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PAPER

Nickel-catalyzed C–P coupling of aryl mesylates and tosylates with H(O)PR^{1}R^2†

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A method was developed for the nickel-catalyzed phosphonylation of aryl mesylates and tosylates with H(O)PR^{1}R^2. To the best of our knowledge, this is the first example of nickel-catalyzed C–P coupling of aryl mesylates and tosylates. Most of the substrates gave moderate to good yields under our catalytic system.

Introduction

Aromatic organophosphorus compounds have attracted considerable interest due to their wide applications in organic synthesis,[1] polymers,[2] medicinal chemistry,[3] and photoelectric materials.[4] Particularly in organic synthesis, arylphosphines play an important role in organometallic catalysis[5] and organocatalysis.[6] Continuing efforts have been made to construct C–P bonds directly through the coupling of aryl halides with secondary phosphines, their boranes, stannanes, potassium and lithium salts.[7] Much attention has also been concentrated on the development of metal-catalyzed C–P couplings to obtain arylphosphonates and arylphosphine oxides.[8] The transition-metal-catalyzed Arbuzov reaction[9] and Hirao reaction[10] are the two most widely-used methods employed for the synthesis of arylphosphonates. In addition, oxidative phosphonylations of alkynes, arylboronic acids and aryltrifluoroborates to prepare alkynyl and aryl phosphonates catalyzed by Pd or Cu have recently become feasible.[11] The synthesis of vinyl phosphonates has also been realized by various transition-metal catalyzed additions of the H–P bond.[12]

For the preparation of arylphosphine oxides, one of the most frequently employed methods involves the treatment of diaryl phosphoryl chloride with Li or Mg aromatics,[13] however this method suffers from a lack of tolerance for functional groups. Another method is the metal-catalyzed coupling of aryl halides and triflates with air-stable diarylphosphine oxides,[10n,z,14] which avoids the use of very air sensitive reagents. Alternatively, the utilization of aryl mesylates and tosylates as substrates is attractive in cross-coupling reactions,[15–18] because phenol derivatives are readily available and may be used as a directing group for the introduction of other functional groups on the aromatic ring. In addition, aryl mesylates and tosylates are more stable in comparison to their corresponding triflates and can be readily prepared from common and cheap industrial chemicals, thus allowing access to a wider substrate scope. Although aryl mesylates and tosylates have been used in nickel-catalyzed cross-coupling reactions to form C–C,[16] C–N,[17] C–B[18] and C–S[16a] bonds, to the best of our knowledge, these substrates have not been studied in transition metal-catalyzed cross-coupling reactions to construct C–P bonds. P-arylation using aryl mesylates and tosylates as coupling partners remains a challenge in this field, however we envisage that it would greatly expand the scope of transition-metal-catalyzed C–P couplings.

Results and discussion

Our initial studies to achieve the construction of C(sp^2)–P bonds with aryl sulfonates were performed using phenyl mesylate with diphenylphosphine oxide. Through the evaluation of several kinds of ligands (see Table 1 and Table S1 in ESI†), we found that $NiCl_2$(dppf) with an excess of dppf was the only catalyst that exhibited activity in the cross-coupling of phenyl mesylates with diphenylphosphine oxide (Table 1, entry 1). It is noteworthy that $NiCl_2$(dppp) with an excess of dppp was not effective in this reaction (Table 1, entry 2), which is probably due the smaller bite angle of Ni–dppp compared to Ni–dppf.[19] Reducing the quantity of dppf resulted in a very low reaction yield (Table 1, entries 3–4), which was caused by premature decomposition of the catalyst.[15c,16a] A significant difference in product yield was observed when using readily prepared $NiCl_2$(dppf) as catalyst and generation of this complex *in situ* in DMF (Table 1, entries 1, 5), which perhaps indicated that the Ni–dppf complex could not be formed sufficiently in the aforementioned solvent. Several dipolar aprotic solvents were screened (Table 1, entries 6–11) and the highest yield was obtained when DMF was used as the reaction solvent. DMSO completely inhibited the reaction and the use of HMPA resulted in a poor yield (Table 1, entries 9–10), the results of which were due to the rapid decomposition

