Cooperative Carbon Monoxide to Formyl Reduction at a Trifunctional PBB Frustrated Lewis Pair

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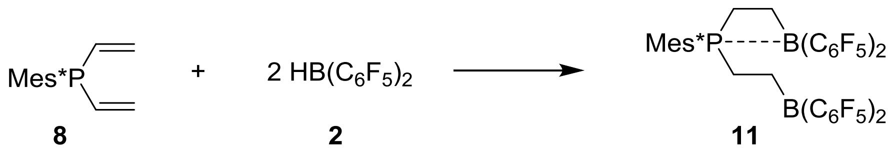
Supporting information

General information

All experiments were carried out in a dry argon atmosphere using an MBraun glovebox and/or standard Schlenk techniques. All solvents were dried and stored under an argon atmosphere before use. NMR spectra were measured on a Varian INOVA 500 MHz spectrometer (^{1}H 500 MHz; ^{13}C, 126 Hz; ^{11}B, 160 MHz; ^{19}F, 470 Hz) or a Varian UNITY plus 600 MHz spectrometer (^{1}H 600 MHz; ^{13}C, 151 Hz; ^{11}B, 192 MHz; ^{19}F, 564 Hz). Chemical shifts are given relative to $SiMe_4$ and referenced to the respective residual solvent signal (^{1}H NMR and ^{13}C NMR) or an external standard [δ ($BF_3{\cdot}OEt_2$) = 0 for ^{11}B NMR, δ ($CFCl_3$) = 0 for ^{19}F NMR]. NMR assignments were supported by additional 2D NMR experiments. IR were measured on Varian 1300 FT-IR and melting points were measured on TA-instruments DSC Q-20. X-Ray diffraction: For compounds **13** and **22** data sets were collected with a Nonius Kappa CCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, 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 **14**, **18**, **21**, **23** and **24** data sets 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**). *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: For compound **13** one badly disordered dichloromethane molecule and for compound **24** one half disordered dichloromethane molecule were found in the asymmetrical unit. The program SQUEEZE (A. L. Spek J. Appl. Cryst., 2003, 36, 7-13) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecules. Compound **18** crystallized with two half molecules in the asymmetric unit. For compound **22** one C_6F_5 group was found disordered over two positions. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. The hydrogen positions at P1 and B2 atoms in compound **24** were refined freely. CCDC deposition numbers are 1537867 to 1537873.

Unless otherwise noted, all chemicals were purchased from commercially available sources. Compound **8** was prepared according to the literature [Hasegawa, Y.; Kehr, G.; Ehrlich, S.; Grimme, S.; Daniliuc, C. G.; Erker, G. *Chem. Sci.* **2014**, *5*, 797.].

Generation of compound 11(in situ)



A solution of phosphane **8** (16.5 mg, 0.05 mmol, 1.0 eq.) and borane **2** (34.6 mg, 0.10 mmol, 2.0 eq.) in dichloromethane-d$_2$ (1 mL) was stirred for 15 min at room temperature to give a yellow solution, which was characterized by NMR experiments

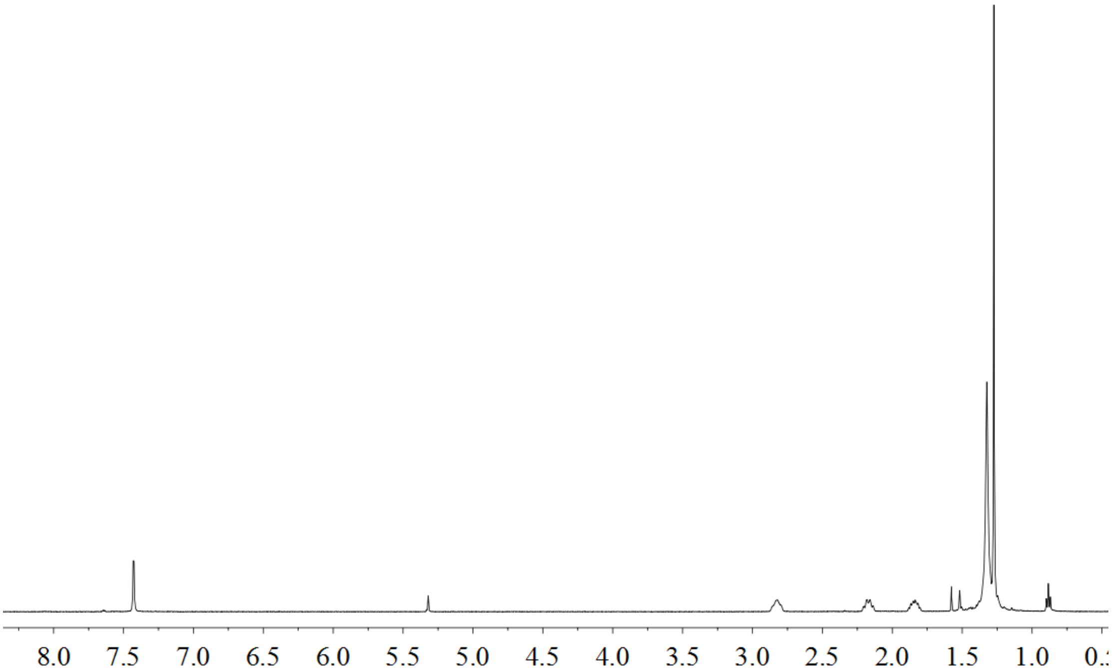
[Mes*: 2,4,6-tri(tert-butyl)phenyl]
^{1}H NMR (500 MHz, 299K, dichloromethane-d$_2$) δ = 7.43 (d, $^4J_{PH}$ = 2.9 Hz, 2H, *m*-Mes*), 2.83, 2.17 (each m, each 2H, PCH$_2$), 1.84 (m), 1.31 (dm, $^3J_{PH}$ ~ 41 Hz)(each 2H, BCH$_2$), 1.32 (br, 18H, *o*-^{t}Bu), 1.27 (s, 9H, *p*-^{t}Bu).

^{13}C{^{1}H} NMR (126 MHz, 299K, dichloromethane-d$_2$) δ = 157.9 (br, *o*-Mes*), 152.1 (d, $^4J_{PC}$ = 2.9 Hz, *p*-Mes*), 147.8 (dm, $^1J_{FC}$ ~ 245 Hz, C$_6$F$_5$), 142.3 (dm, $^1J_{FC}$ ~ 255 Hz, C$_6$F$_5$), 137.8 (dm, $^1J_{FC}$ ~ 250 Hz, C$_6$F$_5$), 125.4 (d, $^1J_{PC}$ = 10.2 Hz, *i*-Mes*), 125.2 (br, *m*-Mes*), 116.4 (br, *i*-C$_6$F$_5$), 39.2 (br, *o*-^{t}Bu), 34.9 (d, $^4J_{PC}$ = 1.0 Hz, *p*-^{t}Bu), 33.9 (br, *o*-^{t}Bu), 30.9 (s, *p*-^{t}Bu), 29.4 (d, $^1J_{PC}$ = 26.6 Hz, PCH$_2$), 19.8 (br, BCH$_2$).

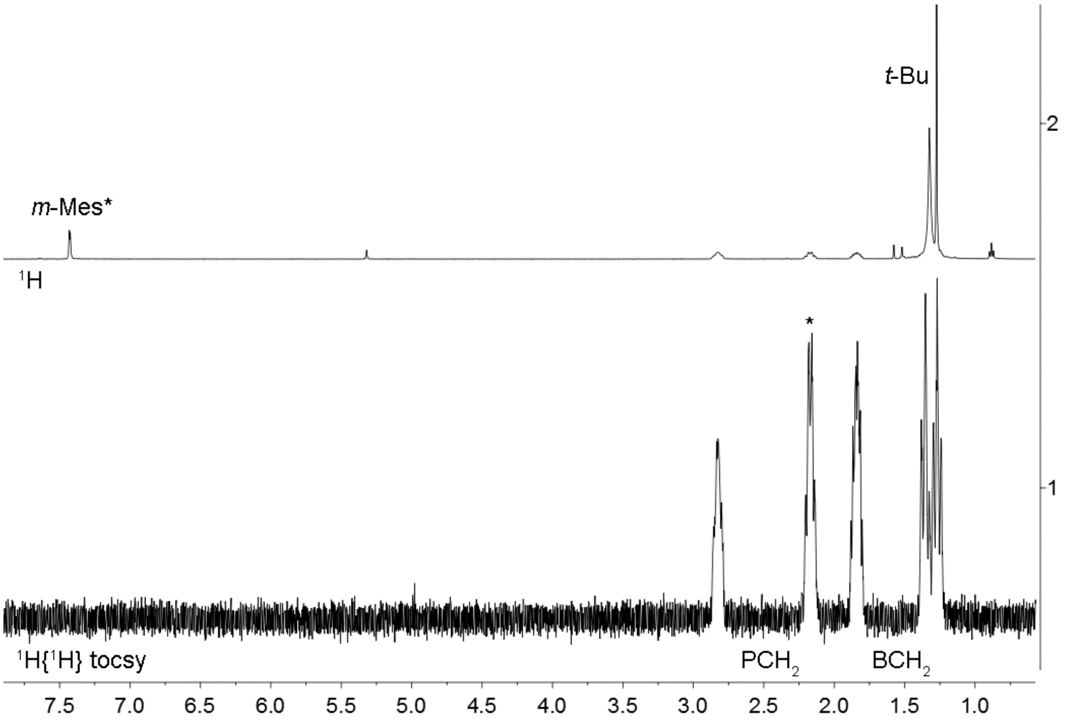
^{11}B{^{1}H} NMR (160 MHz, 299K, dichloromethane-d$_2$) δ = 39.2 ($\nu_{1/2}$ ~ 1000 Hz).

^{19}F NMR (470 MHz, 299K, dichloromethane-d$_2$) δ = -128.9 (br m, 2F, *o*-C$_6$F$_5$), -152.5 (br, 1F, *p*-C$_6$F$_5$), -163.0 (br m, 2F, *m*-C$_6$F$_5$), [$\Delta\delta^{19}F_{m,p}$ = 10.5].

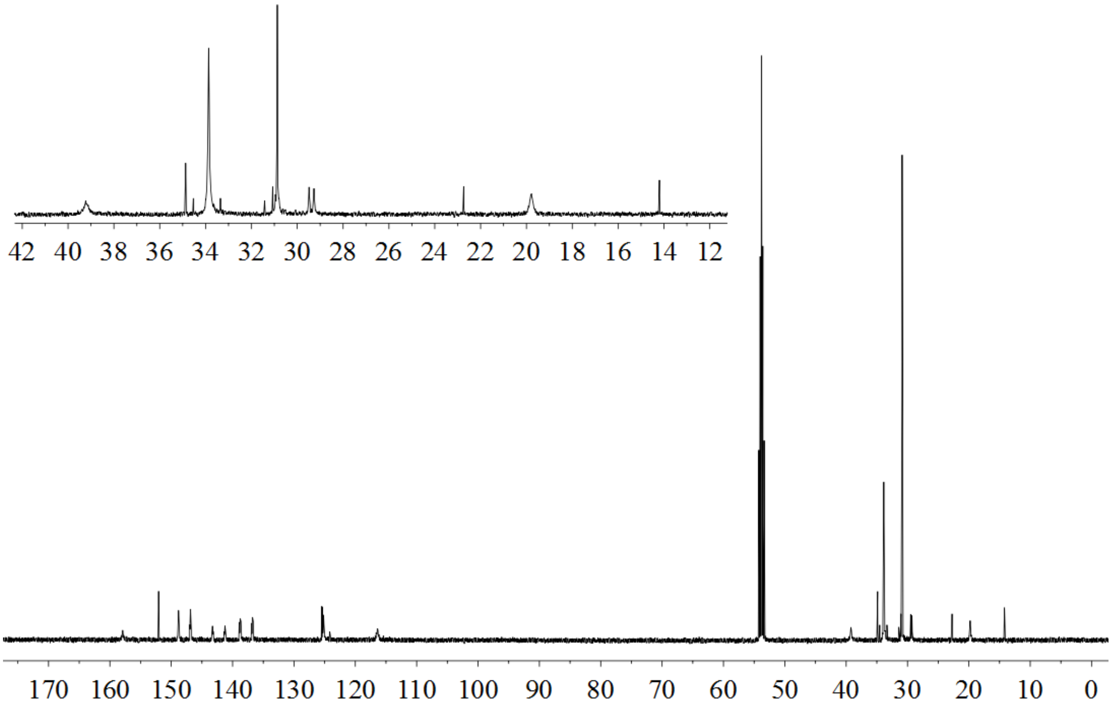
^{31}P NMR (202 MHz, 299K, dichloromethane-d$_2$) δ = 23.6 (br t, J_{PH} ~ 41 Hz).
^{31}P{^{1}H} NMR (202 MHz, 299K, dichloromethane-d$_2$) δ = 23.6 ($\nu_{1/2}$ ~ 20 Hz).



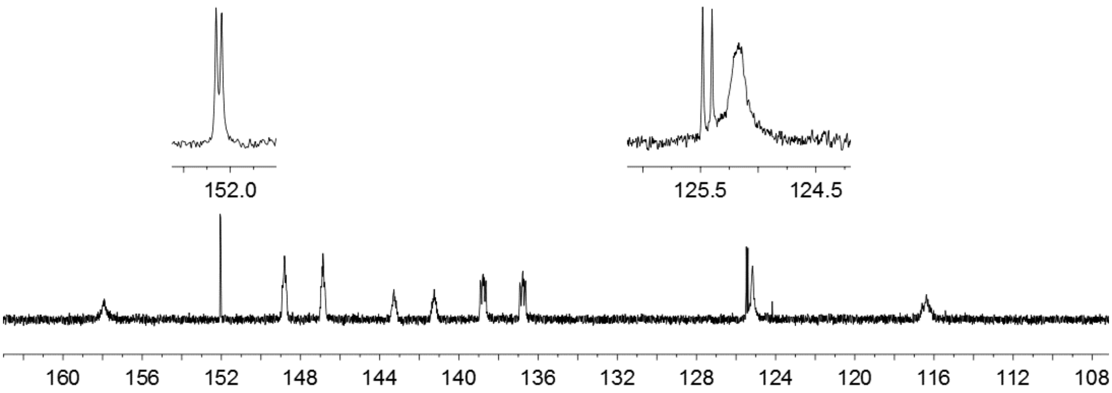
^{1}H NMR (500 MHz, 299K, dichloromethane-d$_2$) spectrum of compound **11** [admixed with pentane]



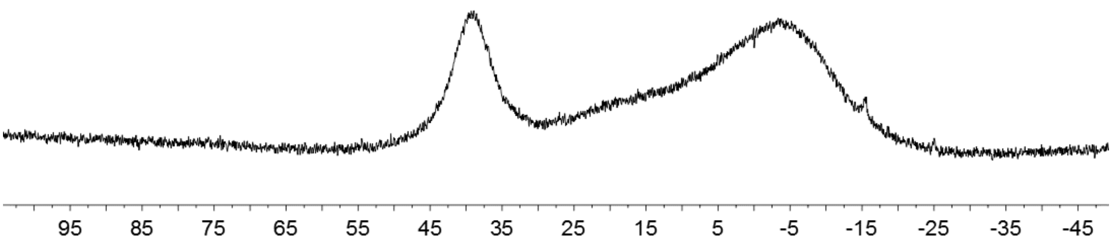
(1) **^{1}H{^{1}H} tocsy** and (2) **^{1}H NMR** (500 MHz, 299K, dichloromethane-d$_2$) sprectra of compound **11** (* irradiation point)



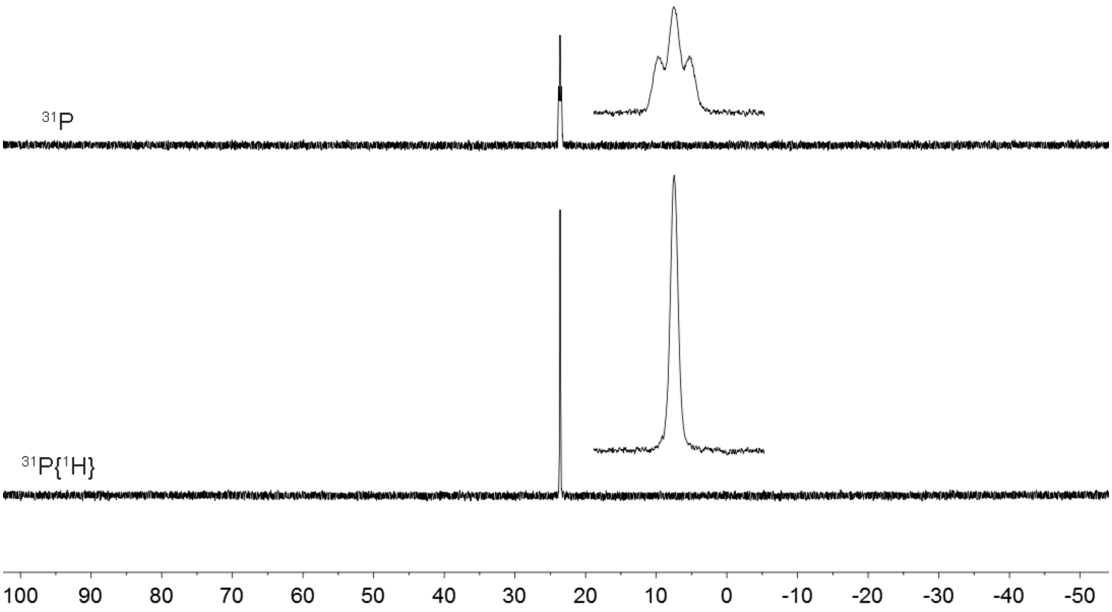
$^{13}C\{^{1}H\}$ NMR (126 MHz, 299K, dichloromethane-d_2) spectrum of compound **11** [admixed with pentane]



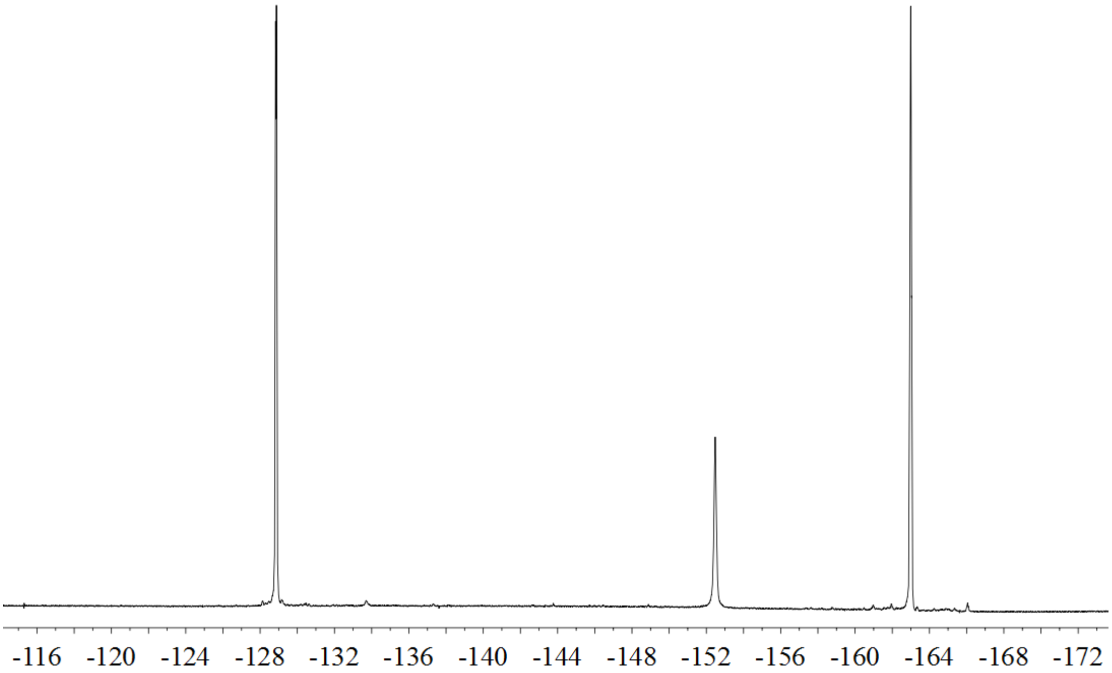
$^{13}C\{^{1}H\}$ NMR (126 MHz, 299K, dichloromethane-d_2) spectrum of compound **11**



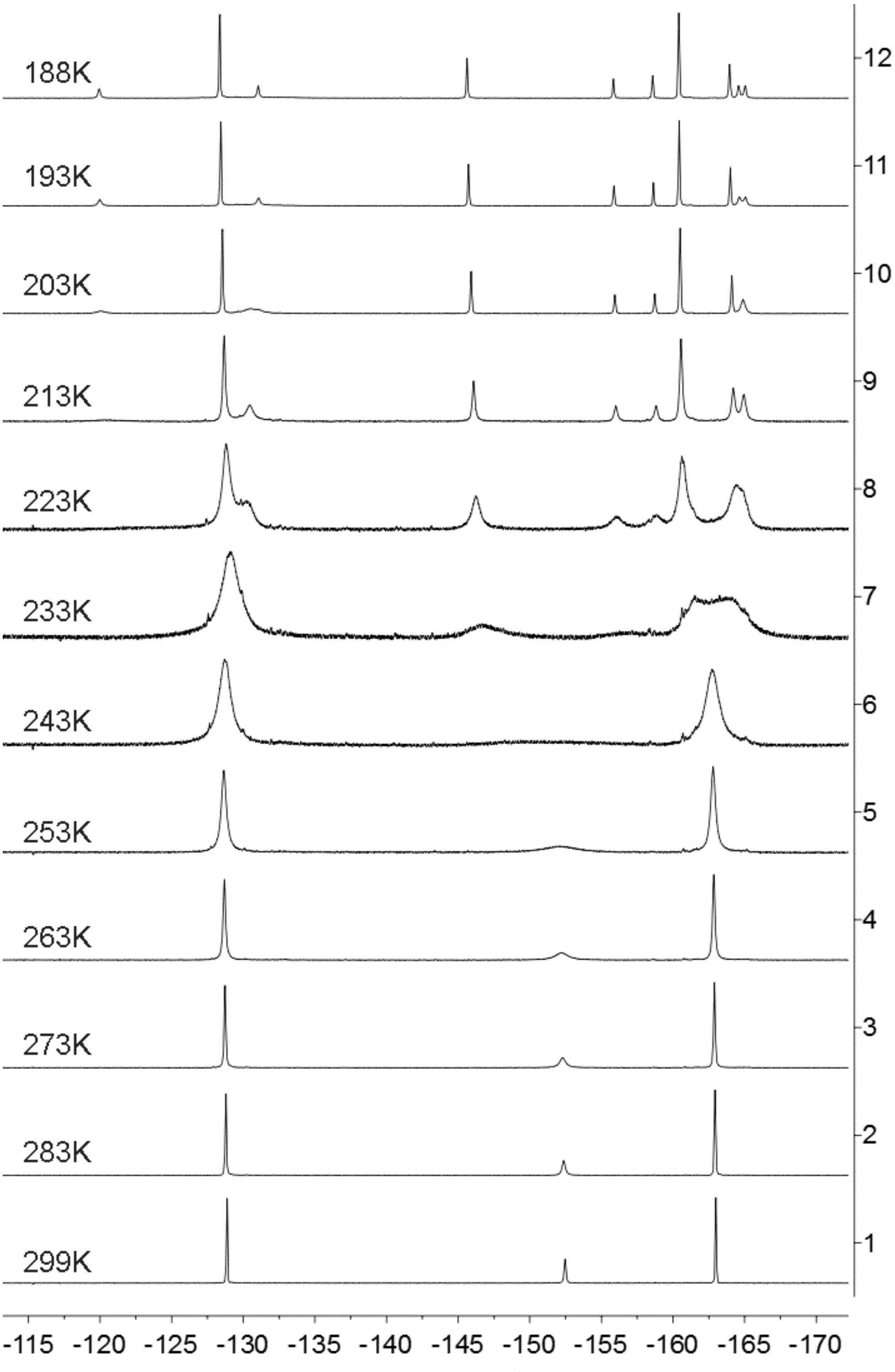
$^{11}B\{^{1}H\}$ NMR (160 MHz, 299K, dichloromethane-d_2) spectrum of compound **11**



(bottom) **^{31}P{^{1}H}** and (top) **^{31}P NMR** (202 MHz, 299K, dichloromethane-d$_2$) spectra of compound **11**



^{19}F NMR (470 MHz, 299K, dichloromethane-d$_2$) spectrum of compound **11**

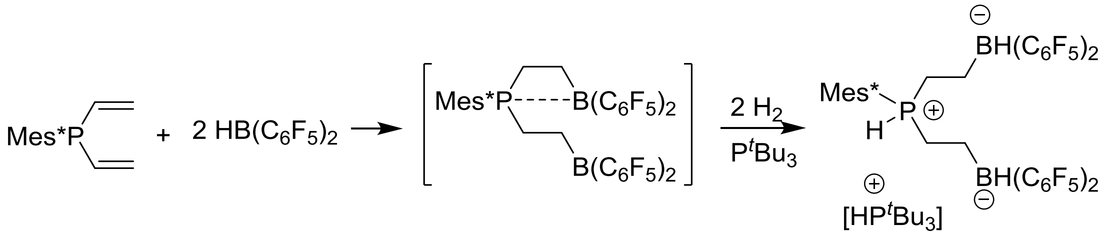


^{19}**F DNMR** (470 MHz, dichloromethane-d$_2$) of compound **11** at variable temperatures

(1) Coalescence of *p*-BC_6F_5 resonances at $\delta^{19}F$ -145.9 and -157.3 (203K) [Comment: -157.3 center between -155.9 and -158.7]
$\Delta G^\ddagger\ [T_c, \Delta\nu(T)] = RT_c(22.96 + \ln(T_c/\Delta\nu))$ [J/mol]
T_c = coalescence temperature [K]: 243 K (^{19}F, *p*-BC_6F_5)
$\Delta\nu$ = chemical shift difference [Hz] (^{19}F, *p*-BC_6F_5, 203 K): 5370 Hz
R = 8.314 J/(mol·K); 1 J = 0.239 cal
$\Delta G^\ddagger$ [243 K, $\Delta\nu$(203 K) = 5370 Hz] = 40132 J/mol = 9.6 ± 0.4 kcal/mol

(2) Coalescence of *p*-BC_6F_5 resonances at $\delta^{19}F$ -155.9 and -158.7 (203K):
$\Delta G^\ddagger\ [T_c, \Delta\nu(T)] = RT_c(22.96 + \ln(T_c/\Delta\nu))$ [J/mol]
T_c = coalescence temperature [K]: 233 K (^{19}F, *p*-BC_6F_5)
$\Delta\nu$ = chemical shift difference [Hz] (^{19}F, *p*-BC_6F_5, 203 K): 1310 Hz
R = 8.314 J/(mol·K); 1 J = 0.239 cal
$\Delta G^\ddagger$ [243 K, $\Delta\nu$(203 K) = 5370 Hz] = 41132 J/mol = 9.8 ± 0.4 kcal/mol

Synthesis of compound 12



8 **2** **11** **12**

A solution of phosphane **8** (66.1 mg, 0.20 mmol, 1.0 eq.) and borane **2** (138.4 mg, 0.40 mmol, 2.0 eq.) in dichloromethane (4 mL) was stirred for 15 min at room temperature to give a yellow solution. Then P*ᵗ*Bu3 (40.5 mg, 0.2 mmol, 1.0 eq.) in dichloromethane (1 mL) was added to the yellow solution. Subsequently the yellow solution was exposed to H_2 gas (1.5 bar) and stirred at room temperature for 12 h to give a colorless solution. Then all volatiles were removed in vacuo to give a white foam. After crystallization from pentane/ dichloromethane and drying of the collected precipitate in vacuo, compound **12** was obtained as a white solid (125.3 mg, 0.102 mmol, 51 %).
Anal. Calcd. for $C_{58}H_{68}B_2F_{20}P_2$: C, 56.70; H, 5.58. Found: C, 56.44; H 5.43.
Melting point: 127 °C

[Mes*: 2,4,6-tri(tert-butyl)phenyl]
^{1}H NMR (500 MHz, 299 K, dichloromethane-d$_2$) δ = 7.50 (d, $^4J_{PH}$ = 3.6 Hz, 2H, *m*-Mes*), 6.36 (d quint, $^1J_{PH}$ = 466.8 Hz, $^3J_{HH}$ = 5.9 Hz, 1H, PH^{Mes*}), 5.17 (d, $^1J_{PH}$ = 430.8 Hz, 1H, PH^{tBu}), 2.63 (br m, 2H, BH), 2.44/2.18 (each m, each 2H, PCH$_2$), 1.64 (d, $^3J_{PH}$ = 15.8 Hz, 27H, ^{t}Bu^P), 1.40 (br, 9H, *o*-^{t}Bu), 1.30 (s, 9H, *p*-^{t}Bu), 0.91/0.72 (each m, each 2H, BCH$_2$).

^{1}H NMR (500 MHz, 233 K, dichloromethane-d$_2$) δ = 7.48, 7.40 (each br, each 1H, *m*-Mes*), 6.20 (br dm, $^1J_{PH}$ ~ 466 Hz, 1H, PH^{Mes*}), 5.25 (d, $^1J_{PH}$ = 433.4 Hz, 1H, PH^{tBu}), 2.53 (br m, 2H, BH), 2.38/2.07 (each m, each 2H, PCH$_2$), 1.59 (d, $^3J_{PH}$ = 15.7 Hz, 27H, ^{t}Bu^P), 1.45, 1.16 (each s, each 9H, *o*-^{t}Bu), 1.25 (s, 9H, *p*-^{t}Bu), 0.80/0.58 (each m, each 2H, BCH$_2$).

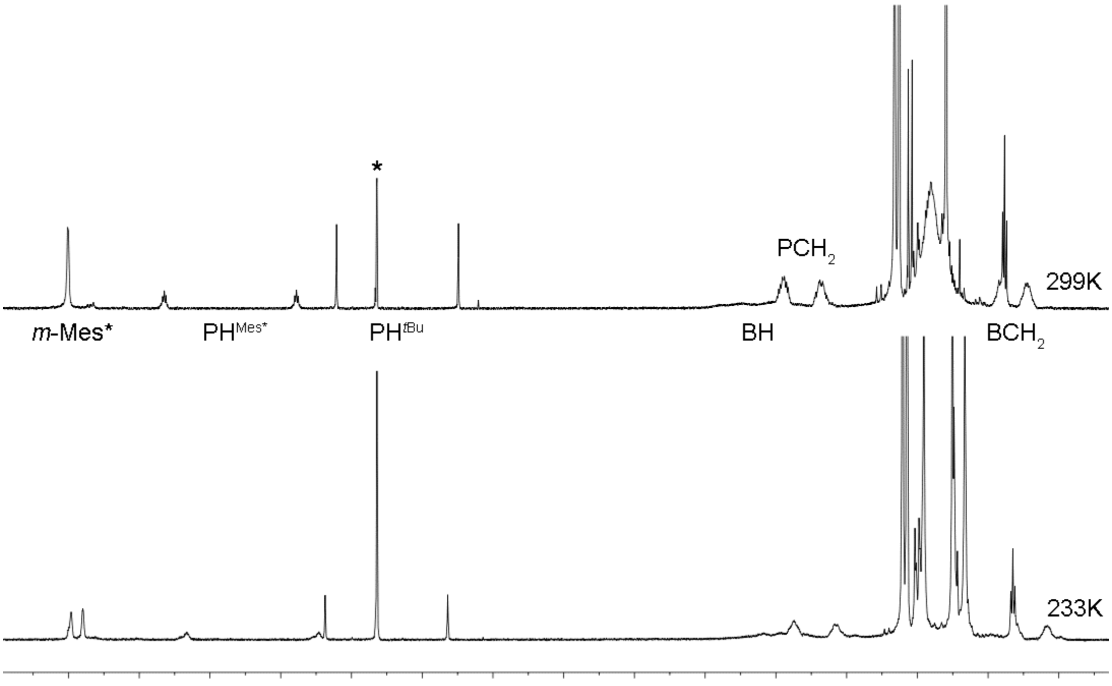
^{13}C{^{1}H} NMR (126 MHz, 299 K, dichloromethane-d$_2$) δ = n.o. (*o*-Mes*), 155.6 (d, $^4J_{PC}$ = 3.5 Hz, *p*-Mes*),125.3 (br, *m*-Mes*), 111.8 (d, $^1J_{PC}$ = 64.9 Hz, *i*-Mes*), 38.9 (d, $^3J_{PC}$ = 3.3 Hz, *o*-^{t}Bu), 38.1 (d, $^1J_{PC}$ = 33.6 Hz, ^{t}Bu^P), 35.3 (d, $^5J_{PC}$ = 1.0 Hz, *p*-^{t}Bu), 33.6 (br, *o*-^{t}Bu), 30.7 (*p*-^{t}Bu), 30.4 (^{t}Bu^P), 27.6 (d, $^1J_{PC}$ = 33.7 Hz, PCH$_2$), 18.5 (br, BCH$_2$), [C_6F_5 not listed].

