Functional group chemistry at intramolecular frustrated Lewis pairs: substituent exchange at the Lewis acid site with 9-BBN

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[‡] X-ray crystal structure analyses.

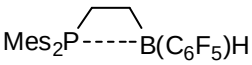
Supporting Information

Experimental work carried out by the Erker group:

General information

All reactions were carried out under argon atmosphere with Schlenk-type glassware. Solvents were dried using a Grubbs-type system [A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* 1996, **15**, 1518], which uses activated basic alumina and/or molecular sieves as drying agents in combination with copper metal as oxygen scavenger. Pentane, toluene and dichloromethane were dried in this manner. Cyclopentane and n-hexane were dried over $LiAlH_4$. Dimesitylvinylphosphane (**1**) [P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme, D. W. Stephan, *Chem. Commun.* **2007**, 5072-5074], bis(pentafluorophenyl)borane [D. J. Parks, R. E. v H. Spence, W. E. Piers, *Angew. Chem.* **1995**, *107*, 895-897; *Angew. Chem. Int. Ed. Engl*. **1995**, *34*, 809-811; W. E. Piers, D. J. Parks, G. P. A. Yap, *Organometallics* **1998**, *17*, 5492-5503] and (2-[bis(pentafluorophenyl)-boryl]ethyl)dimesitylphosphane (**2**) [P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme, D. W. Stephan, *Chem. Commun.* **2007**, 5072-5074] were prepared according to modified literature procedures. The following instruments were used for physical characterization of the compounds. Elemental analyses: Foss-Heraeus CHN-O-Rapid and Vario EL III CHNS instrument. NMR: Bruker Avance 400 (^{1}H, 400 MHz; ^{11}B: 128 MHz; ^{13}C, 100 MHz; ^{29}Si: 79 MHz), Varian Inova 500 (^{1}H, 500 MHz; ^{13}C, 126 MHz, ^{31}P, 202 MHz, ^{11}B, 160 MHz, ^{19}F, 470 MHz), Varian UnityPlus 600 (^{1}H, 600 MHz; ^{13}C, 151 MHz, ^{31}P, 243 MHz, ^{11}B, 192 MHz, ^{19}F, 564 MHz). Assignments of the resonances were supported by 2D experiments. **X-Ray diffraction:** Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (Nonius B.V., 1998); 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 50% probability, *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

Compound 4



Dimesitylvinylphosphane (364.4 mg, 1.23 mmol, 1.00 eq.) and bispentafluorophenylborane (425.3 mg, 1.23 mmol, 1.00 eq.) were dissolved in pentane (30 mL). After this solution was stirred for 15 min 9-borabicyclononane (150.0 mg, 1.23 mmol, 1.00 eq.) was added to the solution and the solution was stirred over night at room temperature. The formed white precipitate was isolated and washed with pentane (30 mL) and dissolved in dichloromethane (30 mL). The solvent was removed and the remaining white solid was dried *in vacuo* (yield 462.5 mg, 79 %). Anal. calc. for $C_{26}H_{27}BF_5P$ (476.27 g/mol): C 65.57, H 5.71; found: C 65.07, H 5.76. IR (KBr): $\tilde{\upsilon}$ = 3468 (w), 2953 (m), 2926 (m), 2736 (w), 2429 (m), 1638 (m), 1606 (m), 1560 (m), 1510 (s), 1463 (s), 1406 (m), 1381 (m).1277 (m), 1191 (m), 1137 (m), 1087 (s), 1029 (m), 965 (s), 910 (m), 850 (m), 772 (w), 736 (w), 713 (w), 624 (w), 552 (w), 460 (w), 421 (w).

Decomp.: 187 °C (DSC).

^{1}H NMR (600 MHz, [D$_6$]-benzene, 299 K): δ = 7.34 (s, 1H, m-Mes^a), 6.44 (s, 1H, m'-Mes^a), 6.43 (s, 1H, m-Mes^b), 5.97 (s, 1H, m'-Mes^b), 3.62 (br, 1H, BH), 3.35 (s, 3H, o-$CH_3{}^a$), 3.16/ 2.56 (each m, each 1H, CH_2P), 2.37 (s, 3H, p-$CH_3{}^a$), 2.12 (s, 3H, o-$CH_3{}^b$), 1.92/1.36 (each m, each 1H, CH_2B), 1.89 (s, 3H, o'-$CH_3{}^b$), 1.80 (s, 3H, p-$CH_3{}^b$), 1.27 (s, 3H, o'-$CH_3{}^a$).

^{13}C{^{1}H} NMR (151 MHz, [D$_6$]-benzene, 299 K): δ = 144.8 (br, o-Mes^a), 141.5 (o'-Mes^a), 141.4 (br, o-Mes^b), 141.1 (p-Mes^a), 139.6 (o'-Mes^b), 139.5 (p-Mes^b), 132.0 (br, m'-Mes^a), 131.9 (br, m-Mes^b), 131.0 (br, m-Mes^a), 130.6 (br, m'-Mes^b), 126.9 (br d, $^1J_{PC}$ ~ 50 Hz, i-Mes^b), 126.6 (br d, $^1J_{PC}$ ~ 54 Hz, i-Mes^a), 30.9 (br, CH_2P), 24.3 (o-$CH_3{}^a$), 24.1 (o'-$CH_3{}^b$), 23.8 (o-$CH_3{}^b$), 21.4 (o'-$CH_3{}^a$), 20.9 (p-$CH_3{}^a$), 20.3 (p-$CH_3{}^b$), 12.7 (br, CH_2B), [C_6F_5 not listed].

^{31}P NMR (243 MHz, [D$_6$]-benzene, 299 K): δ = 12.6 (br m).

^{31}P{^{1}H} NMR (243 MHz, [D$_6$]-benzene, 299 K): δ = 12.6 ($\nu_{1/2}$ ~ 30 Hz).

^{11}B NMR (192 MHz, [D$_6$]-benzene, 299 K): δ = -15.8 ($\nu_{1/2}$ ~ 600 Hz).

^{11}B{^{1}H} NMR (192 MHz, [D$_6$]-benzene, 299 K): δ = -15.8 ($\nu_{1/2}$ ~ 620 Hz).

^{19}F NMR (564 MHz, [D$_6$]-benzene, 299 K): δ = -124.0 (m, 1F, o-C_6F_5), -128.2 (m, 1F, o-C_6F_5), -160.1 (m, 1F, p-C_6F_5), -164.3 (m, 1F, m-C_6F_5), -164.9 (m, 1F, m-C_6F_5), [$\Delta\delta^{19}F_{pm}$ = 4.2, 4.8].

^{19}F, ^{19}F GCOSY (564 MHz/ 564 MHz, [D$_6$]-benzene, 299 K): δ^{19}F/ δ^{19}F = -124.0/-164.9 (o-C_6F_5/ m-C_6F_5), -128.2/-164.3 (o-C_6F_5/ m-C_6F_5), -160.1/-164.3, -164.9 (p-C_6F_5/m-C_6F_5, m-C_6F_5).

^{1}H, ^{1}H GCOSY (600 MHz/ 600 MHz, [D$_6$]-benzene, 299 K): δ^1H/ δ^1H = 7.34/6.44, 3.35, 2.37, 1.27 (m-Mes^a/ m'-Mes^a, o-$CH_3{}^a$, p-$CH_3{}^a$, o'-$CH_3{}^a$), 6.44/3.35, 2.37, 1.27 (m'-Mes^a/o-

CH_3^a, p-CH_3^a, o'-CH_3^a), 6.43/5.97, 2.12, 1.89, 1.80 (m-Mes^b/ m'-Mes^b, o-CH_3^b, o'-CH_3^b, p-CH_3^b), 5.97/2.12, 1.89, 1.80 (m'-Mes^b/o-CH_3^b, o'-CH_3^b, p-CH_3^b), 3.35/2.37, 1.27 (o-CH_3^a/p-CH_3^a, o'-CH_3^a), 3.16/2.56, 1.92, 1.36 (CH_2P/ CH_2P, CH_2B, CH_2B), 2.56/1.92 (CH_2P/ CH_2B), 2.37/1.27 (p-CH_3^a/ o'-CH_3^a), 1.92/1.36 (CH_2B/CH_2B).

^{1}H, ^{13}C GHSQC (600 MHz/ 151 MHz, [D_6]-benzene, 299 K): δ^1H/ δ^{13}C = 7.34/131.0 (m-Mes^a/ m-Mes^a), 6.44/132.0 (m'-Mes^a/ m'-Mes^a), 6.43/131.9 (m-Mes^b/m-Mes^b), 5.97/130.6 (m'-Mes^b/m'-Mes^b), 3.35/24.3 (o-CH_3^a/o-CH_3^a), 3.16/30.9 (CH_2P/CH_2P), 2.56/30.9 (CH_2P/CH_2P), 2.37/20.9 (p-CH_3^a/p-CH_3^a), 2.12/23.8 (o-CH_3^b/o-CH_3^b), 1.92/12.7 (CH_2B/CH_2B), 1.89/24.1 (o'-CH_3^b/o'-CH_3^b), 1.80/20.3 (p-CH_3^b/p-CH_3^b), 1.36/12.7 (CH_2B/CH_2B), 1.27/21.4 (o'-CH_3^a/ o'-CH_3^a).

^{1}H, ^{13}C GHMBC (600 MHz/ 151 MHz, [D_6]-benzene, 299 K): δ^1H/ δ^{13}C = 7.34/144.8, 132.0, 126.6, 24.3, 20.9 (m-Mes^a/o-Mes^a, m'-Mes^a, i-Mes^a, o-CH_3^a, p-CH_3^a), 6.44/141.5, 131.0, 126.6, 21.4, 20.9 (m'-Mes^a/o'-Mes^a, m-Mes^a, i-Mes^a, o'-CH_3^a, p-CH_3^a), 6.43/141.5, 130.6, 126.9, 23.8, 20.3 (m-Mes^b/o'-Mes^b, m'-Mes^b, i-Mes^b, o-CH_3^b, p-CH_3^b) , 5.97/139.6, 131.9, 126.9, 24.1, 20.3 (m'-Mes^b/o'-Mes^b, m-Mes^b, i-Mes^b, o'-CH_3^b, p-CH_3^b), 3.35/144.8, 131.0, 126.6 (o-CH_3^a/o-Mes^a, m-Mes^a, i-Mes^a), 3.16/126.6, 12.7 (CH_2P/i-Mes^a, CH_2B), 2.37/141.1, 132.0, 131.0 (p-CH_3^a/ p-Mes^a, m'-Mes^a, m-Mes^a), 2.12/141.4, 131.9, 126.9 (o-CH_3^b/o-Mes^b, m-Mes^b, i-Mes^b), 1.92/30.9 (CH_2B/CH_2P), 1.89/139.6, 130.6, 126.9 (o'-CH_3^b/o'-Mes^b, m'-Mes^b, i-Mes^b), 1.80/139.5, 131.9, 130.6 (p-CH_3^b/p-Mes^b, m-Mes^b, m'-Mes^b), 1.27/141.5, 132.0, 126.6 (o'-CH_3^a/ o'-Mes^a, m'-Mes^a, i-Mes^a).

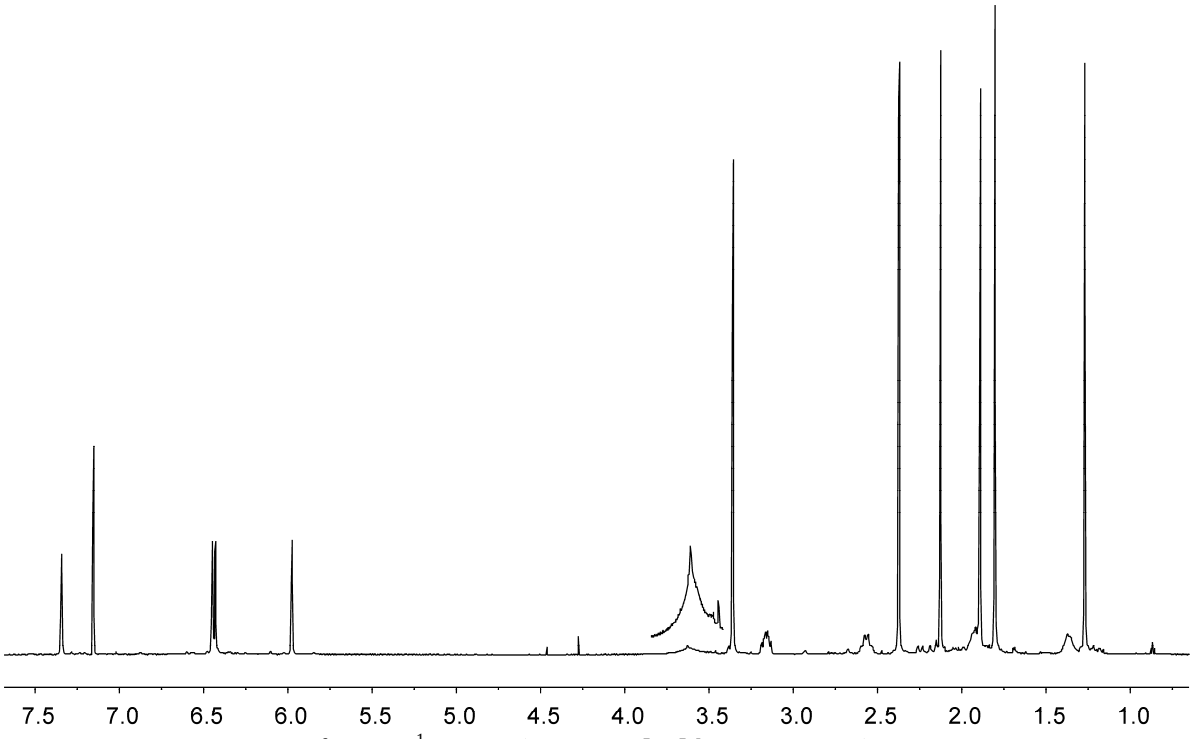


figure 1: ^{1}H NMR (600 MHz, $[D_6]$-benzene, 299 K).

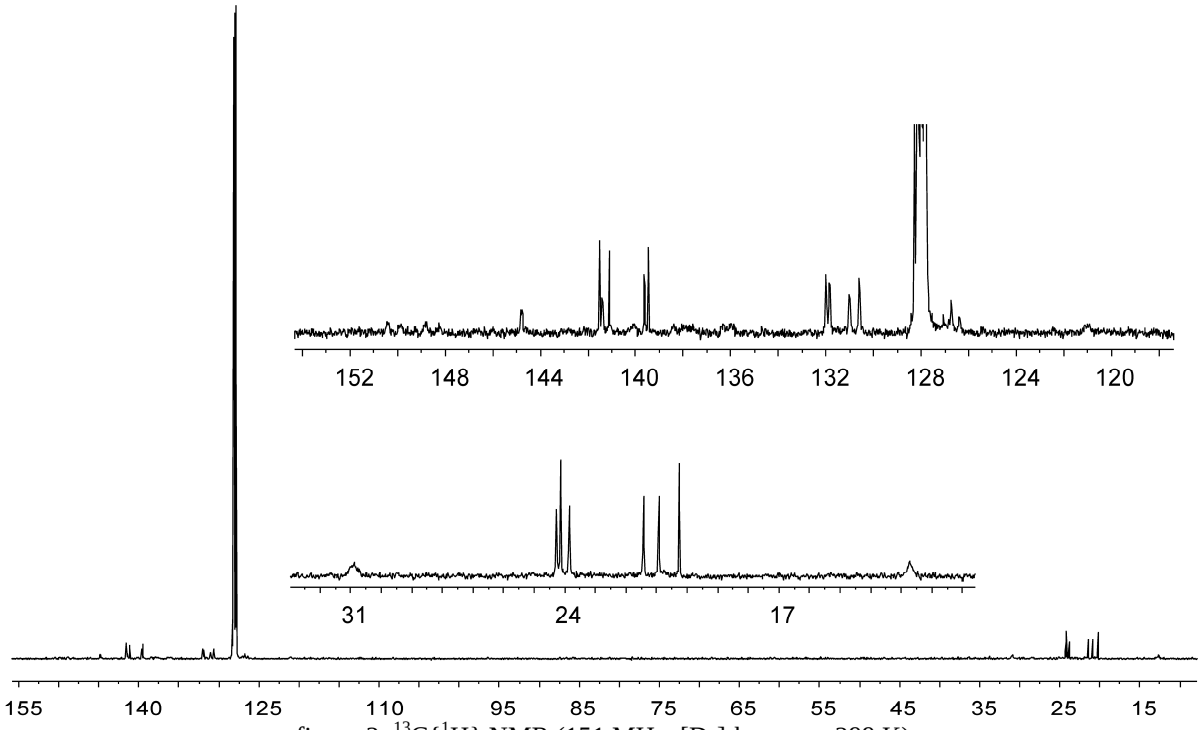


figure 2: $^{13}C\{^{1}H\}$ NMR (151 MHz, $[D_6]$-benzene, 299 K).

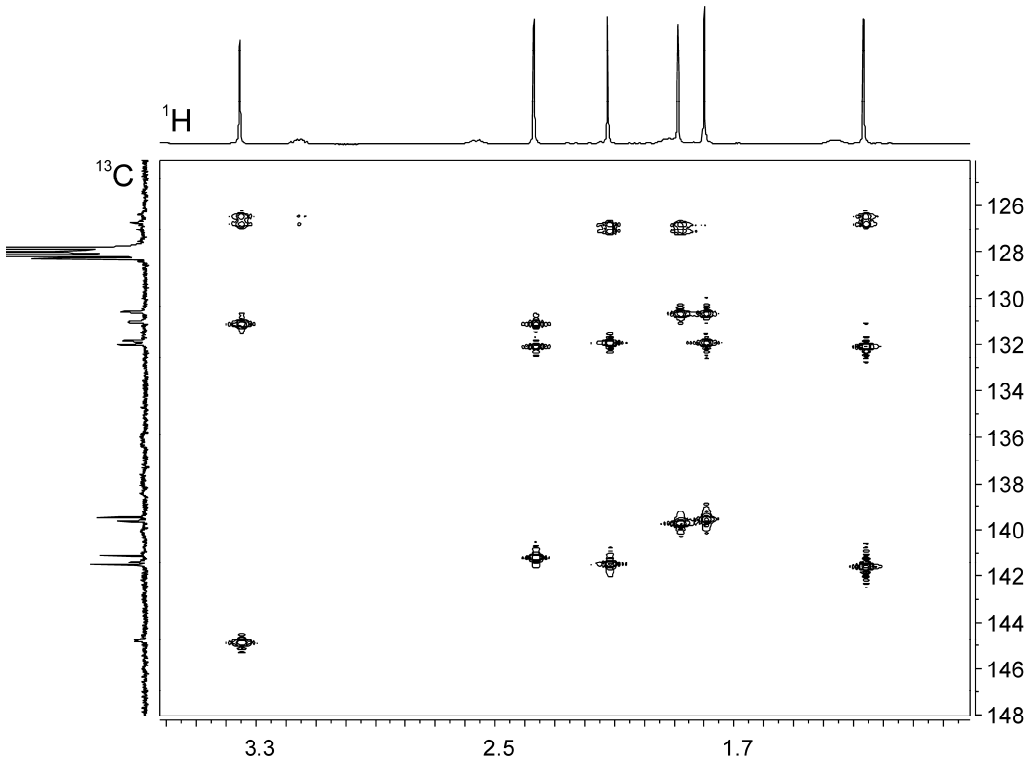


figure 3: ^{1}H, ^{13}C GHMBC (600 MHz/ 151 MHz, [D_6]-benzene, 299 K).

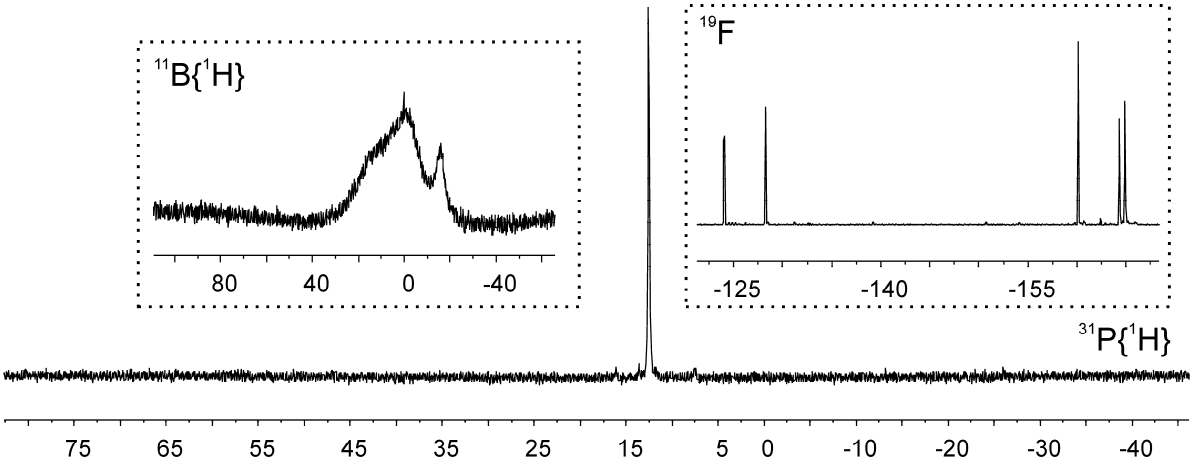
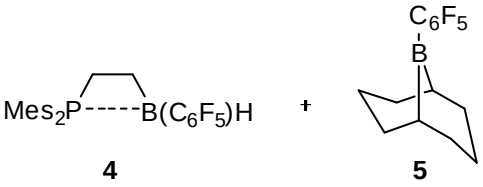


figure 4: : ^{31}P{^{1}H}NMR (243 Mhz, [D_6]-benzene, 299 K), ^{11}B{^{1}H} NMR (192 MHz, [D_6]-benzene, 299 K) and ^{19}F NMR (564 MHz, [D_6]-benzene, 299 K).

Mixture of compound 4 and 5



Dimesitylvinylphosphane (24.3 mg, 0.08 mmol, 1.00 eq.) and bispentafluorophenylborane (28.4 mg, 0.08 mmol, 1.00 eq.) were dissolved in [D_6]-benzene (0.8 mL). After 15 min 9-borabicyclononane (10 mg, 0.08 mmol, 1.00 eq.) was added to the solution and the solution was stored over night. The mixture of compound **4** and **5** (ratio ca. 1:1 from ^{19}F NMR) could be obtained as a colourless solution.

NMR data compound 4 (in the mixture):

^{1}H NMR (500 MHz, [D_6]-benzene, 299 K): δ = 7.34 (s, 1H, m-Mes^{a}), 6.44 (s, 1H, m'-Mes^{a}), 6.43 (s, 1H, m-Mes^{b}), 5.97 (s, 1H, m'-Mes^{b}), 3.62 (br, 1H, BH), 3.35 (s, 3H, o-CH_3^{a}), 3.15/2.56 (each m, each 1H, CH_2P), 2.37 (s, 3H, p-CH_3^{a}), 2.12 (s, 3H, o-CH_3^{b}), 1.92/1.36 (each m, each 1H, CH_2B), 1.89 (s, 3H, o'-CH_3^{b}), 1.80 (s, 3H, p-CH_3^{b}), 1.26 (s, 3H, o'-CH_3^{a}).

^{13}C{^{1}H} NMR (126 MHz, [D_6]-benzene, 299 K): δ = 144.8 (br, o-Mes^{a}), 141.5 (o'-Mes^{a}), 141.4 (br, o-Mes^{b}), 141.1 (p-Mes^{a}), 139.6 (o'-Mes^{b}), 139.5 (p-Mes^{b}), 132.0 (br, m'-Mes^{a}), 131.9 (br, m-Mes^{b}), 131.0 (br, m-Mes^{a}), 130.6 (br, m'-Mes^{b}), 126.9 (br d, $^{1}J_{PC}$ ~ 45 Hz, i-Mes^{b}), 126.6 (br d, $^{1}J_{PC}$ ~ 45 Hz, i-Mes^{a}), 30.9 (br, CH_2P), 24.3 (o-CH_3^{a}), 24.1 (o'-CH_3^{b}), 23.8 (o-CH_3^{b}), 21.5 (o-CH_3^{a}), 20.9 (p-CH_3^{a}), 20.3 (p-CH_3^{b}), 12.7 (CH_2B), [C_6F_5 not listed].

^{31}P NMR (202 MHz, [D_6]-benzene, 299 K): δ = 12.6 (br m).

^{31}P{^{1}H} NMR (202 MHz, [D_6]-benzene, 299 K): δ = 12.6 ($\nu_{1/2}$ = 30 Hz).

^{11}B NMR (160 MHz, [D_6]-benzene, 299 K): δ = -15.4 ($\nu_{1/2}$ = 600 Hz).

^{11}B{^{1}H} NMR (160 MHz, [D_6]-benzene, 299 K): δ = -15.8 ($\nu_{1/2}$ = 620 Hz).

^{19}F NMR (470 MHz, [D_6]-benzene, 299 K): δ = -124.0 (m, 1F, o-C_6F_5), -128.2 (m, 1F, o-C_6F_5), -160.1 (m, 1F, p-C_6F_5), -164.3 (m, 1F, m-C_6F_5), -164.9 (m, 1F, m-C_6F_5), [$\Delta\delta^{19}F_{pm}$ = 4.2, 4.8].