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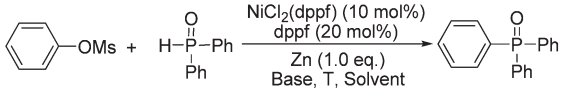
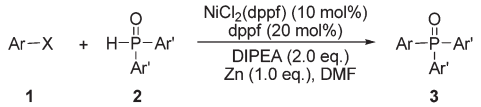
Table 1 Reaction condition screening[a]

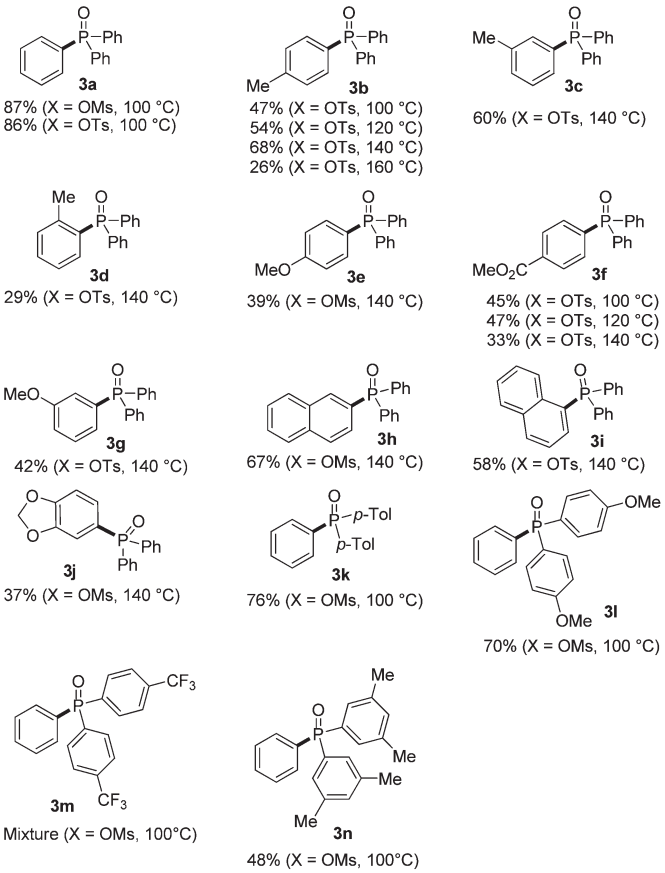


Entry	Base	*T* (°C)	Solvent	Yield (%)
1	—	100	DMF	74
2[b]	—	100	DMF	0
3[c]	—	100	DMF	14
4[d]	—	100	DMF	52
5[e]	—	100	DMF	26
6	—	100	1,4-Dioxane	30
7	—	100	DMA	30
8	—	100	NMP	50
9	—	100	DMSO	0
10	—	100	HMPA	31
11	—	80	DME	27
12	—	120	DMF	57
13	—	80	DMF	69
14[f]	—	100	DMF	0
15[g]	—	100	DMF	74
16	DIPEA	100	DMF	87
17	NEt_3	100	DMF	78
18	DABCO	100	DMF	84

[a] Unless otherwise stated, reaction conditions: phenyl mesylate (0.50 mmol), $Ph_2P(O)H$ (0.60 mmol), $NiCl_2$(dppf) (50 μmol), dppf (0.10 mmol), zinc dust (0.50 mmol), base (1.0 mmol), solvent (3 mL) under N_2, reaction time was 36 h. [b] $NiCl_2$(dppp) (10 mol%) instead of $NiCl_2$(dppf), dppp (20 mol%) instead of dppf. [c] Without added dppf. [d] dppf (0.05 mmol). [e] $NiCl_2$ (10 mol%) instead of $NiCl_2$(dppf), and added dppf (0.15 mmol). [f] No zinc dust. [g] Zinc dust (1.0 mmol).

