Supporting Information

Bronsted acid/organic photoredox cooperative catalysis: Easy

access to tri- and tetra-substituted alkenylphosphorus

compounds from alcohols and P-H species

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1. General Information

Unless otherwise noted, all commercially available compounds were used as received. All solvents were purified according to standard procedures. The ¹H NMR and spectra was recorded at 400MHz, ¹³C NMR was recorded at 101MHz. ³¹P NMR was recorded at 162 MHz. ¹H and ¹³C NMR Chemical shifts were calibrated to tetramethylsilane as an external reference. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet); coupling constants (*J*) are in Hertz (Hz). The data with an asterisk (*) indicate peaks of the by-products **3'**. IR spectra were recorded on a Thermo Scientific Nicolet iS-5 FT-IR spectrometer and are reported in terms of frequency of absorption (cm⁻¹). HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected. The starting materials **1a**, **2a** purchased from *Energy-chemical Ltd. p*-Toluenesulfonic acid purchased from *MERYER CO. LTD. tert*-Butyl hydroperoxide was purchased from *Sigma-Aldrich LLC*. Other phosphine oxides **2**¹, (*R*_P)-menthylphosphine oxide ² and alcohols³ were readily prepared according to the related literatures. The LEDs were TORNADO (23W), CoolDaylight purchased from *Philips N.V.*

2. Screening reaction conditions

I	OH Ph + HP(O)Ph ₂ Ph	Conditions Visible-light Pt	Ph P(C))Ph ₂ + Pł	Ph J P(O)P	'h ₂
	1a 2a		3a		Ja	
Entry	Cat.(mol	%)	Sol.	[O]	Yield (%) b	3a/3a' ^c
1	TsOH (20), RI	$hBH^+(2)$	i-PrOH	air	11	94/6
2	TsOH (20), RI	$hBH^+(2)$	i-PrOH	O_2	23	91/9
3	TsOH (20), Rł	$\mathrm{BH}^{+}(2)$	i-PrOH	$K_2S_2O_8$	20	79/21
4	TsOH (20), Rł	$\mathrm{BH}^{+}(2)$	i-PrOH	DDQ	trace	_/_
5	TsOH (20), Rł	$\mathrm{BH}^{+}(2)$	<i>i</i> -PrOH	TBHP	80 (98)	>99/1
6	TFA (20), Rh	$\mathrm{BH}^{+}(2)$	<i>i</i> -PrOH	TBHP	20	69/31
7	PhCO ₂ H (20), F	$hBH^{+}(2)$	<i>i</i> -PrOH	TBHP	20	69/31
8	$HNTf_{2}$ (20), RI	$nBH^{+}(2)$	<i>i</i> -PrOH	TBHP	77	98/2
9	TsOH (20), Eo	sin Y (2)	<i>i</i> -PrOH	TBHP	60	92/8
10	TsOH (20), Eo	sin B (2)	<i>i</i> -PrOH	TBHP	26	97/3
11	TsOH (20), Eosin B (2)	(alcohol soluble)	<i>i</i> -PrOH	TBHP	32	97/3
12	TsOH (20), Rł	$\mathrm{BH}^{+}(2)$	CH ₃ CN	TBHP	59	79/21
13	TsOH (20), Rł	$\mathrm{BH}^{+}(2)$	DCE	TBHP	35	97/3
14	TsOH (20), Rł	$\mathrm{BH}^{+}(2)$	DMF	TBHP	25	74/26
15	TsOH (20), Rł	$\mathrm{BH}^{+}(2)$	Tol.	TBHP	10	94/6
16	TsOH (20), Rł	$\mathrm{BH}^{+}(2)$	t-BuOH	TBHP	35	74/26
17	TsOH (20), Rh	1000000000000000000000000000000000000	EtOH	TBHP	63	81/19

Table 1. Optimization of the Reaction Conditions^{*a*}

18	TsOH (20)	<i>i</i> -PrOH	TBHP	60	48/52
19	$RhBH^{+}(2)$	<i>i</i> -PrOH	TBHP	trace	_/_
20	TsOH (10), RhBH ⁺ (2)	<i>i</i> -PrOH	TBHP	36	>99/1
21	TsOH (20), RhBH ⁺ (1)	<i>i</i> -PrOH	TBHP	83	90/10
22 ^d	TsOH (20), RhBH ⁺ (2)	<i>i</i> -PrOH	TBHP	8	96/4
23 ^e	TsOH (20), RhBH ⁺ (2)	<i>i</i> -PrOH	TBHP	51	95/5

^{*a*} Experimental conditions see the General method. ^{*b*} Isolated yields. ^{*c*} The ratio of **3a/3a'** was determined by ³¹P NMR. ^{*d*} Performed at room temperature. ^{*e*} Performed at 50 °C. Result in the parentheses was carried out with 4.0 equivalent (8.0 h later, the second 2.0 equivalent TBHP was then added) of TBHP.

3a'was known compounds, while cannot be isolated in this reaction. Thus, we also prepared **3a**' according to the literature ⁴ and set its data as reference to analysis the ratio between **3a/3a'** by NMR. 1H NMR (400 MHz, CDCl3) δ 7.66 – 7.51 (m, 4H), 7.44 – 7.35 (m, 2H), 7.33 – 7.26 (m, 4H), 7.23 – 7.15 (m, 4H), 7.15 – 7.08 (m, 4H), 7.07 – 7.01 (m, 2H), 4.70 (dt, *J* = 11.8, 7.1 Hz, 1H), 3.10 (dd, *J* = 11.0, 7.2 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 143.96 (d, *J*_{C-P} = 7.2 Hz), 131.39 (d, *J*_{C-P} = 2.2 Hz), 130.78, 130.68, 128.49, 128.36, 127.91, 126.50, 44.55 (d, *J*_{C-P} = 2.7 Hz), 36.60 (d, *J*_{C-P} = 70.4 Hz). ³¹P NMR (162 MHz, Chloroform-d) δ = 30.21.

	H + H + H +	TSOH (x mol%), TBHP, Rhodamine B (y mol%) <i>i-</i> PrOH, Temp.		+ 0 3x'	
Entry	х	у	Temp. (°C)	Yield (%) ^b	3x/3x' ^c
1	25	2	80	32	>99/1
2	30	2	80	34	>99/1
3	20	5	80	34	>99/1
4	20	10	80	28	>99/1
5	20	2	60	36	>99/1

Table 2. Optimization of the Reaction Conditions with 2x^{*a*}

^{*a*} Experimental conditions see the General method. ^{*b*} Isolated yields. ^{*c*} The ratio of **3x/3x'** was determined by ³¹P NMR.

Figure 1. Structures of Organic Photoredox Catalysts.



3. General Procedure for the substituted alkenylphosphorus compounds.

Alcohol 1 (0.2 mmol), phosphine oxide 2 (0.6 mmol), TsOH 20 mol%, Rhodamine B (2 mol%) and 2 mL ^{*i*}PrOH were added into a tube. The reaction was stirred at 80 °C under N₂ for 30 min. 2 eq. TBHP (~5.5mol/L in decane) was injected into the tube. 8 h later the second 2.0 eq. TBHP was then added. All of the reactions were performed under two white LED (23 W). After complete conversion, volatiles were removed under reduced pressure. The residue was purified *via* PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 2:3) or column chromatography (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 1:1) to afford the corresponding products **3a-3aa**. In most examples, pure **3** can be isolated by column chromatography or PTLC. The R_f value of **3** and **3'** almost was same. Thus in few case **3'** and **3** were isolated as a mixture. Then the desired product **3** can also further purified by recrystallization with EtOAc-petroleum ether (60-90 °C). **3'** cannot be isolated from **3**, while the HRMS and ³¹P NMR was obtained in this report (for the reactions with lower chemoselectivity).

