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A Versatile Protocol for the Quantitative and Smooth Conversion of Phosphane Oxides into Synthetically Useful Pyrazolylphosphonium Salts

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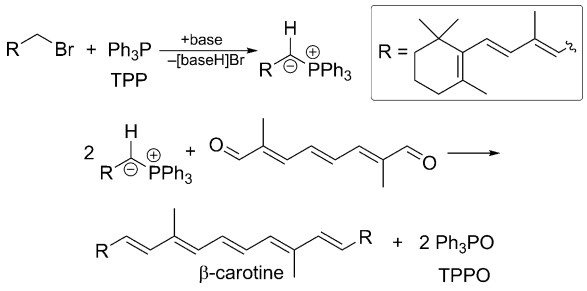
Dedicated to Professor Joseph Grobe on the occasion of his 80th birthday.

A convenient protocol for the smooth conversion of the resistant P–O bond in phosphane oxides into a reactive P–N bond of synthetically useful pyrazolylphosphonium salts is described. A highly charged, oxophilic, phosphorus-centered trication is employed and the reactions are conducted at room temperature with quantitative yields. The resulting pyrazolylphosphonium cations are valuable synthetic intermediates and are used for the synthesis of a variety of organophosphorus compounds. This represents a new approach towards the transformation of the rather inert phosphoryl group under very mild reaction and workup conditions and aims towards alternatives to existing reduction methods for phosphane oxide functionalization.

Introduction

The Wittig reaction is the key step of the industrial-scale production of carotenoids, such as β-carotene (provitamin A; Scheme 1).[1] However, the formation of stoichiometric



Scheme 1. The Wittig reaction as the key step in the industrial production of β-carotene.[1d]

amounts of triphenylphosphane oxide (TPPO) is a major problem because there are very few applications for this by-product. The recycling of TPPO has been identified as a major factor for the economic efficiency of the Wittig reaction.[2] Although facilities for the recycling of TPPO have been installed[1b] and catalytic Wittig reactions are being developed,[3] most TPPO is still disposed of as waste.[1b] There is a persistent need for more efficient recycling methods and alternative applications of TPPO and other phosphane oxides, which motivates research in this field.[4]

Supplemented by academic research, which has been largely triggered by the development of new synthetic routes to tertiary phosphanes as ligands in transition-metal-mediated reactions, a plethora of reduction methods for functionalized phosphane oxides were developed.[5] Such methods are being continuously optimized towards better cost efficiency, higher yields, and more viable reaction conditions. Notably, the reduction of phosphane oxides still represents the only major exception to the paradigm that the phosphoryl group generally resists chemical transformations.[6a] Alternative, nonreductive transformations of the resistant P–O bond of phosphane oxides are sought and are addressed in this contribution.[5m]

The selective cleavage of the thermodynamically favoured P–O bond [$E(D)_{P-O} = 128–139$ kcal mol^{-1}][6a] in close vicinity to a much weaker P–C bond [$E(D)_{P-C} \approx 65$ kcal mol^{-1} for tetracoordinate phosphorus atoms][6b] is a major challenge. More than half a century after the Wittig reaction gained industrial importance,[7] examples of such transformations are still extremely rare (Scheme 2). Phosphane oxides can be transformed into the corresponding dihalophosphoranes (Scheme 2a) by reacting them with Group IV–VI halides and oxyhalides (e.g., thionyl chloride,[8] phosphoryl chloride,[9] phosphorus pentachloride,[10] oxalyl chloride,[11] diphosgene,[11] and phosgene[12]) to implement reactive P–Cl bonds. Phosphane sulfides (strong P–O vs. weak P–S bonds) have been obtained from the corresponding oxides upon reaction with P_4S_{10},[13,5l] Lawesson's reagent,[14] or related derivatives[15] (Scheme 2b)[5l]. Iminophosphoranes are intermediates in the industrial manufacturing of carbodiimides from isocyanates with phosphane oxides as catalysts;[16] these highly reactive intermediates are only isolable in rare cases.

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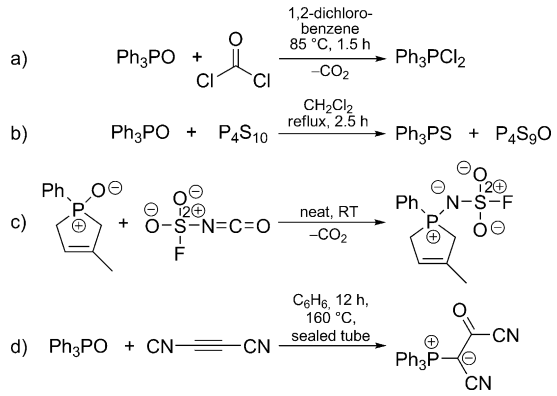


Scheme 2. Selected examples for the transformation of phosphane oxides.

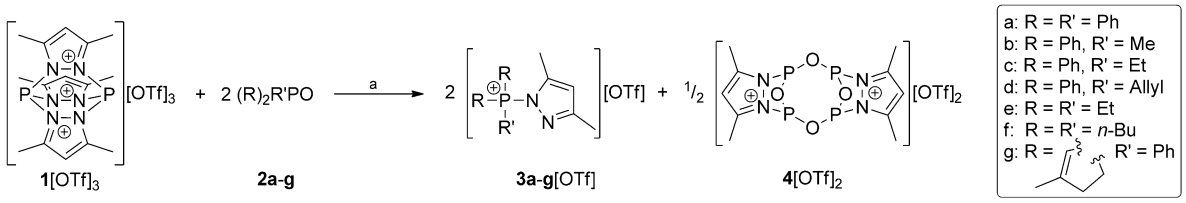
The example shown in Scheme 2c, represents one of the very rare cases for which a P–O bond is substituted by a much weaker P–N bond.[17] A reversed Wittig reaction to form an ylide is observed when dicyanoalkyne is reacted with TPPO at elevated temperatures in benzene to exchange a P–O bond for a P–C bond (Scheme 2d).[18]

Herein, we report a versatile and attractive concept to easily obtain value-added products from unreactive phosphane oxides. This novel approach uses the recently reported Janus head type diphosphorus trication $\mathbf{1}^{3+}$ (Scheme 3), which is easily accessible in one step and on a large scale from comparably cheap and commercially available starting materials. In previous work we showed that trication $\mathbf{1}^{3+}$ exhibited very unusual reactivity towards water.[19] We have now found that trication $\mathbf{1}^{3+}$ is highly oxophilic and can be used for the facile and clean transformation of phosphane oxides **2a**–**g** into pyrazolylphosphonium cations **3a**–**g**$^{+}$ under very smooth reaction conditions at room temperature. This approach allows the transformation of the P–O bond in phosphane oxides into a much more reactive P–N bond and offers a convenient protocol for the transformation of functional phosphane oxides. The resulting pyrazolylphosphonium triflate salts **3a**–**g**[OTf] can be easily isolated in quantitative yields and a series of selected transformation reactions prove their utility as precursors for further syntheses.

