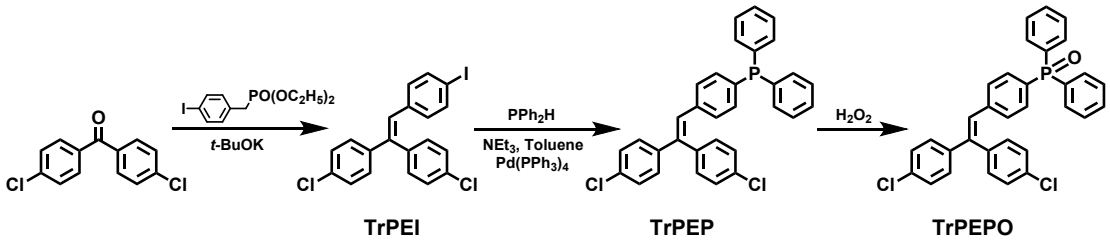
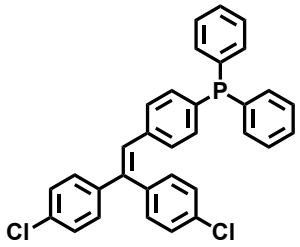
Supporting Information

1 Synthetic details

The synthetic procedures and the synthetic details for TrPEP and TrPEPO are listed in scheme S1. Bis(4-chlorophenyl)methanone was purchased from Sigma–Aldrich Chemical Co.. Diethyl (4-iodobenzyl)phosphonate, *t*-BuOK, diphenylphosphine, $Pd(PPh_3)_4$ and K_2CO_3 were purchased from Aladdin Chemical Co.. All chemicals were of analytical grade and used as received. Compound TrPEI was synthesized according to previous reports.[1] All these final compounds are conformed by ^1H NMR spectroscopy, high-resolution EI mass spectroscopy and elemental analysis and all solvents were distilled and purified according to the standard procedures before use.



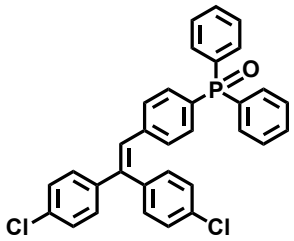
Scheme S1 Synthetic routes for compounds TrPEP and TrPEPO.



(4-(2,2-bis(4-chlorophenyl)vinyl)phenyl)diphenylphosphane (TrPEP)

Diphenylphosphine in hexane solution (1.0 M, 2.1 mL) was added in a dropwise manner to a mixture of TrPEI (902.0 mg, 2.0 mmol), $Pd(PPh_3)_4$ (69.2 mg, 0.06 mmol) and Et_3N (12 mL) in degassed toluene (50 mL) under an argon atmosphere. The resulting mixture was further refluxed and stirred for 12 hours. After filtration, the filtrate was poured into water and extracted with CH_2Cl_2. Further purification was carried out by chromatography on silica gel with CH_2Cl_2–hexane (1:3, v/v) as eluent.

Yield: 842.6 mg (82.7%). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 6.91 (s, 1H), 6.99 (d, 7.0 Hz, 2H), 7.08 (d, 7.6 Hz, 2H), 7.18 (d, 8.4 Hz, 2H), 7.20 (d, 8.5 Hz, 2H), 7.27–7.34 (m, 14H); High Resolution EI–MS: m/z found: 508.0914 $[M]^+$; calcd for $C_{32}H_{23}Cl_2P$: 508.0907. Anal. calcd for $C_{32}H_{23}Cl_2P$: C 75.44, H 4.55; found: C 75.71, H 4.54.



