Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Direct synthesis of a geminal zwitterionic phosphonium/hydridoborate system – developing an alternative tool for generating frustrated *Lewis* pair hydrogen activation systems

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Supporting Information

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General Procedures

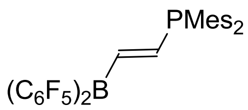
Standard Schlenk-type glassware (or glove box) was applied for the syntheses compounds involving air- and/or moisture-sensitive under an atmosphere of argon. Solvents were purified and stored under an argon atmosphere. NMR spectra were recorded on the following instruments: Agilent VNMRS 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{19}F: 470 MHz, ^{11}B: 160 MHz, ^{31}P: 202 MHz), Agilent DD2 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{19}F: 564 MHz, ^{11}B: 192 MHz, ^{31}P: 243 MHz). Bruker AV 400 (^{1}H: 400 MHz, ^{13}C: 101 MHz). ^{1}H NMR and ^{13}C NMR: chemical shift δ is given relative to TMS and referenced to the solvent signal. ^{19}F NMR: chemical shift δ is given relative to $CFCl_3$ (external reference); ^{11}B NMR: chemical shift δ is given relative to $BF_3{\cdot}Et_2O$ (external reference). NMR assignments are supported by additional 2D NMR experiments. Elemental analyses were performed on a Elementar Vario El III, while IR spectra Varian 3100 FT-IR (Excalibur Series) and melting points DSC Q20 (TA Instruments). Mass spectra were recorded by a MicroTof (Bruker Daltonics) machine. The methods used were the electron impact time of flight or the electrospray ionization time of flight. X-Ray diffraction: Data sets were collected with a Nonius Kappa CCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr*. **2003**, *A59*, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*. **1990**, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, 2000). Thermals ellipsoids are shown with 30% probability. *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: For the compounds **8** and **9** a badly disordered half pentane molecule was found in the asymmetrical unit and could not be satisfactorily refined. The compounds **13** and **14** crystallized with a badly disordered dichloromethane molecule in the asymmetrical unit. The program SQUEEZE (A. L. Spek, J. Appl. Cryst., 2003, 36, 7-13) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecule. Compound **12** crystallized with a disordered over two positions dichloromethane molecule. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. CCDC deposition numbers are 1034881 to 1034888 and 1045775.

Materials

Bis(pentafluorophenyl)borane (*Piers'* borane) was prepared according to the procedure described in the literature [Parks, D. J.; Spence, R. E. von H.; Piers, W. E. *Angew. Chem. Int. Ed.* **1995**, *34*, 809-811; Parks, D. J.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5492-5503.]. Dimesitylethynylphosphane (**4**) was prepared according to the procedure described in the literature [Zhao, X.; Lough, A. J.; Stephan, D. W. *Chem. Eur. J.* **2011**, *17*, 6731-6743.].

Preparation and Characterization of compounds

Synthesis of compound 5.



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Scheme S1

The combination of a toluene (2.0 mL) solution of dimesitylethynylphosphane (**4**) (206 mg, 0.70 mmol) with a toluene (2.0 mL) solution of bis(pentafluorophenyl)borane (242 mg, 0.70 mmol) give instantaneously a yellow solution. After stirring the reaction mixture at r.t. for 30 min, it was stored at r.t. overnight to obtain some deep yellow crystalline material. The solid was collected and dried *in vacuo* to give compound **5** (340 mg, 0.53 mmol, 76%). Single crystals of compound **5** suitable for the X-ray crystal structure analysis were obtained by storing a saturated toluene solution of compound **5** at r.t. for several days.

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 3012 (w), 2968 (w), 2924 (w), 2859 (w), 1645 (m), 1605 (m), 1518 (s), 1474 (s), 1381 (w), 1308 (w), 1216 (w), 1172 (w), 1137 (w), 1081 (w), 997 (w), 970 (m), 853 (w), 679 (w), 637 (w), 553 (w).

Melting point: 193 ºC.

Elemental analysis: calc. for $C_{32}H_{24}BF_{10}P$ (640.30 g/mol): C, 60.03; H, 3.78. Found: C, 59.96; H, 3.70.

^{1}H NMR (600 MHz, 299K, [d_2]-CH_2Cl_2): δ = 8.30 (dd, $^2J_{PH}$ = 29.0, $^3J_{HH}$ = 18.1 Hz, 1H, PCH), 6.91 (d, $^4J_{PH}$ = 2.5 Hz, 4H, *m*-Mes), 6.66 (dd, $^3J_{HH}$ = 18.1 Hz, $^3J_{PH}$ = 9.9 Hz, 1H, BCH), 2.29 (s, 12H, *o*-CH_3^{Mes}), 2.27 (s, 6H, *p*-CH_3^{Mes}).

^{13}C{^{1}H} NMR (151 MHz, 299K, [d_2]-CH_2Cl_2): δ = 172.1 (d, $^1J_{PC}$ = 19.9 Hz, PCH), 147.5 (dm, $^1J_{FC}$ ≈ 250 Hz, C_6F_5), 143.5 (d, $^2J_{PC}$ = 14.4 Hz, *o*-Mes), 142.8 (dm, $^1J_{FC}$ ≈ 250 Hz, C_6F_5), 140.5 (d, $^4J_{PC}$ = 1.2 Hz, *p*-Mes), 137.8 (dm, $^1J_{FC}$ ≈ 250 Hz, C_6F_5), 134.9 (br, BCH), 130.2 (d, $^3J_{PC}$ = 5.5 Hz, *m*-Mes), 127.2 (d, $^1J_{PH}$ = 3.1 Hz, *i*-Mes), 114.6 (br, *i*-C_6F_5), 23.1 (d, $^3J_{PC}$ = 12.9 Hz, *o*-CH_3^{Mes}), 21.1 (*p*-CH_3^{Mes}).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, [d_2]-CH_2Cl_2): δ^{1}H / δ^{13}C = 8.30 / 172.1 (PCH), 6.91 / 130.2 (*m*-Mes), 6.66 / 134.9 (BCH), 2.29 / 23.1 (*o*-CH_3^{Mes}), 2.27 / 21.1 (*p*-CH_3^{Mes}).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, [d_2]-CH_2Cl_2): δ^{1}H / δ^{13}C = 8.30 /

127.2 (PCH / *i*-Mes), 6.91 / 130.2, 127.2, 23.1, 21.1 (*m*-Mes / *m*-Mes, *i*-Mes, *o*-CH_3^{Mes}, *p*-CH_3^{Mes}), 6.66 / 172.1, 114.6 (BCH / PCH, *i*-C_6F_5), 2.29 / 143.5, 130.2, 127.2 (*o*-CH_3^{Mes} / *o*-Mes, *m*-Mes, *i*-Mes), 2.27 / 140.5, 130.2 (*p*-CH_3^{Mes} / *p*-Mes, *m*-Mes).

^{11}B{^{1}H} NMR (192 MHz, 299K, [d_2]-CH_2Cl_2): δ = 53.2 ($\nu_{1/2}$ ≈ 1300 Hz).

^{31}P NMR (243 MHz, 299K, [d_2]-CH_2Cl_2): δ = -7.7 (br d, $^{2}J_{PH}$ = 29.0 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299K, [d_2]-CH_2Cl_2): δ = -7.7 (t, J_{PF} ≈ 4 Hz).

^{31}P{^{1}H, ^{19}F} NMR (243 MHz, 299K, [d_2]-CH_2Cl_2): δ = -7.7 (s).

^{19}F NMR (564 MHz, 299K, [d_2]-CH_2Cl_2): δ = -130.3 (m, 2F, *o*-C_6F_5), -150.1 (br, 1F, *p*-C6F_5), -162.6 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 12.5].

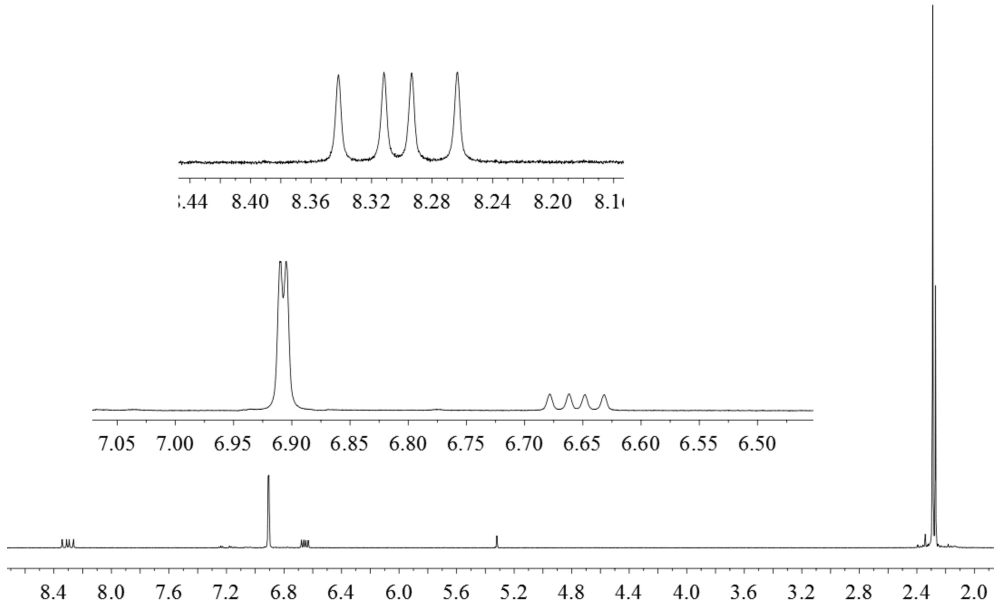


Figure S1 ^{1}H NMR (600 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **5**

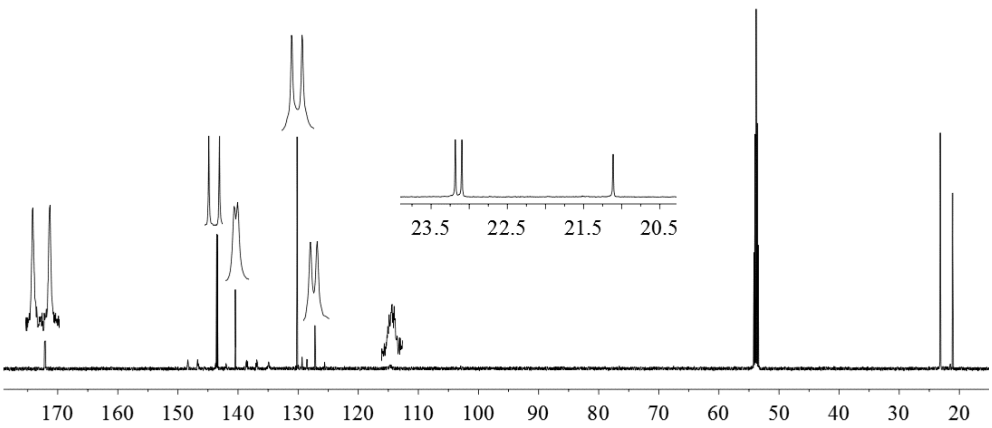


Figure S2 ^{13}C{^{1}H} NMR (151 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **5**

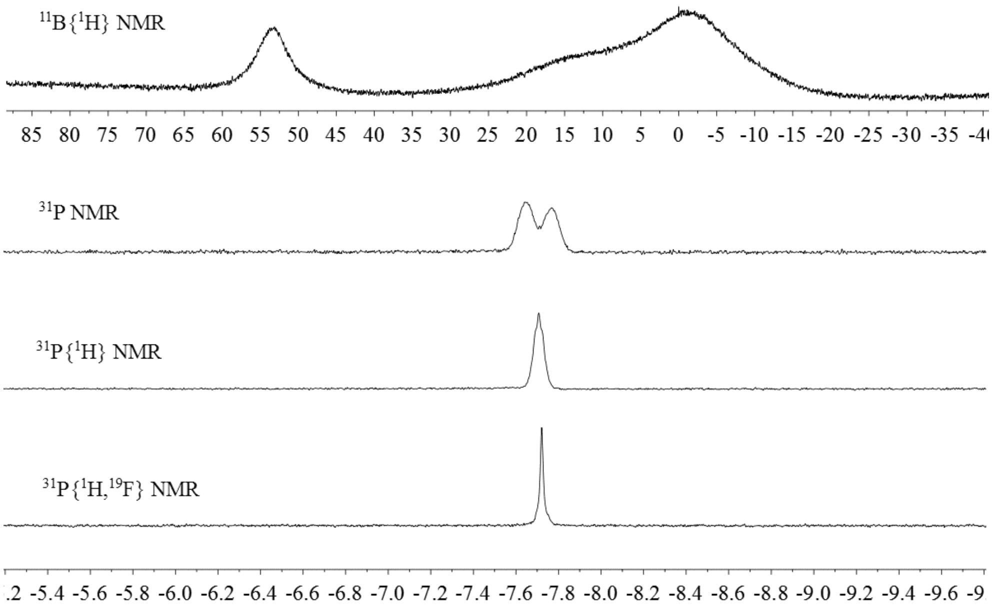


Figure S3 $^{11}B\{^{1}H\}$ NMR (192 MHz, 299K, [d_2]-CH_2Cl_2), ^{31}P and $^{31}P\{^{1}H\}$, $^{31}P\{^{1}H,^{19}F\}$ NMR (243 MHz, 299K, [d_2]-CH_2Cl_2) spectra of compound **5**

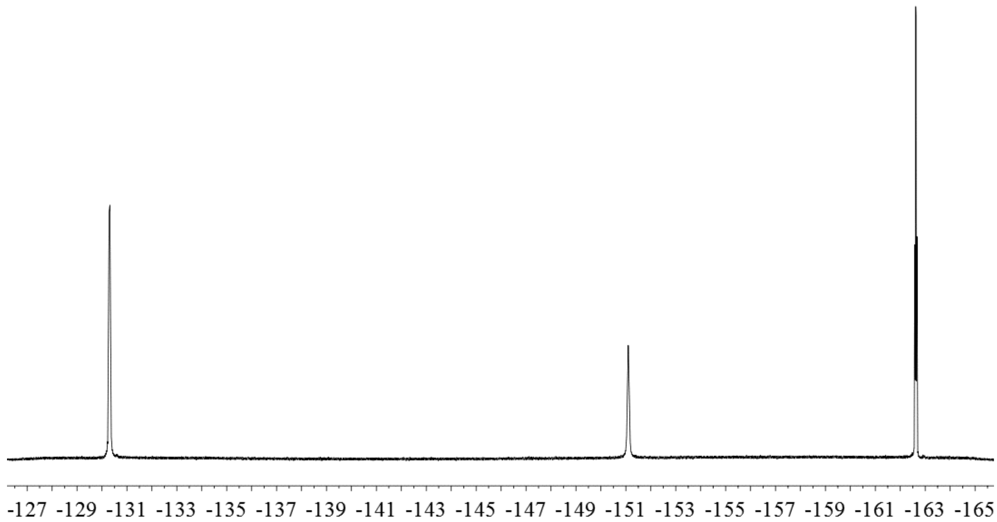


Figure S4 ^{19}F NMR (564 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **5**

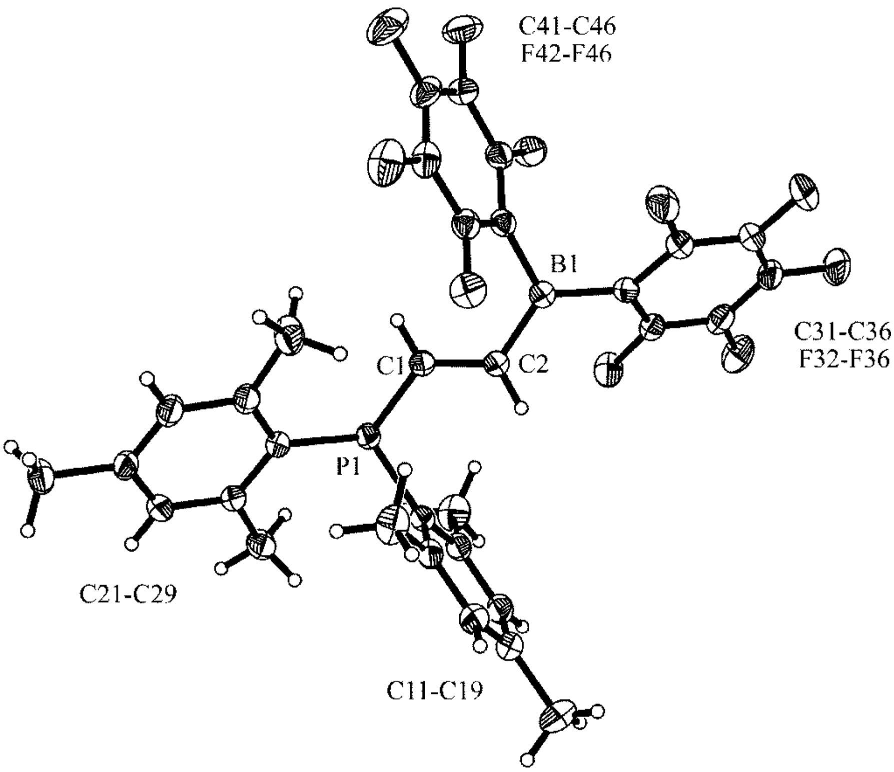
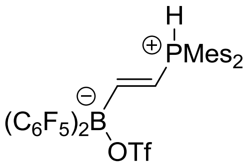


Figure S5 X-Ray crystal structure analysis of compound **5**: formula $C_{32}H_{24}BF_{10}P$, *M* = 640.29, yellow crystal, 0.30 x 0.17 x 0.10 mm, *a* = 7.7849(1), *b* = 22.0042(4), *c* = 17.4037(3) Å, *β* = 93.534(1) °, *V* = 2975.6(1) Å^3, ρ_{calc} = 1.322 gcm^{-3}, μ = 1.405 mm^{-1}, empirical absorption correction (0.694 ≤ T ≤ 0.872), *Z* = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, *T* = 223(2) K, ω and φ scans, 29825 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.67 Å^{-1}, 7331 independent (R_{int} = 0.055) and 5257 observed reflections [$I>2\sigma(I)$], 403 refined parameters, *R* = 0.058, wR^2 = 0.144, max. (min.) residual electron density 0.26 (-0.24) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Synthesis of compound 6.



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Scheme S2

Triflic acid (75 mg, 0.50 mmol) was added to a toluene solution (10 mL) of compound **5** (320 mg, 0.50 mmol). The reaction mixture was stirred at r.t. for 30 min to give a light yellow solution. Subsequently all volatiles were removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (2 mL). Then pentane (10 mL) was added to form a suspension. Compound **6** (260 mg, 0.33 mmol, 66%) was obtained as white powder after filtration of the suspension and drying of the residue *in vacuo* overnight. Single crystals of compound **6** suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **6** in CH_2Cl_2 at -30 °C.

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 2977 (w), 2928 (w), 1645 (w), 1605 (w), 1516 (m), 1468 (vs), 1350 (m), 1242 (m) 1216 (s), 1201 (s), 1100 (m), 1006 (w), 973 (m), 631 (s).

Melting point: 203 °C.

Elemental analysis: calc. for $C_{33}H_{25}BF_{13}O_3PS$ (790.38): C, 50.15; H, 3.19. Found: C, 49.92; H, 3.00.

^{1}H NMR (600 MHz, 299 K, [d_2]-CH_2Cl_2): δ = 7.90 (d, $^1J_{PH}$ = 475.3 Hz, 1H, PH), 7.67 (dd, $^3J_{PH}$ = 37.6, $^3J_{HH}$ = 19.0 Hz, 1H, BCH), 7.09 (d, $^4J_{PH}$ = 4.6 Hz, 4H, *m*-Mes), 6.43 (ddd, $^2J_{PH}$ = 36.6, $^3J_{HH}$ = 19.0, $^3J_{HH}$ = 2.6 Hz, 1H, PCH), 2.37 (s, 6H, *p*-CH_3^{Mes}), 2.31 (s, 12H, *o*-CH_3^{Mes}).

^{13}C{^{1}H} NMR (151 MHz, 299 K, [d_2]-CH_2Cl_2): δ = 174.1 (br, BCH), 148.0 (dm, $^1J_{FC}$ ≈ 240 Hz, C_6F_5), 146.7 (d, $^4J_{PC}$ = 2.8 Hz, *p*-Mes), 144.1 (d, $^2J_{PC}$ = 10.0 Hz, *o*-Mes), 140.2 (dm, $^1J_{FC}$ ≈ 250 Hz, C_6F_5), 137.3 (dm, $^1J_{FC}$ ≈ 250 Hz, C_6F_5), 132.1 (d, $^3J_{PC}$ = 11.2 Hz, *m*-Mes), 119.0 (d, $^1J_{FC}$ = 318.0 Hz, CF_3), 117.9 (br, *i*-C_6F_5), 111.2 (d, $^1J_{PC}$ = 86.0 Hz, *i*-Mes), 107.9 (d, $^1J_{PC}$ = 68.8 Hz, PCH), 21.9 (d, $^3J_{PC}$ = 8.2 Hz, *o*-CH_3^{Mes}), 21.5 (d, $^5J_{PC}$ = 1.3 Hz, *p*-CH_3^{Mes}).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, [d_2]-CH_2Cl_2): δ^{1}H / δ^{13}C = 7.67 / 174.1 (BCH), 7.09 / 132.1 (*m*-Mes), 6.43 / 107.9 (PCH), 2.37 / 21.5 (*p*-CH_3^{Mes}), 2.31 / 21.9 (*o*-CH_3^{Mes}).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, [d_2]-CH_2Cl_2) [selected traces]: δ^{1}H / δ^{13}C = 7.90 / 144.1, 111.2 (PH / *o*-Mes, *i*-Mes), 2.37 / 146.7, 132.1 (*p*-CH_3^{Mes} / *p*-Mes, *m*-Mes), 2.31 / 144.1, 132.1, 111.2 (*o*-CH_3^{Mes} / *o*-Mes, *m*-Mes, *i*-Mes).

^{11}B{^{1}H} NMR (192 MHz, 299K, [d_2]-CH_2Cl_2): δ = 0.7 ($\nu_{1/2} \approx$ 450 Hz).

^{31}P NMR (243 MHz, 299 K, [d_2]-CH_2Cl_2): δ = -16.8 (dt, $^{1}J_{PH} \approx$ 475 Hz, $^{2}J_{PH} \approx {}^{3}J_{PH} \approx$ 37 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, [d_2]-CH_2Cl_2): δ = -16.8 ($\nu_{1/2} \approx$ 10 Hz).

^{19}F NMR (564 MHz, 299 K, [d_2]-CH_2Cl_2): δ = -78.6 (s, 3F, CF_3), -133.6 (m, 4F, *o*-C_6F_5), -158.7 (t, $^{3}J_{FF}$ = 20.2 Hz, 2F, *p*-C_6F_5), -165.1 (m, 4F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 6.4].

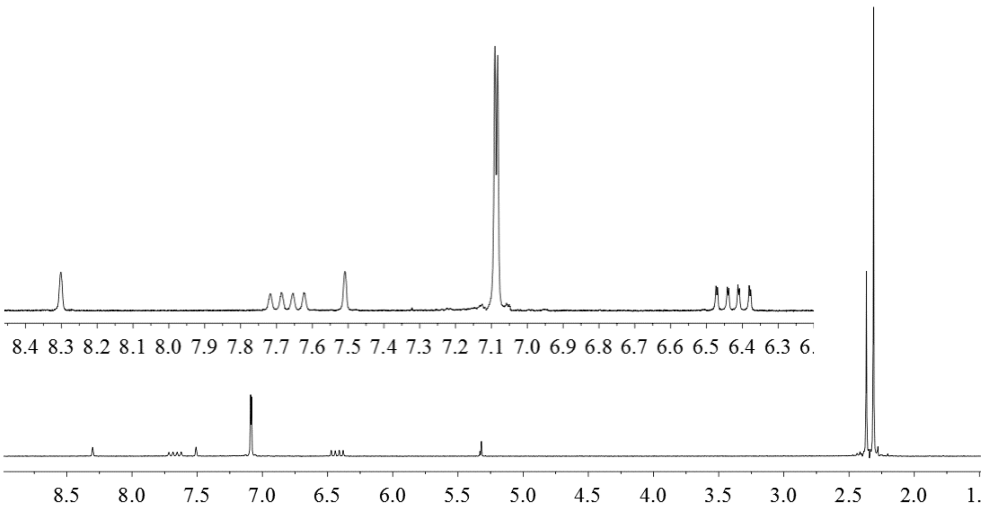


Figure S6 ^{1}H NMR (600 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **6**

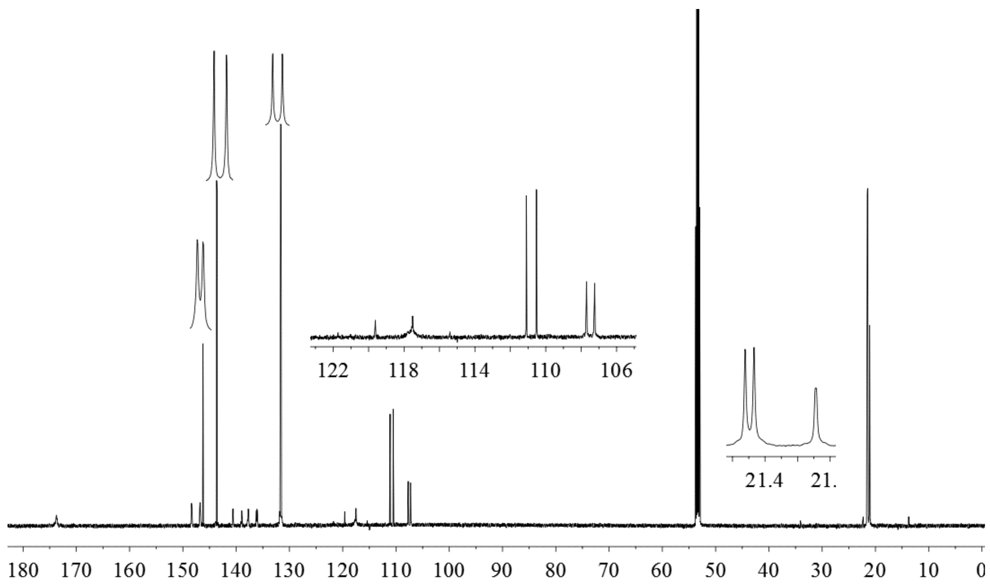


Figure S7 $^{13}C\{^{1}H\}$ NMR (151 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **6**

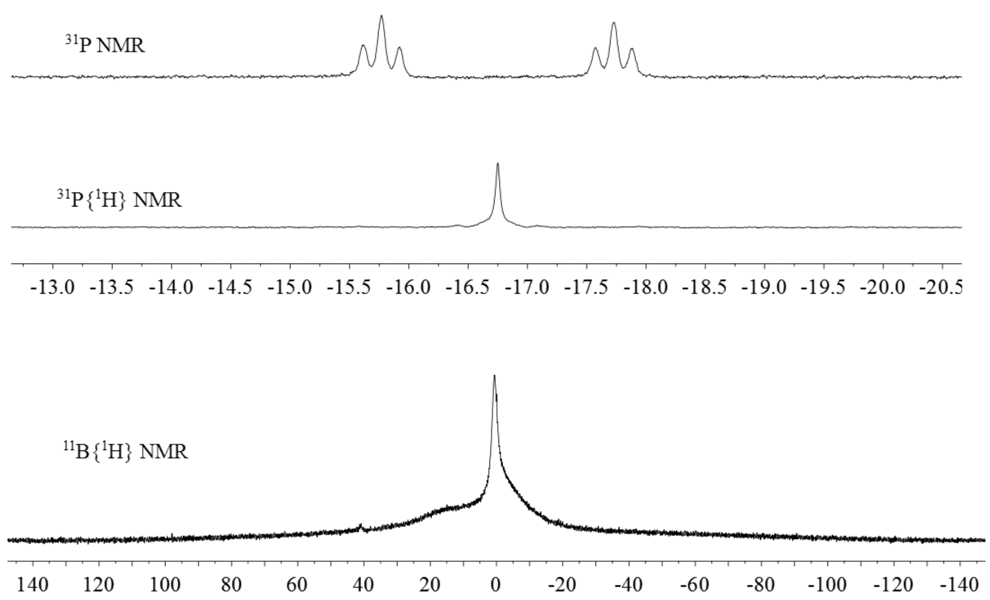


Figure S8 $^{11}B\{^{1}H\}$ NMR (192 MHz, 299K, [d_2]-CH_2Cl_2), ^{31}P and $^{31}P\{^{1}H\}$ NMR (243 MHz, 299K, [d_2]-CH_2Cl_2) spectra of compound **6**

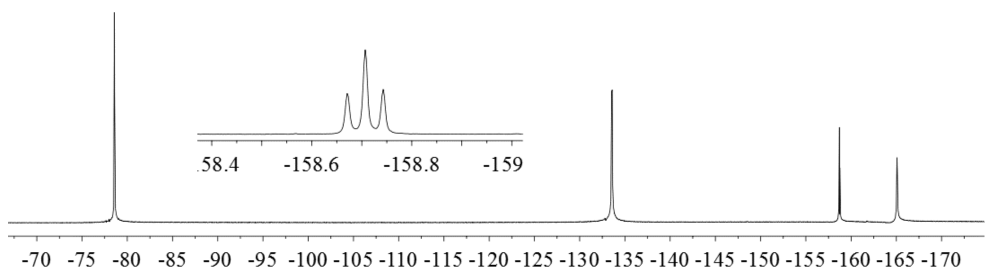


Figure S9 ^{19}F NMR (564 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **6**

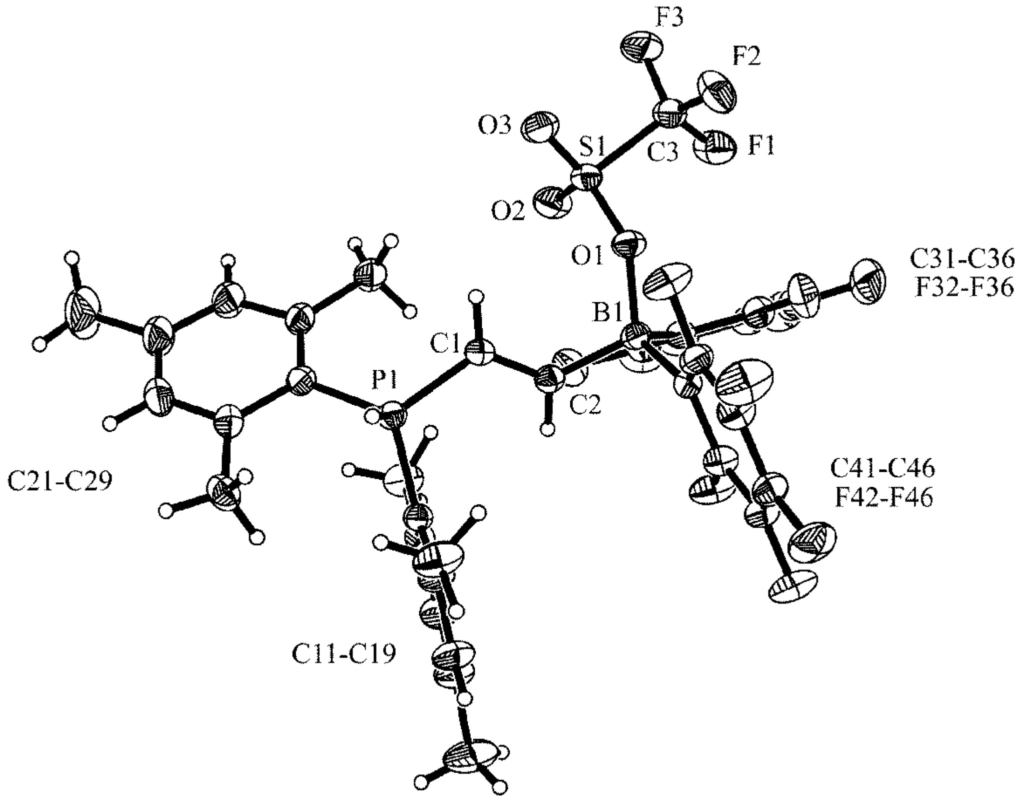
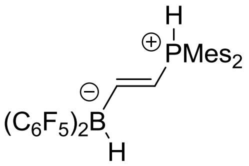


Figure S10 X-Ray crystal structure analysis of compound **6**: formula $C_{33}H_{25}BF_{13}O_3PS$, *M* = 790.37, colourless crystal, 0.24 x 0.18 x 0.14 mm, *a* = 10.8338(1), *b* = 16.5708(2), *c* = 19.0605(3) Å, *β* = 91.147(1) °, *V* = 3421.1(1) Å^3, ρ_{calc} = 1.535 gcm^{-3}, μ = 0.247 mm^{-1}, empirical absorption correction (0.943 ≤ T ≤ 0.966), *Z* = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, *T* = 223(2) K, ω and φ scans, 20225 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.62 Å^{-1}, 6883 independent (R_{int} = 0.037) and 5583 observed reflections [$I > 2\sigma(I)$], 479 refined parameters, *R* = 0.056, wR^2 = 0.138, max. (min.) residual electron density 0.35 (-0.35) e.Å^{-3}, the hydrogen at P1 atom was refined freely; others were calculated and refined as riding atoms.

Synthesis of compound 7.



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Scheme S3

Excess of $Me_2Si(H)Cl$ (0.2 mL, 1.8 mmol) was slowly added to a CH_2Cl_2 (4 mL) solution of compound **6** (320 mg, 0.40 mmol). Then the reaction mixture was stirred at r.t. for 1 h. Subsequently all volatiles were removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (2 mL). Then pentane (10 mL) was added to give a suspension. The solution was removed by cannula to give compound **7** (200 mg, 0.31 mmol, 78%) as white powder which was dried *in vacuo* overnight.

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 2963 (m), 2926 (m), 2325 (m, ν_{PH}/ν_{BH}), 1639 (w), 1605 (w), 1509 (s), 1464 (vs), 1274 (m), 1191 (w), 1097 (s), 969 (s), 819 (w), 649 (w).

Melting point: 139 °C.

Elemental analysis: calc. for $C_{32}H_{26}BF_{10}P$ (642.32): C, 59.84; H, 4.08. Found: C, 59.69; H, 3.96.

^{1}H NMR (500 MHz, 299 K, [d_2]-CH_2Cl_2): δ = 8.02 (dd, $^3J_{PH}$ = 37.9, $^3J_{HH}$ = 18.3 Hz, 1H, BCH), 7.82 (d, $^1J_{PH}$ = 469.3 Hz, 1H, PH), 7.05 (d, $^4J_{PH}$ = 4.6 Hz, 4H, *m*-Mes), 5.74 (dd, $^2J_{PC}$ = 41.1, $^3J_{HH}$ = 18.3 Hz, 1H, PCH), 3.24 (1:1:1:1 q partially relaxed, $^1J_{BH}$ ≈ 90 Hz, 1H, BH), 2.35 (s, 6H, *p*-CH_3^{Mes}), 2.33 (s, 12H, *o*-CH_3^{Mes}).

^{13}C{^{1}H} NMR (126 MHz, 299 K, [d_2]-CH_2Cl_2): δ = 189.1 (br, BCH), 148.0 (dm, $^1J_{FC}$ ≈ 230 Hz, C_6F_5), 145.9 (d, $^4J_{PC}$ = 2.8 Hz, *p*-Mes), 143.9 (d, $^2J_{PC}$ = 9.8 Hz, *o*-Mes), 138.5 (dm, $^1J_{FC}$ ≈ 250 Hz, C_6F_5), 137.1 (dm, $^1J_{FC}$ ≈ 240 Hz, C_6F_5), 131.9 (d, $^3J_{PC}$ = 11.0 Hz, *m*-Mes), 123.9 (br, *i*-C_6F_5), 112.8 (d, $^1J_{PC}$ = 84.9 Hz, *i*-Mes), 101.5 (d, $^1J_{PC}$ = 68.1 Hz, PCH), 21.9 (d, $^3J_{PC}$ = 8.0 Hz, *o*-CH_3^{Mes}), 21.5 (d, $^5J_{PC}$ = 1.4 Hz, *p*-CH_3^{Mes}).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, [d_2]-CH_2Cl_2): δ^{1}H / δ^{13}C = 8.02 / 189.1 (BCH), 7.05 / 131.9 (*m*-Mes), 5.74 / 101.5 (PCH), 2.35 / 21.5 (*p*-CH_3^{Mes}), 2.33 / 21.9 (*o*-CH_3^{Mes}).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, [d_2]-CH_2Cl_2) [selected traces]: δ^{1}H / δ^{13}C = 7.82 / 143.9 (PH / *o*-Mes), 2.35 / 145.9, 131.9 (*p*-CH_3^{Mes} / *p*-Mes, *m*-Mes), 2.33 / 143.9, 131.9, 112.8 (*o*-CH_3^{Mes} / *o*-Mes, *m*-Mes, *i*-Mes).

^{11}B NMR (160 MHz, 299K, [d_2]-CH_2Cl_2): δ = -21.6 (d, $^1J_{BH}$ = 89.0 Hz).

^{11}B{^{1}H} NMR (160 MHz, 299K, [d_2]-CH_2Cl_2): δ = -21.6 ($\nu_{1/2} \approx$ 60 Hz).

^{31}P NMR (202 MHz, 299 K, [d_2]-CH_2Cl_2): δ = -18.3 (br dm, $^1J_{PH} \approx$ 469 Hz).

^{31}P{^{1}H} NMR (202 MHz, 299 K, [d_2]-CH_2Cl_2): δ = -18.3 (1:1:1:1 q partially relaxed, $^3J_{PB} \approx$ 25 Hz).

^{19}F NMR (470 MHz, 299 K, [d_2]-CH_2Cl_2): δ = -134.0 (m, 2F, *o*-C_6F_5), -164.1 (t, 1F, $^3J_{FF}$ = 20.0 Hz, *p*-C_6F_5), -167.5 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 3.4].

