

Supporting Information
for

**Synthesis of ethoxy dibenzooxaphosphorin oxides through
Palladium-catalyzed C(sp²)-H activation/C-O formation**

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This paper is dedicated to Professor Bong Rae Cho (Korea University) on the occasion of his
honorable retirement.

**Experimental procedures, characterization data, and ¹H and ¹³C NMR
spectra of new compounds**

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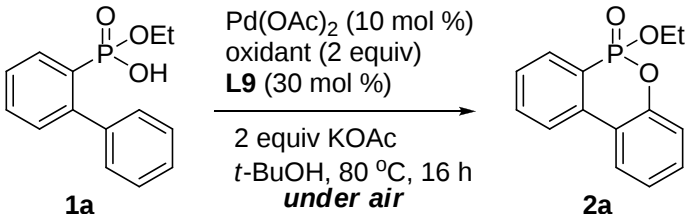
1. Experimental Section

1.1 General

Reactions were carried out in oven-dried glassware under air atmosphere. Commercial available reagents were used without purification. All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography using silica gel pre-coated glass plates, which were visualized with UV light and then, developed using either iodine or a solution of anisaldehyde. Flash column chromatography was carried out using silica gel (230-400 mesh). ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker DPX FT spectrometer. Deuterated chloroform was used as the solvent and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent (δ 7.24 for ^1H and δ 77.0 for ^{13}C). Infrared spectra were recorded on a JASCO FT/IR-460 plus FT-IR spectrometer as either a thin film or as a solid suspended in a potassium bromide pellet. Mass spectrometry was performed on a GC/HRMS spectrometer by electron impact (EI) ionization techniques from the KBSI. Melting points were determined in open capillary tube using Electrothermal 9100 apparatus.

1.2. Additional data for reaction optimization

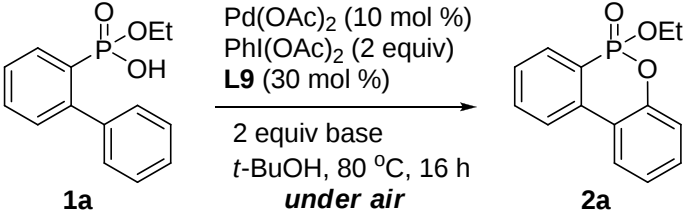
Table 1: Effect of oxidant.^a

					
entry	oxidant	yield ^b [%]	entry	oxidant	yield ^b [%]
1	K ₂ S ₂ O ₈	0	6	CuCl ₂	0
2	BQ	0	7	CuBr	0
3	[PhCO ₂] ₂	0	8	AgOAc	0
4	PhI(TFA) ₂	0	9	Ag ₂ CO ₃	0
5	Cu(OAc) ₂	0	10	Ag ₂ O	0

^aReaction condition : **1a** (0.2 mmol), Pd(OAc)₂ (10 mol %), *t*-BuOH (2.5 mL), 100 °C for 16 h.

^b¹H NMR yield using CH₂Br₂ as an internal standard.

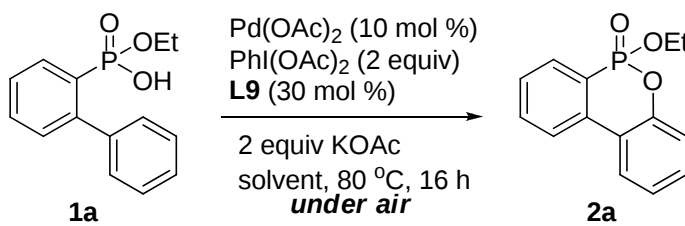
Table 2: Effect of base.^a

					
entry	base	yield ^b [%]	entry	base	yield ^b [%]
1	KHCO ₃	31	10	CsOAc	51
2	K ₂ HPO ₄	35	11	CsF	52
3	K ₂ CO ₃	17	12	CsOPiv	46
4	KOH	33	13	LiOAc	9
5	KF	39	14	LiPF ₆	12
6	KPF ₆	0	15	Li ₃ PO ₄	8
7	Na ₂ CO ₃	26	16	LiF	8
8	NaOAc	42	17	LiI	5
9	NaF	9			

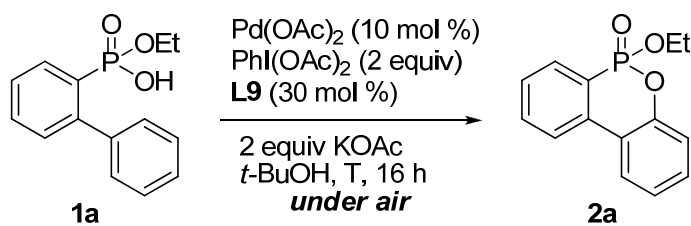
^aReaction condition : **1a** (0.2 mmol), Pd(OAc)₂ (10 mol %), *t*-BuOH (2.5 mL), 100 °C for 16 h.

^b¹H NMR yield using CH₂Br₂ as an internal standard.

Table 3: Effect of solvent.^a

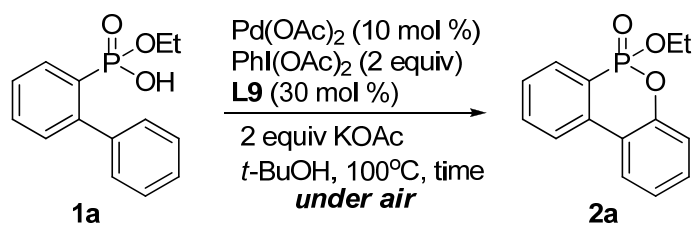
					
entry	base	yield ^b [%]	entry	base	yield ^b [%]
1	DCE	7	6	HFIP	0
2	dioxane	0	7	THF	7
3	CH ₃ CN	4	8	toluene	6
4	<i>t</i> -AmOH	26	9	TFA	42
5	DMF	9	10	MeOH	14

^aReaction condition : **1a** (0.2 mmol), Pd(OAc)₂ (10 mol %), solvent (2.5 mL), 100 °C for 16 h.^b¹H NMR yield using CH₂Br₂ as an internal standard.**Table 4:** Effect of temperature.^a

					
entry	T [°C]	yield ^b [%]	entry	T [°C]	yield ^b [%]
1	60	20			
2	100	61			
3	120	50			
4	140	8			
5	160	7			

^aReaction condition : **1a** (0.2 mmol), Pd(OAc)₂ (10 mol %), *t*-BuOH (2.5 mL), 16 h.^b¹H NMR yield using CH₂Br₂ as an internal standard.

Table 5: Effect of time.^a

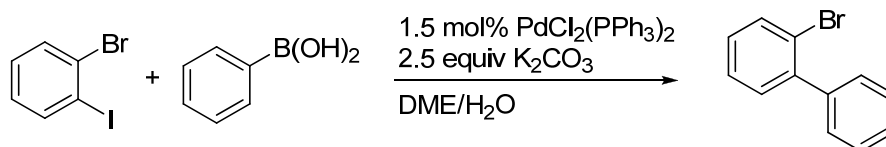


entry	t [h]	yield ^b [%]
1	1	32
2	2	40
3	4	45
4	8	51
5	12	61(55)

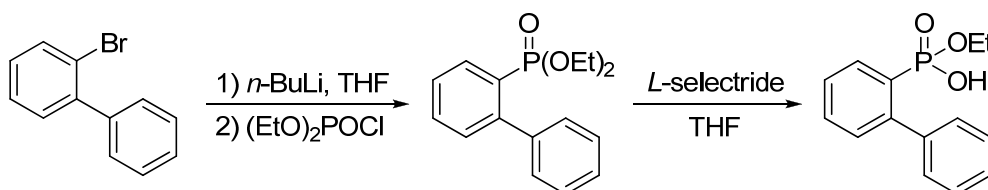
^aReaction condition : **1a** (0.2 mmol), Pd(OAc)₂ (10 mol %), *t*-BuOH (2.5 mL), 100 °C

^b¹H NMR yield using CH₂Br₂ as an internal standard.

1.3. Preparation of 1,1'-biphenylphosphonic acid monoethyl esters (1a) ^[1-4]



To a solution of PdCl₂(PPh₃)₂ (31.6 mg, 0.045 mmol) and potassium carbonate (1.04 g, 7.5 mmol) in water (1.2 mL) and DME (10.0 mL) were added 2-bromoiodobenzene (0.85 g, 3.0 mmol) and substrated phenylboronic acid (4.5 mmol). The reaction mixture was stirred at 80 °C for 5 h in oil bath until substrate disappeared on TLC. When the reaction was complete, water (10.0 mL) and ether (10.0 mL) were added. The aqueous layer was separated and extracted with ether (10.0 mL x 3). The combined organic layer was washed with brine and the organic fraction was dried with MgSO₄, filtered and concentrated under reduced pressure. The crude product was then purified by flash column chromatography (hexane) on silica gel, producing the title compound as a colorless oil (607.0 mg, 87%).

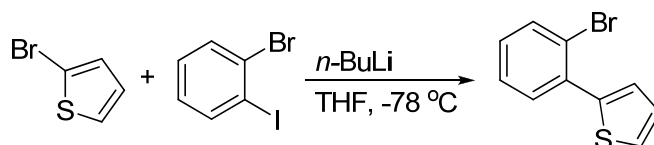


To a solution of 2-bromo-1,1'-biphenyl (2.60 mmol) in dry THF (8.7 mL) was added *n*-BuLi (2.5 M solution in *n*-hexane, 1.3 mL, 3.1 mmol) at 0 °C under nitrogen atmosphere. The mixture was stirred at 0 °C for 30 min and then, diethyl chlorophosphate (0.38 mL, 2.60 mmol) was added at 0 °C. The solution was stirred for 1 h at 0 °C, warmed to 25 °C and stirred for 3 h. When the reaction was complete, the solution was quenched with ammonium chloride. The aqueous layer was separated and extracted with ether (10 mL x 3) and the organic fraction was dried with MgSO₄, filtered and concentrated under reduced pressure. The crude product was then purified by flash column chromatography (ethyl acetate:hexane = 1:1) on silica gel, producing the title compound as a colorless oil (580.0 mg, 77%).

A solution of 1,1'-biphenylphosphonic acid diethyl ester (580.0 mg, 2.0 mmol) in THF (6.7 mL) was treated with *L*-selectride (1.0 M solution in THF, 4.0 mL, 4.0 mmol) at 50 °C for 30 min. When the reaction was complete, the solution was quenched by addition of water.