(4-(2,2-bis(4-chlorophenyl)vinyl)phenyl)diphenylphosphine oxide (TrPEPO)

To the TrPEP (509.0 mg 1.0 mmol) in 20 ml THF, 0.1 ml H_2O_2 aqueous (30 wt%) solution was added in a dropwise manner. After stirring for 5 minutes at room temperature, the mixture was poured into 100 ml water and extracted with CH_2Cl_2. Further purification was carried out by chromatography on silica gel with ethyl acetate–hexane (2:1, v/v) as eluent. Yield: 479.5 mg (91.3%). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 6.94 (s, 1H), 7.08-7.11 (m, 4H), 7.21 (d, 8.5 Hz, 2H), 7.28-7.31 (m, 4H), 7.42-7.47 (m, 6H), 7.53–7.55 (m, 2H), 7.62–7.66 (m, 4H); High solution EI–MS: m/z found: 524.0856 $[M]^+$; calcd for $C_{32}H_{23}Cl_2OP$: 524.0864 Elemental analyses (%) calcd for $C_{32}H_{23}Cl_2OP$: C 73.15, H 4.41; found: C 72.92, H 4.32.

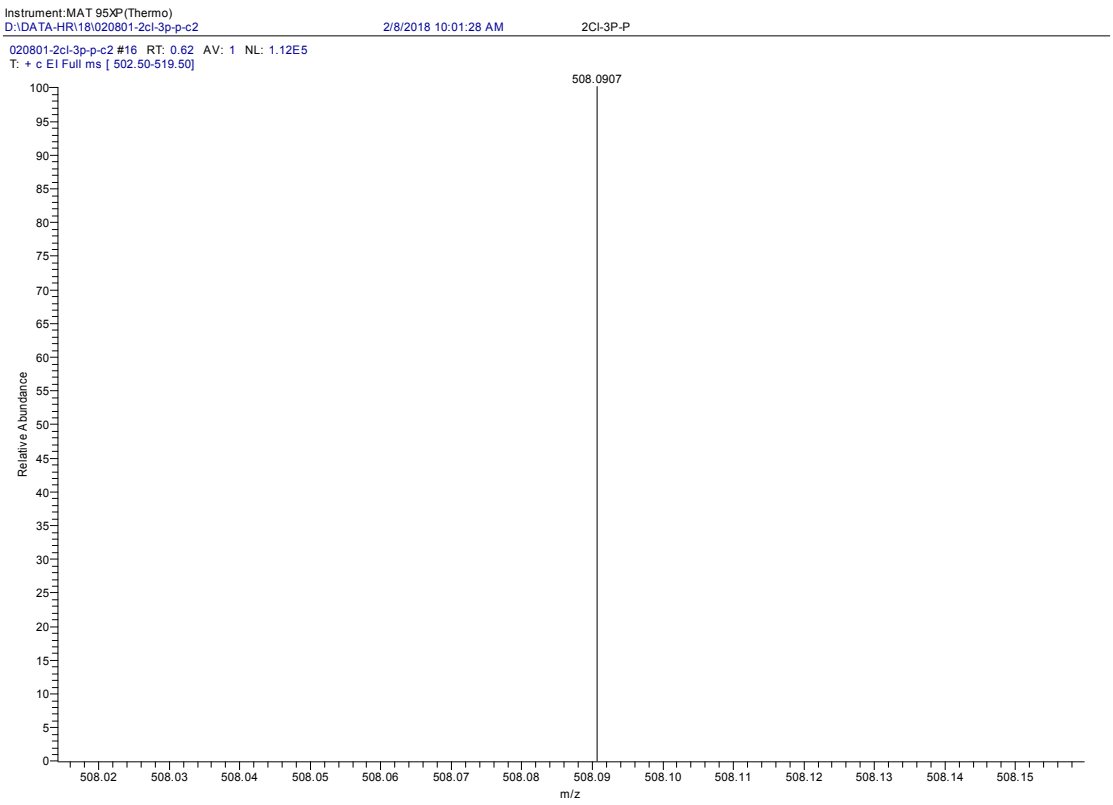


Figure S1 High Resolution EI mass spectrum of compound TrPEP.