^{19}F, ^{19}F GCOSY (470 MHz/ 470 MHz, [D_6]-benzene, 299 K): δ^{19}F/ δ^{19}F = -124.0/-164.3, -164.9 (o-C_6F_5/ m-C_6F_5), -128.2/-164.3, -164.9 (o-C_6F_5/ m-C_6F_5), -160.1/-164.3, -164.9 (p-C_6F_5/m-C_6F_5, m-C_6F_5).

^{1}H, ^{1}H GCOSY (500 MHz/ 500 MHz, [D_6]-benzene, 299 K): δ^{1}H/ δ^{1}H = 7.34/6.44, 3.35, 2.37, 1.26 (m-Mes^{a}/ m'-Mes^{a}, o-CH_3^{a}, p-CH_3^{a}, o'-CH_3^{a}), 6.44/3.35, 2.37, 1.26 (m'-Mes^{a}/o-CH_3^{a}, p-CH_3^{a}, o'-CH_3^{a}), 6.43/5.97, 2.12, 1.89, 1.80 (m-Mes^{b}/ m'-Mes^{b}, o-CH_3^{b}, o'-CH_3^{b}, p-CH_3^{b}), 5.97/2.12, 1.89, 1.80 (m'-Mes^{b}/o-CH_3^{b}, o'-CH_3^{b}, p-CH_3^{b}), 3.35/2.37, 1.26 (o-CH_3^{a}/p-CH_3^{a}, o'-CH_3^{a}), 3.15/2.56, 1.92, 1.36 (CH_2P/ CH_2P, CH_2B, CH_2B), 2.56/1.92 (CH_2P/ CH_2B), 2.37/1.26 (p-CH_3^{a}/ o'-CH_3^{a}), 2.12/1.89, 1.80 (o-CH_3^{b}/o'-CH_3^{b}, p-CH_3^{b}).

^{1}H, ^{13}C GHSQC (500 MHz/ 126 MHz, [D$_6$]-benzene, 299 K): δ^{1}H/ δ^{13}C = 7.34/131.0 (m-Mes^{a}/ m-Mes^{a}), 6.44/132.0 (m'-Mes^{a}/ m'-Mes^{a}), 6.43/131.9 (m-Mes^{b}/m-Mes^{b}), 5.97/130.6 (m'-Mes^{b}/m'-Mes^{b}), 3.35/24.3 (o-CH_3^{a}/o-CH_3^{a}), 3.15/30.9 (CH_2P/CH_2P), 2.56/30.9 (CH_2P/CH_2P), 2.37/20.9 (p-CH_3^{a}/p-CH_3^{a}), 2.12/23.8 (o-CH_3^{b}/o-CH_3^{b}), 1.92/12.7 (CH_2B/CH_2B), 1.89/24.1 (o'-CH_3^{b}/o'-CH_3^{b}), 1.80/20.3 (p-CH_3^{b}/p-CH_3^{b}), 1.36/12.7 (CH_2B/CH_2B), 1.26/21.5 (o'-CH_3^{a}/ o'-CH_3^{a}).

^{1}H, ^{13}C GHMBC (500 MHz/ 126 MHz, [D$_6$]-benzene, 299 K): δ^{1}H/ δ^{13}C = 7.34/144.8, 132.0, 126.6, 24.3, 20.9 (m-Mes^{a}/o-Mes^{a}, m'-Mes^{a}, i-Mes^{a}, o-CH_3^{a}, p-CH_3^{a}), 6.44/141.5, 131.0, 126.6, 21.5, 20.9 (m'-Mes^{a}/o'-Mes^{a}, m-Mes^{a}, i-Mes^{a}, o-CH_3^{a}, p-CH_3^{a}), 6.43/141.4, 130.6, 126.9, 23.8, 20.3 (m-Mes^{b}/o-Mes^{b}, m'-Mes^{b}, i-Mes^{b}, o-CH_3^{b}, p-CH_3^{b}) , 5.97/139.6, 131.9, 126.9, 24.1, 20.3 (m'-Mes^{b}/o'-Mes^{b}, m-Mes^{b}, i-Mes^{b}, o'-CH_3^{b}, p-CH_3^{b}), 3.35/144.8, 131.0, 126.6 (o-CH_3^{a}/o-Mes^{a}, m-Mes^{a}, i-Mes^{a}), 3.15/126.6, 12.7 (CH_2P/i-Mes^{a}, CH_2B), 2.38/141.1, 132.0, 131.0 (p-CH_3^{a}/ p-Mes^{a}, m'-Mes^{a}, m-Mes^{a}), 2.12/141.4, 131.9, 126.9 (o-CH_3^{b}/o-Mes^{b}, m-Mes^{b}, i-Mes^{b}), 1.92/30.9 (CH_2B/CH_2P), 1.89/139.6, 130.6, 126.9 (o'-CH_3^{b}/o'-Mes^{b}, m'-Mes^{b}, i-Mes^{b}), 1.80/139.5, 131.9, 130.6 (p-CH_3^{b}/p-Mes^{b}, m-Mes^{b}, m'-Mes^{b}), 1.26/141.5, 132.0, 126.6 (o'-CH_3^{a}/ o'-Mes^{a}, m'-Mes^{a}, i-Mes^{a}).

NMR data compound 5 (in the mixture):

^{1}H NMR (500 MHz, [D$_6$]-benzene, 299 K): δ = 2.04 (m, 2H, CHB), 1.87/1.84 (each m, each 4H, CH_2), 1.86/1.22 (each m, each 2H, CH_2).

^{13}C{^{1}H} NMR (126 MHz, [D$_6$]-benzene, 299 K): δ = 33.8 (CH_2), 32.7 (br, BCH), 23.2 (CH_2), [C_6F_5 not listed].

^{11}B NMR (160 MHz, [D$_6$]-benzene, 299 K): δ = 85.1 ($\nu_{1/2}$ ~ 280 Hz).

^{11}B{^{1}H} NMR (160 MHz, [D$_6$]-benzene, 299 K): δ = 85.1 ($\nu_{1/2}$ ~ 300 Hz).

.**^{19}F NMR (470 MHz, [D$_6$]-benzene, 299 K):** δ = -131.2 (m, 2F, o-C_6F_5), -150.8 (m, 1F, p-C_6F_5), -162.4 (m, 2F, m-C_6F_5), [$\Delta\delta^{19}F_{pm}$= 11.6] .

^{19}F, ^{19}F GCOSY (470 MHz/ 470 MHz, [D$_6$]-benzene, 299 K): δ^{19}F/ δ^{19}F = -131.2/-150.8, -162.4 (o-C_6F_5/ p-C_6F_5, m-C_6F_5), -150.8/-162.4 (p-C_6F_5/ m-C_6F_5).

^{1}H, ^{13}C GHSQC (500 MHz/ 126 MHz, [D$_6$]-benzene, 299 K): δ^{1}H/ δ^{13}C = 2.04/32.7 (CHB/CHB), 1.87/33.8 (CH_2/CH_2), 1.84/33.8 (CH_2/CH_2), 1.86/23.2 (CH_2/CH_2) 1.22/23.2 (CH_2/CH_2).

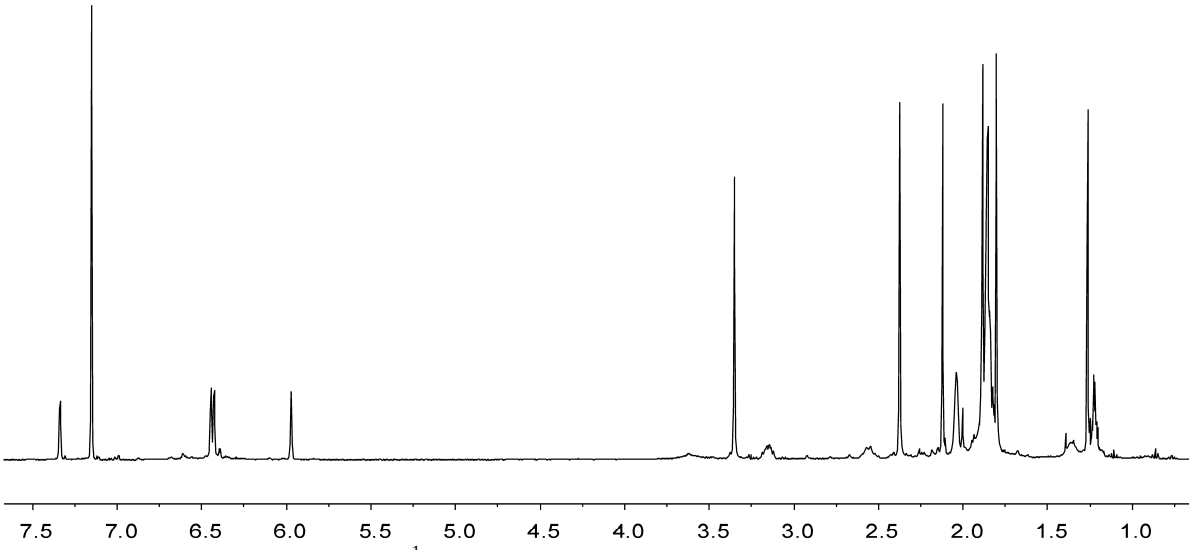


figure 5: ^{1}H-NMR (500 MHz, [D_6]-benzene, 299 K).

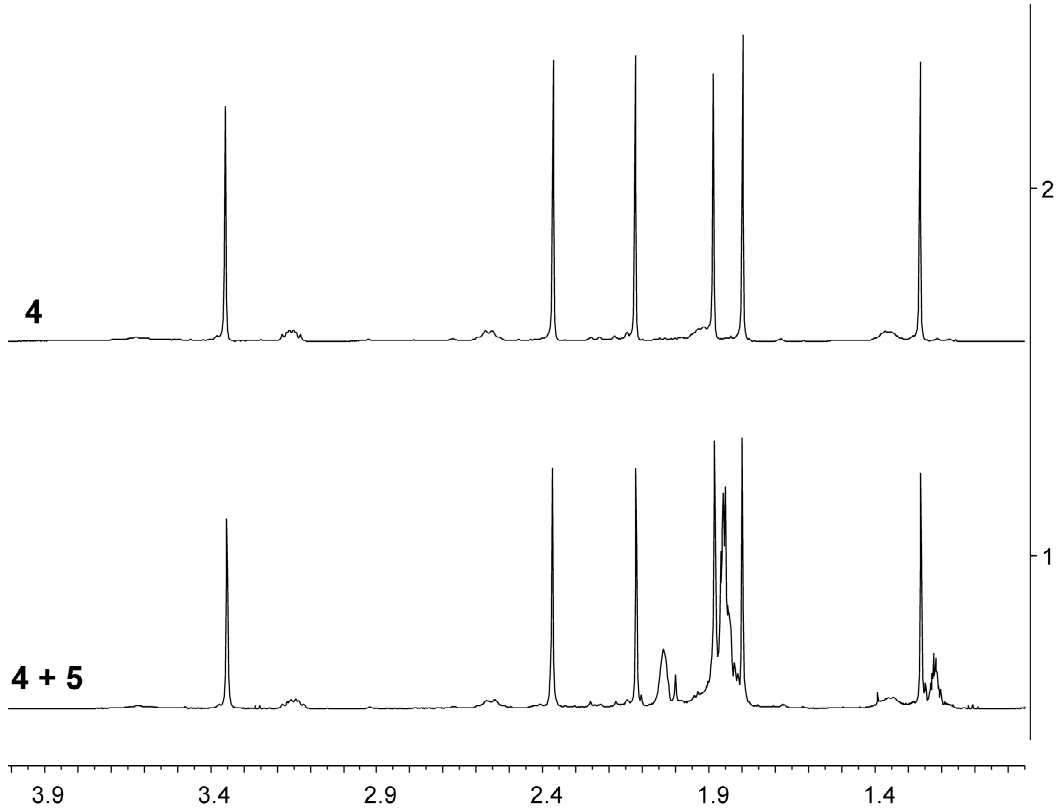


figure 6: ^{1}H-NMR (500 MHz, [D_6]-benzene, 299 K) alkyl region: (1) Reaction mixture of compound **4** and **5**; (2) Compound **4**.

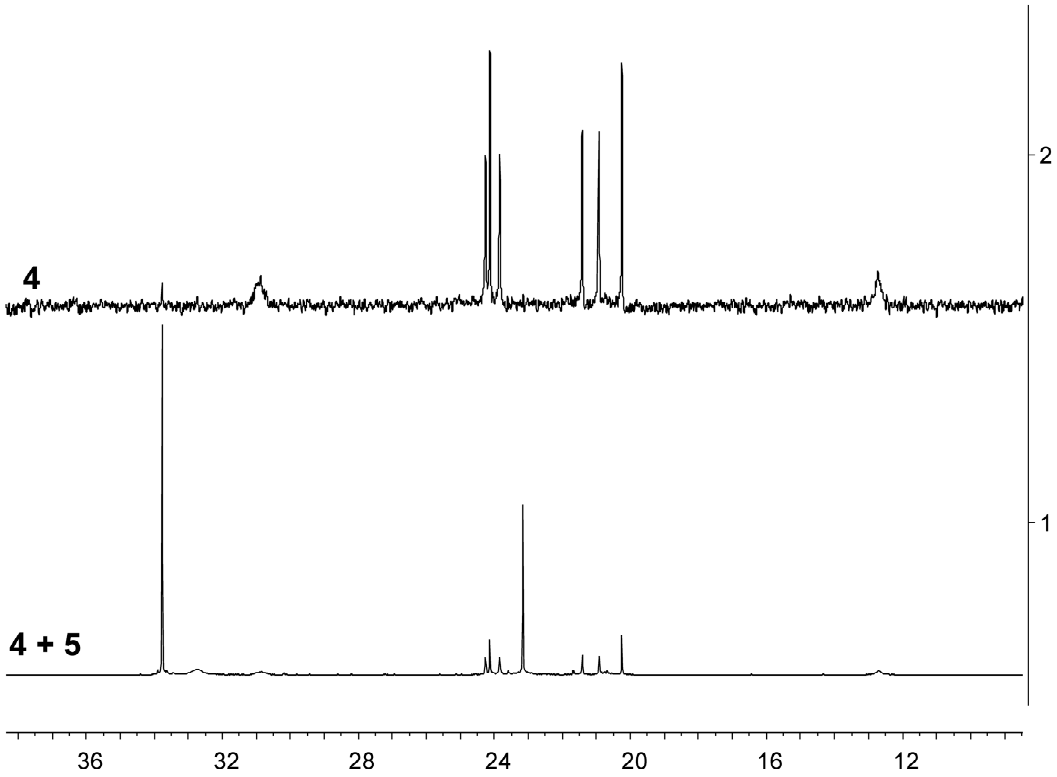


figure 7: $^{13}C\{^{1}H\}$ NMR (126 MHz, $[D_6]$-benzene, 299 K) alkyl region: (1) Reaction mixture of compound **4** and **5**; (2) Compound **4**.

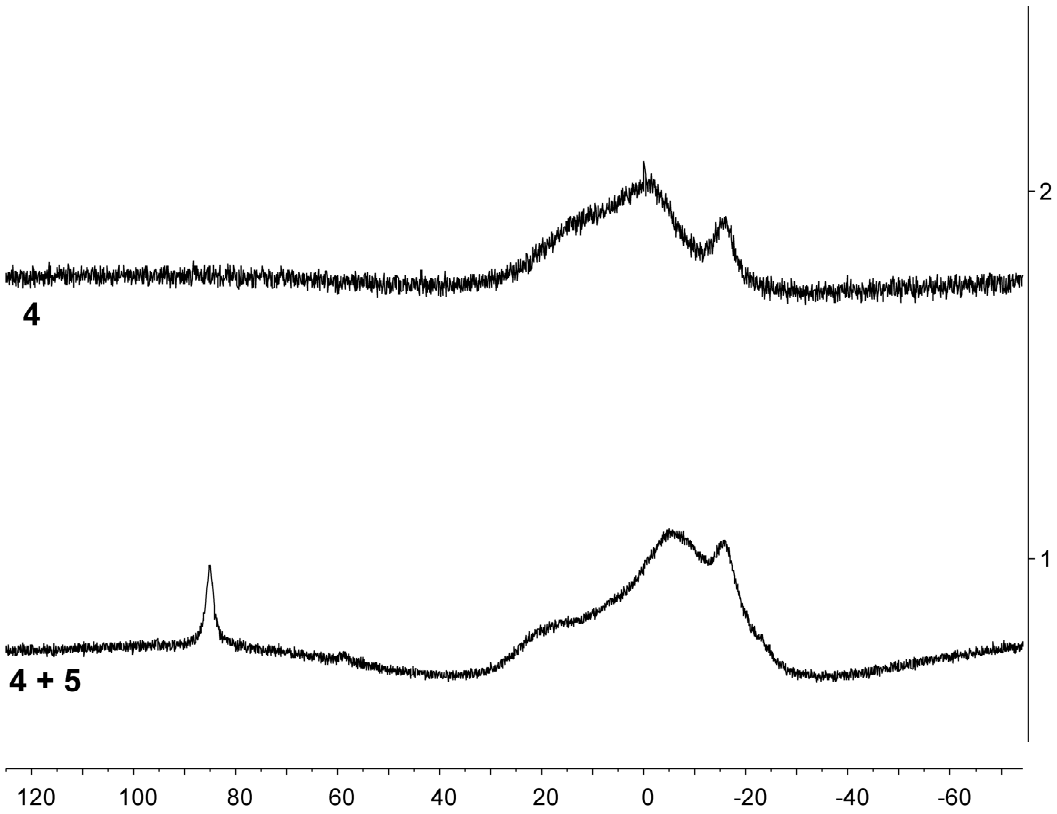


figure 8: $^{11}B\{^{1}H\}$ NMR (160 MHz, $[D_6]$-benzene, 299 K): (1) Reaction mixture of compound **4** and **5**; (2) Compound **4**.

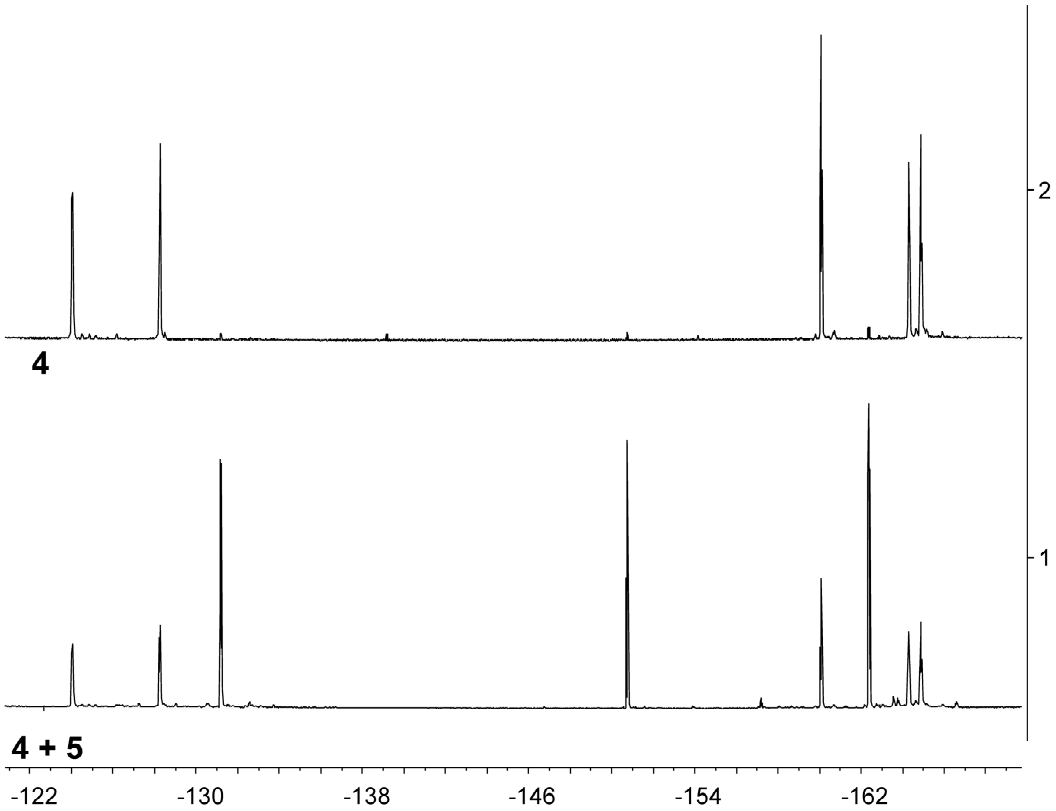
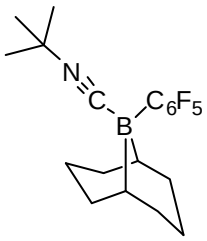


figure 9: ^{19}F NMR (470 MHz, [D_6]-benzene, 299 K): (1) Reaction mixture of compound **4** and **5**; (2) Compound **4**.

Compound 6



Dimesitylvinylphosphane (341.7 mg, 1.15 mmol, 1.00 eq.) and bispentafluorophenylborane (398.8 mg, 1.15 mmol, 1.00 eq.) were dissolved in pentane (30 mL). After this solution was stirred for 15 min 9-borabicyclononane (140.7 mg, 1.15 mmol, 1.00 eq.) was added to the solution and the solution was stirred over night at room temperature. The solution above the white precipitate was separated and *tert*-butylisocyanide (132 µL, 1.15 mmol, 1.00 eq.) was added. The mixture was stirred for 2 h at room temperature and then stored at -40 °C to start the crystallization. The product was isolated as colourless crystals and was dried *in vacuo* (yield 223.3 mg, 52%). Crystals of **6** suitable for X-ray crystal structure analysis were obtained by crystal growth in pentane at -40 °C. Anal. calc. for $C_{19}H_{23}BF_5N$ (371.20 g/mol): C 61.48, H 6.25, N 3.77; found: C 61.36, H 6.17, N 3.76. IR (KBr): $\tilde{\upsilon}$ = 3744 (w), 2983 (m), 2919 (m), 2670 (w), 2451 (w), 2261 (m), 1638 (m), 1513 (s), 1457 (s), 1375 (s), 1273 (m), 1238 (m), 1206 (m), 1091 (s), 967 (s), 916 (m), 888 (m), 866 (m), 814 (w), 779 (m), 737 (s), 625 (w), 540 (m), 521 (m), 431 (w).

M. p.: 126 °C (DSC).

^{1}H NMR (500 MHz, [D$_6$]-benzene, 299 K): δ = 2.27/1.77 (each m, each 1H, CH_2)[1], 2.09/1.69 (each m, each 1H, CH_2)[1], 2.15/1.96 (each m, each 2H, CH_2)[1], 2.05/2.00 (each m, each 2H, CH_2)[1], 1.97 (m, 2H, CHB)[1], 0.69 (s, 9H, CH_3), [[1] from the GHSQC experiment].

^{13}C{^{1}H} NMR (126 MHz, [D$_6$]-benzene, 299 K): δ = 132.9 (br, C≡N), 120.2 (br, i-C_6F_5), 58.6 (CCH_3), 34.5 (CH_2), 30.8 (CH_2), 28.6 (CH_3), 24.65 (CH_2), 24.62 (CH_2), 22.1 (br, CHB), [C_6F_5 not listed].

^{11}B NMR (160 MHz, [D$_6$]-benzene, 299 K): δ = -16.6 ($\nu_{1/2}$ ~ 140 Hz).

^{11}B{^{1}H} NMR (160 MHz, [D$_6$]-benzene, 299 K): δ = -16.6 ($\nu_{1/2}$ ~ 140 Hz).

^{19}F NMR (470 MHz, [D$_6$]-benzene, 299 K): δ = -132.5 (m, 2F, o-C_6F_5), -159.3 (m, 1F, p-C_6F_5), -164.3 (m, 2F, m-C_6F_5), [$\Delta\delta^{19}F_{pm}$ = 5.0].

^{19}F, ^{19}F GCOSY (470 MHz/ 470 MHz, [D$_6$]-benzene, 299 K): δ^{19}F/ δ^{19}F = -132.5/-159.3, -164.3 (o-C_6F_5/ p-C_6F_5, m-C_6F_5), -159.3/-164.3 (p-C_6F_5, m-C_6F_5).

^{1}H, ^{13}C GHSQC (500 MHz/ 126 MHz, [D$_6$]-benzene, 299 K): δ^1H/ δ^{13}C = 2.27/24.62 (CH_2/CH_2), 2.15/34.5 (CH_2/CH_2), 2.09/24.65 (CH_2/CH_2), 2.05/30.8 (CH_2/CH_2), 2.00/30.8 (CH_2/CH_2), 1.97/22.1 (CHB/CHB), 1.96/34.5 (CH_2/CH_2), 1.77/24.62 (CH_2/CH_2), 1.69/24.65 (CH_2/CH_2), 0.69/28.6 (CH_3/CH_3).

