SUPPORTING INFORMATION

The Frustrated *Lewis* Pair Pathway to Methylene Phosphonium Systems

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General Procedures.

All reactions involving air- and moisture sensitive compounds were carried out under a dry argon atmosphere (argon 4.8, *WESTFALEN*) in oven- or flame-dried glassware with standard Schlenk techniques or in an *MBraun* (MB 150B-G) glove box. *n*-Pentane, tetrahydrofuran (THF), diethylether, toluene, and dichloromethane were dried using a solvent drying system described by Grubbs et al.[S1]. Dichloromethane-d_2 [CD_2Cl_2] was distilled from calcium hydride [CaH_2] and benzene-d_6 [C_6D_6] was purchased distilled from sodium-potassium alloy. Tipp: 2,4,6-triisopropylphenyl; mes*: 2,4,6-tri-*tert*-butylphenyl.

The following instruments were used for physical characterization of the compounds.

Mass Spectrometer: Orbitrap LTQ XL (Thermoscientific) was used for ESI measurements.

Infrared Spectroscopy: *Varian* 3100 FT-Infrared Spectrometer (Excalibur Series).

NMR spectra: Data sets were recorded on a *Varian* Inova 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{19}F: 470 MHz, ^{11}B: 160 MHz, ^{31}P: 202 MHz) and on a *Varian* UnityPlus 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{19}F: 564 MHz, ^{11}B: 192 MHz, ^{31}P: 243 MHz). ^{1}H NMR chemical shifts δ are given relative to the respective residual solvent peaks ($CDHCl_2$ at 5.32; $CHCl_3$ at 7.24, C_6D_5H at 7.15). ^{13}C NMR chemical shifts δ are given relative to the solvent peaks (CD_2Cl_2 at 53.8, C_6D_6 at 128.0). ^{19}F NMR: chemical shifts δ are given relative to $CFCl_3$ ($\delta^{19}F = 0$, external reference), ^{11}B NMR: relative to $BF_3{\cdot}Et_2O$ ($\delta^{11}B = 0$, external reference), ^{31}P NMR: relative to H_3PO_4 (85% in H_2O) ($\delta^{31}P = 0$, 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, sept = septet, oct = octet, m = multiplet, br = broad signal. Coupling constants are given in Hertz (Hz).

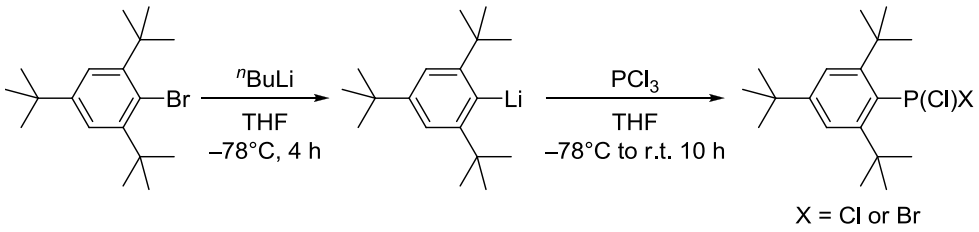
X-Ray Crystal Structure Analyses: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (Nonius B.V., 1998); data reduction Denzo-SMN[S2]; absorption correction, Denzo[S3]; structure solution SHELXS-97[S4]; structure refinement SHELXL-97[S5] and graphics, XP (BrukerAXS, 2000). Thermal ellipsoids are shown with 30% probability, *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special*

features: Compound **5a** crystallized with two independent molecules per asymmetric unit. One t-Bu group was found disordered over two positions. Several restraints (SADI, SIMU, SAME, ISOR) were used in order to improve refinement stability. The hydrogen atoms at P1 and B1 in compound **8a** were refined freely. Two t-Bu groups and the vinyl group are disordered over two positions. Several restraints (SADI, SIMU, ISOR and SAME) were used in order to improve refinement stability. One t-Bu group was found in compound **10a** disordered over two positions. One t-Bu group was found in compound **7a** disordered over two positions. Several restraints (SADI, SIMU, SAME, ISOR) were used in order to improve refinement stability. For the compound **11a** two t-Bu groups and one dichloromethane($-d_2$) molecule were found disordered over two positions. Several restraints (SADI, SIMU, SAME, ISOR) were used in order to improve refinement stability. (CCDC: 952207 - 95209 and 967611 - 967613)

Preparation of the starting materials.

Bis(pentafluorophenyl)borane was prepared according to the following modified literature procedures[S6]. Dihalo(2,4,6-triisopropylphenyl)phosphane [tippPXY] [X, Y = Cl or Br; tipp: tri(isopropyl)phenyl] was synthesized according to a modified literature procedure[S7]. 2-Bromo-1,3,5-tri-*tert*-butylbenzene [mes*Br] was prepared according to the following literature procedure[S8].

Preparation of dihalo(2,4,6-tri-*tert*-butylphenyl)phosphane [mes*P(Cl)X].



Dihalo-tri-*tert*-butylphenylphosphane [mes*P(Cl)X] was prepared according to a modified literature procedure[S9]. Phosphorus trichloride was distilled right before use. 1-Bromo-2,4,6-tri-*tert*-butylbenzene was dissolved in dried THF (50 mL) containing 20 g of activated molecular sieves 4A and kept still in the dark for 2 days before the reaction.

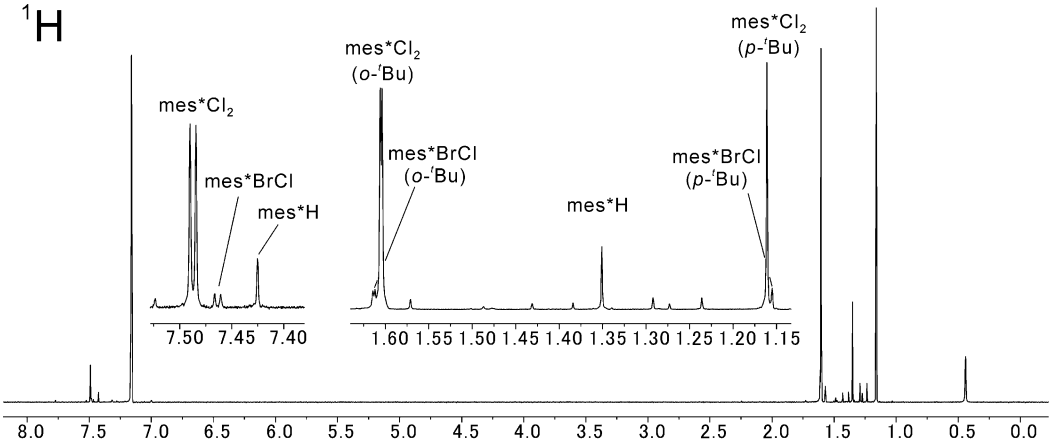
A solution of 1-bromo-2,4,6-tri-*tert*-butylbenzene [mes*Br] (7.8 g, 23.9 mmol) in dry, degassed THF (200 mL) was added to a 400-mL Schlenk flask. The flask was cooled to and maintained at −78°C for 10 min. *n*-Butyl lithium (15.0 mL, 1.6 M *n*-hexane solution: 24.0 mmol) was added via a syringe over a period of a few minutes and the resulting mixture was stirred for 4 h at −78°C. Then the solution was transferred via a cannula to a second 400-mL Schlenk flask containing a stirred solution of phosphorous trichloride (12 mL, 137 mmol, 5.7 eq.) in THF (100 mL) over a period of 30 min. The temperature of the

both Schlenk flasks was maintained at −78°C throughout this process. After addition was complete, the flask was maintained at −78°C for 3 h and then gradually raised to 0°C over 10 h. All volatiles, including excess phosphorous trichloride and *n*-butyl bromide were removed in vacuo (0.1 mbar) for 12 h at 0°C. The obtained residue was dissolved in *n*-pentane (50 mL) and filtered through a pad of Celite® resulting in a crude light yellow solid (7.59 g, mixture of mes*PCl_2 : mes*PClBr : mes*H = 83:6:10 [^{1}H NMR]).

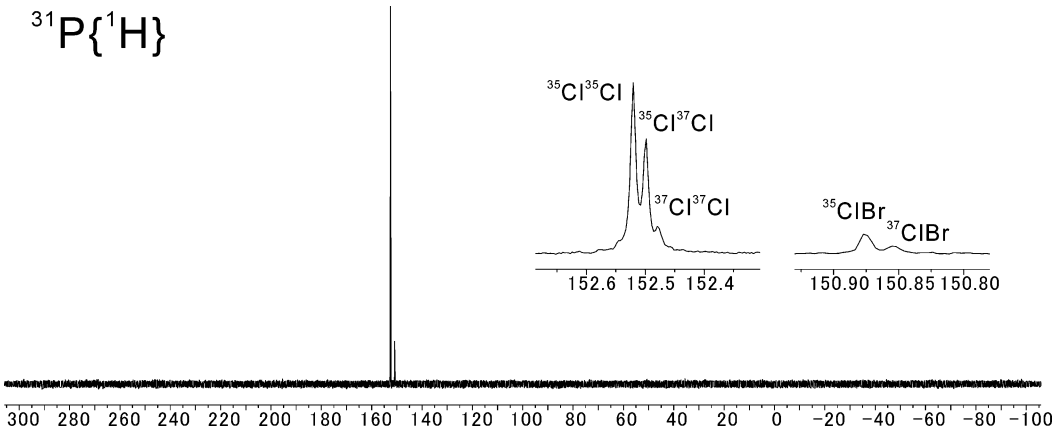
Comment: The crude compound was employed in the next step without further purification. It should be noted that all purification attempts including crystallization and sublimation rather deteriorated the purity of the product. Washing with diethyl ether or *n*-pentane would only slightly increase the purity at a cost of losing the majority of the product. Since the product very slowly decomposes at room temperature even under an argon atmosphere, one should keep it in a fridge at −35°C for a long-time storage.

^{1}H NMR (500 MHz, 299 K, benzene-d_6): mes*PCl_2: δ = 7.48 (d, $^4J_{PH}$ = 2.8 Hz, 2H, *m*-mes*), 1.59 (d, $^5J_{PH}$ = 1.0 Hz, 18 H, *o*-^{t}Bu), 1.151 (s, 9H, *p*-^{t}Bu). mes*PBrCl: δ = 7.45 (d, $^4J_{PH}$ = 2.9 Hz, 2H, *m*-mes*), 1.60 (d, $^5J_{PH}$ = 1.2 Hz, 18 H, *o*-^{t}Bu), 1.145 (s, 9H, *p*-^{t}Bu). mes*H: δ = 7.42 (s, 1H, mes*-H), 1.34 (s, 9 H, ^{t}Bu).

^{31}P{^{1}H} NMR (202 MHz, 299 K, benzene-d_6): δ = 152.52 ($P^{35}Cl^{35}Cl$, 57%), 152.50 ($P^{35}Cl^{37}Cl$, 34%), 152.48 ($P^{37}Cl^{37}Cl$, 9%) (mes*PCl_2, 92%), 150.88 (mes*$PBr^{35}Cl$, 71%), 150.85 (mes*$PBr^{37}Cl$, 29%)(mes*PBrCl, 8%).

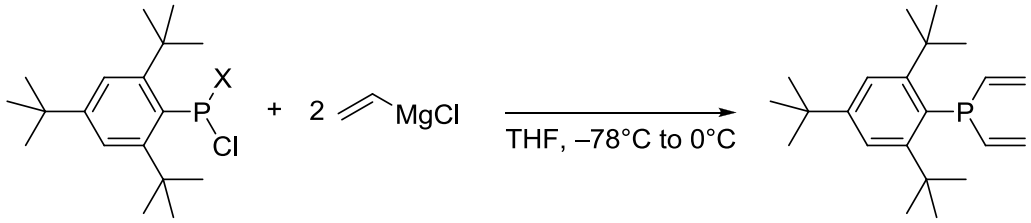


^{1}H NMR (500 MHz, 299 K, benzene-d_6) of dihalo-tri-tert-butylphenylphosphane.



$^{31}P\{^1H\}$ NMR (500 MHz, 299 K, benzene-d_6) of dihalo-tri-tert-butylphenylphosphane.

Preparation of (2,4,6-tri-*tert*-butylphenyl)divinylphosphane [mes*P(CHCH$_2$)$_2$] 6a.



X = Cl or Br **6a**

Dihalo(2,4,6-tri-*tert*-butylphenyl)phosphane [3.6 g, 9.7 mmol in terms of mes*PX$_2$, where mes*PCl$_2$:mes*PClBr:mes*H = 0.85:0.08:0.07 (^{1}H NMR)] was dissolved in THF (100 mL) and cooled down to −78°C. Vinyl magnesium chloride (13 mL, 1.6 M THF solution: 20.8 mmol) was added dropwise to the solution at −78°C and stirred vigorously at −78°C for 5 h and then stirred for another 16 h while very slowly raising the reaction temperature to 0°C. The volatiles were removed in vacuo. The obtained residue was dissolved in *n*-pentane (20 mL) and filtered through a pad of Celite®. All the volatiles were evaporated in vacuo which gave a crude brown oil [3.10 g, 91% purity (^{1}H NMR)]. The crude product (1.40 g) was further purified by column chromatography using silica gel (4 cm x 50 cm, eluent: *n*-pentane:triethylamine = 100:1), which gave **6a** as a colorless oil [0.70 g, 95% purity (^{1}H NMR), 50% yield]. The progress of column chromatography was monitored by TLC (Rf = 0.45: eluent = *n*-pentane, TLC = Silica gel 60 F$_{254}$.).

Comment: The compound could also be purified by the following conditions: silica gel, 4 cm x 42 cm, eluent: *n*-pentane, the column was kept under an argon atmosphere. The fractions (monitored by TLC) were collected under air and quickly dried in vacuo, which gave the product as a colorless oil (>99% purity (^{1}H NMR), yield 3%).

HRMS: $M+H^+$ ($C_{22}H_{35}PH^+$): calc. 331.2554, found 331.2549.

^{1}H NMR (600 MHz, 299 K, benzene-d_6): δ = 7.65 (d, $^4J_{PH}$ = 2.3 Hz, 2H, *m*-mes*), 6.56 (ddd, $^2J_{PH}$ = 19.7 Hz, $^3J_{HH}$ = 18.5 Hz, $^3J_{HH}$ = 12.3 Hz, 2H, =CH), 5.43 (ddd, $^3J_{PH}$ = 25.3 Hz, $^3J_{HH}$ = 12.3 Hz, $^2J_{HH}$ = 1.7 Hz, 2H, $=CH_2^E$), 5.22 (ddd, $^3J_{HH}$ = 18.5 Hz, $^3J_{PH}$ = 9.0 Hz, $^2J_{HH}$ = 1.7 Hz, 2H, $=CH_2^Z$), 1.65 (d, $^5J_{PH}$ = 0.4 Hz, 18H, *o*-^{t}Bu), 1.28 (s, 9H, *p*-^{t}Bu).

^{1}H NMR (500 MHz, 299 K, dichloromethane-d_2): δ = 7.48 (d, $^4J_{PH}$ = 2.4 Hz, 2H, *m*-mes*), 6.61 (ddd, $^2J_{PH}$ = 19.5 Hz, $^3J_{HH}$ = 18.5 Hz, $^3J_{HH}$ = 12.3 Hz, 2H, =CH), 5.56 (ddd, $^3J_{PH}$ = 25.6 Hz, $^3J_{HH}$ = 12.3 Hz, $^2J_{HH}$ = 1.6 Hz, 2H, $=CH_2^E$), 5.19 (ddd, $^3J_{HH}$ = 18.5 Hz, $^3J_{PH}$ = 9.1 Hz, $^2J_{HH}$ = 1.6 Hz, 2H, $=CH_2^Z$), 1.51 (m, 18H, *o*-^{t}Bu), 1.32 (s, 9H, *p*-^{t}Bu).

^{1}H{^{31}P} NMR (600 MHz, 299 K, benzene-d_6) [selected resonances]: δ = 7.65 (s, 2H, *m*-mes*), 6.56 (dd, $^3J_{HH}$ = 18.5 Hz, $^3J_{HH}$ = 12.3 Hz, 2H, =CH), 5.43 (dd, $^3J_{HH}$ = 12.3 Hz, $^2J_{HH}$ = 1.7 Hz, 2H, $=CH_2^E$), 5.22 (dd, $^3J_{HH}$ = 18.5, $^2J_{HH}$ = 1.7 Hz, 2H, $=CH_2^Z$), 1.65 (s, 18H, *o*-^{t}Bu).

^{13}C{^{1}H} NMR (151 MHz, 299 K, benzene-d_6): δ = 158.9 (d, $^2J_{PC}$ = 13.6 Hz, *o*-mes*), 151.0 (d, $^4J_{PC}$ = 2.4 Hz, *p*-mes*), 139.6 (d, $^1J_{PC}$ = 22.9 Hz, =CH), 129.1 (d, $^1J_{PC}$ = 33.9 Hz, *i*-mes*), 123.7 (d, $^3J_{PC}$ = 7.5 Hz, *m*-mes*), 120.9 (d, $^2J_{PC}$ = 20.3 Hz, $=CH_2$), 39.8 (d, $^3J_{PC}$ = 4.2 Hz, *o*-^{t}Bu^C), 35.0 (d, $^5J_{PC}$ = 0.9 Hz, *p*-^{t}Bu^C), 34.4 (d, $^4J_{PC}$ = 7.0 Hz, *o*-^{t}Bu^{CH3}), 31.3 (*p*-^{t}Bu^{CH3}).

^{1}H,^{1}H GCOSY (600 MHz/600 MHz, 299 K, benzene-d_6) [selected traces]: δ^1H/ δ ^{1}H: 6.56/5.43 (=CH/$=CH_2^E$), 6.56/5.22 (=CH/$=CH_2^Z$), 5.43/5.22 ($=CH_2^E$/$=CH_2^Z$).

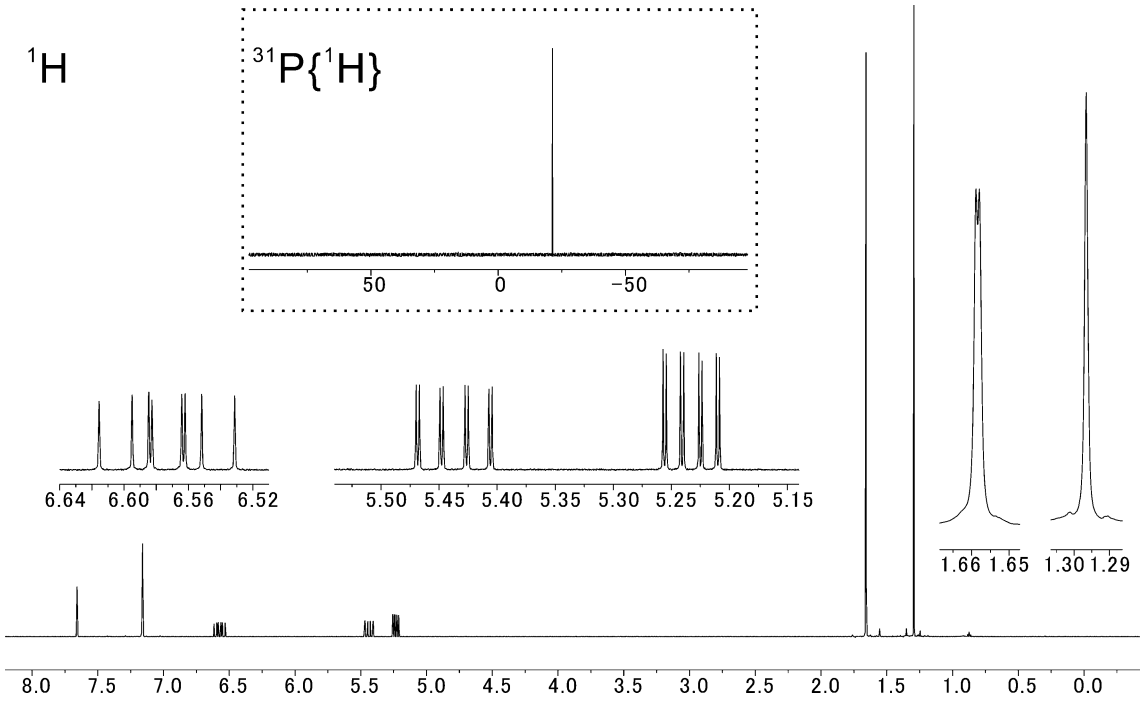
^{1}H{^{1}H} 1D NOESY (600 MHz, 299 K, benzene-d_6) [selected experiments]: $\delta^1H_{irr}/\delta^1H_{res}$: 5.43/ 6.56, 5.22 ($=CH_2^E$ / =CH, $=CH_2^Z$), 5.22/5.43 ($=CH_2^Z$/$=CH_2^E$).

^{1}H,^{13}C GHSQC (600 MHz/151 MHz, 299 K, benzene-d_6) [selected traces]: δ^1H/δ^{13}C: 7.65/123.7 (*m*-mes*), 6.56/139.6 (=CH), 5.43/120.9 ($=CH_2^E$), 5.22/120.9 ($=CH_2^Z$), 1.65/34.4 (*o*-^{t}Bu), 1.28/31.3 (*p*-^{t}Bu).

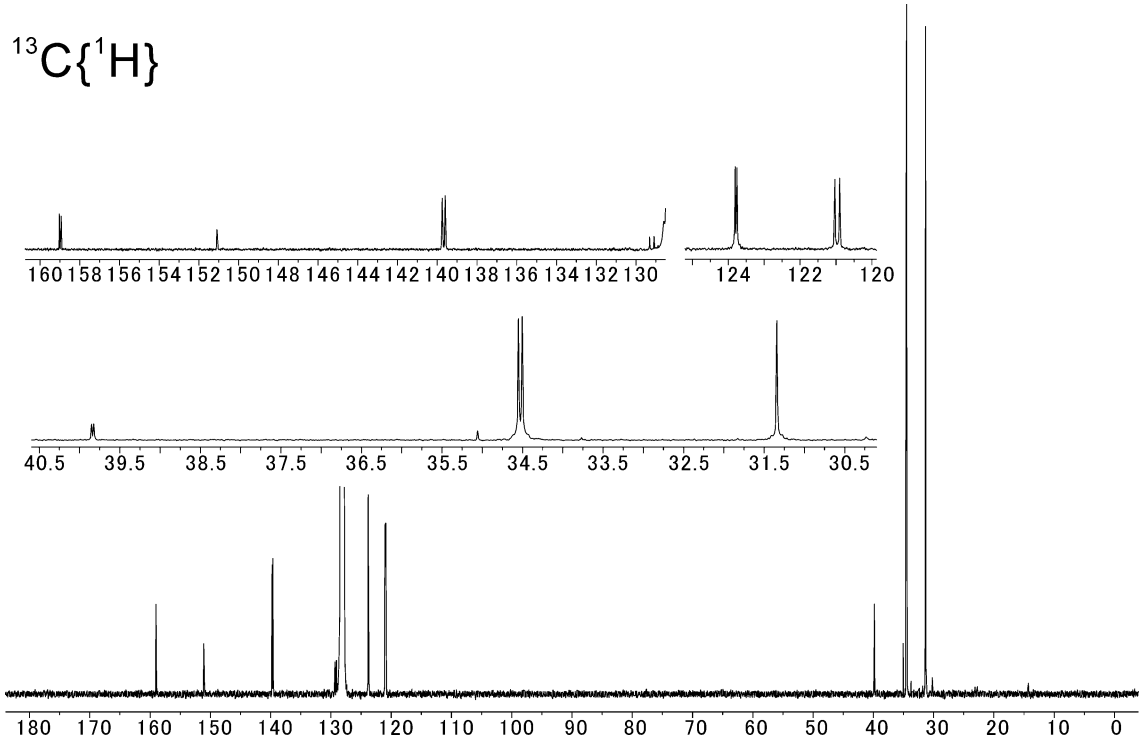
^{1}H,^{13}C GHMBC (600 MHz/151 MHz, 299 K, benzene-d_6) [selected traces]: δ^1H/δ^{13}C: 7.65/129.1, 123.7 (*m*-mes*/*i*-mes*, *m*-mes*), 1.65/158.9 (*o*-^{t}Bu/*o*-mes*).

^{31}P{^{1}H} NMR (243 MHz, 299 K, benzene-d_6): δ = –21.4 ($\nu_{1/2}$ ~ 1.0 Hz).

^{31}P{^{1}H} NMR (202 MHz, 299 K, dichloromethane-d_2): δ = –21.6 ($\nu_{1/2}$ ~ 2 Hz).

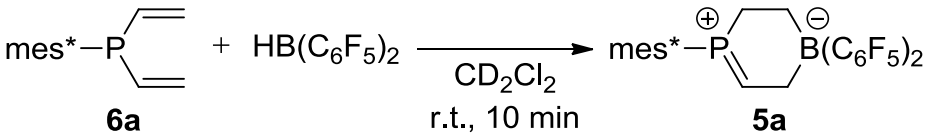


^{1}H NMR (600 MHz, 299 K, benzene-d_6) and ^{31}P{^{1}H} NMR (243 MHz, 299 K, benzene-d_6) spectra of **6a**.



^{13}C NMR (151 MHz, 299 K, benzene-d_6) spectrum of **6a**.

Preparation of Phosphonium Borata Zwitterionic Compound 5a.



6a **5a**

(1) *NMR scale:* Inside a glove box: slowly over 3 min a dichloromethane-d_2 (0.3 mL) solution of bis(pentafluorophenyl)borane (22.3 mg, 0.064 mmol) was added to a pre-cooled (–35°C) dichloromethane-d_2 (0.3 mL) solution of (2,4,6-tri-*tert*-butylphenyl)divinylphosphane (**6a**) (21.1 mg, 0.064 mmol) in an NMR tube. The reaction mixture was shaken while the addition to avoid the second hydroboration. The reaction was left at about 10 min at room temperature and then the NMR spectra were obtained at –40°C. (The formation of compound **5a** was nearly quantitative).

^{1}H NMR (600 MHz, 233 K, dichloromethane-d_2): δ = 8.10 (br t, $^{3}J_{HH}$ = 5.8 Hz, 1H, P=CH), 7.58 (d, $^{4}J_{PH}$ = 4.6 Hz, 2H, *m*-mes*), 2.75 (br dm, $^{2}J_{PH}$ = 21.0 Hz, 2H, PCH_2), 2.27 (br d, $^{3}J_{PH}$ = 53.9 Hz, 2H, $^{-}CH_2B$), 1.95 (br dm, $^{3}J_{PH}$ = 29.8 Hz, 2H, BCH_2), 1.47 (s, 18H, *o*-^{t}Bu), 1.28 (s, 9H, *p*-^{t}Bu).

^{1}H{sel-^{31}P: δ 148.8} NMR (500 MHz, 233 K, dichloromethane-d_2)[selected resonances]: δ = 8.10 (br t, $^{3}J_{HH}$ = 5.8 Hz, 1H, P=CH), 7.58 (s, 2H, *m*-mes*), 2.75 (br m, 2H, PCH_2), 2.27 (br, 2H, $^{-}CH_2B$), 1.95 (br, 2H, BCH_2).

^{13}C{^{1}H} NMR (151 MHz, 233 K, dichloromethane-d_2): δ = 172.1 (d, $^{1}J_{PC}$ = 112.2 Hz, P=CH), 157.9 (d, $^{2}J_{PC}$ = 5.2 Hz, *o*-mes*), 157.2 (d, $^{4}J_{PC}$ = 2.8 Hz, *p*-mes*), 148.2 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 137.8 (dm, $^{1}J_{FC}$ ~ 245 Hz, *p*-C_6F_5), 136.4 (dm, $^{1}J_{FC}$ ~ 245 Hz, *m*-C_6F_5), 126.1 (br, *i*-C_6F_5), 123.8 (d, $^{3}J_{PC}$ = 12.6 Hz, *m*-mes*), 113.2 (d, $^{1}J_{PC}$ = 65.7 Hz, *i*-mes*), 38.1 (d, $^{3}J_{PC}$ = 2.4 Hz, *o*-^{t}Bu^{C}), 35.5 (*p*-^{t}Bu^{C}), 32.6 (*o*-^{t}Bu^{CH3}), 32.4 (d, $^{1}J_{PC}$ = 39.4 Hz, PCH_2), 30.6 (br, $^{-}CH_2B$), 30.4 (*p*-^{t}Bu^{CH3}), 18.6 (br, BCH_2).

^{1}H,^{1}H GCOSY (600 MHz/600 MHz, 233 K, dichloromethane-d_2) [selected traces]: δ^{1}H/δ^{1}H: 8.10/2.27 (P=CH/$^{-}CH_2B$), 7.58/1.47, 1.28 (*m*-mes*/*o*-^{t}Bu, *p*-^{t}Bu), 2.75/2.27 (PCH_2/$^{-}CH_2B$), 2.75/1.95 (PCH_2/BCH_2).

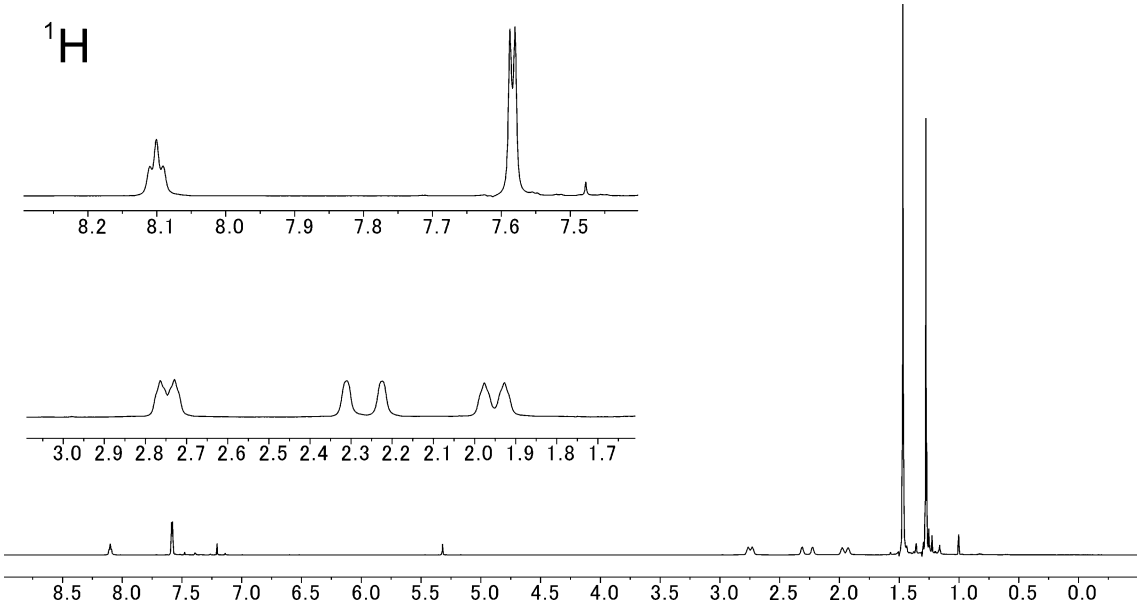
^{1}H,^{13}C GHSQC (600 MHz/151 MHz, 233 K, dichloromethane-d_2) [selected traces]: δ^{1}H/δ^{13}C: 8.10/172.1 (P=CH), 7.58/123.8 (*m*-mes*), 2.75/32.4 (PCH_2), 2.27/30.4 ($^{-}CH_2B$), 1.95/18.6 (BCH_2), 1.47/32.6 (*o*-^{t}Bu), 1.28/30.4 (*p*-^{t}Bu).

^{1}H,^{13}C GHMBC (600 MHz/151 MHz, 233 K, dichloromethane-d_2) [selected traces]: δ^{1}H/δ^{13}C: 8.10/32.4 (P=CH/PCH_2), 7.58/157.9, 157.2, 123.8, 113.2, 38.1, 35.5 (*m*-mes*/*o*-mes*, *p*-mes*, *m*-mes*, *i*-mes*, *o*-^{t}Bu^{C}, *p*-^{t}Bu^{C}), 1.47/157.9, 38.1, 32.6 (*o*-^{t}Bu/*o*-mes*, *o*-^{t}Bu^{C}, *o*-^{t}Bu^{CH3}), 1.28/157.2, 35.5, 30.4 (*p*-^{t}Bu/*p*-mes*, *p*-^{t}Bu^{C}, *p*-^{t}Bu^{CH3}).

