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Aryne insertion into the P=O bond: one-pot synthesis of quaternary phosphonium triflates†

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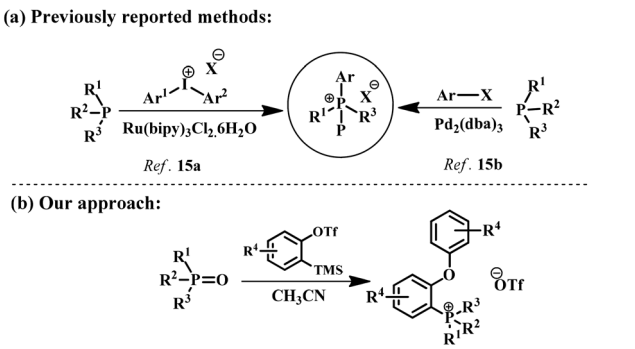
A novel transition-metal free synthetic strategy has been developed for the direct synthesis of quaternary phosphonium triflates *via* insertion of aryne into phosphine oxide. This methodology provides good yields of quaternary phosphonium salts and one of the synthesized phosphonium salts has been unambiguously established by single crystal XRD study. Preliminary mechanistic studies suggest that the reaction proceeds *via* a sequential [2 + 2] cycloaddition followed by the *o*-arylation and protonation pathway.

Introduction

Organophosphorus compounds are an important class of organic compounds that have gained much attention among chemists due to their broad spectrum of applications in various promising areas, such as medicinal chemistry,[1] organic synthesis,[2] natural products,[3] materials chemistry,[4] catalysis and coordination chemistry.[5] Aryl substituted organophosphorus compounds and their derivatives have particularly gained importance as targets for synthesis due to their unique physicochemical and biological properties, which are influenced by the C(sp^2)–P bond between the phosphorus and the arene. Therefore, the construction of the C(sp^2)–P bond is one of the most important and fundamental methods to synthesize organophosphorus compounds in organic synthesis. The classical synthetic methods for the construction of the C–P bond rely on the transition-metal-catalyzed cross-coupling reactions as well as reactions of phosphine reagents with C(sp^2)-halides or pseudo halides.[6] Later on, various Cu,[7] Ni[8] and Mn[9] catalyzed or mediated synthetic strategies have been developed for the synthesis of aryl substituted organophosphorus compounds. Among organophosphorus compounds, quaternary aryl phosphonium salts are also promising compounds,[10] which are extensively used as Lewis acid reagents,[11] phase-transfer catalysts,[12] ionic liquids,[13] and anti-cancer agents[14] as well as in drug delivery.[15] Although there are several methods for the synthesis of organophosphorus compounds, synthetic methods for quaternary phosphonium salts are very rare (Scheme 1).[16] In this regard, metal-catalyzed coupling of phosphines with aryl halides and hypervalent iodine is known but it requires high reaction temperatures and expensive reagents. Therefore, the development of a reliable synthetic strategy for the synthesis of quaternary phosphonium salts *via* the construction of the C(sp^2)–P bond from readily available starting materials under mild reaction conditions is still a challenge for chemists.

On the other hand, arynes are highly reactive transient intermediates, which have emerged as powerful synthons for various carbocycles,[17] heterocycles[18] and natural products.[19] Although there are several synthetic protocols for the generation of arynes, the use of 2-(trimethylsilyl) aryltriflates[20] as mild aryne precursors has led to the rapid growth of this field. Due to their high reactivity, arynes undergo various interesting reactions including nucleophilic addition,[21] [2 + 2] cycloaddition and Diels–Alder reactions.[22] Additionally, this intermediate could be used for the direct *ortho*-functionalization of



Scheme 1 Reported and our approach for the quaternary phosphonium salt.

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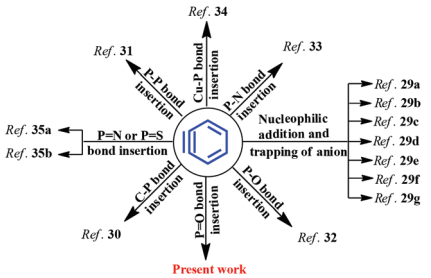


Scheme 2 Reported synthetic protocols for the synthesis of organophosphorus compounds using the aryne precursor.

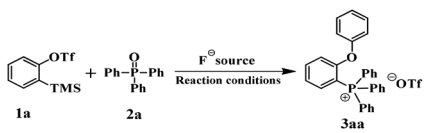
arenes *via* aryne insertion into the σ-bond and the π-bond. Aryne insertion into the methylene–carbonyl σ-bond,[23] C=C bond,[24] C=O bond,[25] various amides including DMF,[25f,g,26] and halogens[27] for the synthesis of functionalized arenes has also been reported. These insertion reactions are preferred as they do not require any transition metal catalysts as well as harsh reaction conditions for the synthesis of functionalized arenes. Interestingly, aryne insertion into the S=O[28] bond is also known and several sulfur containing compounds have been synthesized. Additionally, the synthesis of organophosphorus compounds from aryne precursors is another interesting area of aryne chemistry, where several organophosphorus compounds have been synthesized and reported (Scheme 2).

In this regard, nucleophilic addition by phosphine to highly electrophilic arynes followed by the trapping of anions is one of the most common strategies for their synthesis.[29] Additionally, the insertion of arynes into the methylene–phosphorus σ bond,[30] and into the P–P,[31] P–O,[32] P–N,[33] Cu–P,[34] P=S and P=N[35] bonds for the synthesis of organophosphorus compounds is known (Scheme 2). However, studies on the insertion of the P=O bond into arynes for the synthesis of organophosphorus compounds are rare. As a continuation of our research on aryne chemistry,[28c,36] here we report a synthetic protocol for the direct synthesis of quaternary phosphonium triflates from phosphine oxides *via* aryne insertion into the P=O bond.

Results and discussion

Initially, the reaction conditions were screened by using a model reaction between Kobayashi's precursor **1a** and triphenylphosphine oxide **2a** in acetonitrile with a variety of fluoride sources at room temperature for 24 h and the results are shown in Table 1 (entries 1–3). From these preliminary investigations, it was seen that CsF showed better results in comparison with KF or TBAF and afforded the desired product **3aa** in 71% yield (Table 1, entry 2). Additionally, 18-crown-6 was separately used as an additive with KF and CsF during our optimization studies under the same reaction conditions (Table 1, entries 4 and 5). Although addition of 18-crown-6 with KF gave slightly improved results, they were comparatively lower than the best results already achieved. On the other hand, use of 18-crown-6 with CsF did not result in any significant improvement in yield. Few more optimization studies were performed by changing the reaction medium, that is using DMF, dioxane and DMSO instead of CH_3CN; nevertheless, the results were not impressive (Table 1, entries 6–8). The amount of fluoride used as the source was also optimized and 3 equiv. were found to be optimum to obtain high yield under the same reaction conditions (Table 1, entries 9 and 10). Slight modifications of the reaction temperature as well as reaction time compared to our previous reaction conditions were also done to investigate the progress of our reaction (Table 1, entries 11 and 12). It was

Table 1 Optimization studies for the synthesis of (2-phenoxyphenyl)triphenylphosphonium triflates[a]



Entry	Fluoride source (equiv.)	Solvent	Additive	Temp. (°C)	Time (hours)	Yield[b] (%)
1	KF (3)	CH_3CN	—	rt	24	52
2	**CsF (3)**	**CH_3CN**	**—**	**rt**	**24**	**71**
3	TBAF (3)	CH_3CN		rt	24	Trace
4	KF (3)	CH_3CN	18-Crown-6	rt	24	62
5	CsF (3)	CH_3CN	18-Crown-6	rt	24	70
6	CsF (3)	DMF	—	rt	24	ND
7	CsF (3)	Dioxane	—	rt	24	ND
8	CsF (3)	DMSO	—	rt	24	Trace
9	CsF (4)	CH_3CN	—	rt	24	72
10	CsF (2)	CH_3CN	—	rt	24	65
11	CsF (3)	CH_3CN	—	60	12	65
12	KF (3)	CH_3CN	—	rt	48	69
13	—	CH_3CN	—	rt	24	ND

[a] Conditions: *o*-Silyl aryl triflate **1a** (2 mmol), triphenylphosphineoxide **2a** (1 mmol), fluoride source (3 mmol), solvent (4 mL) stirred at rt to 60 °C. [b] Isolated yield; ND: not detected.

seen that KF requires more reaction time for the synthesis of **3aa**. A control experiment was also performed using **1a** and **2a** without any fluoride source in acetonitrile at room temperature for 24 h. Under these reaction conditions, the desired product **3aa** was not obtained (Table 1, entry 13).

