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‡Graphical Abstract

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The Chan-Evans-Lam *N*-Arylation of Phosphonic/Phosphinic amides

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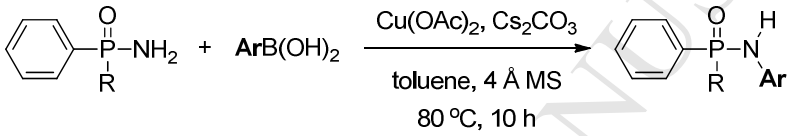

A general and efficient arylation protocol of phosphinamides and phosphonamides was herein demonstrated. And various unreported *N*-aryl phosphinamides and phosphonamides were successfully prepared through the Chan-Evans-Lam reaction with high efficiency (up to 88% yields) and good functional groups tolerance (30 examples). The stoichiometric copper(II)-mediated transformation required for no organic ligands or co-catalysts.

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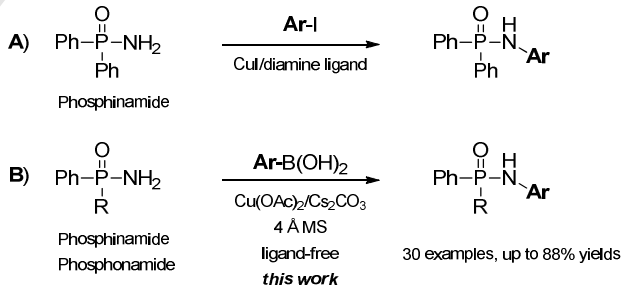
ABSTRACT

A stoichiometric copper(II)-mediated arylation protocol of phosphinamides and phosphonamides was herein demonstrated. Various unreported *N*-aryl phosphinamides and phosphonamides were successfully prepared through Chan-Evans-Lam reaction with high efficiency (up to 88% yields) and good functional groups tolerance (30 examples) in the absence of any ligands or co-catalysts.

1. Introduction

Constructions of carbon-hetero bonds have gained widespread research interests. Despite great contributions have been made for higher efficiency,[1] Chan-Evans-Lam reactions have been considered as a powerful tool in the field for the advantages including stable reagents, easy-to-workup procedure and good compatibility.[2] Arylboronic acids have been generally coupled in the presence of different transition metal-catalysts, such as Cu,[3] Ni,[4] and Au,[5] for the formations of various carbon-hetero bonds such as C-N,[3, 6] C-O,[7] C-P[8] and C-S bonds[9]. Amines, amides, azides have been arylated successfully with arylboronic acids for the generation of Ar-N bonds under mild conditions.

Be aware of those phosphonic amides and phosphinic amides have attracted extensive attention in the fields of synthetic and pharceutical chemistry[10] for not only the unique structures, but also the versatile roles in the clinical chemistry, explorations for the derivations of the useful compounds have been carried out and inter or intra-molecular annulation towards heterocycles like benzazaphosphole 1-oxides and phosphaisoquinoline 1-oxides have been realized by kinds of synthetic tools.[11] However, arylation of phosphonic amides and phosphinic amides reamined unexplored except the only example from Guo,[12] wherein aryl iodides were successfully applied as the arylation reagents of phosphinic amides in the presence of CuI and (±)-*trans*-cyclohexane-1,2-diamine (Scheme 1, **A**)). Thus, to enrich the diversity of the –P(=O)-N- backboned molecules, novel methodologies are still severely required. Within this context, we wish to demonstrate a general arylation method towards *N*-aryl phosphonic amides and *N*-aryl phosphinic amides with assistance of a simple Cu(II)-salt without participation of any organic ligands (Scheme 1, **B**)).



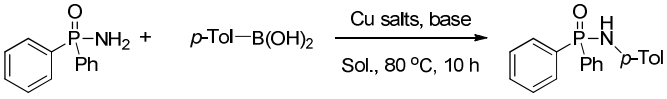
Scheme 1. Arylation of phosphonic/phosphinic amides

2. Results and discussions

Firstly, reactions between *P*,*P*-diphenyl phosphinamide (**1a**) and *p*-tolyl boronic acid (**2a**) were carried out for the optimal conditions as summarized in Table 1. With a stoichiometric 1.0 equivalent of $Cu(OAc)_2$ and 2.0 equivalents of K_2CO_3, optimization on the effect of different solvents was conducted. Alcoholic solvents and chlorinated solvents such as methyl alcohol (entry 1), *tert*-butyl alcohol (entry 2), chloroform (entry 3) and DCE (1,2-dichloro ethane for entry 4) could not provide satisfactory results, for no reaction or only trace product **3aa** was detected after 10 hours. Other solvents, such as DMF (*N*,*N*-dimethyl formamide, entry 5) and DMSO (dimethyl sulfoxide, entry 6) offered the similar effects to the transformation. To our satisfactory, participation of toluene provided the *N*-(4-methylphenyl)-*P*,*P*-diphenyl phosphinamide (**3aa**) in 58% yield (entry 7). Sodium carbonate gave analogous performance with potassium carbonate, while cesium carbonate afforded superior effect for 62% of **3aa** was smoothly isolated in toluene (entries 8 and 9). But involvement of CsOAc offered **3aa** in 48% yield,

inferior to the results obtained from Cs_2CO_3 (entry 10). Disappointingly, organic bases, such as triethyl amine and pyridine, failed to make the arylation protocol proceed in the Cu(II)-catalyzed system (entry 11 and 12). Other Cu(II) or Cu(I) catalysts, such as $CuSO_4$, $CuCl_2$, CuI and CuBr were proved useless to the transformation and trace **3aa** were detected after 10 hours (entries 13 – 16). Increased loading of $Cu(OAc)_2$ (2.0 equiv.) furnished the corresponding *N*-arylated phosphinamide **3aa** in 75% yield (entry 17), while 48% yield of **3aa** was observed with reduced loading of $Cu(OAc)_2$ (entry 18). To our delight, addition of powdered molecular sieves (4 Å, 100 wt%) raised the yield of **3aa** to 85% (entry 19). Inner atmosphere also had significant impact over the arylation protocol (entry 19, note e)), for 73% of **3aa** was furnished under the dioxygen atmosphere probably because of the homo-coupling of **2a**. If the the reaction was conducted in the presence reduced amount of 4 Å MS (50 wt%), the yield of **3aa** was slightly lower, up to 83% (entry 20), whereas increased loading of MS (200 wt%) led to the dramatic decrease in the efficiency of the coupling reaction, for 75% **3aa** was successfully isolated (entry 21). This probably resulted from insufficient stirring of the mixture.

Table 1. Optimization of the reaction conditions[a]



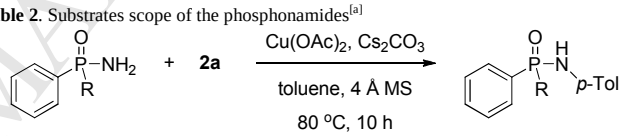
1a **2a** **3aa**

Entry	[Cu] (equiv.)	Base	Sol.	Yield [b]
1	$Cu(OAc)_2$ (1.0)	K_2CO_3	CH_3OH	n.d.[c]
2	$Cu(OAc)_2$ (1.0)	K_2CO_3	*t*BuOH	n.d.
3	$Cu(OAc)_2$ (1.0)	K_2CO_3	$CHCl_3$	trace
4	$Cu(OAc)_2$ (1.0)	K_2CO_3	DCE	trace
5	$Cu(OAc)_2$ (1.0)	K_2CO_3	DMF	trace
6	$Cu(OAc)_2$ (1.0)	K_2CO_3	DMSO	20%
7	$Cu(OAc)_2$ (1.0)	K_2CO_3	toluene	58%
8	$Cu(OAc)_2$ (1.0)	Na_2CO_3	toluene	56%
9	$Cu(OAc)_2$ (1.0)	Cs_2CO_3	toluene	62%
10	$Cu(OAc)_2$ (1.0)	CsOAc	toluene	48%
11	$Cu(OAc)_2$ (1.0)	Et_3N	toluene	n.d.
12	$Cu(OAc)_2$ (1.0)	pyridine	toluene	n.d.
13	$CuCl_2$ (1.0)	Cs_2CO_3	toluene	trace
14	$CuSO_4$ (1.0)	Cs_2CO_3	toluene	trace
15	CuI (1.0)	Cs_2CO_3	toluene	trace
16	CuBr (1.0)	Cs_2CO_3	toluene	trace
17	$Cu(OAc)_2$ (2.0)	Cs_2CO_3	toluene	75%
18	$Cu(OAc)_2$ (0.5)	Cs_2CO_3	toluene	48%
19[d]	**$Cu(OAc)_2$ (2.0)**	**Cs_2CO_3**	**toluene**	**85% (73%)[e]**
20[f]	$Cu(OAc)_2$ (2.0)	Cs_2CO_3	toluene	83%
21[g]	$Cu(OAc)_2$ (2.0)	Cs_2CO_3	toluene	75%

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), [Cu], base (2.0 equiv.), under air atmosphere or noted, in sol. (2.0 mL) at 80 °C for 10 h. [b] Isolated yields. [c] Stands for no reaction. [d] 4Å molecular sieves (powdered, 100wt%) was added. [e] The yield in the parentheses was obtained under O_2 (1 atm) atmosphere. [f] 50 wt% 4Å molecular sieves was added. [g] 200 wt% 4Å molecular sieves was added.

