

Cyclopropane Formation under Frustrated Lewis Pair Conditions

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^{\$} X-ray crystal structure analysis

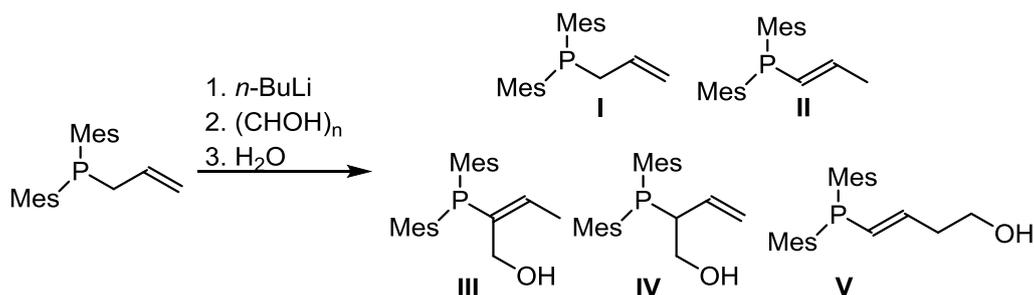
Supporting Information

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 a *Bruker* AV 300 (¹H: 300 MHz, ¹³C: 76 MHz, ³¹P: 122 MHz, ¹¹B: 96 MHz, ¹⁹F: 282 MHz), a *Bruker* AV 400 (¹H: 400 MHz, ¹³C: 101 MHz, ³¹P: 162 MHz), a *Varian* VNMR 500 MHz (¹H: 500 MHz, ¹³C: 126 MHz, ¹⁹F: 470 MHz, ¹¹B: 160 MHz, ³¹P: 202 MHz) and on a *Agilent* DD2-600 MHz (¹H: 600 MHz, ¹³C: 151 MHz, ¹⁹F: 564 MHz, ¹¹B: 192 MHz, ³¹P: 243 MHz). ¹H NMR and ¹³C NMR: chemical shifts δ are given relative to TMS and referenced to the solvent signal. ¹⁹F NMR: chemical shifts δ are given relative to CFC1₃ ($\delta = 0$, external reference), ¹¹B NMR: chemical shifts δ are given relative to BF₃·Et₂O ($\delta = 0$, external reference), ³¹P NMR: chemical shifts δ are given relative to H₃PO₄ (85% in D₂O) ($\delta = 0$, 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 a *Elementar Vario El III*. X-Ray diffraction: Data sets for the compounds **9** and **12** 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). For the compounds **V** and **10** data sets 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). *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: Compound **9** crystallized with a disordered over two positions cyclopropane group. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. For the compounds **10** and **12** a badly disordered dichloromethane molecule and one half toluene molecule, respectively, were 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. CCDC deposition numbers are 1419592 to 1419595.

Starting materials. Bis(pentafluorophenyl)borane $\text{HB}(\text{C}_6\text{F}_5)_2$ [(a) R. E. von H. Spence, W. E. Piers, Y. E. Sun, M. Parvez, L. R. MacGillivray and M. J. Zaworotko, *Organometallics*, 1998, **17**, 2459; (b) D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492; (c) D. J. Parks, R. E. von H. Spence and W. E. Piers, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 809]. Tris(pentafluorophenyl)borane $\text{B}(\text{C}_6\text{F}_5)_3$ was purchased. Allyldimesitylphosphane was synthesized as reported in the following literature [P. Spies, G. Kehr, K. Bergander, B. Wibbeling, R. Fröhlich and G. Erker, *Dalton Trans.*, 2009, 1534].

Preparation of phosphinobutenols.



1st Experiment: Allyldimesitylphosphane (**I**) (3.24 g, 10.44 mmol) was dissolved in dry THF (50 mL). The solution was cooled to $-78\text{ }^{\circ}\text{C}$ and *n*-BuLi (1.6 M in *n*-hexane) (6.53 mL, 10.44 mmol) was added slowly. After stirring at this temperature for 30 min, paraformaldehyde (CHOH)_n (626 mg, 20.87 mmol) was added at once under an atmosphere of argon. Then the dry ice bad was removed and the reaction mixture was stirred first for 48 h at ambient temperature and then to complete the reaction for 2 h at $60\text{ }^{\circ}\text{C}$. The reaction was quenched with distilled H₂O (20 mL) and the organic layer was extracted with CH₂Cl₂ (1 × 50 mL, 2 × 25 mL) and subsequently the combined organic phases were dried with Na₂SO₄. After removing all volatiles by using a rotary evaporator a yellow oil (3.8 g) was obtained. Further purification was carried out by column chromatography using silica gel (50 cm x Ø 4 cm, eluent: ethyl acetate/ *n*-pentane 3:7 and 1% NEt₃): three fractions were obtained, each dried *in vacuo*.

Fraction 1: Yellow oil (1.08 g), a mixture, which contains mostly allyldimesitylphosphane (**I**) and (*E*)-(prop-1-enyl)dimesitylphosphane (**II**) [(R_f: 0.95, (4:1 (¹H))].

Fraction 2: Yellow oil (0.7 g), a mixture of compounds 2-(dimesitylphosphino)but-2-en-1-ol (**III**) and 2-(dimesitylphosphino)but-3-en-1-ol (**IV**) [R_f: 0.62, (2:1 (¹H))].

Fraction 3: Slightly yellow oil (1.20 g, 34%), (*E*)-4-(dimesitylphosphino)but-3-en-1-ol (**V**) [R_f : 0.35], which crystallized upon standing for two weeks as a white crystalline solid.

(*E*)-(Prop-1-enyl)dimesitylphosphane (**II**) was obtained by column chromatography of *fraction 1* on silica gel (eluent: CH₂Cl₂/cyclohexane 3:10) as a yellow oil (0.08 g, 2%).

2-(Dimesitylphosphino)but-2-en-1-ol (**III**) was obtained by column chromatography of *fraction 2* [R_f : 0.6] on silica gel (eluent: ethylacetate/ *n*-pentane 1:5) as a colorless oil (0.16 g, 5%).

HRMS (MicroTof): [M+H]⁺ (C₂₂H₂₉OPH⁺): Calcd.: 314.2034, Found: 314.2029.

Elemental analysis: Calcd. for C₂₂H₂₉OP: C, 77.62; H, 8.59. Found C, 76.81; H, 8.31.

2-(Dimesitylphosphino)but-3-en-1-ol (**IV**) was obtained by column chromatography of *fraction 2* on silica gel [R_f : 0.48] (eluent: ethylacetate/ *n*-pentane 1:5) as a colorless oil (0.33 g, 9%).

2nd Experiment: A solution of allyldimesitylphosphane (**I**) (1 g, 3.22 mmol) in THF (20 mL) was precooled to -78 °C and *n*-BuLi (1.6 M in *n*-hexane) (2.11 mL, 3.38 mmol) was added. After 30 min stirring, *p*-formaldehyde (CHOH)_n (0.1 g, 3.38 mmol) was added quickly and the mixture was warmed to 0 °C. After 1 h stirring, HCl (1 M, 10 mL) and ethylacetate (50 mL) were added to the reaction mixture. Then the organic layer was separated and washed twice with distilled H₂O (2 × 50 mL), dried with Na₂SO₄ and all volatiles were removed using a rotary evaporator. The obtained colorless oil was purified by column chromatography (see *1st Experiment*). Only (*E*)-4-(dimesitylphosphino)but-3-en-1-ol (**V**) was isolated as a slight yellow oil which crystallized upon several days as a white crystalline solid (0.2 g, 18%).

Elemental analysis: Calcd. for C₂₂H₂₉OP: C, 77.62; H, 8.59. Found: C, 76.98; H, 8.40.

3rd Experiment: *n*-BuLi (1.6M in *n*-hexane) (4.23 mL, 6.76 mmol) was added dropwise to a solution of allyldimesitylphosphane (**I**) (2 g, 6.44 mmol) in THF (40 mL) at $-78\text{ }^{\circ}\text{C}$. After 1 h, *p*-formaldehyde (0.2 g, 6.76 mmol) was added. The temperature of solution was allowed to rise to ambient temperature and stirring was continued for 16 h. Then the solution was heated for 1 h at $65\text{ }^{\circ}\text{C}$. Subsequently a mixture of H₂O (30 mL) and of HCl in diethyl ether (2M) (3.45 mL, 6.9 mmol) was added. After 10 min, the reaction mixture was extracted four times with CH₂Cl₂ (4 × 30 mL) and the combined organic phases were dried with Na₂SO₄. Further workup was carried out as described in *1st Experiment*.

Fraction 1: Yellow oil (0.3 g), mixture of allyldimesitylphosphane (**I**) and (*E*)-(prop-1-enyl)dimesitylphosphane (**II**).

Fraction 2: Colorless oil (0.50 g), 2-(dimesitylphosphino)but-3-en-1-ol (**IV**). Colorless oil (0.50 g, 23%).

HRMS (MicroTof): [M+H]⁺ (C₂₂H₂₉OPH⁺): Calcd.: 314.2034, Found: 314.2027.

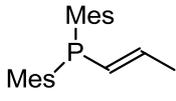
Elemental analysis: Calcd. for C₂₂H₂₉OP: C, 77.62; H, 8.59. Found: C, 76.92; H, 8.58.

Fraction 3: Slightly yellow oil, (*E*)-4-(dimesitylphosphino)but-3-en-1-ol (**V**), which completely crystallized after storing for 2 days at ambient temperature. The quality of the obtained crystals (1.02 g, 47%) was suitable for the X-ray crystal structure analysis.

[*Comment:* the phosphanyl alcohols seem to react with air, therefore the column purification should be done quickly. All fractions were collected on air, followed by fast drying *in vacuo*.]

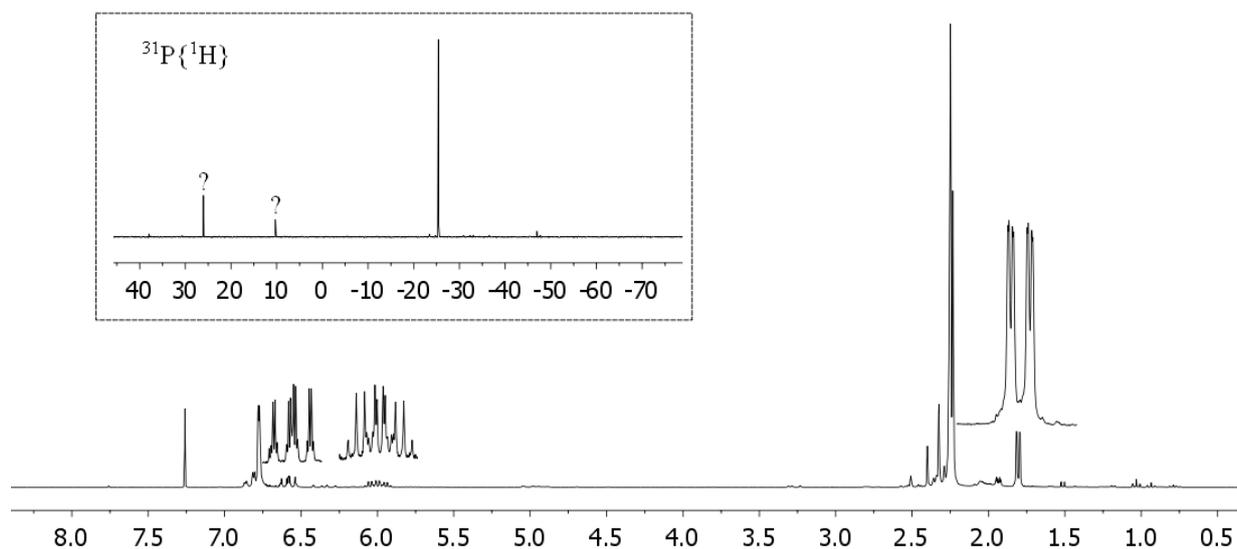
(E)-(Prop-1-enyl)dimesitylphosphane (II). From 1st Experiment: Yellow oil (0.08 g, 2%).

The solution of the oil in CDCl₃ was admixed with some compounds not identified yet.

 **¹H NMR** (300 MHz, 299 K, CDCl₃): δ = 6.78 (m, 4H, *m*-Mes), 6.58 (ddq, ³J_{HH} = 16.2 Hz, ²J_{PH} = 12.2 Hz, ⁴J_{HH} = 1.6 Hz, 1H, PCH), 6.00 (ddq, ³J_{HH} = 16.2 Hz, ³J_{PH} = 14.7 Hz, ³J_{HH} = 6.5 Hz, 1H, =CH), 2.25 (s, 12H, *o*-CH₃^{Mes}), 2.23 (s, 6H, *p*-CH₃^{Mes}), 1.81 (ddd, ³J_{HH} = 6.5 Hz, ⁴J_{HH} = 1.6 Hz, ⁴J_{PH} = 0.5 Hz, 3H, CH₃).

³¹P{¹H} NMR (121 MHz, 299 K, CDCl₃): δ = -25.4 (ν_{1/2} ~ 1 Hz).

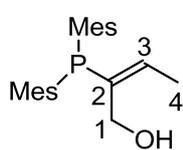
³¹P NMR (121 MHz, 299 K, CDCl₃): δ = -25.4 (br t, J_{PH} ~ 13 Hz).



¹H NMR (300 MHz, 299 K, CDCl₃) and **³¹P{¹H}** NMR (121 MHz, 299 K, CDCl₃) spectra of compound **II**. [? not identified yet].

2-(Dimesitylphosphino)but-2-en-1-ol (III). From 1st Experiment: Colorless oil (0.16 g, 5%).

The solution of the oil in CDCl₃ was admixed with 2-(dimesitylphosphino)but-3-en-1-ol (IV) (ca. 10% (³¹P)).



¹H NMR (400 MHz, 299 K, CDCl₃) δ = 6.82 (d, ⁴J_{HH} = 2.7 Hz, 4H, *m*-Mes), 5.62 (m, 1H, 3-H), 4.43 (d, ³J_{PH} = 11.8 Hz, 2H, 1-H), 2.26 (s, 18H, *o,p*-CH₃^{Mes}), 1.90 (br, 1H, OH)^t, 1.80 (dd, ³J_{HH} = 7.0 Hz, *J* = 2.4 Hz, 3H, 4-H), [^t

tentative assignment].

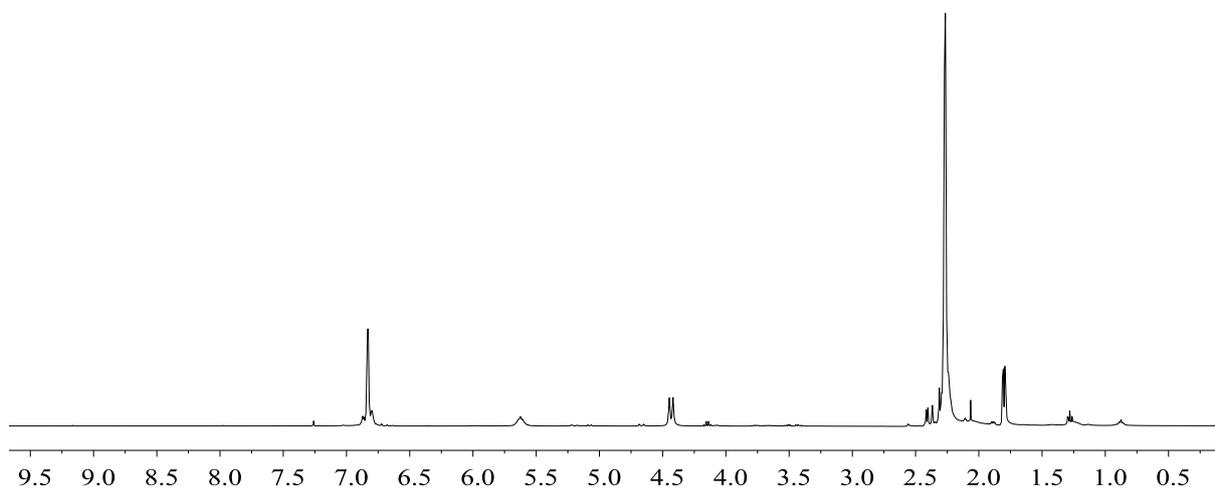
¹³C{¹H} NMR (101 MHz, 299 K, CDCl₃): δ = 142.7 (d, ²J_{PC} = 14.9 Hz, *o*-Mes), 137.9 (br, *p*-Mes), 136.3 (d, ¹J_{PC} = 13.1 Hz, C2), 133.6 (br, C3), 129.8 (d, ³J_{PC} = 3.7 Hz, *m*-Mes), 129.7 (br d, ¹J_{PC} ~ 20 Hz, *i*-Mes), 61.6 (d, ²J_{PC} = 30.9 Hz, C1), 22.3 (d, ³J_{PC} = 15.2 Hz, *o*-CH₃^{Mes}), 20.8 (*p*-CH₃^{Mes}), 15.2 (d, ³J_{PC} = 4.4 Hz, C4).

¹H, ¹H GCOSY (400 MHz/ 400 MHz, 299 K, CDCl₃) [selected traces]: $\delta^1\text{H}/ \delta^1\text{H}$ = 5.61/ 1.80 (3-H/ 4-H), 1.80/ 4.43, 5.61 (4-H/ 1-H, 3-H)

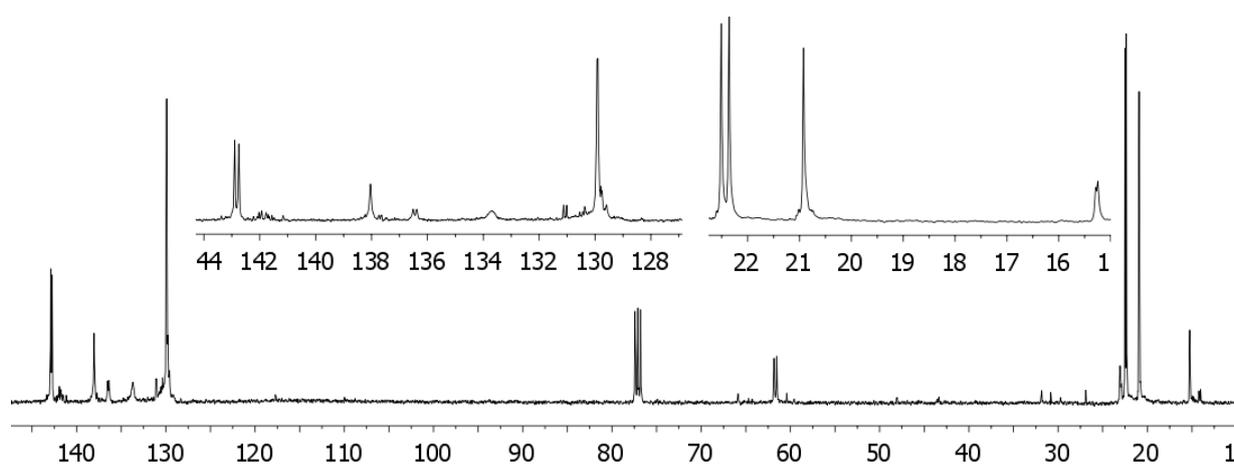
¹H, ¹³C GHSQC (400 MHz/ 101 MHz, 299 K, CDCl₃): $\delta^1\text{H}/ \delta^{13}\text{C}$ = 6.82/ 129.8 (*m*-Mes), 5.62/ 133.6 (C3), 4.43/ 61.6 (C1), 2.26/ 22.3 (*o*-CH₃^{Mes}), 2.26/ 20.8 (*p*-CH₃^{Mes}), 1.80/ 15.2 (C4).

¹H, ¹³C GHMBC (400 MHz/ 101 MHz, 299 K, CDCl₃) [selected traces]: $\delta^1\text{H}/ \delta^{13}\text{C}$ = 6.82/ 142.7, 129.8, 129.7 (*m*-Mes/ *o*-Mes, *m*-Mes, *i*-Mes), 2.26/ 142.7, 129.8, 129.7 (*o*-CH₃^{Mes}/*o*-Mes, *m*-Mes, *i*-Mes), 1.80/ 136.3, 133.6 (4-H/ C2, C3).

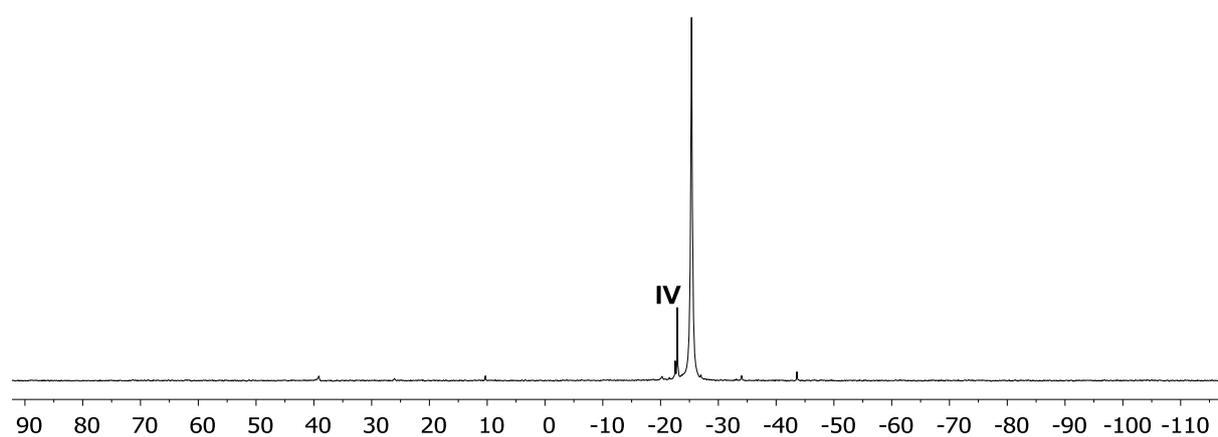
³¹P{¹H} NMR (162 MHz, 299 K, CDCl₃): δ = -25.4 ($\nu_{1/2}$ ~ 50 Hz).



^1H NMR (400 MHz, 299 K, CDCl_3) spectrum of compound **III**.



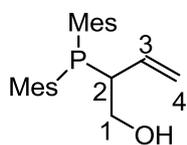
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 299 K, CDCl_3) spectrum of compound **III**.



$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, 299 K, CDCl_3) spectrum of compound **III**. [admixed with compound **IV**].

2-(Dimesitylphosphino)but-3-en-1-ol (IV). From 1st Experiment: Colorless oil (0.33 g, 9%).

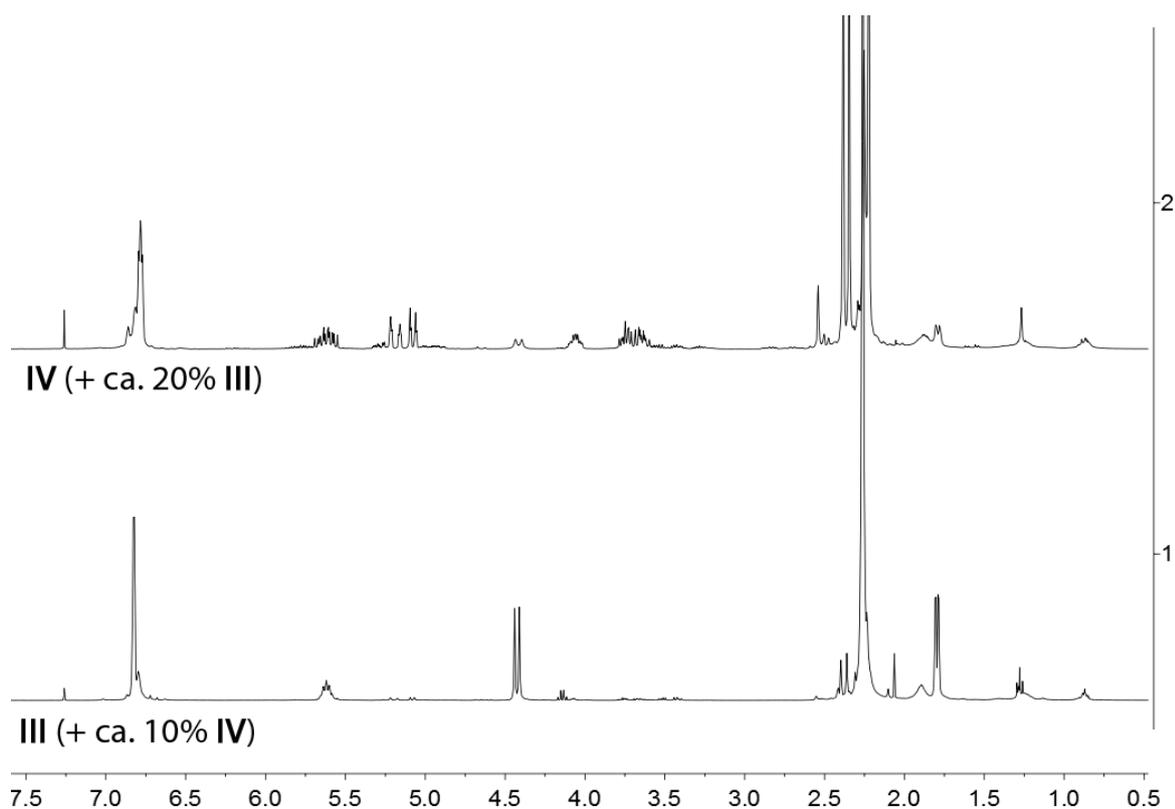
The solution of the oil in CDCl₃ was admixed with 2-(dimesitylphosphino)but-2-en-1-ol (III) (ca.: 20% (¹H)).



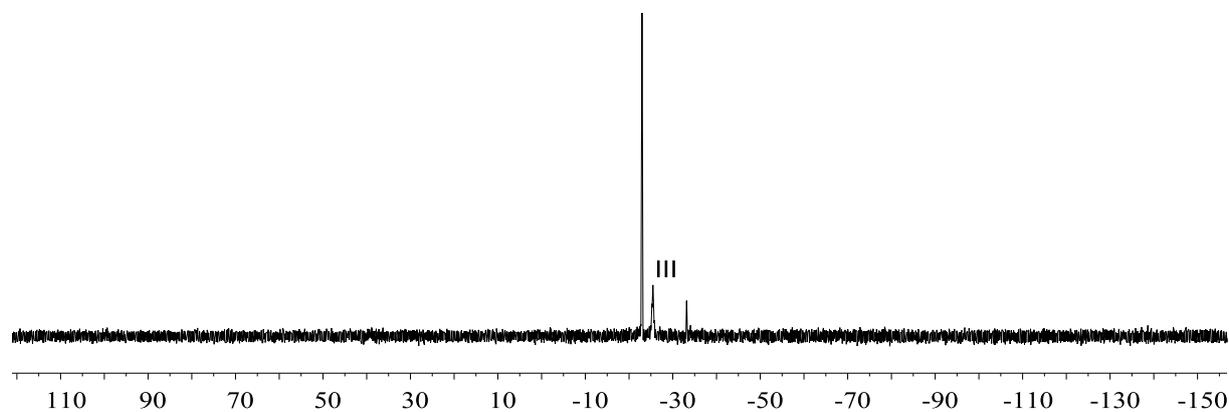
¹H NMR (300 MHz, 299 K, CDCl₃) data are consistent to those listed below.

³¹P{¹H} NMR (121 MHz, 299 K, CDCl₃): $\delta = -23.0$ ($\nu_{1/2} \sim 2$ Hz).

