SUPPORTING INFORMATION

Reactions of Phosphine Oxides with Bromophosphoranimines; Synthesis and Unusual Rearrangements of O-Donor Stabilized Phosphoranimine Cations.

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Experimental

General. All reactions and manipulations were carried out under an atmosphere of purified nitrogen or argon (BOC) using standard Schlenk techniques or an inert-atmosphere glovebox (M-Braun). Hexanes and Et_2O were dried and collected using a Grubbs-type solvent purification system using filtration through an alumina column impregnated with deoxygenated catalysts and CH_2Cl_2, $CDCl_3$, CD_2Cl_2, dichloroethane and 1,2-dichlorobenzene, were dried at reflux over CaH_2. ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$, ^{29}Si and ^{19}F NMR spectra were obtained on a JOEL Lambda 300 and JEOL Eclipse 300 spectrometers (300, 75.4, 121, 59.6 and 282 MHz, respectively) and on a Varian 400 (400, 100, 161, 79.5 and 376 MHz, respectively) and were referenced either to protic impurities in the solvent (^{1}H) or externally to $SiMe_4$ ($^{13}C\{^{1}H\}$, ^{29}Si), 85% H_3PO_4 ($^{31}P\{^{1}H\}$) or CCl_3F (^{19}F) in $CDCl_3$. ^{31}P NMR integrations are approximate and are estimated to be accurate to within ca. ±10% in the case of identical coordination numbers (e.g. R_4P^+ and $R_3P{=}E$) and within ±20% in the case of mixed coordination numbers (e.g. $R_3P{=}E$ and R_3P). Elemental analyses were carried out by the Laboratory for Microanalysis, University of Bristol, however completely satisfactory results could often not be obtained, with measured values for carbon consistently lower than predicted, likely due to incomplete combustion (as previously reported for similar compounds).[1] Compounds **1e**, AgOTf, $AgPF_6$, DMAP, H_2NSiPh_3, $[Ph_4P]Br$, $^{i}Pr_3P$, $^{t}Bu_3P$ and $Ph_3P{=}NSiMe_3$ were purchased from commercial sources and used as received. **1e** was purified by sublimation and $Ph_3P{=}NSiMe_3$ was recrystallized from hexanes and dried under reduced pressure before use, phosphoranimines **2a-c**,[2] $AgBPh_4$,[3] Me_3P,[4] Et_3P[5] were synthesized by known procedures.

X-ray diffraction experiments on [**4a**]OTf, **5**, [**8**]OTf, [**3d**]OTf, [**3e**]OTf, [**4d**]OTf) and [**4a**]PF_6 were carried out at 100K on a Bruker APEX II diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Data collections were performed using a CCD area detector from a single crystal mounted on a glass fibre. Intensities were integrated[6] from several series of exposures measuring 0.5° in ω or ϕ. Absorption corrections were based on equivalent reflections using SADABS or TWINABS.[7] The structures were solved using SHELXS and refined against all F_o^2 data with hydrogen atoms riding in calculated positions using SHELXL.[8] Crystal structure and refinement data are given in Tables 1 to 4.

The structures of [**4a**]OTf, **5** and [**8**]OTf were non-merohedral twins containing 2, 3 and 2 domains respectively. These were indexed independently and integrated simultaneously using the APEX II software.[9] Refinement proceeded smoothly to give the structures shown to give ratios of 0.57:0.43, 0.64:0.24:0.10 and 0.52:0.48 respectively for the different domains.

For structures where potential ambiguity exists in identifying P and Si ([**4a**]OTf and [**4a**]PF_6), both options were refined. The difference in R_1 was low in each case when the elements were swapped; the one with the lower R_1 was retained in each case.

In all reactions below species denoted as A and B have been assigned as the salts [**3**]$^+$ (or [**7**]$^+$) and [**4**]$^+$ (or [**8**]$^+$), respectively, C and D are unidentified, but have analogues observed in most reactions between **1** and **2** (or **5**) (See Figure 1 in the main text).

Typical Synthesis of Phosphine Oxides (1a–d). Compounds **1a–d** have all been previously reported,[10–13] however the following provides a general synthesis. CAUTION: Dry mixtures of hydrogen peroxide and organic material are potentially explosive, do not heat or undertake further manipulations of the dry product until complete decomposition of H_2O_2 (δ_H = 9.5) has been confirmed by ^{1}H NMR. To a rapidly stirred solution of Et_3P (16.0 g, 136 mmol) and I_2 (~10 mg) in CH_2Cl_2 (50 mL) cooled to 0 °C was added H_2O_2 (20.6 g, 30% in H_2O, 203 mmol) over 1 h. The solution was then warmed to room temperature and stirred for a further 1 h, followed by addition of NaI (~10 mg) and refluxed for 3 d to decompose any remaining H_2O_2. The solution was then reduced to dryness, analyzed by ^{1}H NMR to confirm complete decomposition of H_2O_2, redissolved in CH_2Cl_2, dried over $MgSO_4$, and again reduced to dryness to give a crude, pale yellow solid which was sublimed at 80 °C under reduced pressure to give Et_3P=O as a white crystalline solid (13.8 g, 76 %). ^{1}H NMR ($CDCl_3$): δ = 1.13 (dt, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 7.7 Hz, 9H, CH_3) and 1.68 ppm (dq, $^2J_{PH}$ = 11.8, Hz, $^3J_{HH}$ = 7.7 Hz, 6H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): 5.8 (d, $^2J_{PC}$ = 4.8 Hz, CH_3) and 19.7 ppm. ^{31}P{^{1}H} ($CDCl_3$): 53.2 ppm (s). **1d** was isolated as a crude liquid which was purified by distillation at 80 °C under reduced pressure. In all cases purity was confirmed by ^{1}H and ^{31}P{^{1}H} NMR.

Reaction of 1a with 2a. To 0.75 mL of a 0.27 M solution of **1a** (0.2 mmol) in CH_2Cl_2 was added 0.75 mL of a 0.27 M solution of **2a** (0.2 mmol) in CH_2Cl_2 and the mixture stirred. Monitoring by ^{31}P{^{1}H} NMR after 10 min revealed consumption of starting materials to give 4 sets of signals: A (72%): δ = 35.7 (d, J_{PP} = 28.8 Hz), 95.0 ppm (d, J_{PP} = 28.8 Hz), B (15%): δ = 25.0 (d, J_{PP} = 20.9 Hz), 40.9 ppm (d, J_{PP} = 20.9 Hz), C (2%): δ = 28.4 (d, J_{PP} = 15.1 Hz), 29.0 (d, J_{PP} = 32.5 Hz), 46.8 ppm (dd, J_{PP} = 32.5, 15.1 Hz), D (3%): 30.8 (dd, J_{PP} = 10.6, 6.7 Hz), 51.8 ppm (dd, J_{PP} = 10.6, 6.7 Hz). After 5 h, signals for A and D were no longer observed, with 86% conversion to B, increasing to 96% conversion to B after 2 d. Attempts to isolate crystalline material after 9 d proved unsuccessful, likely due to slight decomposition to an insoluble white solid which was present in very small quantities from the reaction and on redissolution of any isolated solid.

Reaction of 1a with 2a in the presence of AgOTf; Synthesis of [Me_3P=N−PMe_2−$OSiMe_3$]OTf ([4a]OTf). In the absence of light, a solution of **1a** (92 mg, 1.0 mmol) in CH_2Cl_2 (4 mL) was added to AgOTf (257 mg, 1.0 mmol), immediately followed by **2a** (228 mg, 1.0 mmol) in CH_2Cl_2 (1 mL) and the reaction stirred for 15 min to give an off-white precipitate (AgBr), and allowed to settle. After 50 min, ^{31}P{^{1}H} NMR of the reaction solution revealed formation of 4 sets of signals: A (9%): δ = 37.7 (d, J_{PP} = 28.8 Hz), 94.2 ppm (d, J_{PP} = 28.8 Hz), B (78%): δ = 25.3 (d, J_{PP} = 17.2 Hz), 40.0 ppm (d, J_{PP} = 17.2 Hz), C (3%): δ = 28.6 (d, J_{PP} = 11.4 Hz), 30.5 (d, J_{PP} = 31 Hz), 45.5 ppm (dd, J_{PP} = 31, 11.4 Hz), D: (8%): δ = 30.8 (dd, J_{PP} = 11.7, 7.4 Hz), 51.3 [**4a**]$^{+}$ ppm (dd, J_{PP} = 11.7, 7.4 Hz). The solution was filtered, then stirred and monitored by ^{31}P{^{1}H} NMR, showing complete consumption of A after 6 h and only signals for B after 2 d. The solvent was then removed under reduced pressure to give a white solid, which was recrystallized from hexane (3 mL) diffusing into a solution of the solid in CH_2Cl_2 (1 mL) at −40 °C to give [**4a**]OTf as a white crystalline solid (308 mg, 79%). ^{1}H NMR ($CDCl_3$): δ = 0.29 (s, 9H, $SiMe_3$), 1.74 (d, $^{2}J_{PH}$ = 14.2 Hz, 6H, PMe_2), 1.78 ppm (d, $^{2}J_{PH}$ = 13.5 Hz, 9H, PMe_3). ^{13}C{^{1}H} NMR ($CDCl_3$):