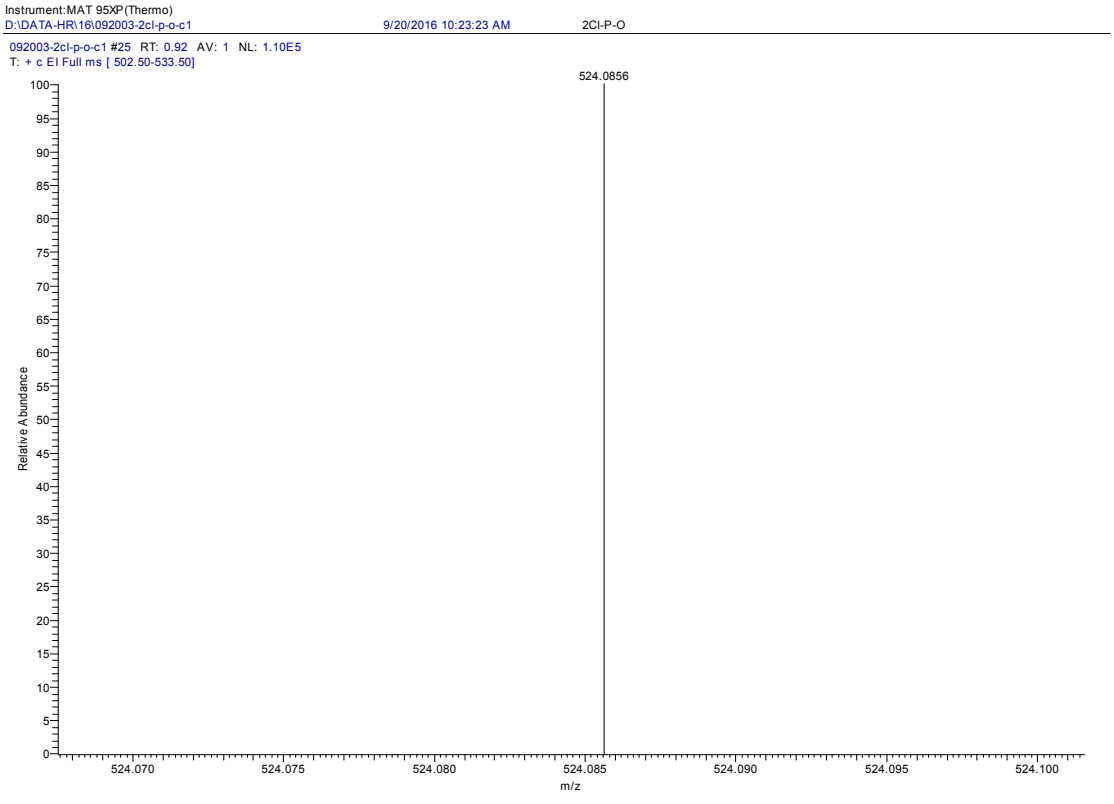


Figure S2 High Resolution EI mass spectrum of compound TrPEPO.

2 Physical measurements and instrumentations

^{1}H NMR spectra for TrPEP and TrPEPO were obtained on a Bruker AVANCE 600 Nuclear Magnetic Resonance Spectrometer with chemical shifts recorded relative to tetramethylsilane (TMS). Single-crystal X-ray data for TrPEP and TrPEPO was determined on an Oxford Diffraction Germini S Ultra X-ray Single Crystal Diffractometer using a (Cu) X-ray source. Positive ion EI mass spectra were achieved on a Thermo MAT95XP high resolution mass spectrometer. The elemental analyses were performed with a Vario EL analyzer. UV-vis absorption spectra were achieved on an Ocean Optics Maya2000PRO spectrometer with Ocean Optics reflection probes R600-125F. For the photochromic cycle in solution state, UV and white light sources are Ocean Optics LLS-365-LED (365 nm, typical output power: 1.1 mW) and Ocean Optics DH2000-BAL Halogen Light Source (typical output power: 615 μW) respectively. Steady state fluorescence spectra measured with a Horiba Scientific Fluorolog-3 spectrofluorometer. Luminescent quantum yields were performed on the Horiba Scientific Fluorolog-3 spectrofluorometer with a Horiba Scientific Quanta-φ calibrated integrating sphere. TD-DFT Calculations were performed at B3LYP/6-31G* level with Gaussian 09 software package based on their single-crystal structures. The time-dependent density functional theory (TD-DFT) method at the same level to compute the low-energy singlet–singlet transitions for the compounds.

