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Radical Arylation of Triphenyl Phosphite Catalyzed by Salicylic Acid: Mechanistic Investigations and Synthetic Applications

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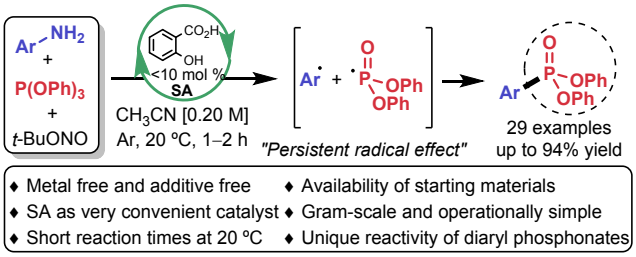


ABSTRACT: A straightforward and scalable methodology to synthesize diphenyl arylphosphonates at 20 ºC within 1-2 h is reported, using inexpensive SA as the catalytic promoter of the reaction. Mechanistic investigations suggest that the reaction proceeds *via* radical-radical coupling, consistent with the so-called Persistent Radical Effect. The reaction tolerated a wide range of functional groups and heteroaromatic moieties. The synthetic usefulness and the unique reactivity of the obtained phosphonates were demonstrated in different one-step transformations.

INTRODUCTION

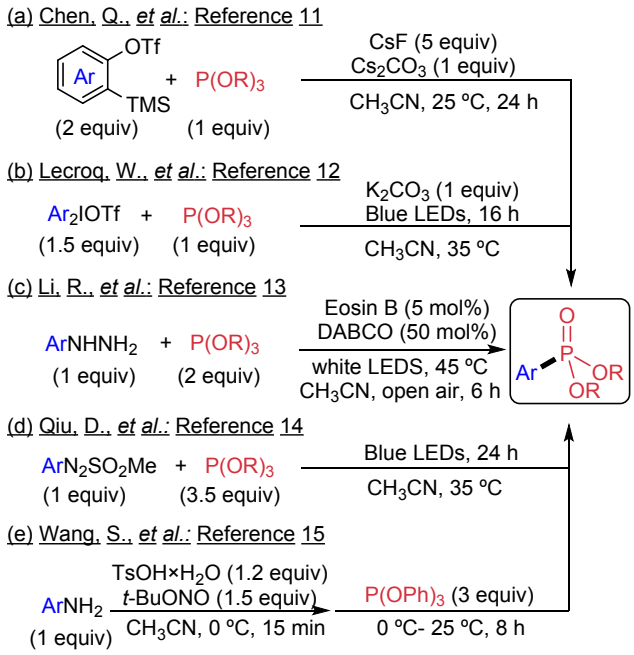
Aryl phosphonates are privileged scaffolds among pharmaceuticals, agrochemicals, and organic materials; as well as being versatile building blocks in organic synthesis or ligands in transition-metal (TM) catalysis.[1] Traditionally, these organophosphorus compounds were prepared by reaction of electrophilic dialkyl chlorophosphonates with organolithium[2] or Grignard reagents.[3] Since the seminal contribution of Hirao and coworkers,[4] the TM-catalyzed cross-coupling of (pseudo)haloarenes with *H*-phosphonates or trialkyl

phosphites has been one of the most extensively used strategies to prepare aryl phosphonates.[5-7] Given the recent advancements in visible light photocatalysis,[8] the room temperature preparation of aryl phosphonates has also been accomplished using this methodology. In this frame, the photoinduced reductive generation of aryl radicals trapped by trisubstituted phosphites has been successfully implemented,[9] as well as the single-electron oxidation of arenes to obtain radical cations that easily add nucleophilic phosphites.[10] In addition, intensive efforts have been made recently in the development of TM-free synthesis of aryl phosphonates at room temperature. In this context, one successful approach relied on the nucleophilic addition of dialkyl phosphites to *in situ* generated arynes from 2-(trimethylsilyl)aryl triflates (Kobayashi precursors, Scheme 1a).[11] It has been also recently reported that the combination of diaryliodonium salts with phosphites can form an electron donor-acceptor complex, upon irradiation with blue light in the presence of a base, leading to the desired aryl phosphonates (Scheme 1b).[12] The photoinduced oxidation of arylhydrazines to produce aryl radicals that were trapped with trialkyl phosphites was also recently developed,[13] using an organic photocatalyst and 1,4-diazabicyclo[2.2.2]octane (DABCO) as additive under aerobic conditions (Scheme 1c). The visible light-driven generation of aryl radicals from arylazo sulfones in the absence of photocatalyst, which was trapped with triaryl phosphites, is another elegant approach recently reported (Scheme 1d).[14] Furthermore, a Sandmeyer-type reaction of *in situ* formed diazonium salts with triaryl phosphites promoted by stoichiometric amounts of *p*-toluene sulfonic acid (TsOH), has also allowed the efficient preparation of aryl phosphonates (Scheme 1e).[15] *Despite these remarkable contributions, a TM-free synthesis of aryl phosphonates at room temperature, from readily available starting materials, without stoichiometric additives or excess of reagents, is still desired.*

Given the high reactivity and low selectivity of aryl radicals, a sustained catalytic aryl radical generation is a more convenient approach for a successful synthetic transformation.[16,17] We have recently demonstrated that aryl radicals can be catalytically generated from readily available anilines that are *in situ* transformed into diazonium salts with *tert*-butyl nitrite (TBN),[18] by using salicylic acid (SA) as a catalyst at room temperature.[19] *We do think that SA is a very convenient catalyst because is inexpensive, non-toxic, and a renewable feedstock derived from natural salicin.* As part of our ongoing

program, we decided to explore these mild and environmentally benign conditions to obtain diphenyl arylphosphonates.

Scheme 1. Context of the TM-free synthesis of diaryl phosphonates

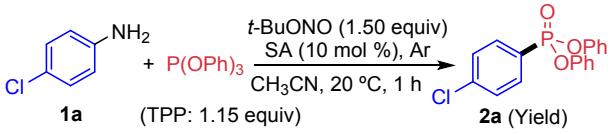


RESULTS AND DISCUSSION

Since at 60 ºC the diazonium salts can react with CH_3CN to form acetamides *via N*-arenenitrilium salts (Ritter reaction),[20] we carefully controlled the reaction temperature at 20 ºC. We were pleased to observe how the addition of 10 mol % of salicylic acid (SA) significantly accelerated the formation of phosphonate **2a** in CH_3CN (Table 1, entries 1-2). *Importantly, the reaction was complete within 1 h without preforming of the diazonium salt, and without requiring an excess of triphenyl phosphite (TPP) or any other additive.* We have seen that the presence of minor amounts of H_2O is not critical for the success of the reaction, but its addition to the reaction media was not beneficial neither (entry 3). The reaction performance was worst under air atmosphere, which is in accordance with the intermediacy of radicals, as also suggested by its complete inhibition in the presence of 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO, entries 4-5). Given the precedents in the photogeneration of aryl radicals from aryl diazonium salts,[21] we carefully checked that the ambient light was not promoting the reaction (entry 6). *Importantly, no reaction was observed using $P(OEt)_3$ (entry 7), and the addition of TPP after the formation of the*

diazonium salt was detrimental to the reaction yield (entry 8). When stoichiometric amounts of the more acidic p-TsOH were used to promote the reaction, in analogy to the conditions reported by Wang and coworkers but without preforming the diazonium salt,[15] only 38% of ***2a*** *was obtained (entry 9).*[22] We have also confirmed that with both hydroxyl groups free in the SA, the formation of **2a** is more efficient (entries 10-11). Remarkably, the reaction is complete after only 30 min under our optimal reaction conditions (entry 12 and Figure S3), and only 2 mol % of SA is enough to efficiently promote the reaction (Figure S4) with about 1 equivalent of TPP. These conditions represent a significant improvement over the method shown in Scheme 1e,[15] where 3 equivalents of TPP are required in a sequential procedure (preformation of the diazonium salt) that uses stoichiometric amounts of *p*-TsOH and needs about 8 h for completion.

Table 1. Reaction optimization and control experiments.[a]



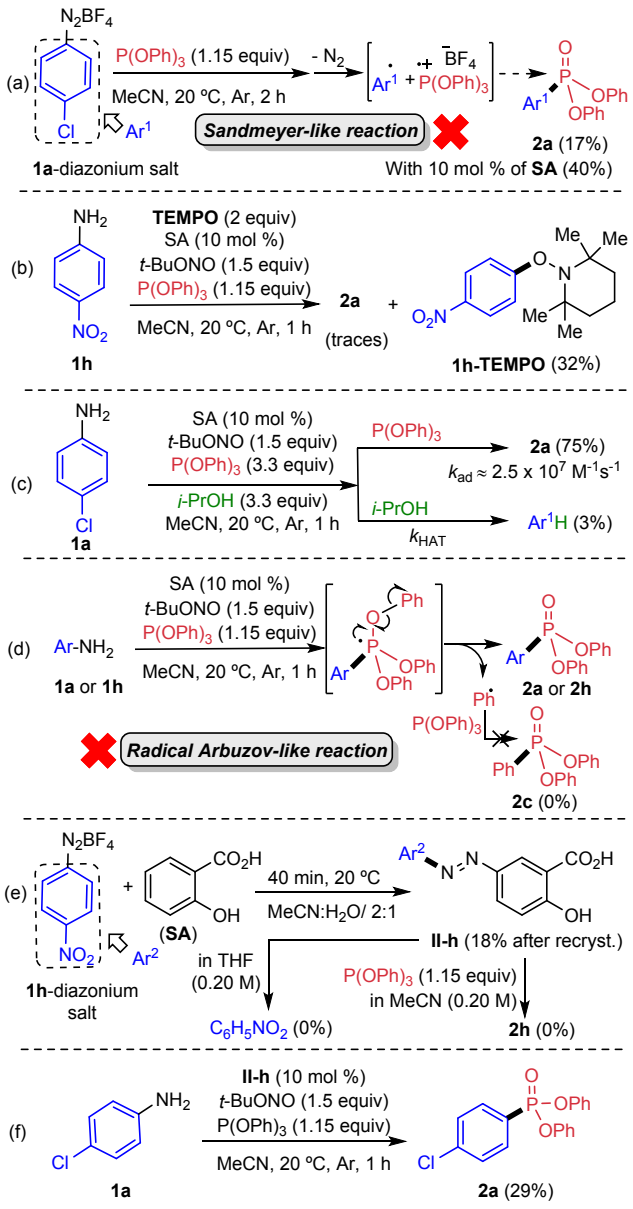
1a (TPP: 1.15 equiv) **2a** (Yield)

Entry	Deviation from above	Yield[b]
1	Without SA	27%
2	**none**	**94%**
3	in 3:1 CH_3CN: H_2O	88%
4	Without an Ar atmosphere	64%
5	+ TEMPO (2.0 equiv)	traces
6	Protected from light	93%
7	With $P(OEt)_3$ as phosphite	0%
8[c]	TPP added to the diazonium salt	45%
9	*p*-TsOH•H_2O (1.2 equiv) instead of SA	38%
10	With Methyl salicylate instead of SA	37%
11	With *O*-Acetyl SA instead of SA	48%
12	**After 30 min**	**93%**

[a]Reactions with 0.30 mmol of aniline in 1.5 mL of CH_3CN. [b]Determined by GC, using adamantane as the internal standard (Figure S1). [c]TPP was added 30 min after the other reactants.

To gather information about our arylation of TPP, we conducted a series of experiments. When the isolated pure diazonium salt of **1a** reacted with TPP in MeCN at 20 ºC, only 17% of **2a** was obtained, being improved to 40% in the presence of SA (Scheme 2a). *This experiment excludes a direct single-electron transfer (SET) between the diazonium salt and TPP as the main pathway under our optimized conditions (Sandmeyer-like reaction),[23] as proposed by Wang and coworkers under the conditions shown in Scheme 1e*.[15] The formation of diazo anhydrides (Ar-N=N-O-N=N-Ar)[24] or triazene intermediates (ArN=N-NHAr)[25] and their radical fragmentation could explain the background reaction. The *p*-nitrophenyl radical was trapped by TEMPO (Scheme 2b) and a competitive experiment in the presence of 2-propanol ($k_{HAT} \approx 10^6\ M^{-1}s^{-1}$)[26] allowed us to estimate the rate constant for the addition of the *p*-chlorophenyl radical to the TPP (Scheme 2c). This very fast reaction ($k \approx 2.2\ x10^7\ M^{-1}s^{-1}$) indicates that TPP is functioning as a very efficient radical trap under our reaction conditions, competing favorably with the other possible radical side-reactions. It has been known for a long time that phenyl radicals react very rapidly with trimethyl phosphite to give dimethyl phenylphosphonate, likely through a radical Arbuzov-like mechanism.[27] However, in a reaction of aryl radical with TPP, this pathway involves the cleavage of a stronger O-C(sp^2) bond to furnish the desired product and the phenyl radical. More importantly, this phenyl radical would eventually be trapped by TPP, and we never observed the formation of **2c** when we submitted anilines **1a** or **1h** to our reaction conditions (Scheme 2d). Trying to identify the catalytically active species of the process, we put into reacting the diazonium salt of **1h** with SA. After careful crystallization, we only isolated the azo compound **II-h** in a rather low yield (Scheme 2e).[28] However, this tan azo compound was unreactive with stoichiometric amounts of TPP, as well as in THF solution, and resulted catalytically inactive in the studied reaction (Scheme 2f).

