Supporting Information

Divergent synthesis of oxaphospholenes and phosphacoumarines *via* the reaction of 2-alkenylphenols with PCl_3 or PCl_5

D.A. Tatarinov,[a,b] E.A. Mikulenkova,[a,b] I.A. Litvinov,[a] Kh. R. Khayarov[b] and V.F. Mironov[a]

[a]*Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, Arbuzov Str. 8, Kazan, 420088, Russian Federation*

[b]*Institute of Chemistry, Kazan Federal University, Kremlevskaya Str. 18, Kazan, 420008, Russian Federation*

Correspondence to: datint@iopc.ru, datint@mail.ru

Table of Contents

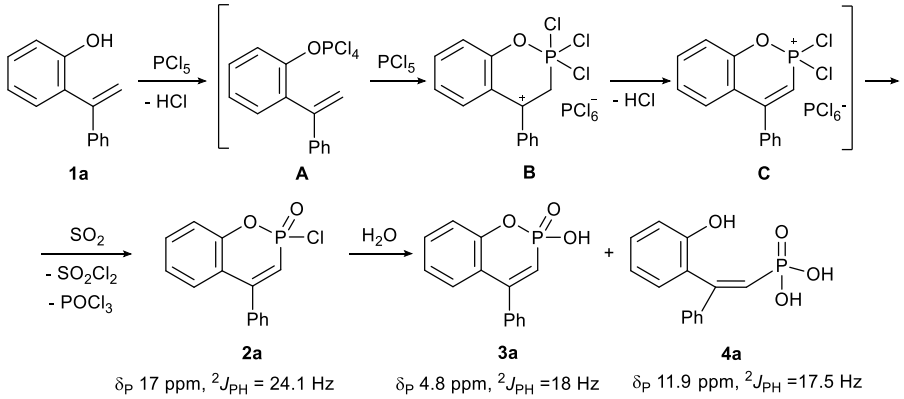
1. General information

Commercially available reagents were used. Commercially available solvents were purified by standard procedures. All reactions were run under an argon atmosphere unless performed in aqueous solutions. Column chromatography was performed using silica gel (70-230 mesh).
NMR experiments were carried out on 400 MHz [400.1 MHz (^{1}H), 100.6 MHz (^{13}C)], 600 MHz [600.1 MHz (^{1}H), 150.9 MHz (^{13}C)] spectrometers. Chemical shifts are reported on the δ (ppm) scale relative to the residual ^{1}H and ^{13}C signal of $CDCl_3$, DMSO-d_6 or MeOH-d_4 Coupling constants (*J*) are reported in Hertz and refer to apparent peak multiplications. The abbreviations s, d, t, q, and m stand for singlet, doublet, triplet, quartet, and multiplet in that order. The ESI MS measurements were performed using an AmazonX ion trap mass spectrometer (Bruker Daltonic GmbH, Germany) in the positive or negative mode in the mass range of 70–3000. MALDI mass spectra were recorded in a positive or negative ion mode on a Bruker Ultraflex III TOF/TOF mass spectrometer for 10-3 mg/mL solutions in EtOH. IR spectra were recorded for thin films or KBr pellets. The elemental analysis was carried out on a CHNS analyzer EuroEA3028-HT-OM (Eurovector SpA, Italy). The samples were weighed on Sartorius CP2P (Germany) microbalances in tin capsules. Callidus 4.1 software was used to perform quantitative measurements and evaluate the data received.

2. Additional experimental details.

2.1. The reaction of 2-alkenylphenol 1a with phosphorus pentachloride

The reaction of 2-alkenylphenol **1a** and phosphorus pentachloride probably involves initial phosphorylation of the phenolic hydroxyl followed by ring-closure via intermediates **A** and **B** to dichlorophosphonium hexachlorophosphate **C**. Hydrolysis of the reaction mixture after a sulfur dioxide treatment resulted in the cyclic phosphonic acid **3a**.[1]



Scheme S1. Proposed pathway for reaction of 2-alkenylphenols with phosphorus pentachloride with formation of phosphacoumarins.

Additionally, a signal with a chemical shift of 12.6 ppm was observed in the ^{31}P NMR spectra of the reaction mixture (Fig. S1 ESI). Upon analysis of the ^{1}H NMR spectra (Fig S2 ESI) of the reaction mixture, it was identified as the acyclic phosphonate **4a** but was not isolated. Phosphonate **4a** could be formed through hydrolysis with ring-opening from compound **3a** in the same manner as described previously. [2]

Figure S1. ^{31}P-{^{1}H} (**A**) and ^{31}P NMR (**B**) spectra for the reaction mixture of compound **1a** with PCl_5 after hydrolysis.

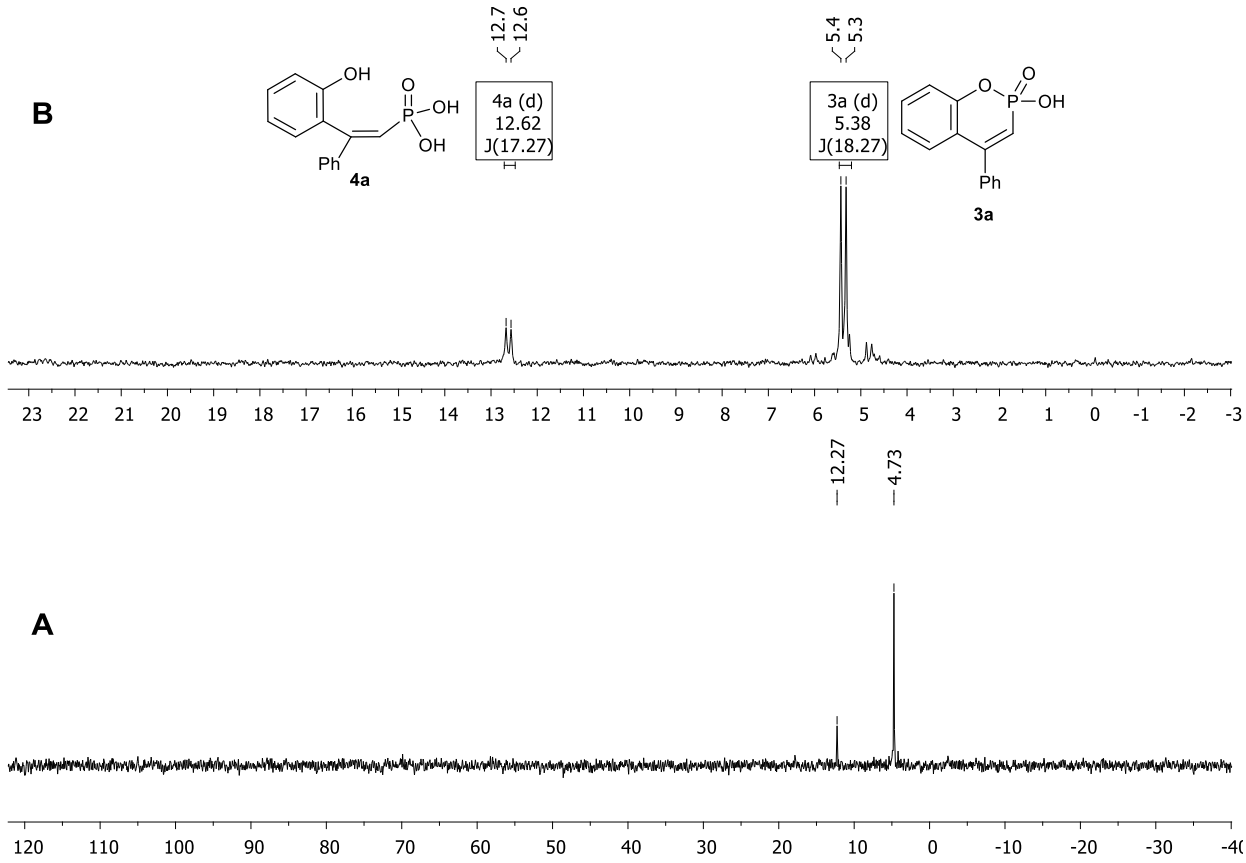


Figure S2. ^{1}H NMR spectra for the reaction mixture of compound **1a** with PCl_5 after hydrolysis.

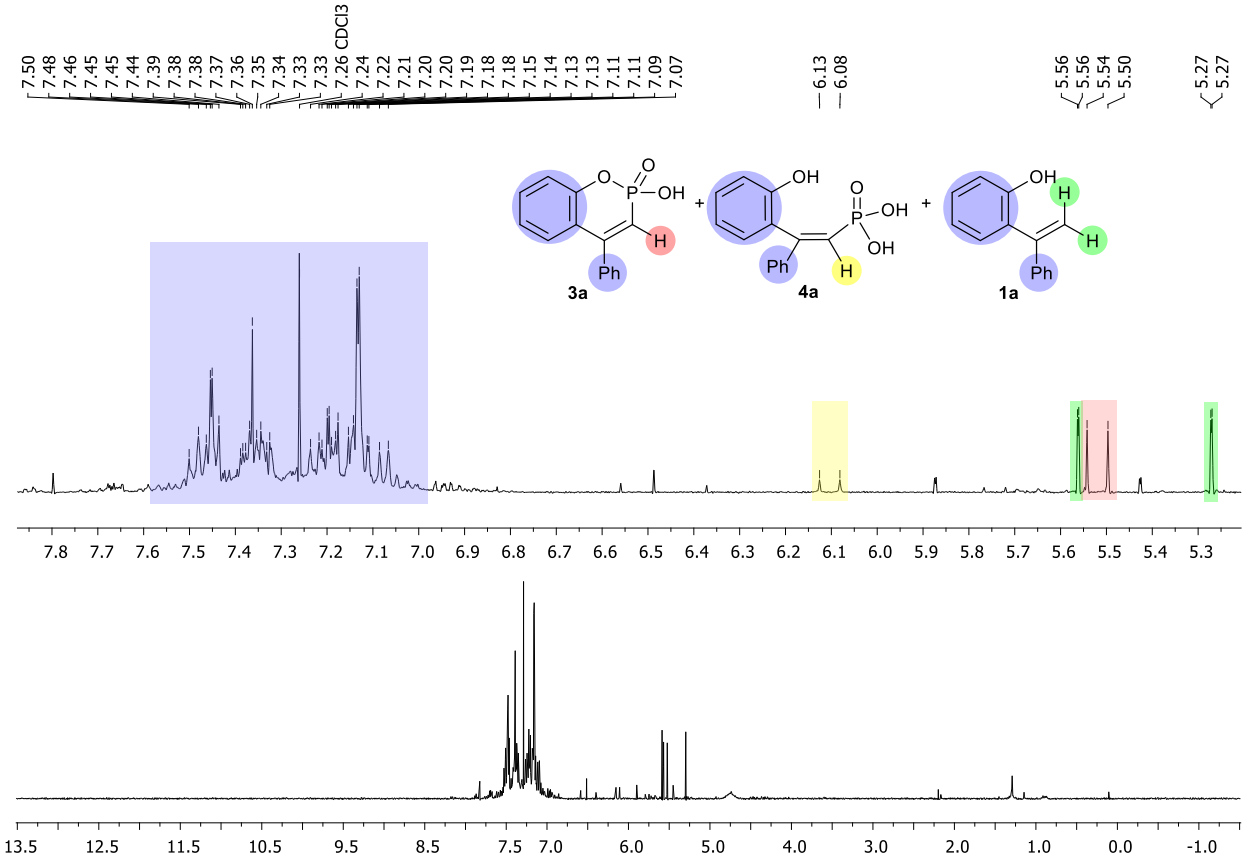


Table S1. Optimization of conditions for reaction of **1a** with phosphorus pentachloride.

Entry	Reagent ratio [a]			Reaction conditions		Conversion of 3a % [b]
	1a	PCl_5 (**x** equiv.)	Py (**y** equiv.)	T, °C	Time, h	
1	1	2	–	10 → 23	10	40
2	1	1	–	60	10	35
3	1	1	1	10 → 23	1	37
4	1	1	2	10 → 23	1	45
5	1	1	2	10 → 23	10	40
6	1	2	2	10 → 23	2	60

[a] Reaction conditions: **1a** (0.5 mmol) in benzene (5 ml) was added to phosphorus pentachloride (**x** equiv.) and pyridine (**y** equiv.) in benzene (5 ml) and stirred under argon atmosphere for the time and at the temperature indicated in the table. [b] Determined on the basis of integral intensities of the signals in the ^{31}P NMR spectra for the reaction mixtures.

2.2. The reaction of 2-alkenylphenol 1a with phosphorus trihloride

Figure S3. ^{31}P-{^{1}H} and ^{31}P NMR spectra for the reaction mixture of 2-alkenylphenol **1a** with an excess of PCl_3.

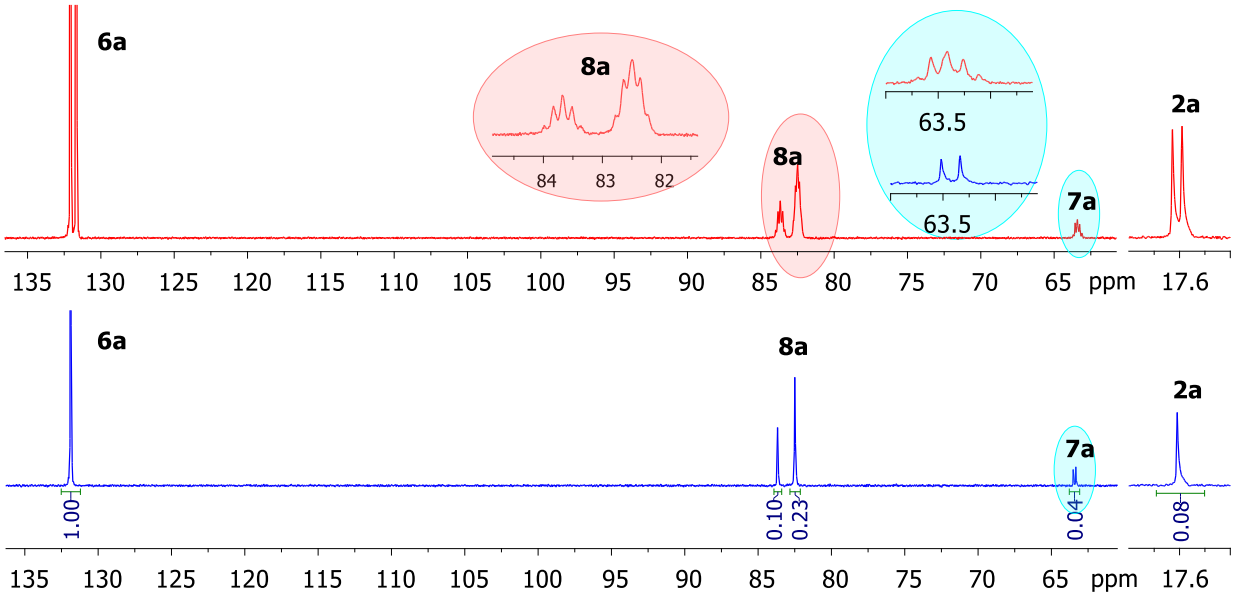
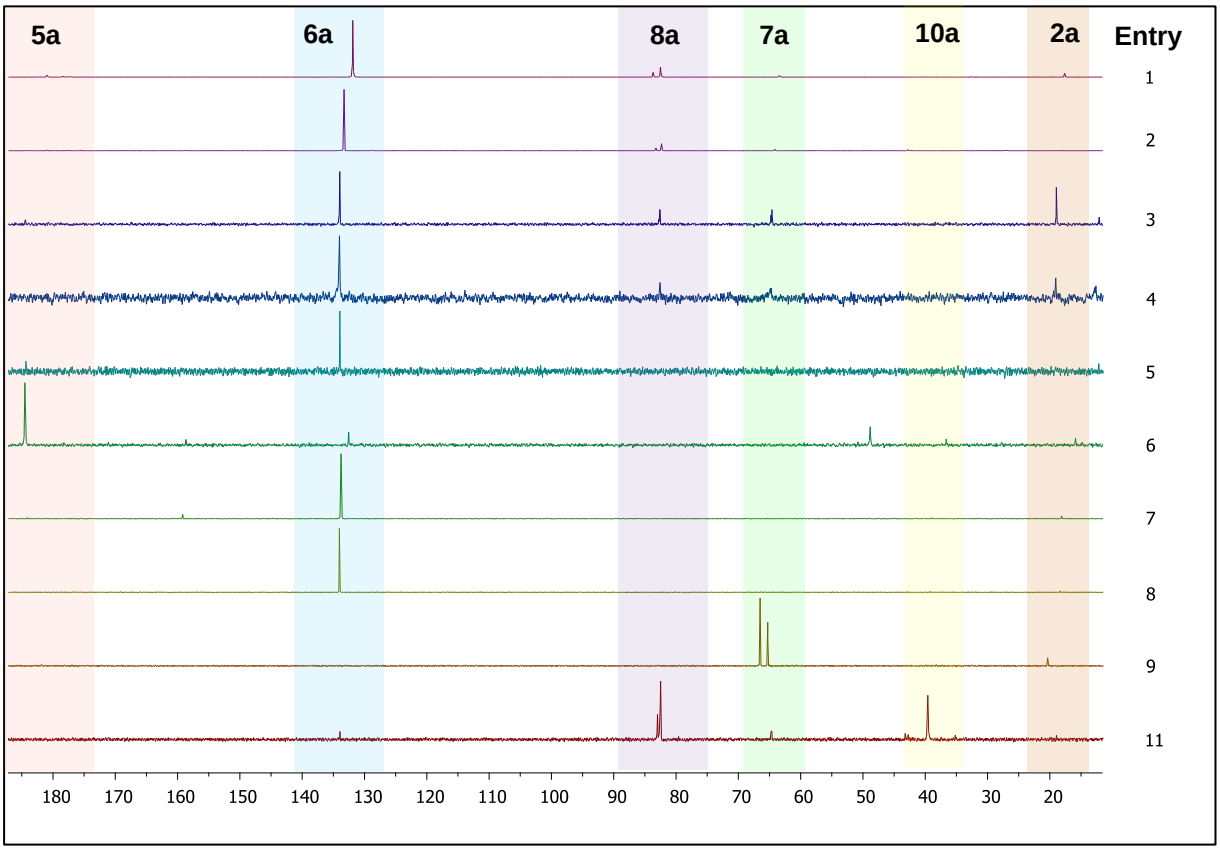


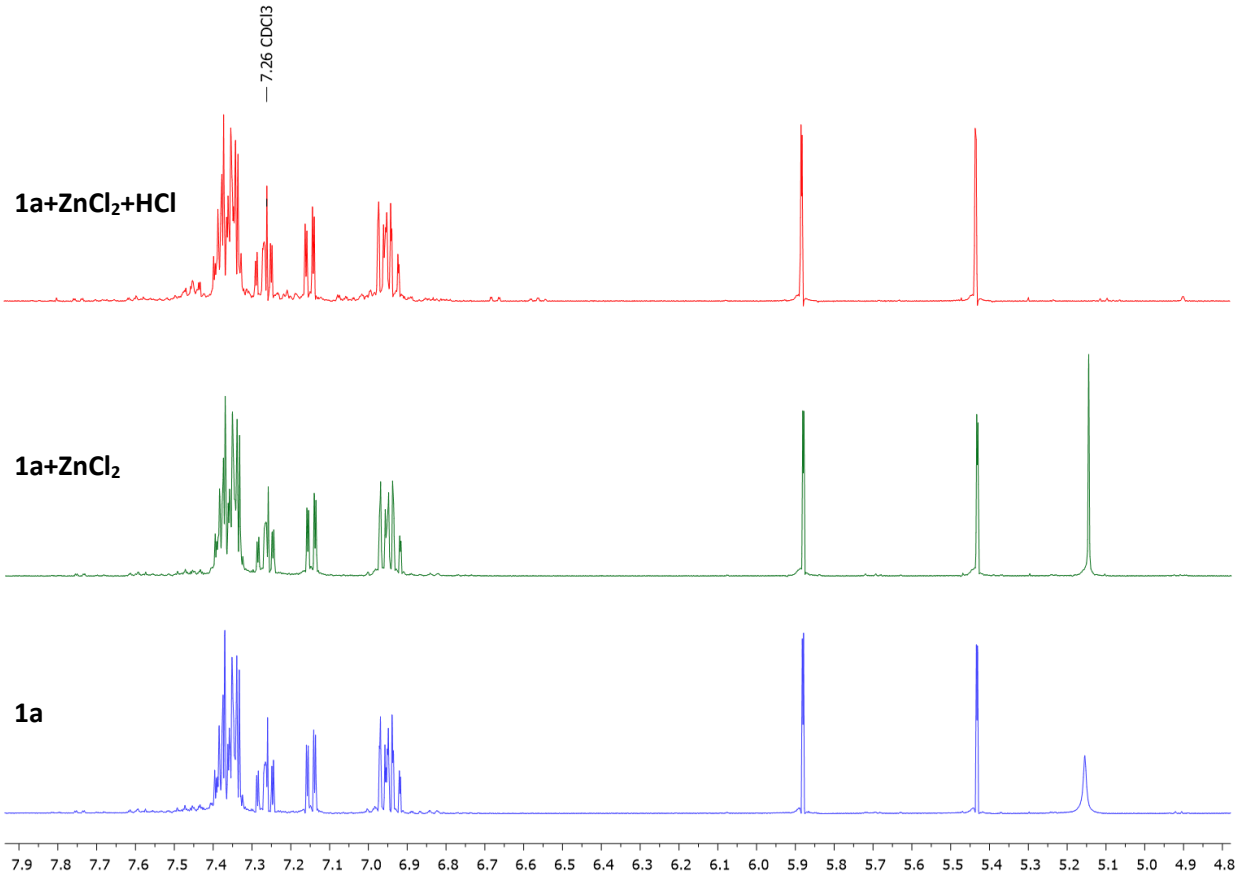
Figure S4. Stack of ^{31}P NMR spectra of the reaction of **1a** with PCl_3 at different conditions.



2.3. The interaction of 2-alkenylphenol 1a with $ZnCl_2$

Alkenes are known to form π-complexes in the reaction with Lewis acids.[3] The interaction of 2-alkenylphenol **1a** with zinc chloride was studied by ^{1}H NMR. No significant changes in chemical shifts or coupling constant of both protons at the double bond and aromatic fragment could be detected (Fig. S5). Zinc chloride can be assumed to form a complex with hydrogen chloride and thereby prevent its removal from the reaction medium.

Figure S5. ^{1}H NMR spectra monitoring of interaction of 2-alkenylphenol **1a** with $ZnCl_2$



2.4. The reaction of 1a with ethyl dichlorophosphite in the presence of $ZnCl_2$

Figure S6a. ^{31}P-{^{1}H} spectra for the reaction mixture of **1a** with ethyl dichlorophosphite in the presence of $ZnCl_2$.

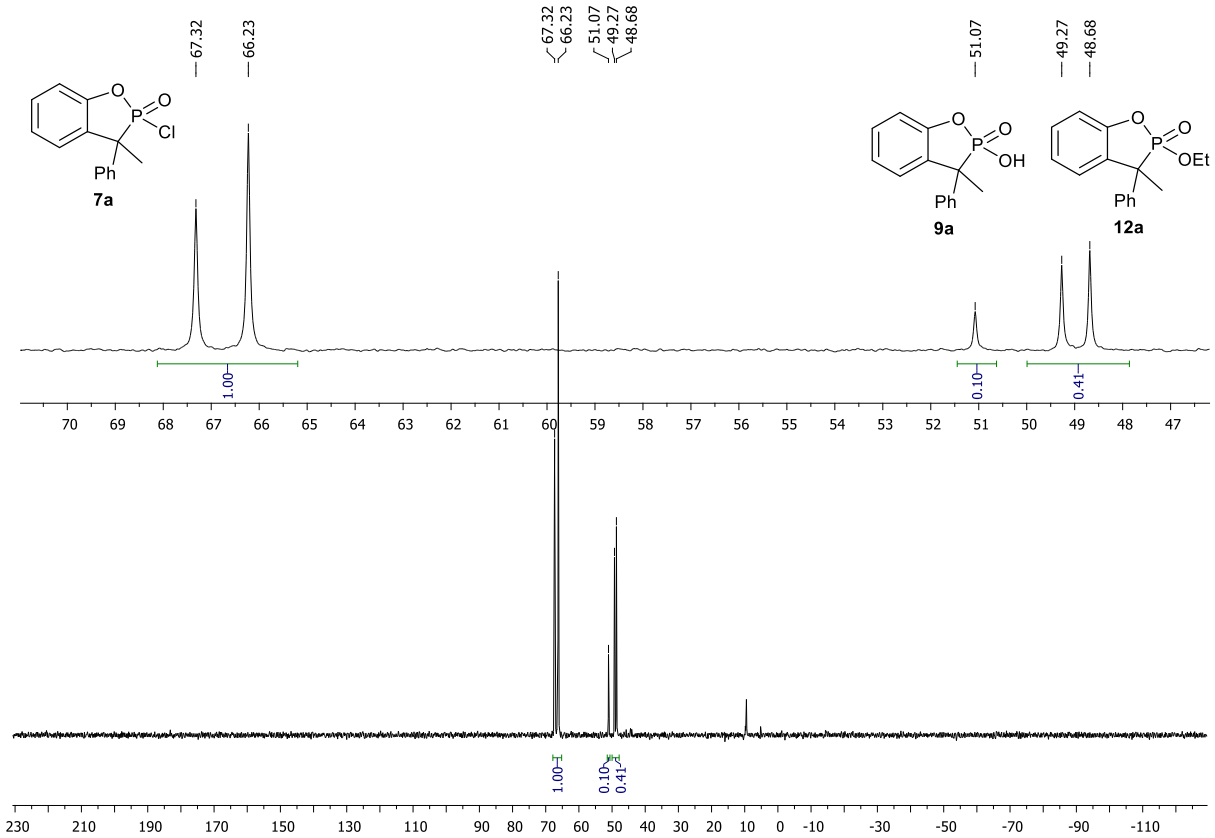
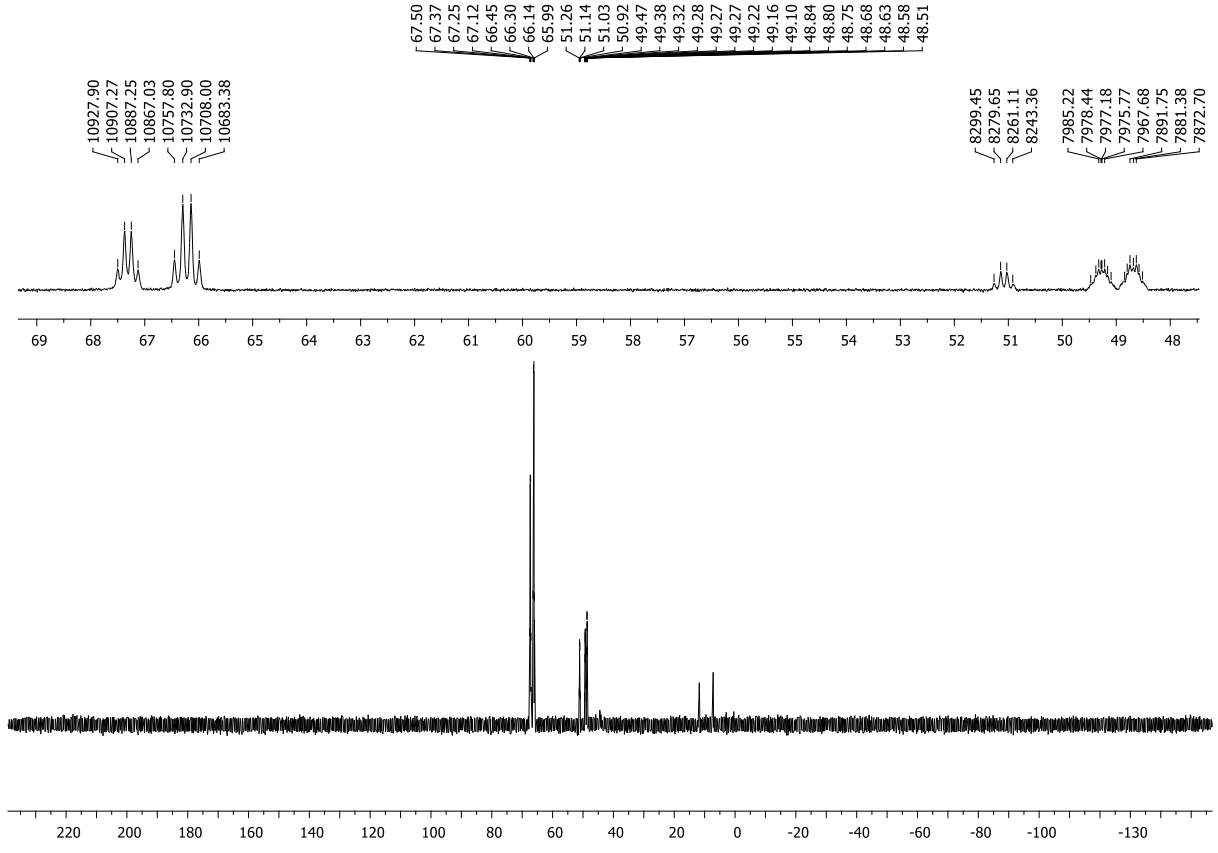
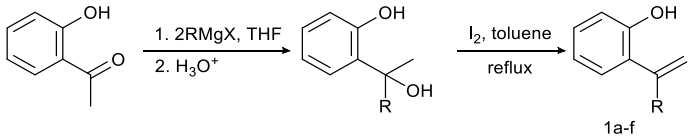


Figure S6b. ^{31}P NMR spectra for the reaction mixture of **1a** with ethyl dichlorophosphite in the presence of $ZnCl_2$.



3. Experimental section

General procedure for synthesis of substrates 1a-h:



R=Ph(**1a**), 4-MeC_6H_4(**1b**), 4-MeOC_6H_4(**1c**), 4-ClC_6H_4(**1d**), 2-MeC_6H_4(**1e**), Me(**1f**)

Compounds **1a-h** were synthesized by a similar procedure to that reported in the previous literature.[4] To a magnesium turning 0.528 g (22 mmol) in anhydrous THF (30 ml) was added dropwise a solution of appropriate aryl halides (22 mmol) to keep a gentle reflux. 2-Hydroxyacetophenone (14.7 mmol) was added to the resulting solution at 0 ºC. The solution was warmed to reflux temperature and stirred for 12 h. The reaction mixture was cooled to 0 °C and then 5 ml 15% AcOH aq. was added. The aqueous layer was separated by a separating funnel and extracted with CH_2Cl_2 (3×20mL). The organic layer was collected, dried over Na_2SO_4, and the solvents were removed on rotary evaporator. The obtained residue was dissolved in toluene (10 mL), and then 10.0 mg I_2 was added. The mixture was stirred at reflux temperature for 12 h. The reaction mixture was cooled to room temperature, washed with aq. $Na_2S_2O_3$ and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by silica gel flash column chromatography (hexane/ethyl acetate = 10:1 to 4:1) to afford the products **1a-f**.

2-(1-Phenylvinyl)phenol (1a): Yellow liquid (88%, 2.54 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 5H), 7.34 – 7.28(m, 1H), 7.20 (dd, *J* = 7.6, *J* = 1.7 Hz, 1H), 7.03 – 6.95 (m, 2H), 5.92 (d, *J* = 1.2 Hz, 1H), 5.47 (d, *J* = 1.1 Hz, 1H), 4.93 (br.s, 1H).

2-[1-(4-Methoxyphenyl)vinyl]phenol (1b): Yellow liquid (85%, 2.82 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.30 – 7.26 (m, 1H), 7.17 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.99 – 6.94 (m, 2H), 6.91 – 6.87 (m, 2H), 5.80 (d, *J* = 1.0 Hz, 1H), 5.34 (d, *J* = 1.0 Hz, 1H), 3.84 (s, 3H).

2-[1-(4-Methylphenyl)vinyl]phenol (1c): Yellow liquid (80%, 2.45 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 3H), 7.21 – 7.17 (m, 3H), 7.01 – 6.94 (m, 2H), 5.86 (s, 1H), 5.40 (s, 1H), 2.40 (s, 3H).

2-[1-(2-Methylphenyl)vinyl]phenol (1d): White liquid. Yields 70% (2.16 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.31 – 7.24 (m, 3H), 7.23 – 7.19 (m, 2H), 7.07 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.92 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.88 (td, *J* = 7.6, 1.2 Hz, 1H), 5.68 (d, *J* = 1.6 Hz, 1H), 5.53 (d, *J* = 1.6 Hz, 1H), 5.49 (br.s, 1H).

2-[1-(4-Chlorophenyl)vinyl]phenol (1e): Yellow liquid (79%, 2.67 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 5H), 7.11 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.98 – 6.91 (m, 2H), 5.88 (d, *J* = 1.0 Hz, 1H), 5.44 (d, *J* = 0.9 Hz, 1H), 5.13 (br.s, 1H).

2-(1-Methylethenyl)phenol (1f): Prepared according to the reported procedure[4] from magnesium turning (1.58 g, 65.8 mmol), MeI (4.1 ml, 65.9 mmol), 2-hydroxyacetophenone (3.62 ml, 30.1 mmol) in anhydrous Et_2O (30 ml). Colorless oil (56 %, 2.48 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ

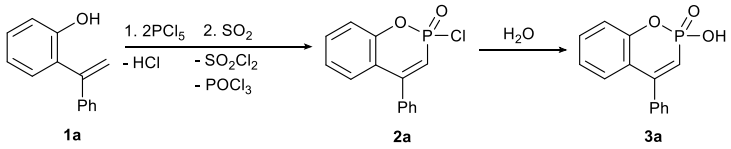
7.19 (s, 1H). 7.18 (s, 1H), 6.98 - 6.96 (m, 1H), 6.93 (td, *J* = 7.5, 1.3 Hz, 1H), 5.42 (m, *J* = 1.5 Hz, 1H), 5.19 (m, *J* = 1.9, 0.9 Hz), 2.16 (dd, *J* = 1.5, 0.9 Hz, 2H).

2-(but-2-en-2-yl)phenol (1g): Prepared according to the literature procedure [4] from magnesium turning (1.58 g, 65.8 mmol), EtBr (4.9 ml, 65.9 mmol) and 2-Hydroxyacetophenone (2.65 ml, 22 mmol) in anhydrous Et_2O (50 ml). Colorless oil (62 %, 2.02 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.16 (m, 1H), 7.15 – 7.10 (m, 1H), 7.08 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.04 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.96 – 6.93 (m, 1H), 6.92 (d, *J* = 1.3 Hz, 1H), 6.91 – 6.83 (m, 1H), 5.81 (q, *J* = 6.8 Hz, 1H), 5.66 (q, *J* = 6.4 Hz, 1H), 5.53 (s, 1H), 5.16 (s, 1H), 2.02 – 1.98 (m, 4H), 1.83 (d, *J* = 6.7 Hz, 2H), 1.55 (s, 1H), 1.51 (dd, *J* = 6.8, 1.5 Hz, 3H).

2-(2-Phenylvinyl)phenol (1h):[5]
Off-white solid (30%, 0.230 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 3H), 7.32 – 7.21 (m, 4H), 7.19 – 7.12 (m, 1H), 7.08 – 6.97 (m, 2H), 6.85 (td, J = 7.5, 0.7 Hz, 1H), 6.70 (dd, *J* = 8.0, 1.0 Hz, 1H), 5.10 – 4.71 (br s, 1H).

2-vinylphenol (1i): Prepared from the 2-hydroxybenzaldehyde directly via Wittig reaction according to a literature method.[6] Colorless oil (47%, 0.190 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 6.97 – 6.87 (m, 3H), 6.79 (d, *J* = 8.1 Hz, 1H), 5.74 (d, *J* = 17.7 Hz, 1H), 5.37 (d, *J* = 11.2 Hz, 1H).

Reaction of 2-alkenylphenol with PCl_5



1a **2a** **3a**

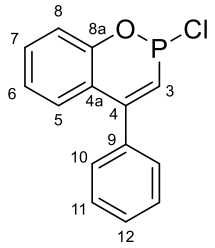
To a stirred mixture of PCl_5 (209 mg, 1 mmol) and pyridine (0.081 ml, 79mg, 1 mmol) in benzene (5 ml) was added dropwise a solution of 2-(1-Phenylvinyl)phenol **1a** (98 mg; 0.5 mmol) in benzene (5 ml) at 10°C under stream of argon. After stirring for an additional 30 min, a solution was warmed to ambient temperature and stirred for 2 hours. A yellow viscous layer was formed under a clear liquid. A gentle stream of sulphur dioxide was passed through the reaction mixture until yellow viscous layer disappears. All volatile components were removed in vacuo. The residue was dissolved in acetone (10 ml) and water (0.2 ml, 10 mmol) mixture. The resulting white precipitate was separated by filtration and dried to give compound **3a** as a white powder. Yield (60%, 77 mg). The spectral data are consistent with those previously described.[1] ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.54 – 7.47 (m, 3H, $H^{5,10}$), 7.44 (t, *J* = 7.5 Hz, 1H,H^7), 7.39 – 7.34 (m, 2H, H^{11}), 7.27 (dd, *J* = 8.1, 1.0 Hz, 1H, H^8), 7.16 – 7.05 (m, 2H, $H^{6,12}$), 6.26 (d, *J* = 17.6 Hz, 1H, H^3). ^{31}P NMR (162 MHz, DMSO-d_6) δ 4.78 (d, *J* = 16.8 Hz). ESI-MS m/z: $[M]^+$ 259.09.

General procedure for synthesis of 2-chloro-4-aryl-2*H*-benzo[*e*][1,2]oxaphosphinine 6a-g

To a stirred solution of PCl_3 (0.1 ml, 0.165 g, 1.2 mmol) and triethylamine (0.17 ml, 0.121 g, 1.2 mmol) in dry toluene (5 ml) was added dropwise by the syringe a solution of appropriate 2-alkenylphenol **1a-g (**1 mmol) in toluene (5 ml) under argon atmosphere at 0**°**C. The reaction

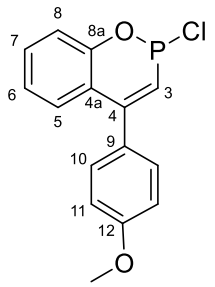
mixture was stirred at reflux until complete as determined by TLC (hexane + ethyl acetate (10:1)) and then warmed to ambient temperature. The precipitate of triethylammonium chloride was filtered off. A solvent was removed in vacuum, the residue was dried in vacuum (60 °C, 0.1 Torr) to obtain crude compounds **6a-g**.

2-chloro-4-phenyl-2*H*-benzo[*e*][1,2]oxaphosphinine (6a)



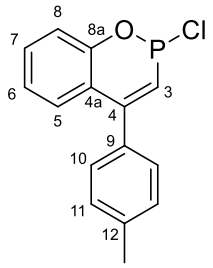
White waxy mass (96%, 0.250 g). ^{1}H NMR (500 MHz, $CDCl_3$,) δ: 7.48 – 7.37 (m, 4H, H^{10-12}), 7.28 – 7.24 (m, 2H, $H^{5,7,8}$), 7.13 (t, J = 7.7 Hz, 1H, H^{6}), 6.51 (d, J = 65.5 Hz, 1H, H^{3}). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 149.51 (d, $^{2}J_{CP}$ = 11.8 Hz, C^{8a}), 147.60 (d, $^{2}J_{CP}$ = 4.9 Hz, C^{4}), 139.19 (s, C^{9}), 132.53 (s, C^{12}), 131.23 (s, C^{7}), 128.92 (d, $^{4}J_{CP}$ = 2.3 Hz, C^{Ar}), 128.87 (s, C^{Ar}), 128.66 (s, C^{Ar}), 124.00 (s, C^{6}), 123.24 (d, $^{1}J_{CP}$ = 51.9 Hz, C^{3}), 122.71 (d, $^{3}J_{CP}$ = 7.5 Hz, C^{4a}), 120.44 (d, $^{3}J_{CP}$ = 1.2 Hz, C^{8}). ^{31}P NMR (162 MHz, $CDCl_3$) δ 133.36 (d, J = 65.5 Hz). Anal. Calcd for $C_{14}H_{10}ClOP$ (%): C 64.51; H 3.87; Cl 13.60, P 11.88. Found (%): C 64.53; H 3.79; Cl 13.65, P 11.87. ESI-MS m/z: $[M+H]^{+}$ 261.09.

2-chloro-4-(4-methoxyphenyl)-2*H*-benzo[*e*][1,2]oxaphosphinine (6b)



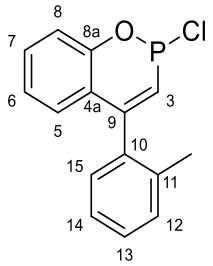
Red waxy mass (96%, 0.250 g). Yield: 91% (0.265 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (t, J = 7.7 Hz, 1H, H^{7}), 7.38 – 7.31 (m, 3H, $H^{5,10}$), 7.28 (d, J = 7.9 Hz, 1H, H^{8}), 7.15 (t, J = 7.1 Hz, 1H, H^{6}), 6.99 (d, J = 8.2 Hz, 2H, H^{11}), 6.49 (d, J = 66.5 Hz, 1H, H^{3}), 3.88 (s, 1H, CH_3O). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.13 (s, C^{12}), 149.56 (d, $^{2}J_{CP}$ = 11.6 Hz, C^{8a}), 147.15 (d, $^{2}J_{CP}$ = 4.9 Hz, C^{4}), 131.26 (d, $^{3}J_{CP}$ = 2.1 Hz, C^{9}), 130.97 (s, C^{Ar}), 130.07 (s, C^{Ar}), 128.79 (s, C^{Ar}), 123.77 (s, C^{Ar}), 122.70 (d, $^{3}J_{CP}$ = 7.5 Hz, C^{4a}), 122.08 (d, $^{1}J_{CP}$ = 51.7 Hz, C^{3}), 120.25 (d, $^{3}J_{CP}$ = 1.4 Hz, C^{8}), 113.93 (s, C^{11}), 55.46 (s, OCH_3). ^{31}P NMR (243 MHz, $CDCl_3$) δ 133.60 (d, J = 66.7 Hz). Anal. Calcd for $C_{15}H_{12}ClO_2P$ (%): C 61.98; H 4.16; Cl 12.20, P 10.66. Found (%): C 61.93; H 4.17; Cl 12.15, P 10.57. ESI-MS m/z: $[M+H]^{+}$ 290.92.

2-chloro-4-(p-tolyl)-2*H*-benzo[*e*][1,2]oxaphosphinine (6c)



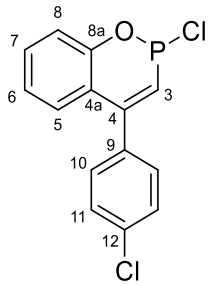
Yellow waxy mass (94%, 0.258 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (m, J = 7.8, 7.2, 1.6 Hz, 1H, H^{7}), 7.29 – 7.27 (m, 1H, H^{Ar}), 7.27 – 7.24 (m, 4H, H^{Ar}), 7.24 – 7.22 (m, 1H, H^{Ar}), 7.11 (t, J = 7.4 Hz, 1H, H^{6}), 6.46 (d, J = 66.1 Hz, 1H, H^{3}), 2.41 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.51 (d, $^{2}J_{CP}$ = 11.8 Hz, C^{8a}), 147.58 (d, $^{2}J_{CP}$ = 5.0 Hz, C^{4}), 138.88 (s, C^{12}), 136.17 (d, $^{3}J_{CP}$ = 2.2 Hz, C^{9}), 131.07 (s, C^{Ar}), 129.26 (s, C^{Ar}), 128.89 (s, C^{Ar}), 128.73 (s, C^{Ar}), 123.86 (s, C^{Ar}), 122.72 (d, $^{3}J_{CP}$ = 7.8 Hz, C^{4a}), 122.62 (d, $^{1}J_{CP}$ = 51.9 Hz, C^{3}), 120.31 (d, $^{3}J_{CP}$ = 1.7 Hz, C^{8}), 21.34 (s, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$) δ 133.69 (d, J = 66.0 Hz). Anal. Calcd for $C_{15}H_{12}ClOP$ (%): C 65.59; H 4.40; Cl 12.91, P 11.28. Found (%): C 65.53; H 4.49; Cl 12.95, P 11.27. ESI-MS m/z: $[M+H]^{+}$ 274.91.

