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Iridium-Catalyzed Phosphoramidation of Arene C−H Bonds with Phosphoryl Azide

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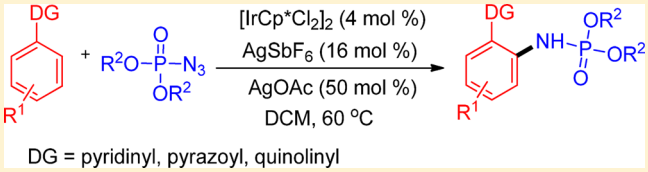
Supporting Information

ABSTRACT: An iridium-catalyzed phosphoramidation of arene C−H bonds with phosphoryl azide as the amino source is described. The direct C−H phosphoramidation of arenes bearing pyridinyl, pyrazoyl, and quinolinyl as the directing group has good functional group tolerance and occurs smoothly under mild conditions, providing *N*-aryl phosphoramidates in good yields.

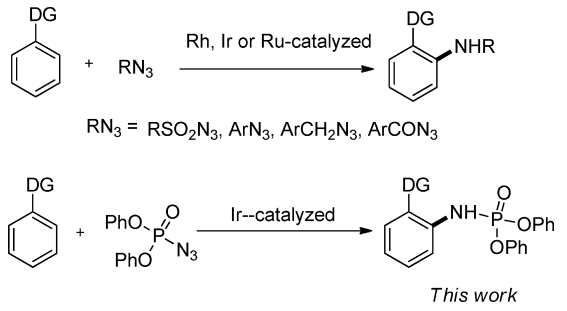


Phosphoramidates are key structural units that exist in various kinds of bioactive molecules and pharmaceuticals.[1] Thus, the composition of phosphoramidate is of great significance and a variety of approaches have been explored. The conventional methods were usually limited to the reaction of suitable phosphorus halides with amines.[2] The Cu- or I_2-catalyzed oxidative coupling of phosphites with amines were also described.[3] The Staudinger-phosphite reaction furnishes an alternative approach for phosphoramidate formation using organic azides.[4] However, among those methods, direct approaches to access *N*-aryl phosphoramidates were less studied.[5]

Recently, notable advances have been achieved in the direct amination of C−H bonds.[6] Especially, organic azides were proven to be "energetic reagents" for the direct C−H amination since nitrogen as the sole byproduct is released during the "NR" transfer process.[7] For example, elegant approaches for Rh- or Ru-catalyzed direct amidation of arene C−H bonds with sulfonyl, alkyl, or aryl azides were disclosed by Chang.[8] Subsequently, we[9n] and other groups also described the C−H amidation of arenes with sulfonyl azides.[9] Recently, iridium catalysts also attracted special attention for C−H amidation. Chang developed the Ir-catalyzed direct C−H amidation with sulfonyl azides or acyl azides.[10] However, the phosphoramidation of an arene C−H bond with phosphoryl azide has not been reported before. Herein, we disclose the Ir-catalyzed C−H phosphoramidation of an arene with a phosphoryl azide to provide *N*-aryl phosphoramidate (Scheme 1).

First, we chose 2-phenylpyridine (**1a**) and diphenyl phosphorazidate (**2a**) as the model reaction. After several catalysts were screened, a 20% yield of product **3aa** was obtained in the presence of $[IrCp^*Cl_2]_2$, while no product was observed using $[RhCp^*Cl_2]_2$ or $[RuCl_2(p\text{-cymene})]_2$ as the catalyst (Table 1, entries 3−4). Next, we attempted to elevate the yield by investigating the additive. We found the yield could be increased to 50% with the combination of $AgSbF_6$ and

Scheme 1. Direct Amidation of C−H Bonds with Organic Azides



AgOAc (Table 1, entry 8). To our delight, increasing the amount of AgOAc to 50 mol % led to a 75% yield of product (Table 1, entry 18). Further studies disclosed the solvent was crucial. Among the solvents screened such as DCM, DCE, EA, THF, dioxane, and CH_3CN, DCM was the best, whereas only a trace of product was observed in THF, dioxane, or CH_3CN. Control experiments showed that the product **3aa** was not obtained without $[IrCp^*Cl_2]_2$ and a trace of product was observed in the absence of $AgSbF_6$ (Table 1, entries 19 and 20). It is noted that the reaction could be performed to access **3aa** in an acceptable 67% yield on a 1 mmol scale.

Next, we attempted to explore the substrate scope of this protocol. As illustrated in Table 2, the C−H phosphoramidation of arene with phosphoryl azide ran smoothly, affording the products in good yields. Substituents such as methoxy, chloro, fluoro, trifluoromethyl, and carboxylate groups in the *ortho*-, *meta*-, and *para*-position on the 2-arylpyridine were well tolerated. Notably, a halogen group which is available for further transformation was compatible (Table 2, **3ha**−**3ja**).

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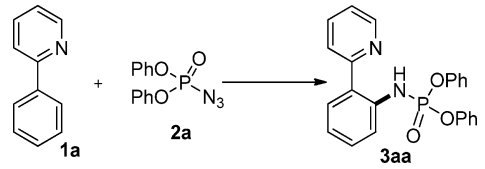
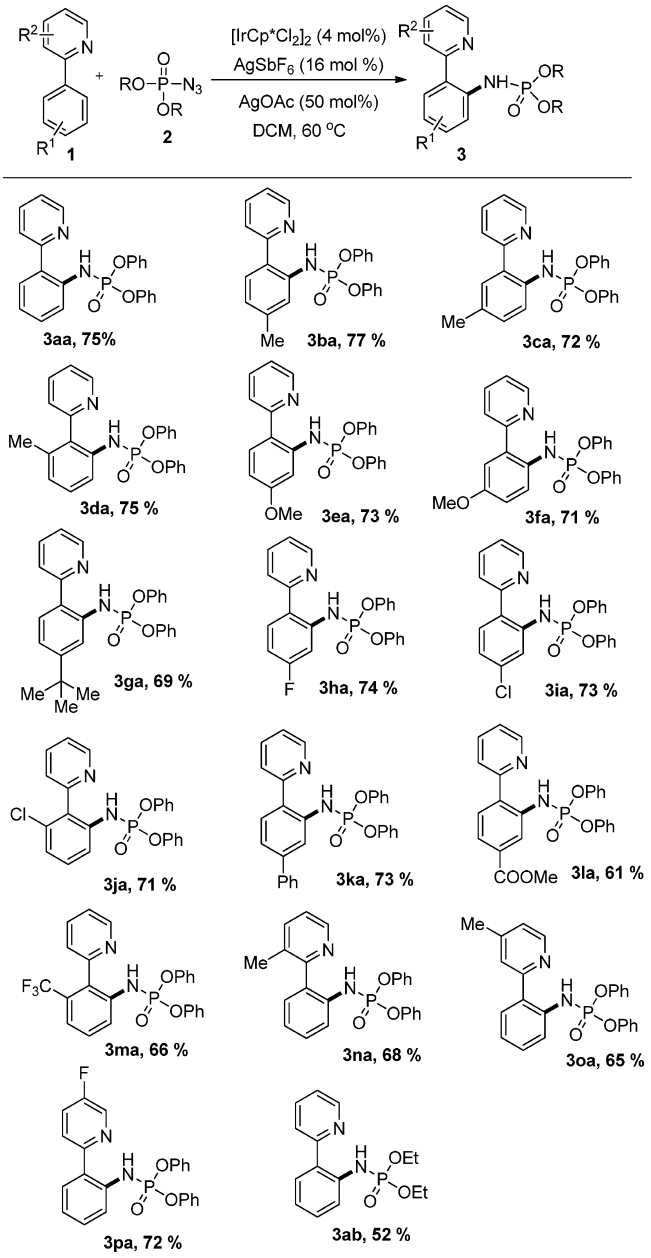
Table 1. Screening of Conditions for Phosphoramidation[a]



