

Supporting Information

for

***N*-Phosphinoylaminophthalimide: A Phosphinoyl Radical Precursor Applied in Phosphinoyl-Substituted Phenanthridine and Ketone Synthesis**

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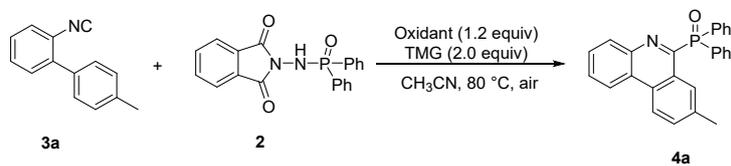
(A) General information

All reactions were carried out by standard procedures under air condition at room temperature unless stated otherwise. All hydrazine materials are commercially available unless stated otherwise. All solvents were freshly distilled prior to use in synthesis unless otherwise noted. Flash column chromatography was performed using silica gel (200-300 mesh). ^1H , ^{13}C and ^{19}F NMR spectra were measured on Bruker Avance IIDMX 400 MHz spectrometers (400 MHz for ^1H NMR, 101 MHz for ^{13}C NMR and 289 MHz for ^{19}F NMR). Chemical shifts are reported in parts per million (ppm) relative to TMS (0.00) for the ^1H NMR, residual signals in solvents (CDCl_3 at δ 77.16 ppm) for the ^{13}C NMR and CFCl_3 (0.00 ppm) for the ^{19}F NMR measurements. Coupling constant (J) are quoted in Hz.

(B) Optimization of Reaction Conditions

1. Optimization for the formation of **4a**

(a) Optimization on additive



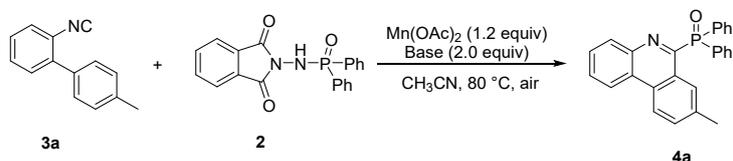
Under air atmosphere, dry CH₃CN (2.0 mL) was added to an oven-dried reaction tube charged with 2-isocyano-4'-methyl-1,1'-biphenyl **3a** (1.0 equiv, 0.2 mmol), *N*-phosphinoylaminophthalimide **2** (1.5 equiv, 0.3 mmol), TMG (2.0 equiv, 0.4 mmol) and additive (1.2 equiv); then the reaction mixture was stirred at 80 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH₄Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (PE:EA = 2:1) to give the desired product **4a**.

Table S1. Optimization on additive.

Entry	Additive	Time/h	Yield/%
1	Cu(acac) ₂	24	15
2	Cu(OTf) ₂	26	9
3	Cu ₂ O	24	17
4	MnSO ₄	23	34
5	Mn(OAc)₂	24	55
6	Mn(acac) ₃	24	51
7	Mn(OTf) ₂	25	13

8	MnBr ₂	25	11
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(b) Optimization on base

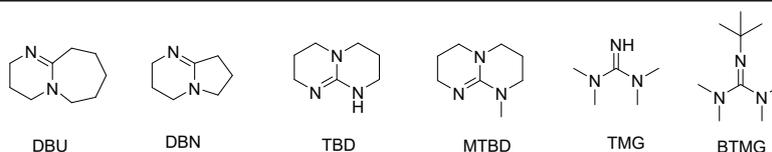


Under air atmosphere, dry CH₃CN (2.0 mL) was added to an oven-dried reaction tube charged with 2-isocyano-4'-methyl-1,1'-biphenyl **3a** (1.0 equiv, 0.2 mmol), *N*-phosphinoylaminophthalimide **2** (1.5 equiv, 0.3 mmol), Mn(OAc)₂ (1.2 equiv, 0.24 mmol) and base (2.0 equiv); then the reaction mixture was stirred at 80 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH₄Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (PE:EA = 2:1) to give the desired product **4a**.

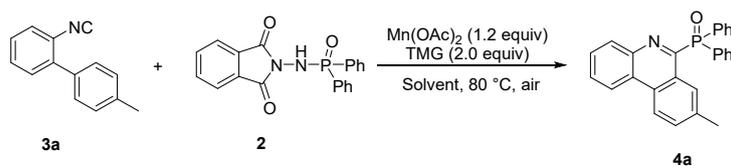
Table S2. Optimization on base.

Entry	Base	Time/h	Yield/%
1	Cs ₂ CO ₃	23	9
2	EtONa	23	3
3	Et ₃ N	24	14
4	^t BuOK	24	19
5	BTMG	24	18
6	DABCO	24	28
7	DMAP	22	17

8	DIPEA	23	31
9	DBU	24	50
10	DBN	23	51
11	TBD	25	39
12	MTBD	21	53
13	TMG	22	55



(c) Optimization on solvent



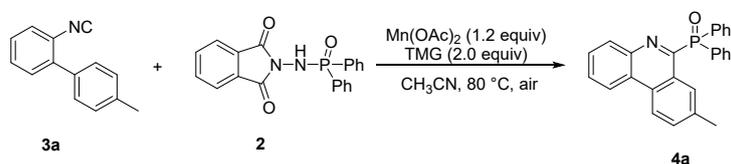
Under air atmosphere, dry solvent (2.0 mL) was added to an oven-dried reaction tube charged with 2-isocyano-4'-methyl-1,1'-biphenyl **3a** (1.0 equiv, 0.2 mmol), *N*-phosphinoylaminophthalimide **2** (1.5 equiv, 0.3 mmol), $\text{Mn}(\text{OAc})_2$ (1.2 equiv, 0.24 mmol) and TMG (2 equiv 0.4 mmol); then the reaction mixture was stirred at 80 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH_4Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (PE:EA = 2:1) to give the desired product **4a**.

Table S3. Optimization on solvent.

Entry	Solvent	Time/h	Yield/%
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1	CH₃CN	24	55
2	Dioxane	23	38
3	THF	31	19
4	Toluene	24	24
5	DMSO	24	41
6	DMF	23	41

(d) Optimization on ratio of **3a** and **2**

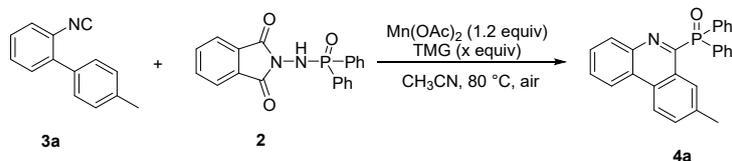


Under air atmosphere, dry CH₃CN (2.0 mL) was added to an oven-dried reaction tube charged with 2-isocyano-4'-methyl-1,1'-biphenyl **3a** (1.0 equiv, 0.2 mmol), *N*-phosphinoylaminophthalimide **2**, Mn(OAc)₂ (1.2 equiv, 0.24 mmol) and TMG (2 equiv 0.4 mmol); then the reaction mixture was stirred at 80 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH₄Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (PE:EA = 2:1) to give the desired product **4a**.

Table S4. Optimization on ratio of **3a** and **2**.

Entry	3a:2	Time/h	Yield/%
1	1:1.0	24	45
2	1:1.2	24	51
3	1:1.5	24	55

(e) Optimization on base equivalent

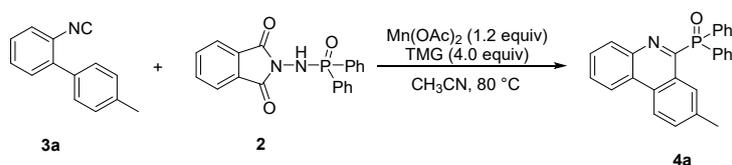


Under air atmosphere, dry CH_3CN (2.0 mL) was added to an oven-dried reaction tube charged with 2-isocyano-4'-methyl-1,1'-biphenyl **3a** (1.0 equiv, 0.2 mmol), *N*-phosphinoylaminophthalimide **2** (1.5 equiv, 0.3 mmol), $\text{Mn}(\text{OAc})_2$ (1.2 equiv, 0.24 mmol) and TMG (x equiv); then the reaction mixture was stirred at $80\text{ }^\circ\text{C}$ heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH_4Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (PE:EA = 2:1) to give the desired product **4a**.

Table S5. Optimization on base equivalent.

Entry	x	Time/h	Yield/%
1	2	24	55
2	3	24	61
3	3.5	24	66
4	4	24	75
5	4.5	24	56
6	5	22	64
7	6	22	72

(f) Optimization on atmosphere

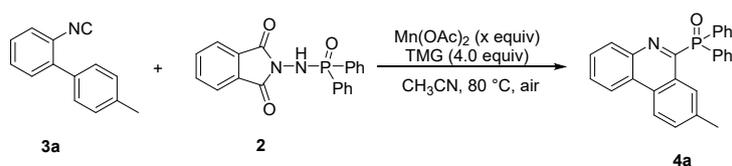


Under different atmosphere, dry CH₃CN (2.0 mL) was added to an oven-dried reaction tube charged with 2-isocyano-4'-methyl-1,1'-biphenyl **3a** (1.0 equiv, 0.2 mmol), *N*-phosphinoylaminophthalimide **2** (1.5 equiv, 0.3 mmol), Mn(OAc)₂ (1.2 equiv, 0.24 mmol) and TMG (4 equiv, 0.8 mmol) and a stirring bar; then the reaction mixture was stirred at 80 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH₄Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (PE:EA = 2:1) to give the desired product **4a**.

Table S6. Optimization on atmosphere.

Entry	Atmosphere	Time/h	Yield/%
1	N ₂	23	41
2	O ₂	24	55
3	air	24	75

(g) Optimization on additive equivalent



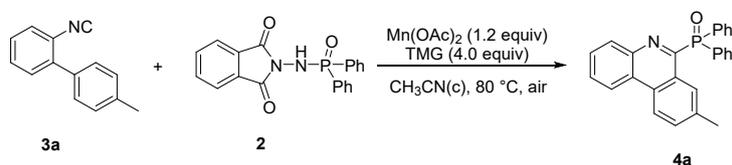
Under air atmosphere, dry CH₃CN (2.0 mL) was added to an oven-dried reaction tube charged with 2-isocyano-4'-methyl-1,1'-biphenyl **3a** (1.0 equiv, 0.2 mmol), *N*-phosphinoylaminophthalimide **2** (1.5 equiv, 0.3 mmol), Mn(OAc)₂ (x equiv) and TMG (4.0 equiv); then the reaction mixture was stirred at 80 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH₄Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed

with 10 mL brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (PE:EA = 2:1) to give the desired product **4a**.