For gram-scale reaction: 1,1-diphenylethan-1-ol (0.79 g, 4 mmol), HP(O)Ph₂ (2.43 g, 12 mmol), TsOH (0.14 g, 0.8 mmol) and Rhodamine B (0.04 g, 0.08 mmol) were added into a 100 mL round-bottomed flask charged with N₂. 40 mL *i*-PrOH was injected into the flask under N₂. The reaction mixture was stirred at 80°C for 30 min under light irradiating. Then 1.5 mL TBHP (~5.5 M in decane, ~8 mmol) was added dropwise. After stirred for 8 h, the second TBHP (~5.5 M in decane, ~8 mmol) was injected. After complete conversion, volatiles were removed under reduced pressure. The residue was purified *via* column chromatography (Petroleum ether (bp: 60 – 90 °C)/EtOAc = 1/1) to afford the corresponding products **3a.** (1.3 g, 3.4 mmol, 85% yield, **3a/3a'** > 99/1).

4. Preparation of (2,2-diphenylvinyl)phosphines.

In a 25 mL flask, **3a** (1 mmol) was placed with a magnetic stir bar under N_2 atmosphere. Toluene

(6 mL) and HSiCl₃ (3 mmol) were then added by a syringe. The reaction mixture was heated at 120 °C in an oil bath for 12h. After cooling, the resulting solution was carefully quenched with 10% aq. NaOH and stirred until excess HSiCl₃ was consumed. The resulting mixture was diluted with water and extracted with ethyl acetate (25 mL * 3). The combined organic layer was dried over Na₂SO₄ and volatiles were removed in vacuo. The desired phosphine **4** (353.5 mg, 97%) was obtained in an analytically pure form ^{2b}.

5. General methods for the control experiments.



a) **3a'** was prepared according to the literature.⁴ **3a** (0.2 mmol) was dissolved in 2mL ^{*i*}PrOH, Rhodamine B (2 mol%), TsOH (20 mol%). The mixture was stirred for 30 min under N₂ at 80°C, and 0.4 mmol TBHP was added dropwise. 12 h later volatiles were removed under reduced pressure the crude product was confirmed by ³¹P NMR.

b) **Top**: 1,1-Diphenylethylene (0.2 mmol), **2a** (0.6 mmol) and Rhodamine B (2 mol%) was dissolved in 2 mL ^{*i*}PrOH. The mixture was stirred for 30 min under N₂ at 80°C, and 0.4 mmol TBHP was added dropwise. 12 h later, the desired product **3a** was obtained by PTLC. **Middle:** 1,1-Diphenylethylene(0.2 mmol), **2a** (0.6 mmol), Rhodamine B (2 mol%) and TsOH (20 mol%) was dissolved in 2 mL ^{*i*}PrOH. The mixture was stirred for 30 min under N₂ at 80°C, and 0.4 mmol TBHP was added dropwise. 12 h later, the desired product **3a** was obtained by PTLC. **Bottom**: 1,1-Diphenylethylene (0.2 mmol), **2a**(0.6 mmol), Rhodamine B (2 mol%) and TsOH(20 mol%) was dissolved in 2 mL ^{*i*}PrOH. The mixture was stirred for 30 min under N₂ at room temperature, and 0.4 mmol TBHP was added dropwise. 12 h later, the desired product 3a was obtained by PTLC.

c) **1a** (0.2 mmol), **2a** (0.6 mmol), Rhodamine B (2 mol%), TsOH(20 mol%) and TEMPO (0.4 mmol) was dissolved in 2 mL ^{*i*}PrOH. The mixture was stirred for 30 min under N₂ at 80 °C, and 0.4 mmol TBHP was added dropwise. After 12h, only a trace amount of **3a** and **3a**' can be detected by NMR.

6. Stern-Volmer fluorescence quenching experiments

We investigated the emission and excitation spectra of the photocatalyst Rhodamine B. A solution of Rhodamine B (0.5 mM) in *i*PrOH was chosen as the model. The fluorescence excitation spectrum was obtained with the detection wavelength of 581 nm (Figure 2), and the fluorescence emission spectrum was excited at 571 nm (Figure 3).



Figure 2. The fluorescence excitation spectrum of Rhodamine B.



Figure 3. The fluorescence emission spectrum of Rhodamine B excited at 571 nm.

In a typical experiment, appropriate amount of HP(O)Ph2 was added to 3 mL of solution of Rhodamine



B (0.5 mM). And the solution was added to a 1.0 cm quartz cuvette. The emission of the sample was collected (Figure 4). The solution was excited at 571 nm, and the emission intensity at 581 nm was observed (Figure 5).

Figure 4. The fluorescence emission spectra of Rhodamine B with different concentration of added HP(O)Ph₂ excited at 571 nm.



Figure 5. Rhodamine B emission quenching by HP(O)Ph₂. Linear quenching is observed.

7. Determine the configuration of phosphorus atom for 3y.

We have tried to confirm the absolute configuration of the phosphorus atoms. In our

original experiment, when (R_P)-O-(-)-menthyl H-phenylphosphinate (R_P/S_P > 99/1) was selected as starting material, only one isomer (determined by ³¹P NMR (δ = 29.0 ppm), ¹H NMR and ¹³C NMR) was detected.



Additionally, when the reaction was conducted by using mixture of O-(-)-menthyl *H*-phenylphosphinate ($\mathbf{R}_{\mathbf{P}}/\mathbf{S}_{\mathbf{P}} = 7/3$), two isomer can be obviously detected by ³¹P NMR ($\delta = 29.0$ and 29.8, the ratio is also 7/3), ¹H NMR and ¹³C NMR. Moreover, we also analysis the ratio of the residual O-(-)-menthyl *H*-phenylphosphinate, and the ratio is also $\mathbf{R}_{\mathbf{P}}/\mathbf{S}_{\mathbf{P}} = 7/3$. These result revealed that the phosphorus atom in O-(-)-menthyl *H*-phenylphosphinate is stable under the reaction condition. Then we preliminary come to the conclusion that the configuration is retention.





8. Analytical Data for All New Compounds

(2,2-diphenylvinyl)diphenylphosphine oxide (3a)



Known compound⁵. Following the general procedure, **3a** was isolated as white solid. Mp: 206-208 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.64 (m, 4H), 7.38 – 7.26 (m, 11H), 7.24 – 7.19 (m, 2H), 7.09 (ddd, J = 14.3, 7.8, 6.1 Hz, 3H), 6.78 (d, $J_{\text{H-P}} = 18.1$ Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 162.06 (d, $J_{\text{C-P}} = 2.3$ Hz), 141.98 (d, $J_{\text{C-P}} = 16.3$ Hz), 138.10 (d, $J_{\text{C-P}} = 6.7$ Hz), 134.47 (d, $J_{\text{C-P}} = 105.9$ Hz), 131.15 (d, $J_{\text{C-P}} = 2.8$ Hz), 130.95 (d, $J_{\text{C-P}} = 9.4$ Hz), 130.40 (d, J = 1.8 Hz), 129.16 (d, $J_{\text{C-P}} = 89.3$ Hz), 128.46 , 128.41 , 128.38 , 128.29 , 127.67 , 120.66 (d, $J_{\text{C-P}} = 103.7$ Hz). ³¹P NMR (162 MHz, CDCl₃) δ 19.31. IR (KBr): 3053.45, 1630.77, 1584.62, 1560.53, 1172.50, 1114.59, 1098.54, 696.44 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₆H₂₂OP 381.1408, found 381.1408.

(2,2-di-p-tolylvinyl)diphenylphosphine oxide (3b)



Following the general procedure. **3b** was isolated as white solid. Mp: 203-205 °C ¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.63 (m, 4H), 7.39 – 7.33 (m, 2H), 7.33 – 7.27 (m, 4H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.11 (dd, *J* = 8.0, 6.2 Hz, 4H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.70 (d, *J*_{H-P} = 18.5 Hz, 1H), 2.35 (s, 3H), 2.22 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 162.05, 139.29 (d, *J*_{C-P} = 16.4 Hz), 139.16 (d, *J*_{C-P} = 125.3 Hz), 135.42 (d, *J*_{C-P} = 6.9 Hz), 134.75 (d, *J*_{C-P} = 105.6 Hz), 131.04, 130.96, 130.35, 129.12, 128.38, 128.31, 128.28, 128.19, 119.01 (d, *J*_{C-P} = 104.9 Hz), 21.35 (d, *J*_{C-P} = 4.3 Hz). ³¹P NMR (162 MHz, CDCl₃) δ = 19.67. IR (KBr): 3022.34, 1610.17, 1580.64, 1553.90, 1275.39, 1181.43, 1115.01, 750.16 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₈H₂₆OP 409.1721, found 409.1730. For **3b'** the ³¹P NMR (162 MHz, CDCl₃) δ = 29.86.

