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Silver-Catalyzed Cascade Radical Cyclization: A Direct Approach to 3,4-Disubstituted Dihydroquinolin-2(1*H*)-ones through Activation of the P−H Bond and Functionalization of the C(sp^2)−H Bond

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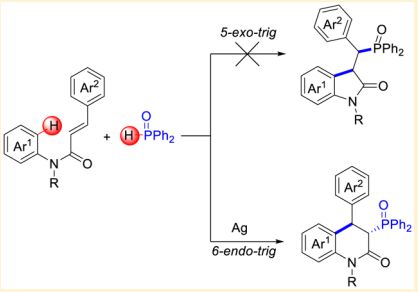
Supporting Information

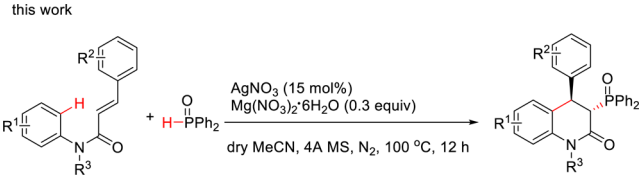
ABSTRACT: A silver-catalyzed cascade cyclization of cinnamamides with diphenylphosphine oxide was developed, in which activation of the P−H bond and functionalization of the C(sp^2)−H bond occurred. A direct method for the synthesis of 3,4-disubstituted dihydroquinolin-2(1*H*)-ones was developed.



C−P bond formation has attracted much of the attention of organic synthetic chemists, because phosphine-containing compounds are widely found in organic compounds such as pharmaceuticals, natural products, and materials.[1] Considerable effort has been spent on the research for the construction of the C−P bond.[2] Therefore, to develop easily operational and highly effective methods for construction of the C−P bond is highly desirable. Radical reaction is one of the most powerful tools in organic synthesis, especially for construction of heterocycles. Great progress has recently been made in radical cyclization for the synthesis of 3,3-disubstituted oxindoles via the 5-*exo-trig* pathway.[3] In 2013, Yang[1c] reported a silver-catalyzed carbon−phosphorus functionalization of alkenes, providing an effective strategy toward phosphorylated oxindoles. Recently, our group reported a series of tandem radical cyclizations to access 3,3-disubstituted oxindoles through decarboxylation and alkylation, trifluoromethylation, and cyanomethylation of arylacrylamides.[4] The synthesis of the 6-*endo-trig* pathway has been researched less extensively for the 6-membered ring than the 5-membered ring.[5] 3,4-Dihydroquinolin-2(1*H*)-one is a common-structure unit, and its derivatives can be used to prepare many important pharmaceuticals and natural products.[6] Much effort has been spent on the synthesis of substituted 3,4-dihydroquinolin-2(1*H*)-ones, and in most of these methods, transition metal catalysts were used.[6] However, these methods usually require multiple steps or complicated starting materials. Recently, Duan, Taylor, Hayashi, Zhao, Mai, and Xu reported several radical cyclizations for construction of the 6-membered ring through the 6-*endo-trig* pathway.[7] However, it is still highly desirable for general and direct access to the 6-membered ring.

Herein, we report a silver-catalyzed cascade P−H bond activation and C(sp^2)−H bond functionalization and provide a direct approach to valuable 3,4-disubstituted dihydroquinolin-2(1*H*)-ones through an intermolecular radical addition and an intramolecular 6-*endo-trig* cyclization procedure (Scheme 1).

Scheme 1. Silver-Catalyzed Cascade Cyclization of Cinnamamides with Diphenylphosphine Oxide



Initially, the cascade radical phosphonation−cyclization of *N*-methyl-*N*-phenylcinnamamide (**1a**) and diphenylphosphine oxide was investigated in the presence of 10 mol % $AgNO_3$ with 0.5 equiv of $Mg(NO_3)_2{\cdot}6H_2O$ in 1 mL of dry MeCN at 100 °C for 12 h. To our delight, the desired product 3-(diphenylphosphoryl)-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one (**2a**) was obtained with 36% yield (Table 1, entry 1). Encouraged by this result, we optimized the reaction conditions for this radical cyclization. However, better results were not obtained when Ag_2CO_3 or AgOAc was loaded (Table 1, entries 2 and 3). Our results showed that $Mg(NO_3)_2{\cdot}6H_2O$

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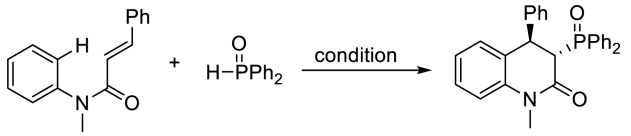
Table 1. Optimization of Reaction Conditions[a]



1a 2a

entry	catalyst (mol %)	additive (equiv)	t (°C)	time (h)	yield (%)[b]
1	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	100	12	36
2	Ag_2CO_3 (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	100	12	26
3	AgOAc (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	100	12	11
4	$AgNO_3$ (10)	$Zn(NO_3)_2·6H_2O$ (0.5)	100	12	33
5	$AgNO_3$ (10)	$NaNO_3$ (0.5)	100	12	29
6[c]	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	100	12	18
7[d]	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	100	12	26
8	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (1.0)	100	12	31
9	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.3)	100	12	64
10	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.1)	100	12	42
11	$AgNO_3$ (15)	$Mg(NO_3)_2·6H_2O$ (0.3)	100	12	75
12	$AgNO_3$ (20)	$Mg(NO_3)_2·6H_2O$ (0.3)	100	12	59
13	$AgNO_3$ (15)	$Mg(NO_3)_2·6H_2O$ (0.3)	80	12	53
14	$AgNO_3$ (15)	$Mg(NO_3)_2·6H_2O$ (0.3)	120	12	69
15	$AgNO_3$ (15)	$Mg(NO_3)_2·6H_2O$ (0.3)	100	6	46
16	$AgNO_3$ (15)	$Mg(NO_3)_2·6H_2O$ (0.3)	100	18	72
17[e]	$AgNO_3$ (15)	$Mg(NO_3)_2·6H_2O$ (0.3)	100	12	78
18[e]	$AgNO_3$ (20)		100	12	trace
19[e]		$Mg(NO_3)_2·6H_2O$ (0.3)	100	12	nd[f]

