# **Supporting Information for:**

# Phosphorous(V) Lewis Acids: Water-Base Tolerant P<sub>3</sub>-trimethylated trications

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### 1. General Remarks

Unless otherwise indicated all manipulations were conducted under inert nitrogen atmosphere. TRIPHOS 1 and 2 (Bis(diphenylphosphinoethyl)phenylphosphine and 1,1,1-Tris(diphenylphosphinomethyl)ethane), methyl triflate, methyl iodide and all the reagents for the catalysis screening were purchased from commercial sources and used as received unless otherwise stated. NMR spectra were recorded with a Bruker AV-400 spectrometer (400 MHz <sup>1</sup>H; 100 MHz <sup>13</sup>C; 128 MHz <sup>11</sup>B; 376 MHz <sup>19</sup>F; 79 MHz <sup>29</sup>Si, 162 MHz <sup>31</sup>P). <sup>1</sup>H NMR chemical shifts are reported in ppm relative to *proteo* impurities in the deuterated solvents and <sup>13</sup>C NMR chemical shifts using the solvent resonances unless otherwise stated. <sup>11</sup>B NMR spectra were referenced to external BF<sub>3</sub>:Et<sub>2</sub>O, <sup>19</sup>F to Cl<sub>3</sub>CF, <sup>29</sup>Si to Si(CH<sub>3</sub>)<sub>4</sub> and <sup>31</sup>P to 85% H<sub>3</sub>PO<sub>4</sub>. Coupling constants *J* are given in Hertz (Hz), while the multiplicity of the signals are indicated as "s", "d", "t", "q", "pent", "sept" or "m" for singlet, doublet, triplet, quartet, pentet, septet or multiplet, respectively. Mass spectra were recorded on a Waters QTOF mass spectrometer. MeOTf is a strong methylated agent (handled in the fumehood or glovebox at all times) and was quenched with a NaOH solution.

### 2. Catalyst synthesis

## 2.1 Synthesis of [6][OTf]<sub>3</sub> and [7][OTf]<sub>3</sub>



Methyl trifluoromethanesulfonate (0.4 mL, 3.66 mmol, 6.2 eq.) was added to a solution of Bis(diphenylphosphinoethyl)phenylphosphine (314.7 mg, 0.59 mmol, 1.0 eq.) in  $CH_2Cl_2$  (3 mL). The reaction mixture was left to stir at ambient temperature for 20 h, after which time a white precipitate settled out of solution. 3 mL of *n*-pentane was added to the solution, and after stirring for 2 h the supernatant was decanted and the remaining solid was washed with *n*-pentane (3 x 3 mL). The solid was dried *in vacuo* to afford a white microcrystalline solid. Yield: 531 mg (88%). Diffraction-quality single crystals can be obtained by vapour diffusion of diethyl ether into saturated DMF solutions.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 298K): δ 7.76 (m, 15H; Ar-H), 7.65 (m, 8H; Ar-H), 7.55 (m, 2H; Ar-H), 3.42 (m, 2H; CH<sub>2</sub>), 3.04 (m, 6H; CH<sub>2</sub>), 2.63 (d,  ${}^{2}J_{PH}$  = 14 Hz, 6H; Ph<sub>2</sub>P-CH<sub>3</sub>), 2.62 ppm (d,  ${}^{2}J_{PH}$  = 14 Hz, 3H; PhP-CH<sub>3</sub>). <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 377 MHz, 298K): δ -78.8 ppm (s, 9F; O<sub>3</sub>SCF<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz, 298K): δ 33.4 (t,  ${}^{3}J_{PP}$  = 58 Hz, 1P), 25.7 ppm (d,  ${}^{3}J_{PP}$  = 58 Hz, 2P). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125 MHz, 298K): δ 135.8 (m, 5C; *p*-Ph), 132.9 (dd,  ${}^{2/3}J_{PC}$  = 15 Hz,  ${}^{2/3}J_{PC}$  = 15 Hz, o/m-Ph), 132.6 (d,  ${}^{2/3}J_{PC}$  = 10 Hz, o/m-Ph), 130.9 (dd,  ${}^{2/3}J_{PC}$  = 13 Hz,  ${}^{2/3}J_{PC}$  = 12 Hz, 10C; o/m-Ph), 118.3 (d,  ${}^{1}J_{PC}$  = 87 Hz, 2C; *i*-Ph<sub>2</sub>P), 117.1 (d,  ${}^{1}J_{PC}$  = 86 Hz, 2C; *i*-Ph<sub>2</sub>P), 115.9 (d,  ${}^{1}J_{PC}$  = 84 Hz, 1C; *i*-PhP), 16.6 (m, 4C; CH<sub>2</sub>), 6.5 (d,  ${}^{1}J_{PC}$  = 55 Hz, 2C; Ph<sub>2</sub>P-CH<sub>3</sub>), 2.6 ppm (d,  ${}^{1}J_{PC}$  = 52 Hz, 1C; PhP-CH<sub>3</sub>).

HRMS (DART-TOF+): Unable to observe [M]<sup>+</sup> peak due to fragmentation.

**Elemental analysis** calcd. (%) for C<sub>40</sub>H<sub>42</sub>F<sub>9</sub>O<sub>9</sub>P<sub>3</sub>S<sub>3</sub>: C, 46.79; H, 4.12. (found: C, 45.99; H, 4.08).





Figure S3. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of compound [6][OTf]<sub>3</sub>.



Figure S4. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of compound [6][OTf]<sub>3</sub>.