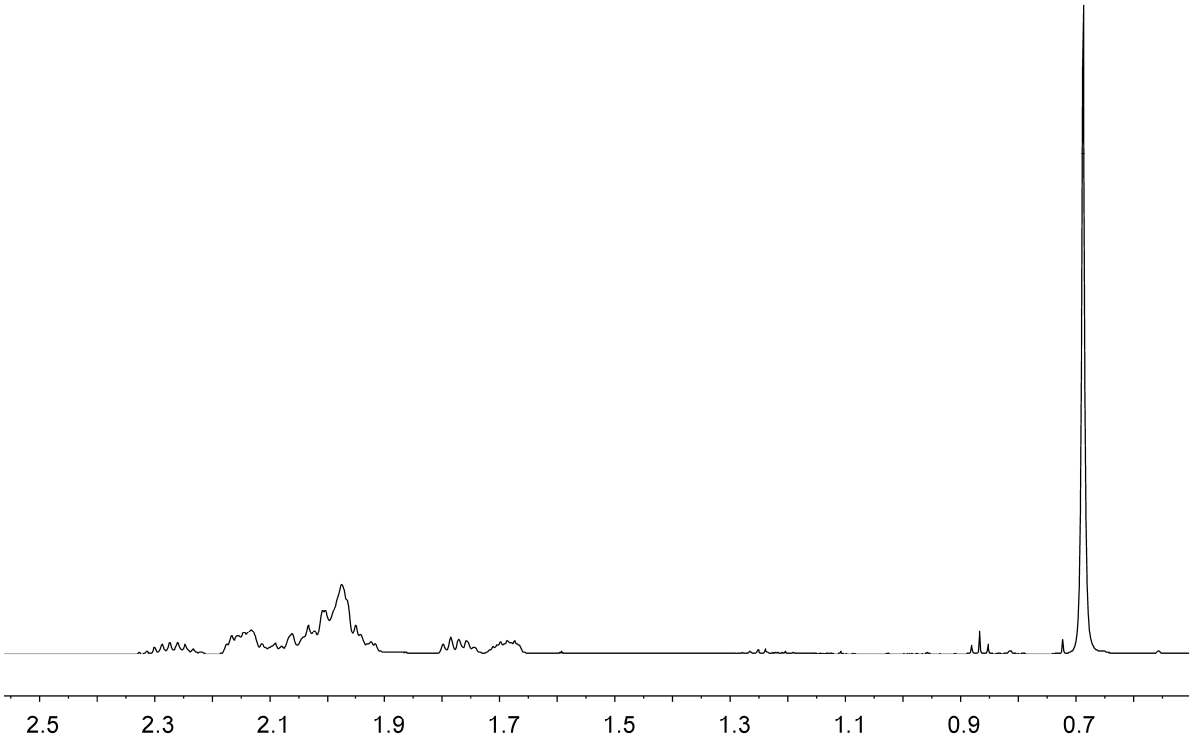


figure 10: ^{1}H NMR (500 MHz, [D_6]-benzene, 299 K).

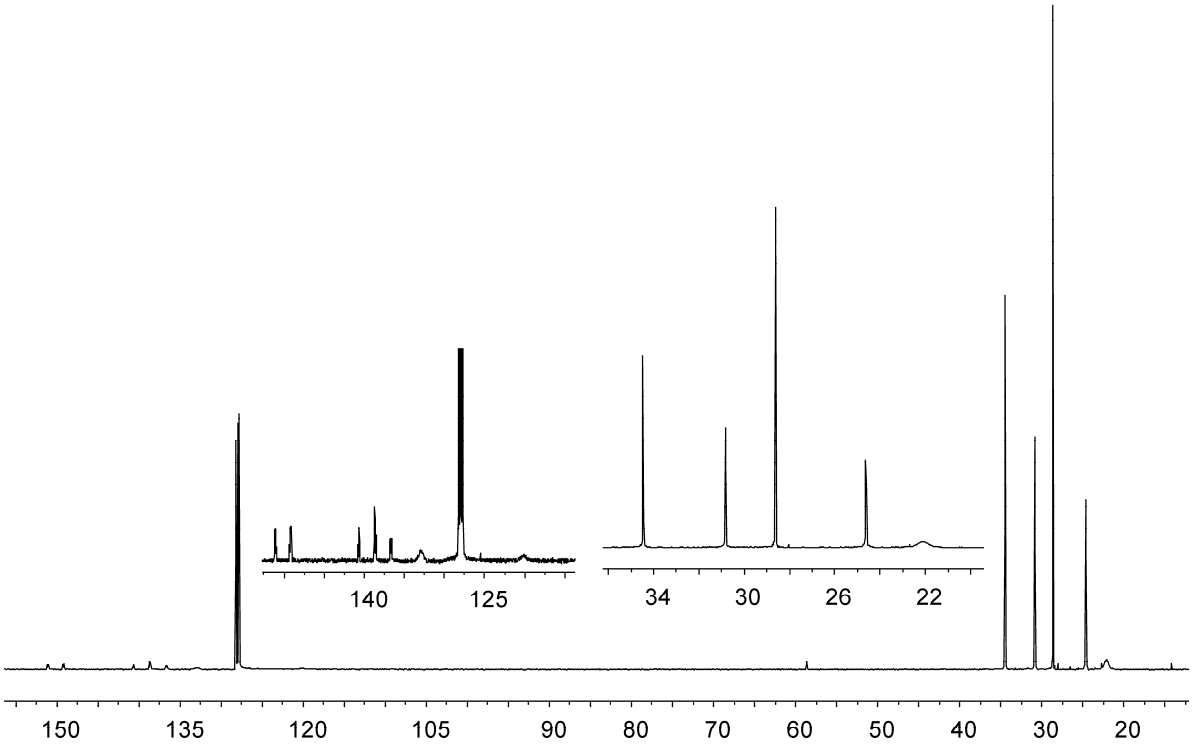


figure 11: ^{13}C{^{1}H} NMR (126 MHz, [D_6]-benzene, 299 K).

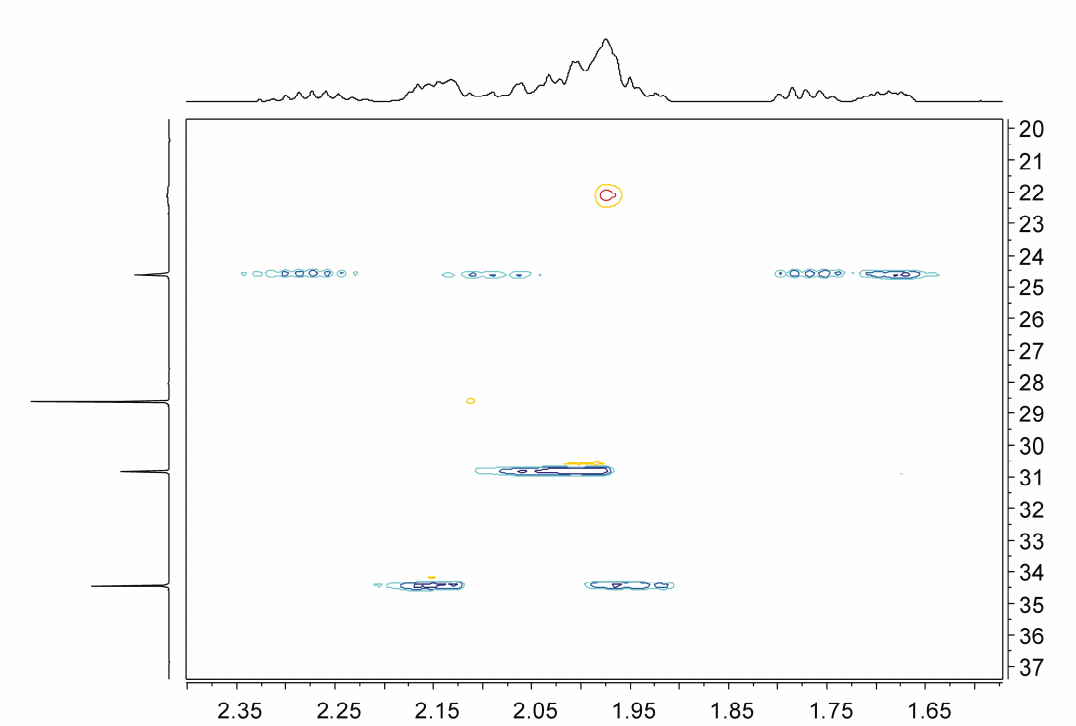


figure 12: ^{1}H, ^{13}C GHSQC (500 MHz/ 126 MHz, [D_6]-benzene, 299 K).

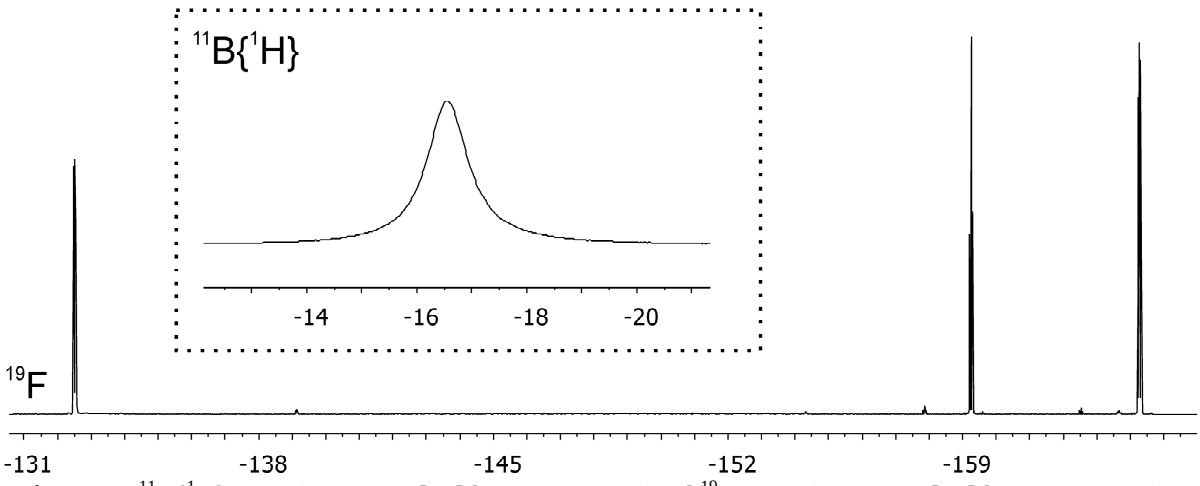
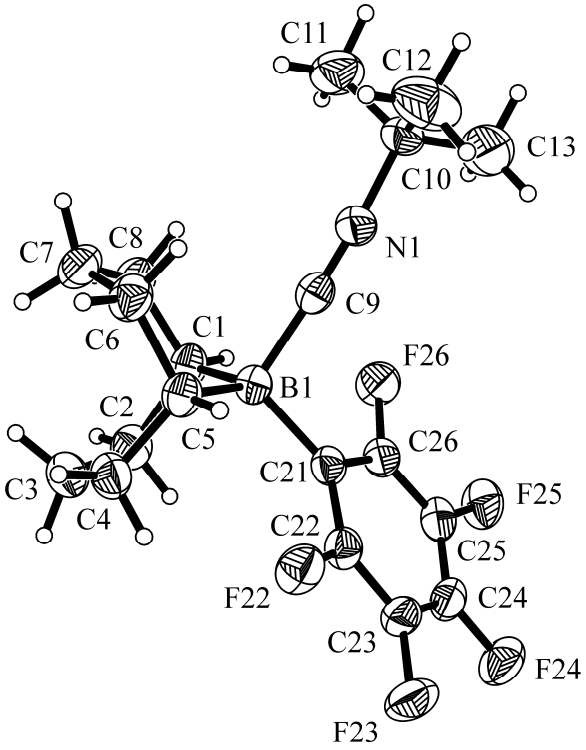
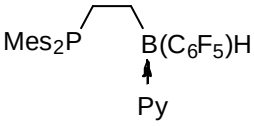


figure 13: $^{11}B\{^{1}H\}$NMR (160 MHz, [D_6]-benzene, 299 K) and ^{19}F NMR (470 MHz, [D_6]-benzene, 299 K).

X-ray crystal structure analysis of 6: formula $C_{19}H_{23}BF_5N$, M = 371.19, colourless crystal, 0.42 x 0.35 x 0.18 mm, a = 27.7049(7), b = 9.8068(2), c = 13.6633(5) Å, β = 93.373(2) °, V = 3705.84(18) Å^3, ρ_{calc} = 1.331 gcm^{-3}, μ = 0.956 mm^{-1}, empirical absorption correction (0.689 ≤ T ≤ 0.846), Z = 8, monoclinic, space group $C2/c$ (No. 15), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 11474 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 3167 independent (R_{int} = 0.030) and 3026 observed reflections [I>2σ(I)], 238 refined parameters, R = 0.038, wR^2 = 0.101, max. (min.) residual electron density 0.22 (-0.15) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Compound 7



Compound **4** (200.0 mg, 0.42 mmol, 1.00 eq.) and pyridine (17 µL, 0.42 mmol, 1.00 eq.) were dissolved in toluene (20 mL). After stirring for one day the solvent was removed *in vacuo* and the remaining crude product was dissolved in pentane (20 mL). The solution was stored over night at -40 °C. The pentane was removed *via* cannula and the remaining white precipitate was dried *in vacuo*. The remaining solid was dissolved in dichloromethane (20 mL) and afterwards dried *in vacuo*. The product could be obtained as a white solid (168.8 mg, 72%). Anal. calc. for $C_{31}H_{32}BF_5NP$ (476.27 g/mol): C 67.04; H 5.81; N 2.52; found: C 66.60; H 5.62; N 2.35. IR (KBr): 3131 (w), 3019 (m), 2729 (w), 2373 (m), 2713 (w), 1936 (w), 1855 (w), 1733 (w), 1625 (s), 1601 (s), 1533 (m), 1512 (s), 1467 (s), 1374 (s), 1277 (s), 1215 (m), 1173 (s), 1140 (s), 1083 (s), 1051 (s), 1024 (s), 972 (s), 902 (m), 848 (s), 795 (m), 754 (s), 689 (s), 613 (m), 553 (m).
M. p.: 146 °C (DSC).

^{1}H NMR (600 MHz, [D$_6$]-benzene, 299 K): δ = 7.90 (m, 2H, o-Py), 6.70 (m, 2H, m-Mes^{a}), 6.68 (m, 2H, m-Mes^{b}), 6.55 (m, 1H, p-Py), 6.18 (m, 2H, m-Py), 3.98 (br, 1H, BH), 2.75/2.49 (each m, each 1H, CH_2P), 2.46 (s, 6H, o-CH_3^{a}), 2.43 (s, 6H, o-CH_3^{b}), 2.08 (s, 6H, p-$CH_3^{a/b}$), 1.39/1.26 (each m, each 1H, CH_2B).

^{13}C{^{1}H} NMR (151 MHz, [D$_6$]-benzene, 299 K): δ = 146.3 (o-Py), 142.4 (d, $^{2}J_{PC}$ = 12.7 Hz, o-Mes^{b}), 142.1 (d, $^{2}J_{PC}$ = 12.8 Hz, o-Mes^{a}), 139.5 (p-Py), 137.02, 137.00 (p-Mes$^{a/b}$), 135.5 (d, $^{1}J_{PC}$ = 24.6 Hz, i-Mes^{b}), 135.1 (d, $^{1}J_{PC}$ = 25.1 Hz, i-Mes^{a}), 130.3 (d, $^{3}J_{PC}$ = 2.5 Hz, m-Mes^{a}), 130.2 (d, $^{3}J_{PC}$ = 2.6 Hz, m-Mes^{b}), 125.0 (m-Py), 26.7 (d, $^{1}J_{PC}$ = 16.3 Hz, CH_2P), 23.49 (d, $^{3}J_{PC}$ = 12.7 Hz, o-CH_3^{a}), 23.47 (d, $^{3}J_{PC}$ = 12.9 Hz, o-CH_3^{b}), 20.82, 20.80 (p-$CH_3^{a,b}$), 19.1 (br, CH_2B), [C_6F_5 not listed].

^{31}P NMR (243 MHz, [D$_6$]-benzene, 299 K): δ = -16.2 (s).

^{31}P{^{1}H} NMR (243 MHz, [D$_6$]-benzene, 299 K): δ = -16.2 ($\nu_{1/2}$ ~ 7 Hz).

^{11}B NMR (192 MHz, [D$_6$]-benzene, 299 K): δ = -3.1 ($\nu_{1/2}$ ~ 350 Hz).

^{11}B{^{1}H} NMR (192 MHz, [D$_6$]-benzene, 299 K): δ = -3.1 ($\nu_{1/2}$ ~ 300 Hz).

^{19}F NMR (564 MHz, [D$_6$]-benzene, 299 K): δ = -133.6 (m, 2F, o-C_6F_5), -159.4 (m, 1F, p-C_6F_5), -164.2 (m, 2F, m-C_6F_5), [$\Delta\delta^{19}F_{pm}$ = 4.8].

^{19}F, ^{19}F GCOSY (564 MHz/ 564 MHz, [D$_6$]-benzene, 299 K): δ^{19}F/ δ^{19}F = -133.6/-164.2 (o-C_6F_5/ m-C_6F_5), -159.4/-164.2 (p-C_6F_5/ m-C_6F_5).

^{1}H, ^{1}H GCOSY (600 MHz/ 600 MHz, [D$_6$]-benzene, 299 K): δ^{1}H/ δ^{1}H = 7.90/6.55, 6.18 (o-Py/p-Py, m-Py), 6.70/2.46, 2.08 (m-Mes^{a}/o-CH_3^{a}, p-CH_3^{a}), 6.68/2.43, 2.08 (m-Mes^{b}/o-CH_3^{b},

p-CH_3^b), 6.55/6.18 (p-Py/m-Py), 2.75/2.49, 1.39, 1.26 (CH_2P/ CH_2P, CH_2B, CH_2B), 2.49/1.39, 1.26 (CH_2P/ CH_2B, CH_2B), 2.46/2.08 (o-CH_3^a/p-CH_3^a), 2.43/2.08 (o-CH_3^b/p-CH_3^b).

^{1}H, ^{13}C GHSQC (600 MHz/ 151 MHz, [D_6]-benzene, 299 K): δ^1H/ δ^{13}C = 7.90/146.3 (o-Py/ o-Py), 6.70/130.3 (m-Mes^a/m-Mes^a), 6.68/130.2 (m-Mes^b/m-Mes^b), 6.55/139.5 (p-Py/p-Py), 6.18/125.0 (m-Py/m-Py), 2.75/26.7 (CH_2P/CH_2P), 2.49/26.7 (CH_2P/CH_2P), 2.46/23.49 (o-CH_3^a/o-CH_3^a), 2.43/23.47 (o-CH_3^b/o-CH_3^b), 2.08/20.82, 20.80 (p-$CH_3^{a,b}$/ p-$CH_3^{a,b}$), 1.39/19.1 (CH_2B/CH_2B), 1.26/19.1 (CH_2B/CH_2B).

^{1}H, ^{13}C GHMBC (600 MHz/ 151 MHz, [D_6]-benzene, 299 K): δ^1H/ δ^{13}C = 7.90/146.3, 139.5, 125.0 (o-Py/o-Py, p-Py, m-Py), 6.70/ 135.1, 130.3, 23.49, 20.82, 20.80 (m-Mes^a/i-Mes^a, m-Mes^a, o-CH_3^a, p-CH_3^a), 6.68/135.5, 130.2, 23.47, 20.82, 20.80 (m-Mes^b/i-Mes^b, m-Mes^b, o-CH_3^b, p-CH_3^b), 6.55/146.3 (p-Py/o-Py), 6.18/146.3, 125.0 (m-Py/o-Py, m-Py), 2.75/135.5, 135.1, 19.1 (CH_2P/i-Mes^b, i-Mes^a, CH_2B), 2.46/142.1, 135.1, 130.3 (o-CH_3^a/o-Mes^a, i-Mes^a, m-Mes^a) 2.43/142.4, 135.5, 130.2 (o-CH_3^b/o-Mes^b, i-Mes^b, m-Mes^b), 2.08/137.02, 137.00, 130.3, 130.2 (p-$CH_3^{a,b}$/ p-$Mes^{a/b}$, m-Mes^a, m-Mes^b), 1.39/26.7 (CH_2B/CH_2P), 1.26/26.7 (CH_2B/CH_2P).

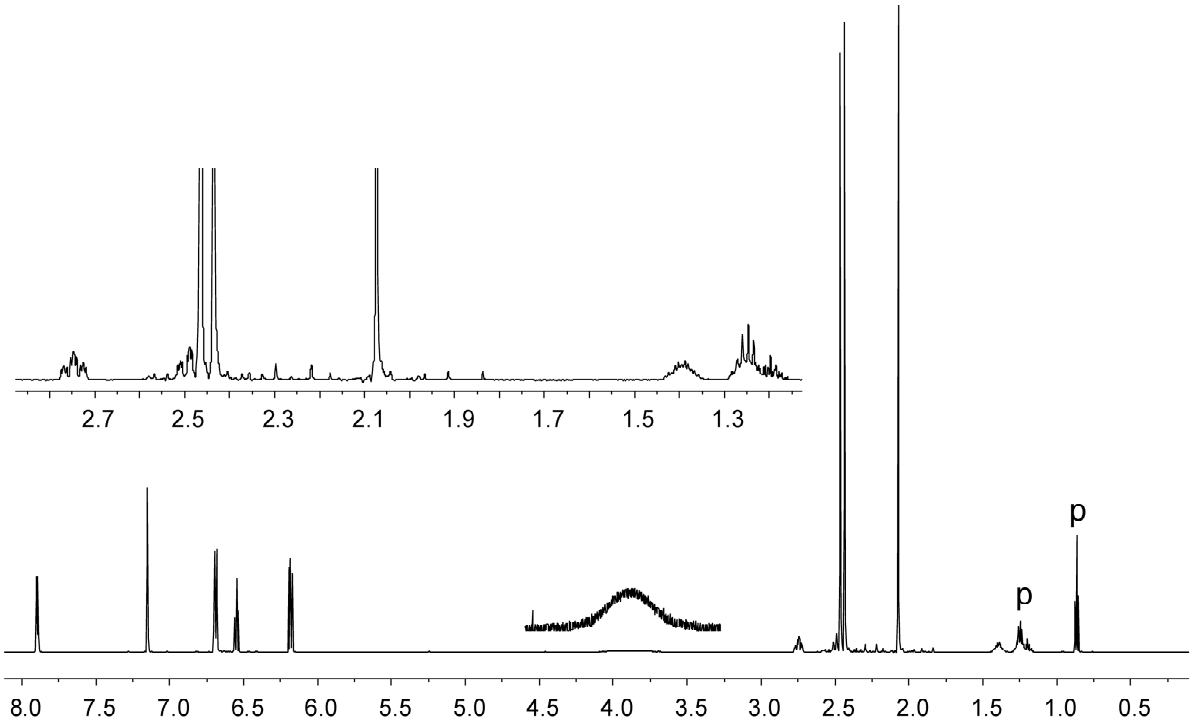


figure 14: ^{1}H NMR (600 MHz, [D_6]-benzene, 299 K) [p: pentane].

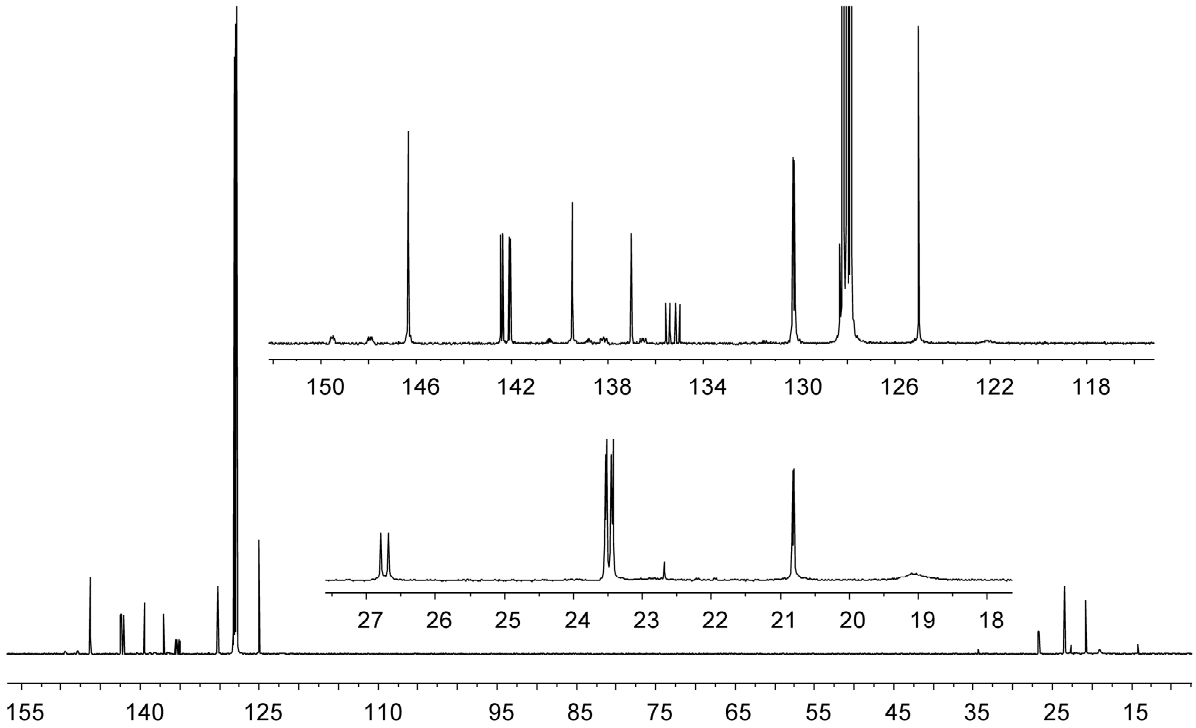


figure 15: $^{13}C\{^{1}H\}$ NMR (151 MHz, $[D_6]$-benzene, 299 K).

