Unusual Borane Addition to Conjugated Dienylphosphanes under Frustrated Lewis Pair Conditions

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$ X-Ray crystal structure analysis

Supporting Information

Materials and Methods: 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. NMR spectra were recorded on: *Bruker* AV 300 (^{1}H: 300 MHz, ^{13}C: 76 MHz, ^{31}P: 122 MHz, ^{11}B: 96 MHz, ^{19}F: 282 MHz), *Bruker* AV 400 (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{31}P:162 MHz), *Varian* VNMR 500 MHz (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{19}F: 470 MHz, ^{11}B: 160 MHz, ^{31}P: 202 MHz) and *Agilent* DD2-600 MHz (^{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 shifts δ are given relative to TMS and referenced to the solvent signal. ^{19}F NMR: chemical shifts δ are given relative to $CFCl_3$ (δ = 0, external reference), ^{11}B NMR: chemical shifts δ are given relative to $BF_3{\cdot}Et_2O$ (δ = 0, external reference), ^{31}P NMR: chemical shifts δ are given relative to H_3PO_4 (85% in D_2O) (δ = 0, external reference). NMR assignments were supported by additional 2D NMR experiments. The splitting patterns in the NMR spectra are reported as follows: s = singlet, d

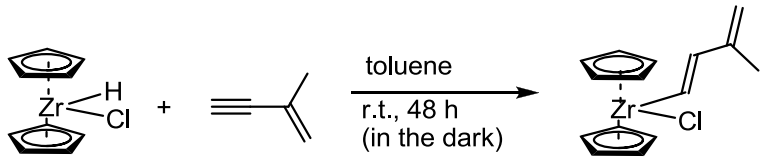
= doublet, t = triplet, q = quartet, m = multiplet, br = broad signal. Coupling constants are given in Hertz (Hz). High Resolution Mass Spectrometry (HRMS) was recorded on Orbitrap (*Thermoscientific LTQ XL*) and MicroTof (*Bruker Daltonics*). Elemental analyses were performed on an *Elementar Vario El III*.

X-Ray diffraction: Data sets for compounds **13a** and **13c** were collected with a Nonius KappaCCD 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); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, 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). For compounds **9c**, **10** and **13b** 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) and graphics, XP (BrukerAXS, 2000). *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: For compounds **13a** and **13c** one disordered dichloromethane molecule was found in the asymmetrical unit and could not be satisfactorily refined. 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 molecules. Compound **13a** present one mesityl group and one phenyl group disordered over two positions. Compound **13c** contains one disordered over two positions ^{t}Bu group. Several restraints (SADI, SAME, ISOR and

SIMU) were used in order to improve refinement stability. CCDC deposition numbers are 1423877 to 1423881.

Starting materials: Bis(pentafluorophenyl)borane $HB(C_6F_5)_2$ [(a) R. E von H. Spence, W. E. Piers, Y. E. Sun, M. Parvez, L. R. MacGillivray, M. J. Zaworotko, *Organometallics* 1998, **17**, 2459; (b) D. J. Parks, W. E. Piers, G. P. A. Yap, *Organometallics* 1998, **17**, 5492; (c) D. J. Parks, R. E. von H. Spence, W. E. Piers, *Angew. Chem. Int. Ed. Engl.* 1995, **34**, 809; (d) R. E. von H. Spence, D. J. Parks, W. E. Piers, M.-A. McDonald, M. J. Zaworotko, S. J. Rettig, *Angew. Chem. Int. Ed. Engl.* 1995, **34**, 1230] Tris(pentafluorophenyl)borane $B(C_6F_5)_3$, Ph_2PCl and 2-Methylbut-1-en-3-yne were purchased. Mes_2PCl, Mes_2PBr and (*p*-tolylethynyl)lithium were available. Compound **8** and **11** were synthesized similar as reported in the following literature [M. D. Fryzuk, G. S. Bates, C. Stone, *J. Org. Chem.* 1991, **56**, 7201]. Diphenyldienylphosphane **9b** was prepared similar to the procedure reported in the literature [M. D. Fryzuk, G. S. Bates, C. Stone, *J. Org. Chem.* 1988, **53**, 4425]. Borane **12c** was synthesized in a similar procedure reported earlier [R. E. H. Spence, W. E. Piers, Y. Sun, M. Parvez, L. R. MacGillivray and M. J. Zavorotko, *Organometallics* 1998, **17**, 2459]. 2-(*tert*-Butyl)ethenyl-bis(pentaflurophenyl)-borane **12b** and (*E*)-styryl-bis(pentafluorophenyl)-borane **12a** were prepared according a literature procedure [O. Ekkert, O. Tuschewitzki, C. G. Daniliuc, G. Kehr. G. Erker, *Chem. Commun.* 2013, **49**, 6992].

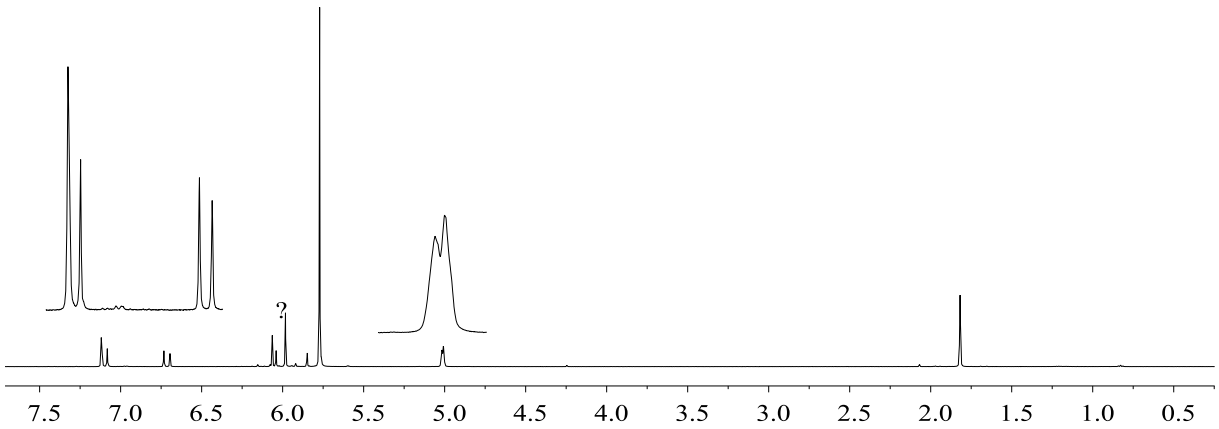
Synthesis of zirconium dienyl complex 8.



8

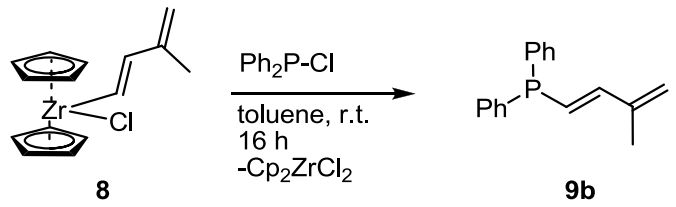
Schwartz reagent $Cp_2Zr(Cl)H$ (3g, 11.63 mmol) was added slowly in three portions (every 2h one portion) to a solution of 2-methylbut-1-en-3-yne (0.77 g, 11.65 mmol) in dry toluene (40 mL) inside of a glove box [Comment: the used Schlenk flask should be covered with aluminum foil]. The stirring was continued at ambient temperature until a homogenous red solution was obtained. Then, the volume of the solution was reduced to 20 mL and *n*-pentane (40 mL) was added. After standing at -30 °C for 2 days, yellow crystals were obtained, which were filtered (at -30 °C) via canula, washed with *n*-pentane (10 mL) and dried *in vacuo*. Yield: 3.7 g (98%).

^{1}H NMR (500 MHz, 299K, C_6D_6): δ = 7.13, 6.75 (each d, $^3J_{HH}$ = 18.6 Hz, each 1H, =CH), 5.80 (s, 10H, Cp), 5.05, 504 (each m, each 1H, $=CH_2$), 1.85 (s, 3H, CH_3).



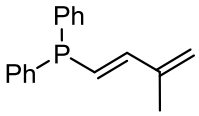
^{1}H NMR (500 MHz, 299K, C_6D_6) spectrum of complex **8**. [? unidentified compounds].

Synthesis of diphenyldienylphosphane 9b.



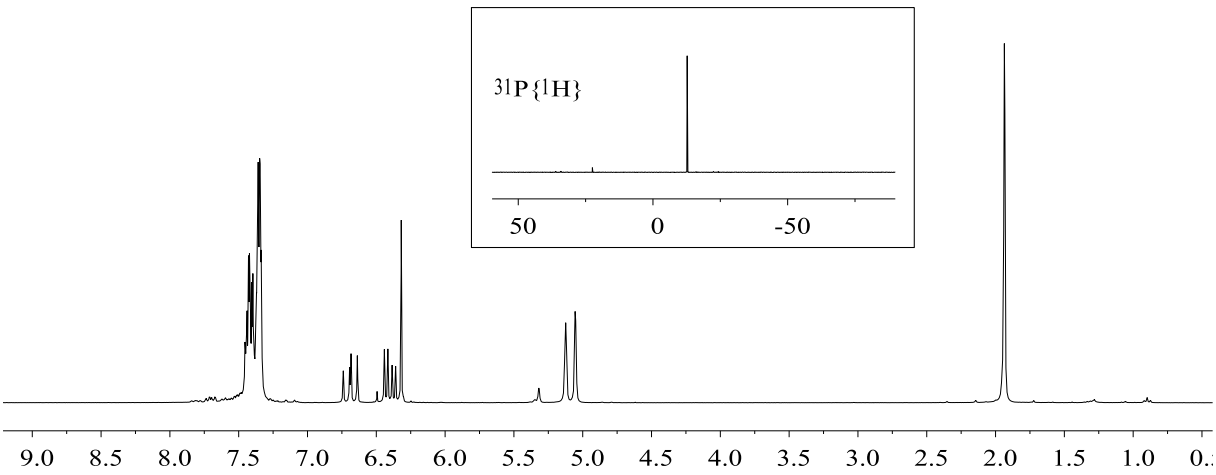
8 **9b**

Zirconocene complexe **8** (0.5 g, 1.543 mmol) and diphenylchlorophosphane (0.324 g, 1.466 mmol) were mixed and dissolved in toluene (5 mL) to give a red solution. After 20 min the formation of a colorless precipitate was observed and the suspension became yellow. After 16 h the reaction mixture was filtered over a short column (Silica-Gel 1 cm x Ø 0.5 cm) and rinsed with *n*-pentane (10 mL). After drying the filtrate *in vacuo* compound **9b** was obtained as a slight yellow oil (0.25 g, 68%).



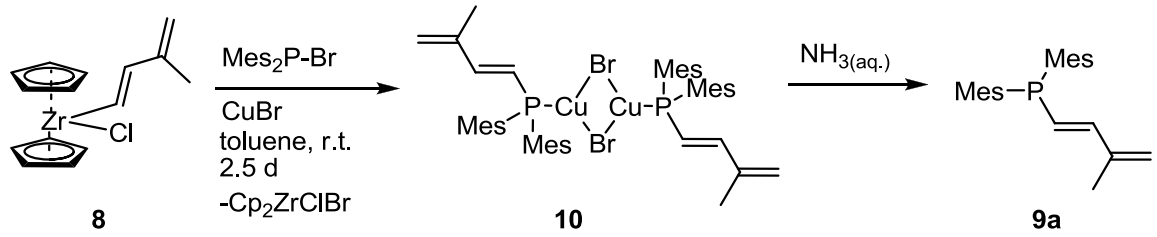
^{1}H NMR (300 MHz, 299K, CD_2Cl_2): δ = 7.42 (4H), 7.35 (6H)(each m, Ph), 6.69 (dd, $^{3}J_{HH,trans}$ = 16.9, J_{PH} = 13.7 Hz, 1H, =CH), 6.40 (dd, $^{3}J_{HH,trans}$ = 16.9, J_{PH} = 8.4 Hz, 1H, =CH), 5.12, 5.05 (each m, each 1H, =CH_2), 1.94 (s, 3H, CH_3).

^{31}P{^{1}H} NMR (121 MHz, 299 K, $CDCl_3$): δ = -12.7 ($\nu_{1/2}$ ~ 1 Hz)



^{1}H NMR (300 MHz, 299K, $CDCl_3$) and **^{31}P{^{1}H} NMR** (121 MHz, 299 K, $CDCl_3$) spectra of compound **9b** (admixed with Cp_2ZrCl_2).

Synthesis of dimesityldienylphosphane copper complex 10



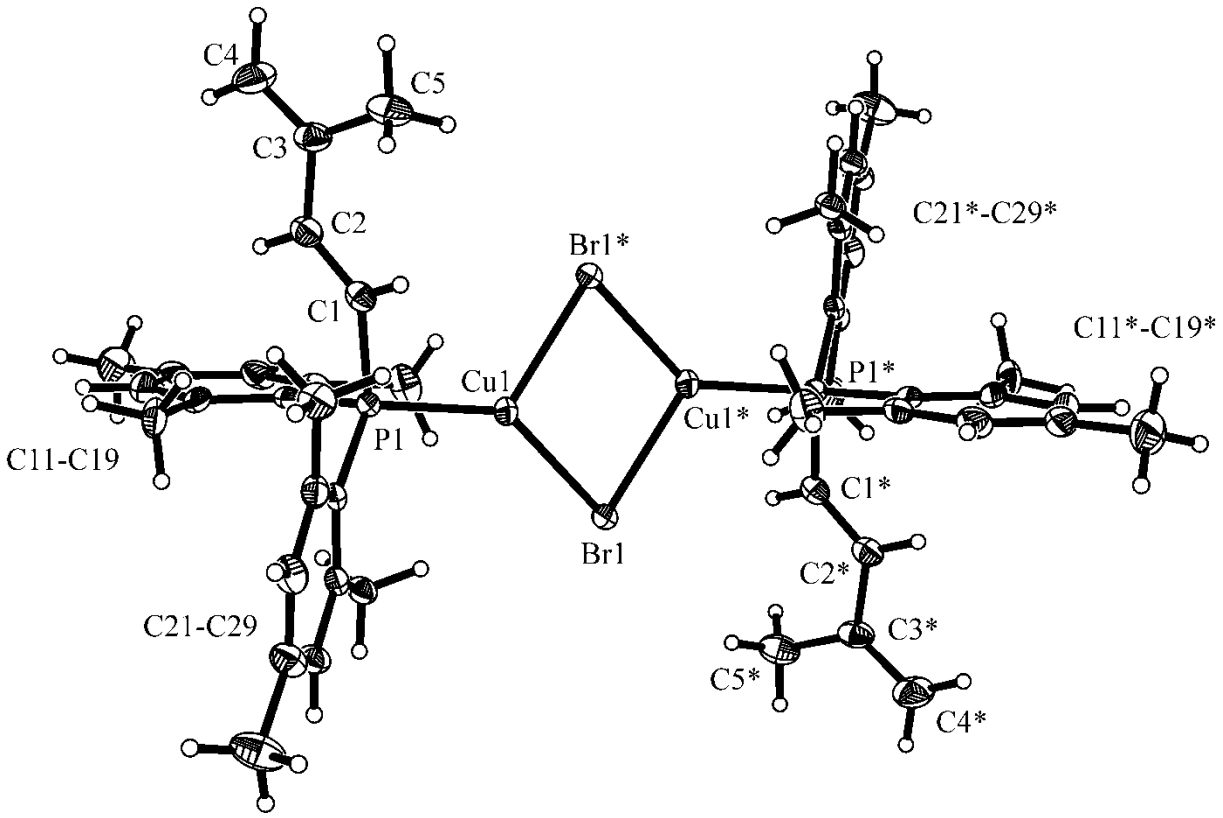
8 **10** **9a**

Mes_2PBr (5.05 g, 14.45 mmol) and CuBr (2.08 g, 14.49 mmol) were added to a solution of compound **8** (4.78 g, 14.75 mmol) in toluene (50 mL). This reaction mixture was stirred for 2.5 days at room temperature, then the volume was reduced *in vacuo* to 1/3 and *n*-pentane (50 mL) was added. The obtained brown-grey suspension was filtered via canula, passed through a frit filled with Al_2O_3 (2 cm x Ø 2 cm) and washed with CH_2Cl_2 (20 mL). Drying of the filtrate *in vacuo* gave complex **10** as a yellow solid (5.9 g, 85%). Single crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane to a saturated solution of compound **10** in toluene at ambient temperature.

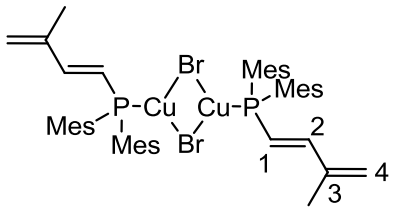
HRMS (Orbitrap)**:** [**9a**+H]$^+$ ($C_{23}H_{29}PH^+$): Calcd.: 337.2085, Found: 314.2073; [2x**9a**+Cu]$^+$ ($C_{46}H_{58}P_2Cu^+$): Calcd.: 735.3310, Found: 735.3291.

Elemental analysis: Calcd. for $C_{46}H_{58}Br_2P_2Cu_2$: C, 57.56; H, 6.09. Found: C, 56.74; H, 6.22.

X-ray crystal structure analysis of compound 10: formula $C_{46}H_{58}Br_2Cu_2P_2$, M = 959.76, colourless crystal, 0.240 x 0.166 x 0.125 mm, a = 11.3422(5), b = 13.9434(7), c = 15.1495(7) Å, α = 81.832(2), β = 71.968(2), γ = 76.313(2)°, V = 2207.3(2) Å^3, ρ_{calc} = 1.444 gcm^{-3}, μ = 2.876 mm^{-1}, empirical absorption correction (0.545 ≤ T ≤ 0.715), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 100(2) K, ω and φ scans, 37445 reflections collected (±h, ±k, ±l), 8069 independent (R_{int} = 0.037) and 6828 observed reflections [I>2σ(I)], 483 refined parameters, R = 0.025, wR^2 = 0.063, max. (min.) residual electron density 0.73 (-0.30) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.



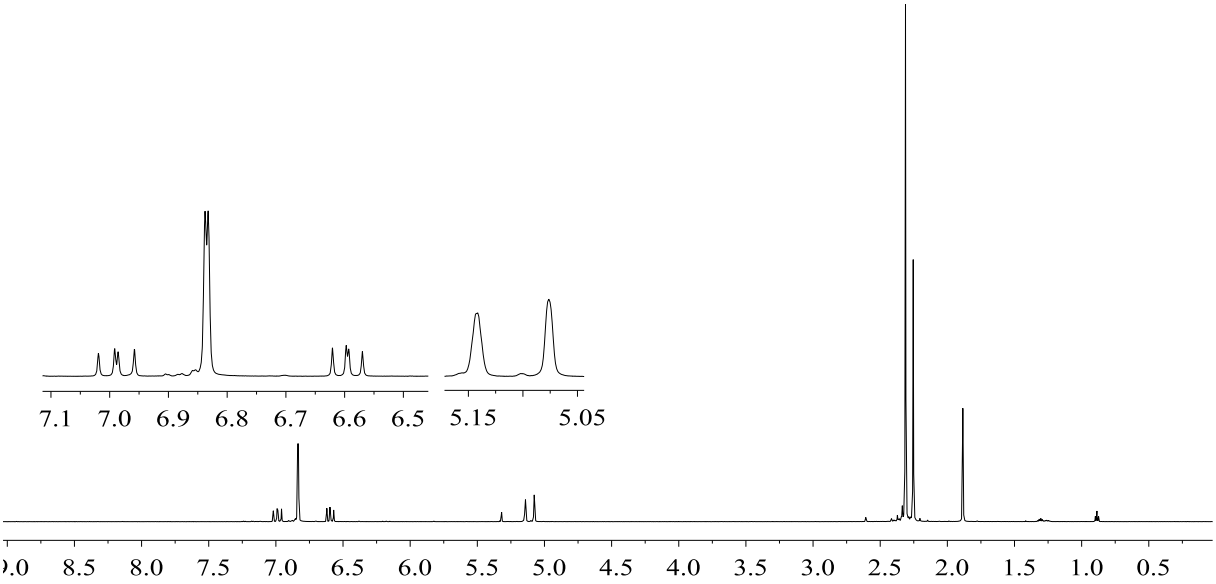
NMR characterization of a solution of the yellow solid in CD_2Cl_2:



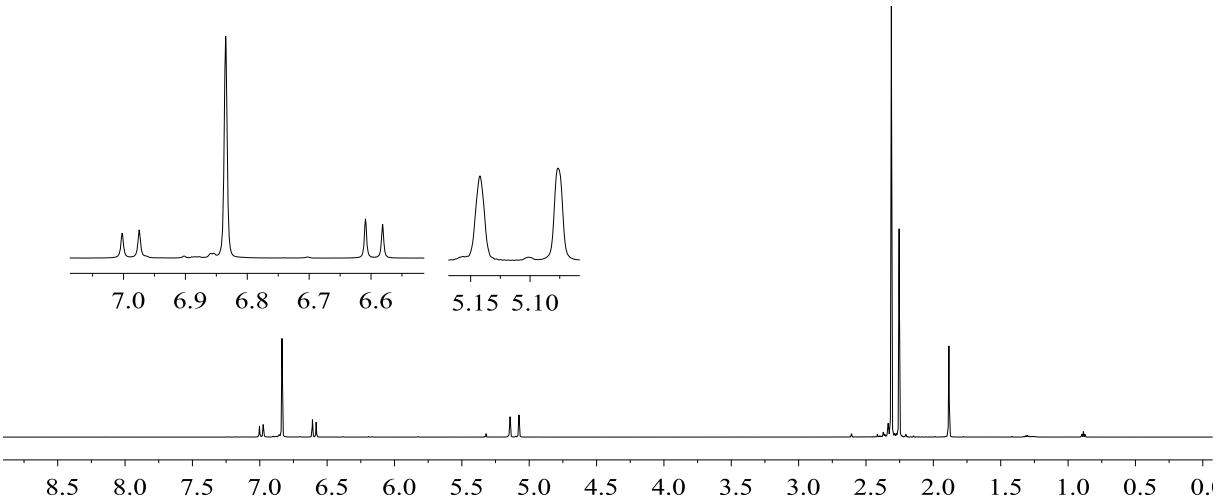
^{1}H NMR (600 MHz, 299K, CD_2Cl_2): δ = 6.99 (dd, $^3J_{PH}$ = 20.1 Hz, $^3J_{HH}$ = 16.6 Hz, 1H, =CH), 6.83 (d, $^4J_{PH}$ = 3.4 Hz, 4H, *m*-Mes), 6.60 (dd, $^3J_{HH}$ = 16.6 Hz, $^2J_{PH}$ = 14.0 Hz, 1H, PCH), 5.14, 5.08 (each m, each 1H, =CH_2), 2.31 (s, 12H, *o*-CH_3^{Mes}), 2.25 (s, 6H, *p*-CH_3^{Mes}), 1.88 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 299K, CD_2Cl_2): δ = 145.6 (d, $^2J_{PC}$ = 17.9 Hz, =CH), 142.4 (d, $^3J_{PC}$ = 18.0 Hz, =C), 141.6 (d, $^2J_{PC}$ = 10.5 Hz, *o*-Mes), 139.9 (d, $^4J_{PC}$ = 1.7 Hz, *p*-Mes), 131.0 (d, $^3J_{PC}$ = 6.9 Hz, *m*-Mes), 127.2 (d, $^1J_{PC}$ = 36.8 Hz, *i*-Mes), 122.2 (d, $^1J_{PC}$ = 37.5 Hz, PCH), 120.3 (=CH_2), 24.2 (d, $^3J_{PC}$ = 10.9 Hz, *o*-CH_3^{Mes}), 21.0 (*p*-CH_3^{Mes}), 18.5 (CH_3).

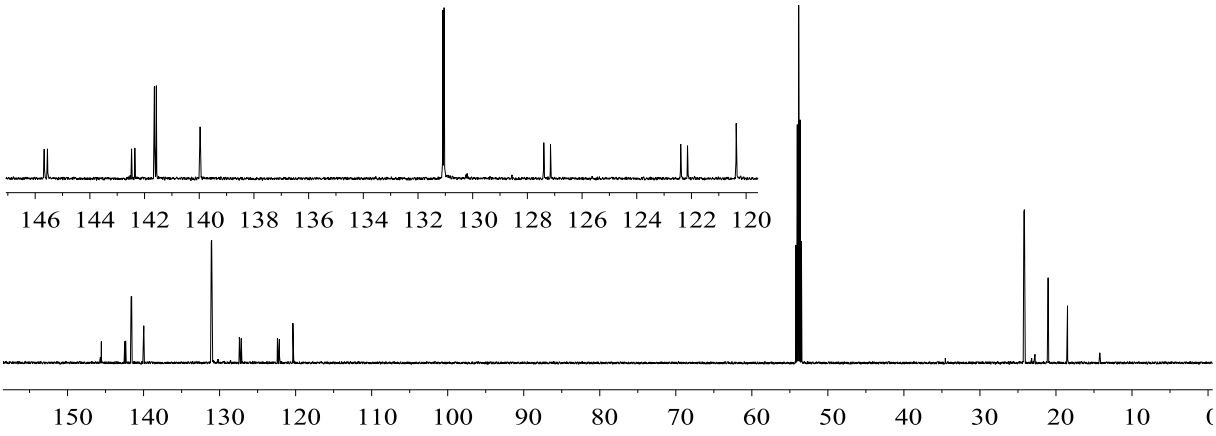
^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = -22.3 ($\nu_{1/2}$ ~ 70 Hz).