Results and Discussion

The reaction of TPPO (**2a**) with **1**[OTf]$_3$ in CH_2Cl_2 in a ratio of 2:1 at ambient temperature resulted in the formation of a colourless precipitate, which was isolated by filtration in quantitative yield and identified as analytically pure **4**[OTf]$_2$ (Scheme 3).[19,20] Compound **4**[OTf]$_2$ itself represents a very viable reagent, however, its applicability will be addressed elsewhere. By-product **4**[OTf]$_2$ can be conveniently hydrolyzed with water to quantitatively yield 3,5-dimethylpyrazolium triflate and P_4O_6, which can be easily separated. Oxidation of P_4O_6 with O_2 to P_4O_{10} and subsequent reaction with water yields pure H_3PO_4. After removal of the solvent from the filtrate, the colourless residue obtained was investigated by means of multinuclear NMR spectroscopy in CD_2Cl_2. The $^{31}P\{^1H\}$ NMR spectrum exclusively displayed a singlet ($\delta =$ 41.3 ppm) at lower field than that of **2a** ($\delta = 26.0$ ppm)[21] The ^1H NMR spectrum showed only one set of resonances, revealing the presence of phenyl groups and an asymmetrically substituted 3,5-dimethylpyrazolyl fragment ($\delta = 7.97$ (m, 3H), 7.79 (m, 6H), 7.71 (m, 6H), 6.37 (d, ^4J(H,P) = 3.2 Hz, 1H), 2.29 (s, 3H), 1.75 ppm (d, ^4J(H,P) = 0.7 Hz, 3H). In accordance with the results from the ^{13}C and ^{19}F NMR spectroscopy investigations, the formation of triphenyl-3,5-dimethyl-1-pyrazolyl-phosphonium triflate (**3a**[OTf]; Scheme 3) was deduced. Compound **3a**[OTf] was obtained in quantitative yield and was analytically pure without the need for further purification. Suitable crystals for X-ray single-crystal structure determination were obtained by slow diffusion of *n*-hexane into a CH_2Cl_2 solution at low temperatures (−32 °C).[20] In cation **3a**$^{+}$ (Figure 1) the coordination sphere at the phosphorus atom possesses almost ideal tetrahedral geometry (angles span 108.2(9)–111.2(1)°). The P–N bond length (1.683(2) Å) is in the typical range of P(tetravalent)–N(sp^2) bonds if the P atom is tetravalent (e.g., $[(PMe_3)_2NH]^{2+}$ 1.655 and 1.661 Å;[22] [*t*Bu$_2$P(H)pyrrole]$^{+}$ 1.669 Å;[23] Ph$_2$P(BH$_3$)pyrrole 1.711 Å;[24] and $[PMe_3DMAP]^{2+}$, DMAP = 4-dimethylaminopyridine, 1.720 Å[25]) and does not significantly depend on the substituents on phosphorus (compare **3c**$^{+}$ and **3e**$^{+}$; Figure 1; see the Supporting Information for further details and natural bond orbital analysis of **3a**$^{+}$). We extended our approach to a series of phosphane oxides (Scheme 3). Under identical conditions, compounds **2b**–**g** were transformed into the corresponding pyrazolylphosphonium salts **b**–**g**[OTf] in only moderate purity (90%). Further purification reduced the yields drastically. However, by applying a slight excess of **1**[OTf]$_3$ (1.1 equiv),[20] phosphonium salts **3b**–**g**[OTf] were obtained in quantitative yields in satisfying purities (>97%) after filtration and removal of the solvent. To the best of our knowledge, only derivative **3b**[I] has been described in the literature and was prepared in very low yield (28%) from (3,5-dimethylpyrazolyl)diphenylphosphane and a 25-fold excess of MeI.[26]

Having prepared pyrazolylphosphonium salts **3a**–**g**[OTf] on a multigram scale, we proceeded to investigate the synthetic potential of this class of compounds, which had not been as-



Scheme 3. Preparation of pyrazolylphosphonium salts **3a**–**g**[OTf]. a: CH_2Cl_2, ambient temperature, 15–20 h.[31]

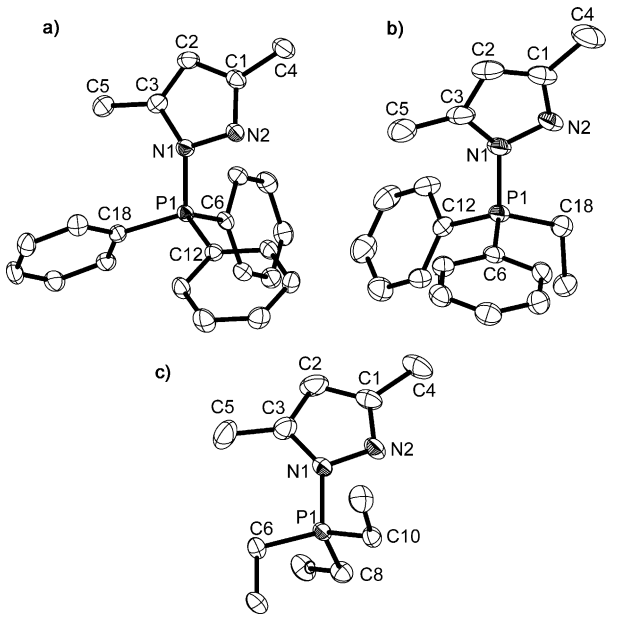
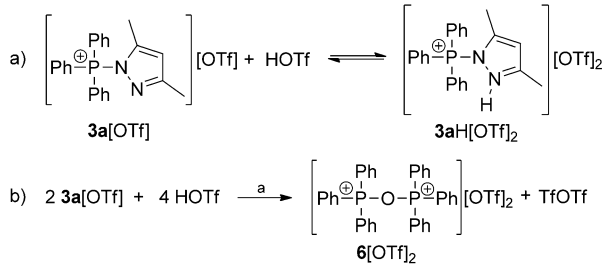


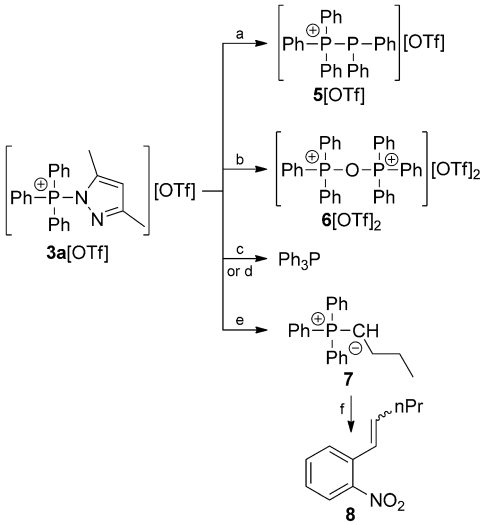
Figure 1. ORTEP plot of the molecular structures of cations a) $\mathbf{3a}^+$, b) $\mathbf{3c}^+$ and c) $\mathbf{3e}^+$ in **3a**[OTf], **3c**[OTf], and **3e**[OTf], respectively. Thermal ellipsoids are drawn at the 50% probability level (hydrogen atoms and counterions are omitted for clarity). Selected bond lengths [Å] and angles [°]: $\mathbf{3a}^+$: P1–N1 1.683(2); N1-P1-C6 108.16(9), N1-P1-C12 109.86(8), N1-P1-C18 108.26(9), C6-P1-C12 109.52(9), C6-P1-C18 110.74(9), C12-P1-C18 110.26(9); $\mathbf{3c}^+$: P1–N1 1.688(2); N1-P1-C6 110.7(1), N1-P1-C12 108.6(1), N1-P1-C18 106.5(1), C6-P1-C12 110.7(1), C6-P1-C18 111.0(1), C12-P1-C18 109.2(1); $\mathbf{3e}^+$: P1–N1 1.683(2); N1-P1-C6 106.4(1), N1-P1-C8 108.1(1), N1-P1-C10 109.0(1), C6-P1-C8 109.6(1), C6-P1-C10 110.6(1), C8-P1-C10 113.0(1).