Thus, we optimized our reaction conditions of the aryne precursor (2 equiv.) and phosphine oxide (1 equiv.) for the synthesis of quaternary phosphonium triflate using 3 equiv. of CsF as the fluoride source and acetonitrile as the reaction medium, and the reaction was set at room temperature for 24 h. The quaternary phosphonium triflate **3aa** as obtained from our optimization studies was characterized by ^{1}H NMR and ^{13}C NMR spectra and HRMS analysis. This solid product, **3aa**, was crystallized from ethyl acetate and finally the composition and configuration of the product was confirmed by X-ray crystal structure analysis (Fig. 1).

The optimized reaction conditions, as obtained from our initial investigations, were applied for our generalization studies, and the results are shown in Table 2. A set of structurally diverse organophosphorus compounds were synthesized using the aryne precursor *o*-silyl aryl triflate **1a** with a wide range of phosphine oxides. Both aryl and alkyl substituted phosphine oxides were considered in this investigation. Electron-rich and electron-deficient $Ar_3P{=}O$ smoothly participated in our reaction processes for the synthesis of quaternary phosphonium triflates and all were well-tolerated under the reaction conditions.

Electron-rich $Ar_3P{=}O$ gave a comparatively higher yield than electron-deficient $Ar_3P{=}O$. Additionally, phosphine oxides with alkyl substitutions also took part in our reaction process with aryne precursor **1a** and afforded the corresponding quaternary phosphonium triflates in good yields. Interestingly, alkyl-substituted phosphine oxides afforded higher yields than aryl-substituted phosphine oxides. Another symmetrical aryne precursor, 4,5-dimethoxy-2-(trimethylsilyl) phenyl trifluoromethanesulfonate **2b**, was also investigated in our reaction process with phosphine oxides bearing both aliphatic and aromatic substituents, providing our targeted quaternary phosphonium triflates in good yields.

To investigate the substrate scope of arynes, mono substituted β-trimethylsilyltriflates, *i.e.* 4-methyl-2-(trimethylsilyl) phenyl trifluoromethanesulfonate **1c**, 3-methoxy-2-(trimethylsilyl) phenyl trifluoromethanesulfonate **1d** and 1-(trimethylsilyl)-2-naphthyl trifluoromethanesulfonate **1e**, were used for the synthesis of quaternary phosphonium triflates. The aryne

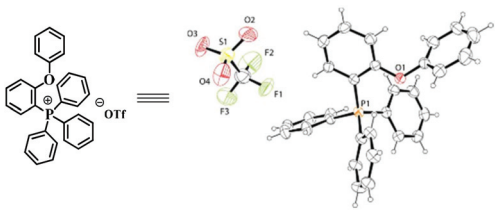
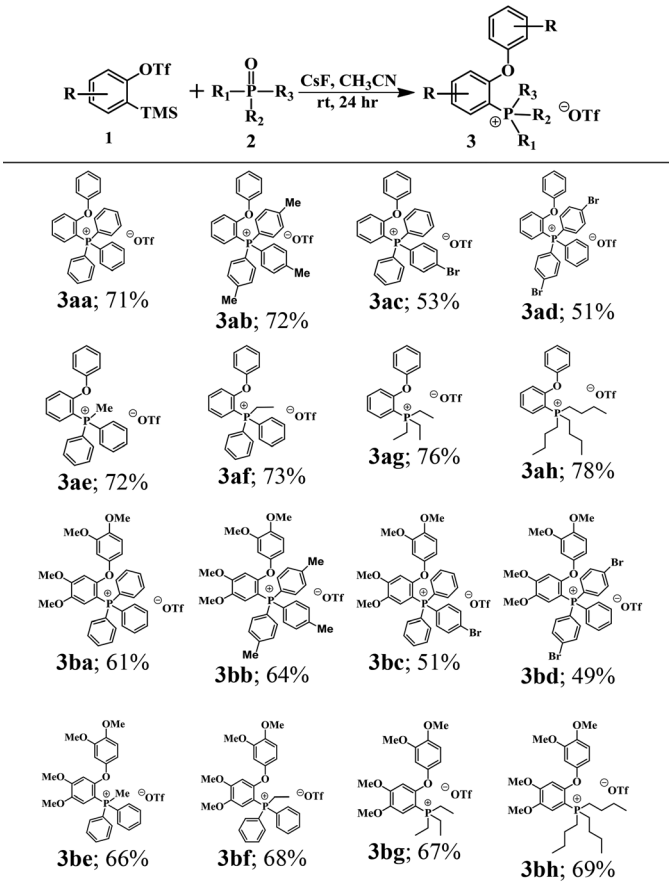


Fig. 1 Crystal structure of **3aa**.

Table 2 Synthesis of quaternary phosphonium triflates from aryne precursors and phosphine oxides[a]

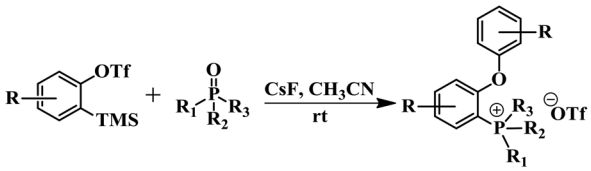


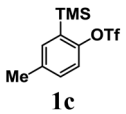
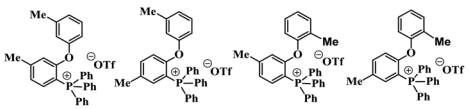
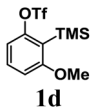
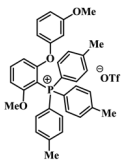
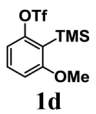
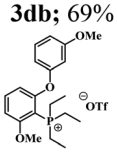
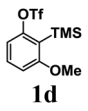
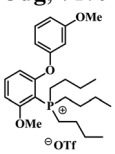
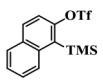
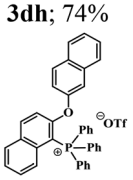
[a] Conditions: *o*-Silyl aryl triflate **1** (2 mmol), phosphine oxide **2** (1 mmol), fluoride source (2 mmol), solvent (4 mL) stirred at room temperature for 24 h.

derived from **1c** undergoes two possible attacks from phosphine oxide **2a** followed by another two possible additions of arynes to each, giving four phosphonium salts **3ca**, **3ca′**, **3c′a** and **3c′a′** as a mixture of regioisomers. The regioisomers are difficult to separate into individual isomers by column chromatography and are presented as mixtures. Interestingly, single regioisomers **3db**, **3dg** and **3dh** were obtained in good yields when unsymmetrical benzyne precursor 3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1d** was treated with phosphine oxides **2b**, **2g** and **2h**. The electronic effect of the –OMe group of the aryne generated from **1d** played an important role in the formation of single regioisomers *via* allowing single side attack of the respective phosphine oxides. Similarly, the aryne precursor 1-(trimethylsilyl)-2-naphthyl trifluoromethanesulfonate **1e** also showed regioselectivity and afforded the regioisomer **3ea** when treated with phosphine oxide **2a** under our optimized reaction conditions (Table 3).