Table 2 Substrate scope of the nickel-catalyzed coupling of aryl mesylates and tosylates with diarylphosphine oxides[ab]



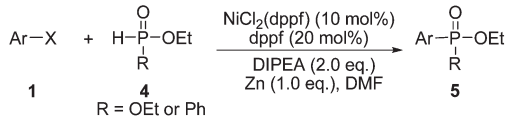


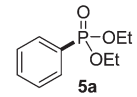
[a] Reaction conditions: **1** (0.50 mmol), **2** (0.60 mmol), $NiCl_2$(dppf) (50 μmol), dppf (0.10 mmol), DIPEA (95 μL, 1.0 mmol), zinc dust (0.50 mmol), 3 mL DMF, under N_2, reaction time was 36 h. [b] Isolated yields.

of nickel catalyst in these solvents.[20] The solvent DME also gave a poor result (Table 1, entry 11). Changes in reaction temperature had an effect on the reaction outcome with both increases and decreases in temperature leading to a drop in yield (Table 1, entries 12–13). The cross-coupling reaction with diphenylphosphine oxide did not occur in the absence of zinc dust (Table 1, entry 14). However, increasing the amount of zinc dust had no effect on the reaction yield (Table 1, entry 15). This may mean excess zinc dust is functionalized as a reducing agent for *in situ* generating Ni(0) catalyst before the start of catalytic cycle. In consideration of the possibility of nickel-catalyzed cross-couplings of aryl mesylates with primary amines and secondary amines to form C–N bonds, some tertiary amines were chosen as bases, and the results revealed that the added-base promoted the cross coupling of C–P bond formation (Table 1, entries 16–18). Among these tertiary amines, DIPEA provided the best result. Through the screening of reaction conditions, $NiCl_2$(dppf)/dppf/Zn/DIPEA/DMF was found to be the optimized catalytic system for the cross-coupling of aryl mesylate with diarylphosphine oxide.

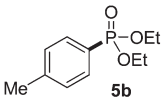
With the optimized reaction conditions in hand, a variety of aryl mesylates and tosylates were examined for the nickel-catalyzed coupling of C–P bonds with diarylphosphine oxides (Table 2). We found that there was no remarkable difference in reactivity between phenyl mesylate and phenyl tosylate (Table 2, **3a**). For the cross coupling of aryl mesylates and tosylates with diarylphosphine oxide, temperature plays a prominent role in determining reaction yield when using substituted phenyl tosylates (Table 2, **3b**, **3f**). For example, an increase in reaction temperature improved the product yield when using *p*-tolyl tosylate. However, when the reaction was performed at 160 °C, the yield decreased sharply, probably resulting from the decomposition of the Ni–dppf complex. The catalysis of electron-rich and deficient substrates gave lower yields than the corresponding electron-neutral substrates (Table 2, **3a**, **3b**, **3e**, **3f**). It is well known that electron-donating groups usually hinder the oxidative addition step whilst electron-withdrawing groups retard the reductive elimination step. Thus, the results may suggest that both the oxidative addition and reductive elimination are the kinetically important steps for our catalytic system. The *meta*-substituted substrates showed moderate reactivity, while the *ortho*-substituted substrate showed reduced reactivity (Table 2, **3c**, **3d**, **3g**). Fused-ring aromatic mesylates and tosylates gave the corresponding products in moderate yields (Table 2, **3h**, **3i**). Substituent effects of diarylphosphine oxides on the reaction outcome were also investigated. The introduction of an

Table 3 Scope of the nickel-catalyzed coupling of aryl mesylates and tosylates with diethyl phosphonate and ethyl phenylphosphinate[ab]

