Supplementary Material (ESI) for Dalton Transactions

Addition Reactions to the Intramolecular Mesityl$_2$ P-CH$_2$-CH$_2$-B(C$_6$F$_5$)$_2$ Frustrated Lewis Pair

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Supporting Information

General considerations.

All manipulations were performed under Ar using Schlenk-type glassware or in a glove box. Solvents were dried according to the procedure by Grubbs[30] or were distilled from appropriate drying agents and stored under an argon atmosphere.

Melting points were obtained with a DSC Q20 (*TA Instruments*). IR spectra were recorded on a *Varian* 3100 FT-IR (Excalibur Series). Elemental analyses were performed on a *Elementar Vario El III*. NMR spectra were recorded on a *Bruker* AC 200 P (^{11}B: 64.0 MHz, ^{31}P: 81.0 MHz), *Bruker* ARX 300 (^{19}F: 282.4 MHz, ^{31}P: 121.4); *Varian* Inova 500 (^{1}H: 499.9 MHz, ^{13}C: 125.7 MHz, ^{19}F: 470.3 MHz, ^{11}B: 160.4 MHz, ^{31}P: 202.3 MHz) and on a *Varian* UnityPlus 600 (^{1}H: 599.9 MHz, ^{13}C: 150.8 MHz, ^{19}F: 564.4 MHz, ^{11}B: 192.4 MHz, ^{31}P: 242.7 MHz). ^{1}H NMR and ^{13}C NMR: chemical shifts δ are given relative to TMS and referenced to the solvent signal. ^{19}F NMR: chemical shifts δ are given relative to $CFCl_3$ (external reference), ^{11}B NMR: chemical shifts δ are given relative to $BF_3{\cdot}Et_2O$ (external reference), ^{31}P NMR: chemical shifts δ are given relative to H_3PO_4 (85% in H_2O) (external reference). NMR assignments were supported by additional 2D NMR experiments. X-ray structure analyses: Data sets were collected with Nonius KappaCCD diffractometers, in case of Mo-radiation equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307-326), absorption correction Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Cryst.* **2003**, *A59*, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122), graphics XP (BrukerAXS, 2000). Thermal ellipsoids are shown on the 50% probability level. CCDC numbers 722646-767250.

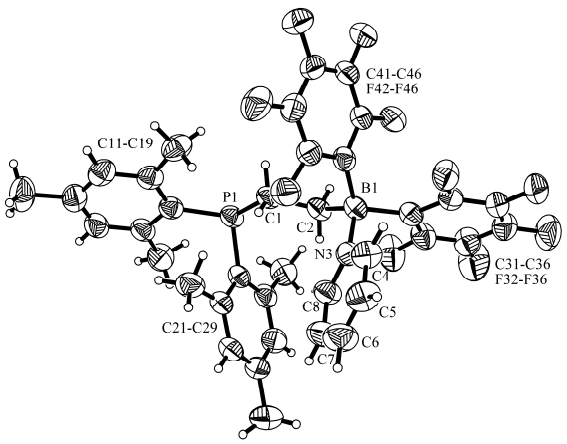
Materials.

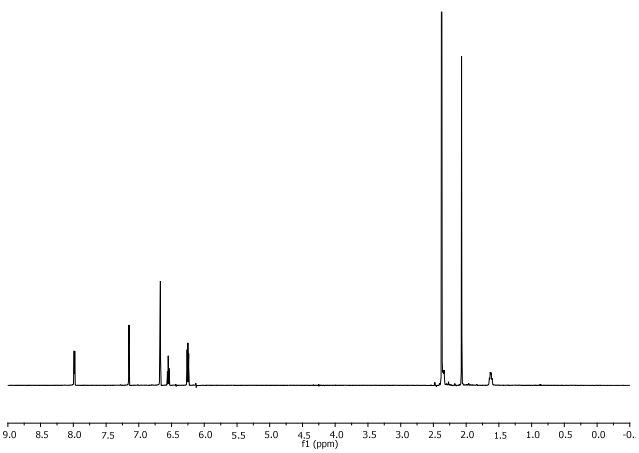
Dimesitylvinylphosphine (P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme and D. W. Stephan, *Chem. Commun*., **2007**, 5072) and HB(C$_6$F$_5$)$_2$ (a) D. J. Parks, R. E. von H. Spence and W. E. Piers, *Angew. Chem.*, 1995, **107**, 895; *Angew. Chem. Int. Ed. Engl*., 1995, **34**, 809; b) W. E. Piers, D. J. Parks and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492) and phenylazide (V. A. Gilyarov, V. Y. Kovtun, M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, *5*, 1159-1161) were prepared according to literature procedures. The following substrates were distilled from appropiate drying agents prior to use: pyridine (KOH), pivalonitrile (molecular sieves), phenylisocyanate (P_2O_5). Benzaldehyde was distilled prior to use. *tert*-Butylisocyanide and nitrosobenzene were used as received.

Compound 5. Dimesitylvinylphosphine (100 mg, 0.34 mmol) and bis(pentafluorophenyl)borane (117 mg, 0.34 mmol) were dissolved in pentane (8 mL) and stirred for 15 minutes. Upon addition of pyridine (27 µL, 0.34 mmol) the solution became immediately colourless, and within two hours a white precipitate had formed. After stirring the reaction mixture overnight, the precipitate was isolated *via cannula* filtration. Then the residue was washed three times with pentane (3 mL) and all volatiles were removed *in vacuo* to yield **5** (159 mg, 65%) as a white powder. Crystals suitable for X-ray analysis were obtained by gas diffusion of heptane into a benzene solution of **5**. mp 193 °C (DSC). $\tilde{\nu}$ (KBr) /cm^{-1} = 3022 (m), 2950 (m), 2917 (s), 2859 (m), 2735 (w), 2389 (w), 2359 (w), 2010 (w), 1944 (w), 1856 (w), 1712 (w), 1647 (m), 1602 (m), 1523 (w), 1438 (w), 1362 (m), 1278 (vs), 1217 (m), 1185 (vs), 1158 (m), 1122 (s), 1027 (w), 949 (m), 909 (s), 857 (vs), 834 (vs), 792 (vs), 768 (s), 721 (s), 694 (s), 666 (s), 632 (m), 615 (m), 555 (s). Found: C, 61.36; H, 4.49; N, 1.90. Calc. for $C_{37}H_{31}BF_{10}NP$: C, 61.60; H, 4.33; N, 1.94. ^{1}H NMR (600 MHz, 298 K, benzene-d$_6$) δ = 7.99 (2H, m, *o*-Py), 6.67 (4H, d, $^{4}J_{PH}$ = 2.1 Hz, *m*-Mes), 6.56 (1H, m, *p*-Py), 6.26 (2H, m, *m*-Py), 2.37 (12H, s, *o*-CH_3^{Mes}), 2.35 (2H, m, $^{P}CH_2$), 2.07 (6H, s, *p*-CH_3^{Mes}), 1.62 (2H, m, $^{B}CH_2$). ^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d$_6$) δ = 148.3 (dm, $^{1}J_{FC}$ = 238 Hz, C_6F_5), 145.3 (*o*-Py), 142.2 (d, $^{2}J_{PC}$ = 12.8 Hz, *o*-Mes), 140.6 (*p*-Py), 139.8 (dm, $^{1}J_{FC}$ = 247 Hz, C_6F_5), 137.4 (dm, $^{1}J_{FC}$ = 248 Hz, C_6F_5), 137.4 (*p*-Mes), 134.4 (d, $^{1}J_{PC}$ = 24.6 Hz, *i*-Mes), 130.3 (d, $^{3}J_{PC}$ = 2.6 Hz, *m*-Mes), 125.3 (*m*-Py), 24.4 (d, $^{1}J_{PC}$ = 15.8 Hz, $^{P}CH_2$), 121.9 (br, *i*-C_6F_5), 23.2 (d, $^{3}J_{PC}$ = 13.2 Hz, *o*-CH_3^{Mes}), 20.7 (*p*-CH_3^{Mes}), 20.0 (br, $^{B}CH_2$). ^{1}H,^{1}H GCOSY (600 MHz / 600 MHz, 298 K, benzene-d$_6$) δ (^{1}H, ^{1}H) = 7.99 / 6.56, 6.26 (*o*-Py / *p*-Py, *m*-Py), 6.67 / 2.37, 2.07 (*m*-Mes / *o*-CH_3^{Mes}, *p*-CH_3^{Mes}), 6.56 / 7.99, 6.26 (*p*-Py / *o*-Py, *m*-Py), 6.26 / 7.99, 6.56 (*m*-Py / *p*-Py / *o*-Py), 2.37 / 6.67 (*o*-CH_3^{Mes} / *m*-Mes), 2.35 / 1.62 ($^{P}CH_2$ / $^{B}CH_2$), 2.07 / 6.67 (*p*-CH_3^{Mes} / *m*-Mes), 1.62 / 2.35 ($^{B}CH_2$ / $^{P}CH_2$). ^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 298 K, benzene-d$_6$) δ (^{1}H) / δ (^{13}C) = 7.99 / 145.3 (*o*-Py), 6.67 / 130.3 (*m*-Mes), 6.56 / 140.6 (*p*-Py), 6.26 / 125.3 (*m*-Py), 2.37 / 23.2 (*o*-CH_3^{Mes}), 2.35 / 24.2 ($^{P}CH_2$), 2.07 / 20.7 (*p*-CH_3^{Mes}), 1.62 / 20.0 ($^{B}CH_2$). ^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 298 K, benzene-d$_6$) δ (^{1}H) / δ (^{13}C) = 7.99 / 145.3, 140.6, 125.3 (*o*-Py / *o*-Py, *p*-Py, *m*-Py), 6.67 / 134.4, 130.3, 23.2, 20.7 (*m*-Mes / *i*-Mes, *m*-Mes, *o*-CH_3^{Mes}, *p*-CH_3^{Mes}), 6.56 / 145.3 (*p*-Py / *o*-Py), 6.26 / 145.3, 125.3 (*m*-Py / *o*-Py, *p*-Py), 2.37 / 142.2, 134.4, 130.3, 23.2 (*o*-CH_3^{Mes} / *o*-Mes, *i*-Mes, *m*-

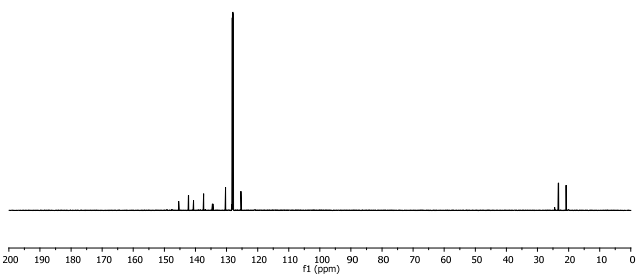
Mes, *o*-CH_3^{Mes}), 2.35 / 24.4, 20.0 ($^{P}CH_2$ / $^{P}CH_2$, $^{B}CH_2$), 2.07 / 142.2, 137.4, 134.4, 130.3, 20.7 (*p*-CH_3^{Mes} / *o*-Mes, *p*-Mes, *i*-Mes, *m*-Mes, *p*-CH_3^{Mes}), 1.62 / 24.4 ($^{B}CH_2$ / $^{P}CH_2$). $^{11}B\{^1H\}$ NMR (64 MHz, 300 K, benzene-d_6) δ = –0.2 ($\nu_{1/2}$ = 450 Hz). $^{31}P\{^1H\}$ NMR (81 MHz, 300 K, benzene-d_6) δ = –16.1 ($\nu_{1/2}$ = 6 Hz). $^{19}F\{^1H\}$ NMR (282 MHz, 298 K, benzene-d_6) δ = –131.9 (2F, *o*-C_6F_5), –157.4 (1F, *p*-C_6F_5), –163.1 (2F, *m*-C_6F_5).

