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Rhodium(III)-Catalyzed C−H Activation and Annulation with 1-Alkynylphosphine Sulfides: A Mild and Regioselective Access for the Synthesis of Bulky Phosphine Ligands

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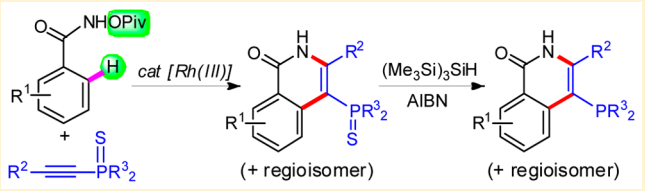
Supporting Information

ABSTRACT: We reported herein rhodium(III)-catalyzed C−H activation and annulation reactions for the synthesis of bulky phosphine ligands by using 1-alkynylphosphine sulfides as key starting materials. In the presence of $[Cp^*RhCl_2]_2$ (5 mol %) and CsOAc (2.0 equiv), various *N*-(pivaloyloxy)benzamides (3.0 equiv) could react smoothly with 1-alkynylphosphine sulfides at 40 °C in MeOH/CF_3CH_2OH cosolvent without external oxidant. Using $[Cp^{Ph}RhCl_2]_2$ as catalyst, the reaction can be performed under less loading of benzamides (2.0 equiv) and milder reaction conditions (25 °C) with higher regioselectivity. In a sequential cyclization/desulfidation process, this new method provides a variety of bulky heteroarylphosphines with an isoquinolin-1(2*H*)-one motif.



INTRODUCTION

Organophosphines have been widely used in modern organic synthesis, especially as ligands for a variety of transition-metal-catalyzed reactions including cross-coupling reactions[1] and asymmetric transformations.[2] Meanwhile, phosphine-containing motifs have important roles in the fields of agrochemical and medicinal chemistry as well as material science.[3] Thus, creation of new organophosphine species and development of novel methods to construct organophosphines have evoked considerable attention from both academic and industrial communities. However, the available literature methods are mostly limited to the addition of phosphine halides to an organometallic reagent[4] and the transition-metal-catalyzed C−P cross-coupling of aryl halides with arylphosphines.[5]

Recently, 1-alkynylphosphines and their derivatives have been emerging as useful building blocks for the construction of new phosphines.[6] In this context, two main catalytic routes have been reported: (i) additions of nucleophiles (such as hydrophosphines, thiols, and amines) to the C−C triple bond of 1-alkynylphosphine derivatives result in the formation of functionalized alkenylphosphines (Scheme 1, a),[7] and (ii) [2 + 2 + 2] cycloadditions of 1-alkynylphosphine derivatives with other unsaturated bonds lead to the construction of cyclic compounds bearing a phosphorus substituent (Scheme 1, b).[8] In addition, the group of Yorimitsu and Oshima described an elegant example of Pd(II)-catalyzed annulation of 1-alkynylphosphine sulfides with 2-iodoanilines, followed by desulfidation for the synthesis of indolylphosphines (Scheme 1, c).[9] In this method, a heteroaromatic ring was formed with concomitant incorporation of a phosphorus moiety. Despite these impressive advances, the development of new and efficient methodologies for the synthesis of new phosphines under mild and environmentally friendly conditions remains highly desirable.

Arguably, Rh(III)-catalyzed oxidative coupling of C−H bonds with alkynes has been identified as a straightforward and efficient way to construct (hetero)cyclic compounds in recent years.[10] Among these reports, the redox-neutral C−H activation/annulation reactions have received much attention in which an oxidative functional group acts as both a directing group and an internal oxidant.[11] In this regard, the syntheses of a variety of heterocycles including isoquinolones,[12] isoquinolines,[13] indoles,[14] furans,[15] pyridines,[16] and isocoumarins[17] were realized under mild reaction conditions with a broader functional group tolerance through the utilization of internal oxidants. In particular, *N*-(pivaloyloxy)benzamides and their derivatives are one of the most popular substrates in Rh(III)-catalyzed redox-neutral C−H activation reactions, and they can react with a plethora of coupling partners.[12,18] As a continuation of our interest in metal-catalyzed direct C−H annulation with alkynes,[19] we herein disclose our recent development of oxidative coupling of *N*-(pivaloyloxy)benzamides with 1-alkynylphosphine sulfides via Rh(III) catalysis (Scheme 1, d). The reactions afford a new type of bulky phosphine containing an isoquinolin-1(2*H*)-one motif after desulfidation. As far as we know, this is the first time that 1-alkynylphosphine derivatives emerge in the redox-neutral C−H

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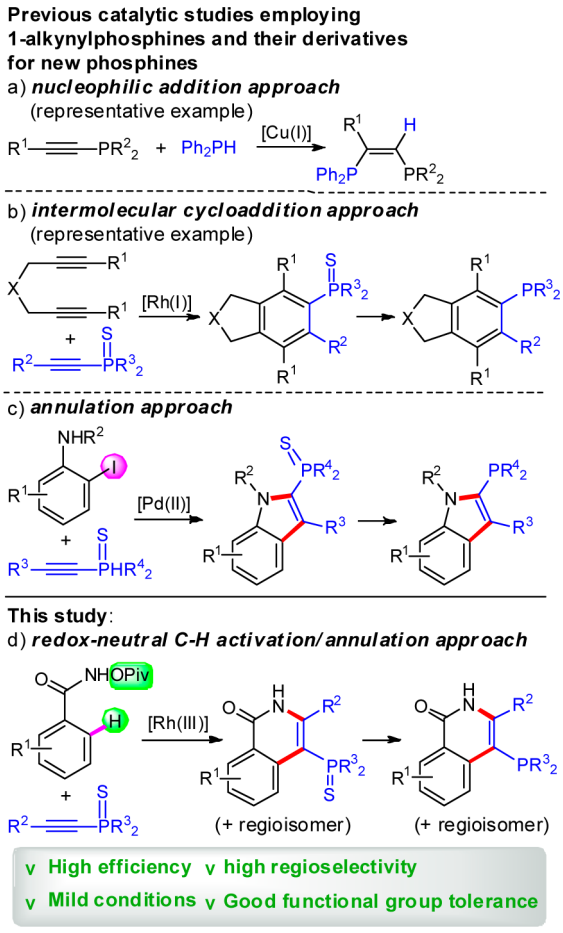
Scheme 1



activation/annulation strategy, which provides a novel method for construction of new bulky phosphines that are difficult to synthesize by other methods.

RESULTS AND DISCUSSION

We commenced our investigations with the coupling of different *N*-protected benzamides **1** and diphenyl(phenylethynyl)-phosphine sulfide (**2a**) (Table 1). We were pleased to find that the reaction starting from *N*-(pivaloyloxy)benzamide (**1a**) indeed did proceed, leading to the annulation products. In the presence of $[Cp^*RhCl_2]_2$ catalyst (5 mol %) and CsOAc additive (2.0 equiv), the conversion was smooth to furnish a mixture of regioisomers in a high combined yield with a cosolvent system of MeOH/CF_3CH_2OH (1:1) at 40 °C. However, the regioselectivity was relative low (1:3.1), favoring the cyclization product **4aa** in which the alkyne carbon linked to the aryl group being connected with the nitrogen atom (entry 1). The structures of **3aa** and **4aa** were established by ^1H and ^{13}C NMR analysis, mass spectrometry, and finally confirmed through X-ray analysis (see Figures S1 and S2 in the Supporting Information for details). It was found that the choice of the leaving group on the hydroxamic acid type compound was crucial, as indicated by substrates bearing other leaving groups such as OMe (**1b**), OAc (**1c**), and OC(O)Ph (**1d**) were not suitable for this transformation (entries 2−4). Further experiments showed that reducing the loading of catalyst or additive, employing AgOAc as additive, or lowering the reaction temperature led to inferior results (entries 5−8). To improve the regioselectivity, complexes $[Cp^tRhCl_2]_2$, $[Cp^ERhCl_2]_2$, and $[Cp^{Ph}RhCl_2]_2$, which differ in the steric and electronic effects of ligands, were then synthesized and examined as catalyst for this reaction. The former two complexes, which were demonstrated as high reactive catalysts for Rh(III)-catalyzed oxidative annulation reactions before,[20] turned out to be inactive in the present transformation (entries 9 and 10). Interestingly, almost quantitative conversion was achieved in the presence of $[Cp^{Ph}RhCl_2]_2$ as catalyst (entry 11). However, a considerable number of an indole derivative **5aa**, which was also observed in a small amount under $[Cp^*RhCl_2]_2$ catalysis (entry 1), was generated in this catalytic system. The formation of byproduct was a result of the annulation of methyl phenylcarbamate (generated *in situ* from Lossen rearrangement of **1a** in MeOH)[21] with **2a**. Its structure was confirmed through X-ray analysis of an analogue subsequently prepared (see below). Whereas the combined yield of **3aa** and **4aa** was decreased, the ratio of **3aa**:**4aa** was raised to 1:15 when the reaction was performed at room temperature (entry 12). By increasing the ratio of CF_3CH_2OH in the cosolvent, the yield of the desired products was improved but sacrificing the regioselectivity a little to 1:7.1 (entry 13). Moreover, reducing the loading of **1a** did not affect the result (entry 14). Finally, $[Ru(p\text{-Cymene})Cl_2]_2$ displayed no catalytic activity under the present reaction conditions (entry 15).

With the promising optimal conditions, we first explored the scope of *N*-(pivaloyloxy)benzamides with diverse arene substituents under both $[Cp^*RhCl_2]_2$ and $[Cp^{Ph}RhCl_2]_2$ catalysis (Scheme 2). The electronic nature of substituents strongly affected the reaction efficiency and regioselectivity. *Para*-substituted electron-deficient groups resulted in the desired products **4ha**−**4oa** in good to excellent yields (70−99%) as well as excellent regioselectivity (1:29−1:100, **3**:**4**) in all cases for both catalytic systems. In comparison, subtrates bearing electron-rich groups at the *para* position (Me, **1e**; OMe, **1f**; and Ph, **1g**) led to lower yields (21−67%) due to the formation of significant quantities of byproducts **5**, as exemplified by the *p*-OMe substituted substrate, affording the indole byproduct **5fa** in 44% isolated yield via $[Cp^{Ph}RhCl_2]_2$ catalysis. The molecular structure of **5fa** was determined by single-crystal X-ray diffraction analysis, which is depicted in Figure S3 (see the Supporting Information for details). Meanwhile, a relatively lower regioselectivity (1:5.2−1:9.1, **3**:**4**) was observed for electron-rich substrates. It is worthy to note that, from the synthetic point of view, the resulting two regioisomers could be easily separated by silica gel column chromatography. For the *meta*-methyl group substituted substrate **1p**, the annulation took place at the less hindered site. The two catalysts showed similar reactivity, but $[Cp^{Ph}RhCl_2]_2$ provided a much higher level of regioselectivity for **4pa** than $[Cp^*RhCl_2]_2$, improving to 1:21 from 1:4.8. In addition, the reaction proceeded smoothly with disubstituted *N*-(pivaloyloxy)-benzamides. For example, 3,4-dichloro- (**1q**) and 3-methyl-4-nitro- (**1r**) substituted substrates provided the corresponding regioisomers **4qa** and **4ra** exclusively in excellent yields. *β*-Naphthyl derivative (**1s**) was also suitable for the present catalytic system, giving product **4sa** as the only regioisomer, albeit in moderate yield. Disappointedly, the cyclization reaction failed to take place when substrates with *ortho*-methyl and chloride substituents were used, presumably due to the steric hindrance. Various functional groups commonly encountered in organic synthesis were well tolerated, such as alkoxy (**1f**), halides (**1h-j**), nitro (**1k**), trifluoromethyl (**1l**), ester (**1m**), ketone (**1n**), and cyano (**1o**).

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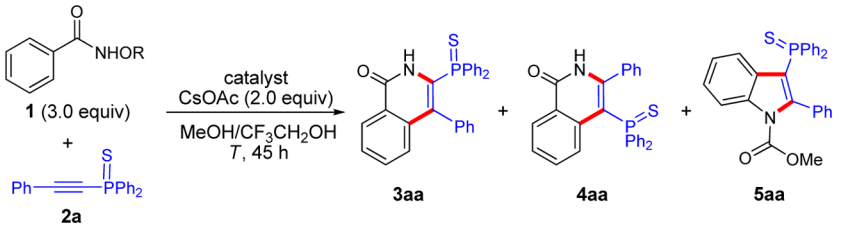
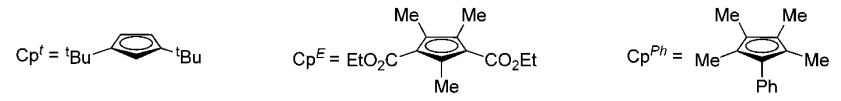
Table 1. Optimization of Reaction Conditions[a]



entry	R	catalyst (mol %)	MeOH/CF_3CH_2OH (v/v)	T / °C	Yield (%)[b] 3aa + 4aa (3aa : 4aa)	5aa
1	Piv (**1a**)	$[Cp^*RhCl_2]_2$ (5)	1:1	40	93 (1 : 3.1)	7
2	Me (**1b**)	$[Cp^*RhCl_2]_2$ (5)	1:1	40	8 (0 : 100)	0
3	Ac (**1c**)	$[Cp^*RhCl_2]_2$ (5)	1:1	40	18 (1 : 2.0)	0
4	C(O)Ph (**1d**)	$[Cp^*RhCl_2]_2$ (5)	1:1	40	42 (1 : 3.3)	2
5	Piv (**1a**)	$[Cp^*RhCl_2]_2$ (4)	1:1	40	84 (1 : 2.8)	10
6[c]	Piv (**1a**)	$[Cp^*RhCl_2]_2$ (5)	1:1	40	55 (1 : 4.7)	4
7[d]	Piv (**1a**)	$[Cp^*RhCl_2]_2$ (5)	1:1	40	81 (1 : 2.9)	18
8	Piv (**1a**)	$[Cp^*RhCl_2]_2$ (5)	1:1	25	55 (1 : 4.4)	5
9	Piv (**1a**)	$[Cp^tRhCl_2]_2$ (5)	1:1	40	4 (2.2 : 1)	5
10	Piv (**1a**)	$[Cp^ERhCl_2]_2$ (5)	1:1	40	42 (1 : 6.7)	10
11	Piv (**1a**)	$[Cp^{Ph}RhCl_2]_2$ (5)	1:1	40	63 (1 : 6.8)	35
12	Piv (**1a**)	$[Cp^{Ph}RhCl_2]_2$ (5)	1:1	25	67 (1 : 15)	33
13	Piv (**1a**)	$[Cp^{Ph}RhCl_2]_2$ (5)	1:3	25	80 (1 : 7.1)	18
14[e]	Piv (**1a**)	$[Cp^{Ph}RhCl_2]_2$ (5)	1:3	25	81 (1 : 7.1)	18
15	Piv (**1a**)	$[(p\text{-Cymene})RuCl_2]_2$ (5)	1:1	40	0	0



[a]Reactions in 0.1 mmol scale (0.1 M). [b]Yield and ratio (**3aa**:**4aa**) of crude reaction mixture determined by ^{31}P NMR (internal standard: trimethyl phosphate). [c]CsOAc (1.0 equiv). [d]AgOAc (0.5 equiv). [e]**1a**, 2.0 equiv.