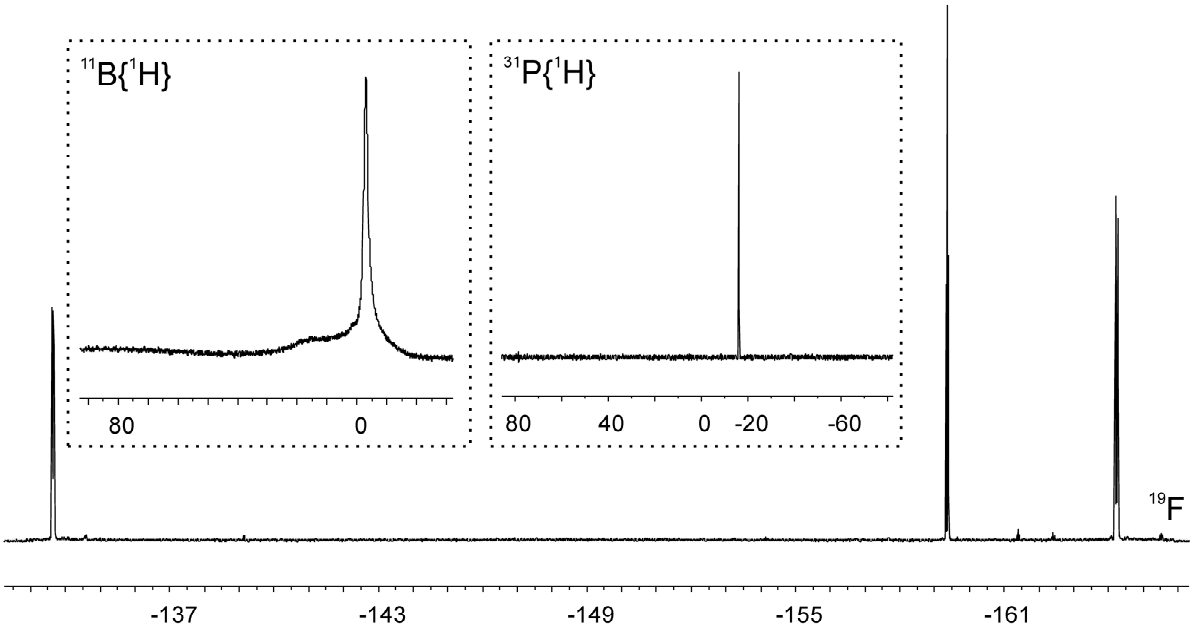
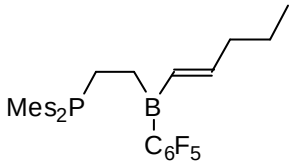


figure 16: ^{19}F NMR (564 MHz, $[D_6]$-benzene, 299 K), $^{31}P\{^{1}H\}$ NMR (243 MHz, $[D_6]$-benzene, 299 K) and $^{11}B\{^{1}H\}$ NMR (192 MHz, $[D_6]$-benzene, 299 K).

Compound 8



Compound **4** (62.8 mg, 0.13 mmol, 1.00 eq.) and 1-pentyne (13 µL, 0.13 mmol, 1.00 eq.) were dissolved in 0.8 mL C_6D_6. After one day the desired product was formed as a yellow solution.

^{1}H NMR (600 MHz, [D$_6$]-benzene, 299 K): δ = 6.64 (m, 4H, m-Mes), 6.52 (dt, $^{3}J_{HH}$ = 17.4 Hz, $^{3}J_{HH}$ = 6.2 Hz 1H, =CH), 6.43 (d, $^{3}J_{HH}$ = 17.4 Hz 1H, =CHB), 2.71 (m, 2H, CH_2P), 2.33 (s, 12H, o-CH_3), 2.04 (s, 6H, p-CH_3), 1.97 (m, 2H, $^{=}CH_2$), 1.81 (m, 2H, CH_2B), 1.25 (sex, $^{3}J_{HH}$ = 7.5 Hz, 2H, CH_2), 0.76 (t, $^{3}J_{HH}$ = 7.5 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, [D$_6$]-benzene, 299 K): δ = 161.9 (=CH), 142.2 (d, $^{2}J_{PC}$ = 12.7 Hz, o-Mes), 138.0 (p-Mes), 135.2 (br, =CHB), 132.9 (d, $^{1}J_{PC}$ = 19.2 Hz, i-Mes), 130.4 (d, $^{3}J_{PC}$ = 3.3 Hz, m-Mes), 38.5 ($^{=}CH_2$), 23.9 (br d, $^{2}J_{PC}$ = 15.6 Hz, CH_2B), 23.7 (d, $^{1}J_{PC}$ = 11.9 Hz, CH_2P), 23.3 (d, $^{3}J_{PC}$ = 12.7 Hz, o-CH_3), 21.5 (CH_2), 20.8 (p-CH_3), 13.8 (CH_3), [C_6F_5 not listed].

^{31}P NMR (243 MHz, [D$_6$]-benzene, 295 K): δ = -11.4 (t, $^{3}J_{PH}$ ~ 17 Hz).

^{31}P{^{1}H} NMR (243 MHz, [D$_6$]-benzene, 295 K): δ = -11.4 ($\nu_{1/2}$ ~ 10 Hz).

^{11}B NMR (192 MHz, [D$_6$]-benzene, 299 K): δ = 63.6 ($\nu_{1/2}$ ~ 1000 Hz).

^{11}B{^{1}H} NMR (192 MHz, [D$_6$]-benzene, 299 K): δ = 63.6 ($\nu_{1/2}$ ~ 1000 Hz).

^{19}F NMR (564 MHz, [D$_6$]-benzene, 299 K): δ = -131.8 (m, 2F, o-C_6F_5), -154.0 (m, 1F, p-C_6F_5), -162.4 (m, 2F, m-C_6F_5), [$\Delta\delta^{19}F_{pm}$ = 8.4].

^{19}F, ^{19}F GCOSY (564 MHz/ 564 MHz, [D$_6$]-benzene, 299 K): δ^{19}F/ δ^{19}F = -131.8/-162.4 (o-C_6F_5/ m-C_6F_5), -154.0/-162.4 (p- C_6F_5/m- C_6F_5).

^{1}H, ^{1}H GCOSY (600 MHz/ 600 MHz, [D$_6$]-benzene, 299 K): δ^{1}H/ δ^{1}H = 6.64/2.33, 2.04 (m-Mes/o-CH_3, p-CH_3), 6.52/6.43, 1.97 (=CH/=CHB, $^{=}CH_2$), 2.71/1.81 (CH_2P/CH_2B), 2.33/2.04 (o-CH_3/p-CH_3), 1.97/1.25 ($^{=}CH_2$/CH_2), 1.25/0.76 (CH_2/CH_3).

^{1}H, ^{13}C GHSQC (600 MHz/ 151 MHz, [D$_6$]-benzene, 299 K): δ^{1}H/ δ^{13}C = 6.64/130.4 (m-Mes/m-Mes), 6.52/161.9 (=CH/=CH), 6.43/135.2 (=CHB/=CHB), 2.71/23.7 (CH_2P/CH_2P), 2.33/23.3 (o-CH_3/o-CH_3), 2.04/20.8 (p-CH_3/p-CH_3), 1.97/38.5 ($^{=}CH_2$/$^{=}CH_2$), 1.81/23.9 (CH_2B/CH_2B), 1.25/21.5 (CH_2/CH_2), 0.76/13.8 (CH_3/CH_3).

^{1}H, ^{13}C GHMBC (400 MHz/ 100 MHz, [D$_6$]-benzene, 296 K): δ^{1}H/ δ^{13}C = 6.64/132.9, 130.4, 23.3, 20.8 (m-Mes/i-Mes, m-Mes, o-CH_3, p-CH_3), 6.52/38.5, 21.5 (=CH/$^{=}CH_2$, CH_2), 6.43/161.9, 38.5, 23.9 (=CHB/=CH, CH_2, CH_2B), 2.71/132.9, 23.9 (CH_2P/i-Mes, CH_2B), 2.33/142.2, 132.9, 130.4 (o-CH_3/o-Mes, i-Mes, m-Mes), 2.04/138.0, 130.4 (p-CH_3/ p-Mes, m-

Mes), 1.97/161.9, 135.2, 21.5, 13.8 ($^{=}CH_2$/=CH, =CHB, CH_2, CH_3), 1.81/135.2, 23.7 (CH_2B/=CHB, CH_2P), 1.25/161.9, 38.5, 13.8 (CH_2/=CH, $^{=}CH_2$, CH_3), 0.76/ 38.5, 21.5 (CH_3/$^{=}CH_2$, CH_2).

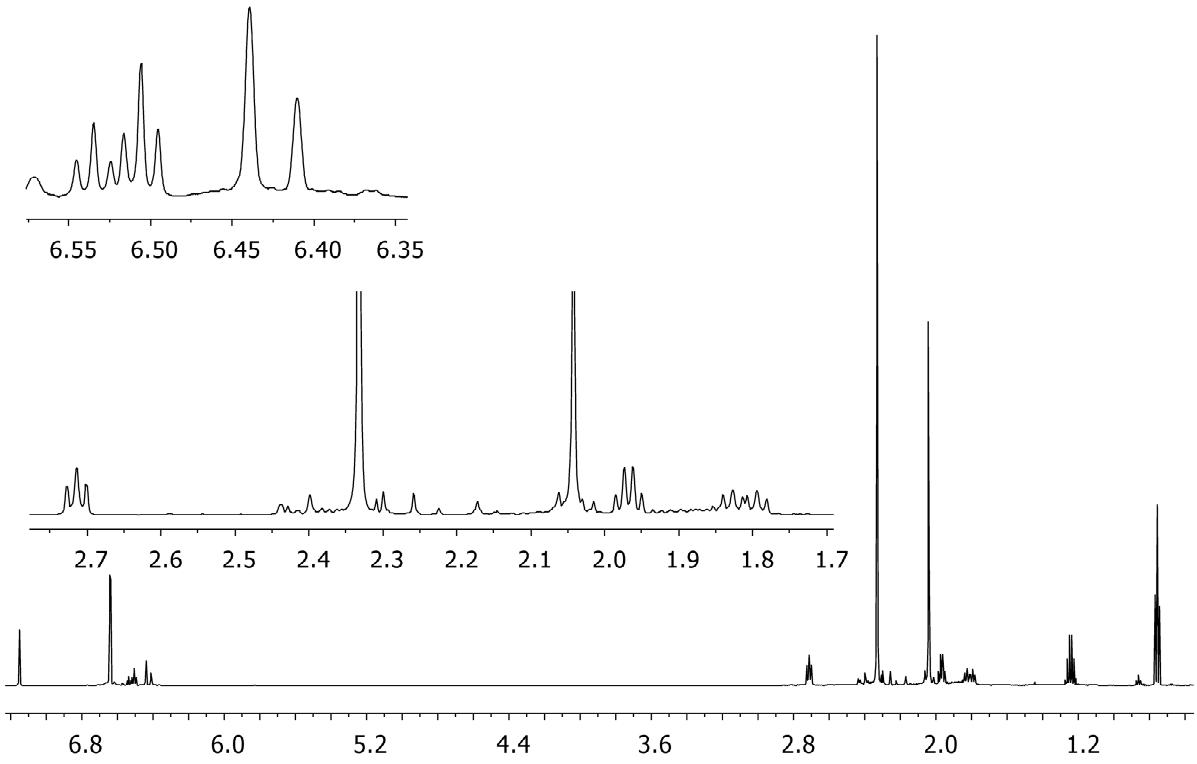


figure 17: ^{1}H NMR (600 MHz, [D_6]-benzene, 299 K).

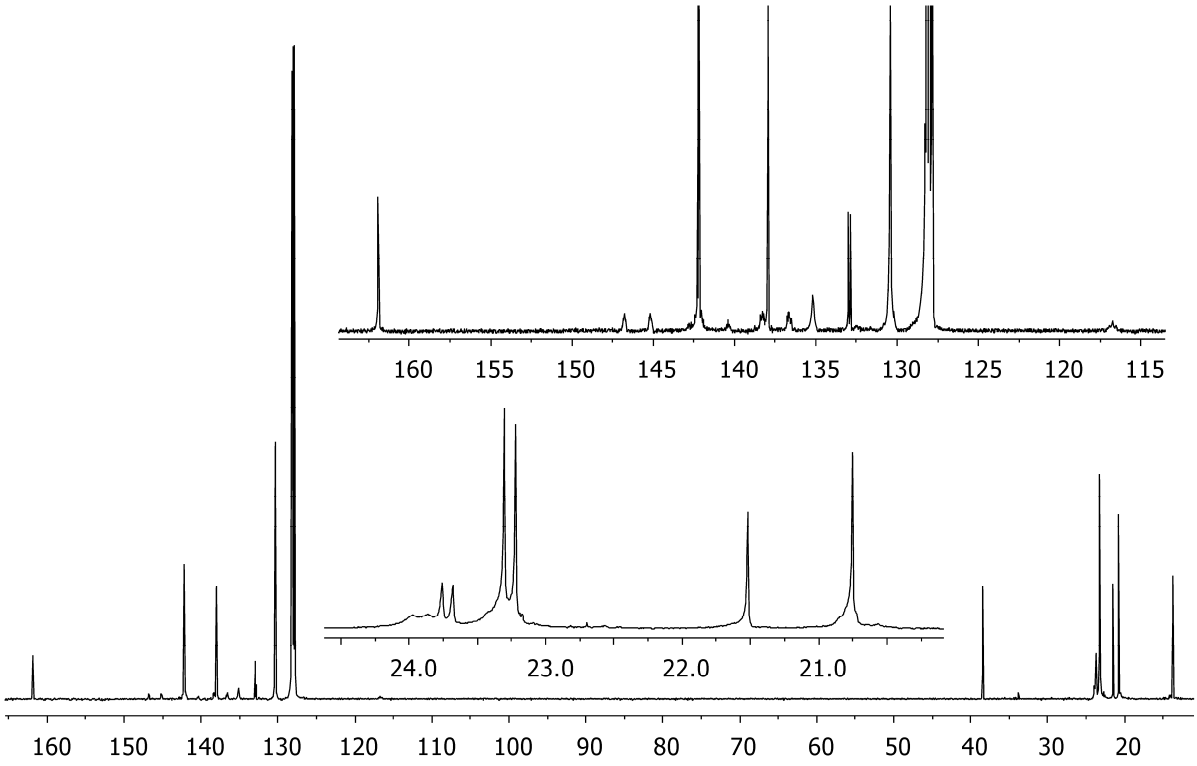


figure 18: $^{13}C\{^{1}H\}$ NMR (151 MHz, [D_6]-benzene, 299 K).

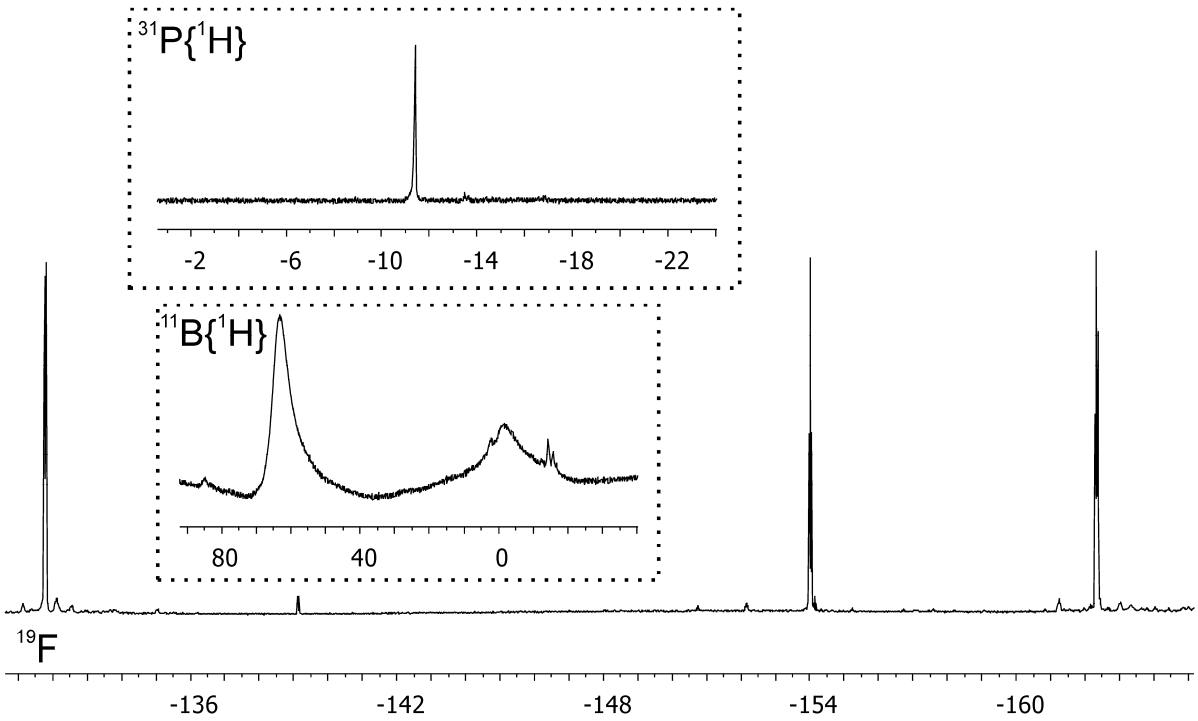
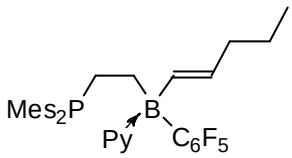


figure 19: ^{19}F NMR (564 MHz, [D_6]-benzene, 299 K), $^{31}P\{^1H\}$ NMR (243 MHz, [D_6]-benzene, 299 K) and $^{11}B\{^1H\}$ NMR (192 MHz, [D_6]-benzene, 299 K).

Compound 9



Compound **4** (100.0 mg, 0.21 mmol, 1.00 eq.) and 1-pentyne (20.8 µL, 0.21 mmol, 1.00 eq) were dissolved in toluene (20 mL) and stirred over night. Pyridine (17 µL, 0.21 mmol, 1.00 eq.) was added and the reaction mixture was again stirred over night. The solvent was removed *in vacuo* and to the remaining crude product pentane (10 mL) was added. The solution was stored at -40 °C over night, and the formed white crystals were separated by removal of the pentane through cannula. The product was dried *in vacuo* (105.9 mg, 81 %). Crystals suitable for X-ray crystal structure analysis were obtained by crystal growth in pentane at -40 °C. Anal. calc. for $C_{36}H_{40}BF_5NP$ (544.39 g/mol): C 69.35; H 6.47; N 2.25; found: C 68.32; H 6.40; N 2.01. IR (KBr): $\tilde{\upsilon}$ = 3021 (w), 2966 (m), 2918 (m), 2879 (m), 2830 (m), 2730 (w), 2359 (w), 1734 (w), 1644 (m), 1623 (s), 1603 (m), 1558 (m), 1515 (s), 1456 (s), 1376 (m), 1274 (m), 1215 (m), 1174 (s), 1121 (w), 1086 (s), 1015 (s), 960 (s), 920 (m), 890 (m), 848 (m), 827 (m), 767 (m), 734 (m), 697 (s), 617 (w), 599 (w), 555 (m), 483 (w), 432 (w).

M. p.: 131 °C (DSC).

^{1}H NMR (600 MHz, [D$_6$]-benzene, 299 K): δ = 7.94 (m, 2H, o-Py), 6.71 (m, 1H, p-Py), 6.70 (m, 2H, m-Mes^{a}), 6.67 (m, 2H, m-Mes^{b}), 6.35 (m, 2H, m-Py), 6.21 (d, $^{3}J_{HH}$ = 17.3 Hz, 1H, =CHB), 5.46 (dt, $^{3}J_{HH}$ = 17.3 Hz, $^{3}J_{HH}$ = 6.5 Hz 1H, =CH), 2.48/1.80 (each m, each 1H, CH_2P), 2.43 (s, 6H, o-CH_3^{a}), 2.34 (s, 6H, o-CH_3^{b}), 2.18 (m, 2H, $^{=}CH_2$), 2.08 (s, 3H, p-CH_3^{a}), 2.07 (s, 3H, p-CH_3^{b}), 1.54/1.22 (each m, each 1H, CH_2B), 1.44 (sex, $^{3}J_{HH}$ = 7.4 Hz, 2H, CH_2), 0.93 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, [D$_6$]-benzene, 299 K): δ = 145.2 (o-Py), 142.20 (d, $^{2}J_{PC}$ = 12.5 Hz o-Mes^{a},), 142.16 (d, $^{2}J_{PC}$ = 12.8 Hz, o-Mes^{b}), 139.4 (p-Py), 138.9 (br, =CHB), 137.8 (=CH), 137.1 (p-Mes^{a}), 137.0 (p-Mes^{b}), 135.3 (d, $^{1}J_{PC}$ = 25.3 Hz, i-Mes^{b}), 135.0 (d, $^{1}J_{PC}$ = 25.0 Hz, i-Mes^{a}), 130.3 (d, $^{3}J_{PC}$ = 2.5 Hz, m-Mes^{a}), 130.2 (d, $^{3}J_{PC}$ = 2.5 Hz, m-Mes^{b}), 124.8 (m-Py), 38.9 ($^{=}CH_2$), 24.6 (d, $^{1}J_{PC}$ = 16.0 Hz, CH_2P), 23.43 (d, $^{3}J_{PC}$ = 13.0 Hz, o-CH_3^{a}), 23.41 (d, $^{3}J_{PC}$ = 13.0 Hz, o-CH_3^{b}), 23.1 (CH_2), 21.6 (br, CH_2B), 20.8 (p-$CH_3^{a,b}$), 14.1 (CH_3), [C_6F_5 not listed].

^{31}P NMR (243 MHz, [D$_6$]-benzene, 299 K): δ = -15.9 (s).

^{31}P{^{1}H} NMR (243 MHz, [D$_6$]-benzene, 299 K): δ = -15.9 ($\nu_{1/2}$ ~ 4 Hz).

^{11}B NMR (192 MHz, [D$_6$]-benzene, 299 K): δ = 0.5 ($\nu_{1/2}$ ~ 540).

^{11}B{^{1}H} NMR (192 MHz, [D$_6$]-benzene, 299 K): δ = 0.5 ($\nu_{1/2}$ ~ 500 Hz).

^{19}F NMR (564 MHz, [D$_6$]-benzene, 299 K): δ = -132.3 (m, 2F, o-C_6F_5), -159.8 (m, 1F, p-C_6F_5), -164.2 (m, 2F, m- C_6F_5), [$\Delta\delta^{19}F_{pm}$ = 4.4].

^{19}F, ^{19}F GCOSY (564 MHz/ 564 MHz, [D$_6$]-benzene, 299 K): δ^{19}F/ δ^{19}F = -132.3/-164.2 (o-C_6F_5/m-C_6F_5), -159.8/-164.2 (p-C_6F_5/m-C_6F_5).

^{1}H, ^{1}H GCOSY (600 MHz/ 600 MHz, [D$_6$]-benzene, 299 K): δ^{1}H/ δ^{1}H = 7.94/6.71, 6.35 (o-Py/ p-Py, m-Py), 6.71/6.35 (p-Py/m-Py), 6.70/2.43, 2.08 (m-Mes^a/o-CH_3^a, p-CH_3^a), 6.67/2.34, 2.07 (m-Mes^b/o-CH_3^b, p-CH_3^b), 6.21/5.46, 2.18 (=CHB/=CH, $^{=}CH_2$), 5.46/2.18 (=CH/$^{=}CH_2$), 2.48/1.80, 1.54, 1.22 (CH_2P/CH_2P, CH_2B, CH_2B), 2.43/2.08 (o-CH_3^a/p-CH_3^a), 2.34/2.07 (o-CH_3^b/p-CH_3^b), 2.18/1.44 ($^{=}CH_2$/CH_2), 1.80/1.54, 1.22 (CH_2P/CH_2B, CH_2B), 1.54/1.22 (CH_2B/CH_2B), 1.44/0.93 (CH_2/CH_3).

^{1}H, ^{13}C GHSQC (600 MHz/ 151 MHz, [D$_6$]-benzene, 299 K): δ^{1}H/ δ^{13}C = 7.94/145.2 (o-Py/o-Py), 6.71/139.4 (p-Py/p-Py), 6.70/130.3 (m-Mes^a/m-Mes^a), 6.67/130.2 (m-Mes^b/m-Mes^b), 6.35/124.8 (m-Py/m-Py), 6.21/138.9 (=CHB/=CHB), 5.46/137.8 (=CH/=CH), 2.48/24.6 (CH_2P/CH_2P), 2.43/23.43 (o-CH_3^a/o-CH_3^a), 2.34/23.41 (o-CH_3^b/o-CH_3^b), 2.18/38.9 ($^{=}CH_2$/$^{=}CH_2$), 2.08, 2.07/20.8 (p-CH_3^a, p-CH_3^b/p-$CH_3^{a,b}$), 1.80/24.6 (CH_2P/CH_2P), 1.54/21.6 (CH_2B/CH_2B), 1.44/23.1 (CH_2/CH_2), 1.22/21.6 (CH_2B/CH_2B), 0.94/14.1 (CH_3/CH_3).