[a]Reaction condition: **1a** (0.1 mmol), diphenylphosphine oxide (0.2 mmol), dry MeCN (1 mL), under N_2 atmosphere unless otherwise noted. [b]Isolated yield. [c]DMF (1 mL) was used. [d]DCE (1 mL) was used. [e]4 Å MS (20 mg) was added. [f]Not detected.

was more effective compared to nitrates such as $Zn(NO_3)_2·6H_2O$ and $NaNO_3$ (Table 1, entries 4 and 5). Different solvents were tested, and MeCN produced the best result (Table 1, entries 1, 6, and 7). Additionally, an increase in the amount of $Mg(NO_3)_2·6H_2O$ led to a decrease in product yield, while a reduction in the amount of $Mg(NO_3)_2·6H_2O$ to 0.3 equiv led to a higher product yield (Table 1, entries 8–10). In the following study, 15 mol % was found to be the ideal amount of $AgNO_3$ (Table 1, entries 11 and 12). Furthermore, reaction temperature and time were investigated. The highest yield was obtained when the reaction was conducted at 100 °C for 12 h (Table 1, entries 13–16). The yield increased to 78% when 4 Å MS was added (Table 1, entry 17). Without the presence of $Mg(NO_3)_2·6H_2O$, trace amounts of **2a** were detected (Table 1, entry 18). Product was not obtained in the absence of $AgNO_3$ (Table 1, entry 19). The results show that $Mg(NO_3)_2·6H_2O$ is unable to promote the reaction without $AgNO_3$.

With the optimized reaction condition in hand, we then studied the scope of the radical cyclization of diphenylphosphine oxide with a series of cinnamamides. As shown in Figure 1, electron-withdrawing and electron-donating groups on

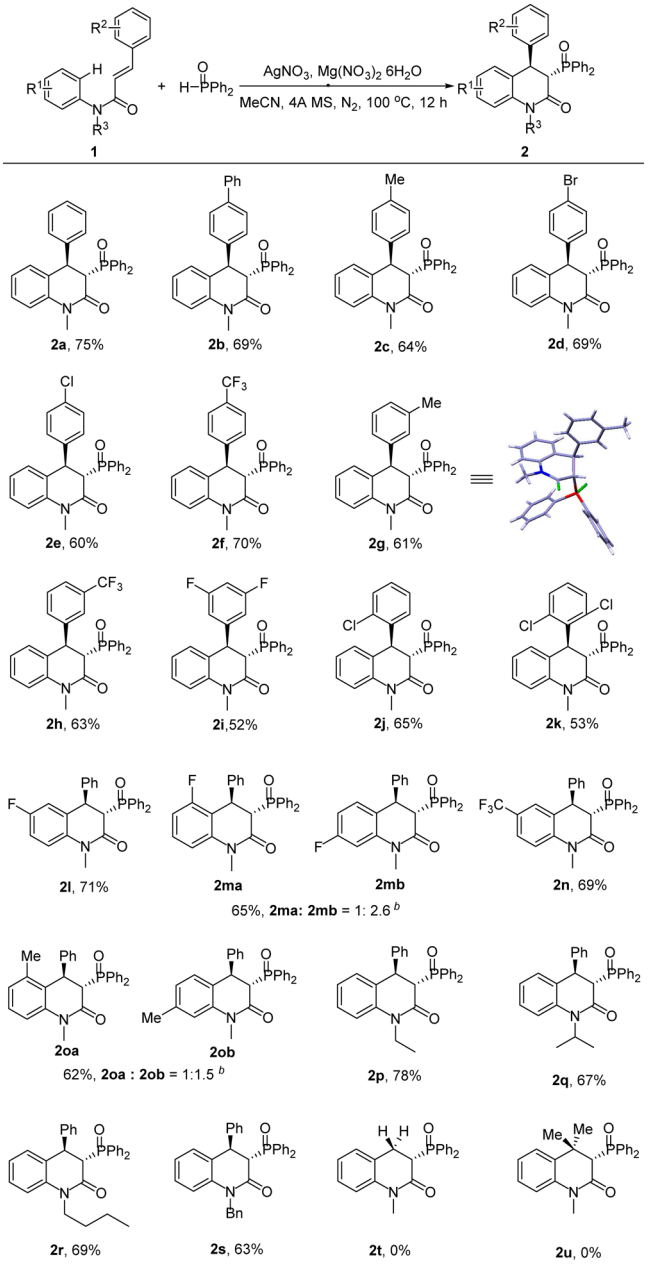


Figure 1. Silver-mediated cascade cyclization of cinnamamides with diphenylphosphine oxide. Standard conditions: cinnamamide (0.1 mmol), diphenylphosphine oxide (0.2 mmol), $AgNO_3$ (15 mol %), $Mg(NO_3)_2·6H_2O$ (0.3 equiv), 4 Å MS (20 mg), dry MeCN (1 mL), 100 °C, 12 h under N_2 atmosphere. An isolated yield was provided. A superscript b indicates the ratio of **2** to its isomer determined by ^1H NMR analysis of the crude product.