Then, we also investigated the reaction scope with several different (1-alkynyl)diphenylphosphine sulfides (Table 2). Benzamide **1a** was readily annulated with 1-alkynylphosphine sulfides **2b**−**2d** irrespective of the electronic nature of arene substituents. As expected, the regioselectivity was improved dramatically when $[Cp^{Ph}RhCl_2]_2$ was applied as catalyst (entries 1−3). In the cases of 4-chloro and 4-nitro substituted substrates **1i** and **1k**, high efficiency and excellent selectivity was achieved in the reaction with **2b**−**2d** to deliver the major regioisomers **4ib**−**d** and **4kb**−**d**, respectively (entries 6−8 and 11−13). Under the current reaction conditions, terminal alkyne derivatives such as ethynyldiphenylphosphine sulfides failed to afford the corresponding cycloadducts.

The reactions of **1a** and **1i** with alkyl substituted 1-alkynylphosphine sulfides **2e** and **2f** were facile under $[Cp^*RhCl_2]_2$ catalysis, leading to the corresponding products in excellent yields (Table 2, entries 4, 5, 9, and 10), but **1k** exhibited relative lower reactivity (entries 14 and 15). $[Cp^{Ph}RhCl_2]_2$ was less efficient for these transformations (entries 4, 5, and 10). It was interesting to observe that the regioselectivity was changed strongly depending on the arene substituents of the benzamides. For example, while the reaction occurred highly regioselectively (1:8.4−1:12) with substrates bearing a 4-nitro group (entries 14 and 15), the selectivity was decreased to 1:2.1−1:2.4 when a 4-chloro substituted substrate was examined (entries 9 and 10), and especially, the selectivity reversed (1.7:1−1.8:1), affording **3ae** and **3af**, in which the phosphine sulfide group is close to the nitrogen atom, as major regioisomers (entries 4 and 5) in the case of **1a** as substrate. It is also observed that the selectivity of products derived from alkyl 1-alkynylphosphine sulfides decreased dramatically as compared to the corresponding aryl substituted analogues, which might be ascribed to the combined effect of the electronic and steric nature of the substituents.[12e,12j,22]

Next, the bulkier (1-alkynyl)dicyclohexylphosphine sulfide **2h** was tested for the annulation reactions. It was less reactive than the corresponding diphenyl analogue **2a** under the same conditions. The desired products were obtained in moderate yield with the unreacted **2h** remaining. Moreover, the regioisomer **3ah** was obtained as the major product in a ratio of 2.5:1 (see Table S1 in the Supporting Information for details). The conversion was not improved much after many trials. However, it was interesting to observe that changing the additive CsOAc (2.0 equiv) to AgOAc (0.5 equiv) generated **3ah** exclusively. Scheme 3 illustrates the results of the reactions of several substituted benzamides **1** with **2h**. Based on the conversion of **2h**, the yields of all the substrates were acceptable. Benzamides containing electron-rich groups (**1e**, **1p**, and **1w**) were more reactive than those bearing electron-deficient substituents (**1h** and **1r**). Again, the annulation occurred at the less hindered site for the *meta*-methyl group substituted substrate **1p**.

Several experiments were conducted to obtain further insights into the mechanistic information on the catalytic process. When **1k** was treated in deuterated MeOH in the absence of alkyne, no deuteration was observed (eq 1). If the same reaction was performed in the presence of alkyne **2a**, no deuterium incorporation was detected in both unreacted **1k** and the product **4ka** (eq 2).[12g] These results suggest that cleavage of the *ortho* C−H bond is an irreversible process. Furthermore, consistent with previous

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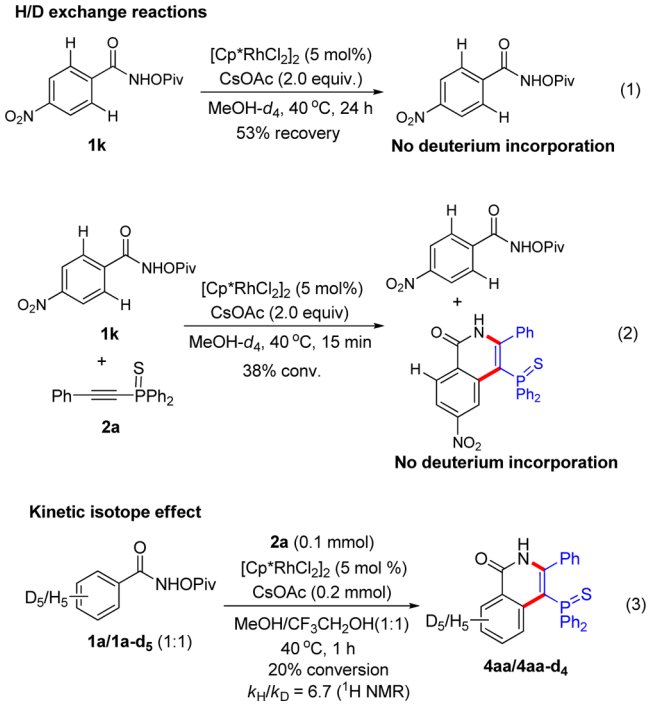
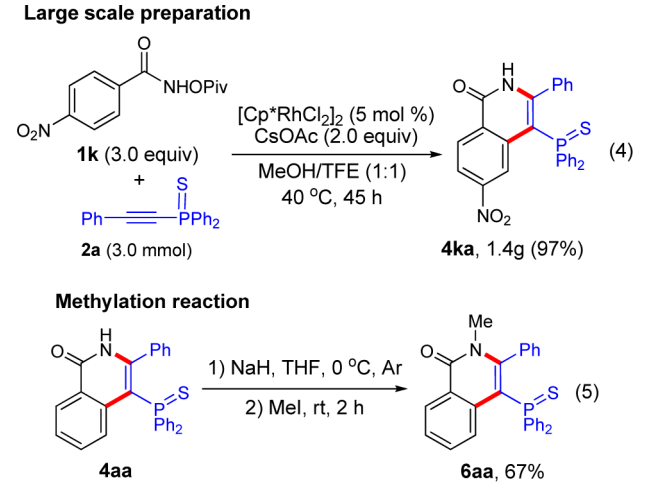
observations,[12e,f] a significant primary kinetic isotope effect (KIE) of k_H/k_D = 6.7 was observed for an intermolecular competitive coupling of **2a** with a 1:1 mixture of **1a** and **1a-d_5** at a low conversion (eq 3), suggesting that the C−H bond activation was involved in the rate-determining step.

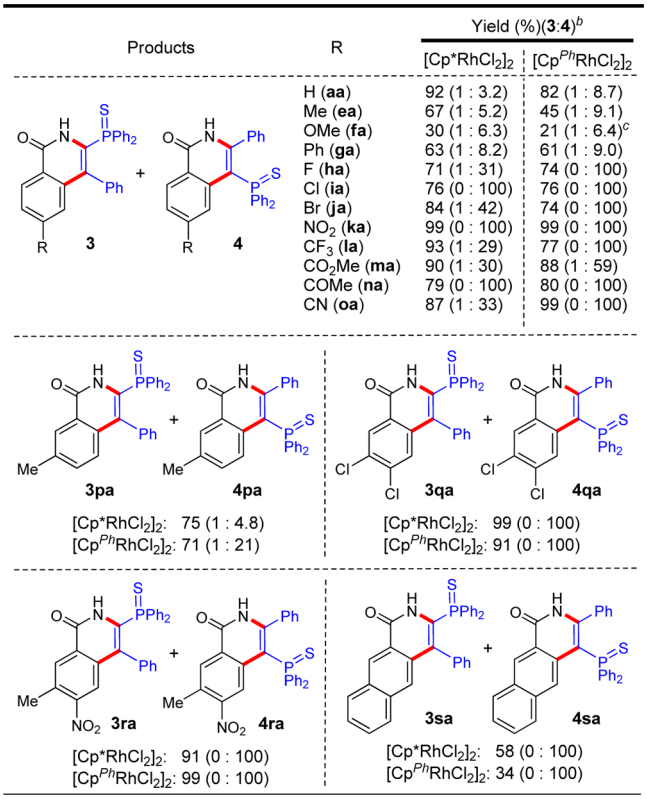


To our delight, the reactions can be easily performed on a large scale: **4ka** was isolated in 97% yield on a 3.0 mmol scale (eq 4). In addition, methylation reaction of **4aa** with MeI was performed to give the deprotonated product **6aa** in good yield (eq 5).



Importantly, the resulting annulated phosphine sulfide products underwent radical desulfidation reactions[8d,9,23] cleanly and smoothly (Scheme 4). In the presence of 10 mol % of AIBN with 1.5 equiv of tris(trimethylsilyl)silane (TTMSS) at 80 °C in toluene for 12 h, the corresponding trivalent phosphines **4aa-S**, **4ia-S**, **4ab-S**, and **6aa-S** were obtained in good to high yields. Bulkier phosphine sulfide **3ah** was less reactive; a higher loading of TTMSS (3.0 equiv) was necessary for complete desulfidation. Note that, while all the desulfidation products were relatively stable and thus could be isolated by quick silica gel column chromatography, they would be oxidized by air very slowly without further protection in the solid state.

Scheme 2. Substrate Scope of *N*-(Pivaloyloxy)benzamides[a]



[a]Reaction conditions: (1) $[Cp^*RhCl_2]_2$ as catalyst: **1** (0.6 mmol, 3.0 equiv), **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol, 5 mol %), CsOAc (0.4 mmol, 2.0 equiv), MeOH/CF_3CH_2OH (1.0 mL/1.0 mL), 40 °C, 45 h; (2) $[Cp^{Ph}RhCl_2]_2$ as catalyst: **1** (0.4 mmol, 2.0 equiv), **2a** (0.2 mmol), $[Cp^{Ph}RhCl_2]_2$ (0.01 mmol, 5 mol %), CsOAc (0.4 mmol, 2.0 equiv), MeOH/CF_3CH_2OH (0.5 mL/1.5 mL), 25 °C, 45 h. [b]Combined yields of isolated products, ratio of crude reaction mixture determined by ^{31}P NMR (internal standard: trimethyl phosphate). [c]As exemplified, the byproduct **5fa** was isolated in 44% yield. For the NMR yields of byproducts **5** in the other reactions listed in Scheme 2, see Table S3 in the Supporting Information for details.

CONCLUSION

In summary, we have established a Rh(III)-catalyzed redox-neutral C−H activation/annulation of *N*-(pivaloyloxy)-benzamides with 1-alkynylphosphine sulfides, followed by desulfidation, to afford a new type of bulky phosphines with an isoquinolin-1(2*H*)-one motif. This conceptually new method is featured by high efficiency and regioselectivity, broader functional group tolerance, and mild reaction conditions, which offers a novel access for construction of new bulky phosphines that are difficult to synthesize by other methods. A new rhodium complex $[Cp^{Ph}RhCl_2]_2$ was developed, which could enable this transformation with higher regioselectivity even at room temperature. It is believed that the synthetic utility of 1-alkynylphosphine derivatives will have more applications in C−H activation to create novel functionalized phosphines, which can be applicable to various fields of chemical science. Further studies on the transition-metal-catalyzed oxidative coupling of the C−H bond with 1-alkynylphosphine sulfides and the application of new organophines as ligands in organic synthesis are currently underway in our laboratory and will be reported in due course.

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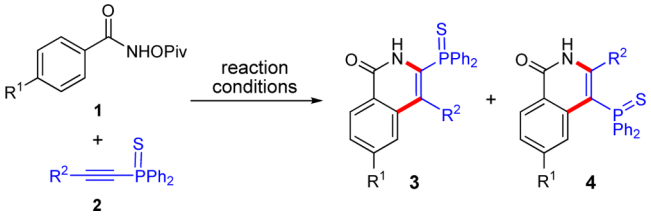
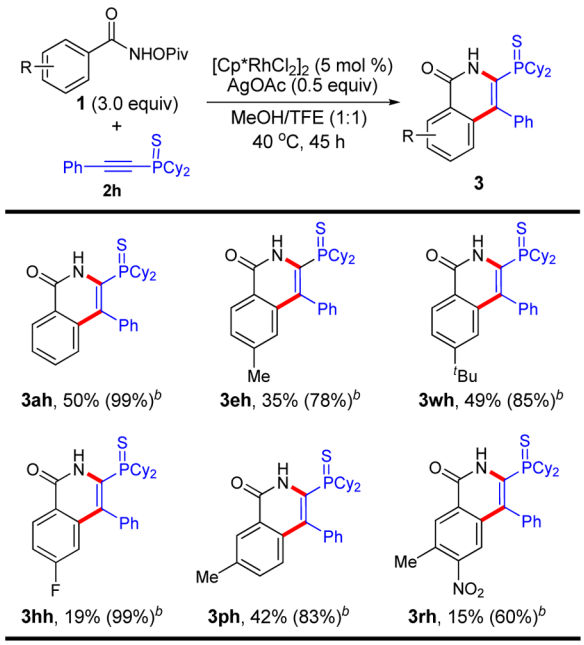
Table 2. Substrate Scope of (1-Alkynyl)diphenylphosphine Sulfides[a]



entry	R^1	R^2	yield (%) (3:4)[b,c] $[Cp^*RhCl_2]_2$	yield (%) (3:4)[b,c] $[Cp^{Ph}RhCl_2]_2$
1	H (**1a**)	*p*-MeC_6H_4 (**2b**)	96 (1:2.3)	75 (1:11)
2		*p*-$MeOC_6H_4$ (**2c**)	88 (1:3.3)	69 (1:10)
3		*p*-FC_6H_4 (**2d**)	76 (1:3.1)	65 (1:8.6)
4		*n*Bu (**2e**)	98 (1.8:1)	48 (1:1.3)
5		*n*Hex (**2f**)	91 (1.7:1)	42 (1:1.3)
6	Cl (**1i**)	*p*-MeC_6H_4 (**2b**)	67 (1:40)	
7		*p*-$MeOC_6H_4$ (**2c**)	92 (1:59)	
8		*p*-FC_6H_4 (**2d**)	72 (1:36)	
9		*n*Bu (**2e**)	91 (1:2.4)	
10		*n*Hex (**2f**)	96 (1:2.1)	62 (1:3.6)
11	NO_2 (**1k**)	*p*-MeC_6H_4 (**2b**)	89 (0:100)	
12		*p*-$MeOC_6H_4$ (**2c**)	99 (0:100)	
13		*p*-FC_6H_4 (**2d**)	99 (0:100)	
14		*n*Bu (**2e**)	50 (1:12)	
15		*n*Hex (**2f**)	69 (1:8.4)	

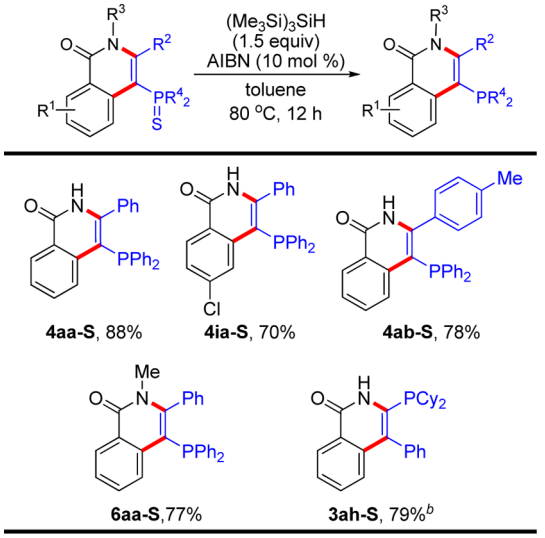
[a]Reaction conditions: see Scheme 2 for details. [b]Combined yields of isolated products, ratio of crude reaction mixture determined by ^{31}P NMR (internal standard: trimethyl phosphate). [c]For the NMR yields of byproducts **5** in the other reactions listed in this table, see Table S4 in the Supporting Information for details.