(2,2-di-m-tolylvinyl)diphenylphosphine oxide (3c)



Following the general procedure, **3c** was isolated as white solid. Mp: 168-170 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (dd, J = 12.0, 6.7 Hz, 4H), 7.41 – 7.30 (m, 6H), 7.26 – 7.12 (m, 4H), 7.07 – 6.97 (m, 3H), 6.93 (d, J = 7.4 Hz, 1H), 6.77 (d, J = 18.2 Hz, 1H), 2.33 (s, 3H), 2.15 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 162.45 (d, $J_{C-P} = 2.7$ Hz), 141.95 (d, $J_{C-P} = 16.3$ Hz), 138.17, 138.11, 137.08, 134.58 (d, $J_{C-P} = 105.8$ Hz), 131.06 (d, $J_{C-P} = 2.8$ Hz), 130.42, 129.66 (d, $J_{C-P} = 264.4$ Hz), 129.55 (d, $J_{C-P} = 267.7$ Hz), 129.17 (d, $J_{C-P} = 51.1$ Hz), 127.55 (d, $J_{C-P} = 12.5$ Hz), 125.68, 120.31 (d, $J_{C-P} = 104.5$ Hz), 21.57, 21.35. ³¹P NMR (162 MHz, CDCl₃) δ 19.32. IR (KBr): 3053.93, 2975.64, 2922.81, 1589.27, 1563.49, 1275.38,

1098.33, 749.38, 560.57 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: $C_{28}H_{26}OP$ 409.1721, found 409.1729. For **3c'** the ³¹P NMR (162 MHz, CDCl₃) δ = 30.18.

(2,2-di-o-tolylvinyl)diphenylphosphine oxide (3d)



Following the general procedure. The mixture of **3d** and **3d'** was isolated by column chromatography (Petroleum ether (bp: 60-90 °C)/ethyl acetate). The pure **3d** was obtained by recrystallization with EtOAc-petroleum ether (60-90 °C) as white solid. Mp: 195-196 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (dd, J = 11.7, 7.4 Hz, 4H), 7.61 (dd, J = 7.5, 1.4 Hz, 1H), 7.37 – 7.27 (m, 6H), 7.20 – 7.16 (m, 2H), 7.13 – 7.06 (m, 3H), 7.06 – 7.00 (m, 1H), 6.67 (d, J = 7.4 Hz, 1H), 6.62 (d, J = 19.9 Hz, 1H), 2.38 (s, 3H), 1.64 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 162.40, 141.11 (d, $J_{C-P} = 16.1$ Hz), 138.17 (d, $J_{C-P} = 6.8$ Hz), 135.35, 135.04, 132.14, 131.05, 130.86, 130.46 (d, $J_{C-P} = 9.3$ Hz), 129.59 (d, $J_{C-P} = 20.4$ Hz), 128.40 (d, $J_{C-P} = 31.4$ Hz), 127.99 (d, $J_{C-P} = 11.9$ Hz), 125.63 (d, $J_{C-P} = 101.4$ Hz), 125.24 (d, $J_{C-P} = 86.7$ Hz), 21.25, 20.01.³¹P NMR (162 MHz, CDCl₃) $\delta = 17.84$. IR (KBr): 3010.68, 1582.84, 1437.11, 1275.36, 1260.64, 1187.13, 1114.89, 749.67 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₈H₂₆OP 409.1721, found 409.1726. For **3d'**: the ³¹P NMR (162 MHz, CDCl₃) $\delta = 29.96$, the ¹H NMR (401 MHz, CDCl₃) 5.02 – 4.89 (m, 1H), 2.98 (dd, J = 10.7, 7.0 Hz, 2H) was typical data. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₈H₂₈OP 411.1878, found 411.1888.

(2,2-bis(4-chlorophenyl)vinyl)diphenylphosphine oxide (3e)



Following the general procedure. The mixture of **3e** and **3e'** was isolated by column chromatography (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 1:1). The pure **3e** was obtained by recrystallization with EtOAc-petroleum ether (60-90 °C) as white solid. Mp: 185-186 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.62 (m, 4H), 7.43 (td, *J* = 7.3, 1.5 Hz, 2H), 7.39 – 7.32 (m, 4H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.25 – 7.11 (m, 4H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 17.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 159.07 (d, *J*_{C-P} = 2.4 Hz), 139.63 (d, *J*_{C-P} = 16.0 Hz), 135.89 (d, *J*_{C-P} = 6.8 Hz), 135.33 (d, *J*_{C-P} = 94.9 Hz), 133.74 (d, *J*_{C-P} = 106.4 Hz), 131.48 (d, *J*_{C-P} = 1.4 Hz), 131.28 (d, *J*_{C-P} = 2.8 Hz), 130.74 (d, *J*_{C-P} = 9.7 Hz), 129.35, 128.64, 128.38, 128.26, 127.84, 121.67 (d, *J*_{C-P} = 102.2 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 19.23. IR (KBr): 3050.10, 1679.40, 1589.99, 1549.35, 1171.31, 1115.61, 1013.49, 751.92 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₆H₂₀OPCl₂ 449.0629, found 449.0630. For **3e'**: the ³¹P NMR (162 MHz, CDCl₃) δ = 29.56. the ¹H NMR (401 MHz, CDCl₃) 4.68^{*} (dt, *J* = 11.0, 7.2 Hz, 1H), 3.02^{*} (dd, *J* = 10.9, 7.3 Hz, 2H) was typical data. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₆H₂₂Cl₂OP 451.0785, found 451.0786.

(2,2-bis(4-bromophenyl)vinyl)diphenylphosphine oxide (3f)



Following the general procedure, **3f** was isolated as white solid, Mp: 190-192 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.63 (m, 4H), 7.49 – 7.40 (m, 4H), 7.35 (td, *J* = 7.5, 2.8 Hz, 4H), 7.25 – 7.13 (m, 4H), 7.11 – 7.03 (m, 2H), 6.81 (d, *J* = 17.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 159.27, 140.16 (d, *J*_{C-P} = 16.3 Hz), 136.43 (d, *J*_{C-P} = 6.6 Hz), 133.86 (d, *J*_{C-P} = 106.3 Hz), 131.89, 131.80, 131.47, 130.98, 130.32 (d, *J*_{C-P} = 113.4 Hz), 128.57, 128.45, 124.35, 123.44, 121.93 (d, *J*_{C-P} = 102.1 Hz) ³¹P NMR (162 MHz, CDCl₃) δ 19.29. IR (KBr): 3005.76, 1589.45, 1454.25, 1275.38, 1260.64, 1115.81, 1009.88, 749.87 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₆H₂₀OPBr₂ 536.9619, found 536.9614.

(2,2-bis(4-fluorophenyl)vinyl)diphenylphosphine oxide (3g)



Following the general procedure. **3g** was isolated as white solid, Mp: 163-165 °C., ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.64 (m, 4H), 7.42 – 7.37 (m, 2H), 7.37 – 7.31 (m, 4H), 7.31 – 7.26 (m, 2H), 7.24 – 7.19 (m, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 6.78 (t, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 17.8 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 164.44 (d, *J*_{C-F} = 71.3 Hz), 161.95 (d, *J*_{C-F} = 69.8 Hz), 159.54 (d, *J*_{C-P} = 2.3 Hz), 137.69 (dd, *J* = 16.2, 3.2 Hz), 134.00 (d, *J* = 106.3 Hz), 133.78 (dd, *J* = 6.8, 3.2 Hz), 132.16 (d, *J*_{C-P} = 8.2 Hz), 131.18 (d, *J*_{C-P} = 2.5 Hz), 130.72 (d, *J*_{C-P} = 9.6 Hz), 130.03 (d, *J*_{C-P} = 8.5 Hz), 128.27 (d, *J*_{C-P} = 12.0 Hz), 120.80 (d, *J*_{C-P} = 103.0 Hz), 115.40 (d, *J*_{C-P} = 21.7 Hz), 114.59 (d, *J*_{C-P} = 21.7 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 19.21. IR (KBr): 3055.29, 1585.76, 1570.56, 1182.08, 1115.91, 1014.04, 695.50 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₆H₂₀OPF₂ 417.1220, found 417.1229.