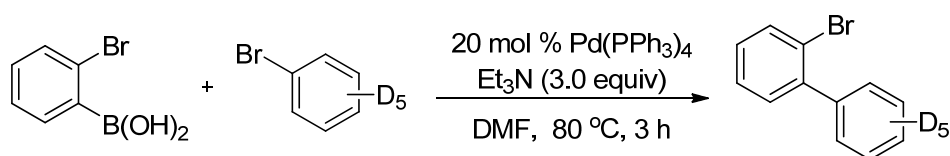
The aqueous layer was extracted with ethyl acetate (20 mL x 3) to remove impurities, then acidified to pH 1 with 1 N HCl (10 mL) and extracted with ethyl acetate (20 mL x 5). The combined organic layer was dried with MgSO₄ and concentrated under reduced pressure. Then, the crude product was dried in vacuum to afford 1,1'-biphenylphosphonic acid monoethyl ester (420.0 mg, 80%) as a white crystalline solid.

1.4. Preparation of 2-(thiophene-2-yl)phenylphosphonic acid monoethyl ester (1n)^[5]

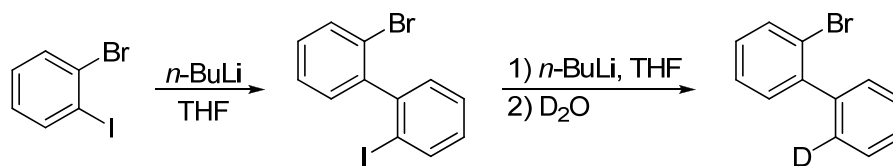


To a solution of 2-bromothiophene (9.0 mmol) in dry THF (30 mL) was added *n*-BuLi (2.5 M solution in *n*-hexane, 3.8 mL, 9.45 mmol) at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 30 min and then, 1-bromo-2-iodobenzene (9.0 mmol) was dropwise at -78 °C. The mixture was warmed to 25 °C and stirred for 1 h. When the reaction was complete, the solution was quenched with ammonium chloride. The aqueous layer was extracted with ethyl ether (3 x 20 mL) and the combined organic layer was dried over MgSO₄ and concentrated under reduced pressure. The crude product was then purified by flash column chromatography (hexane) on silica gel, producing the title compound as a yellow oil (1.70 g, 79%).

1.5. Preparation of isotopically labeled compounds.^[6-7]



2-Bromophenylboronic acid (3.0 mmol) and bromobenzene-*d*₅ (3.0 mmol) in presence of tetrakis(triphenylphosphine)palladium (69.3 mg, 20 mol %) and triethylamine (911.0 mg, 6.0 mmol) in DMF (18 mL) were heated at 80 °C. After 3 h, it was allowed to cool to 25 °C and extracted with Et₂O (3 x 20 mL). Then, organic layer was washed with water and dried over MgSO₄ and concentrated under reduced pressure. The crude product was then purified by flash column chromatography (hexane) on silica gel, producing the title compound as a colorless oil (572.0 mg, 80%).

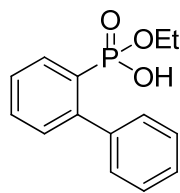


To a solution of 2-bromoiodobenzene (10 mmol) in THF (20 mL) was added *n*-BuLi (2.5 M solution in *n*-hexane, 2.0 mL, 5.0 mmol) at -78 °C under nitrogen atmosphere. The reaction mixture was then warmed to 25 °C over a two hours and hydrolyzed with a 1.0 M aqueous hydrochloric acid solution (20 mL). After the aqueous layer was extracted with diethyl ether (3 x 40 mL), the combined organic layer was dried over MgSO₄ and concentrated under reduced pressure. Upon crystallization from ethanol, 2-bromo-2'-iodobiphenyl was obtained as a colorless needle (2.58 g, 73%).

To a solution of 2-bromo-2'-iodobiphenyl (2.0 mmol) in THF (8.0 mL) was added *n*-BuLi (2.5 M solution in *n*-hexane, 0.8 mL, 2.0 mmol) at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 1 h and then, quenched by D₂O (3.0 mmol). After being stirred for 30 min, the mixture was poured into cold water and extracted with dichloromethane (3 x 15 mL). The combined organic layer was dried over MgSO₄ and concentrated under reduced pressure. The crude was purified by flash column chromatography (hexane) on silica gel, producing 2-bromo-2'-deuterio-1,1'-biphenyl as a colorless oil (0.31 g, 66%).

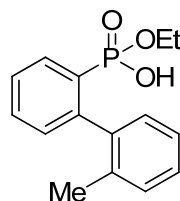
1.6. Preparation of 6-ethoxy-6*H*-dibenz[*c,e*]oxaphosphorin-6-oxide **2a**.

1,1'-Biphenylphosphonic acid monoethyl ester **1a** (52.4 mg, 0.2 mmol), Pd(OAc)₂ (4.49 mg, 0.02 mmol), *N*-acetyl-L-leucine (10.4 mg, 0.06 mmol), PhI(OAc)₂ (128.8 mg, 0.4 mmol), KOAc (39.3 mg, 0.4 mmol) and *t*-BuOH (2.5 mL) were added to a 2.5 mL screw-top v-vial. The reaction mixture was stirred at 100 °C for 12 h under air atmosphere. After celite filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1/1) to yield **2a** (28.9 mg, 55%) as a yellow oil.



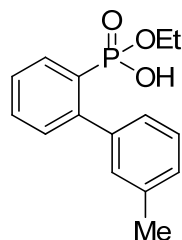
1a

1,1'-Biphenyl phosphonic acid monoethyl ester (1a) : White solid, m.p. 107-125 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.21 (br, 1H), 8.05 (ddd, $J = 14.8, 7.7, 1.2$ Hz, 1H), 7.58-7.53 (m, 1H), 7.46-7.30 (m, 7H), 3.70 (m, 2H), 0.95 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.1 (d, $J = 9.9$ Hz), 141.4 (d, $J = 4.3$ Hz), 133.5 (d, $J = 10.2$ Hz), 132.0 (d, $J = 2.9$ Hz), 131.3 (d, $J = 14.3$ Hz), 129.4, 127.5, 127.4, 127.3 (d, $J = 192.7$ Hz), 126.8 (d, $J = 14.8$ Hz), 61.5 (d, $J = 6.2$ Hz), 15.7 (d, $J = 7.3$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 20.81; IR (film): 3056, 2981, 2801, 2359, 1469, 1199, 1040, 988, 754, 701 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{O}_3\text{P}$: 262.0759; found : 262.0760.



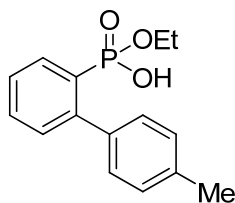
1b

2'-Methyl-1,1'-biphenyl phosphonic acid monoethyl ester (1b) : White solid, m.p. 83-87 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.11 (br, 1H), 8.03-8.00 (m, 1H), 7.55-7.50 (m, 1H), 7.41-7.36 (m, 1H), 7.23-7.12 (m, 5H), 3.74-3.57 (m, 2H), 2.02 (s, 3H), 1.01 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.4 (d, $J = 10.2$ Hz), 140.4 (d, $J = 4.1$ Hz), 136.3, 133.2 (d, $J = 10.4$ Hz), 131.8 (d, $J = 2.9$ Hz), 130.8 (d, $J = 14.5$ Hz), 130.0, 129.3, 127.8 (d, $J = 194.5$ Hz), 127.6, 126.7 (d, $J = 15.2$ Hz), 124.5, 61.3 (d, $J = 6.6$ Hz), 20.3, 15.9 (d, $J = 6.9$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 20.35; IR (film): 3057, 2980, 2309, 1468, 1198, 1040, 988, 760 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{17}\text{O}_3\text{P}$: 276.0915; found : 276.0916.



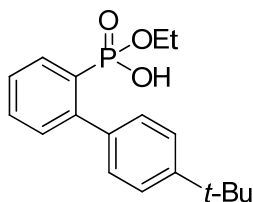
1c

3'-Methyl-1,1'-biphenyl phosphonic acid monoethyl ester (1c) : White solid, m.p. 80-87 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.08 (br, 1H), 8.03 (ddd, $J = 14.8, 7.7, 1.0$ Hz, 1H), 7.51 (tt, $J = 11.3, 1.5$ Hz, 1H), 7.41-7.37 (m, 1H), 7.32-7.29 (m, 1H), 7.24-7.23 (m, 3H), 3.72 (p, $J = 7.2$ Hz, 2H), 2.37 (s, 3H), 0.98 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.2 (d, $J = 10.1$ Hz), 141.3 (d, $J = 4.3$ Hz), 136.9, 133.5 (d, $J = 10.1$ Hz), 131.9 (d, $J = 2.8$ Hz), 131.2 (d, $J = 14.4$ Hz), 130.1, 128.1, 127.4, 127.3 (d, $J = 192.4$ Hz), 126.7 (d, $J = 15.1$ Hz), 126.3, 61.4 (d, $J = 6.3$ Hz), 21.4, 15.7 (d, $J = 7.4$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 20.84; IR (film): 2980, 2904, 2297, 1467, 1200, 1143, 1042, 989, 790 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{17}\text{O}_3\text{P}$: 276.0915; found : 276.0916.



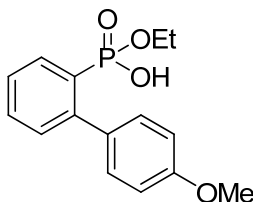
1d

4'-Methyl-1,1'-biphenyl phosphonic acid monoethyl ester (1d) : White solid, m.p. 80-85 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.08 (br, 1H), 8.03 (dd, $J = 14.7, 7.1$ Hz, 1H), 7.52 (t, $J = 7.5$ Hz, 1H), 7.40-7.28 (m, 4H), 7.17 (s, 1H), 7.15 (s, 1H), 3.70 (m, 2H), 2.36 (s, 3H), 0.97 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.2 (d, $J = 10.1$ Hz), 138.5 (d, $J = 4.2$ Hz), 137.0, 133.6 (d, $J = 10.1$ Hz), 131.9 (d, $J = 2.2$ Hz), 131.4 (d, $J = 14.3$ Hz), 129.3, 128.2, 126.6 (d, $J = 14.8$ Hz), 126.3, 61.5 (d, $J = 6.2$ Hz), 21.3, 15.8 (d, $J = 7.4$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 20.81; IR (film): 2981, 2925, 2331, 1469, 1200, 1041, 989, 821, 765 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{17}\text{O}_3\text{P}$: 276.0915; found : 276.0916.