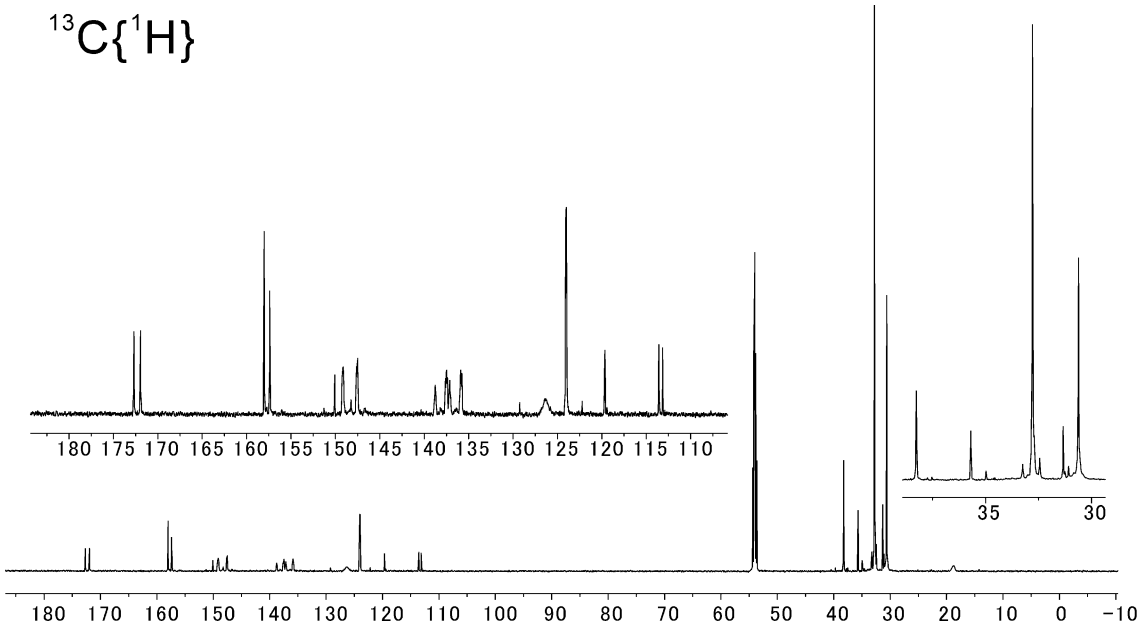
^{11}B{^{1}H} NMR (192 MHz, 233 K, dichloromethane-d_2): δ = –15.8 ($\nu_{1/2}$ ~ 120 Hz).

^{19}F NMR (564 MHz, 233 K, dichloromethane-d_2): δ = −133.9 (m, 2F, *o*-C_6F_5), −162.4 (t, $^3J_{FF}$ ~ 20 Hz, 1F, *p*-C_6F_5), −165.6 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{pm}$ = 3.2].

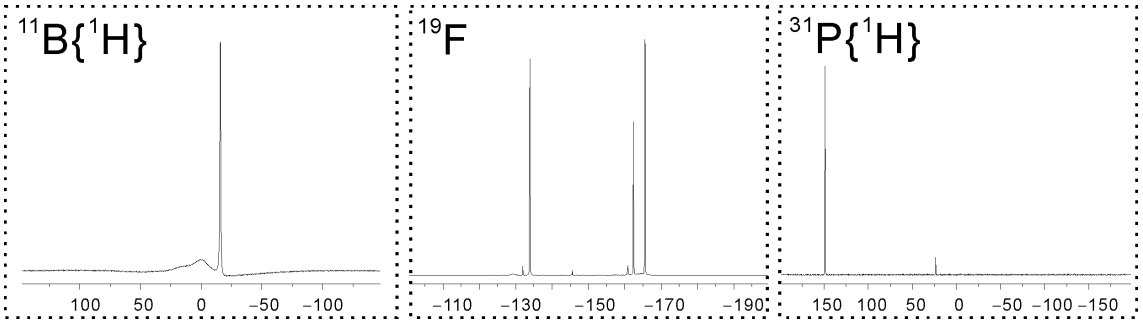
^{31}P{^{1}H} NMR (243 MHz, 233 K, dichloromethane-d_2): δ = 148.8 ($\nu_{1/2}$ ~ 40 Hz).



^{1}H NMR (600 MHz, 233 K, dichloromethane-d_2) spectrum of **5a**.



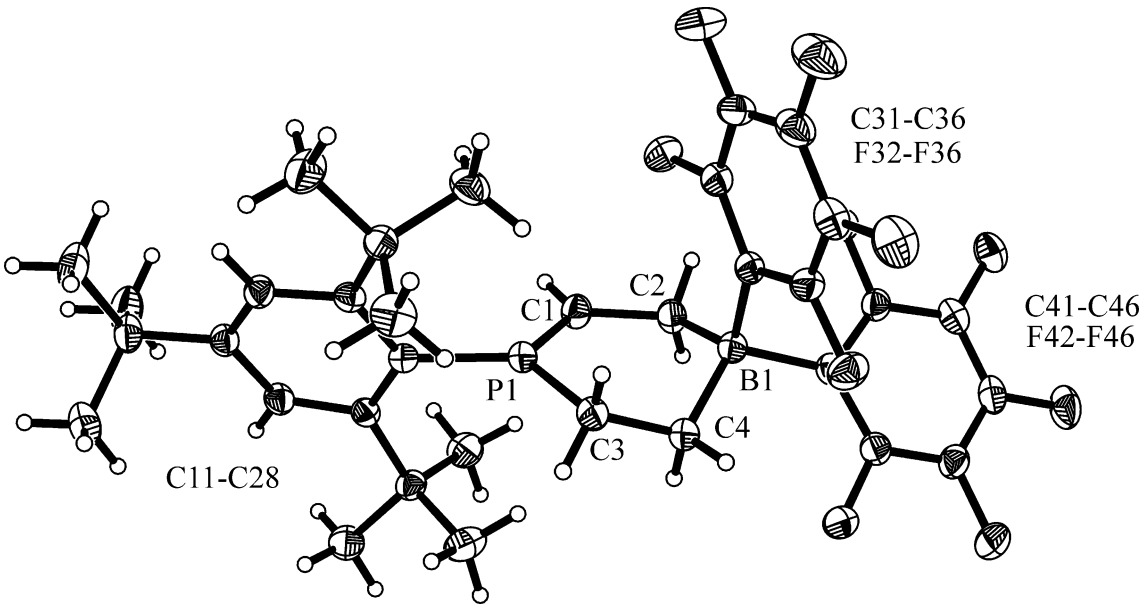
^{13}C{^{1}H} NMR (151 MHz, 233 K, dichloromethane-d_2) spectrum of **5a**.



$^{11}B\{^1H\}$ NMR (192 MHz, 233 K, dichloromethane-d_2), ^{19}F NMR (564 MHz, 233 K, dichloromethane-d_2) and $^{31}P\{^1H\}$ NMR (243 MHz, 233 K, dichloromethane-d_2) spectra of **5a**.

(2) *Preparative scale:* Inside a glove box: bis(pentafluorophenyl)borane (150 mg, 0.43 mmol) was added to a solution of **6a** (141 mg. 0.43 mmol) in dichloromethane (1 mL) and then the reaction mixture was kept in a fridge at −35°C. After 8 days crystals of **5a** (100 mg, 35%) suitable for the X-ray crystal structure analysis were obtained. **HRMS:** $M+H^+$ ($C_{34}H_{36}BF_{10}PH^+$): calc. 677.25667, found 677.25638.

X-ray crystal structure analysis of compound **5a**: formula $C_{34}H_{36}BF_{10}P$, M = 676.41 colourless crystal, 0.30 x 0.05 x 0.03 mm, a = 13.2615(8), b = 14.2777(9), c = 17.5650(15) Å, α = 101.998(4), β = 96.776(6), γ = 91.480(6)°, V = 3226.1(4) Å^3, ρ_{calc} = 1.393 gcm^{-3}, μ = 1.486 mm^{-1}, empirical absorption correction ($0.664 \leq T \leq 0.956$), Z = 4, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 40714 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 11064 independent (R_{int} = 0.059) and 8445 observed reflections [$I>2\sigma(I)$], 1033 refined parameters, R = 0.049, wR^2 = 0.127, max. (min.) residual electron density 0.26 (-0.28) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

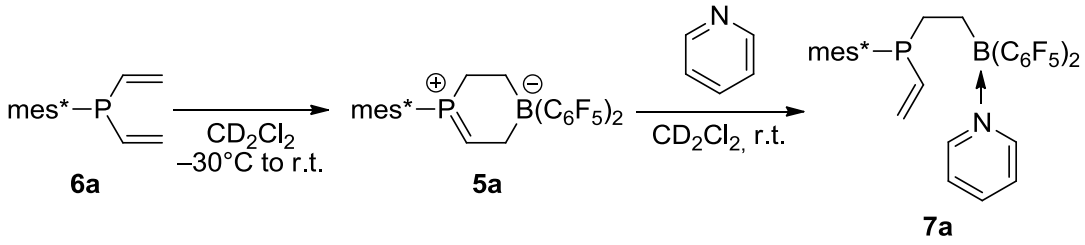


(3) *Preparative scale:* Inside a glove box: a dichloromethane (50 mL) solution of bis(pentafluorophenyl)borane (346 mg, 1.00 mmol) was added slowly (over ca. 5 min) to a dichloromethane (50 mL) solution of (2,4,6-tri-*tert*-butylphenyl)divinylphosphane (**6a**) (330 mg, 1.00 mmol) which gave a yellowish reaction solution. The solvent was removed in vacuo for 1 h at 0°C, then the obtained residue was dissolved in a minimum amount of dichloromethane (ca. 3 mL) and put into a fridge (–35°C) for a few days. The solution was concentrated to ca. 1.5 mL. Then *n*-pentane (1.5 mL) was added to give a suspension. After filtration compound **5a** (277 mg, 41%) was isolated as a white powder.

Elemental analysis: Calcd. for $C_{34}H_{36}BF_{10}P$: C, 60.37; H, 5.36. Found: C 59.72, H 5.44.

Melting point (DSC): 113°C

Preparation of Pyridine Adduct 7a.



1st experiment: Inside a glove box: a precooled (–35°C) solution of bis(pentafluorophenyl)borane (9.5 mg, 0.026 mmol, 1.0 eq.) in dichloromethane-d_2 (0.25 mL) was slowly added to a precooled (–35°C) dichloromethane-d_2 solution (0.25 mL) of **6a** (9.1 mg, 0.027 mmol, 1.0 eq.). Then the reaction mixture was transferred to an NMR tube. After 1 min at room temperature, pyridine (2.2 µL, 0.27 mmol, 1.0 eq.) was added which gave the pyridine adduct **7a** almost quantitatively.

HRMS: $M+H^+$ ($C_{39}H_{41}BF_{10}NPH^+$): calc. 756.29895, found 756.29672.

^{1}H NMR (500 MHz, 299 K, dichloromethane-d_2): δ = 8.63 (m, 2H, *o*-Py), 8.12 (m, 1H, *p*-Py), 7.65 (m, 2H, *m*-Py), 7.37 (d, $^4J_{PH}$ = 1.9 Hz, 2H, *m*-mes*), 6.60 (ddd, $^2J_{PH}$ = 21.7 Hz, $^3J_{HH}$ = 18.5 Hz, $^3J_{HH}$ = 12.5 Hz, 1H, =CH), 5.37 (ddd, $^3J_{PH}$ = 19.3 Hz, $^3J_{HH}$ = 12.5 Hz, $^2J_{HH}$ = 1.9 Hz, 1H, $=CH_2^E$), 4.89 (ddd, $^3J_{HH}$ = 18.5 Hz, $^3J_{PH}$ = 6.1 Hz, $^2J_{HH}$ = 1.9 Hz, 1H, $=CH_2^Z$), 1.81, 1.51 (each m, each 1H, PCH_2)[a], 1.49, 1.19 (each m, each 1H, BCH_2)[a], 1.43 (s, 18H, *o*-^{t}Bu^{CH3}), 1.26 (s, 9H, *p*-^{t}Bu^{CH3}), [[a] from ghsqc experiment].

^{13}C{^{1}H} NMR (126 MHz, 299 K, dichloromethane-d_2): δ = 158.7 (d, $^2J_{PC}$ = 12.4 Hz, *o*-mes*), 150.2 (d, $^4J_{PC}$ = 2.3 Hz, *p*-mes*), 146.2 (*o*-Py), 142.2 (*p*-Py), 142.0 (d, $^1J_{PC}$ = 28.9 Hz, =CH), 132.5 (d, $^1J_{PC}$ = 41.2 Hz, *i*-mes*), 126.5 (*m*-Py), 124.4 (*i*-C_6F_5), 122.9 (d, $^3J_{PC}$ = 7.0 Hz, *m*-mes*), 118.3 (d, $^2J_{PC}$ = 15.9 Hz, $=CH_2$), 39.4 (d, $^3J_{PC}$ = 4.0 Hz, *o*-^{t}Bu^C), 35.0 (d, $^5J_{PC}$ = 0.8 Hz, *p*-^{t}Bu^C), 34.2 (d, $^4J_{PC}$ = 7.4 Hz, *o*-^{t}Bu^{CH3}), 31.2 (*p*-^{t}Bu^{CH3}), 26.1 (d, $^1J_{PC}$ = 21.1 Hz, PCH_2), 21.5 (br, BCH_2), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (500 MHz/500 MHz, 299 K, dichloromethane-d_2) [selected traces]: δ^{1}H/ δ^{1}H: 8.63/8.12, 7.65 (*o*-Py/*p*-Py, *m*-Py), 6.60/5.37, 4.89 (=CH/=CH_2^E, =CH_2^Z), 1.81/1.51, 1.49, 1.19 (PCH_2/PCH_2', BCH_2, BCH_2).

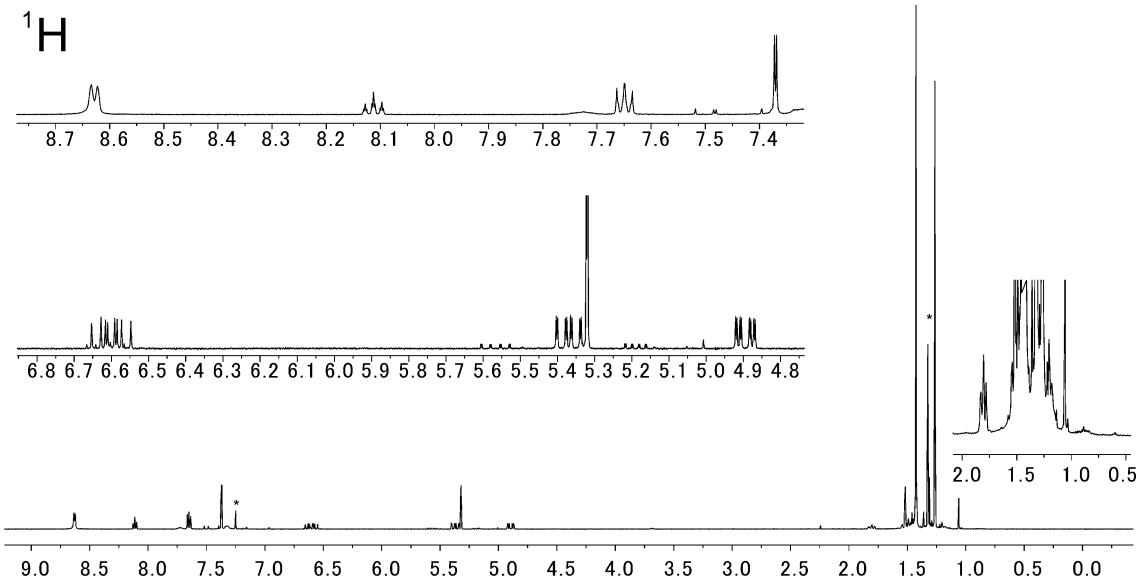
^{1}H,^{13}C GHSQC (500 MHz/126 MHz, 299 K, dichloromethane-d_2) [selected traces]: δ^{1}H/δ^{13}C: 8.63/146.42(*o*-Py), 8.12/142.2 (*p*-Py), 7.65/126.5 (*m*-Py), 7.37/122.9 (*m*-mes*), 6.60/142.0 (=CH), 5.37/118.3 (=CH_2^E), 4.89/118.3 (=CH_2^Z), 1.81/26.1 (PCH_2), 1.51/26.1 (PCH_2'), 1.49/21.5 (BCH_2), 1.43/34.2 (*o*-^{t}Bu), 1.26/31.2 (*p*-^{t}Bu), 1.19/21.5 (BCH_2').

^{1}H,^{13}C GHMBC (500 MHz/126 MHz, 299 K, dichloromethane-d_2) [selected traces]: δ^{1}H/δ^{13}C: 7.37/132.5, 122.9, 39.4, 35.0 (*m*-mes*/*i*-mes*, *m*-mes*, *o*-^{t}Bu^C, *p*-^{t}Bu^C), 1.43/158.7, 39.4, 34.2 (*o*-^{t}Bu^{CH3}/*o*-mes*, *o*-^{t}Bu^C, *o*-^{t}Bu^{CH3}), 1.26/150.2, 35.0, 31.2 (*p*-^{t}Bu^{CH3}/*p*-mes*, *p*-^{t}Bu^C, *p*-^{t}Bu^{CH3}).

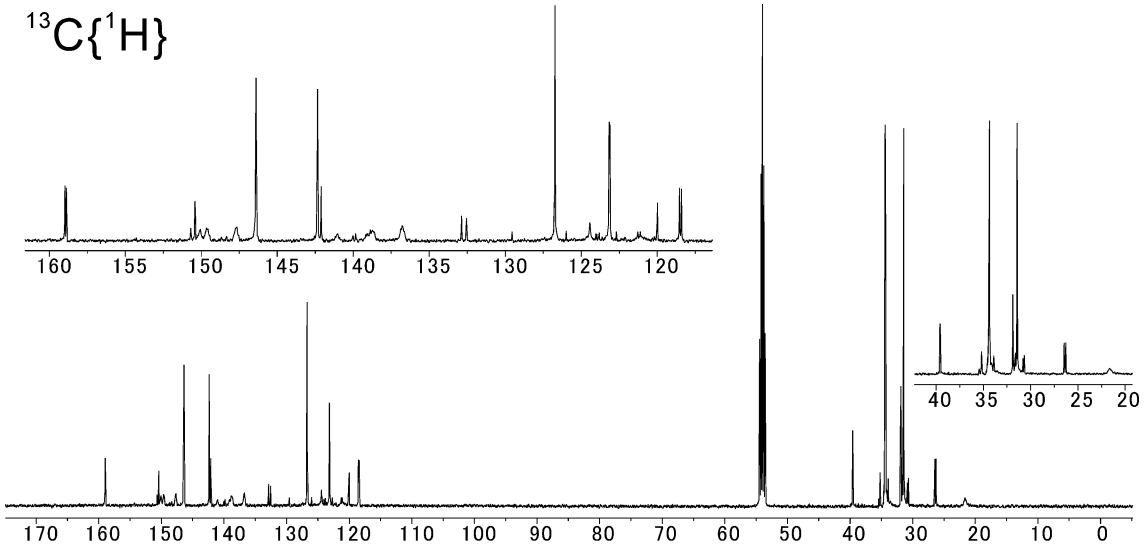
^{11}B{^{1}H} NMR (160 MHz, 299 K, dichloromethane-d_2): δ = –0.7 ($\nu_{1/2}$ ~ 250 Hz).

^{19}F NMR (470 MHz, 299 K, dichloromethane-d_2): δ = –132.0 (m, 4F, *o*-C_6F_5), –159.1 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), –159.2 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), –164.5 (m, 4F, *m*-C_6F_5). [$\Delta\delta^{19}F_{pm}$ = 5.4, 5.3]

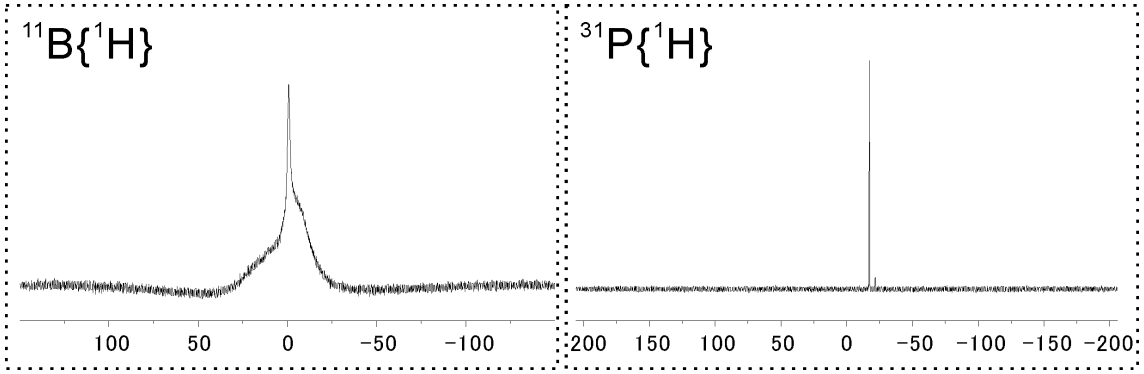
^{31}P{^{1}H} NMR (202 MHz, 299 K, dichloromethane-d_2): δ = –17.3 ($\nu_{1/2}$ ~ 8 Hz).



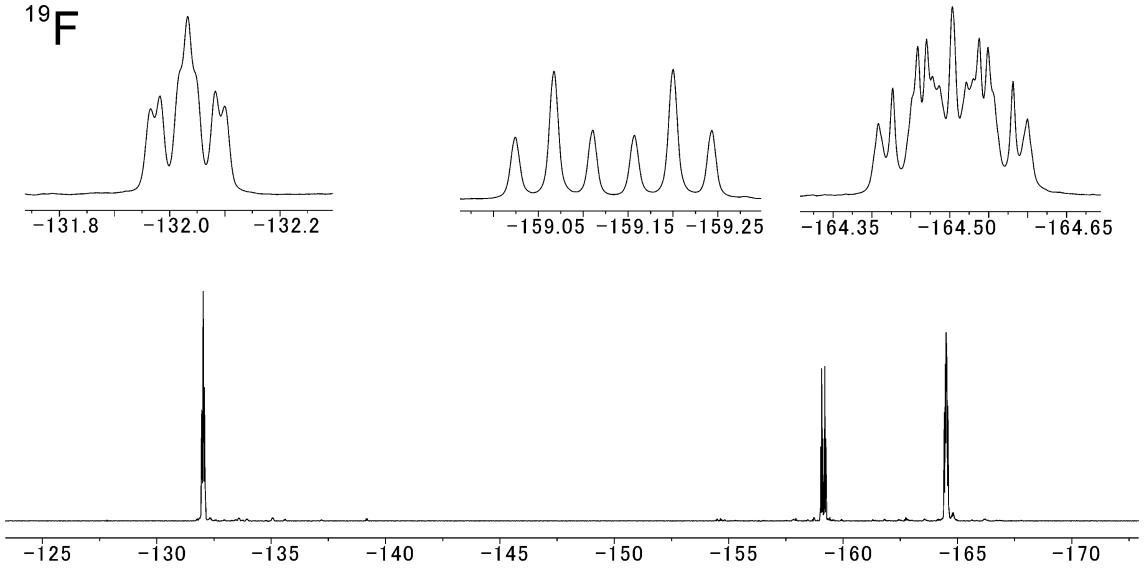
^{1}H NMR (500 MHz, 299 K, dichloromethane-d_2) spectrum of **7a**.



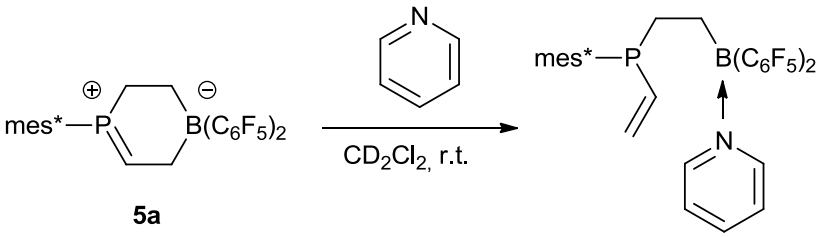
$^{13}C\{^1H\}$ NMR (126 MHz, 299 K, dichloromethane-d_2) spectrum of **7a**.



$^{11}B\{^1H\}$ NMR (160 MHz, 299 K, dichloromethane-d_2) and $^{31}P\{^1H\}$ NMR (202 MHz, 299 K, dichloromethane-d_2) spectra of **7a**.



^{19}F NMR (470 MHz, 273 K, dichloromethane-d_2) spectrum of **7a**.



5a **7a**

*2nd experiment (starting from compound **5a**)*: Inside a glove box: Pyridine (7.9 µL, 0.098 mmol) was added to a precooled (–35°C) solution of **5a** (66.6 mg, 0.098 mmol, 1.0 eq.) in dichloromethane-d_2 (0.5 mL) Then the reaction mixture was transferred to an NMR tube. After the NMR measurements, the solution was evaporated and then the obtained residue was dissolved in a minimum amount of *n*-pentane (ca. 2 mL). Slow diffusion of the solvent at –35°C gave crystals of **7a** (659 mg, 89%) which were suitable for the X-ray crystal structure analysis.

Calcd. for $C_{39}H_{41}BF_{10}NP$: C, 62.00; H, 5.47; N, 1.85. Found: C, 62.10; H, 5.62; N, 1.63.

^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2): δ = 8.64 (d, $^{3}J_{HH}$ = 5.7 Hz, 2H, *o*-Py), 8.12 (tt, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H, *p*-Py), 7.66 (m, 2H, *m*-Py), 7.38 (d, $^{4}J_{PH}$ = 1.9 Hz, 2H, *m*-mes*), 6.61 (ddd, $^{2}J_{PH}$ = 21.7 Hz, $^{3}J_{HH}$ = 18.5 Hz, $^{3}J_{HH}$ = 12.5 Hz, 1H, =CH), 5.38 (ddd, $^{3}J_{PH}$ = 19.3 Hz, $^{3}J_{HH}$ = 12.5 Hz, $^{2}J_{HH}$ = 1.9 Hz, 1H, =CH_2^E), 4.90 (ddd, $^{3}J_{HH}$ = 18.5 Hz, $^{3}J_{PH}$ = 6.0 Hz, $^{2}J_{HH}$ = 1.9 Hz, 1H, =CH_2^Z), 1.81, 1.51 (each m, each 1H, PCH_2)[a], 1.49, 1.19 (each m, each 1H, BCH_2)[a], 1.44 (s, 18H, *o*-$^{t}Bu^{CH3}$), 1.27 (s, 9H, *p*-$^{t}Bu^{CH3}$), [[a] from ghsqc experiment].

^{13}C{^{1}H} NMR (151 MHz, 299 K, dichloromethane-d_2): δ = 158.7 (d, $^{2}J_{PC}$ = 12.3 Hz, *o*-mes*), 150.2 (d, $^{4}J_{PC}$ = 2.3 Hz, *p*-mes*), 146.2 (*o*-Py), 142.2 (*p*-Py), 142.1 (d, $^{1}J_{PC}$ = 29.0 Hz, =CH), 132.5 (d, $^{1}J_{PC}$ = 41.2 Hz, *i*-mes*), 126.5 (*m*-Py), 123.0 (d, $^{3}J_{PC}$ = 6.9 Hz, *m*-mes*), 118.3 (d, $^{2}J_{PC}$ = 15.8 Hz, =CH_2), 39.4 (d, $^{3}J_{PC}$ = 4.1 Hz, *o*-$^{t}Bu^{C}$), 35.0 (d, $^{5}J_{PC}$ = 0.8 Hz, *p*-$^{t}Bu^{C}$), 34.2 (d, $^{4}J_{PC}$ = 7.3 Hz, *o*-$^{t}Bu^{CH3}$), 31.3 (*p*-$^{t}Bu^{CH3}$), 26.2 (d, $^{1}J_{PC}$ = 21.1 Hz, PCH_2), 21.5 (br, BCH_2), [C_6F_5 not listed].

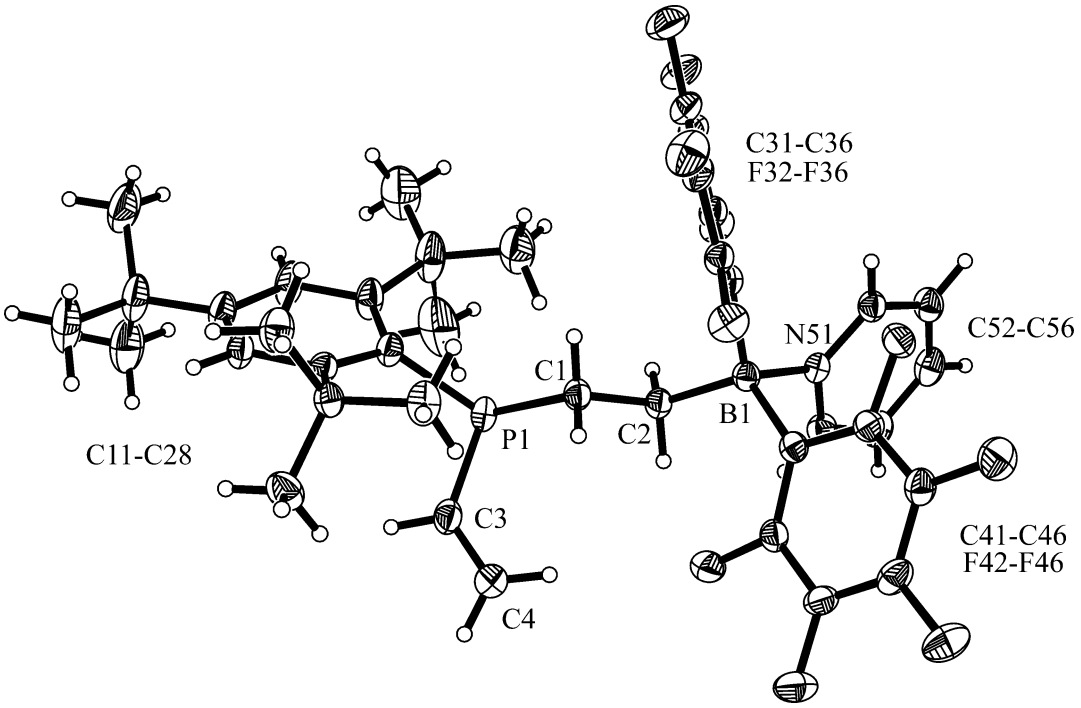
^{11}B{^{1}H} NMR (192 MHz, 299 K, dichloromethane-d_2): δ = –0.6 ($\nu_{1/2}$ ~ 270 Hz).

^{19}F NMR (564 MHz, 299 K, dichloromethane-d_2): δ = –132.0 (m, 4F, *o*-C_6F_5), –159.1 (t, $^{3}J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), –159.2 (t, $^{3}J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), –164.5 (m, 4F, *m*-C_6F_5). [$\Delta\delta^{19}F_{pm}$ = 5.4, 5.3]

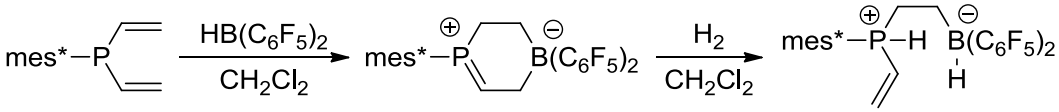
^{31}P{^{1}H} NMR (243 MHz, 299 K, dichloromethane-d_2): δ = –17.3 ($\nu_{1/2}$ ~ 8 Hz).

X-ray crystal structure analysis of compound **7a**: formula $C_{39}H_{41}BF_{10}NP$, *M* = 755.51 colourless crystal, 0.10 x 0.05 x 0.02 mm, *a* = 38.3733(7), *b* = 9.7770(2), *c* = 22.7086(6) Å, *β* = 117.195(1)°, *V* = 7577.9(3) Å^3, ρ_{calc} = 1.324 gcm^{-3}, µ = 1.331 mm^{-1}, empirical absorption correction (0.878 ≤ T ≤ 0.973), *Z* = 8, monoclinic, space group *C*2/*c* (No. 15), λ = 1.54178 Å, *T* = 223(2) K, ω and φ scans, 36118 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 6534 independent (R_{int} = 0.079) and 4516 observed

reflections [$I>2\sigma(I)$], 509 refined parameters, R = 0.051, wR^2 = 0.141, max. (min.) residual electron density 0.39 (-0.26) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Preparation of Phosphonium Hydridoborate 8a.



6a **5a** **8a**

A dichloromethane solution (20 mL) of bis(pentafluorophenyl)borane (71.0 mg, 0.21 mmol) was slowly added to a dichloromethane solution (20 mL) of **6a** (70.0 mg, 0.21 mmol) at room temperature and the reaction mixture was stirred for 10 min. Then the reaction solution was cooled to –40°C, concentrated to ca. 1 mL in vacuo and subsequently reacted with dry H_2 (1.5 bar after evacuation of argon) for 1 h. After slowly warming to room temperature under dihydrogen pressure, the solution was stirred for another 30 min and then the solvent was removed in vacuo. Crystallization attempt from dichloromethane/*n*-pentane gave crystals suitable for the X-ray crystal structure analysis (**8a**: 70 mg, 49%).

Calcd. for $C_{34}H_{38}BF_{10}P$: C, 60.19; H, 5.65. Found: C, 59.81; H, 5.36.

HRMS: M+H$^+$ ($C_{39}H_{41}BF_{10}PH^+$): calc. 756.29895, found 756.29875.

^{1}H NMR (500 MHz, 273 K, dichloromethane-d_2): δ = 7.59 (d, $^{4}J_{PH}$ = 4.6 Hz, 2H, *m*-mes*), 7.18 (dm, $^{1}J_{PH}$ ~ 484 Hz, 1H, PH), 6.51 (m, 1H, =CH)[a], 6.47[a], 5.98 (each m, each 1H, =CH_2), 2.72 (br, 1H, BH), 2.70, 2.49 (each m, each 1H, PCH_2), 1.45 (br, 18H, *o*-^{t}Bu^{CH3}), 1.31 (s, 9H, *p*-^{t}Bu^{CH3}), 1.10, 0.99 (each m, each 1H, BCH_2), [[a] from ghsqc experiment].

