaction of the P/B-system **4** (64.2 mg, 0.1 mmol, 1 eq) with bis(phenylethynyl)mesitylphosphane (**1a**) (35.2 mg, 0.1 mmol, 1 eq) in C_6D_6 (1 mL) at 70 °C for 4 hours gave a mixture of compound **2a**, **1a**, **5a** and **6a** (ratio ca. 63 : 20 : 14 : 3 (^{31}P)) and traces of not identified compounds.

[Comment: comparable results were obtained using the same amounts of the reactants but the reaction was carried out in toluene (3 mL) at room temperature for 4 days or alternatively in *n*-pentane (3 mL) at 70 °C for one day]

Compound 2a:

^{1}H NMR (500 MHz, 299 K, C_6D_6): δ^1H = 7.24 (m, 2H, *o*-Ph^5), 7.20 (m, 2H, *o*-Ph^2), 6.96 (m, 2H, *m*-Ph^5), 6.85 (m, 1H, *p*-Ph^5), 6.78 (m, 2H, *m*-Ph^2), 6.61 (m, 1H, *p*-Ph^2), 6.53 (d, $^4J_{PH}$ = 2.4 Hz, 4H, *m*-mes), 6.34 (d, $^4J_{PH}$ = 3.1 Hz, 2H, *m*-mes^1), 2.76 (m, 2H, PCH_2), 2.61 (m, 2H, CH_2), 2.34 (s, 6H, *o*-$CH_3^{mes,1}$), 2.14 (s, 12H, *o*-CH_3^{mes}), 2.02 (s, 6H, *p*-CH_3^{mes}), 1.68 (s, 3H, *p*-$CH_3^{mes,1}$).

^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6): δ^{13}C = 166.9 (br, C2), 151.3 (br, C3), 148.4 (dd, J_{PC} = 17.0 Hz, J_{PC} = 15.3 Hz, C4), 146.3 (d, $^2J_{PC}$ = 15.4 Hz, *o*-mes^1), 145.4 (d, $^1J_{PC}$ = 8.3 Hz, C5), 141.7 (d, $^2J_{PC}$ = 13.3 Hz, *o*-

[1] a) J. D. Parks, R. E. V. H. Spence and W. E. Piers, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 809; W. E. Piers, J. D. Parks and G. P. A. Yap, *Organometallics* 1998, **17**, 5492.

[2] H. Lang and L. Zsolnai, *Chem. Ber*., 1991, **124**, 259; J. Möbus, Q. Bonnin, K. Ueda, R. Fröhlich, K. Itami, G. Kehr and G. Erker, *Angew. Chem. Int. Ed*. 2012, **51**, 1954; J. Möbus, K. Malessa, H. Frisch, C. G. Daniliuc, R. Fröhlich, G. Kehr and G. Erker, *Heteroat. Chem*., 2014, **25**, 396.

[3] P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme and D. W. Stephan, *Chem. Commun*. 2007, 5072.

mes), 141.3 (d, $^{4}J_{PC}$ = 1.8 Hz, *p*-mes[1]), 139.5 (d, $^{2}J_{PC}$ = 15.8 Hz, *i*-Ph[2]), 137.5 (*p*-mes), 136.9 (d, $^{2}J_{PC}$ = 17.9 Hz, *i*-Ph[5]), 132.8 (d, $^{1}J_{PC}$ = 21.1 Hz, *i*-mes), 130.3 (d, $^{3}J_{PC}$ = 2.8 Hz, *m*-mes), 129.5 (d, $^{3}J_{PC}$ = 6.2 Hz, *m*-mes[1]), 129.3 (d, $^{3}J_{PC}$ = 7.8 Hz, *o*-Ph[5]), 129.2 (d, $^{3}J_{PC}$ = 9.2 Hz, *o*-Ph[2]), 128.7 (*m*-Ph[5]), 128.4 (*m*-Ph[2]), 127.9 (*p*-Ph[2]), 126.8 (*p*-Ph[5]), 122.7 (d, $^{1}J_{PC}$ = 3.4 Hz, *i*-mes[1]), 31.5 (dd, $^{1}J_{PC}$ = 19.0 Hz, *J* = 4.7 Hz, PCH_2), 27.9 (dm, $^{2}J_{PC}$ = 22.2 Hz, CH_2), 23.0 (d, $^{3}J_{PC}$ = 13.1 Hz, *o*-CH_3^{mes}), 22.0 (br d, $^{3}J_{PC}$ = 14.1 Hz, *o*-$CH_3^{mes,1}$), 20.8 (*p*-$CH_3^{mes,1}$), 20.7 (*p*-CH_3^{mes}), [C_6F_5 not listed].

$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, C_6D_6): $\delta^{11}B$ = 60.5 ($\nu_{1/2} \approx 3000$ Hz).

^{19}F NMR (470 MHz, 299 K, C_6D_6): $\delta^{19}F$ = −128.2 (br m, 2F, *o*-C_6F_5), −146.8 (br, 1F, *p*-C_6F_5), −161.5 (br, 2F, *m*-C_6F_5). [$\Delta\delta^{19}F_{p,m}$ = 14.7].

$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, C_6D_6): $\delta^{31}P$ = 16.9 ($\nu_{1/2}$ ~ 10 Hz, 1P, P-1), −21.9 ($\nu_{1/2}$ ~ 15 Hz, 1P, $Pmes_2$).

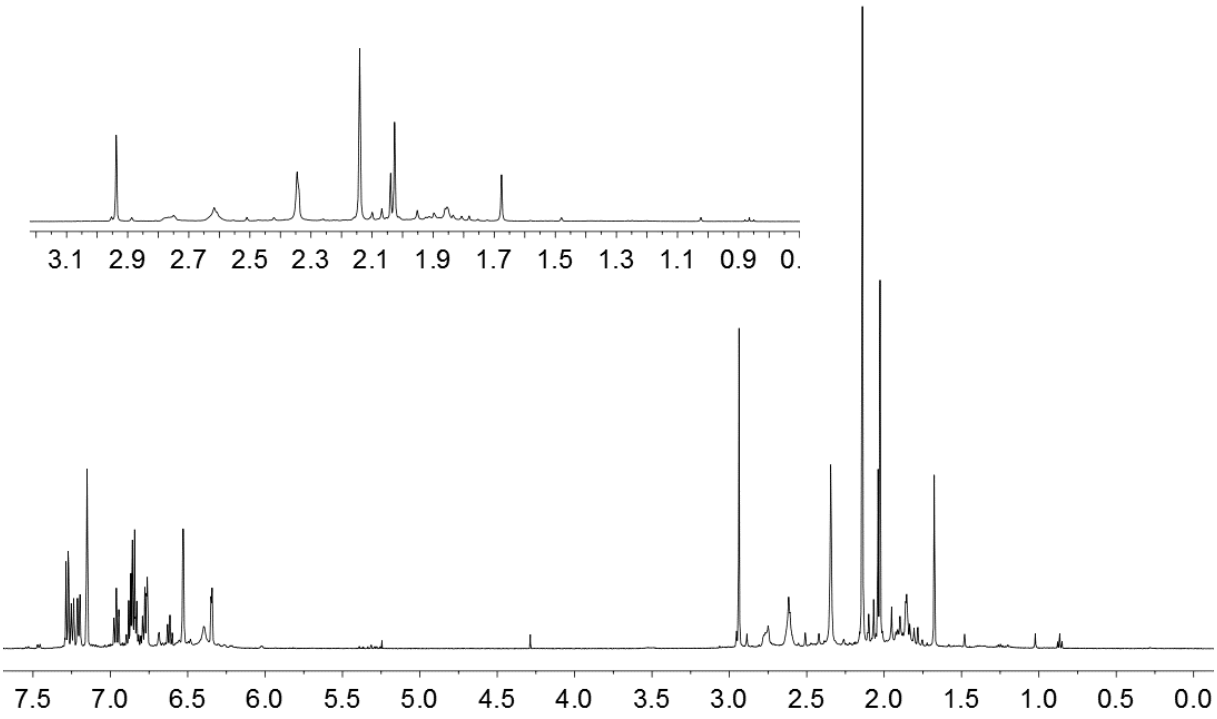
Compound 6a:

[Characterization by selected NMR experiments and in comparison with compound **6b**]

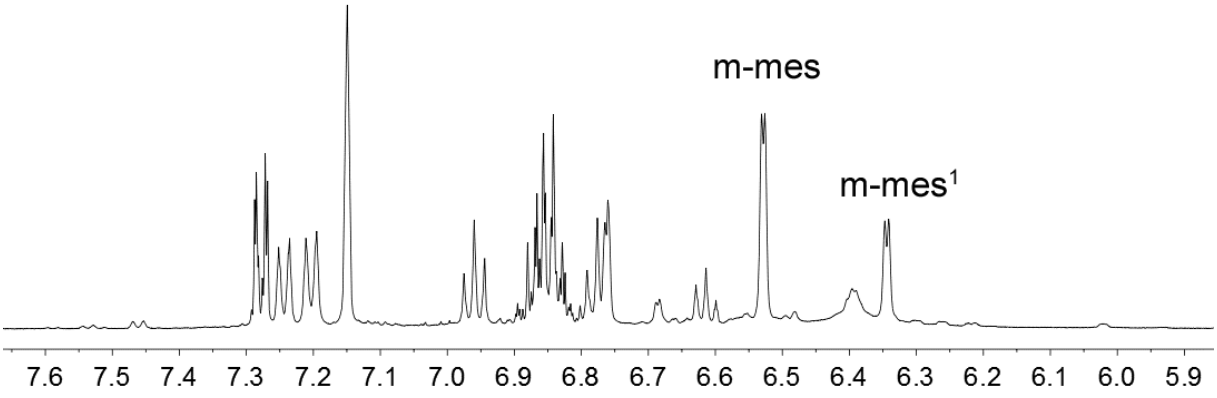
$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, C_6D_6): $\delta^{11}B$ = −7.2 ($\nu_{1/2} \approx 150$ Hz).

^{19}F NMR (470 MHz, 299 K, C_6D_6): $\delta^{19}F^{t}$ = −118.9 (dm, J_{PF} = 224.2 Hz), −136.5 (m), −140.4 (m), −142.2 (m)(each 1F, *o*-C_6F_5), −159.5 (t, $^{3}J_{FF}$ = 20.3 Hz), −160.9 (t, $^{3}J_{FF}$ = 20.8 Hz)(each 1F, *p*-C_6F_5), −163.4 (m), −164.6 (m), −165.2 (m), −165.3 (m)(each 1F, *m*-C_6F_5), [^{t} tentative assignment]

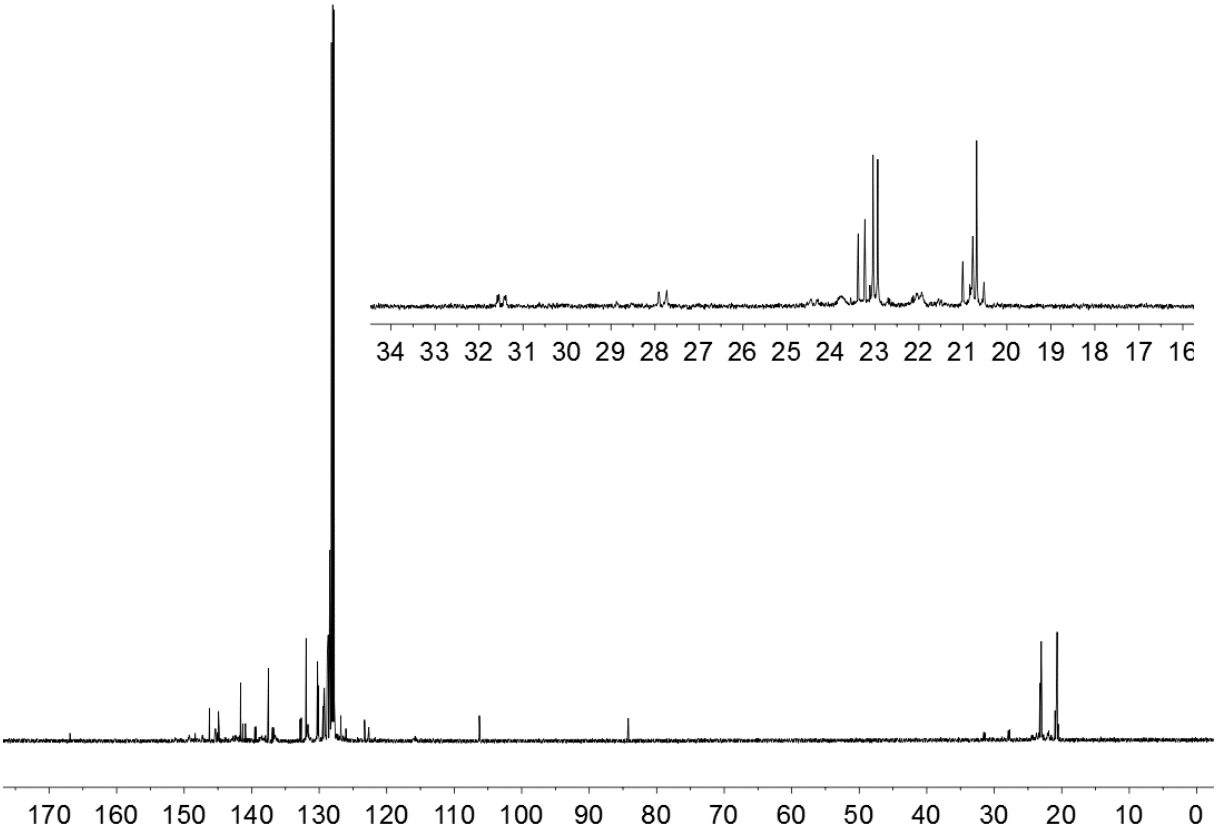
$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, C_6D_6): $\delta^{31}P$ = 38.4 (br d, J_{PF} = 221.3 Hz, 1P, Pmes), −6.0 (m, 1P, $Pmes_2$).



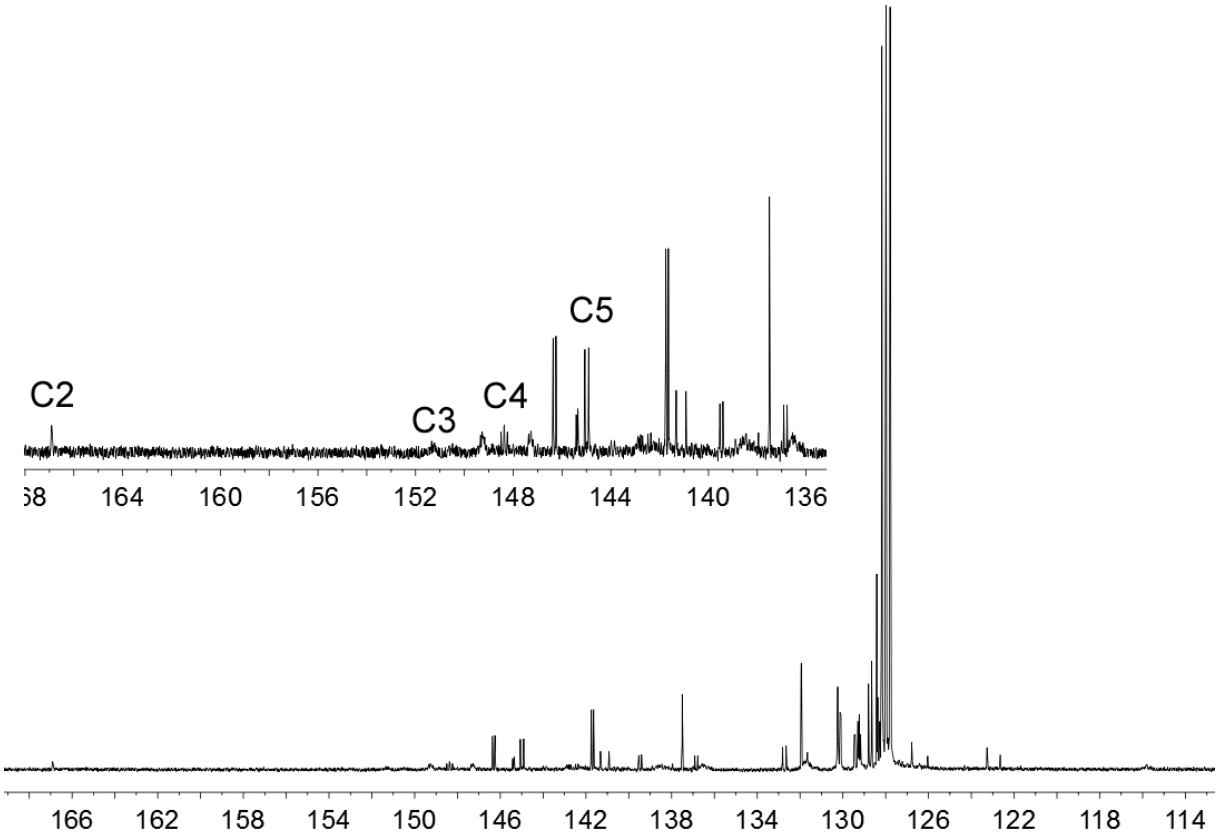
^{1}H NMR (500 MHz, 299 K, C_6D_6) spectrum of the reaction mixture.



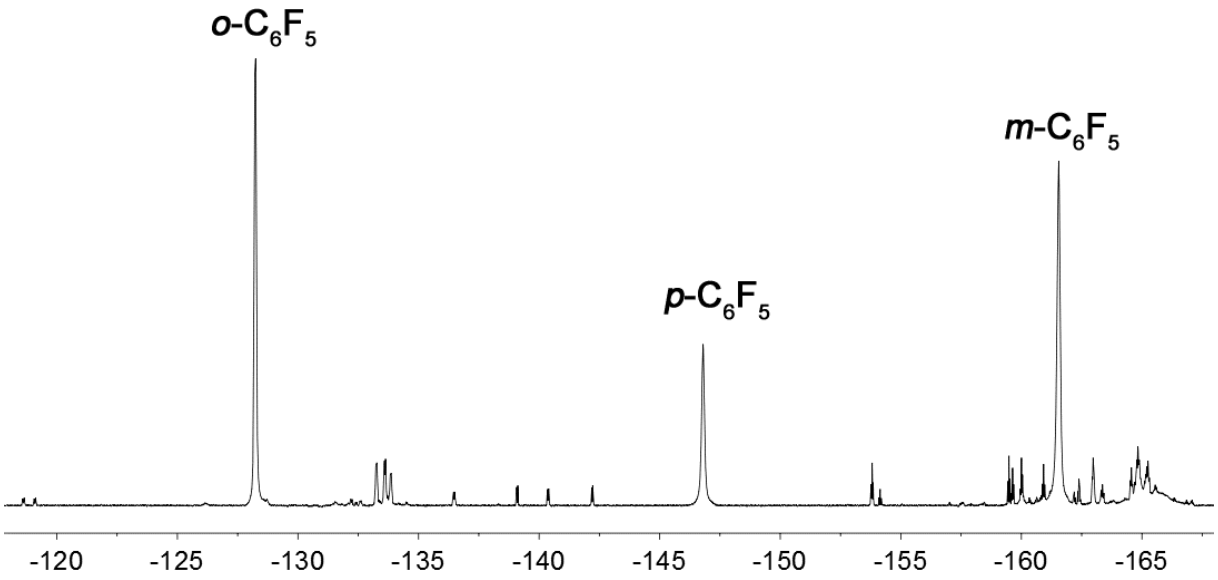
^{1}H NMR (500 MHz, 299 K, C_6D_6) spectrum of the reaction mixture.



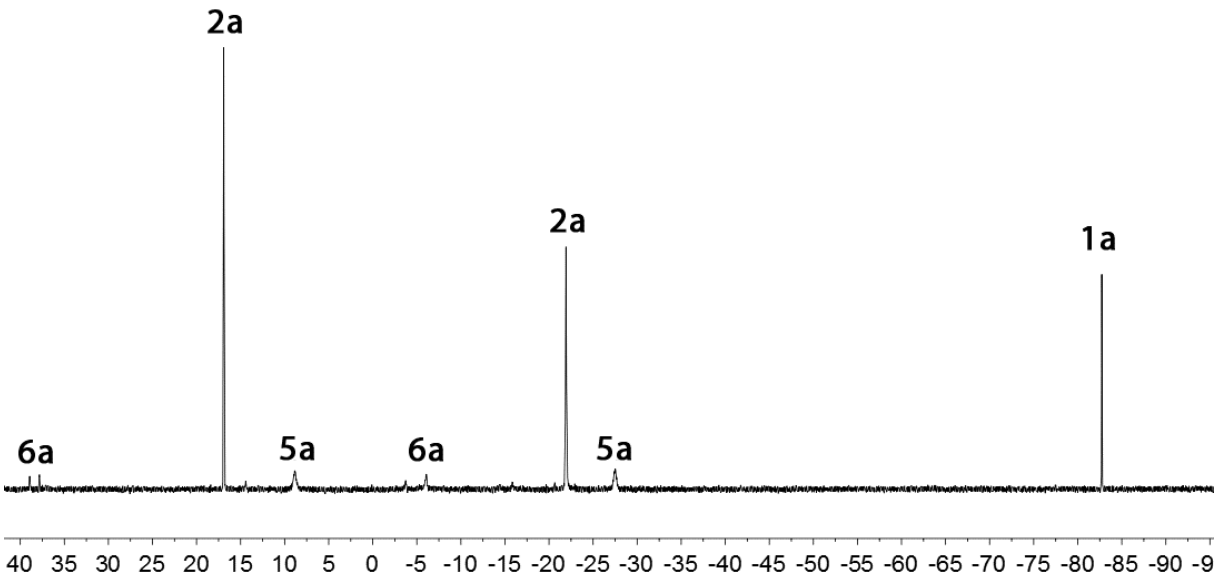
^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6) spectrum of the reaction mixture.



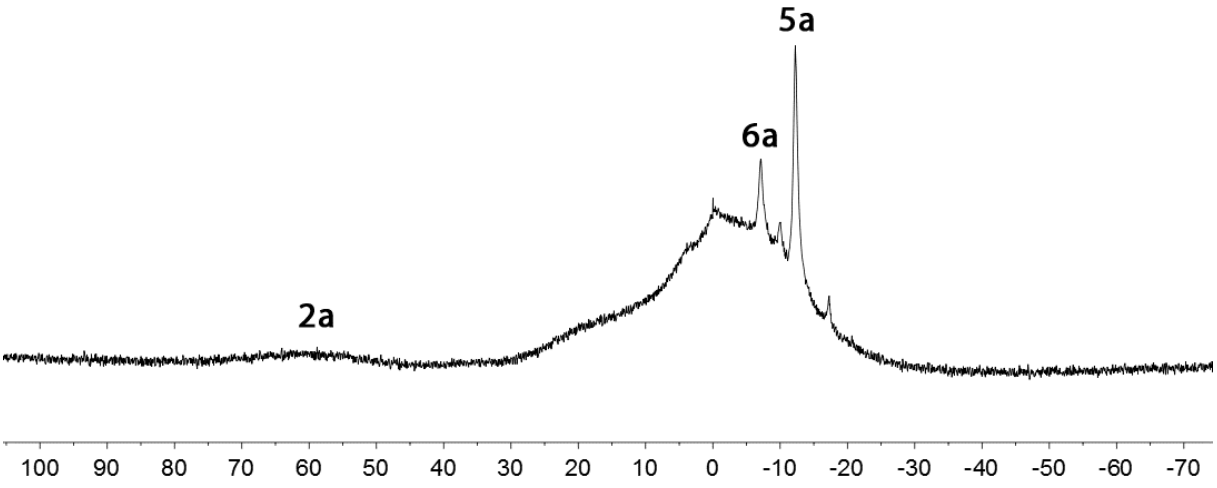
$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, C_6D_6) spectrum of the reaction mixture.



^{19}F NMR (470 MHz, 299 K, C_6D_6) spectrum of the reaction mixture.



$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, C_6D_6) spectrum of the reaction mixture.



$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, C_6D_6) spectrum of the reaction mixture.

Preparation of compound 2a:

A solution of dimesitylvinylphosphane (59 mg, 0.2 mmol, 1 eq) in toluene (2 mL) was added to bis(pentafluorophenyl)borane (69 mg, 0.2 mmol, 1 eq). The obtained solution was stirred for 30 min at room temperature. Subsequently, bis(phenylethynyl)-mesitylphosphane (**1a**) (70 mg, 0.2 mmol, 1 eq) was added to the reaction mixture and the resulting green solution was stirred at room temperature for 4 days. After removal of all volatiles *in vacuo*, the residue was suspended in *n*-pentane (5 mL). The supernatant was separated, dried *in vacuo* to give compound **2a** as a brown solid (93 mg, 0.09 mmol, 47%).

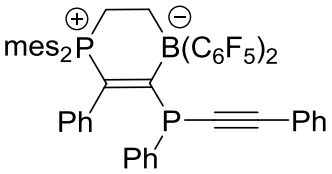
Elemental analysis: calc. for $C_{57}H_{47}BF_{10}P_2$: C: 68.82, H: 4.76; found: C: 69.16, H: 4.90.

IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 4376 (w), 3516 (w), 3433 (w), 3020 (w), 2960 (m), 2921 (m), 2731 (w), 2358 (w), 2176 (w), 1643 (w), 1603 (m), 1513 (s), 1457 (s), 1381 (m), 1313 (w), 1269 (m), 1244 (m), 1080 (m), 1028 (w), 969 (m), 850 (m), 754 (m), 698 (s), 639 (w), 554 (w), 503 (w).

Melting point: 118 °C.

[Comment: the ^{1}H, ^{19}F, ^{31}P NMR resonances of a solution of the brown solid in C_6D_6 were consistent to those given for compound **2a** (*in situ* reaction, see above).]

Characterization of compound 5a



Dimesitylvinylphosphane (30 mg, 0.1 mmol, 1 eq) and bis(pentafluorophenyl)-borane (35 mg, 0.1 mmol, 1 eq) were each dissolved in C_6D_6 (each: 0.5 mL). Then the solution of the phosphane was added to the borane solution and the reaction mixture was stirred for 15 min before bis(phenylethynyl)mesityl-phosphane (**1a**) (35 mg, 0.1 mmol, 1 eq) was added. The reaction mixture was heated at 70 °C for 2 h. After cooling to room temperature the benzene solution was covered with *n*-pentane (3 mL) and crystalline material was formed. The obtained crystals were suitable for the X-ray structure analysis of compound **5a**.

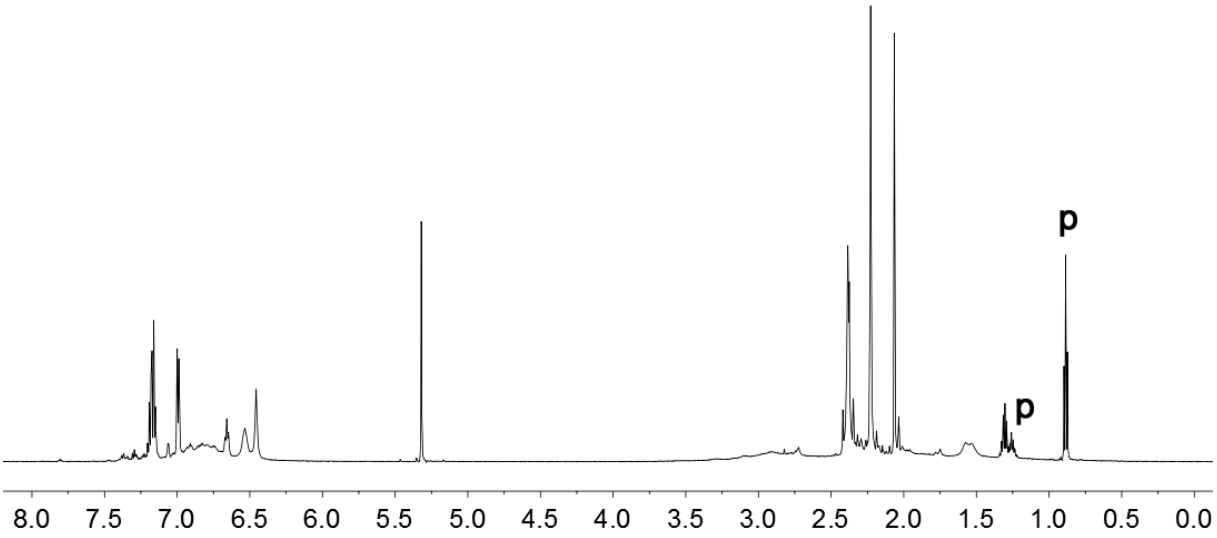
IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3022 (w), 2960 (w), 2923 (w), 2162 (w, $\nu_{C\equiv C}$), 1950 (w), 1641 (m), 1604 (m), 1557 (w), 1513 (s), 1450 (s), 1382 (m), 1269 (m), 1182 (w), 1082 (s), 1030 (w), 976 (s), 925 (w), 847 (s), 791 (w), 757 (m), 701 (m), 638 (w), 599 (w), 554 (w).