cinnamamides were all well tolerated, and the corresponding products were obtained in moderate to good yields (Figure 1, **2a–k**). Moreover, the positions of the substituent groups have no effect on the efficiency of the reaction. Similarly, cinnamamides with substituent groups such as F, Me, and CF_3 on aniline reacted well in this cyclization process, producing the corresponding products in moderate yields

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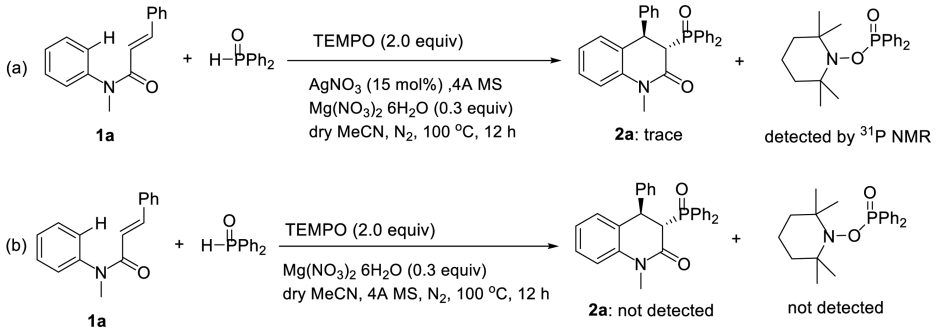
Scheme 2. Mechanism Study

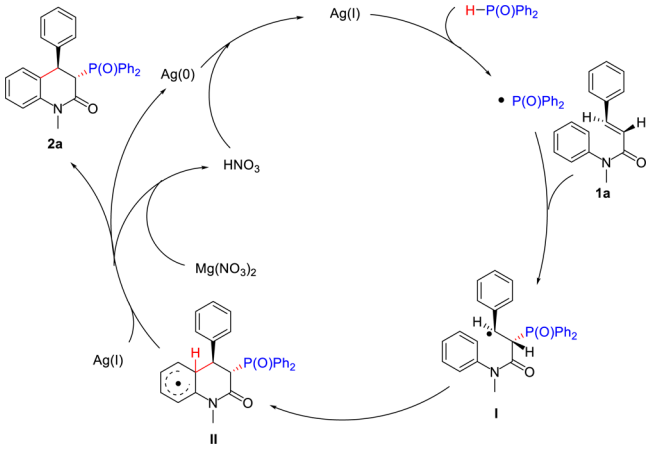


(Figure 1, **2l–o**). However, two isomers were obtained when a substituent group was at the *meta* position of aniline, which were difficult to separate (Figure 1, **2ma** and **2mb**, **2oa** and **2ob**). We found that a series of *N*-protected groups (such as Me, Et, *n*-Bu, *i*-Pr, and Bn) were well tolerated, and the corresponding products were obtained in moderate to good yields (Figure 1, **2a**, **2q–s**).

Control experiments were performed to further investigate the mechanism of this reaction. First, 2.0 equiv of radical inhibitor 2,2,6,6-tetramethylpiperidine oxide (TEMPO) was added to this reaction system under standard conditions. As we expected, traces of **2a** were detected (Scheme 2a). Meanwhile, TEMPO-P(O)Ph_2 adduct was detected by ^{31}P NMR (δ 33.5, mass calcd for $C_{21}H_{29}NO_2P$ $[M + H]^+$: 358.18, found 358.92).[8] If TEMPO was added in the absence of $AgNO_3$, no TEMPO-P(O)Ph_2 was observed (Scheme 2b). The results suggest that this reaction may go through a radical procedure.

On the basis of both our results and literature,[1c,e,9a–c] a plausible reaction mechanism for this transformation is proposed (Scheme 3). First, a P-centered radical is generated

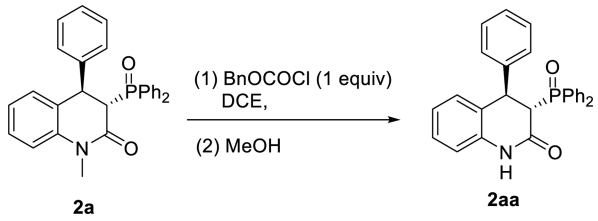
Scheme 3. Plausible Mechanism



as diphenylphosphine oxide and is oxidized by Ag(I).[1c,e] Then, the P-centered radical selectively attacks the α-position of the carbonyl group of **1a**, giving radical **I** which is stabilized by the phenyl group.[9b,c] Next, intermediate **II** is formed via an intramolecular 6-membered cyclization.[9a–c] Then, the products **2a**, HNO_3, and Ag(0) were generated after a single electron transfer from **II** to Ag(I).[9b] Finally, Ag(I) was regenerated in the presence of HNO_3.[9b]

To study the utilities of the products, a demethylation reaction of **2a** was carried out,[10] and the product 3-(diphenylphosphoryl)-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one (**2aa**) was obtained with 52% yield (Scheme 4). A new

Scheme 4. Demethylation Reaction of 2a



method to phenylphosphoryl-substituted 3,4-dihydroquinolin-2(1*H*)-one was performed, which includes the regeneration of NH, providing the possibility for inhibition of other functional groups.

In summary, we have disclosed a method for the silver-catalyzed cascade of P-central radical addition and cyclization of *N*-methyl-*N*-phenyl-cinnamamides with diphenylphosphine oxide, providing direct access to various functional 3,4-dihydroquinolin-2(1*H*)-ones. This is one of the most efficient methods for construction of 6-membered rings via the 6-*endo*-*trig* pathway. It also increases the efficiency of functionalization of the C(sp^2)–H bond.