entry	catalyst	additive (mol %)	solvent	yield (%)
1	$[IrCp^*Cl_2]_2$	$AgSbF_6$ (16)	DCM	20
2	$[IrCp^*Cl_2]_2$	$AgNTf_2$ (16)	DCM	21
3	$[RhCp^*Cl_2]_2$	$AgSbF_6$ (16)	DCM	0
4	$[RuCl_2(p\text{-cymene})]_2$	$AgSbF_6$ (16)	DCM	0
5	$[IrCp^*Cl_2]_2$	$AgSbF_6$ (50)	DCM	25
6	$[IrCp^*Cl_2]_2$	$AgSbF_6$ (16)/ $Cu(OAc)_2$ (20)	DCM	trace
7	$[IrCp^*Cl_2]_2$	$AgSbF_6$ (16)/ HOAc (20)	DCM	trace
8	$[IrCp^*Cl_2]_2$	$AgSbF_6$ (16)/ AgOAc (20)	DCM	50
9	$[IrCp^*Cl_2]_2$	$AgSbF_6$ (16)/ NaOAc (20)	DCM	30
10	$[IrCp^*Cl_2]_2$	$AgSbF_6$ (16)/ CsOAc (20)	DCM	33
11	$[IrCp^*Cl_2]_2$	$AgSbF_6$ (16)/ $AgBF_4$ (20)	DCM	36
12	$[IrCp^*Cl_2]_2$	$AgSbF_6$ (16)/ AgOAc (20)	THF	trace
13	$[IrCp^*Cl_2]_2$	$AgSbF_6$ (16)/ AgOAc (20)	DCE	45
14	$[IrCp^*Cl_2]_2$	$AgSbF_6$ (16)/ AgOAc (20)	acetone	35
15	$[IrCp^*Cl_2]_2$	$AgSbF_6$ (16)/ AgOAc (20)	EA	40
16	$[IrCp^*Cl_2]_2$	$AgSbF_6$ (16)/ AgOAc (20)	dioxane	trace
17	$[IrCp^*Cl_2]_2$	$AgSbF_6$ (16)/ AgOAc (20)	CH_3CN	trace
18	**$[IrCp^*Cl_2]_2$**	**$AgSbF_6$ (16)/ AgOAc (50)**	**DCM**	**75**
19	$[IrCp^*Cl_2]_2$	AgOAc (50)	DCM	trace
20	–	$AgSbF_6$ (16)/ AgOAc (50)	DCM	0

[a]Conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), catalyst (4 mol %), additive, and solvent (1.0 mL) under Ar, 24 h, 60 °C.

Table 2. Scope of 2-Aryl Pyridine[a]



[a]Conditions: **1** (0.1 mmol), **2** (0.2 mmol), $[IrCp^*Cl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), AgOAc (50 mol %) and DCM (1.0 mL) under Ar, 24 h, 60 °C.

Particularly, the reaction exhibited good regioselectivity. For example, when arylpyridines **1c** and **1f** were submitted to the procedure, the sole products **3ca** and **3fa** were obtained due to less steric hindrance. Substrates substituted on the pyridine motif were also applicable to this phosphoramidation procedure. The desired products were obtained in good yields when substitutions occurred at the 3-, 4-, or 5-position of pyridine (Table 2, **3na**, **3oa**, and **3pa**). The diethyl phosphorazidate was also a proper substrate for this process, albeit a moderate yield was obtained (Table 2, **3ab**).

Next, we tried to further investigate other directing groups instead of pyridine (Table 3). To our delight, the desired products were obtained in moderate yields when pyrazole group was used as the directing group. As expected, benzo[*h*]quinolone was also a good partner in the Ir-catalyzed C−H phosphoramidation process, providing the diphenyl benzo[*h*]quinolin-10-ylphosphoramidate **5fa** in 55% yield.

To access some insights into the mechanism, a series of preliminary isotopic experiments were conducted. A significant H/D scrambling was observed in the *ortho*-position of 2-phenylpyridine **1a** when it was treated with a catalytic amount of $[IrCp^*Cl_2]_2$ and $AgSbF_6$ in DCM and D_2O (Scheme 2, eq 1). When the reaction was performed in the presence of diphenyl phosphorazidate in DCM/D_2O, deuterium incorporation was also observed in the unreacted **1a** (Scheme 2, eq 2). These results suggested that the sp^2 C−H bond cleavage in this phosphoramidation is a reversible process. In addition, the result that the D-incorporation is higher in the phosphoramidated product (40% D) than in the recovered starting material (10% D) also showed that C−H activation occurs faster than the exchange of substrate coordinated to the catalyst. Moreover, the kinetic isotope effect (k_H/k_D = 1.04) was determined by an intermolecular competition experiment with isotopically labeled **1a′** (Scheme 2, eq 3). It also indicated that cleavage of the sp^2 C−H bond in this phosphoramidation