Selected NMR Experiments:

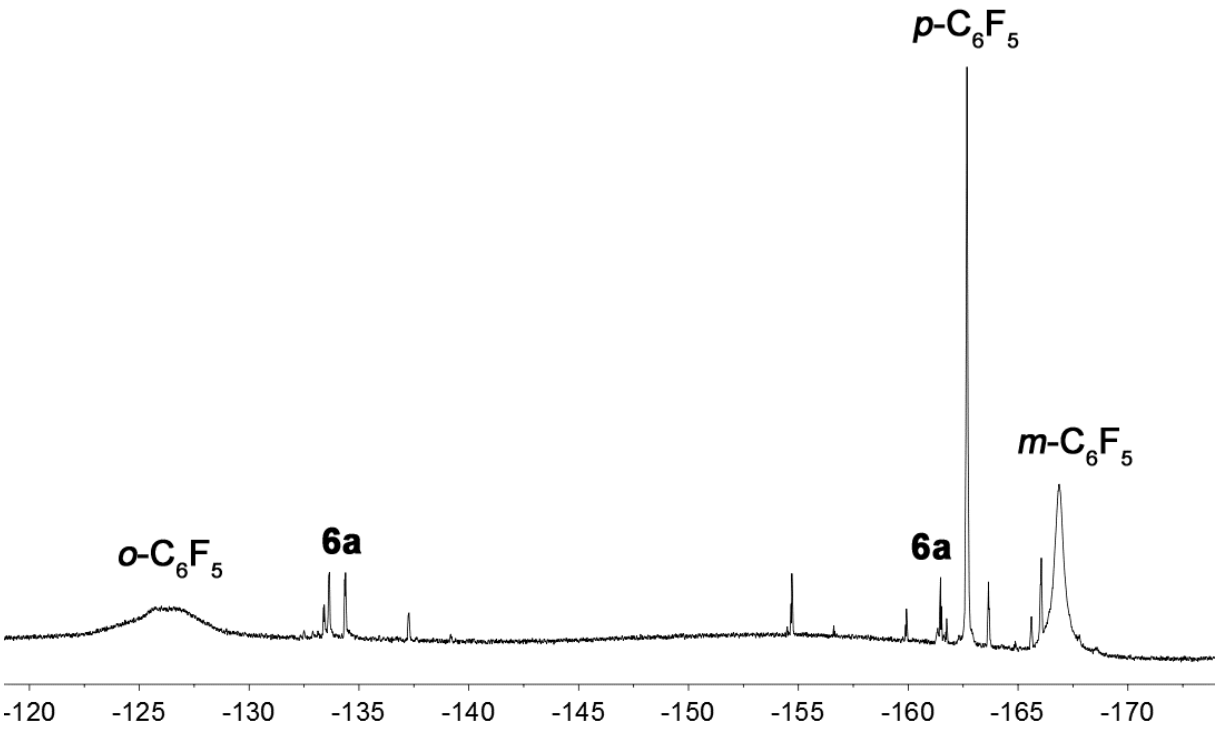
$^{11}B\{^1H\}$ NMR (192 MHz, 299 K, CD_2Cl_2): $\delta^{11}B$ = –12.6 ($\nu_{1/2}$ ~ 60 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): $\delta^{19}F$ = –126.3 (br, 2F, *o*-C_6F_5), –162.7 (br t, $^3J_{FF}$ = 18.7 Hz, 1F, *p*-C_6F_5), –166.9 (br, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 4.2].

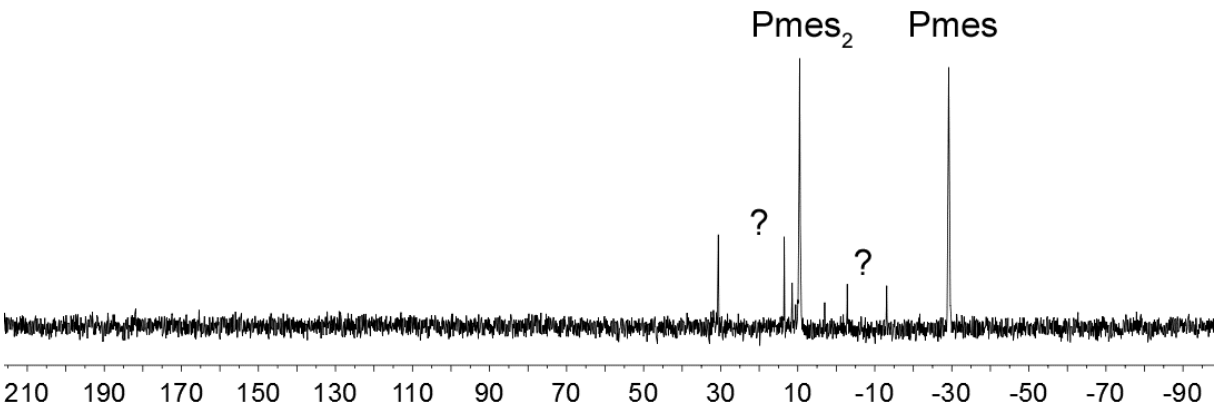
$^{31}P\{^1H\}$ NMR (243 MHz, 299 K, CD_2Cl_2): $\delta^{31}P$ = 9.5 ($\nu_{1/2}$ ~ 70 Hz, 1P, $Pmes_2$), –29.2 ($\nu_{1/2}$ ~ 100 Hz, 1P, Pmes).



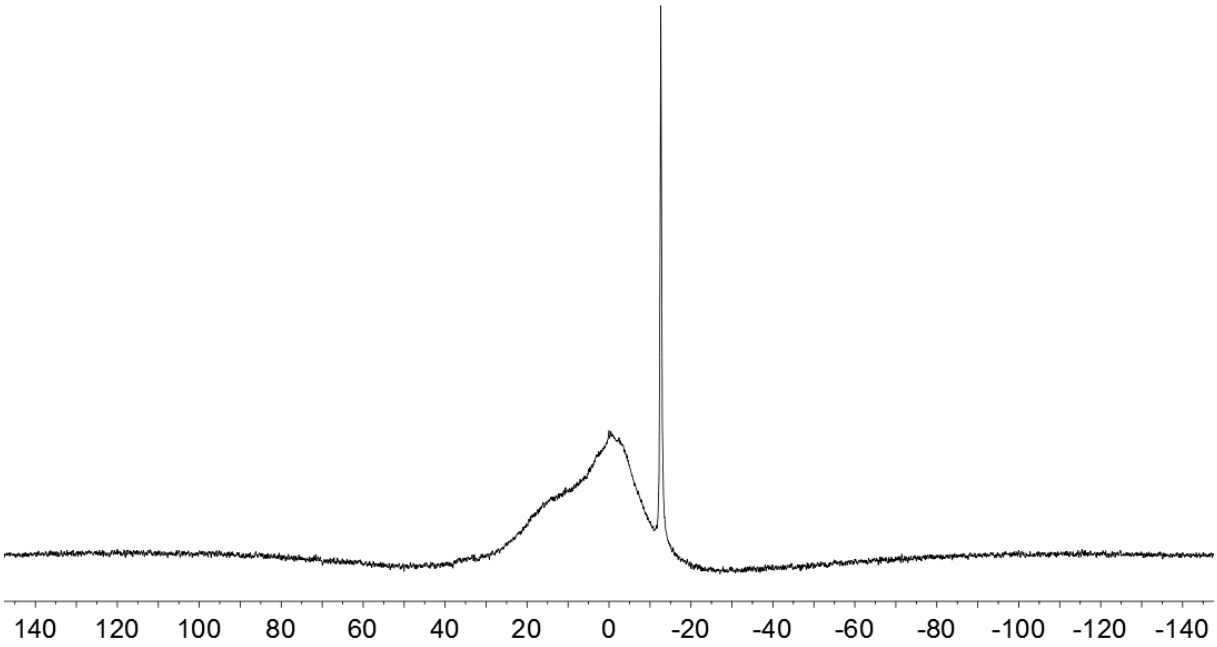
^1H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound **5a**. [p = *n*-pentane]



^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of **5a**.

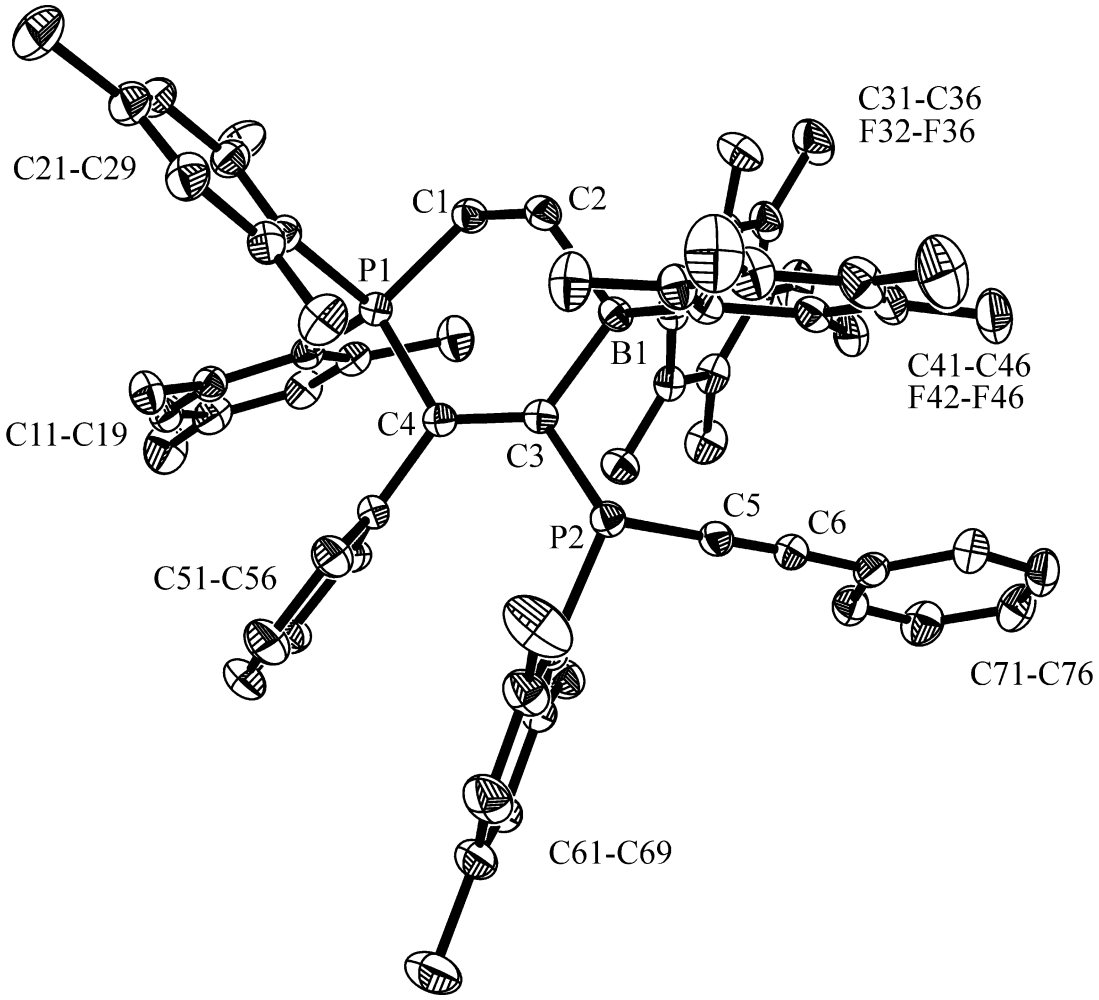


$^{31}P\{^1H\}$ NMR (243 MHz, 299 K, CD_2Cl_2) spectrum of compound **5a**.[?: not identified yet]

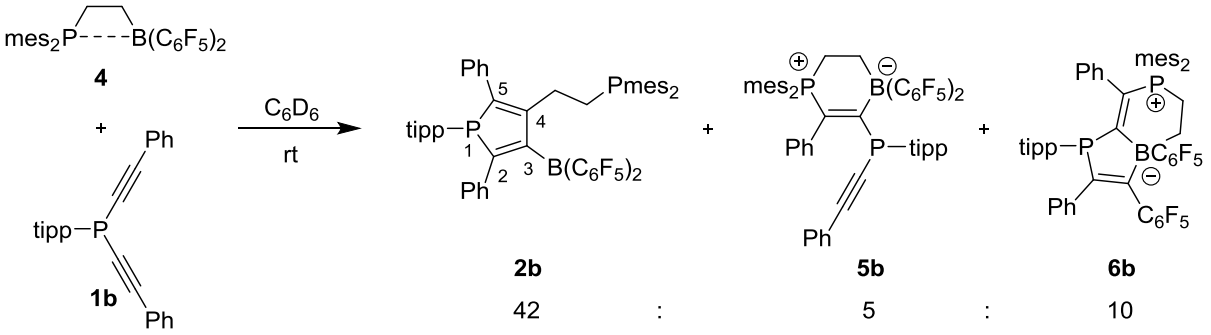


$^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of compound **5a**.

X-ray crystal structure analysis of compound 5a: formula $C_{57}H_{47}BF_{10}P_2$, M = 994.70, colourless crystal, 0.18 x 0.14 x 0.12 mm, a = 11.3490(2), b = 12.5217(3), c = 20.7425(4) Å, α = 103.336(2), β = 93.017(2), γ = 108.594(1)°, V = 2692.9(1) Å^3, ρ_{calc} = 1.227 gcm^{-3}, μ = 0.151 mm^{-1}, empirical absorption correction (0.973 ≤ T ≤ 0.982), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 26432 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 9162 independent (R_{int} = 0.048) and 7876 observed reflections [I>2σ(I)], 640 refined parameters, R = 0.057, wR^2 = 0.160, max. (min.) residual electron density 0.37 (-0.23) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.


C31-C36
F32-F36
C21-C29
C1
C2
P1
B1
C41-C46
F42-F46
C11-C19
C4
C3
C5
C6
P2
C51-C56
C71-C76
C61-C69

Reaction of compound 4 with bis(phenylethynyl)(2,4,6-triisopropylphenyl)phosphane (1b)



tipp: 2,4,6-triisopropylphenyl

The *in situ* reaction of the P/B-system **4** (64.2 mg, 0.1 mmol, 1 eq) with bis(phenylethynyl)(2,4,6-triisopropylphenyl)phosphane (**1b**) (43.7 mg, 0.1 mmo, 1 eq) in C_6D_6 (1 mL) at room temperature for 2 days gave a mixture of compound **1b**, **4, 2b**, **5b** and **6b** (ratio ca. 31 : 12 : 42 : 5 : 10 (^{31}P)) and traces of not identified compounds.

[Comment: comparable results were obtained using the same amounts of the reactants but the reaction was carried out in toluene (3 mL) at room temperature for 6 days or alternatively in *n*-pentane (3 mL) at 70 °C for 2.5 days]

Compound 2b:

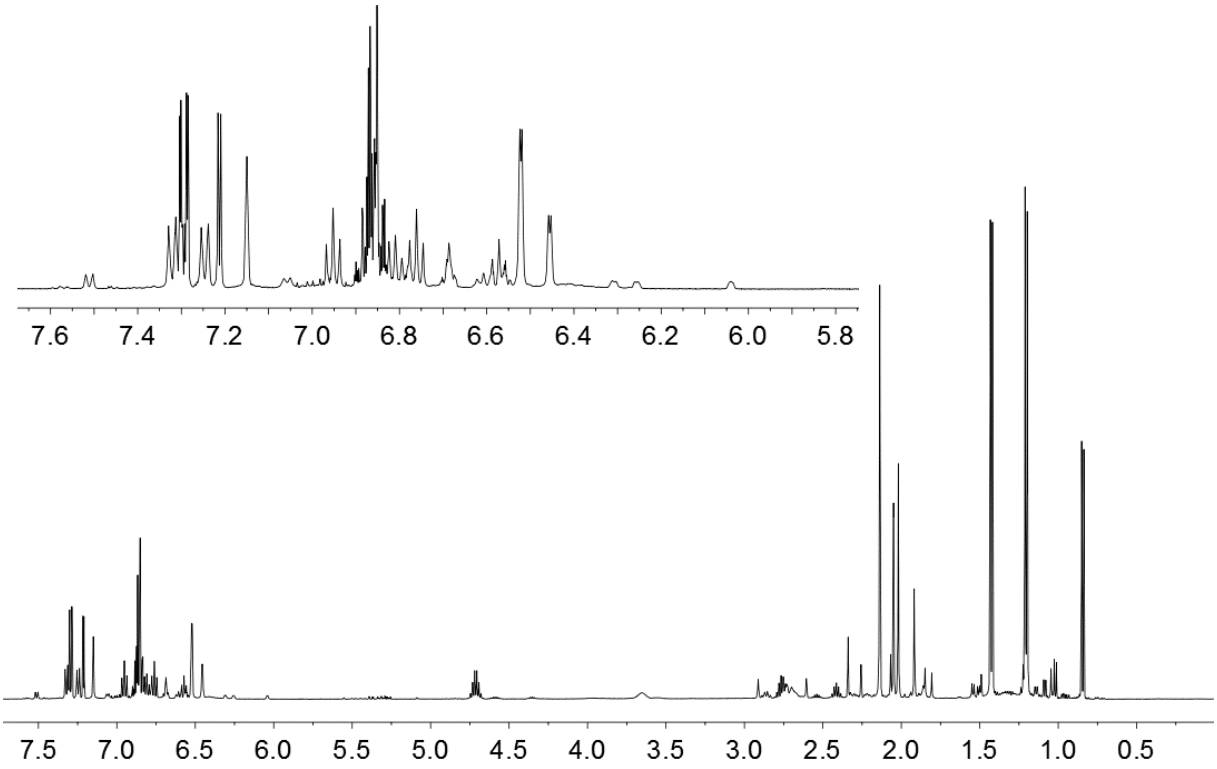
^{1}H NMR (500 MHz, 299 K, C_6D_6): δ^1H = 7.32 (m, 2H, *o*-Ph^5), 7.25 (m, 2H, *o*-Ph^2), 6.95 (m, 2H, *m*-Ph^5), 6.85 (m, 2H, *m*-tipp), 6.81 (m, 1H, *p*-Ph^5), 6.76 (m, 2H, *m*-Ph^2), 6.57 (m, 1H, *p*-Ph^2), 6.52 (dm, $^4J_{PH}$ = 2.6 Hz, 4H, *m*-mes), 3.65 (br, 2H, *o*-CH^{iPr}), 2.74 (m, 2H, PCH$_2$), 2.69 (m, 2H, CH$_2$), 2.41 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, *p*-CH^{iPr}), 2.14 (s, 12H, *o*-CH$_3^{mes}$), 2.02 (s, 6H, *p*-CH$_3^{mes}$), 1.20 (d, $^3J_{HH}$ = 6.9 Hz, *o*-CH$_3^{iPr}$), 0.84 (d, $^3J_{HH}$ = 6.9 Hz, *p*-CH$_3^{iPr}$).

^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6): δ^{13}C = 167.1 (d, $^1J_{PC}$ = 6.0 Hz, C2), 157.4 (d, $^2J_{PC}$ = 14.3 Hz, *o*-tipp), 152.8 (d, $^4J_{PC}$ = 1.8 Hz, *p*-tipp), 150.2 (br d, $^2J_{PC}$ = 14.7 Hz, C3), 147.2 (d, J_{PC} = 11.2 Hz, C5), 147.2 (dd, J_{PC} = 17.8 Hz, J_{PC} = 15.7 Hz, C4), 141.7 (d, $^2J_{PC}$ = 13.4 Hz, *o*-mes), 139.1 (d, $^2J_{PC}$ = 16.4 Hz, *i*-Ph^2), 137.5 (*p*-mes), 136.6 (d, $^2J_{PC}$ = 17.7 Hz, *i*-Ph^5), 132.8 (d, $^1J_{PC}$ = 21.7 Hz, *i*-mes), 130.9 (d, $^3J_{PC}$ = 7.2 Hz, *m*-tipp), 130.3 (d, $^3J_{PC}$ = 3.0 Hz, *m*-mes), 129.8 (d, $^3J_{PC}$ = 9.3 Hz, *o*-Ph^{2,5}), 128.5 (*m*-Ph^5), 128.2 (*m*-Ph^2), 128.0 (*p*-Ph^2), 126.8 (*p*-Ph^5), 122.6 (d, $^3J_{PC}$ = 6.2 Hz, *m*-tipp), 120.6 (d, $^1J_{PC}$ = 6.2 Hz, *i*-tipp), 34.2 (*p*-CH^{iPr}), 33.2 (d, $^3J_{PC}$ = 15.8 Hz, *o*-CH^{iPr}), 31.7 (dd, $^1J_{PC}$ = 19.7 Hz, $^4J_{PC}$ = 5.4 Hz, PCH$_2$), 27.7 (dd, J_{PC} = 22.5 Hz, J_{PC} = 1.6 Hz, CH$_2$), 25.4, 25.0 (*o*-CH$_3^{iPr}$), 23.4 (*p*-CH$_3^{iPr}$), 23.0 (d, $^3J_{PC}$ = 13.5 Hz, *o*-CH$_3^{mes}$), 20.7 (*p*-CH$_3^{mes}$), [C_6F_5 not listed].

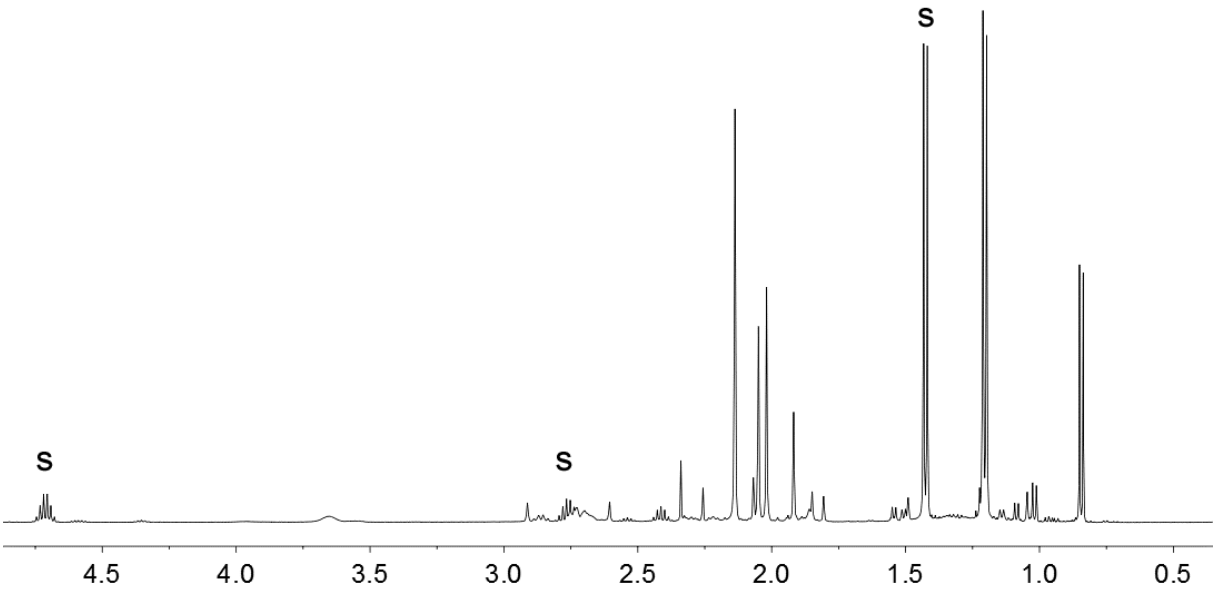
^{11}B{^{1}H} NMR (160 MHz, 299 K, C_6D_6): δ^{11}B = 60.0 ($\nu_{1/2} \approx$ 3000 Hz).

^{19}F NMR (470 MHz, 299 K, C_6D_6): δ^{19}F = −128.3 (br m, 2F, *o*-C_6F_5), −146.8 (br, 1F, *p*-C_6F_5), −161.7 (br m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 14.9].

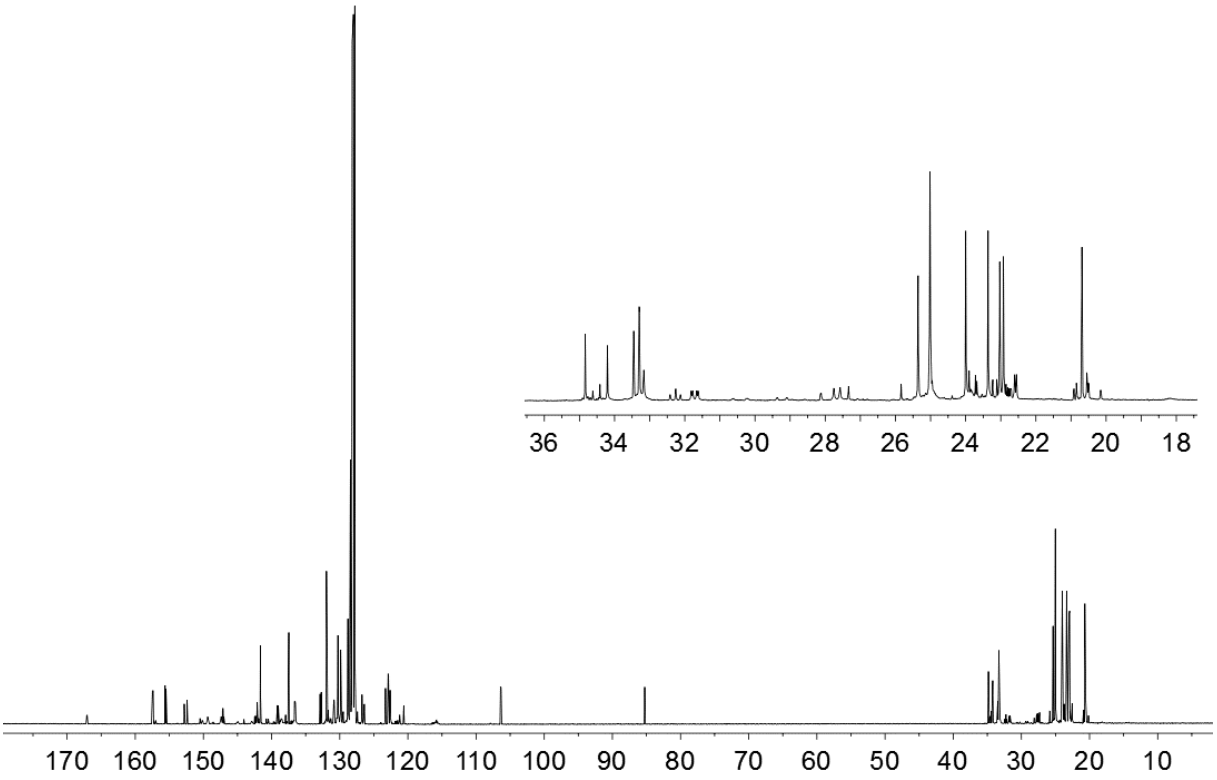
$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, C_6D_6): $\delta^{31}P$ = 10.8 ($\nu_{1/2}$ ~ 10 Hz, 1P, P-1), −21.9 ($\nu_{1/2}$ ~ 15 Hz, 1P, $Pmes_2$).



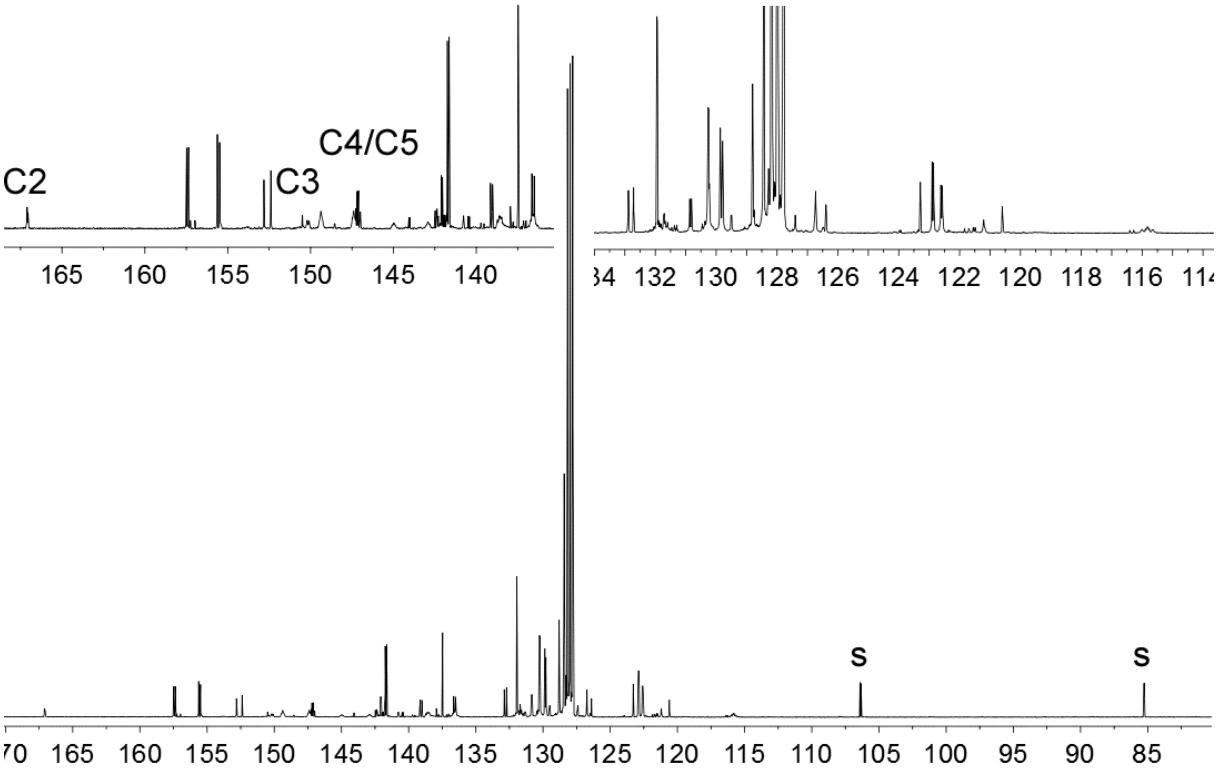
^{1}H NMR (500 MHz, 299 K, C_6D_6) spectrum of the reaction mixture.



