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π-Insertion Reactions of Benzynes into P=N and P=S Double Bonds

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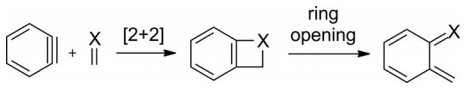
The π-insertion reactions of in situ generated benzynes into the P=N bonds of *N*-benzyl and *N*-aryl iminophosphoranes and the P=S bonds of phosphane sulfides have been examined by using the Kobayashi benzyne precursors, (2-trimethylsilyl)phenyl triflates. The reactions with iminophosphoranes afforded (2-aminophenyl)phosphonium triflates under mild conditions, most probably by a [2+2]/retro [2+2] cycloaddition sequence and further N-protonation by the solvent (CH_3CN) or N-phenylation by a second molecule of benzyne. The final products of the analogous reactions with *P*-OCH_3-substituted iminophosphoranes were the respective (2-aminophenyl)phosphane oxides, as result of a final O-demethylation event of the putative phosphonium triflate. The reactions with phosphane sulfides involve a final S-phenylation step to yield (2-phenylthio)phenylphosphonium salts.

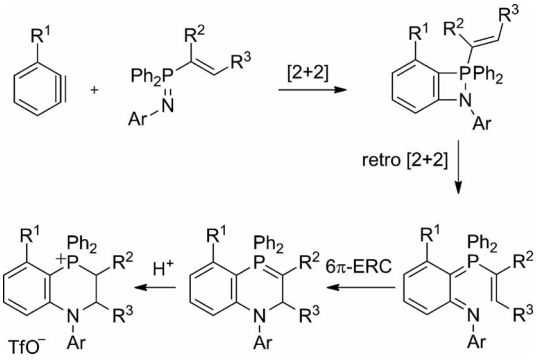
Introduction

The reactions of the highly reactive arynes have been extensively developed as powerful tools in organic synthesis.[1] The innovation of fluoride-induced in situ generation of arynes from (2-trialkylsilyl)aryl triflates under mild conditions[2] has naturally resulted in rapid progress in aryne chemistry during recent years. The [2+2] cycloadditions of arynes, also considered as π-insertions of arynes into double bonds, initially provide highly strained benzannulated four-membered rings. The reactions between arynes and alkenes afford stable benzocyclobutenes.[3] Cycloadditions between arynes and compounds containing carbon–heteroatom double bonds have been far less widely studied and are still challenging. In this context, several publications reported the insertion of arynes into the C=O double bonds of aldehydes,[4] ketones,[5] and amides,[6] as well as into the C=S bonds of thiones and thioureas,[7] the C=Se bonds of selones,[8] the C=N bonds of imines,[9] and the C=P bonds of alkylidenephosphoranes.[10] As a consequence of their considerable ring strain, the adducts of these reactions tend to undergo a further ring-opening event to afford *ortho*-heteroxylylene reactive intermediates (Scheme 1), which can then be trapped by subsequent reagents. This global sequence of reactions most often results in a tandem strategy for the facile construction of a wide range of benzofused heterocycles.



Scheme 1. General π-insertion reaction of benzyne into C=X double bonds.

In the context of our interest in the chemistry of iminophosphoranes[11] and their *P*-vinyl derivatives,[12] we have recently reported that the reaction of benzynes with *P*-alkenyl-*N*-aryl iminophosphoranes yielded the respective 1,4-benzazaphosphorinium triflates.[13] We rationalized these conversions by a mechanistic sequence in which the first step is a π-insertion of benzyne into the P=N bond of the iminophosphorane, followed by a retro [2+2] cycloaddition/6π-electrocyclization/protonation cascade (Scheme 2).



Scheme 2. Mechanistic explanation of the reaction between benzynes and *P*,*P*-alkenyl-substituted iminophosphoranes to yield 1,4-benzazaphosphorinium triflates.

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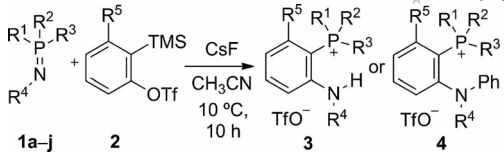
To the best of our knowledge, this was the first report of a π-insertion reaction of benzyne into a heteroatom–heteroatom double bond. In view of those results, we considered it worthwhile to examine the feasibility of the reaction between benzynes and the P=N bonds of more simple iminophosphoranes and to extend the study of this reactivity to the P=S moieties of phosphane sulfides. The process proved to be of broad scope and leads to the formation of a range of organophosphorus compounds decorated with *ortho*-amino and *ortho*-phenylthio groups in high yields under very mild reaction conditions.

Results and Discussion

To test the feasibility of our proposal, we first prepared a series of iminophosphoranes **1** by the stoichiometric reaction of azides and phosphanes under the standard conditions of the Staudinger imination reaction.[14] In this way, the starting materials **1** were obtained in good yields (90–96%) and high purity (>95% by ^{1}H and ^{31}P NMR analysis) and were used successfully in the following reactions without further purification. The treatment of the iminophosphoranes **1** with either the commercially available benzyne precursor 2-(trimethylsilyl)phenyl triflate (**2a**) or the easily prepared 3-methoxy analog **2b**[2b,2c] in the presence of CsF with acetonitrile as solvent gave rise to the phosphonium triflates **3** and/or **4** (Scheme 3, Table 1). Compounds **4** result from the incorporation of a second equivalent of benzyne at the nitrogen atom of the phosphonium triflates **3**. After extensive optimization experiments with iminophosphoranes **1b** and **1c**, the best reaction conditions to obtain **3** were established as those in which the **1**/benzyne precursor/CsF ratio is 1:1.3:3 with a reaction time of 10 h in acetonitrile at 10 °C. Attempts to improve the product yields by using 1,4 dioxane or a toluene/acetonitrile (4:1) mixture as solvent or the KF/18-crown-6 system as a fluoride source failed. The utilization of 2.6 equiv. of benzyne precursor **2** afforded phosphonium triflates **4** as the main reaction products (Table 1).



Scheme 3. Reaction of benzynes with iminophosphoranes to give (2-aminoaryl)phosphonium triflates.

The reactions with the *P*,*P*,*P*-triphenyl iminophosphoranes provided exclusively the (2-aminophenyl)phosphonium triflates **3a**–**3c** in good yields (Table 1, Entries 1–3). However, the standard reaction conditions were not adequate for *P*-methyl-*P*,*P*-diphenyl iminophosphoranes **1d** and **1e** and resulted in complex mixtures in which **4** and the starting material were present. As **4** are derivatives of **3**, we tried to direct the process towards the formation of **4**. Thus, when 2.6 equiv. of benzyne precursor were used, the respective (2-phenylamino)phenyl phosphonium triflates **4a** and **4b** were isolated in high yields (Table 1, Entries 4 and 5). In general, the reactions of *P*,*P*-dimethyl-*P*-phenyl iminophosphoranes **1f**–**1j** with benzyne precursor **2a** (Table 1, Entries 6–12) gave similar results. Thus, with 1.3 equiv. of **2a**, mixtures of **3** and **4** were obtained, except in the case of the sterically shielded *N*-(2,6-dimethylphenyl) derivative (Table 1, Entry 8), which exclusively yielded **3f**. In contrast, the utilization of 2.6 equiv. of **2a** gave rise to the respective *N*-phenylated compounds **4**. The utilization of the unsymmetrical 3-methoxybenzyne [generated in situ from 3-methoxy-2-(trimethylsilyl)phenyl triflate] resulted in regioselective reactions, which led to the exclusive formation of the **3g** and **3h** regioisomers (Table 1, Entries 13 and 14). Similar regioselectivities are well known in the use of this and other alkoxy-substituted benzynes and are rationalized in terms of electronic and steric factors in the initial step of comparable stepwise reactions, which determine the more favorable attack at the *meta* position of the alkoxy substituent.[15]

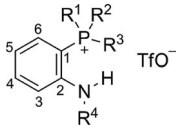
A careful scrutiny of the analytical and spectroscopic data allowed the unambiguous structural assignment of the phosphonium triflates **3** (see Exp. Sect.). The dissociation

Table 1. Phosphonium triflates **3** and **4**.

Entry	**1**	R^1	R^2	R^3	R^4	**2**	R^5	Equiv. **2**	Yield of **3** [%][a]	Yield of **4** [%][a]
1	**1a**	C_6H_5	C_6H_5	C_6H_5	$C_6H_5CH_2$	**2a**	H	1.3	**3a**, 70	–
2	**1b**	C_6H_5	C_6H_5	C_6H_5	4-$CH_3C_6H_4$	**2a**	H	1.3	**3b**, 56	–
3	**1c**	C_6H_5	C_6H_5	C_6H_5	4-$CH_3OC_6H_4$	**2a**	H	1.3	**3c**, 65	–
4	**1d**	C_6H_5	C_6H_5	CH_3	4-$CH_3OC_6H_4$	**2a**	H	2.6	–	**4a**, 74
5	**1e**	C_6H_5	C_6H_5	CH_3	4-BrC_6H_4	**2a**	H	2.6	–	**4b**, 87
6	**1f**	C_6H_5	CH_3	CH_3	4-$CH_3C_6H_4$	**2a**	H	1.3	**3d**, 54[b]	–
7	**1g**	C_6H_5	CH_3	CH_3	4-$CH_3OC_6H_4$	**2a**	H	1.3	**3e**, 56[b]	–
8	**1h**	C_6H_5	CH_3	CH_3	2,6-$(CH_3)_2C_6H_3$	**2a**	H	1.3	**3f**, 75	–
9	**1f**	C_6H_5	CH_3	CH_3	4-$CH_3C_6H_4$	**2a**	H	2.6	–	**4c**, 65
10	**1g**	C_6H_5	CH_3	CH_3	4-$CH_3OC_6H_4$	**2a**	H	2.6	–	**4d**, 72
11	**1i**	C_6H_5	CH_3	CH_3	4-BrC_6H_4	**2a**	H	2.6	–	**4e**, 76
12	**1j**	C_6H_5	CH_3	CH_3	4-$NO_2C_6H_4$	**2a**	H	2.6	–	**4f**, 69
13	**1g**	C_6H_5	CH_3	CH_3	4-$CH_3OC_6H_4$	**2b**	OCH_3	1.3	**3g**, 72	–
14	**1h**	C_6H_5	CH_3	CH_3	2,6-$(CH_3)_2C_6H_3$	**2b**	OCH_3	1.3	**3h**, 48	–

[a] Yields of isolated products. [b] Compounds **4** were also detected (<10%).

Table 2. Selected $^{13}C\{^1H\}$ NMR spectroscopic data of phosphonium triflates **3** in $CDCl_3$ (298 K). The spectra were measured at 100 or 75 MHz. Chemical shifts (δ) are given in ppm, and coupling constants (J) are in Hz.

