Frustrated Lewis Pair Mediated C-O or C-H Bond Activation of Ethers

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1. Materials and Methods

**General Remarks.**

All manipulations were performed in a Glovebox MB Unilab produced by MBraun or using standard Schlenk techniques under an inert atmosphere of purified Argon (purchased from Westfalen AG) or dried, oxygen-free nitrogen. Dry, oxygen-free solvents (drying agents in brackets; [CaH$_2$]: C$_6$D$_5$Br, CH$_2$Cl$_2$, C$_6$H$_5$F, 1,2-C$_6$H$_4$F$_2$, [sodium]: n-hexane, [sodium/benzophenone]: Et$_2$O were employed. Pentane (Aldrich) was dried employing a Grubbs-type column system (Innovative Technology), degassed and stored over molecular sieves (4 Å) in the glovebox. Deuterated benzene (C$_6$D$_6$) was purchased from Sigma-Aldrich and distilled from sodium prior to use. Deuterated dichloromethane (CD$_2$Cl$_2$, ampoule) was purchased from Sigma-Aldrich and stored over molecular sieves for at least two days prior to use. Reagents such as Ph$_2$PH, Cy$_2$PH, t-Bu$_2$PH and Bz$_2$O were purchased from Aldrich chemical company and distilled prior to use. B(C$_6$F$_5$)$_3$ was purchased from Boulder Scientific and used without further purification. Cyclohexyl vinyl ether (TCI) was stored for 16 h over molecular sieves (4 Å) in the glovebox before use. Reagents 1-(tert-butoxy)-4-fluorobenzene and trityltriflate were synthesized following literature known procedures. All glassware was oven-dried at temperatures above 180°C prior to use. NMR spectra were measured at 26 °C on a Bruker AVANCE 400 MHz or a Varian 500 MHz spectrometer equipped with an HFX AutoX triple resonance indirect probe (used for $^{13}$C{$^1$H, $^{19}$F} experiments). 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) or externally ($^{31}$P, $^{11}$B and $^{19}$F NMR experiments were referenced to 85% H$_3$PO$_4$, BF$_3$(OEt)$_2$, and CFCl$_3$, respectively). Chemical shifts ($\delta$) are reported in ppm. Coupling constants ($J$) are reported in Hz. Assignments of individual resonances were done using 2D techniques (HMBC, HSQC, HH-COSY) when necessary. Elemental analyses (C, H, N) were performed at the University of Toronto employing a Perkin Elmer 2400 Series II CHNS Analyzer. Mass spectra where recorded on a Thermo Scientific Orbitrap LTQ XL at the Organisch Chemisches Institut, University of Münster, Germany. Parent cations were separated and fragmented using appropriate potentials in order to obtain exact masses of the fragment-cations.
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 either on a Bruker AXS APEX II CCD diffractometer utilizing MoKα radiation (1, [Ph₂TrtPH][OTf], 4, 4'•1,2-C₆H₄F₂, 6 and 7) or a Bruker SMART CCD diffractometer utilizing CuKα radiation ([Cy₂TrtPH][OTf], 5). The Bruker APEX II CCD diffractometer was equipped with a rotation anode at 153(2) K using graphite-monochromated MoKα radiation (λ = 0.71073 Å) with a scan width of 0.3°. The Bruker SMART CCD diffractometer was equipped with a rotation anode at 153(2) K using graphite-monochromated CuKα radiation (λ = 1.54178 Å) focused with a Goebel mirror system and was operated with a scan width of 0.5°. In some cases, data collection strategies were determined using Bruker Apex software and optimized to provide >99.5% complete data to a 2θ value of at least 55°. Data reduction was done using the Bruker SMART 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 against $F^2$ using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms bonded to carbon atoms were generated with idealized geometries and isotropically refined using a riding model. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Further details are given in tables S1 and S2 (pages S17 and S18).
S2. Synthesizes and Spectroscopic Data

S2.1. Synthesis of \([t\text{-}Bu_3\text{PCH}_2\text{Ph}][\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3]\) (1)

In the glove box, a 20 mL vial equipped with a stir bar was charged with a solution of B(\text{C}_6\text{F}_5)_3 (0.189 g, 0.370 mmol) in pentane (10 mL). A solution of dibenzyl ether (0.073 g, 0.370 mmol) in pentane (3 mL) was added to the vial. After 5 min, a solution of \(t\text{-}Bu_3\text{P}\) (0.075 g, 0.370 mmol) in pentane (2 mL) was added dropwise over 5 min at ambient temperature. The solution gradually became pale-yellow and white precipitate was observed. The mixture was allowed to stir overnight. The precipitate was allowed to settle and the pale-yellow solution was decanted. The white precipitate was collected and dried \textit{in vacuo} (86%).

\(^1\text{H}\) NMR (400 MHz, CD$_2$Cl$_2$, 298 K): \(\delta\) 7.46 (m, 5H, Ph-CH$_2$P), 7.43 (d, 2H, \(^3\)J$_{\text{HH}}$ = 7.2 Hz, o-Ph$_{\text{borate}}$), 7.27 (t, 2H, \(^3\)J$_{\text{HH}}$ = 7.2 Hz, m-Ph$_{\text{borate}}$), 7.15 (t, 1H, \(^3\)J$_{\text{HH}}$ = 7.2 Hz, p-Ph$_{\text{borate}}$), 4.30 (s, 2H, CH$_2$OB(\text{C}_6\text{F}_5)_3), 3.71 (d, 2H, \(^2\)J$_{\text{PH}}$ = 13 Hz, CH$_2$P), 1.63 (d, 27H, \(^3\)J$_{\text{PH}}$ = 14 Hz, \(t\text{-}Bu\)); \(^19\text{F}\) NMR (377 MHz, CD$_2$Cl$_2$, 298 K): \(\delta\) -133.7 (m, 2F, o-\text{C}_6\text{F}_5), -163.7 (t, 1F, \(^3\)J$_{\text{FF}}$ = 21 Hz, p-\text{C}_6\text{F}_5), -167.1 (m, 2F, m-\text{C}_6\text{F}_5); \(^31\text{P}\{^1\text{H}\}\) NMR (162 MHz, CD$_2$Cl$_2$, 298 K): \(\delta\) 48.8 (s, CH$_2$P); \(^11\text{B}\) NMR (128 MHz, CD$_2$Cl$_2$, 298 K): \(\delta\) -2.66 (s, OB(\text{C}_6\text{F}_5)_3); \(^13\text{C}\{^1\text{H}\}\) NMR (101 MHz, CD$_2$Cl$_2$, 298 K): \(\delta\) 148.2 (dm, \(^1\)J$_{\text{CF}}$ = 240 Hz, \text{C}_6\text{F}_5), 145.1 (ipso-PhCH$_2$OB), 138.6 (dm, \(^1\)J$_{\text{CF}}$ = 231 Hz, \text{C}_6\text{F}_5), 136.9 (dm, \(^1\)J$_{\text{CF}}$ = 245 Hz, \text{C}_6\text{F}_5), 131.6 (d, \(^3\)J$_{\text{CP}}$ = 4.4 Hz, o-PhCH$_2$P), 130.0 (d, \(^4\)J$_{\text{CP}}$ = 2.1 Hz, m-PhCH$_2$P), 129.6 (d, \(^5\)J$_{\text{CP}}$ = 2.6 Hz, p-PhCH$_2$P), 129.1 (d, \(^2\)J$_{\text{CP}}$ = 8.4 Hz, ipso-PhCH$_2$P), 127.8 (m-PhCH$_2$OB), 126.7 (o-PhCH$_2$OB), 125.7 (p-PhCH$_2$OB), 66.6 (PhCH$_2$OB), 40.8 (d, \(^1\)J$_{\text{CP}}$ = 26 Hz, \(t\text{-}Bu\)), 30.9 (\(t\text{-}Bu\)), 25.7 (d, \(^1\)J$_{\text{CP}}$ = 33 Hz, CH$_2$P); \textbf{elemental analysis} calcd (%) for C$_{44}$H$_{41}$BF$_{15}$OP: C 57.9; H 4.5; Found: C 57.8; H 4.9.

S2.2. Synthesis of \([t\text{-}Bu_3\text{PH}][\text{CyOB}(\text{C}_6\text{F}_5)_3]\) (2)

In the glove box, a 20 mL vial equipped with a stir bar was charged with a solution of B(\text{C}_6\text{F}_5)_3 (0.189 g, 0.370 mmol) in pentane (10 mL). To the vial, \(t\text{-}Bu_3\text{P}\) (0.075 g, 0.370 mmol) in pentane (2 mL) was added at once. A solution of cyclohexyl vinyl
ether (0.047 g, 0.370 mmol) in pentane (3 mL) was then added to the same vial over 5 minutes. The solution gradually became pale-pink and precipitate was observed. The mixture was allowed to stir overnight. The precipitate was allowed to settle and the solution was decanted. The pale-pink precipitate was collected and dried \textit{in vacuo} (80\%).