Beyond our expectations, substituted phosphonamides showed good compatibility in the Cu(II)-mediated system and coupled with *p*-tolyl boronic acid (**2a**) smoothly under the optimal conditions, which was shown in Table 2. For instance, *P*-Phenyl-*P*-methoxy phosphonamide (**1b**) reacted with *p*-tolyl boronic acid (**2a**) successfully, offering the desired arylated product **3ba** in 79% yield (entry 1). In a similar pattern, other alkoxy decorated phosphonamides, including *P*-ethoxy (entry 2), *P*-isopropoxy (entry 3), *P*-butoxy (entry 4), *P*-(2-methoxyethoxy) (entry 5) underwent the arylation reaction readily, providing the corresponding *N*-(*p*-tolyl) phosphonamides **3ca** – **3fa** in yields from 75% to 83%. It was noteworthy that *P*-phenyl-*P*-cyclohexyloxy phosphonamide (**1g**) produced the desired product **3ga** in satisfactory 85% yield (entry 6), superior to *P*-isopropoxy did despite the similar steric hindrance. Unsaturated carbon-carbon triple bond was also well tolerated in the reaction, which was exemplified by the formation of *N*-(*p*-tolyl)-*P*-diphenyl-*P*-(2-butynyloxy) phosphonamide (**3ha**), in a ratio up to 88% (entry 7). Other substituents, such as benzyloxy groups, were also found compatible in the system. For example, benzyloxy, 3-fluorobenzyloxy, 4-chlorobenzyloxy, 2-bromobenzyloxy groups gave an access to the desired *N*-arylated phosphonamides **3ia** – **3la** in yields ranging from 79% to 83% (entries 8 -11). *N*-(*p*-tolyl)-*P*-(4-morpholinyl)-*P*-phenyl phosphinamide was favorably generated under the Cu(II)-catalysis in 56% yield (entry 12).

Table 2. Substrates scope of the phosphonamides[a]



1b - 1m **3ba - 3ma**

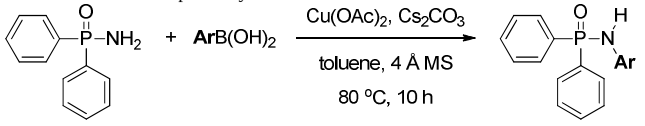
Entry	**1**	R	**3**	Yield [b]
1	**1b**	CH_3O-	**3ba**	79%
2	**1c**	CH_3CH_2O-	**3ca**	83%
3	**1d**	$(CH_3)_2CHO$-	**3da**	78%
4	**1e**	$CH_3(CH_2)_3O$-	**3ea**	78%
5	**1f**	$CH_3O(CH_2)_2O$-	**3fa**	75%
6	**1g**	cyclo-$C_6H_{11}CH_2O$-	**3ga**	85%
7	**1h**	$CH_3C{\equiv}CCH_2O$-	**3ha**	88%
8	**1i**	$C_6H_5CH_2O$-	**3ia**	83%
9	**1j**	3-$FC_6H_5CH_2O$-	**3ja**	79%
10	**1k**	4-$ClC_6H_5CH_2O$-	**3ka**	81%
11	**1l**	2-$BrC_6H_5CH_2O$-	**3la**	81%
12	**1m**	4-Morpholinyl-	**3ma**	56%

[a] Reaction conditions: **1** (0.5 mmol), **2a** (0.6 mmol), $Cu(OAc)_2$ (1.0 mmol), Cs_2CO_3 (1.0 mmol), 4Å MS (100 wt%), in toluene (3.5 mL) at 80 °C for 10 h. [b] Isolated yields.

Successively, the tolerance of the functional groups of aryl boronic acids was also checked in the system as shown in Table 3. Phenyl boronic acid (**2b**) coupled with phosphinamide **1a** readily, offering *N*,*P*,*P*-triphenyl phosphinamide (**3ab**) in acceptable 76% yield (entry 1). Tolyl boronic acids were well-tolerated in the

system, for *N*-(2-methylphenyl), *N*-(3-methylphenyl) and *N*-(2,4-dimethylphenyl) phosphinamides 3ac – 3ae were furnished in yields ranging from 76% to 82% (entries 2 – 4). Other alkyl substituted phenyl groups were also compatible in the protocol, for *N*-(2-ethylphenyl), *N*-(4-ethylphenyl), *N*-(4-isopropylphenyl), *N*-(4-*tert*butylphenyl) phosphinamides **3af** – **3ai** in yields from 75% - 79% (entries 5 – 8). Electron-sufficient phenyl groups also provided good performance in the reaction, as exemplified with 3-methoxyphenyl and 4-methoxyphenyl boronic acids **1j** and **1k** afforded the corresponding products **3aj** – **3ak** in good yields, up to 83% (entries 9 and 10). Halogenated phenyl groups fused boronic acids, such as 4-fluorophenyl, 4-chlorophenyl and 4-bromophenyl boronic acids furnished the desired *N*-arylated phosphinamides **3al** – **3an** in yields up to 80% (entries 11 – 13). Electron-deficient phenyl groups, such as 4-trifluoromethylphenyl, 2-nitrophenyl substituted phosphinic amides **3ao** and **3ap** were readily prepared in 81% and 65% yields, respectively (entries 14 and 15). Pleasingly, polyaryl and heteroaryl, like *N*-(1-napthylation) and *N*-(2-pyridinylation) were achieved by the Cu(II)-catalysis in yields of 76% and 46%, separately (entries 16 and 17).

Table 3. Substrates scope on aryl boronic acids[a]

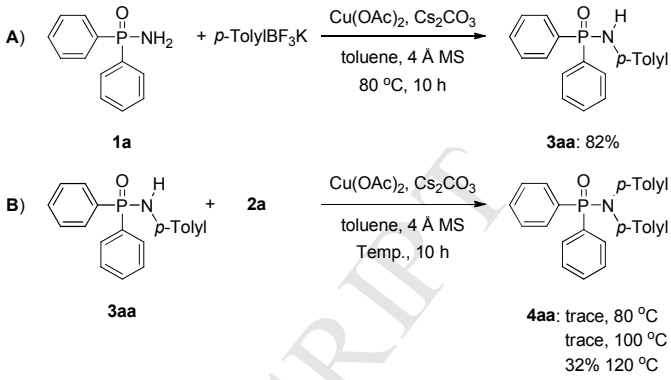


1a **2b - 2r** **3ab - 3ar**

Entry	**2**	Ar	**3**	Yield[b]
1	**2b**	C_6H_5	**3ab**	76%
2	**2c**	2-$CH_3C_6H_5$	**3ac**	82%
3	**2d**	3- $CH_3C_6H_5$	**3ad**	79%
4	**2e**	2,4-$(CH_3)_2C_6H_4$	**3ae**	76%
5	**2f**	2-$C_2H_5C_6H_5$	**3af**	77%
6	**2g**	4-$C_2H_5C_6H_5$	**3ag**	79%
7	**2h**	4-*i*PrC_6H_5	**3ah**	75%
8	**2i**	4-*t*BuC_6H_5	**3ai**	75%
9	**2j**	3-$CH_3OC_6H_5$	**3aj**	79%
10	**2k**	4-$CH_3OC_6H_5$	**3ak**	83%
11	**2l**	4-FC_6H_5	**3al**	80%
12	**2m**	4-ClC_6H_5	**3am**	75%
13	**2n**	4-BrC_6H_5	**3an**	70%
14	**2o**	4-$CF_3C_6H_5$	**3ao**	81%
15	**2p**	2-$NO_2C_6H_5$	**3ap**	65%
16	**2q**	1-Naphthyl	**3aq**	76%
17	**2r**	2-Pyridinyl	**3ar**	46%

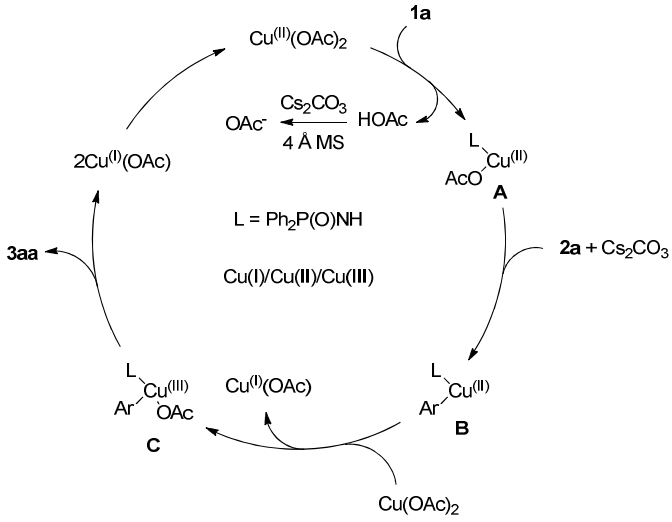
[a] Reaction conditions: **1** (0.5 mmol), **2a** (0.6 mmol), $Cu(OAc)_2$ (1.0 mmol), Cs_2CO_3 (1.0 mmol), 4Å MS (100 wt%), in toluene (3.5 mL) at 80 °C for 10 h. [b] Isolated yields.