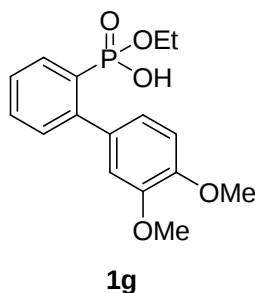
1e

4'-tert-Butyl- 1,1'-biphenyl phosphonic acid monoethyl ester (1e) : Ivory solid, m.p. 100-123 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.28 (br, 1H), 8.06 (ddd, $J = 15.0, 7.7, 1.0$ Hz, 1H), 7.55 (tt, $J = 11.3, 1.4$ Hz, 1H), 7.44-7.33 (m, 6H), 3.72 (p, $J = 7.1$ Hz, 2H), 1.34 (s, 9H), 0.89 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.3, 146.1 (d, $J = 10.1$ Hz), 138.4 (d, $J = 4.2$ Hz), 133.6 (d, $J = 10.4$ Hz), 132.1 (d, $J = 2.9$ Hz), 131.4 (d, $J = 14.3$ Hz), 129.0, 126.8 (d, $J = 193.6$ Hz), 126.7 (d, $J = 15.0$ Hz), 124.5, 61.6 (d, $J = 6.5$ Hz), 34.6, 31.4, 15.5 (d, $J = 7.5$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 21.35; IR (film): 3056, 2963, 2308, 1591, 1471, 1195, 1041, 989, 835, 756 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{23}\text{O}_3\text{P}$: 318.1385; found : 318.1388.

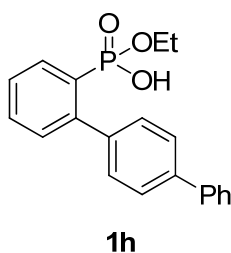


1f

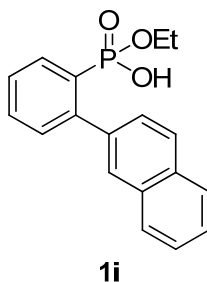
4'-Methoxy- 1,1'-biphenyl phosphonic acid monoethyl ester (1f) : White solid, m.p. 120-123 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.67 (br, 1H), 8.03 (ddd, $J = 14.8, 7.7, 0.9$ Hz, 1H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.41-7.37 (m, 3H), 7.30 (t, $J = 6.6$ Hz, 1H), 6.90 (d, $J = 8.7$ Hz, 2H), 3.82 (s, 3H), 3.73 (p, $J = 5.8$ Hz, 2H), 0.99 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.0, 145.8 (d, $J = 14.3$ Hz), 130.6, 127.2 (d, $J = 192.2$ Hz), 126.5 (d, $J = 15.0$ Hz), 113.0, 61.5 (d, $J = 6.2$ Hz), 55.2, 15.8 (d, $J = 7.3$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 21.21; IR (film): 3057, 2904, 2295, 1517, 1244, 1179, 1038, 988, 768 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{17}\text{O}_4\text{P}$: 292.0864; found : 292.0981.



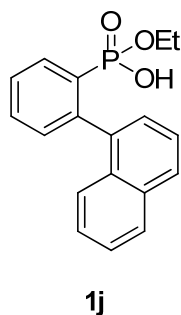
3',4'-Dimethoxy- 1,1'-biphenyl phosphonic acid monoethyl ester (1g) : Yellow solid, m.p. 128-135 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.23 (br, 1H), 8.07 (dd, $J = 14.8, 7.7$ Hz, 1H), 7.64-7.50 (m, 7H), 7.46-7.33 (m, 5H), 3.77 (m, 2H), 0.94 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.4, 147.9, 145.9 (d, $J = 10.1$ Hz), 134.1 (d, $J = 4.3$ Hz), 133.7 (d, $J = 10.1$ Hz), 132.0 (d, $J = 2.8$ Hz), 131.4 (d, $J = 14.2$ Hz), 127.2 (d, $J = 192.0$ Hz), 126.6 (d, $J = 15.0$ Hz), 121.5, 113.3, 110.3, 61.6 (d, $J = 6.2$ Hz), 55.9 (d, $J = 3.5$ Hz), 15.8 (d, $J = 7.3$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 21.25; IR (film): 3057, 2835, 2362, 2254, 1605, 1520, 1470, 1247, 1141, 1029, 732 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{19}\text{O}_5\text{P}$: 322.0970; found : 322.0966.



4'-Phenyl-1,1'-biphenyl phosphonic acid monoethyl ester (1h) : White solid, m.p. 166-175 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.23 (br, 1H), 8.07 (dd, $J = 14.8, 7.7$ Hz, 1H), 7.64-7.50 (m, 7H), 7.46-7.33 (m, 5H), 3.77 (m, 2H), 0.94 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 144.5 (d, $J = 9.4$ Hz), 140.7 (d, $J = 3.9$ Hz), 139.8, 138.8, 133.0 (d, $J = 9.2$ Hz), 131.5, 131.2 (d, $J = 13.2$ Hz), 129.8, 129.4 (d, $J = 181.6$ Hz), 128.5, 127.4, 126.9 (d, $J = 13.9$ Hz), 126.6, 125.6, 60.2 (d, $J = 5.6$ Hz), 15.8 (d, $J = 7.0$ Hz) ; ^{31}P NMR (161 MHz, CDCl_3) δ 21.02; IR (film): 3056, 2981, 2348, 1591, 1470, 1195, 1038, 988, 841, 751 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{20}\text{H}_{19}\text{O}_3\text{P}$: 338.1072; found : 338.1070.

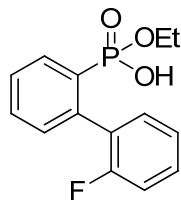


2-(Naphthalen-2-yl)phenylphosphonic acid monoethyl ester (1i) : White solid, m.p. 109-125 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.60 (br, 1H), 8.05 (ddd, $J = 14.8, 7.7, 0.92$ Hz, 1H), 7.87 (s, 1H), 7.83-7.80 (m, 2H), 7.60-7.54 (m, 2H), 7.48-7.37 (m, 4H), 3.61 (p, $J = 7.3$ Hz, 2H), 0.81 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.0 (d, $J = 9.9$ Hz), 138.8 (d, $J = 4.3$ Hz), 133.5 (d, $J = 10.1$ Hz), 132.8, 132.6, 131.9 (d, $J = 2.9$ Hz), 131.5 (d, $J = 14.4$ Hz), 128.0 (d, $J = 53.2$ Hz), 127.9 (d, $J = 64.9$ Hz), 127.5 (d, $J = 192.9$ Hz), 126.9, 126.9 (d, $J = 14.7$ Hz), 126.0, 61.4 (d, $J = 6.4$ Hz), 15.7 (d, $J = 7.2$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 20.85; IR (film): 3055, 2981, 2364, 1481, 1394, 1196, 1039, 1030, 879, 770 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{17}\text{O}_3\text{P}$: 312.0915; found : 312.0917.



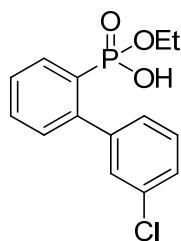
2-(Naphthalen-1-yl)phenylphosphonic acid monoethyl ester (1j) : White solid, m.p. 146-152 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.04 (br, 1H), 8.04 (ddd, $J = 14.8, 7.7, 1.0$ Hz, 1H), 7.87 (d, $J = 1.1$ Hz, 1H), 7.84-7.79 (m, 3H), 7.60-7.54 (m, 2H), 7.48-7.37 (m, 4H), 3.60 (p, $J = 7.2$ Hz, 2H), 0.80 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.0 (d, $J = 9.6$ Hz), 138.1 (d, $J = 3.6$ Hz), 133.5 (d, $J = 10.5$ Hz), 133.4, 132.5, 132.0 (d, $J = 14.2$ Hz), 131.5 (d, $J = 14.4$ Hz), 128.0 (d, $J = 53.2$ Hz), 127.9 (d, $J = 64.9$ Hz), 127.5 (d, $J = 192.9$ Hz), 129.9, 127.9, 127.8, 127.1, 126.5, 125.5 (d, $J = 20.5$ Hz), 124.7, 61.2 (d, $J = 6.6$ Hz), 15.2 (d, $J = 7.2$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 20.80; IR (film): 3056, 2981, 2368, 2264, 1655, 1393,

1198, 1041, 990, 779 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{17}\text{O}_3\text{P}$: 312.0915; found : 312.0912.



1k

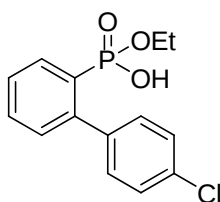
2'-Fluoro- 1,1'-biphenyl phosphonic acid monoethyl ester (1k) : Yellow solid, m.p. 72-91 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 11.40 (br, 1H), 8.01 (ddd, $J = 14.6, 7.7, 1.1$ Hz, 1H), 7.58-7.53 (m, 1H), 7.46-7.41 (m, 1H), 7.37-7.28 (m, 3H), 3.74 (p, $J = 7.2$ Hz, 2H), 1.03 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.7 (d, $J = 245.9$ Hz), 139.2 (d, $J = 9.3$ Hz), 133.5 (d, $J = 9.8$ Hz), 132.2 (d, $J = 2.3$ Hz), 131.8 (d, $J = 2.8$ Hz), 131.5 (d, $J = 14.1$ Hz), 129.5 (d, $J = 8.0$ Hz), 128.3 (d, $J = 192.8$ Hz), 127.5 (d, $J = 15.0$ Hz), 123.0 (d, $J = 3.5$ Hz), 115.0 (d, $J = 22.3$ Hz), 61.5 (d, $J = 6.1$ Hz), 15.8 (d, $J = 7.3$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 19.93; IR (film): 3060, 2982, 2328, 1469, 1210, 1094, 1037, 989, 757, 684 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{14}\text{FO}_3\text{P}$: 280.0665; found : 280.0666.