EXPERIMENTAL SECTION

General Information. All reagents were commercially available AR reagents. Alkenes were prepared according to methods in the literature.[9] Cyclization reactions were carried out under an N_2 atmosphere. TLC was used to detect the progress of reactions and to separate the products. HRMS data were recorded by a TOF LC/MS. ^{1}H NMR, ^{19}F NMR, ^{31}P NMR, and ^{13}C NMR spectra were recorded using a 400 MHz spectrometer at room temperature, with TMS as the internal standard. Chemical shifts (δ) were determined in ppm downfield from tetramethylsilane.

Experimental Procedure for the Radical Cyclization of Cinnamamides with Diphenylphosphine Oxide. *N*-Methyl-*N*-phenylcinnamamide (**1**) (0.1 mmol, 1 equiv), diphenylphosphine oxide (0.2 mmol, 2.0 equiv), $AgNO_3$ (15 mol %), $Mg(NO_3)_2{\cdot}6H_2O$ (0.3 equiv), dry MeCN (1 mL), 4 Å MS (20 mg), and a stir bar were added to a sealed tube. The sealed tube was degassed by alternating vacuum evacuation and N_2 backfill three times. Then, the sealed tube was heated at 100 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and concentrated in vacuum. The residue was purified by TLC on silica gel (GF254) using petroleum and ethyl acetate as solvents to give the corresponding products **2**.

3-(Diphenylphosphoryl)-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (***2a***). A white solid (32.6 mg, 75%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.08–7.98 (m, 2H), 7.67–7.54 (m, 3H), 7.45–7.39 (m, 1H), 7.33–7.23 (m, 6H), 7.22–7.12 (m, 3H), 7.06–6.99 (m, 3H),

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6.63 (d, J = 8.1 Hz, 1H), 4.70 (d, J = 12.5 Hz, 1H), 4.25 (d, J = 15.2 Hz, 1H), 3.02 (s, 3H). ^{31}P NMR (162 MHz, DMSO): δ 26.49 (s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 142.0, 141.8, 139.3, 133.3, 132.3, 132.2, 131.8, 131.7, 131.4, 131.4, 131.1, 131.0, 130.7, 129.7, 129.6, 128.9, 128.8, 128.6, 128.4, 127.6, 127.5, 127.1, 127.0, 125.3, 123.9, 114.6, 52.1, 51.6, 41.3, 41.3, 29.5. HRMS (ESI): m/z calcd for $C_{28}H_{25}NO_2P$ $(M + H)^+$ 438.1617, found 438.1618.

4-([1,1′-Biphenyl]-4-yl)-3-(diphenylphosphoryl)-1-methyl-3,4-dihydroquinolin-2(1H)-one (**2b**). A white solid (35.2 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30−8.13 (m, 3H), 7.57−7.47 (m, 5H), 7.44 (d, J = 7.8 Hz, 2H), 7.39 (t, J = 6.9 Hz, 3H), 7.33−7.27 (m, 2H), 7.19−7.04 (m, 8H), 6.31 (d, J = 6.6 Hz, 1H), 5.19 (d, J = 12.0 Hz, 1H), 4.24 (d, J = 16.6 Hz, 1H), 3.01 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.50 (s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 140.0, 139.8, 139.6, 139.1, 138.3, 132.3, 131.3, 131.2, 131.2, 130.8, 130.7, 130.4, 130.4, 130.1, 130.0, 129.7, 128.7, 128.6, 127.7, 127.7, 127.6, 127.4, 126.7, 126.6, 126.4, 126.2, 126.0, 124.2, 123.0, 113.6, 51.1, 50.6, 40.0, 40.0, 28.5. HRMS (ESI): m/z calcd for $C_{34}H_{29}NO_2P$ $(M + H)^+$ 514.1930, found 514.1931.

3-(Diphenylphosphoryl)-1-methyl-4-(p-tolyl)-3,4-dihydroquinolin-2(1H)-one (**2c**). A white solid (30.1 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26−8.16 (m, 1H), 7.58−7.47 (m, 3H), 7.37−7.32 (m, 1H), 7.32−7.26 (m, 1H), 7.14−7.02 (m, 7H), 6.98 (d, J = 7.6 Hz, 1H), 6.93 (s, 1H), 6.76 (d, J = 7.7 Hz, 1H), 6.31−6.24 (m, 1H), 5.08 (d, J = 12.2 Hz, 1H), 4.19 (dd, J = 16.6, 1.1 Hz, 1H), 2.98 (d, J = 1.2 Hz, 3H), 2.25 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.46. ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 139.3, 138.9, 138.8, 136.7, 132.2, 132.2, 131.8, 131.7, 131.4, 131.4, 131.1, 131.0, 129.6, 129.6, 128.8, 128.6, 128.3, 127.6, 127.5, 126.9, 125.5, 123.9, 114.5, 52.1, 51.6, 40.9, 40.9, 29.5, 20.9. HRMS (ESI): m/z calcd for $C_{29}H_{26}NNaO_2P$ $(M + Na)^+$ 474.1593, found 474.1595.