1,1,1-Tris(diphenylphosphinomethyl)ethane (117.0 mg, 0.19 mmol, 1 eq.) was dissolved in 2 mL  $CH_2Cl_2$  at room temperature. To this homogeneous solution was added excess MeOTf (~1.5 mL). This solution was stirred for 5 minutes, then 1 mL of pentane was added. A white solid precipitated from the reaction mixture, and the heterogeneous solution was stirred for 30 minutes. After this time, the solvent was removed *in vacuo*, and the white solid washed with  $CH_2Cl_2$  (2 x 2 mL) and pentane (2 x 5 mL). The white solid was dried again, yielding analytically pure product. Yield: 197 mg (94%). Diffraction-quality single crystals can be obtained by vapour diffusion of diethyl ether into saturated DMF solutions. Trace DMF can be observed by  ${}^{13}C{}^{1}H$  NMR spectroscopy.

<sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 MHz, 298K):  $\delta$  7.74 (m, 6H, Ar), 7.58 (m, 24H, Ar), 2.81 (d, <sup>2</sup>J<sub>PH</sub> = 14 Hz, 6H, CH<sub>2</sub>) 2.77 (d, <sup>2</sup>J<sub>PH</sub> = 14 Hz, 9H, CH<sub>3</sub>), 1.87 ppm (s, 3H, CH<sub>3</sub>). <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 376 MHz, 298K):  $\delta$  -79.2 ppm (s, CF<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 161 MHz, 298K):  $\delta$  18.6 ppm (s). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 126 MHz, 298K):  $\delta$  136.2 (d, <sup>4</sup>J<sub>PC</sub> = 3 Hz, Ar), 133.2 (d, <sup>3</sup>J<sub>PC</sub> =11 Hz, Ar), 131.2 (d, <sup>2</sup>J<sub>PC</sub> = 13 Hz, Ar), 42.4 (q, <sup>2</sup>J<sub>PC</sub> = 5 Hz, C), 39.2 (dt, <sup>1</sup>J<sub>PC</sub> = 48 Hz, <sup>3</sup>J<sub>PC</sub> = 9 Hz, CH<sub>2</sub>) 26.8 (s, CH<sub>3</sub>), 7.5 ppm (d, <sup>1</sup>J<sub>PC</sub> = 52 Hz, CH<sub>3</sub>). HRMS (DART-TOF+): Unable to observe [M]<sup>+</sup> peak due to fragmentation. Elemental analysis calcd. (%) for C<sub>47</sub>H<sub>48</sub>F<sub>9</sub>O<sub>9</sub>P<sub>3</sub>S<sub>3</sub>: C, 50.54; H, 4.33. (found: C, 50.22; H, 4.29).



Figure S8. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of compound [7][OTf]<sub>3</sub>.

# 2.2 Synthesis of [Ph<sub>2</sub>PMe(CH<sub>2</sub>)<sub>3</sub>MePPh<sub>2</sub>][OTf]<sub>2</sub>



Methyl Trifluoromethanesulfonate (0.08 mL, 0.73 mmol, 2 eq.) was added to a solution of diphenylphosphinopropane (dppp, 157 mg, 0.38 mmol, 1 eq.) in  $CH_2CI_2$  (3 mL). The reaction mixture was left to stir at ambient temperature for 24 h. The volume was reduced in vacuo to 1 mL and 3 mL of *n*-pentane was added to induce precipitation. The supernatant was decanted and the solid was washed with *n*-pentane (3 x 5 mL). The solid was dried *in vacuo* to afford a white microcrystalline solid. (225 mg, 80% Yield).

<sup>1</sup>**H NMR (CD<sub>3</sub>CN, 400MHz, 298K):** δ 7.72 (m, 20H; Ar-H) 3.65 (m, 4H; -C*H*<sub>2</sub>-), 2.43 (d, *J* = 14 Hz, 6H; P-C*H*<sub>3</sub>), 1.70 ppm (m, 2H; -C*H*<sub>2</sub>-).

<sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 377 MHz, 298K): δ -79.2 ppm (s, 6F; O<sub>3</sub>SCF<sub>3</sub>).

<sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 162 MHz, 298K): δ 22.3 ppm (s).

<sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 101 MHz, 298K):  $\delta$  136.0 (t, J = 2 Hz, 4C; p-Ph), 133.3 (pent., J = 4 Hz, 8C; o-Ph), 131.1 (m, 8C; m-Ph), 119.8 (d, J = 87 Hz, 4C; i-Ph), 23.8 (dd, J = 72 Hz, J = 37 Hz, 2C;  $-CH_2$ -), 16.4 (s, 1C;  $-CH_2$ -), 6.8 ppm (d, J = 56 Hz, 2C; P-CH<sub>3</sub>).

**HRMS (ESI-QTOF+):** Unable to observe  $[M]^+$  peak due to fragmentation. **Elemental analysis** calcd. (%) for  $C_{31}H_{32}F_6O_6P_2S_2$ : C, 50.27; H, 4.36. (found: C, 49.72; H, 4.32).





#### 3. Stability in the presence of water/aniline



**General procedure**: In a J. Young NMR tube, the catalyst was dissolved in MeCN (0.05 mL), followed by the addition of H<sub>2</sub>O (5  $\mu$ L, 10 eq.) and aniline (23  $\mu$ L, 10 eq.). The NMR tube was sealed and heated in an oil bath at 60 °C for 18 h. Multinuclear NMR analysis post heating revealed no decomposition in each case.





**Figure S13.** <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H} and <sup>19</sup>F-NMR spectra of **[6][OTf]**<sub>3</sub> with H<sub>2</sub>O/PhNH<sub>2</sub> in MeCN. Blue (after 5 min at RT), red (after 18 h at 60 °C).