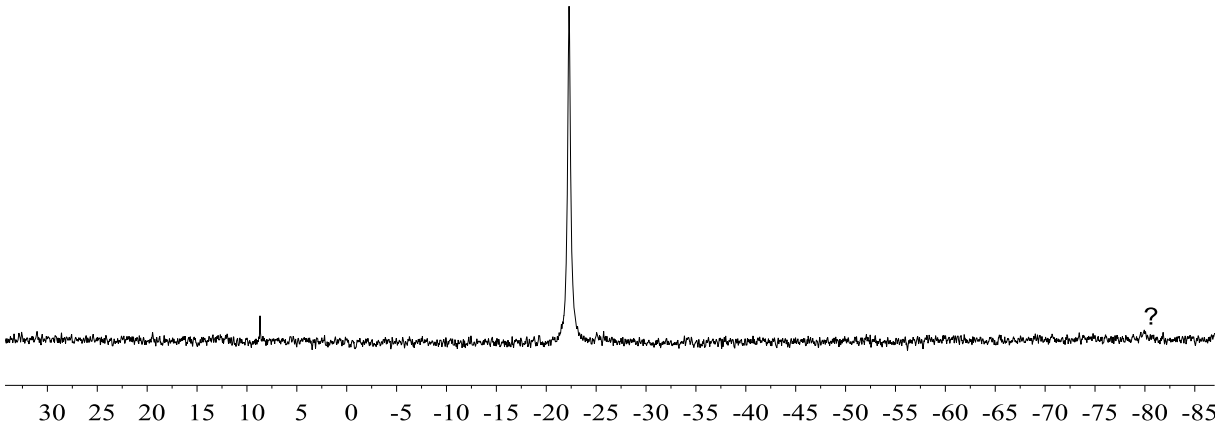
^{1}H NMR (600 MHz, 299K, CD_2Cl_2) spectrum of copper complex **10**.



^{1}H{^{31}P} NMR (600 MHz, 299K, CD_2Cl_2) spectrum of copper complex **10**.



^{13}C{^{1}H} NMR (151 MHz, 299K, CD_2Cl_2) spectrum of copper complex **10**.



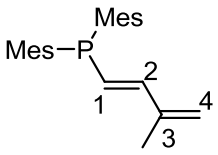
$^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, CD_2Cl_2) spectrum of copper complex **10**. [? not identified].

Dimesityldienylphosphane 9a

Concentrated aqueous NH_4OH solution (10 mL) was added to a solution of compound **10** (2.87 g, 2.99 mmol) in toluene (50 mL) under argon. The organic phase was separated by using a canula and dried with Na_2SO_4. Then all volatiles were removed *in vacuo* to give compound **9a** as a yellow oil (2.01 g, 99%), which crystallized after a few days.

Elemental analysis: Calcd. for $C_{23}H_{29}P$: C, 82.11; H, 8.69. Found: C, 79.09; H, 8.61.

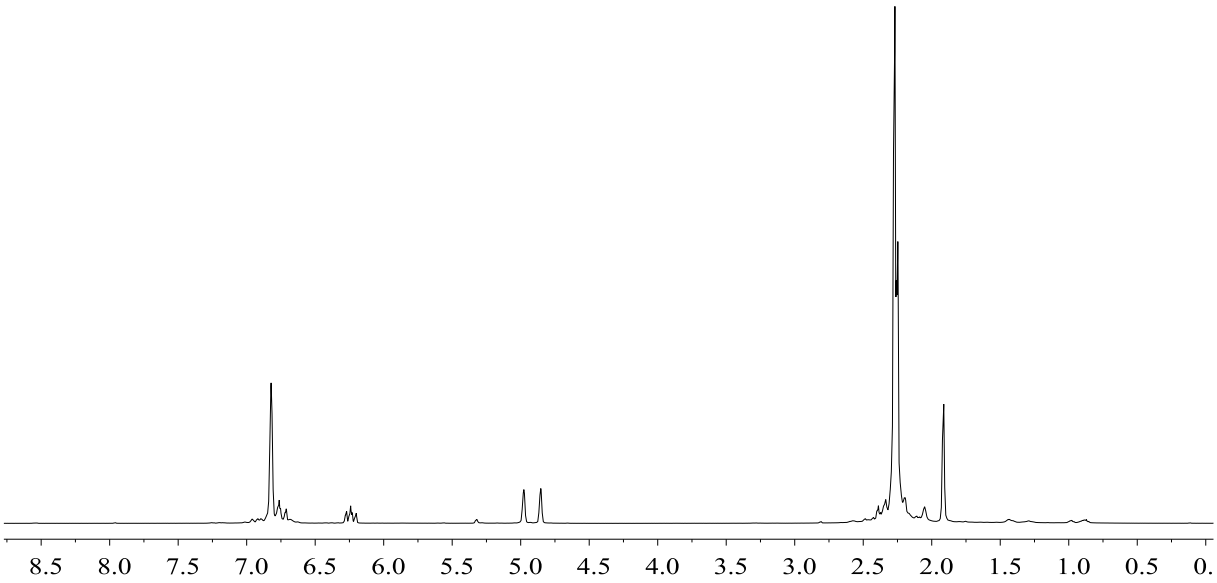
NMR characterization of a solution of the yellow solid in CD_2Cl_2:



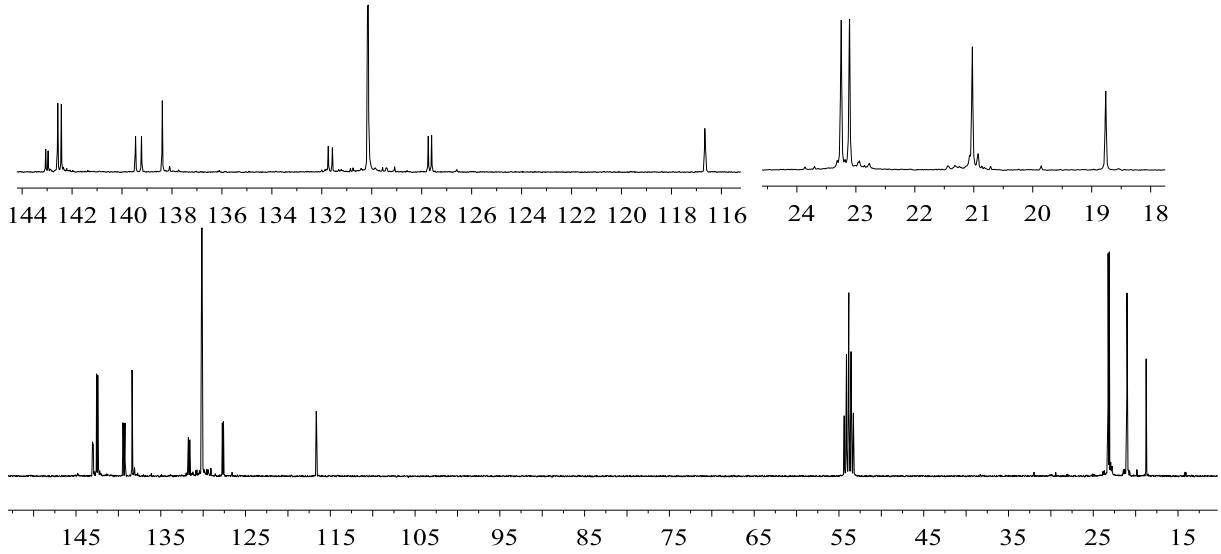
^{1}H NMR (400 MHz, 299 K, CD_2Cl_2): δ = 6.82 (m, 4H, *m*-Mes), 6.76 (dd, $^{3}J_{HH,trans}$ = 16.5 Hz, $^{2}J_{PH}$ = 11.6 Hz, 1H, PCH), 6.24 (dd, $^{3}J_{PH}$ = 20.7 Hz, $^{3}J_{HH,\ trans}$ = 16.5 Hz, 1H, =CH), 4.98, 4.85 (each br m, each 1H, $=CH_2$), 2.27 (s, 12H, *o*-CH_3^{Mes}), 2.25 (s, 6H, *p*-CH_3^{Mes}), 1.91 (m, 3H, CH_3).

$^{13}C\{^{1}H\}$ NMR (101 MHz, 299 K, CD_2Cl_2): δ = 143.0 (d, $^{3}J_{PC}$ = 9.6 Hz, =C), 142.5 (d, $^{2}J_{PC}$ = 14.4 Hz, *o*-Mes), 139.3 (d, $^{1}J_{PC}$ = 24.1 Hz, =CH), 138.4 (*p*-Mes), 131.6 (d, $^{1}J_{PC}$ = 16.6 Hz, *i*-Mes), 130.1 (d, $^{3}J_{PC}$ = 3.4 Hz, *m*-Mes), 127.7 (d, $^{2}J_{PC}$ = 13.5 Hz, PCH), 116.6 (d, $^{4}J_{PC}$ = 2.3 Hz, $=CH_2$), 23.2 (d, $^{3}J_{PC}$ = 14.2 Hz, *o*-CH_3^{Mes}), 21.0 (*p*-CH_3^{Mes}), 18.7 (CH_3).

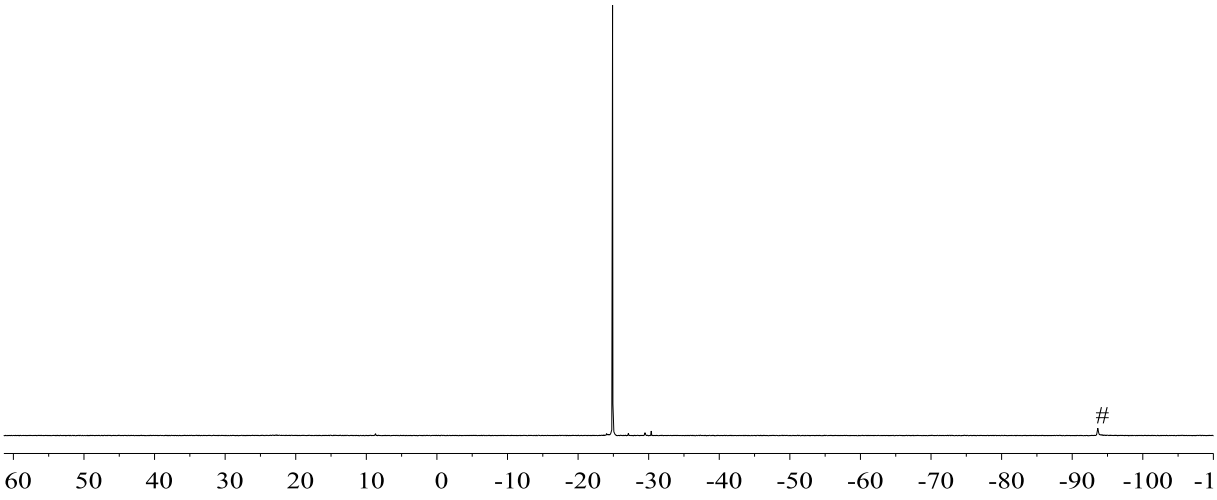
$^{31}P\{^{1}H\}$ NMR (162 MHz, 299 K, CD_2Cl_2): δ = -24.9 ($\nu_{1/2}$ ~ 2 Hz).



^{1}H NMR (400 MHz, 299 K, CD_2Cl_2) spectrum of compound **9a**.

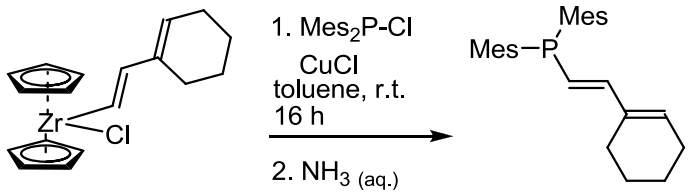


^{13}C{^{1}H} NMR (101 MHz, 299 K, CD_2Cl_2) spectrum of compound **9a**.



^{31}P {^{1}H} NMR (162 MHz, 299 K, CD_2Cl_2) spectrum of compound **9a**. [$^{\#}$ Mes_2PH].

Synthesis of dimesityldienylphosphane 9c.



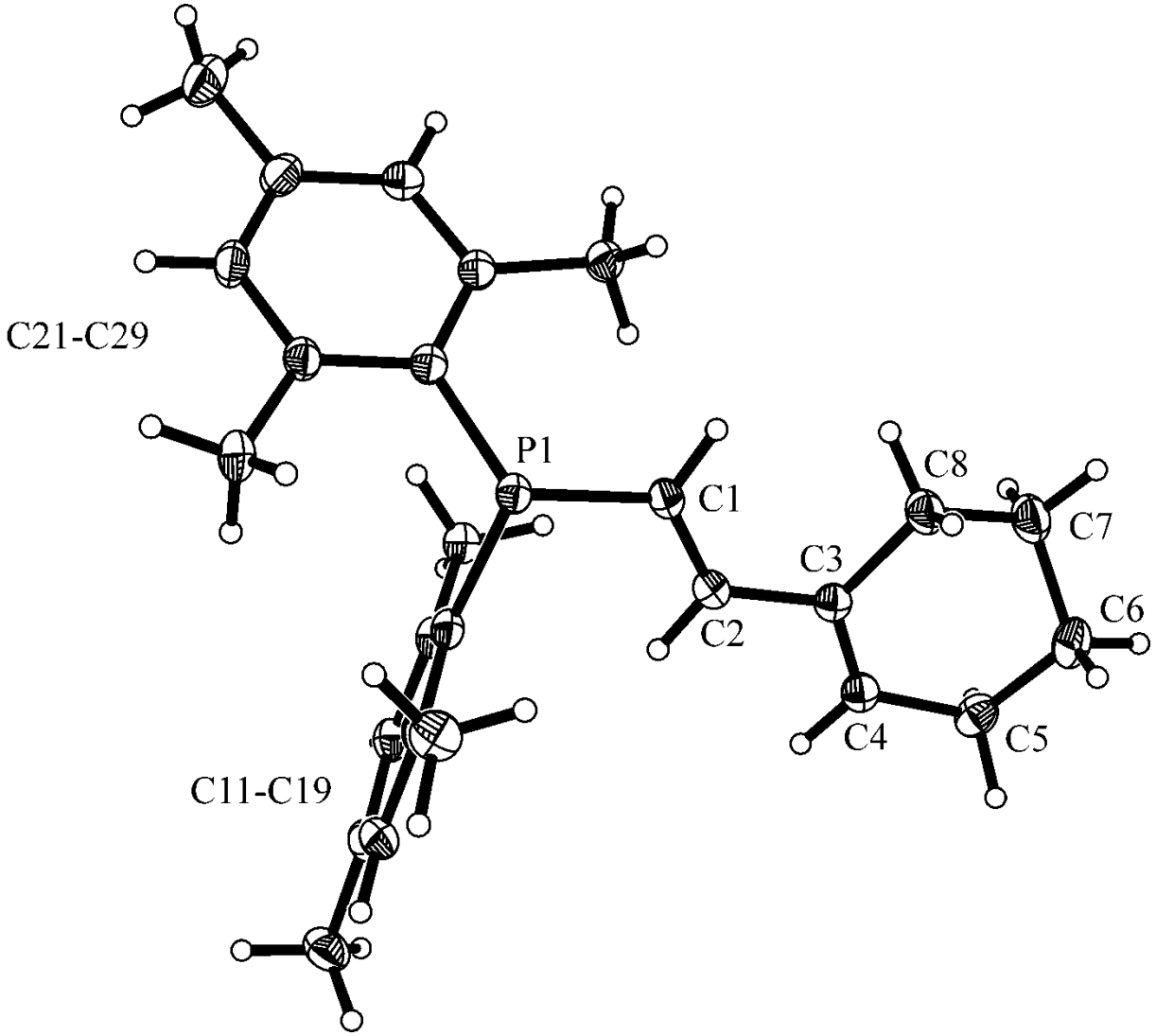
11 **9c**

Compound **9c** was synthesized in a similar way as described for compound **9a**, but using Mes_2PCl and CuCl: Mes_2PCl (1.00 g, 3.28 mmol) and CuCl (0.324 g, 3.27 mmol) were added to a solution of compound **11** (1.21 g, 3.32 mmol) in toluene (6 mL). The reaction mixture was stirred for 16 h at room temperature, then the volume was reduced *in vacuo* to 1/2 and *n*-pentane (30 mL) was added. The obtained suspension was filtered through a frit filled with Al_2O_3 (2 cm x Ø 2 cm) and washed with CH_2Cl_2 (20 mL). Subsequently concentrated aqueous NH_4OH solution (10 mL) was added to the filtrate (argon atmosphere). The organic phase was separated and dried with Na_2SO_4. Finally all volatiles were removed *in vacuo* to give compound **9c** as a slight yellow oil, which crystallized after several days (0.89 g, 72%). The quality of the obtained crystals was suitable for the X-ray crystal structure analysis.

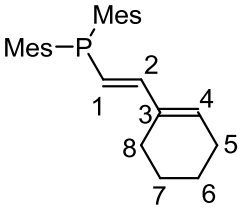
Elemental analysis (crystalline material): Calcd. for $C_{26}H_{33}P$: C, 82.94; H, 8.83. Found: C, 80.49; H, 8.92.

X-ray crystal structure analysis of compound 9c: formula $C_{26}H_{33}P$, M = 376.49, colourless crystal, 0.194 x 0.142 x 0.091 mm, a = 12.6725(3), b = 10.3622(3), c = 16.8729(5) Å, β = 99.970(1)°, V = 2182.2(1) Å^3, ρ_{calc} = 1.146 gcm^{-3}, μ = 1.144 mm^{-1}, empirical absorption correction ($0.809 \leq T \leq 0.903$, Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 100(2) K, ω and φ scans, 35075 reflections collected ($\pm h$, $\pm k$, $\pm l$), 3996 independent (R_{int} = 0.056) and 3471 observed reflections [$I>2\sigma(I)$], 250 refined parameters, R = 0.037, wR^2 =

0.099, max. (min.) residual electron density 0.40 (-0.26) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.



NMR characterization of a solution of the yellow solid in CD_2Cl_2:



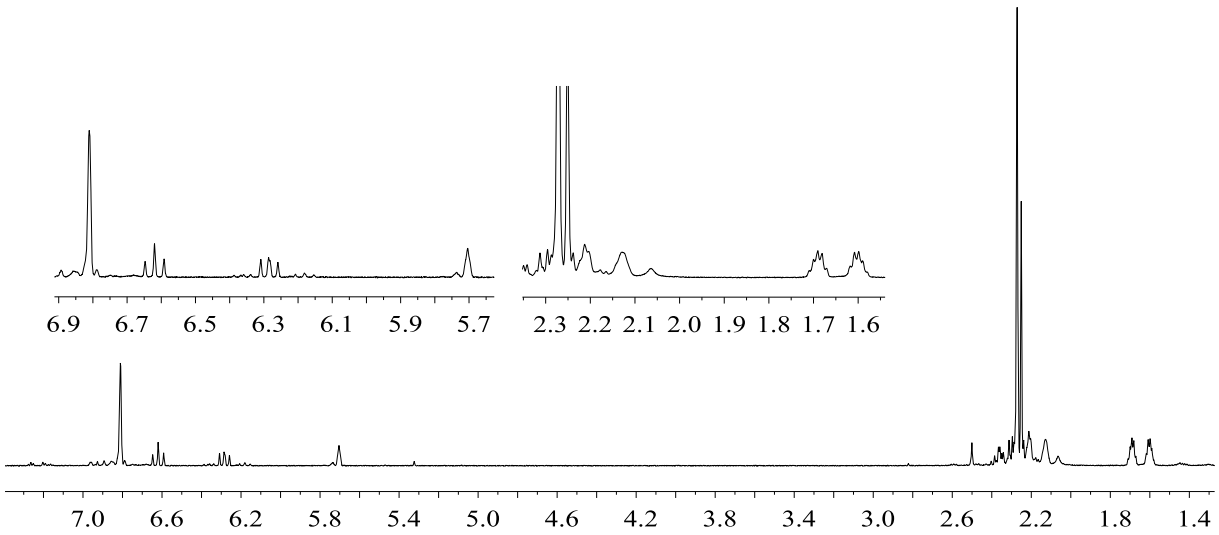
^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 6.81 (m, 4H, *m*-Mes), 6.62 (t, $^{3}J_{HH,trans}$ = $^{2}J_{PH}$ = 16.6 Hz, 1H, PCH), 6.28 (dd, $^{3}J_{HH,trans}$ = 16.7, $^{3}J_{PH}$ = 13.4 Hz, 1H, 2-H), 5.70 (m, 1H, 4-H), 2.27 (s, 12H, *o*-CH_3^{Mes}), 2.25 (s, 6H, *p*-CH_3^{Mes}), 2.21 (m, 2H, 8-H), 2.12 (m, 2H, 5-H), 1.69 (m, 2H, 7-H), 1.60 (m, 2H, 6-H).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = 142.3 (d, $^{2}J_{PC}$ = 14.3 Hz, *o*-Mes), 141.7 (d, $^{2}J_{PC}$ = 29.1 Hz, C2), 138.1 (*p*-Mes), 136.9 (d, $^{3}J_{PC}$ = 11.7 Hz, C3), 132.5 (d, $^{1}J_{PC}$ = 16.9 Hz, *i*-

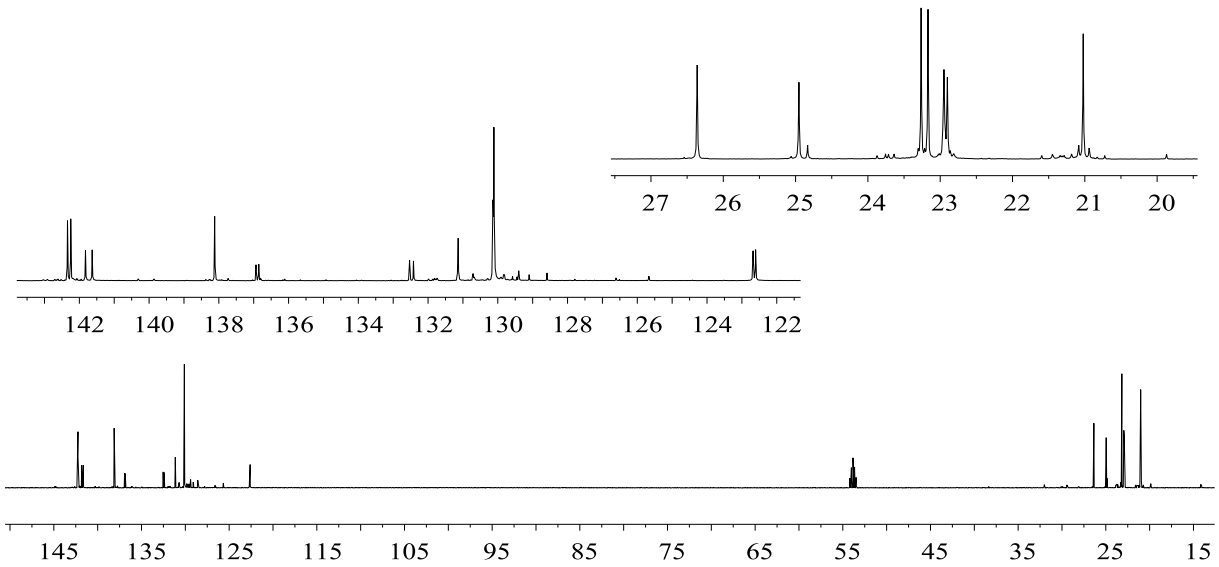
Mes), 131.1 (d, $^{4}J_{PC}$ = 1.6 Hz, C4), 130.1 (d, $^{3}J_{PC}$ = 3.2 Hz, *m*-Mes), 122.6 (d, $^{1}J_{PC}$ = 11.1 Hz, C1), 26.3 (C5), 24.9 (C8), 23.2 (d, $^{3}J_{PC}$ = 14.3 Hz, *o*-CH_3^{Mes}), 22.91, 22.86 (C6,7), 21.0 (*p*-CH_3^{Mes}).

$^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, CD_2Cl_2): δ = -24.3 ($\nu_{1/2}$ ~ 2 Hz).

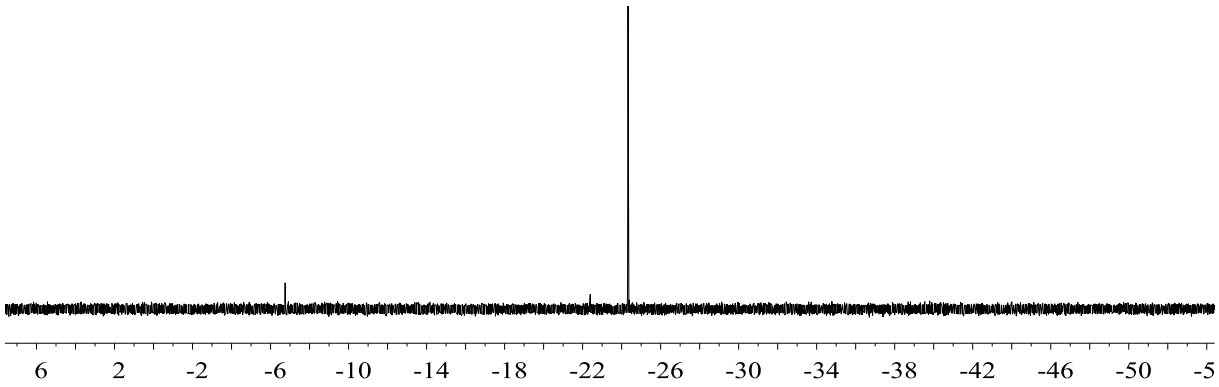
^{31}P NMR (243 MHz, 299 K, CD_2Cl_2): δ = -24.3 (br t, *J* ~ 16 Hz).



^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound **9c**.

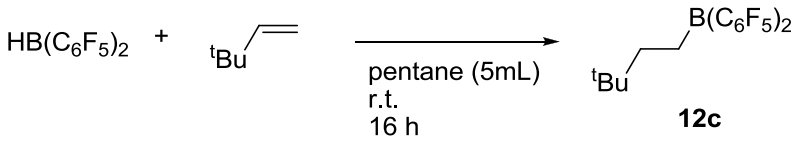


$^{13}C\{^{1}H\}$ NMR (202 MHz, 299 K, CD_2Cl_2) spectrum of compound **9c**.



$^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, CD_2Cl_2) spectrum of compound **9c**.

Synthesis of compound 12c.