^{1}H, ^{13}C GHMBC (600 MHz/ 151 MHz, [D$_6$]-benzene, 299 K): δ^{1}H/ δ^{13}C = 7.94/145.2, 139.4, 124.8 (o-Py/o-Py, p-Py, m-Py), 6.71/145.2 (p-Py/o-Py), 6.70/135.0, 130.3, 23.43, 20.8 (m-Mes^a/i-Mes^a, m-Mes^a, o-CH_3^a, p-CH_3^a), 6.67/135.3, 130.2, 23.41, 20.8 (m-Mes^b/i-Mes^b, m-Mes^b, o-CH_3^b, p-CH_3^b), 6.35/145.2, 124.8 (m-Py/o-Py, m-Py), 6.21/137.8, 38.9, 21.6 (=CHB/=CH, $^{=}CH_2$, CH_2B), 5.46/138.9, 38.9, 23.1 (=CH/=CHB, $^{=}CH_2$, CH_2), 2.43/142.20, 135.0, 130.3 (o-CH_3^a/o-Mes^a, i-Mes^a, m-Mes^a), 2.34/142.16, 135.3, 130.2 (o-CH_3^b/o-Mes^b, i-Mes^b, m-Mes^b), 2.18/138.9, 137.8, 23.1, 14.1 ($^{=}CH_2$/=CHB, =CH, CH_2, CH_3), 2.08/137.1, 130.3 (p-CH_3^a/p-Mes^a, m-Mes^a), 2.07/137.0, 130.2 (p-CH_3^b/p-Mes^b, m-Mes^b), 1.44/137.8, 38.9, 14.1 (CH_2/=CH, $^{=}CH_2$, CH_3), 0.93/38.9, 23.1 (CH_3/$^{=}CH_2$, CH_2).

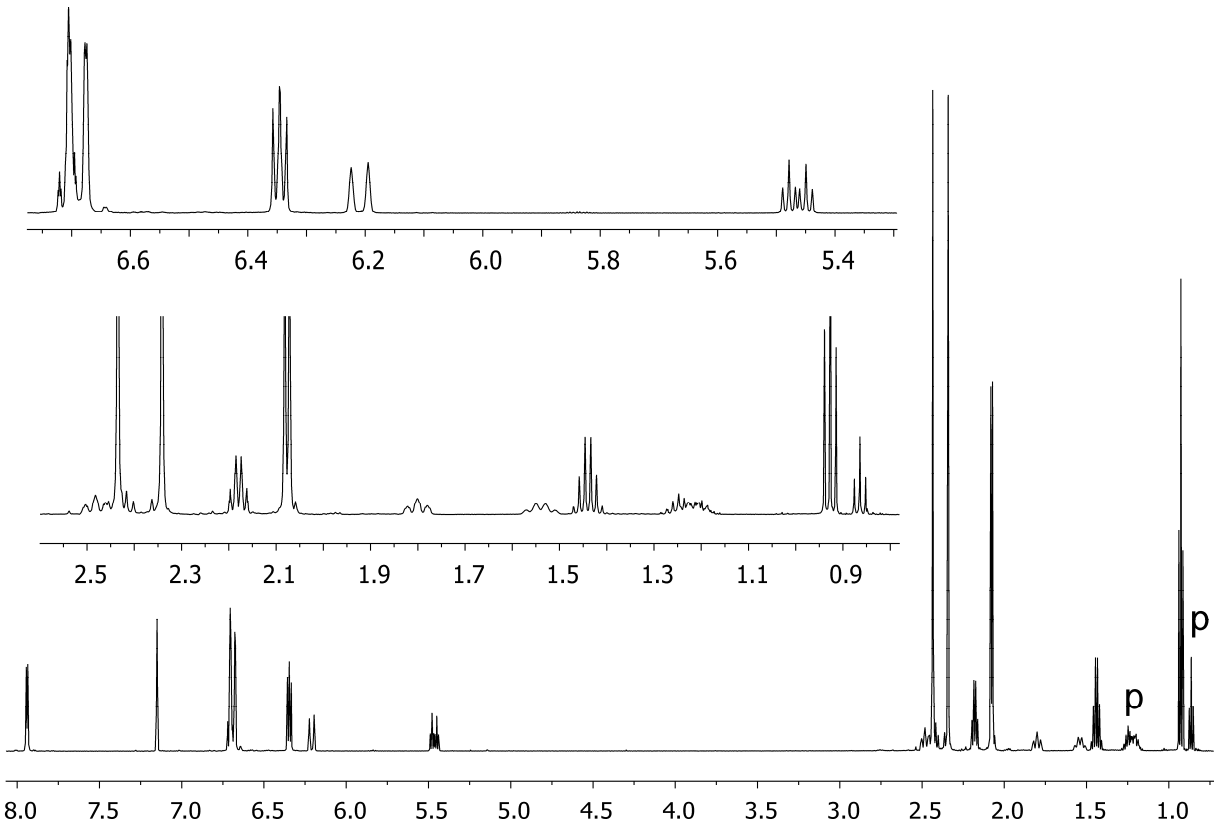


figure 20: ^{1}H NMR (600 MHz, [D_6]-benzene, 299 K) [p: pentane].

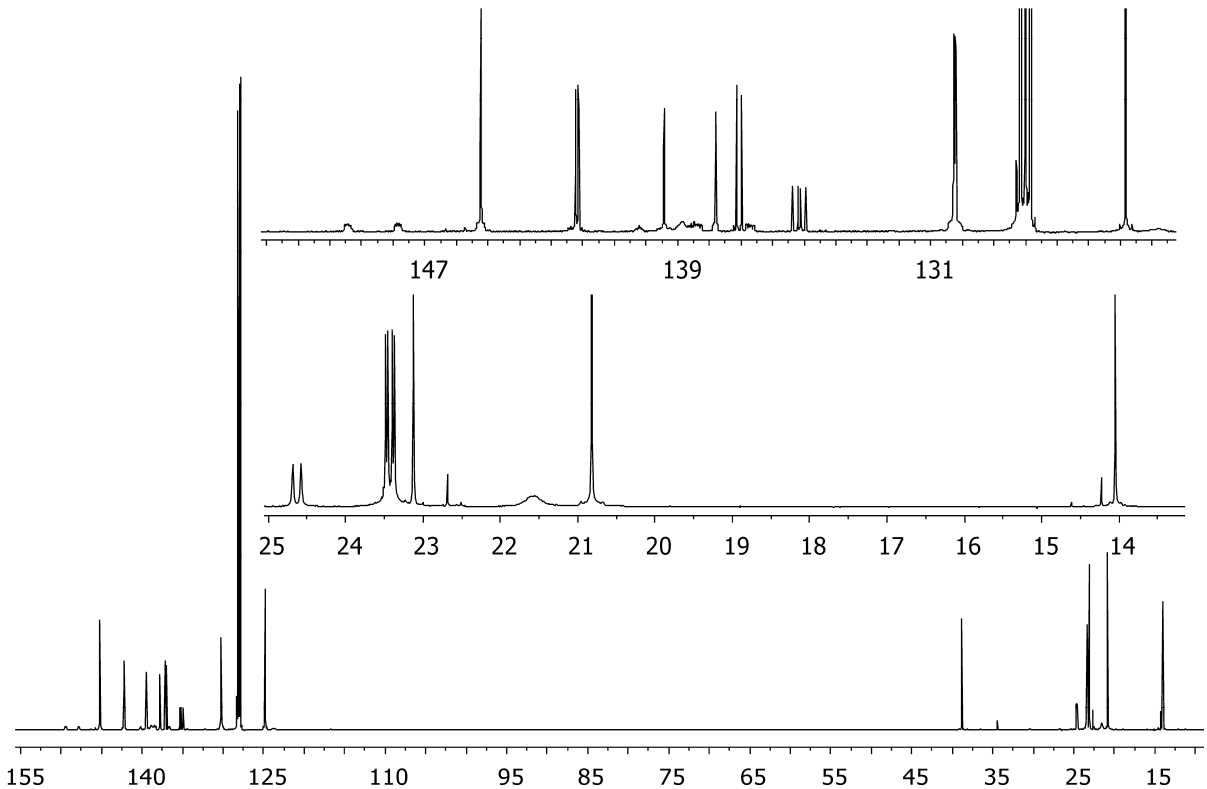


figure 21: $^{13}C\{^{1}H\}$ NMR (151 MHz, [D_6]-benzene, 299 K).

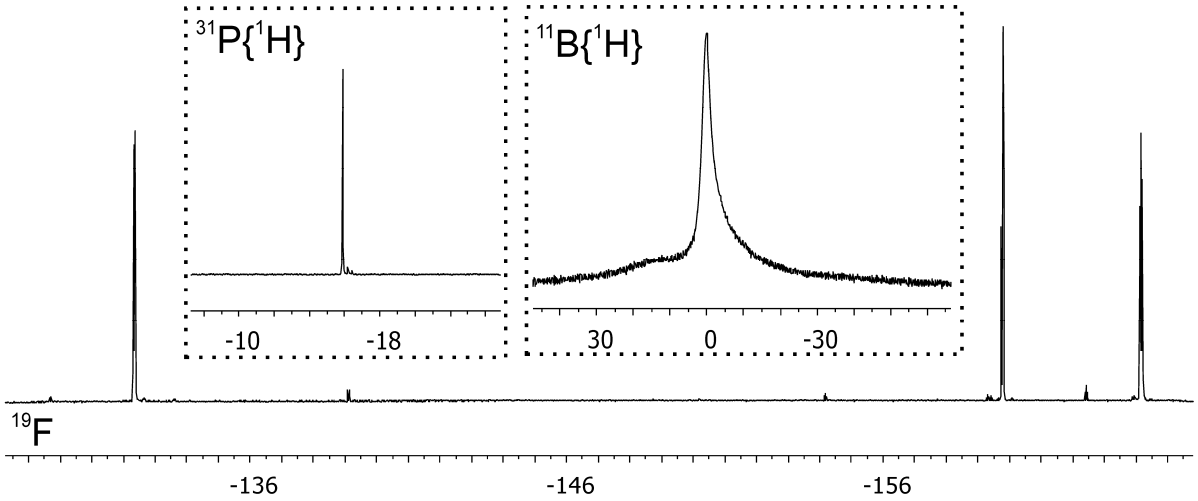
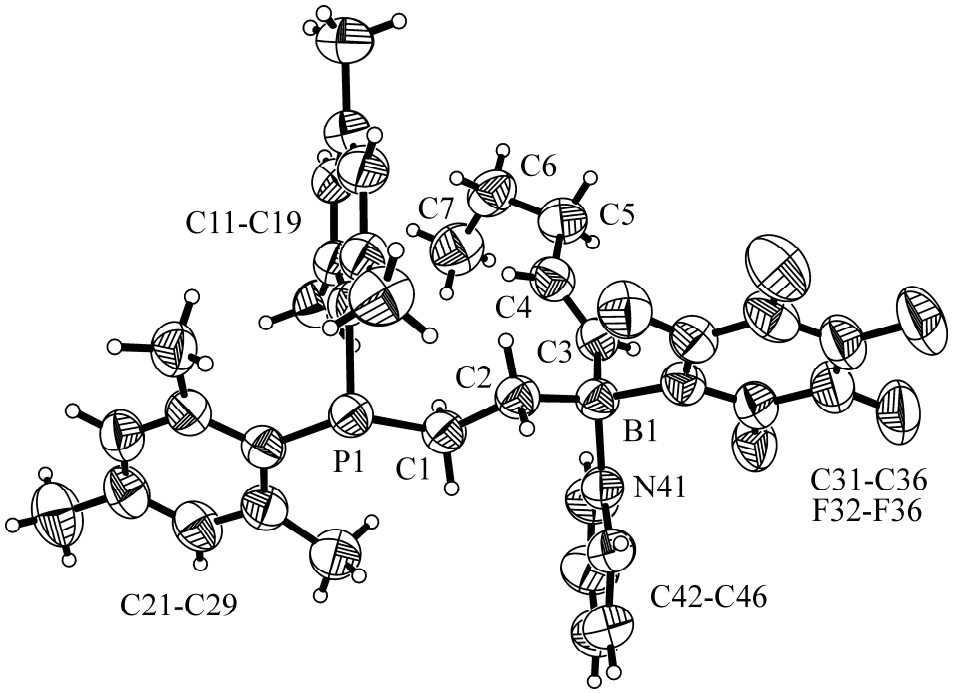
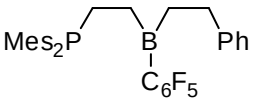


figure 22: ^{19}F NMR (564 MHz, [D_6]-benzene, 299 K), $^{31}P\{^1H\}$ NMR (243 MHz, [D_6]-benzene, 299 K) and $^{11}B\{^1H\}$ NMR (192 MHz, [D_6]-benzene, 299 K).

X-ray crystal structure analysis of 9: formula $C_{36}H_{40}BF_5NP$, M = 623.47, colourless crystal, 0.23 x 0.15 x 0.05 mm, a = 7.5810(2), b = 16.8998(4), c = 31.7784(8) Å, β = 98.408(1) º, V = 3315.73(13) Å^3, ρ_{calc} = 1.249 gcm^{-3}, μ = 1.188 mm^{-1}, empirical absorption correction (0.771 ≤ T ≤ 0.943), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 28006 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 5714 independent (R_{int} = 0.064) and 4354 observed reflections [I>2σ(I)], 404 refined parameters, R = 0.053, wR^2 = 0.141, max. (min.) residual electron density 0.15 (-0.27) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Compound 10



Compound **4** (54.1 mg, 0.11 mmol, 1.00 eq.) and styrene (13 µL, 0.11 mmol, 1.00 eq.) were dissolved in 0.8 mL C_6D_6. After one day the desired product was formed as a clear solution (ratio of product and remaining styrene from ^{1}H-NMR = 1:0.2).

^{1}H NMR (600 MHz, [D$_6$]-benzene, 299 K): δ = 7.12 (m, 2H, m-Ph), 7.03 (m, 2H, o-Ph), 7.02 (m, 1H, p-Ph), 6.58 (m, 4H, m-Mes), 2.62 (m, 2H, CH_2P), 2.59 (m, 2H, CH_2Ph), 2.26 (s, 12H, o-CH_3), 2.00 (s, 6H, p-CH_3), 1.81 (dm, $^3J_{PH}$ = 28.5 Hz, 2H, ^{P}CH_2B), 1.80 (m, 2H, ^{Ph}CH_2B).

^{13}C{^{1}H} NMR (151 MHz, [D$_6$]-benzene, 299 K): δ = 144.4 (i-Ph), 142.1 (d, $^2J_{PC}$ = 11.5 Hz, o-Mes), 138.7 (p-Mes), 131.1 (d, $^1J_{PC}$ = 10.7 Hz, i-Mes), 130.5 (d, $^3J_{PC}$ = 4.3 Hz, m-Mes), 128.6 (m-Ph), 128.1 (o-Ph), 125.9 (s, p-Ph), 31.6 (d, *J* = 7.3 Hz, CH_2Ph), 29.9 (br, ^{Ph}CH_2B), 24.6 (CH_2P). 24.2 (br d, $^2J_{PC}$ = 17.0 Hz, ^{P}CH_2B), 23.0 (d, $^3J_{PC}$ = 11.0 Hz, o-CH_3), 20.7 (p-CH_3), [C_6F_5 not listed].

^{31}P NMR (243 MHz, [D$_6$]-benzene, 299 K): δ = -3.4 (t, $^3J_{PH}$ = 28.5 Hz).

^{31}P{^{1}H} NMR (243 MHz, [D$_6$]-benzene, 299 K): δ = -3.4 ($\nu_{1/2}$ ~ 10 Hz).

^{11}B NMR (192 MHz, [D$_6$]-benzene, 299 K): δ = 58.8 ($\nu_{1/2}$ ~ 1000 Hz).

^{11}B{^{1}H} NMR (192 MHz, [D$_6$]-benzene, 299 K): δ = 58.8 ($\nu_{1/2}$ ~ 950 Hz).

^{19}F NMR (564 MHz, [D$_6$]-benzene, 299 K): δ = -132.0 (m, 2F, o-C_6F_5), -154.6 (m, 1F, p-C_6F_5), -162.7 (m, 2F, m-C_6F_5), [$\Delta\delta^{19}F_{pm}$ = 8.1].

^{19}F, ^{19}F GCOSY (564 MHz/ 564 MHz, [D$_6$]-benzene, 299 K): δ^{19}F/ δ^{19}F = -132.0/-162.7 (o-C_6F_5/m-C_6F_5), -154.6/-162.7 (p-C_6F_5/m-C_6F_5).

^{1}H, ^{1}H GCOSY (600 MHz/ 600 MHz, [D$_6$]-benzene, 299 K): δ^1H/ δ^1H = 7.12/7.03, 7.02 (m-Ph/o-Ph, p-Ph) 7.03/2.59 (o-Ph/CH_2Ph), 6.58/2.26, 2.00 (m-Mes/o-CH_3, p-CH_3), 2.62/1.81 (CH_2P/ ^{P}CH_2B), 2.59/1.80 (CH_2Ph/ ^{Ph}CH_2B), 2.26/2.00 (o-CH_3/p-CH_3).

^{1}H, ^{13}C GHSQC (600 MHz/ 151 MHz, [D$_6$]-benzene, 299 K): δ^1H/ δ^{13}C = 7.12/128.6 (m-Ph/m-Ph), 7.03/128.1 (o-Ph/o-Ph), 7.02/125.9 (p-Ph/p-Ph), 6.58/130.5 (m-Mes/m-Mes), 2.62/24.6 (CH_2P/CH_2P), 2.59/31.6 (CH_2Ph/CH_2Ph), 2.26/23.0 (o-CH_3/o-CH_3), 2.00/20.7 (p-CH_3/p-CH_3), 1.81/24.2 (^{P}CH_2B/ ^{P}CH_2B), 1.80/29.9 (PhCH_2B/ PhCH_2B).

^{1}H, ^{13}C GHMBC (600 MHz/ 151 MHz, [D$_6$]-benzene, 299 K): δ^1H/ δ^{13}C = 7.12/144.4, 128.6 (m-Ph/i-Ph, m-Ph), 7.03/125.9, 31.6 (o-Ph/p-Ph, CH_2Ph) 7.02/128.1 (p-Ph/o-Ph), 6.58/142.1, 131.1, 23.0, 20.7 (m-Mes/o-Mes, i-Mes, o-CH_3, p-CH_3), 2.62/131.1, 24.2 (CH_2P/i-Mes, ^{P}CH_2B), 2.59/144.4, 128.1, 29.9 (CH_2Ph/i-Ph, o-Ph, ^{Ph}CH_2B), 2.26/142.1,

131.1 130.5 (o-CH_3/o-Mes, i-Mes, m-Mes), 2.00/138.7, 130.5 (p-CH_3/p-Mes, m-Mes), 1.81/ 29.9, 24.6 ($^{P}CH_2B$/ $^{Ph}CH_2B$, CH_2P), 1.80/144.4, 31.6, 24.2 ($^{Ph}CH_2B$/ i-Ph, $PhCH_2$, $^{P}CH_2B$).

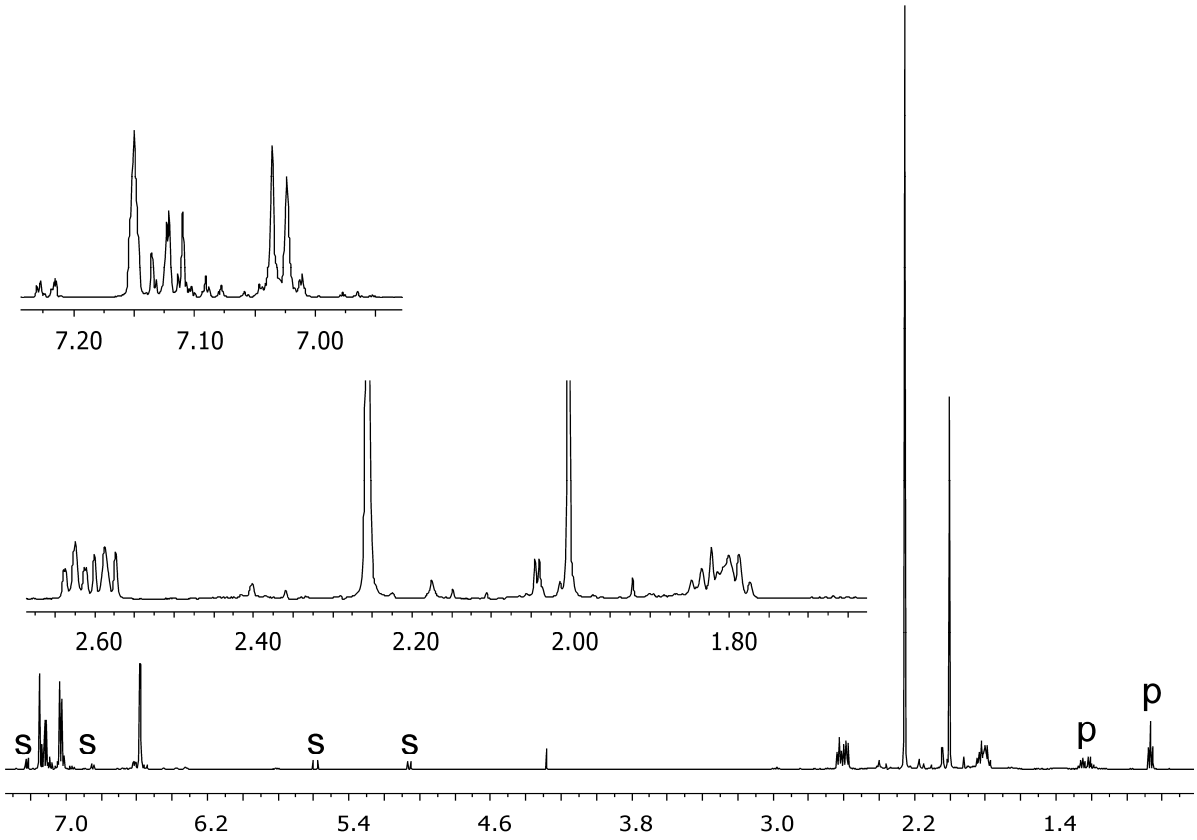


figure 23: ^{1}H NMR (600 MHz, [D_6]-benzene, 299 K) [p: pentane, s: styrene].

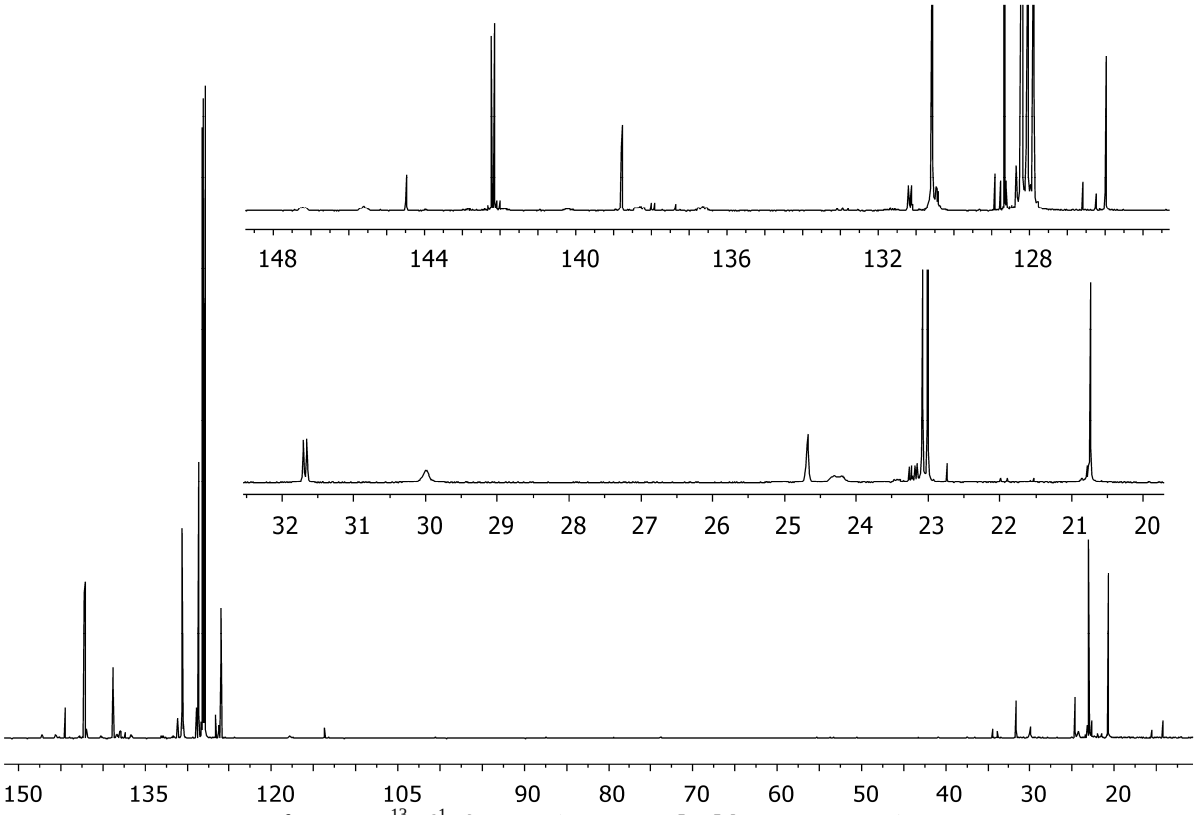


figure 24: $^{13}C\{^{1}H\}$ NMR (151 MHz, $[D_6]$-benzene, 299 K).