At present, the exact mechanism for the synthesis of quaternary phosphoniumtriflates from arynes and phosphine oxides is not clear; however based on a previous report[28a] and

Table 3 Synthesis of quaternary phosphonium triflates from unsymmetrical benzyne precursors[a]



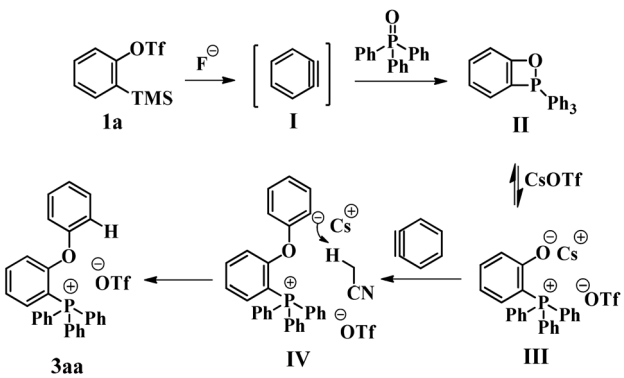
Entry	Benzyne precursor (**1c–e**)	Quaternary phosphonium triflates (**3ca–3ea**)
1	 **1c**	 Mixture of **3ca**, **3ca'**, **3c'a**, **3c'a'** (65%)
2	 **1d**	 **3db;** 69%
3	 **1d**	 **3dg**; 71%
4	 **1d**	 **3dh**; 74%
5	 **1e**	 **3ea**; 64%

[a] Conditions: *o*-Silyl aryl triflate **1** (2 mmol), phosphine oxide **2** (1 mmol), fluoride source (2 mmol), solvent (4 mL) stirred at room temperature for 24 h.

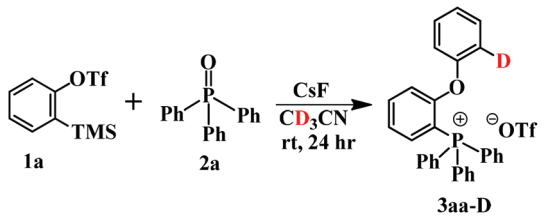
our observations, a plausible reaction mechanism is proposed in Scheme 3. As shown in Scheme 3, the *in situ* generated benzyne undergoes insertion into the P=O π-bond of triphenylphosphine oxide to form intermediate **II**. Due to the ring strain, the four-membered ring of **II** undergoes ring opening in the presence of the Cs–salt to form the 1,4-zwitterionic intermediate **III**. The oxygen anion of **III** traps another benzyne to give **IV** followed by protonation from acetonitrile to give our desired quaternary phosphonium triflate **3aa**.

To support our proposed mechanism, we performed an independent experiment using **1a** and **2a** in CD_3CN under the optimized reaction conditions (Scheme 4).

This experiment gave the desired *o*-aryloxotriphenyl phosphonium triflate **3aa-D** in 53% yield with deuterium incorporation at the *ortho* position of the phenoxy group of **3aa**, which



Scheme 3 Plausible reaction mechanism for the synthesis of quaternary phosphonium triflates.



Scheme 4 Isotope tracer experiment.

was confirmed by HRMS analysis. This result clearly indicates that the proton source at the aryl ring is acetonitrile.

Conclusions

In conclusion, we have developed a transition-metal-free protocol for the synthesis of *o*-aryloxotriphenylphosphonium triflates *via* arynes. A series of aryl phosphonium salts have been synthesized using this one-pot synthetic strategy in good yields and with excellent functional group tolerance. This synthetic strategy has been accomplished through the P–O bond cleavage and the formation of C–O and C–P bonds in a single operation.

Experimental section

General remarks

All reactions involving oxygen or moisture-sensitive compounds were carried out under an argon atmosphere using oven-dried or flame-dried glassware. All other solvents and reagents were purified according to standard procedures or were used as received from TCI, Aldrich, Merck and Spectrochem. The reactions were monitored by thin-layer chromatography (TLC) using aluminium-backed silica gel plates (0.2 mm thickness); the chromatograms were visualized with ultraviolet light (254 nm). Flash column chromatography was performed with silica gel 60 (100–200 mesh). HRMS data were recorded by electrospray ionization with a Q-TOF mass analyzer.

General procedure for the synthesis of *o*-aryloxotriphenyl phosphonium triflate from triphenyl-phosphineoxide and silyltriflate

An oven-dried round bottomed flask (50 mL capacity) equipped with a magnetic stir bar was evacuated and purged with argon. Triphenylphosphineoxide (0.5 mmol, 1 equiv.), aryne precursor (1 mmol, 2 equiv.), CsF (2 mmol, 4 equiv.) and CH_3CN (4 mL) were added sequentially at room temperature and allowed to stir for 24 h. After completion of the reaction, water (10 mL) was added to the reaction mixture and the organic layer was extracted with EtOAc (2 × 20 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed, and the residue was purified by column chromatography on silica gel using DCM/methanol as the eluent.

Characterization of quaternary phosphonium triflates

(2-Phenoxyphenyl)triphenylphosphonium trifluoromethanesulfonate (3aa). Using the general experimental procedure with triphenylphosphineoxide (0.139 g; 0.5 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.24 mL; 1 mmol), and CsF (0.227 g; 1.5 mmol) in acetonitrile (4 mL), **3aa** was obtained as a colorless solid (0.153 g, 71% yield) after purification by flash chromatography using DCM/MeOH (98 : 2) as the eluent; mp 216–220 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64–7.88 (m, 16H), 7.20–7.39 (m, 4H), 7.14 (m, 1H), 6.99 (dd, J_1 = 5.7 Hz, J_2 = 8.4 Hz, 1H), 6.50 (d, J = 8.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.4, 152.5, 138.3 (d, J = 1.9 Hz), 136.3 (d, J = 9 Hz), 135.2 (d, J = 3.0 Hz), 133.9 (d, J = 10.5 Hz), 130.4 (d, J = 13.2 Hz), 130.2, 125.9, 124.4 (d, J = 12.6 Hz), 119.5, 117.8 (d, J = 91.7 Hz), 116.9 (d, J = 6.3 Hz), 107.1 (d, J = 93.2 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz): δ 21.6; IR ($CHCl_3$): 2927, 1586, 1573, 1449, 1468, 1441, 1272, 1151, 1109, 1031, 755, 721, 690, 637 cm^{-1}; HRMS (+ESI) calcd for $C_{30}H_{24}OP^+$ [M − OTf]$^+$: 431.1559; found: 431.1577.

2-Methyl-5-[(2-phenoxyphenyl)di-*p*-tolylphosphonio]benzen-1-ide-trifluoromethanesulfonate (3ab). Using the general experimental procedure with tris(4-methylphenyl)phosphineoxide (0.160 g; 0.5 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.24 mL; 1 mmol), and CsF (227 g; 1.5 mmol) in acetonitrile (4 mL), **3ab** was obtained as a light yellow gummy product (0.170 g, 72% yield) after purification by flash chromatography using DCM/MeOH (98 : 2) as the eluent; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74–7.80 (m, 1H), 7.46–7.57 (m, 12H), 7.31–7.36 (m, 1H), 7.22–7.29 (m, 3H), 7.13 (m, 1H), 6.99 (dd, J_1 = 5.8 Hz, J_2 = 8.2 Hz, 1H), 6.55 (d, J = 7.6 Hz, 2H), 2.49 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.2 (d, J = 1.4 Hz), 152.7, 146.4 (d, J = 2.9 Hz), 137.9 (d, J = 2.0 Hz), 136.2 (d, J = 8.9 Hz), 133.7 (d, J = 10.9 Hz), 131.0 (d, J = 13.6 Hz), 130.1, 125.7, 124.3 (d, J = 12.6 Hz), 119.4, 117.0 (d, J = 6.3 Hz), 114.7 (d, J = 94.5 Hz), 108.1 (d, J = 93.0 Hz), 21.7; ^{31}P NMR ($CDCl_3$, 202 MHz): δ 20.9; IR ($CHCl_3$): 2923, 1713, 1598, 1572, 1490, 1469, 1444, 1377, 1259, 1159, 1108, 1031, 807, 758 cm^{-1}; HRMS (+ESI) calcd for $C_{33}H_{30}OP^+$ [M − OTf]$^+$: 473.2029; found: 473.2030.