sessed previously. We found that phosphonium cation $\mathbf{3a}^+$ was prone to nucleophilic substitution of the pyrazole moiety, that is, it served well as the synthetic equivalent of a $[R_3P^{2+}]$ synthon. Treating **3a**[OTf] with diphenylphosphane or **2a** in the presence of trifluoromethanesulfonic acid (HOTf) gave phosphanylphosphonium salt **5**[OTf] (79%) and phosphonium anhydride $\mathbf{6}[OTf]_2$ (83%), respectively, in very good yields (Scheme 5). The addition of HOTf is necessary to sequester the 3,5-dimethylpyrazole moiety into 3,5-dimethylpyrazolium triflate. 3,5-Dimethylpyrazole may otherwise act as a nucleophile and initiate side reactions.[32] Furthermore, protonation of monocation $\mathbf{3a}^+$ to dication $\mathbf{3a}H^{2+}$ may also occur under these conditions (Scheme 4). Quantum chemical calculations



Scheme 4. a) Hypothetical protonation of monocation $\mathbf{3a}^+$ and b) observed reaction of **3a**[OTf] with HOTf; a: 1,2-difluorobenzene, RT, −2 3,5-dimethylpyrazolium triflate, 86% isolated yield of $\mathbf{6}[OTf]_2$.

[B3LYP/6-311G(2d)][27] show that protonation of the free lone pair of the pyrazole moiety in $\mathbf{3a}^+$ (gas-phase proton affinity of $\mathbf{3a}^+$: 160.3 kcal mol^{-1})[28] leads to weakening of the P–N bond. The optimized molecular structure of $\mathbf{3a}H^{2+}$ features a significantly longer P–N bond (1.7699 Å) than that in $\mathbf{3a}^+$ (calcd: 1.6998 Å, exptl: 1.683(2) Å) and a smaller Wiberg bond index[29] ($\mathbf{3a}^+$: WBI = 0.7785; $\mathbf{3a}H^{2+}$: WBI = 0.6708). Hence, the addition of a Brønsted acid renders the pyrazol moiety an excellent leaving group. Attempts to isolate $\mathbf{3a}H[OTf]_2$ from reaction mixtures containing **3a**[OTf] and HOTf failed. Instead, we were able to verify the formation of phosphonium anhydride $\mathbf{6}[OTf]_2$ (isolated yield 86%) and trifluoromethanesulfonic anhydride (Scheme 4, bottom) in excellent yields. The latter originates from the dehydration of HOTf, the oxygen atom of which is transferred to form phosphonium anhydride $\mathbf{6}[OTf]_2$. Furthermore, compound **3a**[OTf] could be reduced to TPP electrochemically (Scheme 5). A cyclic voltammogram of **3a**[OTf]



Scheme 5. Preparation of phosphanylphosphonium salt **5**[OTf], bis(triphenylphosphonium) anhydride $\mathbf{6}[OTf]_2$, Ph_3P, ylide **7**, and alkene **8** from **3a**[OTf]. a) HOTf, Ph_2PH, − 3,5-dimethylpyrazolium triflate, CH_2Cl_2, RT, 12 h, 79%; b) Ph_3PO, 2 HOTf, − 3,5-dimethylpyrazolium triflate, CH_2Cl_2, RT, 12 h 83%; c) galvanostatic electrolysis: 25 mA, 2.86 mA cm^{-2}, Pt mesh, divided cell; d) $LiAlH_4$, Et_2O, RT, 48 h, 90%; e) 2 *n*BuLi, − lithium 3,5-dimethylpyrazolate, Et_2O, −95 °C→RT, 4 h; f) 2-nitrobenzaldehyde, − **2a**, RT, 12 h, 74%.

showed a single irreversible peak at −2.11 V (CH_3CN, supporting electrolyte [*n*Bu_4N][OTf], Pt electrode, 0.1 V s^{-1}, range: −2.3 to −0.5 V, referenced to ferrocene). Galvanostatic electrolysis (25 mA, 2.86 mA cm^{-2}, Pt mesh, divided cell) afforded conversion to TPP, as confirmed by NMR spectroscopy.[31] As anticipated, compound **3a**[OTf] was also cleanly reduced to TPP with $LiAlH_4$ in Et_2O (90% yield).[30,31] In addition, we could also demonstrate that the reaction of **3a**[OTf] with two equivalents of *n*BuLi (Scheme 5) gave ylide **7** quantitatively in solution. Addition of 2-nitrobenzaldehyde resulted in the formation of alkene **8** (74% yield, 7:3 ratio of Z to E isomer) through a Wittig reaction.[31]

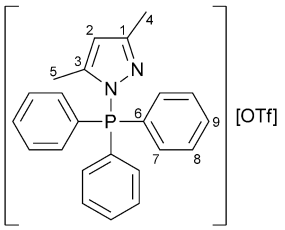
Conclusion

We have developed a versatile method for the conversion of phosphane oxides into pyrazolylphosphonium cations, which were shown to be valuable synthetic intermediates amenable to a number of subsequent transformations to a variety of organophosphorus compounds. Our protocol enables the clean transformation of the P–O bond in phosphane oxides into a much more reactive P–N bond under very mild reaction conditions at room temperature. The resulting pyrazolylphosphonium triflate salts are easily isolated in quantitative yields. This represents a new approach towards the transformation of the rather inert phosphoryl group and aims to provide alternatives to existing reduction methods for phosphane oxide functionalization. Furthermore, our protocol might also be applicable to the transformation of functional phosphane oxides by providing a novel synthetic route to tertiary phosphanes, which are used as ligands in transition metal-mediated reactions. A detailed investigation to address this aspect is currently underway.

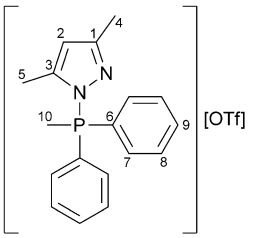
Experimental Section

All reactions were performed in a glove box or by using standard Schlenk techniques under an inert Ar atmosphere. Dry, oxygen-free solvents were employed. Compound **1**$[OTf]_3$ was prepared according to a previously described method.[19] All phosphane oxides were sublimed prior to use. All new compounds were fully characterized by ^{31}P, ^{1}H, ^{19}F, and ^{13}C NMR spectroscopy; Raman and IR spectroscopy; mass spectrometry; melting points; and elemental analyses. NMR spectra were measured on a Bruker AVANCE 400 spectrometer (^{1}H: 400.03 MHz; ^{13}C: 100.59 MHz; ^{31}P: 161.94 MHz) at 300 K. Chemical shifts were referenced to tetramethylsilane (TMS) or H_3PO_4 (85%). Assignments of individual resonances were possible by using 2D techniques (HMBC, HSQC) and phosphorus-decoupled proton NMR spectroscopy investigations ($^{1}H\{^{31}P\}$) if necessary. IR and Raman spectra were recorded by using a Bruker Vertex 70 instrument equipped a RAM II module. An attenuated total reflectance (ATR) unit (diamond) was used to record IR spectra. The intensities are reported relative to the most intense peak. Raman spectra were obtained by employing an Nd:YAG laser (1064 nm, 10–200 mW). The intensities are reported in percent relative to the most intense peak and are given in parentheses. Mass spectra were recorded on a Thermo Scientific Orbitrap LTQ XL instrument at the Organisch-Chemisches Institut, WWU Münster. Parent cations were separated and fragmented by using appropriate potentials to obtain high-resolution mass data of the fragment cations. Melting points were recorded on a thermoelectric melting point apparatus in sealed capillaries under an argon atmosphere. Elemental analyses were performed on a Vario EL III CHNS elemental analyzer at the IAAC, University of Münster