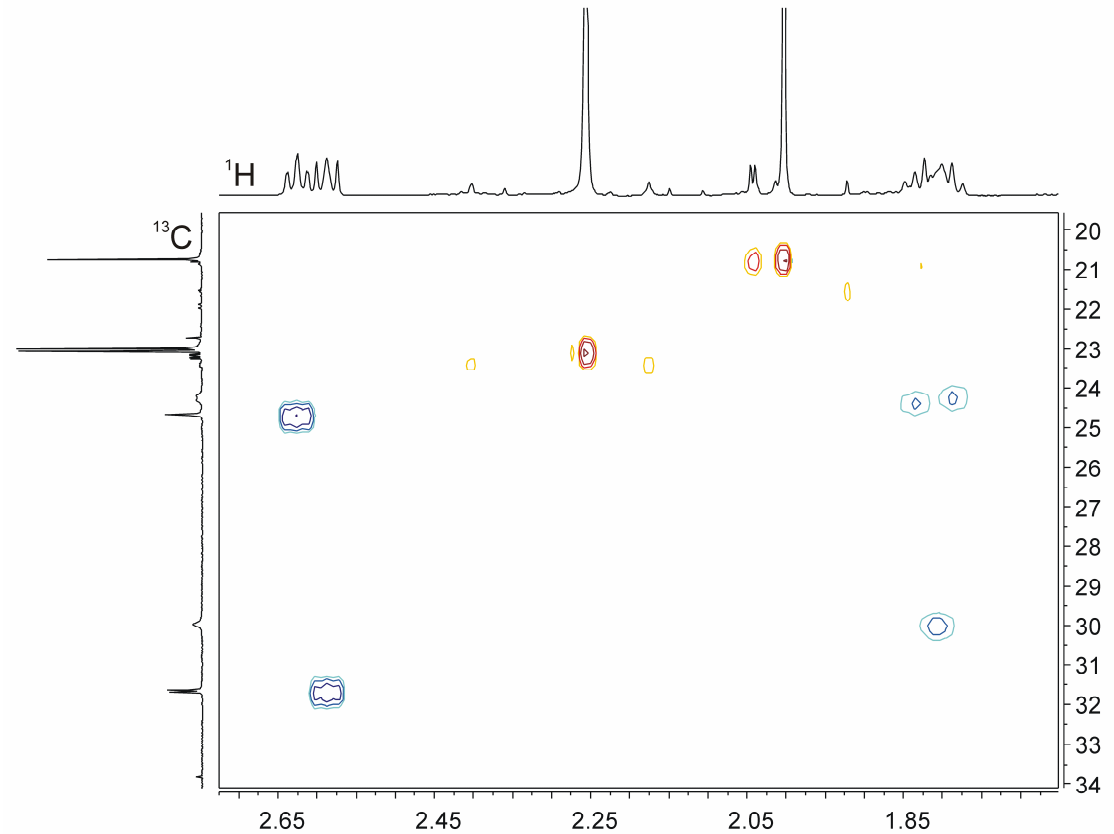


figure 25: ^{1}H, ^{13}C GHSQC (600 MHz/ 151 MHz, $[D_6]$-benzene, 299 K).

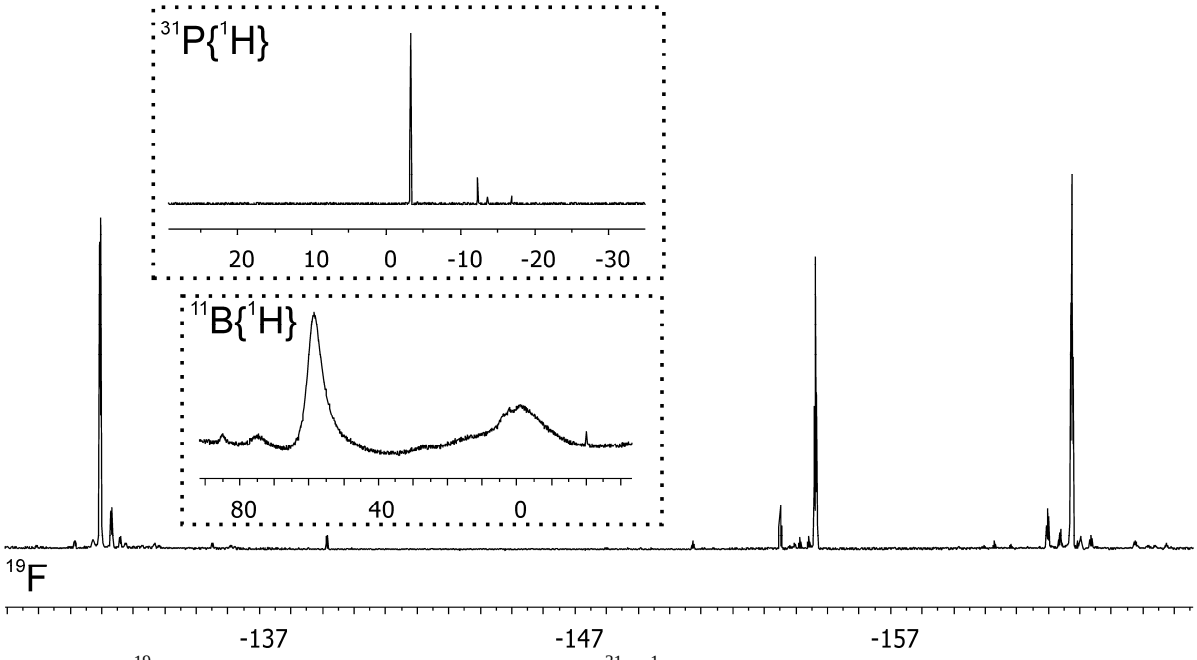
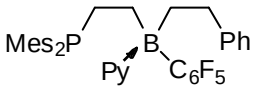


figure 26: ^{19}F NMR (564 MHz, $[D_6]$-benzene, 299 K), $^{31}P\{^1H\}$ NMR (243 MHz, $[D_6]$-benzene, 299 K) and $^{11}B\{^1H\}$ NMR (192 MHz, $[D_6]$-benzene, 299 K).

Compound 11



Compound **4** (100.0 mg, 0.21 mmol, 1.00 eq.) and styrene (24.0 µL, 0.21 mmol, 1.00 eq) were dissolved in toluene (20 mL) and stirred over night. Pyridine (17 µL, 0.21 mmol, 1.00 eq.) was added and the reaction mixture was again stirred over night. The solvent was removed *in vacuo* and to the remaining crude product pentane (10 mL) was added. The solution was stored at -40 °C over night, and the resulting colourless solid was separated by removal of the pentane through cannula and dried *in vacuo* (77.0 mg, 56 %). IR (KBr): $\tilde{\upsilon}$ = 4067 (w), 3022(s), 2960(s), 2920 (s), 2730 (w), 2320 (w), 2091 (w), 2005 (w), 1943 (w), 1869 (w), 1734 (w), 1641 (s), 1603 (s), 1514 (s), 1456 (s), 1375 (m), 1277 (s), 1217 (m), 1175 (m), 1083 (s), 1028 (m), 961 (s), 850 /s), 803 (m), 766 (m), 698 (s), 613 (m), 553 (m), 502 (w).

M. p.: 58 °C (DSC).

^{1}H NMR (500 MHz, [D$_6$]-benzene, 299 K): δ = 7.74 (m, 2H, o-Py), 7.18 (m, 2H, m-Ph), 7.14 (m, 2H, o-Ph), 7.06 (m, 1H, p-Ph), 6.72 (m, 2H, m-Mes^{a}), 6.671 (m, 1H, p-Py), 6.668 (m, 2H, m-Mes^{b}), 6.30 (m, 2H, m-Py), 2.45 (s, 6H, o-CH_3^{a}), 2.41/1.90 (each m, each 1H, CH_2P), 2.35 (s, 6H, o-CH_3^{b}), 2.26/2.13 (each m, each 1H, CH_2Ph), 2.09 (s, 3H, p-CH_3^{a}), 2.07 (s, 3H, p-CH_3^{b}), 1.46/1.26 (each m, each 1H, $^{Ph}CH_2$B), 1.43/1.15 (each m, each 1H, $^{P}CH_2$B).

^{13}C{^{1}H} NMR (126 MHz, [D$_6$]-benzene, 299 K): δ = 146.9 (i-Ph), 144.9 (o-Py), 142.2 (d, $^{2}J_{PC}$ = 12.7 Hz, o-Mes^{a}), 142.1 (d, $^{2}J_{PC}$ = 12.7 Hz, o-Mes^{b}), 139.3 (p-Py), 137.3 (p-Mes^{a}), 136.9 (p-Mes^{b}), 135.3 (d, $^{1}J_{PC}$ = 25.5 Hz, i-Mes^{b}), 135.0 (d, $^{1}J_{PC}$ = 24.5 Hz, i-Mes^{a}), 130.29 (d, $^{3}J_{PC}$ = 2.7 Hz, m-Mes^{a}), 130.26 (d, $^{3}J_{PC}$ = 2.6 Hz, m-Mes^{b}), 128.44 (m-Ph), 128.36 (o-Ph), 125.4 (p-Ph), 124.8 (m-Py), 32.8 (CH_2Ph), 26.6 (br, $^{Ph}CH_2$B), 24.1 (d, $^{1}J_{PC}$ = 15.9 Hz, CH_2P), 23.08 (d, $^{3}J_{PC}$ = 12.9 Hz, o-CH_3^{b}), 23.06 (d, $^{3}J_{PC}$ = 13.1 Hz, o-CH_3^{a}), 20.813, 20.810 (p-$CH_3^{a,b}$), 20.5 (br, $^{P}CH_2$B), [C_6F_5 not listed].

^{31}P NMR (202 MHz, [D$_6$]-benzene, 299 K): δ = -15.9 (s).

^{31}P{^{1}H} NMR (202 MHz, [D$_6$]-benzene, 299 K): δ = -15.9 ($\nu_{1/2}$ ~ 3 Hz).

^{11}B NMR (160 MHz, [D$_6$]-benzene, 299 K): δ = 1.6 ($\nu_{1/2}$ ~ 490 Hz).

^{11}B{^{1}H} NMR (160 MHz, [D$_6$]-benzene, 299 K): δ = 1.6 ($\nu_{1/2}$ ~ 470 Hz).

^{19}F NMR (470 MHz, [D$_6$]-benzene, 299 K): δ = -132.6 (m, 2F, o-C_6F_5), -159.2 (m, 1F, p-C_6F_5), -164.0 (m, 2F, m-C_6F_5), [$\Delta\delta^{19}F_{pm}$ = 4.8].

^{19}F, ^{19}F GCOSY (470 MHz/ 470 MHz, [D$_6$]-benzene, 299 K): δ^{19}F/ δ^{19}F = -132.6/-159.2, -164.0 (o-C_6F_5/p-C_6F_5, m-C_6F_5), -159.2/-164.0 (o-C_6F_5/m-C_6F_5).

^{1}H, ^{1}H GCOSY (500 MHz/ 500 MHz, [D$_6$]-benzene, 299 K): δ^{1}H/ δ^{1}H = 7.74/6.671, 6.30 (o-Py/p-Py, m-Py), 7.18/7.14, 7.06 (m-Ph/o-Ph, p-Ph), 7.14/7.06 (o-Ph/p-Ph) 6.72/2.45, 2.09 (m-Mes^{a}/o-CH$_3$^{a}, p-CH$_3$^{a}), 6.671/6.30 (p-Py/m-Py), 6.668/2.35, 2.07 (m-Mes^{b}/o-CH$_3$^{b}, p-CH$_3$^{b}), 2.45/2.09 (o-CH$_3$^{a}/p-CH$_3$^{a}), 2.41/1.90, 1.43, 1.15 (CH$_2$P/CH$_2$P, ^{P}CH$_2$B, ^{P}CH$_2$B), 2.35/2.07 (o-CH$_3$^{b}/p-CH$_3$^{b}), 2.26/2.13, 1.46, 1.26 (CH$_2$Ph/CH$_2$Ph,^{Ph}CH$_2$B, ^{Ph}CH$_2$B), 2.13/1.46, 1.26 (CH$_2$Ph/^{Ph}CH$_2$B, ^{Ph}CH$_2$B), 1.90/1.43, 1.15 (CH$_2$P/^{P}CH$_2$B, ^{P}CH$_2$B), 1.46/1.26 (^{Ph}CH$_2$B /^{Ph}CH$_2$B), 1.43/1.15 (^{P}CH$_2$B /^{P}CH$_2$B).

^{1}H, ^{13}C GHSQC (500 MHz/ 299 MHz, [D$_6$]-benzene, 233 K): δ^{1}H/ δ^{13}C = 7.74/144.9 (o-Py/o-Py), 7.18/128.44 (m-Ph/m-Ph), 7.14/128.36 (o-Ph/o-Ph), 7.06/125.4 (p-Ph/p-Ph), 6.72/130.29 (m-Mes^{a}/m-Mes^{a}), 6.671/139.3 (p-Py/p-Py), 6.668/130.26 (m-Mes^{b}/m-Mes^{b}), 6.30/124.8 (m-Py/m-Py), 2.45/23.06 (o-CH$_3$^{a}/o-CH$_3$^{a}), 2.41/24.1 (CH$_2$P/CH$_2$P), 2.35/23.08 (o-CH$_3$^{b}/o-CH$_3$^{b}), 2.26/32.8 (CH$_2$Ph/CH$_2$Ph), 2.09, 2.07/20.813, 20.810 (p-CH$_3$^{a}, p-CH$_3$^{b}/p-CH$_3$$^{a/b}$, p-CH$_3$$^{a/b}$), 1.90/24.1 (CH$_2P/CH_2$P), 1.46/26.6 (^{Ph}CH$_2$B /^{Ph}CH$_2$B), 1.43/20.5 (^{P}CH$_2$B /^{P}CH$_2$B), 1.26/26.6 (^{Ph}CH$_2$B /^{Ph}CH$_2$B), 1.15/20.5 (^{P}CH$_2$B /^{P}CH$_2$B).

^{1}H, ^{13}C GHMBC (500 MHz/ 126 MHz, [D$_6$]-benzene, 299 K): δ^{1}H/ δ^{13}C = 7.74/144.9, 139.3, 124.8 (o-Py/o-Py, p-Py, m-Py), 7.18/146.9, 128.44 (m-Ph/i-Ph, m-Ph), 7.14/128.36, 125.4, 32.8 (o-Ph/o-Ph, p-Ph, CH$_2$Ph), 6.72/135.0, 130.29, 23.06, 20.813, 20.810 (m-Mes^{a}/i-Mes^{a}, m-Mes^{a}, o-CH$_3$^{a}, p-CH$_3$$^{a/b}$), 6.671/144.9 (p-Py/o-Py), 6.668/135.3, 130.26, 23.08, 20.813, 20.810 (m-Mes^{b}/i-Mes^{b}, m-Mes^{b}, o-CH$_3$^{b}, p-CH$_3$$^{a/b}$), 6.30/144.9, 124.8 (m-Py/o-Py, m-Py), 2.45/142.2, 135.0, 130.29 (o-CH$_3$^{a}/o-Mes^{a}, i-Mes^{a}, m-Mes^{a}), 2.35/142.1, 135.3, 130.26 (o-CH$_3$^{b}/o-Mes^{b}, i-Mes^{b}, m-Mes^{b}), 2.26/146.9, 128.36, 26.6 (CH$_2$Ph/i-Ph, o-Ph, ^{Ph}CH$_2$B), 2.13/146.9, 128.36, 26.6 (CH$_2$Ph/i-Ph, o-Ph, ^{Ph}CH$_2$B), 2.09/137.3, 130.29 (p-CH$_3$^{a}/p-Mes^{a}, m-Mes^{a}), 2.07/136.9, 130.26 (p-CH$_3$^{b}/p-Mes^{b}, m-Mes^{b}), 1.90/135.3, 135.0, 20.5 (CH$_2$P/i-Mes^{b}, i-Mes^{a}, ^{P}CH$_2$B), 1.46/146.9, 32.8, 20.5 (^{Ph}CH$_2$B, i-Ph, CH$_2$Ph, ^{P}CH$_2$B), 1.26/146.9, 32.8, 20.5 (^{Ph}CH$_2$B, i-Ph, CH$_2$Ph, ^{P}CH$_2$B), 1.15/26.6, 24.1 (^{P}CH$_2$B /^{Ph}CH$_2$B, CH$_2$P).

^{13}C{^{1}H} NMR (126 MHz, [D$_6$]-benzene, 299 K): δ = 146.9 (i-Ph), 144.9 (o-Py), 142.2 (d, $^{2}J_{PC}$ = 12.7 Hz, o-Mes^{a}), 142.1 (d, $^{2}J_{PC}$ = 12.7 Hz, o-Mes^{b}), 139.3 (p-Py), 137.3 (p-Mes^{a}), 136.9 (p-Mes^{b}), 135.3 (d, $^{1}J_{PC}$ = 25.5 Hz, i-Mes^{b}), 135.0 (d, $^{1}J_{PC}$ = 24.5 Hz, i-Mes^{a}), 130.29 (d, $^{3}J_{PC}$ = 2.7 Hz, m-Mes^{a}), 130.26 (d, $^{3}J_{PC}$ = 2.6 Hz, m-Mes^{b}), 128.44 (m-Ph), 128.36 (o-Ph), 125.4 (p-Ph), 124.8 (m-Py), 32.8 (CH$_2$Ph), 26.6 (br, ^{Ph}CH$_2$B), 24.1 (d, $^{1}J_{PC}$ = 15.9 Hz, CH$_2$P,), 23.08 (d, $^{3}J_{PC}$ = 12.9 Hz, o-CH$_3$^{b}), 23.06 (d, $^{3}J_{PC}$ = 13.1 Hz, o-CH$_3$^{a}), 20.813, 20.810 (p-

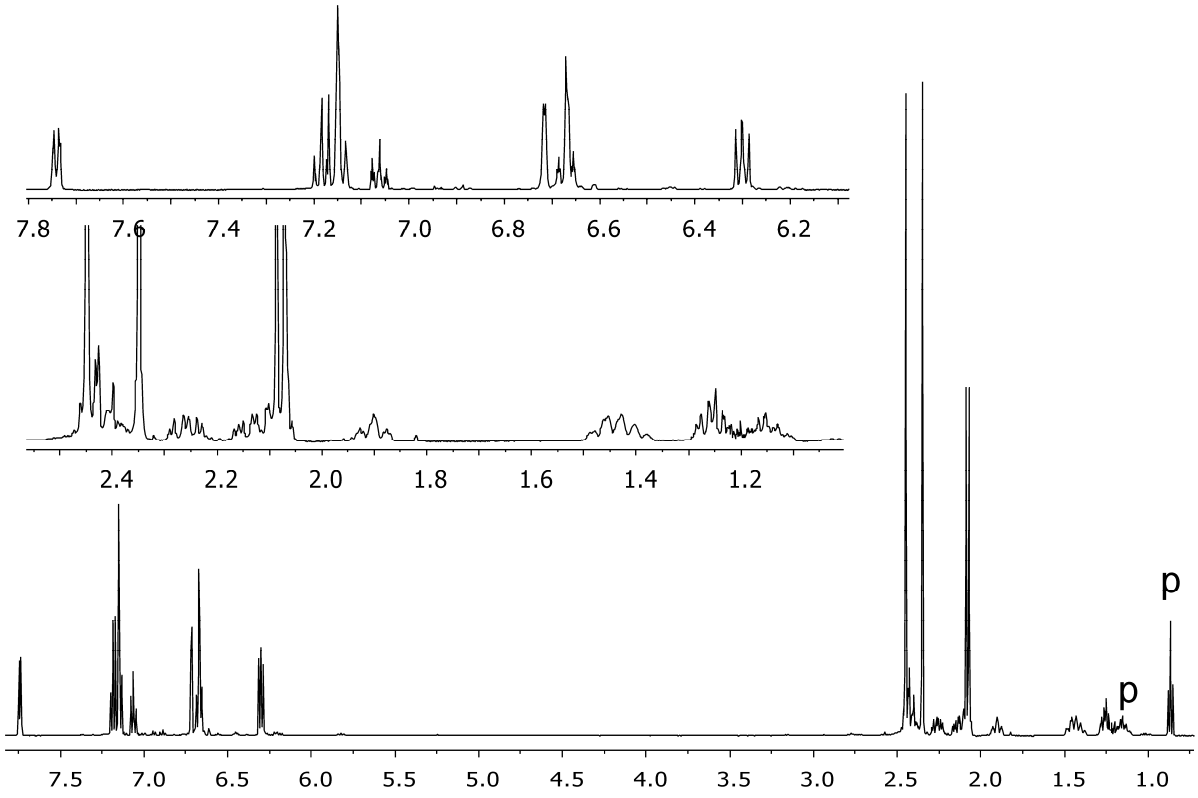


figure 27: ^{1}H NMR (500 MHz, [D_6]-benzene, 299 K).

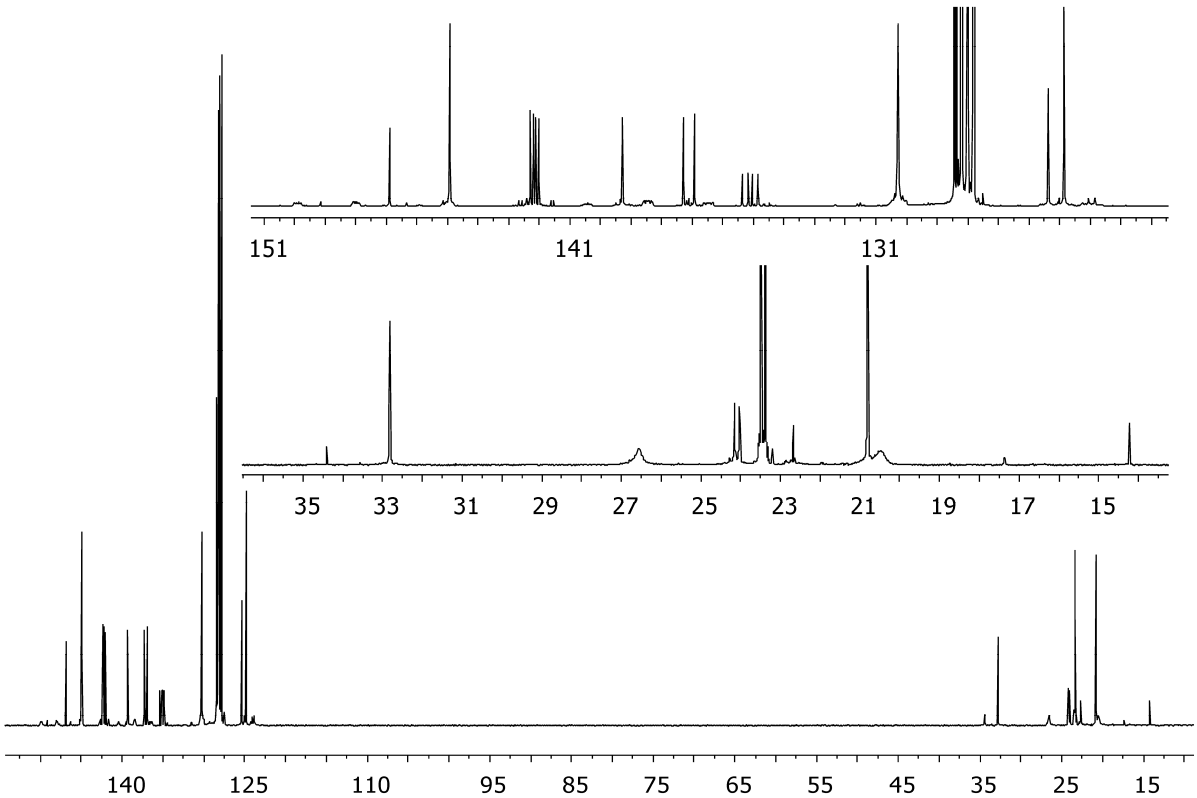


figure 28 ^{13}C{^{1}H} NMR (126 MHz, [D_6]-benzene, 299 K).