^{13}C{^{1}H} NMR (126 MHz, 273 K, dichloromethane-d_2): δ = 159.4 (br, *o*-mes*), 157.0 (d, $^{4}J_{PC}$ = 3.5 Hz, *p*-mes*), 139.6 (=CH_2), 126.0 (br, *m*-mes*), 121.9 (d, $^{1}J_{PC}$ = 70.9 Hz, =CH), 108.3 (d, $^{1}J_{PC}$ = 73.7 Hz, *i*-mes*), 39.0 (d, $^{3}J_{PC}$ = 3.4 Hz, *o*-^{t}Bu^{C}), 35.4 (*p*-^{t}Bu^{C}), 33.7 (*o*-^{t}Bu^{CH3}), 30.6 (*p*-^{t}Bu^{CH3}), 28.1 (d, $^{1}J_{PC}$ = 37.5 Hz, PCH_2), 18.0 (br, BCH_2), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (500 MHz/500 MHz, 273 K, dichloromethane-d_2) [selected traces]: δ^{1}H/ δ ^{1}H: 7.18/2.70, 2.49 (PH/PCH_2, PCH_2'), 2.72/2.49, 1.10, 0.99 (PCH_2/ PCH_2', BCH_2, BCH_2').

^{1}H,^{13}C GHSQC (500 MHz/126 MHz, 273 K, dichloromethane-d_2) [selected traces]: δ^{1}H/δ^{13}C: 7.59/126.0 (*m*-mes*), 6.51/121.9 (=CH), 6.51/139.6 (=CH_2), 5.98/139.6 (=CH_2'), 2.70/28.1 (PCH_2), 2.49/28.1 (PCH_2'), 1.45/33.7 (*o*-^{t}Bu^{CH3}), 1.31/30.6 (*p*-^{t}Bu^{CH3}), 1.10/28.1 (BCH_2), 0.99/28.1 (BCH_2').

^{1}H,^{13}C GHMBC (500 MHz/126 MHz, 273 K, dichloromethane-d_2) [selected traces]: δ^{1}H/δ^{13}C: 7.59/126.0, 108.3, 39.0, 35.4 (*m*-mes*/*m*-mes*, *i*-mes*, *o*-^{t}Bu^{C}, *p*-^{t}Bu^{C}), 1.45/159.4, 39.0, 33.7 (*o*-^{t}Bu^{CH3}/*o*-mes*, *o*-^{t}Bu^{C}, *o*-^{t}Bu^{CH3}), 1.31/157.0, 35.4, 30.6 (*p*-^{t}Bu^{CH3}/*p*-mes*, *p*-^{t}Bu^{C}, *p*-^{t}Bu^{CH3}).

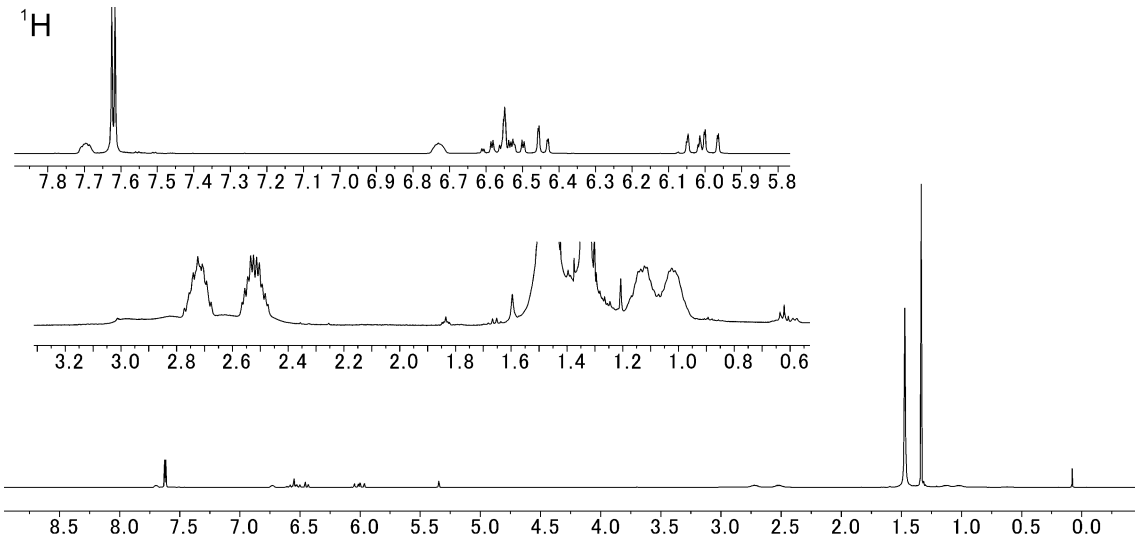
^{11}B{^{1}H} NMR (160 MHz, 273 K, dichloromethane-d_2): δ = –20.6 ($\nu_{1/2}$ ~ 65 Hz).

^{11}B NMR (160 MHz, 273 K, dichloromethane-d_2): δ = –20.6 (d, $^{1}J_{BH}$ ~ 88 Hz).

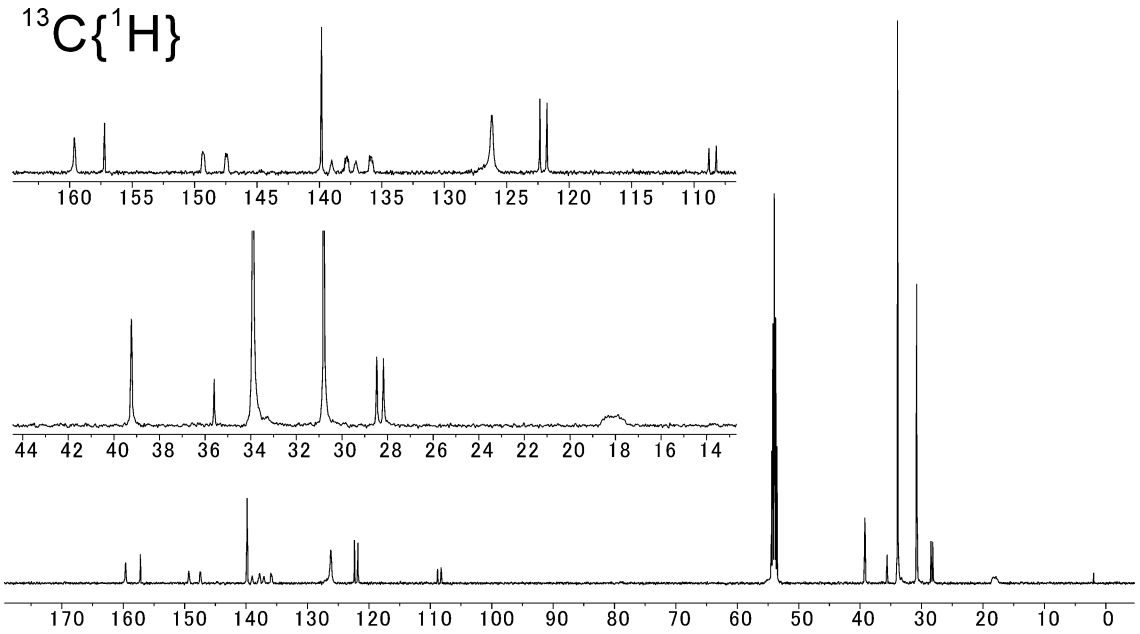
^{19}F NMR (470 MHz, 273 K, dichloromethane-d_2): δ = –134.0 (m, 4F, *o*-C_6F_5), –163.90, 163.94 (each t, each $^{3}J_{FF}$ = 21 Hz, each 1F, *p*-C_6F_5), –166.7 (m, 4F, *p*-C_6F_5), [$\Delta\delta^{19}F_{pm}$ = 2.8].

^{31}P NMR (202 MHz, 273 K, dichloromethane-d_2): δ = 4.2 (d, $^{1}J_{PH}$ ~ 484 Hz).

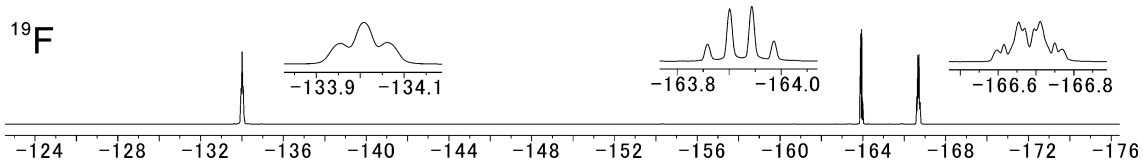
^{31}P{^{1}H} NMR (202 MHz, 273 K, dichloromethane-d_2): δ = 4.2 ($\nu_{1/2}$ ~ 60 Hz).



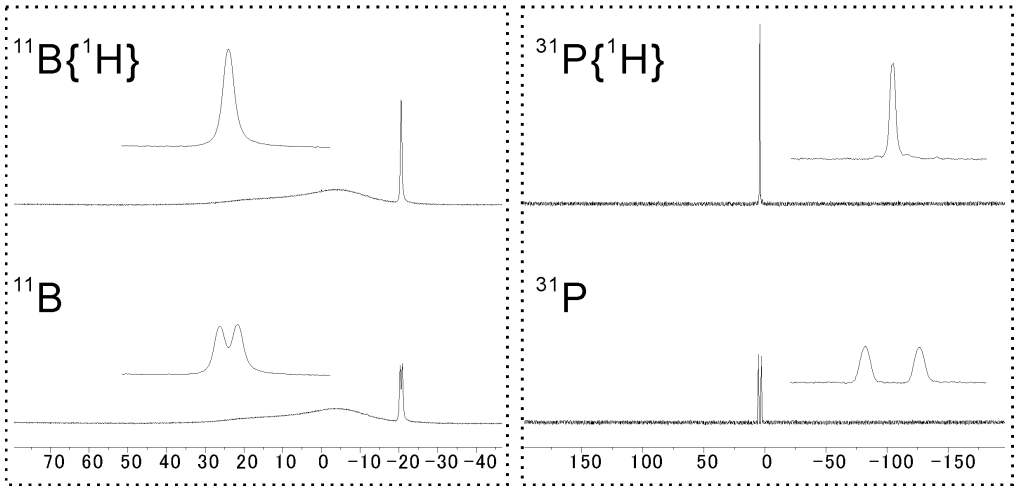
^{1}H NMR (500 MHz, 273 K, dichloromethane-d_2) spectrum of **8a**.



$^{13}C\{^1H\}$ NMR (126 MHz, 273 K, dichloromethane-d_2) spectrum of **8a**.

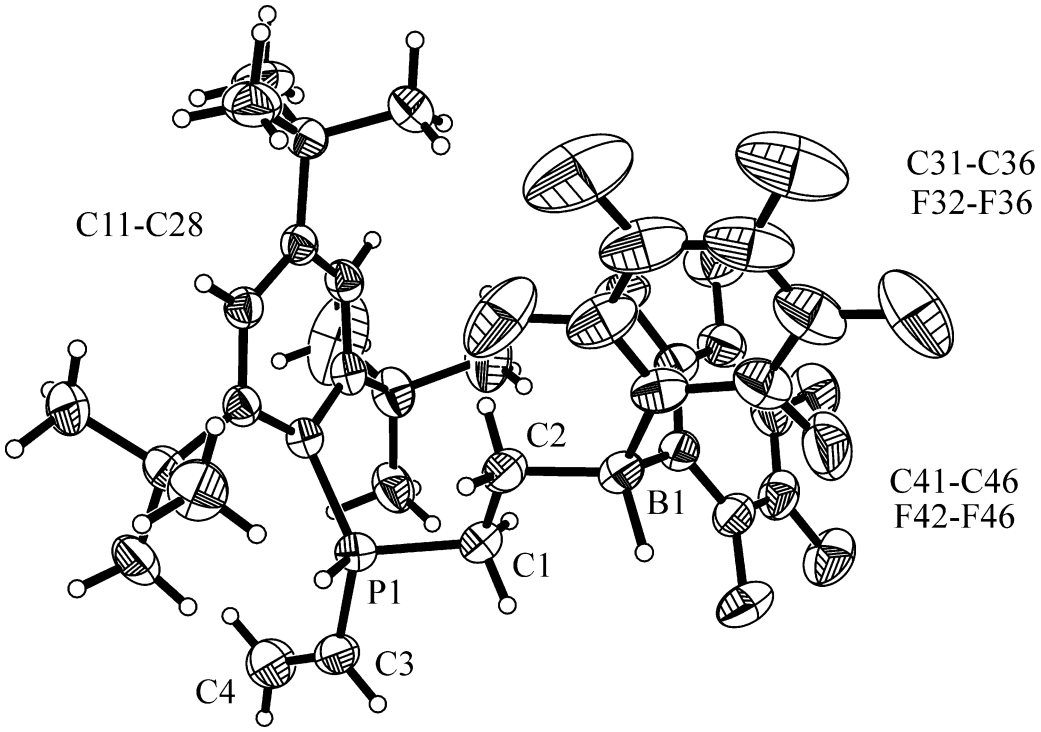


^{19}F NMR (470 MHz, 273 K, dichloromethane-d_2) and spectrum of **8a**.



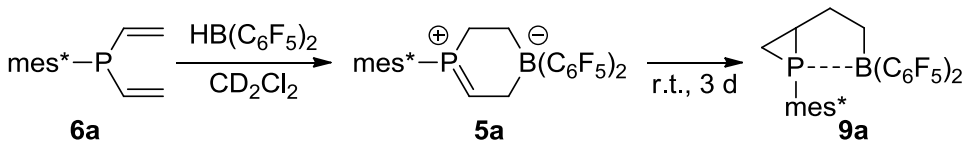
^{11}B NMR, $^{11}B\{^1H\}$ NMR (160 MHz, 273 K, dichloromethane-d_2), ^{31}P NMR and $^{31}P\{^1H\}$ NMR (202 MHz, 273 K, dichloromethane-d_2) spectra of **8a**.

X-ray crystal structure analysis of comound **8a**: formula $C_{34}H_{38}BF_{10}P$, M = 678.42 colourless crystal, 0.25 x 0.17 x 0.12 mm, a = 10.7438(4), b = 17.8343(5), c = 18.5450(5) Å, β = 106.201(2)°, V = 3412.26(18) Å^3, ρ_{calc} = 1.321 gcm^{-3}, μ = 1.405 mm^{-1}, empirical absorption correction ($0.720 \leq T \leq 0.849$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 23360 reflections collected ($\pm h, \pm k, \pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 5881 independent (R_{int} = 0.040) and 4915 observed reflections [$I>2\sigma(I)$], 492 refined parameters, R = 0.061, wR^2 = 0.164, max. (min.) residual electron density 0.25 (-0.43) e.Å^{-3}, the hydrogen atoms at P1 and B1 were refined freely, others hydrogen atoms were calculated and refined as riding atoms.



Preparation of Phosphirane 9a.

(a) Preparation and NMR Data.



(1) *NMR scale:* Inside a glove box: a dichloromethane-d_2 solution (0.3 mL) of bis(pentafluorophenyl)borane (4.5 mg, 0.013 mmol) was slowly added to a dichloromethane-d_2 solution (0.3 mL) of **6a** (4.0 mg, 0.012 mmol) while permanently shaking. The reaction mixture was

transferred to a NMR tube which was sealed and left at room temperature for 3 days to eventually give compound **9a** (> 99% conversion).

^{1}H NMR (500 MHz, 299 K, dichloromethane-d_2): δ = 7.43 (dd, $^{4}J_{HH}$ = 3.8 Hz, $^{4}J_{PH}$ = 2.2 Hz, 1H, *m*-mes*), 7.38 (dd, $^{4}J_{HH}$ = 3.8 Hz, $^{4}J_{PH}$ = 2.2 Hz, 1H, *m*'-mes*), 2.52, 2.05 (each m, each 1H, CH_2), 2.39 (m, 1H, PCH), 1.74, 1.35 (each m, each 1H, PCH_2), 1.63, 1.55 (each m, each 1H, BCH_2)[a], 1.47 (s, 9H, *o*-^{t}Bu), 1.34 (s, 9H, *o*'-^{t}Bu), 1.28 (s, 9H, *p*-^{t}Bu).

^{13}C{^{1}H} NMR (126 MHz, 299 K, dichloromethane-d_2): δ = 158.5 (d, $^{2}J_{PC}$ = 6.2 Hz, *o*-mes*), 157.0 (*o*'-mes*), 152.6 (*p*-mes*), 148.5 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 140.1 (dm, $^{1}J_{FC}$ ~ 246 Hz, C_6F_5), 137.5 (dm, $^{1}J_{FC}$ ~ 256 Hz, C_6F_5), 125.7 (d, $^{3}J_{PC}$ = 7.8 Hz, *m*'-mes*), 125.3 (d, $^{3}J_{PC}$ = 8.1 Hz, *m*-mes*), 121.9 (*i*-mes*), 120.0 (br, *i*-C_6F_5), 39.1 (d, $^{3}J_{PC}$ = 1.0 Hz, *o*'-^{t}Bu^{C}), 38.5 (d, $^{3}J_{PC}$ = 1.1 Hz, *o*-^{t}Bu^{C}), 35.2 (d, $^{1}J_{PC}$ = 3.7 Hz, PCH), 35.1 (*p*-^{t}Bu^{C}), 34.2 (*o*-^{t}Bu^{CH3}), 33.6 (*o*'-^{t}Bu^{CH3}), 33.3 (br, *o*-^{t}Bu^{CH3}), 31.0 (*p*-^{t}Bu^{CH3}) , 27.3 (d, $^{3}J_{PC}$ = 11.6 Hz, CH_2), 26.4 (d, $^{1}J_{PC}$ = 13.8 Hz, PCH_2), 23.8 (br, BCH_2).

^{1}H,^{1}H GCOSY (600 MHz/600 MHz, 299 K, dichloromethane-d_2) [selected traces]: δ^{1}H/ δ ^{1}H: 7.43/7.38 (*m*-mes*/*m*'-mes*), 2.52/2.39, 2.05, 1.63, 1.55 (CH_2/PCH, CH_2', BCH_2, BCH_2'), 2.39/1.74, 1.35 (PCH/PCH_2, PCH_2').

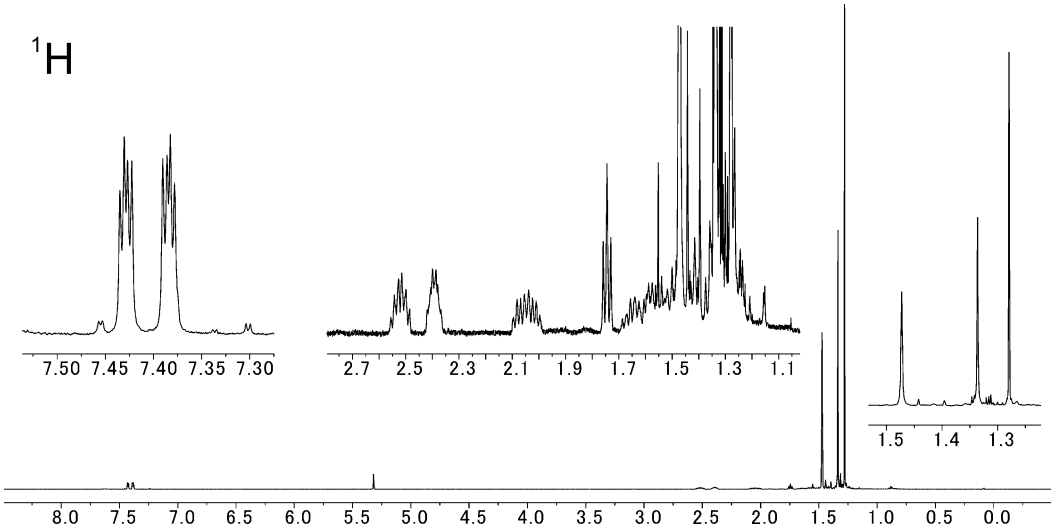
^{1}H,^{13}C GHSQC (500 MHz/126 MHz, 299 K, dichloromethane-d_2) [selected traces] δ^{1}H/δ^{13}C: 7.43/125.3 (*m*-mes*), 7.38/125.7 (*m*'-mes*), 2.52/27.3 (CH_2), 2.39/35.2 (PCH), 2.05/27.3 (CH_2), 1.74/26.4 (PCH_2), 1.63/23.8 (BCH_2), 1.55/23.8 (BCH_2'), 1.47/33.3 (*o*-^{t}Bu^{CH3}), 1.35/26.4 (PCH_2'), 1.34/33.6 (*o*'-^{t}Bu^{CH3}), 1.28/31.0 (*p*-^{t}Bu^{CH3}).

^{1}H,^{13}C GHMBC (500 MHz/126 MHz, 299 K, dichloromethane-d_2) [selected traces]: δ^{1}H/δ^{13}C: 7.43/125.7, 121.9, 38.5, 35.1 (*m*-mes*/*m*'-mes*, *i*-mes*, *o*-^{t}Bu^{C}, *p*-^{t}Bu^{C}), 7.38/125.3, 121.9, 39.1, 35.1 (*m*'-mes*/*m*-mes*, *i*-mes*, *o*'-^{t}Bu^{C}, *p*-^{t}Bu^{C}), 2.52/35.2, 26.4, 23.8 (CH_2/PCH, PCH_2, BCH_2), 1.47/158.5, 38.5, 33.3 (*o*-^{t}Bu/*o*-mes*, *o*-^{t}Bu^{C}, *o*-^{t}Bu^{CH3}), 1.34/157.0, 39.1, 33.6 (*o*'-^{t}Bu/*o*'-mes*, *o*'-^{t}Bu^{C}, *o*'-^{t}Bu^{CH3}), 1.28/152.6, 35.1, 31.0 (*p*-^{t}Bu/*p*-mes*, *p*-^{t}Bu^{C}, *p*-^{t}Bu^{CH3}).

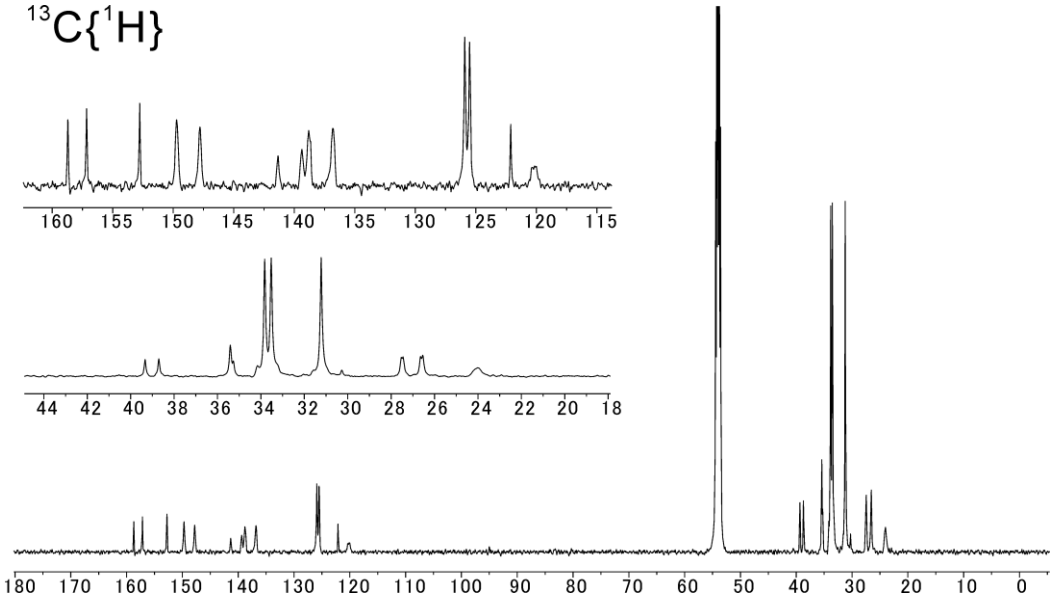
^{11}B{^{1}H} NMR (160 MHz, 299 K, dichloromethane-d_2): δ = 1.5 ($\nu_{1/2}$ ~ 300 Hz).

^{19}F NMR (470 MHz, dichloromethane-d_2): δ = –128.5 (br, 2F, *o*-C_6F_5), –158.3 (br, 1F, *p*-C_6F_5), –164.8 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{pm}$ = 6.5].

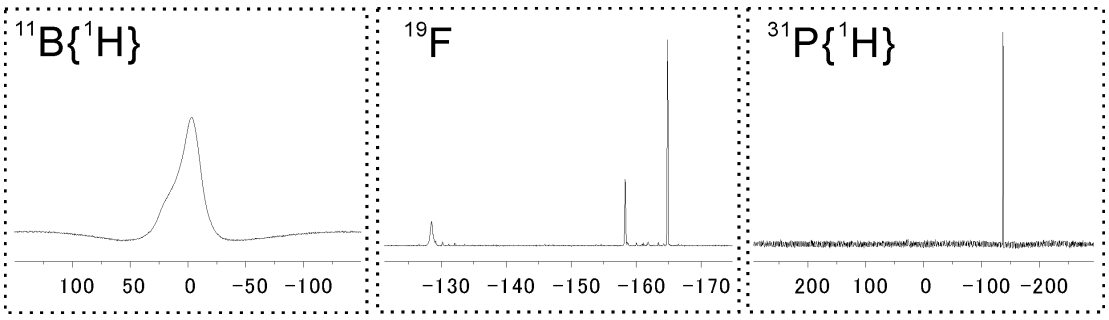
^{31}P{^{1}H} NMR (202 MHz, 299 K, dichloromethane-d_2): δ = –137.5 ($\nu_{1/2}$ ~ 40 Hz).



^{1}H NMR (500 MHz, 299 K, dichloromethane-d_2) spectrum of **6b**.

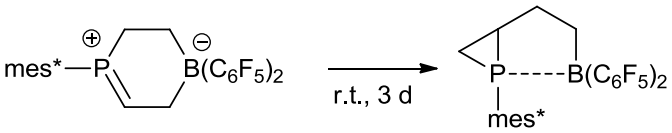


^{13}C{^{1}H} NMR (126 MHz, 299 K, dichloromethane-d_2) spectrum of **9a**.



^{11}B{^{1}H} NMR (160 MHz, 299 K, dichloromethane-d_2), ^{19}F NMR (470 MHz, 299 K, dichloromethane-d_2) and ^{31}P{^{1}H} NMR (202 MHz, 299 K, dichloromethane-d_2) spectra of **9a**.

(2) *Preparative scale:* Inside a glove box: a dichloromethane solution (15 mL) of bis(pentafluorophenyl)borane (520 mg, 1.50 mmol) was slowly added to a precooled (–35°C) dichloromethane solution (15 mL) of **6a** (500 mg, 1.51 mmol) while permanent shaking. After the reaction mixture was stored at room temperature for 3 days, all volatiles were removed in vacuo to give compound **9a** (830 mg, 82% isolated yield). **HRMS:** $M+H^+$ ($C_{34}H_{36}BF_{10}PH^+$): calc. 677.25634, found 677.25667. [*Comment:* since isomerization from **5a** to **9a** is extremely air sensitive, one should be very careful not to allow any contact with the air.]

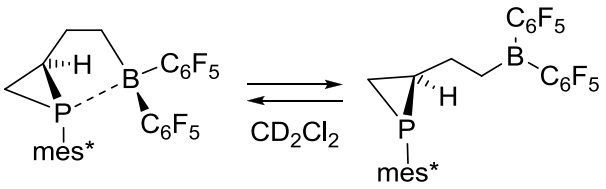


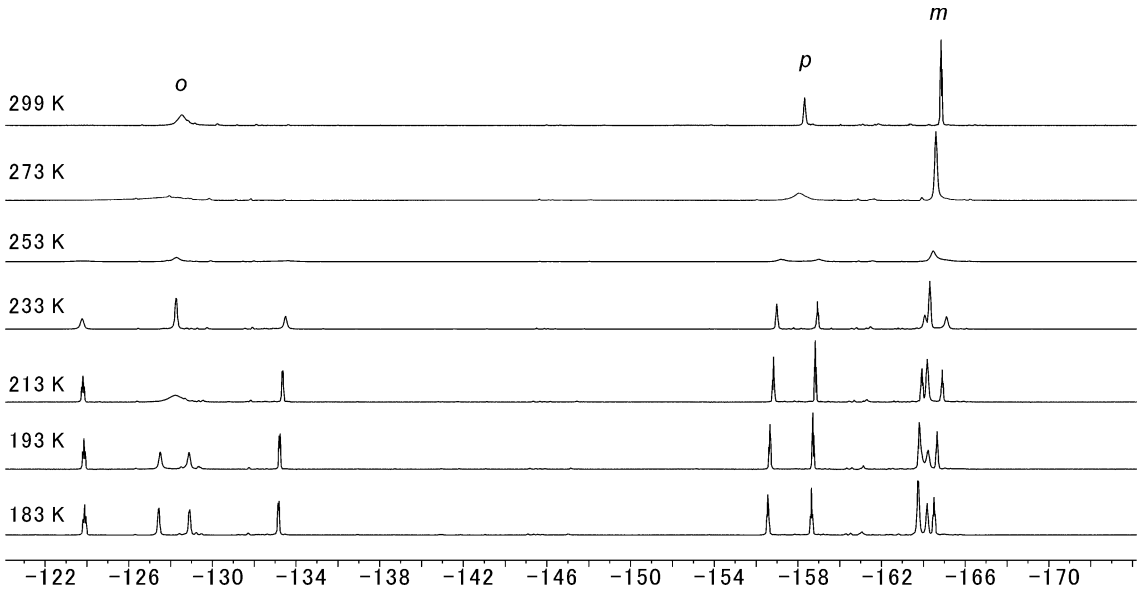
5a **9a**

(3) *Preparative scale (starting from **5a**):* Inside a glove box: **5a** (100 mg, 0.148 mmol) was dissolved in dichloromethane (15 mL) and kept for 3 days at room temperature to give compound **9a** (98 mg, 98%).

Elemental analysis: Calcd. for $C_{34}H_{36}BF_{10}P$: C, 60.37; H, 5.36. Found: C, 59.78; H, 5.41.

(b) Dynamic NMR Experiments.





^{19}F NMR (470 MHz, 299K to 183 K, dichloromethane-d_2) spectra of **9a**.

$\Delta G^{\ddagger} = RT_c(22.96 + \ln(T_c/\delta\nu))$

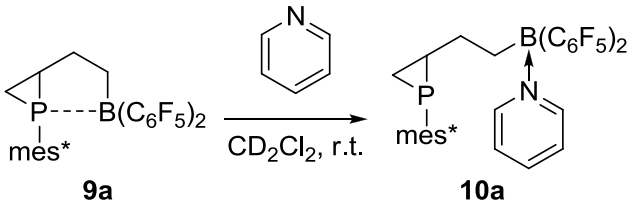
T_c = coalescence temperature [K]: 263 K (^{19}F, *p*-C_6F_5)

$\delta\nu$ = chemical shift difference [Hz] (^{19}F, *p*-C_6F_5, 183 K): 980 Hz

R = 8.314 J/(mol K); 1 J = 0.239 cal

$\Delta G^{\ddagger}$[263K, $\Delta\nu$(183K) = 980Hz] = 47328 J/mol = 11.3 ± 0.3 kcal mol^{-1}

Preparation of Pyridine Adduct 10a.



9a **10a**

Inside a glove box: pyridine (24.2 μL, 0.30 mmol) was added to a dichloromethane solution (2 mL) of **9a** (200 mg, 0.30 mmol) and the obtained reaction mixture was shaken for ca. 10 seconds. After crystallization of the reaction mixture from dichloromethane at −35°C by slow evaporation of the solvent, product **10a** was obtained as a crystalline solid (67.5 mg, 30% yield). The obtained crystals were suitable for the X-ray crystal structure analysis.

Elemental analysis: Calcd. for $C_{39}H_{41}BF_{10}NP$: C, 62.00; H, 5.47; N, 1.85. Found: C, 62.07; H, 5.53 N, 1.57.

HRMS: $M+H^+$ ($C_{39}H_{41}BF_{10}NPH^+$): calc. 756.29895, found 756.29672.