General procedure for preparation of compounds **3a**–**g**[OTf]: A solution of phosphane oxide (3.00 mmol, 2 equiv) in CH_2Cl_2 (10 mL) was added to a suspension of **1**$[OTf]_3$ (1.311 g, 1.65 mmol, 1.1 equiv) in CH_2Cl_2 (20 mL). The resulting pale yellow solution was stirred for 15 h at ambient temperature. Precipitate **4**$[OTf]_2$ was filtered off. The reaction of tri-*n*-butylphosphane oxide required an additional reaction time of 5 h. After removal of all volatile compounds from the filtrate in vacuo, the targeted pyrazolylphosphonium salts **3a**–**g**[OTf] were obtained in quantitative yield.

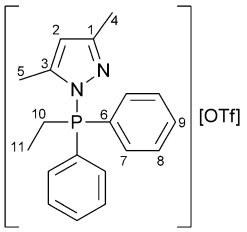


Synthesis of **3a**[OTf]: Compound **3a**[OTf] was prepared according to the general procedure; however, excess **1**$[OTf]_3$ was not required. A 2:1 stoichiometry of **2a**/**1**$[OTf]_3$ was applied. Typically, this reaction was performed on a scale of 10 mmol of **1**$[OTf]_3$ or more. M.p. 148–151 °C; ^{1}H NMR (CD_2Cl_2, 300 K): $\delta = 7.97$ (m, 3H; C9-H), 7.79 (m, 6H; C8-H), 7.71 (m, 6H; C7-H), 6.37 (d, $^{4}J(H,P) = 3.2$ Hz, 1H; C2-H), 2.29 (s, 3H; C4-H), 1.75 ppm (d, $^{4}J(H,P) = 0.7$ Hz, 3H; C5-H); ^{13}C NMR (CD_2Cl_2, 300 K): $\delta = 159.0$ (d, $^{3}J(C,P) = 12.9$ Hz, 1C; C1), 150.3 (d, $^{2}J(C,P) = 7.6$ Hz, 1C; C3), 137.2 (d, $^{4}J(C,P) = 3.1$ Hz, 3C; C9), 134.9 (d, $^{2}J(C,P) = 11.6$ Hz, 6C; C7), 131.0 (d, $^{3}J(C,P) = 13.9$ Hz, 6C; C8), 121.4 (q, $^{1}J(C,F) = 321.7$ Hz, 1C; CF_3), 118.0 (d, $^{1}J(C,P) = 102.4$ Hz, 3C; C6), 114.9 (d, $^{3}J(C,P) = 5.5$ Hz, 1C; C2), 14.0 (s, 1C; C4), 13.7 ppm (s, 1C; C5); ^{31}P NMR (CD_2Cl_2, 300 K): $\delta = 41.3$ ppm; $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2, 300 K): $\delta = -78.8$ ppm (s, CF_3); Raman (300 mW, 300 K): 3074 (56), 2994 (6), 2929 (23), 1587 (77), 1480 (6), 1437 (13), 1226 (5), 1189 (7), 1101 (21), 1029 (55), 1000 (100), 755 (16), 696 (14), 616 (19), 585 (9), 573 (14), 349 (14), 314 (16), 282 (9), 266 (6), 250 (14), 207 (9), 179 cm^{-1} (10); IR (300 K, ATR): $\tilde{\nu} = 2961$ (w), 1611(w), 1581 (m), 1482 (w), 1440 (s), 1410 (w), 1376 (w), 1259 (vs), 1223 (w), 1146 (w), 1110 (m), 1028 (m), 996 (w), 960 (w), 821 (w), 755 (w), 726 (s), 687 (m), 635 (m), 571 (m), 534 (w), 515 (m), 475 (vw), 437 (vw), 425 cm^{-1} (w); MS (ESI-EM): *m/z* calcd for $C_{23}H_{22}N_2P$ [M^+]: 357.15151; found: 357.1512; *m/z* calcd for $C_{18}H_{15}P$ [M^+ −3,5-dimethylpyrazole radical]: 262.0906; found: 262.0903; *m/z* calcd for $C_{12}H_{10}P$ [$M+$ −3,5-dimethylpyrazole radical−phenyl radical]: 185.0515; found: 185.0511; elemental analysis calcd (%) for $C_{24}H_{22}F_3N_2O_3PS$: C 56.98, H 4.38, N 5.53; found: C 56.78, H 4.30, N 5.94.



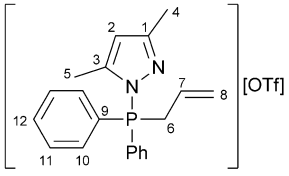
Synthesis of **3b**[OTf]: M.p. 133–136 °C; ^{1}H NMR (CD_2Cl_2, 300 K): $\delta =$ 7.94 (m, 2H; C9-H), 7.77 (m, 4H; C8-H), 7.67 (m, 4H; C7-H), 6.29 (d, $^{4}J(H,P) = 2.8$ Hz, 1H; C2-H), 3.08 (d, $^{3}J(H,H) = 13.4$ Hz, 2H; C10-H), 2.30 (s, 3H; C4-H), 1.82 ppm (3H; C5-H); ^{13}C NMR (CD_2Cl_2, 300 K): $\delta =$ 158.2 (d, $^{3}J(C,P) = 13.0$ Hz, 1C; C1), 149.1 (d, $^{2}J(C,P) = 7.6$ Hz, 1C; C3), 136.6 (d, $^{4}J(C,P) = 3.0$ Hz, 2C; C9), 132.8 (d, $^{2}J(C,P) = 12.0$ Hz, 4C; C7), 130.7 (d, $^{3}J(C,P) = 13.9$ Hz, 4C; C8), 120.9 (q, $^{1}J(C,F) = 321.2$ Hz, 1C; CF_3), 118.1 (d, $^{1}J(C,P) = 98.4$ Hz, 2C; C6), 114.2 (d, $^{3}J(C,P) = 5.1$ Hz, 1C; C2), 13.5 (s, 1C; C4), 12.9 (d, $^{1}J(C,P) =$ 68.6 Hz, 1C; C10), 12.8 ppm (s, 1C; C5); ^{31}P NMR (CD_2Cl_2, 300 K): $\delta = 49.3$ ppm; $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2, 300 K): $\delta = -78.9$ ppm (s, CF_3); Raman (60 mW, 300 K): 3069 (52), 3031 (9), 2937 (26), 2918 (8), 1590 (45), 1576 (10), 1440 (11), 1227 (8), 1191 (8), 1164 (8), 1116 (22), 1032 (66), 1020 (7), 999 (100), 757 (22), 694 (21), 615 (25), 585 (16), 574 (6), 553 (8), 384 (5), 350 (21), 316 (18); IR (300 K, ATR): $\tilde{\nu} = 3073$ (vw), 1581 (m), 1482 (w), 1440 (s), 1408 (w), 1376 (w), 1259 (vs), 1224 (w), 1193 (w), 1145 (w), 1110 (m), 1066 (w), 1029 (m), 996 (w), 960 (w), 821 (m), 756 (w), 727 (vs), 687 (s), 635 cm^{-1} (s); MS (ESI-EM): *m/z* calcd for $C_{18}H_{20}N_2P$ [M^+]: 295.13586; found: 295.13559; *m/z* calcd. for $C_{14}H_{14}P$ [M^+ −3,5-dimethylpyrazole]: 199.06711; found: 199.06675.