1.1 (d, $^4J_{PC}$ = 1.56 Hz, $SiMe_3$), 17.1 (dd, $^1J_{PC}$ = 70.8, $^3J_{PC}$ = 2.3, Me_3P), 19.1 (dd, $^1J_{PC}$ = 95.0 Hz, $^3J_{PC}$ = 1.6 Hz, Me_2P) 120.7 ppm (q, $^1J_{FC}$=320.8 Hz, CF_3). $^{31}P\{^1H\}$ ($CDCl_3$): 24.2 (d, $^2J_{PP}$ = 20.4 Hz, $^1J_{CP}$ = 70.9 Hz, Me_3P), 40.0 ppm (d, $^2J_{PP}$ = 20.4 Hz, $^1J_{CP}$ = 94.9 Hz, $^2J_{SiP}$ = 10.1 Hz, , Me_2P). ^{19}F NMR ($CDCl_3$): 78.3 ppm (s, OTf). $^{29}Si\{^1H\}$ ($CDCl_3$): 24.9 ppm (d, $^2J_{PSi}$ = 10.1 Hz). Anal. Calcd for $C_9H_{24}F_3NO_4P_2SSi$ (389.38): %C, 27.76; %H, 6.21; %N, 3.60 Found: %C, 26.86; %H, 6.02; %N, 3.81

Reaction of 1a with 2b. To a solution of **1a** (92.1 mg, 1.0 mmol) in CH_2Cl_2 (0.75 mL) was added a solution of **2b** (290 mg, 1.0 mmol) in CH_2Cl_2 (2.75 mL) and the solution stirred. Monitoring by $^{31}P\{^1H\}$ NMR after 50 min revealed consumption of starting materials to give 4 sets of signals: A (65%): δ = 24.3 (d, J_{PP} = 30.0 Hz), 95.7 ppm (d, J_{PP} = 30.0 Hz), B (8%): δ = 28.6 (d, J_{PP} = 11.5 Hz), 29.2 ppm (d, J_{PP} = 11.5 Hz), C (12%): δ = 18.1 (d, J_{PP} = 34.9 Hz), 31.0 (d, J_{PP} = 7.8 Hz), 32.2 ppm (dd, J_{PP} = 34.9, 7.8 Hz). C□ (13%): δ = 19.4 (d, J_{PP} = 33.8 Hz), 31.2 (d, J_{PP} = 9.4 Hz), 31.8 ppm (dd, J_{PP} = 33.8, 9.4 Hz). After 2 d signals for A were no longer observed, with 87 % conversion to B, increasing to 91% after 8 d.

Reaction of 1a with 2c. To 0.75 mL of a 0.27 M solution of **2c** (0.2 mmol) in CH_2Cl_2 was added 0.75 mL of a 0.27 M solution of **1a** (0.2 mmol) in CH_2Cl_2 and the mixture stirred. $^{31}P\{^1H\}$ NMR after 14 h revealed partial conversion (67%) to a new species appearing as two broad doublet resonances: δ = 1.6 (d, J_{PP} = 24.5 Hz), 26.4 ppm (d, J_{PP} = 24.5 Hz), along with two others at δ = −17.5 (br, 13%), 83.3 (br, 10%). $^{31}P\{^1H\}$ NMR after 38 h showed 93% conversion to two very broad resonances δ = 1.3, 29.9 ppm. Pure material could not be isolated due to the product forming an impure oil on precipitation or removal of the solvent under reduced pressure.

Reaction of 1a with 2c in the presence of AgOTf. To 0.75 mL of a 0.27 M solution of **2c** (0.2 mmol) in CH_2Cl_2 was added 0.75 mL of a 0.27 M solution of **1a** (0.2 mmol) in CH_2Cl_2 and the mixture quickly added to AgOTf (51 mg, 0.27 mmol) in the absence of light and the mixture stirred. After 6 h, $^{31}P\{^1H\}$ NMR of the reaction solution revealed formation of three sets of resonances: A (44%): δ = −26.3 (d, J_{PP} = 30.8 Hz), 103.9 ppm (d, J_{PP} = 30.8 Hz) (both resonances showed a considerable degree of broadening), B (34%): δ = –0.7 (d, J_{PP} = 23.0 Hz), 28.3 ppm (d, J_{PP} = 23.0 Hz) along with a broad resonance at δ = 82.4 ppm (11%) and unreacted **2c**. After 3 d, 95% of the $^{31}P\{^{1}H\}$ NMR intensity was attributed to a species at δ = –10.3 (d, J_{PP} = 26.1 Hz), 36.0 ppm (d, J_{PP} = 26.1 Hz). Pure material could not be isolated due to the product forming an impure oil on precipitation or removal of the solvent under reduced pressure.

Synthesis of $BrMe_2P{=}NSiPh_3$ (5). To a stirred solution of H_2NSiPh_3 (10.1 g, 37 mmol) in Et_2O (200 mL) at –5 °C was added ^{n}BuLi solution (23 mL of a 1.6 M solution in hexanes, 37 mmol) dropwise over 10 min and the solution stirred at 25 °C for 1 h. The reaction mixture was then cooled to –5 °C before addition of $ClSiMe_3$ (4.67 mL, 37 mmol) dropwise over 5 min, and the reaction mixture stirred for 30 min at room temperature. The reaction mixture was then cooled to –5 °C before addition of further ^{n}BuLi solution (23 mL of a 1.6 M solution in hexanes, 37 mmol) dropwise over 10 min, and then stirred at room temperature for 30 min. This was followed by cooling to –5 °C before the dropwise addition of PCl_3 (3.2 mL, 37 mmol) over 5 min and warming to room temperature for 1 h. The reaction mixture was then cooled to –5 °C, followed by dropwise addition of MeLi solution (46 mL of a 1.6 M solution in hexanes, 74 mmol) over 20 min and the solution stirred for 1 h. The solvent was then removed from the reaction mixture under reduced pressure and the resultant residues redissolved in CH_2Cl_2 (250 mL), filtered through Celite and the solution reduced to dryness under reduced pressure. The resultant solid was then sublimed at 110 °C under vacuum, reprecipitated from hexane and re-sublimed at 80 °C under vacuum to yield an impure white solid: $Me_2P{-}N(SiMe_3)(SiPh_3)$ (**6**) (5.1 g, 13 mmol, 34%). The crude solid was then dissolved in CH_2Cl_2 (100 mL) and cooled to –5 °C in a foil-wrapped flask to prevent exposure to light, followed by dropwise addition of Br_2 (0.70 mL, 2.2 g, 13 mmol) in CH_2Cl_2 (10 mL) over 30 min. The solvent and $BrSiMe_3$ were removed under reduced pressure to give a yellow solid. $BrMe_2P{=}NSiPh_3$ (**5**) (1.9 g, 12 %) was then isolated as a white crystalline solid from hexane diffusing into a saturated CH_2Cl_2 solution of the crude product. ^{1}H NMR ($CDCl_3$): δ = 2.05 (d, $^{2}J_{PH}$ = 13.63 Hz, 6H, PMe_2), 7.3 (m, 9H, $SiPh_3$), 7.7 ppm (m, 6H, $SiPh_3$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): 28.7 (d, $^{1}J_{PC}$ = 80.2 Hz,

PMe_2), 127.5 (s, *m*-C), 127.5 (s, *p*-C), 127.5 (s, *o*-C), 127.5 ppm (d, $^3J_{PC}$ = 5.5 Hz, *i*-C). $^{31}P\{^1H\}$ ($CDCl_3$): 12.0 ppm (s, d, $^1J_{CP}$ = 80.4 Hz, d, $^2J_{SiP}$ = 12.8 Hz). $^{29}Si\{^1H\}$ ($CDCl_3$): −26.5 ppm (d, $^2J_{PSi}$ = 13.1 Hz). Anal. Calcd for $C_{20}H_{21}BrNPSi$ (414.35): %C, 57.97; %H, 5.11; %N, 3.38; Found: %C, 59.73; %H, 5.54; %N, 3.77

Reaction of 1a with 5. To 0.75 mL of a 0.27 M solution of **1a** in CH_2Cl_2 was added 0.75 mL of a 0.27 M solution of **5** in CH_2Cl_2 and the mixture stirred. Monitoring by $^{31}P\{^1H\}$ NMR after 10 min revealed consumption of starting materials to give 4 sets of signals: A (20%): δ = 40.1 (d, J_{PP} = 33.5 Hz), 95.6 ppm (d, J_{PP} = 33.5 Hz), B (42%): δ = 25.4 (d, J_{PP} = 24.2 Hz), 42.5 ppm (d, J_{PP} = 24.2 Hz), C (38%): δ = 28.2 (d, J_{PP} = 20.4 Hz), 31.4 (d, J_{PP} = 35.9 Hz), 48.2 ppm (dd, J_{PP} = 31.4, 20.4 Hz), D (3%): 30.8 (dd, J_{PP} = 10.5, 6.8 Hz), 51.8 ppm (dd, J_{PP} = 10.5, 6.8 Hz). After 23 h, signals for A and D were no longer observed, with 93% conversion to B. Complete conversion to B was observed by $^{31}P\{^1H\}$ NMR after 9 d.

Reaction of 1a with 5 in the presence of AgOTf; Preparation of [Me_3P=N−PMe_2−$OSiPh_3$]OTf ([8]OTf). In the absence of light, a solution of **1a** (92 mg, 1.0 mmol) in CH_2Cl_2 (0.75 mL) was added to AgOTf (51 mg, 0.2 mmol), immediately followed by **5** (228 mg, 0.2 mmol). The reaction was then stirred for 15 h and allowed to settle for five min, after which $^{31}P\{^1H\}$ NMR of the reaction solution revealed formation of 3 sets of signals: A (6%): δ = 41.4 (d, J_{PP} = 32.8 Hz), 94.8 ppm (d, J_{PP} = 32.8 Hz), B (73%): δ = 25.5 (d, J_{PP} = 17.2 Hz), 41.3 ppm (d, J_{PP} = 17.2 Hz), C (21%): δ = 28.4 (d, J_{PP} = 16.3 Hz), 33.3 (d, J_{PP} = 36 Hz), 46.6 ppm (dd, J_{PP} = 36, 16.3 Hz). The solution was then filtered and stirred for a further 24 h after which $^{31}P\{^1H\}$ NMR showed only signals for B. The solvent was removed under reduced pressure and [**8**]$^+$ recrystallized from Et_2O diffusing into a filtered solution of the solid product in CH_2Cl_2 (0.8 mL) at −40 °C (73 mg, 65%). ^1H NMR ($CDCl_3$): δ = 1.52 (d, $^3J_{PH}$ = 13.5 Hz, 9H, Me_3P), 1.73 (d, $^2J_{PH}$ = 14.2 Hz, 6H, Me_2P), 7.5 ppm (m, 15H, Ph_3Si). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 17.0 (dd, $^1J_{PC}$ = 71.0, $^3J_{PC}$ = 2.2 Hz, PMe), 19.1 ppm (dd, $^1J_{PC}$ = 94.8, $^3J_{PC}$ = 1.6 Hz, PMe) 127−136 ppm (m, $SiPh_3$). $^{31}P\{^1H\}$ ($CDCl_3$): 25.3 (d, $^2J_{PP}$ = 22.4 Hz, Me_3P), 41.3 ppm (d, $^2J_{PP}$ = 22.4 Hz, Me_2P). ^{19}F NMR ($CDCl_3$):

δ = 78.3 ppm (s, OTf).