Scheme 3. Substrate Scope of *N*-(Pivaloyloxy)benzamides with (1-Alkynyl)dicyclohexylphosphine Sulfide 2h[a]



[a]Reactions in 0.1 mmol scale (0.1 M); isolated yields of **3** are given. [b]Yields in parentheses were based on the conversion of **2h**.

Scheme 4. Desulfidation of Phosphorothioylisoquinolin-1(2*H*)-one[a]



[a]Reactions in 0.1 mmol scale (0.05 M); isolated yields are given. [b]$(Me_3Si)_3SiH$ (3.0 equiv).

EXPERIMENTAL SECTION

General Procedures. All the reactions were carried out under an argon atmosphere using standard Schlenk techniques. ^1H NMR (400 MHz), $^{13}C\{^1H\}$ NMR (100 MHz), ^{31}P NMR (162 MHz), and ^{19}F NMR (376 MHz) were recorded with $CDCl_3$ or DMSO-d_6 as solvent. Chemical shifts of ^1H, $^{13}C\{^1H\}$, ^{31}P, and ^{19}F NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references, and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.00 ppm; DMSO-d_6: δ_H = 2.50 ppm, δ_C = 39.52 ppm). IR spectra were recorded as KBr disks on an FT-IR spectrometer. HRMS were done on Q-TOF mass spectrometers. $[Cp^*RhCl_2]_2$,[24] $[Cp^tRhCl_2]_2$,[25] $[Cp^ERhCl_2]_2$,[26] and $[Cp^{Ph}RhCl_2]_2$[27] were prepared from $RhCl_3{\cdot}xH_2O$ following literature procedures. The substrates **1a**,[28] **1b**,[29] **1c**,[28] and **1d**[28] were prepared according to the literature. **1e**−**1w** were prepared by the same way as that for **1a**. The substrates **2a**−**2h** were prepared according to the literature.[30]

*3,4-Dichloro-N-(pivaloyloxy)benzamide (**1q**).* m.p.: 165−167 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 9.51 (s, 1H), 7.88 (s, 1H), 7.61 (d, J = 7.3 Hz, 1H), 7.51 (d, J = 7.9 Hz, 1H), 1.34 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 176.9, 164.5, 137.3, 133.4, 130.9, 130.5, 129.6, 126.5, 38.5, 27.0; IR (cm^{-1}): ν 3170, 3016, 2976, 1787, 1662, 1589, 1558, 1528, 1470, 1373, 1307, 1270, 1160, 1074, 1031, 926, 890, 870, 742; HRMS (ESI): Calcd for $C_{12}H_{14}Cl_2NO_3$ $[M + H]^+$ 290.0345, Found: 290.0351.

*Diphenyl(p-tolylethynyl)phosphine Sulfide (**2b**).* m.p.: 101−103 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 15.2 Hz, 2H), 8.00 (dd, J = 15.4, 16.7 Hz, 2H), 7.53−7.45 (m, 8H), 7.19 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.2, 133.9 (d, J = 98.7 Hz), 132.4 (d, J = 1.8 Hz), 131.7 (d, J = 2.9 Hz), 130.8 (d, J = 12.3 Hz), 129.3, 128.6 (d, J = 13.7 Hz), 117.1 (d, J = 4.2 Hz), 106.4 (d, J = 26.8 Hz), 81.2 (d, J = 154.5 Hz), 21.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 20.10; IR (cm^{-1}): ν 3049, 2919, 2169, 1436, 1102, 857, 819, 775, 748, 715, 690, 650; HRMS (ESI): Calcd for $C_{21}H_{18}PS$ $[M + H]^+$ 333.0861, Found: 333.0866.

*((4-Fluorophenyl)ethynyl)diphenylphosphine Sulfide (**2d**).* m.p.: 149−151 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 15.1 Hz, 2H), 7.98 (d, J = 15.3 Hz, 2H), 7.58 (dd, J = 8.3, 5.5 Hz, 2H), 7.54−7.44 (m, 6H), 7.06 (t, J = 8.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.7 (d, J = 253.5 Hz), 134.6 (dd, J = 8.9, 1.6 Hz), 133.5 (d, J = 98.8 Hz), 131.8 (d, J = 3.0 Hz), 130.7 (d, J = 12.2 Hz), 128.6 (d, J = 13.8 Hz), 116.2−116.2 (m), 116.0 (d, J = 22.4 Hz), 104.6 (d, J = 26.3 Hz), 81.8 (d, J = 151.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 20.27; ^{19}F NMR

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(376 MHz, $CDCl_3$): δ −106.21; IR (cm^{-1}): ν 3047, 2171, 1896, 1645, 1592, 1504, 1477, 1433, 1313, 1289, 1152, 1097, 994, 863, 832, 789, 749, 690, 651; HRMS (ESI): Calcd for $C_{20}H_{15}FPS$ $[M + H]^+$ 337.0611, Found: 337.0613.

*Hex-1-ynyldiphenylphosphine Sulfide (**2e**).* m.p.: 74−76 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 15.2 Hz, 2H), 7.91 (dd, J = 15.2, 1 Hz, 2H), 7.50−7.42 (m, 6H), 2.48 (td, J = 7.1, 4.0 Hz, 2H), 1.67−1.58 (m, 2H), 1.50−1.40 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 134.0 (d, J = 98.3 Hz), 131.6 (d, J = 2.7 Hz), 130.7 (d, J = 12.2 Hz), 128.5 (d, J = 13.6 Hz), 110.3 (d, J = 26.5 Hz), 73.8 (d, J = 158.0 Hz), 29.6, 22.0, 19.7 (d, J = 3.1 Hz), 13.4; ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.40; IR (cm^{-1}): ν 3045, 2957, 2929, 2866, 2194, 1437, 1103, 752, 719, 691, 661, 591; HRMS (ESI): Calcd for $C_{18}H_{20}PS$ $[M + H]^+$ 299.1018, Found: 299.1022.

General Procedure for the Reaction of *N*-(Pivaloyloxy)-benzamides with (1-Alkynyl)diphenylphosphine Sulfides. *General Procedure A.* **1** (0.60 mmol, 3.0 equiv), **2** (0.2 mmol), and $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol, 5.0 mol %) were successively added to a flame-dried 25 mL reaction vessel with a stir bar, and CsOAc (76.8 mg, 0.4 mmol, 2.0 equiv) was weighed into the vessel in the glovebox. After that, no special care was taken to exclude air. Then, dry MeOH (1.0 mL) and dry CF_3CH_2OH (1.0 mL) were added, and the mixture was stirred at 40 °C for 45 h. Afterward, it was diluted with CH_2Cl_2 and transferred to a round-bottom flask and then evaporated under reduced pressure. Trimethyl phosphate (28.0 mg, 0.2 mmol) was added. Then, the appropriate amount of $CDCl_3$ was added to make sure the crude mixture was all dissolved. After ^{31}P NMR was taken, purification was performed by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1:20 to 1:2).

General Procedure B. **1** (0.40 mmol, 2.0 equiv), **2** (0.2 mmol), and $[Cp^{Ph}RhCl_2]_2$ (7.4 mg, 0.01 mmol, 5.0 mol %) were successively added to a flame-dried 25 mL reaction vessel with a stir bar, and CsOAc (76.8 mg, 0.4 mmol, 2.0 equiv) was weighed into the vessel in the glovebox. After that, no special care was taken to exclude air. Then, dry MeOH (0.5 mL) and dry CF_3CH_2OH (1.5 mL) were added, and the mixture was stirred at 25 °C for 45 h. Afterward, it was diluted with CH_2Cl_2 and transferred to a round-bottom flask and then evaporated under reduced pressure. Trimethyl phosphate (28.0 mg, 0.2 mmol) was added. Then, the appropriate amount $CDCl_3$ was added to make sure the crude mixture was all dissolved. After ^{31}P NMR was taken, purification was performed by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1:20 to 1:2).

*3-(Diphenylphosphorothioyl)-4-phenylisoquinolin-1(2H)-one (**3aa**).* This compound was obtained as a white solid in 22% yield (19.2 mg) by following the general procedure A. m.p.: 198−200 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 10.20 (d, J = 8.1 Hz, 1H), 8.41−8.32 (m, 1H), 7.71−7.64 (m, 2H), 7.56−7.51 (m, 6H), 7.41−7.36 (m, 4H), 7.13 (t, J = 7.4 Hz, 1H), 6.94 (t, J = 7.5 Hz, 2H), 6.78−6.76 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 160.2 (d, J = 7.8 Hz), 138.0 (d, J = 11.5 Hz), 133.1, 132.7 (d, J = 3.1 Hz), 131.9 (d, J = 1.8 Hz), 131.7 (d, J = 11.6 Hz), 131.2, 130.3 (d, J = 89.2 Hz), 129.0, 128.7 (d, J = 13.2 Hz), 127.9, 127.7, 126.8, 126.7, 126.3, 126.2 (d, J = 87.5 Hz), 125.3 (d, J = 8.7 Hz); ^{31}P NMR (162 MHz, DMSO-d_6): δ 42.97; IR (cm^{-1}): ν 3447, 3269, 3186, 3056, 1663, 1481, 1436, 1331, 1100, 848, 749, 718, 695; HRMS (ESI): Calcd for $C_{27}H_{21}NOPS$ $[M + H]^+$ 438.1076, Found: 438.1079.

*4-(Diphenylphosphorothioyl)-3-phenylisoquinolin-1(2H)-one (**4aa**).* This compound was obtained as a white solid in 70% yield (61.0 mg) by following the general procedure A and 74% yield (64.4 mg) by following the general procedure B, respectively. m.p.: 299−301 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 11.75 (s, 1H), 8.28 (d, J = 7.9 Hz, 1H), 7.79 (d, J = 8.3 Hz, 1H), 7.70 (dd, J = 13.3, 7.5 Hz, 4H), 7.44−7.40 (m, 3H), 7.36−7.32 (m, 1H), 7.22−7.12 (m, 6H), 7.09 (d, J = 7.3 Hz, 1H), 7.05−7.01 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 161.9, 150.1 (d, J = 14.9 Hz), 136.7 (d, J = 9.0 Hz), 134.6 (d, J = 85.6 Hz), 133.9 (d, J = 3.8 Hz), 131.1 (d, J = 10.5 Hz), 130.8, 130.4, 130.2 (d, J = 2.7 Hz), 129.7, 127.9 (d, J = 12.6 Hz), 127.6, 127.5, 126.7, 126.4, 125.6 (d, J = 8.8 Hz), 103.3 (d, J = 101.2 Hz); ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.80; IR (cm^{-1}): ν 3448, 3052, 1654, 1605, 1579, 1548, 1484, 1437, 1339, 1093, 772, 754, 698; HRMS (ESI): Calcd for $C_{27}H_{21}NOPS$ $[M + H]^+$ 438.1076, Found: 438.1079.

*Methyl 3-(Diphenylphosphorothioyl)-2-phenyl-1H-indole-1-carboxylate (**5aa**).* This compound was obtained as a white solid in 18% yield (16.5 mg) by following the general procedure B. m.p.: 195−197 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 13.9 Hz, 2H), 7.71 (dd, J = 13.9, 1.2 Hz, 4H), 7.36−7.28 (m, 4H), 7.23−7.18 (m, 4H), 7.10 (d, J = 7.3 Hz, 1H), 7.07−7.02 (m, 3H), 6.95 (t, J = 7.5 Hz, 2H), 3.65 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.5, 144.4 (d, J = 17.1 Hz), 136.3 (d, J = 9.9 Hz), 132.9, 132.0 (d, J = 11.1 Hz), 131.1, 131.0 (d, J = 3.2 Hz), 130.1, 128.9 (d, J = 9.9 Hz), 128.2, 128.1 (d, J = 13.3 Hz), 127.1, 125.2, 123.4, 122.6, 114.9, 111.0 (d, J = 101.7 Hz), 53.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.22; IR (cm^{-1}): ν 3417, 3048, 2918, 2848, 1745, 1619, 1541, 1436, 1352, 1323, 1330, 1267, 1218, 1094, 747, 692; HRMS (ESI): Calcd for $C_{28}H_{22}NO_2PS$ $[M + H]^+$ 468.1182, Found: 468.1184.

*4-(Diphenylphosphorothioyl)-6-methyl-3-phenylisoquinolin-1(2H)-one (**4ea**).* This compound was obtained as a white solid in 56% yield (51.0 mg) by following the general procedure A and 41% yield (37.4 mg) by following the general procedure B, respectively. m.p.: 293−295 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 11.64 (s, 1H), 8.14 (d, J = 7.7 Hz, 1H), 7.75−7.70 (m, 4H), 7.52 (s, 1H), 7.44 (d, J = 6.8 Hz, 2H), 7.26−7.19 (m, 3H), 7.15 (m, 4H), 7.09 (d, J = 7.0 Hz, 1H), 7.04−7.01 (m, 2H), 2.00 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 162.0, 150.2 (d, J = 15.3 Hz), 140.9, 136.8 (d, J = 8.7 Hz), 134.7 (d, J = 85.6 Hz), 134.1 (d, J = 3.9 Hz), 131.2 (d, J = 10.5 Hz), 130.5, 130.4 (d, J = 1.9 Hz), 129.8, 128.0 (d, J = 12.6 Hz), 127.8, 127.7, 126.8, 123.4 (d, J = 8.4 Hz), 103.3 (d, J = 101.2 Hz), 21.4 (one signal missing due to overlap); ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.71; IR (cm^{-1}): ν 3417, 2956, 2921, 1651, 1558, 1435, 1306, 1089, 748, 698; HRMS (ESI): Calcd for $C_{28}H_{23}NOPS$ $[M + H]^+$ 452.1232, Found: 452.1233.

*4-(Diphenylphosphorothioyl)-6-methoxy-3-phenylisoquinolin-1(2H)-one (**4fa**).* This compound was obtained as a white solid in 26% yield (24.4 mg) by following the general procedure A and 18% yield (16.8 mg) by following the general procedure B, respectively. m.p.: 306−308 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 11.62 (s, 1H), 8.16 (d, J = 8.8 Hz, 1H), 7.77−7.72 (m, 4H), 7.43 (d, J = 7.4 Hz, 2H), 7.24−7.16 (m, 7H), 7.11−7.08 (m, 1H), 7.04−6.98 (m, 3H), 3.28 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 161.4, 160.7, 150.8 (d, J = 15.2 Hz), 138.7 (d, J = 8.5 Hz), 134.7 (d, J = 85.4 Hz), 133.9 (d, J = 3.7 Hz), 131.1 (d, J = 10.3 Hz), 130.3, 129.7, 128.6, 127.9 (d, J = 12.6 Hz), 127.6, 119.2 (d, J = 8.8 Hz), 115.9, 109.7 (d, J = 7.4 Hz), 102.9 (d, J = 101.6 Hz), 54.9 (one signal missing due to overlap); ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.71; IR (cm^{-1}): ν 3416, 2955, 2922, 1649, 1556, 1456, 1243, 1090, 739, 705; HRMS (ESI): Calcd for $C_{28}H_{23}NO_2PS$ $[M + H]^+$ 468.1182, Found: 468.1184.