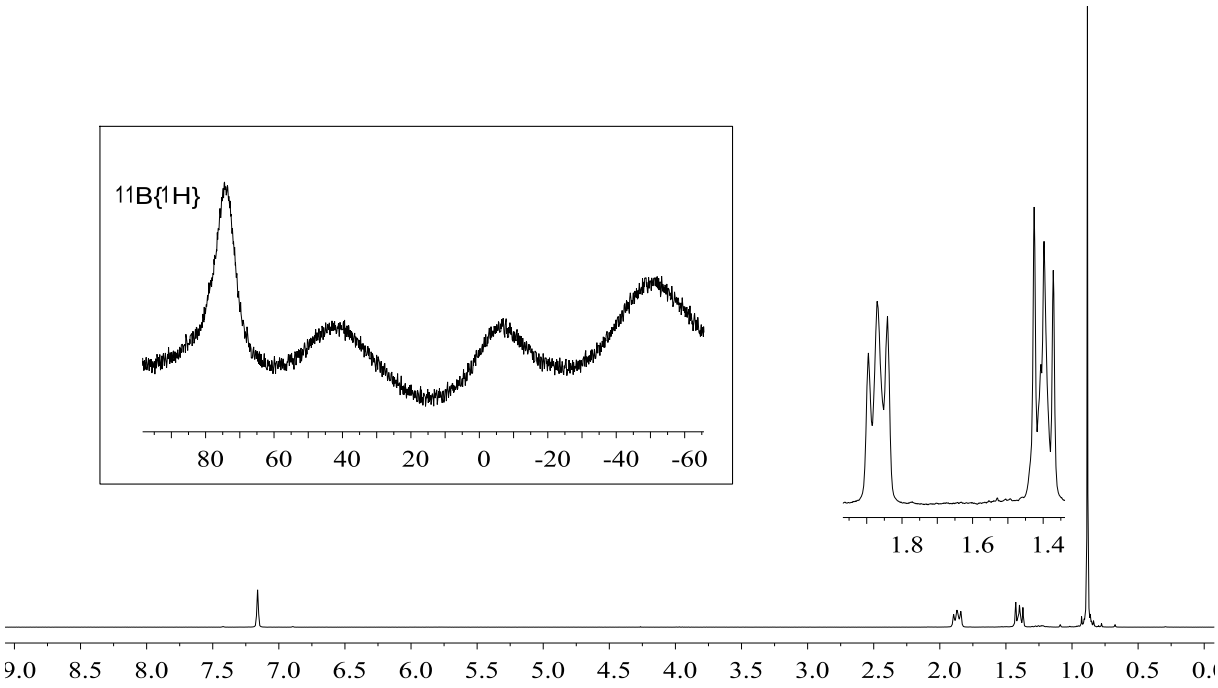


Inside of a glove box a solution of 3,3-dimethylbut-1-ene (127.1 mg, 1.51 mmol) in *n*-pentane (2 mL) was added to a suspension of $HB(C_6F_5)_2$ (402 mg, 1.16 mmol) in *n*-pentane (3 mL). After 16 h stirring the reaction mixture was filtered and all volatiles of the filtrate were removed *in vacuo* to give a colorless oil (480 mg, 96%).

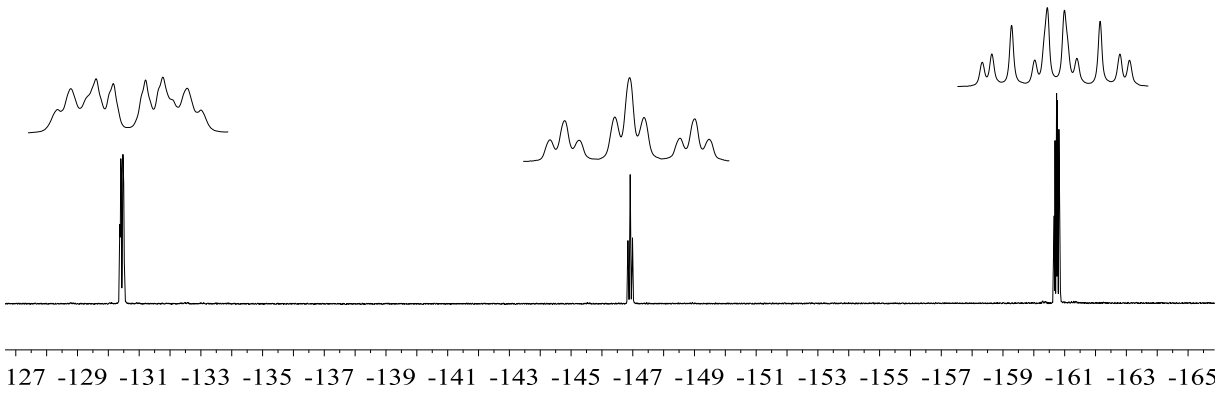
^{1}H NMR (300 MHz, 299 K, C_6D_6): δ = 1.86, 1.39 (each m, each 2H, CH_2), 0.87 (s, 9H, ^{t}Bu).

$^{11}B\{^{1}H\}$ NMR (96 MHz, 299 K, C_6D_6): δ = 73.8 ($\nu_{1/2}$ ~ 700 Hz).

$^{19}F\{^{1}H\}$ NMR (282 MHz, 299 K, C_6D_6): δ = -130.4 (m, 2F, *o*-C_6F_5), -146.9 (tt, *J* = 20.9, 4.8 Hz, 1F, *p*-C_6F_5), -160.8 (m, 2F, *m*-C_6F_5).

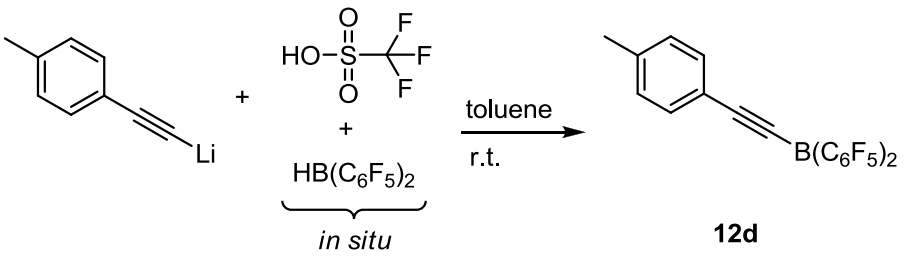


^{1}H NMR (300 MHz, 299 K, C_6D_6) and **^{11}B{^{1}H} NMR** (96 MHz, 299 K, C_6D_6) spectra of compound **12c**.



^{19}F NMR (282 MHz, 299 K, C_6D_6) spectrum of compound **12c**.

Synthesis of compound 12d.



Trifluoromethanesulfonic acid (163.0 mg, 1.09 mmol) and $HB(C_6F_5)_2$ (375.7 mg, 1.09 mmol) were solved in dry toluene (4 mL). Immediately a gas evolution was observed. After 5 min reaction time a clear yellow solution was obtained. This solution was added to (*p*-tolylethynyl)lithium (132.6 mg, 1.09 mmol) at ambient temperature. The formation of a red brown solution and a white solid were observed. After 2h stirring the reaction mixture was filtered through celite, all volatiles of the filtrate were removed *in vacuo* to give a brown viscous residue which was washed trice with *n*-pentane (2 × 2 mL). After drying *in vacuo* a grey white powder was obtained (180 mg, 36%).

[*Comment*: Compound **12d** slowly decomposes at room temperature and should be stored in the fridge at -30°C].

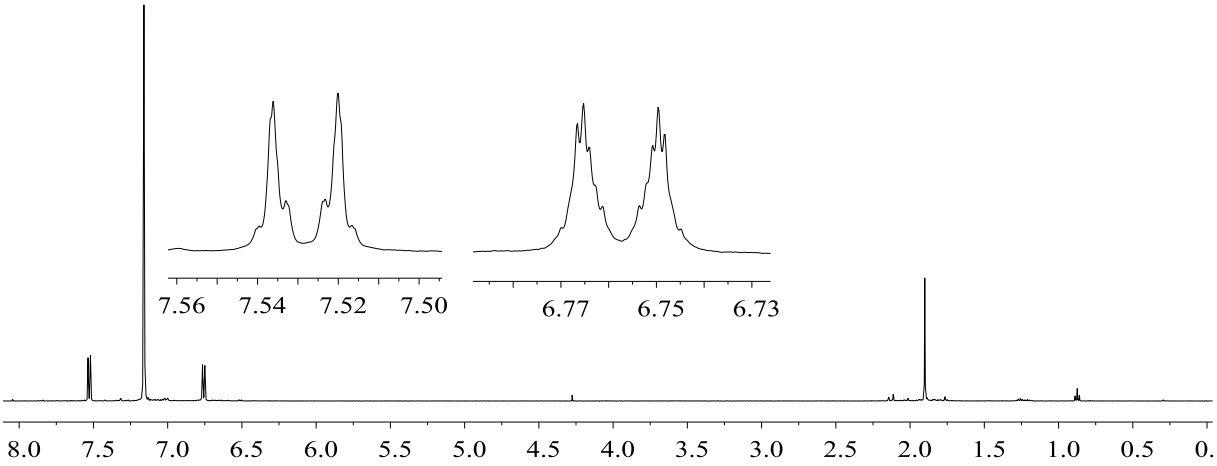
Elemental analysis: Calcd. for $C_{21}H_7BF_{10}$: C, 54.82; H, 1.53. Found: C, 54.40; H, 1.54.

^{1}H NMR (500 MHz, 299 K, C_6D_6): δ = 7.52 (m, 2H, *o*-Tol), 6.75 (m, 2H, *m*-Tol), 1.89 (s, 3H, CH_3).

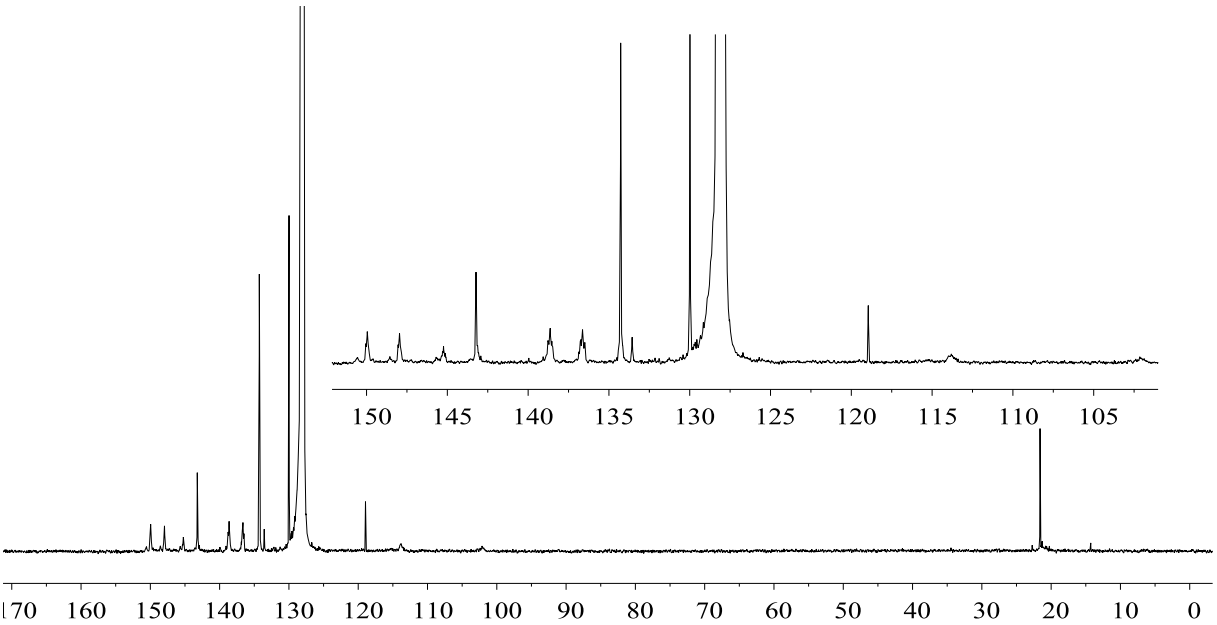
^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6): δ = 148.9 (dm, J_{FC} = 250 Hz, C_6F_5), 144.0 (dm, J_{FC} = 259 Hz, C_6F_5), 143.2 (*p*-Tol), 137.5 (dm, J_{FC} = 252 Hz, C_6F_5), 134.2 (*o*-Tol), 133.5 (≡C), 129.9 (*m*-Tol), 118.9 (*i*-Tol), 113.7 (m, *i*-C_6F_5), 102.1 (br, ≡CB), 21.5 (CH_3).

^{11}B{^{1}H} NMR (160 MHz, 299 K, C_6D_6): δ = 47.2 ($\nu_{1/2}$ ~ 800 Hz).

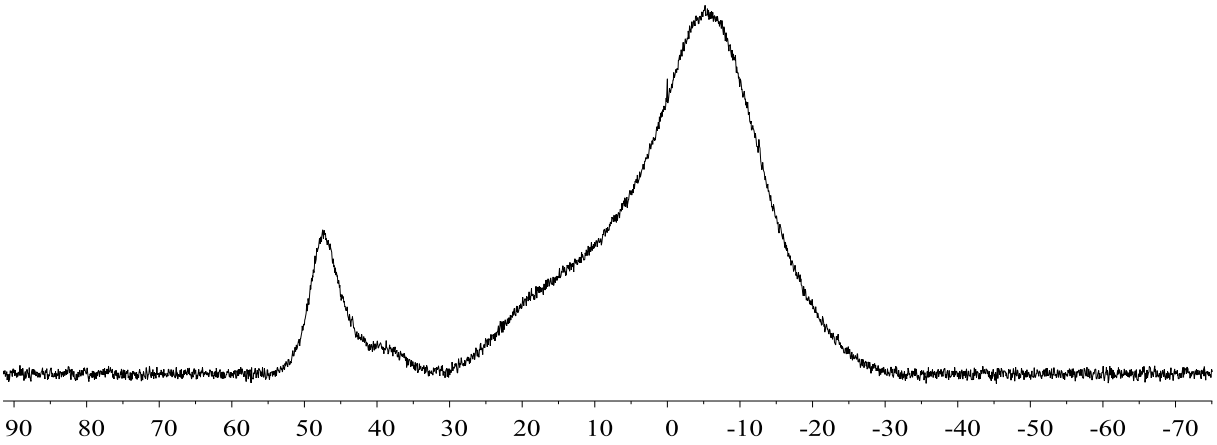
^{19}F NMR (470 MHz, 299 K, C_6D_6): δ = -128.8 (m, 2F, *o*-C_6F_5), -146.3 (tt, *J* = 20.9, 5.8 Hz, 1F, *p*-C_6F_5), -161.6 (m, 2F, *m*-C_6F_5).



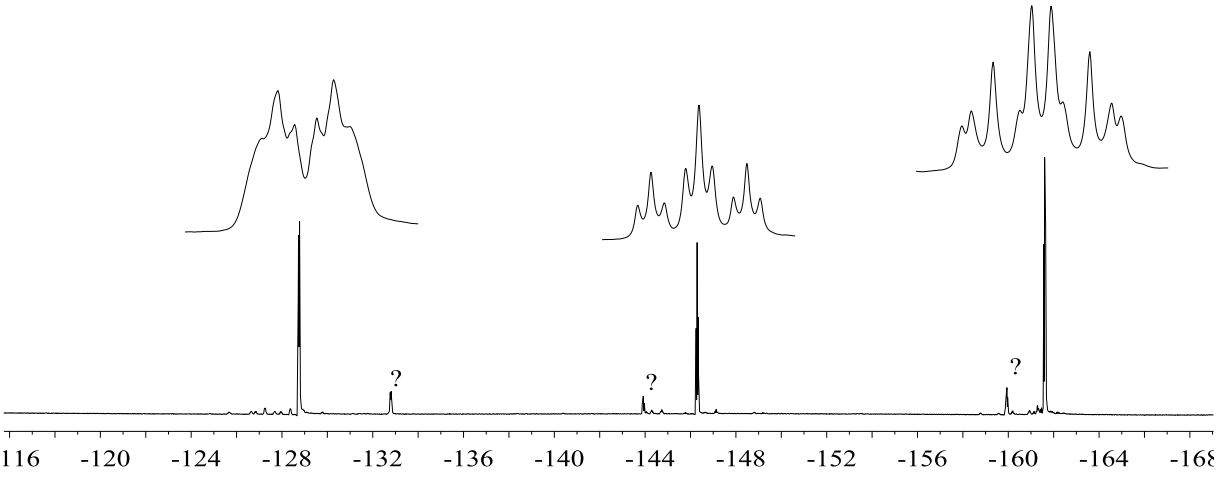
^{1}H NMR (500 MHz, 299 K, C_6D_6) spectrum of compound **12d**.



^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6) spectrum of compound **12d**.

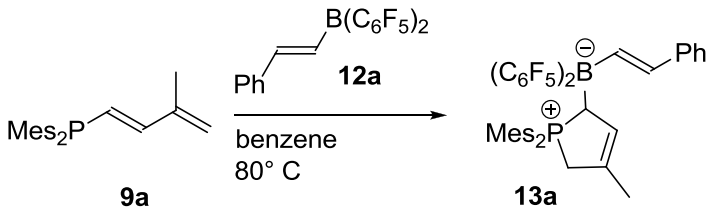


^{11}B{^{1}H} NMR (160 MHz, 299 K, C_6D_6) spectrum of compound **12d**.



^{19}F NMR (470 MHz, 299 K, C_6D_6) spectrum of compound **12d**. [? not identified].

Synthesis of compound 13a.

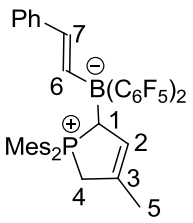


(*E*)-Styryl-bis(pentafluorophenyl)borane **12a** (133.2 mg, 0.297 mmol) and phosphane **9a** (100 mg, 0.297 mmol) were dissolved in benzene (0.7 mL) and then heated for 3 days at 80 °C. The formed precipitate was collected, washed with *n*-pentane (3 × 1 mL) and dried *in vacuo* to give a colorless solid (167 mg, 72%).

HRMS (MicroTof)**:** M+Na$^+$ ($C_{43}H_{36}BF_{10}PNa^+$): Calcd.: 807.2386, Found: 807.2388.

Elemental analysis: Calcd. for $C_{43}H_{36}BF_{10}P$: C, 65.83; H, 4.63. Found: C, 66.38; H, 4.77.

NMR characterization of a solution of the colorless solid in CD_2Cl_2:



^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 7.41 (d, $^3J_{HH,trans}$ = 17.9 Hz, 1H, =CHB), 7.31 (m, 2H, o-Ph), 7.28 (m, 2H, m-Ph), 7.12 (m, 1H, *p*-Ph), 7.08, 6.38 (each m, each 1H, *m*-Mes^b), 6.94, 6.84 (each m, each 1H, *m*-Mes^a), 6.22 (d, $^3J_{PH}$ = 32.4 Hz, 1H, =CH), 5.92 (d, $^3J_{HH,trans}$ = 17.9 Hz, 1H,

=CHPh), 4.95 (d, $^{2}J_{PH}$ = 15.5 Hz, 1H, BCH), 3.51 (br d, $^{2}J_{HH}$ = 15.8 Hz), 2.64 (dd, $^{2}J_{HH}$ = 15.8, $^{2}J_{PH}$ = 11.5 Hz)(each 1H, CH_2), 2.91, 1.97 (each s, each 3H, *o*-$CH_3^{Mes,a}$), 2.81, 1.78 (each s, each 3H, *o*-$CH_3^{Mes,b}$), 2.27 (s, 3H, *p*-$CH_3^{Mes,b}$), 2.24 (s, 3H, *p*-$CH_3^{Mes,a}$), 1.63 (s, 3H, Me).

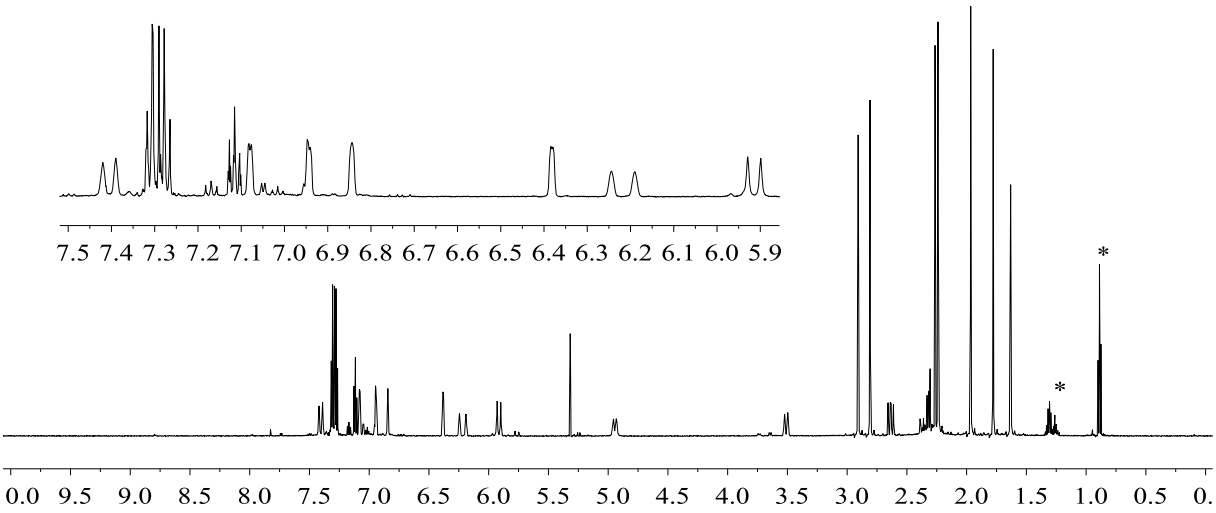
$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2): δ = 143.9 (d, $^{4}J_{PC}$ = 2.9 Hz, *p*-Mes^b), 143.2 (d, $^{2}J_{PC}$ = 9.0 Hz), 141.7 (d, $^{2}J_{PC}$ = 9.5 Hz)(*o*-Mes^a), 143.1 (d, $^{4}J_{PC}$ = 2.7 Hz, *p*-Mes^a), 142.4 (d, $^{2}J_{PC}$ = 10.8 Hz), 142.0 (d, $^{2}J_{PC}$ = 8.5 Hz)(*o*-Mes^b), 141.8 (*i*-Ph), 141.5 (br, =CHB), 138.6 (dm, J_{FC} = 248 Hz, C_6F_5), 133.9 (=CHPh), 133.1 (d, $^{3}J_{PC}$ = 10.7 Hz, *m*-Mes^a), 132.1 (d, $^{3}J_{PC}$ = 11.2 Hz), 130.9 (dm, $^{3}J_{PC}$ = 10.7 Hz)(*m*-Mes^b), 131.7 (d, $^{2}J_{PC}$ = 12.7 Hz, =C), 131.4 (br, =CH), 128.8 (m-Ph), 125.9 (p-Ph), 125.7 (o-Ph), 122.4 (d, $^{1}J_{PC}$ = 69.8 Hz, *i*-Mes^a), 119.1 (d, $^{1}J_{PC}$ = 68.0 Hz, *i*-Mes^b), 41.3 (d, $^{1}J_{PC}$ = 52.8 Hz, CH_2), 37.6 (br, BCH), 25.3 (br d, $^{3}J_{PC}$ = 2.7 Hz), 22.5 (d, $^{3}J_{PC}$ = 8.1 Hz)(*o*-$CH_3^{Mes,b}$), 23.9, 22.3 (d, $^{3}J_{PC}$ = 6.7 Hz)(*o*-$CH_3^{Mes,a}$), 20.9 (m, *p*-$CH_3^{Mes,a}$), 20.8 (*p*-$CH_3^{Mes,b}$), 19.5 (d, $^{3}J_{PC}$ = 10.3 Hz, Me), [C_6F_5 not listed].

$^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2): δ = -11.5 ($\nu_{1/2}$ ~ 60 Hz).

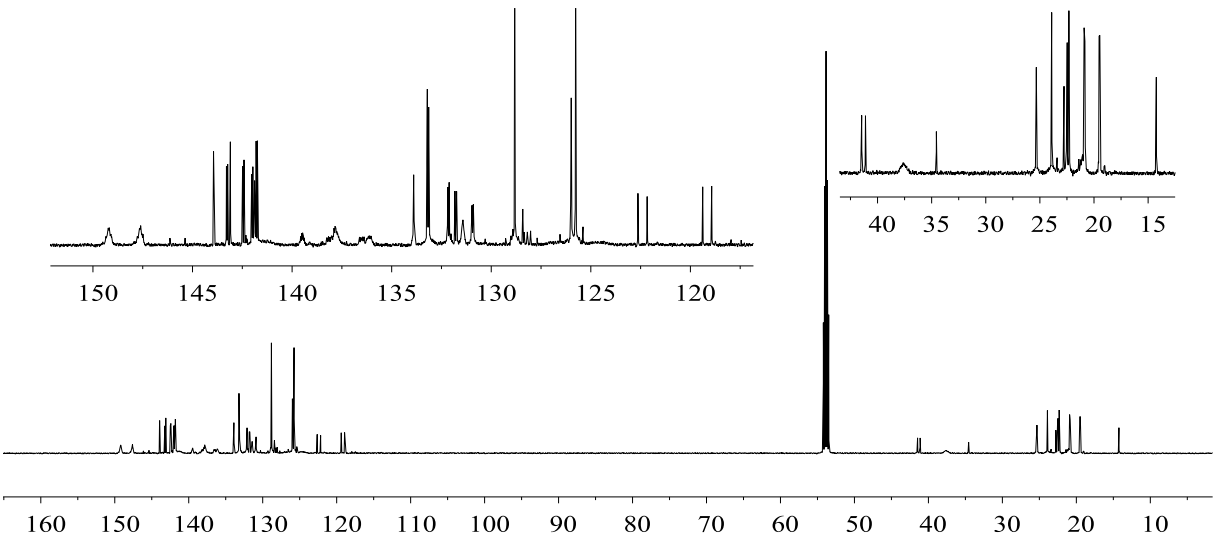
^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = -130.1, -132.6 (each br, each 2F, *o*-C_6F_5), -162.9, -163.5 (each t, J_{FC} = 20.3 Hz, each 1F, *p*-C_6F_5), -166.4, -166.5 (each br, each 2F, *m*-C_6F_5).

^{19}F NMR (470 MHz, 193 K, CD_2Cl_2): δ = -125.0, -130.7, -132.9, -136.4 (each m, each 1F, *o*-C_6F_5), -162.1, -162.8 (each br t, J_{FF} ~ 21 Hz, each 1F, *p*-C_6F_5), -165.2, -165.3, -166.1, -166.5 (each m, each 1F, *m*-C_6F_5).

