Copper-Catalyzed Diphenylation of P(O)-OH Bonds with Cyclic Diaryliodonium Salts

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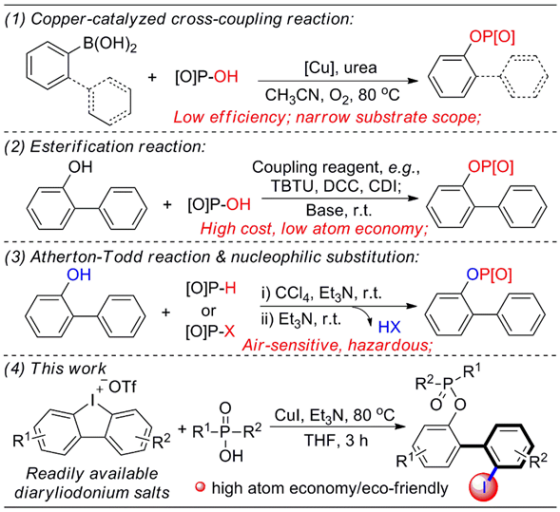
Abstract: A copper-catalyzed diphenylation of P(O)-OH bonds with cyclic diaryliodonium salts is described. The valuable 2'-iodo substituted biaryl phosphinic/phosphoric acid esters are obtained in good to excellent yields, which could be further transformed to diversified building blocks for the synthesis of bioactive compounds, pharmaceuticals and functional materials.

Introduction

Organophosphorus compounds have been recognized as the important intermediates in biological chemistry, asymmetric catalysis, and functional materials for a half century, due to their unique structural features and potential pharmacological activities.[1,2] Since then, a number of natural products with phosphoryl moieties have been isolated and synthesized. Engel, Imamoto, Quin and Toy *et al.* have summarized the synthesis, application and importance of this valuable compounds comprehensively.[3] The direct cross-coupling reaction of P(O)-H/P(O)-X compounds with nucleophiles and the reactions of P(O)-OH compounds with aryl boronic acids or 2-aryl substituted phenols are the straightforward protocols for forming *O*-biaryl organophosphorus compounds. Unfortunately, from the available protocols, P(O)-H and P(O)-X compounds are air/moisture-sensitive and toxic, and the coupling reagents (e.g., TBTU, DCC, CDI) and R-X are more expensive and not environment-benign.[4] In 2013, Prabhu *et al.* reported a green, direct cross-coupling of phosphites with alcohols in the presence of I_2/H_2O_2 at room temperature.[5a] In 2016, Chen and Han further reported an efficient procedure based on iron-catalyzed dehydrogenative coupling of P(O)−H compounds with alcohols.[5b] Although there are a large number of studies on the phosphorylation of nucleophiles, the use of phenols as starting materials is rare.

Diaryliodonium salts, due to their reactivity and practical applications, have been utilized as reactants since they were exploited in the last century. Moreover, it features a rich hypervalent chemistry.[6] Additionally, as a reactant, the combination of diaryliodonium salts with nucleophilic reagent has been employed as both intra- and intermolecular reaction.[6-9]

Compared to linear aryliodonium compounds, although cyclic diphenyleneiodonium salt was discovered for a half century, they are more inert and have not attracted much attention to their application as building blocks.[6a-b] In 2013, Huang *et al.* have presented an efficient method for the formation of functionalized carbazoles via the copper-catalyzed amine insertion into cyclic diphenyleneiodonium compounds.[6c] Later, Zhang and co-workers have further disclosed a divergent transition metal-catalyzed coupling of benzoic acid and their derivatives with cyclic diaryliodonium salts for the selective synthesis of 2'-iodo-[1,1'-biphenyl]-2-yl benzoate, 2'-alkynyl-[1,1'-biphenyl]-2-yl 2-aminobenzoate, and triphenylene derivatives.[6d,7h,10a,10c] Although the arylation of P(O)-OH bonds with linear aryliodonium compounds via the assistance of a base was reported, a stoichiometric amount of iodobenzene is released after the reaction, and the recovery of iodobenzene increases the burden in purification.[8a] Herein, we demonstrate an efficient direct cross-coupling reaction of P(O)-OH bonds with cyclic diphenyliodonium species to construct functionalized 2'-iodo-[1,1'-biaryl]-2-yl phosphonates and phosphates, catalyzed by cheap copper species under mild conditions.



Scheme 1. Synthesis of *O*-biaryl organophosphorus compounds.

Results and Discussion

To test our initial hypothesis, the reaction of cyclic diaryliodonium salt (**1a**) and diphenylphosphinic acid (**2a**) was investigated to delineate reaction parameters. The reaction of **1a** with **2a** was carried out at 80 °C in toluene under N_2 atmosphere with the addition of $Cu(OTf)_2$, and K_3PO_4 and the corresponding coupling product of 2'-iodo-[1,1'-biphenyl]-2-yl diphenylphosphinate (**3a**) was generated in 81% yield. Besides $Cu(OTf)_2$, other copper sources, such as $CuCl_2$, Cu powder, $Cu(OAc)_2$, CuI, and CuCl were further tested (**Table 1**, entries 2-6), and most of them give the product in satisfactory yields. We then chose CuI (89% yield) as the catalyst for further optimization. When we slightly changed the solvent from toluene to THF, **3a** was obtained in 92% yield. To our surprise, Et_3N is much more effective than K_3PO_4 in a shortened time (**Table 1**, entry 9). This phenomenon may be caused by the fact that the

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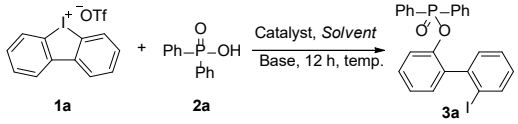
reaction of inorganic bases with P(O)-OH compounds could form the corresponding inorganic salts in the reaction, which inhibited the cross-coupling process. When the reaction was performed at 60 °C, **3a** was only generated in 86% yield. We further optimized the amount of base and catalyst, and the optimal condition was obtained at a "diphenyl phosphinic acid/Et_3N/CuI molar ratio" of 1:1.5:0.1 (**Table S5**).

Table 1. Optimization of the reaction conditions.[a]

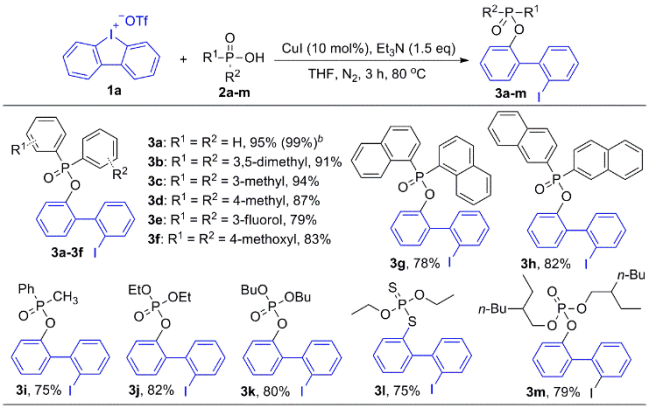


Entry	Cat.	*T* (°C)	Base	Solvent	Yield [b]
1	$Cu(OTf)_2$	80	K_3PO_4	Toluene	81%
2	$CuCl_2$	80	K_3PO_4	Toluene	84%
3	Cu	80	K_3PO_4	Toluene	80%
4	$Cu(OAc)_2$	80	K_3PO_4	Toluene	82%
5	CuI	80	K_3PO_4	Toluene	89%
6	CuCl	80	K_3PO_4	Toluene	86%
7	CuI	80	K_3PO_4	THF	92%
8	**CuI**	**80**	**Et_3N**	**THF**	**99% [c] (95) [d]**
9	-	80	Et_3N	THF	N.D. [e]
10	CuI	60	Et_3N	THF	86%

[a] Reaction conditions: cyclic diaryliodonium salt (**1a,** 0.24 mmol), diphenylphosphinic acid (**2a,** 0.2 mmol), catalyst (10 mol%), and base (1.5 equiv), THF (1.0 mL), under N_2 atmosphere, 80 °C , 12 h. [b] ^{31}P NMR yield. [c] 3 h. [d] Isolated yield. [e] N.D. = Not detected.

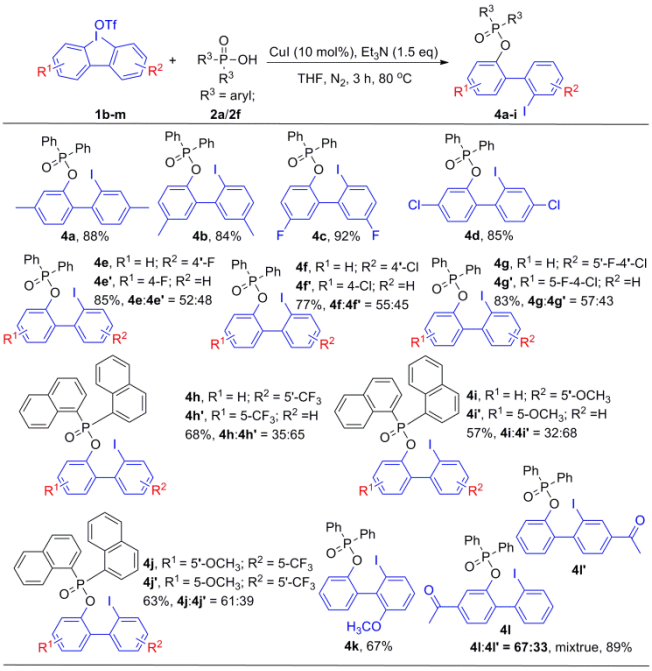
As shown in **Table 2**, the present copper-catalyzed cross-coupling reaction can be applied to a variety of P(O)-OH compounds. It is clear that *bis*(3,5-dimethylphenyl)phosphinic acid, *di-m*-tolylphosphinic acid, *di-p*-tolylphosphinic acid, *bis*(3-fluorophenyl)phosphinic acid, and *bis*(4-methoxyphenyl)phosphinic acid can react efficiently with [1,1'-biphenyl]-2,2'-diyliodonium triflates (**1a**) under the optimized reaction conditions, affording the corresponding coupling products of **3b**−**3f** in 79-95% isolated yields. In addition, special diarylphosphinic acid such as *di*-(naphthalen-1-yl)phosphinic acid (**2g**) and *di*-(naphthalen-2-yl)phosphinic acid (**2h**) could also afford the desired products of **3g** and **3h** in 78 and 82% yields, respectively. To our delight, 2'-iodo-[1,1'-biphenyl]-2-yl methyl(phenyl)phosphinate (**3i**) was synthesized in 75% yield when phenylmethylphosphinic acid (**2i**) was used as the phosphorylation reagent. For most cases, electron-donating or electron-withdrawing groups which are located on the aryl ring of P(O)-OH compounds do not change the yields of the cross-coupling products significantly. In addition, dialkyl hydrogen phosphate such as diethyl hydrogen phosphate, dibutyl hydrogen phosphate and *O,O*-diethyl *S*-hydrogen phosphorodithioate also show positive results toward the reaction, and the expected products were generated in 75-82% yields. Furthermore, *bis*-(2-ethylhexyl) (2'-iodo-[1,1'-biphenyl]-2-yl) phosphate (**3m**) was synthesized in 79% yield through the reaction of *bis*-(2-ethylhexyl) hydrogen phosphate with [1,1'-biphenyl]-2,2'-iodonium triflate (**1a**).

