Electronic Supplementary Material (ESI) for Chemical Science.

Electrophilic *Bis*-Fluorophosphonium Dications: Lewis Acid Catalysts from Diphosphines

Michael H. Holthausen, Rashi R. Hiranandani and Douglas W. Stephan

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using 5, [Ph_3PF][$B(C_6F_5)_4$] and 9a-e as catalysts

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using 5, [Ph_3PF][$B(C_6F_5)_4$] and 9a-e as catalysts

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using 5, [Ph_3PF][$B(C_6F_5)_4$] and 9a-e as catalysts

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1. Materials and Methods

General Remarks

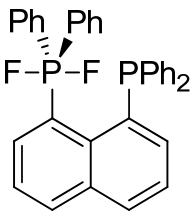
All manipulations were performed in a glove box MB Unilab produced by MBraun or using standard Schlenk techniques[S1] under an inert atmosphere of anhydrous N_2. Dry, oxygen-free solvents (CH_2Cl_2, *n*-pentane, toluene) were prepared using an Innovative Technologies solvent purification system. Fluorobenzene (C_6H_5F) was distilled from CaH_2 and stored over molecular sieves (4 Å) prior to use. Deuterated dichloromethane (CD_2Cl_2) and bromobenzene (C_6D_5Br) were purchased from Sigma-Aldrich, distilled from CaH_2 and stored over molecular sieves (4 Å) for at least two days prior to use. Reagents such as 1,8-Bis(diphenylphosphino)naphthalene, 1,1-Bis(diphenylphosphino)methane, 1,2-Bis(diphenylphosphino)ethane, 1,3 Bis(diphenylphosphino) propane, 1,4-Bis(diphenylphosphino)butane, 1,5-Bis(diphenylphosphino)pentane, XeF_2, Et_3PO, Et_3SiH, Ph_3P, 1-fluoropentane, 1,1-diphenylethylene, phenol and benzophenone were purchased either from Sigma-Aldrich, Strem Chemicals or Alfa Aesar and, if applicable, distilled prior to use. Compound $[Et_3Si][B(C_6F_5)_4]*2(C_7H_8)$ was prepared according to a literature known procedure.[S2] All glassware was oven-dried at temperatures above 180°C prior to use. NMR spectra were measured on a Bruker AVANCE 400 (^{1}H: 400 MHz, ^{11}B: 128 MHz, ^{13}C: 101 MHz, ^{31}P: 162 MHz, ^{19}F: 377 MHz) or Agilent DD2 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz, ^{31}P: 202 MHz, ^{19}F: 471 MHz) at ambient temperature. All ^{13}C NMR spectra were exclusively recorded with composite pulse decoupling. Assignments of the carbon atoms in the ^{13}C spectra were performed via indirect deduction from the cross-peaks in 2D correlation experiments (HMBC; HSQC). Chemical shifts were referenced to $\delta_{TMS} = 0.00$ ppm (^{1}H, ^{13}C), $\delta_{BF3*OEt2} = 0.00$ ppm (^{11}B), $\delta_{CFCl3} = 0.00$ ppm (^{19}F) and $\delta_{H3PO4(85\%)} = 0.00$ ppm (^{31}P, externally). Chemical shifts (δ) are reported in ppm, multiplicity is reported as follows (s = singlet, d = doublet, t = triplet, m = multiplet) and coupling constants (*J*) are reported in Hz. Assignments of individual resonances were done using 2D techniques (HMBC, HSQC, HH-COSY) when necessary. Yields of products in solution were determined by integration of all resonances observed in the respective NMR spectra if not stated otherwise. High-resolution mass spectra (HRMS) were obtained on a micro mass 70S-250 spectrometer (EI), an ABI/Sciex QStar Mass Spectrometer (DART), or on a JOEL AccuTOF-DART (DART). Elemental analyses (C, H, N) were performed at the University of Toronto employing a Perkin Elmer 2400 Series II CHNS Analyzer.

X-ray Diffraction Studies.

Single crystals were coated with Paratone-N oil, mounted using a glass fibre pin and frozen in the cold nitrogen stream of the goniometer. Data sets were collected on a Siemens Smart System CCD diffractometer which was equipped with a rotation anode using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) Data reduction was performed using the Bruker SMART[S3] software package. Data sets were corrected for absorption effects using SADABS routine (empirical multi-scan method). Structure solutions were found with the SHELXS-97 package using the direct method and were refined with SHELXL-97[S4] against F^2 using first isotropic and anisotropic thermal parameters for all non-hydrogen atoms. The unit cell of **4** contains 5 molecules CH_2Cl_2 which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON due to their high degree of disorder. Hydrogen atoms bonded to carbon atoms were generated with idealized geometries and isotropically refined using a riding model. Further details are given in tables S3.1 and S3.2 (pages S54-S55).

2. Syntheses and Spectroscopic Data

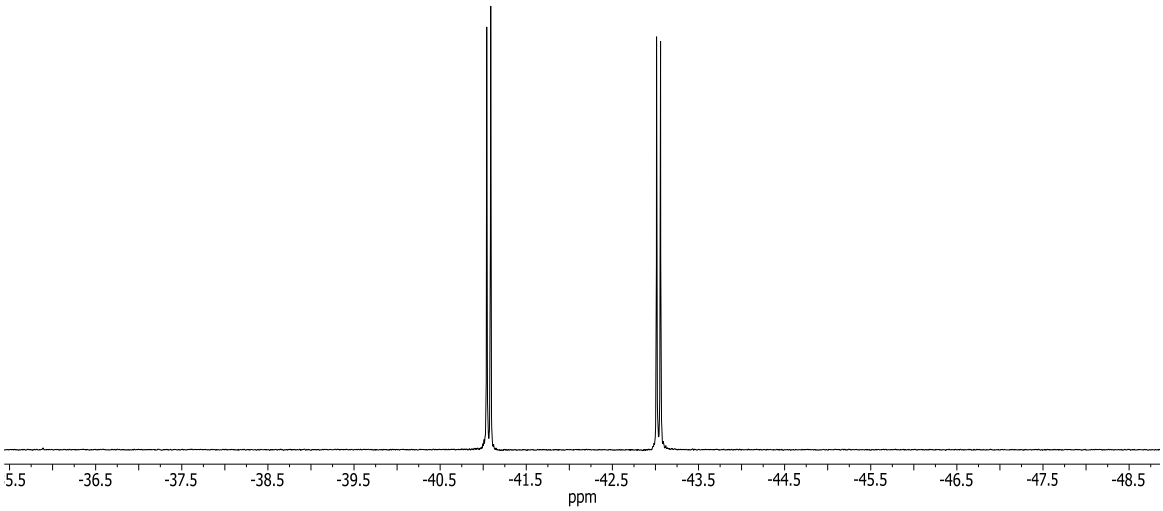
2.1. Preparation of $(C_{10}H_6)(Ph_2PF_2)(Ph_2P)$ (1)



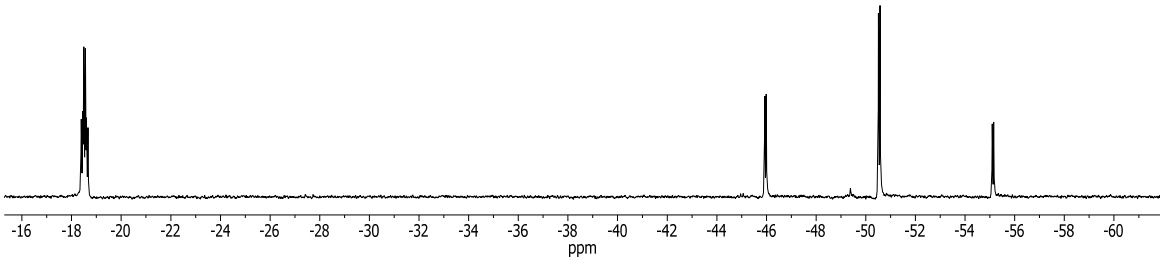
1

XeF_2 (76 mg, 0.45 mmol, 0.9 eq.) was added portionwise to a solution of 1,8-bis(diphenylphosphino)naphthalene (248 mg, 0.50 mmol, 1.0 eq.) in CH_2Cl_2 (15 mL) at −35 °C. The solution was slowly warmed to ambient temperature and stirred for one hour. All volatiles were removed *in vacuo* and the remaining yellowish solid was washed with *n*-pentane (3 x 3 mL) yielding **1** as a colourless material (208 mg, 87% yield).

^{1}H NMR (CD_2Cl_2, [ppm]): δ = 6.94 - 7.00 (4H, m, Ph), 7.16 - 7.24 (8H, m, Ph), 7.26 - 7.37 (8H, m, Ph), 7.44 - 7.49 (1H, m, naphthyl), 7.51 - 7.55 (1H, m, naphthyl), 7.78 - 7.82 (1H, m, naphthyl), 7.85 - 7.91 (2H, m, naphthyl), 7.91 - 7.96 (1H, m, naphthyl); **^{13}C{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 124.8 (1C, d, *p*-naphthyl, $^4J_{CP}$ = 23.5 Hz), 125.9 (1C, d, *p*-naphthyl, $^4J_{CP}$ = 6.1 Hz), 128.3 (4C, s(br), Ph), 128.5 (4C, m, Ph), 130.4 (4C, s(br), Ph), 131.5 (1C, m, naphthyl), 131.8 (1C, m, naphthyl), 133.2 (4C, d, Ph, $^nJ_{CP}$ = 18.0 Hz), 134.0 (1C, t, naphthyl, $^nJ_{CF}$ = 10.5 Hz), 134.2 (4C, s(br), Ph), 135.1 (1C, m, naphthyl), 135.5 (1C, m, naphthyl), 137.1 (1C, t, naphthyl, $^nJ_{CF}$ = 1.8 Hz), 137.7 (2C, d, *i*-Ph, $^1J_{CP}$ = 12.3 Hz), 139.4 (2C, d, *i*-Ph, $^1J_{CP}$ = 212.4 Hz), resonances for the quaternary carbon atoms of the naphthyl-moiety were not observed; **^{19}F{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −42.0 (2F, dd, $^1J_{FP}$ = 742 Hz, $^5J_{FP}$ = 17 Hz); **^{31}P{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −55.5 (1P, td, $^1J_{PF}$ = 742 Hz, $^4J_{PP}$ = 10 Hz), −18.5 (1P, $^5J_{PF}$ = 17 Hz, td, $^4J_{PP}$ = 10 Hz); **elemental analysis** for $C_{34}H_{26}F_2P_2$: calcd.: C 76.4, H 4.9, found: C 76.3, H 5.3; **ESI MS**: m/z: 515.1479 (calcd. for $M-F^+$: 515.1488).

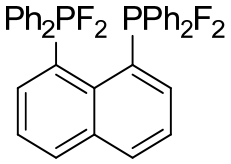


$^{19}F\{^{1}H\}$ NMR spectrum of compound **1** (CD_2Cl_2).



$^{31}P\{^{1}H\}$ NMR spectrum of compound **1** (CD_2Cl_2).

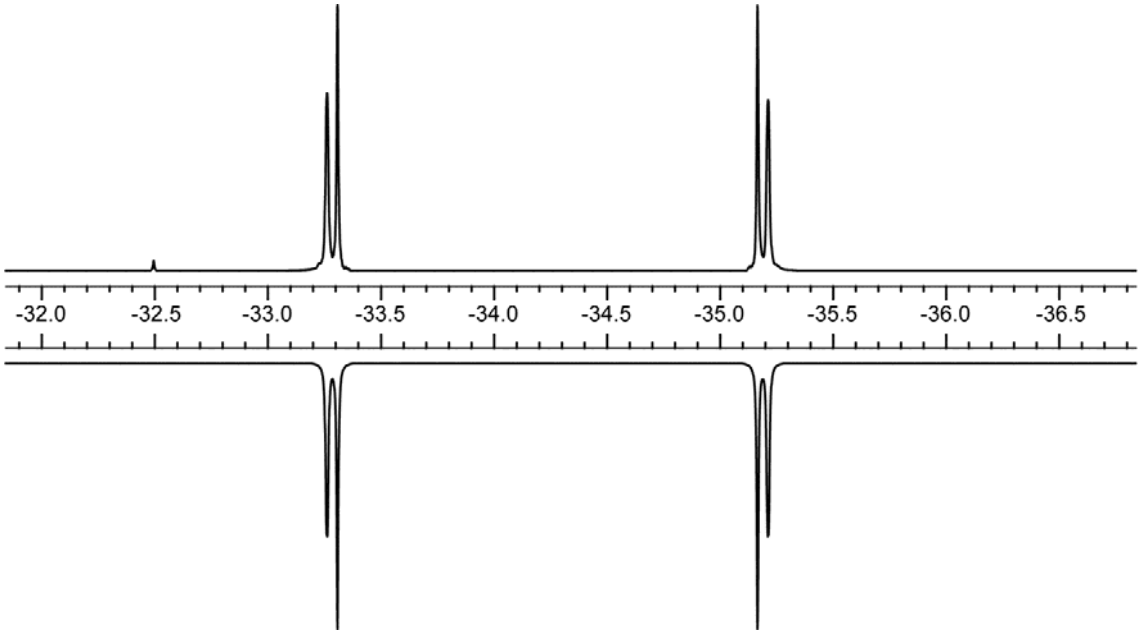
2.2. Preparation of $(C_{10}H_6)(Ph_2PF_2)_2$ (2)



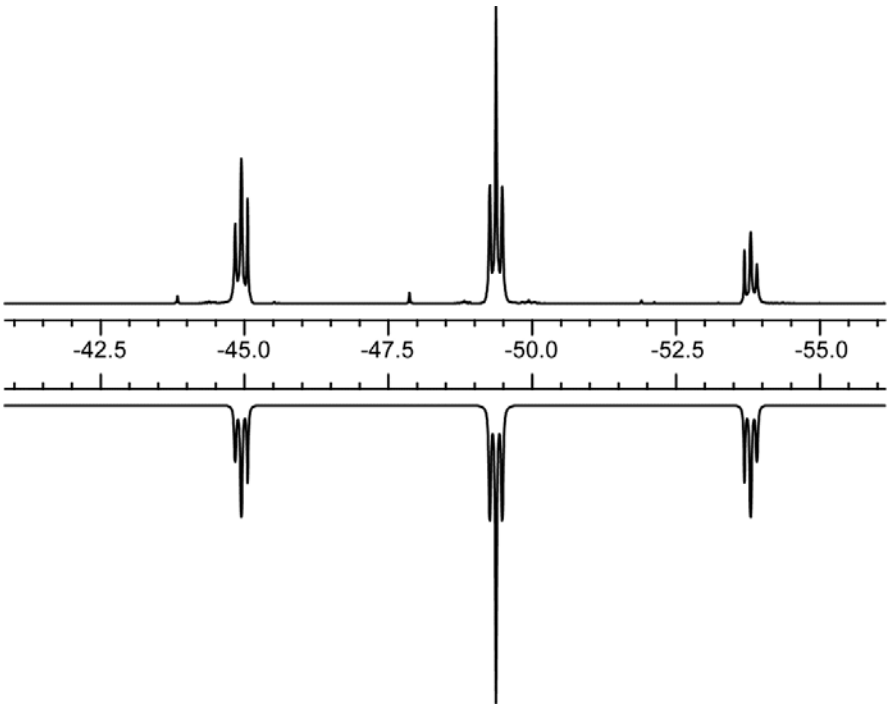
2

XeF_2 (406 mg, 2.4 mmol, 2.2 eq.) was added portionwise to a yellow solution of 1,8-bis(diphenylphosphino)naphthalene (496 mg, 1.00 mmol, 1.0 eq.) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at ambient temperature for six hours giving a colourless solution. All volatiles were removed *in vacuo* yielding **2** as a colourless solid (509 mg, 95% yield).

^{1}H NMR (CD_2Cl_2, [ppm]): δ = 7.05 - 7.13 (8H, m, *m*-Ph), 7.21 - 7.27 (4H, m, *p*-Ph), 7.33 - 7.42 (8H, m, *o*-Ph), 7.44 - 7.50 (2H, m, *p*-naphthyl), 7.94 - 8.01 (2H, m, *m*-naphthyl), 8.46 - 8.57 (2H, m, *o*-naphthyl); **^{13}C{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 125.0 (2C, d, *p*-naphthyl, $^4J_{CP}$ = 20.9 Hz), 128.1 (8C, d, *m*-Ph, $^3J_{CP}$ = 17.2 Hz), 130.3 (4C, d, *p*-Ph, $^4J_{CP}$ = 3.5 Hz), 133.3 (8C, dt, *o*-Ph, $^2J_{CP}$ = 12.8 Hz, $^3J_{CF}$ = 8.1 Hz), 133.8 (2C, m, *m*-$C_{naphthyl}$H), 137.4 (2C, dtdt, *i*-naphthyl, $^1J_{CP}$ = 202.4 Hz, $^2J_{CF}$ = 31.6 Hz, $^3J_{CP}$ = 3.6 Hz, $^4J_{CF}$ = 3.6 Hz), 138.5 (2C, dt, *o*-$C_{naphtyl}$H, $^2J_{CP}$ = 14.5 Hz, $^3J_{CF}$ = 14.5 Hz), 139.8 (4C, dt, *i*-Ph, $^1J_{CP}$ = 182.3 Hz, $^2J_{PF}$ = 28.4 Hz), resonances for the quaternary carbon atoms of the naphthyl-moiety were not observed; **^{19}F{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −34.3 (4F, X_2X_2' part of AA'X_2X_2' spin system, $^1J_{AX} = {}^1J_{A'X'}$ = 717 Hz, $^5J_{A'X} = {}^5J_{AX'}$ = −18 Hz, $^6J_{XX'}$ = 0 Hz); **^{31}P{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −49.4 (2P, AA' part of AA'X_2X_2' spin system, $^5J_{AA'}$ = 3 Hz); **elemental analysis** for $C_{34}H_{26}F_4P_2$: calcd.: C 71.2, H 4.6, found: C 71.0, H 5.0; **ESI MS**: m/z: 553.1 (calcd. for $M-F^+$: 553.1).

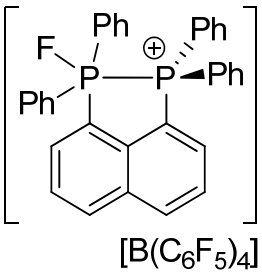


^{19}F{^{1}H} NMR spectrum of compound **2** (CD_2Cl_2, upwards) and simulated spectrum (downwards).



$^{31}P\{^{1}H\}$ NMR spectrum of compound **2** (CD_2Cl_2, upwards) and simulated spectrum (downwards).

2.3. Preparation of $[(C_{10}H_6)(Ph_2PF)(Ph_2P)][B(C_6F_5)_4]$ (3)

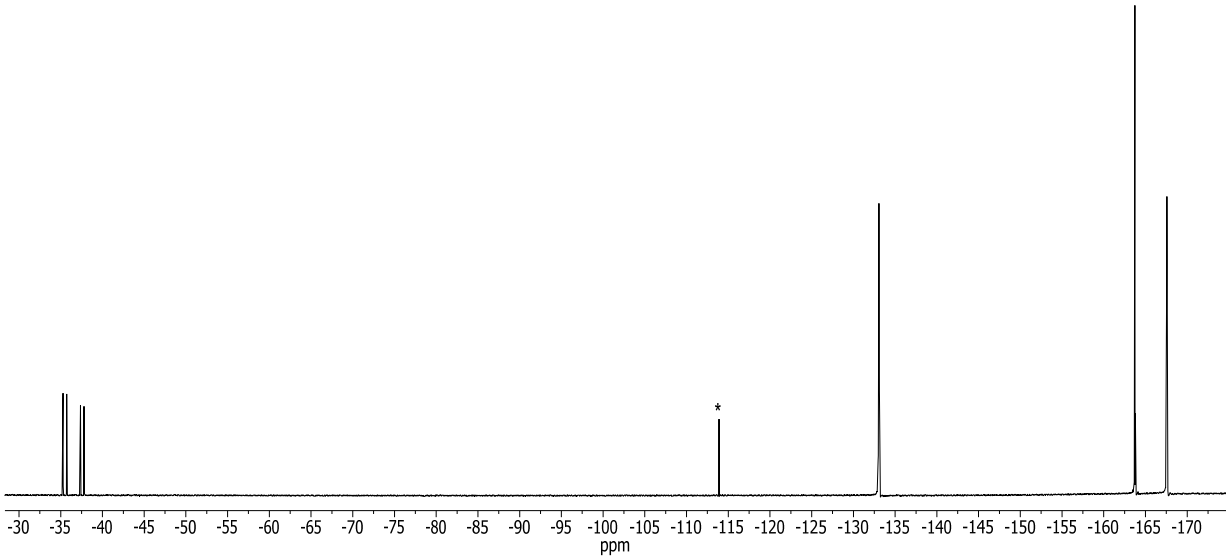


3

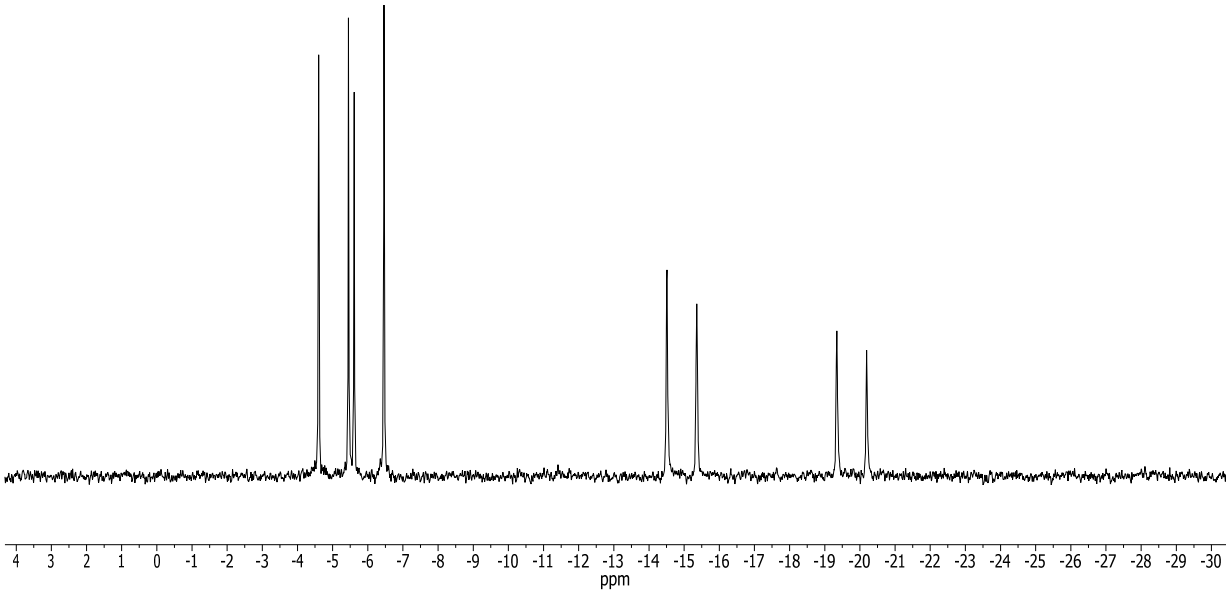
Freshly prepared $[Et_3Si][B(C_6F_5)_4]*2(C_7H_8)$ (196 mg, 0.20 mmol, 1.0 eq.) was added portion wise to a solution of **1** (107 mg, 0.20 mmol, 1.0 eq.) in C_6H_5F (5 mL). The clear, yellowish reaction mixture was stirred for 30 min at ambient temperature. Addition of *n*-pentane (10 mL) gave a colourless precipitate. The supernatant was removed and the residue was washed with *n*-pentane (3 x 3 mL). Removal of all volatiles *in vacuo* gave **3** as colourless, microcrystalline solid (208 mg, 87% yield).