4-(4-Bromophenyl)-3-(diphenylphosphoryl)-1-methyl-3,4-dihydroquinolin-2(1H)-one (**2d**). A white solid (35.3 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26−8.14 (m, 2H), 7.60−7.47 (m, 3H), 7.35 (d, J = 6.5 Hz, 3H), 7.29 (s, 1H), 7.16−7.03 (m, 6H), 6.92 (d, J = 7.6 Hz, 2H), 6.28 (d, J = 6.9 Hz, 1H), 5.10 (d, J = 11.8 Hz, 1H), 4.14 (d, J = 16.5 Hz, 1H), 2.97 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.42. ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 140.9, 140.8, 139.2, 133.1, 132.4, 132.3, 132.1, 132.0, 131.7, 131.6, 131.5, 131.5, 131.1, 131.0, 130.5, 129.5, 129.5, 128.8, 128.7, 128.6, 127.6, 127.5, 124.7, 124.1, 121.1, 114.7, 52.0, 51.5, 40.8, 40.8, 29.5. HRMS (ESI): m/z calcd for $C_{28}H_{24}BrNO_2P$ $(M + H)^+$ 516.0723, found 516.0725.

4-(4-Chlorophenyl)-3-(diphenylphosphoryl)-1-methyl-3,4-dihydroquinolin-2(1H)-one (**2e**). A white solid (29.5 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25−8.15 (m, 2H), 7.60−7.48 (m, 3H), 7.34 (d, J = 6.0 Hz, 1H), 7.29 (s, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.16−7.04 (m, 6H), 6.98 (d, J = 7.8 Hz, 2H), 6.29 (d, J = 6.7 Hz, 1H), 5.12 (d, J = 11.9 Hz, 1H), 4.15 (d, J = 16.5 Hz, 1H), 2.97 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.11. ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 140.4, 140.3, 139.2, 133.2, 133.0, 132.3, 132.3, 132.2, 131.7, 131.6, 131.5, 131.4, 131.1, 131.0, 130.6, 129.6, 129.5, 129.1, 128.8, 128.7, 128.6, 128.5, 127.6, 127.5, 124.8, 124.0, 114.7, 52.1, 51.6, 40.7, 40.7, 29.5. HRMS (ESI): m/z calcd for $C_{28}H_{23}ClNNaO_2P$ $(M + Na)^+$ 494.1047, found 494.1048.

3-(Diphenylphosphoryl)-1-methyl-4-(4-(trifluoromethyl)phenyl)-3,4-dihydroquinolin-2(1H)-one (**2f**). A white solid (37.7 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19−8.07 (m, 2H), 7.52−7.41 (m, 3H), 7.30−7.25 (m, 1H), 7.25−7.20 (m, 1H), 7.07−6.97 (m, 6H), 6.96−6.90 (m, 2H), 6.87−6.80 (m, 2H), 6.22 (dd, J = 7.4, 1.8 Hz, 1H), 5.05 (d, J = 11.9 Hz, 1H), 4.08 (dd, J = 16.6, 1.1 Hz, 1H), 2.91 (d, J = 1.1 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.48. ^{19}F NMR (376 MHz, $CDCl_3$): δ −115.59. ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 161.8 (d, J = 244.5 Hz), 139.2, 137.7, 137.6, 133.3, 132.3, 131.9 (d, J = 265.8 Hz), 131.7, 131.6, 131.4, 131.1, 131.0, 130.6, 129.5, 128.8, 128.7, 128.7, 128.6, 128.5, 127.60, 127.5, 125.1, 124.0, 115.9, 115.7, 114.6, 52.3, 51.7, 40.6, 29.5. HRMS (ESI): m/z calcd for $C_{29}H_{24}F_3NO_2P$ $(M + H)^+$ 506.1491, found 506.1490.

3-(Diphenylphosphoryl)-1-methyl-4-(3-(trifluoromethyl)phenyl)-3,4-dihydroquinolin-2(1H)-one (**2g**). A white solid (31.6 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27−8.16 (m, 2H), 7.59−7.49 (m, 3H), 7.45 (d, J = 7.8 Hz, 1H), 7.38−7.32 (m, 2H), 7.32−7.27 (m, 2H), 7.22 (d, J = 7.8 Hz, 1H), 7.16−7.06 (m, 6H), 6.31 (dd, J = 7.7, 1.5 Hz, 1H), 5.22 (d, J = 11.9 Hz, 1H), 4.16 (dd, J = 16.7, 1.1 Hz, 1H), 3.00 (d, J = 1.1 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.15. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.63. ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 142.9, 142.8, 139.3, 133.1, 132.4, 132.3, 132.1, 131.7, 131.6, 131.5, 131.5, 131.4, 131.1, 131.0, 130.5, 129.5, 129.5, 129.5, 128.9, 128.8, 128.7, 127.6, 127.5, 124.2, 124.2, 124.2, 124.1, 124.1, 124.0, 124.0, 123.9, 123.9 (d, J = 271.0 Hz), 114.8, 52.2, 51.7, 41.2, 41.2, 29.5. HRMS (ESI): m/z calcd for $C_{29}H_{24}F_3NO_2P$ $(M + H)^+$ 506.1491, found 506.1492.

3-(Diphenylphosphoryl)-1-methyl-4-(m-tolyl)-3,4-dihydroquinolin-2(1H)-one (**2h**). A white solid (27.4 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25−8.17 (m, 2H), 7.57−7.48 (m, 3H), 7.37−7.33 (m, 1H), 7.31−7.26 (m, 1H), 7.16−7.03 (m, 7H), 6.97 (d, J = 7.6 Hz, 1H), 6.91 (s, 1H), 6.78 (d, J = 7.7 Hz, 1H), 6.28 (dd, J = 7.5, 1.7 Hz, 1H), 5.11 (d, J = 12.2 Hz, 1H), 4.19 (dd, J = 16.6, 1.0 Hz, 1H), 2.98 (d, J = 1.1 Hz, 3H), 2.24 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.37. ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 142.0, 141.8, 139.4, 138.6, 133.5, 132.4, 132.2, 132.2, 131.8, 131.7, 131.4, 131.3, 131.1, 131.0, 130.8, 129.9, 129.6, 128.8, 128.7, 128.6, 128.3, 127.9, 127.9, 127.6, 127.4, 125.4, 123.9, 123.9, 114.6, 52.2, 51.7, 41.2, 41.2, 29.5, 21.5. HRMS (ESI): m/z calcd for $C_{29}H_{27}NO_2P$ $(M + H)^+$ 452.1774, found 452.1776.

