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Cobalt-catalyzed oxidative arylmethylation of phosphorylamides

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ABSTRACT

A cobalt-catalyzed strategy for *N*-arylmethylation of phosphorylamides was herein achieved with the assistance of azodiisobutyronitrile as the radical initiator and di-*tert*-butyl peroxide as the oxidant. Both methylarenes and diaryl methanes were compatible under the oxidative conditions, expressing broad substrate scope (51 examples) and high efficiency (up to 87% yield).

1. Introduction

Phosphorylamides [1], which possess -P(O)-N- unit, have been appealing research topic not only because of their unique architecture, but also for the extraordinary pharmaceutical and material properties [2]. Additionally, -P(O)-N-backboned molecules have been elaborately designed for asymmetric syntheses [3], and some biologically active heterocycles have been successfully prepared from the principal intermediates [4]. However, novel methodologies are still highly demanded in the light of diversification requirement which was driven by the nature of screening process. Despite the rapid growth have been witnessed in the field [1–9], the direct modifications of the NH_2 group on the phosphorylamides remained underexploited due to the facile cleavage of P-N bonds [10] and superior stability of their N-H bonds relative to other amides [11], which means the direct *N*-functionalization of the amides has remained a great challenge. Benzylation attracted our attention due to a recent description of a benzylated compound that can function as a flame retardant (BA-DOPO, Scheme 1) [6b,6c].

Traditional means of benzylic functionalization involving pre-activated substrates suffer from requiring harsh conditions and tedious steps and generating halogenated waste [6,7] among other issues. However, benzylic C-H bonds, which are highly reactive [12], have been directly oxidized to construct different C(sp^3)-N bonds because direct functionalization is more environmentally friendly and atom/step economical. Amines [13], amides [14], sulfonamides [14c,15], and sulfoximines [16] can be readily benzylated by straightforward procedures. Based on the previous successfully established arylation [8], methylation (alkylation) [9] of phosphorylamides, we wish to describe our durative studies on benzylation of the same substrates by (di)arylmethanes. Beyond our expectations, simple transferring the conditions of methylation (alkylation) for arylmethylation gave benzylated product in trace amount. Therefore, cobalt catalysts, which were considered cheaper and more environmentally benign, were turned to for the arrival of the useful transformation. Additionally, the oxidative methodology possessed the advantages including high substrate generality and P-N bond reservation under the oxidative conditions.

2. Results and discussions

Firstly, the conditions for the reaction between diphenyl

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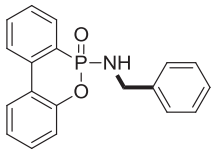
0040-4020/

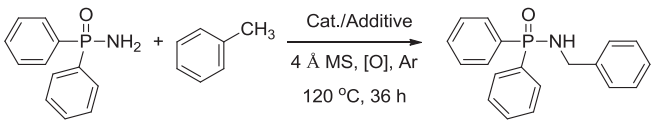


BA-DOPO
Flame retardant

Scheme 1. Useful N-benzyl phosphorylamide.

phosphinamide (**1a**) and toluene (**2a**) were optimized, as shown in Table 1. Under the standard methylation/alkylation conditions, the combination of CuI/1,10-phenanthroline was capable to make the arylmethylation reaction happen in the presence of DCP (dicumyl peroxide) with low efficiency, and **3aa** was detected in trace amount after 36 h at 120 °C (entry 1). Other copprous catalysts, such as CuCl and CuBr did not make the reaction occur in the presence of 1,10-phenanthroline under the oxidative conditions (entries 2 and 3). Palladium catalysts, which were exemplified by $PdCl_2$ and $Pd(OAc)_2$, failed to offer positive effect to the transformation, and no reaction was detected (entries 4 and 5), either did AgOAc (entry 6). Gratifyingly, iron catalysts in general gave positive performance in the system. Employment of $FeCl_2$, $FeBr_2$, $FeBr_3$ rendered the benzylation of phosphorylamide **1a** take place smoothly, forming the desired product **3aa** in yields from 25% to 28% (entries 7–9). The best performance of the arylmethylation protocol was obtained with the assistance of cobalt-catalysts. And

Table 1
Optimization of the reaction conditions.[a]



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

Entry	Cat.	Additive	[O]	Yield[b]
1	CuI	Phen[c]	DCP	trace
2	CuCl	Phen	DCP	n.d.[d]
3	CuBr	Phen	DCP	n.d.
4	$PdCl_2$	Phen	DCP	n.d.
5	$Pd(OAc)_2$	Phen	DCP	n.d.
6	AgOAc	Phen	DCP	n.d.
7	$FeCl_2$	Phen	DCP	20%
8	$FeCl_3$	Phen	DCP	25%
9	$FeBr_3$	Phen	DCP	28%
10	$CoCl_2$	Phen	DCP	38%
11	$CoBr_2$	Phen	DCP	42%
12	$NiCl_2$	Phen	DCP	n.d.
13	$NiBr_2$	Phen	DCP	n.d.
14	$CoBr_2$	TMEDA	DCP	35%
15	$CoBr_2$	DMEDA	DCP	32%
16	$CoBr_2$	AIBN	DCP	68%
17	$CoBr_2$	AIBN	DTBP	82%
18	$CoBr_2$	AIBN	TBHP	72%
19	$CoBr_2$	AIBN	DTBP	78%[e]
20	–	AIBN	DTBP	n.d.
21	$CoBr_2$	AIBN	DTBP	42%[f]

[a] Reactions conditions: **1a** (0.3 mmol), **2a** (3.0 mL, ca. 30 mmol), cat. (10 mol%), 4 Å molecular sieves (MS, powdered, 200 wt%), additive (0.2 equiv.), [O] (2.0 equiv.) at 120 °C under argon (1 atm) in a sealed tube for 36 h.
[b] Isolated yields.
[c] For 1,10-phenanthroline.
[d] For not detected.
[e] At 140 °C.
[f] No 4 Å MS added.

$CoBr_2$ offered superior effect to $CoCl_2$ did for higher 42% of **3aa** was isolated in the $CoBr_2$-mediated system (entries 10 and 11). Disappointingly, $NiCl_2$ and $NiBr_2$ failed to provide positive effect to the strategy and no reaction was checked at 120 °C for 36 h (entries 12 and 13). Successive screening on the additives was also conducted. And diamine ligands, for example, tetramethylethylenediamine (TMEDA) and *N,N′*-dimethylethylenediamine (DMEDA) afforded the similar effect to 1,10-phenanthroline did, and 35% and 32% of **3aa** was isolated, respectively (entries 14 and 15). Beyond our expectations, participation of AIBN (azodiisobutyronitrile), which was regarded as the radical initiator generally, dramatically increased the yield of **3aa** up to 68% (entry 16). And replacement of DTBP (di-*tert*-butyl peroxide) with DCP led to higher efficiency of the transformation, and 82% of **3aa** was separated successfully (entry 17). However, TBHP (*tert*-butyl hydroperoxide) gave inferior effect to that DTBP did (entry 18). Elevated temperature (140 °C) did not provide positive effect to the protocol and decreased yield of **3aa** was observed (entry 19). No doubt, no reaction was detected without an addition of the cobalt catalyst to the system (entry 20). Moreover, decreased efficiency of the transformation (42% yield of **3aa**) was observed if the reaction was conducted without addition of 4 Å MS, probably due to the absorption of the H_2O, which was generated in situ under the oxidative conditions (entry 21).

Following the successful establishment of the optimal conditions, the substrate scope and limitations of the phosphonamides were evaluated in the $CoBr_2$-catalyzed systems (Table 2).

Alkoxyl substituted phosphonamides, such as *P*-methoxy-, *P*-ethoxy-, *P*-isopropoxy- and *P*-*n*-butoxy-*P*-phenyl phosphonamides (**1b** – **1e**) coupled efficiently with **2a** in the Co-catalyzed system, and they provided the corresponding *N*-benzyl amides **3ba** – **3ea** in 70%–76% yields. Additionally, *P*-cyclohexyloxy-*P*-phenyl phosphonamide (**1f**) provided **3fa** in 79% yield. In a similar fashion, *P*-methoxyethoxy-*P*-phenyl phosphonamide (**1g**) and *P*-chloropropoxy-*P*-phosphonamide (**1h**) readily coupled with **2a** and furnished **3ga** and **3ha** in 66% and 69% yields, respectively. (Un) substituted benzyloxy-decorated phosphonamides were also well tolerated in the system. For instance, *P*-benzyloxy-, *P*-(2-fluorobenzyloxy)-, *P*-(4-chlorobenzyloxy)- and *P*-(4-bromobenzyloxy)-*P*-phenyl phosphonamides (**1i** – **1l**) were smoothly benzylated to afford corresponding products in **3ia** – **3la** in yields of 76%–80%. Similarly, the flame retardant BA-DOPO (**3ma**) was also provided in 68% yield by the oxidative protocol.

Furthermore, the scope of methylarenes in the oxidative system was also examined. To our satisfaction, 2-methyltoluene (**2b**), 3-methyltoluene (**2c**), 4-methyltoluene (**2d**) and mesitylene (**2e**) smoothly underwent the phosphorylamidation reaction and provided **3ab** – **3ae** in yields from 82% to 87%. In addition, varying the methyl groups on the methylarenes did not affect the efficiency of the reaction. *p*-*tert*-Butyltoluene (**2f**) and *p*-methoxytoluene (**2g**) were also tolerated, and **3af** and **3ag** were isolated in 80% and 70% yields, respectively. Halogenated toluenes could also serve as benzylating agents for 4-fluoro-, 2-chloro-, 3-chloro-, 4-chloro-, and 4-bromotoluenes (**2h** – **2l**), which easily coupled with **1a** to give **3ah** – **3al** in 72%–87% yields. *p*-Trifluoromethyltoluene (**2m**) and *p*-methylbenzoic methyl ester (**2n**) underwent amidation, and **3am** and **3an** were obtained in moderate yields. Polyarenes 1-methylnaphthalene (**2o**) and 2-methylnaphthalene (**2p**) provided **3ao** and **3ap** in 67% and 62% yields, respectively. However, electron-deficient methylarenes and methylheteroarenes, like 4-nitrotoluene (**2q**), *p*-tolunitrile (**2r**), 2-methylfuran (**2s**) and 2-methylpyridine (**2t**), failed to couple with **1a** under the oxidative reaction conditions. Contrary to our expectations, phosphinamidation occurred at the benzylic position of ethylbenzene (**2u**) and afforded **3au** in 62% yield.

Encouraged by the broad substrate scope and high efficiency of

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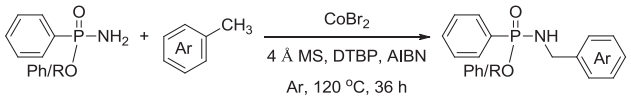
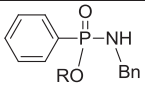
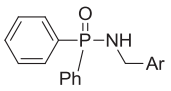
Table 2
Substrates scope of the phosphonamides.[a]



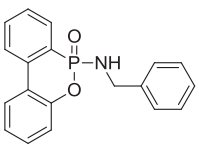
1a- 1l **2a - 2u** **3ba - 3ma**
3ab - 3au



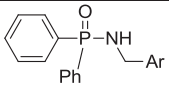
3ba: R = CH_3, 73%
3ca: R = C_2H_5, 76%
3da: R = $(CH_3)_2CH$, 70%
3ea: R = *n*-C_4H_9, 72%
3fa: R = cyclo-C_6H_{11}, 79%
3ga: R = $CH_3OC_2H_4$, 66%
3ha: R = ClC_3H_6, 69%
3ia: R = Bn, 80%
3ja: R = 2-FBn, 77%
3ka: R = 4-ClBn, 79%
3la: R = 4-BrBn, 76%



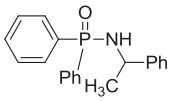
3aq: Ar = 4-NO_2Ph, n.d.
3ar: Ar = 4-CNPh, n.d.
3as: Ar = 2-furanyl, n.d.
3at: Ar = 2-pyridinyl, n.d.



3ma: BA-DOPO: 68%



3ab: Ar = 2-tolyl, 82%
3ac: Ar = 3-tolyl, 87%
3ad: Ar = 4-tolyl, 86%
3ae: Ar = 3,5-$(CH_3)_2$Ph, 82%
3af: Ar = 4-*t*BuPh, 80%
3ag: Ar = 4-MeOPh, 70%
3ah: Ar = 4-FPh, 83%
3ai: Ar = 2-ClPh, 84%
3aj: Ar = 3-ClPh, 80%
3ak: Ar = 4-ClPh, 87%
3al: Ar = 4-BrPh, 74%
3am: Ar = 4-CF_3Ph, 70%
3an: Ar = 4-$CH_3OC(O)$Ph, 68%
3ao: Ar = 1-naphthyl, 67%
3ap: Ar = 2-naphthyl, 62%



3au: 62%

[a]Reaction conditions: **1** (0.5 mmol), **2** (5.0 mL, ca. 30 mmol), $CoBr_2$ (10 mol%), 4 Å molecular sieves (MS, powdered, 200 wt%), DTBP (2.0 equiv.) and AIBN (0.2 equiv.) at 120 °C under argon (1 atm) in a sealed tube for 36 h.

the method, the amidation protocol was further extended to diphenyl methanes possessing benzylic C-H bonds (Table 3).