X-ray crystal structure analysis for **5**. Crystal data for $C_{37}H_{31}BF_{10}NP$ (**5**), M = 721.41, monoclinic, space group $P2_1/n$ (No. 14), a = 16.1539(6), b = 12.4332(4), c = 17.1214(7) Å, β = 95.333(2)°, V = 3423.9(2) Å^3, D_c = 1.400 g cm^{-3}, μ = 1.451 mm^{-1}, Z = 4, λ = 1.54178 Å, T = 223(2) K, 26661 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 6016 independent (R_{int} = 0.055), and 4855 observed reflections [I ≥ 2σ(I)], 457 refined parameters, R = 0.047, wR^2 = 0.153.

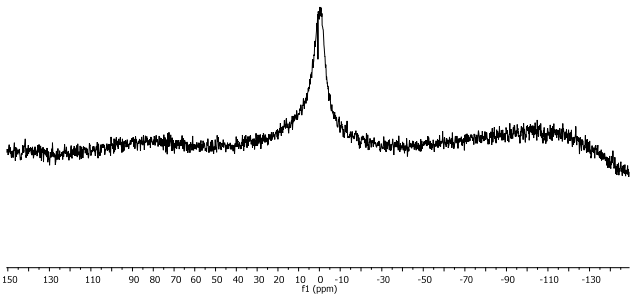




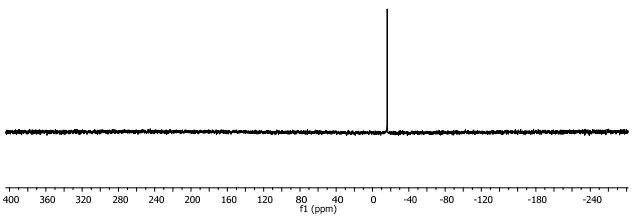
^1H NMR (600 MHz, 298 K, benzene-d_6) of **5**.



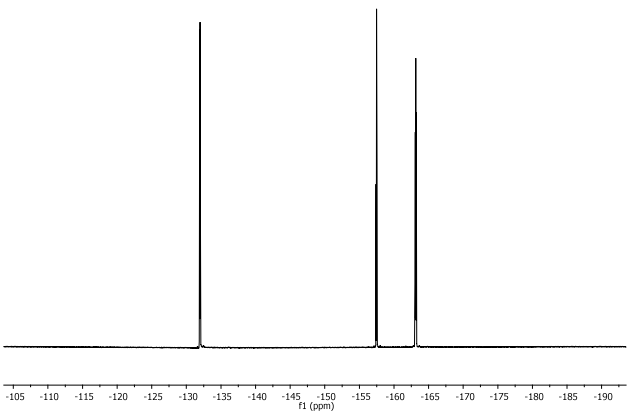
$^{13}C\{^1H\}$ NMR (151 MHz, 298 K, benzene-d_6) of **5**.



$^{11}B\{^1H\}$ NMR (64 MHz, 300 K, benzene-d_6) of **5**.



$^{31}P\{^1H\}$ NMR (81 MHz, 300 K, benzene-d_6) of **5**.



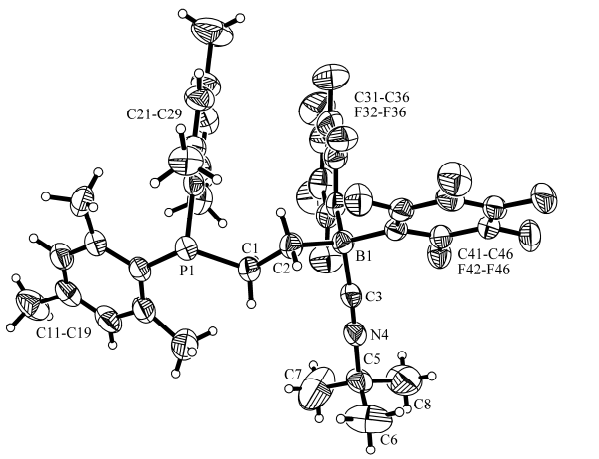
$^{19}F\{^1H\}$ NMR (282 MHz, 298 K, benzene-d_6) of **5**.

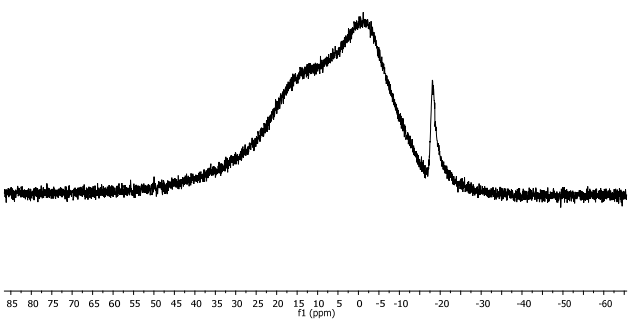
Compound 6. To a solution of dimesitylvinylphosphine (100 mg, 0.34 mmol) and bis(pentafluorophenyl)borane (117 mg, 0.34 mmol) in pentane (5 mL) *tert*-butylisocyanide (42 μL, 0.36 mmol) was added. The solution was immediately decolourized and stirred for 2 days. Removal of all volatiles *in vacuo* yielded **6** (178 mg, 74%) as a white solid. Crystals suitable for X-ray analysis were obtained from heptane at –36°C. mp 142 °C (DSC). $\tilde{\nu}$ (KBr)/cm^{-1} = 3475 (w), 3414 (w), 2984 (m), 2921 (m), 2287 (s, CN), 1644 (s), 1604 (m), 1516 (vs), 1469 (vs), 1376 (s), 1284 (s), 1237 (m), 1181 (m), 1091 (vs), 1027 (w), 986 (vs), 940 (m), 850 (s), 785 (m), 737 (w), 713 (w), 676 (w), 614 (w), 554 (w), 535 (w). Found C, 60.96; H, 4.79; N, 1.87. Calc. for $C_{37}H_{35}BF_{10}NP$: C, 61.26; H, 4.86; N, 1.93.

^1H NMR (600 MHz, 298 K, benzene-d_6) δ = 6.68 (4H, d, $^4J_{PH}$ = 2.0 Hz, *m*-Mes), 2.54 (2H, m, $^{P}CH_2$), 2.41 (12H, s, *o*-CH_3^{Mes}), 2.08 (6H, s, *p*-CH_3^{Mes}), 1.62 (2H, br m, $^{B}CH_2$), 0.75 (9H, s, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (151 MHz, 298 K, benzene-d_6) δ = 148.2 (dm, $^1J_{FC}$ = 246 Hz, *o*-C_6F_5), 142.0 (d, $^2J_{PC}$ = 13 Hz, *o*-Mes), 140.0 (dm, $^1J_{FC}$ = 250 Hz, *p*-C_6F_5), 137.5 (dm, $^1J_{FC}$ = 250 Hz, *m*-C_6F_5), 137.5 (*p*-Mes), 134.4 (d, $^1J_{PC}$ = 24.1 Hz, *i*-Mes), 130.4 (*m*-Mes), 127.8 (C≡N), 117.4 (*i*-C_6F_5), 59.6

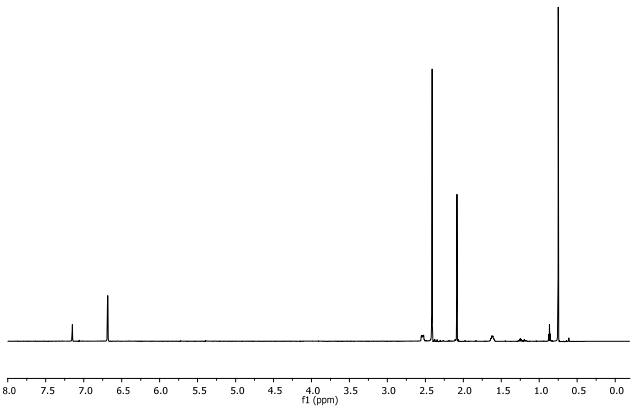
($\underline{C}(CH_3)_3$, 28.2 ($C(\underline{C}H_3)_3$), 26.7 (d, $^1J_{PC}$ = 17.0 Hz, $^PCH_2$), 23.4 (d, $^3J_{PC}$ = 13.0 Hz, *o*-CH_3^{Mes}), 20.8 (*p*-CH_3^{Mes}), 17.9 (br, $^BCH_2$). ^1H,^{13}C GHSQC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ (^1H) / δ (^{13}C) = 6.68 / 130.4 (*m*-Mes) 2.54 / 26.7 ($^PCH_2$), 2.41 / 23.4 (*o*-CH_3^{Mes}), 2.08 / 20.8 (*p*-CH_3^{Mes}), 1.62 / 17.9 ($^BCH_2$), 0.75 / 28.2 ($C(CH_3)_3$). ^1H,^{13}C GHMBC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ (^1H) / δ (^{13}C) = 6.68 / 142.0, 134.4, 130.4, 23.4, 20.8 (*m*-Mes/ *o*-Mes, *i*-Mes, *m*-Mes, *o*-CH_3^{Mes}, *p*-CH_3^{Mes}), 2.54 / 134.4, 23.4 ($^PCH_2$ / *i*-Mes, *o*-CH_3^{Mes}), 2.41 / 142.0, 134.4, 130.4, 26.7, 23.4 (*o*-CH_3^{Mes}/ *o*-Mes, *i*-Mes, *m*-Mes, $^PCH_2$, *o*-CH_3^{Mes}), 2.08 / 142.0, 137.5, 134.4, 130.4 (*p*-CH_3^{Mes} / *o*-Mes, *p*-Mes, *i*-Mes, *m*-Mes), 1.62 / 26.7 ($^BCH_2$ / $^PCH_2$), 0.75 / 59.6, 28.2 ($C(CH_3)_3$ / $\underline{C}(CH_3)_3$, $C(\underline{C}H_3)_3$). $^{11}B\{^1H\}$ NMR (192 MHz, 298 K, benzene-d_6) δ = –18 ($\nu_{1/2}$ = 230 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, 300 K, benzene-d_6) δ = –18.7 ($\nu_{1/2}$ = 9 Hz). $^{19}F\{^1H\}$ NMR (564 MHz, 298 K, benzene-d_6) δ = –133.0 (2F, *o*-C_6F_5), –157.5 (1F, *p*-C_6F_5), –163.3 (2F, *m*-C_6F_5).

X-ray crystal structure analysis for **6**. Crystal data for $C_{37}H_{35}BF_{10}NP$ (**6**), M = 725.44, triclinic, space group $P\bar{1}$ (No. 2), a = 10.4592(4), b = 13.2592(5), c = 14.5233(7) Å, α = 99.281(2), β = 99.394(2), γ = 110.205(3)°, V = 1812.55(13) Å^3, D_c = 1.329 g cm^{-3}, μ = 1.371 mm^{-1}, Z = 2, λ = 1.54178 Å, T = 223(2) K, 21458 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 6332 independent (R_{int} = 0.47), and 5367 observed reflections [I ≥ 2σ(I)], 460 refined parameters, R = 0.056, wR^2 = 0.164.

