

Supporting Information

**Palladium(II)-catalyzed Oxidative C(sp³)-P Bond Formation via
C(sp³)-H Bond Activation**

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I. General remarks

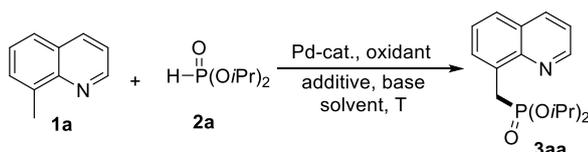
NMR spectra were obtained on a Bruker AMX-600 or Bruker AMX-400. The ^1H NMR chemical shifts were measured relative to CDCl_3 or DMSO-d_6 as the internal reference (CDCl_3 : $\delta = 7.260$ ppm; DMSO : $\delta = 2.500$ ppm). The ^{13}C NMR chemical shifts were given using CDCl_3 as the internal standard (CDCl_3 : $\delta = 77.16$ ppm). High-resolution mass spectra (HR-MS) were obtained with a Bruker-impact II (ESI^+).

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. 8-Methylquinoline **1a**, 8-ethylquinoline **1x**, H-phosphonates **2a-2f**, and diphenylphosphine oxide **2g** were purchased from Adamas-beta[®]. Substituted 8-methylquinolines **1b-1w** [1-7] and functionalized diarylphosphine oxides **2h-2k** [8] were prepared according to the literatures. All solvents were dried according to standard methods prior to use.

II. Optimization of the reaction conditions.

A Schlenk test tube equipped with a magnetic stir bar was charged with Pd-catalyst, 8-methylquinoline **1a** (0.5 mmol, 2.0 equiv.), oxidant (3.0 equiv.), base (2.0 equiv.), additive and solvent (2.0 mL) under N_2 . The resulting mixture was stirred for 10 min at 120 °C, and then diisopropyl phosphite **2a** (0.25 mmol, 1.0 equiv) in solvent (1 mL) was added dropwise via a syringe pump. After addition, the mixture was stirred at 120 °C for indicated time. After cooling to room temperature, the reaction solution was diluted with 20 mL of CH_2Cl_2 , then filtered through a celite pad and concentrated under vacuum. The residue was purified by column chromatography on silica gel (100-200 mesh) to provide the desired product **3aa**.

Table S1. Optimization of reaction condition.^[a]



entry	Pd-cat.	oxidant	base	additive	solvent	Yield (%)
1	$\text{Pd}(\text{OAc})_2$	AgOAc	NaOAc	BQ	<i>t</i> -AmylOH	72
2	$\text{Pd}(\text{TFA})_2$	AgOAc	NaOAc	BQ	<i>t</i> -AmylOH	51

3	Pd(PPh ₃) ₄	AgOAc	NaOAc	BQ	<i>t</i> -AmylOH	trace
4	Pd(<i>dba</i>) ₂	AgOAc	NaOAc	BQ	<i>t</i> -AmylOH	43
5	Pd(<i>dppf</i>)Cl ₂	AgOAc	NaOAc	BQ	<i>t</i> -AmylOH	26
6	[RhCp*Cl] ₂	AgOAc	NaOAc	BQ	<i>t</i> -AmylOH	trace
7	-	AgOAc	NaOAc	BQ	<i>t</i> -AmylOH	n.d
8	Pd(OAc) ₂	Ag ₂ CO ₃	NaOAc	BQ	<i>t</i> -AmylOH	40
9	Pd(OAc) ₂	AgTFA	NaOAc	BQ	<i>t</i> -AmylOH	21
10	Pd(OAc) ₂	Ag ₂ O	NaOAc	BQ	<i>t</i> -AmylOH	trace
11	Pd(OAc) ₂	Cu(OAc) ₂	NaOAc	BQ	<i>t</i> -AmylOH	n.d
12	Pd(OAc) ₂	Mn(OAc) ₃ ·2H ₂ O	NaOAc	BQ	<i>t</i> -AmylOH	n.d
13	Pd(OAc) ₂	K ₂ S ₂ O ₈	NaOAc	BQ	<i>t</i> -AmylOH	n.d
14	Pd(OAc) ₂	-	NaOAc	BQ	<i>t</i> -AmylOH	n.d
15	Pd(OAc) ₂	AgOAc	NaOAc	BQ	<i>t</i> -BuOH	32
16	Pd(OAc) ₂	AgOAc	NaOAc	BQ	1,4-dioxane	34
17	Pd(OAc) ₂	AgOAc	NaOAc	BQ	DMSO	trace
18	Pd(OAc) ₂	AgOAc	NaOAc	BQ	ethyl glyme	22
19	Pd(OAc) ₂	AgOAc	NaOAc	1,4-naphthoquinone	<i>t</i> -AmylOH	46
20	Pd(OAc) ₂	AgOAc	NaOAc	1,2,4,5-tetrachlorobenzoquinone	<i>t</i> -AmylOH	trace
21	Pd(OAc) ₂	AgOAc	NaOAc	2,6-ditertbutyl-1,4-benzoquinone	<i>t</i> -AmylOH	trace
22	Pd(OAc) ₂	AgOAc	NaOAc	2,3,5-trimethyl-1,4-benzoquinone	<i>t</i> -AmylOH	trace
23	Pd(OAc) ₂	AgOAc	NaOAc	anthraquinone	<i>t</i> -AmylOH	trace
24	Pd(OAc) ₂	AgOAc	NaOAc	NMMI	<i>t</i> -AmylOH	trace
25	Pd(OAc) ₂	AgOAc	NaOAc	maleic anhydride	<i>t</i> -AmylOH	trace
26	Pd(OAc) ₂	AgOAc	NaOAc	DDQ	<i>t</i> -AmylOH	trace
27	Pd(OAc) ₂	AgOAc	NaOAc	BQ+X-phos (20 mol%)	<i>t</i> -AmylOH	trace
28	Pd(OAc) ₂	AgOAc	NaOAc	BQ+S-phos (20 mol%)	<i>t</i> -AmylOH	trace
29	Pd(OAc) ₂	AgOAc	NaOAc	-	<i>t</i> -AmylOH	n.d
30	Pd(OAc) ₂	AgOAc	NaOAc	BQ (0.2 equiv)	<i>t</i> -AmylOH	21
31	Pd(OAc) ₂	AgOAc	NaOAc	BQ (2 equiv)	<i>t</i> -AmylOH	44
32	Pd(OAc) ₂	AgOAc	NaOAc	BQ (4 equiv)	<i>t</i> -AmylOH	43
33	Pd(OAc) ₂	AgOAc	-	BQ	<i>t</i> -AmylOH	n.d
34	Pd(OAc) ₂	AgOAc	LiOAc	BQ	<i>t</i> -AmylOH	52
35	Pd(OAc) ₂	AgOAc	KOAc	BQ	<i>t</i> -AmylOH	28
36	Pd(OAc) ₂	AgOAc	CsOAc	BQ	<i>t</i> -AmylOH	trace
37	Pd(OAc) ₂	AgOAc	NaHCO ₃	BQ	<i>t</i> -AmylOH	49
38	Pd(OAc) ₂	AgOAc	PivONa	BQ	<i>t</i> -AmylOH	26
39	Pd(OAc) ₂	AgOAc	PhCOONa	BQ	<i>t</i> -AmylOH	46
40	Pd(OAc) ₂	AgOAc	K ₂ CO ₃	BQ	<i>t</i> -AmylOH	trace
41	Pd(OAc) ₂	AgOAc	K ₃ PO ₄	BQ	<i>t</i> -AmylOH	trace
42	Pd(OAc) ₂	AgOAc	NEt ₃	BQ	<i>t</i> -AmylOH	trace
43	Pd(OAc) ₂	AgOAc	DBU	BQ	<i>t</i> -AmylOH	trace
44^[b]	Pd(OAc)₂	AgOAc	NaOAc	BQ	<i>t</i>-AmylOH	71
45 ^[c]	Pd(OAc) ₂	AgOAc	NaOAc	BQ	<i>t</i> -AmylOH	41

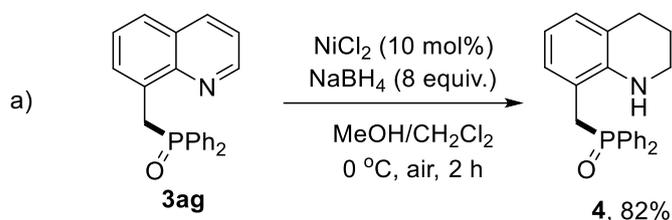
46 ^[d]	Pd(OAc) ₂	AgOAc	NaOAc	BQ	<i>t</i> -AmylOH	62
47 ^[e]	Pd(OAc) ₂	AgOAc	NaOAc	BQ	<i>t</i> -AmylOH	60
48 ^[f]	Pd(OAc) ₂	AgOAc	NaOAc	BQ	<i>t</i> -AmylOH	55
49 ^[g]	Pd(OAc) ₂	AgOAc	NaOAc	BQ	<i>t</i> -AmylOH	44

^a Reaction was carried out using **1a** (0.5 mmol), Pd-cat. (0.025 mmol), base (0.5 mmol), oxidant (0.75 mmol), additive (0.25 mmol) in solvent (2 mL) for 10 hours at 120 °C, and **2a** (0.25 mmol) dissolved in *t*-AmylOH (1 mL) was added dropwise to the reaction mixture over 8 hours. [b] **1a** (0.25 mmol), **2a** (0.75 mmol); [c] feeding time 4 hour, total reaction time 6 hours; [d] feeding time 6 hour, total reaction time 8 hours; [e] feeding time 16 hour, total reaction time 24 hours. [f] 110 °C; [g] 130 °C.

III. General procedure for Pd-catalyzed cross-coupling of 8-methylquinolines **1** with H-phosphonates or diarylphosphine oxides **2**.

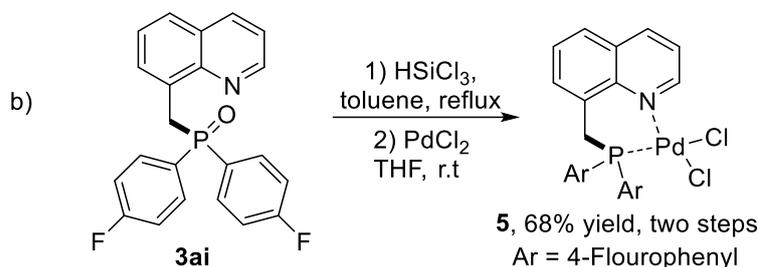
In a 25 mL rubber-sealed tube, a mixture of 8-methylquinolines **1** (0.5 mmol, 2.0 equiv), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 10 mol%), AgOAc (125 mg, 0.75 mmol, 3.0 equiv.), 1,4-benzoquinone (27 mg, 0.25 mmol, 1.0 equiv.) and NaOAc (41 mg, 2 equiv) in *t*-AmylOH (2.0 mL) was stirred at 120 °C under N₂ for 10 min. Then H-phosphonates or diarylphosphine oxides **2** (0.25 mmol, 1.0 equiv) in *t*-AmylOH (1 mL) was added dropwise via a syringe pump in 8 h. After addition, the mixture was stirred at the same temperature for another 2 h. After cooling to room temperature, the mixture was filtered through a celite pad and concentrated under vacuum. The residue was purified by column chromatography on silica gel (100-200 mesh) to provide the desired product **3**.