^{1}H NMR (CD_2Cl_2, [ppm]): δ = 6.67 - 6.65 (4H, m, Ph), 7.09 - 7.16 (4H, m, Ph), 7.20 - 7.28 (4H, m, Ph), 7.44 - 7.49 (8H, m, Ph), 7.82 - 7.94 (2H, m, naphthyl), 8.09 - 8.15 (1H, m, naphthyl), 8.46 - 8.51 (1H, m, naphthyl), 8.58 - 8.62 (1H, m, naphthyl), 8.98 - 9.05 (1H, m, naphthyl); **^{11}B{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −16.6 (s); **^{13}C{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 115.6 (1C, d, *i*-naphthyl, $^{1}J_{CP}$ = 20.9), 118.0 (1C, ddd, *i*-napthyl, $^{1}J_{CP}$ = 140.0 Hz, $^{2}J_{CF}$ = 40.7 Hz, $^{3}J_{CP}$ = 20.9 Hz), 121.1 (2C, dd, *i*-Ph, $^{1}J_{CP}$ = 40.5 Hz, $^{4}J_{CF}$ = 3.0 Hz), 125.0 (2C, ddd, *i*-Ph, ddd,

$^{1}J_{CF}$ = 38.7 Hz, $^{5}J_{CP}$ = 1.6 Hz, $^{6}J_{CF}$ = 1.6 Hz), 128.8 - 129.2 (6C, m, Ph / naphthyl), 129.7 (4C, d, Ph, J_{CP} = 10.4 Hz), 130.0 (4C, dd, Ph, J_{CP} = 17.1 Hz, J_{CF} = 1.7 Hz), 131.9 (2C, d, Ph, J_{CP} = 3.1 Hz), 132.4 (4C, dd, Ph, J_{CP} = 9.1 Hz, J_{CP} = 0.9 Hz), 132.7 (2C, m, Ph), 134.7 (1C, ddd, naphthyl, J_{CP} = 11.7 Hz, J_{CF} = 9.9 Hz, J_{CP} = 2.2 Hz), 136.7 (8C, d(br), C_6F_5, $^{1}J_{CF}$ = 246 Hz), 137.6 - 137.9 (2C, m, naphthyl), 138.6 (4C, d(br), C_6F_5, $^{1}J_{CF}$ = 237 Hz), 143.3 (1C, ddd, naphthyl, J_{CP} = 16.7 Hz, $J_{CF/P}$ = 13.5 Hz, $J_{CF/P}$ = 10.6 Hz), 148.5 (8C, d(br), C_6F_5, $^{1}J_{CF}$ = 241 Hz), resonances for the quaternary carbon atoms of the naphthyl-moiety were not observed; **^{19}F{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −167.6 (8F, m, *m*-C_6F_5), −163.7 (4F, t, *p*-C_6F_5, $^{3}J_{FF}$ = 20 Hz), −133.1 (8F, m, *o*-C_6F_5), −36.5 (1F, dd, PF, $^{1}J_{FP}$ = 783 Hz, $^{2}J_{FP}$ = 164 Hz); **^{31}P{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −17.4 (1P, dd, PPh_2F, $^{1}J_{PF}$ = 783 Hz, $^{1}J_{PP}$ = 138 Hz), −5.5 (1P, dd, PPh_2, $^{2}J_{PF}$ = 164 Hz, $^{1}J_{PP}$ = 138 Hz); **elemental analysis** for $C_{58}H_{26}F_{21}BP_2$: calcd.: C 58.3, H 2.2, found: C 57.7, H 2.3; **ESI MS**: m/z: 515.1487 (calcd. for M^+: 515.1488).

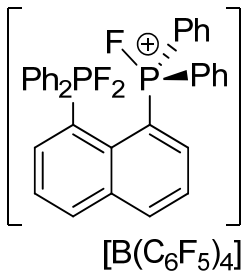


$^{19}F\{^{1}H\}$ NMR spectrum of compound **3** (CD_2Cl_2), * indicates traces of C_6H_5F.



$^{31}P\{^{1}H\}$ NMR spectrum of compound **3** (CD_2Cl_2).

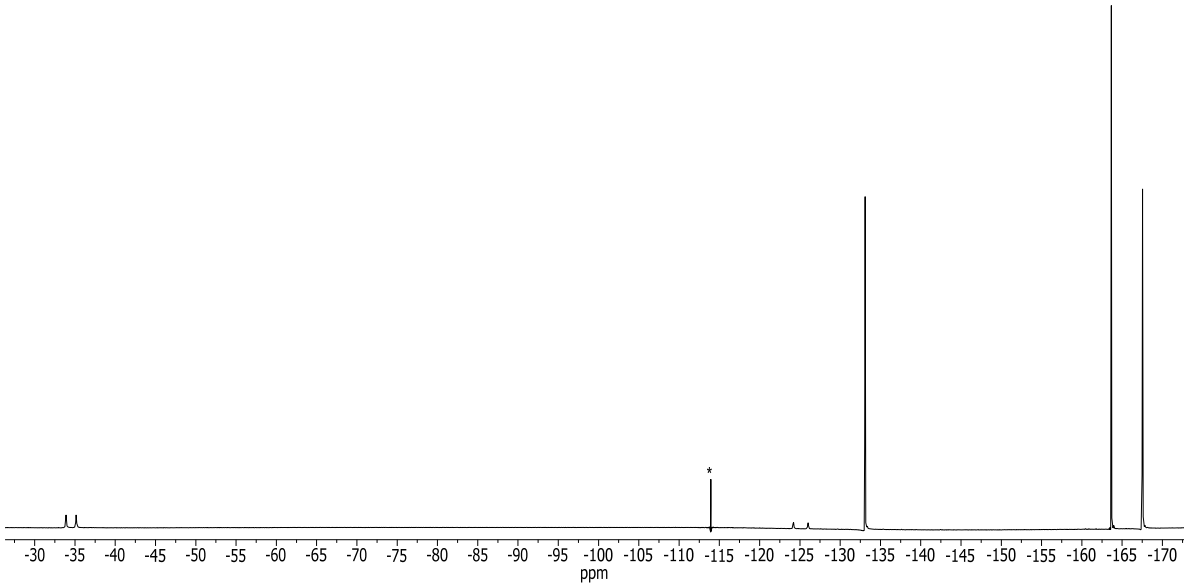
2.4. Preparation of $[(C_{10}H_6)(Ph_2PF)(Ph_2PF_2)][B(C_6F_5)_4]$ (4)



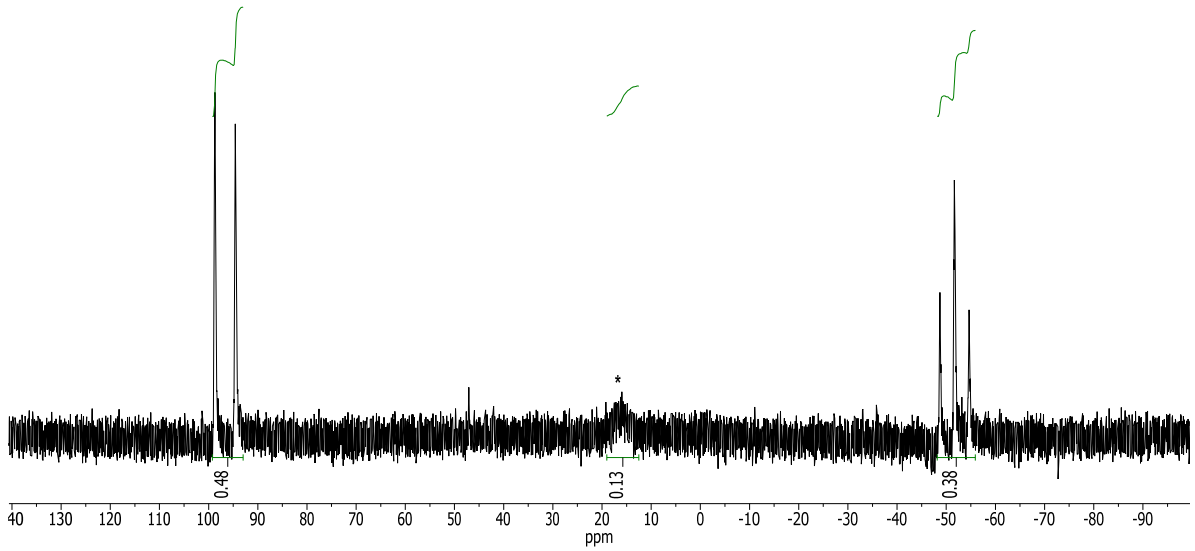
4

Freshly prepared $[Et_3Si][B(C_6F_5)_4]*2(C_7H_8)$ (156 mg, 0.16 mmol, 1.0 eq.) was added portionwise to a solution of **2** (85 mg, 0.16 mmol, 1.0 eq.) in C_6H_5F (5 mL). The clear, yellowish solution was stirred for 30 min at ambient temperature. Addition of *n*-pentane (10 mL) gave a colourless precipitate. The supernatant was removed and the residue was washed with *n*-pentane (3 x 3 mL). Removal of all volatiles *in vacuo* gave **4** as colourless, microcrystalline solid (189 mg, 96% yield). Single crystals of **4**, as its dichloromethane solvate **4***(CH_2Cl_2), were obtained by slow diffusion of *n*-pentane into a CH_2Cl_2 solution at −35 °C and were suitable of X-ray single crystal structure determination. Portions of the crystalline material were isolated by decanting the supernatant and either removing remaining volatiles *in vacuo* or by evaporating in one atmosphere of N_2. Both samples were investigated by ^{1}H NMR spectroscopy. While 0.7 equivalent CH_2Cl_2 solvate were observed in the ^{1}H NMR spectrum of the sample that was dried *in vacuo*, the latter indicated the presence of one CH_2Cl_2 solvate molecule. This indicates that the solvate molecules are only weakly bound.

^{1}H NMR (CD_2Cl_2, [ppm]): δ = 7.12 - 7.27 (4H, m(br), Ph), 7.32 - 7.48 (12H, m(br), Ph), 7.52 - 7.68 (4H, m(br), Ph), 7.68 - 7.80 (2H, m(br), naphthyl), 7.82 - 7.92 (1H, m(br), naphthyl), 8.20 - 8.31 (1H, m(br), naphthyl), 8.36 - 8.47 (1H, m(br), naphthyl), 8.78 - 8.90 (2H, m(br), naphthyl); **^{11}B{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −16.7 (s); **^{13}C{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 116.0 (s(br)), 119.1 (s(br)), 119.9 (s(br)), 123.5 (s(br)), 127.0 (s(br)), 127.9 (s(br)), 132.8 (s(br)), 134.7 (s(br)), 136.1 (8C, d(br), C_6F_5, $^{1}J_{CF}$ = 244 Hz), 136.6 (s(br)), 137.8 (4C, d(br), C_6F_5, $^{1}J_{CF}$ = 236 Hz), 142.5 (s(br)), 148.1 (8C, d(br), C_6F_5, $^{1}J_{CF}$ = 242 Hz); **^{19}F{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −167.3 (8F, m, *m*-C_6F_5), −163.4 (4F, m, *p*-C_6F_5), −132.8 (8F, m, *o*-C_6F_5), −125.0 (d(br), $^{1}J_{PF}$ = 1012 Hz), −34.5 (d(br), $^{1}J_{PF}$ = 717 Hz); **^{31}P{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −51.7 (t(br), $^{1}J_{PF}$ = 717 Hz), 96.6 (d(br), $^{1}J_{PF}$ = 1012 Hz); **elemental analysis** for $C_{82}H_{26}F_{43}B_2P_2$: calcd.: C 56.5, H 2.1, found: C 56.5, H 1.5; **ESI MS**: m/z: 529.1 (calcd. for $[M+H_2O-2HF]^+$: 529.1).

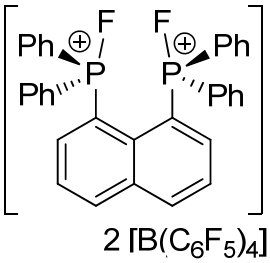


^{19}F{^{1}H} NMR spectrum of compound **4** (CD_2Cl_2), * indicates traces of C_6H_5F.



$^{31}P\{^{1}H\}$ NMR spectrum of compound **4** (CD_2Cl_2). *despite several tested workup procedures the broad resonance at 16 ppm persisted. Based on this, it is tentatively assigned to an isomer of **4** which is present in small amounts only. This isomer is assumed to feature a bridging P−F−P interaction caused by coordination of the σ^*(P−F) acceptor orbital of the phosphonium moiety to one of the fluoro-groups of the adjacent difluorophosphorane.

2.5. Preparation of $[(C_{10}H_6)(Ph_2PF)_2][B(C_6F_5)_4]_2$ (5)

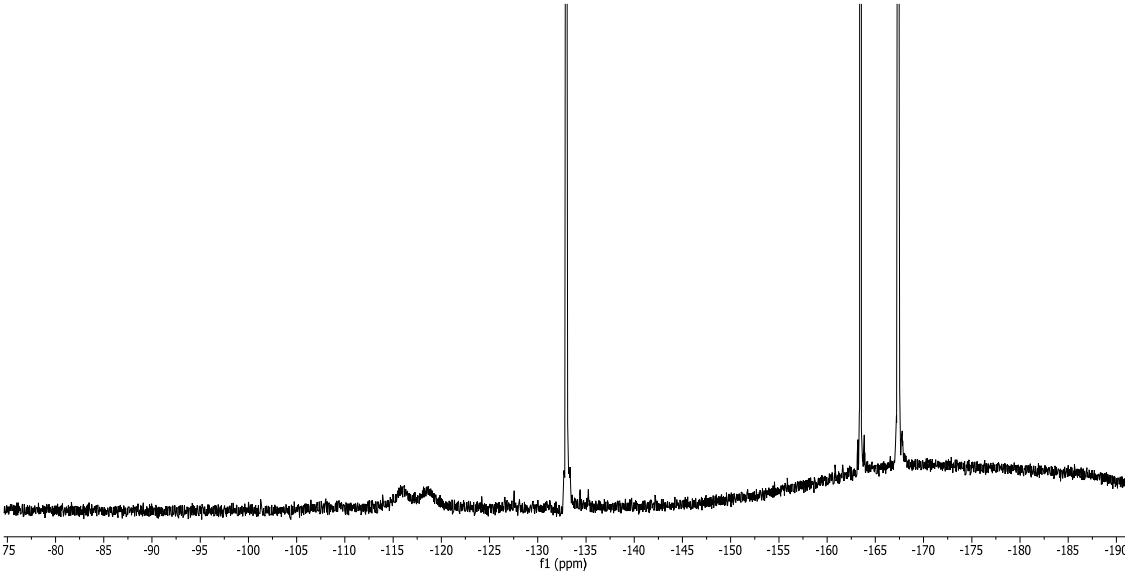


5

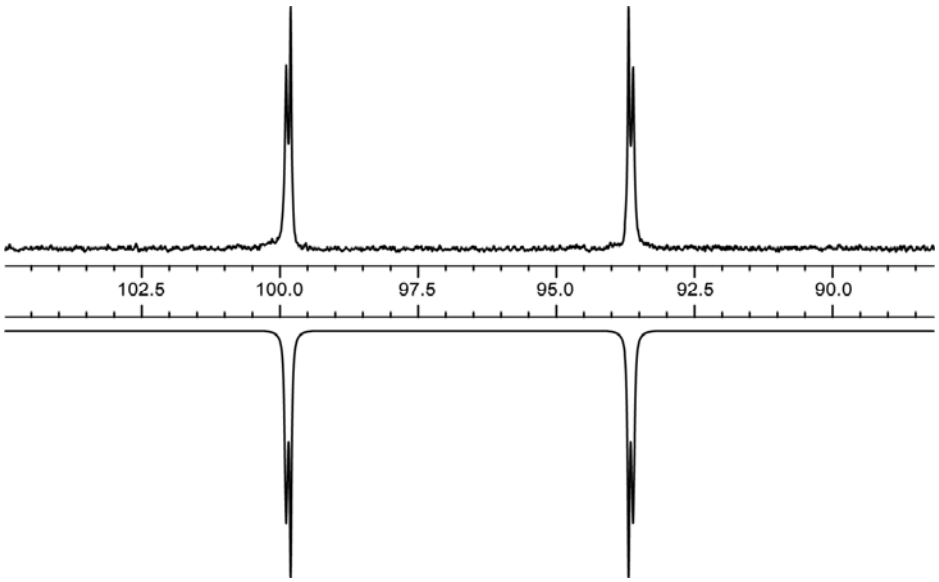
Freshly prepared $[Et_3Si][B(C_6F_5)_4]*2(C_7H_8)$ (1029 mg, 1.05 mmol, 2.0 eq.) was added to a solution of **2** (281 mg, 0.53 mmol, 1.0 eq.) in C_6H_5F (10 mL). Instantly the formation of a colourless oil was observed. The supernatant was removed and the residue was washed with *n*-pentane (3 x 3 mL). During this process, the oil turned into a colourless, microcrystalline solid. Removal of all volatiles *in vacuo* gave **5** was colourless, microcrystalline solid (842 mg, 84% yield).

^{1}H NMR (CD_2Cl_2, [ppm]): δ = 7.39 - 7.48 (8H, m, *o*-Ph), 7.67 - 7.76 (8H, m, *m*-Ph), 7.96 – 8.06 (6H, m, *p*-Ph/*p*-naphthyl), 8.08 - 8.18 (2H, m, *o*-naphthyl), 8.73 – 8.80 (2H, m, *m*-naphthyl); **^{11}B{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −16.7 (s); **^{13}C{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 111.1 (2C, dd, *i*-naphthyl, $^{1}J_{CP}$ = 106.9 Hz, $^{2}J_{CF}$ = 16.0 Hz), 116.9 (4C, dd, *i*-Ph, $^{1}J_{CP}$ = 109.8 Hz, $^{2}J_{CF}$ = 15.0 Hz), 123.8 (4C, s(br), C_6F_5), 127.9 (2C, d, *p*-$C_{naphthyl}$H, $^{4}J_{CP}$ = 17.3 Hz), 131.3 (8C, d, *m*-Ph, $^{3}J_{CP}$ = 14.7 Hz), 133.4 (8C, d, *o*-Ph, $^{2}J_{CP}$ = 13.1 Hz), 136.2 (16C, d(br), C_6F_5, $^{1}J_{CF}$ = 246 Hz), 138.1 (8C, d(br), C_6F_5, $^{1}J_{CF}$ = 243 Hz), 139.2 (4C, s, *p*-Ph), 142.5 - 142.6 (2C, m,

m-$C_{naphthyl}H$), 145.2 (2C, d(br), *o*-$C_{naphthyl}H$), 148.1 (16C, d(br), $^1J_{CF}$ = 242 Hz), resonances for the quaternary carbon atoms of the naphthyl-moiety were not observed; **$^{19}F\{^1H\}$ NMR (CD_2Cl_2, [ppm]):** δ = −167.4 (16F, m, *m*-C_6F_5), −163.4 (8F, m, *p*-C_6F_5), −132.9 (16F, m, *o*-C_6F_5), −117.1 (2F, XX' part of AA'XX' spin system, $^1J_{AX} = {}^1J_{A'X'}$ = 1004 Hz, $^5J_{A'X} = {}^5J_{AX'}$ = −13 Hz, $^6J_{XX'}$ was not determined due to broad $^{19}F\{^1H\}$ resonance); **$^{31}P\{^1H\}$ NMR (CD_2Cl_2, [ppm]):** δ = 96.8 (2P, AA' part of AA'XX' spin system, $^5J_{AA'}$ = 3 Hz); **elemental analysis** for $C_{82}H_{26}B_2F_{42}P_2$: calcd.: C 52.0, H 1.4, found: C 52.8, H 1.7; **ESI MS**: m/z: 529.1469 (calcd. for $[M-2F+H_2O]^+$: 529.1469), 543.1626 (calcd. for $[M+e^-]^+$: 543.1478).

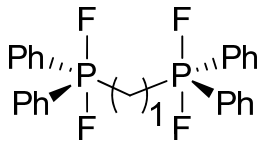


$^{19}F\{^1H\}$ NMR spectrum of compound **5** (CD_2Cl_2).



$^{31}P\{^1H\}$ NMR spectrum of compound **5** (CD_2Cl_2, upwards) and simulated spectrum (downwards).

2.6. Preparation of $(CH_2)_1(Ph_2PF_2)_2$ (8a)[S5]



8a

A solution of XeF_2 (480 mg, 2.84 mmol, 2.2 eq.) in CH_2Cl_2 (5 mL) was added dropwise to a solution of 1,1-bis(diphenylphosphino)methane (503 mg, 1.31 mmol, 1.0 eq.) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at ambient temperature for 15 min. giving a colourless solution. All volatiles were removed *in vacuo* yielding a white solid (579 mg, 96% yield). Single crystals of **8a**, suitable for X-ray single crystal structure determination were obtained by slow diffusion of *n*-pentane into a CH_2Cl_2 solution. Multi-nuclear magnetic resonance experiments were in accordance to literature reported values.[S5]

^{1}H NMR (CD_2Cl_2, [ppm]): δ = 3.57 (2H, m, CH_2), 7.37 (8H, m, *m*-Ph), 7.46 (4H, m, *p*-Ph), 7.88 (8H, m, *o*-Ph);**^{13}C{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 46.3 (1C, td, CH_2, $^1J_{CP}$ = 132 Hz, $^2J_{CF}$ = 35 Hz), 128.6 (8C, dm, *m*-Ph, $^3J_{CP}$ = 16 Hz), 131.9 (4C, d, *p*-Ph, $^4J_{CP}$ = 5 Hz), 134.9 (8C, m, *o*-Ph), 136.1 (4C, dt, *i*-Ph, $^1J_{PF}$ = 232 Hz, $^2J_{CF}$ = 32 Hz); **^{19}F{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = –27.7 (4F, X_2X_2' part of AA'X_2X_2' spin system, $^1J_{AX} = {}^1J_{A'X'}$ = 644 Hz, $^3J_{A'X} = {}^3J_{AX'}$ = –18 Hz, $^4J_{XX'}$ = –7 Hz); **^{31}P{1H} NMR (CD_2Cl_2, [ppm]):** δ = –46.8 (2P, AA' part of AA'X_2X_2' spin system, $^2J_{AA'}$ = 26 Hz); **elemental analysis** for $C_{25}H_{22}F_4P_2$: calcd.: C 65.2, H 4.8, found: C 64.9, H 5.0; **DART MS**: m/z: 441.1 (calcd. for $M-F^+$: 441.1).

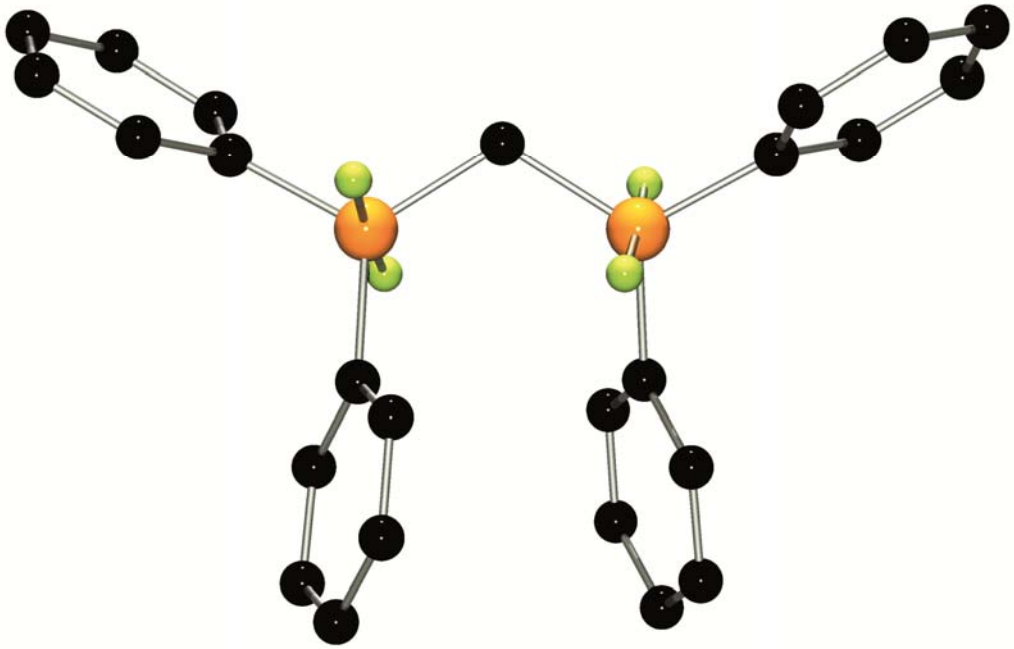
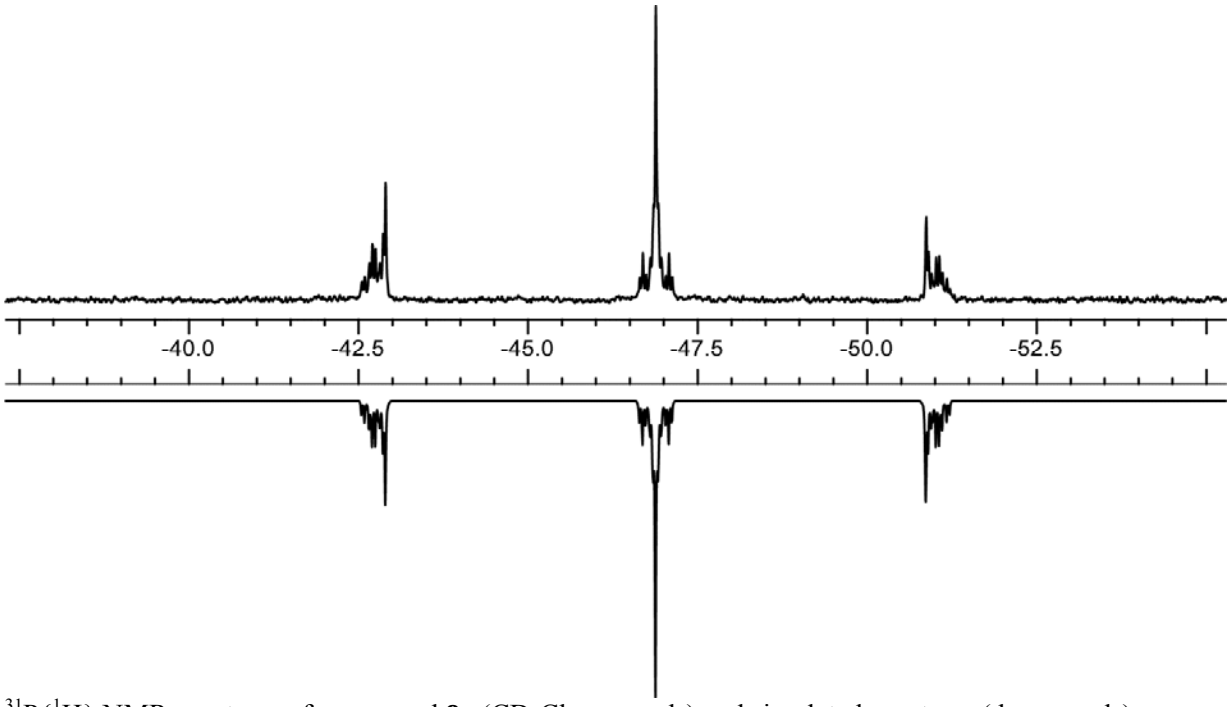
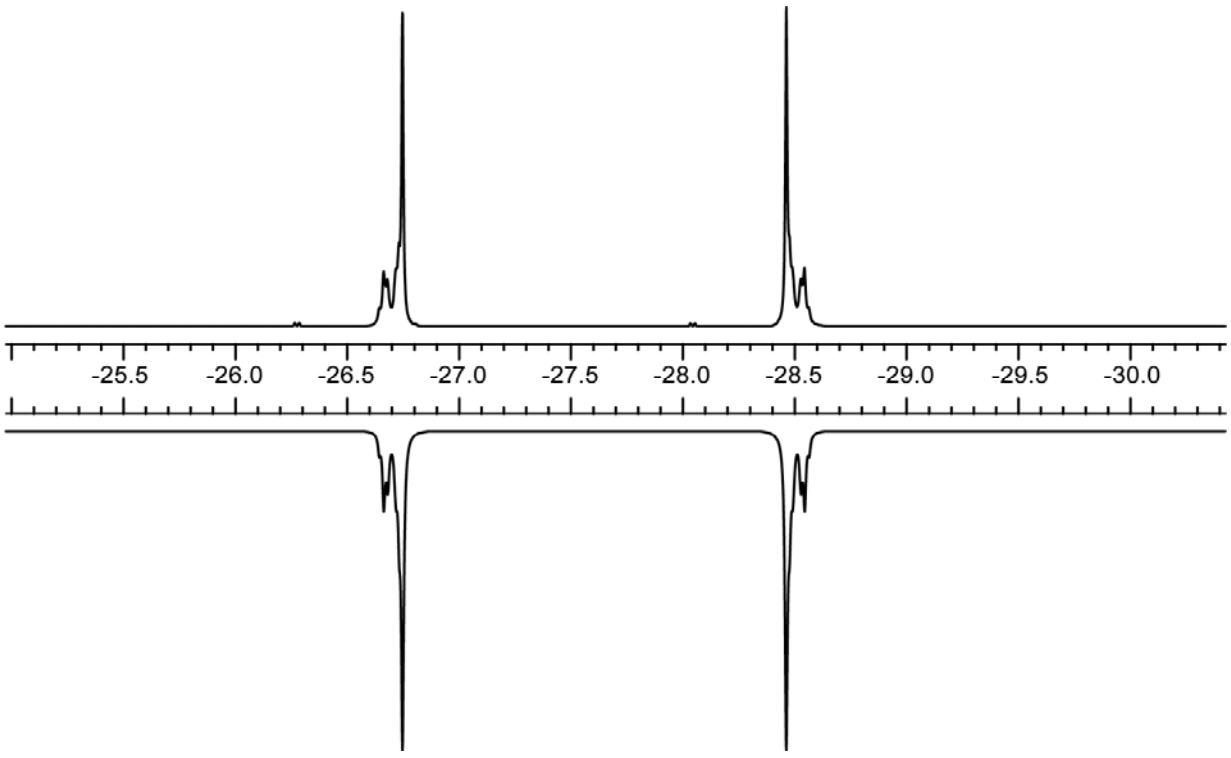