Table 2. Scope of P(O)-OH compounds. [a]



[a] Reaction conditions: P(O)-OH compound (**2,** 0.2 mmol), [1,1'-biphenyl]-2,2'-iodonium triflate (**1a,** 0.24 mmol), , CuI (10 mol%), and Et_3N (1.5 equiv), THF (1.0 mL) under N_2 atmosphere, 80 °C , 3 h, isolated yield. [b] ^{31}P NMR yield.

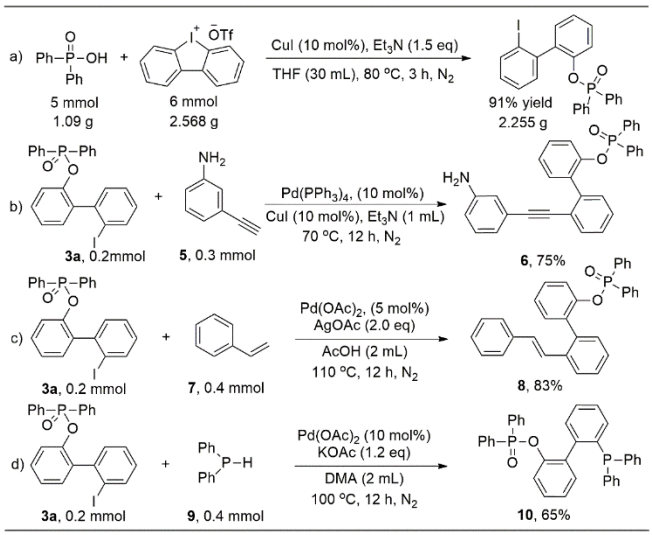
Table 3. Scope of cyclic diaryliodonium salts [a]



[a] Reaction conditions: cyclic diaryliodonium salt (**1,** 1.2 equiv), P(O)-OH compound (1.0 equiv), CuI (10 mol%), and Et_3N (1.5 equiv), THF (1.0 mL), under N_2 atmosphere, 80 °C , 3 h.

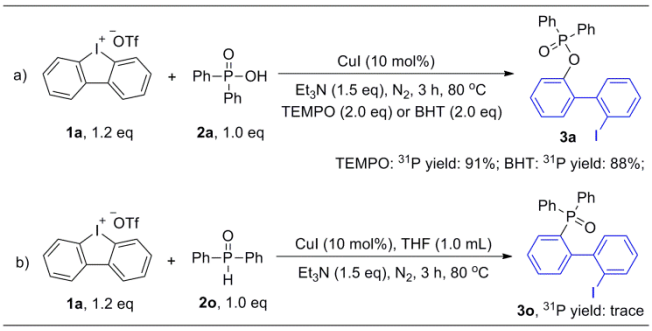
As depicted in **Table 3**, a range of substituted cyclic diaryliodonium salts (**1b**-**1j**) were prepared according to the Olofsson's method and subjected to the optimized reaction protocol with diarylphosphinic acids.[9] It is clear that symmetric cyclic diaryliodonium triflates such as 4,4'-dimethyl-[1,1'-biphenyl]-2,2'-iodonium triflate (**1b**), 5,5'-dimethyl-[1,1'-biphenyl]-2,2'- iodonium triflate (**1c**), 5,5'-difluoro-[1,1'-biphenyl]-2,2'-iodonium triflate (**1d**) and 4,4'-dichloro-[1,1'-biphenyl]-2,2'-iodonium triflate (**1e**), exhibit high reactivity toward diphenyl phosphinic acid, giving the corresponding products in 84% to 92% yields. For the symmertric cyclic diaryliodonium salts, electron-donating groups and electron-withdrawing groups on the aryls do not have a significant effect on the yield of products (**4a-d**). When 4-*H*-4'-fluoro-[1,1'-biphenyl]-2,2'-iodonium triflate (**1f**) is applied, the reaction of it with diphenyl phosphinic acid affords the corresponding products of **4e** with **4e**' (at a ratio of

52/48) in 85% yield. As for 4'-chloro-2'-iodo-[1,1'-biphenyl]-2-yl diphenylphosphinate (**4f**), 4-chloro-2'-iodo-[1,1'-biphenyl]-2-yl diphenylphosphinate (**4f'**), 4'-chloro-5'-fluoro-2'-iodo-[1,1'-biphenyl]-2-yl diphenyl phosphinate (**4g**) and 4-chloro-5-fluoro-2'-iodo-[1,1'-biphenyl]-2-yl diphenylphosphinate (**4g**'), they were obtained in 77% (**4f** with **4f'** at a ratio of 55/45) and 83% yields (**4g** with **4g**' at a ratio of 57/43), respectively, through the reaction of 4-*H*-4'-chloro-[1,1'-biphenyl]-2,2'-iodonium triflate (**1g**) and 4-*H*-4'-chloro-5'-fluoro-[1,1'-biphenyl]-2,2'-iodonium triflate (**1h**) with **2a**. Moreover, the reactions of 5-*H*-5'-trifluoromethyl-[1,1'-biphenyl]-2,2'-iodonium triflate (**1i**), 5-*H*-5'-methoxy-[1,1'-biphenyl]-2,2'-iodonium triflate (**1j**) and 5-methoxy-5'-trifluoromethyl- [1,1'-biphenyl]-2,2'-iodonium triflate (**1k**) with di(naphthalen-1-yl)phosphinic acid (**2f**) could also proceed efficiently, giving the coupling products (**4h** with **4h**' at a ratio of 35/65, **4i** with **4i**' at a ratio of 32/68, **4j** with **4j**' at a ratio of 61/39) in 57-68% yields. The phenomenon may be ascribed to the fact that electron-poor aryl groups are transferred more readily than electron-rich aryl groups in the arylation reaction of unsymmetric diaryliodonium salts with P(O)−OH compounds.[10] To our surprise, when 6-*H*-6'-methoxy-[1,1'-biphenyl]-2,2'-iodonium triflate (**1l**) was used for the reaction, there is only 2'-iodo-6'-methoxy-[1,1'-biphenyl]-2-yl diphenylphosphinate (**4k**) generated in 67% yield after the reaction. However, a mixture was obtained when 4-*H*-4'-acetyl-[1,1'-biphenyl]-2,2'-iodonium triflate (**1m**) was adopted as the coupling partner for the reaction. Except for **4l** and **4l'** (**4l**:**4l'**=67:33), all the products generated from the reaction could be easily separated via the short silica-gel column.



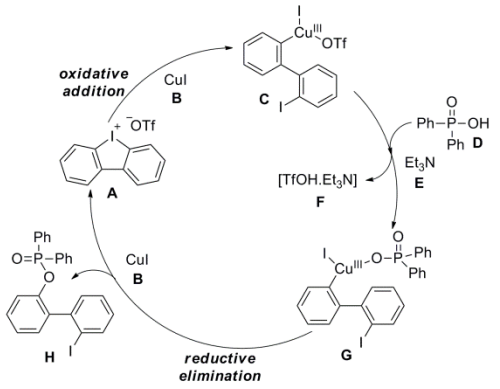
Scheme 2. Large-scale production and selective functionalization of **3a**

We further performed a large-scale reaction of [1,1'- biphenyl]-2,2'-iodonium triflate (**1a**, 6 mmol) with diphenyl phosphinic acid (**2a**, 5 mmol) and afforded **3a** in 91% yield (2.255 g) (**Scheme 2**). In the presence of $Pd(PPh_3)_4$, CuI and Et_3N, **3a** could react efficiently with 3-ethynyl aniline to afford 2'-((3-aminophenyl)ethynyl)-[1,1'-biphenyl]-2-yl diphenyl phosphinate (**6**) in 75% yield.[11a] In addition, we further performed the reaction of **3a** with styrene via the catalysis of palladium in the presence of a stoichiometric amount of silver, and the expected product (**8**) was obtained in 83% yield.[11b] Interestingly, 2'-(diphenylphosphino)-[1,1'-biphenyl]-2-yl diphenylphosphinate (**10**) could also be synthesized in 65% yield via the nucleophilic substitution reaction of **3a** with diphenylphosphine.[11c]



Scheme 3. Control experiments

Control experiments were performed for the reaction in order to gain the insight of the reaction mechanism. As depicted in Scheme 3, the reactions of [1,1'-biphenyl]-2,2'-iodonium triflate (**1a**) with diphenyl phosphinic acid (**2a**) in the presence of the radical scavenger 2,2,6,6-tetramethylpiperidine *N*-oxyl (TEMPO) or 2,6-*di-tert*-butyl-4-methylphenol (BHT) were performed under the optimized reaction conditions. As confirmed by GC, GC-MS, and ^{31}P NMR analysis, the coupling product of **3a** was generated in 91% (TEMPO: 2.0 equivalent) and 88% (BHT: 2.0 equivalent) yields, respectively. It is hence deduced that the reaction possibly occurs not through the radical path. In addition, we further operated the reaction of [1,1'-biphenyl]-2,2'-iodonium triflate(**1a**) with diphenyl phosphine oxide (**2o**), and the coupling product of **3o** was not observed after the reaction. This phenomenon might be ascribed to the stronger acidity of P(O)-OH bond than P-H bond of the starting materials.



Scheme 4. Plausible mechanism for the selective diphenylation of P(O)-OH compounds with cyclic diaryliodonium salts.

A plausible mechanism for the reaction is proposed as illustrated in Scheme 4.[6c] The cyclic diaryliodonium salt (**A**) first undergoes the oxidative addition with CuI (**B**) to generate intermediate **C**. In the presence of a base, P(O)-OH compound (**B**) could easily proceed the ion exchange reaction to form the corresponding intermediate (**G**) with the release of one molecule of triethylammonium triflate (**F**). Finally, the catalytic cycle is completed via the reductive elimilation of **G** accompanied by the regeneration of CuI (**B**) as a catalytically active species.

Conclusions

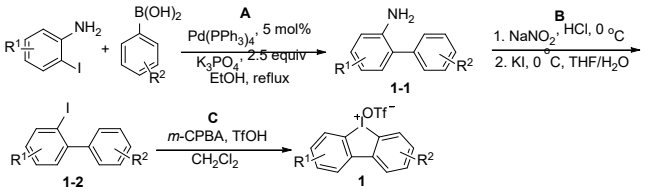
In summary, we have developed an efficient copper-catalyzed selective diphenylation of P(O)-OH bonds with cyclic diaryliodonium salts. The salient features of the reaction include its broad substrate scope, high step economy, and good chemoselectivity. To the best of our knowledge, it is the first time to realize the diphenylation of P(O)-OH bonds under mild conditions, and the present synthetic method also exhibits high potential for the construction of biologically active molecules, chiral catalytic ligands, and organophosphorus compounds.

Experimental Section

General Considerations:

All solvents used in the reactions were freshly distilled. The other reagents were recrystallized or distilled as necessary. All reactions were performed under an atmosphere of dry nitrogen unless specified otherwise. ^{1}H (400 MHz), ^{13}C (100 MHz), ^{31}P (160 MHz) and ^{19}F (376 MHz) spectra were recorded on a 400 MHz spectrometer in $CDCl_3$ or DMSO-*d6*. ^{1}H NMR chemical shifts were reported using TMS as internal standard while ^{13}C NMR chemical shifts were reported relative to $CDCl_3$ or DMSO-*d6*. The electron ionization method was used for HRMS measurements, and the mass analyzer type was double-focusing.