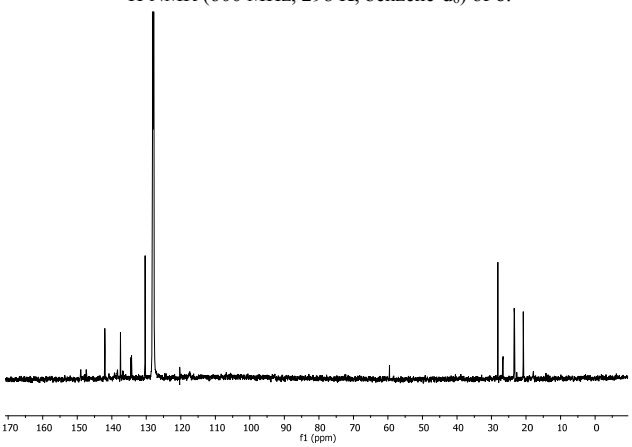




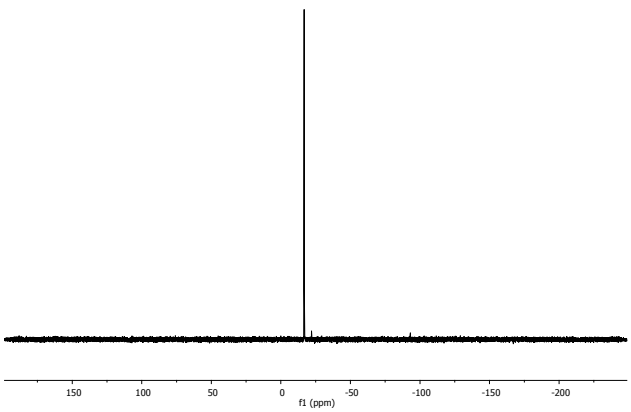
$^{11}B\{^1H\}$ NMR (192 MHz, 298 K, benzene-d_6) of **6**.



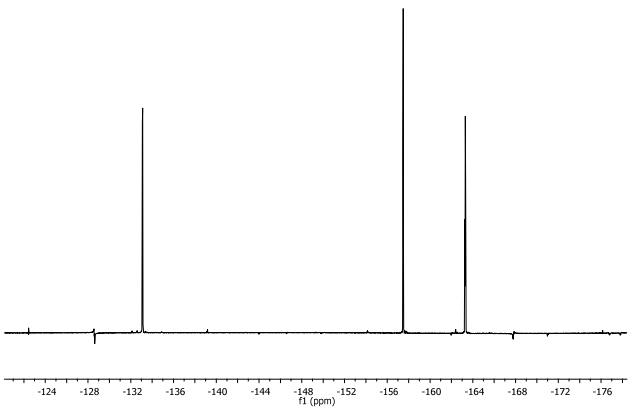
^1H NMR (600 MHz, 298 K, benzene-d_6) of **6**.



$^{13}C\{^1H\}$ NMR (151 MHz, 298 K, benzene-d_6) of **6**.



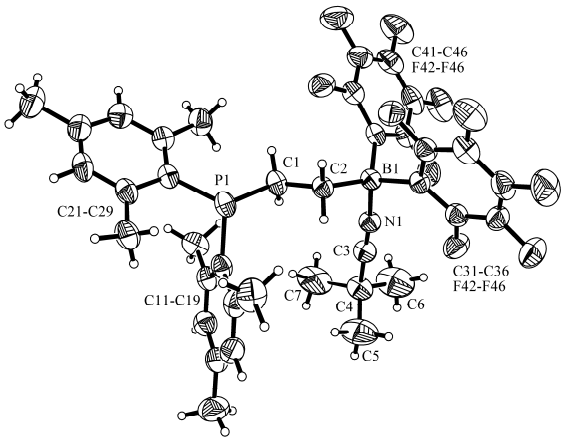
$^{31}P\{^1H\}$ NMR (121 MHz, 300 K, benzene-d_6) of **6**.

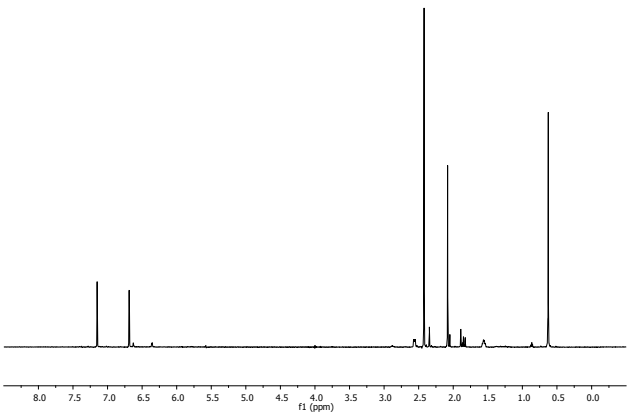


$^{19}F\{^1H\}$ NMR (564 MHz, 298 K, benzene-d_6) of **6**.

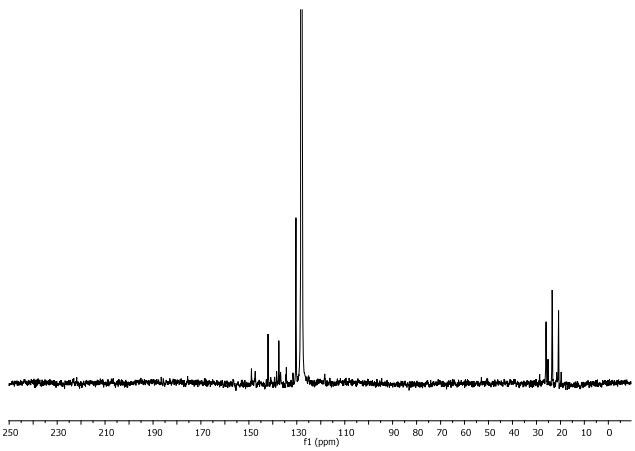
Compound 7. Dimesitylvinylphosphine (80 mg, 0.27 mmol) and bis(pentafluorophenyl)borane (94 mg, 0.27 mmol) were dissolved in pentane (6 mL) and stirred for 15 minutes. Upon addition of pivalonitrile (28 µL, 0.27 mmol) at room temperature the solution became immediately colourless. After stirring the reaction mixture for 3 hours, a white powder started to precipitate. The reaction mixture was stirred overnight, then the precipitate was isolated *via cannula* filtration and washed three times with pentane (2.5 mL). All volatiles were removed *in vacuo* to yield a white powder (118 mg, 60%). Crystals suitable for X-ray analysis were grown by slow diffusion of heptane into a benzene solution of **7**. mp 143 °C (DSC). $\tilde{\nu}$ (KBr)/cm^{-1} = 3593 (w), 2876 (s), 2733 (w), 2329 (s, CN), 1734 (w), 1644 (m), 1604 (m), 1557 (w), 1520 (w), 1450 (w), 1371 (m), 1283 (m), 1235 (m), 1183 (m), 1126 (s), 1096 (s), 1032 (m), 970 (m), 910 (m), 881 (m), 852 (s), 829 (s), 780 (s), 748 (m), 678 (m), 690 (s), 647 (s), 598 (s), 553 (vs). Found C, 60.95; H, 4.83; N, 2.05. Calc. for $C_{37}H_{35}BF_{10}NP$: C, 61.26; H, 4.86; N, 1.93. ^{1}H NMR (600 MHz, 298 K, benzene-d$_6$) δ = 6.69 (4H, d, $^4J_{PH}$ = 2.1 Hz, *m*-Mes), 2.56 (2H, m, ^{P}CH$_2$), 2.42 (12H, s, *o*-CH$_3^{Mes}$), 2.08 (6H, s, *p*-CH$_3^{Mes}$), 1.56 (2H, m, ^{B}CH$_2$), 0.63 (9H, s, C(CH$_3$)$_3$. ^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d$_6$) δ = 148.1 (dm, $^1J_{FC}$ = 242 Hz, C_6F_5), 142.0 (d, $^2J_{PC}$ = 12.8 Hz, *o*-Mes), 139.8 (dm, $^1J_{FC}$ = 246 Hz, C_6F_5), 137.5 (dm, $^1J_{FC}$ = 248 Hz, C_6F_5), 137.4 (*p*-Mes), 134.4 (d, $^1J_{PC}$ = 24 Hz, *i*-Mes), 130.3 (*m*-Mes), 121.0 (C≡N), 118.3 (br, *i*-C_6F_5), 28.6 (br, C(CH$_3$)$_3$), 25.9 (br, C(CH$_3$)$_3$), 25.1 (d, $^1J_{PC}$ = 16.0 Hz, ^{P}CH$_2$), 23.3 (d, $^3J_{PC}$ = 12.9 Hz, *o*-CH$_3^{Mes}$), 20.7 (*p*-CH$_3^{Mes}$), 19.6 (br, ^{B}CH$_2$). ^{1}H,^{1}H GCOSY (600 MHz / 600 MHz, 298 K, benzene-d$_6$) δ (^{1}H, ^{1}H) = 6.69 / 2.42, 2.08 (*m*-Mes / *o*-CH$_3^{Mes}$, *p*-CH$_3^{Mes}$), 2.56 / 1.56 (^{P}CH$_2$ / ^{B}CH$_2$), 2.42 / 6.69 (*o*-CH$_3^{Mes}$ / *m*-Mes), 2.08 / 6.69 (*p*-CH$_3^{Mes}$ / *m*-Mes), 1.56 / 2.56 (^{B}CH$_2$ / ^{P}CH$_2$). ^{1}H TOCSY (600 MHz, 298 K, benzene-d$_6$) δ ^{1}H$_{irr}$ / δ ^{1}H$_{res}$ = 6.69 / 2.42, 2.08 (*m*-Mes / *o*-CH$_3^{Mes}$, *p*-CH$_3^{Mes}$), 2.56 / 1.56 (^{P}CH$_2$ / ^{B}CH$_2$). ^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 298 K, benzene-d$_6$) δ (^{1}H) / δ (^{13}C) = 6.69 / 130.3 (*m*-Mes), 2.56 / 25.1 (^{P}CH$_2$), 2.42 / 23.3 (*o*-CH$_3^{Mes}$), 2.08 / 20.7 (*p*-CH$_3^{Mes}$), 1.56 / 19.6 (^{B}CH$_2$), 0.63 / 25.9 (C(CH$_3$)$_3$. ^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 298 K, benzene-d$_6$) δ (^{1}H) / δ (^{13}C) = 6.69 / 134.4, 130.3, 23.3, 20.7 (*m*-Mes / *i*-Mes, *m*-Mes, *o*-CH$_3^{Mes}$, *p*-CH$_3^{Mes}$), 2.42 / 142.0, 134.4, 130.3, 23.3 (*o*-CH$_3^{Mes}$ / *o*-Mes, *i*-Mes, *m*-Mes, *o*-CH$_3^{Mes}$); 2.08 / 137.4, 134.4, 130.3, 20.7 (*p*-CH$_3^{Mes}$ / *p*-Mes, *m*-Mes, *i*-Mes, *p*-CH$_3^{Mes}$); 0.63 / 121.0, 28.6, 25.1 (C(CH$_3$)$_3$ / C≡N, C(CH$_3$)$_3$, C(CH$_3$)$_3$. ^{11}B{^{1}H} NMR (192 MHz, 298 K, benzene-d$_6$) δ = –1.2. ^{31}P{^{1}H} NMR (243 MHz, 298 K, benzene-d$_6$) δ = –16.4 ($\nu_{1/2}$ = 50 Hz). ^{19}F{^{1}H} NMR (564 MHz, 298 K, benzene-d$_6$) δ = –134.7 (2F, *o*-C_6F_5), –157.6 (1F, *p*-C_6F_5), –163.5 (2F, *m*-C_6F_5).