Figure 2.6.1. POV-ray depiction of **8a**. P: orange, F: yellow-green, C: black.

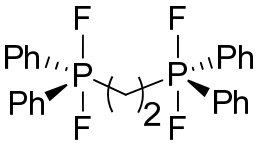


$^{31}P\{^{1}H\}$ NMR spectrum of compound **8a** (CD_2Cl_2, upwards) and simulated spectrum (downwards).



$^{19}F\{^{1}H\}$ NMR spectrum of compound **8a** (CD_2Cl_2, upwards) and simulated spectrum (downwards).

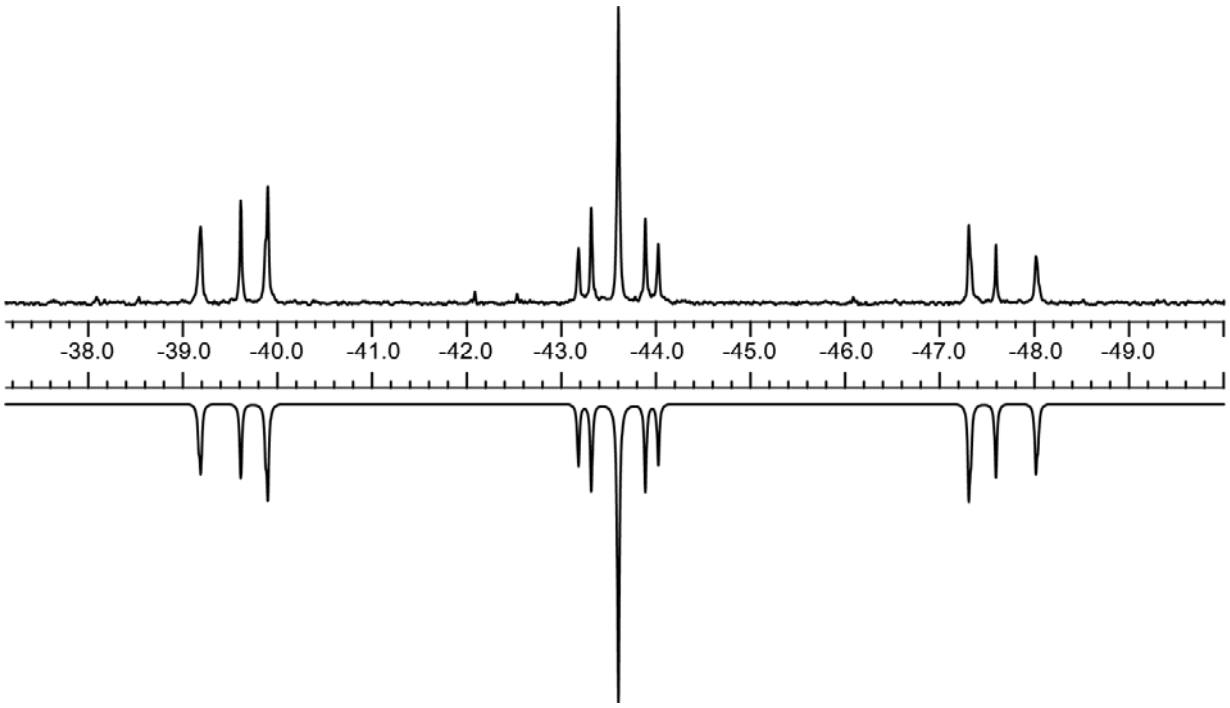
2.7. Preparation of $(CH_2)_2(Ph_2PF_2)_2$ (8b)[S5]



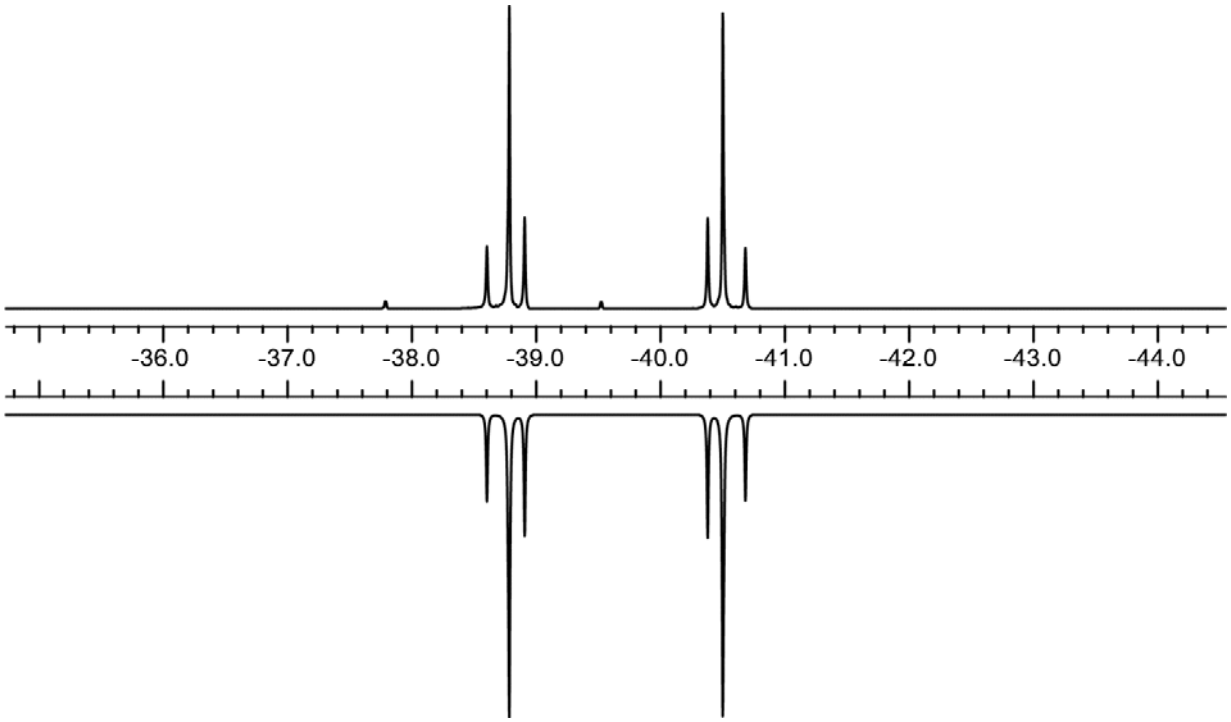
8b

A solution of XeF_2 (103 mg, 0.61 mmol, 2.4 eq.) in CH_2Cl_2 (5 mL) was added dropwise to a solution of 1,2 bis(diphenylphosphino)ethane (99 mg, 0.25 mmol, 1.0 eq.) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at ambient temperature for 15 min giving a colourless solution. All volatiles were removed *in vacuo* yielding a white solid (117 mg, 99% yield). Multi-nuclear magnetic resonance experiments were in accordance to literature reported values.[S5]

^{1}H NMR (CD_2Cl_2, [ppm]): δ = 2.74 (4H, m, CH_2), 7.46 (8H, m, *m*-Ph), 7.52 (4H, m, *p*-Ph), 7.97 (8H, m, *o*-Ph); **^{13}C{1H} NMR (CD_2Cl_2, [ppm]):** δ = 31.0 (2C, dm, CH_2, $^1J_{CP}$ = 126 Hz), 128.8 (8C, dm, *m*-Ph, $^3J_{CP}$ = 15 Hz), 132.0 (4C, s(br), *p*-Ph), 134.5 (8C, m, *o*-Ph), 135.8 (4C, dt, *i*-Ph, $^1J_{PF}$ = 172 Hz, $^2J_{CF}$ = 26 Hz); **^{19}F{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = –39.7 (4F, X_2X_2' part of AA'X_2X_2' spin system, $^1J_{AX} = {}^1J_{A'X'}$ = 653 Hz, $^4J_{A'X} = {}^4J_{AX'}$ = –6 Hz, $^5J_{XX'}$ = 0 Hz); **^{31}P{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −43.6 (2P, AA' part of AA'X_2X_2' spin system, $^3J_{AA'}$ = 115 Hz); **elemental analysis** for $C_{26}H_{24}F_4P_2$: calcd.: C 65.8, H 5.1, found: C 65.5, H 5.5; **DART MS**: m/z: 455.1 (calcd. for $M-F^+$: 455.1).

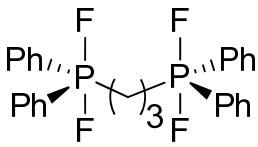


^{31}P{^{1}H} NMR spectrum of compound **8b** (CD_2Cl_2, upwards) and simulated spectrum (downwards).



$^{19}F\{^{1}H\}$ NMR spectrum of compound **8b** (CD_2Cl_2, upwards) and simulated spectrum (downwards).

2.8. Preparation of $(CH_2)_3(Ph_2PF_2)_2$ (8c)[S6]

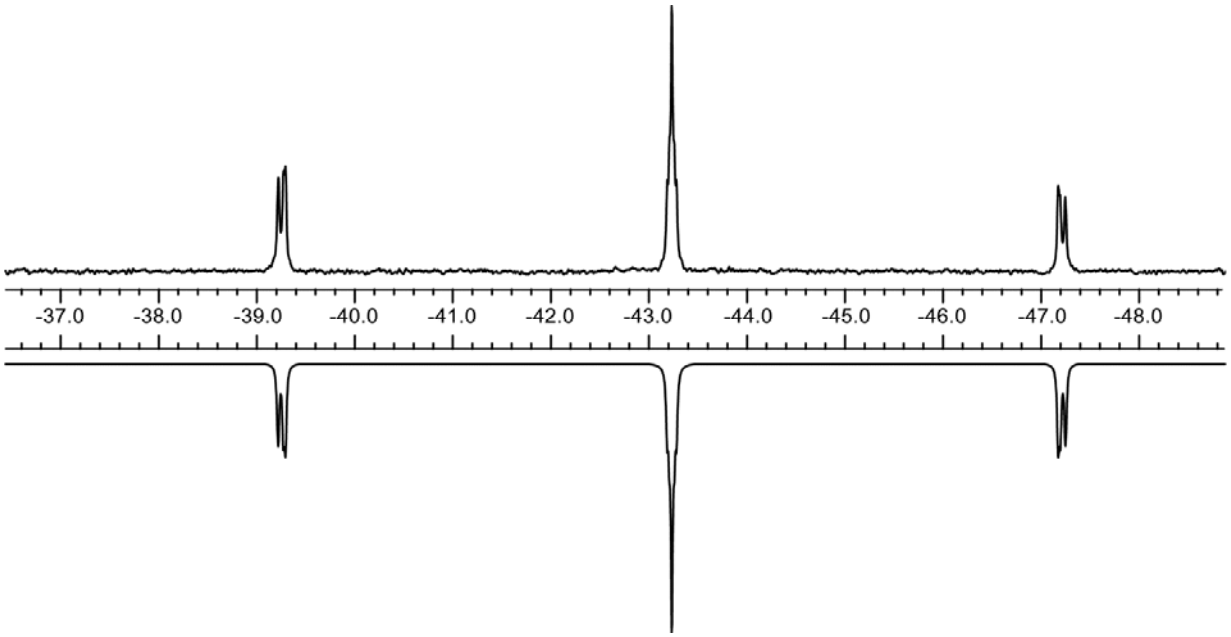


8c

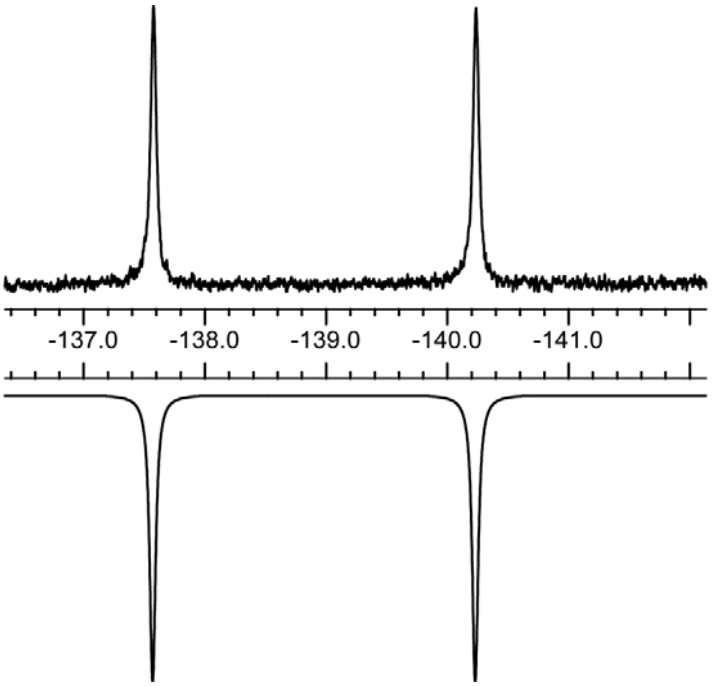
A solution of XeF_2 (112 mg, 0.56 mmol, 2.1 eq.) in CH_2Cl_2 (5 mL) was added dropwise to a solution of 1,3 bis(diphenylphosphino)propane (131 mg, 0.32 mmol, 1.0 eq.) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at ambient temperature for 15 min giving a colourless solution. All volatiles were removed *in vacuo* yielding a white solid (142 mg, 88% yield). Multi-nuclear magnetic resonance experiments were in accordance to literature reported values.[S6]

^{1}H NMR (CD_2Cl_2, [ppm]): δ = 2.20 (2H, m, CH_2), 2.53 (4H, m, P-CH_2), 7.45 (8H, m, *m*-Ph), 7.52 (4H, m, *p*-Ph), 7.92 (8H, m, *o*-Ph); **^{13}C {^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 19.6 (1C, m, CH_2), 37.6 (1C, dm, P-CH_2, $^{1}J_{CP}$ = 111 Hz), 128.7 (8C, dm, *m*-Ph, $^{3}J_{CP}$ = 16 Hz), 131.8 (4C,m, *p*-Ph), 134.2 (8C, m, *o*-Ph), 136.3 (4C, dt, *i*-Ph, $^{1}J_{CP}$ = 172 Hz, $^{2}J_{CF}$ = 26 Hz); **^{19}F{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = –39.0 (4F, X_2X_2' part of AA'X_2X_2' spin system, $^{1}J_{AX} = {}^{1}J_{A'X'}$ = 644 Hz, $^{5}J_{A'X} = {}^{5}J_{AX'}$ = −2 Hz, $^{6}J_{XX'}$ = 0 Hz); **^{31}P{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −43.2 (2P, AA' part of

AA'X_2X_2' spin system, $^4J_{AA'}$ = 12 Hz); **elemental analysis** for $C_{27}H_{26}F_4P_2$: calcd.: C 66.4, H 5.4, found: C 66.3, H 5.0; **DART MS**: m/z: 469.2 (calcd. for $M-F^+$: 469.2).

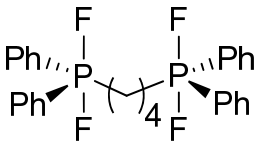


$^{31}P\{^1H\}$ NMR spectrum of compound **8c** (CD_2Cl_2, upwards) and simulated spectrum (downwards).



$^{19}F\{^1H\}$ NMR spectrum of compound **8c** (CD_2Cl_2, upwards) and simulated spectrum (downwards).

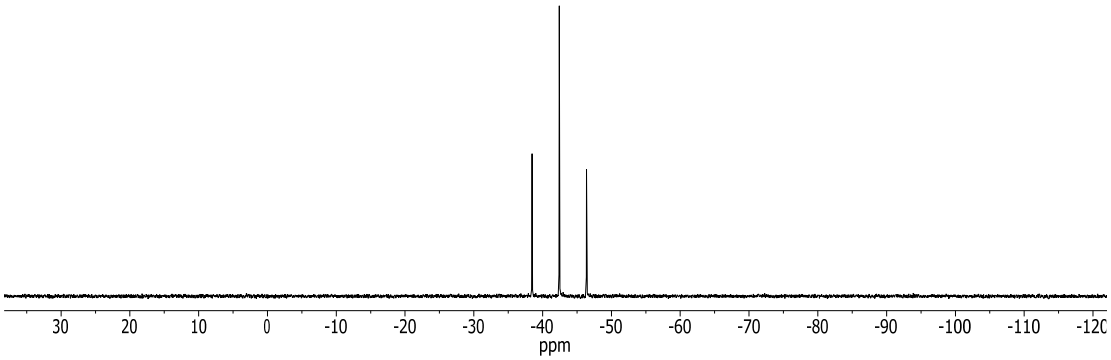
2.9. Preparation of $(CH_2)_4(Ph_2PF_2)_2$ (8d)[S6]



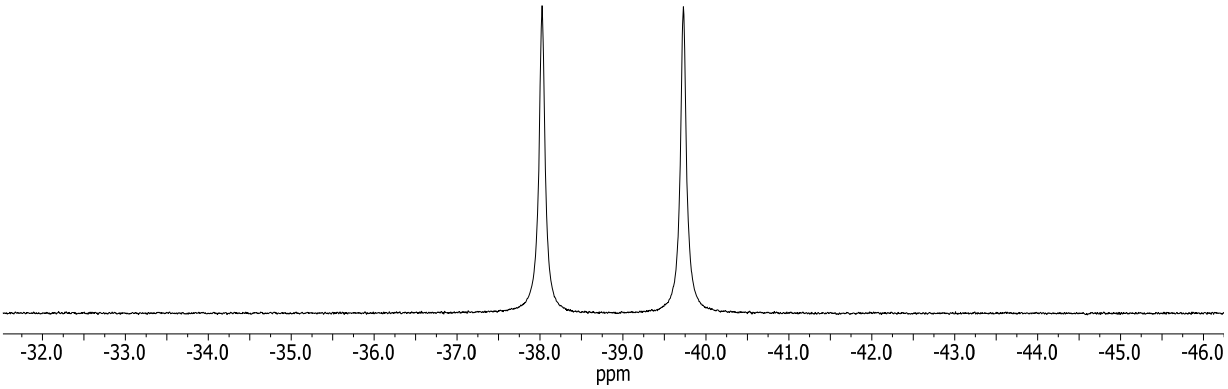
8d

A solution of XeF_2 (86 mg, 0.51 mmol, 2.1 eq.) in CH_2Cl_2 (5 mL) was added dropwise to a solution of 1,4 bis(diphenylphosphino)butane (104 mg, 0.24 mmol, 1.0 eq.) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at ambient temperature for 15 min giving a colourless solution. All volatiles were removed *in vacuo* yielding a white solid (121 mg, 98% yield). Multi-nuclear magnetic resonance experiments were in accordance to literature reported values.[S6]

^{1}H NMR (CD_2Cl_2, [ppm]): δ = 1.80 (4H, m, CH_2), 2.42 (4H, m, P-CH_2), 7.44 (8H, m, *m*-Ph), 7.50 (4H, m, *p*-Ph), 7.90 (8H, m, *o*-Ph); **^{13}C{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 25.6 (2C, m, CH_2), 36.0 (2C, dtd, P-CH_2, $^1J_{CP}$ = 130 Hz, $^2J_{CF}$ = 29 Hz, $^4J_{CP}$ = 1 Hz), 128.6 (8C, dt, *m*-Ph, $^3J_{CP}$ = 15 Hz, $^4J_{CF}$ = 1 Hz), 131.7 (4C, m, *p*-Ph), 134.2 (8C, m, *o*-Ph), 136.4 (4C, dt, *i*-Ph, $^1J_{PF}$ = 171 Hz, $^2J_{CF}$ = 28 Hz); **^{19}F{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = –38.9 (4F, X_2X_2' part of AA'X_2X_2' spin system, $^1J_{AX} = {}^1J_{A'X'}$ = 641 Hz, $^6J_{A'X} = {}^6J_{AX'}$ = 0 Hz, $^7J_{XX'}$ = 0 Hz); **^{31}P{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −42.4 (2P, AA' part of AA'X_2X_2' spin system, $^5J_{AA'}$ = 0 Hz); **elemental analysis** for $C_{27}H_{28}F_4P_2$: calcd.: C 66.9, H 5.6, found: C 66.9, H 6.0; **DART MS**: m/z: 483.2 (calcd. for $M-F^+$: 483.2).

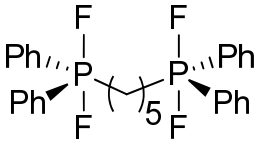


^{31}P{^{1}H} NMR spectrum of compound **8d** (CD_2Cl_2).



$^{19}F\{^{1}H\}$ NMR spectrum of compound **8d** (CD_2Cl_2).