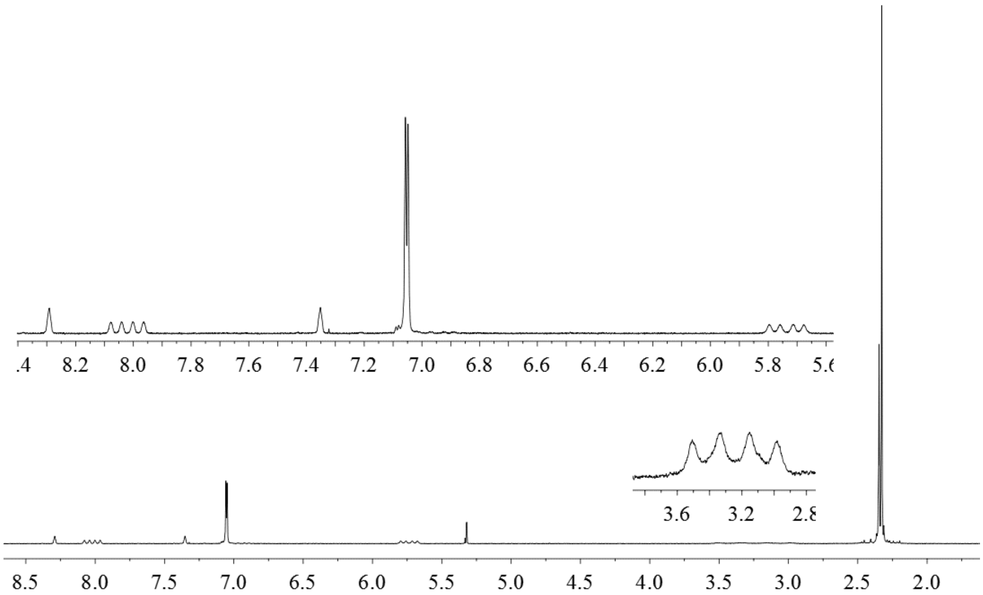


Figure S11 ^{1}H NMR (500 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **7**

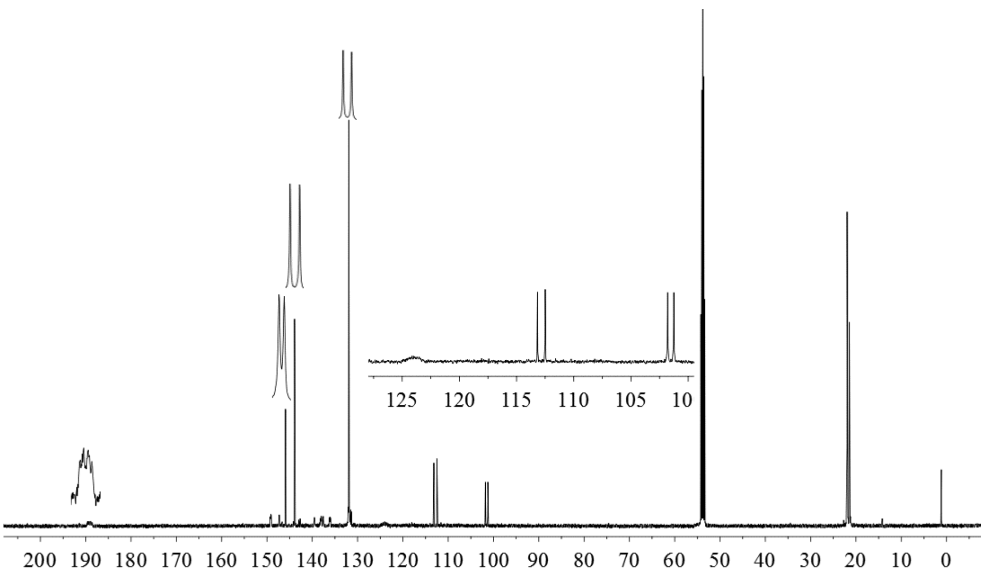


Figure S12 ^{13}C{^{1}H} NMR (126 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **7**

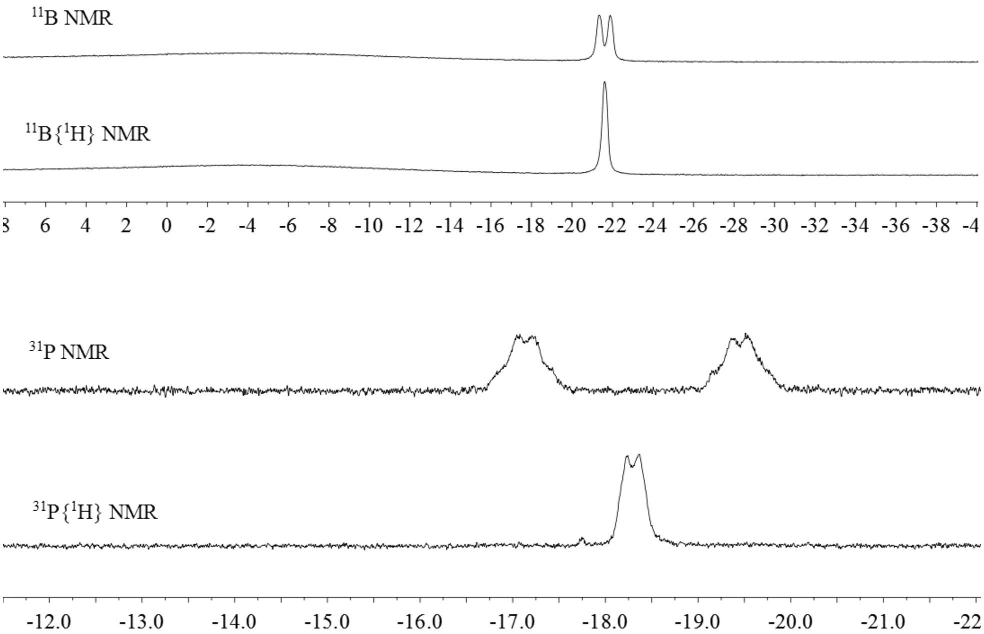


Figure S13 ^{11}B, ^{11}B{^{1}H} NMR (160 MHz, 299K, [d_2]-CH_2Cl_2), ^{31}P and ^{31}P{^{1}H} NMR (202 MHz, 299K, [d_2]-CH_2Cl_2) spectra of compound **7**

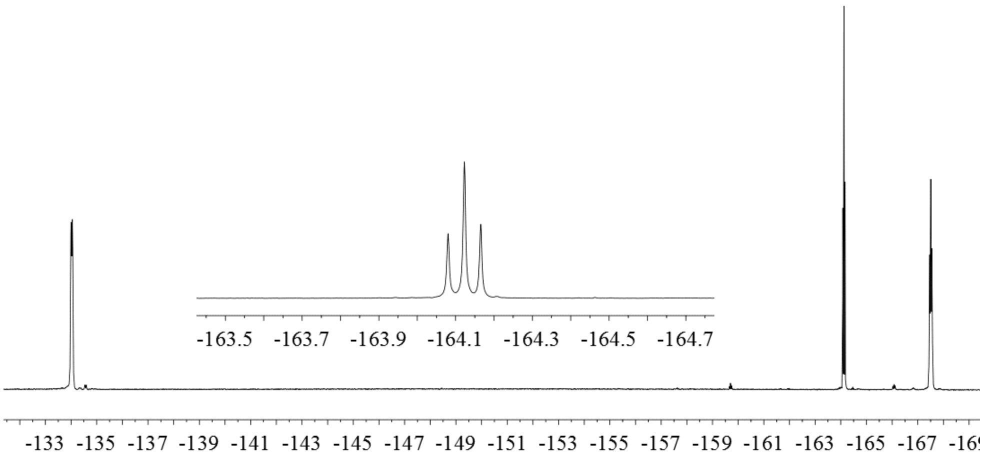
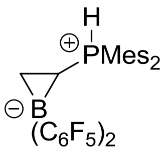


Figure S14 ^{19}F NMR (470 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **7**

Synthesis of compound 8.



8

Scheme S4

Heating a solution of compound **7** (200 mg, 0.31 mmol) in toluene (10 mL) at 110 °C for 30 min gave a deep yellow solution. Then all volatiles were removed *in vacuo* and the residue was dissolved in pentane (5 mL). Subsequently the solution was stored at -30 °C overnight to give yellow crystalline material. The solid was collected and dried *in vacuo* overnight to give compound **8** (150 mg, 0.23 mmol, 75%). Single crystals of compound **8** suitable for the X-ray crystal structure analysis were obtained by storing solution of compound **8** in pentane at -30 °C for several days.

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 2959 (w), 2927 (w), 2872 (w), 1643 (w), 1603 (w), 1512 (s), 1471 (vs), 1382 (w), 1250 (m), 1285 (w), 1250 (w), 1170 (w), 1116 (m), 1084 (w), 971 (s), 911 (w), 851 (w), 755 (w), 685 (w), 650 (w), 557 (w).

Melting point: 108 °C.

Elemental analysis: calc. for $C_{32}H_{26}BF_{10}P$ (642.32): C, 59.84; H, 4.08. Found: C, 59.51; H, 4.44.

^{1}H NMR (500 MHz, 299 K, [d_2]-CH_2Cl_2): δ = 6.97 (d, $^{4}J_{PH}$ = 4.1 Hz, 2H, *m*-Mes^{a}), 6.94 (dd, $^{1}J_{PH}$ = 464.4 Hz, $^{3}J_{HH}$ = 11.6 Hz, 1H, PH), 6.92 (d, $^{3}J_{PH}$ = 4.0 Hz, 2H, *m*-Mes^{b}), 2.41 (s, 6H, *o*-$CH_3^{Mes,b}$), 2.36 (s, 6H, *o*-$CH_3^{Mes,a}$), 2.32 (s, 3H, *p*-$CH_3^{Mes,a}$), 2.29 (s, 3H, *p*-$CH_3^{Mes,b}$), 1.17 (m, 1H, CH), 1.00 (dm, $^{3}J_{PH}$ = 30.8 Hz, 1H, CH_2), 0.85 (m, 1H, CH_2).

^{13}C{^{1}H} NMR (126 MHz, 299 K, [d_2]-CH_2Cl_2): δ = 144.2 (d, $^{4}J_{PC}$ = 2.7 Hz), 144.1 (d, $^{4}J_{PC}$ = 2.7 Hz) (*p*-Mes^{a,b}), 143.0 (d, $^{2}J_{PC}$ = 10.0 Hz, *o*-Mes^{a}), 142.7 (d, $^{2}J_{PC}$ = 9.5 Hz, *o*-Mes^{b}), 131.5 (d, $^{3}J_{PC}$ = 7.8 Hz, *m*-Mes^{a}), 131.4 (d, $^{3}J_{PC}$ = 7.6 Hz, *m*-Mes^{b}), 118.1 (d, $^{1}J_{PC}$ = 79.0 Hz, *i*-Mes^{b}), 117.8 (d, $^{2}J_{PC}$ = 78.3 Hz, *i*-Mes^{a}), 22.1 (d, $^{3}J_{PC}$ = 6.9 Hz, *o*-$CH_3^{Mes,b}$), 22.0 (d, $^{3}J_{PC}$ = 7.0 Hz, *o*-$CH_3^{Mes,a}$), 21.23 (d, $^{5}J_{PC}$ = 1.3 Hz, *p*-$CH_3^{Mes,a}$), 21.18 (d, $^{5}J_{PC}$ = 1.3 Hz, *p*-$CH_3^{Mes,b}$), 12.4 (br, CH_2), 4.2 (br d, $^{1}J_{PC}$ = 62.3 Hz, CH), [C_6F_5 not listed].

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, [d_2]-CH_2Cl_2): δ^{1}H / δ^{13}C =6.97, 6.92 / 131.5, 131.4 (*m*-Mes^{a,b}), 2.41 / 22.1 (*o*-$CH_3^{Mes,b}$), 2.36 / 22.0 (*o*-$CH_3^{Mes,a}$), 2.32 / 21.23 (*p*-$CH_3^{Mes,a}$), 2.29 / 21.18 (*p*-$CH_3^{Mes,b}$), 1.17 / 4.2 (CH), 1.00, 0.85 / 12.4 (CH_2).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, [d_2]-CH_2Cl_2) [selected traces]: δ^{1}H / δ^{13}C = 6.94 / 143.0, 142.7, 118.1, 117.8, 4.2 (PH / *o*-Mes^{a}, *o*-Mes^{b}, *i*-Mes^{b}, *i*-Mes^{a}, CH), 2.41 / 142.7, 131.4, 118.1 (*o*-$CH_3^{Mes,b}$ / *o*-Mes^{b}, *m*-Mes^{b}, *i*-Mes^{b}), 2.36 / 143.0, 131.5, 117.8 (*o*-$CH_3^{Mes,a}$ / *o*-Mes^{a}, *m*-Mes^{a}, *i*-Mes^{a}).

^{11}B{^{1}H} NMR (160 MHz, 299K, [d_2]-CH_2Cl_2): δ = -23.8 ($\nu_{1/2} \approx$ 60 Hz).

^{31}P NMR (202 MHz, 299 K, [d_2]-CH_2Cl_2) δ = -1.1 (br dd, $^{1}J_{PH} \approx$ 465 Hz, $^{2}J_{PH} \approx$ 31 Hz).

^{31}P{^{1}H} NMR (202 MHz, 299 K, [d_2]-CH_2Cl_2) δ = -1.1 ($\nu_{1/2} \approx$ 10 Hz).

^{19}F NMR (470 MHz, 299 K, [d_2]-CH_2Cl_2) δ = -130.9 (m, 2F, *o*), -160.5 (t, $^{3}J_{FF}$ = 20.1 Hz, 1F, *p*), -165.6 (m, 2F, *m*) (C_6F_5) [$\Delta\delta^{19}F_{mp}$ = 5.1]; -133.3 (m, *o*), -162.1 (t, $^{3}J_{FF}$ = 20.1 Hz, 1F, *p*), -166.4 (m, 2F, *m*) (C_6F_5) [$\Delta\delta^{19}F_{mp}$ = 4.3].

^{19}F,^{19}F GCOSY (470 MHz / 470 MHz, 299 K, [d_2]-CH_2Cl_2) δ^{19}F / δ^{19}F = -130.9 / -165.6 (*o* / *m*), -160.5 / -165.6 (*p* / *m*) (C_6F_5); -133.3 / -166.4 (*o* / *m*), -162.1 / -166.4 (*p* / *m*) (C_6F_5).

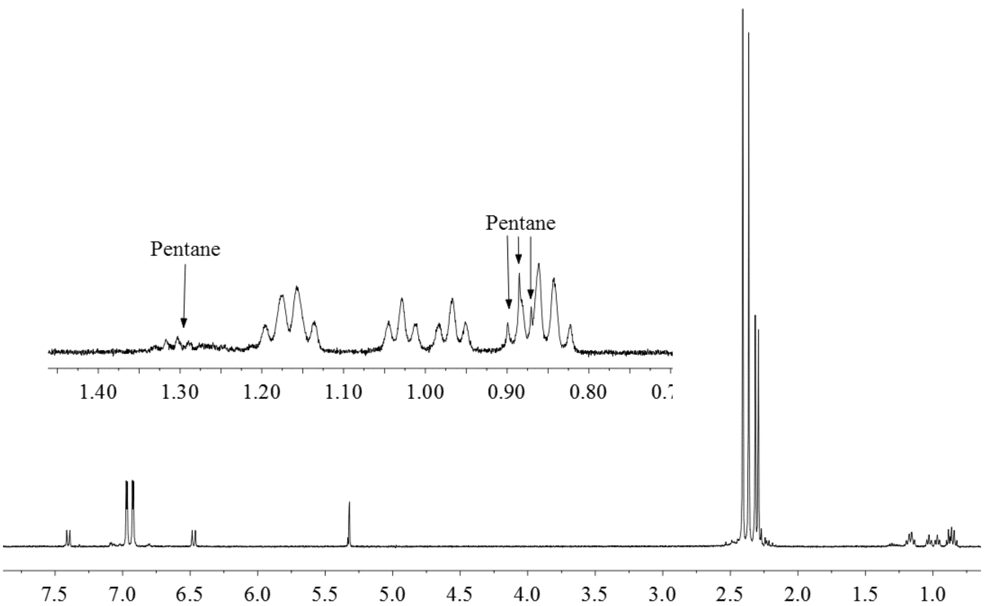


Figure S15 ^{1}H NMR (500 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **8**

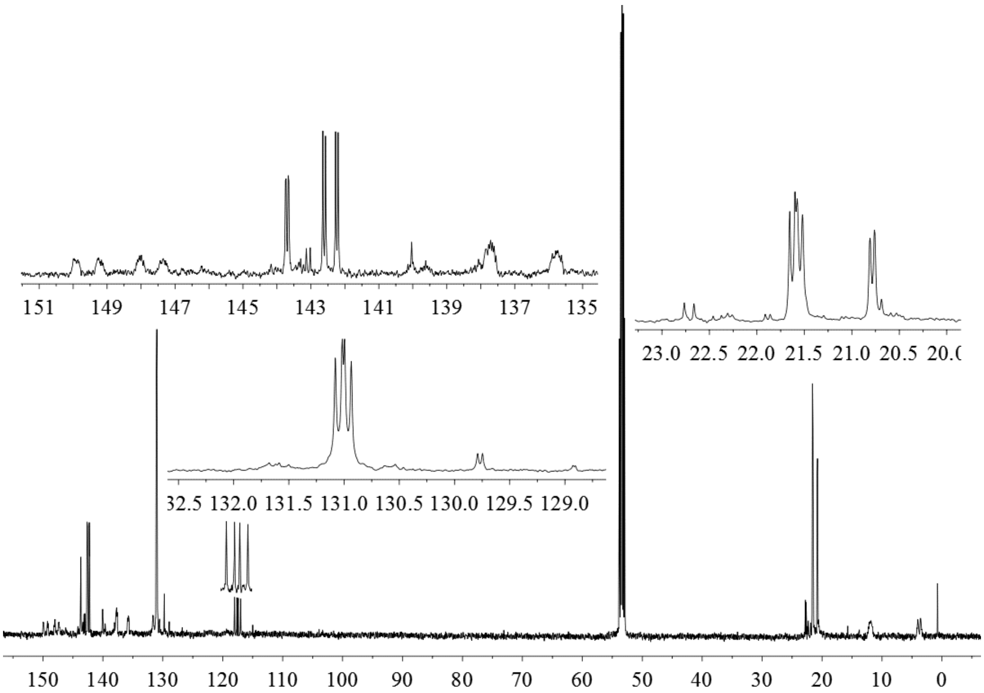


Figure S16 $^{13}C\{^1H\}$ NMR (126 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **8**

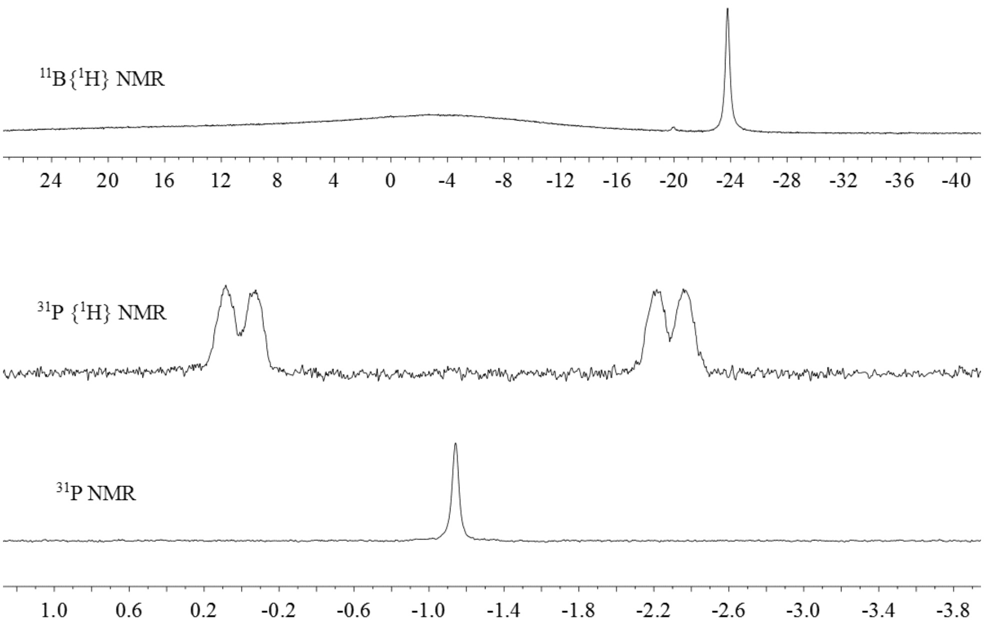


Figure S17 $^{11}B\{^1H\}$ NMR (160 MHz, 299K, [d_2]-CH_2Cl_2), ^{31}P and $^{31}P\{^1H\}$ NMR (202 MHz, 299K, [d_2]-CH_2Cl_2) spectra of compound **8**

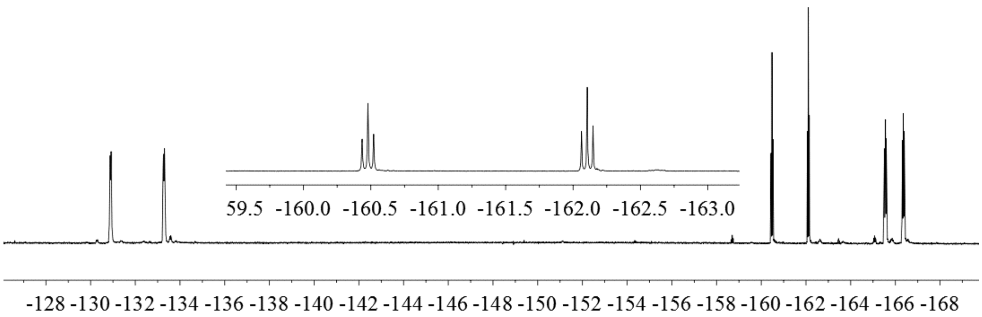


Figure S18 ^{19}F NMR (470 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **8**

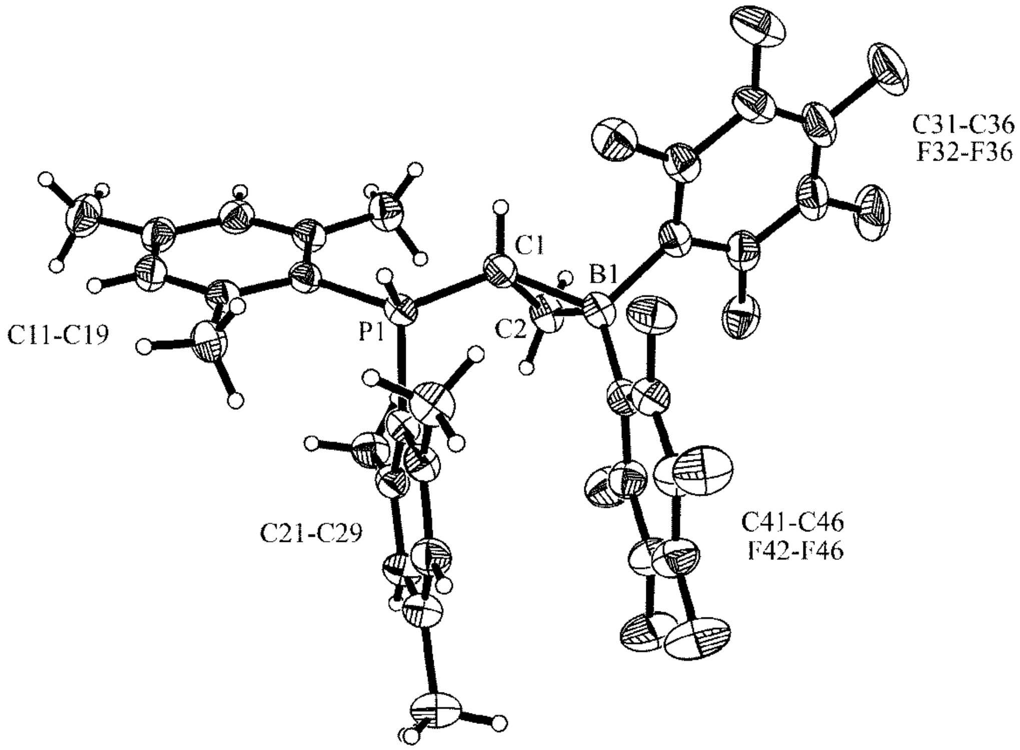
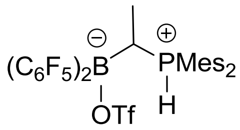


Figure S19 X-Ray crystal structure analysis of compound **8**: formula $C_{32}H_{26}BF_{10}P$, M = 642.31, colourless crystal, 0.22 x 0.12 x 0.06 mm, a = 9.8988(1), b = 12.2385(1), c = 13.9479(1) Å, α = 90.586(1), β = 107.262(1), γ = 99.498(1)°, V = 1588.4(1) Å^3, ρ_{calc} = 1.343 gcm^{-3}, μ = 1.485 mm^{-1}, empirical absorption correction (0.735 ≤ T ≤ 0.916), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 21483 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 5515 independent (R_{int} = 0.038) and 4932 observed reflections [I>2σ(I)], 407 refined parameters, R = 0.050, wR^2 = 0.155, max. (min.) residual electron density 0.36 (-0.33) e.Å^{-3}, the hydrogen at P1 atom was refined freely; others were calculated and refined as riding atoms.

Synthesis of compound 9.



9

Scheme S5

Triflic acid (30 mg, 0.20 mmol) was added to the CH_2Cl_2 (5 mL) solution of compound **8** (128 mg, 0.20 mmol). The color of the yellow solution disappeared immediately. After stirring the reaction mixture at r.t. for another 10 min, all volatiles were removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (1 mL) and then pentane (5 mL) was added. After storing this solution at -30 °C overnight, some colorless solid was obtained. The solid was collected and dried *in vacuo* overnight to give compound **9** (120 mg, 0.15 mmol, 75%). Single crystals of **9** suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **9** in CH_2Cl_2 at -30 °C.

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 2963 (w), 2921 (w), 1648 (w), 1607 (w), 1520 (m), 1470 (s), 1357 (m), 1241 (s), 1241 (m), 1212 (s), 1156 (m), 1096 (s), 1004 (m), 980 (s), 838 (w), 781 (w), 630 (m).

Melting point: 191 °C.

Elemental analysis: calc. for $C_{33}H_{27}BF_{13}O_3PS$ (792.39): C, 50.02; H, 3.43. Found: C, 49.91; H, 3.43.

^{1}H NMR (600 MHz, 273 K, [d_2]-CH_2Cl_2): 7.45 (dd, $^1J_{PH}$ = 469.0, $^3J_{HH}$ = 12.8 Hz, 1H, PH), 7.10 (d, $^4J_{PH}$ = 3.9 Hz, 1H, *m*-Mes^a), 7.02 (d, $^4J_{PH}$ = 2.6 Hz, 1H, *m'*-Mes^a), 6.99 (d, $^4J_{PH}$ = 4.7 Hz, 1H, *m*-Mes^b), 6.66 (s, 1H, *m'*-Mes^b), 3.72 (m, 1H, CH), 2.78 (s, 3H, *o*-$CH_3^{Mes,a}$), 2.65 (s, 3H, *o*-$CH_3^{Mes,b}$), 2.31 (s, 3H, *p*-$CH_3^{Mes,a}$), 2.29 (s, 3H, *o'*-$CH_3^{Mes,a}$), 2.24 (s, 3H, *o'*-$CH_3^{Mes,b}$), 2.23 (s, 3H, *p*-$CH_3^{Mes,b}$), 1.67 (dd, $^3J_{PH}$ = 24.2, $^3J_{HH}$ = 6.9 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 273 K, [d_2]-CH_2Cl_2): δ = 145.3 (d, $^4J_{PC}$ = 2.8 Hz, *p*-Mes^b), 145.1 (d, $^4J_{PC}$ = 2.8 Hz, *p*-Mes^a), 144.3 (d, $^2J_{PC}$ = 8.6 Hz, *o'*-Mes^a), 143.9 (d, $^2J_{PC}$ = 10.4 Hz, *o*-Mes^a), 143.8 (d, $^2J_{PC}$ = 7.8 Hz, *o*-Mes^b), 142.7 (d, $^2J_{PC}$ = 10.5 Hz, *o'*-Mes^b), 133.3 (d, $^3J_{PC}$ = 12.0 Hz, *m*-Mes^a), 132.1 (d, $^3J_{PC}$ = 9.7 Hz, *m'*-Mes^a), 131.0 (d, $^3J_{PC}$ = 11.0 Hz, *m'*-Mes^b), 130.9 (d, $^3J_{PC}$ = 10.3 Hz, *m*-Mes^b), 114.8 (d, $^1J_{PC}$ = 76.0 Hz, *i*-Mes^b), 111.6 (d, $^1J_{PC}$ = 76.5 Hz, *i*-Mes^a), 22.5 (d, $^3J_{PC}$ = 6.4 Hz, *o,o'*-$CH_3^{Mes,a}$), 22.3 (br d, $^{3}J_{PC}$ = 6.3 Hz, *o'*-$CH_3^{Mes,b}$), 21.7 (br d, $^{3}J_{PC}$ = 10.0 Hz, *o*-$CH_3^{Mes,b}$), 21.1 (d, $^{5}J_{PC}$ = 1.4 Hz, *p*-$CH_3^{Mes,a}$), 20.9 (d, $^{5}J_{PC}$ = 1.3 Hz, *p*-$CH_3^{Mes,b}$), 19.5 (br, CH), 14.9 (m, CH_3), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (600 MHz / 600 MHz, 273 K, [*d*$_2$]-CH_2Cl_2) [selected traces]: δ^{1}H / δ^{1}H = 7.10, 7.02 / 2.78, 2.31, 2.29 (*m,m'*-Mes^{a} / *o*-$CH_3^{Mes,a}$, *p*-$CH_3^{Mes,a}$, *o'*-$CH_3^{Mes,a}$), 6.99, 6.66 / 2.65, 2.29, 2.23 (*m,m'*-Mes^{b} / *o*-$CH_3^{Mes,b}$, *o'*-$CH_3^{Mes,b}$, *p*-$CH_3^{Mes,b}$).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 273 K, [*d*$_2$]-CH_2Cl_2): δ^{1}H / δ^{13}C = 7.10 / 133.3 (*m*-Mes^{a}), 7.02 / 132.1 (*m'*-Mes^{a}), 6.99 / 130.9 (*m*-Mes^{b}), 6.66 / 131.0 (*m'*-Mes^{b}), 3.72 / 19.5 (CH), 2.78, 2.29 / 22.4 (*o,o'*-$CH_3^{Mes,a}$), 2.65 / 21.7 (*o*-$CH_3^{Mes,b}$), 2.31 / 21.1 (*p*-$CH_3^{Mes,a}$), 2.24 / 22.3 (*o'*- $CH_3^{Mes,b}$), 2.23 / 20.9 (*p*-$CH_3^{Mes,b}$), 1.67 / 14.9 (CH_3).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 273 K, [*d*$_2$]-CH_2Cl_2) [selected traces]: δ^{1}H / δ^{13}C = 7.45 / 144.3, 143.9, 143.8, 142.7, 114.8, 111.6 (PH / *o,o'*-Mes^{a}, *o,o'*-Mes^{a}, *i*-Mes^{a,b}), 7.10 / 132.1, 111.6, 22.5 (*m*-Mes^{a} / *m'*-Mes^{a}, *i*-Mes^{a}, *o,o'*-$CH_3^{Mes,a}$), 6.99 / 131.0, 114.8, 22.3, 21.7 (*m*-Mes^{b} / *m*-Mes^{b}, *i*-Mes^{b}, *o'*-$CH_3^{Mes,b}$, *o*-$CH_3^{Mes,b}$).

^{11}B{^{1}H} NMR (192 MHz, 299K, [*d*$_2$]-CH_2Cl_2): δ = 3.6 (the peak is too broad for detection at low temperature).

^{31}P NMR (243 MHz, 273 K, [*d*$_2$]-CH_2Cl_2): δ = -1.2 (br d, $^{1}J_{PH}$ ≈ 470 Hz).

^{31}P{^{1}H} NMR (243 MHz, 273 K, [*d*$_2$]-CH_2Cl_2): δ = -1.2 ($\nu_{1/2}$ ≈ 15 Hz).

^{19}F NMR (564 MHz, 233 K, [*d*$_2$]-CH_2Cl_2): δ = -76.8 (s, 3F, CF_3), -131.5, -133.7, -134.0, -136.7 (each br, each 1F, *o*-C_6F_5), -157.6, -159.3 (each br, each 1F, *p*-C_6F_5), -163.3, -164.4, -164.7, -165.3 (each br, each 1F, *m*-C_6F_5).

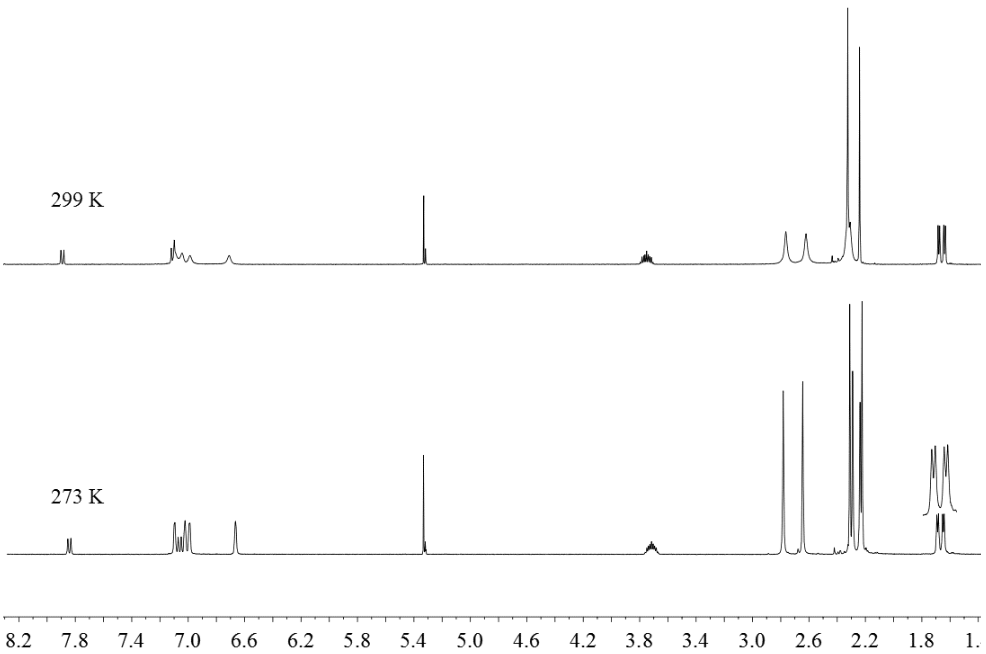


Figure S20 ^{1}H NMR (600 MHz, top:299K; bottom: 273K, [d_2]-CH_2Cl_2) spectra of compound **9**

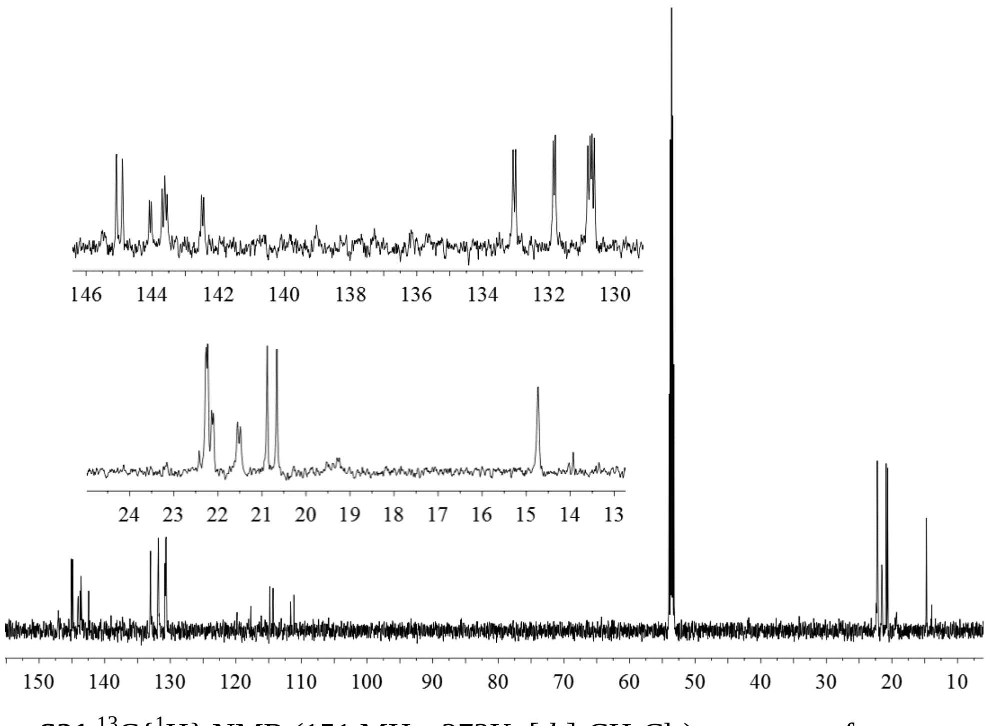


Figure S21 $^{13}C\{^{1}H\}$ NMR (151 MHz, 273K, [d_2]-CH_2Cl_2) spectrum of compound **9**

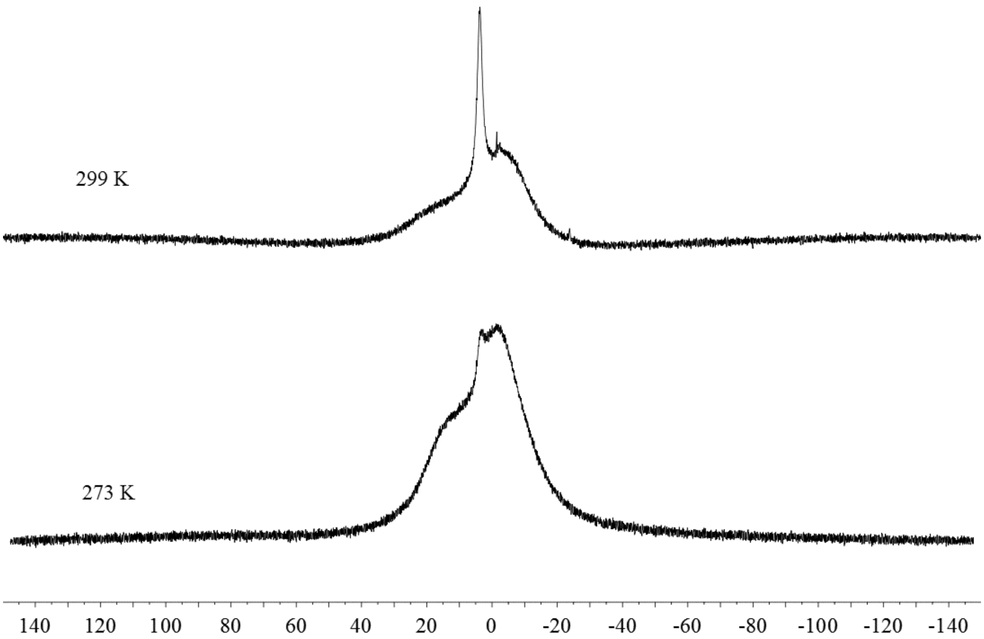


Figure S22 $^{11}B\{^1H\}$ NMR (192 MHz, top: 299K; bottom:273K, [d_2]-CH_2Cl_2) spectra of compound **9**

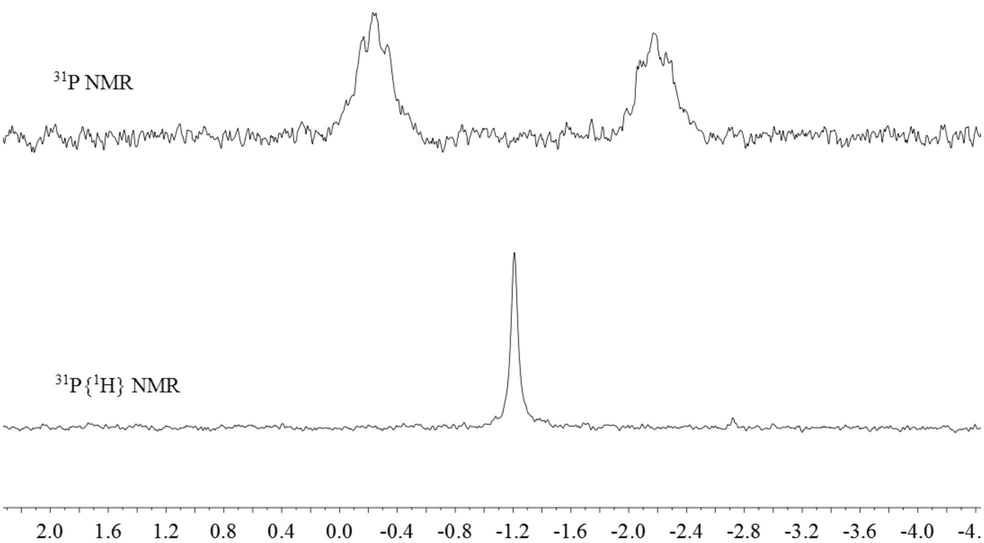


Figure S23 ^{31}P and $^{31}P\{^1H\}$ NMR (243 MHz, 273K, [d_2]-CH_2Cl_2) spectra of compound **9**

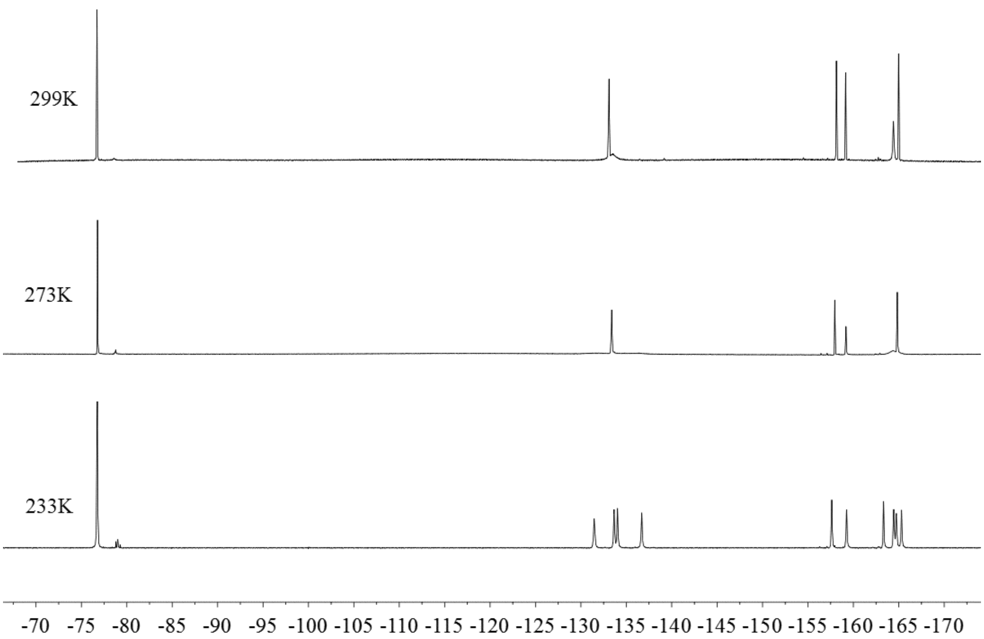


Figure S24 ^{19}F NMR (564 MHz, top: 299K; mid: 273K, bottom: 233K, [d_2]-CH_2Cl_2) spectra of compound **9**

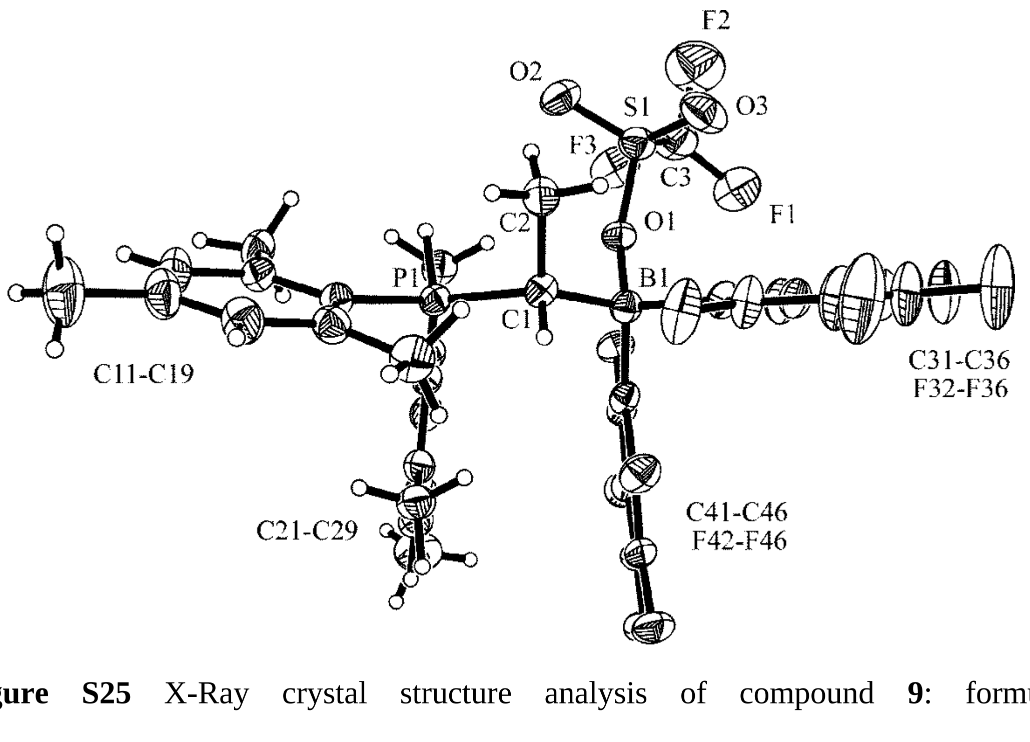
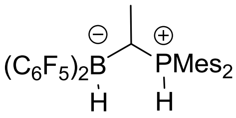


Figure S25 X-Ray crystal structure analysis of compound **9**: formula $C_{33}H_{27}BF_{13}O_3PS$, *M* = 792.39, colourless crystal, 0.16 x 0.09 x 0.03 mm, *a* = 13.0550(5), *b* = 18.7048(8), *c* = 15.4615(6) Å, *β* = 103.848(3) °, *V* = 3665.8(3) Å^3, ρ_{calc} = 1.436 gcm^{-3}, μ = 2.102 mm^{-1}, empirical absorption correction (0.729 ≤ T ≤

0.939), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 26571 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 $Å^{-1}$, 6159 independent (R_{int} = 0.092) and 3853 observed reflections [I>2σ(I)], 508 refined parameters, R = 0.053, wR^2 = 0.153, max. (min.) residual electron density 0.32 (-0.32) e.$Å^{-3}$, the hydrogen at P1 atom was refined freely; others were calculated and refined as riding atoms.