X-ray crystal structure analysis for **7**. Crystal data for $C_{37}H_{35}BF_{10}NP$ (**7**), M = 725.44, monoclinic, space group $P2_1/n$ (No. 14), a = 9.5576(1), b = 22.3280(3), c = 16.9958(4) Å, β = 104.650(1)°, V = 3509.02(10) Å^3, D_c = 1.373 g cm^{-3}, µ = 0.159 mm^{-1}, Z = 4, λ = 0.71073 Å, T = 223(2) K, 20451 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 6989 independent (R_{int} = 0.051), and 5030 observed reflections [I ≥ 2σ(I)], 491 refined parameters, R = 0.074, wR^2 = 0.179.

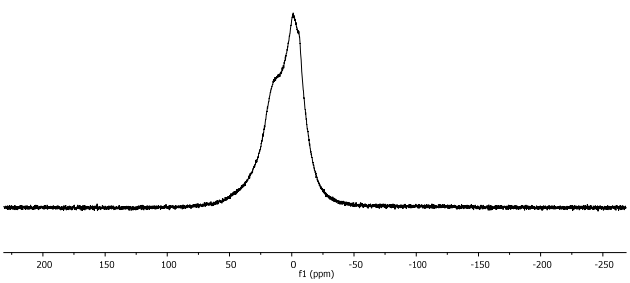




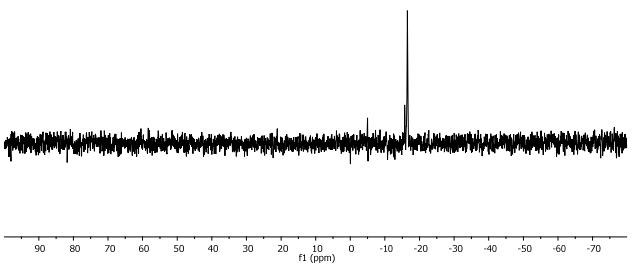
^{1}H NMR (600 MHz, 298 K, benzene-d$_6$) of **7**.



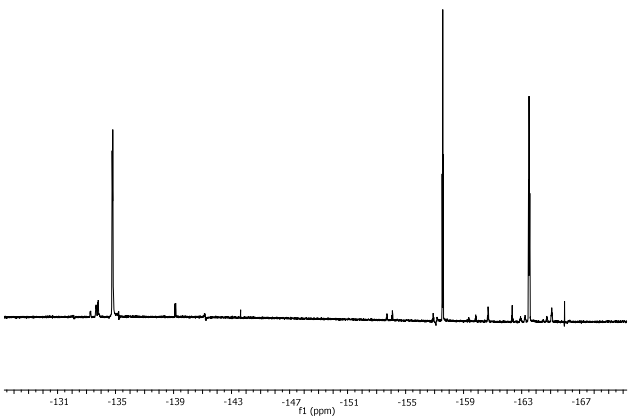
^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d$_6$) of **7**.



^{11}B{^{1}H} NMR (192 MHz, 298 K, benzene-d$_6$) of **7**.



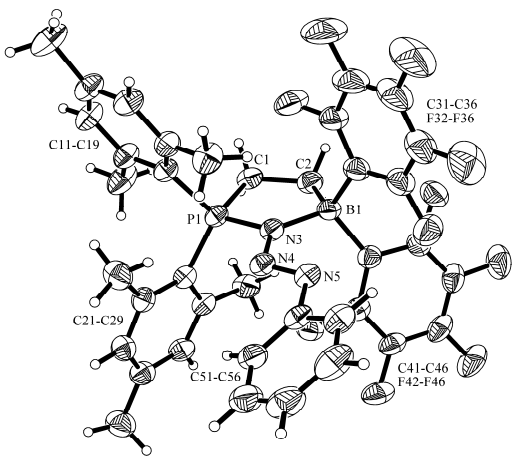
$^{31}P\{^{1}H\}$ NMR (243 MHz, 298 K, benzene-d_6) of **7**.

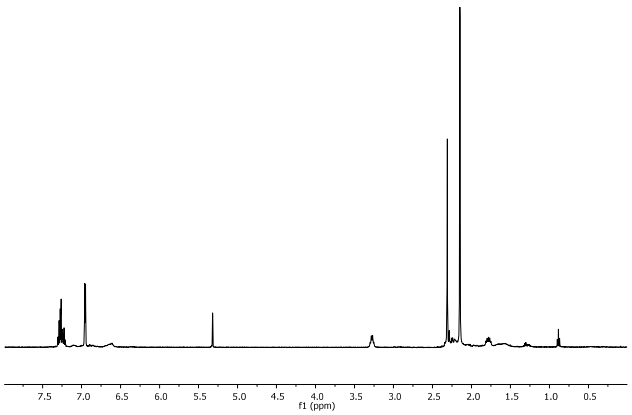


$^{19}F\{^{1}H\}$ NMR (564 MHz, 298 K, benzene-d_6) of **7**.

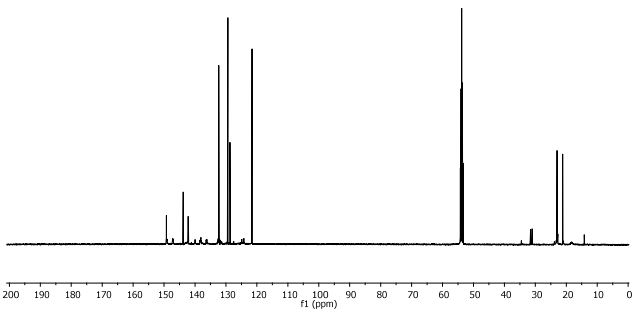
Compound 8. Dimesitylvinylphosphine (100 mg, 0.34 mmol) and bis(pentafluorophenyl)borane (117 mg, 0.34 mmol) were dissolved in pentane (8 mL) and stirred for 15 minutes. After addition of phenylazide (40 mg, 0.34 mmol) the reaction mixture became immediately cloudy. The reaction mixture was stirred for 2 days, then the precipitate was collected *via cannula* filtration and washed three times with pentane (3 mL). All volatiles were removed *in vacuo* to yield **8** (201 mg, 77%). Crystals suitable for X-ray analysis were obtained by slow diffusion of heptane into a benzene solution of **8**. dp 162 °C (DSC). $\tilde{\nu}$ (KBr)/cm^{-1} = 3205 (s), 2967 (vs), 2934 (vs), 2737 (w), 1715 (w), 1642 (vs), 1605 (vs), 1557 (w), 1518 (m), 1439 (w), 1381 (w), 1330 (w), 1272 (s), 1250 (m), 1224 (m), 1190 (w), 1136 (s), 1032 (w), 980 (m), 893 (m), 851 (s), 834 (vs), 773 (m), 732 (s), 689 (s), 652 (s), 559 (s). Found C, 59.50; H, 4.10; N, 5.13. Calc. for $C_{38}H_{31}BF_{10}N_3P$: C, 59.94; H, 4.10; N, 5.52. ^{1}H NMR (500 MHz, 298 K, dichloromethane-d_2) δ = 7.28 (2H, m, *m*-Ph), 7.26 (2H, m, *o*-Ph), 7.23 (1H, m, *p*-Ph), 6.95 (4H, d, $^{4}J_{PH}$ = 4.6 Hz, *m*-Mes), 3.28 (2H, m, $^{P}CH_2$), 2.31 (6H, s, *p*-CH_3^{Mes}), 2.15 (12H, s, *o*-CH_3^{Mes}), 1.78 (2H, m, $^{B}CH_2$). $^{13}C\{^{1}H\}$ NMR (126 MHz, 298 K, dichloromethane-d_2) δ = 149.2 (*i*-Ph), 148.0 (dm, $^{1}J_{FC}$ = 240 Hz, C_6F_5), 143.8 (*p*-Mes), 142.2 (d, $^{2}J_{PC}$ = 11.0 Hz, *o*-Mes), 139.0 (dm, $^{1}J_{FC}$ = 240 Hz, C_6F_5), 137.2 (dm, $^{1}J_{FC}$ = 241 Hz, C_6F_5), 132.2 (d, $^{3}J_{PC}$ = 11.8 Hz, *m*-Mes), 131.4 (br, *i*-C_6F_5), 129.3 (*m*-Ph), 128.6 (*p*-Ph), 124.5 (d, $^{1}J_{PC}$ = 87.5 Hz, *i*-Mes), 121.5 (*o*-Ph), 31.2 (d, $^{1}J_{PC}$ = 66.2 Hz, $^{P}CH_2$), 22.9 (d, $^{3}J_{PC}$ = 5.2 Hz, *o*-CH_3^{Mes}), 21.1 (d, $^{5}J_{PC}$ = 1.5 Hz, *p*-CH_3^{Mes}), 18.2 (br, $^{B}CH_2$). $^{1}H,^{1}H$ GCOSY (500 MHz / 500 MHz, 298 K, dichloromethane-d_2) δ (^{1}H, ^{1}H) = 6.95 / 2.31, 2.15 (*m*-Mes / *p*-CH_3^{Mes}, o CH_3^{Mes}), 3.28 / 1.78 ($^{P}CH_2$ / $^{B}CH_2$), 2.31 / 6.95 (*p*-CH_3^{Mes} / *m*-Mes), 2.15 / 6.95 (*o*-CH_3^{Mes} / *m*-Mes), 1.78 / 3.28 ($^{B}CH_2$ / $^{P}CH_2$). ^{1}H TOCSY (500 MHz, 298 K, C_6D_6) δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 6.95 / 2.31, 2.15 (*m*-Mes / *p*-CH_3^{Mes}, *o*-CH_3^{Mes}), 3.28 / 1.78 ($^{P}CH_2$ / $^{B}CH_2$), 2.31 / 6.95 (*p*-CH_3^{Mes} / *m*-Mes), 2.15 / 6.95 (*o*-CH_3^{Mes} / *m*-Mes), 1.78 / 3.28 ($^{B}CH_2$ / $^{P}CH_2$). $^{1}H,^{13}C$ GHSQC (500 MHz / 126 MHz, 298 K, dichloromethane-d_2) δ (^{1}H) / δ (^{13}C) = 7.28 / 129.3 (*m*-Ph), 7.26 / 121.5 (*o*-Ph), 7.23 / 128.6 (*p*-Ph), 6.95 / 132.2 (*m*-Mes), 3.28 / 31.2 ($^{P}CH_2$), 2.31 / 21.1 (*p*-CH_3^{Mes}), 2.15 / 22.9 (*o*-CH_3^{Mes}), 1.78 / 18.2 ($^{B}CH_2$). $^{1}H,^{13}C$ GHMBC (500 MHz / 126 MHz, 298 K, dichloromethane-d_2) δ (^{1}H) / δ (^{13}C) = 7.28 / 149.2, 129.3 (*m*-Ph / *i*-Ph, *m*-Ph), 7.26 / 128.6, 121.5 (*o*-Ph / *p*-Ph, *o*-Ph), 7.23 / 121.5 (*p*-Ph / *o*-Ph), 6.95 / 142.2, 132.2, 124.5, 22.9, 21.1 (*m*-Mes/ *o*-Mes, *m*-Mes, *i*-Mes, *o*-CH_3^{Mes}, *p*-CH_3^{Mes}), 2.31 / 143.8, 132.2, 124.5 (*p*-CH_3^{Mes} / *p*-Mes, *m*-Mes, *i*-Mes), 2.15 / 142.2, 132.2, 124.5 (*o*-CH_3^{Mes} / *o*-Mes, *m*-Mes, *i*-Mes), 1.78 / 31.2 ($^{B}CH_2$ / $^{P}CH_2$). $^{11}B\{^{1}H\}$ NMR (160 MHz, 298 K, dichloromethane-d_2) δ = –5.4 ($\nu_{1/2}$ = 210 Hz). $^{31}P\{^{1}H\}$ NMR (202 MHz, 298 K, dichloromethane-d_2) δ = +50 ($\nu_{1/2}$ ~ 1600 Hz). ^{19}F NMR (470 MHz, 298 K, dichloromethane-d_2) [all resonances are broad] δ = –132.7 (2F, *o*-C_6F_5), –162.1 (1F, *p*-C_6F_5), –166.3 (2F, *m*-C_6F_5).