Table S7. Optimization on additive equivalent.

Entry	x	Time/h	Yield/%
1	1.0	24	59
2	1.2	24	75
3	1.5	24	61
4	2.0	24	63

(h) Optimization on concentration



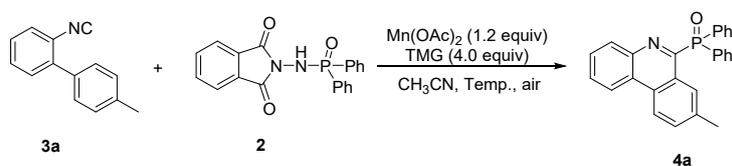
Under air atmosphere, dry CH₃CN was added to an oven-dried reaction tube charged with 2-isocyano-4'-methyl-1,1'-biphenyl **3a** (1.0 equiv, 0.2 mmol), *N*-phosphinoylaminophthalimide **2** (1.5 equiv, 0.3 mmol), Mn(OAc)₂ (1.2 equiv, 0.24 mmol) and TMG (4.0 equiv, 0.8 mmol); then the reaction mixture was stirred at 80 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH₄Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (PE:EA = 2:1) to give the desired product **4a**.

Table S8. Optimization on concentration.

Entry	c/M	Time/h	Yield/%
1	0.27	23	70
2	0.20	23	77

3	0.16	23	78
4	0.13	24	80
5	0.10	24	75
6	0.08	24	76
7	0.07	24	69
8	0.05	24	73

(i) Optimization on temperature



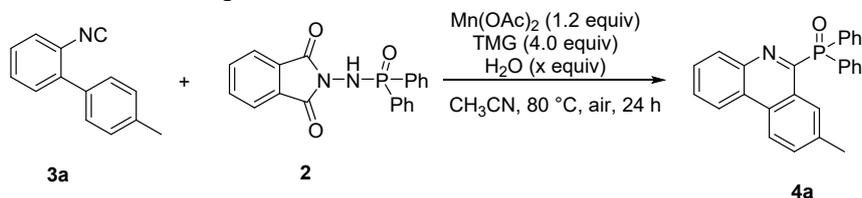
Under air atmosphere, dry CH₃CN (1.5 mL) was added to an oven-dried reaction tube charged with 2-isocyano-4'-methyl-1,1'-biphenyl **3a** (1.0 equiv, 0.2 mmol), *N*-phosphinoylaminophthalimide **2** (1.5 equiv, 0.3 mmol), Mn(OAc)₂ (1.2 equiv, 0.24 mmol) and TMG (4.0 equiv, 0.8 mmol); then the reaction mixture was stirred and heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH₄Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (PE:EA = 2:1) to give the desired product **4a**.

Table S9. Optimization on temperature.

Entry	Temp/°C	Time/h	Yield/%
1	60	23	32
2	70	23	62
3	80	23	80

4	90	23	54
5	100	23	56

(i) Optimization on H₂O equivalent



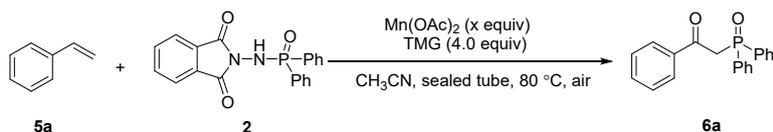
Under air atmosphere, dry CH₃CN (1.5 mL) was added to an oven-dried reaction tube charged with 2-isocyano-4'-methyl-1,1'-biphenyl **3a** (1.0 equiv, 0.2 mmol), *N*-phosphinoylaminophthalimide **2** (1.5 equiv, 0.3 mmol), Mn(OAc)₂ (1.2 equiv, 0.24 mmol), TMG (4.0 equiv, 0.8 mmol) and H₂O (x equiv); then the reaction mixture was stirred at 80 °C and heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH₄Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (PE:EA = 2:1) to give the desired product **4a**.

Table S10. Optimization on temperature.

Entry	x	Yield/%
1	0.5	63
2	1.0	55
3	1.5	54
4	2.0	52
5	0	80

2. Optimization for the formation of **6a**

(a) Optimization on additive equivalent

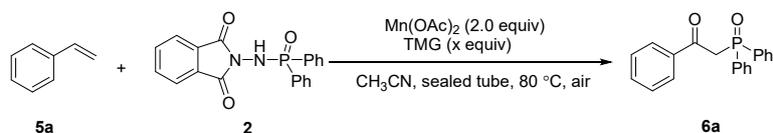


Under air atmosphere, dry CH_3CN (1.5 mL) was added to an oven-dried sealed tube charged with styrene **5a** (1.0 equiv, 0.2 mmol), *N*-phosphinoylaminophthalimide **2** (1.5 equiv, 0.3 mmol), Mn(OAc)_2 (x equiv) and TMG (4.0 equiv); then the reaction mixture was stirred at 80 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH_4Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (PE:EA = 1:2) to give the desired product **6a**.

Table S11. Optimization on additive equivalent.

Entry	x	Time/h	Yield/%
1	1.2	36	43
2	1.5	36	43
3	1.8	36	44
4	2.0	36	48
5	2.5	35	46

(b) Optimization on base equivalent



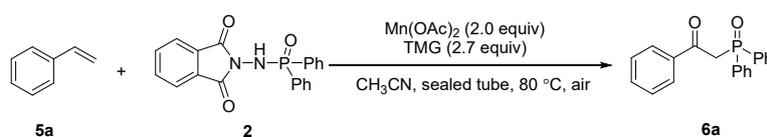
Under air atmosphere, dry CH_3CN (1.5 mL) was added to an oven-dried sealed tube charged with styrene **5a** (1.0 equiv, 0.2 mmol), *N*-phosphinoylaminophthalimide **2** (1.5 equiv, 0.3 mmol), Mn(OAc)_2 (2.0 equiv, 0.4 mmol) and TMG (x equiv); then the reaction mixture was stirred at 80 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH_4Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for

three times. The combined organic phase was continually washed with 10 mL brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (PE:EA = 1:2) to give the desired product **6a**.

Table S12. Optimization on base equivalent.

Entry	x	Time/h	Yield/%
1	2.0	36	41
2	2.5	36	48
3	2.7	36	52
4	3.0	35	50
5	4.0	36	48

(c) Optimization on ratio of **5a** and **2**



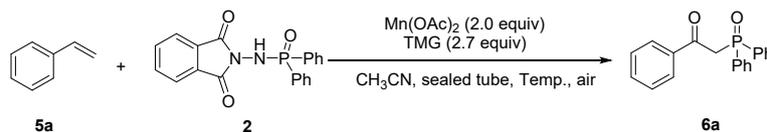
Under air atmosphere, dry CH₃CN (1.5 mL) was added to an oven-dried sealed tube charged with styrene **5a** (1.0 equiv, 0.2 mmol), *N*-phosphinoylaminophthalimide **2**, Mn(OAc)₂ (2.0 equiv, 0.4 mmol) and TMG (2.7 equiv, 0.54 mmol); then the reaction mixture was stirred at 80 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH₄Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (PE:EA = 1:2) to give the desired product **6a**.

Table S13. Optimization on ratio of **5a** and **2**.

Entry	5a:2	Time/h	Yield/%
1	1.0	36	34

2	1.5	36	52
3	1.8	36	63
4	2.0	36	63
5	1.8	12	63

(d) Optimization on temperature

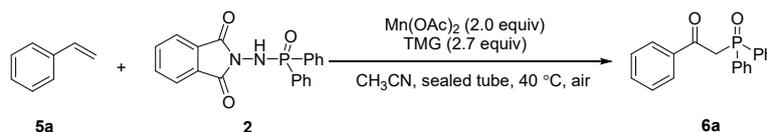


Under air atmosphere, dry CH₃CN (1.5 mL) was added to an oven-dried sealed tube charged with styrene **5a** (1.0 equiv, 0.2 mmol), *N*-phosphinoylaminophthalimide **2** (1.8 equiv, 0.36 mmol), Mn(OAc)₂ (2.0 equiv, 0.4 mmol) and TMG (2.7 equiv 0.54 mmol); then the reaction mixture was stirred at different temperature heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH₄Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (PE:EA = 1:2) to give the desired product **6a**.

Table S14. Optimization on temperature.

Entry	Temp/°C	Time/h	Yield/%
1	40	12	33
2	60	12	55
3	70	12	59
4	80	12	63

(e) Optimization on time

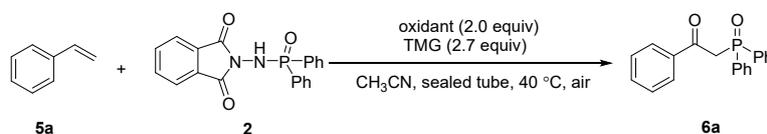


Under air atmosphere, dry CH₃CN (1.5 mL) was added to an oven-dried sealed tube charged with styrene **5a** (1.0 equiv, 0.2 mmol), *N*-phosphinoylaminophthalimide **2** (1.8 equiv, 0.36 mmol), Mn(OAc)₂ (2.0 equiv, 0.4 mmol) and TMG (2.7 equiv 0.54 mmol); then the reaction mixture was stirred at 40 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH₄Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (PE:EA = 1:2) to give the desired product **6a**.

Table S15. Optimization on time.

Entry	Time/h	Yield/%
1	12	33
2	24	40
3	36	60
4	48	68

(f) Optimization on additive



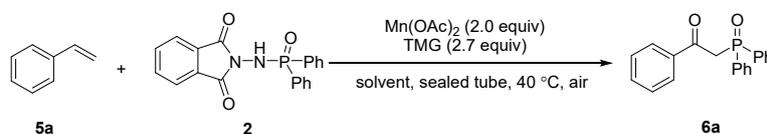
Under air atmosphere, dry CH₃CN (1.5 mL) was added to an oven-dried sealed tube charged with styrene **5a** (1.0 equiv, 0.2 mmol), *N*-phosphinoylaminophthalimide **2** (1.8 equiv, 0.36 mmol), TMG (2.7 equiv, 0.54 mmol) and additive (2 equiv); then the reaction mixture was stirred at 40 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated

aqueous NH_4Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (PE:EA = 1:2) to give the desired product **6a**.

Table S16. Optimization on additive.