(2-(4-bromophenyl)-2-phenylvinyl)diphenylphosphine oxide (3h)



Following the general procedure. The mixture of **3h** and **3h**' was isolated by column chromatography (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 1:1). The pure **3h** was obtained by recrystallization with EtOAc-petroleum ether (60-90 °C) as white solid. Mp: 178-180 °C. **3h-1**: ¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.62 (m, 4H), 7.47 – 7.39 (m, 2H), 7.39 – 7.28 (m, 9H), 7.15 (dd, *J* = 52.3, 7.9 Hz, 4H), 6.82 (d, *J* = 17.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 160.61, 141.30 (d, *J*_{C-P} = 15.9 Hz), 137.00 (d, *J*_{C-P} = 6.9 Hz), 134.17 (d, *J*_{C-P} = 106.0 Hz), 131.99, 131.37 (d, *J*_{C-P} = 2.0 Hz), 131.03, 130.93, 130.85, 129.88, 128.57 (d, *J*_{C-P} = 7.7 Hz), 128.35 (d, *J*_{C-P} = 13.2 Hz), 123.21, 121.36 (d, *J*_{C-P} = 102.8 Hz). **3h-2**: ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.59 (m, 4H), 7.48 – 7.43 (m, 2H), 7.41 – 7.35 (m, 2H), 7.35 – 7.29 (m, 4H), 7.23 – 7.14 (m, 5H), 7.12 – 7.06 (m, 2H), 6.77 (d, *J* = 17.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 160.57 , 140.79 (d, *J*_{C-P} = 16.4 Hz), 137.45 (d, *J*_{C-P} = 6.7 Hz), 134.10 (d, *J*_{C-P} = 106.1 Hz),

131.20 (d, $J_{C-P} = 68.4$ Hz), 131.13 (d, $J_{C-P} = 2.8$ Hz), 130.27 (d, $J_{C-P} = 100.4$ Hz), 130.21 (d, $J_{C-P} = 1.2$ Hz), 129.13 (d, $J_{C-P} = 118.7$ Hz), 128.81 , 128.27 (d, $J_{C-P} = 12.1$ Hz), 127.69 , 125.75 (d, $J_{C-P} = 366.5$ Hz), 121.14 (d, $J_{C-P} = 103.3$ Hz). ³¹P NMR (162 MHz, CDCl₃) δ 19.18. IR (KBr): 2975.69, 2927.80, 1638.59, 1483.39, 1275.20, 1179.81, 1090.40, 749.70 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₆H₂₁BrOP 459.0513, found 459.0514. For **3h**': the ³¹P NMR (162 MHz, CDCl₃) δ = 29.84^{*}. the ¹H NMR (401 MHz, CDCl₃) 4.72-4.62^{*} (m, 1H), 3.12 – 3.01^{*} (m, 2H) was typical data. HRMS^{*} (ESI/[M+H]⁺) Calcd. for: C₂₆H₂₃OPBr 461.0670, found 461.0665.

(1,1-diphenylprop-1-en-2-yl)diphenylphosphine oxide (3i)



Following the general procedure. The mixture of **3i** and **3i'** was isolated by column chromatography (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 1:1). The pure **3i** was obtained by recrystallization with EtOAc-petroleum ether (60-90 °C) as white solid. Mp: 172-174 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.56 (m, 4H), 7.38 – 7.24 (m, 9H), 7.20 – 7.08 (m, 4H), 6.95 – 6.87 (m, 3H), 1.89 (d, *J* = 13.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.70 (d, *J*_{C-P} = 8.8 Hz), 142.38 (d, *J*_{C-P} = 15.0 Hz), 140.83 (d, *J*_{C-P} = 7.6 Hz), 134.45 , 133.43 , 131.08 (d, *J*_{C-P} = 9.2 Hz), 130.73 (d, *J*_{C-P} = 2.6 Hz), 130.24 (d, *J*_{C-P} = 1.8 Hz), 128.37 (d, *J*_{C-P} = 130.4 Hz), 128.22 , 128.12 , 128.01 , 127.33 , 127.16 (d, *J*_{C-P} = 95.9 Hz), 21.51 (d, *J*_{C-P} = 12.5 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 27.75. IR (KBr): 2976.21, 2925.59, 1639.18, 1438.28, 1275.38, 1172.99, 1093.48, 750.00 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₇H₂₄OP 395.1565, found 395.1566. For **3i'**: the ³¹P NMR (162 MHz, CDCl₃) δ = 30.52^{*}. HRMS^{*} (ESI/[M+H]⁺) Calcd. for: C₂₇H₂₄OP 395.1565, found 395.1721, found 397.1730.

(1,1-diphenylbut-1-en-2-yl)diphenylphosphine oxide (3j)



Following the general procedure. The mixture of **3j** and **3j**' was isolated by column chromatography (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 1:1). The pure **3j** was obtained by recrystallization with EtOAc-petroleum ether (60-90 °C) as white solid. Mp: 217-219 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.76 – 7.60 (m, 4H), 7.37 – 7.24 (m, 9H), 7.23 – 7.07 (m, 4H), 6.95 – 6.84 (m, 3H), 2.36 (dq, *J* = 16.6, 7.3 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.91 (d, *J*_{C-P} = 9.3 Hz), 142.62 (d, *J*_{C-P} = 15.4 Hz), 140.98 (d, *J*_{C-P} = 7.7 Hz), 135.26 , 134.39 (d, *J*_{C-P} = 101.6 Hz), 134.34 , 131.18 (d, *J*_{C-P} = 9.1 Hz), 130.62 (d, *J*_{C-P} = 2.8 Hz), 129.98 , 128.34 , 128.33 , 128.01 , 127.59 (d, *J*_{C-P} = 60.2 Hz), 127.49 (d, *J*_{C-P} = 9.1 Hz), 26.42 (d, *J*_{C-P} = 11.7 Hz), 14.83 (d, *J*_{C-P} = 2.1 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 27.21. IR (KBr): 3054.91, 2975.57, 2928.15, 1639.06, 1488.58, 1275.97, 1175.97, 1094.12, 699.53 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₈H₂₆OP 409.1721, found 409.1732. For **3j**': the ³¹P NMR (162 MHz, CDCl₃) δ = 30.50^{*}, HRMS^{*} (ESI/[M+H]⁺) Calcd. for: C₂₈H₂₈OP 411.1878, found 411.1875.

(1,1-diphenylpent-1-en-2-yl)diphenylphosphine oxide (3k)



Following the general procedure. The mixture of **3k** and **3k'** was isolated by column chromatography (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 1:1). The pure **3k** was obtained by recrystallization with EtOAc-petroleum ether (60-90 °C) as white solid. Mp: 172-174 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.64 (m, 4H), 7.37 – 7.23 (m, 9H), 7.22 – 7.09 (m, 4H), 6.94 – 6.83 (m, 3H), 2.34 – 2.23 (m, 2H), 1.36 (dq, *J* = 14.8, 7.3 Hz, 2H), 0.54 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 158.52 (d, *J*_{C-P} = 9.2 Hz), 142.86 (d, *J*_{C-P} = 15.6 Hz), 141.23 (d, *J*_{C-P} = 7.9 Hz), 134.58 (d, *J*_{C-P} = 101.6 Hz), 133.54 (d, *J*_{C-P} = 92.9 Hz), 131.27 (d, *J*_{C-P} = 9.1 Hz), 130.68 (d, *J*_{C-P} = 2.9 Hz), 130.32 (d, *J*_{C-P} = 1.4 Hz), 128.71 (d, *J*_{C-P} = 0.8 Hz), 128.40 , 128.09 , 127.97 , 127.65 (d, *J*_{C-P} = 13.5 Hz), 127.39 , 35.35 (d, *J*_{C-P} = 11.6 Hz), 23.46 (d, *J*_{C-P} = 2.4 Hz), 139.1³¹P NMR (162 MHz, CDCl₃) δ 26.70. IR (KBr): 3054.42, 2974.44, 2928.66, 1437.54, 1180.97, 1095.68, 699.29 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₉H₂₈OP 423.1878, found 423.1872. For **3j'**: the ³¹P NMR (162 MHz, CDCl₃) δ = 30.50^{*}, HRMS^{*} (ESI/[M+H]⁺) Calcd. for: C₂₉H₃₀OP 425.2034, found 425.2035.