However, $CHCl_3$ proved to be crucial to the oxidative protocol while the loading of **4** was reduced (1.5 equiv.) in the presence of $CoBr_2$. Similar to toluene, diphenyl methane (**4a**) smoothly underwent the oxidative amidation reaction with diphenyl phosphinamide (**1a**) and phosphonamides **1b** – **1l** and generated corresponding derivatives **5aa** – **5al** in yields from 62% to 78%. The substrate scope of diaryl methanes with various functional groups was then explored. Symmetric diaryl methanes, such as di-(*p*-tolyl) methane (**4b**), di-(*p*-methoxyphenyl) methane (**4c**) and di-(*p*-fluorophenyl) methane (**4d**), were well tolerated under the oxidative amidation conditions, and they afforded **5ab** – **5ad** in 68%–72% yields. Gratifyingly, asymmetric diaryl methanes were also well tolerated in the system, and phosphinamino groups were successfully installed at the benzylic positions of the substrates. (*o*-Methylphenyl) phenyl methane (**4e**), (*m*-methylphenyl) phenyl methane (**4f**), (*p*-methylphenyl) phenyl methane (**4g**), (*4*-methoxylphenyl) phenyl methane (**4h**), (*4*-fluorophenyl) phenyl methane (**4i**), (*4*-chlorophenyl) phenyl methane (**4j**), (*4*-bromophenyl) phenyl methane (**4k**), (*4*-trifluoromethylphenyl) phenyl methane (**4l**) and (*4*-tolyl) (4-fluorophenyl) methane (**4m**) furnished corresponding *N*-methyl phosphinamides **5ae** – **5al** in yields of 58%–73%.

To further elucidate the newly developed protocol, competitive reactions were conducted in the Co(II)-system, and the results are shown in Scheme 2. The reaction of a mixture of equal amounts of (0.25 mmol) *P,P*-diphenyl phosphinamide (**1a**) and *P*-phenyl-*P*-methoxy phosphonamide (**1b**) with **2a** (5.0 mL) was carried out to evaluate the difference in reactivity of the amino groups. After 8 h, **3aa** and **3ba** were isolated in 18% and 16% yields, respectively, while 30% and 27% yields were obtained after 12 h, indicating that the two amino groups exhibited almost the same reactivities under these conditions (Eq. (1)). Notably, the reaction between **1a** and a mixture of **2a** (2.5 mL) and **2u** (2.5 mL) provided 65% of **3aa** and trace **3au**. The result proved that the benzyl C-H bonds of toluene are more reactive that those of ethylbenzene (Eq. (2)). Similarly, a comparison of the benzylic C-H bonds of **2a** and **4a** was conducted based on the reaction of **1a** with equal amounts of **2a** and **4a** (2.5 mL). After 36 h, a trace amount of **3aa** was found, while **5aa** was isolated in 68% yield, which was in accordance with the fact that diaryl methane generally performed better than methylarenes under these reaction conditions (Eq. (3)).

Mechanistic studies were conducted with the addition of TEMPO (2,2,6,6-tetramethyl piperidinyl -1-oxide) in the protocol and trace **3aa** was detected. However, attempts for isolation of the TEMPO-benzyl adduct failed probably due to the instability of the intermediate in the system. Results that the yields of **3aa** were depressed severely indicated that the reaction likely took place through a single-electron transfer (SET) pathway. Exemplified with

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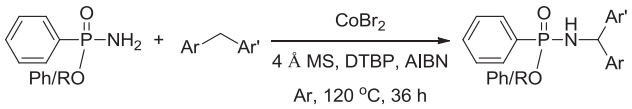
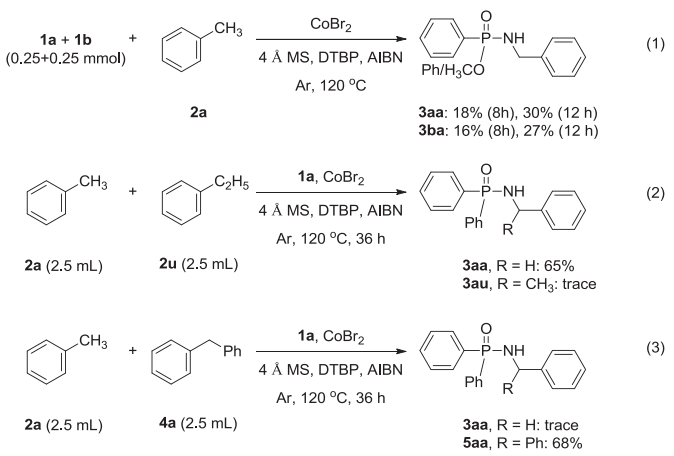
Table 3
Substrates scope on aryl boronic acids.[a]



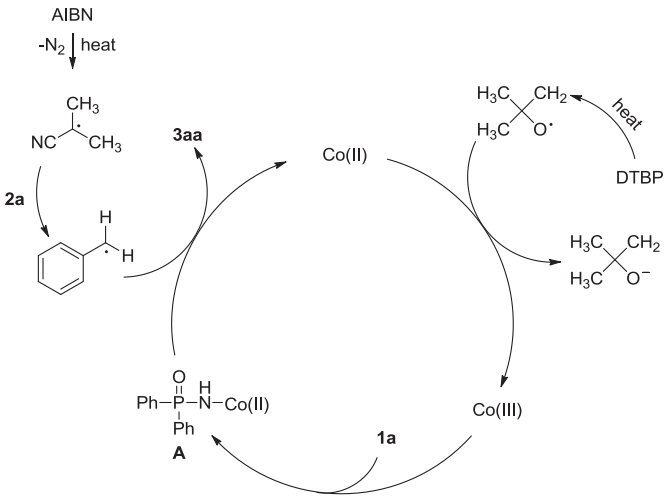
5aa: Ph, 78%
5ba: R = Me, 68%
5ca: R = Et, 72%
5da: R = *i*Pr, 69%
5ea: R = *n*Bu, 70%
5fa: R = cyclohexyl, 62%
5ga: R = $MeOC_2H_4$, 70%
5ha: R = ClC_3H_6, 68%
5ia: R = Bn, 72%
5ja: R = 2-FBn, 75%
5ka: R = 4-ClBn, 70%
5la: R = 4-BrBn, 70%

5ab: Ar = Ar' = *p*-tolyl, 72%
5ac: Ar = Ar' = 4-MeOPh, 68%
5ad: Ar = Ar' = 4-FPh, 65%
5ae: Ar = Ph, Ar' = *o*-tolyl, 70%
5af: Ar = Ph, Ar' = *m*-tolyl, 71%
5ag: Ar = Ph, Ar' = *p*-tolyl, 73%
5ah: Ar = Ph, Ar' = 4-MeOPh, 65%
5ai: Ar = Ph, Ar' = 4-FPh, 63%
5aj: Ar = Ph, Ar' = 4-ClPh, 67%
5ak: Ar = Ph, Ar' = 4-BrPh, 65%
5al: Ar = Ph, Ar' = 4-CF_3Ph, 58%
5am: Ar = *p*-tolyl, Ar' = 4-FPh, 70%

[a]Conditions: **1** (0.5 mmol), **4** (1.5 equiv.), $CoBr_2$ (10 mol%), 4 Å molecular sieves (MS, powdered, 200 wt%), DTBP (2.0 equiv.) and AIBN (0.2 equiv.) in $CHCl_3$ (5.0 mL) at 120 °C under argon (1 atm) in a sealed tube for 36 h.



Scheme 2. Competitive reactions.



Scheme 3. Proposed mechanism.

the reaction between **1a** and **2a** in the presence of CuI, a plausible radical mechanism of the phosphorylamidation of benzylic C-H bonds was proposed as shown in Scheme 3. Initially, Co(II) was oxidized into Cu(III) by the free-radical particle (^{t}BuO•), which was generated easily by heating from DTBP. Then, coordination of Co(III) and **1a** led to the successful formation of the key liganded intermediate **A**. The in situ formed intermediate **A** interacted with a benzyl radical particle, which was produced from isobutyronitrile radical by AIBN with a release of a N_2 molecule under heating, affording the desired benzylated phosphorylamide **3aa** and the Co(II), which entered the next catalytic circle. In the same manner, cobalt-mediated transformation would occur through the Co(II)/Co(III)-circle under the oxidative conditions.

3. Conclusion

In conclusion, we have disclosed a $CoBr_2$-catalyzed oxidative arylmethylation of phosphorylamides, offering broad functional group tolerance for methylarenes and diaryl methanes, and provide a general and efficient avenue for the preparation of phosphinamide and phosphonamide derivatives. Additionally, further explorations on the synthetic and clinical applications of the products are ongoing in our laboratory.

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 ($\delta = 7.26$ ppm for ^{1}H NMR and $\delta = 77.16$ 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

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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-benzyl phosphorylamides **3** (**5**)

Under the argon stomosphere, a Schlenk tube (35 mL) equipped with a magnetic bar was charged with a solution of **1** (0.5 mmol), MS (4 Å, powdered, 200 wt%), $CoBr_2$ (10 mol%), AIBN (0.2 equiv.) in **2** or **4** (5.0 mL, ca. 30 equiv.), then DTBP (2.0 equiv.) was added dropwise to the system and the mixture was allowed to stir at 120 °C for 36 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 ethyl acetate as eluent to give the corresponding products **3** or **5** in noted yields.

4.2.2. Procedures for control reactions (Scheme 2)

Under the argon stomosphere, a Schlenk tube (35 mL) equipped with a magnetic bar was charged with a solution of **1a** (0.5 mmol), or a mixture of **1a** (0.25 mmol) and **1b** (0.25 mmol), MS (4 Å, powdered, 200 wt%), $CoBr_2$ (10 mol%), AIBN (0.2 equiv.) in a mixture of **2a** and **2u** (2.5 mL + 2.5 mL) or **2a** and **4a** (2.5 mL + 2.5 mL) or **2a** (5.0 mL, ca. 30 equiv.), then DTBP (2.0 equiv.) was added dropwise to the system and the mixture was allowed to stir at 120 °C for noted time. 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 ethyl acetate as eluent to give the corresponding results.

4.2.3. N-Benzyl-P,P-diphenylphosphinamide (3aa)

Colorless oil (75.4 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99–7.89 (m, 4H), 7.54–7.40 (m, 6H), 7.40–7.30 (m, 4H), 7.29–7.23 (m, 1H), 4.13 (t, J = 7.2 Hz,2H), 3.32–3.19 (m, 1H)(ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.6 ($J_{C\text{-}P}$ = 8.3 Hz), 132.3 ($J_{C\text{-}P}$ = 9.5 Hz), 132.2 ($J_{C\text{-}P}$ = 129.3 Hz), 132.1 ($J_{C\text{-}P}$ = 2.6 Hz), 128.8, 128.7 ($J_{C\text{-}P}$ = 12.5 Hz), 127.8, 127.5, 44.8 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) δ = 23.7 (ppm). MS (EI): m/z = 77.0 (21), 91.1 (15), 106.1 (100), 155.1 (19), 201.1 (54), 202.0 (45), 307.1 (15). IR (in KBr): ν = 3748, 3170, 1437, 1182, 1115, 1067, 845, 725, 692, 554, 519 (cm^{-1}). HRMS (ESI) (m/z) [$C_{19}H_{18}NOP + H^+$]: Calcd. 308.1204, Found. 308.1208.

4.2.4. N-Benzyl-P-methyl-P-phenylphosphonamide (3ba)

White solid (95.1 mg, 73% yield). m.p.: 59–60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73 (dd, J = 12.7, 7.5 Hz, 2H), 7.48–7.41 (m, 1H), 7.40–7.33 (m, 2H), 7.25–7.12 (m, 5H), 4.06–3.91 (m, 2H), 3.63 (d, J = 11.1 Hz, 3H), 3.36–3.18 (m, 1H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.6 ($J_{C\text{-}P}$ = 6.3 Hz), 132.0 ($J_{C\text{-}P}$ = 2.9 Hz), 131.6 ($J_{C\text{-}P}$ = 9.8 Hz), 130.3 ($J_{C\text{-}P}$ = 173.3 Hz), 128.6, 128.5 ($J_{C\text{-}P}$ = 14.0 Hz), 127.5, 127.4, 51.4 ($J_{C\text{-}P}$ = 5.8 Hz), 44.9 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) δ = 24.0 (ppm). MS (EI): m/z = 77.1 (8), 91.0 (7), 106.1 (100), 141.0 (6), 155.0 (17), 261.0 (8). IR (in KBr): ν = 3208, 2945, 1443, 1207, 1128, 1034, 857, 750, 698, 552, 517 (cm^{-1}). HRMS (ESI) (m/z) [$C_{14}H_{16}NO_2P + H^+$]: Calcd. 262.0997, Found. 262.0990.

4.2.5. N-Benzyl-P-ethyl-P-phenylphosphonamide (3ca)

Yellowish oil (105.1 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 (dd, J = 12.6, 7.6 Hz, 2H), 7.47–7.40 (m, 1H), 7.40–7.32 (m, 2H), 7.25–7.11 (m, 5H), 4.09–3.91 (m, 4H), 3.30–3.15 (m, 1H), 1.23 (d, J = 6.9 Hz, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.7 ($J_{C\text{-}P}$ = 6.5 Hz), 131.9 ($J_{C\text{-}P}$ = 2.9 Hz), 131.6 ($J_{C\text{-}P}$ = 9.7 Hz), 130.9 ($J_{C\text{-}P}$ = 172.8 Hz), 128.6, 128.5 ($J_{C\text{-}P}$ = 14.5 Hz), 127.5, 127.4, 60.8 ($J_{C\text{-}P}$ = 5.6 Hz), 44.9, 16.4 ($J_{C\text{-}P}$ = 6.8 Hz) (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) δ = 22.4 (ppm). MS (EI): m/z = 77.1 (13), 94.0 (10), 106.1 (100), 141.0 (21), 246.0 (14), 275.1 (33). IR (in KBr): ν = 3664, 3210, 2940, 1444, 1207, 1127, 1036, 754, 697, 555, 518 (cm^{-1}). HRMS (ESI) (m/z) [$C_{15}H_{18}NO_2P + H^+$]: Calcd. 276.1153, Found. 276.1150.