2-chloro-4-(o-tolyl)-2*H*-benzo[*e*][1,2]oxaphosphinine (6d)



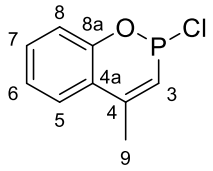
White waxy mass (91%, 0.247 g). Mixture of two diastereomers with an equal ratio d_1 and d_2. (From here on, the designations for d_1 and d_2 are given only for signals that are different for each isomer.) The hindered rotation of the *o*-tolyl substituent relative to the double bond causes diastereoisomerism similar to the previously one described for phosphinines.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 – 7.38 (m, 2H, H^{Ar}), 7.36 – 7.33 (m, 5H, H^{Ar}), 7.31 – 7.21 (m, 4H, H^{Ar}), 7.09 (td, J = 7.4, 1.4 Hz, 2H, H^{Ar}), 7.03 (d, J = 7.4 Hz, 1H, H^{12}), 6.97 – 6.89 (m, 2H, H^{6}), 6.43 (d, J = 64.4 Hz, 1H, H^{3} (d_1)), 6.38 (d, J = 62.8 Hz, 1H, H^{3} (d_2)), 2.34 (s, 3H, CH_3 (d_1)), 1.98 (s, 3H, CH_3 (d_2)). ^{13}C NMR (101 MHz, $CDCl_3$,) δ: 148.89 (d, $^{2}J_{CP}$ = 12.9 Hz, C^{8a} (d_1)), 148.51 (d, $^{2}J_{CP}$ = 12.3 Hz, C^{8a} (d_2)), 147.69 (d, $^{2}J_{CP}$ = 5.0 Hz, C^{4} (d_1)), 147.09 (d, $^{2}J_{CP}$ = 5.1 Hz, C^{4} (d_2)), 138.63 (s, C^{11} (d_1)), 138.35 (s, C^{11} (d_2)), 136.18 (s, C^{9} (d_1)), 135.50 (s, C^{9} (d_2)), 131.26 (s, C^{13} (d_1)), 131.20 (s, C^{13} (d_2)), 130.51 (s, C^{7} (d_2)), 130.18 (s, C^{7} (d_1)), 129.38 (s, C^{Ar}), 128.72 (s, C^{Ar}), 128.54 (s, C^{Ar}), 128.41 (s, C^{Ar}), 128.33 (s, C^{Ar}), 128.09 (s, C^{Ar}), 126.28 (s, C^{Ar}), 125.85 (s, C^{Ar}), 124.23 (s, C^{6} (d_1)), 124.12 (s, C^{6} (d_2)), 123.81 (d, $^{1}J_{CP}$ = 52.4 Hz, C^{3} (d_1)), 123.79 (d, $^{1}J_{CP}$ = 52.7 Hz, C^{3} (d_2)), 122.56 (s, C^{4a} (d_1)), 122.48 (s, C^{4a} (d_2)), 120.35 (d, $^{3}J_{CP}$ = 2.0 Hz, C^{8} (d_2)), 120.26 (d, $^{3}J_{CP}$ = 2.0 Hz, C^{8} (d_1)), 19.84(s, CH_3 (d_1)), 19.43(s, CH_3 (d_2)). ^{31}P NMR (243 MHz, $CDCl_3$) δ 136.75 (d, J = 62.3 Hz, (d_1)), 134.21 (d, J = 64.2 Hz, (d_2)). Anal. Calcd for $C_{15}H_{12}ClOP$ (%): C 65.59; H 4.40; Cl 12.91, P 11.28. Found (%): C 65.51; H 4.34; Cl 12.93, P 11.22. ESI-MS m/z: $[M+H]^{+}$ 274.90.

2-chloro-4-(4-chlorophenyl)-2*H*-benzo[*e*][1,2]oxaphosphinine (6e)



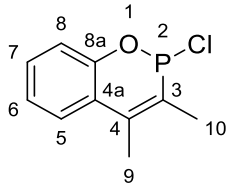
White waxy mass (97%, 0.286 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 – 7.23 (m, 3H, H^{Ar}), 7.21 – 7.14 (m, 2H, H^{Ar}), 7.11 (d, J = 8.1 Hz, 1H, H^{Ar}), 7.08 – 7.04 (m, 1H, H^{Ar}), 7.00 (t, J = 7.5 Hz, 1H, H^{6}), 6.35 (d, J = 65.0 Hz, 1H, H^{3}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.01 (d, $^{2}J_{CP}$ = 11.7 Hz, C^{8a}), 147.22 (d, $^{2}J_{CP}$ = 4.8 Hz, C^{4}), 138.55 (d, $^{3}J_{CP}$ = 1.8 Hz, C^{9}), 135.55 (s, C^{12}), 130.74 (s, C^{Ar}), 128.87 (s, C^{Ar}), 128.48 (s, C^{Ar}), 128.25 (s, C^{Ar}), 123.54 (s, C^{6}), 121.99 (d, $^{1}J_{CP}$ = 51.7 Hz, C^{3}), 119.82 (d, $^{3}J_{CP}$ = 1.5 Hz, C^{8}), 118.91 (d, $^{3}J_{CP}$ = 8.1 Hz, C^{4a}). ^{31}P NMR (162 MHz, $CDCl_3$) δ 131.34 (d, J = 64.6 Hz). Anal. Calcd for $C_{14}H_9Cl_2OP$ (%): C 56.98; H 3.07; Cl 24.03, P 10.50. Found (%): C 56.91; H 3.05; Cl 24.09, P 10.55. ESI-MS m/z: $[M+H]^+$ 294.85.

2-chloro-4-methyl-2*H*-benzo[*e*][1,2]oxaphosphinine (6f)



White waxy mass (93%, 0.185 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (dd, J = 7.8, 1.2 Hz, 1H, H^{5}), 7.41 (td, J = 8.1, 1.3 Hz, 1H, H^{7}), 7.26 – 7.19 (m, 2H, $H^{6,8}$), 6.37 (d, J = 63.8 Hz, 1H, H^{3}), 2.40 (dd, J = 2.7, 1.1 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.81 (d, $^{2}J_{CP}$ = 13.0 Hz, C^{8a}), 142.92 (d, $^{2}J_{CP}$ = 4.9 Hz, C^{4}), 130.98 (s, C^{Ar}), 125.80 (s, C^{Ar}), 124.12 (s, C^{Ar}), 123.00 (d, $^{3}J_{CP}$ = 8.5 Hz,C^{4a}), 122.45 (d, $^{1}J_{CP}$ = 48.4 Hz, C^{3}), 120.30 (d, $^{3}J_{CP}$ = 1.8 Hz, C^{8}), 22.33 (d, $^{3}J_{CP}$ = 2.0 Hz, C^{9}).^{31}P NMR (243 MHz, $CDCl_3$) δ 137.48 (d, J = 63.7 Hz). Anal. Calcd for C_9H_8ClOP (%): C 54.43; H 4.06; Cl 17.85, P 15.60. Found (%): C 54.41; H 4.05; Cl 17.89, P 15.55. ESI-MS m/z: $[M+H]^+$ 199.93.

2-chloro-3,4-dimethyl-2*H*-benzo[*e*][1,2]oxaphosphinine (6g)

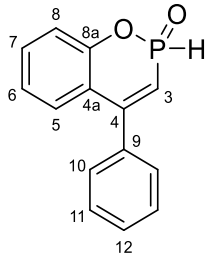


To a flask, containing 2-alkenylphenol **1g** (0.2 g, 1.4 mmol) was added PCl_3 in a one portion and stirred at reflux under stream of argon for 2 hours. An excess of PCl_3 was removed in vacuo to give compound **6g** as yellow waxy mass (92%, 0.274 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.7 Hz, 1H, H^{5}), 7.42 (t, J = 6.8 Hz, 1H, C^{7}), 7.29 (t, J = 7.1 Hz, 1H, H^{6}), 7.25 (d, J = 7.9 Hz, 1H, H^{8}), 2.35 (br.s, 3H, CH_3), 2.21 (d, J = 14.1 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.32 (d, $^{2}J_{CP}$ = 11.2 Hz, C^{8a}), 136.30 (d, $^{2}J_{CP}$ = 6.6 Hz, C^{4}), 129.18 (s, C^{Ar}), 129.11 (d, $^{1}J_{CP}$ = 43.9 Hz, C^{3}), 125.06 (s, C^{Ar}), 123.89 (s, C^{Ar}), 123.29 (d, $^{3}J_{CP}$ = 7.0 Hz, C^{4a}), 119.67 (d, $^{3}J_{CP}$ = 1.8 Hz, C^{8}), 15.19 (s, CH_3), 14.70 (s, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$) δ 137.94 (q, J = 13.6 Hz). Anal. Calcd for $C_{10}H_{10}ClOP$ (%): C 56.49; H 4.74; Cl 16.67, P 14.57. Found (%): C 56.41; H 4.75; Cl 16.64, P 14.53. ESI-MS m/z: $[M+H]^+$ 213.95.

General procedure for synthesis of 4-arylbenzo[*e*][1,2]oxaphosphinine 2-oxide 11a-g

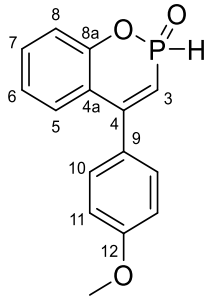
Compounds **6a-g** (0.5 mmol) were dissolved in aqueous THF and stirred for 30 min under an argon atmosphere. The solvent and all volatile components were removed on rotary evaporator. The residue was subjected dry-column flash chromatography on silica gel (230-400 mesh) with gradient elution from hexane to ethyl acetate.

4-phenylbenzo[*e*][1,2]oxaphosphinine 2-oxide (11a)



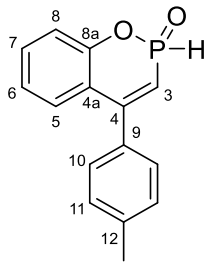
Light yellow oil (88%, 0.103 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, J = 611.9 Hz, 1H, P-H), 7.49 – 7.45 (m, 3H, H^{Ar}), 7.39 – 7.45 (m, 1H, H^{Ar}), 7.37 (m, 2H, H^{Ar}), 7.29 (d, J = 8.2 Hz, 1H, H^{Ar}), 7.21 (dd, J = 8.0, 1.2 Hz, 1H, H^{Ar}), 7.10 (br.t, 1H, H^{Ar}), 6.18 (d, J = 27.6 Hz, 1H, H^{3}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.64 (s, C^{4}), 150.28 (d, $^{2}J_{CP}$ = 9.7 Hz, C^{8a}), 138.24 (d, $^{3}J_{CP}$ = 15.5 Hz, C^{9}), 131.86 (s, C^{7}), 129.53 (s, C^{5}), 129.28 (s, C^{12}), 128.66 (s, C^{10}), 128.36 (s, C^{11}), 123.95 (s, C^{6}), 121.39 (d, $^{3}J_{CP}$ = 15.6 Hz, C^{4a}), 119.61 (d, $^{3}J_{CP}$ = 6.4 Hz, C^{8}), 112.54 (d, $^{1}J_{CP}$ = 112.9 Hz, C^{3}). ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.87 (dd, J = 610.4, 26.9 Hz). IR (neat) ν (cm^{-1}): 3407, 3026, 2956, 2923, 2852, 2730, 2302, 1803, 1701, 1589, 1605, 1512, 1451, 1406, 1377, 1205, 1109, 1020, 996, 902, 868, 831. Anal. Calcd for $C_{14}H_{11}O_2P$ (%): C 69.42; H 4.58; P 12.79. Found (%): C 69.44; H 4.55; P 12.84. ESI-MS m/z: $[M+H]^+$ 243.07.

4-(4-methoxyphenyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (11b)



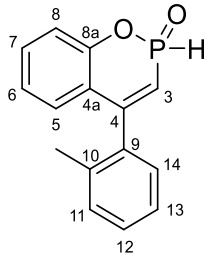
Red oil (90%, 0.123 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, J = 614.1 Hz, 1H, P-H), 7.40 (s, 1H, H^{Ar}), 7.26 (s, 3H, H^{Ar}), 7.10 (s, 2H, H^{Ar}), 6.97 (s, 2H, H^{Ar}), 6.13 (d, J = 26.2 Hz, 1H, H^{3}), 3.87 (s, 3H, CH_3O). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.38 (s, C^{12}), 155.06 (s, C^{4}), 150.24 (d, $^{2}J_{CP}$ = 9.0 Hz, C^{8a}), 131.69 (s, C^{7}), 130.40 (d, $^{3}J_{CP}$ = 15.9 Hz, C^{9}), 129.86 (s, C^{Ar}), 129.50 (s, C^{Ar}), 123.86 (s, C^{6}), 121.52 (d, $^{3}J_{CP}$ = 15.4 Hz, C^{4a}), 119.61 (d, $^{3}J_{CP}$ = 6.0 Hz, C^{8}), 114.05 (s, C^{Ar}), 111.84 (d, $^{1}J_{CP}$ = 113.8 Hz, C^{3}), 55.72 (s, CH_3O). ^{31}P NMR (162 MHz, $CDCl_3$) δ 11.28 (dd, J = 607.6, 27.7 Hz). IR (neat) ν (cm^{-1}): 3060, 3004, 2933, 2957, 2838, 1607, 1592, 1551, 1510, 1479, 1447, 1418, 1340, 1290, 1252, 1217, 1179, 1108, 1064, 1032, 954, 919, 890, 836, 799, 766, 753, 737, 703, 563. Anal. Calcd for $C_{15}H_{13}O_3P$ (%): C 66.18; H 4.81; P 11.38. Found (%): C 66.23; H 4.79; P 11.37. ESI-MS m/z: $[M+H]^+$ 272.91.

4-(p-tolyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (11c)



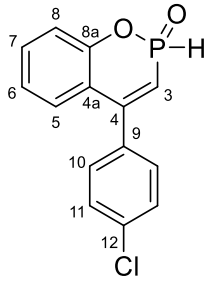
Light yellow oil (97%, 0.124 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.01 (d, J = 610.1 Hz, 1H, P-H), 7.41 (t, J = 7.7 Hz, 1H, H^7), 7.29 – 7.27 (m, 5H, $H^{5,10,11}$), 7.25 (dd, J = 7.9, 1.7 Hz, 1H, H^8), 7.10 (t, J = 7.6 Hz, 1H, H^6), 6.16 (d, J = 27.7 Hz, 1H, H^3), 2.43 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.62 (s, C^4), 150.41 (d, $^2J_{CP}$ = 9.7 Hz, C^{8a}), 139.42 (s, C^{Ar}), 135.49 (d, $^3J_{CP}$ = 15.7 Hz, C^9), 131.77 (s, C^{Ar}), 129.62 (s, C^{Ar}), 129.36 (s, C^{Ar}), 128.41 (s, C^{Ar}), 123.89 (s, C^{Ar}), 121.61 (d, $^3J_{CP}$ = 15.6 Hz, C^{4a}), 119.68 (d, $^3J_{CP}$ = 6.3 Hz, C^8), 112.36 (d, $^1J_{CP}$ = 113.0 Hz, C^3), 21.33 (s, CH_3). ^{31}P NMR (243 MHz, $CDCl_3$) δ 11.01 (dd, J = 612.3, 27.6 Hz). IR (neat) ν (cm^{-1}): 3208, 3059, 3030, 2922, 2869, 2732, 2408, 2246, 1911, 1802, 1607, 1591, 1552, 1510, 1480, 1449, 1407, 1377, 1339, 1291, 1273, 1213, 1197, 1108, 1038, 1019, 954, 916, 889, 840. Anal. Calcd for $C_{15}H_{13}O_2P$ (%): C 70.31; H 5.11; P 12.09. Found (%): C 70.29; H 5.13; P 12.04. ESI-MS m/z: $[M+H]^+$ 256.90.

4-(o-tolyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (11d)



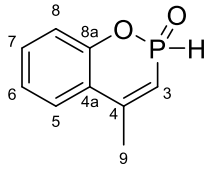
White oil (87%, 0.112 g). Mixture of two diastereomers with an equal ratio (d_1 and d_2). The hindered rotation of the *o*-tolyl substituent relative to the double bond causes diastereoisomerism similar to the previously one described for phosphinines.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (d, J = 609.7 Hz, 1H, P-H (d_1)), 8.09 (d, J = 613.5 Hz, 1H, P-H (d_2)), 7.42 – 7.21 (m, 11H, H^{Ar}), 7.09 (d, J = 7.5 Hz, 1H, H^{Ar}), 7.04 (t, J = 7.6 Hz, 2H, H^{Ar}), 6.88 (dd, J = 7.9, 1.7 Hz, 1H, H^8 (d_1)), 6.87 (dd, J = 7.9, 1.7 Hz, 1H, H^8 (d_2)), 6.14 (d, J = 28.4 Hz, 1H, H^3 (d_1)), 6.08 (d, J = 26.6 Hz, 1H, H^3 (d_2)), 2.22 (s, 3H, CH_3 (d_1)), 2.05 (s, 3H, CH_3 (d_2)). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.90 (s, C^4 (d_1)), 155.81 (s, C^4 (d_2)), 150.44 (d, $^2J_{CP}$ = 9.6 Hz, C^{8a} (d_1)), 149.95 (d, $^2J_{CP}$ = 9.7 Hz, C^{8a} (d_2)), 137.90 (d, $^3J_{CP}$ = 15.7 Hz, C^9), 135.47 (s, C^{10} (d_1)), 135.13 (s, C^{10} (d_2)), 131.95 (s, C^{Ar}), 131.91 (s, C^{Ar}), 130.58 (s, C^{Ar}), 130.35 (s, C^{Ar}), 129.16 (s, C^{Ar}), 129.06 (s, C^{Ar}), 128.96 (s, C^{Ar}), 128.91 (s, C^{Ar}), 128.80 (s, C^{Ar}), 128.78 (s, C^{Ar}), 128.19 (br.s, C^{Ar}), 126.39 (s, C^{Ar}), 126.08 (s, C^{Ar}), 124.21 (s, C^{Ar}), 124.12 (s, C^{Ar}), 121.34 (d, $^3J_{CP}$ = 15.4 Hz, C^{4a} (d_1)), 121.28 (d, $^3J_{CP}$ = 15.6 Hz, C^{4a} (d_2)), 119.61 (d, $^3J_{CP}$ = 6.5 Hz, C^8 (d_1)), 119.50 (d, $^3J_{CP}$ = 6.8 Hz, C^8 (d_2)), 113.12 (d, $^1J_{CP}$ = 109.6 Hz, C^3 (d_1)), 113.05 (d, $^1J_{CP}$ = 110.1 Hz, C^3 (d_2)), 19.71 (s, CH_3 (d_1)), 19.62 (s, CH_3 (d_2)). ^{31}P NMR (243 MHz, $CDCl_3$) δ 11.32 (dd, J = 609.4, 26.4 Hz, d_1), 10.40 (dd, J = 612.7, 27.9 Hz, d_2). IR (neat) ν (cm^{-1}): 3177, 3063, 2955, 2926, 2868, 2739, 2410, 2240, 1957, 1922, 1811, 1717, 1685, 1604, 1594, 1555, 1479, 1447, 1383, 1338, 1287, 1272, 1243, 1216, 1147, 1118, 1103, 1038, 1017, 945, 915, 887, 834, 810. Anal. Calcd for $C_{15}H_{13}O_2P$ (%): C 70.31; H 5.11; P 12.09. Found (%): C 70.27; H 5.09; P 12.14. ESI-MS m/z: $[M+H]^+$ 256.91.

4-(4-chlorophenyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (11e)



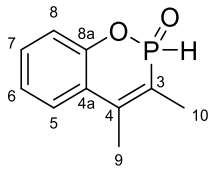
Light yellow oil (93%, 0.129 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, J = 616.6 Hz, 1H, P-H), 7.43 – 7.33 (m, 3H, $H^{5,10}$), 7.27 – 7.20 (m, 3H, $H^{7,11}$), 7.11 (dd, J = 8.0, 1.9 Hz, 1H, H^{8}), 7.05 (t, J = 7.1 Hz, 1H, H^{6}), 6.13 (d, J = 27.1 Hz, 1H, H^{3}). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.03 (s, C^{4}), 149.97 (d, $^{2}J_{CP}$ = 9.8 Hz, C^{8a}), 136.36 (d, $^{3}J_{CP}$ = 15.8 Hz, C^{9}), 135.20 (s, C^{12}), 131.88 (s, C^{7}), 129.59 (s, C^{10}), 129.00 (s, C^{5}), 128.75 (s, C^{11}), 123.89 (s, C^{6}), 120.87 (d, $^{3}J_{CP}$ = 15.5 Hz, C^{4a}), 119.52 (d, $^{3}J_{CP}$ = 6.5 Hz, C^{8}), 112.89 (d, $^{1}J_{CP}$ = 112.5 Hz, C^{3}). ^{31}P NMR (243 MHz, $CDCl_3$) δ 10.74 (dd, J = 619.2, 25.6 Hz). IR (neat) ν (cm^{-1}): 3442, 2926, 2854, 1806, 1598, 1510, 1487, 1447, 1399, 1216, 1181, 1144, 1092, 1038, 1014, 943, 921, 902, 831, 814, 759, 713, 638, 553, 500. Anal. Calcd for $C_{14}H_{10}ClO_2P$ (%): C 60.78; H 3.64; Cl 12.81; P 11.20. Found (%): C 60.77; H 3.62; Cl 12.85; P 11.15. ESI-MS m/z: $[M+H]^+$ 276.85.

4-methylbenzo[*e*][1,2]oxaphosphinine 2-oxide (11f)



Light yellow oil (95%, 0.086 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (d, J = 611.5 Hz, 1H, P-H), 7.50 (d, J = 6.9 Hz, 1H, H^{5}), 7.38 (t, J = 6.8 Hz, 1H, H^{7}), 7.18 (m, 2H, $H^{6,8}$), 6.07 (d, J = 26.4 Hz, 1H, H^{3}), 2.36 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.52 (s, C^{4}), 149.96 (d, $^{2}J_{CP}$ = 9.7 Hz, C^{8a}), 131.64 (s, C^{7}), 126.46 (s, C^{5}), 124.06 (s, C^{6}), 121.43 (d, $^{3}J_{CP}$ = 16.1 Hz, C^{4a}), 119.35 (d, $^{3}J_{CP}$ = 6.7 Hz, C^{8}), 111.80 (d, $^{1}J_{CP}$ = 114.9 Hz, C^{3}), 22.83 (d, $^{3}J_{CP}$ = 16.7 Hz, C^{9}). ^{31}P NMR (243 MHz, $CDCl_3$) δ 11.73 (br.d, J = 611.5 Hz). IR (neat) ν (cm^{-1}): 3855, 3751, 3736, 3690, 3650, 3402, 3229, 3065, 2979, 2414, 1685, 1603, 1561, 1486, 1446, 1376, 1344, 1276, 1206, 1126, 1091, 1063, 1041, 1016, 961, 926, 854, 832, 789, 758, 735, 704, 663, 613, 595. Anal. Calcd for $C_9H_9O_2P$ (%): C 60.01; H 5.04; P 17.19. Found (%): C 60.05; H 5.03; P 17.22. ESI-MS m/z: $[M+H]^+$ 181.01.

3,4-dimethylbenzo[*e*][1,2]oxaphosphinine 2-oxide (11g)



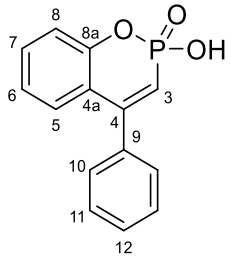
Light yellow oil (97%, 0.094 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, J = 594.9 Hz, 1H, P-H), 7.49 (d, J = 7.5 Hz, 1H, H^{5}), 7.30 (t, J = 7.0 Hz, 1H, H^{7}), 7.17 – 7.12 (m, 2H, $H^{6,8}$), 2.24 (s, 3H, CH_3), 2.14 (d, J = 15.4 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.41 (d, $^{2}J_{CP}$ = 8.9 Hz, C^{8a}), 144.03 (d, $^{2}J_{CP}$ = 3.9 Hz, C^{4}), 129.94 (s, C^{7}), 125.90 (s, C^{5}), 123.97 (s, C^{6}), 122.28 (d, $^{3}J_{CP}$ = 16.7 Hz, C^{4a}), 119.14 (d, $^{1}J_{CP}$ = 113.7 Hz, C^{3}), 118.98 (d, $^{3}J_{CP}$ = 6.1 Hz, C^{8}), 15.41 (d, $^{2}J_{CP}$ = 12.5 Hz, C^{10}), 13.64 (d, $^{3}J_{CP}$ = 16.5 Hz, C^{9}). ^{31}P NMR (243 MHz, $CDCl_3$) δ 15.87 (d, J = 594.3 Hz). IR (neat) ν (cm^{-1}): 3822, 3209, 3073, 2959, 2926, 2859, 2734, 2393, 1963, 1919, 1799, 1710, 1603,

1567, 1485, 1447, 1382, 1312, 1290, 1277, 1214, 1170, 1153, 1124, 1094, 1073, 1034, 1023, 996, 959, 912, 863, 839, 797, 756, 736, 701, 650, 608. Anal. Calcd for $C_{10}H_{11}O_2P$ (%): C 61.86; H 5.71; P 15.95. Found (%): C 61.89; H 5.75; P 15.91. ESI-MS m/z: $[M+H]^+$ 195.01.

General procedure for 2-hydroxy-4-aryl/alkylbenzo[*e*][1,2]oxaphosphinine 2-oxide 3a-g synthesis

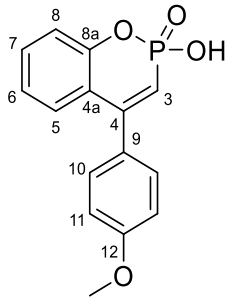
Dry oxygen was passed through the stirred solution of compounds **6a-g** (0.5 mmol) in toluene (5 ml) for 1h and additionally stirred in a tightly closed flask overnight. A solvent was evaporated and the residue was crystallized from wet acetone to give compounds **3a-g** a white powders.

2-hydroxy-4-phenylbenzo[*e*][1,2]oxaphosphinine 2-oxide (3a)



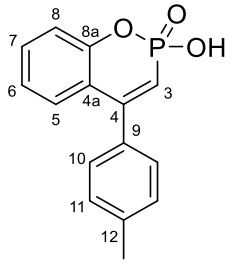
White powder. Yield: 53% (0.068 g). The spectral data are the same for this compound obtained by the reaction of **1a** with PCl_5.

2-hydroxy-4-(4-methoxyphenyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (3b)



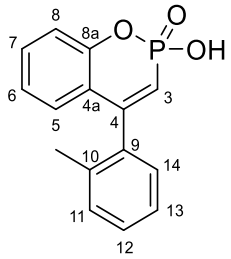
White solid (69%, 0.098 g.); mp: 95-98 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.25 (br. s, 1H, OH), 7.38 (t, J = 7.7 Hz, 1H, H^7), 7.31 (d, J = 8.6 Hz, 2H, H^{10}), 7.28 – 7.23 (m, 2H, $H^{5,8}$), 7.08 (t, J = 7.6 Hz, 1H, H^6), 6.97 (d, J = 8.6 Hz, 2H, H^{11}), 6.14 (d, J = 18.0 Hz, 1H, H^3), 3.87 (s, 3H, CH_3O). ^{13}C NMR (101 MHz, $CDCl_3$ / DMSO-d_6) δ 159.45 (s, C^4), 152.48 (s, C^{12}), 151.05 (d, $^2J_{CP}$ = 7.1 Hz, C^{8a}), 130.51 (d, $^3J_{CP}$ = 19.1 Hz, C^9), 130.14 (s, C^5), 129.18 (s, C^{10}), 128.45 (s, C^7), 122.47 (s, C^6), 121.74 (d, $^3J_{CP}$ = 16.0 Hz, C^{4a}), 118.69 (d, $^3J_{CP}$ = 7.1 Hz, C^8), 113.34 (s, C^{11}), 113.00 (d, $^1J_{CP}$ = 172.3 Hz, C^3), 54.73 (s, CH_3O).^{31}P NMR (243 MHz, $CDCl_3$) δ 12.57 (d, J = 17.7 Hz). IR (neat) ν (cm^{-1}): 3403, 3062, 3001, 2958, 2933, 2837, 2359, 1802, 1607, 1552, 1510, 1480, 1446, 1417, 1342, 1292, 1251, 1215, 1179, 1107, 1031, 957, 903, 860, 833, 799, 755, 703, 653, 613, 594, 554, 542, 508, 430. Anal. Calcd for $C_{15}H_{13}O_4P$ (%): C 62.51; H 4.55; P 10.75. Found (%): C 62.55; H 4.49; P 10.73. MALDI MS: m/z $[M+H]^+$ 288.9

2-hydroxy-4-(p-tolyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (3c)



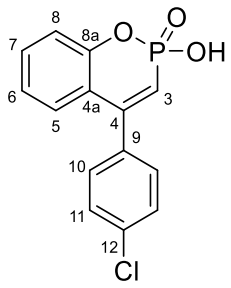
White solid (45%, 0.061 g.); mp: 237-240 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.46 – 7.40 (m, 1H, H^5), 7.32 – 7.28 (m, 2H, H^{10}), 7.28 – 7.23 (m, 3H, H^{6-8}), 7.13 (d, J = 4.1 Hz, 2H, H^{11}), 6.20 (d, J = 17.8 Hz, 1H, H^3), 2.38 (s, 3H, CH_3). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 151.74 (s, C^4), 151.29 (d, $^{2}J_{CP}$ = 7.1 Hz, C^{8a}), 138.33 (s, C^{12}), 135.62 (d, $^{3}J_{CP}$ = 18.7 Hz, C^9), 130.92 (s, C^{Ar}), 129.19 (s, C^{Ar}), 128.53 (s, C^{Ar}), 128.23 (s, C^{Ar}), 123.18 (s, C^{Ar}), 121.99 (d, $^{3}J_{CP}$ = 16.0 Hz, C^{4a}), 119.22 (d, $^{3}J_{CP}$ = 6.8 Hz, C^8), 115.41 (d, $^{1}J_{CP}$ = 168.7 Hz, C^3), 20.78 (s, CH_3). ^{31}P NMR (243 MHz, DMSO-d_6) δ 5.98 (d, J = 17.8 Hz). IR (KBr) ν (cm^{-1}): 3855, 3843, 3752 3737, 3691, 3677, 3026, 2921, 2863, 2734, 2364, 2304, 1907, 1804, 1709, 1655, 1592, 1552, 1510, 1480, 1446, 1376, 1341, 1212, 1105, 1066, 1038, 1019, 954, 900, 858, 802, 751, 704, 627, 612, 562, 546, 510, 483, 437. Anal. Calcd for $C_{15}H_{13}O_3P$ (%): C 66.18; H 4.81; P 11.38. Found (%): C 66.15; H 4.86; P 11.37. MALDI MS: m/z $[M]^+$ 272.8. ESI-MS m/z: $[M+H]^+$ 273.07.

2-hydroxy-4-(o-tolyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (3d)



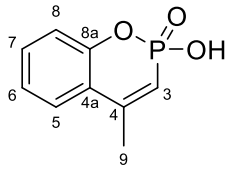
White solid (60%, 0.081 g.); mp: 80-82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 – 7.33 (m, 2H, $H^{7,12}$), 7.30 – 7.24 (m, 3H, $H^{5,13,14}$), 7.19 (dd, J = 7.6, 1.3 Hz, 1H, H^{11}), 7.02 (t, J = 8.2 Hz, 1H, H^6), 6.87 (dd, J = 7.9, 1.6 Hz, 1H, H^8), 6.09 (d, J = 18.2 Hz, 1H, H^3), 2.13 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.40 (s, C^4), 151.02 (d, $^{2}J_{CP}$ = 7.0 Hz, C^{8a}), 138.03 (d, $^{3}J_{CP}$ = 19.2 Hz, C^9), 135.29 (s, C^{10}), 131.22 (s, C^{Ar}), 130.24 (s, C^{Ar}), 128.69 (s, C^{Ar}), 128.66 (s, C^{Ar}), 128.49 (s, C^{Ar}), 126.01 (s, C^{Ar}), 123.62 (s, C^{Ar}), 121.42 (d, J = 16.6 Hz, C^{4a}), 119.21 (d, $^{3}J_{CP}$ = 7.7 Hz, C^8), 112.26 (d, $^{1}J_{CP}$ = 173.9 Hz, C^3), 19.51 (s, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$) δ 12.26 (d, J = 18.1 Hz). IR (KBr) ν (cm^{-1}): 3852, 3836, 3743, 3060, 3019, 2924, 2854, 2738, 2360, 2320, 1707, 1604, 1593, 1557, 1479, 1447, 1382, 1339, 1216, 1118, 1101, 1000, 954, 902, 853, 813, 797, 760, 728, 705, 667, 645, 586, 571, 539, 483, 462, 432. Anal. Calcd for $C_{15}H_{13}O_3P$ (%): C 66.18; H 4.81; P 11.38. Found (%): C 66.21; H 4.83; P 11.35. MALDI MS: m/z $[M]^+$ 272.8. ESI-MS m/z: $[M+H]^+$ 273.07.

4-(4-chlorophenyl)-2-hydroxybenzo[*e*][1,2]oxaphosphinine-2-oxide(3e)



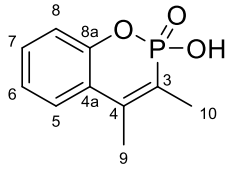
White solid (54%, 0.078 g.); mp: 227-230 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.55 (d, J = 8.0 Hz, 2H, H^{10}), 7.44 (t, J = 7.7 Hz, 1H, H^{7}), 7.39 (d, J = 8.1 Hz, 2H, H^{11}), 7.26 (d, J = 8.1 Hz, 1H, H^{5}), 7.14 (t, J = 7.5 Hz, 1H, H^{6}), 7.08 (d, J = 7.7 Hz, 1H, H^{8}), 6.29 (d, J = 17.2 Hz, 1H, H^{3}). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 151.37 (d, $^{2}J_{CP}$ = 7.0 Hz, C^{8a}), 150.67 (s, C^{4}), 137.38 (d, $^{3}J_{CP}$ = 18.9 Hz, C^{9}), 133.77 (s, C^{12}), 131.33 (s, C^{Ar}), 130.43 (s, C^{Ar}), 128.88 (s, C^{Ar}), 128.54 (s, C^{Ar}), 123.55 (s, C^{6}), 121.80 (d, $^{3}J_{CP}$ = 16.2 Hz, C^{4a}), 119.49 (d, $^{3}J_{CP}$ = 6.4 Hz, C^{8}), 116.54 (d, $^{1}J_{CP}$ = 168.2 Hz, C^{3}). ^{31}P NMR (162 MHz, DMSO-d_6) δ 4.34 (d J = 17.2 Hz). IR (KBr) ν (cm^{-1}): 3856, 3839, 3736, 3430, 2953, 2926, 2854, 2362, 2337, 2113, 1637, 1595, 1551, 1508, 1487, 1479, 1458, 1447, 1399, 1385, 1340, 1220, 1125, 1107, 1088, 1041, 1027, 1015, 963, 944, 904, 857, 830, 810, 780, 764, 752, 710, 693, 669, 622, 595, 560, 523, 449, 410. Anal. Calcd for $C_{14}H_{10}ClO_3P$ (%): C 57.46; H 3.44; Cl 12.11; P 10.58. Found (%): C 57.47; H 3.42; Cl 12.15; P 10.55.ESI-MS m/z: $[M+H]^+$ 293.04.

2-hydroxy-4-methylbenzo[*e*][1,2]oxaphosphinine 2-oxide (3f)



Light yellow solid (37%, 0.036 g.); mp: 153-155 °C. ^{1}H NMR (400 MHz, MeOH-d_4) δ: 7.54 (dd, J = 7.8, 1.2 Hz, 1H, H^{5}), 7.37 (ddt, J = 8.4, 7.1, 1.3 Hz, 1H, H^{7}), 7.17 (t, J = 7.6 Hz, 1H, H^{6}), 7.12 (dd, J = 8.2, 1.2 Hz, 1H, H^{8}), 6.06 (d, J = 18.0 Hz, 1H, H^{3}), 2.33 (s, 3H, CH_3). ^{13}C NMR (101 MHz, MeOH-d_4) δ: 151.81 (d, $^{2}J_{CP}$ = 7.0 Hz, C^{8a}), 151.63 (s, C^{4}), 131.91 (s, C^{Ar}), 127.33 (s, C^{Ar}), 124.55 (s, C^{Ar}), 122.83 (d, $^{3}J_{CP}$ = 16.8 Hz, C^{4a}), 119.65 (d, $^{3}J_{CP}$ = 7.6 Hz, C^{8}), 112.32 (d, $^{1}J_{CP}$ = 173.1 Hz, C^{3}), 22.66 (d, $^{3}J_{CP}$ = 20.3 Hz, CH_3). ^{31}P NMR (243 MHz, $CDCl_3$) δ: 10.39 (d, J = 17.9 Hz). IR (neat) ν (cm^{-1}): 3700, 3063, 3033, 2959, 2926, 2855, 2297, 2255, 1921, 1743, 1606, 1561, 1486, 1447, 1377, 1345, 1276, 1190, 1126, 1089, 1042, 1014, 985, 936, 861, 833, 792, 758, 734, 706, 646, 617, 594, 578, 553, 512, 477, 449, 409. Anal. Calcd for $C_9H_9O_3P$ (%): C 55.11; H 4.63; P 15.79. Found (%): C 55.15; H 4.62; P 15.72. ESI-MS m/z: $[M-H]^-$ 194.82.

2-hydroxy-3,4-dimethylbenzo[*e*][1,2]oxaphosphinine 2-oxide (3g)

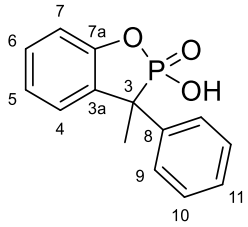


The residue, obtained after evaporation of the reaction mixture was washed with THF to give pure compound **4f**. Light yellow solid (43%, 0.045 g.); mp: >300 °C. ^{1}H NMR (600 MHz, MeOH-d_4) δ: 7.46 (dd, J = 8.0, 1.6 Hz, 1H, H^{5}), 7.20 (m, 1H, H^{7}), 7.06 (td, J = 7.7, 1.4 Hz, 1H, H^{6}), 6.99 (dd, J = 8.0, 1.4 Hz, 1H, H^{8}), 2.16 (dq, J = 1.9, 1.0 Hz, 3H, CH_3), 2.12 (dq, J = 13.4, 1.0 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, MeOH-d_4) δ: 152.59 (d, $^{2}J_{CP}$ = 6.9 Hz, C^{8a}), 138.23 (d, $^{2}J_{CP}$ = 5.7 Hz, C^{4}), 129.25 (s, C^{7}), 127.01 (d, $^{1}J_{CP}$ = 165.7 Hz, C^{3}), 126.60 (s, C^{5}), 126.35 (d, $^{3}J_{CP}$ = 17.1 Hz, C^{4a}), 123.29 (s, C^{6}), 119.77 (d, $^{3}J_{CP}$ = 6.4 Hz, C^{8}), 15.14 (d, $^{3}J_{CP}$ = 14.8 Hz, C^{9}), 14.07 (d, $^{2}J_{CP}$ = 10.4 Hz, C^{10}). ^{31}P NMR (243 MHz, MeOH-d_4) δ 8.25 (q, J = 13.2 Hz). IR (neat) ν (cm^{-1}): 3453, 2399, 2114, 1624, 1485, 1447, 1382, 1290, 1182, 1126, 1073, 909, 859, 755, 523, 479, 422, 408. Anal. Calcd for $C_{10}H_{11}O_3P$ (%): C 57.15; H 5.28; P 14.74. Found (%): C 57.19; H 5.25; P 14.79. ESI-MS m/z: m/z $[M+H]^+$ 210.93.

General procedure for 2-hydroxy-3*H*-benzo[*d*][1,2]oxaphosphole 2-oxides 9a-g synthesis

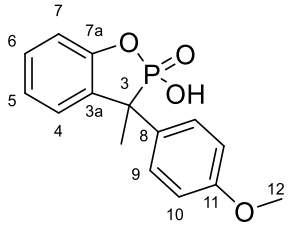
A solution of 2-alkenylphenol **1a-g** (1 mmol) in CH_2Cl_2 (1 ml) was added dropwise by the syringe to a stirred solution of phosphorus trichloride (1 mmol) in CH_2Cl_2 (20 ml) at 0°C and stirred for 20 minutes. Then $ZnCl_2$ (45 mg, 30 mol%, 0.33 mmol) was added and the reaction mixture was stirred at this temperature until total consumption of 2-alkenylphenol was determined by TLC (hexane + ethyl acetate (10:1)). The reaction mixture was filtered and dissolved in aqueous EtOH. The solvent and all volatile components were removed on rotary evaporator. The products **9a-g** were isolated by silica gel column chromatography using gradient elution from hexane to ethyl acetate.

2-hydroxy-3-methyl-3-phenyl-3*H*-benzo[*d*][1,2]oxaphosphole 2-oxide (9a)



Brown solid (56%, 0.146 g.); mp: 152-154 °C. ^{1}H NMR (400 MHz, MeOH-d$_4$) δ: 7.28 (t, J = 6.7 Hz, 1H, H^6), 7.25 – 7.17 (m, 5H, H^{4,9,10}), 7.08 – 7.05 (m, 2H, H^{5,11}), 7.04 (d, J = 7.8 Hz, 1H, H^7), 1.86 (d, J = 16.8 Hz, 3H, CH$_3$). ^{13}C NMR (101 MHz, MeOH-d$_4$) δ: 152.95 (d, $^2J_{CP}$ = 10.9 Hz, C^{7a}), 141.62 (d, $^2J_{CP}$ = 4.0 Hz, C^8), 135.30 (d, $^2J_{CP}$ = 6.9 Hz, C^{3a}), 129.05 (s, C^{11}), 128.24 (d, $^4J_{CP}$ = 1.9 Hz, C^{10}), 128.12 (d, $^3J_{CP}$ = 4.9 Hz, C^9), 126.74 (d, $^4J_{CP}$ = 2.4 Hz, C^6), 126.44 (d, $^3J_{CP}$ = 13.6 Hz, C^4), 123.47 (s, C^5), 113.27 (d, $^3J_{CP}$ = 10.7 Hz, C^7), 44.39 (d, $^1J_{CP}$ = 122.7 Hz, C^3), 23.38 (d, $^2J_{CP}$ = 2.1 Hz, CH$_3$). ^{31}P NMR (162 МГц, CDCl$_3$) δ 44.67 (q, J = 16.1 Hz). IR (neat) ν (cm^{-1}): 3949, 3912, 3898, 3863, 3851, 3836, 3800, 3767, 3743, 3500, 3061, 2958, 2931, 2873, 2455, 2329, 1952, 1906, 1804, 1622, 1553, 1495, 1475, 1460, 1446, 1402, 1381, 1343, 1279, 1215, 1129, 1108, 1073, 1035, 956, 868, 842, 819, 796, 753, 699, 678, 617, 596, 572, 513, 480, 433, 420. Anal. Calcd for C$_{14}$H$_{13}$O$_3$P (%): C 64.62; H 5.04; P 11.90. Found (%): C 64.69; H 5.05; P 11.97. ESI-MS m/z: [M+H]$^+$ 261.07.

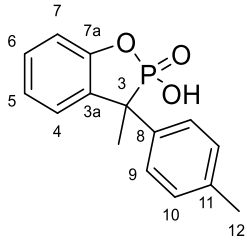
2-hydroxy-3-(4-methoxyphenyl)-3-methyl-3*H*-benzo[*d*][1,2]oxaphosphole 2-oxide (9b)



White solid (32%, 0.093 g.); mp: 185-189 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 7.21 – 7.12 (m, 1H, H^6), 7.06 (d, J = 8.5 Hz, 2H, H^9), 6.96 – 6.91 (m, 2H, H^{4,5}), 6.88 (d, J = 7.5 Hz, 1H, H^7), 6.77 (d, J = 8.4 Hz, 2H, H^{10}), 1.68 (d, J = 16.2 Hz, 3H, CH$_3$). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ: 157.16 (d, $^5J_{CP}$ = 1.8 Hz, C^{11}), 153.49 (d, $^2J_{CP}$ = 8.9 Hz, C^{7a}), 137.07 (s, C^{3a}), 135.84 (d, $^2J_{CP}$ = 3.7 Hz, C^8), 128.85 (d, $^3J_{CP}$ = 4.6 Hz, C^9), 127.71 (s, C^6), 125.83 (d,$^3J_{CP}$ = 12.1 Hz, C^4), 121.33 (s, C^5), 112.91 (s, C^{10}), 112.49 (d, $^2J_{CP}$ = 9.1 Hz, C^7), 55.04 (s, OCH$_3$), 42.43 (d, $^1J_{CP}$ = 120.6 Hz, C^3), 24.17 (s, CH$_3$). ^{31}P-{^{1}H} NMR (162 MHz, DMSO-d$_6$) δ: 36.33 (s). IR (KBr) ν (cm^{-1}): 3378, 3063, 2964, 2932, 2836, 2433, 2260, 2128, 1802, 1608, 1586, 1511, 1475, 1459, 1380, 1293, 1251, 1185,

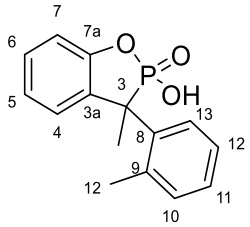
1130, 1116, 1076, 1028, 869, 835, 794, 753, 656, 596, 573, 545, 504. Anal. Calcd for $C_{15}H_{15}O_4P$ (%): C 62.07; H 5.21; P 10.67. Found (%): C 62.09; H 5.25; P 10.61. ESI-MS m/z: $[M-H]^-$ 289.06.

2-hydroxy-3-methyl-3-(p-tolyl)-3*H*-benzo[*d*][1,2]oxaphosphole 2-oxide (9c)



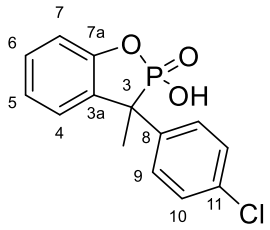
White solid (83%, 0.227 g.); mp: 87-90 °C. ^{1}H NMR (400 MHz, MeOH-d$_4$) δ: 7.19 (td, J = 7.6, 1.8 Hz, 1H, H^6), 7.03 (m, 3H, H^{4,9}), 6.99 (m, 2H, H^{10}), 6.96 (m, 2H, H^{5,7}), 2.19 (d, J = 1.8 Hz, 3H, $C_6H_4\underline{CH_3}$), 1.79 (d, J = 16.9 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, MeOH-d$_4$) δ: 153.33 (d, $^2J_{CP}$ = 11.4 Hz, C^{7a}), 139.27 (d, $^2J_{CP}$ = 5.1 Hz, C^8), 136.76 (d, $^5J_{CP}$ = 2.7 Hz, C^{11}), 136.02 (d, $^2J_{CP}$ = 7.5 Hz, C^{3a}), 129.42 (s, C^6), 129.36 (d, $^4J_{CP}$ = 1.3 Hz, C^{10}), 128.57 (d, $^3J_{CP}$ = 4.9 Hz, C^9), 126.81 (d, $^3J_{CP}$ = 13.6 Hz, C^4), 123.85 (s, C^5), 113.75 (d, $^3J_{CP}$ = 10.6 Hz, C^7), 44.55 (d, $^1J_{CP}$ = 125.1 Hz, C^3), 24.19 (d, J = 1.8 Hz, CH_3), 20.78 (s, C^{12}). ^{31}P NMR (162 МГц, $CDCl_3$) δ 48.84 (q, J = 17.4 Hz). IR (KBr) ν (cm^{-1}): 3902, 3854, 3837, 3821, 3807, 3746, 3586, 3519, 3221, 3060, 3028, 2984, 2925, 2874, 2612, 2360, 2342, 2155, 1910, 1803, 1707, 1608, 1588, 1513, 475, 1459, 1416, 1366, 1279, 1231, 1126, 1106, 1072, 1021, 987, 862, 845, 807, 776, 756, 717, 688, 658, 642, 597, 570, 532, 494. Anal. Calcd for $C_{15}H_{15}O_3P$ (%): C 65.69; H 5.51; P 11.29. Found (%): C 65.76; H 5.55; P 11.27. ESI-MS m/z: $[M-H]^-$ 273.05.