3 Luminescent quantum yields and ^{1}H NMR spectra

Table S1 Luminescent quantum yields for TrPEP in THF/water mixed solvent system and for TrPEPO in ethanol/water mixed solvent system

TrPEP in mixed solvent systems	**Luminescent quantum**	**TrPEPO in mixed solvent systems**	**Luminescent quantum**
Water Fraction % (v/v)	**yield**	**Water Fraction % (v/v)**	**yield**
90	18.1%	90	29.3%
80	3.5%	80	22.9%
70	0.7%	70	17.5%

60	0	60	4.7%
50	0	50	1.8%
40	0	40	0.2%
30	0	30	0
20	0	20	0
10	0	10	0
0	0	0	0

Table S2 Luminescent quantum yields for TrPEP and TrPEPO in solid states

Sample	Maximum emission wavelength /nm	Luminescent quantum yield
TrPEP	500	91.3%
TrPEPO	455	77.4%

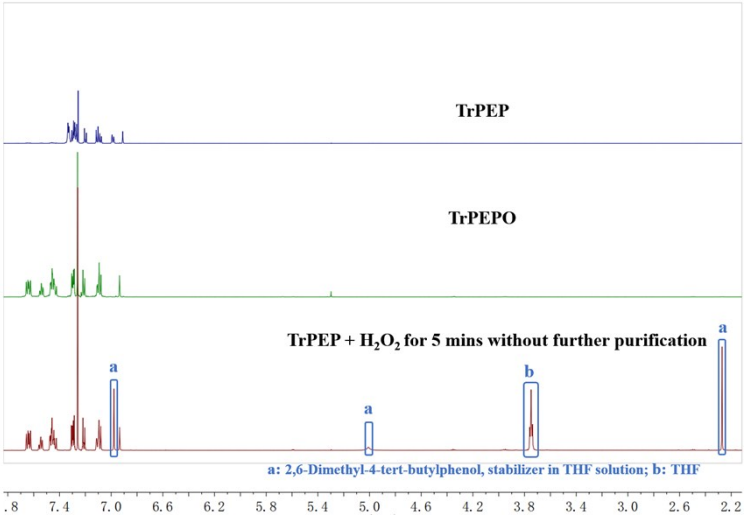


Figure S3 ^{1}H NMR spectra for pure TrPEP, pure TrPEPO and oxidation products of TrPEP mixed with equimolar H_2O_2 for 5 minutes.

4. Single crystal data of TrPEP and TrPEPO

Single-crystal X-ray analyses for compounds TrPEP and TrPEPO were carried out with an Oxford Diffraction Gemini S Ultra X-ray single-crystal diffractometer using graphite-monochromatized Cu-Kα radiation (λ = 1.54184 Å). The single crystal structures for these two compounds were solved with Olex2 v1.2 program and

expanded using Fourier techniques. In addition, non-H atoms of these compounds were further refined with anisotropic thermal parameters. The hydrogen atoms were added in idealized positions and refined with fixed geometry according to their carrier atoms.

Crystal data for TrPEP; $C_{32}H_{23}Cl_2P$, Formula Weight = 509.37 g/mol, monoclinic, space group $P2_1/c$, T = 296.80(10) K, Z = 4, a = 13.4074(4) Å, b = 11.4312(3) Å, c = 18.1544(5) Å, α = 90 °, β = 110.539(3) °, γ = 90 °, V = 2605.52(13) $Å^3$, ρ_c = 1.299 g cm^{-3}, $\mu(Cu_{K\alpha})$ = 2.956 mm^{-1}, F(000) = 1056.0 . Reflections collected 7481, Independent reflections 3800 (R_{int} = 0.0263). R_1 = 0.0426 (I ＞ 2σ(I)) and wR_2 = 0.1157, GOF =1.092.