General procedure for the preparation of cyclic diaryliodoniums [6g]



A: [1,1'-Biphenyl]-2-amine (1a-1): To a stirred solution of 2-iodoaniline (1.0 g, 4.57 mmol) in EtOH (10 mL) was added phenylboronic acid (0.68 g, 5.48 mmol), K_3PO_4 (2.91g, 13.7 mmol) and $Pd(PPh_3)_4$ (52.76 mg, 45.66 μmol). The reaction proceeded at a reflux for 12h under argon atmosphere before EtOH was removed by rotary evaporation. The residue was extracted with EtOAc, and the combined organic layers were washed with H_2O and brine, dried over anhydrous Na_2SO_4, concentrated by rotary evaporation. The crude product was purified by column chromatography on a silica gel (PE/EtOAc = 20/1) to afford **1a-1** (750 mg, 97% yield) as a yellow liquid.

B: 2-Iodo-1,1'-biphenyl (1a-2): To a stirred solution of **1a-1** (750 mg, 4.43 mmol) in THF (10 mL) was added 4 M aqueous HCl (11.1 mL), and the solution was cooled with an ice bath. $NaNO_2$ (458.2 mg, 6.65 mmol) dissolved in H_2O (5 mL) was added dropwise. KI (2.21 g, 13.3 mmol) dissolved in H_2O (5 mL) was added after 20 min. The reaction mixture was stirred for 10 min with the ice bath, then slowly warmed up to r.t. and stirred for 1 h. The mixture was extracted with EtOAc, and the combined organic layers were washed with H_2O and brine. Then the organic layer was washed with 1M aqueous $Na_2S_2O_3$ until the color of the organic layer didn't change, dried over anhydrous Na_2SO_4, concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel (PE) to afford **1a-2** (1.1 g, 85% yield) as a colorless liquid.

C: Dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (1a): To a stirred solution of **1a-2** (1.1 g, 3.93 mmol) in anhydrous CH_2Cl_2 (10 mL) was added *m*-CPBA (1.02 g, 5.89 mmol), TfOH (1.04 mL, 11.78 mmol). The solution was stirred for 1h at r.t. CH_2Cl_2 was removed by rotary evaporation before Et_2O (15 mL) was added, and the mixture was stirred for 20 min, and filtered. The collected solid was washed with Et_2O three times, dried in vacuo to afford **1a** (1.68 g, 98% yield) as a white powder. Compounds of **1b**-**1m** were synthesized by the general procedure **A**, **B**, **C**. **1a** (yield: 81%),[6g] **1b** (yield: 75%),[12a] **1c** (yield: 69%),[10b] **1d** (yield: 43%),[12b] **1e** (yield: 65%),[12a] **1f** (yield: 46%),[12b] **1g** ((yield: 60%),[12b] **1i** ((yield: 71%),[12c] **1j** ((yield: 68%),[12b] **1l** ((yield: 36%),[12b] **1m** ((yield: 77%),[6i] **1h** (yield: 29%) and **1k** (yield: 55%) are new compounds.

General procedure for the synthesis of P(O)-OH compounds with cyclic diaryliodoniums: A mixture of P(O)-OH compounds (0.2 mmol), cyclic diaryliodoniums (1.2 equiv), CuI (10 mol%), and Et_3N (1.5 equiv) was dissolved in THF under N_2 atmosphere, stirred at 80 °C for 3 h. Upon completion of the reaction, the mixture was concentrated under vacuum. Removal of the solvent under a reduced pressure gave the crude product; pure product was obtained by passing the crude product through a short silica gel column using Hexane/EtOAc (2:1-10:1) as eluent.

Analytical data for compounds

*4-H-4'-chloro-5'-fluoro-[1,1'-biphenyl]-2,2'-iodonium triflate (**1h**)*: According to the general procedure, gave product **1h** (636 mg, 29%) as a ashen powder. ^{1}H NMR (400 MHz, DMSO-*d6*, 25 °C, TMS): δ = 8.62-8.65 (m, 1H), 8.38 (d, *J* = 3.6 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.99-8.01 (m, 1H), 7.78 (t, *J* = 10.8 Hz, 1H), 7.68 (t, *J* = 11.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-*d6*, 25 °C, TMS): δ = 158.5 (s), 155.9 (s), 140.0 (s), 139.9 (d, *J* = 3.4 Hz), 131.7 (s), 131.2 (s), 130.8 (s), 128.5 (s), 127.8 (s), 121.7 (dd, *J* = 527.8 Hz, *J* = 535.9 Hz), 122.6 (s), 121.1 (d, *J* = 320.1 Hz), 120.1 (d, *J* = 7.3 Hz). ^{19}F NMR (376MHz, DMSO-*d6*, 25 °C): δ = -77.8 (s), -110.5 (s). HRMS (ESI) *m*/*z*: calcd. for $C_{13}H_7ClF_4IO_3S$ $[M+H]^+$: 480.8785, found: 480.8780.

*5-Methoxy-5'-trifluoromethyl-[1,1'-biphenyl]-2,2'-iodonium triflate (**1k**)*: According to the general procedure, gave product **1k** (1322 mg, 55%) as a off-white powder. ^{1}H NMR (400 MHz, DMSO-*d6*, 25 °C, TMS): δ = 8.72 (d, *J* = 2.0 Hz, 1H), 8.57 (d, *J* = 8.8 Hz, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 7.93-7.95 (m, 1H), 7.72 (d, *J* = 2.4 Hz, 1H) , 3.92 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d6*, 25 °C, TMS): δ = 161.7 (s), 143.2 (s), 133.5 (s), 132.1 (s), 131.7 (s), 128.9 (s), 126.0 (d, *J* = 2.8 Hz), 125.6 (s), 124.0 (s), 123.3 (d, *J* = 2.8 Hz), 122.7 (d, *J* = 14.0 Hz), 119.5 (s), 118.3 (s), 115.1 (s), 56.6 (s). ^{19}F NMR (376MHz, DMSO-*d6*, 25 °C): δ = -60.9 (s), -77.8 (s). HRMS (ESI) *m*/*z*: calcd. for $C_{15}H_{10}F_6IO_4S$ $[M+H]^+$: 526.9249, found: 526.9244.

*2'-Iodo-[1,1'-biphenyl]-2-yl diphenylphosphinate (**3a**)*: According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **3a** (94.2 mg, 0.196 mmol, 95%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.98-8.00 (m, 1H), 7.63-7.69 (m, 2H), 7.52-7.55 (m, 1H), 7.46-7.51 (m, 1H), 7.33-7.44 (m, 6H), 7.24-7.31 (m, 3H), 7.13-7.20 (m, 3H), 7.07-7.11 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 147.8 (d, ^{1}J (C,P) = 8.1 Hz), 142.9 (s), 138.9 (s), 135.8 (d, ^{1}J (C,P) = 6.2 Hz), 132.4 (d, ^{1}J (C,P) = 3.0 Hz), 132.1 (d, ^{1}J (C,P) = 2.8 Hz), 132.0 (d, ^{1}J (C,P) = 10.6 Hz), 131.4 (d, ^{1}J (C,P) = 10.7 Hz), 131.1 (d, ^{1}J (C,P) = 1.7 Hz), 130.3 (d, ^{1}J (C,P) = 39.6 Hz), 129.5 (s), 129.1 (s), 128.6 (s), 128.5 (s), 128.3 (s), 128.2 (s), 127.8 (s), 124.2 (s), 120.5 (d, ^{1}J (C,P) = 3.8 Hz), 100.2 (s). ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ = 30.0. HRMS (ESI) *m*/*z*: calcd. for $C_{24}H_{19}IO_2P$ $[M+H]^+$: 497.0167, found: 497.0165.

*2'-Iodo-[1,1'-biphenyl]-2-yl bis(3,5-dimethylphenyl)phosphinate (**3b**)*: According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **3b** (100.5 mg, 0.182 mmol, 91%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25.94 °C, TMS): δ = 8.00-8.03 (m, 1H), 7.52-7.56 (m, 1H), 7.38-7.42 (m, 1H), 7.26-7.31 (m, 3H), 7.09-7.23 (m, 5H), 7.01-7.05 (m, 3H), 2.27 (s, 6H), 2.21 (s, 6H); ^{13}C NMR (100 MHz,

$CDCl_3$, 25 ºC, TMS): δ = 148.0 (d, ^1J (C,P) = 7.9 Hz), 143.2 (s), 138.8 (s), 138.2 (d, ^1J (C,P) = 14.2 Hz), 137.9 (d, ^1J (C,P) = 14.2 Hz), 135.6 (d, ^1J (C,P) = 6.5 Hz), 134.2 (d, ^1J (C,P) = 3.1 Hz), 133.9 (d, ^1J (C,P) = 3.1 Hz), 131.0 (d, ^1J (C,P) = 17.3 Hz), 130.9 (d, ^1J (C,P) = 136.7 Hz), 130.6 (d, ^1J (C,P) = 136.0 Hz), 129.5 (d, ^1J (C,P) = 3.5 Hz), 129.4 (s), 129.2 (s), 129.1 (d, ^1J (C,P) = 80.9 Hz), 128.9 (d, ^1J (C,P) = 10.6 Hz), 127.8 (s), 123.9 (s), 120.3 (d, ^1J (C,P) = 3.9 Hz), 100.3 (s), 21.3 (d, ^1J (C,P) = 10.6 Hz). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 31.0. HRMS (ESI) *m*/*z*: calcd. for $C_{28}H_{27}IO_2P$ $[M+H]^+$: 553.0793, found: 553.0791.

*2'-Iodo-[1,1'-biphenyl]-2-yl di-m-tolylphosphinate (**3c**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **3c** (98.5 mg, 0.188 mmol, 94%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25.94 ºC, TMS): δ = 8.00-8.02 (m, 1H), 7.43-7.55 (m, 3H), 7.36-7.40 (m, 1H), 7.26-7.31 (m, 3H), 7.09-7.25 (m, 8H), 2.32 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 147.9 (d, ^1J (C,P) = 8.0 Hz), 143.0 (s), 138.9 (s), 138.3 (d, ^1J (C,P) = 13.2 Hz), 138.0 (d, ^1J (C,P) = 13.4 Hz), 135.7 (d, ^1J (C,P) = 6.3 Hz), 133.2 (d, ^1J (C,P) = 2.9 Hz), 132.9 (d, ^1J (C,P) = 3.0 Hz), 132.3 (d, ^1J (C,P) = 10.4 Hz), 131.8 (d, ^1J (C,P) = 10.3 Hz), 131.1 (d, ^1J (C,P) = 7.1 Hz), 131.0 (d, ^1J (C,P) = 137.4 Hz), 130.6 (d, ^1J (C,P) = 136.0 Hz), 129.5 (s), 129.2 (s), 129.1 (s), 128.6 (d, ^1J (C,P) = 5.1 Hz), 128.5 (d, ^1J (C,P) = 8.5 Hz), 128.3 (d, ^1J (C,P) = 1.7 Hz), 128.1 (s), 127.8 (s), 124.1 (s), 120.4 (s), 100.3 (s), 21.4 (d, ^1J (C,P) = 9.3 Hz). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 30.6. HRMS (ESI) *m*/*z*: calcd. for $C_{26}H_{23}IO_2P$ $[M+H]^+$: 525.0480, found: 525.0477.