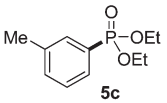




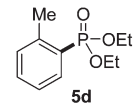
92% (X = OMs)
0% (X = OMs)[c]



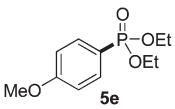
89% (X = OTs)



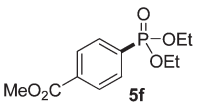
87% (X = OTs)



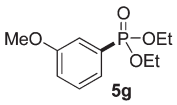
29% (X = OTs)



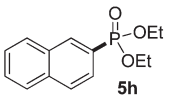
36% (X = OMs)



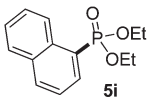
trace (X = OTs)



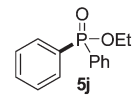
71% (X = OTs)



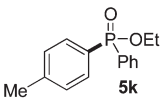
84% (X = OMs)



55% (X = OTs)



86% (X = OTs)



83% (X = OTs)

[a] Reaction conditions: **1** (0.50 mmol), **2** (0.60 mmol), $NiCl_2$(dppf) (50 μmol), dppf (0.10 mmol), DIPEA (95 μL, 1.0 mmol), zinc dust (0.50 mmol), 3 mL DMF, under N_2, reaction time was 36 h, reaction temperature was 100 °C. [b] Isolated yields. [c] No zinc dust.

electron-neutral group and an electron-donating group at the *para*-position of the aromatic ring did not significantly affect the yields of the C–P coupling products (Table 2, **3k**, **3l**). However when the strong electron-withdrawing trifluoromethyl group was present at the *para*-position of the phenyl ring, an inseparable mixture of products were obtained (Table 2, **3m**). The cross-coupling of di(3,5-dimethylphenyl)phosphine oxide gave a moderate yield (Table 2, **3n**).

This catalytic system was also adapted to the cross coupling reaction of aryl mesylates and tosylates with diethyl phosphonate and ethyl phenylphosphinate (Table 3). For most examples, the Ni-catalyzed reaction of aryl mesylates and tosylates with diethyl phosphonate furnished the corresponding arylphosphonates in good yields. When diethyl phosphinate was utilized in the reaction using optimized conditions with a substrate possessing a *para*-substituted electron-neutral group, the desired phosphonate was isolated in good yield (Table 3, **5a**, **5b**). *Meta*-substituted substrates and fused-ring aryl substrate also gave good yields (Table 3, **5c**, **5g**, **5h**). *Ortho*-steric effects make the reaction sluggish (Table 3, **5d**, **5i**). This method is not suitable for substrates bearing an electron-donating group or an electron-withdrawing group in the *para*-position of the phenyl ring (Table 3, **5e**, **5f**), probably due to similar reasons (as discussed previously) for the reaction with diarylphospine oxides. Ethyl diarylphosphinates could also be prepared in good yields by employing the same catalytic system for the cross coupling of tosylates with ethyl arylphosphinate (Table 3, **5j**, **5k**). In addition, some well-known chiral phosphine ligands can be synthesized from compounds **3j**,[13b] **5c**, **5g**.[21]

Conclusions

In summary, we have developed a method for C(sp^2)–P coupling *via* nickel-catalyzed coupling of aryl mesylates and tosylates with H(O)PR^1R^2 to prepare arylphosphonates, diarylphosphinates, and arylphosphine oxides. Our studies have expanded the scope of transition-metal-catalyzed P-arylation. The catalytic system of this reaction with tolerance to a broader range of substituents on the substrates is under further investigation.