Scheme 2. Mechanistic investigations



The redox potentials of TPP, $P(OEt)_3$ and SA were measured by cyclic voltammetry (CV, Figure S5) to examine their different reactivities (entries 2 and 7 of Table 1). Considering the experimental values obtained, the salicyloyl radical (SA$^{\bullet}$, $E^{ox}_{p/2}$ =+1.97 V vs SCE) would be able to oxidize TPP ($E^{ox}_{p/2}$ = +1.85 V vs SCE) but the oxidation of $P(OEt)_3$ is slightly unfavored ($E^{ox}_{p/2}$ = +2.04 V vs SCE). As shown in Figure 1 (left), the onset potential of the mixture of SA and TPP was found to be like the one of the SA alone, but higher current density was achieved. This result suggests that after the oxidation of the SA, an electron transfer occurs from TPP to SA$^{\bullet}$. On the contrary, when a similar experiment was conducted with $P(OEt)_3$, the onset potential for the oxidation of the mixture started at least 400 mV

before than the one of SA alone (Figure 1, right). This significant difference suggests that $P(OEt)_3$ reacts directly with SA (not with SA•), resulting in the consumption of the SA before the catalytic cycle starts.[29]

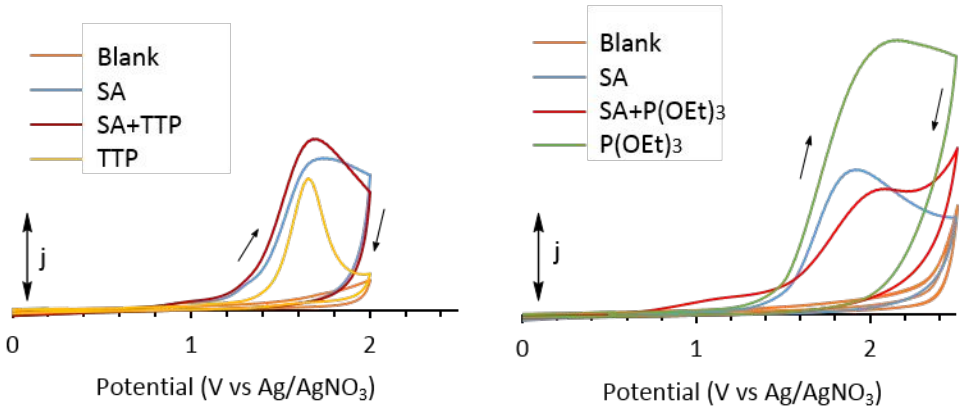
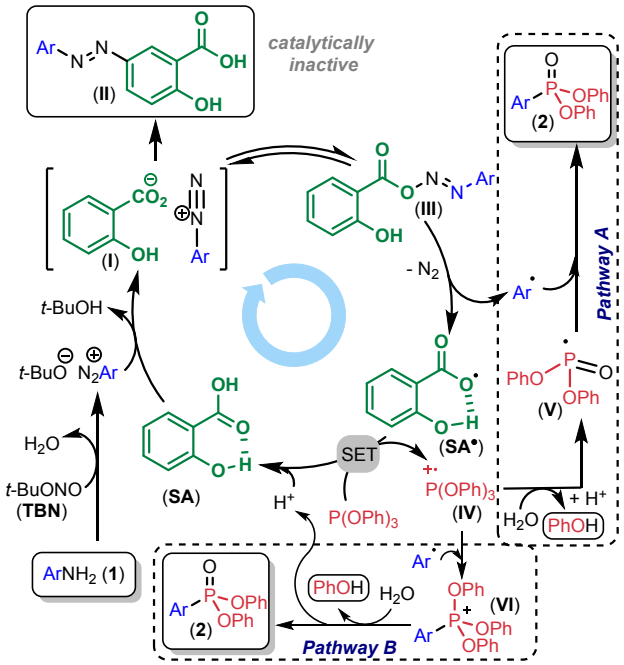


Figure 1. Cyclic voltammograms. See SI for more details.

Based on our experimental investigations and literature precedents, we propose the mechanism depicted in Scheme 3. The reaction of aniline **1** with TBN in the presence of SA would form the diazonium salt **I**. This intermediate would lead to the azo compound **II**, which is catalytically inactive, or to the aryl diazobenzoate **III**.[30] Based on literature precedents, acyloxydiazoaryls decompose easily to generate N_2 and aryl radicals.[31,32] The fragmentation of **III** would lead to the aryl radicals and to the salicyloyl radical SA•, likely stabilized by an intramolecular H-bond. We have then shown by CV measurements that the SET between TPP and SA• is feasible, enabling the turnover of the SA and producing the phosphoniumyl radical cation **IV**.[33] We speculate that hydrolysis of **IV** would produce phenol (almost 1 equiv of phenol in the formation of **2a**, see SI) and the phosphanyl radical **V**, which is stabilized by electron-donation from the two phenoxy groups and can be considered a persistent radical. We thus propose that nucleophilic radical **V** serves as an efficient trap of the aryl radicals, which are σ-sp^2 radicals and therefore more electrophilic than common π-alkyl radicals (pathway A).[34] *This highly selective cross-coupling is consistent with the reaction between a transient aryl radical and a longer-lived phosphanyl radical, being both generated at equal rates within the catalytic cycle (Persistent Radical Effect).*[35] Alternatively, aryl radical can also be trapped by the radical cation **IV** to obtain the quaternary phosphonium intermediate

VI, which after hydrolysis could provide the product **2**, with concomitant formation of phenol and deprotonation (pathway B).[14]

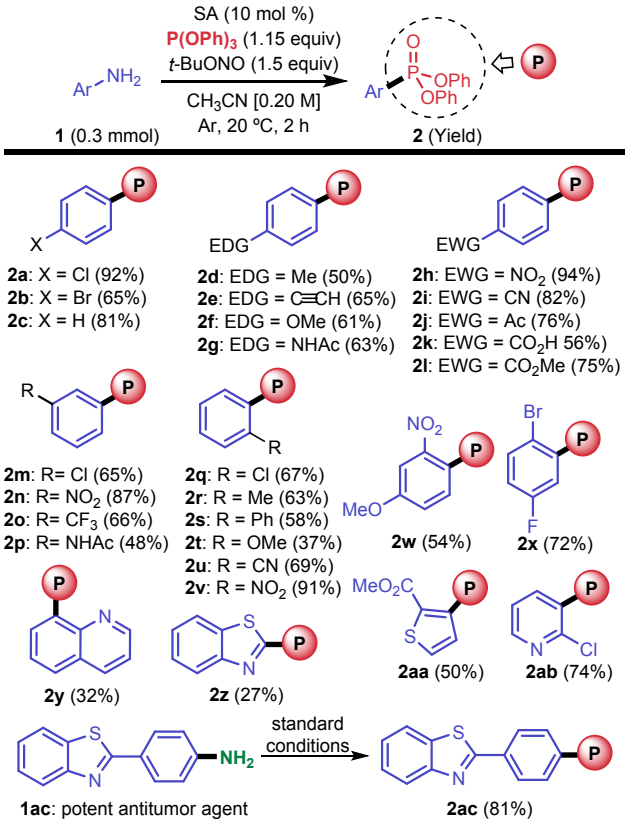
Scheme 3. Plausible mechanism



Having identified the optimal conditions for the radical arylation of TPP, we examined the scope of the reaction with diversely substituted anilines. As shown in Scheme 4, unsubstituted aniline and halogen-containing anilines at the *ortho*-, *metha*- or *para*- position, ready for further functionalization, afforded the phosphonates (**2a**, **2b**, **2c**, **2m**, **2q, 2x**) in good-to-excellent yields. Anilines bearing electron-donating groups (methyl, ethynyl, phenyl, methoxy, *N*-acetyl) were also suitable substrates, leading to the expected phosphonates (**2d-2g**, **2p, 2r-2s**) in moderate-to-good yields. However, the yield dropped when the electron-rich 2-methoxy aniline (**1t**) was used to obtain compound **2t**. On the other hand, a variety of electron-withdrawing groups in the aniline remained intact (NO_2, CN, Ac, CO_2H, CO_2Me, CF_3), affording the corresponding products in good-to-excellent yields (**2h-2l**, **2n-2o**, **2u-2v**). Electron-donating- and electron-withdrawing-groups could also be successfully combined in the same aniline, as exemplified by the product **2w**. More importantly, the reaction was not restricted to anilines since heteroaryl amines were also suitable substrates. While 8-aminoquinoline and 2-aminobenzothiazole gave the corresponding phosphonates (**2y** and **2z**) in rather low yields, the thiophene-derived **2aa** and

pyridine-phosphonate **2ab** were obtained in moderate-to-good yields. Furthermore, the 2-(4-aminophenyl)benzothiazole (**1ac**), which exhibits a potent anti-breast cancer activity,[36] was smoothly transformed into the phosphonate **2ac** under our optimized conditions.

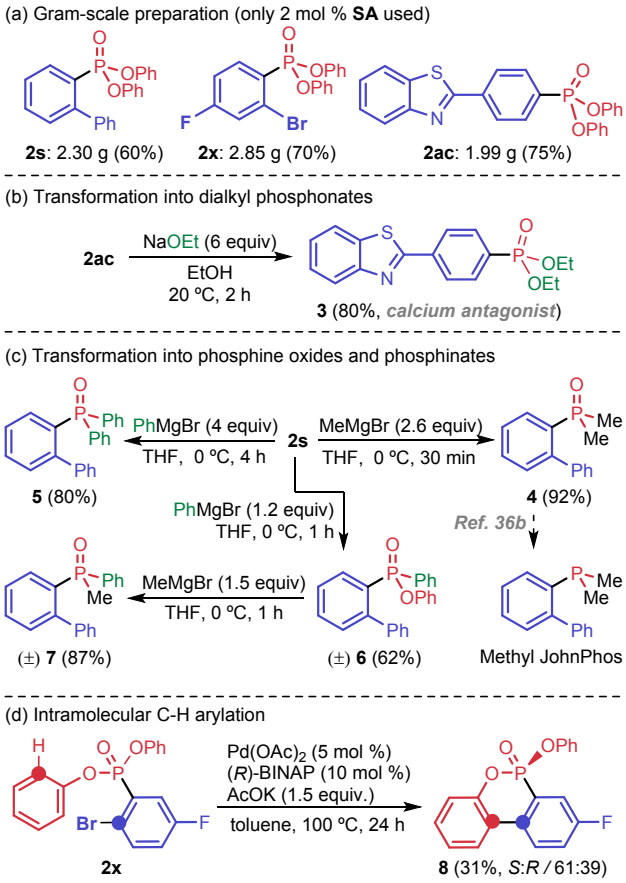
Scheme 4. Reaction scope



We further carried out the preparation of phosphonates **2s**, **2x** and **2ac** on the gram scale, using only 2 mol % of SA (Scheme 5a). Remarkably, we obtained similar yields of isolated pure products than in 0.30 mmol-scale, even after recrystallization (see SI for details). With these diphenyl arylphosphonates in gram-quantities, we explored the underexploited reactivity of this family of compounds. To overcome the limitation of this methodology to triaryl phosphites we examined the transesterification of diphenyl phosphonates into dialkyl phosphonates (Scheme 5b). This two-step protocol provided a convenient TM-free approach to the calcium channel blocker compound **3**,[37] which is analogous to the pharmaceutical fostedil. We also studied the transformation of diaryl phosphonates into phosphine derivatives since they can be used as ligands in TM catalysis and their preparation usually requires expensive and multistep procedures. It is known that the reaction of dialkyl

phosphonates with Grignard reagents is limited by Arbuzov-like decomposition of the starting material,[38a] and this limitation was recently circumvented by the use of stoichiometric amounts of NaOTf as additive.[38b] In stark contrast, we have observed that diphenyl phosphonate **2s** smoothly reacted with MeMgBr at 0 ºC, in the absence of additives, obtaining dimethyl(aryl)phosphine oxide **4** in excellent yield (Scheme 5c). Importantly, compound **4** can be easily transformed by one-step reduction into Methyl JohnPhos, a Buchwald-type ligand.[38b] Under similar conditions but using an excess of PhMgBr and longer reaction time, compound **5** was prepared in excellent yield. It is worthy of mention that compound **5** and some derivatives have been used as "platform molecules" for the Pd-catalyzed $R_2(O)P$-directed $C(sp^2)$–H activation, introducing a wide range of functionalities at the adjacent phenyl ring.[39] Moreover, by only reducing the amount of PhMgBr and running the reaction over 30 min at 0 ºC, we obtained the racemic phosphinate **6** in an unoptimized but useful synthetic yield. The reaction of this compound with MeMgBr allowed the efficient preparation of chiral, albeit racemic, tertiary phosphine oxide **7**. The results shown in Scheme 5c support diaryl phosphonates as convenient synthetic precursors for the preparation of tertiary phosphine oxides by reaction with Grignard reagents.[40] Finally, we explored an intramolecular C-H arylation reaction with diaryl phosphonate **2x** (Scheme 5d). Using (*R*)-BINAP as chiral ligand and $Pd(OAc)_2$ we obtained the *P*-chiral biaryl phosphonate **8**. Although in an unoptimized yield and enantioselectivity, this reaction demonstrates the straightforward access to chiral biaryl phosphonates in only two steps from readily available starting materials.[41]

Scheme 5. Scale-up and follow-up reactions



CONCLUSION

In summary, we have demonstrated that SA efficiently catalyzes the arylation of TPP, using readily available anilines as starting materials and TBN for the *in situ* formation of diazonium salts, without thermal or photochemical activation. Our mechanistic studies supported the intermediacy of transient aryl radicals which rapidly coupled with the longer-lived phosphanyl radical, being the SA regenerated by SET between the TPP and the SA•. The protocol was easily adapted for the gram-scale preparation of three diphenyl arylphosphonates and we examined the unique reactivity of these compounds by straightforward transformations into dialkyl phosphonates, phosphinates, phosphine oxides, and cyclic *P*-chiral biaryl phosphonates.