Synthesis of **3c**[OTf]: M.p. 82–85 °C; ^{1}H NMR (CD_2Cl_2, 300 K): $\delta =$ 7.93 (m, 2H; C9-H), 7.78 (m, 4H; C8-H), 7.70 (m, 4H; C7-H), 6.30 (dq, $^{4}J(H,P) = 2.4$ Hz, $^{4}J(H,H) = 0.7$ Hz, 1H; C2-H), 3.43 (dq, $^{3}J(H,H) =$



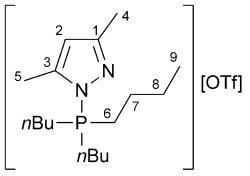
7.4 Hz, ^{2}J(H,P) = 13.2 Hz, 2H; C10-H), 2.32 (s, 3H; C4-H), 1.79 (d, ^{4}J(H,P) = 0.7 Hz, 3H; C5-H), 1.43 ppm (dt, ^{3}J(H,H) = 7.4 Hz, ^{3}J(H,P) = 21.9 Hz, 3H; C11-H); ^{13}C NMR (CD_2Cl_2, 300 K): δ = 158.5 (d, ^{3}J(C,P) = 12.3 Hz, 1C; C1), 149.3 (d, ^{2}J(C,P) = 6.3 Hz, 1C; C3), 136.9 (d, ^{4}J(C,P) = 3.1 Hz, 2C; C9), 133.4 (d, ^{2}J(C,P) = 11.5 Hz, 4C; C7), 131.1 (d, ^{3}J(C,P) = 13.2 Hz, 4C; C8), 121.2 (q, ^{1}J(C,F) = 320.8 Hz, 1C; CF_3), 117.1 (d, ^{1}J(C,P) = 94.5 Hz, 2C; C6), 114.4 (d, ^{3}J(C,P) = 5.4 Hz, 1C; C2), 21.2 (d, ^{1}J(C,P) = 61.8 Hz, 1C; C10), 13.8 (s, 1C; C4), 13.3 (s, 1C; C5), 6.7 ppm (d, ^{2}J(C,P) = 5.3 Hz, 1C; C11); ^{31}P NMR (CD_2Cl_2, 300 K): δ = 51.8 ppm; ^{19}F{^{1}H} NMR (CD_2Cl_2, 300 K): δ = −78.9 ppm (s, CF_3); Raman (81 mW, 300 K): 3063 (67), 2937 (59), 2899 (8), 1589 (62), 1579 (5), 1443 (13), 1225 (11), 1194 (11), 1163 (9), 1115 (40), 1033 (80), 998 (100), 755 (32), 686 (29), 616 (34), 585 (22), 574 (8), 545 (14), 348 (22), 313 (28), 264 cm^{-1} (13); IR (300 K, ATR): $\tilde{\nu}$ = 3065 (vw), 2929 (w), 1580 (m), 1440 (m), 1408 (w), 1258 (vs), 1222 (w), 1145 (m), 1118 (w), 1075 (w), 1028 (s), 996 (w), 961 (m), 844 (w), 747 (m), 689 (m), 634 cm^{-1} (vs); MS (ESI-EM): *m/z* calcd for $C_{19}H_{22}N_2P$ [M^+]: 309.1515; found: 309.1512; *m/z* calcd. for $C_{14}H_{14}P$ [M^+−3,5-dimethylpyrazole]: 213.0828; found: 213.0823, *m/z* calcd for C_8H_8P [M^+−3,5-dimethylpyrazole−benzene]: 135.0358; found: 135.0355.

Synthesis of **3d**[OTf]: M.p. liquid at RT; ^{1}H NMR (CD_2Cl_2, 300 K): δ = 7.94 (m, 2H; C12-H), 7.77 (m, 4H; C11-H), 7.68 (m, 4H; C10-H), 6.31 (m, ^{4}J(H,P) = 2.8 Hz, coupling to C4-H and C5-H not resolved, 1H; C2-H), 5.84 (m, 1H; C7-H), 5.40–5.49 (m, 2H; C8-H), 4.29 (m, 1H; C6), 2.34 (s, 3H; C4-H), 1.74 ppm (d, ^{4}J(H,H) = 1.0 Hz, 3H; C5-H); ^{13}C NMR (CD_2Cl_2, 300 K): δ = 158.7 (d, ^{3}J(C,P) = 12.6 Hz, 1C; C1), 149.6 (d, ^{2}J(C,P) = 6.1 Hz, 1C; C3), 137.1 (d, ^{4}J(C,P) = 3.0 Hz, 2C; C12), 133.7 (d, ^{2}J(C,P) = 10.7 Hz, 4C; C10), 131.1 (d, ^{3}J(C,P) = 13.7 Hz, 4C; C11), 127.1 (d, ^{3}J(C,P) = 14.6 Hz, 1C; C8), 122.8 (d, ^{2}J(C,P) = 10.0 Hz, 1C; C7), 121.1 (q, ^{1}J(C,F) = 322.1 Hz, 1C; CF_3), 116.9 (d, ^{1}J(C,P) = 94.2 Hz, 2C; C9), 114.6 (d, ^{3}J(C,P) = 5.3 Hz,1C; C2), 32.7 (s, ^{1}J(C,P) = 60.8 Hz, 1C; C6), 13.9 (s, 1C; C4), 13.3 ppm (s, 1C; C5); ^{31}P NMR (CD_2Cl_2, 300 K): δ = 45.2 ppm (s); ^{19}F{^{1}H} NMR (CD_2Cl_2, 300 K): δ = −78.9 ppm (s, CF_3); Raman (100 mW, 300 K): 3067 (34), 2934 (25), 1637 (18), 1589 (36), 1440 (9), 1307 (5), 1224 (7), 1165 (8), 1111 (15), 1031 (61), 999 (100), 756 (19), 701 (11), 616 (15), 586 (16), 348 (17), 313 (14), 252 cm^{-1} (7); IR (300 K, ATR): $\tilde{\nu}$ = 2930 (w), 2361 (w), 1580 (w), 1440 (m), 1408 (w), 1258 (vs), 1222 (w), 1146 (m), 1118 (w), 1076 (vw), 1027 (vs), 996 (w), 962 (m), 834 (w), 742 (m), 727 (w), 688 (m), 645 (vs), 571 (vw), 551 (w), 516 (m), 500 (vw), 450 cm^{-1} (vw); MS (ESI-EM): *m/z* calcd for $C_{20}H_{22}N_2P$ [M^+]: 321.1515; found: 321.1497; *m/z* calcd for $C_{15}H_{14}P$ [M^+−3,5-dimethylpyrazole]: 225.0828; found: 225.0812.