IV. Procedure for derivatization reactions of products **3**.



To a mixture of **3ag** (0.2 mmol, 68.6 mg) and NiCl₂ (10 mol %, 2.6 mg) in MeOH (1.6 mL) and CH₂Cl₂ (0.8 mL), NaBH₄ (1.6 mmol, 60.8 mg) was added in portions with stirring at 0 °C for 1 h. After addition, the mixture was stirred at the same temperature for another 1 h. After

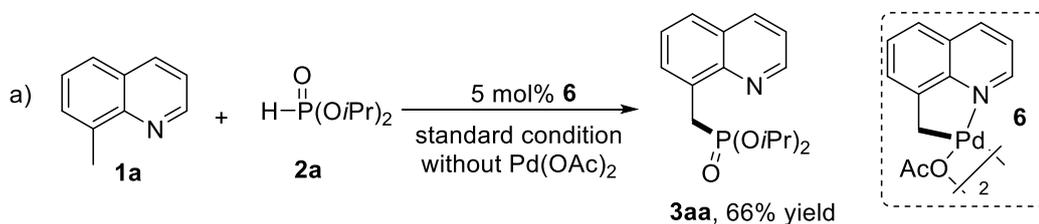
the removal of the solvents, the residue was purified by flash column chromatography on silica gel to provide the product **4** as a white solid (57 mg, 82% yield).



In a 25 mL Schlenk test tube, **3ai** (0.2 mmol, 76 mg) were suspended in anhydrous toluene (2 mL), then NEt_3 (2 mmol, 278 μL) and HSiCl_3 (1 mmol, 100 μL) were added by syringe. Subsequently, the mixture was refluxed for 3 h. The mixture was then quenched by saturated sodium bicarbonate solution (1 mL). The aqueous phase was separated and extracted three times with toluene. The combined organic fractions were concentrated in vacuo to give the corresponding phosphine as a white solid. Without further purification, the phosphine was redissolved in anhydrous THF (10 mL), and then PdCl_2 (0.2 mmol, 35.5 mg) was added under nitrogen atmosphere. The resulting mixture was stirred at room temperature for 24 h. Finally, the suspension was filtrated. The filter cake was washed with THF and dried in vacuo to give the target palladium complex **5** as a brown solid (73.3 mg, 68% yield over two steps).

V. Mechanism study.

(a) Reaction in Scheme 5a.



1) Preparation of palladacycle **6**:

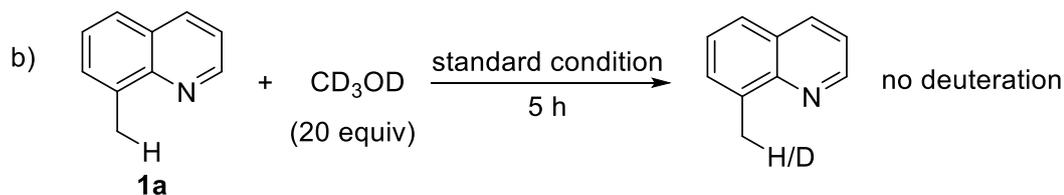
8-Methylquinoline (186 mg, 1.3 mmol) and Pd(OAc)_2 (291 mg, 1.3 mmol) were suspended in glacial acetic acid (20 mL). The mixture was refluxed for 1.5 h, and then filtered. Water (150 mL) was added to the filtrate, and the mixture was allowed to sit overnight. The

precipitated product was collected by filtration and recrystallized from CH₂Cl₂/hexane to yield **6** as a bright orange solid.

2) Coupling Reaction between **1a** and **2a** in the presence of intermediate **6**:

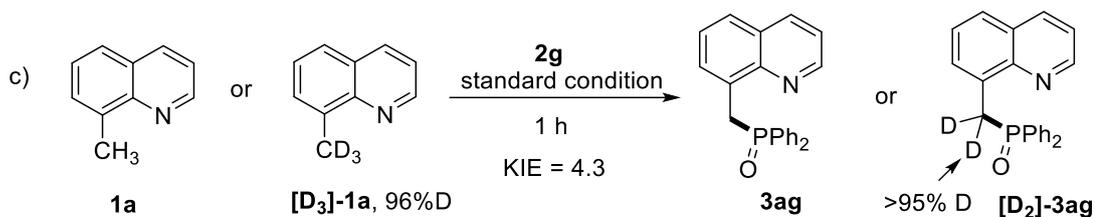
In a 25 mL sealed tube, a mixture of 8-methylquinoline **1a** (0.5 mmol, 2.0 equiv), **6** (7.6 mg, 0.0125 mmol, 5 mol%), AgOAc (125 mg, 0.75 mmol, 3.0 equiv.), 1,4-benzoquinone (27 mg, 0.25 mmol, 1.0 equiv.) and NaOAc (41 mg, 2 equiv) in *t*-AmylOH (2.0 mL) was stirred at 120 °C under N₂ for 10 min. Then **2a** (0.25 mmol, 1.0 equiv) in *t*-AmylOH (1 mL) was added dropwise via a syringe pump in 8 h. After addition, the mixture was stirred at the same temperature for another 2 h. After cooling to room temperature, the mixture was filtered through a celite pad and concentrated under vacuum. The residue was purified by column chromatography on silica gel (100-200 mesh) to provide the desired product **3aa** (66% yield).

(b) Reaction in Scheme 5b.

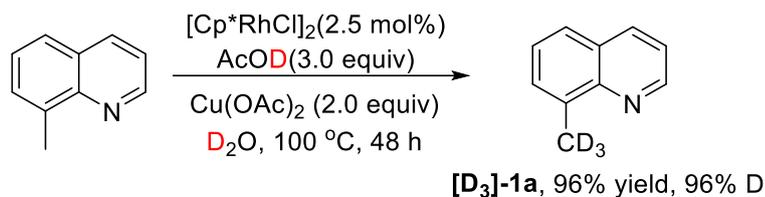


In a 25 mL sealed tube, a mixture of 8-methylquinoline **1a** (0.5 mmol, 2.0 equiv), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 10 mol%), AgOAc (125 mg, 0.75 mmol, 3.0 equiv.), 1,4-benzoquinone (27 mg, 0.25 mmol, 1.0 equiv.), NaOAc (41 mg, 2 equiv) and CD₃OD (207 μ L, 5 mmol, 20 equiv) in *t*-AmylOH (2.0 mL) was stirred at 120 °C under N₂ for 5 hours. After cooling to room temperature, the mixture was filtered through a celite pad and concentrated under vacuum. The residue was purified by column chromatography on silica gel (100-200 mesh) to recover the starting material **1a**, and no deuteration of the methyl C–H bonds was detected via ¹H NMR test.

(c) Reaction in Scheme 5c.



1) Preparation of **[D₃]-1a**

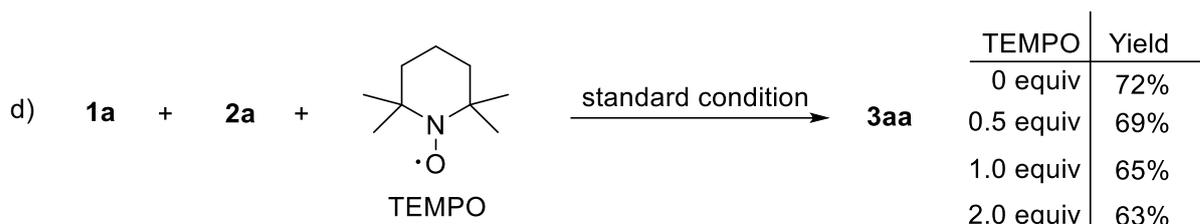


A Schlenk test tube equipped with a magnetic stir bar was charged with 8-methylquinoline (**1a**) (43.0 mg, 0.3 mmol), $[\text{RhCp}^*\text{Cl}_2]_2$ (4.6 mg, 0.0075 mmol, 2.5 mol %), AcOD (54.1 mg, 0.9 mmol, 300 mol %), $\text{Cu}(\text{OAc})_2$ (109.0 mg, 0.6 mmol, 200 mol %) and D_2O (1 mL) under air. The reaction mixture was heated at 100 °C for 20 h. After cooling down, the reaction mixture was extracted with EtOAc (10 mL). The organic layer was dried over MgSO_4 , and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 10:1) to afford **[D₃]-1a** (42.1 mg, 96% D) in 96% yield.

2) Procedure for the parallel KIE experiments

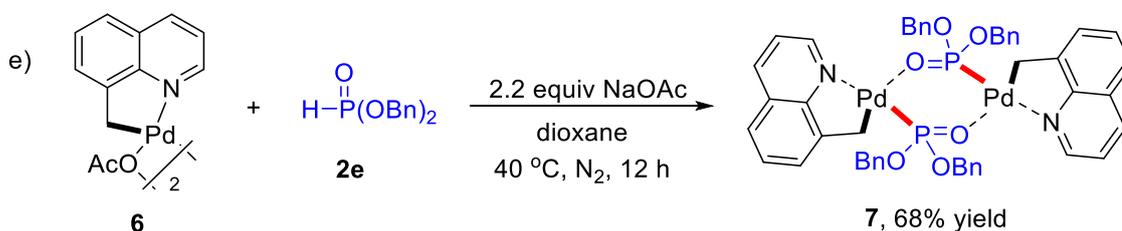
In a 25 mL sealed tube, a mixture of 8-methylquinoline **1a** or 8-methylquinoline-*d*₃ **[D₃]-1a** (0.25 mmol, 1.0 equiv), $\text{Pd}(\text{OAc})_2$ (5.6 mg, 0.025 mmol, 10 mol%), AgOAc (125 mg, 0.75 mmol, 3.0 equiv.), 1,4-benzoquinone (27 mg, 0.25 mmol, 1.0 equiv.) and NaOAc (41 mg, 2 equiv) in *t*-AmylOH (2.0 mL) was stirred at 120 °C under N_2 for 10 min. Then diphenylphosphine oxides **2g** (152 mg, 0.75 mmol, 3.0 equiv) in *t*-AmylOH (1 mL) was added dropwise via an automatic syringe. After one hour, both reactions were rapidly quenched in ice water. The reactions mixtures were filtered through a celite pad and concentrated under vacuum. The residues were purified by column chromatography on silica gel (100-200 mesh) to provide the desired product **3ag** (14.6 mg, 17% yield) and **[D₂]-3ag** (3.3 mg, 4% yield).

(d) Reaction in Scheme 5d.