4.2.6. N-Benzyl-P-isopropyl-P-phenylphosphonamide (3da)

Yellowish oil (101.4 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (dd, J = 12.6, 7.5 Hz, 2H), 7.46–7.40 (m, 1H), 7.40–7.33 (m, 2H), 7.25–7.13 (m, 5H), 4.75–4.63 (m, 1H), 4.03–3.95 (m, 2H), 3.01 (bs, 1H), 1.25 (dd, J = 9.6, 7.0 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.7 ($J_{C\text{-}P}$ = 7.3 Hz), 131.9 ($J_{C\text{-}P}$ = 2.9 Hz), 131.6 ($J_{C\text{-}P}$ = 9.7 Hz), 131.5 ($J_{C\text{-}P}$ = 172.9 Hz), 128.6, 128.5 ($J_{C\text{-}P}$ = 14.2 Hz), 127.5, 127.4, 69.7 ($J_{C\text{-}P}$ = 5.6 Hz), 45.0, 24.3 ($J_{C\text{-}P}$ = 4.3 Hz) (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) δ = 21.1 (ppm). MS (EI): m/z = 77.1 (5), 91.0 (6), 106.1 (100), 141.0 (11), 246.1 (7), 289.1 (4). IR (in KBr): ν = 3666, 3212, 2965, 1445, 1268, 1206, 1030, 755, 696, 555, 516 (cm^{-1}). HRMS (ESI) (m/z) [$C_{16}H_{20}NO_2P + H^+$]: Calcd. 290.1310, Found. 290.1315.

4.2.7. N-Benzyl-P-butyl-P-phenylphosphonamide (3ea)

Yellowish oil (108.8 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 (dd, J = 12.7, 7.5 Hz, 2H), 7.48–7.41 (m, 1H), 7.41–7.34 (m, 2H), 7.25–7.13 (m, 5H), 4.06–3.88 (m, 4H), 3.18–3.01 (m, 1H), 1.62–1.53 (m, 2H), 1.37–1.28 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.7 ($J_{C\text{-}P}$ = 6.6 Hz), 132.0 ($J_{C\text{-}P}$ = 2.9 Hz), 131.6 ($J_{C\text{-}P}$ = 9.7 Hz), 130.9 ($J_{C\text{-}P}$ = 173.0 Hz), 128.6, 128.5 ($J_{C\text{-}P}$ = 14.3 Hz), 127.5, 127.4, 64.6 ($J_{C\text{-}P}$ = 5.8 Hz), 45.0, 32.6 ($J_{C\text{-}P}$ = 6.8 Hz), 19.0, 13.8 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) δ = 22.2 (ppm). MS (EI): m/z = 77.0 (9), 91.0 (8), 106.1 (100), 141.0 (11), 246.0 (10), 303.1 (5). IR (in KBr): ν = 3667, 3211, 2961, 1445, 1267, 1207, 1026, 754, 698, 555,519 (cm^{-1}). HRMS (ESI) (m/z) [$C_{17}H_{22}NO_2P + H^+$]: Calcd. 304.1466, Found. 304.1463.

4.2.8. N-Benzyl-P-cyclohexyl-P-phenylphosphonamide (3fa)

Yellowish oil (129.9 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 (dd, J = 12.8, 7.5 Hz, 2H), 7.54–7.47 (m, 1H), 7.47–7.40 (m, 2H), 7.32–7.20 (m, 5H), 4.55–4.42 (m, 1H), 4.07 (t, J = 7.7 Hz, 2H), 3.15–3.01 (m, 1H), 1.96–1.85 (m, 2H), 1.79–1.66 (m, 2H), 1.61–1.45 (m, 3H), 1.37–1.19 (m, 3H), (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.8 ($J_{C\text{-}P}$ = 7.0 Hz), 131.8 ($J_{C\text{-}P}$ = 3.0 Hz), 131.7 ($J_{C\text{-}P}$ = 172.9 Hz), 131.6 ($J_{C\text{-}P}$ = 9.7 Hz), 128.6, 128.4 ($J_{C\text{-}P}$ = 14.2 Hz), 127.4, 127.3, 74.5 ($J_{C\text{-}P}$ = 5.9 Hz), 45.0, 34.0 ($J_{C\text{-}P}$ = 7.0 Hz), 25.3, 23.8 ($J_{C\text{-}P}$ = 7.2 Hz) (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) δ = 21.0 (ppm). MS (EI): m/z = 77.0 (7), 91.0 (9), 106.1 (100), 141.0 (13), 223.1 (11), 329.1 (4). IR (in KBr): ν = 3662, 3212, 2962, 1447, 1207, 1130, 1040, 754, 697, 556, 518 (cm^{-1}). HRMS (ESI) (m/z)[$C_{19}H_{24}NO_2P + H^+$]: Calcd. 330.1623, Found. 330.1629.

4.2.9. N-Benzyl-P-(2-methoxyethyl)-P-phenyl phosphonamide (3ga)

Yellowish oil (100.8 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 (dd, J = 13.1, 7.3 Hz, 2H), 7.55–7.49 (m, 1H), 7.48–7.41 (m, 2H), 7.35–7.19 (m, 5H), 4.28–4.08 (m, 4H), 3.62–3.58 (m, 2H), 3.35 (s, 3H), 3.33–3.24 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.7 ($J_{C\text{-}P}$ = 6.9 Hz), 132.0 ($J_{C\text{-}P}$ = 2.8 Hz), 131.7 ($J_{C\text{-}P}$ = 9.8 Hz), 130.7 ($J_{C\text{-}P}$ = 174.3 Hz), 128.6, 128.5 ($J_{C\text{-}P}$ = 14.4 Hz), 127.5, 127.4, 71.9 ($J_{C\text{-}P}$ = 6.2 Hz), 63.7 ($J_{C\text{-}P}$ = 5.8 Hz), 59.0, 44.9 (ppm). ^{31}P NMR

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(100 MHz, $CDCl_3$) $\delta = 23.1$ (ppm). MS (EI): $m/z = 77.0$ (11), 91.1 (9), 106.1 (100), 199.0 (15), 246.1 (21), 305.1 (15). IR (in KBr): $\nu = 3211$, 2889, 1445, 1205, 1128, 1045, 957, 849, 752, 698, 559 (cm^{-1}). HRMS (ESI) (m/z) [$C_{16}H_{20}NO_3P + H^+$]: Calcd. 306.1259, Found. 306.1263.

4.2.10. N-Benzyl-P-(3-chloropropyl)-P-phenyl phosphonamide (3ha)

Yellowish oil (111.2 mg, 69% yield). ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.74$ (dd, $J = 12.1$, 8.1 Hz, 2H), 7.50–7.43 (m, 1H), 7.42–7.35 (m, 2H), 7.27–7.13 (m, 5H), 4.18–3.95 (m, 4H), 3.61–3.50 (m, 2H), 3.30–3.10 (m, 1H), 2.09–1.97 (m, 2H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 139.6$ ($J_{C\text{-}P} = 6.4$ Hz), 132.2 ($J_{C\text{-}P} = 2.7$ Hz), 131.6 ($J_{C\text{-}P} = 9.8$ Hz), 130.4 ($J_{C\text{-}P} = 173.4$ Hz), 128.7, 128.6 ($J_{C\text{-}P} = 14.3$ Hz), 127.5, 61.3 ($J_{C\text{-}P} = 5.5$ Hz), 45.0, 41.1, 33.3 ($J_{C\text{-}P} = 6.8$ Hz) (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 22.9$ (ppm). MS (EI): $m/z = 77.0$ (8), 91.1 (9), 106.1 (100), 141.0 (13), 217.0 (9), 246.1 (11), 323.1 (4). IR (in KBr): $\nu = 3661$, 3210, 2966, 1443, 1267, 1205, 1128, 1032, 754, 698, 554 (cm^{-1}). HRMS (ESI) (m/z)[$C_{16}H_{19}ClNO_2P + H^+$]: Calcd. 324.0920, Found. 324.0915.

4.2.11. N,P-Dibenzyl-P-phenylphosphonamide (3ia)

White solid (135.1 mg, 80% yield). m.p.: 54–55 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.75$ (dd, $J = 12.6$, 7.6 Hz, 2H), 7.47–7.40 (m, 1H), 7.39–7.32 (m, 2H), 7.29–7.11 (m, 10H), 5.03–4.92 (m, 2H), 4.04–3.88 (m, 2H), 3.32–3.19 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 139.6$ ($J_{C\text{-}P} = 6.6$ Hz), 136.7 ($J_{C\text{-}P} = 7.3$ Hz), 132.1 ($J_{C\text{-}P} = 2.9$ Hz), 131.6 ($J_{C\text{-}P} = 9.8$ Hz), 130.5 ($J_{C\text{-}P} = 173.4$ Hz), 128.6, 128.5 ($J_{C\text{-}P} = 13.3$ Hz), 128.3, 127.9, 127.5, 127.4, 66.2 ($J_{C\text{-}P} = 5.3$ Hz), 44.9 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.1$ (ppm). MS (EI): $m/z = 77.1$ (5), 91.1 (26), 106.0 (100), 141.0 (10), 231,1 (7), 246.0 (8), 337.1 (3). IR (in KBr): $\nu = 3659$, 3283, 2984, 2901, 1267, 1205, 1047, 800, 754, 692, 590 (cm^{-1}). HRMS (ESI) (m/z) [$C_{20}H_{20}NO_2P + H^+$]: Calcd. 338.1310, Found. 338.1318.

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

Yellowish oil (136.4 mg, 77% yield). ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.83$ (dd, $J = 12.9$, 7.6 Hz, 2H), 7.55–7.49 (m, 1H), 7.47–7.38 (m, 3H), 7.34–7.19 (m, 6H), 7.11 (t, $J = 7.5$ Hz, 1H), 7.04 (t, $J = 9.1$ Hz, 1H), 5.22–5.06 (m, 2H), 4.13–4.00 (m, 2H), 3.39–3.21 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 160.8$ ($J_{C\text{-}F} = 248.2$ Hz), 139.5 ($J_{C\text{-}P} = 6.7$ Hz), 132.2 ($J_{C\text{-}P} = 2.9$ Hz), 131.6 ($J_{C\text{-}P} = 9.9$ Hz), 130.4 ($J_{C\text{-}F} = 3.7$ Hz), 130.3 ($J_{C\text{-}P} = 173.4$ Hz), 130.2 ($J_{C\text{-}F} = 8.2$ Hz), 128.7, 128.6 ($J_{C\text{-}P} = 13.6$ Hz), 127.5, 127.4, 124.3 ($J_{C\text{-}F} = 3.6$ Hz), 124.0 (dd, $J_{C\text{-}P} = 14.4$ Hz, $J_{C\text{-}F} = 7.5$ Hz), 115.5 ($J_{C\text{-}F} = 21.0$ Hz), 60.3 ($J_{C\text{-}P} = 4.7$ Hz), 44.9 (ppm). ^{19}F NMR (376 MHz, $CDCl_3$) $\delta = -118.2$ (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.3$ (ppm). MS (EI): $m/z = 77.0$ (6), 106.1 (100), 109.1 (21), 141.0 (5), 249.1 (8), 355.1 (5). IR (in KBr): $\nu = 3661$, 3221, 2985, 1445, 1267, 1194, 1039, 755, 695, 554, 512 (cm^{-1}). HRMS (ESI) (m/z)[$C_{20}H_{19}FNO_2P + H^+$]: Calcd. 356.1216, Found. 356.1222.

4.2.13. N-Benzyl-P-(4-chlorobenzyl)-P-phenylphosphonamide (3ka)

White solid (146.6 mg, 79% yield). m.p.: 81–82 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.82$ (dd, $J = 12.9$, 7.6 Hz, 2H), 7.56–7.51 (m, 1H), 7.49–7.42 (m, 2H), 7.33–7.20 (m, 9H), 5.08–4.96 (m, 2H), 4.14–3.98 (m, 2H), 3.25–3.08 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 139.5$ ($J_{C\text{-}P} = 6.3$ Hz), 135.2 ($J_{C\text{-}P} = 7.2$ Hz), 134.2, 132.2 ($J_{C\text{-}P} = 2.9$ Hz), 131.6 ($J_{C\text{-}P} = 9.9$ Hz), 130.3 ($J_{C\text{-}P} = 173.2$ Hz), 129.3, 128.8, 128.7, 128.6 ($J_{C\text{-}P} = 14.3$ Hz), 127.5, 65.4 ($J_{C\text{-}P} = 5.2$ Hz), 45.0 (ppm). ^{31}P NMR (162 MHz, $CDCl_3$) $\delta = 23.4$ (ppm). MS (EI): $m/z = 77.0$ (9), 91.1 (4), 106.1 (100), 125.0 (16), 140.0 (5), 371.0 (11). IR (in KBr): $\nu = 3659$, 3278, 2984, 2904, 1266, 1204, 1060, 801, 754, 700, 591 (cm^{-1}). HRMS (ESI) (m/z)[$C_{20}H_{19}ClNO_2P + H^+$]: Calcd. 372.0920, Found. 372.0926.