4-(3,5-Difluorophenyl)-3-(diphenylphosphoryl)-1-methyl-3,4-dihydroquinolin-2(1H)-one (**2i**). A white solid (26.1 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26−8.15 (m, 2H), 7.64−7.48 (m, 3H), 7.38−7.27 (m, 2H), 7.16−7.05 (m, 6H), 6.63 (t, J = 8.7 Hz, 1H), 6.57 (d, J = 7.0 Hz, 2H), 6.31 (d, J = 7.3 Hz, 1H), 5.11 (d, J = 11.8 Hz, 1H), 4.14 (d, J = 16.7 Hz, 1H), 2.98 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.98. ^{19}F NMR (376 MHz, $CDCl_3$): δ −108.66. ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 163.3 (d, J = 247.9 Hz), 163.2 (d, J = 247.7 Hz), 145.9, 139.3, 133.1, 132.4, 132.4, 132.1, 131.7, 131.6, 131.5, 131.5, 131.1, 131.0, 130.4, 129.6, 129.4, 129.0, 128.8, 128.7, 127.7, 127.5, 124.1, 123.9, 114.8, 110.3, 110.3, 110.1, 110.1, 103.0, 102.7, 102.5, 51.9, 51.4, 41.0, 29.5. HRMS (ESI): m/z calcd for $C_{28}H_{22}F_2NNaO_2P$ $(M + Na)^+$ 496.1248, found 496.1249.

4-(2-Chlorophenyl)-3-(diphenylphosphoryl)-1-methyl-3,4-dihydroquinolin-2(1H)-one (**2j**). A white solid (30.5 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10−7.98 (m, 2H), 7.49−7.38 (m, 3H), 7.29 (dd, J = 8.0, 1.2 Hz, 1H), 7.26−7.19 (m, 2H), 7.15−6.97 (m, 7H), 6.95−6.90 (m, 1H), 6.43 (dd, J = 7.8, 1.4 Hz, 1H), 6.32 (d, J = 7.8 Hz, 1H), 5.41 (d, J = 12.2 Hz, 1H), 4.23 (dd, J = 16.3, 0.9 Hz, 1H), 2.92 (d, J = 1.0 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.45. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 139.3, 137.5, 137.3, 132.1, 132.1, 131.2, 131.1, 131.1, 130.7, 130.6, 130.4, 130.4, 130.3, 130.2, 129.9, 129.2, 128.9, 128.7, 127.8, 127.8, 127.7, 127.5, 127.5, 126.6, 126.5, 126.1, 123.1, 123.1, 113.6, 48.8, 48.3, 37.8, 37.8, 28.5. HRMS (ESI): m/z calcd for $C_{28}H_{24}ClNO_2P$ $(M + H)^+$ 472.1228, found 472.1226.

4-(2,6-Dichlorophenyl)-3-(diphenylphosphoryl)-1-methyl-3,4-dihydroquinolin-2(1H)-one (**2k**). A white solid (27.0 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09−8.00 (m, 2H), 7.49−7.30 (m, 6H), 7.23−7.11 (m, 4H), 7.10−7.06 (m, 2H), 7.01 (t, J = 8.0 Hz, 1H), 6.93−6.87 (m, 1H), 6.45 (dd, J = 6.0, 2.9 Hz, 1H), 6.18 (dd, J = 20.1, 2.1 Hz, 1H), 4.06 (dd, J = 16.5, 2.3 Hz, 1H), 2.95 (d, J = 1.2 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.74. ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 140.2, 139.0, 138.9, 132.5, 132.2, 132.0, 131.9, 131.7, 131.7, 131.6, 131.5, 131.3, 130.3, 129.2, 128.9, 128.7, 128.5, 128.2, 127.7, 127.6, 123.3, 122.9, 114.5, 49.3, 48.8, 37.3, 29.6. HRMS (ESI): m/z calcd for $C_{28}H_{23}Cl_2NO_2P$ $(M + H)^+$ 506.0838, found, 506.0840.

3-(Diphenylphosphoryl)-6-fluoro-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (**2l**). A white solid (32.2 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25−8.04 (m, 2H), 7.55−7.39 (m, 3H), 7.27−7.22 (m, 1H), 7.20−7.05 (m, 7H), 7.02 (dd, J = 8.3, 2.9 Hz, 1H), 7.00−6.93 (m, 2H), 6.78−6.64 (m, 1H), 6.17 (dd, J = 9.0, 4.5 Hz, 1H), 5.01 (d, J = 12.1 Hz, 1H), 4.11 (dd, J = 16.6, 1.0 Hz, 1H), 2.91 (d, J = 1.1 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.20. ^{19}F NMR (376 MHz, $CDCl_3$): δ −119.18. ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 159.0 (d, J = 243.0 Hz), 141.3, 141.2, 135.7, 135.7, 133.1, 132.3, 132.3, 132.1, 131.7, 131.6, 131.6, 131.6, 131.2, 131.1, 130.7, 129.7, 129.1, 128.8,

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128.7, 127.7, 127.6, 127.4, 127.0, 116.5, 116.3, 115.9, 115.8, 114.9, 114.7, 51.8, 51.3, 41.3, 29.7. HRMS (ESI): m/z calcd for $C_{28}H_{24}FNO_2P$ $(M + H)^+$ 456.1523, found 456.1524.