³¹P NMR (121 MHz, 299 K, CDCl₃): $\delta = -23.0$ ($\nu_{1/2} \sim 20$ Hz).



(1) ¹H NMR (400 MHz, 299 K, CDCl₃) and (2) ¹H NMR (300 MHz, 299 K, CDCl₃)



³¹P NMR (121 MHz, 299 K, CDCl₃) spectrum of compound IV.

From 3rd Experiment: Colorless oil (0.50 g, 23%). The solution of the oil in CDCl₃ was admixed with 2-(dimesitylphosphino)but-2-en-1-ol (**III**) (ca.: 8% (¹H)).

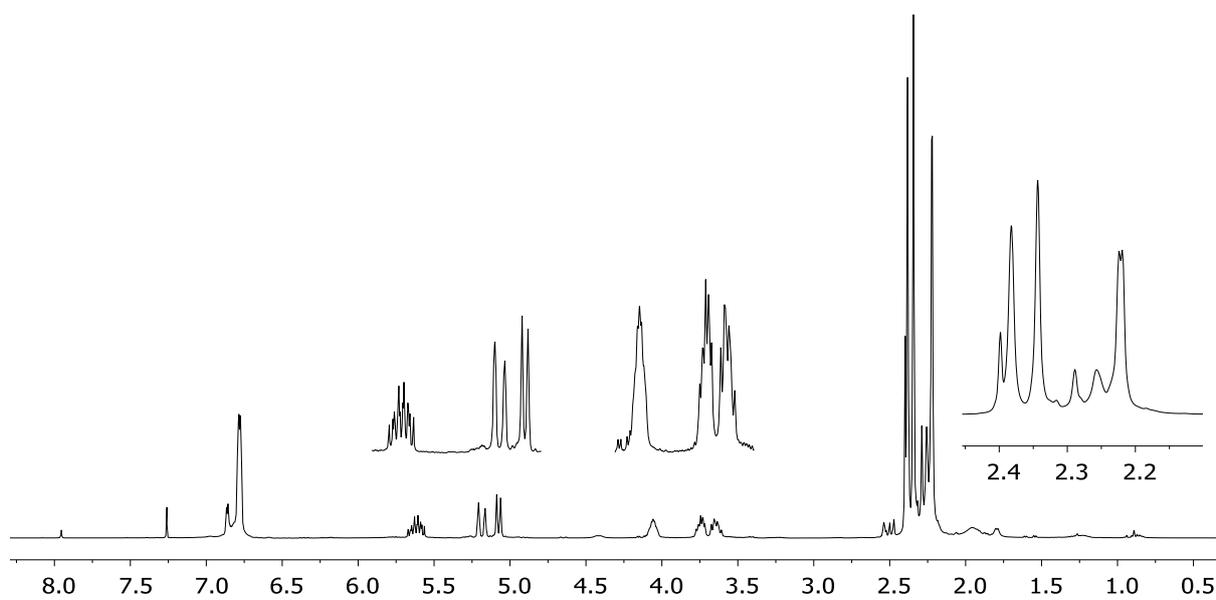
¹H NMR (400 MHz, 299 K, CDCl₃): δ = 6.79 (d, ⁴J_{HH} = 2.6 Hz, 2H, *m*-Mes^a), 6.77 (d, ⁴J_{HH} = 2.6 Hz, 2H, *m*-Mes^b), 5.62 (m, 1H, 3-H), 5.19 (dm, ³J_{HH} = 17.3 Hz, 1H, 4-H^Z), 5.07 (dm, ³J_{HH} = 10.3 Hz, 1H, 4-H^E), 4.06 (m, 1H, 2-H), 3.74, 3.65 (each m, each 1H, 1-H), 2.38 (s, 6H, *o*-CH₃^{Mes,a}), 2.34 (s, 6H, *o*-CH₃^{Mes,b}), 2.224 (s, 3H, *p*-CH₃^{Mes,a}), 2.219 (s, 3H, *p*-CH₃^{Mes,b}), 1.96 (br, 1H, OH)^t, [^t tentative assignment].

¹³C{¹H} NMR (101 MHz, 299 K, CDCl₃): δ 143.2 (d, ²J_{PC} = 14.8 Hz, *o*-Mes^b), 142.1 (d, ²J_{PC} = 14.6 Hz, *o*-Mes^a), 138.2 (*p*-Mes^b), 137.7 (*p*-Mes^a), 137.1 (d, ²J_{PC} = 11.6 Hz, C3), 130.8 (d, ¹J_{PC} = 25.5 Hz, *i*-Mes^a), 130.3 (br d, ³J_{PC} = 2.6 Hz, *m*-Mes^a), 129.9 (d, ¹J_{PC} = 22.0 Hz, *i*-Mes^b), 129.7 (d, ³J_{PC} = 3.7 Hz, *m*-Mes^b), 117.7 (d, ³J_{PC} = 10.4 Hz, C4), 64.4 (d, ²J_{PC} = 40.1 Hz, C1), 43.4 (d, ¹J_{PC} = 17.3 Hz, C2), 23.0 (d, ³J_{PC} = 15.0 Hz), 23.0 (d, ³J_{PC} = 13.5 Hz)(*o*-CH₃^{Mes,ab}), 20.8 (*p*-CH₃^{Mes,b}), 20.7 (*p*-CH₃^{Mes,a}).

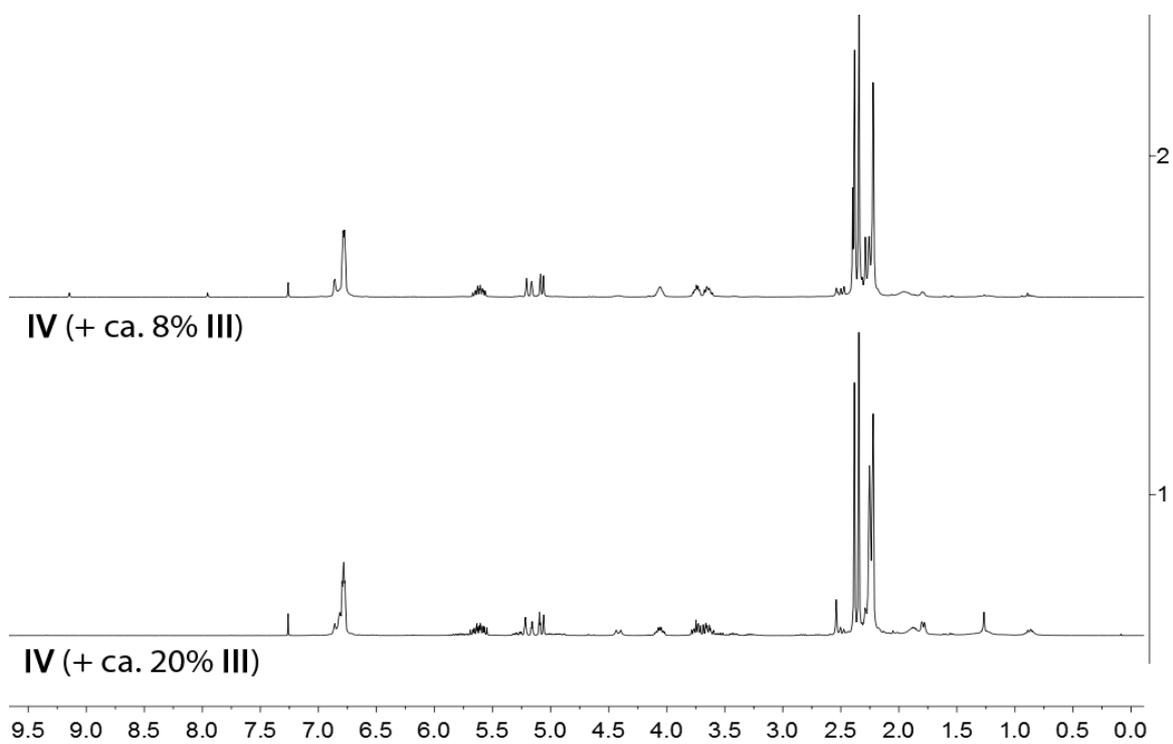
¹H,¹H GCOSY (400 MHz/ 400 MHz, 299 K, CDCl₃) [selected traces]: $\delta^1\text{H}/ \delta^1\text{H} = 6.79/ 2.38$, 2.224 (*m*-Mes^a/ *o*-CH₃^{Mes,a}, *p*-CH₃^{Mes,b}), 5.62/ 5.19, 5.07, 4.06 (3-H/ 4-H^E, 4-H^Z, 2-H).

¹H,¹³C GHSQC (400 MHz/ 101 MHz, 299 K, CDCl₃): $\delta^1\text{H}/ \delta^{13}\text{C} = 6.79/ 130.3$ (*m*-Mes^a), 6.77/ 129.7 (*m*-Mes^b), 5.62/ 137.1 (C3), 5.19, 5.07/ 117.7 (C4), 4.06/ 43.4 (C2), 3.74, 3.65/64.4 (C1), 2.38/ 23.0 (*o*-CH₃^{Mes,a}), 2.34/ 23.0 (*o*-CH₃^{Mes,b}), 2.224/ 20.7 (*p*-CH₃^{Mes,a}), 2.219/ 20.8 (*p*-CH₃^{Mes,b}).

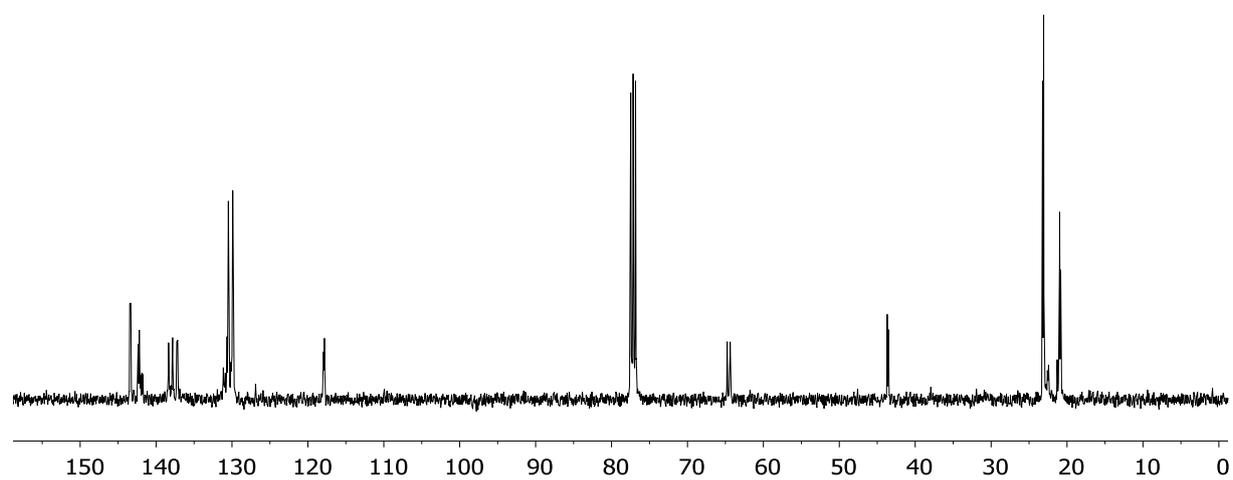
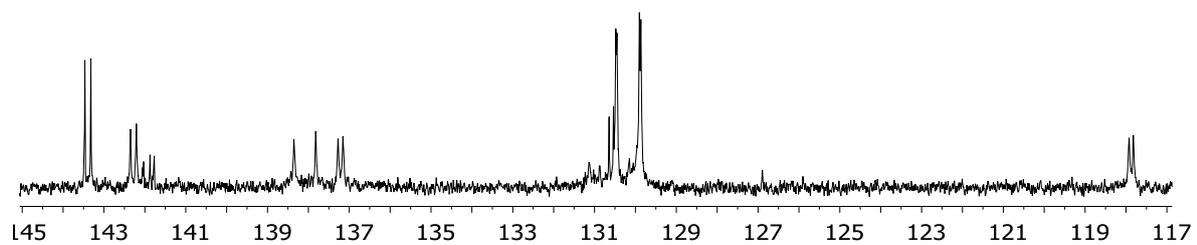
¹H,¹³C GHMBC (400 MHz/ 101 MHz, 299 K, CDCl₃) [selected traces]: $\delta^1\text{H}/ \delta^{13}\text{C} = 6.79/ 130.8$, 130.3, 23.0, 20.7 (*m*-Mes^a/ *i*-Mes^a, *m*-Mes^a, *o*-CH₃^{Mes,a}, *p*-CH₃^{Mes,a}), 6.77/ 129.9, 129.7, 23.0, 20.8 (*m*-Mes^b/ *i*-Mes^b, *m*-Mes^b, *o*-CH₃^{Mes,b}, *p*-CH₃^{Mes,b}), 2.224/ 137.7, 130.3 (*p*-CH₃^{Mes,a}/ *p*-Mes^a, *m*-Mes^a), 2.219/ 138.2, 129.7 (*p*-CH₃^{Mes,b}/ *p*-Mes^b, *m*-Mes^b).



^1H NMR (400 MHz, 299 K, CDCl_3) spectrum of compound **IV**.



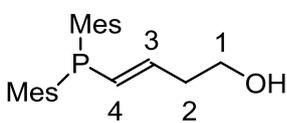
(1) ^1H NMR (300 MHz, 299 K, CDCl_3) and (2) ^1H NMR (400 MHz, 299 K, CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 299 K, CDCl_3) spectrum of compound IV.

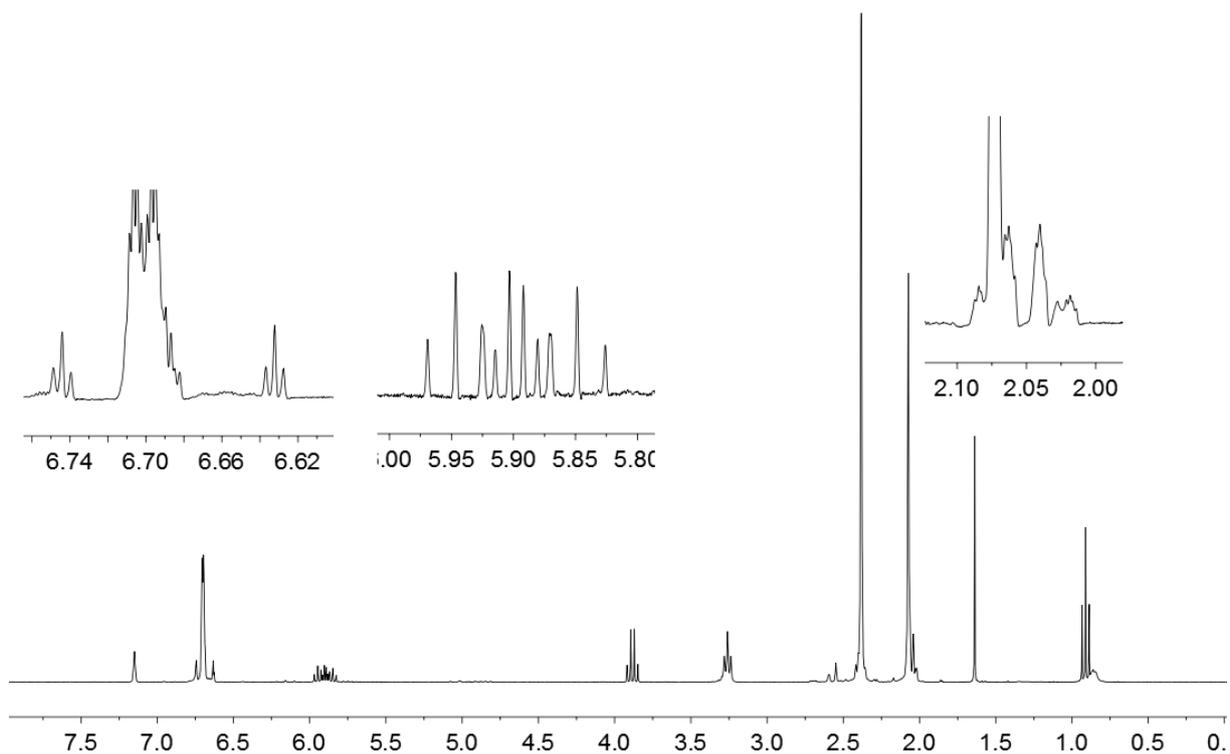
(E)-4-(Dimesitylphosphino)but-3-en-1-ol (V).

From 1st Experiment: light yellow oil (1.20 g, 34%). A solution of the oil in C₆D₆ was analyzed by NMR experiments (admixed with ethyl acetate).

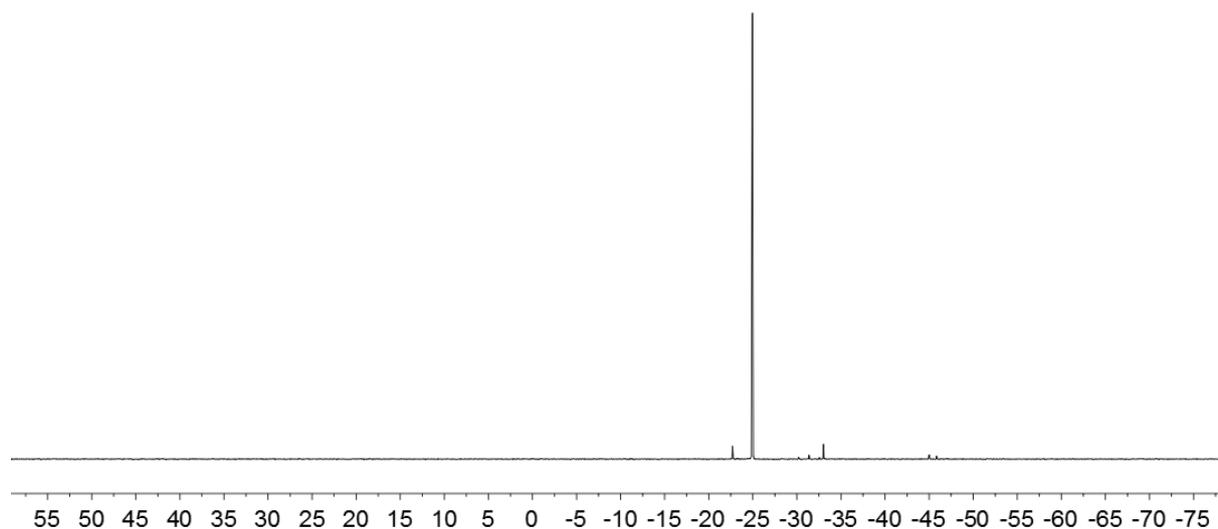
**¹H NMR** (300 MHz, 299 K, C₆D₆): $\delta = 6.70$ (dm, $^4J_{\text{HH}} = 2.6$ Hz, 4H, *m*-Mes), 6.69 (ddt, $^2J_{\text{PH}} = 17.2$ Hz, $^3J_{\text{HH}} = 16.3$ Hz, $^4J_{\text{HH}} = 1.3$ Hz, 1H, 4-H), 5.90 (ddt, $^3J_{\text{HH}} = 16.3$ Hz, $^3J_{\text{PH}} = 13.3$ Hz, $^3J_{\text{HH}} = 6.8$ Hz, 1H, 3-H), 3.26 (t, $^3J_{\text{HH}} = 6.5$ Hz, 2H, 1-H), 2.38 (s, 12H, *o*-CH₃^{Mes}), 2.07 (s, 6H, *p*-CH₃^{Mes}), 2.05 (m, 2H, 2-H), 0.86 (br, OH)[†], [[†] tentative assignment].

³¹P{¹H} NMR (121 MHz, 299K, C₆D₆): $\delta = -25.0$ ($\nu_{1/2} \sim 2$ Hz).

³¹P NMR (121 MHz, 299K, C₆D₆): $\delta = -25.0$ (tm, $J_{\text{PH}} \sim 15.0$ Hz).



¹H NMR (300 MHz, 299 K, C₆D₆) spectrum of compound V.



$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, 299K, C_6D_6) spectrum of compound **V**.

From 2nd Experiment: White crystalline solid (0.2 g, 18%). A solution of the crystals in CDCl_3 was analyzed by NMR experiments (admixed with traces of ethyl acetate).

^1H NMR (400 MHz, 299 K, CDCl_3): δ = 6.80 (dm, $^4J_{\text{HH}} = 2.4$ Hz, 4H, *m*-Mes), 6.72 (ddm, $^2J_{\text{PH}} = 16.4$ Hz^t, $^3J_{\text{HH}} = 15.6$ Hz^t, 1H, 4-H), 5.88 (m, 1H, 3-H), 3.66 (t, $^3J_{\text{HH}} = 6.5$ Hz, 2H, 1-H), 2.41 (q_m, $^3J_{\text{HH}} = 6.5$ Hz, 2H, 2-H), 2.27 (s, 12H, *o*-CH₃^{Mes}), 2.25 (s, 6H, *p*-CH₃^{Mes}), 1.78 (br, 1H, OH)^t, [^t tentative assignment].

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 299K, CDCl_3): δ = 141.7 (d, $^2J_{\text{PC}} = 14.2$ Hz, *o*-Mes), 137.7 (*p*-Mes), 137.0 (br d, $^2J_{\text{PC}} = 29.8$ Hz, C3), 131.7 (br d, $^1J_{\text{PC}} \sim 18$ Hz, *i*-Mes), 130.5 (br, C4), 129.7 (d, $^3J_{\text{PC}} = 3.3$ Hz, *m*-Mes), 61.5 (C1), 38.2 (d, $^3J_{\text{PC}} = 11.2$ Hz, C2), 23.0 (d, $^3J_{\text{PC}} = 13.8$ Hz, *o*-CH₃^{Mes}), 20.8 (*p*-CH₃^{Mes}).

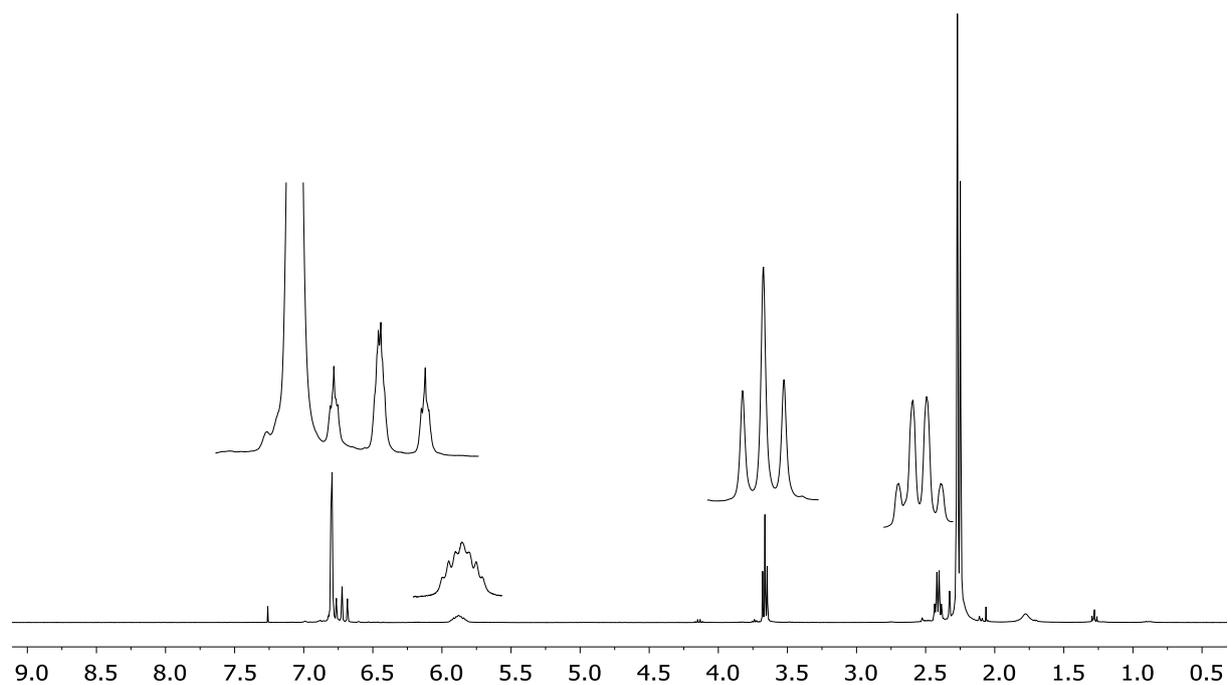
$^1\text{H}, ^1\text{H}$ GCOSY (400 MHz/ 400 MHz, 299 K, CDCl_3) [selected trace]: $\delta^1\text{H}/ \delta^1\text{H} = 5.88/ 6.72$, 2.41 (3-H/ 4-H, 2-H).

$^1\text{H}, ^{13}\text{C}$ GHSQC (400 MHz/ 101 MHz, 299 K, CDCl_3): $\delta^1\text{H}/ \delta^{13}\text{C} = 6.80/ 129.7$ (*m*-Mes), 6.72/ 130.5 (C4), 5.88/ 137.0 (C3), 3.66/ 61.5 (C1), 2.41/ 38.2 (C2), 2.27/ 23.0 (*o*-CH₃^{Mes}), 2.25/ 20.8 (*p*-CH₃^{Mes}).

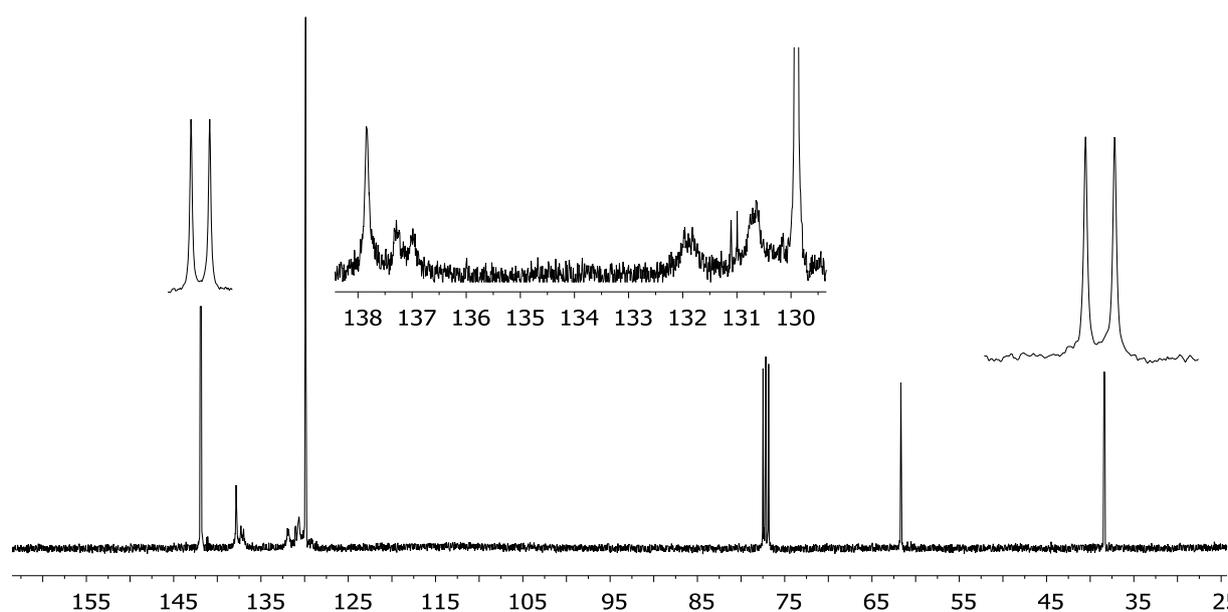
$^1\text{H}, ^{13}\text{C}$ GHMBC (400 MHz/ 101 MHz, 299 K, CDCl_3) [selected traces]: $\delta^1\text{H}/ \delta^{13}\text{C} = 6.80/$
131.7, 129.7, 23.0, 20.8 (*m*-Mes/ *i*-Mes, *m*-Mes, *o*- CH_3^{Mes} , *p*- CH_3^{Mes}), 2.27/ 141.7, 131.7,
129.7 (*o*- CH_3^{Mes} / *o*-Mes, *i*-Mes, *m*-Mes), 2.25/ 137.7, 129.7 (*p*- CH_3^{Mes} / *p*-Mes, *m*-Mes).