#### [7][OTf]<sub>3</sub> (28 mg, 1 eq.)



**Figure S14.** <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H} and <sup>19</sup>F-NMR spectra of **[7][OTf]**<sub>3</sub> with H<sub>2</sub>O/PhNH<sub>2</sub> in MeCN. Blue (after 5 min at RT), red (after 18 h at 60 °C)

## 4. Catalyst applications in reductive aminations

## 4.1 Catalyst screening



**General procedure**: A J. Young NMR tube was loaded with a solution of the catalyst in MeCN (0.5 mL), followed by the addition of benzaldehyde (25 µL, 0.241 mmol, 1.00 eq.), aniline (26 µL, 0.289 mmol, 1.20 eq.), dimethylphenylsilane (45 µL, 0.289 mmol, 1.20 eq.) and mesitylene as internal standard (25 µL, 0.179 mmol, 0.74 eq.). The J. Young NMR tube was then sealed, and the initial reaction mixture was monitored by multinuclear NMR spectroscopy. Thus, the J. Young NMR tube was heated up at 100°C for 18 h in an oil bath and then the reaction mixture was monitored again by multinuclear NMR spectroscopy. The determination of the <sup>1</sup>H NMR yields was based on the relative integral of the benzylic protons of BnNHPh ( $\overline{0}$ = 4.32 ppm) and the methyl signal of mesitylene ( $\overline{0}$  = 2.26 ppm). The product distribution was then confirmed by GC-MS analysis (PhC(H)=NPh (R<sub>t</sub> = 14.46 min): m/z 181.1 [M]<sup>+</sup>, 77.0 [Ph]<sup>+</sup>; BnNHPh (R<sub>t</sub> = 14.99 min): m/z 183.1 [M]<sup>+</sup>, 91.0 [Bn]<sup>+</sup>; (PhMe<sub>2</sub>Si)<sub>2</sub>O (R<sub>t</sub> = 14.62 min): m/z 286.1 [M]<sup>+</sup>, 271.1 [M-CH<sub>3</sub>]<sup>+</sup>). The data were in agreement with those reported in the literature.<sup>3</sup>

| Entry | Catalyst                               | Time (h) | Yield (%) <sup>b</sup> |
|-------|--|----------|------------------------|
| 1     | None                                   | 18       | 0                      |
| 2     | 5 mol% [6][OTf] <sub>3</sub>           | 5        | 82                     |
| 3     | 5 mol% [7][OTf] <sub>3</sub>           | 5        | 93                     |
| 4     | 15 mol% [Ph <sub>3</sub> PMe][OTf]     | 5        | 58                     |
| 5     | 7.5 mol%<br>[Ph2PMe(CH2)3MePPh2][OTf]2 | 5        | 20                     |

#### Reductive amination in absence of the catalyst

Upon heating the reaction mixture at 100 °C for 18 h, no reaction was observed.



**Figure S15.** *In situ* <sup>1</sup>H spectra of the standard reductive amination without catalyst. Blue (after 5 min), red (after 18h at 100 °C).

#### Reductive amination with [6][OTf]<sub>3</sub> (12.4 mg, 0.012 mmol, 0.05 eq.)

Upon heating the reaction mixture at 100 °C for 5 h, minimal degradation of the catalyst was observed and significant BnNHPh formation was detected (82%).



**Figure S16.** *In situ* <sup>1</sup>H, <sup>31</sup>P and <sup>19</sup>F NMR spectra of the standard reductive amination with **[6][OTf]**<sub>3</sub> (5 mol%). Blue (after 5 min), red (after 5 h at 100 °C).

#### **Reductive amination with [7][OTf]**<sub>3</sub> (13.4 mg, 0.012 mmol, 0.05 eq.)

Upon heating the reaction mixture at 100 °C for 5 h, no degradation of the catalyst was observed and significant BnNHPh formation was detected (93%).



**Figure S17.** *In situ* <sup>1</sup>H, <sup>31</sup>P and <sup>19</sup>F NMR spectra of the standard reductive amination with **[7][OTf]**<sub>3</sub> (5 mol%). Blue (after 5 min), red (after 5 h at 100 °C).

#### **Reductive amination with [Ph<sub>3</sub>PMe][OTf]** (15.3 mg, 0.036 mmol, 0.15 eq.)

Upon heating the reaction mixture at 100 °C for 18 h, no degradation of the catalyst was observed and significant BnNHPh formation was detected (93%).



**Figure S18.** In situ <sup>1</sup>H NMR spectra of the standard reductive amination with [Ph<sub>3</sub>PMe][OTf] (15 mol%). Blue (after 5 min), red (after 18h at 100 °C).

The disparity among the catalysts was further confirmed by repeating the standard reductive amination (general procedure) with **[6][OTf]**<sub>3</sub> (5 mol%), **[7][OTf]**<sub>3</sub> (5 mol%) or [Ph<sub>3</sub>PMe][OTf] (15 mol%) and monitoring BnN(H)Ph formation upon heating at 100 °C.



**Graph S1.** *In situ* monitoring of the standard reductive amination with **[6][OTf]**<sub>3</sub> (red), **[7][OTf]**<sub>3</sub> (blue) or [Ph<sub>3</sub>PMe][OTf] (green) after heating at 100 °C each hour.

# **Reductive amination with [Ph<sub>2</sub>PMe(CH<sub>2</sub>)<sub>3</sub>MePPh<sub>2</sub>][OTf]<sub>2</sub> (13.4 mg, 0.018 mmol, 0.075 eq.)**

Upon heating the reaction mixture at 100 °C for 24 h, no degradation of the catalyst was observed and BnNHPh formation was detected (41%).



**Figure S19.** In situ <sup>1</sup>H NMR spectra of the standard reductive amination with  $[Ph_2PMe(CH_2)_3MePPh_2][OTf]_2$  (7.5 mol%). Blue (after 5 min), red (after 24 h at 100 °C).