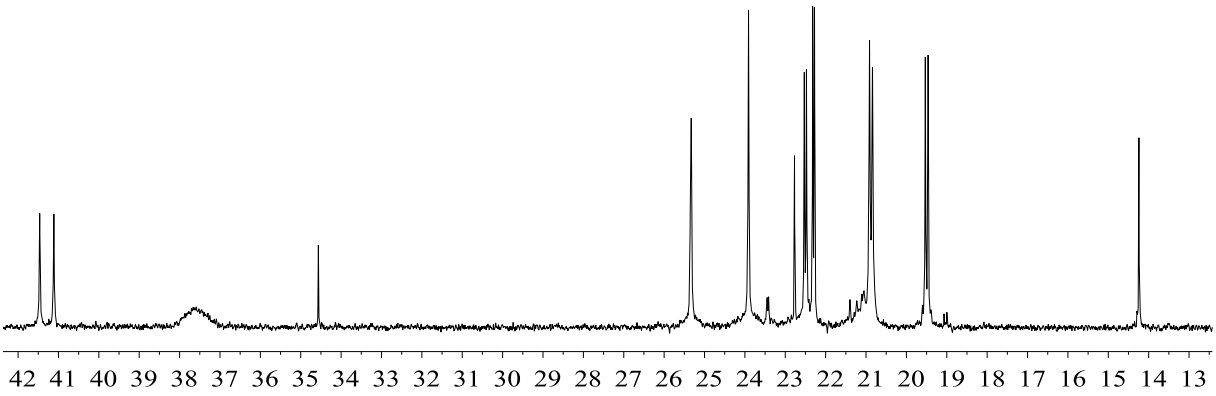
$^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, CD_2Cl_2): δ = 48.3 ($\nu_{1/2}$ ~ 8 Hz).



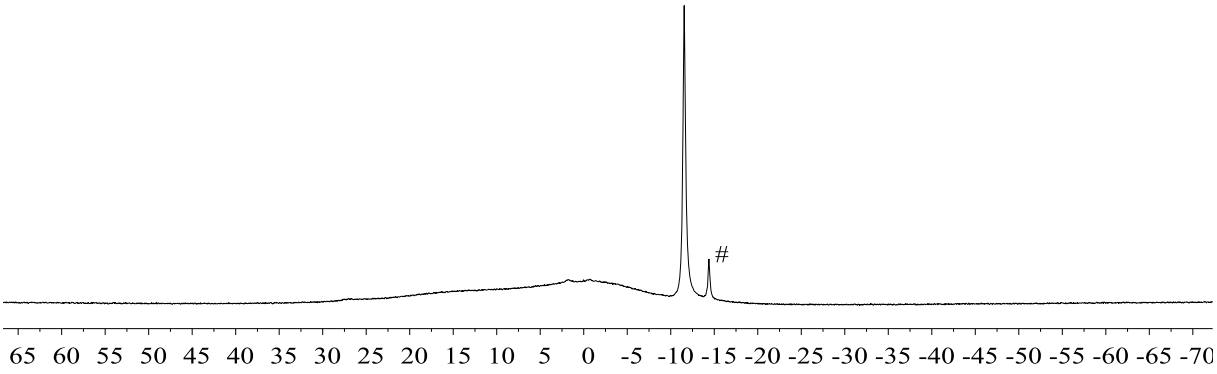
^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound **13a**. [* *n*-pentane].



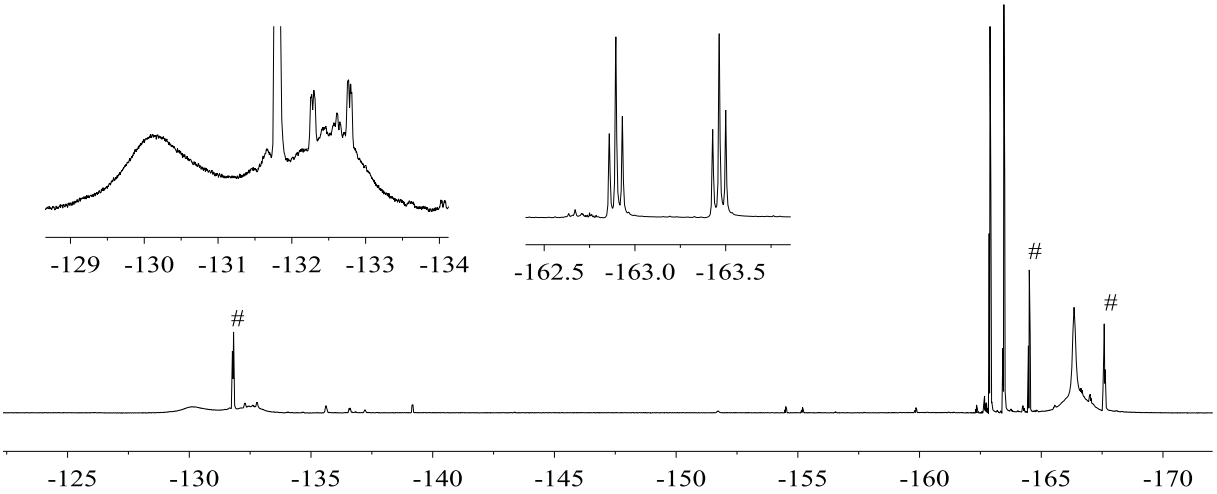
^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **13a**.



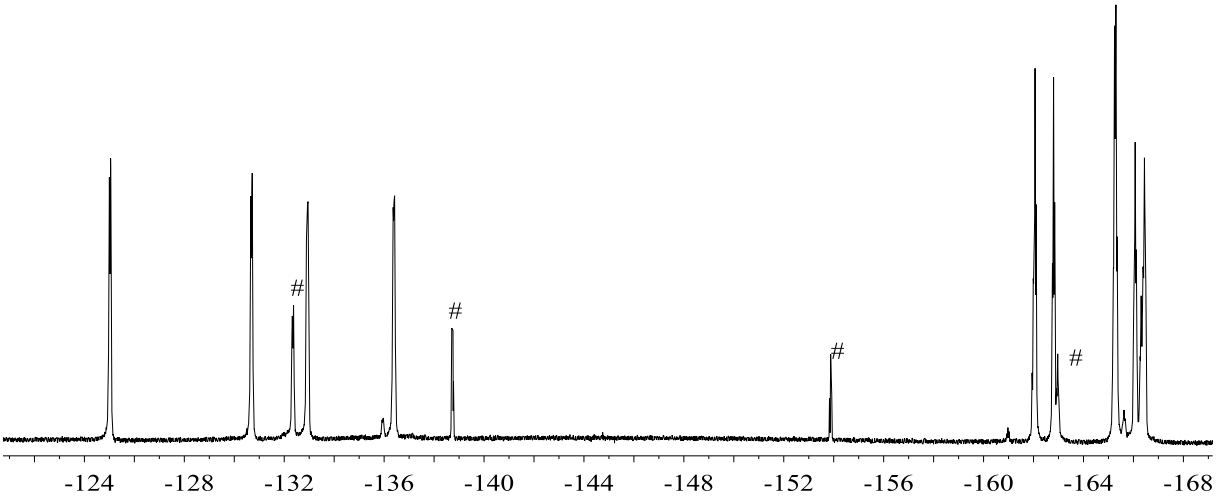
^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **13a**.



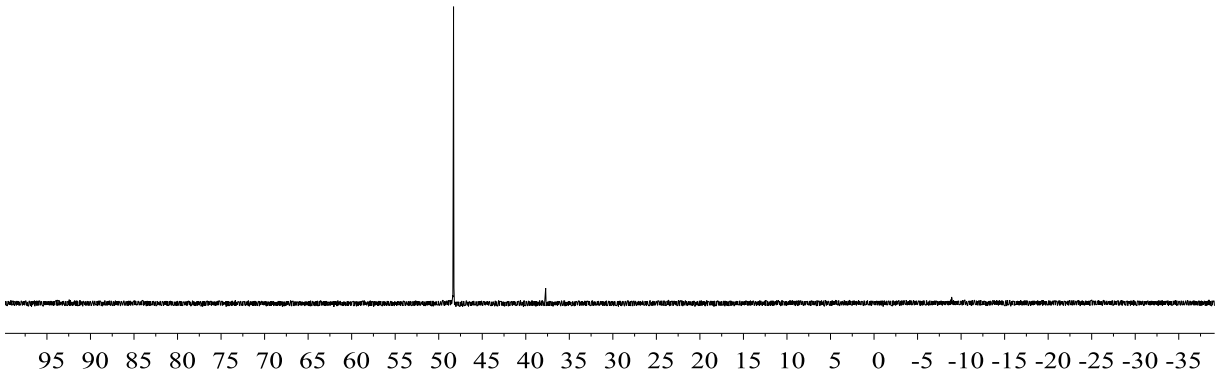
$^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of compound **13a**. [# not identified].



^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **13a**. [# not identified].



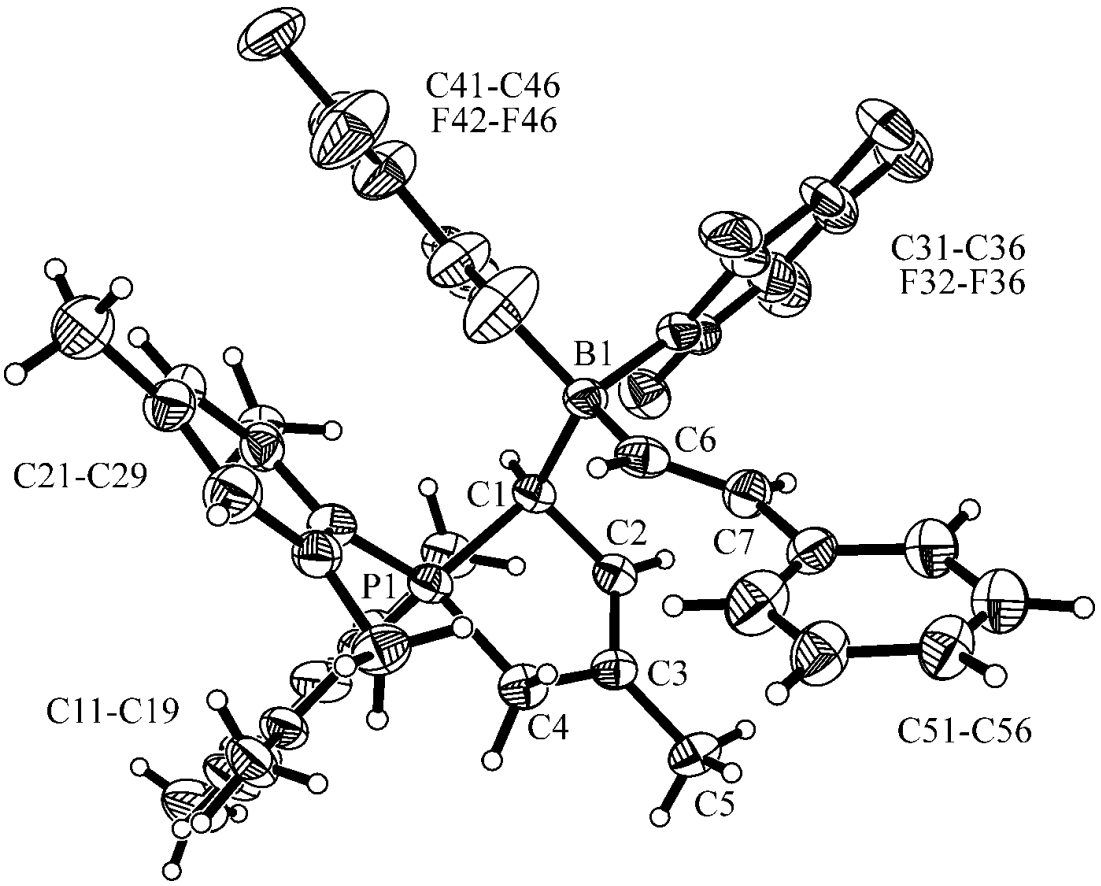
^{19}F NMR (564 MHz, 193 K, CD_2Cl_2) spectrum of compound **13a**. [# not identified].



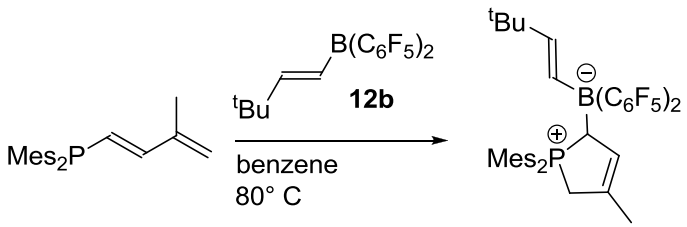
$^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, CD_2Cl_2) spectrum of compound **13a**.

Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane to a saturated solution of compound **13a** in toluene and 1 drop CH_2Cl_2 at -30 °C.

X-ray crystal structure analysis of compound 13a: formula $C_{43}H_{36}BF_{10}P$, M = 784.50, colourless crystal, 0.15 x 0.12 x 0.05 mm, a = 11.2806(4), b = 12.2184(4), c = 17.1300(8) Å, α = 75.251(1), β = 78.781(1), γ = 88.548(3)°, V = 2238.9(2) Å^3, ρ_{calc} = 1.164 gcm^{-3}, μ = 0.129 mm^{-1}, empirical absorption correction (0.980 ≤ T ≤ 0.993), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 17590 reflections collected ($\pm h$, $\pm k$, $\pm l$), 7575 independent (R_{int} = 0.080) and 4121 observed reflections [$I>2\sigma(I)$], 634 refined parameters, R = 0.101, wR^2 = 0.312, max. (min.) residual electron density 0.38 (-0.34) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.



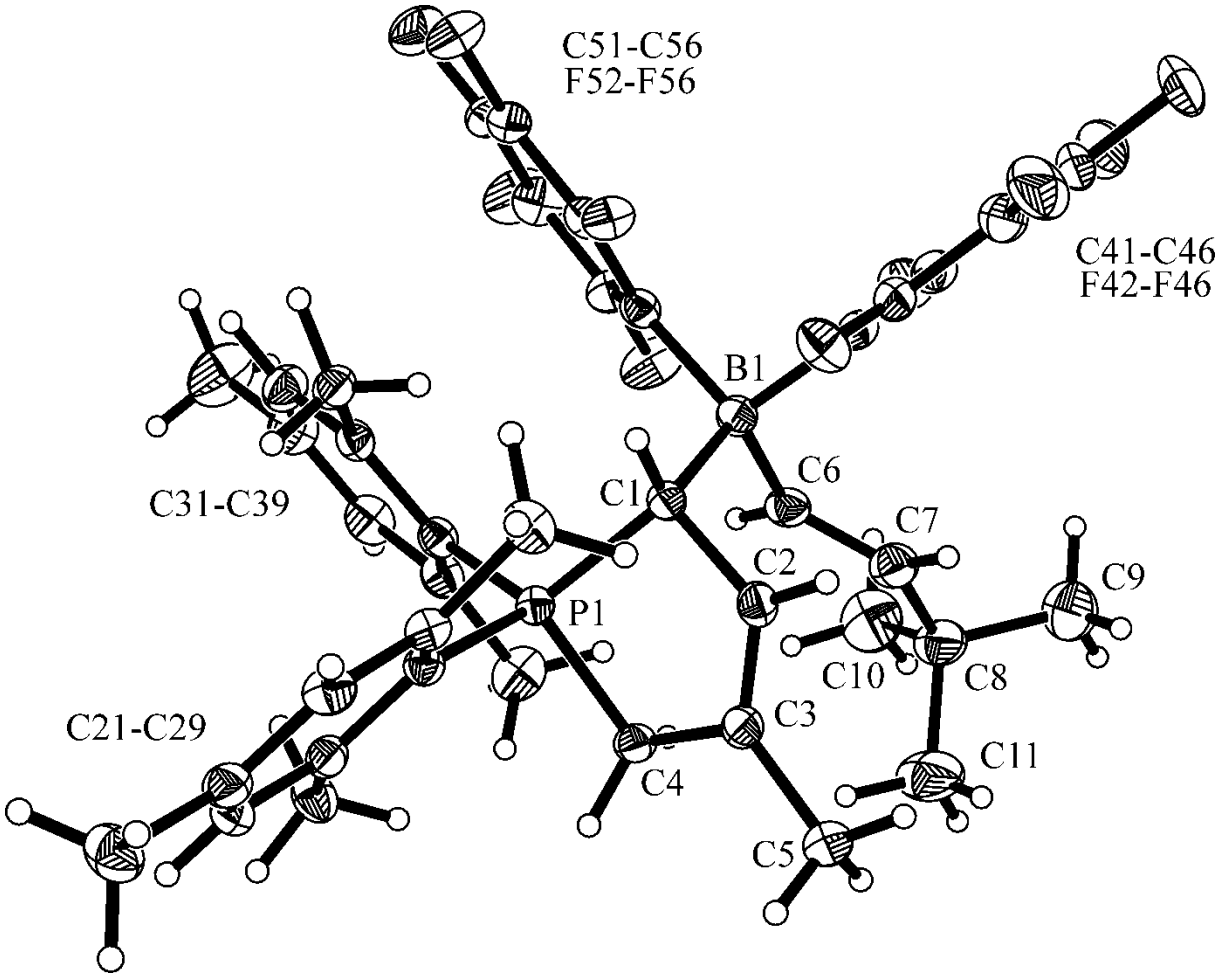
Synthesis of compound 13b.



9a **13b**

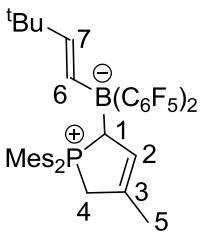
1st Experiment (X-ray crystal structure analysis): (*E*)-(3,3-dimethylbut-1-enyl)bis(pentafluorophenyl)borane **12b** (80 mg, 0.187 mmol) and phosphane **9a** (62.9 mg, 0.187 mmol) were dissolved in C_6D_6 (0.7 mL) and heated in a sealed NMR tube for 1 day at 80 °C. Subsequently the reaction mixture was characterized by NMR experiments. After 2 weeks colorless crystals were obtained inside the NMR tube, which were suitable for the X-ray crystal structure analysis.

X-ray crystal structure analysis of compound 13b: formula $C_{41}H_{40}BF_{10}P \cdot C_6H_6$, M = 842.62, colourless crystal, 0.253 x 0.128 x 0.072 mm, a = 11.2089(2), b = 30.0074(6), c = 12.2976(2) Å, β = 95.073(1)°, V = 4120.1(1) Å^3, ρ_{calc} = 1.358 gcm^{-3}, μ = 1.277 mm^{-1}, empirical absorption correction ($0.738 \leq T \leq 0.914$, Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 100(2) K, ω and φ scans, 71754 reflections collected ($\pm h$, $\pm k$, $\pm l$), 7294 independent (R_{int} = 0.052) and 6053 observed reflections [$I>2\sigma(I)$], 542 refined parameters, R = 0.038, wR^2 = 0.101, max. (min.) residual electron density 0.49 (-0.25) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.



2nd Experiment (NMR scale): (*E*)-(3,3-dimethylbut-1-enyl)bis(pentafluorophenyl)borane **12b** (63.6 mg, 0.149 mmol) and phosphane **9a** (50 mg, 0.149 mmol) were dissolved in CD_2Cl_2 (0.7 mL) and heated in a sealed NMR tube for 1d at 60 °C. Then the NMR tube was opened,

the reaction solution was refilled in a vial and *n*-pentane (3 mL) was added. The formed precipitate was collected by filtration and dried *in vacuo* to give a colorless powder (57 mg, 50%).



^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 7.01, 6.37 (each m, each 1H, *m*-Mes^{b}), 6.94, 6.86 (each m, each 1H, *m*-Mes^{a}), 6.31 (dm, $^{3}J_{HH,trans}$ = 17.6 Hz, 1H, =CHB), 6.18 (d, $^{3}J_{PH}$ = 32.3 Hz, 1H, =CH), 4.90 (d, $^{3}J_{HH,trans}$ = 17.6 Hz, 1H, =CH^{t}Bu), 4.81 (d, $^{2}J_{PH}$ = 16.6 Hz, 1H, BCH), 3.88 (dm, $^{2}J_{HH}$ = 15.6 Hz, 1H, CH_2), 2.88, 1.74 (each s, each 3H, *o*-$CH_3^{Mes,b}$), 2.87, 1.98 (each s, each 3H, *o*-$CH_3^{Mes,a}$), 2.75 (dd, $^{2}J_{HH}$ = 15.6 Hz, $^{2}J_{PH}$ = 11.7 Hz, 1H, CH_2), 2.25 (d, *J* = 0.8 Hz, 3H, *p*-$CH_3^{Mes,a}$), 2.23 (s, 3H, *p*-$CH_3^{Mes,b}$), 1.76 (m, 3H, Me), 0.94 (s, 9H, ^{t}Bu).

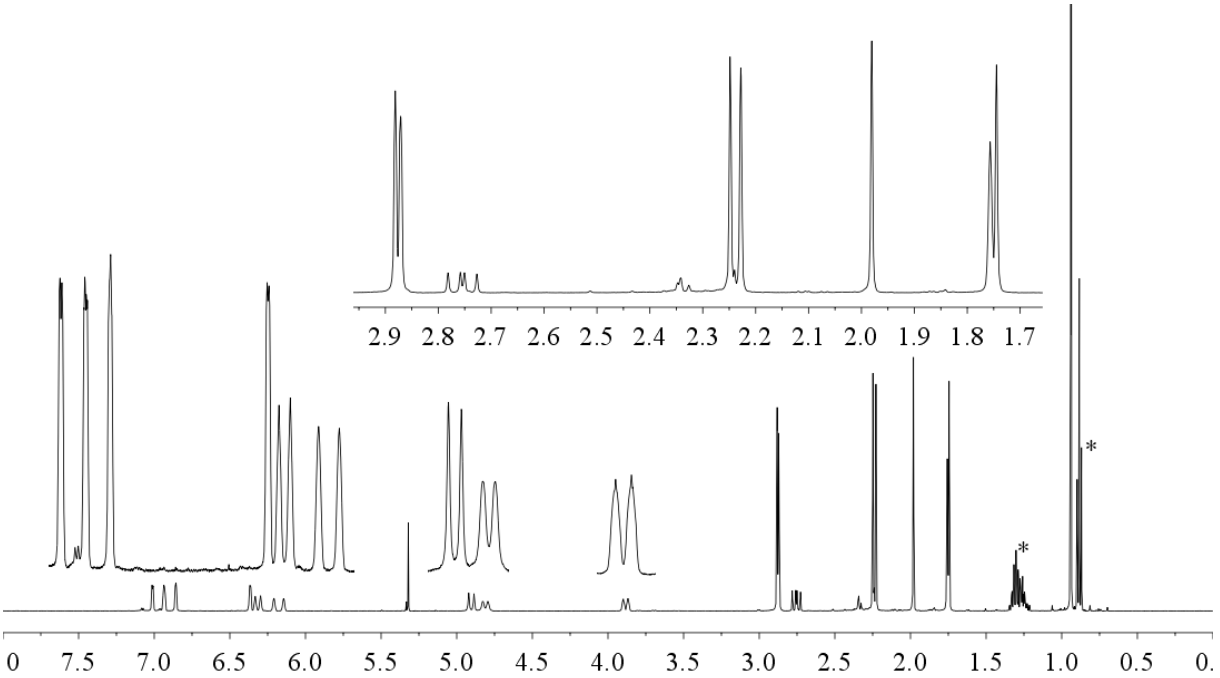
^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 145.5 (=CH^{t}Bu), 143.7 (d, $^{4}J_{PC}$ = 2.9 Hz, *p*-Mes^{b}), 143.3 (d, $^{2}J_{PC}$ = 9.0 Hz), 141.7 (d, $^{2}J_{PC}$ = 9.2 Hz)(*o*-Mes^{a}), 142.9 (d, $^{4}J_{PC}$ = 2.8 Hz, *p*-Mes^{a}), 142.3 (d, $^{2}J_{PC}$ = 10.8 Hz), 141.9 (d, $^{2}J_{PC}$ = 8.5 Hz)(*o*-Mes^{b}), 133.14 (d, $^{3}J_{PC}$ = 9.9 Hz), 133.05 (d, $^{3}J_{PC}$ = 11.3 Hz)(*m*-Mes^{a}), 132.4 (m, =CH), 131.8 (d, $^{3}J_{PC}$ = 11.1 Hz), 130.9 (d, $^{3}J_{PC}$ = 10.5 Hz)(*m*-Mes^{b}), 130.6 (d, $^{2}J_{PC}$ = 12.8 Hz, =C), 122.9 (d, $^{1}J_{PC}$ = 69.8 Hz, *i*-Mes^{a}), 119.6 (d, $^{1}J_{PC}$ = 67.1 Hz, *i*-Mes^{b}), 41.4 (d, $^{1}J_{PC}$ = 52.1 Hz, CH_2), 36.8 (br, BCH), 33.9 (^{t}Bu), 30.1 (^{t}Bu), 25.3 (d, $^{3}J_{PC}$ = 2.9 Hz), 22.5 (d, $^{3}J_{PC}$ = 8.0 Hz)(*o*-$CH_3^{Mes,b}$), 23.7 (d, $^{3}J_{PC}$ = 1.4 Hz), 22.3 (d, $^{3}J_{PC}$ = 6.5 Hz)(*o*-$CH_3^{Mes,a}$), 20.9 (d, $^{5}J_{PC}$ = 1.4 Hz, *p*-$CH_3^{Mes,a}$), 20.8 (br, *p*-$CH_3^{Mes,b}$), 19.6 (d, $^{3}J_{PC}$ = 10.1 Hz, Me), n.o. (=CB), [C_6F_5 not listed].

^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2): δ = -11.3 ($\nu_{1/2}$ ~ 70 Hz).

