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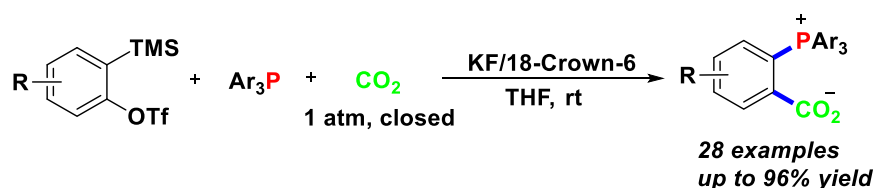
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Multicomponent reaction of phosphines, benzyne and CO₂: facile synthesis of stable zwitterionic phosphonium inner-salts

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Abstract: The first synthesis of benzyne derived stable zwitterions is reported. Benzyne generated in situ from 2-(trimethylsilyl)aryl triflates undergo multicomponent reaction with phosphines and CO₂ to produce the stable 1,5-zwitterionic species in moderate to excellent isolated yields, which provides a novel method for the preparation of phosphonium inner-salts under mild and transition-metal free conditions.

Introduction:

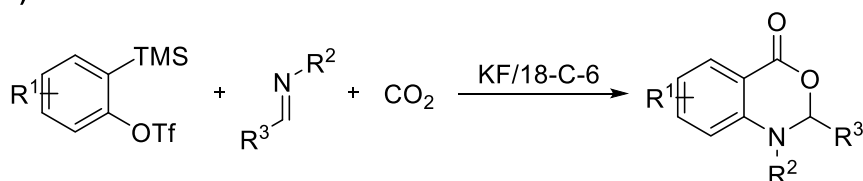
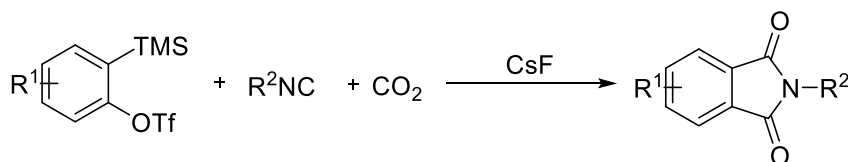
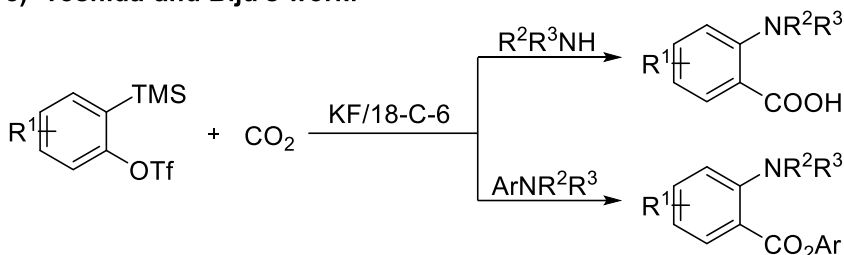
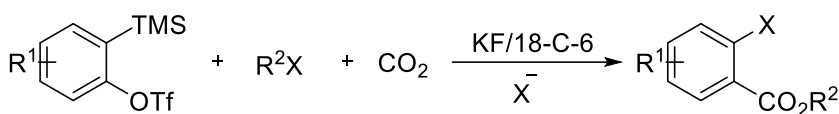
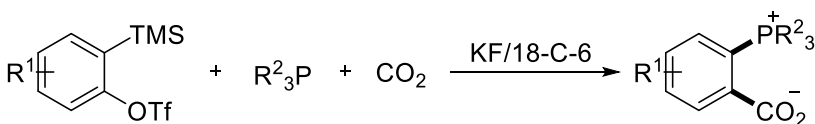
The past two decades have witnessed remarkable progress in benzyne chemistry.¹ As one of the most versatile building blocks, benzyne have been used widely in a broad variety of reactions, such as pericyclic reactions,² insertion reactions,³ multicomponent

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4 reactions (MCRs)⁴ and others.⁵ These reactions provide efficient
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6 methods for the construction of carbon-carbon and carbon-
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8 heteroatom bonds. In particular, the highly electrophilic properties of
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10 benzyne enable them to be readily attacked by different nucleophiles
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12 to generate an aryl anion or 1,3-zwitterionic species, which can
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14 further react with the third electrophilic component to produce
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16 various 1,2-disubstituted benzene derivatives.
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22 On the other hand, the utilization of CO₂ as non-toxic, renewable,
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24 inexpensive and easy-available one carbon (C1) feedstock to prepare
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26 value-added chemicals has received considerable attention in recent
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28 years.⁶ Generally, CO₂ is used as an electrophile regardless of its
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30 intrinsic thermodynamic and kinetic stability. Although several
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32 excellent MCRs involving benzyne, CO₂ and different nucleophiles
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34 have been reported in recent years, the studies of the incorporation of
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36 CO₂ in the reaction of benzyne are still very limited. In 2006,
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38 Yoshida, Kunai and coworkers reported the first incorporation of CO₂
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40 in MCR of benzyne⁷ (Scheme 1, eq. a). They found that imines can
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42 be employed as nucleophiles to trigger the three-component coupling
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44 involving benzyne and CO₂, giving benzoxazinones efficiently.
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46 Later, Biju and coworkers⁸ reported an interesting MCR of
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48 isocyanides, benzyne and CO₂ to produce phthalimides as the final
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50 products, which were assumed to be formed through fluoride-induced
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rearrangement of the iminoisobenzofuranone intermediates (Scheme 1, eq. b). In 2008, Yoshida and coworkers⁹ documented a concise three-component coupling of benzyne, secondary amines and CO₂, furnishing anthranilic acids directly (Scheme 1, eq. c). Interestingly, with the introduction of aromatic tertiary amines to the reaction, Biju and coworkers¹⁰ developed a novel substrate-controlled switchable MCR involving benzyne and CO₂, delivering two different types of 2-aminoaryl benzoates selectively (Scheme 1, eq. c). Recently, Jiang and coworkers^{11a} disclosed a new three-phase four-component coupling reaction involving benzyne. In that reaction, KCl was used as nucleophile to attack the carbon-carbon triple bond of benzyne and trigger the MCR of benzyne with incorporation of CO₂, giving *o*-chlorobenzoates as the major products. More interestingly, the same group uncovered^{11b} that allyl bromides can function as unconventional nucleophiles to alter the MCR of benzyne to provide the bromocarboxylation products (Scheme 1, eq. d). In these aforementioned MCRs, the benzyne-derived zwitterionic species are the key intermediates, which readily undergo the following nucleophilic attack to furnish the corresponding products.

Scheme 1. MCRs involving benzyne and CO₂

a) Yoshida's work:**b) Biju's work:****c) Yoshida and Biju's work:****d) Jiang's work:****e) This work:**

However, these zwitterions are unstable and have not been successfully prepared. With our continuing interest in benzyne chemistry,¹² we found that phosphines, benzyne and CO₂ can undergo three-component coupling reaction to produce zwitterionic species as the unexpected final products.¹³ These stable zwitterions, also named as phosphonium salts, are a unique type of P(V) compounds that used widely as organocatalysts,¹⁴ organic reagents,¹⁵ ionic liquids,¹⁶ ligands¹⁷ and others¹⁸ in organic chemistry. Herein, we

would like to report our preliminary results on the synthesis of zwitterionic phosphonium inner-salts through MCR involving benzyne and CO₂.

Results and Discussion:

To start our investigation, the commercially available Kobayashi's precursor **1a**¹⁹ and triphenylphosphine **2a** were selected as the model substrates for the optimization of the reaction (Table 1). To our delight, with 2.0 equiv of KF and 18-crown-6 as additives, the MCR smoothly proceeded in THF under 1 atm CO₂ at room temperature to provide phosphonium inner-salt **3aa** in 91% NMR yield (Table 1, entry 1). Encouraged by this success, other common fluoride sources were subsequently tested for the reaction. In the absence of 18-crown-6, KF or CsF cannot promote the coupling (Table 1, entries 2 and 3). Tetrabutylammonium difluorotriphenylsilicate (TBAT) promoted the reaction in high yield (Table 1, entry 4). Both tetrabutylammonium fluoride (TBAF) and tetramethylammonium fluoride (TMAF) showed low efficiency (Table 1, entries 5 and 6). Shorten the reaction time to 10 h, the reaction yield was slightly improved to 94% (Table 1, entry 7). A brief screening of the reaction media showed that THF was still the best choice in terms of yield (Table 1, entries 8-11). Reducing KF and 18-crown-6 to 1.5 equiv, the product can still be formed in 90% yield (Table 1, entry 12).

However, lowering the additives loading to 1.2 equiv resulted in obvious decrease of the reaction yield (Table 1, entry 13). Finally, in the presence of 1.5 equiv KF/18-crown-6 and prolonged the reaction time to 24 h, the desired product was obtained in 96% NMR yield and 91% isolated yield (Table 1, entry 14).