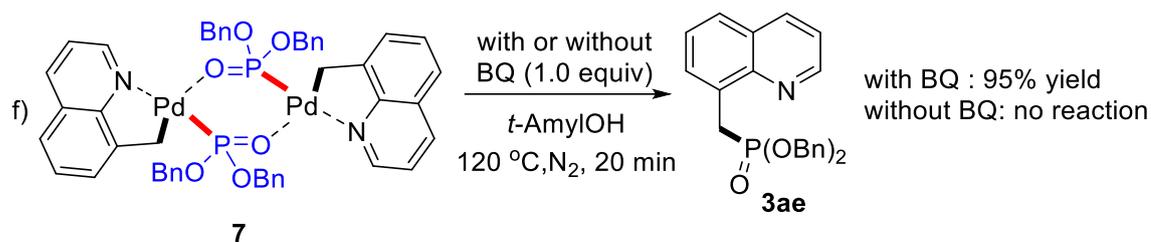
In a 25 mL sealed tube, a mixture of 8-methylquinoline **1a** (0.5 mmol, 2.0 equiv), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 10 mol%), AgOAc (125 mg, 0.75 mmol, 3.0 equiv.), 1,4-benzoquinone (27 mg, 0.25 mmol, 1.0 equiv.), NaOAc (41 mg, 2 equiv) and 2,2,6,6-tetramethylpiperidine *N*-oxide (indicated equivalents) in *t*-AmylOH (2.0 mL) was stirred at 120 °C under N₂ for 10 min. Then **2a** (0.25 mmol, 1.0 equiv) in *t*-AmylOH (1 mL) was added dropwise via a syringe pump in 8 h. After addition, the mixture was stirred at the same temperature for another 2 h. After cooling to room temperature, the mixture was filtered through a celite pad and concentrated under vacuum. The residue was purified by column chromatography on silica gel (100-200 mesh) to provide the desired product **3aa**.

(e) Reaction in Scheme 5e.



A Schlenk test tube equipped with a magnetic stir bar was charged with palladium complex **6** (64 mg, 0.10 mmol, 1.0 equiv), NaOAc (18 mg, 0.22 mmol, 2.2 equiv), dioxane (2.0 mL) and **2e** (52.4 mg, 0.2 mmol, 2.0 equiv). The reaction was stirred at 40 °C for 12 h. After cooling to room temperature, the reaction mixture was filtered through a celite pad and concentrated under vacuum. The residues were purified by column chromatography on silica gel (100-200 mesh) to provide complex **7** (62 mg, 68% yield). Single crystal of **7**, which was suitable for X-ray crystallographic analysis, was obtained by evaporation from an ethyl ether/chloroform solution.

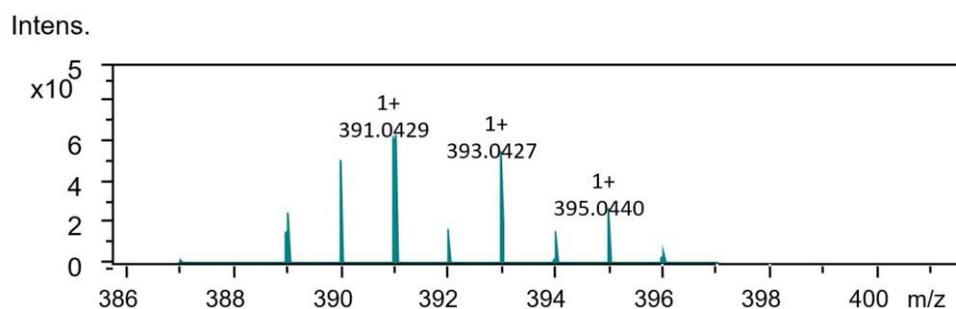
(f) Reaction in Scheme 5f.



WITH BQ: A Schlenk test tube equipped with a magnetic stir bar was charged with palladium complex **7** (51 mg, 0.10 mmol, 1.0 equiv), BQ (10.8 mg, 0.1 mmol, 1.0 equiv) and t-AmylOH (2 mL) under an N₂ atmosphere. The resulting mixture was heated at 120 °C for 20 minutes. After being cooled to ambient temperature, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to provide the product **3ae** (95% yield).

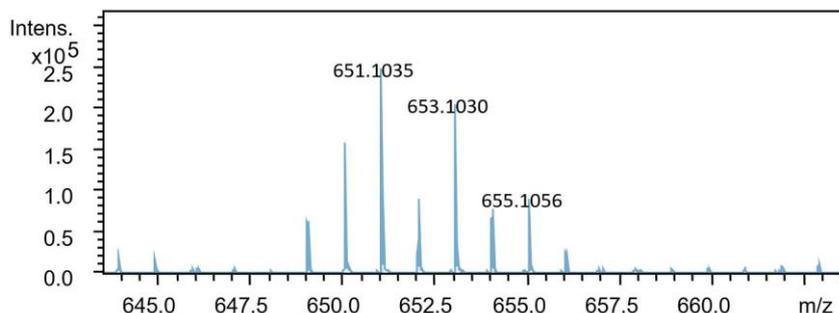
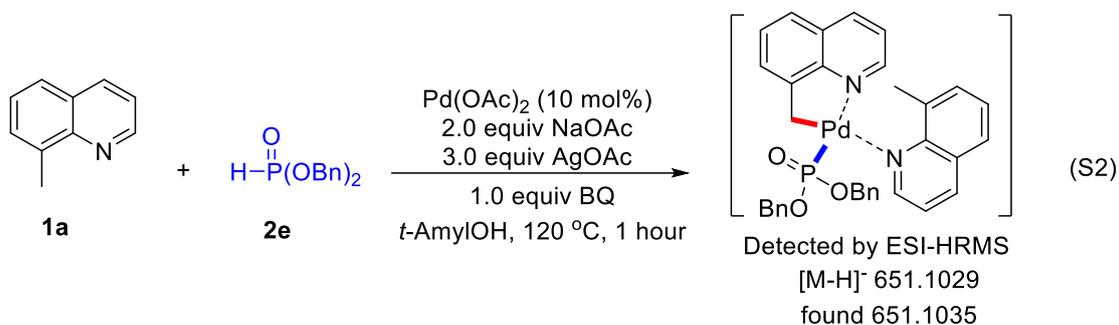
WITHOUT BQ: A Schlenk test tube equipped with a magnetic stir bar was charged with palladium complex **7** (51 mg, 0.10 mmol, 1.0 equiv) and t-AmylOH (2 mL) under an N₂ atmosphere. The resulting mixture was heated at 120 °C for 20 minutes. After being cooled to ambient temperature, the reaction mixture was monitored by TLC and showed that no reaction occurred in the system.

(g) ESI-HRMS analysis



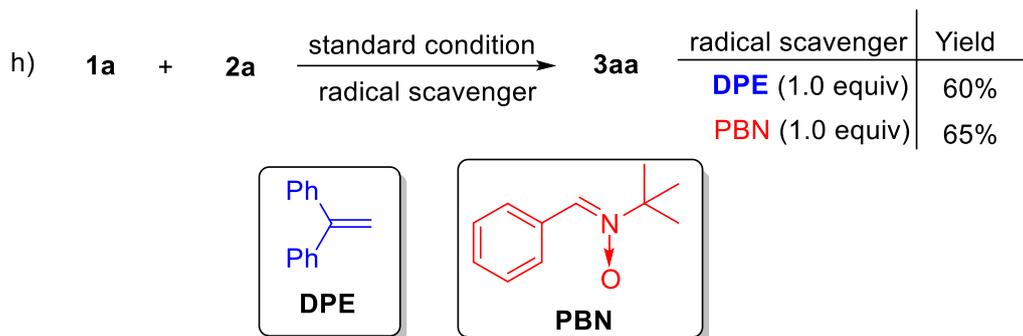
In a 25 mL sealed tube, a mixture of 8-methylquinoline **1a** (0.5 mmol, 2.0 equiv), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 10 mol%), AgOAc (125 mg, 0.75 mmol, 3.0 equiv.), 1,4-benzoquinone

(27 mg, 0.25 mmol, 1.0 equiv.) and NaOAc (41 mg, 2 equiv) in *t*-AmylOH (2.0 mL) was stirred at 120 °C under N₂ for 10 min. Then dibenzyl phosphite **2e** (0.25 mmol, 1.0 equiv) in *t*-AmylOH (1 mL) was added dropwise via a syringe pump. After addition for 30 mins, the reaction mixture was detected by ESI-HRMS. HRMS (ESI): calcd for C₂₀H₁₇N₂Pd [M]⁺ 391.0427, found 391.0429.



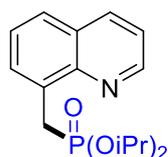
In a 25 mL sealed tube, a mixture of 8-methylquinoline **1a** (0.5 mmol, 2.0 equiv), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 10 mol%), AgOAc (125 mg, 0.75 mmol, 3.0 equiv.), 1,4-benzoquinone (27 mg, 0.25 mmol, 1.0 equiv.) and NaOAc (41 mg, 2 equiv) in *t*-AmylOH (2.0 mL) was stirred at 120 °C under N₂ for 10 min. Then dibenzyl phosphite **2e** (0.25 mmol, 1.0 equiv) in *t*-AmylOH (1 mL) was added dropwise via a syringe pump. After addition for 1 hour, the reaction mixture was detected by ESI-HRMS. HRMS (ESI): calcd for C₃₄H₃₀N₂O₃PPd [M-H]⁻ 651.1029, found 651.1035.

(h) Other radical scavengers



In a 25 mL sealed tube, a mixture of 8-methylquinoline **1a** (0.5 mmol, 2.0 equiv), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 10 mol%), AgOAc (125 mg, 0.75 mmol, 3.0 equiv.), 1,4-benzoquinone (27 mg, 0.25 mmol, 1.0 equiv.), NaOAc (41 mg, 2 equiv) and DPE (1.0 equivalent) or PBN (1.0 equivalent) in *t*-AmylOH (2.0 mL) was stirred at 120 °C under N₂ for 10 min. Then **2a** (0.25 mmol, 1.0 equiv) in *t*-AmylOH (1 mL) was added dropwise via a syringe pump in 8 h. After addition, the mixture was stirred at the same temperature for another 2 h. After cooling to room temperature, the mixture was filtered through a celite pad and concentrated under vacuum. The residue was purified by column chromatography on silica gel (100-200 mesh) to provide the desired product **3aa**.

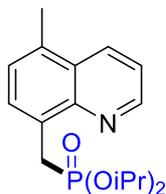
VI. Experimental data for the described substances.