1l

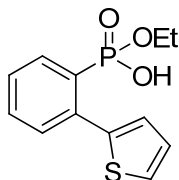
3'-Chloro- 1,1'-biphenyl phosphonic acid monoethyl ester (1l) : White solid, m.p. 75-83 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 12.67 (br, 1H), 8.03 (dd, $J = 14.7, 7.6$ Hz, 1H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.46-7.41 (m, 2H), 7.34-7.28 (m, 4H), 3.78 (p, $J = 7.2$ Hz, 2H), 1.03 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.4 (d, $J = 9.7$ Hz), 143.0 (d, $J = 4.3$ Hz), 133.5 (d, $J = 9.9$ Hz), 133.3, 132.1 (d, $J = 2.9$ Hz), 131.0 (d, $J = 14.2$ Hz), 128.7, 127.8, 127.5, 127.3 (d, $J = 193.1$ Hz), 127.9 (d, $J = 14.9$ Hz), 61.5 (d, $J = 6.5$ Hz), 15.8 (d, $J = 7.3$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 20.43; IR (film): 3061, 2982, 2359, 1462, 1200, 1039, 990, 909, 734,

697 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{14}\text{ClO}_3\text{P}$: 296.0369; found : 296.0367.



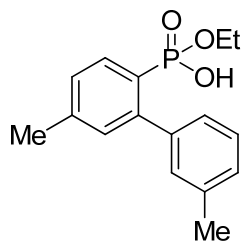
1m

4'-Chloro- 1,1'-biphenyl phosphonic acid monoethyl ester (1m) : White solid, m.p. 130-132 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 12.58 (br, 1H), 8.02 (ddd, $J = 14.8, 7.7, 1.0$ Hz, 1H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.43 (td, $J = 11.4, 3.5$ Hz, 1H), 7.38-7.36 (m, 2H), 7.34-7.26 (m, 3H), 3.75 (p, $J = 7.2$ Hz, 2H), 1.01 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.4 (d, $J = 10.0$ Hz), 139.7 (d, $J = 4.3$ Hz), 133.5 (d, $J = 2.5$ Hz), 133.4, 132.1 (d, $J = 2.8$ Hz), 131.2 (d, $J = 14.1$ Hz), 130.8, 127.7, 127.2 (d, $J = 192.6$ Hz), 127.2 (d, $J = 14.9$ Hz), 61.6 (d, $J = 6.3$ Hz), 15.8 (d, $J = 7.2$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 20.38; IR (film): 2982, 2285, 1469, 1200, 1039, 990, 831, 764 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{14}\text{ClO}_3\text{P}$: 296.0369; found : 296.0370.



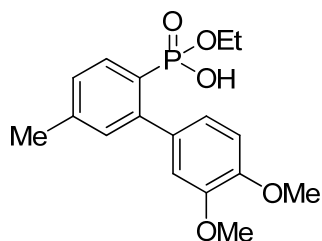
1n

2-(Thiophene-2-yl)phenylphosphonic acid monoethyl ester (1n) : Brown solid, m.p. 91-101 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 12.64 (br, 1H), 8.08 (ddd, $J = 14.8, 7.8, 1.2$ Hz, 1H), 7.53 (tt, $J = 11.3, 1.5$ Hz, 1H), 7.50-7.46 (m, 1H), 7.44-7.39 (m, 2H), 7.32 (dd, $J = 5.1, 1.2$ Hz, 1H), 3.83 (m, 2H), 1.06 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.4 (d, $J = 5.0$ Hz), 138.2 (d, $J = 8.9$ Hz), 134.1 (d, $J = 9.8$ Hz), 132.3 (d, $J = 13.5$ Hz), 132.0 (d, $J = 2.9$ Hz), 128.7, 128.0 (d, $J = 192.6$ Hz), 127.4 (d, $J = 14.7$ Hz), 127.0, 125.8, 61.8 (d, $J = 6.3$ Hz), 15.9 (d, $J = 7.5$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 20.44; IR (film): 3059, 2982, 2903, 2288, 1590, 1471, 1199, 1143, 1039, 849, 766, 701 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{12}\text{H}_{13}\text{O}_3\text{PS}$: 268.0323; found : 268.0321.



3a

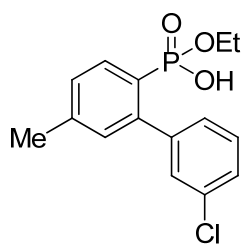
3'-Methyl-5-methyl-1,1'-biphenyl phosphonic acid monoethyl ester (3a) : White solid, m.p. 77-81 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.07 (br, 1H), 7.91 (dd, $J = 14.6, 7.9$ Hz, 1H), 7.24-7.18 (m, 4H), 7.14-7.12 (m, 2H), 3.69 (p, $J = 7.2$ Hz, 2H), 2.40 (s, 3H), 2.36 (s, 3H), 0.95 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.2 (d, $J = 10.6$ Hz), 142.3 (d, $J = 3.1$ Hz), 141.4 (d, $J = 4.0$ Hz), 136.9, 133.7 (d, $J = 10.7$ Hz), 132.1 (d, $J = 14.7$ Hz), 130.1, 128.0, 127.4, 127.3 (d, $J = 15.3$ Hz), 126.5, 124.1 (d, $J = 194.9$ Hz), 61.3 (d, $J = 6.3$ Hz), 21.5, 21.4, 15.7 (d, $J = 7.4$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 21.48; IR (film): 3030, 2980, 2297, 1603, 1392, 1196, 1041, 987, 789, 664 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{19}\text{O}_3\text{P}$: 290.1072; found : 290.1071.



3b

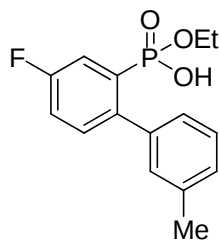
3',4'-Dimethoxy-5-methyl-1,1'-biphenyl phosphonic acid monoethyl ester (3b) : White solid, m.p. 40-50 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.87 (br, 1H), 7.92 (dd, $J = 7.9, 14.6$ Hz, 1H), 7.22-7.20 (m, 1H), 7.16 (d, $J = 5.2$, 1H), 7.09 (d, $J = 1.5$, 1H), 7.00-6.97 (m, 1H), 7.00-6.97 (m, 1H), 6.90-6.82 (m, 1H), 3.894 (s, 3H), 3.889 (s, 3H), 3.71 (p, $J = 7.2$ Hz, 2H), 2.41 (s, 3H), 0.97 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.1 (d, $J = 47.0$ Hz), 145.8 (d, $J = 10.6$ Hz), 142.5 (d, $J = 3.2$ Hz), 134.2 (d, $J = 5.1$ Hz), 133.8 (d, $J = 10.4$ Hz), 132.2 (d, $J = 14.6$ Hz), 127.3 (d, $J = 15.4$ Hz), 125.0, 123.1, 121.5, 113.2, 110.3, 61.4 (d, $J = 6.2$ Hz), 55.9, 55.8, 21.5, 15.8 (d, $J = 7.3$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 21.87; IR (film): 2936, 2254, 1603, 1517, 1248, 1171, 1029, 732 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{17}\text{H}_{21}\text{O}_5\text{P}$:

336.1127; found : 336.1123.



3c

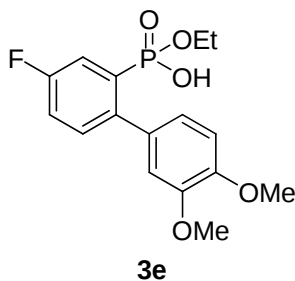
3'-Chloro-5-methyl-1,1'-biphenyl phosphonic acid monoethyl ester (3c) : Yellow solid, m.p. 107-110 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.66 (br, 1H), 7.90 (dd, $J = 14.5$, 7.9 Hz, 1H), 7.34-7.22 (m, 4H), 7.10 (d, $J = 4.8$ Hz, 1H), 3.75 (p, $J = 7.2$ Hz, 2H), 2.40 (s, 3H), 1.01 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.4 (d, $J = 10.2$ Hz), 143.1 (d, $J = 4.0$ Hz), 142.6 (d, $J = 2.9$ Hz), 133.7 (d, $J = 10.3$ Hz), 133.2, 131.9 (d, $J = 14.5$ Hz), 129.4, 128.7, 127.9 (d, $J = 15.3$ Hz), 127.8, 127.4, 124.2 (d, $J = 195.5$ Hz), 61.4 (d, $J = 6.4$ Hz), 21.5, 15.8 (d, $J = 7.3$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 20.87; IR (film): 3065, 2982, 2355, 1619, 1436, 1270, 1034, 771, 618 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{16}\text{ClO}_3\text{P}$: 310.0526; found : 310.0529.



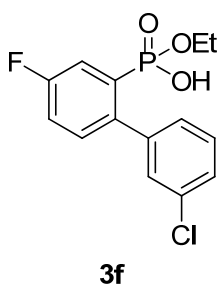
3d

3'-Methyl-1,1'-biphenyl-4-fluoro phosphonic acid monoethyl ester (3d) : White solid, m.p. 93-95 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.65 (br, 1H), 7.70 (ddd, $J = 9.0$, 15.9, 2.7 Hz, 1H), 7.31-7.20 (m, 5H), 7.15 (d, $J = 7.0$ Hz, 1H), 3.74 (p, $J = 7.2$ Hz, 2H), 2.37 (s, 3H), 1.00 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.2 (dd $J = 21.2$, 248.3 Hz), 142.3 (dd, $J = 3.6$, 9.5 Hz), 140.2 (d, $J = 3.9$ Hz), 137.1, 133.2 (dd, $J = 7.0$, 17.1 Hz), 130.2, 129.4 (dd, $J = 193.5$, 23.2 Hz), 128.3, 127.5, 126.6, 120.2 (dd, $J = 10.7$, 23.2 Hz), 118.8 (dd, $J = 2.8$, 20.8 Hz), 61.8 (d, $J = 6.4$ Hz), 21.4, 15.7 (d, $J = 7.3$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 18.80 (d, $J =$

7.7 Hz); IR (film): 2981, 2349, 1469, 1389, 1213, 1038, 993, 788, 707 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{16}\text{FO}_3\text{P}$: 294.0821; found : 294.0823.