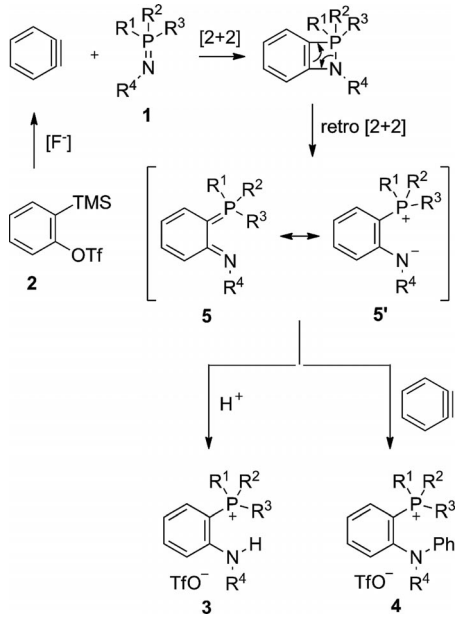


	$\delta_{C\text{-}1}$ ($^1J_{P,C}$)	$\delta_{C\text{-}2}$ ($^2J_{P,C}$)	$\delta_{C\text{-}3}$ ($^3J_{P,C}$)	$\delta_{C\text{-}4}$ ($^4J_{P,C}$)	$\delta_{C\text{-}5}$ ($^3J_{P,C}$)	$\delta_{C\text{-}6}$ ($^2J_{P,C}$)
3a	97.51 (91.4)	151.09 (5.1)	113.92 (7.9)	137.79	118.93 (13.2)	136.02 (10.5)
3b	104.97 (91.7)	149.54 (4.4)	120.80 (7.7)	137.45	123.04 (12.9)	136.05 (10.5)
3c	102.76 (91.7)	150.47 (4.5)	119.23 (7.5)	137.44	122.01 (13.0)	135.94 (10.4)
3d	115.27 (91.0)	149.03 (4.4)	126.58 (7.5)	136.47 (2.1)	125.57 (12.8)	133.80 (10.3)
3e	113.26 (90.7)	149.82 (4.4)	125.00 (7.6)	136.46 (1.6)	124.67 (12.9)	133.71 (10.1)
3f	102.78 (88.6)	149.05 (4.5)	115.91 (7.6)	136.98 (2.2)	121.25 (12.6)	133.64 (9.5)
3g	97.79 (93.0)	152.13	105.08 (4.6)	137.00	115.87 (6.7)	163.15
3h	92.19 (92.5)	152.30 (2.4)	103.38 (6.1)	137.39	110.59 (7.8)	163.63

of the P=N bond of **1** and the incorporation of its two termini into the adjacent carbon atoms of the benzyne unit to give the salts **3** is evidenced by the following key NMR spectroscopic data. First, the *ortho*-disubstituted pattern of the new benzene ring is present in their ^1H NMR spectra. Second, the phosphorus atom is coupled to all of the carbon atoms of that ring in their $^{13}C\{^1H\}$ NMR spectra (see Table 2), and there is no ^{31}P–^{13}C coupling for the *ortho*- and NC_{ipso} carbon atoms of the *N*-aryl ring, which was present in **1**. Moreover, the NH proton is clearly appreciable in the ^1H NMR spectra of **3**, whereas the singlet at $\delta \approx$ 18 ppm in their $^{31}P\{^1H\}$ NMR spectra is typical of phosphonium salts and is remarkably deshielded with respect to those of the starting iminophosphoranes **1** ($\Delta\delta$ = 7.00–20.94 ppm). Finally, the triflate anion is clearly revealed in their $^{13}C\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra. For instance, the signals of the respective carbon and fluorine atoms of the anionic moiety of **3h** appear at δ_C = 120.73 ppm (q, $^1J_{F,C}$ = 320.3 Hz) and δ_F = –78.22 ppm.

Compounds **4** were characterized by examination of their HRMS and NMR spectroscopic data, which are in some aspects comparable with those of the analogous triflates **3**.

The formation of products **3** and **4** is reasonably explained by a mechanism analogous to that reported for the reaction of iminophosphoranes with acetylenic esters[16] and propargylic phosphonium salts (Scheme 4).[17] First, the iminophosphorane **1** reacts with the in situ generated benzyne to yield the formal [2+2] cycloadduct, which then undergoes a retro [2+2] cycloaddition. The resulting *ortho*-phosphazaxylylene **5** (or its amidophosphonium betaine canonical form **5′**) intermediate could act either as a base to abstract a proton from the acetonitrile[7c,18] solvent to give **3** or as a nucleophile with a second equivalent of benzyne to give **4**.

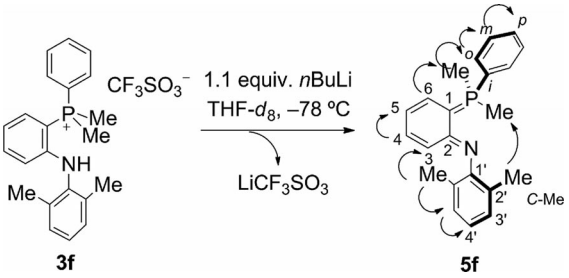


Scheme 4. Proposed mechanism for the formation of phosphonium triflates **3** and **4**.

The (2-aminophenyl)phosphonium salts **3** and **4** can be envisaged as precursors of the corresponding (2-aminophenyl)phosphanes by reduction with sodium naphthalenide.[19] (*ortho*-Amino)phosphanes are important hemilabile P,N-ligands in transition-metal catalysis and are commonly prepared through multistep syntheses.[20] The one-pot procedure reported here for the preparation of this compound class represents a significant improvement as the insertion reaction occurs under mild reaction conditions with readily accessible reagents that are compatible with a variety of functional groups.

To gain insight into the structure of species **5** (Scheme 4) formed in the insertion of benzyne into the P=N linkage of iminophosphoranes **1**, we undertook a variable-temperature multinuclear magnetic resonance study of the deprotonation of phosphonium triflate **3f** with 1.1 equiv. of *n*BuLi in [D_8]THF as solvent. The analysis of the ^1H, ^7Li, ^{13}C, and ^{31}P NMR spectra of a 0.1 M sample in the temperature range –30 to –120 °C showed the existence of the neutral compound **5f** [δ_P(–30 °C) = 11.09 ppm, Scheme 5] in solution. Although the ^7Li NMR spectrum of the freshly prepared sample measured at –110 °C consisted of four signals at δ_{Li} = 0.41, 1.23, 1.35, 1.40 ppm plus that of the LiBr present in the organolithium base solution used (δ_{Li} =

–0.25 ppm), these signals disappear upon standing of the sample at low temperature owing to crystallization (Figure S46). This crystallization has no effect on the other spectra, except for the large intensity decrease of the quartet arising from the triflate anion in the ^{13}C NMR spectrum (Figure S48; δ_C = 120.56 ppm, $^1J_{F,C}$ = 319.4 Hz). The dearomatized phosphorus ylide structure of **5f** was identified from the standard combination of 1D [^1H, $^1H(^{31}P)$, ^{13}C, DEPT135, ^{31}P] and 2D [COSY45, heteronuclear multiple quantum coherence (HMQC), HMBC, ROESY] NMR spectroscopy at –30 °C (see Supporting Information).

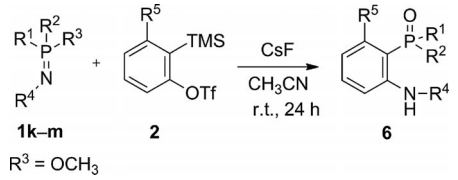


Scheme 5. Formation of **5f** by deprotonation of **3f** and numbering scheme used. The arrows indicate the NOEs observed in the 2D ROESY spectrum (mixing time 200 ms, 30 °C).

The ^1H and ^{31}P NMR spectra of **5f** are temperature-dependent. The ^{31}P NMR signal broadens in the temperature range 30 to –80 °C, coalesces at –90 °C, and splits into two signals at lower temperature (Figure S44). At –120 °C, two relatively narrow signals ($W_{1/2}$ < 25 Hz) are observed at δ_P = 11.51 and 17.88 ppm in a ratio of 65:35. The ^1H NMR spectra showed similar features. At –120 °C, the signals in the aromatic region and those of the C–Me groups appear almost duplicated (ratio of 65:35 from integration of the 5-H peak) owing to the presence of two species (Figure S43). Most importantly, at this temperature, the P–Me protons generate two equally intense doublets at δ_H = 2.58 ($^2J_{P,H}$ = 13.4 Hz) and 2.64 ppm ($^2J_{P,H}$ = 14.6 Hz). These doublets collapse into two singlets in the $^1H\{^{31}P\}$ spectrum (Figure S43 top). This chemical inequivalence of the methyl groups linked to the prochiral phosphorus atom is attributed to restricted rotation about the N–Ar bond.[21] This atropisomerism leads to a chiral axis that renders the P–Me groups diastereotopic.

As far as the reaction products are concerned, only a very small number of (2-amino)phenyl phosphonium salts have been described previously, all of which were prepared by following the aryl halide–phosphane coupling method of Horner and co-workers.[22] Thus, the Ni^{II}-catalyzed reaction between 2-chloro(bromo)anilines and tertiary phosphanes (basically triphenylphosphane) at temperatures ranging from 200 to 220 °C resulted in the respective (2-amino)-phenyl phosphonium salts.[23]

Next, we extended these reactions to the utilization of *P*-methoxy-substituted iminophosphoranes (**1k**–**1m**, R^3 = OCH_3), prepared by Staudinger imination reactions between methyl diphenylphosphinite (for **1k** and **1l**) or trimethyl phosphite (for **1m**) and aryl azides.[24] Their reactions with **2** were conducted in acetonitrile at room temperature for 24 h in an optimized **1**/**2**/CsF ratio of 1:1.3:3 to afford the respective 2-(arylamino)phenylphosphane oxides **6a**–**6c** (Scheme 6; Table 3, Entries 1–3) or the phosphonate **6d** (Scheme 6; Table 3, Entry 4).



Scheme 6. Reaction of benzynes with *P*-methoxy derivatives to give phosphane oxides.

Table 3. (2-Arylamino)phenylphosphane oxides **6a**–**6c** and phosphonate **6d**.

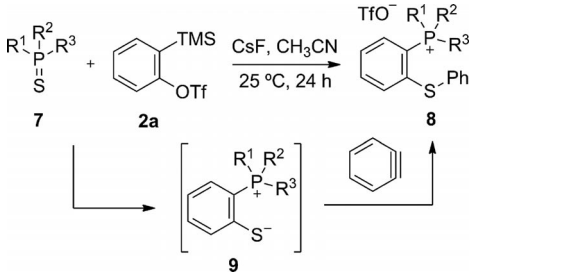
Entry	**1**	$R^1 = R^2$	R^4	**2**	R^5	Yield of **6** [%]
1	**1k**	C_6H_5	4-$CH_3C_6H_4$	**2a**	H	**6a**, 90
2	**1l**	C_6H_5	4-BrC_6H_4	**2a**	H	**6b**, 86
3	**1l**	C_6H_5	4-BrC_6H_4	**2b**	OCH_3	**6c**, 42
4	**1m**	OCH_3	4-$CH_3C_6H_4$	**2a**	H	**6d**, 45

The analytical and spectroscopic data of **6** were consistent with their structures. Their ^1H and $^{13}C\{^1H\}$ NMR spectra showed the absence of one methoxy group from the respective *P*-methoxy iminophosphorane precursor. Their $^{31}P\{^1H\}$ NMR spectra show a singlet in the δ = 36.23–38.75 ppm interval for **6a**–**6c** and at δ = 24.45 ppm for **6d**.