Synthesis of **3e**[OTf]: M.p. 55–58 °C; ^{1}H NMR (CD_2Cl_2, 300 K): δ = 6.20 (d, ^{4}J(H,P) = 2.4 Hz, 1H; C2-H), 2.80 (dq, ^{3}J(H,H) = 7.6 Hz, ^{2}J(H,P) = 11.8 Hz, 6H; C6-H), 2.49 (s, 3H; C5-H), 2.24 (s, 3H; C4-H), 1.28 ppm (dt, ^{3}J(H,H) = 7.6 Hz, ^{3}J(H,P) = 20.3 Hz, 9H; C7-H); ^{13}C NMR (CD_2Cl_2, 300 K): δ = 157.7 (d, ^{3}J(C,P) = 11.2 Hz, 1C; C1), 148.0 (d, ^{2}J(C,P) = 6.2 Hz, 1C; C3), 121.2 (q, ^{1}J(C,F) = 321.1 Hz, 1C; CF_3), 113.8 (d, ^{4}J(C,P) = 5.2 Hz, 1C; C2), 16.0 (d, ^{1}J(C,P) = 54.1 Hz, 3C; C6), 13.7 (s, 1C; C4), 13.0 (s, 1C; C5), 5.6 ppm (d, ^{2}J(C,P) = 5.5 Hz, 3C; C7); ^{31}P NMR (CD_2Cl_2, 300 K): δ = 79.0 ppm (1P); ^{19}F{^{1}H} NMR (CD_2Cl_2, 300 K): δ = −78.9 ppm (s, CF_3); Raman (80 mW, 300 K): 2993 (17), 2970 (7), 2.952 (10), 2932 (100), 2.894 (8), 2761 (8), 1576 (5), 1467 (26), 1442 (6), 1392 (7), 1225 (13), 1064 (7), 1032 (77), 978 (9), 758 (28), 650 (22), 584 (32), 522 (18), 441 (7), 348 (37), 315 cm^{-1} (20); IR (300 K, ATR): $\tilde{\nu}$ = 2969 (w), 2931 (m), 1612 (vw), 1575 (m), 1467 (w), 1408 (m), 1315 (vw), 1303 (w), 1258 (vs), 1223 (w), 1150 (m), 1085 (w), 1026 (s), 961 (m), 872 (w), 811 (w), 793 (s), 766 (m), 731 (m), 635 cm^{-1} (m); MS (ESI-EM): *m/z* calcd for $C_{11}H_{22}N_2P$ [M^+]: 213.15151; found: 213.15117; *m/z* calcd for $C_6H_{14}P$ [M^+−3,5-dimethylpyrazole]: 117.08276; found: 117.08239. Single crystals suitable for single-crystal X-ray analysis were obtained by slow diffusion of Et_2O into a solution of **3e**[OTf] in CH_2Cl_2.

Synthesis of **3f**[OTf]: M.p. oil at RT; ^{1}H NMR (CD_2Cl_2, 300 K): δ = 6.20 (d, ^{4}J(H,P) = 2.4 Hz, 1H; C2-H), 2.74 (m, 6H; C6-H), 1.54 (m, 6H; C7-H), 1.50 (m, 6H; C8–H), 0.95 ppm (t, ^{3}J(H,H) = 7.1 Hz, 9H; C9-H), 2.48 (3H, s, C5–H), 2.24 (3H, s, C4–H); ^{13}C NMR (CD_2Cl_2, 300 K): δ = 157.4 (d, ^{3}J(C,P) = 11.3 Hz, 1C; C1), 147.7 (d, ^{2}J(C,P) = 6.5 Hz, 1C; C3), 121.3 (q, ^{1}J(C,F) = 320.7, 1C; CF_3), 113.8 (d, ^{3}J(C,P) = 5.0 Hz, 1C; C2), 23.9 (d, ^{3}J(C,P) = 16.7 Hz, 3C; C8), 23.5 (d, ^{2}J(C,P) = 4.7 Hz, 3C; C7), 22.6 (d, ^{1}J(C,P) = 52.4 Hz, 3C; C6), 13.4 ppm (s, 3C; C9); ^{31}P NMR (CD_2Cl_2, 300 K): δ = 73.5 ppm (s); ^{19}F{^{1}H} NMR (CD_2Cl_2, 300 K): δ = −78.9 ppm (s, CF_3); Raman (80 mW, 300 K): 3112 (5), 2937 (100), 2876 (25), 1449 (30), 1302 (7), 1224 (12), 1101 (7), 1051 (8), 1031 (91), 868 (8), 755 (32), 587 (24), 574 (8), 348 (21), 312 cm^{-1} (16); IR (300 K, ATR): $\tilde{\nu}$ = 2963 (w), 2935 (vw), 2875 (w), 2361 (w), 1577 (w), 1465 (w), 1408 (w), 1256 (vs), 1222 (w), 1150 (s), 1099 (vw), 1079 (w), 1028 (s), 967 (w), 903 (w), 832 (w), 778 (vw), 755 (w), 718 (w), 636 (vs), 573 (w), 516 (m), 449 cm^{-1} (w); MS (ESI-EM): *m/z* calcd for $C_{17}H_{34}N_2P$ [M^+]: 297.2454; found: 297.2445; *m/z* calcd. for $C_{12}H_{26}P$ [M^+−3,5-dimethylpyrazole]: 201.1767; found: 201.1760; *m/z* calcd for $C_8H_{18}P$ [M^+−3,5-dimethylpyrazole−butene]: 145.1141; found: 145.1136.



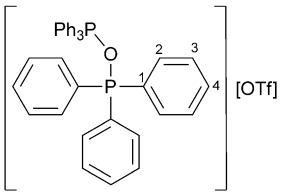
Synthesis of **3g**[OTf]: M.p. 49–52 °C; ^{1}H NMR (CD_2Cl_2, 300 K): δ = 7.83 (m, 2H; C9-H), 7.67 (m, 4H; C8-H), 7.62 (m, 4H; C7-H), 6.58 (ddt, pseudo sext, ^{2}J(H,P) = 30.6 Hz, ^{4}J(H,H) = 1.5 Hz, ^{4}J(H,H) = 1.5 Hz, 1H; C10-H), 6.23 (dt, ^{4}J(P,H) = 2.4 Hz, ^{4}J(H,H) = 0.7 Hz, 1H; C2-H), 3.71 (dddd, ^{2}J(H,H) = 16.3 Hz, ^{2}J(H,P) = 16.3 Hz, ^{3}J(H,H) = 8.3 Hz, ^{3}J(H,H) = 2.7 Hz, 1H; C13-H), 3.34 (dddd, broad, $\nu_{1/2}$ = 6.2 Hz, ^{3}J(H,P) = 17.8 Hz, ^{2}J(H,H) = 17.8 Hz ^{3}J(H,H) = 9.2 Hz, second ^{3}J(H,H) is not resolved, 1H; C12-H), 3.22 (m, 1H; C12-H), 3.13 (dddd, ^{2}J(H,H) = 16.3 Hz, ^{2}J(H,P) = 6.7 Hz, ^{3}J(H,H) = 9.2 Hz, ^{3}J(H,H) = 4.6 Hz, 1H; C13-H), 2.37 (s, 3H, C14-H), 2.29 (s, 3H, C4-H), 2.18 ppm (d ^{4}J(H,H) = 0.7 Hz, 3H; C5-H); the assignment of the coupling constants was confirmed by a ^{1}H{^{31}P} spectrum; ^{13}C NMR (CD_2Cl_2, 300 K): δ = 183.2 (d, ^{2}J(C,P) = 27.5 Hz, 1C; C14), 158.1 (d, ^{3}J(C,P) = 12.2 Hz, 1C; C1), 148.0 (d, ^{2}J(C,P) = 7.3 Hz, 1C; C3), 136.6 (d, ^{4}J(C,P) = 3.4 Hz, 1C; C19), 132.4 (d, ^{2}J(C,P) = 12.9 Hz, 2C; C7), 130.8 (d, ^{3}J(C,P) = 14.5 Hz, 2C; C8), 121.3 (q, ^{1}J(C,F) = 321.1 Hz, 1C; CF_3), 120.6 (d, ^{1}J(C,P) = 97.8 Hz, 1C; C6), 113.5 (d, ^{3}J(C,P) = 5.3 Hz, 1C; C2), 107.2 (d, ^{1}J(C,P) = 95.9 Hz, 1C; C10), 36.7 (d, ^{2}J(C,P) = 8.4 Hz, 1C; C12), 24.1