\textbf{1H NMR} (400 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 5.05 (d, 1H, $^1J_{PH} = 427$ Hz, PH), 3.19 (br s, 1H, CyCH-O), 1.67 (d, 27H, $^3J_{PH} = 16$ Hz, t-Bu$_3$), 1.56 (m, 4H, Cy), 1.30 (m, 3H, Cy), 1.10 (m, 4H, Cy); $^{19}$F NMR (377 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ -132.4 (m, 2F, o-C$_6$F$_5$), -164.4 (t, 1F, $^3J_{FF} = 20$ Hz, p-C$_6$F$_5$), -167.5 (m, 2F, m-C$_6$F$_5$); $^{31}$P$^{1}$H NMR (162 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 60.7 (s, PH); $^{11}$B NMR (128 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ -3.45 (s, OB(C$_6$F$_5$)$_3$); $^{13}$C$^{1}$H NMR (125 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 72.3 (CyCHOB), 37.8 (d, $^1J_{CP} = 26$ Hz, t-Bu), 35.8 (Cy), 30.0 (t-Bu), 29.8 (Cy), 26.5 (Cy), 25.2 (Cy); \textbf{elemental analysis} calcd (\%) for C$_{36}$H$_{39}$BF$_{15}$OP: C 53.09; H 4.83; Found: C 52.83; H 4.63; N 0.21.

\section*{S2.3. Synthesis of [(t-Bu$_3$PH)][p-C$_6$H$_4$FOB(C$_6$F$_5$)$_3$] (3)}

In the glove box, a 20 mL vial equipped with a stir bar was charged with a solution of B(C$_6$F$_5$)$_3$ (0.379 g, 0.740 mmol) in pentane (10 mL), then a solution of 1-(tert-butoxy)-4-fluorobenzene (0.124 g, 0.740 mmol) in pentane (3 mL) was added. After 5 min, a solution of t-Bu$_3$P (0.149 g, 0.740 mmol) in pentane (2 mL) was added dropwise over 10 min at ambient temperature. The solution gradually became pale-yellow and the formation of a white precipitate was observed. After 5h stirring at room temperature, the solvent was reduced \textit{in vacuo} to yield a white precipitate that was collected (88\%).

\textbf{1H NMR} (400 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 6.72 (m, 2H, o-C$_6$H$_4$F), 6.61 (m, 2H, m-C$_6$H$_4$F), 5.08 (d, 1H, $^1J_{PH} = 430$ Hz, PH), 1.66 (d, 27H, $^3J_{PH} = 15.5$ Hz, t-Bu$_3$); $^{19}$F NMR (377 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ -129.6 (m, 1F, CyH$_4$F), -134.0 (m, 6F, o-C$_6$F$_5$), -162.6 (t, 3F, $^3J_{FF} = 21.4$ Hz, p-C$_6$F$_5$), -166.8 (m, 6F, m-C$_6$F$_5$); $^{31}$P$^{1}$H NMR (162 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 60.1 (s, PH); $^{11}$B NMR (128 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ -3.53 (s, OB(C$_6$F$_5$)$_3$); $^{13}$C$^{1}$H NMR (101 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 156.8 (ipso-C$_6$H$_4$F), 155.2 (d, $^1J_{CF} = 234$ Hz, p-C$_6$H$_4$F), 147.9 (dm, $^1J_{CF} = 241$ Hz, C$_6$F$_5$), 138.5 (dm, $^1J_{CF} = 246$ Hz, C$_6$F$_5$), 136.3 (dm, $^1J_{CF} = 242$ Hz, C$_6$F$_5$), 123.7 (ipso-C$_6$F$_5$), 118.9 (d, $^3J_{CF} = 7.6$ Hz,
\( o\)-C\(_6\)H\(_4\)F, 114.2 (d, \( ^2J_{CF} = 22.3 \) Hz, \( m\)-C\(_6\)H\(_4\)F), 37.6 (d, \( ^1J_{CF} = 28.8 \) Hz, \( t\)-Bu), 29.9 (\( t\)-Bu); \n
**elemental analysis** calcd (%) for C\(_{36}\)H\(_{32}\)BF\(_{16}\)OP: C 52.32; H 3.90; Found: C 51.94; H 4.08.

Observation of isobutylene

\(^1\)H NMR (400 MHz, C\(_6\)D\(_5\)Br, 298 K)

Crude reaction mixture showing the presence of isobutylene in solution

2.4. Study of Mixtures of \( R_2PH \) and Trt[OTf]

2.4.1. Reaction of \( R_2PH \) (\( R = \text{Ph, Cy} \)) and Trt[OTf]

A solution of \( R_2PH \) (\( R = \text{Ph: 931 mg, R = Cy: 991 mg}, 5.00 \text{ mmol, 1.0 eq.} \)) in CH\(_2\)Cl\(_2\) (10 mL) was added dropwise to a solution of Trt[OTf] (1.962 g 5.00 mmol, 1.0 eq.) in CH\(_2\)Cl\(_2\) (10 mL) within 15 min. In the course of the addition the initial red reaction mixture turned yellow. The addition of Et\(_2\)O (15 mL) led to the formation of a colourless precipitate. The supernatant was removed and the residue was washed with Et\(_2\)O (2 x 15 mL) and dried \textit{in vacuo} yielding \([\text{Ph}_2\text{TrtPH}][\text{OTf}]\) ([Cy\(_2\)TrtPH][OTf]) as colourless, microcrystalline solid ([Ph\(_2\)TrtPH][OTf]:
2.446 g, 85%; [Cy₂TrtPH][OTf]: 2.593 g, 88%). Single crystals of both compounds, suitable for X-ray single crystal structure determination, were obtained by diffusion of Et₂O into CH₂Cl₂ solutions of the respective compounds at −35°C.

S2.4.2. Characterisation data of [Ph₂TrtPH][OTf]

1H NMR (CD₂Cl₂, 26°C, [ppm]): δ = 7.26 (4H, m, H7), 7.30 (6H, m, H3), 7.42 (6H, m, H4), 7.44 (4H, m, H8), 7.46 (3H, m, H5), 7.68 (2H, m, H9), 9.54 (1H, d, PH, 1JHP = 513.1 Hz); 13C{1H} NMR (CD₂Cl₂, 26°C, [ppm]): δ = 62.5 (1C, d, C1, 1JC = 42.7 Hz), 121.3 (1C, quart., CF₃, 1JC = 320.6 Hz), 117.1 (2C, d, C6, 1JC = 77.8 Hz), 129.7 (6C, d, C4, 4JC = 1.4 Hz), 129.8 (3C, d, C5, 5JC = 2.4 Hz), 130.4 (4C, d, C8, 3JC = 12.7 Hz), 131.0 (6C, d, C3, 3JC = 7.2 Hz), 135.4 (2C, d, C9, 4JC = 2.0 Hz), 135.5 (4C, d, C7, 2JC = 9.6 Hz), 137.4 (3C, d, C2, 2JC = 2.7 Hz); 31P{1H} NMR (CD₂Cl₂, 26°C, [ppm]): δ = 8.9 (s); 19F{1H} NMR (CD₂Cl₂, 26°C, [ppm]): δ = −78.8 (s); MS-ESI-MS: 429.1766 (M⁺), calcd. for C31H26P: 429.1767.

Figure S1. Molecular structure of the cation of [Ph₂TrtPH][OTf] (orange: P, black: C, grey: H; some hydrogen atoms are omitted for clarity).
S2.4.3. Characterisation data of [Cy₂TrtPH][OTf]

**1H NMR (CD₂Cl₂, 26°C, [ppm]):** δ = 0.98 (2H, m, H7), 1.06 (2H, m, H8), 1.18 (2H, m, H8), 1.20 (2H, m, H9), 1.48 (2H, m, H7), 1.54 (2H, m, H7), 1.63 (2H, m, H9), 1.67 (2H, m, H8), 1.76 (2H, m, H8), 1.90 (2H, m, H7), 2.22 (2H, ddd, H2, \(^3J_{HH} = 5\) Hz, \(^3J_{HH} = 12\) Hz, \(^3J_{HP} = 13\) Hz), 7.40 (3H, m, H5), 7.46 (6H, m, H3), 7.46 (6H, m, H4), 7.87 (1H, d, PH, \(^1J_{HP} = 467.3\) Hz); **\(^{13}C\{^1H\} NMR (CD₂Cl₂, 26°C, [ppm]):** δ = 25.3 (2C, s, C9), 26.7 (2C, d, C8, \(^3J_{CP} = 12.9\) Hz), 27.5 (2C, d, C8, \(^3J_{CP} = 12.7\) Hz), 27.7 (2C, d, C7, \(^2J_{CP} = 3.5\) Hz), 30.7 (2C; d, C7, \(^2J_{CP} = 4.6\) Hz), 32.2 (2C, d, C6, \(^1J_{CP} = 37.3\) Hz), 60.3 (1C, d, C1, \(^1J_{CP} = 38.1\) Hz), 129.2 (3C, s(br), C5), 129.4 (6C, s(br), C3), 130.0 (6C, s, C4), 138.4 (3C, s(br), C2); **\(^{31}P\{^1H\} NMR (CD₂Cl₂, 26°C, [ppm]):** δ = 19.4 (s); **\(^{19}F\{^1H\} NMR (CD₂Cl₂, 26°C, [ppm]):** δ = −78.7 (s); **MS-ESI-MS:** 441.2704 (M⁺), calcd. for C₃₁H₃₈P: 441.2706.