X-ray crystal structure analysis for **8**. Crystal data for $C_{38}H_{31}BF_{10}N_3P$ * 2 C_6H_6 (**8**), M = 917.65, monoclinic, space group $P2_1/c$ (No. 14), a = 15.8351(4), b = 13.8395(4), c = 21.6049(7) Å, β = 109.595(1)°, V = 4460.5(2) Å^3, D_c = 1.366 g cm^{-3}, μ = 1.250 mm^{-1}, Z = 4, λ = 1.54178 Å, T = 223(2) K, 43759 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 7883 independent (R_{int} = 0.053), and 6856 observed reflections [I ≥ 2σ(I)], 592 refined parameters, R = 0.046, wR^2 = 0.132.

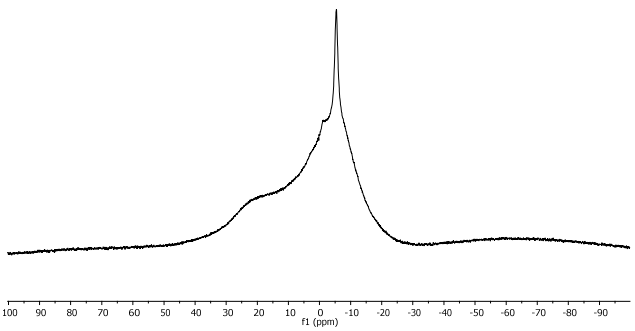




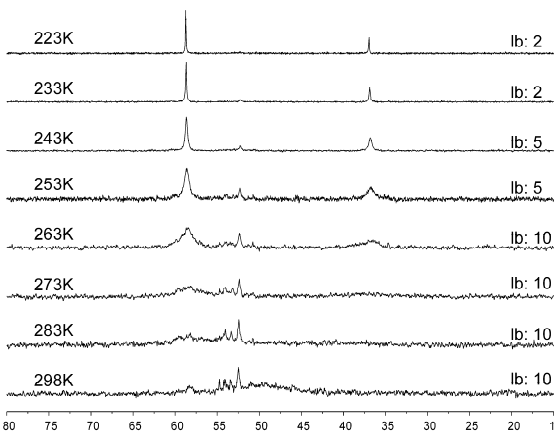
^{1}H NMR (500 MHz, 298 K, dichloromethane-d_2) of **8**.



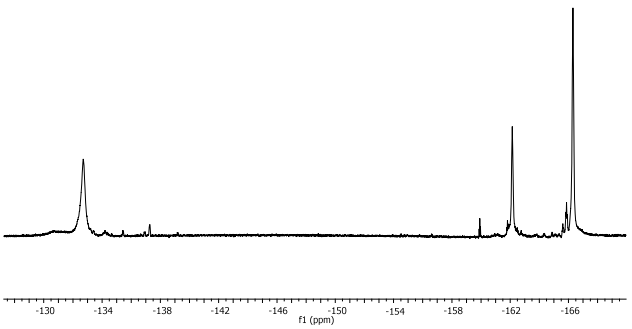
^{13}C{^{1}H} NMR (126 MHz, 298 K, dichloromethane-d_2) of **8**.



^{11}B{^{1}H} NMR (160 MHz, 298 K, dichloromethane-d_2) of **8**.



Variable temperature ^{31}P{^{1}H} NMR (202 MHz, dichloromethane-d_2) of **8** (lb: line broadening).

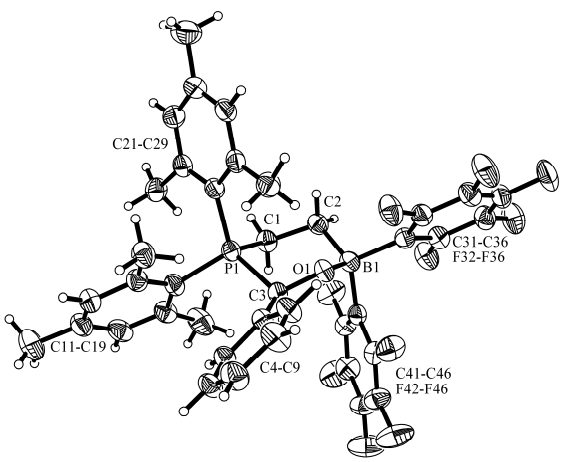


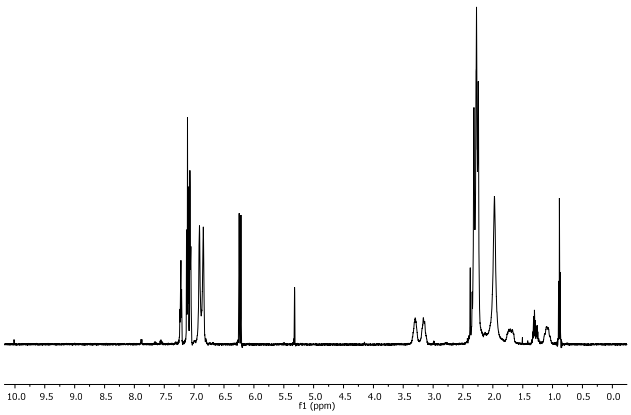
^{19}F NMR (470 MHz, 298 K, dichloromethane-d_2) of **8**.

Compound 9. Dimesitylvinylphosphine (100 mg, 0.34 mmol) and bis(pentafluorophenyl)borane (117 mg, 0.34 mmol) were dissolved in pentane (8 mL) and stirred for 15 minutes. Upon addition of benzaldehyde (34 µL, 0.34 mmol) the solution turned colourless and after 1 hour a white precipitate had formed. The precipitate was isolated *via cannula* filtration after 5 hours, washed twice with pentane (2 mL) and dried *in vacuo* to afford **9** (218 mg, 86%). Crystals suitable for X-ray diffraction were grown by slow diffusion of heptane into a benzene solution of **6**. mp 197 °C (DSC). $\tilde{\nu}$ (KBr)/cm^{-1} = 3205 (m), 2974 (s), 2935 (s), 2881 (m), 2822 (w), 2774 (m), 2592 (w), 2537 (w), 2392 (w), 2359 (w), 2342 (w), 2214 (w), 1969 (w), 1901 (w), 1776 (w), 1737 (w), 1697 (w), 1639 (vs), 1604 (vs), 1556 (w), 1516 (vs), 1474 (vs), 1399 (s), 1380 (s), 1306 (m), 1277 (s), 1234 (s), 1204 (m), 11482 (w), 1123 (s), 1089 (s), 1031 (m), 1009 (m), 969 (s), 946 (s), 862 (s), 789 (s), 769 (m), 741 (s), 700 (s), 653 (m), 619 (w), 593 (s), 569 (m), 552 (s), 520 (m). Found C, 62.29; H, 3.86. Calc. for $C_{39}H_{32}BF_{10}OP$: C, 62.59; H, 4.31. ^{1}H NMR (500 MHz, 298 K, dichloromethane-d_2) δ = 7.22 (1H, m, *p*-Ph), 7.11 (2H, m, *m*-Ph), 7.06 (2H, m, *o*-Ph), 6.91, 6.85 (each 2H, each br, *m*-Mes), 6.23 (1H, d, $^{2}J_{PH}$ = 15.3 Hz, CH), 3.30, 3.15 (each 1H, each m, $^{P}CH_2$), 2.32, 2.24 (each 3H, each s, *p*-CH_3^{Mes}), 2.27, 1.97 (each 6H, each br, *o*-CH_3^{Mes}), 1.70, 1.09 (each 1H, each m, $^{B}CH_2$). ^{13}C{^{1}H} NMR (126 MHz, 298 K, dichloromethane-d_2) δ = 148.6 (dm, $^{1}J_{FC}$ = 240 Hz, C_6F_5), 148.2 (dm, $^{1}J_{FC}$ = 243 Hz, C_6F_5), 144.2, 143.4 (*p*-Mes), 142.7, 142.6 (each br, *o*-Mes), 139.0 (dm, $^{1}J_{FC}$ = 251 Hz, 2 × C_6F_5), 137.2 (dm, $^{1}J_{FC}$ = 248 Hz, 2 × C_6F_5), 137.1 (*i*-Ph), 132.5, 131.4 (each br d, each $^{3}J_{PC}$ = 10.2 Hz, *m*-Mes), 128.8 (d, $^{5}J_{PC}$ = 3.8 Hz, *p*-Ph), 127.9 (d, $^{4}J_{PC}$ = 4.7 Hz, *m*-Ph), 127.7 (d, $^{3}J_{PC}$ = 3.2 Hz, *o*-Ph), 123.1, 124.2 (each br, *i*-C_6F_5), 123.4 (d, $^{1}J_{PC}$ = 55.5 Hz, *i*-Mes), 121.0 (d, $^{1}J_{PC}$ = 56.8 Hz, *i*-Mes), 85.5 (d, $^{1}J_{PC}$ = 29.6 Hz, CH), 28.9 (d, $^{1}J_{PC}$ = 42.5 Hz, $^{P}CH_2$), 24.3, 24.0 (br, *o*-CH_3^{Mes}), 21.1, 21.0 (br, *p*-CH_3^{Mes}), 13.8 (br, $^{B}CH_2$). ^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 298 K, dichloromethane-d_2) δ (^{1}H, ^{1}H) = 7.22 / 7.11, 7.06, 6.23 (*p*-Ph / *m*-Ph, *o*-Ph, CH), 7.11 / 7.22, 7.06, 6.23 (*m*-Ph / *p*-Ph, *o*-Ph, CH), 7.06 / 7.22, 7.11, 6.23 (*o*-Ph / *p*-Ph, *m*-Ph, CH), 6.91 / 2.32, 1.97 (*m*-Mes / *p*-CH_3^{Mes}, *o*-CH_3^{Mes}), 6.85 / 2.27, 2.24 (*m*-Mes / *p*-CH_3^{Mes}, *o*-CH_3^{Mes}), 6.23 / 7.22, 7.11, 7.06 (CH / *p*-Ph, *m*-Ph, *o*-Ph), 3.30 / 3.15, 1.70, 1.09 ($^{P}CH_2$ / $^{P}CH_2$, $^{B}CH_2$, $^{B}CH_2$), 3.15 / 3.30, 1.70, 1.09 ($^{P}CH_2$ / $^{P}CH_2$, $^{B}CH_2$, $^{B}CH_2$), 2.32 / 6.91 (*p*-CH_3^{Mes} / *m*-Mes), 2.27 / 6.85 (*o*-CH_3^{Mes} / *m*-