2-hydroxy-3-methyl-3-(o-tolyl)-3*H*-benzo[*d*][1,2]oxaphosphole 2-oxide (9d)



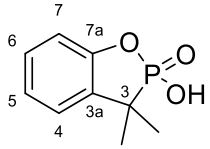
Light brown oil (63%, 0.173 g.). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.24 (t, J = 7.8 Hz, 1H, H^6), 7.13 – 7.04 (m, 3H, H^{4,10,11}), 7.06 – 6.99 (m, J = 16.6, 7.5 Hz, 3H, H^{5,12,13}), 6.98 (d, J = 7.9 Hz, 1H, H^7), 2.05 (s, 3H, $C_6H_4\underline{CH_3}$), 1.86 (d, J = 17.4 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.33 (d, $^2J_{CP}$ = 12.5 Hz, C^{7a}), 138.72 (d, $^3J_{CP}$ = 4.1 Hz, C^9), 137.97 (d, $^2J_{CP}$ = 5.1 Hz, C^8), 134.87 (d, $^2J_{CP}$ = 8.2 Hz, C^{3a}), 132.72 (d, J = 3.3 Hz, C^{Ar}), 128.85 (s, C^6), 128.15 (d, J = 6.4 Hz, C^{13}), 127.34 (d, J = 3.4 Hz, C^{Ar}), 126.29 (d, $^3J_{CP}$ = 15.3 Hz, C^4), 125.75 (d, J = 2.5 Hz, C^{Ar}), 123.55 (s, C^5), 113.51 (d, $^3J_{CP}$ = 12.0 Hz, C^7), 44.44 (d, $^1J_{CP}$ = 124.9 Hz, C^3), 25.39 (s, CH_3), 22.77 (s, $C_6H_4\underline{CH_3}$). ^{31}P-{^{1}H} NMR (243 МГц, D_2O) δ: 42.92 (s). IR (neat) ν (cm^{-1}): 3421, 3064, 3019, 2958, 2435, 2299, 1921, 1605, 1592, 1554, 1478, 1450, 1379, 1341, 1196, 1118, 1103, 1047, 956, 908, 852, 819, 807, 755, 728, 666, 645, 622, 597, 566, 519, 499, 470. Anal. Calcd for $C_{15}H_{15}O_3P$ (%): C 65.69; H 5.51; P 11.29. Found (%): C 65.67; H 5.59; P 11.23. ESI-MS m/z: $[M-H]^-$ 273.06.

3-(4-chlorophenyl)-2-hydroxy-3-methyl-3H-benzo[*d*][1,2]oxaphosphole 2-oxide (9e)



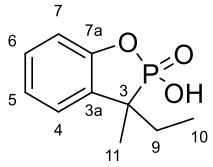
Yellow oil (85%, 0.25 g.). ^{1}H NMR (400 MHz, MeOH-d_4) δ: 7.23 (t, J = 7.6 Hz, 1H, H^6), 7.19 – 7.11 (m, J = 8.5 Hz, 2H, H^{10}), 7.11 – 7.06 (m, J = 2.4 Hz, 2H, H^9), 7.04 (t, J = 7.6 Hz, 1H, H^5), 6.98 (d, J = 8.1 Hz, 1H, H^4), 6.94 (d, J = 8.1 Hz, 1H, H^7), 1.79 (d, J = 17.4 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, MeOH-d_4) δ: 152.17 (d, $^{2}J_{CP}$ = 11.7 Hz, C^{7a}), 139.71 (d, $^{2}J_{CP}$ = 5.2 Hz, C^8), 134.22 (d, $^{2}J_{CP}$ = 7.4 Hz, C^{3a}), 132.87 (d, $^{3}J_{CP}$ = 3.6 Hz, C^9), 129.99 (s, C^{11}), 129.93 (s, C^{10}), 128.62 (d, J = 2.4 Hz, C^6), 126.46 (d, $^{3}J_{CP}$ = 13.9 Hz, C^4), 124.51 (s, C^5), 113.77 (d, $^{3}J_{CP}$ = 11.0 Hz, C^7), 44.27 (d, $^{1}J_{CP}$ = 125.5 Hz, C^3), 23.75 (s, CH_3). ^{31}P NMR (162 МГц, $CDCl_3$) δ 42.12 (q, J = 17.0 Hz). IR (neat) ν (cm^{-1}): 3921, 3591, 3518, 2926, 2361, 1700, 1607, 1492, 1474, 1459, 1414, 1401, 1384, 1202, 1168, 1095, 1073, 1013, 866, 842, 802, 755, 719, 594, 499. Anal. Calcd for $C_{14}H_{12}ClO_3P$ (%): C 57.07; H 4.10; P 10.51. Found (%): C 57.06; H 4.19; P 10.53. ESI-MS m/z: $[M-H]^-$ 293.03.

2-hydroxy-3,3-dimethyl-3*H*-benzo[*d*][1,2]oxaphosphole 2-oxide (9f)



White solid (35%, 0.077 g.); mp: 81-83 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.21 (t, J = 7.8 Hz, 1H, H^6), 7.17 (d, J = 7.7 Hz, 1H, H^4), 7.08 (t, J = 7.6 Hz, 1H, H^5), 7.01 (d, J = 8.0 Hz, 1H, H^7), 1.53 (d, J = 17.8 Hz, 6H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 150.94 (d, $^{2}J_{CP}$ = 12.2 Hz, C^{7a}), 134.49 (d, $^{2}J_{CP}$ = 8.8 Hz, C^{3a}), 128.77 (s, C^6), 124.03 (s, C^5), 123.90 (s, C^4), 113.55 (d, $^{3}J_{CP}$ = 11.5 Hz, C^7), 34.61 (d, $^{1}J_{CP}$ = 127.1 Hz, C^3), 24.00 (s, CH_3). ^{31}P NMR (243 МГц, $CDCl_3$) δ 53.74 (m, J = 17.9 Hz). IR (neat) ν (cm^{-1}): 3257, 3085, 3047, 2992, 2974, 2934, 2874, 2386, 2350, 2289, 1905, 1712, 1609, 1587, 1474, 1455, 1392, 1373, 1300, 1284, 1194, 1155, 1112, 1086, 1021, 924, 859, 812, 766, 751, 667, 589, 561, 547, 522, 497, 431. Anal. Calcd for $C_9H_{11}O_3P$ (%): C 54.55; H 5.60; P 15.63. Found (%): C 54.56; H 5.69; P 15.65. MALDI MS: m/z $[M+Na]^+$ 220.8.

3-ethyl-2-hydroxy-3-methyl-3*H*-benzo[*d*][1,2]oxaphosphole 2-oxide (9g)



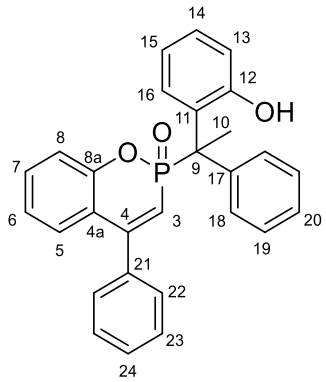
White solid (30%, 0.064 g.); mp: 87-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.08 (t, J = 7.8 Hz, 1H, H^6), 7.03 – 6.92 (m, 2H, $H^{4,5}$), 6.83 – 6.73 (m, 1H, H^7), 1.75 (s, 2H, H^9), 1.36 (d, J = 18.7 Hz, 3H, H^{11}), 0.85 (s, 3H, H^{10}). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.65 (d, $^{2}J_{CP}$ = 12.4 Hz, C^{7a}), 134.09 (d, $^{2}J_{CP}$ = 8.4 Hz, C^{3a}), 128.14 (s, C^6), 124.56 (d, J = 14.6 Hz, C^4), 122.83 (s, C^5), 113.19 (d, J = 10.8 Hz, C^7), 38.98 (d, J = 129.7 Hz, C^3), 30.80 (s, C^9), 20.95 (s, C^{10}), 9.74 (d, $^{2}J_{CP}$ = 4.3 Hz, C^{11}). ^{31}P-{^{1}H} NMR (243 МГц, $CDCl_3$) δ 49.48 (s). IR (neat) ν (cm^{-1}): 3482, 3070, 3044, 3012, 2971, 2930, 2881, 2856, 2742, 2614, 2431, 2401, 2349, 2306, 2252, 2177, 2086, 2049, 1940, 1902, 1866, 1610, 1587, 1459, 1474, 1384, 1335, 1308, 1280, 1195, 1170, 1118, 1081, 1047, 1022, 980, 934,

910, 861, 806, 752, 666, 595. Anal. Calcd for $C_{10}H_{13}O_3P$ (%): C 56.61; H 6.18; P 14.60. Found (%): C 56.59; H 6.29; P 14.65. MALDI MS: m/z $[M+H]^+$ 213.8.

General procedure for synthesis of compounds 10a-g

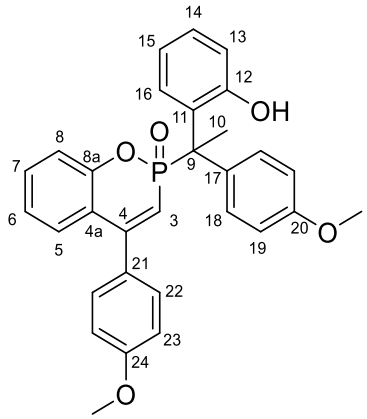
To a stirred solution of PCl_3 (0.87 ml, 1.37 g, 10 mmol) was added dropwise by the syringe an appropriate 2-alkenylphenol **1a-g (**1 mmol) under argon atmosphere at 80°C. The reaction mixture was stirred at reflux for 30 min and then an excess of PCl_3 was evaporated. The residue was dissolved in CH_2Cl_2 and a second portion of appropriate 2-alkenylphenols **1a-g** (1 mmol) solution in CH_2Cl_2 was added dropwise at ambient temperature. The reaction mixture was stirred for an additional 30 min and evaporated. Dissolving of the residue in wet acetone give a white precipitate of compounds **10a-c,e,f** which collected by filtration in a high yields. Compounds **10d,g** were purified by silica gel column chromatography (hexane + ethyl acetate (4:1)).

2-(1-(2-hydroxyphenyl)-1-phenylethyl)-4-phenylbenzo[*e*][1,2]oxaphosphinine 2-oxide (10a)



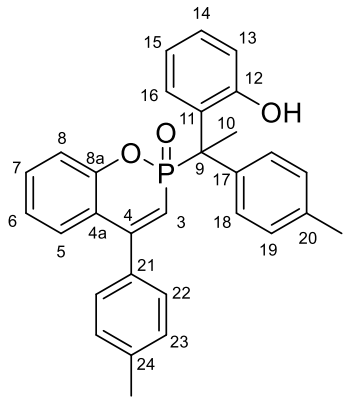
A mixture of two diastereomers d_1 and d_2 with a ratio of 5:1. White solid (87%, 0.38 g.); mp: 194-196 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (d, J = 7.7 Hz, 2H, $H^{18,22}$), 7.45 – 7.37 (m, 7H, H^{Ar}), 7.35 – 7.31 (m, 1H, H^{Ar}), 7.29 (dd, J = 8.1, 0.8 Hz, 1H, H^{Ar}), 7.26 – 7.22 (m, 6H, H^{Ar}), 7.10 (t, J = 7.6 Hz, 1H, H^{Ar}), 6.97 (t, J = 7.2 Hz, 1H, H^6), 6.97 (dd, J = 8.3, 1.2 Hz, 1H, H^8), 6.31(d, J = 23.3 Hz, H^3(d_2)), 5.84 (d, J = 21.1 Hz, 1H, H^3 (d_1)), 2.01(d, J = 16.8 Hz, H^{10} (d_2)), 1.81 (d, J = 18.3 Hz, 3H, H^{10} (d_1)). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.14 (d, $^2J_{CP}$ = 4.2 Hz, C^4 (d_1)), 156.08 (s, C^{12} (d_1)), 151.42 (d, $^2J_{CP}$ = 11.0 Hz, C^{8a} (d_1)), 141.35 (d, $^2J_{CP}$ = 5.0 Hz, C^{11} (d_1)), 138.56 (s, C^{21} (d_1)), 131.82 (s, C^{Ar} (d_2)), 138.40 (s, C^{17} (d_1)), 131.82 (s, C^7 (d_1)), 131.59 (s, C^{Ar} (d_2)), 130.01 (s, C^{Ar} (d_1)), 129.99 (s, C^{Ar} (d_1)), 129.56 (s, C^{Ar} (d_1)), 129.21 (s, C^{Ar} (d_2)), 129.10 (s, C^{Ar} (d_1)), 129.02 (s, C^{Ar} (d_1)), 128.62 (s, C^{Ar} (d_1)), 128.41 (s, C^{Ar} (d_1)), 128.35 (s, C^{Ar} (d_2)), 128.29 (s, C^{Ar} (d_2)), 127.92 (d, $^3J_{CP}$ = 7.0 Hz, C^{16} (d_2)), 127.76 (d, $^3J_{CP}$ = 7.0 Hz, C^{16} (d_1)), 127.20 (s, C^5 (d_1)), 127.11 (s, C^{Ar} (d_2)), 125.93 (s, C^{Ar} (d_2)), 123.79 (s, C^6 (d_1)), 123.41 (s, C^{Ar} (d_2)),120.97 (d, $^2J_{CP}$ = 13.1 Hz, C^{4a} (d_1)), 120.63 (s, C^{Ar} (d_1)), 120.53 (s, J = 2.0 Hz, C^{Ar} (d_1)), 120.22 (s, C^{Ar} (d_2)), 119.37 (d, $^3J_{CP}$ = 6.7 Hz, C^8 (d_1)), 119.34 (s, C^{Ar} (d_2)), 119.25 (s, C^{Ar} (d_2)), 119.19 (s, C^{Ar} (d_2)), 113.24 (d, $^1J_{CP}$ = 113.6 Hz, C^3 (d_2)), 110.93 (d, $^1J_{CP}$ = 119.0 Hz, C^3 (d_1)), 51.65 (d, $^2J_{CP}$ = 99.1 Hz, C^9 (d_1)), 26.41 (s, C^{10} (d_1)), 18.41 (s, C^{10} (d_2)). ^{31}P-{^{1}H} NMR (243 MHz, $CDCl_3$) δ: 38.40 (s, d_2), 38.45 (s, d_1). IR (neat) ν (cm^{-1}): 3330, 3060, 3027, 2956, 2923, 2870, 2851 , 2366, 1945, 1799, 1718, 1654, 1601, 1524, 1485, 1447, 1400, 1384 , 1264, 1221, 1194, 1122, 1079, 1059 , 1031, 952, 874, 820, 804. Anal. Calcd for $C_{28}H_{23}O_3P$ (%): C 76.70; H 5.29; P 7.06. Found (%): C 76.69; H 5.32; P 7.05. MALDI MS: m/z $[M+H]^+$ 439.15.

2-(1-(2-hydroxyphenyl)-1-(4-methoxyphenyl)ethyl)-4-(4-methoxyphenyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (10b)



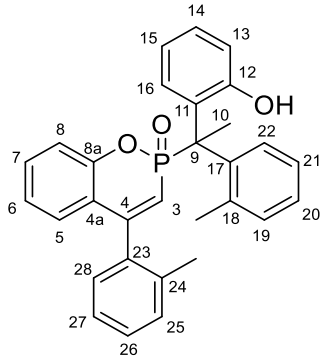
Mixture of two diastereomers d_1 and d_2 with ratio 10:1. White solid (81%, 0.404 g.); mp: 187-189 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 7.49 (d, J = 8.3 Hz, 2H, H^{22} (d_1)), 7.42 (t, J = 7.7 Hz, 1H, H^7 (d_1)), 7.33 – 7.22 (m, 5H, $H^{5,14,16,18}$ (d_1)), 7.19 (d, J = 8.5 Hz, 2H, H^{23} (d_1)), 7.10 (t, J = 7.5 Hz, 1H, H^{15} (d_1)), 7.04 (d, J = 7.7 Hz, (d_2)), 6.98 (d, J = 7.7 Hz, 2H, H^{23} (d_1)), 6.96 – 6.88 (m, J = 14.8, 6.7 Hz, 4H, $H^{6,13,19}$ (d_1)), 6.76 (d, J = 8.7 Hz, (d_2)) 6.20 (d, J = 24.0 Hz, H^3 (d_2)), 5.72 (d, J = 21.3 Hz, 1H, H^3 (d_1)), 3.85 (s, CH_3O (d_2)), 3.84 (s, 3H, CH_3O (d_1)), 3.82 (s, 3H, CH_3O (d_1)), 3.72 (s, CH_3O (d_2)), 1.93 (d, J = 18.2 Hz, H^{10}(d_2)), 1.76 (d, J = 18.2 Hz, 3H, H^{10} (d_1)). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.39 (s, C^{20} (d_1)), 158.59 (s, C^{24} (d_1)), 156.30 (d, $^2J_{CP}$ = 4.0 Hz, C^4 (d_1)), 155.77 (s, C^{12} (d_1)), 151.55 (d, $^2J_{CP}$ = 10.8 Hz, C^{8a} (d_1)), 133.14 (d, $^2J_{CP}$ = 5.1 Hz, C^{11} (d_1)), 131.72 (s, C^7 (d_1)), 130.85 (d, J = 15.8 Hz, C^{21} (d_1)), 130.01 (d, J = 2.1 Hz, C^{Ar} (d_1)), 129.89 (s, C^{Ar} (d_1)), 129.77 (s, C^{Ar} (d_2)), 129.64 (s, C^{Ar} (d_1)), 129.21 (s, C^{Ar} (d_2)), 129.14 (s, C^{Ar} (d_2)), 129.02 (s, C^{Ar} (d_2)), 128.94 (s, C^{Ar} (d_1)), 128.86 (s, C^{Ar} (d_1)), 125.87 (s, C^{17} (d_1)), 123.74 (s, C^6 (d_1)), 121.25 (d, $^3J_{CP}$ = 13.3 Hz, C^{4a} (d_1)), 120.74 (s, C^{Ar} (d_1)), 120.64 (s, C^{Ar} (d_1)), 119.41 (d, $^2J_{CP}$ = 6.4 Hz, C^8 (d_1)), 114.06 (s, C^{Ar} (d_1)), 113.86 (s, C^{Ar} (d_1)), 110.13 (d, $^1J_{CP}$ = 118.8 Hz, C^3 (d_1)), 55.46 (s, CH_3O (d_1)), 55.29 (s, CH_3O (d_1)), 51.00 (d, $^1J_{CP}$ = 98.5 Hz, C^9 (d_1)), 26.65 (s, C^{10}(d_1)). ^{31}P-{^{1}H} NMR (162 MHz, $CDCl_3$) δ: 43.03 (s, d_2), 40.35 (s, d_1). IR (KBr) ν (cm^{-1}): 3840, 3808, 3737, 3691, 3677, 3651, 3631, 3441, 3105, 3069, 3032, 2992, 2964, 2928, 2854, 2837, 2690, 2592, 2488, 2050, 1954, 1912, 1898, 1882, 1815, 1775, 1736, 1719, 1648, 1606, 1590, 1544, 1510, 1476, 1449, 1414, 1371, 1340, 1295, 1279, 1253, 1215, 1184, 1168, 1105, 1061, 1032, 949, 936, 886, 869, 855, 845, 832, 814, 793, 765, 753, 747, 722, 706, 667, 652, 637, 614, 589, 577, 561, 543, 507, 487, 458, 435, 417. Anal. Calcd for $C_{30}H_{27}O_5P$ (%): C 72.28; H 5.46; P 6.21. Found (%): C 72.26; H 5.42; P 6.25. MALDI MS: m/z $[M-H]^-$ 497.27.

2-(1-(2-hydroxyphenyl)-1-(p-tolyl)ethyl)-4-(p-tolyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (10c)



Mixture of two diastereomers d_1 and d_2 with ratio 10:1. White solid (80%, 0.374 g.); mp: 219-221 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.45 – 7.41 (m, 3H, H^{Ar} (d_1)), 7.37 (d, J = 8.2 Hz, 1H, H^{Ar} (d_1)), 7.32 – 7.28 (m, 3H, H^{Ar} (d_1)), 7.25 (dd, J = 7.9, 1.5 Hz, 1H, H^7 (d_1)), 7.23 – 7.21 (m, 2H, H^{Ar} (d_1)), 7.18 – 7.13 (m, 5H, H^{Ar} (d_1)), 7.09 (t, J = 7.6 Hz, 1H, H^6 (d_1)), 7.02 – 6.98 (m, 2H, H^{Ar} (d_1)), 6.24 (d, J = 24.2 Hz, H^3 (d_2)), 5.59 (d, J = 21.3 Hz, 1H, H^3 (d_1)), 2.42 (s, CH_3 (d_2)), 2.40 (s, 3H, CH_3 (d_1)), 2.34 (s, 3H, CH_3 (d_1)), 2.27 (s, CH_3 (d_2)), 1.86 (d, J = 17.8 Hz, C^{10} (d_2))1.76 (d, J = 17.9 Hz, 3H, C^{10} (d_1)). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.42 (d, $^2J_{CP}$ = 3.7 Hz, C^4 (d_1)), 156.36 (s, C^{12} (d_1)), 151.48 (d, $^2J_{CP}$ = 11.2 Hz, C^{8a} (d_1)), 139.25 (s, C^{24} (d_1)), 138.39 (d, $^2J_{CP}$ = 4.7 Hz, C^{11} (d_1)), 136.96 (d, $^3J_{CP}$ = 1.2 Hz, C^{17} (d_1)), 136.84 (s, C^{20} (d_1)), 135.64 (d, J = 15.7 Hz, C^{21} (d_1)), 131.83 (s, C^7 (d_1)), 131.62 (s, (d_2)), 130.17 (d, J = 1.7 Hz, C^{Ar} (d_1)), 129.71 (s, C^{Ar} (d_1)), 129.48 (s, C^{Ar} (d_1)), 129.35 (s, C^{Ar} (d_1)), 129.33 (s, C^{Ar} (d_1)), 128.93 (d, J = 6.1 Hz, C^{Ar} (d_1)), 128.41 (s, C^5(d_1)), 128.31 (s, (d_2)), 127.42 (d, $^3J_{CP}$ = 7.0 Hz, C^{16} (d_1)), 125.36 (s, C^{4a} (d_1)), 123.82 (s, C^6 (d_1)), 121.07 (s, (d_2)), 120.78 (d, J = 1.0 Hz, C^{Ar} (d_1)), 119.38 (d, $^2J_{CP}$ = 6.5 Hz, C^8 (d_1)), 119.29 (s, (d_2)), 109.84 (d, $^1J_{CP}$ = 118.8 Hz, C^3(d_1)), 51.17 (d, $^1J_{CP}$ = 99.0 Hz, C^9 (d_1)), 26.96 (s. C^{10} (d_1)), 21.41 (s, CH_3 (d_2)), 21.39 (s, CH_3 (d_1)), 21.18 (s, CH_3 (d_1)), 21.04 (s, CH_3 (d_1)). ^{31}P-{^{1}H} NMR (162 MHz, $CDCl_3$) δ: 42.57 (s, d_2), 39.43 (s, d_1). IR (KBr) ν (cm^{-1}): 3427, 3149, 2975, 2916, 2876, 2611, 2359, 2344, 1905, 1795, 1605, 1589, 1549, 1511, 1482, 1455, 1445, 1408, 1378, 1340, 1293, 1272, 1263, 1242, 1228, 1211, 1202, 1142, 1106, 1074, 1038, 1021, 946, 899, 880, 869, 851, 817, 803, 782, 754, 719, 703, 649, 640, 615, 581, 560, 512, 482, 461, 447, 436, 427, 404. Anal. Calcd for $C_{30}H_{27}O_3P$ (%): C 77.24; H 5.83; P 6.64. Found (%): C 77.26; H 5.82; P 6.68. MALDI MS: m/z $[M+H]^+$ 467.1.

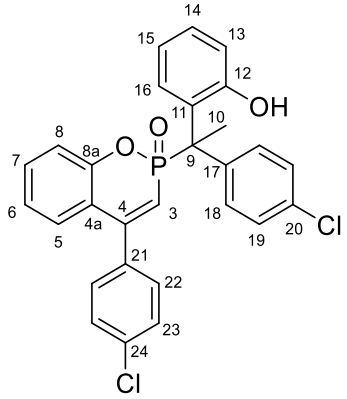
2-(1-(2-hydroxyphenyl)-1-(o-tolyl)ethyl)-4-(o-tolyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (10d)



A mixture of four diastereomers. The major isomers ratio is 3:2 (54% (d_2) 36% (d_1)). The minor isomers (d_3, d_4) content is less than 10%. White solid (85%, 0.39 g); mp: 176-178 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.45 – 8.36 (m, 2H, H^{Ar}, d_1 and d_2), 7.46 – 7.19 (s, 24H, H^{Ar}, d_1 and d_2), 7.13 – 6.93 (m, 12H, H^{Ar}, d_1 and d_2), 6.91 – 6.84 (m, 2H, H^{Ar}, d_1 and d_2), 5.55 (d, J = 20.3 Hz, 1H, H^3

(d_2)), 5.52 (d, J = 19.6 Hz, 1H, H^3 (d_2)), 2.22 (s, 3H, CH_3 (d_2)), 2.11 (s, CH_3 (d_4)), 2.08 (d, CH_3 (d_3)), 2.07 (s, CH_3 (d_1)), 1.90 (d, J = 19.3 Hz, 3H, H^{10} (d_2)), 1.86 (d, J = 19.4 Hz, 3H, H^{10} (d_1)), 1.61 (br. s, 6H, d_1+d_2+d_3+d_4 CH_3).^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.90 (s, C^{12} (d_2)), 156.55 (s, C^{Ar} (d_1)), 156.33 (s, C^4 (d_2)), 151.75 (d, $^2J_{CP}$ = 11.9 Hz, Hz, C^{8a} (d_1)), 151.44 (d, $^2J_{CP}$ = 11.1 Hz, C^{8a} (d_2)), 138.49 (s, C^{Ar} (d_2)), 138.33 (s, C^{Ar} (d_1)), 138.10 (s, C^{Ar} (d_1)), 136.58 (s, C^{Ar} (d_2)), 135.57 (s, C^{Ar} (d_2)), 135.04 (s, C^{Ar} (d_1)), 134.89 (s, C^{Ar} (d_2)), 134.17 (s, C^{Ar} (d_2)), 134.05 (s, C^{Ar} (d_1)), 133.70 (s, C^{Ar} (d_2)), 131.99 (s, C^{Ar} (d_2)), 130.64, 130.54 (s, C^{Ar} (d_2)), 130.36 (s, C^{Ar} (d_2)), 130.28 (s, C^{Ar} (d_2)), 129.55(s, C^{Ar} (d_1)), 129.45 (s, C^{Ar} (d_1)), 129.23 (s, C^{Ar} (d_2)), 129.00 (s, C^{Ar} (d_2)), 128.93 (s, C^{Ar} (d_2)), 128.82 (d, J = 5.7 Hz, C^{Ar} (d_2)), 128.67(s, C^{Ar} (d_2)), 128.45 (s, C^{Ar} (d_2)), 128.25 (s, C^{Ar} (d_2)), 128.18 (s, C^{Ar} (d_1)), 127.39 (s, C^{Ar} (d_2)), 126.49 (s, C^{Ar} (d_1)), 126.33 (s, C^{Ar} (d_2)), 126.20 (s, C^{Ar} (d_2)), 126.14(s, C^{Ar} (d_1)), 125.01 (d, $^3J_{CP}$ = 9.7 Hz, C^{4a} (d_2)), 124.08 (s, C^{Ar} (d_2)), 124.00(s, C^{Ar} (d_1)), 123.82(s, C^{Ar} (d_1)), 121.33 (s, C^{Ar} (d_2)), 121.26(s, C^{Ar} (d_1)), 120.95(s, C^{Ar} (d_1)), 120.78(s, C^{Ar} (d_1)), 119.97 (d, $^1J_{CP}$ = 111.4 Hz, C^3 (d_2)), 119.24 (d, $^3J_{CP}$ = 4.0 Hz, C^8 (d_2)), 110.21 (d, $^1J_{CP}$ = 119.0 Hz, C^3 (d_2)), 52.71 (d, $^1J_{CP}$ = 92.3 Hz, C^9 (d_1), 52.34 (d, $^1J_{CP}$ = 97.6 Hz, C^9 (d_2)), 22.83 (s, C^{10} (d_2)), 22.68(s, C^{10} (d_1)), 21.21 (s, CH_3 (d_2)), 20.04 (s, CH_3 (d_2)), 19.86 (s, CH_3 (d_1)), 19.71 (s, CH_3 (d_1)). ^{31}P NMR (243 MHz, $CDCl_3$) δ: 38.79 (d_1), 38.82 (d_2), 39.31(d_3), 39.51(d_4) (m). IR (neat) ν (cm^{-1}): 3061, 2926, 2871, 2856 2731, 2606, 2487, 2365, 2246, 2109, 1920, 1808, 1777, 1730, 1593, 1555, 1505, 1481, 1450, 1382, 1340, 1295, 1271, 1222, 1198, 1118, 1102, 1038, 943, 900, 869, 847, 818. Anal. Calcd for $C_{30}H_{27}O_3P$ (%): C 77.24; H 5.83; P 6.64. Found (%): C 77.28; H 5.79; P 6.61. ESI-MS m/z: $[M-H]^-$ 465.29.

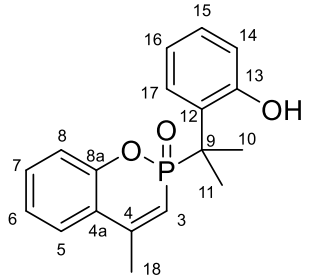
4-(4-chlorophenyl)-2-(1-(4-chlorophenyl)-1-(2-hydroxyphenyl)ethyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (10e)



Mixture of two diastereomers d_1 and d_2 with ratio 8:1. White solid (83%, 0.42 g); mp: 235-237 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, J = 7.7 Hz, 2H, H^{Ar} (d_1)), 7.44 (t, J = 7.6 Hz, 1H, H^7 (d_1)), 7.39 – 7.30 (m, J = 10.8, 8.5 Hz, 4H, H^{Ar} (d_1)), 7.25 – 7.19 (m, 2H, H^{Ar} (d_1)), 7.18 – 7.07 (m, 5H, H^{Ar} (d_1)), 7.08 – 7.00 (m, (d_2)), 6.97 – 6.89 (m, J = 14.0, 7.6 Hz, 2H, $H^{13,15}$ (d_1)), 6.84 (d, J = 7.9 Hz, H^{Ar} (d_2)) 6.22 (d, J = 22.9 Hz, H^3 (d_2)), 5.81 (d, J = 20.8 Hz, 1H, H^3 (d_1)), 1.99 (d, J = 17.0 Hz, H^{10} (d_2)), 1.74 (d, J = 18.4 Hz, 3H, H^{10} (d_1)). The signals of minor isomer (d_2) did not recognized in ^{13}C NMR spectra.^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.94 (d, $^2J_{CP}$= 4.0 Hz, C^4), 155.06 (s, C^{12}), 151.37 (d, $^2J_{CP}$ = 10.8 Hz, C^{8a}), 139.94 (s, C^{24}), 136.92 (s, C^{Ar}), 136.76 (s, C^{Ar}), 135.44 (s, C^{Ar}), 133.20 (s, C^{Ar}), 132.19 (s, C^7), 130.27 (d, J = 2.5 Hz, C^{Ar}), 129.85 (s, C^{Ar}), 129.42 (s, C^{Ar}), 129.35 (s, C^{Ar}), 129.28 (s, C^5), 129.01 (s, C^{Ar}), 128.97 (s, C^{Ar}), 128.84 (s, C^{Ar}), 125.91 (d,

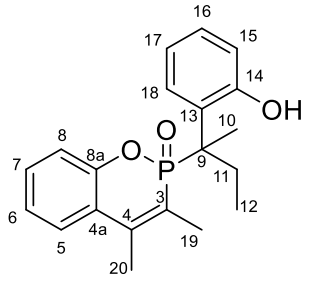
$^{3}J_{CP}$ = 3.7 Hz, C^{4a}), 124.07 (s, C^{6}), 120.87 (s, C^{Ar}), 119.57 (d, $^{3}J_{CP}$ = 6.4 Hz, C^{8}), 111.51 (d, $^{1}J_{CP}$ = 119.5 Hz, C^{3}), 51.30 (d, $^{1}J_{CP}$ = 99.3 Hz, C^{9}), 26.24 (s, C^{10})). ^{31}P-{^{1}H} NMR (243 MHz, $CDCl_3$) δ: 40.66 (s, d_2), 39.21 (s, d_1). IR (neat) ν (cm^{-1}): 3408, 3066, 2975, 2935, 2877, 2728, 2606, 2490, 2364, 2314, 2247, 2128, 1904, 1791, 1711, 1592, 1551, 1489, 1481,1449, 1400, 1375,1341, 1296,1273, 1219, 1181, 1108, 1092,1037, 1014, 943, 902, 869, 850, 815, 766, 752, 733, 715, 691, 648, 622, 598, 560. Anal. Calcd for $C_{28}H_{21}Cl_2O_3P$ (%): C 66.29; H 4.17; Cl 13.97; P 6.11. Found (%): C 66.22; H 4.19; Cl 13.93; P 6.16. MALDI MS: m/z $[M+H]^+$ 507.2.

2-(2-(2-hydroxyphenyl)propan-2-yl)-4-methylbenzo[*e*][1,2]oxaphosphinine 2-oxide (10f)



Yellow oil (90%, 0.283 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.52 (d, J = 7.8 Hz, 1H, H^{17}), 7.39 (t, J = 7.6 Hz, 1H, H^{7}), 7.27 – 7.22 (m, J = 6.9 Hz, 1H, H^{5}), 7.20 – 7.13 (m, 3H, H^{14-16}), 7.05 (d, J = 8.0 Hz, 1H, H^{8}), 6.93 (t, J = 7.6 Hz, 1H, H^{6}), 5.77 (d, J = 23.0 Hz, 1H, H^{3}), 2.34 (s, 3H, H^{18}), 1.75 (d, J = 15.7 Hz, 3H, H^{10}), 1.51 (d, J = 18.0 Hz, 3H, H^{11}). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.97 (d, $^{3}J_{CP}$ = 3.8 Hz, C^{13}), 152.22 (s, C^{4}), 150.85 (d, $^{2}J_{CP}$ = 10.7 Hz, C^{8a}), 131.77 (s, C^{7}), 129.55 (s, C^{Ar}), 127.99 (d, $^{3}J_{CP}$ = 6.2 Hz, C^{17}), 126.62 (s, C^{5}), 126.05 (s, C^{12}), 123.98 (s, C^{6}), 121.37 (d, $^{3}J_{CP}$ = 13.9 Hz, C^{4a}), 121.26 (s, C^{Ar}), 120.67 (s, C^{Ar}), 119.16 (d, $^{3}J_{CP}$ = 6.6 Hz, C^{8}), 108.25 (d, $^{1}J_{CP}$ = 114.0 Hz, C^{3}), 41.11 (d, $^{1}J_{CP}$ = 98.4 Hz, C^{9}), 23.36 (s, CH_3), 22.91 (d, J = 15.7 Hz, C^{18}), 20.73 (d, J = 3.8 Hz, CH_3). ^{31}P-{^{1}H} NMR (243 MHz, $CDCl_3$) δ: 44.07 (s). IR (neat) ν (cm^{-1}): 3073, 2975, 2958, 2927, 2855, 2772, 2626, 2347, 2305, 2120, 2073, 1918, 1802, 1716, 1604, 1574, 1563, 1509, 1486, 1446, 1391, 1376, 1343, 1289, 1278, 1239, 1220, 1193, 1163, 1153, 1125, 1090, 1042, 1001, 929, 851, 789, 737, 761, 704, 662, 612, 596, 574, 556, 519, 509, 504, 470, 448, 443, 429, 410. Anal. Calcd for $C_{18}H_{19}O_3P$ (%): C 68.78; H 6.09; P 9.85. Found (%): C 68.72; H 6.12; P 9.76. ESI-MS m/z: $[M+H]^+$ 314.97.

2-(2-(2-hydroxyphenyl)butan-2-yl)-3,4-dimethylbenzo[*e*][1,2]oxaphosphinine 2-oxide (10g)



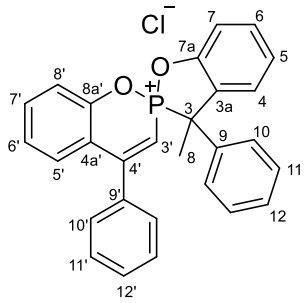
Minor isomers (d_2) content less than 10%. Yellow oil (74%, 0.25 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (d, J = 7.9 Hz, 1H, H^{18}), 7.34 (t, J = 7.7 Hz, 1H, H^{7}), 7.26 – 7.20 (m, 1H, H^{16}), 7.19 – 7.13 (m, 2H, $H^{15,17}$), 7.02 (dd, J = 8.0, 1.5 Hz, 2H, $H^{5,8}$), 6.88 (t, J = 7.5 Hz, 1H, H^{6}), 3.12 – 2.99 (m, 1H, CH_2), 2.20 (s, J = 11.5 Hz, 3H, CH_3), 1.99 – 1.90 (m, 1H, CH_2), 1.52 (d, J = 12.4 Hz, 3H, CH_3), 1.30 (d, J = 19.1 Hz, 3H, H^{10}), 0.64 (t, J = 7.4 Hz, 3H, H^{12}). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.11 (d, $^{3}J_{CP}$ = 3.4 Hz, C^{14}), 150.55 (d, $^{2}J_{CP}$ = 10.0 Hz, C^{8a}), 146.15 (s, C^{4}), 146.09 (d, $^{2}J_{CP}$ = 4.4 Hz, C^{13}), 130.55 (s, C^{7}), 129.57 (s, C^{Ar}), 129.06 (d, $^{3}J_{CP}$ = 6.6 Hz, C^{18}), 126.41 (s, C^{5}), 123.94

(s, C^{6}), 122.56 (d, $^{3}J_{CP}$ = 14.6 Hz, C^{4a}), 120.86 (d, $^{4}J_{CP}$ = 2.7 Hz, C^{17}), 120.78 (s, C^{Ar}), 118.62 (d, $^{3}J_{CP}$ = 6.7 Hz, C^{8}), 117.66 (d, $^{1}J_{CP}$ = 106.2 Hz, C^{3}), 46.46 (d, $^{1}J_{CP}$ = 93.0 Hz, C^{9}), 23.12 (d, $^{2}J_{CP}$ = 4.6 Hz, C^{10}), 19.19 (s, C^{10}), 15.75 (d, $^{3}J_{CP}$ = 13.0 Hz, C^{20}), 14.85 (d, $^{2}J_{CP}$ = 9.8 Hz, C^{19}), 7.46 (d, $^{3}J_{CP}$ = 10.7 Hz, C^{12}). ^{31}P-{^{1}H} NMR (243 MHz, $CHCl_3$) δ: 48.26 (s). IR (neat) ν (cm^{-1}): 3242, 3076, 2975, 2931, 2880, 2856, 2619, 2453, 2362, 2339, 2065, 1948, 1914, 1717, 1679, 1641, 1604, 1580, 1484, 1449, 1381, 1285, 1229, 1205, 1164, 1151, 1118, 1087, 1067, 1037, 1010, 980, 940, 925, 885, 864, 850, 836, 810, 753, 666, 605, 599. Anal. Calcd for $C_{20}H_{23}O_3P$ (%): C 70.16; H 6.77; P 9.05. Found (%): C 70.12; H 6.79; P 9.06. MALDI MS: m/z $[M-H]^-$ 341.0.

3-methyl-3,4'-diphenyl-3*H*-spiro[benzo[*d*][1,2]oxaphosphole-2,2'-benzo[*e*][1,2]oxaphosphinin]-2-ium chloride (8a)

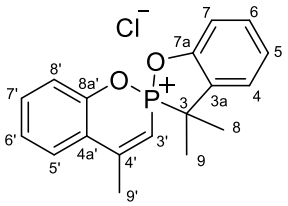
Yield >99%. Obtained by treatment with sulfinyl chloride (0.05 ml, 82 mg, 0.7 mmol) of compounds **10a** (70 mg, 0.16 mmol) in a solution of $CDCl_3$ (0.6 ml) and not isolated.

Mixture of two diastereomers d_1 and d_2 with ratio 5:2. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (t, *J* = 7.0 Hz, 1H, H^{Ar}), 7.63 – 7.26 (m, 17H, H^{Ar}), 7.23 – 7.17 (m, 2H, H^{Ar}), 7.01 – 6.92 (m, 1H, H^{Ar}), 5.23 (d, *J* = 28.6 Hz, 1H, H^{3} (d_1)), 2.41 (d, *J* = 20.6 Hz, 3H, H^{8}(d_1)), 2.32 (d, *J* = 23.5 Hz, H^{8}(d_2)). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.98 (s, $C^{4'}$(d_1)), 151.47 (d, $^{2}J_{CP}$ = 8.0 Hz, C^{7a} (d_1)), 149.25 (d, $^{2}J_{CP}$ = 14.0 Hz, $C^{8a'}$(d_1)), 136.11 (d, $^{3}J_{CP}$ = 17.6 Hz, $C^{9'}$(d_1)), 135.77 (s, C^{Ar}(d_1)), 135.32 (s, C^{Ar}(d_2)), 132.65 (s, C^{9}(d_1)), 131.92 (s, C^{Ar}), 131.60 (s, C^{Ar}), 131.52 (s, C^{Ar}), 131.05 (s, C^{Ar}), 130.38 (d, $^{3}J_{CP}$ = 3.8 Hz, C^{10}(d_1)), 130.09 (d, $^{3}J_{CP}$ = 4.3 Hz, C^{10}(d_2)), 129.62 (d, *J* = 3.8 Hz, C^{Ar}(d_2)), 129.44 (d, *J* = 3.3 Hz, C^{Ar}(d_1)), 129.11 (s, C^{Ar}), 129.03 (s, C^{Ar}), 128.89 (s, C^{Ar}), 128.41 (s, C^{3a}), 128.35 (s, C^{Ar}), 128.29 (s, C^{Ar}), 128.26 (s, C^{Ar}), 127.92 (s, C^{Ar}), 127.73 (s, C^{Ar}), 127.67 (s, C^{Ar}), 127.35 (s, C^{Ar}), 126.97 (s, C^{Ar}), 126.68 (s, C^{Ar}), 125.97 (d, $^{3}J_{CP}$ = 14.4 Hz, C^{4}(d_2)), 125.79 (d, $^{3}J_{CP}$ = 13.7 Hz, C^{4}(d_1)), 119.66 (d, $^{3}J_{CP}$ = 7.6 Hz, $C^{8'}$(d_1)), 119.10 (d, $^{3}J_{CP}$ = 14.6 Hz, $C^{4a'}$), 118.93 (d, $^{3}J_{CP}$ = 7.6 Hz, $C^{8'}$(d_2)), 114.72 (d, $^{3}J_{CP}$ = 10.4 Hz, C^{7}(d_2)), 114.54 (d, $^{3}J_{CP}$ = 10.2 Hz, C^{7}(d_1)), 93.04 (d, $^{1}J_{CP}$ = 120.3 Hz, $C^{3'}$(d_2)), 92.79 (d, $^{1}J_{CP}$ = 121.6 Hz, $C^{3'}$(d_1)), 50.74 (d, $^{1}J_{CP}$ = 79.8 Hz, C^{3}(d_1)), 23.19 (d, $^{2}J_{CP}$ = 5.2 Hz, C^{8}(d_2)), 20.03 (d, $^{2}J_{CP}$ = 4.1 Hz, C^{8}(d_1)). ^{31}P NMR (243 MHz, $CDCl_3$) δ: 82.89 (s, d_2), 82.09 (s, d_1).



3,3,4'-trimethyl-3*H*-spiro[benzo[*d*/[1,2]oxaphosphole-2,2'-benzo[*e*][1,2]oxaphosphinin]-2-ium chloride (8f)

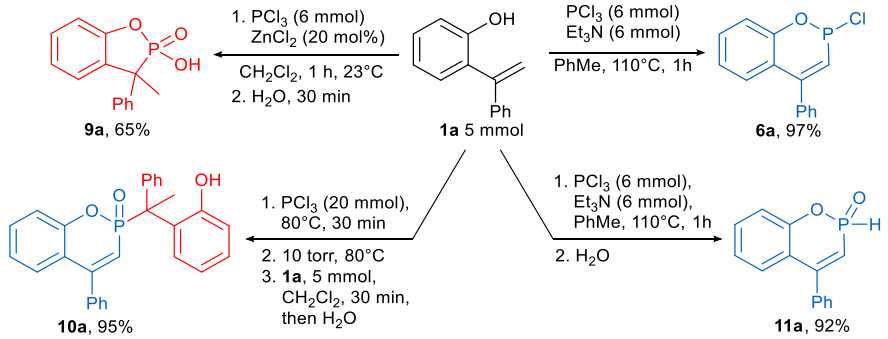
Yield >99%. Obtained by the treatment with sulfinyl chloride (0.05 ml, 82 mg, 0.7 mmol) of compound **10f** (50 mg, 0.16 mmol) in a solution of $CDCl_3$ and not isolated.