dibutyl(2,2-diphenylvinyl)phosphine oxide (31)



Following the general procedure. **31** was isolated as colorless sticky oil, ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.35 (m, 5H), 7.35 – 7.26 (m, 5H), 6.31 (d, *J* = 13.3 Hz, 1H), 1.54 – 1.40 (m, 8H), 1.28 (dq, *J* = 13.6, 6.8 Hz, 4H), 0.85 (t, *J* = 7.3 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 158.32 (d, *J*_{C-P} = 2.4 Hz), 141.57 (d, *J*_{C-P} = 15.3 Hz), 138.81 (d, *J*_{C-P} = 5.7 Hz), 129.73 (d, *J*_{C-P} = 1.3 Hz), 129.23, 128.89, 128.37, 128.18, 127.90, 120.50 (d, *J*_{C-P} = 91.5 Hz), 29.19 (d, *J*_{C-P} = 69.9 Hz), 24.12 (d, *J*_{C-P} = 15.1 Hz), 23.87 (d, *J*_{C-P} = 3.7 Hz), 13.59. ³¹P NMR (162 MHz, CDCl₃) δ 38.95. IR (KBr): 2975.07, 2928.76, 1639.25, 1444.09, 1275.37, 1260.72, 1157.76, 1090.11, 750.00 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₂H₃₀OP 341.2034, found 341.2030.

dicyclopentyl(2,2-diphenylvinyl)phosphine oxide (3m)



Following the general procedure. **3m** was isolated as white solid. Mp: 148-150 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.29 (m, 8H), 7.28 – 7.24 (m, 2H), 6.21 (d, *J* = 15.4 Hz, 1H), 1.90 – 1.75 (m, 10H), 1.68 (dqd, *J* = 10.2, 5.3, 2.2 Hz, 4H), 1.53 (tq, *J* = 7.8, 3.8 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 158.70, 142.61 (d, *J*_{C-P} = 14.5 Hz), 138.88 (d, *J*_{C-P} = 5.3 Hz), 129.84 (d, *J*_{C-P} = 1.2 Hz), 129.05, 128.57,

128.41, 127.96, 127.79, 120.27 (d, $J_{C-P} = 88.1 \text{ Hz}$), 38.80 (d, $J_{C-P} = 72.6 \text{ Hz}$), 27.54 (d, $J_{C-P} = 1.5 \text{ Hz}$), 26.71 (d, $J_{C-P} = 9.6 \text{ Hz}$), 26.45 (d, $J_{C-P} = 1.4 \text{ Hz}$), 26.29 (d, $J_{C-P} = 9.4 \text{ Hz}$). ³¹P NMR (162 MHz, CDCl₃) δ 43.62. IR (KBr): 3056.95, 2946.21, 2864.18, 1589.25, 1490.32, 1442.96, 1168.73, 1073.94, 1031.88, 755.99 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₄H₃₀OP 365.2034, found 365.2025.

dicyclohexyl(2,2-diphenylvinyl)phosphine oxide (3n)



Following the general procedure **3n** was isolated as white solid. Mp: 134-136 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.30 (m, 8H), 7.26 (dd, *J* = 7.7, 2.0 Hz, 2H), 6.00 (d, *J*_{H-P} = 19.2 Hz, 1H), 1.92 – 1.79 (m, 8H), 1.72 – 1.61 (m, 4H), 1.47 – 1.33 (m, 4H), 1.24 – 1.17 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 160.85, 142.91 (d, *J*_{C-P} = 14.5 Hz), 138.51 (d, *J*_{C-P} = 5.3 Hz), 130.03 (d, *J*_{C-P} = 1.4 Hz), 129.08, 128.42, 128.40, 127.94, 127.58, 117.36 (d, *J*_{C-P} = 84.8 Hz), 36.89 (d, *J*_{C-P} = 69.8 Hz), 26.66 (d, *J*_{C-P} = 3.0 Hz), 26.66 (d, *J*_{C-P} = 5.3 Hz), 26.25 (d, *J*_{C-P} = 2.9 Hz), 26.05 (d, *J*_{C-P} = 1.4 Hz), 25.31 (d, *J*_{C-P} = 3.0 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 42.87. IR (KBr): 3054.55, 3022.59, 2926.29, 2851.00, 1681.96, 1588.64, 1568.54, 1444.73, 1275.06, 1176.02, 763.47 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₆H₃₄OP 393.2347, found 393.2345.

(2,2-diphenylvinyl)diisopropylphosphine oxide (30)



Following the general procedure **30** was isolated as colorless sticky oil, ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.28 (m, 8H), 7.26 – 7.22 (m, 2H), 6.01 (d, *J* = 19.6 Hz, 1H), 2.01 – 1.86 (m, 2H), 1.16 (td, *J* = 15.5, 7.2 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 161.61, 143.01 (d, *J*_{C-P} = 14.5 Hz), 138.45, 130.14, 129.13, 128.52, 128.43, 127.97, 127.56, 116.72 (d, *J*_{C-P} = 84.8 Hz), 26.86 (d, *J*_{C-P} = 69.5 Hz), 16.17 (d, *J*_{C-P} = 95.9 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 47.55. IR (KBr): 3055.77, 2956.37, 2928.23, 2867.44, 1588.49, 1570.91, 1490.43, 1257.98, 1176.64, 1072.84, 695.66 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₀H₂₆OP 313.1721, found 313.1715.

(2,2-diphenylvinyl)di-p-tolylphosphine oxide (3p)



Following the general procedure. The mixture of **3p** and **3p**' was isolated by column chromatography (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 1:1). The pure **3p** was obtained by recrystallization with EtOAc-petroleum ether (60-90 °C) as white solid. Mp: 168-169 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.55 (ddt, *J* = 11.6, 8.0, 1.5 Hz, 4H), 7.36 – 7.30 (m, 5H), 7.21 (dt, *J* = 8.4, 1.6 Hz, 2H), 7.11 (tt, *J* = 8.5, 6.2 Hz, 7H), 6.75 (d, *J* = 18.0 Hz, 1H), 2.32 (s, 6H).¹³C NMR (101 MHz, CDCl₃) δ 161.35 (d, *J*_{C-P} = 2.3 Hz), 142.18 (d, *J*_{C-P} = 15.9 Hz), 141.41, 138.18 (d, *J*_{C-P} = 6.7 Hz), 131.39 (d, *J*_{C-P} = 108.3 Hz), 130.95 (d, *J*_{C-P} = 9.7 Hz), 130.36 (d, *J*_{C-P} = 1.4 Hz), 129.07 (d, *J*_{C-P} = 12.2 Hz), 128.98 (d, *J*_{C-P} = 92.5 Hz), 128.38 (d, *J*_{C-P} = 4.7 Hz), 127.57, 121.11 (d, *J*_{C-P} = 103.1 Hz), 21.59 (d, *J*_{C-P} = 1.4 Hz).³¹P NMR (162 MHz, CDCl₃) δ 19.85. IR (KBr): 2977.30, 1601.37, 1560.53, 1275.43, 1260.55, 1179.19, 1099.01, 750.13 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₈H₂₆OP 409.1721, found 409.1725. For **3p'**: the ³¹P NMR (162 MHz, CDCl₃) δ = 31.52^{*}, the ¹H NMR (401 MHz, CDCl₃) 4.17-4.07^{*} (m, 1H), 3.07^{*} (dd, *J* = 11.1, 7.1 Hz, 2H) was typical data. HRMS^{*} (ESI/[M+H]⁺) Calcd. for: C₂₈H₂₈OP 411.1878, found 411.1881.