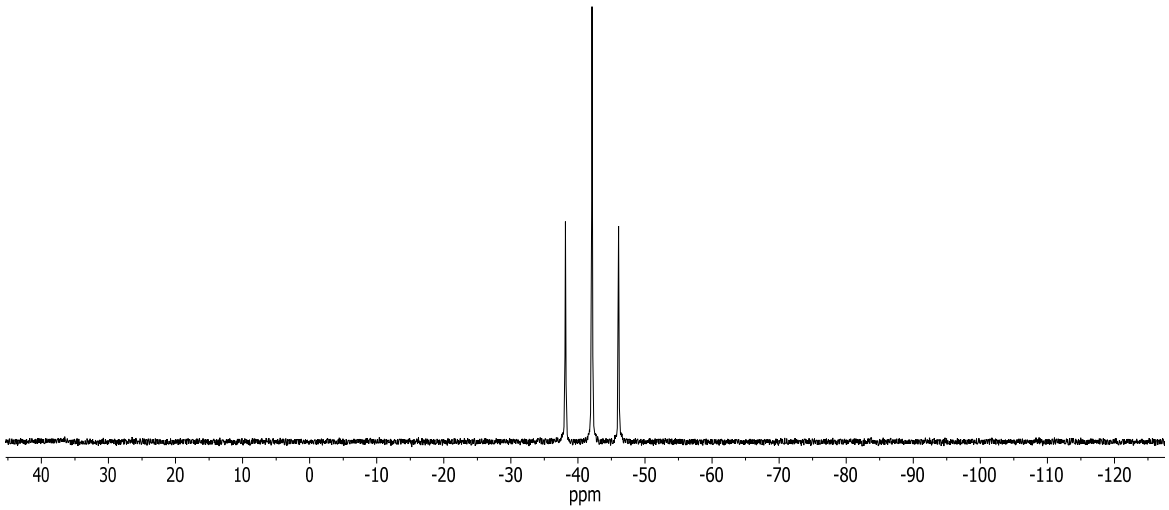
2.10. Preparation of $(CH_2)_5(Ph_2PF_2)_2$ (8e)



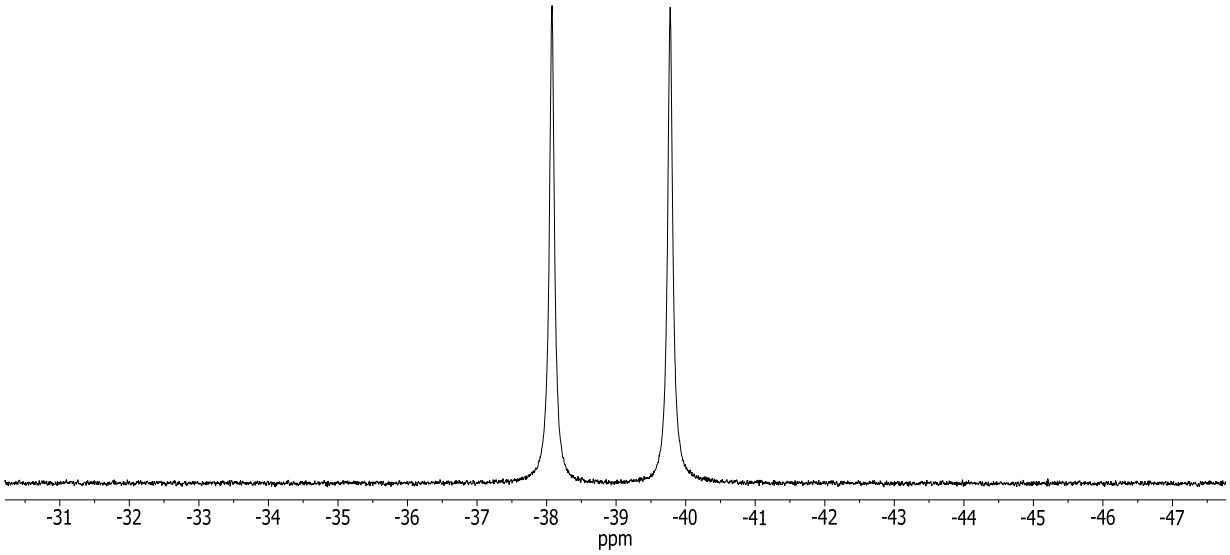
8e

A solution of XeF_2 (86 mg, 0.51 mmol, 2.2 eq.) in CH_2Cl_2 (5 mL) was added dropwise to a solution of 1,4 bis(diphenylphosphino)pentane (101 mg, 0.23 mmol, 1.0 eq.) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at ambient temperature for 15 min giving a colourless solution. All volatiles were removed *in vacuo* yielding a white solid (118 mg, 99% yield).

^{1}H NMR (CD_2Cl_2, [ppm]): δ = 1.47 (2H, p, CH_2, $^{3}J_{HH}$ = 10 Hz), 1.76 (4H, m, CH_2), 2.41 (4H, s(br), P-CH_2), 7.45 (8H, m, *m*-Ph), 7.51 (4H, m, *p*-Ph), 7.95 (8H, m, *o*-Ph); **^{13}C{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 24.0 1C, CH_2), 32.5 (2C, t, CH_2, $^{2}J_{CP}$ = 21 Hz) 36.2 (2C, dt, P-CH_2, $^{1}J_{CP}$ = 128 Hz, $^{2}J_{CF}$ = 24 Hz, $^{4}J_{CP}$ = 1 Hz), 128.6 (8C, dt, *m*-Ph, $^{3}J_{CP}$ = 16 Hz, $^{4}J_{CF}$ = 2 Hz), 131.7 (4C, d, *p*-Ph, $^{4}J_{CP}$ = 4 Hz), 134.2 (8C, dt, *o*-Ph, $^{2}J_{CP}$ = 12 Hz, $^{3}J_{CF}$ = 10 Hz), 136.5 (4C, dt, *i*-Ph, $^{1}J_{PF}$ = 172 Hz, $^{2}J_{CF}$ = 25 Hz); **^{19}F{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = –38.9 (4F, X_2X_2' part of AA'X_2X_2' spin system, $^{1}J_{AX}$ = $^{1}J_{A'X'}$ = 641 Hz, $^{7}J_{A'X}$ = $^{7}J_{AX'}$ = 0 Hz, $^{8}J_{XX'}$ = 0 Hz); **^{31}P{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −42.1 (2P, AA' part of AA'X_2X_2' spin system, $^{5}J_{AA'}$ = 0 Hz); **elemental analysis** for $C_{29}H_{30}F_4P_2$: calcd.: C 67.4, H 5.9, found: C 67.8, H 6.2; **DART MS**: m/z: 497.2 (calcd. for $M-F^+$: 497.2).



$^{31}P\{^{1}H\}$ NMR spectrum of compound **8e** (CD_2Cl_2).

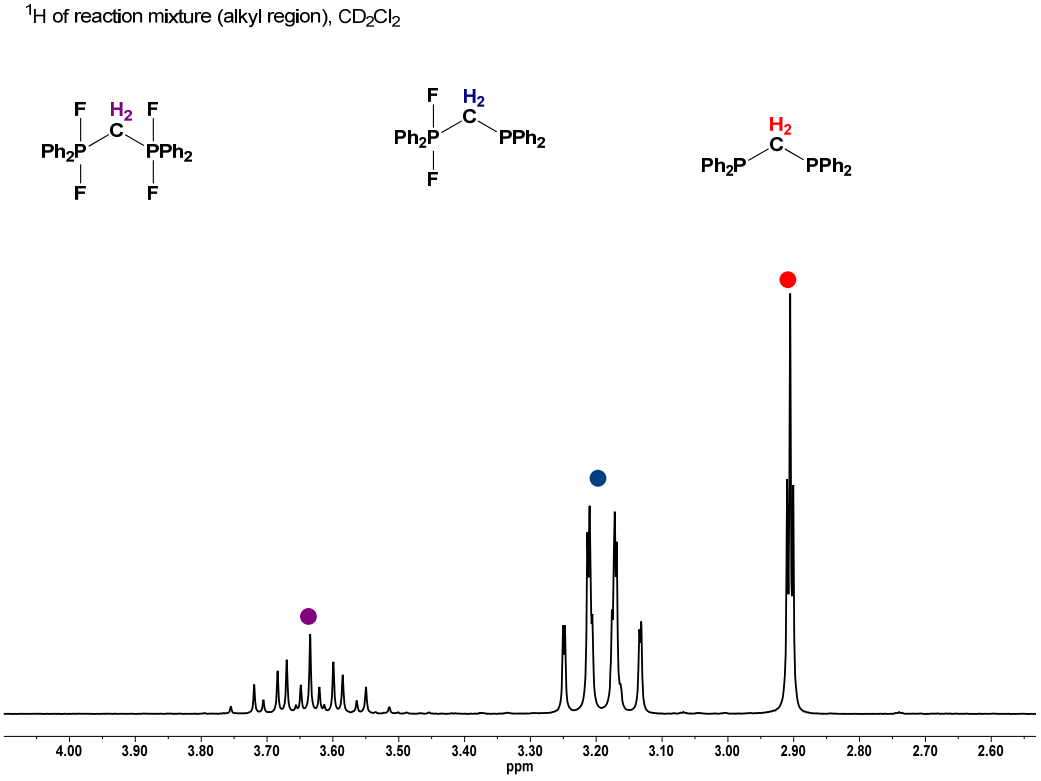


$^{19}F\{^{1}H\}$ NMR spectrum of compound **8e** (CD_2Cl_2).

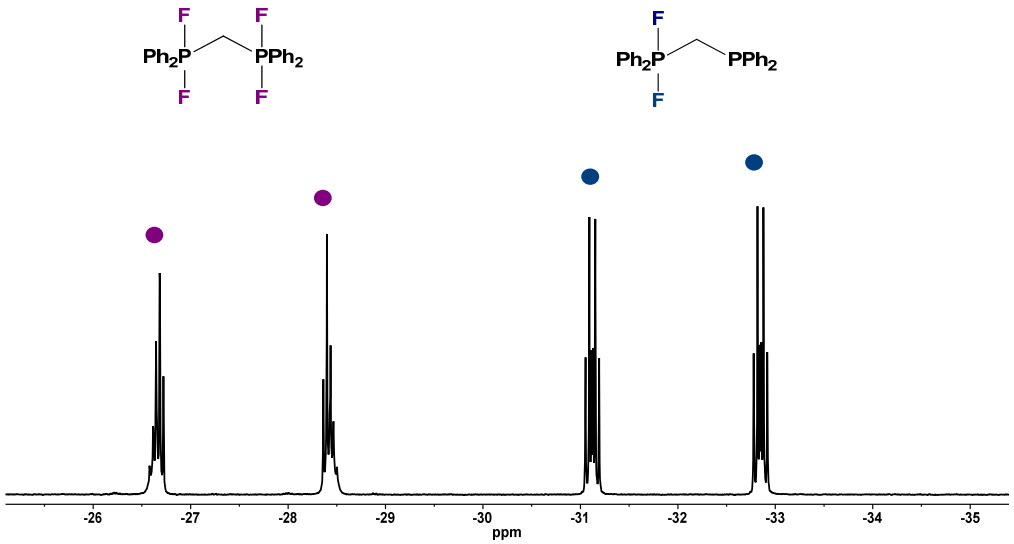
2.11. Attempted stepwise oxidation of 1,1-bis(diphenylphosphino)methane

A solution of XeF_2 (15 mg, 0.089 mmol, 1.0 eq.) in CH_2Cl_2 (2 mL) was added dropwise to a solution of 1,1-bis(diphenylphosphino)methane (35 mg, 0.089 mmol, 1.0 eq.) in CH_2Cl_2 (2 mL) at −35 °C. The reaction mixture was stirred for one hour and all volatiles were removed *in vacuo* yielding a white solid. The residue was dissolved in CD_2Cl_2 and investigated by multi-nuclear magnetic resonance spectroscopy which indicated the presence of 1,1-bis(diphenylphosphino)methane, monophosphorane $(CH_2)_1(Ph_2P)(Ph_2PF_2)$ and bisphosphorane **8a** a 1 : 2 : 1 ratio.

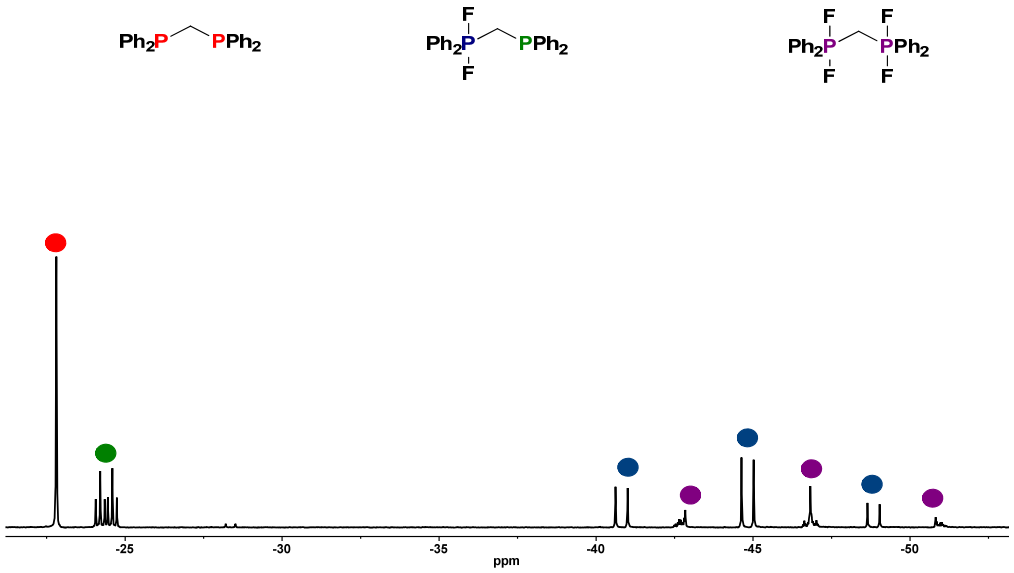
^{1}H NMR (CD_2Cl_2, [ppm]): δ 2.91 (t, $(CH_2)_1(Ph_2P)_2$, $^2J_{HP}$ = 4 Hz), 3.19 (m, $(CH_2)_1(Ph_2P)(Ph_2PF_2)$), 3.63 (m, **8a**), 7.37 (8H, m, *m*-Ph), 7.32-7.98 ($(CH_2)_1(Ph_2P)_2$, $(CH_2)_1(Ph_2P)(Ph_2PF_2)$, **8a**); **^{19}F{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ –32.0 (dd, $(CH_2)_1(Ph_2P)(Ph_2PF_2)$, $^1J_{FP}$ = 650 Hz, $^3J_{FP}$ = 16 Hz), –27.5 (m, **8a**); **^{31}P{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ −46.8 (m, **8a**), −44.8 (td, $(CH_2)_1(Ph_2P)(Ph_2PF_2)$, $^1J_{PF}$ = 650 Hz, $^2J_{PP}$ = 63 Hz), δ -24.40 (dt, $(CH_2)_1(Ph_2P)(Ph_2PF_2)$, $^2J_{PP}$ = 63 Hz, $^3J_{PF}$ = 16 Hz,), -22.81 (s, $(CH_2)_1(Ph_2P)_2$).



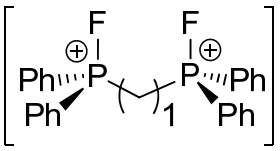
^{19}F of reaction mixture, CD_2Cl_2



^{31}P {1H} of reaction mixture, CD_2Cl_2



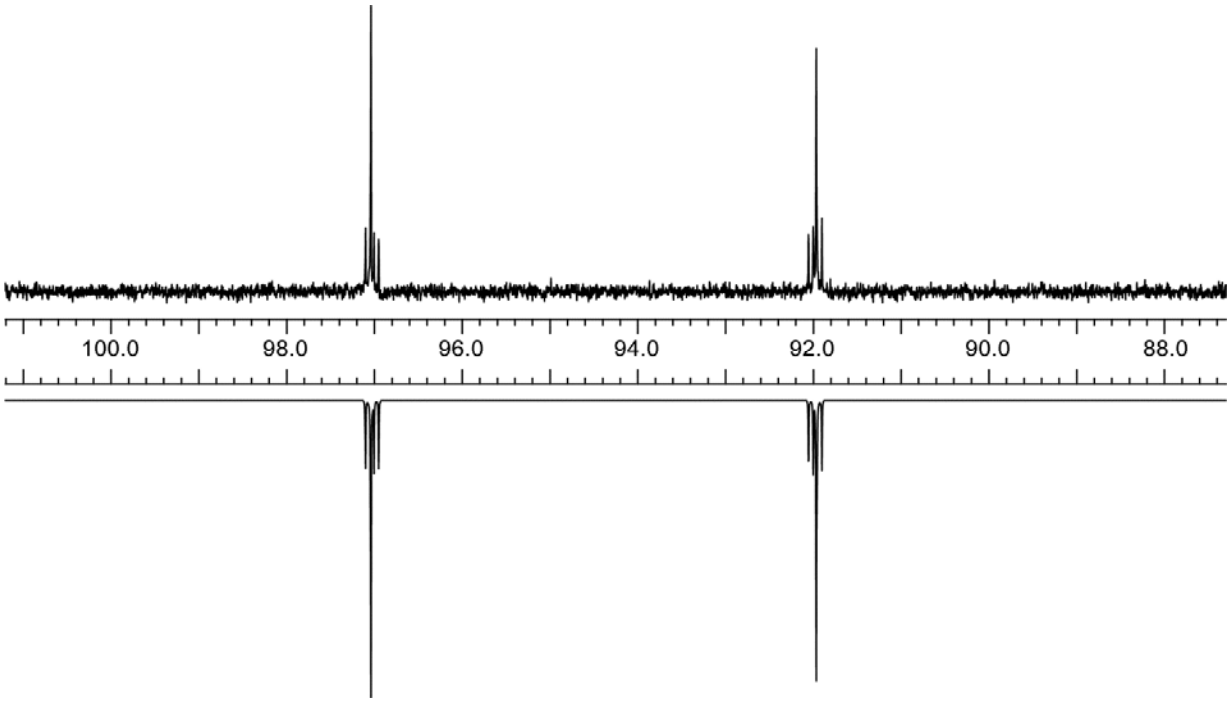
2.12. Preparation of $[(CH_2)_1(Ph_2PF)_2][B(C_6F_5)_4]_2$ (9a)



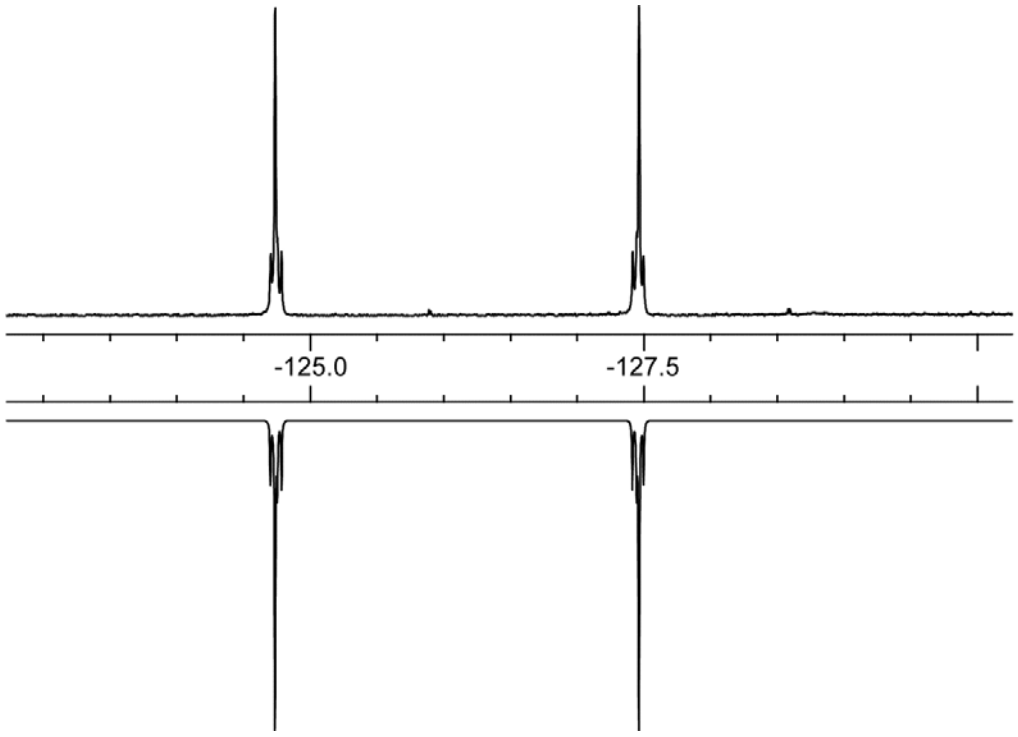
9a

Freshly prepared $[Et_3Si][B(C_6F_5)_4]*2(C_7H_8)$ (411 mg, 0.42 mmol, 1.8 eq.) was added to a solution of **8a** (104 mg, 0.23 mmol, 1.0 eq.) in toluene (5 mL). The formation of a brown oil was observed. The supernatant was removed and the residue was washed with *n*-pentane (3 x 3 mL). During this process, the oil turned into a white solid. The residue was dissolved in CH_2Cl_2 (2 mL) and addition of *n*-pentane (3 mL) resulted in the precipitation of **9a**. The supernatant was removed and the residue was dried *in vacuo* to afford **9a** as a white solid (349 mg, 93% yield).

^{1}H NMR (CD_2Cl_2, [ppm]): δ = 4.78 (2H, m, CH_2), 7.73 (8H, m, *o*-Ph), 7.82 (8H, m, *m*-Ph), 8.15 (4H, t, *p*-Ph, $^3J_{HH}$ = 8 Hz); **^{11}B{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −16.7 (s); **^{13}C{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 25.8 (1C, tt, CH_2, $^1J_{CP}$ = 60 Hz, $^2J_{CF}$ = 16 Hz), 111.8 (4C, dm, *i*-Ph, $^1J_{CP}$ = 115 Hz), 123.8 (8C, m(br), *i*-C_6F_5), 132.0 (8C, dm, *m*-Ph, $^3J_{CP}$ = 15 Hz), 134.9 (8C, dm, *o*-Ph, $^2J_{CP}$ = 14 Hz), 136.2 (16C, dt, *p*-C_6F_5, $^1J_{CF}$ = 241 Hz, $^3J_{FF}$ = 14 Hz), 138.1 (8C, dt, *p*-C_6F_5, $^1J_{CF}$ = 238 Hz, $^3J_{FF}$ = 12 Hz), 148.1 (16C, d(br), $^1J_{CF}$ = 238 Hz); **^{19}F{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −167.1 (16F, m, *m*-C_6F_5), −163.1 (8F, m, *p*-C_6F_5), −133.0 (16F, m, *o*-C_6F_5), −126.3 (2F, XX' part of AA'XX' spin system, $^1J_{AX} = {}^1J_{A'X'}$ = 1024 Hz, $^3J_{A'X} = {}^3J_{AX'}$ = 3 Hz, $^4J_{XX'}$ = 12 Hz); **^{31}P{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 94.5 (2P, AA' part of AA'XX' spin system, $^5J_{AA'}$ = 20 Hz); **elemental analysis** for $C_{73}H_{22}B_2F_{42}P_2$: calcd.: C 49.2, H 1.2, found: C 49.2, H 1.1; **ESI MS**: m/z: 417.1161 (calcd. for $[M-2F+HO_2]^+$: 417.1173)

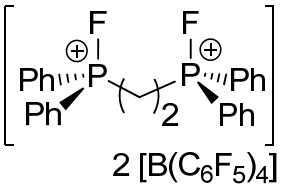


$^{31}P\{^{1}H\}$ NMR spectrum of compound **9a** (CD_2Cl_2, upwards) and simulated spectrum (downwards).



$^{19}F\{^{1}H\}$ NMR spectrum of compound **9a** (CD_2Cl_2, upwards) and simulated spectrum (downwards).