Synthesis of compound 10 - starting from compound 9 and $Me_2Si(H)Cl$.



10

Scheme S6

Excess of $Me_2Si(H)Cl$ (0.1 mL, 0.90 mmol) was slowly added to a CH_2Cl_2 (2 mL) solution of compound **9** (125 mg, 0.16 mmol). Then the reaction mixture was stirred at 90 °C for 0.5 h. Subsequently all volatiles were removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (1 mL). Then pentane (5 mL) was added. The obtained solution was stored at -30 °C overnight to give crystalline material. The solid was collected and dried *in vacuo* overnight to give compound **10** (91 mg, 0.14 mmol, 88%). This compound was characterized by ^{1}H, ^{11}B, $^{11}B\{^{1}H\}$, ^{31}P, $^{31}P\{^{1}H\}$ and ^{19}F NMR which are consistent with the NMR data given for the compound **10** prepared according to the following procedure.

Alternative way to synthesize compound 10 - starting from compound 8 and H_2.

Compound **8** (200 mg, 0.31 mmol) was dissolved in toluene (4.0 mL). Then the solution was degassed and purged with H_2 gas (2.5 bar). After heating it at 90 °C overnight, the color of the reaction mixture turned from deep yellow to light yellow. Subsequently all volatiles were removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (2 mL). Pentane (10 mL) was added to form a suspension. The solid was filtrated off to give a clear solution which was then stored at -30 °C overnight to give colorless crystalline material. The solid was collected and dried *in vacuo* overnight to give compound **10** (130 mg, 0.20 mmol, 65%).

Single crystals of compound **10** suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a CH_2Cl_2 solution of compound **10** at -30 °C.

IR (KBr): $\tilde{\nu}$ / cm^{-1} =2965 (m), 2934 (w), 2875 (w), 2364 (w, ν_{BH}/ν_{PH}), 1647 (m), 1606 (m), 1519 (s), 1467 (vs), 1356 (m), 1285 (m), 1211 (s), 1096 (s), 966 (s), 630 (w).

Melting point: 138 °C.

Elemental analysis: calc. for $C_{32}H_{28}BF_{10}P$ (644.33): C, 59.65; H, 4.38. Found: C, 59.40; H, 4.07.

^{1}H NMR (600 MHz, 233 K, [d_2]-CH_2Cl_2): δ = 7.06 (dd, $^{1}J_{PH}$ = 463.9, $^{3}J_{HH}$ = 13.7 Hz, 1H, PH), 7.02 (s, 1H, *m*-Mes^{a}), 6.96 (s, 1H, *m'*-Mes^{a}), 6.75 (d, $^{4}J_{PH}$ = 4.0 Hz, 2H, *m*,*m*'-Mes^{b}), 3.26 (m, 1H, CH), 2.89 (br, 1H, BH), 2.65 (s, 3H, *o*-$CH_3^{Mes,a}$), 2.60 (s, 3H, *o*-$CH_3^{Mes,b}$), 2.27 (s, 6H, *p*-$CH_3^{Mes,a}$, *o'*-$CH_3^{Mes,b}$), 2.23 (s, 3H, *o'*-$CH_3^{Mes,a}$), 2.16 (s, 3H, *p*-$CH_3^{Mes,b}$), 1.13 (dd, $^{3}J_{PH}$ = 25.7, $^{3}J_{HH}$ = 6.7 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 233 K, [d_2]-CH_2Cl_2): δ = 144.1 (d, $^{4}J_{PC}$ = 2.6 Hz, *p*-Mes^{b}), 143.9 (d, $^{4}J_{PC}$ = 2.5 Hz, *p*-Mes^{a}), 143.5 (br d, $^{2}J_{PC}$ = 10.6 Hz, *o*-Mes^{a}), 143.3 (br d, $^{2}J_{PC}$ = 7.9 Hz, *o*-Mes^{b}), 143.1 (br d, $^{2}J_{PC}$ = 7.1 Hz, *o'*-Mes^{a}), 142.9 (br d, $^{2}J_{PC}$ = 10.7 Hz, *o'*-Mes^{b}), 132.0 (br d, $^{3}J_{PC}$ = 10.9 Hz, *m*-Mes^{a}), 131.2 (br d, $^{3}J_{PC}$ = 8.9 Hz, *m'*-Mes^{a}), 130.6 (br d, $^{3}J_{PC}$ = 11.4 Hz, *m'*-Mes^{b}), 130.0 (br d, $^{3}J_{PC}$ = 10.2 Hz, *m*-Mes^{b}), 115.3 (d, $^{1}J_{PC}$ = 77.5 Hz, *i*-Mes^{b}), 113.9 (d, $^{1}J_{PC}$ = 68.1 Hz, *i*-Mes^{a}), 22.6 (br d, $^{3}J_{PC}$ = 7.6 Hz, *o*-$CH_3^{Mes,b}$), 22.1 (br d, $^{3}J_{PC}$ = 5.9 Hz, *o'*-$CH_3^{Mes,b}$), 22.0 (m, *o,o'*-$CH_3^{Mes,a}$), 20.9 (*p*-$CH_3^{Mes,a}$), 20.6 (*p*-$CH_3^{Mes,b}$), 17.3 (br, CH), 15.8 (br, CH_3), [C_6F_5 not listed].

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 233 K, [d_2]-CH_2Cl_2): δ^{1}H / δ^{13}C = 7.02 / 132.0 (*m*-Mes^{a}), 6.96 / 131.2 (*m'*-Mes^{a}), 6.75 / 130.6, 130.0 (*m,m'*-Mes^{b}), 3.26 / 17.3 (CH), 2.65, 2.23 / 22.0 (*o,o'*-$CH_3^{Mes,a}$), 2.60 / 22.6 (*o*-$CH_3^{Mes,b}$), 2.27 / 22.1, 20.9 (*o'*-CH_3^{Mesb}, *p*-$CH_3^{Mes,a}$), 2.16 / 20.6 (*p*-$CH_3^{Mes,b}$), 1.13 / 15.8 (CH_3).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 233 K, [d_2]-CH_2Cl_2) [selected traces]: δ^{1}H / δ^{13}C = 7.06 / 143.5, 143.3, 143.1, 142.9, 115.3, 113.9, 17.3 (PH / *o*-Mes^{a}, *o*-Mes^{b}, *o'*-Mes^{a}, *o'*-Mes^{b}, *i*-Mes^{b}, *i*-Mes^{a}, CH), 7.02 / 131.2, 113.9, 20.9, 22.0 (*m*-Mes^{a} / *m'*-Mes^{a}, *i*-Mes^{a}, *p*-$CH_3^{Mes,a}$, *o,o'*-$CH_3^{Mes,a}$), 6.75 / 130.6, 130.0, 22.6, 22.1, 20.6 (*m,m'*-Mes^{b} / *m,m'*-Mes^{b}, *i*-Mes^{b}, *o,o'*-$CH_3^{Mes,b}$, *p*-$CH_3^{Mes,b}$).

^{11}B NMR (192 MHz, 233K, [d_2]-CH_2Cl_2) δ = -20.1 (br d, $^{1}J_{BH}$ ≈ 85 Hz).

^{11}B{^{1}H} NMR (192 MHz, 233K, [d_2]-CH_2Cl_2): δ = -20.1 ($\nu_{1/2}$ ≈ 150 Hz).

^{11}B NMR (192 MHz, 299K, [d_2]-CH_2Cl_2) δ = -20.0 (d, $^{1}J_{BH}$ = 90.5 Hz).

^{11}B{^{1}H} NMR (192 MHz, 299K, [d_2]-CH_2Cl_2): δ = -20.0 ($\nu_{1/2}$ ≈ 50 Hz).

^{31}P NMR (243 MHz, 233 K, [d_2]-CH_2Cl_2): δ = 6.3 (br d, $^{1}J_{PH}$ ≈ 466 Hz).

^{31}P{^{1}H} NMR (243 MHz, 233 K, [d_2]-CH_2Cl_2): δ = 6.3 ($\nu_{1/2}$ ≈ 80 Hz).

^{31}**P NMR** (243 MHz, 299 K, [d_2]-CH_2Cl_2): δ = 6.8 (br d, $^1J_{PH}$ ≈ 467 Hz).

^{31}**P{^{1}H} NMR** (243 MHz, 299 K, [d_2]-CH_2Cl_2): δ = 6.8 ($\nu_{1/2}$ ≈ 10 Hz).

^{19}**F NMR** (564 MHz, 233 K, [d_2]-CH_2Cl_2): δ = -131.4 (br, 2F, *o*), -163.2 (br t, $^3J_{FF}$ = 21.0 Hz, 1F, *p*), -166.3 (br m, 2F, *m*) (C_6F_5) [$\Delta\delta^{19}F_{mp}$ = 3.1]; -132.2 (br, 2F, *o*), -161.6 (br t, $^3J_{FF}$ = 20.6 Hz, 1F, *p*), -165.3 (br, 2F, *m*) (C_6F_5) [$\Delta\delta^{19}F_{mp}$ = 3.7].

^{19}**F NMR** (564 MHz, 299 K, [d_2]-CH_2Cl_2): δ = -131.4 (m, 2F, *o*), -163.5 (t, $^3J_{FF}$ = 20.0 Hz, 1F, *p*), -166.6 (m, 2F, *m*) (C_6F_5) [$\Delta\delta^{19}F_{mp}$ = 3.1]; -132.4 (m, 2F, *o*), -162.2 (t, $^3J_{FF}$ = 20.1 Hz, 1F, *p*), -165.9 (m, 2F, *m*) (C_6F_5) [$\Delta\delta^{19}F_{mp}$ = 3.7].

^{19}**F,**^{19}**F GCOSY** (564 MHz / 564 MHz, 299 K, [d_2]-CH_2Cl_2) $\delta^{19}F$ / $\delta^{19}F$ = -131.4 / -166.6 (*o* / *m*), -163.5 / -166.6 (*p* / *m*) (C_6F_5); -132.4 / -165.9 (*o* / *m*), -162.2 / -165.9 (*p* / *m*) (C_6F_5).

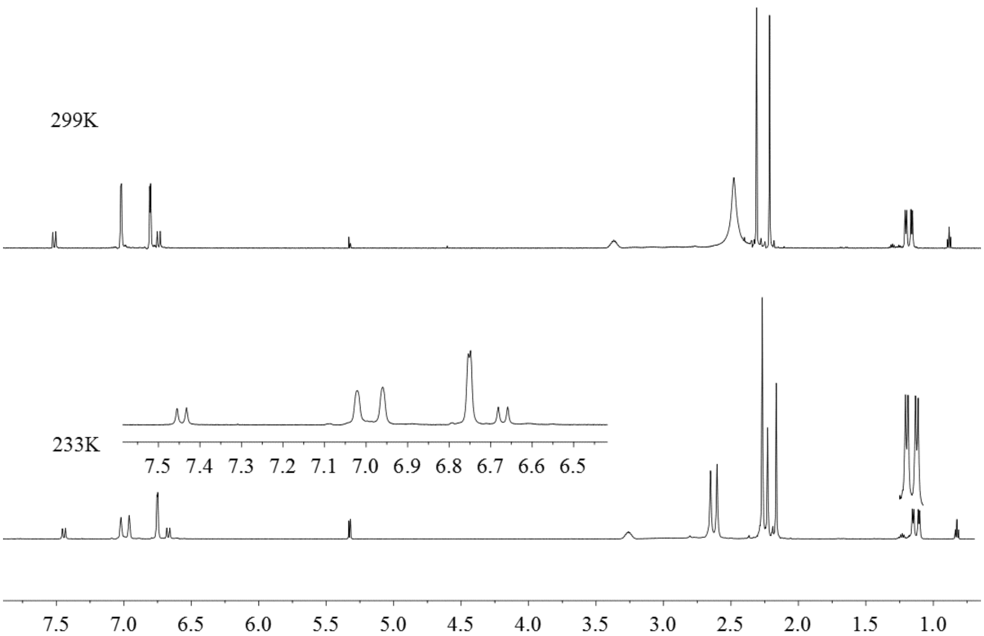


Figure S26 ^{1}H NMR (600 MHz, top: 299 K; bottom: 233 K, [d_2]-CH_2Cl_2) spectra of compound **10**

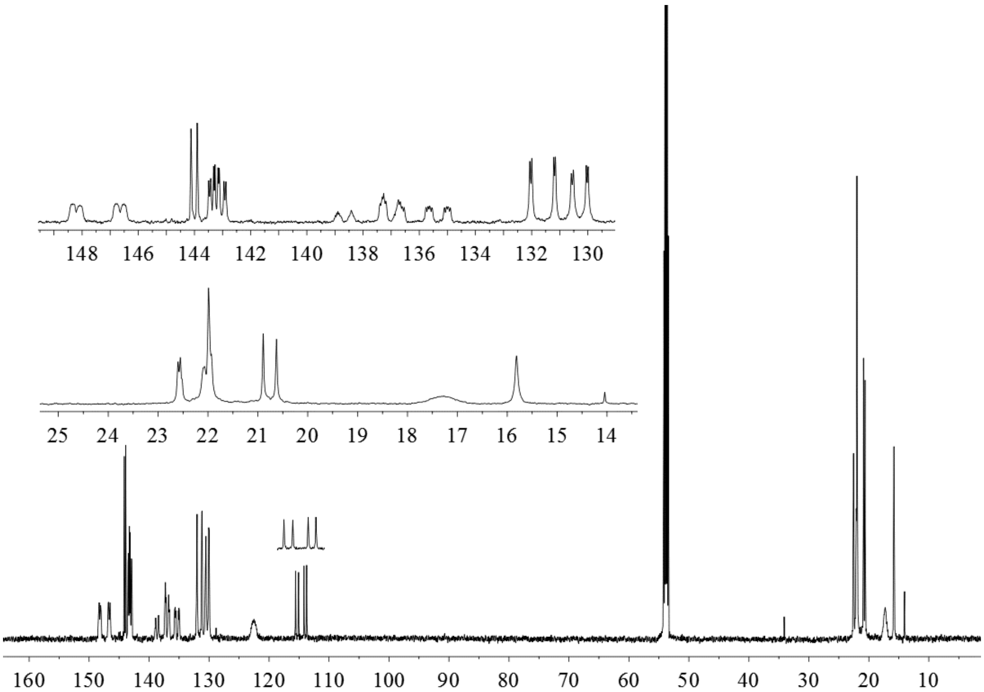


Figure S27 $^{13}C\{^{1}H\}$ NMR (151 MHz, 233K, [d_2]-CH_2Cl_2) spectrum of compound **10**

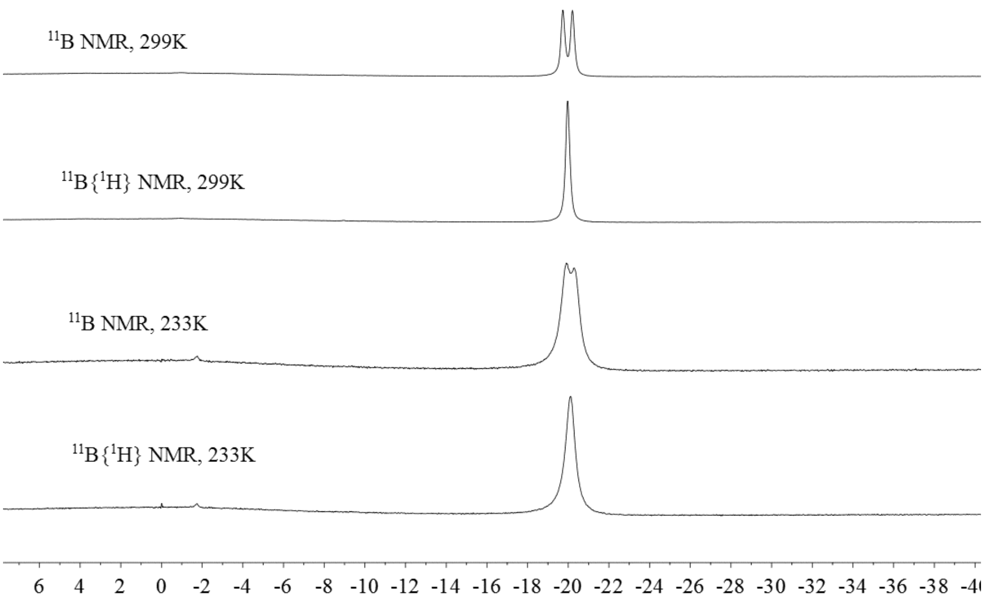


Figure S28 ^{11}B, $^{11}B\{^{1}H\}$ NMR (192 MHz, top 2 line: 299K; bottom 2 line: 233K, [d_2]-CH_2Cl_2) spectra of compound **10**

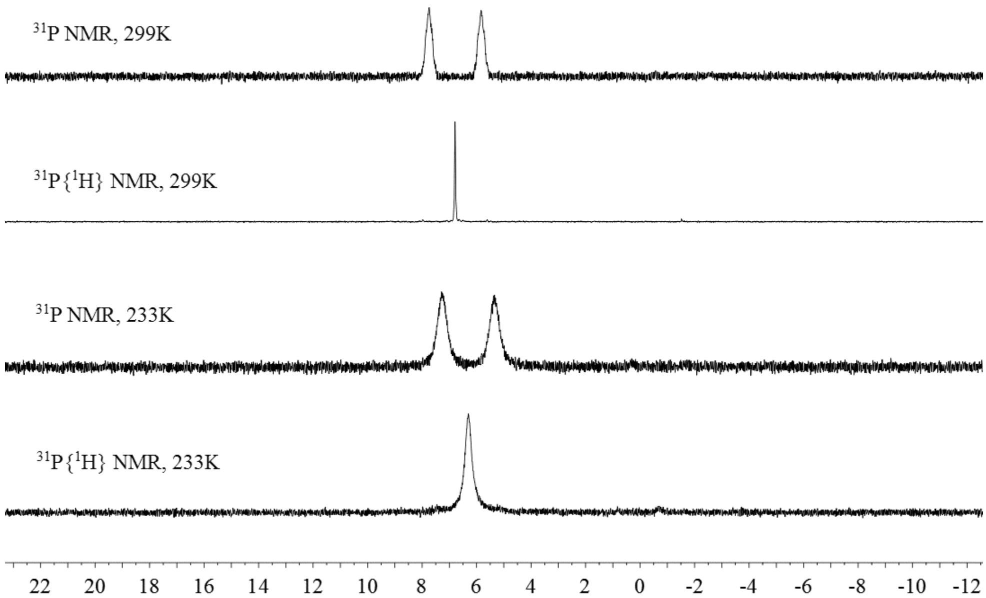


Figure S29 ^{31}P and ^{31}P{^{1}H} NMR (243 MHz, , top 2 line: 299K; bottom 2 line: 233K, [d_2]-CH_2Cl_2) spectra of compound **10**

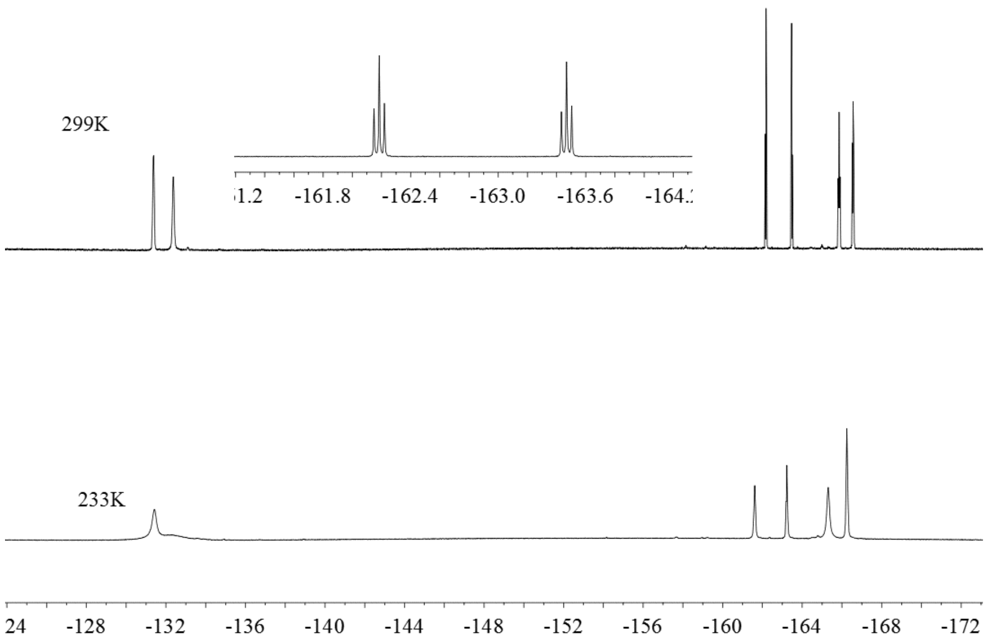


Figure S30 ^{19}F NMR (564 MHz, top: 299K; bottom: 233K, [d_2]-CH_2Cl_2) spectra of compound **10**

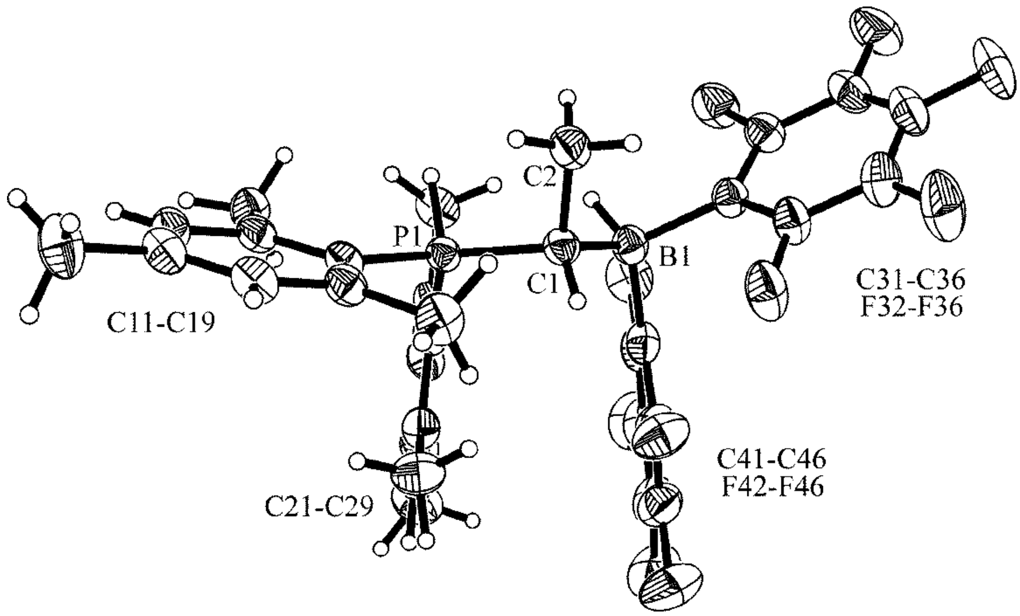


Figure S31 X-Ray crystal structure analysis of compound **10**: formula $C_{32}H_{28}BF_{10}P$, *M* = 644.32, colourless crystal, 0.25 x 0.20 x 0.14 mm, *a* = 8.8140(3), *b* = 24.0603(8), *c* = 14.3592(4) Å, *β* = 104.377(2) °, *V* = 2949.7(2) Å^3, ρ_{calc} = 1.451 gcm^{-3}, μ = 1.600 mm^{-1}, empirical absorption correction (0.690 ≤ T ≤ 0.807), *Z* = 4, monoclinic, space group $P2_1$/n (No. 14), λ = 1.54178 Å, *T* = 223(2) K, ω and φ scans, 18372 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 5076 independent (R_{int} = 0.034) and 4770 observed reflections [*I*>2σ(*I*)], 656 refined parameters, *R* = 0.057, wR^2 = 0.135, max. (min.) residual electron density 0.26 (-0.20) e.Å^{-3}, the hydrogen at P1, P1A, B1 and B1A atoms were refined freely, but with distance restraints (DFIX); others were calculated and refined as riding atoms.

Control reaction: reaction of compound **10** with water (NMR scale).

A small amount of H_2O was added to the CD_2Cl_2 solution (1 mL) of compound **10** (15 mg). The mixture was stored at r.t. for one day and then characterized by NMR experiments.

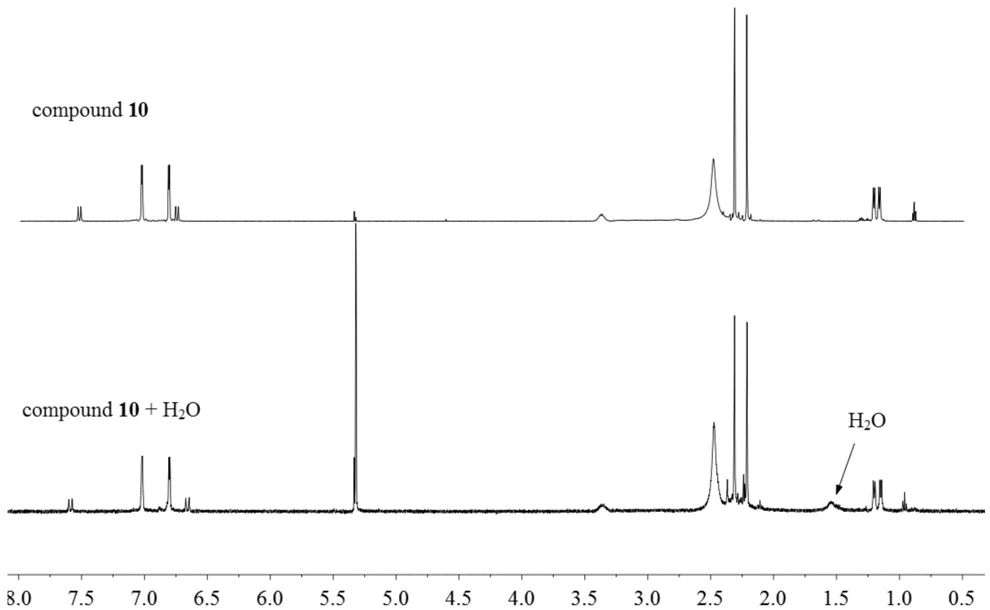


Figure S32 ^{1}H NMR (600 MHz, 299 K, [d_2]-CH_2Cl_2) spectra of top: compound **10**; bottom: compound **10** + H_2O

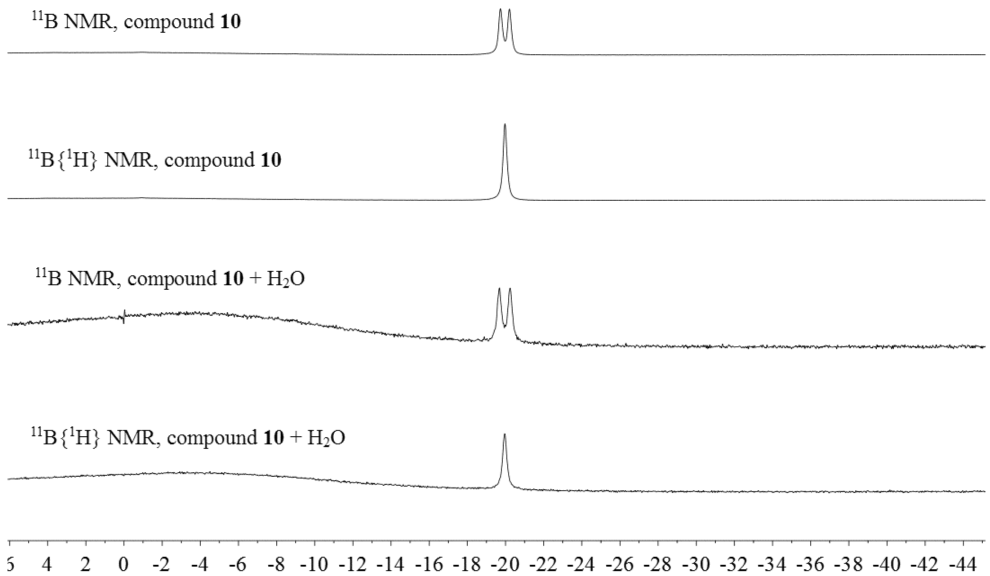


Figure S33 ^{11}B, ^{11}B{^{1}H} NMR (192 MHz, 299K, [d_2]-CH_2Cl_2 spectra of top 2: compound **10**; bottom 2: compound **10** + H_2O

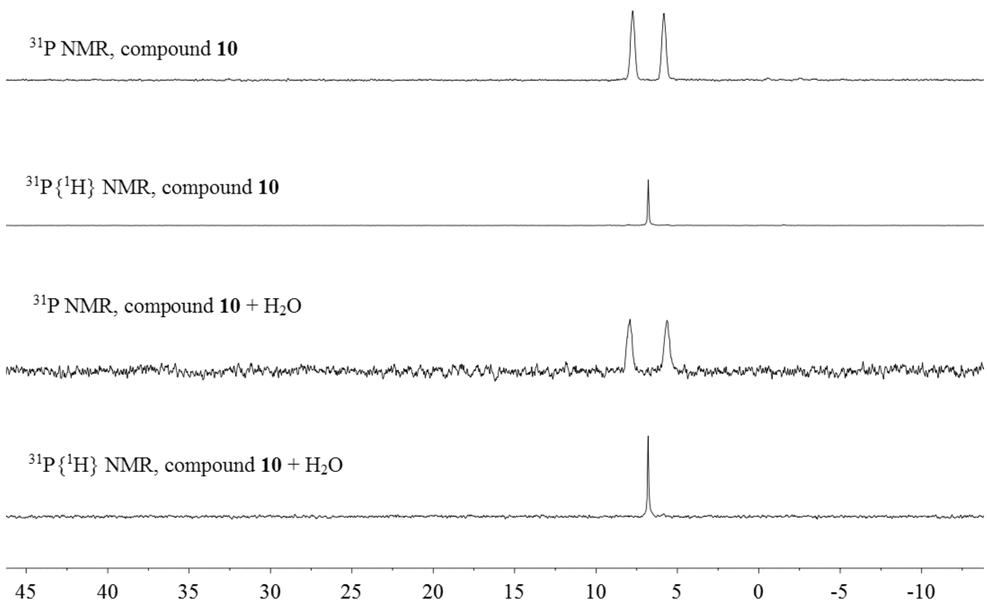


Figure S34 ^{31}P, ^{31}P{^{1}H} NMR (243 MHz, 299K, [d_2]-CH_2Cl_2 spectra of top 2: compound **10**; bottom 2: compound **10** + H_2O

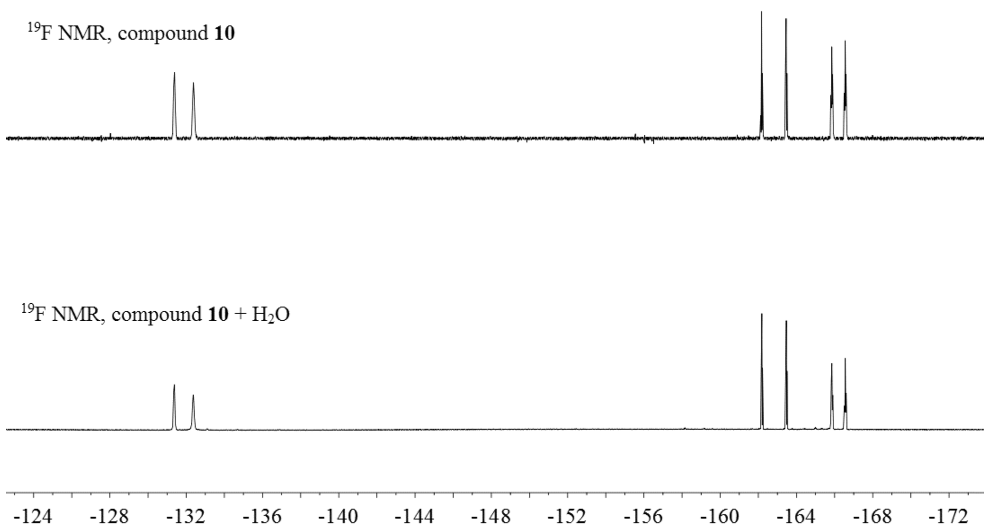
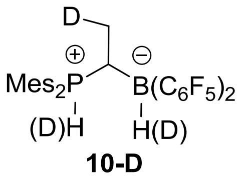


Figure S35 ^{19}F NMR (564 MHz, 299 K, [d_2]-CH_2Cl_2) spectra of top: compound **10**; bottom: compound **10** + H_2O

Synthesis of compound 10-D.



Scheme S7

Compound **8** (100 mg, 0.15 mmol) was dissolved in toluene (2 mL). Subsequently the solution was degassed and then purged with D_2 gas (1.0 bar). After heating at 90 °C overnight the color of the solution turned from deep yellow to light yellow. Then all volatiles were removed *in vacuo* and the obtained residue was dissolved in CH_2Cl_2 (1 mL) and pentane (5 mL) was added to form a suspension. The solid was then filtrated off and the solution was stored in fridge (-30 °C) overnight to give colorless crystalline material. The solid was collected and dried *in vacuo* overnight to give compound **10**-D (60 mg, ≈ 60%).

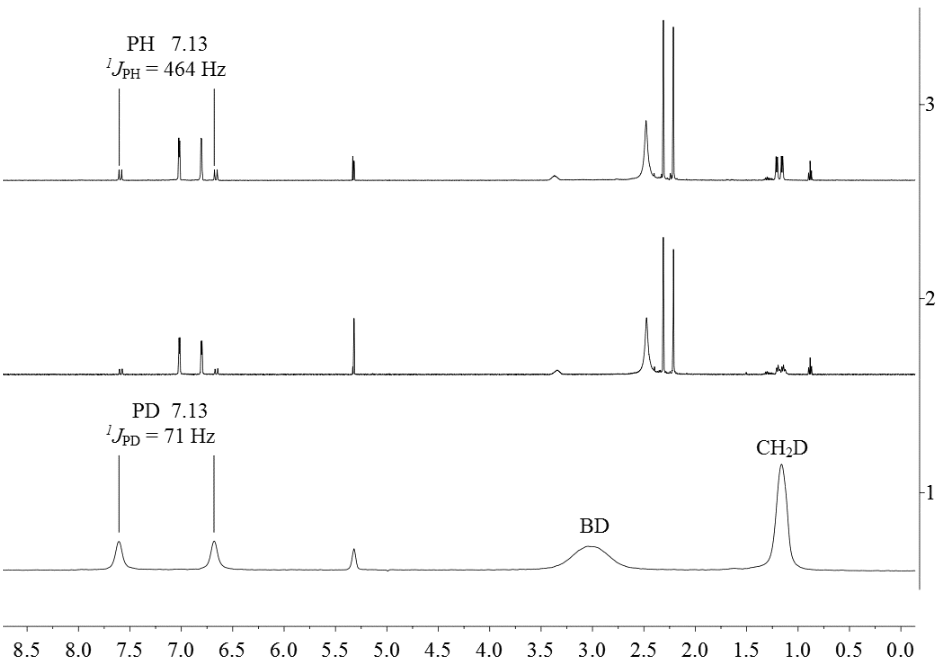
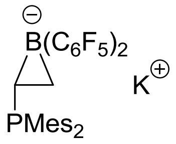


Figure S36 (3): ^{1}H NMR (500 MHz, 299K, [d_2]-CH_2Cl_2) of compound **10**

(2): ^{1}H NMR (500 MHz, 299K, [d_2]-CH_2Cl_2) of compound **10**-D

(1): ^{2}H NMR (77 MHz, 299K, CH_2Cl_2) of compound **10**-D

Synthesis of compound 11



11

Scheme S8

KH (16 mg, 0.40 mmol) was added to the THF solution (4 mL) of compound **8** (200 mg, 0.31 mmol). The reaction mixture was stirred at r.t. for 0.5 h (some gas bubbles were observed during the reacion). Then all volatiles were removed *in vacuo* and the residue was dissolved in CH_2Cl_2/pentane (1 mL/5 mL). Subsequently the solution was stored at -30 °C overnight to give a colorless crystalline material. The solid was collected and dried *in vacuo* for 1 h to give compound **11** with coordinating ¼ THF (140 mg, ≈ 0.2 mmol, ≈ 50 %).

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 2958(m), 1642(w), 1603(m), 1513(s), 1458(vs), 1376(w), 1279(w), 1165(w), 1112(w), 1053(w), 963(m), 791(w), 612(w), 570(w).

Decomposition point: 99 °C.

^{1}H NMR (500 MHz, 299 K, [d_8]-THF): δ = 6.56 (m, 4H, *m*-Mes^{a,b}), 3.62 (m, 1H, THF), 2.35 (s, 6H, *o*-$CH_3^{Mes,a}$), 2.21 (s, 6H, *o*-$CH_3^{Mes,b}$), 2.13 (s, 3H, *p*-$CH_3^{Mes,b}$), 2.12 (s, 3H, *p*-$CH_3^{Mes,a}$), 1.78 (m, 1H, THF), 1.62 (m, 1H, CH), 0.61 (dt, $^3J_{PH}$ = 25.4, $^3J_{HH}$ ≈ $^2J_{HH}$ = 7.0 Hz, 1H, CH_2), 0.18 (td, $^3J_{PH}$ = 10.1 Hz, $^3J_{HH}$ = 10.1 Hz, $^2J_{HH}$ = 7.0 Hz, 1H, CH_2).

^{13}C{^{1}H} NMR (126 MHz, 299 K, [d_8]-THF): δ = 143.0 (d, $^2J_{PC}$ = 13.4 Hz, *o*-Mes^b), 142.3 (d, $^2J_{PC}$ = 12.5 Hz, *o*-Mes^a), 141.3 (d, $^1J_{PC}$ = 33.6 Hz, *i*-Mes^a), 138.9 (d, $^1J_{PC}$ = 20.7 Hz, *i*-Mes^b), 135.5 (*p*-Mes^b), 134.8 (*p*-Mes^a), 129.8 (d, $^3J_{PC}$ = 1.8 Hz, *m*-Mes^a), 129.3 (d, $^3J_{PC}$ = 2.8 Hz, *m*-Mes^b), 68.2 (THF), 26.4 (THF), 23.6 (d, $^3J_{PC}$ = 11.8 Hz, *o*-$CH_3^{Mes,a}$), 22.8 (d, $^3J_{PC}$ = 14.4 Hz, *o*-$CH_3^{Mes,b}$), 21.1 (*p*-$CH_3^{Mes,b}$), 20.9 (*p*-$CH_3^{Mes,a}$), 14.5 (br, CH_2), 12.3 (br, CH), [C_6F_5 not listed].