*2'-Iodo-[1,1'-biphenyl]-2-yl di-p-tolylphosphinate (**3d**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **3d** (91.2 mg, 0.174 mmol, 87%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25.94 ºC, TMS): δ = 7.99-8.01 (m, 1H), 7.49-7.55 (m, 3H), 7.36-7.40 (m, 1H), 7.27-7.30 (m, 3H), 7.05-7.20 (m, 8H), 2.33 (d, *J* = 12.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 148.0 (d, ^1J (C,P) = 7.9 Hz), 142.9 (s), 142.8 (d, ^1J (C,P) = 2.9 Hz), 142.6 (d, ^1J (C,P) = 2.9 Hz), 138.9 (s), 135.7 (d, ^1J (C,P) = 6.0 Hz), 131.9 (d, ^1J (C,P) = 10.9 Hz), 131.4 (d, ^1J (C,P) = 10.9 Hz), 131.1 (d, ^1J (C,P) = 9.2 Hz), 129.4 (d, ^1J (C,P) = 11.4 Hz), 129.3 (s), 129.2 (s), 129.1 (s), 128.9 (s), 128.1 (d, ^1J (C,P) = 141.3 Hz), 127.8 (s), 127.6 (d, ^1J (C,P) = 139.9 Hz), 124.0 (s), 120.5 (d, ^1J (C,P) = 3.9 Hz), 100.3 (s), 21.7 (d, ^1J (C,P) = 6.0 Hz). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 31.0. HRMS (ESI) *m*/*z*: calcd. for $C_{26}H_{23}IO_2P$ $[M+H]^+$: 525.0480, found: 525.0478.

*2'-Iodo-[1,1'-biphenyl]-2-yl bis(3-fluorophenyl)phosphinate (**3e**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **3e** (84.1 mg, 0.158 mmol, 79%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25.94 ºC, TMS): δ = 7.91-8.01 (m, 1H), 7.50-7.53 (m, 1H), 7.36-7.48 (m, 3H), 7.24-7.34 (m, 4H), 7.10-7.22 (m, 6H), 6.98-7.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 163.5 (s), 161.1 (s), 160.9 (s), 147.4 (d, ^1J (C,P) = 8.1 Hz), 142.6 (s), 135.8 (d, ^1J (C,P) = 6.2 Hz), 133.8 (d, ^1J (C,P) = 6.0 Hz), 132.8 (d, ^1J (C,P) = 138.9 Hz), 132.7 (d, ^1J (C,P) = 138.9 Hz), 132.4 (d, ^1J (C,P) = 5.6 Hz), 131.2 (s), 130.9 (s), 130.6 (m, C-F), 129.7 (s), 129.5 (s), 128.0 (s), 127.7 (dd, ^1J (C,P) = 3.3 Hz; ^2J (C,P)= 3.3 Hz), 127.3 (dd, ^1J (C,P) = 2.3 Hz; ^2J (C,P) = 3.2 Hz), 124.7 (s), 120.5 (d, ^1J (C,P) = 3.5 Hz), 120.0 (dd, ^1J (C,P) = 2.8 Hz; ^2J (C,P) = 2.5 Hz), 119.7 (dd, ^1J (C,P) = 2.8 Hz; ^2J (C,P) = 2.5 Hz), 118.5 (m, C-F), 100.1 (s). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 26.2 (dd, ^1J = 6.72 Hz; ^1J = 6.72 Hz). ^{19}F NMR (376MHz, $CDCl_3$, 25 ºC): δ = -110.6 (dd, ^1J = 2.26 Hz; ^2J = 3.76 Hz), -111.0 (dd, ^1J = 2.26 Hz; ^2J = 2.26 Hz). HRMS (ESI) *m*/*z*: calcd. for $C_{24}H_{17}F_2IO_2P$ $[M+H]^+$: 532.9979, found: 532.9976.

*2'-Iodo-[1,1'-biphenyl]-2-yl bis(4-methoxyphenyl)phosphinate (**3f**)*: According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **3f** (82.3 mg, 0.166 mmol, 83%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25.94 ºC, TMS): δ = 7.99-8.01 (m, 1H), 7.52-7.58 (m, 3H), 7.36-7.40 (m, 1H), 7.27-7.33 (m, 3H), 7.09-7.20 (m, 4H), 6.84-6.87 (m, 2H), 6.74-6.77 (m, 2H), 3.80 (d, *J* = 9.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 162.5 (d, ^1J (C,P) = 22.8 Hz), 147.9 (s), 143.0 (s), 138.9 (s), 135.7 (d, ^1J (C,P) = 6.0 Hz), 133.9 (s), 133.8 (s), 133.4 (s), 133.3 (s), 131.1 (d, ^1J (C,P) = 11.3 Hz), 129.5 (s), 129.1 (s), 127.9 (s), 124.0 (s), 122.8 (d, ^1J (C,P) = 145.9 Hz), 122.3 (d, ^1J (C,P) = 145.1 Hz), 120.6 (d, ^1J (C,P) = 4.0 Hz), 114.1 (d, ^1J (C,P) = 14.5 Hz), 113.8 (d, ^1J (C,P) = 14.6 Hz), 100.3 (s), 55.3 (d, ^1J (C,P) = 2.9 Hz). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 31.0. HRMS (ESI) *m*/*z*: calcd. for $C_{26}H_{23}IO_4P$ $[M+H]^+$: 557.0379, found: 557.0376.

*2'-Iodo-[1,1'-biphenyl]-2-yl di(naphthalen-1-yl)phosphinate (**3g**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **3g** (93.0 mg, 0.156 mmol, 78%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25.94 ºC, TMS): δ = 8.34-8.42 (m, 1H), 8.25-8.31 (m, 2H), 7.89-8.00 (m, 3H), 7.74-7.82 (m, 3H), 7.49-7.58 (m, 2H), 7.35-7.43 (m, 3H), 7.25-7.30 (m, 2H), 7.15-7.19 (m, 1H), 7.11-7.14 (m, 2H), 7.05-7.08 (m, 1H), 6.99-7.09 (m, 1H), 6.83-6.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 148.1 (d, ^1J (C,P) = 7.8 Hz), 142.3 (s), 138.6 (s), 136.0 (d, ^1J (C,P) = 6.2 Hz), 133.9 (d, ^1J (C,P) = 8.7 Hz), 133.8 (d, ^1J (C,P) = 3.1 Hz), 133.6 (d, ^1J (C,P) = 2.2 Hz), 133.5 (d, ^1J (C,P) = 3.1 Hz), 133.4 (s), 132.7 (d, ^1J (C,P) = 25.9 Hz), 132.6 (d, ^1J (C,P) = 25.1 Hz), 131.2 (s), 130.8 (s), 129.5 (s), 129.1 (s), 128.9 (s), 128.8 (d, ^1J (C,P) = 1.8 Hz), 128.7 (d, ^1J (C,P) = 1.4 Hz), 128.3 (s), 128.1 (d, ^1J (C,P) = 133.9 Hz), 128.0 (d, ^1J (C,P) = 133.4 Hz), 127.6 (d, ^1J (C,P) = 11.8 Hz), 127.3 (s), 126.3 (d, ^1J (C,P) = 6.6 Hz), 126.2 (d, ^1J (C,P) = 5.1 Hz), 126.1 (s), 125.3 (s), 124.8 (s), 124.6 (d, ^1J (C,P) = 14.5 Hz), 124.5 (d, ^1J (C,P) = 15.0 Hz), 120.6 (d, ^1J (C,P) = 3.6 Hz), 100.3 (s). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 30.8. HRMS (ESI) *m*/*z*: calcd. for $C_{32}H_{23}IO_2P$ $[M+H]^+$: 597.0480, found: 597.0478.

*2'-Iodo-[1,1'-biphenyl]-2-yl di(naphthalen-2-yl)phosphinate (**3h**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **3h** (97.7 mg, 0.164 mmol, 82%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25.94 ºC, TMS): δ = 8.38-8.42 (m, 1H), 8.06-8.11 (m, 2H), 7.87-7.88 (m, 1H), 7.74-7.84 (m, 4H), 7.68-7.71 (m, 1H), 7.59-7.66 (m, 2H), 7.49-7.58 (m, 4H), 7.34-7.40 (m, 2H), 7.21-7.30 (m, 1H), 7.12-7.20 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 147.9 (d, ^1J (C,P) = 7.8 Hz), 143.0 (s), 139.0 (s), 135.8 (d, ^1J (C,P) = 6.3 Hz), 135.0 (d, ^1J (C,P) = 2.5 Hz), 134.8 (d, ^1J (C,P) = 2.5 Hz), 134.1 (d, ^1J (C,P) = 9.8 Hz), 133.6 (d, ^1J (C,P) = 10.1 Hz), 132.5 (s), 132.3 (d, ^1J (C,P) = 2.5 Hz), 132.2 (s), 131.2 (s), 131.1 (s), 129.6 (s), 129.3 (s), 129.2 (s), 129.0 (s), 128.3 (d, ^1J (C,P) = 149.8 Hz), 128.1 (d, ^1J (C,P) = 168.3 Hz), 128.6 (s), 128.5 (s), 128.4 (s), 128.3 (d, ^1J (C,P) = 2.9 Hz), 128.0 (s), 127.8 (d, ^1J (C,P) = 7.0 Hz), 126.8 (d, ^1J (C,P) = 6.2 Hz), 126.6 (d, ^1J (C,P) = 11.6 Hz), 126.2 (d, ^1J (C,P) = 11.5 Hz), 125.3 (s), 124.2 (s), 120.4 (d, ^1J (C,P) = 3.8 Hz), 100.4 (s). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 30.1. HRMS (ESI) *m*/*z*: calcd. for $C_{32}H_{23}IO_2P$ $[M+H]^+$: 597.0480, found: 597.0478.

*2'-Iodo-[1,1'-biphenyl]-2-yl methyl(phenyl)phosphinate (**3i**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **3i** (65.1 mg, 0.15 mmol, 75%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.95-7.99 (m, 1H), 7.50-7.64 (m, 2H), 7.28-7.50 (m, 7H), 7.17-7.24 (m, 2H), 7.09-7.12 (m, 1H), 1.44-1.67 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 147.9 (d, ^1J (C,P) = 8.4 Hz), 147.7 (d, ^1J (C,P) = 8.5 Hz), 142.9 (s), 142.7 (s), 139.1 (s), 136.0 (d, ^1J (C,P) = 5.5 Hz), 135.7 (d, ^1J (C,P) = 5.7 Hz), 132.5 (d, ^1J (C,P) = 2.5 Hz), 132.3 (d, ^1J (C,P) = 2.8 Hz), 131.5 (s), 131.3 (d, ^1J (C,P) = 131.2 Hz), 131.2 (d, ^1J (C,P) = 133.3 Hz), 131.3 (d, ^1J (C,P) = 2.9 Hz), 131.2 (d, ^1J (C,P) = 3.7 Hz), 131.0 (s), 130.9 (s), 129.6 (d, ^1J (C,P) = 7.3 Hz), 129.1 (d, ^1J (C,P) = 4.9 Hz), 128.7 (s), 128.6 (s), 128.4 (s), 128.3 (s), 127.8 (d, ^1J (C,P) = 2.0 Hz), 124.4 (d, ^1J (C,P) = 9.1 Hz), 120.9 (d, ^1J (C,P) = 3.4 Hz), 120.8 (d, ^1J (C,P) = 3.6 Hz), 100.2 (s),

99.7 (s), 16.6 (d, ^1J (C,P) = 10.2 Hz), 15.7 (d, ^1J (C,P) = 8.5 Hz). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 41.8 (d, J = 6.4). HRMS (ESI) m/z: calcd. for $C_{19}H_{17}IO_2P$ $[M+H]^+$: 435.0011, found: 435.0007.