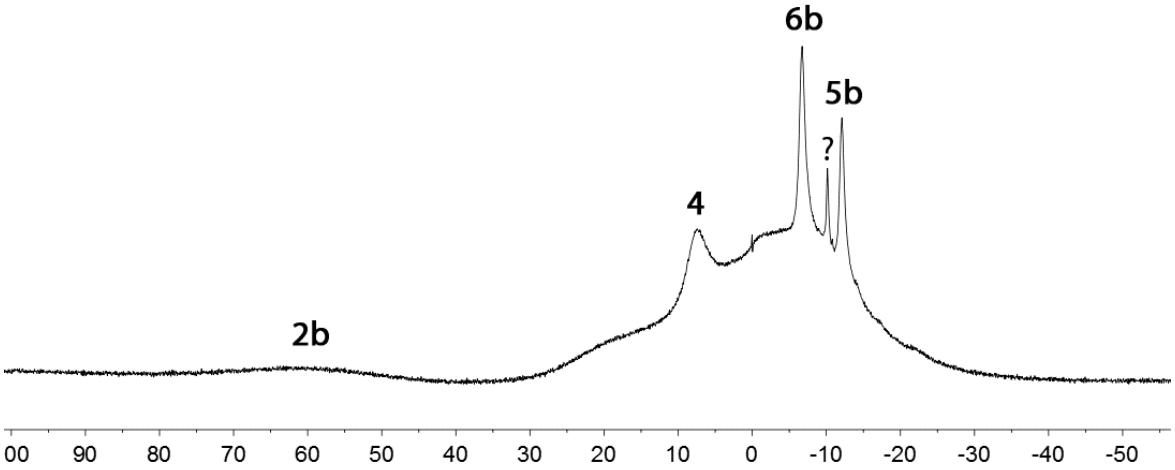
^{1}H NMR (500 MHz, 299 K, C_6D_6) spectrum of the reaction mixture. [s : **1b**]



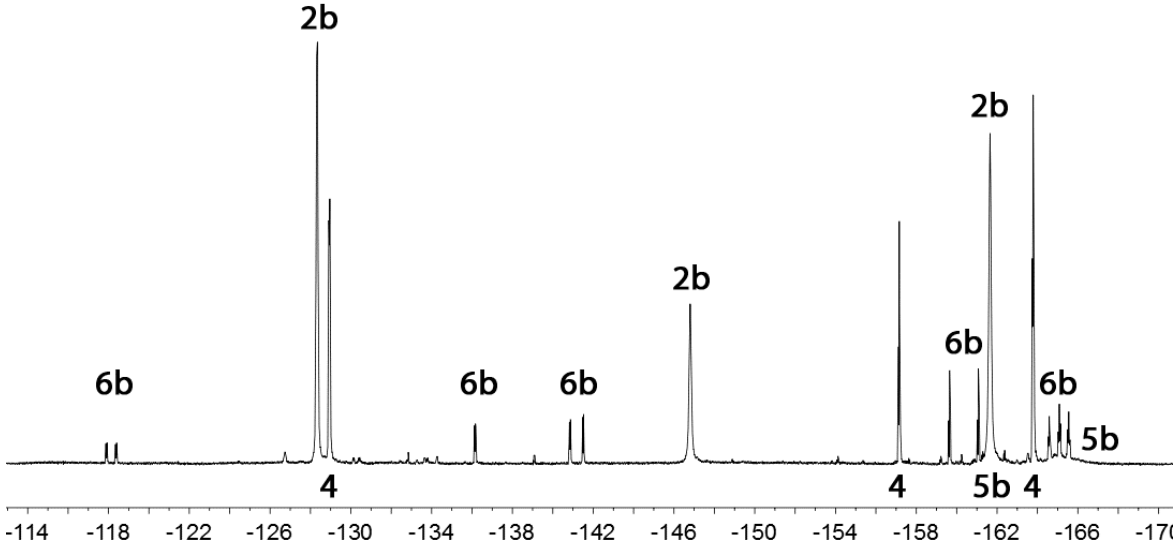
$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, C_6D_6) spectrum of the reaction mixture.



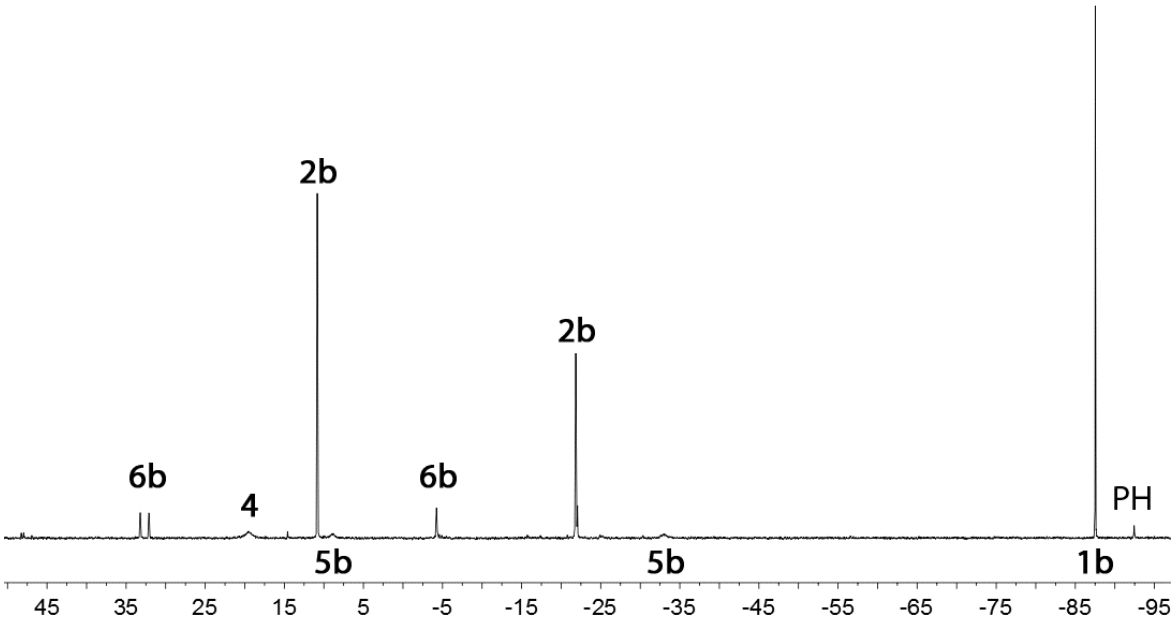
$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, C_6D_6) spectrum of the reaction mixture. [s = **1b**]



$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, C_6D_6) spectrum of the reaction mixture (?: not identified yet).

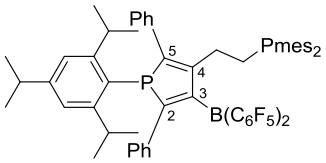


^{19}F NMR (470 MHz, 299 K, C_6D_6) spectrum of the reaction mixture (the resonances of **5b** are broad or masked by the *p*-C_6F_5 resonance of compound **2b**).



^{31}P NMR (202 MHz, 299 K, C_6D_6) spectrum of the reaction mixture (PH: assigned as $HPmes_2$).

Preparation of compound 2b



A solution of dimesitylvinylphosphane (148 mg, 0.5 mmol, 1 eq) in toluene (5 mL) was added to bis(pentafluorophenyl)-borane (173 mg, 0.5 mmol, 1 eq) and the solution was stirred for 1 h. After addition of bis(phenylethynyl)(2,4,6-triisopropyl-phenyl)phosphane (**1b**) (219 mg, 0.5 mmol, 1 eq) the reaction mixture was stirred for 6 days at room temperature, then all volatiles were removed *in vacuo* and the obtained residue suspended in *n*-pentane (5 mL). The supernatant was separated from the solid material and dried *in vacuo* to give compound **2b** as a green solid (300 mg, 0.3 mmol, 57%). (The separated solid material was used for the characterization of compounds **5b** and **6b** (see below).)

Elemental analysis: Calc. for $C_{63}H_{59}BF_{10}P_2$: C: 70.13, H: 5.51; found: C: 69.54, H: 5.78.

IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3020 (w), 2962 (m), 2961 (m), 2868 (m), 2730 (w), 1645 (m), 1603 (m), 1559 (w), 1516 (s), 1473 (s), 1457 (s), 1381 (m), 1312 (m), 1270 (m), 1152 (m), 1080 (s), 1029 (m), 973 (s), 880 (w), 851 (w), 752 (m), 699 (s), 641 (m), 554 (w).

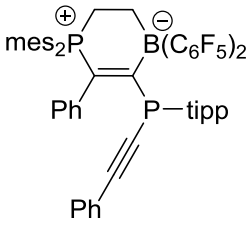
Melting point: 154 °C.

$^{11}B\{^1H\}$ NMR (160 MHz, 299 K, C_6D_6): $\delta^{11}B$ = 60.0 ($\nu_{1/2} \approx$ 2900 Hz).

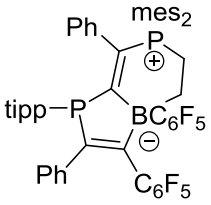
^{19}F NMR (470 MHz, 299 K, C_6D_6): $\delta^{19}F$ = −128.4 (m, 2F, *o*-C_6F_5), −146.8 (br, 1F, *p*-C_6F_5), −161.7 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 14.9].

$^{31}P\{^1H\}$ NMR (202 MHz, 299 K, C_6D_6): $\delta^{31}P$ = 10.8 ($\nu_{1/2}$ ~ 25 Hz, 1P, P-1), −21.9 ($\nu_{1/2}$ ~ 30 Hz, 1P, $Pmes_2$).

Characterization of compound 5b and 6b



5b



6b

The solution of the solid obtained from the preparation of compound **2b** (see above) in C_6D_6 showed a mixture of compounds **5b** and **6b** (ratio ca. 1 : 1 (^{31}P)).

Compound 5b:

[Characterization by selected NMR experiments and in comparison with compound **5a**]

^{11}B{^{1}H} NMR (160 MHz, 299 K, C_6D_6): δ^{11}B = −12.1 ($\nu_{1/2}$ ~ 150 Hz).

^{19}F NMR (470 MHz, 299 K, C_6D_6): δ^{19}F = −120.8, −124.0, −126.2, −127.2 (each br, each 1F, *o*-C_6F_5), −161.6 (br, 1F, *p*-C_6F_5), −165.8 (br, 2F, *m*-C_6F_5),[$\Delta\delta^{19}F_{p,m}$ = 4.2].

^{31}P{^{1}H} NMR (202 MHz, 299 K, C_6D_6): δ^{31}P = 9.0 ($\nu_{1/2}$ ~ 130 Hz, 1P, $Pmes_2$), −33.1 ($\nu_{1/2}$ ~ 150 Hz, 1P, P-tipp).

Compound 6b:

^{1}H NMR (500 MHz, 299 K, C_6D_6): δ^{1}H = 7.52 (m, 2H, *o*-Ph^4), 7.06 (br m, 2H, *o*-Ph^6), 6.83 (m, 1H, *m'*-tipp), 6.82 (m, 2H, *m*-Ph^4), 6.69 (m, 1H, *p*-Ph^4), 6.68 (dm, $^4J_{PH}$ = 5.4 Hz, 1H, *m*-tipp), 6.60 (m, 2H, *m*-Ph^6), 6.56 (m, 1H, *m*-mes^a), 6.54 (m, 1H, *p*-Ph^6), 6.30 (d, $^4J_{PH}$ = 3.4 Hz, 1H, *m*-mes^b), 6.25 (d, $^4J_{PH}$ = 3.7 Hz, 1H, *m'*-mes^b), 6.03 (br, 1H, *m'*-mes^a), 4.59 (dsept, $^4J_{PH}$ = 12.9 Hz, $^3J_{HH}$ = 6.8 Hz, 1H, *o*-CH^{iPr}), 4.35 (sept, $^3J_{HH}$ = 6.7 Hz, 1H, *o*-CH^{iPr}), 3.56, 2.65 (each m, each 1H, PCH_2), 2.91 (s, 3H, *o*-$CH_3^{mes,b}$), 2.25, 1.32 (each m, each 1H, BCH_2), 2.60 (s, 3H, *o*-$CH_3^{mes,a}$), 2.54 (sept, $^3J_{HH}$ = 6.7 Hz, 1H, *p*-CH^{iPr}), 1.85 (s, 3H, *p*-$CH_3^{mes,b}$), 1.80 (s, 3H, *p*-$CH_3^{Mes,a}$), 1.54, 1.51 (each d, $^3J_{HH}$ = 6.6 Hz, each 3H, *o'*-CH_3^{iPr}), 1.49 (s, 3H, *o'*-$CH_3^{mes,b}$), 1.22, 1.09 (each d, $^3J_{HH}$ = 6.8 Hz, each 3H, *o*-CH_3^{iPr}), 1.04 (s, 3H, *o'*-$CH_3^{mes,a}$), 1.02 (d, $^3J_{HH}$ = 7.0 Hz, 6H, *p*-CH_3^{iPr}).

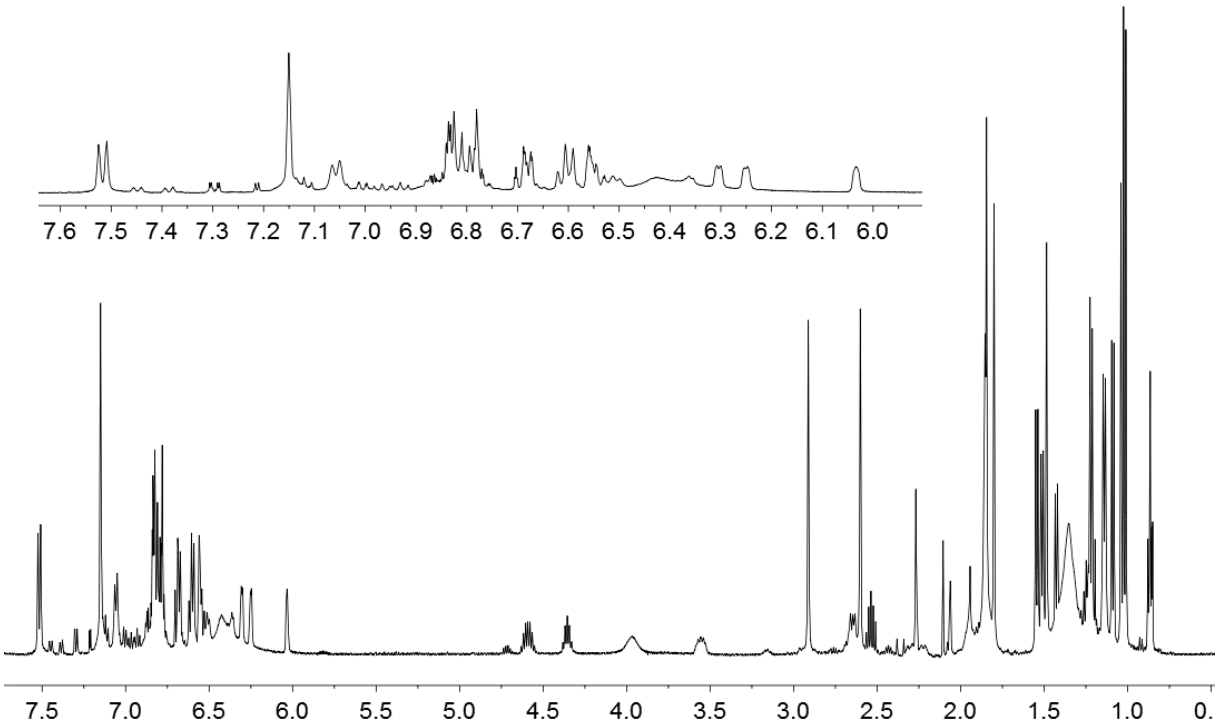
^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6): δ^{13}C = 157.1 (d, $^2J_{PC}$ = 34.7 Hz, *o*-tipp), 155.4 (dd, *J* = 5.1 Hz, *J* = 2.4 Hz, *o'*-tipp), 150.5 (d, $^4J_{PC}$ = 7.2 Hz, *p*-tipp), 148.6 (br d, $^1J_{PC}$ = 3.5 Hz, C4), 144.0 (d, $^2J_{PC}$ = 7.8 Hz, *o'*-mes^a), 142.4 (d, $^4J_{PC}$ = 2.6 Hz, *p*-mes^a), 141.9 (d, $^2J_{PC}$ = 9.9 Hz, *o*-mes^b), 141.73 (d, $^2J_{PC}$ = 10.1 Hz, *o*-mes^a), 141.66 (d, $^4J_{PC}$ = 3.1 Hz, *p*-mes^b), 140.5 (d, $^2J_{PC}$ = 9.6 Hz, *o'*-mes^b), 139.7 (d, $^2J_{PC}$ = 23.5 Hz, *i*-Ph^4), 139.1 (dd, $^2J_{PC}$ = 16.7 Hz, $^3J_{PC}$ = 2.5 Hz, *i*-Ph^6), 131.9 (d, $^3J_{PC}$ = 11.0 Hz, *m'*-mes^b), 131.7 (d, $^3J_{PC}$ = 10.6 Hz, *m*-mes^a), 131.4 (d, $^3J_{PC}$ = 10.3 Hz, *m'*-mes^a), 130.4 (d, $^3J_{PC}$ = 11.0 Hz, *m*-mes^b), 130.3 (*o*-Ph^4), 129.2 (dd, $^1J_{PC}$ = 77.9 Hz, *J* = 4.1 Hz, *i*-mes^b), 128.8 (d, $^3J_{PC}$ = 7.0 Hz, *o*-Ph^4), 127.8 (*m*-Ph^4), 127.4 (*m*-Ph^6), 127.1

(dd, $^{1}J_{PC}$ = 29.2 Hz, *J* = 8.8 Hz, *i*-tipp), 126.8 (*p*-Ph^{6}), 126.8 (*p*-Ph^{4}), 123.6 (dd, $^{1}J_{PC}$ = 73.7 Hz, *J* = 3.6 Hz, *i*-mes^{a}), 121.5 (d, $^{3}J_{PC}$ = 7.8 Hz, *m*-tipp), 121.2 (d, $^{3}J_{PC}$ = 4.6 Hz, *m'*-tipp), 116.2 (dd, $^{1}J_{PC}$ = 62.9 Hz, $^{2}J_{PC}$ = 16.2 Hz, C6), 34.4 (*p*-CH^{iPr}), 32.28 (d, $^{3}J_{PC}$ = 36.8 Hz, *o*-CH^{iPr}), 32.27 (*o'*-CH^{iPr}), 30.4 (br d, $^{1}J_{PC}$ = 48.3 Hz, *J* = 4.0 Hz, PCH_2), 28.8 (br d, J_{PC} = 44.1 Hz, CH_2), 28.1 (d, $^{4}J_{PC}$ = 2.5 Hz), 25.9 (*o'*-CH_3^{iPr}), 27.4, 23.7 (*o*-CH_3^{iPr}), 25.0 (d, $^{3}J_{PC}$ = 4.5 Hz, *o*-$CH_3^{mes,a}$), 23.8 (m, *o*-$CH_3^{mes.b}$), 23.9 (*p*-CH_3^{iPr}), 22.8 (d, $^{3}J_{PC}$ = 5.2 Hz, *o'*-$CH_3^{mes,a}$), 22.7 (d, $^{3}J_{PC}$ = 3.6 HZ, *o'*-$CH_3^{mes,b}$), 20.2 (d, $^{5}J_{PC}$ = 1.5 Hz, *p*-$CH_3^{mes,b}$), 20.5 (d, $^{5}J_{PC}$ = 1.3 Hz, *p*-$CH_3^{mes,a}$). [C_6F_5 not listed, C3,5 not located]

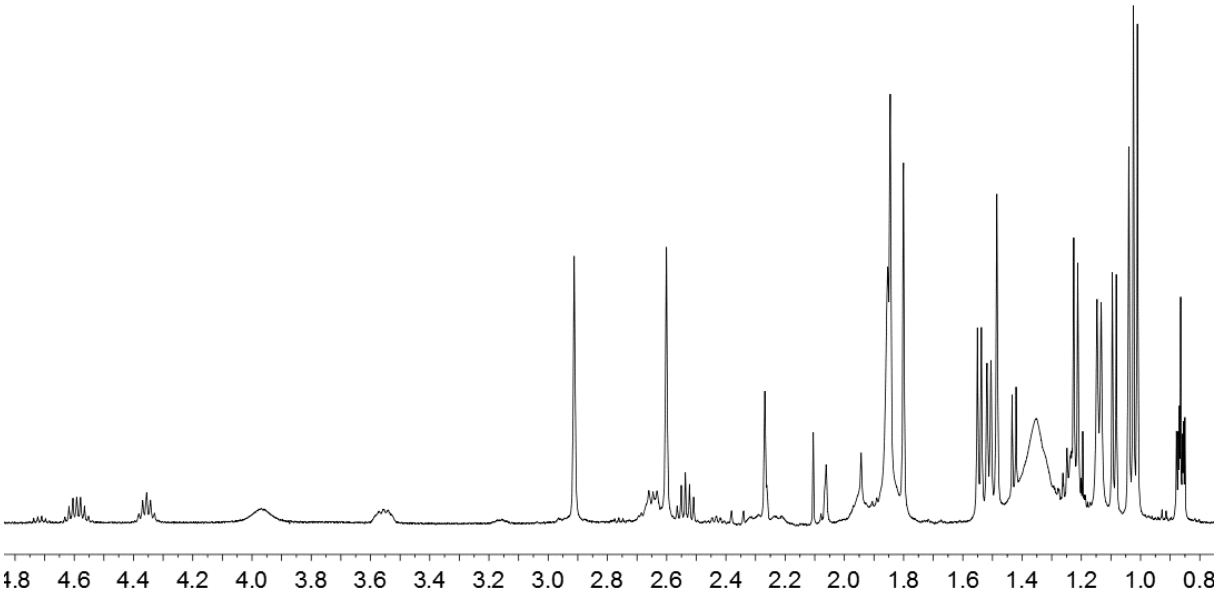
$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, C_6D_6): $\delta^{11}B$ = –6.7 ($\nu_{1/2} \approx$ 140 Hz).

^{19}F NMR (470 MHz, 299 K, C_6D_6): $\delta^{19}F$ = –118.2 (dm, J_{PF} = 226.3 Hz, *o*), –136.1 (m, *o'*), –161.1 (t, $^{3}J_{FF}$ = 20.8 Hz, *p*), –164.6 (m, *m*), –165.6 (m, *m'*)(each 1F, BC_6F_5)[$\Delta\delta^{19}F_{p,m}$ = 3.5, 4.5], –140.8 (m, *o*), –141.5 (m, *o'*), –159.7 (t, $^{3}J_{FF}$ = 21.2 Hz, *p*), –163.8 (m, *m'*), –165.1 (m, *m*)(each 1F, C_6F_5)[$\Delta\delta^{19}F_{p,m}$ = 4.1, 5.4].

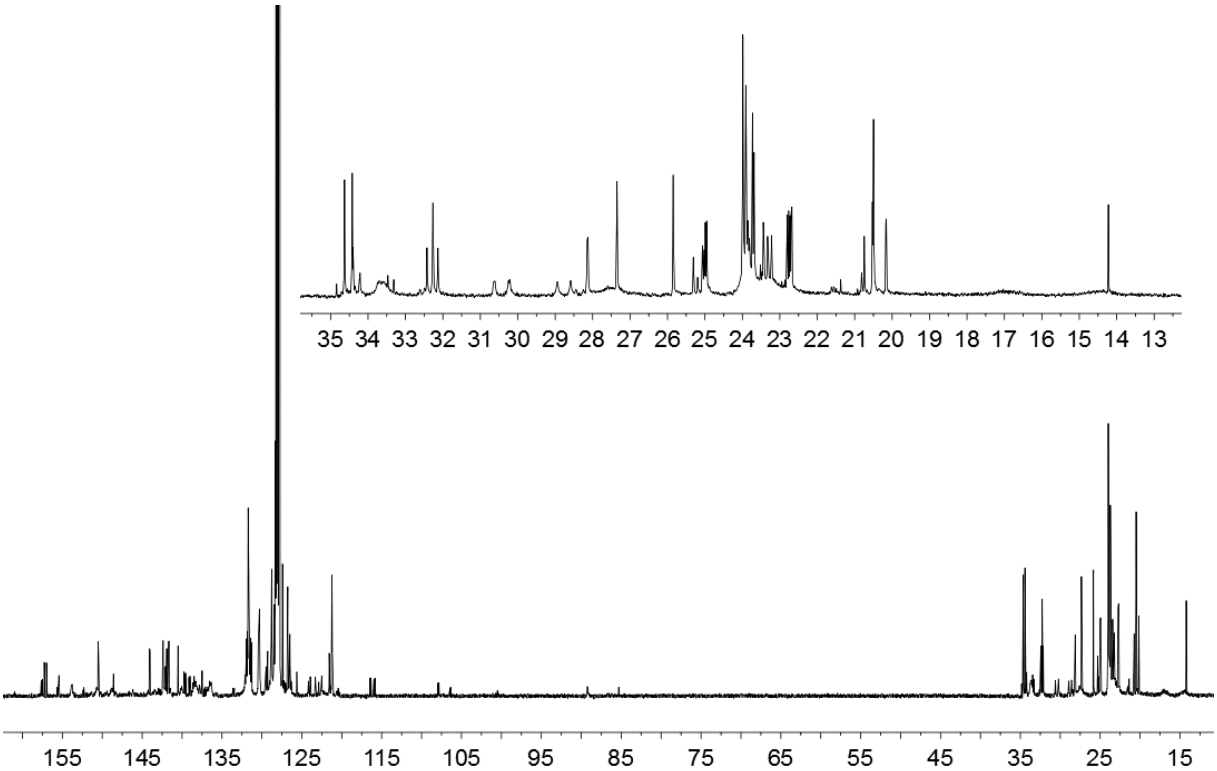
$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, C_6D_6): $\delta^{31}P$ = 32.7 (dd, J_{PF} = 226.1 Hz, $^{3}J_{PP}$ = 9.8 Hz, 1P, P-tipp), –4.2 (dm, $^{3}J_{PP}$ = 9.8 Hz, 1P, $Pmes_2$).



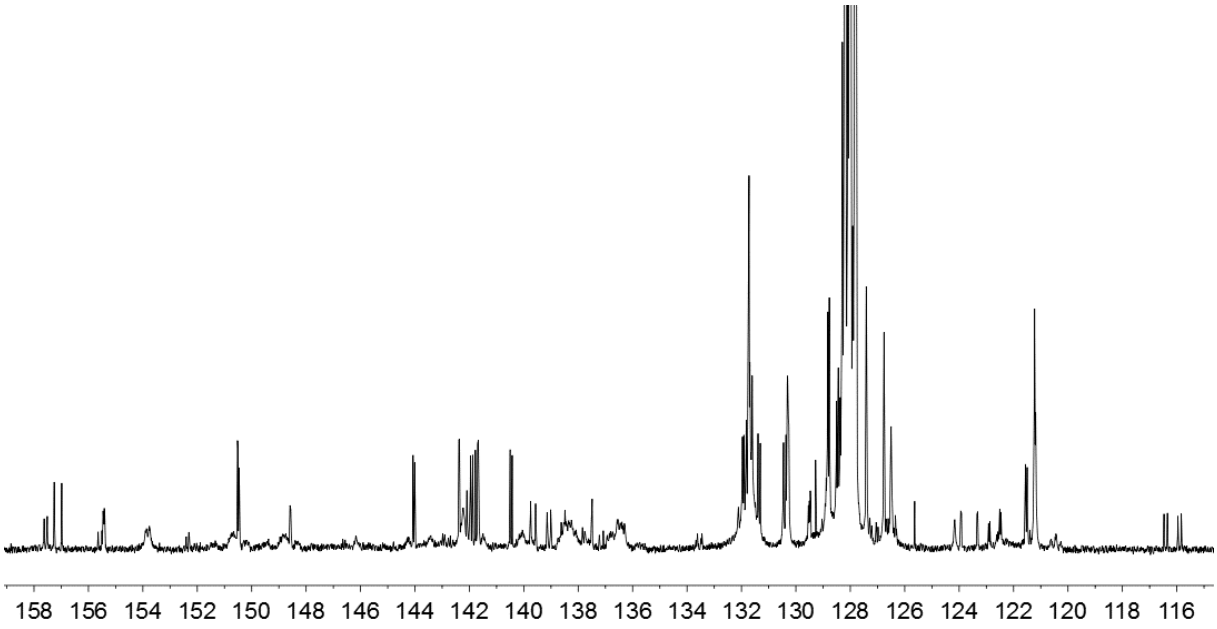
^{1}H NMR (500 MHz, 299 K, C_6D_6) spectrum of the mixture of compounds **5b** and **6b**.



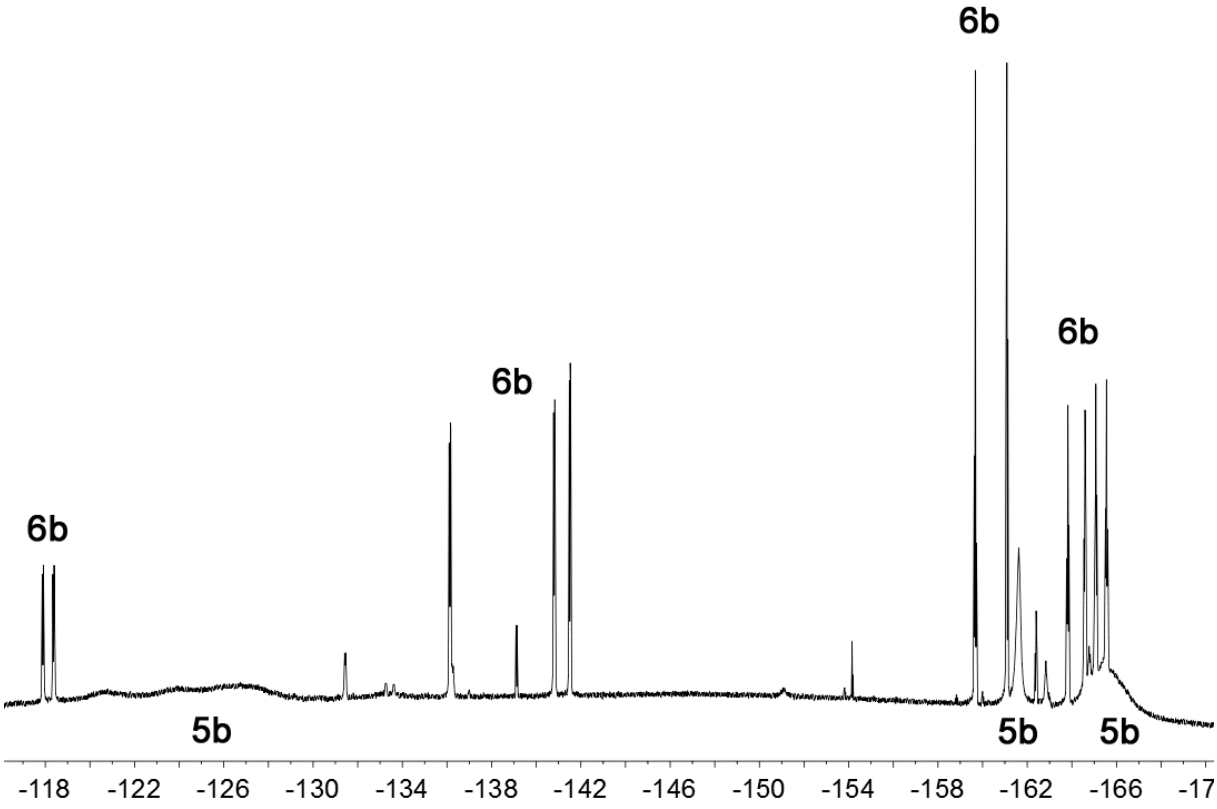
^{1}H NMR (500 MHz, 299 K, C_6D_6) spectrum of the mixture of compounds **5b** and **6b**.