^{13}C{^{1}H} NMR (126 MHz, 233 K, dichloromethane-d$_2$) δ = 159.7 (d, $^2J_{PC}$ = 5.1 Hz), 157.1 (d, $^2J_{PC}$ = 7.1 Hz)(*o*-Mes*), 154.9 (d, $^5J_{PC}$ = 2.9 Hz, *p*-Mes*), 125.8, 124.1 (br, *m*-Mes*), 110.8 (d, $^{1}J_{PC}$ = 65.5 Hz, *i*-Mes*), 38.3 (*o*-^{t}Bu), 37.3 (d, $^{1}J_{PC}$ = 27.2 Hz, ^{t}Bu^{P}), 34.8 (*p*-^{t}Bu), 32.9, 32.7 (*o*-^{t}Bu), 30.2 (*p*-^{t}Bu), 29.7 (^{t}Bu^{P}), 26.6 (d, $^{1}J_{PC}$ = 32.6 Hz, PCH$_2$), 17.8 (br, BCH$_2$), [C$_6$F$_5$ not listed].

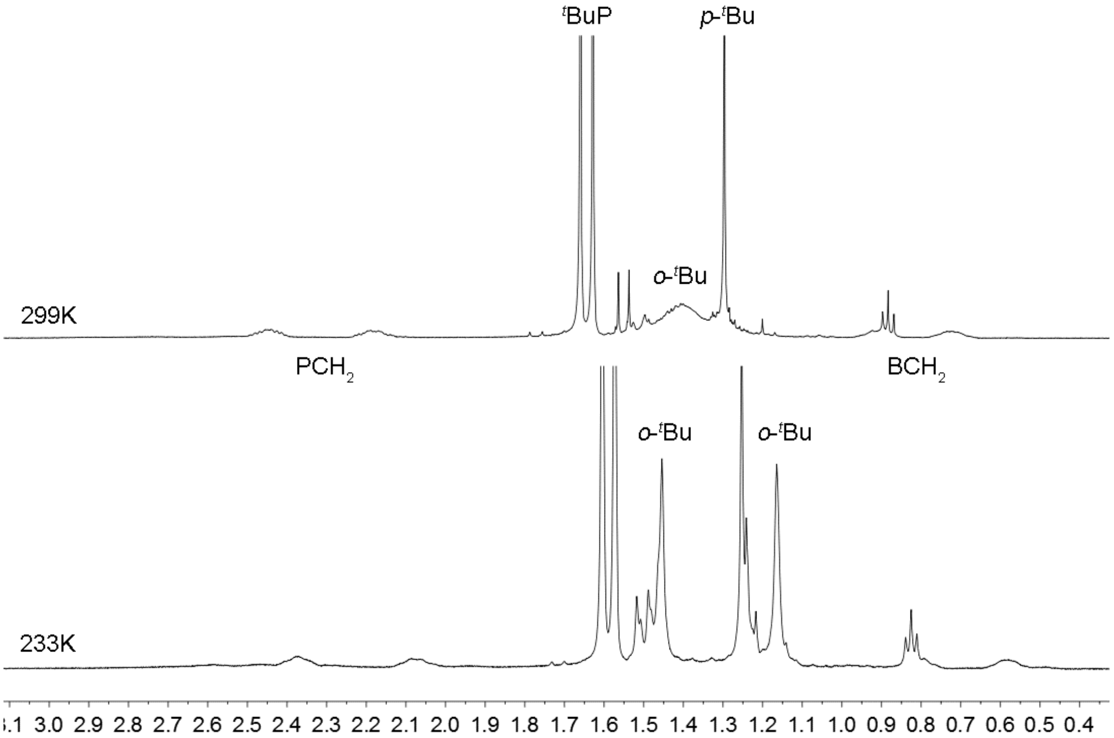
^{11}B NMR (160 MHz, 299K, dichloromethane-d$_2$) δ = -20.2 (br d, $^{1}J_{BH}$ ~ 87 Hz).
^{11}B{^{1}H} NMR (160 MHz, 299K, dichloromethane-d$_2$) δ = -20.2 ($\nu_{1/2}$ ~ 80 Hz).

^{19}F NMR (470 MHz, 299 K, dichloromethane-d$_2$) δ = -133.3, -133.5 (each m, each 2F, *o*-C$_6$F$_5$), -164.78, -164.83 (each t, ^{3}J$_{FF}$ = 22.2 Hz, each 1F, *p*-C$_6$F$_5$), -167.1, -167.2 (each m, each 2F, *m*-C$_6$F$_5$). [$\Delta\delta^{19}$F$_{m,p}$ ~ 2.3]

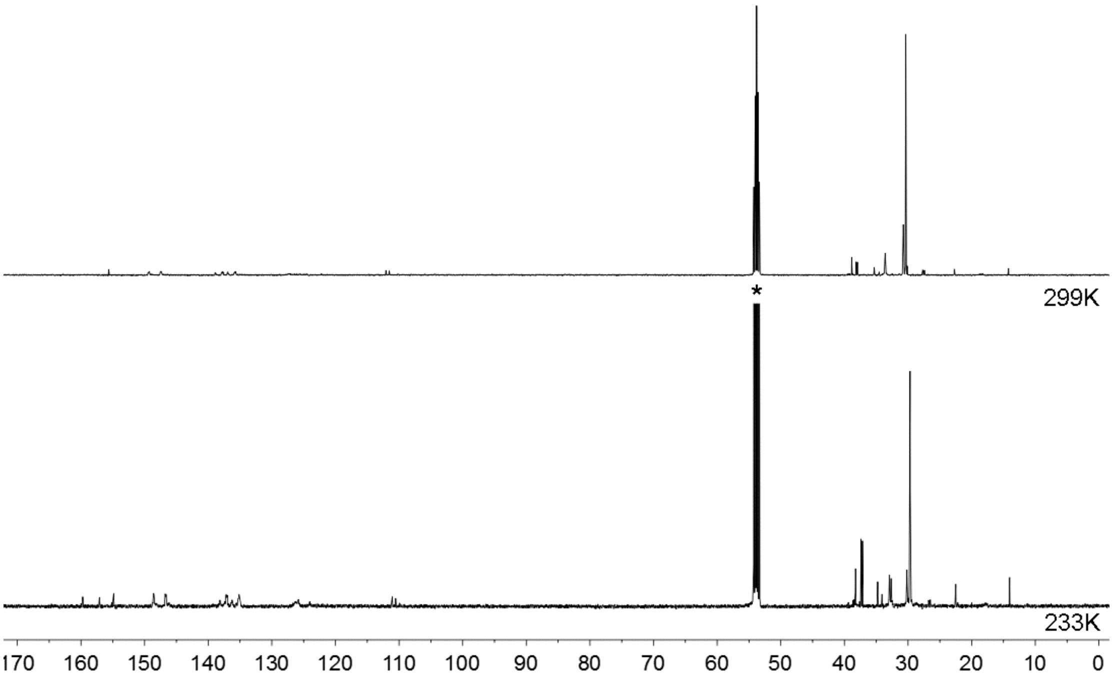
^{31}P NMR (202 MHz, 299K, dichloromethane-d$_2$) δ = 59.6 (dm, $^{1}J_{PH}$ ~ 431 Hz, P^{t}Bu), 29.1 (br d, $^{1}J_{PH}$ ~ 467 Hz, PMes*).
^{31}P{^{1}H} NMR (202 MHz, 299K, dichloromethane-d$_2$) δ = 59.6 ($\nu_{1/2}$ ~ 3 Hz, P^{t}Bu), 29.1 ($\nu_{1/2}$ ~ 70 Hz, PMes*).



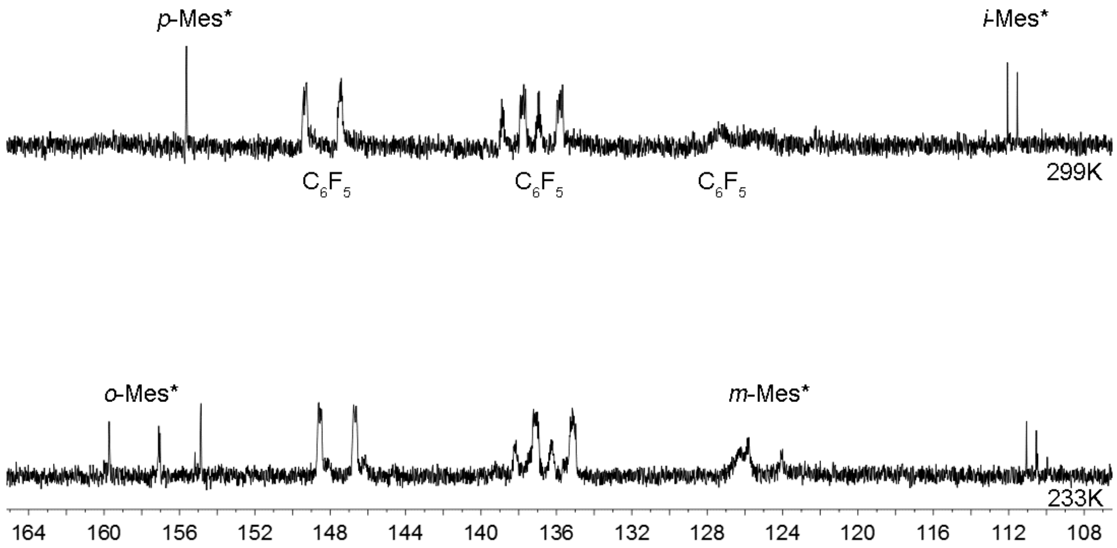
^{1}H NMR (500 MHz, dichloromethane-d$_2$) spectra of compound **12** at (bottom) 233K and (top) 299K.



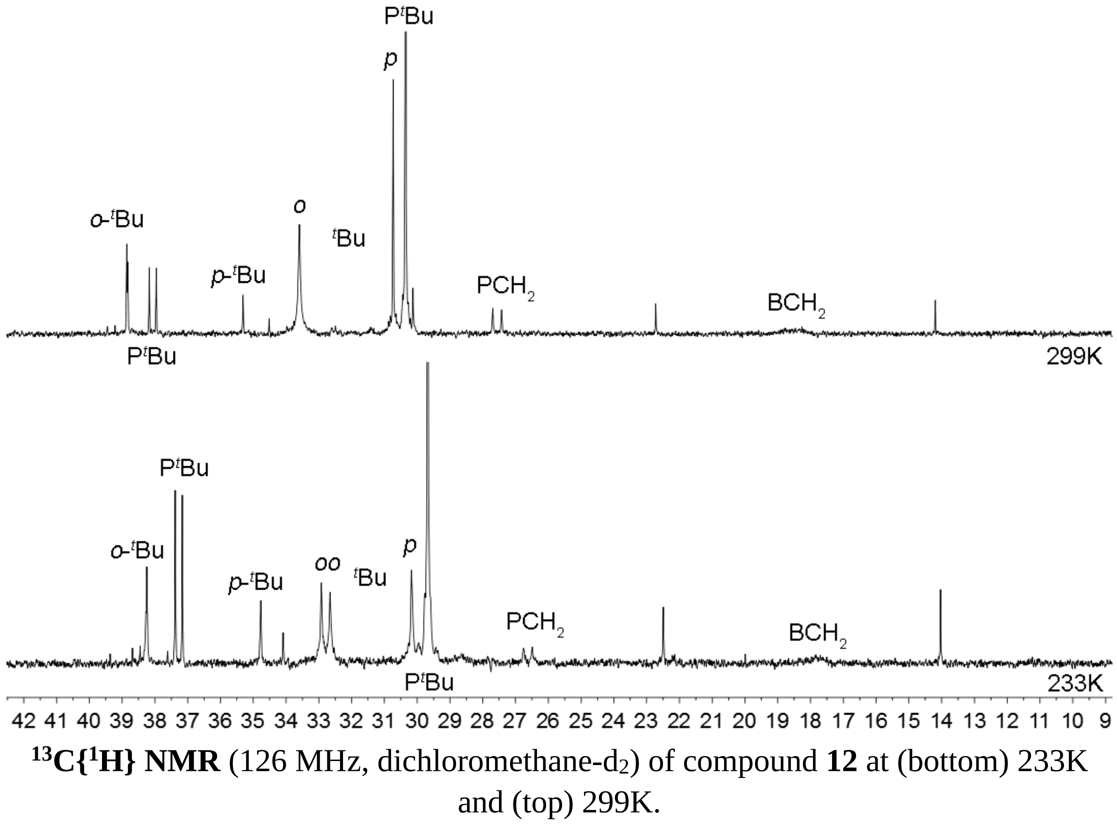
^{1}H NMR (500 MHz, dichloromethane-d$_2$) spectra of compound **12** at (bottom) 233K and (top) 299K.



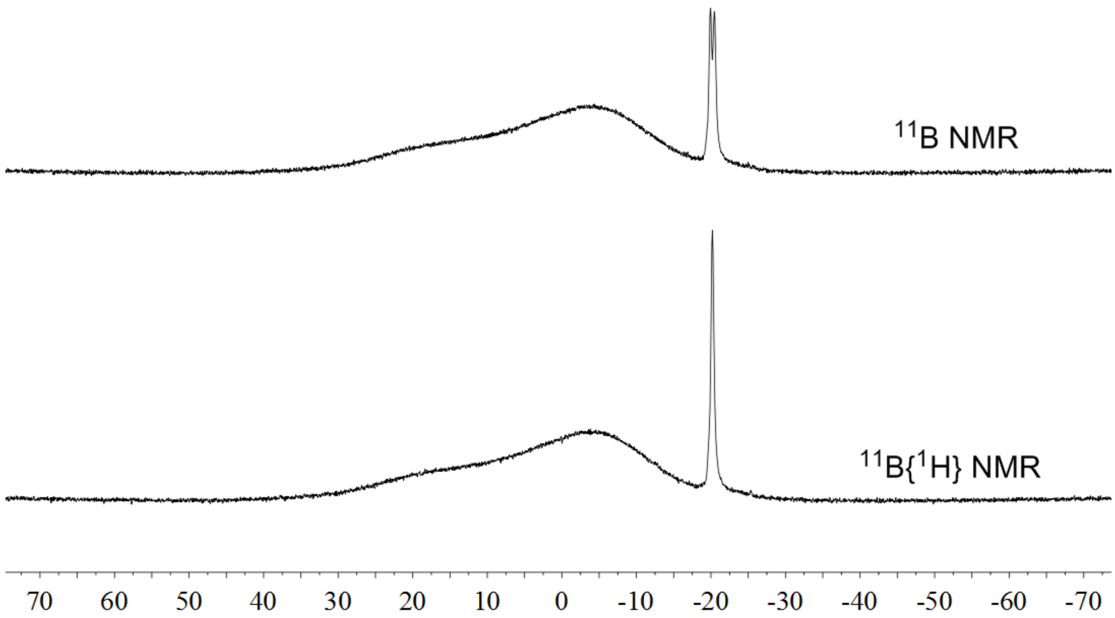
^{13}C{^{1}H} NMR (126 MHz, dichloromethane-d$_2$*) of compound **12** at (bottom) 233K and (top) 299K.



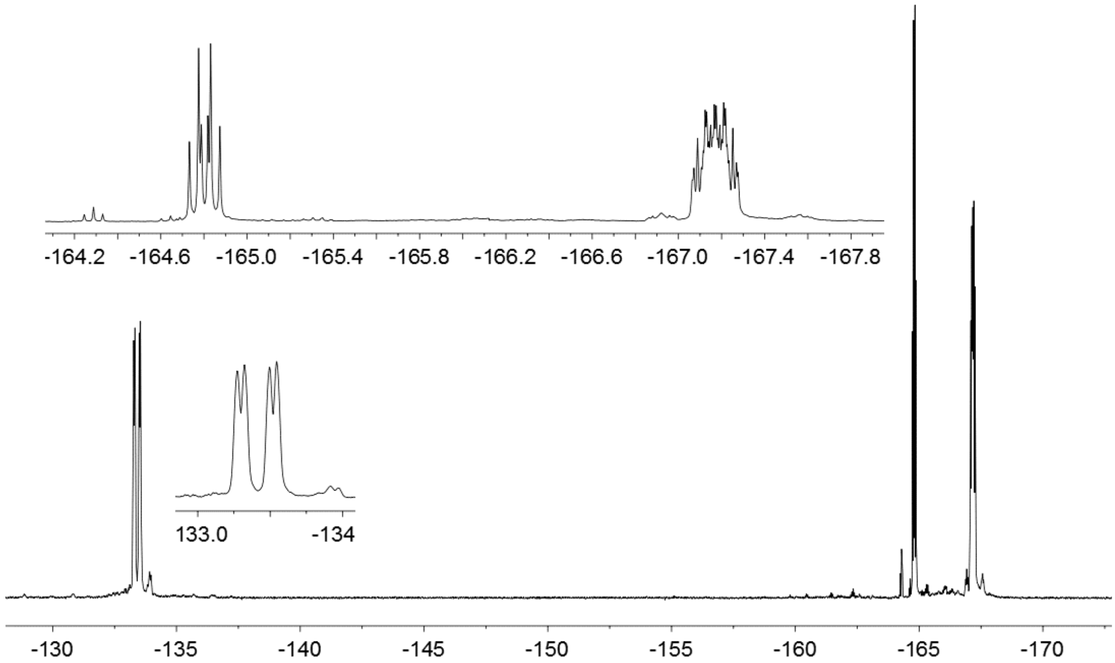
$^{13}C\{^1H\}$ NMR (126 MHz, dichloromethane-d$_2$) of compound **12** at (bottom) 233K and (top) 299K.



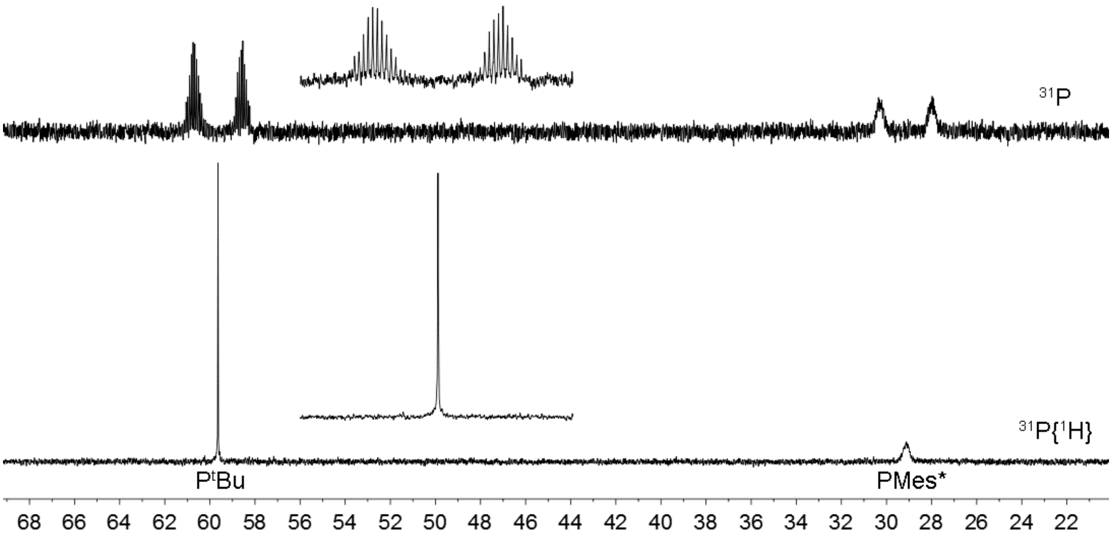
$^{13}C\{^1H\}$ NMR (126 MHz, dichloromethane-d$_2$) of compound **12** at (bottom) 233K and (top) 299K.



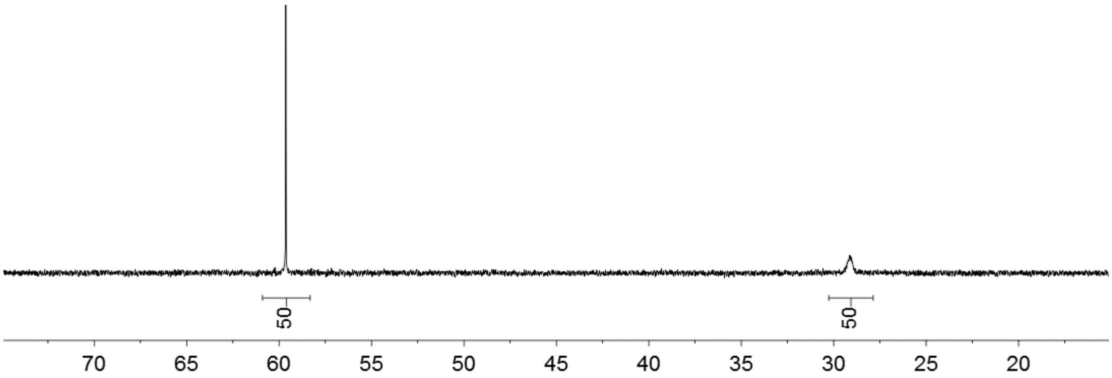
(bottom) **^{11}B{^{1}H}** and (top) **^{11}B NMR** (160 MHz, 299K, dichloromethane-d_2) spectra of compound **12**



^{19}F NMR (470 MHz, 299 K, dichloromethane-d_2) spectrum of compound **12**

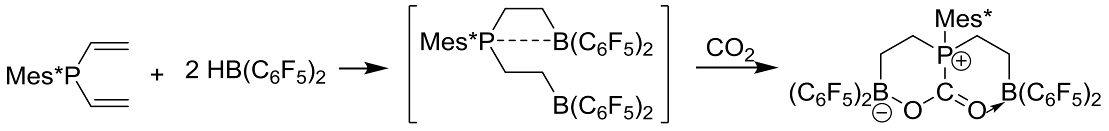


(bottom) **^{31}P{^{1}H}** and (top) **^{31}P NMR** (202 MHz, 299K, dichloromethane-d$_2$) spectra of compound **12**



^{31}P{^{1}H} NMR (202 MHz, 299K, dichloromethane-d$_2$) spectrum of compound **12**

Synthesis of compound 13



8 **2** **11** **13**

A solution of phosphane **8** (66.1 mg, 0.20 mmol, 1.0 eq.) and borane **2** (138.4 mg, 0.40 mmol, 2.0 eq.) in dichloromethane (4 mL) was stirred for 15 min at room temperature to give a yellow solution. Then the solvent was removed in vacuo and the obtained residue was dissolved in pentane (4 mL). The resulting solution was cooled to -78 °C (dry ice / isopropanol) and evacuated carefully. Then the dry ice bath was removed and the reaction mixture was exposed to CO_2 gas (2.0 bar) and stirred at room temperature for 8 h to give a white suspension. The precipitate was collected by filtration using a filter cannula, washed with pentane (1 mL × 2) and dried in vacuo to give compound **13** as a white solid (158.0 mg, 0.148 mmol, 74 %).
Anal. Calcd. for $C_{49}H_{51}B_2F_{20}P_2$: C, 52.94; H, 3.50. Found: C, 53.01; H, 3.34.
Melting point: 153 ^{o}C

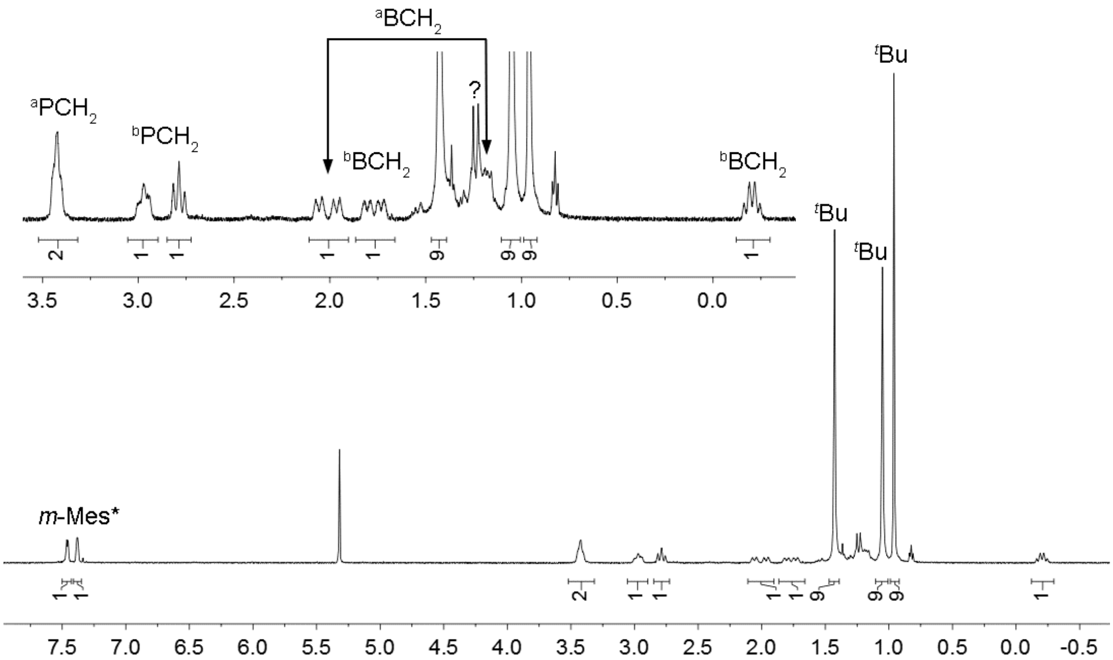
[Mes*: 2,4,6-tri(tert-butyl)phenyl]
^{1}H NMR (500 MHz, 233 K, dichloromethane-d_2) δ = 7.46 (d, $^{4}J_{PH}$ = 6.2 Hz), 7.38 (d, $^{4}J_{PH}$ = 6.2 Hz)(each 1H, *m*-Mes*), 3.42 (m, 2H, ^{a}PCH$_2$), 2.97/2.79 (each m, each 1H, ^{b}PCH$_2$), 2.01 (br dd, $^{3}J_{PH}$ = 45.5 Hz, $^{2}J_{HH}$ = 16.2 Hz)/1.19 (m) (each 1H, ^{a}BCH$_2$), 1.77 (br dd, $^{3}J_{PH}$ = 35.9 Hz, $^{2}J_{HH}$ = 15.4 Hz)/-0.20 (m) (each 1H, ^{b}BCH$_2$), 1.43, 1.05 (each s, each 9H, *o*-^{t}Bu), 0.96 (s, 9H, *p*-^{t}Bu).

^{13}C{^{1}H} NMR (126 MHz, 233 K, dichloromethane-d_2) δ = 179.2 (d, $^{1}J_{PC}$ = 82.4 Hz, C=O), 162.8 (d, $^{2}J_{PC}$ = 3.9 Hz), 161.2 (d, $^{2}J_{PC}$ = 8.7 Hz) (*o*-Mes*), 156.8 (d, $^{4}J_{PC}$ = 4.4 Hz, *p*-Mes*), 127.3 (d, $^{3}J_{PC}$ = 14.0 Hz), 125.9 (d, $^{3}J_{PC}$ = 12.1 Hz) (*m*-Mes*), 101.4 (d, $^{1}J_{PC}$ = 79.0 Hz, *i*-Mes*), 40.2, 40.1 (each d, $^{3}J_{PC}$ = 2.8 Hz, *o*-^{t}Bu), 34.4 (d, $^{5}J_{PC}$ = 1.2 Hz, *p*-^{t}Bu), 32.9, 32.6 (*o*-^{t}Bu), 34.4 (*p*-^{t}Bu), 24.5 (d, $^{1}J_{PC}$ = 31.4 Hz, ^{a}PCH$_2$), 23.6 (d, $^{1}J_{PC}$ = 44.1 Hz, ^{b}PCH$_2$), 14.5 (br, ^{a}BCH$_2$), 10.8 (br, ^{b}BCH$_2$), [C_6F_5 not listed].

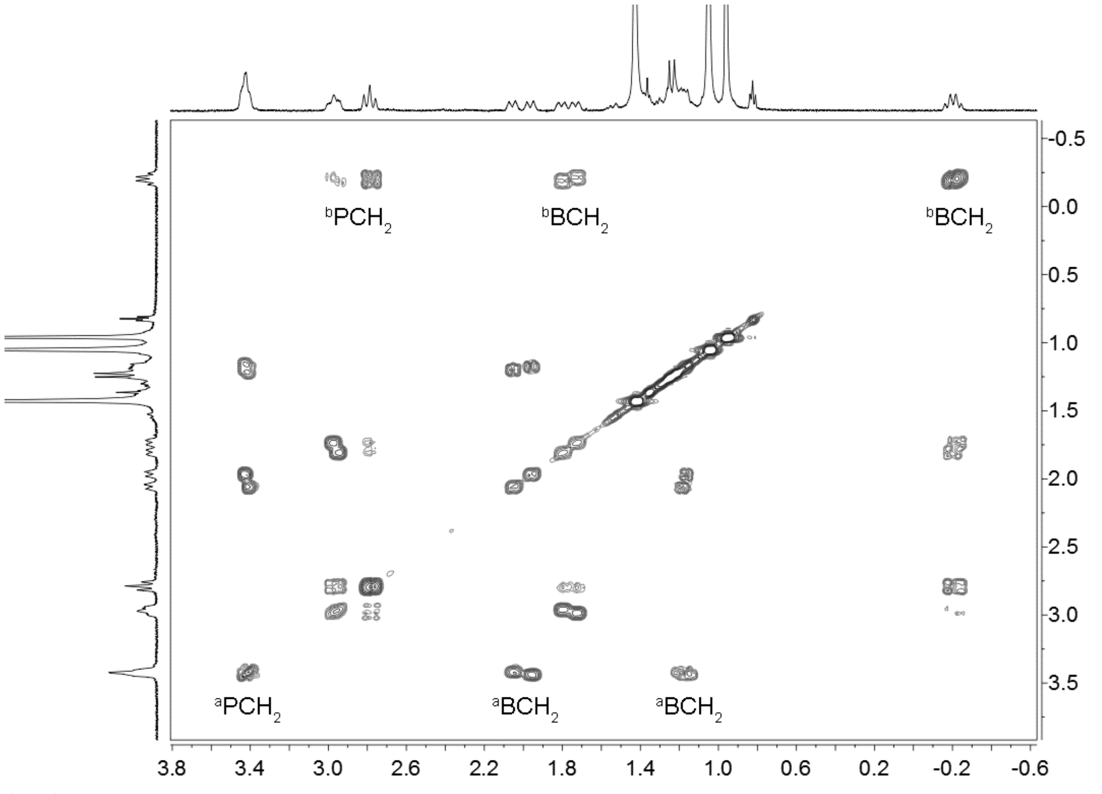
^{11}B{^{1}H} NMR (160 MHz, 299K, dichloromethane-d_2) δ = 7.7 ($\nu_{1/2}$ ~ 1600 Hz).
^{10}B{^{1}H} NMR (54 MHz, 299K, dichloromethane-d_2) δ = 7.7 ($\nu_{1/2}$ ~ 700 Hz).