The formation of phosphane oxides **6** most probably occurs via the corresponding (2-arylamino)phenylphosphonium triflate of structure similar to that of **3**. A subsequent cleavage of the O–CH_3 bond in an Arbuzov-like manner finally leads to the respective phosphane oxides **6a**–**6c** (R^1 = R^2 = C_6H_5) or dimethyl phosphonate **6d** (R^1 = R^2 = OCH_3). This latter transformation is quite usual in the chemistry of *P*-alkoxyphosphonium salts.[25] (*ortho*-Amino)phosphane oxides **6** are good candidates as ligands for metal complexes.[26] Transition-metal complexes containing this structural motif have found application, for example, as initiators for catalytic ring-opening oligomerization and olefin polymerization and as catalysts for cross-coupling reactions.[27]

The isolation of products **6** in these reactions seems to indicate that the strong P=O bond is probably not easily involved in reactions with benzynes (similar to those experienced by its P=N analogs **3**). Nevertheless, we reasoned that compounds bearing weaker and more nucleophilic P=S bonds could be suitable candidates for similar benzyne insertion reactions. Therefore, we next tested similar reactions with the three phosphane sulfides **7a**–**7c** under comparable reaction conditions. The first experiment with **7a** showed the formation of *P*-[(2-phenylthio)phenyl]triphenylphosphonium triflate (**8a**) as the major product, although in low yield (35%), accompanied by unreacted phosphane sulfide.

Therefore, we increased the amount of benzyne precursor **2a** to 2.6 equiv. and obtained the respective *S*-phenylated compounds **8** in good yields (Scheme 7, Table 4). The spectroscopic and analytical data support the formulation of **8**. Their NMR spectra show an *ortho*-substituted phenylphosphonium moiety and they are similar to those of **3** and **4**.



Scheme 7. Reaction of benzyne with phosphane sulfides.

Table 4. 2-(Phenylthio)phenylphosphonium triflates **8**.

7	R^1	R^2	R^3	Yield of **8** [%]
7a	C_6H_5	C_6H_5	C_6H_5	**8a**, 70
7b	C_6H_5	C_6H_5	CH_3	**8b**, 87
7c	C_6H_5	CH_3	CH_3	**8c**, 73

Similar to those of iminophosphoranes, the reactions of phosphane sulfides **7** with benzyne most probably proceed by a [2+2] cycloaddition followed by ring opening to give the betaines **9**, which undergo addition to a second molecule of benzyne to afford the phenylthiophosphonium salts **8**. To the best of our knowledge, the reaction of the P=S linkage with formal acetylenes has no precedent in the literature.

An exhaustive examination of the chemical literature revealed that a small number of alkyl [(2-methylthio)phenyl]diphenylphosphonium salts have been prepared by *P*-quaternization of the respective triarylphosphanes with reactive alkyl halides.[28] In addition, we found that the synthesis of **8a** by palladium-mediated aryl–PPh_3 coupling has been previously reported.[29] This is the only example that we are aware of for the preparation of a (2-arylthio)phenyl triaryl phosphonium salt, although it yielded only a few crystals that permitted an X-ray crystal study. In contrast, the procedure shown in Scheme 7 represents a simple and efficient method to access this family of compounds in high yield.

Conclusions

Herein, we have shown a facile and mild method for the preparation of *P*-(2-arylamino)phenyl and *P*-(2-phenylthio)phenyl phosphonium triflates by reactions of iminophosphoranes and phosphane sulfides with (2-trialkylsilyl)-aryl triflates in the presence of CsF. These reactions most probably involve the initial π-insertion of the in situ generated benzyne into the P=N and P=S bonds of the organophosphorus reagents, followed by a retro [2+2] cycloaddition and further protonation or reaction with a second equivalent of benzyne. Variable-temperature NMR spectroscopic studies showed that prior to protonation, the reaction product exists as a dearomatized phosphorus ylide stabilized by extended conjugation through a 1,3-cyclohexadiene moiety and a carbon–nitrogen double bond. The participation of phosphane sulfides in this pathway with a formal carbon–carbon triple bond is described for the first time. The methodology described here allows an easy entry to a variety of *ortho*-functionalized organophosphorus compounds such as (*o*-aminophenyl)- and (*o*-phenylthio)-phenylphosphonium salts, and (*o*-aminophenyl)phosphane oxides, which can be used as precursors or directly as hemilabile chelating ligands in coordination chemistry.

Experimental Section

General: All reactions were performed under nitrogen in HPLC grade solvents (Scharlab), which were nitrogen-saturated, dried, and deoxygenated by using an Innovative Technology Inc. PureSolv 400 solvent purification system. Column chromatography was performed with the indicated solvent and silica gel (70–200 μm) as the stationary phase. Thin layer chromatography (TLC) was performed with silica gel plates. All melting points were determined with a Kofler hot-plate melting point apparatus. IR spectra were determined as Nujol emulsions or films with a Nicolet 380 FTIR spectrophotometer. NMR spectra were recorded at 25 °C with a Bruker AC200 (200 MHz), Avance 300 (300 MHz), or Avance 400 (400 MHz) spectrometer. Variable-temperature multinuclear magnetic resonance spectra were measured with a Bruker Avance 500 spectrometer (500 MHz) equipped with a 5 mm direct $^1H/^{31}P/BB$ triple resonance broadband (TBO) probe. ^1H and ^{13}C chemical shifts are reported in ppm, referenced to residual H and C in the deuterated solvent (chloroform, THF) as the internal standard. ^7Li, ^{19}F, and ^{31}P chemical shifts were externally referenced to 1 M LiBr in D_2O, trifluorotoluene, and 85% H_3PO_4, respectively. *J* values are given in Hz. A set of two complementary $^{31}P/^7Li$-selective band-pass/stop frequency filters was used for the measurement of NMR spectra involving ^{31}P and ^7Li nuclei. Standard Bruker software was used for acquisition and processing routines. Signals in the ^1H and ^{13}C NMR spectra of the synthesized compounds were assigned with the aid of $^1H\{^{31}P\}$, DEPT, and two-dimensional experiments (HMQC). NMR samples of **5f** were prepared by using Schlenk techniques. Mass spectra were recorded with an Agilent VL (ESI) mass spectrometer.

Materials: Commercially available reagents were used throughout without purification unless otherwise stated. Compounds **1a**,[30] **1b**,[31] **1c**,[32] **1m**,[33] **7a**,[34] **7b**,[35] and **7c**[36] were prepared according to published procedures.

General Procedure for the Preparation of the Phosphonium Triflates 3: A solution of **2** (0.39 mmol) in anhydrous CH_3CN (5 mL) was added over 2 h to a mixture of **1** (0.3 mmol) and CsF (0.9 mmol) in anhydrous CH_3CN (10 mL) at 0 °C. The resulting mixture was stirred at 10 °C for 10 h. The reaction mixture was then filtered through a short pad of Celite to remove insoluble substances. After concentration of the filtrate under vacuum, the residue was purified by chromatography on silica and then recrystallized to afford **3**.

***P*-[2-(Benzylamino)phenyl]-*P*,*P*,*P*-triphenylphosphonium Triflate (3a):** The general procedure with **1a** (0.11 g, 0.3 mmol) in anhy-

drous CH_3CN (5 mL), **2a** (0.12 g, 0.39 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **3a** as a white solid, which was purified by flash column chromatography [gradient eluents: chloroform/methanol 9:1 (v/v) then ethanol; R_f = 0.19, TLC, chloroform/methanol 9:1 (v/v)] and recrystallized from dichloromethane/diethyl ether; 0.12 g, 70%; white prisms; m.p. 196–198 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.85 (s, 1 H, NH), 4.19 (s, 2 H, CH_2), 6.75–6.77 (m, 2 H, Ar H), 6.84–6.99 (m, 3 H, Ar H), 7.13–7.19 (m, 3 H, Ar H), 7.62–7.69 (m, 7 H, Ar H), 7.72–7.77 (m, 6 H, Ar H), 7.85–7.89 (m, 3 H, Ar H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = 47.96 (CH_2), 97.51 (d, $^1J_{P,C}$ = 91.4 Hz, C-1), 113.92 (d, $^3J_{P,C}$ = 7.9 Hz, C-3), 117.07 (d, $^1J_{P,C}$ = 88.8 Hz, C-*i*), 118.93 (d, $^3J_{P,C}$ = 13.2 Hz, C-5), 127.18 (C-2′ or C-3′), 127.79 (C-4′), 128.76 (C-2′ or C-3′), 130.99 (d, $^3J_{P,C}$ = 12.9 Hz, C-*m*), 134.24 (d, $^2J_{P,C}$ = 10.4 Hz, C-*o*), 135.75 (d, $^4J_{P,C}$ = 2.7 Hz, C-*p*), 136.02 (d, $^2J_{P,C}$ = 10.5 Hz, C-6), 136.76 (C-1′), 137.79 (C-4), 151.09 (d, $^2J_{P,C}$ = 5.1 Hz, C-2) ppm; CF_3SO_3 not observable. ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, 25 °C): δ = –78.06 ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 20.54 ppm. IR (Nujol): $\tilde{\nu}$ = 3414 (w), 1440 (m), 1264 (s), 1031 (m), 908 (vs), 733 (vs) cm^{-1}. HRMS (ESI): calcd. for $C_{31}H_{27}NP$ [M – OTf]$^+$ 444.1876; found 444.1881.

***P*,*P*,*P*-Triphenyl-*P*-[2-(4-methylphenylamino)phenyl]phosphonium Triflate (3b):** The general procedure with **1b** (0.11 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2a** (0.12 g, 0.39 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **3b** as a yellow solid, which was purified by flash column chromatography [gradient eluents: chloroform/methanol 9:1 (v/v) then ethanol; R_f = 0.23, TLC, chloroform/methanol 9:1 (v/v)] and recrystallized from dichloromethane/diethyl ether; 0.1 g, 56%; yellow prisms; m.p. 163–165 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.24 (s, 3 H, CH_3), 5.19 (s, 1 H, NH), 6.48 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, Ar H), 6.97 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, Ar H), 7.10–7.15 (m, 2 H, Ar H), 7.36 (m, 1 H, Ar H), 7.61–7.72 (m, 1 H, Ar H), 7.73–7.80 (m, 12 H, Ar H), 7.85–7.88 (m, 3 H, Ar H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = 20.82 (CH_3), 104.97 (d, $^1J_{P,C}$ = 91.7 Hz, C-1), 117.45 (d, $^1J_{P,C}$ = 89.6 Hz, C-*i*), 120.56 (C-2′), 120.80 (d, $^3J_{P,C}$ = 7.7 Hz, C-3), 120.97 (q, $^1J_{F,C}$ = 321.1 Hz, CF_3SO_3), 123.04 (d, $^3J_{P,C}$ = 12.9 Hz, C-5), 130.24 (C-3′), 131.04 (d, $^3J_{P,C}$ = 12.9 Hz, C-*m*), 134.14 (d, $^2J_{P,C}$ = 10.4 Hz, C-*o*), 134.59 (C-1′), 135.67 (d, $^4J_{P,C}$ = 3.0 Hz, C-*p*), 136.05 (d, $^2J_{P,C}$ = 10.5 Hz, C-6), 137.45 (C-4), 149.54 (d, $^2J_{P,C}$ = 4.4 Hz, C-2) ppm; C-4′ not observable. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 20.65 ppm. IR (Nujol): $\tilde{\nu}$ = 3397 (s), 1439 (s), 1275 (vs), 1030 (s), 752 (m), 723 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{31}H_{27}NP$ [M – OTf]$^+$ 444.1876; found 444.1897.