4.2.14. N-Benzyl-P-(4-bromobenzyl)-P-phenylphosphonamide (3la)

White solid (158.2 mg, 76% yield), m.p. 75–76 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.81$ (dd, $J = 12.9$, 7.5 Hz, 2H), 7.57–7.50 (m, 1H), 7.49–7.41 (m, 4H), 7.32–7.17 (m, 7H), 5.05–4.93 (m, 2H), 4.13–3.97 (m, 2H), 3.30–3.17 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 139.5$ ($J_{C\text{-}P} = 6.4$ Hz), 135.8 ($J_{C\text{-}P} = 7.2$ Hz), 132.3 ($J_{C\text{-}P} = 3.0$ Hz), 131.8, 131.6 ($J_{C\text{-}P} = 9.9$ Hz), 130.3 ($J_{C\text{-}P} = 173.2$ Hz), 129.6, 128.8, 128.7 ($J_{C\text{-}P} = 14.3$ Hz), 127.5(3), 127.5(0), 122.3, 65.5 ($J_{C\text{-}P} = 5.2$ Hz), 45.0 (ppm). ^{31}P NMR (162 MHz, $CDCl_3$) $\delta = 23.3$ (ppm). MS (EI): $m/z = 77.1$ (7), 90.1 (4), 106.0 (100), 169.0 (12), 336.1 (5), 415.0 (6). IR (in KBr): $\nu = 3664$, 2982, 2890, 1263, 1199, 1047, 800, 757, 690, 555, 520 (cm^{-1}). HRMS (ESI) (m/z)[$C_{20}H_{19}BrNO_2P + H^+$]: Calcd. 416.0415, Found. 416.0412.

4.2.15. 6-(Benzylamino)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**3ma**)

White solid (108.9 mg, 68% yield), m.p. 149–150 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 8.00–7.87$ (m, 3H), 7.68 (t, $J = 7.7$ Hz,1H),7.46 (t, $J = 6.6$ Hz,1H),7.35 (t, $J = 7.6$ Hz,1H),7.31–7.20 (m, 7H), 7.27–7.20 (m, 1H),4.14–3.99 (m, 2H), 3.72–3.60 (m, 1H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 150.0$ ($J_{C\text{-}P} = 7.2$ Hz), 139.0 ($J_{C\text{-}P} = 6.3$ Hz), 137.3 ($J_{C\text{-}P} = 7.3$ Hz), 133.0 ($J_{C\text{-}P} = 2.3$ Hz), 130.4, 130.3 ($J_{C\text{-}P} = 9.4$ Hz), 128.7, 128.4 ($J_{C\text{-}P} = 14.6$ Hz), 127.6, 127.5, 125.0, 124.4, 123.8 ($J_{C\text{-}P} = 11.4$ Hz), 123.4, 122.2 ($J_{C\text{-}P} = 11.7$ Hz), 120.7 ($J_{C\text{-}P} = 6.4$ Hz), 45.2 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) $\delta = 14.8$ (ppm). MS (EI): $m/z = 77.1$ (6), 90.1 (4), 106.0 (100), 169.0 (17), 215.1 (10), 321.0 (3). IR (in KBr): $\nu = 3154$, 2887, 1642, 1472, 1227, 1148, 925, 899, 782, 757 (cm^{-1}). HRMS (ESI) (m/z)[$C_{19}H_{16}NO_2P + H^+$]: Calcd. 322.0997, Found. 322.0992.

4.2.16. N-(2-Methylbenzyl)-P,P-diphenylphosphinamide (3ab)

White solid (131.4 mg, 82% yield). m.p. 105–106 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 8.01–7.89$ (m, 4H), 7.54–7.38 (m, 7H), 7.24–7.12 (m, 3H), 4.13 (t, $J = 6.6$ Hz, 2H), 3.08–2.96 (m, 1H), 2.28 (s, 3H)(ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 137.4$ ($J_{C\text{-}P} = 9.0$ Hz), 136.1, 132.2 ($J_{C\text{-}P} = 129.0$ Hz), 132.1 ($J_{C\text{-}P} = 9.5$ Hz), 132.0 ($J_{C\text{-}P} = 2.7$ Hz), 130.4, 128.7 ($J_{C\text{-}P} = 12.6$ Hz), 127.8, 127.5, 126.3, 42.2, 19.1 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.9$ (ppm). MS (EI): $m/z = 77.1$ (15), 104.1 (13), 120.1 (100), 201.0 (62), 230.0 (43), 321.1 (36). IR (in KBr): $\nu = 3661$, 3184, 2921, 1437, 1269, 1184, 1116, 1072, 754, 698, 554 (cm^{-1}). HRMS (ESI) (m/z)[$C_{20}H_{20}NOP + H^+$]: Calcd. 322.1361, Found. 322.1354.

4.2.17. N-(3-Methylbenzyl)-P,P-diphenylphosphinamide (3ac)

White solid (139.1 mg, 87% yield). m.p. 59–60 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.93$ (dd, $J = 11.6$, 7.7 Hz, 4H), 7.52–7.40 (m, 6H), 7.24–7.19 (m, 1H), 7.18–7.12 (m, 2H), 7.09–7.04 (m, 1H), 4.08 (t, $J = 7.2$ Hz, 2H), 3.31–3.21 (m, 1H), 2.32 (s, 3H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 139.6$ ($J_{C\text{-}P} = 8.4$ Hz), 138.4, 132.9, 132.3 ($J_{C\text{-}P} = 129.2$ Hz), 132.2 ($J_{C\text{-}P} = 9.5$ Hz), 132.0 ($J_{C\text{-}P} = 2.7$ Hz), 128.7 ($J_{C\text{-}P} = 12.6$ Hz), 128.6, 128.2, 124.8, 44.7, 21.5 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.8$ (ppm). MS (EI): $m/z = 77.0$ (11), 104.1 (8), 120.1 (100), 155.1 (12), 201.0 (43), 321.1 (27). IR (in KBr): $\nu = 3665$, 3174, 2919, 1439, 1271, 1186, 1117, 1072, 756, 697, 554 (cm^{-1}). HRMS (ESI) (m/z) [$C_{20}H_{20}NOP + H^+$]: Calcd. 322.1361, Found. 322.1365.

4.2.18. N-(4-Methylbenzyl)-P,P-diphenylphosphinamide (3ad)

White solid (137.8 mg, 86% yield). m.p.: 102–103 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.94$ (dd, $J = 11.7$, 7.6 Hz, 4H), 7.51–7.41 (m, 6H), 7.25 (d, $J = 7.9$ Hz, 2H), 7.13 (d, $J = 7.6$ Hz, 2H), 4.08 (t, $J = 7.2$ Hz, 2H), 3.23–3.11 (m, 1H), 2.33 (s, 3H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 139.5$ ($J_{C\text{-}P} = 8.6$ Hz), 138.3, 132.4 ($J_{C\text{-}P} = 129.1$ Hz), 132.3 ($J_{C\text{-}P} = 9.5$ Hz), 132.0 ($J_{C\text{-}P} = 2.7$ Hz), 129.2, 128.7 ($J_{C\text{-}P} = 12.6$ Hz), 125.7, 44.7, 21.4 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.6$ (ppm). MS (EI): $m/z = 77.0$ (8), 105.1 (5), 120.1 (100), 155.1 (14), 201.0 (62), 321.1 (26). IR (in KBr): $\nu = 3660$, 3177, 2920, 1439, 1269, 1186, 1117,

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1072, 754, 696, 555 (cm^{-1}). HRMS (ESI) (m/z)[$C_{20}H_{20}NOP + H^+$]: Calcd. 322.1361, Found. 322.1354.

4.2.19. N-(3,5-Dimethylbenzyl)-P,P-diphenylphosphinamide (3ae)

White solid (137.0 mg, 82% yield). m.p. 120–121 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.94$ (dd, $J = 11.8$, 7.7 Hz, 4H), 7.52–7.41 (m, 6H), 6.95 (s, 2H), 6.90 (s, 1H), 4.05 (t, $J = 7.2$ Hz, 2H), 3.24–3.11 (m, 1H), 2.29 (s, 6H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 139.5$ ($J_{C-P} = 8.6$ Hz), 138.3, 132.4 ($J_{C-P} = 129.1$ Hz), 132.3 ($J_{C-P} = 9.5$ Hz), 132.0 ($J_{C-P} = 2.7$ Hz), 129.2, 128.7 ($J_{C-P} = 12.6$ Hz), 125.7, 44.7, 21.4 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.6$ (ppm). MS (EI): $m/z = 77.0$ (7), 91.0 (5), 134.1 (100), 155.1 (8), 201.0 (35), 335.1 (20). IR (in KBr): $\nu = 3661$, 3180, 2980, 1444, 1267, 1190, 1072, 756, 698, 555, 518 (cm^{-1}). HRMS (ESI) (m/z) [$C_{21}H_{22}NOP + H^+$]: Calcd. 336.1517, Found. 336.1514.

4.2.20. N-(4-tert-Butylbenzyl)-P,P-diphenylphosphinamide (3af)

White solid (145.4 mg, 80% yield). m.p.: 150–151 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.94$ (dd, $J = 10.5$, 8.6 Hz, 4H), 7.52–7.40 (m, 6H), 7.35 (d, $J = 7.9$ Hz, 2H), 7.30 (d, $J = 7.8$ Hz, 2H), 4.10 (t, $J = 7.1$ Hz, 2H), 3.29–3.12 (m, 1H), 1.30 (s, 9H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 150.5$, 136.6 ($J_{C-P} = 8.8$ Hz), 132.3 ($J_{C-P} = 129.2$ Hz), 132.2 ($J_{C-P} = 9.5$ Hz), 132.0 ($J_{C-P} = 2.6$ Hz), 128.7 ($J_{C-P} = 12.6$ Hz), 127.6, 125.6, 44.4, 34.6, 31.4 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.6$ (ppm). MS (EI): $m/z = 77.0$ (7), 91.0 (6), 132.1 (8), 146.1 (15), 162.1 (100), 201.0 (33), 363.1 (27). IR (in KBr): $\nu = 3667$, 3180, 2910, 1439, 1187, 1114, 1069, 760, 691, 550, 520 (cm^{-1}). HRMS (ESI) (m/z) [$C_{23}H_{26}NOP + H^+$]: Calcd. 364.1830, Found. 364.1825.

4.2.21. N-(4-Methoxybenzyl)-P,P-diphenylphosphinamide (3ag)

Brownish oil (118.4 mg, 70% yield). ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.93$ (dd, $J = 11.3$, 7.8 Hz, 4H), 7.53–7.40 (m, 6H), 7.28 (d, $J = 8.2$ Hz, 2H), 6.86 (d, $J = 7.9$ Hz, 2H), 4.06 (t, $J = 7.1$ Hz, 2H), 3.78 (s, 3H), 3.22–3.12 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 159.1$, 132.3 ($J_{C-P} = 129.4$ Hz), 132.2 ($J_{C-P} = 9.5$ Hz), 132.0 ($J_{C-P} = 2.6$ Hz), 131.8 ($J_{C-P} = 8.5$ Hz), 129.1, 128.7 ($J_{C-P} = 12.5$ Hz), 114.1, 55.4, 44.2 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.7$ (ppm). MS (EI): $m/z = 77.0$ (7), 136.0 (100), 155.1 (9), 201.1 (23), 337.1 (15). IR (in KBr): $\nu = 3667$, 2985, 1512, 1439, 1269, 1180, 1115, 1068, 756, 698, 519 (cm^{-1}). HRMS (ESI) (m/z)[$C_{20}H_{20}NO_2P + H^+$]: Calcd. 338.1310, Found. 338.1306.

4.2.22. N-(4-Fluorobenzyl)-P,P-diphenylphosphinamide (3ah)

Yellowish oil (135.5 mg, 83% yield). ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.92–7.83$ (m, 4H), 7.48–7.36 (m, 6H), 7.33–7.27 (m, 2H), 6.94 (t, $J = 8.3$ Hz, 2H), 4.03 (t, $J = 7.6$ Hz, 2H), 3.61–3.47 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 162.2$ ($J_{C-P} = 245.5$ Hz), 135.5 (dd, $J_{C-P} = 7.9$ Hz, $J_{C-F} = 3.7$ Hz), 132.3 ($J_{C-P} = 9.6$ Hz), 132.2 ($J_{C-P} = 2.8$ Hz), 132.1 ($J_{C-P} = 129.1$ Hz), 129.5 ($J_{C-F} = 8.1$ Hz), 128.8 ($J_{C-P} = 12.6$ Hz), 115.6 ($J_{C-F} = 21.4$ Hz), 44.2 (ppm). ^{19}F NMR (376 MHz, $CDCl_3$) $\delta = -115.1$ (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 24.0$ (ppm). MS (EI): $m/z = 77.0$ (8), 95.0 (7), 124.1 (100), 155.1 (12), 201.1 (24), 325.1 (8). IR (in KBr): $\nu = 3173$, 2984, 1601, 1508, 1439, 1267, 1184, 1117, 822, 754, 696 (cm^{-1}). HRMS (ESI) (m/z)[$C_{19}H_{17}FNOP + H^+$]: Calcd. 326.1110, Found. 326.1116.