### 4.2 Aldehyde scope



**General procedure**: A NMR tube was loaded with a solution of the catalyst in MeCN (0.5 mL), followed by the addition of aldehyde (0.241 mmol, 1.00 eq.), aniline (26  $\mu$ L, 0.289 mmol, 1.20 eq.), dimethylphenylsilane (45  $\mu$ L, 0.289 mmol, 1.20 eq.) and mesitylene as internal standard (25  $\mu$ L, 0.179 mmol, 0.74 eq.). The reaction mixture was heated to 100 °C and monitored by multinuclear NMR spectroscopy. The determination of the <sup>1</sup>H NMR yields was based on the relative integral of the benzylic protons of ArCH<sub>2</sub>NHPh and the methyl signal of mesitylene ( $\delta$  = 2.26 ppm).



**Figure S20.** <sup>1</sup>H NMR (CD<sub>3</sub>CN) spectrum of crude reaction mixture of N-(2,4,6-trimethylbenzyl)aniline. Bottom (after 5 min), top (after 5 h at 100 °C). Data in agreement with those reported in the literature.<sup>4</sup>



**Figure S21.** <sup>1</sup>H NMR (CD<sub>3</sub>CN) spectrum of crude reaction mixture of *N*-(4-bromobenzyl)aniline. Bottom (after 5 min), top (after 5 h at 100 °C). Data in agreement with those reported in the literature.<sup>5</sup>



**Figure S22.** <sup>1</sup>H NMR (CD<sub>3</sub>CN) spectrum of crude reaction mixture of 4- ((phenylamino)methyl)benzonitrile. Bottom (after 5 min), top (after 5 h at 100 °C). Data in agreement with those reported in the literature.<sup>6</sup>



 $\dot{0.5}$   $\dot{10.0}$   $\dot{9.5}$   $\dot{9.0}$   $\dot{8.5}$   $\dot{8.0}$   $\dot{7.5}$   $\dot{7.0}$   $\dot{6.5}$   $\dot{6.0}$   $\dot{5.5}$   $\dot{5.0}$   $\dot{4.5}$   $\dot{4.0}$   $\dot{3.5}$   $\dot{3.0}$   $\dot{2.5}$   $\dot{2.0}$   $\dot{1.5}$   $\dot{1.0}$   $\dot{0.5}$   $\dot{0.0}$  **Figure S23.** <sup>1</sup>H NMR (CD<sub>3</sub>CN) spectrum of crude reaction mixture of *N*-(2chlorobenzyl)aniline. Bottom (after 5 min), top (after 5 h at 100 °C). Data in agreement with those reported in the literature.<sup>3</sup>



**Figure S24.** <sup>1</sup>H NMR (CD<sub>3</sub>CN) spectrum of crude reaction mixture of *N*-(4-methoxybenzyl)aniline. Bottom (after 5 min), top (after 5 h at 100 °C). Data in agreement with those reported in the literature.<sup>3</sup>



**Figure S25.** <sup>1</sup>H NMR (CD<sub>3</sub>CN) spectrum of crude reaction mixture of methyl 4-((phenylamino)methyl)benzoate. Bottom (after 5 min), middle (after 5 h at 100 °C), top (after 24h at 100 °C). Note: imine precipitated at room temperature after 5 min. Data in agreement with those reported in the literature.<sup>7</sup>

#### 4.3 Aniline scope



**General procedure**: A NMR tube was loaded with a solution of the catalyst in MeCN (0.5 mL), followed by the addition of benzaldehyde (25  $\mu$ L, 0.241 mmol, 1.00 eq.), aniline (0.289 mmol, 1.20 eq.), dimethylphenylsilane (45  $\mu$ L, 0.289 mmol, 1.20 eq.) and mesitylene as internal standard (25  $\mu$ L, 0.179 mmol, 0.74 eq.). The reaction mixture was heated to 100 °C for 5 h. The determination of the <sup>1</sup>H NMR yields was based on the relative integral of the benzylic protons of BnNHR' and the methyl signal of mesitylene ( $\delta$  = 2.26 ppm).



**Figure S26.** <sup>1</sup>H NMR (CD<sub>3</sub>CN) spectrum of crude reaction mixture of *N*-benzyl-(2-bromophenyl)amine. Bottom (after 5 min), top (after 5 h at 100 °C). Data in agreement with those reported in the literature.<sup>3</sup>



**Figure S27.** <sup>1</sup>H NMR (CD<sub>3</sub>CN) spectrum of crude reaction mixture of *N*-benzyl-(2-fluorophenyl)amine. Bottom (after 5 min), top (after 5 h at 100 °C). Data in agreement with those reported in the literature.<sup>8</sup>



**Figure S28.** <sup>1</sup>H NMR (CD<sub>3</sub>CN) spectrum of crude reaction mixture of *N*-benzyl-(2,6-diisopropylphenyl)amine. Bottom (after 5 min), top (after 5 h at 100 °C). Data in agreement with those reported in the literature.<sup>9</sup>



**Figure S29.** <sup>1</sup>H NMR (CD<sub>3</sub>CN) spectrum of crude reaction mixture of *N*-benzyl-(3-trifluoromethylphenyl)amine. Bottom (after 5 min), top (after 5 h at 100 °C). Data in agreement with those reported in the literature.<sup>10</sup>



**Figure S30.** <sup>1</sup>H NMR (CD<sub>3</sub>CN) spectrum of crude reaction mixture of *N*-benzyl-(4-chlorophenyl)amine. Bottom (after 5 min), top (after 5 h at 100 °C). Data in agreement with those reported in the literature.<sup>11</sup>



**Figure S31.** <sup>1</sup>H NMR (CD<sub>3</sub>CN) spectrum of crude reaction mixture of *N*-benzyl-(4-hexylphenyl)amine, t = 24 h. Bottom (after 5 min), top (after 5 h at 100 °C). Data in agreement with those reported in the literature.<sup>12</sup>

## 4.4 Recycling experiment

A NMR tube was loaded with a solution of the catalyst in MeCN (0.5 mL), followed by the addition of benzaldehyde (25  $\mu$ L, 0.241 mmol, 1.00 eq.), aniline (26  $\mu$ L, 0.289 mmol, 1.20 eq.) dimethylphenylsilane (45  $\mu$ L, 0.289 mmol, 1.20 eq.) and mesitylene as internal standard (25  $\mu$ L, 0.179 mmol, 0.74 eq.). The reaction mixture was heated to 100 °C for 24 h and monitored by multinuclear NMR spectroscopy. Then, a mixture of benzaldehyde, aniline, dimethylphenylsilane, and mesitylene, containing the same amounts as in initial loading, was added to the NMR tube and the mixture was heated to 100 °C for 24 h. This procedure was repeated 4 times. The determination of the <sup>1</sup>H NMR yields was based on the relative integral of the benzylic protons of BnNHR and the methyl signal of mesitylene ( $\delta$  = 2.26 ppm).