**Figure S2.** Molecular structure of the cation of [Cy₂TrtPH][OTf] (orange: P, black: C, grey: H, some hydrogen atoms are omitted for clarity).
S2.4.4. Preparation of FLP system 4

A solution of \(t\)-BuPH (1.462 g, 10.00 mmol, 1.0 eq.) in 1,2-C\(_6\)H\(_4\)F\(_2\) (10 mL) was added dropwise to a solution of Trt[OTf] (4.316 g 11.00 mmol, 1.1 eq.) in 1,2-C\(_6\)H\(_4\)F\(_2\) (50 mL) within 10 min at –30°C. In the course of the addition the initial red reaction mixture turned yellow. The reaction mixture was stirred for 5 min at –30°C and warmed to ambient temperature. \(n\)-Hexane was added (50 mL) leading to the formation of a yellow precipitate. The supernatant was removed and the residue was washed with \(n\)-hexane (2 x 15 mL) and dried in vacuo yielding 4 as a colourless, microcrystalline solid (5.150 g, 96%). Single crystals of 4, suitable for X-ray single crystal structure determination, were obtained by diffusion of \(n\)-hexane into a CH\(_2\)Cl\(_2\) solution at –35°C.

\(^1\)H NMR (CD\(_2\)Cl\(_2\), 26°C, [ppm]): \(\delta = 1.60\) (18H, d, \(H11, 3J_{HP} = 16.2\) Hz), 4.75 (1H, d, \(H1, 2J_{HP} = 472\) Hz), 5.97 (2H, m, H2), 6.80 (2H, m, H3), 7.14 (4H, m, H7), 7.34 (2H, m, H9), 7.35 (4H, m, H8); \(^{13}\)C\{\(^1\)H\} NMR (CD\(_2\)Cl\(_2\), 26°C, [ppm]): \(\delta = 28.5\) (6C, s, C11), 35.9 (2C, d, C10, \(1J_{CP} = 27.8\) Hz), 35.8 (1C, d, C1, \(1J_{CP} = 36.6\) Hz), 120.8 (2C, d, C2 \(2J_{CP} = 8.6\) Hz), 121.1 (1C, quart., CF\(_3\), \(1J_{CF} = 321.2\) Hz), 125.5 (1C, d, C4, \(4J_{CP} = 10.8\) Hz), 128.5 (2C, s, C9), 128.7 (4C, s, C8), 132.9 (2C, d, C7, \(7J_{CP} = 11.4\) Hz), 132.9 (2C, d, C3, \(3J_{CP} = 11.3\) Hz), 140.8 (2C, d, C6 \(6J_{CP} = 4.1\) Hz), 145.0 (1C, d, C5, \(5J_{CP} = 11.2\) Hz); \(^{31}\)P\{\(^1\)H\} NMR (CD\(_2\)Cl\(_2\), 26°C, [ppm]): \(\delta = 36.9\) (s); \(^{31}\)P\{\} NMR (CD\(_2\)Cl\(_2\), 26°C, [ppm]): \(\delta = 36.9\) (dm, \(1J_{PP} = 472\) Hz); \(^{19}\)F\{\(^1\)H\} NMR (CD\(_2\)Cl\(_2\), 26°C, [ppm]): \(\delta = –78.9\) (s); MS-ESI-MS: 389.2394 (M\(^+\)), calcd. for C\(_{27}\)H\(_{34}\)P: 389.2393.

S2.4.5. Isomerization of 4 to 4’

A solution of 4 (269 mg, 0.50 mmol, 1.0 eq.) in CH\(_2\)Cl\(_2\) was stirred at ambient temperature. The progress of the reaction was monitored by means of \(^{31}\)P\{\(^1\)H\} NMR spectroscopy after 1 d (i), 5 d (ii) and 14 d (iii) reaction time. The slow isomerization of 4 to a trityl species of type C (4’) accompanied by formation of some amounts of \([t\)-Bu\(_2\)PH\(_2\)][OTf] was observed.

(i) \(^{31}\)P\{\(^1\)H\} NMR (CH\(_2\)Cl\(_2\), C\(_6\)D\(_6\)-capillary, 26°C, [ppm]): \(\delta = 20.2\) (s, \([t\)-Bu\(_2\)PH\(_2\)]\(^+\), 2%), 37.3 (s, 4, 97%), 43.3 (s, 4’, 1%).
(ii) $^{31}$P{$_1^1$H} NMR (CH$_2$Cl$_2$, C$_6$D$_6$-capillary, 26°C, [ppm]): $\delta = 20.1$ (s, $[t$-$Bu_2$PH]$^+$, 18%), 37.1 (s, 4, 60%), 43.2 (s, 4’, 22%).

(iii) $^{31}$P{$_1^1$H} NMR (CH$_2$Cl$_2$, C$_6$D$_6$-capillary, 26°C, [ppm]): $\delta = 20.1$ (s, $[t$-$Bu_2$PH]$^+$, 26%), 37.1 (s, 4, 35%), 43.3 (s, 4’, 39%).

Figure S3. $^{31}$P{$_1^1$H} NMR spectra of a solution of 4 (CH$_2$Cl$_2$, C$_6$D$_6$-capillary, ambient temperature) after A: 1 d, B: 5 d and C: 14 d.

The formation of 4’ can be explained by the phosphane-induced isomerization in scheme S1.

Scheme S1. Proposed mechanism for the isomerization of 4 to 4’.

A deprotonation of 4 by $t$-$Bu_2$PH proceeds either at the phosphonium moiety (pK$_a$ $t$-$Bu_3$PH$^+$: 11.4) to give phosphane intermediate I-1 (I) or at the carbon atom in $\alpha$-position (compare pK$_a$ Ph$_3$P-C$H_2$-CH=CHPh$^+$: 15.6).$^{[12]}$ The latter would result in the formation of ylidene phosphorane intermediate I-2 (II). Several resonance structures rendering the delocalization of the formal
negative charge of I-2 on the six-membered rings of the trityl-group and the central carbon atom are feasible (e.g. I-3). The two-fold phenyl-substituted carbon atom is assumed to constitute the most basic side. Thus, protonation of I-2 occurs at this position yielding isomerization product 4’. The catalytic amounts of $t$-BuP$_2$H required for this isomerization reaction form via the equilibrium dissociation of 4 into $t$-Bu$_2$PH and Trt[OTf] (II). This is supported by a significantly accelerated isomerization of 4 to 4’ in the presence of additional $t$-Bu$_2$PH.

S2.4.6. Isomerization of 4 to 4’ in the Presence of $t$-Bu$_2$PH

A solution of $t$-Bu$_2$PH (88 mg, 0.60 mmol, 2.0 eq.) in 1,2-C$_6$H$_4$F$_2$ (2 mL) was added dropwise to a solution of Trt[OTf] (118 mg, 0.30 mmol, 1.0 eq.) in 1,2-C$_6$H$_4$F$_2$ (4 mL) within 5 min. The initially deep red reaction mixtures turned rapidly to a yellow colour. The reaction mixture was stirred for 12 h at ambient temperature and investigated by means of $^{31}$P{$^1$H} NMR spectroscopy. Slow diffusion of Et$_2$O into the reaction mixture at –30°C yielded single crystals of 4’ suitable for X-ray single crystal structure determination. Compound 4’ was isolated as colourless, crystalline material by filtration and removing all volatiles in vacuo (40 mg, 24%).

$^{31}$P{$^1$H} NMR (1,2-C$_6$H$_4$F$_2$, C$_6$D$_6$-capillary, 26°C, [ppm]): $\delta$ = 19.9 (s, $t$-Bu$_2$PH), 41.8 (s, 4’).

S2.4.7. Characterisation data of 4’

$^1$H NMR (CD$_2$Cl$_2$, 26°C, [ppm]): $\delta$ = 1.50 (18H, d, H11, $^3$$J_{HF}$ = 17.0 Hz), 5.65 (1H, s, H5), 7.12 (4H, m, H7), 7.22 (1H, d, PH, $^1$$J_{HP}$ = 485.5 Hz), 7.28 (2H, m, H9), 7.32 (4H, m, H8), 7.45 (2H, m, H3), 7.78 (2H, m, H2, $\Delta$$\nu_{1/2}$ = 28 Hz); $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$, 26°C, [ppm]): $\delta$ = 27.9 (6C, s, C11), 34.7 (2C, d, C10, $^1$$J_{CP}$ = 34.0 Hz), 57.3 (1C, s, C5), 113.6 (1C, d, C1, $^1$$J_{CP}$ = 72.6 Hz), 121.3 (1C, quart. CF$_3$, $^1$$J_{CF}$ = 320.2 Hz), 127.4 (2C, s, C9), 129.1 (4C, s, C8), 129.7 (4C, s, C7), 131.7 (2C, d, C3, $^2$$J_{CP}$ = 11.8 Hz), 142.7 (2C, s, C4), 152.3 (1C, d, C4, $^2$$J_{CP}$ = 2.3 Hz), C2 was not detected presumably due to a significant line broadening; $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$, 26°C, [ppm]): $\delta$ = 42.8 (s); $^{19}$F{$^1$H} NMR (CD$_2$Cl$_2$, 26°C, [ppm]): $\delta$ = –78.9 (s).
Figure S4. Molecular structure of the cation of 4′•1,2-C₆H₄F₂; (hydrogen atoms of t-Bu-, and phenyl-substituents as well as solvate molecules are omitted for clarity); selected bond lengths [Å] and angles [°]: P1–C5 1.783(2), P1–C20 1.843(2), P1–C24 1.839(2), C5–C6 1.397(3), C5–C4 1.400(3), C6–C7 1.379(3), C4–C3 1.381(3), C3–C2 1.394(3), C7–C2 1.395(3), C1–C2 1.520(3); C4–C5–P1 117.4(2), C6–C5–P1 123.1(1), C5–P1–P20 110.8(1), C5–P1–P24 110.7(1), C20–P1–C24 120.0(1).