*Methyl 3-(Diphenylphosphorothioyl)-5-methoxy-2-phenyl-1H-indole-1-carboxylate (**5fa**).* This compound was obtained as a white solid in 44% yield (44.1 mg) by following the general procedure B. m.p.: 175−176 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 7.99 (d, J = 8.9 Hz, 1H), 7.80−7.74 (m, 4H), 7.43−7.36 (m, 2H), 7.34−7.26 (m, 4H), 7.16 (d, J = 6.7 Hz, 2H), 7.08−7.01 (m, 1H), 7.00−6.92 (m, 3H), 6.36 (s, 1H), 3.63 (s, 3H), 3.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 155.0, 150.8, 144.9 (d, J = 16.9 Hz), 132.1 (d, J = 90.8 Hz), 131.6 (d, J = 11.0 Hz), 131.2, 130.7, 130.4 (d, J = 9.8 Hz), 130.0, 129.3 (d, J = 9.6 Hz), 128.2 (d, J = 12.7 Hz), 128.2, 126.8, 115.8, 113.5, 109.8 (d, J = 102.7 Hz), 104.1, 54.8, 54.0; ^{31}P NMR (162 MHz, DMSO-d_6): δ 29.10; IR (cm^{-1}): ν 3415, 2923, 1740, 1616, 1468, 1439, 1321, 1164, 1096, 1066, 743, 694; HRMS (ESI): Calcd for $C_{29}H_{25}NO_3PS$ $[M + H]^+$ 498.1287, Found: 498.1296.

*4-(Diphenylphosphorothioyl)-3,6-diphenylisoquinolin-1(2H)-one (**4ga**).* This compound was obtained as a white solid in 57% yield (58.0 mg) by following the general procedure A and 54% yield (55.9 mg) by following the general procedure B, respectively. m.p.: 307−309 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 11.76 (s, 1H), 8.33 (dd, J = 8.3, 1.2 Hz, 1H), 8.00 (s, 1H), 7.82−7.77 (m, J = 13.4, 7.0 Hz, 4H), 7.71 (dd, J = 8.3, 1.6 Hz, 1H), 7.45 (d, J = 7.1 Hz, 2H), 7.36−7.32 (m, 3H), 7.27−7.19 (m, 6H), 7.13−7.09 (m, 1H), 7.06−7.02 (m, 2H), 6.96−6.92 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 161.8, 150.6 (d, J = 15.3 Hz), 142.5, 139.2, 136.9 (d, J = 8.7 Hz), 134.8 (d, J = 85.5 Hz), 133.9 (d, J = 3.6 Hz), 131.2 (d, J = 10.6 Hz), 130.3, 129.7, 128.9, 128.3, 128.0 (d, J = 12.5 Hz), 127.6, 127.5, 126.9, 126.2 (d, J = 6.9 Hz), 125.0, 124.5

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(d, J = 8.8 Hz), 103.4 (d, J = 101.5 Hz) (one signal missing due to overlap); ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.83; IR (cm^{-1}): ν 3414, 3053, 2908, 1655, 1609, 1556, 1436, 1397, 1310, 1093, 757, 699; HRMS (ESI): Calcd for $C_{33}H_{25}NOPS$ $[M + H]^+$ 514.1389, Found: 514.1391.

4-(Diphenylphosphorothioyl)-6-fluoro-3-phenylisoquinolin-1(2H)-one (**4ha**). This compound was obtained as a white solid in 69% yield (63.0 mg) by following the general procedure A and 74% yield (67.0 mg) by following the general procedure B, respectively. m.p.: 289−291 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.84 (s, 1H), 8.31 (br s, 1H), 7.79−7.69 (m, 4H), 7.48−7.40 (m, 3H), 7.34−7.00 (m, 10H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 162.0 (d, J = 248.5 Hz), 161.2, 151.5 (d, J = 15.0 Hz), 139.2 (dd, J = 10.6, 8.8 Hz), 134.2 (d, J = 85.8 Hz), 133.6 (d, J = 3.5 Hz), 131.1 (d, J = 10.5 Hz), 130.5 (d, J = 2.5 Hz), 130.3, 130.1 (d, J = 10.4 Hz), 129.9, 128.0 (d, J = 12.4 Hz), 127.6, 122.6 (d, J = 8.7 Hz), 114.8 (d, J = 23.4 Hz), 112.8 (dd, J = 25.2, 7.0 Hz), 102.7 (dd, J = 101.2, 3.1 Hz); ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.84; ^{19}F NMR (376 MHz, DMSO-d_6): δ −106.87; IR (cm^{-1}): ν 3415, 3050, 2922, 1655, 1612, 1580, 1438, 1412, 1303, 1092, 856, 697; HRMS (ESI): Calcd $C_{27}H_{20}FNOPS$ for $[M + H]^+$ 456.0982, Found: 456.0976.

6-Chloro-4-(diphenylphosphorothioyl)-3-phenylisoquinolin-1(2H)-one (**4ia**). This compound was obtained as a white solid in 76% yield (71.6 mg) by following the general procedure A and 76% yield (71.8 mg) by following the general procedure B, respectively. m.p.: 301−303 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.87 (s, 1H), 8.24 (d, J = 8.4 Hz, 1H), 7.76−7.71 (m, 5H), 7.49−7.41 (m, 3H), 7.28−7.00 (m, 9H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 161.3, 151.4 (d, J = 14.9 Hz), 138.2 (d, J = 8.8 Hz), 136.2, 134.2 (d, J = 85.6 Hz), 133.6 (d, J = 3.6 Hz), 131.1 (d, J = 10.6 Hz), 130.5 (d, J = 1.5 Hz), 130.3, 129.9, 128.8, 128.0 (d, J = 12.5 Hz), 127.6, 126.8 (d, J = 6.7 Hz), 126.5, 124.3 (d, J = 8.5 Hz), 102.5 (d, J = 101.1 Hz); ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.65; IR (cm^{-1}): ν 3414, 3042, 2921, 1654, 1598, 1437, 1301, 1092, 833, 788, 695; HRMS (ESI): Calcd for $C_{27}H_{20}ClNOPS$ $[M + H]^+$ 472.0686, Found: 472.0685.

6-Bromo-4-(diphenylphosphorothioyl)-3-phenylisoquinolin-1(2H)-one (**4ja**). This compound was obtained as a white solid in 82% yield (84.6 mg) by following the general procedure A and 74% yield (76.3 mg) by following the general procedure B, respectively. m.p.: 313−315 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.89 (s, 1H), 8.14 (dd, J = 8.5, 1.2 Hz, 1H), 7.91 (d, J = 1.4 Hz, 1H), 7.77−7.72 (m, 4H), 7.57 (dd, J = 8.5, 1.8 Hz, 1H), 7.43 (d, J = 7.1 Hz, 2H), 7.26−7.22 (m, 2H), 7.19−7.15 (m, 4H), 7.13−7.09 (m, 1H), 7.05−7.01 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 161.5, 151.3 (d, J = 14.8 Hz), 138.3 (d, J = 8.8 Hz), 134.1 (d, J = 85.7 Hz), 133.6 (d, J = 3.7 Hz), 131.1 (d, J = 10.6 Hz), 130.4 (d, J = 2.6 Hz), 130.3, 130.0 (d, J = 7.0 Hz), 129.9, 129.2, 128.8, 128.0 (d, J = 12.7 Hz), 127.6, 125.3, 124.5 (d, J = 8.4 Hz), 102.5 (d, J = 101.0 Hz); ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.59; IR (cm^{-1}): ν 3415, 3047, 2917, 1658, 1592, 1435, 1396, 1306, 1090, 996, 882, 795, 696; HRMS (ESI): Calcd for $C_{27}H_{20}BrNOPS$ $[M + H]^+$ 516.0181, Found: 516.0175.

4-(Diphenylphosphorothioyl)-6-nitro-3-phenylisoquinolin-1(2H)-one (**4ka**). This compound was obtained as a yellow solid in 99% yield (95.8 mg) by following the general procedure A and 99% yield (96.0 mg) by following the general procedure B, respectively. m.p.: 290−292 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.15 (s, 1H), 8.63 (s, 1H), 8.46 (d, J = 8.8 Hz, 1H), 8.14 (d, J = 8.8 Hz, 1H), 7.81−7.76 (m, 4H), 7.47 (d, J = 7.2 Hz, 2H), 7.24−7.11 (m, 7H), 7.08−7.04 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 161.1, 152.1 (d, J = 14.3 Hz), 148.0, 137.5 (d, J = 8.9 Hz), 133.9 (d, J = 85.9 Hz), 133.3 (d, J = 3.7 Hz), 131.3 (d, J = 10.6 Hz), 130.6 (d, J = 1.4 Hz), 130.3, 130.1, 129.7 (d, J = 8.3 Hz), 128.9, 128.0 (d, J = 12.6 Hz), 127.7, 122.7 (d, J = 6.8 Hz), 119.8, 103.7 (d, J = 101.2 Hz); ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.57; IR (cm^{-1}): ν 3478, 3415, 3054, 2920, 1662, 1616, 1525, 1438, 1344, 1093, 789, 741, 696; HRMS (ESI): Calcd for $C_{27}H_{20}N_2O_3PS$ $[M + H]^+$ 483.0928, Found: 483.0927.

4-(Diphenylphosphorothioyl)-3-phenyl-6-(trifluoromethyl)isoquinolin-1(2H)-one (**4la**). This compound was obtained as a white solid in 90% yield (90.4 mg) by following the general procedure A and 77% yield (77.4 mg) by following the general procedure B, respectively. m.p.: 320−322 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.04 (s, 1H), 8.42 (d, J = 8.3 Hz, 1H), 8.07 (s, 1H), 7.79−7.74 (m, 4H), 7.70 (d, J = 8.3 Hz, 1H), 7.47 (d, J = 7.3 Hz, 2H), 7.27−7.09 (m, 7H), 7.05 (t, J = 7.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 161.3, 151.5 (d, J = 14.7 Hz), 136.9 (d, J = 8.8 Hz), 134.1 (d, J = 85.6 Hz), 133.5 (d, J = 3.6 Hz), 131.2 (d, J = 10.7 Hz), 130.7, 130.5 (d, J = 2.2 Hz), 130.4, 130.2 (q, J = 36.8 Hz), 128.3 (d, J = 8.6 Hz), 128.2, 127.9 (d, J = 12.6 Hz), 127.6, 123.4 (q, J = 272.8 Hz), 124.7 (q, J = 3.3 Hz), 121.9 (q, J = 2.6 Hz), 103.5 (d, J = 100.9 Hz); ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.46; ^{19}F NMR (376 MHz, DMSO-d_6): δ −62.17; IR (cm^{-1}): ν 3414, 3051, 2925, 1661, 1584, 1437, 1302, 1137, 1067, 900, 697; HRMS (ESI): Calcd for $C_{28}H_{20}F_3NOPS$ $[M + H]^+$ 506.0950, Found: 506.0945.

Methyl 4-(Diphenylphosphorothioyl)-1-oxo-3-phenyl-1,2-dihydroisoquinoline-6-carboxylate (**4ma**). This compound was obtained as a white solid in 87% yield (86.6 mg) by following the general procedure A and 88% yield (86.9 mg) by following the general procedure B, respectively. m.p.: 294−296 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.94 (s, 1H), 8.42 (s, 1H), 8.34 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 8.3 Hz, 1H), 7.79−7.74 (m, 4H), 7.47 (d, J = 7.2 Hz, 2H), 7.25−7.10 (m, 7H), 7.04 (t, J = 7.2 Hz, 2H), 3.71 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 165.2, 161.5, 150.8 (d, J = 14.8 Hz), 136.6 (d, J = 8.9 Hz), 134.3 (d, J = 85.8 Hz), 133.7 (d, J = 3.3 Hz), 131.2 (d, J = 10.7 Hz), 131.1, 130.4, 129.9, 129.4 (d, J = 6.4 Hz), 128.6 (d, J = 8.5 Hz), 127.9 (d, J = 12.6 Hz), 127.6, 127.2, 125.7, 103.9 (d, J = 101.1 Hz), 52.2 (one signal missing due to overlap); ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.52; IR (cm^{-1}): ν 3415, 3039, 2956, 1720, 1650, 1548, 1438, 1285, 1089, 757, 735, 697; HRMS (ESI): Calcd for $C_{29}H_{23}NO_3PS$ $[M + H]^+$ 496.1131, Found: 496.1130.

6-Acetyl-4-(diphenylphosphorothioyl)-3-phenylisoquinolin-1(2H)-one (**4na**). This compound was obtained as a white solid in 79% yield (75.4 mg) by following the general procedure A and 80% yield (76.9 mg) by following the general procedure B, respectively. m.p.: 287−289 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.95 (s, 1H), 8.40 (s, 1H), 8.34 (d, J = 8.3 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.81−7.76 (m, 4H), 7.47 (d, J = 7.2 Hz, 2H), 7.24−7.10 (m, 7H), 7.05 (t, J = 7.3 Hz, 2H), 2.12 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.9, 161.5, 150.9 (d, J = 15.0 Hz), 137.3, 136.8 (d, J = 8.5 Hz), 134.4 (d, J = 85.8 Hz), 133.6 (d, J = 3.6 Hz), 131.2 (d, J = 10.6 Hz), 130.4 (d, J = 2.1 Hz), 130.4, 129.9, 129.0 (d, J = 7.0 Hz), 128.4 (d, J = 8.5 Hz), 128.0 (d, J = 12.6 Hz), 127.6, 127.2, 124.1, 103.8 (d, J = 101.3 Hz), 26.3; ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.62; IR (cm^{-1}): ν 3415, 3052, 2920, 1689, 1660, 1551, 1494, 1436, 1308, 1266, 1091, 707, 622; HRMS (ESI): Calcd for $C_{29}H_{23}NO_2PS$ $[M + H]^+$ 480.1182, Found: 480.1183.

4-(Diphenylphosphorothioyl)-1-oxo-3-phenyl-1,2-dihydroisoquinoline-6-carbonitrile (**4oa**). This compound was obtained as a white solid in 84% yield (78.0 mg) by following the general procedure A and 99% yield (92.2 mg) by following the general procedure B, respectively. m.p.: 315−317 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.11 (s, 1H), 8.38 (d, J = 8.2 Hz, 1H), 8.04 (s, 1H), 7.86−7.69 (m, 5H), 7.46 (d, J = 7.3 Hz, 2H), 7.27−7.11 (m, 7H), 7.05 (t, J = 7.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 161.2, 151.8 (d, J = 14.4 Hz), 136.9 (d, J = 8.8 Hz), 134.0 (d, J = 85.7 Hz), 133.4 (d, J = 3.4 Hz), 131.7 (d, J = 6.7 Hz), 131.3 (d, J = 10.7 Hz), 130.7 (d, J = 2.0 Hz), 130.4, 130.1, 128.5 (d, J = 8.4 Hz), 128.1, 118.1, 128.0, 127.7, 117.8, 113.1, 102.8 (d, J = 100.8 Hz); ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.40; IR (cm^{-1}): ν 3417, 3054, 2920, 1663, 1607, 1547, 1438, 1309, 1093, 711, 625; HRMS (ESI): Calcd for $C_{28}H_{20}N_2OPS$ $[M + H]^+$ 463.1028, Found: 463.1026.