7.5 10.0 9.5 9.0 8.5 8.0 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 0.0 **Figure S32.** <sup>1</sup>H NMR (CD<sub>3</sub>CN) spectra of crude reaction mixture of recycling experiment: t = 24 h. a) first addition, b) 24 h at 100 °C, c) after second addition, d) additional 24 h at 100 °C, e) after third addition, f) additional 24 h at 100 °C, q) after fourth addition, h) additional 24 h at 100 °C, i) additional 72 h at 100 °C

#### 4.5 Attempted reductive amination benzaldehyde / t-butylamine



A J. Young NMR tube was loaded with a solution of the **[7][OTf]**<sub>3</sub> (14mg, 0.012 mmol, 0.05 eq.) in MeCN (0.5 mL), followed by the addition of benzaldehyde (25  $\mu$ L, 0.241 mmol, 1.00 eq.), *t*-butylamine (31  $\mu$ L, 0.289 mmol, 1.20 eq.), and dimethylphenylsilane (45  $\mu$ L, 0.289 mmol, 1.20 eq.). The J. Young NMR tube was then sealed and the initial reaction mixture was monitored by multinuclear NMR spectroscopy, revealing no catalyst decomposition. Thus, the J. Young NMR tube was heated up at 100 °C for 18 h and then the reaction mixture was monitored again by multinuclear NMR spectroscopy. Upon heating, minimal imine reduction and catalyst decomposition were observed, with the corresponding triphosphine trioxide present among other unidentified products.<sup>13</sup>



**Figure S33.** In situ  ${}^{1}H/{}^{3}P{}^{1}H{}/{}^{19}F$  NMR spectra of the attempted reductive amination of PhCHO with *t*BuNH<sub>2</sub> using **[7][OTf]**<sub>3</sub> (15 mol%). Blue (after 5 min), red (after 18 h at 100 °C).

#### 4.6 N-benzylidene-aniline hydrosilylation experiment



In a glovebox under nitrogen atmosphere, a J. Young NMR tube was loaded with [7][OTf]<sub>3</sub> (5.5 mg, 0.005 mmol, 0.05 eq.) and *N*-benzylidene aniline (18.0 mg, 0.098 mmol, 1.00 eq.) in anhydrous MeCN (0.5 mL), followed by the addition of dimethylphenylsilane (19  $\mu$ L, 0.118 mmol, 1.20 eq.) and mesitylene as internal standard (10  $\mu$ L, 0.072 mmol, 0.73 eq.). The J. Young NMR tube was then sealed and the initial reaction mixture was monitored by multinuclear NMR spectroscopy. Thus, the J. Young NMR tube was heated up at 100 °C for 5 h and then the reaction mixture was monitored again by multinuclear NMR spectroscopy. Upon heating, no catalyst decomposition was observed and some imine (~20%) had reacted, with BnN(Ph)SiMe<sub>2</sub>Ph identified in the reaction mixture ( $\delta^{1}$ H = 4.64 ppm,  $\delta^{29}$ Si = -1.04 ppm). GC-MS analysis of a small aliquot confirmed the formation of BnN(Ph)SiMe<sub>2</sub>Ph (R<sub>t</sub> = 20.24 min: m/z 317.1 [M]<sup>+</sup>, 91.0 [Bn]<sup>+</sup>), along with some Bn<sub>2</sub>NPh (R<sub>t</sub> = 20.75 min: m/z 273.1 [M]<sup>+</sup>, 91.0 [Bn]<sup>+</sup>) and BnNHPh (from hydrolysis during the GC-Ms analysis). The data were in agreement with those reported in the literature.<sup>3</sup>



**Figure S34.** In situ  ${}^{1}$ H/ ${}^{29}$ Si NMR spectra of the hydrosilylation of N-benzylideneaniline with Me<sub>2</sub>PhSiH using **[7][OTf]**<sub>3</sub> (15 mol%). Blue (after 5 min), red (after 5 h at 100 °C).

#### 4.7 Reductive amination in the presence of PMes<sub>3</sub>

A NMR tube was loaded with a solution of the catalyst in MeCN (0.5 mL), followed by the addition of aldehyde (25  $\mu$ L, 0.241 mmol, 1.00 eq), aniline (26  $\mu$ L, 0.289 mmol, 1.20 eq), dimethylphenylsilane (45  $\mu$ L, 0.289 mmol, 1.20 eq.), mesitylene as internal standard (25  $\mu$ L, 0.179 mmol, 0.74 eq.) and tris(2,4,6-trimethylphenyl)phosphine (PMes<sub>3</sub>, 5 mol%). The reaction mixture was heated to 100 °C and monitored by multinuclear NMR spectroscopy. The determination of the <sup>1</sup>H NMR yields was based on the relative integral of the benzylic protons of BnNHR and the methyl signal of mesitylene ( $\delta$  = 2.26 ppm).