S2.5. Mechanistic investigations of the C−H bond activation by FLP 4 and proposed mechanism

S2.5.1. Competition reaction of 4 with THF and d8-THF

A solution of t-Bu₂PH (9.25 μL, 0.05 mmol, 1.0 eq.), THF (8.1 μL, 0.1 mmol, 2.0 eq.), and d8-THF (8.1 μL, 0.1 mmol, 2.0 eq.) in C₆D₅Br (1 mL) was prepared. Trt[B(C₆F₅)₄] (46 mg, 0.05 mmol, 1.0 eq.) was added to the reaction mixture. The reaction progress was monitored by ¹H and ³¹P NMR spectroscopy. Conversion to 5 and d7-5 was determined by integration of the PH resonances of FLP 4 and the respective products in ¹H NMR spectra. Product distribution was determined by integration of the TrtH resonance. The reaction mixture was investigated after a reaction time of 15 min (16% conversion, ratio 5 / d7-5: 81/19), 30 min (20% conversion, ratio 5 / d7-5: 80/20), 70 min (23% conversion, ratio 5 / d7-5: 79/21), 135 min (47% conversion, ratio 5 / d7-5: 79/21), 350 min (85% conversion, ratio 5 / d7-5: 75/25) and 430 min (100% conversion, ratio 5 / d7-5: 75/25). Figure 2.5.1.1 shows the obtained ¹H NMR spectra.
S2.5.2. Reaction of 4 and THF.

A solution of t-Bu₂PH (9.25 µL, 0.05 mmol, 1.0 eq.) and THF (16.2 µL, 0.2 mmol, 4.0 eq.) in C₆D₅Br (1 mL) was prepared. Trt[B(C₆F₅)₄] (46 mg, 0.05 mmol, 1.0 eq.) was added to the reaction mixture. The reaction progress was monitored by ¹H and ³¹P NMR spectroscopy. Conversion to 5 was determined by integration of the PH resonances of FLP 4 and the respective product in ¹H NMR spectra. The reaction mixture was investigated after a reaction time of 15 min (18% conversion), 30 min (29% conversion), 75 min (36% conversion), 165 min (74% conversion), 285 min (100% conversion). Figure 2.5.2.1 shows the obtained ¹H NMR spectra. From this mixture, 5 was precipitated as a colorless material by careful addition of n-pentanes. The supernatant was removed and the residue was washed with n-pentanes and dried in vacuo giving 5 in 98% yield (44 mg).
Figure 2.5.2.1. $^1$H NMR spectra of the reaction of FLP 4 and THF.

S2.5.3. Characterization Data of 5 (B(C$_6$F$_5$)$_4$-salt)

$^1$H NMR (C$_6$D$_5$Br, 26°C, [ppm]): $\delta = 0.88$ (9H, d, H6, $^3J_{HP} = 16.4$ Hz), 0.97 (9H, d, H6, $^3J_{HP} = 16.8$ Hz), 1.51 - 1.68 (3H, m, H2/3), 1.86 - 1.91 (1H, m, H1), 3.43 - 3.55 (2H, m, H4), 3.94 - 4.04 (1H, m, H1), 4.30 (1H, dd, PH, $^1J_{HP} = 435.0$ Hz, $^3J_{HP} = 4.9$ Hz); $^{11}$B$^1$H NMR (C$_6$D$_5$Br, 26°C, [ppm]): $\delta = -16.2$ (s); $^{13}$C$^1$H NMR (C$_6$D$_5$Br, 26°C, [ppm]): $\delta = 25.0$ (1C, d, C3, $^3J_{CP} = 5.8$ Hz), 26.5 (3C, s, C6), 26.8 (3C, s, C6), 32.1 (1C, d, C2, $^3J_{CP} = 1.8$ Hz), 32.2 (1C, d, C5, $^1J_{CP} = 29.8$ Hz), 34.0 (1C, d, C5, $^1J_{CP} = 28.8$ Hz), 69.7 (1C, d, C4, $^3J_{CP} = 7.3$ Hz), 69.8 (1C, d, C1, $^1J_{CP} = 49.6$ Hz), 136.1 (8C, d(br), C$_6$F$_5$, $^1J_{CF} = 242$ Hz), 138.2 (4C, d(br), C$_6$F$_5$, $^1J_{CF} = 239$ Hz), 148.2 (8C, d(br), C$_6$F$_5$, $^1J_{CF} = 242$ Hz); $^{19}$F$^1$H NMR (C$_6$D$_5$Br, 26°C, [ppm]): $\delta = -165.7$ (8F, m, C$_6$F$_5$), $-161.8$ (4F, m, C$_6$F$_5$), $-131.7$ (8F, m, C$_6$F$_5$); $^{31}$P$^1$H NMR (C$_6$D$_5$Br, 26°C, [ppm]): $\delta = 47.9$ (s); $^{31}$P$^1$H NMR (C$_6$D$_5$Br, 26°C, [ppm]): $\delta = 39.8$ (dm, $^1J_{PH} = 435.0$ Hz); DART-MS: 217.2 (M$^+$), calcd. for C$_{12}$H$_{26}$PO$: 217.2.
S2.5.4. Reaction of 4 and d8-THF.

A solution of t-Bu$_2$PH (9.25 μL, 0.05 mmol, 1.0 eq.) and d8-THF (16.2 μL, 0.2 mmol, 4.0 eq.) in C$_6$D$_5$Br (1 mL) was prepared. Trt[B(C$_6$F$_5$)$_4$] (46 mg, 0.05 mmol, 1.0 eq.) was added to the reaction mixture. The reaction progress was monitored by $^1$H and $^{31}$P NMR spectroscopy. Conversion to d7-5 was determined by integration of the PH resonances of FLP 4 and the respective products in $^1$H NMR spectra. The reaction mixture was investigated after a reaction time of 15 min (9%), 30 min (14% conversion), 80 min (31% conversion), 130 min (61% conversion), 350 min (95% conversion) and 450 min (100% conversion). Figure 2.5.4.1 shows the obtained $^1$H NMR spectra. From this mixture, d7-5 was precipitated as a colorless material by careful addition of n-pentanes. The supernatant was removed and the residue was washed with n-pentanes and dried in vacuo giving d7-5 in 99% yield (45 mg).

Figure 2.5.4.1. $^1$H NMR spectra of the reaction of FLP 4 and d8-THF.
S2.5.5. Characterization Data of d7-5 (B(C₆F₅)₄-salt)

![Structure of d7-5](image)

1H NMR (C₆D₅Br, 26°C, [ppm]): δ = 0.88 (9H, d, H₆, 3J₉P = 16.3 Hz), 0.97 (9H, d, H₆, 3J₉P = 16.8 Hz), 4.29 (1H, d, PH, 1J₉P = 434.8 Hz); ¹¹B{¹H} NMR (C₆D₅Br, 26°C, [ppm]): δ = −16.2 (s); ¹³C{¹H} NMR (C₆D₅Br, 26°C, [ppm]): δ = 26.5 (3C, s, C₆), 26.8 (3C, s, C₆), 32.1 (1C, d, C₅, 1J₉P = 29.9 Hz), 34.0 (1C, d, C₅, 1J₉P = 28.9 Hz), 136.2 (8C, d(br), C₆F₅), 138.1 (4C, d(br), C₆F₅, 1J₉P = 241 Hz), 148.2 (8C, d(br), C₆F₅, 1J₉P = 241 Hz), resonances corresponding to boron or deuterium bound carbon atoms were not observed; ¹⁹F{¹H} NMR (C₆D₅Br, 26°C, [ppm]): δ = −165.7 (8F, m, C₆F₅), −161.8 (4F, m, C₆F₅), −131.7 (8F, m, C₆F₅); ³¹P{¹H} NMR (C₆D₅Br, 26°C, [ppm]): δ = 47.6 (s); ³¹P{¹H} NMR (C₆D₅Br, 26°C, [ppm]): δ = 47.6 (dm, 1J₉P = 434.8 Hz); DART-MS: 224.2 (M⁺), calcd. for C₁₂H₁₉D₇PO⁺: 224.2.

S2.5.6. Reaction of 4 with varying equivalents of Et₂O

A solution of t-Bu₂PH (9.25 µL, 0.05 mmol, 1.0 eq.) and Et₂O (A: 15.7 µL, 0.15 mmol, 3.0 eq.; B: 63 µL, 0.6 mmol, 12.0 eq.; C: 114 µL, 1.1 mmol, 22.0 eq.) in C₆D₅Br (1 mL) was prepared. Trt[B(C₆F₅)₄] (46 mg, 0.05 mmol, 1.0 eq.) was added to the reaction mixture. The reaction progress was monitored by ¹H and ³¹P NMR spectroscopy. Conversion of 4 and formation of 6 or the respective FLP deactivation products (4’ and t-Bu₂PH') was determined by integration of all resonances in the ³¹P NMR spectra of the reaction mixtures. A: Complete conversion of 4 after two days reaction time (36% yield of 6); B: 65% conversion of 4 after eight hours reaction time (40% yield of 6); C: Complete conversion of 4 after six hours reaction time (96% yield of 6). From mixture C, compound 6 was precipitated as a colorless material by careful addition of n-pentanes. The supernatant was removed and the residue was washed with n-pentanes and dried in vacuo giving 6 in 91% yield (41 mg).
Figure 2.5.6.1. $^{31}\text{P}/^{1}\text{H}$ NMR spectra of the reaction of FLP 4 and Et$_2$O (3 eq., A).