^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.89 (d, J = 8.3 Hz, 1H, $H^{5'}$), 7.66 (t, J = 7.3 Hz, 1H, $H^{7'}$), 7.49 (t, J = 7.5 Hz, 1H, $H^{6'}$), 7.45 – 7.41 (m, 1H, H^{6}), 7.39 (d, J = 8.8 Hz, 1H, H^{4}), 7.35 (d, J = 7.7 Hz, 1H, $H^{8'}$), 7.33 (t, J = 7.8 Hz, 1H, H^{5}), 7.15 (d, J = 8.1 Hz, 1H, H^{7}), 7.02 (d, J = 31.5 Hz, 1H, H^{3}), 2.85 (s, 3H, $H^{9'}$), 1.87 (d, J = 20.0 Hz, 3H, H^{8}), 1.83 (d, J = 16.9 Hz, 3H, H^{9}). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.36 (s, $C^{4'}$), 150.42 (d, $^{2}J_{CP}$ = 7.8 Hz, C^{7a}), 148.62 (d, $^{2}J_{CP}$ = 12.5 Hz, $C^{8a'}$), 135.12 (s, C^{Ar}), 130.82 (s, C^{Ar}), 129.82 (d, $^{2}J_{CP}$ = 7.2 Hz, C^{3a}), 128.57 (s, C^{Ar}), 127.24 (s, C^{Ar}), 124.26 (d, $^{3}J_{CP}$ = 14.3 Hz, C^{4}), 119.70 (d, $^{3}J_{CP}$ = 15.8 Hz, $C^{4a'}$), 119.07 (d, $^{3}J_{CP}$ = 7.6 Hz, $C^{8'}$), 114.17 (d, $^{2}J_{CP}$ = 10.3 Hz, C^{7}), 93.29 (d, $^{1}J_{CP}$ = 112.6 Hz, $C^{3'}$), 41.52 (d, $^{1}J_{CP}$ = 82.9 Hz, C^{3}), 24.92 (d, $^{2}J_{CP}$ = 5.0 Hz, C^{8}), 24.61 (d, $^{3}J_{CP}$ = 16.4 Hz, $C^{9'}$), 20.39 (d, $^{2}J_{CP}$ = 3.4 Hz, C^{9}). ^{31}P-{^{1}H} NMR (243 MHz, $CDCl_3$) δ: 87.87 (s).

4. Gram-scale reaction

Additionally, we examined the practical potential of the reaction. The four different standard conditions for the reaction of **1a** with phosphorus trichloride were scaled up from 1 to 5 mmol to provide compounds **6**, **9**, **10** and **11** even with better yields (scheme 10). Furthermore, a solvent volume was reduced twice in the synthesis of **6a** and **11a**. Also, zinc chloride loading was reduced to 20 mol% without affecting the yield of **9a**.



Scheme S2. Gram-scale synthesis of compounds **6, 9, 10** and **11**.

Synthesis of 6a and 11a.

To a stirred solution of PCl_3 (0.52 ml, 0.824 g, 6 mmol) and triethylamine (0.84 ml, 0.607 g, 6 mmol) in dry toluene (10 ml) was added dropwise by the syringe a solution of appropriate 2-alkenylphenol **1a** (0.98 g, 5 mmol) in toluene (5 ml) under an argon atmosphere at 0°C. The reaction mixture was stirred at reflux for 1 h and then cooled down to ambient temperature. The precipitate of triethylammonium chloride was filtered off. A solvent was removed in a vacuum, the residue was dried in a vacuum (60°C, 0.1 Torr) to obtain crude compounds **6a** in 97% (1.26 g) yield.

Compound **6a** was dissolved in aqueous THF and stirred for 30 min under an argon atmosphere. The solvent and all volatile components were removed on a rotary evaporator. The residue was subjected to dry-column flash chromatography with gradient elution from hexane to ethyl acetate to afford the product **11a** in 92% (1.11 g) yield.

Synthesis of 9a.

A solution of 2-alkenylphenol **1a** (5 mmol) in CH_2Cl_2 (5 ml) was added dropwise by the syringe to a stirred solution of phosphorus trichloride (0.52 ml, 0.824 g, 6 mmol) in CH_2Cl_2 (50 ml) at 0°C and stirred for 20 minutes. Then $ZnCl_2$ (136 mg, 20 mol%, 1 mmol) was added and the reaction mixture was stirred at this temperature for 1 h. The reaction mixture was filtered, dissolved in aqueous EtOH and stirred for 0.5 h. The solvent and all volatile components were removed on a rotary evaporator. Product **9a** was isolated by silica gel column chromatography using gradient elution from hexane to ethyl acetate to afford the product **9a** in 65% (0.85 g) yield.

Synthesis of 10a.

To a stirred solution of PCl_3 (1.75 ml, 2.75 g, 20 mmol) was added dropwise by the syringe 2-alkenylphenol **1a (**5 mmol) under an argon atmosphere at 80°C. The reaction mixture was stirred at reflux for 30 min and then an excess of PCl_3 was evaporated. The residue was dissolved in CH_2Cl_2 and a second portion of 2-alkenylphenol **1a** (5 mmol) solution in CH_2Cl_2 was added dropwise at ambient temperature. The reaction mixture was stirred for an additional 30 min and evaporated. The dissolving of the residue in wet acetone gives a white precipitate of compound **10a** which is collected by filtration in a high yield (95%, 4.16 g).

5. X-ray diffraction data.

X-Ray Crystallography. X-ray diffraction analysis of the structures **3e**, **9f, 10b**, **10c**, **10e** and **11c** was performed on a Bruker D8 QUEST automatic three-circle diffractometer with a PHOTON III two-dimensional detector and an IμS DIAMOND microfocus X-ray tube (λ [Mo Kα] = 0.71073 Å) at cooling conditions. Data collection and processing of diffraction data were performed using an APEX3 software package. All of the structures were solved by the direct method using the SHELXT program[8] and refined by the full-matrix least squares method over F2 using the SHELXL program.[9] All of the calculations were performed in the WinGX software package,[10] the calculation of the geometry of the molecules and the intermolecular interactions in the crystals was carried out using the PLATON program[11] and the drawings of the molecules were performed using the ORTEP−3[11] and MERCURY[12] programs. The non-hydrogen atoms were refined in the anisotropic approximation. The positions of the hydrogen atoms H(O) were determined using difference Fourier maps, and these atoms were refined isotropically. The remaining hydrogen atoms were placed in geometrically calculated positions and included in the refinement in the "riding" model. The crystallographic data of structures 1–6 were deposited at the Cambridge Crystallographic Data Center and the registration numbers and the most important characteristics are given in Table S2.

These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

Table S2. Crystal data and structure refinement for structures

	3e	**11c**	**9f**	**10b**	**10c**	**10e**
Moiety Formula	$C_{14}H_{10}ClO_3P$	$C_{15}H_{13}O_2P$	$C_9H_{11}O_3P$, H_2O	$C_{30}H_{27}O_5P$	$C_{30}H_{27}O_3P$	$C_{28}H_{21}Cl_2O_3P$
Sum Formula	$C_{14}H_{10}ClO_3P$	$C_{15}H_{13}O_2P$	$C_9H_{13}O_4P$	$C_{30}H_{27}O_5P$	$C_{30}H_{27}O_3P$	$C_{28}H_{21}Cl_2O_3P$
Formula weight	292.64	256.22	216.16	498.49	466.49	507.32
T (K)	164(2)	100(2)	100(2)	100(2)	135(2)	162(2)
Crystal system	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic
Space group	$P2_1$ (No. 4)	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 19)	P-1 (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	4.5378(3)	11.0159(7)	6.4079(3)	10.4785(5)	11.552(6)	11.4101(5)
b (Å)	10.6153(7)	4.4255(3)	6.8535(3)	12.0901(6)	18.511(4)	18.7328(7)
c (Å)	13.1018(9)	25.0968(16)	22.6667(11)	12.1355(6)	11.652(3)	11.6060(4)
α	90	90	90	71.222(2)	90	90
β	91.716(3)	92.518(3)	90	65.046(2)	107.119(16)	108.346(2)
γ	90	90	90	64.730(2)	90	90
V ($Å^3$)	630.83(7)	1222.31(14)	995.44(8)	1241.50(11)	2381.3(15)	2354.62(16)
Z	2	4	4	2	4	4
ρ calc (mg/mm^3)	1.541	1.392	1.442	1.334	1.301	1.431
μ (mm^{-1})	0.429	0.215	0.262	0.151	0.146	0.373
Crystal size (mm)	0.30x0.20x0.10	0.30x0.30x0.15	0.30x0.20x0.02	0.15x0.10x0.05	0.20x0.20x0.10	0.40x0.20x0.03

θ range for data collection (°)	2.5 < θ < 32.0	2.1 < θ < 32.0	1.8 <θ< 30.3	2.3 <θ< 30.0	2.1 <θ< 32.0	2.1 <θ< 30.0
Reflections collected	38061	45212	24820	59631	77457	90603
Independent reflections	4383 (R_{int} = 0.048),	4248 (R_{int} = 0.055)	2970 (R_{int} = 0.077)	7218 (R_{int} = 0.079)	8158 (R_{int} = 0.103)	6826 (R_{int} = 0.086)
Observed Reflections with I > 2σ (I)	4325	3876	2893	5282	5495	5442
Goodness-of-fit	1.138	1.145	1.066	1.038	1.077	1.135
Final R indexes [I > 2r (I)]	R_1 = 0.0278 wR_2 = 0.0711	R_1 = 0.0433 wR_2 = 0.1144	R_1 = 0.0285 wR_2 = 0.0717	R_1 = 0.0465 wR_2 = 0.1118	R_1 = 0.0574 wR_2 = 0.1386	R_1 = 0.1086 wR_2 = 0.2217
Final R indexes [all data]	R_1 = 0.0281 wR_2 = 0.0712	R_1 = 0.0472 wR_2 = 0.1162	R_1 = 0.0293 wR_2 = 0.0720	R_1 = 0.0718 wR_2 = 0.1206	R_1 = 0.1151 wR_2 = 0.1483	R_1 = 0.1251 wR_2 = 0.2281
Max. and Min. Resd. Dens. (e Å^3)	0.44/-0.28	0.58 /-0.40	0.790/-0.24	0.430/-0.450	0.360/-0.380	0.470/-0.480
Flack parameter	0.023(8)		0.10(4)	-	-	-
CCDC No.	2299771	2299775	2299776	2299774	2299772	2299773

The main geometric parameters of the molecules **3e**, **11c**, **10b**, **c** and **e** are usual. They correspond to the values observed in the previously studied structures of oxaphosphinines with condensed aromatic fragments. [7b] Hence, we will focus on the conformational features of the molecules and crystal structures of these compounds. The geometries of molecules **3e**, **10b**, **10c**, **10e** and **11c** are shown in Figure S7 (A-E).

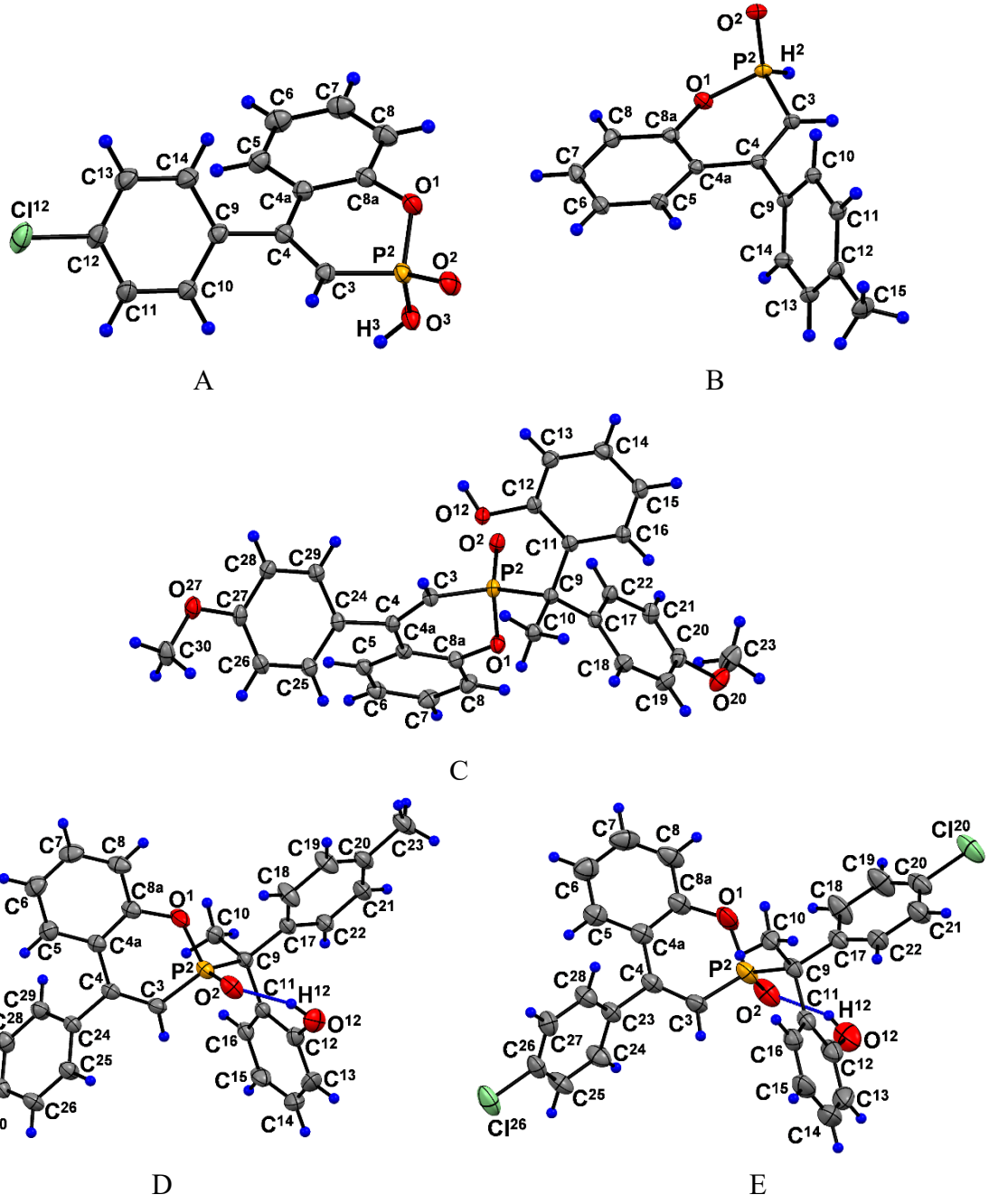


Fig. S7. Geometries of molecules **3e** (A), **11c** (B), **10b** (C), **10c** (D) and **10e** (E) in crystals. Anisotropic displacement ellipsoids are shown at 50% probability.

It should be noted that these compounds are crystalized as individual compounds without the solvent molecules. The asymmetric part of the crystals contained independent molecules. Only **10f** formed the crystal with a water molecule, i.e. it is a crystal hydrate in the solid state.

The conformation of six-membered heterocycles in molecules is determined by a fused planar benzene ring (it is a planar fragment O^1–C^{8a}–C^{4a}–C^4 in the oxaphosphinine heterocycle)

and also a planar fragment P^2–C^3–C^4–C^{4a} at the double C^3=C^4 bond. The P^2 and C^3 atoms are deviated from the O^1–C^{8a}–C^{4a}–C^4 plane on one side by the different distances (Table S3, ESI): by 0.7669(2) and 0.331(1) Å **3e**, –0.5694(4) and –0.235(1) **11c**, 0.8566(4) and 0.294(1) Å **10b**, 0.3295(6) and 0.158(2) Å **10c**, 0.317(1) and 0.135(4) Å **10e**, respectively. Similarly, atoms O^1 and C^{8a} on the same side are deviated from the P^2–C^3–C^4–C^{4a} plane by the different distances (Table S3, ESI). Therefore, in molecules **3e** and **10b**, the heterocycle conformation can be defined as a nonsymmetric *boat*, and in molecules **10c** and **10e** as a flattened nonsymmetric *boat*.

The conformation of the heterocycle in the hydrophosphoryl compound molecule **11c** is also a nonsymmetric *boat*, slightly flattened compared to the conformations of the six-membered heterocycle in **3e** and **10b**. Changes in the planarity of the heterocycle are reflected in changes in the dihedral angle θ between the O^1–C^{8a}–C^{4a}–C^4 and P^2–C^3–C^4–C^{4a} planes, which decreases from values of 16.7-19.9° (in molecules **3e** and **10b**) to values of 12.0° (in molecule **11c**) and 6.6-6.8° (in molecules **10c** and **10e**).

The conformation of the heterocycles in these molecules is defined as *P^2-sofa* by the PLATON software. In contrast to the other four molecules, in molecule **3e**, the hydroxyl group at the phosphorus atom occupies an axial position, while the phosphoryl group is situated in an equatorial position. In molecules **11c**, **10b**, **10c** and **10e**, the phosphoryl group is in the axial position, and the P–C (or P–H) bond is equatorial. This location of the substituents at the phosphorus atom is in accord with the anomeric effect.

The plane of the aromatic substituent at the C^4 atom is turned relative to the P^2–C^3=C^4–C^{4a} plane by the significant angle – from 47.5° (in molecule **3e**) to 67.4° (in molecule **10b**). This evidence excludes almost completely the conjugation between the aromatic substituent and the C^3=C^4 bond.

Table S3. Values of substituent deviations from $O^1C^4C^{4a}C^4$ and $P^2C^3C^4C^{4a}$ planes in benzoxaphosphinine molecules (**3e**, **11c**, **10b**, **10c**, **10e**).

Molecule	Plane*	Atom deviations				
	$O^1C^4C^{4a}C^4$	P^2	O^2	C^3	C^9	O^3 / H^2
3e	± 0.000(1)	0.7669(2)	0.3064(9)	0.331(1)	–	2.2690(9)
11c	± 0.015(1)	–0.5694(4)	–1.9785(9)	–0.235(1)	–	0.30(1)
10b	± 0.008(2)	0.8566(4)	2.309(1)	0.294(2)	0.177(1)	–
10c	± 0.007(2)	–0.3295(6)	–1.633(2)	–0.158(2)	1.074(2)	–
10e	± 0.007(4)	0.317(1)	1.614(3)	0.135(4)	–1.084(4)	–
Molecule	$P^2C^3C^4C^{4a}$	Atom deviations				
		O^1	O^2	C^{8a}	C^9	O^3 / H^2
3e	± 0.0001(9)	–0.6921(9)	–0.8020(9)	–0.341(1)	–	1.4384(8)
11c	± 0.005(2)	0.5028(9)	–1.2897(9)	0.222(1)	–	1.05(1)
10b	± 0.034(2)	–0.792(1)	1.373(1)	–0.407(2)	–1.134(2)	–
10c	±0.005(2)	0.279(2)	–1.211(2)	0.115(2)	1.524(2)	–
10e	± 0.001(4)	–0.277(4)	1.210(3)	–0.121(4)	–1.516(4)	–

*) Dihedral angle (θ, degree) between the planes $O^1C^4C^{4a}C^4$ / $P^2C^3C^4C^{4a}$: 16.56(6) **3e**, 12.03(8) **11c**, 18.8(1) **10b**, 6.8(1) **10c**, 6.6(3) **10e**.

Except for compound **11c**, all the other studied molecules **3e, 10b, 10c, 10e** have hydroxyl groups. Therefore, inter- and intramolecular hydrogen bond formation is observed in the crystals of these compounds. For example, in the crystal of **3e**, intermolecular hydrogen bonds are formed between the hydroxyl group on the phosphorus atom and the phosphoryl group of the neighboring molecule. It leads to an infinite chain of molecules along the *a*-axis of the crystal (Fig. S8).

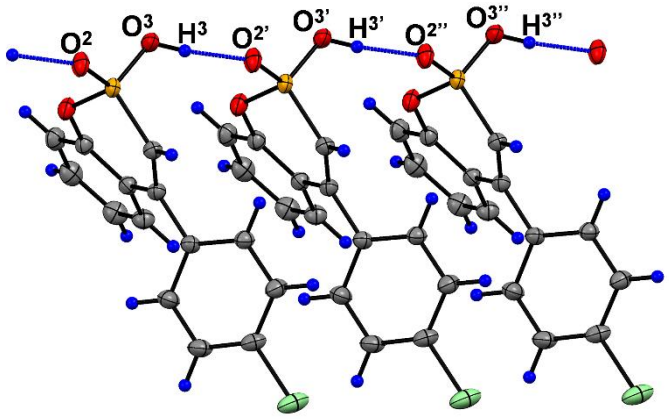


Fig. S8. The hydrogen bonding system (shown as dotted lines) in the crystal **3e**.

An intriguing observation of P-H...O intermolecular contacts of a short length was made within the crystal of **11c** (Fig. S9a). There is a common belief that P-H...X-type bonds do not exist. However, the crystal of **11c** displays the brief interactions between the (x, 1-y, z) coordinates of H2 and O2' atoms at a distance of 2.56(1) Å, as well as a P-H...O2' angle of 162(1)º. Moreover, the distance between P and O2' of 3.85 Å exceeds the sum of their Van der Waals radii. Probably, this contact is determined by the parallel packing of molecules in stacks along the b-axis of the crystal, favorable for stacking interactions of their aromatic rings (Fig. S9b).

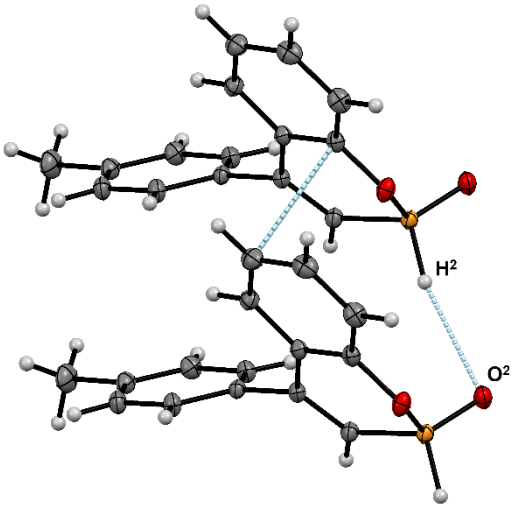


Fig. S9a. The short P-H...O-type intermolecular contacts in the **11c** crystal.

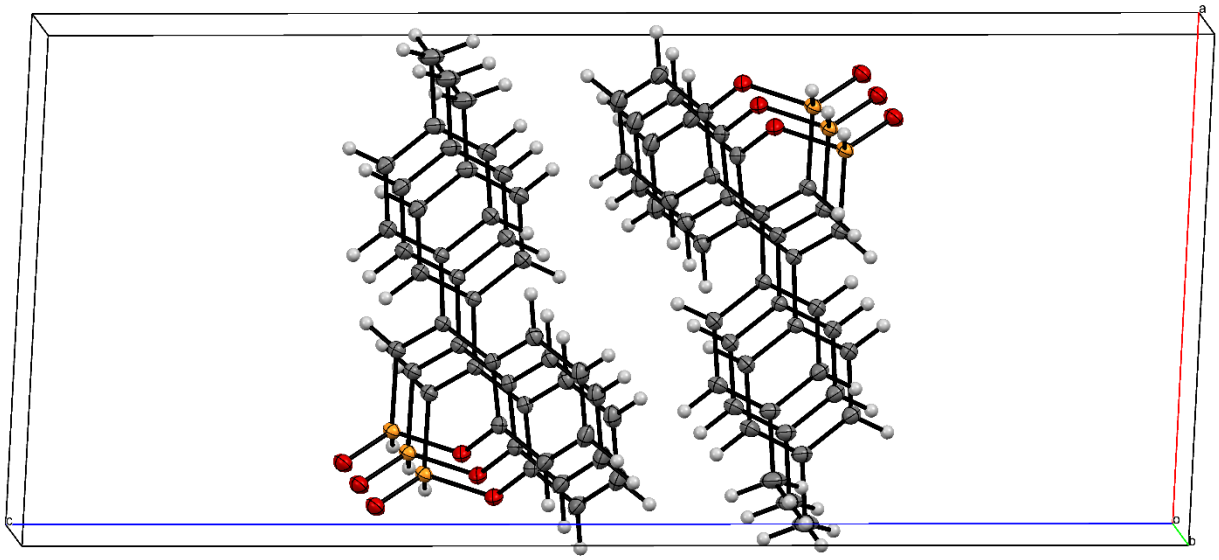


Fig. S9b. Crystal packing fragment of **11c** Projection along the b axis. The interplanar distances between the aromatic rings are 3.3463(5) Å.

The crystals of **10c** and **10e** are isostructural due to the similar steric and electronic properties of the para-tolyl and para-chlorophenyl substituents. Hence, the hydrogen bonding system in both is the same. Only intramolecular H-bonds of the hydroxyl group of the ortho-phenolic substituent to the phosphoryl group (Fig. S7, E) are formed in these crystals. In the crystal of compound **10b**, the 0D-system of hydrogen bonds - centrosymmetric dimer is also realized due to H-bonds of hydroxyl groups of phenolic substituents with phosphoryl groups (Fig. S10).

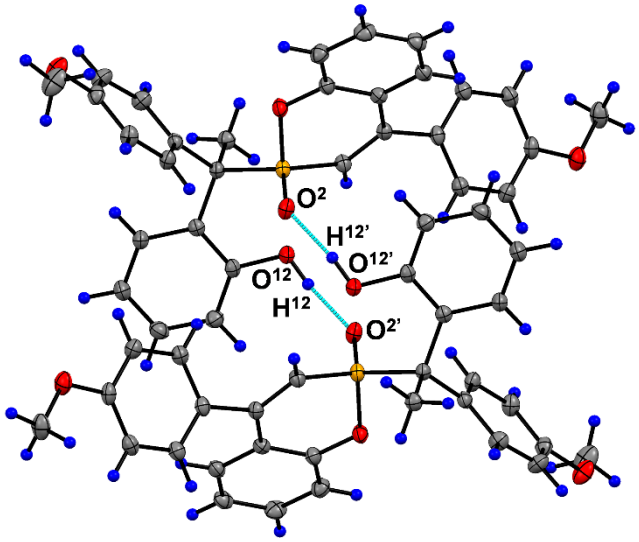


Fig. S10. The hydrogen bonding system (shown as dotted lines) in the crystal of **10b**.

The structure of compound **9f** differs significantly from those discussed above. This molecule contains the oxaphospholane heterocycle with a fused benzene ring (Fig. S11).

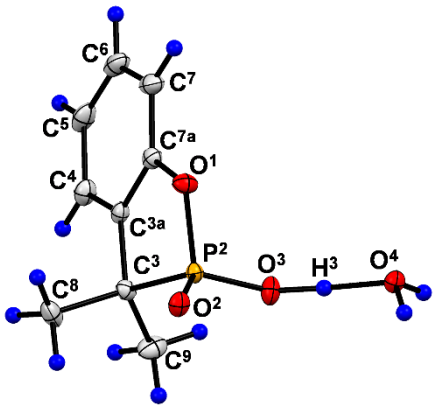


Fig. S11. The geometry of the independent crystal part of the compound **9f**. The anisotropic displacement ellipsoids are shown with a 50% probability.

A fused planar fragment also determines the conformation of the five-membered heterocycle of this molecule. The deviation of the P^2 atom from the O^1–C^{7a}–C^{3a}–C^3 plane is 0.403 Å. Thus, the conformation of the heterocycle is a P^2-*envelope*. The main geometric parameters of the molecule are normal. As mentioned in the experimental part, this compound forms a crystal solvate whose packing is also determined by the hydrogen bonds.

The participation of water molecules in the hydrogen bond formation led to a more complex packing of molecules in the crystal **9f**. As shown in Figure S12, compound molecules form hydrogen-bonded dimers through water molecules. The same water molecules bind the dimers into infinite ribbons along the a-axis of the crystal (Figure S13).

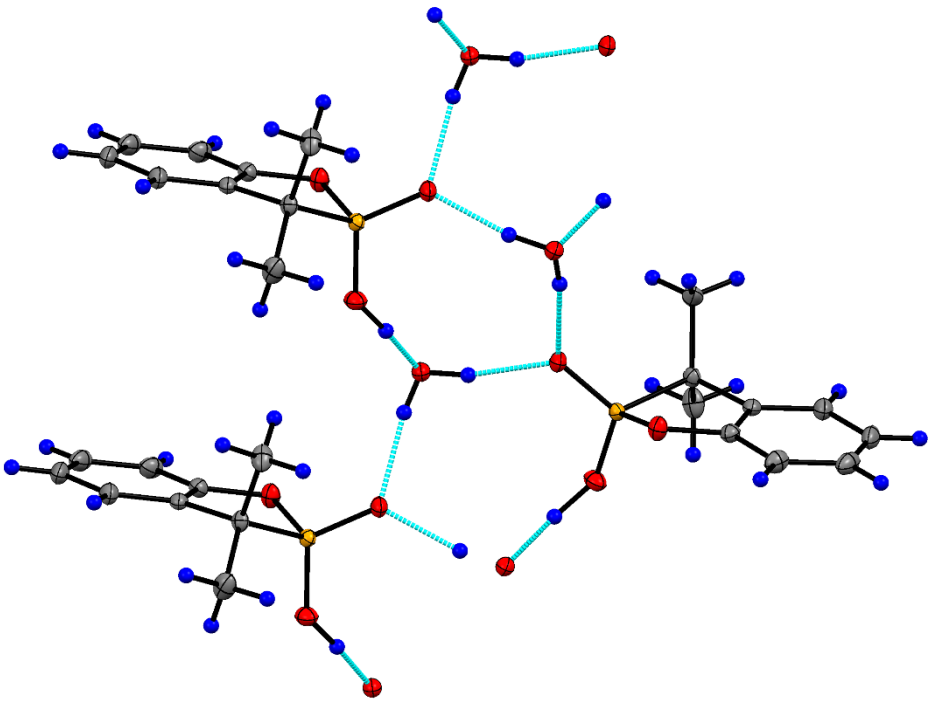


Fig. S12. The hydrogen bonding in the crystal of **9f**.

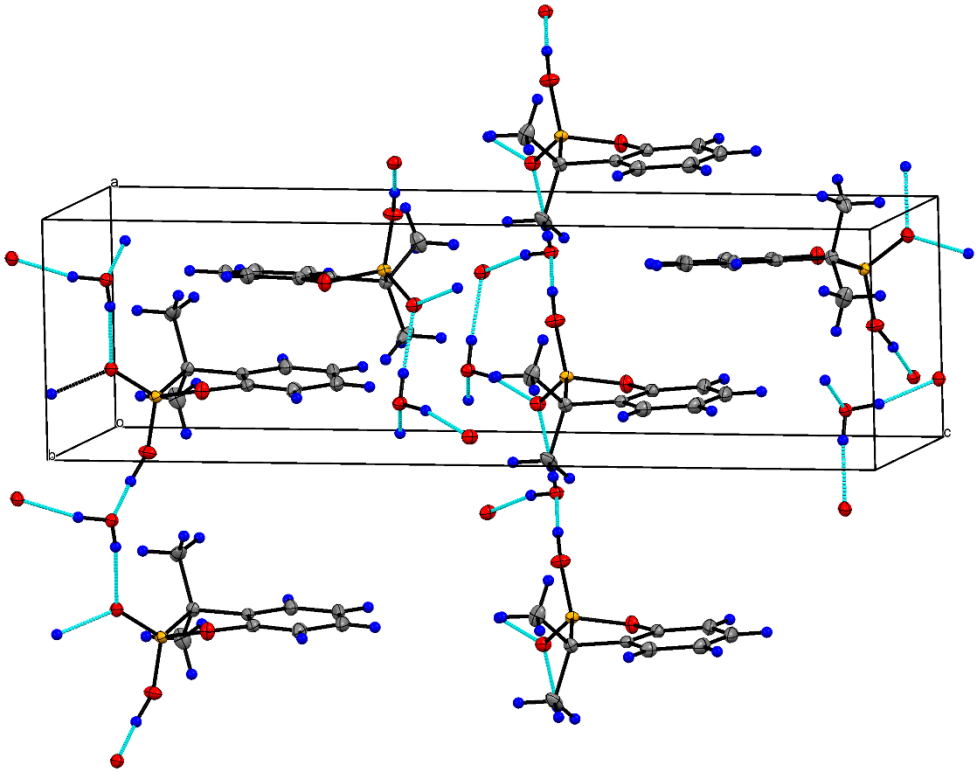


Fig. S13. Fragment of the crystal packing **9f**. Hydrogen bonds are shown as dotted lines.

Attention should be drawn to the fact that crystals **3e** and **9f** are non-centrosymmetric. They contain asymmetric molecules of the corresponding compounds, even though they contain a phosphorus atom as the only chiral centre. Since racemic compounds are obtained in the synthesis, their crystallization is accompanied by a conglomerate separation of the molecules into enantiopure crystals.

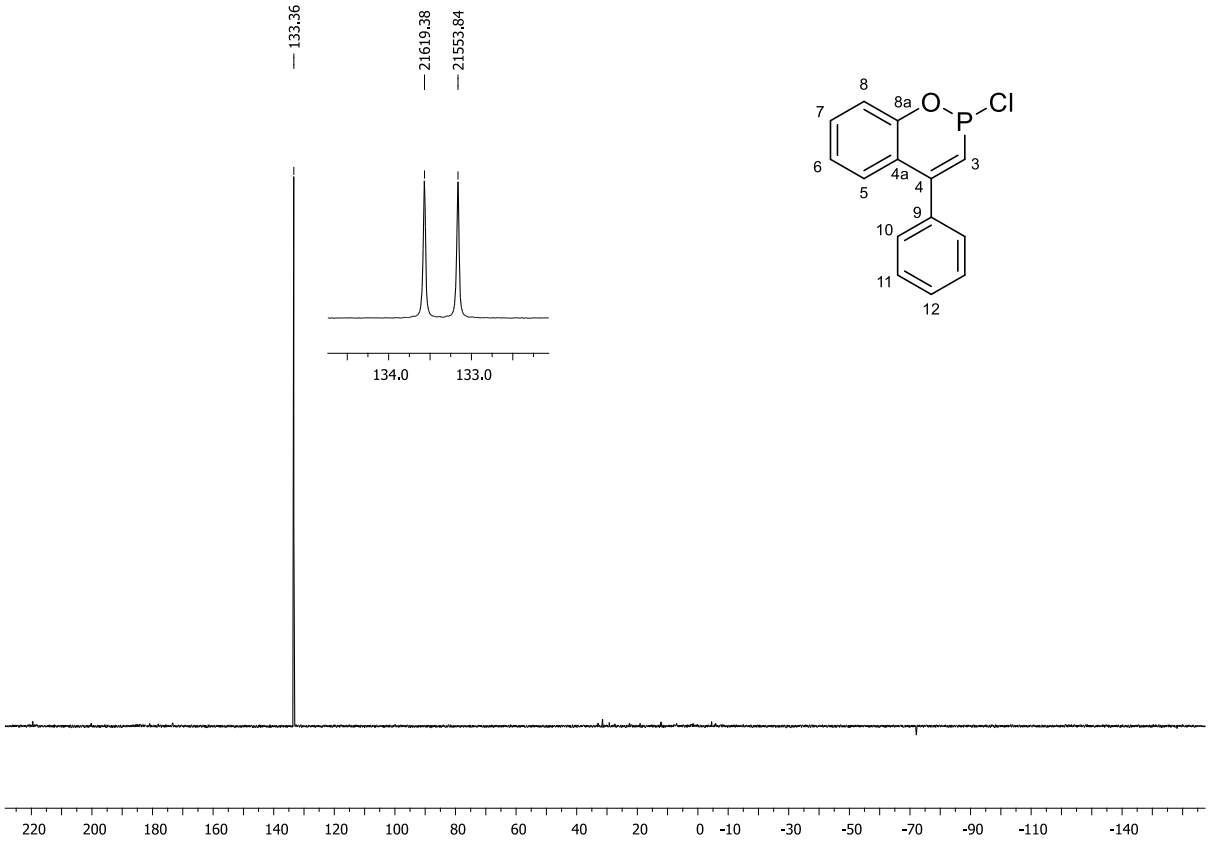
6. References

1. D. Ma, S. Hu, S. Chen, J. Pan, S. Tu, Y. Yin, Y. Gao and Y. Zhao, *Org. Lett.*, 2020, **22**, 8156–8160.
2. V. Nemtarev, V. F. Mironov, A. S. Aniskin, D. S. Baranov, E. V. Mironova, D. B. Krivolapov, R. Z. Musin, S. F. Vasilevskii, N. O. Druzhkov and V. K. Cherkasov, *Russ. Chem. Bull.*, 2013, **62**, 55–70.
3. Y. Yamamoto, *J. Org. Chem.*, 2008, **73**, 5210–5210.
4. K. Sasano, J. Takaya and N. Iwasawa, *J. Am. Chem. Soc.*, 2013, **135**, 10954–10957.
5. L.-Y. Liao, G. Shen, X. Zhang and X.-F. Duan, *Green Chem.*, 2012, **14**, 695.
6. J. Ferguson, F. Zeng and H. Alper, *Org. Lett.*, 2012, **14**, 5602–5605.
7. (a) V. F. Mironov, G. G. Sergeenko, I. Bauer and W. D. Habicher, *Russ. J. Org. Chem.*, 2006, **42**, 1453–1457; (b) V. Mironov, A. Konovalov, I. Litvinov, A. Gubaidullin, R. Petrov, A. A. Shtyrlina, T. A. Zyablikova, R. Z. Musin, N. Azancheev and A. V Il'yasov, *Russ. J. Gen. Chem.*, 1998, **68**, 1414–1442.
8. G.M. Sheldrick, *Acta Crystallogr. Sect. A Found. Adv.* 2015, **71**, 3–8.
9. G.M. Sheldrick, *Acta Crystallogr. Sect. C* 2015, **71**, 3–8.
10. L.J. Farrugia, *J. Appl. Crystallogr.* 2012, **45**, 849–854.
11. A.L. Spek, *Acta Crystallogr. Sect. D Biol. Crystallogr.* 2009, **65**, 148–155.
12. C.F.Macrae, P.R. Edgington, P. McCabe, E. Pidcock, G.P. Shields, R. Taylor, M. Towler, J.V.D. Streek, *J. Appl. Crystallogr.* 2006, **39**, 453–457.

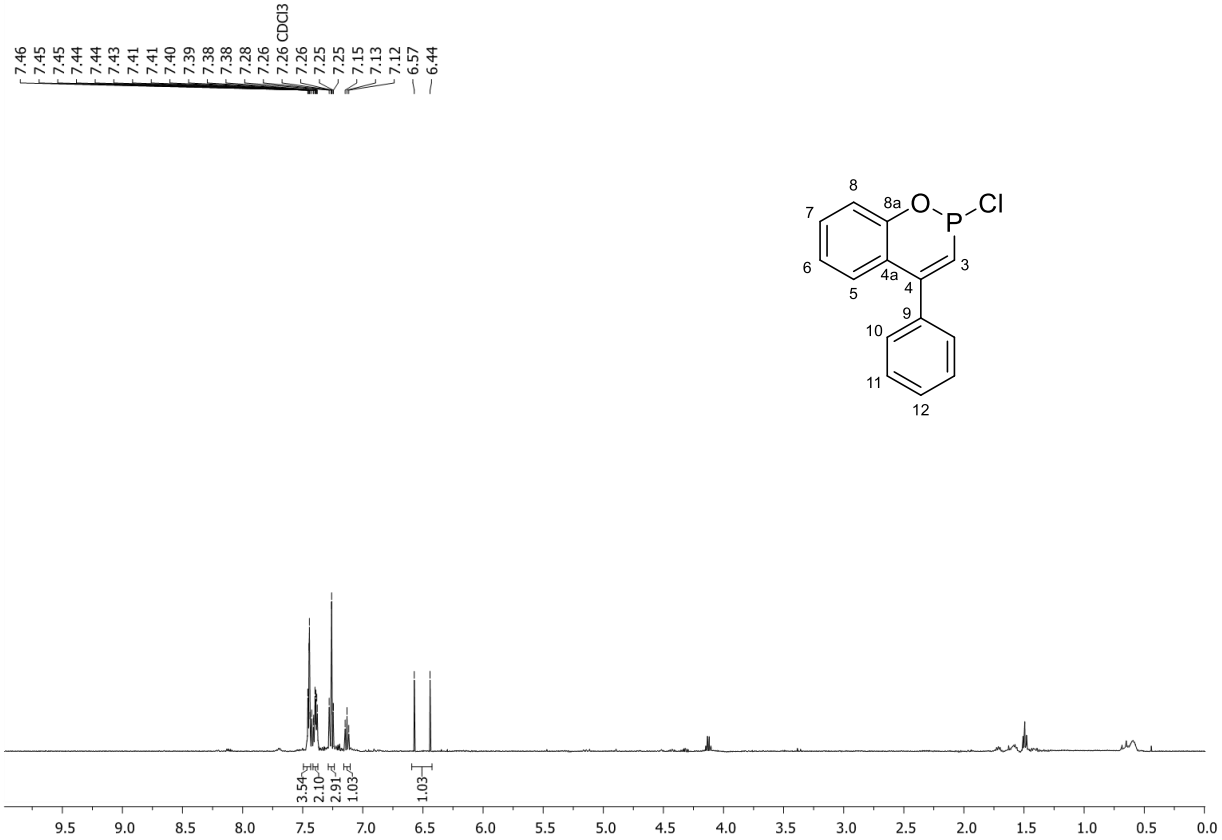
7. Copies of NMR spectra of all products

2-chloro-4-phenyl-2*H*-benzo[*e*][1,2]oxaphosphinine (6a)

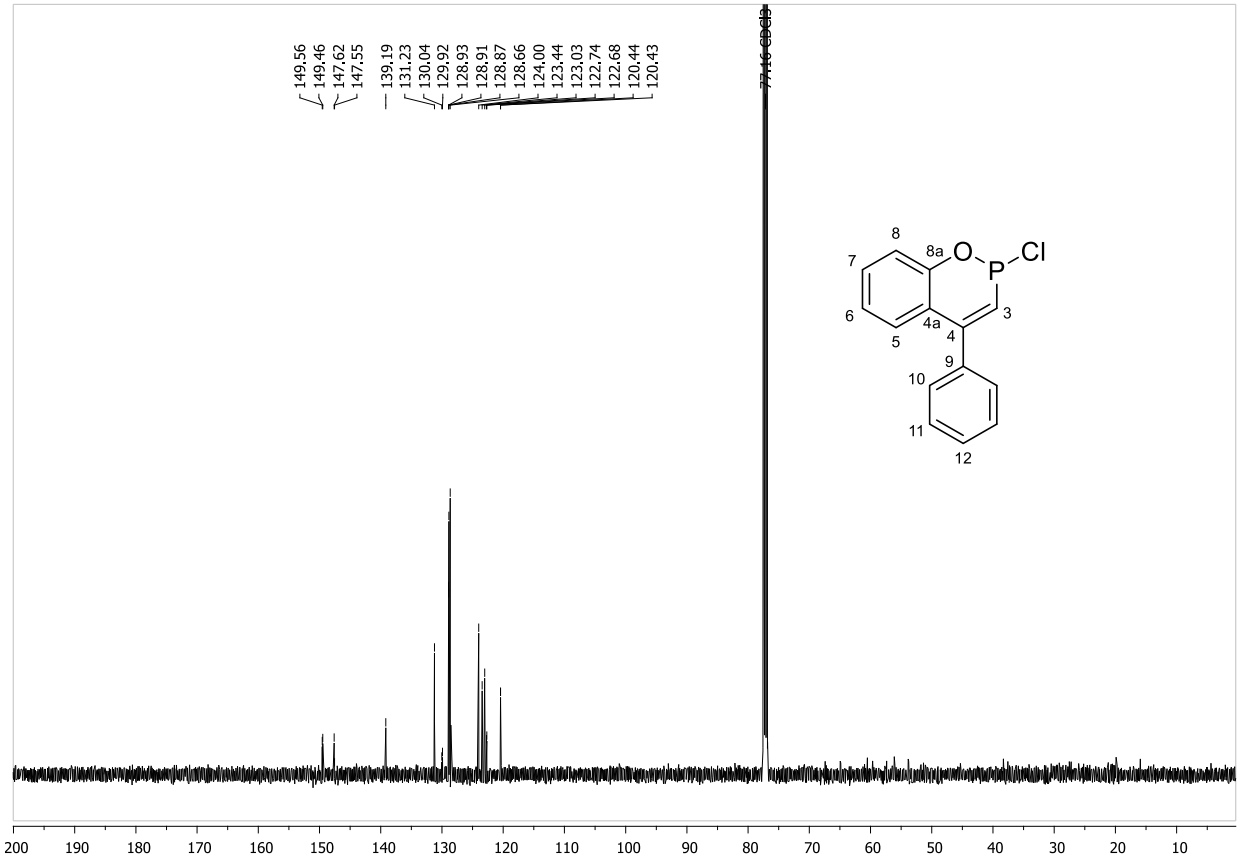
^{31}P NMR (162 MHz, $CDCl_3$) of compound **(6a)**