(4-Bromophenyl)(2-phenoxyphenyl)diphenylphosphonium trifluoromethanesulfonate (3ac). Using the general experimental procedure with bis(4-bromophenyl)triphenylphosphineoxide (0.179 g; 0.5 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.24 mL; 1 mmol), and CsF (227 g; 1.5 mmol) in acetonitrile (4 mL), **3ac** was obtained as a light brown solid (0.135 g, 53% yield) after purification by flash chromatography using DCM/MeOH (98 : 2) as the eluent; mp 181–184 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59–7.89 (m, 15H), 7.22–7.39 (m, 4H), 7.14 (m, 1H), 7.01 (dd, J_1 = 5.8 Hz, J_2 = 8.1 Hz, 1H), 6.55 (dd, J_1 = 0.9, J_2 = 8.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.2 (d, J = 1.5 Hz), 152.4, 138.4 (d, J = 1.9 Hz), 136.2 (d, J = 8.7 Hz), 135.2 (d, J = 14.6 Hz), 135.3, 133.8, 133.7, 133.6, 130.8 (d, J = 3.7 Hz), 130.4 (d, J = 13.1 Hz),

130.1, 125.9, 124.5 (d, J = 12.8 Hz), 119.3, 117.2 (d, J = 91.8 Hz), 117.0 (d, J = 6.3 Hz), 116.9 (d, J = 93.7 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz): δ 21.7; IR ($CHCl_3$): 3012, 1586, 1573, 1489, 1469, 1441, 1388, 1274, 1154, 1109, 1031, 1009, 875, 742, 691 cm^{-1}; HRMS (+ESI) calcd for $C_{30}H_{23}BrOP^+$ [M − OTf]$^+$: 509.0664; found: 509.0685.

Bis(4-bromophenyl)(2-phenoxyphenyl)phenylphosphonium trifluoromethanesulfonate (3ad). Using the general experimental procedure with bis(4-bromophenyl)phenylphosphineoxide (0.268 g; 0.5 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.24 mL; 1 mmol), and CsF (0.227 g; 1.5 mmol) in acetonitrile (4 mL), **3ad** was obtained as a brown gummy product (0.149 g, 51% yield) after purification by flash chromatography using DCM/MeOH (98 : 2) as the eluent; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58–7.89 (m, 14H), 7.24–7.39 (m, 4H), 7.15 (m, 1H), 7.01 (dd, J_1 = 5.9 Hz, J_2 = 8.3 Hz, 1H), 6.55 (d, J = 7.7 Hz, 2H);^{13}C NMR (126 MHz, $CDCl_3$): δ 160.2 (d, J = 1.4 Hz), 152.5, 138.7 (d, J = 1.1 Hz), 136.4 (d, J = 8.9 Hz), 135.5 (d, J = 3.0 Hz), 135.3 (d, J = 11.7 Hz), 133.9 (d, J = 14.2 Hz), 133.8, 131.2 (d, J = 3.7 Hz), 130.6 (d, J = 13.4 Hz), 130.3, 126.0, 124.8 (d, J = 12.9 Hz), 119.3, 117.3 (d, J = 6.3 Hz), 117.0 (d, J = 92.2 Hz), 116.6 (d, J = 94.1 Hz), 106.4 (d, J = 93.8 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz): δ 21.9; IR ($CHCl_3$): 2924, 1573, 1468, 1441, 1387, 1262, 1194, 1155, 1108, 1070, 1030, 1009, 874, 798, 739 cm^{-1}; HRMS (+ESI) calcd for $C_{30}H_{22}Br_2OP^+$ [M − OTf]$^+$: 586.9770; found: 586.9777.

[Methyl(2-phenoxyphenyl)diphenyl]phosphonium trifluoromethanesulfonate (3ae). Using the general experimental procedure with methyldiphenylphosphineoxide (0.108 g; 0.5 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.24 mL; 1 mmol), and CsF (0.227 g; 1.5 mmol) in acetonitrile (4 mL), **3ae** was obtained as a light brown gummy product (0.133 g, 72% yield) after purification by flash chromatography using DCM/MeOH (98 : 2) as the eluent; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64–7.84 (m, 11H), 7.18–7.36 (m, 5H), 6.89 (dd, J_1 = 5.7 Hz, J_2 = 8.4 Hz, 1H), 6.78 (d, J = 7.6 Hz, 2H), 2.98 (d, J = 13.6, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.8 (d, J = 1.6 Hz), 153.0, 137.7 (d, J = 1.8 Hz), 135.5 (d, J = 8.8 Hz), 134.9 (d, J = 2.8 Hz), 132.7 (d, J = 10.8 Hz), 130.4, 130.3 (d, J = 13.2 Hz), 126.1, 124.1 (d, J = 12.7 Hz), 120.1, 118.9 (d, J = 90.7 Hz), 116.6 (d, J = 6.2 Hz), 107.8 (d, J = 91.7 Hz), 9.4 (d, J = 59.3 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz): δ 20.2; IR ($CHCl_3$): 2921, 1588, 1574, 1489, 1471, 1441, 1263, 1162, 1116, 1031, 905, 749, 692, 638 cm^{-1}; HRMS (+ESI) calcd for $C_{25}H_{22}OP^+$ [M − OTf]$^+$: 369.1403; found: 369.1422.

[Ethyl(2-phenoxyphenyl)diphenyl]phosphonium trifluoromethanesulfonate (3af). Using the general experimental procedure with ethyldiphenylphosphineoxide (0.165 g; 0.5 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.24 mL; 1 mmol), and CsF (0.227 g; 1.5 mmol) in acetonitrile (4 mL), **3af** was obtained as a colorless solid (0.139 g, 73% yield) after purification by flash chromatography using DCM/MeOH (98 : 2) as the eluent; mp 148–150 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61–7.81 (m, 12H), 7.29–7.40 (m, 3H), 7.20 (m, 1H), 6.87 (dd, J_1 = 5.5 Hz, J_2 = 8.3 Hz, 1H), 6.69 (d, J = 7.6, 2H), 3.42 (m, 2H) 1.39 (dt, J_1 = 7.5 Hz, J_2 = 20.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.7 (d, J = 1.3 Hz), 152.8, 137.6 (d, J = 1.4 Hz), 135.3 (d, J = 7.8 Hz), 134.7 (d, J = 2.8 Hz), 133.1 (d, J = 10.1 Hz), 130.4, 130.2 (d, J = 12.7 Hz), 126.0, 124.3 (d, J = 12.3 Hz), 119.9, 117.7 (d, J = 87.9 Hz), 116.5 (d, J = 6.2 Hz), 106.9 (d, J = 88.8 Hz), 16.7 (d, J = 53.8 Hz), 7.1 (d, J = 5.3 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz): δ 24.8; IR ($CHCl_3$): 2944, 1587, 1574, 1489, 1471, 1442, 1273, 1154, 1114, 1031, 875, 754, 691, 637cm^{-1}; HRMS (+ESI) calcd for $C_{26}H_{24}OP^+$ [M − OTf]$^+$: 383.1559; found: 383.1563.