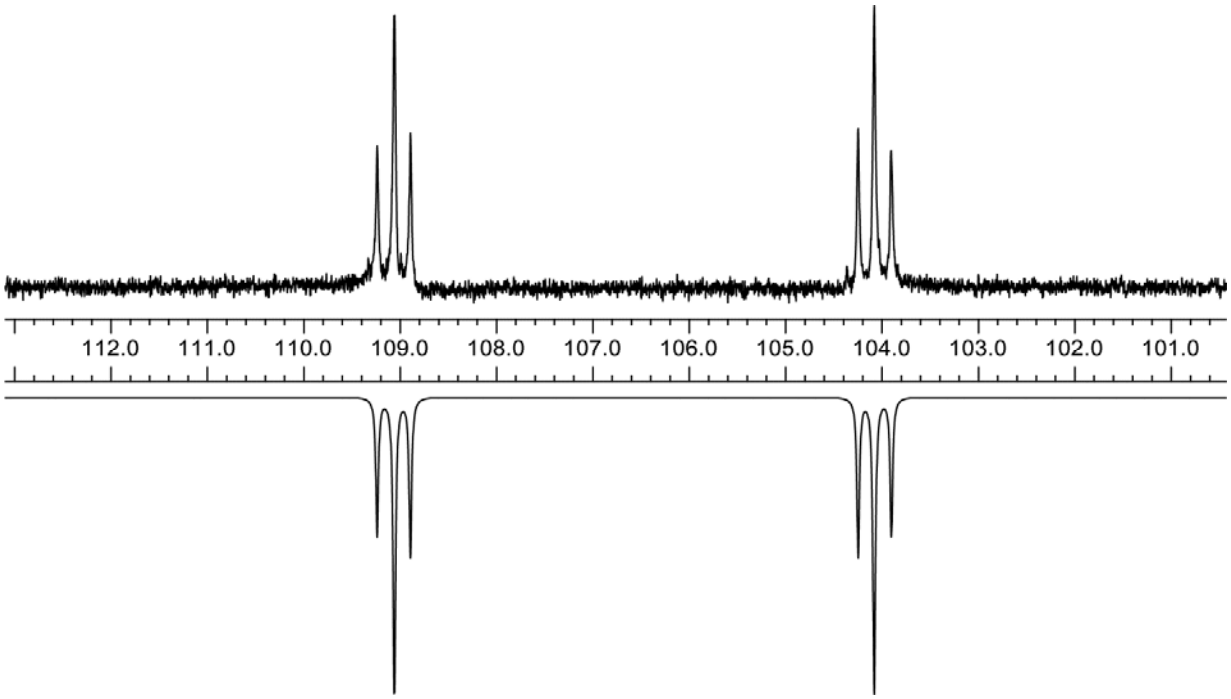
2.13. Preparation of $[(CH_2)_2(Ph_2PF)_2][B(C_6F_5)_4]_2$ (9b)



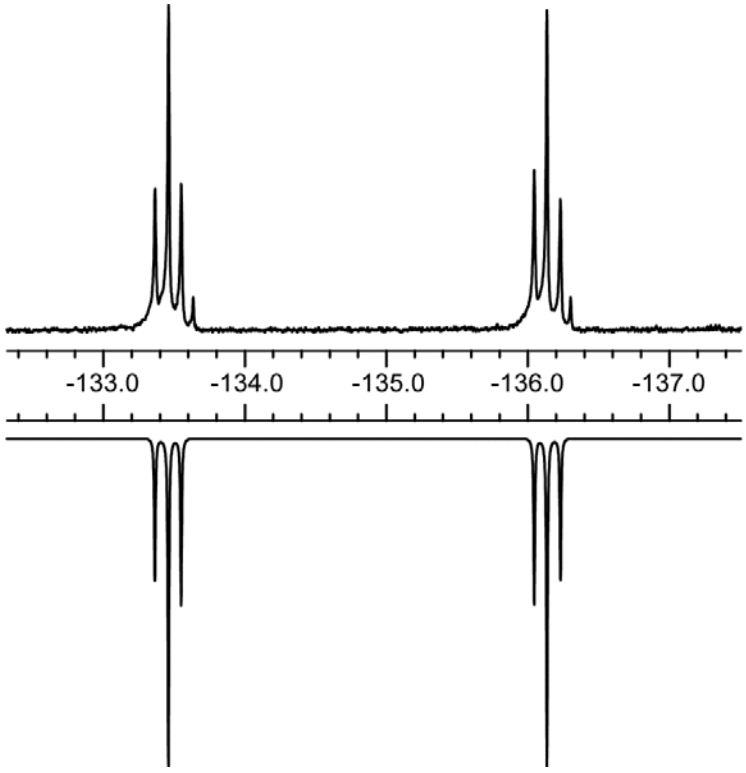
9b

Freshly prepared $[Et_3Si][B(C_6F_5)_4]*2(C_7H_8)$ (283 mg, 0.29 mmol, 1.7 eq.) was added to a solution of **9b** (81 mg, 0.17 mmol, 1.0 eq.) in toluene (5 mL). The solution was stirred for 24 hours, the supernatant was removed, and the residue was washed with *n*-pentane (3 x 3 mL). During this process, the oil turned into a white solid. The residue was dissolved in CH_2Cl_2 (2 mL) and addition of *n*-pentane (3 mL) resulted in the precipitation of **9b**. The supernatant was removed and the residue was dried *in vacuo* to afford **9b** as a white solid (242 mg, 93% yield).

^{1}H NMR (CD_3CN, [ppm]): δ = 3.69 (4H, m, CH_2), 7.85 (8H, m, *o*-Ph), 7.98 (8H, m, *m*-Ph), 8.07 (4H, t, *p*-Ph, $^3J_{CF}$ = 8 Hz); **^{11}B{^{1}H} NMR (CD_3CN, [ppm]):** δ = −16.7 (s); **^{13}C{^{1}H} NMR (CD_3CN, [ppm]):** δ = 18.5 (2C, dd, CH_2, $^1J_{CP}$ = 60 Hz, $^2J_{CF}$ = 11 Hz), 115.5 (4C, dd, *i*-Ph, $^1J_{CP}$ = 103 Hz, $^2J_{CF}$ = 13 Hz), 125.0 (8C, m(br), *i*-C_6F_5), 131.7 (8C, d, *m*-Ph, $^3J_{CP}$ = 15 Hz), 134.7 (8C, dm, *o*-Ph, $^2J_{CP}$ = 13 Hz), 137.3 (16C, dm, C_6F_5, $^1J_{CF}$ = 241 Hz), 139.3 (8C, dm, C_6F_5, $^1J_{CF}$ = 244 Hz), 139.0 (4C, s, *p*-Ph), 149.1 (16C, d(br), C_6F_5 $^1J_{CF}$ = 235 Hz); **^{19}F{^{1}H} NMR (CD_3CN, [ppm]):** δ = −168.3 (16F, m, *m*-C_6F_5), −163.9 (8F, m, *p*-C_6F_5), −138.2 (2F, XX' part of AA'XX' spin system, $^1J_{AX}$ = $^1J_{A'X'}$ = 1008 Hz, $^4J_{A'X}$ = $^4J_{AX'}$ = 0 Hz, $^5J_{XX'}$ = 0 Hz), −133.7 (16F, m, *o*-C_6F_5); **^{31}P{^{1}H} NMR (CD_3CN, [ppm]):** δ = 106.55 (2P, AA' part of AA'XX' spin system, $^3J_{AA'}$ = 70 Hz); **elemental analysis** for $C_{73}H_{22}B_2F_{42}P_2$: calcd.: C 49.5, H 1.35, found: 49.8, H 1.9; **ESI MS**: m/z: 432.1 (calcd. for $[M-2F+H_2O_2]^+$: 432.1)

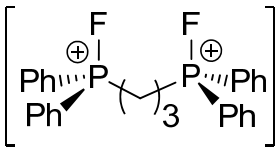


$^{31}P\{^{1}H\}$ NMR spectrum of compound **9b** (CD_3CN, upwards) and simulated spectrum (downwards).



$^{19}F\{^{1}H\}$ NMR spectrum of compound **9b** (CD_3CN, upwards) and simulated spectrum (downwards).

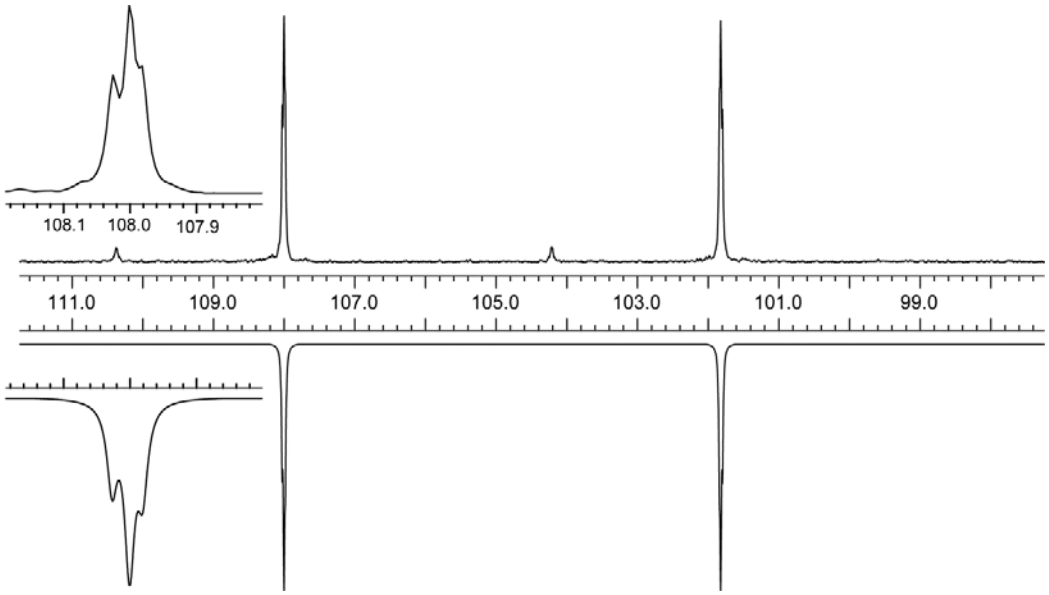
2.14. Preparation of $[(CH_2)_3(Ph_2PF)_2][B(C_6F_5)_4]_2$ (9c)



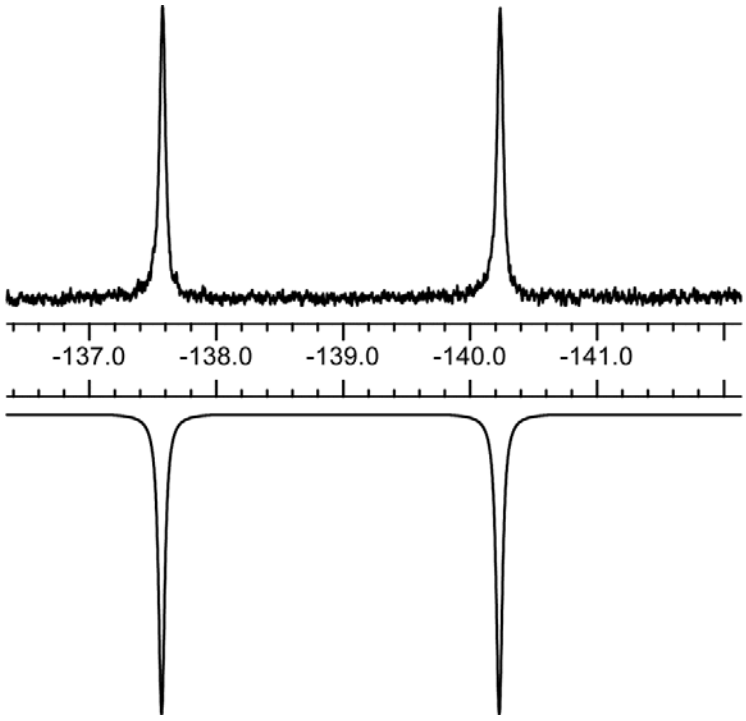
9c

Freshly prepared $[Et_3Si][B(C_6F_5)_4]*2(C_7H_8)$ (176 mg, 0.18 mmol, 1.8 eq.) was added to a solution of **8c** (49 mg, 0.10 mmol, 1.0 eq.) in toluene (5 mL). The formation of a brown oil was observed. The supernatant was removed and the residue was washed with *n*-pentane (3 x 3 mL). During this process, the oil turned into a white solid. The solid was dissolved in dichloromethane (2 mL) and addition of *n*-pentane (3 mL) resulted in the precipitation of **9c**. The supernatant was removed and the residue was dried *in vacuo* to afford **9c** as a white solid (154 mg, 95% yield).

^{1}H NMR (CD_2Cl_2, [ppm]): δ = 2.25 (2H, m (br), CH_2), 3.20 (4H, br, P-CH_2), 7.78 (8H, br, *o*-Ph), 7.81 (8H, br, *m*-Ph), 8.11 (4H, br, *p*-Ph); **^{11}B{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −16.7 (s); **^{13}C{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 14.1 (1C, br, CH_2), 25.9 (2C, d (br), CH_2, $^1J_{CP}$ = 63 Hz), 113.8 (4C, dd, *i*-Ph, $^1J_{CP}$ = 108 Hz, $^2J_{CF}$ = 18 Hz), 123.8 (8C, m(br), *i*-C_6F_5), 131.8 (8C, m, *m*-Ph), 134.9 (8C, dm, *o*-Ph, $^2J_{CP}$ = 14 Hz), 136.6 (16C, dm, C_6F_5, $^1J_{CF}$ = 249 Hz), 138.5 (8C, dm, C_6F_5, $^1J_{CF}$ = 246 Hz), 148.4 (16C, d(br), C_6F_5 $^1J_{CF}$ = 244 Hz); **^{19}F{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −167.2 (16F, m, *m*-C_6F_5), −163.1 (8F, m, *p*-C_6F_5), −138.9 (2F, XX' part of AA'XX' spin system, $^1J_{AX} = {}^1J_{A'X'}$ = 1002 Hz, $^5J_{A'X} = {}^5J_{AX'}$ = −1 Hz, $^6J_{XX'}$ = 0 Hz), −133.0 (16F, m, *o*-C_6F_5); **^{31}P{^{1}H} NMR (CD_2Cl_2,[ppm]):** δ = 104.88 (2P, AA' part of AA'XX' spin system, $^4J_{AA'}$ = 7.5 Hz); **elemental analysis** for $C_{75}H_{26}B_2F_{42}P_2$: calcd.: C 49.8, H 1.45,found: C 49.6, H 1.8; **ESI MS**: m/z: 445.1 (calcd. for $[M-2F+HO_2]^+$: 459.2).

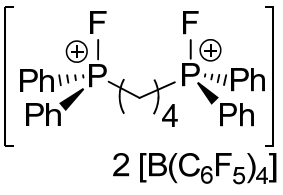


$^{31}P\{^{1}H\}$ NMR spectrum of compound **9c** (CD_2Cl_2, upwards) and simulated spectrum (downwards).



$^{19}F\{^{1}H\}$ NMR spectrum of compound **9c** (CD_2Cl_2, upwards) and simulated spectrum (downwards).

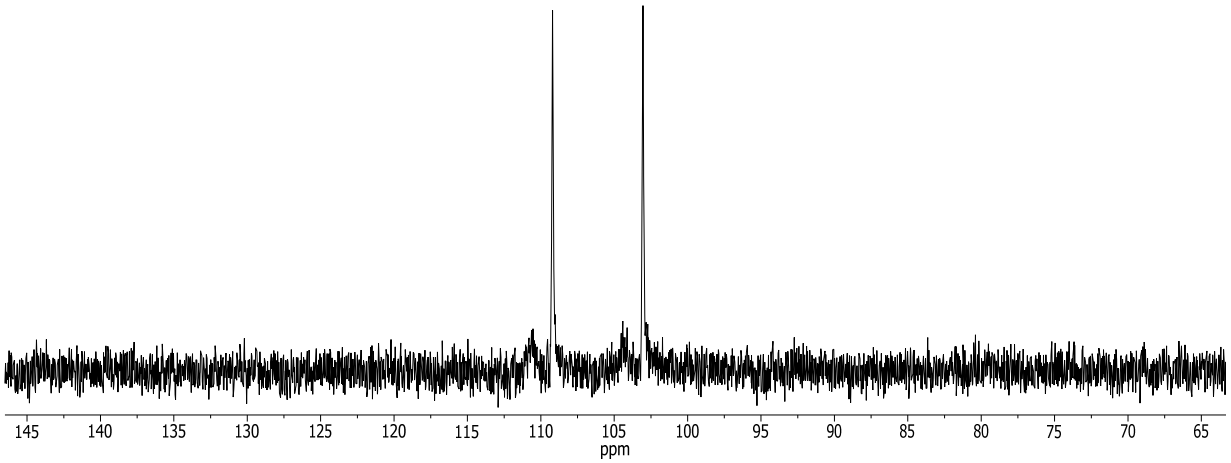
2.15. Preparation of $[(CH_2)_4(Ph_2PF)_2][B(C_6F_5)_4]_2$ (9d)



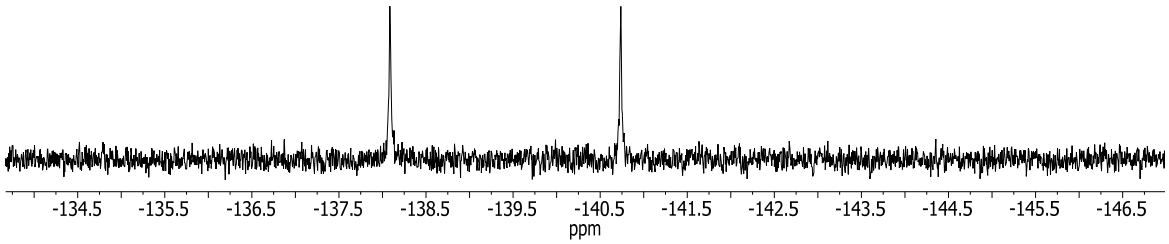
9d

Freshly prepared $[Et_3Si][B(C_6F_5)_4]*2(C_7H_8)$ (254 mg, 0.26 mmol, 1.7 eq.) was added to a solution of **8d** (75 mg, 0.15 mmol, 1.0 eq.) in toluene (5 mL). The formation of a brown oil was observed. The supernatant was removed and the residue was washed with *n*-pentane (3 x 3 mL). During this process, the oil turned into a white solid. The residue was dissolved in dichloromethane (2 mL) and addition of *n*-pentane (3 mL) resulted in the precipitation of **9d**. The supernatant was removed and the residue was dried *in vacuo* to afford **9d** as a white solid (201 mg, 85% yield).

^{1}H NMR (CD_3CN, [ppm]): δ = 1.90 (4H, m, CH_2), 3.27 (4H, m, P-CH_2), 7.80 (8H, m, *o*-Ph), 7.92 (8H, m, *m*-Ph), 8.11 (4H, tm, *p*-Ph, $^3J_{CH}$ = 8 Hz); **^{11}B{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −16.6 (s); **^{13}C{^{1}H} NMR (CD_3CN, [ppm]):** δ = 22.0 (2C, dd, CH_2, $^2J_{CP}$ = 19 Hz, $^3J_{CF}$ = 4 Hz), 24.3 (2C, ddm, P-CH_2, $^1J_{CP}$ = 61 Hz, $^2J_{CF}$ = 12 Hz), 117.3 (4C, dd, *i*-Ph, $^1J_{CP}$ = 101 Hz, $^2J_{CF}$ = 12 Hz), 124.9 (8C, m(br), *i*-C_6F_5), 131.4 (8C, d, *m*-Ph, $^3J_{CP}$ = 14 Hz), 134.2 (8C, dd, *o*-Ph, $^2J_{CP}$ = 12 Hz, $^3J_{CF}$ = 1 Hz), 137.4 (16C, dm, C_6F_5, $^1J_{CF}$ = 244 Hz), 139.3 (8C, dm, C_6F_5, $^1J_{CF}$ = 244 Hz), 139.0 (4C, m, *p*-Ph), 149.2 (16C, d(br), C_6F_5 $^1J_{CF}$ = 239 Hz); **^{19}F{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −167.3 (16F, m, *m*-C_6F_5), −163.3 (8F, m, *p*-C_6F_5), −139.3 (2F, XX' part of AA'XX' spin system, $^1J_{AX}$ = $^1J_{A'X'}$ = 999 Hz, $^6J_{A'X}$ = $^6J_{AX'}$ = 0 Hz, $^7J_{XX'}$ = 0 Hz), −133.0 (16F, m, *o*-C_6F_5); **^{31}P{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 106.13 (2P, AA' part of AA'XX' spin system, $^5J_{AA'}$ = 0 Hz); **elemental analysis** for $C_{76}H_{28}B_2F_{42}P_2$: calcd.: C 50.1, H 1.55, found: C 50.2, H 1.54; **ESI MS**: m/z: 459.1640 (calcd. for $[M-2F+HO_2]^+$: 459.1637).

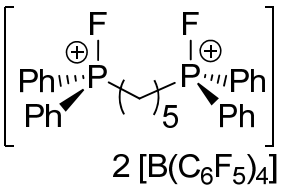


$^{31}P\{^{1}H\}$ NMR spectrum of compound **9d** (CD_2Cl_2).



$^{19}F\{^{1}H\}$ NMR spectrum of compound **9d** (CD_2Cl_2).

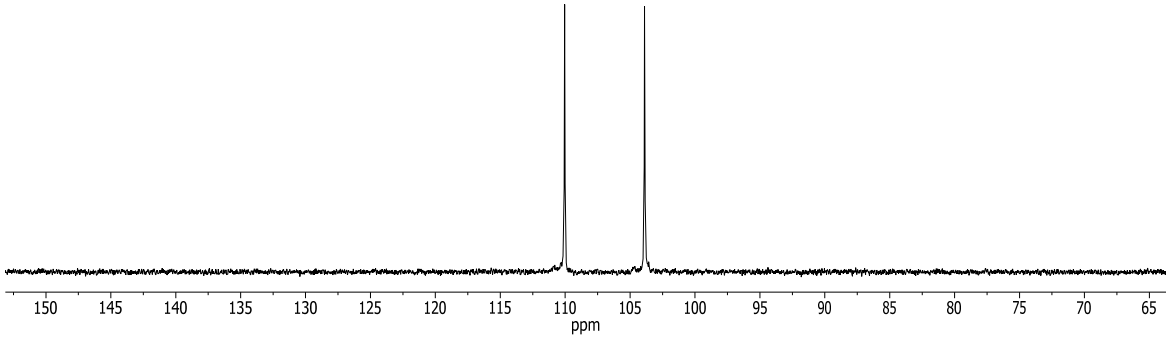
2.16. Preparation of $[(CH_2)_5(Ph_2PF)_2][B(C_6F_5)_4]_2$ (9e)



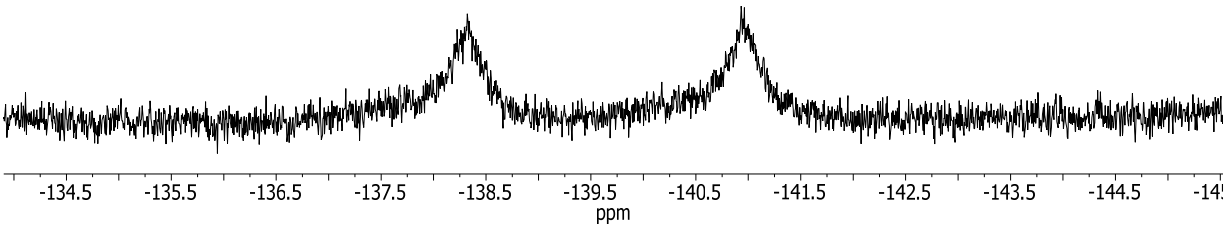
9e

Freshly prepared $[Et_3Si][B(C_6F_5)_4]*2(C_7H_8)$ (343 mg, 0.35 mmol, 1.5 eq.) was added to a solution of **8e** (117 mg, 0.23 mmol, 1.0 eq.) in toluene (5 mL). The formation of a brown oil was observed. The supernatant was removed and the residue was washed with *n*-pentane (3 x 3 mL). During this process, the oil turned into a white solid. The residue was dissolved in dichloromethane (2 mL) and addition of *n*-pentane (3 mL) resulted in the precipitation of **9e**. The supernatant was removed and the residue was dried *in vacuo* to afford **9e** as a white solid (301 mg, 94% yield).

^{1}H NMR (CD_2Cl_2, [ppm]): δ = 1.73 (6H, m (br), CH_2), 2.96 (4H, br, P-CH_2), 7.78 (16H, br, *o*-Ph, *m*-Ph), 8.03 (4H, br, *p*-Ph); **^{11}B{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −16.7 (s); **^{13}C{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 20.81 (1C, br, CH_2), 25.1 (2C, d (br), CH_2, $^1J_{CP}$ = 69 Hz), δ 31.38 (2C, br, CH_2), 115.3 (4C, dm, *i*-Ph, $^1J_{CP}$ = 102 Hz), 124.3 (8C, m(br), *i*-C_6F_5), 131.5 (8C, d, *m*-Ph, $^2J_{CP}$ = 14 Hz), 132.8 (8C, d, *o*-Ph, $^2J_{CP}$ = 11 Hz), 136.7 (16C, dm, C_6F_5, $^1J_{CF}$ = 240 Hz), 138.6 (8C, dm, C_6F_5, $^1J_{CF}$ = 246 Hz), 139.2 (8C, s, *p*-Ph), 148.5 (16C, d(br), C_6F_5 $^1J_{CF}$ = 238 Hz); **^{19}F{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −167.3 (16F, m, *m*-C_6F_5), −163.3 (8F, m, *p*-C_6F_5), −139.7 (2F, XX' part of AA'XX' spin system, $^1J_{AX} = {}^1J_{A'X'}$ = 998 Hz, $^7J_{A'X} = {}^7J_{AX'}$ = 0 Hz, $^8J_{XX'}$ = 0 Hz), −133.0 (16F, m, *o*-C_6F_5); **^{31}P{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 107.0 (2P, AA' part of AA'XX' spin system, $^6J_{AA'}$ = 0 Hz); **elemental analysis** for $C_{77}H_{30}B_2F_{42}P_2$: calcd.: C 50.4, H 1.6, found: C 51.4, H 1.1; **ESI MS**: m/z: 473.2 (calcd. for $[M-2F+HO_2]^+$: 473.2).

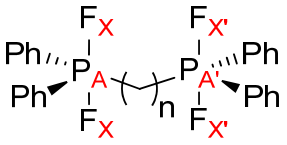


$^{31}P\{^{1}H\}$ NMR spectrum of compound **9e** (CD_2Cl_2).

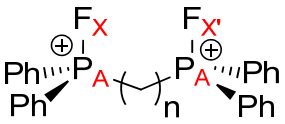


$^{19}F\{^{1}H\}$ NMR spectrum of compound **9e** (CD_2Cl_2).