Reaction of 1b with 2a. To 0.75 mL of a 0.27 M solution of $^{t}Bu_3P{=}O$ in CH_2Cl_2 was added 0.75 mL of a 0.27 M solution of **2a** in CH_2Cl_2 and the mixture stirred. Monitoring by $^{31}P\{^{1}H\}$ NMR after 10 min revealed 2% consumption of starting materials to give a P-P coupled product: δ = 32.0 (d, J_{PP} = 66.3 Hz), 113.3 ppm (d, J_{PP} = 66.3 Hz). After stirring for 40 min conversion increased to 5%, with no further changes by $^{31}P\{^{1}H\}$ NMR after 23 h.

Reaction of 1b with 2a in the presence of 1 equiv. of AgOTf; Synthesis of [$^{t}Bu_3P{=}O{-}PMe_2{=}NSiMe_3$]OTf ([3d]OTf). To mixture of $^{t}Bu_3P{=}O$ (437 mg, 2.0 mmol), and AgOTf (514 mg, 2.0 mmol) was added a solution of **2a** (456 mg, 2.0 mmol) in CH_2Cl_2 (4 mL) dropwise and the solution stirred for 15 h then allowed to stand for 1 h. Analysis of the reaction mixture by $^{31}P\{^{1}H\}$ NMR showed complete conversion to a new species: δ = 32.3 (d, J_{PP} = 66.6 Hz), 113.4 ppm (d, J_{PP} = 66.6 Hz). The reaction mixture was then filtered and the solvent removed under reduced pressure to give a white solid (829 mg, 80%) crystals were grown from Et_2O diffusing into a saturated solution of the crude product in CH_2Cl_2 at −40 °C. ^{1}H NMR ($CDCl_3$) δ = 0.01 (s, d, $^{1}J_{CH}$ = 117.6 Hz, d, $^{2}J_{SiH}$ = 6.3 Hz, 9H, Me_3Si), 1.66 (d, $^{2}J_{PH}$ = 15.6 Hz, $^{1}J_{CH}$ = 117.6 Hz, 27H, $^{t}Bu_3P$), 1.87 ppm (d, $^{2}J_{PH}$ = 13.2 Hz, $^{1}J_{CH}$ = 172.2 Hz, 6H, Me_2P). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 3.04 (d, $^{3}J_{PC}$ = 3.1 Hz, Me_3Si), 21.85 (dd, $^{1}J_{PC}$ = 91.33, $^{3}J_{PC}$ = 1.51 Hz, Me_2P), 28.82 (d, $^{2}J_{PC}$ = 0.97 Hz, Me_3CP), 41.65 (d, $^{1}J_{PC}$ = 34.64 Hz, Me_3Si), 120.9 ppm (q, $^{1}J_{FC}$ = 321.0 Hz, CF_3). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ = 32.7 (d, $^{2}J_{PP}$ = 66.8 Hz, $^{1}J_{CP}$ = 91.3 Hz, $^{2}J_{SiP}$ = 27.7 Hz, Me_2P), 112.9 ppm (d, $^{2}J_{PP}$ = 66.9 Hz, $^{1}J_{CP}$ = 34.8 Hz, $^{t}Bu_3P$). ^{19}F NMR ($CDCl_3$): 78.0 ppm (s, OTf). $^{29}Si\{^{1}H\}$ ($CDCl_3$): −9.0 ppm (d, $^{2}J_{PSi}$ = 27.2 Hz). Anal. Calcd for $C_{18}H_{42}F_3NO_4P_2SSi$ (515.62): %C, 41.93; %H, 8.21; %N, 2.72; Found: %C, 40.07; %H, 8.12; %N, 2.70. No pure product could be obtained (for NMR analysis) due to approximately 5−10% decomposition to one or more species observed by ^{1}H NMR at δ = 1.11 (s, d, $^{1}J_{CH}$ = 120.0 Hz, d, $^{2}J_{SiH}$ = 6.7 Hz), 1.49 (d, J_{PH} = 13.8 Hz) and ^{29}Si NMR at δ = 31.9 (s) ppm with very similar solubility properties.

Reaction of 1b with 2c in the presence of 1 equiv. of AgOTf; Synthesis of

[$^{t}Bu_3P$=O−P(OCH_2CF_3)$_2$=$NSiMe_3$]OTf ([3d]OTf). To mixture of $^{t}Bu_3P$=O (218 mg, 1.0 mmol), and AgOTf (256 mg, 1.0 mmol) was added a solution of **2c** (396 mg, 1.0 mmol) in CH_2Cl_2 (4 mL) dropwise and the solution stirred for 2 h then allowed to stand for 1 h. Analysis of the reaction mixture by $^{31}P\{^1H\}$ NMR showed complete conversion to a new species: δ = −30.9 (d, J_{PP} = 66.8 Hz), 118.5 ppm (d, J_{PP} = 66.8 Hz). The reaction mixture was then filtered and the solvent removed under reduced pressure to give a white solid (532 mg, 79%). Crystals were grown from Et_2O diffusing into a saturated solution of the crude product in CH_2Cl_2 at −40 °C. ^1H NMR ($CDCl_3$) δ = 0.13 (d, $^4J_{PH}$ = 0.89 Hz, 9H, Me_3Si), 1.67 (d, $^2J_{PH}$ = 16.11 Hz, 27H, $^{t}Bu_3P$), 7.5 ppm (m, 6H, CF_3CH_2O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −31.0 (d, $^2J_{PP}$ = 66.9 Hz, $^1J_{CP}$ = 32.8 Hz, Me_2P), 117.8 ppm (d, $^2J_{PP}$ = 66.9 Hz, $^1J_{CP}$ = 30.0 Hz, $^{t}Bu_3P$). ^{19}F NMR ($CDCl_3$): δ = −78.3 (s, 3F, OTf), −74.7 ppm (t, $^2J_{HF}$ = 8.2 Hz, CF_3CH_2O). $^{29}Si\{^1H\}$ ($CDCl_3$): −5.7 ppm (br). No pure product could be obtained due to approximately 5−10% decomposition upon each recrystallisation to one or more species observed by ^1H NMR at δ = 0.52 (s), 1.57 (d, J_{PH} = 14.9 Hz) with very similar solubility properties.

Reaction of 1c with 2a in the presence of AgOTf; Synthesis of [Et_3P=N−PMe_2−$OSiMe_3$]OTf ([4d]OTf). To a solution of **1c** (268 mg, 2.0 mmol) in CH_2Cl_2 (2 mL) was added **2a** (456 mg, 2.0 mmol) in CH_2Cl_2 (1 mL) and the reaction stirred. After 30 min, $^{31}P\{^1H\}$ NMR of the reaction solution revealed formation of 4 sets of signals: A (28%): δ = 35.1 (d, J_{PP} = 35.2 Hz, $^1J_{CP}$ = 88.2 Hz, $^2J_{SiP}$ = 26.1 Hz), 103.8 ppm (d, J_{PP} = 35.2 Hz, $^1J_{CP}$ = 58.2 Hz, $^2J_{CP}$ = 5.5 Hz), B (9%): δ = 39.4 (d, J_{PP} = 12.6 Hz), 40.5 ppm (d, J_{PP} = 12.6 Hz, $^1J_{CP}$ = 66.8 Hz, $^2J_{SiP}$ = 5.2 Hz), C (41%): δ = 28.6 (d, J_{PP} = 33.7 Hz), 43.2 (d, J_{PP} = 8.6 Hz), 45.5 ppm (dd, J_{PP} = 33.7, 8.6 Hz), D: (4%): δ = 51.5 (dd, J_{PP} = 7.6, 5.4 Hz), 51.5 ppm (dd, J_{PP} = 7.6, 5.4 Hz), and starting materials: **2a**: 11.9 ppm (s, 1%) and **1c** 83 ppm (br, 16%). Complete conversion to B was observed by $^{31}P\{^1H\}$ NMR after 3 d. The reaction mixture was then added to a solution of to AgOTf (514 mg, 2.0 mmol) in CH_2Cl_2 (2 mL) and stirred for 1 h to give a pale yellow precipitate (AgBr), which was removed by filtration. The resultant clear solution was reduced to dryness to give a white solid (742 mg) which was then recrystallized from Et_2O (3 mL) diffusing into a solution of the crude product in CH_2Cl_2 (1 mL) at −40°C to give a clear crystals of [**4d**]OTf (354 mg, 41%). ^{1}H NMR ($CDCl_3$): δ = 0.30 (d, $^4J_{PH}$ = 0.4 Hz, 9H, Si*Me*$_3$), (dt, $^2J_{PH}$ = 18.4 Hz, $^3J_{HH}$ = 7.6 Hz, 9H, C*H*$_3$CH$_2$P), 1.75 (d, $^2J_{PH}$ = 14.0 Hz, 6H, P*Me*$_2$), 1.98 ppm (dq, $^2J_{PH}$ = 11.8 Hz, $^3J_{HH}$ = 7.6 Hz, 6H, CH$_3$C*H*$_2$P). ^{13}C{^{1}H} NMR ($CDCl_3$): 1.1 (d, $^4J_{PC}$ = 1.27 Hz, DEPT(+), Si*Me*$_3$), 5.7 (d, $^3J_{PC}$ = 5.3 Hz, DEPT(+), *C*H$_3$CH$_2$P), 18.6 (dd, $^1J_{PC}$ = 66.3, $^3J_{PC}$ = 2.3, DEPT(–), CH$_3$*C*H$_2$P), 19.6 (dd, $^1J_{PC}$ = 95.4 Hz, $^3J_{PC}$ = 1.5 Hz, DEPT(+), P*Me*$_2$) 120.8 ppm (q, $^1J_{FC}$ = 320.8 Hz, CF_3). ^{31}P{^{1}H} ($CDCl_3$): 38.8 (d, $^2J_{PP}$ = 13.6 Hz, Me$_2$P), 40.0 ppm (d, $^2J_{PP}$ = 13.6 Hz, $^1J_{CP}$ = 66.4 Hz, Et$_3$P). ^{19}F NMR ($CDCl_3$): 78.3 ppm (s, OTf). ^{29}Si{^{1}H} ($CDCl_3$): 24.7 ppm (d, $^2J_{PSi}$ = 9.9 Hz). Anal. Calcd for $C_{12}H_{30}F_3NO_4P_2SSi$ (431.46): %C, 33.40; %H, 7.01; %N, 3.25; Found: %C, 32.30; %H, 6.83; %N, 3.68.