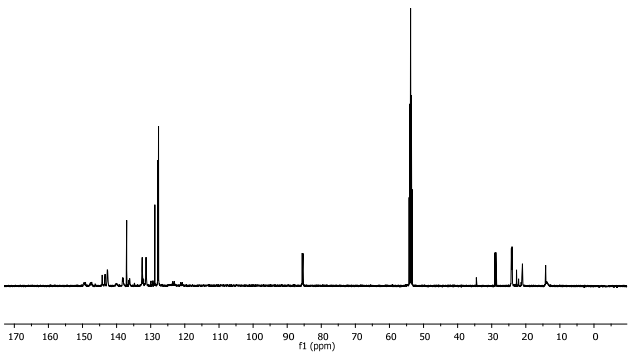
Mes), 2.24 / 6.85 (p-CH_3^{Mes} / m-Mes), 1.97 / 6.91 (o-CH_3^{Mes} / m-Mes), 1.70 / 3.30, 3.15, 1.09 ($^{B}CH_2$ / $^{P}CH_2$, $^{P}CH_2$, $^{B}CH_2$), 1.09 / 3.30, 3.15, 1.70 ($^{B}CH_2$ / $^{P}CH_2$, $^{P}CH_2$, $^{B}CH_2$). $^{1}H,^{13}C$ GHSQC (500 MHz / 126 MHz, 298 K, dichloromethane-d_2) δ (^{1}H) / δ (^{13}C) = 7.22 / 128.8 (p-Ph), 7.11 / 127.9 (m-Ph), 7.06 / 127.7 (o-Ph), 6.91 / 132.5 (m-Mes), 6.85 / 131.4 (m-Mes), 6.23 / 85.5 (CH), 3.30, 3.15 / 28.9 ($^{P}CH_2$), 2.32 / 21.1 (p-CH_3^{Mes}), 2.27 / 24.1 (o-CH_3^{Mes}), 2.24 / 21.0 (p-CH_3^{Mes}), 1.97 / 24.3 (o-CH_3^{Mes}), 1.70, 1.09 / 13.8 ($^{B}CH_2$). $^{1}H,^{13}C$ GHMBC (500 MHz / 126 MHz, 298 K, dichloromethane-d_2) δ (^{1}H) / δ (^{13}C) = 7.22 / 127.9 (p-Ph / m-Ph), 7.11 / 137.1, 127.7 (m-Ph / i-Ph, o-Ph), 7.06 / 128.8, 127.9, 85.5 (o-Ph / p-Ph, m-Ph, CH), 6.23 / 137.1, 127.7, 123.4, 121.0, 85.5 (CH / i-Ph, o-Ph, i-Mes, i-Mes, CH), 2.32 / 144.3, 132.5 (p-CH_3^{Mes} / p-Mes, m-Mes), 2.27 / 143.4, 142.7 (o-CH_3^{Mes} / p-Mes, o-Mes), 2.24 / 143.4, 131.4 (p-CH_3^{Mes} / p-Mes, m-Mes). $^{11}B\{^{1}H\}$ NMR (192 MHz, 298 K, dichloromethane-d_2) δ = –0.3 ($\nu_{1/2}$ = 140 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, 298 K, dichloromethane-d_2) δ = 19.6 ($\nu_{1/2}$ = 70 Hz). $^{19}F\{^{1}H\}$ NMR (564 MHz, 298 K, dichloromethane-d_2) δ = –134.7 (2F, o), –162.5 (1F, p), –166.4 (2F, m) ($C_6F_5^{A}$), –134.7 (2F, o), –161.4 (1F, p), –165.6 (2F, m) ($C_6F_5^{B}$). ^{19}F, ^{19}F GCOSY (564 / 564 MHz, 298 K, dichloromethane-d_2) δ (^{19}F) / δ (^{19}F) = –134.7 / –165.6, –166.4 (o-$C_6F_5^{A/B}$ / m-$C_6F_5^{B}$, m-$C_6F_5^{A}$), –161.4 / –165.6 (p-$C_6F_5^{B}$ / m-$C_6F_5^{B}$), –162.5 / –166.4 (p-$C_6F_5^{A}$ / m-$C_6F_5^{A}$), –165.6 / –134.7, –161.4 (m-$C_6F_5^{B}$ / o-$C_6F_5^{A/B}$, p-$C_6F_5^{A/B}$), –166.4 / –134.7, –162.5 (m-$C_6F_5^{A}$ / o-$C_6F_5^{A/B}$, p-$C_6F_5^{A/B}$).

X-ray crystal structure analysis for **9**. Crystal data for $C_{39}H_{32}BF_{10}OP$ (**9**), M = 748.43, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 11.4602(3), b = 13.8298(4), c = 21.8599(7) Å, V = 3464.63(17) Å^3, D_c = 1.435 g cm^{-3}, μ = 1.470 mm^{-1}, Z = 4, λ = 1.54178 Å, T = 223(2) K, 13725 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 5824 independent (R_{int} = 0.035), and 5536 observed reflections [I ≥ 2σ(I)], 475 refined parameters, R = 0.039, wR^2 = 0.102, Flack 0.00(2).

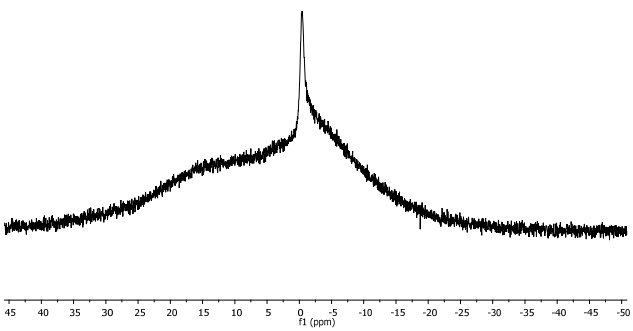




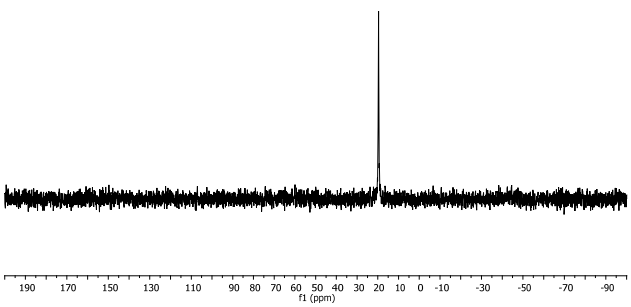
^{1}H NMR (500 MHz, 298 K, dichloromethane-d_2) of **9**.



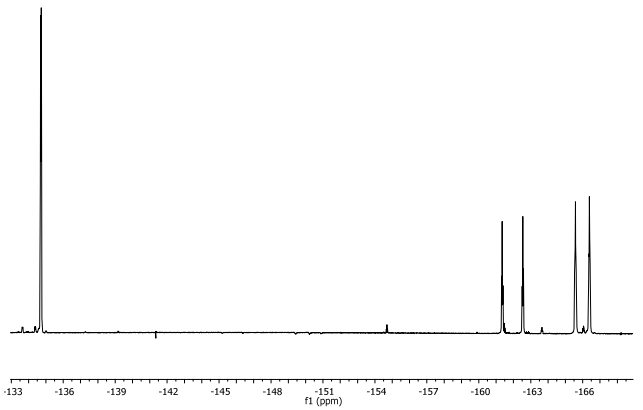
$^{13}C\{^{1}H\}$ NMR (126 MHz, 298 K, dichloromethane-d_2) of **9**.



$^{11}B\{^{1}H\}$ NMR (192 MHz, 298 K, dichloromethane-d_2) of **9**.



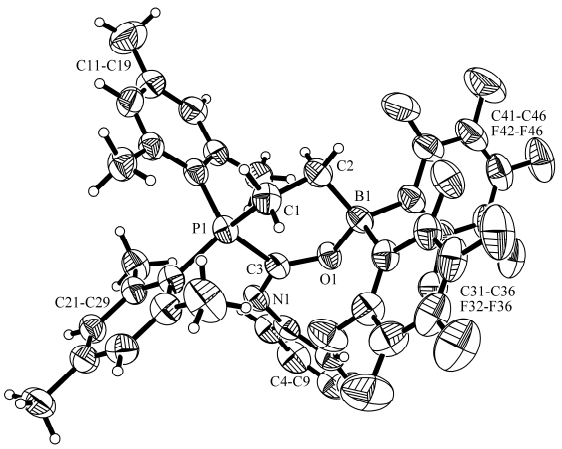
$^{31}P\{^{1}H\}$ NMR (243 MHz, 298 K, dichloromethane-d_2) of **9**.

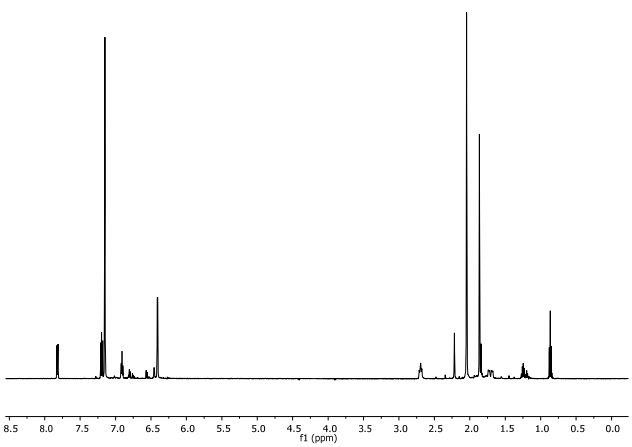


$^{19}F\{^{1}H\}$ NMR (564 MHz, 298 K, dichloromethane-d_2) of **9**.