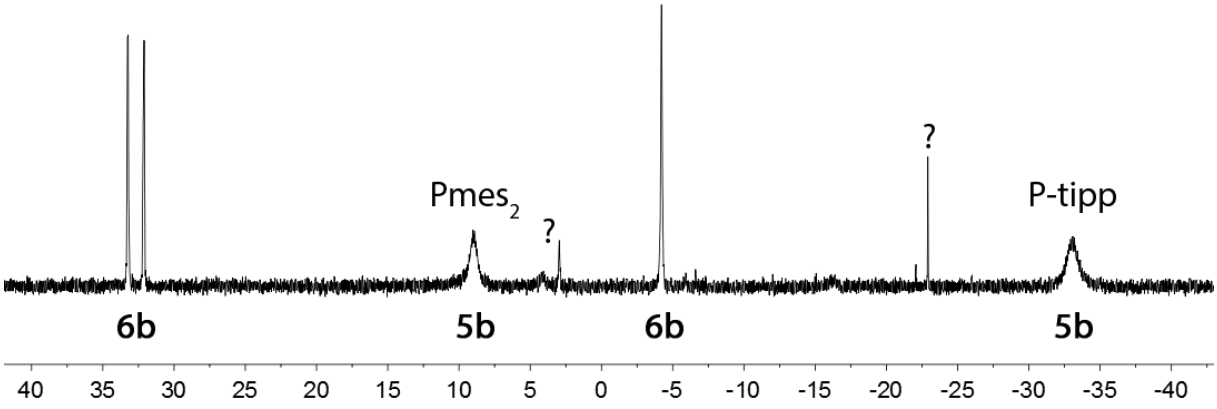
^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6)spectrum of the mixture of compounds **5b** and **6b**.



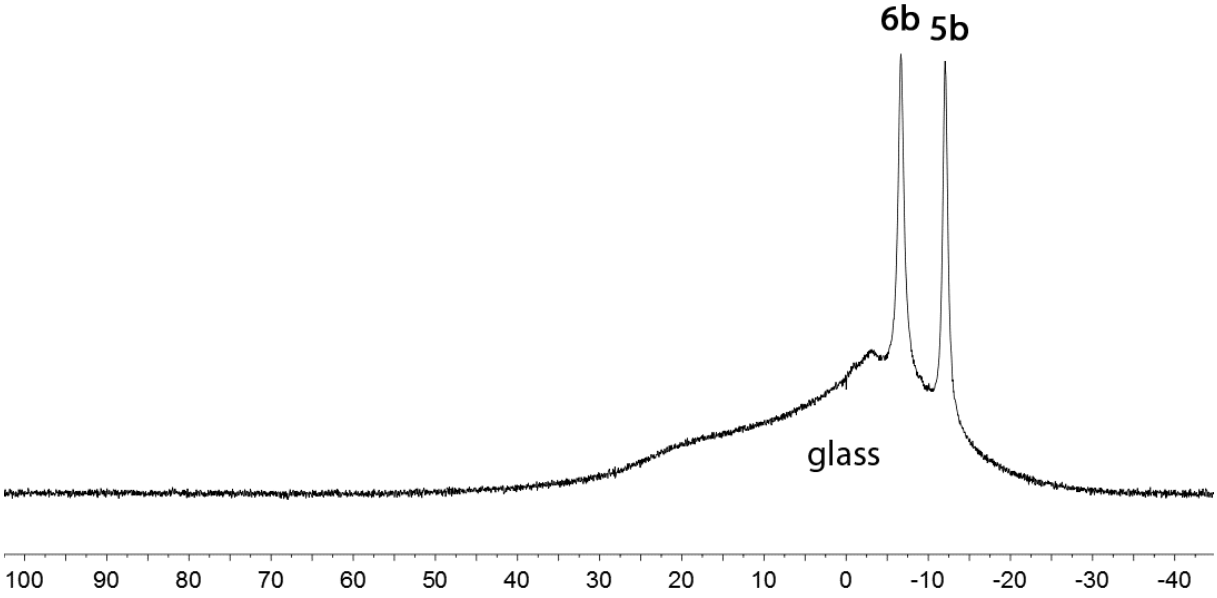
$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, C_6D_6) spectrum of the mixture of compounds **5b** and **6b**.



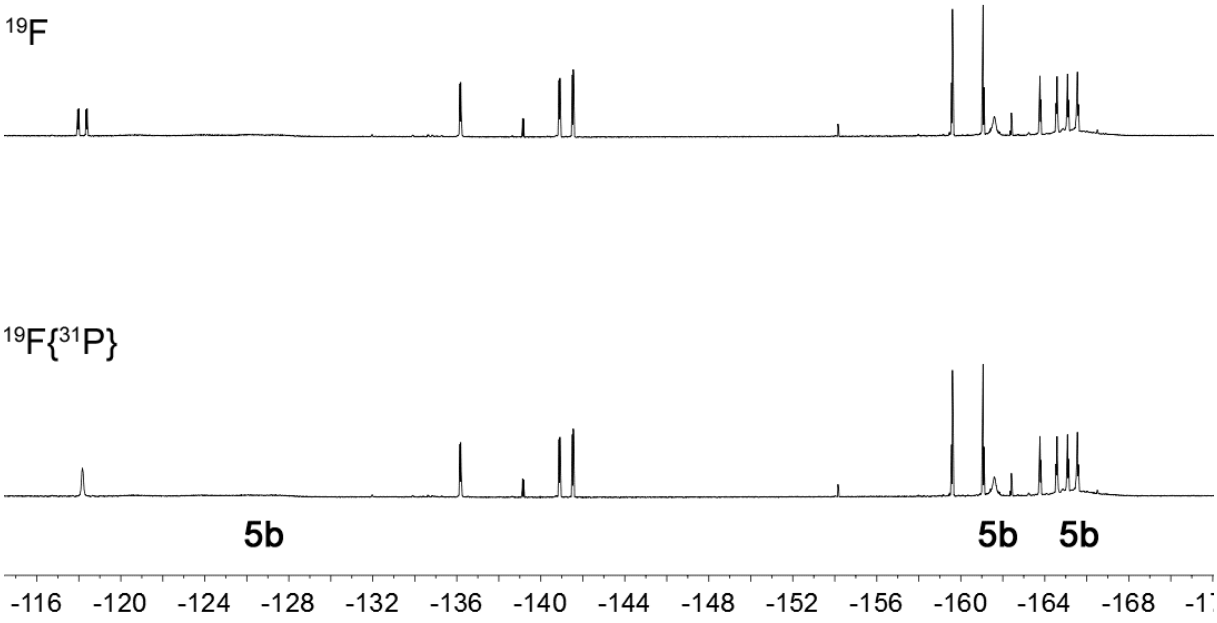
^{19}F NMR (470 MHz, 299 K, C_6D_6) spectrum of the mixture of compounds **5b** and **6b**.



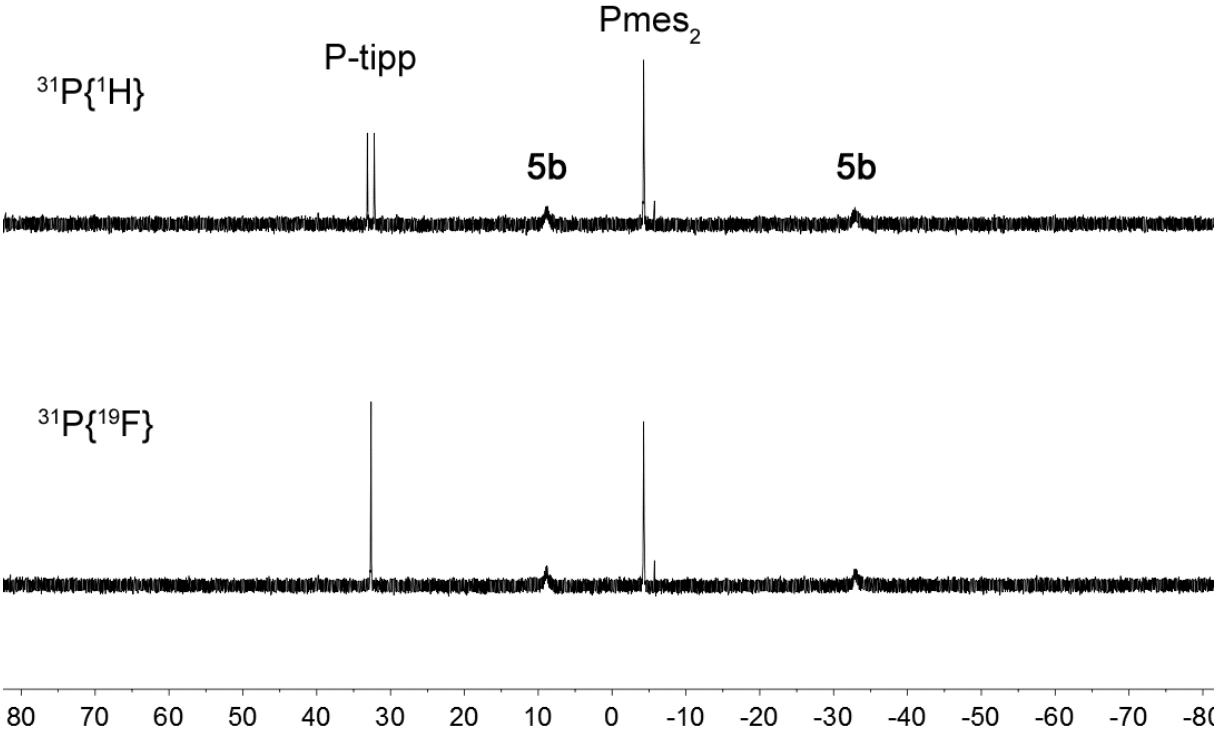
$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, C_6D_6) spectrum of the mixture of compounds **5b** and **6b**. [?: compound not identified yet]



$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, C_6D_6) spectra of the mixture of compounds **5b** and **6b**.

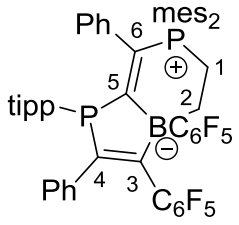


^{19}F NMR and $^{19}F\{^{31}P\}$ NMR (564 MHz, 299 K, C_6D_6) spectra of the mixture of compounds **5b** and **6b**.



$^{31}P\{^{1}H\}$ NMR and $^{31}P\{^{19}F\}$ NMR (243 MHz, 299 K, C_6D_6) spectra of the mixture of compounds **5b** and **6b**.

Isolation of compound 6b



A solution of dimesitylvinylphosphane (30 mg, 0.1 mmol, 1 eq) in *n*-pentane (2 mL) was added to bis(pentafluorophenyl)borane (35 mg, 0.1 mmol, 1 eq) and the solution was stirred for 30 min. After addition of bis(phenylethynyl)(2,4,6-triisopropylphenyl)phosphane (**1b**) (44 mg, 0.1 mmol, 1 eq) the reaction mixture was heated at 70 °C for 2.5 h. After standing at room temperature for 2 days compound **6b** was obtained as yellow crystalline material (15 mg, 7%). Crystals suitable for X-ray crystal structure analysis were obtained from a *n*-pentane (2 mL) solution of the *in situ* reaction mixture at −34 °C.

Elemental analysis: calc. for $C_{63}H_{59}BF_{10}P_2$: C: 70.13, H: 5.51; found: C: 70.08, H: 5.52.

IR (KBr): ν [cm^{-1}] = 2966 (w), 2932 (w), 2871 (w), 1604 (m), 1552 (w), 1514 (s), 1486 (m), 1444 (s); 1381 (m), 1266 (m), 1075 (s), 1028 (m), 980 (s), 961 (s), 930 (m), 844 (m), 796 (m), 754 (s), 701 (s), 642 (m), 601 (m).

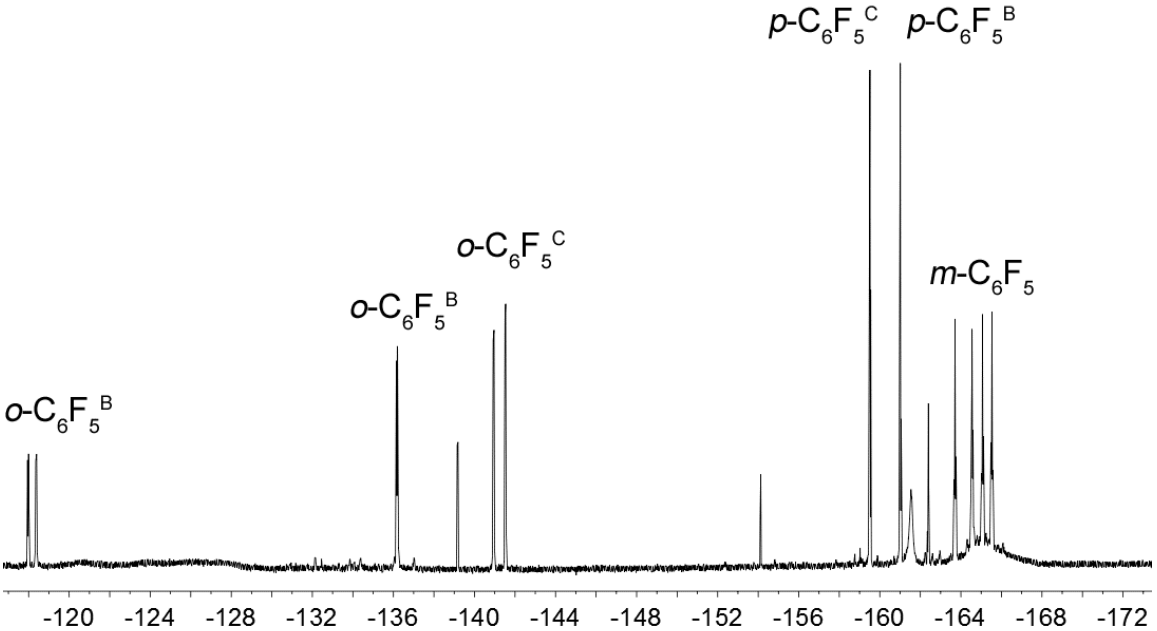
Melting point: 182 °C.

The solution of the crystalline material in C_6D_6 showed a mixture of compounds **5b** and **6b** (ratio ca. 24 : 76 (^{31}P)).

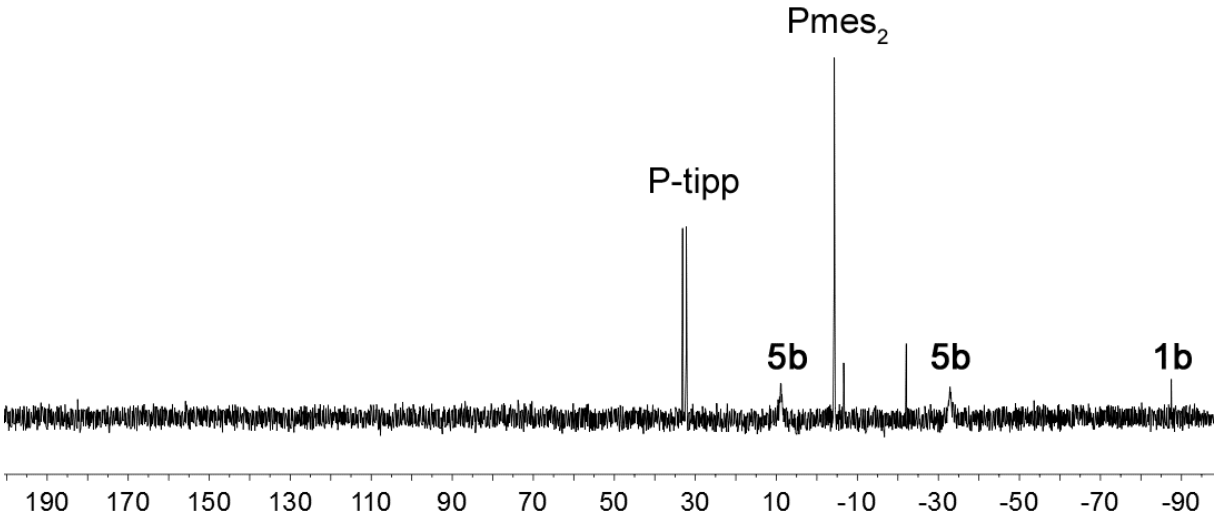
^{11}B{^{1}H} NMR (160 MHz, 299 K, C_6D_6): δ^{11}B = −6.8 ($\nu_{1/2} \approx 140$ Hz).

^{19}F NMR (470 MHz, 299 K, C_6D_6): δ^{19}F = −118.2 (dm, J_{PF} = 226 Hz, 1F, *o*), −136.2 (m, 1F, *o'*), −161.0 (t, $^3J_{FF}$ = 20.8 Hz, 1F, *p*), −164.5 (m, 1F, *m*), −165.5 (m, 1F, *m'*) (BC_6F_5)[$\Delta\delta^{19}F_{p,m}$ = 3.5, 4.5], −140.9 (m, 1F, *o*), −141.5 (m, 1F, *o'*), −159.5 (t, $^3J_{FF}$ = 21.2 Hz, 1F, *p*), −163.7 (m, 1F, *m'*), −165.1 (m, 1F, *m*)(C_6F_5)

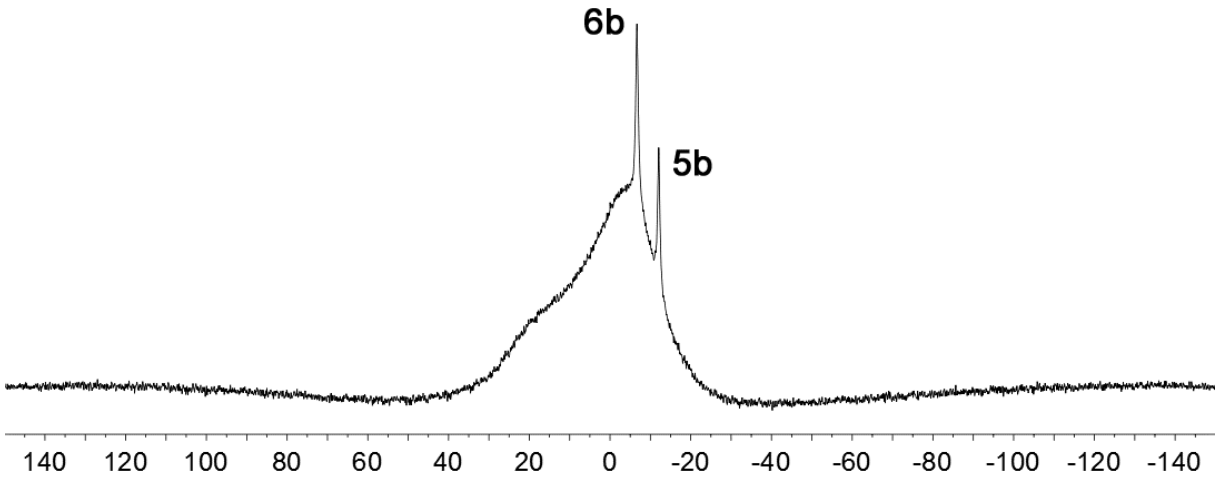
^{31}P{^{1}H} NMR (202 MHz, 299 K, C_6D_6): δ^{31}P = 32.7 (dd, J_{PF} = 225.3 Hz, $^3J_{PP}$ = 9.8 Hz, 1P, P-tipp), −4.3 (dm, $^3J_{PP}$ = 9.8 Hz, 1P, $Pmes_2$).



^{19}F NMR (470 MHz, 299 K, C_6D_6) spectrum of the crystals of compound **6b**.

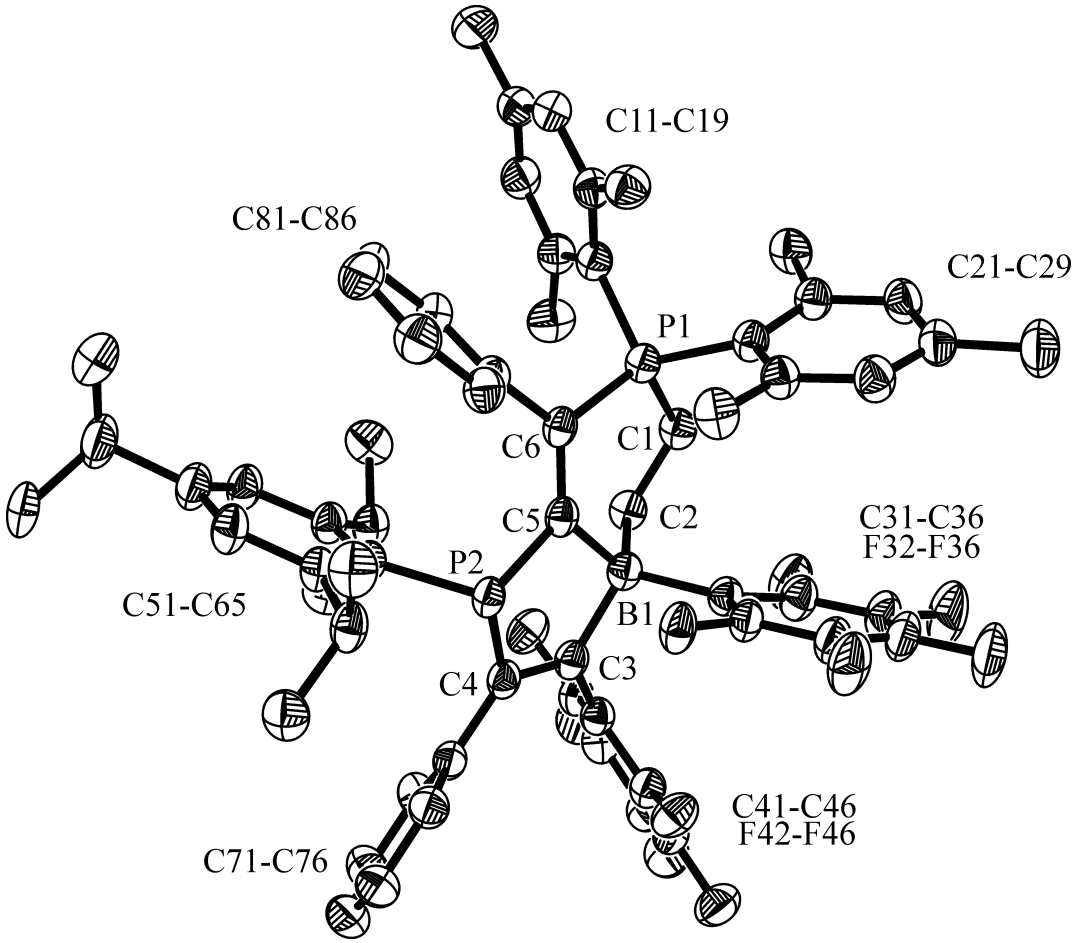


$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, C_6D_6) spectrum of the crystals of compound **6a**.

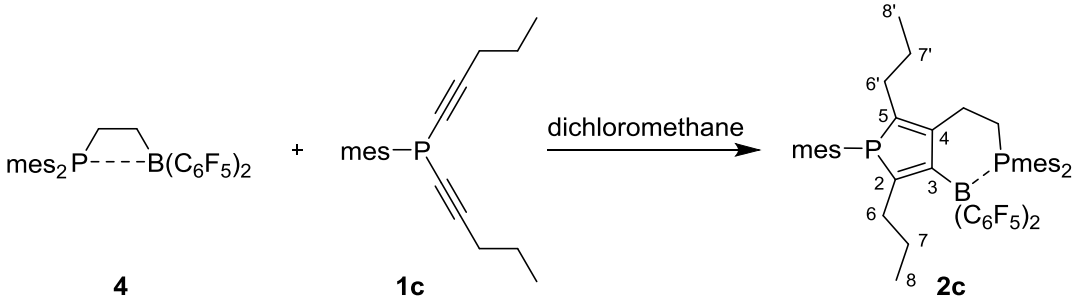


$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, C_6D_6) spectrum of the crystals of compound **6b**.

X-ray crystal structure analysis of compound 6b: formula $C_{63}H_{59}BF_{10}P_2$, *M* = 1078.85, yellow crystal, 0.15 x 0.07 x 0.03 mm, *a* = 13.8113(5), *b* = 14.0951(5), *c* = 16.4458(9) Å, α = 97.778(2), *β* = 99.423(2), γ = 118.030(3)°, *V* = 2703.8(2) Å^3, ρ_{calc} = 1.325 gcm^{-3}, μ = 1.325 mm^{-1}, empirical absorption correction (0.821 ≤ T ≤ 0.960), *Z* = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, *T* = 223(2) K, ω and ϕ scans, 36369 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 9284 independent (R_{int} = 0.066) and 6932 observed reflections [*I*>2σ(*I*)], 718 refined parameters, *R* = 0.054, wR^2 = 0.154, max. (min.) residual electron density 0.28 (-0.20) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.


C11-C19
C81-C86
C21-C29
P1
C6
C1
C5
C2
C31-C36
F32-F36
P2
C51-C65
B1
C4
C3
C41-C46
F42-F46
C71-C76

Preparation of compound 2c



4 **1c** **2c**

A solution of dimesitylvinylphosphane (118 mg, 0.4 mmol, 1 eq) in CH_2Cl_2 (2 mL) was added to bis(pentafluorophenyl)borane (138 mg, 0.4 mmol, 1 eq). After 30 min the yellow solution was added to bis(pentynyl)mesitylphosphane (**1c**) (114 mg, 0.4 mmol, 1 eq) and stirred for 1 day. Subsequently, all volatiles were removed *in vacuo* and the residue was dissolved in *n*-pentane (5 mL). The solvent was removed *in vacuo* to give compound **2c** as an orange solid (290 mg, 0.3 mmol, 78%).

Elemental analysis: cal. for $C_{51}H_{51}BF_{10}P_2$: C: 66.10, H: 5.55, found: C: 66.24, H: 5.55.

IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2958 (m), 2926 (m), 2870 (m), 2733 (w), 2385 (w), 2196 (w), 1734 (w), 1699 (w), 1644 (s), 1604 (s), 1558 (m), 1516 (s), 1457 (s), 1378 (s), 1310 (m), 1271 (m), 1180 (w), 1138 (m), 1083 (s), 1029 (m), 973 (s), 850 (m), 776 (w), 741 (w), 684 (w), 616 (w), 554 (w).

Melting point: 73 °C.