Entry	Additive	Time/h	Yield/%
1	$\text{Cu}(\text{OTf})_2$	49	13
2	Cu_2O	50	7
3	MnSO_4	48	33
4	$\text{Mn}(\text{OAc})_2$	48	68
5	$\text{Mn}(\text{acac})_3$	48	38
6	$\text{Mn}(\text{OTf})_2$	49	29

(g) Optimization on solvent

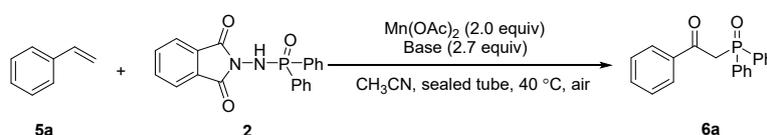


Under air atmosphere, dry solvent (1.5 mL) was added to an oven-dried sealed tube charged with styrene **5a** (1.0 equiv, 0.2 mmol), *N*-phosphinoylaminophthalimide **2** (1.8 equiv, 0.36 mmol), $\text{Mn}(\text{OAc})_2$ (2.0 equiv, 0.4 mmol) and TMG (2.7 equiv 0.54 mmol); then the reaction mixture was stirred at 40 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH_4Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (PE:EA = 1:2) to give the desired product **6a**.

Table S17. Optimization on solvent

Entry	Solvent	Time/h	Yield/%
1	CH₃CN	48	68
2	Dioxane	48	24
3	THF	48	11
4	Toluene	50	trace
5	DMSO	48	41
6	DMF	48	46

(h) Optimization on base

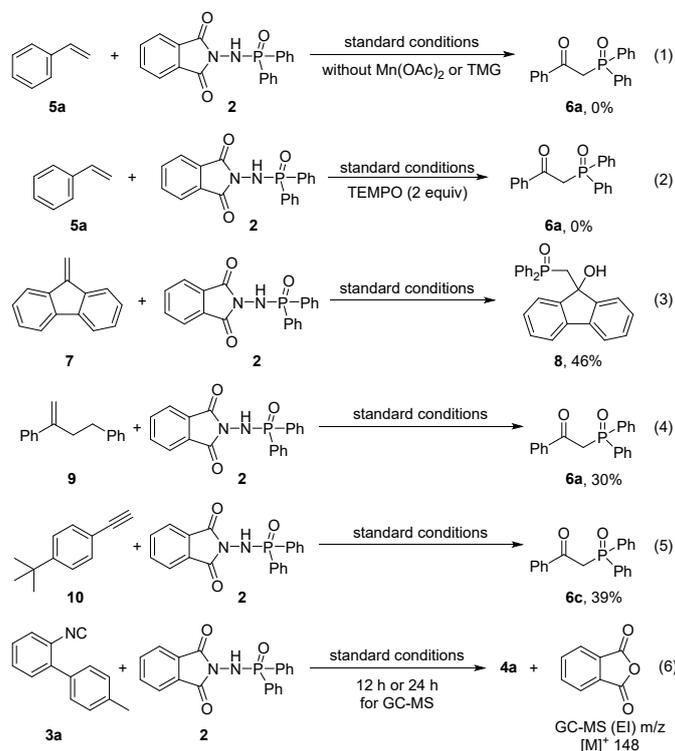


Under air atmosphere, dry CH₃CN (1.5 mL) was added to an oven-dried sealed tube charged with styrene **5a** (1.0 equiv, 0.2 mmol), *N*-phosphinoylaminophthalimide **2** (1.8 equiv, 0.36 mmol), Mn(OAc)₂ (2 equiv, 0.4 mmol) and base (2.7 equiv); then the reaction mixture was stirred at 40 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH₄Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (PE:EA = 1:2) to give the desired product **6a**.

Table S18. Optimization on base.

Entry	Base	Time/h	Yield/%
1	CS ₂ CO ₃	51	9
2	DABCO	48	17
3	DIPEA	48	29
4	DBU	48	49
5	TMG	48	68

(C) Mechanism research



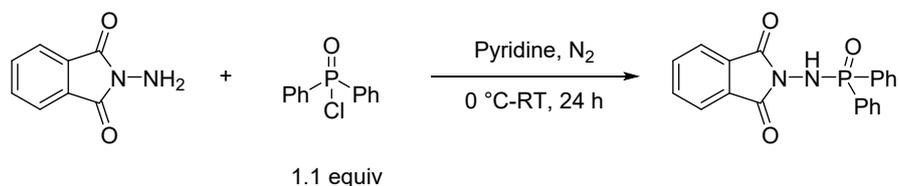
Procedure for control experiments (eq 1, 2): Under air atmosphere, dry CH₃CN (1.5 mL) was added to an oven-dried sealed tube charged with **5a** (1.0 equiv, 0.2 mmol), *N*-phosphinoylaminophthalimide **2** (1.8 equiv, 0.36 mmol), with or without Mn(OAc)₂ (2.0 equiv, 0.4 mmol) or TMG (2.7 equiv 0.54 mmol) and a stirring bar; if needed, TEMPO was added. Then the reaction mixture was stirred at 40 °C in oil bath for 48 h until substrate **6a** was consumed.

Procedure for control experiment (eq 3, 4, 5): Under air atmosphere, dry CH₃CN (1.5 mL) was added to an oven-dried sealed tube charged with **7** (1.0 equiv, 0.2 mmol, 35.6 mg), *N*-phosphinoylaminophthalimide **2** (1.8 equiv, 0.36 mmol), Mn(OAc)₂ (2.0 equiv, 0.4 mmol) and TMG (2.7 equiv 0.54 mmol) and a stirring bar; then the reaction mixture was stirred at 40 °C in oil bath for 48 h. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with 1M HCl. The mixture was then extracted with ethyl acetate for three times. The combined organic phase was continually washed with brine, dried over Na₂SO₄, filtered, and concentrated under

reduced pressure. The resulting residue was purified by flash column chromatography (PE:EA = 6:1) to afford **8** in 46% yield.

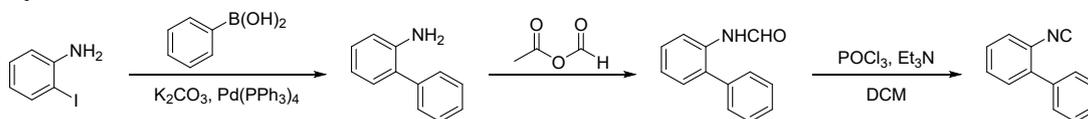
Procedure for control experiments (eq 6): Under air atmosphere, dry CH₃CN (1.5 mL) was added to an oven-dried reaction tube charged with isonitrile **3a** (1.0 equiv, 0.2 mmol), **2** (1.5 equiv, 0.3 mmol), Mn(OAc)₂ (1.2 equiv, 0.24 mmol), TMG (4.0 equiv, 0.8 mmol) and a stirring bar; then the reaction mixture was stirred at 80 °C heated by oil bath for 12 h or 24 h. The reaction mixture was diluted with DCM (7.5 mL) and the obtained solution was tested by GC-MS.

(D) Procedures for starting materials



Add 20 mL of pyridine to a 100 mL round-bottomed flask containing *N*-aminophthalimide (10 mmol) under the atmosphere of N₂, place the reaction in an ice bath, then add diphenylphosphinic chloride (11 mmol, 1.1 equiv) dropwise to the system, stir for 15 min at 0 °C, and then return to the room temperature for 24 h. The reaction was quenched with HCl in an ice bath and washed with DCM, and *N*-phosphinoylaminophthalimide was obtained by filtration.

Synthesis of **3**



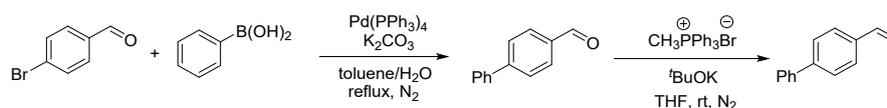
1) Under N₂ atmosphere, toluene:H₂O = 7 ml:7 ml was added to a 100 ml round bottom bottle with 2-iodoaniline (7 mmol, 1.5 g), arylboronic acid (14 mmol), K₂CO₃ (35 mmol, 4.84 g) and Pd(PPh₃)₄ (0.14 mmol, 161.8 mg), then the reaction mixture was stirred at 120 °C heated by oil bath. Upon the completion of the reaction, the mixture

was cooled to room temperature and filter with silica gel. The filtrate concentrated under reduced pressure. The resulting crude mixture was chromatographed on silica gel using petroleum ether/ethyl acetate (PE/EA = 10/1) as eluent to give 2-aminobiphenyl in 88% yield.^[1]

2) Under N₂ atmosphere, Ac₂O (30 mmol) and HCOOH (30 mmol) was added to a 100 ml round bottom bottle. Then the reaction mixture was stirred at 55 °C heated by oil bath for 3 h. 2-aminobiphenyl was added and the mixture was stirred at 55 °C for another 3 h. Upon the completion of the reaction, the mixture was cooled to room temperature and the reaction was quenched with saturated NaHCO₃ and extracted with ethyl acetate (×3), then it was sequentially washed with water (2 × 10 mL), saturated NaHCO₃ (2 × 10 mL) and finally with brine (2 × 10 mL). The organic layer was dried over Na₂SO₄. The mixture concentrated under reduced pressure. The resulting crude mixture was chromatographed on silica gel using ethyl acetate (EA) as eluent to give *N*-biphenyl-2-yl-formamide in 72% yield.^[2]

3) Under N₂ atmosphere, DCM was added to a 100 ml round bottom bottle with *N*-biphenyl-2-yl-formamide (4.4 mmol, 874.8 mg). The reaction mixture was stirred at 0 °C. Then Et₃N (22.2 mmol, 5 equiv), POCl₃ (6.6 mmol, 1.5 equiv) was added to round bottom bottle. After the reaction was completed, the resulting mixture was cooled to 0 °C and aqueous saturated solution of sodium carbonate (5 mL) was added dropwise to quench the reaction. Water (10 mL) was added and organic layer was separated. Aqueous layer was extracted by DCM (20 mL) twice. Combined organic layer was dried over sodium sulfate, and solvent was removed by evaporation. The residue was purified by silica gel column chromatography (PE/EA = 10/1). 2-biphenylisocyanide was obtained in 74% yield.^[3]

Synthesis of 5

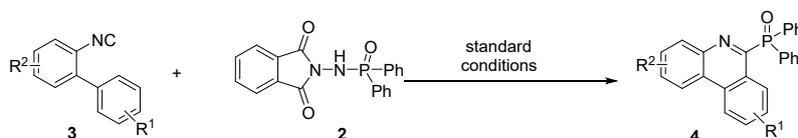


1) Under N₂ atmosphere, 4-bromobenzaldehyde (20 mmol), phenylboronic acid (20 mmol, 1 equiv), tetratriphenylphosphonium palladium (0.3 mmol, 1.5 mol%) and potassium carbonate (40 mmol, 2 equiv) were dissolved in toluene and water (5 : 1) in a 100 mL flask. And the mixture was refluxed and stirred until the 4-bromobenzaldehyde was completely consumed. Then the reaction mixture was cooled to room temperature, quenched with saturated NH₄Cl solution. Ethyl acetate was added, the organic phase was separated and the aqueous phase was extracted several times with additional ethyl acetate. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated. The crude product was purified by column chromatography (PE:EA = 20:1) to obtain the corresponding 4- phenylbenzaldehyde.^[4]