$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, 299 K, CDCl_3): $\delta = -25.3$ ($\nu_{1/2} \sim 15$ Hz).

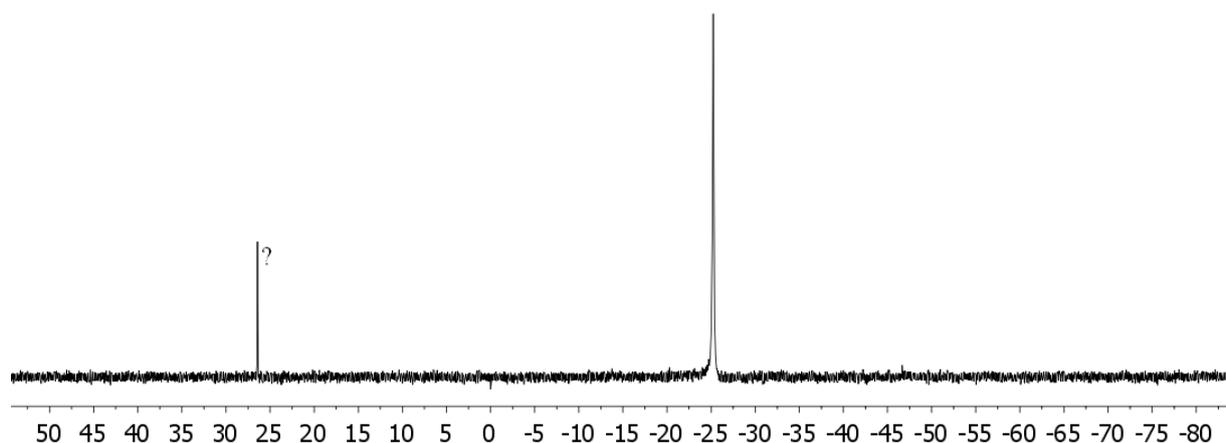
^{31}P NMR (121 MHz, 299 K, CDCl_3): $\delta = -25.3$ ($\nu_{1/2} \sim 40$ Hz).



^1H NMR (400 MHz, 299 K, CDCl_3) spectrum of compound **V**.



$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 299K, CDCl_3) spectrum of compound **V**.



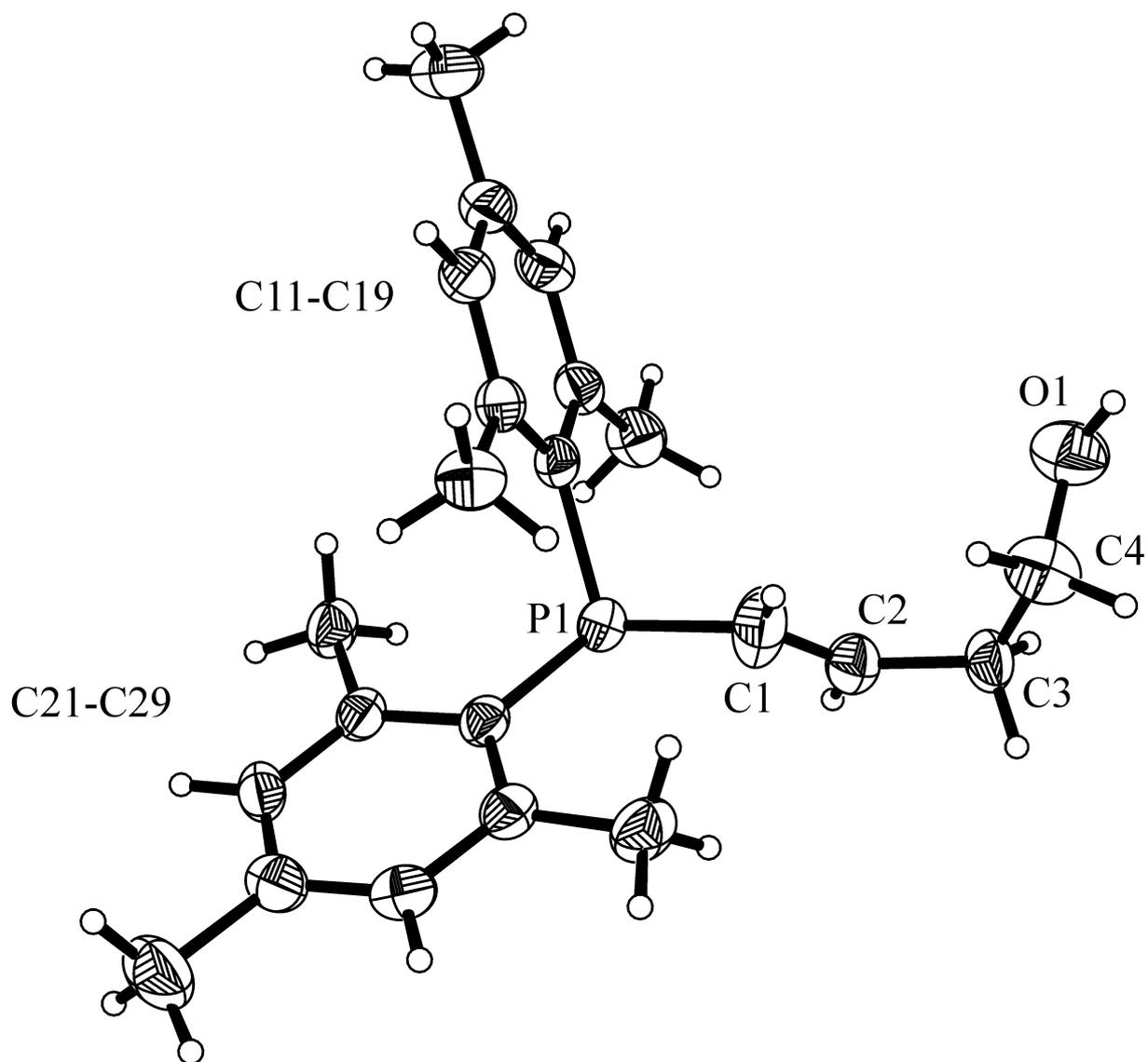
$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, 299 K, CDCl_3) spectra of compound **V**. [? not identified yet].

From 3rd Experiment: white crystalline solid

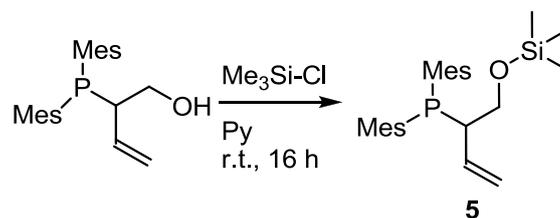
HRMS (MicroTof): $[\text{M}+\text{H}]^+$ ($\text{C}_{22}\text{H}_{29}\text{OPH}^+$): Calcd.: 314.2034, Found: 314.2027.

Melting point (DSC): 61 °C.

X-Ray crystal structure analysis of (*E*)-4-(dimesitylphosphino)but-3-en-1-ol (V**):** formula $\text{C}_{22}\text{H}_{29}\text{OP}$, $M = 340.42$, colourless crystal, 0.11 x 0.05 x 0.03 mm, $a = 15.6981(4)$, $b = 7.4997(2)$, $c = 16.6619(4)$ Å, $\beta = 93.155(1)$ °, $V = 1958.6(1)$ Å³, $\rho_{\text{calc}} = 1.154$ gcm⁻³, $\mu = 0.146$ mm⁻¹, empirical absorption correction ($0.984 \leq T \leq 0.995$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 16993 reflections collected ($\pm h$, $\pm k$, $\pm l$), 3359 independent ($R_{\text{int}} = 0.071$) and 2313 observed reflections [$I > 2\sigma(I)$], 271 refined parameters, $R = 0.072$, $wR^2 = 0.166$, max. (min.) residual electron density 0.25 (-0.21) e.Å⁻³, hydrogen atoms were calculated and refined as riding atoms.



Synthesis of dimesityl(1-(trimethylsilyloxy)but-3-en-2-yl)phosphane (5).



1st Experiment: Trimethylsilyl chloride (0.93 mL, 0.73 mmol) and an excess of pyridine (0.24 mL) were added to a solution of 2-(dimesitylphosphino)but-3-en-1-ol (**IV**) (0.5 g, 1.47 mmol) in *n*-pentane (3 mL). Immediately, in a vigorous reaction, a white precipitate was formed. After 16 h stirring at ambient temperature, all volatiles were removed in *vacuo* and the residue was extracted with *n*-pentane (5x5 mL). Drying in *vacuo* gave a colorless oil, which was purified by column chromatography (CH₂Cl₂/ *n*-pentane 1:1, 1% NEt₃) (0.27 g, 44%).

[*Comment:* Compound **5** lost the trimethylsilyl group during chromatography resulting in the starting material **IV**].

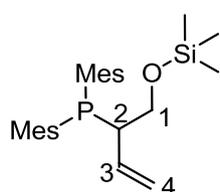
HRMS (MicroTof): M+H⁺ (C₂₅H₃₇OPSiH⁺): Calcd.: 413.2430, Found: 413.2428.

Elemental analysis: Calcd. for C₂₅H₃₇OPSi: C, 72.77; H, 9.04. Found: C, 73.10; H, 8.80.

¹H NMR (400 MHz, 299 K, CDCl₃): δ = 6.77, 6.75 (each d, ⁴J_{PH} = 2.7 Hz, each 2H, *m*-Mes), 5.53 (m, 1H, 3-H), 5.05 (dm, ³J_{HH,trans} = 16.7 Hz), 4.91 (dm, ³J_{HH,cis} = 10.4 Hz)(each 1H, 4-H), 4.14 (m, 1H, 2-H), 3.83, 3.75 (each m, each 1H, 1-H), 2.38, 2.35 (each s, each 6H, *o*-CH₃^{Mes}), 2.22, 2.21 (each s, each 3H, *p*-CH₃^{Mes}), 0.07 (s, ²J_{SiH} = 6.6 Hz, 9H, SiMe₃).

2nd Experiment: Trimethylsilyl chloride (1.57 mL, 1.23 mmol) and an excess of pyridine (0.4 mL) were added to a solution of 2-(dimesitylphosphino)but-3-en-1-ol (**V**) (0.84 g, 2.47 mmol) in *n*-pentane (5 mL). Immediately, in a vigorous reaction, a white precipitate was formed.

After 16 h stirring at ambient temperature, all volatiles were removed *in vacuo* and the residue was extracted with *n*-pentane (5x5 mL). Drying in *vacuo* gave compound **5** as a colorless oil (0.9 g, 89%).



¹H NMR (600 MHz, 299 K, CD₂Cl₂): δ = 6.784, 6.778 (each d, ⁴*J*_{HH} = 3.2 Hz, each 2H, *m*-Mes), 5.54 (dddd, ³*J*_{HH,trans} = 17.1 Hz, ³*J*_{HH,cis} = 10.3 Hz, ³*J*_{HH} = 8.8 Hz, ³*J*_{PH} = 5.5 Hz, 1H, 3-H), 5.03 (dm, ³*J*_{HH,trans} = 17.1 Hz, 1H, 4-H), 4.87 (dm, ³*J*_{HH,cis} = 10.3 Hz, 1H, 4-H), 4.14 (dddd, ³*J*_{HH} ~ ³*J*_{HH} = 8.8 Hz, ³*J*_{HH} = 3.9 Hz, ²*J*_{PH} = 3.6 Hz, 1H, 2-H), 3.82 (ddd, ²*J*_{HH} = 10.4 Hz, ³*J*_{PH} = 7.0 Hz, ³*J*_{HH} = 3.9 Hz, 1H, 1-H), 3.76 (ddd, ²*J*_{HH} = 10.4 Hz, ³*J*_{HH} = 8.8 Hz, ³*J*_{PH} = 4.9 Hz, 1H, 1-H), 2.37, 2.35 (each s, each 6H, *o*-CH₃^{Mes}), 2.22, 2.21 (each s, each 3H, *p*-CH₃^{Mes}), 0.07 (s, ²*J*_{SiH} = 6.4 Hz, 9H, SiMe₃).

¹H{³¹P}NMR (600 MHz, 299 K, CD₂Cl₂): δ = 6.79, 6.78 (each s, each 2H, *m*-Mes), 5.54 (ddd, ³*J*_{HH,trans} = 17.2 Hz, ³*J*_{HH,cis} = 10.4 Hz, ³*J*_{HH} = 8.3 Hz, 1H, 3-H), 5.03 (d, ³*J*_{HH,trans} = 17.1 Hz, 1H, 4-H), 4.87 (d, ³*J*_{HH,cis} = 10.4 Hz, 1H, 4-H), 4.14 (td, ³*J*_{HH} = 8.8 Hz, ³*J*_{HH} = 3.9 Hz, 1H, 2-H), 3.82 (dd, ²*J*_{HH} = 10.4 Hz, ³*J*_{HH} = 3.9 Hz, 1H, 1-H), 3.76 (dd, ²*J*_{HH} = 10.4 Hz, ³*J*_{HH} = 8.8 Hz, 1H, 1-H), 2.37, 2.35 (each s, each 6H, *o*-CH₃^{Mes}), 2.22, 2.21 (each s, each 3H, *p*-CH₃^{Mes}), 0.07 (s, 9H, SiMe₃).

¹³C{¹H} NMR (151 MHz, 299 K, CD₂Cl₂): δ = 144.0 (d, ²*J*_{PC} = 15.0 Hz), 142.4 (d, ²*J*_{PC} = 14.5 Hz)(*o*-Mes), 138.7 (d, ⁴*J*_{PC} = 0.7 Hz), 137.7 (*p*-Mes), 137.7 (d, ²*J*_{PC} = 10.3 Hz, C3), 132.0 (d, ¹*J*_{PC} = 29.5 Hz), 130.9 (d, ¹*J*_{PC} = 19.0 Hz)(*i*-Mes), 130.6 (d, ³*J*_{PC} = 2.7 Hz), 129.8 (d, ³*J*_{PC} = 4.0 Hz)(*m*-Mes), 116.2 (d, ³*J*_{PC} = 10.9 Hz, C4), 65.7 (d, ²*J*_{PC} = 48.9 Hz, C1), 42.7 (d, ¹*J*_{PC} = 16.1 Hz, C2), 23.2 (d, ³*J*_{PC} = 13.9 Hz), 23.1 (d, ³*J*_{PC} = 15.2 Hz)(*o*-CH₃^{Mes}), 21.0, 20.8 (*p*-CH₃^{Mes}), -0.4 (¹*J*_{SiC} = 59.0 Hz, SiMe₃).

¹H,¹H GCOSY (600 MHz/ 600 MHz, 299 K, CD₂Cl₂) [selected trace]: δ¹H/ δ¹H = 4.14/ 5.54, 3.82, 3.76 (2-H/ 3-H, 1-H, 1-H).

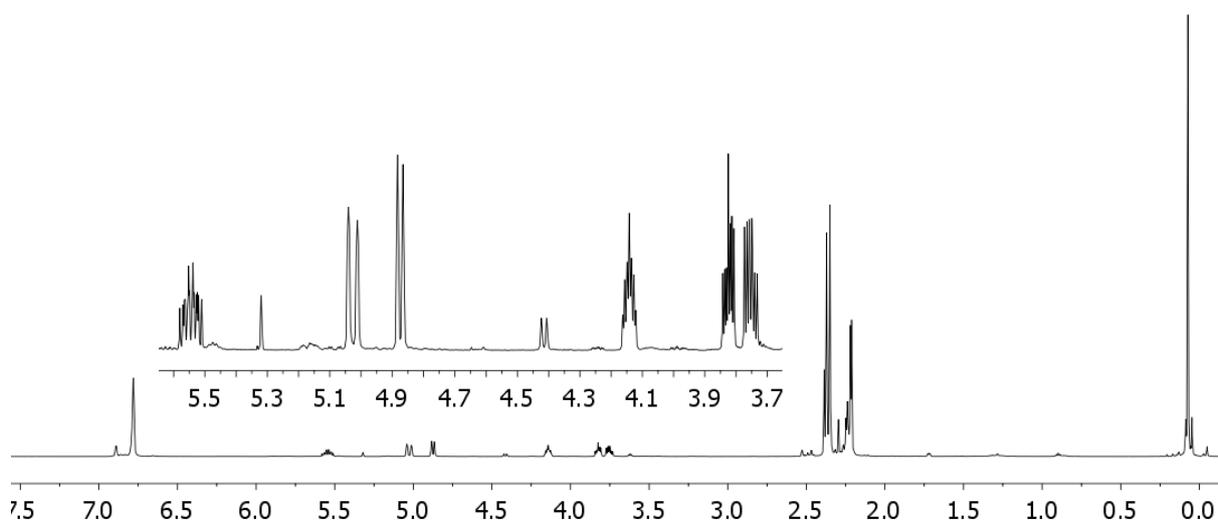
$^1\text{H}, ^{13}\text{C}$ GHSQC (600 MHz/ 151 MHz, 299 K, CD_2Cl_2): $\delta^1\text{H}/ \delta^{13}\text{C} = 6.784/ 130.7, 6.778/ 129.9$ (*m*-Mes^{a,b}), 5.54/ 137.7 (C3), 5.03/ 116.2 (C4), 4.87/ 116.2 (C4), 4.14/ 42.7 (C2), 3.82/ 65.7 (C1), 3.76/ 65.7 (C1), 2.37/ 23.2, 2.35/ 23.1 (*o*-CH₃^{Mes a,b}), 2.22/ 20.8, 2.21/ 21.0 (*p*-CH₃^{Mes a,b}), 0.07/ -0.4 (SiMe₃).

$^1\text{H}, ^{13}\text{C}$ GHMBC (600 MHz/ 151 MHz, 299 K, CD_2Cl_2) [selected traces]: $\delta^1\text{H}/ \delta^{13}\text{C} = 6.79/ 142.4, 130.7, 23.2, 20.8$ (*m*-Mes^a/ *o*-Mes^a, *m*-Mes^a, *o*-CH₃^{Mes a}, *p*-CH₃^{Mes a}), 2.37/ 142.4, 130.7 (*o*-CH₃^{Mes a}/ *o*-Mes^a, *m*-Mes^a).

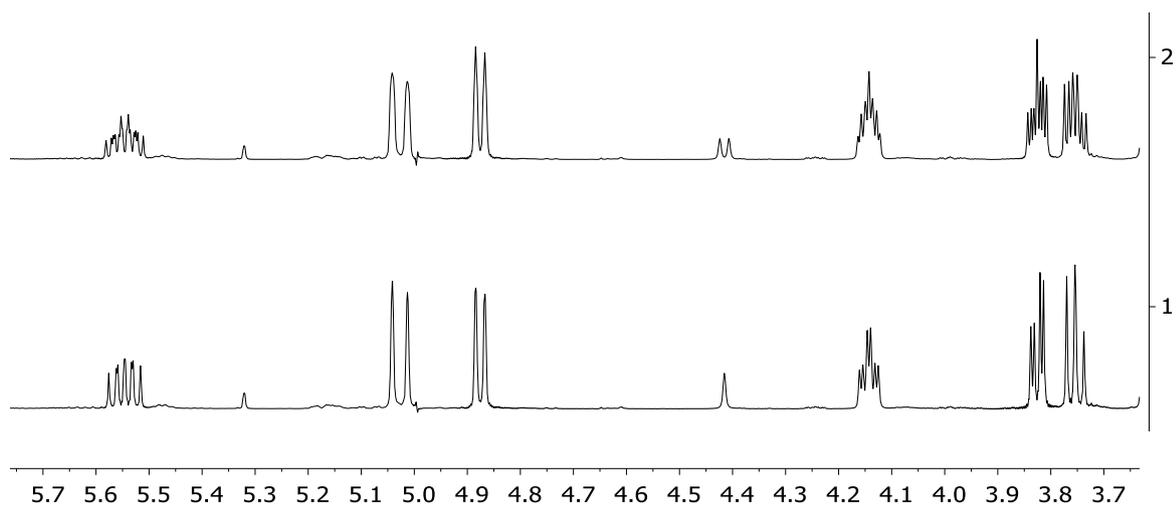
$^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, 299 K, CD_2Cl_2): $\delta = -22.3$ ($\nu_{1/2} \sim 3$ Hz).

$^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, 299 K, CD_2Cl_2): $\delta = -22.3$ ($\nu_{1/2} \sim 20$ Hz).

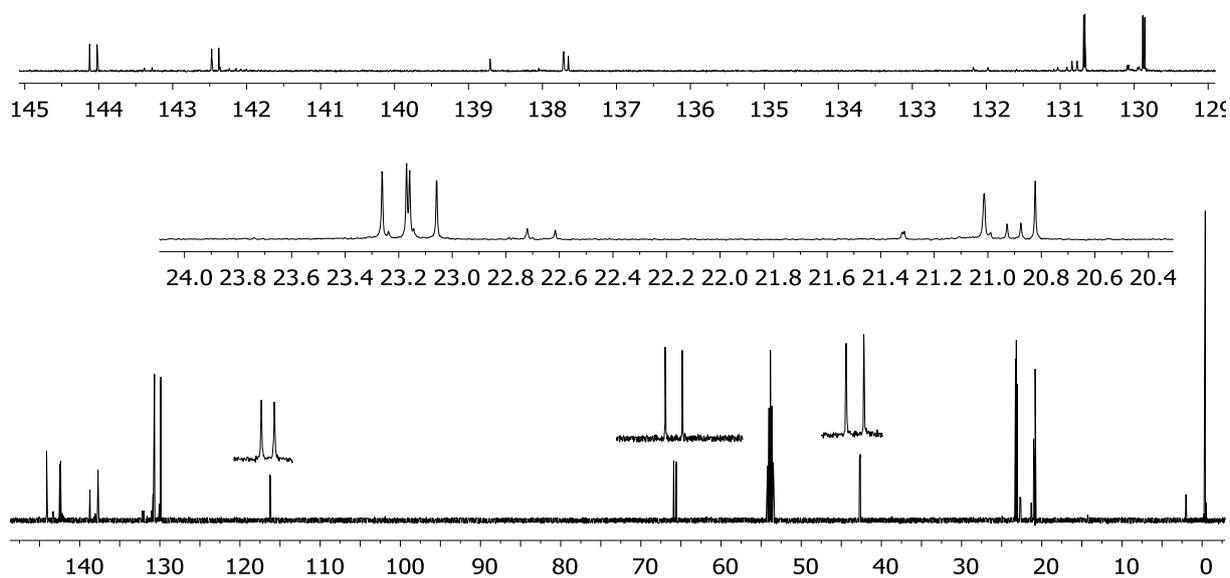
$^{29}\text{Si}\{^1\text{H}\}$ DEPT (119 MHz, 299 K, CD_2Cl_2): $\delta = 17.5$ ($\nu_{1/2} \sim 1$ Hz).



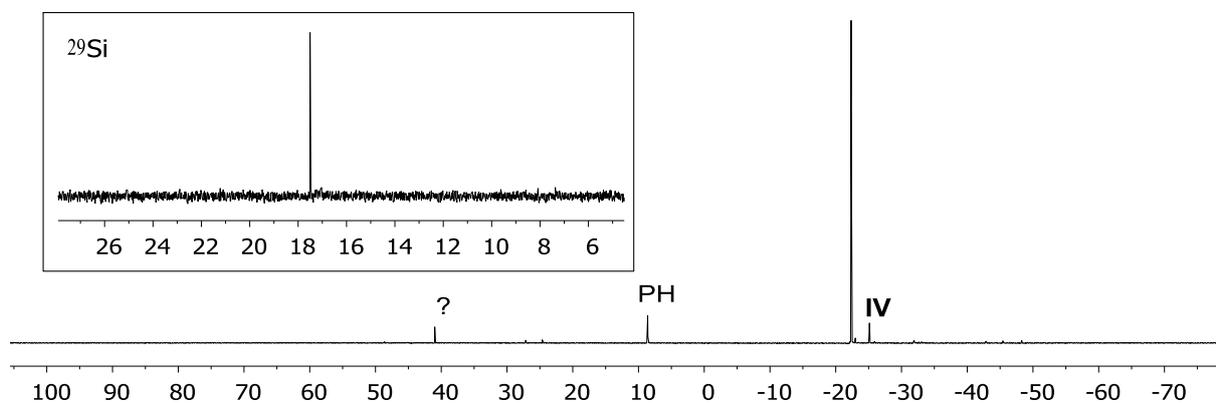
^1H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound **5**.



(2) ^1H NMR (600 MHz, 299 K, CD_2Cl_2) and (1) $^1\text{H}\{^{31}\text{P}\}$ NMR (600 MHz, 299 K, CD_2Cl_2) spectra of compound **5** (selected area).



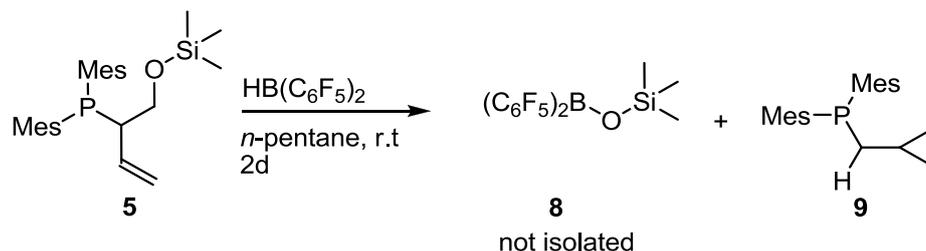
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **5**.



$^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (119 MHz, 299 K, CD_2Cl_2) and $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, 299 K, CD_2Cl_2) spectra of compound **5** (78 mol%). [**?** not identified (5 mol%), **PH** ($J_{\text{PH}} \sim 476$ Hz, 13 mol%), **IV** (4 mol%)].