(2,2-diphenylvinyl)bis(4-methoxyphenyl)phosphine oxide (3q)



Following the general procedure, **3q** was isolated as colorless sticky oil, ¹H NMR (400 MHz, CDCl₃) δ 7.57 (ddd, J = 11.2, 8.7, 2.0 Hz, 4H), 7.38 – 7.28 (m, 5H), 7.23 – 7.19 (m, 2H), 7.16 – 7.07 (m, 3H), 6.82 (dt, J = 8.8, 2.3 Hz, 4H), 6.75 (d, J = 17.7 Hz, 1H), 3.78 (s, 6H).¹³C NMR (101 MHz, CDCl₃) δ 161.80 (d, $J_{C-P} = 2.9$ Hz), 142.21 (d, $J_{C-P} = 15.9$ Hz), 138.16 (d, $J_{C-P} = 6.3$ Hz), 132.75 (d, $J_{C-P} = 11.0$ Hz), 130.35 (d, $J_{C-P} = 1.2$ Hz), 128.96 (d, $J_{C-P} = 87.1$ Hz), 128.31, 128.00 (d, $J_{C-P} = 79.5$ Hz), 126.01 (d, $J_{C-P} = 112.3$ Hz), 121.49 (d, $J_{C-P} = 103.9$ Hz), 113.91 (d, $J_{C-P} = 13.0$ Hz), 55.35. ³¹P NMR (162 MHz, CDCl₃) δ 19.61. IR (KBr): 3056.26, 2930.94, 2837.12, 1596.43, 1568.57, 1292.26, 1252.42, 1116.55, 802.31, 697.85 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₈H₂₆O₃P 441.1620, found 441.1624. For **3q**': the ³¹P NMR (162 MHz, CDCl₃) $\delta = 31.26^*$. HRMS^{*} (ESI/[M+H]⁺) Calcd. for: C₂₈H₂₈O₃P 443.1776, found 443.1771.

(2,2-diphenylvinyl)bis(4-fluorophenyl)phosphine oxide (3r)



Following the general procedure. The mixture of **3r** and **3r'** was isolated by column chromatography (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 1:1). The pure **3r** was obtained by recrystallization with EtOAc-petroleum ether (60-90 °C) as white solid. Mp: 165-167 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.69

- 7.59 (m, 4H), 7.32 (dddd, J = 18.2, 8.3, 6.0, 2.4 Hz, 5H), 7.22 - 7.13 (m, 3H), 7.09 (ddd, J = 8.4, 6.3, 1.6 Hz, 2H), 6.99 (tt, J = 8.7, 1.8 Hz, 4H), 6.72 (d, J = 18.2 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 165.86 (d, $J_{C-F} = 3.4$ Hz), 163.35 (d, $J_{C-F} = 3.4$ Hz), 162.59 (d, $J_{C-P} = 2.8$ Hz), 141.61 (d, $J_{C-P} = 16.5$ Hz), 137.93 (d, $J_{C-P} = 7.0$ Hz), 133.29 (dd, J = 10.8, 8.7 Hz), 130.33 (d, $J_{C-P} = 1.4$ Hz), 130.15 (dd, J = 109.1, 3.4 Hz), 129.38 (d, $J_{C-P} = 91.0$ Hz), 128.52, 128.34, 127.75, 120.09 (d, $J_{C-P} = 105.6$ Hz), 115.73 (dd, $J_{C-P} = 21.4$, 13.2 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 18.05. IR (KBr): 2956.11, 2921.82, 1591.17, 1497.30, 1275.33, 1260.55, 1184.44, 1114.32, 764.17 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₆H₂₀OPF₂ 417.1220, found 417.1218. For **3r'**: the ³¹P NMR (162 MHz, CDCl₃) δ = 28.66^{*}. HRMS^{*} (ESI/[M+H]⁺) Calcd. for: C₂₆H₂₀OPF₂ 419.1376, found 419.1374.

bis(3,5-dimethylphenyl)(2,2-diphenylvinyl)phosphine oxide (3s)



Following the general procedure. **3s** was isolated as colorless sticky oil, ¹H NMR (400 MHz, CDCl₃) δ 7.31 (t, J = 2.3 Hz, 5H), 7.26 (d, J = 12.3 Hz, 4H), 7.19 (dt, J = 8.1, 1.7 Hz, 2H), 7.10 (pd, J = 6.7, 1.8 Hz, 3H), 6.97 (s, 2H), 6.75 (d, J = 17.6 Hz, 1H), 2.25 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 161.02, 142.10 (d, $J_{C-P} = 15.8$ Hz), 138.21 (d, $J_{C-P} = 6.0$ Hz), 137.88 (d, $J_{C-P} = 12.6$ Hz), 134.14 (d, $J_{C-P} = 105.1$ Hz), 132.88 (d, $J_{C-P} = 2.3$ Hz), 130.26, 129.43, 129.28 (d, $J_{C-P} = 10.5$ Hz), 128.61 (d, $J_{C-P} = 9.4$ Hz), 128.40, 128.34, 127.43, 121.11 (d, $J_{C-P} = 102.5$ Hz), 21.34.³¹P NMR (162 MHz, CDCl₃) δ 20.28. IR (KBr): 2919.57, 2857.89, 1600.73, 1585.97, 1274.80, 1260.87, 1182.87, 750.75 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₃₀H₃₀OP 437.2034, found 437.2039. For **3s'**: the ³¹P NMR (162 MHz, CDCl₃) δ = 31.89^{*}. HRMS^{*} (ESI/[M+H]⁺) Calcd. for: C₃₀H₃₀OP 437.2034, found 437.2039. For **3s'**: the ³¹P NMR (162 MHz, CDCl₃) δ = 31.89^{*}.

bis(4-(tert-butyl)phenyl)(2,2-diphenylvinyl)phosphine oxide (3t)



Following the general procedure. The mixture of **3t** and **3t'** was isolated by column chromatography (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 1:1). The pure **3t** was obtained by recrystallization with EtOAc-petroleum ether (60-90 °C). Mp: 231-233 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.56 (m, 4H), 7.31 (td, J = 5.0, 2.1 Hz, 9H), 7.20 – 7.14 (m, 2H), 7.11 – 7.00 (m, 3H), 6.80 (d, J = 17.0 Hz, 1H), 1.27 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 161.11 (d, $J_{C-P} = 2.4$ Hz), 154.24 (d, $J_{C-P} = 2.9$ Hz), 131.69, 130.94, 130.85, 130.62, 130.39 (d, $J_{C-P} = 1.4$ Hz), 129.40, 128.43, 128.38, 128.33, 127.53, 125.26 (d, $J_{C-P} = 12.1$ Hz), 121.68 (d, $J_{C-P} = 103.5$ Hz), 34.91, 31.17. ³¹P NMR (162 MHz, CDCl₃) δ 19.30. IR (KBr): 3056.83, 2962.82, 2904.47, 2876.18, 1598.62, 1530.37, 1493.90, 1392.61, 1267.15, 1188.46, 1092.17, 1015.98, 761.44 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₃₄H₃₈OP 493.2660, found

493.2667. For **3t**²: the ³¹P NMR (162 MHz, CDCl₃) δ = 29.53^{*}, the ¹H NMR (401 MHz, CDCl₃) 4.75 – 4.66^{*} (m, 1H), 3.06^{*} (dd, *J* = 11.0, 7.2 Hz, 2H) was typical data. HRMS^{*} (ESI/[M+H]⁺) Calcd. for: C₃₄H₄₀OP 495.2817, found 495.2821.

(2,2-diphenylvinyl)bis(2-methoxyphenyl)phosphine oxide (3u)



Following the general procedure, **3u** was isolated as colorless sticky oil, ¹H NMR (400 MHz, CDCl₃) δ 7.44 (dd, J = 14.0, 7.6 Hz, 2H), 7.36 (t, J = 7.9 Hz, 2H), 7.29 (p, J = 3.0 Hz, 5H), 7.18 (dt, J = 8.1, 1.9 Hz, 2H), 7.13 – 7.02 (m, 4H), 6.84 (dt, J = 21.6, 7.1 Hz, 4H), 3.73 (s, 6H).¹³C NMR (101 MHz, CDCl₃) δ 160.62, 157.40 (d, $J_{C-P} = 2.4$ Hz), 143.32 (d, $J_{C-P} = 17.8$ Hz), 138.54 (d, $J_{C-P} = 7.2$ Hz), 134.29 (d, $J_{C-P} = 7.7$ Hz), 133.08 (d, $J_{C-P} = 2.0$ Hz), 130.20, 128.67, 128.34, 128.24, 128.11, 123.10, 122.01, 121.52 (d, $J_{C-P} = 108.5$ Hz), 120.54 (d, $J_{C-P} = 12.0$ Hz), 110.82 (d, $J_{C-P} = 6.6$ Hz), 55.69. ³¹P NMR (162 MHz, CDCl₃) δ 18.59. IR (KBr): 3058.06, 2936.70, 2836.18, 1589.06, 1477.34, 1275.81, 1179.94, 1073.89, 756.06 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₈H₂₆O₃P 441.1620, found 441.1611. For **3u'**: the ³¹P NMR (162 MHz, CDCl₃) $\delta = 25.87^*$, HRMS^{*} (ESI/[M+H]⁺) Calcd. for: C₂₈H₂₈O₃P 443.1776, found 443.1779.