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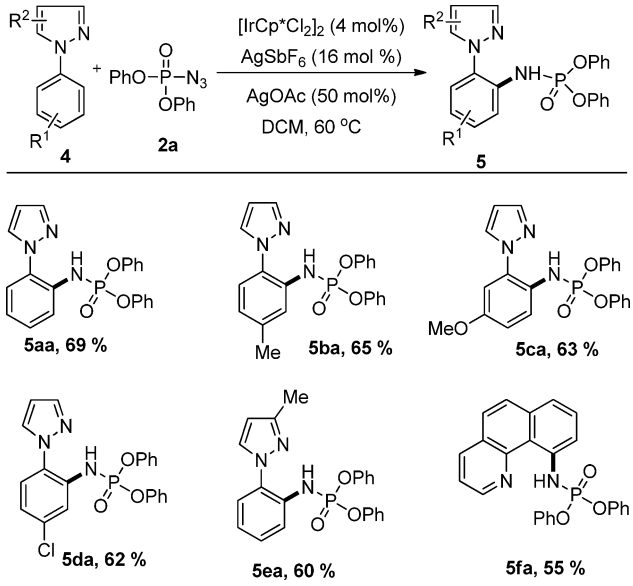
Table 3. Scope of 1-Aryl-1*H*-pyrazole[a]



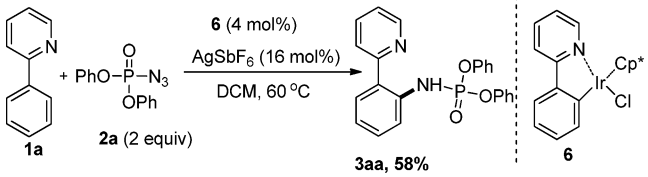
[a]Conditions: **4** (0.1 mmol), **2a** (0.2 mmol), $[IrCp^*Cl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), AgOAc (50 mol %), and DCM (1.0 mL) under Ar, 24 h, 60 °C.

is reversible. Notablely, an iridacyclic intermediate **6**[11a] treated with $AgSbF_6$ could catalyze the direct C−H phosphoramidation of 2-phenylpyridine with diphenyl phosphorazidate (Scheme 3). This result showed that the cationic metallacycle **6** may be the precatalyst in this phosphoramidation.

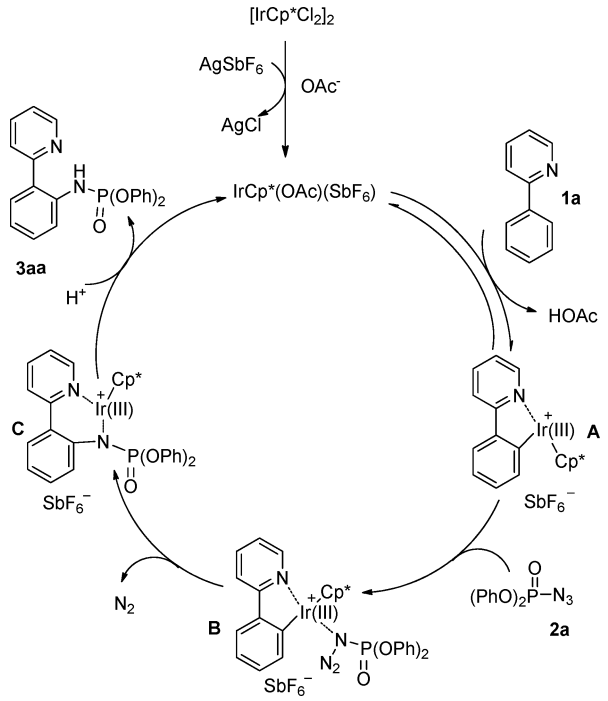
According to the above-mentioned mechanistic experiments and previous studies,[10] we proposed a possible mechanistic pathway in Scheme 4. First, treatment of a dimeric iridium species with $AgSbF_6$ and AgOAc generates the active Ir(III) catalyst, which induces a C−H bond cleavage of **1a** to produce a cyclometalated Ir(III) complex **A**.[11] Subsequently, coordination of the phosphoryl azide to **A** to form the Ir-species **B**, followed by migratory insertion, leads to the intermediate **C**, releasing byproduct N_2. Finally, protonolysis of **C** provides the phosphoramidation product **3aa** and generates the active Ir complex.

In summary, we have developed an iridium-catalyzed phosphoramidation of arene C−H bonds with phosphoryl

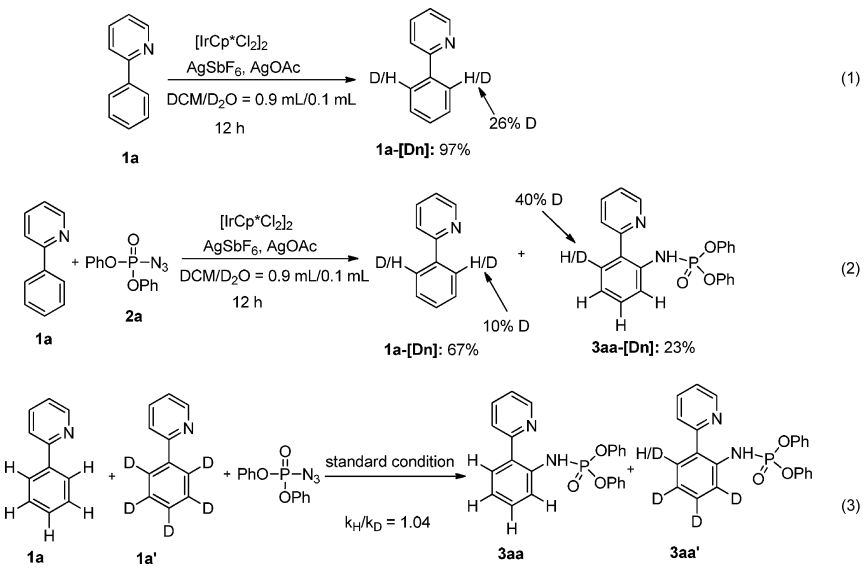
Scheme 3. Direct C−H Phosphoramidation Catalyzed by Iridacyclic Intermediate 6



Scheme 4. Proposed Mechanism



Scheme 2. Deuteration Experiments



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azide. This present reaction is compatible with several directing groups such as pyridinyl, pyrazoyl, and quinolinyl, and the direct C−H phosphoramidation of the substrates with various functional groups (−OMe, −Me, −Cl, −F, $-CF_3$, −COOMe, −*t*-Bu) proceeded smoothly under mild conditions, providing *N*-aryl phosphoramidates in good yields.

EXPERIMENTAL SECTION

General Information. NMR spectra (400 MHz for ^{1}H, 100 MHz for ^{13}C, 162 MHz for ^{31}P) were recorded in $CDCl_3$ at ambient temperature on a NMR spectrometer. Chemical shifts are reported in δ units, parts per million (ppm). Coupling constants (J) are described in Hz. All ^{13}C NMR spectra were accessed with ^{1}H decoupling. HRMS data were performed on a TOF LC/MS.