To take a deeper insight into the reaction, controlled reactions were conducted as shown in Scheme 2. Under the standard conditions, phenylation of phosphinamide **1a** was also realized by the application of potassium trifluoro *p*-tolyl borate, affording the desired product **3aa** in good yield, up to 82% (scheme 2, **A**)). Furthermore, successive arylation of **3aa** was also explored in the system. However, trace product **3aa** was detected at either 80 °C or 100 °C for 10 hours. Elevated reaction temperature at 120 °C gave an access towards *N*,*N*-di-(*p*-tolyl)-*P*-phenyl phosphinamide **4aa** but only 32% yield was obtained (scheme 2, **B**)).



Scheme 2. Control reactions

Based on the literature explorations, possible mechanism for the C-N coupling protocol was proposed, as shown in Scheme 3. First, coordination of substrate **1a** to $Cu(OAc)_2$ occurred, forming a new Cu(II)-centered intermediate **A** with a release of HOAc, which was basified by Cs_2CO_3. Then, with assistance of Cs_2CO_3, **2a**, affording another Cu(II)-complex **B**. In the presence of $Cu(OAc)_2$, the intermediate **B** was transformed into a Cu(III)-centered complex **C**, and a molecular of CuOAc was afforded. And successive reductive elimination step happed on the intermediate **C**, furnishing the desired product **3aa** and anther CuOAc, which was oxidized easily in the air atmosphere to complete the catalytic cycle.



Scheme 3. Proposed mechanism

3. Conclusion

In summary, we have successfully developed an efficient and general Cu(II)-mediated transformation towards *N*-arylated phosphonamides and phosphinamides with aryl boronic acids. The transformation enjoyed good functional group compatibility and high efficiency. The practical and facile methodology offered a promising avenue towards the compounds of great significance

4. Experimental section

4.1 General remarks

All the reagents were purchased from commercial companies and used without further purification.^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer in deuterated chloroform at 25 °C with residue solvent peaks as internal standards (δ = 7.26 ppm for ^{1}H-NMR and δ = 77.16 ppm for ^{13}C-NMR). Chemical shifts (δ) are reported in ppm, and spin-spin coupling constants (*J*) are given in Hz, while multiplicities are abbreviated by s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Mass spectra were recorded on a ThermoFinnigan MAT95XP microspectrometer and High resolution mass spectra (HRMS) were recorded on an Agilent Technologies Accurate Mass Q-TOF 6530 microspectrometer. Infrared (IR) spectra were reported in reciprocal centimeter (cm^{-1}). Melting points were recorded on a national standard melting point apparatus (Model: Taike XT-4) and were uncorrected.

4.2 General Procedure

4.2.1 Procedures towards N-aryl Phosphonic/Phosphinic Amides

A Schlenk tube (35 mL) equipped with a magnetic bar was loaded with the phosphonamides or phosphinamides **1** (0.5 mmol) and $Cu(OAc)_2$ (181 mg, 1.0 mmol) in dry toluene (3.5 mL), then arylboronic acids **2** (0.6 mmol, 1.2 equiv.), Cs_2CO_3 (1.0 mmol, 2.0 equiv.) and 4 Å MS (100 wt%) were added in portions and the reaction mixture was allowed to stir at 80 °C (120 °C for **4aa**) for 10 h. After cooling to room temperature, the mixture was filtered through a short celite pad and washed with dichloromethane (15 mL × 3). The filtrate was concentrated and the oily crude product was purified by column chromatography using silica gel (200-300 mesh) as stationary phase and a petroleum ether and ethyl acetate (3/1) as eluent to give the *N*-aryl phosphonamides or phosphinamides **3** and **4aa** (in sealed tube) in noted yields

4.2.3 P,P-Diphenyl-*N*-(*p*-tolyl) phosphinamide (3aa)

White solid (130.9 mg, 85% yield), m.p. 229 - 230 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.88 (dd, *J* = 12.3, 7.7 Hz, 4H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.48 – 7.42 (m, 4H), 6.91 (dd, *J* = 15.9, 7.3 Hz, 4H), 5.39 (d, *J* = 9.2 Hz, 1H), 2.20 (s, 3H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.8, 132.3 (J_{C-P} = 3.0 Hz), 132.2 (J_{C-P} = 128.0 Hz), 132.1 (J_{C-P} = 10.0 Hz), 131.4, 129.9, 128.9 (J_{C-P} = 13.0 Hz), 118.8 (J_{C-P} = 7.0 Hz), 20.7 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 18.3 ppm. IR (KBr): ν = 3204, 3060, 2943, 2856, 1719, 1515, 1278, 1116, 941, 814, 692, 570, 516 (cm^{-1}). MS (ESI): *m*/z (%) = 218.1, 294.1, 308.1 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 308.1199; found: 308.1208.

4.2.4 *P*-Phenyl-*P*-methoxy-*N*-(*p*-tolyl) phosphonamide (3ba)

White solid (103.5mg, 79% yield). m.p. 115 - 116 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.83 (dd, *J* = 13.5, 7.7 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.41 (dd, *J* = 11.5, 5.8 Hz, 2H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 8.2 Hz, 2H), 6.29 (d, *J* = 5.2 Hz, 1H), 3.83 (d, *J* = 11.3 Hz, 3H), 2.21 (s, 3H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.4, 132.3 (J_{C-P} = 3.0 Hz), 131.5 (J_{C-P} = 10.0 Hz), 131.1, 129.9, 129.8 (J_{C-P} = 177.0 Hz), 128.7 (J_{C-P} = 15.0 Hz), 117.7 (J_{C-P} =6.0 Hz), 51.3 (J_{C-P} = 6.0 Hz), 20.6 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 19.2 ppm. IR (KBr): ν = 3152, 3067, 2957, 2871, 1756, 1514, 1458, 1404, 1273, 1203, 1134, 1093, 1050, 967, 801, 760, 551, 489 (cm^{-1}). MS (ESI): m/z (%) = 155.0, 262.1 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 262.0991; found: 262. 0995.

4.2.5 *P*-Phenyl-*P*-ethoxy-*N*-(*p*-tolyl)-phosphonamide (3ca)

White solid (114.6 mg, 83% yield), m.p. 106 - 108 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.84 (dd, *J* = 13.4, 7.7 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.41 (dd, *J* = 11.3, 7.4 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.43 (d, *J* = 8.0 Hz, 1H), 4.31 – 4.15 (m, 2H), 2.21 (s, 3H), 1.37 (t, *J* = 7.0 Hz, 3H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.7, 132.2 (J_{C-P} = 3.0 Hz), 131.5 (J_{C-P} = 10.0 Hz), 130.8, 130.4 (J_{C-P} = 176.0 Hz), 129.8, 128.6 (J_{C-P} = 13.0 Hz), 117.7 (J_{C-P} = 7.0 Hz), 61.0 (J_{C-P} = 6.0 Hz), 20.6, 16.4 (J_{C-P} = 7.0 Hz) (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 17.2 ppm. IR (KBr): ν = 3160, 3064, 3033, 2927, 2858, 1741, 1615, 1517, 1448, 1384, 1285, 1214, 1133, 1034, 955, 822, 782, 732, 694, 550, 501 (cm-1). MS (ESI): m/z (%) = 77.1 (64), 106.1 (60), 107.1 (100), 141.0 (45), 275.1 (80). HRMS (ESI): m/z calcd for $[M+H]^+$: 276.1148; found: 276.1150.

4.2.6 *P*-Phenyl-*P*-isoproxy-*N*-(*p*-tolyl) phosphonamide (3da)

White solid (112.8 mg, 78% yield). m.p. 188 - 190 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.84 (dd, *J* = 12.9, 7.7 Hz, 2H), 7.47 (d, *J* = 6.8 Hz, 1H), 7.40 (s, 2H), 6.92 (d, *J* = 7.6 Hz, 2H), 6.80 (d, *J* = 7.3 Hz, 2H), 6.33 (d, *J* = 16.3 Hz, 1H), 4.89 (d, *J* = 5.9 Hz, 1H), 2.20 (s, 3H), 1.43 (d, *J* = 5.4 Hz, 3H), 1.29 (d, *J* = 5.5 Hz, 3H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.8, 132.1 (J_{C-P} =2.0 Hz), 131.6 (J_{C-P} = 10.0 Hz), 130.9 (J_{C-P} = 177.0 Hz), 130.6, 129.7, 128.6 (J_{C-P} = 15.0 Hz), 117.7 (J_{C-P} = 6.0 Hz), 70.4 (J_{C-P} = 6.0 Hz), 24.5 (J_{C-P} = 3.0 Hz), 23.9 (J_{C-P} = 5.0 Hz), 20.6 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 16.1 ppm. IR (KBr): ν = 3160, 3044, 3002, 2917, 2868, 1721, 1605, 1428, 1374, 1265, 1214, 1034, 955, 802, 762, 722, 540, 505 (cm^{-1}). MS (ESI): m/z (%) = 77.1 (27), 106.1 (42), 107.1 (76), 247.1 (100), 289.2 (32). HRMS (ESI): m/z calcd for $[M+H]^+$: 290.1304; found: 290.1310.