4.2.23. N-(2-Chlorobenzyl)-P,P-diphenylphosphinamide (3ai)

White solid (143.3 mg, 84% yield). m.p.: 109–110 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.90$ (dd, $J = 10.8$, 8.4 Hz, 4H), 7.52–7.46 (m, 2H), 7.46–7.39 (m, 4H), 7.39–7.35 (m, 1H), 7.35–7.30 (m, 1H), 7.23–7.17 (m, 2H),4.23 (t, $J = 8.1$ Hz, 2H), 3.48–3.37 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 137.1$ ($J_{C-P} = 7.2$ Hz), 133.6, 132.3 ($J_{C-P} = 9.6$ Hz), 132.2 ($J_{C-P} = 129.3$ Hz), 132.1 ($J_{C-P} = 2.7$ Hz), 130.0, 129.6, 128.9, 128.7 ($J_{C-P} = 12.6$ Hz), 127.2, 42.7 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 24.2$ (ppm). MS (EI): $m/z = 77.0$ (12), 125.0 (15), 140.0 (26), 201.0 (28), 306.0 (100), 340.1 (3). IR (in KBr): $\nu = 3174$, 2985, 2901, 1440, 1267, 1184, 1076, 801, 755, 695, 520 (cm^{-1}). HRMS (ESI) (m/z)[$C_{19}H_{17}ClNOP + H^+$]: Calcd. 342.0815, Found. 342.0814.

4.2.24. N-(3-Chlorobenzyl)-P,P-diphenylphosphinamide (3aj)

Yellowish oil (136.7 mg, 80% yield). ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.97–7.87$ (m, 4H), 7.54–7.48 (m, 2H), 7.48–7.41 (m, 4H), 7.33 (s, 1H), 7.28–7.20 (m, 3H), 4.10 (t, $J = 7.7$ Hz, 2H), 3.35–3.23 (m, 1H)(ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 141.8$ ($J_{C-P} = 7.9$ Hz), 134.4, 132.2 ($J_{C-P} = 9.6$ Hz), 132.1 ($J_{C-P} = 4.5$ Hz), 132.0 ($J_{C-P} = 129.2$ Hz), 130.0, 128.7 ($J_{C-P} = 12.6$ Hz), 127.8, 127.6, 126.0, 44.2 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 24.1$ (ppm). MS (EI): $m/z = 77.0$ (8), 125.0 (10), 140.0 (100), 155.1 (10), 201.0 (33), 340.1 (5). IR (in KBr): $\nu = 3175$, 2984, 2901, 1433, 1267, 1185, 1077, 798, 758, 696, 524 (cm^{-1}). HRMS (ESI) (m/z) [$C_{19}H_{17}ClNOP + H^+$]: Calcd. 342.0815, Found. 342.0820.

4.2.25. N-(4-Chlorobenzyl)-P,P-diphenylphosphinamide (3ak)

White solid (149.3 mg, 87% yield). m.p. 130–131 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.92$ (dd, $J = 10.5$, 8.7 Hz, 4H), 7.54–7.41 (m, 6H), 7.34–7.26 (m, 4H), 4.10 (t, $J = 7.8$ Hz, 2H), 3.23–3.12 (m, 1H)(ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 138.2$ ($J_{C-P} = 7.7$ Hz), 133.3, 132.3 ($J_{C-P} = 9.4$ Hz), 132.2, 132.1 ($J_{C-P} = 129.4$ Hz), 129.2, 128.9, 128.8 ($J_{C-P} = 12.6$ Hz), 44.3 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 24.0$ (ppm). MS (EI): $m/z = 77.0$ (10), 125.1 (12), 140.0 (100), 155.1 (7), 201.0 (21), 340.1 (5). IR (in KBr): $\nu = 3175$, 2984, 2903, 1439, 1267, 1182, 1074, 800, 754, 696, 526 (cm^{-1}). HRMS (ESI) (m/z) [$C_{19}H_{17}ClNOP + H^+$]: Calcd. 342.0815, Found. 342.0821.

4.2.26. N-(4-Bromobenzyl)-P,P-diphenyl phosphinamide (3al)

White solid (142.3 mg, 74% yield). m.p. 113–114 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.97–7.87$ (m, 4H), 7.55–7.41 (m, 8H), 7.25 (d, $J = 8.1$ Hz, 2H), 4.09 (t, $J = 7.7$ Hz, 2H), 3.28–3.16 (m, 1H)(ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 138.8$ ($J_{C-P} = 7.6$ Hz), 132.2 ($J_{C-P} = 9.5$ Hz), 132.2 ($J_{C-P} = 2.6$ Hz), 132.1 ($J_{C-P} = 129.4$ Hz), 131.8, 129.6, 128.8 ($J_{C-P} = 12.6$ Hz), 121.4, 44.3 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 24.0$ (ppm). MS (EI): $m/z = 77.0$ (14), 125.0 (10), 155.1 (20), 183.9 (100), 201.0 (67), 384.9 (20). IR (in KBr): $\nu = 3667$, 2984, 2903, 1439, 1269, 1184, 1114, 1070, 754, 698, 524 (cm^{-1}). HRMS (ESI) (m/z) [$C_{19}H_{17}BrNOP$]: Calcd. 386.0309, Found. 386.0306.

4.2.27. P,P-Diphenyl-N-4-trifluoromethylbenzyl phosphinamide (3am)

Yellowish oil (130.9 mg, 70% yield). ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.91$ (dd, $J = 11.7$, 7.9 Hz, 4H), 7.56 (d, $J = 7.8$ Hz, 2H), 7.54–7.41 (m, 8H), 4.18 (t, $J = 8.1$ Hz, 2H), 3.44–3.31 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 143.8$ ($J_{C-P} = 6.3$ Hz), 132.3 ($J_{C-P} = 4.2$ Hz), 132.2 ($J_{C-P} = 9.5$ Hz), 132.1 ($J_{C-P} = 130.3$ Hz), 129.8 (q, $J_{C-F} = 32.2$ Hz), 128.8 ($J_{C-P} = 12.6$ Hz), 128.1, 125.7 (q, $J_{C-F} = 3.4$ Hz), 124.2 (q, $J_{C-F} = 272.0$ Hz), 44.5 (ppm). ^{19}F NMR (100 MHz, $CDCl_3$) $\delta = -62.5$ (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 24.3$ (ppm). MS (EI): $m/z = 77.0$ (7), 125.0 (5), 155.1 (9), 174.0 (34), 202.0 (100), 356.0 (14), 375.1 (58). IR (in KBr): $\nu = 3169$, 1439, 1325, 1269, 1178, 1118, 1069, 856, 754, 696, 555 (cm^{-1}). HRMS (ESI) (m/z)[$C_{20}H_{17}F_3NOP + H^+$]: Calcd. 376.1078, Found. 376.1076.

4.2.28. Methyl 4-(((diphenylphosphoryl)amino)methyl) benzoate (3an)

Yellowish oil (124.4 mg, 68% yield). ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.98$ (d, $J = 8.0$ Hz, 2H), 7.92 (dd, $J = 11.5$, 7.6 Hz, 4H), 7.53–7.40 (m, 8H), 4.18 (t, $J = 7.9$ Hz, 2H), 3.89 (s, 3H), 3.41–3.29 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 167.0$, 144.9 ($J_{C-P} = 7.6$ Hz), 132.3 ($J_{C-P} = 9.4$ Hz), 132.2 ($J_{C-P} = 3.1$ Hz), 132.0 ($J_{C-P} = 129.6$ Hz), 130.1, 129.4, 128.8 ($J_{C-P} = 12.6$ Hz), 127.7, 52.2, 44.6 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 24.3$ (ppm). MS (EI): $m/z = 77.0$ (7), 146.1 (100), 201.0 (34), 350.1 (21) 365.1 (12). IR (in KBr): $\nu = 3667$, 2984,

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1719, 1437, 1271, 1188, 1109, 1070, 756, 700, 527 (cm^{-1}). HRMS (ESI) (m/z)[$C_{21}H_{20}NO_3P + H^+$]: Calcd. 366.1259, Found. 366.1266.

4.2.29. N-(1-Naphthylmethyl)-P,P-diphenyl phosphinamide (3ao)

White solid (120.1 mg, 67% yield). m.p.: 144–145 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 8.05$ (d, $J = 7.8$ Hz, 1H), 8.01–7.91 (m, 4H), 7.87 (d, $J = 7.4$ Hz, 1H), 7.80 (d, $J = 8.1$ Hz, 1H), 7.58–7.39 (m, 10H), 4.60 (t, $J = 6.2$ Hz, 2H), 3.28–3.15 (m, 1H)(ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 135.0$ ($J_{C\text{-}P} = 9.0$ Hz), 133.9, 132.3 ($J_{C\text{-}P} = 128.7$ Hz), 132.2 ($J_{C\text{-}P} = 9.6$ Hz), 132.1 ($J_{C\text{-}P} = 2.7$ Hz), 131.2, 128.9, 128.7 ($J_{C\text{-}P} = 12.6$ Hz), 128.4, 126.6, 126.0, 125.8, 125.6, 123.4, 42.2 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 24.0$ (ppm). MS (EI): $m/z = 77.0$ (4), 115.0 (4), 141.1 (7), 156.1 (100), 201.0 (28), 357.0 (32). IR (in KBr): $\nu = 3666$, 2985, 1440, 1267, 1186, 1116, 1067, 756, 697, 556, 519 (cm^{-1}). HRMS (ESI) (m/z)[$C_{23}H_{20}NOP + H^+$]: Calcd. 358.1361, Found. 358.1356.

4.2.30. N-(2-Naphthylmethyl)-P,P-diphenyl phosphinamide (3ap)

White solid (110.2 mg, 62% yield). m.p. 125–126 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.96$ (dd, $J = 10.8$, 8.3 Hz, 4H), 7.84–7.77 (m, 3H), 7.75 (s, 1H), 7.54–7.41 (m, 9H), 4.29 (t, $J = 7.4$ Hz, 2H), 3.38–3.27 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 137.1$ ($J_{C\text{-}P} = 8.2$ Hz), 133.4, 132.8, 132.3 ($J_{C\text{-}P} = 9.5$ Hz), 132.2 ($J_{C\text{-}P} = 129.2$ Hz), 132.1 ($J_{C\text{-}P} = 2.6$ Hz), 128.8 ($J_{C\text{-}P} = 12.6$ Hz), 128.6, 127.9, 127.8, 126.4, 126.3, 126.1, 126.0, 45.0 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.9$ (ppm). MS (EI): $m/z = 77.0$ (5), 115.1 (4), 141.1 (9), 156.1 (100), 201.0 (23), 357.0 (28). IR (in KBr): $\nu = 3665$, 2984, 1439, 1269, 1186, 1117, 1068, 756, 698, 555, 519 (cm^{-1}). HRMS (ESI) (m/z) [$C_{23}H_{20}NOP + H^+$]: Calcd. 358.1361, Found. 358.1365.

4.2.31. N-(1-Phenylethyl)-P,P-diphenyl phosphinamide (3au)

White solid (99.1 mg, 62% yield). m.p.: 140–141 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.83$ (dd, $J = 11.2$, 7.8 Hz, 2H), 7.74 (dd, $J = 11.4$, 7.9 Hz, 2H), 7.44–7.32 (m, 4H), 7.31–7.13 (m, 7H), 4.38–4.25 (m, 1H), 3.22–3.10 (m, 1H), 1.50 (d, $J = 6.7$ Hz, 3H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 145.2$ ($J_{C\text{-}P} = 6.8$ Hz), 133.4 ($J_{C\text{-}P} = 106.0$ Hz), 132.5 ($J_{C\text{-}P} = 9.6$ Hz), 132.1 ($J_{C\text{-}P} = 108.3$ Hz), 132.0 ($J_{C\text{-}P} = 9.6$ Hz), 131.9 ($J_{C\text{-}P} = 3.2$ Hz), 131.8 ($J_{C\text{-}P} = 2.7$ Hz), 128.7, 128.6 ($J_{C\text{-}P} = 8.9$ Hz), 128.5 ($J_{C\text{-}P} = 8.9$ Hz), 127.2, 126.0, 51.2, 26.1 ($J_{C\text{-}P} = 3.2$ Hz) (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 22.5$ (ppm). MS (EI): $m/z = 77.0$ (11), 105.0 (9), 120.1 (100), 201.0 (23), 321.1 (8). IR (in KBr): $\nu = 3667$, 2982, 1437, 1269, 1188, 1034, 1113, 962, 754, 696, 550 (cm^{-1}). HRMS (ESI) (m/z)[$C_{20}H_{20}NOP + H^+$]: Calcd. 322.1361, Found. 322.1367.

4.2.32. N-Diphenylmethyl-P,P-diphenyl phosphinamide (5aa)

White solid (150.1 mg, 78% yield), m.p. 182–183 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.75$ (dd, $J = 11.1$, 8.2 Hz, 4H), 7.40–7.34 (m, 2H), 7.31–7.24 (m, 4H), 7.24–7.12 (m, 10H), 5.37 (t, $J = 10.8$ Hz, 1H), 3.68–3.55 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 143.4$ ($J_{C\text{-}P} = 4.5$ Hz), 132.4 ($J_{C\text{-}P} = 9.6$ Hz), 132.3 ($J_{C\text{-}P} = 129.5$ Hz), 132.0 ($J_{C\text{-}P} = 2.6$ Hz), 128.6, 128.5 ($J_{C\text{-}P} = 14.2$ Hz), 127.7, 127.3, 58.6 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.1$ (ppm). MS (EI): $m/z = 77.0$ (9), 104.1 (9), 165.1 (10), 182.1 (100), 201.0 (31), 383.1 (4). IR (in KBr): $\nu = 3143$, 2865, 1594, 1447, 1259, 1184, 1112, 935, 803, 696, 539 (cm^{-1}). HRMS (ESI) (m/z)[$C_{25}H_{22}NOP + H^+$]: Calcd. 384.1517, Found. 384.1525.