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 0.0 -0.5 **Figure S35.** <sup>1</sup>H NMR (CD<sub>3</sub>CN) spectra of crude reaction mixture. Bottom (after 5 min), middle (after 5 h at 100 °C), top (after 24 h at 100 °C)



<sup>70</sup> 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -5**Figure S36.** <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>CN) spectra of crude reaction mixture. Bottom (after 5 min), middle (after 5 h at 100 °C), top (after 24 h at 100 °C)

### 5. Gutmann-Beckett tests

[Ph<sub>3</sub>PMe][OTf] (13 mg, 0.03 mmol) was dissolved in CD<sub>3</sub>CN and then added to a separate vial containing Et<sub>3</sub>PO (4 mg, 0.03 mmol). The solution was then transferred to a NMR tube and monitored by  ${}^{31}P{}^{1}H$  NMR spectroscopy (free Et<sub>3</sub>PO in CD<sub>3</sub>CN = 51.05 ppm).



**Figure S37.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum after 1 h at ambient temperature.

[Ph<sub>3</sub>Me][OTf] (95 mg, 0.22 mmol) was dissolved in CD<sub>3</sub>CN and then added to a separate vial containing Et<sub>3</sub>PO (10 mg, 0.07 mmol). The solution was then transferred to a NMR tube and monitored by  ${}^{31}P{}^{1}H{}$  NMR spectroscopy.



Figure S38. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum after 1 h at ambient temperature.

Compound **[7][OTf]**<sub>3</sub> (44 mg, 0.04 mmol) was dissolved in CD<sub>3</sub>CN and then added to a separate vial containing Et<sub>3</sub>PO (6 mg, 0.04 mmol). The solution was then transferred to a NMR tube and monitored by  ${}^{31}P{}^{1}H$  NMR spectroscopy.



Figure S39. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum after 1 h at ambient temperature.

# 6. Computational data

Calculations were performed using the Gaussian09<sup>14</sup> suite of programmes. Structures were optimised at the M06-2X/6-311G(d,p) level with PCM(Dichloromethane) solvation.<sup>15</sup> In all cases, structures were confirmed as minima by frequency analysis and by the absence of imaginary frequencies. Full Cartesian coordinates for the optimised geometries are provided below.

DFT calculations, performed at the M06-2X/6-311G(d,p) level of theory with  $CH_2Cl_2$  solvation (polarizable continuum model) revealed a lower energy LUMO for **[7]**<sup>3+</sup> relative to that of  $[Ph_3PMe]^+$  (-1.986 eV and -1.116 eV, respectively). While the LUMOs are delocalized, there is a prominent contribution from the phosphorus atom (Figure S40).



**Figure S40.** LUMOs of [7]<sup>3+</sup> (a) and  $[Ph_3PMe]^+$  (b) (Isovalue = 0.04). Hydrogen atoms have been omitted for clarity.

# Compound [7]<sup>3+</sup>



| С | 0.903100  | 2.106500  | 0.496700  |
|---|-----------|-----------|-----------|
| Н | 0.385700  | 2.322600  | 1.437700  |
| Н | 1.358400  | 1.122500  | 0.631900  |
| С | -0.096700 | 2.056100  | -0.688400 |
| С | 0.550500  | 1.400600  | -1.916000 |
| Н | -0.204500 | 1.030300  | -2.612200 |
| Н | 1.188300  | 2.099300  | -2.460500 |
| Н | 1.173500  | 0.552800  | -1.624300 |
| С | -1.358700 | 1.269300  | -0.241200 |
| Н | -1.899000 | 1.829200  | 0.530800  |
| Н | -2.035800 | 1.184800  | -1.096400 |
| С | -0.529700 | 3.513300  | -0.983000 |
| Н | 0.354700  | 4.086400  | -1.276500 |
| Н | -0.915400 | 3.984000  | -0.072400 |
| Ρ | -1.274900 | -0.445600 | 0.417800  |
| Ρ | -1.750700 | 3.960200  | -2.272900 |
| Ρ | 2.363600  | 3.210100  | 0.535900  |
| С | -0.855300 | -1.628900 | -0.875000 |
| Н | -1.622100 | -1.561400 | -1.647900 |
| Н | 0.123400  | -1.432200 | -1.309000 |
| Н | -0.877400 | -2.628600 | -0.438100 |
| С | 3.371600  | 3.056300  | -0.954200 |
| Н | 3.518100  | 2.001700  | -1.188500 |
| Н | 2.891900  | 3.549800  | -1.799500 |
| Н | 4.344000  | 3.513900  | -0.767400 |
| С | -0.114600 | -0.551400 | 1.785100  |
| С | -0.383000 | 0.201900  | 2.932700  |
| С | 1.084400  | -1.256300 | 1.659200  |
| С | 0.571700  | 0.282300  | 3.936400  |
| Н | -1.328100 | 0.723600  | 3.043200  |
| С | 2.031100  | -1.172500 | 2.674800  |
| Н | 1.289600  | -1.859500 | 0.782600  |
| С | 1.782100  | -0.393500 | 3.800200  |
| Н | 0.370400  | 0.867500  | 4.824800  |
| Н | 2.964200  | -1.714300 | 2.584300  |