Synthesis of [4a]PF$_6$. To a mixture of $AgPF_6$ (262 mg, 1.0 mmol) and **1a** (96 mg, 1.0 mmol) was added a solution of **2a** (238 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) and the solution stirred 23 h and filtered. ^{31}P{^{1}H} NMR of the filtrate showed complete consumption of starting materials to give to two new species: δ = −143.7 (d, $^1J_{FP}$ = 710.7 Hz), 24.9 (d, J_{PP} = 15.8 Hz), 39.3 ppm (d, J_{PP} = 15.8 Hz) (89%), and −13.9 (td, J = 939.4 Hz, J_{PP} = 54.3 Hz), 41.8 ppm (dt, J_{PP} = 54.3 Hz, J = 12.4 Hz) (11%). The solvent was then removed under reduced pressure to give a white solid (339 mg). [**4a**]PF$_6$ was recrystallised from hexane diffusing into a solution of the crude product in CH_2Cl_2 (202 mg, 52%) to give material suitable for single-crystal x-ray crystallographic analysis.

Reaction between [3d]OTf and an excess of DMAP. To **1b** (44 mg, 0.1 mmol) and AgOTf (51 mg, 0.1 mmol) was added a solution of **2a** (46 mg, 0.1 mmol) in $CDCl_3$ (1 mL) and the mixture stirred for 1 h to give a white precipitate (AgBr) which was removed by filtration. ^{31}P{^{1}H} and ^{1}H NMR confirmed formation of [**3d**]OTf. To the stirred solution of [**3d**]OTf was added DMAP (49 mg, 0.2 mmol) giving complete conversion of [**3d**]OTf to [**9**]OTf and **1b** after 10 min. by ^{31}P{^{1}H} NMR: δ = 25.5 (s, DMAP·PMe$_2$=NSiMe$_3$), 65.4 ppm (s, ^{t}Bu$_3$P=O) and ^{1}H NMR: δ = 0.00 (s, 9H, SiMe$_3$), 1.25 (d, J_{PH} = 12.3 Hz, 27H, ^{t}Bu$_3$P=O), 1.89 (d, J_{PH} = 13.6 Hz, 6H, Me$_2$P), 2.91 (br, 6H, NMe$_3$, DMAP), 3.18 (br, 6H, NMe$_3$, DMAP·PMe$_2$=NSiMe$_3$), 6.41 (br, 2H, *m*-H, DMAP), 6.87 (br, 2H, *m*-H, DMAP·PMe$_2$=NSiMe$_3$), 8.08 (br, 2H, *o*-H, DMAP), 8.52 (br, 2H, *o*-H, DMAP·PMe_2=$NSiMe_3$).

Attempted Reaction between [4a]$^+$ and an excess of DMAP in $CDCl_3$. [**4a**]OTf (78 mg, 0.1 mmol) and DMAP (49 mg, 0.2 mmol) were dissolved in $CDCl_3$ (1 mL) and the solution stirred. No reaction was observed by $^{31}P\{^1H\}$ and ^1H NMR after 4 d.

Attempted Reaction between [4a]$^+$ and an excess of DMAP in 1,2-dichlorobenzene. [**4a**]OTf (78 mg, 0.1 mmol) and DMAP (49 mg, 0.2 mmol) were dissolved in 1,2-dichlorobenzene (0.8 mL) and the solution sealed in a J. Young tap NMR tube. $^{31}P\{^1H\}$ NMR after 14 h at 25 °C, 10 h at 60 °C, 12 h at 100 °C and 10 h at 160 °C showed no reaction of [**4a**]$^+$: δ = 25.3 (d, $^2J_{PP}$ = 19.4 Hz), 40.3 ppm (d, $^2J_{PP}$ = 19.4 Hz).

Thermal Decomposition of [3d]OTf in 1,2-dichlorobenzene. In the absence of light, a solution of **2a** (46 mg, 0.2 mmol) in 1,2-dichlorobenzene (0.6 mL) was added to a mixture of **1b** (44 mg, 0.2 mmol) and AgOTf (51 mg, 0.2 mmol) and the mixture stirred for 1 h and filtered to a J. Young tap NMR tube. $^{31}P\{^1H\}$ NMR showed complete conversion to [**3d**]OTf with resonances at δ = 33.8 (d, $^2J_{PP}$ = 66.5 Hz), 112.7 ppm (d, $^2J_{PP}$ = 66.5 Hz). $^{31}P\{^1H\}$ NMR after heating the reaction mixture to 60 °C for 14 h showed 8% conversion to a new broad resonance around 81 ppm, increasing to 38% after a further 7 h at 100 °C. Heating to 150 °C for a further 14 h gave complete conversion of [**3d**]OTf to a number of broad resonances around 13, 23, 33 and 80 ppm.

Thermal Decomposition of [3d]Br in 1,2-dichlorobenzene. To **1b** (44 mg, 0.2 mmol) was added a solution of **2a** (46mg, 0.2 mmol) in 1,2-dichlorobenzene (0.6 mL) and the mixture transferred to a J. Young tap NMR tube. After 2 h $^{31}P\{^1H\}$ NMR revealed no apparent reaction between **1b** (62.9 ppm) and **2a** (6.7 ppm). After 15 hours at 150 °C, only **2a** had reacted, being completely consumed to give a new resonance at 13 ppm.

Thermal Decomposition of [3d]Br in dichloroethane. To **1b** (44 mg, 0.2 mmol) was added a solution of **2a** (46 mg, 0.2 mmol) in dichloroethane (0.6 mL) and the mixture transferred to a J. Young tap NMR tube. After 20 min $^{31}P\{^1H\}$ NMR revealed 9% conversion of **1b** (63.7 ppm) and **2a** (9.9 ppm) to a new set of resonances at δ = 32.1 (d, $^2J_{PP}$ = 66.7 Hz), 112.9 ppm (d, $^2J_{PP}$ = 66.7 Hz) corresponding to formation of [**3d**]Br. After 14 hours at 20 °C, a new resonance was observed at 23 ppm (s) (3% of the total integral of all resonances), along with 8% reduction in **2a**. The intensity of this new species, increased to 9% after heating to 40 °C for 4 h and 35% after heating to 60 °C for 4 h. These changes were also accompanied by a 90% decrease in intensity of the resonances associated with [**3d**]Br, reducing its concentration to 1%. Heating to 60 °C for a further 14 h gave complete consumption of **2a** and the disappearance of resonances associated with [**3d**]Br.

Reaction between [4a]OTf and excess 2b. In a J. Young tap NMR tube, [**4a**]OTf (39 mg, 0.1 mmol) was dissolved in a solution of **2b** (289 mg, 1.0 mmol) in 1,2-dichlorobenzene (0.8 mL) and the tube sealed and shaken. In addition to **2b** (1.3 ppm) and [**4a**]$^+$ (δ = 25.3 and 40.8 ppm, J_{PP} = 21.2 Hz), $^{31}P\{^1H\}$ NMR of the reaction mixture after 20 min showed conversion to trace quantities of a new species: δ = 17.7 (d, J_{PP} = 32.1 Hz), 28.5 (d, J_{PP} = 13.8 Hz), 45.6 ppm (dd, J_{PP} = 32.1, 13.8 Hz), after 10 h, these signals had increased in intensity to 26% of the integration (not including signals for **2b**) along with formation of two new species: δ = 11.0 (s, 5%), 11.4 ppm (s, 4%). Heating the reaction mixture to 60 °C for 14 h resulted in the species with resonances at δ = 17.7, 28.5 and 45.6 ppm increasing in relative concentration to 42%. No change was observed in the concentration of other species. Heating to 160 °C for 5 h resulted in decomposition to multiple unidentified species, with no apparent decomposition of **2b**. The solvent was removed under reduced pressure and the remaining viscous liquid fully redissolved in $CDCl_3$. $^{31}P\{^1H\}$ NMR of the solution showed no resonances at 1.8 ppm.