4.2.33. N-Diphenylmethyl-P-methyl-P-phenyl phosphonamide (5ba)

White solid (114.5 mg, 68% yield). m.p. 132–133 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.71$ (dd, $J = 12.4$, 7.7 Hz, 2H), 7.51–7.45 (m, 1H), 7.41–7.34 (m, 2H), 7.31–7.18 (m, 8H), 7.16–7.10 (m, 2H), 5.37 (t, $J = 9.3$ Hz, 1H), 3.69–3.59 (m, 1H), 3.56 (d, $J = 10.9$ Hz, 3H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 143.4$ ($J_{C\text{-}P} = 4.1$ Hz), 143.2 ($J_{C\text{-}P} = 5.5$ Hz), 132.0 ($J_{C\text{-}P} = 2.9$ Hz), 131.6 ($J_{C\text{-}P} = 9.8$ Hz), 130.4 ($J_{C\text{-}P} = 175.8$ Hz), 128.6, 128.5, 128.4 ($J_{C\text{-}P} = 14.4$ Hz), 127.4, 127.3, 127.2, 127.1, 58.8, 51.3 ($J_{C\text{-}P} = 6.0$ Hz) (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 22.8$ (ppm). MS (EI): $m/z = 77.1$ (9), 104.0 (5), 155.0 (17), 165.1 (8), 182.1 (100), 260.0 (12), 337.1 (21). IR (in KBr): $\nu = 3184$, 1594, 1450, 1209, 1124, 1028, 912, 750, 700, 554 (cm^{-1}). HRMS (ESI) (m/z) [$C_{20}H_{20}NO_2P + H^+$]: Calcd. 338.1310, Found. 338.1313.

4.2.34. N-Diphenylmethyl-P-ethyl-P-phenyl phosphonamide (5ca)

White solid (126.3 mg, 72% yield). m.p. 121–122 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.72$ (dd, $J = 12.9$, 7.8 Hz, 2H), 7.51–7.44 (m, 1H), 7.41–7.34 (m, 2H), 7.31–7.18 (m, 8H), 7.16–7.10 (m, 2H), 5.37 (t, $J = 9.9$ Hz, 1H), 4.10–4.00 (m, 1H), 3.88–3.78 (m, 1H), 3.60 (t, $J = 9.5$ Hz, 1H), 1.18 (t, $J = 7.0$ Hz, 3H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 143.4$ ($J_{C\text{-}P} = 3.9$ Hz), 143.2 ($J_{C\text{-}P} = 5.6$ Hz), 131.8 ($J_{C\text{-}P} = 2.7$ Hz), 131.6 ($J_{C\text{-}P} = 9.8$ Hz), 130.9 ($J_{C\text{-}P} = 174.1$ Hz), 128.6, 128.5, 128.4 ($J_{C\text{-}P} = 14.4$ Hz), 127.3, 127.2(6), 127.2(1), 60.8 ($J_{C\text{-}P} = 5.7$ Hz), 58.8, 16.2 ($J_{C\text{-}P} = 7.0$ Hz) (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 21.2$ (ppm). MS (EI): $m/z = 77.1$ (11), 104.1 (8), 141.0 (15), 165.1 (10), 182.1 (100), 274.0 (7), 322.0 (10), 351.0 (23). IR (in KBr): $\nu = 3190$, 1596, 1452, 1209, 1126, 1034, 958, 746, 698, 555 (cm^{-1}). HRMS (ESI) (m/z) [$C_{21}H_{22}NO_2P + H^+$]: Calcd. 352.1466, Found. 352.1461.

4.2.35. N-Diphenylmethyl-P-isopropyl-P-phenyl phosphonamide (5da)

White solid (125.7mg, 69% yield). m.p. 148–149 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.61$ (dd, $J = 12.8$, 7.6 Hz, 2H), 7.39–7.33 (m, 1H), 7.29–7.22 (m, 2H), 7.20–7.07 (m, 8H), 7.06–7.01 (m, 2H), 5.32 (t, $J = 9.9$ Hz, 1H), 4.62–4.49 (m, 1H), 3.63–3.49 (m, 1H), 1.19 (d, $J = 6.0$ Hz, 3H), 1.00 (d, $J = 6.0$ Hz, 3H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 143.5$ ($J_{C\text{-}P} = 4.6$ Hz), 143.4 ($J_{C\text{-}P} = 4.0$ Hz), 131.8 ($J_{C\text{-}P} = 174.2$ Hz), 131.7 ($J_{C\text{-}P} = 2.4$ Hz), 131.6 ($J_{C\text{-}P} = 9.8$ Hz), 128.5, 128.4, 128.2 ($J_{C\text{-}P} = 14.3$ Hz), 127.2(7), 127.2(5), 127.1(8), 127.1(4), 69.9 ($J_{C\text{-}P} = 5.9$ Hz), 58.8, 24.3 ($J_{C\text{-}P} = 3.5$ Hz), 23.9 ($J_{C\text{-}P} = 5.1$ Hz) (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 19.8$ (ppm). MS (EI): $m/z = 77.1$ (13), 104.1 (14), 106.1 (17), 165.1 (15), 167.1 (16), 182.1 (100), 246.0 (19), 322.0 (85), 365.1 (15). IR (in KBr): $\nu = 3738$, 3208, 1464, 1200, 1124, 978, 934, 802, 747, 699, 552 (cm^{-1}). HRMS (ESI) (m/z) [$C_{22}H_{24}NO_2P + H^+$]: Calcd. 366.1623, Found. 366.1619.

4.2.36. N-Diphenylmethyl-P-n-butyl-P-phenyl phosphonamide (5ea)

White solid (133.4 mg, 70% yield). m.p. 120–121 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.63$ (dd, $J = 12.9$, 7.6 Hz, 2H), 7.42–7.36 (m, 1H), 7.32–7.25 (m, 2H), 7.21–7.08 (m, 8H), 7.06–7.02 (m, 2H), 5.28 (t, $J = 9.9$ Hz, 1H), 3.93–3.85 (m, 1H), 3.71–3.55 (m, 2H), 1.47–1.35 (m, 2H), 1.23–1.16 (m, 2H), 0.76 (t, $J = 7.4$ Hz, 3H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 143.5$ ($J_{C\text{-}P} = 4.0$ Hz), 143.3 ($J_{C\text{-}P} = 5.4$ Hz), 131.8 ($J_{C\text{-}P} = 3.0$ Hz), 131.6 ($J_{C\text{-}P} = 9.7$ Hz), 131.0 ($J_{C\text{-}P} = 172.6$ Hz), 128.6, 128.5, 128.4 ($J_{C\text{-}P} = 14.4$ Hz), 127.3, 127.2(7), 127.2(1), 64.5 ($J_{C\text{-}P} = 6.0$ Hz), 58.9, 32.4 ($J_{C\text{-}P} = 6.9$ Hz), 18.9, 13,7 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 21.0$ (ppm). MS (EI): $m/z = 104.0$ (5), 141.0 (5), 167.1 (10), 182.1 (100), 246.0 (14), 302.1 (7), 322.0 (36), 379.1 (44). IR (in KBr): $\nu = 3187$, 1448, 1262, 1204, 1100, 1024, 800, 745, 701, 558 (cm^{-1}). HRMS (ESI) (m/z)[$C_{23}H_{26}NO_2P + H^+$]: Calcd. 380.1779, Found. 380.1781.

4.2.37. N-Diphenylmethyl-P-cyclohexyl-P-phenyl phosphonamide (5fa)

White solid (126.5 mg, 62% yield). m.p. 155–156 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.64$ (dd, $J = 12.9$, 7.7 Hz, 2H), 7.41–7.36 (m, 1H), 7.32–7.25 (m, 2H), 7.22–7.09 (m, 8H), 7.07–7.01 (m, 2H), 5.35 (t, $J = 9.9$ Hz, 1H), 4.32–4.22 (m, 1H), 3.36 (t, $J = 9.5$ Hz, 1H), 1.72–1.65 (m, 1H), 1.62–1.33 (m, 5H), 1.29–1.04 (m, 5H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 143.6$ ($J_{C\text{-}P} = 4.8$ Hz), 143.5 ($J_{C\text{-}P} = 4.6$ Hz), 131.9 ($J_{C\text{-}P} = 174.3$ Hz), 131.7 ($J_{C\text{-}P} = 3.1$ Hz), 131.6 ($J_{C\text{-}P} = 9.8$ Hz), 128.6, 128.5, 128.3 ($J_{C\text{-}P} = 14.3$ Hz), 127.3, 127.2, 74.8 ($J_{C\text{-}P} = 5.8$ Hz), 58.8, 33.9 ($J_{C\text{-}P} = 3.1$ Hz), 33.7 ($J_{C\text{-}P} = 4.5$ Hz), 25.3, 23.7, 23.6 (ppm).

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^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 19.6$ (ppm). MS (EI): $m/z = 77.0$ (7), 104.1 (9), 182.1 (100), 223.1 (21), 322.1 (8), 405.2 (11). IR (in KBr): $\nu = 3177$, 2931, 1453, 1262, 1207, 1097, 1022, 801, 744, 696, 563 (cm^{-1}). HRMS (ESI) (m/z)[$C_{25}H_{28}NO_2P + H^+$]: Calcd. 406.1936, Found. 406.1930.

4.2.38. N-Diphenylmethyl-P-(2-methoxyethyl)-P-phenyl phosphonamide (5ga)

White solid (133.1 mg, 70% yield). m.p. 112–113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.71$ (dd, $J = 13.1$, 7.7 Hz, 2H), 7.48–7.42 (m, 1H), 7.37–7.31 (m, 2H), 7.27–7.16 (m, 10H), 5.45 (t, $J = 9.9$ Hz, 1H), 4.12–3.98 (m, 2H), 3.96–3.86 (m, 1H), 3.53–3.41 (m, 2H), 3.29 (s, 3H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 143.4$ ($J_{C-P} = 3.7$ Hz), 143.3 ($J_{C-P} = 4.9$ Hz), 131.9 ($J_{C-P} = 3.1$ Hz), 131.7 ($J_{C-P} = 9.9$ Hz), 130.8 ($J_{C-P} = 176.6$ Hz), 128.6, 128.5, 128.3 ($J_{C-P} = 14.6$ Hz), 127.3, 127.2(6), 127.2(3), 127.2(0), 71.8 ($J_{C-P} = 6.2$ Hz), 63.5 ($J_{C-P} = 6.0$ Hz), 58.9, 58.7 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 22.0$ (ppm). MS (EI): $m/z = 77.1$ (5), 104.0 (7), 167.1 (12), 182.1 (100), 199.0 (7), 322.0 (11), 381.0 (19). IR (in KBr): $\nu = 3700$, 3227, 1448, 1260, 1202, 1100, 1034, 799, 748, 702, 534 (cm^{-1}). HRMS (ESI) (m/z)[$C_{22}H_{24}NO_3P + H^+$]: Calcd. 382.1572, Found. 382.1576.

4.2.39. N-Diphenylmethyl-P-(3-chloropropyl)-P-phenyl phosphonamide (5ha)

White solid (136.7 mg, 68% yield). m.p. 100–101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.64$ (dd, $J = 12.9$, 7.4 Hz, 2H), 7.44–7.39 (m, 1H), 7.35–7.28 (m, 2H), 7.24–7.11 (m, 8H), 7.09–7.04 (m, 2H), 5.31 (t, $J = 9.7$ Hz, 1H), 4.07–3.96 (m, 1H), 3.87–3.78 (m, 1H), 3.69–3.59 (m, 1H), 3.40 (t, $J = 6.4$ Hz, 2H), 1.94–1.83 (m, 2H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 143.3$ ($J_{C-P} = 4.1$ Hz), 143.1 ($J_{C-P} = 5.6$ Hz), 132.1 ($J_{C-P} = 3.1$ Hz), 131.6 ($J_{C-P} = 9.8$ Hz), 130.5 ($J_{C-P} = 174.2$ Hz), 128.7, 128.6, 128.5 ($J_{C-P} = 15.3$ Hz), 127.4, 127.3(6), 127.3(4), 127.2, 61.4 ($J_{C-P} = 5.6$ Hz), 58.9, 41.1, 33.3 ($J_{C-P} = 6.7$ Hz) (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 21.7$ (ppm). MS (EI): $m/z = 77.1$ (5), 104.0 (6), 141.0 (8), 165.1 (9), 182.1 (100), 322.0 (27), 399.0 (26). IR (in KBr): $\nu = 3180$, 2963, 1446, 1262, 1207, 1093, 1024, 804, 694, 562, 528 (cm^{-1}). HRMS (ESI) (m/z)[$C_{22}H_{23}ClNO_2P + H^+$]: Calcd. 400.1233, Found. 400.1230.