Diisopropyl (quinolin-8-ylmethyl)phosphonate (**3aa**)

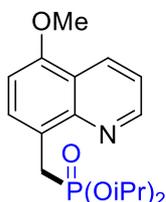
Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3aa** as brown oil (55 mg, 72% yield). ¹H NMR (600 MHz, CDCl₃): δ = 8.92 (d, *J* = 2.4 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.88–7.89 (m, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.38 (dd, *J* = 8.4, 4.2 Hz, 1H), 4.56–4.62 (m, *J* = 2H), 4.00 (d, *J* = 22.8 Hz, 2H), 1.22 (d, *J* = 6.0 Hz, 6H), 1.01 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 149.6, 146.8 (d, *J* = 7.5 Hz), 136.3, 131.5 (d, *J* = 7.5 Hz), 130.8 (d, *J* = 6.0 Hz), 128.5 (d, *J* = 3.0 Hz), 126.9 (d, *J* = 3.0 Hz), 126.3 (d, *J* = 4.5 Hz), 121.1, 70.5 (d, *J* = 7.5 Hz), 28.2 (d, *J* =

139.5 Hz), 24.0 (dd, $J = 61.5, 4.5$ Hz) ppm. ^{31}P NMR (162 MHz, CDCl_3) δ 25.71 ppm. HRMS (ESI $^+$): calcd for $\text{C}_{16}\text{H}_{23}\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$ 308.1416, found 308.1411.



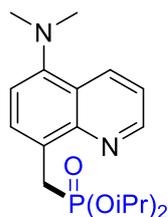
Diisopropyl ((5-methylquinolin-8-yl)methyl)phosphonate (**3ba**)

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3ba** as yellow oil (62 mg, 77% yield). ^1H NMR (600 MHz, CDCl_3): δ = 8.93 (d, $J = 2.4$ Hz, 1H), 8.30 (d, $J = 8.4$ Hz, 1H), 7.77 (dd, $J = 7.2, 3.0$ Hz, 1H), 7.40-7.42 (m, 1H), 7.34 (d, $J = 7.2$ Hz, 1H), 4.58 - 4.63 (m, 2H), 3.96 (d, $J = 22.2$ Hz, 2H), 2.66 (s, 3H), 1.23 (d, $J = 6.0$ Hz, 6H), 1.04 (d, $J = 6.0$ Hz, 6H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 149.0, 147.0 (d, $J = 6.0$ Hz), 133.5 (d, $J = 4.5$ Hz), 132.7, 130.4 (d, $J = 6.0$ Hz), 129.4 (d, $J = 9.0$ Hz), 127.9 (d, $J = 1.5$ Hz), 126.9 (d, $J = 4.5$ Hz), 120.6, 70.5 (d, $J = 7.5$ Hz), 28.2 (d, $J = 139.5$ Hz), 24.0 (dd, $J = 58.5, 6.0$ Hz), 18.7 ppm. HRMS (ESI $^+$): calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$ 322.1572, found 322.1567.



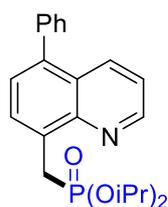
Diisopropyl ((5-methoxyquinolin-8-yl)methyl)phosphonate (**3ca**)

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3ca** as brown oil (63 mg, 75% yield). ^1H NMR (600 MHz, CDCl_3): δ = 8.92 (dd, $J = 4.2, 1.2$ Hz, 1H), 8.57 (dd, $J = 8.4$, 1H), 7.79 (dd, $J = 7.8, 3.6$ Hz, 1H), 7.36 (dd, $J = 8.4, 4.2$ Hz, 1H), 6.84 (d, $J = 8.4$ Hz, 1H), 4.64 - 4.53 (m, 2H), 3.98 (s, 3H), 3.89 (d, $J = 21.6$ Hz, 2H), 1.22 (d, $J = 6.6$ Hz, 6H), 1.02 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 154.2 (d, $J = 3.0$ Hz), 149.6, 146.9, 131.2, 130.7, 122.7, 121.0, 120.1, 104.3 (d, $J = 3.0$ Hz), 70.4 (d, $J = 7.5$ Hz), 55.8, 27.6 (d, $J = 139.5$ Hz), 24.0 (dd, $J = 57, 4.5$ Hz) ppm. HRMS (ESI $^+$): calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_4\text{P}$ $[\text{M}+\text{H}]^+$ 338.1521, found 338.1516.



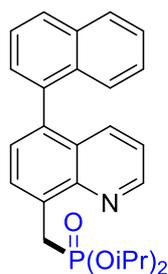
Diisopropyl ((5-(dimethylamino)quinolin-8-yl)methyl)phosphonate (**3da**)

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3da** as yellow oil (46 mg, 53% yield). ^1H NMR (600 MHz, CDCl_3): δ = 8.91 (s, 1H), 8.57 (d, J = 7.2 Hz, 1H), 7.79 (d, J = 4.8 Hz, 1H), 7.38 (dd, J = 7.8, 3.6 Hz, 1H), 7.10 (d, J = 7.8 Hz, 1H), 4.59 – 4.64 (m, 2H), 3.93 (d, J = 22.2 Hz, 2H), 2.87 (s, 6H), 1.23 (d, J = 6.0 Hz, 6H), 1.04 (d, J = 6.0 Hz, 6H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 150.0, 149.0, 133.2, 130.8, 129.6, 125.4, 124.2, 119.9, 114.4, 70.5 (d, J = 7.5 Hz), 45.5, 28.0 (d, J = 139.5 Hz), 24.0 (dd, J = 63.0, 4.5 Hz) ppm. HRMS (ESI⁺): calcd for $\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$ 351.1838, found 351.1832.



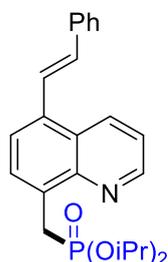
Diisopropyl ((5-phenylquinolin-8-yl)methyl)phosphonate (**3ea**)

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3ea** as brown oil (48 mg, 50% yield). ^1H NMR (600 MHz, CDCl_3): δ = 8.94 (d, J = 2.4 Hz, 1H), 8.23 (d, J = 3.0 Hz, 1H), 7.92-7.94 (m, 1H), 7.47-7.51 (m, 3H), 7.44 (d, J = 7.2 Hz, 3H), 7.33-7.35 (m, 1H), 4.63 – 4.69 (m, 2H), 4.05 (d, J = 22.2 Hz, 2H), 1.27 (d, J = 6.0 Hz, 6H), 1.09 (d, J = 6.0 Hz, 6H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 149.3, 146.9, 139.6, 139.5 (d, J = 3.0 Hz), 134.6, 130.9 (d, J = 9.0 Hz), 130.23, 130.18, 128.6, 127.7, 127.0 (d, J = 4.5 Hz), 126.9 (d, J = 3.0 Hz), 121.0, 70.6 (d, J = 6.0 Hz), 28.5 (d, J = 139.5 Hz), 24.1 (dd, J = 58.5, 6.0 Hz) ppm. HRMS (ESI⁺): calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$ 384.1729, found 384.1723.



Diisopropyl ((5-(naphthalen-1-yl)quinolin-8-yl)methyl)phosphonate (3fa)

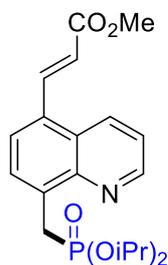
Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3fa** as yellow oil (89 mg, 82% yield). ^1H NMR (600 MHz, CDCl_3): δ = 8.95 (s, 1H), 8.01-8.03 (m, 1H), 7.96 (t, J = 9.0 Hz, 2H), 7.75 (d, J = 6.6 Hz, 1H), 7.56-7.60 (m, 2H), 7.45-7.48 (m, 2H), 7.29-7.30 (m, 2H), 7.23 (d, J = 4.2 Hz, 1H), 4.69 – 4.74 (m, 2H), 4.08-4.18 (m, 2H), 1.30 (d, J = 6.0 Hz, 6H), 1.12 (dd, J = 13.2, 6.0 Hz, 6H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 149.2, 137.8, 137.0, 135.6, 133.8, 132.9, 131.1, 130.6, 128.5, 128.4, 128.3, 126.4, 126.3, 126.1, 125.5, 121.0, 70.7 (d, J = 7.5 Hz), 28.7 (d, J = 139.5 Hz), 24.3 (d, J = 3.0 Hz), 23.9 (t, J = 4.5 Hz) ppm. HRMS (ESI $^+$): calcd for $\text{C}_{26}\text{H}_{29}\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$ 434.1885, found 434.1877.



Diisopropyl (*E*)-((5-styrylquinolin-8-yl)methyl)phosphonate (3ga)

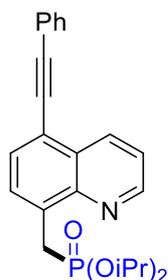
Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3ga** as yellow oil (69 mg, 68% yield). ^1H NMR (600 MHz, CDCl_3): δ = 8.96 (s, 1H), 8.56 (d, J = 7.8 Hz, 1H), 7.90 (s, 1H), 7.78 (d, J = 18.0 Hz, 2H), 7.59 (d, J = 7.8 Hz, 2H), 7.44-7.45 (m, 1H), 7.40 (t, J = 7.2 Hz, 2H), 7.31 (t, J = 7.2 Hz, 1H), 7.17 (d, J = 16.2 Hz, 1H), 4.61-4.66 (m, 2H), 4.03 (d, J = 22.2 Hz, 2H), 1.25 (d, J = 6.0 Hz, 6H), 1.06 (d, J = 6.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 149.4, 146.8 (d, J = 7.0 Hz), 137.4, 134.3 (d, J = 4.0 Hz), 132.6 (d, J = 2.0 Hz), 132.4, 131.2 (d, J = 9.0 Hz), 130.6 (d, J = 6.0 Hz), 129.0, 128.2, 126.9, 126.7 (d, J = 2.0 Hz), 124.4 (d, J = 2.0 Hz), 123.6 (d, J = 4.0 Hz), 120.9, 70.6

(d, $J = 7.0$ Hz), 28.5 (d, $J = 140.0$ Hz), 24.1 (dd, $J = 38.0, 5.0$ Hz) ppm. HRMS (ESI⁺): calcd for C₂₄H₂₉NO₃P [M+H]⁺ 410.1885, found 410.1883.



Methyl (*E*)-3-(8-((diisopropoxyphosphoryl)methyl)quinolin-5-yl)acrylate (**3ha**)

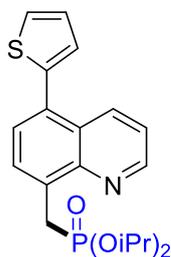
Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3ha** as yellow oil (52 mg, 53% yield, E/Z = 5:1). ¹H NMR (600 MHz, CDCl₃): $\delta = 8.98$ (d, $J = 4.2$ Hz, 1H), 8.54 (d, $J = 8.4$ Hz, 1H), 8.41 (d, $J = 16.2$ Hz, 1H), 7.89–7.91 (m, 1H), 7.80 (d, $J = 7.8$ Hz, 1H), 7.48–7.50 (m, 1H), 6.54 (d, $J = 15.6$ Hz, 1H), 4.58–4.66 (m, 2H), 4.03 (d, $J = 22.8$ Hz, 2H), 3.84 (s, 3H), 1.23 (d, $J = 6.6$ Hz, 6H), 1.05 (d, $J = 6.6$ Hz, 6H) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 167.2, 149.4, 140.1, 134.0$ (d, $J = 9.0$ Hz), 132.6, 131.0 (d, $J = 4.5$ Hz), 130.8, 126.8, 125.2 (d, $J = 4.5$ Hz), 121.6, 121.3, 121.1, 70.8 (d, $J = 6.0$ Hz), 52.0, 29.0 (d, $J = 138.0$ Hz), 24.0 (dd, $J = 51.0, 4.5$ Hz) ppm. HRMS (ESI⁺): calcd for C₂₀H₂₇NO₅P [M+H]⁺ 392.1627, found 392.1629.