| Н         | 2.530000  | -0.319700 | 4.580300  |
|-----------|-----------|-----------|-----------|
| С         | -2.930400 | -0.801000 | 1.033600  |
| С         | -3.072700 | -1.731400 | 2.066900  |
| С         | -4.053500 | -0.205200 | 0.453500  |
| С         | -4.344200 | -2.058000 | 2.520400  |
| Н         | -2.202200 | -2.192600 | 2.519900  |
| С         | -5.318900 | -0.536000 | 0.919700  |
| Н         | -3.962000 | 0.510800  | -0.355200 |
| С         | -5.463600 | -1.459700 | 1.950400  |
| Н         | -4.458700 | -2.777700 | 3.320800  |
| Н         | -6.191200 | -0.071900 | 0.476300  |
| Н         | -6.452700 | -1.714100 | 2.310500  |
| С         | 3.316100  | 2.609800  | 1.946200  |
| С         | 3.188300  | 3.217500  | 3.196700  |
| С         | 4.152000  | 1.501200  | 1.776600  |
| С         | 3.900100  | 2.711200  | 4.277600  |
| Н         | 2.560200  | 4.090200  | 3.330500  |
| С         | 4.868100  | 1.013200  | 2.861200  |
| Н         | 4.257600  | 1.017800  | 0.812000  |
| С         | 4.741600  | 1.616800  | 4.109000  |
| Н         | 3.806800  | 3.183900  | 5.247100  |
| Н         | 5.526800  | 0.163900  | 2.729500  |
| Н         | 5.304400  | 1.234700  | 4.952000  |
| С         | 1.879900  | 4.930000  | 0.776200  |
| С         | 0.832000  | 5.251000  | 1.648900  |
| С         | 2.576000  | 5.943300  | 0.110300  |
| С         | 0.483500  | 6.580000  | 1.845500  |
| Н         | 0.287200  | 4.479600  | 2.182400  |
| С         | 2.216700  | 7.271800  | 0.314100  |
| Н         | 3.390300  | 5.713100  | -0.565500 |
| С         | 1.175700  | 7.588800  | 1.179400  |
| Н         | -0.326100 | 6.827400  | 2.519900  |
| н         | 2.755600  | 8.055700  | -0.202700 |
| H         | 0.902100  | 8.624700  | 1.338500  |
| C         | -1.948400 | 5.750000  | -2.126300 |
| C         | -3.143900 | 6.315900  | -2.581400 |
|           | -0.922600 | 6.563800  | -1.634900 |
|           | -3.307000 | 7.694200  | -2.546000 |
| П         | -3.946700 | 5.688900  | -2.953100 |
|           | -1.100000 | 7.941400  | -1.603200 |
|           | 0.012200  | 0.152600  | -1.209000 |
|           | -2.207000 | 0.000200  | -2.000900 |
|           | -4.232700 | 8,572200  | -2.097500 |
|           | -0.300200 | 0.572200  | 2 021000  |
| $\hat{c}$ | -2.410900 | 3 200000  | -2.031900 |
| c         | -2.001200 | 3 552300  | -0 858000 |
| Ċ.        | -3 880000 | 2 303700  | -2 933800 |
| č         | -5 347000 | 3 004400  | -0 654400 |
| Ĥ         | -3.690700 | 4.269000  | -0.147800 |
| -         |           |           |           |

| С | -5.153500 | 1.761200 | -2.718100 |
|---|-----------|----------|-----------|
| Н | -3.341600 | 2.035800 | -3.828900 |
| С | -5.880500 | 2.115400 | -1.586900 |
| Н | -5.917000 | 3.279800 | 0.223900  |
| Н | -5.570900 | 1.073500 | -3.442400 |
| Н | -6.870400 | 1.702500 | -1.433600 |
| С | -1.150100 | 3.568000 | -3.928200 |
| Н | -0.177100 | 4.042300 | -4.061200 |
| Н | -1.058300 | 2.495100 | -4.086300 |
| Н | -1.853700 | 3.987500 | -4.650200 |
|   |           |          |           |

Total Energy: -2728.81079116 Hartrees

# Compound [Ph3PMe]+



| Ρ | 0.447900  | 0.720900  | -0.153900 |
|---|-----------|-----------|-----------|
| С | 0.990000  | -0.996500 | -0.135400 |
| С | 0.070700  | -2.025800 | 0.068500  |
| С | 2.350700  | -1.277100 | -0.302400 |
| С | 0.517000  | -3.342800 | 0.098700  |
| Н | -0.982000 | -1.806800 | 0.202900  |
| С | 2.783700  | -2.594800 | -0.270100 |
| Н | 3.070800  | -0.478800 | -0.446200 |
| С | 1.867200  | -3.625400 | -0.071300 |
| Н | -0.193200 | -4.144700 | 0.255000  |
| Н | 3.835300  | -2.817000 | -0.399600 |
| Н | 2.210600  | -4.652400 | -0.047800 |
| С | -1.350800 | 0.788100  | -0.137200 |
| С | -2.026200 | 1.112400  | 1.040700  |
| С | -2.058900 | 0.466700  | -1.300200 |
| С | -3.416600 | 1.114700  | 1.051200  |
| С | -3.446500 | 0.472800  | -1.277200 |
| С | -4.122800 | 0.795800  | -0.103200 |
| С | 1.092600  | 1.563300  | 1.299900  |
| С | 1.536800  | 0.825400  | 2.398500  |
| С | 1.094500  | 2.961300  | 1.331900  |
| С | 1.987700  | 1.493500  | 3.531400  |
| Н | 1.533800  | -0.258100 | 2.372400  |
| С | 1.548300  | 3.617000  | 2.467800  |
| С | 1.993900  | 2.883500  | 3.564600  |
| Н | 2.333900  | 0.925700  | 4.385700  |
| Н | 1.554500  | 4.699100  | 2.496300  |
| Н | 2.347600  | 3.399800  | 4.448700  |
| С | 1.070700  | 1.527000  | -1.645000 |
| Н | 0.744800  | 3.538900  | 0.483600  |
| Н | -1.539500 | 0.207700  | -2.216000 |
| Н | -3.999300 | 0.226000  | -2.174700 |
| Н | -5.205700 | 0.799400  | -0.090500 |
| Н | -3.945300 | 1.367200  | 1.961500  |
| Н | -1.476100 | 1.364700  | 1.940000  |
| Н | 0.671700  | 2.539400  | -1.706100 |
| Н | 2.159700  | 1.561500  | -1.607200 |
| Н | 0.756600  | 0.957500  | -2.519800 |