4.2.40. N-Diphenylmethyl-P-benzyl-P-phenyl phosphonamide (5ia)

White solid (148.6 mg, 72% yield). m.p. 140–141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.72$ (dd, $J = 13.0$, 7.5 Hz, 2H), 7.48–7.42 (m, 1H), 7.37–7.30 (m, 2H), 7.29–7.10 (m, 15H), 5.40 (t, $J = 10.0$ Hz, 1H), 5.05–4.96 (m, 1H), 4.79–4.69 (m, 1H), 4.06–3.87 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 143.4$ ($J_{C-P} = 5.1$ Hz), 143.2 ($J_{C-P} = 5.6$ Hz), 136.7 ($J_{C-P} = 8.2$ Hz), 132.0 ($J_{C-P} = 2.9$ Hz), 131.7 ($J_{C-P} = 9.9$ Hz), 130.6 ($J_{C-P} = 174.2$ Hz), 128.6, 128.5(4), 128.5(0), 128.4 ($J_{C-P} = 14.6$ Hz), 128.1, 127.8, 127.3(4), 127.2(9), 127.2(2), 66.0 ($J_{C-P} = 5.5$ Hz), 58.9 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 22.0$ (ppm). MS (EI): $m/z = 77.1$ (4), 91.1 (23), 104.1 (6), 165.1 (7), 182.1 (30), 322.1 (100), 413.0 (2). IR (in KBr): $\nu = 3184$, 1454, 1203, 1124, 1008, 987, 805, 752, 700, 547 (cm^{-1}). HRMS (ESI) (m/z)[$C_{26}H_{24}NO_2P + H^+$]: Calcd. 414.1623, Found. 414.1621.

4.2.41. N-Diphenylmethyl-P-(2-fluorobenzyl)-P-phenyl phosphonamide (5ja)

White solid (161.3 mg, 75% yield). m.p. 138–139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.66$ (dd, $J = 13.0$, 7.5 Hz, 2H), 7.44–7.38 (m, 1H), 7.34–7.26 (m, 2H), 7.24–7.11 (m, 10H), 7.10–7.05 (m, 2H), 7.01–6.91 (m, 2H), 5.39 (t, $J = 9.8$ Hz,1H), 5.04–4.96 (m, 1H), 4.87–4.79 (m, 1H), 3.55–3.46 (m, 1H)(ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 160.7$ ($J_{C-F} = 248.2$ Hz), 143.3 ($J_{C-P} = 4.4$ Hz), 143.1 ($J_{C-P} = 5.5$ Hz), 132.1 ($J_{C-P} = 2.9$ Hz), 131.6 ($J_{C-P} = 10.0$ Hz), 130.4 ($J_{C-P} = 175.0$ Hz), 130.1 ($J_{C-F} = 3.9$ Hz), 130.0 ($J_{C-F} = 8.2$ Hz), 128.7, 128.6, 128.5 ($J_{C-P} = 14.5$ Hz), 127.4, 127.3, 127.2, 124.2 ($J_{C-F} = 3.7$ Hz), 124.0 (dd, $J_{C-F} = 14.6$ Hz, $J_{C-P} = 7.8$ Hz), 115.4 ($J_{C-F} = 21.0$ Hz), 60.3 (t, $J_{C-P} = J_{C-F} = 4.8$ Hz), 58.9 (ppm). ^{19}F NMR (100 MHz, $CDCl_3$) $\delta = -118.2$ (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 22.1$ (ppm). MS (EI): $m/z = 91.1$ (26), 109.0 (37), 121.0 (34), 161.1 (31), 182.1 (40), 282.1 (38), 322.0 (100), 431.0 (2). IR (in KBr): $\nu = 3244$, 1494, 1451, 1259, 1200, 1116, 995, 804, 749, 703, 549 (cm^{-1}). HRMS (ESI) (m/z)[$C_{26}H_{23}FNO_2P + H^+$]: Calcd. 432.1529, Found.432.1534.

4.2.42. N-Diphenylmethyl-P-(4-chlorobenzyl)-P-phenyl phosphonamide (5ka)

White solid (157.4 mg, 70% yield). m.p. 143–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.72$ (dd, $J = 13.0$, 7.7 Hz, 2H), 7.51–7.45 (m, 1H), 7.40–7.33 (m, 2H), 7.29–7.16 (m, 10H), 7.15–7.09 (m, 2H), 7.08–7.02 (m, 2H), 5.37 (t, $J = 10.0$ Hz, 1H), 4.98–4.89 (m, 1H), 4.72–4.63 (m, 1H), 4.06–3.93 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 143.3$ ($J_{C-P} = 3.9$ Hz), 143.1 ($J_{C-P} = 5.7$ Hz), 135.2 ($J_{C-P} = 7.7$ Hz), 134.0, 132.1 ($J_{C-P} = 2.9$ Hz), 131.6 ($J_{C-P} = 9.9$ Hz), 130.3 ($J_{C-P} = 174.8$ Hz), 129.1, 128.7, 128.6, 128.5 ($J_{C-P} = 14.6$ Hz), 127.4, 127.3, 127.2, 65.2 ($J_{C-P} = 5.3$ Hz), 58.9 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 22.2$ (ppm). MS (EI): $m/z = 77.1$ (6), 104.1 (9), 125.0 (27), 165.1 (7), 182.1 (32), 322.1 (100), 447.0 (2). IR (in KBr): $\nu = 3214$, 1453, 1199, 1121, 995, 869, 803, 748, 703, 543 (cm^{-1}). HRMS (ESI) (m/z)[$C_{26}H_{23}ClNO_2P + H^+$]: Calcd. 448.1233, Found. 448.1238.

4.2.43. N-Diphenylmethyl-P-(4-bromobenzyl)-P-phenyl phosphonamide (5la)

White solid (171.6 mg, 70% yield). m.p. 156–157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.72$ (dd, $J = 13.0$, 7.5 Hz, 2H), 7.51–7.46 (m, 1H), 7.41–7.34 (m, 4H), 7.30–7.17 (m, 8H), 7.14–7.08 (m, 2H), 7.02–6.96 (m, 2H), 5.38 (t, $J = 9.9$ Hz, 1H), 4.97–4.89 (m, 1H), 4.71–4.63 (m, 1H), 3.91–3.79 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 143.3$ ($J_{C-P} = 4.2$ Hz), 143.1 ($J_{C-P} = 5.6$ Hz), 135.7 ($J_{C-P} = 7.7$ Hz), 132.2 ($J_{C-P} = 3.1$ Hz), 131.7, 131.6 ($J_{C-P} = 9.9$ Hz), 130.3 ($J_{C-P} = 174.8$ Hz), 129.4, 128.7, 128.6, 128.5 ($J_{C-P} = 14.5$ Hz), 127.4, 127.3(7), 127.3(3), 127.2, 122.2, 65.3 ($J_{C-P} = 5.4$ Hz), 58.9 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 22.2$ (ppm). MS (EI): $m/z = 77.1$ (5), 104.0 (7), 169.0 (14), 182.1 (27), 322.0 (100), 492.0 (2). IR (in KBr): $\nu = 3176$, 1449, 1262, 1198, 1120, 1006, 805, 749, 697, 555 (cm^{-1}). HRMS (ESI) (m/z)[$C_{26}H_{23}BrNO_2P + H^+$]: Calcd. 492.0728, Found. 492.0731.

4.2.44. N-(Di-p-tolylmethyl)-P,P-diphenyl phosphinamide (5ab)

White solid (148.5 mg, 72% yield). m.p. 187–188 °C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.84$ (dd, $J = 11.5$, 8.0 Hz, 4H), 7.48–7.42 (m, 2H), 7.40–7.32 (m, 4H), 7.15 (d, $J = 7.5$ Hz, 4H), 7.09 (d, $J = 7.6$ Hz, 4H), 5.38 (t, $J = 10.7$ Hz, 1H), 3.70–3.57 (m, 1H), 2.32 (s, 6H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 140.7$ ($J_{C-P} = 4.5$ Hz), 136.8, 132.5 ($J_{C-P} = 129.4$ Hz), 132.4 ($J_{C-P} = 9.6$ Hz), 131.9 ($J_{C-P} = 2.6$ Hz), 129.2, 128.5 ($J_{C-P} = 12.7$ Hz), 127.5, 58.2, 21.2 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 22.9$ (ppm). MS (EI): $m/z = 77.1$ (4), 91.1 (3), 118.1 (7), 165.1 (4), 201.0 (16), 210.1 (100), 320.1 (2), 411.1 (3). IR (in KBr): $\nu = 3152$, 2870, 1445, 1181, 1112, 1070, 941, 747, 701, 553 (cm^{-1}). HRMS (ESI) (m/z)[$C_{27}H_{26}NOP + H^+$]: Calcd. 412.1830, Found. 412.1834.

4.2.45. N-(Di-4-methoxyphenylmethyl)-P,P-diphenyl phosphinamide (5ac)

White solid (151.6 mg, 68% yield). m.p.: 224–225 °C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.83$ (dd, $J = 11.8$, 7.7 Hz, 4H), 7.48–7.42 (m, 2H), 7.40–7.33 (m, 4H), 7.17 (d, $J = 8.2$ Hz, 4H), 6.82 (d, $J = 8.2$ Hz, 4H), 5.37 (t, $J = 10.6$ Hz, 1H), 3.78 (s, 6H), 3.62–3.53 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 158.7$, 136.0 ($J_{C-P} = 4.6$ Hz), 132.5 ($J_{C-P} = 129.0$ Hz), 132.4 ($J_{C-P} = 9.6$ Hz), 132.0 ($J_{C-P} = 2.6$ Hz), 128.8, 128.5 ($J_{C-P} = 12.6$ Hz), 113.9, 57.6, 55.4 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.0$ (ppm). MS (EI): $m/z = 77.1$ (3), 134.1 (4), 201.0 (10), 242.0 (100), 443.1 (3). IR (in KBr): $\nu = 3697$, 3143, 1772, 1506, 1447, 1247,

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1187, 1118, 1024, 699, 554 (cm^{-1}). HRMS (ESI) (*m*/*z*) [$C_{27}H_{26}NO_3P + H^+$]: Calcd. 444.1729, Found. 444.1727.

4.2.46. N-(Di-(4-fluorophenyl)methyl)-P,P-diphenyl phosphinamide (5ad)

White solid (136.0 mg, 65% yield). m.p. 183–184 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.87–7.76$ (m, 4H), 7.51–7.45 (m, 2H),7.43–7.34 (m, 4H), 7.25–7.18 (m, 4H), 6.98 (t, $J = 8.0$ Hz, 4H), 5.44 (t, $J = 10.7$ Hz, 1H), 3.60–3.51 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 162.0$ ($J_{C-F} = 246.3$ Hz), 139.0 (t, $J_{C-P} = J_{C-F} = 3.5$ Hz), 132.3 ($J_{C-P} = 9.7$ Hz), 132.1(4) ($J_{C-P} = 129.2$ Hz), 132.1(2) ($J_{C-P} = 2.5$ Hz), 129.4 ($J_{C-F} = 8.1$ Hz), 128.6 ($J_{C-P} = 12.7$ Hz), 115.5 ($J_{C-F} = 21.4$ Hz), 57.4 (ppm). ^{19}F NMR (100 MHz, $CDCl_3$) $\delta = -115.2$ (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.3$ (ppm). MS (EI): *m*/*z* = 77.1 (4), 95.0 (3), 122.0 (6), 155.1 (4), 183.0 (7), 201.0 (24), 218.1 (100), 419.1 (4). IR (in KBr): $\nu = 3143$, 1498, 1445, 1184, 1119, 1075, 1023, 918, 697, 553 (cm^{-1}). HRMS (ESI) (*m*/*z*)[$C_{25}H_{20}F_2NOP + H^+$]: Calcd. 420.1329, Found. 420.1323.

4.2.47. N-(Phenyl(o-tolyl)methyl)-P,P-diphenyl phosphinamide (5ae)

White solid (138.9 mg, 70% yield). m.p. 200–201 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.96–7.88$ (m, 2H), 7.85–7.77 (m, 2H), 7.53–7.40 (m, 5H), 7.36–7.25 (m, 7H), 7.25–7.18 (m, 2H), 7.11–7.06 (m, 1H), 5.62 (t, $J = 11.0$ Hz,1H), 3.71–3.61 (m, 1H), 1.91 (s, 3H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 143.0$ ($J_{C-P} = 4.0$ Hz), 141.2 ($J_{C-P} = 4.5$ Hz), 135.4, 132.7 ($J_{C-P} = 129.2$ Hz), 132.6 ($J_{C-P} = 9.7$ Hz), 132.1 ($J_{C-P} = 9.4$ Hz), 132.0 ($J_{C-P} = 2.5$ Hz), 131.9 ($J_{C-P} = 2.7$ Hz), 131.8 ($J_{C-P} = 131.4$ Hz), 130.6, 128.7, 128.6 ($J_{C-P} = 12.6$ Hz), 128.4 ($J_{C-P} = 12.7$ Hz), 127.9, 127.3, 127.0, 126.4, 55.2, 19.3 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.1$ (ppm). MS (EI): *m*/*z* = 77.1 (8), 104.0 (6), 165.1 (11), 179.1 (18), 196.1 (100), 201.0 (38), 218.0 (18), 306.1 (6), 397.0 (8). IR (in KBr): $\nu = 3148$, 2874, 1445, 1189, 1117, 1067, 936, 741, 696, 550 (cm^{-1}). HRMS (ESI) (*m*/*z*)[$C_{26}H_{24}NOP + H^+$]: Calcd. 398.1674, Found. 398.1669.