(d, ^1J(C,P) = 65.1 Hz, 1C; C13), 22.3 (d, ^3J(H,P) = 18.5 Hz, 1C; C14), 13.8 (s, 1C; C4), 12.8 ppm (s, 1C; C5); ^{31}P NMR (CD_2Cl_2, 300 K): δ = 77.3 ppm; ^{19}F{^{1}H} NMR (CD_2Cl_2, 300 K): $\delta = -78.9$ ppm (s, CF_3); Raman (300 mW, 300 K): 3107 (10), 3063 (53), 3002 (12), 2929 (69), 1591 (60), 1576 (8), 1480 (7), 1442 (22), 1396 (6), 1335 (6), 1303 (7), 1223 (10), 1126 (21), 1031 (86), 998 (100), 778 (7), 756 (31), 714 (18), 615 (22), 598 (13), 574 (16), 510 (6), 456 (6), 391 (6), 348 (20), 328 (7), 314 (23), 285 (8), 263 (14), 228 cm^{-1} (7); IR (300 K, ATR): $\tilde{\nu}$ = 3082 (w), 2930 (vw), 1593 (vw), 1577 (m), 1541 (vw), 1440 (m), 1410 (w), 1375 (w), 1333 (vw), 1260 (vs), 1222 (w), 1199 (vw), 1152 (m), 1124 (w), 1082 (w), 1028 (s), 997 (vw), 963 (m), 922 (w), 892 (m), 855 (w), 811 (w), 776 (w), 756 (s), 727 (w), 696 (w), 635 cm^{-1} (s); MS (ESI-EM): *m/z* calcd for $C_{16}H_{20}N_2P$ [M^+]: 271.1359; found: 271.1349; *m/z* calcd. for $C_{11}H_{12}P$ [M^+−3,5-dimethylpyrazole]: 175.0671; found: 175.0664.

Preparation of TPP from **3a**[OTf]: $LiAlH_4$ (0.19 g, 5.00 mmol) was added to a suspension of **3a**[OTf] (2.53 g, 5.00 mmol) in Et_2O (50 mL). The resulting suspension was stirred for 48 h and filtered. H_2O (15 mL) was added to the filtrate and the aqueous phase was extracted with Et_2O (2×5 mL). The combined organic layers were extracted with HCl (1 M, 10 mL), separated, and dried over $MgSO_4$. All volatile compounds were removed in vacuo. The colourless solid obtained (90%, 1180 mg) showed exclusively the resonances expected for Ph_3P in ^{31}P and ^{1}H NMR spectra.

Preparation of **5**[OTf] from **3a**[OTf]: HOTf (29.5 μL, 0.050 g, 0.33 mmol, 1 equiv) and Ph_2PH (58.0 μL, 0.062 g, 0.33 mmol, 1 equiv) were added successively to a solution of **3a**[OTf] (0.169 g, 0.33 mmol, 1 equiv) in CH_2Cl_2 (5 mL). The mixture was stirred overnight and all volatile compounds were removed in vacuo. The pale yellow solid obtained was dissolved in CH_2Cl_2 and precipitated by slow addition of Et_2O. The resulting suspension was filtered and the precipitate washed with Et_2O (3×2 mL) to give **5**[OTf] (79%, 157 mg). ^{1}H, ^{31}P, and ^{31}P{^{1}H} NMR spectroscopy investigations (CD_2Cl_2, 300 K) showed exclusively the resonances that were previously reported for **5**[OTf].[32]

Preparation of **6**[OTf]$_2$ from **3a**[OTf], Method A: A mixture of Ph_3PO (0.417 g, 1.50 mmol, 1 equiv) and **3a**[OTf] (0.760 g, 1.50 mmol, 1 equiv) were dissolved in CH_2Cl_2 (15 mL) and HOTf (0.266 mL, 0.450 g, 3.00 mmol, 2 equiv) was added dropwise. The mixture was stirred overnight at ambient temperature and reduced to two thirds of its original volume in vacuo. Slow addition of Et_2O gave a colourless precipitate, which was filtered off and washed with Et_2O (2×3 mL) and dried in vacuo. As characterization data for **6**[OTf]$_2$ has never been comprehensively reported, it is given below. X-ray structural analysis of suitable crystals obtained by slow diffusion of *n*-hexane into a solution of **6**[OTf]$_2$ in CH_2Cl_2 at −35 °C gave comparable results (a = 8.6199(4), b = 11.1712(5), c = 19.5323(8) Å; α = 94.6070(10), β = 93.0320(10), γ = 98.9920(10)°; V = 1847.64(14) Å^3) to those previously reported (a = 8.620(2), b = 11.193(3), c = 19.584(6) Å; α = 94.669(5), β = 92.894(5), γ = 99.068(7)°; V = 1856.0(9) Å^3).[33]



Preparation of **6**[OTf]$_2$ from **3a**[OTf], Method B: HOTf (0.354 mL, 0.600 g, 4.00 mmol, 2 equiv) was slowly added to a solution of **3a**[OTf] (1.013 g, 2.00 mmol, 1 equiv) in 1,2-difluorobenzene (10 mL). The reaction mixture was stirred for 24 h, resulting in the formation of a colourless precipitate. After filtration and washing with 1,2-difluorobenzene, the colourless residue (0.418 g) was identified as analytically pure **6**[OTf]$_2$ by means of multinuclear NMR spectroscopy experiments and elemental analysis. The filtrate was reduced to approximately 30% of its original volume. Addition of Et_2O resulted in the formation of a colourless precipitate. This material was isolated dissolved in CH_2Cl_2 and recrystallized by slow addition of Et_2O to yield a second batch of **6**[OTf]$_2$ (0.304 g). The formation of trifluoromethanesulfonic anhydride was confirmed by a ^{19}F NMR spectroscopy investigation of the supernatant of the reaction mixture (1,2-difluorobenzene/C_6D_6 capillary, 300 K). A singlet observed at $\delta = -73.0$ ppm increased in intensity upon addition of a commercial sample of trifluoromethanesulfonic anhydride (0.02 mL). Yield of **6**[OTf]$_2$ 86% (0.722 mg); m.p. > 295 °C (decomp.); ^{1}H NMR (CD_2Cl_2, 300 K): δ = 7.96 (m, 6H; C4-H), 7.72 ppm (m, 24H; C2-H, C3-H); ^{13}C NMR (CD_2Cl_2, 300 K): δ = 138.7 (s, 6C; C4), 134.9 (d, ^2J(C,P) = 11.9 Hz, 12C; C2), 131.6 (d, ^2J(C,P) = 14.1 Hz, 12C; C3), 121.2 (q, ^1J(C,F) = 320.5 Hz, 6C; CF_3), 116.1 ppm (d, ^1J(C,P) = 104.0 Hz, 6C1); ^{31}P{^{1}H} NMR (CD_2Cl_2, 300 K): δ = 75.0 ppm (s, 2P); ^{19}F{^{1}H} NMR (CD_2Cl_2, 300 K): $\delta = -78.7$ ppm (s, 3F; CF_3); Raman (80 mW, 300 K): 3068 (52), 1587 (65), 1225 (6), 1.170 (9), 1.121 (6), 1108 (29), 1.031 (40), 1001 (100), 755 (14), 638 (12), 614 (17), 573 (6), 349 (12), 315 (13), 283 (7), 258 (16), 232 (38), 195 cm^{-1} (6); IR (300 K, ATR): $\tilde{\nu}$ = 3067 (vw), 1586 (w), 1440 (w), 1258 (vs), 1223 (w), 1189 (vw), 1152 (m), 1119 (s), 1104 (vw), 1044 (w), 1028 (vs), 991 (m), 735 (vs), 682 (m), 635 (vs), 572 (w), 525 (m), 516 cm^{-1} (w).