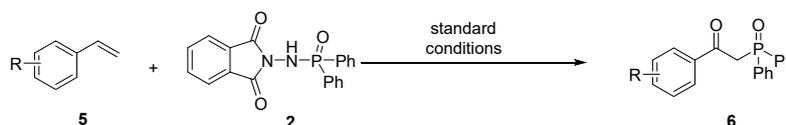
2) Under N₂ atmosphere, after adding triphenylmethylphosphonium bromide (1.3 equiv) to 100 mL round bottom flask, distilled THF was added. The reaction was placed in an ice bath at 0 °C for 5 min, and then ^tBuOK (1.5 equiv) was added. The solution changed from white to yellow, indicating that this step was successful. After stirring for 30 min at 0 °C, 4-phenylbenzaldehyde in THF was added to the mixture, then let the reaction return to room temperature. When the aldehyde was completely consumed by TLC detection, the reaction mixture was quenched with saturated NH₄Cl solution. Ethyl acetate was added, the organic phase was separated and the aqueous phase was extracted several times with additional ethyl acetate. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated. The crude product was purified by column chromatography using PE as the eluting solvent to obtain the corresponding 4-vinylbiphenyl.^[5]

Other olefins, such as 3-methoxystyrene, 2,4-diphenyl-1-butene and etc. were synthesized according to step 2.

(E) General procedure for the synthesis of 4/6

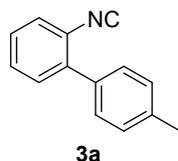


Under air atmosphere, dry CH₃CN (1.5 mL) was added to an oven-dried reaction tube charged with isonitrile **3** (1.0 equiv, 0.2 mmol), **2** (1.5 equiv, 0.3 mmol), Mn(OAc)₂ (1.2 equiv, 0.24 mmol), TMG (4.0 equiv, 0.8 mmol) and a stirring bar; then the reaction mixture was stirred at 80 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH₄Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography using petroleum ether/ethyl acetate as eluent to give the desired product **4**.

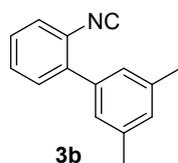


Under air atmosphere, dry CH₃CN (1.5 mL) was added to an oven-dried sealed tube charged with alkene **5** (1.0 equiv, 0.2 mmol), phosphine radical precursors **2** (1.8 equiv, 0.4 mmol), Mn(OAc)₂ (2.0 equiv, 0.4 mmol), TMG (2.7 equiv, 0.54 mmol) and a stirring bar; then the vessel was sealed and the reaction mixture was stirred at 40 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH₄Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography using petroleum ether/ethyl acetate as eluent to give the desired product **6**.

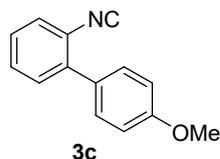
(F) Characterization of products



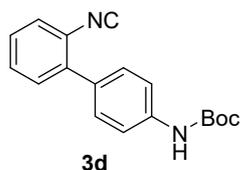
2-isocyano-4'-methyl-1,1'-biphenyl (3a)^[6]: 73% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 9.91 (s, 1H), 8.74 (s, 1H), 8.29 – 7.91 (m, 5H), 7.83 – 7.66 (m, 3H), 7.60 – 7.29 (m, 6H), 7.24 (d, J = 8.5 Hz, 1H), 6.54 (t, J = 5.9 Hz, 1H), 3.23 (dd, J = 25.4, 4.9 Hz, 2H).



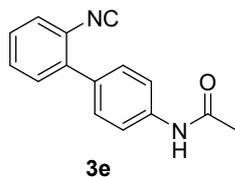
2-isocyano-3',5'-dimethyl-1,1'-biphenyl (3b)^[6]: 51% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.36 (m, 3H), 7.32 (ddd, J = 8.9, 6.3, 2.7 Hz, 1H), 7.08 (d, J = 23.5 Hz, 3H), 2.37 (s, 6H).



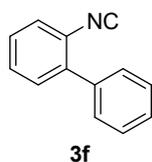
2-isocyano-4'-methoxy-1,1'-biphenyl (3c)^[6]: 80% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.42 (m, 5H), 7.40 – 7.34 (m, 1H), 7.05 (d, J = 8.7 Hz, 2H), 3.91 (s, 3H).



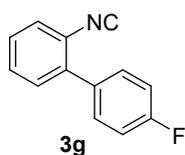
tert-butyl (2'-isocyano-[1,1'-biphenyl]-4-yl)carbamate (3d): 64% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.37 (m, 7H), 7.33 (td, J = 7.7, 2.0 Hz, 1H), 6.69 (s, 1H), 1.53 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 166.3, 152.6, 138.6, 138.2, 131.4, 130.4, 129.6, 129.5, 127.8, 118.3, 80.7, 28.3. HRMS (ESI) m/z calcd for C₁₈H₁₈N₂NaO₂⁺ [M + Na]⁺ 317.1260, found 317.1255.



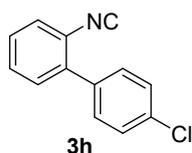
N-(2-isocyano-[1,1'-biphenyl]-4-yl)acetamide (3e): 68% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.64 (d, $J = 8.5$ Hz, 2H), 7.50 – 7.32 (m, 6H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 166.0, 138.2, 132.6, 130.4, 129.6, 128.0, 127.8, 124.4, 119.8, 24.5. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{NaO}^+$ [$\text{M} + \text{Na}$] $^+$ 259.0842, found 259.0839.



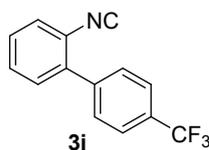
2-isocyano-1,1'-biphenyl (3f)^[6]: 70% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.51 (m, 5H), 7.51 – 7.46 (m, 3H), 7.45 – 7.38 (m, 1H).



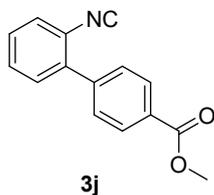
4'-fluoro-2-isocyano-1,1'-biphenyl (3g)^[6]: 47% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.45 (ddd, $J = 13.2, 8.7, 3.2$ Hz, 4H), 7.41 – 7.31 (m, 2H), 7.19 – 7.10 (m, 2H).



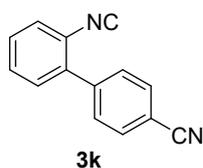
4'-chloro-2-isocyano-1,1'-biphenyl (3h)^[6]: 55% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.45 (m, 2H), 7.45 (s, 4H), 7.38 (dd, $J = 7.8, 6.6$ Hz, 2H).



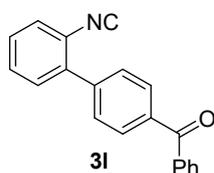
2-isocyano-4'-(trifluoromethyl)-1,1'-biphenyl (3i)^[6]: 49% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, J = 8.2 Hz, 2H), 7.64 (t, J = 6.1 Hz, 2H), 7.58 – 7.47 (m, 2H), 7.47 – 7.42 (m, 2H).



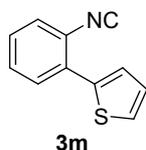
methyl 2'-isocyano-[1,1'-biphenyl]-4-carboxylate (3j)^[6]: 61% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.55 – 7.46 (m, 2H), 7.46 – 7.39 (m, 2H), 3.96 (s, 3H).



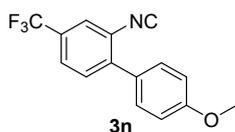
2'-isocyano-[1,1'-biphenyl]-4-carbonitrile (3k)^[6]: 75% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.52 (m, J = 8.9, 1.8 Hz, 2H), 7.47 (dd, J = 7.6, 1.7 Hz, 1H), 7.45 – 7.41 (m, 1H).



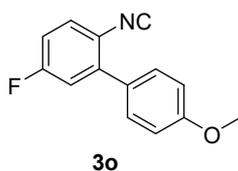
(2'-isocyano-[1,1'-biphenyl]-4-yl)(phenyl)methanone (3l)^[6]: 37% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, J = 7.9 Hz, 2H), 7.86 (d, J = 7.8 Hz, 2H), 7.62 (dd, J = 13.2, 7.4 Hz, 3H), 7.57 – 7.40 (m, 6H).



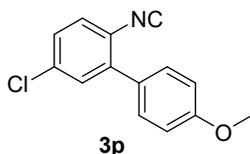
2-(2-isocyano-4'-(trifluoromethyl)-1,1'-biphenyl)thiophene (3m)^[6]: 29% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.55 (m, 2H), 7.55 – 7.35 (m, 4H), 7.33 – 7.18 (m, 1H).



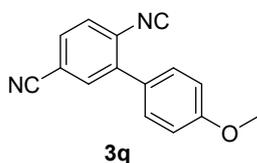
2-isocyano-4'-methoxy-4-(trifluoromethyl)-1,1'-biphenyl (3n): 44% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.73 (s, 1H), 7.68 (d, $J = 8.2$ Hz, 1H), 7.54 (d, $J = 8.2$ Hz, 1H), 7.50 – 7.43 (m, 2H), 7.09 – 6.99 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 160.3, 141.9, 131.1, 130.2, 130.1 (d, $J = 33.7$ Hz), 127.8, 126.1 (d, $J = 3.1$ Hz), 125.0 (d, $J = 3.8$ Hz), 124.7, 124.4, 121.7, 114.2, 55.3. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{10}\text{F}_3\text{NNaO}^+$ [$\text{M} + \text{Na}$] $^+$ 300.0607, found 300.0612.



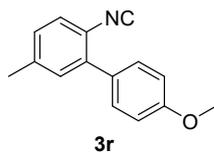
5-fluoro-2-isocyano-4'-methoxy-1,1'-biphenyl (3o): 65% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.46 (dd, $J = 8.5, 4.2$ Hz, 3H), 7.11 (dd, $J = 9.1, 2.6$ Hz, 1H), 7.02 (t, $J = 9.1$ Hz, 3H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.0, 162.2 (d, $J = 251.8$ Hz), 160.1, 141.0 (d, $J = 8.7$ Hz), 130.2, 129.8 (d, $J = 9.3$ Hz), 128.3, 127.8, 117.3 (d, $J = 23.4$ Hz), 114.8 (d, $J = 23.3$ Hz), 114.2, 55.4. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{10}\text{FNNaO}^+$ [$\text{M} + \text{Na}$] $^+$ 250.0639, found 250.0632.