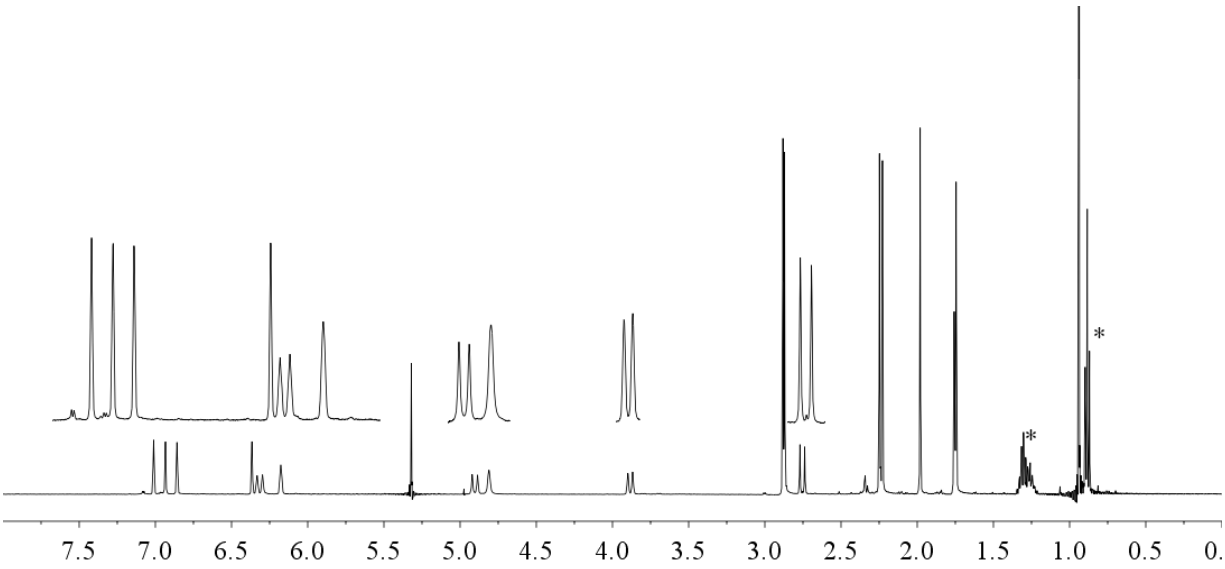
^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ = -124.0, -129.4, -132.6, -137.3 (each br, each 1F, *o*-C_6F_5), -163.7, -164.0 (each t, $^{3}J_{FF}$ = 20.2 Hz, each 1F, *p*-C_6F_5), -166.1 (1F), -167.1 (3F)(each br, *m*-C_6F_5).

^{31}P{^{1}H} NMR (202 MHz, 299 K, CD_2Cl_2): δ = 49.3 ($\nu_{1/2}$ ~ 5 Hz).

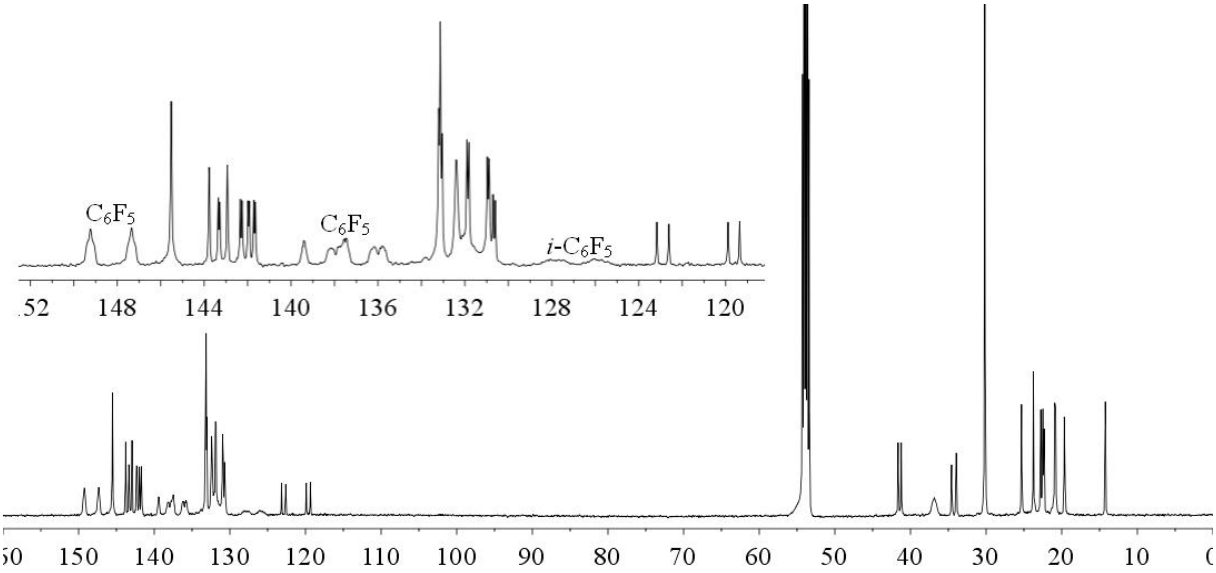
HRMS (MicroTof)**:** M+Na^+ ($C_{41}H_{40}BF_{10}PNa^+$): Calcd.: 787.27002, Found: 787.27027.



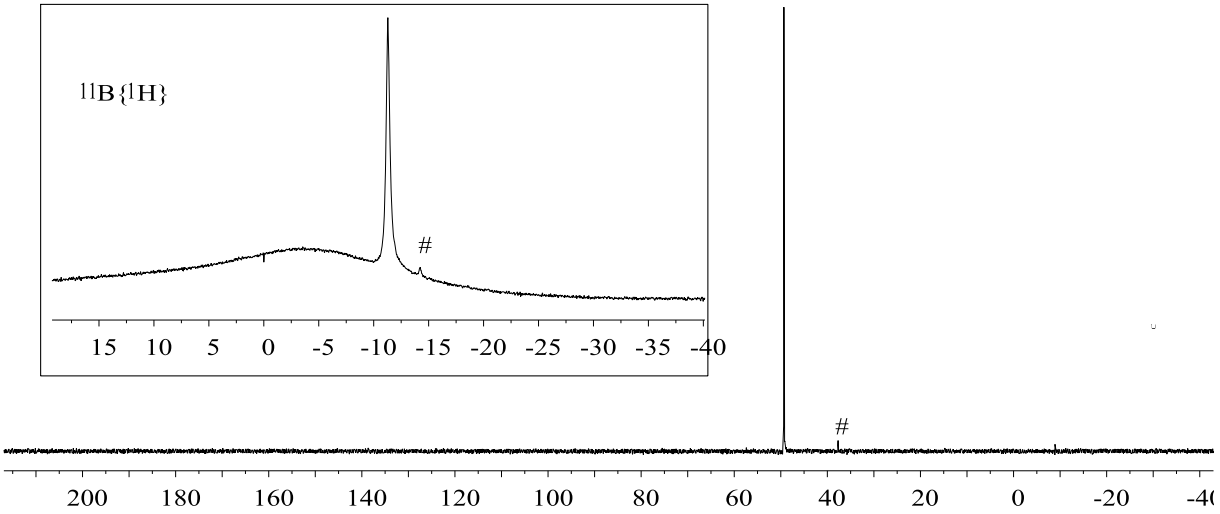
^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of compound **13b**. [* *n*-pentane].



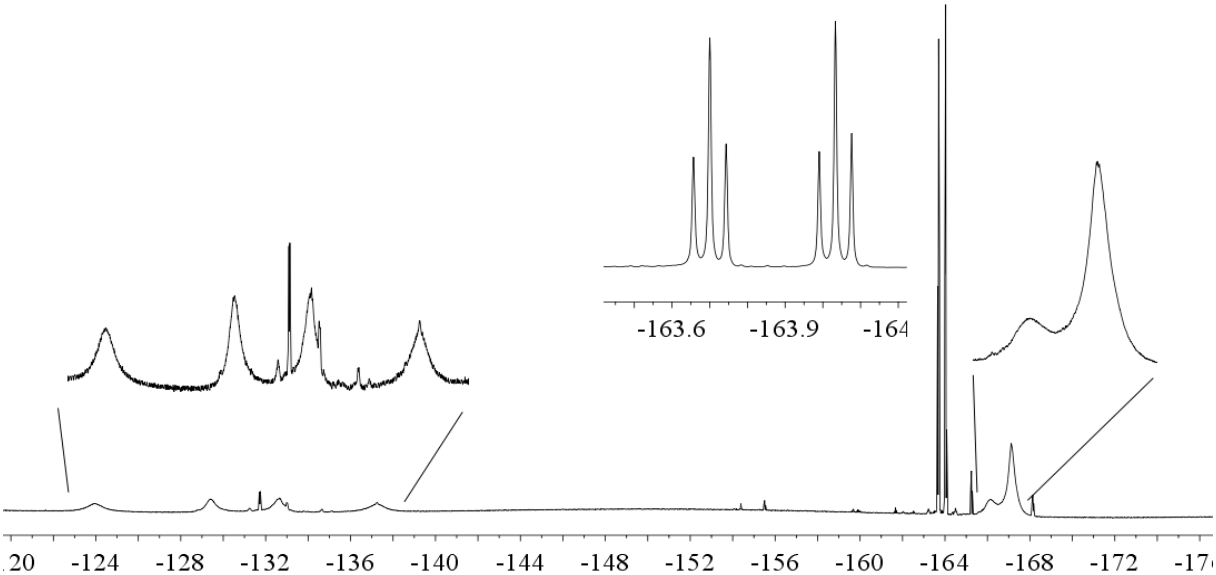
^{1}H{^{31}P} NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of compound **13b**. [* *n*-pentane].



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



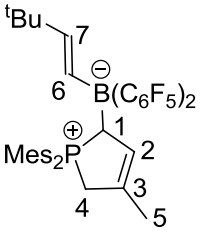
$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, CD_2Cl_2) and **$^{11}B\{^{1}H\}$ NMR** (160 MHz, 299 K, CD_2Cl_2) spectra of compound **13b**. [# not identified].



^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) spectrum of compound **13b**.

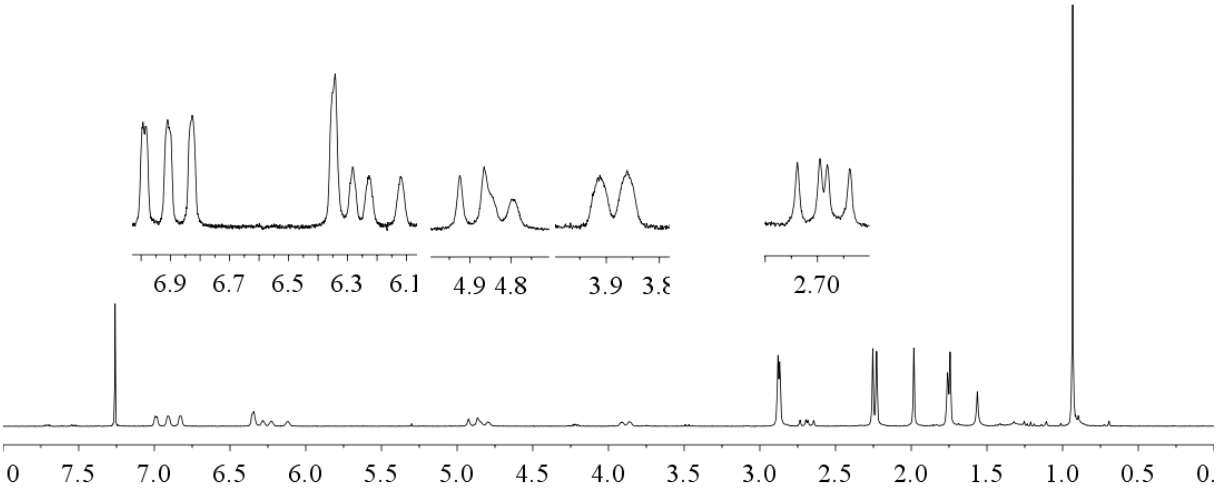
3rd Experiment (preparative scale): (*E*)-(3,3-dimethylbut-1-enyl)bis(pentafluorophenyl)-borane **12b** (392 mg, 0.916 mmol) and phosphane **9a** (308.1 mg, 0.916 mmol) were suspended in benzene (2 mL) and heated for 3.5 days at 80 °C. Then, at ambient temperature, *n*-pentane (5 mL) was added to the reaction mixture. Subsequently the colorless precipitate was collected on a frit (on air), washed with *n*-pentane (5 mL) and dried *in vacuo* (439 mg, 62%). The obtained NMR data were consistent to those listed above (*2nd Experiment).*

4th Experiment: (*E*)-(3,3-dimethylbut-1-enyl)bis(pentafluorophenyl)borane **12b** (63.6 mg, 0.149 mmol) and phosphane **9a** (50 mg, 0.149 mmol) were dissolved in C_6D_6 (0.7 mL) and irradiated with UV-light in a sealed NMR tube for 8 h. Then the NMR tube was opened and the obtained colorless crystals were washed with *n*-pentane (2 mL) and dried *in vacuo* (41.6 mg, 37%).



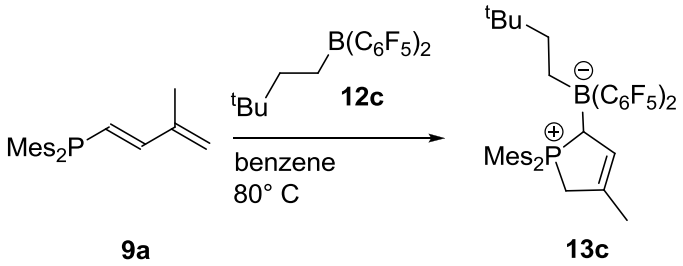
^{1}H NMR (300 MHz, 299 K, $CDCl_3$): δ = 6.99, 6.91, 6.83, 6.35 (each m, each 1H, *m*-Mes), 6.31 (d, $^3J_{HH,trans}$ = 17.8 Hz, 1H, =CHB), 6.17 (d, $^3J_{PH}$ = 32.2 Hz, 1H, =CH), 4.90 (d, $^3J_{HH}$= 17.8 Hz, 1H, =CH^{t}Bu), 4.82 (d, $^3J_{PH}$ = 16.1 Hz, BCH), 3.89 (d, $^2J_{HH}$ = 15.4 Hz), 2.69 (dd, $^2J_{HH}$ = 15.4 Hz, $^2J_{PH}$ = 11.6 Hz, 1H, CH_2), 2.88, 2.87, 2.25, 2.23, 1.98, 1.74 (each s, each 3H, CH_3^{Mes}), 1.76 (s, 3H, Me),.

Elemental analysis: Calcd. for $C_{41}H_{40}BF_{10}P$: C, 64.41; H, 5.27. Found: C, 65.84; H, 5.35.



^{1}H NMR (300 MHz, 299 K, $CDCl_3$) spectrum of compound **13b**.

Synthesis of compound 13c.



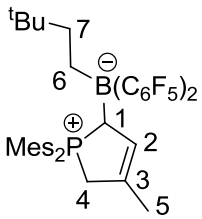
9a **13c**

(*E*)-(3,3-dimethylbutyl)-bis(pentafluorophenyl)borane **12c** (127.8 mg, 0.297 mmol) and phosphane **9a** (100 mg, 0.297 mmol) were dissolved in benzene (2 mL) and heated for 8 h at 80 °C. The formed precipitate was collected, washed with *n*-pentane (2 mL) and crystallized by slow diffusion of *n*-pentane in a solution of the solid in toluene (containing a few drops of CH_2Cl_2) at -30 °C. Then the solution was decanted and the formed colorless crystals were dried *in vacuo* (127 mg, 56%). The obtained crystals were suitable for the X-ray crystal structure analysis.

HRMS (MicroTof)**:** $M+Na^+$ ($C_{41}H_{42}BF_{10}PNa^+$): Calcd.: 789.2857, Found: 789.2864.

Elemental analysis: Calcd. for $C_{41}H_{42}BF_{10}P$: C, 64.24; H, 5.52. Found: C, 65.38; H, 5.71.

NMR characterization of a solution of the colorless crystals in CD_2Cl_2:



^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 6.99 (m), 6.93 (m), 6.85 (m), 6.50 (br)(each 1H, *m*-Mes), 6.26 (br d, $^3J_{PH}$ = 34.1 Hz, 1H, =CH), 4.88 (d, $^2J_{PH}$ = 18.1 Hz, 1H, BCH), 4.07 (br), 2.81 (br m)(each 1H, CH_2), 2.84 (s, 3H), 2.70 (br, 3H), 2.25 (s, 6H), 1.92 (s), 1.77 (br, 3H)(*o*-CH_3^{Mes}), 1.77 (s, 3H, Me), 1.32 (br), 1.01 (br m), 0.50 (br m), 0.42 (br m)(C_2H_4), 0.74 (s, 9H, ^{t}Bu).

^{1}H NMR (500 MHz, 193 K, CD_2Cl_2): δ = 6.92, 6.86, 6.80, 6.31 (each br, each 1H, *m*-Mes), 6.22 (d, $^3J_{PH}$ = 33.4 Hz, 1H, =CH), 4.76 (d, $^2J_{HH}$ = 17.5 Hz, 1H, BCH), 4.12 (d, $^2J_{HH}$ = 16.5 Hz), 2.86 (dd, $^2J_{HH}$ = 16.5 Hz, $^2J_{PH}$ = 12.1 Hz, 1H, CH_2), 2.75, 2.74, 2.17, 2.15, 1.79, 1.52^t

(each s, each 3H, *o*-CH_3^{Mes}), 1.73 (s, 3H, Me), 1.35, 0.95, 0.33, 0.29 (each m, each 1H, C_2H_4), 0.69 (s, 9H, ^{t}Bu), [^{t} tentatively assigned].

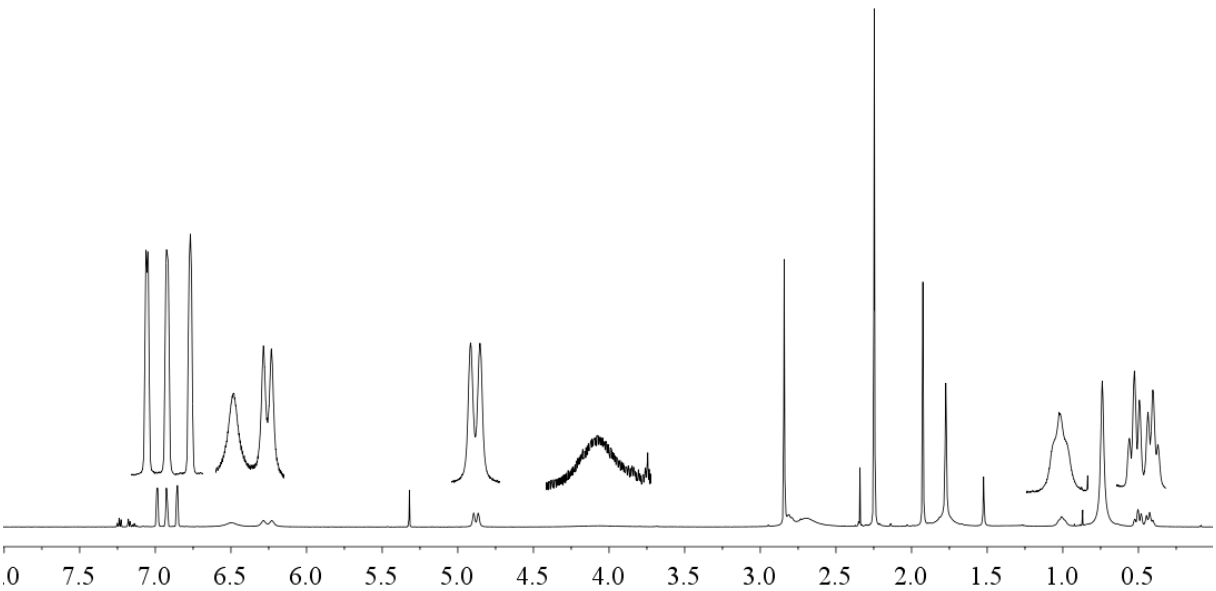
^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = 143.9 (br d, $^4J_{PC}$ = 3.0 Hz), 142.8 (d, $^4J_{PC}$ = 2.8 Hz)(*p*-Mes), 143.2 (d, $^2J_{PC}$ = 9.0 Hz), 142.5 (br), 142.3 (d, $^2J_{PC}$ = 8.5 Hz), 141.7 (d, $^2J_{PC}$ = 9.3 Hz)(*o*-Mes), 134.2 (br, =CH), 133.4 (d, $^3J_{PC}$ = 10.1 Hz), 133.1 (d, $^3J_{PC}$ = 11.5 Hz), 131.9 (d, $^3J_{PC}$ = 11.1 Hz), 131.2 (br)(*m*-Mes), 129.1 (br, =C), 123.5 (d, $^1J_{PC}$ = 71.1 Hz), 119.7 (d, $^1J_{PC}$ = 66.8 Hz)(*i*-Mes), 43.4, 17.6 (br, C_2H_4), 41.5 (br, CH_2), 38.8 (br, BCH), 31.0 (^{t}Bu), 29.6 (^{t}Bu), 25.2 (br), 23.7 (br), 22.9 (d, $^3J_{PC}$ = 8.1 Hz), 22.5 (d, $^3J_{PC}$ = 6.3 Hz), 20.97 (m), 20.85 (m)(CH_3^{Mes}), 19.7 (d, $^3J_{PC}$ = 10.2 Hz, Me). [C_6F_5 not listed].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = -9.6 ($\nu_{1/2}$ ~ 100 Hz).

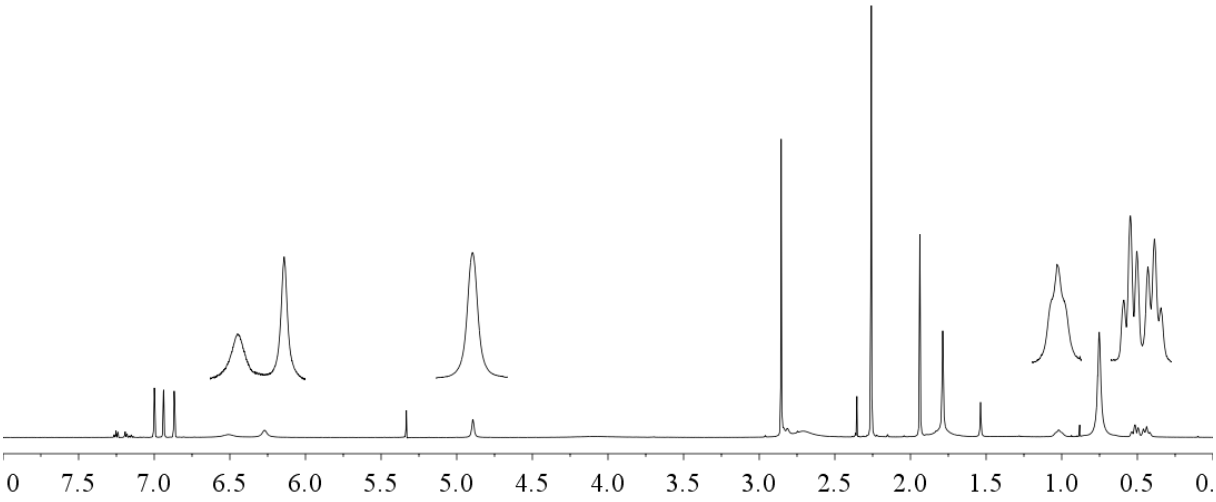
^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = -128.2, -131.4, -131.9, -137.1 (each br, each 1F, *o*-C_6F_5), -163.6 (br), -164.0 (t, $^3J_{FF}$ = 20.3 Hz)(each 1F, *p*-C_6F_5), -167.2 (br, 4F, *m*-C_6F_5).

^{19}F NMR (470 MHz, 193 K, CD_2Cl_2): δ = -128.2, -132.2, -132.6, -137.1 (each m, each 1F, *o*-C_6F_5), -162.9, -163.3 (each t, $^3J_{FF}$ = 21.0 Hz, each 1F, *p*-C_6F_5), -165.67, -165.72, -166.0, -166.7 (each br m, each 1F, *m*-C_6F_5).

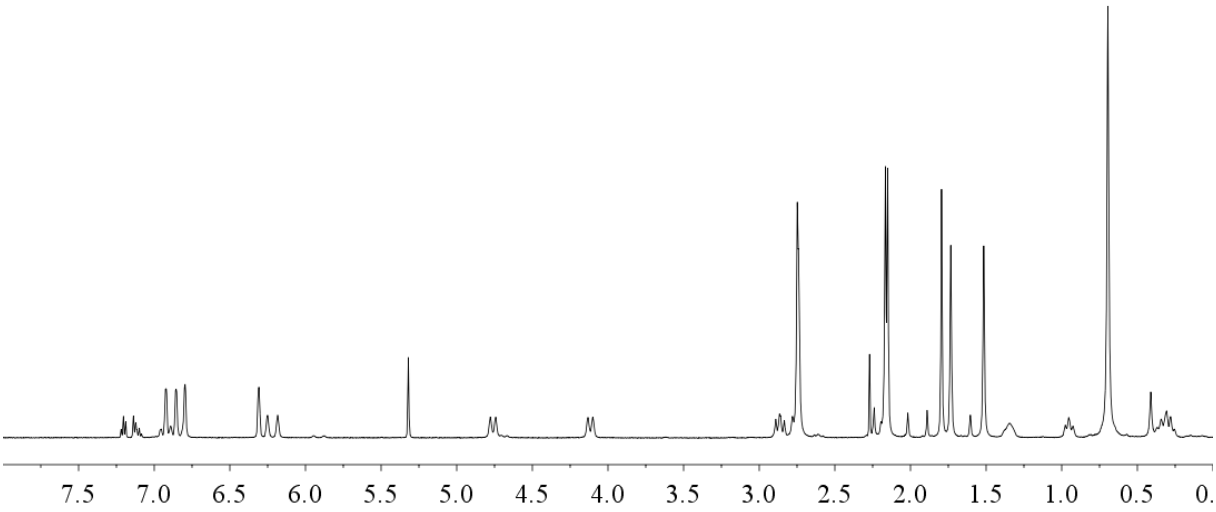
^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = 49.1 ($\nu_{1/2}$ ~ 90 Hz).