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, [d_8]-THF): δ^{1}H / δ^{13}C = 6.56 / 129.8, 129.3 (*m*-Mes^{a,b}), 2.35 / 23.6 (*o*-$CH_3^{Mes,a}$), 2.21 / 22.8 (*o*-$CH_3^{Mes,b}$), 2.13 / 21.1 (*p*-$CH_3^{Mes,b}$), 2.12 / 20.9 (*p*-$CH_3^{Mes,a}$), 1.62 / 14.5 (CH), 0.61, 0.18 / 12.3 (CH_2).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, [d_8]-THF) [selected traces]: δ^{1}H / δ^{13}C = 2.35 / 142.3, 141.3, 129.8 (*o*-$CH_3^{Mes,a}$ / *o*-Mes^a, *i*-Mes^a, *m*-Mes^a), 2.21 / 143.0, 138.9, 129.3 (*o*-$CH_3^{Mes,b}$ / *o*-Mes^b, *i*-Mes^b, *m*-Mes^b).

^{11}B{^{1}H} NMR (160 MHz, 299K, [d_8]-THF): δ = -26.8 ($\nu_{1/2} \approx$ 70 Hz)

^{31}P{^{1}H} NMR (202 MHz, 299 K, [d_8]-THF) δ = -4.4 (m).

^{19}F NMR (470 MHz, 299 K, [d_8]-THF) δ = -130.2 (m, 2F, *o*), -167.7 (t, $^{3}J_{FF}$ = 20.3 Hz, 1F, *p*), -169.7 (m, 2F, *m*) (C_6F_5) [$\Delta\delta^{19}F_{mp}$ = 2.0]; -132.0 (m, 2F, *o*), -167.8 (t, $^{3}J_{FF}$ = 20.2 Hz, 1F, *p*), -169.3 (m, 2F, *m*) (C_6F_5) [$\Delta\delta^{19}F_{mp}$ = 1.5].

^{19}F,^{19}F GCOSY (470 MHz / 470 MHz, 299 K, [d_8]-THF) δ^{19}F / δ^{19}F = -130.2 / -169.7 (*o* / *m*), -167.7 / -169.7 (*p* / *m*) (C_6F_5); -132.0 / -169.3 (*o* / *m*), -167.8 / -169.3 (*p* / *m*) (C_6F_5).

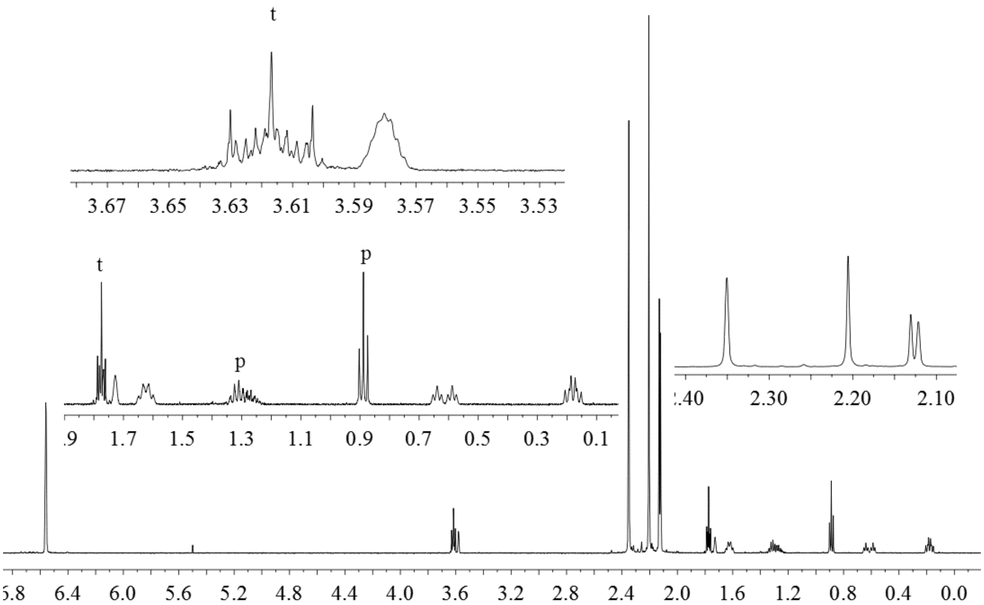


Figure S37 ^{1}H NMR (500 MHz, 299K, [d_8]-THF) spectrum of compound **11** [p: pentane; t: THF]

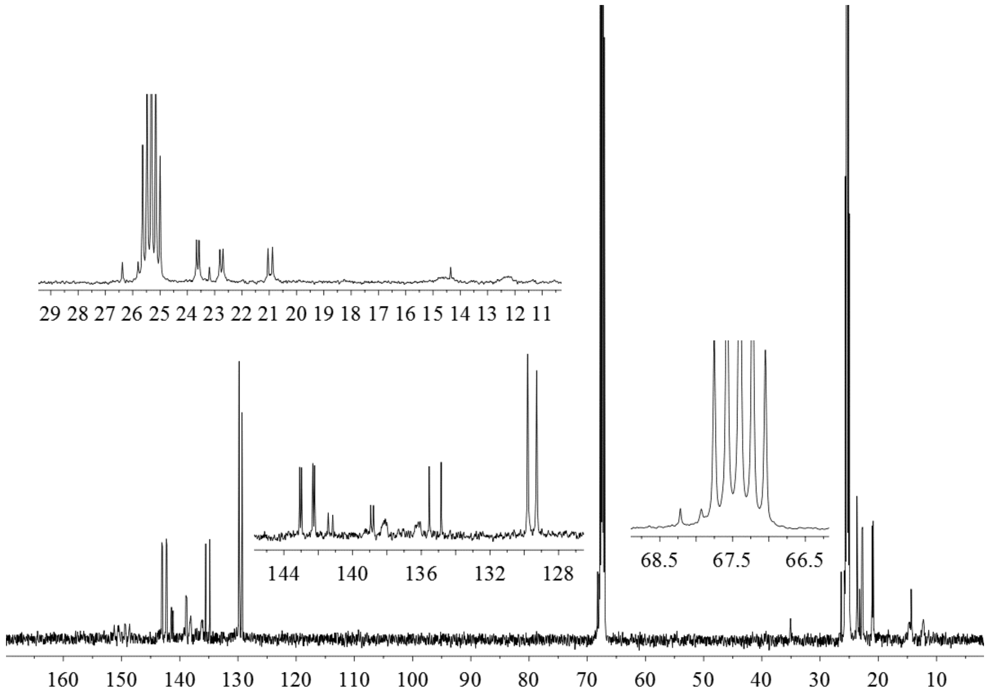


Figure S38 $^{13}C\{^{1}H\}$ NMR (126 MHz, 299K, [d_8]-THF) spectrum of compound **11**

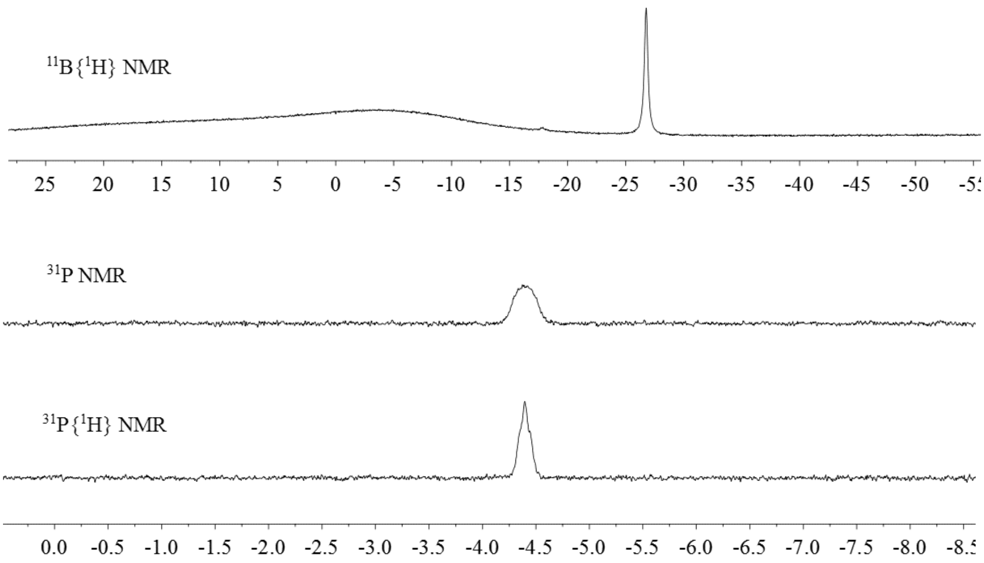


Figure S39 $^{11}B\{^{1}H\}$ NMR (160 MHz, 299K, [d_8]-THF), ^{31}P and $^{31}P\{^{1}H\}$ NMR (202 MHz, 299K, [d_8]-thf) spectra of compound **11**

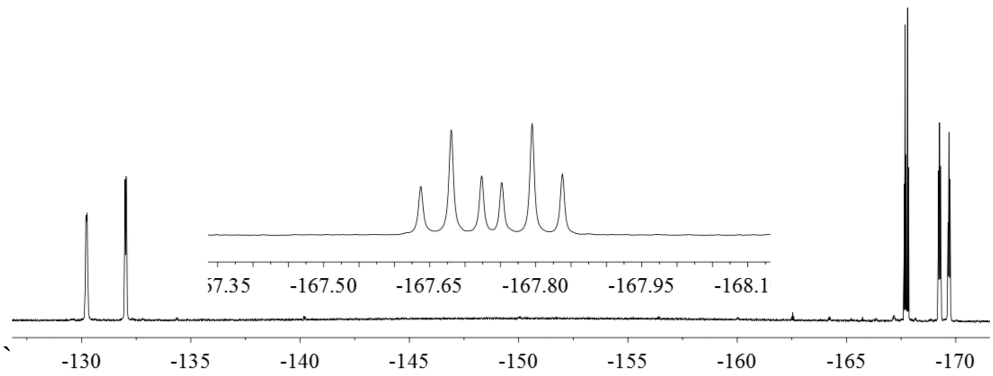
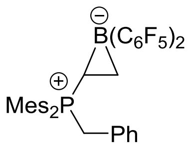


Figure S40 ^{19}F NMR (470 MHz, 299K, [d_8]-THF) spectrum of compound **11**

Synthesis of compound 12



12

Scheme S9

Benzyl bromide (50 mg, 0.29 mmol) was added to a THF solution (5 mL) of compound **11** (200 mg, ≈ 0.28 mmol) to give a suspension immediately. The suspension was stirred at r.t. for 10 min. Then the solid was filtrated off. All volatiles of the solution were removed *in vacuo* and the resulting residue was dissolved in CH_2Cl_2/pentane (1 mL/5 mL). Subsequently the solution was stored at -30 °C overnight to give a colorless crystalline material. The solid was collected and dried *in vacuo* overnight to give compound **12** (160 mg, 0.23 mmol, 82%). Single crystals of compound **12** suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a CH_2Cl_2 solution of compound **12** at -30 °C.

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 2977(w), 2925(w), 1643(w), 1605(w), 1512(m), 1467(vs), 1284(s), 1172(w), 1116(m), 969(s), 865(m), 773(w), 702(w), 557(w), 485(w).

Decomposition point: 105 °C.

Elemental analysis: calc. for $C_{39}H_{32}BF_{10}P$ (732.44 g/mol): C, 63.95; H, 4.40. Found: C, 63.45; H, 4.50.

^{1}H NMR (600 MHz, 299 K, [d_2]-CH_2Cl_2): δ = 7.18 (m, 1H, *p*-Ph), 7.07 (m, 2H, *m*-Ph), 6.95 (m, 2H, *o*-Ph), 6.83 (s, 1H, *m*-Mes^a), 6.79 (s, 1H, *m*-Mes^b), 6.64 (s, 1H, *m'*-Mes^a), 6.44 (s, 1H, *m'*-Mes^b), 4.45, 4.22 (each t, $^2J_{PH} \approx {}^2J_{HH}$ = 13.4 Hz, each 1H, PCH_2), 2.46 (s, 3H, *o'*-$CH_3^{Mes,b}$), 2.23 (s, 3H, *p*-$CH_3^{Mes,a}$), 2.20 (s, 3H, *p*-$CH_3^{Mes,b}$), 2.14 (s, 3H, *o'*-$CH_3^{Mes,a}$), 1.88 (s, 6H, *o*-$CH_3^{Mes,a,b}$), 1.32, 0.69 (each m, each 1H, CH_2), 1.01 (t, $^2J_{PH} \approx {}^3J_{HH}$ = 9.7 Hz, 1H, CH).

^{13}C{^{1}H} NMR (151 MHz, 299 K, [d_2]-CH_2Cl_2): δ = 144.1 (d, $^2J_{PC}$ = 9.0 Hz, *o'*-Mes^a), 143.0 (d, $^4J_{PC}$ = 2.9 Hz, *p*-Mes^b), 142.7 (m, *o*-Mes^b), 142.6 (m, *p*-Mes^a), 140.6 (d, $^2J_{PC}$ = 8.9 Hz, *o'*-Mes^b), 139.8 (d, $^2J_{PC}$ = 8.6 Hz, *o*-Mes^a), 132.0 (d, $^3J_{PC}$ = 10.9 Hz, *m'*-Mes^a), 131.8 (d, $^3J_{PC}$ = 11.3 Hz, *m*-Mes^b), 131.6 (d, $^3J_{PC}$ = 10.3 Hz, *m*-Mes^a), 131.3 (m, *m'*-Mes^b), 131.2 (m, *o*-Ph), 131.0 (d, $^2J_{PC}$ = 6.9 Hz, *i*-Ph)^t, 128.5 (d, $^4J_{PC}$ = 3.6 Hz, *m*-Ph), 128.0 (d, $^5J_{PC}$ = 4.0 Hz, *p*-Ph), 124.2 (d, $^1J_{PC}$ = 69.2 Hz, *i*-Mes^a), 119.4 (d, $^1J_{PC}$ = 81.5 Hz, *i*-Mes^b), 39.3 (d, $^1J_{PC}$ = 49.5 Hz, PCH_2), 24.9 (*o'*-$CH_3^{Mes,b}$), 24.8

(d, $^3J_{PC}$ = 3.8 Hz, *o*-$CH_3^{Mes,b}$), 23.2 (d, $^3J_{PC}$ = 5.3 Hz, *o*-$CH_3^{Mes,a}$), 22.4 (d, $^3J_{PC}$ = 2.9 Hz, *o'*-$CH_3^{Mes,a}$), 21.0 (*p*-$CH_3^{Mes,a}$), 20.6 (*p*-$CH_3^{Mes,b}$), 12.1 (br, CH_2), 10.4 (br d, $^1J_{PC}$ = 59.8 Hz, CH), [C_6F_5 not listed; [t] tentative assignment].

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, [d_2]-CH_2Cl_2): δ^1H / δ^{13}C = 7.18 / 128.0 (*p*-Ph), 7.07 / 128.5 (*m*-Ph), 6.95 / 131.2 (*o*-Ph), 6.83 / 131.6 (*m*-Mes^a), 6.79 / 131.8 (*m*-Mes^b), 6.64 / 132.0 (*m'*-Mes^a), 6.44 / 131.3 (*m'*-Mes^b), 4.45, 4.22 / 39.3 (PCH_2), 2.46 / 24.9 (*o'*-$CH_3^{Mes,b}$), 2.23 / 21.0 (*p*-$CH_3^{Mes,a}$), 2.20 / 20.6 (*p*-$CH_3^{Mes,b}$), 2.14 / 22.4 (*o'*-$CH_3^{Mes,a}$), 1.88 / 23.2 (*o*-$CH_3^{Mes,a}$), 1.88 / 24.8 (*o*-$CH_3^{Mes,b}$), 1.32, 0.69 / 12.1 (CH_2), 1.01 / 10.4 (CH).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, [d_2]-CH_2Cl_2) [selected traces]: δ^1H / δ^{13}C = 7.18 / 131.2 (*p*-Ph / *o*-Ph), 4.45, 4.22 / 131.2, 10.4 (PCH_2 / *o*-Ph, CH), 2.46 / 140.6, 131.3, 119.4 (*o'*-$CH_3^{Mes,b}$ / *o'*-Mes^b, *m'*-Mes^b, *i*-Mes^b), 2.14 / 144.1, 132.0, 124.2 (*o'*-$CH_3^{Mes,a}$ / *o'*-Mes^a, *m'*-Mes^a, *i*-Mes^a).

^{11}B{^{1}H} NMR (192 MHz, 299K, [d_2]-CH_2Cl_2): δ = -23.1 ($\nu_{1/2} \approx$ 100 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, [d_2]-CH_2Cl_2) δ = 33.7 ($\nu_{1/2} \approx$ 10 Hz).

^{19}F NMR (564 MHz, 299 K, [d_2]-CH_2Cl_2) δ = -132.0 (br m, 2F, *o*), -162.2 (t, $^3J_{FF}$ = 19.7 Hz, 1F, *p*-C_6F_5), -166.1 (m, 2F, *m*) (C_6F_5) [$\Delta\delta^{19}F_{mp}$ = 3.9], -128.4, -130.9 (each br, each 1F, *o*), -162.6 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*), -166.0, -167.5 (each br, each 1F, *m*) (C_6F_5) [$\Delta\delta^{19}F_{mp}$ = 3.4, 3.9].

^{19}F NMR (564 MHz, 233 K, [d_2]-CH_2Cl_2) δ = -128.4, -131.0 (each m, each 1F, *o*), -162.2 (t, $^3J_{FF}$ = 20.8 Hz, 1F, *p*), -165.5, -167.1 (each m, each 1F, *m*) (C_6F_5) [$\Delta\delta^{19}F_{mp}$ = 3.3, 4.9], -131.9 (br, 2F, *o*), -161.5 (t, $^3J_{FF}$ = 20.8 Hz, 1F, *p*), -165.4 (m, 2F, *m*) (C_6F_5) [$\Delta\delta^{19}F_{mp}$ = 3.9].

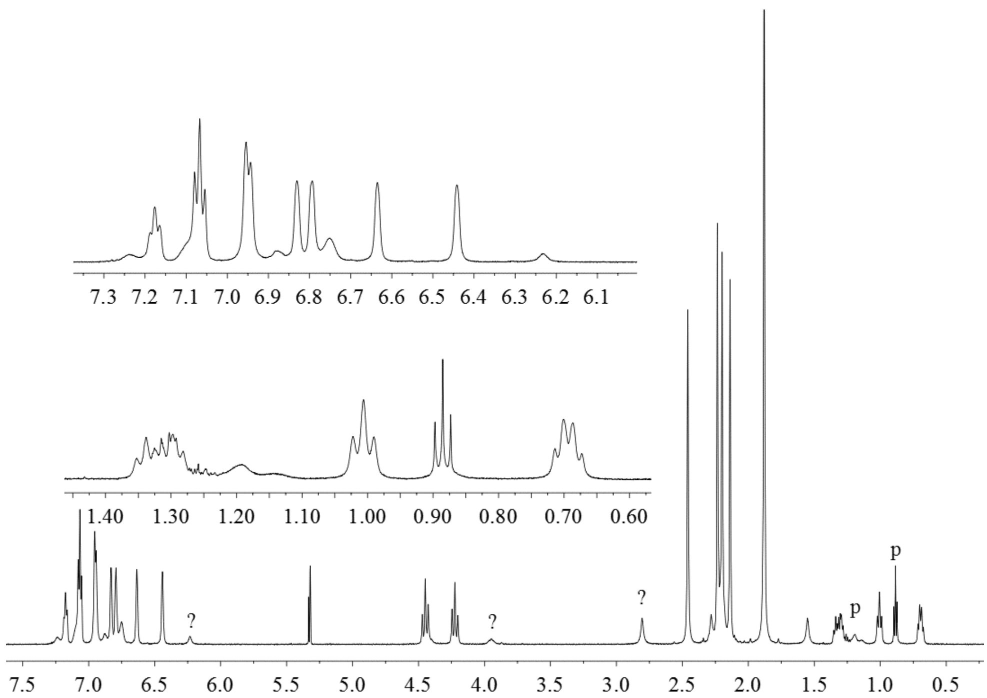


Figure S41 ^{1}H NMR (600 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **12** (?: the compound not yet identified; p: pentane)

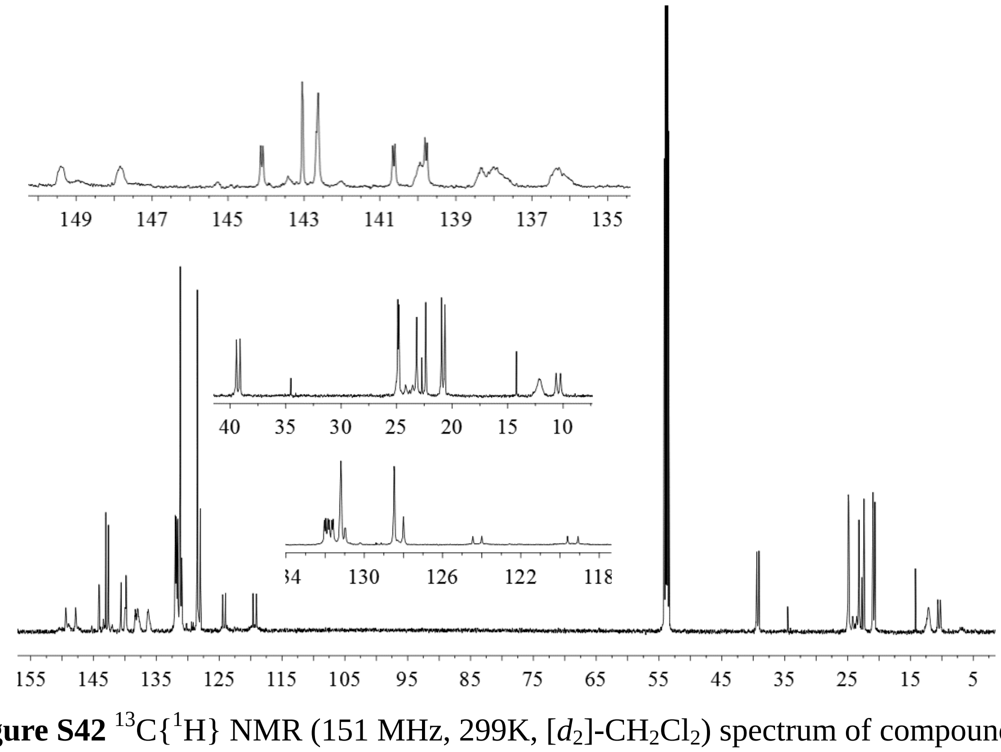


Figure S42 $^{13}C\{^{1}H\}$ NMR (151 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **12**

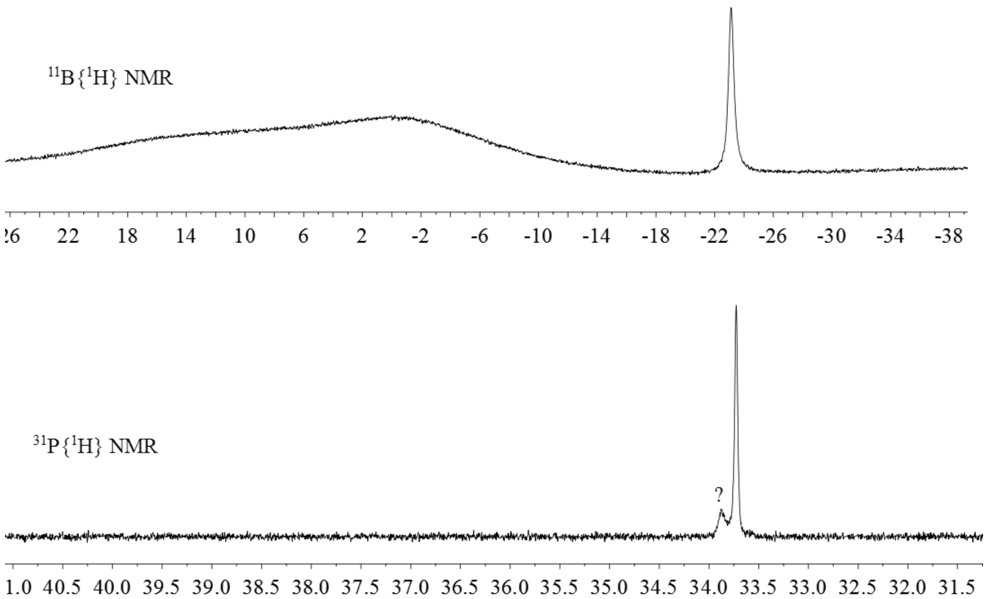


Figure S43 $^{11}B\{^{1}H\}$ NMR (192 MHz, 299K, [d_2]-CH_2Cl_2), $^{31}P\{^{1}H\}$ NMR (243 MHz, 299K, [d_2]-CH_2Cl_2) spectra of compound **12** (?: the compound not yet identified)

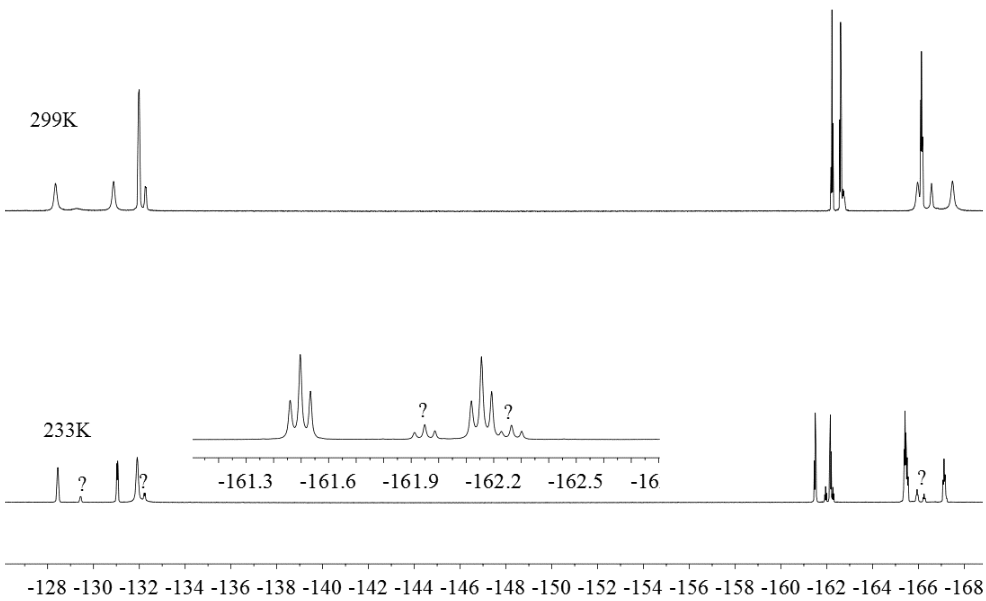


Figure S44 ^{19}F NMR (564 MHz, top: 299K; bottom: 233K, [d_2]-CH_2Cl_2) spectra of compound **12** (?: the compound not yet identified)

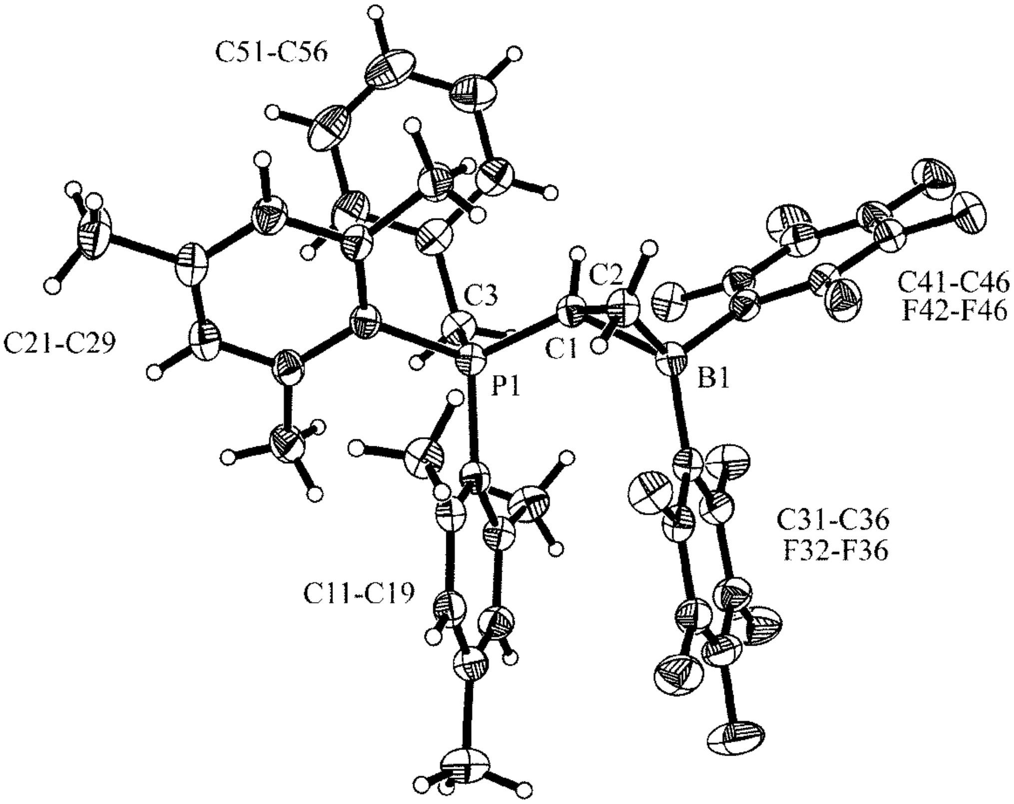
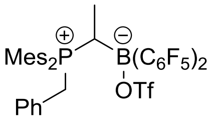


Figure S45 X-Ray crystal structure analysis of compound **12**: formula $C_{39}H_{32}BF_{10}P \cdot CH_2Cl_2$, *M* = 817.35, pale yellow crystal, 0.35 x 0.20 x 0.20 mm, *a* = 11.2185(2), *b* = 11.8258(2), *c* = 15.1455(3) Å, α = 90.266(1), *β* = 108.687(1), γ = 103.129(1)°, *V* = 1847.1(1) Å^3, ρ_{calc} = 1.470 gcm^{-3}, μ = 0.300 mm^{-1}, empirical absorption correction (0.902 ≤ T ≤ 0.942), *Z* = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, *T* = 223(2) K, ω and φ scans, 18017 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.67 Å^{-1}, 8925 independent (R_{int} = 0.050) and 7139 observed reflections [*I*>2σ(*I*)], 521 refined parameters, *R* = 0.060, wR^2 = 0.158, max. (min.) residual electron density 0.33 (-0.34) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Reaction of compound 12 with H_2:

Compound **12** (20 mg, 0.27 mmol) was dissolved in d_8-toluene (1.0 mL). Then the solution was degassed and purged with H_2 gas (2.5 bar). After heating it at 90 °C overnight, the solution was measured by NMR in situ. The analysis (NMR: ^{1}H, ^{11}B, ^{19}F and ^{31}P) showed that compound **12** doesn't react with H_2 under this applied condition.

Synthesis of compound 13



13

Scheme S10

Triflic acid (30 mg, 0.20 mmol) was added to the CH_2Cl_2 (4 mL) solution of compound **12** (150 mg, 0.20 mmol) to give a colorless solution. The solution was stirred at r.t. for 10 min. Then all volatiles were removed *in vacuo* and pentane (5 mL) was added to the residue to give a suspension. Subsequently the solid was collected and dried overnight in *vacuo* to give compound **13** (130 mg, 0.15 mmol, 75%). Crystals of compound **13** suitable for the X-ray single crystal structure analysis were obtained by slow diffusion of pentane to a CH_2Cl_2 solution of compound **13** at -30 °C.

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 2973(w), 1646(w), 1606(w), 1519(s), 1464(vs), 1355(s), 1192(s), 1093(m), 998(m), 973(m), 831(m), 776(m), 698(m), 628(m), 420(w).

Decomposition point: 105 °C.

Melting point: 166 °C.

Elemental analysis: calc. for $C_{40}H_{33}BF_{13}PS$ (882.52 g/mol): C, 54.44; H, 3.77. Found: C, 54.69; H, 3.56.

^{1}H NMR (600 MHz, 299 K, [d_2]-CH_2Cl_2): δ = 7.16 (m, 1H, *p*-Ph), 7.08 (m, 2H, *m*-Ph), 7.02 (s, 2H, *m*-Mes), 6.91 (m, 2H, *o*-Ph), 6.91, 6.38 (each br, each 1H, *m*-Mes), 4.94 (dd, $^2J_{HH}$ = 15.1 Hz, $^2J_{PH}$ = 11.1 Hz, 1H, CH_2), 4.40 (dd, $^2J_{HH} \approx {}^2J_{PH}$ = 15.1 Hz, 1H, CH_2), 3.95 (dq, $^2J_{PH}$ = 19.9 Hz, $^3J_{HH}$ = 6.8 Hz, 1H, CH), 2.84, 2.72, 1.85, 1.57 (each br, each 3H, *o*-CH_3^{Mes}), 2.32, 2.21 (each s, each 3H, *p*-CH_3^{Mes}), 1.84 (dd, $^3J_{PH}$ = 19.8 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 299 K, [d_2]-CH_2Cl_2): δ = 144.1 (d, $^4J_{PC}$ = 3.0 Hz), 143.8 (d, $^4J_{PC}$ = 3.1 Hz) (*p*-Mes), 143.9 (br d, $^2J_{PC}$ = 8.9 Hz), 142.9 (br d, $^2J_{PC}$ = 9.2 Hz), 142.6 (d, $^2J_{PC}$ = 9.1 Hz), 142.3 (d, $^2J_{PC}$ = 10.3 Hz) (*o*-Mes), 134.1 (br d, $^3J_{PC}$ = 11.8 Hz), 133.8 (br d, $^3J_{PC}$ = 11.0 Hz), 132.7 (br d, $^3J_{PC}$ = 11.7 Hz), 131.7 (br d, $^3J_{PC}$ = 11.1 Hz) (*m*-Mes), 132.3 (d, $^2J_{PC}$ = 8.0 Hz, *i*-Ph), 131.3 (d, $^3J_{PC}$ = 6.6 Hz, *o*-Ph), 128.8 (*m*-Ph), 127.9 (d, $^5J_{PC}$ = 2.3 Hz, *p*-Ph), 122.1 (d, $^1J_{PC}$ = 71.4 Hz), 121.2 (d, $^1J_{PC}$ = 71.4 Hz) (*i*-Mes), 119.4 (q, $^1J_{FC}$ = 318.6 Hz, CF_3), 32.0 (d, $^1J_{PC}$ = 43.3 Hz, CH_2), 26.2, 24.8, 23.8, 23.1 (*o*-CH_3^{Mes}), 25.1 (br, CH), 20.9, 20.6 (*p*-CH_3^{Mes}), 17.2 (CH_3), [C_6F_5 not listed].

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, [d_2]-CH_2Cl_2): δ^1H / δ^{13}C = 7.16 / 127.9 (*p*-Ph), 7.08 / 128.8 (*m*-Ph), 7.02 / 132.7, 134.1 , 6.91 / 133.8 , 6.38 / 131.7 (*m*-Mes), 691 / 131.3 (*o*-Ph), 4.94, 4.40 / 32.0 (CH_2), 3.95 / 25.1 (CH), 2.84 / 26.2, 2.72 / 23.1, 1.85 / 23.8, 1.57 / 24.8 (*o*-CH_3^{Mes}), 2.32 / 20.9 , 2.21 / 20.6 (*p*-CH_3^{Mes}), 1.84 / 17.2 (CH_3).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, [d_2]-CH_2Cl_2) [selected traces]: δ^1H / δ^{13}C = 2.72 / 143.9, 134.1, 122.1 (*o*-CH_3^{Mes} / *o*-Mes, *m*-Mes, *i*-Mes), 1.57 / 142.3, 131.7, 121.2 (*o*-CH_3^{Mes} / *o*-Mes, *m*-Mes, *i*-Mes).

^{11}B{^{1}H} NMR (192 MHz, 299K, [d_2]-CH_2Cl_2): δ = 5.1 ($\nu_{1/2} \approx$ 400 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, [d_2]-CH_2Cl_2) δ = 38.6 ($\nu_{1/2} \approx$ 10 Hz).

^{19}F NMR (564 MHz, 233 K, [d_2]-CH_2Cl_2) δ = -75.9 (m, 3F, CF_3), -129.7, -136.0 (each br, each 1F, *o*), -158.7 (t, $^3J_{FF}$ = 20.4 Hz, *p*), -165.5 (m, 2F, *m*) (C_6F_5) [$\Delta\delta^{19}F_{mp}$ = 6.8], -131.5, -132.5 (each br m, each 1F, *o*), -160.9 (t, $^3J_{FF}$ = 20.1 Hz, *p*), -163.9, -166.1 (each m, each 1F, *m*) (C_6F_5) [$\Delta\delta^{19}F_{mp}$ = 3.0, 5.2].