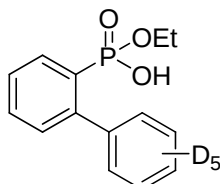


3',4'-Dimethoxy-4-fluoro-1,1'-biphenyl phosphonic acid monoethyl ester (3e) : Yellow solid, m.p. 163-167 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 10.88 (br, 1H), 7.72 (ddd, $J = 15.9, 9.1, 2.8$ Hz, 1H), 7.35-7.29 (m, 1H), 7.26-7.21 (m, 1H), 7.05 (d, $J = 2.0$, 1H), 6.96-6.94 (m, 1H), 6.88-6.86 (m, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.74 (p, $J = 7.2$ Hz, 2H), 1.00 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.2 (dd, $J = 21.3, 248.5$ Hz), 148.2 (d, $J = 60.7$ Hz), 141.9 (dd, $J = 9.5, 3.6$ Hz), 133.4 (dd, $J = 16.7, 7.2$ Hz), 132.9 (d, $J = 4.2$ Hz), 130.3, 128.4, 121.7, 120.3 (dd, $J = 23.3, 10.6$ Hz), 118.9 (dd, $J = 20.6, 3.0$ Hz), 113.3, 110.3, 61.9 (d, $J = 6.3$ Hz), 55.9, 55.8, 15.8 (d, $J = 7.2$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 18.83; IR (film): 2938, 1602, 1482, 1246, 1140, 1026, 765 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{18}\text{FO}_5\text{P}$: 340.0876; found : 340.0878.



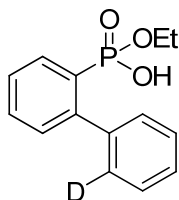
3'-Chloro-4-fluoro-1,1'-biphenyl phosphonic acid monoethyl ester (3f) : Yellow solid, m.p. 163-167 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 10.88 (br, 1H), 7.72 (ddd, $J = 15.9, 9.1, 2.8$ Hz, 1H), 7.35-7.29 (m, 1H), 7.26-7.21 (m, 1H), 7.05 (d, $J = 2.0$, 1H), 6.96-6.94 (m, 1H), 6.88-6.86 (m, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.74 (p, $J = 7.2$ Hz, 2H), 1.00 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.2 (dd, $J = 21.3, 248.5$ Hz), 148.2 (d, $J = 60.7$ Hz),

141.9 (dd, $J = 9.5, 3.6$ Hz), 133.4 (dd, $J = 16.7, 7.2$ Hz), 132.9 (d, $J = 4.2$ Hz), 130.3, 128.4, 121.7, 120.3 (dd, $J = 23.3, 10.6$ Hz), 118.9 (dd, $J = 20.6, 3.0$ Hz), 113.3, 110.3, 61.9 (d, $J = 6.3$ Hz), 55.9, 55.8, 15.8 (d, $J = 7.2$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 18.83; IR (film): 2984, 2287, 1600, 1462, 1212, 995, 786, 701 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{13}\text{ClFO}_3\text{P}$: 314.0275; found : 314.0272.



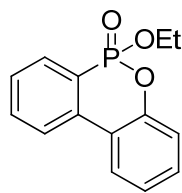
1a-[D₅]

2',3',4',5',6'-pentadeuterio-1,1'-biphenyl phosphonic acid monoethyl ester (1a-D₅) : White solid, m.p. 114-118 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.00 (br, 1H), 8.04 (ddd, $J = 14.8, 7.6, 1.2$ Hz, 1H), 7.55 (t, 1H), 7.41 (td, $J = 7.6, 3.5, 1.1$ Hz, 1H), 7.32 (t, 6.8 Hz, 1H), 3.70 (p, $J = 7.2$ Hz, 2H), 0.94 (t, $J = 7.1$ Hz, 3H); ^{31}P NMR (161 MHz, CDCl_3) δ 21.04; IR (film): 3057, 2981, 2903, 2283, 1671, 1475, 1382, 1196, 988, 757 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{10}\text{D}_5\text{O}_3\text{P}$: 267.1073; found : 267.1073.



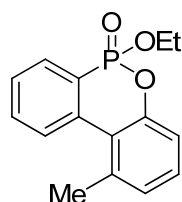
1a-[D₁]

2'-deuterio-1,1'-biphenyl phosphonic acid monoethyl ester (1a-D₁) : White solid, m.p. 110-112 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.20 (br, 1H), 8.05 (ddd, $J = 14.8, 7.7, 1.1$ Hz, 1H), 7.54 (tt, $J = 11.4, 1.5$ Hz, 1H), 7.46-7.30 (m, 6H), 3.70 (p, $J = 7.2$ Hz, 2H), 0.94 (t, $J = 7.1$ Hz, 3H); ^{31}P NMR (161 MHz, CDCl_3) δ 20.93; IR (film): 3055, 2981, 2590, 2309, 1670, 1460, 1196, 1040, 988, 754 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{14}\text{DO}_3\text{P}$: 263.0822; found : 263.0818.



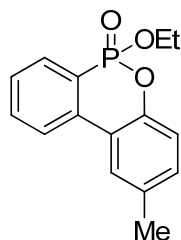
2a

6-Ethoxy-6H-dibenz[c,e]oxaphosphorin-6-oxide (2a) : R_f = 0.4 (EtOAc: hexane = 1:1); Yellow oil (55%, 28.9 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.00-7.93 (m, 3H), 7.74-7.70 (m, 1H), 7.55-7.50 (m, 1H), 7.41-7.37 (m, 1H), 4.26-4.19 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.0 (d, J = 7.6 Hz), 137.0 (d, J = 6.8 Hz), 133.4 (d, J = 2.5 Hz), 130.5, 130.2 (d, J = 9.0 Hz), 128.3 (d, J = 15.5 Hz), 125.2, 124.7, 124.0 (d, J = 12.3 Hz), 122.6 (d, J = 11.9 Hz), 122.5 (d, J = 181.8 Hz), 120.2 (d, J = 6.7 Hz), 63.0 (d, J = 6.6 Hz), 16.3 (d, J = 5.8 Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 10.14; IR (film): 3065, 2983, 2917, 2359, 1476, 1271, 1240, 1205, 1030, 918, 759 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{13}\text{O}_3\text{P}$: 260.0602; found : 260.0599.



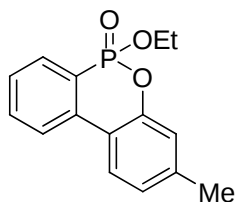
2b

6-Ethoxy-1-methyl-6H-dibenz[c,e]oxaphosphorin-6-oxide (2b) : R_f = 0.4 (EtOAc: hexane = 1:1); Yellow solid (53%, 29.1 mg); m.p. 49-53 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.01 (ddd, J = 15.0, 7.5, 1.1 Hz, 1H), 7.84 (t, J = 7.2 Hz, 3H), 7.70-7.66 (m, 1H), 7.52-7.48 (m, 1H), 7.28-7.24 (m, 1H), 7.12 (d, J = 17.9 Hz, 1H), 4.29-4.14 (m, 2H), 2.70 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.1 (d, J = 8.0 Hz), 137.3 (d, J = 6.4 Hz), 136.7 (d, J = 1.3 Hz), 132.2 (d, J = 2.4 Hz), 130.0 (d, J = 9.8 Hz), 129.2, 128.9 (d, J = 11.8 Hz), 128.5, 127.6 (d, J = 15.6 Hz), 124.9 (d, J = 193.2 Hz), 124.0 (d, J = 2.8 Hz), 117.7 (d, J = 5.9 Hz), 62.9 (d, J = 6.7 Hz), 23.5, 16.3 (d, J = 5.7 Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 10.68; IR (film): 3885, 2981, 1576, 1454, 1422, 1275, 1155, 961, 875, 792 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{15}\text{O}_3\text{P}$: 274.0759; found : 274.0761.



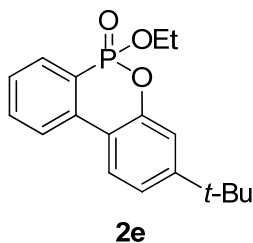
2c

6-Ethoxy-2-methyl-6H-dibenz[c,e]oxaphosphorin-6-oxide (2c) : R_f = 0.4 (EtOAc: hexane = 1:1); Yellow oil (66%, 36.3 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.00-7.93 (m, 2H), 7.72-7.68 (m, 2H), 7.52-7.48 (m, 1H), 7.18 (d, J = 8.3 Hz, 1H), 7.12 (d, J = 8.3 Hz, 1H), 4.24-4.17 (m, 2H), 2.41 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.9 (d, J = 7.9 Hz), 137.1 (d, 7.1 Hz), 134.1, 133.3 (d, J = 2.6 Hz), 131.2, 130.1 (d, J = 9.2 Hz), 128.1 (d, J = 15.5 Hz), 125.5 (d, J = 1.0 Hz), 123.9 (d, J = 12.2 Hz), 122.5 (d, J = 181.7 Hz), 122.2 (d, J = 11.9 Hz), 119.9 (d, J = 6.6 Hz), 62.8 (d, J = 6.6 Hz), 21.0, 16.3 (d, J = 5.8 Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 10.42; IR (film): 3060, 2983, 2297, 1467, 1272, 1200, 1143, 966, 853, 770 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{15}\text{O}_3\text{P}$: 274.0759; found : 274.0761.

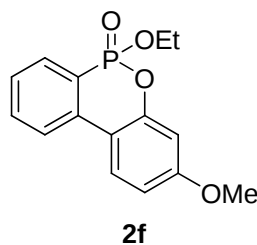


2d

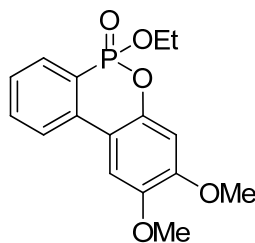
6-Ethoxy-3-methyl-6H-dibenz[c,e]oxaphosphorin-6-oxide (2d) : R_f = 0.4 (EtOAc: hexane = 1:1); Yellow oil (67%, 36.9 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.00-7.91 (m, 2H), 7.81 (d, J = 8.1 Hz, 1H), 7.70 (t, J = 7.8 Hz, 1H), 7.50-7.46 (m, 1H), 7.08 (d, J = 8.2 Hz, 1H), 7.05 (s, 1H), 4.25-4.17 (m, 2H), 2.40 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.8 (d, J = 7.8 Hz), 141.2, 137.2 (d, J = 7.1 Hz), 133.4 (d, J = 2.3 Hz), 130.1 (d, J = 9.1 Hz), 127.8 (d, J = 15.4 Hz), 125.6, 124.9, 123.7 (d, J = 12.0 Hz), 122.0 (d, J = 181.4 Hz), 120.5 (d, J = 6.6 Hz), 119.8 (d, J = 12.1 Hz), 62.9 (d, J = 6.6 Hz), 21.2, 16.3 (d, J = 5.9 Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 10.50; IR (film): 3542, 2982, 2925, 2357, 1621, 1472, 1272, 966, 853, 770 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{15}\text{O}_3\text{P}$: 274.0759; found : 274.0761.