EXPERIMENTAL SECTION

General Remarks. Most commercial chemicals were used as obtained from Sigma-Aldrich, TCI Europe or Alfa-Aesar. However, after the long storage of TPP, it became yellow

and it was purified by washing its solution in EtOAc with a 1 M solution of NaOH. CH_3CN (for analysis, ACS) was purchased from Panreac 99.7% pure. The preparation of starting materials not obtained from commercial sources is detailed below. TLCs were performed on silica gel 60 F_{254}, using aluminum plates and visualized by exposure to ultraviolet light. Flash chromatographies (FC) were carried out on handpacked- columns of silica gel 60 (230–400 mesh). Melting points (mp) were measured in a Riecher Thermovar heating stage microscope and were not corrected. GC yields were determined by GC-FID (6890 Agilent, HP-5 30 m column), using adamantane as the internal standard. LRMS were obtained using a mass spectrometer coupled with a gas chromatographer (GC); the mobile phase was helium (2 $mL \cdot min^{-1}$); HP-1 column of 12 m was used; temperature program starts at 80 ºC for 3 min, then up to 270 ºC at a rate of 15 $ºC \cdot min^{-1}$, and 15 min at 300 ºC (unless other conditions are indicated). NMR spectra were recorded at 300 or 400 MHz for ^1H, at 75 or 101 MHz for ^{13}C, and at 122 or 202 MHz for ^{31}P, using $CDCl_3$ as solvent (unless otherwise stated). For ^1H NMR, TMS was used as an internal standard (0.00 ppm) and for ^{31}P-NMR, H_3PO_4 was the external standard used (0.00 ppm). The data are reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad signal, coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded with ^1H-decoupling $\{^1H\}$ at 101 MHz and referenced to $CDCl_3$ at 77.16 ppm. Enantiomeric ratios were determined by chiral HPLC (1100 Series Agilent Hewlett-Packard, G1311A pump, DAD G1315B detector, Chiral column AD-H Chiralpack, Particle size: 5 µm; Dimensions: 4.6 mm x 250 mm). Exact masses were determined by HRMS (Agilent 7200 de Quadrupole-Time of Flight (Q-TOF)).

Procedure for the synthesis of anilines 1g **and** 1p:[42] Into an oven-dried pressure tube was added the corresponding *N*-(nitrophenyl)acetamide (360.0 mg, 2 mmol) capped with a rubber septum and the system was evacuated and filled with Ar (3 times), then MeOH anhydrous (10 mL) was added, followed by 10% wt Pd/C (100.0 mg, 0.10 mmol) and ammonium formate (252.22 mg, 4 mmol). After 24 h at 20 ºC (water bath), the reaction mixture was filtered through a short plug of Celite, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The corresponding pure products were obtained after FC in silica gel from (50:50 hexane/EtOAc to 100% EtOAc).

N-(4-Aminophenyl)acetamide (**1g**). Compound **1g** was obtained as an off-white solid (169.1 mg, 1.12 mmol, 57 %): TLC (EtOAc 100%) R_f 0.30; ^1H-NMR (300 MHz, CD_3OD) δ

7.33 – 7.25 (m, 2H), 6.78 – 6.71 (m, 1H), 4.87 (s, 2H), 2.08 (s, 3H) ppm; ^{13}C-NMR {^{1}H} (75 MHz, CD_3OD) δ 171.6 (CO), 143.6 (C-NH_2), 132.2 (C-NHAc), 123.4 (2xCH), 117.9 (2xCH), 23.8 (Me).

N-(3-Aminophenyl)acetamide (**1p**). Compound **1p** was obtained as a pale-yellow solid (145.2 mg, 0.96 mmol, 48%): TLC (EtOAc 100%) R_f 0.42; ^{1}H-NMR (300 MHz, CD_3OD) δ 7.18 – 6.98 (m, 2H), 6.87 – 6.80 (m, 1H), 6.51 (ddd, J = 8.0, 2.3, 1.1 Hz, 1H), 4.90 (s, 2H), 2.12 (s, 3H) ppm; ^{13}C-NMR (75 MHz, CD_3OD) δ ^{13}C-NMR {^{1}H} (75 MHz) δ 171.5 (CO), 149.2 (C^3-NH_2), 140.5 (C^1-NHAc), 130.3 (C^5-H), 112.6 (C^6-H), 111.2 (C^4-H), 108.4 (C^2-H), 23.8 (Me).

4-(Benzo[d]thiazol-2-yl)aniline (**1ac**). Aniline **1ac** was synthesized by minor modifications of a reported procedure.[43] Into a pressure tube equipped with a magnetic stirrer were added 4-aminobenzoic acid (1.37 g, 10.0 mmol, 1 equiv.) and polyphosphoric acid (4 g). The reaction mixture was gently heated to obtain a homogeneous mixture, before adding 2-Aminophenol (1.04 mL, 10.0 mmol, 1 equiv.). The tube was closed with a Teflon cap and heated at 220 ºC into a san bath for 3 h. After cooling at room temperature, the reaction mixture was poured into aqueous ammonia (15 mL, 25%v/v). The precipitate was collected by filtration and washed with water (50 mL). The solid product was recrystallized from EtOH (13 mL, 60 ºC to 20 ºC) (1.358 g, 6 mmol, 60%): TLC (hexane/EtOAc 70:30) R_f 0.36; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.05 – 7.79 (m, 2H), 7.38 (dt, J = 38.0, 7.6 Hz, 1H), 6.73 (d, J = 7.9 Hz, 1H) ppm; ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$) δ 168.7 (C^5), 154.3 (C^{10a}), 149.4 (C^1-NH_2), 134.7 (C^{6a}-S), 129.3 (2xC^3-H), 126.2 (C^9-H), 124.66 (C^8-H), 124.04 (C^4), 122.6 (C^6-H), 121.5 (C^{10}-H), 114.9 (2xC^2-H) ppm.

Procedure for the synthesis of 4-chlorobenzenediazonium tetrafluoroborate (1a-diazonium salt) **and 4-nitrobenzenediazonium tetrafluoroborate** (1h-diazonium salt): The corresponding aniline (10.0 mmol) was dissolved in a 50% (w/w aqueous solution) mixture of tetrafluoroboric acid (5 mL, 39.9 mmol, 4 equiv) and water (5 mL). After cooling near to 0 ºC, a freshly-prepared solution of sodium nitrite (700 mg, 10.1 mmol) in H_2O (3 mL), was added in portions (0.25 mL each) during 10 min. The mixture was stirred for an additional 30 min and the thick precipitate formed was collected by filtration, washed with water, and dissolved in the minimal amount of acetone. The diazonium tetrafluoroborate was then precipitated by the addition of Et_2O. The solid was filtered out and dried under vacuum for

several hours. The corresponding diazonium salts were employed directly without further purification.

2-Hydroxy-5-((4-nitrophenyl)diazenyl)benzoic acid (**II-h**): Into and oven-dried round-bottom flask equipped with a magnetic stirrer, 4-nitrophenyl diazonium tetrafluoroborate (1.185 g, 5.0 mmol) and SA (690 mg, 5.0 mmol) were added. The system was evacuated and filled with argon (three times), before adding MeCN (13.20 mL) and water (6.80 mL). Then, the reaction mixture was protected from the light and was stirred for 45 min at 20 ºC (water bath). After this time, the aqueous solution was extracted with Et_2O (3x20 mL), the combined organic layer was dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure without heating. The residue was dissolved in Et_2O and precipitated by the addition of hexane. The solid was filtered out and dried *in vacuo* to give the pure product as a brick-red solid (287.2 mg, 0.90 mmol, 18 %). The spectral data matched that reported.[44]

^{1}H-NMR (500 MHz, Acetone-d_6) δ 8.56 (d, J = 2.5 Hz, 1H), 8.45 (d, J = 9.0 Hz, 2H), 8.22 (dd, J = 8.9, 2.5 Hz, 1H), 8.13 (d, J = 9.0 Hz, 2H), 7.20 (d, J = 8.9 Hz, 1H), 3.42 – 3.12 (m, 1H) ppm; ^{13}C-NMR {^{1}H} (126 MHz, Acetone) δ 172.2, 166.2, 156.7, 149.7, 146.2, 130.0, 128.7, 125.7, 124.2, 119.5, 113.8 ppm.

2,2,6,6-Tetramethyl-1-(4-nitrophenoxy)piperidine (**1h-TEMPO**). *p*-Nitroaniline (41.4 mg, 0.30 mmol), TEMPO (93.9 mg, 0.6 mmol), SA (4.14 mg, 0.04 mmol), TPP (90 µL, 0.345 mmol) and TBN (60 µL, 0.45 mmol), were put into reacting in acetonitrile (1.5 mL). The reaction mixture was then diluted with EtOAc (25 mL), transferred to a round-bottom flask, and the solvent was evaporated *in-vacuo*. The crude mixture was purified by flash column chromatography on silica gel from hexane 100% to 90:10 hexane/EtOAc obtaining the TEMPO-adduct as a white amorphous solid (26.7 mg, 0.096 mmol, 32%): TLC (hexane/EtOAc 90:10) R_f 0.65; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.14 (d, J = 9.5 Hz, 2H), 7.30 (br s, 2H), 1.65 – 1.56 (m, 5H), 1.45 – 1.42 (m, 1H), 1.24 (s, 6H), 0.98 (s, 6H) ppm; ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$) δ 168.8 (C), 141.2 (C), 125.6 (CH), 114.2 (CH), 61.0 (C), 39.8 (CH_2), 32.4 (CH_3), 20.6 (CH_3), 17.0 (CH_2) ppm; LRMS (EI-DIP) m/z (%) 278 (M^+, 11), 263 (43), 149 (20), 125 (100), 97 (40).

General Procedure (GP) for the synthesis of compounds 2: The corresponding aromatic amine (0.30 mmol) and the salicylic acid (SA, 4,14 mg, 0,03 mmol, 10 mol%) were added into an oven-dried Schlenck tube. The system was evacuated and filled with argon

(three times), then acetonitrile (1.5 mL) and the TPP (90.4 μL, 0.35 mmol) were added. The reaction mixture was stirred vigorously until a homogeneous solution was obtained. At this point, *tert*-butyl nitrite (TBN, 60 μL, 0.45 mmol) was added (the solution turned orange after some minutes) and the reaction mixture was stirred for 2 h, keeping the temperature at 20 ºC with an external water bath. For most substrates, the reaction was complete within 1 h, but we ran the reactions over 2 h to use uniform conditions. The mixture was diluted with EtOAc (25 mL), concentrated *in vacuo*, and the residue was purified by FC.

*Diphenyl (4-chlorophenyl)phosphonate (**2a**)*. Following the general procedure, compound **2a** was obtained after FC (from 98:2 hexane/EtOAc to 90:10 hexane/EtOAc) as a yellow liquid (93.18 mg, 0.27 mmol, 92%). The spectral data matched that reported:[15] TLC (hexane/EtOAc 80:20) R_f 0.40; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (dd, J = 13.6, 8.5 Hz, 2H), 7.48 (dd, J = 8.4, 3.8 Hz, 2H), 7.33-7.27 (m, 4H), 7.17 (m, 6H) ppm; ^{13}C NMR {^{1}H} (101, $CDCl_3$) δ 150.3 (d, $^2J_{C\text{-}P}$ = 7.6 Hz, 2xC$^{1'}$-H), 140.1 (d, $^4J_{C\text{-}P}$ = 4.2 Hz, C^4-Cl), 133.9 (d, $^2J_{C\text{-}P}$ = 11.4 Hz, 2xC^2-H), 130.0 (d, $^4J_{C\text{-}P}$ = 5.6 Hz, 4xC$^{3'}$-H), 129.3 (d, $^3J_{C\text{-}P}$ = 16.6 Hz, 2xC^3-H), 125.48 (d, $^1J_{C\text{-}P}$ = 195.8 Hz, C^1-P), 125.47 (2xC$^{4'}$-H), 120.7 (d, $^3J_{C\text{-}P}$ = 4.6 Hz, 4xC$^{2'}$-H) ppm; LRMS (EI) *m/z* (%) 346 (M^++2, 27) 344 (M^+, 100), 251 (M^+-OPh, 42), 77 (100). *For the numbering of the skeleton of compounds **2** used to assign the peaks in ^{13}C NMR, see the structure shown for compound **2n** as example*

*Diphenyl (4-bromophenyl)phosphonate(**2b**)*. Following the general procedure, compound **2b** was obtained after FC (from 95:5 hexane/EtOAc to 80:20 hexane/EtOAc) as a brown liquid (74.98 mg, 0.193 mmol, 65%). The spectral data matched that reported:[15] TLC (hexane/EtOAc 80:20) R_f 0.32; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86–7.76 (m, 2H), 7.67–7.61 (m, 2H), 7.36–7.22 (m, 4H), 7.21–7.12 (m, 6H) ppm; ^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ 150.3 (d, $^2J_{C\text{-}P}$= 7.5 Hz, 2xC$^{1'}$-H), 133.9 (d, $^2J_{C\text{-}P}$ = 11.2 Hz, 2xC^2-H), 132.2 (d, $^3J_{C\text{-}P}$ = 16.4 Hz, 2xC^3-H), 129.9 (4xC$^{3'}$-H), 128.7 (d, $^4J_{C\text{-}P}$ = 4.2 Hz, C^4), 126.0 (d, $^1J_{C\text{-}P}$ = 195.4 Hz, C^1-P), 125.4 (2xC$^{4'}$-H), 120.7 (d, $^3J_{C\text{-}P}$ = 4.5 Hz, 4xC$^{2'}$-H) ppm; LRMS (EI) *m/z* (%) 390 (M^++2, 100), 388 (M^+, 97), 297 (M^++2-OPh, 40) 295 (M^+-OPh, 43), 170, (28), 77 (89).