Reaction of compound 5 with HB(C₆F₅)₂

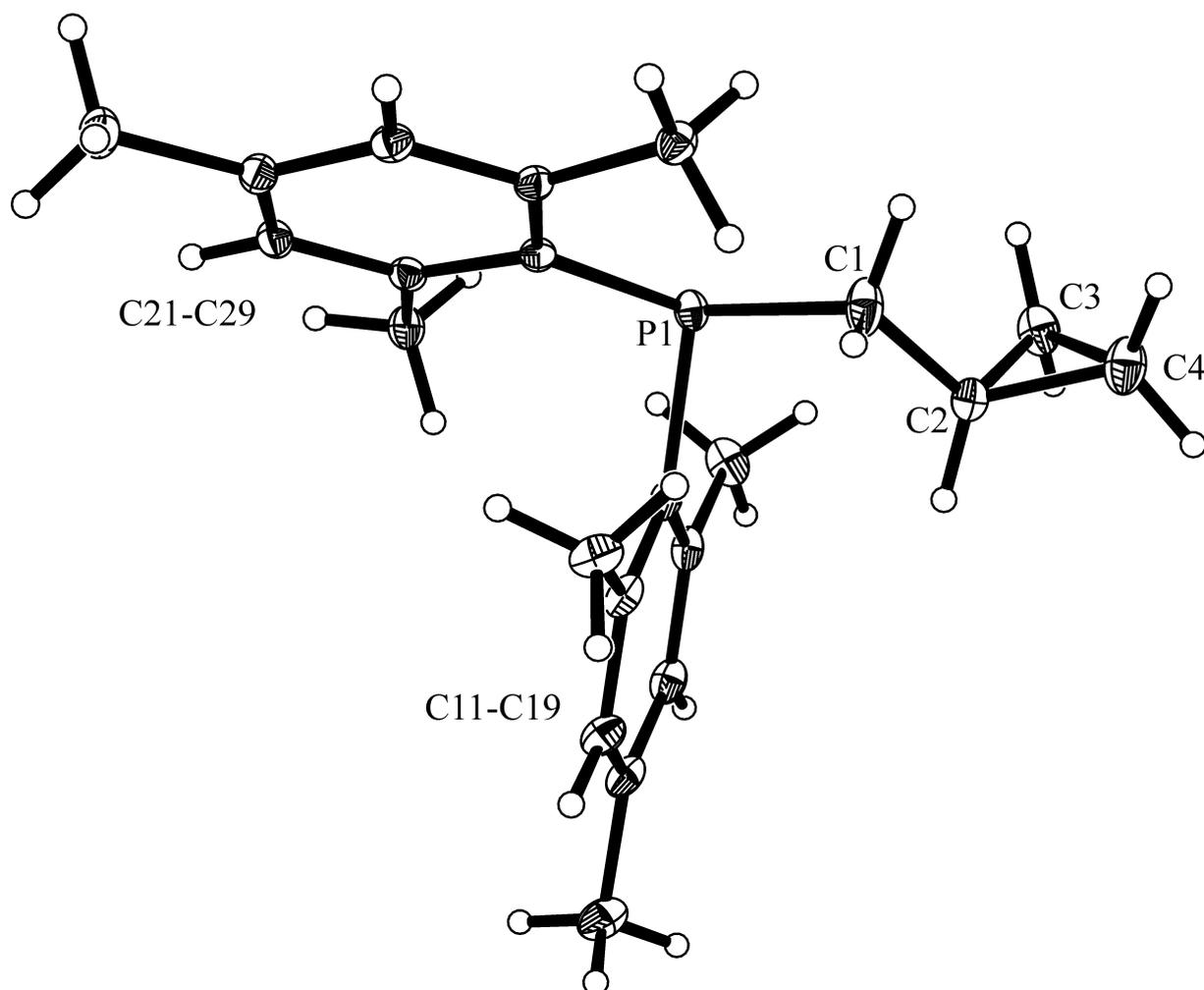
Generation of (cyclopropylmethyl)dimesitylphosphane 9 and siloxyborane 8.



1st Experiment: Preparation of compound 9: HB(C₆F₅)₂ (0.52 g, 1.50 mmol) was added at ambient temperature to a solution of dimesityl(1-(trimethylsilyloxy)but-3-en-2-yl)phosphane 5 (0.58 g, 1.41 mmol) in n-pentane (5 mL). After stirring for 2 days all volatiles were removed in *vacuo*. The collected colorless oil was dissolved in C₆D₆ and analyzed by NMR experiments (before workup: see below).

Then the oil was dissolved in CH₂Cl₂ (2 mL) and purified by column chromatography (Al₂O₃, CH₂Cl₂/ n-pentane, 1:1). After drying compound 9 was isolated as a colorless oil 0.42 g (92%). The obtained oil slowly crystallized over night at room temperature. The formed colorless crystals were suitable for the X-ray crystal structure analysis.

X-Ray crystal structure analysis of compound 9: formula C₂₂H₂₉P, *M* = 324.42, colourless crystal, 0.220 x 0.180 x 0.100 mm, *a* = 8.3322(2), *b* = 8.5865(3), *c* = 13.0867(4) Å, α = 87.833(1), β = 85.945(1), γ = 86.322(1)°, *V* = 931.5(1) Å³, ρ_{calc} = 1.157 gcm⁻³, μ = 1.262 mm⁻¹, empirical absorption correction (0.769 ≤ *T* ≤ 0.884), *Z* = 2, triclinic, space group *P* $\bar{1}$ (No. 2), λ = 1.54178 Å, *T* = 100(2) K, ω and ϕ scans, 23717 reflections collected, 3344 independent (*R*_{int} = 0.044) and 2937 observed reflections [*I* > 2σ(*I*)], 242 refined parameters, *R* = 0.035, *wR*² = 0.092, max. (min.) residual electron density 0.30 (-0.27) e.Å⁻³, hydrogen atoms were calculated and refined as riding atoms.



HRMS (MicroTof): $M+H^+$ ($C_{22}H_{29}PH^+$): Calcd.: 325.2080, Found: 325.2087.

Elemental analysis: Calcd. for $C_{22}H_{29}P$: C, 81.44; H, 9.01. Found: C, 78.05; H, 8.76.

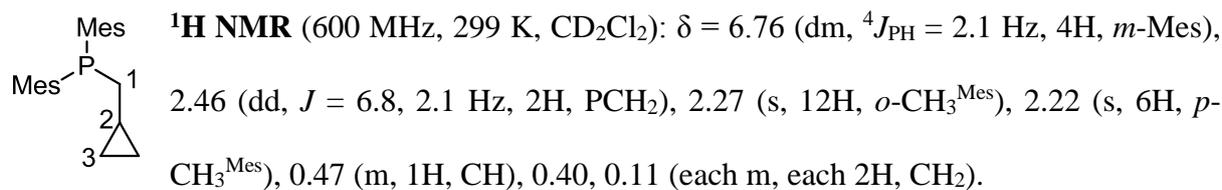
To improve the elemental analysis the crystals of compound **9** were dissolved in dichloromethane and passed through a pipette filled with Al_2O_3 . After removal of the solvent, the obtained white solid was crushed and then dried at 50 °C for 8 h.

Elemental analysis: Calcd. for $C_{22}H_{29}P$: C, 81.44; H, 9.01. Found: C, 80.72; H, 8.58.

A solution of the colorless oil before workup (mixture of compounds **8** and **9**, see below) in C_6D_6 were passed through a pipette filled with Al_2O_3 and then rinsed with dichloromethane (2 mL). After removal of the solvent in vacuo, the obtained white solid was crushed and then dried at 50 °C for 8 h.

Elemental analysis: Calcd. for $C_{22}H_{29}P$: C, 81.44; H, 9.01. Found: C, 81.47; H, 8.76.

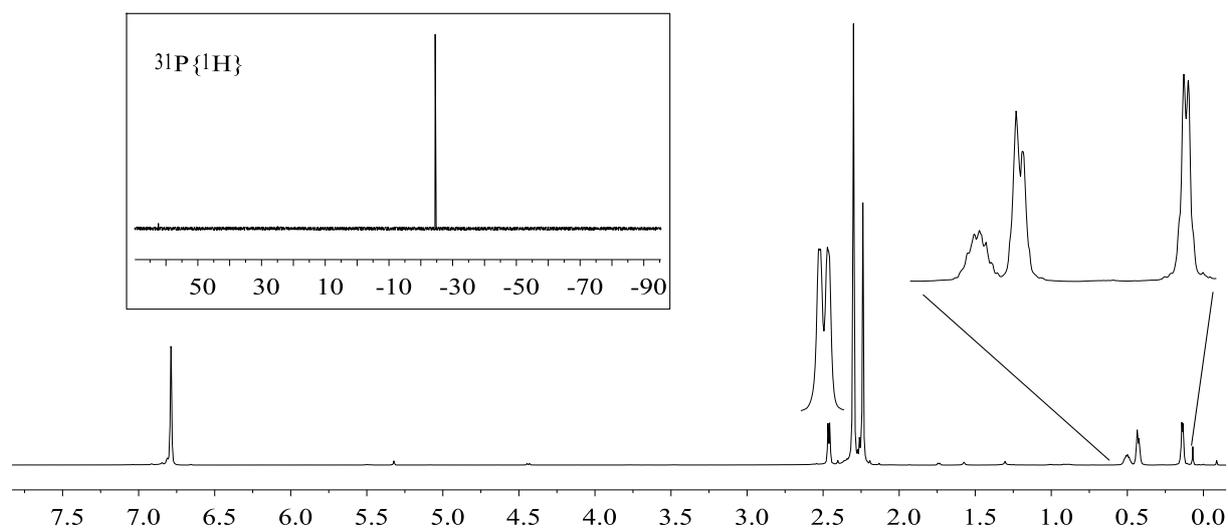
NMR data of the crystalline material in CD₂Cl₂ (compound **9**).



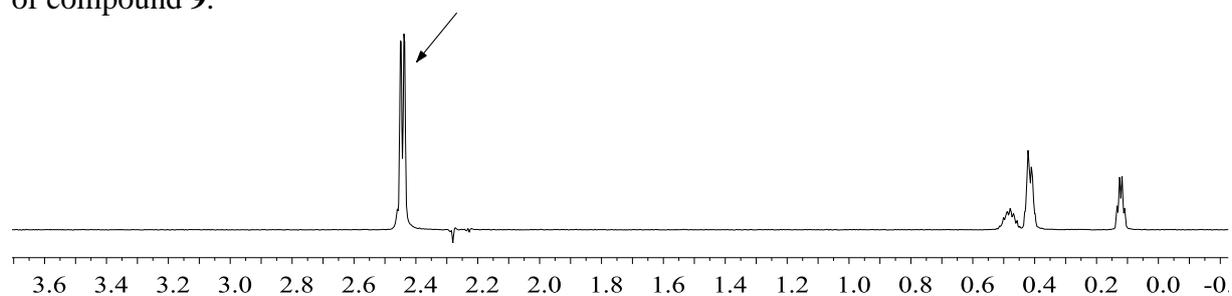
¹³C{¹H} NMR (151 MHz, 299 K, CD₂Cl₂): δ = 142.2 (d, ²J_{PC} = 13.3 Hz, *o*-Mes), 137.7 (*p*-Mes), 134.0 (d, ¹J_{PC} = 22.8 Hz, *i*-Mes), 130.0 (d, ³J_{PC} = 2.8 Hz, *m*-Mes), 33.9 (d, ¹J_{PC} = 16.0 Hz, PCH₂), 23.2 (d, ³J_{PC} = 13.4 Hz, *o*-CH₃^{Mes}), 20.9 (*p*-CH₃^{Mes}), 9.2 (d, ²J_{PC} = 20.5 Hz, CH), 6.5 (d, ³J_{PC} = 10.2 Hz, CH₂).

¹H{¹H} TOCSY (600 MHz, 299 K, CD₂Cl₂)[selected experiments]: δ¹H_{irr}/ δ¹H_{res} = 2.46/0.50, 0.43, 0.14 (1-H/ 2-H, 3-H).

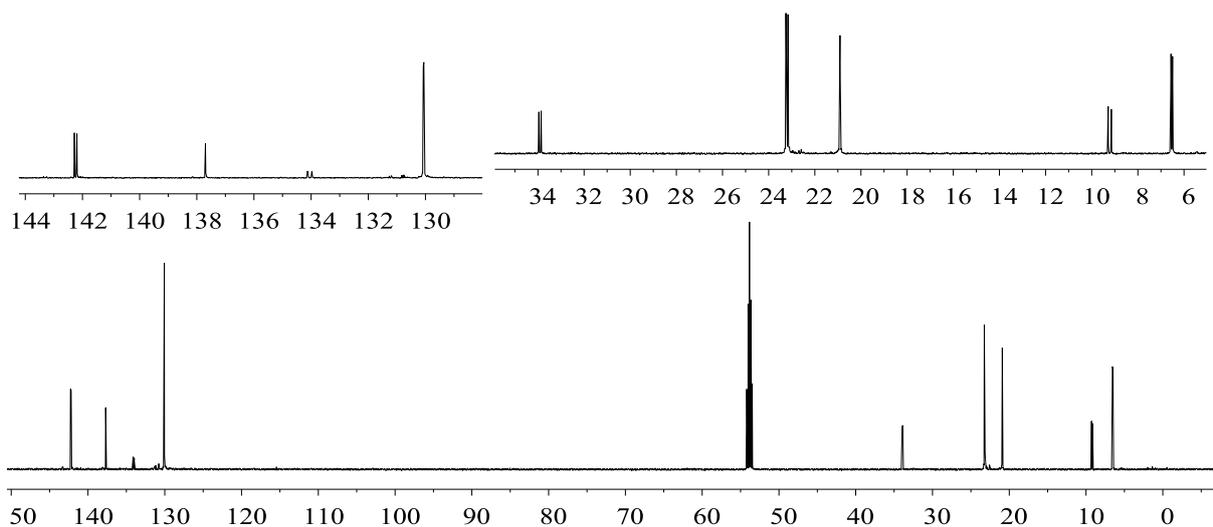
³¹P{¹H} NMR (243 MHz, 299 K, CD₂Cl₂): δ = -24.6 (ν_{1/2} ~ 3 Hz).



¹H NMR (600 MHz, 299 K, CD₂Cl₂) and **³¹P{¹H} NMR** (243 MHz, 299 K, CD₂Cl₂) spectra of compound **9**.



¹H{¹H} TOCSY (600 MHz, 299 K, CD₂Cl₂) spectrum of compound **9** (irradiation (arrow) at 2.46 ppm, response at 0.50, 0.43, 0.14 ppm)



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

Colorless oil before workup (see above): Reaction of compound **5** with $\text{HB}(\text{C}_6\text{F}_5)_2$ resulted in a reaction mixture of compound **9** and borane **8** (1:1 (^1H)).

Borane **8** (in C_6D_6):

^1H NMR (600 MHz, 299 K, C_6D_6): $\delta = 0.04$ (s, $^1J_{\text{SiH}} = 6.7$ Hz, 1H, SiMe_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, C_6D_6): $\delta = 148.2$ (dm, $^1J_{\text{CF}} \sim 245$ Hz, C_6F_5), 143.2 (dm, $^1J_{\text{CF}} \sim 265$ Hz, C_6F_5), 137.4 (dm, $^1J_{\text{CF}} \sim 250$ Hz, C_6F_5), 131.6 (br, $i\text{-C}_6\text{F}_5$), 0.4 ($^1J_{\text{SiC}} = 60.2$ Hz, SiMe_3).

$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, C_6D_6): $\delta = 38.1$ ($\nu_{1/2} \sim 350$ Hz).

^{19}F NMR (564 MHz, 299 K, C_6D_6): $\delta = -133.3$ (m, 2F, $o\text{-C}_6\text{F}_5$), -148.9 (tt, $J_{\text{FF}} = 20.8, 3.6$ Hz, 1F, $p\text{-C}_6\text{F}_5$), -161.3 (m, 2F, $m\text{-C}_6\text{F}_5$). [$\Delta\delta^{19}\text{F}_{\text{m,p}} = 12.5$].

$^1\text{H}, ^{29}\text{Si}$ GHMQC (600 MHz/ 119 MHz, 299 K, C_6D_6): $\delta^1\text{H}/ \delta^{29}\text{Si} = 0.04/ 20.2$ (OSiMe_3).

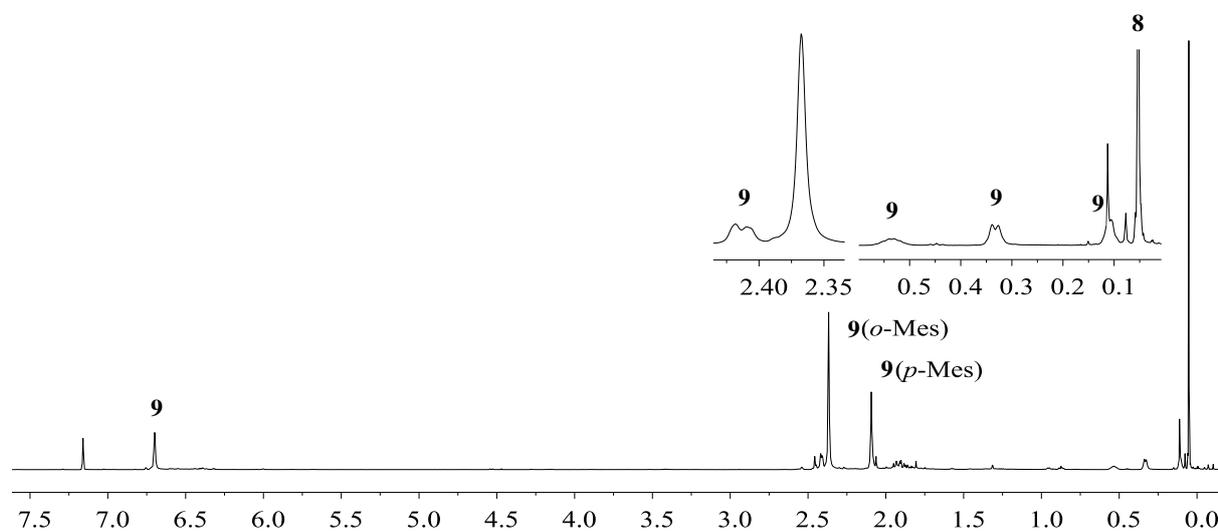
Compound **9** (in C_6D_6):

^1H NMR (600 MHz, 299 K, C_6D_6): $\delta = 6.69$ (s, 4H, $m\text{-Mes}$), 2.40 (m, 2H, PCH_2), 2.36 (s, 12H, $o\text{-CH}_3^{\text{Mes}}$), 2.08 (s, 6H, $p\text{-CH}_3^{\text{Mes}}$), 0.52 (m, 1H, CH), $0.32, 0.10$ (each m, each 2H, CH_2).

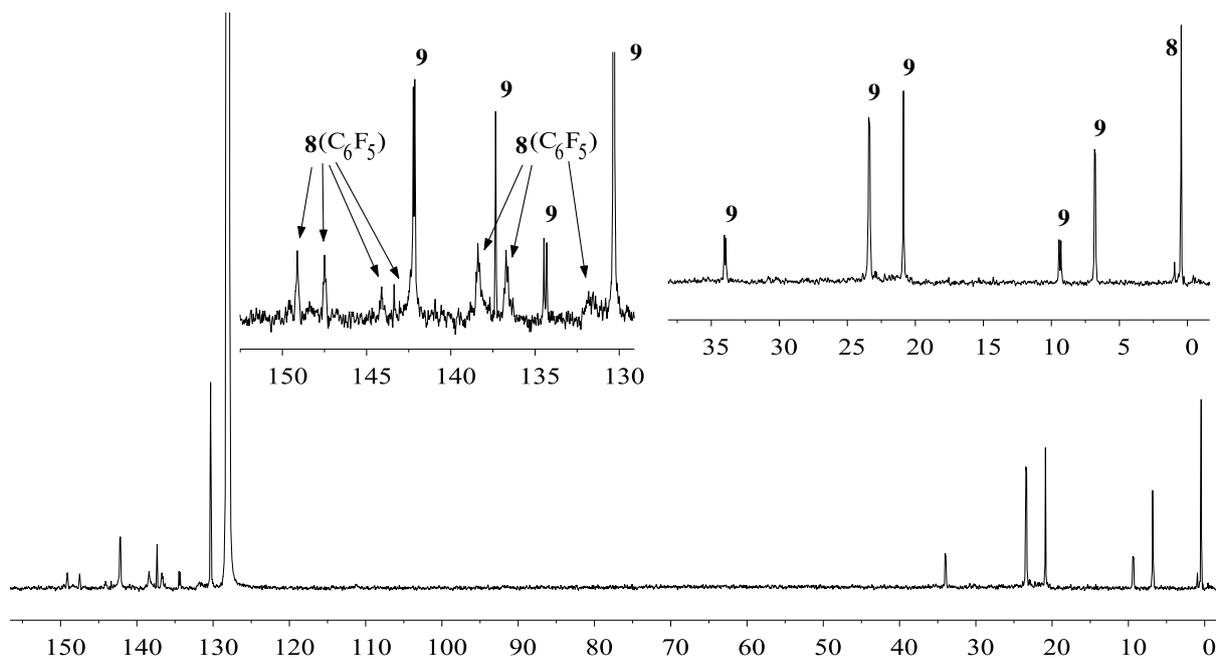
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, C_6D_6): δ = 142.1 (d, $^2J_{\text{PC}}$ = 13.4 Hz, *o*-Mes), 137.3 (*p*-Mes), 134.3 (d, $^1J_{\text{PC}}$ = 24.0 Hz, *i*-Mes), 130.3 (*m*-Mes), 34.9 (d, $^1J_{\text{PC}}$ = 16.0 Hz, PCH_2), 23.3 (d, $^3J_{\text{PC}}$ = 13.6 Hz, *o*- CH_3^{Mes}), 20.8 (*p*- CH_3^{Mes}), 9.3 (d, $^2J_{\text{PC}}$ = 20.5 Hz, CH), 6.7 (d, $^3J_{\text{PC}}$ = 10.2 Hz, CH_2).

$^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, 299 K, C_6D_6): δ = -24.4 ($\nu_{1/2}$ ~ 5 Hz).

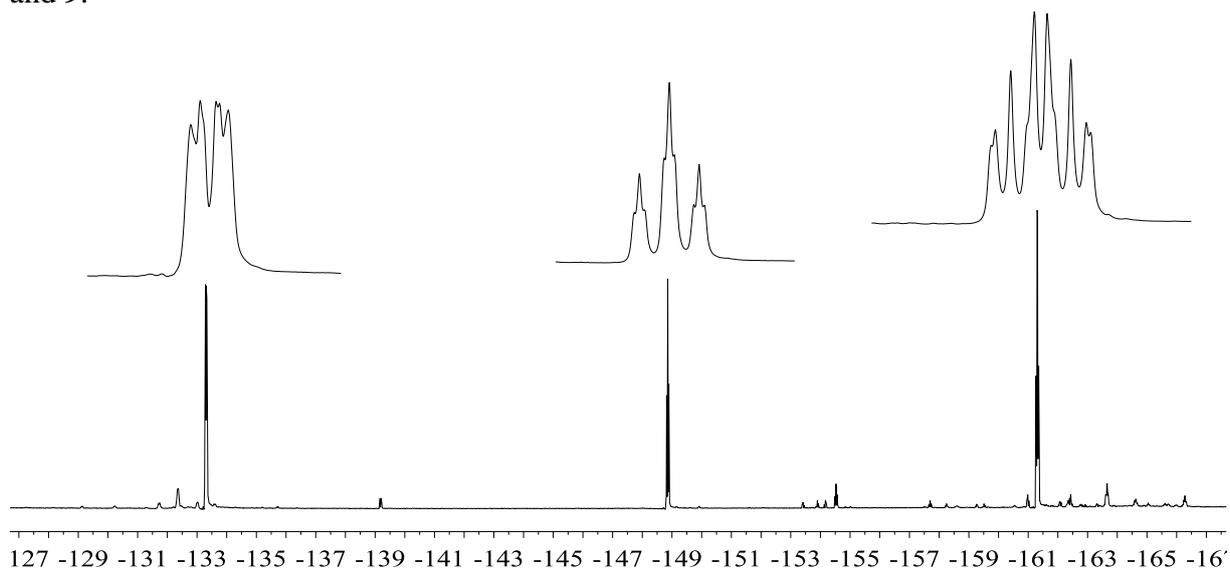
$^1\text{H},^{31}\text{P}$ GHMQC (600 MHz/ 243 MHz, 299 K, C_6D_6): $\delta^1\text{H}/\delta^{31}\text{P}$ = 6.69, 2.40, 2.36, 2.08, 0.52, 0.32, 0.10/ -24.4 (*m*-Mes, PCH_2 , *o*- CH_3^{Mes} , *p*- CH_3^{Mes} , CH, CH_2 , CH_2/P).



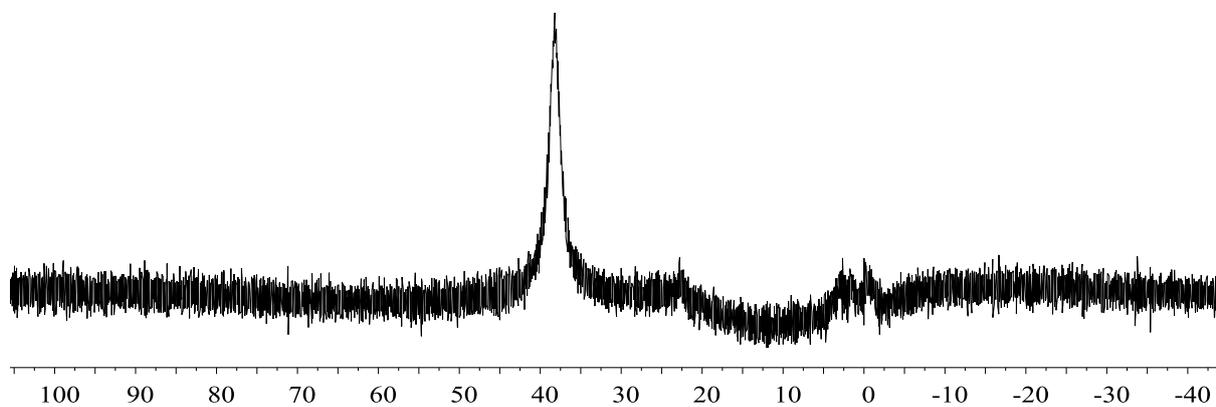
^1H NMR (600 MHz, 299 K, C_6D_6) spectrum of the reaction mixture of compounds **8** and **9**.



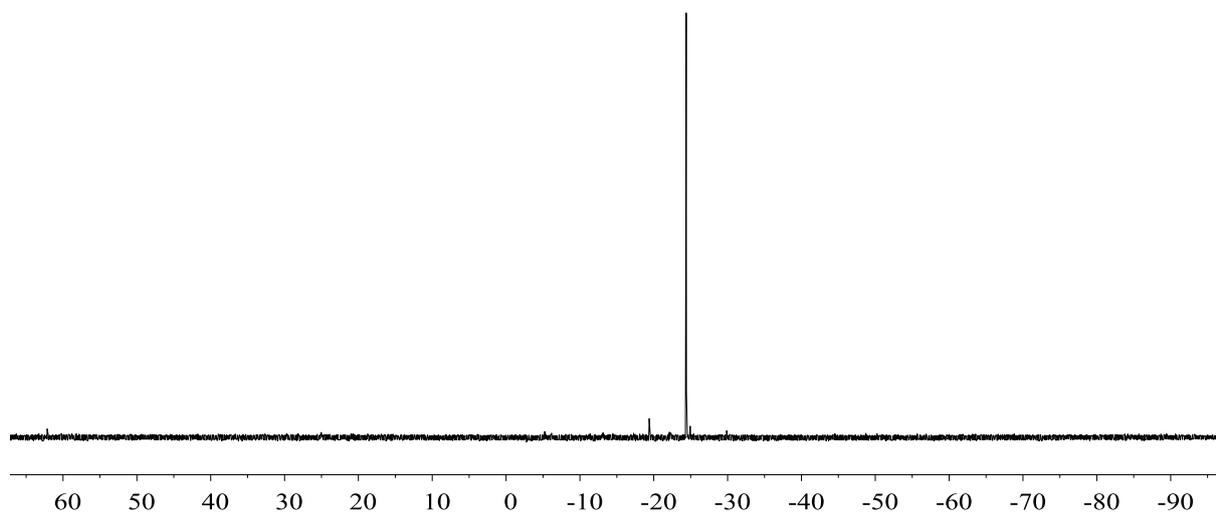
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, C_6D_6) spectrum of the reaction mixture of compounds **8** and **9**.