6-Ethoxy-3-tert-butyl-6H-dibenz[c,e]oxaphosphorin-6-oxide (2e) : R_f = 0.4 (EtOAc: hexane = 1:1); Yellow oil (65%, 40.9 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.97-7.92 (m, 2H), 7.85 (d, J = 8.4 Hz, 1H), 7.72-7.67 (m, 1H), 7.51-7.46 (m, 1H), 7.29 (dd, J = 8.4, 1.8 Hz, 1H), 7.23 (d, J = 2.0 Hz, 1H), 4.26-4.19 (m, 2H), 1.35 (s, 9H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.7, 149.8 (d, J = 7.8 Hz), 137.1 (d, J = 7.2 Hz), 133.3 (d, J = 2.3 Hz), 130.1 (d, J = 9.0 Hz), 127.9 (d, J = 15.4 Hz), 124.7, 123.7 (d, J = 12.3 Hz), 122.1 (d, 181.1 Hz), 121.9, 119.6 (d, J = 11.8 Hz), 117.0 (d, J = 6.8 Hz), 63.0 (d, J = 6.6 Hz), 34.9, 16.3 (d, J = 5.8 Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 10.52; IR (film): 2964, 2905, 2359, 1618, 1472, 1272, 1032, 966, 773, 620 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{21}\text{O}_3\text{P}$: 316.1228; found : 316.1231.

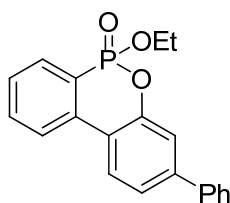


6-Ethoxy-3-methoxy-6H-dibenz[c,e]oxaphosphorin-6-oxide (2f) : R_f = 0.4 (EtOAc: hexane = 2:1); Colorless oil (65%, 38 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.95 (ddd, J = 14.6, 7.6, 1.1 Hz, 1H), 7.89-7.82 (m, 2H), 7.70-7.66 (m, 1H), 7.47-7.43 (m, 1H), 6.84 (dd, J = 8.8, 2.6 Hz, 1H), 6.76 (d, J = 2.6 Hz, 1H), 4.26-4.18 (m, 2H), 3.87 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.3, 151.1 (d, J = 7.5 Hz), 137.2 (d, J = 7.1 Hz), 133.4 (d, J = 2.3 Hz), 130.1 (d, J = 9.4 Hz), 127.3 (d, J = 15.5 Hz), 126.1, 123.3 (d, J = 12.3 Hz), 121.1 (d, J = 181.4 Hz), 115.4 (d, J = 12.0 Hz), 111.5, 104.8 (d, J = 7.2 Hz), 62.9 (d, J = 6.5 Hz), 55.7, 16.4 (d, J = 5.9 Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 10.83; IR (film): 3063, 2978, 2355, 1619, 1436, 1270, 1034, 771, 618 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{15}\text{O}_4\text{P}$: 290.0708; found : 290.0706.



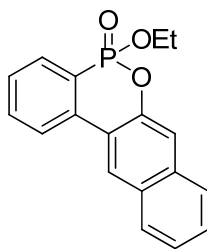
2g

5-Ethoxy-2,3-dimethoxy-6H-dibenz[c,e]oxaphosphorin-5-oxide (2g) : R_f = 0.3 (EtOAc: hexane = 2:1); Yellow solid (68%, 43.5 mg); m.p. 106-111 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.95 (ddd, J = 14.6, 7.5, 1.0 Hz, 1H), 7.83 (t, J = 7.2 Hz, 1H), 7.69 (t, J = 7.8 Hz, 1H), 7.48-7.43 (m, 1H), 7.32 (s, 1H), 4.25-4.18 (m, 2H), 3.95 (d, J = 14.5 Hz, 6H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.9, 146.1, 144.4 (d, J = 7.4 Hz), 137.2 (d, J = 6.9 Hz), 133.3 (d, J = 2.3 Hz), 130.2 (d, J = 9.2 Hz), 127.3 (d, J = 15.5 Hz), 123.3 (d, J = 12.1 Hz), 121.5 (d, J = 181.9 Hz), 114.2 (d, J = 12.0 Hz), 107.1, 103.5 (d, J = 7.2 Hz), 62.9 (d, J = 6.5 Hz), 56.3 (d, J = 25.5 Hz), 16.4 (d, J = 5.8 Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 11.03; IR (film): 3478, 2981, 2937, 1617, 1437, 1274, 1153, 1027, 892, 770 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{17}\text{O}_5\text{P}$: 320.0814; found : 320.0810.



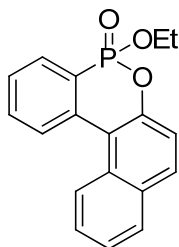
2h

6-Ethoxy-3-phenyl-6H-dibenz[c,e]oxaphosphorin-6-oxide (2h) : R_f = 0.35 (EtOAc: hexane = 1:1); Colorless oil (54%, 36.8 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.02 (m, 3H), 7.75-7.71 (m, 1H), 7.66-7.63 (m, 2H), 7.55-7.46 (m, 5H), 7.43-7.39 (m, 1H), 4.29-4.21 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.3 (d, J = 7.7 Hz), 143.5, 139.2, 136.8 (d, J = 7.2 Hz), 133.5 (d, J = 2.4 Hz), 130.2 (d, J = 9.3 Hz), 129.0, 128.2 (d, J = 15.5 Hz), 128.2, 127.0, 125.6, 124.0 (d, J = 12.2 Hz), 123.2, 122.3 (d, J = 189.9 Hz), 121.4 (d, J = 3.6 Hz), 118.4 (d, J = 6.7 Hz), 63.0 (d, J = 6.6 Hz), 16.4 (d, J = 5.8 Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 10.37; IR (film): 3060, 2982, 1471, 1272, 1188, 1142, 1029, 946, 760, 697 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{20}\text{H}_{17}\text{O}_3\text{P}$: 336.0915; found : 336.0911.



2i

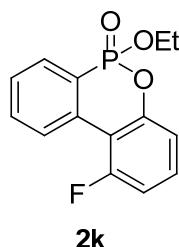
5-Ethoxy-5H-benzo[c]naphtho[2,3-e][1,2]oxaphosphorin-5-oxide (2i) : R_f = 0.35 (EtOAc: hexane = 1:1); Yellow oil (70%, 43.4 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.40 (s, 1H), 8.13 (t, J = 7.2 Hz, 1H), 8.02 (ddd, J = 14.6, 7.5, 1.0 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.76-7.73 (m, 1H), 4.28-4.20 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.7 (d, J = 7.8 Hz), 137.2 (d, J = 6.9 Hz), 134.1, 133.5 (d, J = 2.3 Hz), 130.5, 130.3 (d, J = 9.1 Hz), 128.4, 128.4 (d, J = 15.4 Hz), 127.6, 126.9, 125.8, 125.5, 124.6 (d, J = 12.2 Hz), 123.1, 122.9 (d, J = 11.6 Hz), 116.3 (d, J = 6.8 Hz), 63.0 (d, J = 6.6 Hz), 16.3 (d, J = 5.9 Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 20.87; IR (film): 3477, 2983, 2941, 1596, 1431, 1271, 1158, 1030, 876, 770 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{15}\text{O}_3\text{P}$: 310.0759; found : 310.0760.



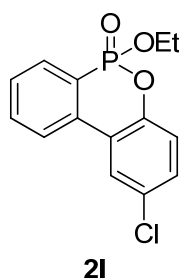
2j

5-Ethoxy-5H-benzo[c]naphtho[1,2-e][1,2]oxaphosphorin-5-oxide (2j) : R_f = 0.4 (EtOAc: hexane = 1:1); Yellow oil (52%, 32.2 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.52 (d, J = 8.5 Hz, 1H), 8.17 (t, J = 7.0 Hz, 1H), 8.08 (ddd, J = 14.8, 7.5, 0.8 Hz, 1H), 7.90 (dd, J = 14.3, 8.0 Hz, 2H), 7.74 (t, J = 7.8 Hz, 1H), 7.60-7.49 (m, 3H), 7.38 (d, J = 8.8 Hz, 1H), 4.30-4.15 (m, 2H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.6 (d, J = 8.0 Hz), 136.8 (d, J = 6.0 Hz), 132.5 (d, J = 2.3 Hz), 131.8, 131.2, 130.4 (d, J = 9.8 Hz), 130.4, 129.4 (d, J = 11.8 Hz), 128.9, 127.8 (d, J = 16.0 Hz), 127.4, 125.6, 125.3, 123.7, 119.4 (d, J = 5.9 Hz), 119.1 (d, J = 12.1 Hz), 63.0 (d, J = 6.8 Hz), 16.3 (d, J = 5.6 Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 10.07;

IR (film): 3726, 3061, 2982, 2926, 2358, 1618, 1380, 1275, 1027, 875, 729 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{15}\text{O}_3\text{P}$: 310.0759; found : 310.0756.

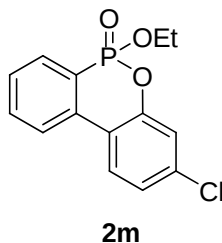


6-Ethoxy-1-fluoro-6H-dibenz[c,e]oxaphosphorin-6-oxide (2k) : R_f = 0.4 (EtOAc: hexane = 1:1); Yellow solid (54%, 29.8 mg); m.p. 72-78 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.27 (t, J = 7.3 Hz, 1H), 8.04-8.00 (m, 1H), 7.72 (t, J = 7.8 Hz, 1H), 7.57-7.52 (m, 1H), 7.09-7.01 (m, 2H), 4.28-4.20 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.6 (d, J = 254.9 Hz), 150.6 (t, J = 7.0 Hz), 133.7 (dd, J = 6.2, 4.1 Hz), 133.4, 130.0, 129.9 (d, J = 3.7 Hz), 128.6 (d, J = 4.2 Hz), 128.4, 128.4 (d, J = 19.4 Hz), 123.0 (d, J = 182.7 Hz), 116.0 (dd, J = 6.3, 3.3 Hz), 112.8 (d, J = 24.6 Hz), 63.2 (d, J = 6.6 Hz), 16.3 (d, J = 5.8 Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 9.87; IR (film): 3063, 2983, 1619, 1433, 1277, 1221, 1010, 796, 609 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{12}\text{FO}_3\text{P}$: 278.0508; found : 278.0509.