Figure 2.5.6.2. $^{31}\text{P}/^{1}\text{H}$ NMR spectra of the reaction of FLP 4 and Et$_2$O (12 eq., B).
Figure 2.5.6.3. $^{31}$P{$^1$H} NMR spectra of the reaction of FLP 4 and Et₂O (22 eq., C).

S2.5.7. Characterization Data of 6 ([B(C₆F₅)₄]-salt)

$^1$H NMR (C₆D₅Br, 26°C, [ppm]): $\delta = 0.93$ (3H, dd, H4, $^3J_{HH} = 7.0$ Hz, $^3J_{HP} = 7.0$ Hz), 0.93 (9H, d, H6, $^3J_{HP} = 16.9$ Hz), 1.01 (9H, d, H6, $^3J_{HP} = 16.9$ Hz), 1.19 (3H, dd, H2, $^3J_{HH} = 7.1$ Hz, $^3J_{HP} = 16.7$ Hz), 2.94 (1H, dquart., H3, $^3J_{HH} = 8.8$ Hz, $^3J_{HP} = 7.0$ Hz), 3.33 (1H, dquart., H3, $^3J_{HH} = 8.8$ Hz, $^3J_{HP} = 7.0$ Hz), 4.03 (1H, dquart., H1, $^2J_{HH} = 4.2$ Hz, $^3J_{HH} = 7.1$ Hz), 4.23 (1H, d, PH, $^1J_{HP} = 431.4$ Hz); $^{11}$B{$^1$H} NMR (C₆D₅Br, 26°C, [ppm]): $\delta = -16.2$ (s);

$^{13}$C{$^1$H} NMR (C₆D₅Br, 26°C, [ppm]): $\delta = 14.5$ (1C, s, C4), 18.1 (1C, d, C2, $^2J_{CP} = 1.2$ Hz), 26.4 (3C, s, C6), 27.1 (3C, s, C6), 32.6 (1C, d, C5 $^1J_{CP} = 29.3$ Hz), 34.4 (1C, d, C5, $^1J_{CP} = 27.3$ Hz), 66.9 (1C, d, C3, $^3J_{CP} = 10.2$ Hz), 69.4 (1C, d, C1, $^1J_{CP} = 56.8$ Hz), 136.2 (8C, d(br), C₆F₅), 148.2 (8C, d(br), C₆F₅, $^1J_{CF} = 241$ Hz), 148.2 (8C, d(br), C₆F₅, $^1J_{CF} = 242$ Hz), resonances corresponding to boron bound carbon atoms were not observed;

$^{19}$F{$^1$H} NMR (C₆D₅Br, 26°C, [ppm]): $\delta = -165.7$ (8F, m, C₆F₅), -161.8 (4F, m, C₆F₅), -131.7 (8F, m, C₆F₅); $^{31}$P{$^1$H} NMR (CD₂Cl₂, 26°C, [ppm]): $\delta = 46.0$ (s); $^{31}$P{$^1$H} NMR (CD₂Cl₂, 26°C, [ppm]): $\delta = 46.0$ (dm, $^1J_{PH} = 431.4$ Hz); MS-ESI-MS: 219.2 (M⁺), calcd. for C₁₂H₂₈PO⁺: 219.2.
S2.5.8. Proposed mechanism for the C–H bond activation with FLP 4.

The proposed mechanism starts with the equilibrium dissociation of FLP 4 into the secondary phosphine and tritylium ion salt (Figure S2.5.8.1). In a second step, the latter effects the hydride abstraction from the substrate. The resulting cationic intermediate is nucleophilically attacked by the phosphine. This results in the formation of the phosphonium-functionalized product. The $S_N1$-type C–H activation is favoured by the adjacent oxygen atom which allows for the formulation of an oxonium ion intermediate. The competition reaction of 4 with THF and d8-THF shows a kinetic isotope effect of $KIE \approx 4$-5. This indicates that the hydride abstraction step determines the product formation. However, separate reactions of 4 with THF and d8-THF, respectively, show comparable conversions indicating a KIE of approximately 1. This indicates that the equilibrium dissociation of FLP 4 constitutes the rate determining step of the reaction sequence. The Lewis base catalysed isomerization of 4 to 4′ (see chapter 2.4.5) is in competition to the C–H bond activation pathway. The reaction of 4 with varying equivalents of Et$_2$O shows that the presence of excess substrate in the reaction mixtures favours the C–H bond activation reaction.

![Figure 2.5.8.1. Proposed mechanism for the C–H bond activation with FLP 4.](image)

S2.6. Reaction of 4 (X = B(C$_6$F$_5$)$_4$) with ethers, thioethers and amines

Dibenzylether (99.1 mg, 0.5 mmol, 10 eq), tetrahydrothiophene (44.1 mg, 0.5 mmol, 10 eq.), tetrahydropyran (43.1 mg, 0.5 mmol, 10 eq.), $N$-methyldiphenylamine (91.6 mg, 0.5 mmol, 10 eq.), diethylsulfide (45.1 mg, 0.5 mmol, 10 eq.) was added to $t$-Bu$_2$PH (7.3 mg, 0.05 mmol, 1.0 eq.) in C$_6$D$_5$Br (0.3 mL). The solution was then transferred to a vial consisting of
[Ph₃C][B(C₆F₅)₄] (46.1 mg, 0.05 mmol, 1.0 eq.) in C₆D₅Br (0.3 mL). The [Ph₃C][B(C₆F₅)₄] was immediately dissolved resulting in a pale yellow solution. The reactions were allowed to proceed for 48 h at ambient temperature. The reaction progress was monitored by ¹H and ³¹P NMR spectroscopy.

The same procedure as above was performed for the reaction with 5,6-Dihydro-4-methoxy-2H-pyran (5.7 mg, 0.05 mmol, 1 eq.) with 2.0 eq. addition of t-Bu₂PH (14.6 mg, 0.10 mmol, 2.0 eq.) in C₆D₅Br (0.3 mL).

**Reaction with dibenzylether:** n-Hexane (2 mL) was added to the solution resulting in a pale orange crude oil that was washed once again with n-hexane (2 mL). The crude product was dissolved in CD₂Cl₂ and characterized by NMR spectroscopy. The product was present in 87% yield while the remainder of the mixture consisted of FLP isomer 4' and t-Bu₂PH₂⁺. Overall formation of the desired product 7 is approximately 79%.

**Reaction with tetrahydropyran:** After complete consumption of FLP 4, the tetrahydropyran was removed under vacuum and the brown crude oil was dissolved in CD₂Cl₂ and characterized by NMR spectroscopy. The desired product 8 was formed in 37% yield while the remainder of the mixture consisted of FLP isomer 4' and t-Bu₂PH₂⁺.

**Reaction with 5,6-dihydro-4-methoxy-2H-pyran:** After complete consumption of FLP 4, remaining substrate was removed under vacuum and the brown crude oil was dissolved in CD₂Cl₂ and characterized by NMR spectroscopy. The desired product 9 was formed in 72% yield while the remainder of the mixture consisted of FLP isomer 4' and t-Bu₂PH₂⁺.

**Reaction with tetrahydrothiophene:** After complete consumption of FLP 4, n-Hexane (2 mL) was added to the solution resulting in a pale pink crude oil that was washed once again with n-hexane (2 mL). The crude product was dissolved in CD₂Cl₂ and characterized by NMR spectroscopy. The product was present in 70% yield while the remainder of the mixture consisted of FLP isomer 4' and t-Bu₂PH₂⁺. Overall formation of the desired product 10 is approximately 63%.

**Reaction with diethylsulphide:** After complete consumption of FLP 4, remaining substrate was removed under vacuum and the brown crude oil was dissolved in CD₂Cl₂ and characterized by NMR spectroscopy. The desired product 11 was formed in 38% yield while the remainder of the mixture consisted of FLP isomer 4' and t-Bu₂PH₂⁺.

**Reaction with N-methyldiphenylamine:** After complete consumption of the FLP 4, n-Hexane (2 mL) was added to the solution resulting in a brown crude oil that was washed once again with
n-hexane (2 mL). The crude product was dissolved in CD$_2$Cl$_2$ and characterized by NMR spectroscopy. The desired product 12 was formed in 47% yield while the remainder of the mixture consisted of FLP isomer 4' and t-Bu$_3$PH$_2^+$.