^{19}F NMR (470 MHz, 299 K, dichloromethane-d_2) δ = -134.6 (br, 4F, *o*-C_6F_5), -157.6, -159.1 (each br, each 1F, *p*-C_6F_5), -164.8 (br, 4F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 7.2, 5.7]
^{19}F NMR (470 MHz, 183 K, dichloromethane-d_2) δ = -131.2 (br, 1F), -134.7 (br m, 2F), -135.3 (br, 2F), -136.3 (br m, 2F), -138.2 (br, 1F)(*o*-C_6F_5), -155.8, -157.3, -157.9, -160.1 (each br t, $^{3}J_{FF}$ ~ 20 Hz, each 1F, *p*-C_6F_5), -162.9 (2F), -163.7 (1F), -164.5 (2F), -164.8 (2F), -165.2 (1F) (each br, *m*-C_6F_5).

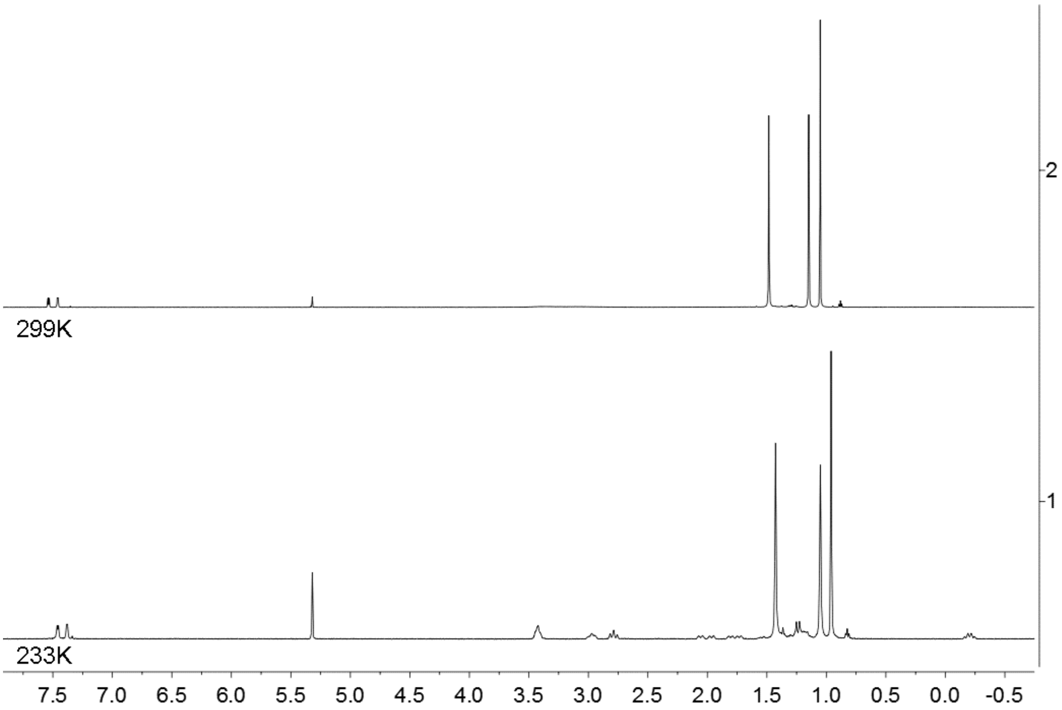
^{31}P{^{1}H} NMR (243 MHz, 299K, dichloromethane-d_2) δ = 15.8 ($\nu_{1/2}$ ~ 5 Hz).



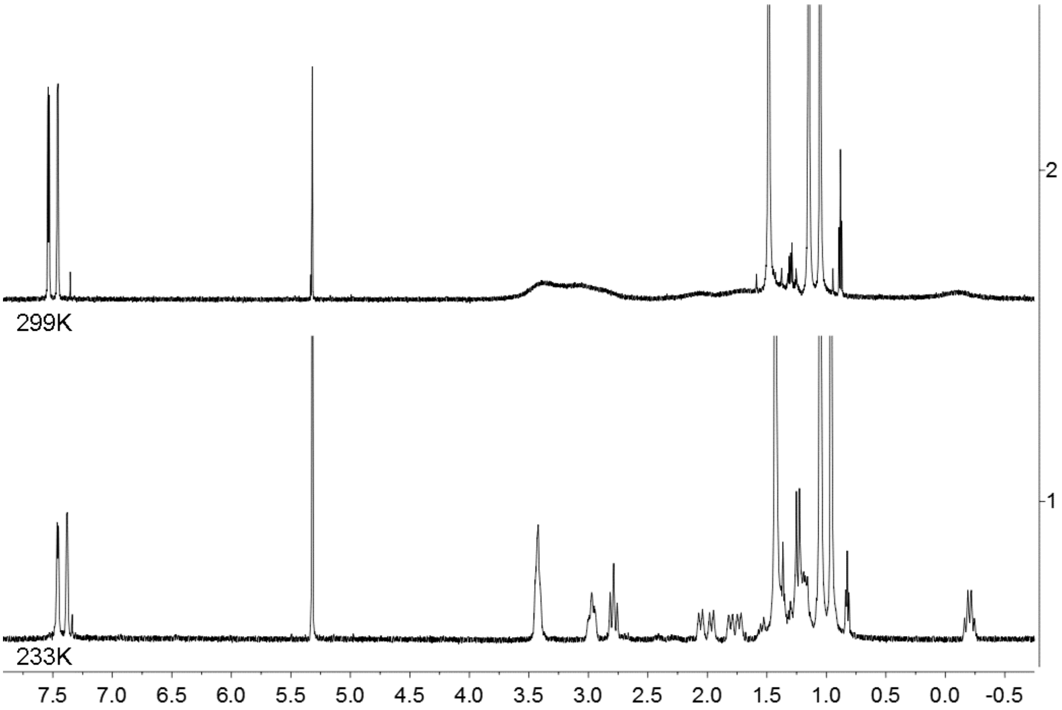
^{1}H NMR (500 MHz, 233 K, dichloromethane-d$_2$) spectrum of compound **13**



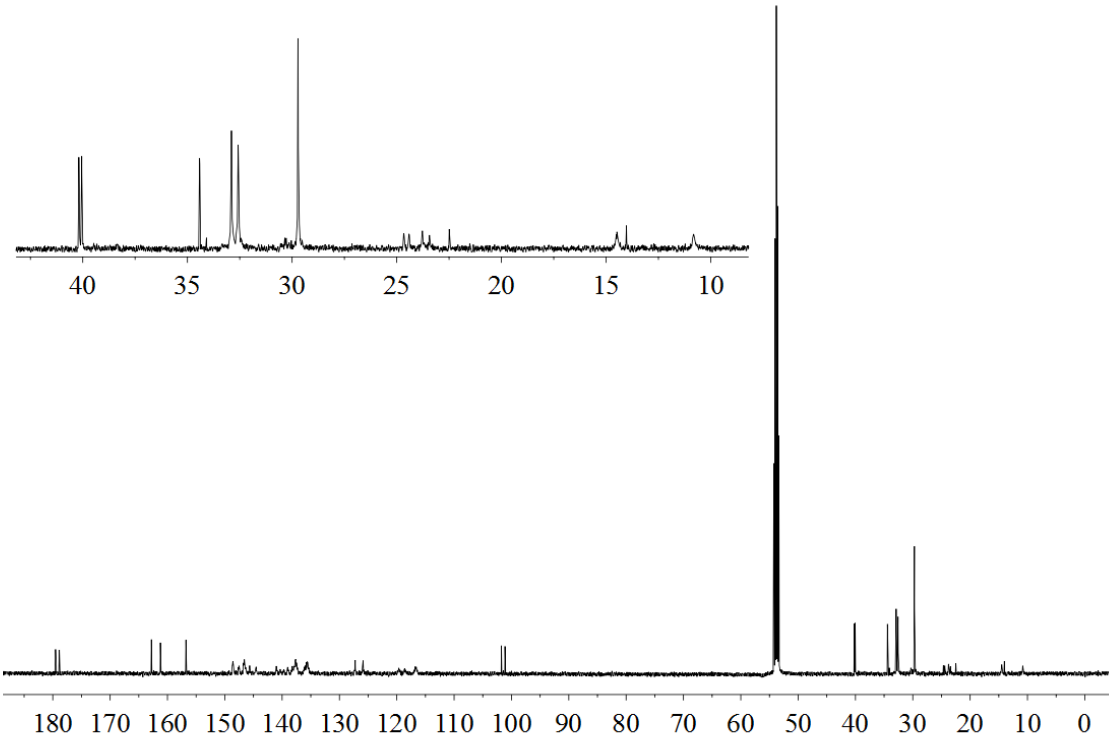
^{1}H,^{1}H cosy NMR (500/500 MHz, 233 K, dichloromethane-d$_2$) spectrum of compound **13**



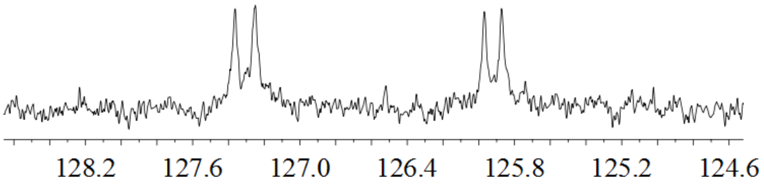
(1) ^{1}**H NMR** (500 MHz, 233 K, dichloromethane-d$_2$) and (2) ^{1}**H NMR** (600 MHz, 299 K, dichloromethane-d$_2$) spectra of compound **13**

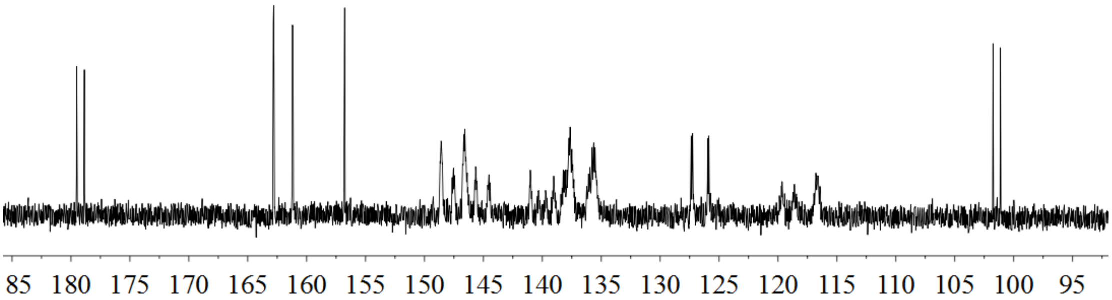


(1) ^{1}**H NMR** (500 MHz, 233 K, dichloromethane-d$_2$) and (2) ^{1}**H NMR** (600 MHz, 299 K, dichloromethane-d$_2$) spectra of compound **13**

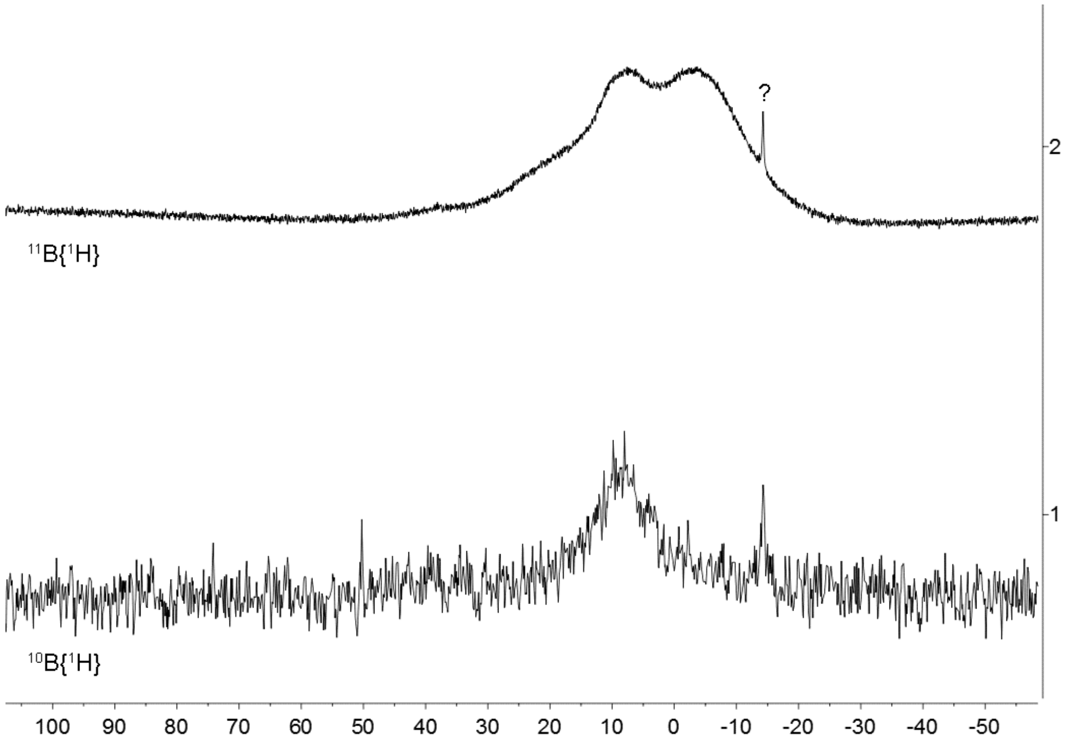


^{13}C{^{1}H} NMR (126 MHz, 233 K, dichloromethane-d$_2$) spectrum of compound **13**

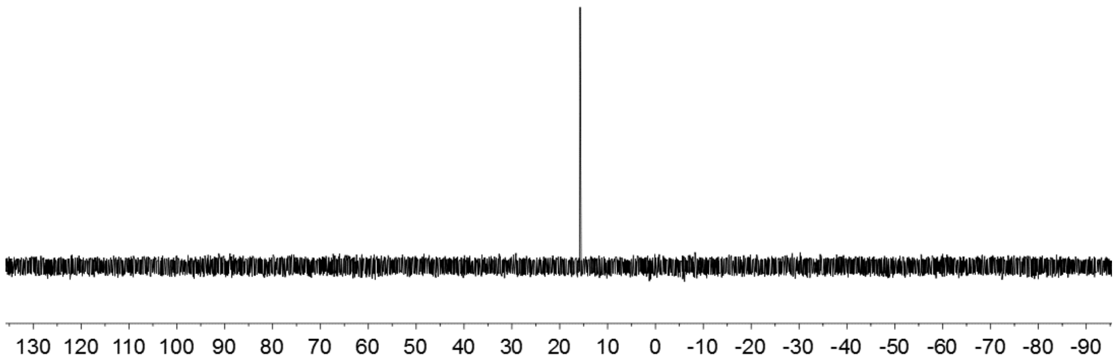




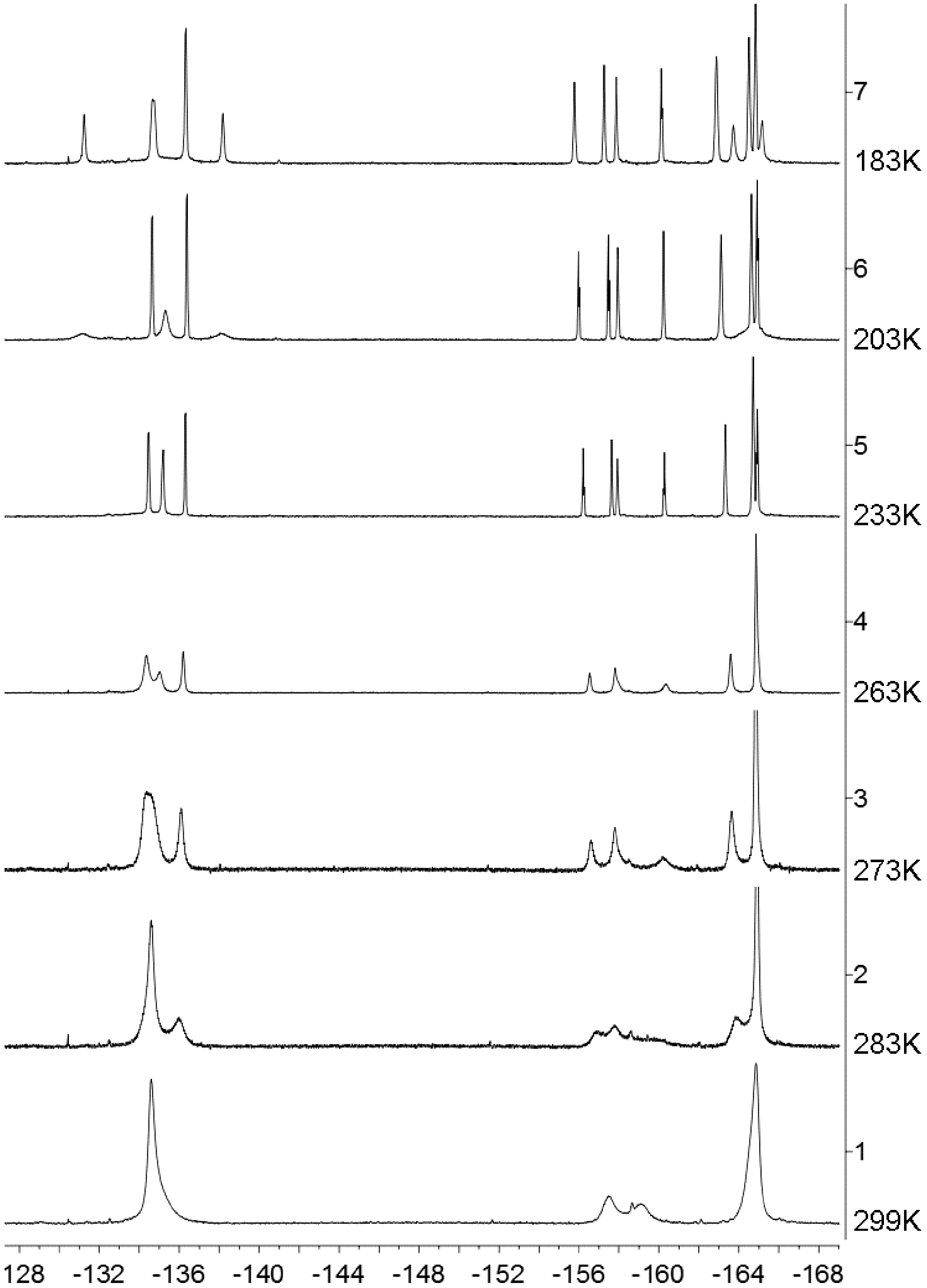
^{13}C{^{1}H} NMR (126 MHz, 233 K, dichloromethane-d$_2$) spectrum of compound **13**



(1) **^{10}B{^{1}H} NMR** (54 MHz, 299K, dichloromethane-d$_2$) and (2) **^{11}B{^{1}H} NMR** (160 MHz, 299K, dichloromethane-d$_2$) spectra of compound **13**



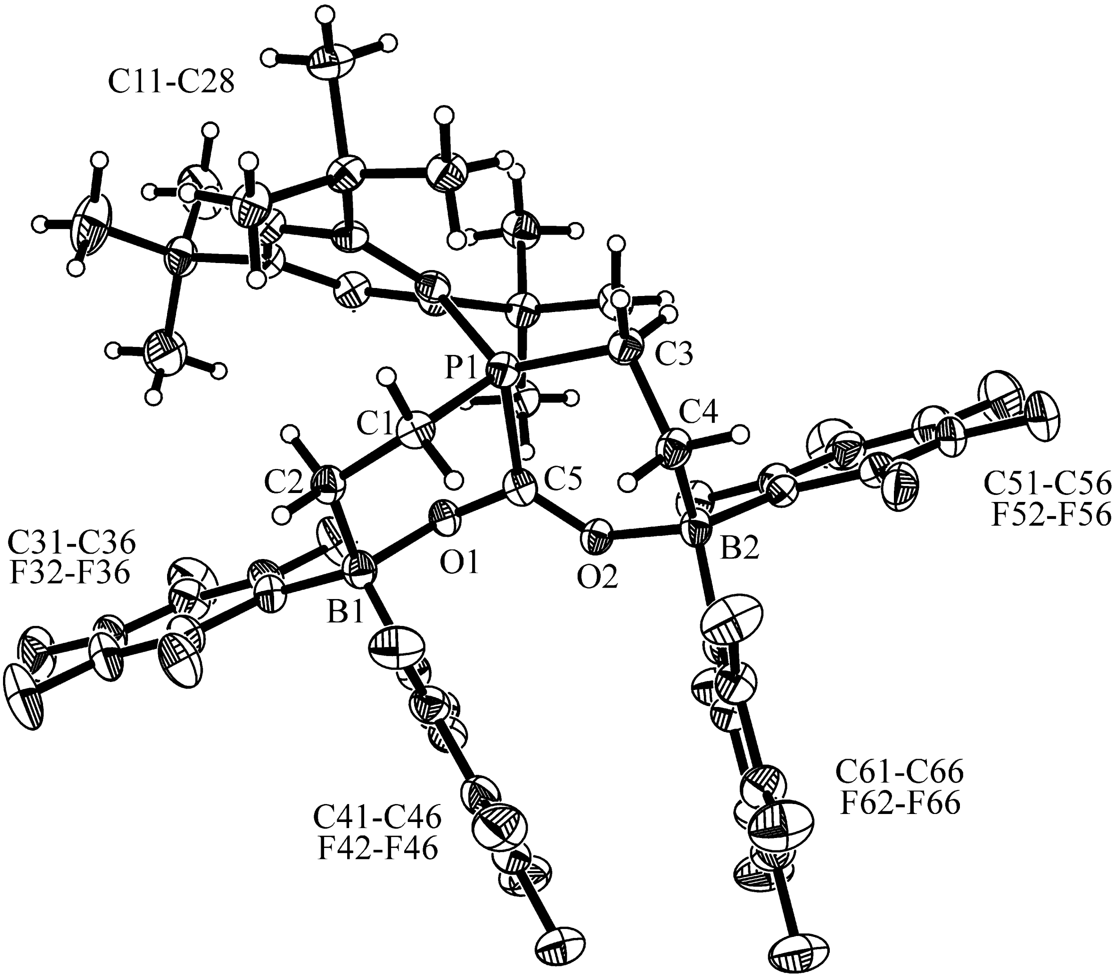
^{31}P{^{1}H} NMR (243 MHz, 299K, dichloromethane-d$_2$) spectrum of compound **13**



^{19}F NMR (470 MHz, dichloromethane-d$_2$) spectra of compound **13** at (1) 299K, (2) 283K, (3) 273K, (4) 263K, (5) 233, (6) 203K, and (7) 183K.

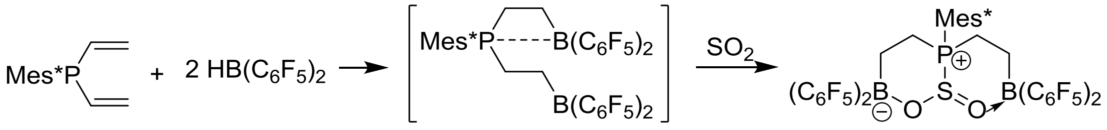
Crystals of compound **13** suitable for the X-ray crystal structure analysis were obtained from slow diffusion of pentane to a solution of the obtained white solid in dichloromethane at -36 °C.

X-ray crystal structure analysis of compound 13: formula $C_{47}H_{37}B_2F_{20}O_2P$, M = 1066.36, colourless crystal, 0.20 x 0.16 x 0.10 mm, a = 13.2824(2), b = 16.3939(3), c = 23.7894(4) Å, β = 95.038(1)°, V = 5160.1(2) Å^3, ρ_{calc} = 1.373 gcm^{-3}, μ = 0.161 mm^{-1}, empirical absorption correction ($0.968 \leq T \leq 0.984$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073Å, T = 223(2) K, ω and φ scans, 39921 reflections collected ($\pm h$, $\pm k$, $\pm l$), 8895 independent (R_{int} = 0.095) and 6383 observed reflections [$I > 2\sigma(I)$], 658 refined parameters, R = 0.070, wR^2 = 0.162, max. (min.) residual electron density 0.30 (-0.32) e.Å^{-3}; hydrogen atoms were calculated and refined as riding atoms.



Molecular structure of compound **13**

Synthesis of compound 14



8 **2** **11** **14**

A solution of phosphane **8** (66.1 mg, 0.20 mmol, 1.0 eq.) and borane **2** (138.4 mg, 0.40 mmol, 2.0 eq.) in dichloromethane (4 mL) was stirred for 15 min at room temperature to give a yellow solution. Then the solvent was removed in vacuo and the obtained residue was dissolved in pentane (4 mL). The resulting solution was cooled to -78 °C (dry ice / isopropanol) and evacuated carefully. Then the dry ice bath was removed and the reaction mixture was exposed to SO_2 gas (1.5 bar) and stirred at room temperature for 2 h to give a white suspension. The precipitate was collected by filtration using a filter cannula, washed with pentane (1 mL × 2) and dried in vacuo to give compound **9** as a white solid (189.0 mg, 0.174 mmol, 87 %).
Anal. Calcd. for $C_{49}H_{51}B_2F_{20}P_2$: C, 50.86; H, 3.43. Found: C, 50.70; H, 3.17.
Decomp.: 119 ^oC

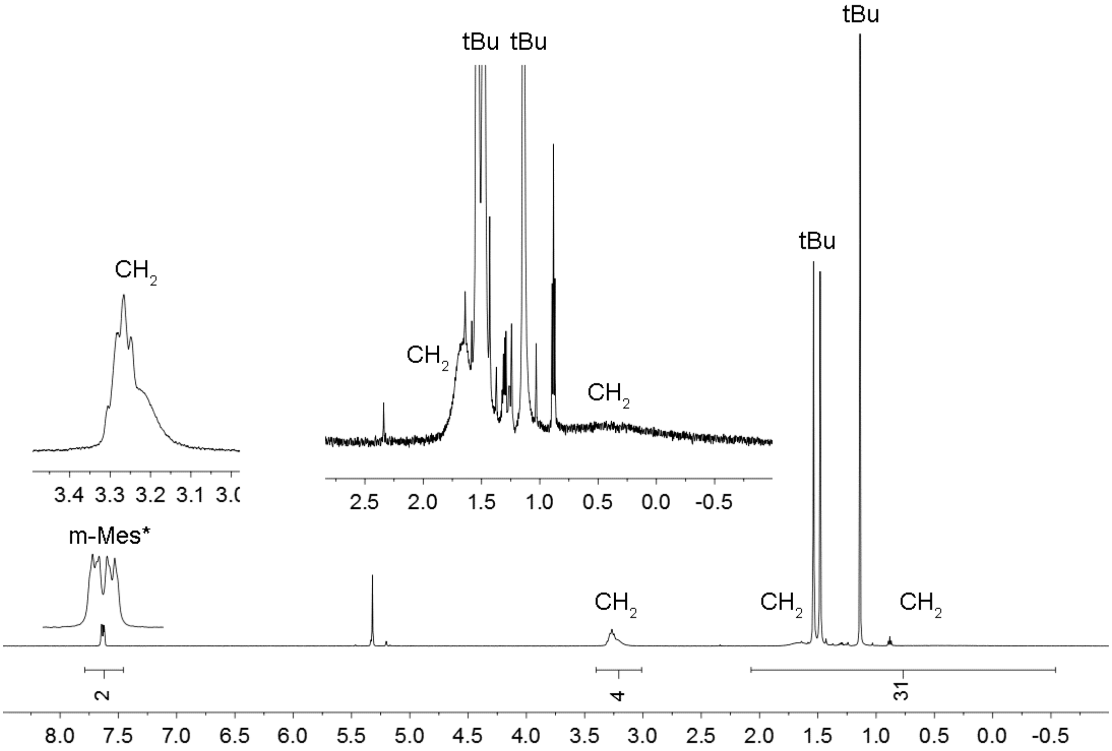
[Mes*: 2,4,6-tri(tert-butyl)phenyl]
[Comment: solubility of the white solid in dichloromethane-d_2 is poor]
^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2) δ = 7.64, 7.62 (each m, each 1H, *m*-Mes*), 3.27 (m), 3.23 (br), 1.66 (br), 0.41 (br) (each 2H, CH_2), 1.54, 1.48 (each s, each 9H, *o*-^{t}Bu), 1.14 (s, 9H, *p*-^{t}Bu).

^{13}C{^{1}H} NMR (151 MHz, 299 K, dichloromethane-d_2) δ = 163.8 (m), 162.3 (d, $^2J_{PC}$ = 5.2 Hz)(*o*-Mes*), 158.3 (d, $^4J_{PC}$ = 4.8 Hz, *p*-Mes*), 128.2, 126.6 (each d, $^3J_{PC}$ = 12.9 Hz, *m*-Mes*), 101.4 (d, $^1J_{PC}$ = 62.8 Hz, *i*-Mes*), 40.6/33.5, 40.5/33.2 (*o*-^{t}Bu), 35.2/30.4 (*p*-^{t}Bu), n.o. (CH_2), [C_6F_5 not listed].

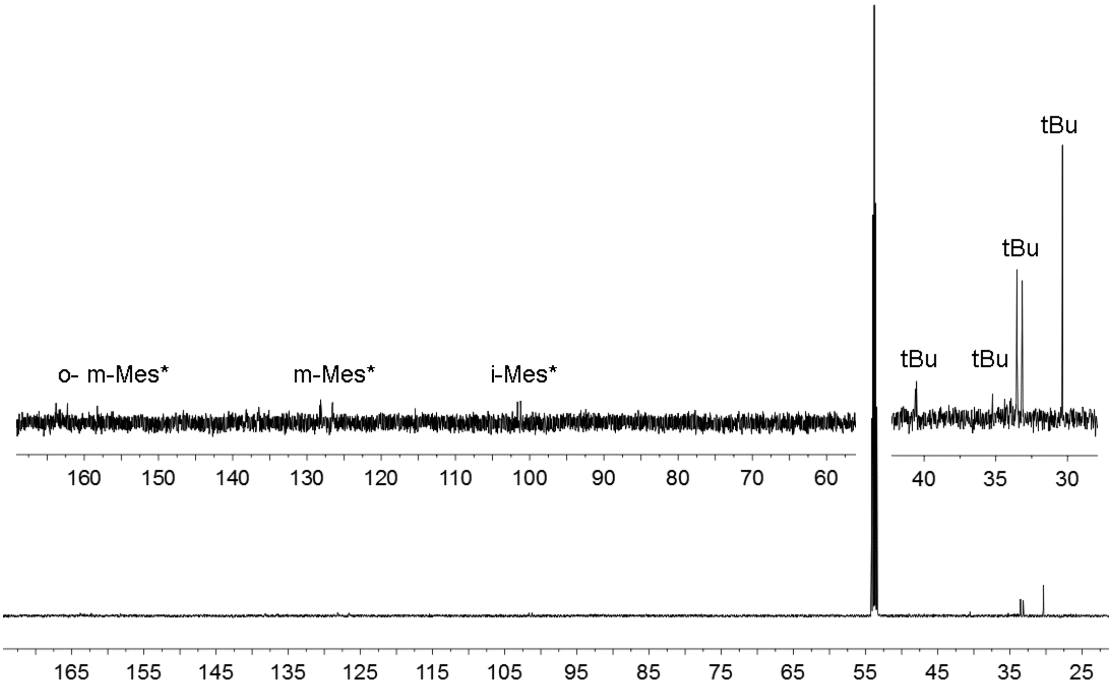
^{10}B{^{1}H} NMR (54 MHz, 299K, dichloromethane-d_2) δ = 4.3 ($\nu_{1/2}$ ~ 500 Hz).
^{11}B{^{1}H} NMR (160 MHz, 299K, dichloromethane-d_2) δ = 4.3 (br).

^{19}F NMR (564 MHz, 299 K, dichloromethane-d_2) δ = -136.0, -136.3 (each br, each 2F, *o*-C_6F_5), -158.3, -159.5 (each br, each 1F, *p*-C_6F_5), -164.5, -164.9 (each br, each 2F, *m*-C_6F_5).