Diphenyl phosphorazidate **2a** is commercially available. The diethyl phosphorazidate **2b** was synthesized according to the reported literature.[12] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.14−4.06 (m, 4H), 1.36−1.32 (m, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 63.7, 63.6, 16.0, 15.9.

Caution: the phosphoryl azides may be explosive, please operate carefully.

Typical Procedure for Iridium-Catalyzed Phosphoramidation of Arene C−H Bonds with Phosphoryl Azide. The mixture of 2-phenylpyridine **1a** (0.1 mmol, 15.5 mg), diphenyl phosphorazidate **2a** (0.2 mmol, 55 mg), $[IrCp^*Cl_2]_2$ (4 mol %, 3.2 mg), $AgSbF_6$ (16 mol %, 6.2 mg), AgOAc (50 mol %, 8.3 mg), and DCM (1.0 mL) was added into a sealed tube. After stirring at 60 °C for 24 h under Ar, the mixture was concentrated and then purified by preparative TLC on GF254 (petroleum/ethyl acetate) to access the product **3aa**.

*Diphenyl (2-(Pyridin-2-yl)phenyl)phosphoramidate (**3aa**).* Colorless liquid (30.1 mg, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.61 (d, J = 12.2 Hz, 1H), 8.48 (d, J = 4.9 Hz, 1H), 7.75−7.68 (m, 4H), 7.41−7.37 (m, 1H), 7.29−7.22 (m, 8H), 7.20−7.17 (m, 1H), 7.14−7.06 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 157.7, 150.6 (d, J = 6.8 Hz), 147.1, 139.4, 137.5, 130.4, 129.7, 128.7, 125.1 (d, J = 1.0 Hz), 124.0 (d, J = 10.0 Hz), 121.9, 121.8 (d, J = 12.4 Hz), 120.5, 120.4, 119.6 (d, J = 2.4 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ −7.49. IR (cm^{-1}) ν 3474, 3065, 1589, 1456, 1433, 1399, 1276, 1162, 1012. HRMS (ESI) m/z calcd for $C_{23}H_{19}N_2NaO_3P$ $(M + Na)^+$ 425.1026, found 425.1028.

*Diphenyl (5-Methyl-2-(pyridin-2-yl)phenyl)phosphoramidate (**3ba**).* Colorless liquid (30.2 mg, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.86 (d, J = 11.7 Hz, 1H), 8.48 (d, J = 4.3 Hz, 1H), 7.79−7.75 (m, 2H), 7.69−7.67 (m, 1H), 7.63−7.61 (m, 1H), 7.31−7.20 (m, 9H), 7.16−7.12 (m, 2H), 7.05 (dd, J = 8.5, 2.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 157.7, 150.7 (d, J = 6.9 Hz), 146.9, 140.7, 139.4, 137.4, 129.7, 128.5, 125.1 (d, J = 0.8 Hz), 122.8, 121.4 (d, J = 10.9 Hz), 121.2 (d, J = 10.1 Hz), 120.5, 120.4, 120.1 (d, J = 2.3 Hz), 21.6. ^{31}P NMR ($CDCl_3$, 162 MHz): δ −7.43. IR (cm^{-1}) ν 3463, 3052, 2924, 1568, 1460, 1424, 1390, 1256, 1142, 1008. HRMS (ESI) m/z calcd for $C_{24}H_{21}N_2NaO_3P$ $(M + Na)^+$ 439.1182, found 439.1182.

*Diphenyl (4-Methyl-2-(pyridin-2-yl)phenyl)phosphoramidate (**3ca**).* Colorless liquid (29.9 mg, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.33 (d, J = 12.2 Hz, 1H), 8.47 (d, J = 4.2 Hz, 1H), 7.77−7.73 (m, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.63 (d, J = 8.3 Hz, 1H), 7.48 (s, 1H), 7.28−7.16 (m, 10H), 7.13−7.09 (m, 2H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 157.8, 150.6 (d, J = 6.9 Hz), 147.2, 137.4, 136.8, 131.1 (d, J = 10.3 Hz), 129.7, 129.2, 125.0 (d, J = 1.1 Hz), 124.1 (d, J = 9.9 Hz), 121.9, 121.6, 120.5, 120.4, 119.6 (d, J = 2.2 Hz), 20.8. ^{31}P NMR ($CDCl_3$, 162 MHz): δ −7.27. IR (cm^{-1}) ν 3460, 3046, 2915, 1548, 1451, 1420, 1250, 1150, 1006. HRMS (ESI) m/z calcd for $C_{24}H_{21}N_2NaO_3P$ $(M + Na)^+$ 439.1182, found 439.1181.

*Diphenyl (3-Methyl-2-(pyridin-2-yl)phenyl)phosphoramidate (**3da**).* Colorless liquid (31.2 mg, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.65 (d, J = 4.2 Hz, 1H), 7.73−7.68 (m, 1H), 7.54 (d, J = 8.1 Hz, 1H), 7.31−7.22 (m, 6H), 7.16−7.08 (m, 7H), 7.00 (d, J = 7.6 Hz, 1H), 6.81 (d, J = 11.3 Hz, 1H), 2.15 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.3, 150.7 (d, J = 6.6 Hz), 149.7, 136.9, 136.8 (d, J = 10.9 Hz), 129.7, 129.5 (d, J = 10.6 Hz), 129.0, 126.0, 125.2 (d, J = 1.1 Hz), 125.1, 122.4, 120.4, 120.3, 116.8 (d, J = 1.5 Hz), 20.9. ^{31}P NMR ($CDCl_3$, 162 MHz): δ −7.48. IR (cm^{-1}) ν 3452, 3038, 2920, 1536, 1463, 1412, 1258, 1154, 1011. HRMS (ESI) m/z calcd for $C_{24}H_{21}N_2NaO_3P$ $(M + Na)^+$ 439.1182, found 439.1180.

*Diphenyl (5-Methoxy-2-(pyridin-2-yl)phenyl)phosphoramidate (**3ea**).* Colorless liquid (31.5 mg, 73%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.61 (d, J = 12.2 Hz, 1H), 8.42 (d, J = 4.1 Hz, 1H), 7.75−7.70 (m, 1H), 7.66−7.64 (m, 2H), 7.30−7.24 (m, 8H), 7.15−7.11 (m, 3H), 6.63 (dd, J = 2.5, 8.8 Hz, 1H), 3.86 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 161.1, 157.6, 150.6 (d, J = 6.9 Hz), 146.8, 141.3, 137.3, 129.7, 125.1, 120.91, 120.90, 120.5, 120.4, 116.6 (d, J = 10.0 Hz), 108.2, 104.4 (d, J = 2.4 Hz), 55.4. ^{31}P NMR ($CDCl_3$, 162 MHz): δ −7.64. IR (cm^{-1}) ν 3458, 3036, 2912, 1521, 1472, 1420, 1251, 1148, 1016. HRMS (ESI) m/z calcd for $C_{24}H_{21}N_2NaO_4P$ $(M + Na)^+$ 455.1131, found 455.1130.