*Diethyl (2'-iodo-[1,1'-biphenyl]-2-yl) phosphate (**3j**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 5:1) gave product **3j** (70.0 mg, 0.162 mmol, 82%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.92-7.94 (m, 1H), 7.38-7.47 (m, 3H), 7.32-7.34 (m, 1H), 7.22-7.27 (m, 2H), 7.03-7.07 (m, 1H), 3.96-4.05 (m, 2H), 3.71-3.85 (m, 2H), 1.23-1.27 (m, 3H), 1.09-1.13 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 147.5 (d, ^1J (C,P) = 4.5 Hz), 142.7 (s), 138.7 (s), 135.9 (d, ^1J (C,P) = 7.1 Hz), 131.2 (s), 130.9 (s), 129.6 (d, ^1J (C,P) = 1.4 Hz), 129.1 (s), 127.8 (s), 124.7 (s), 119.8 (d, ^1J (C,P) = 2.3 Hz), 99.9 (s), 64.6 (d, ^1J (C,P) = 6.6 Hz), 64.3 (d, ^1J (C,P) = 6.5 Hz), 16.1 (d, ^1J (C,P) = 6.7 Hz), 15.9 (d, ^1J (C,P) = 6.7 Hz). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = -7.2. HRMS (ESI) m/z: calcd. for $C_{16}H_{19}IO_4P$ $[M+H]^+$: 433.0066, found: 433.0065.

*Dibutyl (2'-iodo-[1,1'-biphenyl]-2-yl) phosphate (**3k**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 5:1) gave product **3k** (78.0 mg, 0.16 mmol, 80%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.91-7.93 (m, 1H), 7.37-7.43 (m, 2H), 7.31-7.33 (m, 1H), 7.19-7.27 (m, 2H), 7.02-7.07 (m, 1H), 3.86-3.98 (m, 2H),3.64-3.77 (m, 2H), 1.54-1.61 (m, 2H), 1.41-1.48 (m, 2H), 1.29-1.37 (m, 2H), 1.18-1.28 (m, 2H), 0.82-0.90 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 147.6 (d, ^1J (C,P) = 6.4 Hz), 142.8 (s), 138.7 (s), 135.9 (d, ^1J (C,P) = 7.3 Hz), 131.1 (s), 130.9 (s), 129.6 (d, ^1J (C,P) = 1.2 Hz), 129.1 (s), 127.8 (s), 124.6 (s), 119.8 (d, ^1J (C,P) = 2.2 Hz), 100.0 (s), 68.3 (d, ^1J (C,P) = 6.7 Hz), 68.0 (d, ^1J (C,P) = 6.6 Hz), 32.1 (d, ^1J (C,P) = 6.8 Hz), 32.0 (d, ^1J (C,P) = 6.9 Hz), 18.6 (d, ^1J (C,P) = 10.6 Hz), 13.6 (d, ^1J (C,P) = 4.0 Hz). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 7.1. HRMS (ESI) m/z: calcd. for $C_{20}H_{27}IO_4P$ $[M+H]^+$: 489.0692, found: 489.0690.

*O,O-diethyl S-(2'-iodo-[1,1'-biphenyl]-2-yl) phosphorodithioate (**3l**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 5:1) gave product **3l** (69.6 mg, 0.15 mmol, 75%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.91-7.93 (m, 1H), 7.64-7.80 (m, 1H), 7.38-7.44 (m, 3H), 7.30-7.32 (m, 1H), 7.21-7.23 (m, 1H), 7.05-7.09 (m, 1H), 3.90-4.33 (m, 4H), 1.23-1.30 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 147.6 (d, ^1J (C,P) = 5.9 Hz), 145.2 (s), 138.8 (s), 135.2 (d, ^1J (C,P) = 4.4 Hz), 130.8 (d, ^1J (C,P) = 2.4 Hz), 130.6 (s), 129.3 (s), 129.0 (d, ^1J (C,P) = 2.9 Hz), 128.8 (d, ^1J (C,P) = 2.4 Hz), 128.6 (d, ^1J (C,P) = 5.9 Hz), 127.8 (s), 100.6 (s), 64.3 (d, ^1J (C,P) = 5.9 Hz), 64.1 (d, ^1J (C,P) = 6.1 Hz), 15.9 (d, ^1J (C,P) = 4.1 Hz), 15.8 (d, ^1J (C,P) = 4.1 Hz). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 89.0. HRMS (ESI) m/z: calcd. for $C_{16}H_{19}IO_2PS_2$ $[M+H]^+$: 464.9609, found: 464.9606.

*2'-Iodo-[1,1'-biphenyl]-2-yl di(octan-3-yl) phosphate (**3m**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **3m** (94.8 mg, 0.158 mmol, 79%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.90-7.93 (m, 1H), 7.36-7.42 (m, 2H), 7.31-7.33 (m, 1H), 7.18-7.26 (m, 2H), 7.02-7.06 (m, 1H), 3.75-3.87 (m, 2H), 3.53-3.68 (m, 2H), 1.13-1.40 (m, 18H), 0.75-0.90 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 147.6 (d, ^1J (C,P) = 6.5 Hz), 142.8 (s), 138.7 (s), 135.8 (d, ^1J (C,P) = 7.4 Hz), 131.1 (s), 131.0 (s), 129.6 (s), 129.1 (s), 127.8 (s), 124.6 (s), 119.6 (d, ^1J (C,P) = 2.1 Hz), 100.0 (s), 70.5 (d, ^1J (C,P) = 7.1 Hz), 70.2 (d, ^1J (C,P) = 6.9 Hz), 39.9 (d, ^1J (C,P) = 7.7 Hz), 39.8 (d, ^1J (C,P) = 3.0 Hz), 39.7 (d, ^1J (C,P) = 3.1 Hz), 29.8 (d, ^1J (C,P) = 1.5 Hz), 29.7 (d, ^1J (C,P) = 4.5 Hz), 28.8 (d, ^1J (C,P) = 4.1 Hz), 28.7 (s), 23.1 (d, ^1J (C,P) = 1.5 Hz), 23.0 (s), 22.7 (s), 14.1 (d, ^1J (C,P) = 1.6 Hz), 11.5 (s), 10.9 (s), 10.8 (d, ^1J (C,P) = 3.5 Hz). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = -6.9. HRMS (ESI) m/z: calcd. for $C_{28}H_{43}IO_4P$ $[M+H]^+$: 601.1944, found: 601.1941.

*2'-Iodo-4,4'-dimethyl-[1,1'-biphenyl]-2-yl diphenylphosphinate (**4a**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **4a** (92.2 mg, 0.176 mmol, 88%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.72-7.73 (m, 1H), 7.56-7.61 (m, 2H), 7.27-7.42 (m, 7H), 7.15-7.20 (m, 2H), 7.04-7.06 (m, 1H), 6.94-6.98 (m, 2H), 6.86-6.89 (m, 1H), 2.27 (d, J = 27.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 147.8 (d, ^1J (C,P) = 8.2 Hz), 139.9 (s), 139.8 (s), 139.3 (s), 139.0 (s), 132.7 (d, ^1J (C,P) = 6.1 Hz), 132.2 (d, ^1J (C,P) = 2.9 Hz), 132.0 (s), 131.9 (s), 131.8 (d, ^1J (C,P) = 2.9 Hz), 131.5 (s), 131.4 (d, ^1J (C,P) = 138.2 Hz), 131.4 (s), 131.0 (d, ^1J (C,P) = 137.7 Hz), 130.9 (d, ^1J (C,P) = 1.9 Hz), 128.6 (d, ^1J (C,P) = 5.8 Hz), 128.4 (s), 128.2 (d, ^1J (C,P) = 13.5 Hz), 125.0 (s), 100.4 (s), 21.4 (s), 20.6 (s). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 29.7. HRMS (ESI) m/z: calcd. for $C_{26}H_{23}IO_2P$ $[M+H]^+$: 525.0480, found: 525.0478.

*2'-Iodo-5,5'-dimethyl-[1,1'-biphenyl]-2-yl diphenylphosphinate (**4b**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **4b** (88.0 mg, 0.168 mmol, 84%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.82-7.85 (m, 1H), 7.65-7.71 (m, 2H), 7.34-7.50 (m, 7H), 7.22-7.27 (m, 2H), 7.06-7.09 (m, 1H), 6.88-6.96 (m, 3H), 2.27 (d, J = 18.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 145.5 (d, ^1J (C,P) = 8.0 Hz), 142.7 (s), 138.6 (s), 137.7 (s), 135.4 (d, ^1J (C,P) = 6.0 Hz), 133.7 (s), 132.3 (d, ^1J (C,P) = 2.8 Hz), 132.0 (d, ^1J (C,P) = 4.4 Hz), 131.9 (s), 131.5 (s), 131.4 (s), 131.3 (d, ^1J (C,P) = 124.9 Hz), 130.9 (d, ^1J (C,P) = 137.9 Hz), 130.0 (s), 129.9 (s), 128.6 (s), 128.5 (s), 128.1 (d, ^1J (C,P) = 13.6 Hz), 120.4 (d, ^1J (C,P) = 3.6 Hz), 96.0 (s), 20.9 (s), 20.8 (s). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 29.8. HRMS (ESI) m/z: calcd. for $C_{26}H_{23}IO_2P$ $[M+H]^+$: 525.0480, found: 525.0477.

*5,5'-Difluoro-2'-iodo-[1,1'-biphenyl]-2-yl diphenylphosphinate (**4c**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **4c** (97.9 mg, 0.184 mmol, 92%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.86-7.90 (m, 1H), 7.65-7.70 (m, 2H), 7.50-7.57 (m, 2H), 7.36-7.48 (m, 5H), 7.27-7.32 (m, 2H), 7.01-7.06 (m, 1H), 6.82-6.87 (m, 2H), 6.70-6.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 163.7 (s), 161.2 (s), 160.0 (s), 157.5 (s), 143.5 (d, ^1J (C,P) = 8.8 Hz), 136.2 (s), 132.6 (d, ^1J (C,P) = 2.8 Hz), 132.4 (d, ^1J (C,P) = 2.9 Hz), 131.8 (d, ^1J (C,P) = 10.5 Hz), 131.3 (d, ^1J (C,P) = 10.6 Hz), 130.7 (d, ^1J (C,P) = 136.1 Hz), 130.3 (d, ^1J (C,P) = 138.6 Hz), 128.7 (d, ^1J (C,P) = 13.5 Hz), 128.4 (d, ^1J (C,P) = 13.5 Hz), 122.6 (d, ^1J (C,P) = 3.4 Hz), 118.3 (d, ^1J (C,P) = 22.4 Hz), 117.5 (d, ^1J (C,P) = 23.8 Hz), 116.9 (d, ^1J (C,P) = 21.4 Hz), 116.5 (d, ^1J (C,P) = 22.9 Hz), 92.6 (d, ^1J (C,P) = 3.4 Hz). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 31.3. HRMS (ESI) m/z: calcd. for $C_{24}H_{17}F_2IO_2P$ $[M+H]^+$: 532.9979, found: 532.9976.