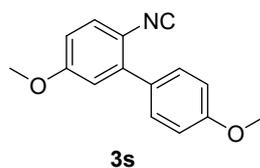
5-chloro-2-isocyano-4'-methoxy-1,1'-biphenyl (3p): 71% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.42 (m, 2H), 7.40 (dd, $J = 5.4, 3.1$ Hz, 2H), 7.30 (dd, $J = 8.5, 2.2$ Hz, 1H), 7.04 – 6.98 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.1, 140.1, 135.3, 130.4, 130.1, 129.0, 128.0, 127.7, 114.2, 55.4. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{10}\text{ClNNaO}^+$ [$\text{M} + \text{Na}$] $^+$ 266.0343, found 266.0342.



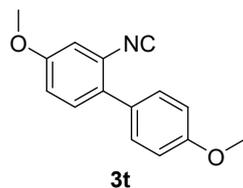
6-isocyano-4'-methoxy-[1,1'-biphenyl]-3-carbonitrile (3q): 64% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.69 (m, 1H), 7.67 – 7.54 (m, 2H), 7.44 (d, $J = 8.7$ Hz, 2H), 7.04 (d, $J = 8.7$ Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 160.4, 139.8, 134.2, 131.0, 130.1, 128.7, 127.7, 126.9, 117.3, 114.4, 113.5, 55.4. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{10}\text{N}_2\text{NaO}^+$ [$\text{M} + \text{Na}$] $^+$ 257.0685, found 257.0685.



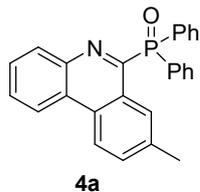
2-isocyano-4'-methoxy-5-methyl-1,1'-biphenyl (3r): 74% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, J = 8.6 Hz, 2H), 7.34 (d, J = 8.0 Hz, 1H), 7.20 (s, 1H), 7.12 (d, J = 8.1 Hz, 1H), 7.00 (d, J = 8.6 Hz, 2H), 3.86 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.6, 139.8, 138.2, 131.0, 130.1, 129.5, 128.3, 127.6, 113.9, 55.3, 21.3. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{13}\text{NNaO}^+$ $[\text{M} + \text{Na}]^+$ 246.0889, found 246.0882.



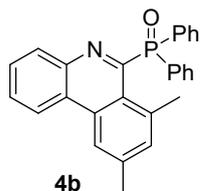
2-isocyano-4',5-dimethoxy-1,1'-biphenyl (3s): 53% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, J = 8.7 Hz, 2H), 7.38 (d, J = 8.7 Hz, 1H), 6.99 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 2.7 Hz, 1H), 6.82 (dd, J = 8.7, 2.8 Hz, 1H), 3.84 (d, J = 7.8 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.7, 159.7, 159.7, 139.9, 130.0, 129.3, 129.1, 117.5, 115.2, 113.9, 113.1, 55.5, 55.2. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{13}\text{NNaO}_2^+$ $[\text{M} + \text{Na}]^+$ 262.0838, found 262.0843.



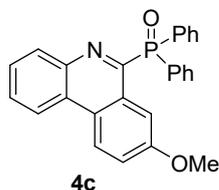
2-isocyano-4,4'-dimethoxy-1,1'-biphenyl (3t): 65% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, J = 8.7 Hz, 2H), 7.30 (d, J = 8.3 Hz, 1H), 6.99 (d, J = 8.8 Hz, 4H), 3.85 (d, J = 4.2 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.0, 159.4, 158.8, 131.3, 131.2, 130.2, 129.2, 116.2, 114.0, 112.6, 55.8, 55.4. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{13}\text{NNaO}_2^+$ $[\text{M} + \text{Na}]^+$ 262.0838, found 262.0842.



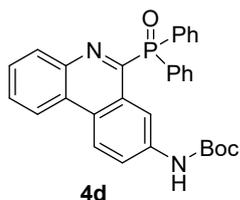
(8-methylphenanthridin-6-yl)diphenylphosphine oxide (4a)^[6]: 80% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 8.50 (dt, *J* = 8.1, 2.4 Hz, 2H), 8.05 – 8.00 (m, 1H), 7.98 – 7.90 (m, 4H), 7.64 (td, *J* = 7.8, 7.1, 4.0 Hz, 3H), 7.49 (td, *J* = 7.3, 1.4 Hz, 2H), 7.46 – 7.38 (m, 4H), 2.54 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 156.2 (d, *J* = 128.7 Hz), 142.4 (d, *J* = 23.4 Hz), 138.0, 133.6, 132.9, 132.5, 132.3 (d, *J* = 9.2 Hz), 131.6 (d, *J* = 2.5 Hz), 131.0, 130.4 (d, *J* = 6.8 Hz), 128.6, 128.2, 128.1, 128.0, 127.6, 124.4 (d, *J* = 2.4 Hz), 121.9 (d, *J* = 6.8 Hz), 21.9.



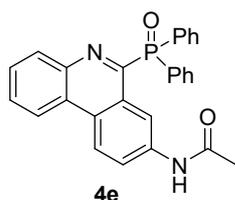
(7,9-dimethylphenanthridin-6-yl)diphenylphosphine oxide (4b)^[6]: 40% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.54 (s, 1H), 8.33 (s, 1H), 7.93 – 7.17 (m, 14H), 2.95 (s, 3H), 2.55 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 156.6 (d, *J* = 129.4 Hz), 141.3 (d, *J* = 24.2 Hz), 140.7, 137.5, 135.4, 134.4, 134.3, 133.3, 132.0 (d, *J* = 8.9 Hz), 131.1, 130.4, 128.5 (d, *J* = 30.1 Hz), 128.0 (d, *J* = 12.2 Hz), 125.5 (d, *J* = 23.6 Hz), 124.2, 122.2, 120.0, 24.9, 21.8.



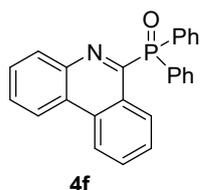
(8-methoxyphenanthridin-6-yl)diphenylphosphine oxide (4c)^[6]: 83% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 9.02 (d, *J* = 2.5 Hz, 1H), 8.54 – 8.32 (m, 2H), 8.11 – 7.92 (m, 5H), 7.71 – 7.57 (m, 2H), 7.54 – 7.47 (m, 2H), 7.44 (ddd, *J* = 9.2, 5.9, 2.7 Hz, 5H), 3.92 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 158.8, 155.4 (d, *J* = 129.5 Hz), 142.0 (d, *J* = 23.1 Hz), 133.5, 132.5, 132.3 (d, *J* = 9.2 Hz), 131.6 (d, *J* = 2.3 Hz), 131.0, 129.4 (d, *J* = 23.0 Hz), 128.8, 128.1 (d, *J* = 12.1 Hz), 127.6, 127.0 (d, *J* = 6.7 Hz), 124.5, 122.6, 121.6, 107.5, 55.6.



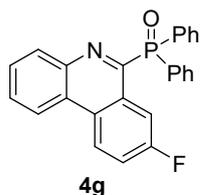
tert-butyl (6-(diphenylphosphoryl)phenanthridin-8-yl)carbamate (4d): 80% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 9.22 (s, 1H), 8.55 (dd, $J = 28.3, 8.3$ Hz, 3H), 8.07 - 7.87 (m, 5H), 7.79 - 7.58 (m, 3H), 7.46 (dt, $J = 28.0, 6.0$ Hz, 6H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.5 (d, $J = 128.9$ Hz), 152.9, 142.0 (d, $J = 23.3$ Hz), 138.6, 133.4, 132.4 (d, $J = 9.2$ Hz), 132.2, 131.6 - 131.6 (m), 130.9, 128.8, 128.5 (d, $J = 22.9$ Hz), 128.1 (d, $J = 12.2$ Hz), 127.8, 124.4 - 124.2 (m), 123.3, 123.1, 121.8, 115.5, 80.6, 28.2. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 28.13. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{27}\text{N}_2\text{NaO}_3\text{P}^+$ $[\text{M} + \text{Na}]^+$ 517.1652, found 517.1653.



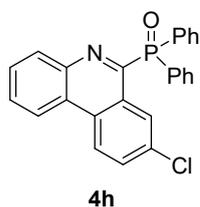
***N*-(6-(diphenylphosphoryl)phenanthridin-8-yl)acetamide (4e):** 81% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 9.48 (s, 1H), 9.27 (s, 1H), 8.62 (d, $J = 8.1$ Hz, 1H), 8.55 - 8.35 (m, 2H), 7.97 (d, $J = 6.9$ Hz, 1H), 7.92 - 7.74 (m, 4H), 7.72 - 7.59 (m, 2H), 7.48 - 7.23 (m, 6H), 2.03 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.5, 155.3 (d, $J = 130.1$ Hz), 142.2 (d, $J = 23.7$ Hz), 138.6, 132.3 (d, $J = 9.3$ Hz), 132.1 (d, $J = 105.6$ Hz), 131.9 (m), 131.1, 129.1, 128.7 (d, $J = 6.6$ Hz), 128.3, 128.2, 128.1, 124.8, 124.3 (m), 123.1, 122.0, 116.6, 24.4. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 29.20. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{21}\text{N}_2\text{NaO}_2\text{P}^+$ $[\text{M} + \text{Na}]^+$ 459.1233, found 459.1224.



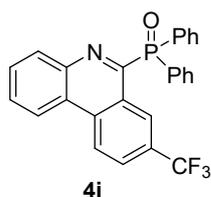
phenanthridin-6-yl diphenylphosphine oxide (4f)^[6]: 65% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 9.51 (d, $J = 8.3$ Hz, 1H), 8.64 (d, $J = 8.4$ Hz, 1H), 8.58 (dd, $J = 6.2, 3.3$ Hz, 1H), 8.05 (dd, $J = 6.1, 3.4$ Hz, 1H), 8.00 - 7.89 (m, 4H), 7.87 - 7.80 (m, 1H), 7.70 (td, $J = 5.5, 2.6$ Hz, 3H), 7.55 - 7.48 (m, 2H), 7.47 - 7.39 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.8 (d, $J = 128.4$ Hz), 142.7 (d, $J = 23.3$ Hz), 133.4, 132.5 (d, $J = 6.8$ Hz), 132.3 (d, $J = 9.2$ Hz), 131.6 (d, $J = 2.5$ Hz), 131.1, 131.0, 128.8, 128.6, 128.5, 128.2, 128.1, 127.8, 127.8 (d, $J = 23.2$ Hz), 124.3 (m), 122.0.