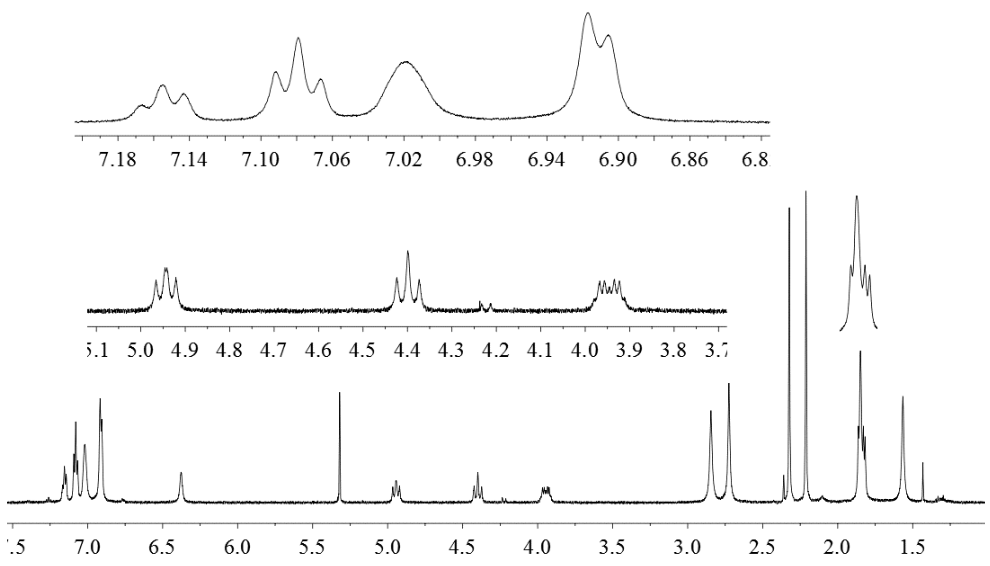


Figure S46 ^{1}H NMR (600 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **13**

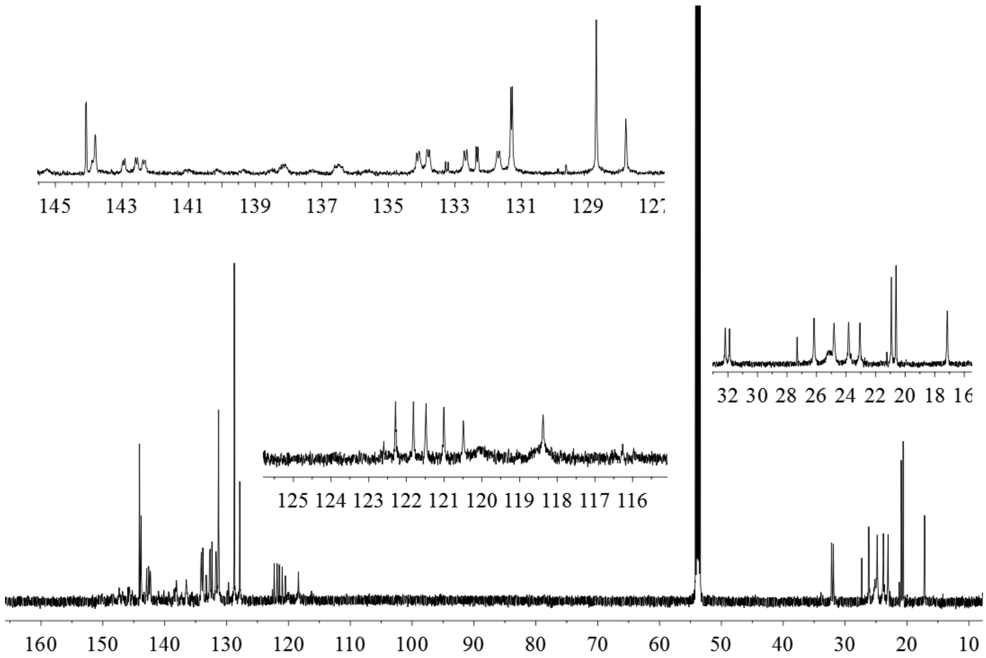


Figure S47 $^{13}C\{^1H\}$ NMR (151 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **13**

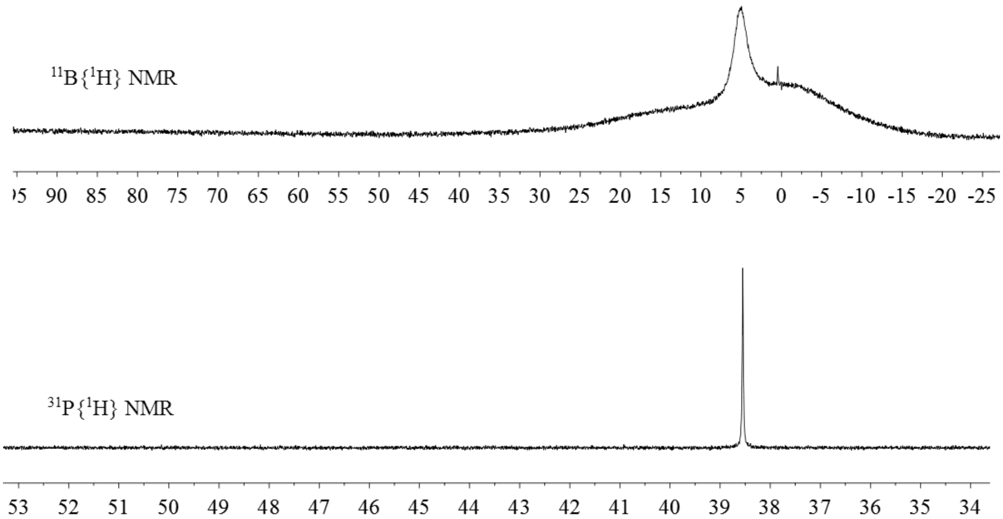


Figure S48 $^{11}B\{^1H\}$ NMR (192 MHz, 299K, [d_2]-CH_2Cl_2), $^{31}P\{^1H\}$ NMR (243 MHz, 299K, [d_2]-CH_2Cl_2) spectra of compound **13**

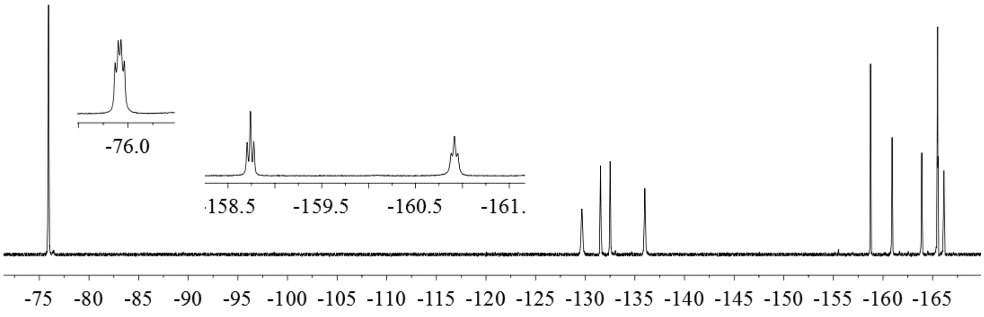


Figure S49 ^{19}F NMR (564 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **13**

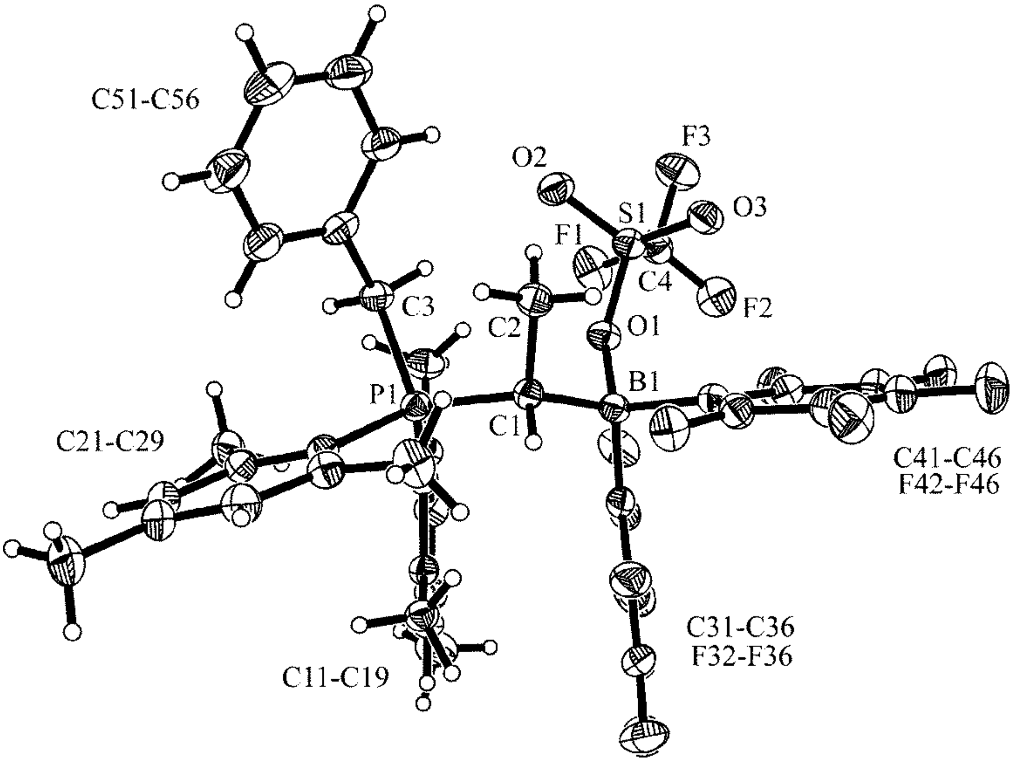
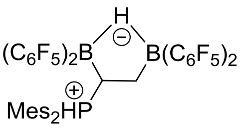


Figure S50 X-Ray crystal structure analysis of compound **13**: formula $C_{40}H_{33}BF_{13}O_3PS$, M = 882.50, colourless crystal, 0.18 x 0.14 x 0.04 mm, a = 18.0651(3), b = 10.2032(1), c = 23.1974(4) Å, β = 107.174(1) °, V = 4085.14(11) Å^3, ρ_{calc} = 1.435 gcm^{-3}, μ = 0.215 mm^{-1}, empirical absorption correction (0.962 $\leq$ T $\leq$ 0.991), Z = 4, monoclinic, space group $P2_1$/n (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 25089 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.67 Å^{-1}, 9948 independent (R_{int} = 0.044) and 6930 observed reflections [I>2σ(I)], 539 refined parameters, R = 0.072, wR^2 = 0.194, max. (min.) residual electron density 0.35 (-0.28) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Synthesis of compound 14



14

Scheme S11

Mixing of compound **8** (200 mg, 0.31 mmol) and $HB(C_6F_5)_2$ (107 mg, 0.31 mmol) in CH_2Cl_2 (10 mL) gave a suspension. The reaction mixture was stirred at r.t. for another 1h. Then the solid was collected and dried *in vacuo* overnight to give compound **14** (200 mg, 0.20 mmol, 65%). Single crystals of compound **14** suitable for the X-ray single crystal structure analysis were obtained by storing a saturated CH_2Cl_2 solution of compound **14** at r.t. for several days.

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 2982(w), 2933(w), 1645(w), 1607(w), 1517(m), 1463(vs), 1379(w), 1291(m), 1136(m), 1089(s), 971(s), 856(w), 740(w), 672(w), 481(w).

Melting point: 165 °C.

Elemental analysis: calc. for $C_{44}H_{27}B_2F_{20}P$ (988.25 g/mol): C, 53.48; H, 2.75. Found: C, 53.83; H, 2.38.

^{1}H NMR (600 MHz, 299 K, [d_2]-CH_2Cl_2): δ = 7.07 (d, $^3J_{PH}$ = 4.3 Hz, 1H, *m*-Mes^a), 7.01 (dd, $^1J_{PH}$ = 460.8, $^3J_{HH}$ = 12.9 Hz, 1H, PH), 6.88 (d, $^3J_{PH}$ = 4.3 Hz, 1H, *m*-Mes^b), 4.09 (br, 1H, CH), 2.50 (s, 6H, *o*-$CH_3^{Mes,a}$), 2.34 (s, 3H, *p*-$CH_3^{Mes,a}$), 2.29 (s, 6H, *o*-$CH_3^{Mes,b}$), 2.25 (s, 3H, *p*-$CH_3^{Mes,b}$), 2.09 (br, 2H, BH, CH_2), 1.87 (dt, $^3J_{PH}$ = 27.5, $^3J_{HH} \approx {}^2J_{HH}$ = 13.0 Hz, 1H, CH_2).

^{13}C{^{1}H} NMR (151 MHz, 299 K, [d_2]-CH_2Cl_2): δ = 145.4 (*p*-Mes^{a,b}), 143.4 (br d, $^2J_{PC}$ = 8.0 Hz), 143.3 (br d, $^2J_{PC}$ = 8.1 Hz) (*o*-Mes^{a,b}), 132.1 (d, $^3J_{PC}$ = 10.5 Hz, *m*-Mes^a), 131.6 (d, $^3J_{PC}$ = 10.6 Hz, *m*-Mes^b), 114.5 (d, $^1J_{PC}$ = 69.3 Hz, *i*-Mes^b), 114.0 (d, $^1J_{PC}$ = 78.5 Hz, *i*-Mes^a), 22.7 (d, $^3J_{PC}$ = 7.2 Hz, *o*-$CH_3^{Mes,a}$), 22.6 (d, $^3J_{PC}$ = 7.3 Hz, *o*-$CH_3^{Mes,b}$), 22.2 (br, CH_2), 21.3 (*p*-$CH_3^{Mes,a}$), 21.1 (*p*-$CH_3^{Mes,b}$), 20.7 (br, CH), [C_6F_5 not listed].

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, [d_2]-CH_2Cl_2): δ^{1}H / δ^{13}C = 7.07 / 132.1 (*m*-Mes^a), 6.88 / 131.6 (*m*-Mes^b), 4.09 / 20.7 (CH), 2.50 / 22.7 (*o*-$CH_3^{Mes,a}$), 2.34 / 21.3 (*p*-$CH_3^{Mes,a}$), 2.29 / 22.6 (*o*-$CH_3^{Mes,b}$), 2.25 / 21.1 (*p*-$CH_3^{Mes,b}$), 2.09, 1.87 / 22.2 (CH_2).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, [d_2]-CH_2Cl_2) [selected traces]: δ^{1}H /

$\delta^{13}C$ = 7.01 / 143.4, 143.3, 114.5, 114.0 (PH / *o*-Mes[a], *o*-Mes[b], *i*-Mes[b], *i*-Mes[a]), 2.50 / 143.4, 132.1, 114.0 (*o*-$CH_3^{Mes,a}$ / *o*-Mes[a], *m*-Mes[a], *i*-Mes[a]), 2.29 / 143.3, 131.6, 114.5 (*o*-$CH_3^{Mes,b}$ / *o*-Mes[b], *m*-Mes[b], *i*-Mes[b]).

$^{11}B\{^1H\}$ NMR (192 MHz, 299K, [d_2]-CH_2Cl_2): δ = 4.1 ($\nu_{1/2} \approx$ 400 Hz).

^{31}P NMR (243 MHz, 299 K, [d_2]-CH_2Cl_2) δ = -2.2 (br d, $^1J_{PH} \approx$ 460 Hz).

$^{31}P\{^1H\}$ NMR (243 MHz, 299 K, [d_2]-CH_2Cl_2) δ = -2.2 ($\nu_{1/2} \approx$ 10 Hz).

^{19}F NMR (564 MHz, 233 K, [d_2]-CH_2Cl_2) δ = -127.7 (br m, 2F), -131.2 (br, 2F), -133.6 (br, 4F) (*o*-C_6F_5), -156.0 (t, $^3J_{FF}$ = 20.2 Hz, 1F), -156.7 (t, $^3J_{FF}$ = 20.1 Hz, 1F), -158.2 (br, 2F) (*p*-C_6F_5), -163.0 (m, 2F), -165.0 (m, 6F) (*m*-C_6F_5).

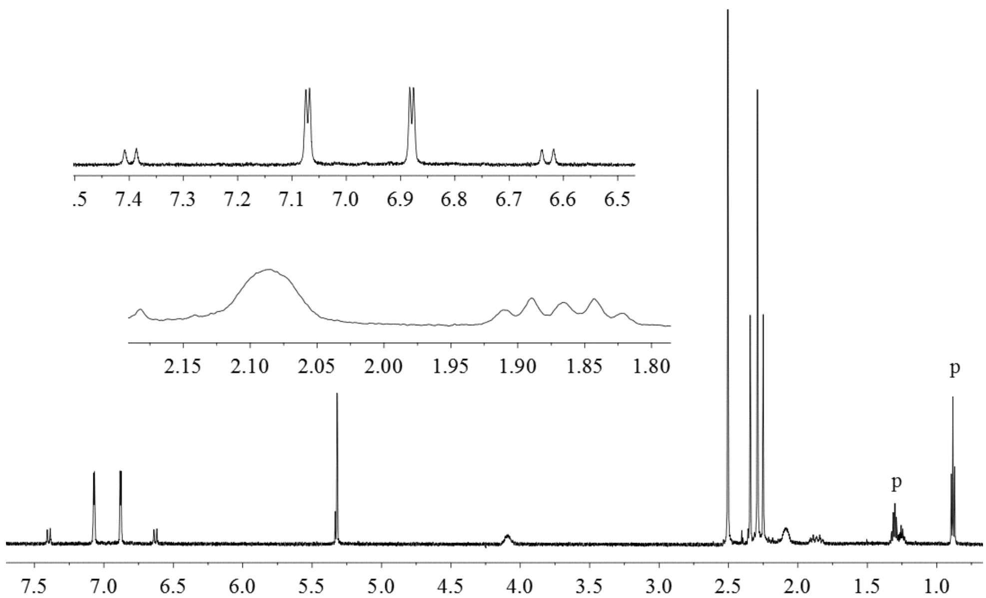


Figure S51 ^1H NMR (600 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **14** (p: pentane)

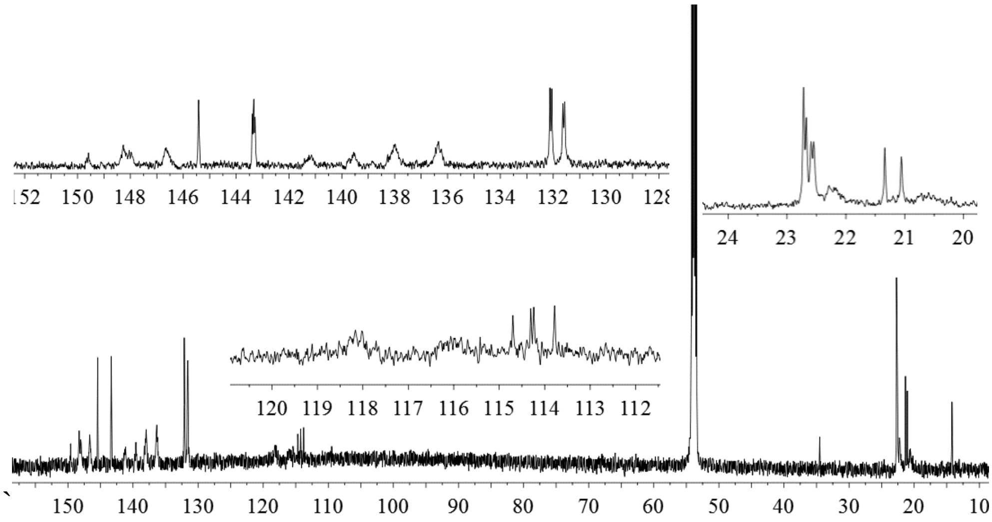


Figure S52 $^{13}C\{^1H\}$ NMR (151 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **14**

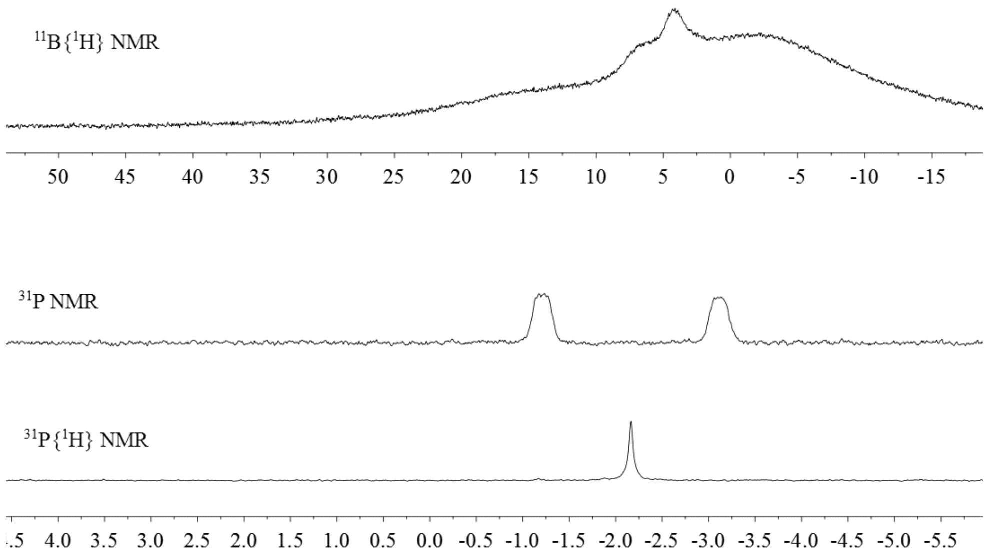


Figure S53 $^{11}B\{^1H\}$ NMR (192 MHz, 299K, [d_2]-CH_2Cl_2), ^{31}P and $^{31}P\{^1H\}$ NMR (243 MHz, 299K, [d_2]-CH_2Cl_2) spectra of compound **14**

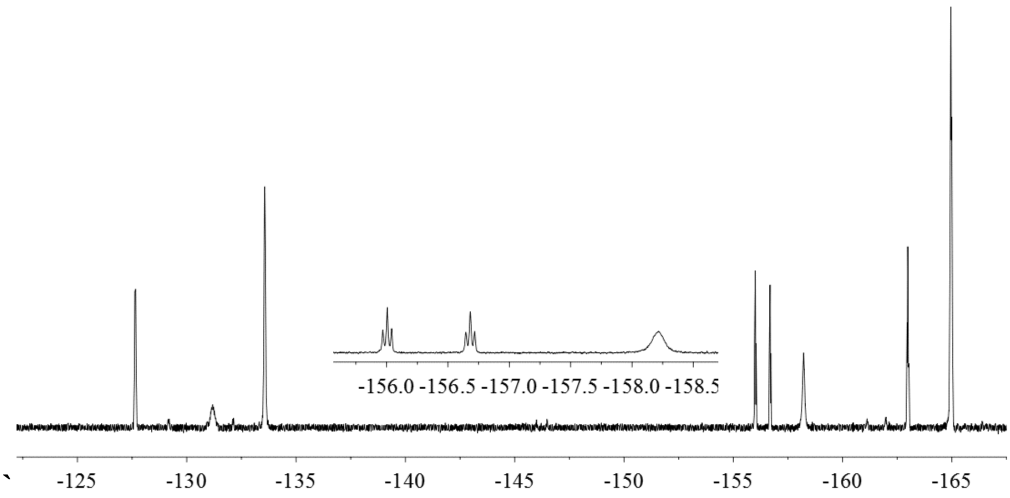


Figure S54 ^{19}F NMR (564 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of compound **14**

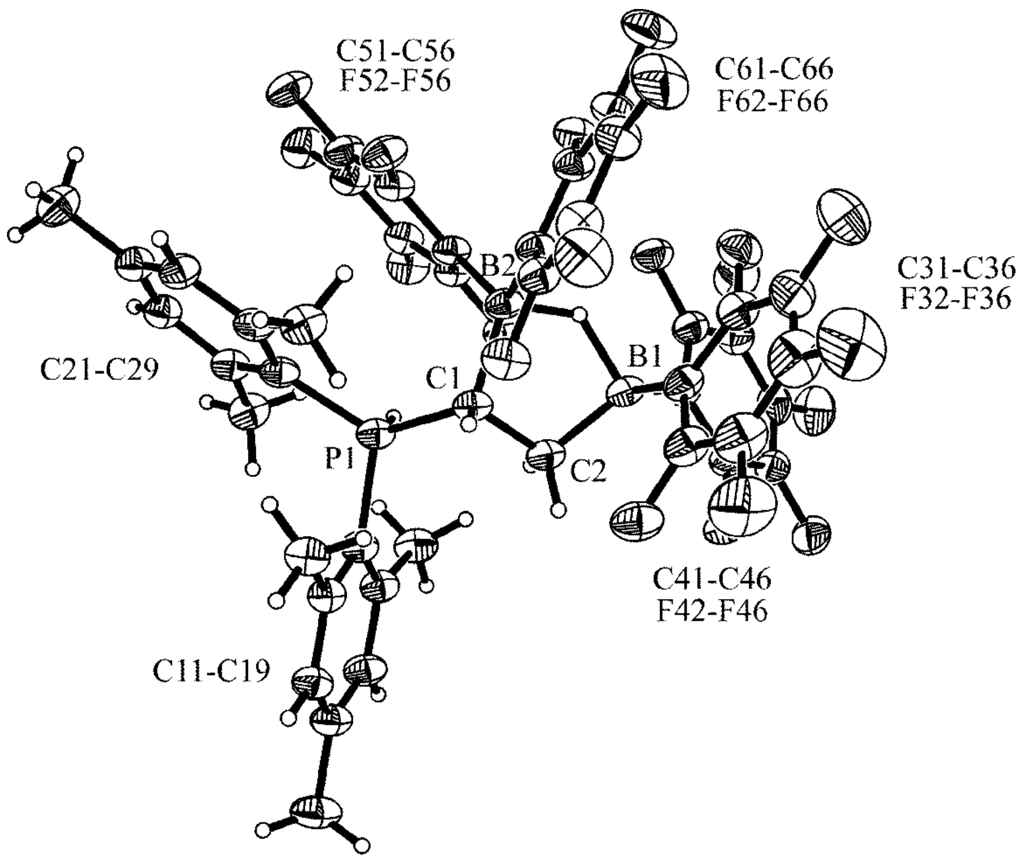
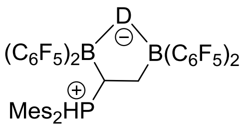


Figure S55 X-Ray crystal structure analysis of compound **14**: formula $C_{44}H_{27}B_2F_{20}P$, M = 988.25, colourless crystal, 0.15 x 0.08 x 0.05 mm, a = 14.7699(5), b = 16.8329(5), c = 17.5277(7) Å, β = 99.020(2) °, V = 4303.9(3) Å^3, ρ_{calc} = 1.525 gcm^{-3}, μ = 1.663 mm^{-1}, empirical absorption correction (0.788 ≤ T ≤ 0.921), Z = 4, monoclinic, space group $P2_1$/n (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 37324 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 $Å^{-1}$, 7449 independent (R_{int} = 0.052) and 5736 observed reflections [I>2σ(I)], 618 refined parameters, R = 0.044, wR^2 = 0.124, max. (min.) residual electron density 0.28 (-0.27) e.$Å^{-3}$, the hydrogen at P1 atom and the hydrogen between B1 and B2 atoms were refined freely; others were calculated and refined as riding atoms.

Synthesis of compound 14-D.



14-D

Scheme S12

Mixing of compound **8** (146 mg, 0.20 mmol) and $DB(C_6F_5)_2$ (69 mg, 0.20 mmol) in CH_2Cl_2 (10 mL) gave a suspension, which was stirred at r.t. for 2h. Then the solid was collected and dried *in vacuo* overnight to give compound **14-D** (130 mg, 0.12 mmol, 60%) as a colorless solid.

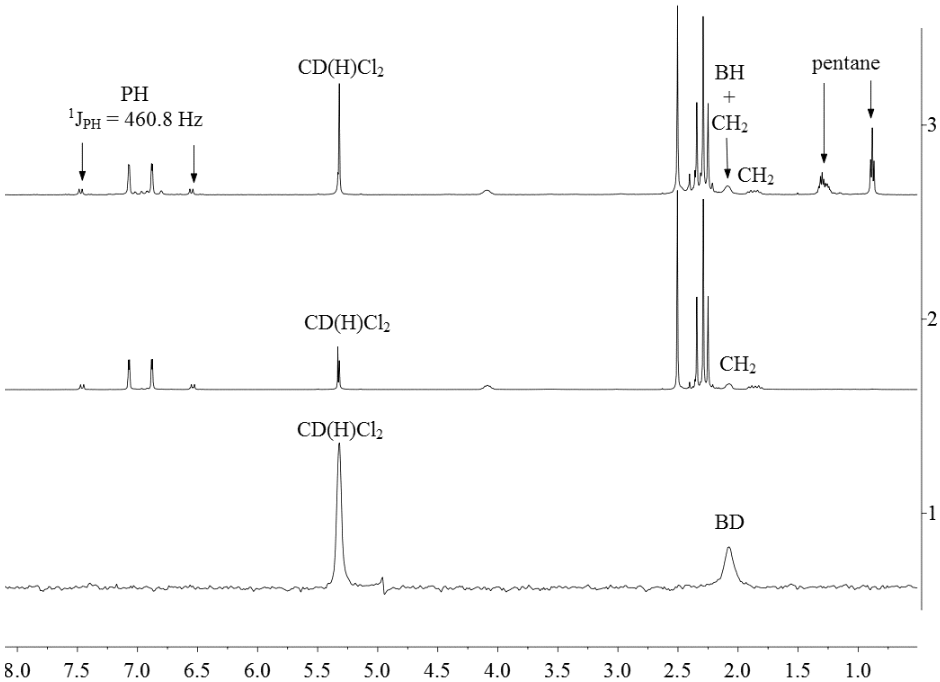
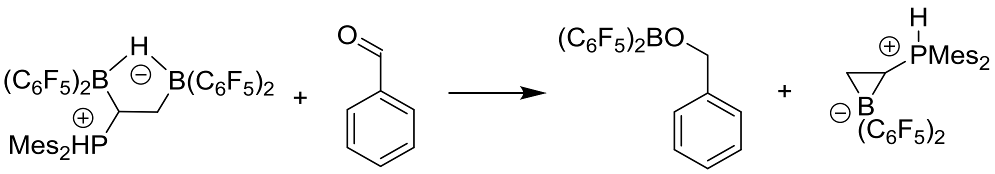


Figure S56 (3): ^{1}H NMR (500 MHz, 299K, [d_2]-CH_2Cl_2) of compound **14**

(2): ^{1}H NMR (500 MHz, 299K, [d_2]-CH_2Cl_2) of compound **14-**D

(1): ^{2}H NMR (77 MHz, 299K, CH_2Cl_2) of compound **14**-D

Reaction of compound 14 with benzaldehyde – generation of compound 8



Scheme S13

Benzaldehyde (22 mg, 0.20 mmol) was added slowly to a solution of compound **14** (198 mg, 0.20 mmol) in CD_2Cl_2 (4 mL). Then the reaction mixture was stirred at r.t. overnight and then characterized by NMR experiments.

$PhCH_2OB(C_6F_5)_2$:

^{1}H NMR (600 MHz, 299 K, [d_2]-CH_2Cl_2): δ = 7.39 (m, 2H, *m*-Ph), 7.35 (m, 2H, *o*-Ph),7.34 (m, 1H, *p*-Ph), 5.28 (s, 2H, $PhCH_2$).

^{13}C{^{1}H} NMR (151 MHz, 299 K, [d_2]-CH_2Cl_2): δ = 137.1 (*i*-Ph), 129.0 (*m*-Ph), 128.7 (*p*-Ph), 127.2 (*o*-Ph), 72.5 ($PhCH_2$).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, [d_2]-CH_2Cl_2): δ^{1}H / δ^{13}C = 7.39 / 129.0 (*m*-Ph), 7.35 / 127.2 (*o*-Ph), 7.34/ 128.7 (*p*-Ph), 5.28 / 72.5 ($PhCH_2$).

^{11}B{^{1}H} NMR (192 MHz, 299K, [d_2]-CH_2Cl_2): δ = 40.8 ($\nu_{1/2}$ ≈ 300 Hz).

^{19}F NMR (564 MHz, 233 K, [d_2]-CH_2Cl_2) δ = -132.0 (m, 4F, *o*), -149.8 (br, 2F, *p*), -161.7 (br, 4F, *m*)[$\Delta\delta^{19}F_{mp}$ = 11.9].

Compound **8**:

^{1}H NMR (600 MHz, 299 K, [d_2]-CH_2Cl_2): δ = 6.97 (d, $^4J_{PH}$ = 4.1 Hz, 2H, *m*-Mes^a), 6.93 (dd, $^1J_{PH}$ = 464.1 Hz, $^3J_{HH}$ = 11.6 Hz, 1H, PH), 6.92 (d, $^4J_{PH}$ = 3.8 Hz, 2H, *m*-Mes^b), 2.41 (s, 6H, *o*-$CH_3^{Mes,b}$), 2.36 (s, 6H, *o*-$CH_3^{Mes,a}$), 2.32 (s, 3H, *p*-$CH_3^{Mes,a}$), 2.29 (s, 3H, *p*-$CH_3^{Mes,b}$), 1.16 (m, 1H, CH), 1.00 (dt, $^3J_{PH}$ = 30.8 Hz, $^2J_{HH}$ ≈ $^3J_{HH}$ = 8.4 Hz), 0.85 (m)(each 1H, CH_2).

^{13}C{^{1}H} NMR (151 MHz, 299 K, [d_2]-CH_2Cl_2): δ = 144.2 (d, $^4J_{PC}$ = 2.8 Hz, *p*-Mes^a), 144.1 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Mes^b), 143.0 (d, $^2J_{PC}$ = 9.9 Hz, *o*-Mes^a), 142.7 (d, $^2J_{PC}$ = 9.5

Hz, *o*-Mes[b]), 131.5 (d, $^3J_{PC}$ = 9.6 Hz, *m*-Mes[a]), 131.4 (d, $^3J_{PC}$ = 9.9 Hz, *m*-Mes[b]), 118.1 (d, $^1J_{PC}$ = 79.0 Hz, *i*-Mes[b]), 117.8 (d, $^1J_{PC}$ = 78.3 Hz, *i*-Mes[a]), 22.1 (d, $^3J_{PC}$ = 7.0 Hz, *o*-$CH_3^{Mes,b}$), 22.0 (br d, $^3J_{PC}$ = 6.9 Hz, *o*-$CH_3^{Mes,a}$), 21.23 (d, $^5J_{PH}$ = 1.3 Hz, *p*-$CH_3^{Mes,a}$), 21.18 (d, $^5J_{PH}$ = 1.2 Hz, *p*-$CH_3^{Mes,b}$), 12.4 (br, CH_2), 4.2 (br d, $^2J_{PC}$ = 60.1 Hz, CH), [C_6F_5 not listed].

^{11}B{^{1}H} NMR (192 MHz, 299K, [d_2]-CH_2Cl_2): δ = -23.8 ($\nu_{1/2}$ ≈ 60 Hz).

^{31}P NMR (243 MHz, 299 K, [d_2]-CH_2Cl_2) δ = -1.2 (br dd, $^1J_{PH}$ ≈ 465 Hz, $^3J_{HH}$ ≈ 31 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, [d_2]-CH_2Cl_2) δ = -1.2 ($\nu_{1/2}$ ≈ 10 Hz).

^{19}F NMR (564 MHz, 233 K, [d_2]-CH_2Cl_2) δ = -130.9 (m, 2F, *o*), -160.5 (t, $^3J_{FF}$ = 20.2 Hz, 1F, *p*), -165.6 (m, 2F, *m*)[$\Delta\delta^{19}F_{mp}$ = 5.1]; -133.3 (m, 2F, *o*), -162.1 (t, $^3J_{FF}$ = 20.2 Hz, 1F, *p*), -166.4 (m, 2F, *m*)[$\Delta\delta^{19}F_{mp}$ = 4.3].

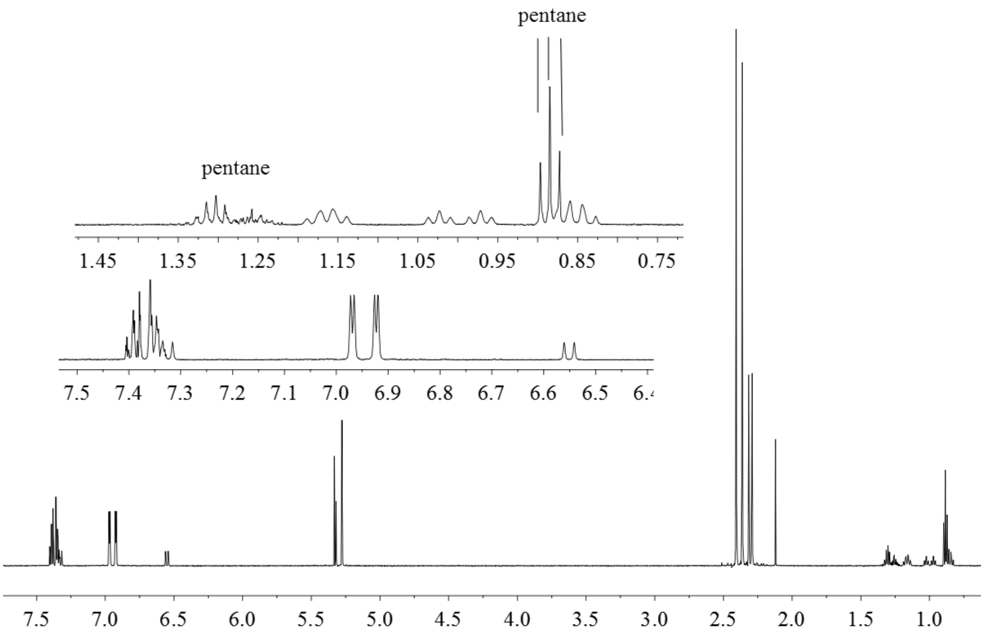


Figure S57 ^{1}H NMR (600 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of the mixture of compound **8** and $PhCH_2OB(C_6F_5)_2$ (b)

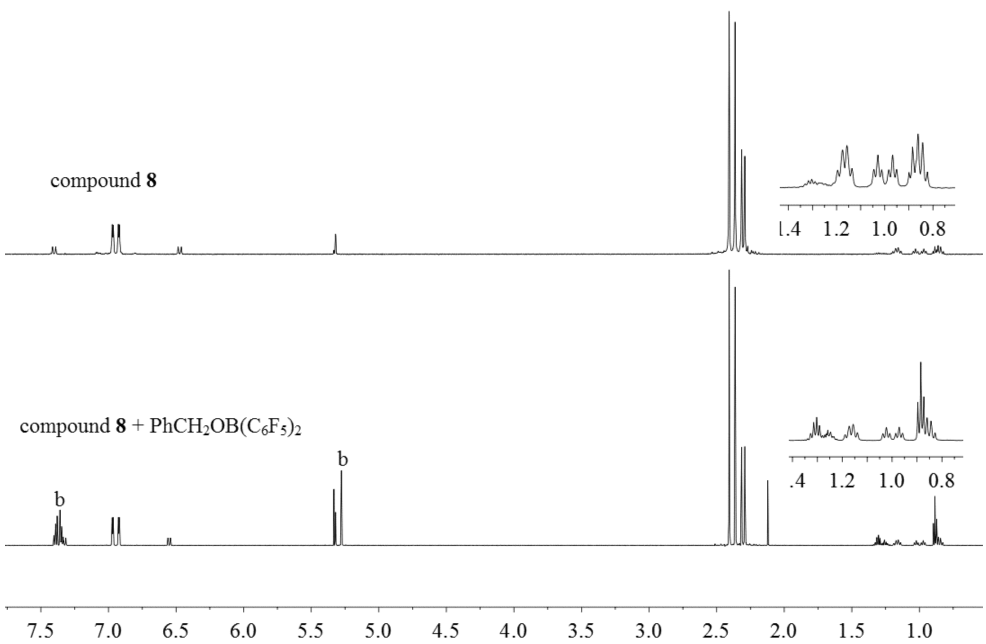


Figure S58 ^{1}H NMR spectra of compound **8** (top, 500 MHz, 299K, [d_2]-CH_2Cl_2) and the mixture of compound **8** and $PhCH_2OB(C_6F_5)_2$ (b) (bottom: 600 MHz, 299K, [d_2]-CH_2Cl_2)

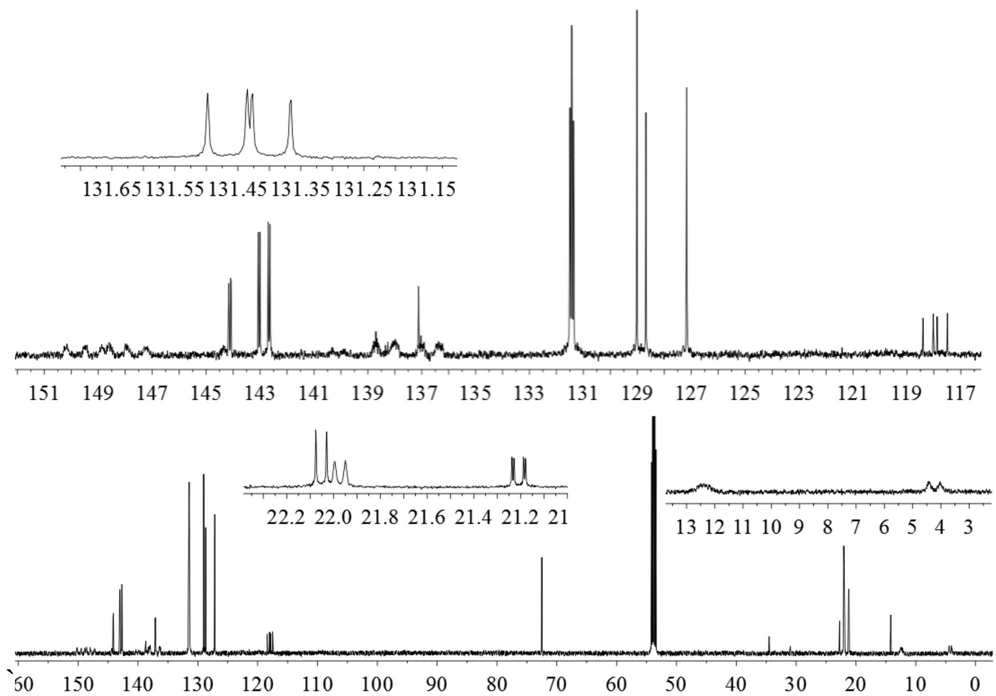


Figure S59 ^{13}C{^{1}H} NMR (151 MHz, 299K, [d_2]-CH_2Cl_2) spectrum of the mixture of compound **8** and $PhCH_2OB(C_6F_5)_2$

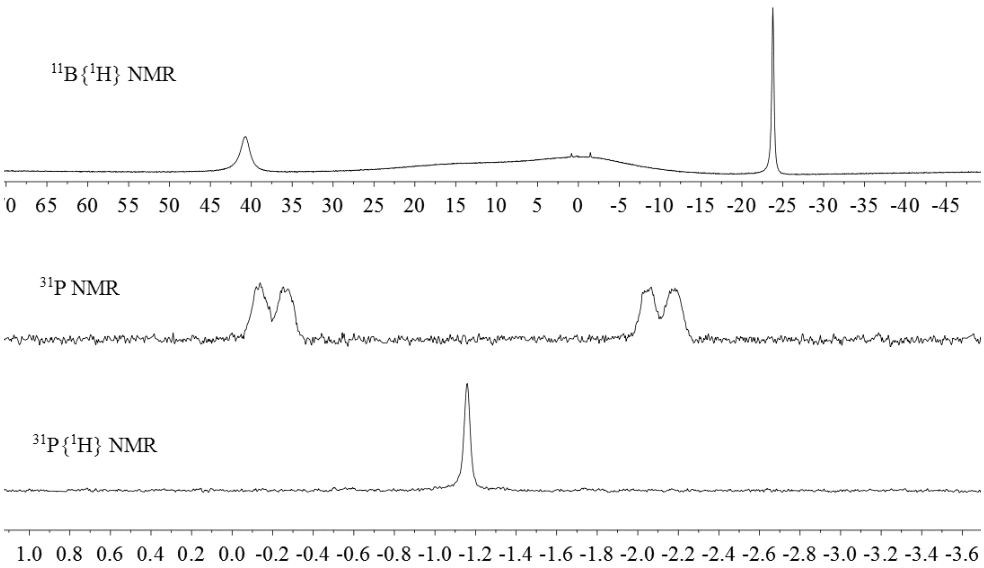


Figure S60 $^{11}B\{^{1}H\}$ NMR (192 MHz, 299K, [d_2]-CH_2Cl_2), ^{31}P and $^{31}P\{^{1}H\}$ NMR (243 MHz, 299K, [d_2]-CH_2Cl_2) spectra of the mixture of compound **8** and $PhCH_2OB(C_6F_5)_2$