Diisopropyl ((5-(phenylethynyl)quinolin-8-yl)methyl)phosphonate (**3ia**)

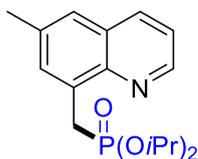
Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3ia** as pale yellow oil (56 mg, 55% yield). ¹H NMR (600 MHz, CDCl₃): $\delta = 8.99$ (s, 1H), 8.74 (d, $J = 8.4$ Hz, 1H), 7.88 (dd, $J = 7.8, 3.6$ Hz, 1H), 7.78 (d, $J = 7.2$ Hz, 1H), 7.63 (dd, $J = 7.2, 1.8$ Hz, 2H), 7.51 (dd, $J = 7.8, 3.0$ Hz, 1H), 7.37–7.42 (m, 3H), 4.60–4.66 (m, 2H), 4.03 (d, $J = 22.2$ Hz, 2H), 1.24 (d, $J = 6.0$ Hz, 6H), 1.06 (d, $J = 6.0$ Hz, 6H) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 149.8, 146.2, 135.2, 132.6$ (d, $J = 7.5$ Hz), 131.8, 130.5 (d, $J = 4.5$ Hz), 128.8, 128.6, 123.1, 121.7, 120.2 (d, $J = 3.0$ Hz), 95.0, 86.4, 70.7 (d, $J = 6.0$ Hz),

28.7 (d, $J = 139.5$ Hz), 24.0 (dd, $J = 51.0, 4.5$ Hz) ppm. HRMS (ESI⁺): calcd for C₂₄H₂₇NO₃P [M+H]⁺ 408.1729, found 408.1722.



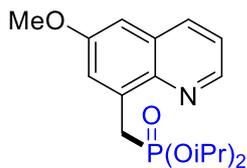
Diisopropyl ((5-(thiophen-2-yl)quinolin-8-yl)methyl)phosphonate (**3ja**)

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3ja** as pale yellow oil (39 mg, 40% yield). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.95$ (dd, $J = 4.0, 1.6$ Hz, 1H), 8.53 (dd, $J = 8.4, 2.1$ Hz, 1H), 7.90 (dd, $J = 7.6, 3.6$ Hz, 1H), 7.60 (d, $J = 7.6$ Hz, 1H), 7.38-7.45 (m, 2H), 7.17-7.19 (m, 2H), 4.61-4.69 (m, 2H), 4.03 (d, $J = 22.4$ Hz, 2H), 1.26 (d, $J = 6.4$ Hz, 6H), 1.09 (d, $J = 6.4$ Hz, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 149.5, 146.9$ (d, $J = 7.0$ Hz), 140.6, 134.4, 131.8 (d, $J = 9.0$ Hz), 131.6 (d, $J = 4.0$ Hz), 130.1 (d, $J = 7.0$ Hz), 128.1 (d, $J = 4.0$ Hz), 127.8, 127.6, 127.2 (d, $J = 2.0$ Hz), 126.2, 121.3, 70.6 (d, $J = 6.0$ Hz), 28.5 (d, $J = 139.0$ Hz), 24.1 (dd, $J = 37.0, 5.0$ Hz) ppm. HRMS (ESI⁺): calcd for C₂₀H₂₅NO₃PS [M+H]⁺ 390.1293, found 390.1287.



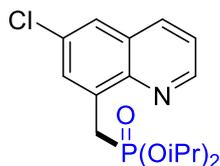
Diisopropyl ((6-methylquinolin-8-yl)methyl)phosphonate (**3ka**)

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3ka** as brown oil (44 mg, 55% yield). ¹H NMR (600 MHz, CDCl₃): $\delta = 8.85$ (d, $J = 3.6$ Hz, 1H), 8.03 (d, $J = 8.4$ Hz, 1H), 7.73 (s, 1H), 7.47 (s, 1H), 7.33-7.35 (m, 1H), 4.58 – 4.62 (m, 2H), 3.95 (d, $J = 22.2$ Hz, 2H), 2.52 (s, 3H), 1.23 (d, $J = 6.0$ Hz, 6H), 1.03 (d, $J = 6.0$ Hz, 6H) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 148.7, 145.4$ (d, $J = 6.0$ Hz), 136.1 (d, $J = 4.5$ Hz), 135.6, 133.1 (d, $J = 6.0$ Hz), 131.0 (d, $J = 9.0$ Hz), 128.6, 125.8 (d, $J = 4.5$ Hz), 121.1, 70.5 (d, $J = 7.5$ Hz), 28.1 (d, $J = 139.5$ Hz), 24.0 (dd, $J = 64.5, 4.5$ Hz), 21.7 ppm. HRMS (ESI⁺): calcd for C₁₇H₂₅NO₃P [M+H]⁺ 322.1572, found 322.1566.



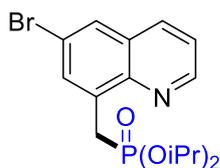
Diisopropyl ((6-methoxyquinolin-8-yl)methyl)phosphonate (3la)

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3la** as brown oil (59 mg, 70% yield). ^1H NMR (600 MHz, CDCl_3) δ : = 8.77 (d, J = 3.0 Hz, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.56 (s, 1H), 7.32-7.34 (m, 1H), 6.98 (s, 1H), 4.60-4.65 (m, 2H), 3.95 (d, J = 22.2 Hz, 2H), 3.91 (s, 3H), 1.24 (d, J = 6.0 Hz, 6H), 1.06 (d, J = 6.0 Hz, 6H) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 157.3 (d, J = 3.0 Hz), 147.1, 143.0 (d, J = 7.5 Hz), 135.0, 133.2 (d, J = 9.0 Hz), 129.7 (d, J = 3.0 Hz), 123.1 (d, J = 7.5 Hz), 121.5, 104.7 (d, J = 3.0 Hz), 70.6 (d, J = 6.0 Hz), 55.6, 28.2 (d, J = 139.5 Hz), 24.0 (dd, J = 57.0, 4.5 Hz) ppm. HRMS (ESI⁺): calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_4\text{P}$ $[\text{M}+\text{H}]^+$ 338.1521, found 338.1515.



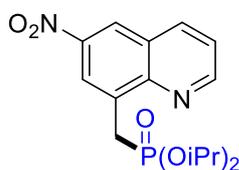
Diisopropyl ((6-chloroquinolin-8-yl)methyl)phosphonate (3ma)

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3ma** as brown oil (45 mg, 53% yield). ^1H NMR (600 MHz, CDCl_3) δ : = 8.92 (s, 1H), 8.06 (d, J = 7.2 Hz, 1H), 7.82 (s, 1H), 7.70 (s, 1H), 7.42 (s, 1H), 4.63-4.66 (m, 2H), 3.96 (d, J = 22.2 Hz, 2H), 1.25 (d, J = 4.2 Hz, 6H), 1.09 (d, J = 4.2 Hz, 6H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 149.8, 145.2 (d, J = 7.5 Hz), 135.4, 134.0 (d, J = 9.0 Hz), 132.0 (d, J = 4.5 Hz), 131.4 (d, J = 7.5 Hz), 129.1 (d, J = 1.5 Hz), 125.4 (d, J = 4.5 Hz), 122.0, 70.8 (d, J = 7.5 Hz), 28.2 (d, J = 139.5 Hz), 24.0 (dd, J = 51.0, 4.5 Hz) ppm. HRMS (ESI⁺): calcd for $\text{C}_{16}\text{H}_{22}\text{ClNO}_3\text{P}$ $[\text{M}+\text{H}]^+$ 342.1026, found 342.1022.



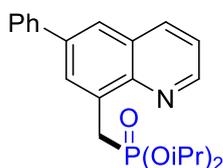
Diisopropyl ((6-bromoquinolin-8-yl)methyl)phosphonate (3na)

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3na** as brown oil (43 mg, 45% yield). ¹H NMR (600 MHz, CDCl₃): δ = 8.93 (s, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.95 (s, 1H), 7.88 (s, 1H), 7.40-7.43 (m, 1H), 4.63 – 4.67 (m, 2H), 3.96 (dd, *J* = 22.2, 2.4 Hz, 2H), 1.25 (d, *J* = 6.0 Hz, 6H), 1.10 (d, *J* = 6.0 Hz, 6H) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 149.8, 145.3 (d, *J* = 7.5 Hz), 135.5, 134.1, 134.0 (d, *J* = 6.0 Hz), 129.6 (d, *J* = 3.0 Hz), 128.8 (d, *J* = 3.0 Hz), 122.0, 120.2 (d, *J* = 6.0 Hz), 70.8 (d, *J* = 7.5 Hz), 28.2 (d, *J* = 139.5 Hz), 24.0 (dd, *J* = 48.0, 4.5 Hz) ppm. HRMS (ESI⁺): calcd for C₁₆H₂₂BrNO₃P [M+H]⁺ 386.0521, found 386.0514.



Diisopropyl ((6-nitroquinolin-8-yl)methyl)phosphonate (**3oa**)

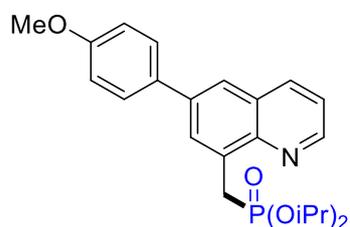
Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3oa** as brown oil (39 mg, 44% yield). ¹H NMR (600 MHz, CDCl₃): δ = 9.10 (d, *J* = 3.6 Hz, 1H), 8.69 (s, 1H), 8.62 (s, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 7.56-7.58 (m, 1H), 4.66-4.71 (m, 2H), 4.05 (d, *J* = 22.8 Hz, 2H), 1.27 (d, *J* = 6.0 Hz, 6H), 1.16 (d, *J* = 6.0 Hz, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 153.0, 148.7 (d, *J* = 6.0 Hz), 145.1 (d, *J* = 5.0 Hz), 138.3, 134.9 (d, *J* = 9.0 Hz), 127.3 (d, *J* = 2.0 Hz), 123.7 (d, *J* = 7.0 Hz), 123.3 (d, *J* = 3.0 Hz), 122.9, 71.0 (d, *J* = 7.0 Hz), 28.7 (d, *J* = 139.0 Hz), 24.0 (dd, *J* = 24.0 Hz, 5.0 Hz) ppm. HRMS (ESI⁺): calcd for C₁₆H₂₂N₂O₅P [M+H]⁺ 353.1266, found 353.1260.