***P*,*P*,*P*-Triphenyl-*P*-[2-(4-methoxyphenylamino)phenyl]phosphonium Triflate (3c):** The general procedure with **1c** (0.11 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2a** (0.12 g, 0.39 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **3c** as a yellow solid, which was purified by flash column chromatography [gradient eluents: chloroform/methanol 9:1 (v/v) then ethanol; R_f = 0.21, TLC, chloroform/methanol 9:1 (v/v)] and recrystallized from dichloromethane/diethyl ether; 0.12 g, 65%; yellow prisms; m.p. 178–180 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.74 (s, 3 H, OCH_3), 5.15 (s, 1 H, NH), 6.58 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H, Ar H), 6.75 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H, Ar H), 7.03–7.08 (m, 2 H, Ar H), 7.15–7.19 (m, 1 H, Ar H), 7.60–7.65 (m, 1 H, Ar H), 7.70–7.80 (m, 12 H, Ar H), 7.86–7.90 (m, 3 H, Ar H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = 55.64 (OCH_3), 102.76 (d, $^1J_{P,C}$ = 91.7 Hz, C-1), 115.06 (C-3′), 117.42 (d, $^1J_{P,C}$ = 89.3 Hz, C-*i*), 119.23 (d, $^3J_{P,C}$ = 7.5 Hz, C-3), 122.01 (d, $^3J_{P,C}$ = 13.0 Hz, C-5), 123.82 (C-2′), 131.07 (d, $^3J_{P,C}$ = 12.9 Hz, C-*m*), 132.42 (C-1′), 134.21 (d, $^2J_{P,C}$ = 10.4 Hz, C-*o*), 135.60 (d, $^4J_{P,C}$ = 2.8 Hz, C-*p*), 135.94 (d, $^2J_{P,C}$ = 10.4 Hz, C-6), 137.44 (C-4), 150.47 (d, $^2J_{P,C}$ = 4.5 Hz, C-2), 157.90 (C-4′) ppm; CF_3SO_3 not observable. ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, 25 °C): δ = –78.27 ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 20.89 ppm. IR (Nujol): $\tilde{\nu}$ = 3493 (w), 1440 (s), 1262 (vs), 1031 (s), 731 (vs), 636 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{31}H_{27}NOP$ [M – OTf]$^+$ 460.1825; found 460.1847.

***P*,*P*-Dimethyl-*P*-[2-(4-methylphenylamino)phenyl]-*P*-phenylphosphonium Triflate (3d):** The general procedure with **1f** (0.07 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2a** (0.12 g, 0.39 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **3d** as a white solid, which was purified by successive preparative TLC [eluent: chloroform/methanol 9:1 (v/v), R_f = 0.24] and recrystallized from dichloromethane/diethyl ether; 0.08 g, 54%; white prisms; m.p. 101–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.22 (s, 3 H, CH_3), 2.52 [d, $^2J_{H,P}$ = 13.6 Hz, 6 H, $P(CH_3)_2$], 5.91 (s, 1 H, NH), 6.52 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, Ar H), 6.93 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, Ar H), 7.31–7.35 (m, 2 H, Ar H), 7.56–7.73 (m, 7 H, Ar H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ = 9.99 [d, $^1J_{P,C}$ = 58.3 Hz, $P(CH_3)_2$], 20.64 (CH_3), 115.27 (d, $^1J_{P,C}$ = 91.0 Hz, C-1), 117.92 (C-2′), 120.67 (q, $^1J_{F,C}$ = 320.1 Hz, CF_3SO_3), 121.50 (d, $^1J_{P,C}$ = 88.4 Hz, C-*i*), 125.57 (d, $^3J_{P,C}$ = 12.8 Hz, C-5), 126.58 (d, $^3J_{P,C}$ = 7.5 Hz, C-3), 129.99 (C-3′), 130.37 (d, $^3J_{P,C}$ = 12.7 Hz, C-*m*), 131.21 (d, $^2J_{P,C}$ = 10.6 Hz, C-*o*), 131.44 (C-4′), 133.80 (d, $^2J_{P,C}$ = 10.3 Hz, C-6), 134.33 (d, $^4J_{P,C}$ = 2.8 Hz, C-*p*), 136.47 (d, $^4J_{P,C}$ = 2.1 Hz, C-4), 141.37 (C-1′), 149.03 (d, $^2J_{P,C}$ = 4.4 Hz, C-2) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 18.01 ppm. IR (Nujol): $\tilde{\nu}$ = 3284 (w), 1513 (m), 1258 (vs), 1031 (s), 910 (s), 733 (vs) cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{23}NP$ [M – OTf]$^+$ 320.1563; found 320.1576.

***P*,*P*-Dimethyl-*P*-[2-(4-methoxyphenylamino)phenyl]-*P*-phenylphosphonium Triflate (3e):** The general procedure with **1g** (0.08 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2a** (0.12 g, 0.39 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **3e** as a white solid, which was purified by successive preparative TLC [eluent: chloroform/methanol 9:1 (v/v), R_f = 0.19] and recrystallized from dichloromethane/diethyl ether; 0.08 g, 56%; white prisms; m.p. 155–157 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.53 [d, $^2J_{P,H}$ = 13.8 Hz, 6 H, $P(CH_3)_2$], 3.71 (s, 3 H, OCH_3), 5.85 (s, 1 H, NH), 6.59 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H, Ar H), 6.69 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H, Ar H), 7.18–7.30 (m, 2 H, Ar H), 7.53–7.75 (m, 7 H, Ar H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ = 9.92 [d, $^1J_{P,C}$ = 58.2 Hz, $P(CH_3)_2$], 55.63 (OCH_3), 113.26 (d, $^1J_{P,C}$ = 90.7 Hz, C-1), 114.84 (C-3′), 120.44 (C-2′), 120.69 (q, $^1J_{F,C}$ = 320.4 Hz, CF_3SO_3), 121.40 (d, $^1J_{P,C}$ = 88.3 Hz, C-*i*), 124.67 (d, $^3J_{P,C}$ = 12.9 Hz, C-5), 125.00 (d, $^3J_{P,C}$ = 7.6 Hz, C-3), 130.38 (d, $^3J_{P,C}$ = 12.7 Hz, C-*m*), 131.26 (d, $^2J_{P,C}$ = 10.6 Hz, C-*o*), 133.71 (d, $^2J_{P,C}$ = 10.1 Hz, C-6), 134.38 (d, $^4J_{P,C}$ = 2.7 Hz, C-*p*), 136.46 (d, $^4J_{P,C}$ = 1.6 Hz, C-4), 136.62 (C-1′), 149.82 (d, $^2J_{P,C}$ = 4.4 Hz, C-2), 155.40 (C-4′) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 18.28 ppm. IR (Nujol): $\tilde{\nu}$ = 3290 (m), 1511 (vs), 1257 (vs), 1031 (s), 755 (vs), 638 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{23}NOP$ [M – OTf]$^+$ 336.1512; found 336.1516.

***P*,*P*-Dimethyl-*P*-[2-(2,6-dimethylphenylamino)phenyl]-*P*-phenylphosphonium Triflate (3f):** The general procedure with **1h** (0.08 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2a** (0.12 g, 0.39 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **3f** as a white solid, which was purified by flash column chromatography [gradient eluents: chloroform/methanol 9:1 (v/v) then ethanol; R_f = 0.14, TLC, chloroform/methanol 9:1 (v/v)] and recrystallized from dichloromethane/diethyl ether; 0.11 g, 75%; white prisms; m.p. 195–197 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.78 (s, 6 H, CH_3), 2.67 [d, $^2J_{P,H}$ = 14.0 Hz, 6 H, $P(CH_3)_2$], 4.81 (s,

1 H, NH), 6.38 (dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{P,H}$ = 6.1 Hz, 1 H, Ar H), 7.02–7.08 (m, 3 H, Ar H), 7.15 (t, $^3J_{H,H}$ = 7.6 Hz, 1 H, Ar H), 7.48 (t, $^3J_{H,H}$ = 7.6 Hz, 1 H, Ar H), 7.69–7.75 (m, 3 H, Ar H), 7.77–7.81 (m, 1 H, Ar H), 7.90–7.95 (dd, $^3J_{P,H}$ = 8.5 Hz, $^3J_{H,H}$ = 7.1 Hz, 2 H, Ar H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 8.43 [d, $^1J_{P,C}$ = 57.6 Hz, $P(CH_3)_2$], 18.00 (CH_3), 102.78 (d, $^1J_{P,C}$ = 88.6 Hz, C-1), 115.91 (d, $^3J_{P,C}$ = 7.6 Hz, C-3), 120.66 (d, $^1J_{P,C}$ = 84.1 Hz, C-*i*), 120.74 (q, $^1J_{F,C}$ = 320.3 Hz, CF_3SO_3), 121.25 (d, $^3J_{P,C}$ = 12.6 Hz, C-5), 126.78 (C-4′), 129.14 (C-3′), 131.15 (d, $^3J_{P,C}$ = 12.6 Hz, C-*m*), 131.64 (d, $^2J_{P,C}$ = 11.0 Hz, C-*o*), 133.64 (d, $^2J_{P,C}$ = 9.5 Hz, C-6), 134.10 (C-2′), 135.25 (d, $^4J_{P,C}$ = 2.8 Hz, C-*p*), 136.12 (C-1′), 136.98 (d, $^4J_{P,C}$ = 2.2 Hz, C-4), 149.05 (d, $^2J_{P,C}$ = 4.5 Hz, C-2) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 18.40 ppm. IR (Nujol): $\tilde{\nu}$ = 3391 (w), 1449 (m), 1266 (vs), 1030 (s), 738 (vs), 638 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{25}NP$ $[M - OTf]^+$ 334.1719; found 334.1719.