^{1}H NMR (500 MHz, $CDCl_3$) of compound **(6a)**

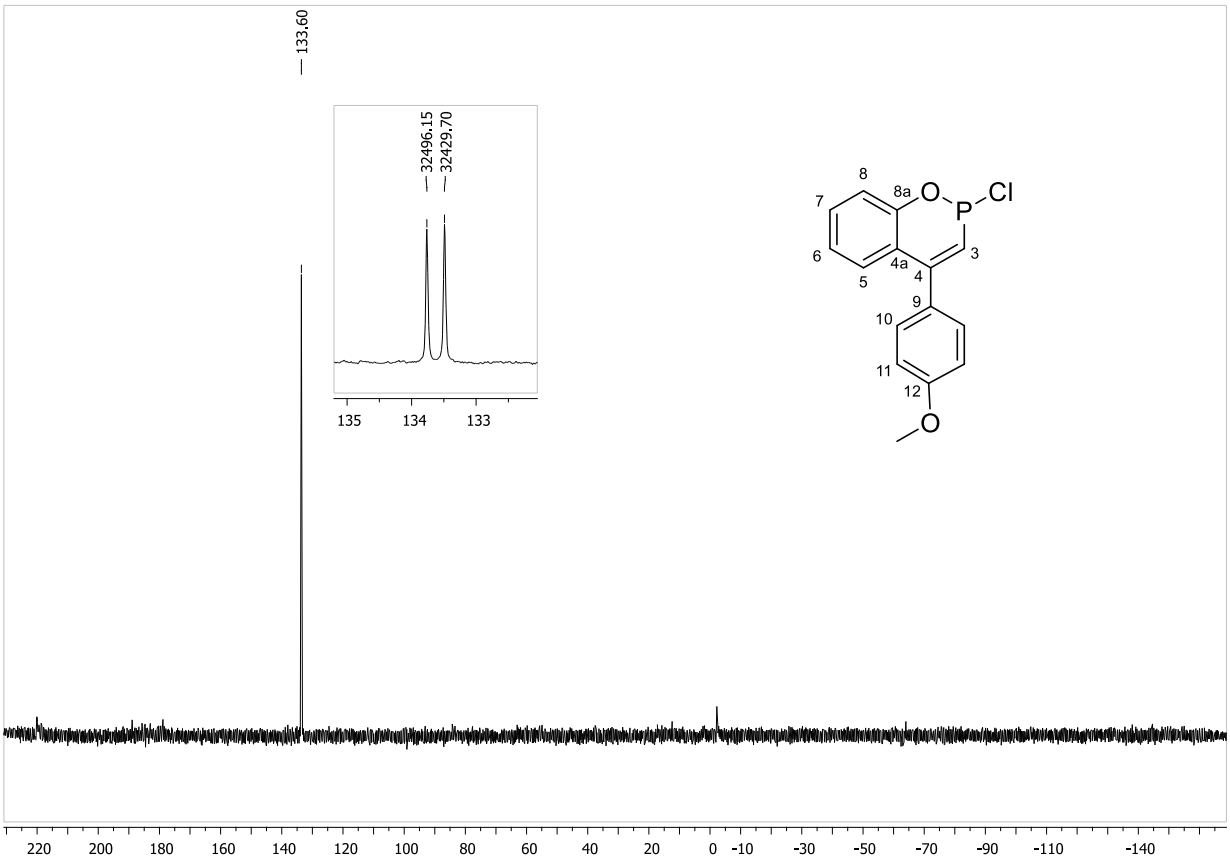


^{13}C NMR (126 MHz, $CDCl_3$) of compound **(6a)**

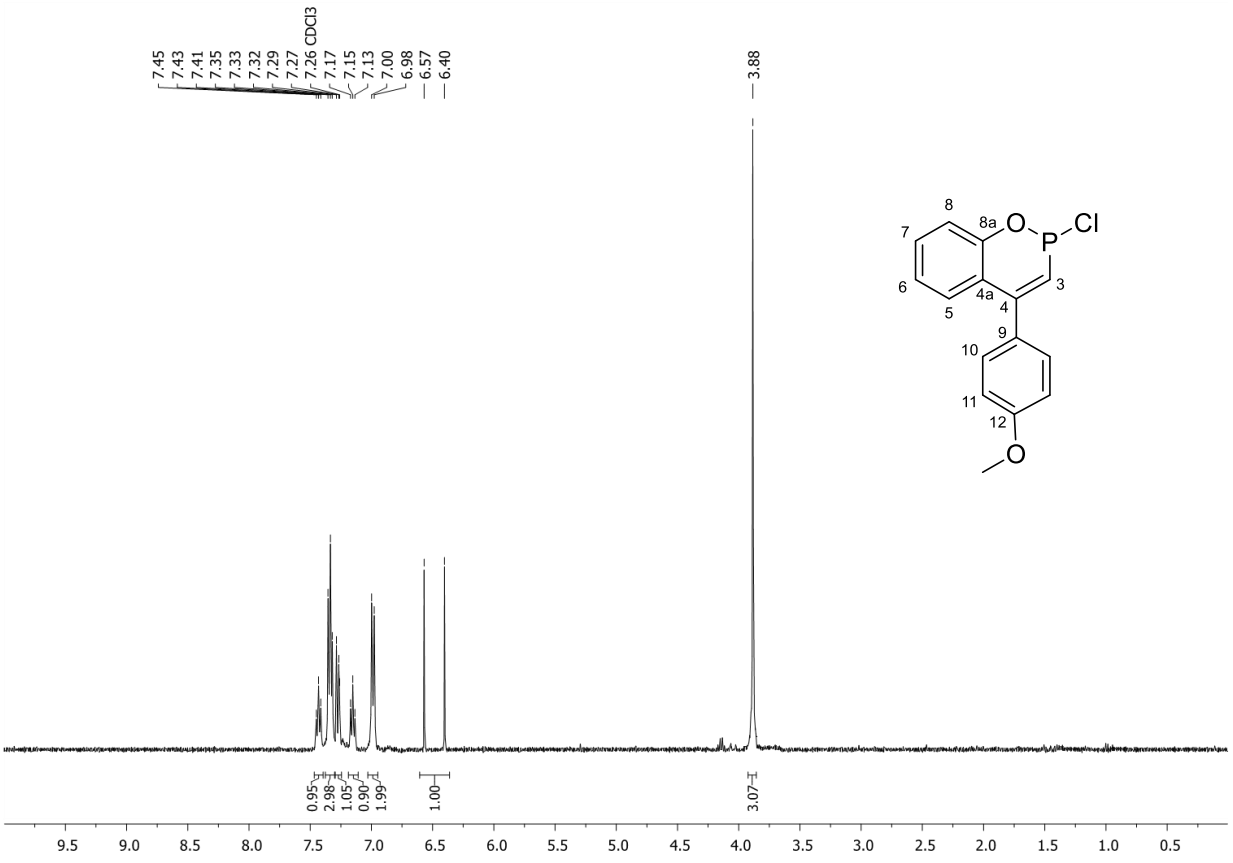


2-chloro-4-(4-methoxyphenyl)-2*H*-benzo[e][1,2]oxaphosphinine (6b)

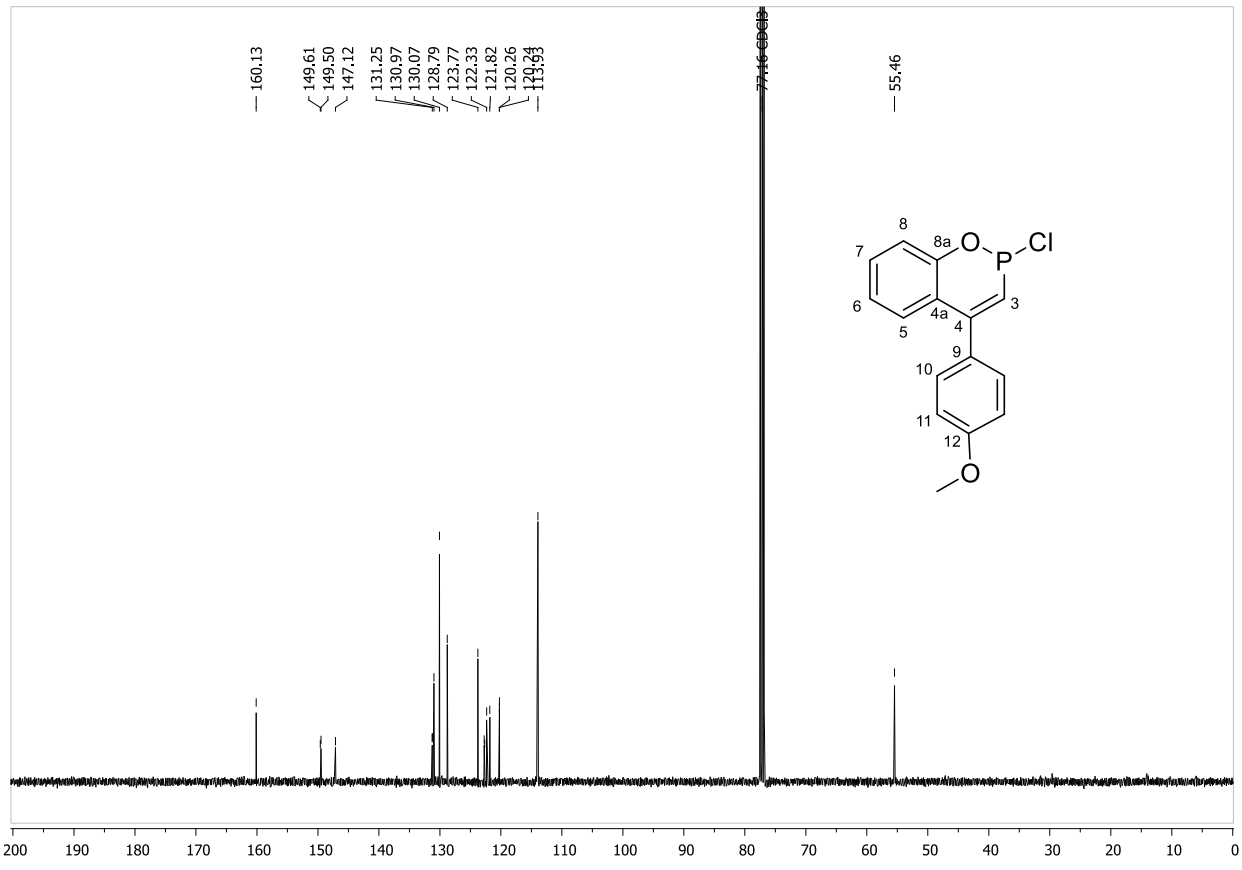
^{31}P NMR (243 MHz, $CDCl_3$) of compound **(6b)**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(6b)**

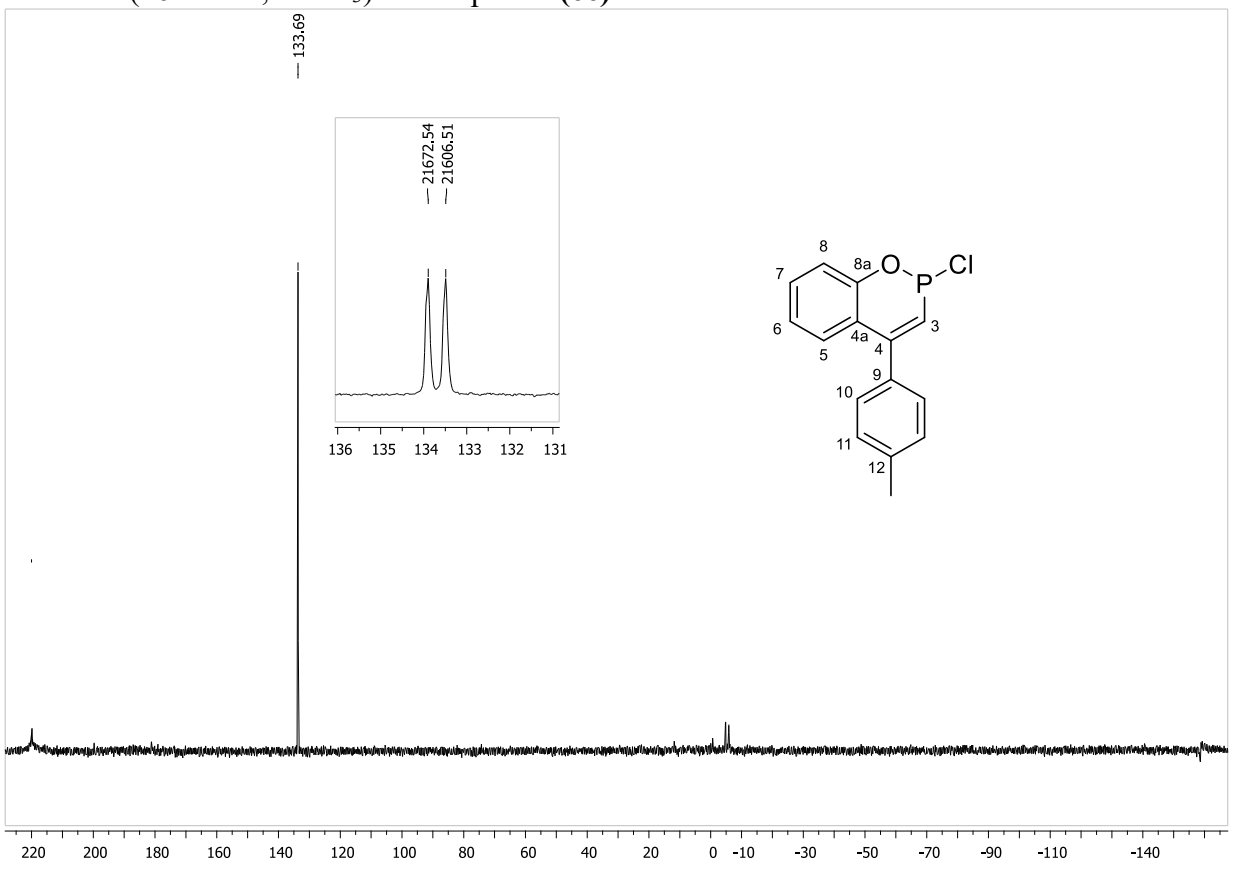


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(6b)**

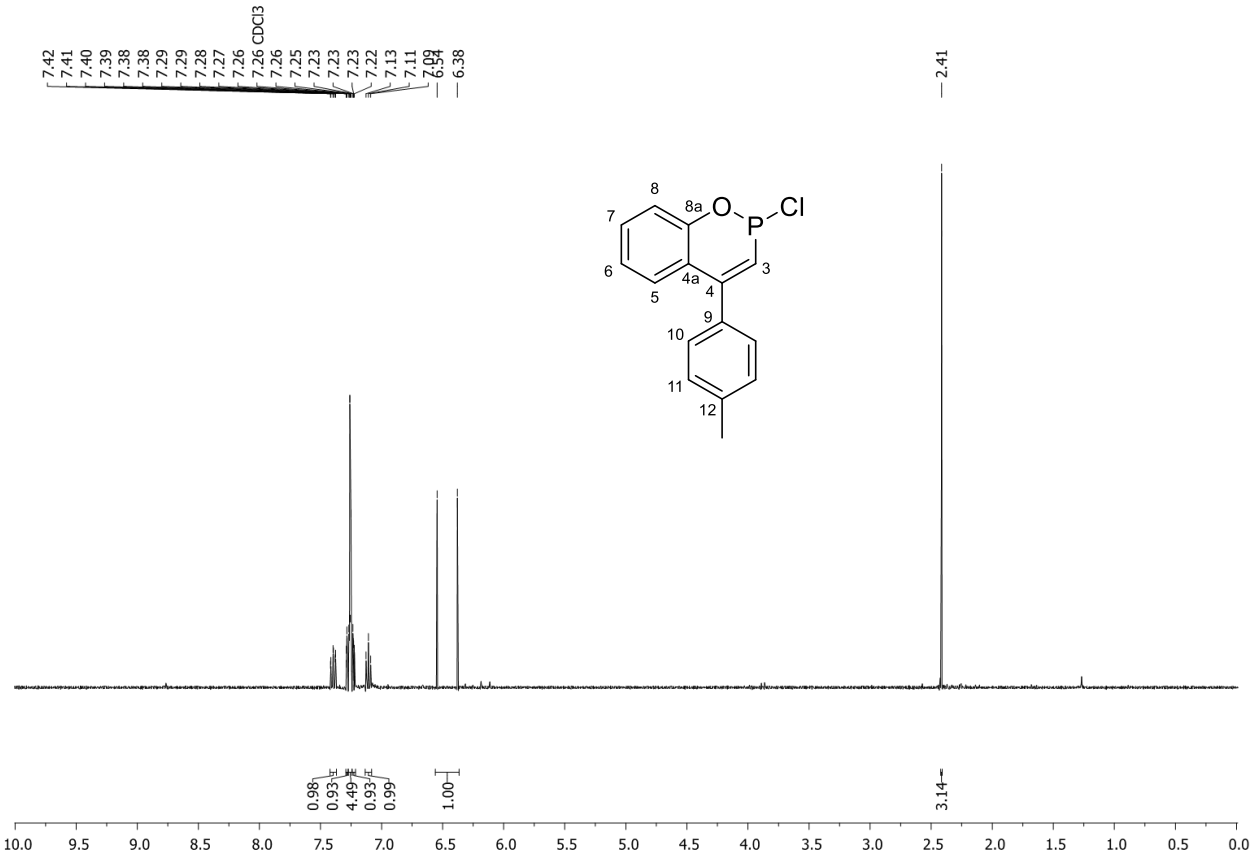


2-chloro-4-(p-tolyl)-2*H*-benzo[e][1,2]oxaphosphinine (6c)

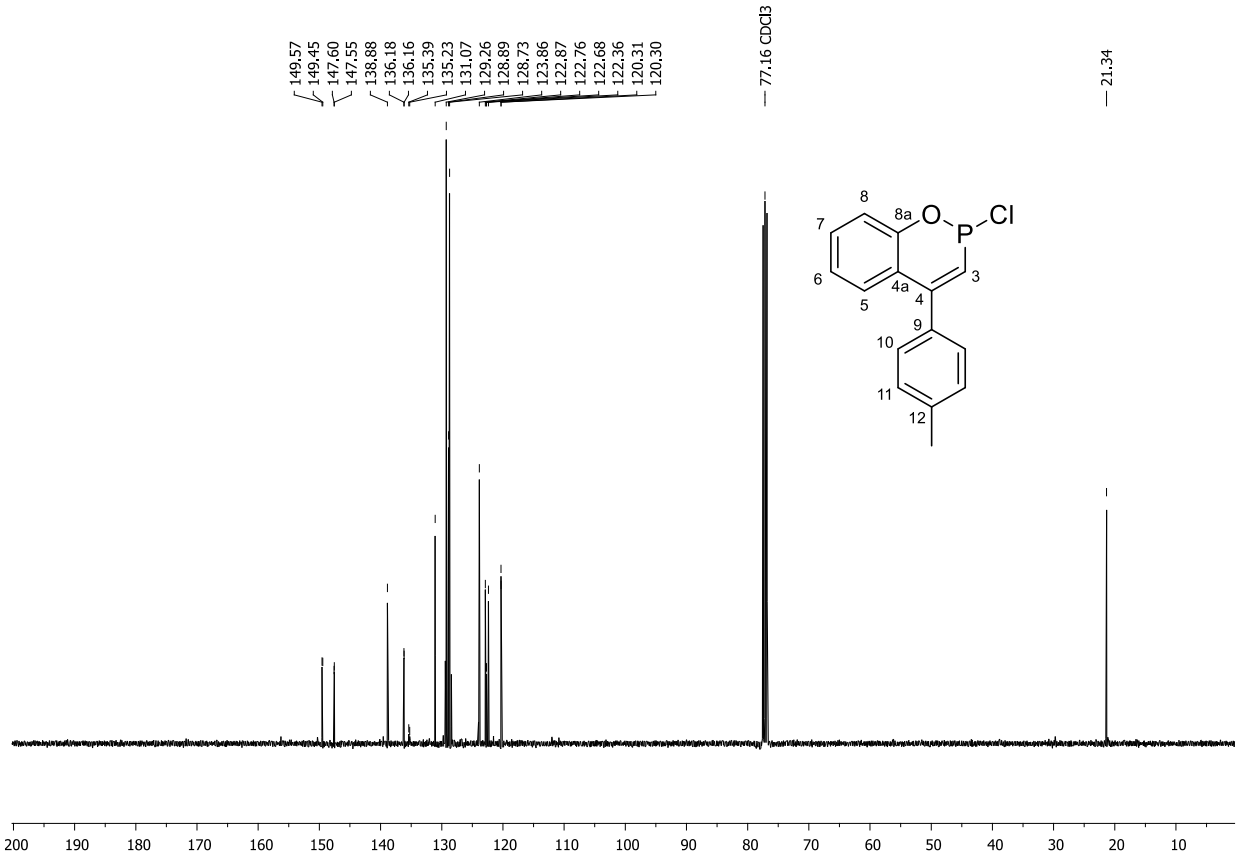
^{31}P NMR (162 MHz, $CDCl_3$) of compound **(6c)**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(6c)**

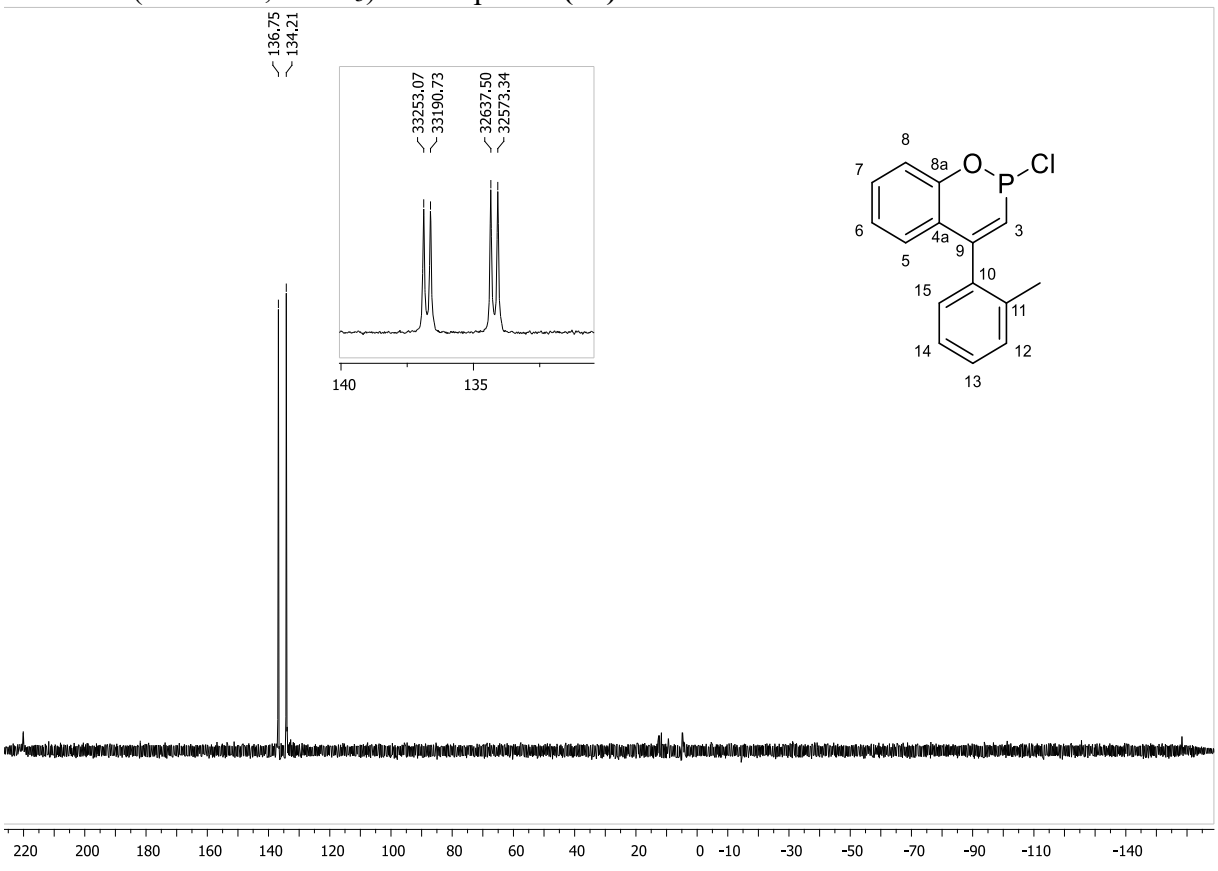


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(6c)**

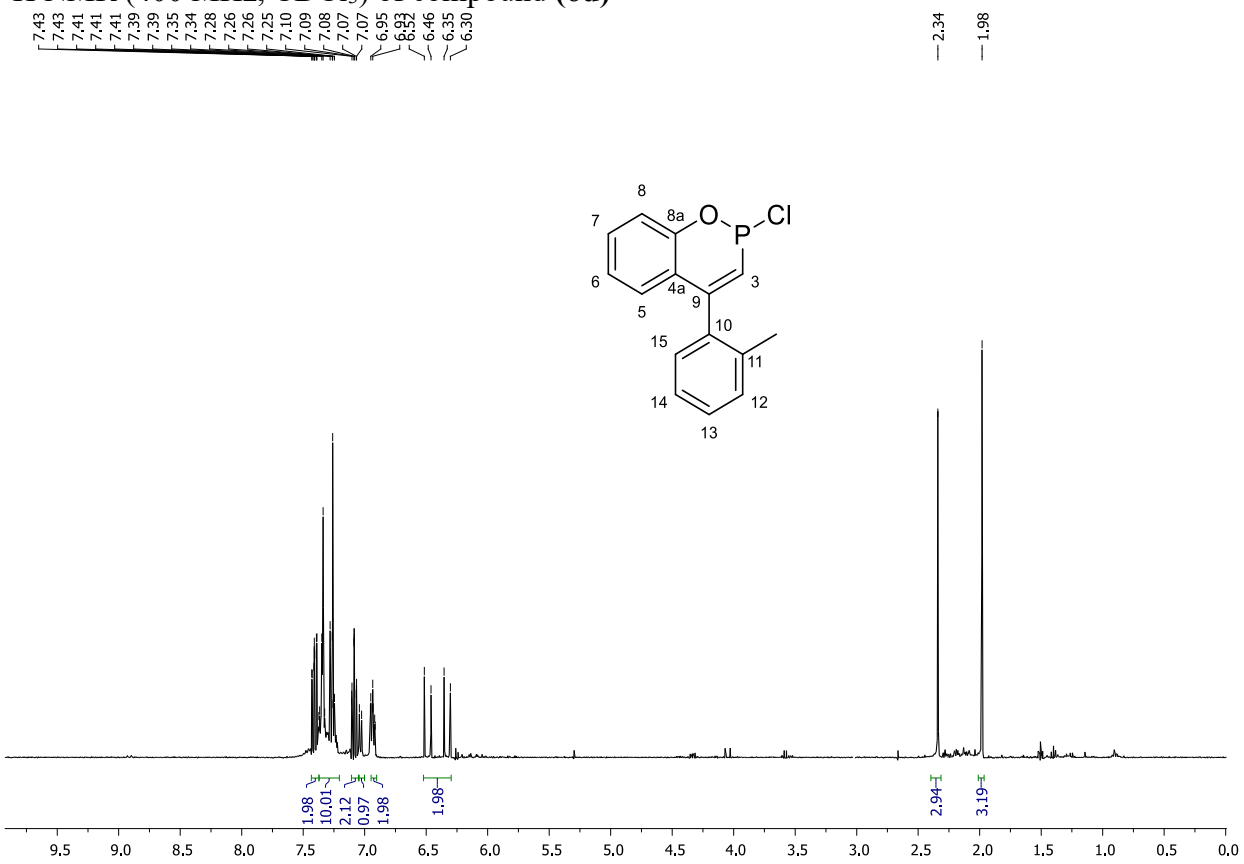


2-chloro-4-(o-tolyl)-2*H*-benzo[*e*][1,2]oxaphosphinine (6d)

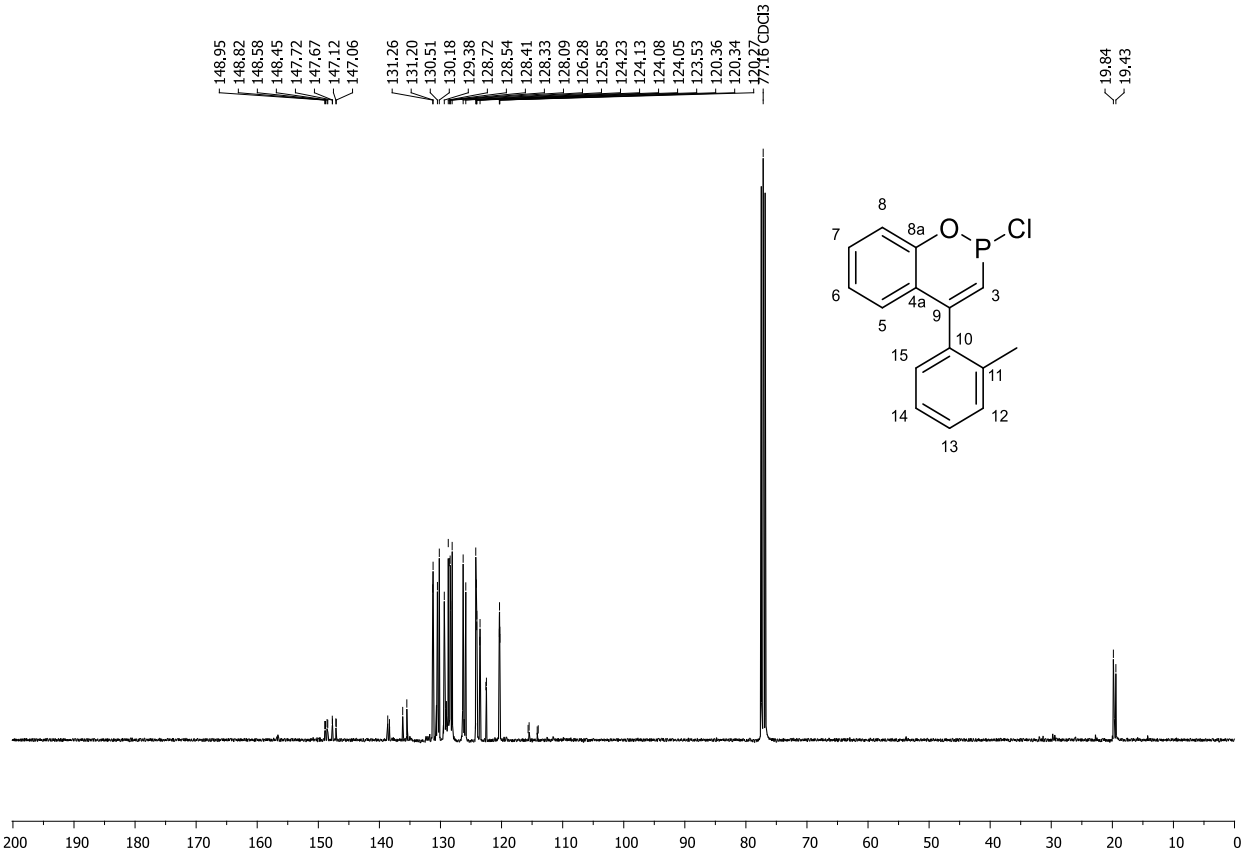
^{31}P NMR (243 MHz, $CDCl_3$) of compound **(6d)**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(6d)**

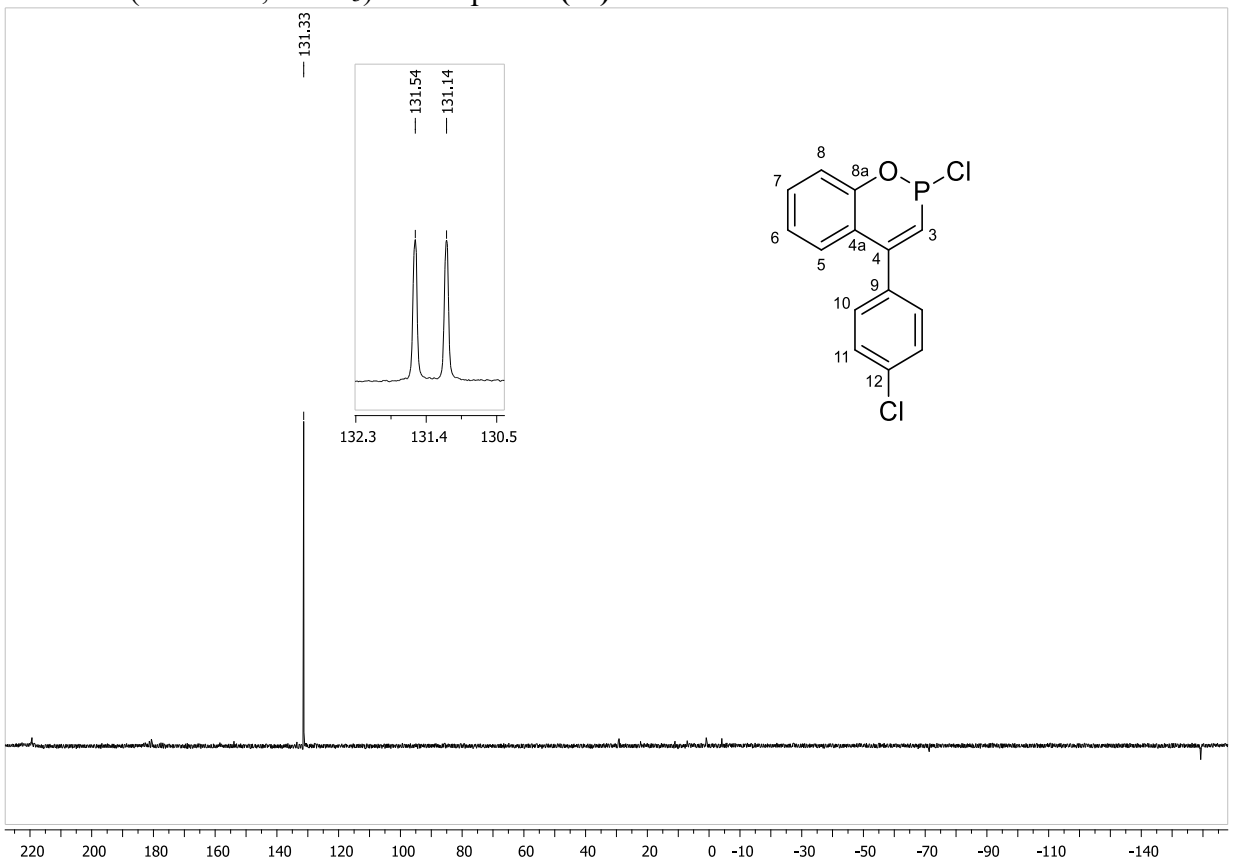


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(6d)**

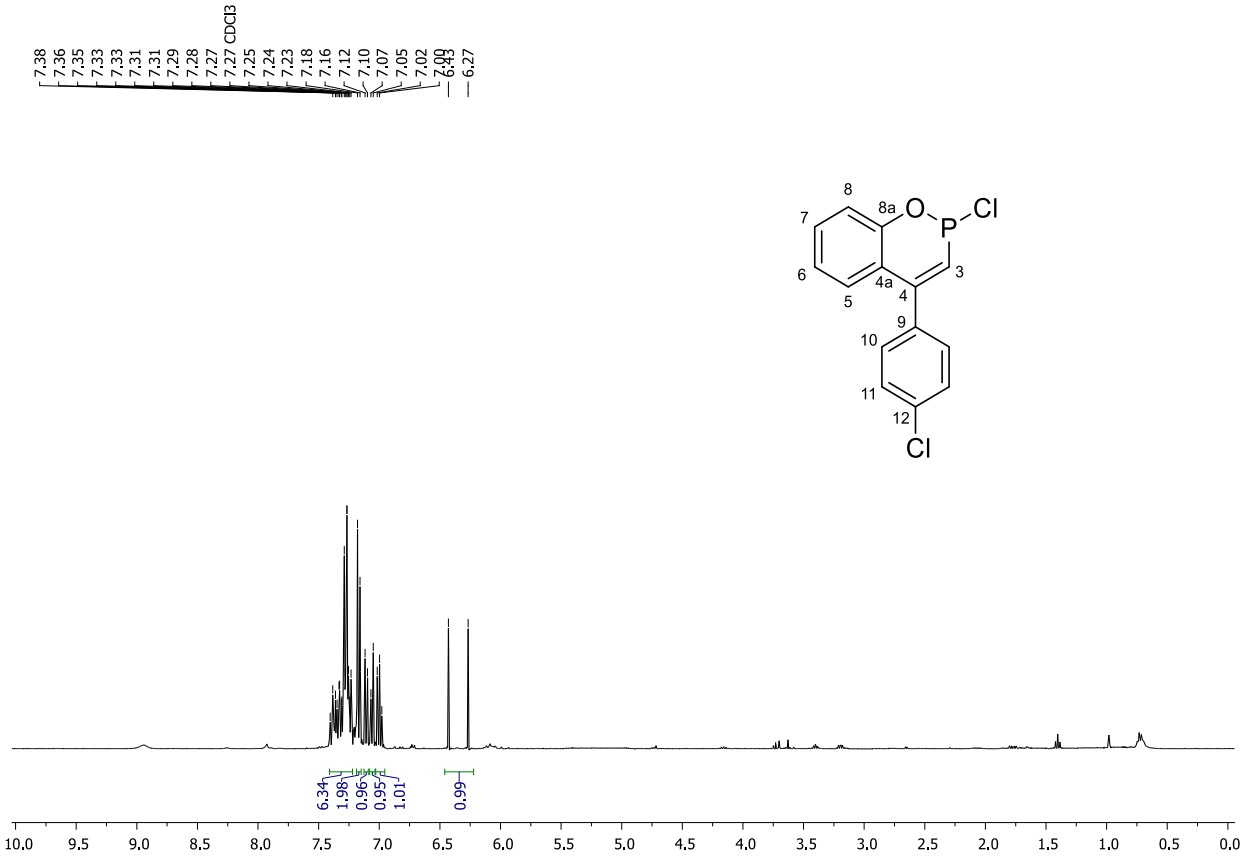


2-chloro-4-(4-chlorophenyl)-2*H*-benzo[*e*][1,2]oxaphosphinine (6e)

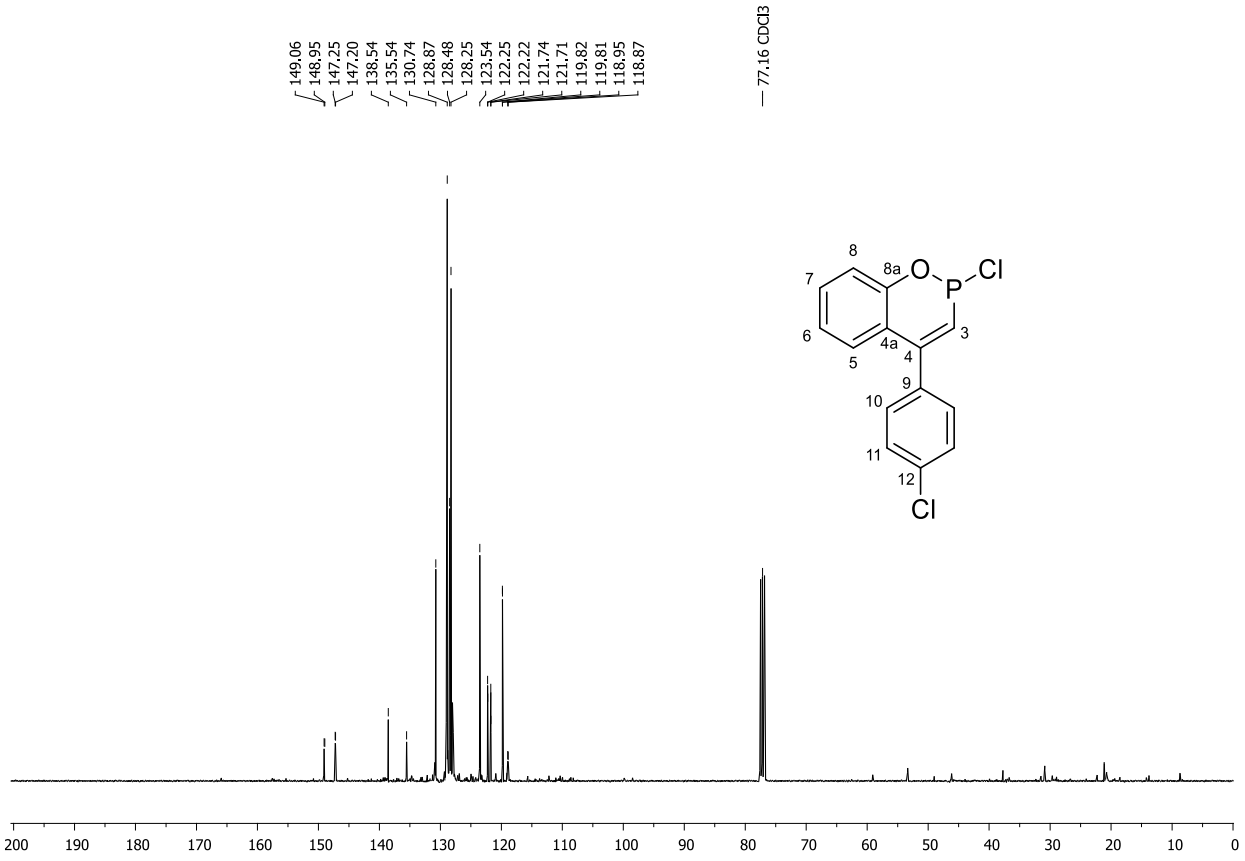
^{31}P NMR (162 MHz, $CDCl_3$) of compound **(6e)**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(6e)**

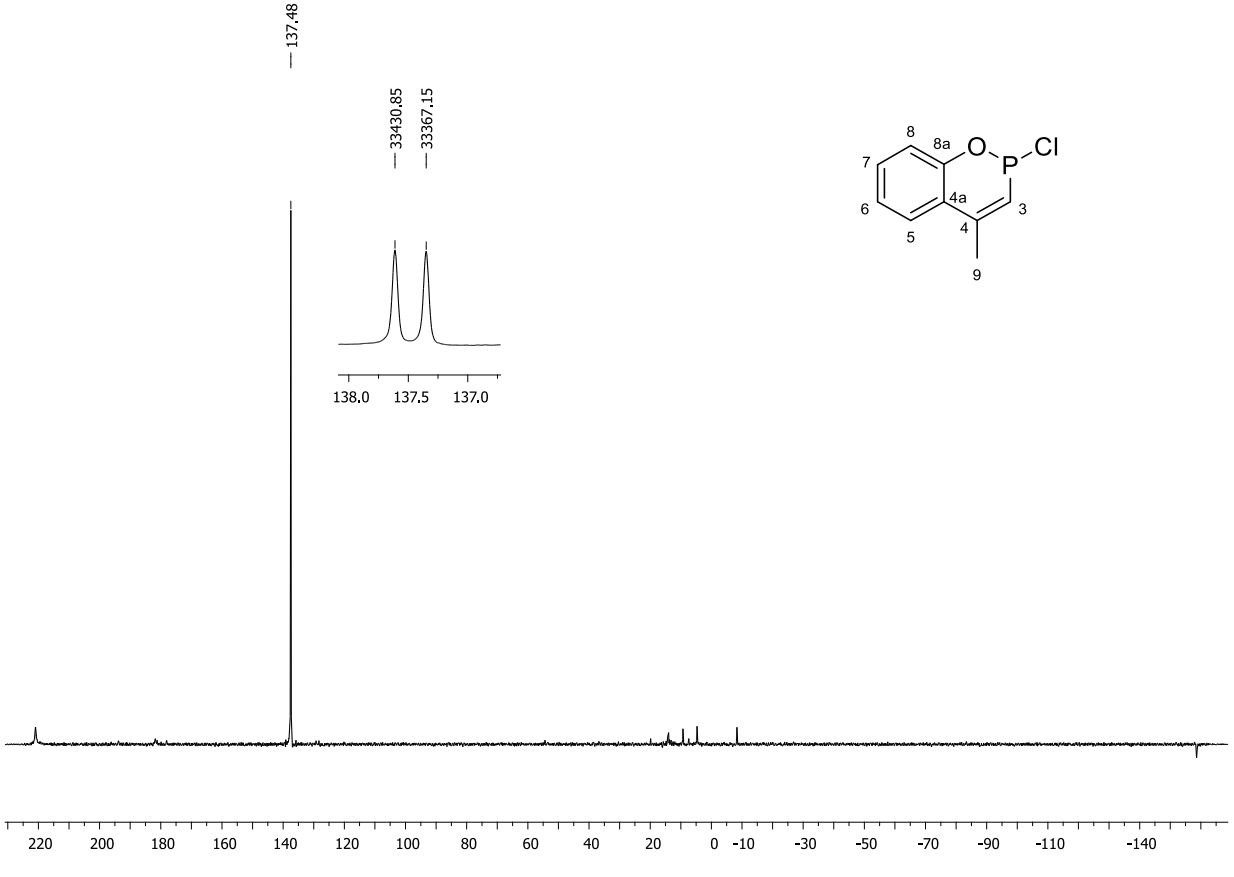


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(6e)**

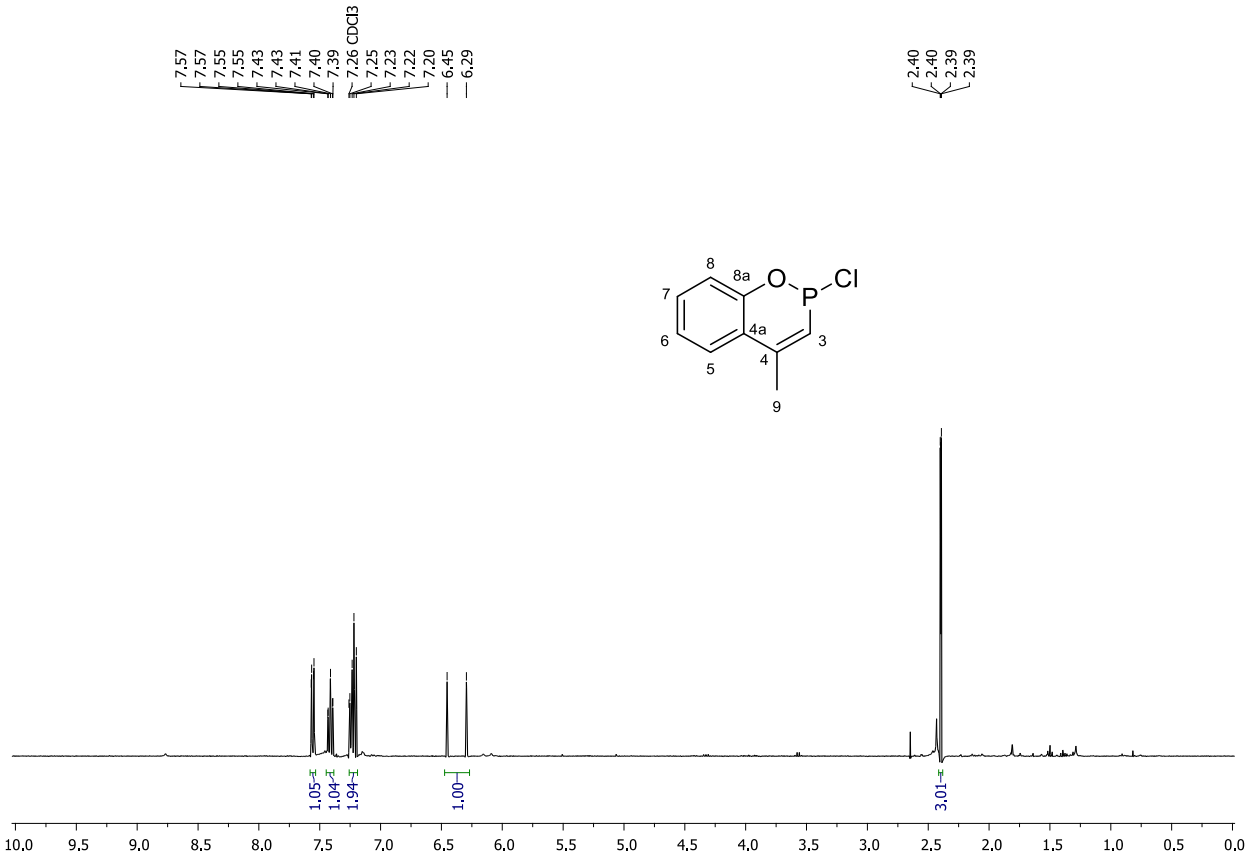


2-chloro-4-methyl-2*H*-benzo[*e*][1,2]oxaphosphinine (6f)