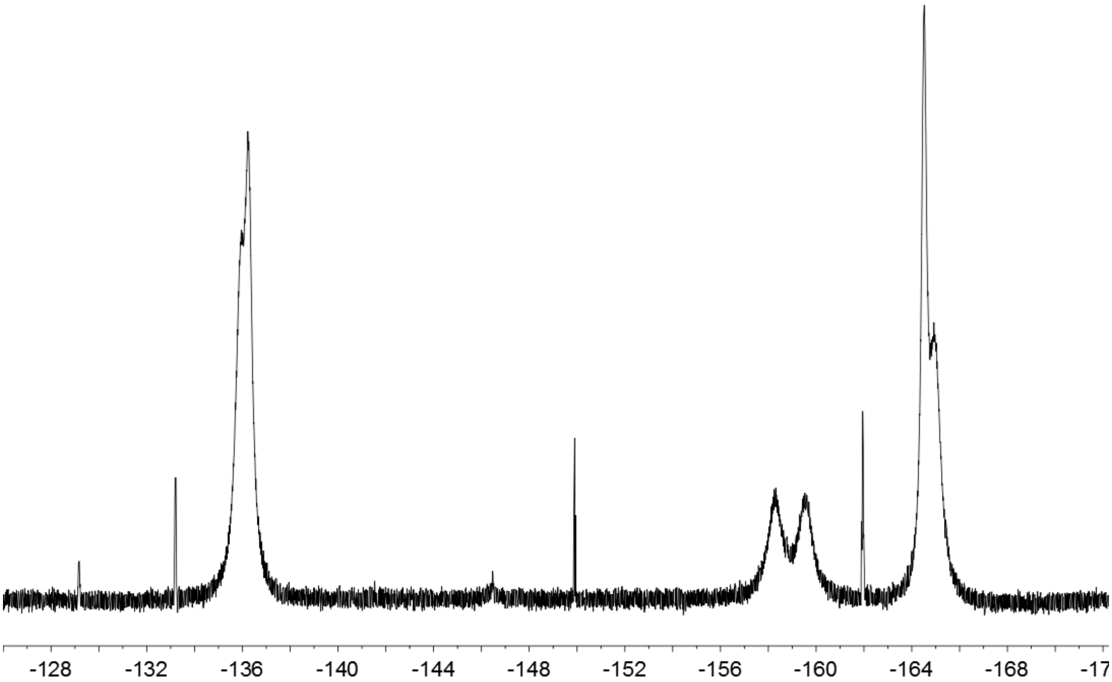
^{31}P{^{1}H} NMR (243 MHz, 299K, dichloromethane-d_2) δ = 45.0 ($\nu_{1/2}$ ~ 6 Hz).



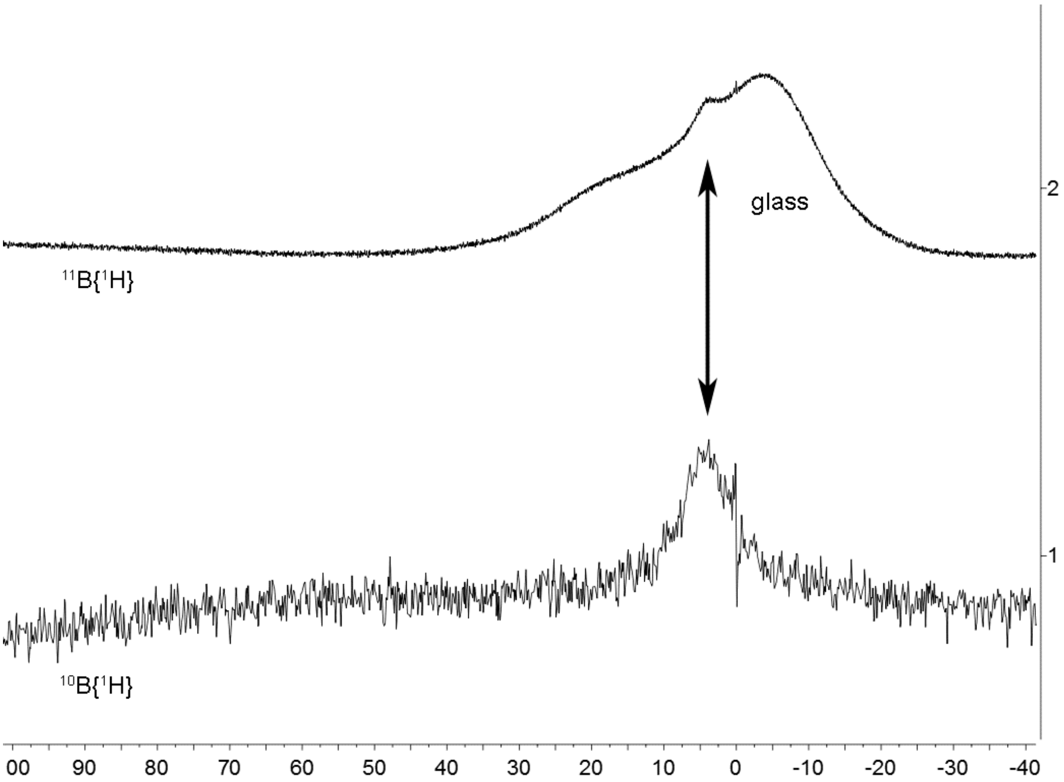
^{1}H NMR (600 MHz, 299 K, dichloromethane-d$_2$) of compound **14**



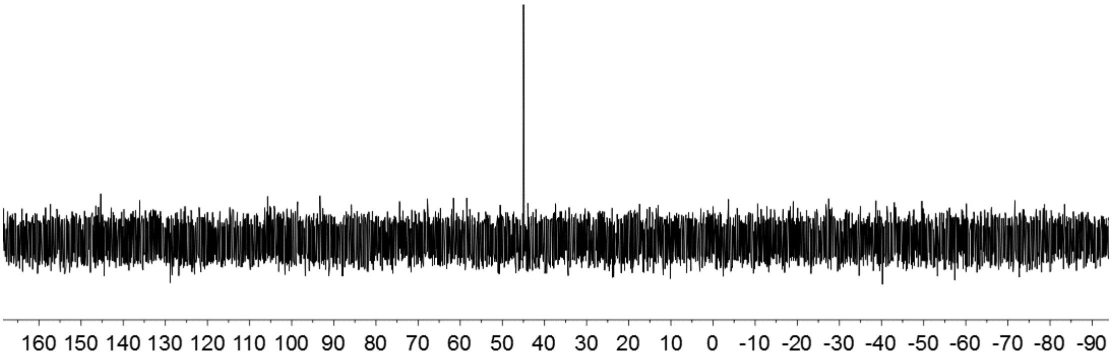
^{13}C{^{1}H} NMR (151 MHz, 299 K, dichloromethane-d$_2$) of compound **14**



^{19}F NMR (564 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound **14**



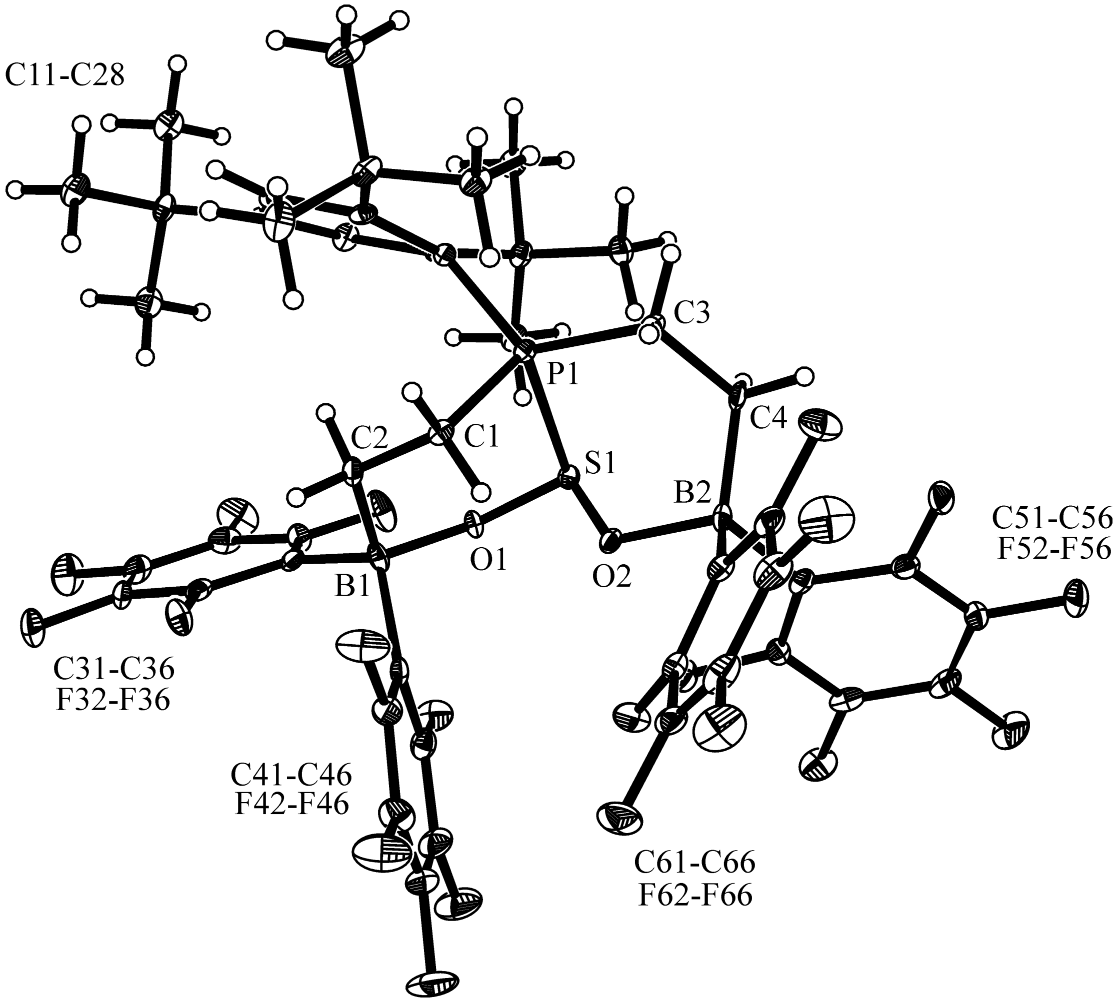
(1) **^{10}B{^{1}H} NMR** (54 MHz, 299K, dichloromethane-d$_2$) and (2) **^{11}B{^{1}H} NMR** (160 MHz, 299K, dichloromethane-d$_2$) spectra of compound **14**



$^{31}P\{^1H\}$ NMR (243 MHz, 299K, dichloromethane-d_2) spectrum of compound **14**

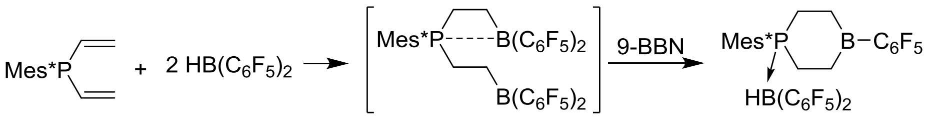
Crystals of compound **14** suitable for the X-ray crystal structure analysis were obtained from slow diffusion of pentane to a solution of the white solid in dichloromethane at -36 °C.

X-ray crystal structure analysis of compound 14: A colorless needle-like specimen of $C_{46}H_{37}B_2F_{20}O_2PS$, approximate dimensions 0.047 mm x 0.079 mm x 0.135 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 831 frames were collected. The total exposure time was 20.77 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 45620 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 8254 were independent (average redundancy 5.527, completeness = 99.8%, R_{int} = 10.05%, R_{sig} = 6.98%) and 5735 (69.48%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.6318(6) Å, b = 14.5000(7) Å, c = 14.8889(8) Å, α = 62.069(2)°, β = 76.457(2)°, γ = 70.196(2)°, volume = 2257.5(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 9954 reflections above 20 σ(I) with $4.843° < 2\theta < 54.97°$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.835. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9700 and 0.9890. The final anisotropic full-matrix least-squares refinement on F^2 with 658 variables converged at R1 = 4.99%, for the observed data and wR2 = 10.28% for all data. The goodness-of-fit was 1.024. The largest peak in the final difference electron density synthesis was 0.341 $e^-/Å^3$ and the largest hole was -0.406 $e^-/Å^3$ with an RMS deviation of 0.073 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.598 g/cm^3 and F(000), 1100 e^-.



Molecular structure of compound **14**

Synthesis of compound 18



8 **2** **11** **18**

A solution of phosphane **8** (174.3 mg, 0.53 mmol, 1.00 eq.) and borane **2** (364.8 mg, 1.06 mmol, 2.00 eq.) in pentane (5 mL) was stirred for 15 min at room temperature. Then 9-borabicyclo[3.3.0]nonane (9-BBN, 64.3 mg, 0.53 mmol, 1.00 eq.) was added and the reaction mixture was stirred for 2 h at room temperature. Subsequently the resulting white precipitate was isolated and washed with pentane (5 × 3 mL) and dried in vacuo to finally give compound **18** as a white solid (376.6 mg, 83%).
Anal. Calcd. for $C_{40}H_{38}B_2F_{15}P$: C, 56.11; H, 4.47. Found: C, 55.57; H, 4.33.
Melting point: 192 °C

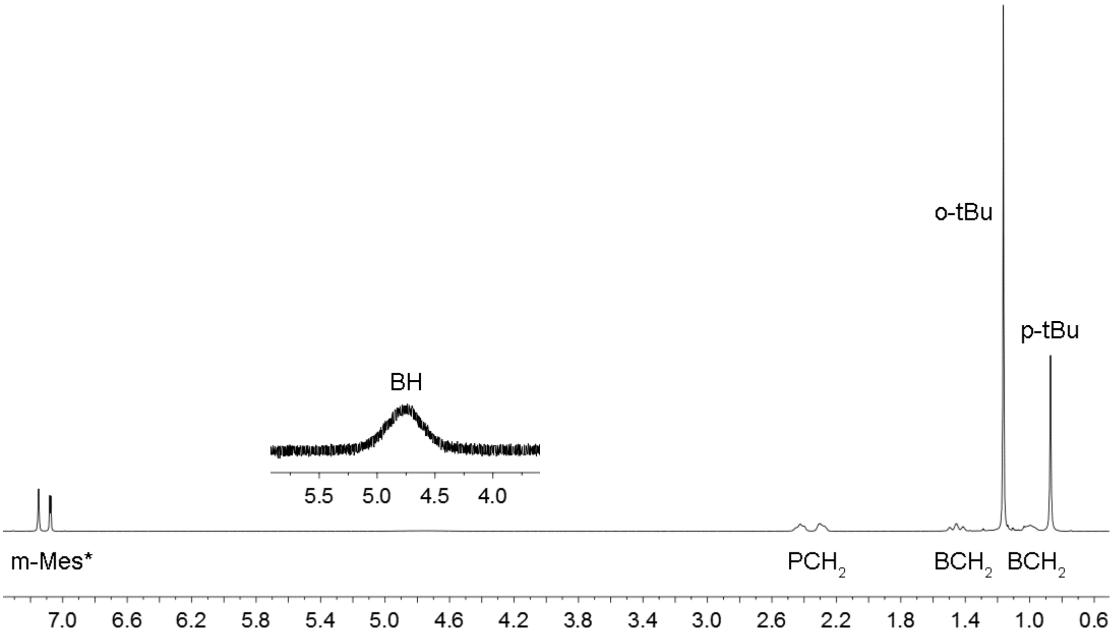
[Mes*: 2,4,6-tri(tert-butyl)phenyl]
^{1}H NMR (500 MHz, 299 K, benzene-d$_6$): δ = 7.08 (d, $^4J_{PH}$ = 3.3 Hz, 2H, *m*-Mes*), 4.75 (br, 1H, BH), 2.42/2.29 (each br m, each 2H, PCH_2), 1.45/1.00 (each br m, each 2H, BCH_2), 1.16 (s, 18H, *o*-^{t}Bu), 0.87 (s, 9H, *p*-^{t}Bu).

^{13}C{^{1}H} NMR (126 MHz, 299 K, benzene-d$_6$): δ = 160.8 (d, $^2J_{PC}$ = 3.2 Hz, *o*-Mes*), 151.2 (d, $^4J_{PC}$ = 3.4 Hz, *p*-Mes*), 124.2 (d, $^3J_{PC}$ = 9.8 Hz, *m*-Mes*), 118.3 (d, $^1J_{PC}$ = 52.6 Hz, *i*-Mes*), 40.2 (d, $^3J_{PC}$ = 2.4 Hz, *o*-^{t}Bu), 34.0 (d, $^5J_{PC}$ = 1.0 Hz, *p*-^{t}Bu), 33.2 (*o*-^{t}Bu), 30.4 (*p*-^{t}Bu), 24.8 (d, $^1J_{PC}$ = 34.5 Hz, PCH_2), 22.8 (br, BCH_2), [C_6F_5 not listed].

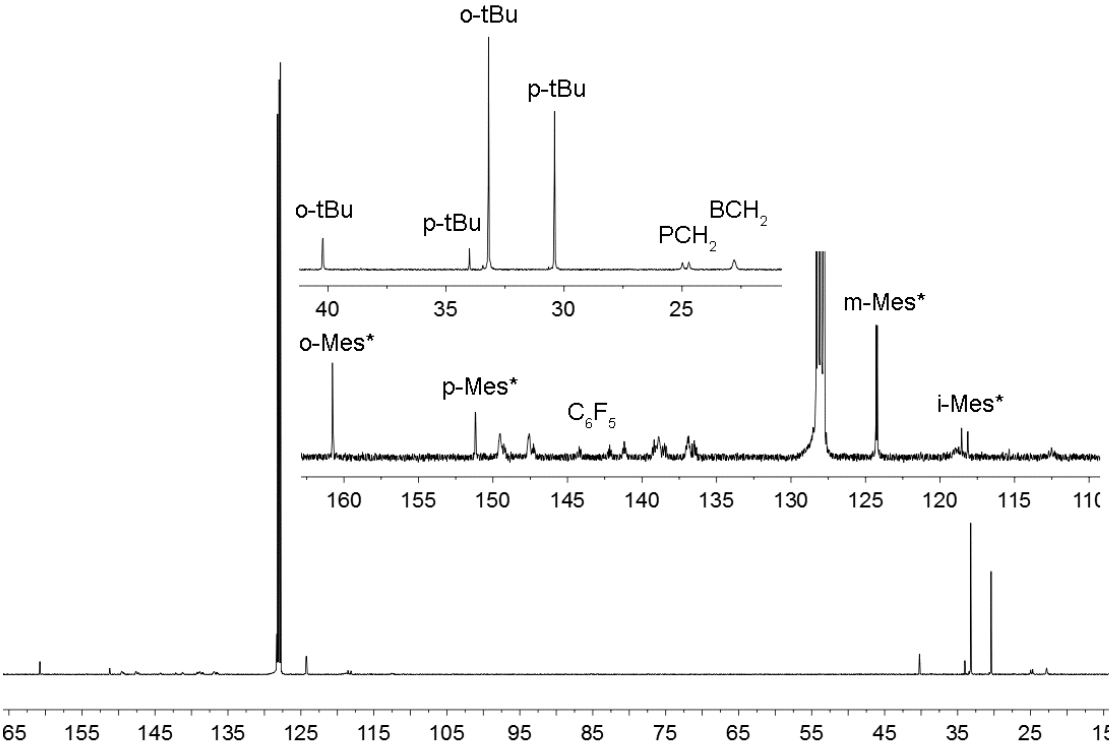
^{11}B{^{1}H} NMR (160 MHz, 299 K, benzene-d$_6$): δ = 77.4 ($\nu_{1/2}$ ~ 2400 Hz, $B(C_6F_5)$), -20.7 ($\nu_{1/2}$ ~ 360 Hz, $B(C_6F_5)_2$).

^{31}P{^{1}H} NMR (202 MHz, 299 K, benzene-d$_6$): δ = 7.3 ($\nu_{1/2}$ ~ 100 Hz).

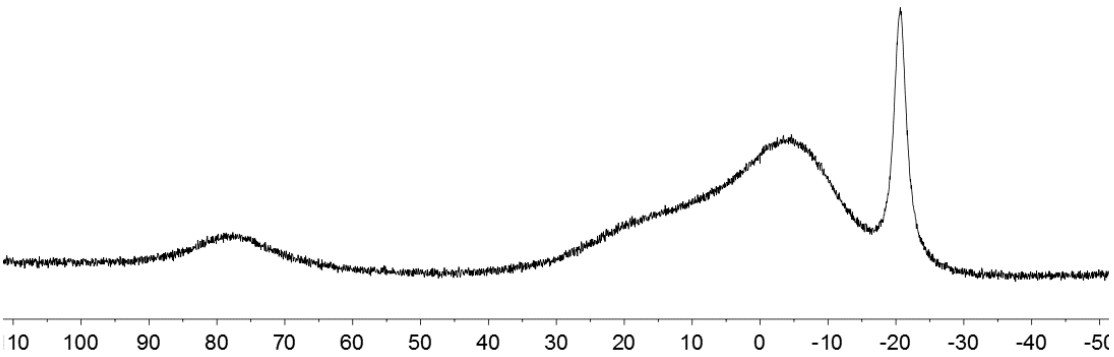
^{19}F NMR (470 MHz, 299 K, benzene-d$_6$): δ = -125.9 (br, 4F, *o*), -157.5 (t, $^3J_{FF}$ = 20.7 Hz, 2F, *p*), -163.0 (br m, 4F, *m*)($B(C_6F_5)_2$)[$\Delta\delta^{19}F_{pm}$ = 5.5], -127.6 (m , 2F, *o*), -148.3 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*), -161.7 (m, 2F, *m*)($B(C_6F_5)$)[$\Delta\delta^{19}F_{p,m}$ = 13.4].



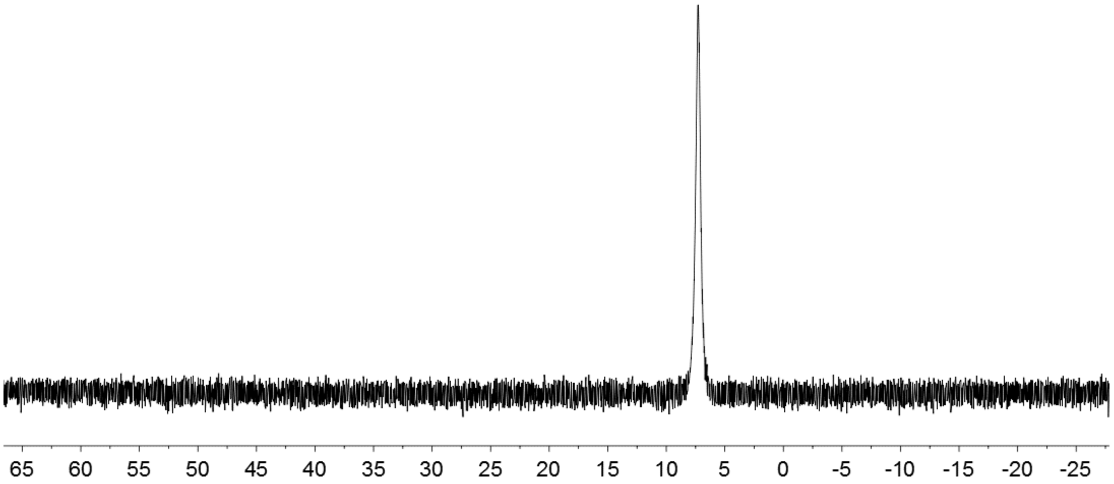
^{1}H NMR (500 MHz, 299 K, C_6D_6) spectrum of compound **18**



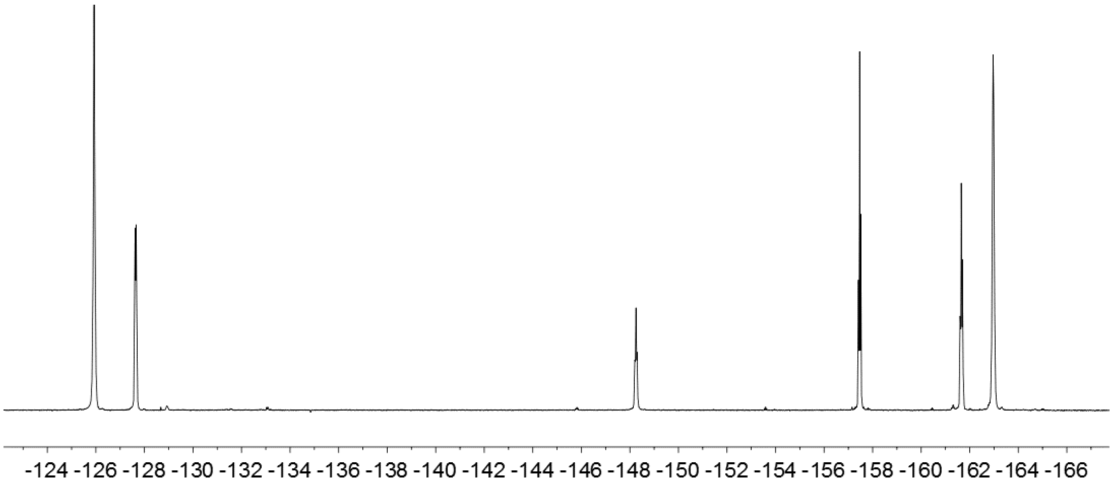
^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6) spectrum of compound **18**



^{11}B{^{1}H} NMR (160 MHz, 299 K, C_6D_6) spectrum of compound **18**



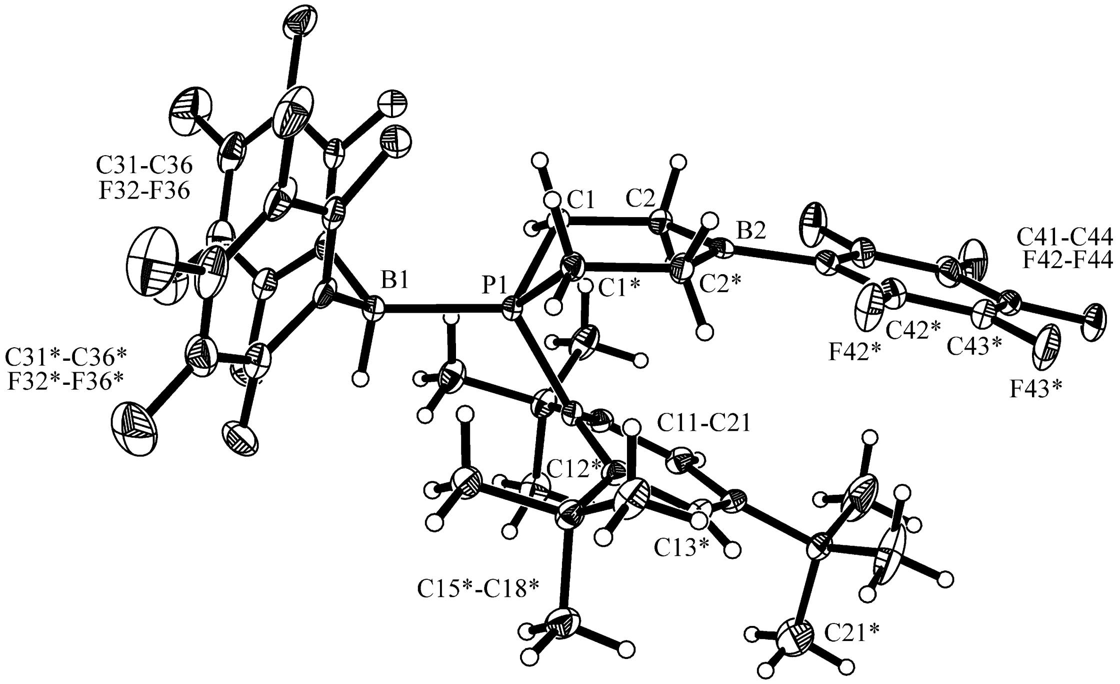
^{31}P{^{1}H} NMR (202 MHz, 299 K, C_6D_6) spectrum of compound **18**



^{19}F NMR (470 MHz, 299 K, C_6D_6) spectrum of compound **18**

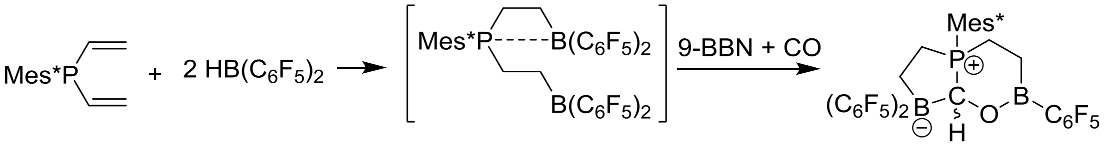
Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of the white solid in CH_2Cl_2/pentane at -35 °C.

X-ray crystal structure analysis of compound 18: A colorless prism-like specimen of $C_{40}H_{38}B_2F_{15}P$, approximate dimensions 0.059 mm x 0.103 mm x 0.134 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1401 frames were collected. The total exposure time was 23.35 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 76841 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 7223 were independent (average redundancy 10.638, completeness = 99.8%, R_{int} = 7.42%, R_{sig} = 3.30%) and 5724 (79.25%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 13.6249(7) Å, $\underline{b}$ = 17.6508(8) Å, $\underline{c}$ = 15.8725(8) Å, β = 91.388(2)°, volume = 3816.1(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 9065 reflections above 20 σ(I) with 4.526° < 2θ < 54.19°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.946. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9770 and 0.9900. The final anisotropic full-matrix least-squares refinement on F^2 with 581 variables converged at R1 = 4.56%, for the observed data and wR2 = 10.10% for all data. The goodness-of-fit was 1.066. The largest peak in the final difference electron density synthesis was 0.334 $e^-/Å^3$ and the largest hole was -0.363 $e^-/Å^3$ with an RMS deviation of 0.054 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.490 g/cm^3 and F(000), 1752 e^-.



Molecular structure of compound **18**

Synthesis of compound 21



8 **2** **11** **21**

A solution of phosphane **8** (66.1 mg, 0.20 mmol, 1.0 eq.) and borane **2** (138.4 mg, 0.40 mmol, 2.0 eq.) in dichloromethane (4 mL) was stirred for 15 min at room temperature to give a yellow solution. Then 9-BBN (24.4 mg, 0.2 mmol, 1.0 eq.) in dichloromethane (1 mL) was added and the obtained reaction mixture was stirred for 1h at room temperature. The resulting solution was cooled to -78 °C (dry ice / isopropanol bath) and evacuated carefully. Then the dry ice bath was removed and the reaction mixture was exposed to CO gas (1.5 bar) and stirred at room temperature for 24 h to give a colorless solution. Then all volatiles were removed in vacuo to give a white foam, which was washed with pentane (1 mL × 2) and dried in vacuo to give compound **21** as a white solid (115.0 mg, 0.130 mmol, 65 %).

Anal. Calcd. for $C_{41}H_{38}B_2F_{15}OP$: C, 55.69; H, 4.33. Found: C, 54.96; H, 4.04.

Melting point: 257 ^{o}C

The NMR data of the obtained white solid in dichloromethane-d_2 showed a mixture of two compounds [major : minor ~ 68 : 32 (^{31}P, 243K); 58 : 42 (^{31}P, 299K)]

[Mes*: 2,4,6-tri(tert-butyl)phenyl]

Major diastereomer

^{1}H NMR (500 MHz, 243 K, dichloromethane-d_2) δ = 7.44 (m, 1H, *m*-Mes*), 7.38 (m, 1H, *m*'-Mes*), 6.26 (d, $^2J_{PH}$ = 12.4 Hz, 1H, OCH), 2.96/2.89, 2.28/1.70 (each m, each 1H, PCH_2), 2.24/0.97, 1.01/-0.30 (each m, each 1H, BCH_2), 1.49 (s, 9H, *o*-$Me^{t\text{-}Bu}$), 1.37 (s, 9H, *o*'-$Me^{t\text{-}Bu}$), 1.14 (s, 9H, *p*-$Me^{t\text{-}Bu}$).