^{1}H NMR (500 MHz, 299 K, dichloromethane-d_2): δ = 8.65 (m, 2H, *o*-Py), 8.12 (m, 1H, *p*-Py), 7.66 (m, 2H, *m*-Py), 7.18 (br, *m*-mes*), 7.17 (br, *m'*-mes*), 1.67, 0.62 (each m, each 1H, CH_2), 1.58 (br, 9H, *o*-^{t}Bu), 1.54 (br, 9H, *o'*-^{t}Bu), 1.38, 1.32 (each m, each 1H, BCH_2)[a], 1.26 (m, 1H, PCH)[a,b], 1.26 (s, 9H, *p*-^{t}Bu), 0.98 (dd, $^2J_{PH}$ = 9.7 Hz, $^2J_{HH}$ = 6.8 Hz), 0.86 (dt, $^2J_{PH}$ = 19.7 Hz, $^2J_{HH} \sim {}^3J_{HH}$ = 6.8 Hz)(each 1H, PCH_2), [[a] from the ghsqc experiment; [b] from the tocsy experiment]

^{13}C{^{1}H} NMR (126 MHz, 299 K, dichloromethane-d_2): δ = 156.0 (br d, $^2J_{PC}$ = 4.0 Hz, *o'*-mes*), 155.8 (br d, $^2J_{PC}$ = 4.0 Hz, *o*-mes*), 148.0 (*p*-mes*), 146.2 (*o*-Py), 142.1 (*p*-Py), 138.9 (d, $^1J_{PC}$ = 58.1 Hz, *i*-mes*), 126.4 (*m*-Py), 122.8 (br, *m*-mes*), 122.4 (br, *m'*-mes*), 39.31 (*o'*-^{t}Bu^C), 39.25 (*o*-^{t}Bu^C), 34.7 (*p*-^{t}Bu^C), 34.0 (d, $^4J_{PC}$ = 8.4 Hz, *o*-^{t}Bu^{CH3}, *o'*-^{t}Bu^{CH3}), 32.5 (d, $^1J_{PC}$ = 39.0 Hz, PCH), 31.4 (*p*-^{t}Bu^{CH3}), 29.3 (d, $^2J_{PC}$ = 16.7 Hz, CH_2), 24.1 (br, BCH_2), 22.4 (d, $^1J_{PC}$ = 38.3 Hz, PCH_2), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (500 MHz/500 MHz, 299 K, dichloromethane-d_2) [selected traces]: δ^1H/ δ^1H: 8.65/8.12, 7.66 (*o*-Py/*p*-Py, *m*-Py), 1.67/1.38, 1.26, 0.98, 0.62 (CH_2/BCH_2, PCH, PCH_2, CH_2'), 1.26/0.98, 0.86, 0.62 (PCH/PCH_2, PCH_2', CH_2').

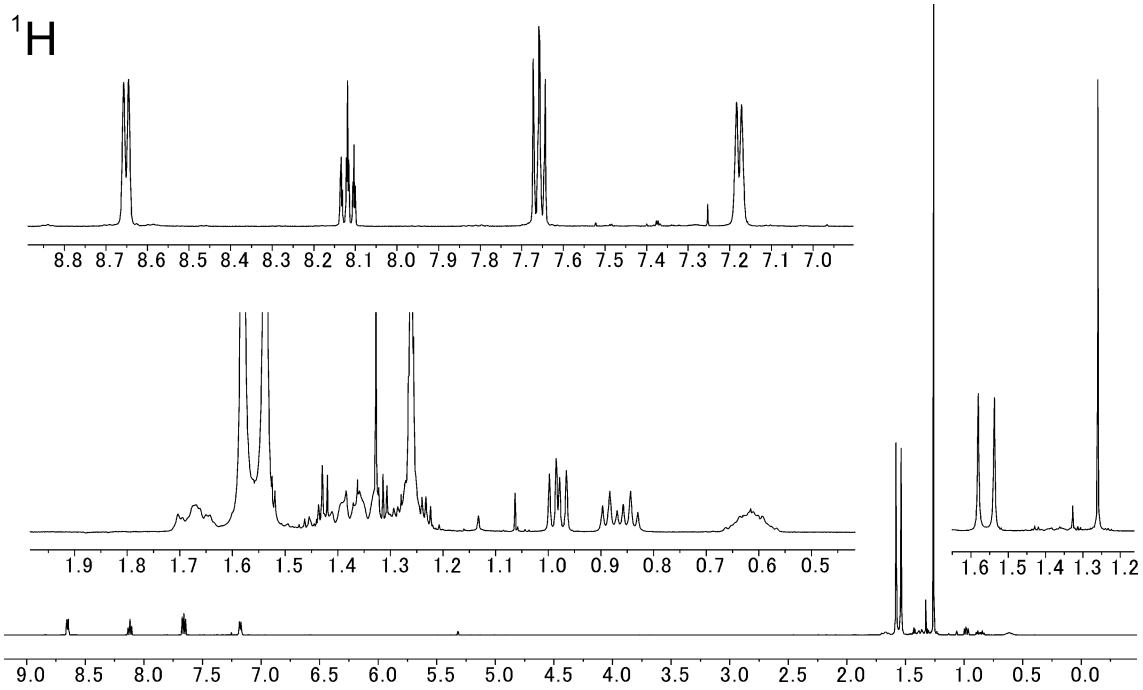
^{1}H,^{13}C GHSQC (500 MHz/126 MHz, 299 K, dichloromethane-d_2) [selected traces]: δ^{1}H/δ^{13}C: 8.65/146.2 (*o*-Py), 8.12/142.1 (*p*-Py), 7.66/126.4 (*m*-Py), 7.18/122.8 (*m*-mes*), 7.17/122.4 (*m'*-mes*), 1.67/29.3 (CH_2), 1.58/34.0 (*o*-^{t}Bu), 1.54/34.0 (*o'*-^{t}Bu), 1.38, 1.32/24.1 (BCH_2), 1.26/32.5 (PCH), 1.26/31.4 (*p*-^{t}Bu), 0.98/22.4 (PCH_2), 0.86/22.4 (PCH_2'), 0.62/29.5 (CH_2').

^{1}H,^{13}C GHMBC (500 MHz/126 MHz, 299 K, dichloromethane-d_2) [selected traces]: δ^{1}H/δ^{13}C: 7.18/138.9, 122.4, 39.25, 34.7 (*m*-mes*/*i*-mes*, *m'*-mes*, *o*-^{t}Bu^{C}, *p*-^{t}Bu^{C}), 7.17/138.9, 122.8, 39.31, 34.7 (*m'*-mes*/*i*-mes*, *m*-mes*, *o'*-^{t}Bu^{C}, *p*-^{t}Bu^{C}), 1.58/155.8, 39.31, 34.0 (*o*-^{t}Bu/*o*-mes*, *o*-^{t}Bu^{C} *o*-^{t}Bu^{CH3}), 1.54/156.0, 39.31, 34.0 (*o'*-^{t}Bu/*o'*-mes*, *o'*-^{t}Bu^{C}, *o'*-^{t}Bu^{CH3}), 1.26/148.0, 34.7, 31.4 (*p*-^{t}Bu/*p*-mes*, *p*-^{t}Bu^{C}, *p*-^{t}Bu^{CH3}), 0.98/138.9, 29.3 (PCH_2/*i*-mes*, CH_2), 0.86/138.9, 32.5, 29.3 (PCH_2'/*i*-mes*, PCH, CH_2).

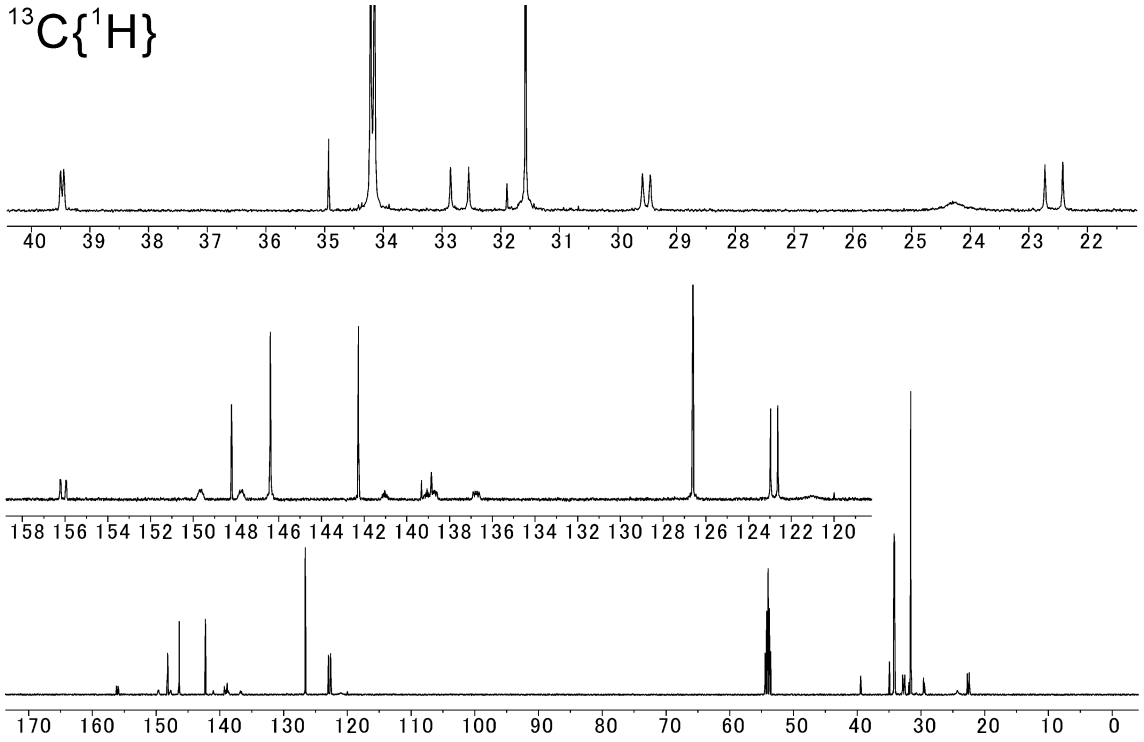
^{11}B{^{1}H} NMR (160 MHz, 299 K, dichloromethane-d_2): δ = –0.6 ($\nu_{1/2}$ ~ 350 Hz).

^{19}F NMR (470 MHz, 299 K, dichloromethane-d_2): δ = –132.2, –132.3 (each m, each 2F, *o*-C_6F_5), –159.1, –159.2 (each t, $^{3}J_{FF}$ = 20.3 Hz, each 1F, *p*-C_6F_5), –164.5, –164.6 (each m, each 2F, *m*-C_6F_5).

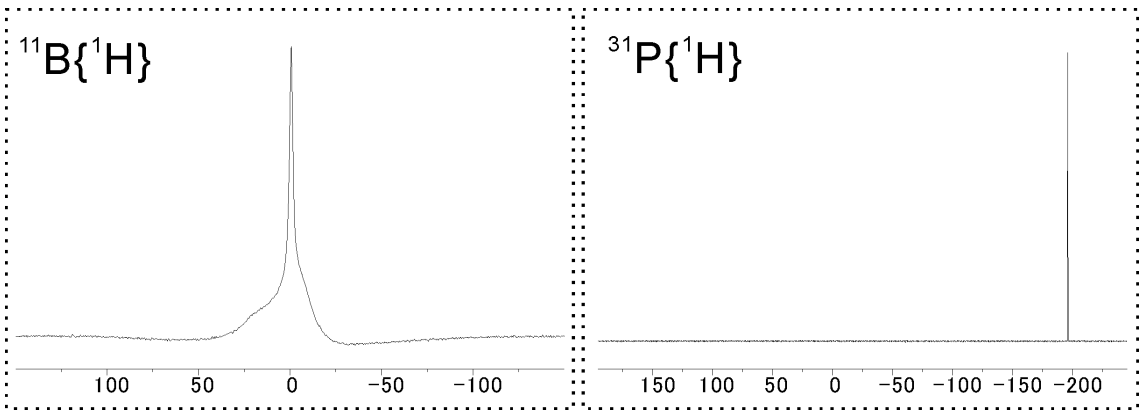
^{31}P{^{1}H} NMR (202 MHz, 299 K, dichloromethane-d_2): δ = –196.2 ($\nu_{1/2}$ ~ 5 Hz).



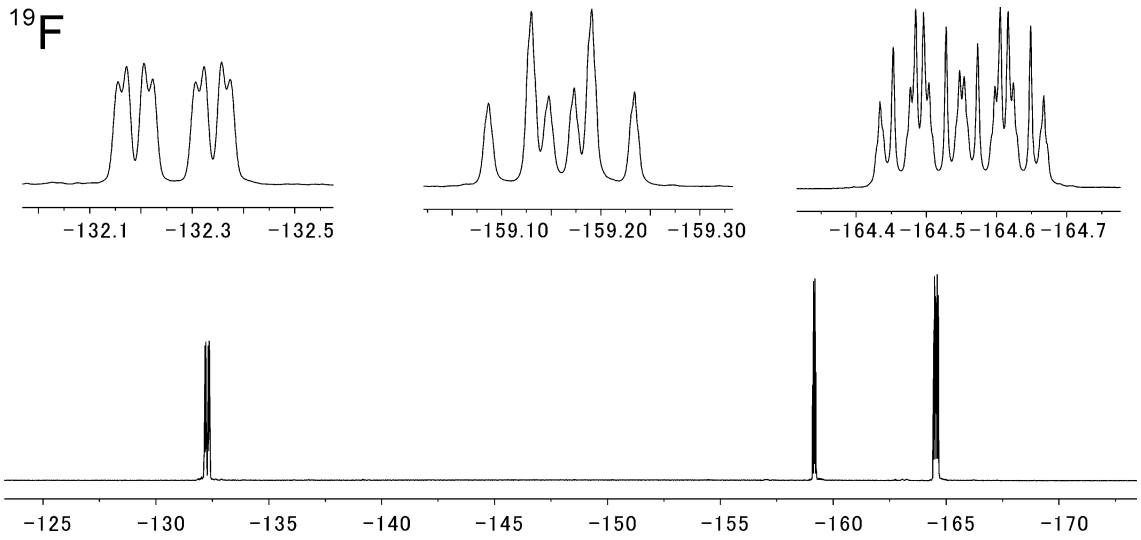
^{1}H NMR (500 MHz, 299 K, dichloromethane-d_2) spectrum of **10a**.



$^{13}C\{^1H\}$ NMR (126 MHz, 299 K, dichloromethane-d_2) spectrum of **10a**.

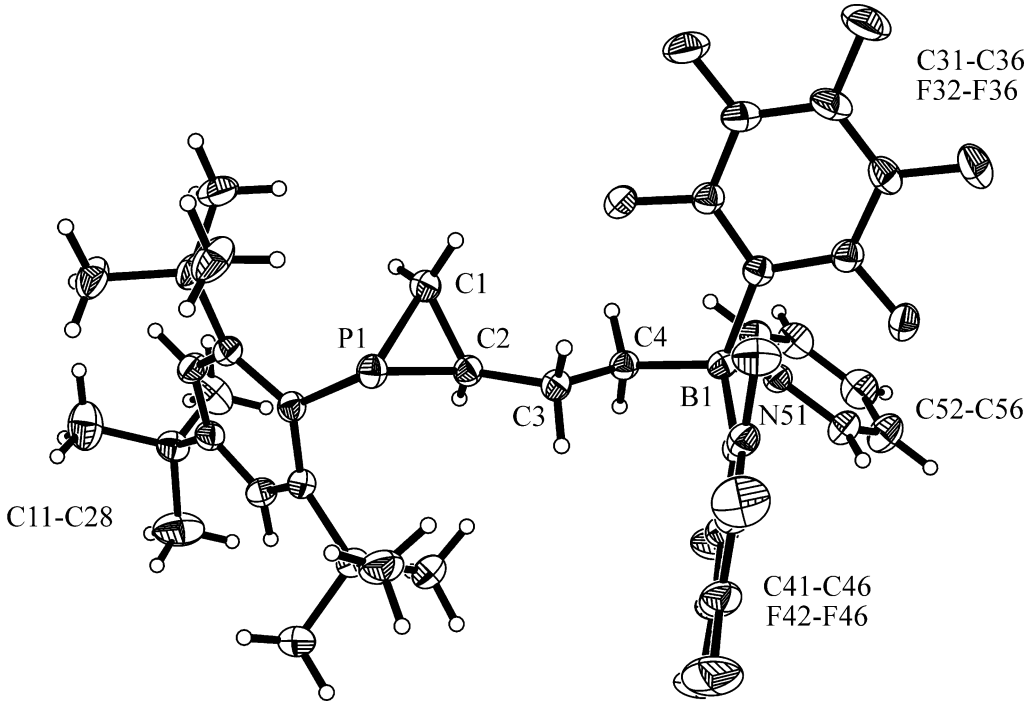


$^{11}B\{^1H\}$ NMR (160 MHz, 299 K, dichloromethane-d_2) and $^{31}P\{^1H\}$ NMR (202 MHz, 299 K, dichloromethane-d_2) spectra of **10a**.

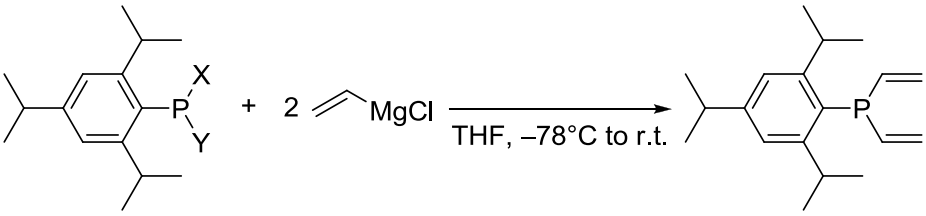


^{19}F NMR (470 MHz, 299 K, dichloromethane-d_2) of **10a**.

X-ray crystal structure analysis of compound **10a**: formula $C_{39}H_{41}BF_{10}NP$, M = 755.51 colourless crystal, 0.23 x 0.10 x 0.03 mm, a = 10.8542(5), b = 13.8552(5), c = 14.0717(10) Å, α = 102.350(2), β = 96.684(6), γ = 111.631(3)°, V = 1876.71(17) Å^3, ρ_{calc} = 1.337 gcm^{-3}, μ = 1.344 mm^{-1}, empirical absorption correction (0.747 ≤ T ≤ 0.960), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 26113 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 6459 independent (R_{int} = 0.047) and 5426 observed reflections [I>2σ(I)], 512 refined parameters, R = 0.045, wR^2 = 0.117, max. (min.) residual electron density 0.30 (-0.22) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Preparation of (2,4,6-triisopropylphenyl)divinylphosphane [tippP(CHCH$_2$)$_2$] 6b.



X, Y = Cl or Br **6b**

Under an argon atmosphere, tippPX$_2$ [tippPCl$_2$ 44%, tippPClBr 45%, tippPBr$_2$ 13% (^{31}P{^{1}H} NMR spectrum), 2.30 g, 6.8 mmol] was dissolved in diethylether (80 mL) and added dropwise to vinyl magnesium chloride (14.9 mL, 1.6 M THF solution: 23.8 mmol) and stirred vigorously at 0°C for 1 h and then at room temperature for 1.5 h. The volatiles were removed in vacuo. The obtained residue was transferred to an alumina gel column (MP Alumina, N, Act. III: 3 cm x 42 cm) for chromatography (eluent: ethyl acetate:*n*-pentane = 580 mL:14 mL). The solutions of the product (TLC [Silica gel 60 F_{254}]: Rf = 0.21: eluent: *n*-pentane) were collected in test tubes, combined and then dried in vacuo (1.60 g or 81% yield).

Comment: THF as solvent and vinyl magnesium bromide (0.7 M THF solution) could also be used in the reaction sequence.

HRMS: M+H$^+$ ($C_{19}H_{29}PH^+$): calc. 289.2080, found 289.2071.

^{1}H NMR (600 MHz, 299 K, benzene-d$_6$): δ = 7.16 (d, $^4J_{PH}$ = 2.5 Hz, 2H, *m*-tipp), 6.54 (td, $^2J_{PH}$ ~ $^3J_{HH}$ = 18.6 Hz, $^3J_{HH}$ = 12.2 Hz, 2H, =CH), 5.46 (ddd, $^3J_{PH}$ = 25.8 Hz, $^3J_{HH}$ = 12.2 Hz, $^2J_{HH}$ = 1.7 Hz, 2H, =CH$_2^E$), 5.36 (ddd, $^3J_{HH}$ = 18.6 Hz, $^3J_{PH}$ = 11.0 Hz, $^2J_{HH}$ = 1.7 Hz, 2H, =CH$_2^Z$), 3.99 (oct, $^3J_{HH}$ ~ $^4J_{PH}$ = 6.8 Hz, 2H, *o*-^{i}Pr^{CH}), 2.75 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, *p*-^{i}Pr^{CH}), 1.27 (d, $^3J_{HH}$ = 6.8 Hz, 12H, *o*-^{i}Pr^{CH3}), 1.19 (d, $^3J_{HH}$ = 6.8 Hz, 6H, *p*-^{i}Pr^{CH3}).

^{1}H NMR (500 MHz, 299 K, dichloromethane-d$_2$): δ = 7.04 (d, $^4J_{PH}$ = 2.5 Hz, 2H, *m*-tipp), 6.60 (ddd, $^3J_{HH}$ = 18.5 Hz, $^2J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 12.1 Hz, 2H, =CH), 5.65 (ddd, $^3J_{PH}$ = 26.8 Hz, $^3J_{HH}$ = 12.1 Hz, $^2J_{HH}$ = 1.7 Hz, 2H, =CH$_2^E$), 5.38 (ddd, $^3J_{HH}$ = 18.5 Hz, $^3J_{PH}$ = 11.4 Hz, $^2J_{HH}$ = 1.7 Hz, 2H, =CH$_2^Z$), 3.75 (oct, $^3J_{HH}$ ~ $^4J_{PH}$ = 6.7 Hz, 2H, *o*-^{i}Pr^{CH}), 2.87 (sept, $^3J_{HH}$ = 7.0 Hz, 1H, *p*-^{i}Pr^{CH}), 1.25 (d, $^3J_{HH}$ = 6.9 Hz, 6H, *p*-^{i}Pr^{CH3}), 1.17 (d, $^3J_{HH}$ = 6.8 Hz, 12H, *o*-^{i}Pr^{CH3}).

^{13}C{^{1}H} NMR (151 MHz, 299 K, benzene-d$_6$): δ = 156.1 (d, $^2J_{PC}$ = 14.0 Hz, *o*-tipp), 151.5 (d, $^4J_{PC}$ = 1.4 Hz, *p*-tipp), 138.2 (d, $^1J_{PC}$ = 16.9 Hz, =CH), 128.7 (d, $^1J_{PC}$ = 12.8 Hz, *i*-tipp), 122.60 (d, $^2J_{PC}$ = 17.6 Hz, =CH$_2$)^t, 122.57 (d, $^3J_{PC}$ = 4.7 Hz, *m*-tipp)^t, 34.7 (*p*-^{i}Pr^{CH}), 32.5 (d, $^3J_{PC}$ = 18.7 Hz, *o*-^{i}Pr^{CH}), 25.0 (d, $^4J_{PC}$ = 0.8 Hz, *o*-^{i}Pr^{CH3}), 24.0 (*p*-^{i}Pr^{CH3}), [^{t} tentatively assigned]

^{13}C{^{1}H} NMR (126 MHz, 299 K, dichloromethane-d$_2$): δ = 155.9 (d, $^2J_{PC}$ = 13.9 Hz, *o*-tipp), 151.5 (*p*-tipp), 138.3 (d, $^1J_{PC}$ = 15.8 Hz, =CH), 128.4 (d, $^1J_{PC}$ = 11.9 Hz, *i*-tipp), 123.1 (d, $^2J_{PC}$ = 18.4 Hz, =CH$_2$),

122.6 (d, $^{3}J_{PC}$ = 4.6 Hz, *m*-tipp), 34.7 (*p*-$^{i}Pr^{CH}$), 32.4 (d, $^{3}J_{PC}$ = 18.6 Hz, *o*-$^{i}Pr^{CH}$), 24.8 (d, $^{5}J_{PH}$ = 0.5 Hz, *o*-$^{i}Pr^{CH3}$), 23.9 (*p*-$^{i}Pr^{CH3}$).

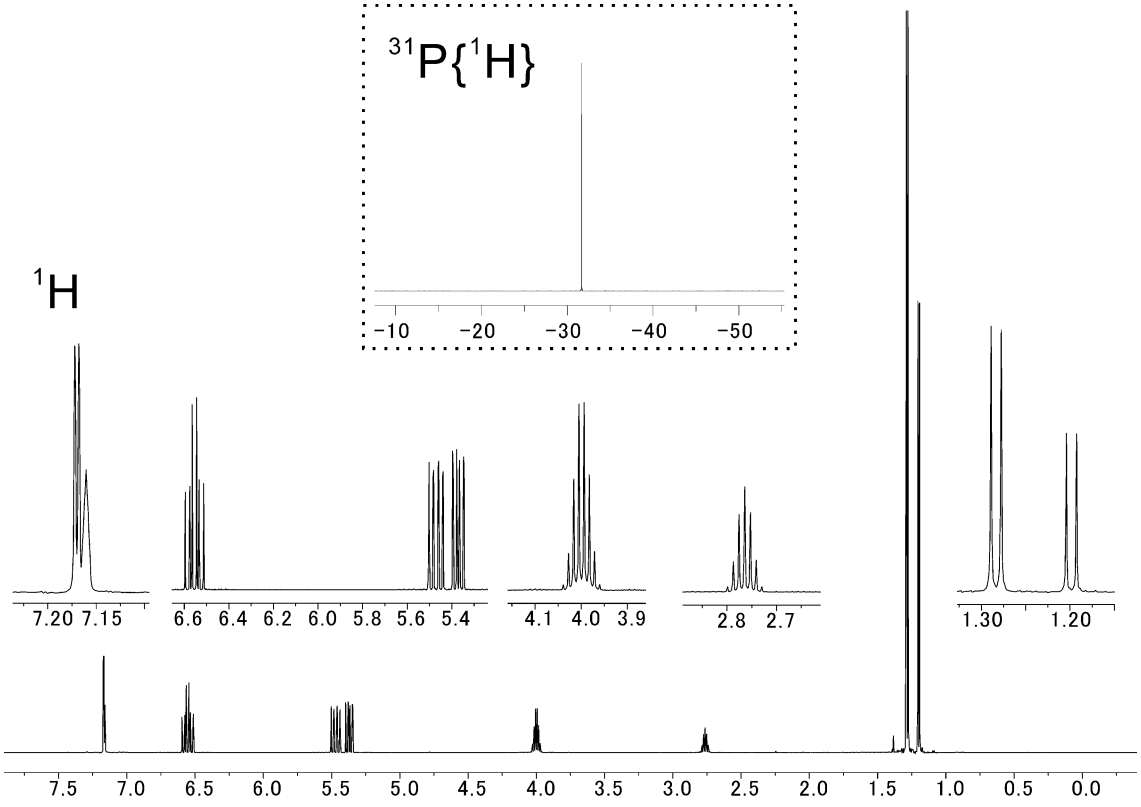
^{1}H,^{1}H GCOSY (600 MHz/600 MHz, 299 K, benzene-d_6) [selected traces]: δ^{1}H/ δ ^{1}H: 6.54/5.46, 5.36 (=CH/=CH_2^E, =CH_2^Z), 3.99/1.27 (*o*-$^{i}Pr^{CH}$/*o*-$^{i}Pr^{CH3}$), 2.75/1.19 (*p*-$^{i}Pr^{CH}$/*p*-$^{i}Pr^{CH3}$).

^{1}H,^{13}C GHSQC (600 MHz/151 MHz, 299 K, benzene-d_6) [selected traces]: δ^{1}H/δ^{13}C: 7.16/122.57 (*m*-tipp), 6.54/138.2 (=CH), 5.46/122.60 (=CH_2^E), 5.36/122.60 (=CH_2^Z), 3.99/32.5 (*o*-$^{i}Pr^{CH}$), 2.75/34.7 (*p*-$^{i}Pr^{CH}$), 1.27/25.0 (*o*-$^{i}Pr^{CH3}$), 1.19/24.0 (*p*-$^{i}Pr^{CH3}$).

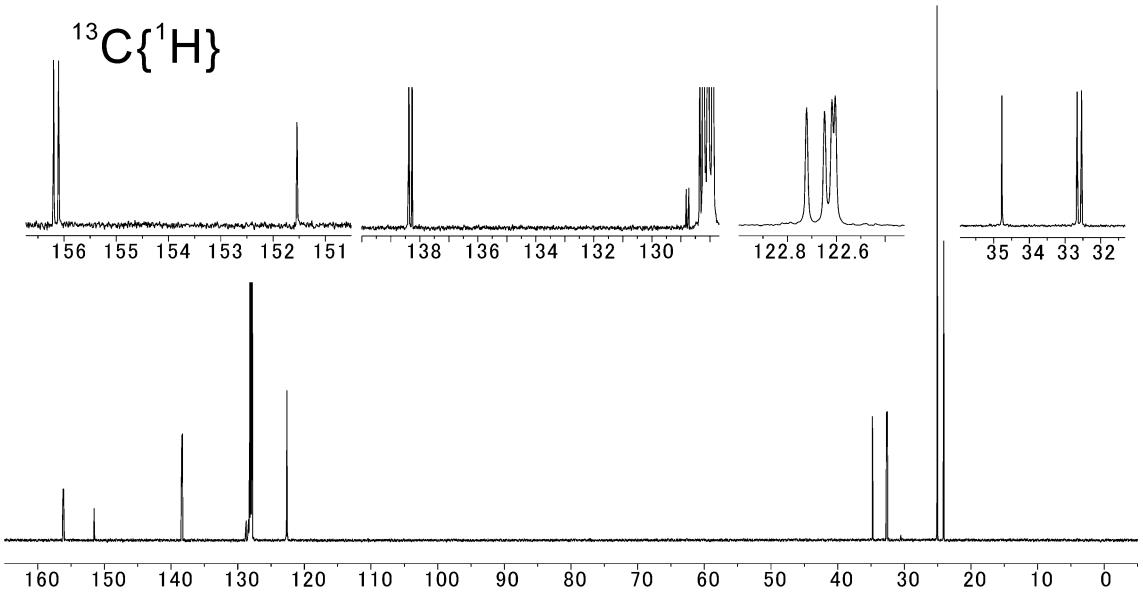
^{1}H,^{13}C GHMBC (600 MHz/151 MHz, 299 K, benzene-d_6) [selected traces]: δ^{1}H/δ^{13}C: 6.54/138.2, 128.7, 122.60 (=CH/=CH, *i*-tipp, =CH_2), 3.99/156.1, 128.7, 122.57, 25.0 (*o*-$^{i}Pr^{CH}$/*o*-tipp, *i*-tipp, *m*-tipp, *o*-$^{i}Pr^{CH3}$), 2.75/151.5, 122.57, 24.0 (*p*-$^{i}Pr^{CH}$/*p*-tipp, *m*-tipp, *p*-$^{i}Pr^{CH3}$).

^{31}P{^{1}H} NMR (243 MHz, 299 K, benzene-d_6): δ = –31.7 ($\nu_{1/2}$ ~ 1 Hz).

^{31}P{^{1}H} NMR (202 MHz, 299 K, dichloromethane-d_2): δ = –32.4 ($\nu_{1/2}$ ~ 2 Hz).



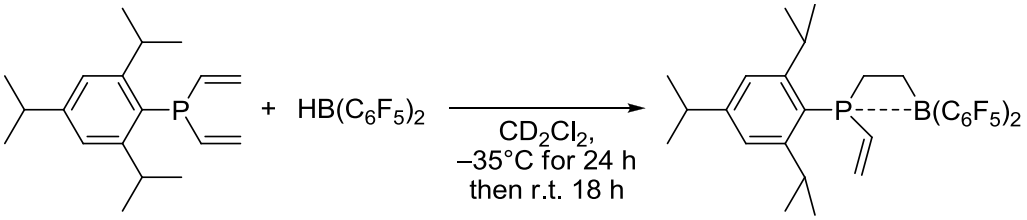
^{1}H NMR (600 MHz, 299 K, benzene-d_6) and ^{31}P{^{1}H} NMR (243 MHz, 299 K, benzene-d_6) spectra of **6b**.



$^{13}C\{^1H\}$ NMR (151 MHz, 299 K, benzene-d_6) of **6b**.

Preparation of P/B Frustrated *Leiws* Pair 4b.

(a) Preparation and NMR Data at Room Temperature.



6b **4b**

(1) *NMR scale:* Inside a glove box: a solution of bis(pentafluorophenyl)borane (28.8 mg, 0.083 mmol, 1.0 eq.) in dichloromethane-d_2 (0.5 mL) was added to a dichloromethane-d_2 solution (0.5 mL) of (2,4,6-triisopropylphenyl)divinylphosphane (**6b**) (23.0 mg, 0.080 mmol, 1.0 eq.). The reaction mixture was kept at –35°C for 24 h, kept at room temperature for 18 h and then transferred to an NMR tube. The reaction gave exclusively compound **4b** which appeared as a pale orange solution in dichloromethane-d_2.

^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2): δ = 7.10 (d, $^4J_{PH}$ = 3.2 Hz, 2H, *m*-tipp), 6.57 (ddd, $^2J_{PH}$ = 25.5 Hz, $^3J_{HH}$ = 18.1 Hz, $^3J_{HH}$ = 12.1 Hz, 1H, =CH), 6.03 (dd, $^3J_{PH}$ = 36.6 Hz, $^3J_{HH}$ = 12.1 Hz, 1H, $=CH_2^E$), 5.51 (ddd, $^3J_{PH}$ = 19.7 Hz, $^3J_{HH}$ = 18.1 Hz, $^2J_{HH}$ = 0.5 Hz, 1H, $=CH_2^Z$), 3.09, 2.70 (each m, each

1H, PCH_2), 3.04 (br m, 2H, *o*-$^{i}Pr^{CH}$), 2.90 (sept, $^{3}J_{HH}$ = 6.9 Hz, 1H, *p*-$^{i}Pr^{CH}$), 2.08 (dm, $^{3}J_{PH}$ = 62.1 Hz, 1H, BCH_2), 2.01 (m, 1H, BCH_2'), 1.25 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, *p*-$^{i}Pr^{CH3}$), 1.12 (br d, $^{3}J_{HH}$ = 6.7 Hz, 6H, *o*-$^{i}Pr^{CH3}$), 0.96 (br d, $^{3}J_{HH}$ = 6.6 Hz, 6H, *o*-$^{i}Pr^{CH3'}$).