***P*,*P*-Dimethyl-*P*-[6-methoxy-2-(4-methoxyphenylamino)phenyl]-*P*-phenylphosphonium Triflate (3 g):** The general procedure with **1g** (0.08 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2b** (0.13 g, 0.39 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **3g** as a white solid, which was purified by flash column chromatography [gradient eluents: chloroform/methanol 9:1 (v/v) then ethanol; R_f = 0.24, TLC, chloroform/methanol 9:1 (v/v)] and recrystallized from dichloromethane/diethyl ether; 0.11 g, 72%; white prisms; m.p. 150–152 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.50 [d, $^2J_{P,H}$ = 14.0 Hz, 6 H, $P(CH_3)_2$], 3.48 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 6.49 (dd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{P,H}$ = 4.8 Hz, 1 H, Ar H), 6.79 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, Ar H), 6.92 (dd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{P,H}$ = 5.2 Hz, 1 H, Ar H), 6.98 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, Ar H), 7.03 (s, 1 H, NH), 7.42 (t, $^3J_{H,H}$ = 8.0 Hz, 1 H, Ar H), 7.51–7.60 (m, 5 H, Ar H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 12.61 [d, $^1J_{P,C}$ = 57.8 Hz, $P(CH_3)_2$], 55.70 (OCH_3), 55.96 (OCH_3), 97.79 (d, $^1J_{P,C}$ = 93.0 Hz, C-1), 105.08 (d, $^3J_{P,C}$ = 4.6 Hz, C-3), 115.04 (C-3′), 115.87 (d, $^3J_{P,C}$ = 6.7 Hz, C-5), 120.81 (q, $^1J_{F,C}$ = 317.7 Hz, CF_3SO_3), 120.87 (C-2′), 126.53 (d, $^1J_{P,C}$ = 91.0 Hz, C-*i*), 129.64 (d, $^2J_{P,C}$ = 10.4 Hz, C-*o*), 129.83 (d, $^3J_{P,C}$ = 12.9 Hz, C-*m*), 133.20 (C-*p*), 136.14 (C-1′), 137.00 (C-4), 152.13 (C-2), 155.44 (C-4′), 163.15 (C-6) ppm. $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$, 25 °C): δ = –78.29 ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 25 °C): δ = 17.92 ppm. IR (Nujol): $\tilde{\nu}$ = 3315 (w), 1511 (s), 1467 (s), 1439 (s), 1265 (vs), 1246 (vs), 1031 (s), 738 (vs), 639 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{25}NO_2P$ $[M - OTf]^+$ 366.1617; found 366.1625.

***P*,*P*-Dimethyl-*P*-[2-(2,6-dimethylphenylamino)-6-methoxy]phenyl-*P*-phenylphosphonium Triflate (3h):** The general procedure with **1h** (0.08 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2b** (0.13 g, 0.39 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **3h** as a white solid, which was purified by flash column chromatography [gradient eluents: chloroform/methanol 9:1 (v/v) then ethanol; R_f = 0.30, TLC, chloroform/methanol 9:1 (v/v)] and recrystallized from dichloromethane/diethyl ether; 0.07 g, 48%; white prisms; m.p. 183–185 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.02 (s, 6 H, CH_3), 2.66 [d, $^2J_{P,H}$ = 14.0 Hz, 6 H, $P(CH_3)_2$], 3.64 (s, 3 H, OCH_3), 5.80 (s, 1 H, NH), 6.07 (dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{P,H}$ = 5.3 Hz, 1 H, Ar H), 6.47 (dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{P,H}$ = 4.9 Hz, 1 H, Ar H), 7.05 (br s, 3 H, Ar H), 7.33 (t, $^3J_{H,H}$ = 8.3 Hz, 1 H, Ar H), 7.59–7.66 (m, 2 H, Ar H), 7.67–7.74 (m, 3 H, Ar H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 12.76 [d, $^1J_{P,C}$ = 57.2 Hz, $P(CH_3)_2$], 18.41 (CH_3), 56.03 (OCH_3), 92.19 (d, $^1J_{P,C}$ = 92.5 Hz, C-1), 103.38 (d, $^3J_{P,C}$ = 6.1 Hz, C-3), 110.59 (d, $^3J_{P,C}$ = 7.8 Hz, C-5), 120.73 (q, $^1J_{F,C}$ = 320.3 Hz, CF_3SO_3), 125.68 (d, $^1J_{P,C}$ = 88.6 Hz, C-*i*), 126.27 (C-4′), 129.05 (C-3′), 129.97 (d, $^2J_{P,C}$ = 10.5 Hz, C-*o*), 130.47 (d, $^3J_{P,C}$ = 12.6 Hz, C-*m*), 133.91 (d, $^4J_{P,C}$ = 2.8 Hz, C-*p*), 134.28 (C-2′), 137.25 (C-1′), 137.39 (C-4), 152.30 (d, $^2J_{P,C}$ = 2.8 Hz, C-2), 163.63 (C-6) ppm. $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$, 25 °C): δ = –78.22 ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 25 °C): δ = 17.56 ppm. IR (Nujol): $\tilde{\nu}$ = 3330 (m), 1467 (vs), 1438 (s), 1262 (vs), 733 (m), 638 (vs) cm^{-1}. HRMS (ESI): calcd. for $C_{23}H_{27}NOP$ $[M - OTf]^+$ 364.1825; found 364.1831.

General Procedure for the Preparation of the Phosphonium Triflates 4: A solution of **2** (0.78 mmol) in anhydrous CH_3CN (5 mL) was added over 2 h to a mixture of **1** (0.3 mmol) and CsF (0.9 mmol) in anhydrous CH_3CN (10 mL) at 0 °C. The resulting mixture was stirred at 10 °C for 10 h. The reaction mixture was then filtered through a short pad of Celite to remove insoluble substances. After concentration of the filtrate under vacuum, the residue was purified by flash column chromatography on silica and then recrystallized to afford **4**.

***P*-Methyl-*P*-{2-[(*N*-4-methoxyphenyl-*N*-phenyl)amino]phenyl}-*P*,*P*-diphenylphosphonium Triflate (4a):** The general procedure with **1d** (0.1 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2a** (0.23 g, 0.78 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **4a** as a yellow solid, which was purified by flash column chromatography [gradient eluents: chloroform/methanol 9:1 (v/v) then ethanol; R_f = 0.2, TLC, chloroform/methanol 9:1 (v/v)] and recrystallized from dichloromethane/diethyl ether; 0.11 g, 74%; yellow prisms; m.p. 158–160 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.91 (d, $^2J_{P,H}$ = 13.7 Hz, 3 H, PCH_3), 3.70 (s, 3 H, OCH_3), 6.58 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, Ar H), 6.67 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, Ar H), 6.72 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, Ar H), 6.87 (t, $^3J_{H,H}$ = $^4J_{H,H}$ = 7.9 Hz, 1 H, Ar H), 7.08 (t, $^3J_{H,H}$ = 7.9 Hz, 2 H, Ar H), 7.26 (ddd, $^3J_{P,H}$ = 15.0 Hz, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.1 Hz, 1 H, Ar H), 7.34–7.42 (m, 6 H, Ar H), 7.49–7.54 (m, 4 H, Ar H), 7.63–7.67 (m, 2 H, Ar H), 7.74 (t, $^3J_{H,H}$ = 7.7 Hz, 1 H, Ar H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 8.89 (d, $^1J_{P,C}$ = 58.8 Hz, PCH_3), 55.47 (OCH_3), 114.97 (C-3′), 116.88 (d, $^1J_{P,C}$ = 87.8 Hz, C-*i*), 119.14 (d, $^1J_{P,C}$ = 88.2 Hz, C-1), 120.91 (q, $^1J_{F,C}$ = 320.9 Hz, CF_3SO_3), 122.15 (C-2′′), 123.42 (C-4′′), 125.52 (C-2′), 126.86 (d, $^3J_{P,C}$ = 12.9 Hz, C-5), 129.56 (C-3′′), 130.22 (d, $^3J_{P,C}$ = 13.0 Hz, C-*m*), 132.63 (d, $^2J_{P,C}$ = 10.4 Hz, C-*o* and C-3), 134.47 (C-*p*), 136.83 (d, $^4J_{P,C}$ = 1.9 Hz, C-4), 137.62 (d, $^2J_{P,C}$ = 10.1 Hz, C-6), 139.18 (C-1′), 147.49 (C-1′′), 153.01 (d, $^2J_{P,C}$ = 4.4 Hz, C-2), 156.39 (C-4′) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 20.30 ppm. IR (Nujol): $\tilde{\nu}$ = 1507 (vs), 1439 (s), 1262 (vs), 1031 (vs), 910 (vs), 734 (vs) cm^{-1}. HRMS (ESI): calcd. for $C_{32}H_{29}NOP$ $[M - OTf]^+$ 474.1981; found 474.1988.

***P*-{2-[(*N*-4-Bromophenyl-*N*-phenyl)amino]phenyl}-*P*-methyl-*P*,*P*-diphenylphosphonium Triflate (4b):** The general procedure with **1e** (0.11 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2a** (0.23 g, 0.78 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **4b** as a yellow solid, which was purified by flash column chromatography [gradient eluents: chloroform/methanol 9:1 (v/v) then ethanol; R_f = 0.2, TLC, chloroform/methanol 9:1 (v/v)] and recrystallized from dichloromethane/diethyl ether; 0.16 g, 87%; yellow prisms; m.p. 158–160 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.95 (d, $^2J_{P,H}$ = 13.5 Hz, 3 H, PCH_3), 6.64 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, Ar H), 6.78 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, Ar H), 6.88 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, Ar H), 7.08–7.13 (m, 4 H, Ar H), 7.29–7.48 (m, 7 H, Ar H), 7.49–7.54 (m, 4 H, Ar H), 7.56–7.68 (m, 2 H, Ar H), 7.78 (t, $^3J_{H,H}$ = 7.8 Hz, 1 H, Ar H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ = 8.84 (d, $^1J_{P,C}$ = 58.6 Hz, PCH_3), 116.91 (C-4′), 117.75 (d, $^1J_{P,C}$ = 87.6 Hz, C-*i*), 118.48 (d, $^1J_{P,C}$ = 95.3 Hz, C-1), 120.90 (q, $^1J_{F,C}$ = 320.9 Hz, CF_3SO_3), 123.17 (C-2′′), 124.45 (C-4′′), 124.62 (C-2′), 127.66 (d, $^3J_{P,C}$ = 12.8 Hz, C-5), 129.84 (C-3′), 130.34 (d, $^3J_{P,C}$ = 13.0 Hz, C-*m*), 132.61 (C-3′′),

132.72 (d, $^2J_{P,C}$ = 10.6 Hz, C-*o*), 133.07 (d, $^2J_{P,C}$ = 8.2 Hz, C-3), 134.56 (C-*p*), 137.08 (C-4), 137.72 (d, $^2J_{P,C}$ = 10.0 Hz, C-6), 145.55 (C-1′ or C-1′′), 146.17 (C-1′ or C-1′′), 151.90 (d, $^2J_{P,C}$ = 4.4 Hz, C-2) ppm. $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$, 25 °C): δ = –78.20 ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 25 °C): δ = 20.81 ppm. IR (Nujol): $\tilde{\nu}$ = 1487 (m), 1261 (s), 1031 (m), 908 (vs), 733 (vs) cm^{-1}. HRMS (ESI): calcd. for $C_{31}H_{26}BrNP$ $[M - OTf]^+$ 522.0981; found 522.0984.