Table 1. Optimization of reaction conditions^a

$\text{1a} + \text{PPh}_3 + \text{CO}_2 \xrightarrow[\text{solvent, } 0^\circ\text{C-rt, } t \text{ (h)}]{[\text{F}] \text{ source}} \text{3aa}$

entry	[F] source (equiv)	solvent	<i>t</i> (h)	yield (%) ^b
1	KF(2)+18-C-6(2)	THF	21	91
2	KF(2)	THF	21	0
3	CsF(2)	THF	21	0
4	TBAT(2)	THF	21	92
5	TBAF(2)	THF	21	45
6	TMAT(2)	THF	21	29
7	KF(2)+18-C-6(2)	THF	10	94
8	KF(2)+18-C-6(2)	CH ₃ CN	10	69
9	KF(2)+18-C-6(2)	DME	10	61
10	KF(2)+18-C-6(2)	Dioxane	10	40
11	KF(2)+18-C-6(2)	Toluene	10	8
12	KF(1.5)+18-C-6(1.5)	THF	10	90
13	KF(1.2)+18-C-6(1.2)	THF	10	75
14	KF(1.5)+18-C-6(1.5)	THF	24	96(91) ^c

^a Reaction conditions: **1a** (0.24 mmol), **2a** (0.2 mmol), CO₂ (1 atm), 0 °C-rt; ^b NMR yield using CH₂Br₂ (0.2 mmol, 14 μL) as internal standard; ^c isolated yield.

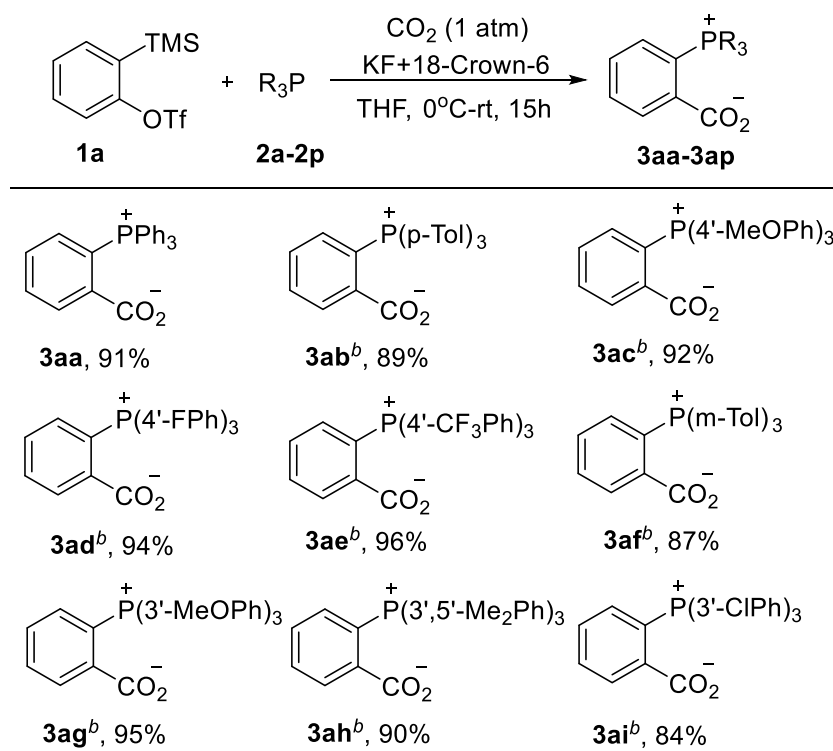
The product **3aa** was crystallized from ethyl acetate and n-hexane,

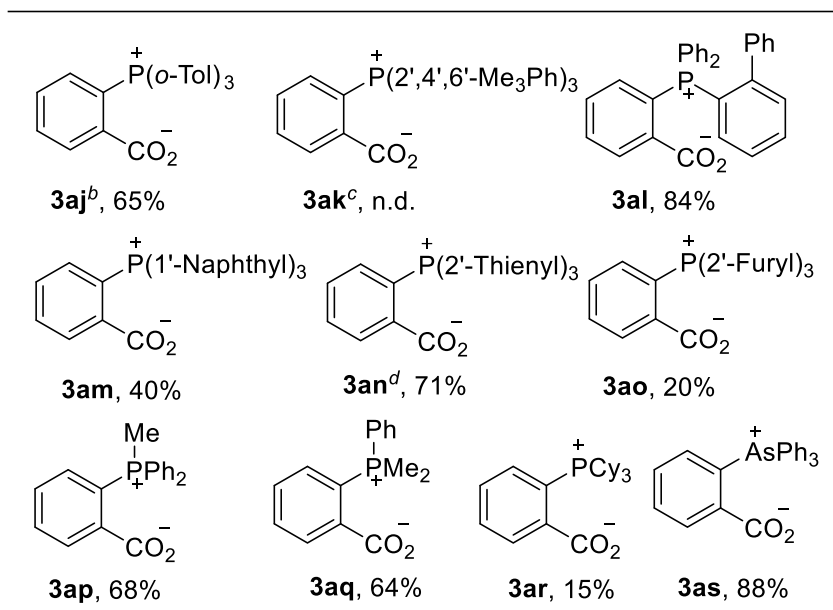
and its structure was clearly confirmed by single-crystal X-ray analysis.²⁰

With the optimized reaction condition in hand, we then examined the scope of phosphines (Scheme 2). Both electron-donating and electron-withdrawing groups substituted triarylphosphines participated in the MCR smoothly to produce the corresponding zwitterionic phosphonium inner-salts in excellent yield (**3ab-3ae**). In addition, triarylphosphines bearing substituent at the meta-position of the benzene ring underwent the reaction to afford the corresponding inner-salts efficiently (**3af-3ai**). However, when tri-*o*-tolylphosphine **2j** was used for the reaction, only trace amount of the desired product was formed under the standard reaction conditions. Pleasingly, the reaction yield can be improved to 65% with elevated reaction temperature and prolonged reaction time (**3aj**). But unfortunately, when the fully *ortho*-substituted triarylphosphine **2k** was employed for the MCR, no desired product was obtained and the starting phosphine **2k** was recovered in high yield (**3ak**). We attributed these results to the dramatic increase of the steric hindrance of triarylphosphines. Interestingly, the bulky phosphines **2l** and **2m** performed the MCR well to give phosphonium inner-salts **3al** and **3am** in 84% and 40% yields, respectively. Heteroaryl substituted phosphine **2n** was proven to be a successful candidate for the reaction,

providing **3an** in 71% yield. However, in case of tri-2-furylphosphine **2o**, the MCR with benzyne and CO₂ was complex and only 20% yield product was obtained (**3ao**). Both mono- and dialkyl-substituted phosphines performed the reaction very well, affording the desired products in satisfactory yield (**3ap** and **3aq**). Surprisingly, when trialkyl-substituted phosphine was used for the reaction, the reaction was complex and the desired product was obtained in very low yield (**3ar**). The similar triarylsarsane was also tested for the MCR and the corresponding arsonium salt **3as** was obtained in 88% yield.