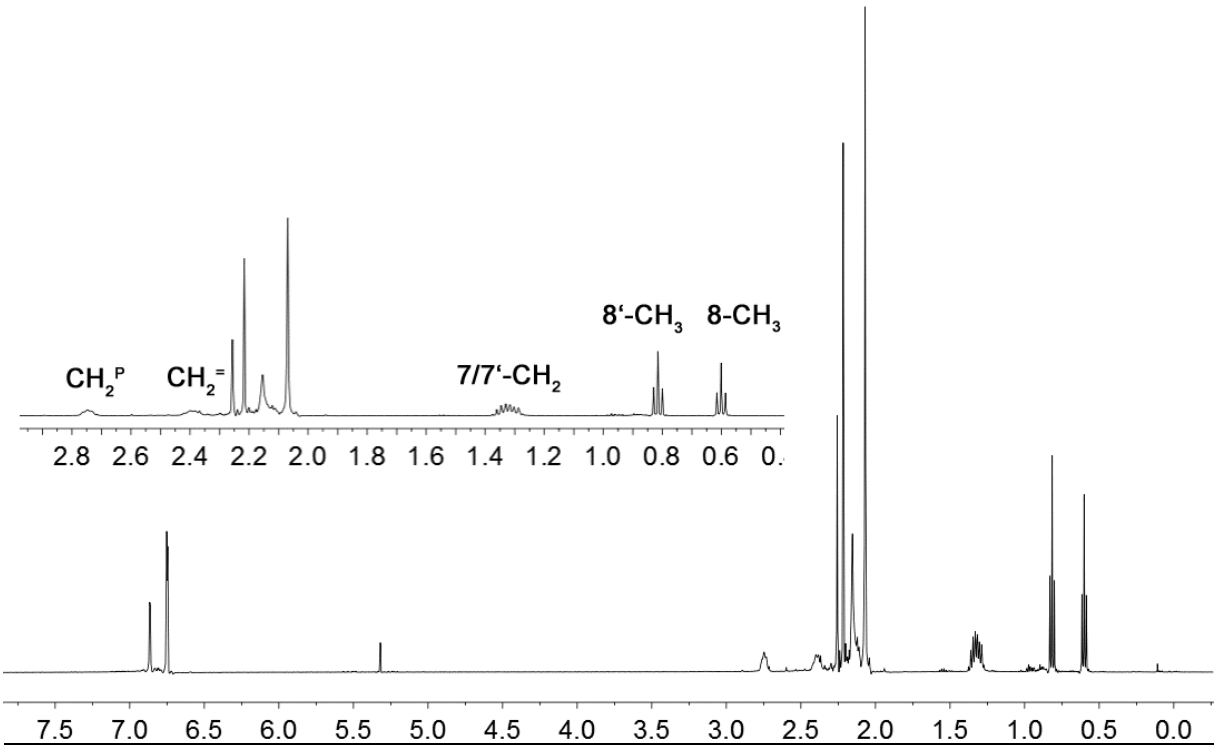
^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ^1H = 6.86 (dm, $^4J_{PH}$ = 2.9 Hz, 2H, *m*-mes^1), 6.75 (dm, $^4J_{PH}$ = 3.2 Hz, 4H, *m*-mes), 2.75 (m, 2H, PCH_2), 2.39 (m, 2H, CH_2), 2.26 (s, 3H, *p*-$CH_3^{mes,1}$), 2.22 (s, 6H, *p*-CH_3^{mes}), 2.15 (br, 6H, *o*-$CH_3^{mes,1}$), 2.16 (m, 2H, 6'-CH_2), 2.12 (m, 2H, 6-CH_2), 2.07 (s, 12H, *o*-CH_3^{mes}), 1.34 (m, 2H, 7'-CH_2), 1.31 (m, 2H, 7-CH_2), 0.81 (t, $^3J_{HH}$ = 7.3 Hz, 3H, 8'-CH_3), 0.60 (t, $^3J_{HH}$ = 7.3 Hz, 3H, 8-CH_3).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ^{13}C = 165.5 (br, C2), 146.7 (d, $^2J_{PC}$ = 14.9 Hz, *o*-Mes^1), 146.1 (br, C3), 145.3 (dd, J_{PC} = 21.6 Hz, J_{PC} = 11.8 Hz, C4), 142.3 (d, $^2J_{PC}$ = 11.1 Hz, *o*-mes), 141.0 (d, $^4J_{PC}$ = 1.8 Hz, *p*-mes^1), 140.7 (d, $^1J_{PC}$ = 6.2 Hz, C5), 138.9 (*p*-mes), 132.5 (*i*-mes), 130.4 (d, $^3J_{PC}$ = 4.8 Hz, *m*-mes), 129.4 (d, $^3J_{PC}$ = 5.3 Hz, *m*-mes^1), 125.4 (d, $^1J_{PC}$ = 9.7 Hz, *i*-mes^1), 33.8 (d, $^2J_{PC}$ = 15.6 Hz, 6-CH_2), 30.3 (d, $^2J_{PC}$ = 16.8 Hz, 6'-CH_2), 29.1 (d, $^1J_{PC}$ = 5.1 Hz, PCH_2), 28.7 (d, $^3J_{PC}$ = 11.6 Hz, 7-CH_2), 26.0 (dd, $^2J_{PC}$ = 14.2 Hz, $^3J_{PC}$ = 3.0 Hz, CH_2), 25.7 (d, $^3J_{PC}$ = 6.1 Hz, 7'-CH_2), 23.4 (d, $^3J_{PC}$ = 10.2 Hz, *o*-CH_3^{mes}), 21.6 (br d, $^3J_{PC}$ = 14.7 Hz, *o*-$CH_3^{mes,1}$), 21.2 (*p*-$CH_3^{mes,1}$), 20.8 (*p*-CH_3^{mes}), 14.4 (d, *J* = 1.0 Hz, 8-CH_3), 14.3 (d, *J* = 1.1 Hz, 8'-CH_3), [C_6F_5 not listed].

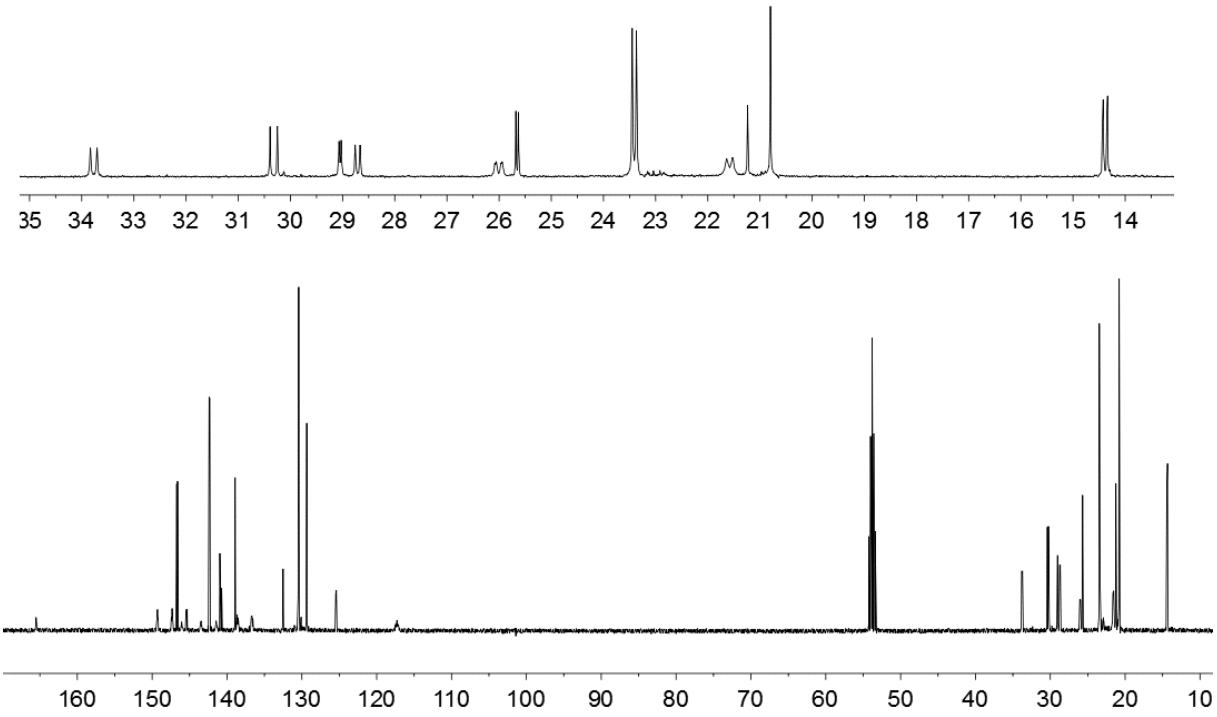
^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2): δ^{11}B = 35.0 ($\nu_{1/2} \approx$ 2500 Hz).

^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ^{19}F = −126.8 (br, 2F, *o*-C_6F_5), −152.4 (br, 1F, *p*-C_6F_5), −162.9 (br, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 10.5].

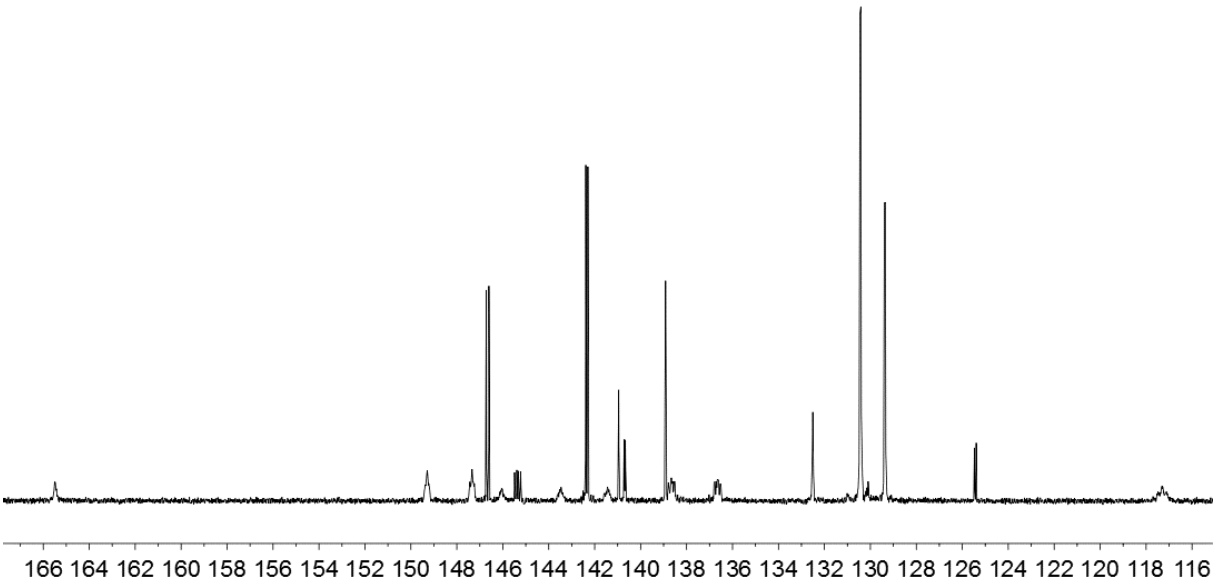
^{31}P{^{1}H} NMR (202 MHz, 299 K, CD_2Cl_2): δ^{31}P = 10.4 ($\nu_{1/2}$ ~ 15 Hz, 1P, P-1), −12.9 ($\nu_{1/2}$ ~ 100 Hz, 1P, $Pmes_2$).



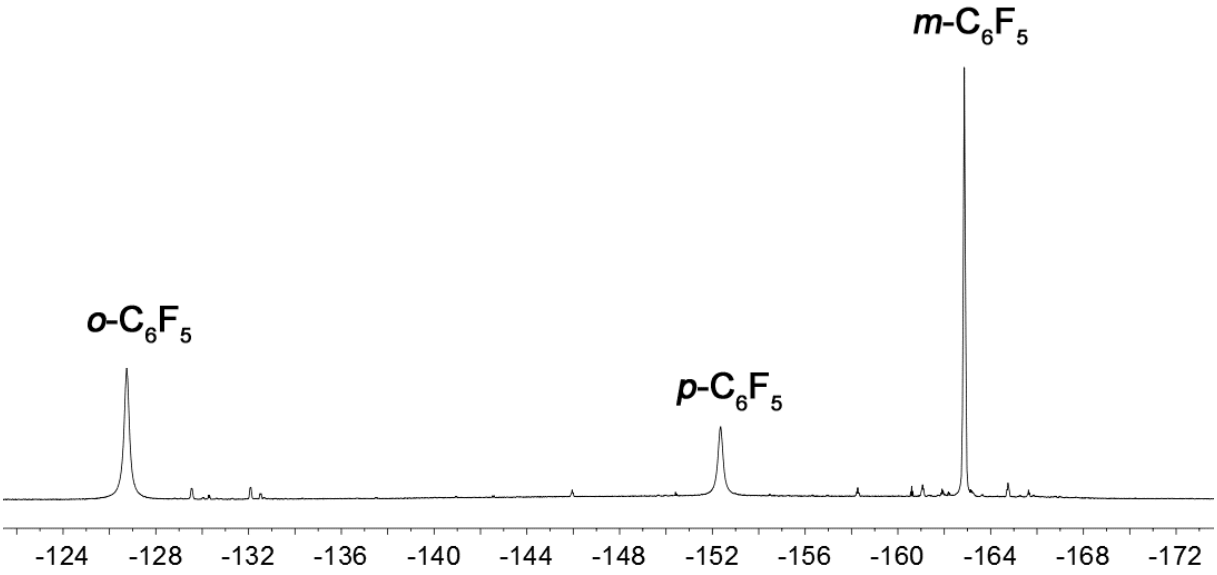
^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of compound **2c**.



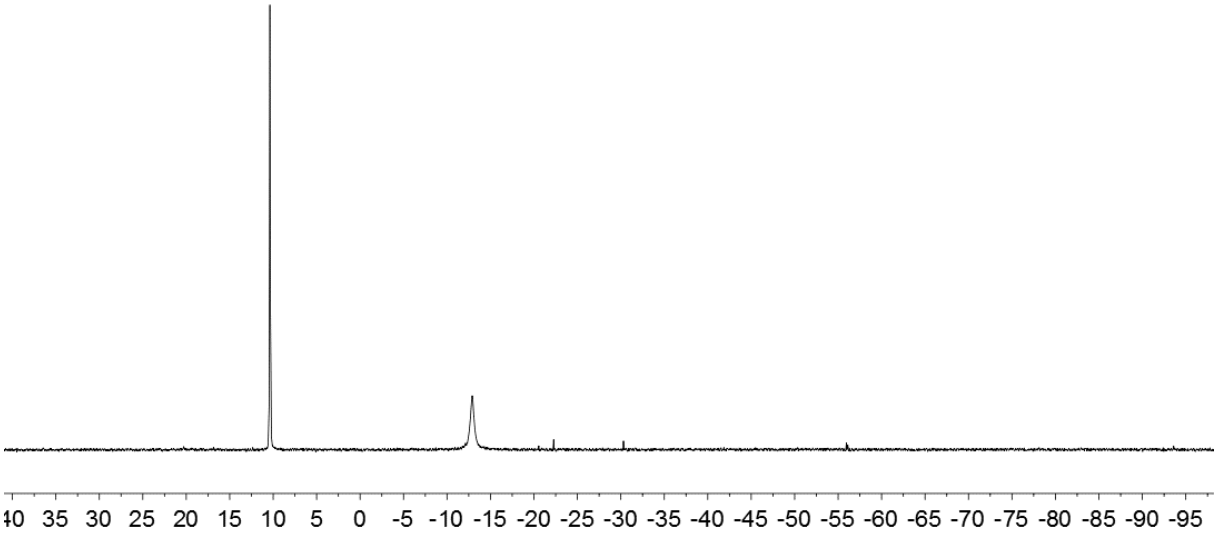
$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) spectrum of compound **2c**.



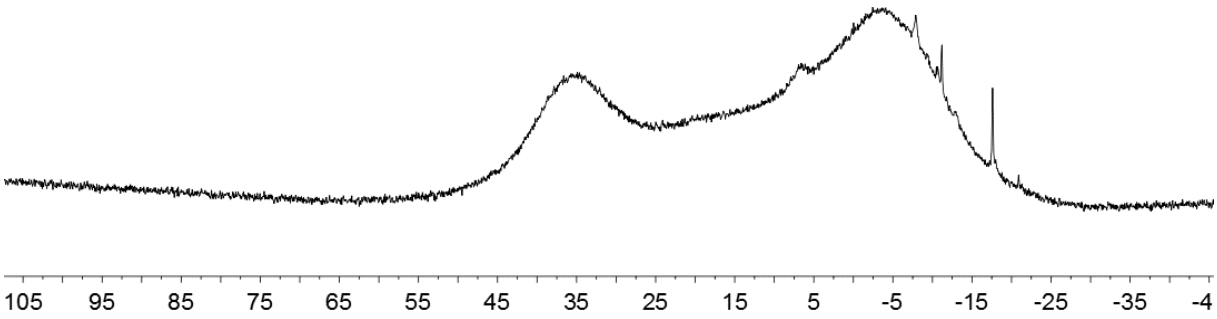
$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) spectrum of compound **2c**.



^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) spectrum of compound **2c**.



$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, CD_2Cl_2) spectrum of compound **2c**.



$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, CD_2Cl_2) spectrum of compound **2c**.

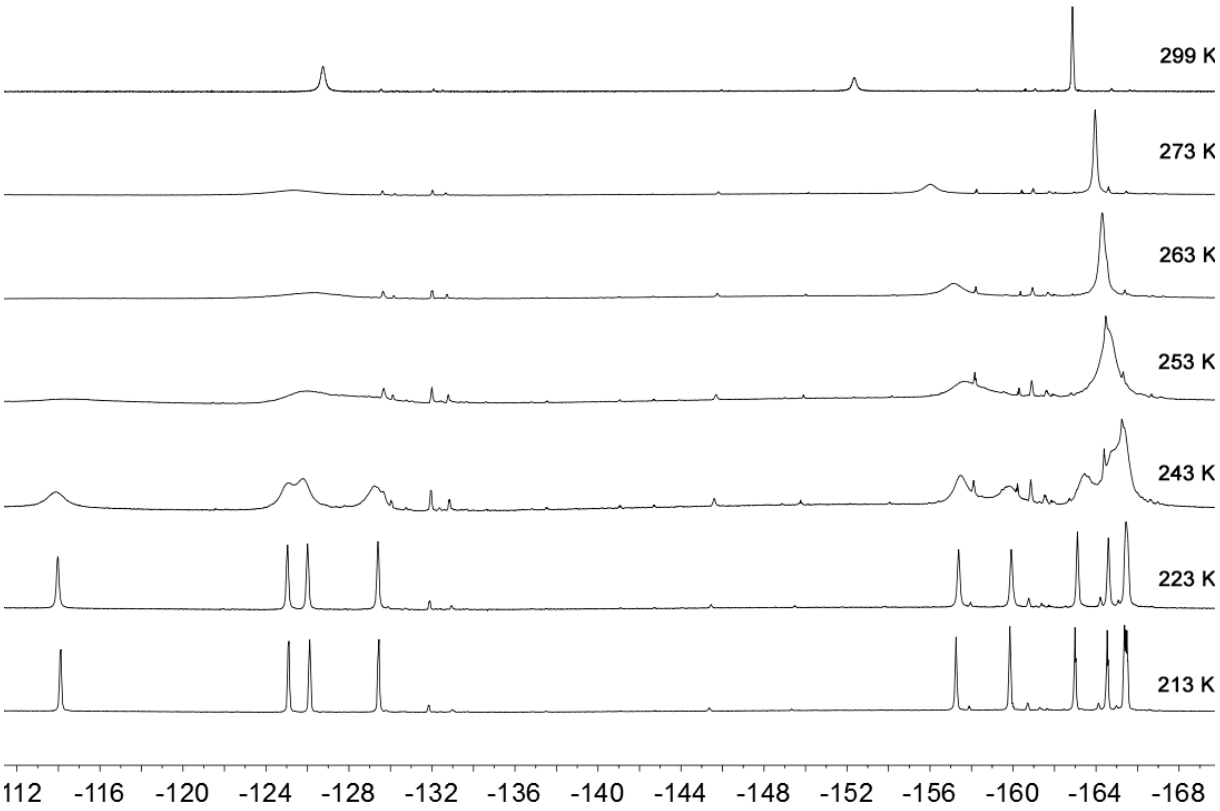
Selected NMR data at low temperature:

$^{11}B\{^{1}H\}$ NMR (160 MHz, 213 K, CD_2Cl_2): $\delta^{11}B = -7.2$ ($\nu_{1/2} \approx 2200$ Hz).

^{19}F NMR (470 MHz, 213 K, CD_2Cl_2): $\delta^{19}F = -114.1$ (br m, 1F, *o*), −129.4 (br m, 1F, *o'*), −157.3 (br m, 1F, *p*), −163.0 (br m, 1F, *m'*), −165.5 (br m, 1F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{p,m}$ = 5.7, 8.2]; −125.1 (br m, 1F, *o*), −126.1 (br m, 1F, *o'*), −159.9 (br m, 1F, *p*), −164.5 (br m, 1F, *m'*), −165.4 (br m, 1F, *m*)(C_6F_5) [$\Delta\delta^{19}F_{p,m}$ = 4.6, 5.5].

$^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2)

	P-1		$Pmes_2$	
	$\delta^{31}P$	$\nu_{1/2}$ (Hz)	$\delta^{31}P$	$\nu_{1/2}$ (Hz)
299K	10.4	15	-12.9	100
273K	7.6	20	-4.4	270
263K	6.7	20	-1.7	320
243K	5.5	20	1.4	200
233K	5.1	15	2.0	130
223K	4.8	15	2.1	70
213K	4.6	15	2.1	50

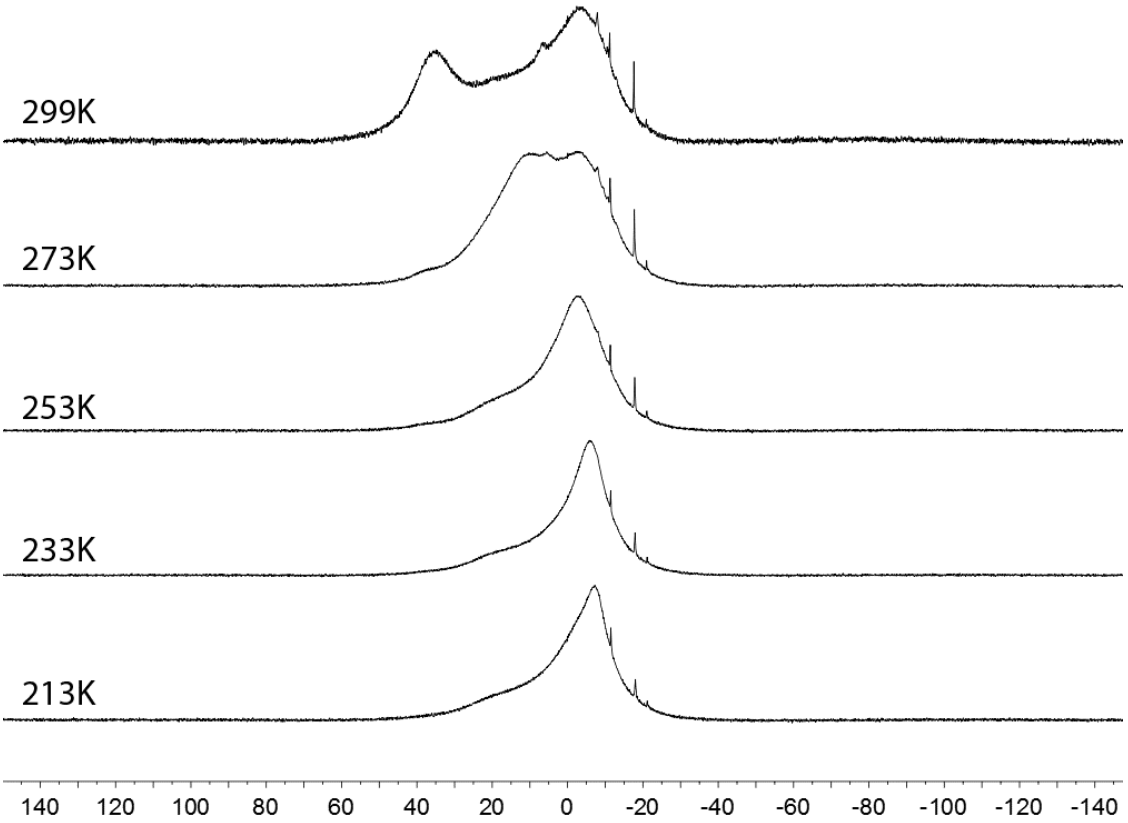


^{19}F NMR (470 MHz, VT, CD_2Cl_2) spectra of compound **2c**.

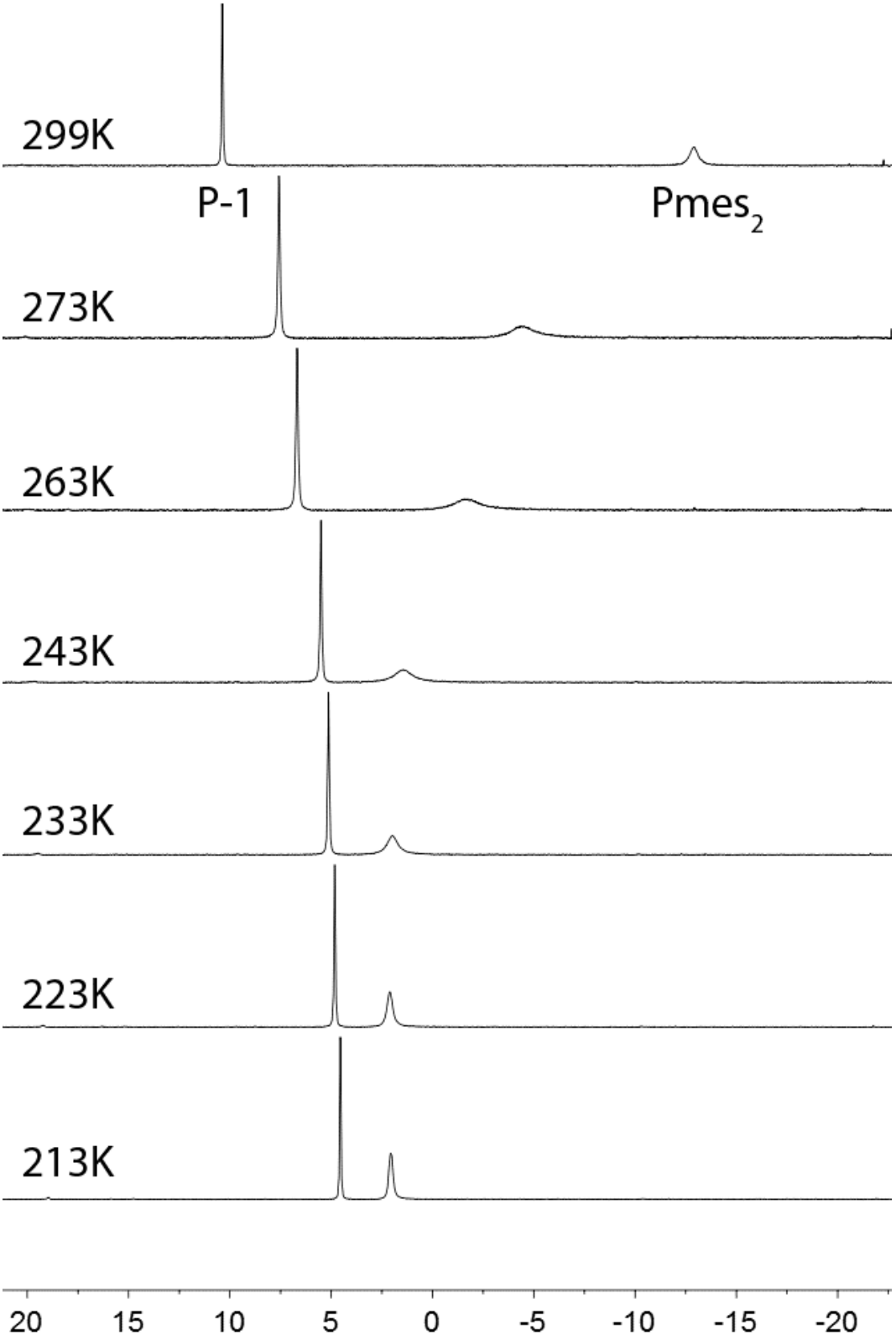
$\Delta G^{\neq} = RT_c(22.96 + \ln(T_c/\Delta\nu)$ [J mol^{-1}]; R = 8.314 J $(mol\ K)^{-1}$; 1 cal = 4.187 J.

^{19}F NMR (470 MHz, CD_2Cl_2): δ^{19}F(*p*-C_6F_5, 299K): –152.4 (br, 2F); δ^{19}F(*p*-C_6F_5, 213K): –157.3, –159.9 (each br m, each 1F).

$\Delta G^{\neq}$(para, T_c = 258 K; $\Delta\nu$(213K) = 1221 Hz) = 11.0 kcal/mol

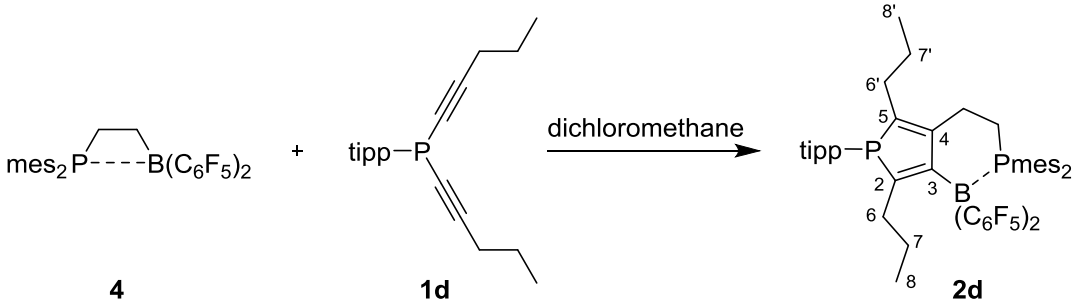


$^{11}B\{^{1}H\}$ NMR (160 MHz, VT, CD_2Cl_2) spectra of compound **2c**.



$^{31}P\{^{1}H\}$ NMR (202 MHz, VT, CD_2Cl_2) spectra of compound **2c**.

Preparation of compound 2d



4 **1d** **2d**

A solution of dimesitylvinylphosphane (89 mg, 0.3 mmol, 1 eq) in dichloromethane (2 mL) was added to bis(pentafluorophenyl)borane (104 mg, 0.3 mmol, 1 eq). Then the solution was stirred for 30 min. After addition of bis(pentynyl)(2,4,6-triisopropylphenyl)phosphane (**1d**) (110 mg, 0.3 mmol, 1 eq) the reaction mixture was stirred at room temperature for 5 days, before all volatiles were removed *in vacuo* and the residue was dissolved in *n*-pentane (5 mL). Removal of the solvent *in vacuo* gave compound **2d** as an orange solid (260 mg, 0.26 mmol, 86%).

Elemental analysis: Calc. for $C_{57}H_{63}BF_{10}P_2$: C: 67.73, H: 6.28; found: C: 68.50, H: 6.81.

IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3747 (w), 2960 (m), 2928 (m), 2869 (m), 2731 (w), 1647 (m), 1603 (m), 1515 (s), 1459 (s), 1381 (m), 1313 (m), 1273 (m), 1243 (m), 1087 (s), 1030 (m), 972 (s), 851 (m), 742 (m), 642 (m), 554 (w).

Melting point: 53 °C.