*3-(Diphenylphosphoryl)-5-fluoro-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (**2ma**) and 3-(Diphenylphosphoryl)-7-fluoro-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (**2mb**).* A white solid (29.4 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22−8.11 (m, 2H), 7.60−7.48 (m, 3H), 7.38−7.14 (m, 10H), 7.12−6.98 (m, 3H), 6.85−6.72 (m, 1H), 6.19 (d, J = 8.1 Hz, 0.72H), 5.99 (d, J = 10.5 Hz, 0.28H), 5.39 (d, J = 12.7 Hz, 0.72H), 5.12 (d, J = 11.8 Hz, 0.28H), 4.19 (dd, J = 16.1, 8.1 Hz, 1H), 3.01 (s, 2H), 2.95 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −112.93, −116.14. ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.61. ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 165.8, 159.8 (d, J = 245.9 Hz), 140.9, 140.9, 140.8, 132.9, 132.4, 131.9, 131.8, 131.7, 131.6, 131.2, 131.1, 131.1, 131.0, 130.9, 130.7, 129.8, 129.3, 129.2, 129.0, 129.0, 128.8, 128.7, 127.8, 127.7, 127.6, 127.4, 127.3, 126.9, 113.7, 113.5, 111.1, 110.8, 110.4, 110.3, 110.1, 102.6, 102.4, 52.1, 51.6, 51.1, 40.7, 34.4, 29.9, 29.6. HRMS (ESI): m/z calcd for $C_{28}H_{24}FNO_2P$ $(M + H)^+$ 456.1523, found 456.1522.

*3-(Diphenylphosphoryl)-1-methyl-4-phenyl-6-(trifluoromethyl)-3,4-dihydroquinolin-2(1H)-one (**2n**).* A white solid (34.7 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19−8.10 (m, 2H), 7.61−7.49 (m, 4H), 7.34−7.29 (m, 2H), 7.28−7.23 (m, 2H), 7.23−7.11 (m, 5H), 7.05−7.00 (m, 2H), 6.39 (d, J = 8.5 Hz, 1H), 5.19 (d, J = 12.0 Hz, 1H), 4.25 (dd, J = 16.7, 1.0 Hz, 1H), 3.05 (d, J = 0.9 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.14. ^{19}F NMR (376 MHz, $CDCl_3$): δ −61.93. ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 142.2, 141.1, 141.0, 132.8, 132.5, 132.4, 131.7, 131.7, 131.7, 131.6, 131.1, 131.0, 130.5, 129.5, 129.2, 128.8, 128.7, 127.8, 127.6, 127.5, 126.9, 126.5, 126.5, 126.0, 125.9, 125.7, 125.6, 125.6, 123.9 (q, J = 270.1 Hz), 114.6, 51.6, 51.1, 41.2, 41.2, 29.7. HRMS (ESI): m/z calcd for $C_{29}H_{24}F_3NO_2P$ $(M + H)^+$ 506.1491, found 506.1490.

*3-(Diphenylphosphoryl)-1,5-dimethyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (**2oa**) and 3-(Diphenylphosphoryl)-1,7-dimethyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (**2ob**).* A white solid (27.8 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36−8.10 (m, 2H), 7.63−7.44 (m, 3H), 7.37−6.83 (m, 14H), 6.16 (d, J = 7.9 Hz, 0.60H), 6.04 (s, 0.40H), 5.26 (d, J = 11.9 Hz, 0.60H), 5.09 (d, J = 12.0 Hz, 0.40H), 4.18 (dd, J = 16.3, 11.3 Hz, 1H), 2.98 (d, J = 4.7 Hz, 3H), 2.36 (s, 2H), 2.24 (s, 1H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.82, 26.76. ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 165.8, 142.0, 141.8, 140.3, 140.2, 139.8, 139.3, 138.2, 137.3, 132.6, 132.2, 131.8, 131.7, 131.6, 131.5, 131.3, 131.3, 131.2, 131.1, 131.0, 130.9, 129.4, 129.0, 128.9, 128.8, 128.7, 128.7, 128.6, 128.0, 127.6, 127.5, 127.4, 127.4, 127.3, 127.2, 127.1, 127.0, 125.8, 124.5, 123.8, 122.3, 115.4, 112.7, 53.0, 52.5, 52.3, 51.8, 40.8, 40.8, 37.8, 37.8, 29.8, 29.6, 21.4, 20.9, 19.3. HRMS (ESI): m/z calcd for $C_{29}H_{27}NO_2P$ $(M + H)^+$ 452.1774, found 452.1775.

*3-(Diphenylphosphoryl)-1-ethyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (**2p**).* A white solid (35.0 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19−8.09 (m, 2H), 7.52−7.39 (m, 3H), 7.29 (dd, J = 7.3, 1.6 Hz, 1H), 7.22−7.17 (m, 1H), 7.16−6.97 (m, 9H), 6.97−6.93 (m, 2H), 6.35 (d, J = 7.8 Hz, 1H), 5.04 (d, J = 12.3 Hz, 1H), 4.07 (dd, J = 16.6, 1.1 Hz, 1H), 3.70 (dd, J = 14.2, 7.2 Hz, 1H), 3.45 (dd, J = 14.2, 7.1 Hz, 1H), 0.80 (t, J = 7.1 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.99. ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 142.0, 141.9, 138.5, 133.4, 132.3, 132.2, 132.2, 131.8, 131.7, 131.4, 131.4, 131.3, 130.9, 129.9, 128.9, 128.8, 128.6, 128.4, 127.7, 127.6, 127.1, 127.1, 125.8, 123.9, 114.9, 52.3, 51.8, 41.5, 41.5, 37.5, 12.2. HRMS (ESI): m/z calcd. for $C_{29}H_{27}NO_2P$ $(M + H)^+$: 452.1774, found 452.1777.