Experimental section

General details

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All reactions were performed in flame-dried glassware under an atmosphere of dry nitrogen, and the workup was carried out in air, unless otherwise stated. CH_2Cl_2, DMF, NMP, DMSO, HMPA, toluene, pyridine and NEt_3 were distilled at atmospheric or reduced pressure over CaH_2 prior to use. Solvents 1,4-dioxane, DME and THF were distilled from sodium benzophenone ketyl prior to use. NaH (65% in mineral oil) was degreased with n-hexane under N_2 prior to use. Activated zinc dust was prepared prior to use according to a literature procedure.[22] Column chromatographic purification of products was carried out using silica gel 60 (200–300 mesh). NMR spectra were recorded on a Varian MERCURY plus-400 (400 MHz, ^{1}H; 100 MHz, ^{13}C; 162 MHz, ^{31}P) spectrometer with chemical shifts reported in ppm relative to the residual deuterated solvent, the internal standard tetramethylsilane, or external 85% H_3PO_4 for ^{31}P. Mass spectrometry analysis was carried out using an electrospray spectrometer Waters 4 micro quadrupole. Melting points were measured with SGW X-4 micro melting point apparatus.

General procedure for Ni-catalyzed cross-coupling of aryl mesylates or tosylates with H(O)PR^1R^2

In a typical reaction, to an oven-dried 25 mL Schlenk tube was added $NiCl_2$(dppf) (50 μmol), dppf (0.10 mmol) and activated Zn dust (0.50 mmol). The tube was sealed with a rubber septum and then degassed by pumping and backfilling with nitrogen three times. DMF (1 mL) was added *via* a syringe. The reaction mixture was stirred at 80 °C for 0.5 h. During this time, the solution of mixture turned from yellow to red. DMF (2 mL) solution containing aryl mesylates or tosylates (0.50 mol), H(O)PR^1R^2 (0.60 mmol), and DIPEA (95 μL, 1.0 mmol) was added *via* a syringe through the rubber septum. The reaction mixture was stirred at 100 °C under a nitrogen atmosphere for 36 h. The reaction mixture was allowed to cool to room temperature and the DMF was evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2 (10 mL) and then washed with 5% HCl (3 × 5 mL) and H_2O (3 × 3 mL), and dried by Na_2SO_4. Solvent was evaporated *in vacuo* and the residue was purified by column

chromatography (silica gel, petroleum ether–ethyl acetate–EtOH). Products **3c**, **3k**, **3l** and **3n** are new compounds.

Phosphoryl triphenyl (3a).[10aa] White solid, ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.45; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.64–7.70 (m, 6H), 7.52–7.56 (m, 3H), 7.43–7.48 (m, 6H).

(4-Methylphenyl)diphenyl phosphine oxide (3b).[10aa] White solid, ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 27.73; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.64–7.69 (m, 4H), 7.49–7.58 (m, 4H), 7.41–7.46 (m, 4H), 7.25–7.28 (m, 2H), 2.39 (s, 3H).

(3-Methylphenyl)diphenyl phosphine oxide (3c). White solid, mp: 123.7–124.2 °C; ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 30.53; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.68–7.63 (m, 4H), 7.56–7.52 (m, 3H), 7.48–7.43 (m, 4H), 7.37–7.33 (m, 3H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 138.7 (d, J = 12.7 Hz), 132.8 (d, J = 142.1 Hz), 133.0 (d, J = 3.6 Hz), 132.4 (d, J = 102.5), 132.7 (d, J = 9.5 Hz), 132.3 (d, J = 10.0 Hz), 132.1 (d, J = 1.9 Hz), 129.4 (d, J = 11.3 Hz), 128.7 (d, J = 12.4 Hz), 128.5 (d, J = 12.9 Hz), 21.66; HR-ESI-MS: $[M + H]^+$ m/z calcd for: 293.1095, found: 293.1108.

(2-Methylphenyl)diphenyl phosphine oxide (3d).[23] White solid, ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 31.71; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.68–7.61 (m, 4H), 7.56–7.38 (m, 7H), 7.27 (ddd, J = 14.0, 7.6, 0.4 Hz, 1H), 7.11 (m, 1H), 7.02 (ddd, J = 14.0, 7.6, 1.2 Hz, 1H), 2.45 (s, 3H).