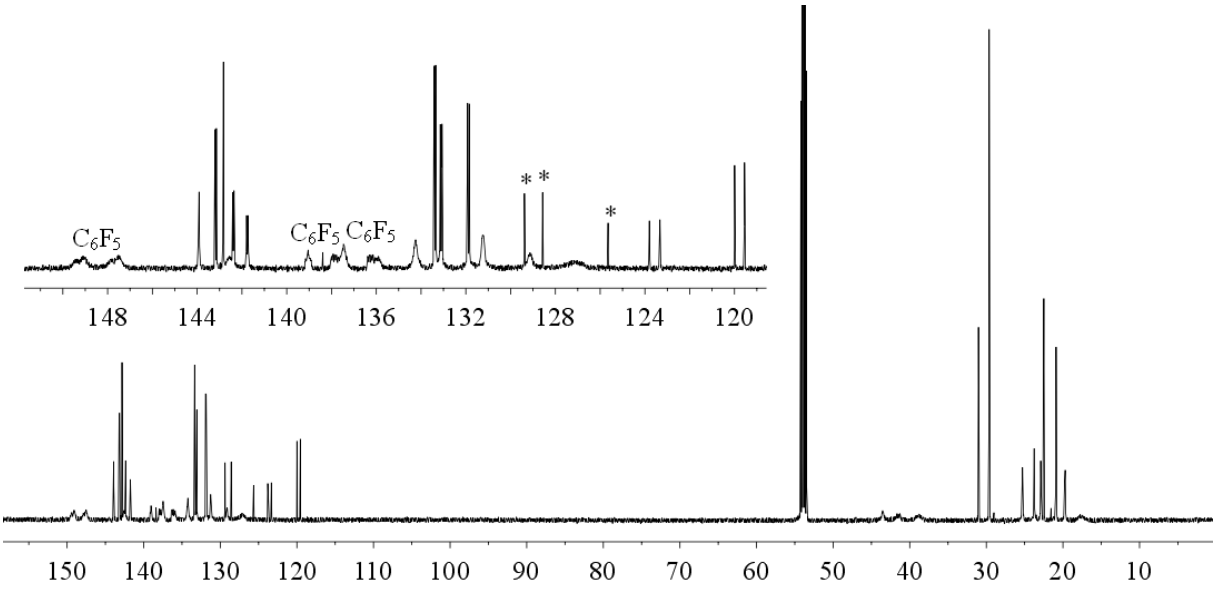
^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound **13c**.



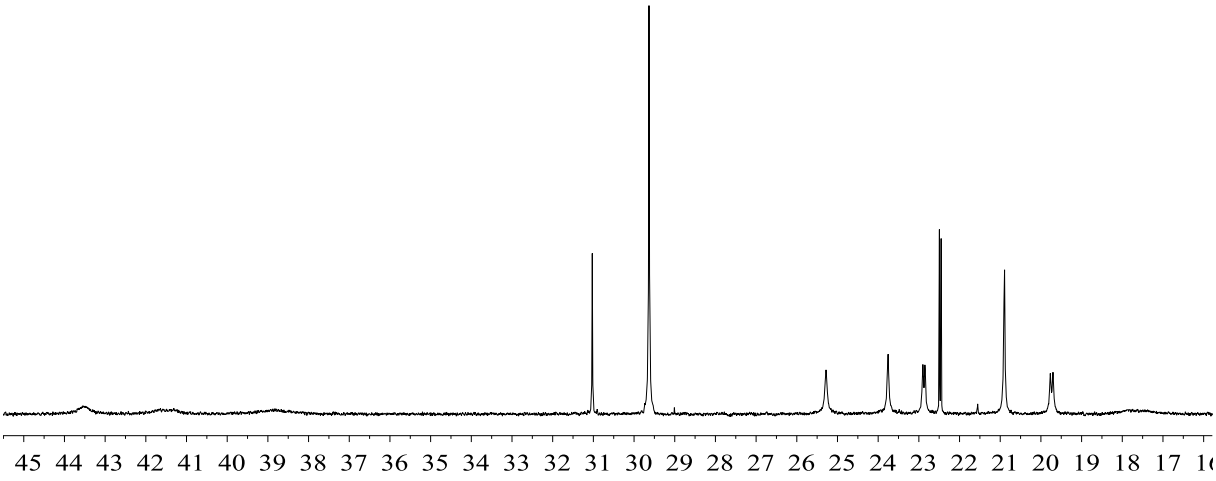
$^{1}H\{^{31}P\}$ NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound **13c**.



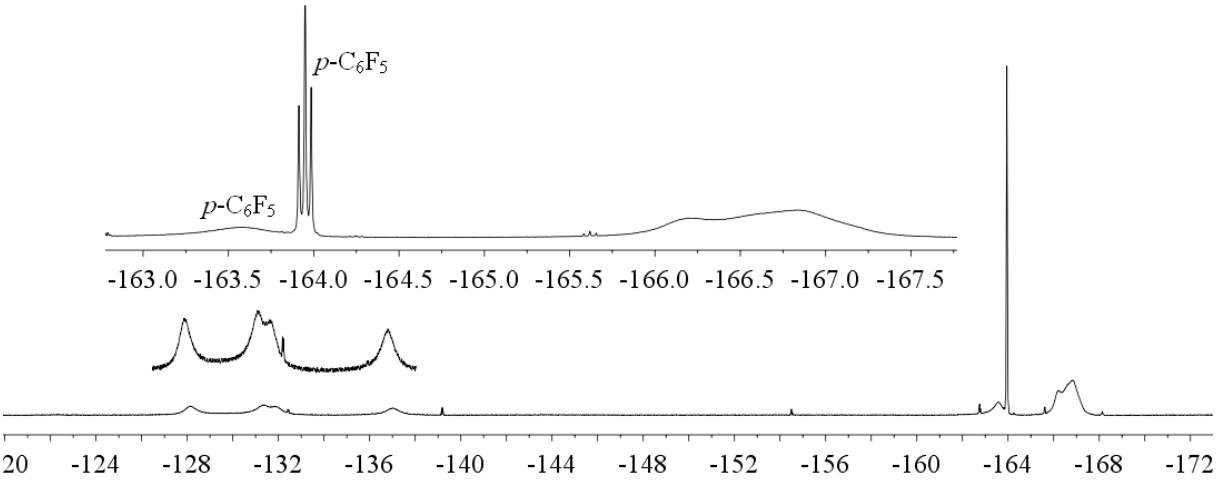
^{1}H NMR (500 MHz, 193 K, CD_2Cl_2) spectrum of compound **13c**.



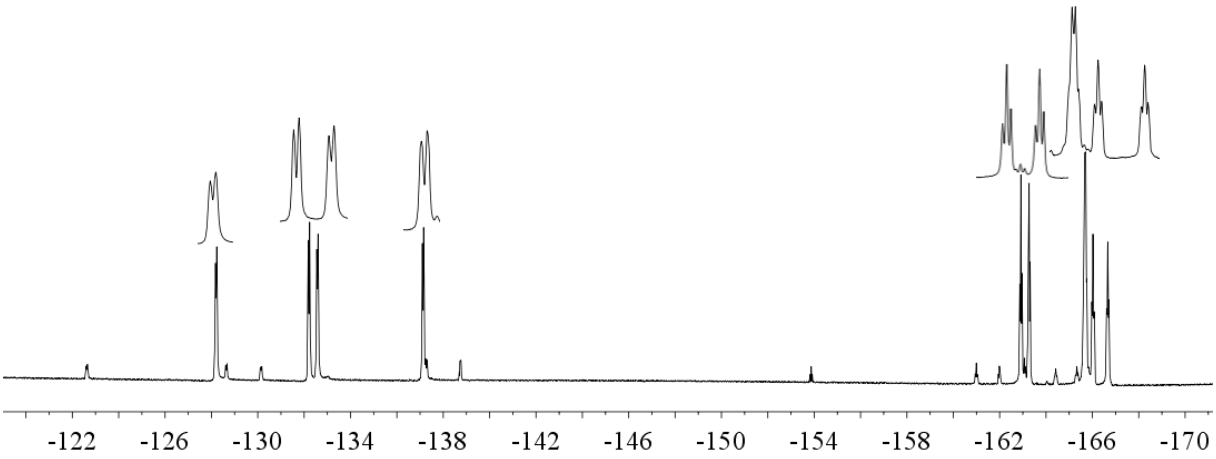
$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **13c**.



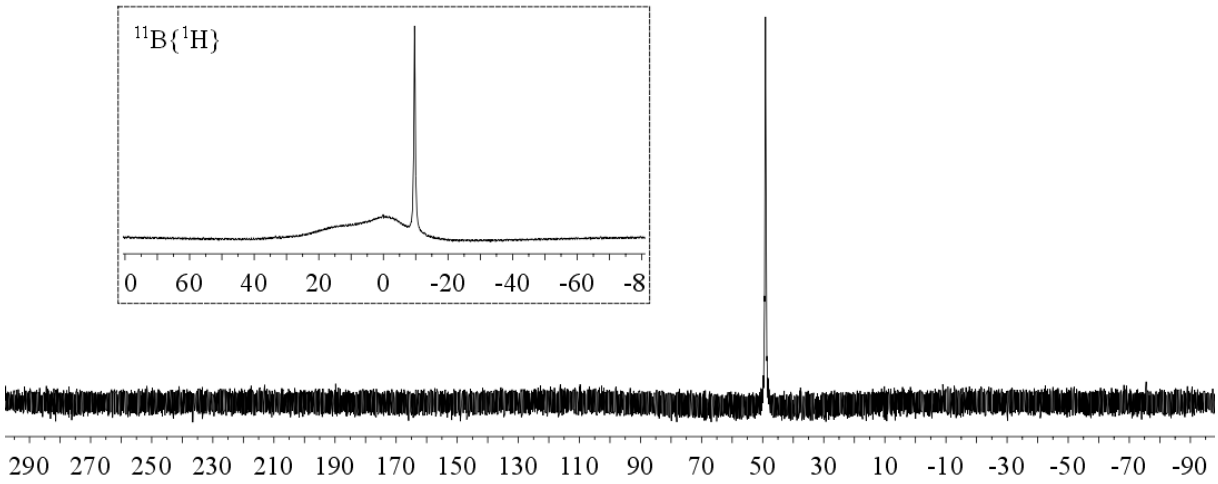
$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **13c**.



^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **13c**.

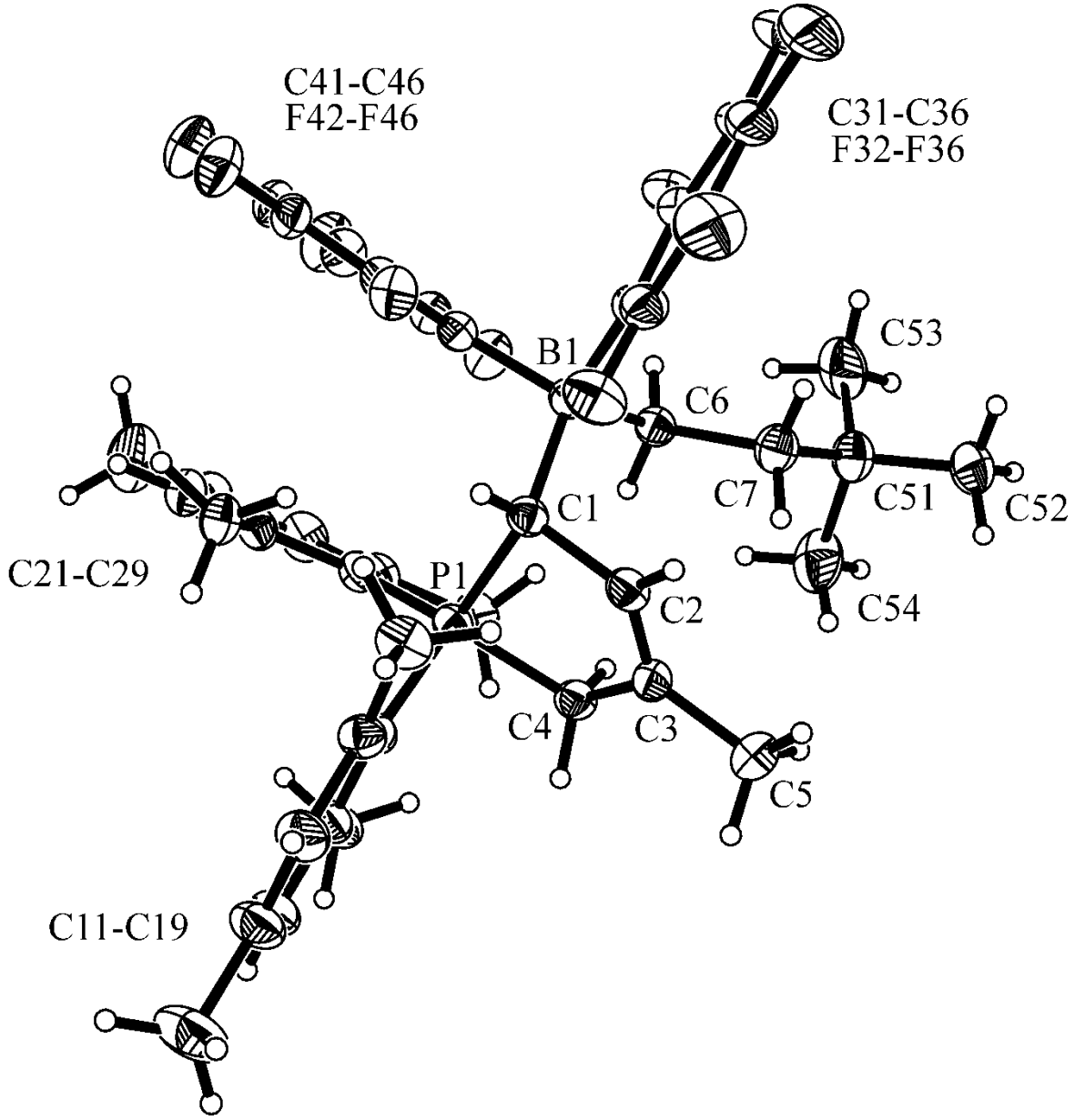


^{19}F NMR (470 MHz, 193 K, CD_2Cl_2) spectrum of compound **13c**.

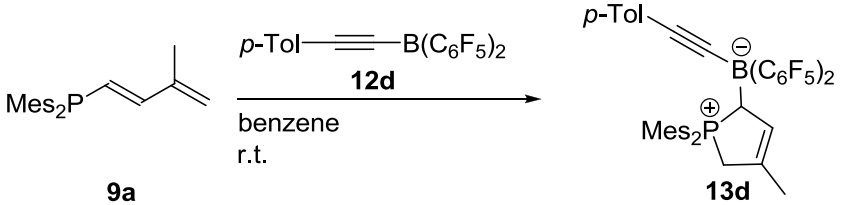


^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2) and **^{31}P{^{1}H} NMR** (243 MHz, 299 K, CD_2Cl_2) spectra of compound **13**.

X-ray crystal structure analysis of compound 13c: formula $C_{41}H_{42}BF_{10}P$, M = 766.53, colourless crystal, 0.20 x 0.06 x 0.03 mm, a = 11.3620(2), b = 12.3977(2), c = 18.5833(5) Å, α = 73.774(1), β = 76.677(1), γ = 88.827(1)°, V = 2443.1(1) Å^3, ρ_{calc} = 1.042 gcm^{-3}, μ = 0.117 mm^{-1}, empirical absorption correction (0.977 ≤ T ≤ 0.996), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 22100 reflections collected (±h, ±k, ±l), 8358 independent (R_{int} = 0.063) and 6068 observed reflections [I>2σ(I)], 513 refined parameters, R = 0.081, wR^2 = 0.230, max. (min.) residual electron density 0.35 (-0.32) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.



Synthesis of compound 13d.

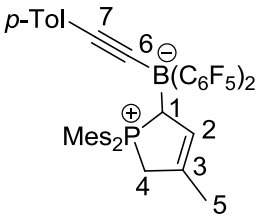


p-Tolylethynyl-bis(pentafluorophenyl)borane **12d** (136.7 mg, 0.297 mmol) and phosphane **9a** (100 mg, 0.297 mmol) were dissolved in benzene (1 mL) and stirred at ambient temperature.

After 3 days *n*-pentane (4 mL) was added to give a sticky solid and a clear orange solution. The orange solution was separated and stored at –30 °C. After two weeks an orange crystalline material was obtained, which was collected and dried *in vacuo* (35 mg, 15%).

HRMS (Orbitrap)**:** $M+H^+$ ($C_{44}H_{36}BF_{10}PH^+$): Calcd.: 797.25682, Found: 797.25467.

Elemental analysis: Calcd. for $C_{44}H_{36}BF_{10}P$: C, 66.35; H, 4.56. Found: C, 66.50; H, 4.91.



^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 7.24 (m, 2H, *o*-Tol), 7.11 (m, 2H, *m*-Tol), 6.98, 6.37 (each m, each 1H, *m*-Mes^b), 6.95, 6.87 (each m, each 1H, *m*-Mes^a), 6.28 (d, $^3J_{PH}$ = 31.8 Hz, 1H, =CH), 4.84 (br m, 1H, BCH), 4.76 (br d, $^2J_{HH}$ = 16.0 Hz, 1H, CH_2), 2.93, 1.75 (s, 3H, *o*-$CH_3^{Mes,b}$), 2.89, 1.95 (s, 3H, *o*-$CH_3^{Mes,a}$), 2.82 (dd, $^2J_{HH}$ = 16.0 Hz, $^2J_{PH}$ = 11.5 Hz, 1H, CH_2), 2.33 (s, 3H, Me^{Tol}), 2.26 (s, 3H, *p*-$CH_3^{Mes,a}$), 2.22 (s, 3H, *p*-$CH_3^{Mes,b}$), 1.91 (s, 3H, Me),.

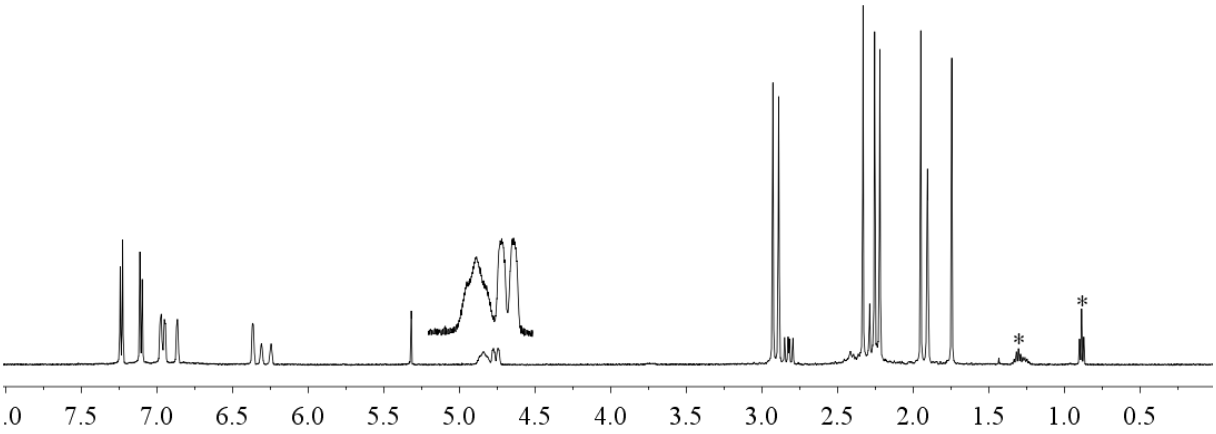
^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 143.9 (d, $^4J_{PC}$ = 2.9 Hz, *p*-Mes^b), 143.5 (d, $^2J_{PC}$ = 8.8 Hz), 142.1 (d, $^2J_{PC}$ = 10.9 Hz)(*o*-Mes^b), 143.1 (d, $^4J_{PC}$ = 2.8 Hz, *p*-Mes^a), 142.9 (d, $^2J_{PC}$ = 8.9 Hz), 141.7 (d, $^2J_{PC}$ = 9.3 Hz)(*o*-Mes^a), 136.9 (*p*-Tol), 133.2 (d, $^3J_{PC}$ = 10.0 Hz), 133.0 (d, $^3J_{PC}$ = 11.4 Hz)(*m*-Mes^a), 132.4 (d, $^2J_{PC}$ = 12.4 Hz, =C), 131.8 (d, $^3J_{PC}$ = 11.4 Hz), 130.7 (d, $^3J_{PC}$ = 10.7 Hz)(*m*-Mes^b), 131.2 (*o*-Tol), 131.0 (br, =CH), 129.3 (*m*-Tol), 124.0 (*i*-Tol), 123.1 (d, $^1J_{PC}$ = 70.5 Hz, *i*-Mes^a), 119.3 (d, $^1J_{PC}$ = 69.2 Hz, *i*-Mes^b), 107.4 (1:1:1:1 q, $^1J_{CB}$ = 76.6 Hz, ≡CB), 96.4 (br, ≡C), 41.8 (d, $^1J_{PC}$ = 52.0 Hz, CH_2), 36.8 (br m, BCH), 25.0 (d, $^3J_{PC}$ = 2.9 Hz), 22.4 (d, $^3J_{PC}$ = 7.9 Hz)(*o*-$CH_3^{Mes,b}$), 23.6, 22.3 (d, $^3J_{PC}$ = 6.6 Hz)(*o*-$CH_3^{Mes,a}$), 21.4 (Me^{Tol}), 20.9 (d, $^5J_{PC}$ = 1.4 Hz, *p*-$CH_3^{Mes,a}$), 20.8 (d, $^5J_{PC}$ = 1.4 Hz, *p*-$CH_3^{Mes,b}$), 19.8 (d, $^3J_{PC}$ = 10.7 Hz, Me). [C_6F_5 not listed].

^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2): δ = -18.1 ($\nu_{1/2}$ ~ 20 Hz).

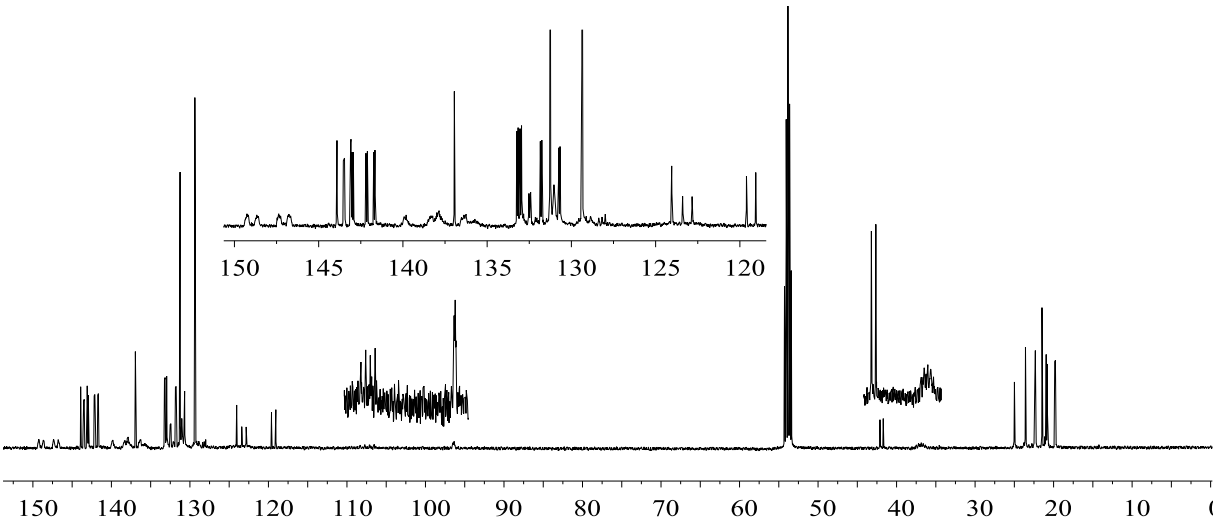
^{31}P{^{1}H} NMR (202 MHz, 299 K, CD_2Cl_2): δ = 49.1 ($\nu_{1/2}$ ~ 10 Hz).

^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ = -127.0 (1F), -132.6 (2F), -134.2 (1F)(each br, *o*-C_6F_5), -162.5, -163.3 (each t, $^3J_{FF}$ = 20.3 Hz, each 1F, *p*-C_6F_5), -165.4 (br, 1F), -166.1 (m, 2F), -167.7 (br, 1F)(*m*-C_6F_5).

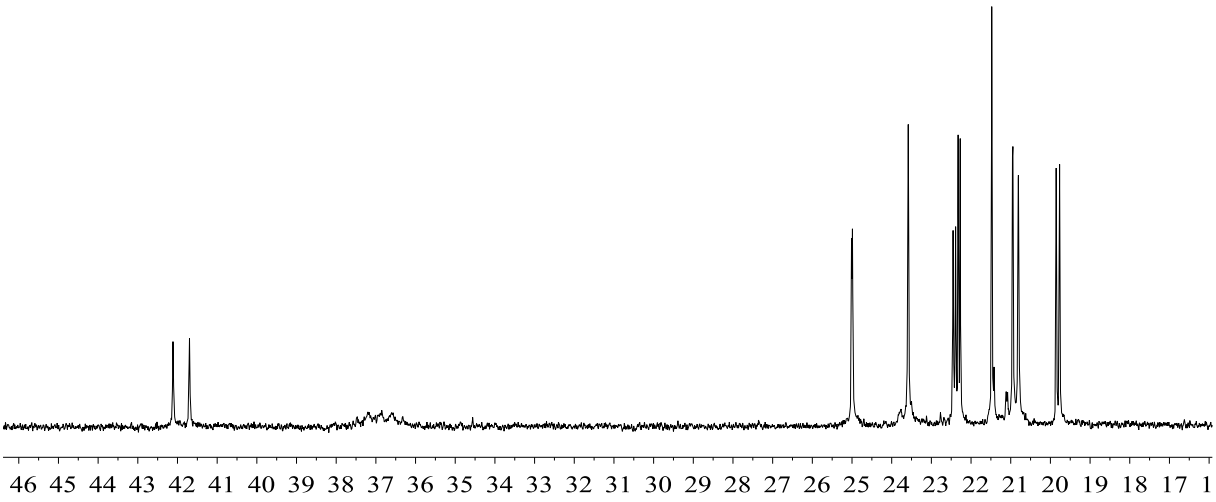
^{19}F NMR (470 MHz, 193 K, CD_2Cl_2): δ = -127.8, -128.4, -134.4, -137.2 (each m, each 1F, *o*-C_6F_5), -161.2, -162.5 (each br t, *J* = 21.4 Hz, each 1F, *p*-C_6F_5), -164.7, -165.0, -165.3, -167.1 (each m, each 1F, *m*-C_6F_5).