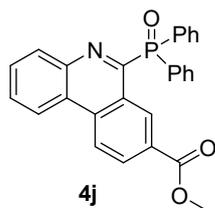
(8-fluorophenanthridin-6-yl)diphenylphosphine oxide (4g)^[6]: 71% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 9.33 (dd, $J = 10.2, 2.6$ Hz, 1H), 8.64 (dd, $J = 9.1, 4.1$ Hz, 1H), 8.56 – 8.48 (m, 1H), 8.11 – 8.03 (m, 1H), 8.01 – 7.90 (m, 4H), 7.72 (ddd, $J = 7.0, 4.7, 1.7$ Hz, 2H), 7.59 (td, $J = 9.3, 2.9$ Hz, 1H), 7.56 – 7.49 (m, 2H), 7.46 (td, $J = 7.4, 3.0$ Hz, 4H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 161.2 (d, $J = 249.5$ Hz), 142.4 (d, $J = 22.8$ Hz), 133.1, 132.3, 132.2, 132.1, 131.8 (d, $J = 2.8$ Hz), 131.2, 129.2, 128.6, 128.3, 128.2, 124.6 (d, $J = 8.6$ Hz), 123.9, 121.9, 120.5 (d, $J = 24.5$ Hz), 113.2 (d, $J = 23.3$ Hz).



(8-chlorophenanthridin-6-yl)diphenylphosphine oxide (4h)^[6]: 78% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 9.67 (d, $J = 1.9$ Hz, 1H), 8.59 – 8.45 (m, 2H), 8.06 (dd, $J = 5.8, 3.7$ Hz, 1H), 8.02 – 7.89 (m, 4H), 7.77 (dd, $J = 8.9, 2.1$ Hz, 1H), 7.71 (dd, $J = 6.1, 3.4$ Hz, 2H), 7.59 – 7.49 (m, 2H), 7.45 (ddd, $J = 7.1, 5.3, 2.3$ Hz, 4H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 155.8 (d, $J = 127.9$ Hz), 142.6 (d, $J = 22.7$ Hz), 133.9, 133.2, 132.3 (d, $J = 9.2$ Hz), 132.1, 131.8, 131.8, 131.1, 130.9 (d, $J = 6.6$ Hz), 129.2, 129.0, 128.7 (d, $J = 23.1$ Hz), 128.2 (d, $J = 12.2$ Hz), 127.6, 123.7, 122.0.

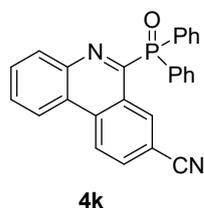


diphenyl(8-(trifluoromethyl)phenanthridin-6-yl)phosphine oxide (4i)^[6]: 61% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 10.03 (s, 1H), 8.77 (d, $J = 8.8$ Hz, 1H), 8.63 (d, $J = 6.8$ Hz, 1H), 8.22 – 7.91 (m, 6H), 7.86 – 7.76 (m, 2H), 7.59 – 7.38 (m, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 133.1, 132.4, 132.3, 132.0, 131.9, 131.3, 129.9, 129.4, 128.3, 128.2, 126.9, 126.3, 123.2, 122.5.



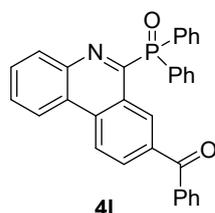
methyl 6-(diphenylphosphoryl)phenanthridine-8-carboxylate (4j)^[6]: 70% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 10.31 (s, 1H), 8.77 – 8.53 (m, 2H), 8.46 (dd, J = 8.7, 1.6 Hz, 1H), 8.18 – 8.06 (m, 1H), 8.00 (dd, J = 11.8, 7.0 Hz, 4H), 7.77 (dq, J = 6.0, 3.7, 2.3 Hz, 2H), 7.59 – 7.39 (m, 6H), 3.99 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 166.5, 157.4 (d, J = 127.4 Hz), 143.3 (d, J = 22.9 Hz), 135.4 (d, J = 6.7 Hz), 132.7 (d, J = 105.1 Hz), 132.4, 131.8 (d, J = 2.5 Hz), 131.1, 130.9, 130.6, 129.8, 129.2, 129.1, 128.2, 128.1, 127.3 (d, J = 23.0 Hz), 123.6 (d, J = 2.2 Hz), 122.6, 122.4, 52.5.



6-(diphenylphosphoryl)phenanthridine-8-carbonitrile (4k)^[6]: 64% yield; ¹H

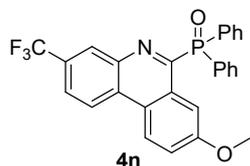
NMR (400 MHz, Chloroform-*d*) δ 10.08 (s, 1H), 8.66 (d, J = 8.5 Hz, 1H), 8.59 – 8.40 (m, 1H), 8.11 (d, J = 7.4 Hz, 1H), 7.97 (dd, J = 11.8, 7.4 Hz, 5H), 7.81 (p, J = 6.9 Hz, 2H), 7.55 (t, J = 7.1 Hz, 2H), 7.48 (dt, J = 7.0, 3.6 Hz, 4H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 156.4 (d, J = 126.6 Hz), 143.7 – 142.7 (m), 134.9 (d, J = 6.6 Hz), 133.8, 132.2, 132.2, 132.1 (d, J = 105.4 Hz), 132.0 (d, J = 2.3 Hz), 130.8 (d, J = 77.5 Hz), 129.6, 128.4, 128.2, 127.1 (d, J = 22.9 Hz), 123.3, 122.5, 118.3, 111.3.



(6-(diphenylphosphoryl)phenanthridin-8-yl)(phenyl)methanone (4l)^[6]: 33%

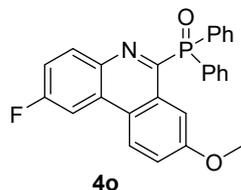
yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 9.80 (s, 1H), 8.74 (d, J = 8.6 Hz, 1H), 8.66 – 8.53 (m, 1H), 8.36 (dd, J = 8.6, 1.6 Hz, 1H), 8.12 – 8.01 (m, 1H), 7.88 (dd, J = 11.8, 7.1 Hz, 4H), 7.80 – 7.70 (m, 4H), 7.60 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.4 Hz, 2H), 7.48 – 7.40 (m, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 195.3, 157.6 (d, J = 127.7 Hz),

143.4 (d, $J = 22.8$ Hz), 136.3 (d, $J = 97.0$ Hz), 135.1 (d, $J = 6.6$ Hz), 132.71 132.6, 132.1 (d, $J = 9.3$ Hz), 131.7 (d, $J = 2.3$ Hz), 131.7, 131.5, 131.2, 131.0, 130.1, 129.8, 129.2, 128.3 (d, $J = 13.2$ Hz), 128.1, 126.3 (d, $J = 23.0$ Hz), 123.6 (d, $J = 2.1$ Hz), 122.9, 122.6.



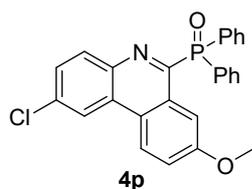
(8-methoxy-3-(trifluoromethyl)phenanthridin-6-yl)diphenylphosphine oxide

(4n): 80% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 9.08 (d, $J = 2.4$ Hz, 1H), 8.53 (dd, $J = 15.6, 8.8$ Hz, 2H), 8.29 (s, 1H), 8.03 – 7.89 (m, 4H), 7.84 (d, $J = 8.6$ Hz, 1H), 7.59 – 7.42 (m, 7H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.7, 157.5 (d, $J = 126.9$ Hz), 141.0 (d, $J = 23.3$ Hz), 133.0, 132.3, 132.2, 131.9 (d, $J = 2.2$ Hz), 131.9, 130.1 (d, $J = 22.5$ Hz), 129.5 (d, $J = 33.0$ Hz), 128.4 (d, $J = 3.9$ Hz), 128.4, 128.2, 126.7, 126.2 (d, $J = 6.6$ Hz), 125.3, 124.4 (d, $J = 2.9$ Hz), 123.9, 123.2, 122.8, 107.8, 55.7. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.89. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{19}\text{F}_3\text{NNaO}_2\text{P}^+$ $[\text{M} + \text{Na}]^+$ 500.0998, found 500.0999.

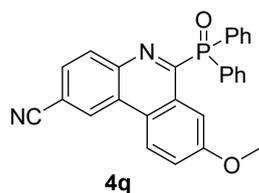


(2-fluoro-8-methoxyphenanthridin-6-yl)diphenylphosphine oxide **(4o)**: 51%

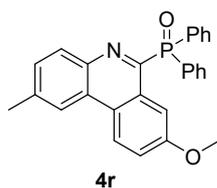
yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.99 (d, $J = 2.3$ Hz, 1H), 8.40 (d, $J = 9.0$ Hz, 1H), 8.05 (ddd, $J = 23.7, 9.5, 4.1$ Hz, 2H), 7.94 (dd, $J = 11.6, 7.4$ Hz, 4H), 7.57 – 7.49 (m, 2H), 7.49 – 7.41 (m, 5H), 7.38 (td, $J = 8.8, 2.5$ Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.7, 161.2, 159.3, 133.5, 133.4, 133.3, 132.3, 132.2, 131.7 (d, $J = 2.3$ Hz), 129.4 (d, $J = 22.9$ Hz), 128.2, 128.1, 123.8, 122.6, 116.8 (d, $J = 24.7$ Hz), 107.6, 106.4 (d, $J = 23.4$ Hz), 55.7. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.91. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{19}\text{FNNaO}_2\text{P}^+$ $[\text{M} + \text{Na}]^+$ 450.1030, found 450.1024



(2-chloro-8-methoxyphenanthridin-6-yl)diphenylphosphine oxide (4p): 79% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 9.01 – 8.99 (m, 1H), 8.52 – 8.23 (m, 2H), 8.05 – 7.83 (m, 5H), 7.58 – 7.49 (m, 3H), 7.45 (ddd, $J = 12.0, 8.3, 2.8$ Hz, 5H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.2, 155.8 (d, $J = 128.4$ Hz), 140.3 (d, $J = 23.3$ Hz), 134.8, 133.3, 132.2 (d, $J = 9.2$ Hz), 132.2, 131.7 (d, $J = 2.4$ Hz), 129.6 (d, $J = 22.8$ Hz), 128.2, 128.2 (d, $J = 9.6$ Hz), 125.9 (d, $J = 6.7$ Hz), 125.5 (d, $J = 2.2$ Hz), 123.6, 122.8, 121.2, 107.6, 55.6. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.80. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{19}\text{ClNNaO}_2\text{P}^+$ $[\text{M} + \text{Na}]^+$ 466.0734, found 466.0725.