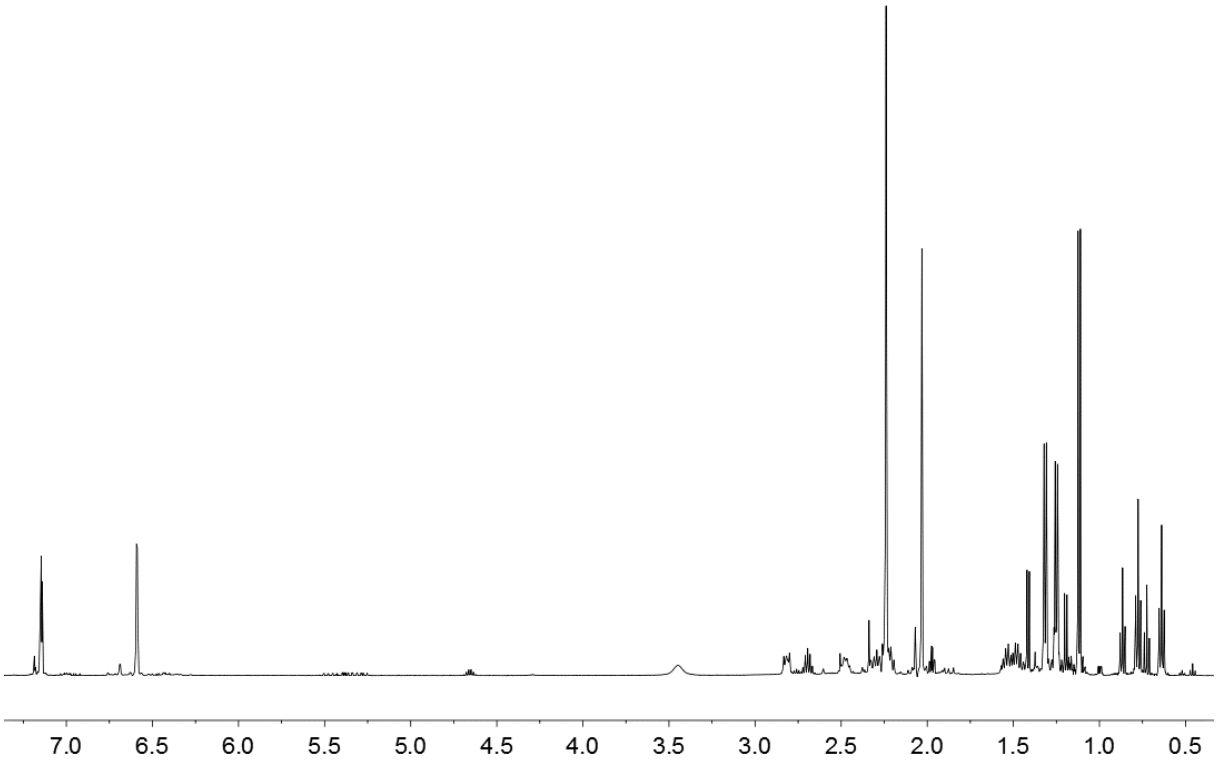
^{1}H NMR (500 MHz, 299 K, C_6D_6): δ^1H = 7.14 (d, $^4J_{PH}$ = 2.9 Hz, 2H, *m*-tipp), 6.59 (d, $^4J_{PH}$ = 2.9 Hz, 4H, *m*-mes), 3.44 (br, 2H, *o*-CH^{iPr}), 2.81 (m, 2H, PCH_2), 2.69 (sept, $^3J_{HH}$ = 7.0 Hz, 1H, *p*-CH^{iPr}), 2.47 (m, 2H, CH_2), 2.29 (m, 2H, 6-CH_2), 2.24 (s, 12 H, *o*-CH_3^{mes}), 2.21 (m, 2H, 6'-CH_2), 2.03 (s, 6H, *p*-CH_3^{mes}), 1.53 (m, 2H, 7-CH_2), 1.48 (m, 2H, 7'-CH_2), 1.32 (d, $^3J_{HH}$ = 7.0 Hz, 6H, *o*-CH_3^{iPr}), 1.25 (d, $^3J_{HH}$ = 6.7 Hz, 6H, *o*-CH_3^{iPr}), 1.12 (d, $^3J_{HH}$ = 7.0 Hz, 6 H, *p*-CH_3^{iPr}), 0.78 (t, $^3J_{HH}$ = 7.3 Hz, 3H, 8'-CH_3), 0.64 (t, $^3J_{HH}$ = 7.3 Hz, 3H, 8-CH_3).

^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6): δ^{13}C = 169.3 (br, C2), 157.6 (d, $^2J_{PC}$ = 13.7 Hz, *o*-tipp), 152.8 (d, $^4J_{PC}$ = 1.7 Hz, *p*-tipp), 147.1 (br, C3), 145.0 (dd, J_{PC} = 24.1 Hz, J_{PC} = 15.0 Hz, C4), 143.2 (d, $^1J_{PC}$ = 7.7 Hz, C5), 142.0 (d, $^2J_{PC}$ = 12.5 Hz, *o*-mes), 138.0 (*p*-mes), 132.9 (d, $^1J_{PC}$ = 12.4 Hz, *i*-mes), 130.4 (d, $^3J_{PC}$ = 3.7 Hz, *m*-mes), 122.9 (d, $^1J_{PC}$ = 5.9 Hz, *i*-tipp), 122.7 (d, $^3J_{PC}$ = 5.3 Hz, *m*-tipp), 34.7 (*p*-CH^{iPr}), 33.4 (d, $^2J_{PC}$ = 15.8 Hz, 6-CH_2), 32.7 (d, $^3J_{PC}$ = 15.3 Hz, *o*-CH^{iPr}), 30.8 (d, $^3J_{PC}$ = 10.5 Hz, 7-CH_2), 30.1 (d, $^2J_{PC}$ = 18.0 Hz, 6'-CH_2), 29.7 (dd, J_{PC} = 11.3 Hz, J_{PC} = 6.9 Hz, PCH_2), 27.2 (dd, J_{PC} = 20.2 Hz, J_{PC} = 3.7 Hz, CH_2), 26.7 (d, $^3J_{PC}$ = 6.1 Hz, 7'-CH_2), 25.3 (*o*-CH_3^{iPr}), 24.8 (*o*-CH_3^{iPr}), 23.8 (*p*-CH_3^{iPr}), 23.3 (d, $^3J_{PC}$ = 12.1 Hz, *o*-CH_3^{mes}), 20.7 (*p*-CH_3^{mes}), 14.1 (d, *J* = 1.2 Hz, 8-CH_3), 13.9 (8'-CH_3), [C_6F_5 not listed]

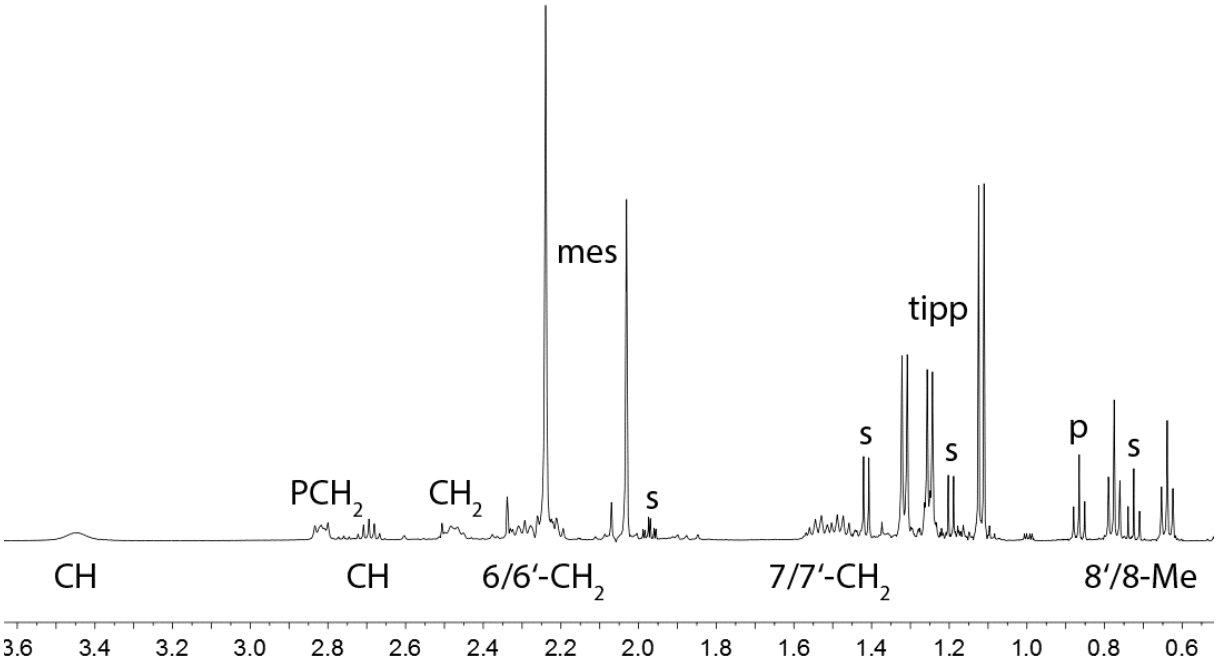
^{11}B{^{1}H} NMR (160 MHz, 299 K, C_6D_6): δ^{11}B = 50.2 ($\nu_{1/2} \approx$ 3200 Hz).

^{19}F NMR (470 MHz, 299 K, C_6D_6): $\delta^{19}F$ = −127.6 (br, 2F, *o*-C_6F_5), −148.4 (br, 1F, *p*-C_6F_5), −161.4 (br m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 13.0].

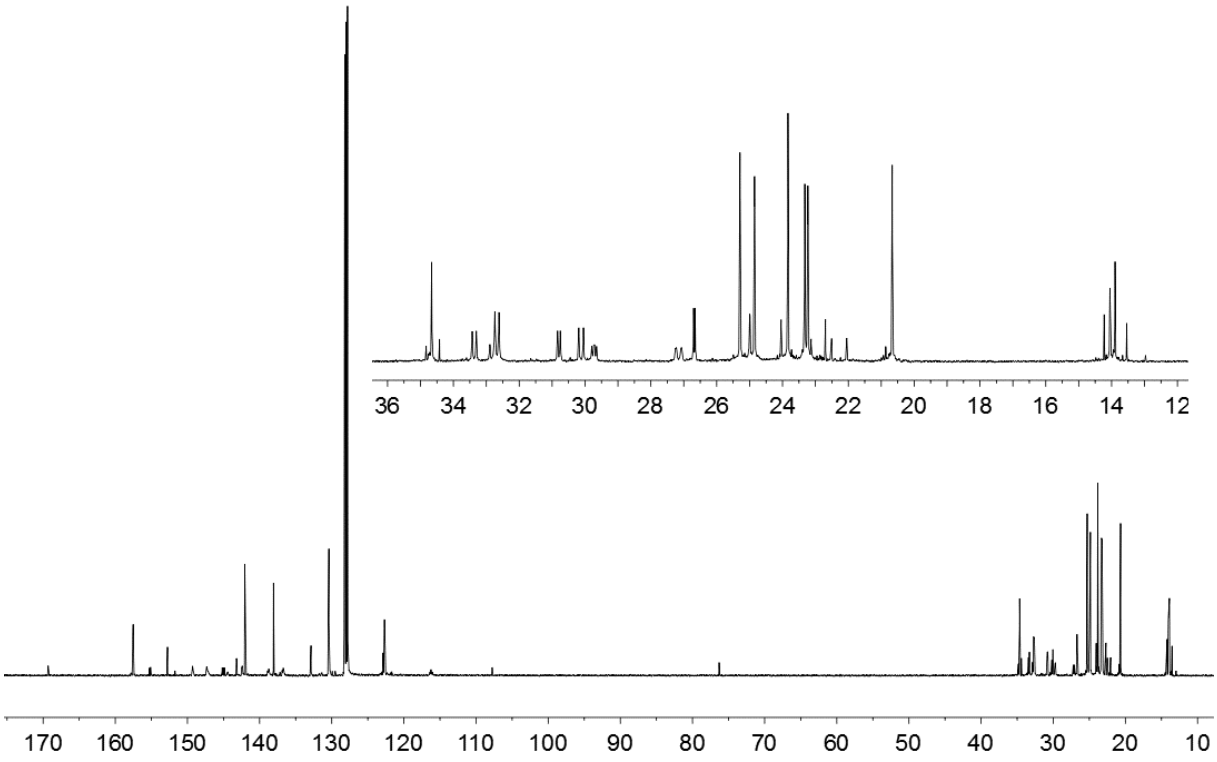
^{31}P{^{1}H} NMR (202 MHz, 299 K, C_6D_6): $\delta^{31}P$ = 4.2 ($\nu_{1/2}$ ~ 10 Hz, 1P, P-1), −17.8 ($\nu_{1/2}$ ~ 60 Hz, 1P, $Pmes_2$).



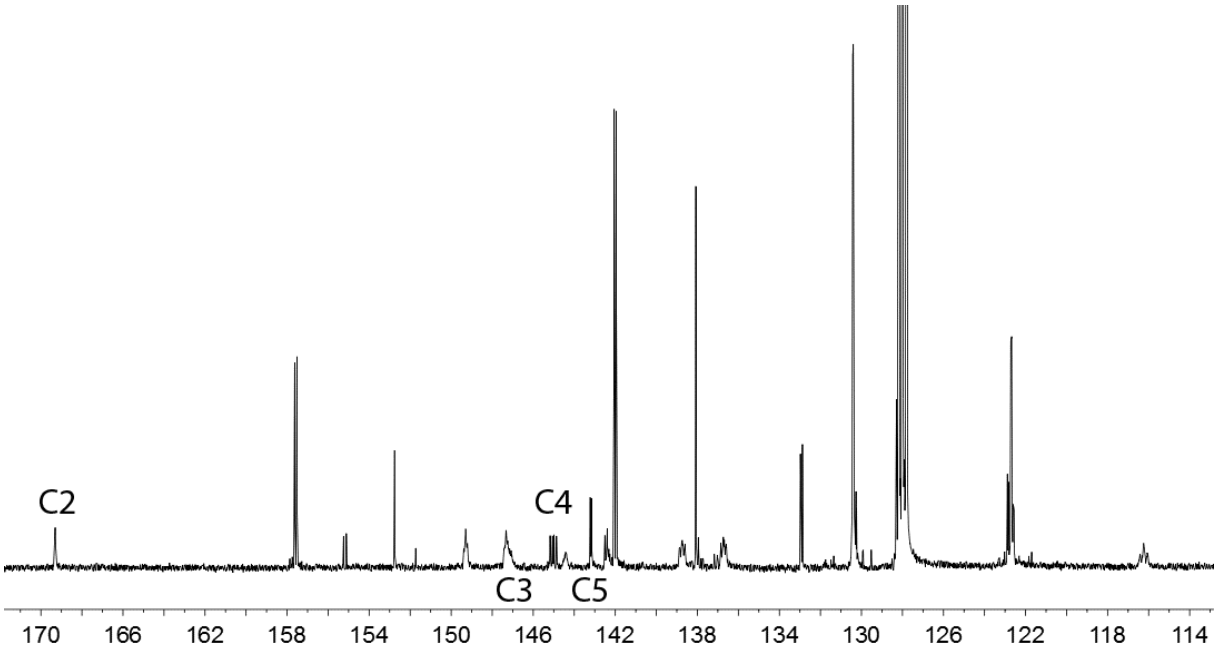
^{1}H NMR (500 MHz, 299 K, C_6D_6) spectrum of compound **2d**.



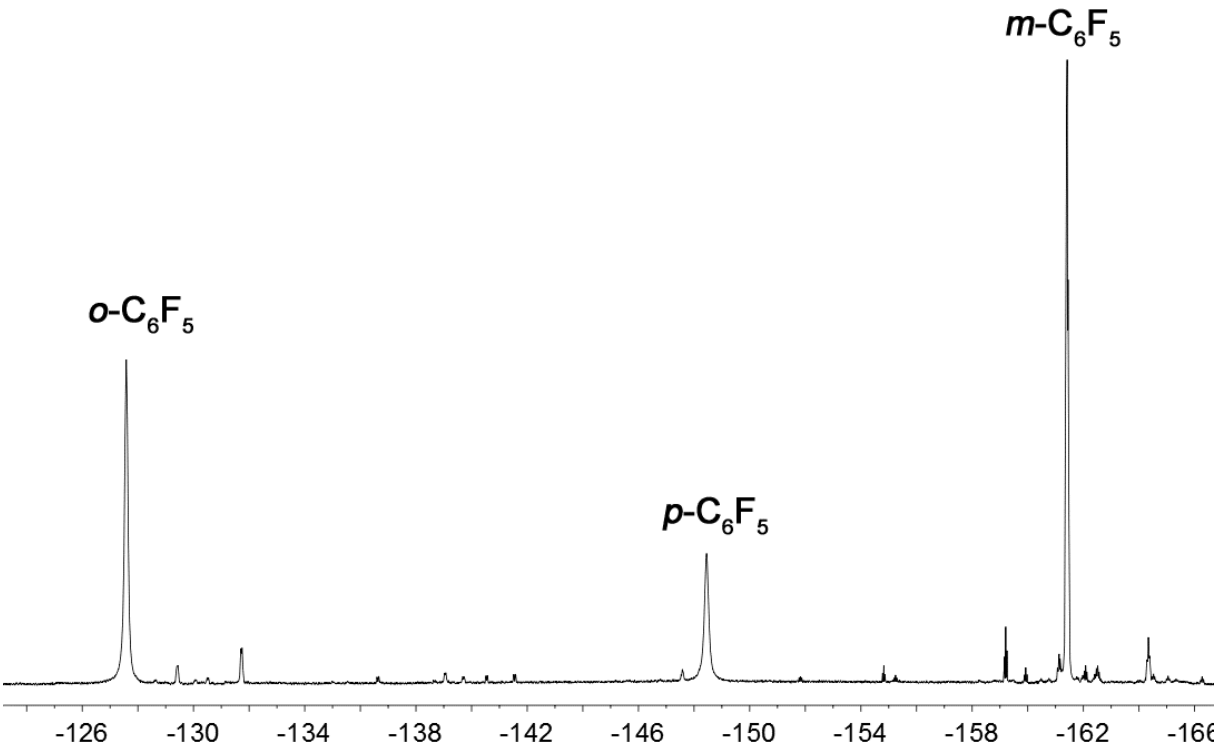
^{1}H NMR (500 MHz, 299 K, C_6D_6) spectrum of compound **2d**. [p = *n*-pentane, s = **1d**]



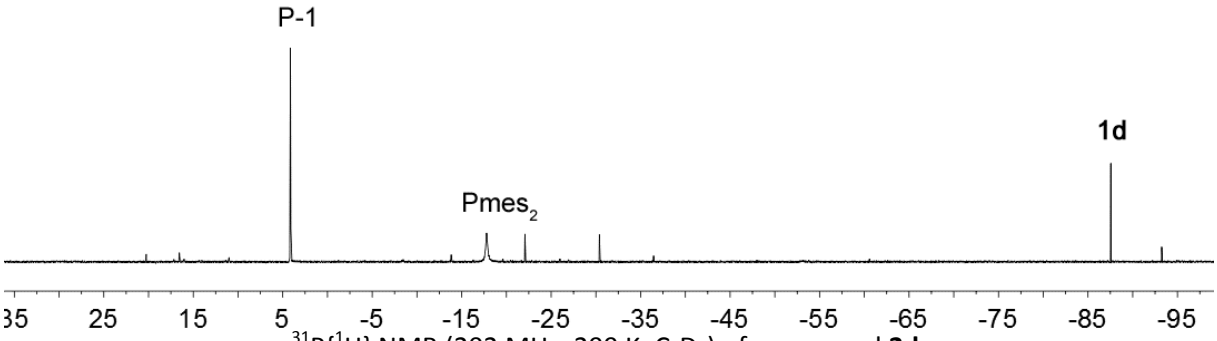
$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, C_6D_6) spectrum of compound **2d**.



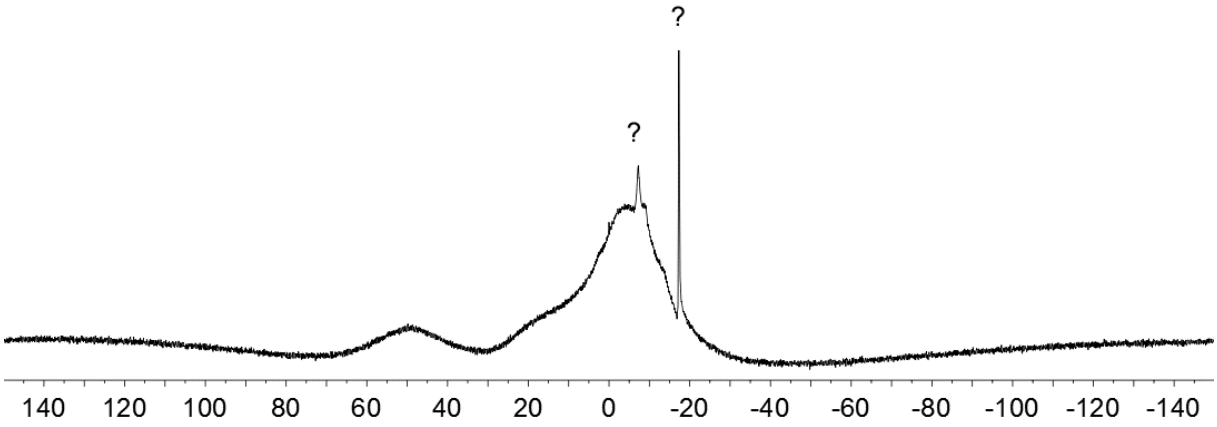
$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, C_6D_6) spectrum of compound **2d**.



^{19}F NMR (470 MHz, 299 K, C_6D_6) spectrum of compound **2d**.



$^{31}P\{^1H\}$ NMR (202 MHz, 299 K, C_6D_6) of compound **2d**.



$^{11}B\{^1H\}$ NMR (160 MHz, 299 K, C_6D_6) spectrum of compound **2d**. [? not identified yet]

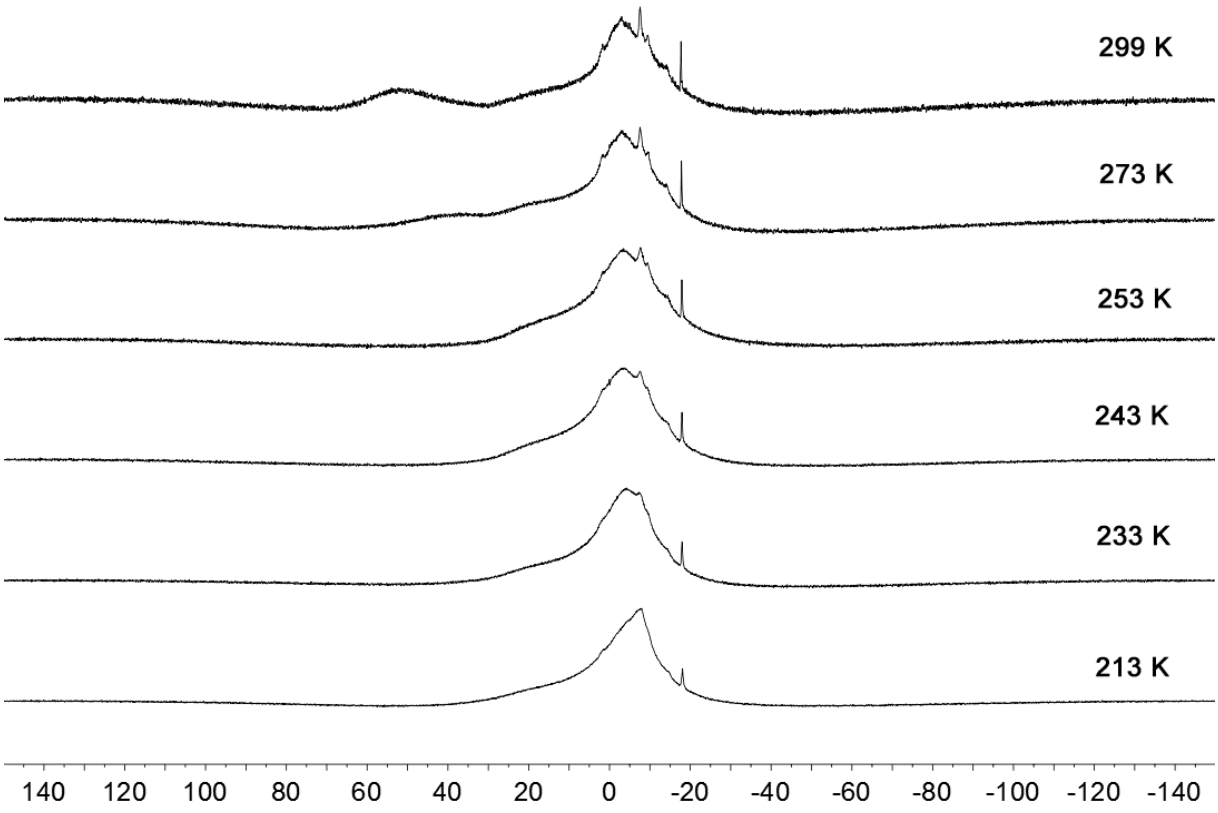
selected NMR data at low temperature:

^{11}B{^{1}H} NMR (160 MHz, 203 K, CD_2Cl_2): $\delta^{11}B = -8.2$ ($\nu_{1/2} \approx 600$ Hz).

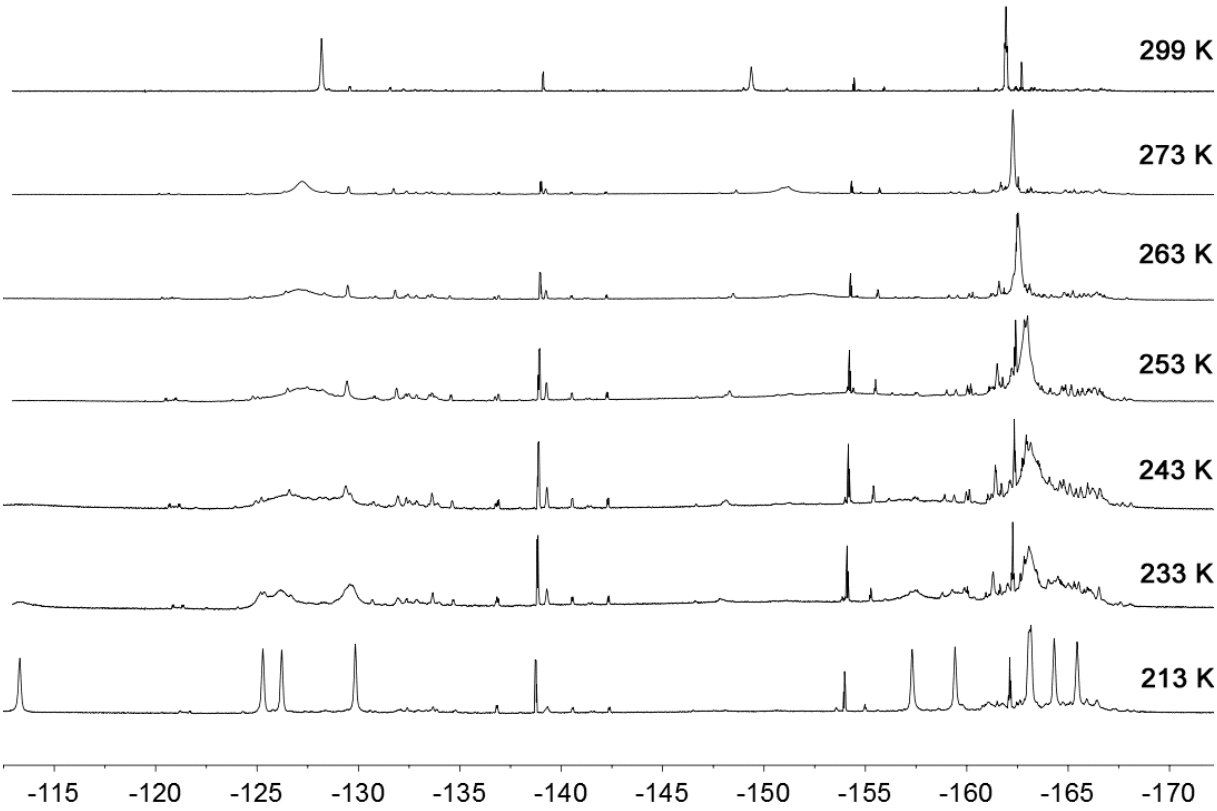
^{19}F NMR (470 MHz, 203 K, CD_2Cl_2): $\delta^{19}F = -113.5, -125.4, -126.3, -129.9$ (each: br, each 1F, *o*-C_6F_5), −157.2, −159.2 (each br m, each 1F, *p*-C_6F_5), −162.9, −163.1, −164.2, −165.4 (each br m, each 1F, *m*-C_6F_5).