Reaction between *in situ* generated [3d]OTf and excess 2b. To AgOTf (25 mg, 0.1 mmol) in the absence of light was added a solution of **1b** (22 mg, 0.1 mmol) in 1,2-dichlorobenzene (0.5 mL) immediately followed by **2a** (23 mg, 0.1 mmol) in 1,2-dichlorobenzene (0.5 mL) and the reaction stirred for 40 min and allowed to settle with $^{31}P\{^1H\}$ NMR of the reaction mixture after 1 h showing 98% conversion to [**3d**]OTf (δ = 32.9 and 113.1 ppm, $^2J_{PP}$ = 66.5 Hz). The mixture was then filtered to a J. Young tap NMR tube containing **2b** (289 mg, 1.0 mmol) and the tube shaken. $^{31}P\{^1H\}$ NMR of the solution after 15 min showed 93% conversion of [**3d**]OTf to a new species (δ_P = 24.1 and 114.7 ppm, J_{PP} = 67.7 Hz) and release of **2a** (δ_P = 6.9 ppm) with no further reaction observed after 7 h at room temperature or after heating the solution to 60 °C for 14 h. Heating the solution to 160 °C for 7 h resulted in decomposition of [**3d**]OTf and the new species with multiple unidentified peaks observed by $^{31}P\{^1H\}$ NMR. The solvent was removed under reduced pressure and the remaining viscous liquid fully redissolved in $CDCl_3$. $^{31}P\{^1H\}$ NMR of the solution showed no resonances at 1.8 ppm.

Reaction between $^tBu_3P$=O (1b) and excess 2b. In a J. Young tap NMR tube, **1b** (22 mg, 0.1 mmol) was dissolved in a solution of **2b** (289 mg, 1.0 mmol) in 1,2-dichlorobenzene (0.8 mL) and the tube sealed and shaken. No reaction was observed by $^{31}P\{^1H\}$ NMR of the reaction mixture after 10 h. Heating the reaction mixture to 60 °C for 14 h also resulted in no reaction. Further heating to 160 °C for 5 h resulted in (10%, relative to **1b**) decomposition to multiple unidentified species between 5 and 25 ppm**.** The solvent was removed under reduced pressure and the remaining viscous liquid fully redissolved in $CDCl_3$. $^{31}P\{^1H\}$ NMR of the solution showed no resonances at 1.8 ppm.

Reaction between Me_3P=O (1a) and excess 2b. In a J. Young tap NMR tube, **1a** (9 mg, 0.1 mmol) was dissolved in a solution of **2b** (289 mg, 1.0 mmol) in 1,2-dichlorobenzene (0.8 mL) and the tube sealed and shaken with complete dissolution of all reagents. After 20 min at 25 °C a small amount of a white precipitate was observed. $^{31}P\{^1H\}$ NMR showed formation of a number of new species: δ = 10.9 (s, 7%), 11.3 (s, 8%), 23.2 (d, J_{PP} = 31.2 Hz, 1%), 95.6 ppm (d, J_{PP} = 31.2 Hz, 1%) and trace amounts of species at δ = 8.6 (s), 18.6 (s), 19.0 (s) and 19.1 ppm (s). After 90 min doublet resonances at 23.2 and 95.6 ppm were no longer observed, with further changes observed after 10 h. No reaction was observed by $^{31}P\{^1H\}$ NMR of the reaction mixture after 10 h. Heating the reaction mixture to 60 °C for 14 h resulted in formation of new resonances at 29.4 (d, J = 3.5 Hz, 2%) and formation of trace amounts of a number of resonances: 17.0 (d, J = 35.4 Hz), 17.9 (d, J = 33.5 Hz), 32.0–33.5 ppm (multiple complex multiplet resonances) and a reduction in intensity of resonances at 10.9 (4%) and 11.3 ppm (4%), and an increase for the resonance at 8.6 ppm to 2%. Further heating to 160 °C for 5 h resulted in complete decomposition of **2b** to multiple unidentified species: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): 21.0 (s, 8%), 21.5 (br, 14%), 21.6 ppm (br, 7%), and a large number of unidentified, and less prominent resonances. The solvent was removed under reduced pressure and the remaining viscous liquid fully redissolved in $CDCl_3$. $^{31}P\{^{1}H\}$ NMR of the solution showed no resonances at 1.8 ppm.

Thermal decomposition of 2b. In a J. Young tap NMR tube, **2b** (289 mg, 1.0 mmol) was dissolved in 1,2-dichlorobenzene (0.8 mL) and the tube sealed and shaken. Analysis of the solution by $^{31}P\{^{1}H\}$ NMR showed the presence of trace amounts (summing to 1% of the total integral) of impurity at δ = 18.6 (s), 19.0 (s) and 19.1 ppm (s) with no change after 10 h at 25 °C. Heating the reaction mixture to 60 °C for 14 h also resulted in a slight increase in the total concentration of the trace impurities to 3%. Further heating to 160 °C for 5 h resulted in 90% decomposition of **2b** to multiple unidentified species: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): 21.1 (br, 26%), 21.6 ppm (br, 50%), and a large number of unidentified, and less prominent broad or complex resonances. The solvent was removed under reduced pressure and the remaining viscous liquid fully redissolved in $CDCl_3$. $^{31}P\{^{1}H\}$ NMR of the solution showed no resonances at 1.8 ppm.

Attempted reaction between 1a and $Ph_3P{=}NSiMe_3$. To 0.75 mL of a 0.27 M solution of **1a** in CH_2Cl_2 was added 0.75 mL of a 0.27 M solution of $Ph_3P{=}NSiMe_3$ in CH_2Cl_2 and the mixture stirred. No reaction was observed by $^{31}P\{^{1}H\}$ NMR after 6 d.

Structural determination of reaction products as rearranged ([4]$^{+}$) or un-rearranged ([3]$^{+}$). It should be noted that the similarity in the X-ray diffraction of N and O or P and Si (due to their similar size and electron densities) raises the question as to the exact arrangement of these atoms within these crystal structures. In all cases, the arrangement given gave the best refinement (measured by R and R_w). In the case of particular concern ([**4a**]$^{+}$), where P and Si are equivalently (methyl-) substituted, the assignment is reinforced by the two salts ([**4a**]PF_6 and [**4a**]OTf) both showing a better refinement for a P–N–P–O–Si arrangement. It was also clear for [**4a**]PF_6 that this was the correct assignment from the thermal ellipsoid parameters for the two possible arrangements, whereby reversing the N and O atoms resulted in unusually large or small values after refinement.

The observed bond lengths also strongly support rearrangement where it is shown by the electron densities and consequential assignments of N vs. O or Si vs. P. The Si–E bond (E = O or N) (1.684(7) to 1.6806(17) Å) is significantly longer than the P–E bond (1.569(5) to 1.587(17) Å) in all examples ([**3d**]$^+$, [**3e**]$^+$, [**4a**]$^+$, [**4d**]$^+$ and [**8**]$^+$), supporting the correct assignment in [**4a**]PF_6 and [**4a**]OTf, where P and Si both possess identical (trimethyl) substituents.

In all the rearranged products ([**4a**]$^+$**,** [**4d**]$^+$ and [**8**]$^+$), the internal N–P(2) and O–Si bond distances (1.555(4) to 1.5670(17) Å and 1.6623(16) to 1.6806(17) Å respectively) are shorter than their respective (equivalently positioned) O–P(2) and N–Si distances (1.574(5) to 1.641(4) Å and 1.684(7) to 1.710(7) Å respectfully) in those that have not rearranged ([**3d**]$^+$ and [**3e**]$^+$). Most significantly for the rearranged products the central P(2)–O distance (1.5597(17) to 1.579(3) Å) is significantly longer than that of P(2)=N distance (1.466(7) to 1.523(5) Å) in those have not rearranged. No significant difference is observed between the P(1)–E (E = O or N) bonds for the different arrangements. Finally, a clear difference between the chemistry of [**3**]$^+$ and [**4**]$^+$ was observed (see section 3a) and this is consistent with their assigned structures.

$^{31}P\{^1H\}$ NMR monitoring data for the reactions between phosphine oxides (1a–e) and phosphoranimines (2a–c or 5). For each of the following reactions, 0.3 mL each of 0.25 M solutions of **1** and **2** in CH_2Cl_2 were quickly syringed into a J. Young tap NMR tube at 25 °C, which was then sealed and shaken to mix the solutions. The reaction was then monitored by $^{31}P\{^1H\}$ NMR spectroscopy, with spectra acquired after 30 min, 60 min, 2 h, 5 h, 10 h, 24 h, 2 d, 5d and 10 d. Details of the observed resonances and their integrals (quoted in percent of the total integral of all resonances observed in each spectrum) are tabulated below. For reactions in the presence of AgOTf (64 mg, 0.25 mmol) or $AgBPh_4$ (107 mg, 0.25 mmol) 1 mL of each solution was added to a foil-wrapped vial containing AgOTf or $AgBPh_4$ and stirred for 30 min, allowed to settle for 10 min, then a 0.6 mL aliquot of the solution filtered to a J. Young tap NMR tube which was then sealed and the reaction monitored from 60 min. For the reaction in the presence of $[Ph_4P]Br$ (524 mg, 1.25 mmol), 1 mL of each solution was added to a vial containing $[Ph_4P]Br$, and the mixture stirred for 5 min until no solid could be observed before transferring 0.6 mL of the solution to J. Young tap NMR tube which was then sealed and the reaction monitored from 30 min.