^{13}C{^{1}H} NMR (126 MHz, 243 K, dichloromethane-d_2) δ = 162.9 (d, $^2J_{PC}$ = 5.5 Hz, *o*-Mes*), 159.4 (d, $^2J_{PC}$ = 4.8 Hz, *o*'-Mes*), 154.6 (d, $^4J_{PC}$ = 4.3 Hz, *p*-Mes*), 125.4 (d, $^3J_{PC}$ = 11.8 Hz, *m*'-Mes*), 124.5 (d, $^3J_{PC}$ = 11.9 Hz, *m*-Mes*), 108.4 (d, $^1J_{PC}$ = 71.1 Hz, *i*-Mes*), 76.9 (br, $^1J_{PC}$ ~ 40 Hz[1], OCH), 40.3 (d, $^3J_{PC}$ = 3.0 Hz, *o*-$C^{t\text{-}Bu}$), 40.1 (d, $^3J_{PC}$ = 2.8 Hz, *o*'-$C^{t\text{-}Bu}$), 34.56 (*p*-$C^{t\text{-}Bu}$), 32.5 (*o*'-$Me^{t\text{-}Bu}$), 31.8 (br, *o*-$Me^{t\text{-}Bu}$), 30.2 (*p*-$Me^{t\text{-}Bu}$), 26.4 (d, $^1J_{PC}$ = 43.7 Hz), 21.4 (d, $^1J_{PC}$ = 50.0 Hz)(PCH_2), 16.4, 10.5 (br, BCH_2), [[1] from the ^{1}H,^{13}C ghsqc NMR experiment; C_6F_5 not listed].

^{11}B{^{1}H} NMR (160 MHz, 243 K, dichloromethane-d_2) δ = 44.9 ($\nu_{1/2}$ ~ 2200 Hz, BO), -12.4 ($\nu_{1/2}$ ~ 90 Hz).

^{19}F NMR (470 MHz, 268 K, dichloromethane-d$_2$) δ = -132.8 (m, 2F, *o*)^t, -159.4 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*), -164.2 (m, 2F, *m*)(B(C_6F_5)$_2$), [Δδ^{19}F$_{m,p}$ = 4.8], -133.5 (m, 2F, *o*), -153.1 (t, $^3J_{FF}$ = 20.0 Hz, 1F, *p*), -162.8 (m, 2F, *m*)(B(C_6F_5))[Δδ^{19}F$_{m,p}$ = 9.7], -134.4 (m, 2F, *o*), -162.5 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*), -165.8 (m, 2F, *m*)(B(C_6F_5)$_2$)[Δδ^{19}F$_{m,p}$ = 3.3], [^{t} tentative assignment].

^{31}P{^{1}H} NMR (202 MHz, 243 K, dichloromethane-d$_2$) δ = 26.2 ($\nu_{1/2}$ ~ 40 Hz).
^{31}P{^{1}H} NMR (202 MHz, 299 K, dichloromethane-d$_2$) δ = 26.4 ($\nu_{1/2}$ ~ 100 Hz).

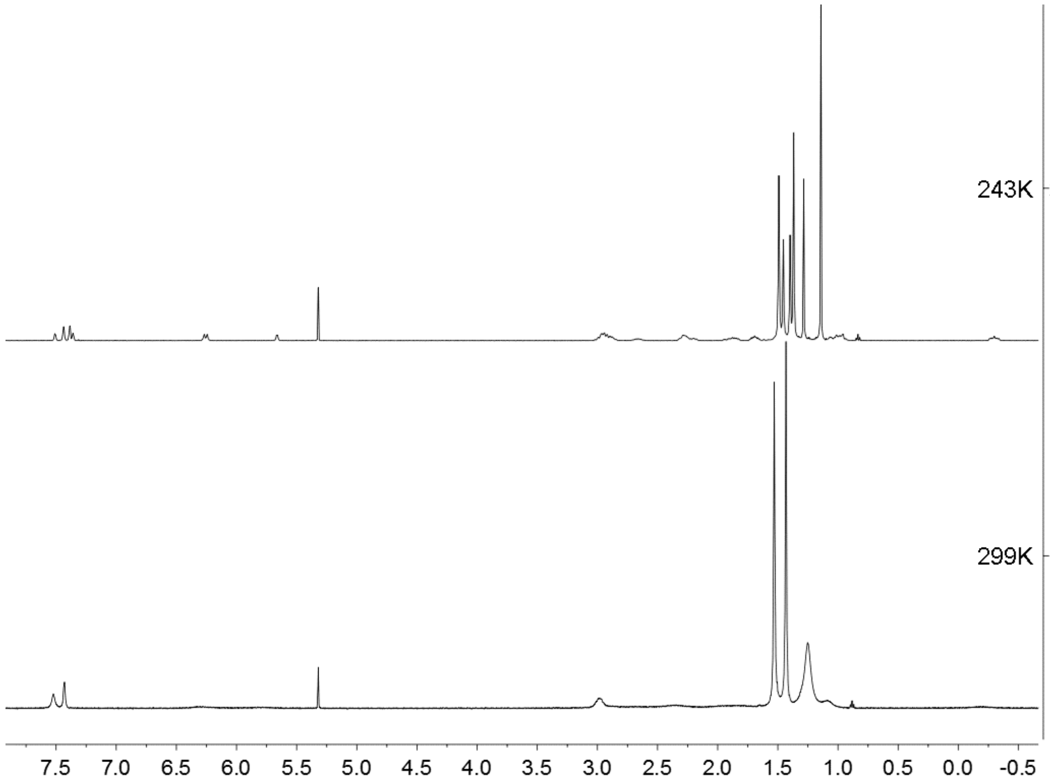
Minor diastereomer
^{1}H NMR (500 MHz, 243 K, dichloromethane-d$_2$) δ = 7.51 (m, 1H, *m*-Mes*), 7.36 (m, 1H, *m*'-Mes*), 5.66 (d, $^2J_{PH}$ = 3.0 Hz, 1H, OCH), 2.95/2.66, 2.92/1.86 (each m, each 1H, PCH$_2$), 1.89/1.35, 1.44/1.11 (each m, each 1H, BCH$_2$), 1.45 (s, 9H, *o*-Me$^{t\text{-Bu}}$), 1.40 (s, 9H, *o'*-Me$^{t\text{-Bu}}$), 1.29 (s, 9H, *p*-Me$^{t\text{-Bu}}$).

^{13}C{^{1}H} NMR (126 MHz, 243 K, dichloromethane-d$_2$) δ = 161.5 (d, $^2J_{PC}$ = 6.4 Hz, *o*-Mes*), 160.2 (d, $^2J_{PC}$ = 6.3 Hz, *o'*-Mes*), 154.8 (d, $^4J_{PC}$ = 4.3 Hz, *p*-Mes*), 125.5 (d, $^3J_{PC}$ = 11.6 Hz, *m*-Mes*), 125.2 (d, $^3J_{PC}$ = 12.8 Hz, *m'*-Mes*), 113.0 (d, $^1J_{PC}$ = 73.0 Hz, *i*-Mes*), 75.9 (br, OCH), 40.9 (d, $^3J_{PC}$ = 2.6 Hz, *o*-C$^{t\text{-Bu}}$), 40.5 (d, $^3J_{PC}$ = 3.0 Hz, *o'*-C$^{t\text{-Bu}}$), 34.57 (*p*-C$^{t\text{-Bu}}$), 33.1 (*o'*-Me$^{t\text{-Bu}}$), 32.9 (*o*-Me$^{t\text{-Bu}}$), 30.3 (*p*-Me$^{t\text{-Bu}}$), 35.9 (d, $^1J_{PC}$ = 57.0 Hz), 17.5 (d, $^1J_{PC}$ = 34.0 Hz)(PCH$_2$), 20.5, 13.1 (br, BCH$_2$), [C_6F_5 not listed].

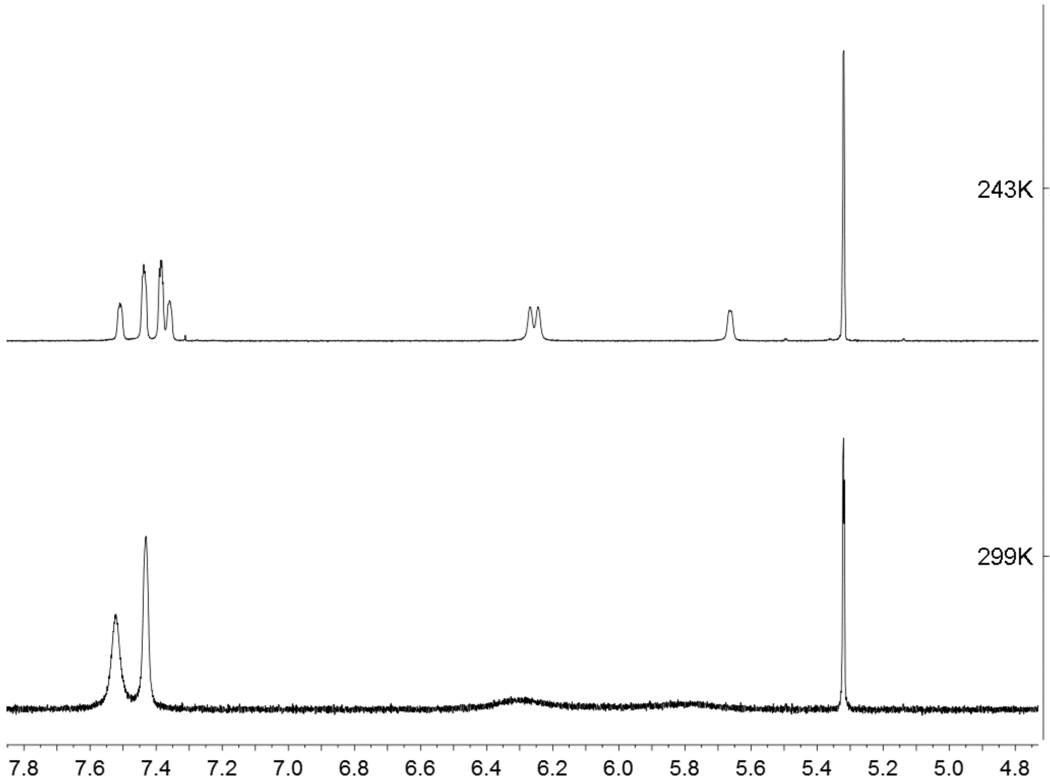
^{11}B{^{1}H} NMR (160 MHz, 243 K, dichloromethane-d$_2$) δ = 44.9 ($\nu_{1/2}$ ~ 2200 Hz, BO), -9.0 ($\nu_{1/2}$ ~ 100 Hz).

^{19}F NMR (470 MHz, 268 K, dichloromethane-d$_2$) δ = -132.2 (br, 2F, *o*), -151.4 (t, $^3J_{FF}$ = 20.0 Hz, 1F, *p*), -162.7 (m, 2F, *m*)(B(C_6F_5))[Δδ^{19}F$_{m,p}$ = 11.3], -132.9, -133.6 (each br, each 1H, *o*)^t, -162.1 (t, $^3J_{FF}$ = 19.7 Hz, 1F, *p*), -166.4 (m, 2F, *m*-B(C_6F_5)$_2$)[Δδ^{19}F$_{m,p}$ = 4.3], -133.5 (br, 2F, *o*)^t, -161.9 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*), -165.2 (m, 2F, *m*)(B(C_6F_5)$_2$)[Δδ^{19}F$_{m,p}$ = 3.3], [^{t} tentative assignment].

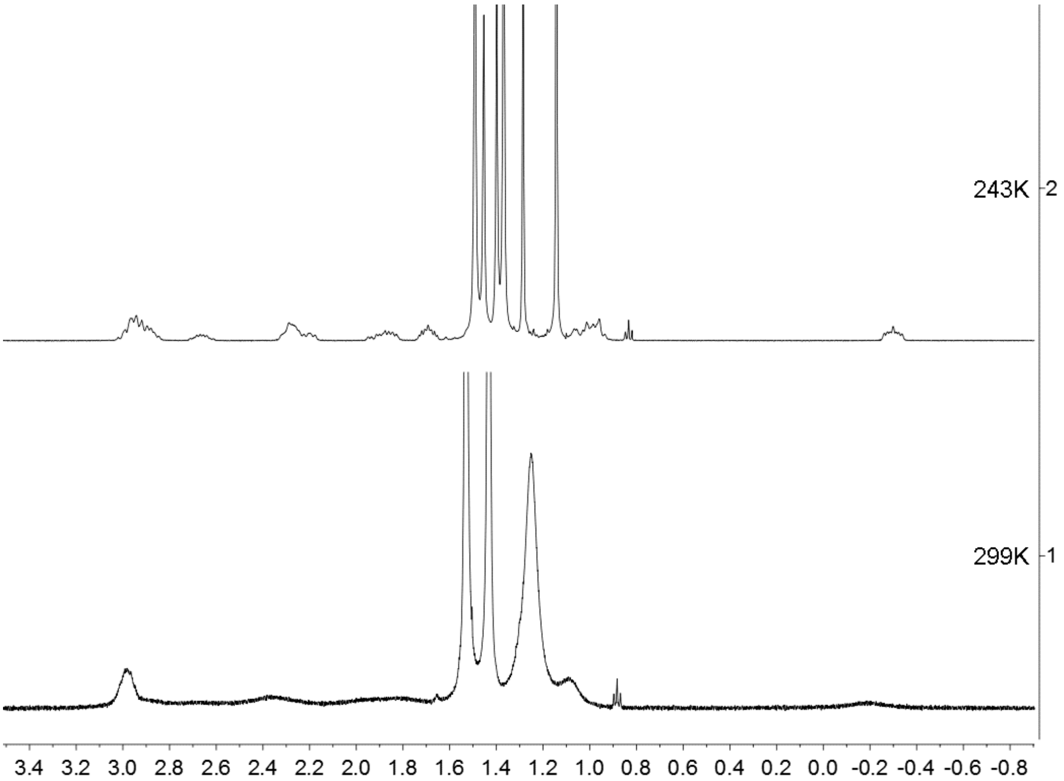
^{31}P{^{1}H} NMR (202 MHz, 243 K, dichloromethane-d$_2$) δ = 34.8 ($\nu_{1/2}$ ~ 15 Hz).
^{31}P{^{1}H} NMR (202 MHz, 299 K, dichloromethane-d$_2$) δ = 34.4 ($\nu_{1/2}$ ~ 140 Hz).



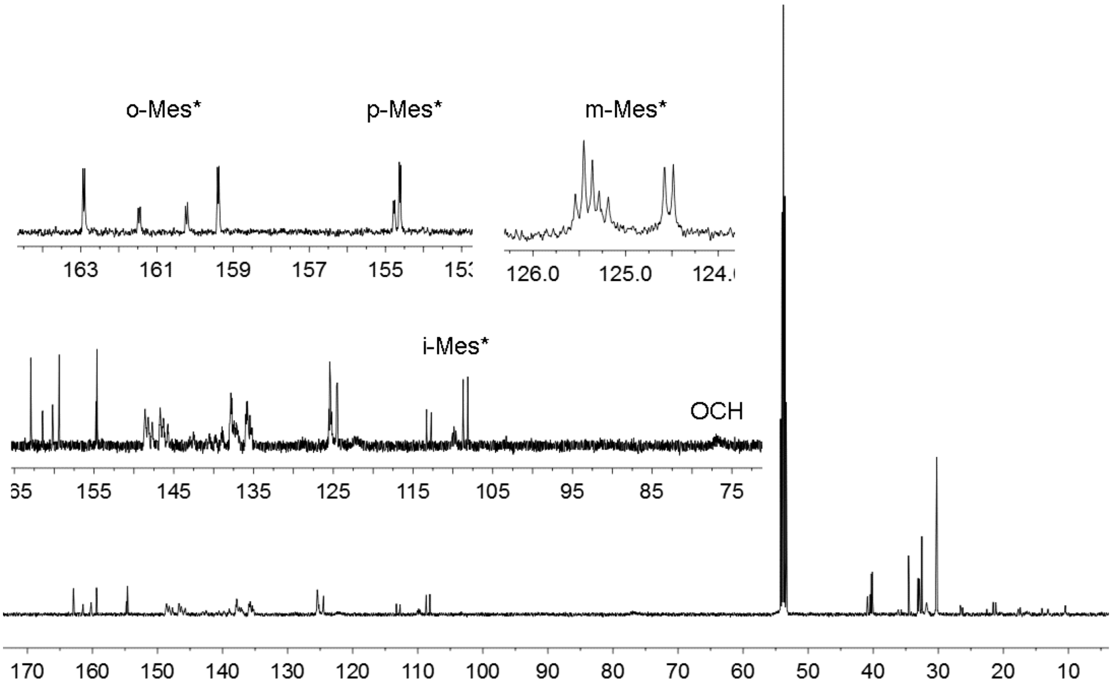
^{1}**H NMR** (500 MHz, dichloromethane-d$_2$) spectra of compound **21** at (1) 299K and (2) 243K.



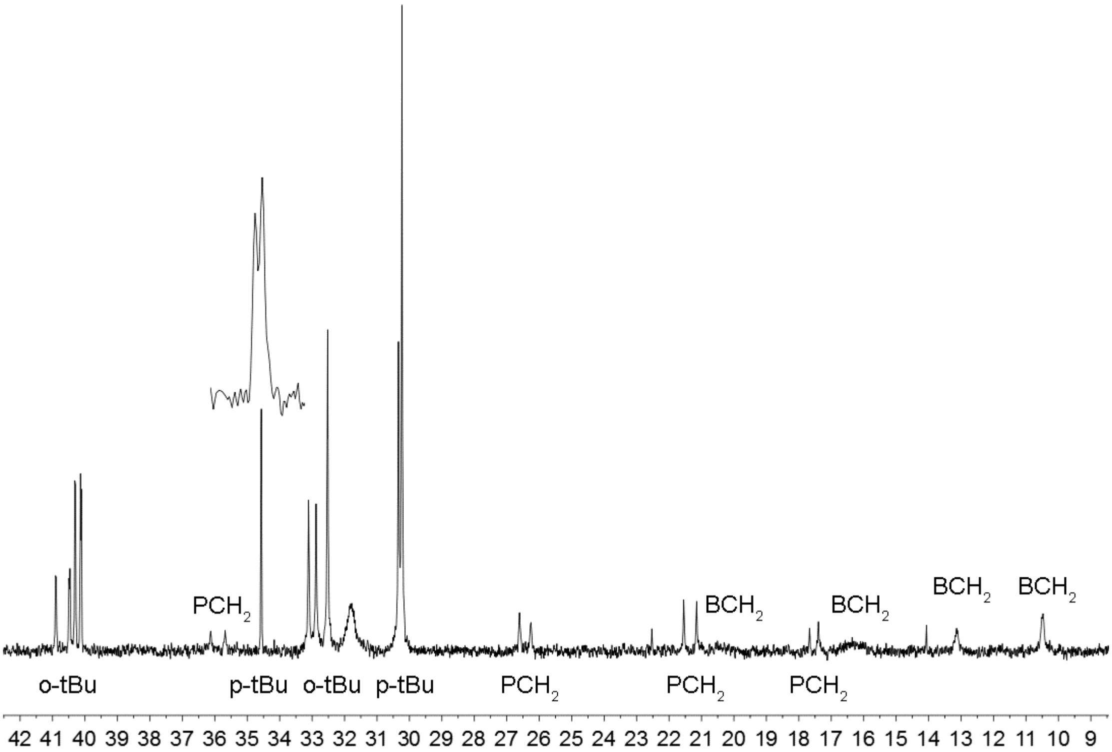
^{1}**H NMR** (500 MHz, dichloromethane-d$_2$) spectra of compound **21** at (1) 299K and (2) 243K.



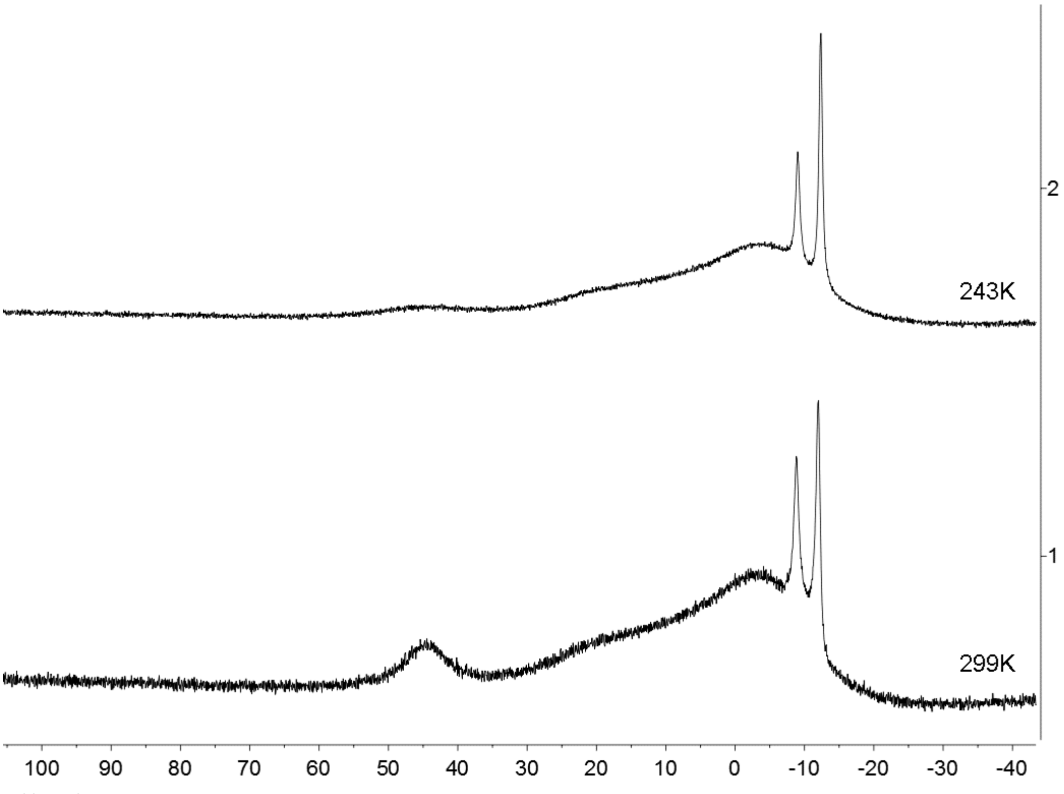
^{1}H NMR (500 MHz, dichloromethane-d$_2$) spectra of compound **21** at (1) 299K and (2) 243K.



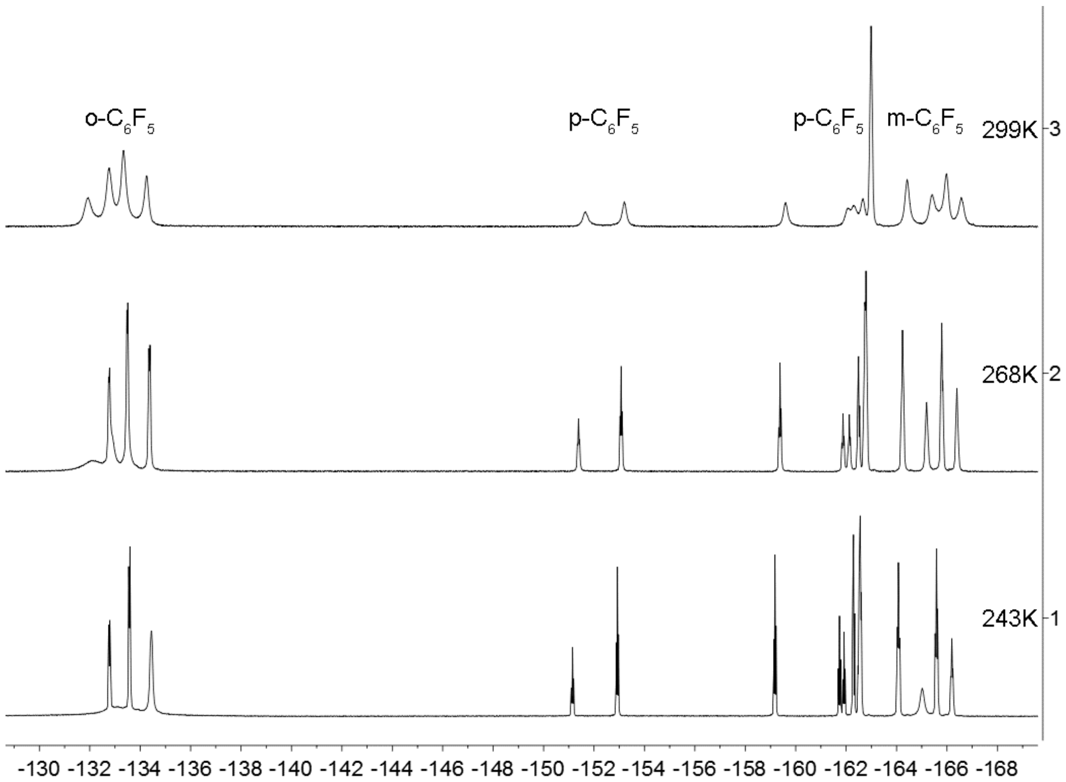
^{13}C{^{1}H} NMR (126 MHz, 243 K, dichloromethane-d$_2$) spectrum of compound **21**



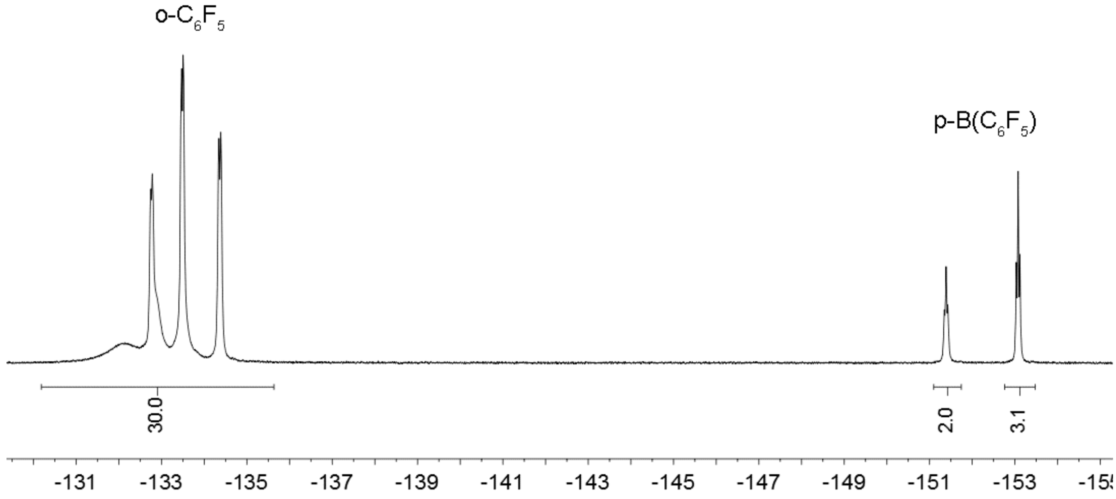
$^{13}C\{^1H\}$ NMR (126 MHz, 243 K, dichloromethane-d_2) spectrum of compound **21**



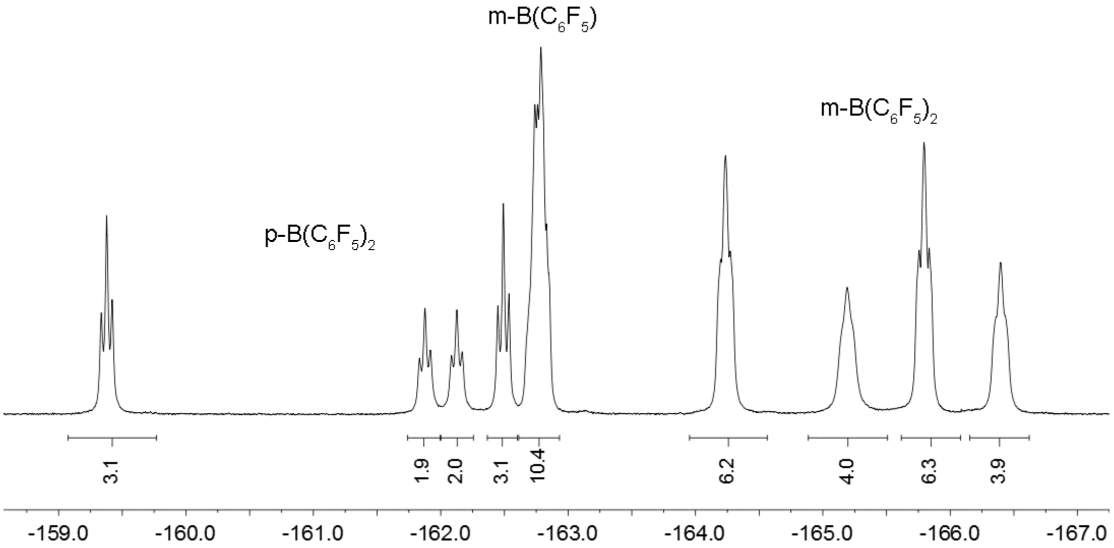
$^{11}B\{^1H\}$ NMR (160 MHz, dichloromethane-d_2) spectra of compound **21** at (1) 299K and (2) 243K.