Triethyl(2-phenoxyphenyl)phosphonium trifluoromethanesulfonate (3ag). Using the general experimental procedure with triethylphosphineoxide (0.067 g; 0.5 mmol), 2-(trimethylsilyl) phenyl trifluoromethanesulfonate (0.24 mL; 1 mmol), and CsF (0.227 g; 1.5 mmol) in acetonitrile (4 mL), **3ag** was obtained as a light yellow gummy product (0.109 g, 76% yield) after purification by flash chromatography using DCM/MeOH (98 : 2) as the eluent; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (ddd, J_1 = 1.4 Hz, J_2 = 7.8 Hz, J_3 = 12.2 Hz, 1H), 7.57 (t, J = 7.9 Hz, 1H), 7.40 (t, J = 7.9 Hz, 2H), 7.31 (dt, J_1 = 1.7 Hz, J_2 = 7.5 Hz, 1H), 7.23 (m, 1H), 6.99 (d, J = 7.7 Hz, 2H), 6.83 (dd, J_1 = 4.9 Hz, J_2 = 8.3 Hz, 1H), 2.58 (m, 6H), 1.22 (dt, J_1 = 7.6 Hz, J_2 = 19.4 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.2 (d, J = 1.1 Hz), 153.0, 136.5, 134.1 (d, J = 5.9 Hz), 130.4, 125.8, 124.1 (d, J = 10.9 Hz), 119.6, 116.3 (d, J = 5.9 Hz), 104.9 (d, J = 80.4 Hz), 12.4 (d, J = 50.9 Hz), 5.6 (br); ^{31}P NMR ($CDCl_3$, 202 MHz): δ 36.0; IR ($CHCl_3$): 2949, 1595, 1575, 1475, 1442, 1267, 1156, 1089, 1031, 874, 755, 638 cm^{-1}; HRMS (+ESI) calcd for $C_{18}H_{24}OP^+$ [M − OTf]$^+$: 287.1559; found: 287.1574.

Tributyl(2-phenoxyphenyl)phosphonium trifluromethanesulfonate (3ah). Using the general experimental procedure with tributylphosphineoxide (0.109 g; 0.5 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.24 mL; 1 mmol), and CsF (0.227 g; 1.5 mmol) in acetonitrile (4 mL), **3ah** was obtained as a pale yellow gummy product (0.145 g, 78% yield) after purification by flash chromatography using DCM/MeOH (98 : 2) as the eluent; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64–7.73 (m, 2H), 7.49 (t, J = 8.0 Hz, 2H), 7.41 (dt, J_1 = 2.0 Hz, J_2 = 7.6 Hz, 1H), 7.32 (m, 1H), 7.03 (d, J = 7.7, 2H), 6.93 (dd, J_1 = 4.9 Hz, J_2 = 8.2 Hz, 1H), 2.57–2.65 (m, 6H), 1.50 (m, 12H), 0.94 (t, J = 7.0 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.3, 153.4, 136.7 (d, J = 1.6 Hz), 134.1 (d, J = 6.1 Hz), 130.7, 126.2, 124.5 (d, J = 11.1 Hz), 119.6, 116.9 (d, J = 5.9 Hz), 106.5 (d, J = 79.9 Hz), 23.9 (d, J = 4.6 Hz), 23.7 (d, J = 16.3 Hz), 13.3; ^{31}P NMR ($CDCl_3$, 202 MHz): δ 29.9; IR ($CHCl_3$): 2962, 1595, 1574, 1491, 1474, 1443, 1263, 1153, 1031, 873, 755, 637 cm^{-1}; HRMS (+ESI) calcd for $C_{24}H_{36}OP^+$ [M − OTf]$^+$: 371.2498; found: 371.2509.

2-(3,4-Dimethoxyphenoxy)-4,5-dimethoxyphenyltriphenyl phosphonium trifluromethanesulfonate (3ba). Using the general experimental procedure with triphenylphosphineoxide (0.189 g; 0.5 mmol), 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.29 mL, 1 mmol), and CsF (0.227 g; 1.5 mmol) in acetonitrile (4 mL), **3ba** was obtained as a brown solid (0.168 g, 61% yield) after purification by flash chromatography using DCM/MeOH (90 : 10) as the eluent; mp 184–186 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70–7.85 (m, 15H),

6.70 (d, J = 8.8 Hz, 1H), 6.45–6.52 (m, 2H), 6.16 (dd, J_1 = 2.7 Hz, J_2 = 8.7 Hz, 1H), 5.97 (t, J = 2.6 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.70 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 157.5, 157.1 (d, J = 1.5 Hz), 149.9, 146.8, 146.6, 145.7 (d, J = 15.3 Hz), 135.0, 134.9, 134.0 (d, J = 10.6 Hz), 130.3 (d, J = 13 Hz), 118.6 (d, J = 91.9 Hz), 111.4, 110.9, 103.8, 101.0 (d, J = 8.6 Hz), 94.7 (d, J = 100.8 Hz), 56.7, 56.6, 56.2, 56.1; ^{31}P NMR ($CDCl_3$, 202 MHz): δ 20.9; IR ($CHCl_3$): 3010, 1576, 1505, 1440, 1389, 1267, 1222, 1199, 1150, 1066, 1031, 948, 754, 693 cm^{-1}; HRMS (+ESI) calcd for $C_{34}H_{32}O_5P^+$ [M − OTf]$^+$: 551.1982; found: 551.1988.

[2-(3,4-Dimethoxyphenoxy)-4,5-dimethoxyphenyl]tri-*p*-tolylphosphonium trifluoromethanesulfonate (3bb). Using the general experimental procedure with tris(4-methylphenyl) phosphineoxide (0.160 g; 0.5 mmol), 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.29 mL; 1 mmol), and CsF (0.227 g; 1.5 mmol) in acetonitrile (4 mL), **3bb** was obtained as a brown gummy product (0.189 g, 64% yield) after purification by flash chromatography using DCM/MeOH (90 : 10) as the eluent; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45–7.56 (m, 12H), 6.71 (d, J = 8.8 Hz, 1H), 6.51 (d, J = 14.6 Hz, 1H), 6.46 (d, J = 5.8 Hz, 1H), 6.19 (dd, J_1 = 2.7 Hz, J_2 = 8.7 Hz, 1H), 5.92 (d, J = 2.8 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.68 (s, 3H), 3.63 (s, 3H), 2.47 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 157.1 (d, J = 2.7 Hz), 156.7 (d, J = 1.6 Hz), 149.7, 146.7 (d, J = 20.2 Hz), 146.2 (d, J = 2.8 Hz), 145.6 (d, J = 15.2 Hz), 142.2 (d, J = 2.7 Hz), 133.8 (d, J = 10.9 Hz), 131.9 (d, J = 10.2 Hz), 130.9 (d, J = 13.5 Hz), 129.1 (d, J = 12.6 Hz), 120.8 (q, J = 321.2 Hz for OTf), 116.5 (d, J = 11.1 Hz), 115.8, 115.1, 111.2 (d, J = 60.7 Hz), 103.6, 101.2 (d, J = 8.5 Hz), 95.9 (d, J = 100.5 Hz), 56.7, 56.5, 56.1, 55.9, 21.7; ^{31}P NMR ($CDCl_3$, 202 MHz): δ 20.2; IR ($CHCl_3$): 2925, 1599, 1502, 1442, 1388, 1273, 1222, 1199, 1152, 1031, 993, 808, 754, 665, 638 cm^{-1}; HRMS (+ESI) calcd for $C_{37}H_{38}O_5P^+$ [M − OTf]$^+$: 593.2451; found: 593.2454.

(4-Bromophenyl)(2-(3,4-dimethoxyphenoxy)-4,5-dimethoxyphenyl)diphenylphosphonium trifluoromethanesulfonate (3bc). Using the general experimental procedure with (4-bromophenyl)diphenylphosphineoxide (0.179 g; 0.5 mmol), 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.29 mL; 1 mmol), and CsF (0.227 g; 1.5 mmol) in acetonitrile (4 mL), **3bc** was obtained as a light brown solid (0.160 g, 51% yield) after purification by flash chromatography using DCM/MeOH (90 : 10) as the eluent; mp 114–116 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60–7.87 (m, 14H), 6.70 (d, J = 8.8 Hz, 1H), 6.50 (d, J = 14.7 Hz, 1H), 6.47 (d, J = 6.0 Hz, 1H), 6.17 (dd, J_1 = 2.7 Hz, J_2 = 8.7 Hz, 1H), 5.97 (d, J = 2.7 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.70 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 157.8 (d, J = 2.7 Hz), 157.0 (d, J = 1.5 Hz), 149.9, 146.8, 146.6, 145.9 (d, J = 15.5 Hz), 135.4 (d, J = 11.5 Hz), 135.1 (d, J = 2.8 Hz), 134.0 (d, J = 10.5 Hz), 133.6 (d, J = 13.6 Hz), 130.7 (d, J = 3.7 Hz), 130.4 (d, J = 13.2 Hz), 120.8 (q, J = 321.4 Hz for OTf), 118.2 (d, J = 92.2 Hz), 117.8 (d, J = 94.2 Hz), 116.5 (d, J = 11.2 Hz), 111.4, 110.9, 103.7, 101.2 (d, J = 8.8 Hz), 94.3 (d, J = 101.3 Hz), 56.8, 56.6, 56.2, 56.1; ^{31}P NMR ($CDCl_3$, 202 MHz): δ 20.9; IR ($CHCl_3$): 2922, 1602, 1574, 1504, 1439, 1388, 1264, 1222, 1031 cm^{-1}; HRMS (+ESI) calcd for $C_{34}H_{31}BrO_5P^+$ [M − OTf]$^+$: 629.1087; found: 629.1095.