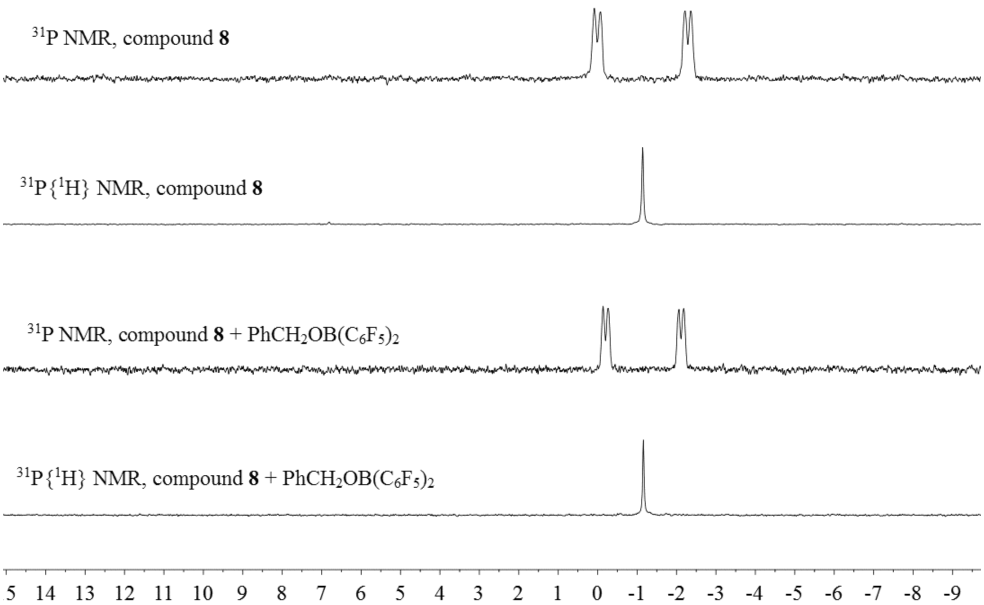


Figure S61 ^{31}P and $^{31}P\{^{1}H\}$ NMR spectra of compound **8** (top two lines, 202 MHz, 299K, [d_2]-CH_2Cl_2) and the mixture of compound **8** and $PhCH_2OB(C_6F_5)_2$ (bottom two lines: 243 MHz, 299K, [d_2]-CH_2Cl_2)

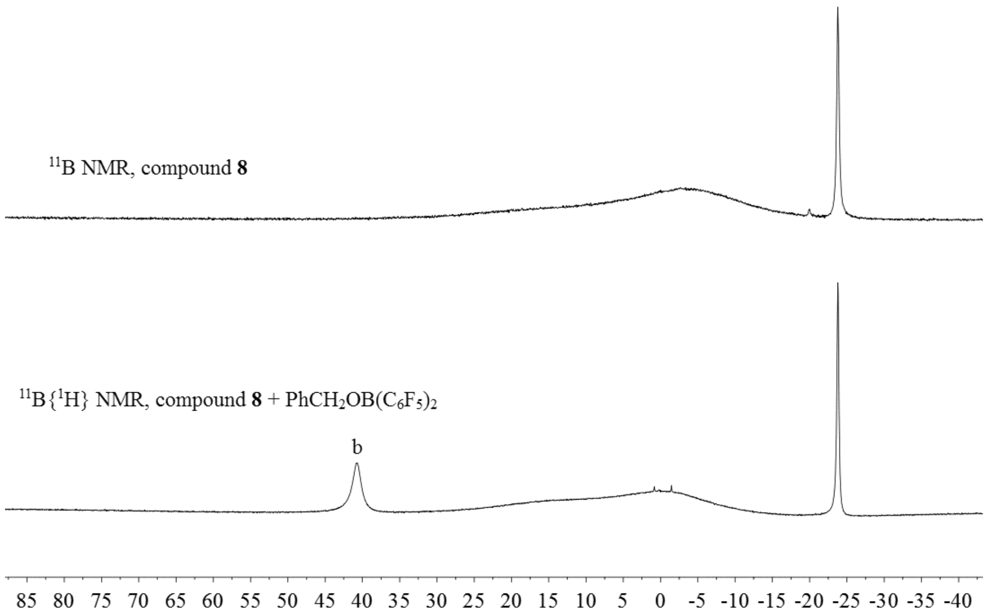


Figure S62 $^{11}B\{^{1}H\}$ NMR spectra of compound **8** (top, 160 MHz, 299K, [d_2]-CH_2Cl_2) and the mixture of compound **8** and $PhCH_2OB(C_6F_5)_2$ (b) (bottom: 192MHz, 299K, [d_2]-CH_2Cl_2)

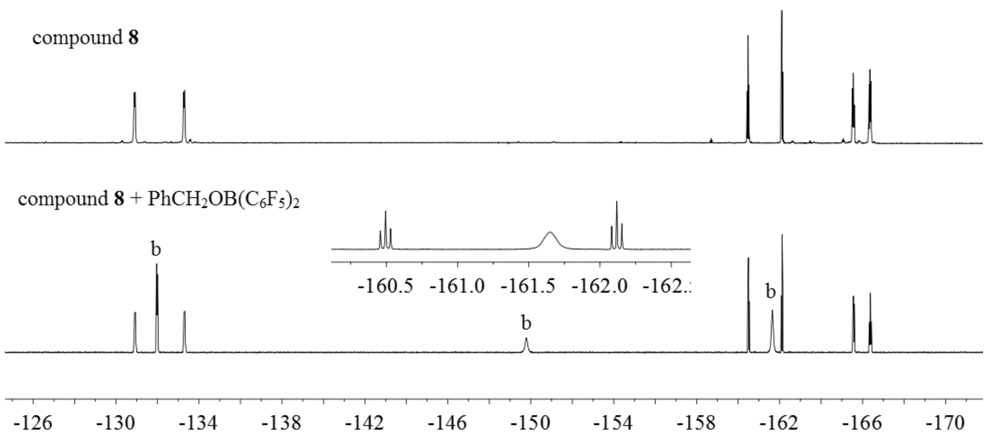
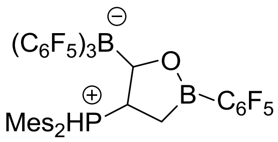


Figure S63 ^{19}F NMR spectra of compound **8** (top, 470 MHz, 299K, [d_2]-CH_2Cl_2) and the mixture of compound **8** and $PhCH_2OB(C_6F_5)_2$ (b) (bottom: 564 MHz, 299K, [d_2]-CH_2Cl_2)

Synthesis of compound 22



Scheme S14

Compound **14** (300 mg, 0.30 mmol) was dissolved in CH_2Cl_2 (10 mL). Then the solution was degassed and purged with CO gas (2.5 bar). After heating the reaction mixture at 80 °C overnight, all volatiles were removed *in vacuo* at rt and the remaining residue was purified by column chromatography [silica gel, CH_2Cl_2] to give compound **22** (183 mg, 0.18 mmol, 60%). Single crystals of compound **22** suitable for the X-ray single crystal structure analysis were obtained by storing a saturated CH_2Cl_2 solution of compound **22** at r.t. for several days.

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 2976(w), 2928(w), 1650(w), 1606(w), 1516(m), 1460(vs), 1397(w), 1321(w), 1275(m), 1088(s), 977(s), 853(w), 772(w), 684(w), 419(w).

Melting point: 213 °C.

Elemental analysis: calc. for $C_{45}H_{27}B_2F_{20}OP$ (1016.26 g/mol): C, 53.18; H, 2.68. Found: C, 53.06; H, 2.77.

^{1}H NMR (600 MHz, 203 K, [d_2]-CH_2Cl_2): δ = 7.26 (s, 1H, *m*-Mes^{a}), 7.05 (s, 1H, *m*-Mes^{b}), 6.99 (s, 2H, *m'*-Mes^{a,b}), 6.97 (dd, $^{1}J_{PH}$ = 456.8, $^{3}J_{HH}$ = 13.1 Hz, 1H, PH), 6.09 (d, $^{3}J_{PH}$ = 30.3 Hz, 1H, BCH), 3.90 (m, 1H, PCH), 2.74 (s, 3H, *o*-$CH_3^{Mes,a}$), 2.58 (s, 3H, *o*-$CH_3^{Mes,b}$), 2.37 (s, 3H, *p*-$CH_3^{Mes,a}$), 2.25 (s, 3H, *p*-$CH_3^{Mes,b}$), 2.14 (s, 3H, *o'*-$CH_3^{Mes,b}$), 1.96 (s, 3H, *o'*-$CH_3^{Mes,a}$), 1.47 (dd, $^{3}J_{PH}$ = 33.2, $^{2}J_{HH}$ = 19.2 Hz,), 1.21 (dm, $^{3}J_{PH}$ = 34.8 Hz)(each 1H, CH_2).

^{13}C{^{1}H} NMR (151 MHz, 203 K, [d_2]-CH_2Cl_2): δ = 146.5 (*p*-Mes^{a}), 145.6 (*p*-Mes^{b}), 144.3 (br m, *o'*-Mes^{b}), 144.2 (br m, *o*-Mes^{a}), 143.6 (d, $^{2}J_{PC}$ = 11.1 Hz, *o*-Mes^{b}), 142.1 (d, $^{2}J_{PC}$ = 11.4 Hz, *o'*-Mes^{a}), 132.6 (d, $^{3}J_{PC}$ = 12.5 Hz, *m*-Mes^{b}), 131.5 (d, $^{3}J_{PC}$ = 10.1 Hz, *m'*-Mes^{b}), 131.4 (d, $^{3}J_{PC}$ = 10.8 Hz, *m'*-Mes^{a}), 130.7 (d, $^{3}J_{PC}$ = 10.2 Hz, *m*-Mes^{a}), 111.2 (d, $^{1}J_{PC}$ = 80.1 Hz, *i*-Mes^{a}), 107.7 (br d, $^{1}J_{PC}$ = 73.9 Hz, *i*-Mes^{b}), 84.2 (br, BCH), 32.3 (br d, $^{1}J_{PC}$ = 33.9 Hz, PCH), 25.7 (br, CH_2), 22.4 (d, $^{3}J_{PC}$ = 6.4 Hz, *o*-$CH_3^{Mes,b}$), 22.1 (d, $^{3}J_{PC}$ = 7.2 Hz, *o*-$CH_3^{Mes,a}$), 21.5 (d, $^{3}J_{PC}$ = 8.7 Hz, *o'*-$CH_3^{Mes,b}$), 21.1 (*p*-$CH_3^{Mes,a}$), 20.9 (m, *o'*-$CH_3^{Mes,a}$), 20.8 (*p*-$CH_3^{Mes,b}$), [C_6F_5 not listed].

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 203 K, [d_2]-CH_2Cl_2): δ^{1}H / δ^{13}C = 7.26 /

130.7 (*m*-Mes^a), 7.05 / 132.6 (*m*-Mes^b), 6.99 / 131.5, 131.4 (*m'*-Mes^{b,a}), 6.09 / 84.2 (BCH), 3.90 / 32.3 (PCH), 2.74 / 22.1 (*o*-$CH_3^{Mes,a}$), 2.58 / 22.4 (*o*-$CH_3^{Mes,b}$), 2.37 / 21.1 (*p*-$CH_3^{Mes,a}$), 2.25 / 20.8 (*p*-$CH_3^{Mes,b}$), 2.14 / 21.5 (*o'*-$CH_3^{Mes,b}$), 1.96 / 20.9 (*o'*-$CH_3^{Mes,a}$), 1.47, 1.21 / 25.7 (CH_2).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 203 K, [d_2]-CH_2Cl_2)[selected traces]: δ^1H / δ^{13}C =2.74 / 144.2, 130.7, 111.2 (*o*-$CH_3^{Mes,a}$ / *o*-Mes^a, *m*-Mes^a, *i*-Mes^a), 2.58 / 143.6, 132.6, 107.7 (*o*-$CH_3^{Mes,b}$ / *o*-Mes^b, *m*-Mes^b, *i*-Mes^b), 2.37 / 146.5, 131.4, 130.7 (*p*-$CH_3^{Mes,a}$ / *p*-Mes^a, *m'*-Mes^a, *m*-Mes^a), 2.25 / 145.6, 132.6, 131.5 (*p*-$CH_3^{Mes,b}$ / *p*-Mes^b, *m*-Mes^b, *m'*-Mes^b).

^{11}B{^{1}H} NMR (192 MHz, 299K, [d_2]-CH_2Cl_2): δ = 45.1 ($\nu_{1/2} \approx$ 1300 Hz), -12.7 (d, *J* ≈ 12 Hz).

^{11}B{^{1}H} NMR (192 MHz, 203K, [d_2]-CH_2Cl_2): δ = 42.7 ($\nu_{1/2} \approx$ 2500 Hz), -12.9 ($\nu_{1/2} \approx$ 100 Hz).

^{31}P NMR (243 MHz, 203 K, [d_2]-CH_2Cl_2) δ = -5.6 (br d, $^1J_{PH} \approx$ 460 Hz).

^{31}P{^{1}H} NMR (243 MHz, 203 K, [d_2]-CH_2Cl_2) δ = -5.6 ($\nu_{1/2} \approx$ 60 Hz).

^{19}F NMR (564 MHz, 203 K, [d_2]-CH_2Cl_2) δ = -128.3 (m, 2F, *o*), -158.9 (br t, $^3J_{FF}$ = 19.1 Hz, 1F, *p*), -164.4, -164.9 (each m, each 1F, *m*)[$\Delta\delta^{19}F_{mp}$ = 5.5, 6.0], -128.1 (m, 1F, *o*), -131.6 (br, 1F, *o'*), -160.3 (br t, $^3J_{FF}$ = 19.4 Hz, 1F, *p*), -164.2 (m, 1F, *m*), -164.8 (m, 1F, *m'*)[$\Delta\delta^{19}F_{mp}$ = 3.9, 4.5], -129.9 (m, 1F, *o*), -136.0 (br, 1F, *o'*), -161.8 (br t, $^3J_{FF}$ = 18.6 Hz, 1F, *p*), -165.2 (m, 1F, *m'*), -166.1 (m, 1F, *m*)[$\Delta\delta^{19}F_{mp}$ = 3.4, 4.3](B(C_6F_5)$_3$); -129.4 (br m, 2F, *o*), -147.4 (br t, $^3J_{FF}$ = 19.2 Hz, 1F, *p*), -161.6 (m, 2F, *m*)(BC_6F_5)[$\Delta\delta^{19}F_{mp}$ = 14.2].

^{19}F,^{19}F GCOSY (564 MHz / 564 MHz, 203 K, [d_2]-CH_2Cl_2) δ^{19}F / δ^{19}F = -128.3 / -164.4, -164.9 (*o* / *m*), -158.9 / -164.4, -164.9 (*p* / *m*) (B(C_6F_5)$_3$); -128.1 / 164.2 (*o* / *m*), -131.6 / -164.8 (*o'* / *m'*), -160.3 / -164.2, -164.8 (*p* / *m*, *m'*) (B(C_6F_5)$_3$); -129.9 / 166.1 (*o* / *m*), -136.0 / -165.2 (*o'* / *m'*), 161.8 / 166.1, 165.2 (*p* / *m*, *m'*) (B(C_6F_5)$_3$); -129.4 / -161.6 (*o* / *m*), -147.4 / -161.6 (*p* / *m*) [B(C_6F_5)].

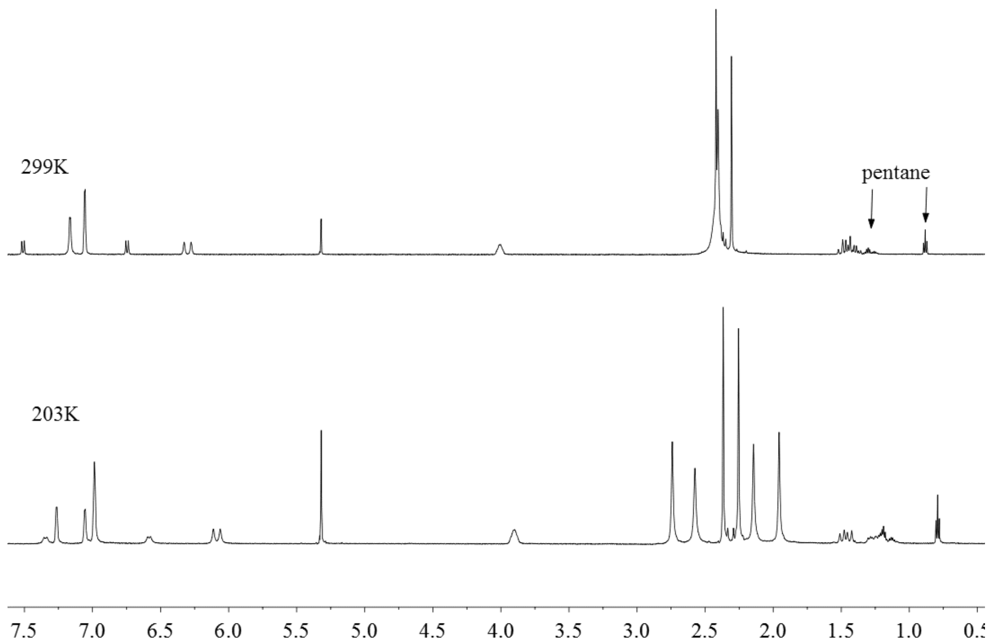


Figure S64 ^{1}H NMR (600 MHz, top: 299 K; bottom: 203 K, [d_2]-CH_2Cl_2) spectra of compound **22**

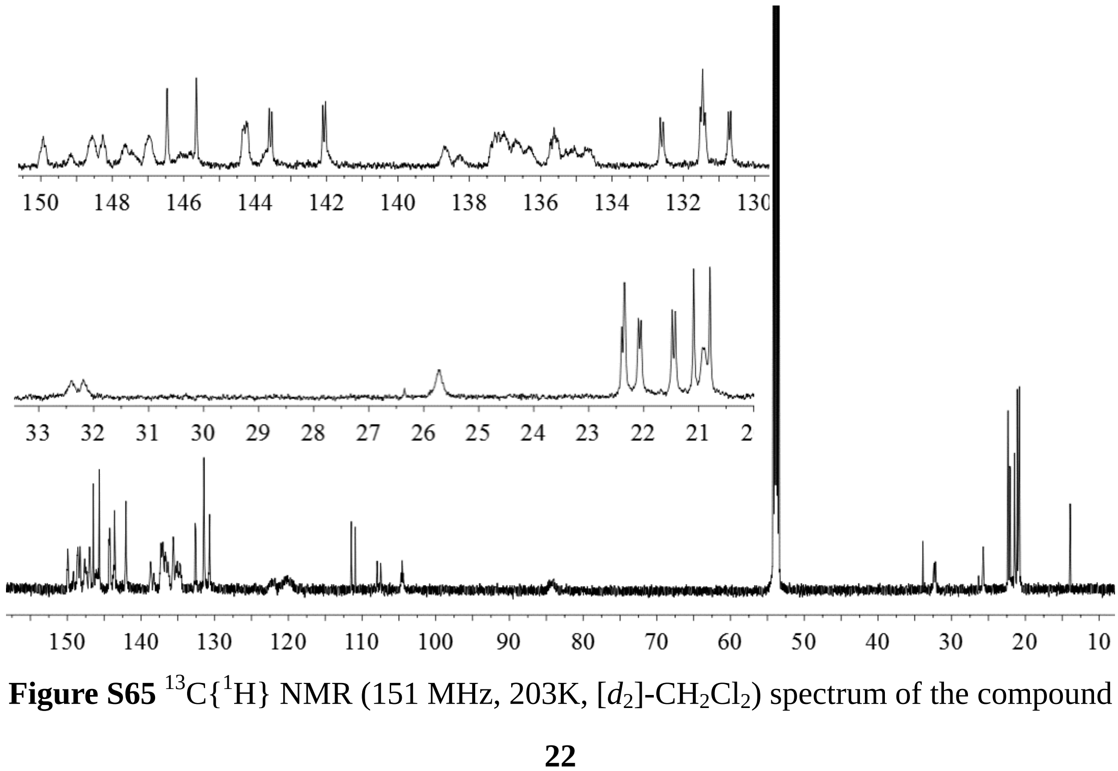


Figure S65 ^{13}C{^{1}H} NMR (151 MHz, 203K, [d_2]-CH_2Cl_2) spectrum of the compound **22**

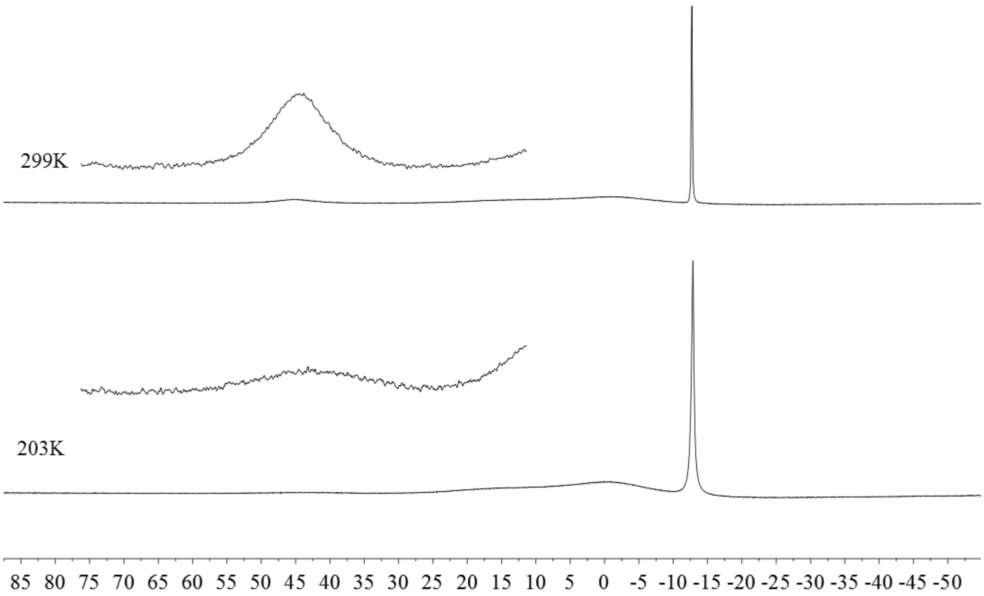


Figure S66 $^{11}B\{^1H\}$ NMR (192 MHz, top: 299 K; bottom: 203 K, [d_2]-CH_2Cl_2) spectra of compound **22**

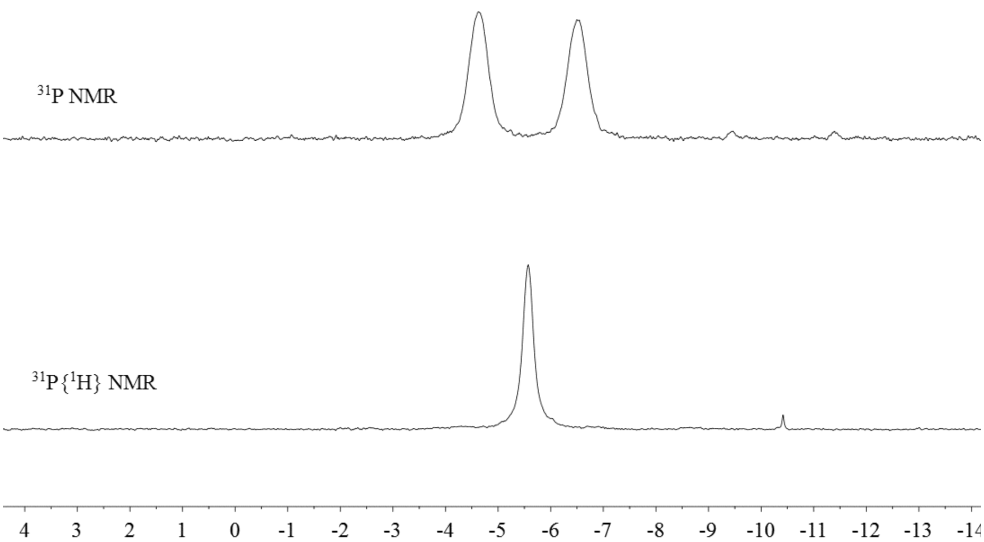


Figure S67 ^{31}P and $^{31}P\{^1H\}$ NMR (243 MHz, 203K, [d_2]-CH_2Cl_2) spectra of the compound **22**

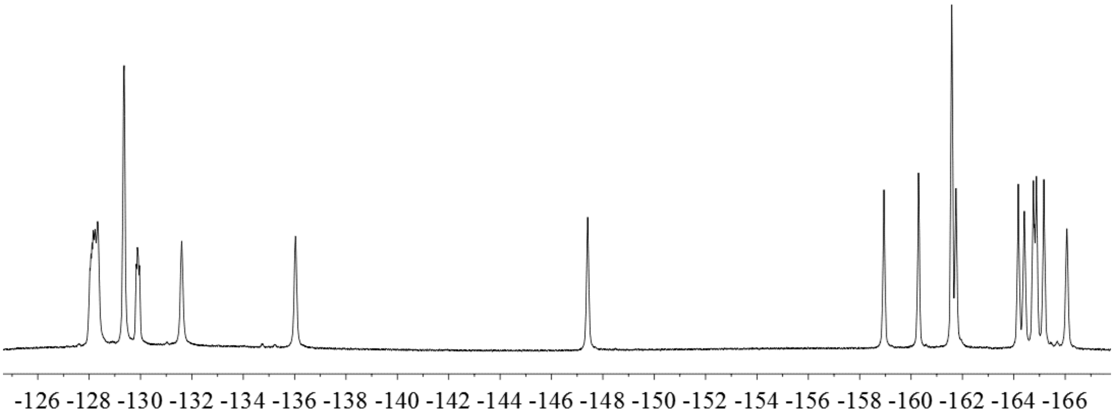
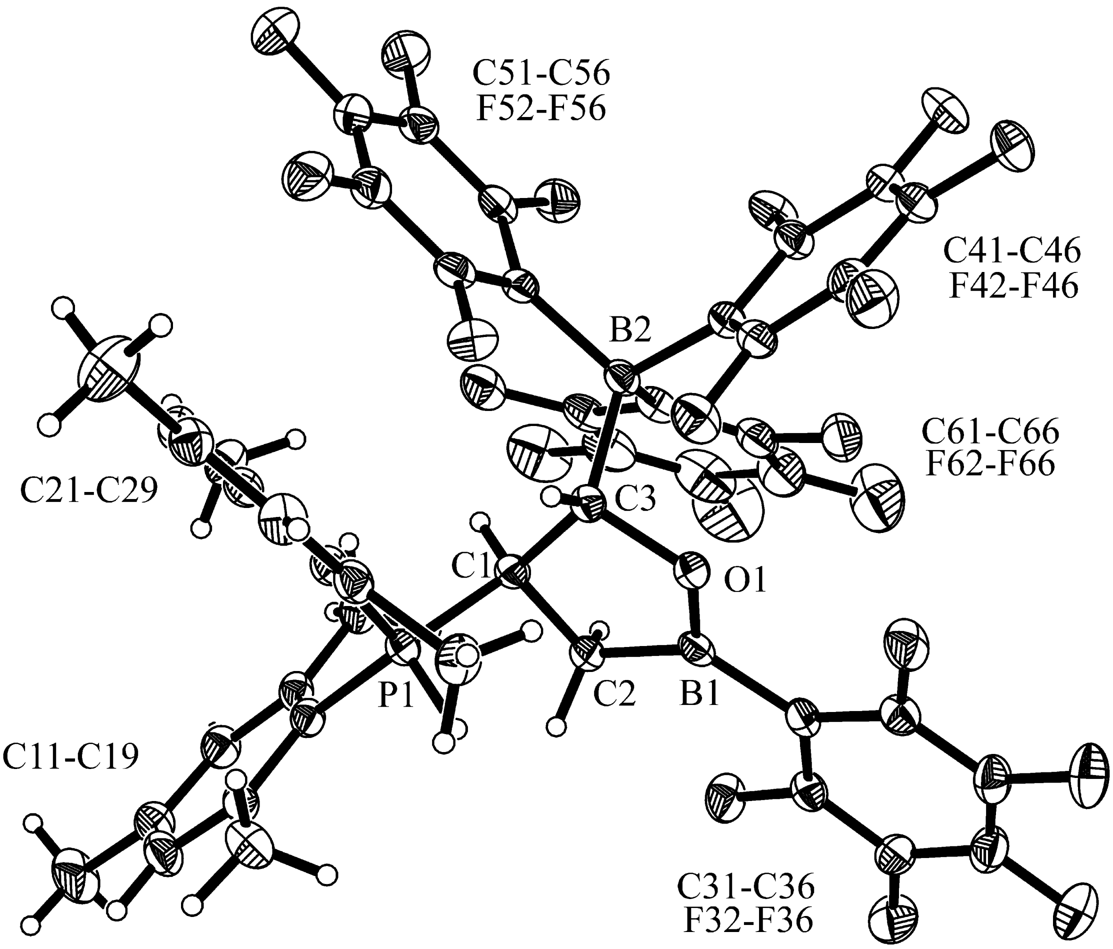


Figure S68 ^{19}F NMR (564 MHz, 203K, [d_2]-CH_2Cl_2) spectrum of compound **22**

Figure S69 X-Ray crystal structure analysis of compound **22**: formula $C_{45}H_{27}B_2F_{20}OP$, M = 1016.26, colourless crystal, 0.13 x 0.13 x 0.08 mm, a = 11.7085(2), b = 20.9557(4), c = 17.8664(3) Å, β = 107.975(1) °, V = 4169.7(1) Å^3, ρ_{calc} = 1.619 gcm^{-3}, μ = 0.194 mm^{-1}, empirical absorption correction (0.975 ≤ T ≤ 0.984), Z = 4, monoclinic, space group $P2_1$/n (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 21611 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 7293 independent (R_{int} = 0.080) and 4897 observed reflections [I>2σ(I)], 632 refined parameters, R = 0.066, wR^2 = 0.156, max. (min.) residual electron density 0.36 (-0.31) e.Å^{-3}, the hydrogen at P1 atom was refined freely; others were calculated and refined as riding atoms.



*Control reaction: In situ reaction of compound **14** with carbon monoxide (NMR scale).*

22 **i-22**
(tentatively assigned)

Scheme S15

Compound **14** (22 mg, 0.030 mmol) was dissolved in CD_2Cl_2 (2 mL). Then the solution was degassed and purged with CO gas (2.5 bar). After heating the reaction mixture at 80 °C overnight, the CO gas was released at r.t. and the obtained solution was transferred to a NMR tube. The sample was then characterized by NMR experiments.

Comment: A mixture of compound **22** and a second compound which was tentatively assigned as the isomer **i-22** was observed (conversion ≈ 81%; **22** : **i-22** ≈ 80 : 20). The NMR data of compound **22** are consistent with those listed above. Compound **i-22** was characterized by selected resonances:

^{1}H NMR (500 MHz, 299 K, [d_2]-CH_2Cl_2)[selected resonances]: δ = 6.39 (dd, $^{1}J_{PH}$ = 463.6, $^{3}J_{HH}$ = 12.7 Hz, PH), 6.39 (br t, $^{3}J_{HH}$ = 7.7 Hz, BCH), 2.82 (br, PCH)[1], 2.52 (CH_2)[1], [[1] assigned from gcosy and ghsqc experiment]

^{13}C{^{1}H} NMR (126 MHz, 299 K, [d_2]-CH_2Cl_2)[selected resonances]: δ = 89.0 (BCH), 31.0 (CH_2), 27.5 (PCH), [assigned from ghsqc experiment]

^{1}H,^{13}C GCOSY (500 MHz / 500 MHz, 299 K, [d_2]-CH_2Cl_2)[selected traces]: δ^{1}H / δ^{1}H = 7.46 / 2.82 (PH / PCH), 2.52 / 6.39, 2.82 (CH_2 / BCH, PCH).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, [d_2]-CH_2Cl_2)[selected traces]: δ^{1}H / δ^{13}C = 6.39 / 89.4 (BCH), 2.82 / 27.5 (PCH), 2.52 / 31.0 (CH_2).

^{11}B NMR (160 MHz, 299K, [d_2]-CH_2Cl_2): δ = -12.7 ($B(C_6F_5)_3$).

^{31}P NMR (202 MHz, 299 K, [d_2]-CH_2Cl_2): δ = -9.8 (br dm, $^{1}J_{PH}$ ≈ 464 Hz).

^{31}P{^{1}H} NMR (202 MHz, 299 K, [d_2]-CH_2Cl_2): δ = -9.8 ($\nu_{1/2}$ ≈ 10 Hz).

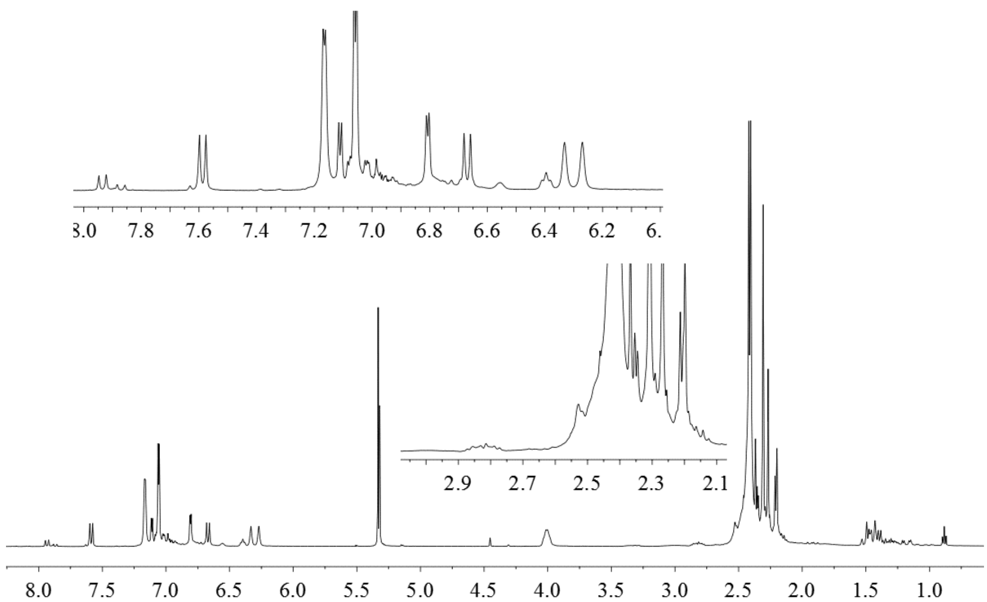


Figure S70 ^{1}H NMR (500 MHz, 299 K, [d_2]-CH_2Cl_2) of the *in situ* reaction of compound **14** with carbon monoxide

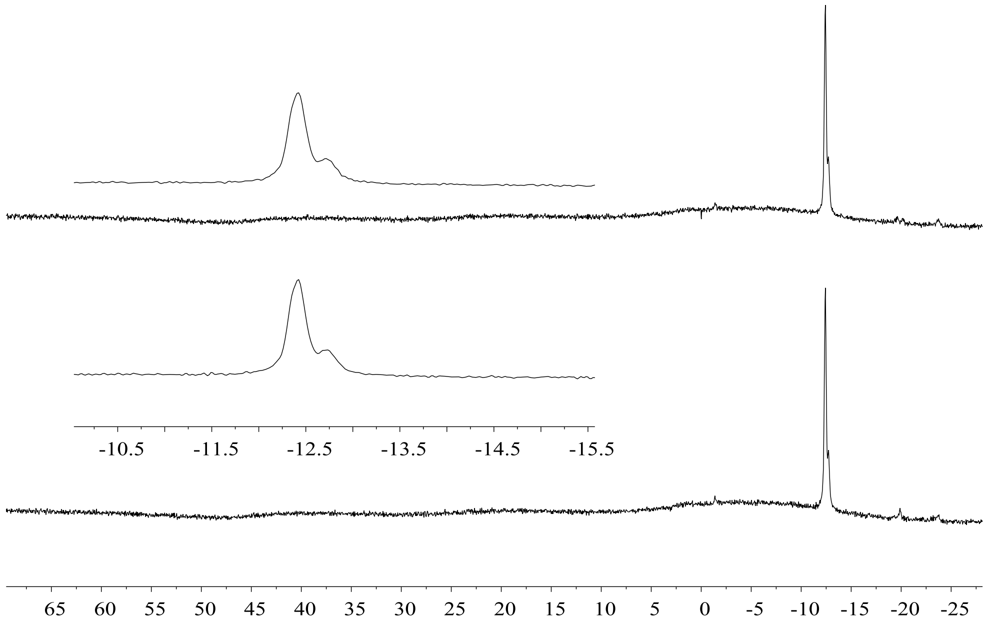


Figure S71 ^{11}B NMR (160 MHz, 299K, [d_2]-CH_2Cl_2) of the *in situ* reaction of compound **14** with carbon monoxide

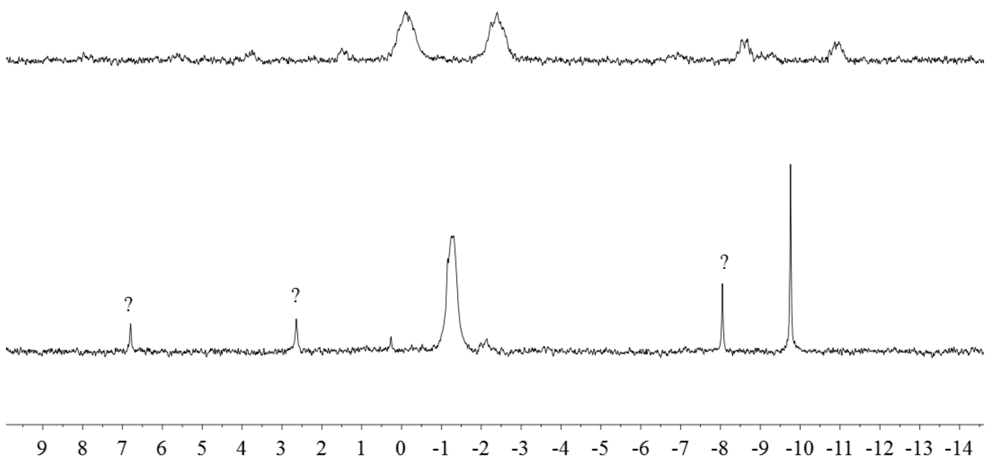
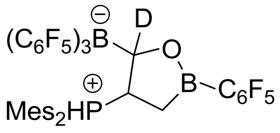


Figure S72 $^{31}P\{^1H\}$ NMR (202 MHz, 299 K, [d_2]-CH_2Cl_2) of the *in situ* reaction of compound **14** with carbon monoxide (?: compounds not yet identified)

Synthesis of compound 22-D.



Scheme S16

Compound **14-D** (80 mg, 0.074 mmol) was dissolved in CH_2Cl_2 (5 mL). Then the solution was degassed and purged with CO gas (2.5 bar). After heating the reaction mixture at 80 °C overnight, all volatiles were removed *in vacuo* at rt and the remaining residue was purified by column chromatography [silica gel, CH_2Cl_2] to give compound **22-D** (40 mg, 0.039 mmol, 53%).

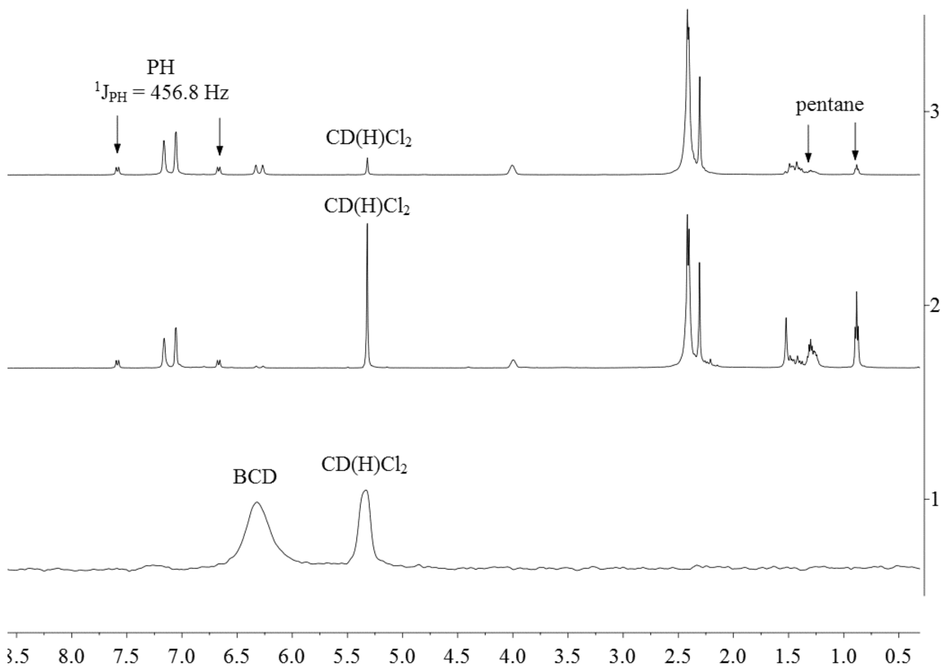


Figure S73 (3): ^{1}H NMR (500 MHz, 299K, [d_2]-CH_2Cl_2) of compound **22**

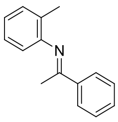
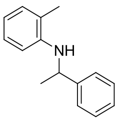
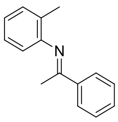
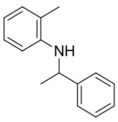
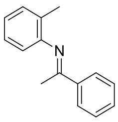
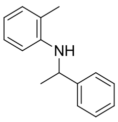
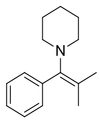
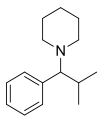
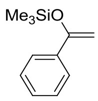
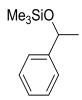
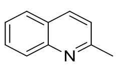
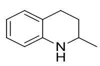
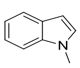
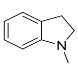
(2): ^{1}H NMR (500 MHz, 299K, [d_2]-CH_2Cl_2) of compound **22-**D

(1): ^{2}H NMR (77 MHz, 299K, CH_2Cl_2) of compound **22**-D

Compound 10 catalyzed hydrogenation reaction

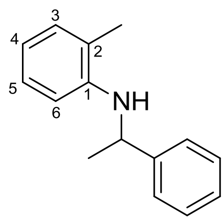
General procedure: compound **10** (X mmol) and the respective substrate were mixed in CD_2Cl_2 (2 mL) using a special ampule (10 mL) (Spies, P.; Schwendemann, S.; Lange, S.; Kehr, G.; Fröhlich, R.; Erker, G. *Angew. Chem. Int. Ed.* **2008**, *47*, 7543-7546.) with magnetic stirrer. Subsequently the ampule was put into an autoclave and H_2 gas (50 bar) was applied. Then the reaction mixture was stirred at 90 °C for Y h. The obtained reaction mixture was directly characterized by ^{1}H NMR spectroscopy. The conversion was estimated by integration of suitable ^{1}H NMR signals.