*3-(Diphenylphosphoryl)-1-isopropyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (**2q**).* A white solid (31.0 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33−8.18 (m, 2H), 7.57−7.50 (m, 3H), 7.46−7.42 (m, 1H), 7.32−7.27 (m, 1H), 7.25−7.15 (m, 3H), 7.14−6.98 (m, 8H), 6.51−6.41 (m, 1H), 5.09 (d, J = 11.5 Hz, 1H), 4.31−4.15 (m, 2H), 1.20 (d, J = 6.8 Hz, 3H), 1.12 (d, J = 7.0 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.97. ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 141.3, 141.2, 141.1, 140.8, 140.0, 132.2, 132.1, 131.8, 131.7, 131.5, 131.4, 131.2, 131.2, 129.9, 128.8, 128.7, 128.6, 128.2, 127.8, 127.7, 127.3, 127.0, 124.1, 116.6, 53.3, 52.8, 50.1, 41.2, 41.2, 20.4, 18.9. HRMS (ESI): m/z calcd. for $C_{30}H_{28}NNaO_2P$ $(M + Na)^+$: 488.1750, found 488.1751.

*1-Butyl-3-(diphenylphosphoryl)-4-phenyl-3,4-dihydroquinolin-2(1H)-one (**2r**).* A white solid (32.9 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21−8.08 (m, 2H), 7.50−7.40 (m, 3H), 7.30 (dd, J = 7.2, 1.7 Hz, 1H), 7.24−7.19 (m, 1H), 7.16−7.10 (m, 2H), 7.10−6.98 (m, 7H), 6.97−6.94 (m, 2H), 6.31 (d, J = 7.8 Hz, 1H), 5.05 (d, J = 12.3 Hz, 1H), 4.11 (dd, J = 16.6, 1.0 Hz, 1H), 3.81−3.64 (m, 1H), 3.28−3.16 (m, 1H), 1.29−0.98 (m, 4H), 0.76 (t, J = 7.2 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.04. ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 142.0, 141.8, 138.5, 133.4, 132.4, 132.2, 132.2, 131.8, 131.7, 131.4, 131.4, 131.3, 130.9, 130.0, 129.9, 128.8, 128.8, 128.6, 128.4, 127.7, 127.5, 127.2, 127.1, 125.7, 123.9, 114.9, 52.3, 51.7, 42.0, 41.4, 41.3, 28.8, 20.1, 13.7. HRMS (ESI): m/z calcd. for $C_{31}H_{30}NNaO_2P$ $(M + Na)^+$: 502.1906, found 502.1908.

*1-Benzyl-3-(diphenylphosphoryl)-4-phenyl-3,4-dihydroquinolin-2(1H)-one (**2s**).* A white solid (32.2 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25−8.13 (m, 2H), 7.60−7.51 (m, 3H), 7.3−7.21 (m, 5H), 7.20−7.11 (m, 8H), 7.05−6.97 (m, 4H), 6.93 (dd, J = 6.5, 2.7 Hz, 2H), 6.51−6.44 (m, 1H), 5.38 (d, J = 15.7 Hz, 1H), 5.07 (d, J = 12.1 Hz, 1H), 4.32 (dd, J = 15.9, 0.8 Hz, 1H), 4.18 (d, J = 15.7 Hz, 1H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.22. ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 141.6, 141.5, 138.2, 136.0, 133.1, 132.3, 132.3, 132.1, 131.8, 131.7, 131.6, 131.6, 131.4, 131.3, 130.8, 129.9, 129.9, 128.9, 128.8, 128.7, 128.4, 128.3, 127.8, 127.7, 127.6, 127.3, 127.3, 127.1, 125.6, 124.0, 115.4, 52.1, 51.6, 45.0, 41.4, 41.4. HRMS (ESI): m/z calcd. for $C_{34}H_{29}NO_2P$ $(M + H)^+$: 514.1930, found 514.1931.

*3-(Diphenylphosphoryl)-4-phenyl-3,4-dihydroquinolin-2(1H)-one (**2aa**).* A white solid (27.8 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 8.20−8.10 (m, 2H), 7.60−7.47 (m, 3H), 7.34−7.19 (m, 5H), 7.18−7.15 (m, 1H), 7.11−7.02 (m, 4H), 6.97 (dd, J = 5.7, 3.3 Hz, 2H), 6.18 (dd, J = 5.6, 3.5 Hz, 1H), 5.12 (d, J = 13.1 Hz, 1H), 4.06 (d, J = 16.7 Hz, 1H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.10. ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 142.7, 142.6, 136.2, 132.7, 132.3, 132.3, 131.9, 131.8, 131.7, 131.7, 131.6, 131.5, 130.1, 129.3, 129.2, 129.0, 128.8, 128.6, 128.3, 127.7, 127.6, 127.2, 127.1, 124.0, 123.6, 115.5, 51.8, 51.3, 41.8, 41.8. HRMS (ESI): m/z calcd. for $C_{27}H_{22}NNaO_2P$ $(M + Na)^+$: 446.1280, found 446.1283.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01879.

^{1}H, ^{31}P, ^{19}F, and ^{13}C NMR spectra of compounds **2a**−**s** (PDF)

X-ray crystal structure of **2g** (CIF)

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Notes

The authors declare no competing financial interest.

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