***P*,*P*-Dimethyl-*P*-phenyl-*P*-[2-(*N*-phenyl-*N*-4-methylphenyl)amino]-phenylphosphonium Triflate (4c):** The general procedure with **1f** (0.07 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2a** (0.23 g, 0.78 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **4c** as a white solid, which was purified by flash column chromatography [gradient eluents: chloroform/methanol 9:1 (v/v) then ethanol; R_f = 0.33, TLC, chloroform/methanol 9:1 (v/v)] and recrystallized from dichloromethane/diethyl ether; 0.11 g, 65%; white prisms; m.p. 183–185 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.21 (s, 3 H, CH_3), 2.32 [d, $^2J_{P,H}$ = 13.6 Hz, 6 H, $P(CH_3)_2$], 6.53 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, Ar H), 6.66 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar H), 6.88 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, Ar H), 6.93 (t, $^3J_{H,H}$ = 8.4 Hz, 1 H, Ar H), 7.11 (t, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar H), 7.23 (t, $^3J_{H,H}$ = 6.7 Hz, 1 H, Ar H), 7.38–7.45 (m, 4 H, Ar H), 7.51–7.59 (m, 2 H, Ar H), 7.72 (t, $^3J_{H,H}$ = 7.7 Hz, 1 H, Ar H), 7.98 (dd, $^3J_{P,H}$ = 14.9 Hz, $^3J_{H,H}$ = 7.9 Hz, 1 H, Ar H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 9.96 [d, $^1J_{P,C}$ = 57.8 Hz, $P(CH_3)_2$], 20.70 (CH_3), 118.11 (d, $^1J_{P,C}$ = 86.8 Hz, C-1 or C-*i*), 120.62 (d, $^1J_{P,C}$ = 88.5 Hz, C-1 or C-*i*), 120.78 (q, $^1J_{F,C}$ = 320.4 Hz, CF_3SO_3), 122.50 (C-2′′), 123.10 (C-2′), 123.72 (C-4′′), 127.57 (d, $^3J_{P,C}$ = 12.5 Hz, C-5), 129.58 (C-3′′), 129.82 (d, $^3J_{P,C}$ = 13.1 Hz, C-*m*), 130.24 (C-3′), 130.96 (d, $^2J_{P,C}$ = 10.7 Hz, C-*o*), 132.36 (d, $^3J_{P,C}$ = 8.0 Hz, C-3), 133.67 (d, $^4J_{P,C}$ = 3.0 Hz, C-*p*), 133.93 (C-4′), 135.92 (d, $^2J_{P,C}$ = 9.8 Hz, C-6), 136.63 (d, $^4J_{P,C}$ = 2.4 Hz, C-4), 144.32 (C-1′ or C-1′′), 147.37 (C-1′ or C-1′′), 151.83 (d, $^2J_{P,C}$ = 4.0 Hz, C-2) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 18.08 ppm. IR (Nujol): $\tilde{\nu}$ = 1508 (s), 1259 (vs), 1030 (s), 933 (m), 734 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{27}H_{27}NP$ $[M - OTf]^+$ 396.1876; found 396.1876.

***P*,*P*-Dimethyl-*P*-phenyl-*P*-[2-(*N*-phenyl-*N*-4-methoxyphenyl)amino]-phenylphosphonium Triflate (4d):** The general procedure with **1g** (0.08 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2a** (0.23 g, 0.39 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **4d** as a white solid, which was purified by flash column chromatography [gradient eluents: chloroform/methanol 9:1 (v/v) then ethanol; R_f = 0.3, TLC, chloroform/methanol 9:1 (v/v)] and recrystallized from dichloromethane/diethyl ether; 0.12 g, 72%; white prisms; m.p. 171–173 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.33 [d, $^2J_{P,H}$ = 13.6 Hz, 6 H, $P(CH_3)_2$], 3.72 (s, 3 H, OCH_3), 6.56–6.64 (m, 6 H, Ar H), 6.92 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, Ar H), 7.10 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, Ar H), 7.22 (t, $^3J_{H,H}$ = 8.0 Hz, 1 H, Ar H), 7.41–7.46 (m, 4 H, Ar H), 7.52–7.58 (m, 2 H, Ar H), 7.72 (t, $^3J_{H,H}$ = 8.0 Hz, 1 H, Ar H), 7.97 (dd, $^3J_{P,H}$ = 14.9 Hz, $^3J_{H,H}$ = 8.0 Hz, 1 H, Ar H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 9.96 [d, $^1J_{P,C}$ = 58.5 Hz, $P(CH_3)_2$], 55.51 (OCH_3), 114.91 (C-3′), 117.76 (d, $^1J_{P,C}$ = 86.9 Hz, C-1 or C-*i*), 120.73 (d, $^1J_{P,C}$ = 88.4 Hz, C-1 or C-*i*), 120.78 (q, $^1J_{F,C}$ = 320.4 Hz, CF_3SO_3), 122.07 (C-2′′), 123.48 (C-4′′), 124.93 (C-2′), 127.36 (d, $^3J_{P,C}$ = 12.7 Hz, C-5), 129.58 (C-3′′), 129.84 (d, $^3J_{P,C}$ = 12.9 Hz, C-*m*), 130.93 (d, $^2J_{P,C}$ = 10.6 Hz, C-*o*), 132.09 (d, $^3J_{P,C}$ = 8.0 Hz, C-3), 133.80 (d, $^4J_{P,C}$ = 2.8 Hz, C-*p*), 135.90 (d, $^2J_{P,C}$ = 9.9 Hz, C-6), 136.62 (d, $^4J_{P,C}$ = 2.1 Hz, C-4), 139.87 (C-1′), 147.79 (C-1′′), 152.02 (d, $^2J_{P,C}$ = 3.9 Hz, C-2), 156.41 (C-4′) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 18.08 ppm. IR (Nujol): $\tilde{\nu}$ = 1507 (s), 1260 (vs), 1031 (vs), 911 (s), 732 (vs) cm^{-1}. HRMS (ESI): calcd. for $C_{27}H_{27}NOP$ $[M - OTf]^+$ 412.1825; found 412.1830.

***P*-{2-[(*N*-4-bromophenyl-*N*-Phenyl)amino]phenyl}-*P*,*P*-dimethyl-*P*-phenylphosphonium Triflate (4e):** The general procedure with **1i** (0.09 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2a** (0.23 g, 0.78 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **4e** as a yellow solid, which was purified by flash column chromatography [gradient eluents: chloroform/methanol 9:1 (v/v) then ethanol; R_f = 0.2, TLC, chloroform/methanol 9:1 (v/v)] and recrystallized from dichloromethane/diethyl ether; 0.14 g, 76%; white prisms; m.p. 163–165 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.39 [d, $^2J_{P,H}$ = 13.6 Hz, 6 H, $P(CH_3)_2$], 6.52 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, Ar H), 6.69 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, Ar H), 6.96 (t, $^3J_{H,H}$ = 7.8 Hz, 1 H, Ar H), 7.11 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, Ar H), 7.13 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, Ar H), 7.22 (dd, $^3J_{H,H}$ = 7.7 Hz, $^4J_{P,H}$ = 5.6 Hz, 1 H, Ar H), 7.36–7.39 (m, 4 H, Ar H), 7.50–7.57 (m, 1 H, Ar H), 7.62 (t, $^3J_{H,H}$ = 7.7 Hz, 1 H, Ar H), 7.75 (t, $^3J_{H,H}$ = 7.7 Hz, 1 H, Ar H), 8.08 (dd, $^3J_{P,H}$ = 14.7 Hz, $^3J_{H,H}$ = 7.7 Hz, 1 H, Ar H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 9.22 (d, $^1J_{P,C}$ = 55.8 Hz, PCH_3), 10.53 (d, $^1J_{P,C}$ = 57.6 Hz, PCH_3), 116.63 (C-4′), 118.53 (d, $^1J_{P,C}$ = 86.7 Hz, C-1 or C-*i*), 120.28 (d, $^1J_{P,C}$ = 87.9 Hz, C-1 or C-*i*), 120.74 (q, $^1J_{F,C}$ = 320.5 Hz, CF_3SO_3), 122.83 (C-2′′), 124.06 (C-2′), 124.36 (C-4′′), 128.20 (d, $^3J_{P,C}$ = 12.9 Hz, C-5), 129.83 (C-3′′), 129.92 (d, $^3J_{P,C}$ = 13.1 Hz, C-*m*), 130.83 (d, $^2J_{P,C}$ = 10.7 Hz, C-*o*), 132.48 (C-3′) 132.52 (d, $^3J_{P,C}$ = 8.2 Hz, C-3), 133.73 (d, $^4J_{P,C}$ = 3.0 Hz, C-*p*), 136.09 (d, $^2J_{P,C}$ = 9.6 Hz, C-6), 136.82 (d, $^4J_{P,C}$ = 2.4 Hz, C-4), 145.80 (C-1′ or C-1′′), 146.46 (C-1′ or C-1′′), 150.79 (d, $^2J_{P,C}$ = 3.9 Hz, C-2) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 18.15 ppm. IR (Nujol): $\tilde{\nu}$ = 1487 (vs), 1260 (vs), 1031 (vs), 911 (s), 731 (vs) cm^{-1}. HRMS (ESI): calcd. for $C_{26}H_{24}BrNP$ $[M - OTf]^+$ 460.0824; found 460.0825.

***P*-{2-[(*N*-4-nitrophenyl-*N*-phenyl)amino]phenyl}-*P*,*P*-dimethyl-*P*-phenylphosphonium Triflate (4f):** The general procedure with **1j** (0.08 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2a** (0.23 g, 0.78 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **4f** as a yellow solid, which was purified by flash column chromatography [gradient eluents: chloroform/methanol 9:1 (v/v) then ethanol; R_f = 0.2, TLC, chloroform/methanol 9:1 (v/v)] and recrystallized from dichloromethane/diethyl ether; 0.12 g, 69%; white prisms; m.p. 124–126 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.34 (d, $^2J_{P,H}$ = 14.0 Hz, 3 H, PCH_3), 2.47 (d, $^2J_{P,H}$ = 13.6 Hz, 3 H, PCH_3), 6.76 (d, $^3J_{H,H}$ = 9.2 Hz, 2 H, Ar H), 6.77 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, Ar H), 7.04 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, Ar H), 7.18 (dd, $^3J_{H,H}$ = 8.1 Hz, $^3J_{H,H}$ = 7.4 Hz, 2 H, Ar H), 7.28–7.40 (m, 5 H, Ar H), 7.44–7.50 (m, 1 H, Ar H), 7.72 (t, $^3J_{H,H}$ = 7.9 Hz, 1 H, Ar H), 7.83 (t, $^3J_{H,H}$ = 7.9 Hz, 1 H, Ar H), 7.86 (d, $^3J_{H,H}$ = 9.2 Hz, 2 H, Ar H), 8.14 (ddd, $^3J_{P,H}$ = 14.8 Hz, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H, Ar H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 9.33 (d, $^1J_{P,C}$ = 57.6 Hz, PCH_3), 10.10 (d, $^1J_{P,C}$ = 58.1 Hz, PCH_3), 119.16 (d, $^1J_{P,C}$ = 86.4 Hz, C-1 or C-*i*), 120.06 (d, $^1J_{P,C}$ = 87.5 Hz, C-1 or C-*i*), 120.31 (C-2′), 120.71 (q, $^1J_{F,C}$ = 320.5 Hz, CF_3SO_3), 123.89 (C-2′′), 125.35 (C-3′), 125.80 (C-4′′), 129.30 (d, $^3J_{P,C}$ = 12.3 Hz, C-5), 129.86 (d, $^3J_{P,C}$ = 13.2 Hz, C-*m*), 130.15 (C-3′′), 130.89 (d, $^2J_{P,C}$ = 10.7 Hz, C-*o*), 132.96 (d, $^3J_{P,C}$ = 7.9 Hz, C-3), 133.97 (d, $^4J_{P,C}$ = 2.4 Hz, C-*p*), 136.48 (d, $^2J_{P,C}$ = 9.4 Hz, C-6), 137.14 (C-4), 142.21 (C-4′), 144.35 (C-1′′), 149.22 (d, $^2J_{P,C}$ = 3.6 Hz, C-2), 152.19 (C-1′) ppm. $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$, 25 °C): δ = –78.30 ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 18.76 ppm. IR (Nujol): $\tilde{\nu}$ = 1492 (m), 1270 (s), 1031 (m), 908 (vs), 732 (vs) cm^{-1}. HRMS (ESI): calcd. for $C_{26}H_{24}N_2O_2P$ $[M - OTf]^+$ 427.1570; found 427.1581.