Species are labeled A–D to identify where analogous sets of ^{31}P signals are observed in more than one reaction. Signals from A and B correspond the cations [**3**]$^+$ and [**4**]$^+$, the species responsible for signals C and D are unknown. Neither appear to be the intermediate [**10**]$^+$ proposed in Scheme 9. The results of these reactions are given in the following tables:

1a ($Me_3P{=}O$) + **2a** ($BrMe_2P{=}NSiMe_3$)

$^{31}P\{^{1}H\}$ NMR Signals									
	δ	m	*J*	*δ*	m	*J*	*δ*	m	*J*
	ppm		Hz	ppm		Hz	ppm		Hz
2a	11.3	br. s.	-						
A ([**3a**]$^+$)	35.8	d	28.8	95.2	d	28.8			
B ([**4a**]$^+$)	25.1	d	20.9	41.0	d	20.9			
C	28.6	d	15.0	29.2	d	32.1	46.9	dd	32.1, 15.0
D	31.0	dd	10.3, 7.3	52.0	dd	10.3, 7.3			
Others	22.9	br. s.	-						
	37.5	br. s.	-						

$^{31}P\{^{1}H\}$ NMR Integration (%)									
	30 min	60 min	2 h	5 h	10 h	24 h	2 d	5 d	10 d
2a	6	5	3	1	0	0	0	0	0
A ([**3a**]$^+$)	58	38	17	2	0	0	0	0	0
B ([**4a**]$^+$)	18	33	51	67	72	79	87	92	89
C	13	18	23	26	24	18	10	7	7
D	3	3	3	0	0	0	0	0	0
Others	2	3	4	4	4	3	3	1	4

1a ($Me_3P{=}O$) + **2a** ($BrMe_2P{=}NSiMe_3$) + AgOTf

$^{31}P\{^{1}H\}$ NMR Signals									
	δ	m	*J*	*δ*	m	*J*	*δ*	m	*J*
	ppm		Hz	ppm		Hz	ppm		Hz
A ([**3a**]$^+$)	37.3	d	28.6	94.0	d	28.6			
B ([**4a**]$^+$)	25.0	d	17.4	39.8	d	17.4			
C	28.3	d	11.4	30.3	d	32.5	45.5	dd	32.5, 11.4
D	30.6	dd	11.6, 7.21	51.0	dd	11.6, 7.21			
Others	23.0	br. s.	-						

$^{31}P\{^{1}H\}$ NMR Integration (%)									
	30 min	60 min	2 h	5 h	10 h	24 h	2 d	5 d	10 d
A ([**3a**]$^+$)		16	4	0	0	0	0	0	0
B ([**4a**]$^+$)		72	85	92	92	96	96	96	97
C		3	3	5	5	5	4	4	3
D		8	6	4	3	0	0	0	0
Others		2	1	0	0	0	0	0	0

1a ($Me_3P{=}O$) + **2b** ($BrMePhP{=}NSiMe_3$)

$^{31}P\{^{1}H\}$ NMR Signals	δ ppm	m	J Hz	δ ppm	m	J Hz	δ ppm	m	J Hz
2b	3.6	s	-						
A ([**3b**]$^+$)	24.0	d	29.7	95.7	d	29.7			
B ([**4b**]$^+$)	28.5	d	11.8	29.1	d	11.8			
C	18.0	d	34.7	30.8	d	7.6	32.1	dd	34.7, 7.6
C'	19.3	d	33.6	31.0	d	9.3	31.7	dd	33.6, 9.3
Others	37.4	bs	-						

$^{31}P\{^{1}H\}$ NMR Integration (%)	30 min	60 min	2 h	5 h	10 h	24 h	2 d	5 d	10 d
2b	5	5	4	3	1	0	0	0	0
A ([**3b**]$^+$)	63	49	36	19	9	2	0	0	0
B ([**4b**]$^+$)	5	9	17	32	48	68	81	89	91
C	13	17	19	19	17	13	8	4	3
C'	14	19	24	27	24	17	12	6	4
Others	0	0	0	0	0	0	0	0	3

1a ($Me_3P{=}O$) + **2b** ($BrMePhP{=}NSiMe_3$) + AgOTf

$^{31}P\{^{1}H\}$ NMR Signals	δ ppm	m	J Hz	δ ppm	m	J Hz	δ ppm	m	J Hz
A ([**3b**]$^+$)	25.2	d	29.8	94.5	d	29.8			
B ([**4b**]$^+$)	27.9	d	10.9	29.2	d	10.9			
C	18.6	d	34.7	30.2	d	7.0	32.1	dd	34.7, 7.0
C'	19.8	d	33.8	30.4	d	8.8	31.6	dd	33.8, 8.8
Others									

$^{31}P\{^{1}H\}$ NMR Integration (%)	30 min	60 min	2 h	5 h	10 h	24 h	2 d	5 d	10 d
A ([**3b**]$^+$)		52	32	10	3	1	0	0	0
B ([**4b**]$^+$)		20	31	46	59	74	84	93	100
C		15	20	21	16	11	7	3	0
C'		13	18	23	22	15	9	4	0
Others		0	0	0	0	0	0	0	0

1a ($Me_3P{=}O$) + **2c** ($Br\{CF_3CH_2O\}_2P{=}NSiMe_3$)

$^{31}P\{^1H\}$ NMR Signals	δ ppm	m	J Hz	δ ppm	m	J Hz
2c	−34.0	s	-			
1a	42.9	s	-			
A ([**3c**]$^+$)	−26.3	d	32.0	105.1	d	32.0
B ([**4c**]$^+$)	2.5	d	23.7	25.4	d	23.7
Others	−34.0	s	-			
	−17.7	br. s.	-			
	−2.4	s	-			
	10.3	s	-			
	11.2	s	-			
	27.5	d	15.5			
	83.8	s	-			

$^{31}P\{^1H\}$ NMR Integration (%)	30 min	60 min	2 h	5 h	10 h	24 h	2 d	5 d	10 d
2c	33	30	25	16	12	9	8	7	6
1a	28	18	12	13	13	13	12	10	9
A ([**3c**]$^+$)	16	16	12	3	1	0	0	0	0
B ([**4c**]$^+$)	17	29	41	53	59	64	70	73	83
Others	5	8	10	15	16	14	10	9	2

1a ($Me_3P{=}O$) + **2c** ($Br\{CF_3CH_2O\}_2P{=}NSiMe_3$) + AgOTf

$^{31}P\{^1H\}$ NMR Signals	δ ppm	m	J Hz	δ ppm	m	J Hz
2c	−34.1	s	-			
A ([**3c**]$^+$)	−26.4	d	31.5	104.3	d	31.5
B ([**4c**]$^+$)	2.4	d	23.6	25.4	d	23.6
Others	−17.7	s	-			
	−2.4	s	-			
	10.3	s	-			
	27.6	d	15.6			
	38.7	d	31.9			
	83.3	s	-			

$^{31}P\{^1H\}$ NMR Integration (%)	30 min	60 min	2 h	5 h	10 h	24 h	2 d	5 d	10 d
2c		32	27	21	21	18	17	15	13
A ([**3c**]$^+$)		31	27	8	1	0	0	0	0
B ([**4c**]$^+$)		32	40	48	54	63	65	68	73
Others		6	7	23	25	19	18	17	14

1a ($Me_3P{=}O$) + **5** ($BrMe_2P{=}NSiPh_3$)

$^{31}P\{^{1}H\}$ NMR Signals	δ ppm	m	J Hz	δ ppm	m	J Hz	δ ppm	m	J Hz
5	14.1	s	-						
A ([**7**]$^+$)	31.7	d	34.6	95.8	d	34.6			
B ([**8**]$^+$)	25.6	d	23.8	42.6	d	23.8			
C	31.7	d	35.9	28.5	d	20.2	48.3	dd	35.9, 20.2
D	31.0	dd	10.4, 6.5	52.0	dd	10.4, 6.5			
Others	22.9	br. s.	-						
	37.5	br. s.	-						

$^{31}P\{^{1}H\}$ NMR Integration (%)	30 min	60 min	2 h	5 h	10 h	24 h	2 d	5 d	10 d
5	6	5	4	4	3	3	2	1	0
A ([**7**]$^+$)	52	31	22	17	13	11	8	3	0
B ([**8**]$^+$)	7	17	27	34	40	45	51	66	76
C	29	38	38	34	29	22	19	12	7
D	4	6	2	0	0	0	0	0	0
Others	3	4	7	11	15	19	21	19	17

1a ($Me_3P{=}O$) + **5** ($BrMe_2P{=}NSiPh_3$) + AgOTf

$^{31}P\{^{1}H\}$ NMR Signals	δ ppm	m	J Hz	δ ppm	m	J Hz	δ ppm	m	J Hz
A ([**7**]$^+$)	41.4	d	32.6	94.8	d	32.6			
B ([**8**]$^+$)	25.4	d	20.8	41.2	d	20.8			
C	28.3	d	16.0	32.8	d	35.8	46.5	dd	35.8, 16.0
Others	23.1	s	-						
	27.5	s	-						

$^{31}P\{^{1}H\}$ NMR Integration (%)	30 min	60 min	2 h	5 h	10 h	24 h	2 d	5 d	10 d
A ([**7**]$^+$)		85	78	66	53	33	27	10	5
B ([**8**]$^+$)		1	1	3	7	16	28	45	60
C		8	11	18	24	29	29	24	23
Others		6	9	14	16	22	23	21	12

1c ($Et_3P=O$) + **2a** ($BrMe_2P=NSiMe_3$)

$^{31}P\{^1H\}$ NMR Signals	δ	m	J	δ	m	J	δ	m	J
	ppm		Hz	ppm		Hz	ppm		Hz
2a	11.4	s	-						
A ([**3f**]$^+$)	34.3	d	34.7	104.1	d	34.7			
B ([**4d**]$^+$)	39.3	d	13.4	40.4	d	13.4			
C	28.4	d	33.5	43.2	d	9.1	45.6	dd	33.5, 9.1
D	45.6	dd	8.0, 5.52	51.5	dd	8.0, 5.52			
Others	51.1	s	-						
	56.0	bs							
	68.2	bs	-						

$^{31}P\{^1H\}$ NMR Integration (%)	30 min	60 min	2 h	5 h	10 h	24 h	2 d	5 d	10 d
2a	5	3	2	1	0	0	0	0	0
A ([**3f**]$^+$)	42	28	18	9	4	1	0	0	0
B ([**4d**]$^+$)	5	8	14	25	38	57	74	85	88
C	31	38	43	44	40	27	13	5	2
D	3	3	3	3	3	2	2	0	0
Others	15	20	20	18	15	13	11	10	10