^{19}F NMR (564 MHz, 299 K, C_6D_6) spectrum of the reaction mixture of compounds **8** and **9**.

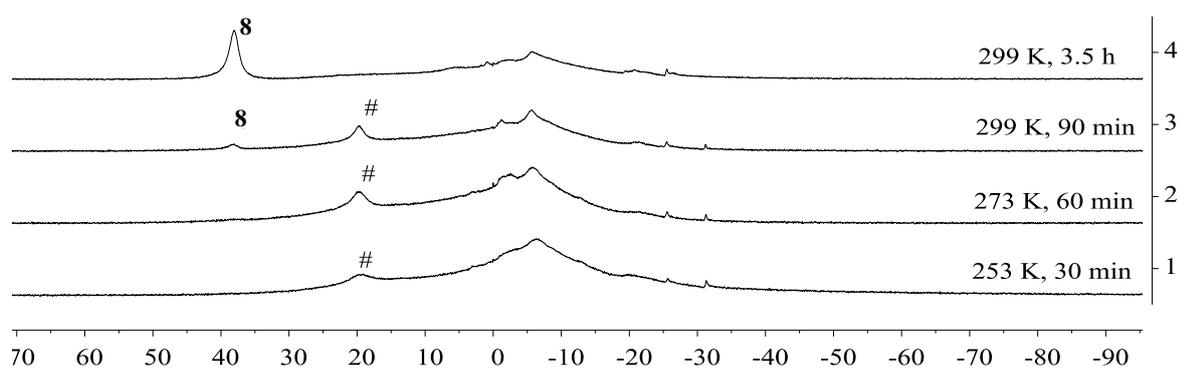


$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, C_6D_6) spectrum of the reaction mixture of compounds **8** and **9**.

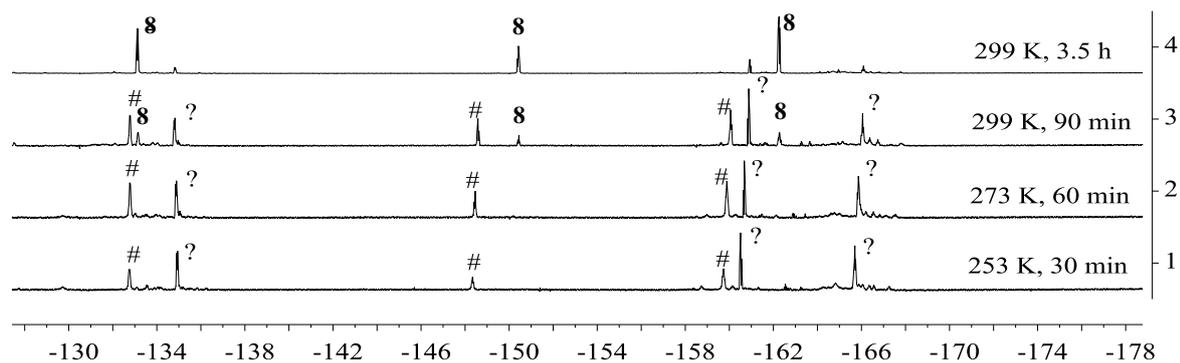


$^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, 299 K, C_6D_6) spectrum of the reaction mixture of compounds **8** and **9**.

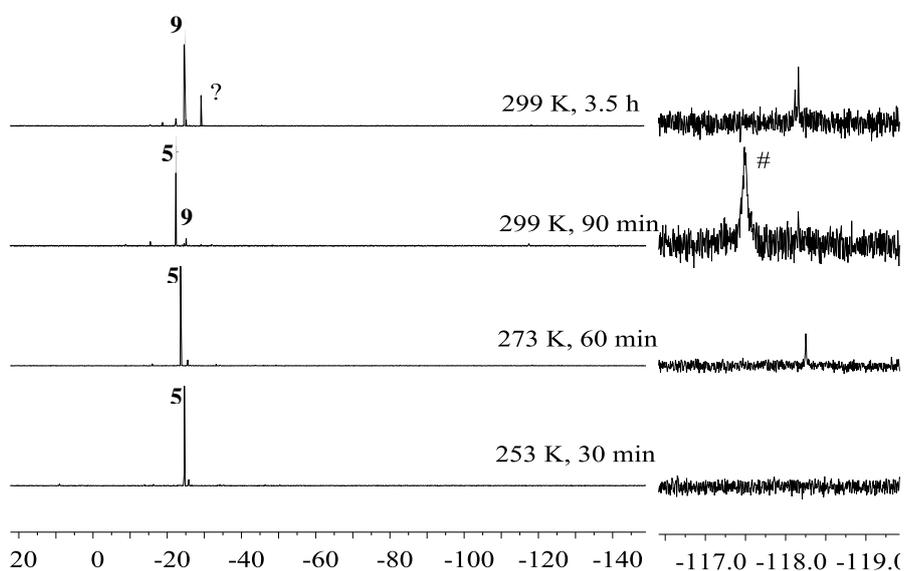
2nd Experiment (reaction monitoring by DNMR). A solution of dimesityl(1-(trimethylsilyloxy)but-3-en-2-yl)phosphane **5** (30 mg, 8.8×10^{-2} mmol) in deuterated dichloromethane (0.3 mL) was added to a Yong-NMR tube filled with a solution of $\text{HB}(\text{C}_6\text{F}_5)_2$ (26 mg, 7.5×10^{-2} mmol) in deuterated dichloromethane (0.3 mL) at -78 °C. The reaction progress was monitored by NMR spectroscopy at various temperatures.



$^{11}\text{B}\{^1\text{H}\}$ VTNMR (160 MHz, CD_2Cl_2) spectra of the reaction of compound **5** with $\text{HB}(\text{C}_6\text{F}_5)_2$. [temperature, overall reaction time; # $\text{HB}(\text{C}_6\text{F}_5)_2$].

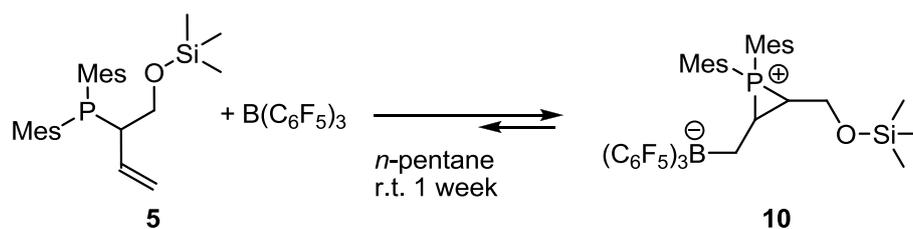


^{19}F VTNMR (470 MHz, 253–299K, CD_2Cl_2) spectra of the reaction of compound **5** with $\text{HB}(\text{C}_6\text{F}_5)_2$. [temperature, overall reaction time; # $\text{HB}(\text{C}_6\text{F}_5)_2$, ? unidentified compound].



$^{31}\text{P}\{^1\text{H}\}$ VTNMR (202 MHz, CD_2Cl_2) spectra of the reaction of compound **5** with $\text{HB}(\text{C}_6\text{F}_5)_2$. [temperature, overall reaction time; ? unidentified compound, # tentatively assigned as phosphiranium intermediate **7** (**5** : **9** : **7** ~ 84 : 6 : 10)].

Synthesis of compound 10.

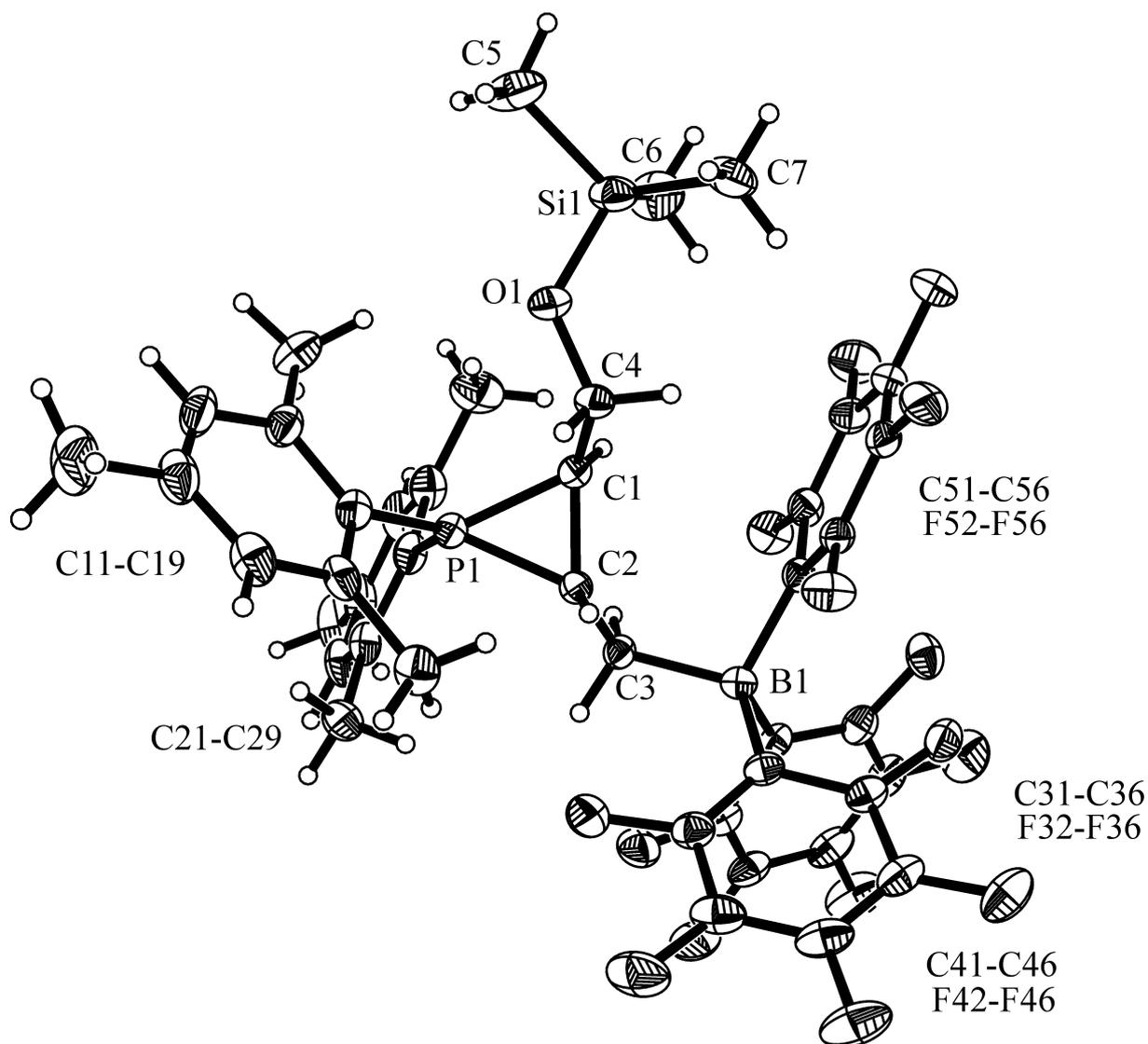


Compound **5** (0.290 g, 0.70 mmol) and tris(pentafluorophenyl)borane (0.360 g, 0.70 mmol) were dissolved in dry *n*-pentane (5 mL) under an atmosphere of argon and stirred for 1 week at ambient temperature. During this time a white precipitate was formed, which was isolated by filtration. It was washed thrice with *n*-pentane (2 mL) and dried *in vacuo* to give a white solid (0.500 g, 77%).

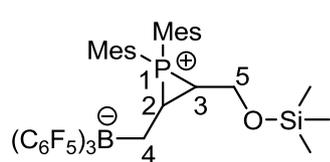
Crystals suitable for the X-ray crystal structure analysis were obtained from a saturated solution of the white solid in CH₂Cl₂ at -30 °C. The crystals were collected, washed with pentane, dried *in vacuo* and dissolved in CD₂Cl₂ for NMR spectroscopic characterization (*Comment*: Compound **10** slowly gives at room temperature in CD₂Cl₂ solution the starting materials back (Compound **5** and B(C₆F₅)₃) (0.25/1 ratio by ¹H NMR)).

Elemental analysis (crystals): Calcd. for C₄₃H₃₇BF₁₅OPSi(1xCH₂Cl₂): C, 52.35; H, 3.89. Found: C, 52.36; H, 3.87.

X-Ray crystal structure analysis of compound 10: formula C₄₃H₃₇BF₁₅OPSi, *M* = 924.60, colourless crystal, 0.23 x 0.10 x 0.05 mm, *a* = 10.8091(2), *b* = 25.3584(3), *c* = 16.9567(4) Å, *β* = 96.133(1) °, *V* = 4621.2(2) Å³, *ρ*_{calc} = 1.329 g cm⁻³, *μ* = 0.177 mm⁻¹, empirical absorption correction (0.960 ≤ *T* ≤ 0.991), *Z* = 4, monoclinic, space group *P*2₁/*c* (No. 14), *λ* = 0.71073 Å, *T* = 223(2) K, *ω* and *φ* scans, 32591 reflections collected (*±h*, *±k*, *±l*), 8012 independent (*R*_{int} = 0.064) and 5621 observed reflections [*I* > 2σ(*I*)], 568 refined parameters, *R* = 0.070, *wR*² = 0.196, max. (min.) residual electron density 0.36 (-0.33) e.Å⁻³, hydrogen atoms were calculated and refined as riding atoms.



A solution of the obtained crystals in CD_2Cl_2 was characterized by NMR experiments. A mixture of compound **10**, compound **5** and $\text{B}(\text{C}_6\text{F}_5)_3$ was observed (**10** : **5** ~ 78 : 22 (^1H)). NMR data of compound **5** are consistent to those listed above.



^1H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 7.12 (1H), 7.07 (2H), 6.97 (1H)(each br, *m*-Mes), 3.56 (ddd, $^3J_{\text{PH}} = 32.5$ Hz, $^2J_{\text{HH}} = 11.2$ Hz, $^3J_{\text{HH}} = 3.3$ Hz, 1H, 5-H), 2.95 (m, 1H, 2-H), 2.75 (ddd, $^3J_{\text{PH}} = 19.7$ Hz, $^2J_{\text{HH}} = 11.2$ Hz, $^3J_{\text{HH}} = 8.8$ Hz, 1H, 5-H), 2.67 (m, 1H, 3-H), 2.67, 2.61, 2.49, 2.45 (each br, each 3H, *o*- CH_3^{Mes}), 2.34, 2.31 (each br, each 3H, *p*- CH_3^{Mes}), 2.34, 0.78 (each m, each 1H, 4-H), -0.18 (s, $^2J_{\text{SiH}} = 6.2$ Hz, 9H, SiMe_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, CD_2Cl_2): $\delta = 148.6$ (dm, $^1J_{\text{FC}} \sim 240$ Hz, C_6F_5), 147.0, 146.0, 145.4, 145.3 (each br, *o*-Mes), 146.2, 146.1 (each d, $^4J_{\text{PC}} = 3.2$ Hz, *p*-Mes), 138.6 (dm, $^1J_{\text{FC}} \sim 240$, C_6F_5), 137.0 (dm, $^1J_{\text{FC}} \sim 250$, C_6F_5), 132.1, 131.7, 131.2, 131.2 (each br, *m*-Mes), 125.3 (br, *i*- C_6F_5), 111.8 (d, $^1J_{\text{PC}} = 80.4$ Hz), 111.2 (d, $^1J_{\text{PC}} = 88.5$ Hz)(*i*-Mes), 60.2 (d, $^2J_{\text{PC}} = 7.0$ Hz, C5), 41.4 (d, $^1J_{\text{PC}} = 2.0$ Hz, C3), 37.9 (d, $^1J_{\text{PC}} = 10.9$ Hz, C2), 23.7 (br), 23.2 (br), 22.9 (br)(*o*- CH_3^{Mes}), 21.5, 21.4 (each d, $J = 0.9$ Hz, *p*- CH_3^{Mes}), 21.5 (br, C4), -1.6 ($^1J_{\text{SiC}} = 59.0$ Hz, SiMe_3).

$^1\text{H}, ^1\text{H}$ GCOSY (600 MHz/ 600 MHz, 299 K, CD_2Cl_2) [selected trace]: $\delta^1\text{H}/ \delta^1\text{H} = 2.95/ 2.67$, 2.34, 0.78 (2-H/ 3-H, 4-H, 4-H).

$^1\text{H}\{^1\text{H}\}$ TOCSY (600 MHz, 299 K, CD_2Cl_2) [selected spectrum]: $\delta^1\text{H}_{\text{irr}}/ \delta^1\text{H}_{\text{res}} = 2.95/ 2.67$, 2.34, 0.79 (2-H / 3-H, 4-H, 4-H).

$^1\text{H}, ^{13}\text{C}$ GHSQC (600 MHz/ 151 MHz, 299 K, CD_2Cl_2): $\delta^1\text{H}/ \delta^{13}\text{C} = 7.12/ 132.1$, 7.07/ 131.7, 6.97/ 131.2 (*m*-Mes), 3.56/ 60.2 (C5), 2.75/ 60.2 (C5), 2.95/ 37.9 (C2), 2.67/ 41.4 (C3), 2.67/ 23.7, 2.61/ 23.2, 2.49/ 22.9, 2.45/ 22.9 (*o*- CH_3^{Mes}), 2.34/ 21.5 (C4), 0.78/ 21.5 (C4), 2.34/ 21.5, 2.31/ 21.4 (*p*- CH_3^{Mes}), -0.18/ -1.6 (SiMe_3).

$^1\text{H}, ^{13}\text{C}$ GHMBC (600 MHz/ 151 MHz, 299 K, CD_2Cl_2) [selected traces]: $\delta^1\text{H}/ \delta^{13}\text{C} = 2.67/ 145.4$, 132.1, 111.8 (*o*- $\text{CH}_3^{\text{Mes}}/ o$ -Mes, *m*-Mes, *i*-Mes), 2.34/ 146.1, 132.1, 131.2 (*p*- $\text{CH}_3^{\text{Mes}}/ p$ -Mes, *m*-Mes, *m*-Mes).

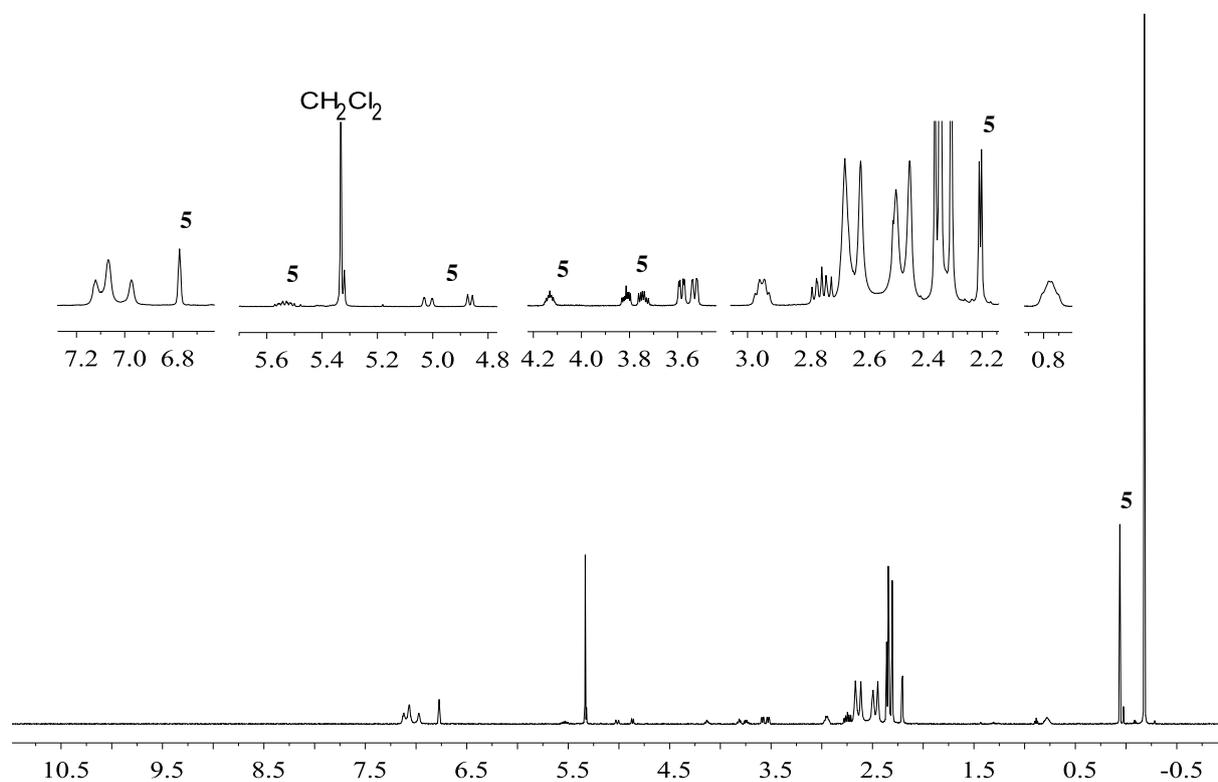
$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, CD_2Cl_2): $\delta = -13.8$ (d, $J \sim 14$ Hz, **10**), 59.1 ($\nu_{1/2} \sim 800$ Hz, $\text{B}(\text{C}_6\text{F}_5)_3$).

^{11}B NMR (192 MHz, 299 K, CD_2Cl_2): $\delta = -13.8$ ($\nu_{1/2} \sim 50$ Hz), 59.1 ($\nu_{1/2} \sim 800$ Hz, $\text{B}(\text{C}_6\text{F}_5)_3$).

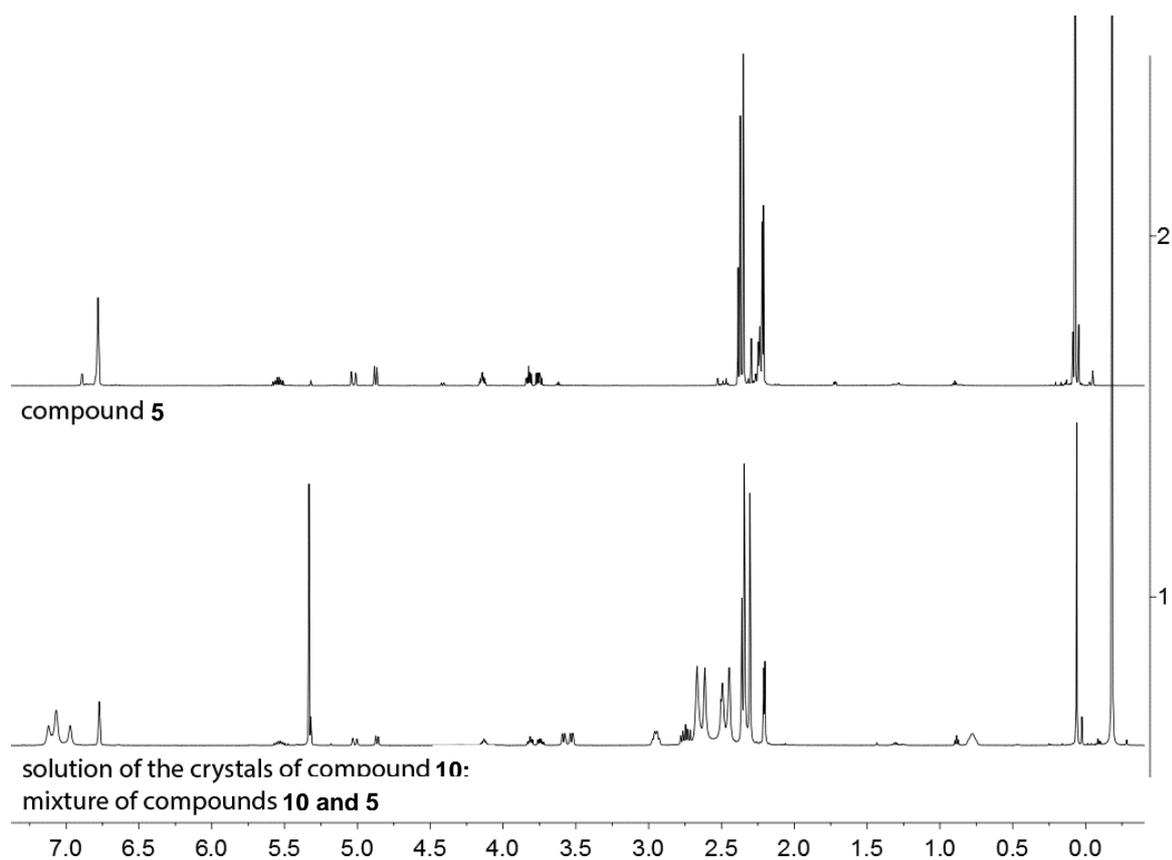
^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): compound **10**: $\delta = -132.4$ (m, 2F, *o*), -162.6 (t, $^3J_{\text{FF}} = 20.3$ Hz, 1F *p*), -166.3 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}\text{F} = 3.7$], $\text{B}(\text{C}_6\text{F}_5)_3$: $\delta = -128.2$ (br m, 2F, *o*), -143.8 (br, 1F *p*), -161.0 (br m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}\text{F} = 17.2$].

$^{29}\text{Si}\{^1\text{H}\}$ DEPT (119 MHz, 299 K, CD_2Cl_2): $\delta = 21.0$ ($\nu_{1/2} \sim 1$ Hz).

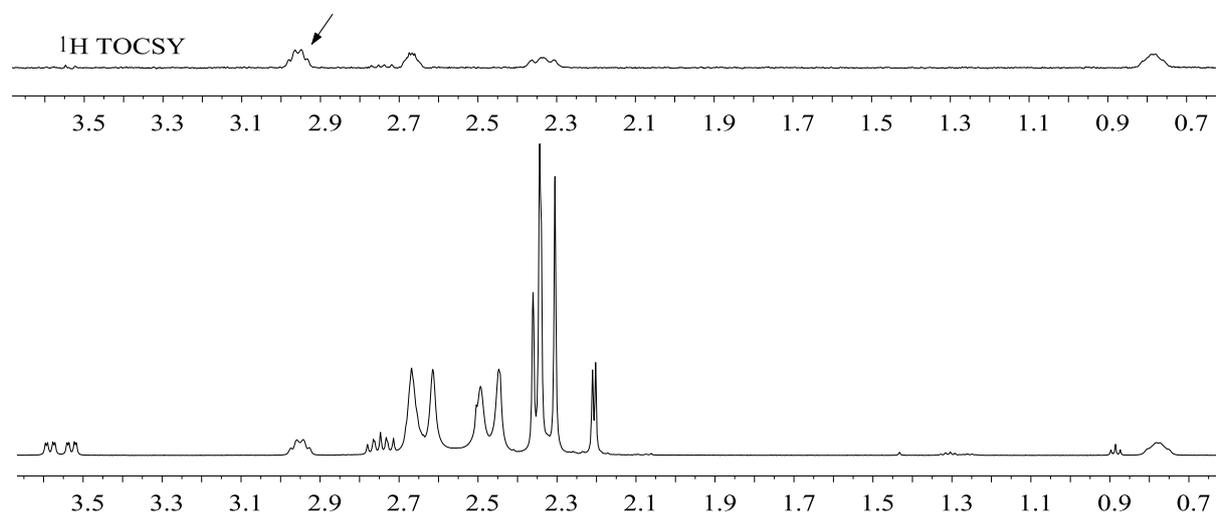
$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 299 K, CD_2Cl_2): $\delta = -114.2$ (m, **10**), -22.4 ($\nu_{1/2} \sim 25$ Hz, **5**). [after 1 week].