Diisopropyl ((6-phenylquinolin-8-yl)methyl)phosphonate (**3pa**)

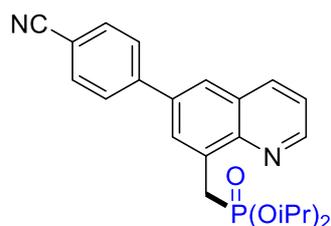
Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3pa** as brown oil (71 mg, 74% yield). ¹H NMR (600 MHz, CDCl₃): δ = 8.93 (d, *J* = 3.6 Hz, 1H), 8.17-8.20 (m, 2H), 7.91 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.38-7.42 (m, 2H), 4.62-4.67 (m, 2H), 4.05 (d, *J* = 22.2 Hz, 2H), 1.24 (d, *J* = 6.0 Hz, 6H), 1.06 (d, *J* = 6.0 Hz, 6H) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 149.6, 146.2 (d, *J* = 6.0 Hz),

140.3, 138.9 (d, $J = 4.5$ Hz), 136.5, 132.0 (d, $J = 9.0$ Hz), 130.5 (d, $J = 7.5$ Hz), 129.0, 128.8 (d, $J = 1.5$ Hz), 127.8, 127.6, 124.4 (d, $J = 3.0$ Hz), 121.5, 70.6 (d, $J = 7.5$ Hz), 28.4 (d, $J = 139.5$ Hz), 24.0 (dd, $J = 57.0, 4.5$ Hz) ppm. HRMS (ESI⁺): calcd for C₂₂H₂₇NO₃P [M+H]⁺ 384.1729, found 384.1722.



Diisopropyl ((6-(4-methoxyphenyl)quinolin-8-yl)methyl)phosphonate (3qa)

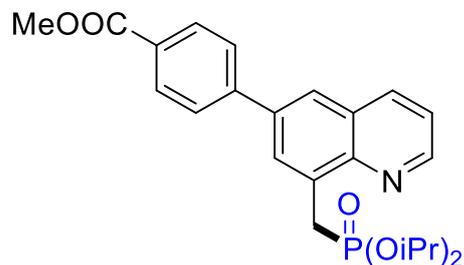
Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3qa** as brown oil (52 mg, 50% yield). ¹H NMR (600 MHz, CDCl₃): $\delta = 8.90$ (d, $J = 4.5$ Hz, 1H), 8.15-8.17 (m, 2H), 7.85 (s, 1H), 7.68 (d, $J = 8.4$ Hz, 2H), 7.38-7.40 (m, 1H), 7.02 (d, $J = 9.0$ Hz, 2H), 4.61-4.66 (m, 2H), 4.04 (d, $J = 22.2$ Hz, 2H), 3.87 (s, 3H), 1.24 (d, $J = 6.0$ Hz, 6H), 1.05 (d, $J = 6.6$ Hz, 6H) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 159.8, 149.1, 145.7, 138.6, 136.6, 132.7, 131.7$ (d, $J = 9.0$ Hz), 130.5, 128.9 (d, $J = 3.0$ Hz), 128.6, 123.6 (d, $J = 3.0$ Hz), 121.4, 114.6, 70.6 (d, $J = 7.5$ Hz), 55.5, 28.4 (d, $J = 139.5$ Hz), 24.0 (dd, $J = 57.0, 4.5$ Hz) ppm. HRMS (ESI⁺): calcd for C₂₃H₂₉NO₄P [M+H]⁺ 414.1834, found 414.1821.



Diisopropyl ((6-(4-cyanophenyl)quinolin-8-yl)methyl)phosphonate (3ra)

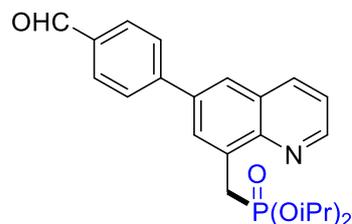
Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3ra** as yellow solid (65 mg, 64% yield). ¹H NMR (600 MHz, CDCl₃): $\delta = 8.97$ (dd, $J = 3.6, 1.2$ Hz, 1H), 8.22 (d, $J = 8.4$ Hz, 1H), 8.18 – 8.19 (m, 1H), 7.93 (s, 1H), 7.84 (d, $J = 8.4$ Hz, 2H), 7.76 (d, $J = 8.4$ Hz, 2H), 7.45-7.47 (m, 1H), 4.61 – 4.67 (m, 2H), 4.06 (d, $J = 22.2$ Hz, 2H), 1.24 (d, $J = 6.0$ Hz, 6H), 1.05 (d, $J = 6.0$ Hz, 6H) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 150.2, 146.3, 144.8, 137.0, 136.9$ (d, $J = 4.5$ Hz), 132.8, 132.7 (d, $J = 7.5$ Hz), 130.0 (d, $J = 7.5$ Hz), 128.7, 128.2, 125.2 (d, $J = 4.5$ Hz), 121.9, 118.9, 111.6, 70.8 (d, $J =$

6.0 Hz), 28.4 (d, $J = 139.5$ Hz), 24.0 (dd, $J = 52.5, 4.5$ Hz) ppm. HRMS (ESI⁺): calcd for C₂₃H₂₆N₂O₃P [M+H]⁺ 409.1681, found 409.1676.



Methyl 4-(8-((diisopropoxyphosphoryl)methyl)quinolin-6-yl)benzoate (**3sa**)

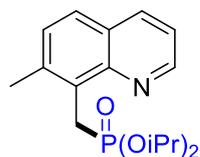
Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3sa** as brown oil (60 mg, 54% yield). ¹H NMR (600 MHz, CDCl₃): $\delta = 8.96$ (d, $J = 2.4$ Hz, 1H), 8.22 (d, $J = 7.8$ Hz, 2H), 8.14 (d, $J = 8.4$ Hz, 2H), 7.96 (s, 1H), 7.81 (d, $J = 7.8$ Hz, 2H), 7.44-7.46 (m, 1H), 4.62-4.68 (m, 2H), 4.07 (d, $J = 22.2$ Hz, 2H), 3.95 (s, 3H), 1.24 (d, $J = 6.6$ Hz, 6H), 1.06 (d, $J = 6.0$ Hz, 6H) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 167.1, 150.0, 146.5$ (d, $J = 7.5$ Hz), 144.8, 137.7 (d, $J = 4.5$ Hz), 136.7, 132.5 (d, $J = 9.0$ Hz), 130.4, 130.2 (d, $J = 7.5$ Hz), 129.5, 128.7, 127.5, 125.0 (d, $J = 4.5$ Hz), 121.7, 70.7 (d, $J = 7.5$ Hz), 52.3, 28.4 (d, $J = 139.5$ Hz), 24.1 (dd, $J = 54.0, 4.5$ Hz) ppm. HRMS (ESI⁺): calcd for C₂₄H₂₉NO₅P [M+H]⁺ 442.1783, found 442.1780.



Diisopropyl ((6-(4-formylphenyl)quinolin-8-yl)methyl)phosphonate (**3ta**)

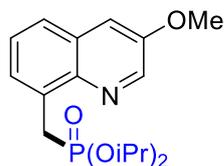
Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3ta** as brown oil (62 mg, 60% yield). ¹H NMR (600 MHz, CDCl₃): $\delta = 10.08$ (s, 1H), 8.96 (d, $J = 2.4$ Hz, 1H), 8.21 (d, $J = 8.4$ Hz, 2H), 7.98-8.00 (m, 3H), 7.91 (d, $J = 7.8$ Hz, 2H), 7.44-7.46 (m, 1H), 4.62-4.67 (m, 2H), 4.06 (d, $J = 22.2$ Hz, 2H), 1.25 (d, $J = 6.0$ Hz, 6H), 1.06 (d, $J = 6.0$ Hz, 6H) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 192.0, 150.2, 146.6$ (d, $J = 7.5$ Hz), 146.3, 137.4 (d, $J = 4.5$ Hz), 136.8, 135.7, 132.6 (d, $J = 9.0$ Hz), 130.5, 130.1 (d, $J = 6.0$ Hz), 128.7, 128.1, 125.3 (d, $J = 3.0$ Hz), 121.8, 70.7 (d, $J = 7.5$ Hz), 28.3 (d, $J =$

139.5 Hz), 24.0 (dd, $J = 55.5, 6.0$ Hz) ppm. HRMS (ESI⁺): calcd for C₂₃H₂₇NO₄P [M+H]⁺ 412.1678, found 412.1672.



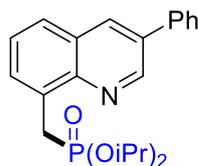
Diisopropyl ((7-methylquinolin-8-yl)methyl)phosphonate (3ua)

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3ua** as brown oil (24 mg, 30% yield). ¹H NMR (600 MHz, CDCl₃): $\delta = 8.92$ (d, $J = 3.0$ Hz, 1H), 8.08 (d, $J = 7.8$ Hz, 1H), 7.61 (dd, $J = 8.4, 1.8$ Hz, 1H), 7.39 (d, $J = 8.4$ Hz, 1H), 7.32-7.34 (m, 1H), 4.54 – 4.62 (m, 2H), 4.08 (d, $J = 23.4$ Hz, 2H), 2.67 (d, $J = 2.4$ Hz, 3H), 1.22 (d, $J = 6.0$ Hz, 6H), 0.97 (d, $J = 6.6$ Hz, 6H) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 149.0, 139.5, 136.5, 130.2, 129.1, 126.8, 126.1$ (d, $J = 4.5$ Hz), 120.2, 70.5 (d, $J = 7.5$ Hz), 27.0 (d, $J = 139.5$ Hz), 24.0 (dd, $J = 78.0, 6.0$ Hz), 21.2 ppm. HRMS (ESI⁺): calcd for C₁₇H₂₅NO₃P [M+H]⁺ 322.1572, found 322.1570.



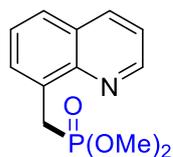
Diisopropyl ((3-methoxyquinolin-8-yl)methyl)phosphonate (3va)

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3va** as yellow oil (42 mg, 50% yield). ¹H NMR (600 MHz, CDCl₃): $\delta = 8.68$ (d, $J = 3.0$ Hz, 1H), 7.70-7.72 (m, 1H), 7.62 (d, $J = 7.8$ Hz, 1H), 7.46 (t, $J = 7.8$ Hz, 1H), 7.37 (s, 1H), 4.57– 4.63 (m, 2H), 3.96 (d, $J = 22.2$ Hz, 2H), 3.94 (s, 3H), 1.22 (d, $J = 6.0$ Hz, 6H), 1.03 (d, $J = 6.0$ Hz, 6H) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 153.2, 143.6, 142.0$ (d, $J = 7.5$ Hz), 131.4 (d, $J = 7.5$ Hz), 129.1 (d, $J = 3.0$ Hz), 128.2 (d, $J = 6.0$ Hz), 127.10 (d, $J = 4.5$ Hz), 125.8 (d, $J = 4.5$ Hz), 112.6, 70.5 (d, $J = 7.5$ Hz), 55.6, 28.4 (d, $J = 139.5$ Hz), 24.0 (dd, $J = 60.0, 6.0$ Hz) ppm. HRMS (ESI⁺): calcd for C₁₇H₂₆NO₄P [M+H]⁺ 338.1521, found 338.1516.