2.17. $^{31}P\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR parameters of 8a-e and 9a-e



8a-e



9a-e

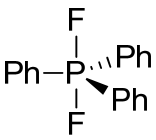
8	Spin system AA'X_2X_2'					
	A (^{31}P)	X (^{19}F)	$^{1}J_{AX} = {}^{1}J_{A'X'}$	$^{n+2}J_{AX} = {}^{n+2}J_{A'X}$	$^{n+1}J_{AA'}$	$^{n+3}J_{XX'}$
a	−46.8	−27.7	664	−18	26	−7
b	−43.6	−39.7	653	−6	115	-
c	−43.2	−39.0	644	−2	12	-
d	−42.4	−38.9	641	-	-	-
e	−42.1	−38.9	641	-	-	-
9	Spin system AA'XX'					
	A (^{31}P)	X (^{19}F)	$^{1}J_{AX} = {}^{1}J_{A'X'}$	$^{n}J_{AX} = {}^{n}J_{A'X}$	$^{n}J_{AA'}$	$^{n}J_{XX'}$
a	94.5	−126.3	1024	3	20	12
b	106.4	−134.8	1008	-	70	-
c	104.9	−138.9	1002	−1	8	-
d	106.1	−139.4	999	-	-	-
e	107.0	−139.7	997	-	-	-

Note: Compounds **8a-c** and **9a-c** showed higher order resonances and their ^{31}P and ^{19}F NMR parameters (CD_2Cl_2) were obtained by means of full-lineshape iteration,[S7] spectra for **9b** were recorded in CD_3CN solution.

Discussion: The ^{31}P NMR resonances of phosphoranes **8a-e** are shifted to higher field with increased length of the (oligo)methylene-linker. A similar trend is observed for the ^{19}F NMR chemical shifts of bisphosphonium ions **9a-e**. For both substance classes, a decrease in the value of the $^{1}J_{PF}$ coupling constant occurs with an increase in (oligo)methylene-linker length. Commonly, highly electrophilic phosphonium ions show $^{1}J_{PF}$ coupling constants above 1000 Hz.[S8] Thus, significant electrophilicity is anticipated for methylene-bridged compound **9a** ($^{1}J_{AX}$ = 1024 Hz) and a stepwise decreases upon utilization of longer (oligo)methylene-linkers seems likely. Only methylene bridged compounds **8a**/**9a** reveal a significant coupling between fluorine atoms ($^{4}J_{XX'}$ = −7 Hz and 12 Hz) and observable P-P couplings occur up to propylene-linked compounds **8c**/**9c**. Remarkable large P-P coupling constants are observed for ethylene-

linked compounds **8b**/**9b** ($^3J_{AA'}$ = 114 Hz and 70 Hz) which might indicate a weak through space interaction between both P moieties.[S9]

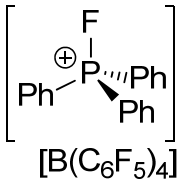
2.18. Preparation of Ph_3PF_2[S10]



XeF_2 (56 mg, 0.33 mmol, 1.1 eq.) was added portion wise to a solution of triphenylphosphine (79 mg, 0.30 mmol, 1.0 eq.) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 30 min at ambient temperature. Removal of all volatiles *in vacuo* gave Ph_3PF_2 as colourless solid (92 mg, 99%). Multi-nuclear magnetic resonance experiments were in accordance to literature reported values.[S10]

^{1}H NMR (CD_2Cl_2, [ppm]): δ = 7.42 - 7.58 (9H, m), 7.94 - 8.06 (6H, m); **^{19}F{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −39.6 (d, $^1J_{FP}$ = 660 Hz); **^{31}P{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −54.9 (t, $^1J_{PF}$ = 660 Hz).

2.19. Preparation of $[Ph_3PF][B(C_6F_5)_4]$[S11]



Freshly prepared $[Et_3Si][B(C_6F_5)_4]$*2(C_7H_8) (139 mg, 0.14 mmol, 1.0 eq.) was added to a solution of Ph_3PF_2 (42 mg, 0.14 mmol, 1.0 eq.) in C_6H_5F (5 mL). Addition of *n*-pentane (5 mL) to the reaction mixture led to the formation of a colourless precipitate. The supernatant was removed and the residue was washed with *n*-pentane (3 x 3 mL). Removal of all volatiles *in vacuo* gave $[Ph_3F][B(C_6F_5)_4]$ as a colourless, microcrystalline solid (119 mg, 87% yield). Multi-nuclear magnetic resonance experiments were in accordance to literature reported values of related AsF_6^- and BF_4^-salts.[S11]

^{1}H NMR (CD_2Cl_2, [ppm]): δ = 7.72 - 7.88 (12H, *m*-/*o*-Ph), 8.02 - 8.10 (3H, *p*-Ph); **^{11}B{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −16.7 (s); **^{13}C{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 131.3 (6C, d, *o*-/*m*-Ph, J_{CP} = 14.4 Hz), 134.3 (6C, dd, *o*-/*m*-Ph, J_{CP} = 13.2 Hz, J_{CF} = 1.1 Hz), 139.0 (3C, dd, *p*-Ph, $J_{CP/F}$ = 2.7 Hz, 1.8 Hz), 116.5 (3C, dd, *i*-Ph, $^1J_{CP}$ = 109.0 Hz, $^2J_{CF}$ = 14.6 Hz), 131.3 (6C, d, *o*-/*m*-Ph, J_{CP} = 14.6 Hz), 134.3 (6C, dd, *o*-/*m*-Ph, J_{CP} = 13.1 Hz, J_{CF} = 1.3 Hz), 136.7 (8C, d(br), C_6F_5, $^1J_{CF}$ = 245 Hz), 138.6 (4C, d(br), C_6F_5, $^1J_{CF}$ = 247 Hz), 139.0 (3C, dd, *p*-Ph, $^4J_{CP}$ = 2.8 Hz, $^5J_{CF}$ = 1.7 Hz), 148.5 (8C, d(br), C_6F_5, $^1J_{CF}$ = 241 Hz); **^{19}F{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −167.6 (8F, m, *m*-C_6F_5), −163.7 (4F, t, *p*-C_6F_5, $^3J_{FF}$ = 20 Hz), −133.2 (8F, m, *o*-C_6F_5), −128.1 (d, $^1J_{FP}$ = 997 Hz); **^{31}P{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −94.8 (d, $^1J_{PF}$ = 997 Hz).

2.20. Reaction of 5, $[Ph_3PF][B(C_6F_5)_4]$, and 9a-e with Et_3PO (Gutmann-Beckett test)

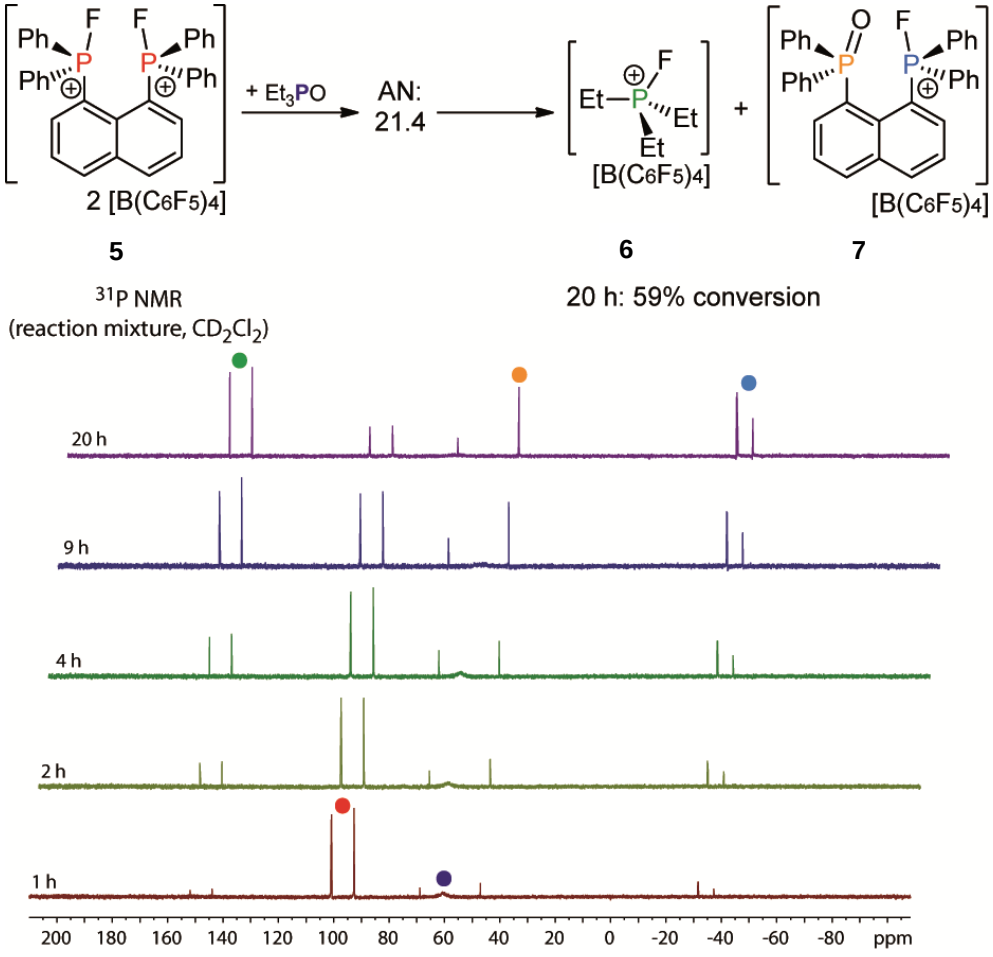
Et_3PO (4 mg, 0.03 mmol, 1.0 eq.) was added to solutions of **5** (57 mg, 0.03 mmol, 1.0 eq.), $[Ph_3PF][B(C_6F_5)_4]$, (58 mg, 0.06 mmol, 1.0 eq.) or **9a-e** (**a**: 53 mg, **b**: 54 mg, **c**: 54 mg, **d**: 55 mg, **e**: 55 mg, 0.03 mmol, 1.0 eq.) in CD_2Cl_2 (1 mL). The reaction mixtures were monitored by means of ^{31}P and ^{19}F NMR spectroscopy for 20 h at ambient temperature. The formation of **6**[S8b] and Ph_3PO[S12] was confirmed by comparison with literature known NMR data.

5 + Et_3PO (1 h):

$^{19}F\{^1H\}$ NMR (CD_2Cl_2, [ppm]): $\delta = -117.2$ (d, **5**, $^1J_{FP} = 991$ Hz); **$^{31}P\{^1H\}$ NMR (CD_2Cl_2, [ppm]):** $\delta = 60.5$ (s(br), Et_3PO), 96.7 (dd, **5**, $^1J_{PF} = 991$ Hz, $^5J_{PF} = 13$ Hz).

5 + Et_3PO (20 h):

^{19}F NMR (CD_2Cl_2, [ppm]): $\delta = -158.5$ (dsept., **6**, $^1J_{FP} = 964$ Hz, $^3J_{FH} = 12$ Hz), −24.5 (d(br), **7**, $^1J_{FP} = 697.0$ Hz); **$^{31}P\{^1H\}$ NMR (CD_2Cl_2, [ppm]):** $\delta = -34.5$ (dd, **7**, $^1J_{FP} = 697$ Hz, $^2J_{PP} = 23$ Hz), 47.1 (dd, **7**, $^2J_{PP} = 23$ Hz, $^3J_{PF} = 2$ Hz), 147.9 (d, **6**, $^1J_{PF} = 964$ Hz).

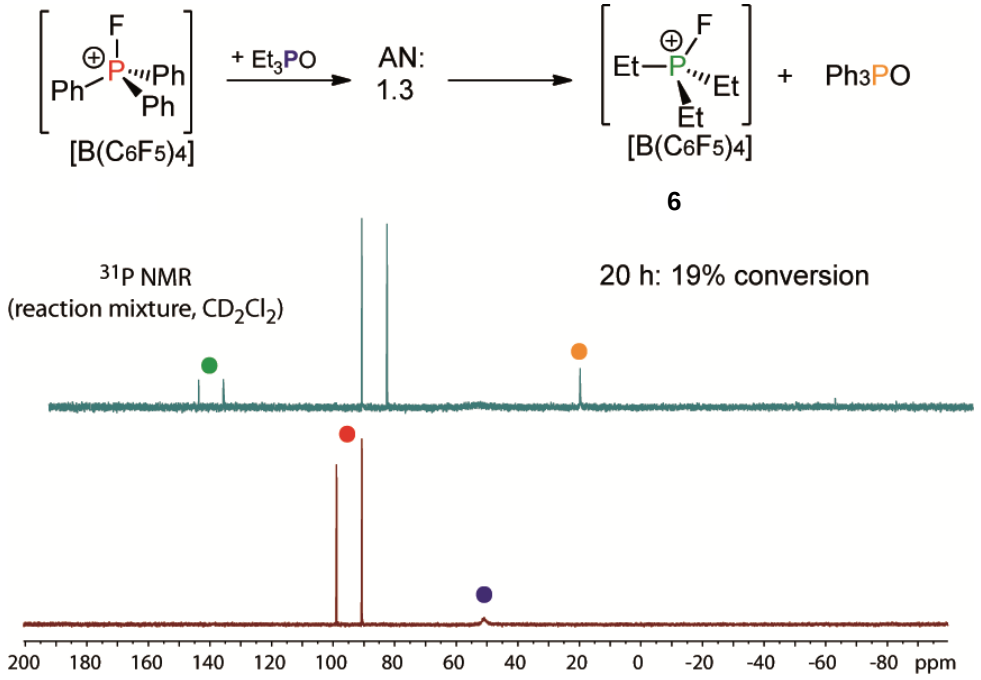


$[Ph_3PF][B(C_6F_5)_4]$ + Et_3PO (1 h):

$^{19}F\{^1H\}$ NMR (CD_2Cl_2, [ppm]): $\delta = -128.1$ (d, $[Ph_3PF]^+$, $^1J_{FP} = 998$ Hz); **$^{31}P\{^1H\}$ NMR (CD_2Cl_2, [ppm]):** $\delta = 51.1$ (s(br), Et_3PO), 94.8 (d, $[Ph_3PF]^+$, $^1J_{PF} = 998$ Hz).

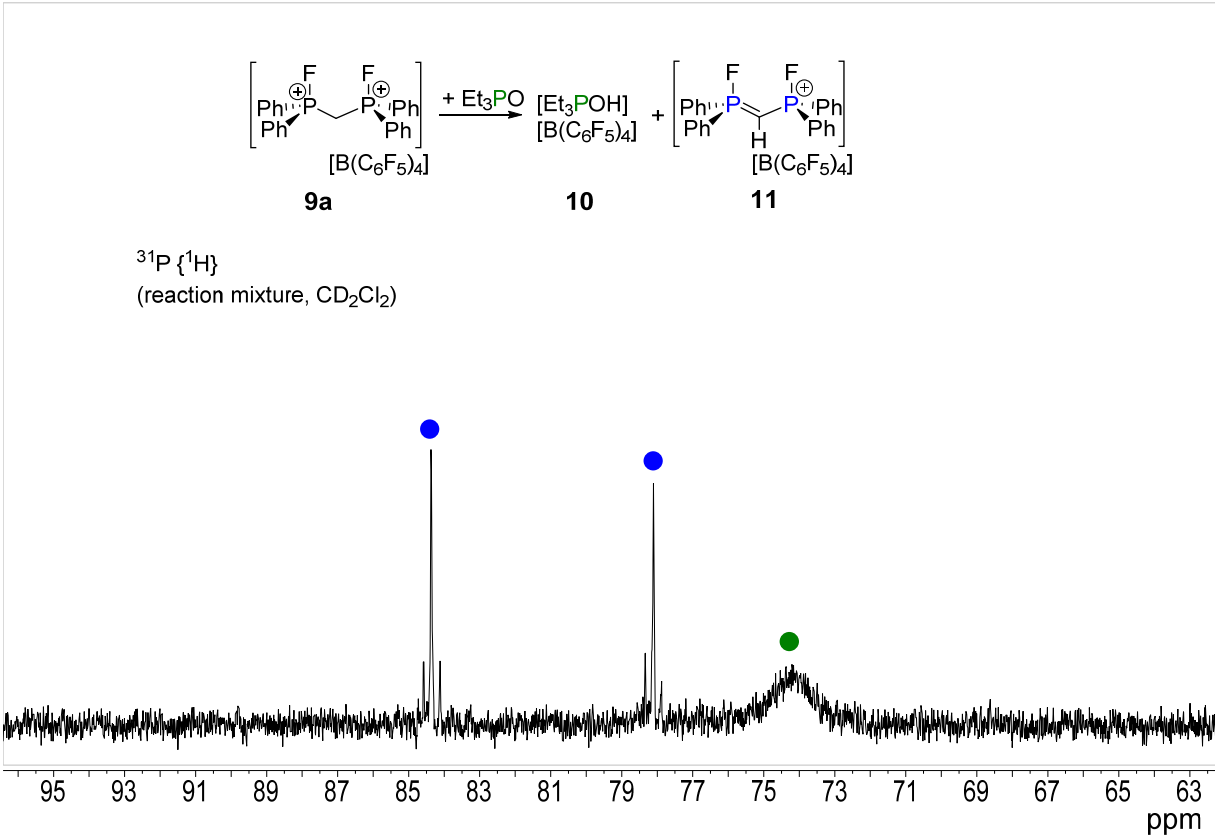
$[Ph_3PF][B(C_6F_5)_4]$ + Et_3PO (20 h):

^{19}F NMR (CD_2Cl_2, [ppm]): $\delta = -158.5$ (dsept., **6**, $^1J_{FP} = 988$ Hz, $^3J_{FH} = 12$ Hz), −128.1 (d, $[Ph_3PF]^+$, $^1J_{FP} = 998$ Hz); **$^{31}P\{^1H\}$ NMR (CD_2Cl_2, [ppm]):** $\delta = -28.0$ (s, Ph_3PO), 94.8 (d, $[Ph_3PF]^+$, $^1J_{PF} = 998$ Hz), 147.4 (d, **6**, $^1J_{PF} = 988$ Hz).



9a + Et_3PO (1 h):

$^{19}F\{^1H\}$ NMR (CD_2Cl_2, [ppm]): $\delta = -99.4$ (dm, **11**, $^1J_{FP} = 1014$ Hz); **$^{31}P\{^1H\}$ NMR (CD_2Cl_2, [ppm]):** $\delta = 74.1$ (s(br), **10**), 81.2 (dm), **11**, $^1J_{PF} = 1014$ Hz).



$^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **9a** and Et_3PO (CD_2Cl_2).

Note:

The deprotonation of **9a** was independently investigated using *t*-Bu_3P as a base. Quantitative transformation to $[t\text{-}Bu_3PH]^+$ and **11** was observed according to ^{1}H, $^{19}F\{^{1}H\}$ and ^{31}P NMR spectroscopy.

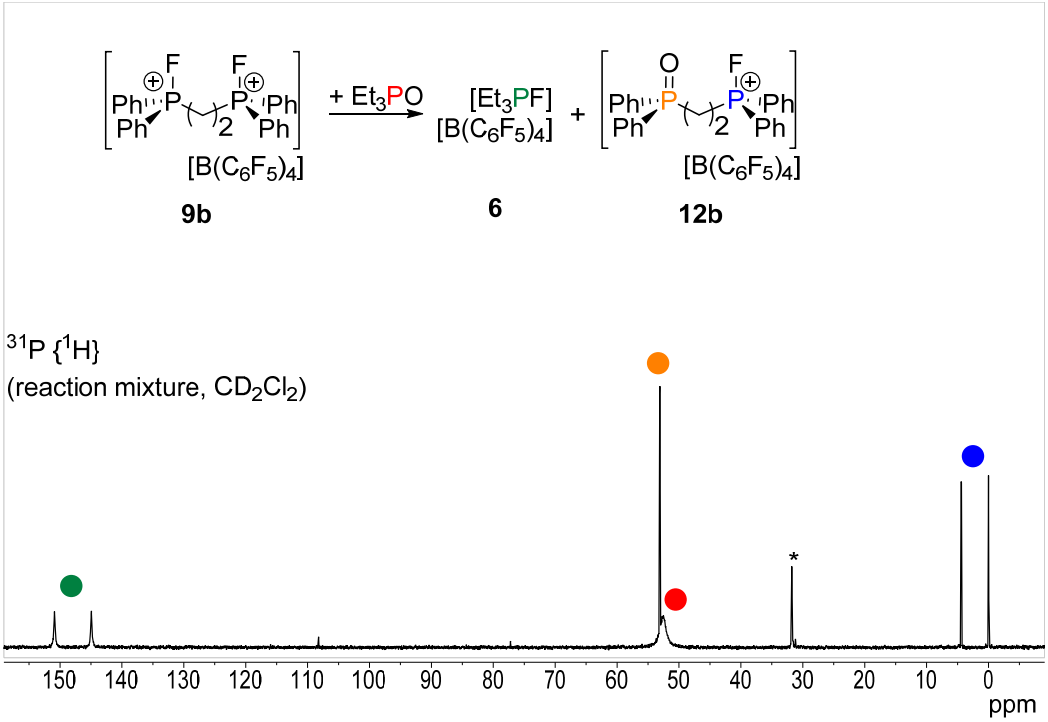
9a + *t*-Bu_3P:

^{19}F NMR (CD_2Cl_2, [ppm]): $\delta = -99.6$ (ddm, **11**, $^{1}J_{FP} = 1013$ Hz, $^{3}J_{FH} = 5.6$ Hz); **$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, [ppm]):** $\delta = 81.5$ (dm, **11**, $^{1}J_{PF} = 1013$ Hz), 61.0 (s(br), $[t\text{-}Bu_3PH]^+$)

^{31}P NMR (CD_2Cl_2, [ppm]): $\delta = 81.5$ (d(br), **11**, $^{1}J_{PF} = 1013$ Hz), 61.0 (dm, $^{1}J_{PH} = 426$ Hz, $[t\text{-}Bu_3PH]^+$)

9b + Et_3PO (1 h):

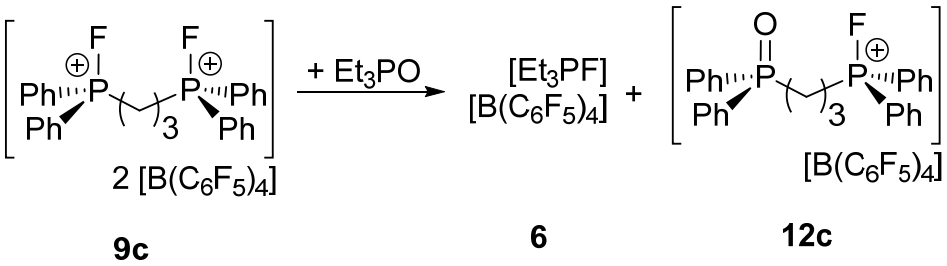
$^{19}F\{^1H\}$ NMR (CD_2Cl_2, [ppm]): $\delta = -159.1$ (d(br), **6**, $^1J_{FP} = 963$ Hz), −44.8 (d(br), **12b**, $^1J_{FP} = 720$ Hz); **$^{31}P\{^1H\}$ NMR (CD_2Cl_2, [ppm]):** $\delta = 2.2$ (dd, **12b**, $^1J_{FP} = 720$ Hz, $^3J_{PP} = 7$ Hz), 53.1 (dd, **12b**, $^3J_{PP} = 7$ Hz, $^4J_{PF} = 2$ Hz), 147.4 (d, **6**, $^1J_{PF} = 963$ Hz).



$^{31}P\{^1H\}$ NMR spectrum of the reaction of **9b** and Et_3PO (CD_2Cl_2). * indicates some amounts of $(CH_2)_2(Ph_2PO)_2$.[S14]

9c + Et_3PO (1 h):

$^{19}F\{^1H\}$ NMR (CD_2Cl_2, [ppm]): $\delta = -159.2$ (d, **6**, $^1J_{FP} = 967$ Hz), −86.4 (d, **12c**, $^1J_{FP} = 823$ Hz); **$^{31}P\{^1H\}$ NMR (CD_2Cl_2, [ppm]):** $\delta = 44.05$ (d, **12c**, $^4J_{PP} = 12$ Hz), 45.2 (dd, **12c**, $^1J_{PF} = 823$ Hz, $^4J_{PP} = 12$ Hz), 148.0 (d, **6**, $^1J_{PF} = 967$ Hz).