1c ($Et_3P=O$) + **2a** ($BrMe_2P=NSiMe_3$) + AgOTf

$^{31}P\{^1H\}$ NMR Signals	δ	m	J	δ	m	J	δ	m	J
	ppm		Hz	ppm		Hz	ppm		Hz
A ([**3f**]$^+$)	35.9	d	33.9	103.2	d	33.9			
B ([**4d**]$^+$)	38.0	d	9.9	40.3	d	9.9			
C	29.9	d	33.7	43.0	d	5.8	44.2	dd	33.7, 5.8
D	45.6	dd	7.5, 5.2	50.1	dd	7.5, 5.2			
Others	75.6	br. s.	-						

$^{31}P\{^1H\}$ NMR Integration (%)	30 min	60 min	2 h	5 h	10 h	24 h	2 d	5 d	10 d
A ([**3f**]$^+$)		38	27	13	6	3	1	0	0
B ([**4d**]$^+$)		6	9	18	28	44	59	76	85
C		28	33	36	32	24	15	4	0
D		13	13	14	13	13	12	9	6
Others		15	18	19	20	17	13	10	9

1d ($^{i}Pr_3P{=}O$) + **2a** ($BrMe_2P{=}NSiMe_3$)

$^{31}P\{^1H\}$ NMR Signals	δ ppm	m	J Hz	δ ppm	m	J Hz
2a	11.4	br. s.	-			
1d	59.4	br. s.	-			
A ([**3g**]$^+$)	33.6	d	45.9	107.6	d	45.9
B ([**4e**]$^+$)	28.1	d	33.7	39.8	d	33.7
Others	24.0	br. s.	-			
	33.1	s	-			
	48.9	s	-			
	51.0	s	-			
	62.6	s	-			

$^{31}P\{^1H\}$ NMR Integration (%)	30 min	60 min	2 h	5 h	10 h	24 h	2 d	5 d	10 d
2a	25	25	24	22	20	17	14	7	1
1d	40	40	40	39	39	38	35	34	33
A ([**3g**]$^+$)	31	30	28	25	22	19	13	7	0
B ([**4e**]$^+$)	3	4	6	9	12	17	20	24	20
Others	2	3	4	5	6	10	17	28	45

1d ($^{i}Pr_3P{=}O$) + **2a** ($BrMe_2P{=}NSiMe_3$) + AgOTf

$^{31}P\{^1H\}$ NMR Signals	δ ppm	m	J Hz	δ ppm	m	J Hz
A ([**3g**]$^+$)	34.1	d	45.4	107.3	d	45.4
B ([**4e**]$^+$)	28.1	d	33.4	39.5	d	33.4
Others	32.8	s	-			
	49.0	s	-			
	51.1	s	-			
	93.2	br. s.	-			
	115.9	s	-			

$^{31}P\{^1H\}$ NMR Integration (%)	30 min	60 min	2 h	5 h	10 h	24 h	2 d	5 d	10 d
A ([**3g**]$^+$)		99	99	99	99	97	95	89	80
B ([**4e**]$^+$)		0	0	0	0	0	1	2	4
Others		1	1	1	1	3	4	10	16

1e ($Ph_3P{=}O$) + **2a** ($BrMe_2P{=}NSiMe_3$)

$^{31}P\{^1H\}$ NMR Signals	δ ppm	m	J Hz	δ ppm	m	J Hz	Δ Ppm	m	J Hz
2a	11.3	br. s.	-						
1e	28.0	s	-						
B ([**4f**]$^+$)	17.5	d	10.5	42.5	d	10.5			
C	18.6	d	11.40	29.3	d	32.91	49.5	dd	34.02, 11.11
Others	23.9	br. s.	-						

$^{31}P\{^1H\}$ NMR Integration (%)	30 min	60 min	2 h	5 h	10 h	24 h	2 d	5 d	10 d
2a	49	49	49	49	49	48	46	42	37
1e	51	51	51	51	52	50	49	47	44
B ([**4f**]$^+$)	0	0	0	0	0	1	2	4	9
C	0	0	0	0	0	2	3	5	8
Others	0	0	0	0	0	0	0	1	3

1e ($Ph_3P{=}O$) + **2a** ($BrMe_2P{=}NSiMe_3$) + AgOTf

$^{31}P\{^1H\}$ NMR Signals	δ ppm	m	J Hz	δ ppm	m	J Hz
A ([**3h**]$^+$)	36.7	d	35.6	58.8	d	35.6
B ([**4f**]$^+$)	17.4	d	10.6	42.4	d	10.6
C	18.7	d	11.5	49.4	dd	34.2, 11.5
D	21.1	dd	9.9, 6.5	55.9	dd	9.9, 6.5
Others	47.3	s	-			

$^{31}P\{^1H\}$ NMR Integration (%)	30 min	60 min	2 h	5 h	10 h	24 h	2 d	5 d	10 d
A ([**3h**]$^+$)		47	28	5	0	0	0	0	0
B ([**4f**]$^+$)		44	62	83	86	91	90	90	90
C		2	3	3	3	5	5	5	5
D		5	5	6	6	3	3	3	3
Others		2	2	2	5	2	2	2	2

1a ($Me_3P=O$) + **2a** ($BrMe_2P=NSiMe_3$) + $AgBPh_4$

$^{31}P\{^1H\}$ NMR Signals	δ ppm	m	J Hz	δ ppm	m	J Hz	δ ppm	m	J Hz
A ([**3a**]$^+$)	37.5	d	28.1	91.5	d	28.1			
B ([**4a**]$^+$)	24.3	d	12.1	38.4	d	12.1			
C	27.6	d	6.4	31.7	d	31.9	43.5	dd	31.9, 6.4
Others	26.6	d	5.7						
	29.8	d	23.4	35.5	d	23.4			
	51.8	d	5.6						
	69.8	s	-						
	96.6	s	-						

$^{31}P\{^1H\}$ NMR Integration (%)	30 min	60 min	2 h	5 h	10 h	24 h	2 d	5 d	10 d
A ([**3a**]$^+$)		3	0	0	0	0	0	0	0
B ([**4a**]$^+$)		44	60	76	85	92	96	97	96
C		41	31	21	13	6	1	0	0
Others		13	9	3	2	2	3	3	4

1a ($Me_3P=O$) + **2a** ($BrMe_2P=NSiMe_3$) + 5 $[Ph_4P]Br$*

$^{31}P\{^1H\}$ NMR Signals	δ ppm	m	J Hz	δ ppm	m	J Hz	δ ppm	m	J Hz
2a	12.8	br. s.	-						
A ([**3a**]$^+$)	37.1	d	29.8	95.2	d	29.8			
B ([**4a**]$^+$)	25.7	d	19.8	41.3	d	19.8			
C	29.1	d	15.2	29.6	d	32.9	46.9	dd	32.9, 15.2
D	31.1	dd	10.9, 6.9	52.2	dd	10.9, 6.9			
Others	32.8	d	17.9	59.1	dd	47.3, 17.9	102.8	d	47.3
	25.4	s	-						
Ph_4PBr	23.4	s	-						

$^{31}P\{^1H\}$ NMR Integration (%)	30 min	60 min	2 h	5 h	10 h	24 h	2 d	5 d	10 d
2a	3	2	1	0	0	0	0	0	0
A ([**3a**]$^+$)	68	47	25	9	3	0	0	0	0
B ([**4a**]$^+$)	6	12	25	39	57	75	81	83	88
C	17	29	42	47	36	23	18	16	11
D	6	9	7	3	2	0	0	0	0
Others	1	0	0	1	2	3	2	1	1

*The singlet resonance at δ = 23.4 ppm due to $[Ph_4P]^+$ was not included in the calculation of percentage integrals.