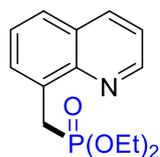
Diisopropyl ((3-phenylquinolin-8-yl)methyl)phosphonate (**3wa**)

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3wa** as brown oil (68 mg, 71% yield). ^1H NMR (600 MHz, CDCl_3): δ = 9.23 (s, 1H), 8.31 (s, 1H), 7.90 (s, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.72 (d, J = 7.8 Hz, 2H), 7.56 (d, J = 7.2 Hz, 1H), 7.53 (t, J = 7.2 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H), 4.62-4.68 (m, 2H), 4.05 (d, J = 22.2 Hz, 2H), 1.25 (d, J = 6.6 Hz, 6H), 1.07 (d, J = 6.6 Hz, 6H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 149.1, 145.9 (d, J = 7.5 Hz), 138.0, 134.0, 133.7, 133.5, 131.5 (d, J = 9.0 Hz), 130.7 (d, J = 7.5 Hz), 129.3, 128.3 (d, J = 3.0 Hz), 128.2, 127.5, 127.1 (d, J = 4.5 Hz), 126.8 (d, J = 4.5 Hz), 70.6 (d, J = 6.0 Hz), 28.4 (d, J = 139.5 Hz), 24.0 (dd, J = 55.5, 4.5 Hz) ppm. HRMS (ESI⁺): calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_3\text{P}$ [M+H]⁺ 384.1729, found 384.1721.



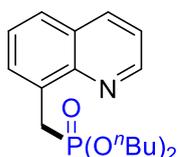
Dimethyl (quinolin-8-ylmethyl)phosphonate (**3ab**)

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/2, v/v) afforded **3ab** as yellow oil (28 mg, 45% yield). ^1H NMR (600 MHz, CDCl_3): δ = 8.96 (d, J = 3.0 Hz, 1H), 8.18 (d, J = 7.8 Hz, 1H), 7.84-7.86 (m, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.44 (dd, J = 7.8, 4.2 Hz, 1H), 4.06 (d, J = 22.2 Hz, 2H), 3.67 (d, J = 10.8 Hz, 6H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 149.7, 146.6 (d, J = 7.5 Hz), 136.5, 130.9 (d, J = 6.0 Hz), 130.8, 128.6 (d, J = 1.5 Hz), 127.3 (d, J = 4.5 Hz), 126.4 (d, J = 3.0 Hz), 121.3, 52.9 (d, J = 6.0 Hz), 26.6 (d, J = 136.5 Hz) ppm. HRMS (ESI⁺): calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_3\text{P}$ [M+H]⁺ 252.0790, found 252.0784.



Diethyl (quinolin-8-ylmethyl)phosphonate (**3ac**)

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/2, v/v) afforded **3ac** as yellow oil (32 mg, 46% yield). ^1H NMR (600 MHz, CDCl_3): δ = 8.94 (d, J = 3.0 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.85-7.86 (m, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.52 (t, J = 7.8 Hz, 1H), 7.39-7.41 (m, 1H), 3.99-4.05 (m, 6H), 1.14 (t, J = 6.6 Hz, 6H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 149.7, 146.7 (d, J = 7.5 Hz), 136.4, 131.2 (d, J = 10.5 Hz), 130.9 (d, J = 7.5 Hz), 128.6 (d, J = 3.0 Hz), 127.1 (d, J = 4.5 Hz), 126.4 (d, J = 4.5 Hz), 121.2, 62.1 (d, J = 6.0 Hz), 27.4 (d, J = 138.0 Hz), 16.4 (d, J = 6.0 Hz) ppm. HRMS (ESI $^+$): calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$ 280.1103, found 280.1101.



Dibutyl (quinolin-8-ylmethyl)phosphonate (**3ad**)

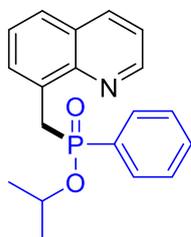
Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3ad** as brown oil (39 mg, 46% yield). ^1H NMR (600 MHz, CDCl_3): δ = 8.93 (d, J = 3.0 Hz, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.85 (dd, J = 6.6, 3.6 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 1H), 7.39-7.41 (m, 1H), 4.03 (d, J = 22.2 Hz, 2H), 3.92-3.97 (m, 4H), 1.43-1.48 (m, 4H), 1.19-1.25 (m, 4H), 0.80 (t, J = 7.2 Hz, 6H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 149.6, 146.7 (d, J = 7.5 Hz), 136.4, 131.3 (d, J = 9.0 Hz), 130.8 (d, J = 6.0 Hz), 128.6 (d, J = 1.5 Hz), 127.0 (d, J = 4.5 Hz), 126.4 (d, J = 4.5 Hz), 121.2, 65.8 (d, J = 6.0 Hz), 32.6 (d, J = 7.5 Hz), 27.2 (d, J = 138.0 Hz), 18.7, 13.7 ppm. HRMS (ESI $^+$): calcd for $\text{C}_{18}\text{H}_{27}\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$ 336.1729, found 336.1724.



Dibenzyl (quinolin-8-ylmethyl)phosphonate (**3ae**)

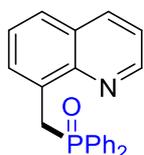
Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3ae** as brown oil (54 mg, 54% yield). ^1H NMR (600 MHz, CDCl_3): δ = 8.87 (d, J = 3.0 Hz, 1H), 8.11 (d, J = 7.8 Hz, 1H), 7.80-7.82 (m, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.36 (dd, J = 8.4, 4.2 Hz, 1H), 7.24-7.26 (m, 6H), 7.14-7.15 (m, 4H), 4.93-4.99 (m, 4H), 4.12 (d, J = 22.2 Hz, 2H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 149.7, 146.6 (d, J

= 7.5 Hz), 136.6 (d, $J = 6.0$ Hz), 136.3, 130.9 (d, $J = 6.0$ Hz), 130.8 (d, $J = 9.0$ Hz), 128.6 (d, $J = 3.0$ Hz), 128.4, 128.2, 127.7, 127.2 (d, $J = 4.5$ Hz), 126.3 (d, $J = 4.5$ Hz), 121.2, 67.5 (d, $J = 7.5$ Hz), 27.7 (d, $J = 136.5$ Hz) ppm. HRMS (ESI⁺): calcd for C₂₄H₂₃NO₃P [M+H]⁺ 404.1416, found 404.1411.



Isopropyl phenyl(quinolin-8-ylmethyl)phosphinate (**3af**)

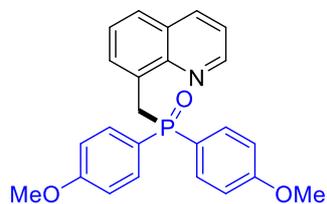
Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3af** as brown oil (41 mg, 51% yield). ¹H NMR (600 MHz, CDCl₃): $\delta = 8.70$ (d, $J = 3.6$ Hz, 1H), 8.02 (d, $J = 8.4$ Hz, 1H), 7.79 (d, $J = 3.6$ Hz, 1H), 7.61-7.66 (m, 3H), 7.45 (t, $J = 7.8$ Hz, 1H), 7.34 (t, $J = 7.2$ Hz, 1H), 7.23-7.27 (m, 3H), 4.52-4.57 (m, 1H), 4.06-4.25 (m, 2H), 1.22 (d, $J = 6.0$ Hz, 3H), 1.13 (d, $J = 6.0$ Hz, 3H) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 149.2$, 146.6 (d, $J = 6.0$ Hz), 136.1, 132.0 (d, $J = 9.0$ Hz), 131.8 [d (132.24, 131.40), $J = 126.0$ Hz], 131.7 (d, $J = 3.0$ Hz), 131.2 (d, $J = 7.5$ Hz), 130.8 (d, $J = 6.0$ Hz), 128.3 (d, $J = 3.0$ Hz), 127.9 (d, $J = 13.5$ Hz), 126.8 (d, $J = 3.0$ Hz), 126.2 (d, $J = 4.5$ Hz), 120.8, 69.9 (d, $J = 6.0$ Hz), 32.1 (d, $J = 96.0$ Hz), 24.3 (dd, $J = 51.0, 4.5$ Hz) ppm. ³¹P NMR (162 MHz, CDCl₃) δ 39.84 ppm. HRMS (ESI⁺): calcd for C₁₉H₂₁NO₂P [M+H]⁺ 326.1310, found 326.1304.



Diphenyl(quinolin-8-ylmethyl)phosphine oxide (**3ag**)

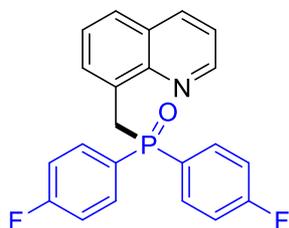
Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3ag** as brown oil (51 mg, 60% yield). ¹H NMR (600 MHz, CDCl₃): $\delta = 8.76$ (t, $J = 1.8$ Hz, 1H), 8.02-8.04 (m, 2H), 7.76-7.79 (m, 4H), 7.65 (d, $J = 7.8$ Hz, 1H), 7.47 (t, $J = 7.8$ Hz, 1H), 7.39 (t, $J = 7.2$ Hz, 2H), 7.28-7.33 (m, 5H), 4.56 (d, $J = 13.8$ Hz, 2H) ppm. ¹³C NMR (150 MHz, CDCl₃) δ 149.2, 146.5 (d, $J = 6.0$ Hz), 136.3, 133.1 [d (133.41, 132.76), $J = 97.5$ Hz], 131.6 (d, $J = 3.0$ Hz), 131.32, 131.3 [d (131.34, 131.28), $J = 9.0$ Hz], 130.8 (d, $J =$

7.5 Hz), 128.4 (d, $J = 1.5$ Hz), 128.3 (d, $J = 12.0$ Hz), 127.0 (d, $J = 1.5$ Hz), 126.5 (d, $J = 3.0$ Hz), 120.9, 31.0 (d, $J = 67.5$ Hz) ppm. ^{31}P NMR (162 MHz, CDCl_3) δ 31.63 ppm. HRMS (ESI $^+$): calcd for $\text{C}_{22}\text{H}_{19}\text{NOP}$ $[\text{M}+\text{H}]^+$ 344.1204, found 344.1198.