$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, dichloromethane-d_2): δ = 154.6 (br d, $^{2}J_{PC}$ = 8.7 Hz, *o*-tipp), 153.9 (d, $^{4}J_{PC}$ = 2.1 Hz, *p*-tipp), 148.0 (dm, $^{1}J_{FC}$ ~ 242 Hz, *o*-C_6F_5), 139.0 (dm, $^{1}J_{FC}$ ~ 252 Hz, *p*-C_6F_5), 137.6 (dm, $^{1}J_{FC}$ ~ 247 Hz, *m*-C_6F_5), 131.9 (d, $^{2}J_{PC}$ = 3.4 Hz, $=CH_2$), 129.2 (d, $^{1}J_{PC}$ = 35.2 Hz, =CH), 123.5 (br d, $^{3}J_{PC}$ = 7.5 Hz, *m*-tipp), 120.6 (d, $^{1}J_{PC}$ = 22.8 Hz, *i*-tipp), 119.7 (br, *i*-C_6F_5), 34.6 (*p*-$^{i}Pr^{CH}$), 32.4 (br d, $^{3}J_{PC}$ = 8.7 Hz, *o*-$^{i}Pr^{CH}$), 28.6 (d, $^{1}J_{PC}$ = 40.1 Hz, PCH_2), 25.9 (br, *o*-$^{i}Pr^{CH3}$), 23.74 (br, *o*-$^{i}Pr^{CH3'}$), 23.70 (*p*-$^{i}Pr^{CH3}$), 18.6 (br, BCH_2).

$^{1}H,^{1}H$ GCOSY (600 MHz/600 MHz, 299 K, dichloromethane-d_2) [selected traces]: $\delta^{1}H$/ δ ^{1}H: 6.57/6.03, 5.51 (=CH/=CH_2^{E}, =CH_2^{Z}), 6.03/5.51 (=CH_2^{E}/=CH_2^{Z}), 3.09/2.70, 2.08 (PCH_2/PCH_2', BCH_2), 3.04/1.12, 0.96 (*o*-$^{i}Pr^{CH}$/*o*-$^{i}Pr^{CH3}$, *o*-$^{i}Pr^{CH3'}$), 2.90/1.25 (*p*-$^{i}Pr^{CH}$/*p*-$^{i}Pr^{CH3}$), 2.70/2.01 (PCH_2'/BCH_2').

$^{1}H\{^{1}H\}$ 1D NOESY (600 MHz, 299 K, dichloromethane-d_2) [selected experiments]: $\delta^{1}H_{irr}/\delta^{1}H_{res}$: 6.57/6.03 (=CH/=$CH_2^{E}$), 6.03/6.57, 5.51 (=$CH_2^{E}$ /=CH, =CH_2^{Z}), 5.51/6.03 (=CH_2^{Z}/=CH_2^{E}).

$^{1}H,^{13}C$ GHSQC (600 MHz/151 MHz, 299 K, dichloromethane-d_2) [selected traces]: $\delta^{1}H/\delta^{13}C$: 7.10/123.5 (*m*-tipp), 6.57/129.2 (=CH), 6.03/131.9 (=CH_2^{E}), 5.51/131.9 (=CH_2^{Z}), 3.09/28.6 (PCH_2), 3.04/32.4 (*o*-$^{i}Pr^{CH}$), 2.90/34.6 (*p*-$^{i}Pr^{CH}$), 2.70/28.6 (PCH_2'), 2.08, 2.01/18.6 (BCH_2), 1.25/23.70 (*p*-$^{i}Pr^{CH3}$), 1.12/25.9 (*o*-$^{i}Pr^{CH3}$), 0.96/23.74 (*o*-$^{i}Pr^{CH3'}$).

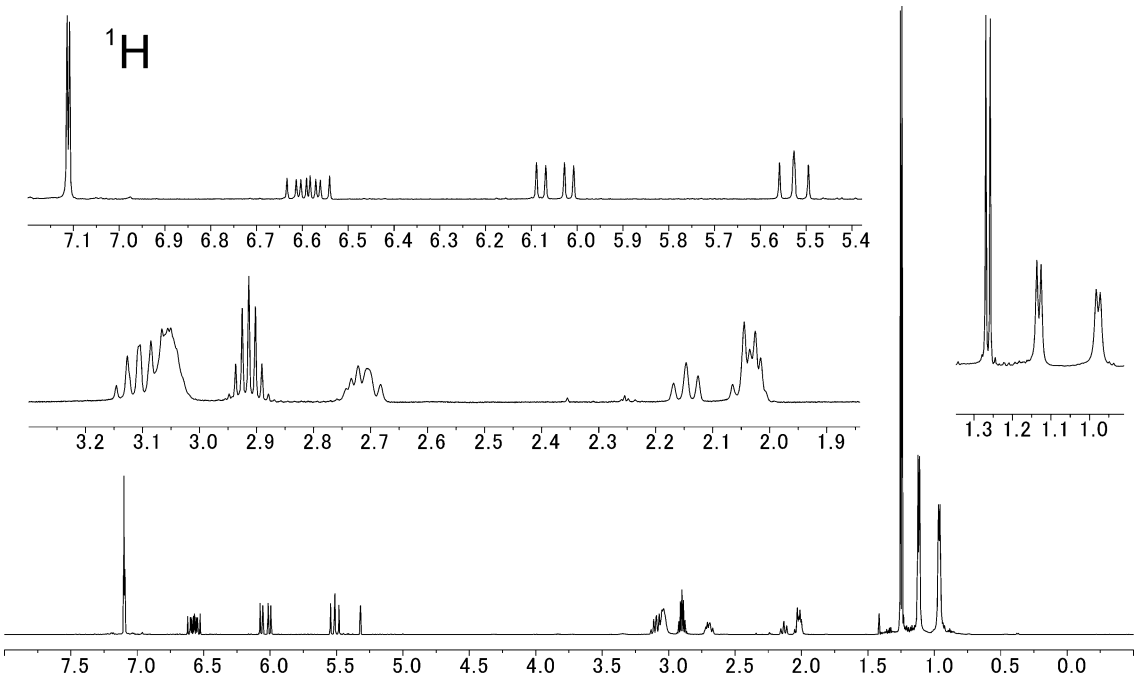
$^{1}H,^{13}C$ GHMBC (600 MHz/151 MHz, 299 K, dichloromethane-d_2) [selected traces]: $\delta^{1}H/\delta^{13}C$: 6.57/131.9, 120.6 (=CH/=CH_2, *i*-tipp), 3.09/129.2, 18.6 (PCH_2/=CH, BCH_2), 2.90/153.9, 123.5, 23.70 (*p*-$^{i}Pr^{CH}$/*p*-tipp, *m*-tipp, *p*-$^{i}Pr^{CH3}$), 1.25/153.9, 34.6, 1.12/154.6, 32.4, 23.74 (*o*-$^{i}Pr^{CH3}$/*o*-tipp, *o*-$^{i}Pr^{CH}$, *o*-$^{i}Pr^{CH3'}$).

$^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, dichloromethane-d_2): δ = 0.7 ($\nu_{1/2}$ ~ 250 Hz).

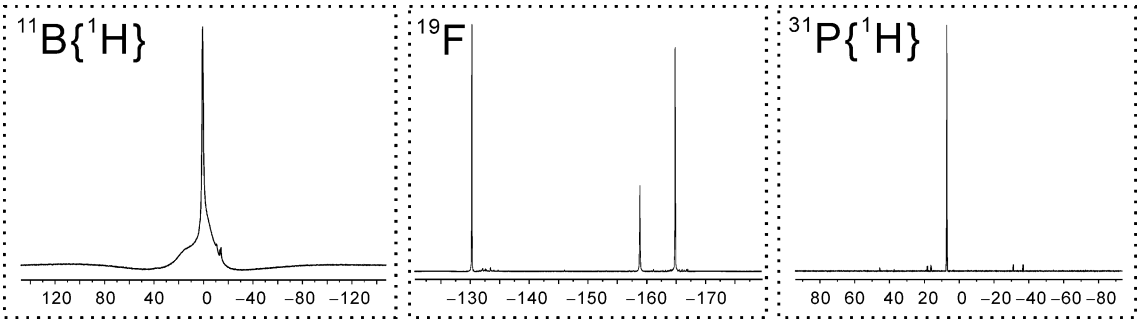
^{19}F NMR (564 MHz, 299 K, dichloromethane-d_2): δ = –130.2 (m, 2F, *o*-C_6F_5), –158.8 (br, 1F, *p*-C_6F_5), –164.8 (br, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{pm}$ = 5.9].

$^{19}F,^{19}F$ GCOSY (564 MHz/564 MHz, 299 K, dichloromethane--d_2) [selected traces]: –130.2/–164.8 (*o*-tipp/*m*-tipp), –158.8/–164.8 (*p*-C_6F_5/*m*-C_6F_5).

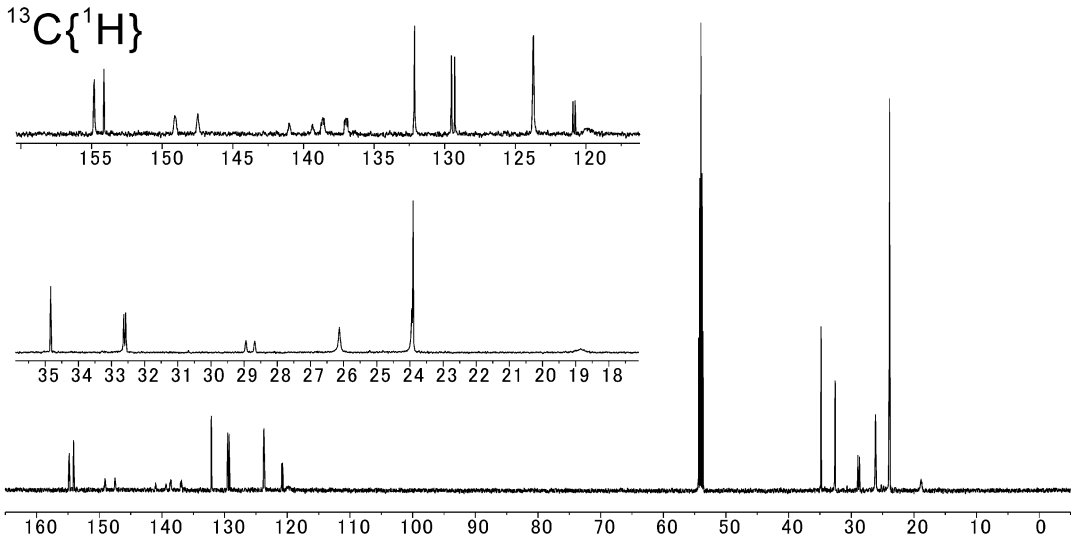
$^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, dichloromethane-d_2): δ = 7.1 ($\nu_{1/2}$ ~ 50 Hz).



^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2) spectrum of **4b**.



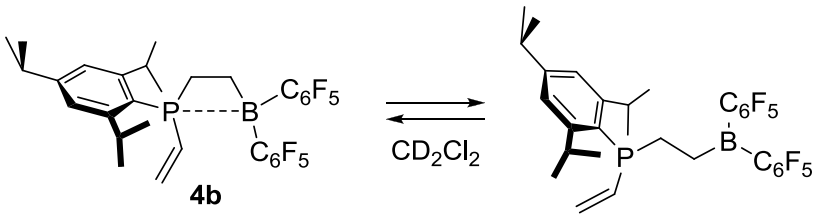
^{11}B{^{1}H} NMR (192 MHz, 299 K, dichloromethane-d_2), ^{19}F NMR (564 MHz, 299 K, dichloromethane-d_2) and ^{31}P{^{1}H} NMR (243 MHz, 299 K, dichloromethane-d_2) spectra of **4b**.

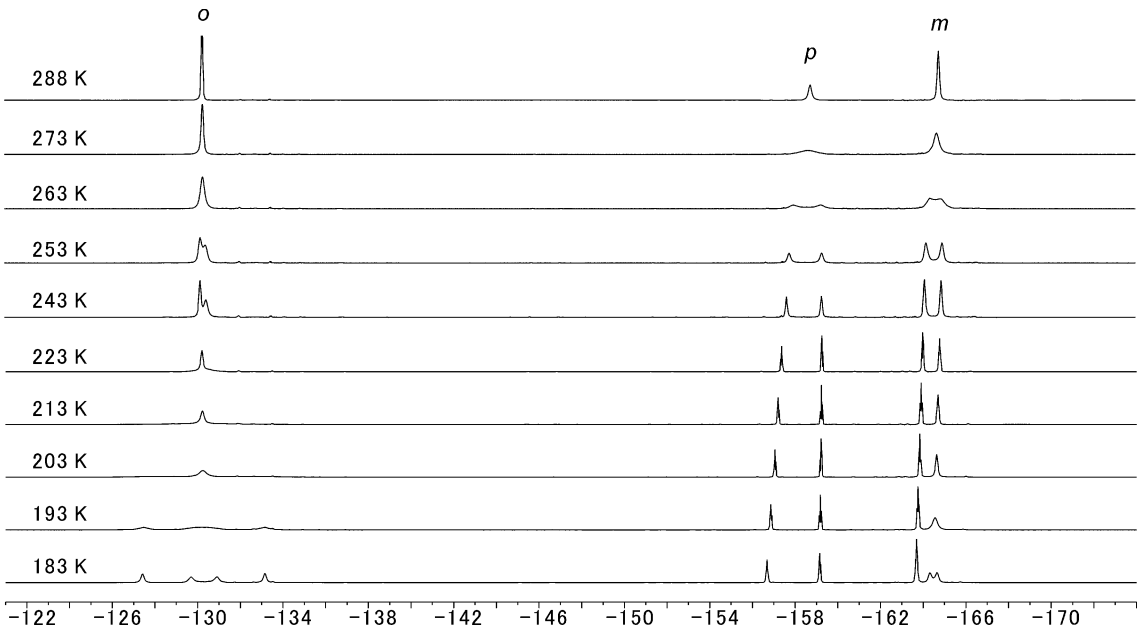


$^{13}C\{^1H\}$ NMR (151 MHz, 299 K, dichloromethane-d_2) spectrum of **3a**.

(2) *Preparative scale:* A solution of bis(pentafluorophenyl)borane (136.6 mg, 0.395 mmol, 1.0 eq.) in dichloromethane (1.5 mL) was added using a cannula to a dichloromethane solution (1.5 mL) of **6b** (111.1 mg, 0.385 mmol) under an argon atmosphere. The reaction mixture was stirred at –35°C for 1 h and then gradually raised to room temperature over a time period of 3 h. After keeping at room temperature for 1 day, the solvent was removed in vacuo (0.1 mbar) at room temperature to give a compound **4b** (237 mg, 97% yield). **HRMS:** $M+H^+$ ($C_{31}H_{30}BF_{10}PH^+$): calc. 635.20967, found 635.20978.

(b) Dynamic NMR Experiments:





^{19}F NMR (470 MHz, 288K to 183 K, dichloromethane-d_2) spectra of **4b**.

$\Delta G^{\ddagger} = RT_c(22.96 + \ln(T_c/\delta\nu))$

T_c = coalescence temperature [K]: 268 K (^{19}F, *p*-C_6F_5)

$\delta\nu$ = chemical shift difference [Hz] (^{19}F, *p*-C_6F_5, 183 K): 1160 Hz

R = 8.314 J/(mol K); 1 J = 0.239 cal

$\Delta G^{\ddagger}$[268K, $\Delta\nu$(183k) = 1160Hz] = 47894 J/mol = 11.4 ± 0.3 kcal/mol

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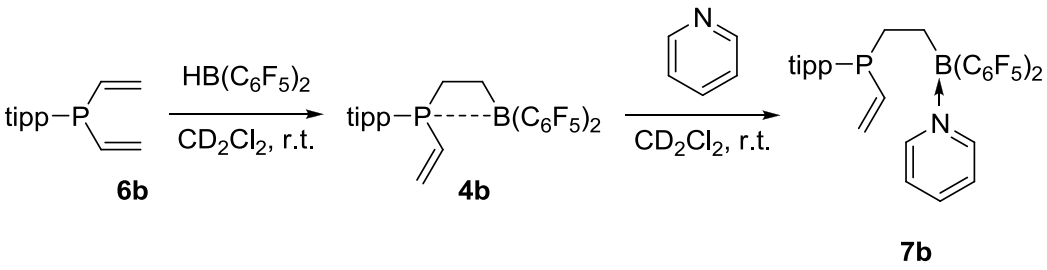
(c) NMR Data at −90°C.

^{1}H NMR (500 MHz, 183 K, dichloromethane-d_2): δ = 7.06 (s, 1H, *m*-tipp), 6.97 (d, $^4J_{PH}$ = 3.6 Hz, 1H, *m*'-tipp), 6.50 (ddd, $^2J_{PH}$ = 27.2 Hz, $^3J_{HH}$ = 18.2 Hz, $^3J_{HH}$ = 12.2 Hz, 1H, =CH), 6.01 (dd, $^3J_{PH}$ = 37.2 Hz, $^3J_{HH}$ = 12.2 Hz, 1H, =CH_2^E), 5.49 (dd, $^3J_{PH}$ = 20.1 Hz, $^3J_{HH}$ = 18.2 Hz, 1H, =CH_2^Z), 3.09 (m, 1H, *o*-^{i}Pr^{CH}), 3.01, 2.62 (each m, each 1H, PCH_2), 2.79 (sept, $^3J_{HH}$ = 7.0 Hz, 1H, *p*-^{i}Pr^{CH}), 2.76 (m, 1H, *o*'-^{i}Pr^{CH}), 2.10 (dm, $^3J_{PH}$ = 69.9 Hz), 1.71 (m)(each 1H, BCH_2), 1.13 (d, $^3J_{HH}$ = 7.0 Hz, 6H, *p*-^{i}Pr^{CH3}), 1.11 (d, $^3J_{HH}$ = 8.7 Hz, 3H, *o*'-^{i}Pr^{CH3}), 1.00 (d, $^3J_{HH}$ = 6.0 Hz, 3H, *o*'-^{i}Pr$^{CH3'}$)^t, 0.94 (d, $^3J_{HH}$ = 5.1 Hz, 3H, *o*-^{i}Pr^{CH3}), 0.60 (d, $^3J_{HH}$ = 5.9 Hz, 3H, *o*-^{i}Pr$^{CH3'}$), [^{t} tentatively assigned].

^{19}F NMR (470 MHz, 183 K, dichloromethane-d_2): δ = −127.4, −129.7, −130.9, −133.1 (each br, each 1F, *o*-C_6F_5), −156.7, −159.2 (each t, $^3J_{FF}$ = 21.2 Hz, $^3J_{FF}$ = 21.3 Hz, each 1F, *p*-C_6F_5), −163.7 (2F), −164.3 (1F), −164.7 (1F) (each br, *m*-C_6F_5).

^{31}P{^{1}H} NMR (202 MHz, 183 K, dichloromethane-d_2): δ = 6.7 ($\nu_{1/2}$ ~ 140 Hz).

Preparation of Pyridine Adduct 7b.



6b **4b** **7b**

(1) *NMR Scale*: NMR-scale: Inside a glove box: a dichloromethane-d_2 solution (0.3 mL) of bis(pentafluorophenyl)borane (25 mg, 0.071 mmol) was added to a dichloromethane-d_2 solution (0.3 mL) of **6b** (20 mL, 0.069 mmol). The reaction mixture was left at room temperature for 15 h. After the formation of **4b**, pyridine (5.6 μL, 0.069 mmol) was added. The reaction solution turned immediately from pale orange to pale yellow and gave the pyridine adduct **7b**. After removal of all volatiles compound **7b** was obtained as a white solid (45.8 mg, 93%).

HRMS: $M+H^+$ ($C_{36}H_{35}BF_{10}NPH^+$): calc. 714.25195, found 714.24972.

^{1}H NMR (500 MHz, 299 K, dichloromethane-d_2): δ = 8.67 (m, 2H, *o*-Py), 8.12 (m, 1H, *p*-Py), 7.65 (m, 2H, *m*-Py), 6.99 (d, $^4J_{PH}$ = 2.1 Hz, 2H, *m*-tipp), 6.62 (td, $^2J_{PH} \sim {}^3J_{HH}$ = 18.7 Hz, $^3J_{HH}$ = 12.4 Hz, 1H, =CH), 5.51 (ddd, $^2J_{PH}$ = 22.0 Hz, $^3J_{HH}$ = 12.4 Hz, $^2J_{HH}$ = 1.9 Hz, 1H, $=CH_2^E$), 5.19 (ddd, $^3J_{HH}$ = 18.7 Hz, $^3J_{PH}$ = 9.0 Hz, $^2J_{HH}$ = 1.9 Hz, 1H, $=CH_2^Z$), 3.78 (m, 2H, *o*-^{i}Pr^{CH}), 2.85 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, *p*-^{i}Pr^{CH}), 1.77, 1.41 (each m, each 1H, PCH_2), 1.68, 1.52 (each m, each 1H, BCH_2), 1.23 (d, $^3J_{HH}$ = 6.9 Hz, 6H, *p*-^{i}Pr^{CH3}), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 6H, *o*-^{i}Pr^{CH3}), 1.06 (d, $^3J_{HH}$ = 6.8 Hz, 6H, *o*-^{i}Pr$^{CH3'}$).

^{13}C{^{1}H} NMR (126 MHz, 299 K, dichloromethane-d_2): δ = 155.9 (d, $^2J_{PC}$ = 12.9 Hz, *o*-tipp), 150.8 (d, $^4J_{PH}$ = 1.4 Hz, *p*-tipp), 146.2 (*o*-Py), 142.2 (*p*-Py), 140.5 (d, $^1J_{PC}$ = 21.0 Hz, =CH), 130.0 (d, $^1J_{PC}$ = 18.2 Hz, *i*-tipp), 126.6 (*m*-Py), 122.4 (d, $^3J_{PC}$ = 4.0 Hz, *m*-tipp), 120.6 (d, $^2J_{PC}$ = 14.6 Hz, $=CH_2$), 34.6 (*p*-^{i}Pr^{CH}), 32.0 (d, $^3J_{PC}$ = 19.3 Hz, *o*-^{i}Pr^{CH}) , 25.0 (*o*-^{i}Pr$^{CH3'}$), 24.4 (*o*-^{i}Pr^{CH3}), 24.4 (d, $^1J_{PC}$ = 12.9 Hz, PCH_2), 24.0 (*p*-^{i}Pr^{CH3}), 23.9 (*p*-^{i}Pr$^{CH3'}$), 21.6 (br, BCH_2), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (500 MHz/500 MHz, 299 K, dichloromethane-d_2) [selected traces]: δ^1H/ δ^1H: 8.67/8.12, 7.65 (*o*-Py/*p*-Py, *m*-Py), 6.62/5.51, 5.19 (=CH/$=CH_2^E$, $=CH_2^Z$), 3.78/1.16, 1.06 (*o*-^{i}Pr^{CH}/*o*-^{i}Pr^{CH3}, *o*-^{i}Pr$^{CH3'}$), 2.85/1.23 (*p*-^{i}Pr^{CH}/*p*-^{i}Pr^{CH3}), 1.77/1.68 (PCH_2/BCH_2), 1.52/1.41 (BCH_2'/PCH_2').

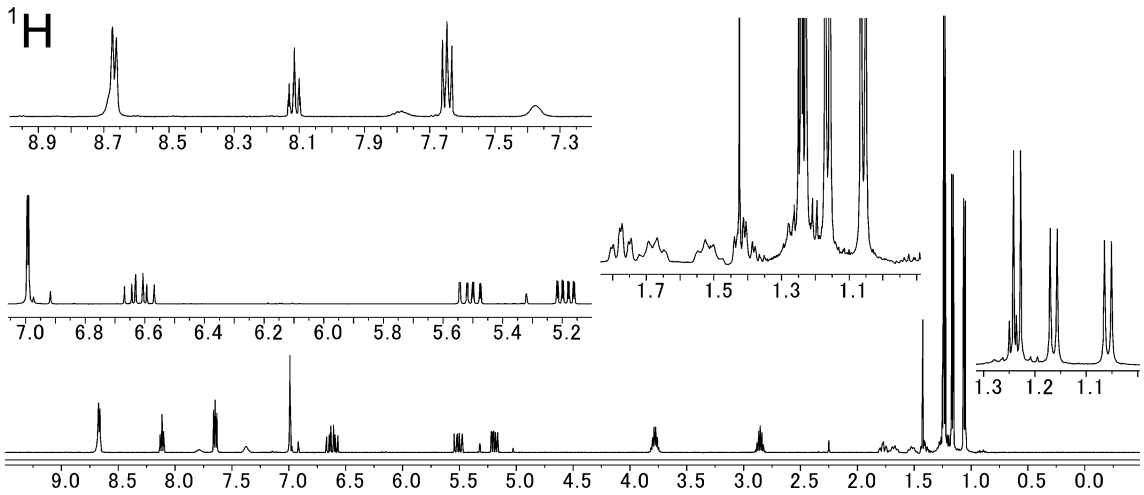
^{1}H,^{13}C GHSQC (500 MHz/126 MHz, 299 K, dichloromethane-d_2) [selected traces]: δ^1H/δ^{13}C: 8.67/146.2 (*o*-Py), 8.12/142.2 (*p*-Py), 7.65/126.6 (*m*-Py), 6.99/122.4 (*m*-tipp), 6.62/140.5 (=CH), 5.51/120.6 ($=CH_2^E$), 5.19/120.6 ($=CH_2^Z$), 3.78/32.0 (*o*-^{i}Pr^{CH}), 2.85/34.6 (*p*-^{i}Pr^{CH}), 1.77/24.4 (PCH_2), 1.68/21.6 (BCH_2), 1.52/21.6 (BCH_2'), 1.41/24.4 (PCH_2'), 1.23/24.0, 23.9 (*p*-^{i}Pr^{CH3}), 1.16/24.4 (*o*-^{i}Pr^{CH3}), 1.06/25.0 (*o*-^{i}Pr$^{CH3'}$).

^{1}H,^{13}C GHMBC (500 MHz/126 MHz, 299 K, dichloromethane-d_2) [selected traces]: δ^{1}H/δ^{13}C: 6.99/130.0, 122.4, 34.6, 32.0 (*m*-tipp/*i*-tipp , *m*-tipp, *p*-^{i}Pr^{CH}, *o*-^{i}Pr^{CH}), 6.62/130.0, 120.6, 24.4 (=CH/*i*-tipp, =CH_2, PCH_2), 2.85/150.8, 122.4, 24.0, 23.9 (*p*-^{i}Pr^{CH}/*p*-tipp, *m*-tipp, *p*-^{i}Pr^{CH3}, *p*-^{i}Pr$^{CH3'}$), 1.16/155.9, 32.0, 25.0 (*o*-^{i}Pr^{CH3}/*o*-tipp, *o*-^{i}Pr^{CH}, *o*-^{i}Pr$^{CH3'}$).

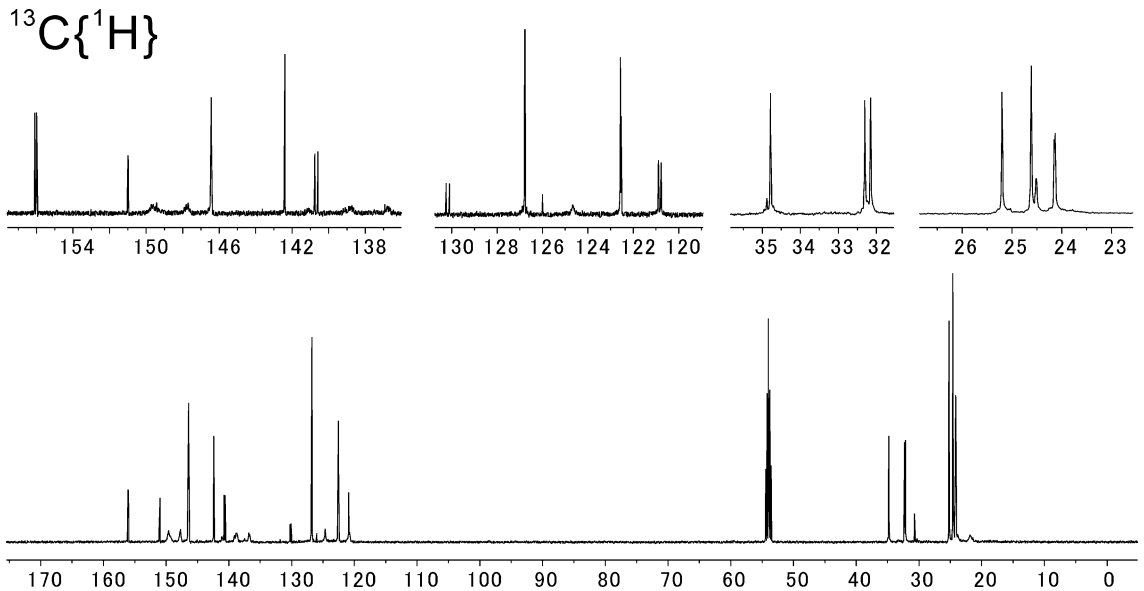
^{11}B{^{1}H} NMR (160 MHz, 299 K, dichloromethane-d_2): δ = –0.6 ($\nu_{1/2}$ ~ 250 Hz).

^{19}F NMR (470 MHz, 299 K, dichloromethane-d_2): δ = –132.0 (m, each 2F, *o*-$C_6F_5^{a}$), –132.2 (m, each 2F, *o*-$C_6F_5^{b}$), –159.0 (t, $^{3}J_{FF}$ = 20.3 Hz, 1F, *p*-$C_6F_5^{a}$), –159.1 (t, $^{3}J_{FF}$ = 20.3 Hz, 1F, *p*-$C_6F_5^{b}$), –164.3 (m, 2F, *m*-$C_6F_5^{a}$), –164.4 (m, 2F, *m*-$C_6F_5^{b}$), [$\Delta\delta^{19}F_{pm}$ = 5.3, 5.3].

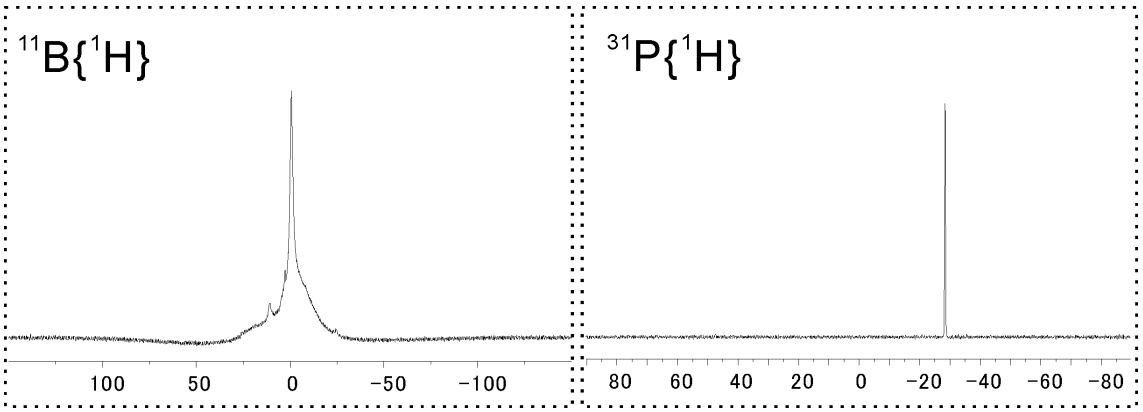
^{31}P{^{1}H} NMR (202 MHz, 299 K, dichloromethane-d_2): δ = –28.4 ($\nu_{1/2}$ ~ 10 Hz).



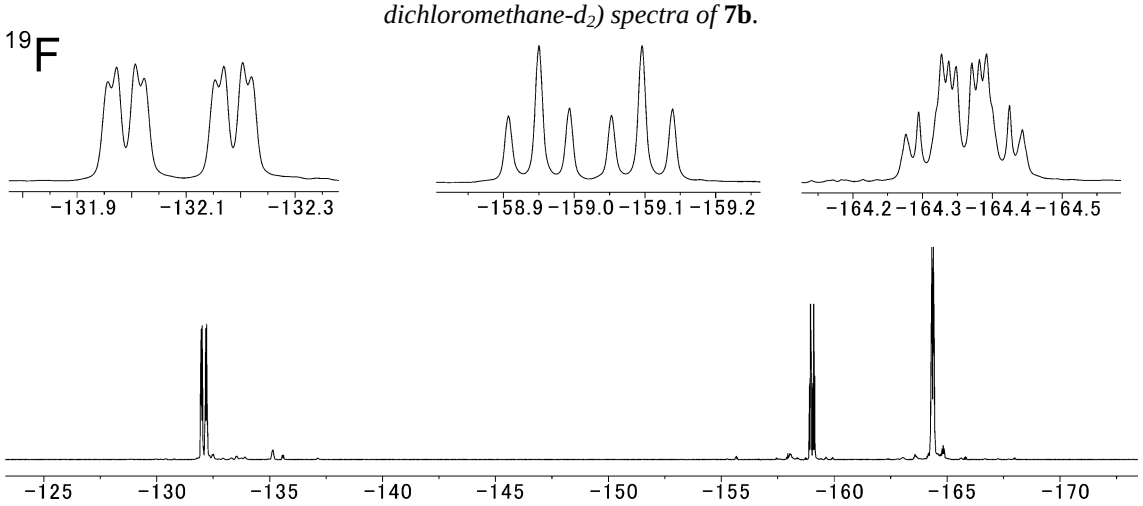
^{1}H NMR (500 MHz, 299 K, dichloromethane-d_2) spectrum of **7b**.