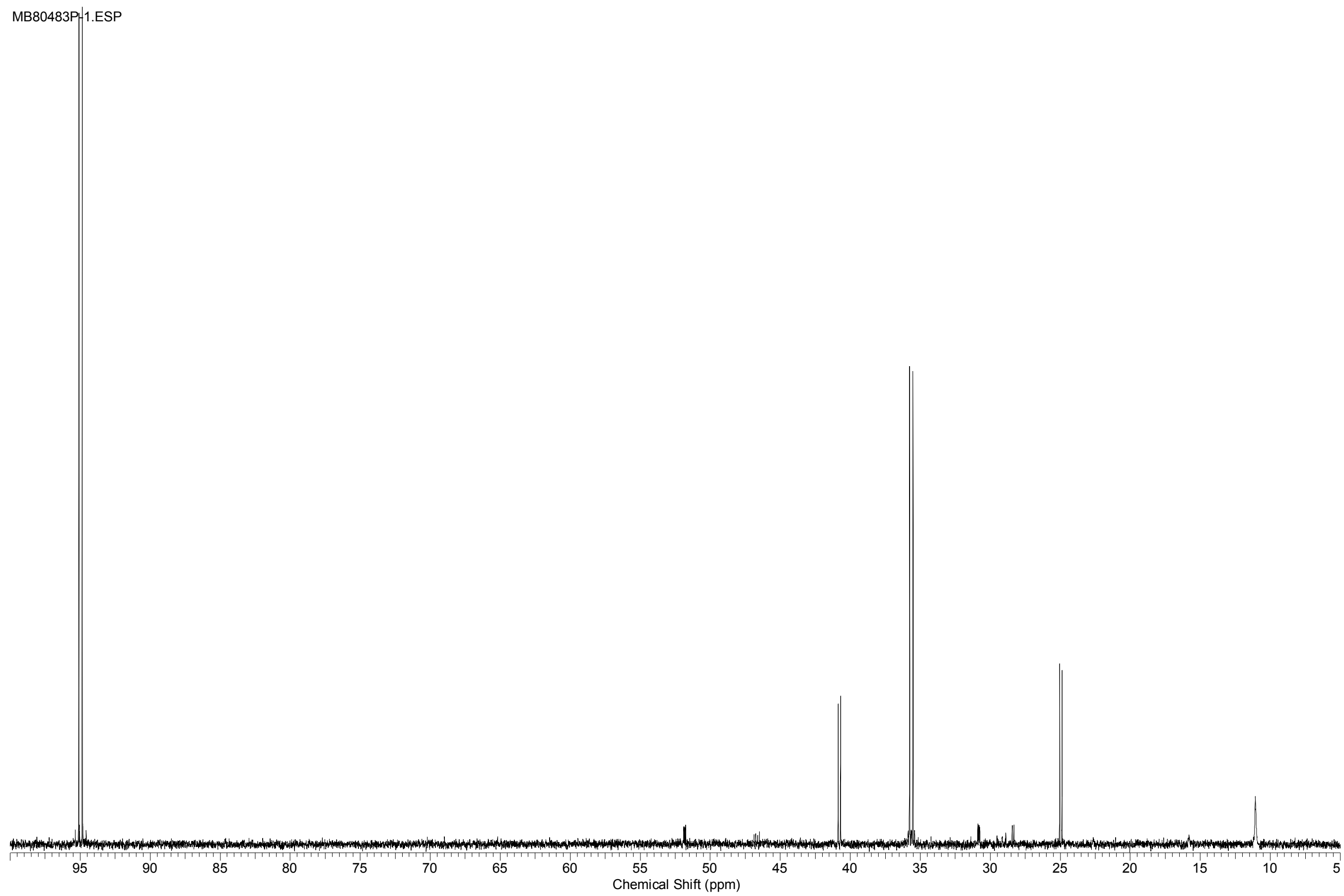

Figure S1. $^{31}P\{^1H\}$ NMR of reaction between **1a** and **2a** in CH_2Cl_2 after 10 min.

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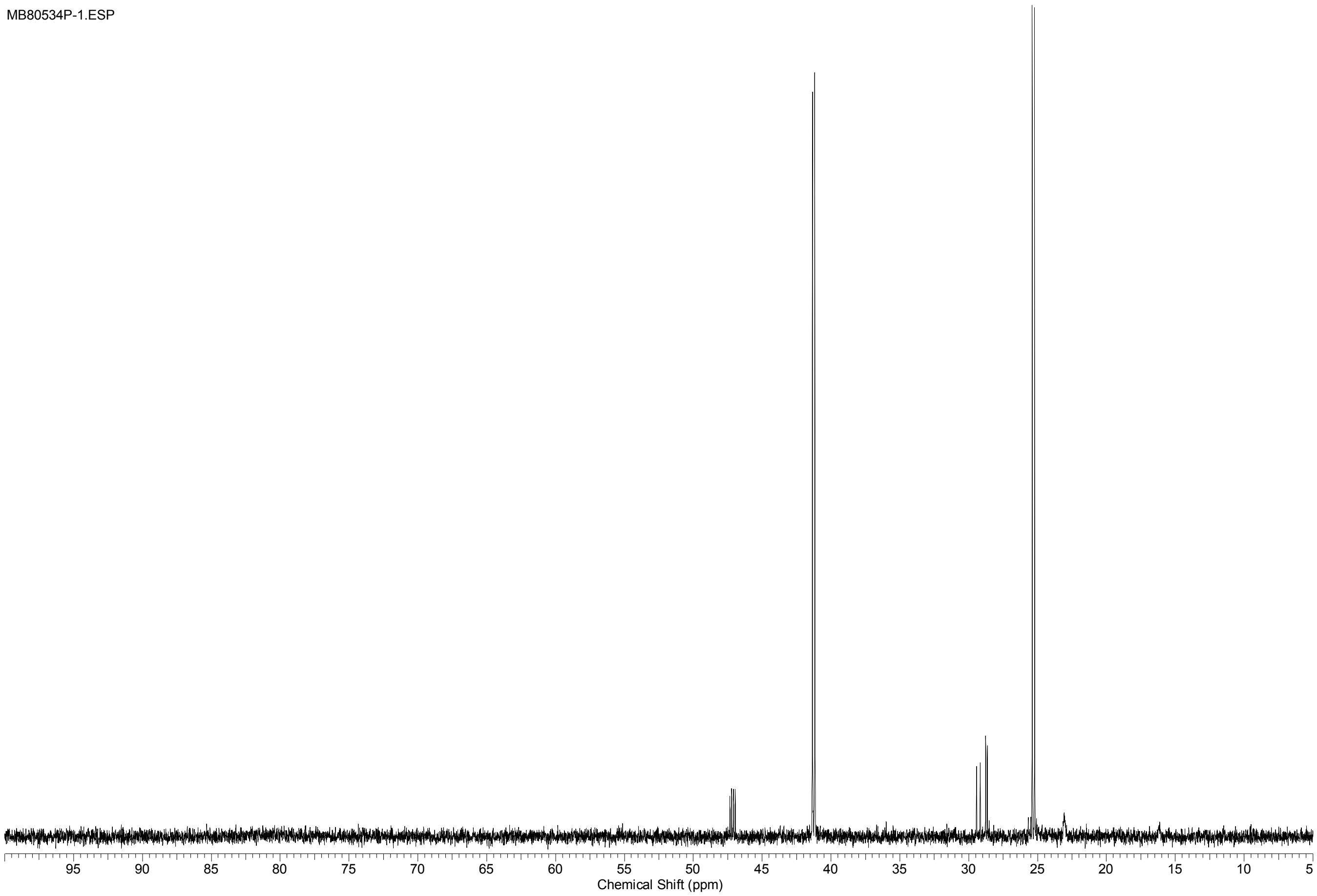

Figure S2. $^{31}P\{^{1}H\}$ NMR of reaction between **1a** and **2a** in CH_2Cl_2 after 5 h.

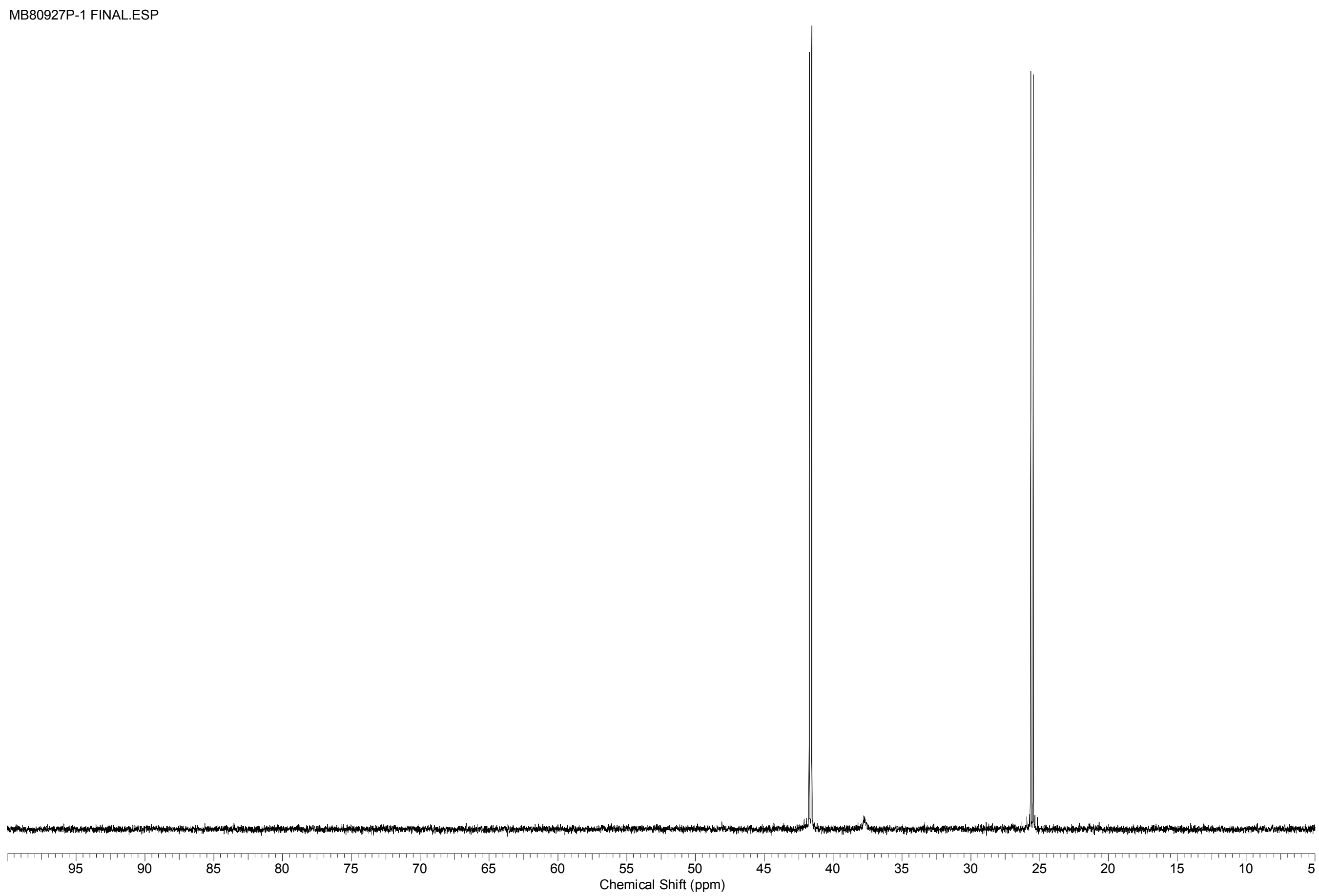

Figure S3. $^{31}P\{^1H\}$ NMR of reaction between **1a** and **2a** in CH_2Cl_2 after 10 d.

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