S2.6.1. Characterization Data of 7 ([B(C$_6$F$_5$)$_4$]-salt)

$^1$H NMR (CD$_2$Cl$_2$, 26°C, [ppm]): $\delta = 1.42$ (9H, d, H12, $^3$J$_{HP} = 17.1$ Hz), 1.47 (9H, d, H12, $^3$J$_{HP} = 16.7$ Hz), 4.52 (1H, d, H2, $^2$J$_{HH} = 11.1$ Hz), 4.94 (1H, d, H2, $^2$J$_{HH} = 11.1$ Hz), 5.18 (1H, d, PH, $^1$J$_{HP} = 436.6$ Hz), 5.82 (1H, d, H1, $^2$J$_{HH} = 7.4$ Hz), 7.32 - 7.36 (2H, m, H4), 7.41 - 7.46 (5H, m, H5/6/9), 7.51 - 7.53 (1H, m, H10), 7.54 - 7.59 (2H, m, H8); $^{11}$B$^1$H NMR (CD$_2$Cl$_2$, 26°C, [ppm]): $\delta = -16.2$ (s); $^{13}$C$^1$H NMR (CD$_2$Cl$_2$, 26°C, [ppm]): $\delta = 28.0$ (3C, s, C12), 28.9 (3C, s, C12), 35.2 (1C, d, C11, $^1$J$_{CP} = 26.3$ Hz), 37.1 (1C, d, C11, $^1$J$_{CP} = 24.1$ Hz), 74.4 (1C, d, C2, $^3$J$_{CP} = 11.4$ Hz), 75.0 (1C, d, C1, $^1$J$_{CP} = 57.0$ Hz), 126.8 (2C, d, C8, $^3$J$_{CP} = 4.0$ Hz), 129.5 (2C, s, C3/4), 129.6 (2C, s, C3/4), 130.0 (1C, s, C6), 130.7 (2C, d, C9, $^3$J$_{CP} = 2.7$ Hz), 131.0 (1C, d, C10, $^5$J$_{CP} = 3.2$ Hz), 132.1 (1C, d, C7, $^1$J$_{CP} = 1.7$ Hz), 134.5 (1C, s, C3), 136.7 (8C, d(br), C$_6$F$_5$, $^1$J$_{CF} = 248$ Hz), 138.6 (4C, d(br), C$_6$F$_5$, $^1$J$_{CF} = 245$ Hz), 148.5 (8C, d(br), C$_6$F$_5$, $^1$J$_{CF} = 241$ Hz), resonances for boron bond carbon atoms were not observed; $^{19}$F$^1$H NMR (C$_6$D$_5$Br, 26°C, [ppm]): $\delta = -167.4$ (8F, m, C$_6$F$_5$), $-163.6$ (4F, m, C$_6$F$_5$), $-133.0$ (8F, m, C$_6$F$_5$); $^{31}$P$^1$H NMR (CD$_2$Cl$_2$, 26°C, [ppm]): $\delta = 52.2$ (s); ESI-HRMS (M$^+$): C$_{12}$H$_{28}$OP$^+$ calcd. 343.2185; found 343.2185.

S2.6.2. Characterization Data of 8 ([B(C$_6$F$_5$)$_4$]-salt)

$^1$H NMR (CD$_2$Cl$_2$, 25 °C, [ppm]): $\delta = 1.55$ (9H, d, H6, $^3$J$_{HP} = 17.7$ Hz), 1.57 (9H, d, $^3$J$_{HP} = 17.7$ Hz), 1.70 - 1.77 (2H, m, H3), 1.82 (1H, m, H4), 1.88 (1H, m, H2), 2.18 (1H, m, H2), 2.21 (1H, m, H4), 3.54 (1H, pseudo t of d, H5, $^1$J$_{HH} = 12.0$ Hz, 2.4 Hz), 4.20 (1H, ddd, H4, $^1$J$_{HH} = 12.0$ Hz, 4.6 Hz, 2.0 Hz), 4.58 (1H, dt, $^2$J$_{HP} = 12.9$ Hz, $^3$J$_{HH} = 6.1$ Hz, H4), 5.74 (1H, dd, $^1$J$_{HP} = 447$ Hz, $^3$J$_{HP} = 9.5$ Hz, PH); $^{19}$F NMR (CD$_2$Cl$_2$, 25 °C, [ppm]): $\delta = -131.7$ (m, 2F, o-
S2.6.3. Characterization Data of 9

\[
\begin{align*}
&\text{\textbf{1H NMR (CD}_2\text{Cl}_2, 25 ^\circ\text{C}, [ppm])}: \delta = 1.45 \ (9\ H, \ d, \ H_7, \ 3J_{HP} = 14.8 \ Hz), \ 1.56 \\
&(9\ H, \ d, \ H_7, \ 3J_{HP} = 14.8 \ Hz), \ 2.27 \ (2H, \ m, \ H_4), \ 2.43 \ (1H, \ m, \ H_5), \ 2.72 \ (1H, \ m, \ H_5), \ 3.60 \ (3H, \ s, \ H_8), \ 4.94 \ (1H, \ d, \ 2J_{HP} = 15.1 \ Hz, \ 3J_{HH} = 4.7 \ Hz, \ H_1), \ 5.32 \ (1H, \ d, \ 3J_{HH} = 4.7 \ Hz, \ H_2);
\end{align*}
\]

\[
\begin{align*}
&\text{\textbf{31P\{1H\} NMR (CD}_2\text{Cl}_2, 25 ^\circ\text{C}, [ppm])}: \delta = 40.3 \ (s);
\end{align*}
\]

\[
\begin{align*}
&\text{\textbf{13C\{1H\} NMR (CD}_2\text{Cl}_2, 25 ^\circ\text{C}, [ppm])}: \delta = 12.6 \ (d, \ 3J_{CP} = 46.7 \ Hz, \ C_4), \ 24.7 \\
&(d, \ 4J_{CP} = 7.4 \ Hz, \ C_5), \ 26.4 \ (d, \ 2J_{CP} = 1.1 \ Hz, \ C_7), \ 27.3 \ (d, \ 2J_{CP} = 1.1 \ Hz, \ C_7), \ 34.2 \ (d, \ 1J_{CP} = 26.8 \\
&\text{Hz, C_6), 36.3 \ (d, \ 1J_{CP} = 26.8 \ Hz, \ C_6), 55.2 \ (C_8), 61.9 \ (d, \ 1J_{CP} = 54.2 \ Hz, \ C_1), 94.9 \ (d, \ 2J_{CP} = 4.2 \\
&\text{Hz, C_2), 159.7 \ (d, \ 3J_{CP} = 7.4 \ Hz, \ C_3}); \ \text{\textbf{ESI-HRMS (MH}^+\text{)}: C}_{14}\text{H}_{28}\text{O}_2\text{P calcd. 259.1821; found 259.1826.}
\end{align*}
\]

S2.6.4. Characterization Data of 10 ([B(C_6F_3)_4]-salt)

\[
\begin{align*}
&\text{\textbf{1H NMR (CD}_2\text{Cl}_2, 25 ^\circ\text{C}, [ppm])}: \delta = 1.50 \ (9\ H, \ d, \ H_6, \ 3J_{HP} = 17.7 \ Hz), \ 1.51 \\
&(9\ H, \ d, \ H_6, \ 3J_{HP} = 17.7 \ Hz), \ 1.93 \ (1H, \ m, \ H_3), \ 2.21 \ (1H, \ m, \ H_2), \ 2.54 \ (1H, \ m, \ H_3), \ 2.69 \ (1H, \ m, \ H_2), \ 3.10 \ (1H, \ m, \ H_4), \ 3.27 \ (1H, \ m, \ H_4), \ 4.01 \ (1H, \ m, \ H_1), \\
&5.77 \ (1H, \ dd, \ PH, \ 1J_{HP} = 447 \ Hz, \ 3J_{HP} = 11.2 \ Hz); \ \text{\textbf{19F NMR (CD}_2\text{Cl}_2, 25 ^\circ\text{C}, [ppm])}: \delta = -133.0 \ (m, \ 2F, \ o-C_6\text{F}_3), \ -163.6 \ (t, \ 1F, \ 3J_{FF} = 20.6 \ Hz, \ p-C_6\text{F}_3), \\
&-167.5 \ (m, \ 2F, \ m-C_6\text{F}_3); \ \text{\textbf{31P\{1H\} NMR (CD}_2\text{Cl}_2, 25 ^\circ\text{C}, [ppm])}: \delta = 47.3 \ (s); \ \text{\textbf{31P NMR (CD}_2\text{Cl}_2, 25 ^\circ\text{C}, [ppm])}: \delta = 47.3 \ (dm, \ 1J_{PH} = 447 \ Hz); \ \text{\textbf{11B NMR (CD}_2\text{Cl}_2, 25 ^\circ\text{C}, [ppm])}: \\
&\delta = -16.7 \ (s, \ B(C_6\text{F}_3)_4); \ \text{\textbf{13C\{1H\} NMR (CD}_2\text{Cl}_2, 25 ^\circ\text{C}, [ppm])}: \delta = 27.4 \ (C_6), \ 31.5 \ (C_3), \ 34.5
\end{align*}
\]
S2.6.5. Characterization Data of 11 ([B(C₆F₅)₄]-salt)

![Diagram of 11 ([B(C₆F₅)₄]-salt)](image)

**¹H NMR (CD₂Cl₂, 25 °C, [ppm]):** δ = 1.38 (3H, t, H₄, J₃HH = 7.5 Hz), 1.65 (9H, d, H₆, J₃HP = 16.6 Hz), 1.66 (9H, d, H₆, J₃HP = 16.6 Hz), 1.86 (3H, dd, J₃HP = 16.3 Hz, J₃HH = 7.5 Hz), 2.82 (2H, m, H₃), 3.59 (1H, dq, J₃HP = 4.8 Hz), 4.84 (2H, dd, J₃HP = 19.7 Hz), 7.24 (2H, t, H₅, J₅H = 8.7 Hz), 7.45 (4H, t, H₄, J₅H = 8.7 Hz); **¹³C {¹H} NMR (CD₂Cl₂, 25 °C, [ppm]):** δ = 13.8 (C₄), 20.8 (C₂), 28.1 (C₆), 28.4 (C₆), 28.6 (d, J₃CP = 4.8 Hz, C₃), 30.0 (d, J₃CP = 36.7 Hz, C₁), 35.5 (d, J₃CP = 30.2 Hz, C₅), 36.5 (d, J₃CP = 30.2 Hz, C₅), 123.9 (br, ipso-C₆F₅), 136.3 (dm, J₃CF = 242 Hz, C₆F₅), 138.1 (dm, J₃CF = 246 Hz, C₆F₅), 148.1 (dm, J₃CF = 233 Hz, C₆F₅); **ESI-HRMS (M⁺):** ESI-HRMS (M⁺): C₁₂H₂₆PS calcd. 235.1644; found 235.1642.