*Diphenyl (4-Methoxy-2-(pyridin-2-yl)phenyl)phosphoramidate (**3fa**).* Colorless liquid (30.6 mg, 71%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.94 (d, J = 12.0 Hz, 1H), 8.49 (d, J = 4.8 Hz, 1H), 7.78−7.75 (m, 1H), 7.68−7.63 (m, 2H), 7.27−7.19 (m, 10H), 7.13−7.09 (m, 2H), 6.98 (dd, J = 8.9, 2.9 Hz, 1H), 3.84 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 157.5, 154.6, 150.6 (d, J = 6.8 Hz), 147.4, 137.5, 132.5, 129.6, 125.8 (d, J = 9.7 Hz), 125.0 (d, J = 1.0 Hz), 122.1, 121.9, 120.9 (d, J = 1.9 Hz), 120.4 (d, J = 4.8 Hz), 115.5, 114.5, 55.7. ^{31}P NMR ($CDCl_3$, 162 MHz): δ −7.03. IR (cm^{-1}) ν 3446, 3027, 2916, 1526, 1468, 1416, 1246, 1130, 1009. HRMS (ESI) m/z calcd for $C_{24}H_{21}N_2NaO_4P$ $(M + Na)^+$ 455.1131, found 455.1133.

*Diphenyl (5-(tert-Butyl)-2-(pyridin-2-yl)phenyl)phosphoramidate(**3ga**).* Colorless liquid (31.6 mg, 69%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.70 (d, J = 12.3 Hz, 1H), 8.49 (d, J = 4.7 Hz, 1H), 7.77−7.69 (m, 3H), 7.64 (dd, J = 8.4, 2.0 Hz, 1H), 7.28−7.23 (m, 8H), 7.18−7.09 (m, 4H), 1.37 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 157.7, 153.8, 150.7 (d, J = 6.8 Hz), 147.1, 139.2, 137.3, 129.7, 128.2, 125.0 (d, J = 1.1 Hz), 121.4 (d, J = 4.8 Hz), 121.1 (d, J = 10.0 Hz), 120.5, 120.4, 118.9, 116.8 (d, J = 2.4 Hz), 34.9, 31.2. ^{31}P NMR ($CDCl_3$, 162 MHz): δ −7.37. IR (cm^{-1}) ν 3442, 3021, 2910, 1512, 1456, 1396, 1240, 1128, 1022. HRMS (ESI) m/z calcd for $C_{27}H_{27}N_2NaO_3P$ $(M + Na)^+$ 481.1652, found 481.1650.

*Diphenyl (5-Fluoro-2-(pyridin-2-yl)phenyl)phosphoramidate (**3ha**).* Colorless liquid (31.1 mg, 74%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.97 (d, J = 11.8 Hz, 1H), 8.47 (d, J = 4.9 Hz, 1H), 7.79−7.75 (m, 1H), 7.70−7.65 (m, 2H), 7.50−7.47 (m, 1H), 7.31−7.23 (m, 8H), 7.21−7.18 (m, 1H), 7.16−7.12 (m, 2H), 6.80−6.76 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 163.6 (d, J_{C-F} = 247.1 Hz), 157.0, 150.5 (d, J = 6.9 Hz), 147.0, 141.6 (d, J = 10.9 Hz), 137.6, 130.2 (d, J = 10.2 Hz), 129.7, 125.1 (d, J = 1.1 Hz), 121.6 (d, J = 13.3 Hz), 120.4, 120.3, 119.9 (q, J_{C-F} = 3.1 Hz, J = 10.1 Hz), 108.8 (d, J_{C-F} = 21.7 Hz), 119.9 (q, J = 2.5 Hz, J_{C-F} = 25.6 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ −8.24. IR (cm^{-1}) ν 3460, 3042, 1529, 1468, 1410, 1251, 1144, 1016. HRMS (ESI) m/z calcd for $C_{23}H_{18}FN_2NaO_3P$ $(M + Na)^+$ 443.0931, found 443.0932.

*Diphenyl (5-Chloro-2-(pyridin-2-yl)phenyl)phosphoramidate (**3ia**).* Colorless liquid (31.8 mg, 73%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.85 (d, J = 11.7 Hz, 1H), 8.48 (d, J = 4.3 Hz, 1H), 7.79−7.75 (m, 2H), 7.69−7.67 (m, 1H), 7.63−7.61 (m, 1H), 7.31−7.20 (m, 9H), 7.16−7.12 (m, 2H), 7.05 (dd, J = 8.5, 2.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.8, 150.4 (d, J = 6.9 Hz), 147.1, 140.8, 137.7, 136.0, 129.8, 129.6, 125.2 (d, J = 1.0 Hz), 122.1 (d, J = 10.0 Hz), 122.0 (d, J = 6.3 Hz), 121.7, 120.4, 120.3, 119.4 (d, J = 2.4 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ −7.64. IR (cm^{-1}) ν 3445, 3036, 1518, 1460, 1401, 1248, 1132, 1010. HRMS (ESI) m/z calcd for $C_{23}H_{18}ClN_2NaO_3P$ $(M + Na)^+$ 459.0636, found 459.0635.

*Diphenyl (3-Chloro-2-(pyridin-2-yl)phenyl)phosphoramidate (**3ja**).* Colorless liquid (30.9 mg, 71%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.63 (d, J = 4.8 Hz, 1H), 7.77−7.72 (m, 1H), 7.63 (d, J = 8.7 Hz, 2H), 7.41 (d, J = 7.9 Hz, 1H), 7.33−7.25 (m, 6H), 7.20−7.12 (m, 7H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 154.3, 150.2 (d, J = 6.6 Hz), 149.1, 138.8 (d, J = 1.7 Hz), 136.8, 133.3 (d, J = 1.4 Hz), 130.0, 129.8, 127.1, 125.3 (d, J = 1.2 Hz), 124.4, 122.9, 120.3, 120.2, 118.0 (d, J = 1.5 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ −8.17. IR (cm^{-1}) ν

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3452, 3025, 1532, 1452, 1409, 1239, 1123, 1002. HRMS (ESI) m/z calcd for $C_{23}H_{18}ClN_2NaO_3P$ $(M + Na)^+$ 459.0636, found 459.0633.