Table S3. Bond distances (Å) for TrPEP

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P01	C00A	1.835(2)	C00B	C00L	1.386(3)
P01	C00B	1.836(2)	C00D	C00G	1.381(3)
P01	C00M	1.831(2)	C00E	C00H	1.377(3)
Cl02	C00F	1.741(2)	C00F	C00H	1.382(3)
Cl03	C00O	1.745(2)	C00F	C00J	1.374(3)
C004	C006	1.388(3)	C00I	C00P	1.383(3)
C004	C008	1.487(3)	C00K	C00O	1.368(4)
C004	C00E	1.388(3)	C00L	C00N	1.378(3)
C005	C008	1.490(3)	C00M	C00S	1.383(4)
C005	C009	1.393(3)	C00M	C00T	1.383(3)
C005	C00I	1.390(3)	C00O	C00P	1.370(4)
C006	C00J	1.381(3)	C00Q	C00U	1.385(4)
C007	C00C	1.473(3)	C00R	C00Z	1.386(4)
C007	C00D	1.400(3)	C00S	C00W	1.385(4)
C007	C00N	1.387(3)	C00T	C00X	1.382(4)
C008	C00C	1.346(3)	C00U	C00Y	1.375(4)
C009	C00K	1.382(3)	C00V	C00W	1.367(4)
C00A	C00Q	1.391(3)	C00V	C00X	1.370(4)
C00A	C00R	1.389(3)	C00Y	C00Z	1.363(4)
C00B	C00G	1.391(3)			

Table S4. Bond angles for TrPEP

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C00A	P01	C00B	102.04(10)	C00J	C00F	Cl02	119.78(18)
C00M	P01	C00A	101.55(10)	C00J	C00F	C00H	121.2(2)
C00M	P01	C00B	103.34(10)	C00D	C00G	C00B	121.61(19)
C006	C004	C008	120.55(19)	C00E	C00H	C00F	119.1(2)
C00E	C004	C006	118.3(2)	C00P	C00I	C005	121.3(2)
C00E	C004	C008	121.12(19)	C00F	C00J	C006	119.1(2)
C009	C005	C008	120.6(2)	C00O	C00K	C009	119.1(2)
C00I	C005	C008	121.91(19)	C00N	C00L	C00B	121.2(2)
C00I	C005	C009	117.5(2)	C00S	C00M	P01	125.38(17)
C00J	C006	C004	121.2(2)	C00T	C00M	P01	117.48(19)
C00D	C007	C00C	125.04(19)	C00T	C00M	C00S	117.1(2)
C00N	C007	C00C	118.36(19)	C00L	C00N	C007	122.1(2)
C00N	C007	C00D	116.59(19)	C00K	C00O	Cl03	118.88(19)
C004	C008	C005	116.08(17)	C00K	C00O	C00P	121.3(2)
C00C	C008	C004	123.57(18)	C00P	C00O	Cl03	119.9(2)
C00C	C008	C005	120.32(19)	C00O	C00P	C00I	119.3(2)
C00K	C009	C005	121.5(2)	C00U	C00Q	C00A	120.5(2)
C00Q	C00A	P01	124.35(18)	C00Z	C00R	C00A	120.7(3)
C00R	C00A	P01	117.46(19)	C00M	C00S	C00W	121.2(2)
C00R	C00A	C00Q	118.2(2)	C00X	C00T	C00M	121.8(3)
C00G	C00B	P01	118.97(16)	C00Y	C00U	C00Q	120.2(3)
C00L	C00B	P01	123.61(17)	C00W	C00V	C00X	119.6(3)
C00L	C00B	C00G	117.20(19)	C00V	C00W	C00S	120.3(3)
C008	C00C	C007	130.0(2)	C00V	C00X	C00T	119.8(3)
C00G	C00D	C007	121.13(19)	C00Z	C00Y	C00U	119.9(3)
C00H	C00E	C004	121.2(2)	C00Y	C00Z	C00R	120.5(3)
C00H	C00F	Cl02	119.06(19)				

Crystal data for TrPEPO; $C_{32}H_{23}Cl_2OP$, Formula Weight = 525.37 g/mol, monoclinic, space group Pc, T = 293(2) K, Z = 4, a = 27.1771(4) Å, b = 9.16128(15) Å, c = 10.88636(13) Å, $\alpha = 90^{o}$, $\beta = 98.5848(13)^{o}$, $\gamma = 90^{o}$, V = 2680.08(7) $Å^3$, $\rho_c = 1.302$ g cm^{-3}, $\mu(Cu_{K\alpha}) = 2.919$ mm^{-1}, F(000) = 1088.0 . Reflections collected 9425, Independent reflections 4731 ($R_{int} = 0.0211$). $R_1 = 0.0351$ ($I > 2\sigma(I)$) and $wR_2 = 0.0974$, GOF =1.051.