4-(Diphenylphosphorothioyl)-7-methyl-3-phenylisoquinolin-1(2H)-one (**4pa**). This compound was obtained as a white solid in 62% yield (56.0 mg) by following the general procedure A and 68% yield (61.1 mg) by following the general procedure B, respectively. m.p.: 299−301 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.66 (s, 1H), 8.07 (s, 1H), 7.76−7.63 (m, 5H), 7.42 (d, J = 7.0 Hz, 2H), 7.21−7.12 (m, 7H), 7.10−7.07 (m, 1H), 7.02 (t, J = 7.3 Hz, 2H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 161.8, 149.1 (d, J = 15.0 Hz), 136.0, 134.7 (d, J = 86.0 Hz), 134.4, 134.0 (d, J = 3.7 Hz), 132.1, 131.1 (d, J = 10.6 Hz), 130.4, 130.2 (d, J = 2.1 Hz), 129.6, 127.9 (d, J = 12.5 Hz), 127.6, 127.5, 126.2, 125.6 (d, J = 8.8 Hz), 103.3 (d, J = 101.1 Hz), 20.6; ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.81; IR (cm^{-1}): ν 3414, 2919, 2853, 1649, 1578, 1434, 1312, 1090, 818, 693; HRMS (ESI): Calcd for $C_{28}H_{23}NOPS$ $[M + H]^+$ 452.1232, Found: 452.1235.

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*6,7-Dichloro-4-(diphenylphosphorothioyl)-3-phenylisoquinolin-1(2H)-one (**4qa**).* This compound was obtained as a white solid in 99% yield (100.2 mg) by following the general procedure A and 91% yield (92.3 mg) by following the general procedure B, respectively. m.p.: 327−329 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.06 (s, 1H), 8.33 (s, 1H), 7.90 (s, 1H), 7.83−7.68 (m, 4H), 7.51−7.40 (m, 2H), 7.25−7.04 (m, 9H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 160.5, 151.7 (d, J = 14.4 Hz), 136.5 (d, J = 8.9 Hz), 134.2, 133.9 (d, J = 85.6 Hz), 133.4 (d, J = 3.7 Hz), 131.2 (d, J = 10.7 Hz), 130.6 (d, J = 2.2 Hz), 130.3, 130.0, 129.1 (d, J = 6.8 Hz), 129.0, 128.04, 128.02 (d, J = 12.6 Hz), 127.6, 125.8 (d, J = 8.5 Hz), 102.3 (d, J = 100.7 Hz); ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.54; IR (cm^{-1}): ν 3414, 3056, 2956, 1659, 1592, 1560, 1439, 1307, 1090, 931, 875, 777, 697; HRMS (ESI): Calcd for $C_{27}H_{19}Cl_2NOPS$ [M + H]$^+$ 506.0296, Found: 506.0289.

*4-(Diphenylphosphorothioyl)-7-methyl-6-nitro-3-phenylisoquinolin-1(2H)-one (**4ra**).* This compound was obtained as a yellow solid in 91% yield (90.6 mg) by following the general procedure A and 99% yield (99.0 mg) by following the general procedure B, respectively. m.p.: 342−344 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.05 (s, 1H), 8.31 (s, 1H), 8.27 (s, 1H), 7.79−7.74 (m, 4H), 7.46 (d, J = 7.3 Hz, 2H), 7.25−7.13 (m, 6H), 7.12−7.10 (m, 1H), 7.05 (t, J = 7.4 Hz, 2H), 2.53 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 160.9, 151.2 (d, J = 14.2 Hz), 150.0, 135.3 (d, J = 8.7 Hz), 133.9 (d, J = 85.5 Hz), 133.4 (d, J = 3.9 Hz), 131.2 (d, J = 10.7 Hz), 130.9, 130.6 (d, J = 2.5 Hz), 130.3, 130.0, 129.4, 128.3 (d, J = 8.3 Hz), 128.1 (d, J = 12.7 Hz), 127.7, 123.4 (d, J = 7.0 Hz), 103.2 (d, J = 100.8 Hz), 19.0; ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.37; IR (cm^{-1}): ν 3416, 2920, 1662, 1523, 1437, 1343, 1309, 1092, 700, 622. HRMS (ESI): Calcd for $C_{28}H_{22}N_2O_3PS$ [M + H]$^+$ 497.1083, Found: 497.1084.

*4-(Diphenylphosphorothioyl)-3-phenylbenzo[g]isoquinolin-1(2H)-one (**4sa**).* This compound was obtained as a white solid in 58% yield (57.0 mg) by following the general procedure A and 34% yield (33.1 mg) by following the general procedure B, respectively. m.p.: 294−296 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.58 (d, J = 2.5 Hz, 1H), 8.96 (s, 1H), 8.22 (s, 1H), 8.15 (d, J = 7.3 Hz, 1H), 7.81−7.76 (m, 4H), 7.55−7.46 (m, 4H), 7.37 (d, J = 7.5 Hz, 1H), 7.20−7.09 (m, 7H), 7.05 (t, J = 7.3 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 162.4, 149.5 (d, J = 15.1 Hz), 134.7 (d, J = 85.5 Hz), 134.1 (d, J = 4.2 Hz), 133.4, 131.9 (d, J = 9.1 Hz), 131.2 (d, J = 10.5 Hz), 130.4, 130.3, 130.2 (d, J = 1.8 Hz), 129.7, 128.9, 128.5, 127.8 (d, J = 12.5 Hz), 127.7, 127.6, 127.3, 126.8 (d, J = 6.4 Hz), 126.5, 124.1 (d, J = 8.5 Hz), 102.9 (d, J = 100.9 Hz); ^{31}P NMR (162 MHz, DMSO-d_6): δ 35.00; IR (cm^{-1}): ν 3416, 2956, 2921, 2851, 1655, 1631, 1561, 1436, 1090, 695. HRMS (ESI): Calcd for $C_{31}H_{23}NOPS$ [M + H]$^+$ 488.1232, Found: 488.1236.

*3-(Diphenylphosphorothioyl)-4-p-tolylisoquinolin-1(2H)-one (**3ab**).* This compound was obtained as a white solid in 29% yield (26.5 mg) by following the general procedure A. m.p.: 172−174 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.11 (d, J = 7.8 Hz, 1H), 8.49 (d, J = 7.8 Hz, 1H), 7.55−7.39 (m, 8H), 7.26−7.22 (m, 4H), 6.83 (d, J = 8.1 Hz, 1H), 6.65 (d, J = 7.6 Hz, 2H), 6.51 (d, J = 7.7 Hz, 2H), 2.21 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.3 (d, J = 8.1 Hz), 138.5 (d, J = 11.2 Hz), 137.5, 132.7, 132.0, 131.8, 131.6, 131.2 (d, J = 86.3 Hz), 131.1, 130.2 (d, J = 3.4 Hz), 128.8, 128.4 (d, J = 13.5 Hz), 127.5, 127.3, 126.7, 126.0 (d, J = 8.3 Hz), 125.8 (d, J = 86.9 Hz), 21.1; ^{31}P NMR (162 MHz, $CDCl_3$): δ 44.30; IR (cm^{-1}): ν 3411, 2957, 2923, 1775, 1642, 1539, 1512, 1437, 1079; HRMS (ESI): Calcd for $C_{28}H_{23}NOPS$ [M + H]$^+$ 452.1232, Found: 452.1230.

*4-(Diphenylphosphorothioyl)-3-p-tolylisoquinolin-1(2H)-one (**4ab**).* This compound was obtained as a white solid in 67% yield (60.2 mg) by following the general procedure A and 69% yield (62.3 mg) by following the general procedure B, respectively. m.p.: 309−311 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.74 (s, 1H), 8.26 (d, J = 7.9 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.70−7.65 (m, 4H), 7.41 (t, J = 7.5 Hz, 1H), 7.35−7.27 (m, 3H), 7.23−7.20 (m, 2H), 7.16−7.13 (m, 4H), 6.79 (d, J = 7.9 Hz, 2H), 2.13 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 161.9, 150.1 (d, J = 15.1 Hz), 139.4, 136.8 (d, J = 8.9 Hz), 134.6 (d, J = 85.8 Hz), 131.2 (d, J = 10.7 Hz), 131.1, 130.8, 130.3, 130.1, 128.1, 127.8 (d, J = 12.6 Hz), 127.5 (d, J = 6.5 Hz), 126.7, 126.3, 125.5 (d, J = 8.9 Hz), 103.3 (d, J = 101.6 Hz), 20.8; ^{31}P NMR (162 MHz, DMSO-d_6): δ 35.03; IR (cm^{-1}): ν 3416, 3049, 2914, 1657, 1548, 1436, 1307, 1090, 767, 704, 619; HRMS (ESI): Calcd for $C_{28}H_{23}NOPS$ [M + H]$^+$ 452.1232, Found: 452.1230.

*6-Chloro-4-(diphenylphosphorothioyl)-3-p-tolylisoquinolin-1(2H)-one (**4ib**).* This compound was obtained as a white solid in 66% yield (64.4 mg) by following the general procedure A. m.p.: 295−297 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.89 (s, 1H), 8.23 (d, J = 8.1 Hz, 1H), 7.79−7.65 (m, 5H), 7.45 (d, J = 7.2 Hz, 1H), 7.33−7.11 (m, 8H), 6.80 (d, J = 7.2 Hz, 2H), 2.13 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 161.4, 151.5 (d, J = 14.8 Hz), 139.7, 138.2 (d, J = 9.0 Hz), 136.2, 134.2 (d, J = 85.9 Hz), 131.2 (d, J = 10.6 Hz), 130.8 (d, J = 3.6 Hz), 130.3, 128.9, 128.2, 127.9 (d, J = 12.5 Hz), 126.8 (d, J = 6.7 Hz), 126.4, 124.3 (d, J = 8.4 Hz), 102.5 (d, J = 101.7 Hz), 20.8, one carbon is not visible due to overlapping peaks; ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.80; IR (cm^{-1}): ν 3417, 3049, 2912, 1657, 1597, 1437, 1305, 1093, 995, 819, 709; HRMS (ESI): Calcd for $C_{28}H_{22}ClNOPS$ [M + H]$^+$ 486.0843, Found: 486.0846.

*4-(Diphenylphosphorothioyl)-6-nitro-3-p-tolylisoquinolin-1(2H)-one (**4kb**).* This compound was obtained as a yellow solid in 89% yield (88.8 mg) by following the general procedure A. m.p.: 308−310 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.14 (s, 1H), 8.63 (s, 1H), 8.45 (d, J = 8.8 Hz, 1H), 8.13 (d, J = 8.8 Hz, 1H), 7.79−7.74 (m, 4H), 7.33 (d, J = 7.7 Hz, 2H), 7.23 (d, J = 7.0 Hz, 2H), 7.18−7.12 (m, 4H), 6.82 (d, J = 7.8 Hz, 2H), 2.14 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 161.1, 152.2 (d, J = 14.2 Hz), 148.0, 139.9, 137.6 (d, J = 9.0 Hz), 133.9 (d, J = 86.0 Hz), 131.3 (d, J = 10.7 Hz), 130.5 (d, J = 2.3 Hz), 130.3, 129.7 (d, J = 8.6 Hz), 129.0, 128.2, 128.0 (d, J = 12.6 Hz), 123.5, 122.7 (d, J = 6.9 Hz), 119.8, 103.7 (d, J = 101.4 Hz), 20.8; ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.74; IR (cm^{-1}): ν 3414, 3051, 1663, 1526, 1437, 1346, 1310, 1092, 827, 745, 708; HRMS (ESI): Calcd for $C_{28}H_{22}N_2O_3PS$ [M + H]$^+$ 497.1083, Found: 497.1084.

*3-(Diphenylphosphorothioyl)-4-(4-methoxyphenyl)isoquinolin-1(2H)-one (**3ac**).* This compound was obtained as a white solid in 20% yield (19.2 mg) by following the general procedure A. m.p.: 223−225 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.15 (s, 1H), 8.54 (d, J = 7.5 Hz, 1H), 7.61−7.43 (m, 8H), 7.36−7.32 (m, 4H), 6.90 (d, J = 7.7 Hz, 1H), 6.60 (d, J = 8.1 Hz, 2H), 6.43 (d, J = 8.4 Hz, 2H), 3.73 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.3 (d, J = 7.9 Hz), 159.0, 138.7 (d, J = 11.0 Hz), 132.7, 132.4, 131.9 (d, J = 11.6 Hz), 131.7 (d, J = 3.0 Hz), 131.2 (d, J = 89.8 Hz), 128.8, 128.5 (d, J = 13.4 Hz), 127.5, 127.3, 126.7, 126.1 (d, J = 95.2 Hz), 125.8, 125.2 (d, J = 3.2 Hz), 113.6, 55.2; ^{31}P NMR (162 MHz, $CDCl_3$): δ 44.10; IR (cm^{-1}): ν 3416, 3259, 2956, 2923, 1669, 1508, 1436, 1325, 1289, 1246, 1100, 1024, 857, 783, 733, 691; HRMS (ESI): Calcd for $C_{28}H_{23}NO_2PS$ [M + H]$^+$ 468.1182, Found: 468.1187.

*4-(Diphenylphosphorothioyl)-3-(4-methoxyphenyl)isoquinolin-1(2H)-one (**4ac**).* This compound was obtained as a white solid in 68% yield (63.5 mg) by following the general procedure B and 63% yield (58.9 mg) by following the general procedure B, respectively. m.p.: 302−303 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.72 (s, 1H), 8.25 (d, J = 7.9 Hz, 1H), 7.78 (d, J = 8.3 Hz, 1H), 7.72−7.67 (m, 4H), 7.42−7.30 (m, 4H), 7.23−7.13 (m, 6H), 6.55 (d, J = 8.8 Hz, 2H), 3.65 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 162.1, 160.3, 150.0 (d, J = 14.9 Hz), 136.9 (d, J = 9.0 Hz), 134.8 (d, J = 86.1 Hz), 132.0, 131.1 (d, J = 10.3 Hz), 130.8, 130.2 (d, J = 2.3 Hz), 127.8 (d, J = 12.4 Hz), 127.4 (d, J = 6.6 Hz), 126.7, 126.4 (d, J = 4.1 Hz), 126.2, 125.5 (d, J = 8.7 Hz), 113.2, 102.9 (d, J = 102.2 Hz), 55.2; ^{31}P NMR (162 MHz, DMSO-d_6): δ 35.09; IR (cm^{-1}): ν 3413, 3014, 2891, 1658, 1607, 1558, 1507, 1432, 1327, 1248, 1091, 1034, 825, 769, 748, 696; HRMS (ESI): Calcd for $C_{28}H_{23}NO_2PS$ [M + H]$^+$ 468.1182, Found: 468.1187.