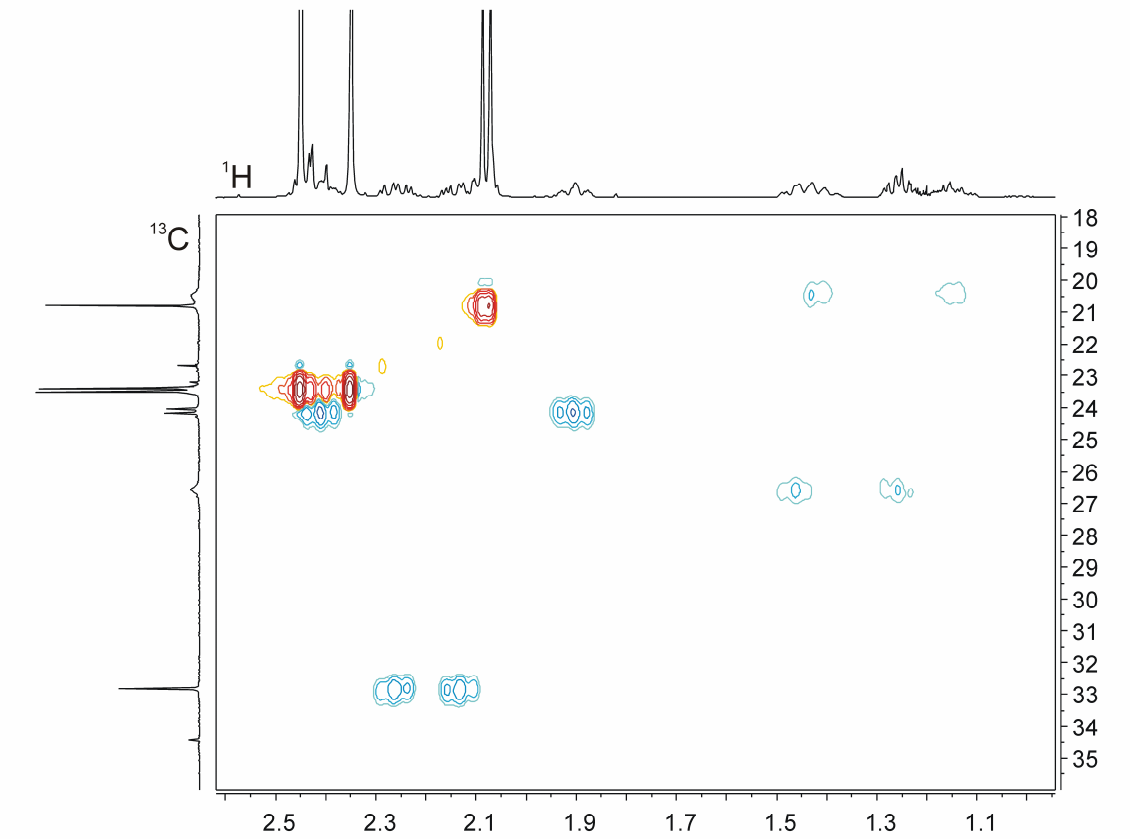


figure 29: ^{1}H, ^{13}C GHSQC (500 MHz/ 299 MHz, [D_6]-benzene, 299 K).

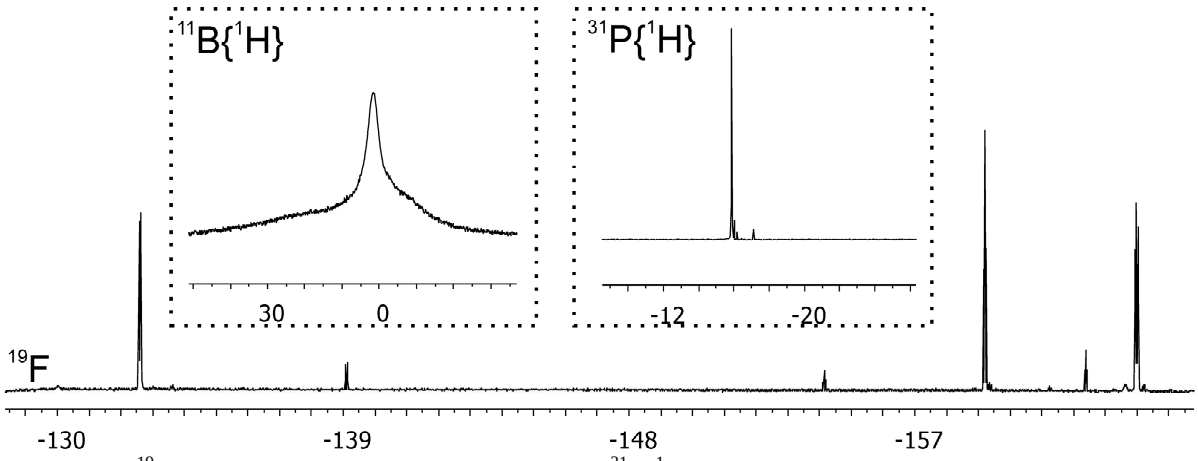
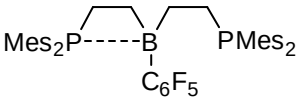


figure 30: ^{19}F NMR (470 MHz, [D_6]-benzene, 299 K), ^{31}P{^{1}H} NMR (202 MHz, [D_6]-benzene, 299 K) and ^{11}B{^{1}H} NMR (160 MHz, [D_6]-benzene, 299 K).

Compound 12



Compound **4** (16.1 mg, 0.03 mmol, 1.00 eq.) and dimesitylvinylphosphane (10.0 mg, 0.03 mmol, 1.00 eq.) were dissolved in 0.8 mL C_6D_6. After five days the desired product was formed (ratio of **12** and remaining dimesitylvinylphosphane from ^{1}H-NMR = 2:1).

^{1}H NMR (600 MHz, [D$_6$]-benzene, 299 K): δ = 6.60 (br, 4H, m-Mes), 2.56 (br m, 2H, CH_2P), 2.26 (br, 12H, o-CH_3), 2.03 (s, 6H, p-CH_3), 1.67 (br dm, $^3J_{PH}$ = 24.8 Hz, 2H, CH_2B).

^{13}C{^{1}H} NMR (151 MHz, [D$_6$]-benzene, 299 K): δ = 142.1 (br d, $^2J_{PC}$ ~ 12 Hz, o-Mes), 138.3 (br, p-Mes), 131.9 (br d, $^1J_{PC}$ ~ 12 Hz, i-Mes), 130.5 (br, m-Mes), 25.0 (br, CH_2P), 23.1 (br d, $^3J_{PC}$ = 12.4 Hz, o-CH_3), 22.4 (br, CH_2B), 20.7 (p-CH_3).

^{31}P NMR (243 MHz, [D$_6$]-benzene, 299 K): δ = -5.5 (m).

^{31}P{^{1}H} NMR (243 MHz, [D$_6$]-benzene, 299 K): δ = -5.5 (m).

^{11}B NMR (192 MHz, [D$_6$]-benzene, 299 K): δ = 40.5 ($\nu_{1/2}$ ~ 1200 Hz).

^{11}B{^{1}H} NMR (192 MHz, [D$_6$]-benzene, 299 K): δ = 40.5 ($\nu_{1/2}$ ~ 620 Hz).

^{19}F NMR (564 MHz, [D$_6$]-benzene, 299 K): δ = -131.5 (br m, 2F, o-C_6F_5), -155.8 (br, 1F, p-C_6F_5), -163.3 (br m, 2F, m-C_6F_5), [$\Delta\delta^{19}F_{pm}$ = 7.5].

^{19}F, ^{19}F GCOSY (564 MHz/ 564 MHz, [D$_6$]-benzene, 299 K): δ^{19}F/ δ^{19}F = -131.5/-163.3 (o-C_6F_5/m-C_6F_5), -155.8/-163.3 (p-C_6F_5/m-C_6F_5).

^{1}H, ^{1}H GCOSY (600 MHz/ 600 MHz, [D$_6$]-benzene, 299 K): δ^1H/ δ^1H = 6.60/2.26, 2.03 (m-Mes, o-CH_3, p-CH_3), 2.56/1.67 (CH_2P/CH_2B).

^{1}H, ^{13}C GHSQC (600 MHz/ 151 MHz, [D$_6$]-benzene, 299 K): δ^1H/ δ^{13}C = 6.60/130.5 (m-Mes/m-Mes), 2.56/25.0 (CH_2P/CH_2P), 2.26/23.1 (o-CH_3/o-CH_3), 2.03/20.7 (p-CH_3/p-CH_3), 1.67/22.4 (CH_2B/CH_2B).

^{1}H, ^{13}C GHMBC (600 MHz/ 151 MHz, [D$_6$]-benzene, 299 K): δ^1H/ δ^{13}C = 6.60/142.1, 131.9, 130.5, 23.1, 20.7 (m-Mes/o-Mes, i-Mes, m-Mes, o-CH_3, p-CH_3), 2.56/131.9, 22.4 (CH_2P/i-Mes, CH_2B), 2.26/142.1, 131.9, 130.5 (o-CH_3/o-Mes, i-Mes, m-Mes), 2.03/142.1, 131.9, 130.5 (p-CH_3/o-Mes, i-Mes, m-Mes), 1.67/25.0 (CH_2B/CH_2P).

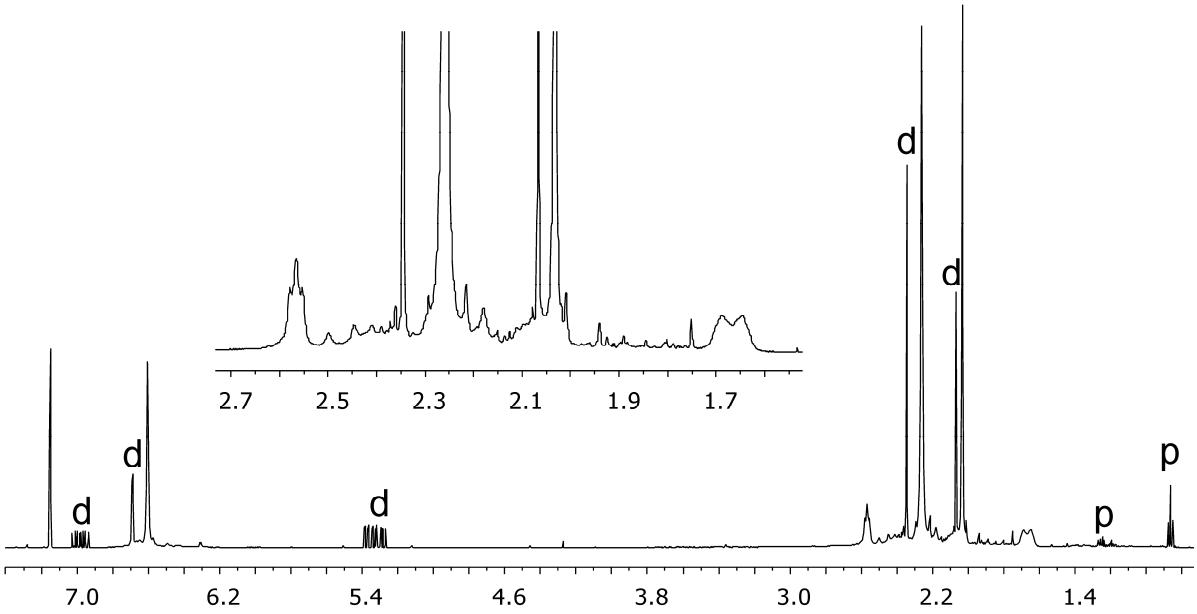


figure 31: ^{1}H NMR (600 MHz, [D_6]-benzene, 299 K) [p: pentane, d: dimesitylvinylphosphane].

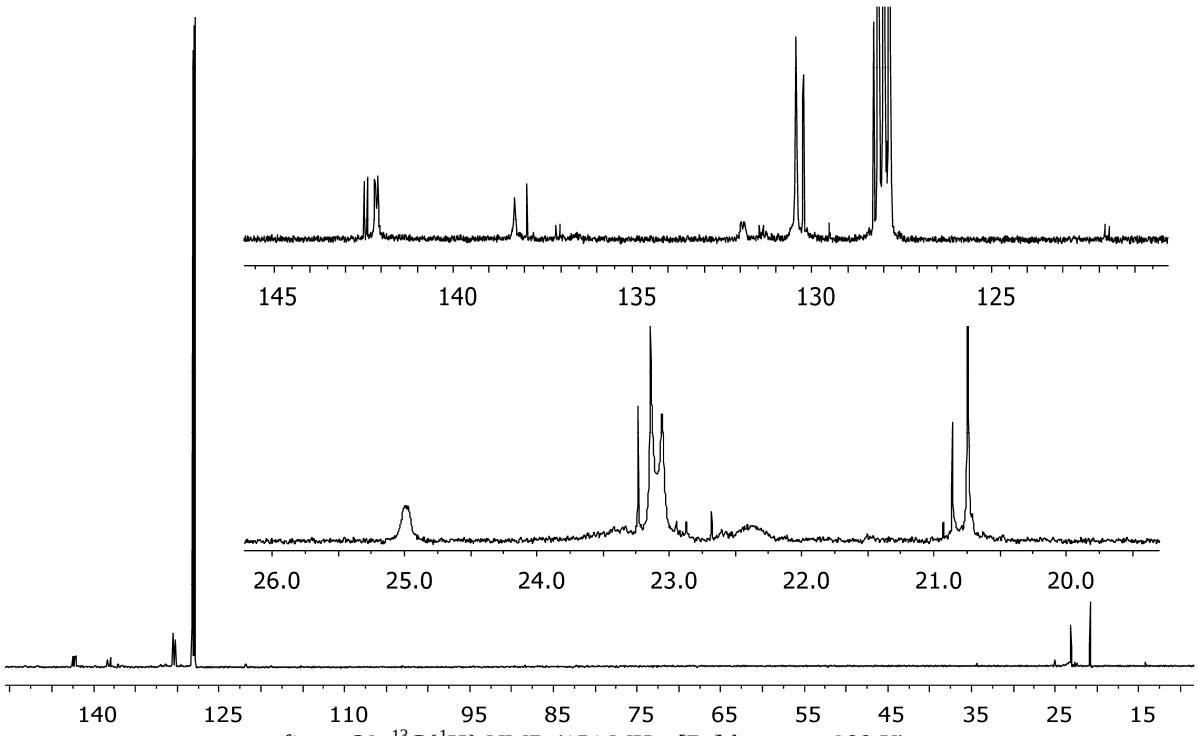


figure 32: $^{13}C\{^{1}H\}$ NMR (151 MHz, [D_6]-benzene, 299 K).

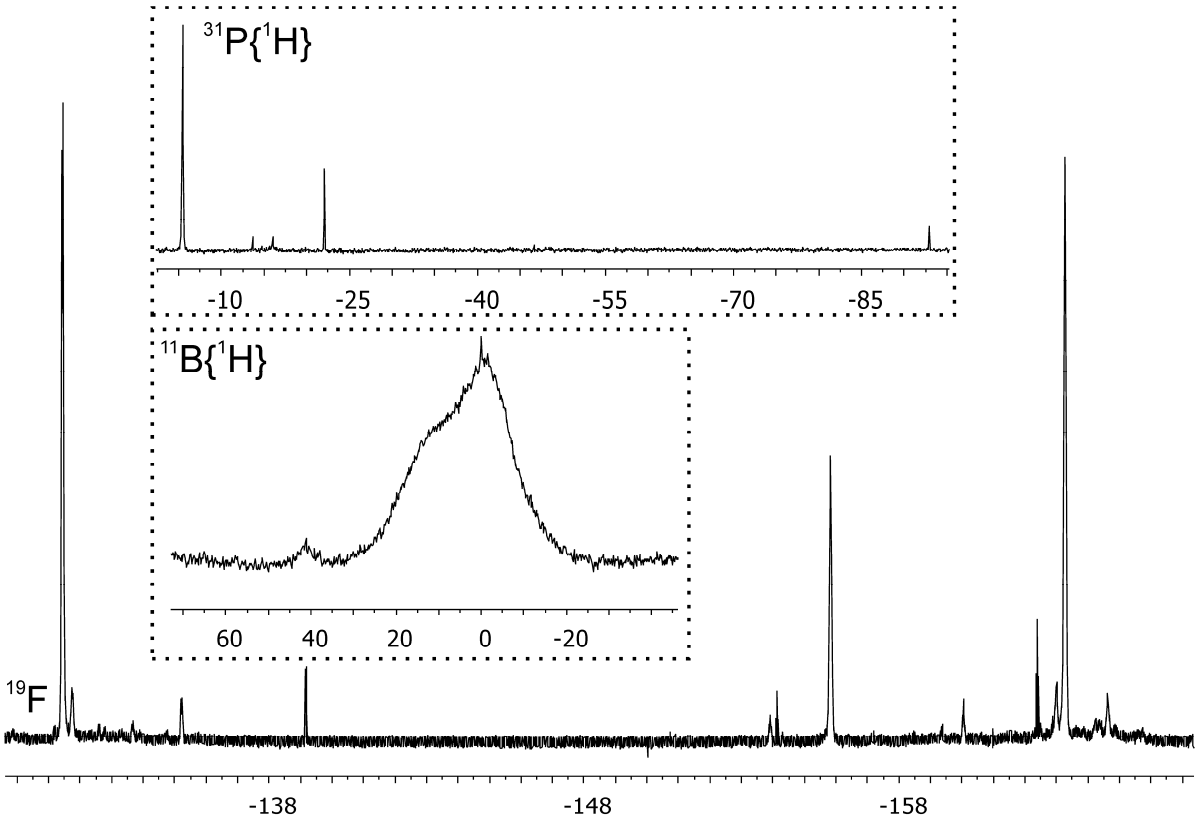


figure 33: ^{19}F NMR (564 MHz, [D_6]-benzene, 299 K), $^{31}P\{^1H\}$ NMR (202 MHz, [D_6]-benzene, 299 K) and $^{11}B\{^1H\}$ NMR (192 MHz, [D_6]-benzene, 299 K).

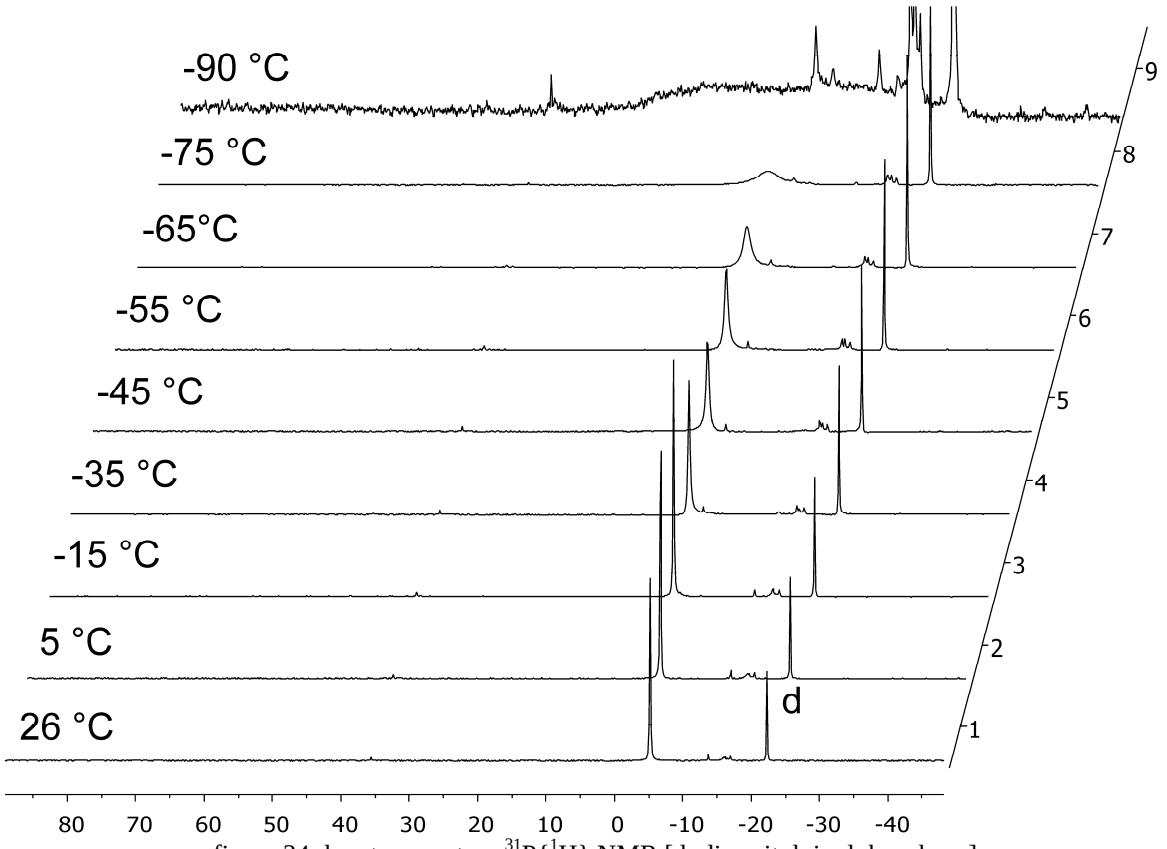
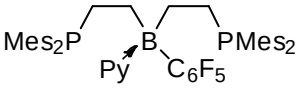


figure 34: low temperature $^{31}P\{^1H\}$ NMR [d: dimesitylvinylphosphane].

Compound 13



Compound **4** (100.0 mg, 0.21 mmol, 1.00 eq.) and dimesitylvinylphosphane (62.2 mg, 0.21 mmol, 1.00 eq.) were dissolved in toluene (10 mL) and stirred for six days. Then pyridine (17 µL, 0.21 mmol, 1.00 eq.) was added and the solution was stirred over night. The solvent was removed *in vacuo* and the remaining crude product was resolved in dichloromethane (10 mL). After removing the dichloromethane the crude product was dissolved in pentane (10 mL) and stored at -40 °C for one day. Since there was no crystallisation observed half of the pentane was removed and the solution was again stored at -40°C. After removing the pentane through cannula filtration the desired product could be obtained as a white solid (68.7 mg, 38%). Crystals suitable for X-ray crystal structure analysis were obtained by the diffusion method of a dichloromethane/heptane solution at -40 °C. Anal. calc. for $C_{51}H_{57}BF_5NP_2$ (851.76 g/mol): C 71.92; H 6.75; N 1.64; found: C 70.46; H 6.53; N 1.34.IR (KBr): $\tilde{\upsilon}$ = 4070 (w), 3745 (w), 2960 (m), 2918 (m), 2730 (w), 2361 (w), 2003 (w), 1923 (w), 1640 (m), 1603 (m), 1558 (m), 1513 (m), 1456 (m), 1375 (m), 1277 (m), 1215 (m), 1172 (m), 1114 (m), 1082 (m), 1027 (m), 970 (m), 849 (m), 806 (m), 769 (m), 692 (m), 614 (m), 554 (m), 407 (m).

M. p.: not observed between 40 and 350 °C (DSC).

^{1}H NMR (500 MHz, [D$_6$]-benzene, 299 K): δ = 7.67 (m, 2H, o-Py), 6.69 (m, 4H, m-Mes^{a}), 6.67 (m, 4H, m-Mes^{b}), 6.62 (m, 1H, p-Py), 6.24 (m, 2H, m-Py), 2.38 (s, 12H, o-CH_3^{a}), 2.34 (s, 12H, o-CH_3^{b}), 2.23/1.87 (each m, each 2H, CH_2P), 2.09 (s, 6H, p-CH_3^{a}), 2.06 (s, 6H, p-CH_3^{b}), 1.29/1.01 (each m, each 2H, CH_2B).

^{13}C{^{1}H} NMR (126 MHz, [D$_6$]-benzene, 299 K): δ = 144.8 (o-Py), 142.2 (d, $^{2}J_{PC}$ = 12.8 Hz, o-Mes^{b}), 142.1 (d, $^{2}J_{PC}$ = 12.7 Hz, o-Mes^{a}), 139.2 (p-Py), 137.1 (p-Mes^{a}), 137.0 (p-Mes^{b}), 135.17 (d, $^{1}J_{PC}$ = 25.1 Hz, i-Mes^{b}), 135.04 (d, $^{1}J_{PC}$ = 25.1 Hz, i-Mes^{a}), 130.23 (d, $^{3}J_{PC}$ = 2.4 Hz, m-Mes^{a}), 130.21 (d, $^{3}J_{PC}$ = 2.5 Hz, m-Mes^{b}), 124.8 (m-Py), 23.8 (d, $^{1}J_{PC}$ = 15.9 Hz, CH_2P), 23.5, 23.4 (o-$CH_3^{a,b}$), 20.8 (p-$CH_3^{a,b}$), 20.1 (br, CH_2B), [C_6F_5 not listed].

^{31}P NMR (202 MHz, [D$_6$]-benzene, 299 K): δ = -15.8 (s).

^{31}P{^{1}H} NMR (202 MHz, [D$_6$]-benzene, 299 K): δ = -15.8 ($\nu_{1/2}$ ~ 3 Hz).

^{11}B NMR (160 MHz, [D$_6$]-benzene, 299 K): δ = 1.5 ($\nu_{1/2}$ ~ 610 Hz).

^{11}B{^{1}H} NMR (160 MHz, [D$_6$]-benzene, 299 K): δ = 1.5 ($\nu_{1/2}$ ~ 660 Hz).

^{19}F NMR (470 MHz, [D$_6$]-benzene, 299 K): δ = -132.7 (m, 2F, o-C_6F_5), -159.5 (m, 1F, p-C_6F_5, -164.0 (m, 2F, m- C_6F_5), [$\Delta\delta^{19}F_{pm}$ = 4.5].