Table S5. Bond distances (Å) for TrPEPO

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P2	C45	1.787(7)	C27	C28	1.420(11)
P2	C33	1.796(8)	C19	C20	1.339(10)
P2	O2	1.474(5)	C20	C21	1.487(10)
P2	C39	1.799(7)	C62	C61	1.389(14)
P1	O1	1.496(5)	C62	C63	1.284(16)
P1	C7	1.801(7)	C62	Cl3	1.753(9)
P1	C1	1.813(6)	C14	C13	1.348(9)
P1	C13	1.822(7)	C14	C15	1.381(10)
C46	C45	1.401(9)	C51	C52	1.346(10)
C46	C47	1.374(9)	C30	C31	1.382(12)
C45	C50	1.425(9)	C30	C29	1.359(12)
C7	C12	1.394(11)	C30	Cl2	1.723(8)
C7	C8	1.308(11)	C10	C11	1.395(15)
C2	C3	1.355(12)	C10	C9	1.253(15)
C2	C1	1.344(10)	C37	C36	1.443(14)
C47	C48	1.435(10)	C37	C38	1.348(12)
C49	C48	1.335(10)	C13	C18	1.384(9)
C49	C50	1.371(11)	C25	C26	1.399(12)
C32	C27	1.390(11)	C25	C24	1.427(16)
C32	C31	1.363(12)	C36	C35	1.311(13)
C54	C53	1.356(10)	C28	C29	1.354(11)
C54	C55	1.419(10)	C33	C38	1.441(10)
C3	C4	1.373(13)	C33	C34	1.360(12)
C12	C11	1.419(12)	C26	C21	1.384(11)
C6	C1	1.376(10)	C21	C22	1.346(12)
C6	C5	1.371(11)	C58	C57	1.410(12)
C17	C16	1.361(10)	C56	C57	1.359(11)
C17	C18	1.398(9)	C56	Cl4	1.759(7)
C59	C60	1.429(13)	C35	C34	1.357(11)
C59	C52	1.484(11)	C24	Cl1	1.722(10)
C59	C64	1.390(11)	C24	C23	1.337(16)
C60	C61	1.416(13)	C5	C4	1.388(13)
C16	C19	1.482(9)	C63	C64	1.365(13)
C16	C15	1.443(9)	C22	C23	1.377(13)
C53	C52	1.497(10)	C44	C39	1.427(9)
C53	C58	1.376(11)	C44	C43	1.423(11)
C8	C9	1.411(13)	C39	C40	1.387(9)

C48	C51	1.464(10)	C40	C41	1.394(11)
C55	C56	1.381(11)	C43	C42	1.362(12)
C27	C20	1.482(10)	C41	C42	1.366(12)