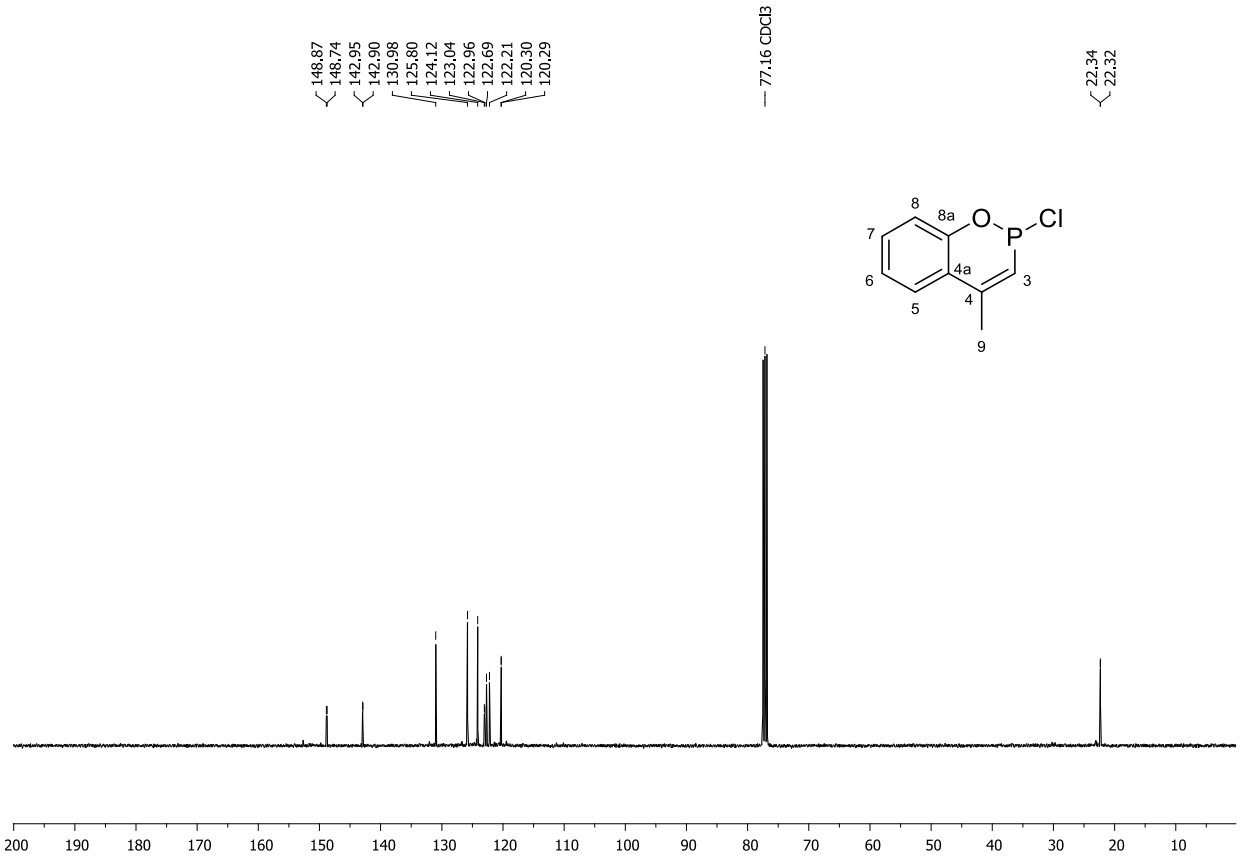
^{31}P NMR (243 MHz, $CDCl_3$) of compound **(6f)**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(6f)**

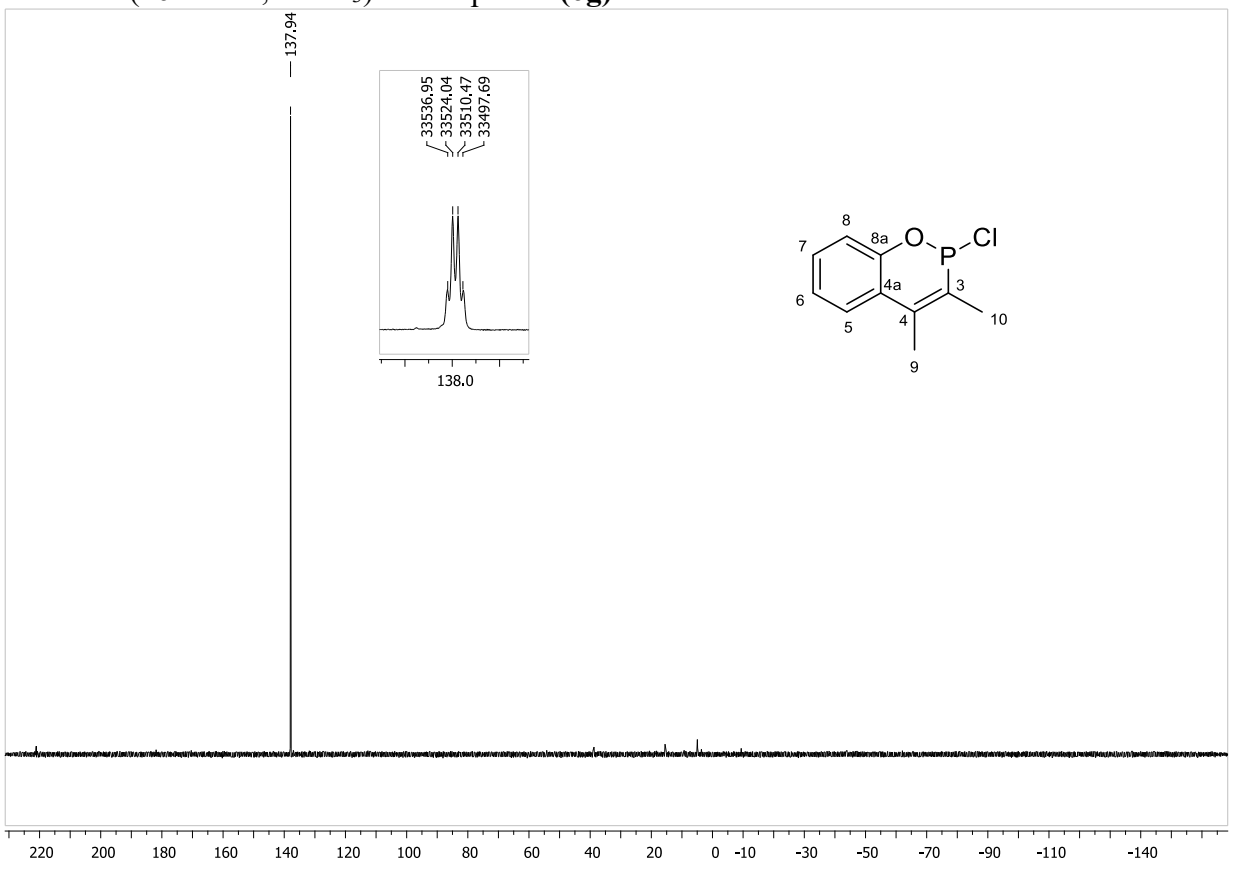


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(6f)**

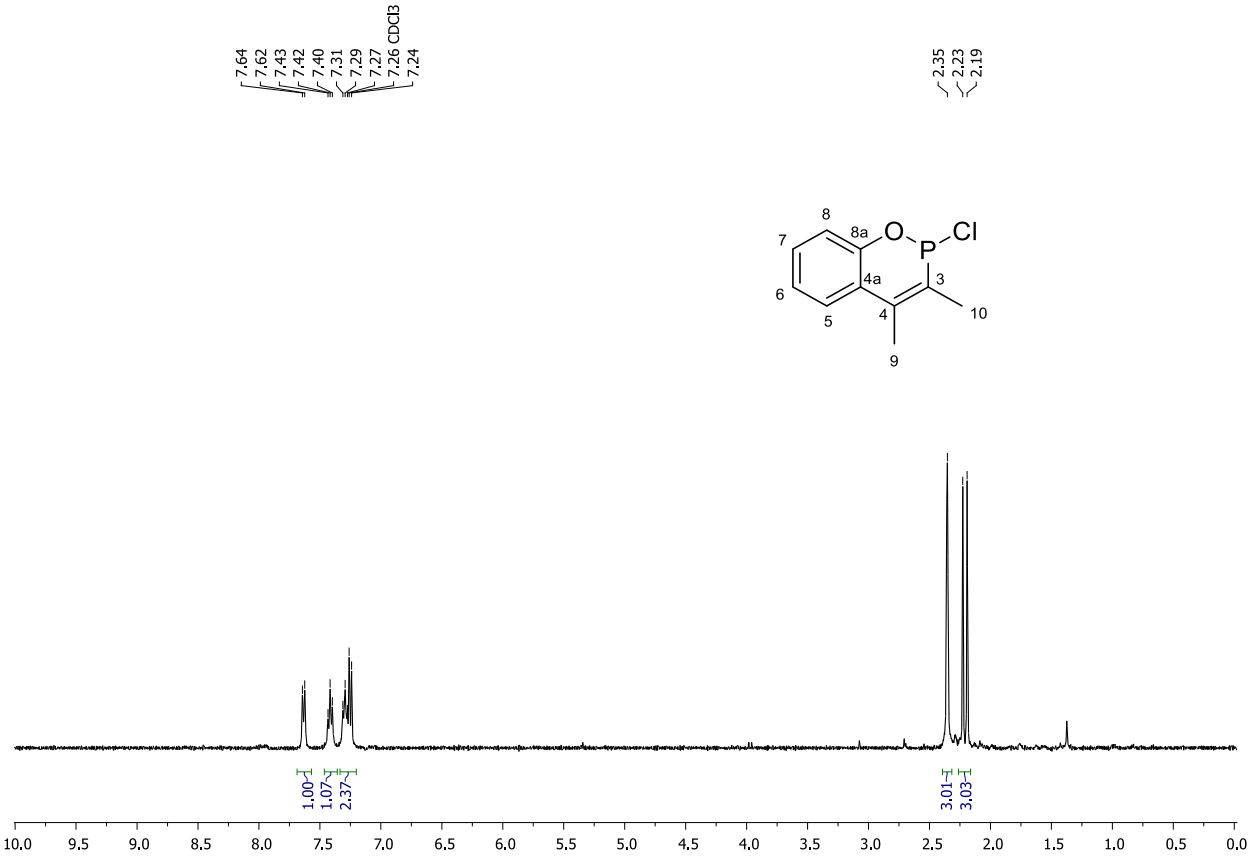


2-chloro-3,4-dimethyl-2*H*-benzo[*e*][1,2]oxaphosphinine (6g)

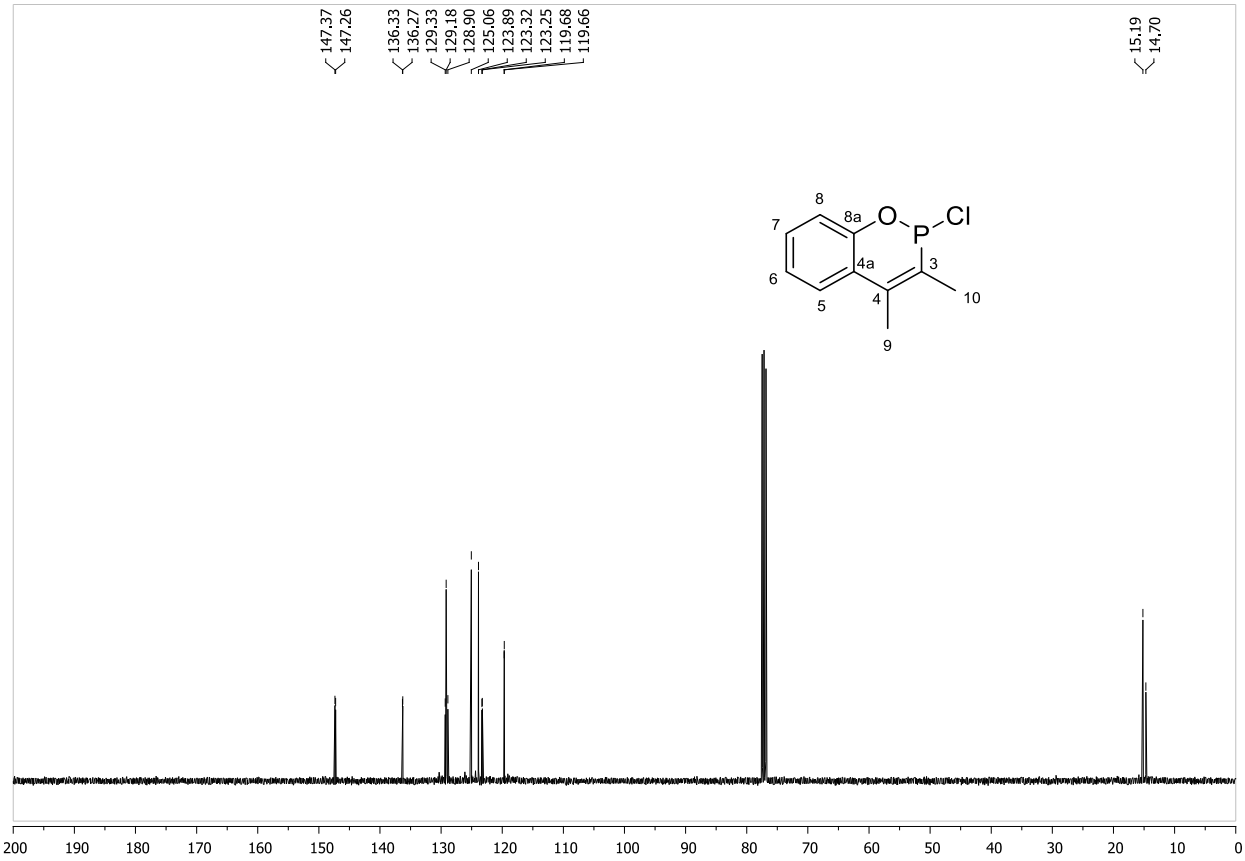
^{31}P NMR (162 MHz, $CDCl_3$) of compound **(6g)**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(6g)**

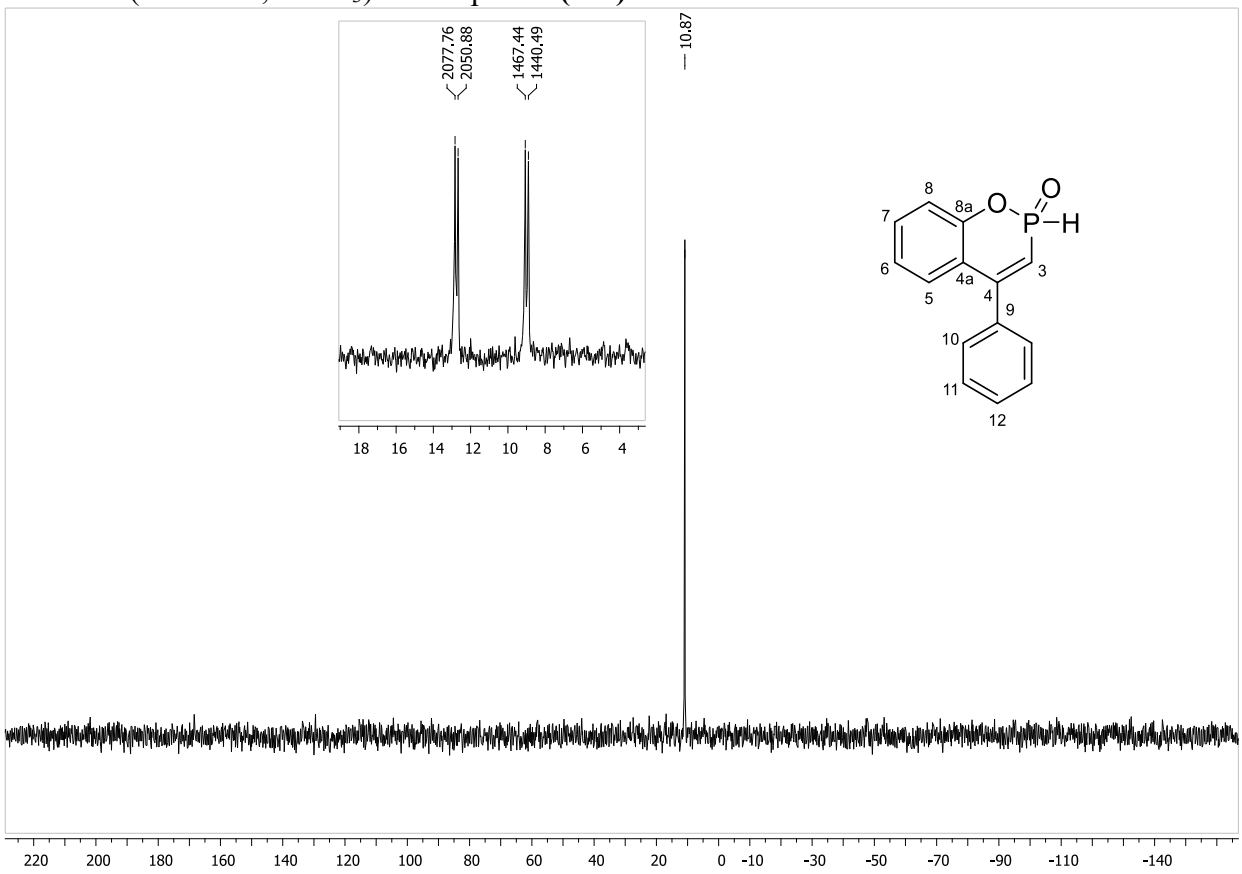


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(6g)**

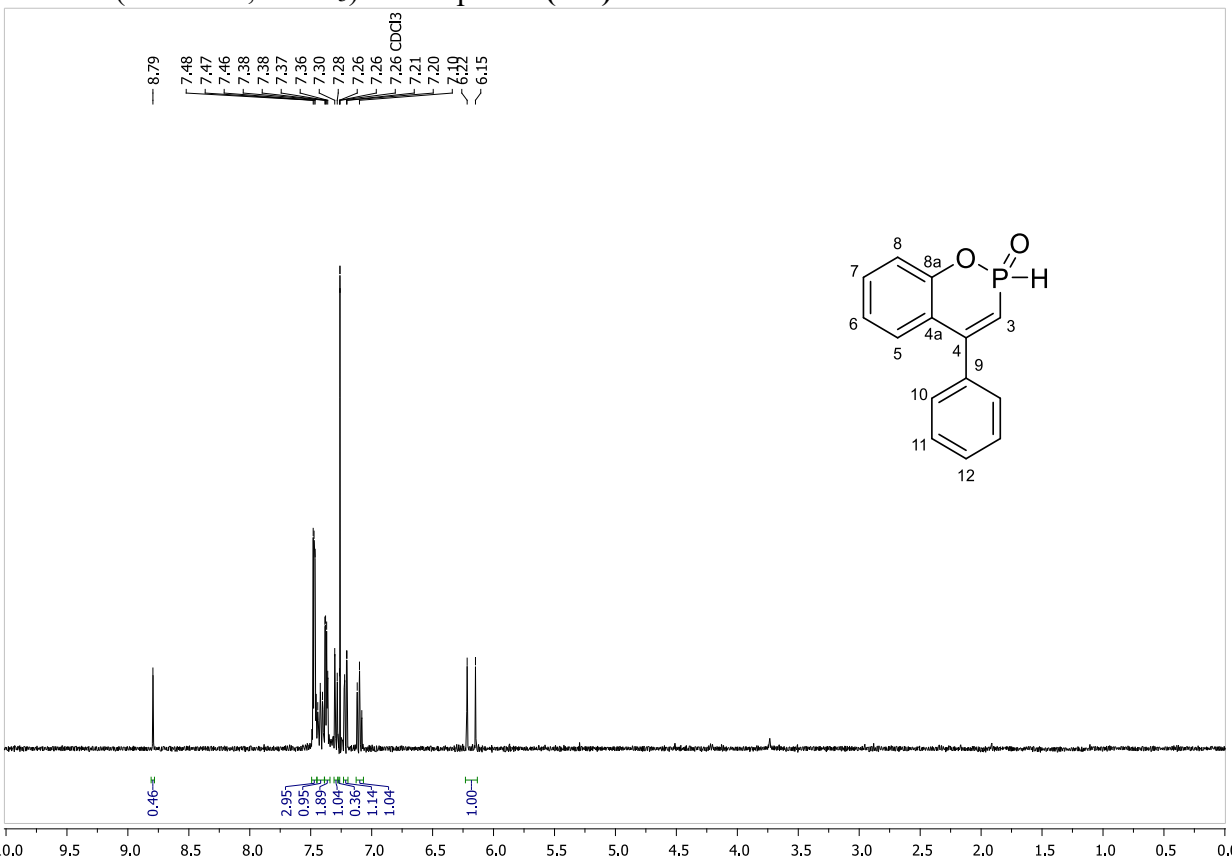


4-phenylbenzo[*e*][1,2]oxaphosphinine 2-oxide (11a)

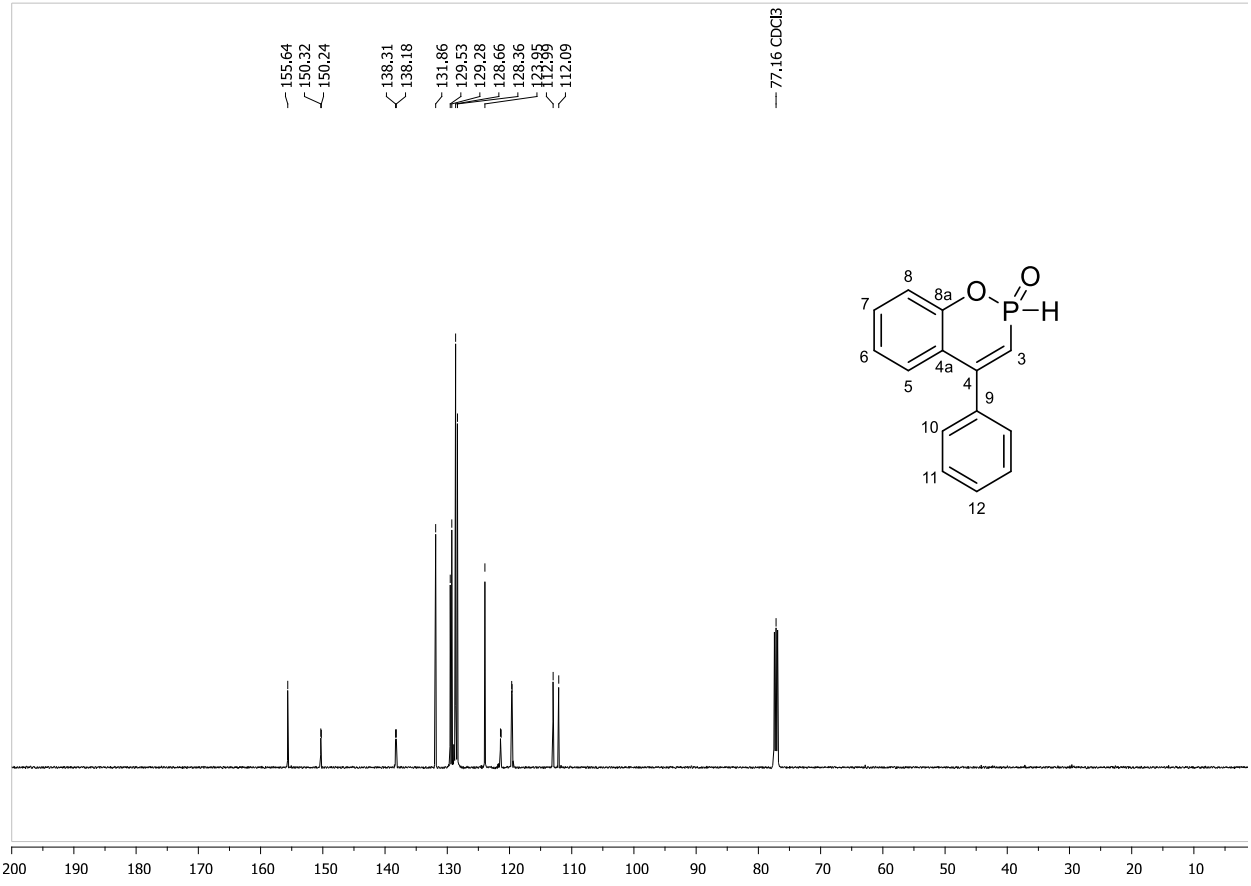
^{31}P NMR (162 MHz, $CDCl_3$) of compound **(11a)**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(11a)**

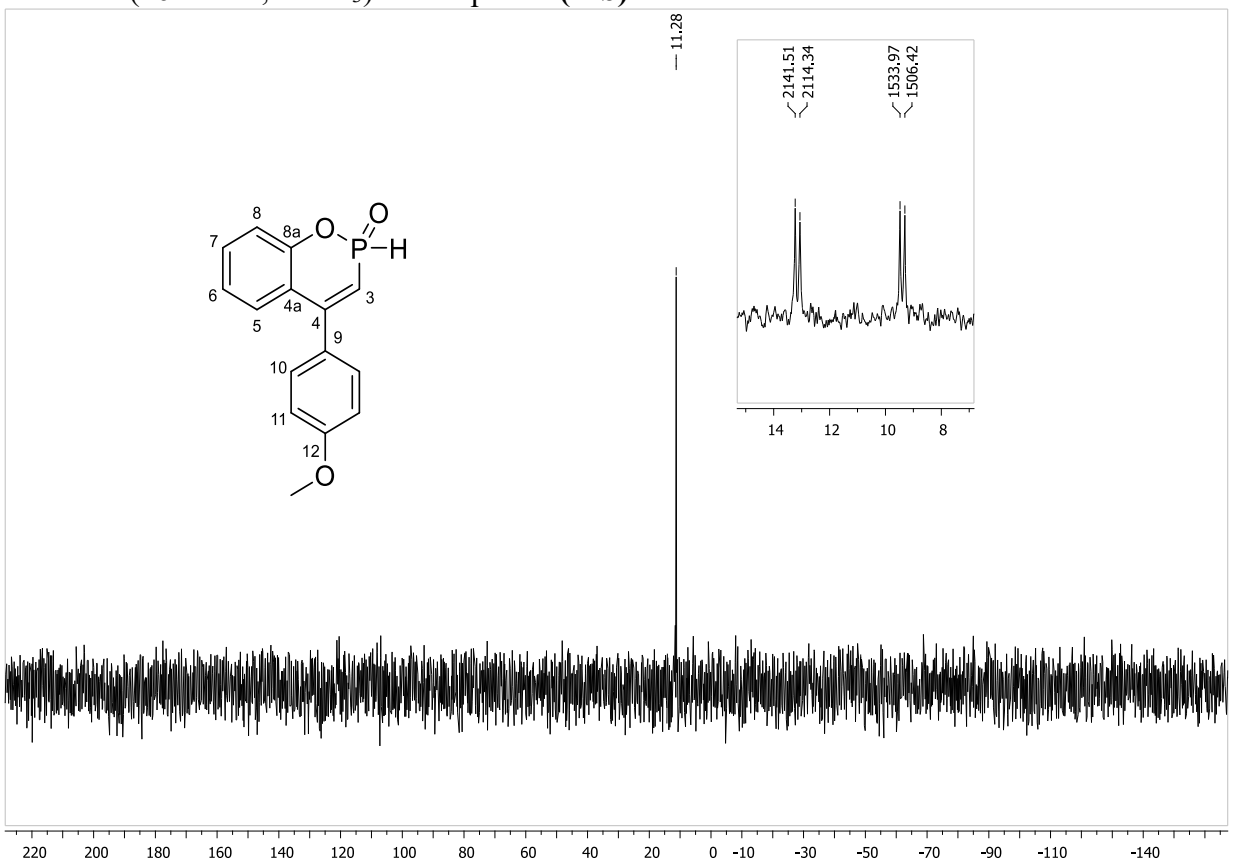


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(11a)**

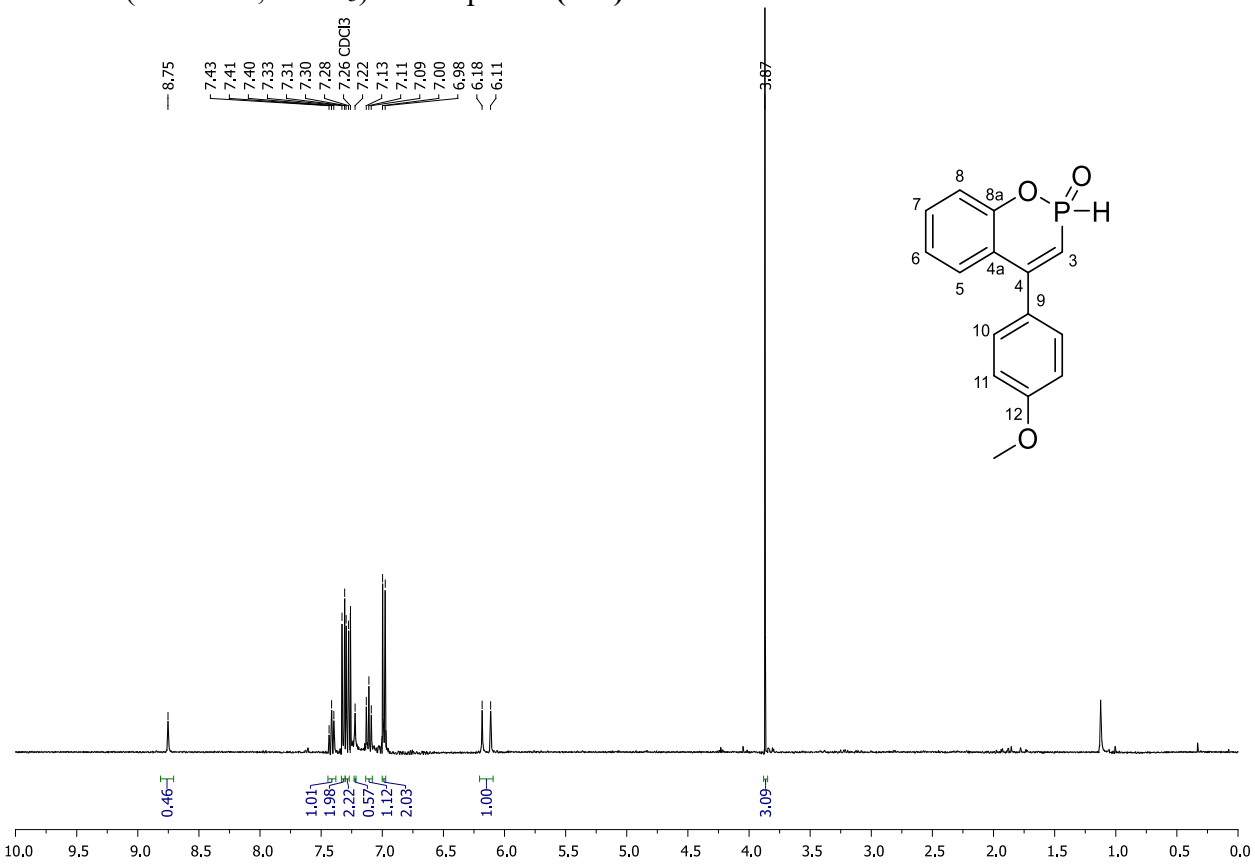


4-(4-methoxyphenyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (11b)

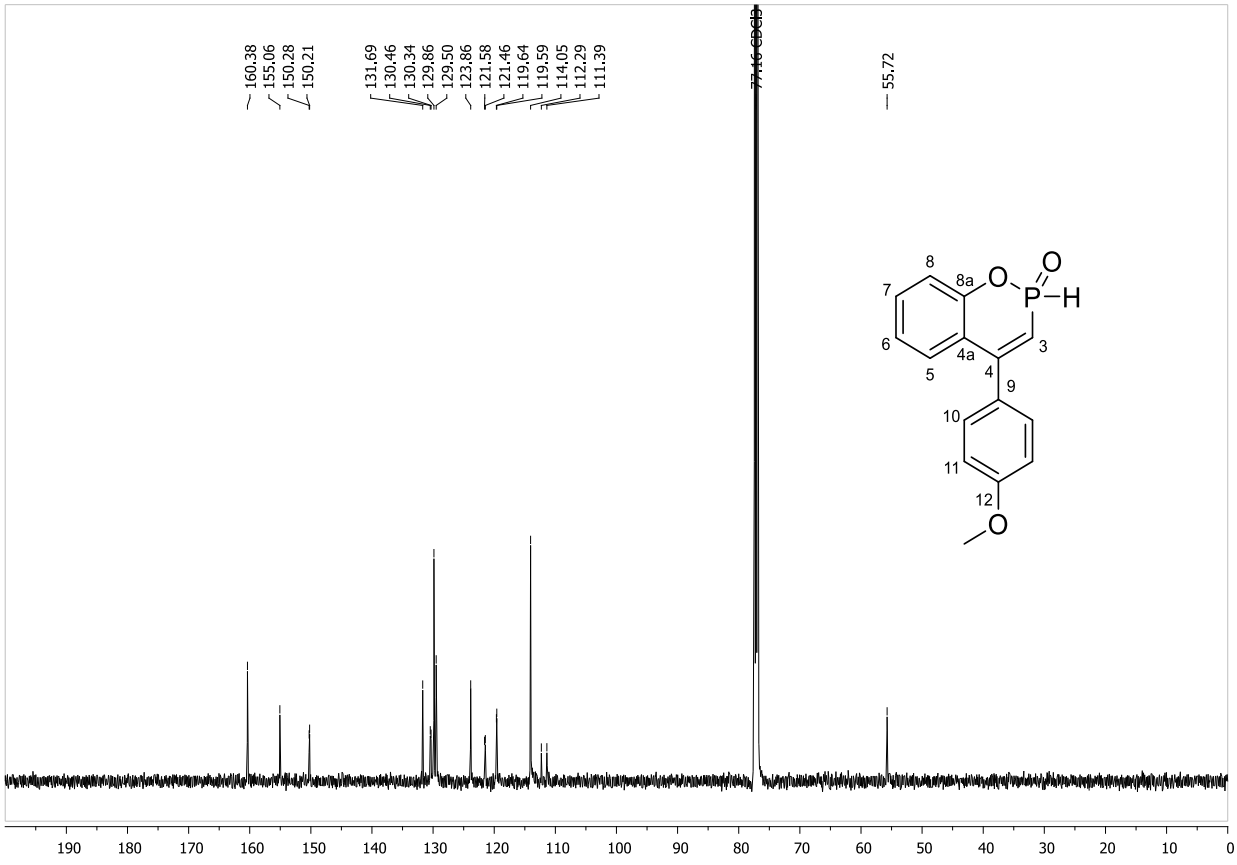
^{31}P NMR (162 MHz, $CDCl_3$) of compound **(11b)**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(11b)**

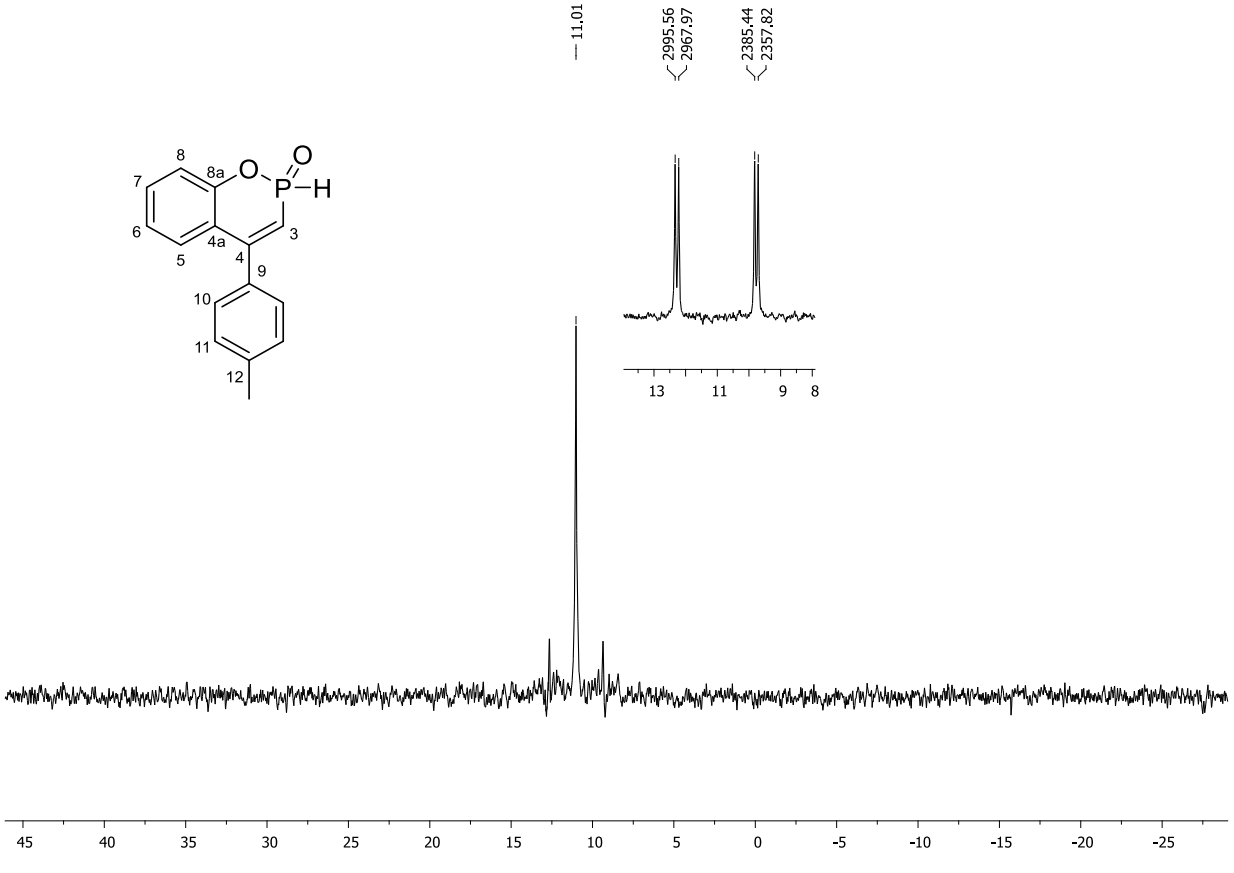


^{13}C NMR (126 MHz, $CDCl_3$) of compound **(11b)**

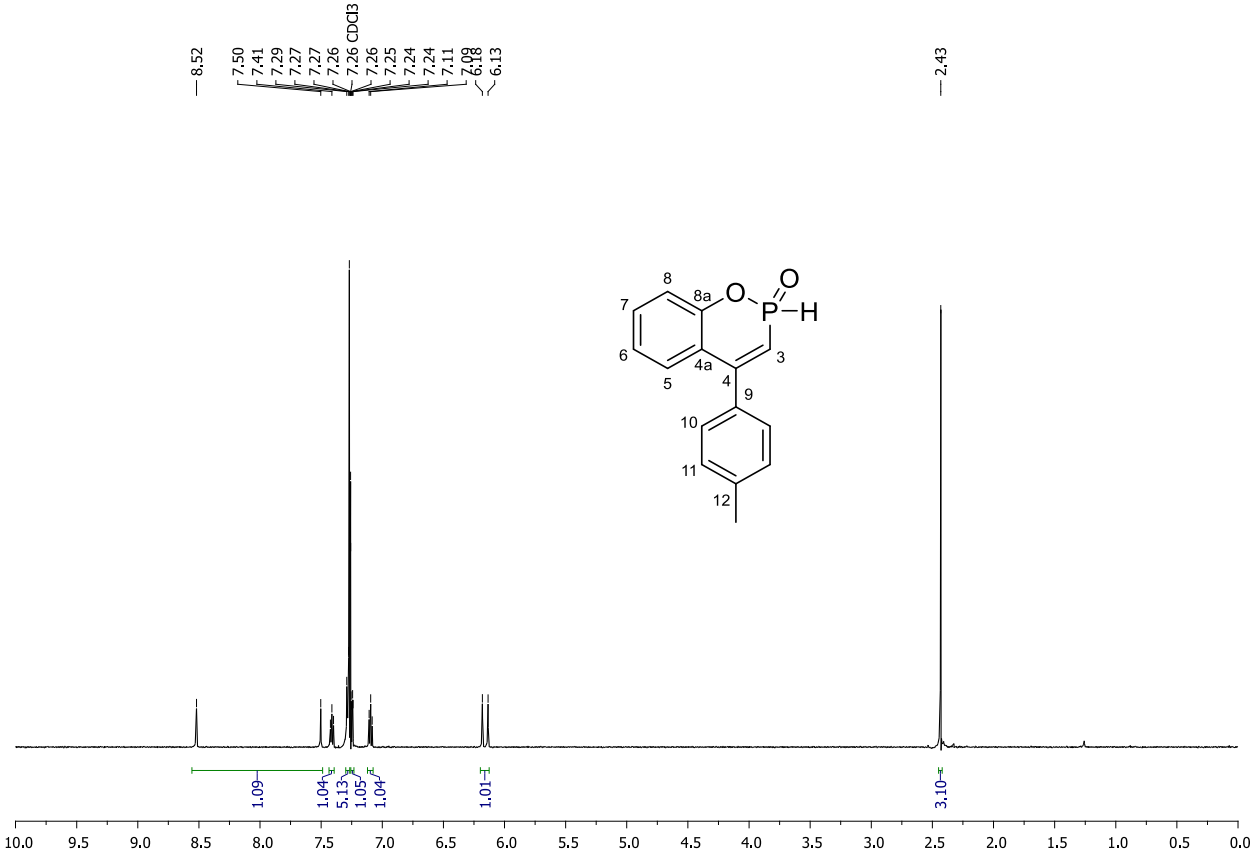


4-(p-tolyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (11c)

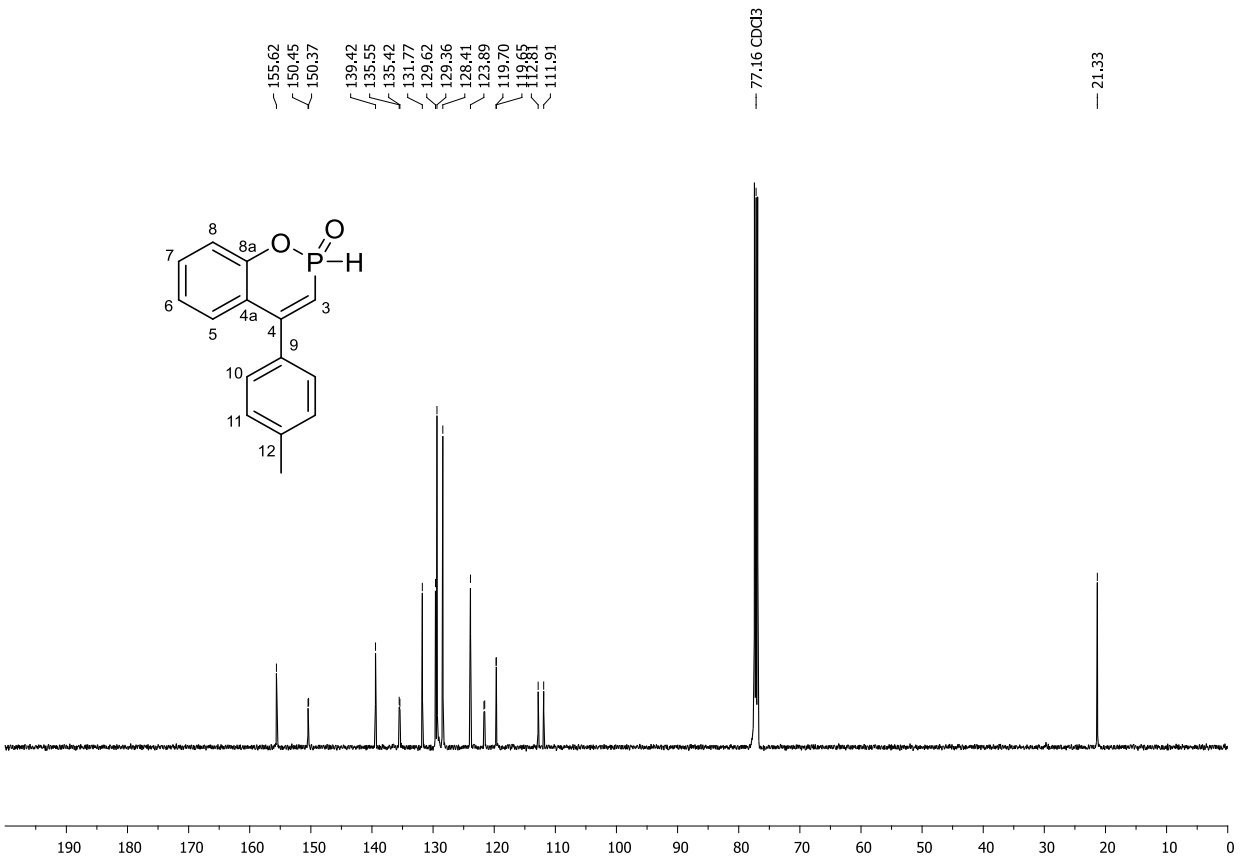
^{31}P NMR (243 MHz, $CDCl_3$) of compound **(11c)**