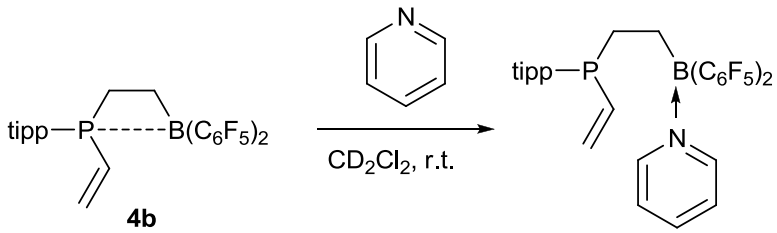
^{13} C{^{1}H} NMR (126 MHz, 299 K, dichloromethane-d_2) spectrum of **7b**.



$^{11}B\{^1H\}$ NMR (160 MHz, 299 K, dichloromethane-d_2), and $^{31}P\{^1H\}$ NMR (202 MHz, 299 K, dichloromethane-d_2) spectra of **7b**.

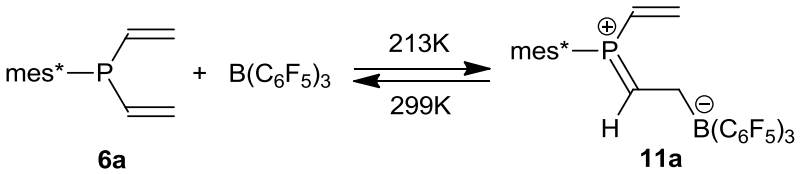


^{19}F NMR (470 MHz, 299 K, dichloromethane-d_2) of **7b**.



(2) *Preparative Scale*: Compound **4b** (150 mg, 0.236 mmol) was dissolved in dichloromethane (1 mL) and then pyridine was added. The reaction solution was left at room temperature for ca. 10 min and then the solvent was removed in vacuo to give compound **7b** (135 mg, 80%).

Preparation of compound 11a.



6a **11a**

(1) *NMR scale:* A solution of tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] (29.1 mg, 0.057 mmol) in dichloromethane-d_2 (0.6 mL) was added to **6a** [17.1 mg, 0.51 mmol; *comment:* **6a** was admixed with $^tBu_3C_6H_3$ (3%)] at rt. Then the reaction mixture was characterized by NMR experiments at 213K: product **11a** was admixed with $B(C_6F_5)_3$ [13 mol%[1], ^{19}F (213K)], a PH-species [2%[1], ^{31}P (213K), not identified yet], and $^tBu_3C_6H_3$ [5%[1], ^1H (213K)] [[1] relative to **11a**].

^1H NMR (600 MHz, 213 K, dichloromethane-d_2): δ = 7.68 (t, $^3J_{HH}$ = 10.3 Hz, 1H, P=CH), 7.61 (d, $^4J_{PH}$ = 5.4 Hz, 2H, *m*-mes*), 7.26 (m, 1H, =CH), 6.48 (dd, $^3J_{PH}$ = 64.2 Hz, $^3J_{HH}$ = 12.3 Hz, 1H, $=CH_2^E$), 5.64 (dd, $^3J_{PH}$ = 34.0 Hz, $^3J_{HH}$ = 18.2 Hz, 1H, $=CH_2^Z$), 3.24 (br d, $^3J_{PH}$ = 46.4 Hz, 2H, BCH_2), 1.30 (s, 18H, *o*-^{t}Bu), 1.26 (s, 9H, *p*-^{t}Bu).

^1H{sel-^{31}P: δ 126.6} NMR (600 MHz, 213 K, dichloromethane-d_2): δ = 7.68 (t, $^3J_{HH}$ = 10.3 Hz, 1H, P=CH), 7.61 (s, 2H, *m*-mes*), 7.26 (dd, $^3J_{HH}$ = 18.1 Hz, $^3J_{HH}$ = 12.3 Hz, 1H, =CH), 6.48 (d, $^3J_{HH}$ = 12.3 Hz, 1H, $=CH_2^E$), 5.64 (d, $^3J_{HH}$ = 18.2 Hz, 1H, $=CH_2^Z$), 3.24 (br m, 2H, BCH_2). 1.30 (s, 18H, *o*-^{t}Bu), 1.26 (s, 9H, *p*-^{t}Bu).

$^{13}C\{^1H\}$ NMR (151 MHz, 213 K, dichloromethane-d_2): δ = 165.3 (d, $^1J_{PC}$ = 113.8 Hz, P=CH), 158.4 (*p*-mes*)^t, 158.3 (d, $^2J_{PC}$ = 7.9 Hz, *o*-mes*)^t, 138.5 (br d, $^2J_{PC}$ = 3.6 Hz, $=CH_2$), 124.4 (d, $^3J_{PC}$ = 14.0 Hz, *m*-mes*), 122.1 (d, $^1J_{PC}$ = 88.2 Hz, =CH), 105.3 (d, $^1J_{PC}$ = 82.5 Hz, *i*-mes*), 38.3 (d, $^3J_{PC}$ = 2.4 Hz, *o*-^{t}Bu^C), 35.5 (*p*-^{t}Bu^C), 33.1 (br, BCH_2), 32.4 (*o*-^{t}Bu^{CH3}), 30.1 (*p*-^{t}Bu^{CH3}), [C_6F_5 not listed; ^{t} tentatively assigned].

^1H,^1H GCOSY (600 MHz/600 MHz, 213 K, dichloromethane-d_2) [selected traces]: δ^1H/ δ^1H: 7.68/7.26, 6.48, 5.64, 3.24 (P=CH/=CH, $=CH_2^E$, $=CH_2^Z$, BCH_2), 7.28/6.48, 5.64 (=CH/$=CH_2^E$, $=CH_2^Z$).

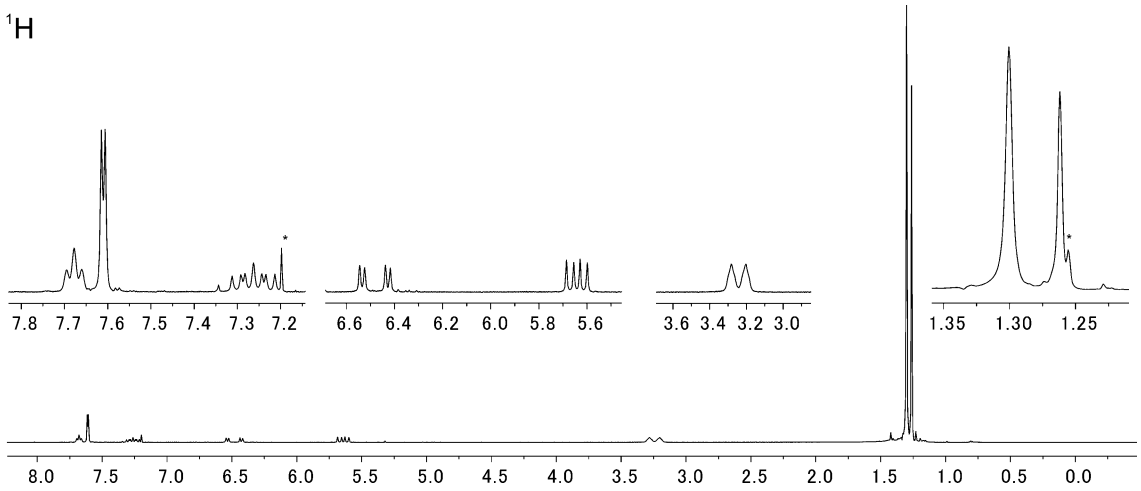
^1H,^{13}C GHSQC (600 MHz/151 MHz, 213 K, dichloromethane-d_2): $\delta^1H/\delta^{13}C$: 7.68/165.3 (P=CH), 7.61/124.4 (*m*-mes*), 7.26/122.1 (=CH), 6.48,5.64/138.5 ($=CH_2$), 3.24/33.1 (BCH_2), 1.30/32.4 (*o*-^{t}Bu), 1.26/30.1 (*p*-^{t}Bu).

^1H,^{13}C GHMBC (600 MHz/151 MHz, 213 K, dichloromethane-d_2) [selected traces]: $\delta^1H/\delta^{13}C$: 7.61/158.4, 158.3, 124.4, 105.3, 38.3, 35.5 (*m*-mes*/*p*-mes*, *o*-mes*, *m*-mes*, *i*-mes*, *o*-^{t}Bu^C, *p*-^{t}Bu^C), 7.28/105.3 (=CH/*i*-mes*), 1.30/158.3, 38.3, 32.4 (*o*-^{t}Bu/*o*-mes*, *o*-^{t}Bu^C, *o*-^{t}Bu^{CH3}), 1.26/158.4, 35.5, 30.1 (*p*-^{t}Bu/*p*-mes*, *p*-^{t}Bu^C, *p*-^{t}Bu^{CH3}).

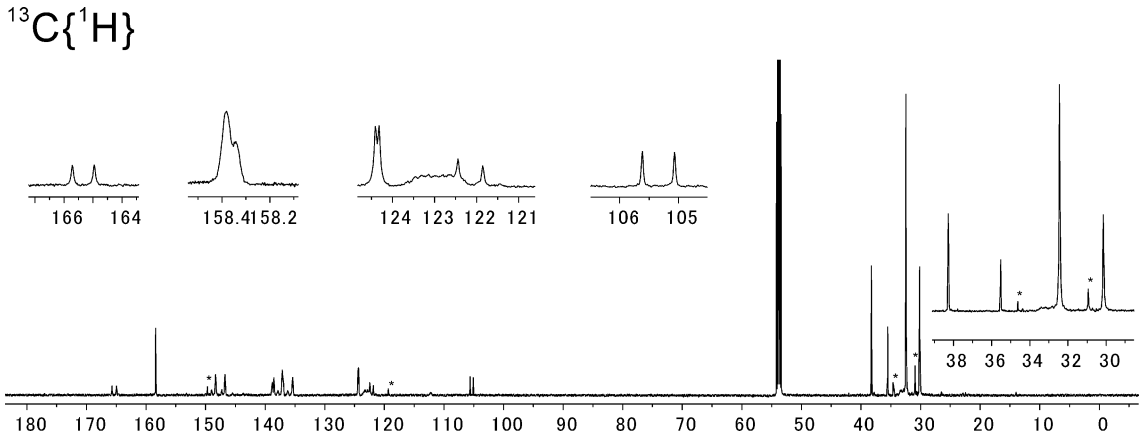
$^{11}B\{^1H\}$ NMR (192 MHz, 213 K, dichloromethane-d_2) : δ = –13.6 (br d, $^3J_{PB}$ ~ 17 Hz).

^{19}F NMR (564 MHz, 213 K, dichloromethane-d_2) : δ = –133.3 (br m, 2F, *o*-C_6F_5), –161.3 (br t, $^3J_{FF}$ = 20.7 Hz, 1F, *p*-C_6F_5) , –165.4 (br m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F$ = 4.1].

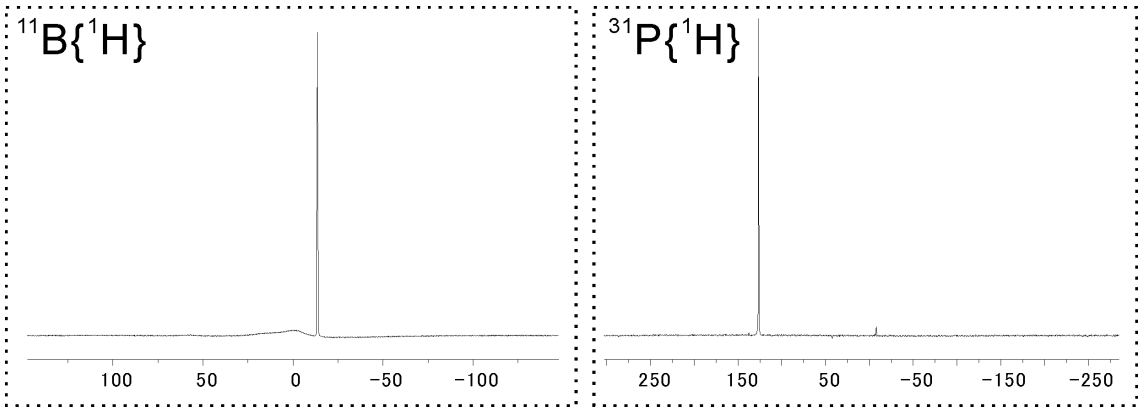
$^{31}P\{^1H\}$ NMR (243 MHz, 213 K, dichloromethane-d_2) :δ = 126.6 (m).



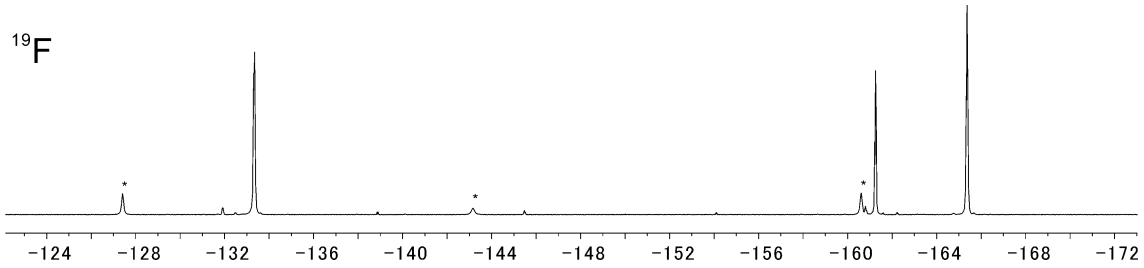
*^{1}H NMR (600 MHz, 213 K, dichloromethane-d_2) spectrum of **11a**. [* ^{t}Bu$_3$C$_6$H$_3$]*



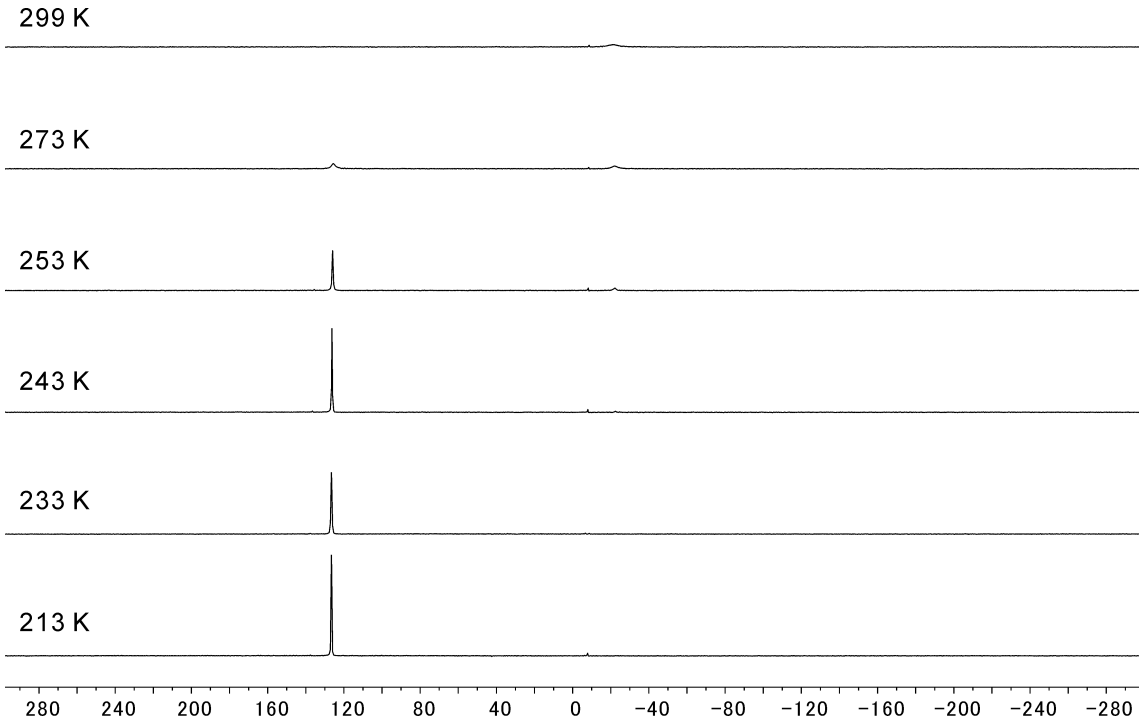
*^{13}C{^{1}H} NMR (151 MHz, 213 K, dichloromethane-d_2) spectrum of **11a**. [* ^{t}Bu$_3$C$_6$H$_3$]*



*^{11}B{^{1}H} NMR (192 MHz, 213 K, dichloromethane-d_2) and ^{31}P{^{1}H} NMR (243 MHz, 213 K, dichloromethane-d_2) spectra of **11a**.*



*^{19}F NMR (564 MHz, 213 K, dichloromethane-d_2) spectra of **11a** [* admixed with $B(C_6F_5)_3$].*

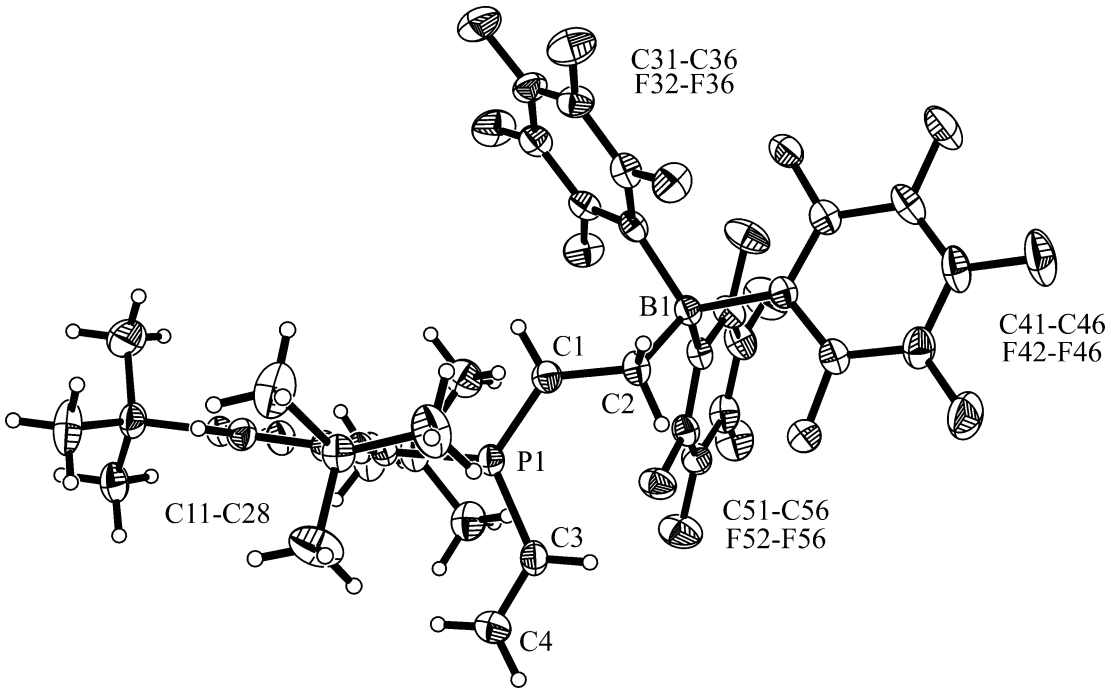


*$^{31}P\{^1H\}$ NMR (243 MHz, 299K to 213 K, dichloromethane-d_2) spectra of **11a**.*

(2) *Preparative scale:* A solution of tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] (512 mg, 1.00 mmol) in dichloromethane-d_2 (1.2 mL) was added to **6a** [331 mg, 0.65 mmol; *comment:* **6a** was admixed with $^tBu_3C_6H_3$ (43%)] and then stored in the fridge at −35°C. First very thin needles were formed after one day and then parallelepiped block crystals appeared after 10 days which were collected and dried (198 mg, 46%). X-ray crystal structure analysis was carried out using a suitable block crystal. [Comment: the block crystals of compound **11a** used for NMR experiments (dichloromethane-d_2, 213K) were admixed with $B(C_6F_5)_3$ [42 mol%[1], ^{19}F (213K)], a PH-species [11%[1], ^{31}P (213K), not identified yet], and $^tBu_3C_6H_3$ [25%[1], ^1H (213K)] [[1] relative to **11a**].

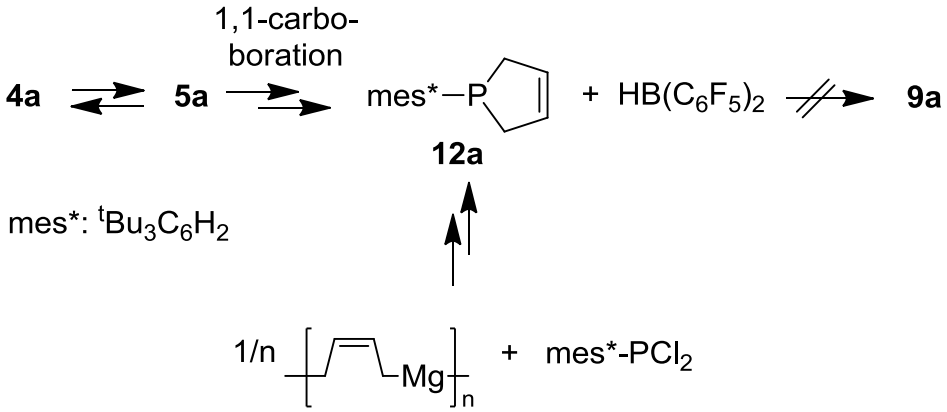
X-ray crystal structure analysis of compound **11a**: formula $C_{40}H_{35}BF_{15}P \times CH_2Cl_2$, M = 927.39 colourless crystal, 0.18 x 0.09 x 0.04 mm, a = 15.4992(3), b = 17.1040(3), c = 15.7066(3) Å, β = 93.555(1)°, V = 4155.8(1) Å^3, ρ_{calc} = 1.482 gcm^{-3}, μ = 0.293 mm^{-1}, empirical absorption correction ($0.949 \leq T \leq 0.988$), Z

= 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 24986 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 7211 independent (R_{int} = 0.066) and 4760 observed reflections [I>2σ(I)], 631 refined parameters, R = 0.079, wR^2 = 0.168, max. (min.) residual electron density 0.39 (-0.42) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

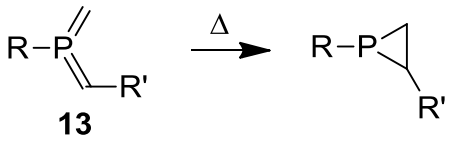


***Comments:* pathway of the 5a → 9a rearrangement.**

So far within this study we were not able to secure the reaction pathway actually taken in the **4a** ⇄ **5a** to **9a** isomerization. We first speculated that the C_4-sequence found in **9a** might be formed from the pair of C_2-units of the starting material by means of a 1,1-carboboration sequence.[S11] This might have given the dihydrophosphole **12a** plus $HB(C_6F_5)_2$ as an intermediate. However we could show that independently synthesized **12a**[S12] did only give a P/B addition with $HB(C_6F_5)_2$ that did not provide a pathway to **9a** even at elevated temperature.

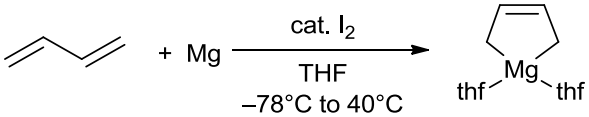


The outcome of these experiments makes it likely that **9a** is formed in a true intramolecular rearrangement sequence. We note that phosphiranes can be obtained by ring closure form bis(methylene)phosphoranes **13**,[S13] sometimes under mild conditions. It needs to be investigated in a future study whether this chemistry provides a viable pathway for the here observed isomerization reaction or not.

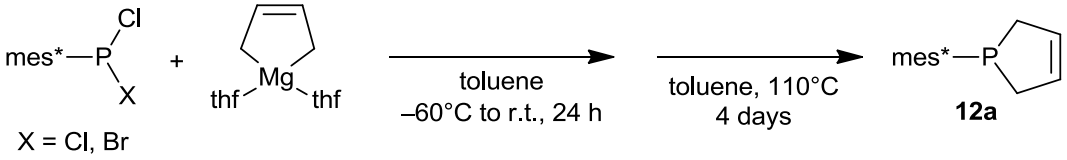


Experiments:

Preparation of compound 12a:



See: K. Fujita, Y. Ohnuma, H, Yasuda and H. Tani, *J. Organomet. Chem.* 1976, **113**, 201-213.



(See**:** W. J. Richter *Angew. Chem. Int. Ed. Engl*. 1982, **21**, 292-293)

Step I: 1-Mes*-2,5-dihydro-1*H*-phosphole (**12a**) was prepared based on the following modified literature procedure: Mes*PCl(X) [3.29 g, 8.8 mmol from mes*PCl_2 : mes*PClBr : mes*H = 83 : 6 : 10 (^{1}H NMR)] in toluene (50 mL) was added dropwise to a suspension of magnesium-butadiene(thf)$_2$ (5.06 g, 23 mmol) in toluene (80 mL) at –60°C over a period of 1 h. Then the reaction mixture was stirred for 20 h while gradually raising the temperature to r.t. The precipitate of the obtained gray suspension was removed by passing through a pad of Celite® on a fritted glass, and the filtrate was collected in a Schlenk flask (100 mL). The volatiles were removed at r.t. in vacuo (0.1 mbar) for 10 h, which gave a slightly yellow oil (1.76 g, 54% crude yield: supposedly the phosphirane isomer).

Step II: The yellow oil (370 mg, 1.10 mmol) from *Step I* was dissolved in toluene (50 mL) and heated at 100°C for 5 days. The progress of the reaction was monitored by ^{31}P{^{1}H} NMR experiments [until the signal from the starting material at δ^{31}P: –182 was not detected anymore [δ^{31}P(product): 5.3]. After the reaction was complete, the volatiles were removed in vacuo. Crystallization of the obtained residue in dichloromethane-d$_2$/*n*-pentane gave compound **12a** (60 mg, 16%). The obtained crystals were suitable for the X-ray crystal structure analysis.

^{1}H NMR (500 MHz, 299 K, dichloromethane-d$_2$): δ = 7.18 (d, $^4J_{PH}$ = 2.4 Hz, 2H, *m*-mes*), 5.68 (dm, $^3J_{PH}$ = 10.8 Hz, 2H, =CH), 2.75 (dm, $^2J_{PH}$ = 25.1 Hz, 2H, CH_2), 2.39 (dm, $^2J_{PH}$ = 15.2 Hz, 2H, CH_2), 1.41 (d, $^5J_{PH}$ = 1.0 Hz, 18H, *o*-^{t}Bu), 1.29 (s, 9H, *p*-^{t}Bu).

^{1}H{sel-^{31}P: δ 5.3} NMR (500 MHz, 299 K, dichloromethane-d$_2$): δ = 7.18 (s, 2H, *m*-mes*), 5.68 (m, 2H, =CH), 2.75 (m, 2H, CH_2), 2.39 (m, 2H, CH_2), 1.41 (s, 18H, *o*-^{t}Bu), 1.29 (s, 9H, *p*-^{t}Bu).

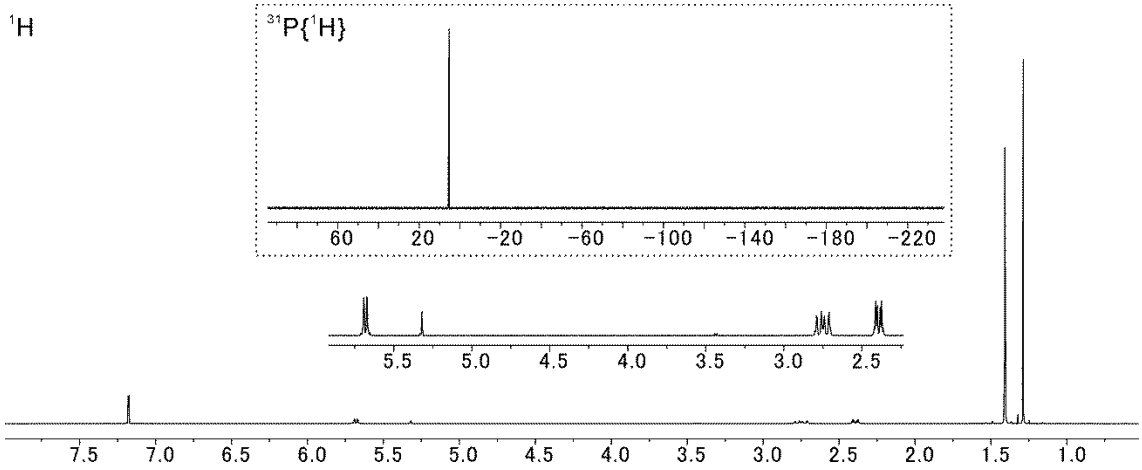
^{13}C{^{1}H} NMR (126 MHz, 299 K, dichloromethane-d$_2$): δ = 155.0 (d, $^2J_{PC}$ = 4.0 Hz, *o*-mes*), 146.8 (*p*-mes*), 142.0 (br d, $^1J_{PC}$ ~ 41 Hz, *i*-mes*), 129.3 (d, $^1J_{PC}$ = 2.6 Hz, =CH), 122.4 (*m*-mes*), 40.6 (d, $^2J_{PC}$ = 16.9 Hz, CH_2), 39.6 (d, $^3J_{PC}$ = 1.7 Hz, *o*-^{t}Bu^C), 34.4 (*p*-^{t}Bu^C), 33.8 (d, $^4J_{PC}$ = 7.6 Hz, *o*-^{t}Bu^{CH3}), 31.4 (*p*-^{t}Bu^{CH3}).

^{1}H,^{1}H GCOSY (500 MHz/500 MHz, 299 K, dichloromethane-d$_2$) [selected trace]: δ^1H/ δ^1H: 5.68/2.75, 2.39 (CH/CH_2, CH_2').

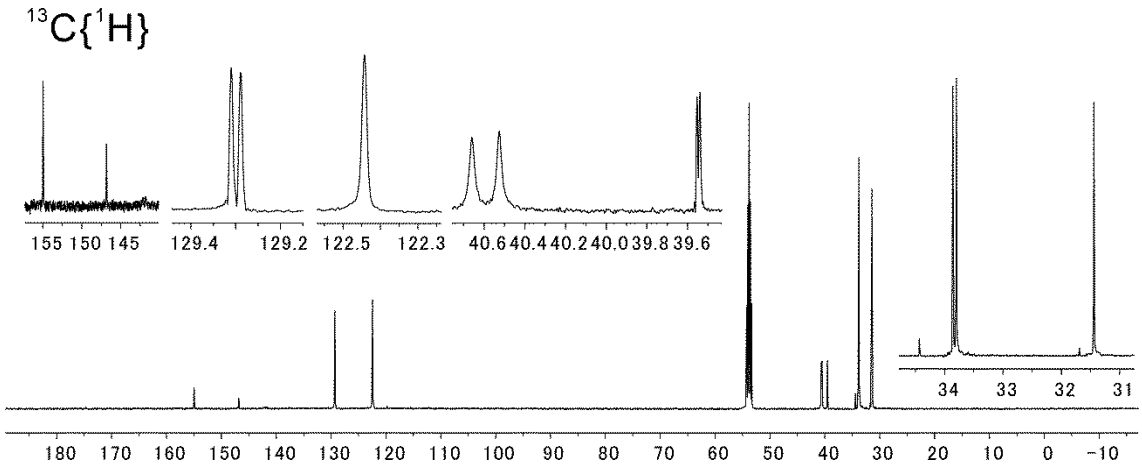
^{1}H,^{13}C GHSQC (500 MHz/126 MHz, 299 K, dichloromethane-d$_2$) [selected traces]: δ^1H/δ^{13}C: 7.18/122.4 (*m*-mes*), 5.68/129.3 (=CH), 2.75,2.39/40.6 (CH_2), 1.41/33.8 (*o*-^{t}Bu), 1.29/31.4 (*p*-^{t}Bu).

^{1}H,^{13}C GHMBC (500 MHz/126 MHz, 299 K, dichloromethane-d$_2$) [selected traces]: δ^1H/δ^{13}C: 7.18/142.0, 122.4, 39.6, 34.4 (*m*-mes*/*i*-mes*, *m*-mes*, *o*-^{t}Bu^C, *p*-^{t}Bu^C), 2.39/141.9, 129.3 (CH_2/*i*-mes*, =CH), 1.41/155.0, 39.6, 33.8 (*o*-^{t}Bu/*o*-mes*, *o*-^{t}Bu^C, *o*-^{t}Bu^{CH3}), 1.29/146.8, 34.4, 31.4 (*p*-^{t}Bu/*p*-mes*, *p*-^{t}Bu^C, *p*-^{t}Bu^{CH3}).