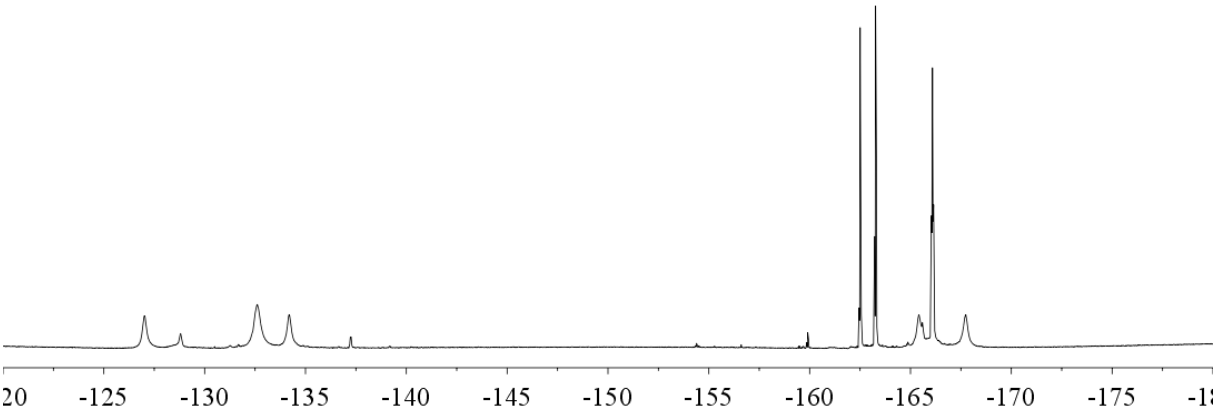
^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of compound **13d**. [* *n*-pentane].



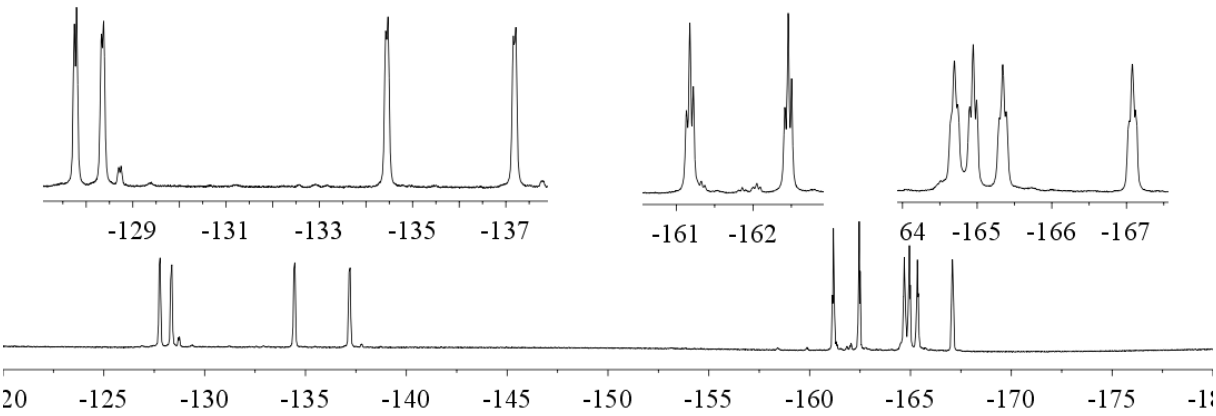
^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2) spectrum of compound **13d**.



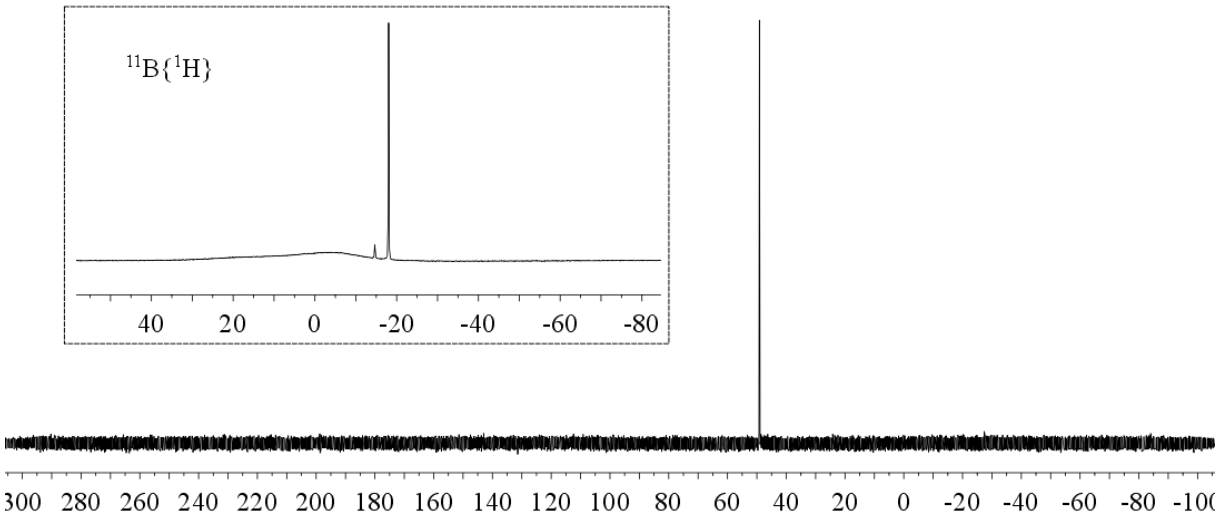
$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) spectrum of compound **13d**.



^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) spectrum of compound **13d**.

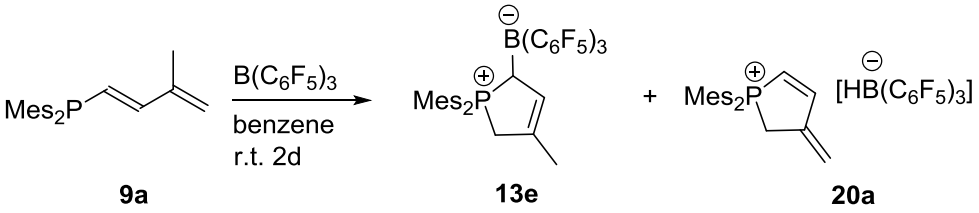


^{19}F NMR (470 MHz, 193 K, CD_2Cl_2) spectrum of compound **13d**.



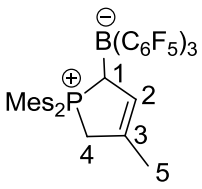
$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, CD_2Cl_2) spectrum of compound **13d**.

Reaction of compound 9a with $B(C_6F_5)_3$.



9a **13e** **20a**

1st Experiment: Tris(pentafluorophenyl)borane (76.1 mg, 0.149 mmol) and phosphane **9a** (50 mg, 0.149 mmol) were dissolved in C_6D_6 (0.7 mL) at room temperature. After 2 days standing at ambient temperature the reaction mixture was characterized by NMR experiments, which showed the formation of compounds **13e** and **20a** (ratio: 45 : 55 (^{31}P)). [Comment: the isolation of the compounds failed].

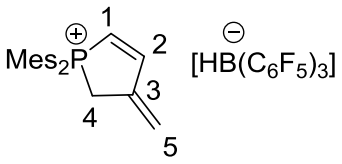


^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 6.51, 6.45, 6.40, 6.25 (each m, each 1H, *m*-Mes), 6.12 (d, $^{3}J_{PC}$ = 34.1 Hz, 1H, =CH), 5.83 (m, 1H, BCH), 2.90, 2.14 (each m, each 1H, CH_2), 2.85 (o), 1.98 (o), 1.97 (o), 1.85 (p), 1.82 (p), 1.64 (o), (each s, each 3H, CH_3^{Mes}), 1.20 (s, 3H, Me).

$^{13}C\{^1H\}$ NMR (151 MHz, 299 K, C_6D_6): δ = 143.9, 142.7 (each d, $^5J_{PC}$ = 2.9 Hz, *p*-Mes), 143.09 (d, $^2J_{PC}$ = 8.6 Hz), 143.05 (d, $^2J_{PC}$ = 11.1 Hz), 142.6 (d, $^2J_{PC}$ = 8.7 Hz), 141.3 (d, $^2J_{PC}$ = 10.0 Hz)(*o*-Mes), 133.6 (d, $^3J_{PC}$ = 11.4 Hz), 133.2 (d, $^3J_{PC}$ = 10.5 Hz), 131.6 (d, $^3J_{PC}$ = 11.4 Hz), 130.7 (d, $^3J_{PC}$ = 10.9 Hz)(*m*-Mes), 132.2 (m, =CH), 130.7 (d, $^2J_{PC}$ = 10.9 Hz, =C), 123.3 (d, $^1J_{PC}$ = 72.3 Hz), 117.6 (d, $^1J_{PC}$ = 67.0 Hz)(*i*-Mes), 39.7 (d, $^1J_{PC}$ = 51.3 Hz, CH_2), 37.2 (br, BCH), 24.4, 23.8, 23.1, 22.4 (each br, *o*-CH_3^{Mes}), 20.4, 20.3 (each d, $^5J_{PC}$ = 1.3 Hz, *p*-CH_3^{Mes}), 18.9 (d, $^3J_{PC}$ = 9.8 Hz, Me), [C_6F_5 not listed].

$^{11}B\{^1H\}$ NMR (192 MHz, 299 K, C_6D_6): δ = -12.8 ($\nu_{1/2}$ ~ 20 Hz).

$^{31}P\{^1H\}$ NMR (243 MHz, 299 K, C_6D_6): δ = 47.9 ($\nu_{1/2}$ ~ 10 Hz).



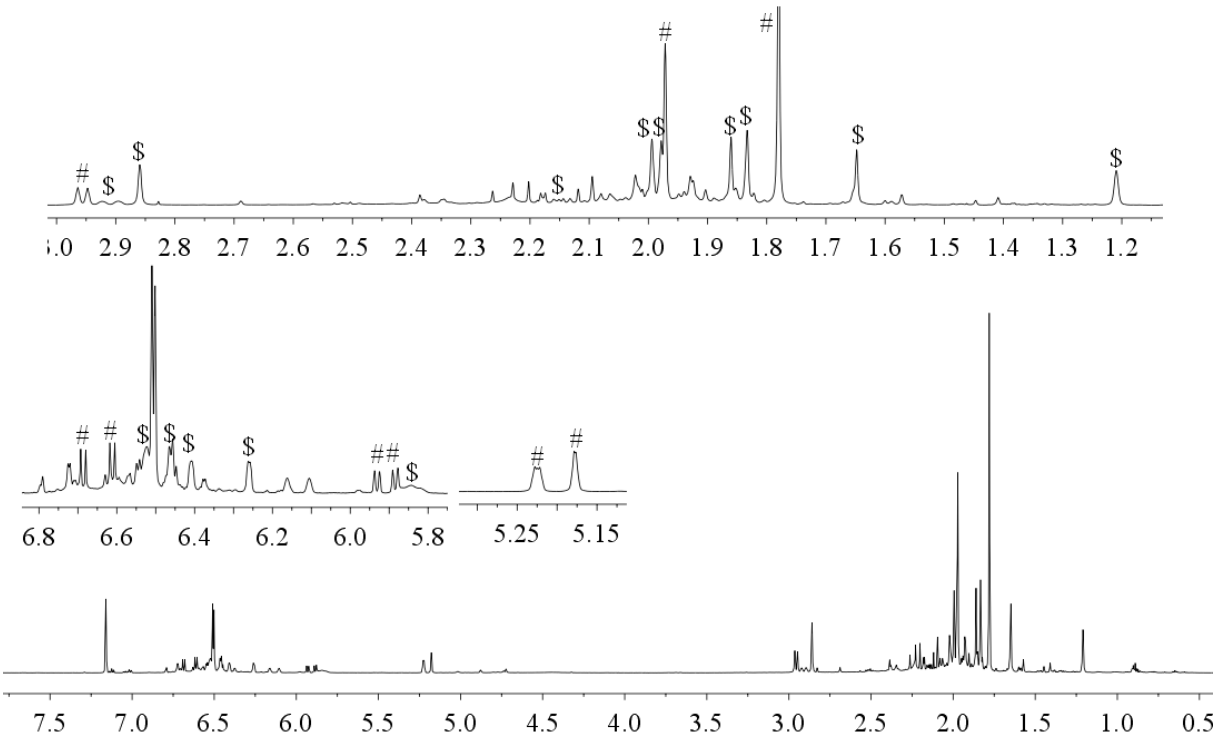
^1H NMR (600 MHz, 299 K, C_6D_6): δ = 6.64 (dd, $^3J_{PH}$ = 44.8 Hz, $^3J_{HH}$ = 7.7 Hz, 1H, =CH), 6.50 (d, $^4J_{HH}$ = 4.7 Hz, 4H, *m*-Mes), 5.90 (dd, $^2J_{PH}$ = 28.1 Hz, $^3J_{HH}$ = 7.7 Hz, 1H, PCH), 5.21, 5.17 (each m, each 1H, =CH_2), 2.95 (dm, *J* = 9.9 Hz, 2H, CH_2), 1.96 (s, 6H, *p*-CH_3^{Mes}), 1.77 (s, 12H, *o*-CH_3^{Mes}).

$^{13}C\{^1H\}$ NMR (151 MHz, 299 K, C_6D_6): δ = 153.5 (d, $^2J_{PC}$ = 10.7 Hz, =CH), 145.6 (d, $^5J_{PC}$ = 2.6 Hz, *p*-Mes), 141.5 (d, $^2J_{PC}$ = 10.6 Hz, *o*-Mes), 140.9 (d, $^2J_{PC}$ = 12.0 Hz, =C), 132.3 (d, $^3J_{PC}$ = 11.9 Hz, *m*-Mes), 121.9 (d, $^3J_{PC}$ = 11.6 Hz, =CH_2), 119.3 (d, $^1J_{PC}$ = 68.4 Hz, PCH), 117.8 (d, $^1J_{PC}$ = 82.8 Hz, *i*-Mes), 32.6 (d, $^1J_{PC}$ = 57.1 Hz, CH_2), 22.3 (d, $^3J_{PC}$ = 5.9 Hz, *o*-CH_3^{Mes}), 20.6 (d, $^5J_{PC}$ = 1.5 Hz, *p*-CH_3^{Mes}), [C_6F_5 not listed].

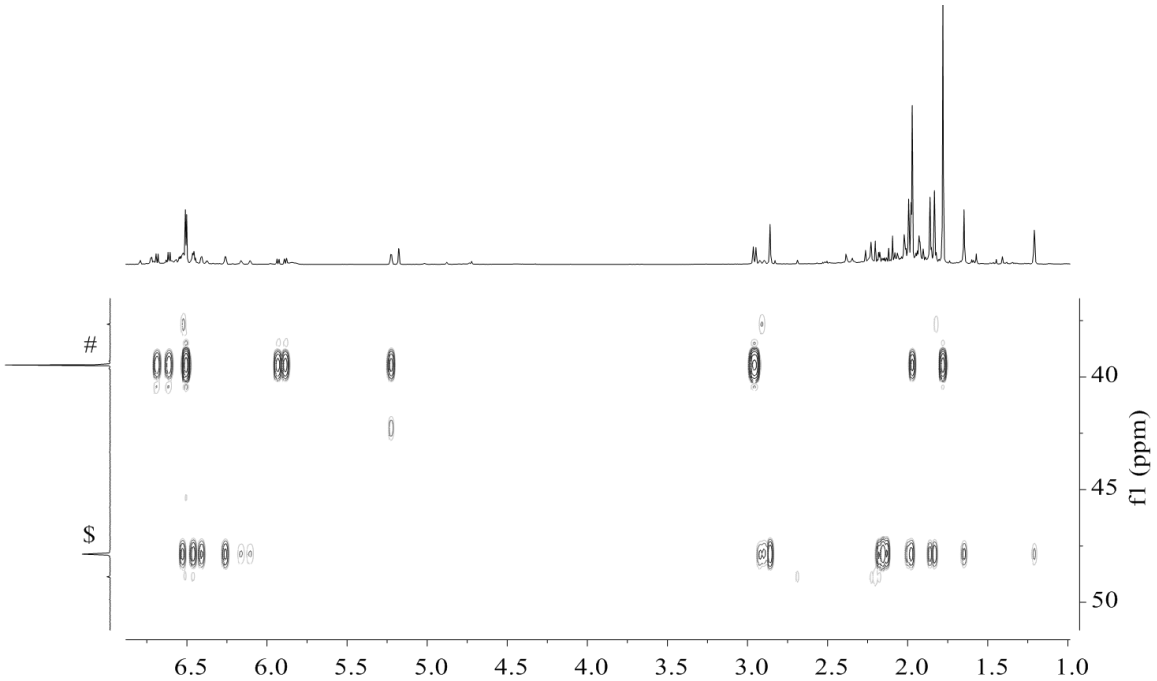
$^{11}B\{^1H\}$ NMR (192 MHz, 299 K, C_6D_6): δ = -24.2 ($\nu_{1/2}$ ~ 300 Hz).

$^{31}P\{^1H\}$ NMR (243 MHz, 299 K, C_6D_6): δ = 39.5 ($\nu_{1/2}$ ~ 3 Hz).

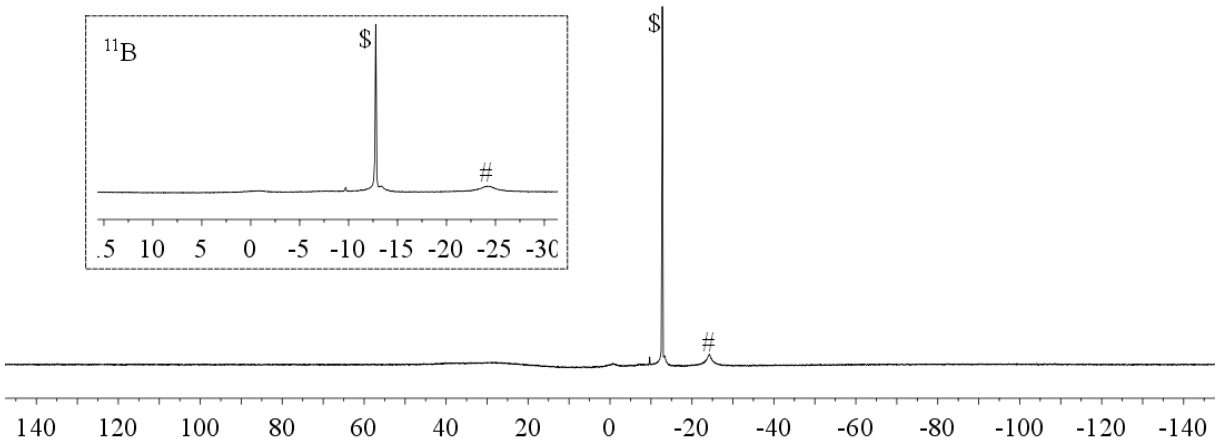
^{31}P NMR (243 MHz, 299 K, C_6D_6): δ = 39.5 (m).



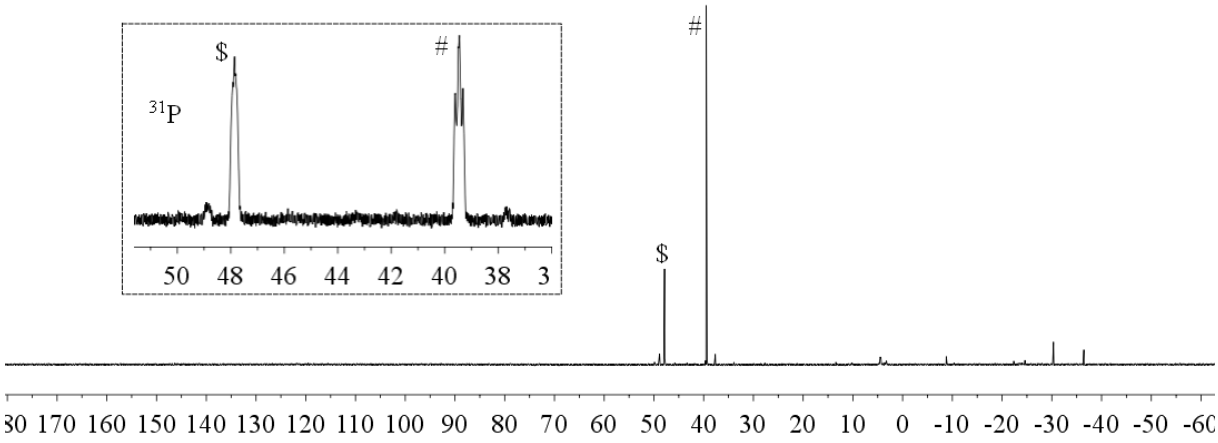
^{1}H NMR (600 MHz, 299 K, C_6D_6) spectrum of the reaction mixture of compounds **13e** ($) and **20a** (#).



^{31}P,^{1}H GHMQC (243 MHz, 600 MHz, 299 K, C_6D_6) spectrum (selected area) of the reaction mixture of compounds of **13e** ($) and **20a** (#).

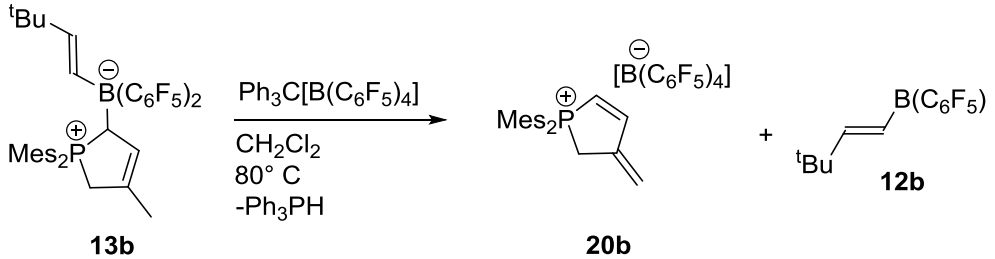


$^{11}B\{^1H\}$ NMR (192 MHz, 299 K, C_6D_6) and **^{11}B NMR** (192 MHz, 299 K, C_6D_6) spectra of the reaction mixture of compounds **13e**($) and **20a** (#).



$^{31}P\{^1H\}$ NMR (243 MHz, 299 K, C_6D_6) and **^{31}P NMR** (243 MHz, 299 K, C_6D_6) spectra of the reaction mixture of compounds **13e** ($) and **20a** (#).

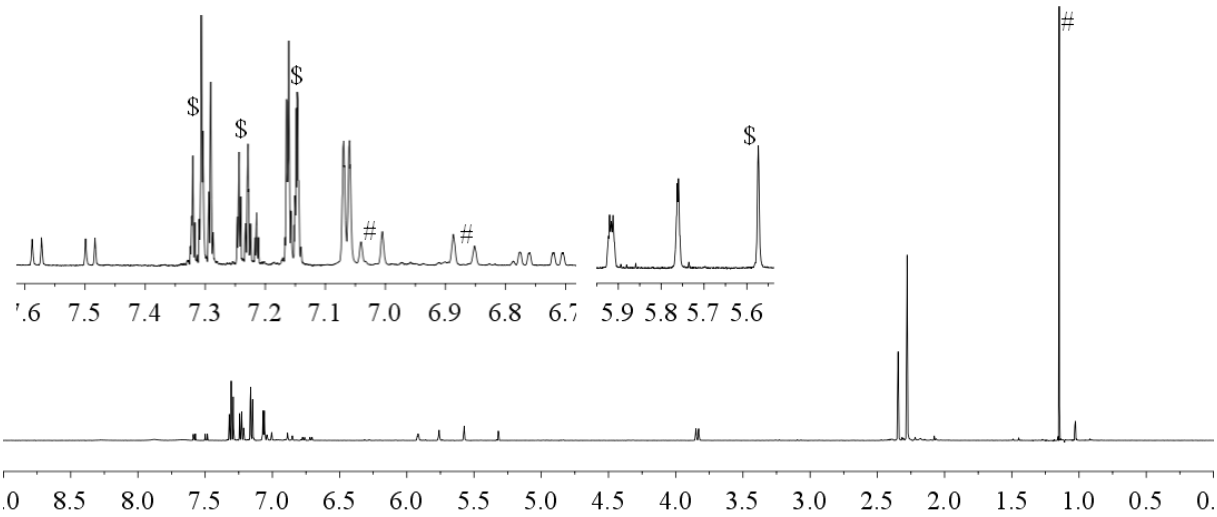
Synthesis of compound 20b.



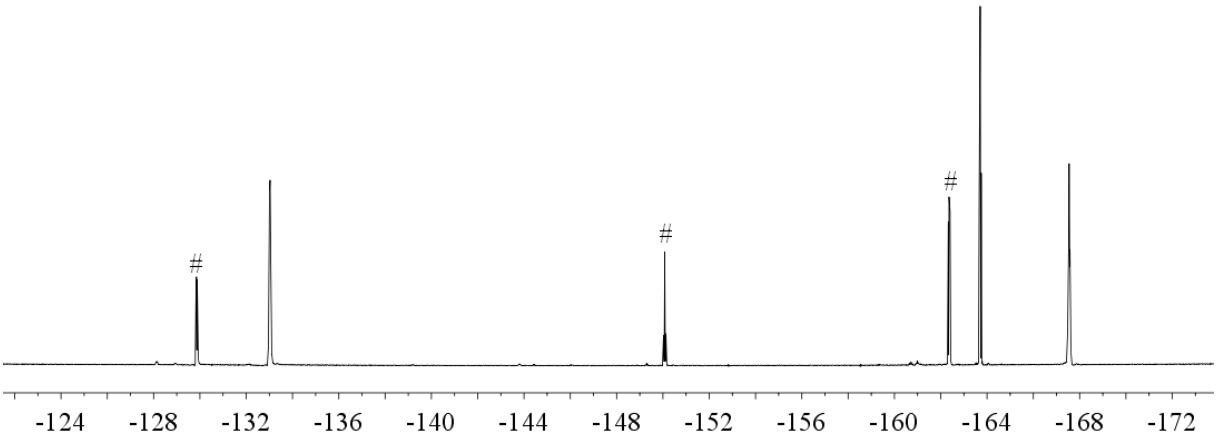
13b **20b**

1st Experiment: Compound **13b** (50 mg, 0.0654 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (60.3 mg, 0.0654 mmol) were dissolved in CD_2Cl_2 (0.7 mL). The orange solution was heated in a sealed NMR tube for 3 days at 80 °C. Then the reaction mixture was characterized by NMR experiments. [triphenylmethane: **^1H NMR** (500 MHz, 299 K, CD_2Cl_2): δ = 7.31 (m), 7.23 (p),

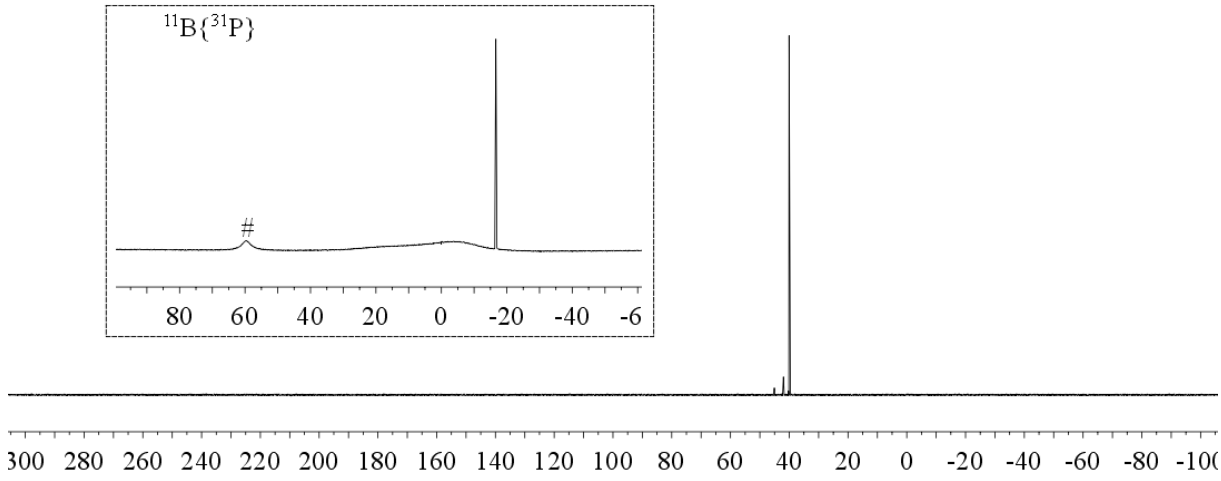
7.15 (o)(each m, 15H, Ph), 5.57 (s, 1H, CH). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, 299 K, CD_2Cl_2): δ = 144.4 (i), 126.7 (p), 128.7 (m), 129.8 (o)(Ph), 57.3 (CH)]



^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of the reaction mixture. [# 2-(*tert*-butyl)ethenylborane **12b**, $ triphenylmethane].