4.2.7 *P*-Phenyl-*P*-(*n*-butoxy)-*N*-(*p*-tolyl) phosphonamide (3ea)

White solid (118.2 mg, 78% yield), m.p. 107 - 109 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.85 (dd, *J* = 13.3, 7.7 Hz, 2H), 7.49 (t, *J* = 7.1 Hz, 1H), 7.41 (d, *J* = 3.0 Hz, 2H), 6.94 (d, *J* = 7.5 Hz, 2H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.10 (s, 1H), 4.27 – 4.02 (m, 2H), 2.21 (s, 3H), 1.74 – 1.67 (m, 2H), 1.47 – 1.38 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.5, 132.2 (J_{C-P} =3.0 Hz), 131.5 (J_{C-P} =10.0 Hz), 130.9, 130.3 (J_{C-P} =177.0 Hz), 129.9, 128.7 (J_{C-P} =15.0 Hz), 117.6 (J_{C-P} = 6.0 Hz), 64.7 (J_{C-P} = 6.0 Hz), 32.5 (J_{C-P} = 7.0 Hz), 20.7, 19.0, 13.8 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 17.3 ppm. IR (KBr): ν = 3180, 3033, 2964, 2925, 2861, 1616, 1522, 1474, 1446, 1384, 1361, 1262, 1219, 1119, 1067, 1025, 950, 808, 742, 670, 543, 500 (cm^{-1}). MS (ESI): m/z (%) = 77.1 (16), 106.6 (30), 107.1 (26), 247.1 (100), 303.2 (65). HRMS (ESI): m/z calcd for $[M+H]^+$: 304.1461; found: 304.1464.

4.2.8 *P*-Phenyl-*P*-(1-methoxyethoxy)-*N*-(*p*-tolyl) phosphonamide (3fa)

White solid (114.4 mg, 75% yield). m.p. 92 - 94 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.86 (dd, *J* = 13.4, 7.6 Hz, 2H), 7.48 (d, *J* = 7.0 Hz, 1H), 7.41 (d, *J* = 2.9 Hz, 2H), 6.95 (d, *J* = 7.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.30 – 6.13 (m, 1H), 4.38 – 4.26 (m, 2H), 3.71 – 3.59 (m, 2H), 3.39 (d, *J* = 1.6 Hz, 3H), 2.21 (s, 3H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.5, 132.3, 131.8 (J_{C-P} = 10.0 Hz), 131.0 (J_{C-P} = 4.0 Hz), 130.0 (J_{C-P} = 139.0 Hz), 129.9, 128.6 (J_{C-P} = 15.0 Hz), 117.8 (J_{C-P} = 6.0 Hz), 71.8 (J_{C-P} = 6.0 Hz), 63.8, 59.0, 20.7 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 18.0 ppm. IR (KBr): ν = 3173, 3060, 3036, 2926, 2875, 1619, 1525, 1478, 1450, 1393, 1284, 1209, 1129, 1039, 955, 803, 747, 704, 549, 502 (cm^{-1}). MS (ESI): m/z (%) = 77.1 (14), 107.1 (50), 229.1 (26), 247.1 (100), 305.1 (32). HRMS (ESI): m/z calcd for $[M+H]^+$: 306.1254; found: 306.1259.

4.2.9 *P*-Phenyl-*P*-cyclohexylmethyl-*N*-(*p*-tolyl) phosphonamide (3ga)

White solid (145.9 mg, 85% yield), m.p. 131 - 132 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.83 (dd, *J* = 13.4, 7.6 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.41 (dt, *J* = 11.2, 5.7 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.1 Hz, 2H), 6.04 (d, *J* = 7.4 Hz, 1H), 4.08 – 3.77 (m, 2H), 2.21 (s, 3H), 1.80 – 1.70 (m, 4H), 1.70 (s, 1H), 1.30 – 1.16 (m, 4H), 1.03 – 0.97 (m, 2H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.5, 132.2 (J_{C-P} =3.0 Hz), 131.5 (J_{C-P} = 10.0 Hz), 130.9, 130.4 (J_{C-P} = 177.0 Hz), 129.8, 128.6 (J_{C-P} = 15.0 Hz), 117.6 (J_{C-P} = 7.0 Hz), 69.7 (J_{C-P} = 7.0 Hz), 38.5 (J_{C-P} = 7.0 Hz), 29.5 (J_{C-P} = 3.0 Hz), 26.5, 25.7, 20.7 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 17.2 ppm. IR (KBr): ν = 3200, 3071, 3030, 2929, 2853, 1615, 1517, 1450, 1392, 1294, 1217, 1124, 1029, 944, 846, 806, 752, 712, 694, 565, 502 (cm^{-1}). MS (ESI): m/z (%) = 77.1 (5), 107.1 (24), 247.1 (100), 248.1 (25), 343.2 (27). HRMS (ESI): m/z calcd for $[M+H]^+$: 344.1774; found: 344.1780.

4.2.10 *P*-Phenyl-*P*-(2-butynyl ester)-*N*-(*p*-tolyl) phosphonamide (3ha)

White solid (131.6 mg, 88% yield), m.p. 198 - 200 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.86 (dd, *J* = 13.6, 7.7 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.41 (dd, *J* = 11.4, 7.2 Hz, 2H), 6.95 (d, *J* = 7.9 Hz, 2H), 6.85 (d, *J* = 7.9 Hz, 2H), 6.07 (d, *J* = 5.9 Hz, 1H), 4.76 (d, *J* = 9.1 Hz, 2H), 2.21 (s, 3H), 1.76 (s, 3H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.3, 132.4 (J_{C-P} = 4.0 Hz), 131.7 (J_{C-P} = 8.0 Hz), 131.2, 129.8, 129.8 (J_{C-P} = 176.0 Hz), 128.6 (J_{C-P} = 15.0 Hz), 118.1 (J_{C-P} = 7.0 Hz), 84.4, 73.7 (J_{C-P} =8.0 Hz), 53.3 (J_{C-P} = 5.0 Hz), 20.6, 3.7 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 18.6 ppm. IR (KBr): ν = 3162, 3060, 3023, 2960, 2923, 1617, 1517, 1443, 1375, 1270, 1212, 1122, 1097, 1018, 975, 948, 806, 754, 701, 659, 554, 502 (cm^{-1}). MS (ESI): m/z (%) = 118.1, 300.1 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 300.1148; found: 300.1151.

4.2.11 *P*-Phenyl-*P*-phenylmethoxy-*N*-(*p*-tolyl) phosphonamide (3ia)

White solid (139.9 mg, 83% yield). m.p. 150-151 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.85 (dd, *J* = 13.6, 7.7 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.33 (m, 7H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 8.1 Hz, 2H), 6.29 (s, 1H), 5.29 – 5.06 (m, 2H), 2.21 (s, 3H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.3, 136.2 (J_{C-P} = 7.0 Hz), 132.4 (J_{C-P} = 3.0 Hz), 131.6 (J_{C-P} = 10.0 Hz), 131.2, 130.0 (J_{C-P} = 176.0 Hz), 129.1, 128.7 (J_{C-P} = 14.0 Hz), 128.7,128.5, 128.3, 117.9 (J_{C-P} = 7.0 Hz), 66.3 (J_{C-P} = 5.0 Hz), 20.7 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 18.0 ppm. IR (KBr): ν = 3201, 3069, 3033, 2954, 2922, 2859, 1615, 1517, 1445, 1386, 1279, 1215, 1126, 998, 947, 810, 742, 701, 640, 559, 527 (cm^{-1}). MS (ESI): m/z (%) = 99.1 (22), 195.1 (25), 196.2 (55), 197.2 (20), 337.2 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 338.1304; found: 338.1309.

4.2.12 *P*-Phenyl-*P*-(*3*-fluorobenzyloxy)-*N*-(*p*-tolyl) phosphonamide (3ja)

White solid (140.3 mg, 79% yield), m.p. 116 - 118 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.80 (dd, *J* = 13.5, 7.6 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.36 (dd, *J* = 11.1, 7.1 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 9.4 Hz, 1H), 6.94 (t, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 7.9 Hz, 2H), 6.76 (d, *J* = 7.5 Hz, 2H), 6.55 (d, *J* = 11.3 Hz, 1H), 5.23 – 4.97 (m, 2H), 2.15 (s, 3H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.0, 160.6, 138.7 (J_{C-F} = 8.0 Hz), 137.4 (J_{C-F} = 5.0 Hz), 132.5 (J_{C-P} = 3.0 Hz), 131.6 (J_{C-P} =10.0 Hz), 131.2, 130.2 (J_{C-F} = 8.0 Hz), 129.9, 129.9 (J_{C-P} = 177.0 Hz), 128.8 (J_{C-F} = 15.0 Hz), 123.5 (J_{C-F} = 4.0 Hz), 117.8 (J_{C-P} = 6.0 Hz), 115.1 (J_{P-C-F}= 21.0 Hz), 64.2 (J_{C-P} = 6.0 Hz), 19.5 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 18.3 ppm. ^{19}F NMR ($CDCl_3$, 370 MHz): = -112.7 ppm. IR (KBr): ν = 3175, 3065, 3035, 2925, 2895, 1599, 1517, 1450, 1380, 1273, 1254, 1214, 1128, 1044, 945, 816, 807, 747, 686, 562, 532 (cm^{-1}). MS (ESI): m/z (%) = 79.0, 118.1, 137.0, 157.0, 356.1 (100). HRMS (ESI): m/z calcd for [M+H]+: 356.1210; found: 356.1220.