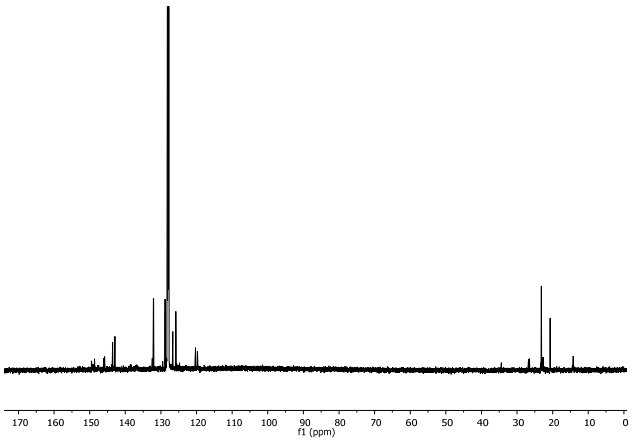
Compound 10. Dimesitylvinylphosphine (100 mg, 0.34 mmol) and bis(pentafluorophenyl)borane (117 mg, 0.34 mmol) were dissolved in pentane (6 mL). Upon addition of phenylisocyanate (185 µL, 1.70 mmol) at room temperature a white solid began to precipitate. After the reaction mixture had been stirred for 3 hours, the solid was isolated *via cannula* filtration and washed twice with pentane (2 mL). Removal of all volatiles *in vacuo* yielded **10** (202 mg, 78%). Crystals suitable for X-ray analysis were grown by slow concentration of a dichloromethane solution at –36 °C. $\tilde{\nu}$ (KBr)/cm^{-1} = 3028 (m), 2970 (vs), 2926 (vs), 2873 (m), 2734 (w), 2260 (w), 1745 (w), 1645 (vs), 1558 (w), 1519 (m), 1443 (w), 1413 (w), 1380 (w), 1274 (vs), 1248 (vs), 1185 (m), 1165 (w), 1096 (m), 1027 (w), 962 (m), 905 (m), 869 (m), 848 (s), 807 (s), 769 (m), 734 (m), 691 (m), 673 (m), 657 (m), 617 (s), 564 (m), 549 (m), 528 (w). Found C, 61.23; H, 4.22; N, 1.88. Calc. for $C_{39}H_{31}BF_{10}NOP$: C, 61.52; H, 4.10; N, 1.84. ^{1}H NMR (600 MHz, 298 K, benzene-d_6) δ = 7.82 (2H, m, *o*-Ph), 7.20 (2H, m, *m*-Ph), 6.91 (1H, m, *p*-Ph), 6.41 (4H, d, $^{4}J_{PH}$ = 4.2 Hz, *m*-Mes), 2.69 (2H, m, $^{P}CH_2$), 2.05 (12 H, s, *o*-CH_3^{Mes}), 1.86 (6H, s, *p*-CH_3^{Mes}), 1.70 (2H, dm, $^{3}J_{PH}$ = 26.3 Hz, $^{B}CH_2$). $^{13}C\{^{1}H\}$ NMR (151 MHz, 298 K, benzene-d_6) δ = 149.1 (d, $^{1}J_{PC}$ = 127.1 Hz, C^{N}), 148.3 (dm, $^{1}J_{FC}$ = 239 Hz, C_6F_5), 145.9 (d, $^{3}J_{PC}$ = 22.7 Hz, *i*-Ph), 143.6 (d, $^{4}J_{PC}$ = 2.9 Hz, *p*-Mes), 142.9 (d, $^{2}J_{PC}$ = 9.1 Hz, *o*-Mes), 139.7 (dm, $^{1}J_{FC}$ = 252 Hz, C_6F_5), 137.6 (dm, $^{1}J_{FC}$ = 252 Hz, C_6F_5), 132.1 (d, $^{3}J_{PC}$ = 11.5 Hz, *m*-Mes), 128.8 (*m*-Ph), 126.6 (*p*-Ph), 125.8 (*o*-Ph), 123.0 (br, *i*-C_6F_5), 120.0 (d, $^{1}J_{PC}$ = 78.9 Hz, *i*-Mes), 26.6 (d, $^{1}J_{PC}$ = 39.9 Hz, $^{P}CH_2$), 23.2 (d, $^{3}J_{PC}$ = 4.4 Hz, *o*-CH_3^{Mes}), 20.7 (*p*-CH_3^{Mes}), 14.4 (br, $^{B}CH_2$). $^{1}H,^{1}H$ GCOSY (600 MHz / 600 MHz, 298 K, benzene-d_6) δ (^{1}H, ^{1}H) = 7.82 / 7.20, 6.91 (*o*-Ph / *m*-Ph, *p*-Ph), 7.20 / 7.82, 6.91 (*m*-Ph / *o*-Ph, *p*-Ph), 6.91 / 7.82, 7.20 (*p*-Ph / *o*-Ph, *m*-Ph), 6.41 / 2.05, 1.86 (*m*-Mes / *o*-CH_3^{Mes}, *p*-CH_3^{Mes}), 2.69 / 1.70 ($^{P}CH_2$ / $^{B}CH_2$), 2.05 / 6.41 (*o*-CH_3^{Mes} / *m*-Mes), 1.86 / 6.41 (*p*-CH_3^{Mes} / *m*-Mes), 1.70 / 2.69 ($^{B}CH_2$ / $^{P}CH_2$). $^{1}H,^{13}C$ GHSQC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ (^{1}H) / δ (^{13}C) = 7.82 / 125.8 (*o*-Ph), 7.20 / 128.8 (*m*-Ph), 6.91 / 126.6 (*p*-Ph), 6.41 / 132.1 (*m*-Mes), 2.69 / 26.6 ($^{P}CH_2$), 2.05 / 23.2 (*o*-CH_3^{Mes}), 1.86 / 20.7 (*p*-CH_3^{Mes}), 1.70 / 14.4 ($^{B}CH_2$). $^{1}H,^{13}C$ GHMBC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ (^{1}H) / δ (^{13}C) = 7.82 / 126.6, 125.8 (*o*-Ph / *p*-Ph, *o*-Ph), 7.20 / 145.9, 128.8 (*m*-Ph / *i*-Ph, *m*-Ph), 6.91 / 125.8 (*p*-Ph / *o*-Ph), 6.41 / 142.9, 132.1, 120.0 (*m*-Mes / *o*-Mes, *m*-Mes, *i*-Mes), 2.05 / 142.9, 132.1, 120.0 (*o*-CH_3^{Mes} / *o*-Mes, *m*-Mes, *i*-Mes), 1.86 / 143.6, 120.0 (*p*-CH_3^{Mes} / *p*-Mes, *i*-Mes), 1.70 / 26.6 ($^{B}CH_2$ / $^{P}CH_2$). $^{11}B\{^{1}H\}$ NMR (192 MHz, 298 K, benzene-d_6) δ = 0.7. $^{31}P\{^{1}H\}$ NMR (243 MHz, 298 K, benzene-d_6) δ = 5.1 ($\nu_{1/2}$ = 3 Hz). $^{19}F\{^{1}H\}$ NMR (564 MHz, 298 K, benzene-d_6) δ = –134.2 (2F, *o*-C_6F_5), –159.2 (1F, *p*-C_6F_5),
–164.2 (2F, *m*-C_6F_5).

X-ray structure analysis for **10**. Crystal data for $C_{39}H_{31}BF_{10}NOP$ * CH_2Cl_2 * ½ C_5H_{12} (**10**), M = 882.43, monoclinic, space group $C2/c$ (No. 15), a = 29.5440(6), b = 14.3430(4), c = 22.6139(7) Å, β = 122.078(1)°, V = 8119.6(4) Å^3, D_c = 1.444 g cm^{-3}, µ = 2.533 mm^{-1}, Z = 8, λ = 1.54178 Å, T = 223(2) K, 57011 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 7244 independent (R_{int} = 0.054), and 6260 observed reflections [I ≥ 2σ(I)], 556 refined parameters, R = 0.062, wR^2 = 0.182.

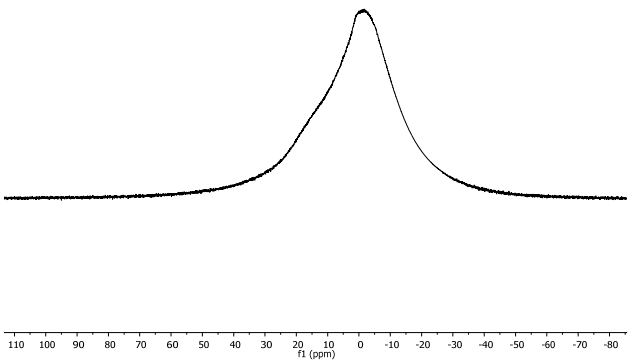




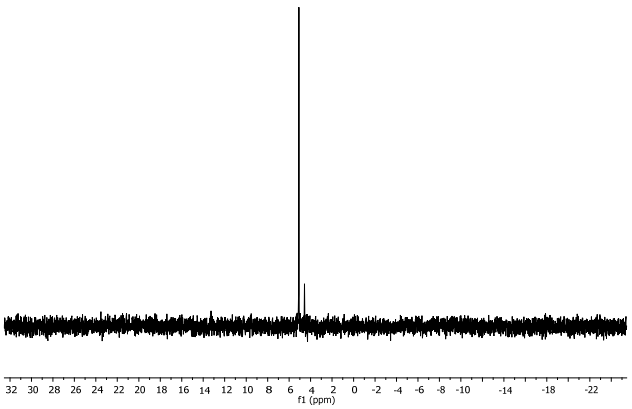
^{1}H NMR (600 MHz, 298 K, benzene-d_6) of **10**.



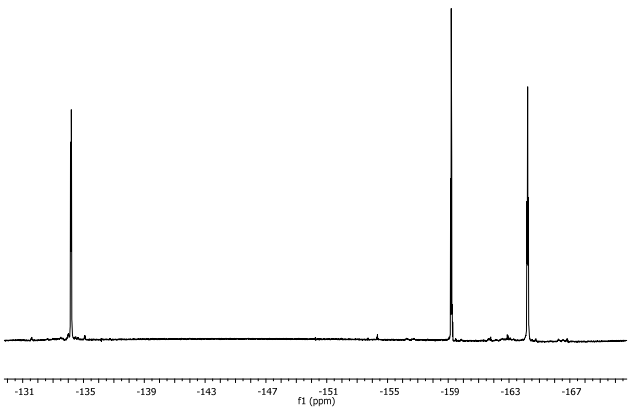
$^{13}C\{^{1}H\}$ NMR (151 MHz, 298 K, benzene-d_6) of **10**.



$^{11}B\{^{1}H\}$ NMR (192 MHz, 298 K, benzene-d_6) of **10**.



$^{31}P\{^{1}H\}$ NMR (243 MHz, 298 K, benzene-d_6) of **10**.

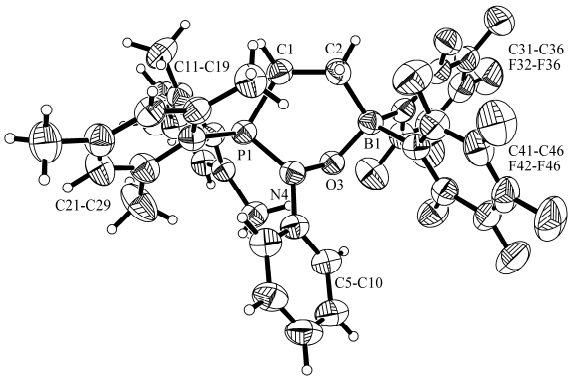


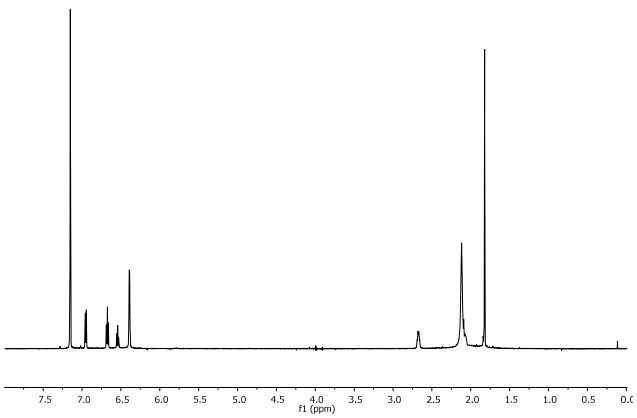
$^{19}F\{^{1}H\}$ NMR (564 MHz, 298 K, benzene-d_6) of **10**.