^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) spectrum of the reaction mixture. [# 2-(*tert*-butyl)etheny-borane **12b**].



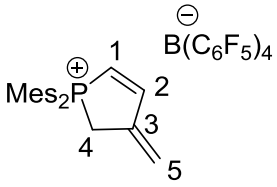
$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, CD_2Cl_2) and **$^{31}P\{^{1}H\}$ NMR** (202 MHz, 299 K, CD_2Cl_2) spectra of the reaction mixture. [# 2-(*tert*-butyl)ethenylborane **12b**].

2nd Experiment: Compound **13b** (214 mg, 0.280 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (258.2 mg, 0.280 mmol) were dissolved in CH_2Cl_2 (5 mL) and heated at 80 °C for 24 h. Then all volatiles were removed *in vacuo* and the orange red residue was washed with *n*-pentane (7 × 1 mL). Then the solid was dried *in vacuo* to give a voluminous orange powder (257 mg, 91%).

[*Comment*: the powder contains some $[Ph_3C][B(C_6F_5)_4]$, which could be not separated (ca. 16 mol% (^{1}H))].

HRMS (Orbitrap)**:** M^+ ($C_{22}H_{26}P^+$): Calcd.: 335.19231, Found: 335.19235.

Elemental analysis: Calcd. for $C_{44}H_{36}BF_{10}P$ + 1/6($[Ph_3C][B(C_6F_5)_4]$): C, 55.68; H, 2.65. Found: C, 55.75; H, 2.64.



^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 7.54 (dd, $^3J_{PH}$ = 44.4, $^3J_{HH}$ = 7.6 Hz, 1H, =CH), 7.05 (d, $^4J_{PH}$ = 4.8 Hz, 4H, *m*-Mes), 6.74 (ddm, $^2J_{PH}$ = 27.8, $^3J_{HH}$ = 7.6 Hz, 1H, PCH), 5.91, 5.76 (each m, each 1H, $=CH_2$), 3.83 (dm, $^2J_{PH}$ = 10.1 Hz, 2H, CH_2), 2.33 (s, 6H, *p*-CH_3^{Mes}), 2.26 (s, 12H, *o*-CH_3^{Mes}).

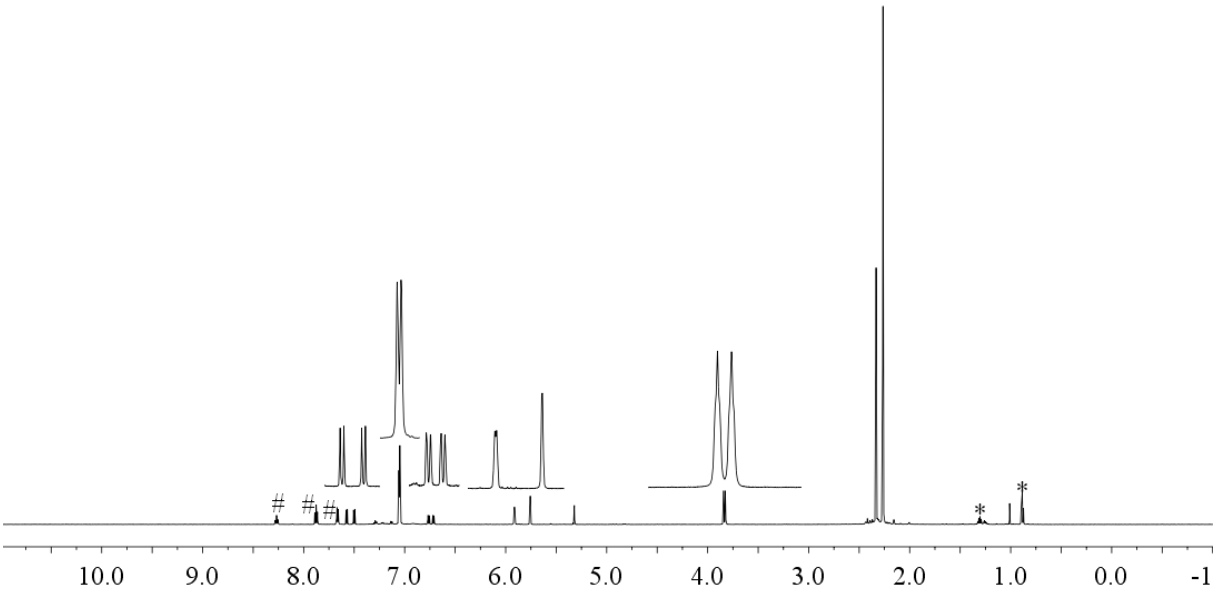
^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = 154.3 (d, $^2J_{PC}$ = 10.9 Hz, =CH), 148.5 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 146.4 (d, $^4J_{PC}$ = 3.0 Hz, *p*-Mes), 142.0 (d, $^2J_{PC}$ = 10.7 Hz, *o*-Mes), 141.2 (d, $^2J_{PC}$ = 11.8 Hz, =C), 138.6 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 136.7 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 132.9 (d, $^3J_{PC}$ = 12.0 Hz, *m*-Mes), 124.4 (br m, *i*-C_6F_5), 122.9 (d, $^3J_{PC}$ = 11.7 Hz, $=CH_2$), 120.2 (d, $^1J_{PC}$ = 69.3 Hz, PCH), 118.1 (d, $^1J_{PC}$ = 82.9 Hz, *i*-Mes), 33.9 (d, $^1J_{PC}$ = 58.1 Hz, CH_2), 23.2 (d, $^3J_{PC}$ = 6.0 Hz, *o*-CH_3^{Mes}), 21.2 (*p*-CH_3^{Mes}).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = -133.1 (m, 2F, *o*-C_6F_5), -163.7 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), -167.6 (br m, 2F, *m*- C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 3.9].

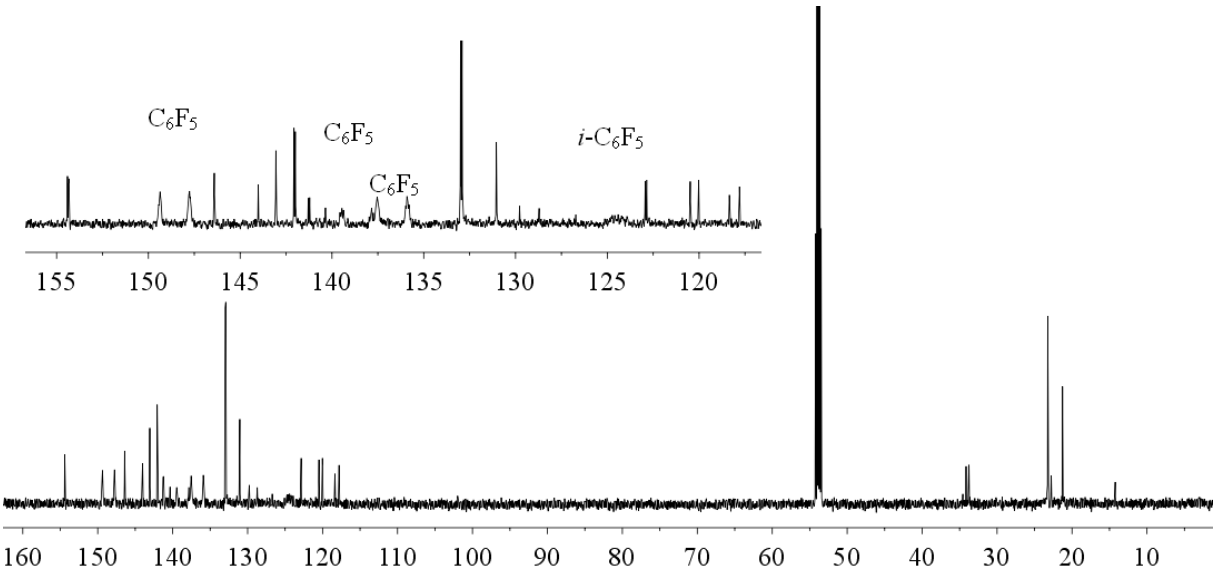
^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = -16.7 ($\nu_{1/2}$ ~ 20 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = 40.0 ($\nu_{1/2}$ ~ 2 Hz).

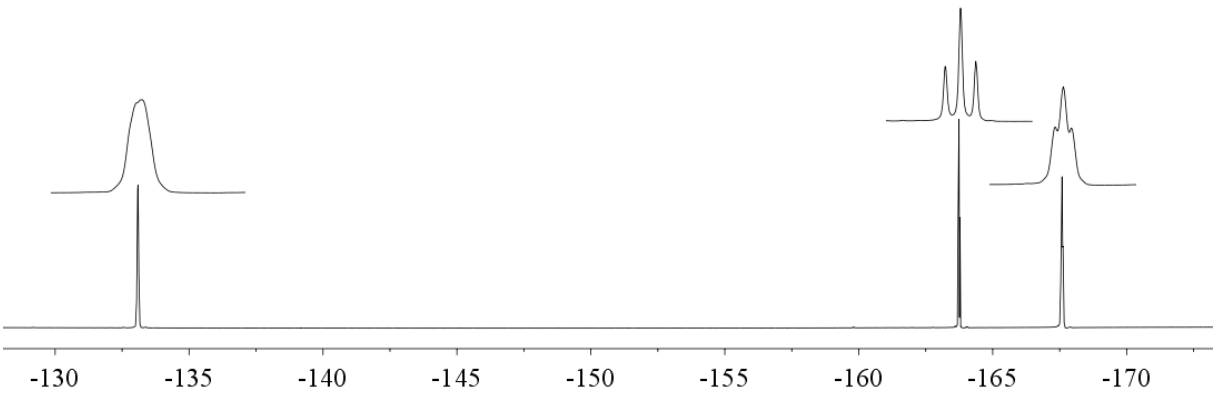
^{31}P NMR (243 MHz, 299 K, CD_2Cl_2): δ = 40.0 (m).



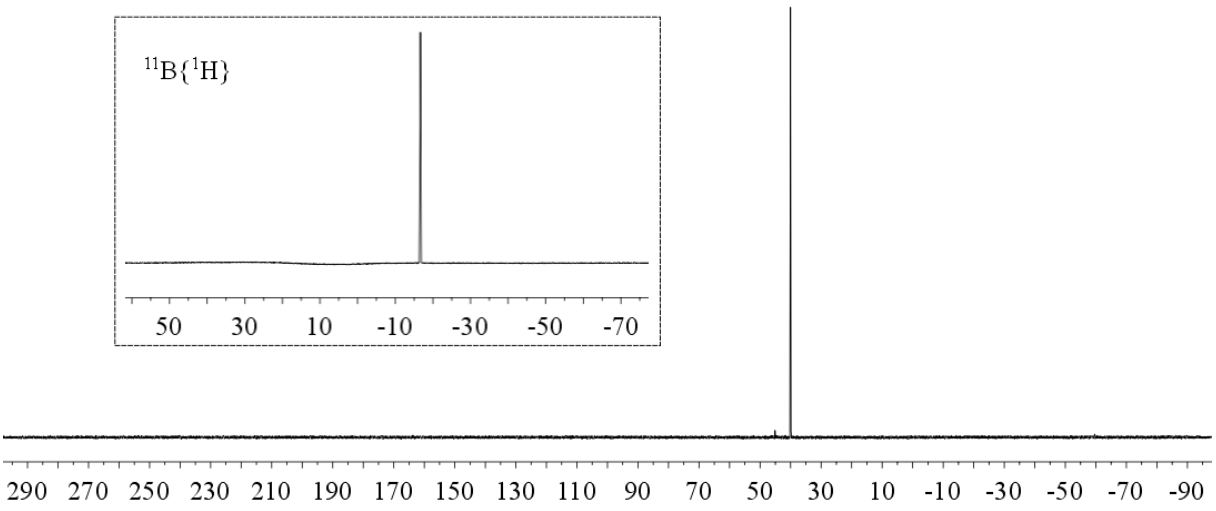
^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound **20b**. [* *n*-pentane, # Ph_3C^+].



^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **20b**.

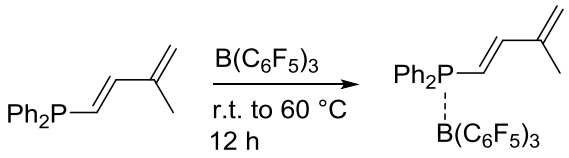


^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **20b**.



$^{11}B\{^1H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) and **$^{31}P\{^1H\}$ NMR** (243 MHz, 299 K, CD_2Cl_2) spectra of compound **20b**.

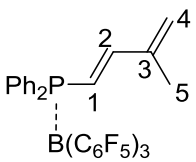
Synthesis of compound 21.



9b **21**

Compound **9b** (30 mg, 0.119 mmol) and tris(pentafluorophenyl)borane (60.9 mg, 0.119 mmol) were mixed together and dissolved in CH_2Cl_2 (1 mL). Then the reaction mixture was stirred at ambient temperature for 24 h and to complete the reaction at 60 °C for 12 h. Subsequently the obtained white suspension was diluted with *n*-pentane (1 mL) and the formed powder was collected by filtration. After drying the solid *in vacuo* compound **21** was obtained as a white powder (49 mg, 54%).

Elemental analysis: Calcd. for $C_{35}H_{17}BF_{15}P$: C, 55.00; H, 2.24. Found: C, 54.89; H, 2.38.



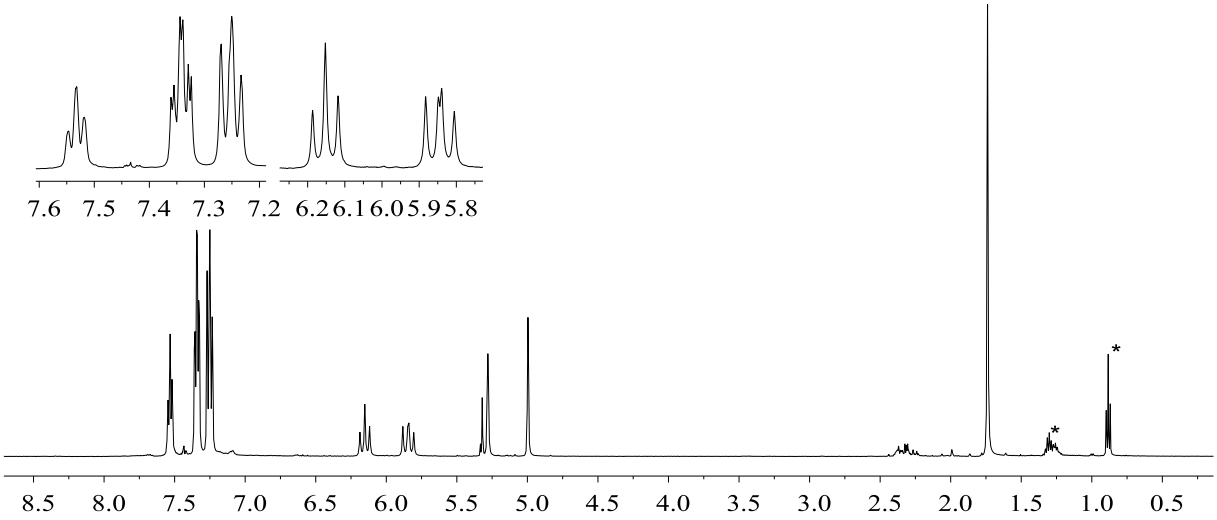
^1H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 7.53 (m, 2H, *p*-Ph), 7.34 (m, 4H, *m*-Ph), 7.25 (m, 4H, *o*-Ph), 6.15 (t, $^3J_{PH}$ = $^3J_{HH,trans}$ = 17.0 Hz, 1H, =CH), 5.84 (dd, $^2J_{PH}$ = 21.6 Hz, $^3J_{HH}$ = 17.0 Hz, 1H, PCH), 5.28, 5.00 (each br, each 1H, $=CH_2$), 1.74 (s, 3H, Me).

$^{13}C\{^1H\}$ NMR (126 MHz, 299 K, CD_2Cl_2)[all resonances are broad]: δ = 152.1 (=CH), 148.7 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 141.1 (d, $^3J_{PC}$ = 15.5 Hz, =C), 140.5 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 137.4 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 134.1 (d, $^2J_{PC}$ = 8.2 Hz, *o*-Ph), 132.4 (*p*-Ph), 129.1 (d, $^3J_{PC}$ = 10.3 Hz, *m*-Ph), 125.3 (d, $^1J_{PC}$ = 56.4 Hz, *i*-Ph), 124.1 (=CH_2), 116.2 (*i*-C_6F_5), 114.0 (d, $^1J_{PC}$ = 57.2 Hz, PCH), 18.0 (Me).

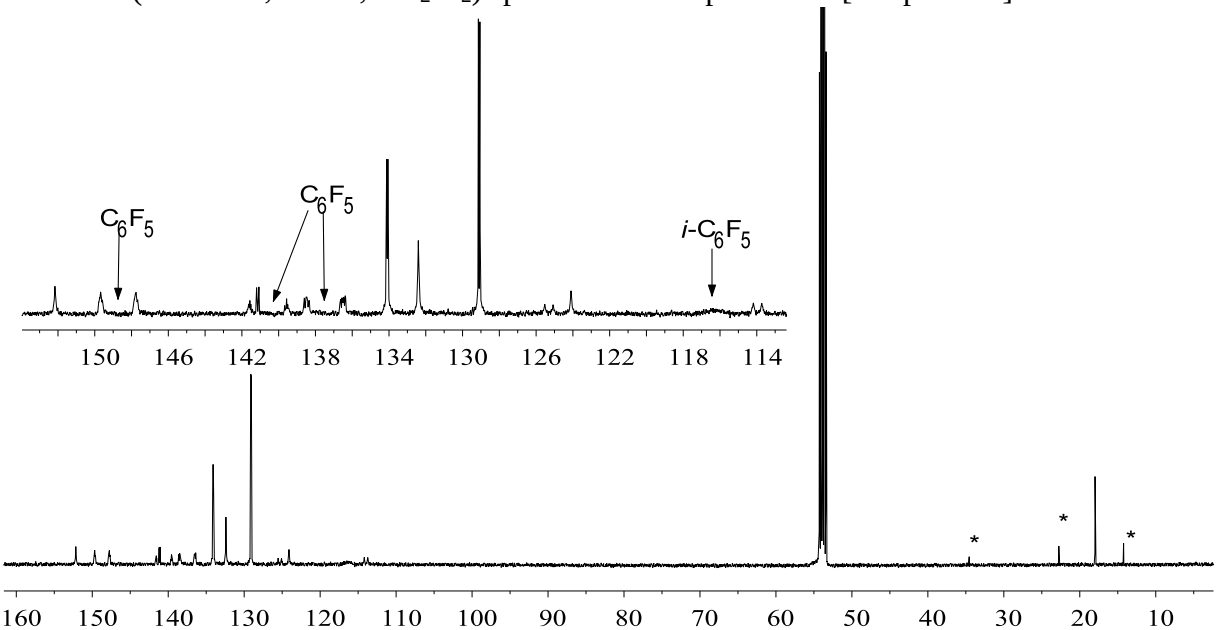
^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ = -127.3 (br, 2F, *o*-C_6F_5), -157.0 (t, *J* = 20.3 Hz, 1F, *p*-C_6F_5), -164.9 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 4.9].

$^{11}B\{^1H\}$ NMR (160 MHz, 299 K, CD_2Cl_2): δ = -9.8 ($\nu_{1/2}$ ~ 200 Hz).

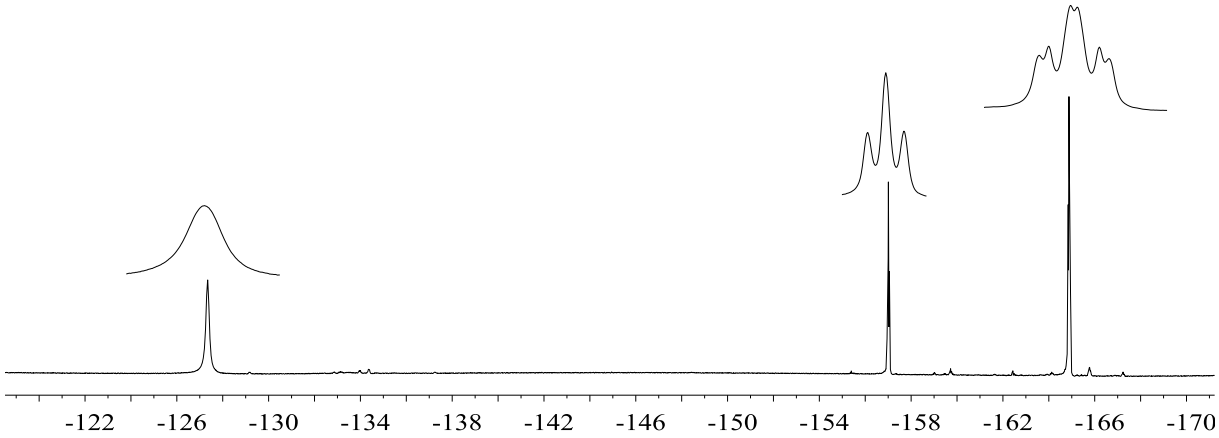
$^{31}P\{^1H\}$ NMR (202 MHz, 299 K, CD_2Cl_2): δ = 13.1 ($\nu_{1/2}$ ~ 150 Hz).



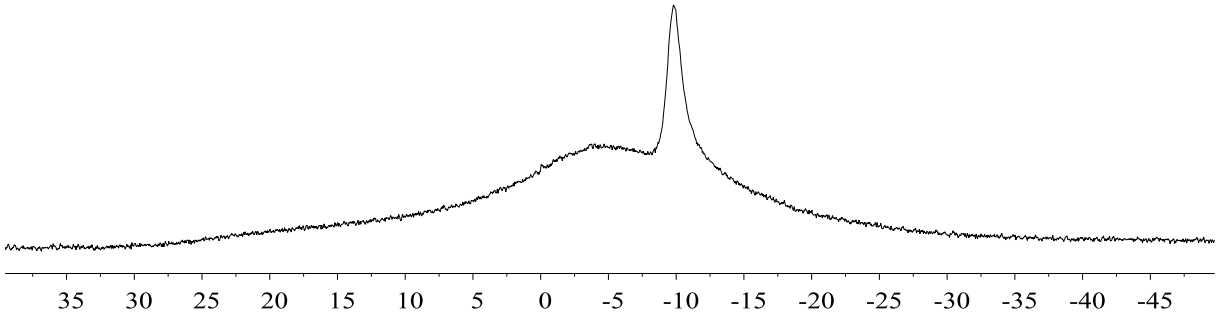
^1H NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of compound **21**. [* *n*-pentane].



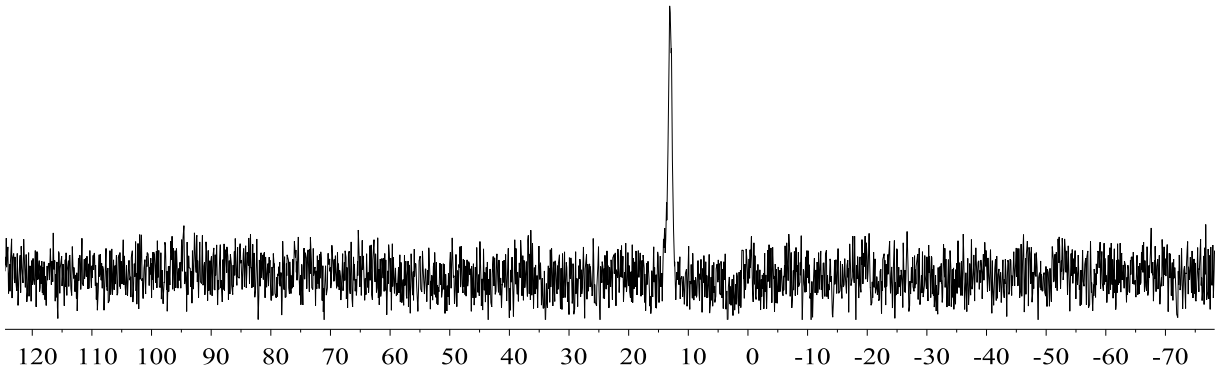
$^{13}C\{^1H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) spectrum of compound **21**. [* *n*-pentane].



^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) spectrum of compound **21**.



^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2) spectrum of compound **21**.



^{31}P{^{1}H} NMR (202 MHz, 299 K, CD_2Cl_2) spectrum of compound **21**.