^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2)

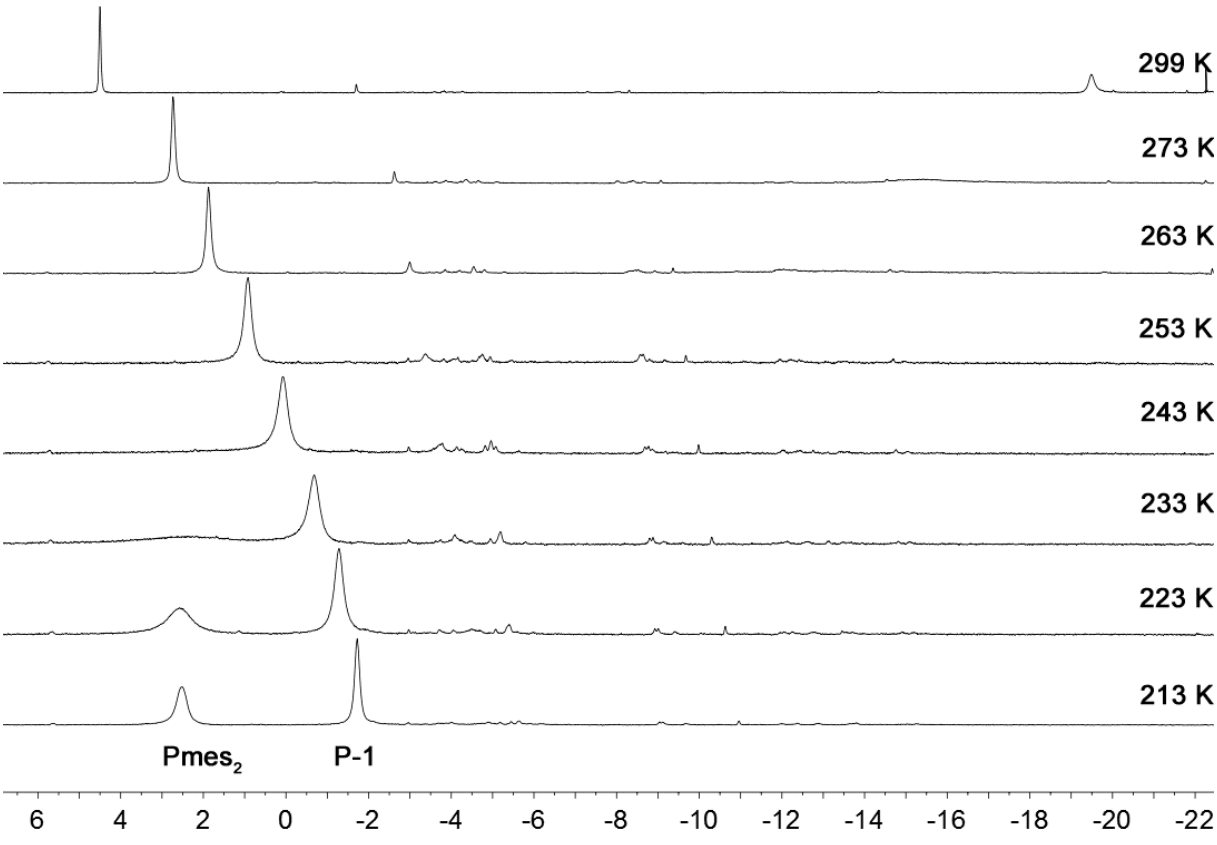
	P-1		$Pmes_2$	
	$\delta^{31}P$	$\nu_{1/2}$ (Hz)	$\delta^{31}P$	$\nu_{1/2}$ (Hz)
299K	4.5	10	−19.5	40
273K	2.7	20	−15.2	410
263K	1.9	30	−12.6	900
253K	0.9	40	−6.6	3500
243K	0.1	60	-	-
233K	−0.7	60	2.3	550
223K	−1.3	60	2.6	140
213K	−1.7	30	2.5	60
203K	−2.1	20	2.4	50



^{11}B{^{1}H} NMR (160 MHz, VT, CD_2Cl_2) spectra of compound **2d**.

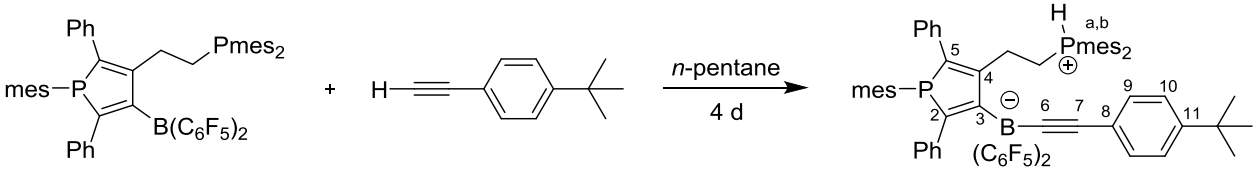


^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) spectra of compound **2d**.



$^{31}P\{^1H\}$ NMR (202 MHz, VT, CD_2I_2) spectra of compound **2d**.

Preparation of compound 9a



A solution of dimesitylvinylphosphane (74 mg, 0.25 mmol, 1 eq) in toluene (3 mL) was added to bis(pentafluorophenyl)borane (87 mg, 0.25 mmol, 1 eq). Then the solution was stirred for 10 min at room temperature. Subsequently, bis(phenylethynyl)mesitylphosphane (**1a**) (88 mg, 0.25 mmol, 1 eq) was added and the green solution was stirred at 70 °C for 2 h. After removal of the solvent *in vacuo*, the residue was dissolved in *n*-pentane (5 mL). The supernatant was separated, 4-*tert*-butylphenylacetylene (45 µL, 0.25 mmol, 1 eq) was added and the reaction mixture was stirred for 4 d. The formed precipitate was collected, dissolved in toluene (4 mL) and covered with *n*-pentane (12 mL). After one day at −32 °C a colorless precipitate was formed and washed with *n*-pentane (2 mL). Drying *in vacuo* gave compound **9a** as a colorless solid (60 mg, 20%). Crystals suitable for the X-ray crystal structure analysis were obtained by covering a solution of compound **9a** in dichloromethane (1 mL) with *n*-pentane (8 mL) at −34 °C.

Exact Mass: Calc. for $C_{69}H_{61}BF_{10}P_2^+$: 1152.4176; found: 1152.4187.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3747 (w), 2957 (m), 2464 (w), 2359 (w), 2153 (w), 1699 (m), 1651 (m), 1604 (m), 1509 (s), 1457 (s), 1396 (w), 1240 (s), 1153 (m), 1085 (s), 975 (s), 912 (m), 848 (m), 748 (s), 700 (s), 642 (m), 564 (w), 521 (w).

Melting point: 134 °C.

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ^1H = 7.33 (m, 2H, *o*-Ph^5), 7.22 (m, 2H, *m*-Ph^5), 7.14 (m, 1H, *p*-Ph^5), 7.14 (dm, $^1J_{PH}$ = 480.2 Hz, 1H, PH), 7.08 (m, 2H, 9-CH), 7.02, 6.85 (each br, each 2H, *o*,*m*-Ph^2), 6.94 (m, 2H, *m*-mes^b), 6.86 (m, 2H, 10-CH), 6.80 (m, 2H, *m*-mes^a), 6.76 (m, 1H, *p*-Ph^2), 6.69 (br m, 1H, *m*-mes^1), 6.52 (br, 1H, *m'*-mes^1), 3.52, 2.82 (each: m, 1H, CH_2), 3.21, 2.87 (each: m, 1H, PCH_2), 2.78 (s, 3H, *o*-$CH_3^{mes,1}$), 2.35 (br, 3H, *p*-$CH_3^{mes,b}$), 2.24 (s, 3H, *p*-$CH_3^{mes,a}$), 2.06 (s, 6H, *p*-$CH_3^{mes,1}$), 1.87 (s, 12H, *o*-$CH_3^{mes,a}$), 1.86 (s, 12H, *o*-$CH_3^{mes,b}$), 1.82 (s, 3H, *o'*-$CH_3^{mes,1}$), 1.07 (s, 9H, *t*Bu).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ^{13}C = 155.8 (br, C3), 151.8 (C2), 149.9 (C11), 148.5 (dd, J_{PC} = 26.1 Hz, J_{PC} = 18.1 Hz, C4), 146.9 (d, $^2J_{PC}$ = 35.1 Hz, *o*-mes^1), 146.6 (br d, $^2J_{PC}$ = 5.2 Hz, *o'*-mes^1), 146.4 (*p*-mes^b), 145.9 (*p*-mes^a), 143.7 (d, $^1J_{PC}$ = 10.1 Hz, C5), 143.6 (br d, $^2J_{PC}$ = 9.8 Hz, *o*-mes^a), 142.9 (br d, $^2J_{PC}$ = 9.7 Hz, *o*-mes^b), 141.0 (d, $^2J_{PC}$ = 19.9 Hz, *i*-Ph^2)140.4 (*p*-mes^1), 139.8 (d, $^2J_{PC}$ = 16.7 Hz, *i*-Ph^5), 132.3 (d, $^3J_{PC}$ = 11.8 Hz, *m*-mes^a), 131.8 (d, $^3J_{PC}$ = 10.2 Hz, *m*-mes^b), 130.4 (9-CH), 129.1 (*m*-Ph^5), 128.9 (br, *m'*-mes^1), 128.7 (br d, $^3J_{PC}$ = 8.8 Hz, *m*-mes^1), 128.3 (br), 126.8 (*o*,*m*-Ph^2), 128.2 (*o*-Ph^5), 126.1 (*p*-Ph^5), 125.6 (10-CH), 125.1 (d, $^1J_{PC}$ = 12.4 Hz, *i*-mes^1), 124.7 (*p*-Ph^2), 124.1 (C8), 113.1 (br, C6), 111.6 (d,

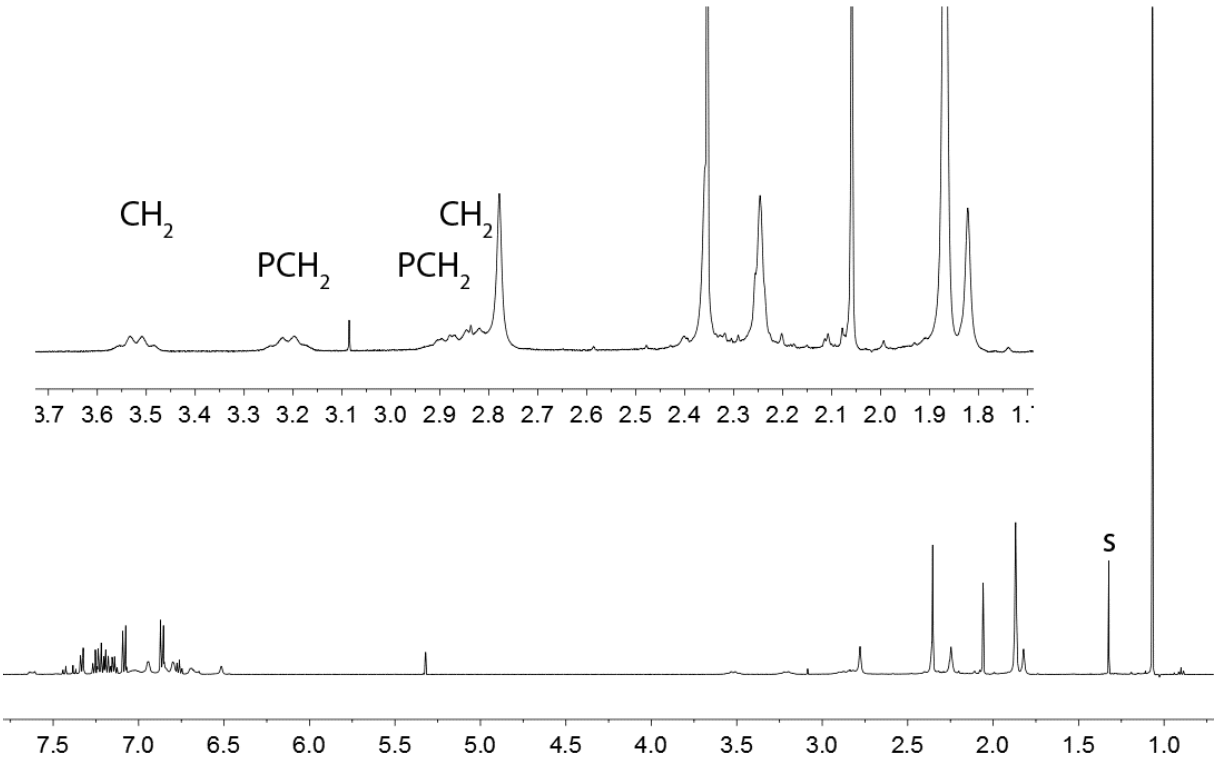
$^{1}J_{PC}$ = 62.3 Hz, *i*-mes^{b}), 111.1 (d, $^{1}J_{PC}$ = 57.3 Hz, *i*-mes^{a}), 92.0 (br, C7), 34.6 (*t*Bu), 31.1 (*t*Bu), 25.8 (CH_2), 24.7 (d, $^{3}J_{PC}$ = 29.6 Hz, *o*-$CH_3^{mes,1}$), 23.0 (dd, $^{1}J_{PC}$ = 37.6 Hz, *J* = 3.9 Hz, PCH_2), 22.4 (br d, $^{3}J_{PC}$ = 5.4 Hz, *o*-$CH_3^{mes,a}$), 21.5 (*p*-$CH_3^{mes,b}$), 21.2 (*p*-$CH_3^{mes,a}$), 21.14 (br d, $^{3}J_{PC}$ = 7.4 Hz, *o*-$CH_3^{mes,b}$), 21.06 (d, $^{5}J_{PC}$ = 7.6 Hz, *p*-$CH_3^{mes,1}$), 18.9 (br, *o'*-$CH_3^{mes,1}$). [C_6F_5 not listed, ^{t} tentative assignement]

$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, CD_2Cl_2): $\delta^{11}B$ = −19.3 ($\nu_{1/2} \approx 50$ Hz).

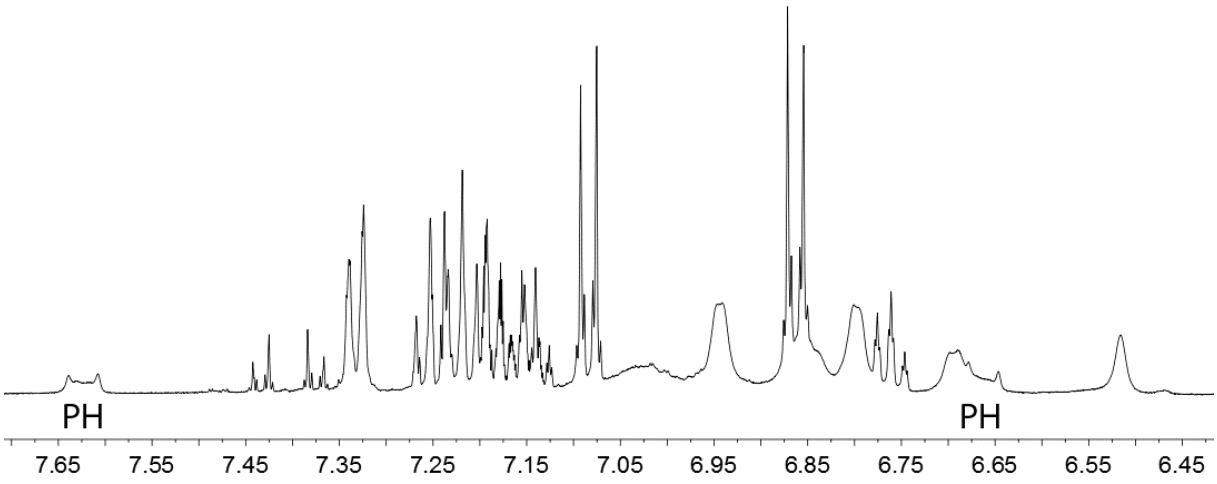
^{19}F NMR (470 MHz, 299 K, C_6D_6): $\delta^{19}F$ = −130.6 (br, 2F, *o*), −163.5 (t, $^{3}J_{FF}$ = 19.9 Hz, 1F, *p*), −167.0 (br m, 2F, m)(C_6F_5)[$\Delta\delta^{19}F_{p,m}$ = 3.5], −130.6 (br, 2F, *o*), −164.8 (t, $^{3}J_{FF}$ = 20.3 Hz, 1F, *p*), −167.9 (mbr , 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{p,m}$ = 3.1].

$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, CD_2Cl_2): $\delta^{31}P$ = 10.2 (t, *J* = 5.6 Hz, 1P, P-1), −13.3 ($\nu_{1/2}$ ~ 2 Hz, 1P, $Pmes_2$).

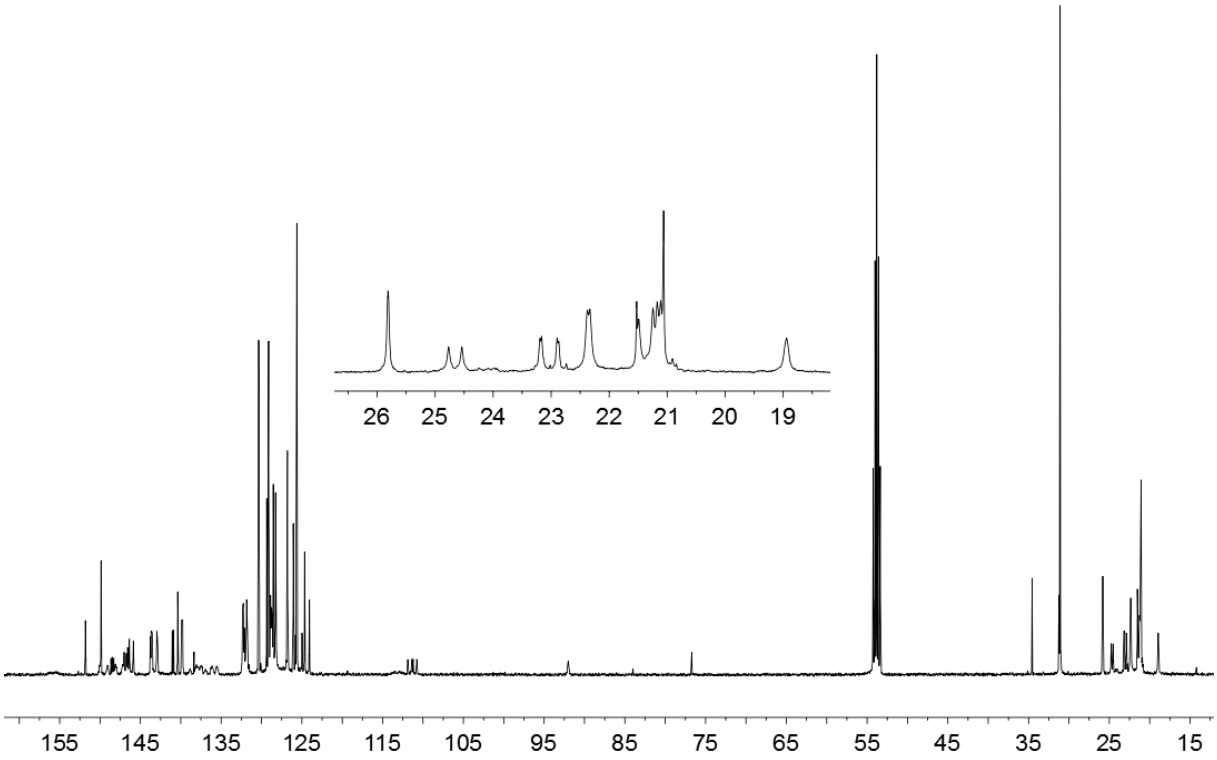
^{31}P NMR (202 MHz, 299 K, CD_2Cl_2): $\delta^{31}P$ = 10.2 ($\nu_{1/2}$ ~ 20 Hz, 1P, P-1), −13.3 (d, $^{1}J_{PH} \approx 480$ Hz, 1P, $Pmes_2$).



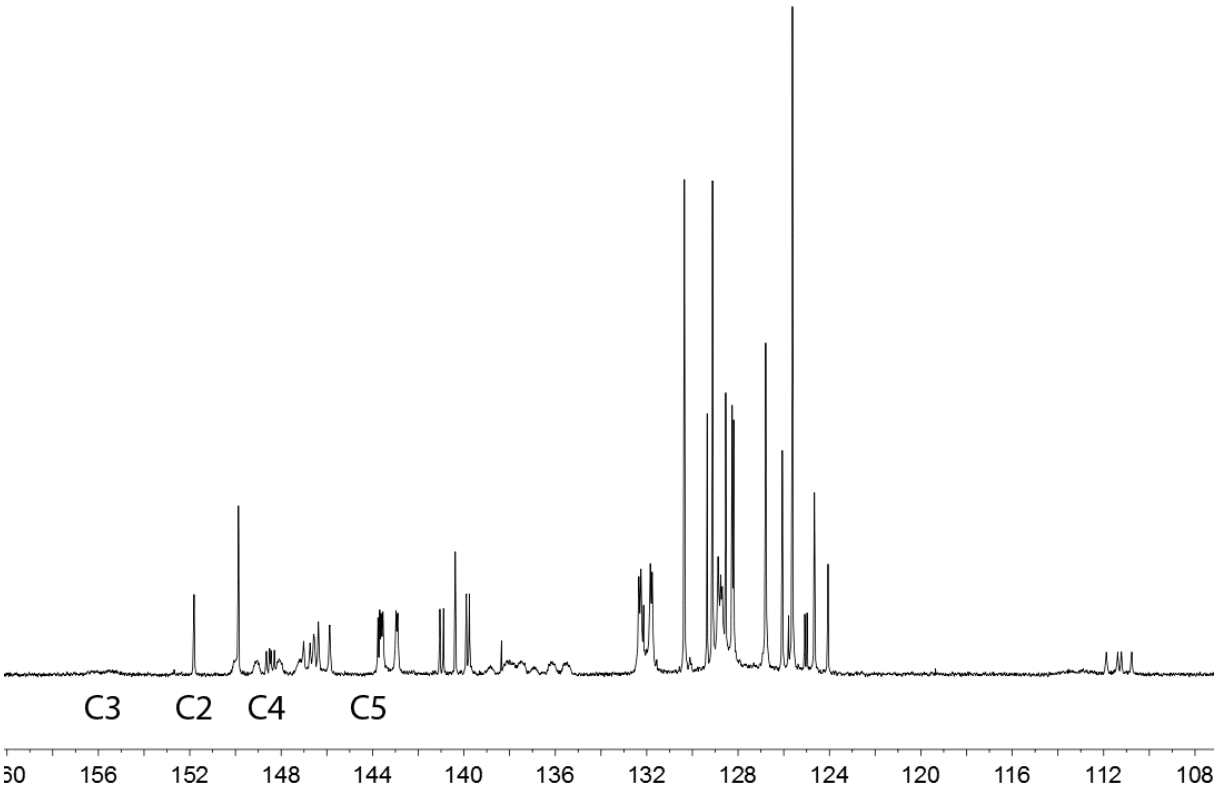
^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of compound **9a**. [s = starting material acetylene]



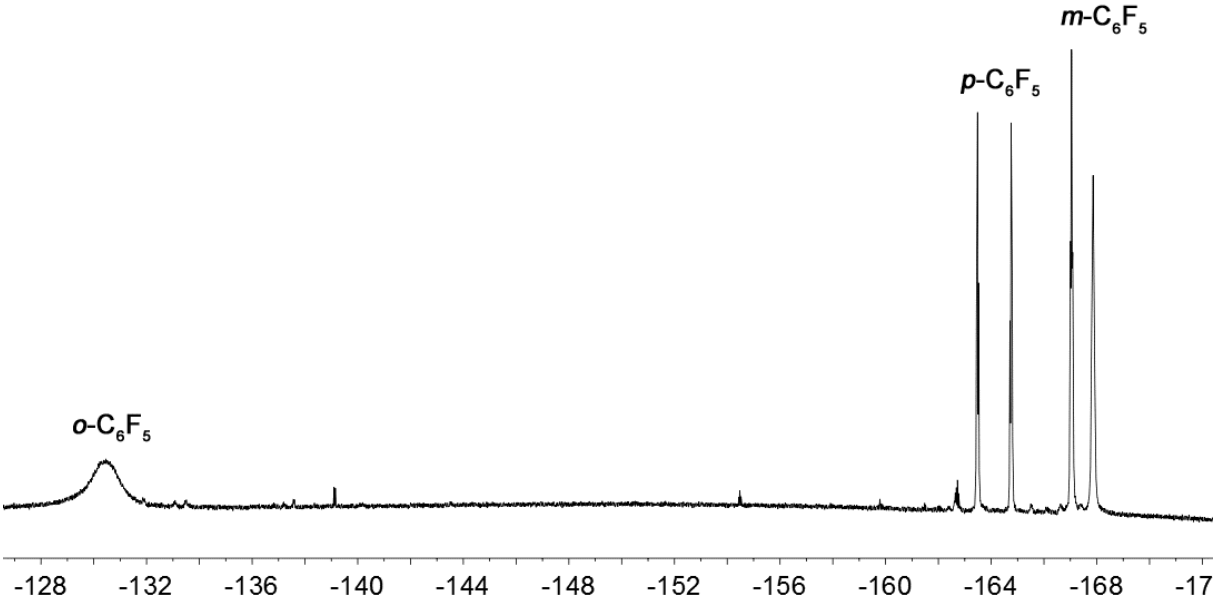
^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of compound **9a**.



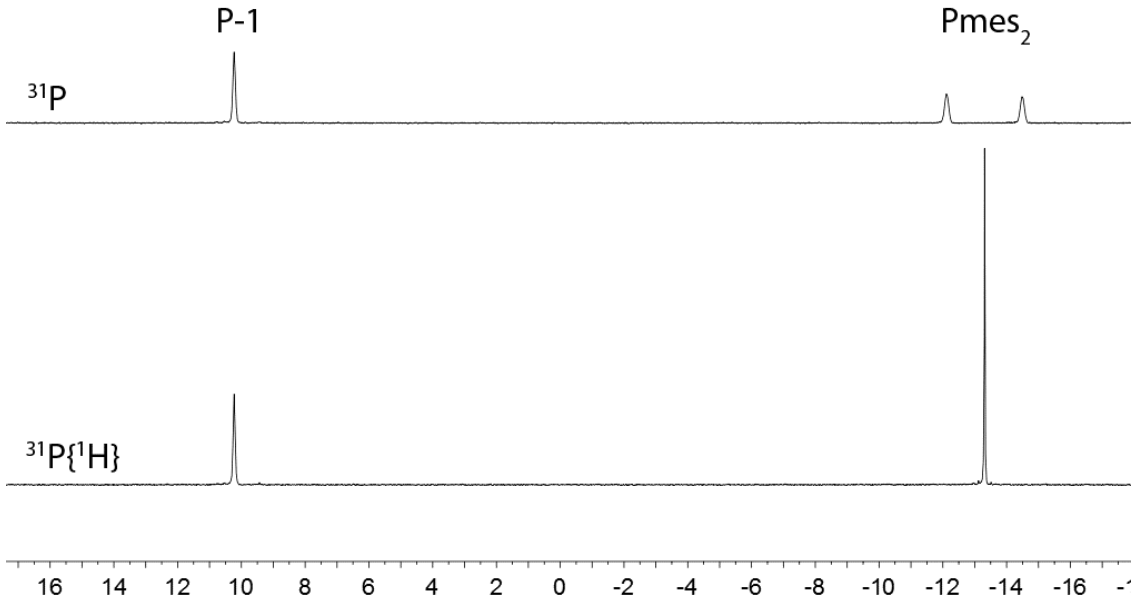
^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2) spectrum of compound **9a**.



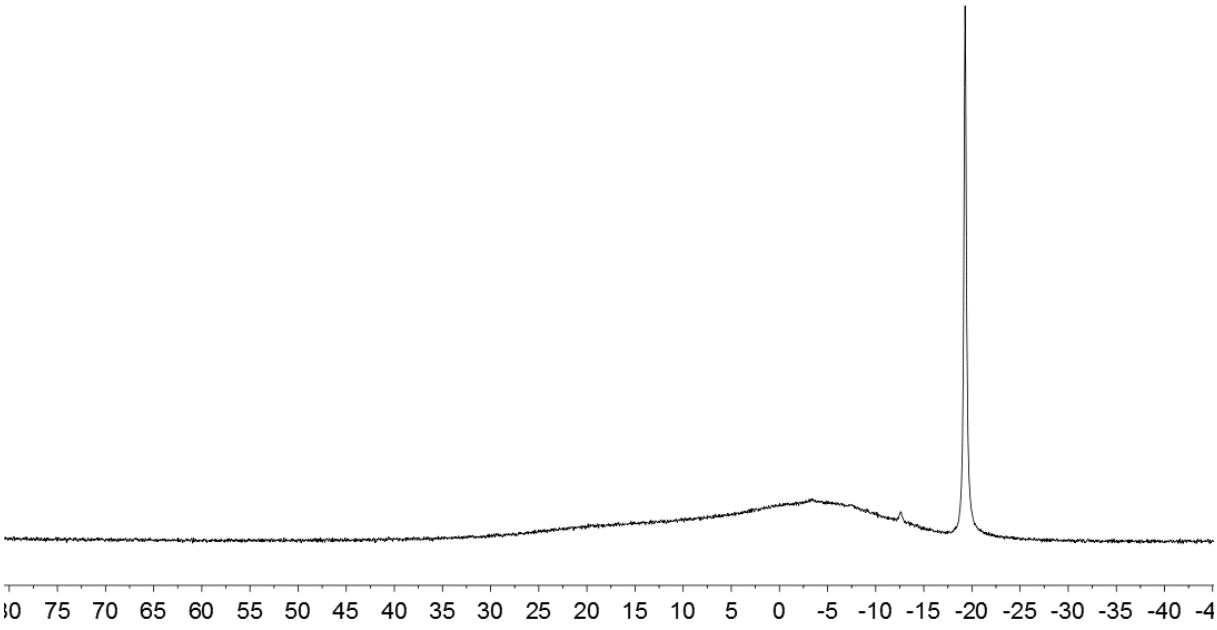
$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) spectrum of compound **9a**.



^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) spectrum of compound **9a**.