*6-Chloro-4-(diphenylphosphorothioyl)-3-(4-methoxyphenyl)isoquinolin-1(2H)-one (**4ic**).* This compound was obtained as a white solid in 90% yield (90.6 mg) by following the general procedure A. m.p.: 305−307 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.87 (s, 1H), 8.22 (d, J = 8.5 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.76−7.71 (m, 4H), 7.53 (d, J = 8.4 Hz, 1H), 7.43 (dd, J = 8.6, 1.6 Hz, 1H), 7.38 (d, J = 8.1 Hz, 2H), 7.28−7.23 (m, 2H), 7.20−7.18 (m, 3H), 6.56 (d, J = 8.2 Hz, 2H), 3.66 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 161.5, 160.5, 151.3 (d, J = 14.9 Hz), 138.4 (d, J = 8.9 Hz), 136.2, 134.3 (d, J = 85.7 Hz), 131.2 (d, J = 10.6 Hz), 130.4 (d, J = 1.6 Hz), 129.4, 128.9, 128.3, 128.0 (d, J = 12.5 Hz), 126.8 (d, J = 6.6 Hz), 126.3, 126.0 (d, J = 4.1 Hz), 124.2

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(d, J = 8.6 Hz), 113.2, 102.1 (d, J = 102.2 Hz), 55.2; ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.87; IR (cm^{-1}): ν 3377, 3049, 2951, 1655, 1600, 1508, 1440, 1311, 1253, 1089, 835, 707; HRMS (ESI): Calcd for $C_{28}H_{22}ClNO_2PS$ [M + H]$^+$ 502.0792, Found: 502.0787.

*4-(Diphenylphosphorothioyl)-3-(4-methoxyphenyl)-6-nitroisoquinolin-1(2H)-one (**4kc**).* This compound was obtained as a yellow solid in 99% yield (101.2 mg) by following the general procedure A. m.p.: 323−325 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.11 (s, 1H), 8.63 (s, 1H), 8.44 (d, J = 8.8 Hz, 1H), 8.12 (d, J = 8.8 Hz, 1H), 7.81−7.76 (m, 4H), 7.42 (d, J = 8.0 Hz, 2H), 7.23−7.17 (m, 6H), 6.59 (d, J = 8.0 Hz, 2H), 3.66 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 161.2, 160.6, 152.0 (d, J = 14.4 Hz), 148.0, 137.7 (d, J = 9.0 Hz), 134.0 (d, J = 86.2 Hz), 132.0, 131.3 (d, J = 10.5 Hz), 130.5 (d, J = 1.8 Hz), 129.6 (d, J = 8.1 Hz), 129.0, 128.0 (d, J = 12.6 Hz), 125.8 (d, J = 3.8 Hz), 123.5, 122.7 (d, J = 7.2 Hz), 119.6, 113.3, 103.2 (d, J = 101.9 Hz), 55.3; ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.82; IR (cm^{-1}): ν 3415, 3051, 1661, 1614, 1527, 1508, 1437, 1346, 1252, 1178, 1090, 839, 794, 746, 706; HRMS (ESI): Calcd for $C_{28}H_{22}N_2O_4PS$ [M + H]$^+$ 513.1032, Found: 513.1030.

*3-(Diphenylphosphorothioyl)-4-(4-fluorophenyl)isoquinolin-1(2H)-one (**3ad**).* This compound was obtained as a white solid in 20% yield (18.6 mg) by following the general procedure A. m.p.: 220−222 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.01 (d, J = 6.1 Hz, 1H), 8.54 (d, J = 7.8 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.56−7.46 (m, 7H), 7.39−7.30 (m, 4H), 6.82 (d, J = 8.0 Hz, 1H), 6.70−6.64 (m, 2H), 6.61 (t, J = 8.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.2 (d, J = 248.7 Hz), 161.2 (d, J = 8.3 Hz), 138.3 (d, J = 11.0 Hz), 133.1 (d, J = 8.2 Hz), 132.9, 132.0, 131.9 (d, J = 11.9 Hz), 130.9 (d, J = 89.6 Hz), 129.2 (t, J = 3.5 Hz), 128.9, 128.7, 128.1 (d, J = 92.2 Hz), 127.3 (d, J = 6.7 Hz), 126.4, 124.7 (d, J = 8.4 Hz), 115.1 (d, J = 21.3 Hz) (one signal missing due to overlap); ^{31}P NMR (162 MHz, $CDCl_3$): δ 43.81; ^{19}F NMR (376 MHz, $CDCl_3$): δ −113.37; IR (cm^{-1}): ν 3418, 3239, 3217, 2923, 1673, 1601, 1507, 1477, 1436, 1330, 1224, 1103, 859, 823, 733, 710, 686; HRMS (ESI): Calcd for $C_{27}H_{20}FNOPS$ [M + H]$^+$ 456.0982, Found: 456.0979.

*4-(Diphenylphosphorothioyl)-3-(4-fluorophenyl)isoquinolin-1(2H)-one (**4ad**).* This compound was obtained as a white solid in 56% yield (50.7 mg) by following the general procedure A and 58% yield (52.4 mg) by following the general procedure B, respectively. m.p.: 305−307 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.80 (s, 1H), 8.26 (d, J = 7.7 Hz, 1H), 7.78−7.69 (m, 5H), 7.46−7.41 (m, 3H), 7.34 (t, J = 7.7 Hz, 1H), 7.27−7.23 (m, 2H), 7.19−7.14 (m, 4H), 6.84 (t, J = 8.5 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 162.6 (d, J = 247.5 Hz), 161.9, 149.0 (d, J = 14.8 Hz), 136.6 (d, J = 8.9 Hz), 134.6 (d, J = 85.5 Hz), 132.9 (d, J = 8.8 Hz), 131.2 (d, J = 10.5 Hz), 130.9, 130.4, 130.4, 130.3 (d, J = 3.7 Hz), 128.0 (d, J = 12.6 Hz), 127.5 (d, J = 6.7 Hz), 126.6 (d, J = 23.3 Hz), 125.7 (d, J = 8.9 Hz), 114.6 (d, J = 21.9 Hz), 103.8 (d, J = 101.1 Hz); ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.70; ^{19}F NMR (376 MHz, DMSO-d_6): δ −110.87; IR (cm^{-1}): ν 3417, 3051, 2914, 1656, 1604, 1508, 1435, 1235, 1092, 767, 709, 668; HRMS (ESI): Calcd for $C_{27}H_{20}FNOPS$ [M + H]$^+$ 456.0982, Found: 456.0979.

*6-Chloro-4-(diphenylphosphorothioyl)-3-(4-fluorophenyl)isoquinolin-1(2H)-one (**4id**).* This compound was obtained as a white solid in 71% yield (69.2 mg) by following the general procedure A. m.p.: 304−306 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.96 (s, 1H), 8.24 (d, J = 8.5 Hz, 1H), 7.80−7.72 (m, 5H), 7.47−7.44 (m, 3H), 7.33−7.27 (m, 2H), 7.24−7.17 (m, 4H), 6.86 (t, J = 8.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 162.7 (d, J = 247.9 Hz), 161.4, 150.3 (d, J = 14.2 Hz), 138.1 (d, J = 8.9 Hz), 136.3, 134.1 (d, J = 85.7 Hz), 132.9 (d, J = 8.9 Hz), 131.2 (d, J = 10.7 Hz), 130.6, 130.0, 128.9, 128.1 (d, J = 12.7 Hz), 126.9 (d, J = 7.0 Hz), 126.6, 124.4 (d, J = 8.7 Hz), 114.6 (d, J = 22.1 Hz), 103.0 (d, J = 100.5 Hz); ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.51; ^{19}F NMR (376 MHz, DMSO-d_6): δ −110.48; IR (cm^{-1}): ν 3373, 3170, 3051, 2918, 1657, 1600, 1508, 1437, 1308, 1233, 1090, 838, 747, 711, 619; HRMS (ESI): Calcd for $C_{27}H_{19}ClFNOPS$ [M + H]$^+$ 490.0592, Found: 490.0589.

*4-(Diphenylphosphorothioyl)-3-(4-fluorophenyl)-6-nitroisoquinolin-1(2H)-one (**4kd**).* This compound was obtained as a white solid in 99% yield (99.7 mg) by following the general procedure A. m.p.: 308−310 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.21 (s, 1H), 8.62 (s, 1H), 8.46 (d, J = 8.8 Hz, 1H), 8.15 (d, J = 8.8 Hz, 1H), 7.83−7.77 (m, 4H), 7.49 (d, J = 6.5 Hz, 2H), 7.29−7.25 (m, 2H), 7.23−7.16 (m, 4H), 6.89 (t, J = 8.5 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 162.9 (d, J = 247.9 Hz), 161.1, 151.0 (d, J = 14.0 Hz), 148.1, 137.5 (d, J = 9.1 Hz), 133.8 (d, J = 85.5 Hz), 132.9 (d, J = 8.8 Hz), 131.4 (d, J = 10.6 Hz), 130.8 (d, J = 2.1 Hz), 129.8, 129.8, 129.0 (d, J = 3.9 Hz), 128.1 (d, J = 12.7 Hz), 123.5, 122.7 (d, J = 7.2 Hz), 120.0, 114.7 (d, J = 22.2 Hz), 104.1 (d, J = 100.2 Hz); ^{31}P NMR (162 MHz, DMSO-d_6): δ 34.46; ^{19}F NMR (376 MHz, DMSO-d_6): δ −110.19; IR (cm^{-1}): ν 3415, 3054, 1661, 1528, 1437, 1347, 1309, 1236, 1093, 999, 842, 745, 708, 620; HRMS (ESI): Calcd for $C_{27}H_{19}FN_2O_3PS$ [M + H]$^+$ 501.0832, Found: 501.0834.

*4-Butyl-3-(diphenylphosphorothioyl)isoquinolin-1(2H)-one (**3ae**).* This compound was obtained as a white solid in 63% yield (52.9 mg) by following the general procedure A and 21% yield (17.2 mg) by following the general procedure B, respectively. m.p.: 192−194 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.66 (d, J = 6.5 Hz, 1H), 8.53 (d, J = 7.8 Hz, 1H), 7.84−7.79 (dd, J = 13.9, 7.3 Hz, 4H), 7.75 (d, J = 7.3 Hz, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.64−7.58 (m, 3H), 7.54−7.50 (m, 4H), 2.65 (t, J = 8.2 Hz, 2H), 0.99−0.90 (m, 2H), 0.87−0.75 (m, 2H), 0.63 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.1 (d, J = 7.9 Hz), 136.8 (d, J = 11.4 Hz), 132.8, 132.4 (d, J = 3.1 Hz), 132.0 (d, J = 11.2 Hz), 131.1 (d, J = 88.0 Hz), 129.2 (d, J = 13.1 Hz), 128.7, 128.3, 127.9 (d, J = 0.9 Hz), 124.5, 124.4 (d, J = 89.1 Hz), 124.4 (d, J = 0.9 Hz), 30.9, 29.7 (d, J = 4.4 Hz), 23.0, 13.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 42.14; IR (cm^{-1}): ν 3413, 3191, 2953, 2864, 1654, 1589, 1432, 1334, 1186, 1104, 1029, 763, 743, 687; HRMS (ESI): Calcd for $C_{25}H_{25}NOPS$ [M + H]$^+$ 418.1389, Found: 418.1392.

*3-Butyl-4-(diphenylphosphorothioyl)isoquinolin-1(2H)-one (**4ae**).* This compound was obtained as a white solid in 35% yield (29.1 mg) by following the general procedure A and 27% yield (22.9 mg) by following the general procedure B, respectively. m.p.: 253−255 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.42 (s, 1H), 8.31 (d, J = 7.4 Hz, 1H), 7.96−7.90 (m, 4H), 7.84 (d, J = 8.3 Hz, 1H), 7.49−7.35 (m, 6H), 7.33 (t, J = 7.2 Hz, 1H), 7.29−7.26 (m, 1H), 2.24−2.21 (m, 2H), 1.55−1.42 (m, 2H), 1.03−0.94 (m, 2H), 0.76 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.2, 150.4 (d, J = 16.4 Hz), 137.1 (d, J = 9.4 Hz), 135.2 (d, J = 84.8 Hz), 131.5, 131.4, 131.2 (d, J = 2.6 Hz), 128.7 (d, J = 12.7 Hz), 128.1 (d, J = 7.1 Hz), 127.0, 126.2, 105.4 (d, J = 98.2 Hz), 33.3 (d, J = 4.5 Hz), 31.4, 22.5, 13.5 (one signal missing due to overlap); ^{31}P NMR (162 MHz, $CDCl_3$): δ 34.67; IR (cm^{-1}): ν 3415, 3039, 2956, 1720, 1650, 1548, 1438, 1285, 1089, 757, 735, 697; HRMS (ESI): Calcd for $C_{25}H_{25}NOPS$ [M + H]$^+$ 418.1389, Found: 418.1392.

*4-Butyl-6-chloro-3-(diphenylphosphorothioyl)isoquinolin-1(2H)-one (**3ie**).* This compound was obtained as a white solid in 26% yield (24.0 mg) by following the general procedure A. m.p.: 190−192 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.66 (d, J = 8.5 Hz, 1H), 8.32 (d, J = 8.6 Hz, 1H), 7.87−7.81 (m, 5H), 7.75−7.69 (m, 3H), 7.65−7.56 (m, 4H), 2.59−2.55 (m, 2H), 0.89−0.78 (m, 2H), 0.71−0.58 (m, 2H), 0.53 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 159.4 (d, J = 8.1 Hz), 138.5, 138.1 (d, J = 11.4 Hz), 132.8, 131.8 (d, J = 11.5 Hz), 130.1 (d, J = 88.5 Hz), 129.6, 129.5 (d, J = 13.2 Hz), 129.1, 126.0, 125.5 (d, J = 87.0 Hz), 124.4, 122.8 (d, J = 8.9 Hz), 30.6, 28.7 (d, J = 2.8 Hz), 22.2, 13.5; ^{31}P NMR (162 MHz, DMSO-d_6): δ 42.08; IR (cm^{-1}): ν 3419, 3186, 2955, 2925, 2863, 1654, 1593, 1464, 1432, 1329, 1184, 1100, 884, 836, 783, 742, 655; HRMS (ESI): Calcd for $C_{25}H_{24}ClNOPS$ [M + H]$^+$ 452.0999, Found: 452.0999.