*Diphenyl phenylphosphonate (**2c**)*. Following the general procedure, compound **2c** was obtained after FC (90:10 hexane/EtOAc) as a dark orange solid (75.18 mg, 0.242 mmol, 81%). The spectral data matched that reported:[15] TLC (hexane/EtOAc 80:20) R_f 0.25; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (dd, J = 14.1, 7.5 Hz, 2H), 7.65–7.55 (m, 1H), 7.49 (td,

J = 7.5, 4.7 Hz, 2H), 7.36–7.24 (m, 4H), 7.23–7.10 (m, 6H) ppm; ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 150.5 (d, $^{2}J_{C\text{-}P}$ = 7.6 Hz) (2xC$^{1'}$), 133.3 (d, $^{4}J_{C\text{-}P}$ = 3.3 Hz) (C^{4}-H), 132.4 (d, $^{2}J_{C\text{-}P}$ = 10.3 Hz) (4xC^{2}-H), 129.8 (4xC$^{3'}$-H), 128.8 (d, $^{3}J_{C\text{-}P}$ = 15.7 Hz) (2xC^{3}-H), 127.0 (d, $^{1}J_{C\text{-}P}$ = 192.9 Hz) (C-P), 125.3 (2xC$^{4'}$-H), 120.7 (d, $^{3}J_{C\text{-}P}$ = 4.6 Hz) (4xC$^{2'}$-H) ppm; LRMS (EI) *m/z* (%) 310 (M^{+}, 78), 309 (M^{+}-H, 100), 217 (41), 170 (33), 77 (46).

*Diphenyl p-tolylphosphonate (**2d**)*. Following the general procedure, compound **2d** was obtained after FC (from 98:2 hexane/EtOAc to 95:5 hexane/EtOAc) as an orange liquid (49.7 mg, 0.15 mmol, 50%). The spectral data matched that reported:[15] TLC (hexane/EtOAc 80:20) R_f 0.50; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.77 (dd, J = 13.8, 8.1 Hz, 2H), 7.33 – 7.23 (m, 6H), 7.18 (dq, J = 7.8, 1.3 Hz, 4H), 7.13 (tt, J = 7.2, 1.1 Hz, 2H), 2.40 (s, 3H) ppm; ^{13}C NMR {^{1}H} (101, $CDCl_3$) δ 150.6 (d, $^{2}J_{C\text{-}P}$ = 7.5 Hz, 2xC$^{1'}$-H), 144.2 (d, $^{4}J_{C\text{-}P}$ = 3.5 Hz, C^{4}-Me), 132.5 (d, $^{2}J_{C\text{-}P}$ = 10.8 Hz, 2xC^{2}-H), 129.9 (4xC$^{3'}$-H), 129.6 (d, $^{3}J_{C\text{-}P}$ = 16.3 Hz, 2xC^{3}-H), 125.2 (2xC$^{4'}$-H), 123.7 (d, $^{1}J_{C\text{-}P}$ = 195.1 Hz, C^{1}-P), 120.8 (d, $^{3}J_{C\text{-}P}$ = 4.6 Hz, 4xC$^{2'}$-H), 21.9 (Me) ppm; LRMS (EI) *m/z* (%) 324 (M^{+}, 81), 323 (M^{+}-H, 100), 231 (M^{+}-OPh, 70), 77 (45).

*Diphenyl (4-ethynylphenyl)phosphonate (**2e**)*. Following the general procedure, compound **2e** was obtained after FC (from 95:10 hexane/EtOAc to 80:20 hexane/EtOAc) as a pale brown solid (65.1 mg, 0,192 mmol, 65%). The spectral data matched that reported:[15] TLC (hexane/EtOAc/AcOH 80:20) R_f 0.28; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, J = 13.8, 8.5 Hz, 1H), 7.60 (dd, J = 8.3, 4.2 Hz, 2H), 7.33 – 7.25 (m, 4H), 7.21 – 7.11 (m, 6H) ppm; ^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ 150.33 (d, $^{2}J_{C\text{-}P}$ = 7.5 Hz, C$^{1'}$), 132.29 (d, $^{3}J_{C\text{-}P}$ = 16.0 Hz, 2xC^{3}-H), 132.28 (d, $^{2}J_{C\text{-}P}$ = 10.7 Hz, 2xC^{2}-H), 129.9 (4xC$^{3'}$-H), 127.3 (d, $^{1}J_{C\text{-}P}$ = 193.8 Hz, C^{1}), 125.4 (d, $^{4}J_{C\text{-}P}$ = 1.3 Hz, 2xC$^{4'}$-H), 120.7 (d, $^{3}J_{C\text{-}P}$ = 4.5 Hz, 4xC$^{2'}$-H), 120.2 (d, $^{4}J_{C\text{-}P}$ = 4.8 Hz, C^{4}), 82.5 (d, $^{5}J_{C\text{-}P}$ = 1.8 Hz, C≡CH), 80.7 (CC-H) ppm; LRMS (EI) *m/z* (%) 334 (M^{+}, 96), 333 (M^{+}-H, 100), 241 (54), 194 (42), 77 (68).

*Diphenyl (4-methoxyphenyl)phosphonate (**2f**)*. Following the general procedure, compound **2f** was obtained after FC (from 90:10 hexane/EtOAc to 70:30 hexane/EtOAc) as a dark orange liquid (62.0 mg, 0.182 mmol, 61%). The spectral data matched that reported:[15] TLC (hexane/EtOAc 80:20) R_f 0.28; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97–7.86 (m, 2H), 7.35–7.27 (m, 4H), 7.24–7.12 (m, 6H), 7.05–6.95 (m, 2H), 3.86 (s, 3H) ppm; ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 163.6 (d, $^{4}J_{C\text{-}P}$ = 3.4 Hz, C^{4}-OMe), 150.6 (d, $^{2}J_{C\text{-}P}$ = 7.4 Hz, 2xC$^{1'}$), 134.5 (d,

$^{2}J_{C\text{-}P}$ = 11.9 Hz, 2xC^{2}-H), 129.8 (4xC$^{3'}$-H), 125.2 (2xC$^{4'}$-H), 120.7 (d, $^{3}J_{C\text{-}P}$ = 4.6 Hz, 4xC$^{2'}$-H), 117.9 (d, $^{1}J_{C\text{-}P}$ = 200.5 Hz, C^{1}-P), 114.3 (d, $^{3}J_{C\text{-}P}$ = 16.9 Hz, 2xC^{3}-H), 55.5 (O$\underline{C}$H$_3$) ppm; LRMS (EI) *m/z* (%) 340 (M$^+$, 73), 247 (M$^+$-OPh, 100), 200 (17), 77 (39).

*Diphenyl (4-acetamidophenyl)phosphonate(**2g**).* Following the general procedure, compound **2g** was obtained after FC (from 50:50 hexane/EtOAc to 100% EtOAc) as an orange sticky oil (69.0 mg, 0.19 mmol, 63%). The spectral data matched that reported:[14] TLC (hexane/EtOAc 50:50) R_f 0.32; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.81 (dd, J = 13.4, 8.4 Hz, 2H), 7.67 (dd, J = 8.4, 4.1 Hz, 2H), 7.32 – 7.16 (m, 4H), 7.17 – 7.05 (m, 6H), 2.07 (s, 3H) ppm; ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 169.5 (CO), 150.3 (d, $^{2}J_{C\text{-}P}$ = 7.5 Hz, C$^{1'}$), 143.3 (d, $^{4}J_{C\text{-}P}$ = 3.6 Hz, C^{4}-NH), 133.4 (d, $^{2}J_{C\text{-}P}$ = 11.4 Hz, 2xC^{2}-H), 129.9 (4xC$^{3'}$-H), 125.4 (2xC$^{4'}$-H), 120.73 (d, $^{3}J_{C\text{-}P}$ = 4.5 Hz, C$^{2'}$-H), 120.61 (d, $^{1}J_{C\text{-}P}$ = 198.6 Hz, C^{1}-P), 119.3 (d, J = 16.1 Hz, 2xC^{3}-H), 24.6 (NHCO$\underline{C}$H$_3$) ppm; LRMS (EI) *m/z (%)* 367 (M$^+$, 100), 325 (25), 274 (64), 232 (86).

*Diphenyl (4-nitrophenyl)phosphonate (**2h**).* Following the general procedure, compound **2h** was obtained after FC (from 95:5 hexane/EtOAc to 70:30 hexane/EtOAc) as an orange liquid (100.2 mg, 0.28 mmol, 94%). The spectral data matched that reported:[15] TLC (hexane/EtOAc 80:20) R_f 0.20; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 – 8.32 (m, 2H), 8.21 – 8.12 (m, 2H), 7.36 – 7.28 (m, 4H), 7.19 (m, 6H) ppm; ^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ 150.8 (d, $^{4}J_{C\text{-}P}$ = 4.0 Hz, C^{4}-NO$_2$), 150.0 (d, $^{2}J_{C\text{-}P}$ = 7.8 Hz, 2xC$^{1'}$), 133.91 (d, $^{1}J_{C\text{-}P}$ = 191.8 Hz, C-P), 133.73 (d, $^{2}J_{C\text{-}P}$ = 11.1 Hz, 2xC^{2}-H), 130.1 (4xC$^{3'}$-H), 126.0 (2xC$^{4'}$-H), 123.7 (d, $^{3}J_{C\text{-}P}$ = 16.1 Hz, 2xC^{3}-H), 120.6 (d, $^{3}J_{C\text{-}P}$ = 4.5 Hz, 4xC$^{2'}$-H) ppm; LRMS (EI) *m/z* (%) 355 (M$^+$, 90), 354 (M$^+$-H, 100), 308 (M$^+$-NO$_2$ 17), 262 (M$^+$-OPh, 15), 215 (37), 77 (89).

*Diphenyl (4-cyanophenyl)phosphonate (**2i**).* Following the general procedure, compound **2i** was obtained after FC (from 85:15 to 80:20 hexane/EtOAc) as pale brown solid (82.4 mg, 0.25 mmol, 82%). The spectral data matched that reported:[15]TLC (hexane/EtOAc 80:20) R_f 0.18; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13–8.02 (m, 2H), 7.84–7.76 (m, 2H), 7.36–7.27 (m, 4H), 7.21–7.14 (m, 6H) ppm; ^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ 150.0 (d, $^{2}J_{C\text{-}P}$ = 7.8 Hz, 2xC$^{1'}$), 132.89 (d, $^{2}J_{C\text{-}P}$ = 10.3 Hz, 2xC^{2}-H), 132.33 (d, $^{3}J_{C\text{-}P}$ = 15.8 Hz, 2xC^{3}-H), 132.07 (d, $^{1}J_{C\text{-}P}$ = 192.5 Hz, C^{1}-P), 130.1 (4xC$^{3'}$-H), 125.8 (d, $^{5}J_{C\text{-}P}$ = 1.4 Hz, 2xC$^{4'}$-H), 120.6 (d, $^{3}J_{C\text{-}P}$ = 4.6 Hz, 4xC$^{2'}$-H), 117.7 (d, $^{5}J_{C\text{-}P}$ = 1.3 Hz, $\underline{C}$N), 117.1 (d, $^{4}J_{C\text{-}P}$ = 3.7 Hz, C^{4}-CN) ppm; LRMS (EI) *m/z* (%) 335 (M$^+$, 79), 334 (M$^+$-1, 90), 242 (M$^+$-OPh, 19), 195 (45), 77 (100).

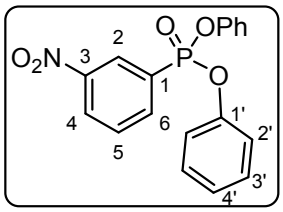
*Diphenyl (4-acetylphenyl)phosphonate (**2j**)*. Following the general procedure, compound **2j** was obtained after FC (from 85:15 to 7:3 hexane/EtOAc) as an orange liquid (79.80 mg, 0.23 mmol, 76%); The spectral data matched that reported:[15] TLC (hexane/EtOAc 80:20) R_f 0.15; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 – 7.99 (m, 4H), 7.34 – 7.26 (m, 4H), 7.22 – 7.14 (m, 6H), 2.63 (s, 3H) ppm; ^{13}C NMR {^{1}H} (75, $CDCl_3$) δ 197.4 (C=O), 150.2 (d, $^2J_{C\text{-}P}$ = 7.7 Hz, 2x$C^{1'}$), 140.5 (d, $^4J_{C\text{-}P}$ = 3.5 Hz, C^4-COMe), 132.7 (d, $^2J_{C\text{-}P}$ = 10.6 Hz, 2xC^2-H), 131.6 (d, $^1J_{C\text{-}P}$ = 191.1 Hz, C-P), 129.9 (d, $^4J_{C\text{-}P}$ = 1.1 Hz, 2x$C^{3'}$-H), 128.3 (d, $^3J_{C\text{-}P}$ = 15.9 Hz, 2xC^3-H), 125.5 (d, $^5J_{C\text{-}P}$ = 1.3 Hz, 2x$C^{4'}$-H), 120.6 (d, $^3J_{C\text{-}P}$ = 4.5 Hz, 4x$C^{2'}$-H), 26.9 ($\underline{C}H_3$) ppm; LRMS (EI) *m/z* (%) 352(M^+, 100), 259 (M^+-OPh, 33), 77 (82).