*Diphenyl (4-(Pyridin-2-yl)-[1,1′-biphenyl]-3-yl)phosphoramidate (**3ka**).* Colorless liquid (34.9 mg, 73%). ^1H NMR ($CDCl_3$, 400 MHz): δ 11.83 (d, J = 12.1 Hz, 1H), 8.49 (d, J = 4.8 Hz, 1H), 8.00 (d, J = 1.7 Hz, 1H), 7.78−7.75 (m, 3H), 7.68−7.66 (m, 2H), 7.47−7.44 (m, 2H), 7.39−7.37 (m, 1H), 7.34−7.32 (m, 1H), 7.27−7.24 (m, 8H), 7.21−7.17 (m, 1H), 7.14−7.10 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 157.4, 150.6 (d, J = 6.8 Hz), 147.1, 142.9, 140.0 (d, J = 8.5 Hz), 137.5, 129.7, 129.0, 128.9, 127.9, 127.1, 125.17, 125.16, 122.7 (d, J = 10.0 Hz), 121.7, 120.52, 120.50, 120.4, 118.0 (d, J = 2.3 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ −8.28. IR (cm^{-1}) ν 3459, 3020, 1541, 1444, 1413, 1242, 1116, 1012. HRMS (ESI) m/z calcd for $C_{29}H_{23}N_2NaO_3P$ $(M + Na)^+$ 501.1339, found 501.1341.

*Methyl 3-((Diphenoxyphosphoryl)amino)-4-(pyridin-2-yl)-benzoate (**3la**).* Colorless liquid (28.0 mg, 61%). ^1H NMR ($CDCl_3$, 400 MHz): δ 11.60 (d, J = 12.1 Hz, 1H), 8.55 (d, J = 4.9 Hz, 1H), 8.44 (d, J = 1.0 Hz, 1H), 7.82−7.72 (m, 4H), 7.30−7.24 (m, 9H), 7.15−7.11 (m, 2H), 3.96 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 166.5, 156.7, 150.5 (d, J = 6.9 Hz), 147.4, 139.5, 137.7, 131.5, 129.7, 128.7, 127.6 (d, J = 9.9 Hz), 125.2 (d, J = 1.0 Hz), 122.7, 122.5 (d, J = 8.6 Hz), 120.6 (d, J = 2.3 Hz), 120.5, 120.4, 52.4. ^{31}P NMR ($CDCl_3$, 162 MHz): δ −8.13. IR (cm^{-1}) ν 3472, 3036, 2918, 1560, 1458, 1418, 1260, 1208, 1120, 1022. HRMS (ESI) m/z calcd for $C_{25}H_{21}N_2NaO_5P$ $(M + Na)^+$ 483.1080, found 483.1080.

*Diphenyl (2-(Pyridin-2-yl)-3-(trifluoromethyl)phenyl)phosphoramidate (**3ma**).* Colorless liquid (31.0 mg, 66%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.67 (d, J = 4.9 Hz, 1H), 7.89 (d, J = 7.7 Hz, 1H), 7.55−7.47 (m, 2H), 7.33−7.25 (m, 5H), 7.19−7.08 (m, 7H), 6.31 (d, J = 10.4 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 153.9, 150.1 (d, J = 6.7 Hz), 149.6, 138.1 (d, J = 1.9 Hz), 137.1, 129.8, 129.5, 129.4, 125.8 (q, J_{C-F} = 2.6 Hz), 125.5, 125.4, 123.3, 122.7, 120.8 (q, J_{C-F} = 5.2 Hz), 120.2, 120.1. ^{31}P NMR ($CDCl_3$, 162 MHz): δ −8.30. IR (cm^{-1}) ν 3466, 3028, 1538, 1462, 1408, 1262, 1125, 1028. HRMS (ESI) m/z calcd for $C_{24}H_{18}F_3N_2NaO_3P$ $(M + Na)^+$ 493.0899, found 493.0897.

*Diphenyl (2-(3-Methylpyridin-2-yl)phenyl)phosphoramidate (**3na**).* Colorless liquid (28.2 mg, 68%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.45 (d, J = 4.2 Hz, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.41−7.37 (m, 1H), 7.34−7.23 (m, 6H), 7.18−7.08 (m, 8H), 2.11 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 156.1, 150.3 (d, J = 6.5 Hz), 146.6, 139.7, 136.8, 132.4, 129.7, 129.4, 128.4 (d, J = 10.4 Hz), 125.2 (d, J = 1.1 Hz), 122.6, 122.1, 120.4, 120.3, 119.6, 19.7. ^{31}P NMR ($CDCl_3$, 162 MHz): δ −7.52. IR (cm^{-1}) ν 3442, 3042, 2909, 1520, 1453, 1420, 1251, 1128, 1006. HRMS (ESI) m/z calcd for $C_{24}H_{21}N_2NaO_3P$ $(M + Na)^+$ 439.1182, found 439.1181.

*Diphenyl (2-(4-Methylpyridin-2-yl)phenyl)phosphoramidate (**3oa**).* Colorless liquid (27.0 mg, 65%). ^1H NMR ($CDCl_3$, 400 MHz): δ 11.69 (d, J = 12.2 Hz, 1H), 8.45 (d, J = 5.0 Hz, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 7.9 Hz, 1H), 7.51 (s, 1H), 7.39−7.35 (m, 1H), 7.28−7.22 (m, 8H), 7.13−7.05 (m, 3H), 7.01 (d, J = 5.0 Hz, 1H) 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 157.4, 150.6 (d, J = 6.8 Hz), 148.6, 146.8, 139.5, 130.2, 129.7, 128.6, 125.0 (d, J = 0.9 Hz), 124.2 (d, J = 10.1 Hz), 122.7, 121.8, 120.5, 120.3, 119.5 (d, J = 2.2 Hz), 21.4. ^{31}P NMR ($CDCl_3$, 162 MHz): δ −7.45. IR (cm^{-1}) ν 3438, 3032, 2912, 1552, 1460, 1411, 1242, 1136, 1018. HRMS (ESI) m/z calcd for $C_{24}H_{21}N_2NaO_3P$ $(M + Na)^+$ 439.1182, found 439.1180.