Preparation of **7** from **3a**[OTf] and subsequent Wittig reaction to **8**: *n*-Butyllithium (1.6 M in *n*-hexane; 5 mL, 8.00 mmol, 2 equiv) was slowly added to a suspension of **3a**[OTf] (2.027 g, 4.00 mmol, 1 equiv) in Et_2O (100 mL) at −95 °C. The mixture was allowed to warm to ambient temperature and was stirred for 5 h. The ^{31}P NMR spectrum of the resulting bright orange solution was recorded and showed only one singlet at δ = 13.4 ppm (Et_2O/C_6D_6 capillary, 300 K; see Figure S2.1 in the Supporting Information) and was consistent with a previously reported chemical shift for **7**.[34] A solution of 2-nitrobenzaldehyde (0.605 g, 4.00 mmol, 1 equiv) in Et_2O (10 mL) was added to the ylide solution and the mixture was stirred overnight. The resulting brown suspension was treated with aqueous HCl (1 M, 3×30 mL). After separation of the organic layer and drying with $MgSO_4$, Et_2O was removed in vacuo and the residue subjected to column chromatography on silica gel (EtOAc/*n*-pentane = 5:95), which gave *cis*/*trans*-**7** (see Figure S2.2 in the Supporting Information)[35] as a 70:30 isomeric mixture (74%, 567 mg).

X-ray data collection and reduction: Suitable single crystals for **3a**[OTf], **3c**[OTf], **3e**[OTf] were obtained by diffusion *of n*-hexane into solutions of the compound in a minimum amount of CH_2Cl_2 at −30 °C. The crystals were coated with Paratone-N oil, mounted by using a glass fibre pin, and frozen in the cold nitrogen stream of the goniometer. X-ray diffraction data for all compounds were collected on a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 153(2) K using graphite-monochromated Cu Kα radiation (λ = 1.54178 Å). Diffraction data were collected over the full sphere with a scan width of 0.5° and exposure times of 20/40 s for **3a**[OTf], 30/60 s for **3c**[OTf], and 5/10 s for **3e**[OTf]. The generator settings were 45 kV and 110 mA. Diffraction data were collected over the full sphere and the frames were integrated by using the Bruker SMART[36] software package with the narrow frame algorithm. Data were corrected for absorption effects by using the SADABS routine (empirical multiscan method). For further crystal and data collection details, see Table 1.

Structure elucidation and refinement: Atomic scattering factors for non-hydrogen elements were taken from the literature. The struc-

Table 1. Crystallographic data and structure refinements of compounds **3a**[OTf], **3c**[OTf], and **3f**[OTf].

	3a[OTf]	**3c**[OTf]	**3e**[OTf]
Formula	$C_{24}H_{22}F_3N_2O_3PS$	$C_{20}H_{22}F_3N_2O_3PS$	$C_{12}H_{22}F_3N_2O_3PS$
Molecular weight	506.47	458.43	362.35
Colour, habit	colourless, block	colourless, irregular	colourless, plate
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P21/c$	$P\bar{1}$
a [Å]	8.8402(1)	8.8201(1)	8.4915(1)
b [Å]	10.2945(2)	11.4535(1)	8.4969(1)
c [Å]	26.1495(4)	21.3641(2)	12.2513(2)
α [°]	99.395(1)	90	81.026(1)
β [°]	97.473(1)	93.729(1)	85.299(1)
γ [°]	92.098(1)	90	81.743(1)
V [Å^3]	2323.81(6)	2153.65(4)	862.47(2)
Z	4	4	2
T [K]	153(1)	153(1)	153(1)
Crystal size [mm]	0.08×0.08×0.07	0.08×0.07×0.04	0.22×0.12×0.04
ρ_{calcd} [g cm^{-3}]	1.448	1.414	1.395
F(000)	1048	952	380
λ [Å]	1.54178 (Cu Kα)	1.54178 (Cu Kα)	1.54178 (Cu Kα)
$\theta_{min/max}$[°]	1.73/68.24	4.15/68.24	3.66/68.18
Index range	$-10 \geq h \geq 10$ $-12 \geq k \geq 12$ $-30 \geq l \geq 31$	$-10 \geq h \geq 9$ $-12 \geq k \geq 10$ $-25 \geq l \geq 22$	$-9 \geq h \geq 10$ $-9 \geq k \geq 10$ $-14 \geq l \geq 14$
μ [mm^{-1}]	2.371	2.491	2.944
Absorption correction	SADABS	SADABS	SADABS
Reflections collected	13584	9856	5056
Reflections unique	7582	3477	2810
R_{int}	0.0332	0.0415	0.0320
Reflections observed, $F > 2\sigma(F)$	6481	2851	2494
Residual density [e Å^{-3}]	0.361/−0.398	0.400/−0.353	0.378/−0.380
Parameters	617	274	204
GooF	1.063	1.053	1.079
R_1, $I > 2\sigma(I)$	0.0407	0.0428	0.0457
wR_2, all data	0.1156	0.1229	0.1315
CCDC	828014	828015	828016

ture was elucidated by using direct methods as implemented in the SHELXS-97 package[37] and were refined with SHELXL-97[38] against F^2 by using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atom positions were calculated and allowed to ride on the carbon atom to which they were bonded by assuming a C–H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.20 times the isotropic temperature factor of the carbon atom to which they were bonded. The locations of the largest peaks in the calculated final difference Fourier map, as well as the magnitude of the residual electron densities in each case, were of no chemical significance. CCDC 828014 (**3a**[OTf]), 828015 (**3c**[OTf]), and 828016 (**3e**[OTf]) contain the supplementary crystallographic data for this paper.[39]

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[30] The structural changes observed on protonation in the gas phase are very likely to be translated into solution because the quantitative gas-phase proton affinity will have little relevance to the behaviour in CH_2Cl_2. However, the absolute value is strongly dependent on a solvate model and we refrain here from a detailed calculation.
[31] a) See the Supporting Information for details on natural bond orbital (NBO) analyses of $\mathbf{3a}^+$ and $\mathbf{3a}H^{2+}$, calculated by using NBO Version 3.1, developed by E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold; b) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899.
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