(2,2-diphenylvinyl)di(naphthalen-2-yl)phosphine oxide (3v)



Following the general procedure **3v** was isolated as colorless sticky oil, ¹H NMR (400 MHz, CDCl₃) δ 8.32 (d, J = 13.7 Hz, 2H), 7.86 – 7.80 (m, 2H), 7.79 – 7.74 (m, 4H), 7.70 (ddt, J = 10.0, 8.4, 1.7 Hz, 2H), 7.55 – 7.45 (m, 4H), 7.35 (qt, J = 7.8, 2.0 Hz, 5H), 7.24 (dt, J = 7.2, 1.9 Hz, 2H), 7.01 – 6.88 (m, 4H).¹³C NMR (101 MHz, CDCl₃) δ 162.23 (d, $J_{C-P} = 2.4$ Hz), 141.89 (d, $J_{C-P} = 16.1$ Hz), 138.00 (d, $J_{C-P} = 6.7$ Hz), 134.41 (d, $J_{C-P} = 2.4$ Hz), 133.06 (d, $J_{C-P} = 8.6$ Hz), 132.66, 131.50 (d, $J_{C-P} = 106.4$ Hz), 130.30 (d, $J_{C-P} = 1.4$ Hz), 129.69, 128.90, 128.71, 128.51, 128.42, 128.24 (d, $J_{C-P} = 11.7$ Hz), 127.91, 127.78, 127.48, 126.75, 125.98 (d, $J_{C-P} = 10.6$ Hz), 120.36 (d, $J_{C-P} = 104.3$ Hz).³¹P NMR (162 MHz, CDCl₃) δ 19.73. IR (KBr): 3053.53, 2925.86, 2853.05, 1675.23, 1587.34, 1490.97, 1342.31, 1272.96, 1180.26, 1086.15, 1029.71, 750.13 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₃₄H₂₆OP 481.1721, found 481.1726. For **3v**': the ³¹P NMR (162 MHz, CDCl₃) $\delta = 30.93^*$, HRMS^{*} (ESI/[M+H]⁺) Calcd. for: C₃₄H₂₈OP 483.1878, found 483.1873.

(2,2-diphenylvinyl)di(naphthalen-1-yl)phosphine oxide (3w)



Following the general procedure, **3w** was isolated as colorless sticky oil, ¹H NMR (400 MHz, CDCl3) δ 8.63 – 8.50 (m, 2H), 7.90 – 7.81 (m, 4H), 7.76 (dd, J = 15.5, 7.1 Hz, 2H), 7.46 (dd, J = 6.4, 3.2 Hz, 4H), 7.32 – 7.17 (m, 7H), 7.11 (d, J = 19.2 Hz, 1H), 6.97 (ddd, J = 9.3, 6.4, 2.2 Hz, 1H), 6.86 (d, J = 7.3 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 160.48 (d, $J_{C-P} = 2.7$ Hz), 142.17 (d, $J_{C-P} = 16.4$ Hz), 137.87 (d, $J_{C-P} = 6.8$ Hz), 133.99 (d, $J_{C-P} = 10.5$ Hz), 133.84 (d, $J_{C-P} = 9.2$ Hz), 133.22 (d, $J_{C-P} = 8.6$ Hz), 132.77 (d, $J_{C-P} = 2.9$ Hz), 129.72 (d, $J_{C-P} = 1.4$ Hz), 129.43 (d, $J_{C-P} = 104.1$ Hz), 129.33, 129.04 (d, $J_{C-P} = 1.6$ Hz), 128.39, 128.32, 127.52 (d, $J_{C-P} = 5.2$ Hz), 127.09, 127.03, 126.21, 124.80 (d, $J_{C-P} = 14.0$ Hz), 122.16 (d, $J_{C-P} = 102.6$ Hz). ³¹P NMR (162 MHz, CDCl₃) δ 23.39. IR (KBr): 3055.33, 2926.68, 2853.53, 2359.68, 1675.57, 1618.71, 1587.83, 1505.82, 1264.68, 1175.95, 1076.46, 773.42 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₃₄H₂₆OP 481.1721, found 481.1723. For **3w**': the ³¹P NMR (162 MHz, CDCl₃) $\delta = 32.76^*$, HRMS^{*} (ESI/[M+H]⁺) Calcd. for: C₃₄H₂₆OP 481.1721, found 481.1723. For **3w**': the ³¹P NMR (162 MHz, CDCl₃) $\delta = 32.76^*$, HRMS^{*} (ESI/[M+H]⁺) Calcd. for: C₃₄H₂₆OP 481.1721, found 481.1723. For **3w**': the ³¹P NMR (162 MHz, CDCl₃) $\delta = 32.76^*$, HRMS^{*} (ESI/[M+H]⁺) Calcd. for: C₃₄H₂₆OP 481.1721, found 481.1723. For **3w**': the ³¹P NMR (162 MHz, CDCl₃) $\delta = 32.76^*$, HRMS^{*} (ESI/[M+H]⁺) Calcd. for: C₃₄H₂₆OP 481.1721, found 481.1723. For **3w**': the ³¹P NMR (162 MHz, CDCl₃) $\delta = 32.76^*$, HRMS^{*} (ESI/[M+H]⁺) Calcd. for: C₃₄H₂₈OP 483.1878, found 483.1874.

6-(2,2-diphenylvinyl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (3x)



Following the general procedure. **3x** was isolated as colorless sticky oil, ¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.47 (m, 4H), 7.35 – 7.22 (m, 5H), 7.22 – 7.16 (m, 2H), 7.16 – 7.11 (m, 2H), 7.11 – 7.07 (m, 2H), 7.07 – 7.02 (m, 2H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.52 (d, *J* = 15.8 Hz, 1H).¹³C NMR (101 MHz, CDCl₃) δ 161.68 (d, *J*_{C-P} = 5.5 Hz), 149.09 (d, *J*_{C-P} = 7.9 Hz), 140.83 (d, *J*_{C-P} = 19.3 Hz), 137.95 (d, *J*_{C-P} = 7.6 Hz), 135.49 (d, *J*_{C-P} = 6.8 Hz), 132.65 (d, *J*_{C-P} = 2.5 Hz), 130.65 (d, *J*_{C-P} = 10.7 Hz), 130.08 (d, *J*_{C-P} = 42.6 Hz), 129.68, 128.60, 128.44, 128.19, 128.14, 128.01, 127.87, 125.93 (d, *J*_{C-P} = 129.9 Hz), 124.62 (d, *J*_{C-P} = 54.6 Hz), 123.39 (d, *J*_{C-P} = 9.8 Hz), 122.51 (d, *J*_{C-P} = 11.6 Hz), 120.49 (d, *J*_{C-P} = 6.6 Hz), 117.83 (d, *J*_{C-P} = 140.9 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 23.71. IR (KBr): 3058.08, 2924.24, 16781.46, 1583.66, 1489.18, 1476.04, 1236.55, 1203.62, 1079.54, 1029.98, 755.75 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₆H₂₀O₂P 395.1201, found 395.1205.