Scheme 2. Substrate scope of triarylphosphine compounds^a



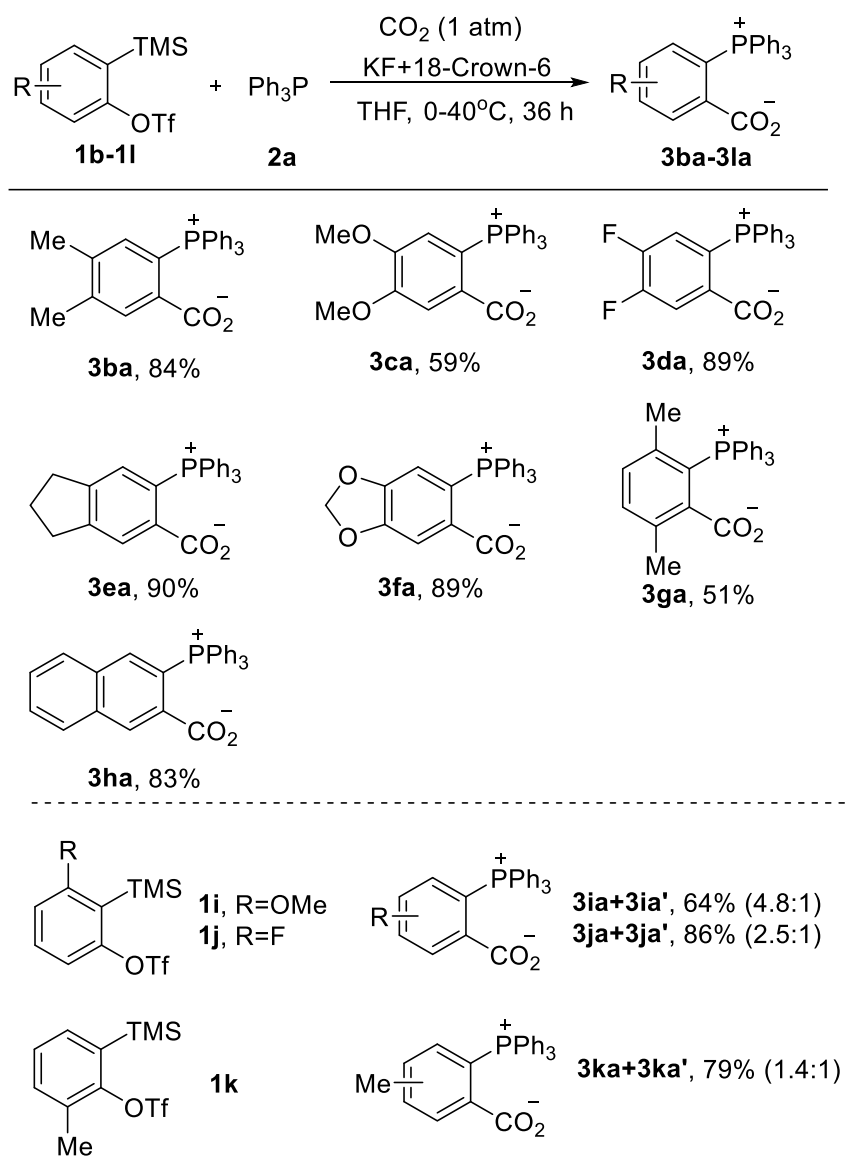


^a Reaction conditions: **1a** (0.24 mmol), **2** (0.2 mmol), CO₂ (1 atm), KF (3.0 mmol), 18-crown-6 (0.3 mmol), 0 °C-rt, 24h and isolated yield. ^b 50 °C, 36 h. ^c Phosphine **2k** was recovered in 90% yield. ^d 0-10 °C, 24 h. n.d. (not detected).

Next, we investigated substituted benzyne precursors for the MCR (Scheme 3). Symmetrical benzynes with both electron-donating and electron-withdrawing groups at 4,5-positions reacted with triphenylphosphine and CO₂ to produce the corresponding phosphonium salts in moderate to high yields (**3ba-3fa**). Notably, 3,6-dimethyl substituted benzyne that with steric hindrance around the carbon-carbon triple bond underwent the MCR to yield **3ga** in 51% yield. The symmetrical naphthalene was suitable reactant for the reaction, furnishing the phosphonium salt in 83% yield (**3ha**). In addition, the unsymmetrical benzynes that derived from precursors **1i**, **1j** and **1k**, underwent the three-component coupling efficiently to provide the corresponding products in

good yields and moderate regioselectivity (**3ia-3ka**). The pure regioisomers **3ia** and **3ia'**, **3ka** and **3ka'** can be obtained via column chromatography. However, regioisomers **3ja** and **3ja'** cannot be isolated completely and only the pure product of the major regioisomer **3ja** was isolated.

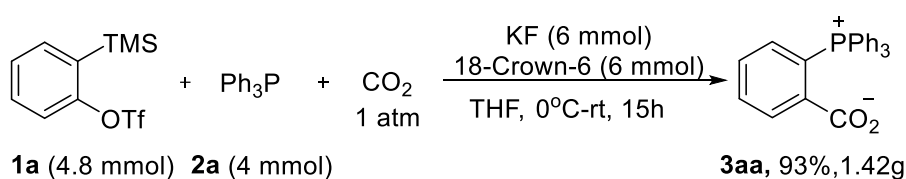
Scheme 3. Substrate scope of benzyne precursors^a



^a Reaction conditions: **1** (0.24 mmol), **2a** (0.2 mmol), CO_2 (1 atm), KF (3.0 mol), 18-crown-6 (0.3 mmol), 40 °C, 36 h and isolated yield.

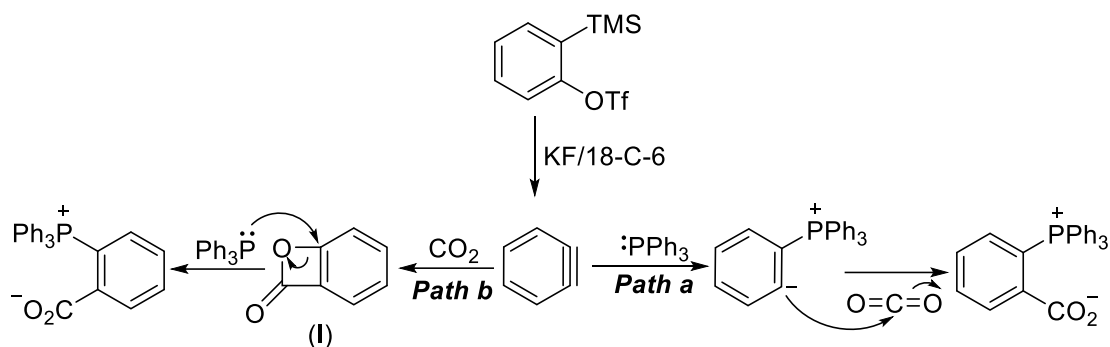
To demonstrate the synthetic utility of this methodology, we carried out the MCR on gram scale by treatment of triphenylphosphine and Kobayashi's precursor **1a** under 1 atm of CO₂. The phosphonium inner-salt **3aa** was obtained in 1.42g and 93% isolated yield under the standard reaction conditions (Scheme 4).

Scheme 4. Gram-scale preparation of **3aa**



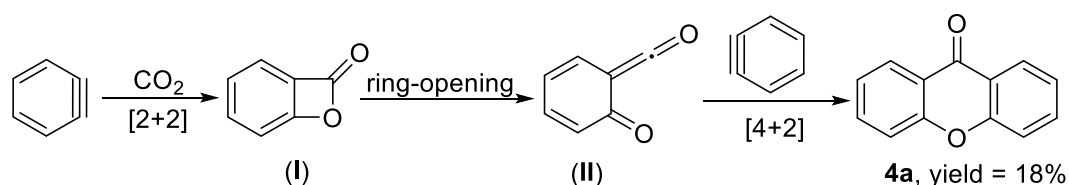
Based on the pioneering studies of three-component coupling reaction involving benzyne and CO₂,⁷⁻¹¹ two plausible reaction mechanisms were proposed as depicted in Scheme 5. For path **a**, the fluoride induced 1,2-elimination of 2-(trimethylsilyl)aryl triflate results in the *in situ* generation of benzyne. The following nucleophilic attack of triphenylphosphine will trigger the tandem reaction and lead to the formation of the final zwitterionic phosphonium inner-salt. For path **b**, benzyne might undergo [2+2] cycloaddition with CO₂ to generate intermediate **I**, which subsequently undergoes ring-opening reaction with triphenylphosphine to produce the final product.

Scheme 5. Proposed mechanism



The control experiment showed that in the absence of triphenylphosphine, benzyne can react with CO_2 to produce xanthone **4a** in 18% yield (Scheme 6). We concluded that benzyne firstly undergo [2+2] reaction with CO_2 to generate intermediate **I**. Owing to the high ring strain of the four-membered ring, **I** undergoes ring-opening reaction to produce ketene intermediate **II**, which couples with the second molecular of benzyne via [4+2] reaction to afford **4a**. This result indicates the possibility of the formation of intermediate **I**.

Scheme 6. The reaction of benzyne and CO_2



Conclusions:

In summary, we have developed an efficient and practical approach for the synthesis of stable zwitterionic phosphonium inner-salts through the three-component coupling reaction of benzynes, phosphines and CO_2 . The presented protocol features mild and transition-metal free conditions, simple operation and ready scalability. Further studies on the synthesis of

chiral P-stereogenic phosphonium inner-salts and their applications in organic synthesis are currently underway in our laboratory.

EXPERIMENTAL SECTION

General experimental methods

Unless otherwise indicated, all reactions were conducted in oven-dried 50 mL Schlenk sealed tube (Synthware) under a CO₂ atmosphere. CO₂ was provided by Shanghai Weichuang Standard Gas and its purity was \geq 99.999%. Benzyne precursors and other commercial available reagents were obtained from commercial suppliers (such as Adamas, Strem, J&K Chemical Co., Energy Chemical. etc), and used without purification. Benzyne precursors **1b**, **1d**, **1e-1g**, and **1j-1k** were prepared according to literature procedures.^{3f, 11b, 21} Anhydrous THF, dioxane, CH₃CN, toluene and DME were obtained from commercial suppliers. ¹H, ¹³C and ³¹P NMR spectra were recorded on a Bruker AVANCE III spectrometer (400 MHz, 100 MHz and 162 MHz, respectively), Chemical shifts are reported parts per million (ppm) referenced to CDCl₃ (δ 7.26 ppm), tetramethylsilane (TMS, δ 0.00 ppm), for ¹H NMR; CDCl₃ (δ 77.16 ppm) or CD₃OD (δ 49.00 ppm) for ¹³C NMR. High-resolution mass spectra (HRMS) were obtained on an LTQ Orbitrap XL mass spectrometry equipped with an ESI source from Thermo Scientific at Keecloud Biotech in Shanghai. X-ray diffraction study for product **3aa** was carried out on Bruker D8 VENTURE

photon II diffractometer with I μ s 3.0 microfocus X-ray source using APEX III program.