Bis(4-bromophenyl)[2-(3,4-dimethoxyphenoxy)-4,5-dimethoxyphenyl]phenylphosphonium trifluoromethanesulfonate (3bd). Using the general experimental procedure with bis(4-bromophenyl)phenylphosphineoxide (0.218 g; 0.5 mmol), 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.29 mL; 1 mmol), and CsF (0.227 g; 1.5 mmol) in acetonitrile (4 mL), **3bd** was obtained as a brown gummy product (0.173 g, 49% yield) after purification by flash chromatography using DCM/MeOH (90 : 10) as the eluent; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62–7.92 (m, 13H), 6.70 (d, J = 8.8 Hz, 1H), 6.55 (d, J = 14.7 Hz, 1H), 6.45 (d, J = 6.0 Hz, 1H), 6.17 (dd, J_1 = 2.7 Hz, J_2 = 8.7 Hz, 1H), 5.95 (d, J = 2.7 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.71 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 157.8 (d, J = 2.7 Hz), 156.9, 149.9, 146.8, 146.6, 145.9 (d, J = 15.5 Hz), 135.5 (d, J = 11.7 Hz), 135.3 (d, J = 2.9 Hz), 134.1 (d, J = 10.7 Hz), 133.8 (d, J = 13.8 Hz), 130.9 (d, J = 3.7 Hz), 130.5 (d, J = 13.3 Hz), 117.8 (d, J = 92.7 Hz), 117.5, 117.0, 116.5 (d, J = 11.3 Hz), 111.1 (d, J = 81.7 Hz), 103.6, 101.2 (d, J = 8.8 Hz), 94.0 (d, J = 101.9 Hz), 56.9, 56.6, 56.2, 56.1; ^{31}P NMR ($CDCl_3$, 202 MHz): δ 21.1; IR ($CHCl_3$): 2924, 1602, 1574, 1505, 1465, 1441, 1262, 1068cm^{-1}; HRMS (+ESI) calcd for $C_{34}H_{30}Br_2O_5P^+$ [M − OTf]$^+$: 707.0192; found: 707.0205.

2-(3,4-Dimethoxyphenoxy)-4,5-dimethoxyphenyl methyl diphenylphosphonium trifluoromethanesulfonate (3be). Using the general experimental procedure with methyldiphenylphosphineoxide (0.108 g; 0.5 mmol), 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.29 mL; 1 mmol), and CsF (0.227 g; 1.5 mmol) in acetonitrile (4 mL), **3be** was obtained as a brown gummy product (0.161 g, 66% yield) after purification by flash chromatography using DCM/MeOH (90 : 10) as the eluent; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64–7.79 (m, 10H), 6.75 (d, J = 8.7 Hz, 1H), 6.65 (d, J = 14.7 Hz, 1H), 6.39 (d, J = 5.8 Hz, 1H), 6.31 (dd, J_1 = 2.7 Hz, J_2 = 8.6 Hz 1H), 6.28 (d, J = 2.7, 1H), 3.84 (s, 3H), 3.76 (s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 2.95 (d, J = 13.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 157.0 (d, J = 2.4 Hz), 156.9, 150.1, 147.1 (d, J = 80.1 Hz), 145.8 (d, J = 15.2 Hz), 134.6 (d, J = 2.9 Hz), 132.8 (d, J = 10.8 Hz), 130.5 (d, J = 9.9 Hz), 130.1 (d, J = 13.1 Hz), 128.6 (d, J = 12.1 Hz), 120.7 (q, J = 320.1 Hz for OTf), 119.9 (d, J = 90.9 Hz), 115.5 (d, J = 11.2 Hz), 111.3 (d, J = 57.1 Hz), 104.1, 101.1 (d, J = 8.7 Hz), 96.1 (d, J = 99.2 Hz), 56.8, 56.4, 56.2, 56.1, 9.9 (d, J = 59.9 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz): 19.34; IR ($CHCl_3$): 2922, 1602, 1504, 1439, 1388, 1355, 1262, 1221, 1030 cm^{-1}; HRMS (+ESI) calcd for $C_{29}H_{30}O_5P^+$ [M − OTf]$^+$: 489.1825; found: 489.1836.

[2-(3,4-Dimethoxyphenoxy)-4,5-dimethoxyphenylethyl] diphenylphosphonium trifluoromethanesulfonate (3bf). Using the general experimental procedure with ethyldiphenylphosphineoxide (0.165 g; 0.5 mmol), 4,5-dimethoxy-2-(trimethylsilyl) phenyl trifluoromethanesulfonate (0.29 mL; 1 mmol), and CsF (0.227 g; 1.5 mmol) in acetonitrile (4 mL), **3bf** was obtained as a pale yellow solid (0.171 g, 68% yield) after purification by flash chromatography using DCM/MeOH (90 : 10) as the eluent; mp: 143–145 °C; ^{1}H NMR (500 MHz, $CDCl_3$):

δ 7.65–7.80 (m, 10H), 6.97 (d, J = 13.5 Hz, 1H), 6.74 (d, J = 8.8 Hz, 1H), 6.36 (d, J = 5.6 Hz, 1H), 6.24 (dd, J_1 = 2.7 Hz, J_2 = 8.7 Hz, 1H), 6.10 (d, J = 2.7, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.75 (s, 3H), 3.71 (s, 3H), 3.40 (m, 2H), 1.36 (dt, J_1 = 7.5 Hz, J_2 = 20.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.8 (d, J = 1.3 Hz), 156.6, 149.9 (d, J = 5.0 Hz), 147.1 (d, J = 1.7 Hz), 146.6 (d, J = 3.8 Hz), 145.9 (d, J = 14.6 Hz), 134.5 (d, J = 2.6 Hz), 133.1 (d, J = 10.1 Hz), 130.0 (d, J = 12.7 Hz), 120.8 (q, J = 319 Hz for OTf), 118.4 (d, J = 88.4 Hz), 114.8, 111.4 (d, J = 7.6 Hz), 111.1, 103.8 (d, J = 4.4 Hz), 100.9 (d, J = 8.5 Hz), 95.5 (d, J = 96.2 Hz), 56.8, 56.4, 56.1, 56.0, 16.8 (d, J = 54.5 Hz), 6.9 (d, J = 5.2 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz): δ 23.9; IR ($CHCl_3$): 2922, 1603, 1506, 1439, 1387, 1261, 1221, 1030, 834 cm^{-1}; HRMS (+ESI) calcd for $C_{30}H_{32}O_5P^+$ [M − OTf]$^+$: 503.1982; found: 503.1967.