*3-Butyl-6-chloro-4-(diphenylphosphorothioyl)isoquinolin-1(2H)-one (**4ie**).* This compound was obtained as a white solid in 65% yield (58.6 mg) by following the general procedure A. m.p.: 250−252 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.80 (s, 1H), 8.16 (d, J = 8.5 Hz, 1H), 8.01−7.96 (m, 4H), 7.57−7.42 (m, 7H), 7.39 (dd, J = 8.5, 1.7 Hz, 1H), 2.06 (d, J = 7.8 Hz, 2H), 1.40−1.32 (m, 2H), 0.85−0.76 (m, 2H), 0.64 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 161.5, 153.2 (d, J = 15.7 Hz), 138.0 (d, J = 9.2 Hz), 136.1, 134.9 (d, J = 84.2 Hz), 131.5 (d, J = 1.5 Hz), 131.0 (d, J = 10.7 Hz), 128.9 (d, J = 12.4 Hz), 128.8, 126.4 (d, J = 7.0 Hz), 125.9, 123.8 (d, J = 8.7 Hz), 102.2 (d, J = 101.2 Hz), 32.5 (d, J = 3.9 Hz), 31.0, 21.9, 13.4; ^{31}P NMR (162 MHz, DMSO-d_6): δ 33.42; IR (cm^{-1}): ν 3423, 3169, 3048, 2924, 2865, 1669, 1596, 1435, 1316, 1096, 931, 814, 746, 696, 624; HRMS (ESI): Calcd for $C_{25}H_{24}ClNOPS$ [M + H]$^+$ 452.0999, Found: 452.0999.

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*3-Butyl-4-(diphenylphosphorothioyl)-6-nitroisoquinolin-1(2H)-one (**4ke**).* This compound was obtained as a yellow solid in 46% yield (42.4 mg) by following the general procedure A. m.p.: 254−256 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.06 (s, 1H), 8.40−8.37 (m, 2H), 8.08−7.01 (m, 5H), 7.53−7.45 (m, 6H), 2.11 (d, J = 7.8 Hz, 2H), 1.43−1.35 (m, 2H), 0.89−0.79 (m, 2H), 0.65 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 161.2, 154.0 (d, J = 15.4 Hz), 148.0, 137.3 (d, J = 9.4 Hz), 134.6 (d, J = 84.5 Hz), 131.6 (d, J = 1.9 Hz), 131.1 (d, J = 10.8 Hz), 130.3 (d, J = 11.0 Hz), 129.2 (d, J = 8.5 Hz), 128.9 (d, J = 12.8 Hz), 122.2 (d, J = 7.3 Hz), 119.3, 103.4 (d, J = 100.8 Hz), 32.6 (d, J = 4.1 Hz), 30.9, 21.9, 13.4; ^{31}P NMR (162 MHz, DMSO-d_6): δ 33.37; IR (cm^{-1}): ν 3415, 2924, 1639, 1617, 1524, 1435, 1343, 1092, 902, 786, 744, 622; HRMS (ESI): Calcd for $C_{25}H_{24}N_2O_3PS$ [M + H]$^+$ 463.1240, Found: 463.1240.

*3-(Diphenylphosphorothioyl)-4-hexylisoquinolin-1(2H)-one (**3af**).* This compound was obtained as a white solid in 57% yield (50.5 mg) by following the general procedure A and 18% yield (16.5 mg) by following the general procedure B, respectively. m.p.: 192−193 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.59 (d, J = 8.2 Hz, 1H), 8.52 (d, J = 7.9 Hz, 1H), 7.84−7.78 (m, 4H), 7.74 (dd, J = 7.0, 1.1 Hz, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.71−7.68 (m, 1H), 7.63−7.57 (m, 3H), 7.53−7.49 (m, 4H), 2.63 (d, J = 7.8 Hz, 2H), 1.15−1.08 (m, 2H), 1.01−0.83 (m, 6H), 0.80 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.2 (d, J = 8.0 Hz), 136.8 (d, J = 11.5 Hz), 132.8, 132.4 (d, J = 3.0 Hz), 132.0 (d, J = 11.2 Hz), 131.1 (d, J = 88.0 Hz), 129.2 (d, J = 13.1 Hz), 128.6, 128.2, 128.0, 124.35, 124.35 (d, J = 8.4 Hz), 124.2 (d, J = 88.4 Hz), 31.4, 29.9 (d, J = 4.3 Hz), 29.6, 29.0, 22.5, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$): δ 42.19; IR (cm^{-1}): ν 3421, 3213, 2954, 2924, 2849, 1670, 1587, 1432, 1330, 1183, 1099, 1027, 744, 711, 641; HRMS (ESI): Calcd for $C_{27}H_{29}NOPS$ [M + H]$^+$ 446.1702, Found: 446.1707.

*4-(Diphenylphosphorothioyl)-3-hexylisoquinolin-1(2H)-one (**4af**).* This compound was obtained as a white solid in 34% yield (30.4 mg) by following the general procedure A and 24% yield (21.1 mg) by following the general procedure B, respectively. m.p.: 250−252 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.43 (s, 1H), 8.32 (d, J = 7.8 Hz, 1H), 7.95−7.90 (m, 4H), 7.84 (d, J = 8.2 Hz, 1H), 7.46−7.37 (m, 6H), 7.32 (d, J = 7.0 Hz, 1H), 7.29−7.25 (m, 1H), 2.25−2.16 (t, J = 8.2 Hz, 2H), 1.54−1.46 (m, 2H), 1.26−1.17 (m, 2H), 1.14−1.07 (m, 2H), 0.97−0.90 (m, 2H), 0.84 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.3, 150.4 (d, J = 16.3 Hz), 137.1 (d, J = 9.3 Hz), 135.3 (d, J = 84.5 Hz), 131.5, 131.5 (d, J = 10.6 Hz), 131.2 (d, J = 1.9 Hz), 128.66 (d, J = 12.7 Hz), 128.74, 128.6, 127.0, 126.2, 105.4 (d, J = 98.5 Hz), 33.6 (d, J = 3.8 Hz), 31.2, 29.4, 29.1, 22.5, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$): δ 34.72; IR (cm^{-1}): ν 3480, 3414, 2924, 1662, 1551, 1470, 1436, 1344, 1260, 1093, 912, 763, 699, 673; HRMS (ESI): Calcd for $C_{27}H_{29}NOPS$ [M + H]$^+$ 446.1702, Found: 446.1707.

*6-Chloro-3-(diphenylphosphorothioyl)-4-hexylisoquinolin-1(2H)-one (**3if**).* This compound was obtained as a white solid in 31% yield (29.8 mg) by following the general procedure A and 13% yield (12.9 mg) by following the general procedure B, respectively. m.p.: 159−161 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.59 (d, J = 8.2 Hz, 1H), 8.44 (d, J = 8.6 Hz, 1H), 7.82−7.77 (m, 4H), 7.63−7.50 (m, 8H), 2.58 (d, J = 8.0 Hz, 2H), 1.18−1.09 (m, 2H), 1.00−0.86 (m, 6H), 0.81 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.5 (d, J = 8.0 Hz), 139.5, 138.3 (d, J = 11.5 Hz), 132.6 (d, J = 2.9 Hz), 131.9 (d, J = 11.3 Hz), 130.8 (d, J = 88.1 Hz), 130.0, 129.2 (d, J = 13.1 Hz), 129.0, 126.3, 126.0 (d, J = 86.4 Hz), 124.0, 123.1 (d, J = 8.9 Hz), 31.3, 29.7 (d, J = 4.3 Hz), 29.5, 28.8, 22.4, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$): δ 42.38; IR (cm^{-1}): ν 3451, 3189, 2925, 2853, 1656, 1599, 1468, 1433, 1328, 1178, 1097, 900, 780, 749, 711, 654 ; HRMS (ESI): Calcd for $C_{27}H_{28}ClNOPS$ [M + H]$^+$ 480.1312, Found: 480.1321.

*6-Chloro-4-(diphenylphosphorothioyl)-3-hexylisoquinolin-1(2H)-one (**4if**).* This compound was obtained as a white solid in 65% yield (62.4 mg) by following the general procedure A and 49% yield (46.5 mg) by following the general procedure B, respectively. m.p.: 214−216 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.80 (s, 1H), 8.16 (d, J = 8.5 Hz, 1H), 7.98 (dd, J = 13.3, 7.2 Hz, 4H), 7.57−7.43 (m, 7H), 7.39 (d, J = 8.5 Hz, 1H), 2.05 (d, J = 7.7 Hz, 2H), 1.41−1.31 (m, 2H), 1.19−1.11 (m, 2H), 1.04−0.96 (m, 2H), 0.81−0.71 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 161.5, 153.2 (d, J = 16.1 Hz), 137.9 (d, J = 9.2 Hz), 136.1, 134.9 (d, J = 84.1 Hz), 131.5, 131.0 (d, J = 10.7 Hz), 128.9 (d, J = 12.6 Hz), 128.8, 126.4 (d, J = 6.7 Hz), 125.9, 123.8 (d, J = 8.4 Hz), 102.1 (d, J = 101.4 Hz), 32.8 (d, J = 4.2 Hz), 30.6, 28.9, 28.3, 21.8, 13.9; ^{31}P NMR (162 MHz, DMSO-d_6): δ 33.42; IR (cm^{-1}): ν 3416, 3022, 2925, 2855, 1668, 1599, 1437, 1404, 1316, 1095, 706, 669; HRMS (ESI): Calcd for $C_{27}H_{28}ClNOPS$ [M + H]$^+$ 480.1312, Found: 480.1324.

*4-(Diphenylphosphorothioyl)-3-hexyl-6-nitroisoquinolin-1(2H)-one (**4kf**).* This compound was obtained as a yellow solid in 62% yield (60.7 mg) by following the general procedure A. m.p.: 239−240 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.05 (s, 1H), 8.40−8.37 (m, 2H), 8.09−8.00 (m, 5H), 7.53−7.45 (m, 6H), 2.11−2.05 (m, 2H), 1.45−1.36 (s, 2H), 1.21−1.11 (m, 2H), 1.05−0.97 (m, 2H), 0.85−0.75 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6):δ 161.2, 154.0 (d, J = 15.4 Hz), 148.0, 137.3(d, J = 9.2 Hz), 134.6 (d, J = 84.3 Hz), 131.6 (d, J = 1.9 Hz), 131.1 (d, J = 10.7 Hz), 129.2 (d, J = 8.5 Hz), 129.0, 128.9, 122.2 (d, J = 6.9 Hz), 119.3, 103.3 (d, J = 101.1 Hz), 32.8 (d, J = 4.1 Hz), 30.6, 28.9, 28.3, 21.8, 13.9; ^{31}P NMR (162 MHz, DMSO-d_6): δ 33.37; IR (cm^{-1}): ν 3416, 2928, 2857, 1671, 1561, 1437, 1347, 1095, 894, 789, 745, 709; HRMS (ESI): Calcd for $C_{27}H_{28}N_2O_3PS$ [M + H]$^+$ 491.1553, Found: 491.1556.

General Procedure for the Reaction of *N*-(Pivaloyloxy)-benzamides with (1-Alkynyl)dicyclohexylphosphine Sulfide. 1 (0.30 mmol, 3.0 equiv), **2h** (0.10 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 5.0 mol %), and AgOAc (8.4 mg, 0.05 mmol, 0.5 equiv) were successively added to a flame-dried 25 mL reaction vessel with a stir bar. After purging with argon gas, dry MeOH (0.5 mL) and dry CF_3CH_2OH (0.5 mL) were added, and the mixture was stirred at 40 °C for 45 h. Afterward, it was diluted with CH_2Cl_2 and transferred to a round-bottom flask and then evaporated under reduced pressure. Trimethyl phosphate (14 mg, 0.1 mmol) was added. Then, the appropriate amount of $CDCl_3$ was added to make sure the crude mixture was all dissolved. After ^{31}P NMR was taken, purification was performed by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1:50 to 1:10).

*3-(Dicyclohexylphosphorothioyl)-4-phenylisoquinolin-1(2H)-one (**3ah**).* This compound was obtained as a white solid in 50% yield (22.4 mg) by following the general procedure. m.p.: 234−236 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.39 (d, J = 7.1 Hz, 1H), 8.51 (dd, J = 6.2, 3.1 Hz, 1H), 7.63−7.53 (m, 5H), 7.31−7.28 (m, 2H), 6.95−6.91 (m, 1H), 1.74−1.55 (m, 12H), 1.54−1.39 (m, 4H), 1.21−1.05 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.3 (d, J = 6.5 Hz), 138.3 (d, J = 10.3 Hz), 135.0 (d, J = 1.3 Hz), 132.6, 131.0, 129.4, 128.8, 128.3, 127.6, 127.0, 126.4, 125.1 (d, J = 64.3 Hz), 121.8 (d, J = 7.4 Hz), 39.5 (d, J = 48.0 Hz), 27.4 (d, J = 2.1 Hz), 26.4 (d, J = 2.9 Hz), 26.0 (d, J = 14.5 Hz), 25.9 (d, J = 14.2 Hz), 25.2; ^{31}P NMR (162 MHz, $CDCl_3$): δ 71.85; IR (cm^{-1}): ν 3418, 3183, 3065, 2928, 2854, 1660, 1484, 1444, 1328, 1105, 1030, 1003, 849, 771, 754, 709; HRMS (ESI): Calcd for $C_{27}H_{33}NOPS$ [M + H]$^+$ 450.2015, Found: 450.2025.

*3-(Dicyclohexylphosphorothioyl)-6-methyl-4-phenylisoquinolin-1(2H)-one (**3eh**).* This compound was obtained as a white solid in 35% yield (16.0 mg) by following the general procedure. m.p.: 232−233 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.35 (d, J = 7.2 Hz, 1H), 8.40 (d, J = 8.1 Hz, 1H), 7.63−7.56 (m, 3H), 7.38 (d, J = 8.1 Hz, 1H), 7.32−7.28 (m, 2H), 6.68 (s, 1H), 2.32 (s, 3H), 1.79−1.54 (m, 12H), 1.54−1.39 (m, 4H), 1.16 (t, J = 10.0 Hz, 4H), 1.11−1.02 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.3 (d, J = 6.5 Hz), 143.3, 138.4 (d, J = 10.4 Hz), 135.0, 131.0, 129.8, 129.3, 128.8, 127.5, 126.1, 124.9 (d, J = 64.5 Hz), 124.7, 121.7 (d, J = 7.3 Hz), 39.3 (d, J = 48.0 Hz), 27.4 (d, J = 2.1 Hz), 26.3 (d, J = 2.9 Hz), 25.9 (d, J = 14.5 Hz), 25.9 (d, J = 14.0 Hz), 25.2, 22.0; ^{31}P NMR (162 MHz, $CDCl_3$): δ 71.82; IR (cm^{-1}): ν 3414, 3186, 2927, 2850, 1656, 1614, 1485, 1445, 1321, 1265, 1107, 1073, 928, 768, 705; HRMS (ESI): Calcd for $C_{28}H_{35}NOPS$ [M + H]$^+$ 464.2172, Found: 464.2178.