*Diphenyl (2-(5-Fluoropyridin-2-yl)phenyl)phosphoramidate (**3pa**).* Colorless liquid (30.2 mg, 72%). ^1H NMR ($CDCl_3$, 400 MHz): δ 10.81 (d, J = 11.9 Hz, 1H), 8.34 (d, J = 2.9 Hz, 1H), 7.74 (d, J = 7.5 Hz, 1H), 7.59 (dd, J = 8.9, 4.2 Hz, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.51−7.46 (m, 1H), 7.42−7.37 (m, 1H), 7.29−7.21 (m, 8H), 7.15−7.06 (m, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 158.0 (d, J_{C-F} = 255.2 Hz), 154.0, 150.3 (d, J = 6.9 Hz), 138.8, 135.3 (d, J_{C-F} = 24.4 Hz), 130.3, 129.7, 128.8, 125.2 (d, J = 1.0 Hz), 124.7 (d, J = 18.4 Hz), 123.7 (d, J = 10.0 Hz), 123.4 (d, J = 4.4 Hz), 122.1, 120.4 (d, J = 4.8 Hz), 119.7 (d, J = 2.2 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ −7.60. IR (cm^{-1}) ν 3467, 3042, 1556, 1470, 1420, 1402, 1262, 1144, 1025. HRMS (ESI) m/z calcd for $C_{23}H_{18}FN_2NaO_3P$ $(M + Na)^+$ 443.0931, found 443.0930.

*Diethyl (2-(Pyridin-2-yl)phenyl)phosphoramidate (**3ab**).* Colorless liquid (15.9 mg, 52%). ^1H NMR ($CDCl_3$, 400 MHz): δ 10.82 (d, J = 11.1 Hz, 1H), 8.63 (d, J = 4.7 Hz, 1H), 7.83−7.74 (m, 2H), 7.67 (d, J = 7.9 Hz, 1H), 7.43 (d, J = 8.2 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.24 (t, J = 6.0 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 4.22−4.05 (m, 4H), 1.31 (t, J = 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 158.1, 147.3, 140.0, 137.4, 130.2, 128.8, 123.6 (d, J = 9.7 Hz), 122.0, 121.6, 121.0, 118.7 (d, J = 2.4 Hz), 62.7 (d, J = 5.0 Hz), 16.1 (d, J = 7.0 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ −1.98. IR (cm^{-1}) ν 3435, 3026, 1533, 1452, 1399, 1242, 1133, 1010. HRMS (ESI) m/z calcd for $C_{15}H_{19}N_2NaO_3P$ $(M + Na)^+$ 329.1026, found 329.1027.

*Diphenyl (2-(1H-Pyrazol-1-yl)phenyl)phosphoramidate (**5aa**).* Colorless liquid (26.9 mg, 69%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.97 (d, J = 10.8 Hz, 1H), 7.76 (dd, J = 8.2, 1.0 Hz, 1H), 7.70−7.68 (m, 2H), 7.34−7.25 (m, 6H), 7.20−7.13 (m, 6H), 7.10−7.06 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 150.3 (d, J = 6.8 Hz), 140.9, 132.7 (d, J = 2.3 Hz), 129.7, 129.5, 128.7 (d, J = 10.6 Hz), 128.1, 125.3 (d, J = 1.1 Hz), 122.6, 122.4, 120.4, 120.3, 107.1. ^{31}P NMR ($CDCl_3$, 162 MHz): δ −8.03. IR (cm^{-1}) ν 3444, 3036, 1541, 1440, 1390, 1236, 1120, 1009. HRMS (ESI) m/z calcd for $C_{21}H_{18}N_3NaO_3P$ $(M + Na)^+$ 414.0978, found 414.0977.

*Diphenyl (5-Methyl-2-(1H-pyrazol-1-yl)phenyl)phosphoramidate (**5ba**).* Colorless liquid (26.3 mg, 65%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.84 (d, J = 10.8 Hz, 1H), 7.67−7.63 (m, 2H), 7.55 (s, 1H), 7.31−7.25 (m, 4H), 7.20−7.13 (m, 7H), 6.87 (dd, J = 8.1, 1.1 Hz, 1H), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 150.4 (d, J = 6.8 Hz), 140.7, 138.3, 132.4 (d, J = 2.3 Hz), 129.7, 129.5, 125.3 (d, J = 1.1 Hz), 123.3, 122.3, 120.7 (d, J = 1.8 Hz), 120.4, 120.3, 106.8. ^{31}P NMR ($CDCl_3$, 162 MHz): δ −7.94. IR (cm^{-1}) ν 3438, 3030, 2920, 1538, 1444, 1401, 1242, 1126, 1012. HRMS (ESI) m/z calcd for $C_{22}H_{20}N_3NaO_3P$ $(M + Na)^+$ 428.1134, found 428.1134.

*Diphenyl (4-Methoxy-2-(1H-pyrazol-1-yl)phenyl)phosphoramidate (**5ca**).* Colorless liquid (26.5 mg, 63%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.51 (d, J = 10.8 Hz, 1H), 7.69−7.62 (m, 3H), 7.29−7.25 (m, 4H), 7.18−7.12 (m, 6H), 6.89 (dd, J = 8.9, 2.8 Hz, 1H), 6.82 (s, 1H), 6.41 (t, J = 2.1 Hz, 1H), 3.81 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 155.2, 150.4 (d, J = 6.7 Hz), 141.0, 129.7, 129.5, 125.8 (d, J = 2.0 Hz), 125.2 (d, J = 0.9 Hz), 121.8 (d, J = 1.6 Hz), 120.3, 120.2, 113.0, 108.9, 107.1, 55.8. ^{31}P NMR ($CDCl_3$, 162 MHz): δ −7.42. IR (cm^{-1}) ν 3446, 3026, 2916, 1532, 1452, 1408, 1236, 1133, 1032. HRMS (ESI) m/z calcd for $C_{22}H_{20}N_3NaO_4P$ $(M + Na)^+$ 444.1084, found 444.1081.

*Diphenyl (5-Chloro-2-(1H-pyrazol-1-yl)phenyl)phosphoramidate (**5da**).* Colorless liquid (26.3 mg, 62%). ^1H NMR ($CDCl_3$, 400 MHz): δ 9.15 (d, J = 10.5 Hz, 1H), 7.77 (d, J = 2.0 Hz, 1H), 7.71−7.66 (m, 2H), 7.32−7.28 (m, 4H), 7.21−7.14 (m, 7H), 6.87 (dd, J = 8.5, 2.2 Hz, 1H), 6.44 (t, J = 2.2 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 150.2 (d, J = 6.8 Hz), 141.3, 133.9 (d, J = 2.0 Hz), 133.5, 129.8, 129.5, 127.1 (d, J = 10.5 Hz), 125.4 (d, J = 1.1 Hz), 123.1, 122.5, 120.3, 120.2, 107.3. ^{31}P NMR ($CDCl_3$, 162 MHz): δ −8.81. IR (cm^{-1}) ν 3442, 3028, 1544, 1460, 1416, 1232, 1112. HRMS (ESI) m/z calcd for $C_{21}H_{17}ClN_3NaO_3P$ $(M + Na)^+$ 448.0588, found 448.0589.