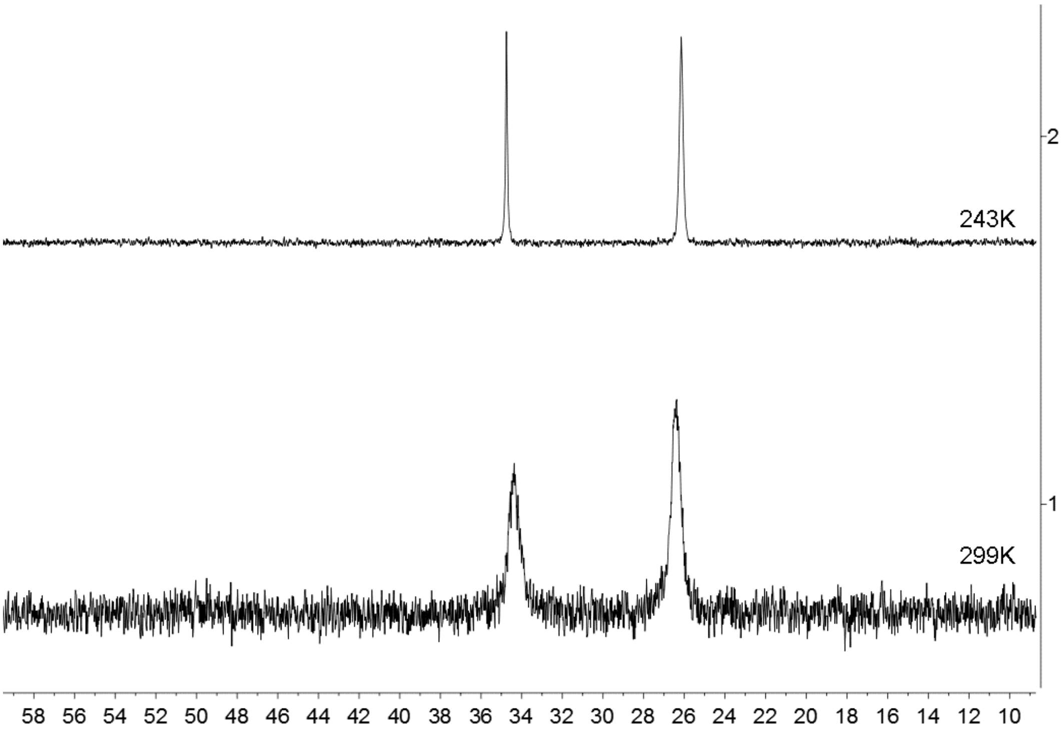
^{19}F NMR (470 MHz, dichloromethane-d$_2$) spectra of compound **21** at (1) 243K, (2) 268K, and (3) 299K



^{19}F NMR (470 MHz, 268K, dichloromethane-d$_2$) spectra of compound **21**



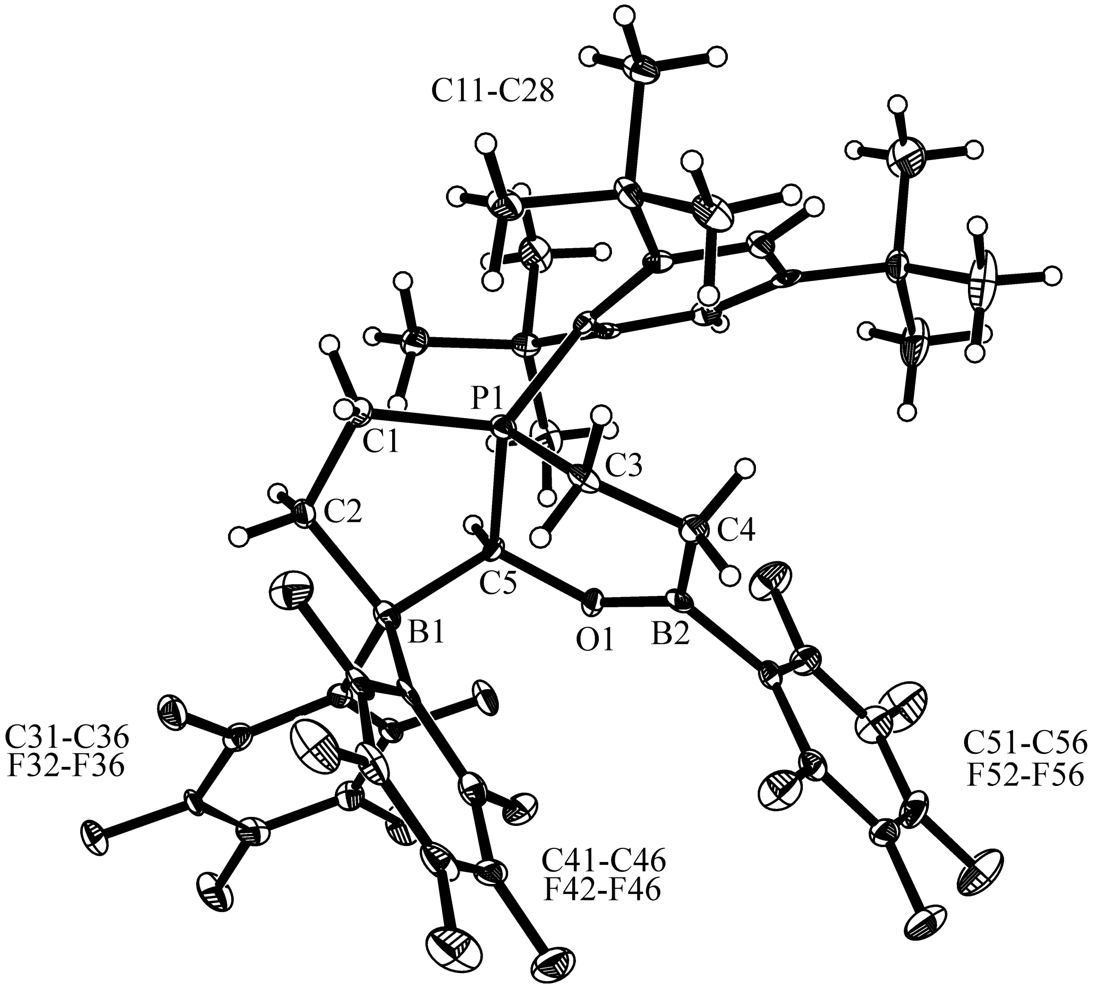
^{19}F NMR (470 MHz, 268K, dichloromethane-d_2) spectra of compound **21**



^{31}P{^{1}H} NMR (202 MHz, dichloromethane-d_2) spectra of compound **21** at (1) 299K and (2) 243K.

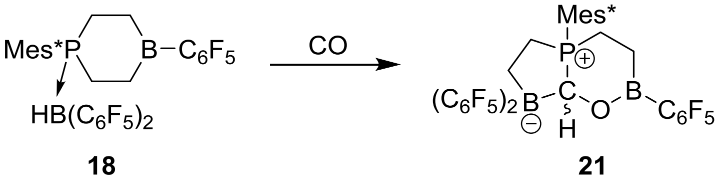
Crystals suitable for the X-ray crystal structure analysis were obtained from slow diffusion of pentane to a solution of the white solid in dichloromethane at -36 °C.

X-ray crystal structure analysis of compound 21: A colorless plate-like specimen of $C_{41}H_{38}B_2F_{15}OP \cdot CH_2Cl_2$, approximate dimensions 0.055 mm x 0.094 mm x 0.201 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 505 frames were collected. The total exposure time was 5.61 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 35075 reflections to a maximum θ angle of 25.03° (0.84 Å resolution), of which 7630 were independent (average redundancy 4.597, completeness = 99.8%, R_{int} = 11.25%, R_{sig} = 8.23%) and 5018 (65.77%) were greater than 2σ(F^2). The final cell constants of a = 11.2486(7) Å, b = 14.9232(9) Å, c = 15.8287(8) Å, α = 63.327(2)°, β = 69.289(2)°, γ = 69.458(2)°, volume = 2161.4(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 5369 reflections above 20 σ(I) with 5.495° < 2θ < 51.42°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.934. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9450 and 0.9840. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{41}H_{38}B_2F_{15}OP \cdot CH_2Cl_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 577 variables converged at R1 = 5.06%, for the observed data and wR2 = 10.09% for all data. The goodness-of-fit was 1.008. The largest peak in the final difference electron density synthesis was 0.354 $e^-/Å^3$ and the largest hole was -0.489 $e^-/Å^3$ with an RMS deviation of 0.066 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.489 g/cm^3 and F(000), 988 e^-.

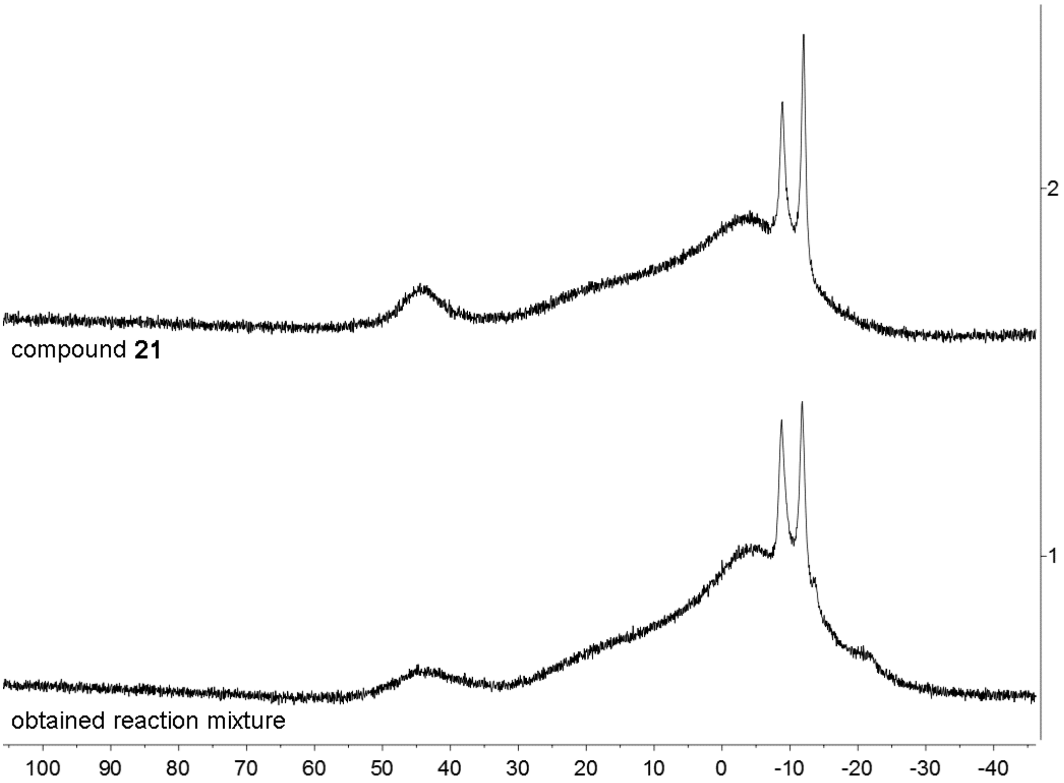


Molecular structure of compound **21**

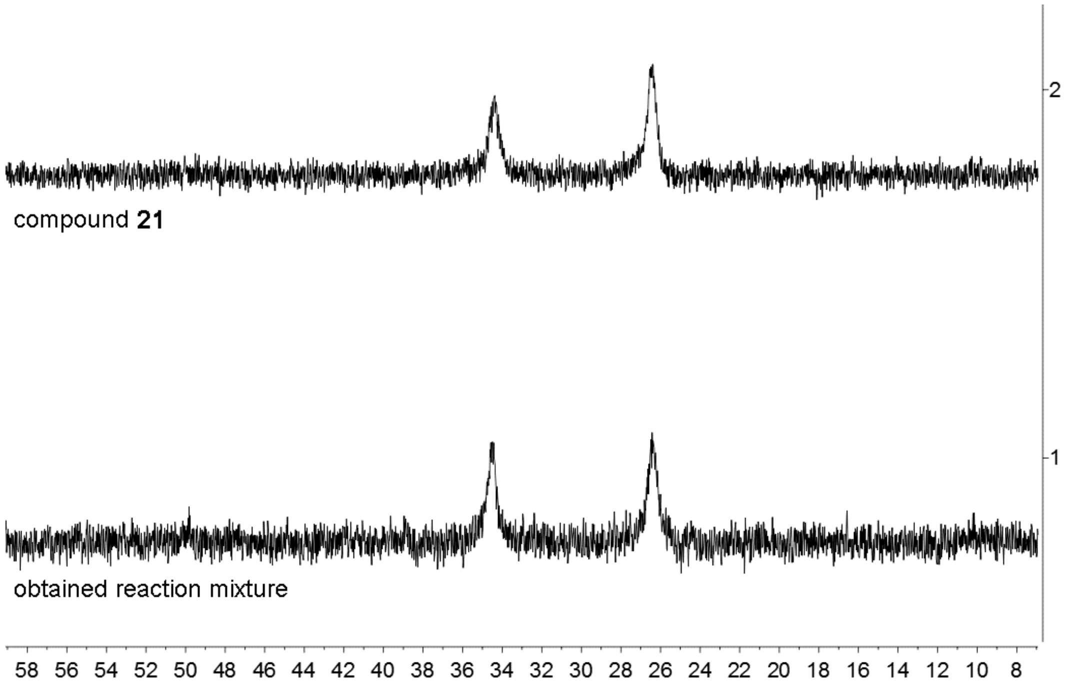
Generation of compound 21 from compound 18 (in situ)



In a J. Young NMR tube: a solution of compound **18** (21.4 mg, 0.025 mmol) in C_6D_6 (1 mL) was cooled to -78 °C (dry ice / isopropanol bath) and evacuated carefully. Then the dry ice bath was removed and the reaction mixture was exposed to CO gas (1.5 bar) and kept for 24 h at room temperature. Then the reaction mixture was characterized by NMR experiments.

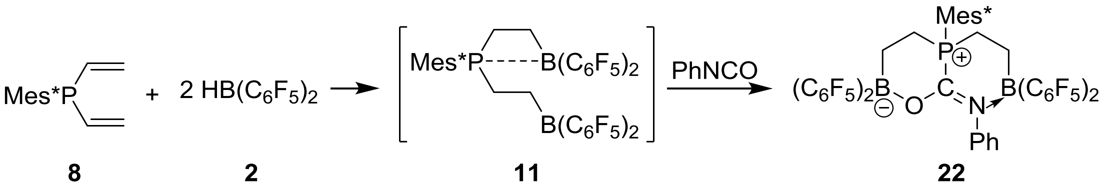


^{11}B{^{1}H} NMR (160 MHz, 299 K_6) spectra of (1) the obtained reaction mixture in benzene-d_6 and (2) the pure compound **21** in dichloromethane-d_2



^{31}P{^{1}H} NMR (202 MHz, 299 K) spectra of (1) the obtained reaction mixture in benzene-d$_6$ (major : minor ~ 52 : 48) and (2) the pure compound **21** in dichloromethane-d$_2$ (major : minor ~ 58 : 42)

Synthesis of compound 22



A solution of phosphane **8** (66.1 mg, 0.20 mmol, 1.0 eq.) and borane **2** (138.4 mg, 0.40 mmol, 2.0 eq.) in dichloromethane (4 mL) was stirred for 15 min at room temperature to give a yellow solution. Then the yellow solution was added to a solution of PhNCO (23.8 mg, 0.20 mmol, 1.0 eq.) in dichloromethane (1 mL) giving a colorless solution. After the reaction mixture was stirred for 1h at room temperature all volatiles were removed in vacuo to give a white solid which was washed with pentane (1 mL × 2) and dried in vacuo to finally give compound **22** as a white solid (182.5 mg, 0.160 mmol, 80 %).

Anal. Calcd. for $C_{53}H_{42}B_2F_{20}NOP$: C, 55.77; H, 3.71; N, 1.23. Found: C, 55.52; H, 3.67; N, 1.02.

Decomp.: 240 ^{o}C

[Mes*: 2,4,6-tri(tert-butyl)phenyl]

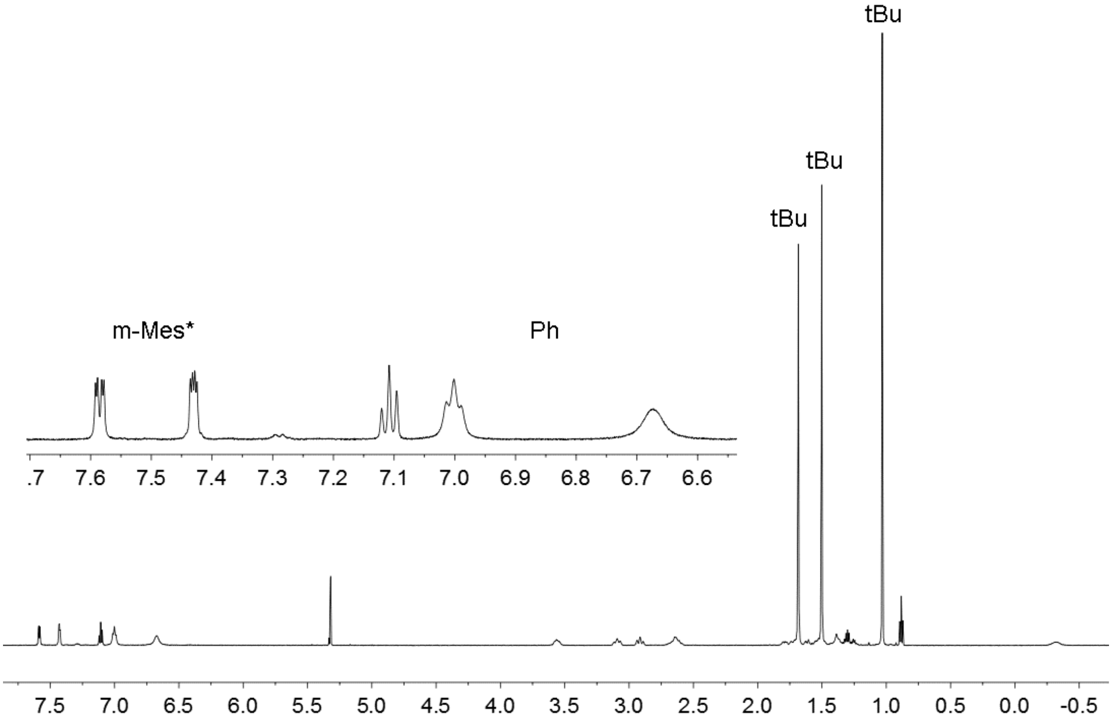
^{1}H NMR (600 MHz, 299K, dichloromethane-d$_2$) δ = 7.59 (dd, $^4J_{PH}$ = 6.2 Hz, $^4J_{HH}$ = 2.2 Hz, 1H, *m*-Mes*), 7.43 (dd, $^4J_{PH}$ = 4.5 Hz, $^4J_{HH}$ = 2.2 Hz, 1H, *m'*-Mes*), 7.11 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *p*-Ph), 7.00 (m, 2H, *m*-Ph), 6.67 (br, 2H, *m*-Ph), 3.56/2.62 (each m, each 1H, ^{a}PCH$_2$), 3.09/2.92 (each m, each 1H, ^{b}PCH$_2$), 2.66/1.58 (each br m, each 1H, ^{a}BCH$_2$), 1.76/-0.32 (each br m, each 1H, ^{b}BCH$_2$), 1.68 (s, 9H, *o'*-^{t}Bu), 1.50 (s, 9H, *o*-^{t}Bu), 1.03 (s, 9H, *p*-^{t}Bu).

^{13}C{^{1}H} NMR (151 MHz, 299K, dichloromethane-d$_2$) δ = 173.7 (d, $^1J_{PC}$ = 87.8 Hz, OCN), 162.6 (br, *o'*-Mes*), 161.8 (d, $^2J_{PC}$ = 10.3 Hz, *o*-Mes*), 156.6 (d, $^4J_{PC}$ = 4.4 Hz, *p*-Mes*), 142.5 (d, $^3J_{PC}$ = 5.9 Hz, *i*-Ph), 129.1 (d, $^3J_{PC}$ = 14.8 Hz, *m*-Mes*), 128.4 (*m*-Ph), 128.3 (*p*-Ph), 125.2 (d, $^3J_{PC}$ = 11.9 Hz, *m'*-Mes*), 124.1 (br, *o*-Ph), 105.2 (d, $^1J_{PC}$ = 77.8 Hz, *i*-Mes*), 41.8 (d, $^3J_{PC}$ = 3.0 Hz, *o*-^{t}Bu), 40.8 (d, $^3J_{PC}$ = 2.8 Hz, *o'*-^{t}Bu), 34.8 (d, $^5J_{PC}$ = 1.5 Hz, *p*-^{t}Bu), 34.6 (*o*-^{t}Bu), 34.1 (*o'*-^{t}Bu), 30.6 (br d, $^1J_{PC}$ = 45.4 Hz, ^{b}PCH$_2$), 30.2 (*p*-^{t}Bu), 27.4 (br d, $^1J_{PC}$ = 32.6 Hz, ^{a}PCH$_2$), 13.9 (br, ^{a}BCH$_2$), 13.5 (br, ^{b}BCH$_2$), [C_6F_5 not listed].

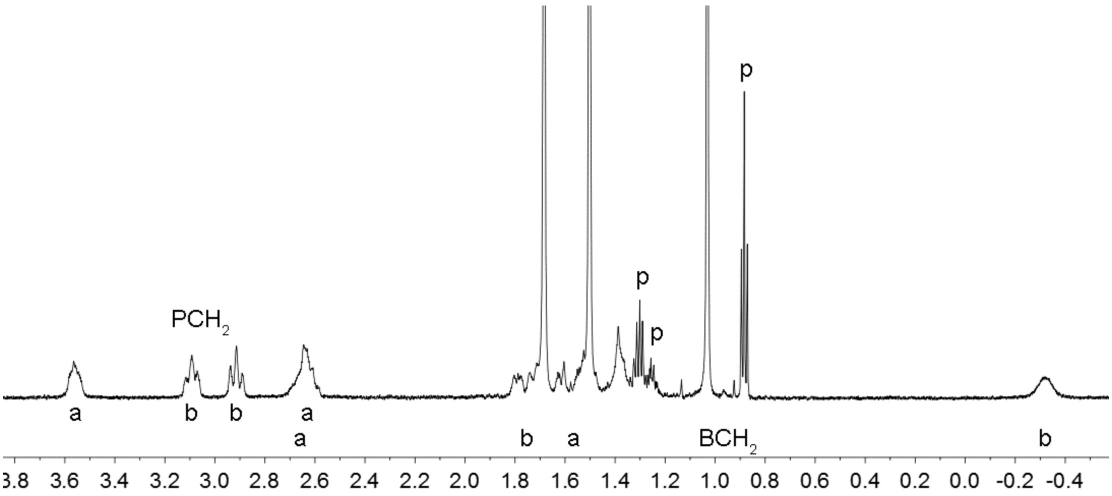
^{11}B{^{1}H} NMR (192 MHz, 299K, dichloromethane-d$_2$) δ = 7.5 ($\nu_{1/2}$ ~ 550 Hz), -3.3 ($\nu_{1/2}$ ~ 350 Hz).

^{19}F NMR (470 MHz, 183K, dichloromethane-d$_2$) δ = -126.4, -129.5, -130.3, -131.3, -131.8, -133.1, -134.4, -136.2 (each br, each 1F, *o*-C_6F_5), -157.0, -158.2, -158.9, -161.6 (each br, each 1F, *p*-C_6F_5), -162.4, -163.3, -164.0, -164.2, -164.4, -165.2, -166.0, -166.2 (each br, each 1F, *m*-C_6F_5).

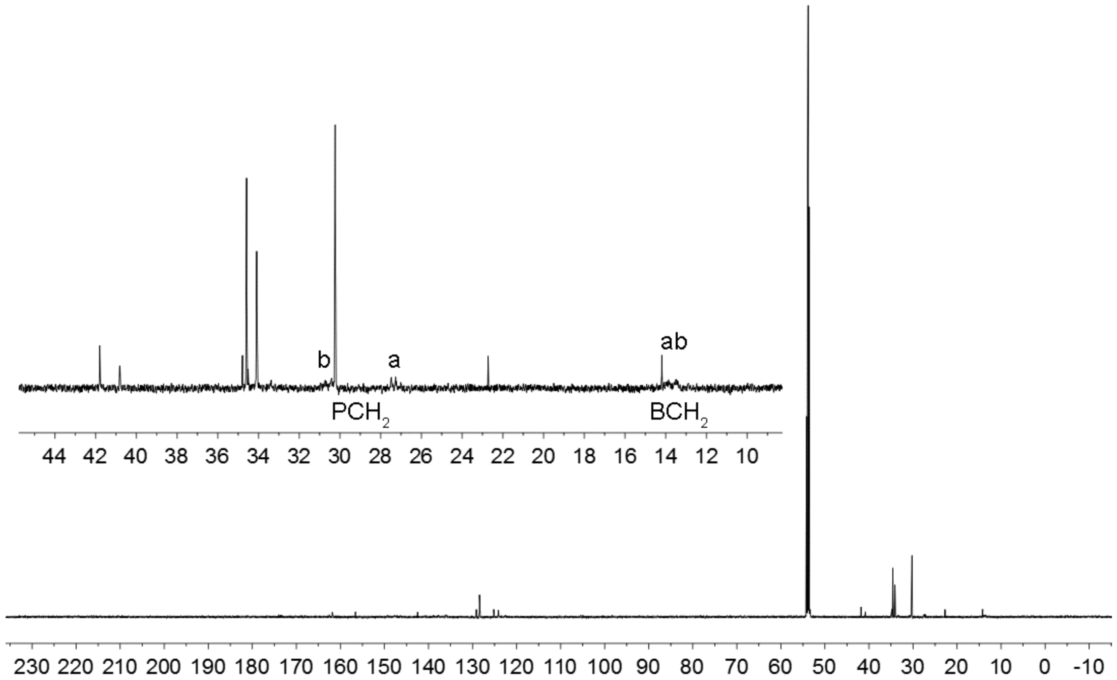
^{31}P{^{1}H} NMR (243 MHz, 299K, dichloromethane-d$_2$) δ = 12.5 ($\nu_{1/2}$ ~ 30 Hz).



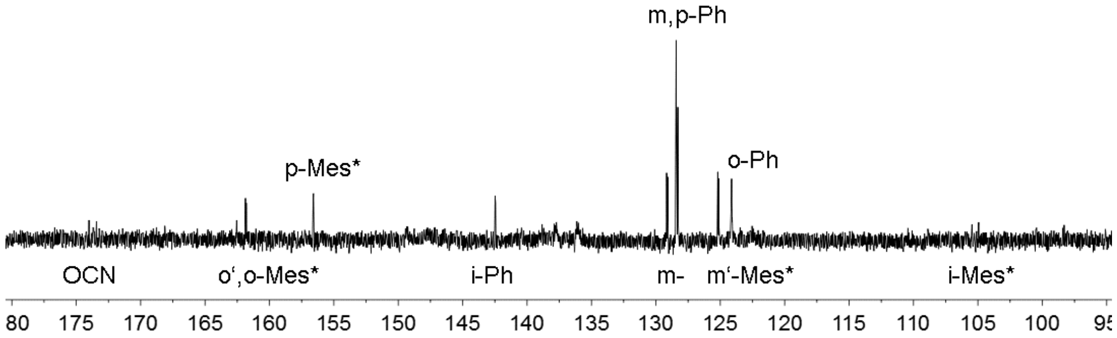
^{1}H NMR (600 MHz, 299K, dichloromethane-d$_2$) spectrum of compound **22**



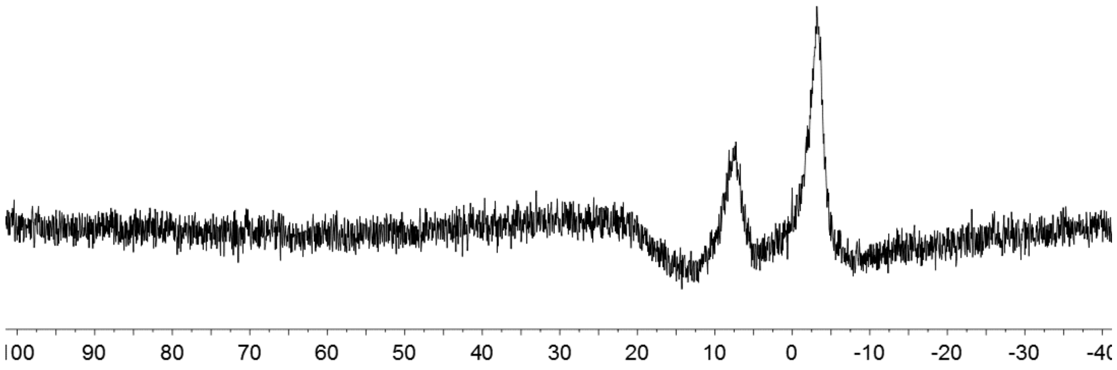
^{1}H NMR (600 MHz, 299K, dichloromethane-d$_2$) spectrum of compound **22**



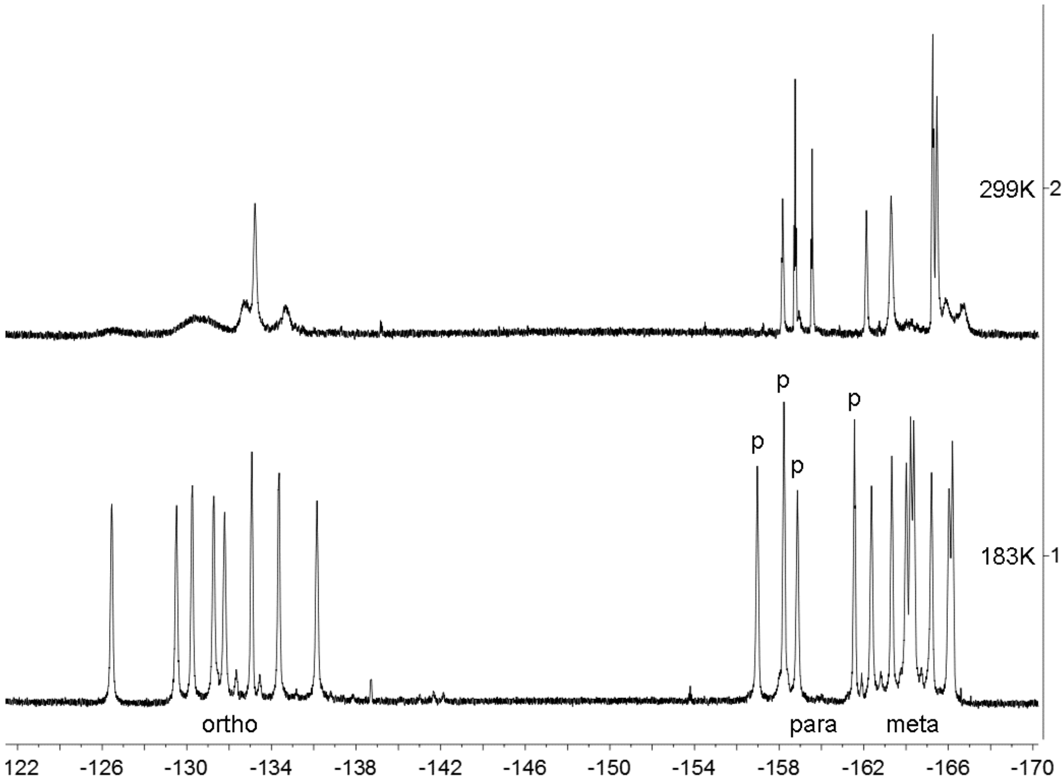
^{13}C{^{1}H} NMR (151 MHz, 299K, dichloromethane-d$_2$) spectrum of compound **22**



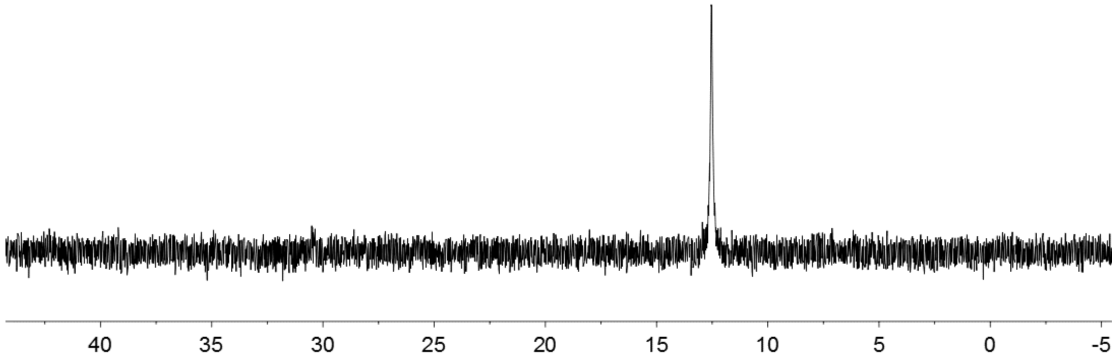
^{13}C{^{1}H} NMR (151 MHz, 299K, dichloromethane-d$_2$) spectrum of compound **22**



^{11}B{^{1}H} NMR (192 MHz, 299K, dichloromethane-d$_2$) spectrum of compound **22**



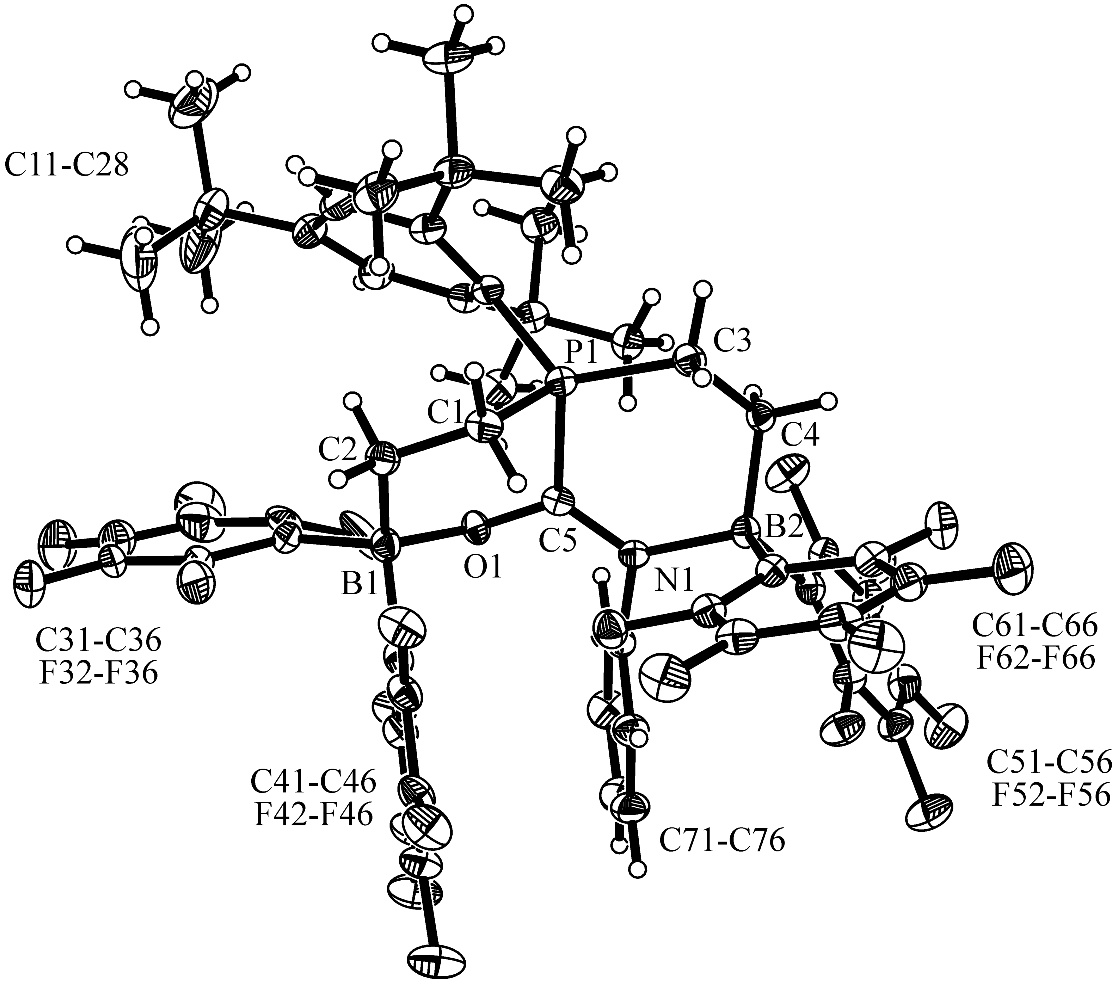
^{19}F NMR (470 MHz, dichloromethane-d$_2$) spectra of compound **22** at (1) 183K and (2) 299K.