*6-tert-Butyl-3-(dicyclohexylphosphorothioyl)-4-phenylisoquinolin-1(2H)-one (**3wh**).* This compound was obtained as a white solid in 49% yield (25.0 mg) by following the general procedure. m.p.: 338−340 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.32 (d, J = 7.2 Hz, 1H), 8.43 (d, J = 8.4 Hz, 1H), 7.63−7.56 (m, 4H), 7.35−7.30 (m, 2H), 6.87 (d, J = 1.6 Hz, 1H), 1.77−1.70 (m, 4H), 1.67−1.57 (m, 8H), 1.54−1.42 (m, 4H), 1.36−1.25 (m, 4H), 1.17 (s, 9H), 1.11−1.02 (m, 2H); ^{13}C{^{1}H}

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NMR (100 MHz, $CDCl_3$): δ 161.2 (d, J = 6.8 Hz), 156.1, 138.2 (d, J = 10.8 Hz), 135.0, 130.9, 129.3, 128.7, 127.2, 126.4, 124.7 (d, J = 64.8 Hz), 124.7, 122.4, 122.2 (d, J = 7.7 Hz), 39.4 (d, J = 48.0 Hz), 35.2, 30.8, 27.4 (d, J = 2.0 Hz), 26.3 (d, J = 2.8 Hz), 25.9 (d, J = 14.4 Hz), 25.9 (d, J = 14.2 Hz), 25.2; ^{31}P NMR (162 MHz, $CDCl_3$): δ 71.67; IR (cm^{-1}): ν 3415, 3182, 2928, 2852, 1661, 1609, 1485, 1446, 1317, 1221, 1108, 1080, 1005, 921, 850, 766, 706; HRMS (ESI): Calcd for $C_{31}H_{41}NOPS$ $[M + H]^+$ 506.2641, Found: 506.2646.

*3-(Dicyclohexylphosphorothioyl)-6-fluoro-4-phenylisoquinolin-1(2H)-one (**3hh**).* This compound was obtained as a white solid in 19% yield (9.0 mg) by following the general procedure. m.p.: 190−192 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.37 (d, J = 7.1 Hz, 1H), 8.51 (dd, J = 8.7, 5.9 Hz, 1H), 7.63−7.57 (m, 3H), 7.32−7.22 (m, 3H), 6.54 (dd, J = 10.4, 2.1 Hz, 1H), 1.81−1.57 (m, 12H), 1.49−1.40 (m, 4H), 1.19−1.14 (m, 4H), 1.11−1.02 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.3 (d, J = 253.1 Hz), 160.5 (d, J = 7.0 Hz), 140.9 (d, J = 9.7 Hz), 134.4, 130.9, 130.8 (d, J = 9.8 Hz), 129.7, 129.1, 126.8 (d, J = 63.0 Hz), 123.6, 121.0 (dd, J = 7.7, 3.4 Hz), 116.8 (d, J = 23.5 Hz), 111.7 (d, J = 23.3 Hz), 39.4 (d, J = 47.9 Hz), 27.4 (d, J = 1.7 Hz), 26.4 (d, J = 3.0 Hz), 25.9 (d, J = 14.5 Hz), 25.9 (d, J = 14.0 Hz), 25.2; ^{31}P NMR (162 MHz, $CDCl_3$): δ 72.29; ^{19}F NMR (376 MHz, $CDCl_3$): δ −104.62; IR (cm^{-1}): ν 3418, 3181, 2923, 2853, 1664, 1611, 1482, 1446, 1341, 1310, 1261, 1092, 1037, 1004, 948, 874, 777, 755, 710; HRMS (ESI): Calcd for $C_{27}H_{32}FNOPS$ $[M + H]^+$ 468.1921, Found: 468.1926.

*3-(Dicyclohexylphosphorothioyl)-7-methyl-4-phenylisoquinolin-1(2H)-one (**3ph**).* This compound was obtained as a white solid in 42% yield (19.6 mg) by following the general procedure. m.p.: 222−223 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.27 (d, J = 6.9 Hz, 1H), 8.22 (s, 1H), 7.50−7.48 (m, 3H), 7.27 (d, J = 8.0 Hz, 1H), 7.17 (d, J = 7.5 Hz, 2H), 6.74 (d, J = 8.3 Hz, 1H), 2.48 (s, 3H), 1.73−1.47 (m, 12H), 1.11−1.03 (m, 4H), 1.00−0.95 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.3 (d, J = 9.1 Hz), 138.8, 135.9 (d, J = 10.4 Hz), 135.0, 134.0, 130.9, 129.3, 128.7, 127.1, 126.7, 126.3, 123.7 (d, J = 65.2 Hz), 122.0 (d, J = 7.4 Hz), 39.3 (d, J = 48.1 Hz), 27.4 (d, J = 2.0 Hz), 26.3 (d, J = 2.8 Hz), 25.9 (d, J = 14.5 Hz), 25.8 (d, J = 14.1 Hz), 25.2, 21.3; ^{31}P NMR (162 MHz, $CDCl_3$): δ 71.45; IR (cm^{-1}): ν 3417, 3169, 2927, 2851, 1657, 1496, 1447, 1331, 1159, 1109, 1077, 1003, 822, 769, 703; HRMS (ESI): Calcd for $C_{28}H_{35}NOPS$ $[M + H]^+$ 464.2172, Found: 464.2178.

*3-(Dicyclohexylphosphorothioyl)-7-methyl-6-nitro-4-phenylisoquinolin-1(2H)-one (**3rh**).* This compound was obtained as a white solid in 15% yield (7.6 mg) by following the general procedure. m.p.: 236−238 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.52 (d, J = 6.9 Hz, 1H), 8.47 (s, 1H), 7.66−7.59 (m, 3H), 7.39 (s, 1H), 7.28 (d, J = 7.5 Hz, 2H), 2.64 (s, 3H), 1.82−1.57 (m, 12H), 1.53−1.39 (m, 4H), 1.19−1.14 (m, 4H), 1.11−0.99 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.8 (d, J = 6.9 Hz), 152.5, 137.1 (d, J = 10.9 Hz), 133.6, 132.0, 131.9, 130.7, 130.0, 129.3, 128.9, 126.9 (d, J = 61.3 Hz), 122.2, 120.9 (d, J = 8.0 Hz), 39.4 (d, J = 47.7 Hz), 27.4 (d, J = 1.6 Hz), 26.4 (d, J = 3.0 Hz), 25.9 (d, J = 14.6 Hz), 25.9 (d, J = 14.0 Hz), 25.2, 19.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 72.70; IR (cm^{-1}): ν 3418, 3178, 2927, 2852, 1672, 1624, 1523, 1488, 1447, 1340, 1128, 1108, 824, 768, 708; HRMS (ESI): Calcd for $C_{28}H_{34}N_2O_3PS$ $[M + H]^+$ 509.2022, Found: 509.2018.

Methylation of 4aa.[31] To a suspension of 60% NaH dispersion (80 mg, 2 mmol) in dry THF (2 mL) at 0 °C under nitrogen was slowly added a solution of **4aa** (87.5 mg, 0.2 mmol) in dry THF (2 mL), and the resulting mixture was stirred at rt for 1 h. MeI (852 mg, 6 mmol) was then added dropwise, and the reaction mixture was stirred at rt for 12 h. The reaction was quenched with water and extracted with CH_2Cl_2. The combined extracts were dried, filtered, and evaporated to dryness in vacuo, and the residue was purified by column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1:50 to 1:10).

*4-(Diphenylphosphorothioyl)-2-methyl-3-phenylisoquinolin-1(2H)-one (**6aa**).* This compound was obtained as a white solid in 67% yield (60.9 mg) by following the general procedure. m.p.: 317−319 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.57−7.51 (m, 4H), 7.41 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 7.8 Hz, 1H), 7.20 (t, J = 6.9 Hz, 2H), 7.12−7.08 (m, 7H), 7.01 (t, J = 7.5 Hz, 2H), 3.10 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.1, 150.5 (d, J = 15.6 Hz), 135.2 (d, J = 9.0 Hz), 134.6 (d, J = 86.1 Hz), 132.8 (d, J = 4.4 Hz), 131.5 (d, J = 10.5 Hz), 130.9, 130.7, 130.1 (d, J = 2.8 Hz), 129.5, 128.3, 128.22, 128.0 (d, J = 12.6 Hz), 127.6, 126.9, 125.4 (d, J = 9.1 Hz), 107.7 (d, J = 99.2 Hz), 34.3; ^{31}P NMR (162 MHz, $CDCl_3$): δ 36.58; IR (cm^{-1}): ν 3415, 3051, 2918, 1658, 1603, 1533, 1476, 1434, 1325, 1182, 1092, 925, 801, 766, 751, 698; HRMS (ESI): Calcd for $C_{28}H_{23}NOPS$ $[M + H]^+$ 452.1233, Found: 452.1239.

General Procedure for Desulfidation.[8d,23] AIBN (16.4 mg, 0.01 mmol) and phosphorothioylisoquinolin-1(2*H*)-ones (0.1 mmol) were placed in a 25 mL reaction flask under argon. Toluene (2.0 mL) and tris(trimethylsilyl)silane (37.1 mg, 0.15 mmol) were sequentially added. The resulting solution was stirred at 80 °C for 12 h. Afterward, it was diluted with CH_2Cl_2 and transferred to a round-bottom flask and then evaporated under reduced pressure. Further purification was performed by flash column chromatography on silica gel.

*4-(Diphenylphosphino)-3-phenylisoquinolin-1(2H)-one (**4aa-S**).* This compound was obtained as a white solid in 88% yield (35.5 mg) by following the general procedure. m.p.: 98−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.35 (s, 1H), 8.29 (d, J = 7.8 Hz, 1H), 7.45−7.28 (m, 11H), 7.24−7.09 (m, 7H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.1, 151.2 (d, J = 51.7 Hz), 138.1 (d, J = 4.2 Hz), 136.3 (d, J = 9.1 Hz), 136.2 (d, J = 15.0 Hz), 131.9, 131.2 (d, J = 17.9 Hz), 129.7, 129.5 (d, J = 5.1 Hz), 128.7, 128.3 (d, J = 5.2 Hz), 128.2, 127.7, 127.6, 126.3, 126.2, 106.9 (d, J = 17.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ −17.04; IR (cm^{-1}): ν 3417, 3051, 2925, 1652, 1606, 1549, 1481, 1432, 1305, 768, 741, 696; HRMS (ESI): Calcd for $C_{27}H_{21}NOP$ $[M + H]^+$ 406.1355, Found: 406.1357.

*6-Chloro-4-(diphenylphosphino)-3-phenylisoquinolin-1(2H)-one (**4ia-S**).* This compound was obtained as a white solid in 70% yield (30.6 mg) by following the general procedure. m.p.: 104−106 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.40 (s, 1H), 8.06 (d, J = 8.5 Hz, 1H), 7.34−7.28 (m, 5H), 7.27−7.22 (m, 5H), 7.16−7.08 (m, 7H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.6, 152.3 (d, J = 50.6 Hz), 139.6 (d, J = 4.0 Hz), 138.6, 135.9 (d, J = 9.3 Hz), 135.5 (d, J = 14.4 Hz), 131.3 (d, J = 18.2 Hz), 129.9, 129.4 (d, J = 4.9 Hz), 129.3, 128.5 (d, J = 5.2 Hz), 128.2, 128.0, 128.0, 126.9, 124.5, 106.3 (d, J = 19.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ −16.75; IR (cm^{-1}): ν 3415, 3055, 2917, 1653, 1598, 1480, 1437, 1302, 1089, 788, 742, 697; HRMS (ESI): Calcd for $C_{27}H_{20}ClNOP$ $[M + H]^+$ 440.0966, Found: 440.0960.

*4-(Diphenylphosphino)-3-p-tolylisoquinolin-1(2H)-one (**4ab-S**).* This compound was obtained as a white solid in 78% yield (32.6 mg) by following the general procedure. m.p.: 145−147 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.59 (s, 1H), 8.42 (d, J = 7.8 Hz, 1H), 7.50−7.39 (m, 7H), 7.37−7.22 (m, 10H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.9, 140.0 (d, J = 1.0 Hz), 138.1 (d, J = 4.5 Hz), 136.2 (d, J = 14.5 Hz), 136.1, 133.6 (d, J = 1.6 Hz), 131.9, 131.3 (d, J = 17.9 Hz), 129.3 (d, J = 4.9 Hz), 129.1 (d, J = 1.6 Hz), 128.7, 128.4 (d, J = 5.2 Hz), 127.70, 127.65, 126.3 (d, J = 1.2 Hz), 126.2, 106.8 (d, J = 16.6 Hz), 21.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ −16.71; IR (cm^{-1}): ν 3413, 3049, 2921, 1650, 1583, 1478, 1432, 1307, 1181, 1091, 1030, 821, 770, 744, 695; HRMS (ESI): Calcd for $C_{28}H_{23}NOP$ $[M + H]^+$ 420.1512, Found: 420.1513.

*4-(Diphenylphosphino)-2-methyl-3-phenylisoquinolin-1(2H)-one (**6aa-S**).* This compound was obtained as a white solid in 77% yield (32.3 mg) by following the general procedure. m.p.: 243−245 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, J = 7.9 Hz, 1H), 7.55−7.54 (m, 3H), 7.48−7.42 (m, 6H), 7.40−7.28 (m, 9H), 3.45 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.2, 153.8 (d, J = 53.4 Hz), 137.2 (d, J = 10.3 Hz), 136.36 (d, J = 16.2 Hz), 136.35 (d, J = 4.0 Hz), 131.3, 131.2, 131.0, 129.0 (d, J = 4.7 Hz), 129.0, 128.8, 128.3 (d, J = 5.0 Hz), 128.1, 127.5, 126.5, 126.1, 108.9 (d, J = 14.0 Hz), 34.9; ^{31}P NMR (162 MHz, $CDCl_3$): δ −16.39; IR (cm^{-1}): ν 3414, 2924, 1647, 1604, 1543, 1476, 1434, 1331, 1050, 1026, 911, 776, 749, 698; HRMS (ESI): Calcd for $C_{28}H_{23}NOP$ $[M + H]^+$ 420.1512, Found: 420.1516.

*3-(Dicyclohexylphosphino)-4-phenylisoquinolin-1(2H)-one (**3ah-S**).* This compound was obtained as a white solid in 79% yield (33.0 mg) by following the general procedure. m.p.: 113−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.48 (s, 1H), 8.49 (d, J = 7.6 Hz, 1H), 7.57−7.50 (m, 2H), 7.45−7.41 (m, 3H), 7.19 (d, J = 5.7 Hz, 2H), 7.08 (d, J = 7.7 Hz, 1H), 2.10−1.97 (m, 2H), 1.81−1.55 (m, 10H), 1.25−1.14 (m, 10H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.1, 138.2 (d, J = 6.7 Hz), 137.1

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(d, J = 8.6 Hz), 135.3 (d, J = 38.0 Hz), 132.5, 131.9 (d, J = 2.3 Hz), 130.6 (d, J = 28.6 Hz), 128.8, 128.1, 127.5, 127.3 (d, J = 5.3 Hz), 126.4 (d, J = 1.5 Hz), 125.8, 34.0 (d, J = 14.5 Hz), 30.9 (d, J = 19.5 Hz), 29.9 (d, J = 8.3 Hz), 26.9, 26.8 (d, J = 6.4 Hz), 26.1; ^{31}P NMR (162 MHz, $CDCl_3$): δ −12.69; IR (cm^{-1}): ν 3414, 2930, 2853, 1665, 1448, 1331, 1174, 1107, 1035, 846, 768, 706; HRMS (ESI): Calcd for $C_{27}H_{33}NOP$ $[M + H]^+$ 418.2294, Found: 418.2302.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02265.

Full experimental procedures, additional experimental data, analytical data, and ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra for all new compounds (PDF)

Crystallographic data for compound **3aa** (CIF)

Crystallographic data for compound **4aa** (CIF)

Crystallographic data for compound **5fa** (CIF)

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Notes

The authors declare no competing financial interest.

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