Table S1 $[P]H^+/[B]H^-$ system **10** catalyzed hydrogenation of an imine, an enamine, a silylenol ether, 2-methylquinoline, and N-methylindole. [a]

entry	substrate	product	substrate mg (mmol)	X mol % **10**	reaction time Y	conversion (isolated)
1			21 (0.1)	20	20h	>99%
2			209 (1.0)	10	36h	>99% (86%)
3			21 (0.1)	5	48h	50%
4			215 (1.0)	10	36h	>99% (60%)
5			192 (1.0)	10	36h	>99% (62%)
6			143 (1.0)	10	36h	>99% (70%)
7			143 (1.0)	10	72h	>99% (65%)

[a] 90 °C, 50 bar H_2, in [d_2]-CH_2Cl_2 solution.

Hydrogenation of 2-tolyl-(1-phenylethylidene)amine



Scheme S17

Following the general procedure compound **10** (64 mg, 0.10 mmol) reacted with 2-tolyl-(1-phenylethylidene)amine (210 mg, 1.0 mmol) at 90 °C for 36 h. *Purification.* All volatiles of the reaction mixture were removed in vacuo and the remaining residue was purified by column chromatography [Silica gel, V(pentane):V(CH_2Cl_2) = 5:1] to give the respective amine (180 mg, 86%) as a colorless oil.

^{1}H NMR (400 MHz, 299K, [d_2]-CH_2Cl_2): δ = 7.37 (m, 2H, *o*-Ph), 7.33 (m, 2H, *m*-Ph), 7.23 (m, 1H, *p*-Ph), 7.03 (dm, $^3J_{HH}$ = 7.4 Hz, 1H, 3-H), 6.91 (tm, $^3J_{HH}$ = 7.2 Hz, 1H, 5-H), 6.56 (tm, $^3J_{HH}$ = 7.4 Hz, 1H, 4-H), 6.34 (d, $^3J_{HH}$ = 8.1 Hz, 1H, 6-H), 4.56 (q, $^3J_{HH}$ = 6.7 Hz, 1H, CH), 3.94 (s, 1H, NH), 2.23 (s, 3H, CH_3^{tol}), 1.56 (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, 299K, [d_2]-CH_2Cl_2): δ = 146.0 (*i*-Ph), 145.5 (C1), 130.2 (C3), 128.9 (*m*-Ph), 127.13 (*p*-Ph), 127.07 (C5), 126.1 (*o*-Ph), 122.1 (C2), 117.0 (C4), 111.2 (C6), 53.5 (CH)[1], 25.5 (CH_3), 17.7 (CH_3^{tol}), [[1] from the ghsqc experiment].

^{1}H,^{1}H GCOSY (400 MHz / 400 MHz, 299 K, [d_2]-CH_2Cl_2) [selected traces]: 7.03 / 6.56, 2.23 (3-H / 4-H, CH_3^{tol}), 6.56 / 7.03, 6.91 (4-H / 3-H, 5-H), 4.56 / 1.56 (CH / CH_3).

^{1}H,^{13}C GHSQC (400 MHz / 101 MHz, 299 K, [d_2]-CH_2Cl_2): δ^{1}H / δ^{13}C = 7.37 / 126.1 (*o*-Ph), 7.33 / 128.9 (*m*-Ph), 7.23 / 127.13 (*p*-Ph), 7.03 / 130.2 (C3), 6.91 / 127.07 (C5), 6.56 / 117.0 (C4), 6.34 / 111.2 (C6), 4.56 / 53.5 (CH), 2.23 / 17.7 (CH_3^{tol}), 1.56 / 25.5 (CH_3).

^{1}H,^{13}C GHMBC (400 MHz / 101 MHz, 299 K, [d_2]-CH_2Cl_2)[selected traces]: δ^{1}H / δ^{13}C = 7.32 / 126.1, 146.0 (*m*-Ph / *m*-Ph, *i*-Ph), 6.56 / 122.1, 111.2 (4-H / C2, C6), 7.03 / 145.5, 127.0 (3-H / C1, C5), 2.23 / 145.5, 130.2, 122.1, 17.7 (CH_3^{tol} / C1, C3, C2, CH_3^{tol}), 1.56 / 146.0, 53.5 (CH_3 / *i*-Ph, CH).

Exact MS: calc. for [$C_{15}H_{17}NH$]: 212.1434. Found [$C_{15}H_{17}NH$]: 212.1443.

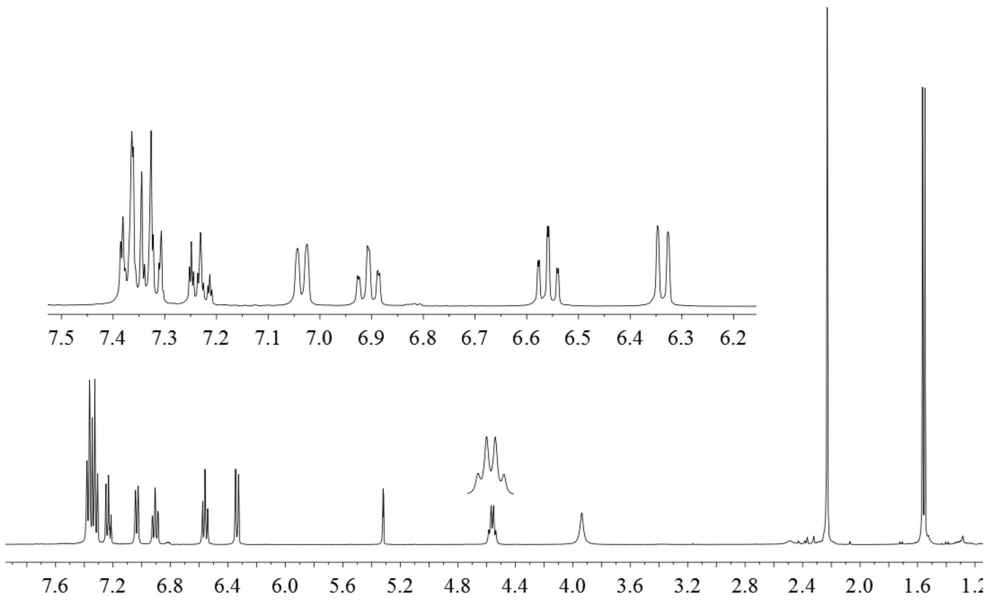


Figure S74 ^{1}H NMR (400 MHz, 299K, [d_2]-CH_2Cl_2)

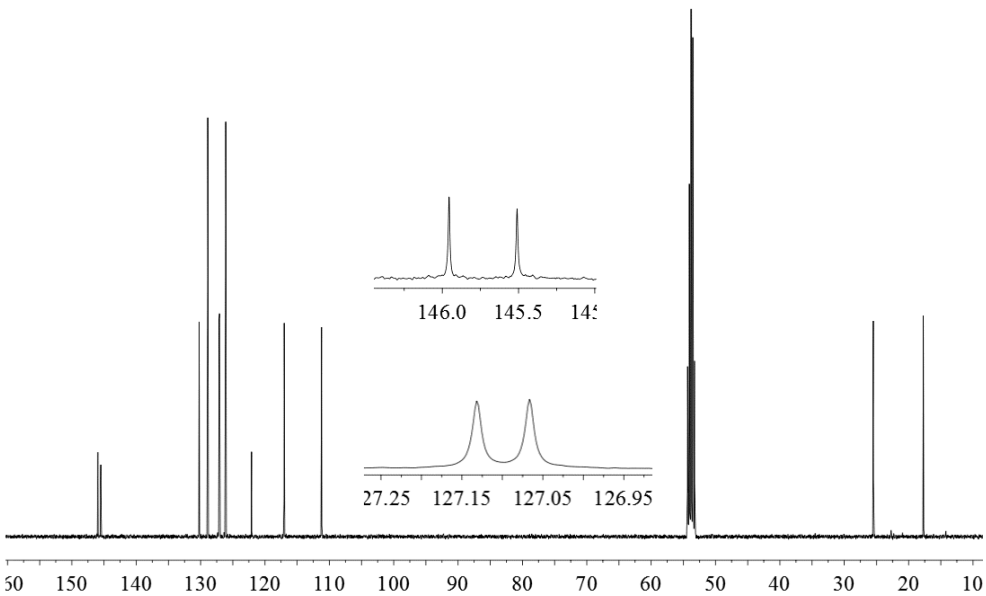
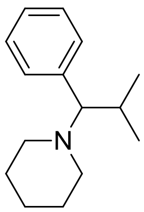


Figure S75 ^{13}C{^{1}H} NMR (101MHz, 299K, [d_2]-CH_2Cl_2)

Hydrogenation of 1-(2-methyl-1-phenylprop-1-en-1-yl)piperidine



Scheme S18

Following the general procedure compound **10** (64 mg, 0.10 mmol) reacted with 1-(2-methyl-1-phenylprop-1-en-1-yl)-piperidine (215 mg, 1.0 mmol) at 90 °C for 36 h. *Purification.* HCl solution (10 mL, 1M in water) was added to the reaction mixture. After 10 min stirring the aqueous phase was separated and treated with NaOH (1M in water). The suspension was exacted with pentane (10 mL × 2). The organic phases were combined and dried with Mg_2SO_4. Then all volatiles were removed by rotary evaporators (40 °C, 700 mbar) to give the respective amine (130 mg, 60%) as a colorless oil.

^{1}H NMR (400 MHz, 299K, [d_2]-CH_2Cl_2): δ = 7.30 (m, 2H, *m*-Ph), 7.24 (m, 1H, *p*-Ph), 7.13 (m, 2H, *o*-Ph), 2.97 (d, $^3J_{HH}$ = 9.6 Hz, 1H, NCH), 2.27 (m, 1H, CH), 2.30, 2.19 (each br, each 2H, NCH_2), 1.51 (m, 4H, CH_2), 1.30 (m, 2H, CH_2), 1.01, 0.68 (each d, $^3J_{HH}$ = 6.6 Hz, each 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, 299K, [d_2]-CH_2Cl_2): δ = 138.5 (*i*-Ph), 129.6 (*o*-Ph), 127.7 (*m*-Ph), 126.8 (*p*-Ph), 77.3 (NCH), 51.1 (NCH_2), 28.2 (CH), 27.0 (CH_2) , 25.3 (CH_2), 20.8, 19.9 (CH_3).

^{1}H,^{1}H GCOSY (400 MHz / 400 MHz, 299 K, [d_2]-CH_2Cl_2) [selected traces]: 2.27 / 1.01, 0.68 (CH / CH_3, CH_3), 2.30 / 1.51 (NCH_2 / CH_2).

^{1}H,^{13}C GHSQC (400 MHz / 101 MHz, 299 K, [d_2]-CH_2Cl_2): δ^{1}H / δ^{13}C = 7.30 / 127.7 (*m*-Ph), 7.24 / 126.8 (*p*-Ph), 7.13 / 129.6 (*o*-Ph), 2.97 / 77.3 (NCH), 2.27 / 28.2 (CH), 2.30, 2.19 / 51.1 (NCH_2), 1.51 / 27.0 (CH_2), 1.30 / 25.3 (CH_2), 1.01 / 20.8 (CH_3), 0.68 / 19.9 (CH_3).

^{1}H,^{13}C GHMBC (400 MHz / 101 MHz, 299 K, [d_2]-CH_2Cl_2) [selected traces]: δ^{1}H / δ^{13}C = 7.30 / 138.5, 127.7 (*m*-Ph / *m*-Ph, *i*-Ph).

Exact MS: calc. for [$C_{15}H_{23}NH$]: 218.1903. Found [$C_{15}H_{23}NH$]: 218.1907.

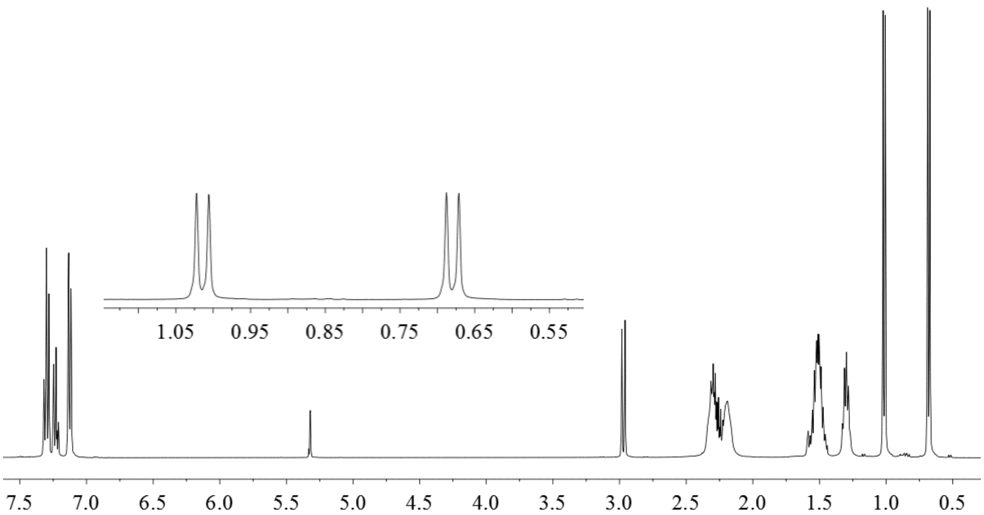


Figure S76 ^{1}H NMR (400 MHz, 299K, [d_2]-CH_2Cl_2)

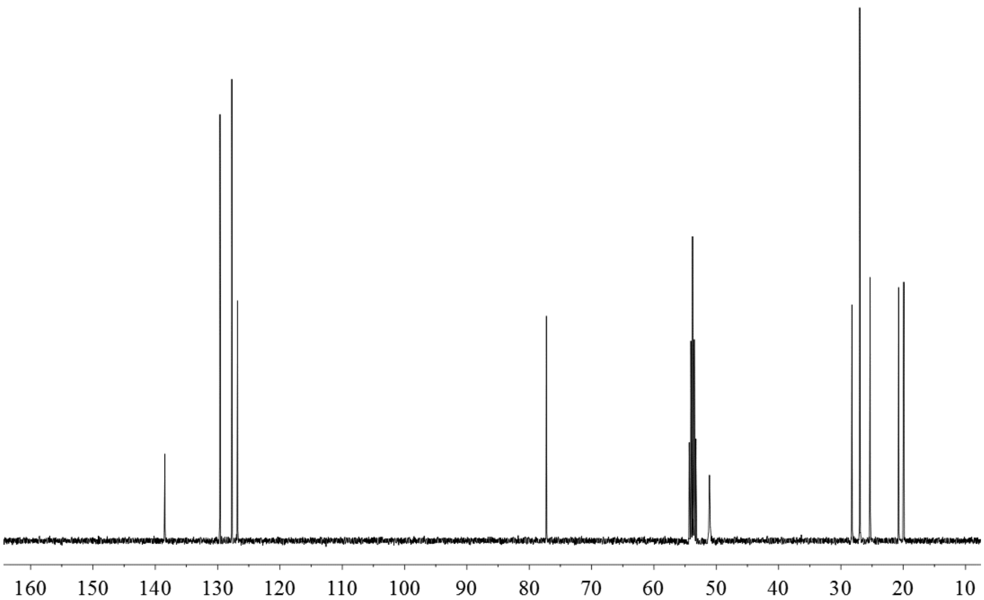


Figure S77 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, [d_2]-CH_2Cl_2)

Hydrogenation of trimethyl((1-phenylvinyl)oxy)silane

Scheme S19

Following the general procedure compound **10** (64 mg, 0.10 mmol) reacted with trimethyl((1-phenylvinyl)oxy)silane (192 mg, 1.0 mmol) at 90 °C for 36 h. *Purification.* Pentane (50 mL) was added to the reaction mixture and the obtained suspension was filtered through Celite. Then all volatiles of the filtrate were removed by rotary evaporator (40 °C, 700 mbar) to give the respective product (120 mg, 62%) as a colorless oil.

[Comment: The used CD_2Cl_2 solution was admixed with ca. 18% of the corresponding alcohol: selected resonances: ^{1}H NMR (400 MHz, 299K, [d_2]-CH_2Cl_2): δ = 4.87 (q, $^3J_{HH}$ = 6.4 Hz, 1H, CH), 1.86 (d, 1H, OH), 1.46 (d, $^3J_{HH}$ = 3.6 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, 299K, [d_2]-CH_2Cl_2): 146.6 (*i*-Ph), 69.9 (CH), 25.5 (CH_3),

^{1}H NMR (400 MHz, 299K, [d_2]-CH_2Cl_2): δ = 7.32 (m, 4H, *o*,*m*-Ph), 7.22 (m, 1H, *p*-Ph), 4.86 (q, $^3J_{HH}$ = 6.4 Hz, 1H, CH), 1.40 (d, $^3J_{HH}$ = 6.4 Hz, 3H, CH_3), 0.07 (s, $^2J_{SiH}$ = 6.5 Hz, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR (101 MHz, 299K, [d_2]-CH_2Cl_2): 147.0 (*i*-Ph), 128.4 (*m*-Ph), 127.1 (*p*-Ph), 125.7 (*o*-Ph), 70.9 (CH), 27.0 (CH_3), 0.1 ($SiMe_3$).

^{1}H,^{13}C GHSQC (400 MHz / 101 MHz, 299 K, [d_2]-CH_2Cl_2): δ^{1}H / δ^{13}C = 7.32 / 125.7 (*o*-Ph), 7.32 / 128.4 (*m*-Ph), 7.22 / 127.1 (*p*-Ph), 4.86 / 70.9 (CH), 1.40 / 27.0 (CH_3), 0.07 / 0.1 ($SiMe_3$).

^{1}H,^{13}C GHMBC (400 MHz / 101 MHz, 299 K, [d_2]-CH_2Cl_2) [selected traces]: δ^{1}H / δ^{13}C = 7.32 / 125.7, 147.0 (*o*-Ph / *o*-Ph, *i*-Ph), 4.86 / 147.0, 125.7, 27.0 (CH / *i*-Ph, *o*-Ph, CH_3), 1.40 / 147.0, 70.9 (CH_3 / *i*-Ph, CH).

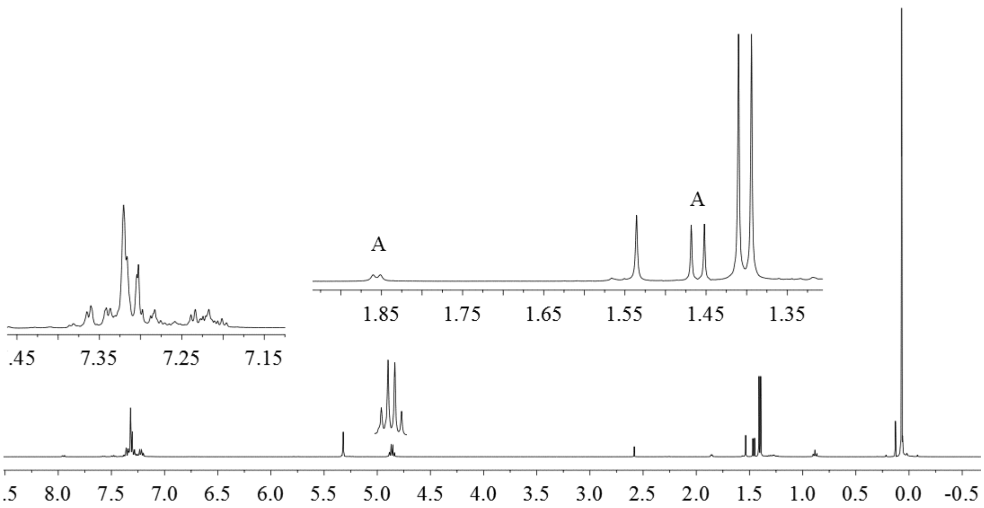


Figure S78 ^{1}H NMR (400 MHz, 299K, [d_2]-CH_2Cl_2) [A: alcohol]

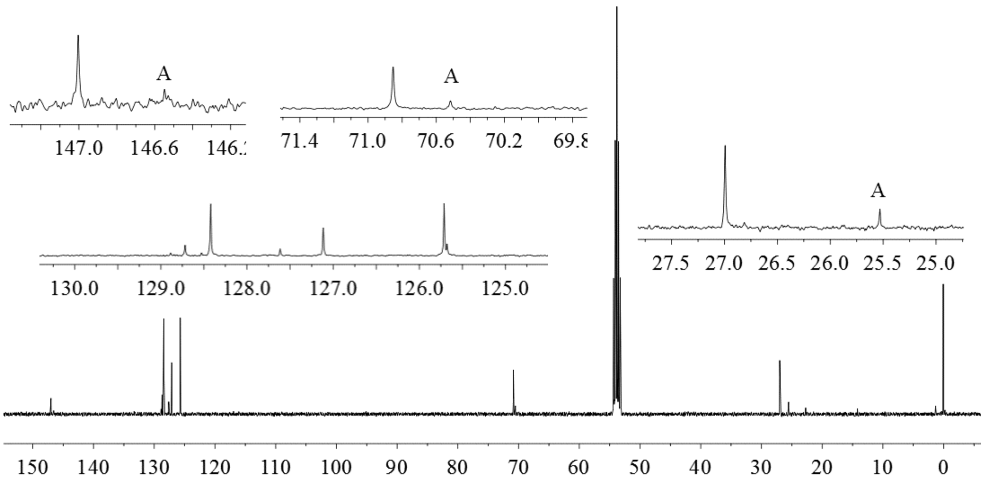
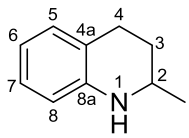


Figure S79 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, [d_2]-CH_2Cl_2) [A: alcohol]

Hydrogenation of Quinaldine



Scheme S20

Following the general procedure compound **10** (64 mg, 0.10 mmol) reacted with quinaldine (143 mg, 1.0 mmol) at 90 °C for 36 h. *Purification.* The reaction mixture was quickly filtered through a short column filled with silica (eluent CH_2Cl_2). Then all volatiles were removed by rotary evaporator (40 °C, 700 mbar) to give the respective product (100 mg, 70%) as a colorless oil.

^{1}H NMR (400 MHz, 299K, [d_2]-CH_2Cl_2): δ = 6.92 (m, 1H, 5-H), 6.91 (m, 1H, 7-H), 6.55 (tm, $^3J_{HH}$ = 7.4 Hz, 1H, 6-H), 6.44 (d, J = 7.8 Hz, 1H, 8-H), 3.67 (br, 1H, NH), 3.38 (m, 1H, 2-H), 2.82, 2.70 (each m, each 1H, 4-H), 1.92, 1.55 (each m, each 1H, C3H), 1.20 (d, $^3J_{HH}$ = 6.3 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, 299K, [d_2]-CH_2Cl_2): δ = 145.3 (C8a), 129.5 (C5), 126.9 (C7), 121.4 (C4a), 117.0 (C6), 114.1 (C8), 47.5 (C2), 30.5 (C3), 26.9 (C4), 22.7 (CH_3).

^{1}H,^{1}H GCOSY (400 MHz / 400 MHz, 299 K, [d_2]-CH_2Cl_2) [selected trace]: δ^{1}H / δ^{1}H =. 3.38 / 1.92, 1.55, 1.20 (2-H / 3-H, 3-H, CH_3).

^{1}H,^{13}C GHSQC (400 MHz / 101 MHz, 299 K, [d_2]-CH_2Cl_2): δ^{1}H / δ^{13}C = 6.92 / 129.5 (C5), 6.91 / 126.9 (C7), 6.55 / 117.0 (C6), 6.44 / 114.1 (C8), 3.38 / 47.5 (C2), 2.82, 2.70 / 26.9 (C4) 1.92, 1.55 / 30.5 (C3), 1.20 / 22.7 (CH_3).

^{1}H,^{13}C GHMBC (400 MHz / 101 MHz, 299 K, [d_2]-CH_2Cl_2) [selected trace]: δ^{1}H / δ^{13}C = 1.92 / 121.4, 47.5, 26.9 (3-H / C4a, C2, C4).

Exact Mass: calc. for [$C_{10}H_{13}NH$]: 148.1121. Found [$C_{10}H_{13}NH$]: 148.1121.

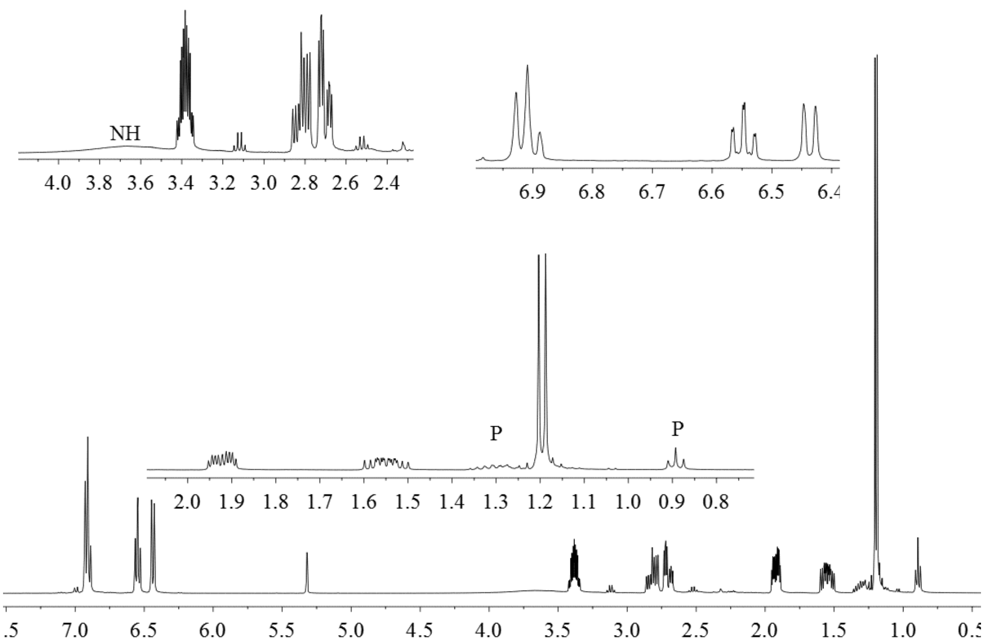


Figure S80 ^{1}H NMR (400 MHz, 299K, [d_2]-CH_2Cl_2) [P: pentane]

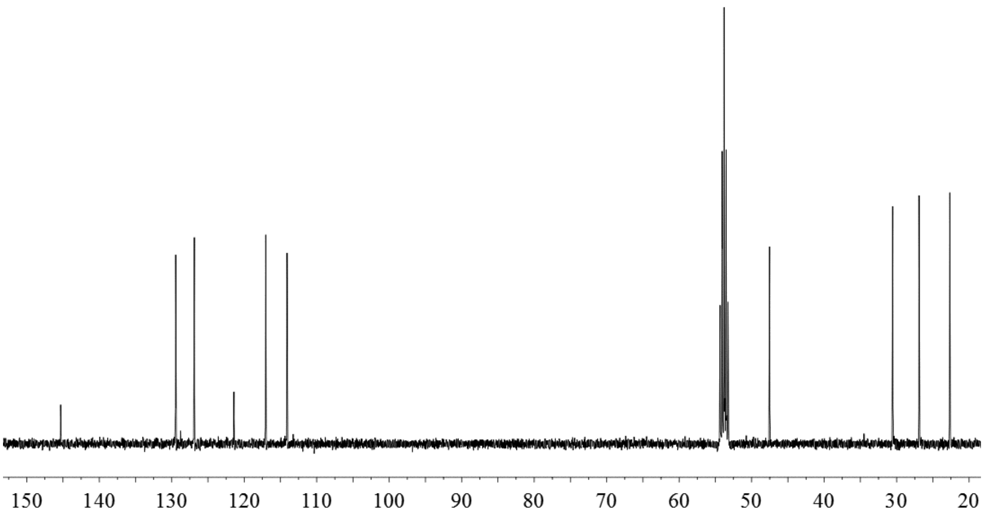
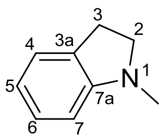


Figure S81 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, [d_2]-CH_2Cl_2)

Hydrogenation of 1-Methylindole



Scheme S21

Following the general procedure compound **10** (64 mg, 0.10 mmol) reacted with 1-methylindole (231 mg, 1.0 mmol) at 90 °C for 72 h. *Purification.* HCl solution (10 mL, 1M in water) was added to the reaction mixture. After 10 min stirring the aqueous phase was separated and treated with NaOH (1M in water). The suspension was exacted with pentane (10 mL × 2). The organic phases were combined and dried with Mg_2SO_4. Then all volatiles were removed by rotary evaporator (40 °C, 700 mbar) to give the respective product (86 mg,, 0.65 mmol, 65%) as a colorless oil.

^{1}H NMR (400 MHz, 299K, [d_2]-CH_2Cl_2): δ = 7.06 (m, 1H, C4H), 7.05 (m, 1H, 6-H), 6.63 (m, 1H, 5-H), 6.46 (d, $^3J_{HH}$ = 7.7 Hz, 1H, 7-H), 3.27 (m, 2H, NCH_2), 2.92 (m, 2H, CH_2), 2.74 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, 299K, [d_2]-CH_2Cl_2): δ = 153.9 (C7a), 130.7 (C3a), 127.5 (C6), 124.5 (124.5), 117.8 (C5), 107.3 (C7), 56.5 (NCH_2), 36.4 (CH_3), 29.0 (CH_2).

^{1}H,^{1}H GCOSY (400 MHz / 400 MHz, 299 K, [d_2]-CH_2Cl_2) [selected traces]: 6.46 / 7.05, 2.74 (7-H / 6-H, CH_3), 7.06 / 2.92 (4-H / CH_2).

^{1}H,^{13}C GHSQC (400 MHz / 101 MHz, 299 K, [d_2]-CH_2Cl_2): δ^{1}H / δ^{13}C = 7.06 / 124.5 (C4), 7.05 / 127.5 (C6), 6.63 / 117.8 (C5), 6.46 / 107.3 (C7), 3.27 / 56.5 (NCH_2), 2.92 / 29.0 (CH_2), 2.74 / 36.4 (CH_3).

^{1}H,^{13}C GHMBC (400 MHz / 101 MHz, 299 K, [d_2]-CH_2Cl_2) [selected traces]: δ^{1}H / δ^{13}C = 2.74 / 153.9, 56.5 (CH_3 / NCH_2, C7a), 2.92 / 130.7, 56.5 (CH_2 / C3a, NCH_2).

Exact MS: calc. for [$C_9H_{11}NH$]: 134.0964. Found [$C_{15}H_{23}NH$]: 134.0964.

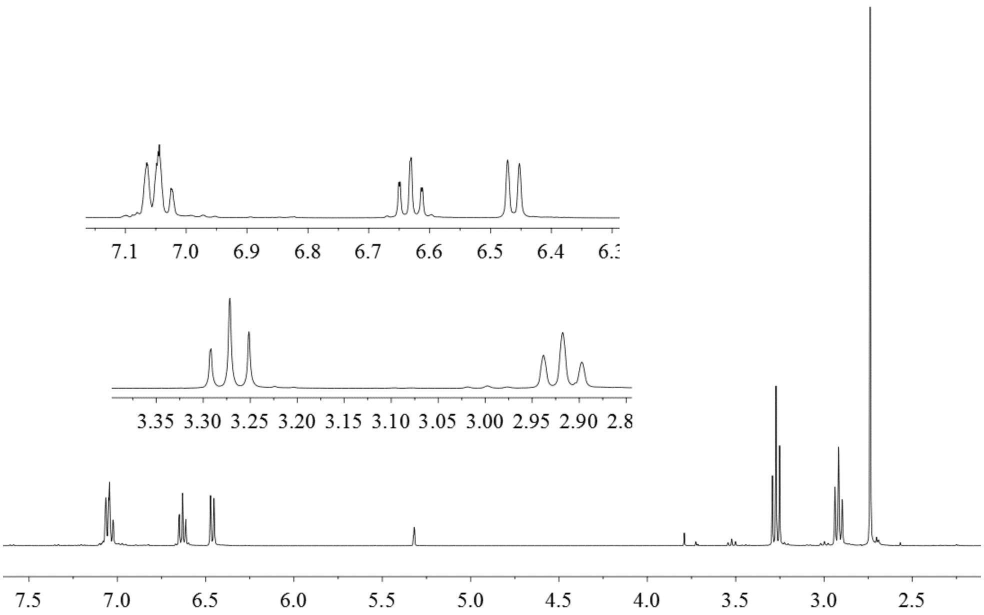


Figure S82 ^{1}H NMR (400 MHz, 299K, [d_2]-CH_2Cl_2)

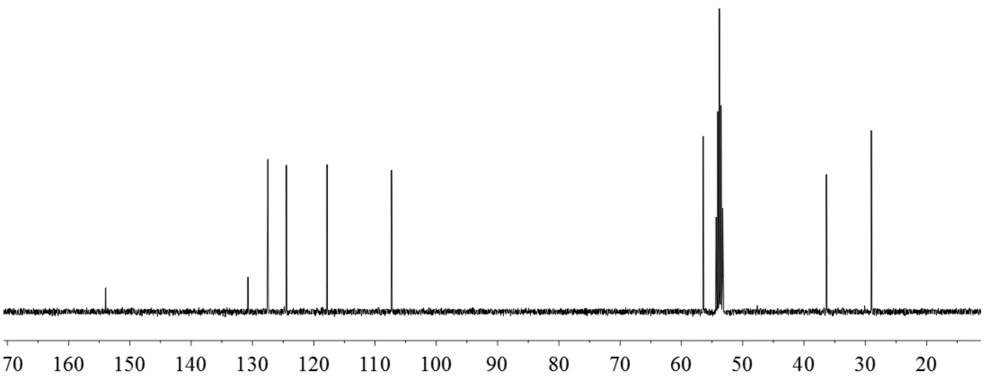


Figure S83 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, [d_2]-CH_2Cl_2)

Theoretical Methods and Technical Details of the Computations

The quantum chemical calculations were carried out with the TURBOMOLE suite of programs.[1] All minimum structures were fully optimized at the dispersion-corrected DFT level using the TPSS density functional[2] along with the polarized triple-zeta (def2-TZVP) sets by Ahlrichs *et al.*[3].

We included the atom pairwise D3 correction with BJ-damping to account for intra- and intermolecular London dispersion interactions.[4] The combined level of theory used for geometry optimization is dubbed TPSS-D3/TZ in the following. For the compounds **8** and **10**, the obtained X-ray structures were used as starting points.

Transition state structures were pre-optimized and verified as such at the HF-3c level.[5] In this method, Hartree-Fock is combined with a small basis set and London dispersion interactions are described within the above mentioned D3 correction (BJ-damping). Shortcomings of the small basis are empirically corrected for by the geometrical counterpoise correction[6] and by a short-range basis set correction.[5] We exploit the efficiency of this method to optimize transition state structures. These transition state geometries were then re-optimized at the TPSS-D3/TZ level making use of the HF-3c Hessian. For TS **8/10** (see Figure S84), we simply used the HF-3c geometry.

The electronic energies used in this work were obtained by applying the B2PLYP double-hybrid DFT functional[7] along with the D3(BJ) correction[4] and the large polarized quadruple-zeta (def2-QZVP) sets by Ahlrichs *et al.*[3] to the geometries obtained by TPSS-D3/TZ (HF-3c for TS **8/10**), respectively. The level of these single-point calculations will be dubbed as B2PLYP-D3/QZ in the following.

The harmonic frequency calculations to identify the transition state and minimum structures were all carried out by HF-3c.

In all DFT treatments, the resolution-of-the-identity approximation has been used[8] for the Coulomb integrals to speed up the computations. The numerical quadrature grid *m5* has been employed for the integration of the exchange-correlation contribution. In the following, we discuss Gibbs free energies at 363.15 K and 1 atm (termed ΔG). The ro-vibrational corrections to the free energy are obtained from a modified rigid rotor, harmonic oscillator statistical treatment[9] based on the harmonic frequencies obtained at the HF-3c level (see above). For the entropy, all frequencies with wavenumbers below 100 cm^{-1} were treated as mixed rigid rotors and harmonic oscillators.

Solvent effects on the thermochemical properties have been obtained by the COSMO-RS method[10] (COSMOtherm software package[11]) based on BP86/TZVP[12] calculations (parametrization from 2012). Solvation contributions to free energies at 363.15 K in toluene solution are computed from the gas phase structures obtained at the above mentioned levels of theory.

The computed free energies are then obtained by

$\Delta G = \Delta E + \Delta G_{RRHO} + \Delta\delta G_{COSMO\text{-}RS,}$

where ΔE is the difference in the electronic energies at the B2PLYP-D3/QZ level and the last two terms refer to the above mentioned ro-vibrational and solvation contributions, respectively, to the free energy.

Discussion of the Computational Results

From our results (see below), it is clear that the reaction of compound **8** with H_2 to form compound **10** is exergonic which is in agreement with the experimental observation. The geminal FLP **15’** is at least as stable as compound **8** as indicated by the lower energy (see Thermodynamic data below) and the similar free energy. A direct hydrogenation of the B-C1 bond seems to be unlikely as the barrier for this reaction is too high ($\Delta G^{‡}$ = +59.2 kcal/mol, see Figure S84).

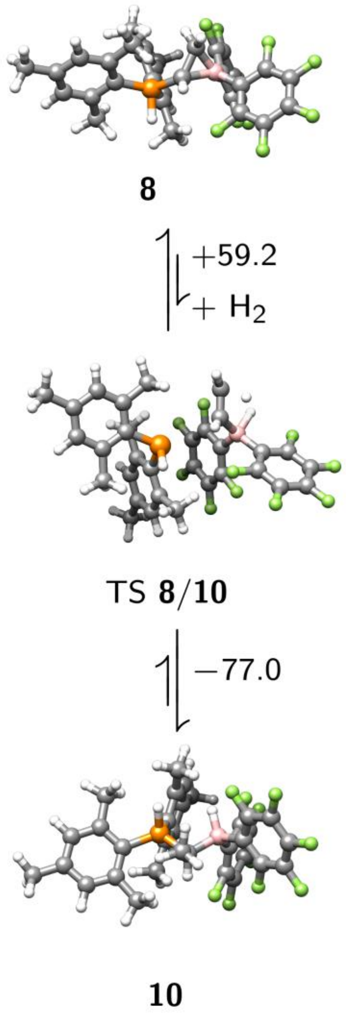


Figure S84: Non-feasible, direct route to zwitterion **10** by hydrogenation of **8**.

The shown numbers are ΔG (kcal/mol) at the B2-PLYP-D3/QZ level (the TS **8/10** geometry was obtained by HF-3c).

An internal conversion from compound **8** to compound **15’** by an intramolecular proton transfer from the P atom to C1 can also be ruled out as it has a barrier of about 55 kcal/mol (see Figure S84). Yet in principle, obtaining compound **10** via FLP **15’** is feasible with a barrier of about 17 kcal/mol.

Thus, if the geminal FLP **15’** could be obtained in a way from compound **8**, the formation of the zwitterion **10** upon exposure to H_2 could be explained in this way.

Instead of an intramolecular proton transfer, a bimolecular one from [P]-H of one compound **8** species to the C1 atom of another molecule **8** is possible (see Figure

S86). The formation of the respective, ionic intermediate **15** is endergonic but still achievable with a ΔG of +20.1 kcal/mol. As a proton transfer reaction is expected to proceed without a significant barrier, we consider the formation of these intermediates as the rate-determining, but feasible step.

From these observations, we can reason that starting from compound **8**, the intramolecular formation of FLP **15'** is kinetically hindered. On the other hand, the intermolecular proton transfer reaction opens up a path to obtain FLP **15'**. This species may then react with molecular hydrogen to form compound **10** according to the right-hand side of Figure S85.