S2.6.6. Characterization Data of 12 ([B(C₆F₅)₄]-salt)

![Diagram of 12 ([B(C₆F₅)₄]-salt)](image)

**¹H NMR (CD₂Cl₂, 25 °C, [ppm]):** δ = 1.57 (18H, d, H₇, J₇H = 16.8 Hz), 4.84 (2H, dd, H₁, J₃HH = 4.5 Hz, J₂HP = 3.1 Hz), 5.41 (1H, dt, PH, J₃HP = 449 Hz, J₃HH = 4.5 Hz), 7.12 (4H, d, H₃, J₃HH = 8.7 Hz), 7.24 (2H, t, H₅, J₅H = 8.7 Hz), 7.45 (4H, t, H₄, J₅H = 8.7 Hz); **¹⁹F NMR (CD₂Cl₂, 25 °C, [ppm]):** δ = -132.9 (m, 2F, o-C₆F₅), -163.5 (t, 1F, J₃FF = 19.4 Hz, p-C₆F₅), -167.3 (m, 2F, m-C₆F₅); **³¹P {¹H} NMR (CD₂Cl₂, 25 °C, [ppm]):** δ = 35.9 (s); **¹³C {¹H} NMR (CD₂Cl₂, 25 °C, [ppm]):** δ = 35.9 (dm, J₃HP = 449 Hz, PH); **¹¹B NMR (CD₂Cl₂, 25 °C, [ppm]):** δ = -16.6 (s, B(C₆F₅)₄); **¹³C {¹H} NMR (CD₂Cl₂, 25 °C, [ppm]):** δ = 27.4 (C₇), 33.6 (d, J₃CP = 29.5 Hz, C₆), 42.3 (d, J₃CP = 48.7 Hz,
C1), 122.4 (C3), 124.0 (br, ipso-C₆F₅), 125.3 (C5), 124.0 (C4), 146.1 (C2), 136.3 (dm, 1JC₆ = 245 Hz, C₆F₅), 138.0 (dm, 1JC₆ = 239 Hz, C₆F₅), 148.3 (dm, 1JC₆ = 239 Hz, C₆F₅); ESI-HRMS (M⁺): 
ESI-HRMS (M⁺): 238.2186, calcd. (C₂₁H₃₁PN): 238.2189.

S2.7. Reaction of 4 (X = O₂SO₂CF₃) with THF, Et₂O and Bn₂O

Ether (Et₂O: 1.556 g, 21.0 mmol, 7.0 eq.; Bz₂O: 4.163 g, 21.0 mmol, 7.0 eq.; THF: 1.514 g, 21.0 mmol, 7.0 eq.) was added dropwise to a suspension of 4 in C₆H₄F₂ (50 mL). The reaction mixtures were stirred for 24 h at ambient temperature giving clear, orange (Et₂O), brown (Bz₂O) or red (THF) solutions. The reaction mixtures were investigated by means of ³¹P{¹H} NMR spectroscopy. The volumes of the reaction mixtures were reduced to approximately 20 mL in vacuo. Et₂O (50 mL) was added leading to the formation of a colourless precipitate of a mixture of 5, 6 or 7 with [t-Bu₂PH₂][OTf]. The separation of both salts was complicated by similar solubilities, however, analytically pure samples of 5 - 7 were obtained by repeated recrystallization steps from CH₂Cl₂ / Et₂O yielding all compounds in variable yields ranging between 10 and 20%.

2.7.1. Characterisation Data of 5 ([OSO₂CF₃]-salt)

1H NMR (CD₂Cl₂, 26°C, [ppm]): δ = 1.54 (9H, d, H₆, 3JHP = 16.5 Hz), 1.58 (9H, d, H₆, 3JHP = 16.5 Hz), 2.09 (1H, m, H₃), 2.17 (1H, m, H₃), 2.48 (1H, m, H₂), 2.62 (1H, m, H₂), 3.93 (1H, m, H₄), 4.04 (1H, m, H₄), 4.75 (1H, m, H₁), 6.41 (1H, dd, PH, 1JHP = 467.7 Hz, 3JHP = 4.7 Hz); ¹³C{¹H} NMR (CD₂Cl₂, 26°C, [ppm]): δ =26.1 (1C, d, C₃, 3JC₆ = 5.5 Hz), 33.0 (1C, s, C₂), 28.0 (3C, s, C₆), 28.4 (3C, s, C₆), 33.4 (1C, d, C₅, 2JC₆ = 32.0 Hz), 35.2 (1C, d, C₅, ²JC₆ = 30.7 Hz), 70.9 (1C, d, C₄, ³JC₆ = 6.9 Hz), 71.3 (1C, d, C₁, ¹JC₆ = 50.9 Hz); ³¹P{¹H} NMR (CD₂Cl₂, 26°C, [ppm]): δ = 39.8 (s); ³¹P{¹H} NMR (CD₂Cl₂, 26°C, [ppm]): δ = 39.8 (dm, ¹JPH = 476.7 Hz); MS-ESI-MS: 217.1715 (M⁺), calcd. for C₁₂H₂₆PO: 219.1716.
**Figure S7.1.1.** Molecular structure of the cation of 5 (OSO$_2$CF$_3$-salt) (orange: P, red: O, black: C, grey: H; some hydrogen atoms are omitted for clarity).

### S2.7.2. Characterisation 6 (O$_2$SOCF$_3$-salt)

**$^1$H NMR (CD$_2$Cl$_2$, 26°C, [ppm]):**

- $\delta = 1.25$ (3H, dd, H4, $^3J_{HH} = 7.0$ Hz, $^3J_{HP} = 7.0$ Hz), 1.55 (9H, d, H6, $^3J_{HP} = 16.2$ Hz), 1.60 (9H, d, H6, $^3J_{HP} = 16.2$ Hz), 1.80 (3H, dd, H2, $^3J_{HH} = 7.2$ Hz, $^3J_{HP} = 16.3$ Hz), 3.52 (1H, dquart., H3, $^2J_{HH} = 8.9$ Hz, $^3J_{HH} = 7.0$ Hz), 3.86 (1H, dquart., H3, $^2J_{HH} = 8.9$ Hz, $^3J_{HH} = 7.0$ Hz), 4.76 (1H, dquart., H1, $^2J_{HP} = 4.8$ Hz, $^3J_{HH} = 7.2$ Hz), 6.23 (1H, d, PH, $^1J_{HP} = 463$ Hz);

**$^{13}$C{$_^1$H} NMR (CD$_2$Cl$_2$, 26°C, [ppm]):**

- $\delta = 15.4$ (1C, s, C4), 19.2 (1C, d, C2, $^2J_{CP} = 1.5$ Hz), 27.9 (3C, s, C6), 28.7 (3C, s, C6), 33.9 (1C, d, C5, $^1J_{CP} = 31.8$ Hz), 35.4 (1C, d, C5, $^1J_{CP} = 29.6$ Hz), 67.4 (1C, d, C3, $^3J_{CP} = 10.3$ Hz), 70.6 (1C, d, C1, $^1J_{CP} = 57.0$ Hz), 121.3 (1C, d, CF$_3$, $^1J_{CF} = 321.2$ Hz);

**$^{31}$P{$_^1$H} NMR (CD$_2$Cl$_2$, 26°C, [ppm]):**

- $\delta = 39.1$ (s);

**$^{19}$F{$_^1$H} NMR (CD$_2$Cl$_2$, 26°C, [ppm]):**

- $\delta = 79.0$ (s); **MS-ESI-MS:** 219.1871 (M$^+$), calcd. for C$_{12}$H$_{28}$PO: 219.1872.
Figure S7.2.1. Molecular structure of the cation of 6 (OSO₂CF₃-salt) (orange: P, red: O, black: C, grey: H; some hydrogen atoms are omitted for clarity).