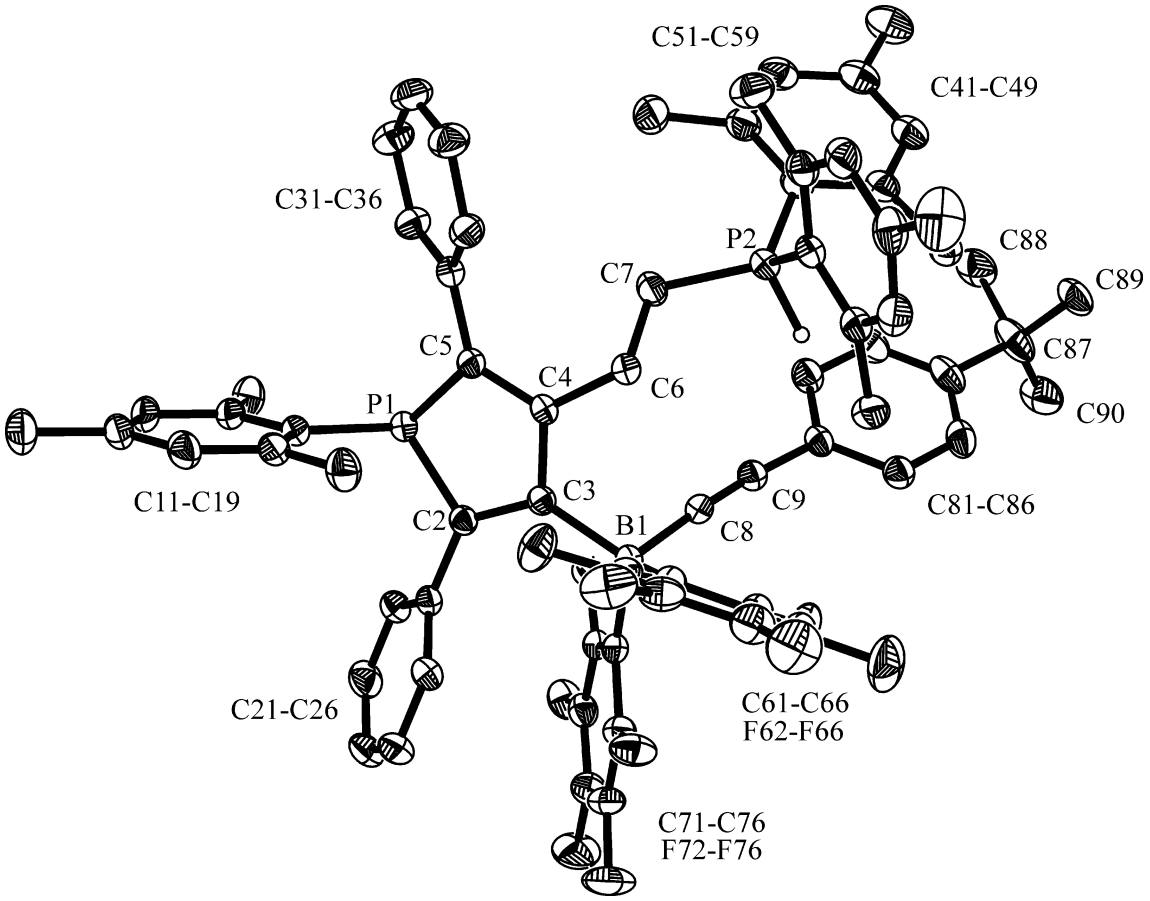
$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, CD_2Cl_2) spectrum of compound **9a**.



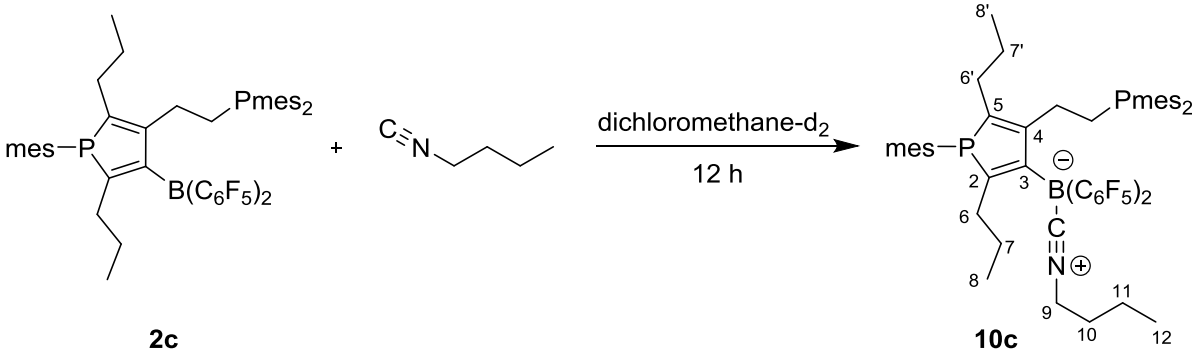
$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, CD_2Cl_2) spectrum of compound **9a**.

X-ray crystal structure analysis of compound 9a: formula $C_{69}H_{61}BF_{10}P_2 \cdot 2 \times CH_2Cl_2$, M = 1322.78, yellow crystal, 0.10 x 0.07 x 0.03 mm, a = 11.1621(3), b = 15.9872(4), c = 19.7607(6) Å, α = 93.009(2), β = 96.384(2), γ = 109.293(2)°, V = 3292.6(2) Å^3, ρ_{calc} = 1.334 gcm^{-3}, μ = 2.683 mm^{-1}, empirical absorption correction (0.775 ≤ T ≤ 0.923), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 49077 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 11528 independent (R_{int} = 0.062) and 8811 observed reflections [I>2σ(I)], 862 refined parameters, R = 0.052,

wR^2 = 0.144, max. (min.) residual electron density 0.82 (-0.47) e.Å^{-3}, the hydrogen atom at P2 was refined freely; others were calculated and refined as riding atoms.



Preparation of compound 10c



2c **10c**

A solution of dimesitylvinylphosphane (30 mg, 0.1 mmol, 1 eq) in CD_2Cl_2 (1 mL) was added to bis(pentafluorophenyl)borane (35 mg, 0.1 mmol, 1 eq). Then the solution was stirred for 5 h and bis(pentynyl)mesitylphosphane (**1c**) (25 mg, 0.1 mmol, 1 eq) was added. The reaction mixture was stirred overnight, before *n*-butylisocyanide (10 µL, 0.1 mmol, 1 eq) was added (*CAUTION: Many isocyanides are toxic compounds that need to be handled with due care.*). The yellow solution was stirred overnight and all volatiles were removed *in vacuo*. The residue was dissolved in *n*-pentane (3 mL) before the solvent was removed *in vacuo* to give compound **10c** as a yellow solid (70.0 mg, 0.07 mmol, 70%).

Elemental Analysis: Calc. for $C_{56}H_{60}BF_{10}NP_2$: C: 66.41, H: 5.99, N: 1.39; found: C: 66.43, H: 5.97, N: 1.92.

IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2961 (m), 2928 (m), 2872 (m), 2732 (w), 2298 (m), 1644 (m), 1603 (m), 1516 (s), 1464 (s), 1379 (m), 1283 (m), 1092 (s), 1027 (m), 977 (s), 850 (m), 775 (w), 712 (w), 616 (w), 553 (w).

Decomposition point: 80 °C.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ^1H = 6.90 (d, $^4J_{PH}$ = 2.7 Hz, 2H, *m*-mes^1), 6.76 (d, $^4J_{PH}$ = 2.3 Hz, 4H, *m*-mes), 3.92 (m, 2H, 9-CH_2), 2.31 (m, 2H, 6-CH_2), 2.28 (s, 3H, *p*-$CH_3^{mes,1}$), 2.24 (br, 4H, *o*-$CH_3^{mes,1}$), 2.22 (m, 2H, CH_2, $PCH_2)^t$, 2.18 (m, 2H, CH_2, $CH_2)^t$, 2.21 (s, 6H, *p*-CH_3^{mes}), 2.16 (s, 12H, *o*-CH_3^{mes}), 1.87 (m, 2H, 6'-CH_2), 1.80 (m, 2H, 10-CH_2), 1.38 (m, 2H, 11-CH_2), 1.34 (m, 2H, 7-CH_2), 1.16 (m, 2H, 7'-CH_2), 0.94 (t, $^3J_{HH}$ = 7.6 Hz, 3H, 12-CH_3), 0.72 (t, $^3J_{HH}$ = 7.5 Hz, 3H, 8-CH_3), 0.64 (t, $^3J_{HH}$ = 7.4 Hz, 3H, 8'-CH_3). [^{t}: tentative assignement]

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ^{13}C = 195.8 (br, C≡N), 156.3 (C2), n.o. (C3), 143.5 (d, $^1J_{PC}$ = 2.8 Hz, C5), 142.5 (dd, J_{PC} = 17.5 Hz, J_{PC} = 14.7 Hz, C4), 142.2 (d, $^2J_{PC}$ = 13.7 Hz, *o*-mes), 141.7 (d, $^4J_{PC}$ = 1.8 Hz, *p*-mes^1), 138.0 (*p*-mes), 132.9 (d, $^1J_{PC}$ = 24.0 Hz, *i*-mes), 130.3 (d, $^3J_{PC}$ = 3.3 Hz, *m*-mes), 129.7 (d, $^3J_{PC}$ = 6.2 Hz, *m*-mes^1), 123.7 (d, $^1J_{PC}$ = 6.0 Hz, *i*-mes^1), 52.8 (9-CH_2), 32.9 (d, $^2J_{PC}$ = 14.1 Hz, 6-CH_2), 30.1 (d, $^2J_{PC}$ = 16.1 Hz, 6'-CH_2), 29.7 (10-CH_2), 29.5 (dd, J_{PC} = 18.8 Hz, J_{PC} = 4.7 Hz, $PCH_2)^t$, 26.0 (dd, J_{PC} = 23.9 Hz, J_{PC} = 3.4 Hz, $CH_2)^t$, 25.9 (d, $^3J_{PC}$ = 9.9 Hz, 7-CH_2), 25.6 (d, $^3J_{PC}$ = 6.8 Hz, 7'-CH_2), 22.8 (d, $^3J_{PC}$ =

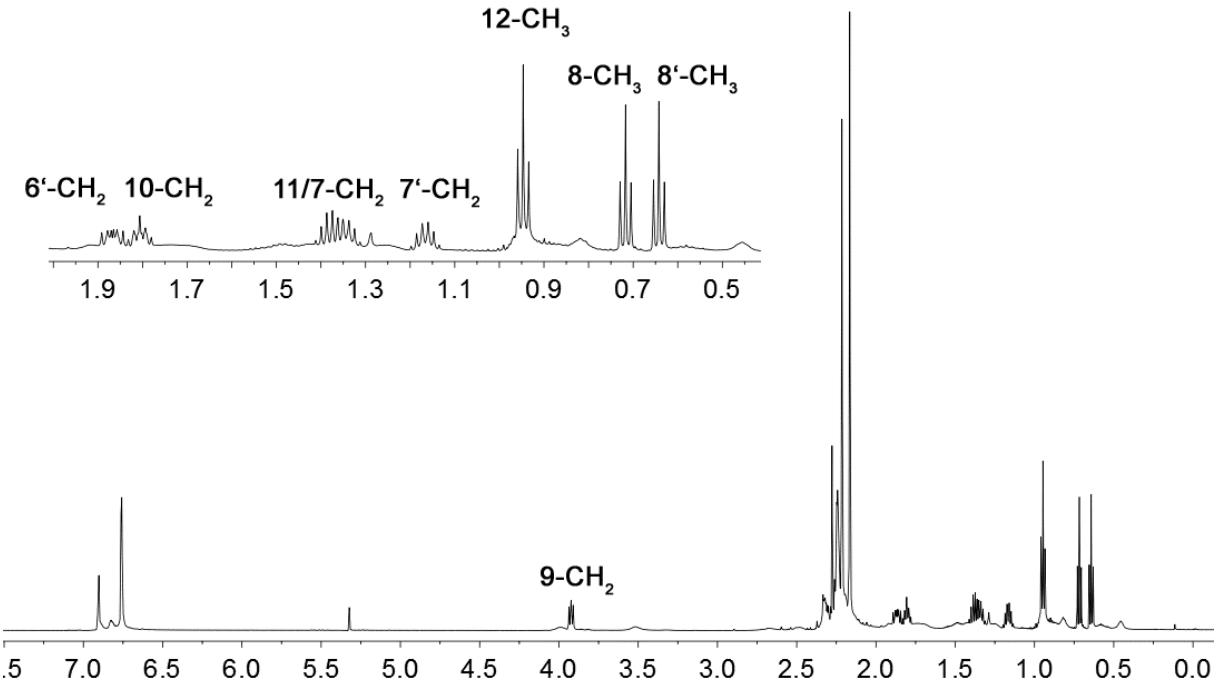
14.2 Hz, *o*-CH_3^{mes}), 21.7 (br, *o*-$CH_3^{mes,1}$), 21.3 (d, *J* = 0.7 Hz, *p*-$CH_3^{mes,1}$), 21.0 (11-CH_2), 20.9 (*p*-CH_3^{mes}), 14.3 (d, *J* = 1.3 Hz, 8-CH_3), 14.2 (d, *J* = 0.7 Hz, 8'-CH_3), 13.8 (12-CH_3), [C_6F_5 not listed]

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): $\delta^{11}B = -17.3$ ($\nu_{1/2} \approx 300$ Hz).

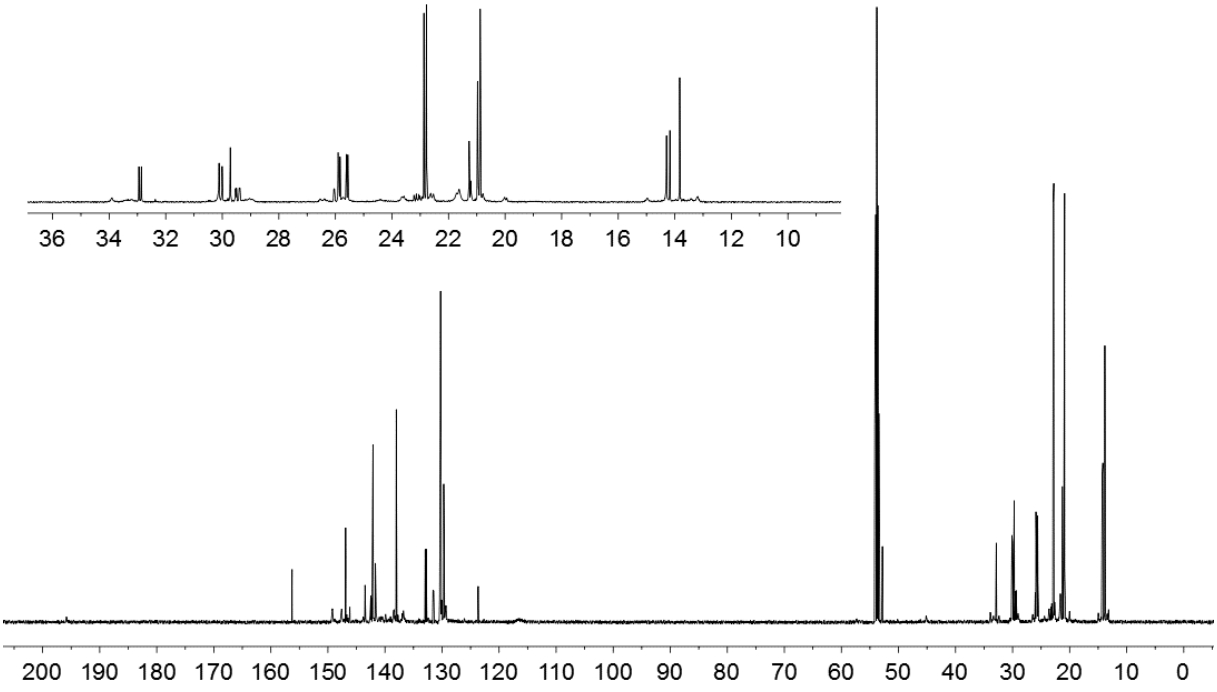
^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): $\delta^{19}F = -135.0$ (m, 2F, *o*-C_6F_5), −158.2 (t, $^3J_{FF}$ = 20.0 Hz, 1F, *p*-C_6F_5), −164.0 (m, 2F, *m*-C_6F_5),[$\Delta\delta^{19}F_{p,m} = 5.8$].

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): $\delta^{31}P = 9.6$ (d, *J* = 1.9 Hz, 1P, P-1), −22.7 ($\nu_{1/2}$ ~ 15 Hz, 1P, $Pmes_2$).

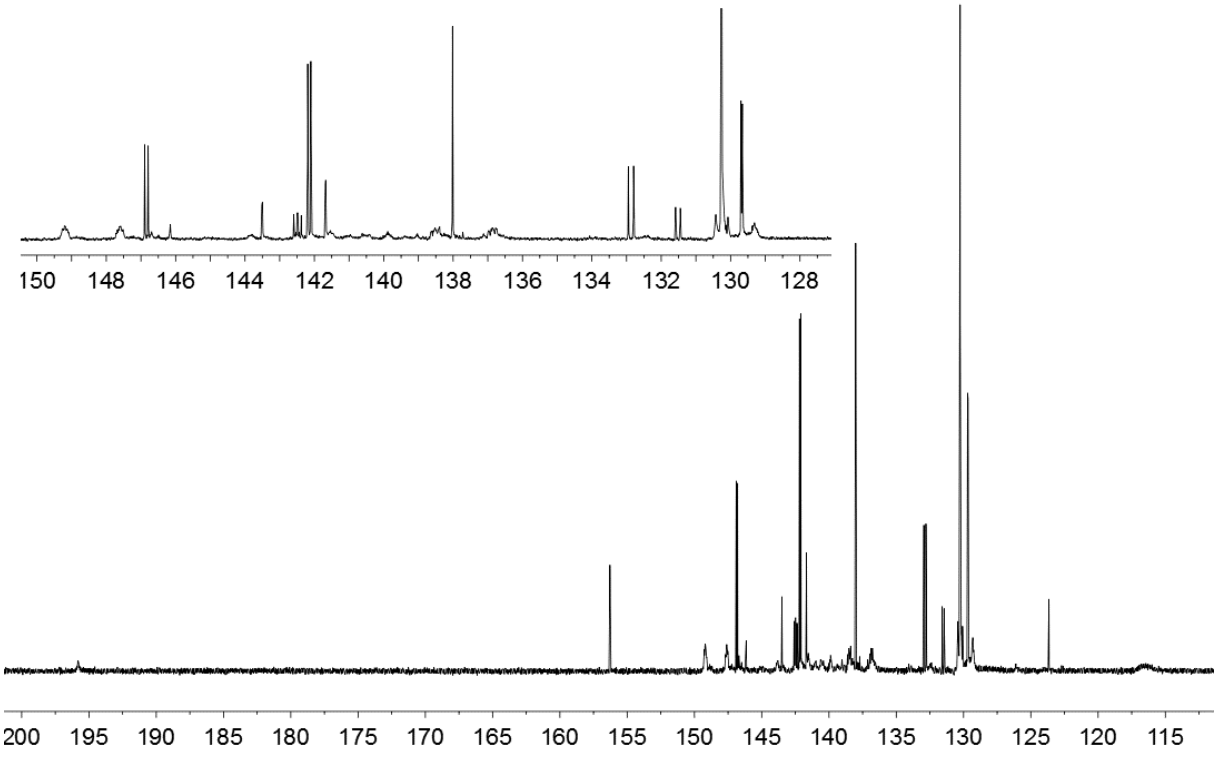
^{31}P NMR (243 MHz, 299 K, CD_2Cl_2): $\delta^{31}P = 9.6$ (quin, J_{PH} = 12.5 Hz, 1P, P-1), −22.7 ($\nu_{1/2}$ ~ 20 Hz, 1P, $Pmes_2$).



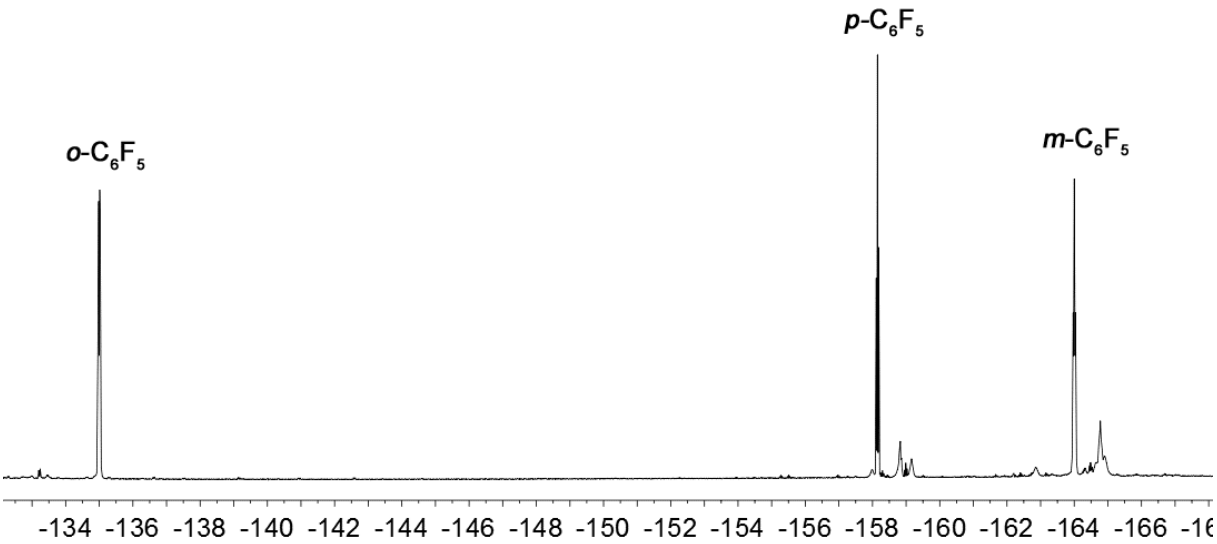
^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound **10c**.



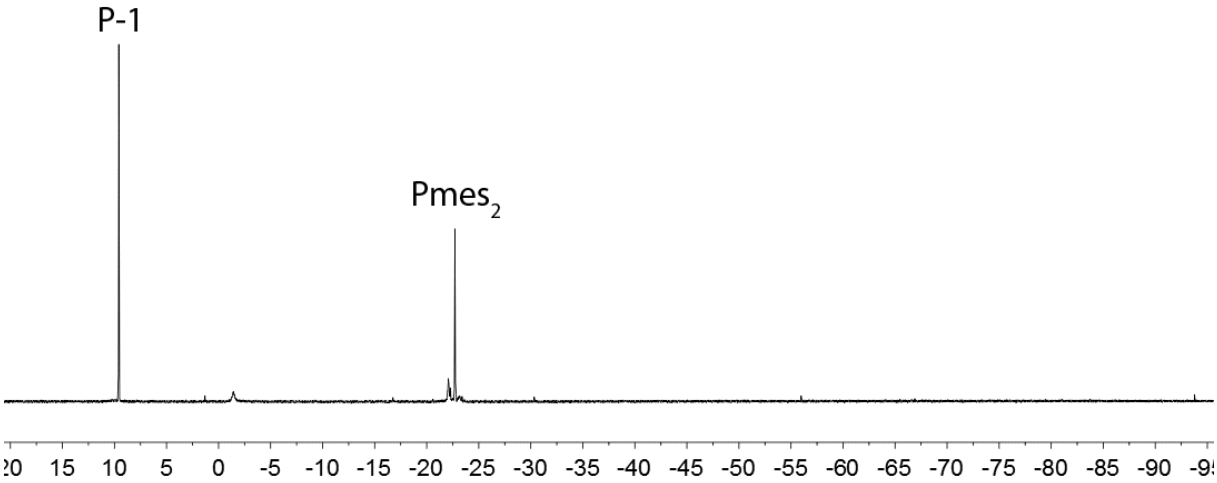
$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **10c**.



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



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



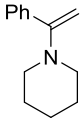
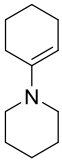
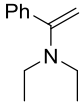
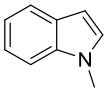
$^{31}P\{^1H\}$ NMR (243 MHz, 299 K, CD_2Cl_2) spectrum of compound **10c**.

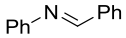
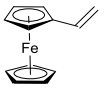
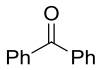
Catalytic Hydrogenation reactions with compound 2c

General Procedure

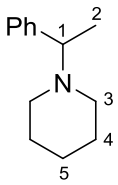
The precatalyst **2c** and the substrate were each dissolved in C_6D_6 (1 mL) and the combined solutions were transferred in a special ampoule (10 mL) equipped with a magnetic stirring bar [P. Spies, S. Schwendemann, G. Kehr, R. Fröhlich and G. Erker, *Angew. Chem. Int. Ed*., 2008, **47**, 7543.]. The ampule was put into an autoclave and purged with H_2 gas. The reaction mixture was stirred (conditions see Table 1) before the pressure was realeased and the conversion rate of the reactions was monitored NMR spectroscopically. After full conversion the products were purified via column chromatography (silica gel), extraction or evaporation (see therefore the corresponding experiments).

Table 1: *Overview of performed hydrogenation reactions and applied conditions with **2c**.*

x mol% 2c (amount)	Substrate (loading)	Pressure [H_2] [bar]	Temperature	Reaction time [h]	Conversion (isolated yield)
25 (37.0 mg)	 32.0 mg (0.12 mmol)	15	r.t.	24	>99% (-)
8 (37.0 mg)	 88.2 mg (0.5 mmol)	50	r.t.	38	>99% (22%)
7.5 (18.5 mg)	 53.0 mg (0.3 mmol)	40	r.t.	41	>99% (37%)
13 (40.0 mg)	 40 µL (0.31 mmol)	50	100 °C	48	>99% (75%)

7.5 **(37.0 mg)**	 90.6 mg (0.5 mmol)	50	r.t.	41.5	>99% (66%)
50 **(46.3 mg)**	 21.3 mg (0.1 mmol)	45	r.t.	20	0
25 **(40.0 mg)**	 21.8 mg (0.12 mmol)	50	50 °C	45	0

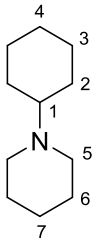
Hydrogenation of *N*-(1-phenylethen-1-yl)piperidine



This amine was not isolated.

^{1}H NMR (200 MHz, 300 K, C_6D_6): δ^1H = 7.28 (m, 2H, *o*-Ph), 7.18 (m, 2H, *m*-Ph), 7.10 (m, 1H, *p*-Ph), 3.25 (q, $^3J_{HH}$ = 6.7 Hz, 1H, 1-CH), 2.28 (m, 4H, 3-CH_2), 1.45 (m, 6H, 4-CH_2, 5-CH_2), 1.21 (d, $^3J_{HH}$ = 6.7 Hz, 3H, 2-CH_3).

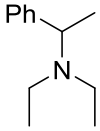
Hydrogenation of *N*-(cyclohex-1-enyl)piperidine



To purify the product all volatiles were removed from the crude reaction mixture under vacuum using a condensate collector. After slow evaporation of the solvent of the colorless condensate the amine was obtained as colorless liquid (18 mg, 0.11 mmol, 22%).

^{1}H NMR (200 MHz, 300 K, C_6D_6): δ^1H = 2.44 (m, 4H, 5-CH_2), 1.97 (m, 1H, 1-CH), 1.74 (m, 4H, 2-CH_2), 1.57 (m, 5H, 3-CH_2, 4-CH_2), 1.39 (m, 4H, 6-CH_2), 1.16 (m, 3H, 4'-CH_2, 7-CH_2).

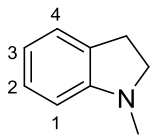
Hydrogenation of *N*-(1-phenylethen-1-yl)diethylamine



The amine was purified via column chromatography (*n*-pentane:EtOAc 10:1) and was obtained as colorless oil (20 mg, 0.11 mmol, 37%).

^{1}H NMR (200 MHz, 300 K, C_6D_6): δ^1H = 7.32 (m, 2H, *o*-Ph), 7.15 (m, 2H, *m*-Ph), 7.04 (m, 1H, *p*-Ph), 3.63 (q, $^3J_{HH}$ = 6.8 Hz, 1H, CH), 2.38 (q, $^3J_{HH}$ = 7.0 Hz, 4H, CH_2), 1.15 (d, $^3J_{HH}$ = 6.8 Hz, 3H, $^{CH}CH_3$), 0.85 (t, $^3J_{HH}$ = 7.0 Hz, 6H, $^{CH2}CH_3$).

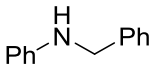
Hydrogenation of *N*-methylindole



Before the pressure was realesed, the autoclave was cooled down to 0 °C for 3 h, to condense all volatiles. After releasing the pressure slowly, 10 mL toluene and 1 M HCl (20 mL) were added to the autoclave and the mixture stirred for 10 min. The organic phase was separated and the aqueous layer was neutralized with 1 M NaOH (21 mL) and extracted with Et_2O (3x20 mL). The organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure *N*-methylindoline was obtained as brown liquid (30 mg, 0.23 mmol, 75%).

^{1}H NMR (200 MHz, 300 K, C_6D_6): δ^1H = 7.06 (m, 2H, 2-CH, 4-CH), 6.65 (dt, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 1.0 Hz, 1H, 3-CH), 6.48 (m, 1H, 1-CH), 3.29 (dt, $^3J_{HHtrans}$ = 7.4 Hz, $^3J_{HHcis}$ = 1.0 Hz, 2H, $^NCH_2$), 2.93 (tm, $^3J_{HH}$ = 8.1 Hz, 2H, CH_2), 2.73 (s, 3H, CH_3).

Hydrogenation of *N*-benzylideneaniline



Toluene (5 mL) and 1 M HCl (20 mL) were added to the crude reaction mixture and the resulting solution was stirred for 10 min before the organic phase was separated. The aqueous layer was neutralized with 1 M NaOH (21 mL) and extracted with Et_2O (3x20 mL). The organic layer was dried over $MgSO_4$ and all volatiles were removed *in vacuo*. The combined organic phases were additionally purified *via* column chromatography (*n*-pentane:EtOAc 10:1) to remove remaining amounts of the catalyst. *N*-benzylaniline was obtained as colorless oil (60 mg, 0.33 mmol, 66%).

^{1}H NMR (200 MHz, 300 K, C_6D_6): δ^1H = 7.16 (m, 5H, *o*-, *m*-, *p*-Ph), 6.77 (m, 2H, *o*-Ph), 6.45 (m, 3H, *m*-, *p*-Ph), 3.94 (m, 2H, CH_2), 3.39 (br, 1H, N-H).