General procedure for synthesis of products:

To an oven-dried 50 mL Schlenk sealed tube (with a Teflon cap) equipped with a magnetic stir bar was added the phosphine **2** (0.20 mmol, 1.0 equiv), KF (18 mg, 0.3 mmol, 1.5 equiv) and 18-crown-6 (80 mg, 0.3 mmol, 1.5 equiv). Then the tube was evacuated under vacuum and charged with CO₂ (1 atm, 3 times). The reaction mixture was dissolved in anhydrous THF (2.0 mL) under protection of CO₂ atmosphere and subsequently cooled the reaction mixture to 0 °C with stirring. At this moment, aryne precursor **1** (0.24 mmol, 1.2 equiv) was added in the stirring solution under protection of CO₂ atmosphere. After the mixture was reacted at 0 °C for 0.5 h, then taking out of the ice-bath, kept stirring at room temperature or 40 °C in oil bath until completion of the reaction which was detected by TLC. The reaction mixture was then diluted with 40 mL dichloromethane and washed with saturated potassium sulfate solution for 12 times (**note**: in order to remove completely the potassium salt generated from KF with 18-C-6 which has closed polarity with **3**). The residue was successively dried with anhydrous sodium sulfate, filtered and evaporated of solvent to give the crude product. The crude product was purified by column chromatography on silica gel (200-300 mesh, DCM:MeOH = 20:1 as eluent) to afford the corresponding

phosphonium inner-salts **3** in moderate to excellent yields.

Procedure for gram-scale synthesis of 3aa: To a 150 mL Schlenk sealed tube with a magnetic stir bar was added the triphenylphosphine **2a** (1.05 g, 4.0 mmol, 1.0 equiv), KF (0.348 g, 6.0 mmol, 1.5 equiv) and 18-crown-6 (1.585 g, 6.0 mmol, 1.5 equiv). Then the tube was evacuated under vacuum and charged with CO₂ (1 atm, 3 times). The reaction mixture was dissolved in anhydrous THF (40 mL) under protection of CO₂ atmosphere and subsequently cooled the reaction mixture to 0 °C with stirring. At this moment, benzyne precursor **1a** (1.43 g, 4.8 mmol, 1.2 equiv) was added in the stirring solution under protection of CO₂ atmosphere. After the mixture was reacted at 0 °C for 0.5 h, then taking out of the ice-bath, kept stirring for 21 h at room temperature until completion of the reaction which was detected by TLC. The reaction mixture was then diluted with 120 mL dichloromethane and washed with saturated potassium sulfate solution for 12 times. The residue was successively dried with anhydrous sodium sulfate, filtered and evaporated of solvent to give the crude product. The crude product was purified by column chromatography on silica gel (200-300 mesh, DCM:MeOH = 20:1 as eluent) to afford the clean *o*-triphenylphosphonium benzoate **3aa** in 1.42 g and 93% isolated yield.

Procedure for the reaction of benzene with CO₂: To an oven-dried 50 mL Schlenk sealed tube (with a Teflon cap) equipped with a magnetic stir bar was added KF (52 mg, 0.9 mmol, 3.0 equiv), 18-crown-6 (238 mg, 0.9

mmol, 3.0 equiv). Then the tube was evacuated under vacuum and charged with CO₂ (1 atm, 3 times). The reaction mixture was dissolved in anhydrous THF (3.0 mL) and subsequently aryne precursor **1a** (89.4, 0.3 mmol, 1.0 equiv) was added to the stirring solution under the protection of CO₂ atmosphere, kept stirring at room temperature for 48 hours. Then, the solvent was evaporated to give the crude product which was purified by flash silica gel chromatography (PE : EA = 15:1) to afford pure **4a** (10.6 mg, 18% yield).

2-(triphenylphosphonio)benzoate (3aa) (known compound)²²: purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (69.5 mg, 91%); m.p.: 233-234 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.53 (dd, *J* = 7.2, 3.6 Hz, 1H), 7.82 (t, *J* = 6.4 Hz, 1H), 7.57-7.33 (m, 16H), 6.99 (dd, *J* = 13.6, 7.6 Hz, 1H).; ¹³C{¹H} NMR (100 Hz, CDCl₃) δ 166.2 , 143.9 (d, *J* = 9.1 Hz), 136.5 (d, *J* = 14.8 Hz), 134.9 (d, *J* = 3.1 Hz), 132.4 (d, *J* = 9.1 Hz), 131.4 (d, *J* = 2.9 Hz), 130.8 (d, *J* = 14.8 Hz), 130.2 (d, *J* = 10.8 Hz), 128.7, 128.6, 122.3 (d, *J* = 113.0 Hz); ³¹P{¹H} NMR (162 MHz, CDCl₃) δ 6.44; HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₅H₂₀O₂P 383.1195, Found 383.1194; IR (KBr, thin film): 3059, 1649, 1628, 1483, 1437, 1354, 1301, 1269, 831, 754, 731, 698 cm⁻¹.

2-(tri-*p*-tolylphosphonio)benzoate (3ab): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (75.5 mg, 89%); m.p.: 159-160 °C; ¹H NMR (400 Hz, CDCl₃) δ 8.49 (dd, *J* = 6.8, 4.4 Hz, 1H),

7.66 (t, $J = 5.6$ Hz, 1H), 7.55-7.47 (m, 1H), 7.28-7.14 (m, 12H), 7.02 (dd, $J = 14.0, 7.6$ Hz, 1H), 2.33 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 Hz, CDCl_3) δ 166.1, 144.1 (d, $J = 3.0$ Hz), 137.1 (d, $J = 12.6$ Hz), 135.1 (d, $J = 2.9$ Hz), 133.6 (d, $J = 10.3$ Hz), 133.2 (d, $J = 10.1$ Hz), 132.8 (d, $J = 8.8$ Hz), 130.9 (d, $J = 13.4$ Hz), 130.1 (d, $J = 13.4$ Hz), 120.4 (d, $J = 98.6$ Hz), 119.9 (d, $J = 95.9$ Hz), 21.7 (d, $J = 1.3$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 10.53; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{26}\text{O}_2\text{P}$ 425.1665, Found 425.1664; IR (KBr, thin film): 3024, 2926, 2866, 1645, 1622, 1564, 1501, 1397, 1379, 1273, 804, 760, 731, 691, 670 cm^{-1} .

2-(tris(4-methoxyphenyl)phosphonio)benzoate (3ac): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (86.9 mg, 92%); m.p.: 134-135 $^{\circ}\text{C}$; ^1H NMR (400 Hz, CDCl_3) δ 8.56 (dd, $J = 6.8, 4.0$ Hz, 1H), 7.78 (t, $J = 7.6$ Hz, 1H), 7.51-7.43 (m, 1H), 7.39-7.30 (m, 6H), 7.00 (dd, $J = 14.0, 7.6$ Hz, 1H), 6.96-6.89 (m, 6H), 3.82 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 Hz, CDCl_3) δ 166.3, 162.0 (d, $J = 2.9$ Hz), 144.7 (d, $J = 8.5$ Hz), 136.1 (d, $J = 14.8$ Hz), 134.6 (d, $J = 11.0$ Hz), 134.5, 130.9 (d, $J = 10.4$ Hz), 130.1 (d, $J = 14.6$ Hz), 122.0 (d, $J = 109.1$ Hz), 119.5 (d, $J = 107.6$ Hz), 114.3 (d, $J = 14.2$ Hz), 55.4; $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 21.16; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{26}\text{O}_5\text{P}$ 473.1512, Found 473.1513; IR (KBr, thin film): 3059, 2932, 2839, 1639, 1595, 1568, 1502, 1458, 1259, 829, 733, 690 cm^{-1} .

2-(tris(4-fluorophenyl)phosphonio)benzoate (3ad): purified by flash

silica gel chromatography (DCM : MeOH = 20:1); white solid (82.0 mg, 94%); m.p.: 128-129 °C; ^1H NMR (400 Hz, CDCl_3) δ 8.48 (dd, $J = 7.2, 4.4$ Hz, 1H), 7.91 (td, $J = 7.6, 1.2$ Hz, 1H), 7.69-7.63 (m, 1H), 7.49-7.36 (m, 6H), 7.27-7.12 (m, 6H), 7.06 (dd, $J = 14.8, 8.0$ Hz, 1H).; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 Hz, CDCl_3) δ 166.2, 164.8 (dd, $J = 255.0, 3.3$ Hz), 141.3 (d, $J = 7.9$ Hz), 136.8 (d, $J = 14.0$ Hz), 135.7 (d, $J = 2.9$ Hz), 135.3 (t, $J = 9.4$ Hz), 132.1 (d, $J = 14.5$ Hz), 131.5 (d, $J = 10.2$ Hz), 122.6 (d, $J = 104.6$ Hz), 120.6 (d, $J = 107.2$ Hz), 116.8 (dd, $J = 21.8, 14.6$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ -0.47; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{17}\text{F}_3\text{O}_2\text{P}$ 437.0913, Found 437.0916; IR (KBr, thin film): 3065, 1673, 1584, 1456, 1396, 1334, 1308, 835, 782, 727, 689 cm^{-1} .