*4,4'-Dichloro-2'-iodo-[1,1'-biphenyl]-2-yl diphenylphosphinate (**4d**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **4d** (96.0 mg, 0.17 mmol, 85%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.91-7.92 (m, 1H), 7.64-7.70 (m, 2H), 7.51-7.56 (m, 2H), 7.38-7.50 (m, 5H), 7.24-7.34 (m, 3H), 7.16-7.19 (m, 1H), 7.06-7.09 (m, 1H), 7.00-7.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 148.0 (d, ^1J (C,P) = 8.2 Hz), 140.4 (s), 138.3 (s), 135.0 (s), 134.2 (s), 133.5 (d, ^1J (C,P) = 5.8 Hz), 132.7 (d, ^1J (C,P) = 3.0 Hz), 132.4 (d, ^1J (C,P) = 2.9 Hz), 131.8 (s), 131.7 (d, ^1J (C,P) = 6.6 Hz), 131.3 (d, ^1J (C,P) = 14.5 Hz), 130.3 (d, ^1J (C,P) = 137.0 Hz), 129.9 (s), 128.9 (d, ^1J (C,P) = 134.1 Hz), 128.8 (d, ^1J (C,P) = 13.6 Hz), 128.5 (d, ^1J (C,P) = 13.5 Hz), 128.2 (s), 124.9 (s), 121.5 (d, ^1J (C,P) = 3.5 Hz), 100.1 (s). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 31.6. HRMS (ESI) m/z: calcd. for $C_{24}H_{17}Cl_2IO_2P$ $[M+H]^+$: 564.9388, found: 564.9385.

*4'-Fluoro-2'-iodo-[1,1'-biphenyl]-2-yl diphenylphosphinate (**4e**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **4e** (45.2 mg,

0.088 mmol, 44%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.66-7.72 (m, 3H), 7.48-7.53 (m, 2H), 7.37-7.47 (m, 5H), 7.26-7.32 (m, 3H), 7.13-7.18 (m, 2H), 7.01-7.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 162.6 (s), 160.1 (s), 147.9 (d, ^{1}J (C,P) = 8.0 Hz), 139.0 (d, ^{1}J (C,P) = 3.4 Hz), 134.9 (d, ^{1}J (C,P) = 5.9 Hz), 132.5 (d, ^{1}J (C,P) = 2.9 Hz), 132.2 (d, ^{1}J (C,P) = 2.9 Hz), 131.9 (s), 131.8 (s), 131.7 (d, ^{1}J (C,P) = 8.0 Hz), 131.1 (d, ^{1}J (C,P) = 137.8 Hz), 130.8 (d, ^{1}J (C,P) = 137.1 Hz), 131.3 (d, ^{1}J (C,P) = 10.6 Hz), 129.8 (s), 128.6 (d, ^{1}J (C,P) = 13.4 Hz), 128.3 (d, ^{1}J (C,P) = 13.5 Hz), 125.7 (d, ^{1}J (C,P) = 23.4 Hz), 120.8 (d, ^{1}J (C,P) = 3.7 Hz), 115.0 (d, ^{1}J (C,P) = 20.8 Hz), 99.6 (d, ^{1}J (C,P) = 8.1 Hz). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 30.3. HRMS (ESI) *m*/*z*: calcd. for $C_{24}H_{18}FIO_2P$ $[M+H]^+$: 515.0073, found: 515.0071.

*4-Fluoro-2'-iodo-[1,1'-biphenyl]-2-yl diphenylphosphinate (**4e'**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **4e'** (42.1 mg, 0.082 mmol, 41%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.97-7.99 (m, 1H), 7.62-7.67 (m, 2H), 7.48-7.53 (m, 1H), 7.31-7.46 (m, 7H), 7.25-7.30 (m, 2H), 7.08-7.16 (m, 3H), 6.85-6.90 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 163.6 (s), 161.1 (s), 148.4 (d, ^{1}J (C,P) = 19.1 Hz), 142.0 (s), 139.0 (s), 132.6 (d, ^{1}J (C,P) = 2.8 Hz), 132.3 (d, ^{1}J (C,P) = 2.9 Hz), 131.9 (d, ^{1}J (C,P) = 10.5 Hz), 131.7 (s), 131.3 (d, ^{1}J (C,P) = 10.6 Hz), 131.2 (s), 130.3 (d, ^{1}J (C,P) = 137.3 Hz), 129.2 (d, ^{1}J (C,P) = 177.0 Hz), 129.3 (s), 128.7 (d, ^{1}J (C,P) = 13.5 Hz), 128.4 (d, ^{1}J (C,P) = 13.6 Hz), 128.0 (s), 111.3 (d, ^{1}J (C,P) = 21.2 Hz), 108.6 (d, ^{1}J (C,P) = 29.0 Hz), 100.5 (s). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 31.0. HRMS (ESI) *m*/*z*: calcd. for $C_{24}H_{18}FIO_2P$ $[M+H]^+$: 515.0073, found: 515.0071.

*4'-Chloro-2'-iodo-[1,1'-biphenyl]-2-yl diphenylphosphinate (**4f**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **4f** (44.4 mg, 0.084 mmol, 42%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.96-7.99 (m, 1H), 7.59-7.67 (m, 3H), 7.48-7.53 (m, 1H), 7.33-7.46 (m, 6H), 7.24-7.30 (m, 2H), 7.08-7.19 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 148.2 (d, ^{1}J (C,P) = 8.1 Hz), 141.9 (s), 139.0 (s), 134.6 (s), 134.4 (d, ^{1}J (C,P) = 6.2 Hz), 132.6 (d, ^{1}J (C,P) = 2.9 Hz), 132.3 (d, ^{1}J (C,P) = 2.9 Hz), 131.9 (s), 131.8 (d, ^{1}J (C,P) = 6.1 Hz), 131.4 (d, ^{1}J (C,P) = 10.7 Hz), 130.8 (d, ^{1}J (C,P) = 137.8 Hz), 131.0 (s), 130.3 (d, ^{1}J (C,P) = 137.2 Hz), 129.4 (s), 128.7 (d, ^{1}J (C,P) = 13.6 Hz), 128.4 (d, ^{1}J (C,P) = 13.6 Hz), 128.0 (s), 124.7 (s), 121.1 (d, ^{1}J (C,P) = 3.7 Hz), 100.0 (d, ^{1}J (C,P) = 7.2 Hz). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 31.0. HRMS (ESI) *m*/*z*: calcd. for $C_{24}H_{18}ClIO_2P$ $[M+H]^+$: 530.9778, found: 530.9775.

*4-Chloro-2'-iodo-[1,1'-biphenyl]-2-yl diphenylphosphinate (**4f'**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **4f'** (38.6 mg, 0.071 mmol, 35%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.94-7.95 (m, 1H), 7.66-7.72 (m, 2H), 7.38-7.54 (m, 7H), 7.24-7.34 (m, 4H), 7.13-7.19 (m, 2H), 7.04-7.06 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 147.7 (d, ^{1}J (C,P) = 8.0 Hz), 141.5 (s), 138.1 (s), 134.8 (d, ^{1}J (C,P) = 6.0 Hz), 133.9 (s), 132.5 (d, ^{1}J (C,P) = 2.9 Hz), 132.2 (d, ^{1}J (C,P) = 2.9 Hz), 131.9 (d, ^{1}J (C,P) = 10.6 Hz), 131.5 (s), 131.3 (d, ^{1}J (C,P) = 10.7 Hz), 131.0 (s), 130.7 (d, ^{1}J (C,P) = 137.3 Hz), 129.7 (d, ^{1}J (C,P) = 133.8 Hz), 129.9 (s), 128.6 (d, ^{1}J (C,P) = 13.5 Hz), 128.4 (d, ^{1}J (C,P) = 13.6 Hz), 128.1 (s), 124.4 (s), 120.9 (d, ^{1}J (C,P) = 3.7 Hz), 100.2 (s). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 30.4. HRMS (ESI) *m*/*z*: calcd. for $C_{24}H_{18}ClIO_2P$ $[M+H]^+$: 530.9778, found: 530.9776.

*5'-Chloro-4'-fluoro-2'-iodo-[1,1'-biphenyl]-2-yl diphenylphosphinate (**4g**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **4g** (51.4 mg, 0.094 mmol, 47%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.59-7.66 (m, 3H), 7.49-7.52 (m, 1H), 7.32-7.46 (m, 6H), 7.26-7.31 (m, 3H), 7.08-7.16 (m, 1H), 7.04-7.07 (m, 1H), 6.96-7.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 147.6 (d, ^{1}J (C,P) = 7.8 Hz), 140.1 (d, ^{1}J (C,P) = 4.0 Hz), 134.0 (d, ^{1}J (C,P) = 5.6 Hz), 132.6 (d, ^{1}J (C,P) = 3.0 Hz), 132.4 (d, ^{1}J (C,P) = 2.8 Hz), 132.1 (s), 131.7 (d, ^{1}J (C,P) = 10.5 Hz), 131.3 (d, ^{1}J (C,P) = 10.6 Hz), 131.2 (s), 131.0 (s), 130.8 (d, ^{1}J (C,P) = 162.8 Hz), 128.6 (d, ^{1}J (C,P) = 13.5 Hz), 128.4 (d, ^{1}J (C,P) = 13.5 Hz), 126.5 (d, ^{1}J (C,P) = 22.9 Hz), 124.6 (s), 121.5 (s), 121.4 (s), 120.9 (s), 120.8 (s), 96.8 (d, ^{1}J (C,P) = 7.0 Hz). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 31.0. HRMS (ESI) *m*/*z*: calcd. for $C_{24}H_{17}ClFIO_2P$ $[M+H]^+$: 548.9683, found: 548.9681.

*5-Chloro-4-fluoro-2'-iodo-[1,1'-biphenyl]-2-yl diphenylphosphinate (**4g'**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **4g'** (39.4 mg, 0.072 mmol, 36%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.90-7.93 (m, 1H), 7.54-7.60 (m, 2H), 7.43-7.48 (m, 1H), 7.27-7.40 (m, 7H), 7.19-7.24 (m, 2H), 7.14-7.16 (m, 1H), 7.02-7.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 140.9 (s), 139.1 (s), 132.7 (d, ^{1}J (C,P) = 3.0 Hz), 132.5 (d, ^{1}J (C,P) = 2.9 Hz), 132.0 (s), 131.9 (s), 131.8 (s), 131.4 (s), 131.3 (s), 130.4 (d, ^{1}J (C,P) = 137.3 Hz), 131.1 (s), 130.0 (d, ^{1}J (C,P) = 137.5 Hz), 129.7 (s), 128.7 (d, ^{1}J (C,P) = 13.7 Hz), 128.5 (d, ^{1}J (C,P) = 13.5 Hz), 128.0 (s), 109.9 (d, ^{1}J (C,P) = 3.7 Hz), 109.7 (d, ^{1}J (C,P) = 3.4 Hz), 100.1 (d, ^{1}J (C,P) = 0.6 Hz), 100.0 (s). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 31.7. HRMS (ESI) *m*/*z*: calcd. for $C_{24}H_{17}ClFIO_2P$ $[M+H]^+$: 548.9683, found: 548.9680.