*4-(Diphenoxyphosphoryl)benzoic acid (**2k**)*. Following the general procedure, compound **2k** was obtained after FC (from 89:10:1 to 69:30:1 hexane/EtOAc/AcOH) as a pale yellow solid (59.54 mg, 0,17 mmol, 56%): TLC (hexane/EtOAc/AcOH 79:20:1) R_f 0.32; ^{1}H NMR (300 MHz, Acetone-d_6) δ 8.25 – 8.09 (m, 4H), 7.42 – 7.32 (m, 4H), 7.29 – 7.15 (m, 6H) ppm; ^{13}C NMR {^{1}H} (75 MHz, Acetone-d_6) δ 166.7 (CO_2H), 151.24 (d, $^2J_{C\text{-}P}$= 7.3 Hz, $C^{1'}$), 135.8 (d, $^4J_{C\text{-}P}$ = 3.3 Hz, C^4), 133.4 (d, $^2J_{C\text{-}P}$= 10.7 Hz, 2xC^2-H), 132.4 (d, $^1J_{C\text{-}P}$= 189.4 Hz, C^1-P), 130.74 (4x$C^{3'}$-H), 130.56 (d, $^3J_{C\text{-}P}$ = 15.8 Hz, 2xC^3-H), 126.22 (d, $^4J_{C\text{-}P}$ = 1.2 Hz, 2x$C^{4'}$-H), 121.42 (d, J = 4.6 Hz, 4x$C^{2'}$-H) ppm; ^{31}P-NMR (202 MHz, Acetone-d_6) δ 11.40 ppm; LRMS (EI) *m/z* (%) 279 (M^+-Ph, 18),167 (25), 149 (100); HRMS (EI-TOF) *m/z* calculated for $C_{19}H_{15}O_5P$ 354.0657, found 354.0652.

*Methyl 4-(diphenoxyphosphoryl)benzoate (**2l**)*. Following the general procedure, compound **2l** was obtained after FC (from 90:10 hexane/EtOAc to 80:20 hexane/EtOAc) as an orange solid (83.14 mg, 0.226 mmol, 75%): TLC (hexane/EtOAc 80:20) R_f 0.18; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20–8.13 (m, 2H), 8.09–7.98 (m, 2H), 7.34–7.24 (m, 4H), 7.21–7.12 (m, 6H), 3.95 (s, 3H) ppm; ^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ 166.1 (CO), 150.2 (d, $^2J_{C\text{-}P}$ = 7.8 Hz, 2x$C^{1'}$), 134.5 (d, $^4J_{C\text{-}P}$ = 3.2 Hz, C^4), 132.4 (d, $^2J_{C\text{-}P}$ = 10.6 Hz, 2xC^2-H), 131.5 (d, $^1J_{C\text{-}P}$ = 191.4 Hz, C^1-P), 130.0 (4x$C^{3'}$-H), 129.7 (d, $^3J_{C\text{-}P}$ = 16.0 Hz, 2xC^3-H), 125.6 (2x$C^{4'}$-H), 120.7 (d, $^2J_{C\text{-}P}$ = 4.6 Hz, $C^{2'}$-H), 52.7 ($\underline{C}H_3$-O) ppm; ^{31}P-NMR (162 MHz, $CDCl_3$) δ 10.04 ppm; LRMS (EI) *m/z* (%) 368 (M^+, 82), 367 (M^+-H, 100), 337 (M^+-OMe, 11), 275 (M^+-OPh, 29), 228 (25), 77 (50); HRMS (EI-TOF) *m/z* calculated for $C_{20}H_{17}O_5P$ 368.0814, found 368.0798.

*Diphenyl (3-chlorophenyl)phosphonate (**2m**)*. Following the general procedure compound **2m** was obtained after FC (from 90:10 to 70:30 hexane/EtOAc) as an orange solid (66.87 mg, 0.194 mmol, 65%): TLC (hexane/EtOAc 80:20) R_f 0.30; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (dt, J = 14.5, 1.6 Hz, 1H), 7.84 (ddt, J = 13.6, 7.5, 1.3 Hz, 1H), 7.59–7.54 (m, 1H), 7.44 (td, J = 7.8, 5.2 Hz, 1H), 7.35–7.10 (m, 10H) ppm; ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 150.2 (d, $^2J_{C\text{-}P}$ = 7.7 Hz, 2xC$^{1'}$), 135.2 (d, $^3J_{C\text{-}P}$ = 21.4 Hz, C^3-Cl), 133.5 (d, $^4J_{C\text{-}P}$ = 3.2 Hz, C^4-H), 132.2 (d, ^2J = 11.2 Hz, C^2-H), 130.41 (d, $^2J_{C\text{-}P}$ = 9.8 Hz, C^6-H), 130.23 (d, $^3J_{C\text{-}P}$ = 17.3 Hz, C^5-H), 129.9 (4xC$^{3'}$-H), 127.0 (d, $^1J_{C\text{-}P}$ = 254.9 Hz, C^1-P), 125.5 (2xC$^{4'}$-H), 120.7 (d, $^3J_{C\text{-}P}$ = 4.6 Hz, 4xC$^{2'}$-H) ppm; LRMS (EI) *m/z* (%) 346 (M^++2H, 34), 344 (M^+, 100), 309 (M^+-Cl, 10), 251 (M^+-OPh, 32), 77 (72); ^{31}P-NMR (162 MHz, $CDCl_3$) δ 9.30 ppm; HRMS (EI-TOF) *m/z* calculated for $C_{18}H_{14}O_3P$ (M^+-Cl) 309.0681, found 309.0675.

*Diphenyl (3-nitrophenyl)phosphonate (**2n**)*.



Following the general procedure compound **2n** was obtained after FC (from 90:10 to 80:20 hexane/EtOAc) as an orange solid (92.3 mg, 0.260 mmol, 87%). The spectral data matched that reported:[14] TLC (hexane/EtOAc 80:20) R_f 0.15; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87–8.77 (m, 1H), 8.53–8.41 (m, 1H), 8.29 (ddt, J = 13.1, 7.6, 1.3 Hz, 1H), 7.73 (ddd, J = 8.6, 7.6, 4.5 Hz, 1H), 7.36–7.28 (m, 4H), 7.23–7.15 (m, 6H) ppm; ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 150.0 (d, $^2J_{C\text{-}P}$ = 7.7 Hz, 2xC$^{1'}$), 148.2 (d, $^3J_{C\text{-}P}$ = 19.2 Hz, C^3-NO_2), 138.0 (d, $^2J_{C\text{-}P}$ = 10.3 Hz, C^6-H), 130.23 (d, ^3J = 16.3 Hz, C^5-H), 130.08 (4xC$^{3'}$-H), 129.6 (d, $^1J_{C\text{-}P}$ = 196.6 Hz, C^1-P), 127.9 (d, $^4J_{C\text{-}P}$ = 3.0 Hz, C^4-H), 127.2 (d, $^2J_{C\text{-}P}$ = 12.0 Hz, C^2-H), 125.8 (2xC$^{4'}$-H), 120.6 (d, $^3J_{C\text{-}P}$ = 4.6 Hz, 4xC$^{2'}$-H) ppm; LRMS (EI-DIP) *m/z* (%) 355 (M^+, 100), 308 (37), 262 (M^+-OPh 17), 207 (24), 77 (64).

*Diphenyl (3-(trifluoromethyl)phenyl)phosphonate (**2o**)*. Following the general procedure, compound **2o** was obtained after FC (90:10 hexane/EtOAc) as an orange liquid (75.10 mg, 0.198/ mmol, 66 %): TLC (hexane/EtOAc 80:20) R_f 0.32; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, J = 14.3 Hz 1H), 8.16 (dd, J = 13.6, 7.6 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.65 (tdt, J = 7.8, 4.3, 0.8 Hz, 1H), 7.36–7.14 (m, 10H) ppm; ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 150.2 (d, $^2J_{C\text{-}P}$ = 7.8 Hz, 2xC$^{1'}$), 135.6 (dd, $^2J_{C\text{-}P}$, $^5J_{C\text{-}F}$ = 10.0,1 Hz, C^6-H), 131.4 (dq, $^2J_{C\text{-}F}$, $^3J_{C\text{-}P}$ = 32, 16.5 Hz, C^3-CF_3), 130.01 (4xC$^{3'}$-H), 129.97 (q, $^3J_{C\text{-}F}$ = 3.6 Hz, C^4-H)129.4 (d, $^3J_{C\text{-}P}$ = 15.9 Hz, C^5-H), 129.3 (dq, $^4J_{C\text{-}P}$, $^3J_{C\text{-}F}$ = 8.6, 3.8 Hz, C^2-H), 126.7 (d, ^1J = 186.2 Hz,

C[1]-P), 125.6 (d, $^{5}J_{C\text{-}P}$ = 1.4 Hz ,2xC[4']-H), 123.5 (qd, $^{1}J_{C\text{-}F}$, $^{4}J_{C\text{-}P}$ = 272, 3 Hz, CF_3), 120.7 (d, $^{3}J_{C\text{-}P}$ = 4.5 Hz, 4xC[2']-H) ppm; ^{31}P-NMR (122 MHz, $CDCl_3$) δ 8.10 ppm; LRMS (EI) *m/z* (%) 378 (M^+, 100), 377 (M^+-H, 98), 285 (28), 238 (45), 77 (85); HRMS (EI-TOF) *m/z* calculated for $C_{19}H_{14}F_3O_3P$ 378.0633, found 378.0615.

*Diphenyl (3-acetamidophenyl)phosphonate (**2p**)*. Following the general procedure, compound **2p** was obtained after FC (from 50:50 hexane/EtOAc to 100% EtOAc) as an orange sticky oil (53.0 mg, 0.144 mmol, 48 %). The spectral data matched that reported:[15] TLC (hexane/EtOAc 50:50): R_f 0.45; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.42 – 8.35 (m, 1H), 7.91 (dt, *J* = 16.0, 1.8 Hz, 1H), 7.60 (ddt, *J* = 13.4, 7.6, 1.3 Hz, 1H), 7.47 (td, *J* = 7.9, 5.6 Hz, 1H), 7.35 – 7.20 (m, 4H), 7.17 – 7.01 (m, 6H), 1.86 (s, 3H) ppm; ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 169.5 (CONHAr), 150.2 (d, $^{2}J_{C\text{-}P}$ = 7.7 Hz, 2xC[2']), 139.7 (d, $^{3}J_{C\text{-}P}$ = 20.2 Hz, C[3]-NHAc), 129.9 (4xC[3']-H), 128.6 (d, $^{1}J_{C\text{-}P}$ = 227.0 Hz, C[1]-P), 126.5 (d, $^{2}J_{C\text{-}P}$ = 8.8 Hz, C[6]-H), 125.6 (2xC[4']-H), 124.6 (C[4]-H), 123.3 (d, $^{3}J_{C\text{-}P}$ = 13.5 Hz, C[5]-H), 120.8 (d, $^{3}J_{C\text{-}P}$ = 4.3 Hz, 4xC[2']-H), 24.2 (NHCO$\underline{C}H_3$) ppm; LRMS (EI) *m/z (%)* 367 (M^+, 48), 325 (100), 232 (15).

*Diphenyl (2-chlorophenyl)phosphonate (**2q**)*. Following the general procedure, compound **2q** was obtained after FC (from 95:5 to 80:20 hexane/EtOAc) as an orange liquid (69,1 mg, 0.20 mmol, 67%). The spectral data matched that reported:[15] TLC (hexane/EtOAc 80:20) R_f 0.28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.09 (m, 1H), 7.57 – 7.47 (m, 2H), 7.41 – 7.32 (m, 1H), 7.34 – 7.21 (m, 8H), 7.19 – 7.11 (m, 2H) ppm; ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 150.3 (d, $^{2}J_{C\text{-}P}$ = 7.6 Hz, C[1']), 137.1 (d, $^{2}J_{C\text{-}P}$ = 2.9 Hz, C[2]-Cl), 137.0 (d, $^{3}J_{C\text{-}P}$ = 8.9 Hz, C[3]-H), 134.7 (d, $^{4}J_{C\text{-}P}$ = 2.7 Hz, C[4]-H), 131.2 (d, $^{2}J_{C\text{-}P}$ = 10.8 Hz, C[6]-H), 129.8 (4xC[3']-H), 126.8 (d, $^{3}J_{C\text{-}P}$ = 14.7 Hz, C[5]-H), 125.9 (d, $^{1}J_{C\text{-}P}$ = 196.5 Hz, C[1]-P), 125.4 (2xC[4']-H), 120.7 (d, $^{2}J_{C\text{-}P}$ = 4.7 Hz, 4xC[2']-H) ppm; LRMS (EI-DIP) *m/z* (%) 346 (M^++2, 21), 344 (M^+, 86), 309 (M^+-Cl, 72), 215 (82), 77 (100).

*Diphenyl o-tolylphosphonate (**2r**)*. Following the general procedure, compound **2r** was obtained after FC (from 95:5 to 85:15 hexane/EtOAc) as an orange liquid. (60.8 mg, 0.19 mmol, 63%). The spectral data matched that reported:[15] TLC (hexane/EtOAc 80:20) R_f 0.28: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (ddd, J = 15.2, 7.7, 1.3 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.35 – 7.09 (m, 13H), 2.76 (d, J = 1.8 Hz, 3H) ppm; ^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ 150.5 (d, $^{2}J_{C\text{-}P}$ = 7.8 Hz, 2xC[1']), 142.2 (d, $^{2}J_{C\text{-}P}$ = 10.6 Hz, C[2]-Me), 134.5 (d, $^{2}J_{C\text{-}P}$ = 11.1 Hz,

C^6-H), 133.4 (d, $^4J_{C\text{-}P}$ = 3.1 Hz, C^4-H), 131.6 (d, $^3J_{C\text{-}P}$ = 15.8 Hz, C^3-H), 129.8 (4xC$^{3'}$-H), 125.79 (d, $^3J_{C\text{-}P}$ = 15.8 Hz, C^5-H), 125.73 (d, $^1J_{C\text{-}P}$ = 188.6 Hz, C-P), 125.1 (d, $^5J_{C\text{-}P}$ = 1.2 Hz, 2xC$^{4'}$-H), 120.5 (d, $^3J_{C\text{-}P}$ = 4.6 Hz, 4xC$^{2'}$-H), 21.6 (d, $^3J_{C\text{-}P}$ = 3.6 Hz, C$\underline{\text{H}}_3$) ppm; LRMS (EI) *m/z* (%) 324 (M$^+$, 100), 288 (18), 231 (25), 212 (30), 77 (54).