2-(tris(4-(trifluoromethyl)phenyl)phosphonio)benzoate (3ae): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (112.5 mg, 96%); m.p.: 97-98 °C; ^1H NMR (400 Hz, CDCl_3) δ 8.50 (dd, $J = 7.6, 3.2$ Hz, 1H), 7.96 (td, $J = 7.6, 1.2$ Hz, 1H), 7.85-7.20 (m, 13H), 7.00 (dd, $J = 12.8, 7.6$ Hz, 1H).; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 Hz, CDCl_3) δ 165.4, 142.5 (d, $J = 11.8$ Hz), 136.6 (d, $J = 15.0$ Hz), 135.9 (d, $J = 3.3$ Hz), 133.0 (qd, $J = 33.0, 2.9$ Hz), 132.2 (d, $J = 15.5$ Hz), 129.3 (d, $J = 12.5$ Hz), 125.8 (d, $J = 1.7$ Hz), 125.6 (d, $J = 2.9$ Hz), 124.5 (d, $J = 124.4$ Hz), 123.2 (q, $J = 271.1$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ -21.57; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{17}\text{F}_9\text{O}_2\text{P}$ 587.0817, Found 587.0811; IR (KBr, thin film): 3070, 1680, 1611, 1400, 1325, 1173, 1130, 1064, 1016, 835, 715,

692 cm⁻¹.

2-(tri-m-tolylphosphonio)benzoate (3af): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (73.8 mg, 87%); m.p.: 164-165 °C; ¹H NMR (400 Hz, CDCl₃) δ 8.55 (dd, *J* = 7.6, 4.0 Hz, 1H), 7.82 (t, *J* = 7.2 Hz, 1H), 7.58-7.44 (m, 1H), 7.35-7.27 (m, 7H), 7.23-7.14 (m, 5H), 6.97 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.31 (s, 9H); ¹³C{¹H} NMR (100 Hz, CDCl₃) δ 166.1 , 144.3 (d, *J* = 8.9 Hz), 138.4 (d, *J* = 12.8 Hz), 136.4 (d, *J* = 14.7 Hz), 134.6 (d, *J* = 3.2 Hz), 132.8 (d, *J* = 9.1 Hz), 132.1 (d, *J* = 2.9 Hz), 130.5 (d, *J* = 14.7 Hz), 130.3 (d, *J* = 10.7 Hz), 129.7 (d, *J* = 9.5 Hz), 128.4, 128.3, 122.5 (d, *J* = 112.3 Hz), 21.6; ³¹P{¹H} NMR (162 MHz, CDCl₃) δ 8.78; HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₈H₂₆O₂P 425.1665, Found 425.1665; IR (KBr, thin film): 3026, 2923, 2867, 1645, 1623, 1564, 1500, 1394, 1381, 1276, 803, 760, 732, 692, 670 cm⁻¹.

2-(tris(3-methoxyphenyl)phosphonio)benzoate (3ag): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (89.7 mg, 95%); m.p.: 93-94 °C; ¹H NMR (400 Hz, CDCl₃) δ 8.51 (dd, *J* = 7.2, 4.0 Hz, 1H), 7.83 (td, *J* = 7.6, 1.2 Hz, 1H), 7.57-7.48 (m, 1H), 7.36-7.29 (m, 3H), 7.07-6.36 (m, 10H), 3.71 (s, 9H); ¹³C{¹H} NMR (100 Hz, CDCl₃) δ 166.1 , 159.3 (d, *J* = 16.6 Hz), 143.9 (d, *J* = 9.4 Hz), 136.5 (d, *J* = 14.8 Hz), 134.9 (d, *J* = 3.1 Hz), 130.7 (d, *J* = 14.8 Hz), 129.9 (d, *J* = 11.1 Hz), 129.8, 129.6, 124.5 (d, *J* = 6.0 Hz), 122.7 (d, *J* = 115.1 Hz), 118.4 (d, *J* = 10.2 Hz), 116.3 (d, *J* = 2.7 Hz), 55.4; ³¹P{¹H} NMR (162 MHz, CDCl₃) δ 3.13;

HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{28}H_{26}O_5P$ 473.1512, found 473.1511;
IR (KBr, thin film): 3058, 2928, 2837, 1636, 1596, 1567, 1502, 1456, 1260,
828, 732, 691 cm^{-1} .

2-(tris(3,5-dimethylphenyl)phosphonio)benzoate (3ah): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (83.9 mg, 90%); m.p.: 95-96 °C; 1H NMR (400 Hz, $CDCl_3$) δ 8.55 (dd, J = 6.8, 4.0 Hz, 1H), 7.73 (t, J = 7.2 Hz, 1H), 7.54-7.45 (m, 1H), 7.14 (s, 3H), 7.06-6.90 (m, 7H), 2.26 (s, 18H); $^{13}C\{^1H\}$ NMR (100 Hz, $CDCl_3$) δ 166.4, 138.3 (d, J = 13.7 Hz), 136.6 (d, J = 14.0 Hz), 134.5 (d, J = 2.9 Hz), 133.7 (d, J = 2.3 Hz), 131.1 (d, J = 10.0 Hz), 130.7 (d, J = 14.3 Hz), 130.3 (d, J = 9.3 Hz), 127.3 (d, J = 97.8 Hz), 121.4 (d, J = 105.7 Hz), 21.5; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 13.11; HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{31}H_{32}O_2P$ 467.2134, Found 467.2138; IR (KBr, thin film): 3028, 2926, 2858, 1655, 1564, 1454, 1393, 1271, 847, 760, 689 cm^{-1} .

2-(tris(3-chlorophenyl)phosphonio)benzoate (3ai): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (81.3 mg; 84%); m.p.: 93-94 °C; 1H NMR (400 Hz, $CDCl_3$) δ 8.48 (dd, J = 7.2, 3.2 Hz, 1H), 7.91 (td, J = 7.6, 1.2 Hz, 1H), 7.67-7.59 (m, 1H), 7.56-7.05 (m, 12H), 6.90 (dd, J = 13.2, 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 Hz, $CDCl_3$) δ 165.6, 142.8 (d, J = 11.3 Hz), 136.6 (d, J = 15.1 Hz), 135.6 (d, J = 3.3 Hz), 135.2, 134.9, 131.9 (d, J = 15.4 Hz), 131.48, 131.46, 130.1, 130.0, 129.3 (d, J = 12.2 Hz), 124.1 (d, J = 122.7 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$)

δ -15.94; HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{25}H_{17}Cl_3O_2P$ 485.0026, Found 485.0030; IR (KBr, thin film): 3063, 1663, 1564, 1468, 1398, 1340, 1300, 835, 777, 725, 685 cm^{-1} .

2-(tri-*o*-tolylphosphonio)benzoate (3aj): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (55.1 mg, 65%); m.p.: 83-84 °C; 1H NMR (400 Hz, $CDCl_3$) δ 8.64 (dd, J = 6.8, 4.4 Hz, 1H), 7.92-7.73 (m, 4H), 7.61-7.48 (m, 5H), 7.45-7.39 (m, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.23 (d, J = 7.2 Hz, 1H), 7.17 (q, J = 6.8 Hz, 2H), 1.78 (s, 3H), 1.75 (s, 3H), 1.62 (s, 3H); $^{13}C\{^1H\}$ NMR (100 Hz, $CDCl_3$) δ 165.7, 145.5 (d, J = 7.9 Hz), 143.4 (d, J = 6.3 Hz), 140.9 (d, J = 11.5 Hz), 138.7 (d, J = 9.3 Hz), 138.6 (d, J = 10.2 Hz), 136.2 (d, J = 10.9 Hz), 135.8 (d, J = 9.7 Hz), 135.5 (d, J = 15.6 Hz), 134.6 (d, J = 3.1 Hz), 134.4 (d, J = 10.8 Hz), 133.3 (d, J = 8.6 Hz), 132.6 (d, J = 2.2 Hz), 132.3, 132.2 (d, J = 16.5 Hz), 131.9 (d, J = 13.0 Hz), 131.7 (d, J = 3.7 Hz), 131.6 (d, J = 3.2 Hz), 130.4 (d, J = 14.7 Hz), 126.8 (d, J = 9.9 Hz), 126.2 (d, J = 14.6 Hz), 126.0 (d, J = 13.9 Hz), 124.4 (d, J = 111.0 Hz), 122.2 (d, J = 108.3 Hz), 120.5 (d, J = 101.0 Hz), 23.0 (d, J = 3.3 Hz), 22.8 (d, J = 2.2 Hz), 22.7 (d, J = 4.4 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 21.76; HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{28}H_{26}O_2P$ 425.1665, Found 425.1661; IR (KBr, thin film): 3061, 2932, 2864, 1726, 1593, 1564, 1474, 1448, 1271, 1223, 806, 760, 721, 692 cm^{-1} .