Table S6. Bond angles for TrPEPO

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C45	P2	C33	107.4(3)	C63	C62	Cl3	121.0(9)
C45	P2	C39	105.5(3)	C13	C14	C15	123.5(6)
C33	P2	C39	105.0(3)	C52	C51	C48	128.5(7)
O2	P2	C45	112.0(3)	C31	C30	Cl2	121.2(7)
O2	P2	C33	114.7(3)	C29	C30	C31	118.8(8)
O2	P2	C39	111.6(3)	C29	C30	Cl2	120.0(6)
O1	P1	C7	111.7(3)	C9	C10	C11	119.6(8)
O1	P1	C1	111.9(3)	C38	C37	C36	118.4(9)
O1	P1	C13	110.8(3)	C32	C31	C30	122.1(8)
C7	P1	C1	107.9(3)	C14	C13	P1	117.3(5)
C7	P1	C13	107.5(3)	C14	C13	C18	120.4(6)
C1	P1	C13	106.8(3)	C18	C13	P1	122.2(5)
C47	C46	C45	122.9(6)	C26	C25	C24	115.7(9)
C46	C45	P2	126.5(5)	C35	C36	C37	119.6(8)
C46	C45	C50	117.1(6)	C62	C61	C60	122.9(9)
C50	C45	P2	116.4(5)	C29	C28	C27	122.0(7)
C12	C7	P1	120.9(6)	C38	C33	P2	117.7(6)
C8	C7	P1	120.1(6)	C34	C33	P2	125.2(6)
C8	C7	C12	118.8(8)	C34	C33	C38	117.0(8)
C1	C2	C3	123.4(7)	C21	C26	C25	123.2(10)
C46	C47	C48	118.5(6)	C37	C38	C33	120.7(9)
C48	C49	C50	124.8(6)	C59	C52	C53	117.6(6)
C31	C32	C27	119.9(8)	C51	C52	C59	123.7(6)
C53	C54	C55	121.0(8)	C51	C52	C53	118.7(7)
C2	C3	C4	118.3(8)	C26	C21	C20	120.4(8)
C7	C12	C11	118.2(8)	C22	C21	C20	124.0(7)
C5	C6	C1	120.0(8)	C22	C21	C26	115.5(8)
C2	C1	P1	119.7(5)	C53	C58	C57	122.3(7)
C2	C1	C6	118.6(6)	C14	C15	C16	117.3(6)
C6	C1	P1	121.7(5)	C55	C56	Cl4	118.7(6)
C16	C17	C18	124.0(6)	C57	C56	C55	123.1(7)
C60	C59	C52	118.3(7)	C57	C56	Cl4	118.2(6)

C64	C59	C60	120.0(8)	C28	C29	C30	120.1(7)
C64	C59	C52	121.6(7)	C36	C35	C34	121.6(9)
C61	C60	C59	114.8(9)	C25	C24	Cl1	119.9(10)
C17	C16	C19	121.9(6)	C23	C24	C25	122.3(9)
C17	C16	C15	117.5(6)	C23	C24	Cl1	117.8(10)
C15	C16	C19	120.3(6)	C10	C11	C12	119.4(8)
C54	C53	C52	120.1(7)	C6	C5	C4	119.8(8)
C54	C53	C58	118.4(7)	C10	C9	C8	122.1(9)
C58	C53	C52	121.3(7)	C3	C4	C5	119.6(7)
C7	C8	C9	121.5(9)	C62	C63	C64	124.5(10)
C47	C48	C51	117.1(6)	C63	C64	C59	119.2(9)
C49	C48	C47	118.1(6)	C56	C57	C58	116.8(7)
C49	C48	C51	124.7(6)	C13	C18	C17	117.1(6)
C49	C50	C45	118.6(6)	C21	C22	C23	125.6(9)
C56	C55	C54	117.6(8)	C35	C34	C33	122.1(9)
C32	C27	C20	121.4(7)	C43	C44	C39	117.0(7)
C32	C27	C28	116.7(7)	C44	C39	P2	116.4(5)
C28	C27	C20	121.7(6)	C40	C39	P2	124.4(5)
C20	C19	C16	130.2(7)	C40	C39	C44	119.2(6)
C27	C20	C21	116.6(6)	C39	C40	C41	121.2(8)
C19	C20	C27	119.6(6)	C24	C23	C22	117.1(10)
C19	C20	C21	123.8(6)	C42	C43	C44	122.0(7)
C61	C62	Cl3	120.5(9)	C42	C41	C40	120.1(9)
C63	C62	C61	118.4(9)	C43	C42	C41	120.3(7)

Reference:

[1] D. Ou, T. Yu, Z. Yang, T. Luan, Z. Mao, Y. Zhang, S. Liu, J. Xu, Z. Chi, M. R. Bryce, *Chem. Sci.*, **2016**, *7*(8), 5302.