4.2.13 *P*-Phenyl-*P*-(*4*-chlorobenzyloxy)-*N*-(*p*-tolyl) phosphonamide (3ka)

White solid (150.7 mg, 81% yield). m.p. 118-120 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.83 (dd, *J* = 13.6, 7.7 Hz, 2H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.29 (s, 4H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.79 (d, *J* = 7.9 Hz, 2H), 6.23 (d, *J* = 5.2 Hz, 1H), 5.24 – 5.01 (m, 2H), 2.12 (s, 3H) (ppm).^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.2, 134.7 (J_{C-P} = 8.0 Hz), 134.4, 132.5 (J_{C-P} = 3.0 Hz), 131.6 (J_{C-P} = 10.0 Hz), 131.3, 129.9 (J_{C-P} = 176.0 Hz), 129.8 (J_{C-P} = 28.0 Hz), 128.9, 128.7 (J_{C-P} = 15.0 Hz), 117.9 (J_{C-P} = 6.0 Hz) 65.6 (J_{C-P} = 6.0 Hz), 20.7 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 18.3 ppm. IR (KBr): ν = 3218, 3052, 2916, 2855, 1065, 1515, 1454, 1490, 1380, 1274, 1210, 1125, 1091, 1018, 938, 808, 748, 697, 546, 494 (cm^{-1}). MS (ESI): m/z (%) = 79.0, 118.1, 157.0, 356.1, 372.1 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 372.0915; found: 372.0915.

4.2.14 *P*-Phenyl-*P*-(2-bromobenzyloxy)-*N*-(*p*-tolyl) phosphonamide (3la)

White solid (168.5 mg, 81% yield), m.p. 121 - 122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 (dd, *J* = 13.5, 7.5 Hz, 2H), 7.47 (dd, *J* = 17.0, 7.6 Hz, 3H), 7.41 – 7.35 (m, 2H), 7.23 (d, *J* = 11.4 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.9 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 2H), 5.91 (d, *J* = 5.4 Hz, 1H), 5.32 – 5.12 (m, 2H), 2.16 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.1, 135.8, 153.7, 132.5 (J_{C-P} = 3.0 Hz), 131.7 (J_{C-P} = 10.0 Hz), 131.4, 129.9, 129.9 (J_{C-P} = 176.0 Hz), 129.8 (J_{C-P} = 7.0 Hz), 128.8 (J_{C-P} = 15.0 Hz), 127.7, 123.1, 118.1 (J_{C-P} = 6.0 Hz), 65.9 (J_{C-P} = 5.0 Hz), 20.7 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 18.1 ppm. IR (KBr): ν = 3142, 3058, 3022, 2923, 2858, 1607, 1517, 1474, 1384, 1277, 1208, 1126, 1064, 1030, 940, 853, 812, 747, 696, 547, 534 (cm^{-1}). MS (ESI): m/z (%) = 79.0, 118.1, 157.0, 352.3, 416.0 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 416.0410; found: 416.0406.

4.2.15 *P*-Phenyl-*P*-(*4*-morpholinyl ester)-*N*-(*p*-tolyl) phosphonamide (3ma)

White solid (88.5 mg, 56% yield), m.p. 193 - 194 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.82 (m, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.48 (dd, *J* = 7.0, 3.1 Hz, 2H), 7.11 – 6.86 (m, 4H), 4.93 (d, *J* = 11.1 Hz, 1H), 3.61 – 3.51 (m, 4H), 3.26 – 3.14 (m, 4H), 2.27 (s, 3H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.3, 132.3 (J_{C-P} = 3.0 Hz), 131.8, 131.4 (J_{C-P} = 10.0 Hz), 131.4 (J_{C-P} = 154.0 Hz), 129.9, 128.9 (J_{C-P} = 14.0 Hz), 119.0 (J_{C-P} = 6.0 Hz), 67.1 (J_{C-P} = 6.0 Hz), 44.8, 20.8 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 16.0 ppm. IR (KBr): ν = 3213, 2965, 2916, 2858, 1517, 1443, 1385, 1294, 1259, 1201, 1116, 1102, 1024, 969, 924, 808, 735, 694, 603, 552, 535, 516 (cm^{-1}). MS (ESI): m/z (%) = 86.1 (25), 107.1 (55), 229.1 (100), 259.1 (52), 316.2 (95). HRMS (ESI): m/z calcd for $[M+H]^+$: 317.1413; found: 317.1417.

4.2.16 *N*,*P*,*P*-Triphenyl phosphinic amide (3ab)

White solid (111.4 mg, 76% yield). m.p. 230 - 232 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.89 (dd, *J* = 12.3, 7.5 Hz, 4H), 7.53 (t, *J* = 7.0 Hz, 2H), 7.49 – 7.43 (m, 4H), 7.14 (t, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 6.89 (t, *J* = 7.3 Hz, 1H), 5.35 (d, *J* = 9.2 Hz, 1H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.5, 132.4 (J_{C-P} = 3.0 Hz), 132.1 (J_{C-P} = 10.0 Hz), 132.1 (J_{C-P} = 129.0

Hz), 129.0 (J_{C-P} = 13.0 Hz), 129.4, 122.0, 118.7 (J_{C-P} = 7.0 Hz) (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 18.4 ppm. IR (KBr): ν = 3111, 3070, 2960, 2930, 2890, 1600, 1494, 1434, 1408, 1270, 1184, 1100, 1031, 930, 803, 748, 694, 525 (cm^{-1}). MS (ESI): m/z (%) = 218.1, 294.1 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 294.1042; found: 294.1051.

4.2.17 *P*,P-Diphenyl-*N*-(*o*-tolyl) phosphinic amide (3ac)

White solid (125.9 mg, 82% yield), m.p. 238-240 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.89 (dd, *J* = 12.2, 7.6 Hz, 4H), 7.53 (t, *J* = 6.0 Hz, 2H), 7.48 – 7.44 (m, 4H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.84 (t, *J* = 7.4 Hz, 1H), 5.04 (d, *J* = 8.7 Hz, 1H), 2.28 (s, 3H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 138.7, 132.4 (J_{C-P} = 30 Hz), 132.2 (J_{C-P} = 129.0Hz), 132.0 (J_{C-P} = 10.0Hz), 130.6, 129.0 (J_{C-P} = 13.0Hz), 127.2, 125.7 (J_{C-P} = 8.0Hz), 122.2, 119.0 (J_{C-P} = 4.0 Hz), 17.9 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 18.6 ppm. IR (KBr): ν = 3194, 3047, 2970, 2905, 1589, 1499, 1439, 1399, 1269, 1188, 1103, 1028, 917, 807, 751, 697, 536 (cm^{-1}). MS (ESI): m/z (%) = 77.1 (25), 106.1 (22), 182.1 (45), 201.1 (55), 307.2 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 308.1199; found: 308.1203.

4.2.18 *P*,*P*-Diphenyl-*N*-(*m*-tolyl) phosphinic amide (3ad)

White solid (121.3 mg, 79% yield), m.p. 248 - 249 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.88 (dd, *J* = 12.2, 7.8 Hz, 4H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.46 (d, *J* = 6.8 Hz, 4H), 7.01 (t, *J* = 7.7 Hz, 1H), 6.81 (s, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.71 (d, *J* = 7.5 Hz, 1H), 5.31 (d, *J* = 8.1 Hz, 1H), 2.19 (s, 3H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.4, 139.3, 132.2 (J_{C-P} = 128.0Hz), 132.2 (J_{C-P} = 3.0Hz), 131.6 (J_{C-P} = 10.0Hz), 129.2, 128.9 (J_{C-P} = 13.0Hz), 122.8, 119.3 (J_{C-P} =6.7Hz), 115.7 (J_{C-P} =6.4Hz), 21.5 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 18.3 ppm. IR (KBr): ν = 3128, 3082, 2966, 2863, 1608, 1484, 1434, 1401, 1285, 1187, 1115, 1024, 947, 792, 726, 693, 620, 525 (cm^{-1}). MS (ESI): m/z (%) = 77.1 (25), 183.1 (20), 201.1 (65), 306.1 (90), 307.2 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 308.1199; found: 308.1202.

4.2.19 *P*,*P*-Diphenyl-*N*-(2,4-dimethylphenyl) phosphinic amide (3ae)

White solid (122.0 mg, 76% yield). m.p. 194-196 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.88 (dd, *J* = 11.1, 8.5 Hz, 4H), 7.52 (t, *J* = 6.9 Hz, 2H), 7.45 (d, *J* = 7.3 Hz, 4H), 7.10 (d, *J* = 8.1 Hz, 1H), 6.93 (s, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 4.93 (d, *J* = 8.4 Hz, 1H), 2.25 (s, 3H), 2.19 (s, 3H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 136.0, 132.3 (J_{C-P} = 128.0 Hz), 132.2 (J_{C-P} = 2.0 Hz), 132.0 (J_{C-P} = 9.0 Hz), 131.7, 131.3, 128.9 (J_{C-P} =13.0 Hz), 127.6, 126.0 (J_{C-P} = 8.0 Hz), 119.4 (J_{C-P} = 4.0 Hz), 20.7, 17.9 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 18.5 ppm. IR (KBr): ν = 3061, 2971, 2923, 2807, 1510, 1429, 1262, 1181, 1106, 1026, 945, 909, 817, 714, 685, 581, 530 (cm-1). MS (ESI): m/z (%) = 201.0, 322.1 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 322.1355; found: 322.1364.