^{1}H NMR (600 MHz, $CDCl_3$) of compound **(11c)**

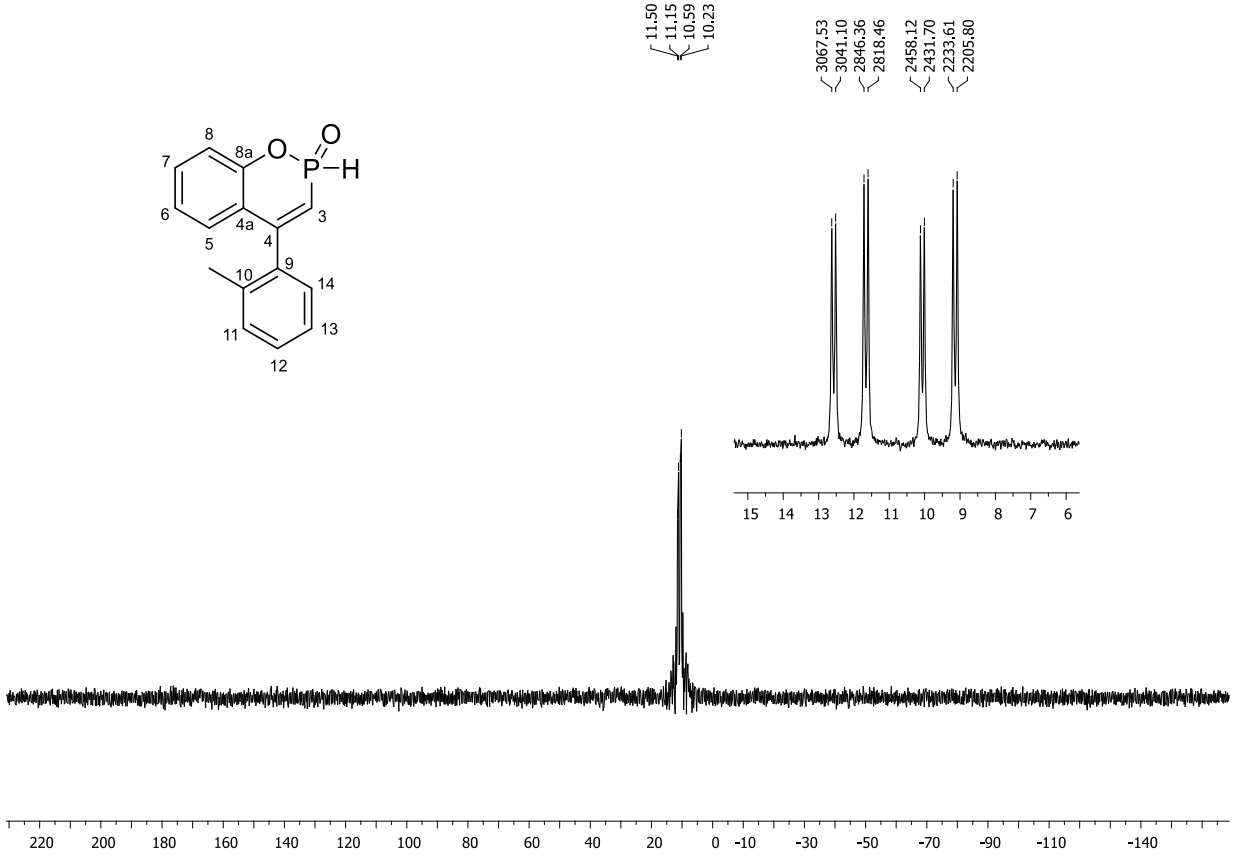


^{13}C NMR (126 MHz, $CDCl_3$) of compound **(11c)**

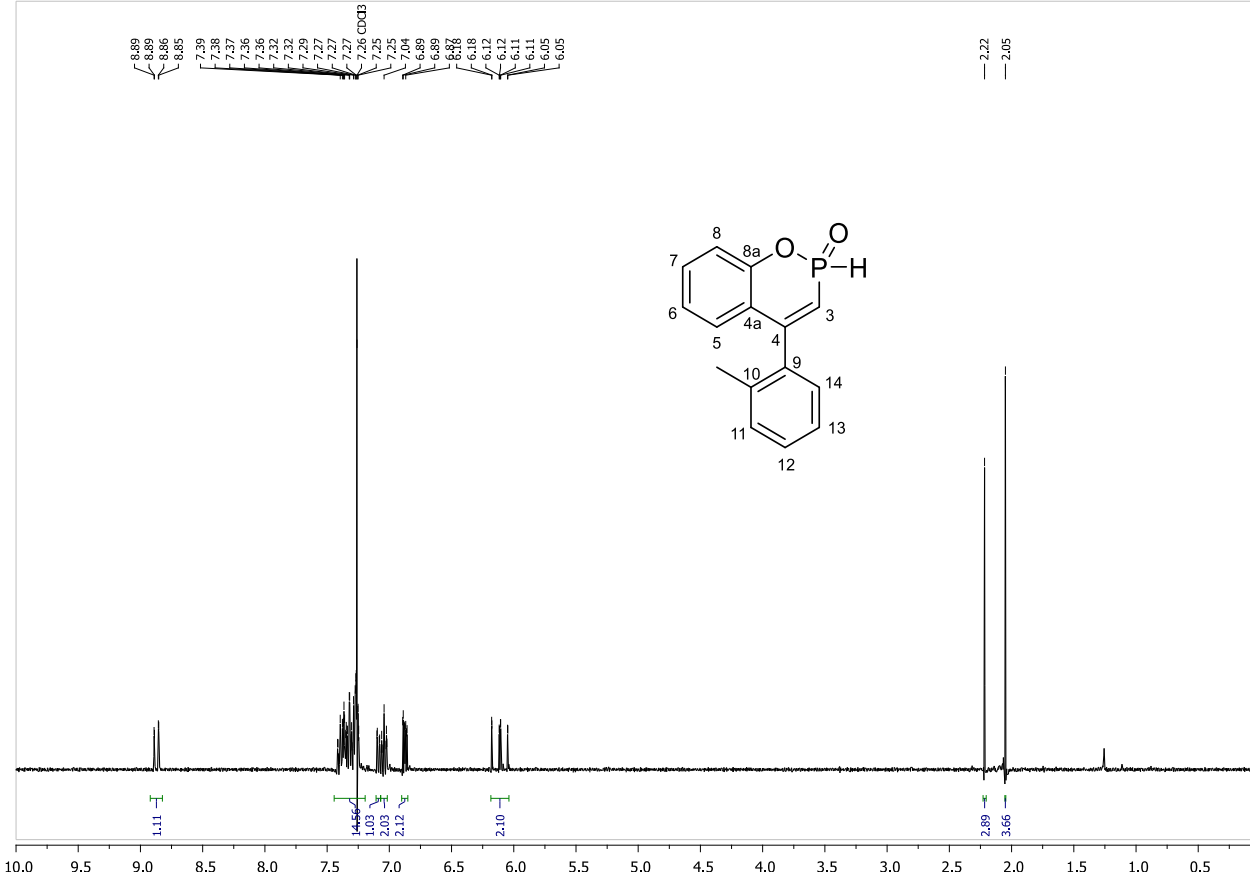


4-(o-tolyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (**11d**)

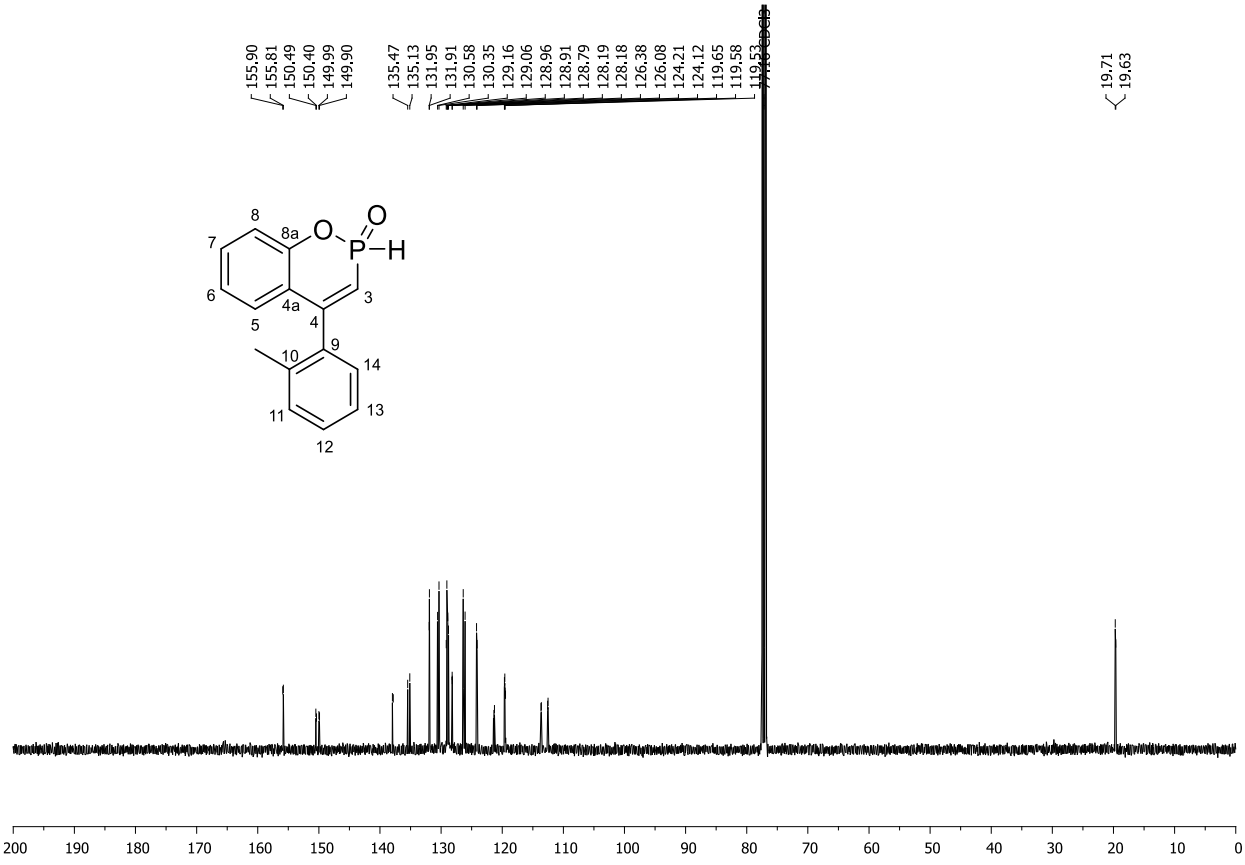
^{31}P NMR (243 MHz, $CDCl_3$) of compound **(11d)**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(11d)**

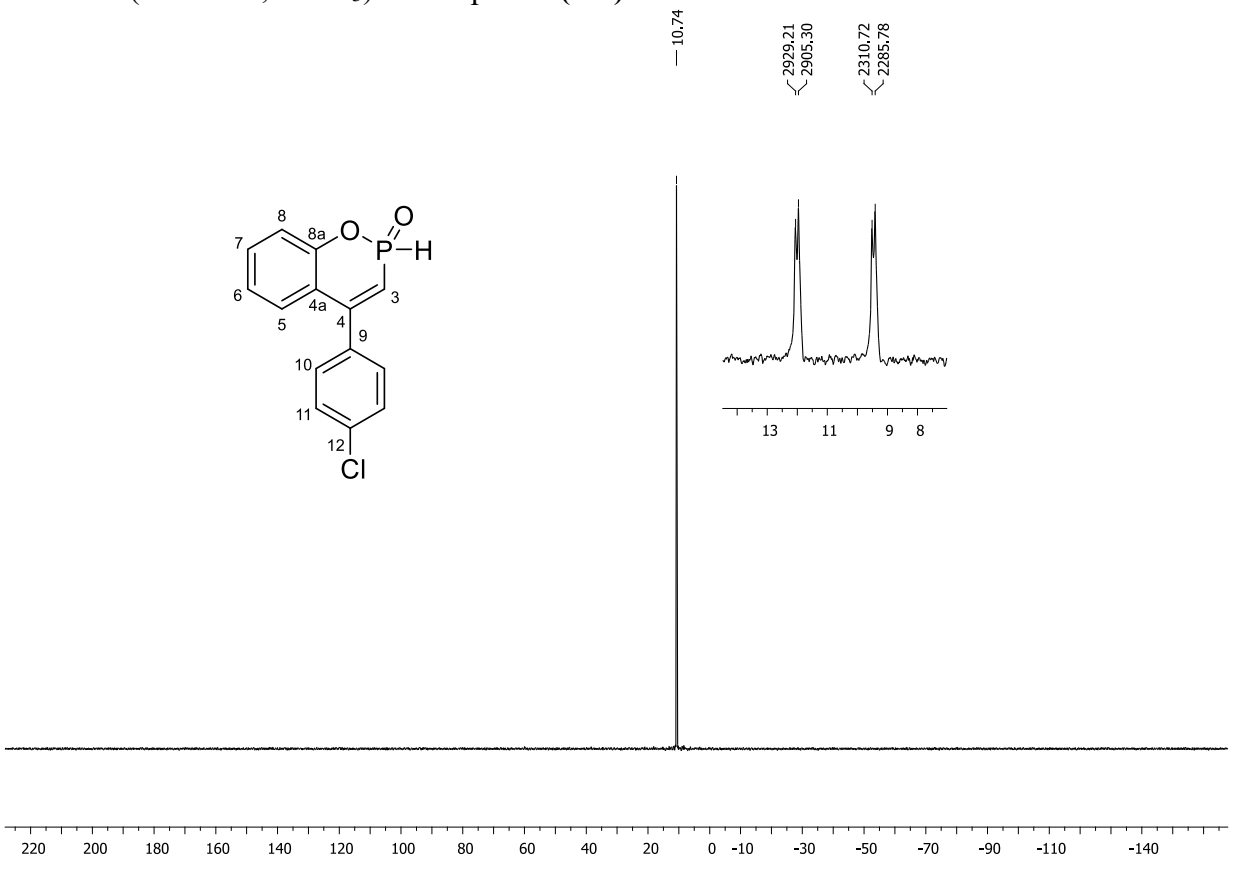


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(11d)**

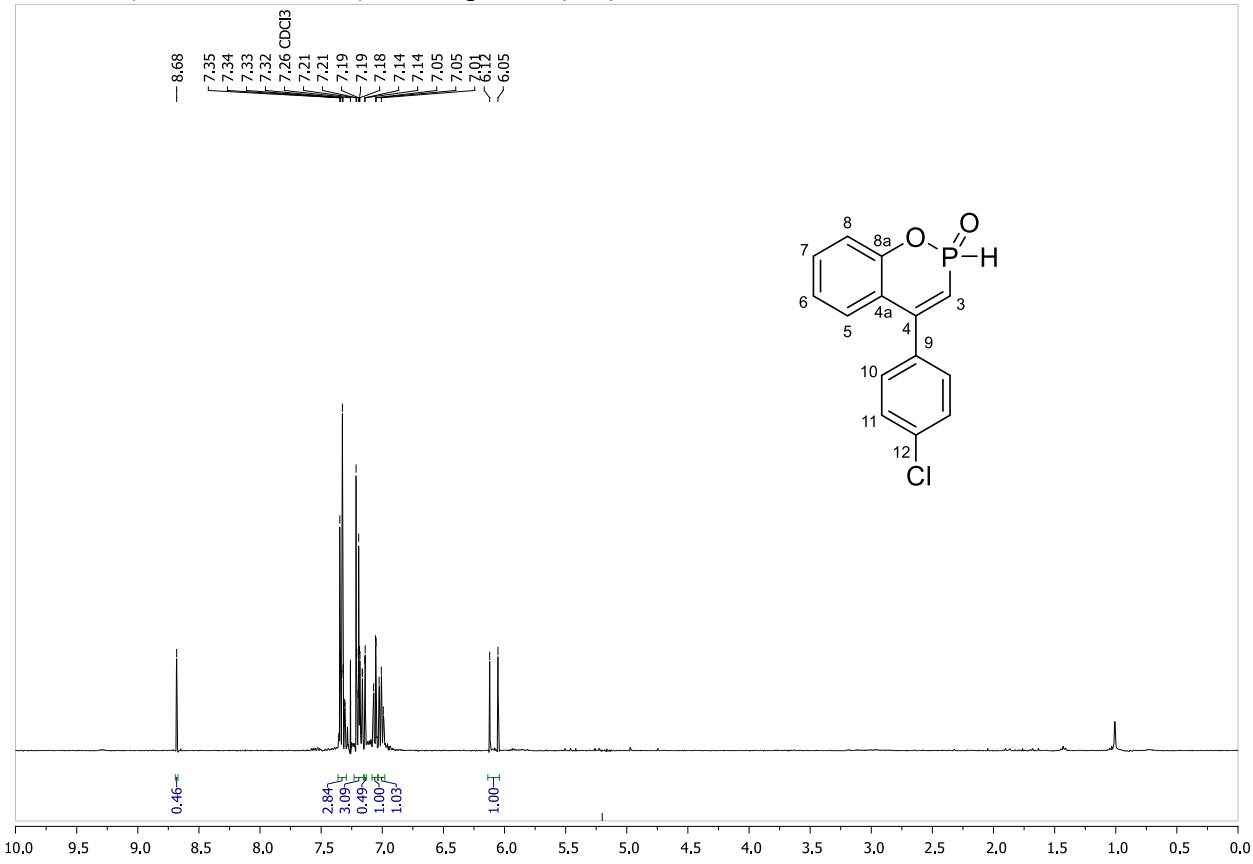


4-(4-chlorophenyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (11e)

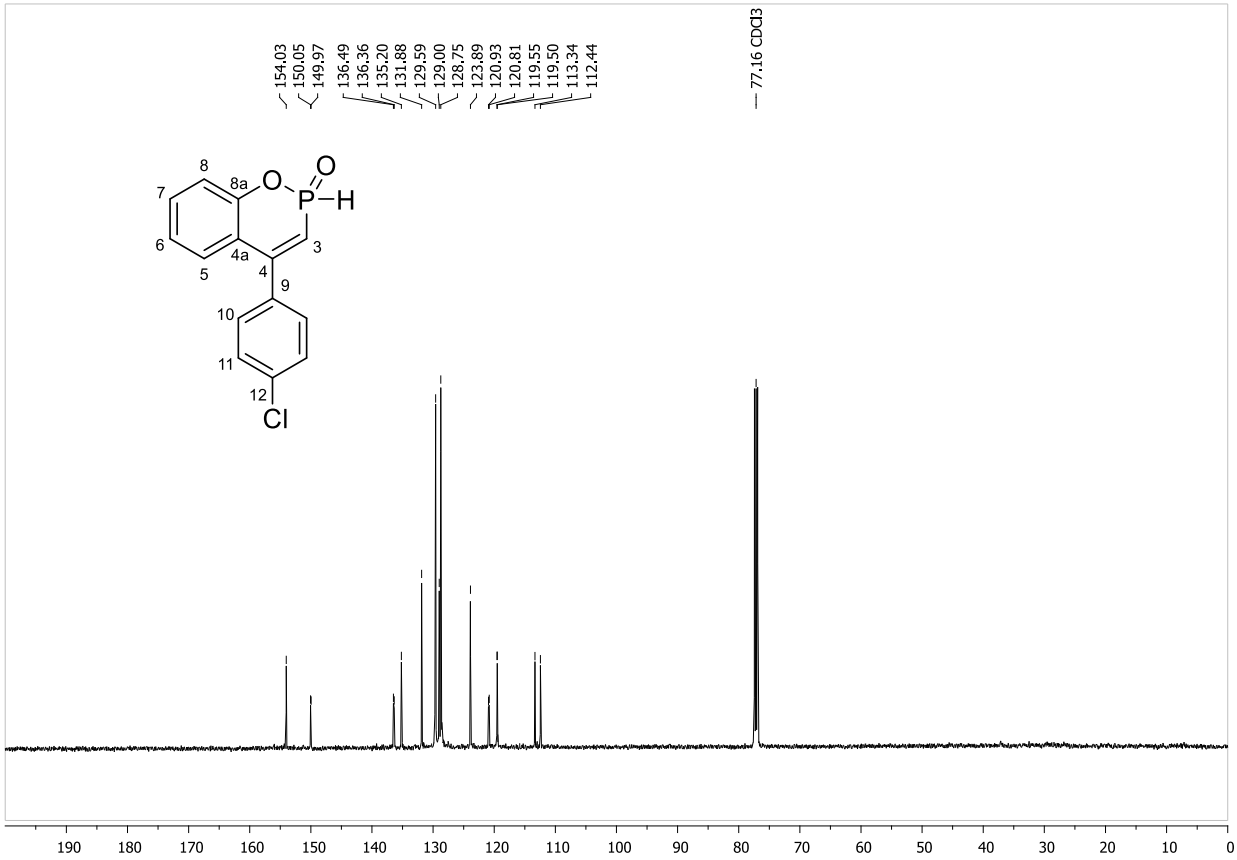
^{31}P NMR (243 MHz, $CDCl_3$) of compound **(11e)**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(11e)**

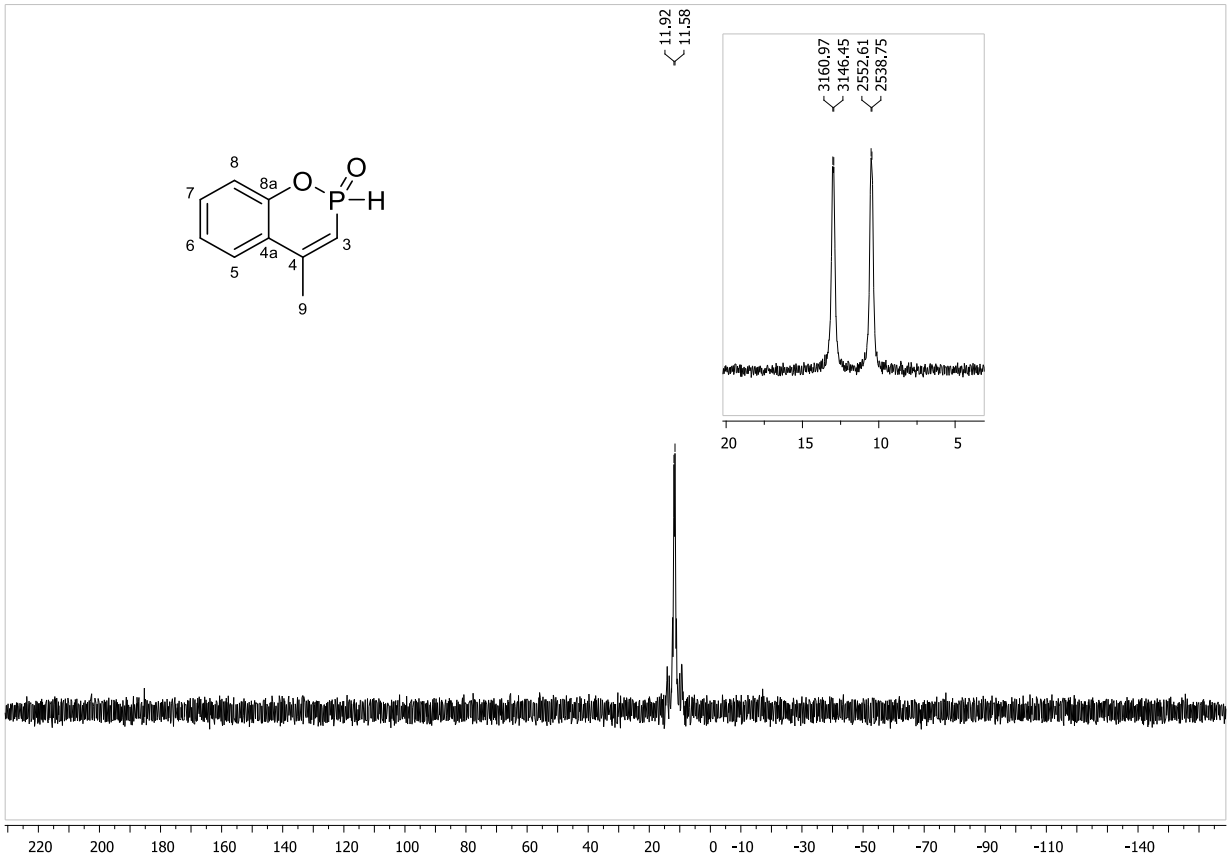


^{13}C NMR (126 MHz, $CDCl_3$) of compound **(11e)**

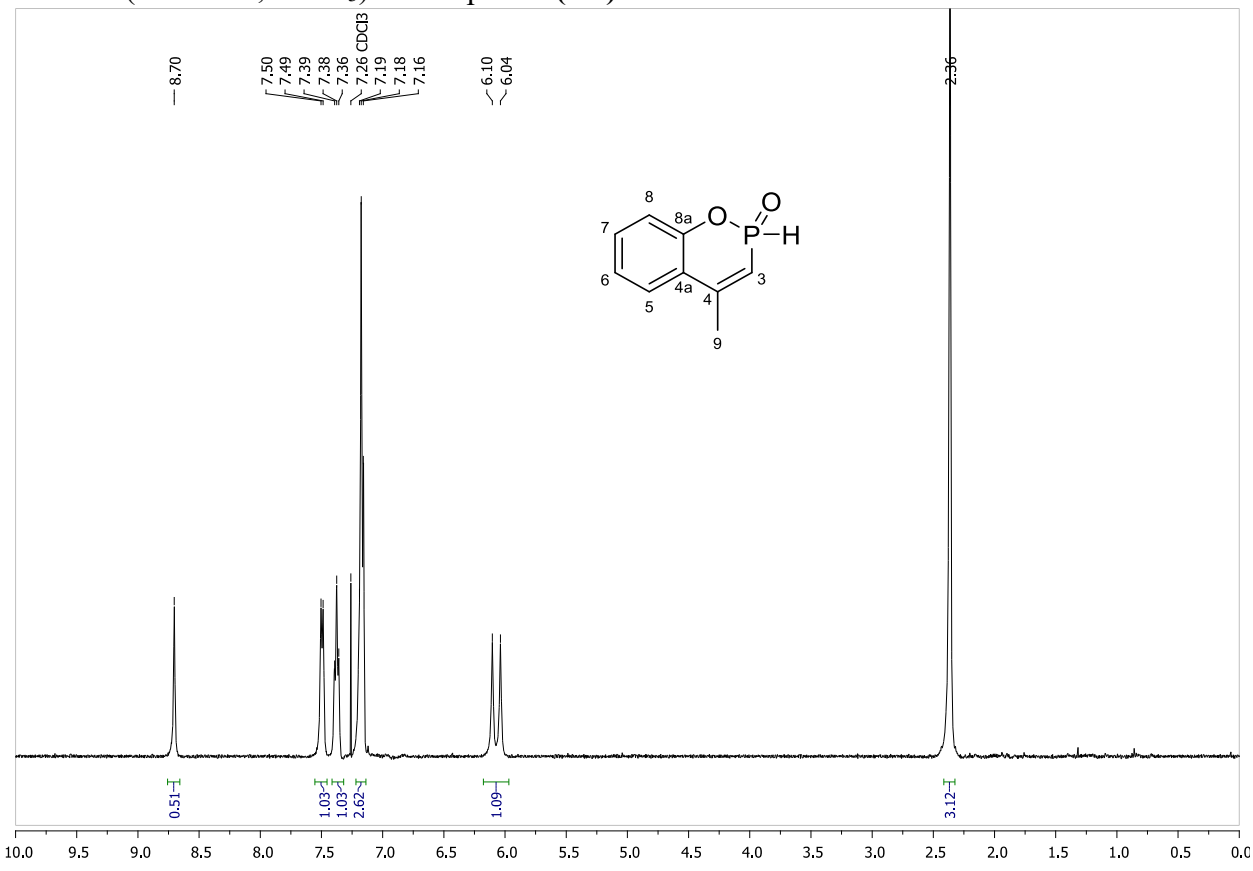


4-methylbenzo[*e*][1,2]oxaphosphinine 2-oxide (11f)

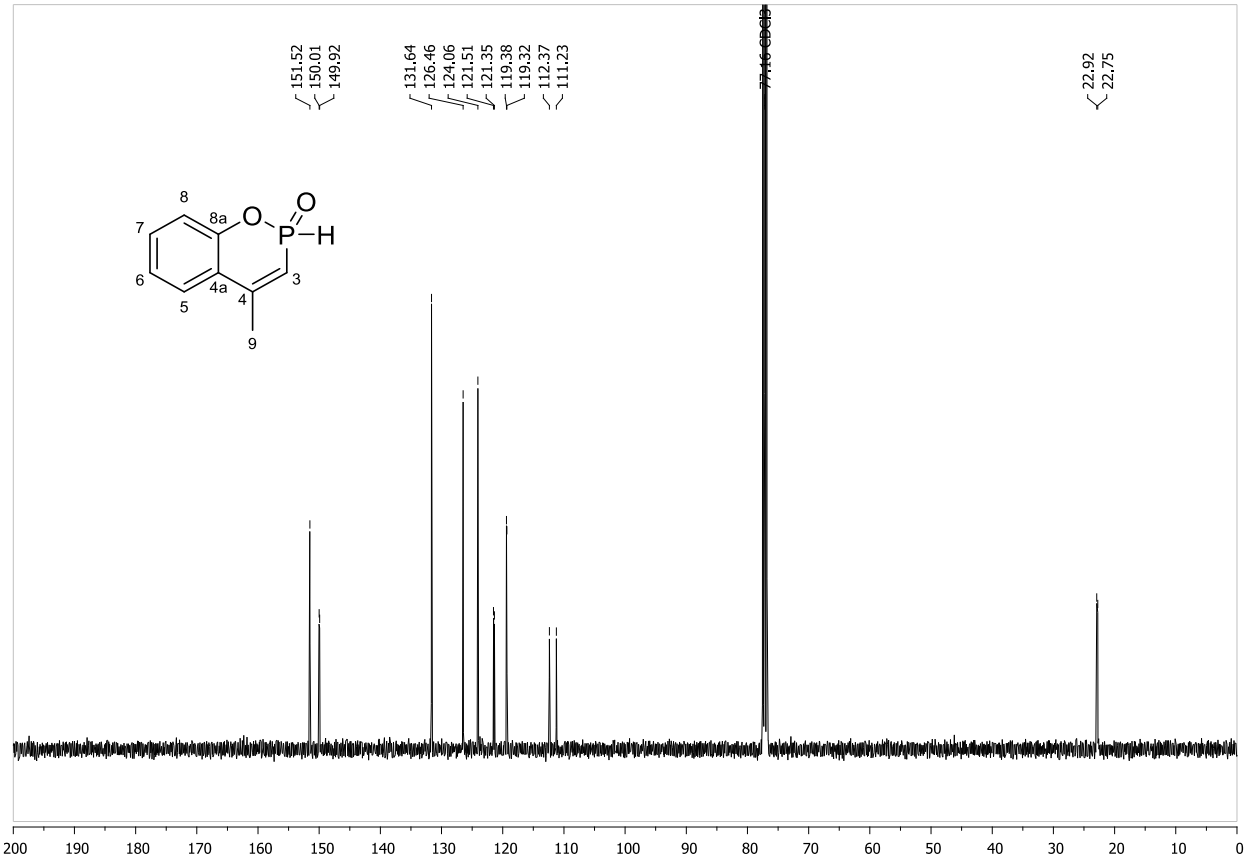
^{31}P NMR (243 MHz, $CDCl_3$) of compound **(11f)**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(11f)**

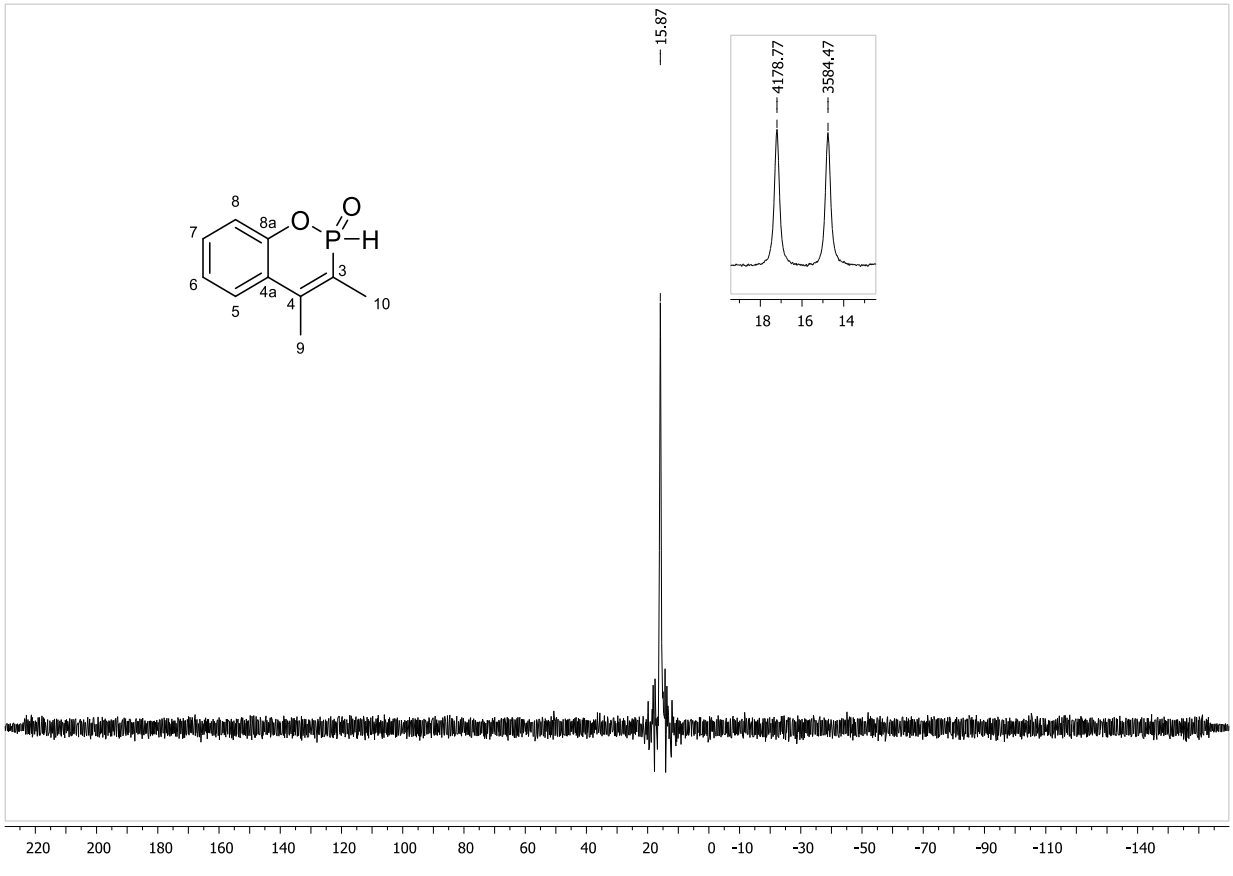


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(11f)**

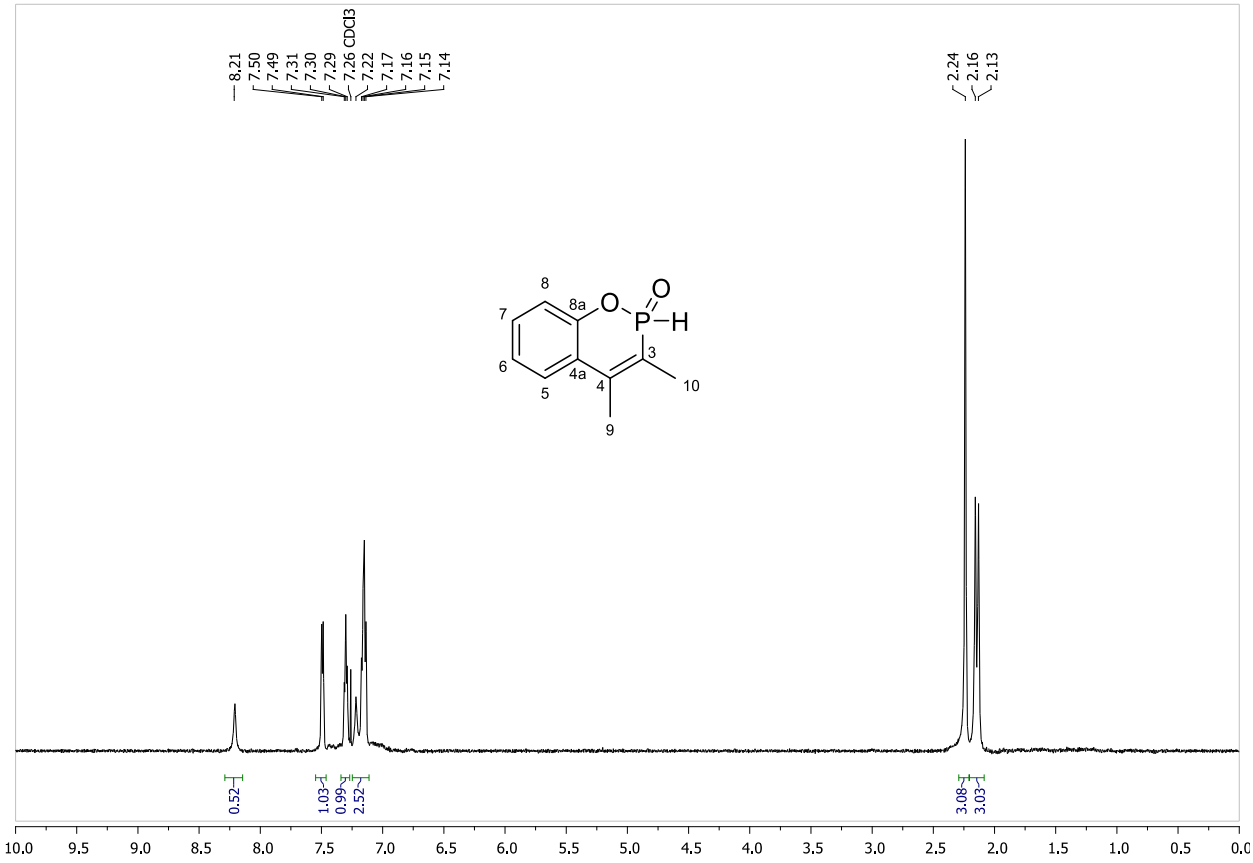


3,4-dimethylbenzo[*e*][1,2]oxaphosphinine 2-oxide (11g)

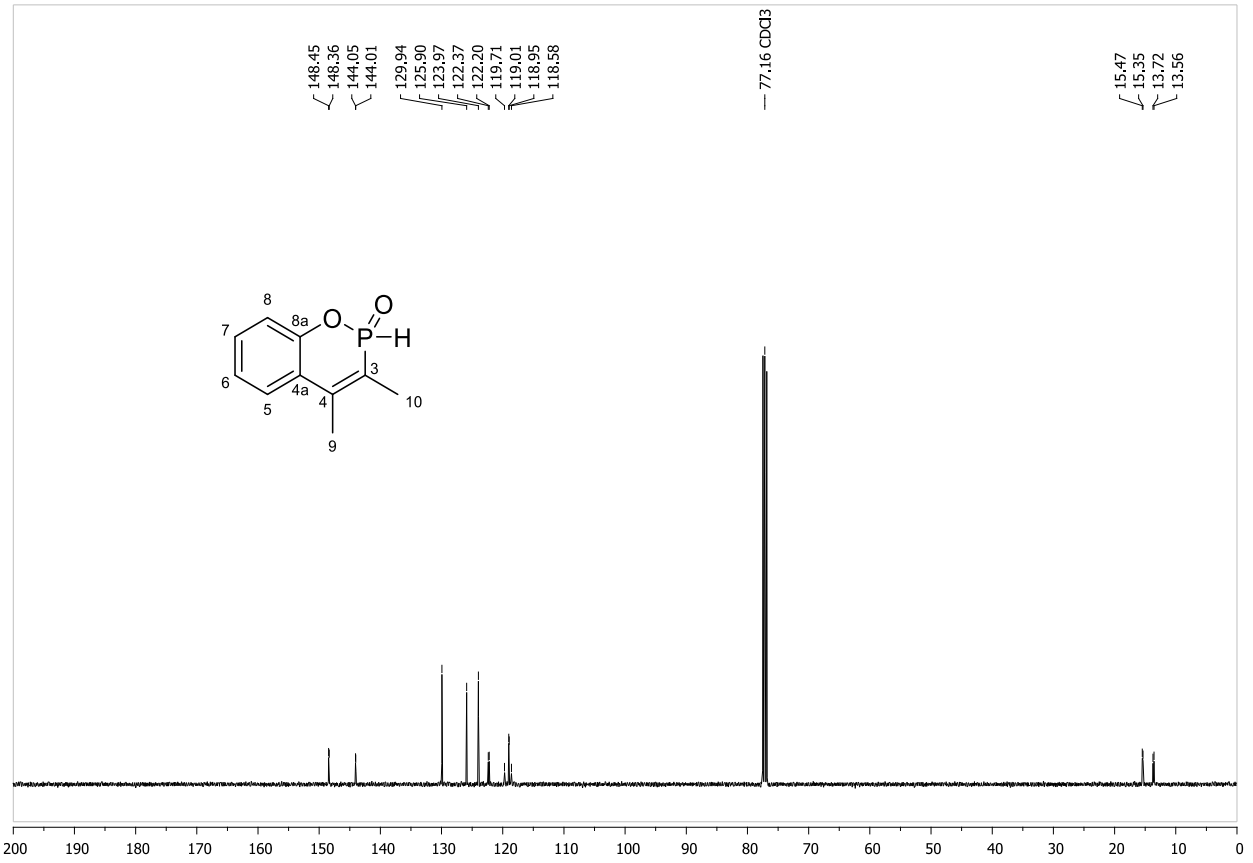
^{31}P NMR (243 MHz, $CDCl_3$) of compound **(11g)**