4.2.48. N-(Phenyl(m-tolyl)methyl)-P,P-diphenyl phosphinamide (5af)

White solid (140.3 mg, 71% yield). m.p. 158–159 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.88–7.78$ (m, 4H), 7.49–7.43 (m, 2H), 7.40–7.34 (m, 4H), 7.31–7.26 (m, 4H), 7.24–7.16 (m, 2H), 7.10–6.99 (m, 3H), 5.42 (t, $J = 10.7$ Hz, 1H), 3.70–3.58 (m, 1H), 2.28 (s, 3H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 143.5$ ($J_{C-P} = 4.5$ Hz), 143.4 ($J_{C-P} = 4.6$ Hz), 138.2, 132.4(4) ($J_{C-P} = 129.2$ Hz), 132.4(3) ($J_{C-P} = 9.5$ Hz), 132.3(8) ($J_{C-P} = 129.5$ Hz), 132.3(5) ($J_{C-P} = 9.5$ Hz), 132.0 ($J_{C-P} = 2.7$ Hz), 128.6, 128.5(0) ($J_{C-P} = 12.3$ Hz), 128.4(6) ($J_{C-P} = 11.2$ Hz), 128.4(3), 128.1, 127.6, 127.2, 124.7, 58.7, 21.6 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.2$ (ppm). MS (EI): *m*/*z* = 77.1 (6), 104.0 (6), 165.1 (9), 196.1 (100), 201.0 (28), 306.1(3), 320.1 (3), 397.0 (5). IR (in KBr): $\nu = 3150$, 2870, 1445, 1192, 1116, 1069, 934, 748, 700, 555 (cm^{-1}). HRMS (ESI) (*m*/*z*)[$C_{26}H_{24}NOP + H^+$]: Calcd. 398.1674, Found. 398.1677.

4.2.49. N-(Phenyl(p-tolyl)methyl)-P,P-diphenyl phosphinamide (5ag)

White solid (145.5 mg, 73% yield). m.p. 177–178 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.88–7.78$ (m, 4H), 7.48–7.42 (m, 2H), 7.40–7.32 (m, 4H), 7.30–7.20 (m, 5H), 7.17–7.12 (m, 2H), 7.12–7.06 (m, 2H), 5.42 (t, $J = 10.8$ Hz, 1H), 3.61 (dd, $J = 10.0$, 6.7 Hz, 1H), 2.31 (s, 3H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 143.6$ ($J_{C-P} = 4.6$ Hz), 140.6 ($J_{C-P} = 4.6$ Hz), 137.0, 132.5(2) ($J_{C-P} = 129.4$ Hz), 132.5(0) ($J_{C-P} = 129.5$ Hz), 132.4 ($J_{C-P} = 9.7$ Hz), 132.0 ($J_{C-P} = 2.6$ Hz), 129.3, 128.5(6), 128.5(2) ($J_{C-P} = 12.5$ Hz), 128.5(0) ($J_{C-P} = 11.6$ Hz), 127.7, 127.6, 127.2, 58.4, 21.2 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.0$ (ppm). MS (EI): *m*/*z* = 77.1 (4), 104.1 (3), 165.1 (6), 196.1 (100), 201.0 (17), 320.1 (2), 397.1 (4). IR (in KBr): $\nu = 3147$, 2870, 1447, 1184, 1115, 1068, 930, 740, 701, 554 (cm^{-1}). HRMS (ESI) (*m*/*z*) [$C_{26}H_{24}NOP + H^+$]: Calcd. 398.1674, Found. 398.1669.

4.2.50. N-((4-Methoxyphenyl)(phenyl)methyl)-P,P-diphenyl phosphinamide (5ah)

White solid (133.7 mg, 65% yield). m.p. 163–164 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.88–7.78$ (m, 4H), 7.49–7.42 (m, 2H), 7.40–7.33 (m, 4H), 7.31–7.22 (m, 5H), 7.17 (d, $J = 8.5$ Hz, 2H), 6.82 (d, $J = 10.7$ Hz, 2H), 5.42 (t, $J = 10.7$ Hz, 1H), 3.78 (s, 3H), 3.58 (dd, $J = 9.7$, 6.6 Hz, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 158.8$, 143.7 ($J_{C-P} = 4.6$ Hz), 135.8 ($J_{C-P} = 4.5$ Hz), 132.6 ($J_{C-P} = 129.3$ Hz), 132.4(4) ($J_{C-P} = 9.7$ Hz), 132.4(3) ($J_{C-P} = 129.7$ Hz), 132.3(9) ($J_{C-P} = 9.6$ Hz), 132.0 ($J_{C-P} = 2.8$ Hz), 128.9, 128.6, 128.5 ($J_{C-P} = 12.1$ Hz), 127.6, 127.3, 114.0, 58.1, 55.4 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.0$ (ppm). MS (EI): *m*/*z* = 77.1 (6), 104.0 (5), 134.1 (3), 201.0 (19), 212.1 (100), 413.1 (4). IR (in KBr): $\nu = 3142$, 1775, 1600, 1449, 1260, 1190, 1118, 1022, 701, 555 (cm^{-1}). HRMS (ESI) (*m*/*z*) [$C_{26}H_{24}NO_2P + H^+$]: Calcd. 414.1623, Found. 414.1618.

4.2.51. N-((4-Fluorophenyl)(phenyl)methyl)-P,P-diphenyl phosphinamide (5ai)

White solid (126.8 mg, 63% yield). m.p. 189–190 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.82$ (dd, $J = 11.8$, 7.7 Hz, 4H), 7.50–7.44 (m, 2H), 7.41–7.34 (m, 4H), 7.33–7.28 (m, 2H), 7.28–7.21 (m, 5H), 6.96 (t, $J = 8.0$ Hz, 2H), 5.44 (t, $J = 10.7$ Hz, 1H), 3.67–3.57 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 162.0$ ($J_{C-F} = 245.9$ Hz), 143.2 ($J_{C-P} = 4.7$ Hz), 139.3 (t, $J_{C-P} = J_{C-F} = 3.3$ Hz), 132.3(8) ($J_{C-P} = 13.3$ Hz), 132.3(5) ($J_{C-P} = 128.8$ Hz), 132.2(9) ($J_{C-P} = 13.3$ Hz), 132.1(2) ($J_{C-P} = 128.9$ Hz), 132.0(6), 129.4 ($J_{C-F} = 8.1$ Hz), 128.7, 128.6 ($J_{C-P} = 12.7$ Hz), 127.6, 127.5, 115.3 ($J_{C-F} = 21.4$ Hz), 58.0 (ppm). ^{19}F NMR (100 MHz, $CDCl_3$) $\delta = -115.5$ (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.2$ (ppm). MS (EI): *m*/*z* = 77.1 (4), 122.0 (3), 165.1 (3), 183.0 (7), 200.1 (100), 201.0 (31), 401.1 (4). IR (in KBr): $\nu = 3148$, 1500, 1444, 1184, 1120, 1071, 1024, 818, 700, 556 (cm^{-1}). HRMS (ESI) (*m*/*z*) [$C_{25}H_{21}FNOP + H^+$]: Calcd. 402.1423, Found. 402.1427.

4.2.52. N-((4-Chlorophenyl)(phenyl)methyl)-P,P-diphenyl phosphinamide (5aj)

White solid (139.4 mg, 67% yield). m.p. 170–171 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.86–7.75$ (m, 4H), 7.48–7.42 (m, 2H), 7.39–7.32 (m, 4H), 7.32–7.18 (m, 9H), 5.41 (t, $J = 10.7$ Hz, 1H), 3.86–3.73 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 143.0$ ($J_{C-P} = 5.1$ Hz), 142.0 ($J_{C-P} = 4.0$ Hz), 133.1, 132.3(6) ($J_{C-P} = 13.5$ Hz), 132.2(9) ($J_{C-P} = 129.1$ Hz), 132.2(6) ($J_{C-P} = 13.4$ Hz), 132.0(7) ($J_{C-P} = 129.3$ Hz), 132.05, 129.2, 128.7, 128.6, 128.5 ($J_{C-P} = 12.8$ Hz), 127.6, 127.5, 58.1 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.3$ (ppm). MS (EI): *m*/*z* = 77.1 (6), 104.1 (3), 138.1 (3), 165.1 (10), 201.0 (27), 216.0 (100), 417.1 (6). IR (in KBr): $\nu = 3152$, 1452, 1200, 1123, 939, 872, 801, 742, 697, 555 (cm^{-1}). HRMS (ESI) (*m*/*z*) [$C_{25}H_{21}ClNOP + H^+$]: Calcd. 418.1128, Found. 418.1134.

4.2.53. N-((4-Bromophenyl)(phenyl)methyl)-P,P-diphenyl phosphinamide (5ak)

White solid (149.3 mg, 65% yield). m.p. 192–193 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.87–7.76$ (m, 4H), 7.50–7.44 (m, 2H), 7.43–7.34 (m, 6H), 7.33–7.28 (m, 2H), 7.27–7.21 (m, 3H), 7.15 (d, $J = 7.7$ Hz, 2H), 5.41 (t, $J = 10.7$ Hz, 1H), 3.70–3.58 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 142.9$ ($J_{C-P} = 4.9$ Hz), 142.5 ($J_{C-P} = 3.9$ Hz), 132.4 ($J_{C-P} = 13.4$ Hz), 132.3(0) ($J_{C-P} = 13.4$ Hz), 132.2(9) ($J_{C-P} = 127.7$ Hz), 132.1(4), 132.0(8) ($J_{C-P} = 129.6$ Hz), 131.7, 129.5, 128.8, 128.6 ($J_{C-P} = 12.7$ Hz), 127.6, 121.3, 58.2 (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.2$ (ppm). MS (EI): *m*/*z* = 77.1 (3), 165.1 (11), 201.0 (29), 260.0 (100), 308.0 (8), 461.0 (5). IR (in KBr): $\nu = 3150$, 1453, 1205, 1102, 998, 937, 807, 746, 692, 554 (cm^{-1}). HRMS (ESI) (*m*/*z*)

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[$C_{25}H_{21}BrNOP + H^+$]: Calcd. 462.0622, Found. 462.0615.

4.2.54. N-((Phenyl)(4-trifluoromethylphenyl)methyl)-P,P-diphenyl phosphinamide (5al)

White solid (131.1 mg, 58% yield). m.p. 199–200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.88–7.75$ (m, 4H), 7.56–7.51 (m, 2H), 7.50–7.44 (m, 2H), 7.43–7.20 (m, 11H), 5.50 (t, $J = 10.6$ Hz, 1H), 3.76–3.67 (m, 1H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 147.3$ ($J_{C-P} = 3.3$ Hz), 142.6 ($J_{C-P} = 4.9$ Hz), 132.4 ($J_{C-P} = 9.7$ Hz), 132.2(6), 132.2(4) ($J_{C-P} = 9.8$ Hz), 132.2(0) ($J_{C-P} = 128.6$ Hz), 132.0 ($J_{C-P} = 129.5$ Hz), 128.9, 128.7 ($J_{C-P} = 12.7$ Hz), 128.6 ($J_{C-P} = 12.7$ Hz), 128.1, 127.8, 127.6, 125.6 (q, $J_{C-F} = 3.7$ Hz), 58.4 (ppm). ^{19}F NMR (100 MHz, $CDCl_3$) $\delta = -62.5$ (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.4$ (ppm). MS (EI): $m/z = 77.1$ (4), 165.1 (4), 201.0 (20), 250.0 (100), 451.0 (5). IR (in KBr): $\nu = 3149$, 2890, 1447, 1302, 1192, 1026, 920, 801, 745, 698, 556 (cm^{-1}). HRMS (ESI) (m/z) [$C_{26}H_{21}F_3NOP + H^+$]: Calcd. 452.1391, Found. 452.1396.

4.2.55. N-((4-Fluorophenyl)(p-tolyl)methyl)-P,P-diphenyl phosphinamide (5am)

White solid (146.2 mg, 70% yield). m.p. 180–181 °C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.88–7.78$ (m, 4H),7.51–7.43 (m, 2H),7.42–7.34 (m, 4H), 7.26–7.21 (m, 2H), 7.12 (bs, 4H), 6.96 (t, $J = 8.0$ Hz, 2H), 5.41 (t, $J = 10.6$ Hz, 1H), 3.59–3.51 (m, 1H), 2.33 (s, 3H) (ppm). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 162.0$ ($J_{C-F} = 245.7$ Hz), 140.4 ($J_{C-P} = 5.2$ Hz), 139.4 (t, $J_{C-P} = J_{C-F} = 3.6$ Hz), 137.2, 132.4(3) ($J_{C-P} = 129.5$ Hz), 132.3(9) ($J_{C-P} = 14.0$ Hz), 132.3(0) ($J_{C-P} = 13.9$ Hz), 132.2(1) ($J_{C-P} = 129.3$ Hz), 132.0(3) ($J_{C-P} = 2.4$ Hz), 132.0(1) ($J_{C-P} = 2.4$ Hz), 129.3(8), 129.3(6) ($J_{C-F} = 7.9$ Hz), 128.6 ($J_{C-P} = 12.7$ Hz), 128.5 ($J_{C-P} = 12.6$ Hz), 127.5, 115.3 ($J_{C-F} = 21.4$ Hz), 57.8, 21.2 (ppm). ^{19}F NMR (100 MHz, $CDCl_3$) $\delta = -115.7$ (ppm). ^{31}P NMR (100 MHz, $CDCl_3$) $\delta = 23.1$ (ppm). MS (EI): $m/z = 77.1$ (4), 122.0 (5), 155.1 (3), 183.0 (7), 201.0 (17), 214.1 (100), 415.1 (3). IR (in KBr): $\nu = 3149$, 1506, 1445, 1181, 1117, 1071, 1021, 724, 694, 554 (cm^{-1}). HRMS (ESI) (m/z) [$C_{26}H_{23}FNOP + H^+$]: Calcd. 416.1580, Found. 416.1577.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.tet.2018.07.006.

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