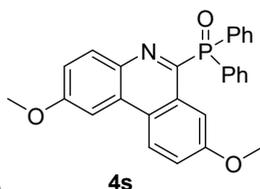


6-(diphenylphosphoryl)-8-methoxyphenanthridine-2-carbonitrile (4q): 49% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 9.07 (s, 1H), 8.82 (s, 1H), 8.48 (d, $J = 9.1$ Hz, 1H), 8.10 (d, $J = 8.5$ Hz, 1H), 7.94 (dd, $J = 11.6, 8.0$ Hz, 4H), 7.80 (d, $J = 8.5$ Hz, 1H), 7.59 – 7.44 (m, 7H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.4 (d, $J = 125.2$ Hz), 159.7, 143.1 (d, $J = 23.0$ Hz), 132.2 (d, $J = 105.1$ Hz), 132.2, 132.2, 132.1, 132.0 (d, $J = 2.4$ Hz), 129.8 (d, $J = 22.2$ Hz), 128.4, 128.2 (d, $J = 147.0$ Hz), 128.2, 125.9 (d, $J = 6.6$ Hz), 134.6, 123.6 (d, $J = 17.8$ Hz), 118.8, 112.0, 108.0, 55.7. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.96. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{19}\text{N}_2\text{NaO}_2\text{P}^+$ $[\text{M} + \text{Na}]^+$ 457.1076, found 457.1064.

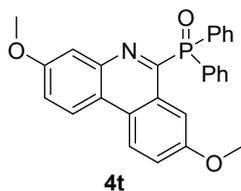


(8-methoxy-2-methylphenanthridin-6-yl)diphenylphosphine oxide (4r): 79% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.98 (d, $J = 2.4$ Hz, 1H), 8.50 (d, $J = 8.5$ Hz, 1H), 8.26 (s, 1H), 8.04 – 7.87 (m, 5H), 7.45 (td, $J = 13.7, 11.0, 4.5$ Hz, 8H), 3.92 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.6, 154.1 (d, $J = 130.5$

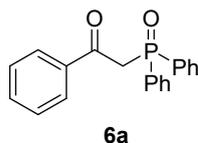
Hz), 140.5 (d, $J = 23.3$ Hz), 139.0, 133.1 (d, $J = 104.5$ Hz), 132.2 (d, $J = 9.1$ Hz), 131.5 (d, $J = 2.4$ Hz), 130.8, 129.5 (d, $J = 23.0$ Hz), 129.4, 128.2, 128.0, 126.7 (d, $J = 6.9$ Hz), 124.5 – 124.2 (m), 123.5, 122.3, 121.1, 107.4, 55.6, 22.1. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.68. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{22}\text{NNaO}_2\text{P}^+$ [$\text{M} + \text{Na}$] $^+$ 446.1280, found 446.1274.



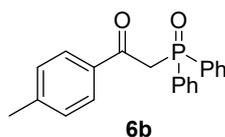
(2,8-dimethoxyphenanthridin-6-yl)diphenylphosphine oxide (4s): 21% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.96 (d, $J = 2.5$ Hz, 1H), 8.47 (dd, $J = 9.2, 1.4$ Hz, 1H), 8.03 – 7.90 (m, 5H), 7.80 (d, $J = 2.6$ Hz, 1H), 7.58 – 7.38 (m, 7H), 7.28 (d, $J = 2.6$ Hz, 1H), 4.01 (s, 3H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.4 (d, $J = 112.4$ Hz), 137.7 (d, $J = 23.5$ Hz), 133.8, 133.2 (d, $J = 104.6$ Hz), 132.3 (d, $J = 9.1$ Hz), 131.5 (d, $J = 2.3$ Hz), 129.6 (d, $J = 23.3$ Hz), 128.2, 128.0, 126.4, 125.9 (d, $J = 2.0$ Hz), 123.6, 122.1, 118.2, 104.5 (d, $J = 562.0$ Hz), 55.6. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.90. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{22}\text{NNaO}_3\text{P}^+$ [$\text{M} + \text{Na}$] $^+$ 462.1230, found 462.1233.



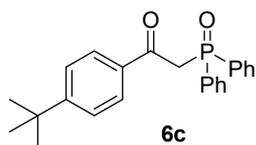
(3,8-dimethoxyphenanthridin-6-yl)diphenylphosphine oxide (4t): 40% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.98 (d, $J = 2.5$ Hz, 1H), 8.47 – 8.29 (m, 2H), 8.04 – 7.89 (m, 4H), 7.47 (dddt, $J = 17.2, 11.8, 9.1, 4.5$ Hz, 7H), 7.41 – 7.28 (m, 2H), 3.92 (d, $J = 4.2$ Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.3, 157.9, 155.6 (d, $J = 129.6$ Hz), 143.6 (d, $J = 23.4$ Hz), 133.1 (d, $J = 104.5$ Hz), 132.3, 132.2, 131.6 (d, $J = 2.4$ Hz), 128.6 (d, $J = 22.9$ Hz), 128.2, 128.1, 127.5 (d, $J = 7.0$ Hz), 122.9 (d, $J = 30.4$ Hz), 122.8, 120.3, 118.8 (d, $J = 2.4$ Hz), 110.2, 107.2, 55.6. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.96. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{22}\text{NNaO}_3\text{P}^+$ [$\text{M} + \text{Na}$] $^+$ 462.1230, found 462.1237.



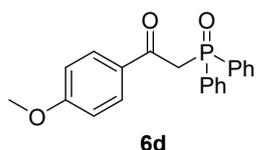
2-(diphenylphosphoryl)-1-phenylethan-1-one (6a)^[7]: 68% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.94 (m, 2H), 7.83 – 7.78 (m, 4H), 7.55 – 7.50 (m, 3H), 7.45 (ddt, $J = 8.6, 4.6, 3.0$ Hz, 5H), 7.40 (d, $J = 7.5$ Hz, 1H), 4.15 (d, $J = 15.4$ Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 192.8 (d, $J = 5.5$ Hz), 136.9, 133.6, 132.1 (d, $J = 2.4$ Hz), 131.1 (d, $J = 9.8$ Hz), 130.4 (d, $J = 9.8$ Hz), 129.2, 128.6, 128.5 (d, $J = 4.0$ Hz), 127.6, 125.4, 43.2 (d, $J = 58.1$ Hz).



2-(diphenylphosphoryl)-1-(p-tolyl)ethan-1-one (6b)^[7]: 70% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, $J = 8.2$ Hz, 2H), 7.84 – 7.77 (m, 4H), 7.54 – 7.49 (m, 2H), 7.48 – 7.42 (m, 4H), 7.20 (d, $J = 8.0$ Hz, 2H), 4.11 (d, $J = 15.3$ Hz, 2H), 2.37 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 192.24 (d, $J = 5.5$ Hz), 144.51, 134.46, 132.01 (d, $J = 2.4$ Hz), 131.97 (d, $J = 103.2$ Hz), 131.04 (d, $J = 9.8$ Hz), 130.30 (d, $J = 9.7$ Hz), 129.33, 129.14, 128.57, 128.45, 125.34, 43.13 (d, $J = 58.2$ Hz), 21.61.

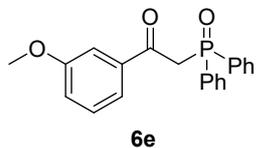


1-(4-(tert-butyl)phenyl)-2-(diphenylphosphoryl)ethan-1-one (6c)^[7]: 64% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, $J = 8.5$ Hz, 2H), 7.80 (dd, $J = 11.5, 7.6$ Hz, 4H), 7.55 – 7.48 (m, 2H), 7.48 – 7.39 (m, 6H), 4.13 (d, $J = 15.3$ Hz, 2H), 1.31 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 192.2, 157.3, 134.4, 132.0 (d, $J = 2.3$ Hz), 132.0 (d, $J = 103.3$ Hz), 131.1 (d, $J = 9.8$ Hz), 129.2, 128.5 (d, $J = 12.3$ Hz), 125.4, 43.4, 42.8, 35.1, 30.9.

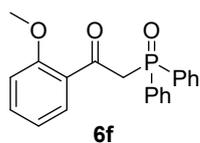


2-(diphenylphosphoryl)-1-(4-methoxyphenyl)ethan-1-one (6d)^[7]: 71% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, $J = 8.9$ Hz, 2H), 7.83 – 7.77 (m, 4H), 7.54

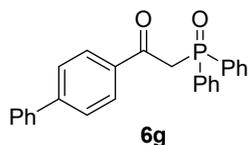
– 7.43 (m, 7H), 6.88 (d, $J = 8.9$ Hz, 1H), 4.09 (d, $J = 15.3$ Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 191.0 (d, $J = 5.4$ Hz), 163.9, 132.0 (d, $J = 2.5$ Hz), 132.0 (d, $J = 103.2$ Hz), 131.7, 131.0 (d, $J = 9.8$ Hz), 130.0, 128.5 (d, $J = 12.3$ Hz), 126.7, 113.8, 113.6, 55.4, 43.1 (d, $J = 58.0$ Hz).



2-(diphenylphosphoryl)-1-(3-methoxyphenyl)ethan-1-one (6e)^[7]: 58% yield; ^1H NMR (400 MHz, Chloroform- d) δ 7.86 – 7.76 (m, 4H), 7.60 (d, $J = 7.7$ Hz, 1H), 7.55 – 7.49 (m, 2H), 7.49 – 7.42 (m, 5H), 7.32 (t, $J = 8.0$ Hz, 1H), 7.08 (dd, $J = 8.1, 2.3$ Hz, 1H), 4.13 (d, $J = 15.3$ Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 192.6 (d, $J = 5.5$ Hz), 159.6, 138.2, 132.1 (d, $J = 2.3$ Hz), 131.9 (d, $J = 103.4$ Hz), 131.1 (d, $J = 9.8$ Hz), 129.5, 128.6, 128.5, 121.3 (d, $J = 165.1$ Hz), 112.6, 55.4, 43.4 (d, $J = 58.1$ Hz).