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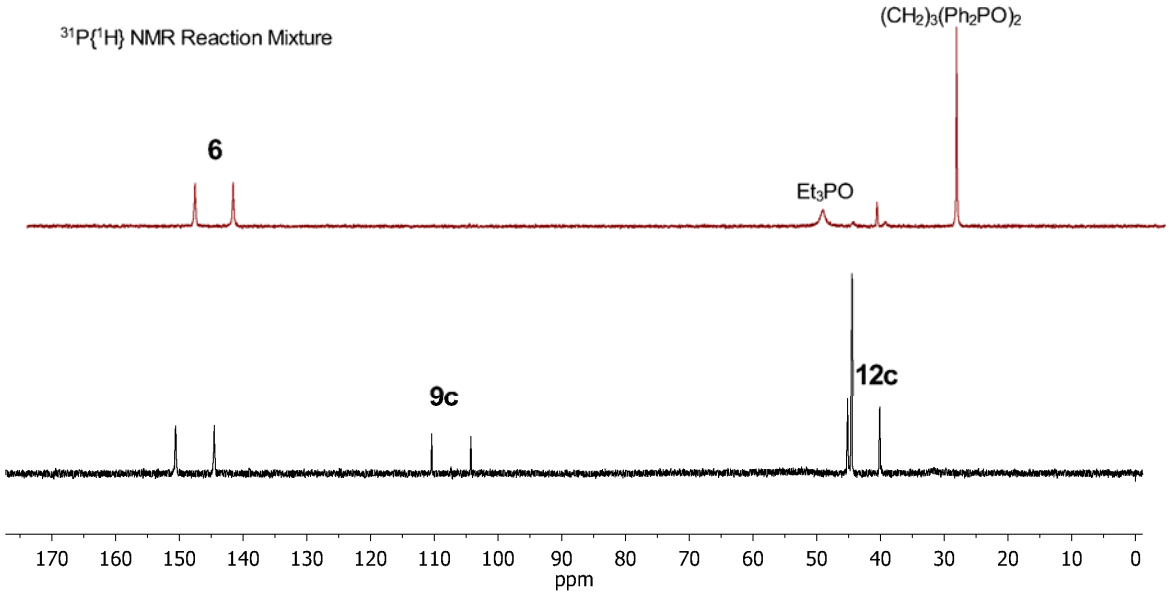


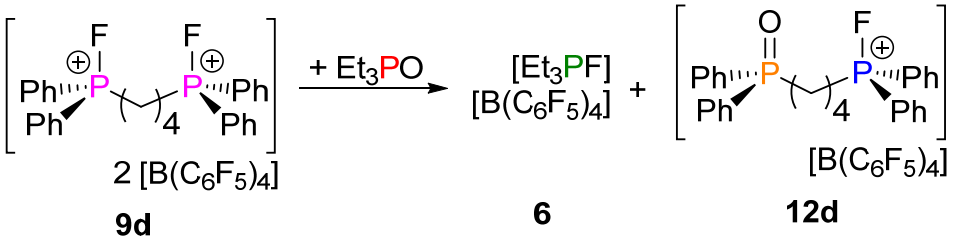
$^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **9c** and Et_3PO (CD_2Cl_2).

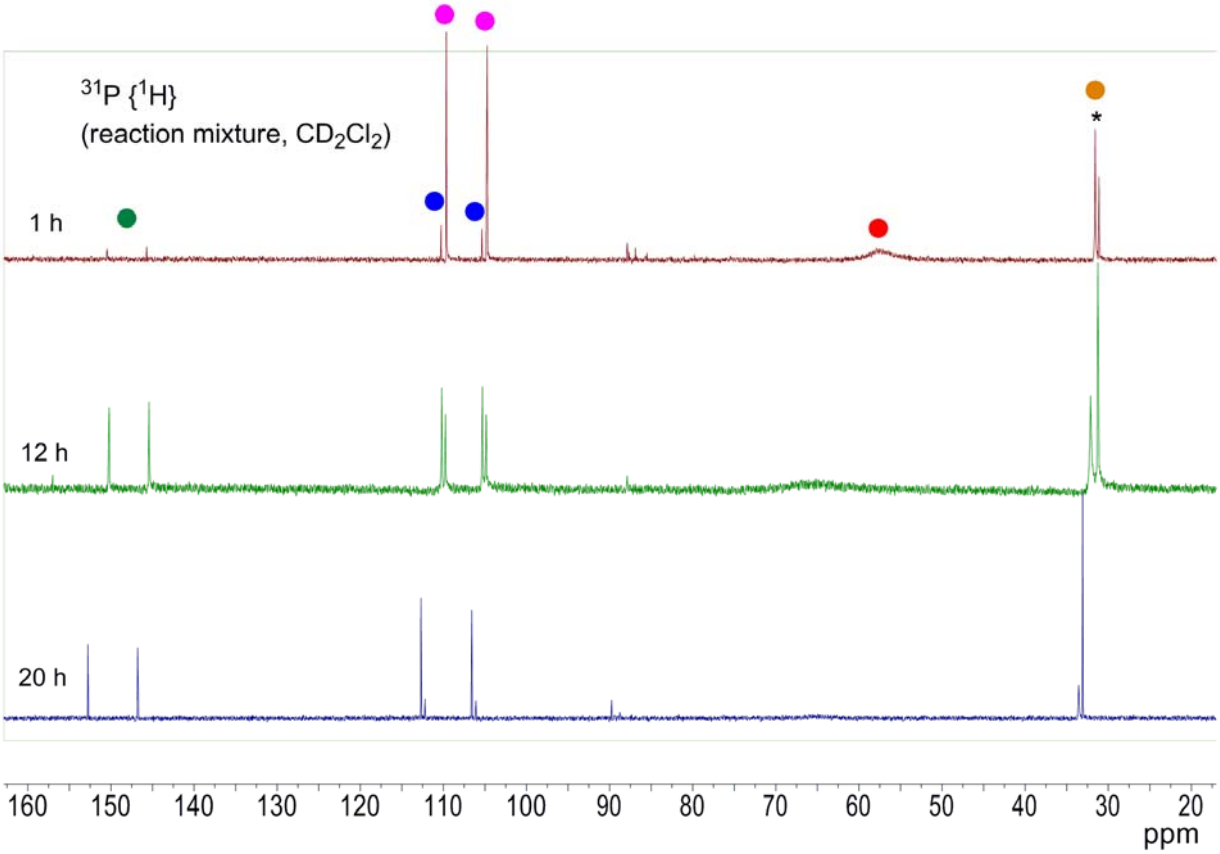
9d + Et_3PO (1 h):

$^{19}F\{^{1}H\}$ NMR (CD_2Cl_2, [ppm]): $\delta = -139.6$ (dt, **9d**, $^{1}J_{FP} = 994$ Hz), **$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, [ppm]):** $\delta = 58.0$ (s(br), Et_3PO), 96.7 (dd, **9d**, $^{1}J_{PF} = 994$ Hz).

9d + Et_3PO (20 h):

$^{19}F\{^{1}H\}$ NMR (CD_2Cl_2, [ppm]): $\delta = -159.2$ (d(br), **6**, $^{1}J_{FP} = 969$ Hz), −136.2 (dt, **12d**, $^{1}J_{FP} = 990$ Hz), **$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, [ppm]):** $\delta = 33.1$ (s, **12d**), 109.6 (d, **12d**, $^{1}J_{PF} = 990$ Hz), 149.8 (d, **6**, $^{1}J_{PF} = 969$ Hz).

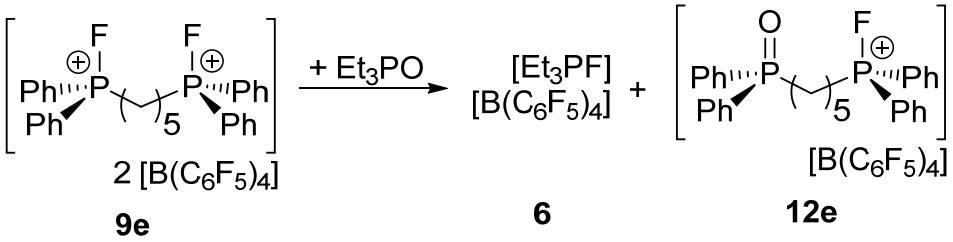


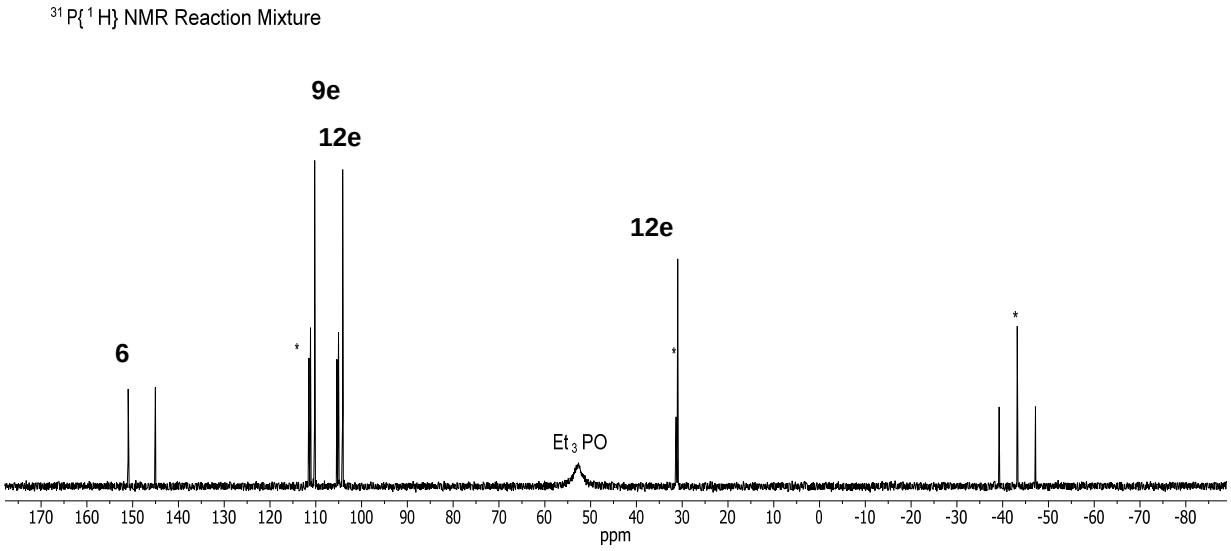


$^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **9d** and Et_3PO (CD_2Cl_2). * indicates some amounts of $(CH_2)_4(Ph_2PO)_2$.

9e + Et_3PO (1 h):

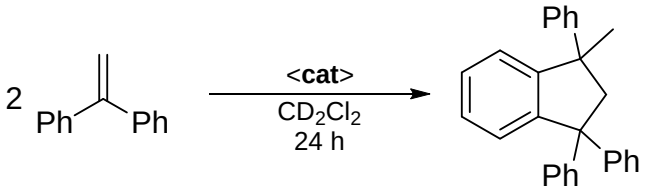
$^{19}F\{^{1}H\}$ NMR (CD_2Cl_2, [ppm]): $\delta = -139.6$ (d, **9e**, $^{1}J_{FP} = 991$ Hz), −139.6 (d, **12e**, $^{1}J_{FP} = 991$ Hz); **$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, [ppm]):** $\delta = 31.8$ (d, **12e**), 52.8 (s(br), Et_3PO), 108.0 (d, **12e**, $^{1}J_{PF} = 991$ Hz), 107.2 (d, **9e**, $^{1}J_{PF} = 991$ Hz).





$^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **9e** and Et_3PO (CD_2Cl_2). * indicates some amounts of $(CH_2)_5(Ph_2PO)_2$ and **8e**

2.21. Friedel-Crafts dimerization of 1,1-diphenylethylene with 5, $[Ph_3PF][B(C_6F_5)_4]$ and 9a-e as catalyst

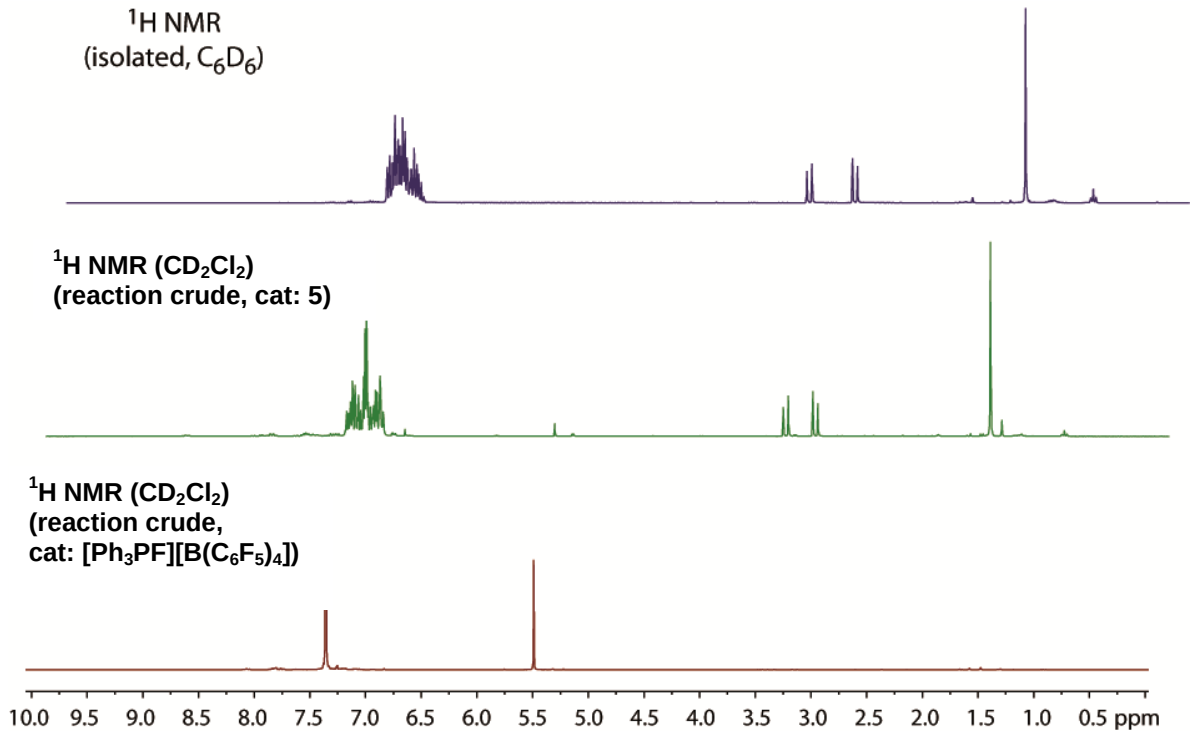


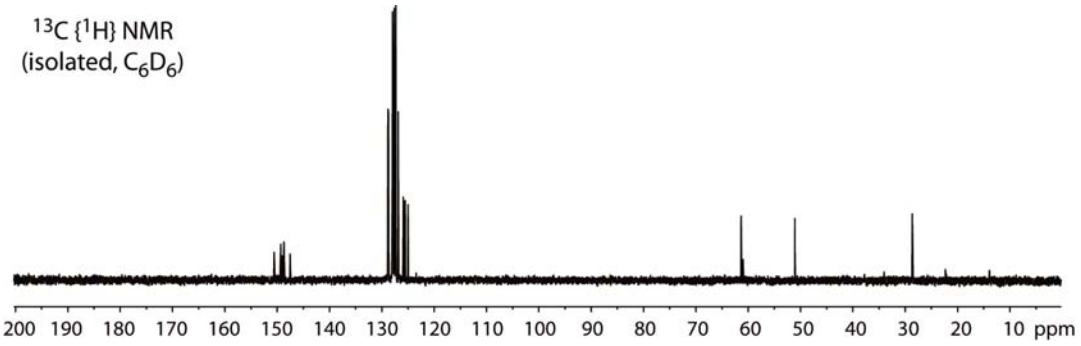
5 (2 mol%): 96% conversion (94% isolated yield)
$[Ph_3PF]^+$ (4 mol%): 1% conversion
9a (2 mol%): 99% conversion
9b (2 mol%): 99% conversion
9c (2 mol%): 99% conversion
9d (2 mol%): 50% conversion
9e (2 mol%): 25% conversion

Catalyst **5** (8 mg, 2 mol%), $[Ph_3PF][B(C_6F_5)_4]$ (8 mg, 4 mol%) or **9a-e** (6mg, 2 mol%) were added to a solution of 1,1-diphenylethylene (32 mg, 0.2 mmol) in CD_2Cl_2 (0.7 mL) at ambient temperature. The reaction mixture was left at ambient temperature for 24 h and investigated by

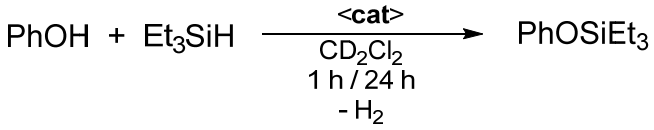
NMR spectroscopy. For catalyst **5**, all volatiles were removed *in vacuo* and the remaining residue was suspended in *n*-pentane. The mixture was filtered through a celite plug and the solvent was removed *in vacuo* giving 1-methyl-1,3,3-triphenyl-2,3-dihydro-1H-indene as a colourless solid (34 mg, 94% yield).[S8b]

^{1}H NMR (C_6D_6, [ppm]): δ = 1.48 (3H, s, CH_3), 3.02 (1H, d, CH_2, $^3J_{HH}$ = 13.5 Hz), 3.42 (1H, d, CH_2, $^3J_{HH}$ = 13.5 Hz), 6.90 - 7.23 (19H, m); **^{13}C{^{1}H} (C_6D_6, [ppm]):** δ = 29.1 (1C, s, CH_3), 51.5 (1C, s, CH_2), 61.4 (1C, s, CPh), 61.8 (1C, s, CPh), 125.4 (1C, s, Ph), 125.9 (1C, s, Ph), 126.0 (1C, s, Ph), 126.3 (1C, s, Ph), 127. 3 (1C, s, Ph), 127.3 (2C, s, Ph), 127.9 (2C, s, Ph), 128.0 (2C, s, Ph), 128.3 (2C, s, Ph), 128.3 (2C, s, Ph), 129.1 (2C, s, Ph), 129.3 (2C, s, Ph), 147.9 (1C, s, Ph), 149.1 (1C, s, Ph), 149.4 (1C, s, Ph), 149.7 (1C, s, Ph), 151.0 (1C, s, Ph).





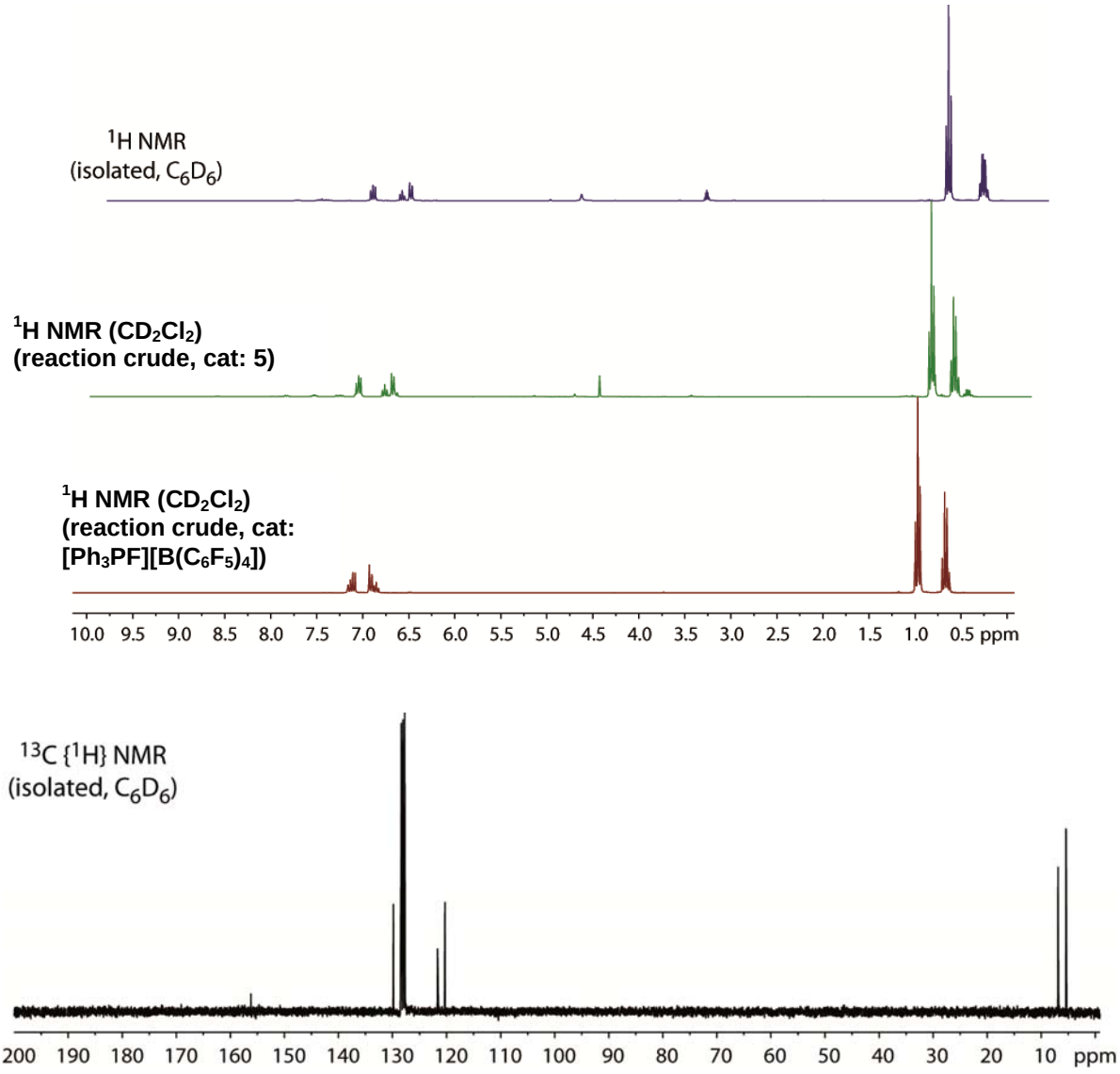
2.22 Dehydrocoupling of Et_3SiH and Phenol with 5, $[Ph_3PF][B(C_6F_5)_4]$ and 9a-e as catalysts.



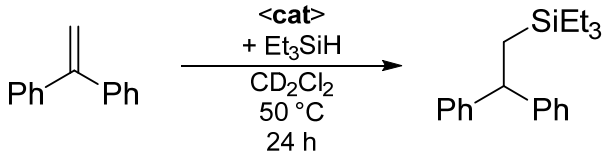
5	(2 mol%): 89% conversion (80% isolated yield)
$[Ph_3PF]^+$	(4 mol%): < 1% conversion
9a	(2 mol%): 99% conversion
9b	(2 mol%): 85% conversion
9c	(2 mol%): 30% conversion
9d	(2 mol%): 19% conversion
9e	(2 mol%): <1% conversion

Catalyst **5** (4 mg, 2 mol%), **9a-e** (6 mg, 2 mol%), or $[Ph_3PF][B(C_6F_5)_4]$ (4 mg, 4 mol%) were added to a solution of Et_3SiH (17 µL, 0.10 mmol) and PhOH (9 mg, 0.10 mmol) in CD_2Cl_2 (0.7 mL) at ambient temperature. The reaction mixture was left at ambient temperature for one hour (**5, 9a**) or 24 h ($[Ph_3PF]^+$) or heated to 50 °C for 24 h for **9b-e** and investigated by NMR spectroscopy. For catalyst **5**, all volatiles were removed *in vacuo* and the remaining residue was suspended in *n*-pentane. The mixture was filtered through a celite plug and the solvent was removed *in vacuo* giving triethyl(phenoxy)silane as a colourless oil (17 mg, 80% yield).[S14]

^1H NMR (C_6D_6, [ppm]): δ = 0.66 (6H, quart., CH_2, $^3J_{HH}$ = 7.8 Hz), 0.96 (9H, t, CH_3, $^3J_{HH}$ = 7.8 Hz), 6.85 (1H, t, *p*-Ph, $^3J_{HH}$ = 7.1 Hz), 6.89 - 6.94 (2H, m, *o-/m*-Ph), 7.07 - 7.15 (2H, m, *o-/m*-Ph); **$^{13}C\{^1H\}$ (C_6D_6, [ppm]):** δ = 5.4 (3C, s, CH_2), 6.9 (3C, s, CH_3), 120.3 (2C, s, *o-/m*-Ph), 121.7 (1C, s, *p*-Ph), 129.8 (2C, s, *o-/m*-Ph), 156.2 (1C, s, *i*-Ph).