S2.7.3. Characterisation data of 7 (OSO₂CF₃-salt)

1H NMR (CD₂Cl₂, 26°C, [ppm]): δ = 1.31 (9H, d, H12, 3JHP = 16.5 Hz), 1.59 (9H, d, H12, 3JHP = 16.5 Hz), 4.57 (1H, d, H2, 2JHH = 11.0 Hz), 4.89 (1H, d, H2, 2JHH = 11.0 Hz), 6.06 (1H, d, H1, 2JHP = 8.9 Hz), 6.46 (1H, d, PH, 1JHP = 466.2 Hz), 7.38 (2H, m, H4), 7.41 (2H, m, H5), 7.43 (1H, m, H6), 7.45 (1H, m, H10), 7.46 (1H, m, H9), 7.66 (2H, m, H8);

13C{1H} NMR (CD₂Cl₂, 26°C, [ppm]): δ = 28.1 (3C, s, C12), 28.7 (3C, s, C12), 35.2 (1C, d, C11, 1JCP = 27.6 Hz), 36.1 (1C, d, C11, 1JCP = 27.1 Hz), 74.3 (1C, d, C2, 3JCP = 11.3 Hz), 75.6 (1C, d, C1, 1JCP = 56.1 Hz), 127.2 (2C, d, C8, 3JCP = 3.6 Hz), 129.0 (2C, s, C4), 129.3 (2C, s, C5), 129.4 (1C, s, C6), 130.2 (1C, s, C10), 130.3 (2C, d, C9, 4JCP = 4.6 Hz), 132.5 (1C, d, C7, 2JCP = 1.4 Hz), 135.6 (1C, s, C3);

31P{1H} NMR (CD₂Cl₂, 26°C, [ppm]): δ = 42.4 (s);

31P{/} NMR (CD₂Cl₂, 26°C, [ppm]): δ = 42.4 (dm, 1JPH = 466.2 Hz);

19F{1H} NMR (CD₂Cl₂, 26°C, [ppm]): δ = −78.8 (s); MS-ESI-MS: 343.2186 (M⁺), calcd. for C₂₂H₃₂PO: 343.2185.
2.8. Preparation of 13 - 15

$t$-Bu$_2$PH (1.462 g, 10.0 mmol, 1.00 eq.) in C$_6$H$_4$F$_2$ (10 mL) was added dropwise to a solution of Trt[OTf] (4.120 g, 10.5 mmol, 1.05 eq.) in C$_6$H$_4$F$_2$ (40 mL) within 20 min at –30°C yielding a deep red reaction mixture. Ether (Et$_2$O: 5.189 g, 70.0 mmol, 7.0 eq.; Bz$_2$O: 13.878 g, 70.0 mmol, 7.0 eq.; thf: 5.047 g, 70.0 mmol, 7.0 eq.) was added dropwise within 10 min at –30°C. The reaction mixtures were stirred for 24 h at ambient temperature giving clear, orange (Et$_2$O), red (thf) or brown (Bz$_2$O) solutions. The volumes of the reaction mixtures were reduced to approximately 25 mL in vacuo. n-Hexane (50 mL) was added leading to the formation of colourless precipitates. The supernatants were removed and the residues were washed with n-Hexane (3 x 20 mL) and dried in vacuo. The ratios of 5 (6, 7) to [t-Bu$_2$PH$_2$][OTf] were determined with the help of $^{31}$P{$_1$H} NMR spectroscopy. One equivalent of $t$-BuOK was added to the mixtures of 5 - 7 with [t-Bu$_2$PH$_2$][OTf]. THF (20 mL) was added and the reaction mixtures were stirred for 12 h at ambient temperatures. All volatiles were removed in vacuo and the remaining brownish to colourless sludge was extracted with benzene (3 x 10 mL). Removing of all volatiles yielded crude products from which analytically pure 13 - 15 was obtained by distillation as viscous, colourless liquids (13: 1.127 g, 53%, 14: 1.810 g, 46%; 15: 2.370 g, 69%).
2.8.1. Characterisation data of 13

$^1$H NMR ($C_6D_6$, 26°C, [ppm]): $\delta = 1.20$ (9H, d, H6, $^3J_{HP} = 10.5$ Hz), 1.37 (9H, d, H6, $^3J_{HP} = 10.5$ Hz), 1.44 (1H, m, H3), 1.56 (1H, m, H3), 1.90 (1H, m, H2), 1.93 (1H, m, H2), 3.42 (1H, m, H4), 3.70 (1H, m, H4), 4.05 (1H, m, H1);

$^{13}$C{$^1$H} NMR ($C_6D_6$, 26°C, [ppm]): $\delta = 26.0$ (1C, d, C3, $^3J_{CP} = 7.2$ Hz), 30.9 (3C, d, C6, $^2J_{CP} = 13.0$ Hz), 31.2 (3C, d, C6, $^2J_{CP} = 13.0$ Hz), 31.5 (1C, d, C2, $^2J_{CP} = 21.7$ Hz), 33.4 (1C, d, C5, $^1J_{CP} = 25.1$ Hz), 34.2 (1C, d, C5, $^1J_{CP} = 23.3$ Hz), 68.5 (1C, d, C4, $^3J_{CP} = 1.5$ Hz), 77.0 (1C, d, C1, $^1J_{CP} = 28.5$ Hz);

$^{31}$P{$^1$H} NMR ($C_6D_6$, 26°C, [ppm]): $\delta = 33.0$ (s);

MS-ESI-MS: 217.1699 (MH$^+$), calcd. for C$_{12}$H$_{26}$PO: 217.1716.

2.8.2. Characterisation data of 14

$^1$H NMR ($C_6D_6$, 26°C, [ppm]): $\delta = 1.05$ (3H, t, H4, $^3J_{HH} = 7.0$ Hz), 1.24 (9H, d, H6, $^3J_{HP} = 10.9$ Hz), 1.40 (9H, d, H6, $^3J_{HP} = 10.9$ Hz), 1.51 (3H, dd, H2, $^3J_{HH} = 7.1$ Hz, $^3J_{HP} = 15.3$ Hz), 2.98 (1H, dquart., H3, $^3J_{HH} = 7.0$ Hz, $^4J_{HP} = 8.6$ Hz), 3.43 (1H, dquart. H3, $^3J_{HH} = 7.0$ Hz), $^1J_{CP} = 2.7$ Hz); 3.81 (1H, dquart. H1, $^3J_{HH} = 7.1$ Hz, $^2J_{HP} = 2.7$ Hz), $^1J_{CP} = 11.0$ Hz);

$^{13}$C{$^1$H} NMR ($C_6D_6$, 26°C, [ppm]): $\delta = 15.8$ (1C, s, C4), 21.0 (1C, d, C2, $^2J_{CP} = 24.5$ Hz), 30.6 (3C, d, C6, $^2J_{CP} = 13.5$ Hz), 31.6 (3C, d, C6, $^2J_{CP} = 13.5$ Hz), 65.1 (1C, d, C3, (3C, d, C6, $^3J_{CP} = 1.0$ Hz), 75.2 (1C, d, C1, (3C, d, C6, $^1J_{CP} = 30.3$ Hz);

$^{31}$P{$^1$H} NMR ($C_6D_6$, 26°C, [ppm]): $\delta = 45.1$ (s); MS-ESI-MS: 219.1855 (MH$^+$), calcd. for C$_{12}$H$_{28}$PO: 219.1872.

2.8.3. Characterisation Data of 15

$^1$H NMR ($C_6D_6$, 26°C, [ppm]): $\delta = 1.14$ (9H, d, H12, $^3J_{HP} = 11.0$ Hz), 1.32 (9H, d, H12, $^3J_{HP} = 10.9$ Hz), 4.42 (1H, d, H2 $^2J_{HH} = 11.2$ Hz), 4.64 (1H, d, H2, $^2J_{HH} = 11.2$ Hz), 5.32 (1H, s, H1), 7.20 (1H, m, H10), 7.33 (2H, m, H9), 7.38 (2H, m, H5), 7.41 (1H, m, H6), 7.42 (2H, m, H4), 7.46 (2H, m, H8);

$^{13}$C{$^1$H} NMR ($C_6D_6$, 26°C, [ppm]): $\delta = 30.9$ (3C, d, C12, $^2J_{CP} = 13.1$ Hz), 31.5 (3C, d, C12, $^2J_{CP} = 12.4$ Hz), 32.9
(1C, d, C11, $^{1}J_{CP} = 23.7$ Hz), 34.5 (1C, d, C11, $^{1}J_{CP} = 26.6$ Hz), 73.0 (1C, s, C2), 82.5 (1C, d, C1, $^{1}J_{CP} = 35.4$ Hz), 127.2 (2C, d, C8, $^{3}J_{CP} = 7.0$ Hz), 127.9 (2C, s, C4), 128.3 (2C, s, C9), 126.5 (1C, s, C6), 128.7 (2C, s, C5), 128.8 (1C, s, C6), 138.9 (1C, s, C3), 142.5 (1C, d, C3, $^{2}J_{CP} = 11.5$ Hz);

$^{31}$P($^1$H) NMR (C$_6$D$_6$, 426°C, [ppm]): $\delta = 55.7$ (s);  **MS-ESI-MS:** 343.2185 (MH$^+$), calcd. for C$_{22}$H$_{32}$PO: 343.2185.
S3. Crystallographic Details

Table S3.1. Crystallographic data and structure refinements of compounds 1, [Ph₂TrtPH][OTf], [Cy₂TrtPH][OTf] and 4[OTf].

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<td>-18 ≤ k ≤ 21</td>
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<td>-19 ≤ l ≤ 20</td>
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<td>0.172</td>
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<td>6584</td>
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<td>0.0349</td>
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<td>5407</td>
<td>4373</td>
<td>4303</td>
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<td>residual density [e Å⁻³]</td>
<td>0.428 - 0.282</td>
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<td>0.359 - 0.313</td>
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<td>1.010</td>
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<td>0.0343</td>
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<td>C₁₃H₃₂F₅O₄PS</td>
<td>C₂₃H₃₂F₅O₄PS</td>
<td>C₁₅H₂₆F₅O₄PS</td>
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<td>8.2485(2)</td>
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<td>V [Å³]</td>
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<td>2467.2(3)</td>
<td>1830.82(4)</td>
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<td>1.310</td>
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<td>F(000)</td>
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<td>3009</td>
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<td>1.026</td>
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<td>1.055</td>
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<td>0.0566</td>
<td>0.0378</td>
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<td>wR&lt;sub&gt;2&lt;/sub&gt; (all data)</td>
<td>0.1710</td>
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S4. References