(4-Methoxyphenyl)diphenyl phosphine oxide (3e).[10aa] White solid, ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 32.91; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.64–7.70 (m, 4H), 7.50–7.54 (m, 2H), 7.42–7.46 (m, 4H), 7.28–7.37 (m, 2H), 7.12–7.17 (m, 1H), 7.06 (dd, J = 8.9, 2.6 Hz), 3.77 (s, 3H).

(4-Carbomethoxyphenyl)diphenyl phosphine oxide (3f).[24] White solid, ^{31}P NMR (100 MHz, $CDCl_3$): δ = 28.9; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, J = 8.2 Hz, 2H), 7.77 (dd, J = 11.4, 8.4 Hz, 2H), 7.64–7.69 (m, 4H), 7.46–7.60 (m, 6H), 3.93 (s, 3H).

(3-Methoxyphenyl)diphenyl phosphine oxide (3g).[10aa] White solid, ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 32.91; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.64–7.70 (m, 4 H), 7.50–7.54 (m, 2H), 7.42–7.46 (m, 4H), 7.28–7.37 (m, 2H), 7.12–7.17 (m, 1H), 7.06 (dd, J = 8.9, 2.6 Hz), 3.77 (s, 3 H).

2-Naphthalenyldiphenyl phosphine oxide (3h).[25] White solid, ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 31.32; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, J = 13.6 Hz, 1H), 7.88 (d, J = 9.6 Hz, 2H), 7.73–7.68 (m, 4H), 7.64–7.46 (m, 10H).

1-Naphthalenyldiphenyl phosphine oxide (3i).[7h] White solid, ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 33.12; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.58 (d, J = 8.2 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.66–7.71 (m, 4H), 7.52–7.56 (m, 2H), 7.43–7.50 (m, 6H), 7.35–7.39 (m, 1H), 7.26–7.32 (m, 1H).

1,3-Benzodioxol-5-yldiphenyl phosphine oxide (3j).[26] White solid, ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 34.53; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.66 (dd, J = 11.6, 7.5 Hz, 4H), 7.54 (d, J = 7.1 Hz, 2H), 7.46 (t, J = 7.1 Hz, 4H), 7.18 (dd, J = 12.6, 8.0 Hz, 1H), 7.07 (d, J = 11.4 Hz, 1H), 6.88 (dd, J = 7.9, 2.1 Hz, 1H), 6.02 (s, 2H).

Bis(4-methylphenyl)phenyl phosphine oxide (3k).[27] Colorless slurry, ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 30.53; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.68–7.62 (m, 2H), 7.53 (dd, J = 11.8, 8.0 Hz, 4H), 7.48 (m, 1H), 7.24 (dd, J = 8.4, 2.4 Hz, 4H), 2.38 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 142.6 (d, J = 2.9 Hz), 133.0 (d, J = 102.5 Hz), 132.2 (d, J = 10.2 Hz), 132.0 (d, J = 8.7 Hz), 131.9 (d, J = 3.2 Hz), 129.4 (d, J = 106.9 Hz), 129.4 (d, J = 12.6 Hz), 128.6 (d, J = 11.8 Hz), 21.7.

Bis(4-methoxypheny1)phenylphosphine oxide (3l).[28] White solid, mp: 96.5–97.4 °C; ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 30.36; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.61–7.54 (m, 2H), 7.56 (dd, J = 11.2, 8.4 Hz, 4H), 7.51–7.49 (m, 1H), 7.45–7.41 (m, 2H), 6.94 (dd, J = 6.4, 1.8 Hz, 4H), 3.83 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 162.6 (d, J = 1.8 Hz), 134.1 (d, J = 11.7 Hz), 133.3 (d, J = 104.3 Hz), 132.2 (d, J = 9.8 Hz), 131.9 (d, J = 2.7 Hz), 128.6 (d, J = 12.4 Hz), 124.0 (d, J = 110.2 Hz), 114.2 (d, J = 12.9 Hz), 55.5.