$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, dichloromethane-d_2): δ = 5.3 ($\nu_{1/2}$ ~ 1 Hz).

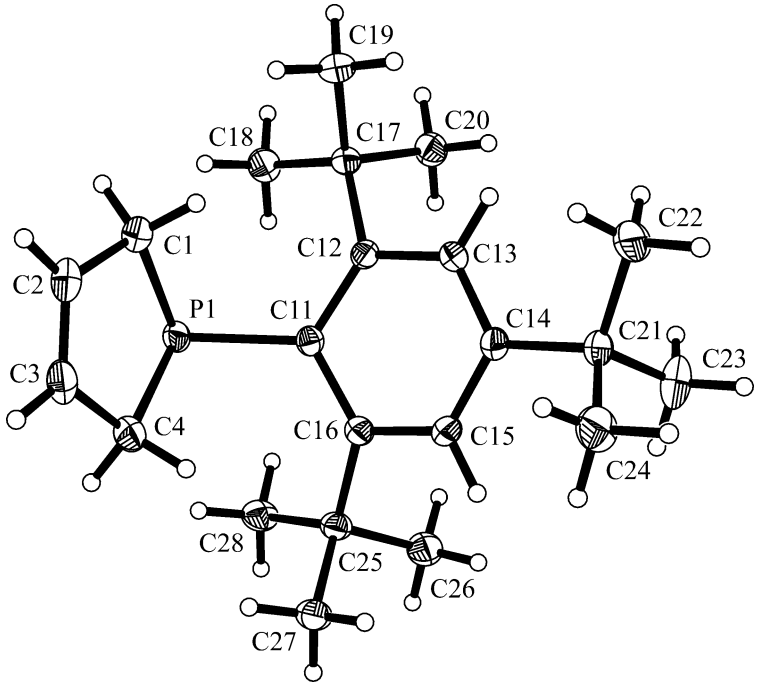


*^{1}H NMR (500 MHz, 299 K, dichloromethane-d_2) and $^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, dichloromethane-d_2) spectra of **12a**.*

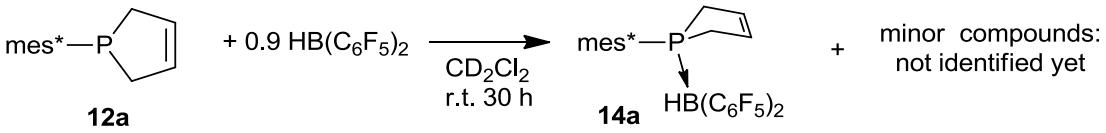


*$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, dichloromethane-d_2) spectrum of **12a**.*

X-ray crystal structure analysis of compound **12a**: formula $C_{22}H_{35}P$, M = 330.47 colourless crystal, 0.20 x 0.15 x 0.10 mm, a = 9.7184(1), b = 11.6807(2), c = 35.4816(5) Å, V = 4027.8(1) Å^3, ρ_{calc} = 1.090 gcm^{-3}, μ = 1.168 mm^{-1}, empirical absorption correction (0.800 ≤ T ≤ 0.982), Z = 8, orthorhombic, space group *P*bca (No. 61), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 23395 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 3477 independent (R_{int} = 0.037) and 3291 observed reflections [I>2σ(I)], 217 refined parameters, R = 0.035, wR^2 = 0.096, max. (min.) residual electron density 0.24 (-0.20) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Reaction of compound 12a with $HB(C_6F_5)_2$



12a **14a**

Inside a glove box: a solution of bis(pentafluorophenyl)borane (8.0 mg, 0.023 mmol) in dichloromethane-d_2 (0.5 mL) was added to 1-mes*-2,5-dihydro-1*H*-phosphole (**12a**) (8.4 mg, 0.025 mmol) and kept at r.t. for 30 h.

^{1}H NMR (500 MHz, 299 K, dichloromethane-d_2): δ = 7.23 (br, 2H, *m*-mes*), 5.63 (d, $^{3}J_{PH}$ = 26.7 Hz, 2H, =CH), 3.87 (br m, 1H, BH), 3.22 (d, $^{2}J_{PH}$ = 6.3 Hz, 4H, CH_2), 1.36 (s, 18H, *o*-^{t}Bu), 1.26 (s, 9H, *p*-^{t}Bu).

^{13}C{^{1}H} NMR (126 MHz, 299 K, dichloromethane-d_2): δ = 161.2 (br, *o*-mes*), 153.2 (br d, $^{4}J_{PC}$ ~ 4.5 Hz, *p*-mes*), n.o. (*i*-mes*), 128.7 (br, =CH), 124.8 (br d, $^{3}J_{PC}$ = 11.7 Hz, *m*-mes*), 34.5 (br, CH_2), 41.3 (d, $^{3}J_{PC}$ = 3.2 Hz, *o*-^{t}Bu^{C}), 34.6 (d, $^{5}J_{PC}$ = 1.5 Hz, *p*-^{t}Bu^{C}), 33.0 (*o*-^{t}Bu^{CH3}), 30.9 (*p*-^{t}Bu^{CH3}), [C_6F_5 not listed].

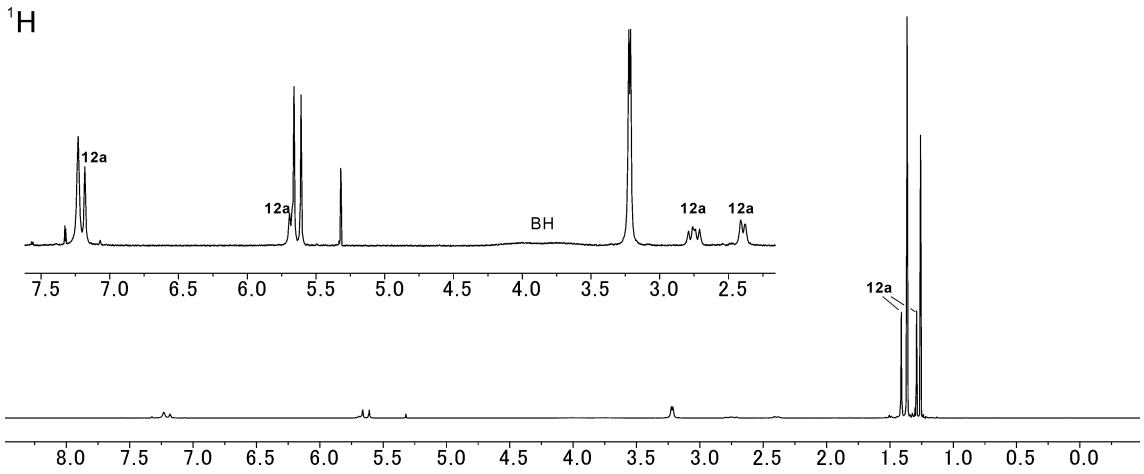
^{10}B{^{1}H} NMR (54 MHz, 299 K, dichloromethane-d_2) : δ = –20.4 ($\nu_{1/2}$ ~ 80 Hz).

^{11}B{^{1}H} NMR (160 MHz, 299 K, dichloromethane-d_2) : δ = –20.4 (br d, $^{1}J_{PB}$ ~ 50 Hz).

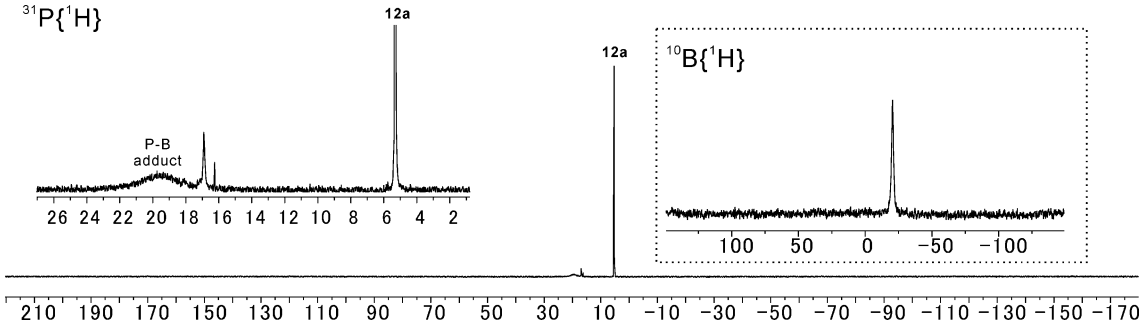
^{11}B NMR (160 MHz, 299 K, dichloromethane-d_2) : δ = –20.4 (br t, $^{1}J_{BH}$ ~ 80 Hz, $^{1}J_{PB}$ ~ 50 Hz).

^{19}F NMR (470 MHz, 299 K, dichloromethane-d_2) : δ = –129.9 (br, 2F, *o*-C_6F_5), –159.4 (br, 1F, *p*-C_6F_5) , –164.5 (br, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 5.1].

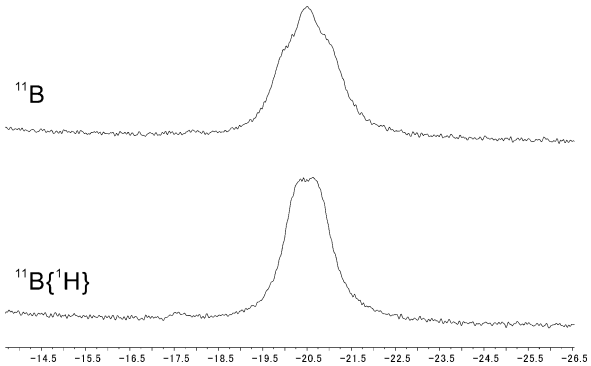
^{31}P{^{1}H} NMR (202 MHz, 299 K, dichloromethane-d_2) :δ = 19.6 ($\nu_{1/2}$ ~ 500 Hz).



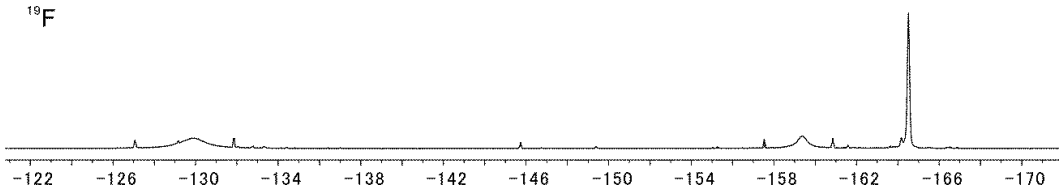
*^{1}H NMR (500 MHz, 299 K, dichloromethane-d_2) spectrum of **12a**×HB(C_6F_5)$_2$*



*^{31}P{^{1}H} NMR (202 MHz, 299 K, dichloromethane-d_2) and ^{10}B{^{1}H} NMR (54 MHz, 299 K, dichloromethane-d_2) spectra of **12a**×HB(C_6F_5)$_2$.*



*^{11}B{^{1}H} and ^{11}B NMR (160 MHz, 299 K, dichloromethane-d_2) spectra of **12a**×HB(C_6F_5)$_2$.*



*^{31}P{^{1}H} NMR (470 MHz, 299 K, dichloromethane-d_2) spectrum of **12a**×HB(C_6F_5)$_2$.*

Theoretical Methods and Technical Details of the Computations.

The quantum chemical calculations have been performed with the TURBOMOLE suite of programs[S14]. As Gaussian AO basis, large triply-polarized triple-zeta (def2-TZVP) sets of Ahlrichs *et al.*[S15] have been employed which avoid most BSSE effects. All geometries have been fully optimized at the DFT level using the TPSS density functional[S16]. We included our standard atom pair-wise DFT-D3 (with BJ-damping) correction for intra- and inter-molecular dispersion (also called van der Waals) interactions[S17]. The final level used for geometry optimization is dubbed TPSS-D3/def2-TZVP in the following. For a detailed description of the dispersion correction, that is of great importance in studies of large molecules, including many illustrative examples[S18], for the most recent chemical applications of this method see Ref.(S19) In all DFT treatments, the RI-approximation has been used[S20] for the Coulomb integrals which speeds the computations up significantly without any significant loss of accuracy. The numerical quadrature grid *m4* (*m5* for PW6B95, see below) has been employed for the integration of the exchange-correlation contribution. We report pure electronic energies *without* zero-point vibrational and thermal corrections as well as free energies G(273.15) that are obtained by a standard rigid-rotor, harmonic vibrational statistical treatment. Vibrational frequencies are computed at the TPSS-D3/def2-TZVP level and are not scaled. Low-lying vibrational modes are treated by a special rigid-rotor approximation in order to avoid numerical artefacts in the entropy calculations[S21]. These calculations are also used to characterize the stationary points as minima.

Single-point energy calculations for the final thermochemical properties were performed at the higher dispersion-corrected PW6B95[S22] hybrid functional level employing the def2-QZVP basis set for all atoms. This final theoretical level should provide relative energies with an estimated accuracy of about 1-2 kcal mol^{-1}[S23].

Wiberg bond indices were calculated according to Ref.(S24).

Solvent effects on the thermochemical properties have been estimated by the COSMO-RS method[S25] (COSMOtherm software package[S26]) based on default BP86/TZVP calculations. Solvation contributions to free energies at 273.15 K in dichloromethane are computed and added to the PW6B95-D3 gas phase values.

Relative energies

Table S1. Contributions to the relative free energies in solution (CH_2Cl_2) at 273.15 K (ΔG(273.15)) for the tri-*tert*-butylphenyl-substituted methylene phosphonium compounds **a**. The last line is relative to the reactants plus H_2. All energies are in kcal mol^{-1}.

	ΔE PW6B95-D3	$\delta\Delta G_{solv.}(CH_2Cl_2)$	δΔG(273.15)	Total ΔG(273.15)
Reactants	0.0	0.0	0.0	0.0
Lewis adduct **15a**	-25.66	-1.06	15.81	-10.91
Intermediate **4a**	-39.75	-0.63	19.38	-21.00
Product **5a**	-35.63	-6.11	19.05	-22.69
H_2 addition product **8a**	-46.38	-13.65	27.58	-32.45

Table S2. Contributions to the relative free energies in solution (CH_2Cl_2) at 273.15 K (ΔG(273.15)) for the 1,3,5-triisopropylphenyl-substituted methylene phosphonium compounds **b**. All energies are in kcal mol^{-1}.

	ΔE PW6B95-D3	$\delta\Delta G_{solv.}(CH_2Cl_2)$	δΔG(273.15)	Total ΔG(273.15)
Reactants	0.0	0.0	0.0	0.0
Intermediate 4**b**	-57.7	-1.6	18.4	-40.9
Product **5b**	-41.8	-5.5	18.6	-28.7
Rotamer of Intermediate **4b'**	-36.0	-1.3	19.6	-17.7

Table S3. Contributions to the relative free energies in solution (CH_2Cl_2) at 273.15 K (ΔG(273.15)) for the methyl-substituted methylene phosphonium compounds **c**. All energies are in kcal mol^{-1}.

	ΔE PW6B95-D3	$\delta\Delta G_{solv.}(CH_2Cl_2)$	δΔG(273.15)	Total ΔG(273.15)
Reactants	0.0	0.0	0.0	0.0
FLP **4c**	-43.14	-2.96	17.24	-28.86
Product **5c**	-17.98	-7.61	17.18	-8.41

Table S4. Contributions to the relative free energies in solution (CH_2Cl_2) at 298.15 K (ΔG(298.15)) the formation of the phosphirane compound **9a** from intermediate **4a**. All energies are in kcal mol^{-1}.

	ΔE PW6B95-D3	$\delta\Delta G_{solv.}(CH_2Cl_2)$	δΔG(298.15)	Total ΔG(298.15)
Intermediate **4a**	0.0	0.0	0.0	0.0
Phosphirane **9a**	-8.68	-0.82	1.72	-7.78

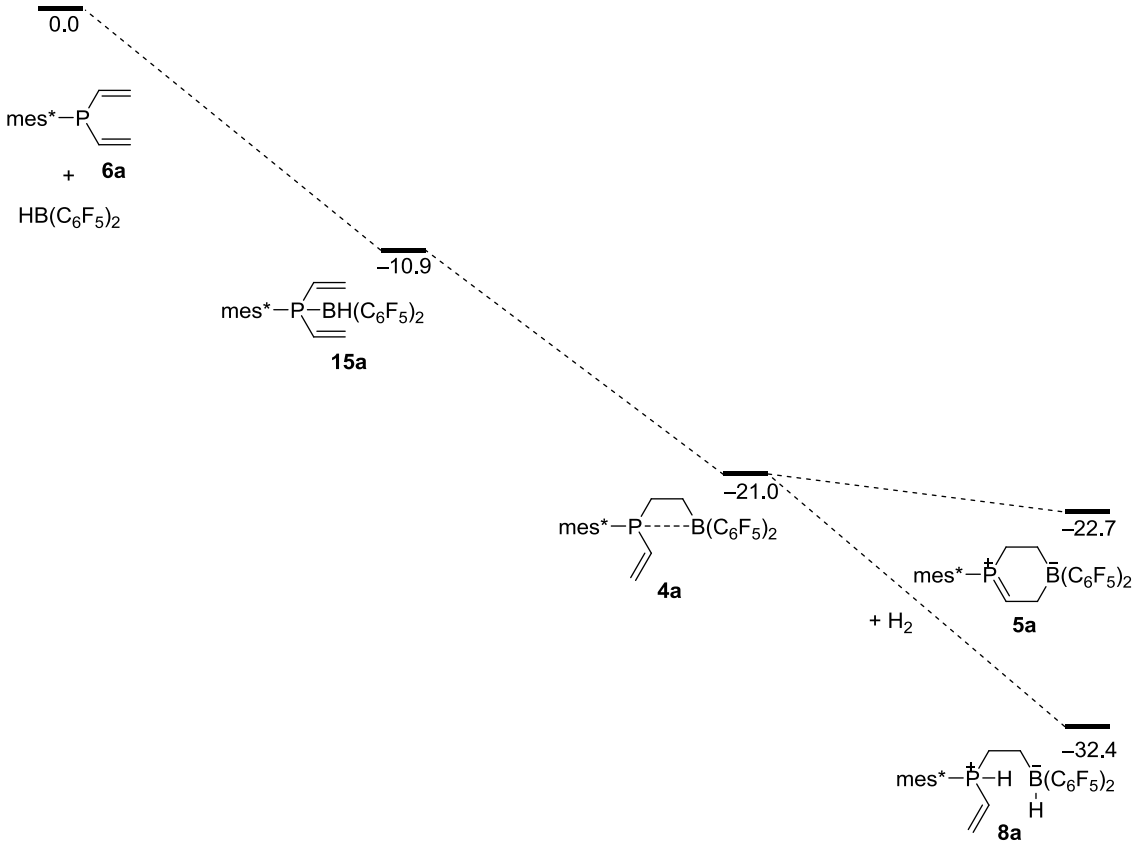


Figure S1. Free energy pathway for the formation (kcal mol^{-1}) of the tri-*tert*-butylphenyl-substituted methylene phosphonium compound **5a**, including the *Lewis* adduct **15a** of the reactants and the product of the activation reaction with H_2 **8a**. The energy of **8a** is relative to the reactants plus H_2. All energies are calculated at 273.15 K in CH_2Cl_2.

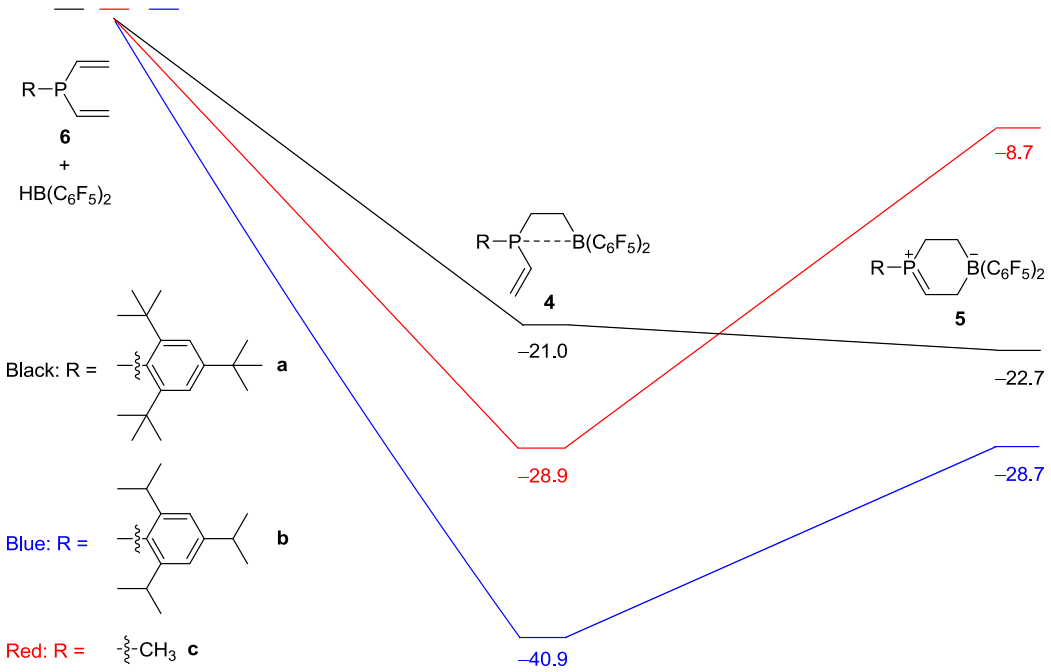


Figure S2. DFT calculated thermodynamics of the **6** + $HB(C_6F_5)_2$ ⇄ **4** ⇄ **5** reaction systems depending on the substituents at phosphorus (energies in kcal mol^{-1}).

Cartesian coordinates of all compounds (in Bohr):

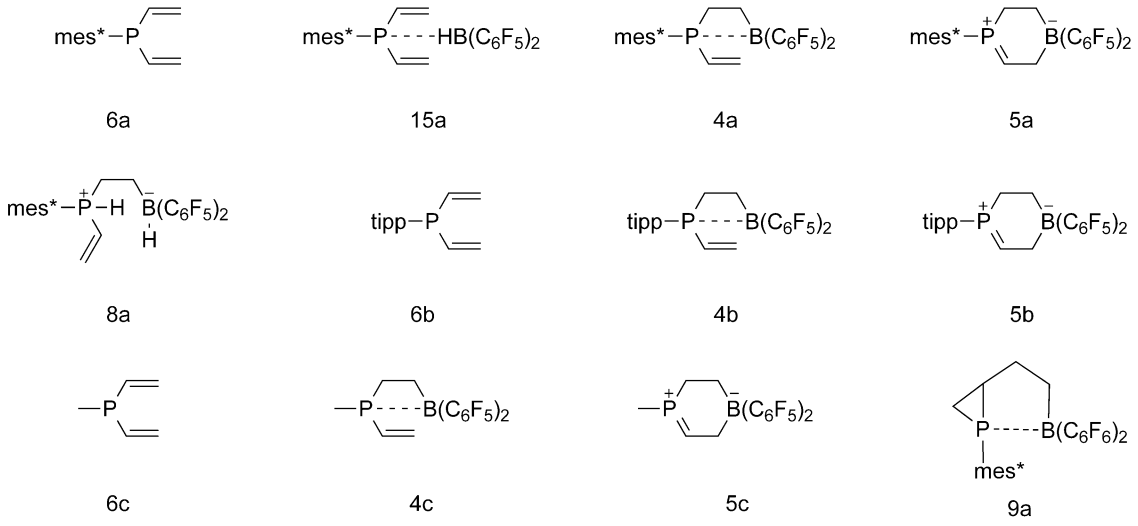


Figure S3. Calculated structures for all available Cartesian coordinates (excluding $HB(C_6F_5)_2$).

$HB(C_6F_5)_2$:

-1.34616037110444	-1.48084473070646	-1.14884985188701	b
-2.65681777914801	-2.92220229066680	-2.26799319392013	h
5.16804921005882	-3.79313834103129	-3.48647893979748	c
6.64320233243162	-1.61375492098911	-3.33250242382957	c
5.59204120226394	0.63840477640391	-2.45034405809476	c
3.07667599622062	0.67002128032382	-1.69976526198958	c
1.50995432131070	-1.47146448265584	-1.80843266783759	c
2.64806581746014	-3.67854524803627	-2.75673084893785	c
6.19553611963323	-5.94986731327499	-4.33306586750853	f
9.06498829124580	-1.67953997246145	-4.03950916550410	f
7.01641451015837	2.73265376373085	-2.35029599506650	f
2.13577535163797	2.90590298680100	-0.93275706029148	f
1.29280925631781	-5.82277631702625	-2.92564710282488	f
-2.73327735350467	2.50045217310545	4.89683414684512	c
-5.26480868944208	3.12977429452951	4.50885005117200	c
-6.51233639906908	2.32054086377729	2.33216368311716	c
-5.19865599478143	0.87849578773735	0.57407777358539	c
-2.63450322508405	0.23480522253737	0.84925165053514	c
-1.47039684753314	1.09176140376131	3.07693724304754	c
-1.56485069837047	3.25263730738850	7.01673396250975	f
-6.49767524953039	4.50227191606774	6.23103542654057	f
-8.94390735373021	2.93876541790471	1.97278262740868	f
-6.46718833376666	0.14079474825352	-1.50205205463339	f
0.94706588632547	0.47485167452616	3.57575792736140	f

6a:

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0.70248341631229	1.98430010826851	1.68238612745454	c
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-0.64703729693893	-1.12249762064064	-1.50001879451137	c
-2.77810305852596	-1.57933984917330	-0.00104949268032	c
-3.23883648266072	-0.36835082706728	2.28501009965377	c
-1.93754786937128	2.59533538615538	4.68154866255409	h
4.68843753753014	0.20922765421319	-1.20639534313345	p
-4.15776323845862	-2.93804353713998	-0.67524911164889	h

-5.58337612756509	-1.04615458199026	3.83881300235220	c
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-5.74036075695368	0.46645737489332	6.31366317283231	c
-7.98198677630199	-0.49840307126992	2.26684537534989	c
-5.44129042853587	-5.05505827301045	2.78960094820266	h
-3.81690016864045	-4.32638423331908	5.62544227641463	h
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-5.89567617843947	2.49987394425282	5.95727243938536	h
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-8.08568178108641	1.50702858982832	1.76696874526828	h
-8.00143113614703	-1.59715685349146	0.51471288795035	h
-9.67496064624572	-0.99123944678272	3.35436178450965	h
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1.32264456811079	-5.83423749467782	-3.25456852756973	h
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-4.98095558869056	-2.63413963215899	-4.24934584894346	h
-3.73308788709673	0.27173789469839	-5.34928292072085	h
-3.49130694220330	-2.49762528208146	-7.23163338880545	h
2.39629841717545	4.14146592997838	2.73081135749567	c
3.55592318151975	5.75046152342604	0.58901140060142	c
0.82193909356412	6.01167776217478	4.33887068057823	c
4.49523142072576	3.09864091836089	4.47784247596467	c
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2.08844130277186	6.38817033241317	-0.72439556294078	h
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0.20079284983769	5.19051280486872	6.13236865767471	h
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7.53276296511580	-3.38175188305854	-4.83932516986842	h
6.92849573662346	-6.38091208707944	-3.14486468424193	h
4.27345450357251	-4.21379430468795	-0.08215715217423	h

15a:

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-4.21717864128502	0.70654613048682	4.79454381313644	h
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-8.69396275174421	-4.56919586378371	3.05145873163500	c
-4.48412961568434	-7.49753832651575	1.95270784511118	h
-2.55617916794771	-6.46586320932380	4.49003375020920	h
-5.44065117368095	-8.07108561126683	5.11117512035426	h
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-2.51789382999896	-4.64890543381302	-5.69120950191918	c
-6.45664220324763	-2.08973104944697	-5.19544262458101	c
-3.56381688163584	1.80111817556962	-6.40900994510072	h
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-3.29905615124784	-0.60024495314246	-8.71348229289850	h
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-6.93172731628226	-2.31552418298236	-7.19829763279262	h
-1.80200311342647	4.26913753226385	2.54027661343759	c
-0.12851560382534	6.08731737962529	1.02771622987930	c
-4.45974364615942	5.52213780481470	2.61097699236173	c
-0.78842966319575	4.14061871445548	5.27604535428658	c
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-0.92484497566143	6.46943126758982	-0.83291733722816	h
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-2.08576931786763	3.15202886754286	6.54411509663953	h
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3.88440666962404	-1.41646218781313	-6.16427213720771	c
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6.98708065391894	-2.77979596605807	0.04392844118214	c
4.87810558117386	-1.61237168066184	1.12888135040336	c
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6.84631867642150	-9.16165048908700	2.58769235118652	f
9.72528109402220	-6.29209624380849	-0.61765738857954	f
8.49150955114837	-1.48719129140363	-1.56505237141028	f
1.43634416873988	-2.26258615572986	3.98094077563656	f
8.84845722852595	6.50068131031986	2.79998866441970	c
10.18733574929688	7.09413533665539	0.61547803896006	c
9.61135763372436	5.83425657161789	-1.61873197440705	c
7.71114465238312	4.01592770962563	-1.61815342149924	c
6.28420553336122	3.36399269592274	0.49988304018129	c
6.95701462868237	4.67297567490757	2.70089057302287	c
9.39710010674086	7.69473002752956	4.97760365509724	f
12.01220460135145	8.85593378214405	0.66361985625411	f
10.89229480290469	6.38046917075532	-3.74932136194956	f
7.28489153532261	2.85446394710535	-3.87158703578585	f
5.76206746042031	4.17809071806954	4.90745830061998	f
2.63782480127539	1.87067905850164	2.35915194101489	h

4a:

-4.01065455784633	0.76410388618925	2.97939329379455	c
-2.27871460597611	1.71995614632331	1.22270869530973	c
-1.92181376960153	0.40239522046120	-1.09577803010195	c
-3.79711348147790	-1.41565421679788	-1.81526124459903	c
-5.44800985107265	-2.29221592765621	0.04224686294916	c
-5.48439963335729	-1.36008855563605	2.51038081527185	c
-4.17255164193701	1.71215266749311	4.78470800517609	h
1.34448565307002	0.14855291309009	-2.36465476361714	p
-6.80515154062187	-3.73955661471361	-0.48157992386754	h

-7.19290001041869	-2.57186413355003	4.49937856123722	c
-6.44173534025211	-5.38000841263595	4.77891071714160	c
-6.94212512747442	-1.28394900019439	7.09034654245750	c
-9.97758960044540	-2.39943720113826	3.63950581476309	c
-6.64227231115945	-6.39231712104261	2.98599940627517	h
-4.47487157996121	-5.55369983744149	5.39742831175359	h
-7.65446924840885	-6.30386245667161	6.18047824185877	h
-4.99311254459842	-1.35090381451739	7.78393945510067	h
-7.54723688912078	0.69471274367202	7.02151222515224	h
-8.14142686777057	-2.26145227737904	8.46440695972191	h
-10.55213914802074	-0.42516651670505	3.40595454412971	h
-10.27632677282628	-3.37414710717261	1.83991169677100	h
-11.21030234533112	-3.27669361723675	5.05351367368671	h
-4.48649318720828	-2.23014209846906	-4.54075417991091	c
-2.86522855051317	-1.04525077732835	-6.62709345725547	c
-4.48853380838833	-5.12579750792444	-4.86771246197611	c
-7.21514416129492	-1.23741572175093	-4.98788368480738	c
-2.64505122602397	0.99284100849430	-6.34861864612888	h
-1.00921630437055	-1.92324396578348	-6.74120176464718	h
-3.80232910581715	-1.33890327716539	-8.44944784286821	h
-2.59324860541105	-5.89992307797474	-4.60563028353171	h
-5.76257917888261	-6.04493034346287	-3.52324739872253	h
-5.13063029655129	-5.60758171672465	-6.77680824926183	h
-8.57065409607930	-2.07376739463895	-3.67312921897778	h
-7.28577580924931	0.81861599162055	-4.76337663430440	h
-7.80458056451062	-1.70780804649058	-6.91682947269883	h
-0.98162553931760	4.22810588495839	1.92500771688619	c
0.01453587394936	5.61247393482201	-0.42193989430059	c
-2.95150784625391	6.03313650557598	3.12347724912251	c
1.12953803613708	3.75566576810705	3.86964170838889	c
1.52836807061430	4.58139702246783	-1.36058761408105	h
-1.50882754421168	5.92285178455518	-1.78794205154706	h
0.79067624898480	7.45054157651646	0.12512168721891	h
-4.60226040466430	6.25924398448318	1.89660759227578	h
-3.59597029498119	5.39175864813282	4.97811491787767	h
-2.07317907924872	7.88982928791065	3.38323176278827	h