***o*-Azaphosphaxylydene (5f):** To a solution of **3f** (49.0 mg, 0.1 mmol) in dry [D_8]THF (1 mL, distilled from sodium/benzophenone immediately prior to use) at –78 °C was added *n*BuLi (1.6 M solution in hexanes; 70 μL, 0.11 mmol). The reaction mixture was stirred for 5 min, and then a portion (0.6 mL) of the yellow solution formed was quickly transferred by syringe to a dried 5 mm NMR tube cooled to –78 °C under an inert atmosphere. The sample was transferred into the bore of the magnet precooled to –50 °C. The extra signals in the spectra correspond to the solvent of the organolithium base, which was not eliminated. ^{1}H NMR (500.13 MHz, [D_8]THF, –30 °C): δ = 1.83 (s, 6 H, CH_3), 2.37 [d, $^2J_{P,H}$ = 14.3 Hz, 6 H, P(CH_3)$_2$], 5.58 (dd, $^3J_{H,H}$ = 7.7 Hz, $^4J_{P,H}$ = 6.5 Hz, 1 H, 3-H), 5.7 (dt, $^3J_{H,H}$ = 7.7 Hz, $^4J_{P,H}$ = 4.1 Hz, 1 H, 5-H), 6.52 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, 4′-H), 6.69 (t, $^3J_{H,H}$ = 7.7 Hz, 1 H, 4-H), 6.77 (t, $^3J_{H,H}$ = 7.7 Hz, $^3J_{P,H}$ = 14.3 Hz, 1 H, 6-H), 6.81 (d, $^3J_{H,H}$ = 7.3 Hz, 2 H, 3′-H), 7.56 (dt, $^3J_{H,H}$ = 7.4, $^4J_{P,H}$ = 2.3 Hz, 2 H, *m*-H), 7.63 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, *p*-H), 7.89 (dd, $^3J_{H,H}$ = 7.4 Hz, $^3J_{P,H}$ = 12.8 Hz, 2 H, *o*-H) ppm. ^{13}C{^{1}H} NMR (125.758 MHz, [D_8]THF, –30 °C): δ = 7.88 [d, $^1J_{P,C}$ = 60.6 Hz, P(CH_3)$_2$], 18.56 (CH_3), 90.61 (d, $^1J_{P,C}$ = 103.0 Hz, C-1), 104.29 (d, $^3J_{P,C}$ = 14.8 Hz, C-5), 111.91 (d, $^3J_{P,C}$ = 8.0 Hz, C-3), 118.34 (C-4′), 127.07 (C-3′), 127.11 (d, $^1J_{P,C}$ = 89.7 Hz, C-*i*), 128.7 (d, $^3J_{P,C}$ = 12.5 Hz, C-*m*), 130.26 (C-2′), 131.3 (d, $^2J_{P,C}$ = 10.1 Hz, C-*o*), 131.83 (d, $^4J_{P,C}$ = 1.7 Hz, C-*p*), 132.86 (d, $^2J_{P,C}$ = 11.9 Hz, C-6), 133.9 (C-4), 153.15 (C-1′), 158.25 (d, $^2J_{P,C}$ = 6.8 Hz, C-2) ppm. ^{31}P{^{1}H} NMR (202.456 MHz, [D_8]-THF, –30 °C): δ = 11.09 ppm.

General Procedure for the Preparation of the 2-(Arylamino)phenylphosphane Oxides 6a–6c and the Phosphonate 6d: A solution of **2** (0.39 mmol) in anhydrous CH_3CN (5 mL) was added over 2 h to a mixture of **1k**–**1m** (0.3 mmol) and CsF (0.9 mmol) in anhydrous CH_3CN (10 mL) at 0 °C. The resulting mixture was stirred at 25 °C for 24 h. The reaction mixture was then filtered through a short pad of Celite to remove insoluble substances. After concentration of the filtrate under vacuum, the residue was purified by chromatography on silica and then recrystallized to afford **6**.

***P*-[2-(4-Methylphenylamino)phenyl]-*P*,*P*-diphenylphosphane Oxide (6a):** The general procedure with **1k** (0.1 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2a** (0.12 g, 0.39 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **6a** as a white solid, which was purified by column chromatography [eluent: hexanes/ethyl acetate 1:1 (v/v), R_f = 0.61] and recrystallized from chloroform/*n*-pentane; 0.1 g, 90%; white prisms; m.p. 147–149 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.28 (s, 3 H, CH_3), 6.64–6.69 (m, 1 H, Ar H), 6.85 (ddd, $^3J_{P,H}$ = 14.4 Hz, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.4 Hz, 1 H, Ar H), 7.00 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar H), 7.05 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar H), 7.24–7.31 (m, 2 H, Ar H), 7.45–7.49 (m, 4 H, Ar H), 7.52–7.58 (m, 2 H, Ar H), 7.64–7.71 (m, 4 H, Ar H), 8.71 (s, 1 H, NH) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ = 20.71 (CH_3), 114.06 (d, $^1J_{P,C}$ = 104.5 Hz, C-1), 114.69 (d, $^3J_{P,C}$ = 7.7 Hz, C-3), 117.49 (d, $^3J_{P,C}$ = 12.9 Hz, C-5), 121.30 (C-2′), 128.44 (d, $^3J_{P,C}$ = 12.3 Hz, C-*m*), 129.62 (C-3′), 131.95 (d, $^4J_{P,C}$ = 2.9 Hz, C-*p*), 131.97 (d, $^2J_{P,C}$ = 9.9 Hz, C-*o*), 132.06 (C-4′), 132.11 (d, $^1J_{P,C}$ = 104.8 Hz, C-*i*), 133.13 (d, $^4J_{P,C}$ = 1.7 Hz, C-4), 133.66 (d, $^3J_{P,C}$ = 11.2 Hz, C-6), 138.64 (C-1′), 150.45 (d, $^2J_{P,C}$ = 4.0 Hz, C-2) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 36.25 ppm. IR (Nujol): $\tilde{\nu}$ = 1591 (vs), 1571 (vs), 1450 (vs), 1118 (s), 726 (vs), 694 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{23}NOP$ [M + H]$^+$ 384.1512; found 384.1518.

***P*-[2-(4-Bromophenylamino)phenyl]-*P*,*P*-diphenylphosphane Oxide (6b):** The general procedure with **1l** (0.12 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2a** (0.12 g, 0.39 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **6b** as a white solid, which was purified by column chromatography [eluent: hexanes/ethyl acetate 1:1 (v/v), R_f = 0.42] and recrystallized from chloroform/*n*-pentane; 0.12 g, 86%; white prisms; m.p. 169–171 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.75–6.79 (m, 1 H, Ar H), 6.88 (ddd, $^3J_{P,H}$ = 15.8 Hz, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.3 Hz, 1 H, Ar H), 6.95 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, Ar H), 7.29 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, Ar H), 7.32–7.37 (m, 2 H, Ar H), 7.44–7.48 (m, 4 H, Ar H), 7.53–7.57 (m, 2 H, Ar H), 7.62–7.67 (m, 4 H, Ar H) ppm; NH not observable. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ = 114.14 (C-4′), 116.01 (d, $^1J_{P,C}$ = 103.0 Hz, C-1), 116.04 (d, $^3J_{P,C}$ = 7.6 Hz, C-3), 118.94 (d, $^3J_{P,C}$ = 12.7 Hz, C-5), 121.58 (C-2′), 128.65 (d, $^3J_{P,C}$ = 12.2 Hz, C-*m*), 131.87 (d, $^1J_{P,C}$ = 104.4 Hz, C-*i*), 132.08 (d, $^2J_{P,C}$ = 10.0 Hz, C-*o*), 132.09 (C-*p* and C-3′), 133.34 (d, $^4J_{P,C}$ = 1.6 Hz, C-4), 133.91 (d, $^2J_{P,C}$ = 10.9 Hz, C-6), 140.84 (C-1′), 149.22 (d, $^2J_{P,C}$ = 2.8 Hz, C-2) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 36.23 ppm. IR (Nujol): $\tilde{\nu}$ = 1591 (vs), 1570 (vs), 1450 (vs), 1119 (m), 728 (vs), 694 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{24}H_{20}BrNOP$ [M + H]$^+$ 448.0460; found 448.0443.

***P*-[2-(4-Bromophenylamino)methoxyphenyl]-*P*,*P*-diphenylphosphane Oxide (6c):** The general procedure with **1l** (0.12 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2b** (0.13 g, 0.39 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **6c** as a white solid, which was purified by column chromatography [eluent: hexanes/ethyl acetate 1:1 (v/v), R_f = 0.70] and recrystallized from chloroform/*n*-pentane; 0.09 g, 66%; white prisms; m.p. 187–189 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.30 (s, 3 H, OCH_3), 6.22 (dd, $^3J_{H,H}$ = 8.1 Hz, $^4J_{P,H}$ = 4.7 Hz, 1 H, Ar H), 6.93 (dd, $^3J_{H,H}$ = 8.5 Hz, $^4J_{P,H}$ = 4.2 Hz, 1 H, Ar H), 7.13 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, Ar H), 7.25–7.29 (m, 1 H, Ar H), 7.37 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, Ar H), 7.42–7.48 (m, 4 H, Ar H), 7.50–7.54 (m, 2 H, Ar H), 7.71–7.77 (m, 4 H, Ar H) ppm; NH not observed. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ = 54.77 (OCH_3), 100.01 (d, $^1J_{P,C}$ = 103.2 Hz, C-1), 101.15 (d, $^3J_{P,C}$ = 5.6 Hz, C-3), 108.30 (d, $^3J_{P,C}$ = 7.9 Hz, C-5), 114.89 (C-4′), 123.37 (C-2′), 128.13 (d, $^3J_{P,C}$ = 12.8 Hz, C-*m*), 131.56 (d, $^4J_{P,C}$ = 3.8 Hz, C-*p*), 131.59 (d, $^2J_{P,C}$ = 10.5 Hz, C-*o*), 132.09 (C-3′), 134.06 (d, $^2J_{P,C}$ = 107.6 Hz, C-*i*), 134.60 (C-4), 140.91 (C-1′), 152.37 (C-6), 161.75 (d, $^2J_{P,C}$ = 2.7 Hz, C-2) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 38.75 ppm. IR (Nujol): $\tilde{\nu}$ = 1583 (s), 1465 (vs), 1118 (m), 774 (s), 749 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{22}BrNO_2P$ [M + H]$^+$ 478.0566; found 478.0571.