^{31}P{^{1}H} NMR (243 MHz, 299K, dichloromethane-d$_2$) spectrum of compound **22**

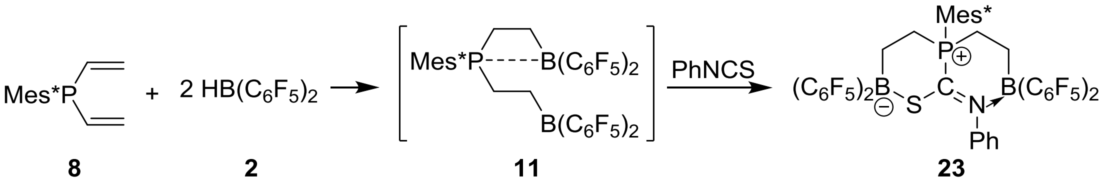
Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of the white solid in dichloromethane at -36 °C.

X-ray crystal structure analysis of compound 22: formula $C_{53}H_{42}B_2F_{20}NOP \cdot 2 \times CH_2Cl_2$, M = 1311.32, colourless crystal, 0.18 x 0.12 x 0.04 mm, a = 11.9911(2), b = 12.2241(2), c = 20.5637(4) Å, α = 85.022(1), β = 80.922(1), γ = 72.511(1)°, V = 2836.4(1) Å^3, ρ_{calc} = 1.535 gcm^{-3}, μ = 0.344 mm^{-1}, empirical absorption correction (0.940 ≤ T ≤ 0.986), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 25959 reflections collected (±h, ±k, ±l), 9787 independent (R_{int} = 0.036) and 7809 observed reflections [I>2σ(I)], 866 refined parameters, R = 0.062, wR^2 = 0.135, max. (min.) residual electron density 0.62 (-0.53) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.



Molecular structure of compound **22**

Synthesis of compound 23



A solution of phosphane **8** (66.1 mg, 0.20 mmol, 1.0 eq.) and borane **2** (138.4 mg, 0.40 mmol, 2.0 eq.) in dichloromethane (4 mL) was stirred for 15 min at room temperature to give a yellow solution. Then the yellow solution was added to a solution of PhNCS (27.0 mg, 0.20 mmol, 1.0 eq.) in dichloromethane (1 mL) giving a bright yellow solution. After the reaction mixture was stirred for 4 days at room temperature, all volatiles were removed in vacuo to give a yellow solid which was washed with pentane (1 mL × 2) and dried in vacuo to finally give compound **23** as a yellow solid (141.2 mg, 0.123 mmol, 61 %).
Decomp.: 196 ^{o}C

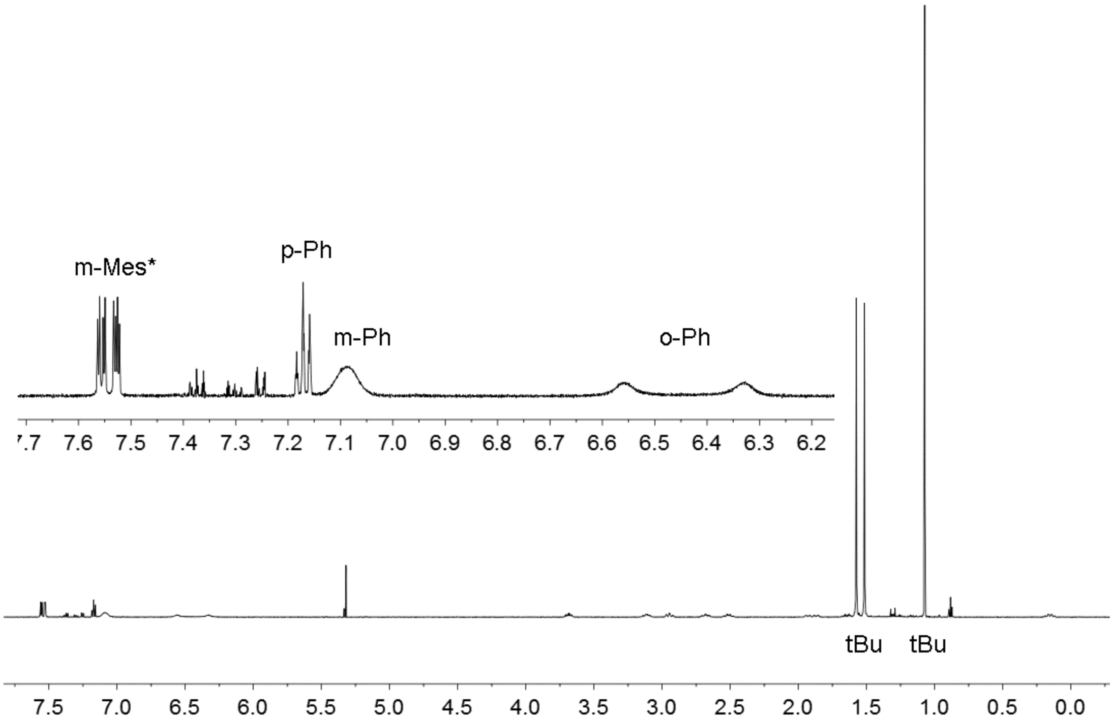
[Mes*: 2,4,6-tri(tert-butyl)phenyl]
^{1}H NMR (600 MHz, 299K, dichloromethane-d$_2$) δ = 7.56 (dd, $^{4}J_{PH}$ = 6.4 Hz, $^{4}J_{HH}$ = 2.2 Hz, 1H, *m*-Mes*), 7.53 (dd, $^{4}J_{PH}$ = 4.4 Hz, $^{4}J_{HH}$ = 2.2 Hz, 1H, *m'*-Mes*), 7.17 (t, $^{3}J_{HH}$ = 7.4 Hz, 1H, *p*-Ph), 7.09 (br, 2H, *m*-Ph)^{t}, 6.56, 6.33 (each br, each 1H, *o*-Ph)^{t}, 3.68/2.51 (each m, each 1H, ^{a}PCH$_2$), 3.11/2.95 (each m, each 1H, ^{b}PCH$_2$), 2.68 (m)/1.60 (dm, $^{3}J_{PH}$ = 44.4 Hz)(each 1H, ^{a}BCH$_2$), 1.90 (ddm, $^{3}J_{PH}$ = 36.4 Hz, J_{HH} = 15.9 Hz)/0.15 (m)(each 1H, ^{b}BCH$_2$), 1.57 (s, 9H, *o'*-^{t}Bu), 1.51 (s, 9H, *o*-^{t}Bu), 1.07 (s, 9H, *p*-^{t}Bu), [^{t} tentative assignment].

^{13}C{^{1}H} NMR (151 MHz, 299K, dichloromethane-d$_2$) δ = 194.2 (br d, $^{1}J_{PC}$ = 61.4 Hz, SCN), 163.2 (d, $^{2}J_{PC}$ = 2.2 Hz, *o'*-Mes*), 161.2 (d, $^{2}J_{PC}$ = 10.9 Hz, *o*-Mes*), 156.2 (d, $^{4}J_{PC}$ = 4.3 Hz, *p*-Mes*), 146.9 (d, $^{3}J_{PC}$ = 8.7 Hz, *i*-Ph)^{t}, 128.7 (d, $^{3}J_{PC}$ = 15.1 Hz, *m*-Mes*), 129.3, 128.61 (each br, *m*-Ph)^{t}, 128.55 (*p*-Ph), 126.4 (d, $^{3}J_{PC}$ = 11.8 Hz, *m'*-Mes*), 124.2, 122.6 (each br, *o*-Ph)^{t}, 107.8 (d, $^{1}J_{PC}$ = 84.4 Hz, *i*-Mes*), 41.9 (d, $^{3}J_{PC}$ = 2.7 Hz, *o*-^{t}Bu), 41.7 (d, $^{3}J_{PC}$ = 2.3 Hz, *o'*-^{t}Bu), 35.0 (*o*-^{t}Bu), 34.7 (d, $^{5}J_{PC}$ = 1.3 Hz, *p*-^{t}Bu), 34.0 (*o'*-Me$^{t\text{-Bu}}$), 33.8 (br d, $^{1}J_{PC}$ ~ 48 Hz ^{b}PCH$_2$), 30.3 (*p*-^{t}Bu), 26.5 (d, $^{1}J_{PC}$ = 29.3 Hz, ^{a}PCH$_2$), 16.8 (br, ^{b}BCH$_2$), 13.4 (br, ^{a}BCH$_2$), [^{t} tentative assignment; C_6F_5 not listed].

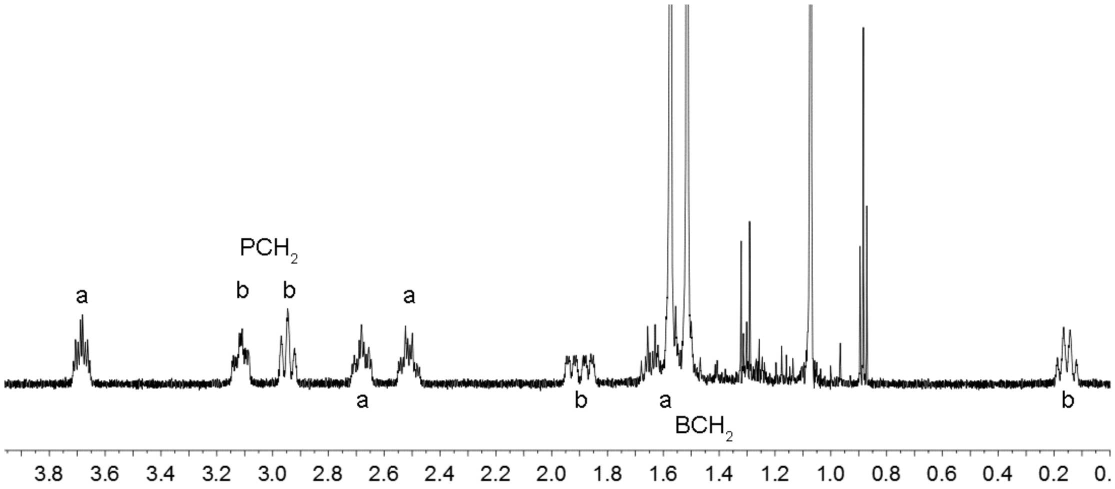
^{11}B{^{1}H} NMR (192 MHz, 299K, dichloromethane-d$_2$) δ = 2.4, -3.2.

^{19}F NMR (564 MHz, 299K, dichloromethane-d$_2$) δ = -128.0 (br), -130.1 (m), -132.6 (m), -132,9 (br)(each 2F, *o*-C_6F_5), -157.6 (br t, $^{3}J_{FF}$ = 18.1 Hz), -158.6 (br t, $^{3}J_{FF}$ = 19.2 Hz), -159.4 (t, $^{3}J_{FF}$ = 19.8 Hz), -160.7 (t, $^{3}J_{FF}$ = 20.1 Hz)(each 1F, *p*-C_6F_5), -162.9, -164.7, -165.0, -165.4 (each br m, each 2F, *m*-C_6F_5).

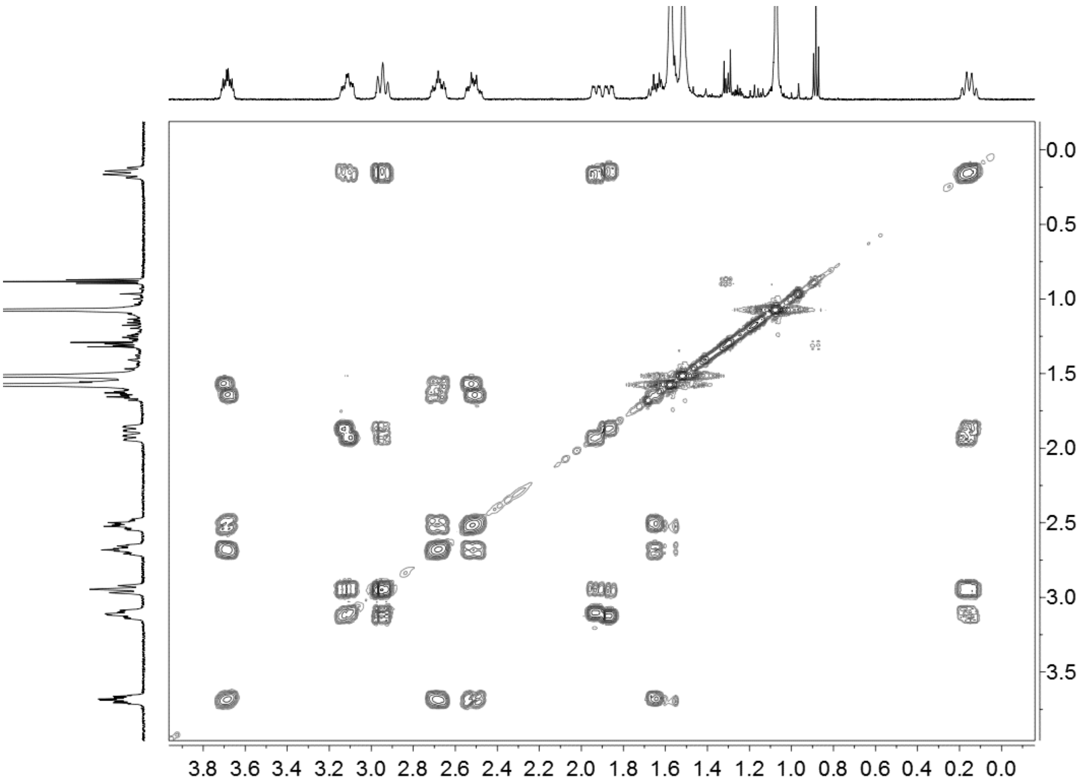
^{31}P{^{1}H} NMR (243 MHz, 299K, dichloromethane-d$_2$) δ = 16.5 ($\nu_{1/2}$ ~ 10 Hz).



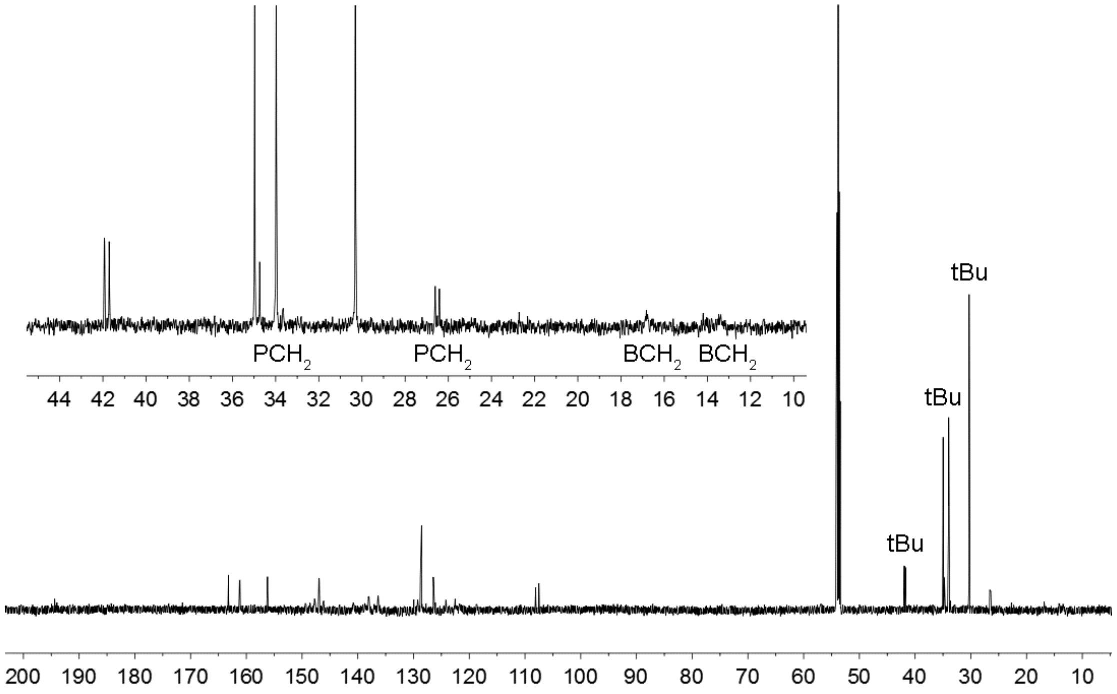
^{1}**H NMR** (600 MHz, 299K, dichloromethane-d$_2$) spectrum of compound **23**



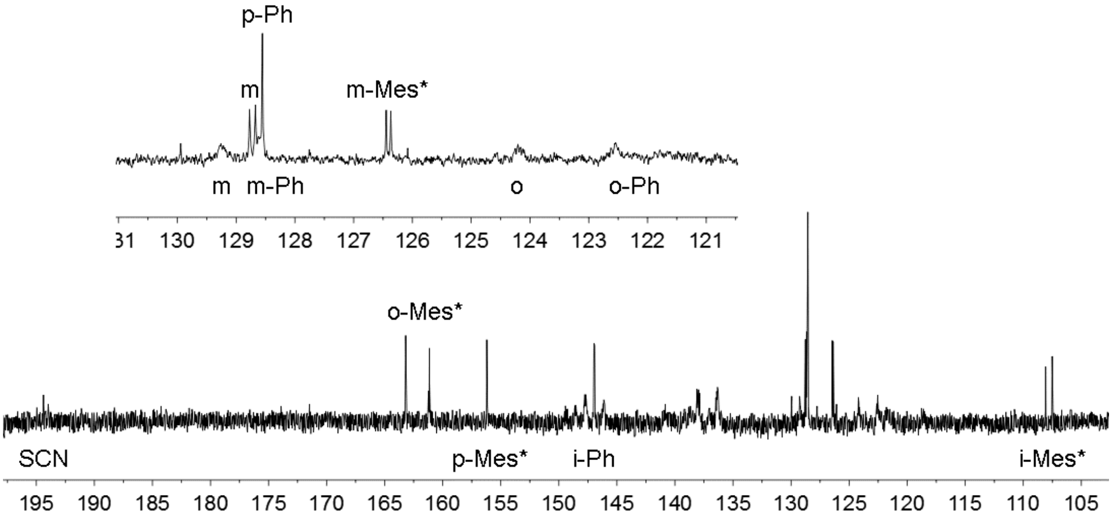
^{1}**H NMR** (600 MHz, 299K, dichloromethane-d$_2$) spectrum of compound **23**



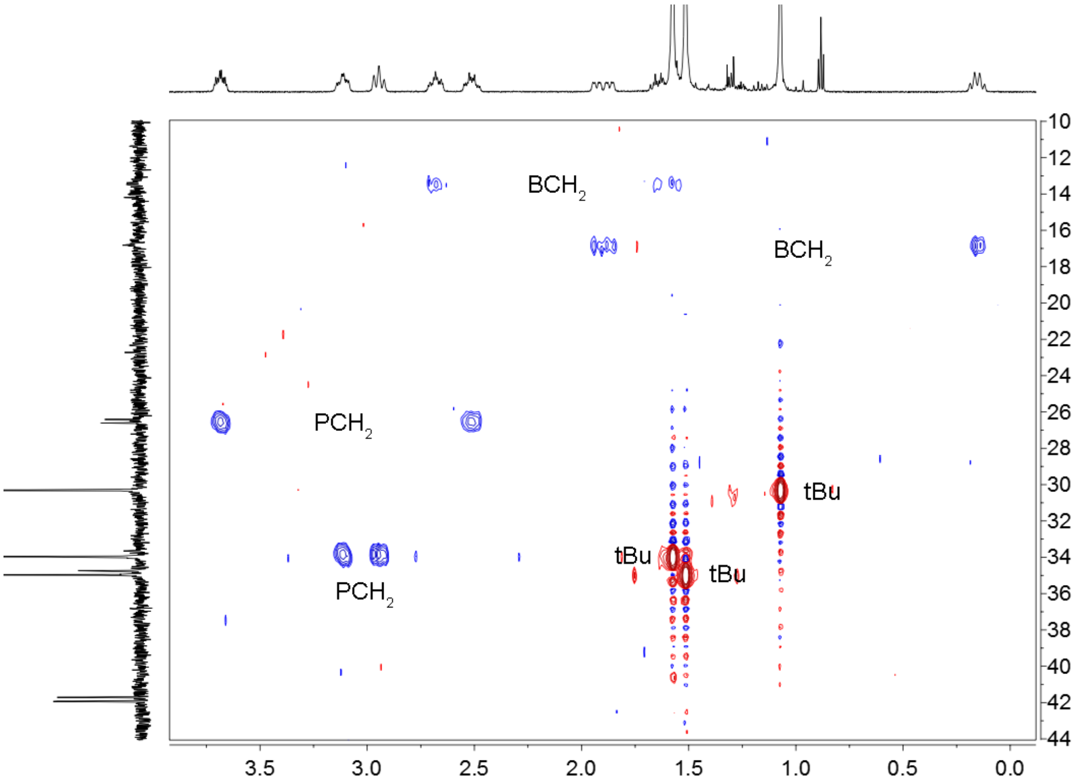
^{1}H,^{1}H cosy (600 MHz, 299K, dichloromethane-d$_2$) spectrum of compound **23**



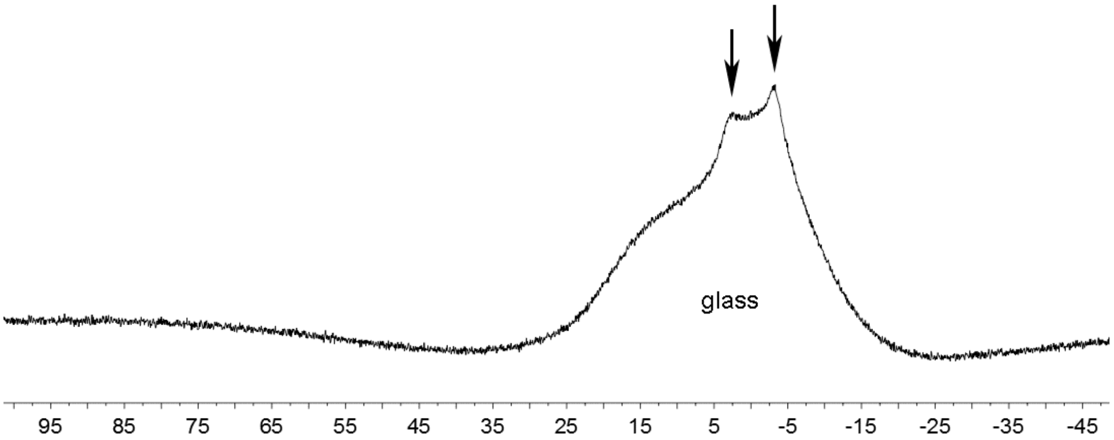
^{13}C{^{1}H} NMR (151 MHz, 299K, dichloromethane-d$_2$) spectrum of compound **23**



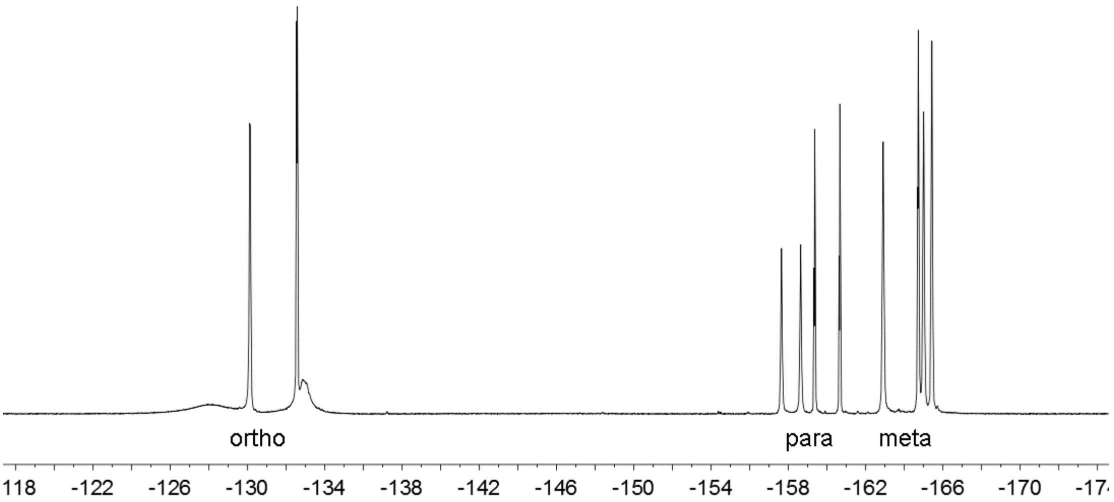
^{13}C{^{1}H} NMR (151 MHz, 299K, dichloromethane-d$_2$) spectrum of compound **23**



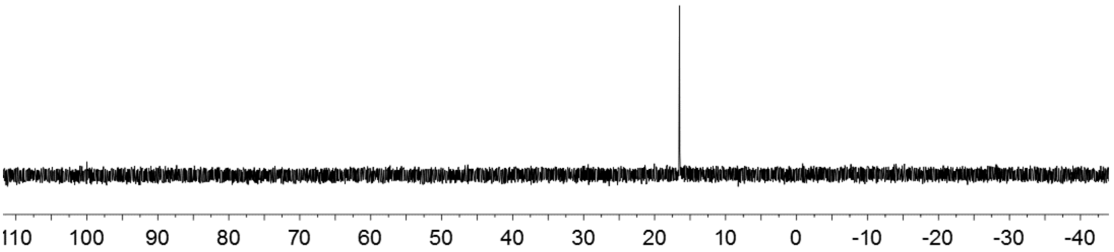
^{1}H,^{13}C ghsqc (600/151 MHz, 299K, dichloromethane-d$_2$) spectrum of compound **23**



$^{11}B\{^{1}H\}$ **NMR** (192 MHz, 299K, dichloromethane-d_2) spectrum of compound **23**



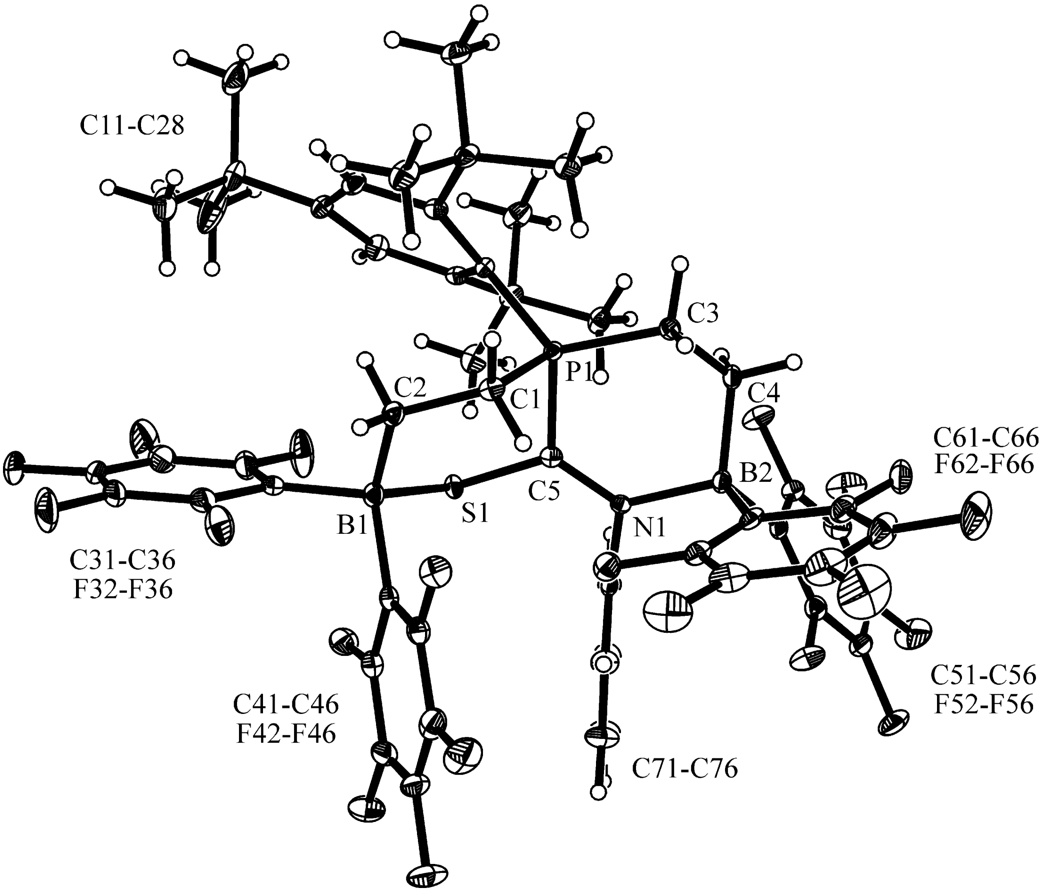
^{19}F **NMR** (564 MHz, 299K, dichloromethane-d_2) spectrum of compound **23**



$^{31}P\{^{1}H\}$ **NMR** (243 MHz, 299K, dichloromethane-d_2) spectrum of compound **23**

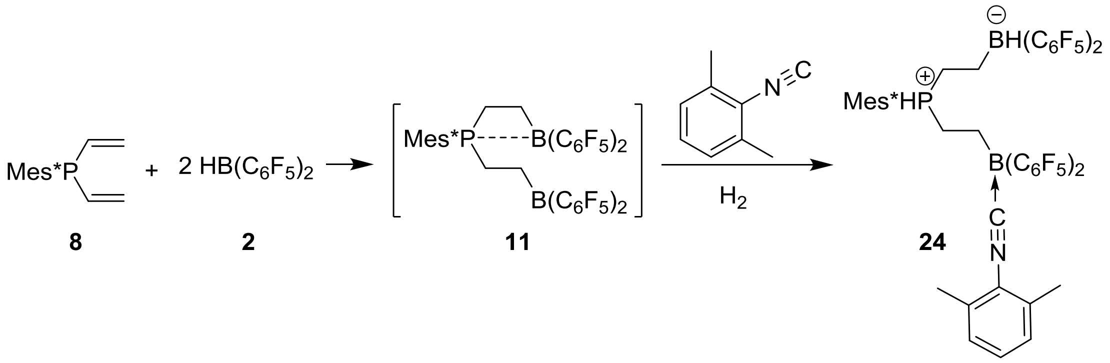
Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of the yellow solid in dichloromethane at -36 ^{o}C.
Anal. Calcd. for $C_{53}H_{42}B_2F_{20}NPS \cdot (CH_2Cl_2)_2$: C, 49.77; H, 3.49; N, 1.06. Found: C, 49.83; H, 3.28; N, 0.89. [from the obtained crystala]

X-ray crystal structure analysis of compound 23: A yellow prism-like specimen of $C_{53}H_{42}B_2F_{20}NPS \cdot 2 \times CH_2Cl_2$, approximate dimensions 0.037 mm x 0.091 mm x 0.155 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1610 frames were collected. The total exposure time was 15.65 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 146830 reflections to a maximum θ angle of 25.42° (0.83 Å resolution), of which 10251 were independent (average redundancy 14.323, completeness = 99.8%, R_{int} = 5.00%, R_{sig} = 1.83%) and 8864 (86.47%) were greater than $2\sigma(F^2)$. The final cell constants of a = 15.6705(6) Å, b = 20.6824(7) Å, c = 18.4644(7) Å, β = 111.5510(10)°, volume = 5566.0(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 9009 reflections above 20 σ(I) with 4.71° < 2θ < 50.84°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.923. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9430 and 0.9860. The final anisotropic full-matrix least-squares refinement on F^2 with 766 variables converged at R1 = 3.59%, for the observed data and wR2 = 9.36% for all data. The goodness-of-fit was 1.036. The largest peak in the final difference electron density synthesis was 0.410 $e^-/Å^3$ and the largest hole was -0.860 $e^-/Å^3$ with an RMS deviation of 0.060 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.584 g/cm^3 and F(000), 2688 e^-.