*Diphenyl [1,1'-biphenyl]-2-ylphosphonate (**2s**)*. Following the general procedure, compound **2s** was obtained after FC (from 95:5 to 80:20 hexane/EtOAc) and further purified by recrystallization from *i*-PrOH as an orange crystalline solid (67.2 mg, 0.174 mmol, 58%): TLC (hexane/EtOAc 80:20) R_f 0.30; mp (*i*-PrOH) 93-95 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 – 8.27 (m, 1H), 7.65 (tt, J = 7.6, 1.6 Hz, 1H), 7.54 (dtd, J = 7.6, 3.8, 1.4 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.45 – 7.38 (m, 4H), 7.25 – 7.17 (m, 4H), 7.13 – 7.05 (m, 2H), 6.93 – 6.86 (m, 4H); ^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ 150.5 (d, $^2J_{C\text{-}P}$ = 8.4 Hz, 2xC$^{1'}$), 146.6 (d, $^2J_{C\text{-}P}$ = 10.0 Hz, C^2), 141.2 (d, $^3J_{C\text{-}P}$ = 4.2 Hz, C^7), 134.6 (d, ^2J = 10.8 Hz, C^6-H), 133.0 (d, $^4J_{C\text{-}P}$ = 3.1 Hz, C^4-H), 131.9 (d, $^3J_{C\text{-}P}$ = 14.9 Hz, C^5-H), 129.7 (2xC^9-H), 129.6 (4xC$^{3'}$-H), 127.8 (C^{10}-H), 127.8 (2xC^8-H), 127.2 (d, $^3J_{C\text{-}P}$= 15.6 Hz, C^3-H), 125. 9 (d, $^1J_{C\text{-}P}$ = 192.4 Hz, C^1-P), 124.9 (d, $^5J_{C\text{-}P}$ = 1.2 Hz, 2xC$^{4'}$-H), 120.5 (d, $^2J_{C\text{-}P}$ = 4.8 Hz, 4xC$^{2'}$-H) ppm; ^{31}P-NMR (122 MHz, $CDCl_3$) δ 11.43 ppm; LRMS (EI-DIP) *m/z* (%) 386 (M$^+$, 42), 293 (M$^+$-OPh), 199 (100); HRMS (ESI-TOF) *m/z* calculated for $C_{24}H_{19}O_3P$ 386.1072, found 386.1071.

*Diphenyl (2-methoxyphenyl)phosphonate (**2t**)*. Following the general procedure, compound **2t** was obtained after FC (from 75:25 to 65:35 hexane/EtOAc) as a brown liquid (37.1 mg, 0.11 mmol, 37%). The spectral data matched that reported:[44] TLC (hexane/EtOAc 80:20) R_f 0.13; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (ddd, J = 15.7, 7.6, 1.8 Hz, 1H), 7.54 (dddd, J = 8.4, 7.4, 1.8, 0.9 Hz, 1H), 7.33 – 7.26 (m, 11H), 7.26 – 7.14 (m, 1H), 7.06 – 6.89 (m, 1H), 3.87 (s, 3H) ppm; ^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ 161.5 (d, $^2J_{C\text{-}P}$ = 2.5 Hz, C^2-OMe), 150.8 (d, $^2J_{C\text{-}P}$ = 7.5 Hz, 2xC$^{1'}$), 135.9 (d, $^3J_{C\text{-}P}$ = 7.9 Hz, C^3-H), 135.5 (d, $^2J_{C\text{-}P}$ = 2.2 Hz, C^6-H), 129.7 (d, $^3J_{C\text{-}P}$ = 1.0 Hz, 4xC$^{3'}$-H), 125.0 (d, $^4J_{C\text{-}P}$ = 1.3 Hz, 2xC$^{4'}$-H), 120.8 (d, $^2J_{C\text{-}P}$ = 4.6 Hz, 4xC$^{2'}$-H), 120.55 (C^4-H), 115.0 (d, $^1J_{C\text{-}P}$ = 192.2 Hz, C^1-P), 111.4 (d, $^3J_{C\text{-}P}$ = 9.9 Hz, C^5-H), 55.9 (O$\underline{\text{C}}$H$_3$) ppm; LRMS (EI-DIP) *m/z* (%) 340 (M$^+$, 27), 309 (M$^+$-OMe, 11), 247 (M$^+$-OPh, 100), 215 (49), 77 (42).

*Diphenyl (2-cyanophenyl)phosphonate (**2u**)*. Following the general procedure, compound **2u** was obtained after FC (80:20 hexane/EtOAc) as a pale orange solid (69.5 mg, 0.207 mmol, 69%). The spectral data matched that reported:[14] TLC (hexane/EtOAc 80:20) *Rf* 0.15; ^{1}H

NMR (300 MHz, $CDCl_3$) δ 8.31–8.21 (m, 1H), 7.91–7.84 (m, 1H), 7.78–7.66 (m, 2H), 7.39–7.23 (m, 8H), 7.21–7.09 (m, 2H) ppm; ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 150.1 (d, $^2J_{C\text{-}P}$ = 8.1 Hz, 2x$C^{1'}$), 135.7 (d, $^2J_{C\text{-}P}$ = 9.5 Hz, C^6-H), 134.8 (d, $^3J_{C\text{-}P}$ = 11.4 Hz, C^3-H), 133.5 (d, $^4J_{C\text{-}P}$ = 2.7 Hz, C^4-H), 132.6 (d, $^3J_{C\text{-}P}$ = 14.9 Hz, C^5-H), 130.0 (d, $^1J_{C\text{-}P}$ = 193.1 Hz, C^1-P), 129.9 (4x$C^{3'}$-H), 125.6 (2x$C^{4'}$-H), 120.6 (d, $^3J_{C\text{-}P}$ = 4.6 Hz, 4x$C^{2'}$-H), 117.1 (d, $^3J_{C\text{-}P}$ = 5.9 Hz, CN), 115.0 (d, $^2J_{C\text{-}P}$ = 4.7 Hz, C^2-CN) ppm; LRMS (EI-DIP) *m/z* (%) 335 (M^+, 100), 242 (M^+-OPh, 33), 195 (55), 170 (17), 77 (51).

*Diphenyl (2-nitrophenyl)phosphonate (**2v**)*. Following the general procedure, compound **2v** was obtained after FC (from 98:2 to 50:50 hexane/EtOAc) as a brown solid (96.9 mg, 0.273 mmol, 91%): TLC (hexane/EtOAc 80:20) R_f 0.18; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35–8.23 (m, 1H), 8.02 (ddd, J = 7.5, 6.2, 1.6 Hz, 1H), 7.82–7.68 (m, 2H), 7.35–7.12 (m, 10H) ppm; ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 151.9 (C^2-NO_2), 150.3 (d, $^2J_{C\text{-}P}$ = 8.3 Hz, 2x$C^{1'}$), 136.3 (d, $^2J_{C\text{-}P}$ = 6.6 Hz, C^6-H), 134.3 (d, $^4J_{C\text{-}P}$ = 2.7 Hz, C^4-H), 132.8 (d, $^3J_{C\text{-}P}$ = 13.9 Hz, C^5-H), 129.9 (4x$C^{3'}$-H), 125.6 (2x$C^{4'}$-H), 124.9 (d, $^3J_{C\text{-}P}$ = 8.9 Hz, C^3-H), 121.9 (d, $^1J_{C\text{-}P}$ = 196.9 Hz, C^1-P), 120.7 (d, $^3J_{C\text{-}P}$ = 4.6 Hz, 4x$C^{2'}$-H) ppm; ^{31}P-NMR (162 MHz, $CDCl_3$) δ 4.70 ppm; LRMS (EI-DIP) *m/z* (%) 355 (M^+, 6), 262 (M^+-OPh, 100), 232 (64), 207 (36); HRMS (EI-TOF) *m/z* calculated for $C_{18}H_{14}NO_5P$ 355.0610, found 355.0619.

*Diphenyl (4-methoxy-2-nitrophenyl)phosphonate (**2w**)*. Following the general procedure, compound **2w** was obtained after FC (from 90:10 to 70:30 hexane/EtOAc) as a pale orange oil (62.4 mg, 0,162 mmol, 54%): TLC (hexane/EtOAc/AcOH 80:20) R_f 0.20; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (dd, J = 14.7, 8.7 Hz, 1H), 7.50 (dd, J = 5.3, 2.5 Hz, 1H), 7.33 – 7.25 (m, 4H), 7.24 – 7.07 (m, 7H), 3.91 (s, 3H) ppm; ^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ 163.8 (d, $^4J_{C\text{-}P}$ = 3.0 Hz, C^4-OMe), 153.3 (d, $^2J_{C\text{-}P}$ = 3.9 Hz, C^2-NO_2), 150.3 (d, $^2J_{C\text{-}P}$ = 8.1 Hz, 2x$C^{1'}$), 138.0 (d, $^3J_{C\text{-}P}$ = 7.8 Hz, C^3-H), 129.8 (d, $^4J_{C\text{-}P}$ = 1.0 Hz, 4x$C^{3'}$-H), 125.4 (d, $^5J_{C\text{-}P}$ = 1.4 Hz, 2x$C^{4'}$-H), 120.6 (d, $^3J_{C\text{-}P}$ = 4.7 Hz, 4x$C^{2'}$-H), 117.4 (d, $^3J_{C\text{-}P}$ = 14.8 Hz, C^5-H), 112.5 (d, $^1J_{C\text{-}P}$ = 204.3 Hz, C^1-P), 111.2 (d, $^2J_{C\text{-}P}$ = 9.9 Hz, C^6-H), 56.3 ($O\underline{C}H_3$); ^{31}P-NMR (162 MHz, $CDCl_3$) δ 5.55 ppm; LRMS (EI) m/z (%) 385 (M^+, 3), 355 (M^+-OMe, 7), 292 (M^+-OPh, 100), 262 (24); HRMS (ESI-TOF) *m/z* calculated for $C_{19}H_{16}NO_6P$ 385.0715, found 385.0716.

*Diphenyl (2-bromo-5-fluorophenyl)phosphonate (**2x**)*. Following the general procedure, compound **2x** was obtained after FC (from 90:10 to 80:20 hexane/EtOAc) as a pale orange

crystalline solid. (87.5 mg, 0.216 mmol, 72%): TLC (hexane/EtOAc 80:20) R_f 0.20; mp (*i*-PrOH/hexane 3:1) 64-66 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (ddd, J = 16.1, 8.4, 3.2 Hz, 1H), 7.69 (ddd, J = 8.7, 6.5, 4.7 Hz, 1H), 7.36 – 7.23 (m, 8H), 7.21 – 7.10 (m, 3H); ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 161.4 (dd, J = 250.9, 20.7 Hz, C^5-F), 150.2 (d, J = 7.6 Hz, 2xC$^{1'}$), 136.4 (dd, J = 14.0, 7.3 Hz, C^3-H), 130.2 (dd, J = 197.7, 6.2 Hz, C^1-P), 129.9 (4xC$^{3'}$-H), 125.6 (2xC$^{4'}$-H), 124.5 (dd, J = 24.6, 9.9 Hz, C^6-H), 121.9 (dd, J = 22.2, 3.1 Hz, C^4-H), 120.6 (d, J = 4.7 Hz, 4xC$^{2'}$-H), 119.6 (t, J = 3.5 Hz, C^2-Br) ppm; ^{31}P-NMR (202 MHz, $CDCl_3$) δ 6.11 (d, J = 7.1 Hz) ppm; LRMS (EI) *m/z* (%) 408 (M^++2 ,56), 406 (M^+, 58), 327 (M^+-Br, 50), 233 (46), 77 (100); HRMS (EI-TOF) *m/z* calculated for $C_{18}H_{13}BrFO_3P$ 405.977, found 405.9773.

*Diphenyl quinolin-8-ylphosphonate (**2y**).* Following the general procedure, compound **2y** was obtained after FC (from 90:10 to 70:30 hexane/EtOAc) as a dark brown solid (34.7 mg, 0.096 mmol, 32%): TLC (hexane/EtOAc/AcOH 80:20) R_f 0.12; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.15 (dd, J = 4.3, 1.7 Hz, 1H), 8.54 (ddd, J = 16.9, 7.1, 1.5 Hz, 1H), 8.24 (dt, J = 8.3, 2.1 Hz, 1H), 8.07 (dt, J = 8.2, 1.5 Hz, 1H), 7.62 (ddd, J = 8.2, 7.1, 3.9 Hz, 1H), 7.53 (dd, J = 8.3, 4.2 Hz, 1H), 7.25 (d, J = 4.4 Hz, 8H), 7.10 (tdd, J = 6.4, 3.2, 1.8 Hz, 2H) ppm; ^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ 151.4 (C^2-H), 150.9 (d, $^2J_{C\text{-}P}$ = 7.5 Hz, 2xC$^{1'}$), 148.0 (d, J = 1.2 Hz, C^{8a}), 146.5 (d, J = 205.0 Hz, C^8), 138.3 (d, J = 8.5 Hz, C^4-H), 134.1 (d, J = 3.4 Hz, C^5-H), 129.6 (C$^{3'}$), 128.4 (d, $^2J_{C\text{-}P}$ = 11.3 Hz, C^7-H), 127.5 (C^{4a}), 125.9 (d, J = 17.1 Hz, C^6-H), 125.0 (d, J = 1.4 Hz, C$^{4'}$-H), 122.1 (C^3-H), 121.0 (d, J = 4.6 Hz, C$^{2'}$-H) ppm; ^{31}P-NMR (122 MHz, $CDCl_3$) δ 10.7 ppm; LRMS (EI-DIP) *m/z* (%) 361 (M^+, 6), 268 (M^+-OPh, 100), 192 (12); HRMS (EI-TOF) *m/z* calculated for $C_{21}H_{16}NO_3P$ 361.0868, found 361.0854.