4.2.20 *P*,*P*-Diphenyl-*N*-(*2*-ethylphenyl) phosphinic amide (3af)

White solid (123.6 mg, 77% yield). m.p. 159 - 160 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.89 (dd, *J* = 12.1, 7.5 Hz, 4H), 7.52 (t, *J* = 6.9 Hz, 2H), 7.46 (d, *J* = 7.3 Hz, 4H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.13 (d, *J* = 7.3 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.88 (t, *J* = 7.3 Hz, 1H), 5.13 (d, *J* = 8.5 Hz, 1H), 2.61 (q, *J* = 7.4 Hz, 2H), 1.29 (t, *J* = 7.5 Hz, 3H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.8, 132.0 (J_{C-P} = 3.0 Hz), 131.9 (J_{C-P} = 129.0 Hz), 131.7 (J_{C-P} = 9.0 Hz), 128.7 (J_{C-P} = 8.0 Hz), 128.2, 126.7, 122.1, 118.9 (J_{C-P} = 4.0 Hz), 24.0, 13.2 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 18.5 ppm. IR (KBr): ν = 3072, 2962, 2920, 2833, 1591, 1501, 1435, 1245, 1115, 1035, 945, 807, 755, 696, 560, 520 (cm^{-1}). MS (ESI): m/z (%) = 77.1 (25), 120.1 (45), 196.1 (23), 201.1 (57), 321.2 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 322.1355; found: 322.1358.

4.2.21 *P*,*P*-Diphenyl-*N*-(*4*-ethylphenyl) phosphinic amide (3ag)

White solid (126.9 mg, 79% yield), m.p. 260 - 261 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.88 (dd, *J* = 11.9, 7.8 Hz, 4H), 7.52 (t, *J* = 6.9 Hz, 2H), 7.46 (d, *J* = 5.9 Hz, 4H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 5.28 (d, *J* = 9.1 Hz, 1H), 2.51 (q, *J* = 7.5 Hz, 2H), 1.14 (t, *J* = 7.5 Hz, 3H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.9, 132.9, 132.2 (J_{C-P} = 129.0 Hz), 132.3 (J_{C-P} =3.0 Hz), 132.1 (J_{C-P} =5.0 Hz), 129.0, 128.8 (J_{C-P} = 11.0 Hz), 118.8 (J_{C-P} =7.0 Hz), 28.1, 15.7 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 18.4 ppm. IR (KBr): ν = 3117, 3042, 2934, 2859, 1613, 1519, 1475, 1291, 1247, 1190, 1120, 829, 735, 690, 582, 512 (cm-1).MS (ESI): m/z (%) = 218.1, 322.1 (100).HRMS (ESI): m/z calcd for [M+H]+: 322.1355; found: 322.1363.

4.2.22 *P*,*P*-Diphenyl-*N*-(*4*-isopropylphenyl) phosphinic amide (3ah)

White solid (125.7 mg, 75% yield). m.p. 212-214 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.88 (dd, *J* = 12.0, 7.6 Hz, 4H), 7.52 (t, *J* = 6.9 Hz, 2H), 7.46 (d, *J* = 7.4 Hz, 4H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 7.7 Hz, 2H), 5.30 (d, *J* = 9.0 Hz, 1H), 2.80 – 2.74 (m, 1H), 1.15 (d, *J* = 6.8 Hz, 6H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 142.5, 138.0, 132.3 (J_{C-P} =3.0 Hz), 132.3 (J_{C-P} = 128.0 Hz), 132.1 (J_{C-P} = 10.0 Hz), 128.9 (J_{C-P} = 13.0 Hz), 127.3, 118.7 (J_{C-P} = 6.0 Hz), 33.4, 24.1 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 18.5 ppm. IR (KBr): ν = 3119, 3046, 2957, 2862, 1619, 1520, 1469, 1270, 1191, 1111, 1026, 946, 807, 742, 693, 567, 518 (cm^{-1}). MS (ESI): m/z (%) = 130.1, 336.1 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 336.1512; found: 336.1522.

4.2.23 *P*,*P*-Diphenyl-*N*-(*4*-(*t*-butyl) phenyl) phosphinic amide (3ai)

White solid (130.9 mg, 75% yield). m.p. 226 - 227 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.89 (dd, *J* = 12.3, 7.5 Hz, 4H), 7.51 (d, *J* = 7.1 Hz, 2H), 7.46 (dd, *J* = 7.4, 3.0 Hz, 4H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 5.31 (d, *J* = 9.1 Hz, 1H), 1.22 (s, 9H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.7, 137.7, 132.3 (J_{C-P} = 129Hz), 132.2 (J_{C-P} = 3.0 Hz), 132.1 (J_{C-P} = 10.0 Hz), 128.9 (J_{C-P} = 13.0 Hz), 126.2, 118.3 (J_{C-P} = 6.0 Hz), 34.2, 31.5 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 18.5 ppm. IR (KBr): ν = 3136, 3034, 2960, 2863, 1625, 1523, 1471, 1288, 1247, 1185, 1104, 1025, 945, 807, 739, 683, 567, 522 (cm^{-1}). MS (ESI): m/z (%) = 218.1, 339.1, 350.1 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 350.1668; found: 350.1676.

4.2.24 *P*,*P*-Diphenyl-*N*-(*3*-methoxyphenyl) phosphinic amide (3aj)

White solid (127.6 mg, 79% yield), m.p. 213 - 214 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.89 (dd, *J* = 12.4, 7.7 Hz, 4H), 7.53 (t, *J* = 7.3 Hz, 2H), 7.46 (td, *J* = 7.1, 2.4 Hz, 4H), 7.03 (t, *J* = 8.1 Hz, 1H), 6.58 – 6.53 (m, 2H), 6.45 (d, *J* = 8.3 Hz, 1H), 5.34 (d, *J* = 9.4 Hz, 1H), 3.64 (s, 3H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.5, 141.7, 132.0 (J_{C-P} = 129.0 Hz),132.4 (J_{C-P} = 2.0 Hz),132.1 (J_{C-P} = 10.0 Hz), 130.1, 128.9 (J_{C-P} = 6.0 Hz),111.2 (J_{C-P} = 7.0 Hz), 107.8, 104.5 (J_{C-P} = 7.0 Hz), 55.2 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 18.4 ppm. IR (KBr): ν = 3135, 3095, 2964, 2893, 1560, 1500, 1450, 1293, 1195, 1123, 1032, 947, 857, 727, 695, 610, 518 (cm^{-1}). MS (ESI): m/z (%) = 79.0, 157.0, 259.5, 324.1 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 324.1148; found: 324.1149.

4.2.25 *P*,*P*-Diphenyl-*N*-(*4*-methoxyphenyl) phosphinic amide (3ak)

White solid (134.1 mg, 83% yield). m.p. 194-195 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.87 (dd, *J* = 12.1, 7.6 Hz, 4H), 7.49 (d, *J* = 7.0 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 4H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.68 (d, *J* = 8.2 Hz, 2H), 5.30 (d, *J* = 8.8 Hz, 1H), 3.68 (s, 3H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 155.1, 133.4, 132.2, 132.2 (J_{C-P} = 128.0 Hz), 131.1, 128.8 (J_{C-P} = 13.0 Hz), 120.8 (J_{C-P} = 6.0 Hz), 114.7, 55.5 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 18.6 ppm. IR (KBr): ν = 3074, 2957, 2905, 2833, 1517, 1284, 1230, 1187, 1110, 1027, 927, 831, 725, 694, 582, 522 (cm^{-1}). MS (ESI): m/z (%) = 218.1, 324.1 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 324.1148; found: 324.1155.

4.2.26 *P*,*P*-Diphenyl-*N*-(*4*-fluorophenyl) phosphinic amide (3al)

White solid (124.4 mg, 80% yield). m.p. 170 - 172 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.84 (dd, *J* = 11.8, 8.0 Hz, 4H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.43 (d, *J* = 7.0 Hz, 4H), 6.99 – 6.94 (m, 2H), 6.80 (t, *J* = 8.1 Hz, 2H), 5.66 (d, *J* = 9.2 Hz, 1H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.3 (J_{C-P} = 239.0 Hz), 136.5, 132.4 (J_{C-P} = 3.0 Hz), 132.1 (J_{C-P} =5.0 Hz), 131.8 (J_{C-P} = 3.0 Hz), 128.9 (J_{C-P} = 3.0 Hz), 120.3 (J_{F-C-P} = 7.0 Hz), 115.9 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 18.9 ppm. ^{19}F NMR ($CDCl_3$, 370 MHz): δ = -121.9 ppm. IR (KBr): ν = 3470, 3265, 2982, 2895, 2351, 2319, 1630, 1548, 1516, 1396, 1046, 694, 644 (cm^{-1}). MS (ESI): m/z (%) = 79.0, 157.0, 312.0 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 312.1148; found: 312.0958.

4.2.27 *P*,*P*-Diphenyl-*N*-(*4*-chlorophenyl) phosphinic amide (3am)

White solid (122.6 mg, 75% yield). m.p. 233 - 234 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ = 8.43 (d, *J* = 11.6 Hz, 1H), 7.81 – 7.76 (m, 4H), 7.59 – 7.55 (m, 2H), 7.52 (d, *J* = 7.2 Hz, 4H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H) (ppm). ^{13}C NMR (DMSO-d_6, 100 MHz) δ = 141.2, 132.5 (J_{C-P} = 129.0 Hz), 132.1 (J_{C-P} = 2.0 Hz), 131.8 (J_{C-P} = 9.0 Hz), 128.9, 128.8, 124.6, 119.8 (J_{C-P} = 7.0 Hz) (ppm). ^{31}P NMR (DMSO-d_6, 160 MHz) δ = 17.0 (ppm). IR (KBr): ν = 3131, 3029, 2923, 2846, 1587, 1450, 1440, 1290, 1193, 1103, 930, 833, 812, 716, 694, 652, 554, 520 cm^{-1}. MS (ESI): m/z (%): 218.1, 328.0 (100). HRMS (ESI) (m/z) $[M+H]^+$: Calcd.328.0653, Found 328.0658.