^{1}H NMR
(isolated, C_6D_6)
^{1}H NMR (CD_2Cl_2)
(reaction crude, cat: 5)
^{1}H NMR (CD_2Cl_2)
(reaction crude, cat:
[Ph_3PF][$B(C_6F_5)_4$])
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
^{13}C {^{1}H} NMR
(isolated, C_6D_6)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

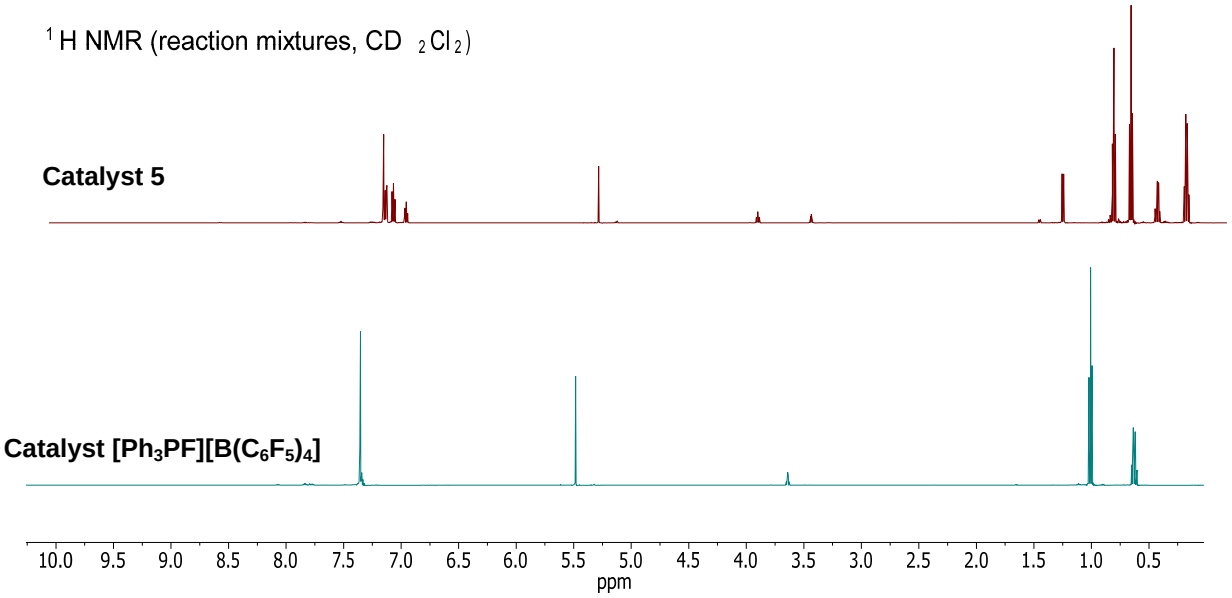
2.23. Hydrosilylation of 1,1-diphenylethylene with Et_3SiH using 5, $[Ph_3PF][B(C_6F_5)_4]$ or 9a-e as catalysts

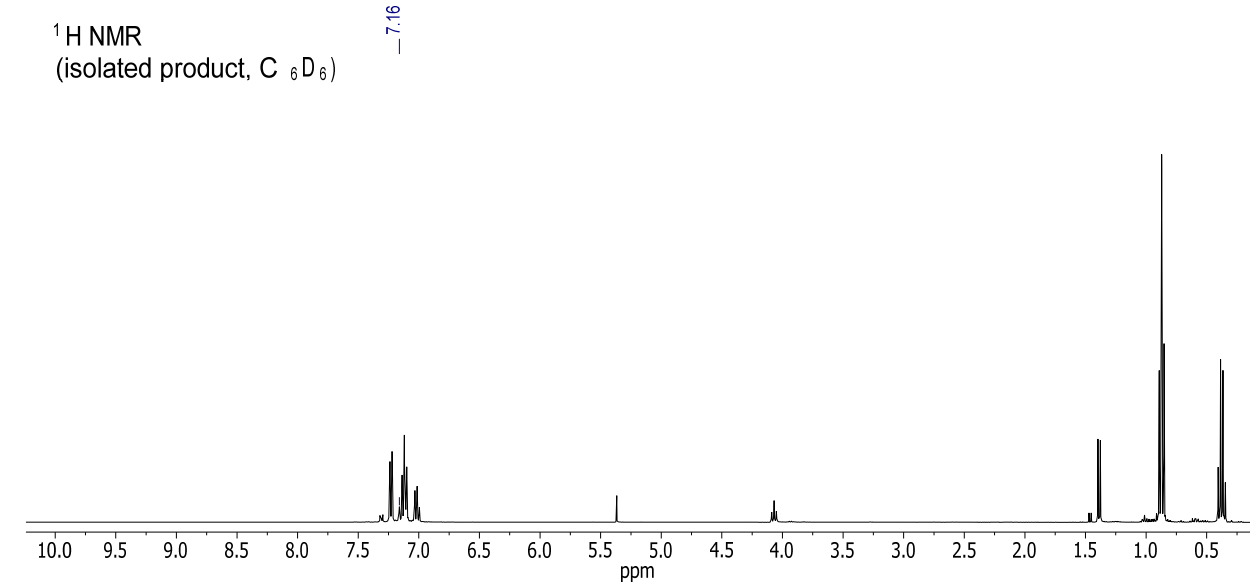


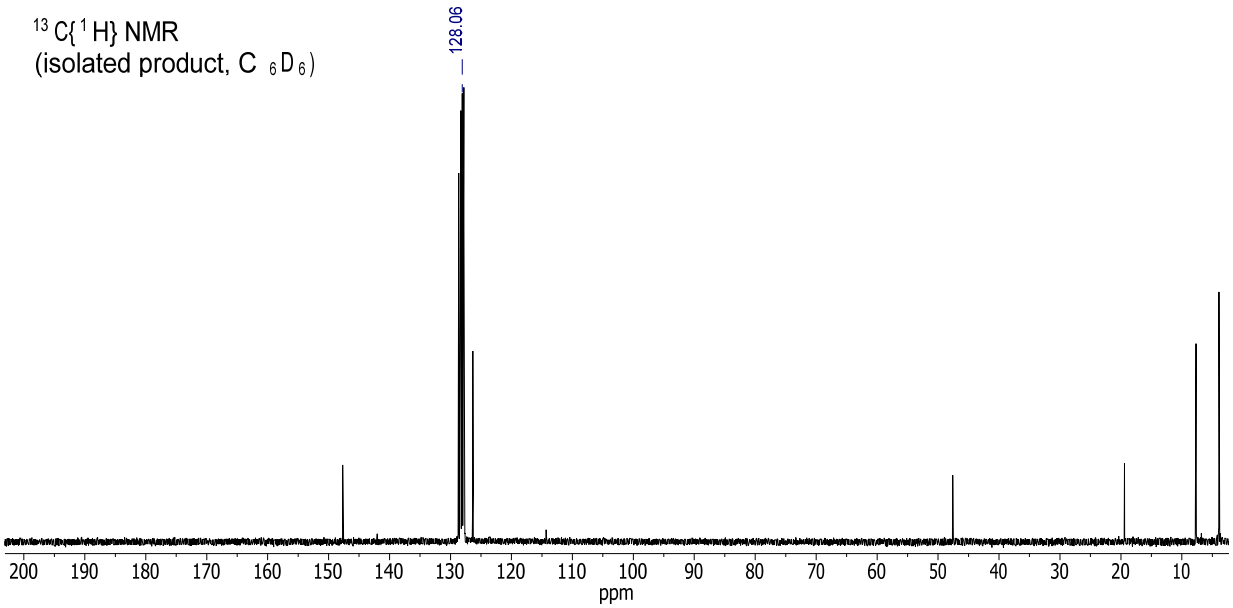
5 (2 mol%): 74% conversion (isolated yield 67%)
$[Ph_3PF]^+$ (4 mol%): 0% conversion
9a (2 mol%): 89% conversion (1h, R.T.)
9b (2 mol%): 72% conversion
9c-e (2 mol%): 0% conversion

Catalyst **5** (4 mg, 2 mol%), $[Ph_3PF][B(C_6F_5)_4]$ (4 mg, 4 mol%) or **9a-e** (6 mg, 2 mol%) were added to a solution of Et_3SiH (18 µL, 0.10 mmol) and 1,1-diphenylethylene (18 mg, 0.10 mmol) in CD_2Cl_2 (0.7 mL). The reaction mixtures were heated to 50 °C for 24 h and investigated by NMR spectroscopy. For catalyst **5**, all volatiles were removed *in vacuo* and the remaining residue was suspended in *n*-pentane. The mixture was filtered through a celite plug and the solvent was removed *in vacuo* giving (2,2-diphenylethyl)triethylsilane as a colourless oil (20 mg, 67% yield).[16]

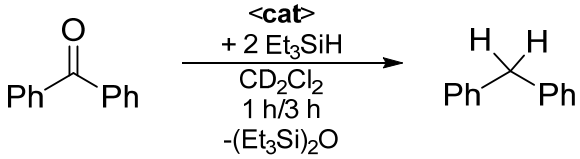
^{1}H NMR (C_6D_6, [ppm]): δ = 0.33 (6H, quart., SiCH_2CH$_3$, $^3J_{HH}$ = 7.8 Hz), 0.83 (9H, t, SiCH$_2$CH_3, $^3J_{HH}$ = 7.9 Hz), 1.34 (2H, s, CH_2, $^3J_{HH}$ = 7.9 Hz), 4.03 (1H, t, CH, $^3J_{HH}$ = 7.9 Hz), 6.94 - 7.00 (2H, m, *p*-Ph), 7.05 - 7.10 (4H, m, *m*-Ph), 7.17 - 7.21 (4H, m, *m*-Ph); **^{13}C{^{1}H} (C_6D_6, [ppm]):** δ = 3.9 (3C, s, SiCH_2CH$_3$), 7.7 (3C, s, SiCH$_2$$CH_3$), 19.4 (1C, s, CH_2), 47.6 (1C, s, CH), 126.3 (2C, s, *p*-Ph), 127.9 (4C, s, *m*-/*o*-Ph), 128.7 (4C, s, *m*-/*o*-Ph), 147.8 (2C, s, *i*-Ph).


^{1}H NMR (reaction mixtures, CD_2Cl_2)
Catalyst 5
Catalyst [Ph_3PF][$B(C_6F_5)_4$]
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm


^{1}H NMR
(isolated product, C_6D_6)
7.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm



2.24. Hydrodeoxygenation of benzophenone in the presence of Et_3SiH using 5, $[Ph_3PF][B(C_6F_5)_4]$ and 9a-e as catalysts

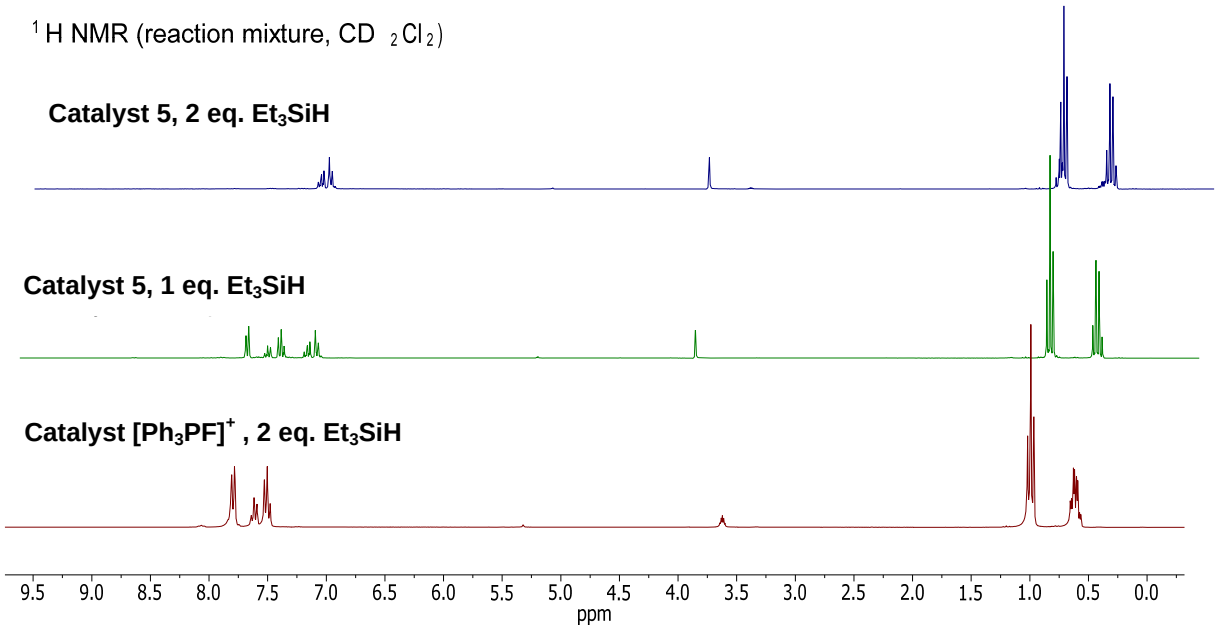


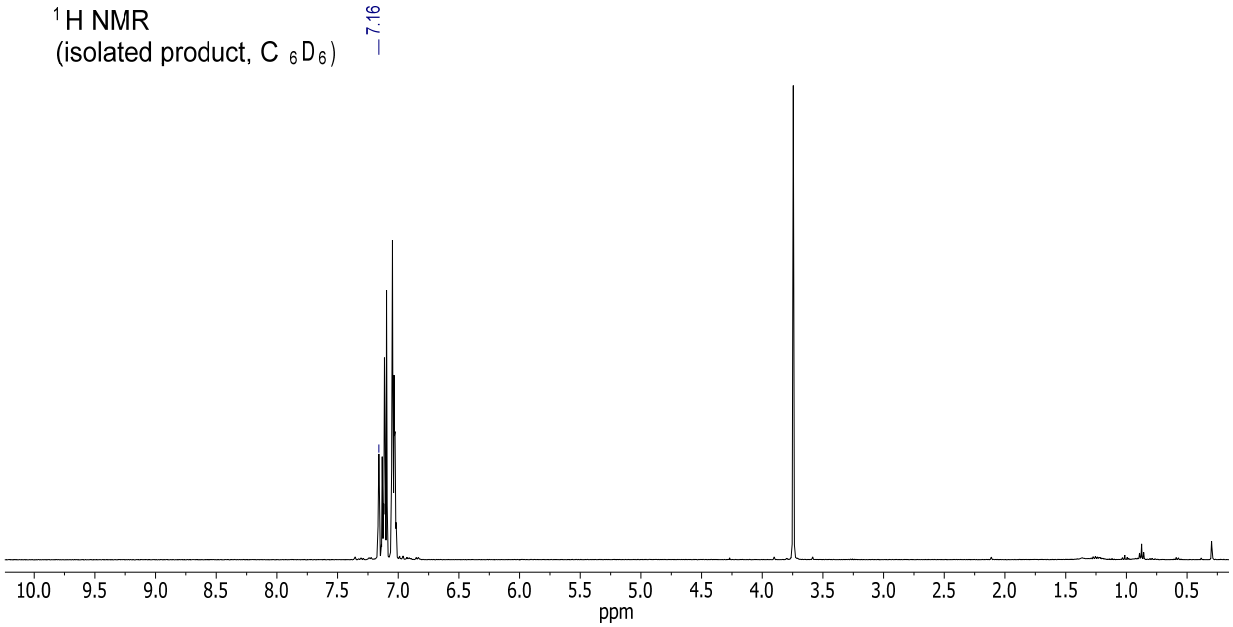
5	(2 mol%): 99% conversion (59% isolated yield)
$[Ph_3PF]^+$	(4 mol%): 0% conversion
9a	(2 mol%): 99% conversion
9b	(2 mol%): 99% conversion
9c	(2 mol%): 93% conversion
9d	(2 mol%): 72% conversion
9e	(2 mol%): 46% conversion

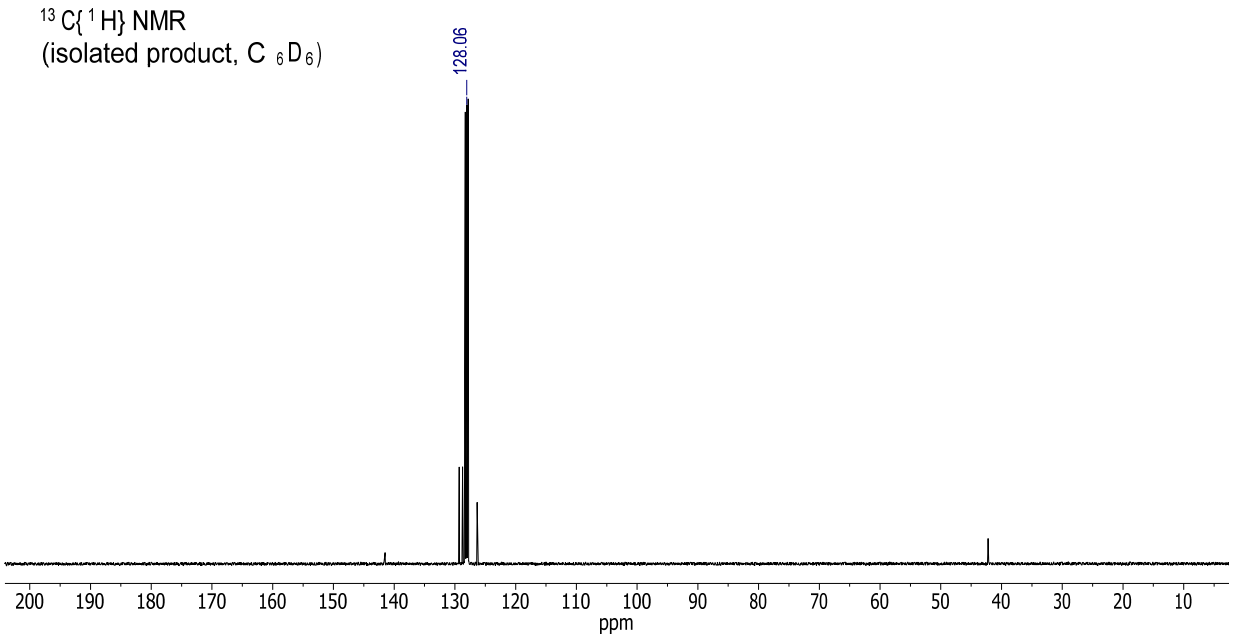
Catalyst **5** (4 mg, 2 mol%), $[Ph_3PF][B(C_6F_5)_4]$ (4 mg, 4 mol%) or **9a-e** (6 mg, 2 mol%) were added to a solution of Et_3SiH (18 µL, 0.10 mmol) and benzophenone (18 mg, 0.10 mmol) in CD_2Cl_2 (0.7 mL). The reaction mixtures were left at ambient temperature for one hour or heated to 50 °C for 36 h for **9c-e** and investigated by NMR spectroscopy. For catalyst **5**, all volatiles were removed *in vacuo* and the remaining residue was suspended in *n*-pentane. The mixture was purified by flash chromatography using a silica column (3 cm). The obtained *n*-pentane fraction

contained mainly $Et_3SiOSiEt_3$ and the product was obtained using Et_2O as an eluent. Removal of all volatiles *in vacuo* gave diphenylmethane as colourless oil (10 mg, 59% yield).

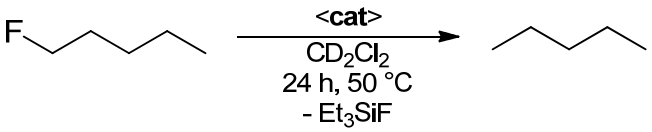
^{1}H NMR (C_6D_6 [ppm]): δ = 3.74 (2H, s, $PhCH_2$), 7.01 - 7.07 (6H, m, Ph), 7.09 - 7.14 (4H, m, Ph); **$^{13}C\{^1H\}$ (C_6D_6, [ppm]):** δ = 42.2 (1C, s, CH_2), 126.3 (1C, s, *p*-Ph), 128.7 (2C, s, *o*-/*m*-Ph), 129.3 (2C, s, *o*-/*m*-Ph), 141.5 (1C, s, *i*-Ph).





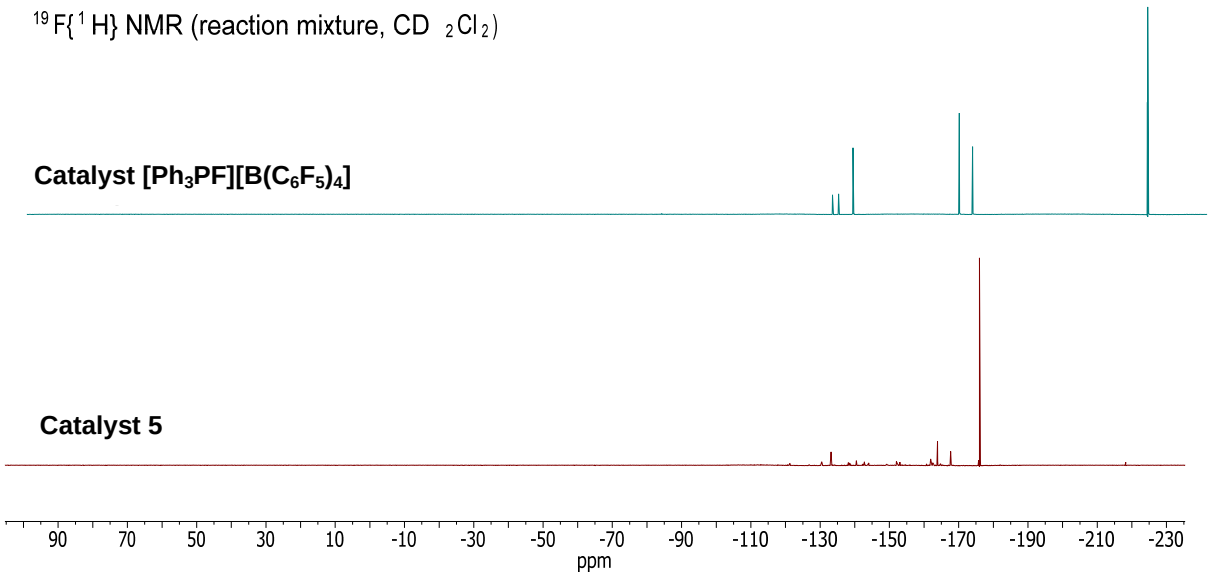


2.25. Hydrodefluorination of fluoropentane in the presence of Et_3SiH using 5, $[Ph_3PF][B(C_6F_5)_4]$ and 9a-e as catalysts



5	(2mol%): 98%
$[Ph_3PF]^+$	(4mol%): 0%
9a	(2mol%): 99% (3 h, R.T.)
9b	(2mol%): 18 %
9c	(2mol%): 4 %
9d-e	(2mol%): 2%

Catalyst **5** (4 mg, 2 mol%), $[Ph_3PF][B(C_6F_5)_4]$ (4 mg, 4 mol%) or **9a-e** (6 mg, 2 mol%) were added to a solution of Et_3SiH (21 µL, 0.12 mmol) and fluoropentane (12 µL, 0.10 mmol) in CD_2Cl_2 (0.7 mL). The reaction mixtures were heated to 50 °C for 24 h and investigated by NMR spectroscopy.[S15] Conversion was determined by means of ^{19}F NMR spectroscopy (Consumption of fluoropentane and formation of Et_3SiF).


$^{19}F\{^{1}H\}$ NMR (reaction mixture, CD_2Cl_2)
Catalyst $[Ph_3PF][B(C_6F_5)_4]$
Catalyst 5
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
ppm

3. Crystallographic Details

Table 3.1. Crystallographic data and details of the structure refinements of compounds **2**, **3** and **4***(CH_2Cl_2)

	2	**3**	**4***(CH_2Cl_2)
formula	$C_{34}H_{26}BF_4P_2$	$C_{58}H_{26}BF_{21}P_2$	$C_{59.25}H_{28.50}BCl_{2.50}F_{23}P_2$
M_r [g mol^{-1}]	572.49	1194.54	1338.70
colour, habit	colourless, block	colourless, block	colourless, block
crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1$	$P2_1/c$
a [Å]	9.206(1)	8.426(1)	18.800(1)
b [Å]	16.745(1)	21.123(3)	17.137(1)
c [Å]	17.632(1)	13.804(2)	17.800(1)
α [°]	90	90	90
β [°]	101.286(3)	95.06(1)	102.564(2)
γ [°]	90	90	90
V [Å^3]	2655.6(3)	2447(1)	5597.6(5)
Z	4	2	4
T [K]	149(2)	150(2)	149(2)
Crystal size [mm]	0.20x0.20x0.20	0.20x0.10x0.10	0.40x0.20x0.20
ρ_c [g cm^{-3}]	1.427	1.621	1.589
F(000)	1184	1196	2674
θ_{min} [°]	1.69	1.48	1.63
θ_{max} [°]	27.55	27.46	27.55
Index range	$-11 \le h \le 11$ $-20 \le k \le 21$ $-22 \le l \le 22$	$-10 \le h \le 10$ $-27 \le k \le 27$ $-17 \le l \le 17$	$-24 \le h \le 24$ $-20 \le k \le 22$ $-22 \le l \le 23$
μ [mm^{-1}]	0.215	0.212	0.315
absorption correction	SADABS	SADABS	SADABS
reflections collected	24302	41120	50339
reflections unique	6136	10858	12911
R_{int}	0.079	0.0787	0.0441
reflection obs. [F>3σ(F)]	3558	7111	8842
residual density [e Å^{-3}]	0.663, –0.287	0.264, –0.266	0.419, –0.357
parameters	361	739	757
GOOF	1.011	0.983	0.989
R_1 [I>2σ(I)]	0.0602	0.0480	0.0458
wR_2 (all data)	0.1615	0.0852	0.1170
CCDC	1041558	1041560	1041561

Table 3.2. Crystallographic data and details of the structure refinement of compound **8a**.

	8a
formula	$C_{25}H_{22}F_4P_2$
M_r [g mol^{-1}]	460.37
color, habit	colourless, block
crystal system	monoclinic
Space group	*C*2
a [Å]	21.097(2)
b [Å]	8.388(1)
c [Å]	6.357(1)
α [°]	90
β [°]	102.383(3)
γ [°]	90
V [Å^3]	1098.7(2)
Z	2
T [K]	150(2)
Crystal size [mm]	0.20x0.20x0.10
ρ_c [g cm^{-3}]	1.391
F(000)	476
θ_{min} [°]	1.98
θ_{max} [°]	27.51
Index range	$-27 \le h \le 27$ $-10 \le k \le 10$ $-8 \le l \le 8$
μ [mm^{-1}]	0.242
absorption correction	SADABS
reflections collected	8224
reflections unique	2417
R_{int}	0.0247
reflection obs. [F>3σ(F)]	2243
residual density [e Å^{-3}]	0.275, –0.182
parameters	141
GOOF	1.048
R_1 [I>2σ(I)]	0.0277
wR_2 (all data)	0.0660
CCDC	1041559

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