Bis(3,5-bismethylphenyl)phenylphosphine oxide (3n). White solid, mp: 158.6–159.2 °C; ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 30.89; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.68–7.63 (m, 2H), 7.55–7.51 (m, 1H), 7.47–7.42 (m, 2H), 7.26 (d, J = 12.4 Hz, 4H), 7.15 (s, 2H), 2.31 (s, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 138.3 (d, J = 12.2 Hz), 133.9 (d, J = 2.3 Hz), 133.1 (d, J = 102.7 Hz), 132.4 (d, J = 102.6 Hz), 132.3 (d, J = 9.7 Hz), 131.9 (d, J = 2.2 Hz), 129.8 (d, J = 10.0 Hz), 128.6 (d, J = 11.7 Hz), 21.56; HR-ESI-MS: $[M + H]^+$ m/z calcd for: 335.1565, found: 335.1574.

Diethyl phenylphosphonate (5a).[9j] Oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (m, 2H), 7.55 (tq, J = 7.5, 1.4 Hz, 1H), 7.47 (m, 2H), 4.12 (m, 4H), 1.32 (td, J = 7.0, 0.5 Hz, 6H).

Diethyl *p*-tolylphosphonate (5b).[9j] Oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, J = 8.9 Hz, 2H), 7.26 (d, J = 8.9 Hz, 2H), 4.04–4.18 (m, 4H), 2.41 (s, 3H), 1.31 (t, J = 6.9 Hz, 6H).

Diethyl *m*-tolylphosphonate (5c).[9j] Oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.67 (m, 2H), 7.27–7.36 (m, 2H), 4.12–4.20 (m, 4H), 2.37 (s, 3H), 1.32 (t, J = 7.0 Hz, 6H).

Diethyl *o*-tolylphosphonate (5d).[9j] Oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.96 (m, 1H), 7.42–7.46 (m, 1H), 7.23–7.28 (m, 2H), 4.12 (m, 4H), 2.57 (s, 3H), 1.33 (t, J = 6.9 Hz, 6H).

Diethyl *p*-methoxyphenylphosphonate (5e).[9j] Oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (dd, J = 13.0, 9.0 Hz, 2H), 6.97 (dd, J = 9.0, 3.0 Hz, 2H), 4.04–4.13 (m, 4H), 3.83 (s, 3H), 1.30 (t, J = 7.3 Hz, 6H).

Diethyl 3-methoxyphenylphosphonate (5g).[9j] Oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.40 (m, 3H), 7.07–7.10 (m, 1H), 4.05–4.18 (m, 4H), 3.85 (s, 3H), 1.33 (t, J = 6.9 Hz, 6H).

Diethyl naphthalen-2-yl phosphonate (5h).[9j] Oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, J = 16.4 Hz, 1H), 7.84–7.93 (m, 3H), 7.71–7.76 (m, 1H), 7.51–7.59 (m, 2H), 4.17–4.23 (m, 4H), 1.32 (t, J = 7.3 Hz, 6H).

Diethyl naphthalen-1-yl phosphonate (5i).[9j] Oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, J = 8.0 Hz, 1H), 8.22 (dd, J = 16.2, 7.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 7.2 Hz, 1H), 7.49–7.61 (m, 3H), 4.02–4.24 (m, 2H), 1.31 (t, J = 7.1 Hz, 6H).

Ethyl diphenylphosphinate (5j).[10n] Oil, ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 25.01; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.64–7.66 (m, 4H), 7.47 (d, J = 7.6 Hz, 4H), 4.16 (m, 2H), 1.38 (m, 3H).

Ethyl (4-methylphenyl)phenylphosphinate (5k).[10n] Oil, ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 24.97; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.66 (d, J = 7.2 Hz, 2H), 7.48–7.51 (m, 3H), 7.39–7.45 (m, 1H), 6.96–6.99 (m, 4H), 4.15 (m, 2H), 2.18 (s, 3H), 1.28 (m, 3H).

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