*Diphenyl benzo[d]thiazol-2-ylphosphonate (**2z**).* Following the general procedure, compound **2z** was obtained after FC (from 90:10 to 70:30 hexane/EtOAc) as a pale pale yellow oil (29.7 mg, 0,081 mmol, 27%): TLC (hexane/EtOAc/AcOH 80:20) R_f 0.21; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, J = 8.4, 1.0 Hz, 1H), 8.01 (ddd, J = 7.9, 1.4, 0.8 Hz, 1H), 7.66 – 7.52 (m, 2H), 7.37 – 7.27 (m, 8H), 7.23 – 7.14 (m, 2H) ppm; ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 157.9 (d,$^1J_{C\text{-}P}$ = 251.2 Hz, C^2), 154.6 (d, $^3J_{C\text{-}P}$ = 30.6 Hz, C^{3a}-N), 150.0 (d, $^2J_{C\text{-}P}$ = 7.6 Hz, C$^{1'}$), 136.9 (C^{7a}), 130.0 (4xC$^{3'}$-H), 127.6 (C^5-H), 127.3 (C^6-H), 125.9 (C^7-H), 125.5 (C^4-H), 122.2 (d, $^5J_{C\text{-}P}$ = 1.9 Hz, 2xC$^{4'}$-H), 120.9 (d, $^4J_{C\text{-}P}$= 4.6 Hz, 4xC$^{2'}$-H) ppm;

^{31}P-NMR (122 MHz, $CDCl_3$) δ -10.28 ppm; LRMS (EI-DIP) *m/z* (%) 367 (M^+, 8), 303 (21), 207 (100); HRMS (EI-TOF) *m/z* calculated for $C_{19}H_{14}NO_3PS$ 367.0432, found 367.0407.

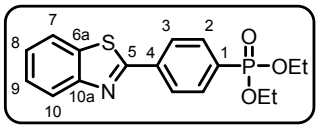
*Methyl 3-(diphenoxyphosphoryl)tiophene-2-carboxylate (**2aa**)*. Following the general procedure, compound **2aa** was obtained after FC (from 90:10 to 70:30 hexane/EtOAc) as an orange liquid (56.2 mg, 0.15 mmol, 50%): TLC (hexane/EtOAc 80:20) *Rf* 0.10; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (t, J = 5.0 Hz, 1H), 7.57 (dd, J = 5.0, 3.4 Hz, 1H), 7.34–7.25 (m, 4H), 7.25–7.19 (m, 4H), 7.18–7.10 (m, 2H), 3.90 (s, 3H) ppm; ^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ 160.8 (CO_2Me), 150.6 (d, $^2J_{C\text{-}P}$ = 8.0 Hz, 2xC$^{1'}$-H), 140.3 (d, $^2J_{C\text{-}P}$ = 15.0 Hz, C^2), 134.7 (d, $^2J_{C\text{-}P}$ = 15.4 Hz, C^4-H), 132.2 (d, $^1J_{C\text{-}P}$ = 201.4 Hz, C^2-P), 130.9 (d, $^3J_{C\text{-}P}$ = 20.8 Hz, C^5-H), 129.8 (4xC$^{3'}$-H), 125.3 (2xC$^{4'}$-H), 120.7 (d, $^3J_{C\text{-}P}$ = 4.7 Hz, 4xC$^{2'}$-H), 53.0 (O-$\underline{C}$H$_3$) ppm; ^{31}P-NMR (162 MHz, $CDCl_3$) δ 11.40 ppm; LRMS (EI) *m/z* (%) 374 (M^+,1), 343 (M^+-OMe, 4), 281 (M^+-OPh, 100), 77 (6); HRMS (EI-TOF) *m/z* calculated for $C_{17}H_{12}O_4PS$ 343.0194 (M^+-OMe), found 343.0164.

*Diphenyl (2-chloropyridin-3-yl)phosphonate (**2ab**)*. Following the general procedure, compound **2ab** was obtained after FC (from 95:5 to 70:30 hexane/EtOAc) as an orange liquid (76.75 mg, 0.22 mmol, 74 %). The spectral data matched that reported:[14] TLC (hexane/EtOAc 80:20) R_f 0.10; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (dt, J = 4.6, 2.2 Hz, 1H), 8.44 (ddd, J = 14.7, 7.6, 2.1 Hz, 1H), 7.38 – 7.22 (m, 9H), 7.19 – 7.12 (m, 2H) ppm; ^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ 153.6 (C^6), 153.1 (d, $^2J_{C\text{-}P}$ = 5.8 Hz, C^2-H), 150.0 (d, $^2J_{C\text{-}P}$ = 7.7 Hz, C$^{1'}$), 146.1 (d, $^2J_{C\text{-}P}$ = 8.6 Hz, C^4-H), 129.9 (4xC$^{3'}$-H), 125.7 (d, $^4J_{C\text{-}P}$ = 1.4 Hz, 2xC$^{4'}$-H), 123.5 (d, $^1J_{C\text{-}P}$ = 186.7 Hz, C^3-P), 122.2 (d, $^3J_{C\text{-}P}$ = 10.9 Hz, C^5-H), 120.6 (d, $^2J_{C\text{-}P}$ = 4.7 Hz, C$^{2'}$-H); LRMS (EI-DIP) *m/z* (%) 347 (M^++2, 21), 345 (M^+, 82), 310 (M^+-Cl, 62), 169 (100).

*Diphenyl (4-(benzo[d]thiazol-2-yl)phenyl)phosphonate (**2ac**)*. Following the general procedure, compound **2ac** was obtained after FC (from 90:10 to 80:20 hexane/EtOAc) as a crystalline pale yellow solid (107.6 mg, 0.24 mmol, 81 %): TLC (hexane/EtOAc 80:20) R_f 0.36; mp (hexane/EtOAc 4:1) 133-135 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 – 8.19 (m, 2H), 8.14 – 8.04 (m, 3H), 7.92 (dt, J = 7.9, 0.9 Hz, 1H), 7.53 (ddd, J = 8.3, 7.2, 1.3 Hz, 1H), 7.43 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 7.35 – 7.27 (m, 4H), 7.25 – 7.11 (m, 6H) ppm; ^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ 166.3 (C^5), 154.1 (C^{10a}-N), 150.3 (d, $^2J_{C\text{-}P}$ = 7.5 Hz, 2xC$^{1'}$), 137.8 (d, $^2J_{C\text{-}P}$ = 3.5 Hz, C^4), 135.3 (C^{6a}-S), 133.1 (d, $^2J_{C\text{-}P}$ = 10.6 Hz, 2xC^2-H), 129.93 (4xC$^{3'}$-H),

129.24 (d, $^{2}J_{C\text{-}P}$ = 192.9 Hz, C^{1}), 127.6 (d, $^{2}J_{C\text{-}P}$ = 16.0 Hz, 2xC^{3}-H), 126.8 (C^{8}-H), 126.0 (C^{9}-H), 125.4 (2x$C^{4'}$-H), 123.7 (C^{7}-H), 121.9 (C^{10}-H), 120.7 (d, $^{2}J_{C\text{-}P}$ = 4.4 Hz, 4x$C^{2'}$-H) ppm; ^{31}P-NMR (162 MHz, $CDCl_3$) δ 10.32 ppm; LRMS (EI-DIP) *m/z* (%) 443 (M^+, 98), 350 (M^+-OPh, 100), 77; HRMS (EI-TOF) *m/z* calculated for $C_{25}H_{18}NO_3PS$ 443.0745, found 443.074.

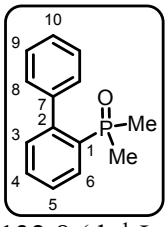
*Diethyl (4-(benzo[d]thiazol-2-yl)phenyl)phosphonate (**3**).* The phosphonate **2ac** (443.5 mg, 1.00 mmol) was added into a flame-dried round bottom flask, and the system was evacuated and filled with argon (three times). EtOH (3 mL, 99.9 %) was then added and the mixture was stirred until a homogeneous solution was obtained. Then, freshly prepared NaOEt (3 mL, 2 M, 6 equiv) was added dropwise, while stirring at 20 ºC (external water bath). After 2 h, NaOH (40 mL, 1 M) was added to the reaction mixture and it was extracted with Et_2O (3x20 mL). The combined organic layers were dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was purified by FC on silica gel (from 90:10 to 70:30 hexane/EtOAc), to obtain the pure product as a pale yellow solid (277.5 mg, 0.80 mmol, 80%). The spectral data matched that reported.[45]



TLC (hexane/EtOAc 80:20) R_f 0.24; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.22 – 8.15 (m, 2H), 8.11 (ddd, *J* = 8.2, 1.3, 0.6 Hz, 1H), 7.98 – 7.88 (m, 3H), 7.52 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.42 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 4.26 – 4.01 (m, 4H), 1.34 (td, *J* = 7.1, 0.6 Hz, 6H); ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$) δ 166.7 (C^{5}), 153.9 (C^{10a}-N), 137.0 (C^{4}), 135.2 (C^{6a}-S), 132.6 (d, $^{2}J_{C\text{-}P}$ = 10.1 Hz, 2xC^{2}-H), 131.1 (d, $^{1}J_{C\text{-}P}$ = 188.3 Hz, C^{1}-P), 127.6 (d, $^{3}J_{C\text{-}P}$ = 15.2 Hz, 2xC^{3}-H), 126.8 (C^{8}-H), 125.92 (C^{9}-H), 123.6 (C^{7}-H), 121.9 (C^{10}-H), 62.5 (d, $^{2}J_{C\text{-}P}$ = 5.5 Hz, O-CH_2), 16.5 (d, $^{3}J_{C\text{-}P}$ = 6.5 Hz, $\underline{C}H_3$).

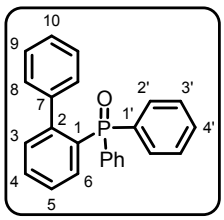
*[1,1'-Biphenyl]-2-yldimethylphosphine oxide (**4**).* Phosphonate **2s** (115.92 mg, 0.30 mmol) was added into a flame-dried round bottom flask equipped with a magnetic stirrer and capped with a rubber septum. The system was evacuated and filled with argon (three times), before adding dry THF (3 mL) and then cooled to 0 ºC with an external ice-water bath. Once the temperature was reached, MeMgBr (400 µL, 2.4 M, 2.6 equiv.) was added dropwise over 5 min, letting the drop fall down the walls of the flask to cool the MeMgBr solution. The reaction was stirred for an additional 30 min, before being quenched with H_2SO_4 (0.5 mL, 0.10 M), while keeping the cooling bath. The reaction mixture was extracted with CH_2Cl_2 (3x10 mL), the combined organic layers were dried over $MgSO_4$, filtered and the solvent was

removed *in vacuo*. The residue was purified by FC on silica gel (from 100% EtOAc to 80:20 EtOAc/MeOH) giving the pure product as a white solid (63.0 mg, 0.28 mmol, 92 %). The spectral data matched that reported.[38b]



TLC (EtOAc/MeOH 90:10) R_f 0.18; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.06 (m, 1H), 7.50 (p, J = 7.4 Hz, 2H), 7.42 – 7.37 (m, 3H), 7.35 – 7.31 (m, 2H), 7.28 – 7.24 (m, 1H), 1.37 (d, J = 13.1 Hz, 6H) ppm; ^{13}C-NMR {^{1}H} (101 MHz, $CDCl_3$) δ 144.5 (d, $^2J_{C\text{-}P}$ = 9.9 Hz, C^2), 141.2 (d, $^3J_{C\text{-}P}$ = 3.3 Hz, C^7), 132.8 (d, $^1J_{C\text{-}P}$ = 94.7 Hz, C^1-P), 132.1 (d, J = 8.3 Hz, C^6-H), 131.3 (d, $^4J_{C\text{-}P}$ = 2.3 Hz, C^4-H), 131.1 (d, $^3J_{C\text{-}P}$ = 9.9 Hz, C^3-H), 129.7 (2xC^9-H), 128.2 (C^{10}-H), 128.2 (2xC^8-H), 127.5 (d, $^3J_{C\text{-}P}$ = 10.7 Hz, C^5-H), 19.0 (d, $^1J_{C\text{-}P}$ = 71.5 Hz, 2xMe-P) ppm; ^{31}P-NMR (202 MHz, $CDCl_3$) δ 36.19 ppm; LRMS (EI): m/z (%) 230 (M^+, 12), 229 (M^+-H, 100), 215 (M^+-Me, 8), 152 (10).