2-([1,1'-biphenyl]-2-yl)diphenylphosphonio)benzoate (3al): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (77.0

mg, 84%); m.p.: 298-299 °C; ^1H NMR (400 Hz, CDCl_3) δ 8.23 (s, 1H), 7.86-7.28 (m, 10H), 7.25-6.60 (m, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 Hz, CDCl_3) δ 167.2, 145.3 (d, $J = 8.4$ Hz), 140.1, 138.7 (d, $J = 4.5$ Hz), 135.8 (d, $J = 13.3$ Hz), 134.2, 134.1, 132.9 (d, $J = 12.0$ Hz), 132.4 (d, $J = 11.0$ Hz), 132.1, 131.5, 131.3, 131.2 (d, $J = 10.1$ Hz), 129.7, 128.7, 128.6, 127.7, 127.6, 127.3, 124.1 (d, $J = 95.6$ Hz), 122.9 (d, $J = 85.4$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 4.24; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{24}\text{O}_2\text{P}$ 459.1508, Found 459.1510; IR (KBr, thin film): 3057, 1641, 1568, 1433, 1344, 1301, 1253, 831, 750, 729, 697 cm^{-1} .

2-(tri(naphthalen-1-yl)phosphonio)benzoate (3am): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (42.6 mg, 40%); m.p.: 110-111°C; ^1H NMR (400 Hz, CDCl_3) δ 8.63 (dd, $J = 6.8, 5.2$ Hz, 1H), 8.48 (dd, $J = 19.6, 7.6$ Hz, 1H), 8.33 (dd, $J = 19.2, 7.2$ Hz, 1H), 8.08 (d, $J = 8.0$ Hz, 1H), 8.05-7.92 (m, 4H), 7.86-7.79 (m, 2H), 7.71 (d, $J = 8.0$ Hz, 2H), 7.63 (td, $J = 8.0, 2.8$ Hz, 1H), 7.53-7.40 (m, 5H), 7.36-7.30 (m, 2H), 7.24-7.16 (m, 2H), 7.12 (t, $J = 7.2$ Hz, 1H), 6.95-6.86 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 Hz, CDCl_3) δ 165.8, 139.8 (d, $J = 9.8$ Hz), 137.9 (d, $J = 10.2$ Hz), 137.7 (d, $J = 9.4$ Hz), 136.3 (d, $J = 16.2$ Hz), 134.9 (d, $J = 3.0$ Hz), 134.5 (d, $J = 2.5$ Hz), 134.3 (d, $J = 3.7$ Hz), 133.9 (d, $J = 14.5$ Hz), 133.8 (d, $J = 4.4$ Hz), 133.7 (d, $J = 4.7$ Hz), 133.3 (d, $J = 3.0$ Hz), 132.7 (d, $J = 11.2$ Hz), 132.2 (d, $J = 5.0$ Hz), 132.1 (d, $J = 4.1$ Hz), 130.4 (d, $J = 4.9$ Hz), 129.9 (d, $J = 2.1$ Hz), 129.7 (d, $J = 1.9$ Hz), 129.5, 127.3, 126.8, 126.4,

126.3, 126.1 (d, $J = 4.0$ Hz), 125.9, 125.6, 125.5 (d, $J = 6.3$ Hz), 125.4 (d, $J = 4.6$ Hz), 125.3 (d, $J = 5.3$ Hz), 125.1 (d, $J = 4.6$ Hz), 124.8 (d, $J = 11.9$ Hz), 121.6 (d, $J = 100.3$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 22.59; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{37}\text{H}_{26}\text{O}_2\text{P}$ 533.1665, found 533.1663; IR (KBr, thin film): 3059, 1726, 1506, 1460, 1275, 833, 802, 773, 692, 675 cm^{-1} .

2-(tri(thiophen-2-yl)phosphonio)benzoate (3an): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (56.8 mg, 71%); m.p.: 217-218 $^\circ\text{C}$; ^1H NMR (400 Hz, CDCl_3) δ 8.37 (dd, $J = 7.6, 2.8$ Hz, 1H), 7.80 (td, $J = 7.2, 2.4$ Hz, 1H), 7.66 (td, $J = 4.8, 0.8$ Hz, 3H), 7.54 (q, $J = 7.6$ Hz, 1H), 7.37 (d, $J = 4.2$ Hz, 3H), 7.17-7.08 (m, 3H), 6.96 (dd, $J = 14.4, 8.0$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 Hz, CDCl_3) δ 165.7 (d, $J = 2.4$ Hz), 139.9 (d, $J = 14.2$ Hz), 137.7 (d, $J = 12.1$ Hz), 135.6 (d, $J = 16.0$ Hz), 135.0 (d, $J = 3.6$ Hz), 133.3, 131.8 (d, $J = 16.6$ Hz), 131.5 (d, $J = 138.7$ Hz), 128.0 (d, $J = 14.0$ Hz), 127.3, 127.2; $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ -53.25; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{14}\text{O}_2\text{PS}_3$ 400.9888, Found 400.9889; IR (KBr, thin film): 3112, 1670, 1459, 1340, 1296, 1220, 1138, 1065, 842, 763, 735, 692 cm^{-1} .

2-(tri(furan-2-yl)phosphonio)benzoate (3ao): purified by preparative thin layer chromatography (DCM : MeOH = 20:1); white solid (14.1 mg, 20%); m.p.: 167-168 $^\circ\text{C}$; ^1H NMR (400 Hz, CDCl_3) δ 8.26 (dd, $J = 7.6, 3.2$ Hz, 1H), 7.76 (tdd, $J = 7.2, 2.4, 0.8$ Hz, 1H), 7.70-7.63 (m, 3H), 7.58-7.51

(m, 1H), 7.03 (br s, 3H), 6.66 (dd, $J = 14.4, 8.0$ Hz, 1H), 6.55-6.50 (m, 3H).; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 Hz, CDCl_3) δ 166.0 (d, $J = 4.0$ Hz), 147.2 (d, $J = 9.0$ Hz), 138.3 (d, $J = 15.2$ Hz), 134.7 (d, $J = 3.5$ Hz), 134.1 (d, $J = 15.2$ Hz), 132.9 (d, $J = 145.8$ Hz), 132.5 (d, $J = 16.9$ Hz), 127.0 (d, $J = 14.9$ Hz), 124.8 (d, $J = 17.5$ Hz), 111.3, 111.2; $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ -90.75; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{14}\text{O}_5\text{P}$ 353.0573, Found 353.0573; IR (KBr, thin film): 3115, 1698, 1454, 1337, 1296, 1215, 1134, 1064, 843, 760, 731, 687 cm^{-1} .

2-(methyldiphenylphosphonio)benzoate (3ap): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (43.5 mg, 68%); m.p.: 254-255 $^{\circ}\text{C}$; ^1H NMR (400 Hz, CDCl_3) δ 8.47 (dd, $J = 6.8, 4.0$ Hz, 1H), 7.76 (t, $J = 7.2$ Hz, 1H), 7.60-7.30 (m, 11H), 6.85 (dd, $J = 14.0, 7.6$ Hz, 1H), 2.83 (d, $J = 13.6$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 Hz, CDCl_3) δ 167.1 (d, $J = 1.0$ Hz), 139.7 (d, $J = 5.8$ Hz), 136.5 (d, $J = 13.2$ Hz), 135.1 (d, $J = 2.9$ Hz), 133.0 (d, $J = 2.6$ Hz), 132.2 (d, $J = 9.3$ Hz), 131.8 (d, $J = 9.6$ Hz), 131.7 (d, $J = 13.8$ Hz), 129.7 (d, $J = 12.5$ Hz), 125.4 (d, $J = 91.7$ Hz), 120.9 (d, $J = 96.6$ Hz), 13.7 (d, $J = 69.6$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 5.17; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{18}\text{O}_2\text{P}$ 321.1039, Found 321.1040; IR (KBr, thin film): 3052, 2958, 2875, 1648, 1624, 1485, 1437, 1355, 1302, 1269, 830, 753, 730, 695 cm^{-1} .

2-(dimethyl(phenyl)phosphonio)benzoate (3aq): purified by preparative thin layer chromatography (DCM : MeOH = 15 : 1); white solid (33.0 mg,

64%); m.p.:174-175°C; ^1H NMR (400 MHz, CDCl_3) δ 8.41 (ddd, $J = 7.6$, 4.4, 1.2 Hz, 1H), 7.81-7.75 (m, 1H), 7.62-7.42 (m, 7H), 2.32 (s, 3H), 2.29 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.8, 142.6 (d, $J = 8.9$ Hz), 134.7 (d, $J = 3.2$ Hz), 133.0 (d, $J = 14.5$ Hz), 131.4 (d, $J = 3.0$ Hz), 130.5 (d, $J = 105.0$ Hz), 130.5 (d, $J = 10.6$ Hz), 130.4 (d, $J = 14.5$ Hz), 129.1 (d, $J = 13.2$ Hz), 128.9 (d, $J = 10.0$ Hz), 123.6 (d, $J = 109.2$ Hz), 16.9, 16.2. $^{31}\text{P}\{\text{H}\}$ NMR (162 MHz, CDCl_3) δ 1.34; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{15}\text{O}_2\text{PNa}$ 281.0702, found 281.0700; IR (KBr, thin film): 3057, 2978, 2912, 1622, 1566, 1442, 1364, 1124, 887, 830, 760, 735, 718, 693 cm^{-1} .