4.2.28 *P*,*P*-Diphenyl-*N*-(*4*-bromophenyl) phosphinic amide (3an)

White solid (130.2 mg, 70% yield). m.p. 241 – 242 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 8.42 (d, *J* = 11.6 Hz, 1H), 7.78 (dd, *J* = 12.0, 7.4 Hz, 4H), 7.62 – 7.55 (m, 2H), 7.53 (d, *J* = 7.3 Hz, 4H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.01 (d, *J* = 8.1 Hz, 2H) (ppm). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 141.6, 132.5 (J_{C-P} = 126.0 Hz), 132.1 (J_{C-P} = 3.0 Hz), 131.7, 131.6, 128.8 (J_{C-P} = 13.0 Hz), 120.3 (J_{C-P} = 7.0 Hz), 112.3 (ppm). ^{31}P NMR (DMSO-d_6, 160 MHz): δ = 17.0 ppm. IR (KBr): ν = 3122, 3000, 2928, 2855, 1615, 1455, 1400, 1235, 1088, 1000, 884, 792, 714, 675, 554, 521 (cm^{-1}).MS (ESI): m/z (%) = 169.1, 338.13 (42), 372.0 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 372.0147; found: 372.0142.

4.2.29 *P*,*P*-Diphenyl-*N*-(*4*-(trifluoromethyl) phenyl) phosphinic amide (3ao)

White solid (146.2 mg, 81% yield). m.p. 160 - 162 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.83 (dd, *J* = 12.5, 7.7 Hz, 4H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.45 (td, *J* = 7.5, 3.2 Hz, 4H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 5.98 (d, *J* = 9.8 Hz, 1H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.0, 132.7 (J_{C-P} = 3.0 Hz), 132.0 (J_{C-P} = 10.0 Hz), 131.3 (J_{C-P} = 130.0 Hz), 129.1 (J_{C-P} = 13.0 Hz), 126.6 (J_{C-F} = 3.7 Hz), 118.1 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 19.0 ppm. ^{19}F NMR ($CDCl_3$, 370 MHz): δ = -61.8 ppm. IR (KBr): ν = 3122, 3000, 2928, 2855, 1615, 1455, 1400, 1235, 1088, 1000, 884, 792, 714, 675, 554, 521 (cm^{-1}). MS (ESI): m/z (%) = 79.0, 157.0, 324.9, 331.1, 362.1 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 362.0916; found: 362.0920.

4.2.30 *P*,*P*-Diphenyl-*N*-(*2*-nitrophenyl) phenyl) phosphinic amide (3ap)

White solid (109.9 mg, 65% yield). m.p. 160 - 162 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.19 (d, *J* = 12.1 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.89 (dd, *J* = 12.6, 7.7 Hz, 4H), 7.58 (t, *J* = 7.6 Hz, 3H), 7.51 (dd, *J* = 7.0, 2.7 Hz, 4H), 7.37 (t, *J* = 7.8 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 1H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 139.2, 136.1, 132.9 (J_{C-P} =3.0 Hz), 131.7 (J_{C-P} = 10.0 Hz), 131.2 (J_{C-P} = 128.0 Hz), 129.3 (J_{C-P} =13.0 Hz), 126.5, 121.1, 120.8 (J_{C-P} = 5.0 Hz), 100.1 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 19.7 ppm. IR (KBr): ν = 3291, 2966, 2923, 2843, 1608, 1497, 1447, 1392, 1261, 1026, 931, 811, 745, 685, 519 (cm^{-1}). MS (ESI): m/z (%) = 218.1, 339.1 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 339.0893; found: 339.0903.

4.2.31 *P*,*P*-Diphenyl-*N*-(1-naphthyl) phosphinic amide (3aq)

White solid (126.6 mg, 76% yield), m.p. 193 - 195 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.96 (d, *J* = 8.2 Hz, 4H), 7.92 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.49 (d, *J* = 8.0 Hz, 4H), 7.44 (d, *J* = 6.3 Hz, 4H), 7.20 (t, *J* = 7.8 Hz, 1H), 5.78 (d, *J* = 7.9 Hz, 1H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 135.5, 134.4, 132.4 (J_{C-P} = 2.0 Hz), 132.1 (J_{C-P} = 10.0 Hz), 132.0 (J_{C-P} = 129.0 Hz), 129.1, 129.0 (J_{C-P} = 13.0 Hz), 126.3 (J_{C-P} = 8.0 Hz), 126.1, 123.2, 120.3, 117.0 (J_{C-P} = 4.0 Hz) (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 19.1 ppm. IR (KBr): ν = 3453, 3403, 3058, 2963, 2914, 1585, 1503, 1450, 1426, 1318, 1253, 1172, 1099, 928, 804, 739, 685, 656, 530 (cm^{-1}). MS (ESI): m/z (%) = 228.2, 322.1, 338.3, 339.3, 344.1 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 344.1199; found: 344.1203.

4.2.32 *P*,*P*-Diphenyl-*N*-(2-pyridinyl) phosphinic amide (3ar)

White solid (67.6 mg, 46% yield), m.p. 191 - 192 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.87 (dd, *J* = 12.5, 7.4 Hz, 4H), 7.66 (s, 1H), 7.51 (t, *J* = 7.0 Hz, 2H), 7.43 (s, 4H), 7.34 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.71 – 6.60 (m, 1H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 154.2, 148.0, 138.1, 132.44(J_{C-P} = 2.0 Hz), 132.00(J_{C-P} = 12.0 Hz), 131.7 (J_{C-P} =129.0 Hz), 128.9 (J_{C-P} = 13.0 Hz), 117.2, 112.1 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 18.9 ppm. IR (KBr): ν = 3514, 3440, 3157, 3065, 3040, 2965, 2848, 2791, 1593, 1450, 1401, 1301, 1263, 1183, 1041, 917, 717, 774, 731, 687, 614, 529 (cm^{-1}). MS (ESI): m/z (%) = 218.1, 295.1 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 295.0995; found: 295.1005.

4.2.33 *P*,*P*-Diphenyl-*N*,*N*-di(*p*-tolyl) phosphinamide (4aa)

White solid (63.7mg, 32% yield). m.p. 160 - 162 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.77 (dd, *J* = 11.9, 7.7 Hz, 4H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 6.6 Hz, 4H), 7.14 (d, *J* = 7.9 Hz, 4H), 6.90 (d, *J* = 7.8 Hz, 4H), 2.18 (s, 6H) (ppm). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 142.3, 134.9, 132.9 (J_{C-P} = 9.0 Hz), 132.0 (J_{C-P} = 132.00 Hz), 131.5 (J_{C-P} = 3.0 Hz), 129.6, 128.2 (J_{C-P} =13.0 Hz), 127.6 (J_{C-P} = 4.0 Hz), 20.9 (ppm). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 24.8 ppm. IR (KBr): ν = 3230, 2963, 2920, 2859, 1603, 1507, 1439, 1257, 1195, 1106, 1025, 806, 693, 623, 558, 509 (cm-1). MS (ESI): m/z (%) = 118.1, 338.3, 338.3, 398.1 (100). HRMS (ESI): m/z calcd for $[M+H]^+$: 398.1668; found: 398.1671.