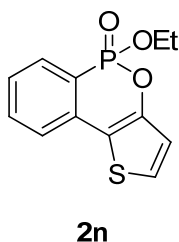


6-Ethoxy-2-chloro-6H-dibenz[c,e]oxaphosphorin-6-oxide (2l) : R_f = 0.4 (EtOAc: hexane = 1:1); White solid (60%, 35.2 mg); m.p. 110-113 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.00 (ddd, J = 14.6, 7.6, 1.1 Hz, 1H), 7.94-7.90 (m, 2H), 7.76-7.72 (m, 1H), 7.59-7.52 (m, 1H), 7.36-7.33 (m, 1H), 7.19 (d, J = 8.6 Hz, 1H), 4.27-4.20 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.4 (d, J = 7.9 Hz), 135.8 (d, J = 7.0 Hz), 133.6 (d, J = 2.4 Hz), 130.2, 130.2, 130.1, 130.0 (d, J = 28.0 Hz), 129.0 (d, J = 15.3 Hz), 125.2 (d, J = 1.0 Hz), 124.1 (d, J = 12.0 Hz), 123.7 (d, J = 60.1 Hz), 121.6 (d, J = 6.7 Hz), 63.2 (d, J = 6.6 Hz), 16.3 (d, J = 5.8

Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 9.87; IR (film): 3060, 2981, 1596, 1243, 1111, 1025, 966, 789, 659 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{12}\text{ClO}_3\text{P}$: 294.0213; found : 294.0210.

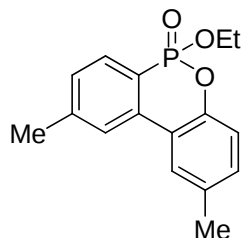


6-Ethoxy-3-chloro-6H-dibenz[c,e]oxaphosphorin-6-oxide (2m) : R_f = 0.4 (EtOAc: hexane = 1:1); White solid (64%, 37.5 mg); m.p. 105-112 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.00 (ddd, J = 14.7, 7.6, 1.0 Hz, 1H), 7.92 (t, J = 7.2 Hz, 1H), 7.90 (d, J = 9.1 Hz, 1H), 7.75-7.70 (m, 1H), 7.57-7.52 (m, 1H), 7.27-7.25 (m, 2H), 4.29-4.20 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.2 (d, J = 7.6 Hz), 136.1 (d, J = 6.8 Hz), 135.6, 133.6 (d, J = 2.3 Hz), 130.3 (d, J = 9.3 Hz), 128.6 (d, J = 15.4 Hz), 126.2 (d, J = 1.0 Hz), 125.1, 124.0 (d, J = 11.9 Hz), 122.2 (d, J = 170.0 Hz), 121.3, 120.4 (d, J = 7.0 Hz), 63.2 (d, J = 6.6 Hz), 16.3 (d, J = 5.8 Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 10.00; IR (film): 3068, 2982, 1601, 1470, 1273, 1081, 1028, 943, 768, 618 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{12}\text{ClO}_3\text{P}$: 294.0213; found : 294.0210.



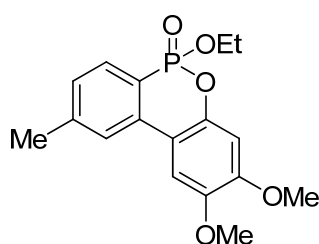
5-Ethoxy-5H-benzo[c]thieno[2,3-e][1,2]oxaphosphorin-5-oxide (2n) : R_f = 0.4 (EtOAc: hexane = 1:1); Yellow solid (52%, 27.8 mg); m.p. 69-73 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.92 (ddd, J = 14.1, 7.6, 0.7 Hz, 1H), 7.64-7.60 (m, 1H), 7.51-7.47 (m, 1H), 7.44-7.39 (m, 1H), 7.26-7.25 (m, 1H), 4.27-4.19 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.5 (d, J = 7.7 Hz), 134.5 (d, J = 7.3 Hz), 133.6 (d, J = 2.3 Hz), 130.4 (d, J = 9.4 Hz), 127.4 (d, J = 15.4 Hz), 124.4, 123.1 (d, J = 11.0 Hz), 120.3 (d, J = 6.6 Hz), 118.5 (d, J = 180.5 Hz), 118.5 (d, J = 13.6 Hz), 63.1 (d, J = 6.6 Hz), 16.3 (d, J = 6.0 Hz); ^{31}P NMR (161

MHz, CDCl₃) δ 13.26; IR (film): 3082, 2982, 2357, 1476, 1272, 1034, 1006, 765, 638 cm⁻¹; HRMS (EI): m/z calcd for C₁₂H₁₁O₃PS : 266.0167; found : 266.0167.



2o

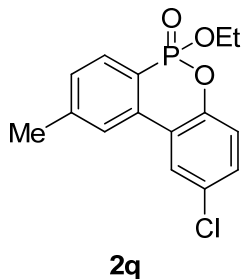
6-Ethoxy-2,9-dimethyl-6H-dibenz[c,e]oxaphosphorin-6-oxide (4a) : R_f = 0.4 (EtOAc: hexane = 1:1); Yellow solid (72%, 41.3 mg); m.p. 112-120 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.86 (dd, J = 14.4, 7.7 Hz, 1H), 7.76 (d, J = 6.0 Hz, 1H), 7.71 (d, J = 1.5 Hz, 1H), 7.33-7.30 (m, 1H), 7.17 (d, J = 8.3 Hz, 1H), 7.10 (d, J = 8.2 Hz, 1H), 4.21-4.14 (m, 2H), 2.50 (s, 3H), 2.41 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 148.0 (d, J = 7.9 Hz), 143.9 (d, J = 2.8 Hz), 137.1 (d, J = 7.3 Hz), 134.0, 131.0 130.2 (d, J = 9.6 Hz), 129.1 (d, J = 16.0 Hz), 125.4, 124.5 (d, J = 12.5 Hz), 122.2 (d, J = 11.8 Hz), 119.8 (d, J = 6.6 Hz), 119.4 (d, J = 184.1 Hz), 62.7 (d, J = 6.6 Hz), 22.1, 21.0, 16.3 (d, J = 5.9 Hz); ³¹P NMR (161 MHz, CDCl₃) δ 11.25; IR (film): 3047, 2981, 2357, 1497, 1271, 1216, 1032, 938, 748, 642 cm⁻¹; HRMS (EI): m/z calcd for C₁₆H₁₇O₃P : 288.0915; found : 288.0913.



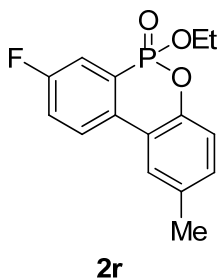
2p

6-Ethoxy-2,3-dimethoxy-9-methyl-6H-dibenz[c,e]oxaphosphorin-6-oxide (4b) : R_f = 0.3 (EtOAc: hexane = 2:1); Yellow solid (70%, 46.7 mg); m.p. 126-130 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.83 (dd, J = 14.4, 7.7 Hz, 1H), 7.61 (d, J = 6.0 Hz, 1H), 7.31 (s, 1H), 7.28-7.26 (m, 1H), 6.74 (s, 1H), 4.23-4.15 (m, 2H), 3.99 (s, 3H), 3.93 (s, 3H), 2.50 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 150.8, 146.0, 144.6 (d, J = 7.5 Hz), 143.9 (d, J = 7.5

Hz), 143.9 (d, $J = 2.6$ Hz), 137.1 (d, $J = 7.5$ Hz), 130.2 (d, $J = 9.6$ Hz), 128.3 (d, $J = 16.0$ Hz), 123.7 (d, $J = 12.5$ Hz), 118.4 (d, $J = 184.2$ Hz), 114.2 (d, $J = 11.9$ Hz), 107.0, 103.4, (d, $J = 7.1$ Hz), 62.8 (d, $J = 6.5$ Hz), 56.5, 56.2, 22.5, 16.4 (d, $J = 5.9$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 11.84; IR (film): 2977, 2937, 2240, 1520, 1272, 1214, 1038, 913, 733, 648 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{17}\text{H}_{19}\text{O}_5\text{P}$: 334.0970; found : 334.0969.

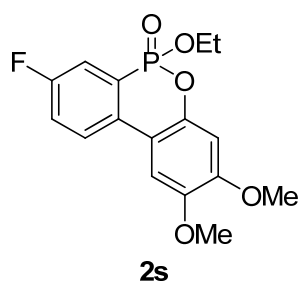


6-Ethoxy-2-chloro-9-methyl-6H-dibenz[c,e]oxaphosphorin-6-oxide (4c) : $R_f = 0.35$ (EtOAc: hexane = 1:1); Yellow solid (64%, 39.7 mg); m.p. 97-100 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.90-7.84 (m, 2H), 7.71 (d, $J = 6.0$ Hz, 1H), 7.39-7.36 (m, 1H), 7.17 (d, $J = 8.7$ Hz, 1H), 4.25-4.17 (m, 2H), 2.51 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.6 (d, $J = 7.9$ Hz), 144.3 (d, $J = 2.4$ Hz), 135.8 (d, $J = 7.3$ Hz), 130.3 (d, $J = 9.5$ Hz), 130.0, 129.9 (d, $J = 15.9$ Hz), 129.8, 125.1, 124.6 (d, $J = 12.4$ Hz), 121.5 (d, $J = 6.7$ Hz), 119.4 (d, $J = 184.7$ Hz), 63.1 (d, $J = 6.6$ Hz), 22.1, 16.3 (d, $J = 5.9$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 10.67; IR (film): 3065, 2982, 2355, 1619, 1436, 1270, 1034, 771, 618 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{14}\text{ClO}_3\text{P}$: 308.0369; found : 308.0371.