*2'-Iodo-5'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl di(naphthalen-1-yl)phosphinate (**4h**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **4h** (31.8 mg, 0.048mmol, 24%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 8.36-8.38 (m, 1H), 8.21-8.27 (m, 2H), 7.94-8.03 (m, 3H), 7.72-7.84 (m, 4H), 7.50-7.55 (m, 2H), 7.35-7.45 (m, 5H), 7.27-7.34 (m, 1H), 7.07-7.12 (m, 1H), 6.99-7.01 (m, 1H), 6.88-6.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 141.4 (s), 138.8 (s), 136.5 (d, ^{1}J (C,P) = 6.4 Hz), 134.1 (d, ^{1}J (C,P) = 3.3 Hz), 133.9 (d, ^{1}J (C,P) = 8.5 Hz), 133.7 (d, ^{1}J (C,P) = 2.3 Hz), 133.6 (d, ^{1}J (C,P) = 2.6 Hz), 133.5 (d, ^{1}J (C,P) = 2.5 Hz), 132.7 (d, ^{1}J (C,P) = 12.4 Hz), 132.4 (d, ^{1}J (C,P) = 11.9 Hz), 130.6 (s), 129.5 (s), 129.1 (s), 128.9 (d, ^{1}J (C,P) = 1.4 Hz), 128.8 (d, ^{1}J (C,P) = 1.5 Hz), 128.6 (d, ^{1}J (C,P) = 3.9 Hz), 128.3 (s), 128.1 (d, ^{1}J (C,P) = 2.9 Hz), 127.8 (s), 127.7 (s), 127.5 (s), 126.7 (d, ^{1}J (C,P) = 3.8 Hz), 126.1 (d, ^{1}J (C,P) = 146.6 Hz), 125.8 (d, ^{1}J (C,P) = 130.8 Hz), 126.4 (s), 126.3 (s), 126.1 (d, ^{1}J (C,P) = 5.4 Hz), 126.0 (d, ^{1}J (C,P) = 2.1 Hz), 124.8 (s), 124.6 (d, ^{1}J (C,P) = 3.9 Hz), 124.4 (s), 120.9 (d, ^{1}J (C,P) = 3.8 Hz), 99.7 (s). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 32.4. ^{19}F NMR (376MHz, $CDCl_3$, 25 ºC): δ = -62.0. HRMS (ESI) *m*/*z*: calcd. for $C_{33}H_{22}F_3IO_2P$ $[M+H]^+$: 665.0354, found: 665.0351.

*2'-Iodo-5-(trifluoromethyl)-[1,1'-biphenyl]-2-yl di(naphthalen-2-yl)phosphinate (**4h'**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **4h'** (58.4 mg, 0.088 mmol, 44%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 8.31-8.33 (m, 1H), 8.19-8.25 (m, 2H), 7.99-8.10 (m, 2H), 7.93-7.95 (m, 1H), 7.75-7.82 (m, 3H), 7.68-7.70 (m, 1H), 7.45-7.52 (m, 1H), 7.38-7.44 (m, 3H), 7.27-7.36 (m, 4H), 7.16-7.20 (m, 1H), 7.10-7.13 (m, 1H), 7.00-7.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 148.0 (s), 143.7 (s), 139.3 (s), 134.7 (d, ^{1}J (C,P) = 6.0 Hz), 134.2 (s), 134.0 (s), 133.9 (d, ^{1}J (C,P) = 1.3 Hz), 133.6 (d, ^{1}J (C,P) = 2.0 Hz), 133.5 (d, ^{1}J (C,P) = 2.7 Hz), 133.5 (d, ^{1}J (C,P) = 3.6 Hz), 133.4 (s), 130.6 (s), 132.7 (d, ^{1}J (C,P) = 12.5 Hz), 132.3 (d, ^{1}J (C,P) = 11.6 Hz), 131.1 (s), 130.1 (s), 128.8 (s), 127.8 (d, ^{1}J (C,P) = 132.5 Hz), 127.6 (s), 127.5 (d, ^{1}J (C,P) = 137.2 Hz), 127.3 (s), 126.8 (s), 126.2 (s), 126.1 (s), 125.9 (d, ^{1}J (C,P) = 4.9 Hz), 125.3 (s), 125.2 (d, ^{1}J (C,P) = 3.0 Hz), 125.0 (d, ^{1}J (C,P) = 3.5 Hz), 124.5 (d, ^{1}J (C,P) = 1.4 Hz), 124.4 (s), 124.3 (s), 121.1 (d, ^{1}J (C,P) = 3.8 Hz), 100.0 (s). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 31.6. ^{19}F NMR (376MHz, $CDCl_3$, 25 ºC): δ = -

62.6. HRMS (ESI) *m*/*z*: calcd. for $C_{33}H_{22}F_3IO_2P$ $[M+H]^+$: 665.0354, found: 665.0352.

*2'-Iodo-5'-methoxy-[1,1'-biphenyl]-2-yl di(naphthalen-1-yl)phosphinate (**4i**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **4i** (23.2 mg, 0.037 mmol, 18%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 8.44-8.49 (m, 1H), 8.12-8.16 (m, 1H), 7.88-7.92 (m, 2H), 7.82-7.85 (m, 2H), 7.77-7.80 (m, 2H), 7.61-7.71 (m, 3H), 7.51-7.60 (m, 4H), 7.34-7.39 (m, 1H), 7.27-7.32 (m, 1H), 7.14-7.20 (m, 2H), 6.73-6.76 (m, 2H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 159.5 (s), 147.7 (d, ^1J (C,P) = 7.9 Hz), 143.8 (s), 139.5 (s), 135.7 (d, ^1J (C,P) = 6.1 Hz), 135.0 (d, ^1J (C,P) = 2.5 Hz), 134.8 (d, ^1J (C,P) = 2.3 Hz), 134.2 (d, ^1J (C,P) = 9.7 Hz), 133.6 (s), 133.5 (s), 132.5 (s), 132.3 (s), 132.2 (s), 132.1 (s), 131.1 (s), 129.7 (s), 129.2 (s), 129.1 (s), 128.6 (d, ^1J (C,P) = 13.2 Hz), 128.4 (d, ^1J (C,P) = 8.8 Hz), 128.3 (d, ^1J (C,P) = 138.8 Hz), 128.2 (d, ^1J (C,P) = 13.5 Hz), 127.9 (d, ^1J (C,P) = 138.1 Hz), 127.8 (d, ^1J (C,P) = 8.6 Hz), 126.7 (s), 126.5 (s), 126.3 (s), 126.1 (s), 120.7 (d, ^1J (C,P) = 3.9 Hz), 116.5 (s), 116.2 (s), 88.6 (s), 55.3 (s). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 30.3. HRMS (ESI) *m*/*z*: calcd. for $C_{33}H_{25}IO_3P$ $[M+H]^+$: 627.0586, found: 627.0583.

*2'-Iodo-5-methoxy-[1,1'-biphenyl]-2-yl di(naphthalen-1-yl)phosphinate (**4i'**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **4i'** (48.8 mg, 0.078 mmol, 39%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 8.37-8.40 (m, 1H), 8.04-8.10 (m, 2H), 7.87-7.89 (m, 1H), 7.75-7.84 (m, 4H), 7.68-7.71 (m, 1H), 7.50-7.63 (m, 6H), 7.30-7.37 (m, 2H), 7.12-7.19 (m, 2H), 6.79-6.82 (m, 1H), 6.69-6.70 (m, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 155.7 (s), 142.9 (s), 139.0 (s), 136.5 (d, ^1J (C,P) = 6.2 Hz), 134.9 (s), 134.7 (d, ^1J (C,P) = 2.3 Hz), 134.2 (d, ^1J (C,P) = 9.7 Hz), 133.7 (d, ^1J (C,P) = 10.0 Hz), 132.3 (d, ^1J (C,P) = 4.0 Hz), 132.1 (s), 131.2 (s), 129.3 (s), 129.2 (s), 129.0 (s), 128.9 (s), 128.6 (s), 128.5 (s), 128.4 (s), 128.3 (s), 128.2 (s), 128.0 (s), 127.3 (d, ^1J (C,P) = 115.6 Hz), 127.2 (d, ^1J (C,P) = 119.7 Hz), 126.9 (s), 126.9 (s), 126.8 (s), 126.3 (s), 126.2 (s), 121.4 (d, ^1J (C,P) = 3.6 Hz), 116.2 (s), 114.4 (s), 100.0 (s), 55.6 (s). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 30.3. HRMS (ESI) *m*/*z*: calcd. for $C_{33}H_{25}IO_3P$ $[M+H]^+$: 627.0586, found: 627.0585.

*2'-Iodo-5'-methoxy-5-(trifluoromethyl)-[1,1'-biphenyl]-2-yl di(naphthalen-1-yl) phosphinate (**4j**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **4j** (54.1 mg, 0.078 mmol, 38%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 8.39-8.43 (m, 1H), 8.09-8.13 (m, 1H), 7.65-7.90 (m, 8H), 7.52-7.61 (m, 6H), 7.39-7.48 (m, 2H), 7.10-7.11 (m, 1H), 6.88-6.91 (m, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 159.6 (s), 150.8 (d, ^1J (C,P) = 7.8 Hz), 135.9 (d, ^1J (C,P) = 7.8 Hz), 135.0 (d, ^1J (C,P) = 2.3 Hz),134.8 (d, ^1J (C,P) = 2.5 Hz), 134.2 (s), 134.1 (s), 133.8 (s), 133.7 (s), 133.6 (s), 132.4 (s), 132.3 (s), 132.1 (s), 131.4 (s), 129.2 (s), 129.1 (s), 129.0 (d, ^1J (C,P) = 3.7 Hz), 128.8 (d, ^1J (C,P) = 13.4 Hz), 128.6 (d, ^1J (C,P) = 9.1 Hz), 128.4 (d, ^1J (C,P) = 7.3 Hz), 128.3 (d, ^1J (C,P) = 6.5 Hz), 128.1 (s), 127.9 (d, ^1J (C,P) = 6.6 Hz), 127.0 (d, ^1J (C,P) = 5.7 Hz), 126.0 (d, ^1J (C,P) = 141.4 Hz), 125.9 (d, ^1J (C,P) = 141.7 Hz), 126.7 (d, ^1J (C,P) = 3.8 Hz), 126.4 (d, ^1J (C,P) = 11.7 Hz), 126.0 (d, ^1J (C,P) = 11.8 Hz), 124.3 (s), 120.9 (d, ^1J (C,P) = 3.9 Hz), 114.0 (s), 99.9 (s), 55.6 (s). ^{19}F NMR (376MHz, $CDCl_3$, 25 ºC): δ = -62.0. ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 31.3. HRMS (ESI) *m*/*z*: calcd. for $C_{34}H_{24}F_3IO_3P$ $[M+H]^+$: 694.0382, found: 694.0381.