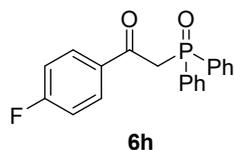


2-(diphenylphosphoryl)-1-(2-methoxyphenyl)ethan-1-one (6f)^[7]: 54% yield; ^1H NMR (400 MHz, Chloroform- d) δ 7.80 – 7.71 (m, 4H), 7.49 (ddd, $J = 13.0, 7.5, 1.5$ Hz, 3H), 7.44 – 7.35 (m, 5H), 6.89 (t, $J = 7.5$ Hz, 1H), 6.80 (d, $J = 8.4$ Hz, 1H), 4.38 (d, $J = 15.5$ Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 194.0 (d, $J = 5.5$ Hz), 158.4, 134.2, 132.7 (d, $J = 10.2$ Hz), 132.7 (d, $J = 102.6$ Hz), 131.8 (d, $J = 2.6$ Hz), 131.1 (d, $J = 9.8$ Hz), 130.7, 128.4, 128.2, 120.6, 111.3, 55.4, 47.0 (d, $J = 60.3$ Hz).

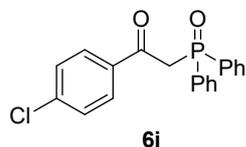


1-([1,1'-biphenyl]-4-yl)-2-(diphenylphosphoryl)ethan-1-one (6g)^[7]: 61% yield; ^1H NMR (400 MHz, Chloroform- d) δ 8.06 (d, $J = 8.3$ Hz, 2H), 7.82 (dd, $J = 12.0, 7.3$ Hz, 4H), 7.63 (d, $J = 8.3$ Hz, 2H), 7.59 (d, $J = 7.3$ Hz, 2H), 7.55 – 7.49 (m, 2H), 7.49 – 7.42 (m, 6H), 7.39 (d, $J = 7.1$ Hz, 1H), 4.17 (d, $J = 15.3$ Hz, 2H). ^{13}C NMR (101 MHz, Chloroform- d) δ 192.4 (d, $J = 5.4$ Hz), 146.3, 139.8, 135.8, 132.2 (d, $J = 2.1$ Hz), 132.0

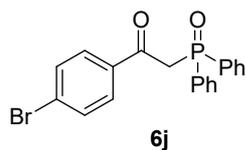
(d, $J = 103.2$ Hz), 131.2 (d, $J = 9.7$ Hz), 130.0, 129.0, 128.7 (d, $J = 12.3$ Hz), 128.4, 127.4, 127.2, 43.5 (d, $J = 57.4$ Hz).



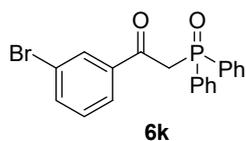
2-(diphenylphosphoryl)-1-(4-fluorophenyl)ethan-1-one (6h)^[7]: 62% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.05 (dd, $J = 8.8, 5.4$ Hz, 2H), 7.80 (dd, $J = 12.0, 7.3$ Hz, 4H), 7.58 – 7.50 (m, 2H), 7.47 (dt, $J = 7.9, 4.0$ Hz, 4H), 7.08 (t, $J = 8.6$ Hz, 2H), 4.11 (d, $J = 15.2$ Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 191.2 (d, $J = 5.5$ Hz), 166.0 (d, $J = 256.1$ Hz), 133.4 (d, $J = 2.6$ Hz), 132.2 (d, $J = 2.1$ Hz), 132.1 (d, $J = 9.8$ Hz), 131.8 (d, $J = 103.4$ Hz), 131.2 – 130.8 (m), 128.6 (d, $J = 12.3$ Hz), 115.6 (d, $J = 22.0$ Hz), 43.6 (d, $J = 56.9$ Hz).



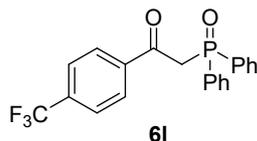
1-(4-chlorophenyl)-2-(diphenylphosphoryl)ethan-1-one (6i)^[7]: 51% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, $J = 8.2$ Hz, 2H), 7.86 – 7.73 (m, 4H), 7.57 – 7.50 (m, 2H), 7.47 (t, $J = 6.7$ Hz, 4H), 7.39 (d, $J = 7.9$ Hz, 2H), 4.11 (d, $J = 13.7$ Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 191.6, 140.2, 135.2, 134.3, 132.2, 131.02 (d, $J = 8.7$ Hz), 130.7, 128.8, 128.6 (d, $J = 11.6$ Hz), 43.6 (d, $J = 59.1$ Hz).



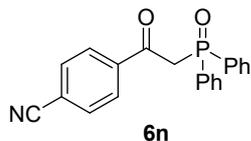
1-(4-bromophenyl)-2-(diphenylphosphoryl)ethan-1-one (6j)^[7]: 51% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, $J = 8.5$ Hz, 2H), 7.79 (dd, $J = 12.1, 7.2$ Hz, 4H), 7.54 (dd, $J = 12.4, 7.6$ Hz, 4H), 7.46 (ddd, $J = 7.1, 5.1, 2.0$ Hz, 4H), 4.10 (d, $J = 15.2$ Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 191.8 (d, $J = 5.4$ Hz), 135.6, 132.2 (d, $J = 2.0$ Hz), 132.2, 131.8, 131.1, 131.0 (d, $J = 9.7$ Hz), 130.8, 129.0, 128.6 (d, $J = 12.3$ Hz), 43.5 (d, $J = 56.5$ Hz).



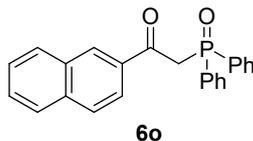
1-(3-bromophenyl)-2-(diphenylphosphoryl)ethan-1-one (**6k**)^[7]: 54% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.96 (d, $J = 7.8$ Hz, 1H), 7.79 (dd, $J = 12.1, 7.3$ Hz, 4H), 7.65 (d, $J = 7.9$ Hz, 1H), 7.57 – 7.51 (m, 2H), 7.47 (dt, $J = 6.9, 3.5$ Hz, 4H), 7.30 (t, $J = 7.9$ Hz, 1H), 4.11 (d, $J = 15.2$ Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 191.6 (d, $J = 5.6$ Hz), 138.6, 136.3, 132.3 (d, $J = 2.2$ Hz), 132.1, 131.1, 131.0, 130.9 (d, $J = 175.3$ Hz), 128.7 (d, $J = 12.3$ Hz), 128.0, 122.8, 43.4 (d, $J = 57.2$ Hz).



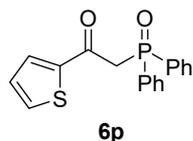
2-(diphenylphosphoryl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (**6l**)^[7]: 41% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, $J = 8.1$ Hz, 2H), 7.80 (dd, $J = 11.5, 7.7$ Hz, 4H), 7.68 (d, $J = 8.1$ Hz, 2H), 7.51 (dt, $J = 26.5, 7.1$ Hz, 6H), 4.17 (d, $J = 15.1$ Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 192.0, 139.5, 134.7 (d, $J = 32.6$ Hz), 132.4, 132.1, 131.0 (d, $J = 9.4$ Hz), 129.6, 128.7 (d, $J = 12.2$ Hz), 125.5 (q, $J = 3.7$ Hz), 123.5 (d, $J = 273.0$ Hz), 43.9 (d, $J = 56.4$ Hz).



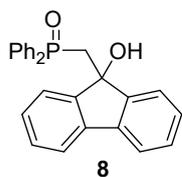
4-(2-(diphenylphosphoryl)acetyl)benzonitrile (**6n**)^[7]: 36% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, $J = 6.3$ Hz, 2H), 7.87 – 7.73 (m, 6H), 7.55 (dd, $J = 20.6, 6.1$ Hz, 6H), 4.18 (s, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 191.7, 139.7, 132.4, 132.3, 131.2 – 130.9 (m), 129.7, 128.8 (d, $J = 8.0$ Hz), 117.8, 116.6, 29.6.



2-(diphenylphosphoryl)-1-(naphthalen-2-yl)ethan-1-one (**6o**)^[7]: 54% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.56 (s, 1H), 7.96 (t, $J = 7.3$ Hz, 2H), 7.88 – 7.78 (m, 7H), 7.62 – 7.40 (m, 9H), 4.27 (d, $J = 15.3$ Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 192.6 (d, $J = 5.1$ Hz), 135.7, 134.3, 132.3, 132.1, 132.0 (d, $J = 103.3$ Hz), 131.9, 131.1 (d, $J = 9.6$ Hz), 129.9, 128.8, 128.6 (d, $J = 12.2$ Hz), 128.3, 127.6, 126.7, 124.1, 43.4 (d, $J = 57.6$ Hz).



2-(diphenylphosphoryl)-1-(thiophen-2-yl)ethan-1-one (6p)^[7]: 69% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 3.8, 0.9 Hz, 1H), 7.84 – 7.77 (m, 4H), 7.65 – 7.59 (m, 1H), 7.54 – 7.43 (m, 6H), 7.08 (dd, *J* = 4.8, 4.0 Hz, 1H), 4.06 (d, *J* = 15.3 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 184.9 (d, *J* = 5.2 Hz), 144.4, 135.0 (d, *J* = 19.6 Hz), 132.2 (d, *J* = 2.6 Hz), 131.1 (d, *J* = 9.9 Hz), 130.4 (d, *J* = 10.0 Hz), 128.6 (d, *J* = 12.4 Hz), 128.4, 125.5 (d, *J* = 180.8 Hz), 44.2 (d, *J* = 57.3 Hz).



((9-hydroxy-9H-fluoren-9-yl)methyl)diphenylphosphine oxide (8): 46% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 (ddd, *J* = 11.7, 8.0, 2.2 Hz, 6H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.47 – 7.38 (m, 4H), 7.33 – 7.25 (m, 3H), 7.09 (td, *J* = 7.5, 0.9 Hz, 2H), 6.03 (s, 1H), 3.13 – 2.93 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 148.3 (d, *J* = 6.5 Hz), 138.7, 134.5, 133.6 (d, *J* = 99.7 Hz), 131.8 (d, *J* = 2.5 Hz), 130.4 (d, *J* = 9.6 Hz), 128.8, 128.6 (d, *J* = 12.0 Hz), 126.1 (d, *J* = 278.8 Hz), 122.8, 119.7, 81.6 (d, *J* = 5.3 Hz), 39.4 (d, *J* = 67.5 Hz). HRMS (ESI) *m/z* calcd for C₂₆H₂₁NaO₂P⁺ [M + Na]⁺ 419.1173, found 419.1171.

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(H) NMR spectra