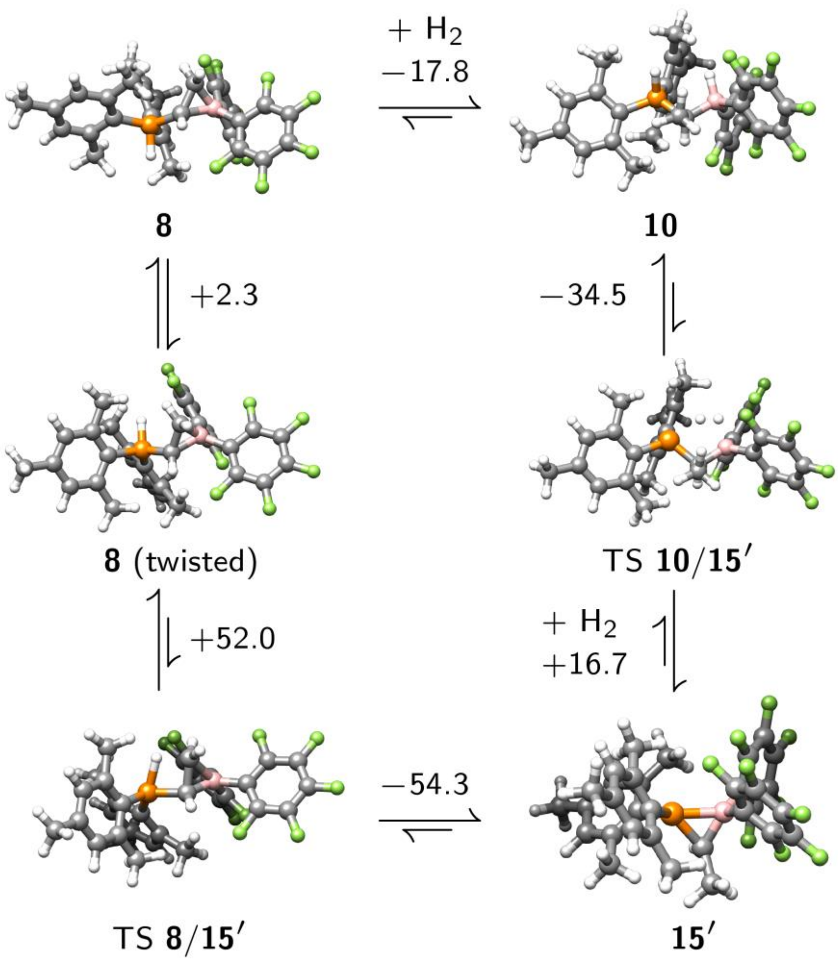


Figure S85: Unfeasible formation of **10** from **8** via the intramolecular proton transfer. The shown numbers are ΔG (kcal/mol) at the B2-PLYP-D3/QZ level of theory. The hydrogenation of the geminal FLP **15'** (right hand side) on the other hand is feasible.

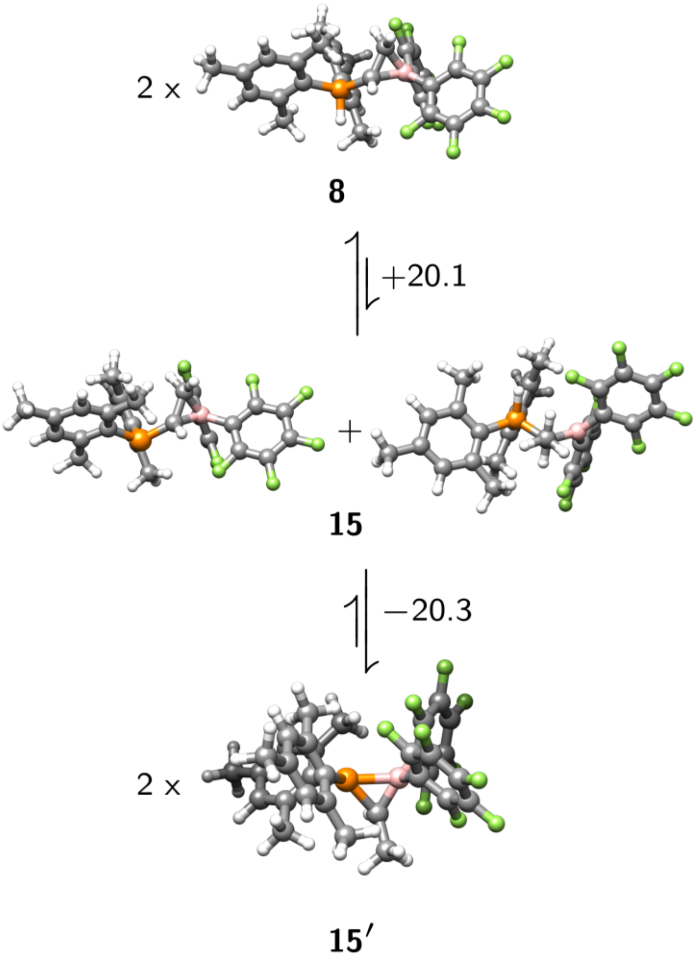


Figure S86: Pathway to form the geminal FLP **15’** from **8** via an intermolecular proton transfer. The shown numbers are ΔG (kcal/mol) at the B2-PLYP-D3/QZ level of theory. The subsequent hydrogenation of FLP **15’** leads to compound **10** as shown in Figure S85.

References

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Thermodynamic data

(B2PLYP-D3/QZ, COSMO-RS(toluene), T=363.15 K, HF-3c frequencies, total energies in Hartree, relative energies in kcal/mol):

compound **8**	+ H_2	-> compound **10**	; difference	
-2599.52852	-1.17113	-2600.74384	-27.73	E_gas
-0.02933	0.00966	-0.02917	-5.96	G_solv
0.40518	-0.00380	0.42662	15.84	G_rovib
-2599.15268	-1.16527	-2600.34640	-17.86	G_tot

compound **8** + H_2 -> TS **8**/**10** ;difference

-2599.52852	-1.17113	-2600.61177	55.14	E_gas
-0.02933	0.00966	-0.02441	-2.97	G_solv
0.40518	-0.00380	0.41254	7.00	G_rovib
-2599.15268	-1.16527	-2600.22364	59.17	G_tot

compound **8** -> compound **15’** ; difference

-2599.52852	-2599.53720	-5.44	E_gas
-0.02933	-0.02479	2.85	G_solv
0.40518	0.40917	2.51	G_rovib
-2599.15268	-2599.15281	-0.08	G_tot

compound **8** -> TS **8**/**15’** ; difference

-2599.52852	-2599.44104	54.89	E_gas
-0.02933	-0.02553	2.39	G_solv
0.40518	0.40031	-3.06	G_rovib
-2599.15268	-2599.06626	54.23	G_tot

compound **15’** + H_2 -> TS **10**/**15’** ; difference

-2599.53720	-1.17113	-2600.68960	11.75	E_gas
-0.02479	0.00966	-0.00149	6.74	G_solv
0.40917	-0.00380	0.42219	10.55	G_rovib
-2599.15281	-1.16527	-2600.29150	16.68	G_tot

2 * compound **8** -> **15** (**8**$_{deprotonated}$ **8**H^+) ; difference

-2599.52852	-2599.01261	-2599.93548	68.37	E_gas
-0.02933	-0.06981	-0.06799	-49.66	G_solv

0.40518		0.39829	0.41432	1.41	G_rovib
-2599.15268		-2598.68413	-2599.58915	20.13	G_tot

15 (**8**$_{deprotonated}$ **8**H^{+}) -> 2 * compound **15'** ; difference

-2599.01261	-2599.93548	-2599.53720	-79.26	E_gas
-0.06981	-0.06799	-0.02479	55.36	G_solv
0.39829	0.41432	0.40917	3.60	G_rovib
-2598.68413	-2599.58915	-2599.15281	-20.30	G_tot

Cartesian coordinates of minimum structures

In Ångström (TPSS-D3/TZ):

Compound **8**

P	-0.5293564	-0.4480629	0.8536251
H	-0.3195612	-1.8124621	1.0821291
B	2.2813318	0.6196008	0.4000056
C	0.9432490	0.3349996	1.3590810
H	1.2010887	-0.0171190	2.3572243
C	1.3838661	1.7585347	1.0249070
H	1.7187756	2.3270625	1.8896196
H	0.7312888	2.3287876	0.3740003
C	-2.0912224	-0.1706369	1.7564709
C	-2.2641688	0.8614201	2.7063114
C	-3.5077155	0.9892084	3.3345239
H	-3.6368460	1.7884182	4.0612242
C	-4.5763135	0.1351934	3.0678779
C	-4.3749768	-0.8920456	2.1427521
H	-5.1868748	-1.5829019	1.9238668
C	-3.1586074	-1.0670216	1.4840876
C	-1.1852215	1.8401871	3.0989130

H	-1.5890515	2.5647189	3.8104510
H	-0.7848954	2.3878109	2.2416454
H	-0.3364931	1.3356891	3.5700513
C	-5.9044424	0.3033270	3.7600453
H	-5.8887183	1.1552663	4.4446995
H	-6.1617374	-0.5937110	4.3348886
H	-6.7075551	0.4630324	3.0315131
C	-3.0398086	-2.2146888	0.5105810
H	-3.9526003	-2.8147837	0.5276251
H	-2.2033309	-2.8766595	0.7646517
H	-2.8774744	-1.8648361	-0.5138537
C	-0.8364905	-0.3497463	-0.9208484
C	-1.4917640	0.7707028	-1.4713041
C	-1.6852606	0.8197225	-2.8533735
H	-2.1684125	1.6953858	-3.2809053
C	-1.2565701	-0.2054851	-3.6969736
C	-0.6262216	-1.3136996	-3.1225775
H	-0.2802772	-2.1207168	-3.7646713
C	-0.4001689	-1.4120197	-1.7509647
C	-1.9981463	1.9139414	-0.6283725
H	-2.0764936	2.8211153	-1.2327258
H	-1.3323049	2.1310563	0.2109538
H	-2.9875616	1.6901179	-0.2131702
C	-1.4193750	-0.1029414	-5.1905452
H	-0.5112454	0.3153861	-5.6412410
H	-2.2535571	0.5527950	-5.4553467
H	-1.5874366	-1.0863661	-5.6396443
C	0.2822836	-2.6485906	-1.2191834
H	-0.4329463	-3.3041508	-0.7055057

H	1.0854602	-2.4148821	-0.5163476
H	0.7173736	-3.2177319	-2.0439039
C	3.6577259	0.2812981	1.1631834
F	2.9210004	-1.7874669	2.1053745
C	3.8904101	-0.8446724	1.9518226
C	5.0949185	-1.0889991	2.6072099
F	5.2648690	-2.1951547	3.3596924
F	7.3117040	-0.3960460	3.0965510
C	6.1398200	-0.1790194	2.4731989
F	6.9704126	1.8415503	1.5550918
C	5.9620489	0.9575672	1.6877446
F	4.6125426	2.2780066	0.3009999
C	4.7377959	1.1599293	1.0564415
C	2.3154541	0.3623563	-1.1894374
F	3.3792709	-1.7511370	-0.8847503
C	2.8965011	-0.7957860	-1.7196738
F	3.5295258	-2.2336121	-3.5137129
C	2.9938319	-1.0746988	-3.0792374
F	2.5555896	-0.4090006	-5.3185176
C	2.5025191	-0.1538363	-3.9980555
F	1.4502551	1.9248629	-4.4125999
C	1.9350907	1.0254747	-3.5309407
F	1.2964167	2.4446875	-1.8120254
C	1.8587834	1.2614758	-2.1606267

Compound **8** (twisted)

C	1.3600865	2.0831804	-1.7737201
C	2.0075298	1.0752238	-1.0537188
C	2.4063498	-0.0136721	-1.8398924

C	2.1490189	-0.1329949	-3.2008956
C	1.4591731	0.8820801	-3.8560188
C	1.0681974	2.0037927	-3.1346032
B	2.2166284	1.0305014	0.5505249
C	3.6778165	0.5687166	1.0361945
C	3.9954029	-0.4473797	1.9369243
C	5.2963363	-0.7642096	2.3231004
C	6.3621075	-0.0422977	1.7968355
C	6.1031751	0.9881796	0.8967591
C	4.7864286	1.2683810	0.5457938
F	3.0160519	-1.2136037	2.4969573
F	5.5323237	-1.7649386	3.1958778
F	7.6253035	-0.3329121	2.1555095
F	7.1253664	1.7024709	0.3870849
F	4.5959675	2.2930611	-0.3224305
F	3.0523656	-1.0576646	-1.2653894
F	2.5298800	-1.2296161	-3.8860524
F	1.1688235	0.7752058	-5.1647778
F	0.3972614	2.9972110	-3.7546445
F	0.9330342	3.2177807	-1.1536186
C	0.8900003	0.5485649	1.4096776
C	1.4142319	1.9956928	1.5214525
P	-0.6025903	0.3938565	0.5034153
C	-2.1444440	0.5044772	1.4578034
C	-2.6846079	-0.6430828	2.0775231
C	-3.8826889	-0.5323685	2.7841934
C	-4.5621661	0.6814037	2.8993228
C	-4.0011023	1.8076972	2.2924659
C	-2.8015205	1.7544205	1.5798259

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C	-0.7010331	-0.8643642	-0.7999564
C	0.0607441	-2.0549633	-0.8167426
C	0.0327453	-2.8457969	-1.9694403
C	-0.7172520	-2.5090608	-3.0944139
C	-1.4961888	-1.3508230	-3.0377649
C	-1.5051967	-0.5199304	-1.9191867
C	0.8985851	-2.5443412	0.3352384
C	-0.6557966	-3.3404617	-4.3483857
C	-2.3543814	0.7277722	-1.9682518
H	-0.6450631	1.5663840	-0.2452749
H	0.9798036	-0.0901294	2.2812090
H	1.8300902	2.2223196	2.4999493
H	0.7816246	2.7906767	1.1417106
H	0.6413232	-3.7471482	-1.9863378
H	-2.1025520	-1.0713905	-3.8967617
H	1.7523567	-3.1115657	-0.0415492
H	0.3134211	-3.2160284	0.9746789
H	1.2847413	-1.7326688	0.9481157
H	-0.4046532	-4.3809987	-4.1242801
H	0.1191002	-2.9485039	-5.0189498
H	-1.6060967	-3.3161182	-4.8900825
H	-3.0298140	0.6848062	-2.8258939
H	-1.7372093	1.6276390	-2.0853872
H	-2.9603346	0.8500994	-1.0643575
H	-4.2909653	-1.4214976	3.2602405
H	-4.5087786	2.7660820	2.3797360

H	-2.4615552	-2.6873098	2.6996968
H	-0.9384135	-1.8969449	2.2750312
H	-2.0489538	-2.4039601	0.9983159
H	-5.6322121	1.0829414	4.7231932
H	-6.3663819	-0.1748343	3.7205293
H	-6.5124750	1.5354011	3.2597546
H	-2.2406491	3.0085805	-0.1071663
H	-1.2536799	3.2526967	1.3369748
H	-2.9076099	3.8744296	1.2802399

Compound **10**

C	0.2299443	-1.7165938	-2.0109996
C	-0.7574310	0.8509266	-0.8444204
P	-0.3493272	-0.8761376	-0.4972191
H	-1.5976260	-1.4593647	-0.2670479
C	0.5275188	-1.2043998	1.0421052
H	1.5926037	-1.0265140	0.9118195
C	0.2631320	-2.6863838	1.3896787
H	0.8568858	-2.9502668	2.2690271
H	0.5205466	-3.3832428	0.5820137
H	-0.7910534	-2.8361238	1.6454048
B	-0.1610910	-0.1461854	2.1383079
H	-1.3323104	-0.0784283	1.8511577
C	-0.1008770	-0.7544833	3.6521110
F	2.1577481	-0.1086486	4.0458018
C	1.0125804	-0.6845391	4.4903498
F	2.1487870	-1.0855497	6.5508010
C	1.0405460	-1.1864363	5.7895959
F	-0.0910117	-2.3046128	7.5529792

C	-0.0942323	-1.8073917	6.3032069
F	-2.3305408	-2.5246436	5.9926189
C	-1.2299975	-1.9153613	5.5060733
F	-2.3484169	-1.5570770	3.4913233
C	-1.2078990	-1.3956222	4.2138917
C	0.4322071	1.3748374	2.0311490
F	-1.7262996	2.2328322	2.5764753
C	-0.4363978	2.4544414	2.2236935
F	-0.9742044	4.7795572	2.2165373
C	-0.0736737	3.7868563	2.0523261
F	1.5959251	5.3789632	1.4831807
C	1.2297519	4.0981137	1.6798860
F	3.4092633	3.3506905	1.1269477
C	2.1432043	3.0661576	1.4998050
F	2.6950024	0.8055422	1.4749739
C	1.7314670	1.7487965	1.6874434
C	1.5385357	-2.2381171	-2.1796170
C	1.8608384	-2.8476908	-3.3961880
H	2.8658095	-3.2461298	-3.5174135
C	0.9539969	-2.9651005	-4.4491947
C	-0.3304912	-2.4572401	-4.2575382
H	-1.0655357	-2.5445133	-5.0548302
C	-0.7114784	-1.8385412	-3.0665671
C	2.6336313	-2.1986665	-1.1396517
H	2.3707972	-2.7736913	-0.2480616
H	2.8702233	-1.1817076	-0.8171442
H	3.5448948	-2.6317817	-1.5587656
C	1.3563874	-3.5995627	-5.7551188
H	1.8239533	-2.8571073	-6.4140549

H	0.4892783	-4.0091577	-6.2809450
H	2.0824108	-4.4028137	-5.5983771
C	-2.1296872	-1.3382671	-2.9562599
H	-2.6575868	-1.4924447	-3.9000739
H	-2.1663249	-0.2712272	-2.7143605
H	-2.6832140	-1.8755009	-2.1763394
C	0.2501354	1.7103320	-1.3387337
C	-0.0438673	3.0584405	-1.5288737
H	0.7442259	3.7181409	-1.8850201
C	-1.3083177	3.5829712	-1.2536315
C	-2.2976059	2.7079377	-0.8029743
H	-3.2895734	3.0971070	-0.5864491
C	-2.0600068	1.3489125	-0.5836837
C	1.6361840	1.2176458	-1.6577111
H	2.3160570	2.0595304	-1.8073881
H	1.6423607	0.6028775	-2.5646140
H	2.0431347	0.6155570	-0.8404038
C	-1.5820437	5.0566554	-1.3960993
H	-0.9683121	5.5006927	-2.1853212
H	-1.3443437	5.5747596	-0.4589919
H	-2.6358297	5.2456715	-1.6200275
C	-3.2063252	0.5140784	-0.0662059
H	-4.0939590	1.1410091	0.0440767
H	-2.9723102	0.0812514	0.9107285
H	-3.4607659	-0.3040178	-0.7491728

Compound **15’**

C	1.1075443	1.6081733	-2.3401826
C	0.2717565	1.6012653	-1.1941824

C	-0.5118408	2.7345277	-0.8919275
C	-0.4556478	3.8422648	-1.7465085
C	0.3498145	3.8667938	-2.8824273
C	1.1256723	2.7365096	-3.1583439
P	0.2696616	0.1051515	-0.1451734
C	-0.2718237	-1.2988621	-1.1828781
C	0.4714896	-2.4710906	-1.4356357
C	-0.0738286	-3.4567693	-2.2642713
C	-1.3319480	-3.3308181	-2.8496802
C	-2.0682737	-2.1818443	-2.5563973
C	-1.5773198	-1.1732184	-1.7282318
C	1.8203432	-2.7353852	-0.8307873
C	-1.8841246	-4.3977659	-3.7595760
C	-2.4848270	-0.0143272	-1.4095322
C	-1.4018765	2.8283737	0.3195114
C	0.4058449	5.0802487	-3.7752727
C	1.9876604	0.4399983	-2.7022395
C	1.7576690	0.2283962	0.9437621
C	3.0723020	-0.5199480	1.0484457
B	0.4422460	0.0255747	1.8535402
C	-0.0602490	1.1823717	2.8321282
C	-1.3937505	1.2795153	3.2394236
C	-1.8684751	2.2556287	4.1079641
C	-0.9772916	3.1939476	4.6247520
C	0.3657620	3.1333604	4.2636164
C	0.7958106	2.1378337	3.3878711
F	-2.3038292	0.4085835	2.7431795
F	-3.1697489	2.3127698	4.4455317
F	-1.4097607	4.1458906	5.4661304

F	1.2334498	4.0273838	4.7719902
F	2.1195293	2.1280489	3.1005618
C	0.1668825	-1.4794000	2.3662526
C	-0.8926898	-2.3201947	2.0163631
C	-1.0247490	-3.6218235	2.4987090
C	-0.0877563	-4.1214585	3.3976647
C	0.9630154	-3.3065167	3.8131619
C	1.0600294	-2.0171285	3.3001320
F	-1.8694039	-1.8984545	1.1854168
F	2.0740828	-1.2484348	3.7667023
F	1.8590735	-3.7699190	4.7035515
F	-0.2039823	-5.3711684	3.8736810
F	-2.0554170	-4.3956475	2.1119567
H	1.9594602	1.2964537	0.8090806
H	3.6500658	-0.0504987	1.8514819
H	3.6666933	-0.4598714	0.1294103
H	2.9424787	-1.5696504	1.3111025
H	0.5118892	-4.3550459	-2.4485845
H	-3.0716653	-2.0710719	-2.9628634
H	1.7404004	-2.8661226	0.2531270
H	2.5141481	-1.9120536	-1.0126504
H	2.2526437	-3.6476359	-1.2494707
H	-1.8441936	-4.0738138	-4.8070692
H	-2.9318450	-4.6128563	-3.5249804
H	-1.3125304	-5.3259993	-3.6735040
H	-3.5051867	-0.2389180	-1.7305800
H	-2.1647480	0.9069694	-1.9069509
H	-2.5024670	0.1760773	-0.3311645
H	1.7693849	2.7315202	-4.0360182

H	-1.0703232	4.7089009	-1.5106334
H	2.6877142	0.7219765	-3.4928577
H	1.3978347	-0.4139815	-3.0520722
H	2.5660136	0.1017393	-1.8360451
H	0.4005837	4.7948961	-4.8323293
H	1.3257855	5.6504997	-3.5956160
H	-0.4413884	5.7466241	-3.5910935
H	-2.2832385	3.4376080	0.0989480
H	-0.8686908	3.3045553	1.1502436
H	-1.7298455	1.8472625	0.6623372

Deprotonated compound **8** (anion of **15**)

C	2.9190927	-0.9083510	-1.6041227
C	2.3197218	0.2581424	-1.1162244
C	1.9186337	1.1494322	-2.1181893
C	2.0555795	0.8924173	-3.4801335
C	2.6317030	-0.2974712	-3.9053808
C	3.0746973	-1.2078883	-2.9532161
B	2.2129735	0.5244841	0.4714603
C	3.6464743	0.3586656	1.2071485
C	4.0026472	-0.6696331	2.0820028
C	5.2448415	-0.7507588	2.7108521
C	6.2049591	0.2235060	2.4614246
C	5.9066114	1.2630202	1.5855205
C	4.6512645	1.3047555	0.9853934
F	3.1356553	-1.6750179	2.3564965
F	5.5379399	-1.7715233	3.5522431
F	7.4157288	0.1615339	3.0618760
F	6.8385499	2.2156716	1.3393417

F	4.4213820	2.3418209	0.1404860
F	1.3735885	2.3518324	-1.8126266
F	1.6343219	1.7913877	-4.4022757
F	2.7491950	-0.5703806	-5.2254726
F	3.6301069	-2.3773224	-3.3536187
F	3.3734644	-1.8470919	-0.7317272
C	0.9035276	0.1865127	1.3944421
C	1.2362096	1.6329356	1.0538231
P	-0.5125874	-0.8536726	0.9577098
C	-0.8154765	-0.4974840	-0.8332836
C	-1.4648908	0.6495372	-1.3378339
C	-1.6429932	0.7863168	-2.7213967
C	-1.2063780	-0.1772811	-3.6270778
C	-0.5847066	-1.3186210	-3.1139283
C	-0.3869939	-1.4959639	-1.7446895
C	-2.0117433	1.7468578	-0.4574852
C	-1.3584774	0.0185948	-5.1152196
C	0.2584800	-2.7786635	-1.2761313
C	-2.1161144	-0.3189860	1.7339748
C	-3.2721303	-1.0229912	1.3005149
C	-4.5170470	-0.7652300	1.8831270
C	-4.6766451	0.1571739	2.9149829
C	-3.5279456	0.8028647	3.3744648
C	-2.2637477	0.5834776	2.8181776
C	-3.2111132	-2.0803699	0.2252329
C	-1.1089283	1.3436940	3.4238494
C	-6.0334705	0.4514801	3.5071524
H	1.2223617	-0.1096514	2.3932661
H	1.5395077	2.2584864	1.8943155

H	0.5742617	2.1451010	0.3654410
H	-3.6104149	1.5103923	4.1997171
H	-5.3838219	-1.3181869	1.5204226
H	-1.4736753	1.9946434	4.2254706
H	-0.5893398	1.9549746	2.6819257
H	-0.3589816	0.6672549	3.8471831
H	-5.9697674	0.6168945	4.5887097
H	-6.7302983	-0.3742650	3.3272318
H	-6.4732833	1.3560763	3.0650036
H	-4.1073007	-2.7089985	0.2634029
H	-2.3245453	-2.7131672	0.3585550
H	-3.1373507	-1.6444714	-0.7769360
H	-2.1247228	1.6883697	-3.0972552
H	-0.2334185	-2.0893413	-3.7988373
H	-2.0234181	2.6948527	-1.0058189
H	-1.4207530	1.8735453	0.4491960
H	-3.0379664	1.5199949	-0.1430380
H	-0.4216752	0.3809641	-5.5562644
H	-2.1378024	0.7541990	-5.3395827
H	-1.6147612	-0.9221788	-5.6153878
H	-0.4809680	-3.4300283	-0.7931462
H	1.0422271	-2.6009224	-0.5378509
H	0.6899467	-3.3159511	-2.1273870

Protonated compound **8** (also dubbed **8**H^+, cation of **15**)

C	-1.8977753	1.3255168	-0.1645610
C	-0.6605677	0.8573056	-0.6855559
C	0.2077622	1.7418179	-1.3681987
C	-0.1705033	3.0776153	-1.5033620

C	-1.3744489	3.5679158	-0.9937418
C	-2.2216495	2.6699265	-0.3365543
P	-0.2210653	-0.8744493	-0.4497727
C	0.8279740	-1.2237191	1.0064086
B	0.5078037	-0.2343225	2.2228564
C	0.9445093	1.2607568	2.0675722
C	0.0605233	2.2970962	2.4077628
C	0.3285777	3.6373337	2.1590904
C	1.5485349	3.9934640	1.5861656
C	2.4813970	3.0044831	1.2703977
C	2.1606353	1.6747325	1.5057331
F	-1.1422184	2.0059263	2.9450335
F	-0.5756054	4.5820831	2.4429879
F	1.8172256	5.2718553	1.3274736
F	3.6571527	3.3438334	0.7296477
F	3.1116260	0.7572890	1.1951852
C	1.5283145	1.3089354	-1.9452772
C	-1.7445538	5.0199380	-1.1262666
C	-2.8748243	0.4520286	0.5821907
C	0.2760750	-1.7267609	-1.9591243
C	1.5933269	-2.1503540	-2.2787571
C	1.7913007	-2.8027816	-3.4974532
C	0.7607267	-3.0462044	-4.4081322
C	-0.5223728	-2.6109783	-4.0717003
C	-0.7915585	-1.9565922	-2.8713165
C	2.8177979	-1.9570012	-1.4141476
C	1.0322473	-3.7276681	-5.7216320
C	-2.2141127	-1.5295057	-2.5976424
C	0.8307942	-2.7457407	1.2779172

C	-0.1630552	-0.7066511	3.5455130
C	0.3241040	-0.2510500	4.7865984
C	-0.2040863	-0.6568401	6.0066240
C	-1.2913853	-1.5326922	6.0214177
C	-1.8269680	-1.9976402	4.8178233
C	-1.2510519	-1.5893953	3.6236246
F	1.3809260	0.5808104	4.8281718
F	0.3125799	-0.2201716	7.1571133
F	-1.8201064	-1.9197674	7.1770069
F	-2.8856725	-2.8131943	4.8278743
F	-1.8452983	-2.0284240	2.4847826
H	-1.4284559	-1.4817266	-0.1032307
H	1.8292161	-0.9146522	0.6854844
H	1.5506469	-2.9642518	2.0713713
H	1.1210600	-3.3143978	0.3905771
H	-0.1478069	-3.1042911	1.5941957
H	2.7986874	-3.1301361	-3.7428597
H	-1.3441025	-2.7842632	-4.7622676
H	2.7946524	-2.5842212	-0.5180533
H	2.9550767	-0.9210084	-1.0959470
H	3.7070040	-2.2398056	-1.9808928
H	1.3245597	-2.9882352	-6.4777160
H	0.1435222	-4.2452354	-6.0917950
H	1.8497785	-4.4481784	-5.6331052
H	-2.8255701	-1.6759900	-3.4900426
H	-2.2812754	-0.4724241	-2.3171459
H	-2.6654105	-2.1237396	-1.7925555
H	0.5037473	3.7561933	-2.0202923
H	-3.1632673	3.0289564	0.0714084

H	2.0767499	2.1718196	-2.3284059
H	1.3970343	0.5954132	-2.7648630
H	2.1596279	0.8344872	-1.1878611
H	-1.0168029	5.5631320	-1.7332040
H	-1.7911652	5.4939188	-0.1389813
H	-2.7328712	5.1305605	-1.5847546
H	-3.7162122	1.0533632	0.9311494
H	-2.4220342	-0.0165902	1.4598231
H	-3.2794237	-0.3474573	-0.0498125

Cartesian coordinates of transition state structures

In Ångström (HF-3c):

TS **8**/**10**

C	-0.4775953	2.0153888	3.0448533
C	-0.3654954	2.2349026	1.6675256
C	-0.1191332	3.5348690	1.2076497
C	0.0297354	4.5717769	2.1196275
C	-0.0649941	4.3551224	3.4860735
C	-0.3257862	3.0702596	3.9346958
P	-0.5602455	0.7890244	0.5373959
C	0.9031993	0.9372558	-0.5707717
C	2.1827453	0.9588749	-0.0090647
C	3.2975398	1.0719581	-0.8283702
C	3.1747099	1.1450911	-2.2068419
C	1.9039982	1.0811737	-2.7588599
C	0.7719480	0.9731719	-1.9633442
C	2.4018985	0.8597151	1.4967567
C	4.4078538	1.2490084	-3.0978093
C	-0.5854760	0.9023950	-2.6575809

C	-0.0047402	3.8759758	-0.2746446
C	0.1263310	5.5048285	4.4701410
C	-0.7790848	0.6317155	3.6164963
C	-2.0978692	-1.9494969	1.0874816
C	-2.0539748	-2.4168892	2.3799099
B	-1.4012657	-2.9744702	-0.0148466
C	-2.5044348	-3.4304595	-1.1113453
C	-3.3699646	-2.5239283	-1.7292237
C	-4.3237263	-2.9242622	-2.6902538
C	-4.4149444	-4.2830206	-3.0526518
C	-3.5482408	-5.2163688	-2.4481090
C	-2.6103261	-4.7714829	-1.4919038
F	-3.3177864	-1.2307843	-1.4311751
F	-5.1310464	-2.0311246	-3.2458986
F	-5.3066490	-4.6789903	-3.9481402
F	-3.6211694	-6.4993438	-2.7736956
F	-1.8159510	-5.6814708	-0.9420203
C	0.0814963	-2.6645686	-0.5662320
C	0.4029518	-2.4941726	-1.9141559
C	1.7300283	-2.2690149	-2.3512291
C	2.7750068	-2.2218963	-1.4119284
C	2.4764942	-2.3922855	-0.0431081
C	1.1418637	-2.6065924	0.3471721
F	-0.5293314	-2.5396781	-2.8554774
F	0.9024012	-2.7810901	1.6419165
F	3.4482623	-2.3586390	0.8589088
F	4.0252943	-2.0328756	-1.8038041
F	1.9871754	-2.1145643	-3.6425943
H	-1.5295822	1.3698927	-0.3279361

H	-0.4147077	2.8853826	4.9918506
H	0.2185656	5.5673975	1.7545612
H	-0.3617296	5.2874849	5.4133404
H	-0.2800474	6.4259870	4.0662297
H	1.1853031	5.6618646	4.6642866
H	-0.0430115	4.9497182	-0.4088502
H	-0.8093154	3.4266836	-0.8432346
H	0.9323693	3.5098984	-0.6836153
H	4.2773783	1.0953611	-0.3806265
H	1.7908154	1.1139363	-3.8298598
H	3.4213642	0.5567713	1.7035720
H	1.7318065	0.1333671	1.9416675
H	2.2225796	1.8162353	1.9795018
H	4.7563169	0.2556526	-3.3743934
H	5.2134001	1.7558560	-2.5784534
H	4.1775768	1.7909438	-4.0083423
H	-1.1475532	1.8194163	-2.5071148
H	-1.1837693	0.0791419	-2.2819572
H	-0.4465542	0.7631090	-3.7227157
H	-0.7899282	0.6723626	4.6986777
H	-0.0355520	-0.0951647	3.3065406
H	-1.7465040	0.2780727	3.2763412
H	-2.8302456	-1.1925350	0.8094859
H	-2.7219366	-2.0539792	3.1486402
H	-1.1254166	-2.8398142	2.7614781
H	-1.9568252	-3.6881649	1.6016623
H	-1.3464996	-4.0199152	0.7677392

In Ångström (TPSS-D3/TZ):

TS **8/15’**

C	-0.9649734	3.1553259	-1.1214863
C	0.2276501	2.4188484	-1.0973432
C	1.1041448	2.7972473	-0.0759504
C	0.8102308	3.7574327	0.8882794
C	-0.4092205	4.4216540	0.8430827
C	-1.2996710	4.1266391	-0.1842611
B	0.3288938	1.1461564	-2.0745004
C	1.8005773	0.0151226	-1.9122550
C	0.3390232	-0.2793377	-1.4666612
P	0.6885648	-0.5978034	0.3060277
C	0.7979657	-2.4042533	0.5706849
C	-0.3578912	-3.2141664	0.6628460
C	-0.2183732	-4.5819873	0.8967420
C	1.0342132	-5.1818751	1.0449666
C	2.1633398	-4.3692099	0.9451740
C	2.0795297	-2.9937437	0.7054758
C	-1.7415953	-2.6436216	0.5098074
C	1.1605850	-6.6658741	1.2765883
C	3.3754686	-2.2247418	0.5906452
F	2.3340220	2.2225065	0.0353436
F	1.6925980	4.0415001	1.8639831
F	-0.7246195	5.3328657	1.7778195
F	-2.4898025	4.7533497	-0.2375791
F	-1.9026185	2.8919827	-2.0647835
C	-0.3990389	0.1887626	1.5477518
C	0.2295401	0.4109697	2.8029908
C	-0.3978536	1.2091841	3.7546074
C	-1.6291319	1.8237611	3.5046846

C	-2.2418903	1.5745792	2.2790958
C	-1.6657104	0.7657135	1.2914287
C	1.5877267	-0.1671825	3.1140059
C	-2.4841800	0.5373716	0.0443206
C	-2.2513658	2.7532707	4.5142398
C	-0.0542461	1.3375300	-3.6028368
C	-1.0567972	0.6221820	-4.2616442
C	-1.3794738	0.8174134	-5.6016746
C	-0.6834918	1.7716060	-6.3399373
C	0.3222661	2.5158760	-5.7261509
C	0.6107768	2.2864243	-4.3851823
F	-1.7949065	-0.2978151	-3.5891201
F	-2.3612589	0.1064829	-6.1875776
F	-0.9795680	1.9730173	-7.6340908
F	1.0009897	3.4353630	-6.4362120
F	1.6046010	3.0220846	-3.8313049
H	-0.1145957	-1.0944150	-2.0229913
H	2.2582799	0.9728913	-1.6516497
H	2.1635011	-0.4244297	-2.8363412
H	-3.2080035	2.0297603	2.0682712
H	0.1018093	1.3755604	4.7069887
H	-3.2159986	-0.2607961	0.2180250
H	-1.8850508	0.2611153	-0.8217209
H	-3.0485176	1.4386231	-0.2065011
H	-3.3037217	2.9408297	4.2840444
H	-1.7316347	3.7194656	4.5157107
H	-2.1833113	2.3433126	5.5273606
H	1.8713129	0.0564050	4.1457167
H	2.3507526	0.2615920	2.4519984

H	1.6075299	-1.2552449	2.9823489
H	-1.1163356	-5.1932572	0.9645608
H	3.1492746	-4.8161479	1.0552815
H	-2.4846166	-3.4441686	0.4689538
H	-1.8302596	-2.0538394	-0.4075372
H	-1.9901049	-1.9844023	1.3481398
H	1.0586520	-7.2134777	0.3311968
H	0.3785434	-7.0297389	1.9504912
H	2.1348037	-6.9188711	1.7042268
H	3.3999888	-1.3571327	1.2563307
H	3.5291975	-1.8548994	-0.4288564
H	4.2157742	-2.8757822	0.8455999
H	2.0877013	-0.2335637	-0.3896883

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H	-1.4450523	-1.2179401	0.4607796
H	-1.4350293	-1.4706877	1.3014299
C	0.1342093	-0.4311828	-2.6311384
C	-0.4286149	1.3455852	-0.3283898
P	-0.3565650	-0.4120631	-0.8560518
C	0.7427607	-1.3828092	0.2814445
H	1.7524777	-0.9780159	0.3749721
C	0.7522431	-2.8251483	-0.2717018
H	1.3871748	-3.4608433	0.3529328
H	1.1126944	-2.8845329	-1.3012024
H	-0.2609130	-3.2434823	-0.2525736
B	0.0055403	-1.3479267	1.7239160
C	0.1024304	-2.6789759	2.6249033
F	2.1756095	-1.8918252	3.4727685

C	1.2097088	-2.8434805	3.4592990
F	2.4855513	-4.0620607	5.0604878
C	1.3957583	-3.9511937	4.2805104
F	0.5893637	-6.0381715	5.0667391
C	0.4340236	-4.9592336	4.2842128
F	-1.6154274	-5.8146610	3.4632851
C	-0.6864077	-4.8423044	3.4656350
F	-1.9354989	-3.6662318	1.8766703
C	-0.8269783	-3.7179327	2.6555039
C	-0.0596081	0.0029038	2.5840134
F	-2.1437723	-0.6580690	3.5170525
C	-1.1454623	0.2577480	3.4248340
F	-2.3861502	1.6379931	4.9188486
C	-1.2949869	1.4281508	4.1605434
F	-0.4212483	3.5436966	4.7830039
C	-0.2978037	2.3972059	4.0950594
F	1.8013331	3.0986217	3.2577088
C	0.8281208	2.1707931	3.3089012
F	2.0581851	0.8242718	1.8555465
C	0.9275106	0.9905131	2.5799835
C	1.3758197	-0.8049953	-3.1952408
C	1.5160575	-0.8106903	-4.5909623
H	2.4804223	-1.1005929	-5.0056612
C	0.4902834	-0.4489802	-5.4561139
C	-0.7285062	-0.0702524	-4.8855184
H	-1.5555669	0.2202056	-5.5307742
C	-0.9280937	-0.0639520	-3.5080771
C	2.6237062	-1.1785759	-2.4276241
H	2.9263172	-2.2042301	-2.6676052

H	2.5096796	-1.1043030	-1.3513454
H	3.4485536	-0.5214703	-2.7250049
C	0.6786599	-0.4608204	-6.9516484
H	1.6889114	-0.7816339	-7.2200743
H	0.5119429	0.5359423	-7.3764079
H	-0.0347272	-1.1409440	-7.4315020
C	-2.2871587	0.3385694	-2.9921383
H	-2.9656984	0.5356322	-3.8264683
H	-2.2340386	1.2430227	-2.3756902
H	-2.7226304	-0.4543777	-2.3729442
C	0.6617482	2.2379727	-0.4911167
C	0.5702290	3.5332092	0.0170477
H	1.4260058	4.1959437	-0.0943432
C	-0.5712948	3.9946353	0.6768541
C	-1.6549182	3.1260241	0.7800698
H	-2.5674509	3.4705337	1.2628346
C	-1.6155027	1.8155548	0.2905020
C	1.9376833	1.8426292	-1.1838701
H	2.6880810	2.6290627	-1.0705173
H	1.7719545	1.6727498	-2.2525046
H	2.3494240	0.9227982	-0.7636455
C	-0.6151726	5.3753714	1.2779047
H	-0.1629429	6.1148124	0.6090859
H	-0.0525708	5.3992307	2.2194745
H	-1.6423425	5.6816882	1.4944114
C	-2.8690800	0.9905015	0.4737147
H	-3.7383160	1.6525314	0.5238170
H	-2.8441965	0.4213673	1.4085194
H	-3.0204494	0.2771189	-0.3373649