2-(tricyclohexylphosphonio)benzoate (3ar): purified by preparative thin layer chromatography (DCM : MeOH = 20 : 1); white solid (12.0 mg, 15%); m.p.:275-276°C; ^1H NMR (400 MHz, CDCl_3) δ 8.39 (dd, $J = 8.0$, 4.4 Hz, 1H), 7.65 (t, $J = 7.6$ Hz, 1H), 7.59-7.46 (m, 2H), 3.29 (q, $J = 12.8$ Hz, 3H), 2.01 (br s, 6H), 1.92-1.59 (m, 16H), 1.50-1.30 (m, 8H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 169.3, 133.3, 133.2, 132.6 (d, $J = 9.1$ Hz), 132.3 (d, $J = 7.9$ Hz), 128.9 (d, $J = 10.7$ Hz), 116.2 (d, $J = 78.6$ Hz), 36.1 (d, $J = 43.1$ Hz), 28.5, 28.4, 27.1, 26.9, 25.7; ^{31}P NMR (162 MHz, CDCl_3) δ 31.61; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{38}\text{O}_2\text{P}$ 401.2609, Found 401.2607; IR (KBr, thin film): 3057, 2830, 2854, 1618, 1585, 1449, 1362, 1271, 895, 852, 825, 754, 731, 696 cm^{-1} .

2-(triphenylarsonio)benzoate (3as): purified by flash silica gel

chromatography (DCM : MeOH = 20:1); white solid (75.0 mg, 88%); m.p.: 187-188 °C; ^1H NMR (400 Hz, CDCl_3) δ 8.59 (d, $J = 7.6$ Hz, 1H), 7.79 (t, $J = 7.6$ Hz, 1H), 7.57-7.35 (m, 16H), 7.03 (d, $J = 7.6$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 Hz, CDCl_3) δ 166.4, 141.8, 133.9, 133.3, 132.2, 131.4, 131.1, 130.6, 129.3, 125.5; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{20}\text{AsO}_2$ 427.0674, Found 427.0672; IR (KBr, thin film): 3058, 1639, 1622, 1564, 1483, 1348, 1271, 827, 766, 745, 689 cm^{-1} .

4,5-dimethyl-2-(triphenylphosphonio)benzoate (3ba): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (68.9 mg; 84%); m.p.: 144-145 °C; ^1H NMR (400 Hz, CDCl_3) δ 8.30 (d, $J = 4.4$ Hz, 1H), 7.58-7.35 (m, 15H), 6.68 (d, $J = 13.6$ Hz, 1H), 2.42 (s, 3H), 2.18 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 Hz, CDCl_3) δ 166.6, 144.9 (d, $J = 3.2$ Hz), 141.3 (d, $J = 7.5$ Hz), 140.0 (d, $J = 14.9$ Hz), 137.6 (d, $J = 14.6$ Hz), 132.5 (d, $J = 9.1$ Hz), 131.8 (d, $J = 11.5$ Hz), 131.5 (d, $J = 2.6$ Hz), 128.7, 128.6, 118.4 (d, $J = 113.0$ Hz), 20.2, 19.9 (d, $J = 1.1$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 6.18; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{24}\text{O}_2\text{P}$ 411.1508, Found 411.1509; IR (KBr, thin film): 3054, 2928, 2862, 1666, 1480, 1438, 1333, 1270, 843, 778, 725, 695, 680 cm^{-1} .

4,5-dimethoxy-2-(triphenylphosphonio)benzoate (3ca): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (52.2 mg, 59%); m.p.: 276-277 °C; ^1H NMR (400 Hz, CDCl_3) δ 8.04 (d, $J = 4.0$ Hz, 1H), 7.56-7.33 (m, 15H), 6.26 (d, $J = 14.0$ Hz, 1H), 4.06 (s, 3H), 3.48

(s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 Hz, CDCl_3) δ 166.2 , 154.2 , 150.7 (d, $J = 18.7$ Hz), 139.1 (d, $J = 10.1$ Hz), 132.4 , 131.2 (d, $J = 2.9$ Hz), 128.6, 128.5, 117.8 (d, $J = 8.6$ Hz), 113.1 (d, $J = 123.2$ Hz), 112.0 (d, $J = 14.4$ Hz), 56.6, 55.6; $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 0.80; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{24}\text{O}_4\text{P}$ 443.1407, Found 443.1407; IR (KBr, thin film): 3061, 2935, 2839, 1644, 1584, 1503, 1439, 1393, 1335, 1283, 1245, 1215, 800, 777, 731, 703, 694 cm^{-1} .

4,5-difluoro-2-(triphenylphosphonio)benzoate (3da): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (74.4 mg, 89%); m.p.: 263-264 $^\circ\text{C}$; ^1H NMR (400 Hz, CDCl_3) δ 8.37-8.27 (m, 1H), 7.61-7.32 (m, 15H), 6.70-6.30 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 Hz, CDCl_3) δ 164.2 , 154.7 (ddd, $J = 260.6, 12.9, 3.3$ Hz), 152.0 (ddd, $J = 253.3, 22.3, 3.3$ Hz), 142.7 (dd, $J = 5.7, 2.7$ Hz), 142.6 (dd, $J = 5.7, 2.8$ Hz), 132.3 (d, $J = 7.7$ Hz), 131.8 (d, $J = 2.9$ Hz), 128.9 (d, $J = 13.2$ Hz), 125.3 (t, $J = 19.4$ Hz), 119.3 (dt, $J = 119.3, 3.3$ Hz), 119.2 (dd, $J = 17.3, 14.2$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 3.63; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{18}\text{F}_2\text{O}_2\text{P}$ 419.1007, Found 419.1008; IR (KBr, thin film): 3029, 1651, 1608, 1495, 1485, 1439, 1407, 1340, 1290, 1184, 1115, 1101, 783, 756, 733, 705, 692 cm^{-1} .

6-(triphenylphosphonio)-2,3-dihydro-1H-indene-5-carboxylate (3ea): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (76.0 mg, 90%); m.p.: 189-190 $^\circ\text{C}$; ^1H NMR (400 Hz, CDCl_3) δ 8.37

(d, $J = 3.6$ Hz, 1H), 7.55-7.31 (m, 15H), 6.75 (d, $J = 13.6$ Hz, 1H), 3.06 (t, $J = 7.6$ Hz, 2H), 2.83 (t, $J = 7.6$ Hz, 2H), 2.20-2.10 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 Hz, CDCl_3) δ 166.6, 152.8 (d, $J = 3.2$ Hz), 147.8 (d, $J = 15.7$ Hz), 142.8 (d, $J = 10.3$ Hz), 132.3 (d, $J = 6.3$ Hz), 131.9 (d, $J = 14.5$ Hz), 130.9 (d, $J = 2.8$ Hz), 128.5, 128.4, 125.9 (d, $J = 12.5$ Hz), 120.5 (d, $J = 115.9$ Hz), 32.83 (d, $J = 10.4$ Hz), 32.81 (d, $J = 10.3$ Hz), 25.5; $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 0.95; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{24}\text{O}_2\text{P}$ 423.1508, Found 423.1509; IR (KBr, thin film): 3057, 2957, 2937, 2843, 1645, 1628, 1557, 1439, 1404, 1337, 1275, 806, 752, 729, 710, 694 cm^{-1} .

6-(triphenylphosphonio)benzo[d][1,3]dioxole-5-carboxylate (3fa): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (75.8 mg, 89%); m.p.: 258-259 $^{\circ}\text{C}$; ^1H NMR (400 Hz, CDCl_3) δ 7.90 (s, 1H), 7.61-7.28 (m, 15H), 6.28 (d, $J = 12.8$ Hz, 1H), 6.14 (s, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 Hz, CDCl_3) δ 153.5 (d, $J = 3.0$ Hz), 150.8, 150.5, 132.4, 131.4 (d, $J = 2.7$ Hz), 128.7, 128.6, 115.0, 114.9, 110.4 (d, $J = 13.3$ Hz), 103.1; $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ -2.40; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{20}\text{O}_4\text{P}$ 427.1094, Found 427.1096; IR (KBr, thin film): 3058, 2925, 2830, 1641, 1582, 1500, 1439, 1397, 1338, 1278, 1239, 1214, 787, 741, 694 cm^{-1} .