2-isopropyl-5-methylcyclohexyl (2,2-diphenylvinyl)(phenyl)phosphinate (3y)



Following the general procedure, 3y was isolated as colorless sticky oil, ¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.39 (m, 2H), 7.32 – 7.24 (m, 6H), 7.19 – 7.12 (m, 3H), 7.12 – 7.02 (m, 4H), 6.56 (d, *J* = 11.0 Hz, 1H), 4.26 – 4.16 (m, 1H), 2.38 – 2.27 (m, 1H), 1.69 – 1.53 (m, 3H), 1.40 – 1.30 (m, 1H), 1.27 – 1.17 (m, 1H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.93 (s, 1H), 0.91 – 0.85 (m, 4H), 0.79 (t, *J* = 12.1 Hz, 1H), 0.70 (d, *J* = 6.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 159.77 (d, *J*_{C-P} = 8.0 Hz), 141.60 (d, *J* _{C-P} = 19.1 Hz), 138.27 (d, *J*_{C-P} = 7.1 Hz), 133.86 (d, *J*_{C-P} = 134.8 Hz), 131.44 (d, *J*_{C-P} = 10.5 Hz), 131.13 (d, *J*_{C-P} = 2.9 Hz), 130.08, 129.29, 128.34, 128.20, 128.05, 127.72, 127.58, 120.96 (d, *J*_{C-P} = 143.1 Hz), 76.21 (d, *J*_{C-P} = 6.7 Hz), 48.97 (d, *J*_{C-P} = 5.6 Hz), 43.21, 34.18, 31.51, 25.83, 22.99, 22.02, 21.34, 1600. ³¹P NMR (162 MHz, CDCl₃) δ 28.95. IR (KBr): 2924.68, 1605.74, 1444.44, 1384.60, 1275.30, 1260.41, 1220.88, 1076.54, 1009.53, 750.83 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₃₀H₃₆O₂P 459.2453, found 459.2455.

2-isopropyl-5-methylcyclohexyl (2,2-diphenylvinyl)(mesityl)phosphinate (3z)



Following the general procedure, **3aa** was isolated as colorless sticky oil, ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.27 (m, 3H), 7.25 (d, *J* = 1.4 Hz, 2H), 7.10 – 7.05 (m, 1H), 7.04 – 6.96 (m, 4H), 6.64 – 6.51 (m, 3H), 4.30 – 4.20 (m, 1H), 2.38 (s, 6H), 2.15 (s, 3H), 1.63 (d, *J* = 15.7 Hz, 4H), 1.25 (d, *J* = 7.1 Hz, 5H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 5.5 Hz, 3H), 0.70 (d, *J* = 6.6 Hz, 3H).¹³C NMR (101 MHz, CDCl₃) δ 156.40 (d, *J*_{C-P} = 8.8 Hz), 142.79 (d, *J*_{C-P} = 12.0 Hz), 141.58 (d, *J*_{C-P} = 18.6 Hz), 140.69 (d, *J*_{C-P} = 2.9 Hz), 138.17 (d, *J*_{C-P} = 7.6 Hz), 130.19 (d, *J*_{C-P} = 13.5 Hz), 129.14 (d, *J*_{C-P} = 1.7 Hz), 129.02, 128.36, 127.79, 127.74, 127.45, 126.88 (d, *J*_{C-P} = 129.5 Hz), 123.86 (d, *J*_{C-P} = 1.4 Hz), 75.65 (d, *J*_{C-P} = 6.3 Hz), 48.99 (d, *J*_{C-P} = 5.8 Hz), 42.53, 34.26, 31.51, 25.92, 23.53 (d, *J*_{C-P} = 3.4 Hz), 23.05, 22.12, 21.35, 21.03 (d, *J*_{C-P} = 1.4 Hz), 16.08. ³¹P NMR (162 MHz, CDCl₃) δ 31.54. IR (KBr): 2953.49, 2924.64, 2853.26, 1683.06, 1605.62, 1444.25, 1275.27, 1181.24, 1076.32, 753.61 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₃₃H₄₂O₂P 501.2922, found 501.2923.

2-isopropyl-5-methylcyclohexyl benzyl(2,2-diphenylvinyl)phosphinate (3aa)



Following the general procedure, **3z** was isolated as colorless sticky oil, ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.38 (m, 3H), 7.37 – 7.34 (m, 3H), 7.33 – 7.31 (m, 1H), 7.31 – 7.27 (m, 1H), 7.25 – 7.23 (m, 1H), 7.23 – 7.20 (m, 1H), 7.20 – 7.18 (m, 2H), 7.18 – 7.16 (m, 1H), 7.13 – 7.09 (m, 2H), 6.14 (d, $J_{H-P} = 12.0$ Hz, 1H), 4.22 – 4.12 (m, 1H), 2.91 – 2.68 (m, 2H), 2.08 – 1.97 (m, 1H), 1.88 – 1.80 (m, 1H), 1.66 – 1.56 (m, 2H), 1.38 – 1.26 (m, 3H), 1.00 – 0.90 (m, 2H), 0.89 (d, J = 7.0 Hz, 3H), 0.80 (d, J = 6.5 Hz, 3H), 0.76 (d, J = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 159.22 (d, $J_{C-P} = 6.2$ Hz), 141.99 (d, $J_{C-P} = 18.4$ Hz), 138.54 (d, $J_{C-P} = 5.8$ Hz), 132.16 (d, $J_{C-P} = 8.2$ Hz), 130.19 (d, $J_{C-P} = 1.5$ Hz), 130.13, 130.07, 129.14, 128.81, 128.27, 128.14 (d, $J_{C-P} = 2.9$ Hz), 128.06, 127.83, 119.56 (d, $J_{C-P} = 128.2$ Hz), 76.60 (d, $J_{C-P} = 7.7$ Hz), 48.64 (d, $J_{C-P} = 5.8$ Hz), 43.55, 38.50 (d, $J_{C-P} = 93.9$ Hz), 34.02, 31.43, 25.64, 22.75, 21.88, 21.15, 15.71. ³¹P NMR (162 MHz, CDCl₃) δ 37.50. IR (KBr): 2953.43, 2924.86, 2867.28, 1588.65, 1493.75, 1275.27, 1011.39, 764.92 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₃₁H₃₈O₂P 473.2609, found 473.2611.

(2,2-diphenylvinyl)diphenylphosphane (4)



Known compound⁶. Following the general procedure, **4** was isolated as white solid, Mp: 121-123 °C, ¹H NMR (400 MHz,CDCl₃) δ 7.42 (tt, J = 7.3, 2.0 Hz, 4H), 7.33 – 7.28 (m, 7H), 7.28 – 7.23 (m, 7H), 7.22 – 7.18 (m, 2H), 6.86 (d, J = 3.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 157.00 (d, $J_{C-P} = 25.6$ Hz), 142.67 (d, $J_{C-P} = 7.3$ Hz), 140.51 (d, $J_{C-P} = 10.6$ Hz), 140.31 (d, $J_{C-P} = 6.8$ Hz), 133.05, 132.86, 130.38 (d, $J_{C-P} = 3.9$ Hz), 128.70 (d, $J_{C-P} = 6.6$ Hz), 128.52, 128.44, 128.28, 128.24, 128.07, 127.71 (d, $J_{C-P} = 11.1$ Hz). ³¹P NMR (162 MHz, CDCl₃) δ -23.57. IR (KBr): 3059.48, 3042.09, 3011.69, 1955.03, 1883.03, 1812.23, 1582.80, 1441.42, 1272.05, 1180.01, 1075.38, 696.98 cm⁻¹. HRMS (ESI/[M+H]⁺) Calcd. for: C₂₆H₂₂P 365.1459, found 365.1456.

9. References

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10. NMR Spectra for New Compounds



















 $^{\rm 31}{\rm P}$ NMR of crude reaction mixture before isolation (3e and 3e')















 $^{\rm 31}{\rm P}$ NMR of crude reaction mixture before isolation (3h and 3h')









 $^{\rm 31}{\rm P}$ NMR of crude reaction mixture before isolation (3i and 3i')







 ^{31}P NMR of crude reaction mixture before isolation (3j and 3j')







³¹P NMR before recrystallization (3k and 3k')



















 $^{\rm 31}{\rm P}$ NMR before recrystallization (3p and 3p')









 $^{\rm 31}{\rm P}$ NMR before recrystallization (3r and 3r')









 $^{\rm 31}{\rm P}$ NMR before recrystallization (3t and 3t')

