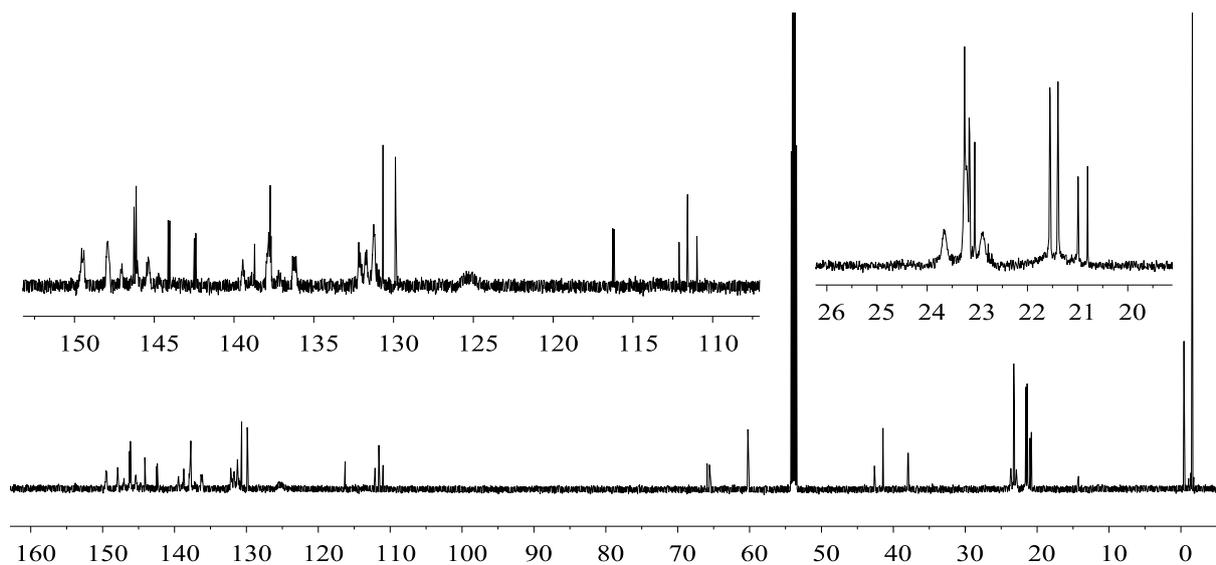
^1H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of the solution of the crystals of compound **10** in CD_2Cl_2 (admixed with compound **5** and CH_2Cl_2).



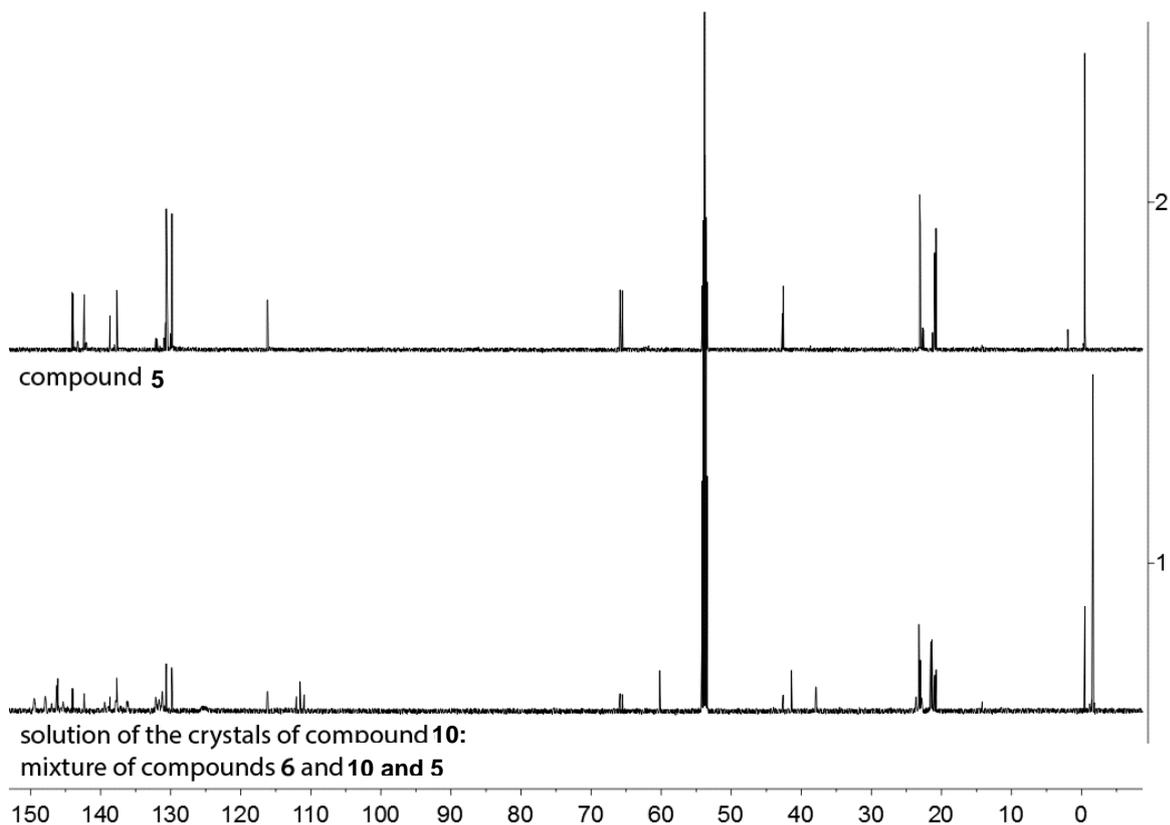
^1H NMR (600 MHz, 299 K, CD_2Cl_2) spectra of compound **10** and **5**. (1) Solution of the crystals of compound **10** in CD_2Cl_2 ; (2) compound **5** (see above).



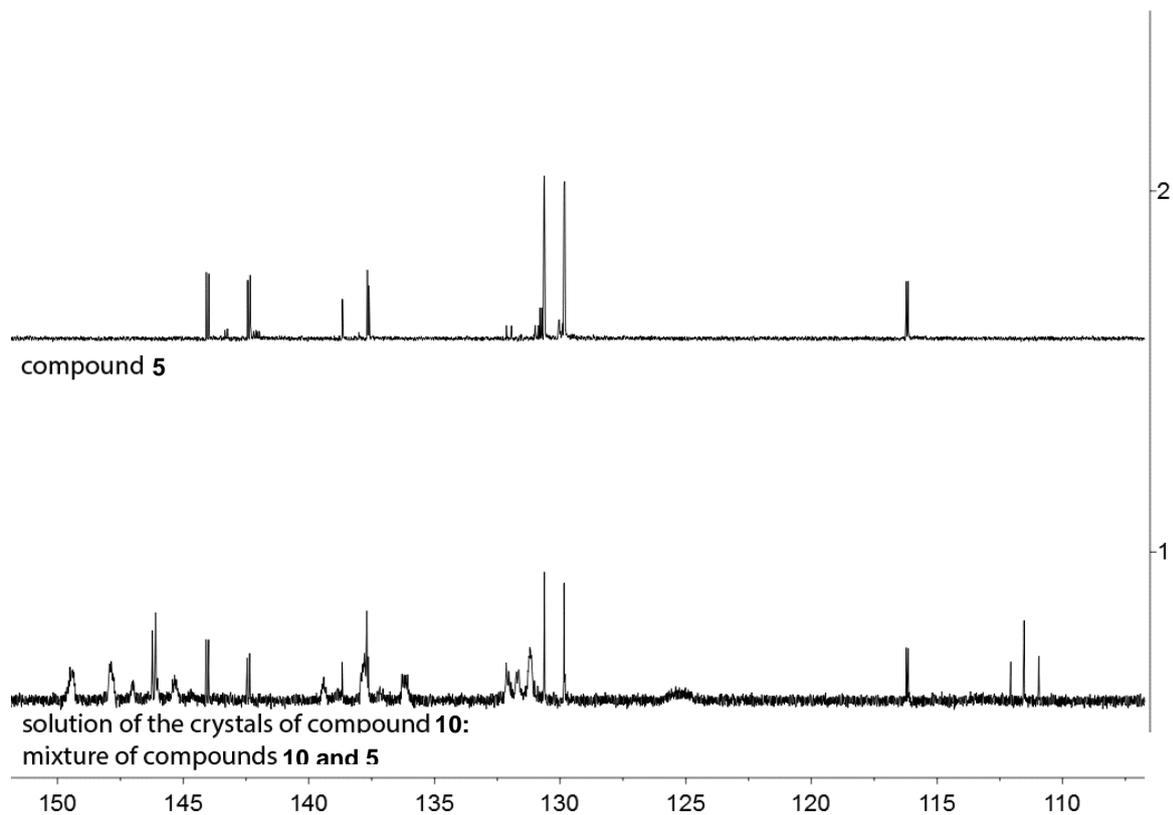
^1H NMR (600 MHz, 299 K, CD_2Cl_2) and $^1\text{H}\{^1\text{H}\}$ TOCSY (600 MHz, 299 K, CD_2Cl_2) spectra of compound **10** (irradiation (arrow) at 2.95 ppm, response at 2.75, 2.67, 2.34, 0.78 ppm).



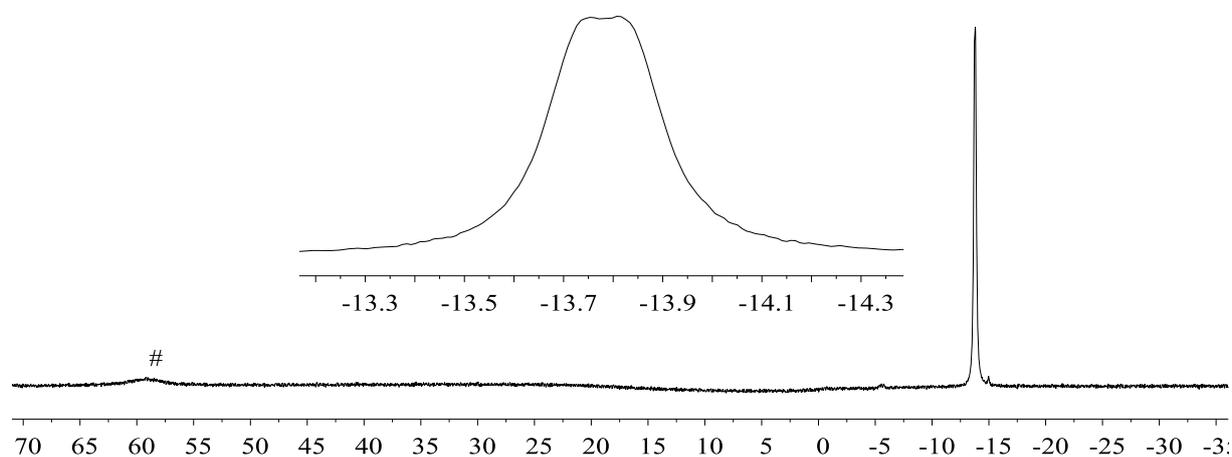
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of the solution of the crystals of compound **10** in CD_2Cl_2 (admixed with compound **5**).



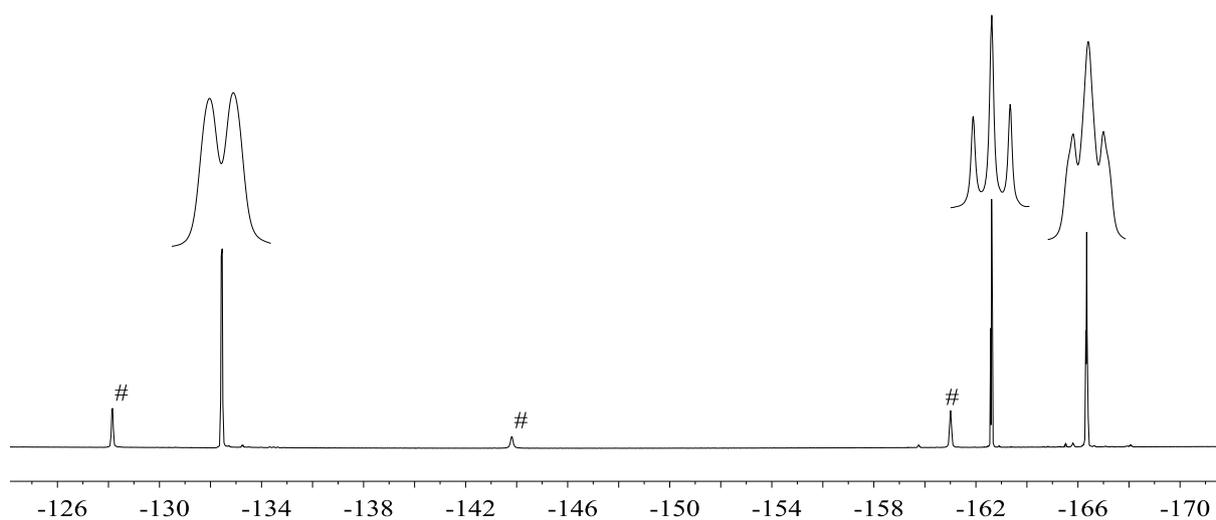
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectra of compound **10** and **5**. (1) Solution of the crystals of compound **10** in CD_2Cl_2 ; (2) compound **5** (see above).



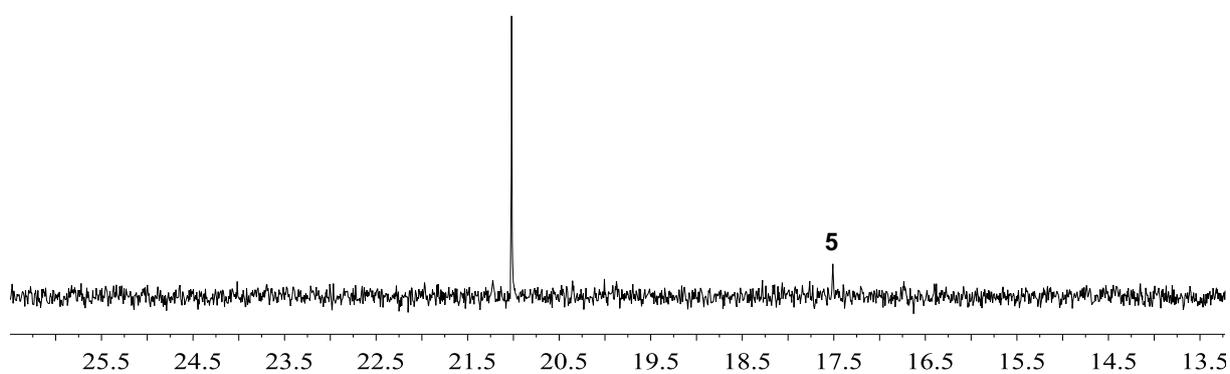
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectra of compounds **10** and **5**. (1) Solution of the crystals of compound **10** in CD_2Cl_2 ; (2) compound **5** (see above).



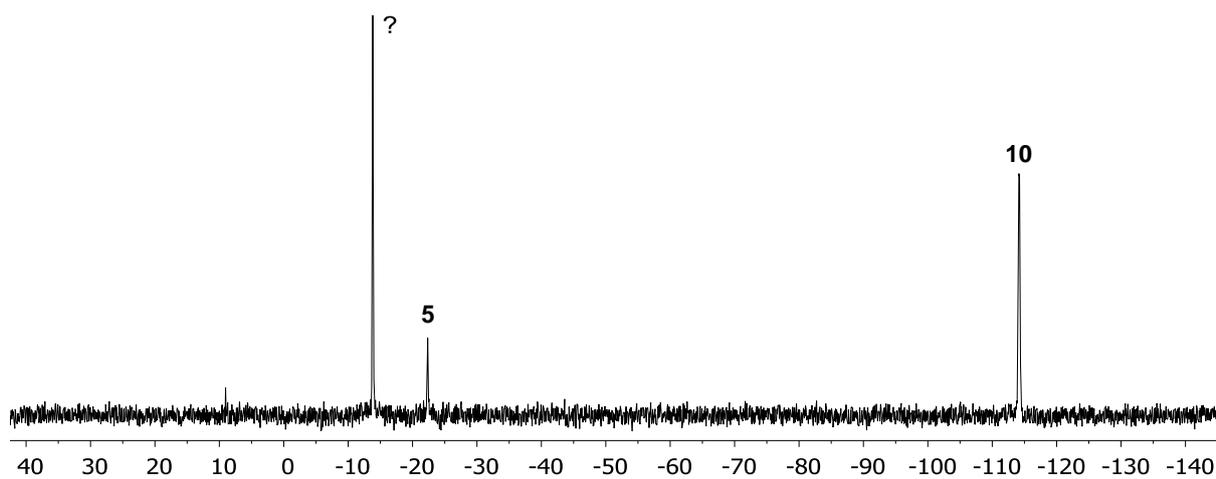
$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of compound **10**. [# $\text{B}(\text{C}_6\text{F}_5)_3$].



^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **10** (# $\text{B}(\text{C}_6\text{F}_5)_3$).



$^{29}\text{Si}\{^1\text{H}\}$ DEPT (119 MHz, 299 K, CD_2Cl_2) spectrum of compound **10**.

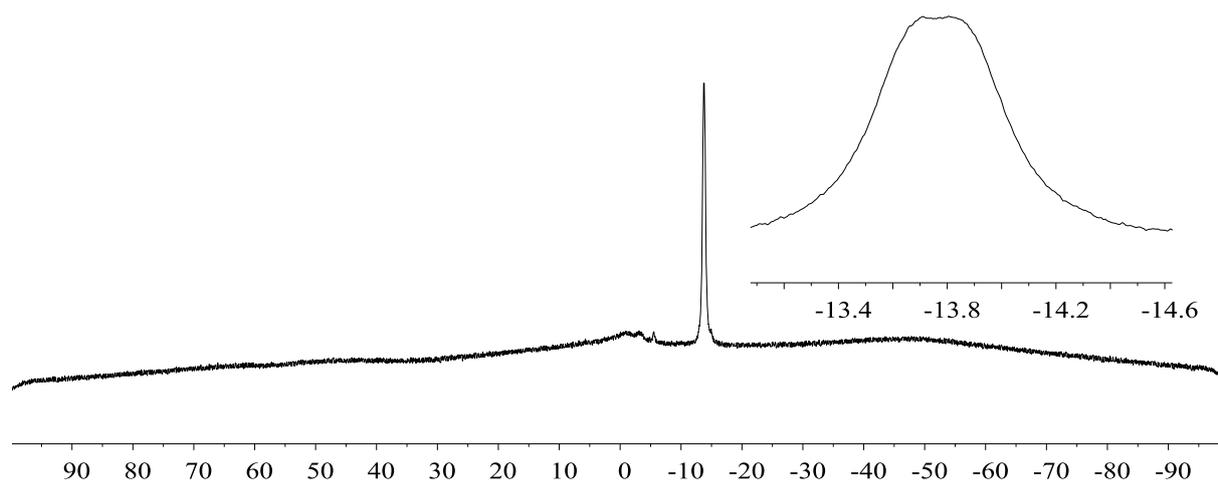


$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 299 K, CD_2Cl_2) spectrum) of compound **10**. [? unidentified compound]. Note: This spectrum was measured after 1 week in CD_2Cl_2 solution.

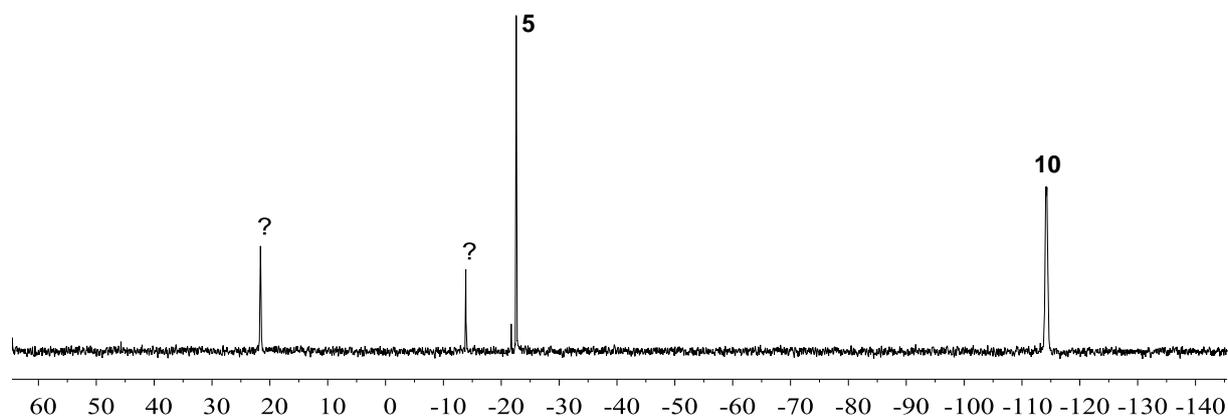
A solution of the obtained white solid (before workup) in CD_2Cl_2 was characterized by NMR experiments.

$^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, 299 K, CD_2Cl_2): $\delta = -13.8$ (d, $J \sim 14$ Hz).

$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, 299K, CD_2Cl_2): $\delta = -114.2$ (m).

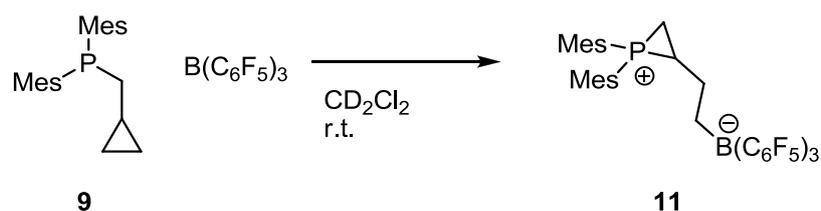


$^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, 299 K, CD_2Cl_2) spectrum of the white solid.



$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, 299 K, CD_2Cl_2) spectrum of the white solid. [? unknown compounds].

Preparation of compound 11.



1st Experiment. Compound **9** (50 mg, 0.1541 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (78.9 mg, 0.1541 mmol) were dissolved in CH_2Cl_2 (2 mL) and stirred at ambient temperature for 30 min. Then all volatiles were removed in *vacuo*. The residue was crystallized from toluene/*n*-pentane solution at $-30\text{ }^\circ\text{C}$ to give a white microcrystalline solid (35 mg, 27%).

Elemental analysis: Calcd. for $\text{C}_{40}\text{H}_{29}\text{BF}_{15}\text{P}$ (+ 1/6 toluene): C, 58.17; H, 3.61. Found: C, 58.64; H, 3.59.

^1H NMR (600 MHz, 299 K, CD_2Cl_2): $\delta = 7.07, 7.05$ (each d, $^4J_{\text{PH}} = 5.8$ Hz, each 2H, *m*-Mes), 3.15 (m, 1H, PCH), 2.61, 2.50 (each s, each 6H, *o*- CH_3^{Mes}), 2.50 (m, 2H, PCH₂) 2.37, 2.33 (each s, each 3H, *p*- CH_3^{Mes}), 1.45 (m, 2H, BCH₂), 1.34, 0.97 (each m, each 1H, CH₂).

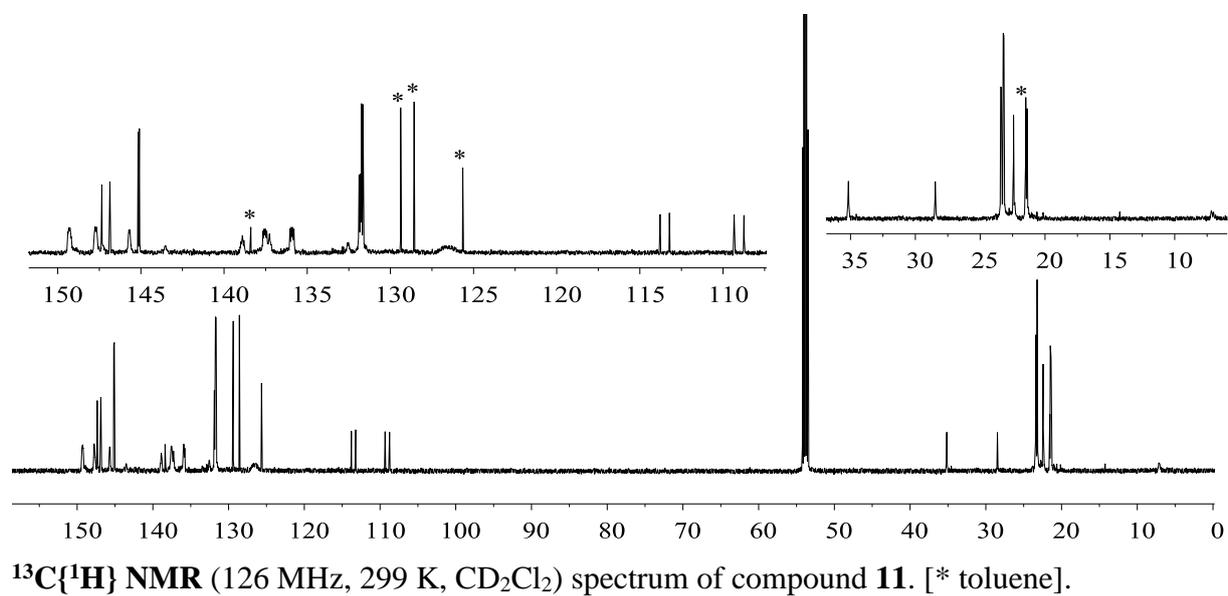
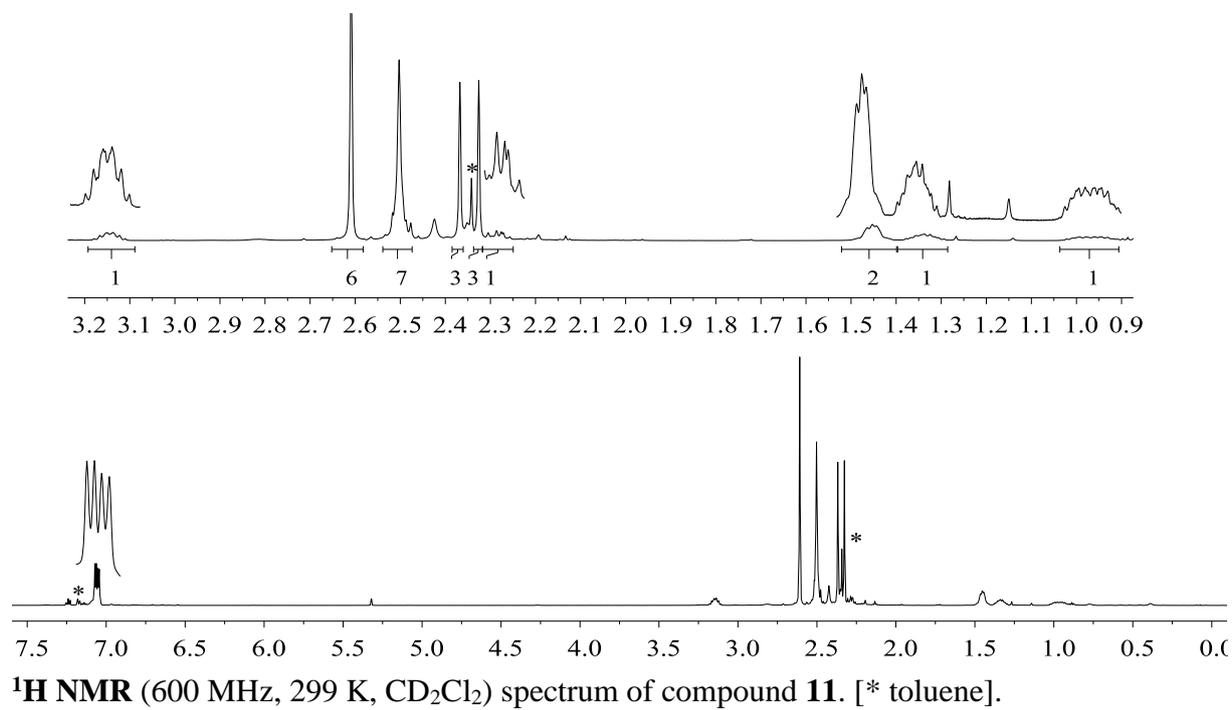
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, CD_2Cl_2): $\delta = 148.4$ (dm, $^1J_{\text{FC}} \sim 240$ Hz, C_6F_5), 147.3, 146.8 (each d, $^4J_{\text{PC}} = 3.3$ Hz, *p*-Mes), 145.7 (br d, $^2J_{\text{PC}} = 10.5$ Hz), 145.1 (d, $^2J_{\text{PC}} = 11.3$ Hz)(*o*-Mes), 138.0 (dm, $^1J_{\text{FC}} \sim 250$ Hz, C_6F_5), 136.7 (dm, $^1J_{\text{FC}} \sim 245$ Hz, C_6F_5), 131.8 (br d, $^3J_{\text{PC}} = 13.8$ Hz), 131.7 (d, $^3J_{\text{PC}} = 13.3$ Hz)(*m*-Mes), 126.5 (br, *i*- C_6F_5), 113.5 (d, $^1J_{\text{PC}} = 84.8$ Hz), 109.0 (d, $^1J_{\text{PC}} = 89.4$ Hz)(*i*-Mes), 35.1 (br d, $^1J_{\text{PC}} = 4.2$ Hz, PCH), 28.4 (d, $J_{\text{PC}} = 5.0$ Hz, CH₂), 23.4, 23.2 (each d, $^3J_{\text{PC}} = 7.9$ Hz, *o*- CH_3^{Mes}), 22.8 (br m, BCH₂), 22.4 (PCH₂), 21.5, 21.3 (each br, *p*- CH_3^{Mes}).