*Diphenyl (2-(3-Methyl-1H-pyrazol-1-yl)phenyl)phosphoramidate (**5ea**).* Colorless liquid (24.3 mg, 60%). ^1H NMR ($CDCl_3$, 400 MHz): δ 9.08 (d, J = 11.2 Hz, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.57 (d, J = 2.4 Hz, 1H), 7.31−7.19 (m, 10H), 7.17−7.12 (m, 2H), 7.07−7.03 (m, 1H), 6.19 (d, J = 2.4 Hz, 1H), 2.31 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 150.6, 150.4 (d, J = 6.8 Hz), 132.5 (d, J = 2.2 Hz), 130.1, 129.7, 127.7, 125.2 (d, J = 1.1 Hz), 122.5, 122.1, 120.4, 120.3, 120.2 (d, J = 1.8 Hz), 106.9, 13.7. ^{31}P NMR ($CDCl_3$, 162 MHz): δ −8.00. IR (cm^{-1}) ν 3432, 3020, 2924, 1523, 1451, 1410, 1250, 1120, 1001. HRMS (ESI) m/z calcd for $C_{22}H_{20}N_3NaO_3P$ $(M + Na)^+$ 428.1134, found 428.1132.

*Diphenyl Benzo[h]quinolin-10-ylphosphoramidate (**5fa**).* Colorless liquid (23.4 mg, 55%). ^1H NMR ($CDCl_3$, 400 MHz): δ 14.11 (d, J = 12.0 Hz, 1H), 8.76 (dd, J = 4.5, 1.8 Hz, 1H), 8.18 (dd, J = 8.0, 1.8 Hz, 1H), 8.18 (dd, J = 8.0, 1.0 Hz, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.68 (t, J = 7.9 Hz, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.48 (dd, J = 8.0, 4.5 Hz, 1H), 7.34−7.28 (m, 8H), 7.13−7.09 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 150.7 (d, J = 6.8 Hz),

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147.9, 145.6, 140.7, 136.3, 135.4, 129.7, 129.2, 128.8, 127.1, 125.3, 125.1 (d, J = 1.0 Hz), 121.3, 120.8, 120.5 (d, J = 4.8 Hz), 117.1 (d, J = 10.6 Hz), 116.0 (d, J = 2.8 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ −7.41. IR (cm^{-1}) ν 3460, 3030, 1565, 1508, 1463, 1421, 1260, 1142, 1028. HRMS (ESI) m/z calcd for $C_{25}H_{19}N_2NaO_3P$ $(M + Na)^+$ 449.1026, found 449.1028.

Procedure of H/D Exchange Experiment on 1a. The mixture of 2-phenylpyridine **1a** (0.1 mmol, 15.5 mg), $[IrCp^*Cl_2]_2$ (4 mol %, 3.2 mg), $AgSbF_6$ (16 mol %, 6.2 mg), AgOAc (50 mol %, 8.3 mg), and DCM/D_2O (0.9 mL/0.1 mL) was added into a sealed tube. After stirring at 60 °C for 12 h under Ar, the mixture was concentrated and then purified by preparative TLC on GF254 (petroleum/ethyl acetate) to access **1a**-[**Dn**]. The D-incorporation of 26% in **1a**-[**Dn**] was estimated by ^{1}H NMR spectroscopy. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.70 (d, J = 4.6 Hz, 1H), 8.00−7.97 (m, 1.74H), 7.77−7.71 (m, 2H), 7.48−7.39 (m, 3H), 7.24−7.21 (m, 1H). MS (ESI) m/z: 156.42, 157.42 $(M + H)^+$, 178.50, 179.58 $(M + Na)^+$.

Procedure of H/D Exchange Experiment on 1a with 2a. The mixture of 2-phenylpyridine **1a** (0.1 mmol, 15.5 mg), diphenyl phosphorazidate **2a** (0.2 mmol, 55 mg), $[IrCp^*Cl_2]_2$ (4 mol %, 3.2 mg), $AgSbF_6$ (16 mol %, 6.2 mg), AgOAc (50 mol %, 8.3 mg), and DCM/D_2O (0.9 mL/0.1 mL) was added into a sealed tube. After stirring at 60 °C for 12 h under Ar, the mixture was concentrated and then purified by preparative TLC on GF254 (petroleum/ethyl acetate) to access **1a**-[**Dn**] and **3aa**-[**Dn**]. The D-incorporation of 10% in **1a**-[**Dn**] and 40% in **3aa**-[**Dn**] was estimated by ^{1}H NMR spectroscopy. **1a**-[**Dn**]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.70 (d, J = 4.7 Hz, 1H), 8.00−7.97 (m, 1.9H), 7.77−7.71 (m, 2H), 7.49−7.39 (m, 3H), 7.24−7.21 (m, 1H). MS (ESI) m/z: 156.58, 157.58 $(M + H)^+$. **3aa**-[**Dn**]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.60 (d, J = 11.2 Hz, 1H), 8.49 (d, J = 4.8 Hz, 1H), 7.80−7.69 (m, 3.6H), 7.41−7.37 (m, 1.0 H), 7.29−7.19 (m, 9H), 7.14−7.07 (m, 3H). MS (ESI) m/z: 403.75, 404.67 $(M + H)^+$, 425.58, 426.33 $(M + Na)^+$.

Procedure of Intermolecular Competition Experiment with Isotopically Labeled 1a′. The mixture of 2-phenylpyridine **1a** (0.05 mmol), **1a**′ (0.05 mmol), diphenyl phosphorazidate **2a** (0.2 mmol), $[IrCp^*Cl_2]_2$ (4 mol %, 3.2 mg), $AgSbF_6$ (16 mol %, 6.2 mg), AgOAc (50 mol %, 8.3 mg), and DCM (1.0 mL) was added into a sealed tube. After stirring at 60 °C for 12 h under Ar, the mixture was concentrated and then purified by preparative TLC on GF254 (petroleum/ethyl acetate) to access **3aa** and **3aa**′. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.61 (d, J = 12.2 Hz, 1H), 8.48 (d, J = 4.8 Hz, 1H), 7.78−7.68 (m, 3.51H), 7.41−7.37 (m, 0.51H), 7.29−7.22 (m, 8H), 7.20−7.17 (m, 1H), 7.14−7.08 (m, 2.52H). MS (ESI) m/z: 403.83, 406.67, 407.67 $(M + H)^+$, 425.75, 428.42, 429.33 $(M + Na)^+$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H, ^{13}C, and ^{31}P NMR spectra of all the products, ESI spectra of compounds **1a**-[**Dn**], **3aa**-[**Dn**], and **3aa**′. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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