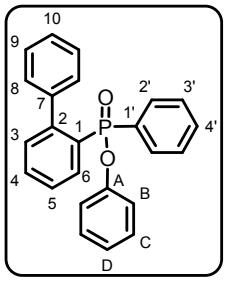
[1,1'-Biphenyl]-2-yldiphenylphosphine oxide (**5**). Phosphonate **2s** (193.2 mg, 0.50 mmol) was added into a flame-dried round bottom flask equipped with a magnetic stirrer and capped with a rubber septum. The system was evacuated and filled with argon (three times), before adding dry THF (3 mL) and then cooled to 0 ºC with an external ice-water bath. Once the temperature was reached, PhMgBr (910 µL, 2.2 M, 4 equiv.) was added dropwise over 5 min, letting the drop fall down the walls of the flask to cool the PhMgBr solution. The reaction was stirred for an additional 4 h, before being quenched with H_2SO_4 (0.5 mL, 0.10 M), while keeping the cooling bath. The reaction mixture was extracted with CH_2Cl_2 (3x10 mL), the combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The residue was purified by FC on silica gel (from 50:50 hexane/EtOAc to 100% EtOAc), giving the pure product as a white solid (141.80 mg, 0.40 mmol, 80 %). The spectral data matched that reported:[46]



TLC (hexane/EtOAc 50:50) R_f = 0.30; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.50 (m, 5H), 7.45 – 7.24 (m, 9H), 7.23 – 7.19 (m, 2H), 7.08 – 6.99 (m, 3H) ppm; ^{13}C-NMR {^{1}H} (101 MHz, $CDCl_3$) δ 147.6 (d, $^2J_{C\text{-}P}$ = 8.5 Hz, C^2), 140.2 (d, $^3J_{C\text{-}P}$ = 4.1 Hz, C^7), 134.0 (d, $^3J_{C\text{-}P}$ = 12.2 Hz, C^3-H), 132.9 (d, $^1J_{C\text{-}P}$ = 104.6 Hz, 2xC$^{1'}$-P), 131.9 (d, $^2J_{C\text{-}P}$ = 9.8 Hz, C^6-H), 131.7 (d, $^4J_{C\text{-}P}$ = 2.5 Hz, C^4-H), 131.52 (d, $^3J_{C\text{-}P}$ = 9.3 Hz, 4xC$^{3'}$-H), 131.50 (d, $^1J_{C\text{-}P}$ = 96.8 Hz, C^1-P), 131.1 (d, $^4J_{C\text{-}P}$ = 2.8 Hz, C$^{4'}$-H), 130.1 (2xC^9-H), 128.0 (d, $^2J_{C\text{-}P}$ = 12.0 Hz, 4xC$^{2'}$-H),

127.1 (2xC^{8}-H), 127.06 (C^{10}-H), 126.5 (d, J = 12.4 Hz, C^{5}-H) ppm; ^{31}P-NMR (162 MHz, $CDCl_3$) δ 32.60 ppm; LRMS (EI) *m/z* (%) 353 (M^+, 43), 277 (100), 199 (27).

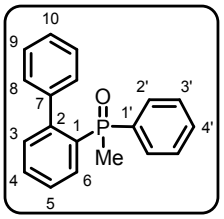
*Phenyl [1,1'-biphenyl]-2-yl(phenyl)phosphinate (**6**)*. Phosphonate **2s** (193.2 mg, 0.50 mmol) was added into a flame-dried round bottom flask equipped with a magnetic stirrer and capped with a rubber septum. The system was evacuated and filled with argon (three times), before adding dry THF (3 mL) and then cooled to 0 ºC with an external ice-water bath. Once the temperature was reached, PhMgBr (273 µL, 2.2 M, 1.2 equiv.) was added dropwise over 5 min, letting the drop fall down the walls of the flask to cool the PhMgBr solution. The reaction was stirred for an additional 1 h, before being quenched with H_2SO_4 (0.5 mL, 0.10 M), while keeping the cooling bath. The reaction mixture was extracted with CH_2Cl_2 (3x10 mL), the combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The residue was purified by FC on silica gel (from 70:30 to 50:50 hexane/EtOAc) giving the pure product as a white solid (113 mg, 0.31 mmol, 62%).



TLC (hexane/EtOAc 50:50) R_f 0.50; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.25 (ddd, J = 13.2, 7.6, 1.5 Hz, 1H), 7.58 (tt, J = 7.6, 1.5 Hz, 1H), 7.50 (tdd, J = 7.6, 2.9, 1.4 Hz, 1H), 7.42 – 7.32 (m, 3H), 7.30 – 7.10 (m, 10H), 7.02 (tt, J = 6.6, 1.1 Hz, 3H) ppm; ^{13}C-NMR {^{1}H} (101 MHz, $CDCl_3$) δ 150.9 (d, $^{2}J_{C\text{-}P}$ = 8.0 Hz, C^{A}), 146.7 (d, $^{2}J_{C\text{-}P}$ = 12.1 Hz, C^{2}), 140.4 (d, $^{3}J_{C\text{-}P}$ = 4.4 Hz, C^{7}), 133.0 (d, $^{2}J_{C\text{-}P}$ = 8.8 Hz, C^{6}-H), 132.2 (d, $^{4}J_{C\text{-}P}$ = 2.7 Hz, C^{4}-H), 131.82 (d, $^{3}J_{C\text{-}P}$ = 10.5 Hz, 2xC$^{3'}$-H), 131.80 (C$^{4'}$-H), 131.6 (d, $^{3}J_{C\text{-}P}$ = 12.4 Hz, C^{3}-H), 131.5 (d, $^{1}J_{C\text{-}P}$ = 120.9 Hz, C^{1}-P), 131.3 (d, $^{1}J_{C\text{-}P}$ = 118.7 Hz, C$^{1'}$-P), 129.9 (2xC^{C}-H), 129.5 (C^{9}-H), 128.0 (d, $^{2}J_{C\text{-}P}$ = 13.6 Hz, 2xC$^{2'}$-H), 127.5 (2xC^{8}-H), 127.40 (C^{10}-H), 127.0 (d, $^{3}J_{C\text{-}P}$ = 12.6 Hz, C^{5}-H), 124.4 (C^{D}-H), 120.7 (d, $^{3}J_{C\text{-}P}$ = 4.8 Hz, 2xC^{B}-H) ppm; ^{31}P-NMR (162 MHz, $CDCl_3$) δ 30.87 ppm; LRMS (EI) *m/z* (%) 370 (M^+, 49), 293 (M^+-Ph, 64), 277 (M^+, 100), 199 (85); HRMS (EI-TOF) *m/z* calculated for $C_{24}H_{19}O_2P$ 370.1123, found 370.1113.

[1,1'-Biphenyl]-2-yl(methyl)(phenyl)phosphine oxide (7). Phosphonate **6** (115.92 mg, 0.30 mmol) was added into a flame-dried round bottom flask equipped with a magnetic stirrer and capped with a rubber septum. The system was evacuated and filled with argon (three times), before adding dry THF (3 mL) and then cooled to 0 ºC with an external ice-water bath. Once the temperature was reached, MeMgBr (18 µL, 2.4 M, 1.5 equiv.) was added dropwise over 5 min, letting the drop fall down the walls of the flask to cool the MeMgBr

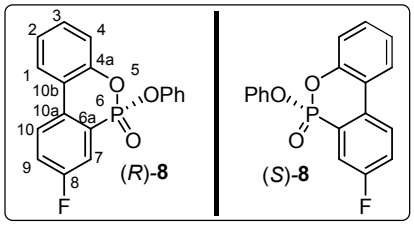
solution. The reaction was stirred for an additional 1 h, before being quenched with H_2SO_4 (0.5 mL, 0.1 M), while keeping the cooling bath. The reaction mixture was extracted with CH_2Cl_2 (3x10 mL), the combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The residue was purified by flash FC on silica gel (from 100% EtOAc to 95:05 EtOAc/MeOH) giving the pure product as a white solid (76.0 mg, 0.26 mmol, 87%).



TLC (100% EtOAc) R_f 0.50; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.92 (ddd, J = 13.2, 7.7, 1.1 Hz, 1H), 7.55 (tt, J = 7.5, 1.4 Hz, 1H), 7.49 – 7.35 (m, 4H), 7.35 – 7.24 (m, 4H), 7.21 (ddd, J = 8.4, 7.1, 1.2 Hz, 2H), 7.11 (dt, J = 6.9, 1.4 Hz, 2H), 1.59 (d, J = 13.4 Hz, 3H); ^{13}C-NMR {^{1}H} (101 MHz, $CDCl_3$) δ 146.1 (d, $^2J_{C\text{-}P}$ = 9.5 Hz, C^2), 140.7 (d, J = 3.9 Hz, C^7), 134.7 (d, J = 102.4 Hz ($C^{1'}$-P), 132.70 (d, J = 9.7 Hz, C^6-H), 131.71 (d, J = 2.8 Hz, C-H), 131.54 (d, J = 9.9 Hz, C^3-H), 131.36 (d, J = 2.8 Hz, C-H), 130.5 (d, J = 9.9 Hz,2x$C^{3'}$-H), 129.9 (2xC^9-H), 128.4 (d, J = 12.1 Hz, 2x$C^{2'}$-H), 127.83 (2xC^8-H), 127.78 (C^{10}-H), 127.17 (d, J = 11.5 Hz, C^5-H), 16.72 (d, J = 74.1 Hz, CH_3); ^{31}P-NMR (162 MHz, $CDCl_3$) δ 28.52 ppm; LRMS (EI) *m/z* (%) 292 (M^+, 21), 291 (M^+-H, 68), 215 (M^+-Ph, 100), 199 (17); HRMS (EI-TOF) *m/z* calculated for $C_{19}H_{17}OP$ 292.1017, found 292.0993.

*8-Fluoro-6-phenoxydibenzo[c,e][1,2]oxaphosphinine 6-oxide (**8**)*. Following a previously reported procedure,[47] the phosphonate **2x** was added into a flame dried pressure tube (81.43, 0.20 mmol), followed by KOAc (29 mg, 0.30 mmol, 1.5 equiv.), *(R_a)*-BINAP (12.45 mg, 0.02 mmol, 10 mol-%) and $Pd(OAc)_2$ (11.25 mg, 0.01 mmol, 5 mol-%). The tube was capped with a rubber septum, and the system was evacuated and filled with argon (three times). Then, dry toluene (1 mL) was added under Ar and the pressure tube was finally capped with a pressure cap. The resulting mixture was stirred at 100 ºC (sand bath) for 24 h. After this time, the tube was cooled to room temperature, and the solvent was removed *in vacuo*. The residue was directly purified by FC on silica gel (from 70:30 to 60:40 hexane/EtOAc), affording the desired product as a white solid (20.0 mg, 0.06 mmol, 31%). The enantiomeric ratio was determined by chiral HPLC: Chiralpak AD-H, 25 ºC, flow rate: 1 mL/min, hexane/*i*-PrOH: 60:40, 254 nm, 8.6 min *(S)*, 9.3 min *(R)*. The absolute configuration was assigned by analogy with compounds shown in the literature.[47] The authentic racemic mixture to determine the enantiomeric ratio by HPLC (see the traces in SI) was obtained with similar yield, using

almost identical conditions, but in the absence of phosphine ligands. The spectral data matched that reported:[48]



TLC (hexane/EtOAc 70:30) R_f 0.24; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.99 (ddd, J = 8.9, 7.4, 4.6 Hz, 1H), 7.90 (dd, J = 7.9, 1.6 Hz, 1H), 7.69 (ddd, J = 16.0, 7.4, 2.8 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.34 – 7.21 (m, 4H), 7.18 – 7.12 (m, 1H), 7.04 (dt, J = 8.4, 1.3 Hz, 2H) ppm; ^{13}C-NMR {^{1}H} (101 MHz, $CDCl_3$) δ 162.1 (dd, $^1J_{C\text{-}F}$ = 252.8, $^3J_{C\text{-}P}$ = 22.3 Hz, C^8-F), 149.6 (2xd, $^2J_{C\text{-}P}$ = 7.8 Hz, C$^{1'}$ and C^{4a}), 133.5 (dd, $^2J_{C\text{-}P}$ = 6.4, $^4J_{C\text{-}F}$ 3.4 Hz, C^{10a}), 130.7 (C^3-H), 129.9 (2xC$^{3'}$-H), 126.9 (dd, $^3J_{C\text{-}P}$ = 14.6, $^3J_{C\text{-}F}$ 7.6 Hz, C^{10}-H), 125.6 (C^1-H), 125.33 (C^2-H), 125.29 (C$^{4'}$-H), 123.8 (dd, $^1J_{C\text{-}P}$ = 182.6, $^3J_{C\text{-}F}$ = 6.8 Hz, C^{6a}), 122.1 (d, $^3J_{C\text{-}P}$ = 11.8 Hz, C^{10b}), 121.6 (dd, $^2J_{C\text{-}F}$ = 22.0, $^4J_{C\text{-}P}$ = 3.0 Hz, C^9-H), 120.7 (d, $^3J_{C\text{-}P}$ = 4.4 Hz, 2xC$^{2'}$-H), 120.4 (d, $^3J_{C\text{-}P}$ = 7.1 Hz, C^4-H), 117.4 (dd, $^2J_{C\text{-}F}$ = 23.1, $^2J_{C\text{-}P}$ = 9.9 Hz, C^7-H) ppm; ^{31}P-NMR (162 MHz, $CDCl_3$) δ 5.04 (d, $^4J_{P\text{-}F}$ = 8.0 Hz); LRMS (EI) *m/z* (%) 326 (M^+, 78), 233 (100), 186 (45); HRMS (EI-TOF) *m/z* calculated for $C_{18}H_{12}FO_3P$ 326.0508, found 326.0511.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. GC-calibrations, mechanistic experiments, gram-scale preparations, HPLC traces of chiral compound **8**, and spectroscopy data (PDF).

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The authors declare no competing financial interest.

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