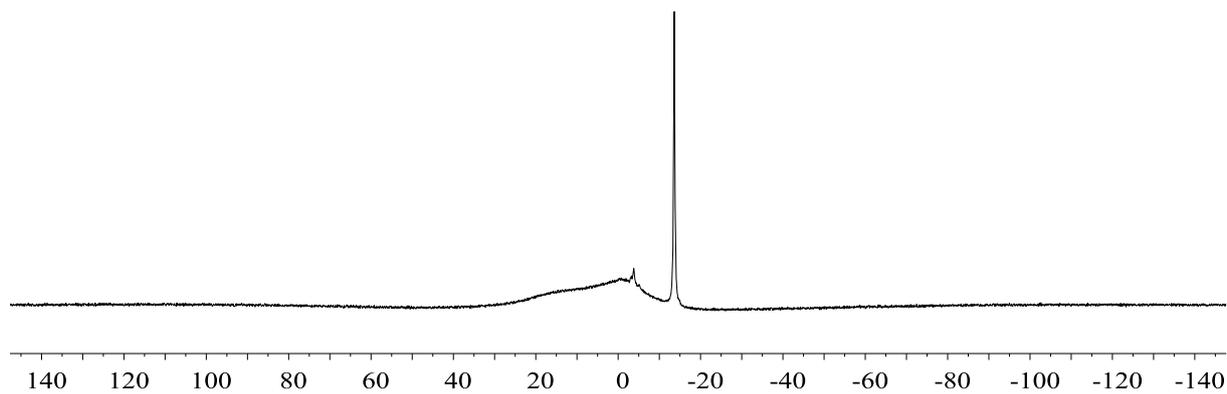
$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, CD_2Cl_2): $\delta = -13.6$ ($\nu_{1/2} \sim 65$ Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): $\delta = -133.1$ (m, 2F, *o*- C_6F_5), -164.0 (t, $^3J_{\text{FF}} = 20.3$ Hz, 1F, *p*- C_6F_5), -167.1 (m, 2F, *m*- C_6F_5). [$\Delta\delta^{19}\text{F}_{\text{m,p}} = 3.1$].

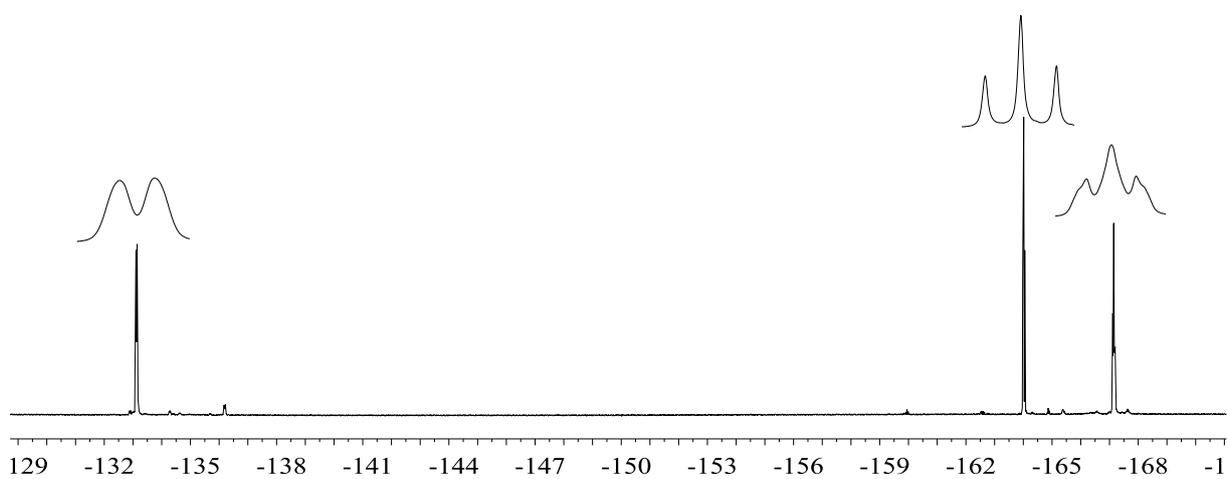
$^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, 299 K, CD_2Cl_2): δ -117.7 ($\nu_{1/2} \sim 2$ Hz).

^{31}P NMR (243 MHz, 299 K, CD_2Cl_2): δ -117.7 (dm, $J \sim 25$ Hz).

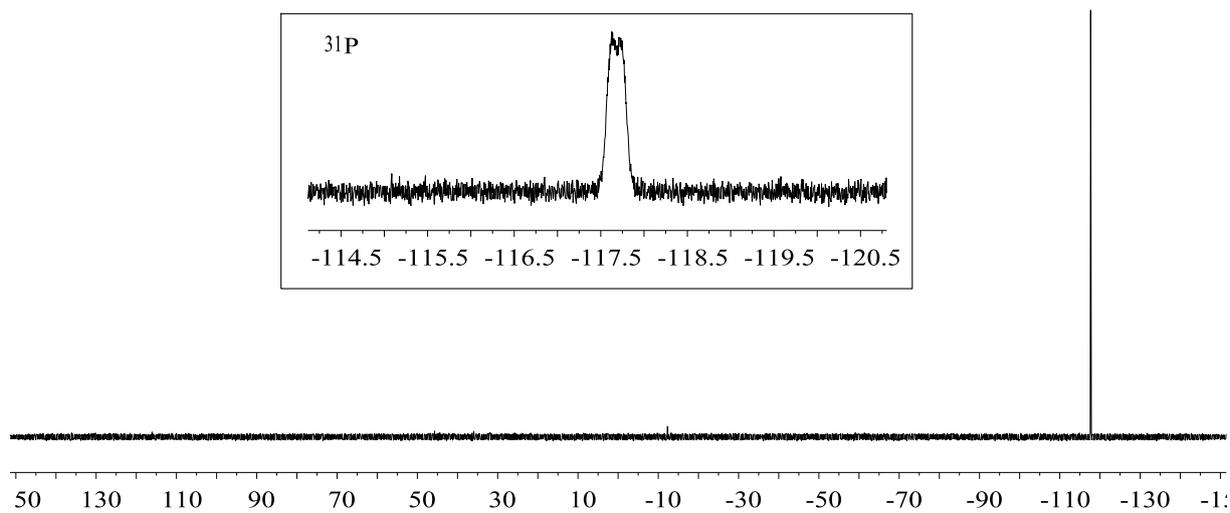




$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of compound **11**.



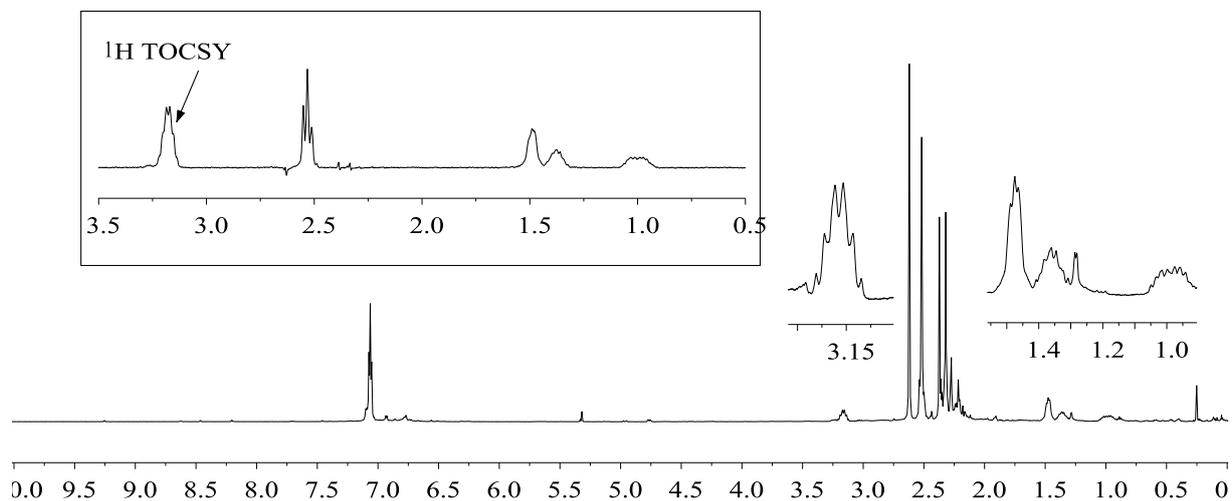
^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **11**.



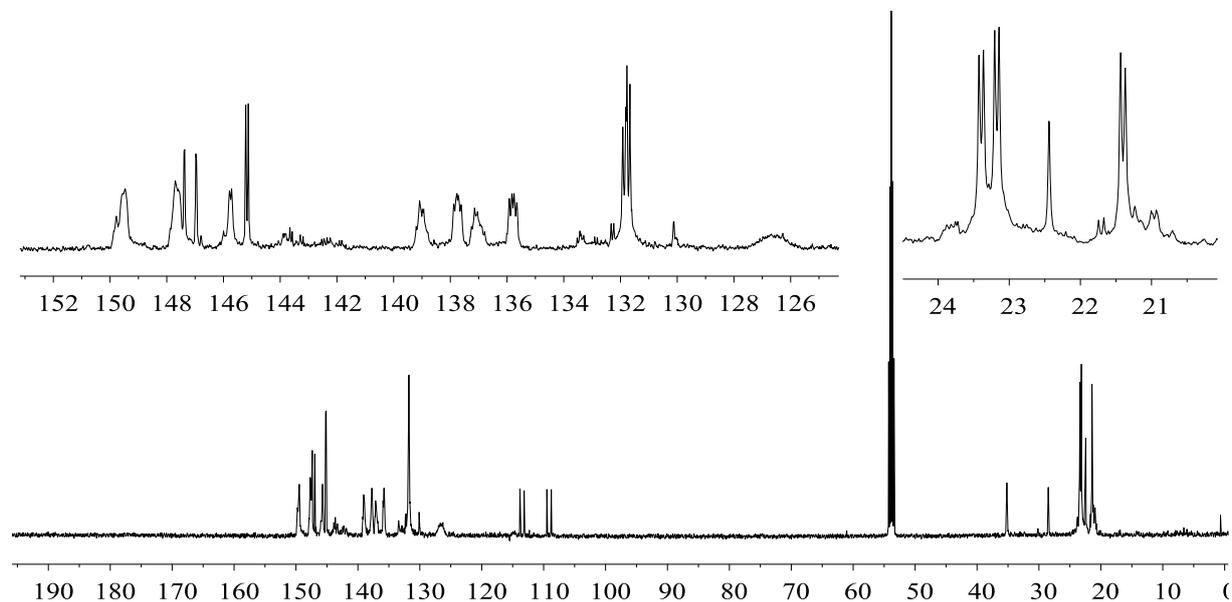
$^{31}\text{P}\{^1\text{H}\}$ NMR (247 MHz, 299 K, CD_2Cl_2) and ^{31}P NMR (247 MHz, 299 K, CD_2Cl_2) spectra of compound **11**.

2nd Experiment (*in situ*, NMR scale). Compound **9** (50 mg, 0.1541 mmol) and B(C₆F₅)₃ (78.9 mg, 0.1541 mmol) were added in a NMR tube and dissolved in deuterated dichloromethane (0.6 mL). After 10 min the reaction mixture was characterized by NMR experiments.

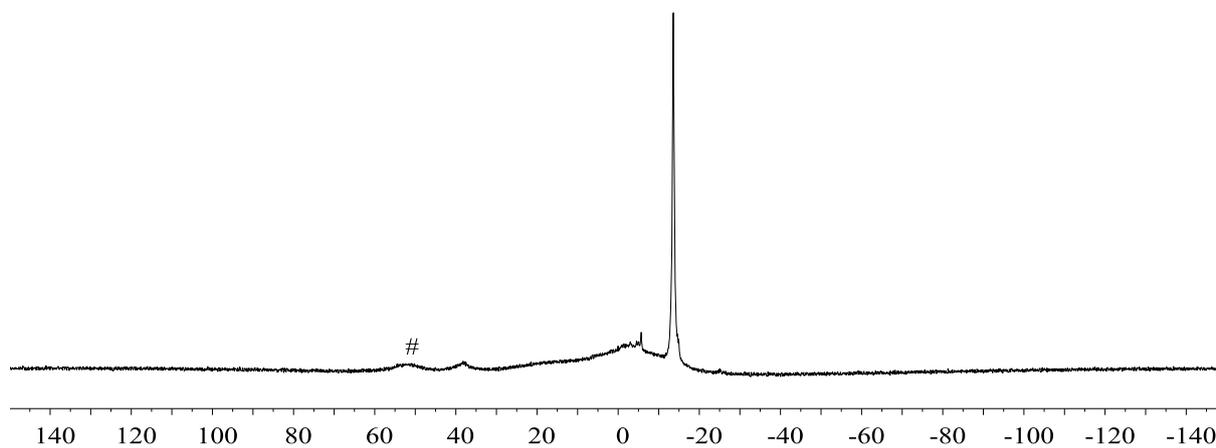
The obtained NMR data are consistent to those listed for compound **11** (see above).



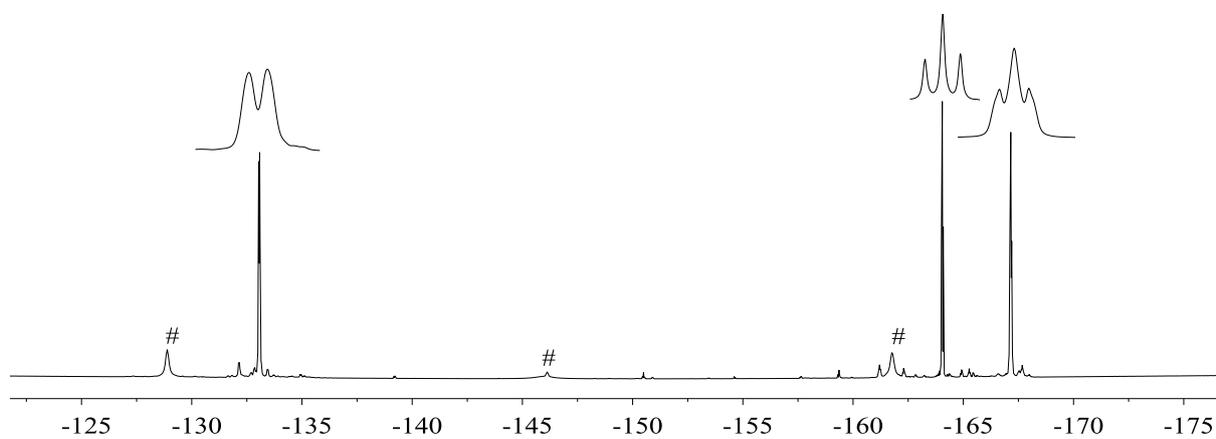
¹H NMR (500 MHz, 299 K, CD₂Cl₂) and ¹H{¹H} TOCSY (500 MHz, 299 K, CD₂Cl₂) spectra of compound **11** (irradiation (arrow) at 3.16 ppm, response at 2.52, 1.47, 1.36, 0.98 ppm).



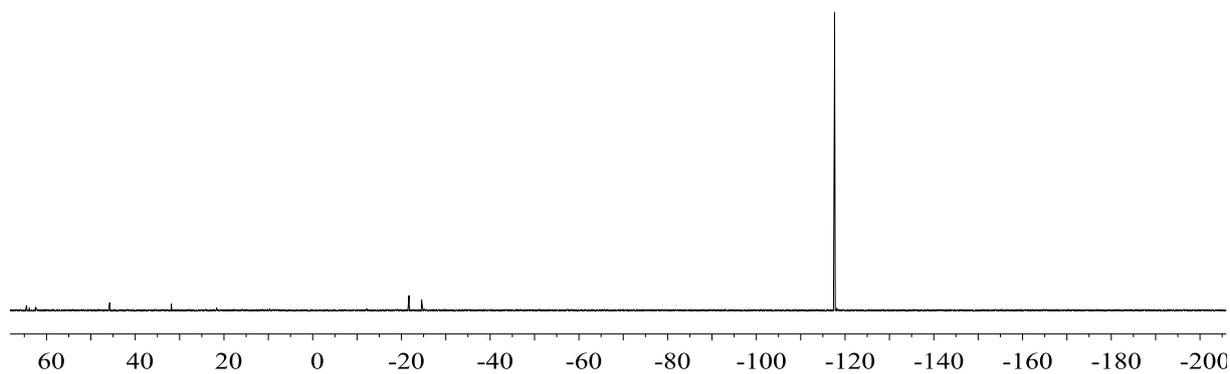
¹³C{¹H} NMR (126 MHz, 299 K, CD₂Cl₂) spectrum of compound **11**.



$^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, 299 K, CD_2Cl_2) spectrum of compound **11**. [# $\text{B}(\text{C}_6\text{F}_5)_3$].

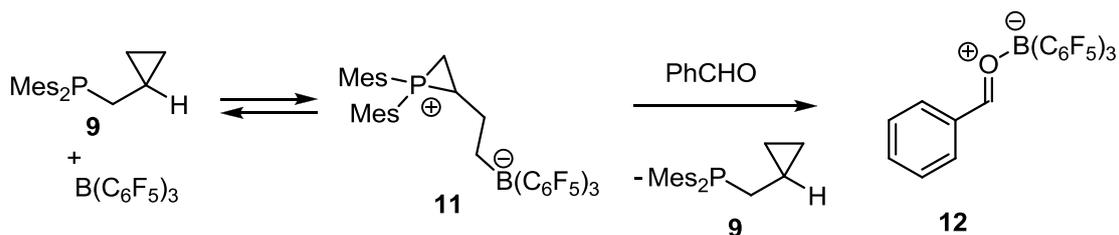


^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) spectrum of compound **11**. [# $\text{B}(\text{C}_6\text{F}_5)_3$].



$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 299 K, CD_2Cl_2) spectrum of compound **11**.

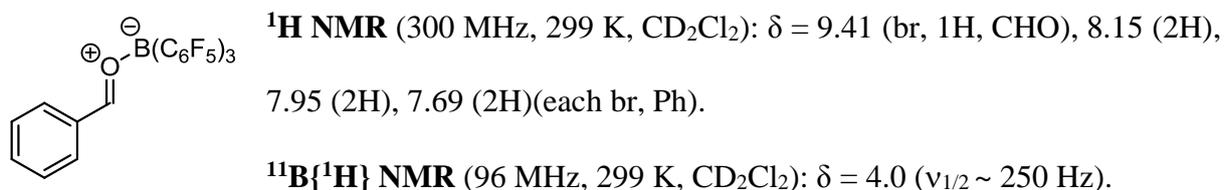
Reaction of compound 11 with benzaldehyde: formation of adduct 12 and compound 9.



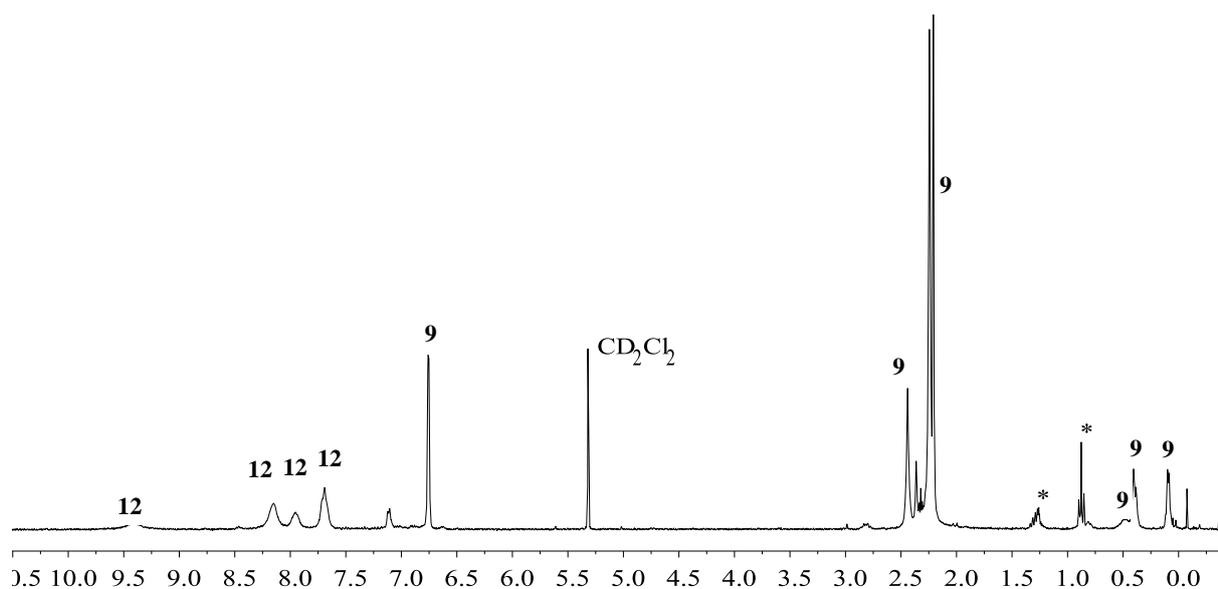
Phosphane **9** (100 mg, 0.308 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (158 mg, 0.308 mmol) were stirred in *n*-pentane (3 mL) for 30 min, then benzaldehyde (33 mg, 0.308 mmol) was added at room temperature. The formation of a white solid was observed. The suspension was stirred for further 16 h. Then all volatiles were removed *in vacuo* giving a viscous white residue (190 mg).

The NMR spectra of the viscous white residue in CD_2Cl_2 show a mixture of compound **9** and the benzaldehyde borane adduct **12** [For a comparison see: D. J. Parks, W. E. Piers, M. Parvez, R. Atencio and M. J. Zavorotko, *Organometallics*, 1998, **17**, 1369; D. J. Morrison and W. E. Piers, *Org. Lett.*, 2003, **5**, 2857].

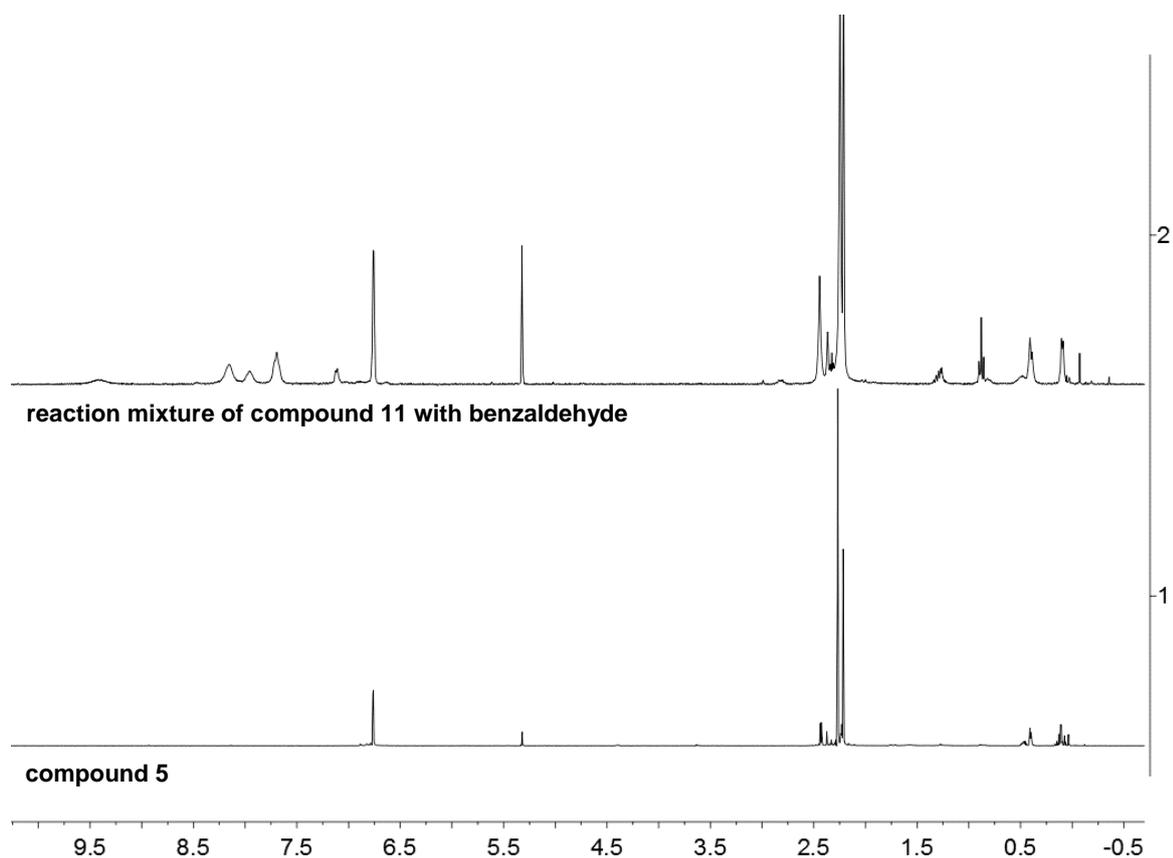
The NMR data of compound **9** were consistent with those listed above.