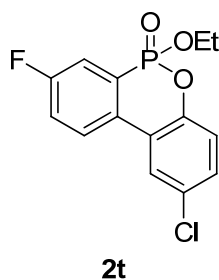


6-Ethoxy-2-methyl-8-floro-6H-dibenz[c,e]oxaphosphorin-6-oxide (4e) : $R_f = 0.35$ (EtOAc: hexane = 1:1); White solid (57%, 33.4 mg); m.p. 102-105 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.98-7.92 (m, 1H), 7.68-7.61 (m, 2H), 7.38 (td, $J = 12.8, 2.8$ Hz, 1H), 7.18 (d, $J = 8.3$ Hz, 1H), 7.12 (d, $J = 8.3$ Hz, 1H), 4.26-4.19 (m, 2H), 2.41 (s, 3H), 1.29 (t, $J = 7.1$ Hz, 3H); ^{13}C

NMR (100 MHz, CDCl₃) δ 161.9 (dd, J = 21.8, 252.1 Hz), 147.4 (d, J = 8.0 Hz), 134.4, 133.4 (dd, J = 6.4, 3.6 Hz), 131.1, 126.6 (dd, J = 14.3, 7.6 Hz), 125.4, 124.6 (dd, J = 182.0, 6.6 Hz), 121.6, 120.9 (dd, J = 21.8, 2.7 Hz), 119.9 (d, J = 6.8 Hz), 116.7 (dd, J = 22.8, 9.9 Hz), 63.2 (d, J = 6.6 Hz), 21.0, 16.3 (d, J = 5.8 Hz); ³¹P NMR (161 MHz, CDCl₃) δ 8.56 (d, J = 7.9 Hz); IR (film): 3539, 3063, 2983, 2926, 1721, 1608, 1488, 1259, 1028, 828 cm⁻¹; HRMS (EI): m/z calcd for C₁₅H₁₄FO₃P : 292.0665; found : 292.0663.



6-Ethoxy-2,3-dimethoxy-8-fluoro-6H-dibenz[c,e]oxaphosphorin-6-oxide (4f) : R_f = 0.30 (EtOAc: hexane = 2:1); Yellow solid (63%, 42.7 mg); m.p. 126-130 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.85-7.80 (m, 1H), 7.63 (ddd, J = 15.7, 7.6, 2.7 Hz, 1H), 7.38 (td, J = 12.8, 2.6 Hz, 1H), 7.26 (s, 1H), 6.75 (s, 1H), 4.28-4.20 (m, 2H), 4.00 (s, 3H), 3.93 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 161.4 (dd, J = 21.8, 251.4 Hz), 150.9, 146.3, 143.9 (d, J = 7.6 Hz), 133.5 (dd, J = 6.1, 3.5 Hz), 125.8 (dd, J = 14.2, 7.5 Hz), 123.5 (dd, J = 182.4, 6.5 Hz), 120.8 (dd, J = 22.0, 2.8 Hz), 116.7 (dd, J = 22.8, 9.7 Hz), 113.6 (d, J = 11.8 Hz), 107.0, 103.5 (d, J = 7.1 Hz), 63.2 (d, J = 6.5 Hz), 56.4 (d, J = 24.9 Hz), 16.4 (d, J = 5.7 Hz); ³¹P NMR (161 MHz, CDCl₃) δ 9.15 (d, J = 7.7 Hz); IR (film): 3065, 2981, 2245, 1618, 1488, 1273, 1241, 1028, 895, 737 cm⁻¹; HRMS (EI): m/z calcd for C₁₆H₁₆FO₅P : 338.0719; found : 338.0721.

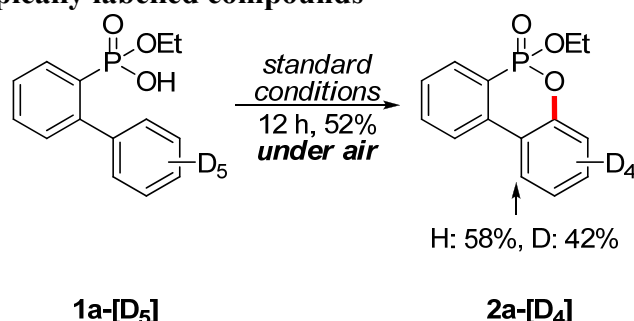


6-Ethoxy-2-chloro-8-fluoro-6H-dibenz[c,e]oxaphosphorin-6-oxide (2t) : R_f = 0.40 (EtOAc: hexane = 1:1); White solid (50%, 31.3 mg); m.p. 127-132 °C; ¹H NMR (400 MHz, CDCl₃) δ

S30

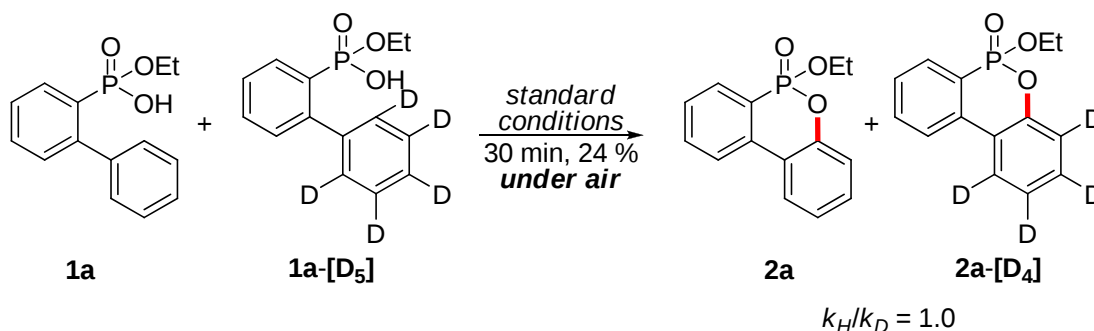
7.94-7.89 (m, 1H), 7.84 (d, $J = 2.4$ Hz, 1H), 7.68 (ddd, $J = 15.7, 10.2, 2.8$ Hz, 1H), 7.42 (td, $J = 12.8, 2.8$ Hz, 1H), 7.36-7.33 (m, 1H), 7.20 (d, $J = 8.7$ Hz, 1H), 4.30-4.22 (m, 2H), 1.31 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.4 (dd, $J = 21.4, 253.8$ Hz), 147.9 (d, $J = 8.2$ Hz), 132.0 (dd, $J = 6.0, 3.6$ Hz), 130.3, 130.1, 126.9 (dd, $J = 14.2, 7.8$ Hz), 125.0, 124.8 (dd, $J = 182.6, 6.6$ Hz), 123.5 (d, $J = 11.6$ Hz), 121.2, 121.1 (dd, $J = 22.0, 2.7$ Hz), 116.9 (dd, $J = 23.0, 9.7$ Hz), 63.5 (d, $J = 6.6$ Hz), 16.3 (d, $J = 5.8$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 7.96 (d, $J = 7.9$ Hz); IR (film): 3568, 3069, 2984, 2315, 1725, 1606, 1477, 1255, 1027, 829 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{11}\text{ClFO}_3\text{P}$: 312.0118; found : 312.0117.

1.7. Studies with isotopically labelled compounds



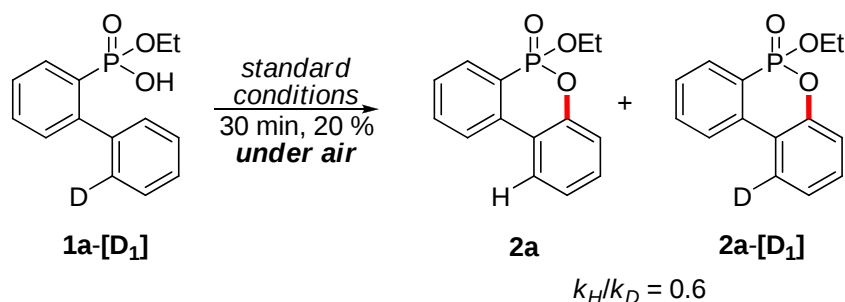
2',3',4',5',6'-Pentadeuterio-1,1'-biphenyl phosphonic acid monoethyl ester **1a-[D₅]** (53.4 mg, 0.2 mmol), $\text{Pd}(\text{OAc})_2$ (4.49 mg, 0.02 mmol), *N*-acetyl-L-leucine (10.4 mg, 0.06 mmol), $\text{PhI}(\text{OAc})_2$ (128.8 mg, 0.4 mmol), KOAc (39.3 mg, 0.4 mmol) and *t*-BuOH (2.5 mL) were added in a 2.5 mL screw-top v-vial. The reaction mixture was stirred at 100 °C for 12 h under air atmosphere. After celite filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1/1) to yield **2a-[d₄]** (27.6 mg,) as a yellow oil.

1.8. Intermolecular competition



1,1'-Biphenylphosphonic acid monoethyl ester **1a** (26.2mg, 0.10 mmol) and 2',3',4',5',6'-pentadeuterio-1,1'-biphenylphosphonic acid monoethyl ester **1a-[D₅]** (26.7 mg, 0.1 mmol), Pd(OAc)₂ (4.49 mg, 0.02 mmol), *N*-acetyl-L-leucine (10.4 mg, 0.06 mmol), PhI(OAc)₂ (128.8 mg, 0.4 mmol), KOAc (39.3 mg, 0.4 mmol) and *t*-BuOH (2.5 mL) were added in a 2.5 mL screw-top v-vial. The reaction mixture was stirred at 100 °C for 30 min under air atmosphere. After celite filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1/1) to yield **2a** and **2a-[d₄]** (12.4 mg, 24%) as a yellow oil. The ratio of **2a** and **2a-[D₄]** was determined to be 0.5 / 0.5 (KIE = 1.0) by ¹H-NMR spectroscopy.

1.9. Intramolecular competition



2'-Deuterio-1,1'-biphenylphosphonic acid monoethyl ester **1a-[D₁]** (52.7 mg, 0.20 mmol), Pd(OAc)₂ (4.49 mg, 0.02 mmol), *N*-acetyl-L-leucine (10.4 mg, 0.06 mmol), PhI(OAc)₂ (128.8 mg, 0.4 mmol), KOAc (39.3 mg, 0.4 mmol) and *t*-BuOH (2.5 mL) were added in a 2.5 mL screw-top v-vial. The reaction mixture was stirred at 100 °C for 30 min under air atmosphere. After celite filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1/1) to yield **2a** and **2a-[d₁]** (10.3 mg, 20%) as a yellow oil. The ratio of **2a** / **2a-[D₁]** was determined to be 0.375 / 0.625 (KIE = 0.6) by ¹H-NMR spectroscopy.

2. References

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3. ^1H and ^{13}C NMR spectra