0.33005269690353	2.98373055152840	5.61529816439229	h
2.50181168063480	2.39993874792366	3.15436104755753	h
2.10410492554533	5.52481745730803	4.32536634990557	h
5.36198355456822	0.93907320969738	-4.60308976100733	c
2.56941962137002	1.42421950970150	-5.35604381811522	c
5.95776521457064	-0.91022429923362	-5.29529481852421	h
6.63014203053250	2.33917439398730	-5.43337188638252	h
1.91153621429343	0.52877628808206	-7.09196813554484	h
2.47008130236423	-4.57432080865288	-4.61705060395027	c
1.50879734145300	-3.26020529344931	-2.69312789454471	c
3.18269117214752	-3.68527003359468	-6.32409339200920	h
2.57175132585894	-6.62431207199916	-4.54720487712765	h
0.81182730670530	-4.24658472727392	-1.02958750804776	h
2.15159481222078	3.44207877293752	-5.44203542448225	h
5.33814221101612	0.95741982012610	-1.49029170780304	b
6.25650241503293	-5.25207453476952	2.60863978959790	c
8.54408554867073	-6.16134761885558	1.67737260843310	c
9.81810221827064	-4.78747720263797	-0.16859154344123	c
8.76543524205093	-2.54401109178892	-1.05701982222859	c
6.46716590417909	-1.57138598177556	-0.20889662605823	c
5.29430261662266	-2.99550590572001	1.67072334439663	c
5.00970914073800	-6.56009858982139	4.40201059202144	f
9.51580035905403	-8.33283564272694	2.56294849673398	f
12.04570842531641	-5.63092009122455	-1.06027439540124	f
10.10838382036795	-1.26307381994313	-2.82724828636708	f
3.07057507725768	-2.19655809288593	2.68120064521241	f
8.11019705392915	5.83638071920939	3.46419014198766	c
8.06709377663284	8.11028113267805	2.14896475917562	c
7.08112078800083	8.14446802695363	-0.28640937540732	c
6.17984759915569	5.91578065529679	-1.35031708446762	c
6.16689431636824	3.56096438211631	-0.12851400381624	c
7.17512330600834	3.65591597317211	2.32723188323149	c
9.03012337626858	5.76793559982281	5.83229548411130	f
8.94366579663995	10.23478676437644	3.21417533809179	f
6.99878747156643	10.32851958655492	-1.58654879860896	f
5.23028393925230	6.16952648208623	-3.71900403289147	f

7.24953898633274	1.56986349612301	3.79875551147528	f

5a:

0.42283509155321	-0.08098534543423	-0.91063376477616	p
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-2.32612378382901	0.82444939099473	-2.08397690356936	c
-3.95893692448778	0.43010960690688	-0.89260407244596	h
-2.59992899638629	2.19988849180472	-4.52772146583790	c
-4.21533061044166	3.48275701065978	-4.38557196063935	h
-3.14851828979733	0.76486914529946	-5.94366735494903	h
3.16027927599318	0.59352636469249	-2.87622737403766	c
4.17726823140474	2.17029487526531	-2.00089775723576	h
4.39002686736594	-1.07331044851856	-2.82133891582889	h
2.23677586285448	1.29422985390792	-5.55221139095999	c
1.51795774792141	-0.42814408144238	-6.46027928869124	h
3.92792520205910	1.84225617308813	-6.60171730327632	h
0.29985654220469	-2.06261835684248	1.84875413037638	c
0.93772956506473	-1.06704989636958	4.27155371606829	c
0.11000180121390	-2.39354874851472	6.39699665111059	c
0.53704296710975	-1.64017458615951	8.24496185656574	h
-1.26647577923894	-4.63401602313842	6.23447234340759	c
-1.64125117391985	-5.66705681706449	3.84014313016394	c
-2.57908350225475	-7.48011463553717	3.70636833046343	h
-0.84692454002800	-4.49505924456203	1.61325760582269	c
2.63016106585584	1.27609670295564	4.66671610801638	c
3.03073893057363	1.87584082529004	7.48953150493846	c
4.29064890689672	3.50924600079064	7.63440753910523	h
3.92019279843992	0.30655790661759	8.50215151529654	h
1.25628635471176	2.36337090927352	8.43620564951981	h
1.54501474969403	3.69344704699792	3.45620001021465	c
-0.41857072063433	4.01270808705523	4.01529727324146	h
1.61218744901185	3.66698238268427	1.39032937769272	h
2.67256863470808	5.32181310832049	4.05596169488556	h
5.26276682440279	0.68850700894566	3.54057419501985	c
6.49922038270046	2.33721727402943	3.73510696559373	h
5.15520377216158	0.20268060793576	1.53693201827839	h

6.13280051648225	-0.90711234807167	4.52934070770313	h
-2.28021104997598	-6.01354422577746	8.56483021866628	c
-1.70771803286192	-4.58659816996431	11.02896501449827	c
0.32886376776995	-4.40454203069797	11.35306842975808	h
-2.50711845517822	-5.63045045028742	12.62619388644318	h
-2.54469906288136	-2.69345281004491	11.02628908887850	h
-5.17544525081531	-6.29733755625057	8.30788943699740	c
-6.08806347015306	-4.44375072246388	8.19614982826935	h
-5.93397689318938	-7.30147001040207	9.95180282765110	h
-5.68325405415814	-7.36799269204914	6.61273458781295	h
-1.06174318326449	-8.66324581721424	8.72144754730767	c
-1.48869248809725	-9.79450052610164	7.04373262444995	h
-1.78503562090896	-9.67419479845702	10.37718349411558	h
0.99510072152888	-8.51633548985510	8.89345968697220	h
-1.19451936588011	-6.00020555510315	-0.87796834052096	c
-3.79579177295260	-5.46454159959130	-2.09129294308129	c
-3.92561475660045	-3.52355200908187	-2.77968281277961	h
-5.31813791597479	-5.78293614255342	-0.72684429747198	h
-4.08615559276856	-6.73731866695506	-3.69851944526549	h
0.91612821875349	-5.48007634887105	-2.82278731190987	c
2.79004875381584	-5.59209589681866	-1.95264356242721	h
0.71745871881867	-3.65092343171702	-3.76419447365057	h
0.81757174207309	-6.90384962822798	-4.32060884488323	h
-1.07109914007245	-8.87414778913700	-0.32385998326711	c
-1.02419001881677	-9.88832576602683	-2.12537172239693	h
-2.72682519032430	-9.55436171472217	0.70875707367441	h
0.62674881558142	-9.37086230794609	0.74881247565972	h
1.00175704856019	5.90290480048488	-3.79233068554181	c
-2.56684900982429	6.10549139176361	-0.99409995338454	f
-0.27051839698325	6.98569167442620	-1.74927992520820	c
-0.66854723145682	9.90922062854481	1.65693472591899	f
0.65393085399217	9.00047975752548	-0.32575523919803	c
3.91510134691236	11.98835324118354	0.43453946312967	f
2.97884953281229	10.05903385111849	-0.93015301928071	c
6.57302876193840	10.10166096414833	-3.59871853756347	f
4.32496327916900	9.08400358697728	-2.96857038031753	c

4.72179345610431	6.26069311047777	-6.31903025975399	f
3.31593729925839	7.06985996585674	-4.32800795705622	c
-0.56181903930524	4.64001824864637	-8.42314578407760	c
-3.28937141785762	7.74596093030808	-6.61949908551848	f
-2.19405970434788	6.70214789366165	-8.69773749493100	c
-4.40518276254665	9.80282588537530	-11.11185768440660	f
-2.82213766024029	7.80939464340070	-10.99901389926920	c
-2.37895327643394	7.85326964616330	-15.46724528321890	f
-1.80257196813020	6.82601006928123	-13.21450080888747	c
0.79323697645591	3.76858308802499	-15.19731378686339	f
-0.19277876514007	4.75567018734397	-13.06402623238993	c
1.94566735122273	1.68100092788781	-10.76754616896544	f
0.37833999153214	3.71869090946905	-10.70945515523269	c

8a:

1.18272418323533	-4.21141373831613	2.60396856378700	p
0.28495797722189	-3.52762389497682	4.98036324450483	h
2.24954819847543	-7.42485257831501	3.05253410640644	c
0.81340882788292	-8.89251837310801	2.97651442632213	h
4.66163823205815	-7.97540880473276	3.53883792709166	c
6.12817128880526	-6.53937779673450	3.59481322679101	h
5.25597064166841	-9.90988824539656	3.88622750734883	h
4.65053818444322	2.92927502662111	2.16376991085764	b
6.33141181921746	2.45568741604098	3.65135729534714	h
3.64677686080708	-1.88691079545845	2.12775493701217	c
5.11634079688884	-2.21687164510149	3.55060206149146	h
4.50415696908999	-2.12647461298738	0.26436039767041	h
2.45161515314051	0.74560730932090	2.44378195809923	c
1.56800930174044	0.86299569192232	4.31844175382684	h
0.93954084486531	0.97616306248786	1.05178348886744	h
-1.45591580491718	-3.48978352152846	0.58302956883957	c
-3.64010083949654	-2.54779523290050	1.86252531787054	c
-5.01381794635046	-0.62545900761031	0.68940162313851	c
-6.59967896944589	0.18525106891335	1.69126597993488	h
-4.40966406786100	0.32311148948858	-1.69103232751334	c
-2.52715243052131	-0.93817509093936	-3.04138499558674	c

-2.17128048074122	-0.38403145063075	-4.98268855475163	h
-1.03128747668585	-2.83816380804990	-2.00182491258000	c
-4.69203783964485	-3.55593957983013	4.40482279657802	c
-7.61770236239477	-3.68026379801229	4.20890127579688	c
-8.20827465589560	-4.77531893974398	2.55641697351167	h
-8.48452849864846	-1.81078573139844	4.09895984800550	h
-8.35799618879659	-4.60256555787121	5.90645909932932	h
-4.04665068944873	-1.76409623440393	6.61898505910234	c
-4.97966766687325	-2.41986753294521	8.34704331781641	h
-4.69863882671277	0.15375330048736	6.20711895665576	h
-2.01604025508508	-1.65463773161379	6.99607727353529	h
-3.86641150896993	-6.29422500835833	5.00205909025194	c
-5.06714120215343	-7.03965034332498	6.51246494437642	h
-1.92604240657373	-6.46766742026024	5.68403805013920	h
-4.09768795249524	-7.51119315519314	3.34398973782412	h
-7.16960068458548	1.70171932609087	-5.28026206131024	c
-8.57962880354270	0.25267324803536	-4.83583869594561	h
-5.85513992326943	0.92053536545403	-6.67345847656637	h
-8.13746514774984	3.31115764977431	-6.15049831735034	h
-3.79405839080308	4.60671354524355	-3.56897562848205	c
-2.39505306091615	3.88310968317740	-4.90697239380531	h
-2.78736368438707	5.26125630077081	-1.88890093621419	h
-4.74257919837688	6.22487071891589	-4.44455234389834	h
-7.70008275501162	3.76493697519009	-1.04725779037629	c
-8.57388934539787	5.40485184194073	-1.95552274548531	h
-6.78790356344968	4.41785407001023	0.69182537062275	h
-9.21508807233336	2.44135660784030	-0.55326216653532	h
0.80528025387267	-4.14316112512061	-3.85181209606731	c
0.38355625206883	-6.26107788671031	-7.34773896705414	h
2.66536698296789	-2.23078143655316	-5.02412005579371	c
3.85685914093702	-1.35185625946823	-3.58311307063770	h
1.67837674136905	-0.71842378294794	-6.02576182052315	h
3.89507114679638	-3.19555508100747	-6.38066533567874	h
2.32144111580747	-6.32935663845679	-2.71407947269827	c
-0.84211101263691	-5.30115820533402	-5.98306026696582	c
-1.92010956108494	-3.85681618699026	-6.99099627595758	h

-2.17670762830626	-6.68227155199938	-5.21171039623467	h
5.81970339484004	2.76829267310989	-0.71168806009001	c
9.28326115372701	0.17982825374688	0.59518509659046	f
8.00765171747730	1.40346143115157	-1.27139689222735	c
11.12277651178822	-0.21066496238598	-4.11747175451200	f
9.00816853168786	1.15487996758016	-3.69609637916249	c
8.69572587979727	2.06732320147368	-8.08322451796397	f
7.78765294037992	2.31155024036611	-5.71764248167418	c
4.34898086935149	4.75338813453672	-7.22890696807574	f
5.58977757086877	3.68373232492583	-5.26966821348361	c
2.46211977246570	5.15890967353468	-2.53836274415388	f
4.66469640231002	3.86519009916142	-2.81390023732346	c
3.63904033749624	5.78901379311648	2.77537193266091	c
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6.60373296956528	12.03044687298071	3.71674505722109	f
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2.27395423929585	10.90116645881355	3.87286241461247	c
0.43174448408652	9.03947345023913	3.66906837506940	c
-2.03126061633257	9.65297366681559	3.97633729171606	f
-0.80428597578389	4.88045974250337	2.92382861339627	f
1.14773926931524	6.56390943691664	3.13121650318339	c
3.30327205846521	-7.33174303672715	-4.23493890315640	h
3.78469465002463	-5.69174476573646	-1.40486015130974	h
1.09723974409524	-7.69699152445619	-1.75812797635427	h
-5.77480380295244	2.57717324735289	-2.86858378890705	c

9a:

-1.82279395222036	3.66090510514781	5.78891725750441	c
0.28583682700860	4.36749757505428	4.38663751504454	c
0.98339904173985	3.16756430988437	2.13311086785730	c
-0.46228338945798	1.04473279680536	1.33992127869316	c
-2.86509566235956	0.58437527874055	2.47568091952152	c
-3.42830892033224	1.86789592940764	4.70827828450956	c
3.16653487317650	4.37826601034018	0.61171928586389	c
5.78840618935726	3.40322247204263	1.44100102254042	c

1.11407681238515	-1.49829907033183	-0.47477133051252	p
1.33425856011771	-4.23366275241717	1.67693311909749	c
1.37267070038723	-6.68077389473058	0.13300894168381	c
-4.98723756258714	-1.06652110203143	1.32535523601923	c
-7.59645166109908	0.10175865279979	1.95489169590998	c
-2.50336960894496	4.86921525812379	8.32538169254216	c
-5.05909865593306	6.26086748430285	8.08456891780857	c
-2.73942100838257	2.76645276557571	10.33714517629080	c
-0.49552403519780	6.77220452952438	9.21007316693578	c
-4.79885422177777	-1.09855415399285	-1.56830090994429	c
-4.99717863736707	-3.79238653746686	2.36315174360033	c
2.78482364112884	3.96010492358129	-2.23419237031965	c
3.15798163885195	7.27785154770507	1.01477985228450	c
1.43791252471649	5.92132336195351	5.04777899773142	h
-5.21085125260277	1.46746991289229	5.63415093105362	h
-4.19163910159331	1.38811473840575	9.81820307614658	h
-0.94568704558774	1.75805543540187	10.55757855812430	h
-3.25645143170942	3.58816195817395	12.16637121795110	h
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-0.32438439556463	8.36676887686203	7.90111168427603	h
-1.03302218711142	7.53075608664883	11.05878935341700	h
-4.94647847164879	7.75589928365830	6.65836465992581	h
-6.57684915726222	4.96610641461764	7.53993216200642	h
-5.57026218512149	7.12292407494227	9.89695276943753	h
-4.84698016587153	0.82116065506692	-2.33708263478561	h
-3.06691298198688	-2.00258114636551	-2.22459505625176	h
-6.37412815478768	-2.17447380971953	-2.36844057792360	h
-3.37155056919089	-4.87285417624032	1.70623063798774	h
-4.99898979423393	-3.78636342120482	4.43299855877049	h
-6.70530091762545	-4.76887671751432	1.71737145647862	h
-8.11775561790053	-0.13852175487529	3.94109700415841	h
-7.65135017077185	2.11841188279924	1.49798441006399	h
-9.03539758311086	-0.86410749832899	0.82382516205584	h
2.89833303172698	1.97269276437012	-2.76394519780393	h
0.94962660601931	4.69381925142414	-2.84678635947833	h
4.27130193573296	4.93246577235126	-3.29505281306351	h

1.27636924473276	8.07967632755727	0.70399842180835	h
3.80426493925488	7.82296158545226	2.90146085622539	h
4.46219430972933	8.12854838266884	-0.34810591908158	h
6.02496359389705	3.60598768191716	3.48784450620482	h
6.07756499031602	1.43109008598720	0.92701839170729	h
7.26258769171119	4.51790897177243	0.50726821159943	h
0.23378135683741	-4.18975924143390	3.40580712238773	h
3.64694657063416	-2.57867515729611	1.64176148952392	c
5.33908706608690	-3.30137692149609	0.73457589353515	h
3.98856863432022	-1.40224685556896	3.28616266113906	h
0.01795565169168	-6.24968997199134	-2.40466709837723	c
1.15028498497974	-3.81760173110285	-3.91825451399798	b
3.33748486748580	-7.26391544975528	-0.18217061888361	h
0.45603096614537	-8.19145372004427	1.21183749405708	h
0.13324015444306	-7.94845387520650	-3.57998511701194	h
-1.98880646581264	-5.96556704966718	-1.99653386609133	h
-0.53205658073091	-2.56144698958772	-6.14870505858377	c
4.03491955707865	-4.32577514872515	-4.92558390071919	c
6.27459252370279	-3.00802163552264	-4.47837089790549	c
8.61935955067445	-3.69402229342070	-5.46503021368974	c
8.80577609822174	-5.78150538251718	-7.04623920486753	c
6.62239254764008	-7.12650614272268	-7.62757050963131	c
4.32787585770312	-6.37468824768520	-6.58512911181856	c
6.29275396340398	-0.87755136379449	-3.05072097025404	f
10.69748270334430	-2.33191981144503	-4.91582001726838	f
11.04425234850380	-6.47037843327506	-8.01935868041325	f
6.74654992420646	-9.12025750306060	-9.19958440930940	f
2.27848398419463	-7.72346859699416	-7.32899968117076	f
0.34285183814193	-0.47056157759056	-7.51474674311976	c
-0.96554008993493	0.66525430084107	-9.49126333569102	c
-3.28589406151225	-0.32703373161571	-10.23135115284920	c
-4.22755469984673	-2.43734781182453	-8.97950096970390	c
-2.85245966281384	-3.50530920637792	-7.00375975504857	c
2.60580018797557	0.57257858936833	-6.93079254786098	f
-0.01259085758868	2.69375062237878	-10.69312091959610	f
-4.58938451316437	0.73064434634350	-12.13136100678020	f

-6.46154739139742	-3.42800388437484	-9.68513615193693	f
-3.91688056612038	-5.56548075876849	-5.92547879675358	f

6b:

-2.06813136615366	1.73112085401689	3.36602612142679	c
0.35235823182511	1.82212097008082	2.29885704970546	c
0.89473595675609	0.33440858612518	0.11858690748370	c
-1.05198271236702	-1.23063272209294	-0.89886373676542	c
-3.42502283788542	-1.22408454040858	0.27556430811151	c
-3.99011308479230	0.22882165080393	2.39487503853996	c
-2.45280677670655	2.88604879790827	5.02480109656642	h
4.13225597473315	0.78652804975403	-1.11972942923179	p
-4.88952727139529	-2.42519601889574	-0.52594183145430	h
-6.59171254046323	0.18285447146164	3.59737415254200	c
-7.25836086000978	-2.47078290652989	4.58449905394866	c
-6.53616722862129	1.47435022338043	5.22048770944118	h
-8.62703138117856	1.14433175877342	1.75471479523092	c
-7.35168564406019	-3.83243459436969	3.02728514388480	h
-5.83948748601214	-3.13987268368509	5.93260632918149	h
-9.10216076316613	-2.45233671642872	5.52670358120522	h
-8.18568603677982	3.05289808054245	1.09076754748002	h
-8.76210667928152	-0.09229788330691	0.09933102408199	h
-10.48085167178202	1.18185466915523	2.67640473868296	h
-0.91484660979227	-3.09331551914831	-3.11710990552895	c
0.22432109573088	-2.15590653828316	-5.61149127395630	c
0.21095220537583	-5.65371422115062	-2.29737082147429	c
-2.90651057504093	-3.48169108891431	-3.54445291302645	h
-0.65202123439116	-0.37923539544668	-6.20541166074356	h
2.26204027553600	-1.88569823862396	-5.50862882933913	h
-0.14745260229615	-3.56779531817826	-7.08184579526771	h
2.22321943914181	-5.50132776689112	-1.88181925794274	h
-0.75765387478374	-6.36632561310076	-0.61359724481571	h
-0.02083573230663	-7.03895133889628	-3.82033607354745	h
2.18898351236530	3.58577316597011	3.69203711726879	c
3.07624418326890	5.89229835040039	2.15127591233347	c
1.04205157457061	4.36299921594687	5.23479129202864	h

4.40756844214921	2.21235018927008	4.98566937852493	c
4.44523968507506	5.36869951409054	0.69670065023689	h
1.47229399344072	6.82714790957538	1.23662292278333	h
3.98192695083694	7.25719803351602	3.42046874699867	h
3.72212413955966	0.61944120971201	6.11535931073526	h
5.76937021699460	1.50616667955129	3.60320002045217	h
5.39056275325432	3.52708174949733	6.25014067635530	h
5.56465533285103	3.10809491280443	-5.66219038393467	c
3.69377727977643	2.41033273497141	-4.10690714168030	c
7.53055734419510	2.64047176994319	-5.29575949907242	h
5.18133199947902	4.19000084974161	-7.36570835440918	h
1.76761748951313	2.99938882855655	-4.52399096094449	h
6.80278242516915	-2.98313511541617	-3.84020464065010	c
5.49269292114807	-2.26826389983341	-1.79768630583198	c
6.91940958855598	-1.81273339417643	-5.52401187555599	h
7.79206584344776	-4.78169220251801	-3.89092398879006	h
5.47101611451604	-3.49535950925433	-0.14116870126733	h

4b:

-4.21959065459353	0.95878052627711	3.23969344562522	c
-1.84742008173420	0.29549277618835	2.28531463082781	c
-1.71979599078720	-0.89757980388304	-0.10428694885468	c
-3.97414863385953	-1.55049821560347	-1.39671414702704	c
-6.28632969029275	-0.84010142813126	-0.35165536667953	c
-6.45406786496269	0.45416576997251	1.94155004473904	c
-4.33030402463191	1.88998814143603	5.06734881909407	h
1.32744267667380	-1.44224862791152	-1.62815452661679	p
-8.01005357964381	-1.32939041193769	-1.35766806705849	h
-8.98918805970096	1.25374069243258	3.01257593694439	c
-10.70678618529635	-1.03911068615708	3.51534865151169	c
-8.61891408353647	2.18689303131919	4.82763999081912	h
-10.30234668427673	3.17435732950573	1.26572087492627	c
-11.15509470126031	-2.02663352555248	1.75142503972204	h
-9.79362230639494	-2.38879236439798	4.78927677478912	h
-12.48978053588223	-0.43087080863092	4.37309155786734	h
-9.10284368782326	4.82786940698262	0.94360997497190	h

-10.72541562005575	2.32346997774147	-0.57429332434888	h
-12.08680224714550	3.80939494723072	2.10088290106027	h
-4.00991746233270	-3.10731811307507	-3.81408440733155	c
-5.25458967741729	-5.69441177313657	-3.32900081520729	c
-5.32276105628581	-1.71361399602770	-6.00067153213617	c
-2.06237618808178	-3.49179420864962	-4.38150245521371	h
-4.27417401710753	-6.71224170437345	-1.81915761033140	h
-7.23561954869848	-5.47269921122889	-2.77240520900003	h
-5.19302510924924	-6.85050780672906	-5.04520263594728	h
-7.32347298238235	-1.39220980631530	-5.57926652859159	h
-4.44790808516353	0.12621411749835	-6.35360468983689	h
-5.21247698397755	-2.83519602293240	-7.73677857184963	h
0.46055760138772	0.67134276049319	3.94723446745614	c
0.59268580698268	-1.48242372530713	5.90728705188173	c
2.14095246470882	0.53306348871648	2.75386369264015	h
0.52876028670590	3.24911038221372	5.27614024400310	c
-1.04420040166877	-1.40325087635314	7.17318713007205	h
0.60362484132479	-3.33464907225971	4.98891481572710	h
2.31312381286347	-1.31357253590610	7.04313804611516	h
0.29874336735789	4.79618105687364	3.92692634557256	h
-0.96186754874732	3.41003337128253	6.70322952727482	h
2.34074093385079	3.48928886348723	6.24371991410175	h
4.03964828872886	0.69833647048042	-4.85373026193396	c
1.40350415237569	-0.58814480667599	-4.99543957569125	c
5.45609261569663	-0.50434995377704	-5.75758221500420	h
4.06754896393392	2.51805029458111	-5.83202738090943	h
1.24586899924848	-2.19829198568276	-6.28172511123375	h
3.16616780512937	-6.14999316531992	-3.11579441859238	c
1.96315665551721	-4.78541154311319	-1.36674605547153	c
3.79791206596946	-5.34418396396137	-4.89564888300418	h
3.57284610176116	-8.13992485496686	-2.81497570682782	h
1.39664391456729	-5.64006823519261	0.41436530812863	h
-0.12201863430282	0.73214879516977	-5.40737299863779	h
4.54040919846024	0.86801046857179	-1.76085845166738	b
9.37779740141174	-3.76966522249012	1.64990006755895	c
11.56233197675845	-3.36222719134019	0.24486430418933	c

11.52247202491320	-1.59514527217067	-1.70488055780979	c
9.29295391368697	-0.29924549010154	-2.22048474730551	c
7.03838672727298	-0.66184478124462	-0.89114588208387	c
7.20375908314168	-2.40821442727836	1.07054262801341	c
9.39170663141561	-5.45546502968159	3.55718552107663	f
13.68839442900510	-4.64348260109593	0.77414468849781	f
13.63530127038750	-1.15124965147181	-3.04901668638538	f
9.39168336609513	1.45148138865331	-4.09017936346594	f
5.16915368291867	-2.84145016598408	2.58067591268690	f
5.43250871896299	7.10531397704620	2.31578715595948	c
3.45164037931262	8.61271872876982	1.47588881146804	c
1.77847890968143	7.64242272140136	-0.30715756365159	c
2.14875322102325	5.20562055128995	-1.21470696685719	c
4.12370941965581	3.60990423409187	-0.47229182666383	c
5.72069425297757	4.66852731197168	1.35557703130555	c
7.03854875777883	8.00287563859789	4.06992624298941	f
3.13385566158666	10.95382212669584	2.39546530015814	f
-0.17679051771112	9.05530653829480	-1.11257671676570	f
0.41634109983195	4.37291592261827	-2.91716825857059	f
7.67880136394219	3.34063125816334	2.32451361478924	f

4b (ROTAMER):

-5.29818405662586	1.02328154956859	3.29351157579230	c
-3.06942922760257	1.39963426546334	1.92689659580886	c
-2.61001568678704	-0.03991530809423	-0.30658034340497	c
-4.59824621224991	-1.62725521447206	-1.22203368611982	c
-6.77555987066320	-1.90591187078398	0.25973713919382	c
-7.15311407280941	-0.68042431278277	2.55118951261954	c
-5.58526837148634	2.12913271055197	5.00387553426076	h
0.65554651889322	-0.08585429923708	-1.62304869486785	p
-8.26070308233832	-3.12702313132421	-0.47142985765495	h
-9.52165763978055	-1.08618010877547	4.11016195773923	c
-9.76862436488808	-3.86110577605794	4.94599417738067	c
-9.33897019364757	0.08463992353187	5.81294737864461	h
-11.89888886698730	-0.21726009222980	2.67531581269892	c
-9.97289840951314	-5.10767881188187	3.30512989358009	h

-8.10146148341531	-4.46998471289287	6.00760415229888	h
-11.43716345229857	-4.10871014759779	6.14587442133274	h
-11.74756808662282	1.76881061328152	2.11799372014992	h
-12.17644203181282	-1.34421435053526	0.96062425732909	h
-13.58015537497964	-0.43921006831069	3.86247040119054	h
-4.88319037686415	-3.05188014252872	-3.74470167311134	c
-3.56351122442153	-1.99013918446811	-6.08819774467549	c
-4.47271027394566	-5.92563490951863	-3.47543575581682	c
-6.90869177681910	-2.82914563459822	-4.13315181599326	h
-3.72292009408447	0.06984328213567	-6.17410928676048	h
-1.57681541466792	-2.52059867861942	-6.16846613230206	h
-4.47852714006657	-2.76848513320520	-7.77454590774005	h
-2.49256107732287	-6.38450677414534	-3.13864890029795	h
-5.59444703866416	-6.68095213208961	-1.91040344777369	h
-5.06539612689939	-6.87838878194403	-5.21613886153124	h
-1.37748375244884	3.47214285701794	3.00199021385753	c
-0.67960010229680	5.46355924827425	1.01690047754181	c
-2.57725454861637	4.44920714654478	4.38158180364976	h
0.88511395259575	2.44440643478048	4.50031844515635	c
0.49879686600752	4.67803265095580	-0.48126162214417	h
-2.38556340321999	6.24171994385593	0.14258040904495	h
0.37501018402172	7.01274084360945	1.89260036451155	h
0.22918131194537	1.19655031834749	6.01418547445378	h
2.16683859787407	1.36670515597115	3.30546388594892	h
1.93802296674072	4.00593394921858	5.35828574002291	h
4.26233234518267	1.39157898777847	-4.40914865139888	c
1.34952775951759	1.51120955392011	-4.63713623700504	c
4.95549475587293	-0.32440779231139	-5.32221265315244	h
5.15744674880350	2.98199987743051	-5.37356266221919	h
0.54738555836482	0.68206575957812	-6.34310196039205	h
2.28714867264596	-4.58223151781482	-4.02120912308065	c
1.16172931269514	-3.42679008157630	-2.08142660091617	c
2.88880051784774	-3.58655818962026	-5.71048086118641	h
2.63624584901336	-6.60567948481903	-3.98418207032616	h
0.61188732899791	-4.52566686116806	-0.43171879264077	h
0.67745273105556	3.45739065842654	-4.46760172384507	h

4.88586029121588	1.27510252602869	-1.39040150636691	b
7.48892971580652	-5.05511281190987	1.73044466194113	c
9.68905136232985	-5.41886239593990	0.33405648124091	c
10.35552800778841	-3.65121289463698	-1.49582191246534	c
8.79031331389506	-1.57557973712260	-1.90023484977480	c
6.55166615026932	-1.13841964833574	-0.57072090838841	c
5.99937796159641	-2.93882573917235	1.27086844380165	c
6.82856323762964	-6.74995459400835	3.51024759615501	f
11.15781384255497	-7.44410618458790	0.75890324870251	f
12.49470731443908	-3.95812556175163	-2.83604049393763	f
9.54748145580967	0.10927888533403	-3.68125217164160	f
3.90193946058630	-2.69700317690555	2.72332633655684	f
7.36031485688973	6.09454852704652	3.73043526938174	c
6.93629713092495	8.42701502085550	2.59494854516975	c
5.78798735404801	8.50283103734635	0.23153670517290	c
5.09083880965244	6.25663546810253	-0.94115947724184	c
5.47205362258553	3.84411676072519	0.09824154826044	c
6.63705693861798	3.89365440726751	2.48560207729344	c
8.44974721359108	5.98961063214281	6.02321065599591	f
7.60609182190891	10.56860964065039	3.76692432834036	f
5.33535979213263	10.74269161178536	-0.88133701857689	f
3.92348319268890	6.54201497248310	-3.20245983026332	f
7.09859800980958	1.73230102776346	3.75738399279386	f

5b:

-0.37377430613973	-0.54628483223364	-0.88254451733385	p
0.21448828311373	3.03535381190100	-5.34421297883178	b
-2.87088954136191	0.34692044716322	-2.53781177891034	c
-4.69849299907823	0.11676139201515	-1.61662853603354	h
-2.61433262192405	1.71765280564883	-4.98751557008111	c
-4.22112844196497	3.00372518667289	-5.18405904328978	h
-2.79681679972711	0.32201691214916	-6.52463658951225	h
2.66749953209343	-0.29404580774086	-2.44052638373706	c
3.81556199346143	1.00224538640774	-1.30356364096139	h
3.56678728721690	-2.16012380060039	-2.34602883054190	h
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-0.62037659398896	-4.82056835129969	6.65199324674801	c
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-2.45385591143870	-7.81273920392808	4.61306522945067	h
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-5.51601334248107	-8.73012770404204	-1.38698368696499	h
-3.60917219748474	-4.58160603049561	-1.37052183597370	h
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-0.57358050291218	1.27827319644012	-2.80239490869135	h
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-0.64405623941465	-6.18074111474973	-0.91524946072859	h
-1.44291118456968	-3.59077744364564	2.80758787579630	h
-2.32980433482120	1.95587778293758	2.55364369036984	c
-2.00755681384110	3.98192703065110	2.80645691627932	h
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-3.79821156132717	3.02065371081849	-2.92280967436093	h
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-5.40615021791624	0.56794714111900	2.30173403918007	c
-7.41140911087651	0.49984280347022	1.80764026981998	h
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-2.86856823919484	-2.27390303481522	-0.16539289425741	c
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-3.73794509494625	-2.52682518650839	-2.03517712882435	h
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-3.26372868837148	5.49920968522815	-1.33096435785259	h
-0.33414614614030	-0.40110296542092	-0.91490480510904	b
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-7.62937352616341	3.69414712328878	2.73441488854610	c
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-8.18458114452018	2.57641437389146	4.38035775539695	h
-7.15990031249966	5.61020429610427	3.34509254388990	h

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