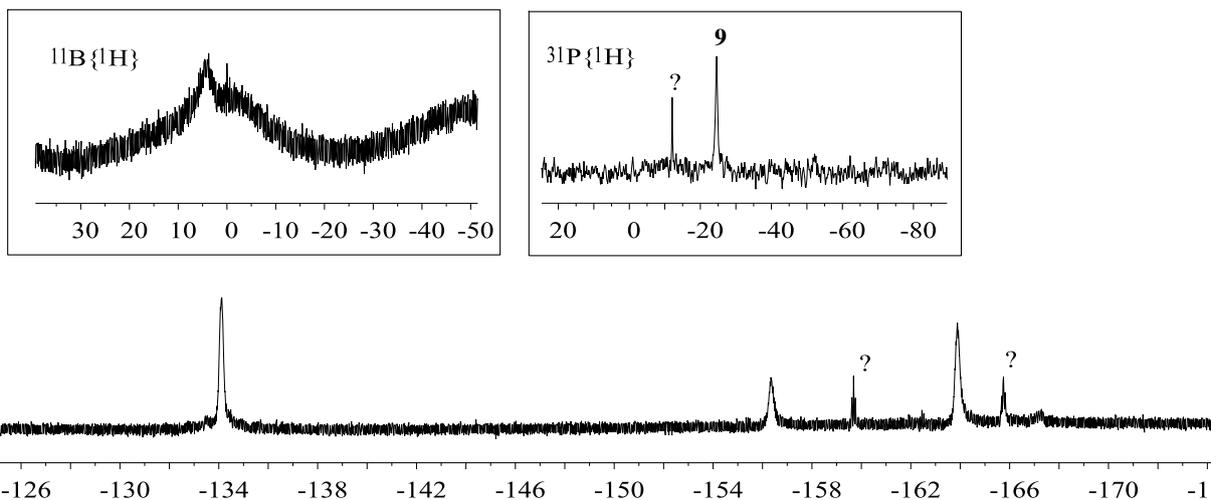
¹⁹F{¹H} NMR (282 MHz, 299 K, CD_2Cl_2): δ = -134.1 (br, 2F, *o*- C_6F_5), -156.3 (br, 1F, *p*- C_6F_5), -163.9 (br, 2F, *m*- C_6F_5). [$\Delta\delta^{19}\text{F}_{\text{m,p}}$ = 7.5].



^1H NMR (300 MHz, 299 K, CD_2Cl_2) spectrum of the reaction mixture of the reaction of compound **11** with benzaldehyde: mixture of compounds **12** and **9**. [* *n*-pentane].



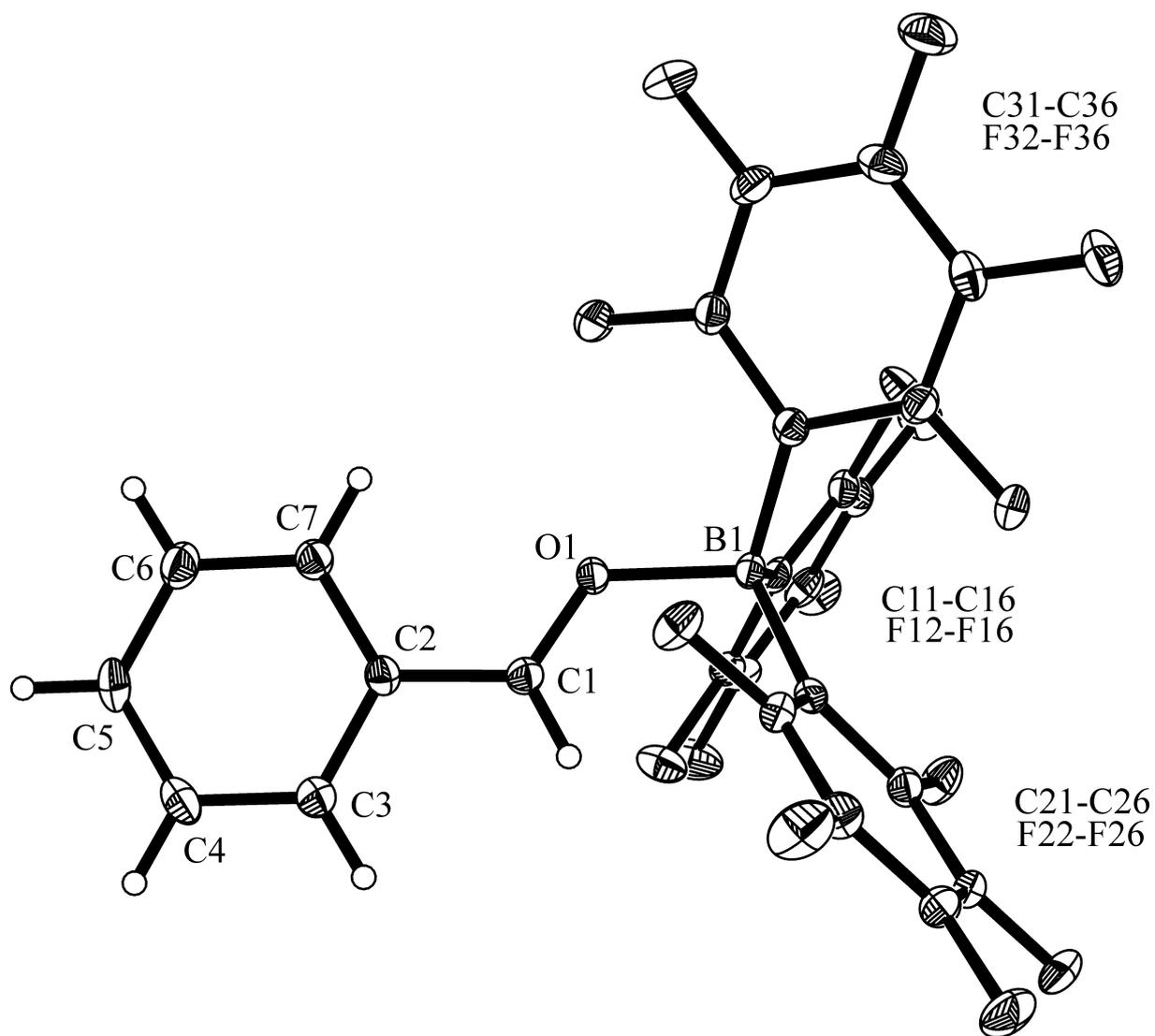
(1) ^1H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound **9**; (2) ^1H NMR (300 MHz, 299 K, CD_2Cl_2) spectrum of the reaction mixture of the reaction of compound **11** with benzaldehyde: mixture of compounds **12** and **9**.



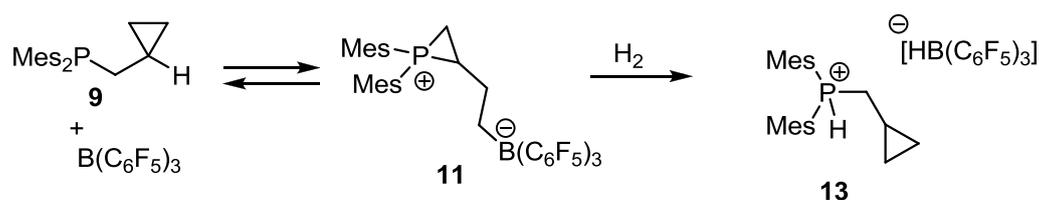
^{19}F NMR (282 MHz, 299 K, CD_2Cl_2), $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, 299 K, CD_2Cl_2) and $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, 299 K, CD_2Cl_2) spectra of the reaction mixture of the reaction of compound **11** with benzaldehyde: mixture of compounds **12** and **9**. [? not identified compound].

After storing the viscous white residue for ca. 4 days at $-30\text{ }^\circ\text{C}$ a few colorless crystals suitable for the X-ray structure analysis were obtained.

X-Ray crystal structure analysis of compound 12 formula $\text{C}_{25}\text{H}_6\text{BF}_{15}\text{O}$, $M = 618.11$, colourless crystal, $0.283 \times 0.251 \times 0.113$ mm, $a = 9.4516(4)$, $b = 12.1427(5)$, $c = 12.2399(4)$ Å, $\alpha = 110.414(1)$, $\beta = 100.070(1)$, $\gamma = 97.111(1)^\circ$, $V = 1267.0(1)$ Å³, $\rho_{\text{calc}} = 1.616$ gcm⁻³, $\mu = 0.174$ mm⁻¹, empirical absorption correction ($0.952 \leq T \leq 0.981$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 100(2)$ K, ω and φ scans, 51651 reflections collected, 5853 independent ($R_{\text{int}} = 0.047$) and 4788 observed reflections [$I > 2\sigma(I)$], 379 refined parameters, $R = 0.036$, $wR^2 = 0.097$, max. (min.) residual electron density 0.37 (-0.26) e.Å⁻³, hydrogen atoms were calculated and refined as riding atoms.

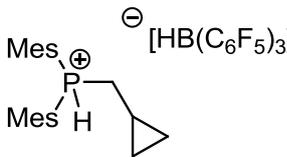


Preparation of compound 13.



Phosphane **9** (100 mg, 0.308 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (158 mg, 0.308 mmol) were dissolved in *n*-pentane (2 mL). Then, after 30 min, the solution was exposed to an H_2 atmosphere (2 bar). The reaction mixture was stirred and the yellow solution turned colorless after 20 min and stirring was continued at ambient temperature for 16 h. The solvent of the obtained emulsion was removed and the separated oil was dried *in vacuo* giving a white foam (249 mg, 96%).

Elemental analysis: Calcd. for $\text{C}_{40}\text{H}_{31}\text{BF}_{15}\text{P}$: C, 57.30; H, 3.73. Found: C, 56.64; H, 3.61.


¹H NMR (400 MHz, 299 K, CD_2Cl_2): $\delta = 7.71$ (dt, $^1J_{\text{PH}} = 476.0$ Hz, $^3J_{\text{HH}} = 7.1$ Hz, 1H, PH), 7.09 (dm, $^4J_{\text{PH}} = 4.8$ Hz, 4H, *m*-Mes), 3.58 (br q 1:1:1:1, $^1J_{\text{BH}} \sim 95$ Hz, 1H, BH), 2.83 (dt, $^2J_{\text{PH}} = 11.2$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, 2H, PCH₂), 2.43 (s, 12H, *o*-CH₃^{Mes}), 2.35 (s, 6H, *p*-CH₃^{Mes}), 0.89 (m, 1H, CH), 0.78, 0.39 (each m, each 2H, CH₂).

¹³C{¹H} NMR (101 MHz, 299 K, CD_2Cl_2): $\delta = 148.5$ (dm, $^1J_{\text{FC}} \sim 235$ Hz, C₆F₅), 147.3 (d, $^4J_{\text{PC}} = 2.9$ Hz, *p*-Mes), 143.5 (d, $^2J_{\text{PC}} = 10.3$ Hz, *o*-Mes), 138.1 (dm, $^1J_{\text{FC}} \sim 245$ Hz, C₆F₅), 136.8 (dm, $^1J_{\text{FC}} \sim 245$ Hz, C₆F₅), 132.5 (d, $^3J_{\text{PC}} = 11.4$ Hz, *m*-Mes), 125.7 (br, *i*-C₆F₅), 111.1 (d, $^1J_{\text{PC}} = 80.0$ Hz, *i*-Mes), 31.1 (d, $^1J_{\text{PC}} = 43.5$ Hz, PCH₂), 22.3 (d, $^3J_{\text{PC}} = 7.4$ Hz, *o*-CH₃^{Mes}), 21.4 (d, $^4J_{\text{PC}} = 1.5$ Hz, *p*-CH₃^{Mes}), 7.1 (d, $^3J_{\text{PC}} = 10.2$ Hz, CH₂), 7.0 (d, $^2J_{\text{PC}} = 2.5$ Hz, CH).

¹H,¹H GCOSY (400 MHz/ 400 MHz, 299 K, CD_2Cl_2) [selected trace]: $\delta^1\text{H}/\delta^1\text{H} = 0.89/2.83$, 0.89, 0.78 (CH/ PCH₂, CH₂, CH₂).

$^1\text{H}, ^{13}\text{C}$ GHSQC (400 MHz/ 101 MHz, 299 K, CD_2Cl_2): $\delta^1\text{H}/ \delta^{13}\text{C} = 7.09/ 132.5$ (*m*-Mes), 2.83/ 31.1 (PCH_2), 2.43/ 22.3 (*o*- CH_3^{Mes}), 2.35/ 21.4 (*p*- CH_3^{Mes}), 0.89/ 7.0 (CH), 0.78/ 7.2 (CH_2), 0.39/ 7.2 (CH_2).

$^1\text{H}, ^{13}\text{C}$ GHMBC (400 MHz/ 101 MHz, 299 K, CD_2Cl_2) [selected traces]: $\delta^1\text{H}/ \delta^{13}\text{C} = 7.71 / 143.5, 111.1, 31.1, 7.0$ ($\text{PH}/$ *o*-Mes, *i*-Mes, PCH_2 , CH), 7.09/ 132.5, 111.1, 22.3, 21.4 (*m*-Mes, *i*-Mes, *o*- CH_3^{Mes} , *p*- CH_3^{Mes}), 2.35/ 147.3, 132.5 (*p*- $\text{CH}_3^{\text{Mes}}/$ *p*-Mes, *m*-Mes).

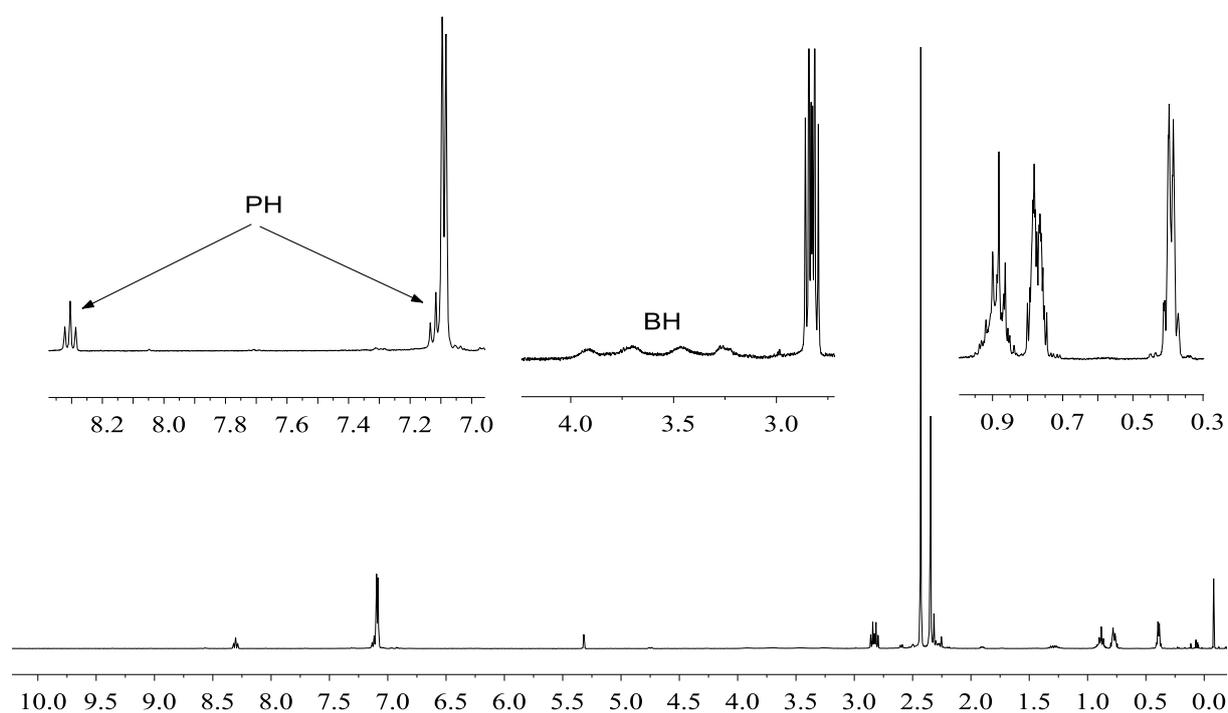
$^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, 299 K, CD_2Cl_2): $\delta = -25.4$ ($\nu_{1/2} \sim 45$ Hz).

^{11}B NMR (96 MHz, 299 K, CD_2Cl_2): $\delta = -25.4$ (d, $^1J_{\text{BH}} \sim 93$ Hz).

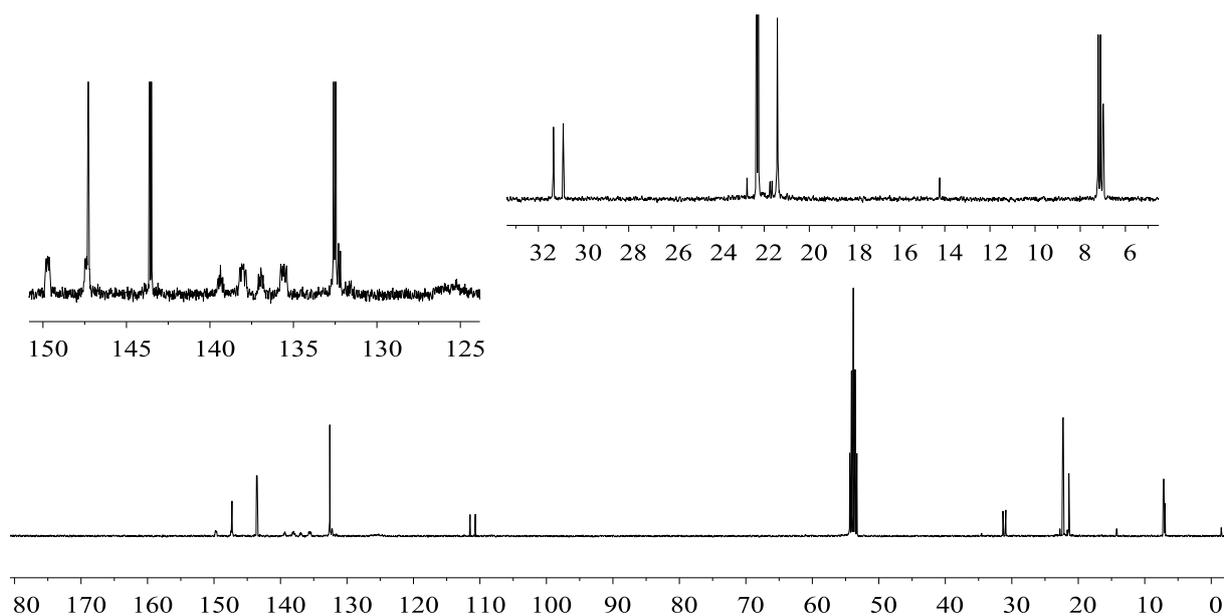
$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, 299 K, CD_2Cl_2): $\delta = -133.9$ (m, 2F, *o*- C_6F_5), -164.6 (t, $J = 20.2$ Hz, 1F, *p*- C_6F_5), -167.5 (m, 2F, *m*- C_6F_5). [$\Delta\delta^{19}\text{F}_{\text{m,p}} = 2.9$].

$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, 299 K, CD_2Cl_2): $\delta -12.2$ ($\nu_{1/2} \sim 2$ Hz).

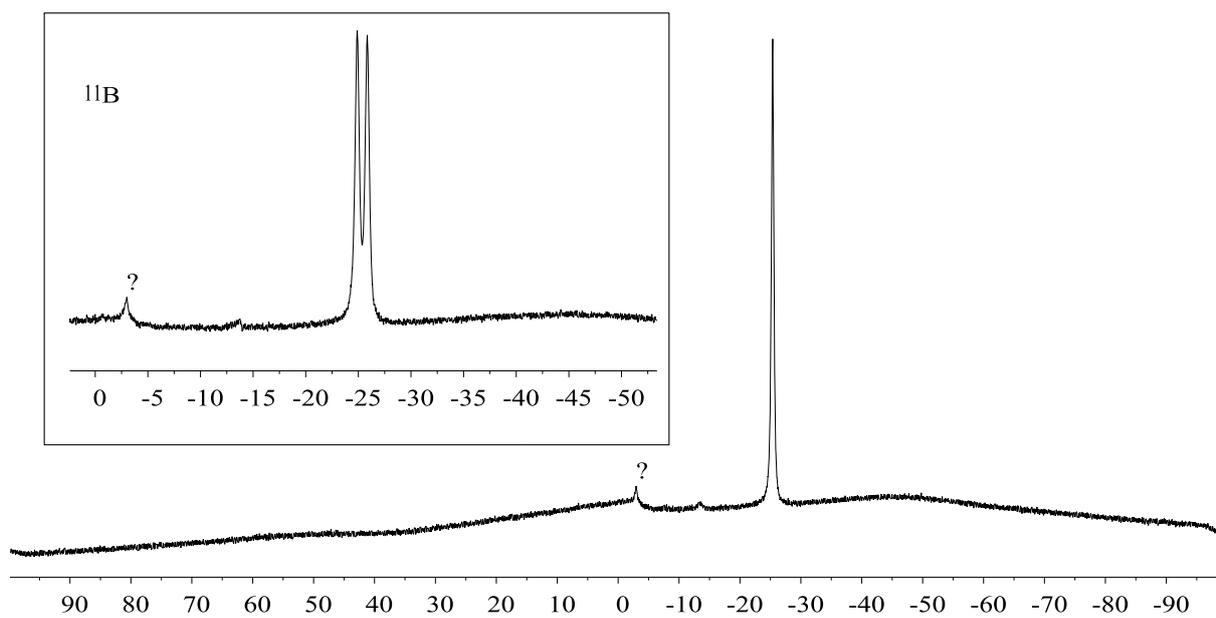
^{31}P NMR (121 MHz, 299 K, CD_2Cl_2): $\delta -12.2$ (dm, $^1J_{\text{PH}} \sim 477$ Hz).



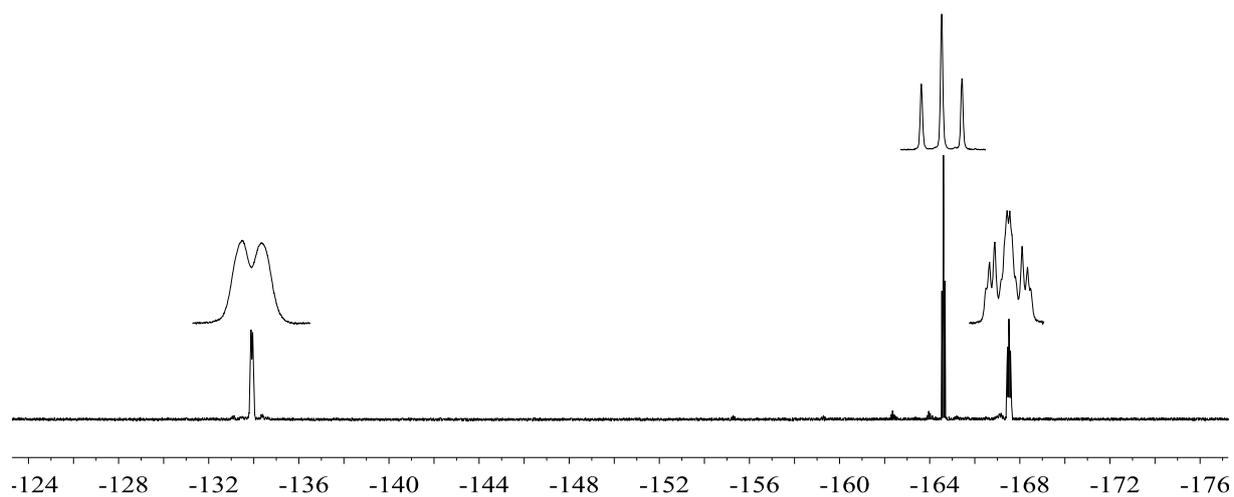
^1H NMR (400 MHz, 299 K, CD_2Cl_2) spectrum of compound **13**.



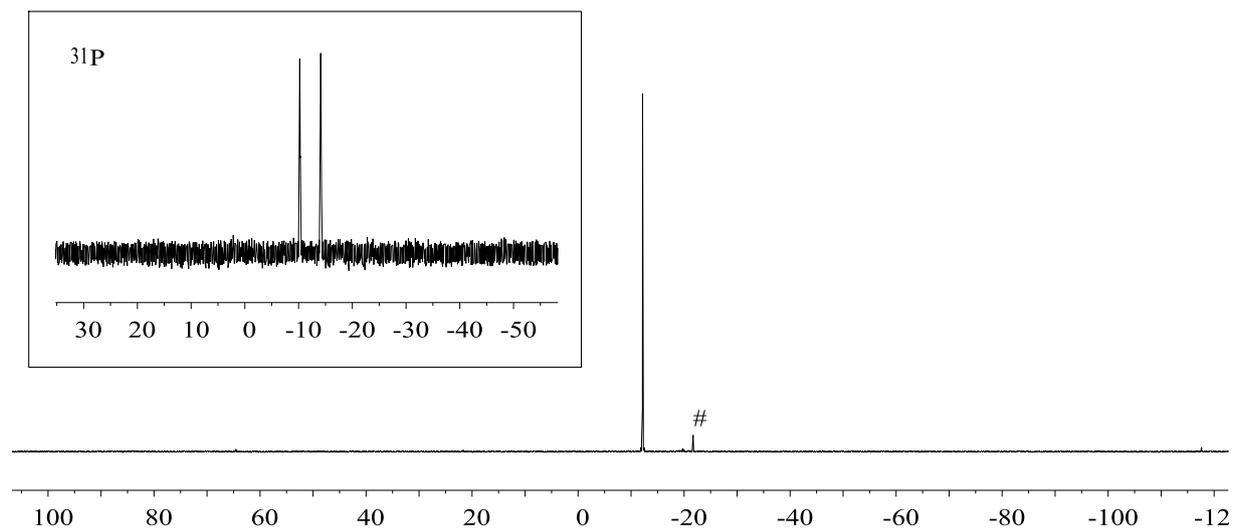
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 299 K, CD_2Cl_2) spectrum of compound **13**.



$^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, 299 K, CD_2Cl_2) and ^{11}B NMR (96 MHz, 299 K, CD_2Cl_2) spectra of compound **13**. [? not identified compound].



^{19}F NMR (282 MHz, 299 K, CD_2Cl_2) spectrum of compound **13**.



$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, 299 K, CD_2Cl_2) and ^{31}P NMR (121 MHz, 299 K, CD_2Cl_2) spectra of compound **13**. [# compound **9**].