[2-(3,4-Dimethoxyphenoxy)-4,5-dimethoxyphenyl triethyl] phosphonium trifluoromethanesulfonate (3bg). Using the general experimental procedure with triethylphosphineoxide (0.067 g; 0.5 mmol), 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.29 mL; 1 mmol), and CsF (0.227 g; 1.5 mmol) in acetonitrile (4 mL), **3bg** was obtained as a light brown gummy product (0.136 g, 67% yield) after purification by flash chromatography using DCM/MeOH (90 : 10) as the eluent; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.01 (d, J = 12.3 Hz, 1H), 6.86 (d, J = 8.8 Hz, 1H), 6.59 (d, J = 2.8 Hz, 1H), 6.49 (dd, J_1 = 2.8 Hz, J_2 = 8.7 Hz, 1H), 6.40 (d, J = 5.2, 1H), 3.95 (s, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 3.73 (s, 3H), 2.58 (m, 6H), 1.25 (dt, J_1 = 7.6 Hz, J_2 = 19.3 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.4, 156.1, 150.7, 148.2, 147.0, 146.4 (d, J = 13.1 Hz), 114.1 (d, J = 8.1 Hz), 112.1, 110.5, 104.1, 101.4 (d, J = 8.0 Hz), 94.4 (d, J = 87.4 Hz), 57.3, 56.6, 56.5, 56.4, 13.1 (d, J = 51.6 Hz), 6.2; ^{31}P NMR ($CDCl_3$, 202 MHz): δ 35.2; IR ($CHCl_3$): 2945, 1603, 1506, 1444, 1386, 1263, 1221, 1031 cm^{-1}; HRMS (+ESI) calcd for $C_{22}H_{32}O_5P^+$ [M − OTf]$^+$: 407.1982; found: 407.2001.

Tributyl[2-(3,4-dimethoxyphenoxy)-4,5-dimethoxyphenyl] phosphonium trifluoromethanesulfonate (3bh). Using the general experimental procedure with tributylphosphineoxide (0.109 g; 0.5 mmol), 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.29 mL; 1 mmol), and CsF (0.227 g; 1.5 mmol) in acetonitrile (4 mL), **3bh** was obtained as a brown gummy product (0.169 g, 69% yield) after purification by flash chromatography using DCM/MeOH (90 : 10) as the eluent; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.87 (d, J = 12.4 Hz, 1H), 6.80 (d, J = 8.8 Hz, 1H), 6.47 (d, J = 2.6 Hz, 1H), 6.41 (dd, J_1 = 2.8 Hz, J_2 = 8.7 Hz, 1H), 6.34 (d, J = 5 Hz, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 3.76 (s, 3H), 3.66 (s, 3H), 2.42 (br s, 6H), 1.41 (br s, 6H), 1.40 (br s, 6 H), 0.84 (brs, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 155.7, 155.6 (d, J = 2.3 Hz), 150.2, 147.6, 146.6, 145.8 (d, J = 13.1 Hz), 120.5 (q, J = 320.7 Hz for OTf), 113.8 (d, J = 8.4 Hz), 111.7, 110.0, 103.4, 101.3 (d, J = 8.3 Hz), 94.7 (d, J = 87.1 Hz), 56.7, 56.1, 56.0, 55.9, 23.6 (d, J = 4.3 Hz), 23.4 (d, J = 16 Hz), 19.4 (d, J = 50.1 Hz), 13.1; ^{31}P NMR ($CDCl_3$, 202 MHz): δ 29.1; IR ($CHCl_3$): 2962, 1603, 1506, 1443, 1386, 1262, 1198, 1031 cm^{-1}; HRMS (+ESI) calcd for $C_{28}H_{44}O_5P^+$ [M − OTf]$^+$: 491.2921; found: 491.2925.

[4-Methyl-2-(*m*-tolyloxy)phenyl]triphenylphosphonium trifluoromethanesulfonate (3ca), [5-methyl-2-(*m*-tolyloxy)phenyl] triphenylphosphonium trifluoromethanesulfonate (3ca′), [4-methyl-2-(*p*-tolyloxy)phenyl]triphenylphosphonium trifluoromethanesulfonate (3c′a), [5-methyl-2-(*p*-tolyloxy)phenyl]triphenylphosphonium trifluoromethanesulfonate (3c′a′), [mixture of four regioisomers 3ca, 3ca′, 3c′a and 3c′a′]. Using the general experimental procedure with triphenylphosphineoxide (0.139 g; 0.5 mmol), 4-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.24 mL; 1 mmol), and CsF (0.227 g; 1.5 mmol) in acetonitrile (4 mL), mixtures of regioisomers **3ca**, **3ca′**, **3c′a** and **3c′a′** were obtained as brown gummy products (0.149 g, 65% yield) after purification by flash chromatography using DCM/MeOH (98 : 2) as the eluent; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53–8.02 (m, 62H), 6.37–7.34 (m, 26 H), 2.38 (s, 3H), 2.37 (s, 3H), 2.29 (s, 3H), 2.28 (s, 3H), 2.23 (s, 3H), 2.21 (s, 3H), 2.20 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.6, 160.3, 158.5, 158.1, 152.8, 152.4, 150.4, 150.1, 150.0, 140.2, 140.1, 138.9, 136.1 (d, J = 8.9 Hz), 135.8 (d, J = 8.6 Hz), 135.3, 135.1, 134.9, 134.1 (m), 133.5 (d, J = 12.3 Hz), 133.3 (d, J = 12.5 Hz), 131.4 (d, J = 9.6 Hz), 130.6 (d, J = 13.5 Hz), 130.3 (d, J = 13 Hz), 129.9 (d, J = 129.9 Hz), 128.7 (d, J = 11.8 Hz), 126.5, 126.2, 125.1 (d, J = 12.9 Hz), 124.8 (d, J = 12.8 Hz), 124.5, 121.9, 121.4, 120.3, 119.9, 119.8, 119.6, 119.4, 118.5 (d, J = 21.5 Hz), 118.4 (d, J = 22.6 Hz), 117.7 (d, J = 21.3 Hz), 117.7 (d, J = 22.3 Hz), 116.9 (d, J = 6.7 Hz), 116.8, 116.5, 116.3 (d, J = 6.5 Hz), 106.6 (d, J = 92.3 Hz), 106.1 (d, J = 92.5, 103.3 (d, J = 95.7 Hz), 102.9 (d, J = 95.6 Hz), 22.5, 21.5, 20.7, 20.6, 20.3, 20.2, 20.1, 20.0; ^{31}P NMR ($CDCl_3$, 202 MHz): δ 21.62, 21.60, 20.93 (one peak is missing due to overlap); IR ($CHCl_3$): 2927, 1586, 1573, 1449, 1468, 1441, 1272, 1151, 1109, 1031, 755, 721, 690, 637 cm^{-1}; HRMS (+ESI) calcd for $C_{32}H_{28}OP^+$ [M − OTf]$^+$: 459.1872; found: 459.1874.

[2-Methoxy-6-(3-methoxyphenoxy)phenyl]tri-*p*-tolyl phosphonium trifluoromethanesulfonate (3db). Using the general experimental procedure with tris(4-methylphenyl)phosphineoxide (0.160 g; 0.5 mmol), 3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.27 mL 1 mmol), and CsF (0.227 g; 1.5 mmol) in acetonitrile (4 mL), **3db** was obtained as a brown gummy product (0.183 g, 69% yield) after purification by flash chromatography using DCM/MeOH (95 : 5) as the eluent; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (t, J = 8.5 Hz, 1H), 7.35–7.51 (m, 12H), 7.06 (m, 1H), 6.91 (dd, J_1 = 5.0 Hz, J_2 = 8.3 Hz, 1H), 6.59 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 6.56 (dd, J_1 = 5.1 Hz, J_2 = 8.1 Hz, 1H), 6.06 (dd, J_1 = 2.2 Hz, J_2 = 8.2 Hz, 1H), 5.89 (t, J = 2.3 Hz, 1H), 3.67 (s, 3H), 3.40 (s, 3H), 2.42 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.5, 161.3, 160.6, 154.5, 145.4 (d, J = 3.1 Hz), 139.1, 133.4 (d, J = 10.9 Hz), 130.4 (d, J = 13.7 Hz), 130.1, 120.8 (q, J = 320.9 Hz for OTf), 117.4 (d, J = 95.5 Hz), 111.1 (d, J = 6.2 Hz), 110.7, 110.3, 107.8 (d, J = 6.1 Hz), 105.0, 95.9 (d, J = 95.6 Hz), 56.3, 55.4, 21.6; ^{31}P NMR ($CDCl_3$, 202 MHz): δ 15.2; IR ($CHCl_3$): 2924, 1735, 1595, 1571, 1467, 1263, 1142, 1031 cm^{-1}; HRMS (+ESI) calcd for $C_{35}H_{34}O_3P^+$ [M − OTf]$^+$: 533.2240; found: 533.2265.