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Supplementary Material

Supporting Information is available *via* Http://

References

1. (a) Li G. Y, Zheng G, Noonan A. F, J. Org. Chem. 2001;66:8677;
(b) Kwong F. Y, Buchwald S. L, Org. Lett. 2002;4:3517;
(c) Bates C. G, Gujadhur R. K, Venkataraman, D. Org. Lett. 2002;4:2803;
(d) Taniguchi N, J. Org. Chem. 2004;69:6904;
(e) Taniguchi N, Onami T, J. Org. Chem. 2004;69:915;
(f) Itoh T, Mase T, Org. Lett. 2004;6:4587;
(g) Fernández-Rodríguez M. A, Shen Q, Hartwig J. F, J. Am. Chem. Soc. 2006;128:2180;
(h) Fernández-Rodríguez M. A, Shen Q, Hartwig J. F, Chem. Eur. J. 2006; 12:7782;
(i) Chen Y.-J, Chen H.-H, Org. Lett. 2006;8:5609;
(j) Kumar S, Engman L, J. Org. Chem. 2006;71:5400;
(k) Zhang Y, Ngeow K. C, Ying J. Y, Org. Lett. 2007;9:3495;
(l) Ranu B. C, Saha A, Jana R, Adv. Synth. Catal. 2007; 349:2690;
(m) Carril M, SanMartin R, Domínguez E, Tellitu I, Chem. Eur. J. 2007; 13: 5100;.
(n) Rout L, Sen T. K, Punniyamurthy T, Angew. Chem. Int. Ed. 2007; 46: 5583;
(o) Lv X, Bao W, J. Org. Chem. 2007;72:3863.
(p) Correa A, Carril M, Bolm C, Angew. Chem. Int. Ed. 2008;47:2880;
(q) Sperotto E, van Klink G. P. M, de Vries J. G, van Koten G, J. Org. Chem. 2008;73:5625;
(r) Rout L, Saha P, Jammi S, Punniyamurthy T. Eur, J. Org. Chem. 2008; 2008:640;
(s) Fernández-Rodríguez M. A, Hartwig J. F, J. Org. Chem. 2009;74:1663;
(t) Wu J.-R, Lin C.-H, Lee C.-F, Chem. Commun. 2009:4450;
(u) Chen C.-K, Chen Y.-W, Lin C.-H, Lin H.-P. Lee C.-F, Chem. Commun. 2010;46:282;
(v) Wang H, Jiang L, Chen T, Li Y, Eur. J. Org. Chem. 2010; 2324;
(w) Kao H.-L, Lee C.-F, Org. Lett. 2011;13:5204;
(x) Huang Y.-B, Yang C.-T, Yi J, Deng X.-J, Fu Y, Liu L, J. Org. Chem. 2011;76:800;
2. (a) Chan D. M. T, Monaco K. L, Wang R.-P, Winters M. P, Tetrahedron Lett. 1998;39:2933;
(b) Evans D. A, Katz J. L, West T. R, Tetrahedron Lett. 1998;39:2937;
(c) Lam P. Y. S, Clark C. G, Saubern S, Adams J, Winters M. P, Chan D. M. T, Combs A, Tetrahedron Lett. 1998;39:2941;
3. (a) Antilla J. C, Buchwald S. L, Org. Lett. 2001;3:2077;
(b) Quach T. D, Batey R. A, Org. Lett. 2003;5:4397;
(c) Chiang G. C. H, Olsson T, Org. Lett. 2004;6:3079;
(d) Singh B. K; Appukkuttan P, Claerhout S, Parmar V. S, Van der Eycken E, Org. Lett. 2006; 8:1863;
(e) Krouželka J, Linhart I, Eur. J. Org. Chem. 2009:6336;
(f) González I, Mosquera J, Guerrero C, Rodríguez R, Cruces J, Org. Lett. 2009;11:1677;
(g) Islam M, Mondal S, Mondal P, Roy A. S, Tuhina K, Mobarok M, Paul S, Salam N, Hossain D, Catal. Lett. 2011; 141: 1171;
(h) Kaboudin B, Abedi Y, Yokomatsu T, Eur. J. Org. Chem. 2011: 6656
(i) Naya L, Larrosa M, Rodríguez R, Cruces J, Tetrahedron Lett. 2012;53: 769.
(j) Bruneau A, Brion J.-D, Alami M, Messaoudi S, Chem. Commun. 2013; 49:8359;
(k) Yu J.-T, Guo H, Yi Y, Fei H, Jiang Y, Adv. Synth. Catal. 2014;356: 749;
4. Raghuvanshi D. S, Gupta A. K, Singh K. N, *Org. Lett.* 2012;14:4326;
5. Qiao J. X, Lam P. Y. S, *Synthesis* 2011:829;
6. (a) Hügel H. M, Rix C. J, Fleck K, Synlett. 2006: 2290;
(b) Kantam M. L, Venkanna G. T, Sridhar C, Sreedhar B, Choudary B. M, J. Org. Chem. 2006; 71: 9522;
(c) Grimes K. D, Gupte A, Aldrich C. C, Synthesis. 2010: 1441;
(d) Zheng Z.-G, Wen J, Wang N, Wu B, Yu X.-Q, Beilstein, J. Org. Chem. 2008;4:40;
(e) Larrosa M, Guerrero C, Rodríguez R, Cruces J, Synlett. 2010:2101;
(f) Sueki S, Kuninobu Y, Org. Lett. 2013;15:1544;
(g) Rossi S. A, Shimkin K. W, Xu Q, Mori-Quiroz L. M, Watson D. A, Org. Lett. 2013;15:2314;
(h) Srivastava V. P, Yadav D. K, Yadav A. K, Watal G, Yadav L. D. S, Synlett. 2013;24:1423;
(i) Gao J, Shao Y, Zhu J, Zhu J, Mao H, Wang X, Lv X, J. Org. Chem. 2014;79:9000;
(j) Moon S.-Y, Nam J, Rathwell K, Kim W.-S, Org. Lett. 2014;16:338;
(k) Nasrollahzadeh M, Ehsani A, Maham M, Synlett. 2014;25:505;
(l) Jiang Y, Huang S, Synlett. 2014;25:407;
(m) Moon S.-Y, Kim U. B, Sung D.-B, Kim W.-S, J. Org. Chem. 2015;80: 1856;
(n) Vantourout J. C, Law R. P, Isidro-Llobet A, Atkinson S. J, Watson A. J. B, J. Org. Chem. 2016;81:3942;
7. (a) Quach T. D, Batey R. A, Org. Lett. 2003;5;1381;
(b) Shade R. E, Hyde A. M, Olsen J.-C, Merlic C. A, J. Am. Chem. Soc. 2010;132:1202;
(c) Zhang L, Zhang G, Zhang M, Cheng J, J. Org. Chem. 2010;75; (21): 7472;
(d) Jacobson C. E, Martinez-Muñoz N, Gorin D. J, J. Org. Chem. 2015;80:7305 and the citations therein;
8. Zhuang R, Xu J, Cai Z, Tang G, Fang M, Zhao Y, Org. Lett. 2011;13:2110;
9. (a) Wang L, Zhou W.-Y, Chen S.-C, He M.-Y, Chen Q, Synlett. 2011: 3041;
(b) Yin P, Liu N, Deng Y.-X, Chen Y, Deng Y, He L, J. Org. Chem. 2012; 77:2649;
(c) Sun N, Zhang H, Mo W, Hu B, Shen Z, Hu X, Synlett. 2013;24:1443;
10. (a) Rewcastle G. W, Baguley B. C, Cain B. F, J. Med. Chem. 1982;25: 1231;
(b) Hrubiec R. T, Shyam K, Cosby L. A, Furubayashi R, Sartorelli A. C, J. Med. Chem. 1986; 29: 1299;
(c) Dillon K. B, Mathey F, Nixon J. F, in Phosphorus: The Carbon Copy; John Wiley & Sons: Chichester, 1998.
(d) Seto H, Kuzuyama T, Nat. Prod. Rep. 1999;16:589;
(e) McCarthy M, Guiry P. J, Tetrahedron 2001;57: 3809;
(f) Tang W, Zhang X, Chem. Rev. 2003;103:3029;
(g) Sørensen M. D, Blæhr L. K. A, Christensen M. K, Høyer T, Latini S, Hjarnaa P.-J. V, Björkling F, Bioorg. Med. Chem. 2003;11:5461;
(h) Methot J. L, Roush W. R, Adv. Synth. Catal. 2004;346:1035;
(i) Grushin V, V. Chem. Rev. 2004;104:1629;
(j) Köhn M, Breinbauer R, Angew. Chem. Int. Ed. 2004;43:3106;
(k) Peng A.-Y, Ding Y.-X, Org. Lett. 2005;7:3299;
(l) Li X, Zhang D, Pang H, Shen F, Fu H, Jiang Y, Zhao Y, Org. Lett. 2005;7:4919;
(m) Mucha A, Kunert A, Grembecka J, Pawełczak M, Kafarski P, Eur. J. Med. Chem. 2006;41:768;
(n) Grabulosa A, Granell J, Muller G, Coord. Chem. Rev. 2007;251:25;
(o) Ruda G. F, Wong P. E, Alibu V. P, Norval S, Read K. D, Barrett M. P, Gilbert I. H, J. Med. Chem. 2010;53:6071;
(p) Li B, Zhou B, Lu H, Ma L, Peng A.-Y, Eur. J. Med. Chem. 2010;45: 1955;
(q) Lühr S, Holz J, Börner A, ChemCatChem. 2011;3:1708;
(r) Stankevič M, Bazan J, J. Org. Chem. 2012;77: 8244;
(s) Han Z. S, Zhang L, Xu Y, Sieber J. D, Marsini M. A, Li Z, Reeves J. T, Fandrick K. R, Patel N. D, Desrosiers J.-N, Qu B, Chen A, Rudzinski D. M, Samankumara L. P, Ma S, Grinberg N, Roschangar F, Yee N. K, Wang G, Song J. J, Senanayake C. H, Angew. Chem. Int. Ed. 2015;54:5474;
(t) Liu L, Zhang A.-A, Wang Y, Zhang F, Zuo Z, Zhao W.-X, Feng C.-L, Ma W, Org. Lett. 2015;17:2046;
(u) Wang L, Du Z, Wu Q, Jin R, Bian Z, Kang C, Guo H, Ma X, Gao L, Eur. J. Org. Chem. 2016:2024;
11. (a) Tang W, Ding Y.-X, J. Org. Chem. 2006;71:8489;

(b) Park S, Seo B, Shin S, Son J. Y, Lee P. H, Chem. Commun. 2013;49: 8671;
(c) Nguyen T. T, Grigorjeva L, Daugulis O, ACS Catal. 2016;6:551;
12. Li J, Zhang S. L, Tao C. Z, Fu Y, Guo Q. X, Chin. Chem. Lett. 2007;18:1033;