*2'-Iodo-5-methoxy-5'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl di(naphthalen-1-yl)phosphinate (**4j'**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **4j'** (34.7 mg, 0.050 mmol, 25%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 8.22-8.34 (m, 2H), 8.08-8.11 (m, 1H), 7.78-7.85 (m, 4H), 7.71-7.74 (m, 1H), 7.48-7.61 (m, 6H), 7.29-7.35 (m, 3H), 7.17-7.20 (m, 1H), 7.06-7.08 (m, 1H), 6.71-6.73 (m, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 160.7 (s), 148.6 (d, ^1J (C,P) = 8.2 Hz), 143.8 (s), 139.7 (s),135.0 (d, ^1J (C,P) = 2.4 Hz), 134.8 (d, ^1J (C,P) = 2.3 Hz), 134.0 (d, ^1J (C,P) = 10.0 Hz), 133.7 d, ^1J (C,P) = 10.1 Hz), 132.4 (s), 132.3 (d, ^1J (C,P) = 1.2 Hz), 132.1 (s), 131.4 (s), 130.6 (s), 130.3 (s), 129.1 (d, ^1J (C,P) = 2.4 Hz), 129.0 (s), 128.7 (s), 128.6 (s), 128.5 (s), 128.3 (s), 127.6 (d, ^1J (C,P) = 153.6 Hz), 127.5 (d, ^1J (C,P) = 154.2 Hz), 127.9 (s), 127.8 (s), 127.0 (d, ^1J (C,P) = 3.1 Hz), 126.2 (d, ^1J (C,P) = 11.4 Hz), 125.8 (d, ^1J (C,P) = 11.2 Hz), 125.4 (d, ^1J (C,P) = 3.4 Hz), 125.3 (s), 125.2 (s), 110.6 (s), 106.6 (d, ^1J (C,P) = 3.8 Hz), 105.8 (s), 55.6 (s). ^{19}F NMR (376MHz, $CDCl_3$, 25 ºC): δ = -62.6. ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 31.0. HRMS (ESI) *m*/*z*: calcd. for $C_{34}H_{24}F_3IO_3P$ $[M+H]^+$: 694.0382, found: 694.0382.

*2'-Iodo-6'-methoxy-[1,1'-biphenyl]-2-yl diphenylphosphinate (**4k**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **4k** (70.4 mg, 0.134 mmol, 67%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.86-7.93 (m, 5H), 7.51-7.56 (m, 2H), 7.43-7.50 (m, 4H), 7.32-7.39 (m, 2H), 7.10-7.13 (m, 1H), 6.98-7.03 (m, 1H), 6.89-6.90 (m, 1H), 6.79-6.82 (m, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 153.2 (s), 143.8 (d, ^1J (C,P) = 8.2 Hz), 142.9 (s), 138.8 (s), 134.1 (s), 132.5 (d, ^1J (C,P) = 3.0 Hz), 132.0 (s), 131.9 (d, ^1J (C,P) = 2.0 Hz), 131.8 (s), 130.3 (s), 129.3 (d, ^1J (C,P) = 159.0 Hz), 129.2 (d, ^1J (C,P) = 162.5 Hz), 128.9 (s), 128.7 (d, ^1J (C,P) = 4.8 Hz), 128.6 (d, ^1J (C,P) = 5.1 Hz), 127.9 (s), 123.2 (d, ^1J (C,P) = 4.8 Hz), 121.3 (d, ^1J (C,P) = 4.3 Hz), 111.8 (s), 100.1 (s), 56.0 (s). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 31.0. HRMS (ESI) *m*/*z*: calcd. for $C_{25}H_{21}IO_3P$ $[M+H]^+$: 527.0273, found: 527.0271.

*4'-Acetyl-2'-iodo-[1,1'-biphenyl]-2-yl diphenylphosphinate (**4l**), 4-Acetyl-2'-iodo-[1,1'-biphenyl]-2-yl diphenylphosphinate (**4l'**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **4l** and **4l'** (93.6 mg, 0.178 mmol, 89%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 8.50-8.51 (m, 2H), 8.02-8.06 (m, 2H), 7.97-8.00 (m, 2H), 7.86-7.88 (m, 1H), 7.77-7.79 (m, 2H), 7.65-7.71 (m, 6H), 7.48-7.54 (m, 4H), 7.33-7.46 (m, 19H), 7.23-7.33 (m, 10H), 7.10-7.20 (m, 6H), 2.64 (s, 3H), 2.56 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 196.9 (s), 196.4 (s), 148.0 (d, ^1J (C,P) = 8.1 Hz), 147.7 (d, ^1J (C,P) = 8.0 Hz), 141.9 (s), 140.4 (d, ^1J (C,P) = 5.8 Hz), 139.0 (s), 138.7 (s), 138.1 (s), 137.4 (s), 135.1 (d, ^1J (C,P) = 5.7 Hz), 132.6 (d, ^1J (C,P) = 2.8 Hz), 132.5 (d, ^1J (C,P) = 2.8 Hz), 132.3 (d, ^1J (C,P) = 2.9 Hz), 132.2 (d, ^1J (C,P) = 2.9 Hz), 131.8 (s), 131.7 (s), 131.5 (s), 131.3 (s), 131.3 (d, ^1J (C,P) = 133.5 Hz), 131.2 (s), 130.8 (d, ^1J (C,P) = 138.0 Hz), 130.7 (d, ^1J (C,P) = 137.3 Hz), 130.6 (s), 130.4 (d, ^1J (C,P) = 130.9 Hz), 129.6 (s), 128.7 (s), 128.6 (s), 128.5 (s), 128.4 (s), 128.3 (s), 128.2 (s), 128.0 (s), 127.6 (s), 124.5 (s), 123.9 (s), 120.9 (d, ^1J (C,P) = 3.5 Hz), 120.8 (d, ^1J (C,P) = 3.7 Hz), 100.4 (s), 99.2 (s), 26.8 (s), 26.7 (s). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 31.2, 30.6. HRMS (ESI) *m*/*z*: calcd. for $C_{25}H_{21}IO_3P$ $[M+H]^+$: 527.0273, found: 527.0271, 527.0270.

*2'-((3-Aminophenyl)ethynyl)-[1,1'-biphenyl]-2-yl diphenylphosphinate (**6**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **6** (72.8 mg, 0.15 mmol, 75%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.47-7.67 (m, 7H), 7.27-7.42 (m, 7H), 7.11-7.24 (m, 6H), 6.97-7.01 (m, 1H), 6.51-6.58 (m, 2H), 6.39-6.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC, TMS): δ = 148.4 (d, ^1J (C,P) = 8.0 Hz), 146.1 (s), 140.2 (s), 132.4 (d, ^1J (C,P) = 6.1 Hz), 132.2 (s), 132.1 (d, ^1J (C,P) = 3.0 Hz), 131.9 (s), 131.8 (s), 131.7 (s), 131.6 (s), 130.8 (s), 130.2 (s), 129.1 (d, ^1J (C,P) = 2.3 Hz), 128.6 (s), 128.5 (s), 128.4 (s), 128.3 (s), 127.9 (s), 127.5 (s), 124.0 (s), 123.8 (s), 123.4 (s), 121.9 (s), 120.5 (d, ^1J (C,P) = 3.8 Hz), 117.7 (s), 115.2 (s), 93.1 (s), 88.2 (s). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ºC): δ = 30.1. HRMS

(ESI) *m*/*z*: calcd. for $C_{32}H_{25}NO_2P$ $[M+H]^+$: 486.1623, found: 486.1620.

*(E)-2'-styryl-[1,1'-biphenyl]-2-yl diphenylphosphinate (**8**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **8** (78.4 mg, 0.166 mmol, 83%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.82-7.84 (m, 1H), 7.63-7.66 (m, 1H), 7.40-7.52 (m, 6H), 7.19-7.33 (m, 12H), 7.08-7.14 (m, 3H), 7.01 (d, *J* = 16.0 Hz, 1H), 6.75 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 148.4 (d, ^1J (C,P) = 7.7 Hz), 137.3 (s), 136.8 (s), 136.1 (s), 132.2 (d, ^1J (C,P) = 6.0 Hz), 132.1 (d, ^1J (C,P) = 2.8 Hz), 132.0 (s), 131.8 (s), 131.7 (d, ^1J (C,P) = 4.1 Hz), 131.5 (s), 131.4 (s), 130.6 (d, ^1J (C,P) = 135.7 Hz), 129.6 (d, ^1J (C,P) = 132.6 Hz), 129.4 (s), 129.1 (s), 128.6 (s), 128.4 (d, ^1J (C,P) = 8.0 Hz), 128.3 (d, ^1J (C,P) = 8.0 Hz), 128.0 (s), 127.6 (s), 127.2 (s), 127.0 (s), 126.6 (s), 124.9 (s), 124.4 (s), 120.9 (d, ^1J (C,P) = 3.7 Hz). ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ = 30.2. HRMS (ESI) *m*/*z*: calcd. for $C_{32}H_{26}O_2P$ $[M+H]^+$: 473.1670, found: 473.1669.

*2'-(Diphenylphosphino)-[1,1'-biphenyl]-2-yl diphenylphosphinate (**10**):* According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 2:1) gave product **10** (72.0 mg, 0.13 mmol, 65%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.58-7.63 (m, 2H), 7.30-7.43 (m, 10H), 7.20-7.27 (m, 6H), 7.08-7.17 (m, 8H), 6.87-6.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 148.1 (d, ^1J (C,P) = 8.0 Hz), 143.9 (s), 143.6 (s), 137.7 (d, ^1J (C,P) = 13.0 Hz), 137.3 (d, ^1J (C,P) = 12.9 Hz), 137.0 (d, ^1J (C,P) = 11.9 Hz), 134.0 (s), 133.7 (d, ^1J (C,P) = 4.6 Hz), 133.6 (d, ^1J (C,P) = 6.6 Hz), 133.2 (d, ^1J (C,P) = 130.5 Hz), 132.3 (d, ^1J (C,P) = 140.8 Hz), 132.3 (d, ^1J (C,P) = 3.3 Hz), 132.0 (d, ^1J (C,P) = 3.4 Hz), 131.7 (d, ^1J (C,P) = 3.1 Hz), 131.6 (s), 131.5 (s), 131.4 (d, ^1J (C,P) = 128.5 Hz), 131.3 (d, ^1J (C,P) = 130.8 Hz), 130.3 (s), 129.0 (s), 128.7 (s), 128.5 (d, ^1J (C,P) = 5.6 Hz), 128.3 (d, ^1J (C,P) = 6.4 Hz), 128.2 (s), 127.9 (s), 123.6 (s), 123.1 (s), 119.8 (d, ^1J (C,P) = 3.7 Hz). ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ = 29.5, -13.3. HRMS (ESI) *m*/*z*: calcd. for $C_{36}H_{29}O_2P$ $[M+H]^+$: 555.1643, found: 555.1640.

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Conflicts of interest

There are no conflicts to declare.

Keywords: P(O)-OH bonds • cyclic diaryliodonium salts • copper catalysis • diphenylation

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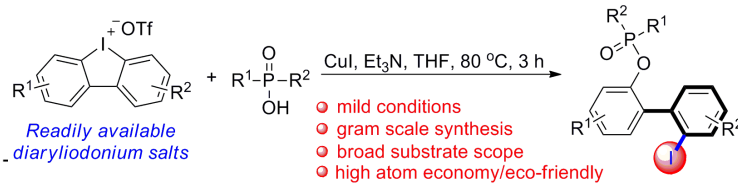

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Page No. – Page No.

Copper-Catalyzed Diphenylation of P(O)-OH Bonds with Cyclic Diaryliodonium Salts

A copper-catalyzed system for the selective diphenylation of P(O)-OH bonds with cyclic diaryliodonium salts is developed. The protocol is practical, representing a direct and simple way to produce functionalized 2'-iodo substituted biaryl phosphinic/phosphoric acid esters from basic starting materials in moderate to good yields.