Triethyl[2-methoxy-6-(3-methoxyphenoxy)phenyl] trifluoromethanesulfonate (3dg). Using the general experimental procedure with triethylphosphineoxide (0.067 g; 0.5 mmol), (1 mmol), 3-methoxy-2-(trimethylsilyl)phenyl trifluorometha-

nesulfonate (0.27 mL 1 mmol), and CsF (0.227 g; 1.5 mmol) in acetonitrile (4 mL), **3dg** was obtained as a yellow gummy product (0.123 g, 71% yield) after purification by flash chromatography using DCM/MeOH (95 : 5) as the eluent; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (t, J = 8.4 Hz, 1H), 7.28 (t, J = 8.5 Hz, 1H), 6.82 (dd, J_1 = 4.4 Hz, J_2 = 8.3 Hz, 1H), 6.76 (m, 1H), 6.51–6.55 (m, 2H), 6.49 (dd, J_1 = 4.1 Hz, J_2 = 8.6 Hz, 1H), 3.96 (s, 3H), 3.77 (s, 3H), 2.57 (m, 6H), 1.23 (dt, J_1 = 7.6 Hz, J_2 = 19.8 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.5, 161.9, 161.3, 154.6, 137.6, 130.9, 120.7 (q, J = 320.6 Hz for OTf), 111.5 (d, J = 5.8 Hz), 111.1 (d, J = 4.3 Hz), 110.3 (d, J = 12.1 Hz), 110.2, 106.5 (d, J = 10.1 Hz), 106.4, 105.9 (d, J = 6.8 Hz), 93.2 (d, J = 79.5 Hz), 56.6 (d, J = 10.6 Hz), 55.5 (d, J = 9.3 Hz), 14.9 (d, J = 51.2 Hz), 6.3; ^{31}P NMR ($CDCl_3$, 202 MHz): δ 37.3; IR ($CHCl_3$): 2946, 1593, 1574, 1468, 1437, 1264, 1142, 1031 cm^{-1}; HRMS (+ESI) calcd for $C_{20}H_{28}O_3P^+$ $[M - OTf]^+$: 347.1771; found: 347.1777.

Tributyl[2-methoxy-6-(3-methoxyphenoxy)phenyl]-phosphonium trifluoromethanesulfonate (3dh). Using the general experimental procedure with tributylphosphineoxide (0.109 g; 0.5 mmol), (1 mmol), 3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.27 mL; 1 mmol), and CsF (0.227 g; 1.5 mmol) in acetonitrile (4 mL), **3dh** was obtained as a yellow gummy product (0.157 g, 73% yield) after purification by flash chromatography using DCM/MeOH (95 : 5) as the eluent; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (t, J = 8.5 Hz, 1H), 7.31 (m, 1H), 6.85 (dd, J_1 = 4.4 Hz, J_2 = 8.1 Hz, 1H), 6.79 (dd, J_1 = 2.1 Hz, J_2 = 8.1 Hz, 1H), 6.49–6.55 (m, 3H), 3.97 (s, 3H), 3.79 (s, 3H), 2.50–2.58 (m, 6H), 1.39–1.52 (m, 12H), 0.88 (t, J = 7.2, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.3, 161.6, 161.3, 154.7, 137.5, 131.0, 120.8 (q, J = 320.5 Hz for OTf), 111.4, 111.0, 110.5 (d, J = 6.1 Hz), 106.6, (d, J = 6.0 Hz), 105.8, 94.4 (d, J = 78.6 Hz), 56.7, 55.5, 24.4 (d, J = 4.8 Hz), 23.7 (d, J = 16.6 Hz), 22.2 (d, J = 49.6 Hz), 13.2; ^{31}P NMR ($CDCl_3$, 202 MHz): δ 30.6; IR ($CHCl_3$): 2961, 1594, 1574, 1467, 1436, 1263, 1141, 1031cm^{-1}; HRMS (+ESI) calcd for $C_{26}H_{40}O_3P^+$ $[M - OTf]^+$: 431.2710; found: 431.2696.

[1-(Naphthalen-2-yloxy)naphthalen-2-yl]triphenyl phosphonium trifluoromethanesulfonate (3ea). Using the general experimental procedure with triphenylphosphineoxide (0.139 g; 0.5 mmol), 1-(trimethylsilyl)-2-napthyl trifluoromethanesulfonate (0.24 mL; 1 mmol), and CsF (0.227 g; 1.5 mmol) in acetonitrile (4 mL), **3ea** was obtained as a colorless solid (0.169 g, 64% yield) after purification by flash chromatography using DCM/MeOH (98 : 2) as the eluent; mp 200–202 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (d, J = 9.1 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.57–7.81 (m, 18H), 7.40–7.53 (m, 3H), 7.10–7.25 (m, 3H), 6.95 (d, J = 2.4 Hz, 1H), 6.65 (dd, J_1 = 2.5 Hz, J_2 = 8.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.9, 151.1, 140.2, 134.8 (d, J = 2.9 Hz), 134.0 (d, J = 10.4 Hz), 133.8 (d, J = 6.1 Hz), 133.5, 130.9, 130.8, 130.4 (d, J = 13.3 Hz), 130.3, 129.0, 127.7, 127.2 (d, J = 16.7 Hz), 126.3, 125.8, 125.6 (d, J = 6.8 Hz), 125.5, 120.3 (d, J = 89.9 Hz), 118.5, 118.4, 115.1, 99.1 (d, J = 91.9 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz): δ 15.6; IR ($CHCl_3$): 3012, 1658, 1595, 1508, 1459, 1439, 1264, 1156, 1030 cm^{-1}; HRMS (+ESI) calcd for $C_{38}H_{28}OP^+$ $[M - OTf]^+$: 531.1872; found: 531.1877.

(2-Phenoxyphenyl)triphenylphosphonium trifluoromethanesulfonate (deuterated) (3aa-D). Using the general experimental procedure with triphenylphosphineoxide (0.070 g; 0.25 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.06 mL; 0.25 mmol), and CsF (0.075 g; 2 mmol) in CD_3CN (4 mL), **3aa-D** was obtained as a light brown gummy product (0.057 g, 53% yield) after purification by flash chromatography using DCM/MeOH (98 : 2) as the eluent; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67–7.85 (m, 16H), 7.21–7.38 (m, 4H), 7.13 (t, J = 7.4 Hz, 1H), 6.99 (dd, J_1 = 5.8 Hz, J_2 = 8.4 Hz, 1H), 6.52 (d, J = 8.3 Hz, ~1.4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.4 (d, J = 1.7 Hz), 152.5 (d, J = 5.4 Hz), 138.3 (d, J = 1.9 Hz), 136.4 (d, J = 8.9 Hz), 135.2 (d, J = 3.0 Hz), 135.1, 134.0 (d, J = 10.6 Hz), 130.5 (d, J = 13.3 Hz), 130.2, 126.0, 124.9, 124.5 (d, J = 12.7 Hz), 119.5, 117.9 (d, J = 91.7 Hz), 116.9 (d, J = 6.3 Hz), 107.2 (d, J = 93.3 Hz); IR ($CHCl_3$): 2924, 1602, 1573, 1466, 1441, 1275, 1108, 1028 cm^{-1}; HRMS (+ESI) calcd for $C_{30}H_{20}DOP^+$ $[M - OTf]^+$: 432.1622; found: 432.1610.

Conflicts of interest

There are no conflicts to declare.

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