Bis(4-methoxyphenyl)(quinolin-8-ylmethyl)phosphine oxide (3ah)

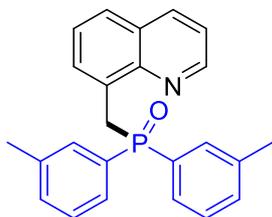
Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/3, v/v) afforded **3ah** as pale yellow oil (71 mg, 70% yield). ^1H NMR (600 MHz, DMSO-d_6): δ = 8.85 (d, $J = 2.4$ Hz, 1H), 8.29 (d, $J = 8.4$ Hz, 1H), 7.80 (d, $J = 7.8$ Hz, 1H), 7.64-7.67 (m, 5H), 7.45-7.49 (m, 2H), 6.97 (d, $J = 8.4$ Hz, 4H), 4.49 (d, $J = 13.8$ Hz, 2H), 3.75 (s, 6H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 162.2 (d, $J = 3.0$ Hz), 149.1, 146.6 (d, $J = 6.0$ Hz), 136.3, 133.1 (d, $J = 10.5$ Hz), 131.3 (d, $J = 6.0$ Hz), 128.4, 126.8 (d, $J = 3.0$ Hz), 126.5 (d, $J = 3.0$ Hz), 125.1, 124.4, 120.8, 113.9 (d, $J = 13.5$ Hz), 55.4, 31.4 (d, $J = 69.0$ Hz) ppm. HRMS (ESI $^+$): calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$ 404.1416, found 404.1413.



Bis(4-fluorophenyl)(quinolin-8-ylmethyl)phosphine oxide (3ai)

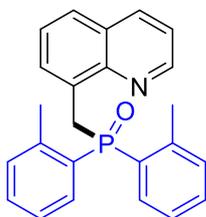
Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3ai** as brown oil (76 mg, 80% yield). ^1H NMR (600 MHz, CDCl_3): δ = 8.75 (dd, $J = 3.6$ Hz, 1.2 Hz, 1H), 8.05 (d, $J = 7.8$ Hz, 1H), 8.00 (d, $J = 5.4$ Hz, 1H), 7.73 – 7.77 (m, 4H), 7.67 (d, $J = 8.4$ Hz, 1H), 7.49 (t, $J = 7.8$ Hz, 1H), 7.30-7.32 (m, 1H), 6.99-7.02 (m, 4H), 4.52 (d, $J = 14.4$ Hz, 2H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 165.0 [dd (165.85, 165.83, 164.18, 164.16), $J = 250.5, 3.0$ Hz], 149.2, 146.3 (d, $J = 6.0$ Hz), 136.4, 133.7 (dd, $J = 10.5, 9.0$ Hz), 131.4 (d, $J = 4.5$ Hz), 130.3 (d, $J = 7.5$ Hz), 129.1 (d, $J = 3.0$ Hz), 128.4, 127.2 (d, $J = 3.0$ Hz), 126.6 (d, $J = 3.0$ Hz), 121.0, 115.7 (dd, $J = 21.0, 12.0$ Hz), 31.3 (d, $J = 69.0$ Hz)

ppm. ^{19}F NMR (376 MHz, CDCl_3) δ : -107.2 ppm. HRMS (ESI^+): calcd for $\text{C}_{22}\text{H}_{17}\text{F}_2\text{NOP}$ $[\text{M}+\text{H}]^+$ 380.1016, found 380.1008.



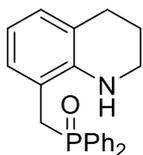
(Quinolin-8-ylmethyl)di-*m*-tolylphosphine oxide (**3aj**)

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3aj** as brown oil (65 mg, 70% yield). ^1H NMR (600 MHz, CDCl_3): δ = 8.80 (d, J = 3.0 Hz, 1H), 8.07 (s, 2H), 7.66 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 11.4 Hz, 2H), 7.57 – 7.60 (m, 2H), 7.50 (t, J = 6.6 Hz, 1H), 7.34 (s, 1H), 7.17-7.22 (m, 4H), 4.56 (d, J = 14.4 Hz, 2H), 2.26 (s, 6H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 149.1, 146.6 (d, J = 6.0 Hz), 138.1 (d, J = 12.0 Hz), 136.4, 133.0 [d (133.29, 132.63), J = 99.0 Hz], 132.3 (d, J = 3.0 Hz), 131.8 (d, J = 9.0 Hz), 131.4 (d, J = 6.0 Hz), 131.0 (d, J = 7.5 Hz), 128.4, 128.3 (d, J = 10.5 Hz), 128.2 (d, J = 12.0 Hz), 126.9 (d, J = 3.0 Hz), 126.6 (d, J = 3.0 Hz), 120.9, 31.0 (d, J = 67.5 Hz), 21.4 ppm. HRMS (ESI^+): calcd for $\text{C}_{24}\text{H}_{23}\text{NOP}$ $[\text{M}+\text{H}]^+$ 372.1517, found 372.1518.



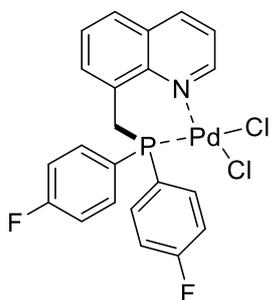
(Quinolin-8-ylmethyl)di-*o*-tolylphosphine oxide (**3ak**)

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v) afforded **3ak** as yellow oil (48 mg, 52% yield). ^1H NMR (600 MHz, CDCl_3): δ = 8.65 (dd, J = 3.6, 1.2 Hz, 1H), 8.01-8.05 (m, 2H), 7.74 (dd, J = 12.6, 7.8 Hz, 2H), 7.65 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 7.2 Hz, 1H), 7.24-7.27 (m, 3H), 7.11 (t, J = 7.2 Hz, 2H), 7.03-7.05 (m, 2H), 4.63 (d, J = 14.4 Hz, 2H), 2.25 (s, 6H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 149.0, 146.7 (d, J = 6.0 Hz), 142.2 (d, J = 7.5 Hz), 136.2, 132.2 (d, J = 10.5 Hz), 131.9 (d, J = 6.0 Hz), 131.6 (d, J = 10.5 Hz), 131.5 (d, J = 3.0 Hz), 130.9 (d, J = 6.0 Hz), 128.3, 126.8 (d, J = 3.0 Hz), 126.4 (d, J = 3.0 Hz), 125.3 (d, J = 12.0 Hz), 120.8, 30.4 (d, J = 67.5 Hz), 21.3 (d, J = 4.5 Hz) ppm. HRMS (ESI^+): calcd for $\text{C}_{24}\text{H}_{23}\text{NOP}$ $[\text{M}+\text{H}]^+$ 372.1517, found 372.1510.



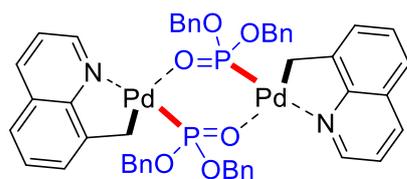
Diphenyl((1,2,3,4-tetrahydroquinolin-8-yl)methyl)phosphine oxide (**4**)

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 3/1, v/v) afforded **4** as a white solid (57 mg, 82% yield). M.p. :135-137 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.71-7.74 (m, 4H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 4H), 6.79 (d, *J* = 7.2 Hz, 1H), 6.44 (d, *J* = 7.2 Hz, 1H), 6.37 (t, *J* = 7.2 Hz, 1H), 5.71 (bs, 1H), 3.59 (d, *J* = 12.6 Hz, 2H), 3.33 (t, *J* = 5.4 Hz, 2H), 2.75 (t, *J* = 6.0 Hz, 2H), 1.85-1.89 (m, 2H) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 145.1 (d, *J* = 3.0 Hz), 132.4 [d (132.69, 132.04), *J* = 97.5 Hz], 132.0 (d, *J* = 3.0 Hz), 131.2 (d, *J* = 9.0 Hz), 129.6 (d, *J* = 6.0 Hz), 128.7 (d, *J* = 10.5 Hz), 128.6 (d, *J* = 3.0 Hz), 123.5 (d, *J* = 3.0 Hz), 117.1 (d, *J* = 9.0 Hz), 116.7 (d, *J* = 1.5 Hz), 42.6, 35.4 (d, *J* = 67.5 Hz), 27.9, 22.0 ppm. HRMS (ESI⁺): calcd for C₂₂H₂₃NOP [M+H]⁺ 348.1517, found 348.1511.



Palladium complex **5**

¹H NMR (600 MHz, DMSO): δ = 9.72 (s, 1H), 8.72 (d, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.97 (d, *J* = 7.2 Hz, 1H), 7.82-7.87 (m, 4H), 7.76 (dd, *J* = 7.8, 5.4 Hz, 1H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 8.4 Hz, 4H), 4.80 (d, *J* = 16.8 Hz, 2H). ¹³C NMR (150 MHz, DMSO) δ = 164.3 [d (165.12, 163.45), *J* = 250.5 Hz], 156.3, 142.1, 140.6, 135.8 (dd, *J* = 12.0, 9.0 Hz), 135.3 (d, *J* = 10.5 Hz), 130.0, 129.5, 127.6, 127.4, 122.3 (d, *J* = 63.0 Hz), 121.9, 116.2 (dd, *J* = 22.5, 13.5 Hz), 26.0 (d, *J* = 33.0 Hz). HRMS (ESI⁺): calcd for C₂₂H₁₆ClF₂NPPd [M-Cl]⁺ 503.9712, found 503.9721.



Palladium complex **7**

Purification via silica gel column chromatography (dichloromethane / methanol = 20/1, v/v) afforded **7** as a pale yellow solid (62 mg, 68% yield). ^1H NMR (600 MHz, CDCl_3): δ = 8.88 (s, 2H), 8.23 (d, J = 7.8 Hz, 2H), 7.60 (t, J = 7.2 Hz, 4H), 7.46-7.49 (m, 10H), 7.25-7.29 (m, 10H), 7.20 (t, J = 7.2 Hz, 4H), 5.31-5.42 (m, 8H), 3.37 (s, 4H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 151.0, 149.8, 148.1, 139.3 (d, J = 3.0 Hz), 137.8 (d, J = 6.0 Hz), 129.3, 128.9, 128.2 (d, J = 4.5 Hz), 127.8 (d, J = 3.0 Hz), 127.5 (d, J = 3.0 Hz), 127.2 (d, J = 4.5 Hz), 123.3 (d, J = 6.0 Hz), 121.1, 64.8 (d, J = 3.0 Hz), 19.6 (d, J = 6.0 Hz) ppm. HRMS (ESI $^+$): calcd for $\text{C}_{48}\text{H}_{45}\text{N}_2\text{O}_6\text{P}_2\text{Pd}_2$ $[\text{M}+\text{H}]^+$ 1019.0823, found 1019.0830.

VII. References

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VIII. Copies of NMR spectra