Dimethyl 2-(4-Methylphenylamino)phenylphosphonate (6d): The general procedure with **1l** (0.07 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2b** (0.12 g, 0.39 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **7c** as a white solid, which was purified by column chromatography [eluent: hexanes/ethyl acetate 1:1 (v/v), R_f = 0.70] and recrystallized from chloroform/*n*-pentane; 0.06 g, 66%; white prisms; m.p. 187–189 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.33 (s, 3 H, CH_3), 3.78 (d, $^3J_{P,H}$ = 11.1 Hz, 6 H, OCH_3), 6.75–6.81 (m, 1 H, Ar H), 7.08–7.15 (m, 4 H, Ar H), 7.17–7.22 (m, 1 H, Ar H), 7.28–7.33 (m, 1 H, Ar H), 7.50 (ddd, $^3J_{P,H}$ = 14.7 Hz, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H, Ar H), 8.33 (s, 1 H, NH) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = 20.85 (CH_3), 52.79 (d, $^2J_{P,C}$ = 5.0 Hz, OCH_3), 108.71 (d, $^1J_{P,C}$ = 183.2 Hz, C-1), 114.36 (d, $^3J_{P,C}$ = 11.9 Hz, C-3), 117.83 (d, $^3J_{P,C}$ = 14.0 Hz, C-5), 121.98 (C-2′), 129.92 (C-3′), 132.79 (C-4′), 133.54 (d, $^2J_{P,C}$ = 6.8 Hz, C-6), 133.99 (d, $^4J_{P,C}$ = 1.6 Hz, C-4), 138.57 (C-1′), 149.52 (d, $^2J_{P,C}$ = 8.3 Hz, C-2) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 24.45 ppm. IR (Nujol): $\tilde{\nu}$ = 1595 (vs), 1516 (vs), 1455 (vs), 1139 (s), 1027 (vs), 823 (s), 790 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{19}NO_3P$ [M + H]$^+$ 292.1097; found 292.1103.

General Procedure for the Preparation of the Phosphonium Triflates 8: A solution of **2a** (0.78 mmol) in anhydrous CH_3CN (5 mL) was

added over 2 h to a mixture of **7** (0.3 mmol) and CsF (0.9 mmol) in anhydrous CH_3CN (10 mL) at 0 °C. The resulting mixture was stirred at 25 °C for 24 h. The reaction mixture was then filtered through a short pad of Celite to remove insoluble substances. After concentration of the filtrate under vacuum, the residue was purified by flash column chromatography on silica and then recrystallized to afford **6**.

***P*,*P*,*P*-Triphenyl-*P*-[2-(phenylthio)phenyl]phosphonium Triflate (8a):** The general procedure with **7a** (0.09 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2a** (0.23 g, 0.78 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **8a** as a white solid, which was purified by flash column chromatography [gradient eluents: chloroform/methanol 9:1 (v/v) then ethanol; R_f = 0.19, TLC, chloroform/methanol 9:1 (v/v)] and recrystallized from dichloromethane/diethyl ether; 0.13 g, 70%; white prisms; m.p. 140–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.90 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, Ar H), 7.19–7.28 (m, 3 H, Ar H), 7.29–7.33 (m, 1 H, Ar H), 7.50 (dd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{P,H}$ = 5.2 Hz, 1 H, Ar H), 7.58 (td, $^3J_{H,H}$ = 7.6 Hz, $^4J_{P,H}$ = 2.8 Hz, 1 H, Ar H), 7.65–7.78 (m, 13 H, Ar H), 7.81–7.84 (m, 3 H, Ar H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ = 118.12 (d, $^1J_{P,C}$ = 90.8 Hz, C-*i*), 118.47 (d, $^1J_{P,C}$ = 94.2 Hz, C-1), 120.71 (q, $^1J_{F,C}$ = 320.9 Hz, CF_3SO_3), 128.89 (C-4′), 129.16 (d, $^3J_{P,C}$ = 12.6 Hz, C-5), 129.79 (C-3′), 130.65 (d, $^3J_{P,C}$ = 13.1 Hz, C-*m*), 131.00 (C-2′), 132.10 (C-1′), 134.17 (d, $^2J_{P,C}$ = 10.3 Hz, C-*o*), 135.08 (d, $^3J_{P,C}$ = 8.7 Hz, C-3), 135.31 (d, $^4J_{P,C}$ = 3.0 Hz, C-*p*), 136.34 (d, $^4J_{P,C}$ = 2.6 Hz, C-4), 137.49 (d, $^2J_{P,C}$ = 11.9 Hz, C-6), 143.46 (d, $^2J_{P,C}$ = 7.1 Hz, C-2) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 22.01 ppm. IR (Nujol): $\tilde{\nu}$ = 1440 (m), 1266 (vs), 1108 (m), 1030 (s), 731 (s), 691 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{30}H_{24}PS$ [M –OTf]$^+$ 447.1331; found 447.1337.

***P*-Methyl-*P*,*P*-diphenyl-*P*-[2-(phenylthio)phenyl]phosphonium Triflate (8b):** The general procedure with **7b** (0.07 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2a** (0.23 g, 0.78 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **8b** as a white solid, which was purified by flash column chromatography [gradient eluents: chloroform/methanol 9:1 (v/v) then ethanol; R_f = 0.17, TLC, chloroform/methanol 9:1 (v/v)] and recrystallized from dichloromethane/diethyl ether; 0.14 g, 87%; white prisms; m.p. 147–149 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.09 (d, $^2J_{P,H}$ = 13.2 Hz, 3 H, PCH_3), 7.03–7.05 (m, 2 H, Ar H), 7.23–7.29 (m, 3 H, Ar H), 7.32 (ddd, $^3J_{P,H}$ = 14.8 Hz, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H, Ar H), 7.45–7.52 (m, 2 H, Ar H), 7.65–7.72 (m, 9 H, Ar H), 7.74–7.78 (m, 2 H, Ar H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ = 10.07 (d, $^1J_{P,C}$ = 58.8 Hz, CH_3), 119.37 (d, $^1J_{P,C}$ = 89.8 Hz, C-*i*), 120.74 (d, $^1J_{P,C}$ = 93.0 Hz, C-1), 120.84 (q, $^1J_{F,C}$ = 320.8 Hz, CF_3SO_3), 128.52 (C-4′), 129.10 (d, $^3J_{P,C}$ = 12.6 Hz, C-5), 129.86 (C-3′), 130.54 (d, $^3J_{P,C}$ = 12.9 Hz, C-*m*), 130.74 (C-2′), 132.85 (d, $^2J_{P,C}$ = 10.5 Hz, C-*o*), 133.05 (C-1′), 134.95 (d, $^4J_{P,C}$ = 2.8 Hz, C-*p*), 135.74 (d, $^3J_{P,C}$ = 8.7 Hz, C-3), 135.95 (d, $^4J_{P,C}$ = 2.3 Hz, C-4), 136.56 (d, $^2J_{P,C}$ = 12.0 Hz, C-6), 141.87 (d, $^2J_{P,C}$ = 7.3 Hz, C-2) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 21.69 ppm. IR (Nujol): $\tilde{\nu}$ = 1440 (m), 1263 (s), 1114 (m), 1030 (s), 909 (s), 732 (vs) cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{22}PS$ [M – OTf]$^+$ 385.1174; found 385.1179.

***P*,*P*-Dimethyl-*P*-phenyl-*P*-[2-(phenylthio)phenyl]phosphonium Triflate (8c):** The general procedure with **7c** (0.05 g, 0.3 mmol) in anhydrous CH_3CN (5 mL), **2a** (0.23 g, 0.78 mmol) in anhydrous CH_3CN (10 mL), and CsF (0.14 g, 0.9 mmol) afforded **8c** as a white solid, which was purified by flash column chromatography [gradient eluents: chloroform/methanol 9:1 (v/v) then ethanol; R_f = 0.17, TLC, chloroform/methanol 9:1 (v/v)] and recrystallized from dichloromethane/diethyl ether; 0.1 g, 73%; white prisms; m.p. 153–155 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.67 [d, $^2J_{P,H}$ = 13.6 Hz, 6 H, $P(CH_3)_2$], 6.95–6.98 (m, 2 H, Ar H), 7.22–7.24 (m, 3 H, Ar H), 7.42–7.45 (m, 1 H, Ar H), 7.52–7.55 (m, 2 H, Ar H), 7.60–7.70 (m, 5 H, Ar H), 7.98–8.06 (m, 1 H, Ar H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = 10.33 (d, $^1J_{P,C}$ = 57.3 Hz, CH_3), 120.76 (q, $^1J_{F,C}$ = 320.4 Hz, CF_3SO_3), 121.86 (d, $^1J_{P,C}$ = 88.6 Hz, C-*i*), 121.89 (d, $^1J_{P,C}$ = 91.5 Hz, C-1), 128.24 (C-4′), 129.47 (d, $^3J_{P,C}$ = 12.1 Hz, C-5), 129.78 (C-2′ or C-3′), 130.12 (d, $^3J_{P,C}$ = 12.1 Hz, C-*m*), 130.20 (C-2′ or C-3′), 131.22 (d, $^2J_{P,C}$ = 11.0 Hz, C-*o*), 133.50 (C-1′), 134.15 (d, $^4J_{P,C}$ = 3.0 Hz, C-*p*), 135.21 (d, $^2J_{P,C}$ = 11.2 Hz, C-6), 135.76 (d, $^4J_{P,C}$ = 2.4 Hz, C-4), 135.92 (d, $^3J_{P,C}$ = 8.6 Hz, C-3), 140.61 (d, $^2J_{P,C}$ = 7.1 Hz, C-2) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 21.01 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –78.27 ppm. IR (Nujol): $\tilde{\nu}$ = 1440 (m), 1257 (vs), 1155 (s), 1029 (s), 744 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{20}PS$ [M –OTf]$^+$ 323.1018; found 323.1024.

Supporting Information (see footnote on the first page of this article): Detailed procedures for the synthesis of **1**, characterization data and copies of the ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of the new compounds.

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