Compound 11. Dimesitylvinylphosphine (100 mg, 0.34 mmol) and bis(pentafluorophenyl)borane (117 mg, 0.34 mmol) were dissolved in pentane (6 mL) and stirred for 15 minutes. After addition of nitrosobenzene (36 mg, 0.34 mmol) the reaction mixture was stirred overnight, whereupon a brownish powder precipitated. The precipitate was collected *via cannula* filtration and washed twice with pentane (2.5 mL). All volatiles were removed *in vacuo* to yield **11** (128 mg, 50%). Crystals suitable for X-ray analysis were obtained by slow diffusion of pentane into a dichloromethane solution of **11** at –36 °C. mp 163 °C (DSC). $\tilde{\nu}$ (KBr)/cm^{-1} = 3026 (m); 2964 (s); 2926 (s); 2883 (s); 2361 (w); 1749 (w); 1642 (vs); 1605 (s); 1557 (w); 1517 (w); 1453 (w); 1376 (w); 1279 (s); 1221 (m); 1186 (w); 1125 (s); 1092 (s); 1033 (w); 961 (m); 925 (m); 857 (s); 825 (m); 789 (vs); 743 (s); 700 (s); 641 (s); 599 (m); 557 (vs).Found C, 60.94; H, 4.29; N, 2.03. Calc. for $C_{38}H_{31}BF_{10}NOP$: C, 60.90; H, 4.17; N, 1.87. ^{1}H NMR (600 MHz, 298 K, benzene-d_6) δ = 6.95 (2H, m, *o*-Ph), 6.67 (2H, m, *m*-Ph), 6.54 (1H, m, *p*-Ph), 6.39 (4H, d, $^{4}J_{PH}$ = 4.0 Hz, *m*-Mes), 2.67 (2H, m, $^{P}CH_2$), 2.12 (12 H, br, *o*-CH_3^{Mes}), 2.09 (2H, m, $^{B}CH_2$), 1.82 (6H, s, *p*-CH_3^{Mes}). ^{13}C NMR (126 MHz, 298 K, benzene-d_6) δ = 148.5 (dm, $^{1}J_{FC}$ = 240 Hz, C_6F_5), 143.6 (d, $^{4}J_{PC}$ = 2.8 Hz, *p*-Mes), 142.9 (d, $^{2}J_{PC}$ = 5.4 Hz, *i*-Ph), 142.2 (d, $^{2}J_{PC}$ = 10.8 Hz, *o*-Mes), 139.1 (dm, $^{1}J_{FC}$ = 245 Hz, C_6F_5), 137.2 (dm, $^{1}J_{FC}$ = 247 Hz, C_6F_5), 131.9 (d, $^{3}J_{PC}$ = 11.5 Hz, *m*-Mes), 128.2 (*m*-Ph), 125.2 (d, $^{5}J_{PC}$ = 1.1 Hz, *p*-Ph), 124.8 (d, $^{1}J_{PC}$ = 76.6 Hz, *i*-Mes), n.o. (*i*-C_6F_5), 121.3 (d, $^{3}J_{PC}$ = 1.5 Hz, *o*-Ph), 28.1 (d, $^{1}J_{PC}$ = 70.1 Hz, $^{P}CH_2$), 22.6 (d, $^{3}J_{PC}$ = 4.0 Hz, *o*-CH_3^{Mes}), 20.6 (d, $^{5}J_{PC}$ = 1.4 Hz, *p*-CH_3^{Mes}), 15.4 (br, $^{B}CH_2$). ^{1}H TOCSY (600 MHz, 298 K, benzene-d_6) δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 6.95 / 6.67, 6.54 (*o*-Ph / *m*-Ph, *p*-Ph), 6.39 / 2.12, 1.82 (*m*-Mes / *o*-CH_3^{Mes}, *p*-CH_3^{Mes}), 2.67 / 2.09 ($^{P}CH_2$ / $^{B}CH_2$). $^{1}H,^{1}H$ GCOSY (600 MHz / 600 MHz, 298 K, benzene-d_6) δ (^{1}H, ^{1}H) = 6.95 / 6.67, 6.54 (*o*-Ph/ *m*-Ph, *p*-Ph), 6.67 / 6.95, 6.54 (*m*-Ph / *o*-Ph, *p*-Ph), 6.54 / 6.95, 6.67 (*p*-Ph / *o*-Ph, *m*-Ph), 6.39 / 2.12, 1.82 (*m*-Mes / *p*-CH_3^{Mes}, *o*-CH_3^{Mes}), 2.67 / 2.09 ($^{P}CH_2$ / $^{B}CH_2$), 2.12 / 6.39 (*o*-CH_3^{Mes} / *m*-Mes), 2.09 / 2.67 ($^{B}CH_2$ / $^{P}CH_2$), 1.82 / 6.39 (*p*-CH_3^{Mes} / *m*-Mes). $^{1}H,^{13}C$ GHSQC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ (^{1}H) / δ (^{13}C) = 6.95 / 121.3 (*o*-Ph), 6.67 / 128.2 (*m*-Ph), 6.54 / 125.2 (*p*-Ph), 6.39 / 131.9 (*m*-Mes), 2.67 / 28.1 ($^{P}CH_2$), 2.12 / 22.6 (*o*-CH_3^{Mes}), 2.09 / 15.4 ($^{B}CH_2$), 1.82 / 20.6 (*p*-CH_3^{Mes}). $^{1}H,^{13}C$ GHMBC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ (^{1}H) / δ (^{13}C) = 6.95 / 142.9, 125.2, 121.3 (*o*-Ph / *i*-Ph, *p*-Ph, *o*-Ph), 6.67 / 142.9, 128.2, 125.2, 121.3 (*m*-Ph / *i*-Ph, *m*-Ph, *p*-Ph, *o*-Ph), 6.54 / 128.2, 121.3 (*p*-Ph / *m*-Ph, *o*-Ph), 6.39 / 131.9, 124.8, 22.6, 20.6 (*m*-Mes / *m*-Mes, *i*-Mes, *o*-CH_3^{Mes}, *p*-CH_3^{Mes}), 1.82 / 143.6, 131.9, 124.8, 20.6 (*p*-CH_3^{Mes} / *p*-Mes, *m*-Mes, *i*-Mes, *p*-CH_3^{Mes}). $^{11}B\{^{1}H\}$ NMR (192 MHz, 298 K, benzene-d_6) δ = 0.4 (br). $^{31}P\{^{1}H\}$ NMR (243 MHz, 298 K, benzene-d_6) δ = 46.9 ($\nu_{1/2}$ = 3 Hz). $^{19}F\{^{1}H\}$ NMR (564 MHz, 298 K, benzene-d_6) δ = –133.1 (2F, *o*-C_6F_5), –161.9 (1F, *p*-C_6F_5), –165.5 (2F, *m*-C_6F_5).

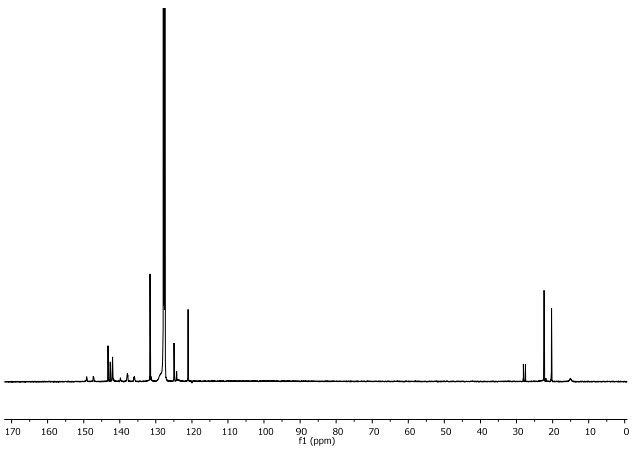
X-ray structure analysis for **11**. Crystal data for $C_{38}H_{31}BF_{10}NOP$ * CH_2Cl_2 (**11**), M = 834.34, monoclinic, space group $P2_1/n$ (No. 14), a = 13.0829(6), b = 15.0592(7), c = 19.0565(9) Å, β = 99.870(1)°, V = 3698.9(3) Å^3, D_c = 1.498 g cm^{-3}, μ = 2.745 mm^{-1}, Z = 4, λ = 1.54178 Å, T = 223(2) K,

27107 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 6490 independent (R_{int} = 0.072), and 4687 observed reflections [I ≥ 2σ(*I*)], 502 refined parameters, *R* = 0.069, wR^2 = 0.197.

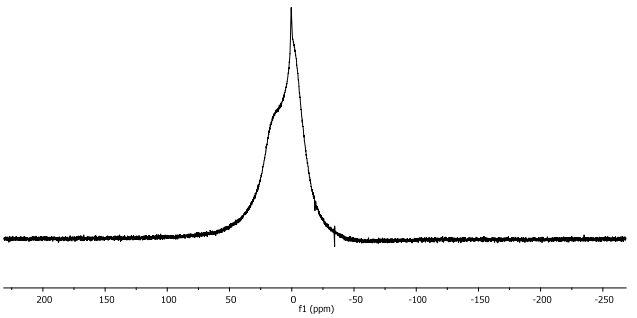




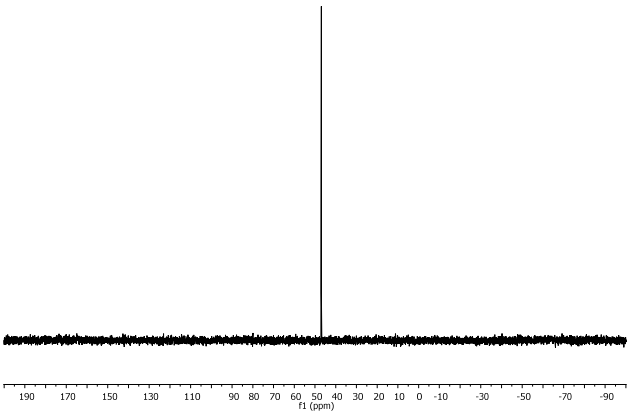
^{1}H NMR (600 MHz, 298 K, benzene-d_6) of **11**.



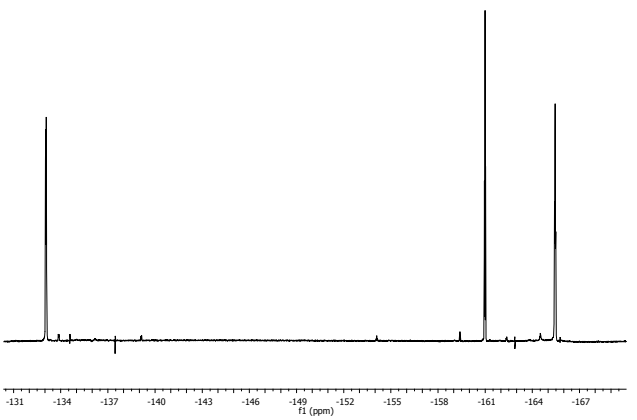
^{13}C NMR (126 MHz, 298 K, benzene-d_6) of **11**.



^{11}B{^{1}H} NMR (192 MHz, 298 K, benzene-d_6) of **11**.



^{31}P{^{1}H} NMR (243 MHz, 298 K, benzene-d_6) of **11**.



^{19}F{^{1}H} NMR (564 MHz, 298 K, benzene-d_6) of **11**.