Molecular structure of compound **23**

Synthesis of compound 24



A solution of phosphane **8** (66.1 mg, 0.20 mmol, 1.0 eq.) and borane **2** (138.4 mg, 0.40 mmol, 2.0 eq.) in dichloromethane (4 mL) was stirred for 15 min at room temperature to give a yellow solution. After the yellow solution was mixed with a solution of (2,6-dimethylphenyl)isocyanide (26.4 mg, 0.2 mmol, 1.0 eq.) in dichloromethane (1 mL), it was cooled to -78 °C (dry ice / isopropanol bath) and evacuated carefully. Then the dry ice bath was removed and the reaction mixture was exposed to H_2 gas (1.5 bar) and stirred at room temperature for 12 h to give a colorless solution. Then all volatiles were removed in vacuo to give a white foam, which was washed with pentane (1 mL × 3) and dried in vacuo to finally give compound **24** as a white solid (136.3 mg, 0.118 mmol, 59 %).

Anal. Calcd. for $C_{55}H_{48}B_2F_{20}NP$: C, 57.17; H, 4.19; N, 1.21; Found. C, 57.62; H, 4.39; N, 0.94.

Melting point: 126 °C

IR(KBr): $\tilde{\upsilon}$ [cm^{-1}] = 2271 (m, CN).

[Mes*: 2,4,6-tri(tert-butyl)phenyl; Ar: 2,6.dimethylphenyl]

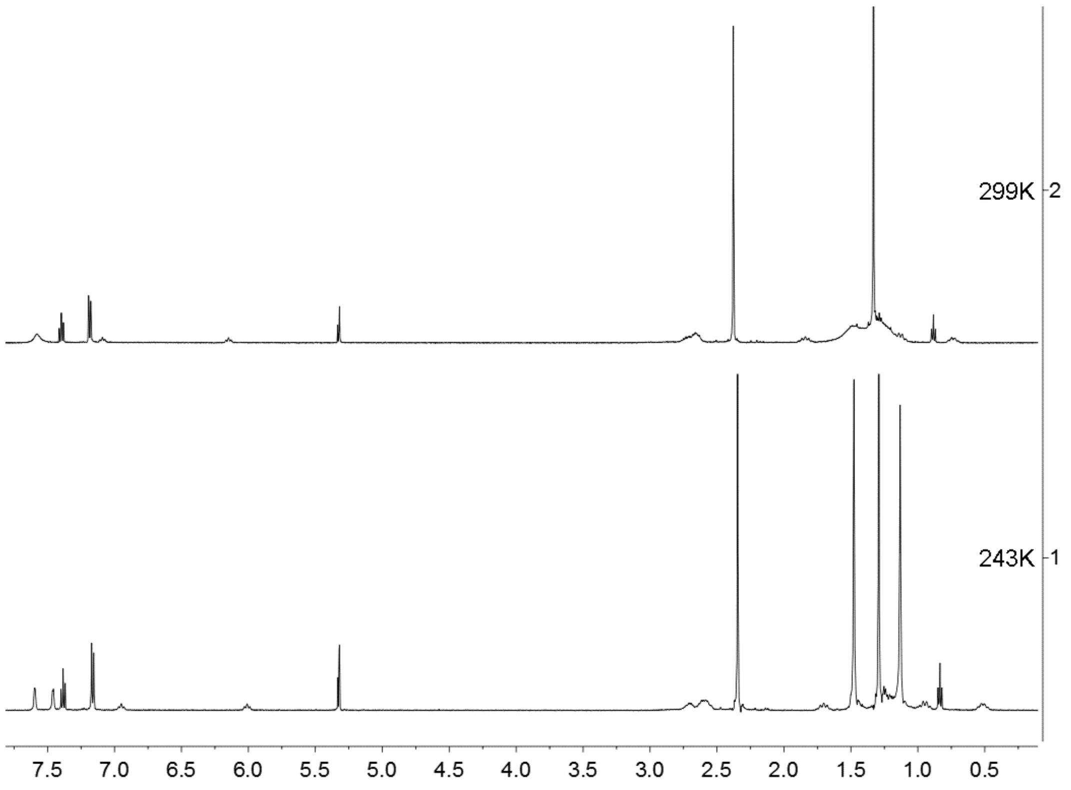
^{1}H NMR (500 MHz, 243 K, dichloromethane-d_2) δ = 7.59 (m, 1H, *m*-Mes*), 7.46 (m, 1H, *m'*-Mes*), 7.38 (t, $^3J_{HH}$ = 7.7 Hz, 1H, *p*-Ar), 7.16 (d, $^3J_{HH}$ = 7.7 Hz, 2H, *m*-Ar), 6.48 (dt, $^1J_{PH}$ = 469.5 Hz, $^3J_{HH}$ = 10.2 Hz, 1H, PH), 2.71/2.62 (each m, each 1H, ^{b}PCH_2), 2.67 (br, 1H, BH), 2.58/1.70 (each m, each 1H, ^{a}PCH_2), 2.35 (s, 6H, *o*-Me^{Ar}), 1.48 (s, 9H, *o*-^{t}Bu), 1.29 (s, 9H, *p*-^{t}Bu), 1.13 (s, 9H, *o'*-^{t}Bu), 1.25/1.18 (each m, each 1H, ^{b}BCH_2), 0.95/0.51 (each m, each 1H, ^{a}BCH_2).

^{13}C{^{1}H} NMR (126 MHz, 243 K, dichloromethane-d_2) δ = 160.9 (d, $^2J_{PC}$ = 5.4 Hz, *o*-Mes*), 157.0 (d, $^2J_{PC}$ = 7.2 Hz, *o'*-Mes*), 156.2 (d, $^4J_{PC}$ = 3.2 Hz, *p*-Mes*), 136.9 (*o*-Ar), 132.4 (*p*-Ar), 128.6 (*m*-Ar), 126.2 (d, $^3J_{PC}$ = 11.8 Hz, *m'*-Mes*), 124.8 (d, $^3J_{PC}$ = 11.4 Hz, *m*-Mes*), 122.3 (br, *i*-Ar), n.o. (CN), 108.9 (d, $^1J_{PC}$ = 68.6 Hz, *i*-Mes*), 38.51 (d, $^3J_{PC}$ = 4.4 Hz, *o*-^{t}Bu), 38.47 (d, $^3J_{PC}$ = 3.0 Hz, *o'*-^{t}Bu), 35.0 (*p*-^{t}Bu), 33.1 (br, *o*-^{t}Bu), 32.9 (br, *o'*-^{t}Bu), 30.2 (*p*-^{t}Bu), 28.0 (br d, $^1J_{PC}$ = 28.5 Hz, ^{b}PCH_2), 22.1 (br d, $^1J_{PC}$ = 47.1 Hz, ^{a}PCH_2), 18.2 (br, ^{b}BCH_2), 18.1 (*o*-Me^{Ar}), 15.7 (br, ^{a}BCH_2), [C_6F^5 not listed]

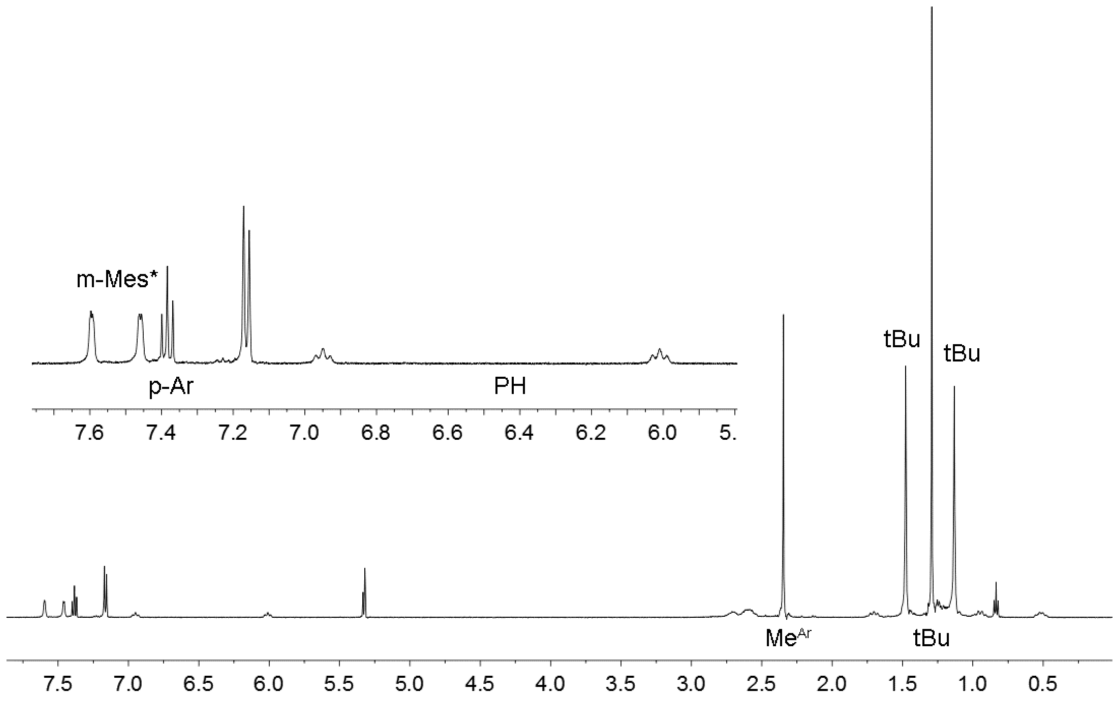
^{11}B NMR (160 MHz, 299K, dichloromethane-d_2) δ = -18.1 ($\nu_{1/2}$ ~ 250 Hz), -20.9 (d, $^1J_{BH}$ ~ 87 Hz, BH).
^{11}B{^{1}H} NMR (160 MHz, 299K, dichloromethane-d_2) δ = -18.1 ($\nu_{1/2}$ ~ 250 Hz), -20.9 ($\nu_{1/2}$ ~ 70 Hz).

^{19}F NMR (470 MHz, 299K, dichloromethane-d_2) δ = -132.1 (m, 2F, *o*), -157.3 (t, $^3J_{FF}$ = 20.0 Hz, 1F, *p*), -163.0 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 5.7], -132.4 (m, 2F, *o*), -156.7 (t, $^3J_{FF}$ = 20.2 Hz, 1F, *p*), -163.5 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 6.8], -133.7, -134.1 (each m, each 2F, *o*), -163.9, -164.1 (each t, $^3J_{FF}$ = 20.1 Hz, each 1F, *p*), 166.7 (m, 4F, *m*)(2 × C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 2.6, 2.8].

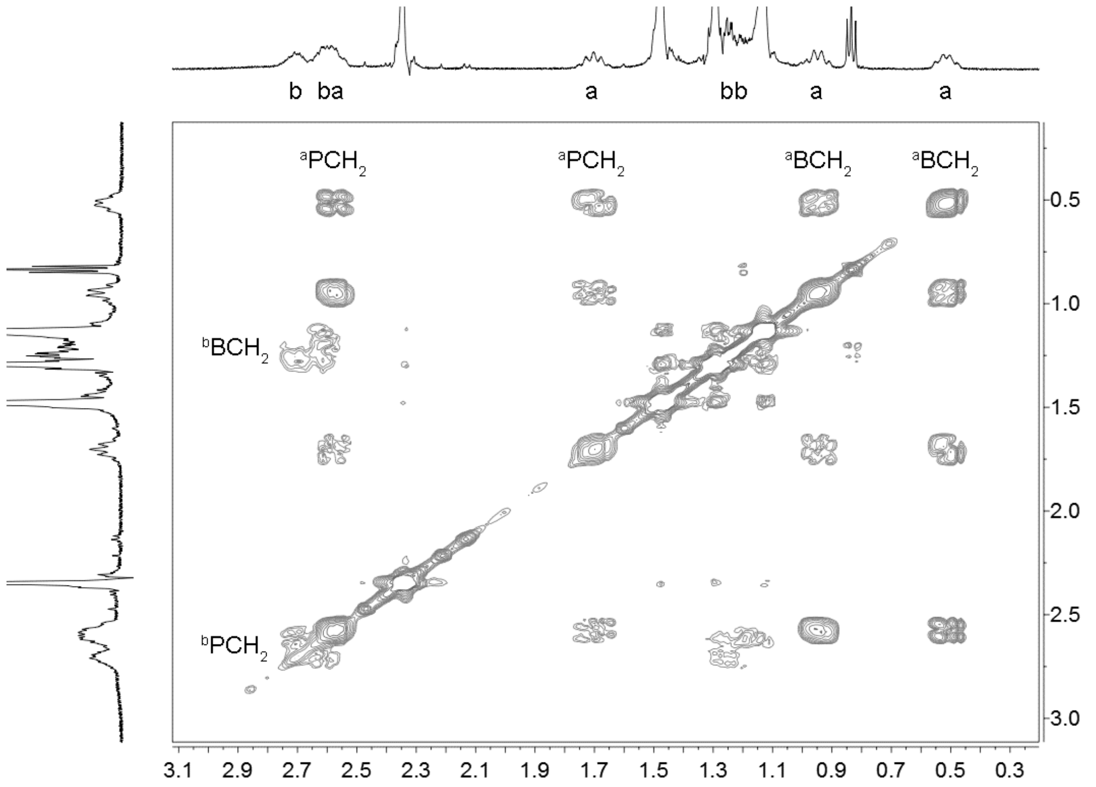
^{31}P NMR (202 MHz, 299K, dichloromethane-d_2) δ = 25.5 (br d, $^1J_{PH}$ ~ 475 Hz).
^{31}P{^{1}H} NMR (202 MHz, 299K, dichloromethane-d_2) δ = 25.5 ($\nu_{1/2}$ ~ 45 Hz).



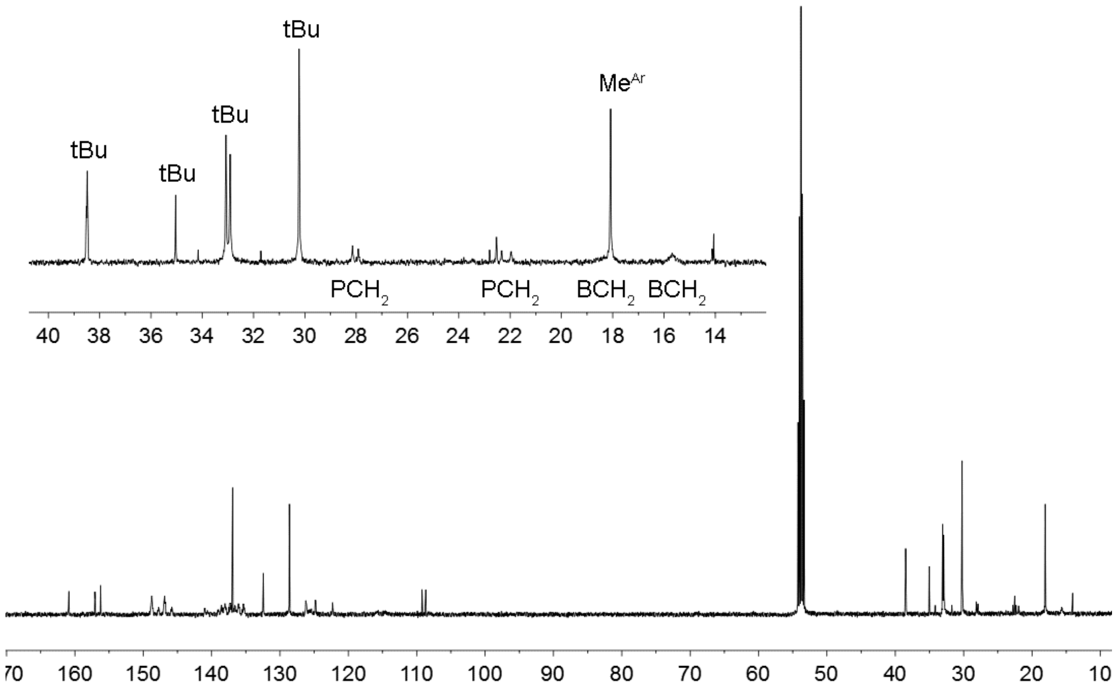
^{1}H NMR (500 MHz, dichloromethane-d_2) spectra of compound **24** at (1) 243K and (2) 299K



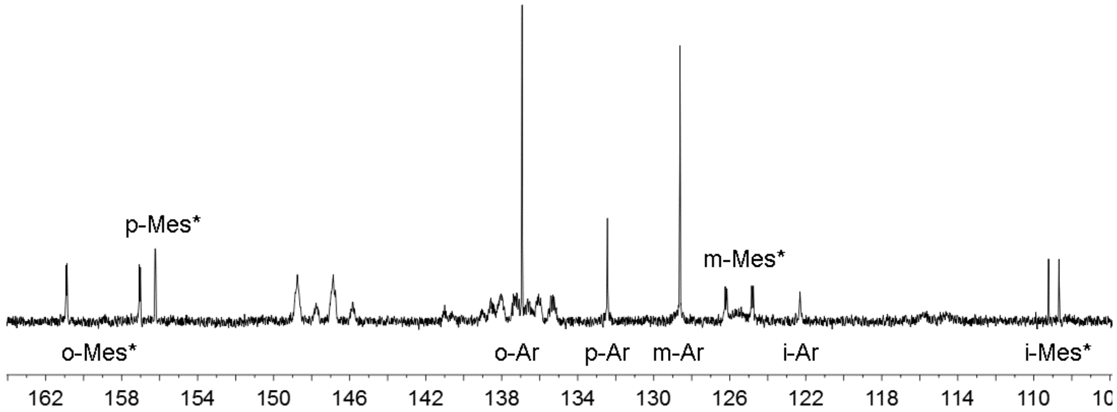
^{1}**H NMR** (500 MHz, 243K, dichloromethane-d$_2$) spectrum of compound **24**



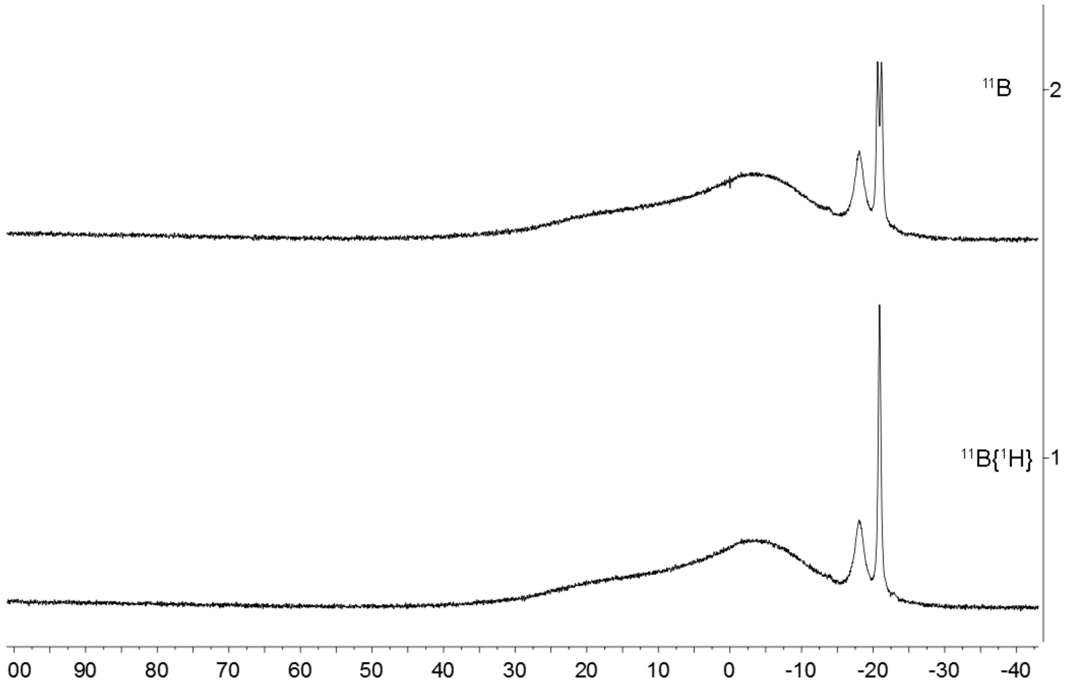
^{1}**H,**^{1}**H cosy** (500 MHz, 243K, dichloromethane-d$_2$) spectrum of compound **24**



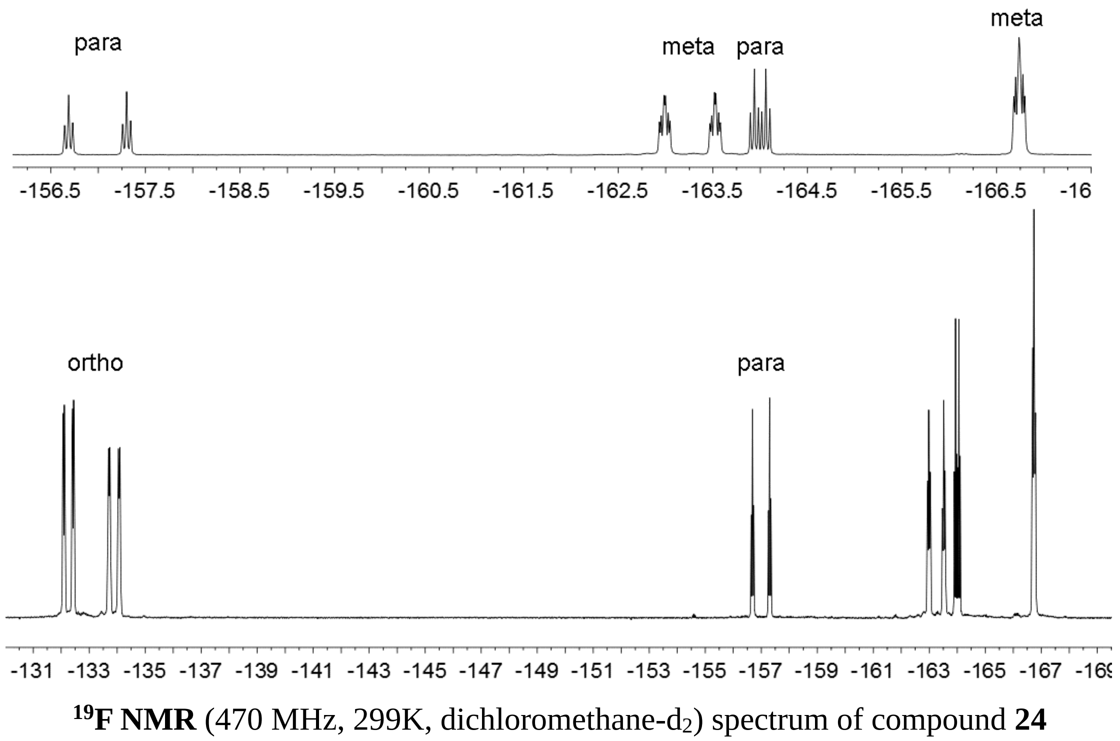
^{13}C{^{1}H} NMR (126 MHz, 243 K, dichloromethane-d_2) spectrum of compound **24**



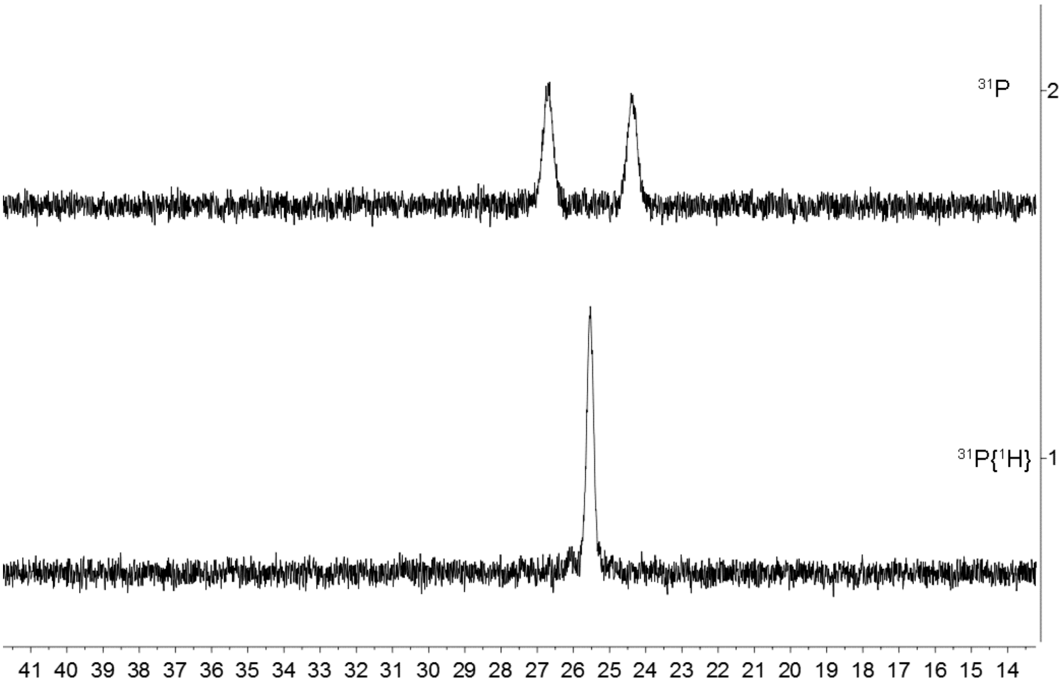
^{13}C{^{1}H} NMR (126 MHz, 243 K, dichloromethane-d_2) spectrum of compound **24**



(1) ^{11}**B{^{1}H}** and (2) ^{11}**B NMR** (160 MHz, 299K, dichloromethane-d$_2$) spectra of compound **24**



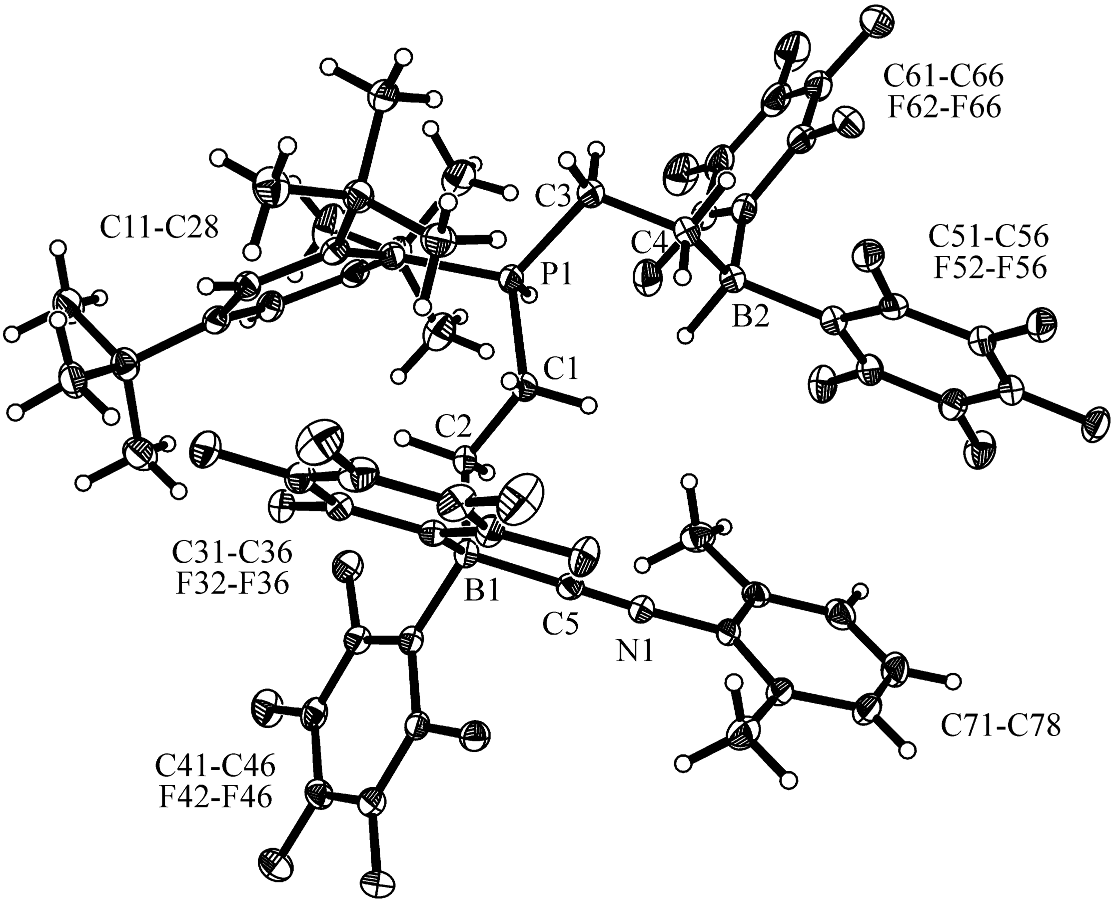
^{19}**F NMR** (470 MHz, 299K, dichloromethane-d$_2$) spectrum of compound **24**



(1) **^{31}P{^{1}H}** and (2) **^{31}P NMR** (202 MHz, 299K, dichloromethane-d_2) spectra of compound **24**

Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of the white solid in dichloromethane at -36 °C.

X-ray crystal structure analysis of compound 24: A colorless plate-like specimen of $C_{55}H_{48}B_2F_{20}NP$, approximate dimensions 0.020 mm x 0.100 mm x 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1949 frames were collected. The total exposure time was 40.53 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 10235 reflections to a maximum θ angle of 68.33° (0.83 Å resolution), of which 10235 were independent (average redundancy 1.000, completeness = 97.4%, R_{int} = 7.91%, R_{sig} = 6.90%) and 6726 (65.72%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.5829(4) Å, b = 13.9854(5) Å, c = 17.6337(6) Å, α = 78.257(2)°, β = 81.650(2)°, γ = 71.145(2)°, volume = 2864.56(17) Å^3, are based upon the refinement of the XYZ-centroids of 8569 reflections above 20 σ(I) with $6.774° < 2\theta < 133.9°$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.854. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8570 and 0.9740. The final anisotropic full-matrix least-squares refinement on F^2 with 731 variables converged at R1 = 5.21%, for the observed data and wR2 = 13.51% for all data. The goodness-of-fit was 1.024. The largest peak in the final difference electron density synthesis was 0.224 e$^-$/Å^3 and the largest hole was -0.370 e$^-$/Å^3 with an RMS deviation of 0.056 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.340 g/cm^3 and F(000), 1180 e$^-$.



Molecular structure of compound **24**