^{19}F, ^{19}F GCOSY (470 MHz/ 470 MHz, [D$_6$]-benzene, 299 K): δ^{19}F/ δ^{19}F = -132.7/-164.0 (o-C_6F_5/ m-C_6F_5), -159.5/-164.0 (p- C_6F_5/m- C_6F_5).

^{1}H, ^{1}H GCOSY (500 MHz/ 500 MHz, [D$_6$]-benzene, 299 K): δ^{1}H/ δ^{1}H = 7.67/6.62, 6.24 (o-Py/p-Py, m-Py), 6.69/2.38, 2.09 (m-Mes^a/o-CH_3^a, p-CH_3^a), 6.67/2.34, 2.06 (m-Mes^b/o-CH_3^b, p-CH_3^b), 6.62/6.24 (p-Py/m-Py), 2.38/2.09 (o-CH_3^a/p-CH_3^a), 2.34/2.06 (o-CH_3^b/p-CH_3^b), 2.23/1.87, 1.29, 1.01 (CH_2P/CH_2P, CH_2B, CH_2B), 1.87/1.29, 1.01 (CH_2P/CH_2B, CH_2B), 1.29/1.01 (CH_2B/ CH_2B).

^{1}H, ^{13}C GHSQC (500 MHz/ 126 MHz, [D$_6$]-benzene, 299 K): δ^{1}H/ δ^{13}C = 7.67/144.8 (o-Py/o-Py), 6.69/130.23 (m-Mes^a/m-Mes^a) 6.67/130.21 (m-Mes^b/m-Mes^b), 6.62/139.2 (p-Py/p-Py), 6.24/124.8 (m-Py/m-Py), 2.38/23.5, 23.4 (o-CH_3^a/o-$CH_3^{a,b}$), 2.34/23.5, 23.4 (o-CH_3^b/o-$CH_3^{a,b}$), 2.23/23.8 (CH_2P/CH_2P), 2.09, 2.06/20.8 (p-CH_3^a, p-CH_3^b/p-$CH_3^{a,b}$), 1.87/23.8 (CH_2P/CH_2P), 1.29/20.1 (CH_2B/CH_2B), 1.01/20.1 (CH_2B/CH_2B).

^{1}H, ^{13}C GHMBC (500 MHz/ 126 MHz, [D$_6$]-benzene, 299 K): δ^{1}H/ δ^{13}C = 7.67/144.8, 139.2, 124.8 (o-Py/o-Py, p-Py, m-Py), 6.69/142.1, 135.04, 130.23, 23.5, 23.4, 20.8 (m-Mes^a/o-Mes^a, i-Mes^a, m-Mes^a, o-CH_3^a, p-CH_3^a), 6.67/142.2, 135.17, 130.21, 23.5, 23.4, 20.8 (m-Mes^b/-Mes^b, i-Mes^b, m-Mes^b, o-CH_3^b, p-$CH_3^{a,b}$), 6.62/144.8 (p-Py/o-Py), 6.24/144.8, 124.8 (m-Py/o-Py, m-Py), 2.39/142.1, 135.04, 130.23 (o-CH_3^a/o-Mes^a, i-Mes^a, m-Mes^a), 2.34/142.2, 135.17, 130.21 (o-CH_3^b/o-Mes^b, i-Mes^b, m-Mes^b), 2.09/137.1, 130.23 (p-CH_3^a/p-Mes^a, m-Mes^a), 2.06/137.0, 130.21 (p-CH_3^b/p-Mes^b, m-Mes^b).

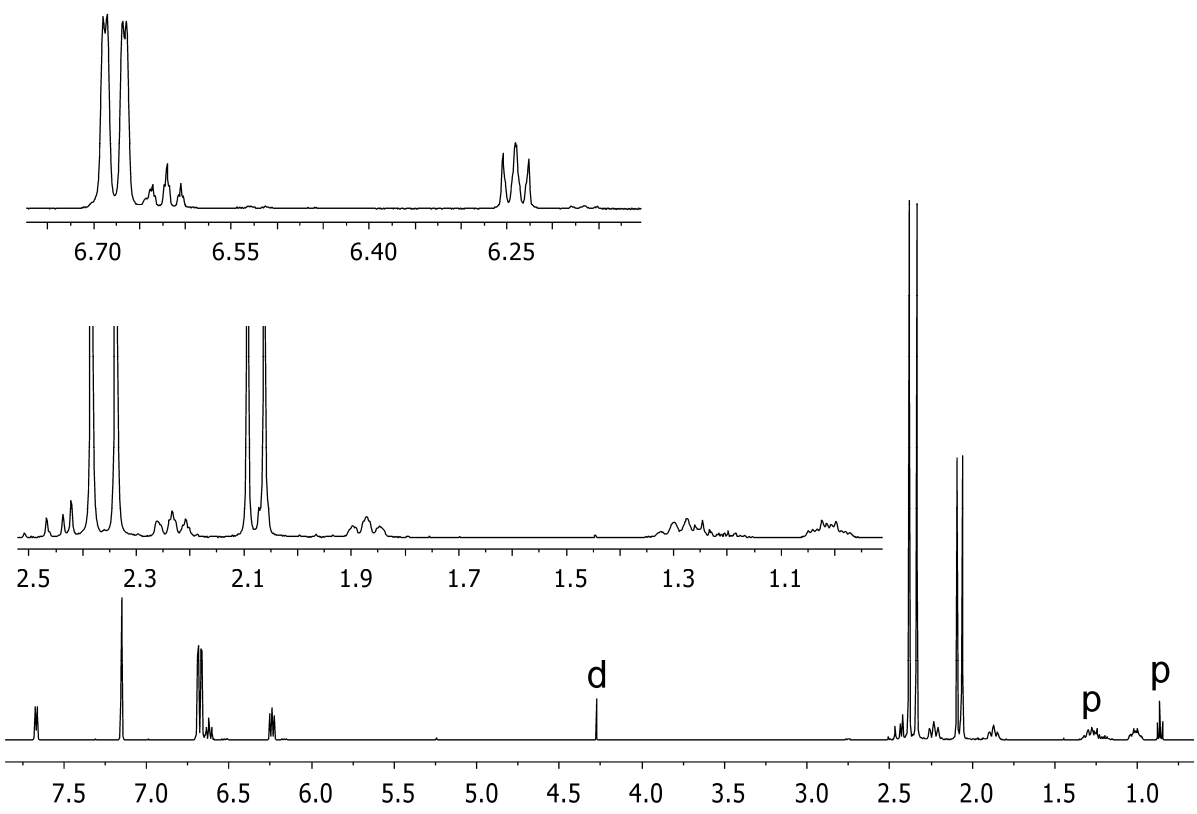


figure 35: ^{1}H NMR (500 MHz, [D_6]-benzene, 299 K) [p: pentane, d: dichloromethane].

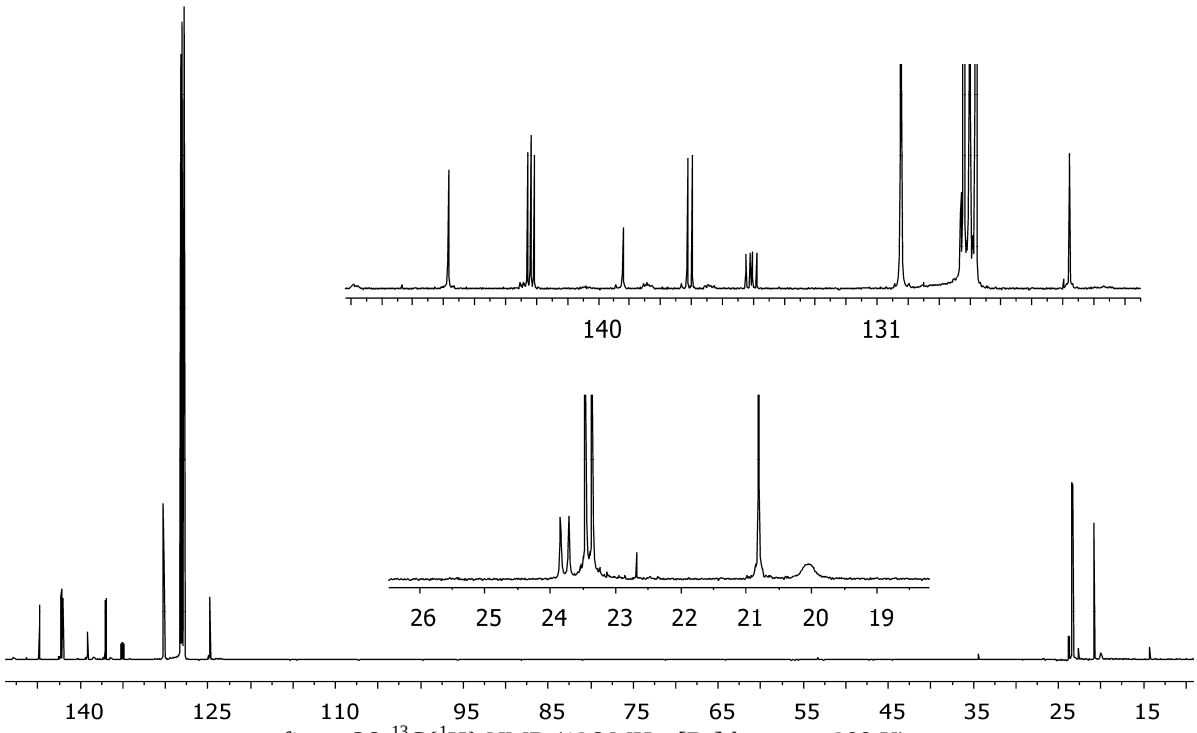


figure 36: ^{13}C{^{1}H} NMR (126 MHz, [D_6]-benzene, 299 K).

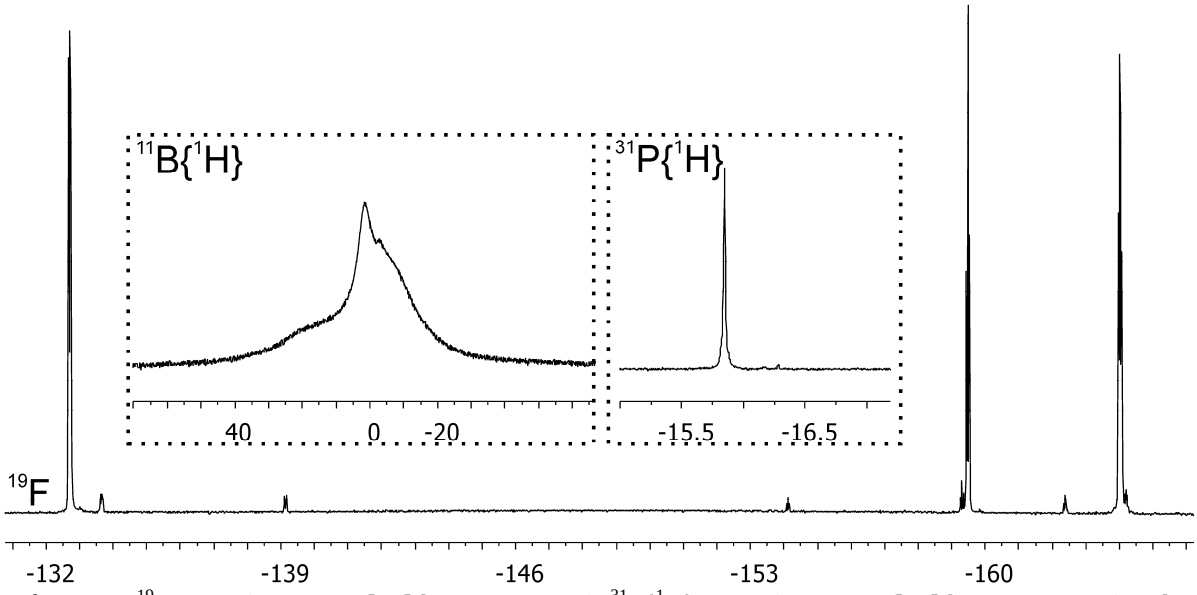
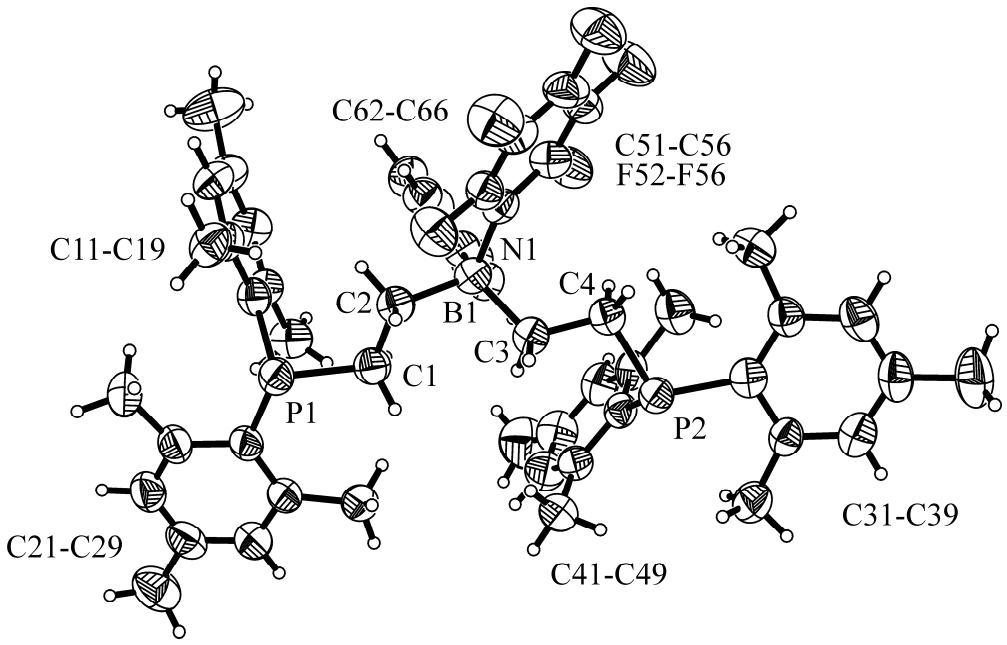


figure 37: ^{19}F NMR (470 MHz, [D_6]-benzene, 299 K), $^{31}P\{^1H\}$ NMR (202 MHz, [D_6]-benzene, 299 K) and $^{11}B\{^1H\}$ NMR (160 MHz, [D_6]-benzene, 299 K).

X-ray crystal structure analysis of 13: formula $C_{51}H_{57}BF_5NP_2$, M = 851.73, colourless crystal, 0.10 x 0.08 x 0.05 mm, a = 10.8480(20), b = 13.0140(30), c = 19.4660(40) Å, α = 95.900(30), β = 92.540(30), γ = 110.500(30) º, V = 2550.9(9) Å^3, ρ_{calc} = 1.109 gcm^{-3}, μ = 1.183 mm^{-1}, empirical absorption correction (0.890 ≤ T ≤ 0.943), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 29514 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 8352 independent (R_{int} = 0.114) and 4806 observed reflections [I>2σ(I)], 553 refined parameters, R = 0.066, wR^2 = 0.176, max. (min.) residual electron density 0.27 (-0.23) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Computational work by the Uhl/Würthwein group:

Quantum Chemical Results

Optimized Cartesian coordinates, total energies (without zero point correction) [au] and numbers of imaginary frequencies (in parenthesis) for the calculated structures at the DFT-level B97-D/def2/TZVP//B97-D/def2-TZVP (EMSL)

Compound 14
-1350.6121234 (0)

14	0	-2.788612	-1.566458	-0.782617
13	0	0.118536	0.519166	0.090355
7	0	1.337586	-1.126933	-0.430441
6	0	2.225951	-1.011441	-1.618478
1	0	1.695865	-0.422970	-2.373773
1	0	2.431031	-2.018037	-2.016596
6	0	2.042373	-1.861679	0.653898
1	0	2.242982	-2.892728	0.321874
1	0	1.378738	-1.885557	1.524214
6	0	3.534089	-0.326799	-1.234205
1	0	4.189009	-0.283267	-2.113799
1	0	3.315543	0.715481	-0.921358
6	0	3.352474	-1.163310	1.001975
1	0	3.125715	-0.159032	1.418329
1	0	3.872993	-1.739055	1.778023
7	0	4.215825	-1.069404	-0.174867
6	0	5.494852	-0.454195	0.158892
1	0	5.379986	0.584075	0.536473
1	0	6.132392	-0.427726	-0.733890
1	0	5.996981	-1.049307	0.932099
6	0	-1.037530	-1.005808	-0.513103
6	0	0.037291	-1.762692	-0.759544
1	0	0.120661	-2.783543	-1.160063
6	0	-3.630355	-1.793067	0.902514
1	0	-3.624628	-0.861664	1.482666
1	0	-3.119408	-2.562054	1.498886
1	0	-4.676451	-2.107337	0.774046
6	0	-2.845856	-3.216974	-1.721425
1	0	-3.882178	-3.554065	-1.869094
1	0	-2.317189	-4.008929	-1.171464
1	0	-2.380206	-3.130577	-2.713625
6	0	-3.724171	-0.251206	-1.775369
1	0	-3.758810	0.705648	-1.237651
1	0	-4.759280	-0.568468	-1.967991
1	0	-3.242007	-0.066364	-2.745532
6	0	0.549624	2.000539	-1.185224
1	0	1.623716	2.245566	-1.100256
1	0	0.405569	1.673958	-2.231181
6	0	0.265393	0.860608	2.058561

1	0	1.121578	0.296950	2.469010
1	0	0.503730	1.922017	2.252085
6	0	-0.261510	3.299427	-0.976749
1	0	-0.133912	3.624529	0.068918
6	0	-0.996154	0.500579	2.876500
1	0	-1.253549	-0.552096	2.677406
6	0	-2.188264	1.359930	2.432862
1	0	-1.959581	2.426077	2.576013
1	0	-3.093839	1.123990	3.008496
1	0	-2.415177	1.204841	1.369341
6	0	-1.758515	3.050275	-1.210234
1	0	-1.926912	2.697197	-2.237741
1	0	-2.347296	3.965812	-1.061324
1	0	-2.148596	2.282579	-0.528893
6	0	0.231929	4.437669	-1.884578
1	0	0.108689	4.154712	-2.940560
1	0	1.297183	4.641682	-1.711545
1	0	-0.332011	5.366357	-1.712332
6	0	-0.765272	0.654249	4.388227
1	0	-0.514442	1.698655	4.625337
1	0	0.070455	0.024059	4.721700
1	0	-1.659720	0.377565	4.965815

9-BBN
-338.5965126 (0)

6	0	1.308786	1.295183	-0.138349
6	0	1.568050	0.000000	-0.938488
6	0	1.308787	-1.295182	-0.138349
6	0	0.000000	-1.306045	0.713523
6	0	-1.308786	-1.295183	-0.138349
6	0	-1.568050	0.000000	-0.938488
6	0	-1.308787	1.295182	-0.138349
6	0	0.000000	1.306045	0.713523
5	0	0.000000	0.000000	1.595592
1	0	1.300941	2.155539	-0.825596
1	0	2.154393	1.456202	0.548525
1	0	0.961650	0.000000	-1.848666
1	0	2.614306	0.000001	-1.276105
1	0	2.154394	-1.456200	0.548526
1	0	1.300944	-2.155539	-0.825594
1	0	0.000001	-2.236185	1.298738
1	0	-2.154392	-1.456202	0.548525
1	0	-1.300941	-2.155539	-0.825595
1	0	-0.961650	0.000000	-1.848666
1	0	-2.614306	-0.000001	-1.276105
1	0	-2.154394	1.456200	0.548526
1	0	-1.300944	2.155539	-0.825594
1	0	-0.000001	2.236185	1.298738
1	0	0.000000	0.000000	2.802340

Compound 15
-495.8155631 (0)

6	0	1.738282	0.848121	-1.570442
6	0	2.148793	1.643890	-0.312667
6	0	1.070506	1.671333	0.794015
6	0	0.357020	0.313847	1.068506
6	0	1.278817	-0.766473	1.715524
6	0	2.433825	-1.266747	0.822550
6	0	2.016303	-1.578750	-0.631477
6	0	1.070843	-0.531783	-1.293108
5	0	-0.142822	-0.280009	-0.310194
6	0	-1.627290	-0.662379	-0.675519
6	0	-2.756213	-0.155189	0.238374
6	0	-4.101001	-0.809353	-0.105902
6	0	-2.859162	1.374177	0.153202
1	0	2.618931	0.709459	-2.216999
1	0	1.022867	1.454056	-2.149115
1	0	3.082785	1.240143	0.088799
1	0	2.373827	2.678541	-0.608514
1	0	0.296641	2.399047	0.504518
1	0	1.515169	2.048708	1.728180
1	0	-0.459295	0.510583	1.777691
1	0	0.645373	-1.626597	1.985240
1	0	1.690075	-0.377808	2.660310
1	0	3.244506	-0.532785	0.826408
1	0	2.855136	-2.178143	1.270593
1	0	1.492751	-2.547696	-0.641864
1	0	2.917992	-1.707874	-1.250577
1	0	0.756249	-0.943650	-2.264261
1	0	-1.636686	-1.771220	-0.699915
1	0	-1.842265	-0.380339	-1.722346
1	0	-2.498357	-0.420794	1.275226
1	0	-4.385490	-0.569459	-1.141046
1	0	-4.041174	-1.902720	-0.017921
1	0	-4.901440	-0.452298	0.556877
1	0	-3.110627	1.677753	-0.873793
1	0	-3.640017	1.760694	0.821856
1	0	-1.907180	1.848286	0.423294

Compound 16
-1532.0495381 (0)

13	0	-0.260845	-0.469645	0.549120
1	0	-0.503946	1.345621	0.595867
1	0	1.068872	0.344960	-0.265888
6	0	-1.808344	-1.078237	-0.526731
6	0	-1.105558	-2.066501	-1.090694
1	0	-1.399979	-2.823208	-1.830907
7	0	0.308772	-2.135348	-0.660463

6	0	1.240139	-1.876501	-1.793432
1	0	0.984519	-0.900527	-2.218491
1	0	1.104971	-2.655422	-2.560077
6	0	2.680655	-1.872676	-1.295265
1	0	3.354921	-1.718194	-2.147066
1	0	2.816420	-1.018827	-0.599032
7	0	3.012229	-3.145342	-0.654922
6	0	4.403552	-3.165019	-0.218288
1	0	4.622220	-2.377103	0.532983
1	0	5.060296	-3.008719	-1.083304
1	0	4.634328	-4.141172	0.226611
6	0	2.105246	-3.396313	0.465279
1	0	2.206627	-2.619912	1.251741
1	0	2.357383	-4.365656	0.913799
6	0	0.656124	-3.426779	-0.011057
1	0	0.512632	-4.248042	-0.731149
1	0	-0.021849	-3.569037	0.837151
6	0	0.169012	-0.814221	2.452917
1	0	-0.293405	-1.755741	2.799997
1	0	1.256792	-0.964597	2.560979
6	0	-0.269887	0.320732	3.407876
1	0	0.214619	1.250970	3.075336
6	0	0.169260	0.046929	4.854347
1	0	-0.113541	0.872182	5.523741
1	0	1.257559	-0.088143	4.912921
1	0	-0.306681	-0.872480	5.226560
6	0	-1.789348	0.536817	3.342643
1	0	-2.317684	-0.388293	3.615817
1	0	-2.110425	0.822109	2.330645
1	0	-2.110383	1.329746	4.031529
5	0	0.557041	1.504178	-0.082205
6	0	0.247014	2.172684	-1.517596
1	0	-0.481306	1.595222	-2.108485
6	0	1.569791	2.199274	-2.322633
1	0	1.832228	1.154784	-2.559199
1	0	1.424671	2.708833	-3.289122
6	0	2.774038	2.845976	-1.598541
1	0	3.694700	2.577888	-2.137955
1	0	2.697274	3.935104	-1.672571
6	0	2.935193	2.442428	-0.113924
1	0	3.672876	3.113827	0.354790
1	0	3.367955	1.429336	-0.075638
6	0	1.626500	2.410983	0.715177
1	0	1.880211	1.999656	1.704261
6	0	0.979170	3.798583	0.948742
1	0	0.147659	3.654504	1.656713
1	0	1.694406	4.479680	1.437918
6	0	0.425835	4.490745	-0.319965
1	0	1.252107	4.946719	-0.874656
1	0	-0.220479	5.325382	-0.011101
6	0	-0.379014	3.565939	-1.263333

1	0	-0.546100	4.093511	-2.216761
1	0	-1.373256	3.398831	-0.821597
14	0	-3.577004	-0.615098	-0.870324
6	0	-4.588193	-0.864680	0.713354
1	0	-4.594248	-1.920314	1.019635
1	0	-5.632040	-0.551521	0.566506
1	0	-4.173437	-0.278604	1.544553
6	0	-4.310959	-1.665917	-2.268479
1	0	-3.739719	-1.543048	-3.199795
1	0	-5.351592	-1.378511	-2.477380
1	0	-4.308683	-2.735090	-2.011946
6	0	-3.605914	1.214238	-1.358157
1	0	-3.169368	1.839206	-0.567282
1	0	-4.633660	1.561474	-1.537055
1	0	-3.023501	1.392407	-2.272346