# Total Energy: -1075.91087413 Hartrees

# 7. Crystallographic analysis of $[6][OTf]_3$ and $[7][OTf]_3$

| Identification code               | [6][OTf] <sub>3</sub>                          |   |  |
|-----------------------------------|--|---|--|
| Empirical formula                 | $C_{40}  H_{43}  F_9  O_{10}  P_3  S_3$        | $C_{40} H_{43} F_9 O_{10} P_3 S_3$                |  |
| Formula weight                    | 1043.83  | 1043.83   |  |
| Temperature                       | 150(2) K                                       |   |  |
| Wavelength                        | 0.71073 Å                                      |   |  |
| Crystal system                    | Triclinic                                      |   |  |
| Space group                       | P-1  |   |  |
| Unit cell dimensions              | a = 13.7550(19) Å                              | $\alpha = 87.306(6)^{\circ}.$                     |  |
|                                   | b = 13.9164(17) Å                              | $\beta = 60.676(6)^{\circ}.$                      |  |
|                                   | c = 13.9779(19) Å                              | γ = 88.417(6)°.                                   |  |
| Volume                            | 2330.2(5) Å <sup>3</sup>                       |   |  |
| Z                                 | 2  |   |  |
| Density (calculated)              | 1.488 Mg/m <sup>3</sup>                        | 1.488 Mg/m <sup>3</sup>                           |  |
| Absorption coefficient            | 0.352 mm <sup>-1</sup>                         | 0.352 mm <sup>-1</sup>                            |  |
| F(000)                            | 1074   | 1074  |  |
| Crystal size                      | 0.140 x 0.070 x 0.070 i                        | 0.140 x 0.070 x 0.070 mm <sup>3</sup>             |  |
| Theta range for data collection   | 2.181 to 26.372°.                              | 2.181 to 26.372°.                                 |  |
| Index ranges                      | -17<=h<=17, -17<=k<=                           | -17<=h<=17, -17<=k<=17, -17<=l<=17                |  |
| Reflections collected             | 37786  | 37786   |  |
| Independent reflections           | 9496 [R(int) = 0.0499]                         | 9496 [R(int) = 0.0499]                            |  |
| Completeness to theta = 25.242°   | 99.6 %   | 99.6 %  |  |
| Absorption correction             | None   | None  |  |
| Refinement method                 | Full-matrix least-square                       | Full-matrix least-squares on F <sup>2</sup>       |  |
| Data / restraints / parameters    | 9496 / 5 / 595                                 | 9496 / 5 / 595                                    |  |
| Goodness-of-fit on F <sup>2</sup> | 1.040  | 1.040   |  |
| Final R indices [I>2sigma(I)]     | R <sub>1</sub> = 0.0543, wR <sub>2</sub> = 0.1 | R <sub>1</sub> = 0.0543, wR <sub>2</sub> = 0.1368 |  |
| R indices (all data)              | R <sub>1</sub> = 0.0889, wR <sub>2</sub> = 0.1 | R <sub>1</sub> = 0.0889, wR <sub>2</sub> = 0.1534 |  |
| Extinction coefficient            | n/a  | n/a   |  |
| Largest diff. peak and hole       | 0.624 and -0.796 e.Å <sup>-3</sup>             | 0.624 and -0.796 e.Å <sup>-3</sup>                |  |

#### Table S1. Crystal data and structure refinement for [6][OTf]<sub>3</sub>.

| Identification code               | [7][OTf] <sub>3</sub>                             |                               |  |
|-----------------------------------|---|-------------------------------|--|
| Empirical formula                 | $C_{50} \ H_{55} \ F_9 \ N \ O_{10} \ P_3 \ S_3$  |                               |  |
| Formula weight                    | 1190.04   |                               |  |
| Temperature                       | 150(2) K  |                               |  |
| Wavelength                        | 0.71073 Å   |                               |  |
| Crystal system                    | Triclinic   |                               |  |
| Space group                       | P-1   |                               |  |
| Unit cell dimensions              | a = 12.7151(9) Å                                  | $\alpha = 77.042(2)^{\circ}.$ |  |
|                                   | b = 14.6939(11) Å                                 | β = 81.897(2)°.               |  |
|                                   | c = 15.3772(12) Å                                 | γ = 72.530(3)°.               |  |
| Volume                            | 2662.3(3) Å <sup>3</sup>                          |                               |  |
| Z                                 | 2   |                               |  |
| Density (calculated)              | 1.485 Mg/m <sup>3</sup>                           |                               |  |
| Absorption coefficient            | 0.319 mm <sup>-1</sup>                            |                               |  |
| F(000)                            | 1232  |                               |  |
| Crystal size                      | 0.160 x 0.100 x 0.060 mm <sup>3</sup>             |                               |  |
| Theta range for data collection   | 1.684 to 27.568°.                                 |                               |  |
| Index ranges                      | -16<=h<=16, -19<=k<=19, -19<=l<=19                |                               |  |
| Reflections collected             | 44853   |                               |  |
| Independent reflections           | 12195 [R(int) = 0.0335]                           |                               |  |
| Completeness to theta = 25.242°   | 99.8 %  |                               |  |
| Absorption correction             | None  |                               |  |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>       |                               |  |
| Data / restraints / parameters    | 12195 / 0 / 688                                   |                               |  |
| Goodness-of-fit on F <sup>2</sup> | 1.035   |                               |  |
| Final R indices [I>2sigma(I)]     | R <sub>1</sub> = 0.0485, wR <sub>2</sub> = 0.1235 |                               |  |
| R indices (all data)              | R <sub>1</sub> = 0.0692, wR <sub>2</sub> = 0.1353 |                               |  |
| Extinction coefficient            | n/a   |                               |  |
| Largest diff. peak and hole       | 2.447 and -0.852 e.Å <sup>-3</sup>                |                               |  |

#### Table S2. Crystal data and structure refinement for [7][OTf]<sub>3</sub>,

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