3,6-dimethyl-2-(triphenylphosphonio)benzoate (3ga): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (41.8 mg, 51%); m.p.: 243-244 $^{\circ}\text{C}$; ^1H NMR (400 Hz, CDCl_3) δ 7.61-7.36 (m, 16H),

7.19 (t, $J = 7.2$ Hz, 1H), 2.75 (s, 3H), 1.69 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 Hz, CDCl_3) δ 167.9, 145.3 (d, $J = 13.0$ Hz), 141.6 (d, $J = 12.3$ Hz), 137.7 (d, $J = 12.3$ Hz), 137.2 (d, $J = 3.2$ Hz), 134.0 (d, $J = 14.9$ Hz), 132.2 (d, $J = 9.6$ Hz), 131.1 (d, $J = 2.8$ Hz), 128.8, 128.7, 121.8 (d, $J = 110.1$ Hz), 23.9 (d, $J = 3.8$ Hz), 21.1; $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ -13.8; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{24}\text{O}_2\text{P}$ 411.1508, Found 411.1508; IR (KBr, thin film): 3057, 2926, 2856, 1663, 1483, 1437, 1329, 1270, 841, 775, 725, 696, 679 cm^{-1} .

3-(triphenylphosphonio)-2-naphthoate (3ha): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (71.7 mg, 83%); m.p.: 247-248 $^\circ\text{C}$; ^1H NMR (400 Hz, CDCl_3) δ 9.03 (d, $J = 3.6$ Hz, 1H), 8.10 (d, $J = 8.0$ Hz, 1H), 7.76-7.34 (m, 19H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 Hz, CDCl_3) δ 166.8, 140.4 (d, $J = 14.7$ Hz), 137.4 (d, $J = 9.5$ Hz), 136.0 (d, $J = 2.6$ Hz), 133.3 (d, $J = 16.4$ Hz), 132.6, 131.5 (d, $J = 2.6$ Hz), 130.5 (d, $J = 10.5$ Hz), 129.9, 129.2, 129.1, 128.8, 128.6, 128.1, 119.5 (d, $J = 114.0$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 5.72; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{22}\text{O}_2\text{P}$ 433.1352, Found 433.1353; IR (KBr, thin film): 3059, 1719, 1586, 1473, 1407, 1325, 1272, 801, 770, 698 cm^{-1} .

2-methoxy-6-(triphenylphosphonio)benzoate (3ia): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (43.7 mg, 53%); m.p.: 208-209 $^\circ\text{C}$; ^1H NMR (400 Hz, CDCl_3) δ 7.43-7.32 (m, 17H), 6.51 (dd, $J = 13.6, 8.0$ Hz, 1H), 4.04 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 Hz, CDCl_3)

δ 164.5 , 160.8 (d, J = 17.0 Hz), 134.1 (d, J = 106.4 Hz), 132.3 (d, J = 18.6 Hz), 132.0 (d, J = 9.3 Hz), 131.5, 130.3 (d, J = 2.9 Hz), 129.7 (d, J = 12.7 Hz), 128.7 (d, J = 14.9 Hz), 128.2 (d, J = 13.0 Hz), 118.0 (d, J = 3.3 Hz), 56.4; $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ -18.43; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{22}\text{O}_3\text{P}$ 413.1301, Found 413.1305; IR (KBr, thin film): 3057, 2928, 2856, 1672, 1483, 1468, 1339, 1263, 831, 756, 725, 694 cm^{-1} .

3-methoxy-2-(triphenylphosphonio)benzoate (3ia'): purified by preparative thin layer chromatography (DCM : MeOH = 20:1); white solid (9.0 mg, 11%); m.p.: 163-164 °C; ^1H NMR (400 Hz, CDCl_3) δ 7.94-7.87 (m, 3H), 7.81-7.75 (m, 6H), 7.67-7.60 (m, 6H), 7.41 (d, J = 8.4 Hz, 1H), 7.16 (dd, J = 12.8, 7.6 Hz, 1H), 7.00 (dt, J = 14.4, 2.0 Hz, 1H), 3.84 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 Hz, CDCl_3) δ 160.8, 160.6, 135.8 (d, J = 3.0 Hz), 134.4 (d, J = 10.2 Hz), 132.3 (d, J = 15.2 Hz), 130.8 (d, J = 12.9 Hz), 126.3 (d, J = 9.9 Hz), 120.6 (d, J = 2.9 Hz), 120.3 (d, J = 11.8 Hz), 118.6 (d, J = 88.7 Hz), 117.4 (d, J = 89.0 Hz), 55.9; $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 23.35; IR (KBr, thin film): 3063, 2924, 2853, 1655, 1585, 1485, 1439, 1272, 1224, 795, 754, 727, 706, 691 cm^{-1} .

2-fluoro-6-(triphenylphosphonio)benzoate (3ja): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (the pure single regio-isomer was isolated in 55% yield, 44.0 mg); m.p.: 100-101 °C; ^1H NMR (400 Hz, CDCl_3) δ 7.59-7.32 (m, 17H), 6.83-6.75 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$

NMR (100 Hz, CD₃OD) δ 165.3 , 162.4 (dd, J = 256.7, 15.9 Hz), 133.2 (d, J = 9.8 Hz), 133.0 (d, J = 3.6 Hz), 132.9 (d, J = 3.0 Hz), 132.2 (dd, J = 17.1, 9.0 Hz), 129.1 (d, J = 13.3 Hz), 125.2 , 124.2 , 123.9 (dd, J = 23.9, 2.8 Hz), 122.2 (dd, J = 102.0, 1.5 Hz); ³¹P{¹H} NMR (162 MHz, CDCl₃) δ -0.51; HRMS (ESI) m/z : [M+H]⁺ Calcd for C₂₅H₁₉FO₂P 401.1101, Found 401.1101; IR (KBr, thin film): 3059, 1652, 1456, 1438, 1334, 1245, 1194, 1150, 1097, 829, 752, 725, 694 cm⁻¹.

2-methyl-6-(triphenylphosphonio)benzoate (3ka): purified by flash silica gel chromatography (DCM : MeOH = 20:1); white solid (35.7 mg, 45%); m.p.: 263-264 °C; ¹H NMR (400 Hz, CDCl₃) δ 7.59 (d, J = 7.6 Hz, 1H), 7.52-7.28 (m, 16H), 6.80 (dd, J = 14.0, 8.0 Hz, 1H), 2.98 (s, 3H); ¹³C{¹H} NMR (100 Hz, CDCl₃) δ 166.8 , 141.2 (d, J = 12.2 Hz), 140.1 (d, J = 10.8 Hz), 138.1 (d, J = 3.3 Hz), 135.1 (d, J = 15.5 Hz), 133.9 (d, J = 106.1 Hz), 132.0 (d, J = 9.3 Hz), 130.4 (d, J = 17.2 Hz), 130.3 (d, J = 2.9 Hz), 128.2 (d, J = 13.0 Hz), 127.9 (d, J = 122.2 Hz), 21.7 (d, J = 1.1 Hz); ³¹P{¹H} NMR (162 MHz, CDCl₃) δ -15.77; HRMS (ESI) m/z : [M+H]⁺ Calcd for C₂₆H₂₂O₂P 397.1352, Found 397.1354; IR (KBr, thin film): 3057, 2922, 2862, 1657, 1629, 1483, 1436, 1337, 1290, 831, 748, 731, 694 cm⁻¹.

3-methyl-2-(triphenylphosphonio)benzoate (3ka'): purified by preparative thin layer chromatography (DCM : MeOH = 20:1); white solid (26.9 mg, 34%); m.p.: 261-262 °C; ¹H NMR (400 Hz, CDCl₃) δ 8.37 (d, J = 6.8 Hz, 1H), 7.70 (td, J = 7.2, 2.0 Hz, 1H), 7.53-7.34 (m, 16H), 1.74 (s,

3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 167.1, 145.4 (d, $J = 10.7$ Hz), 144.9 (d, $J = 12.5$ Hz), 136.2 (d, $J = 13.9$ Hz), 134.1 (d, $J = 3.2$ Hz), 133.5 (d, $J = 102.4$ Hz), 131.3 (d, $J = 9.4$ Hz), 130.7 (d, $J = 2.9$ Hz), 128.8 (d, $J = 13.1$ Hz), 127.9 (d, $J = 11.0$ Hz), 122.2 (d, $J = 112.0$ Hz), 23.9 (d, $J = 3.0$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ -6.38; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{22}\text{O}_2\text{P}$ 397.1352, Found 397.1354; IR (KBr, thin film): 3057, 2930, 2856, 1651, 1585, 1483, 1439, 1344, 1283, 795, 771, 725, 698 cm^{-1} .

9H-xanthen-9-one (4a): known compound;²³ purified by preparative flash chromatography (PE : EA = 15 : 1); white solid (10.6 mg, 18%); ^1H NMR (400 MHz, CDCl_3) δ 8.36 (dd, $J = 7.6, 1.6$ Hz, 2H), 7.74 (ddd, $J = 8.4, 7.2, 1.6$ Hz, 2H), 7.51 (dd, $J = 8.4, 0.8$ Hz, 2H), 7.39 (ddd, $J = 8.0, 7.2, 1.2$ Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 177.3, 156.2, 134.8, 126.8, 123.9, 121.9, 118.0.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: ^1H , ^{13}C and ^{31}P NMR Spectra for all products and the single-crystal X-ray structure analysis of products **3aa**.

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Notes

The authors declare no competing financial interest.

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