^{1}H NMR (600 MHz, $CDCl_3$) of compound **(11g)**

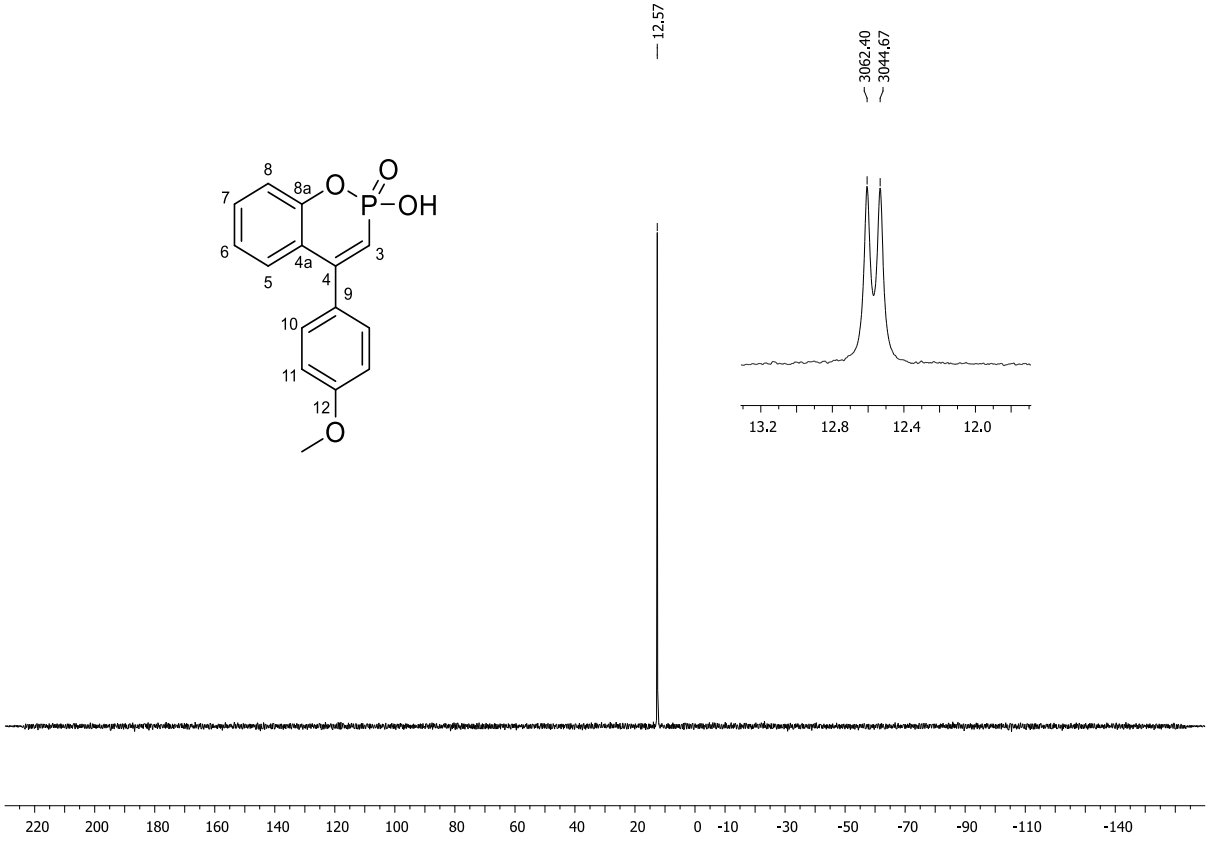


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(11g)**

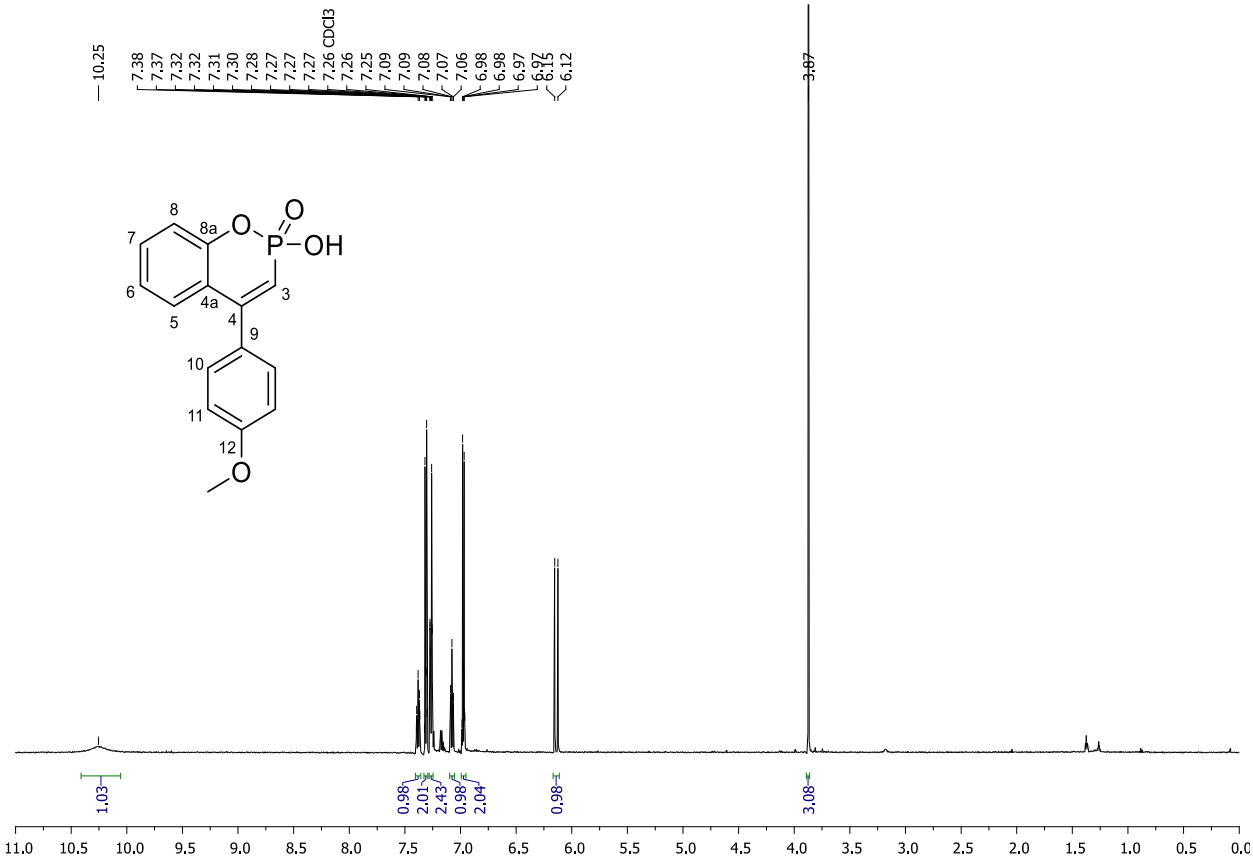


2-hydroxy-4-(4-methoxyphenyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (3b)

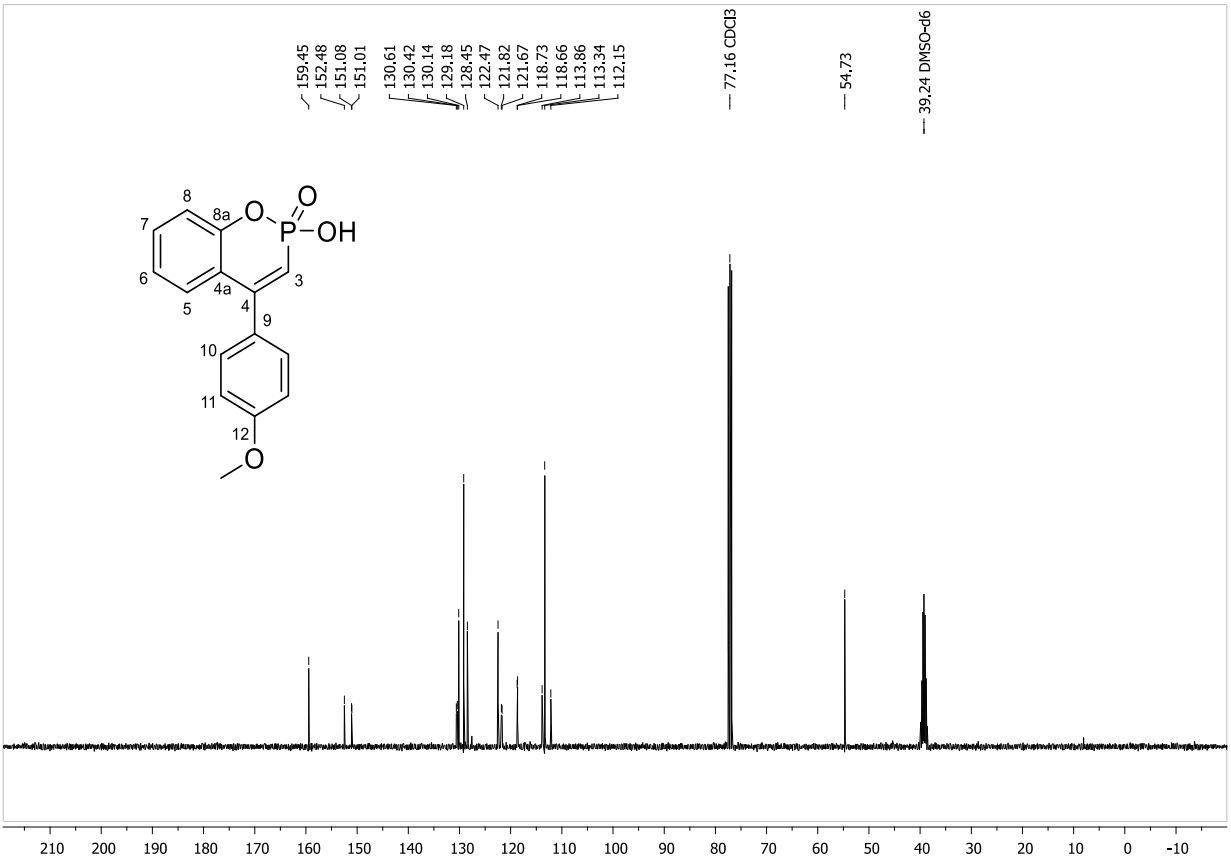
^{31}P NMR (243 MHz, $CDCl_3$) of compound **(3b)**



^{1}H NMR (600 MHz, $CDCl_3$) of compound **(3b)**

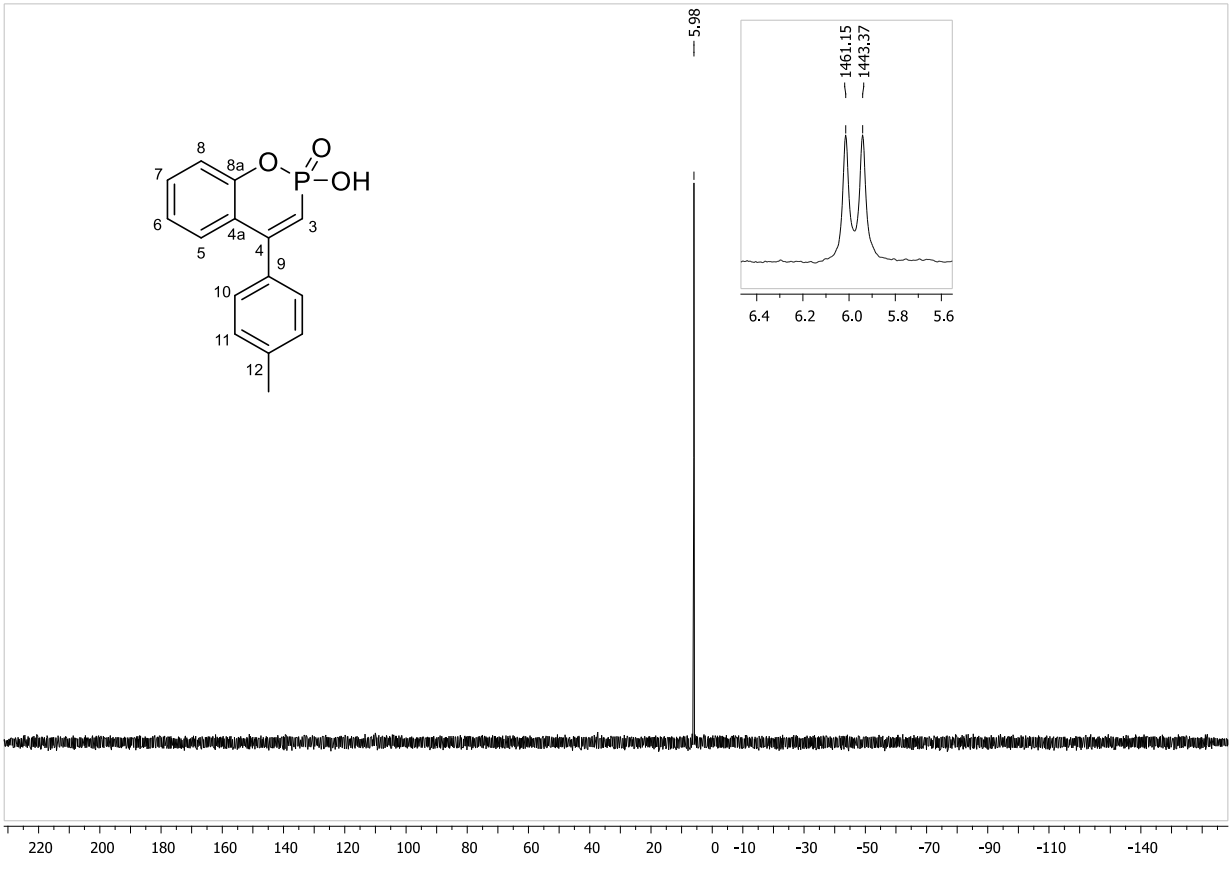


^{13}C NMR (101 MHz, $CDCl_3$ + DMSO-d_6) of compound **(3b)**

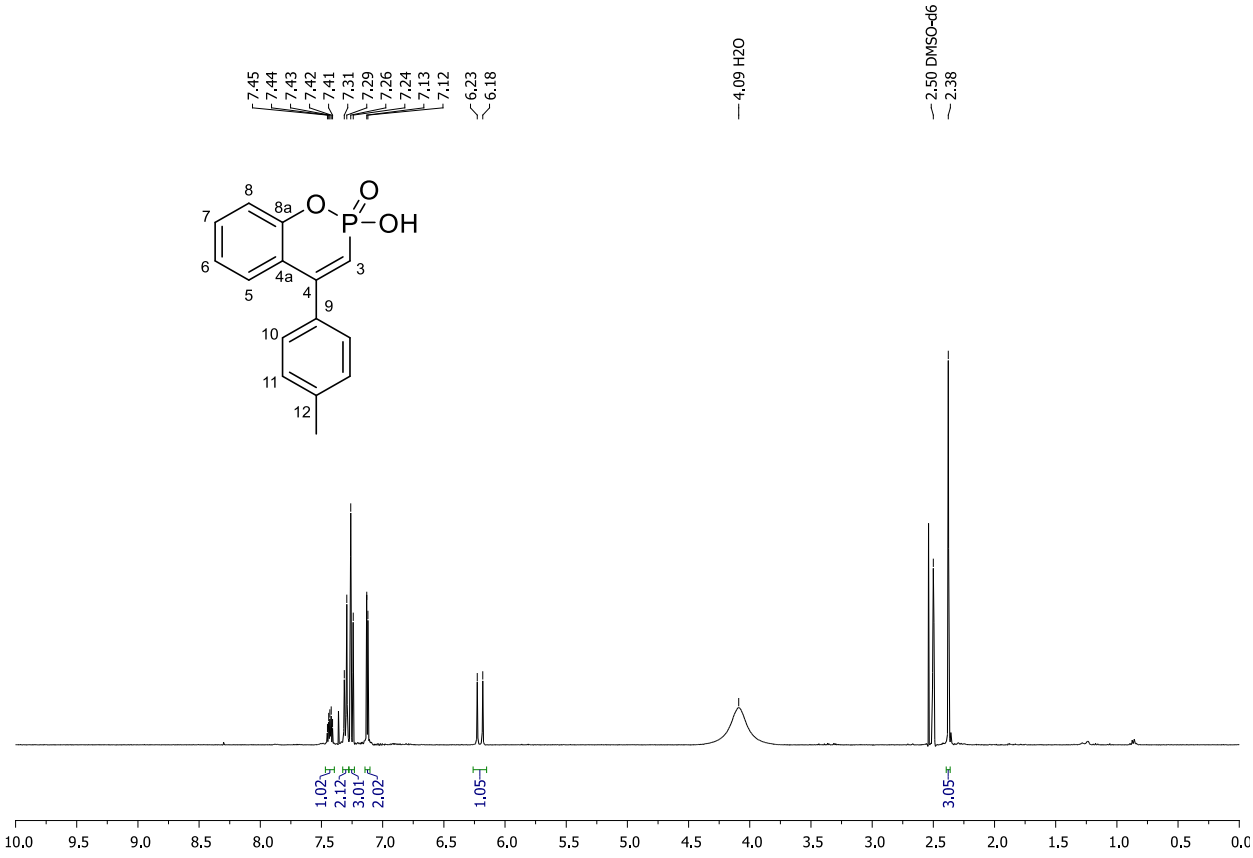


2-hydroxy-4-(p-tolyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (3c)

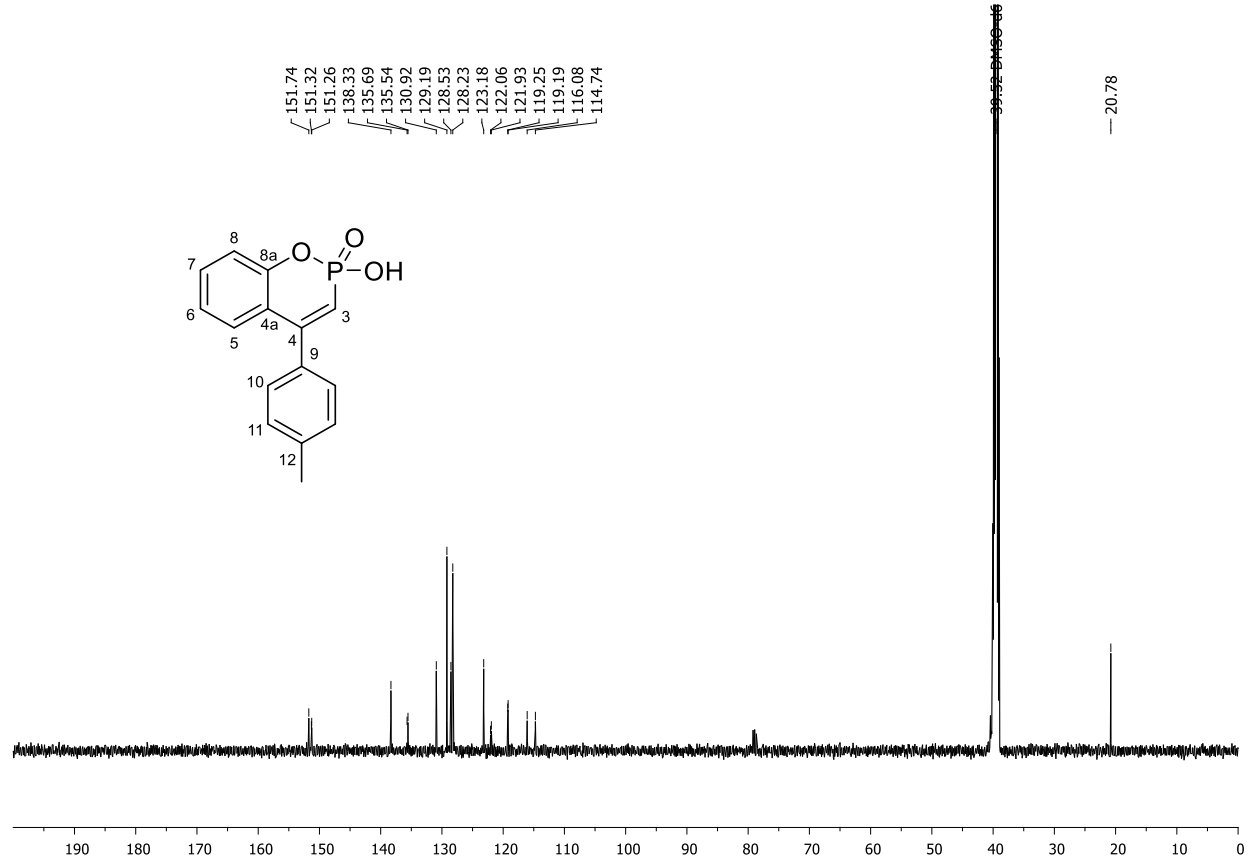
^{31}P NMR (243 MHz, DMSO-d_6) of compound **(3c)**



^{1}H NMR (400 MHz, DMSO-d$_6$) of compound **(3c)**

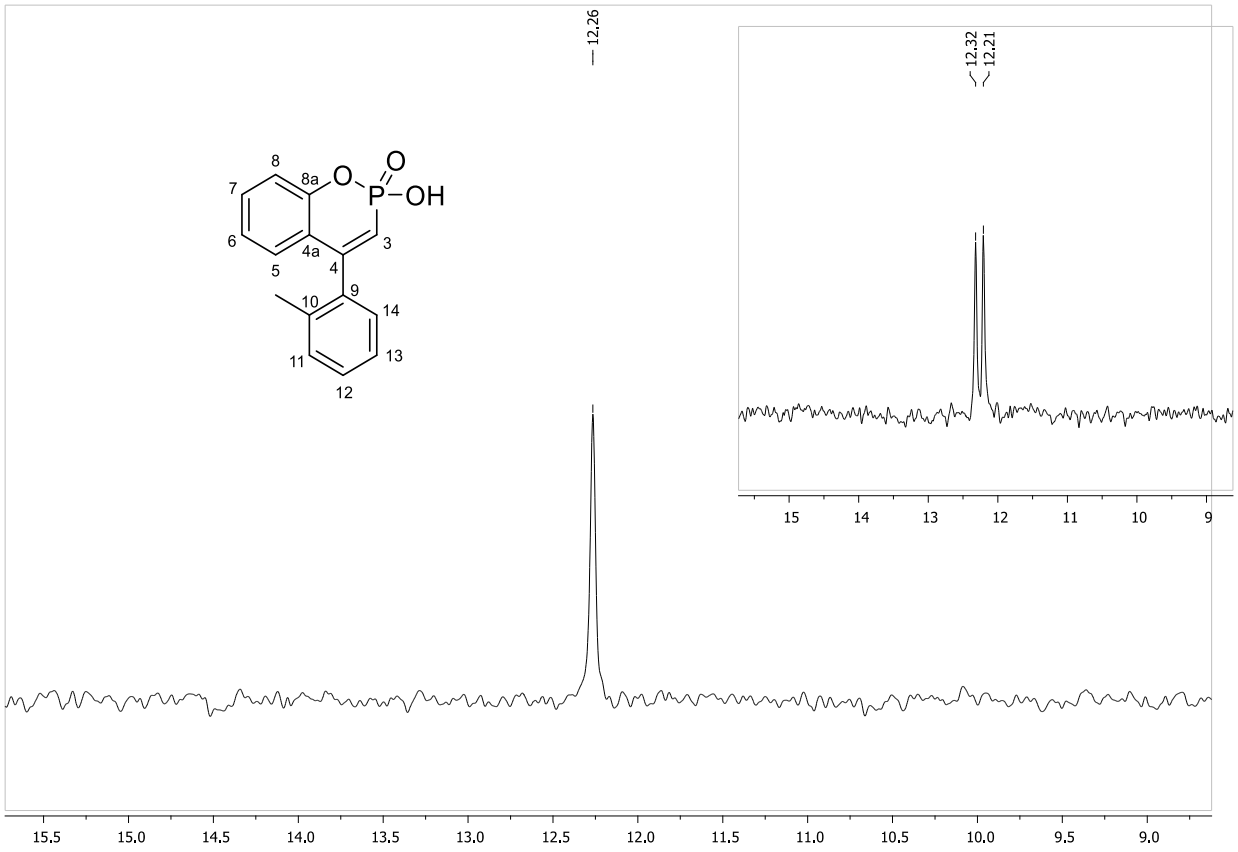


^{13}C NMR (126 MHz, DMSO-d$_6$) of compound **(3c)**

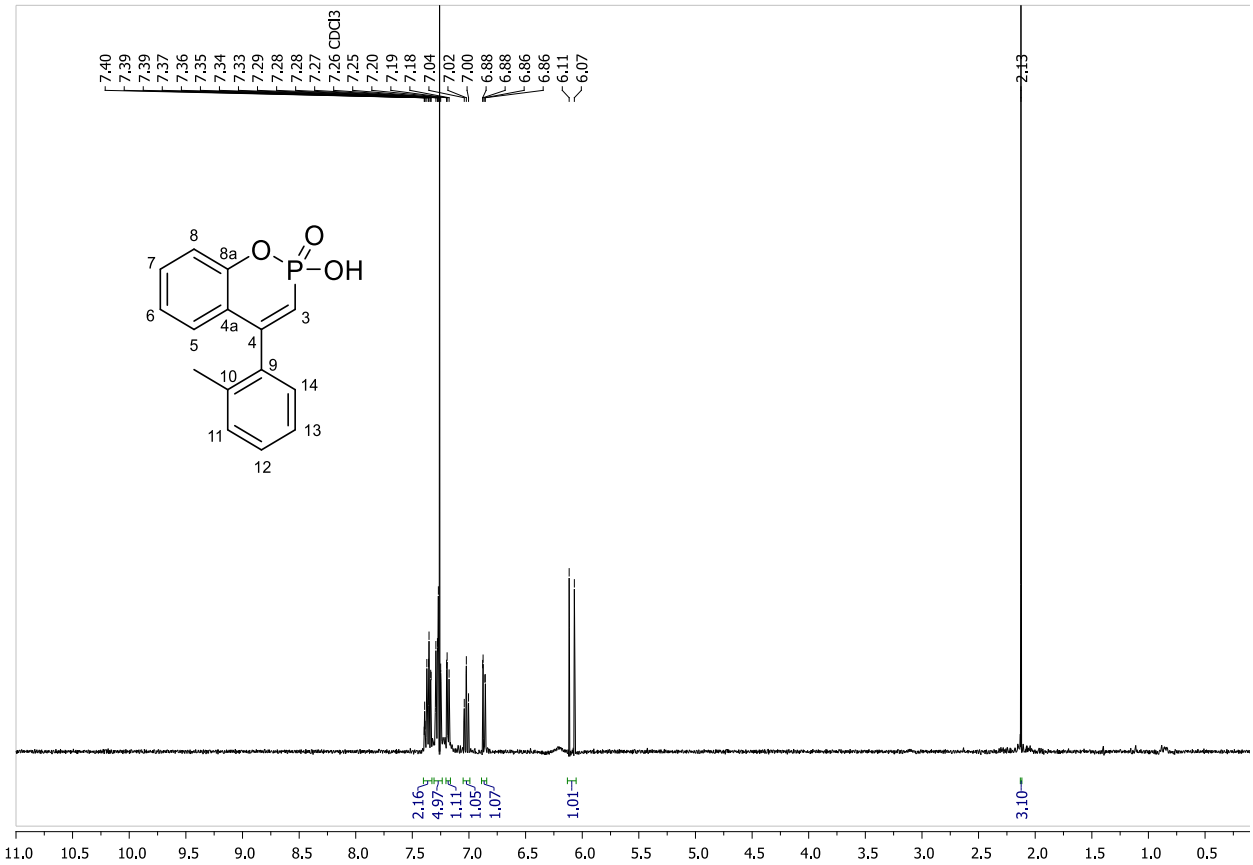


2-hydroxy-4-(o-tolyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (3d)

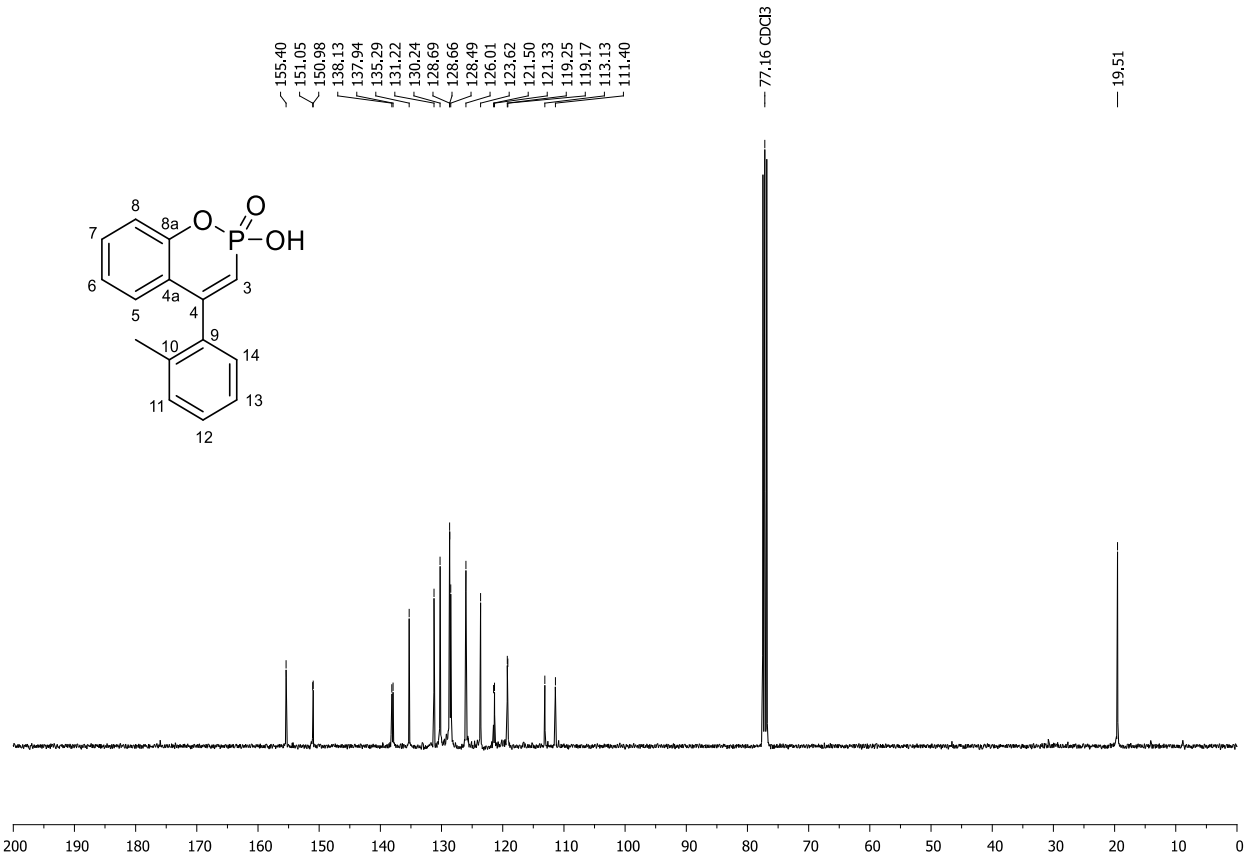
^{31}P NMR (162 MHz, $CDCl_3$) of compound **(3d)**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(3d)**

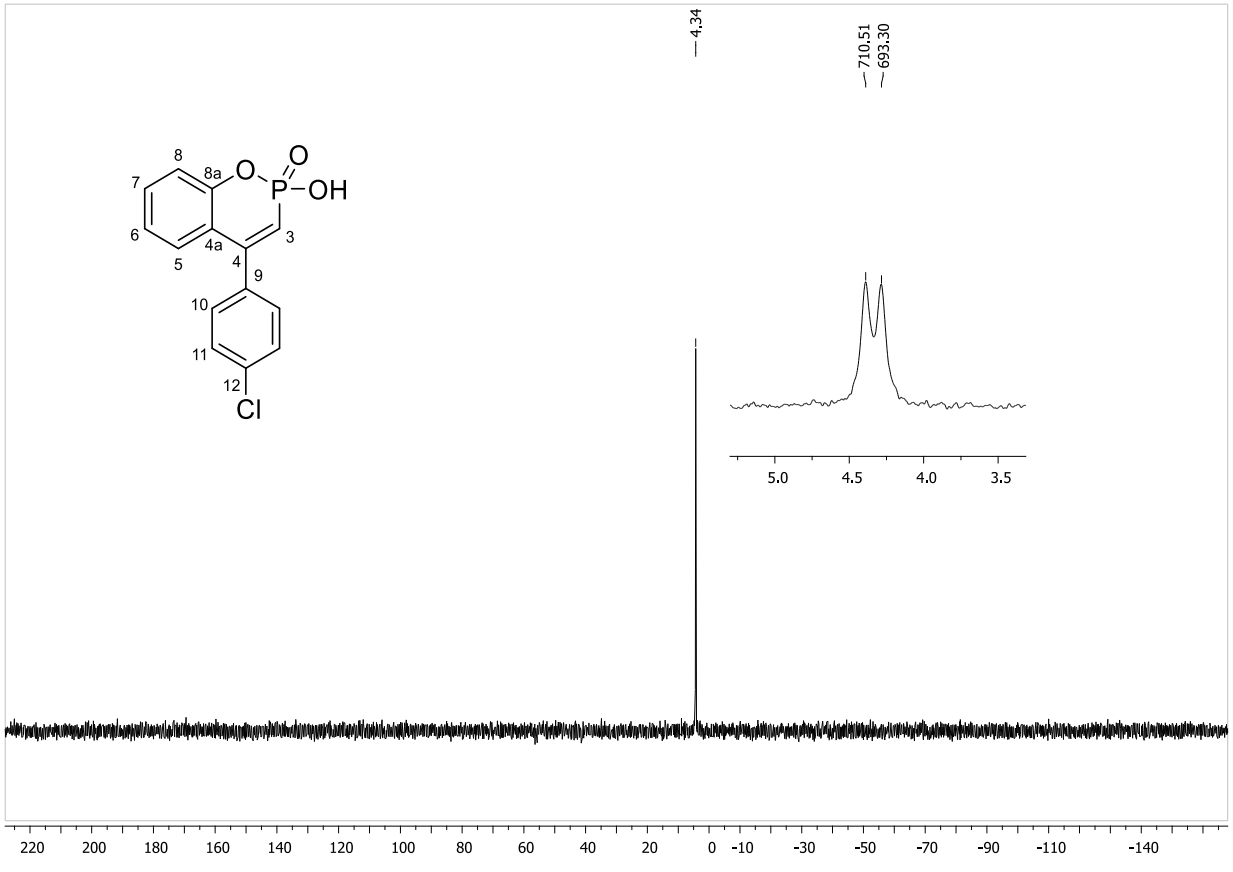


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(3d)**

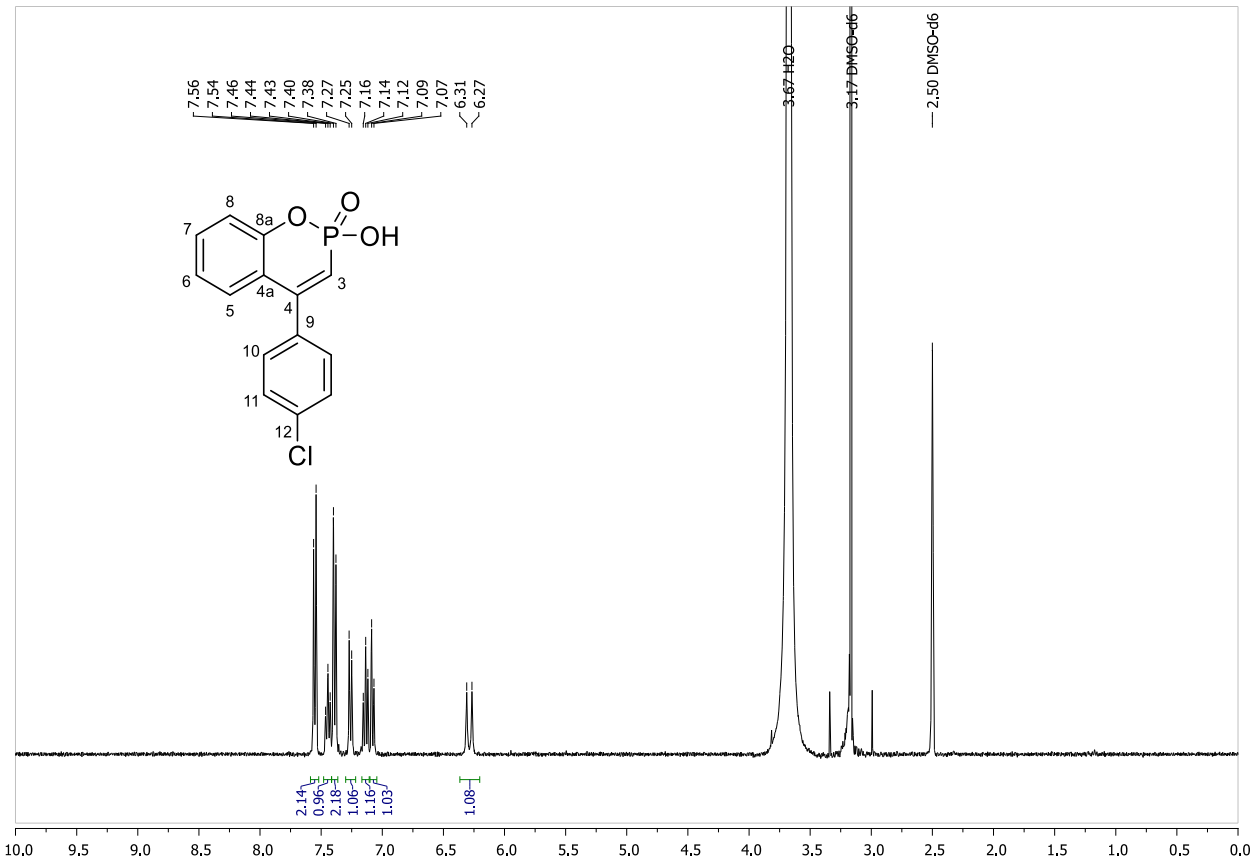


4-(4-chlorophenyl)-2-hydroxybenzo[*e*][1,2]oxaphosphinine-2-oxide (3)

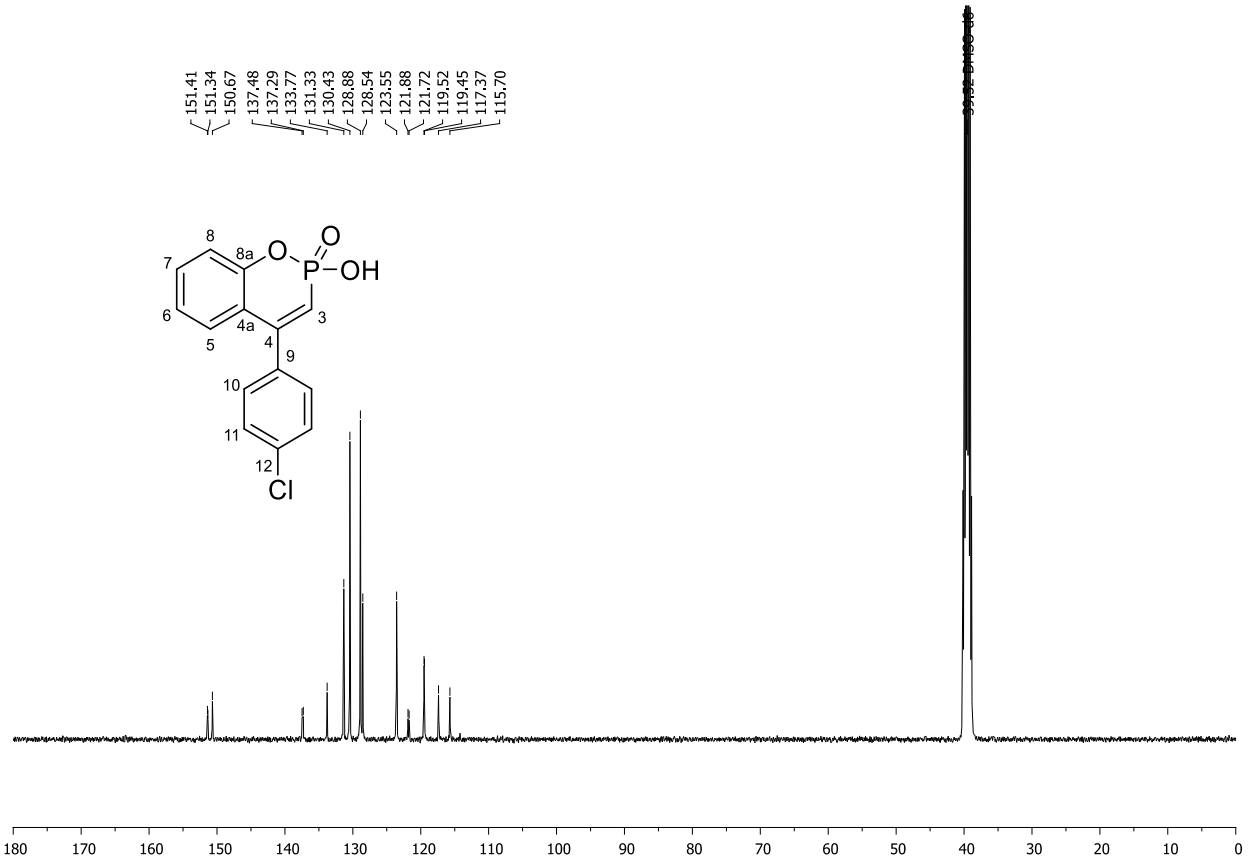
^{31}P NMR (162 MHz, DMSO-d_6) of compound **(3e)**



^{1}H NMR (400 MHz, DMSO-d$_6$) of compound **(3e)**

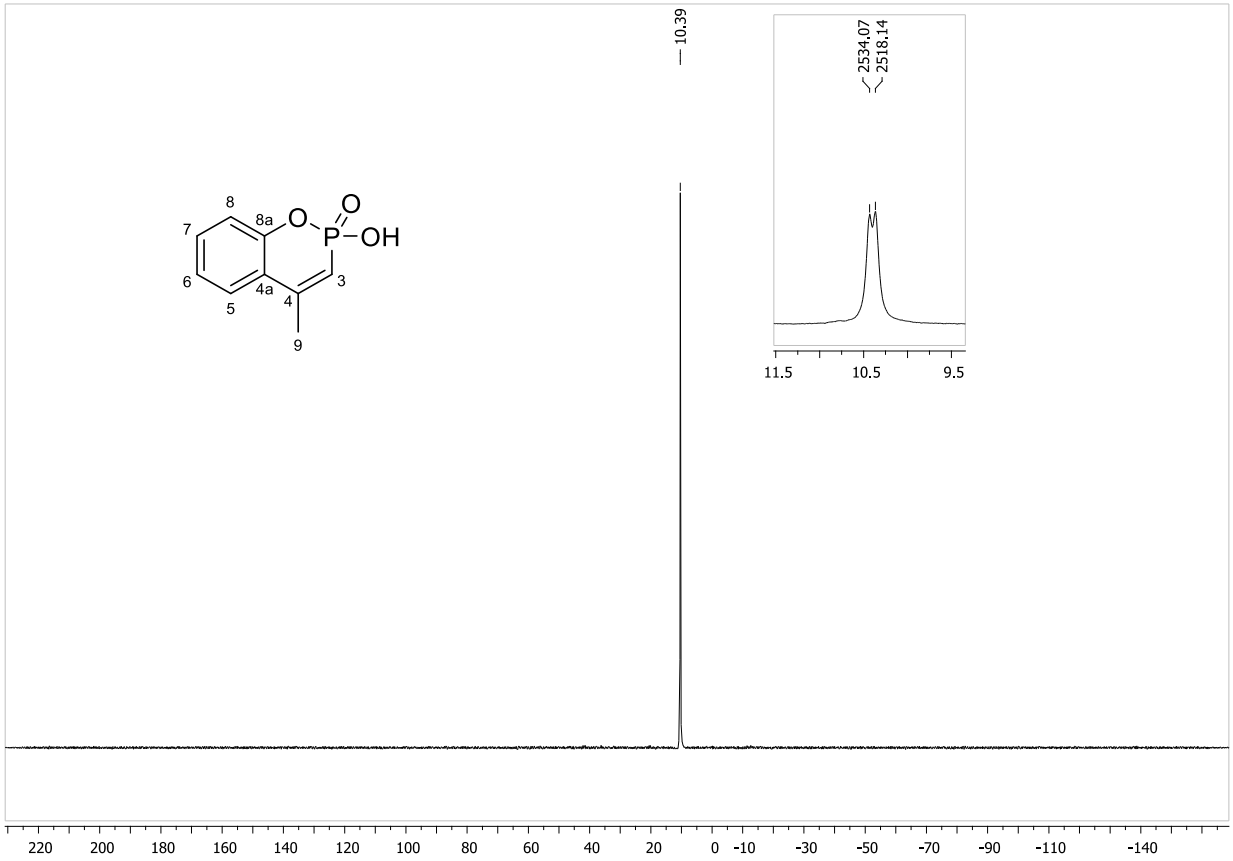


^{13}C NMR (101 MHz, DMSO-d$_6$) of compound **(3e)**

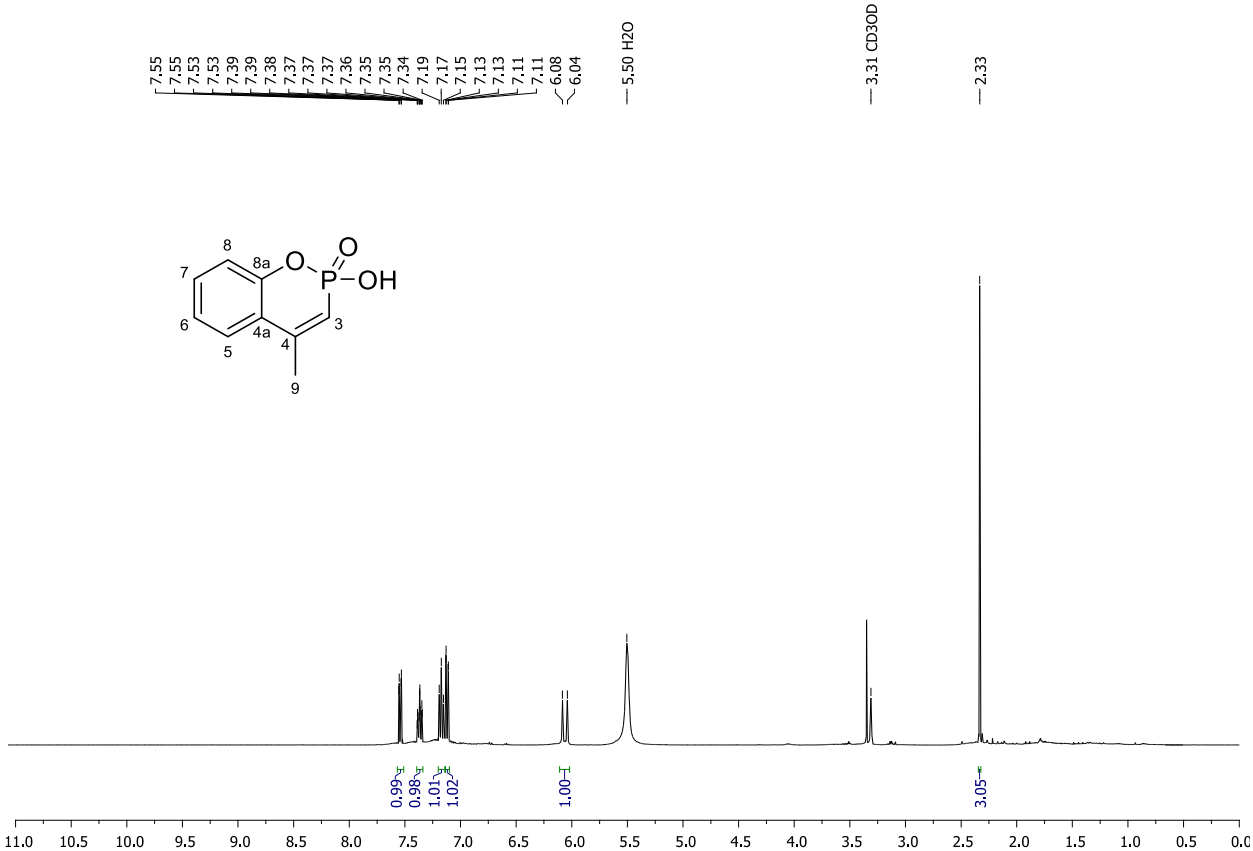


2-hydroxy-4-methylbenzo[*e*][1,2]oxaphosphinine 2-oxide (3f)

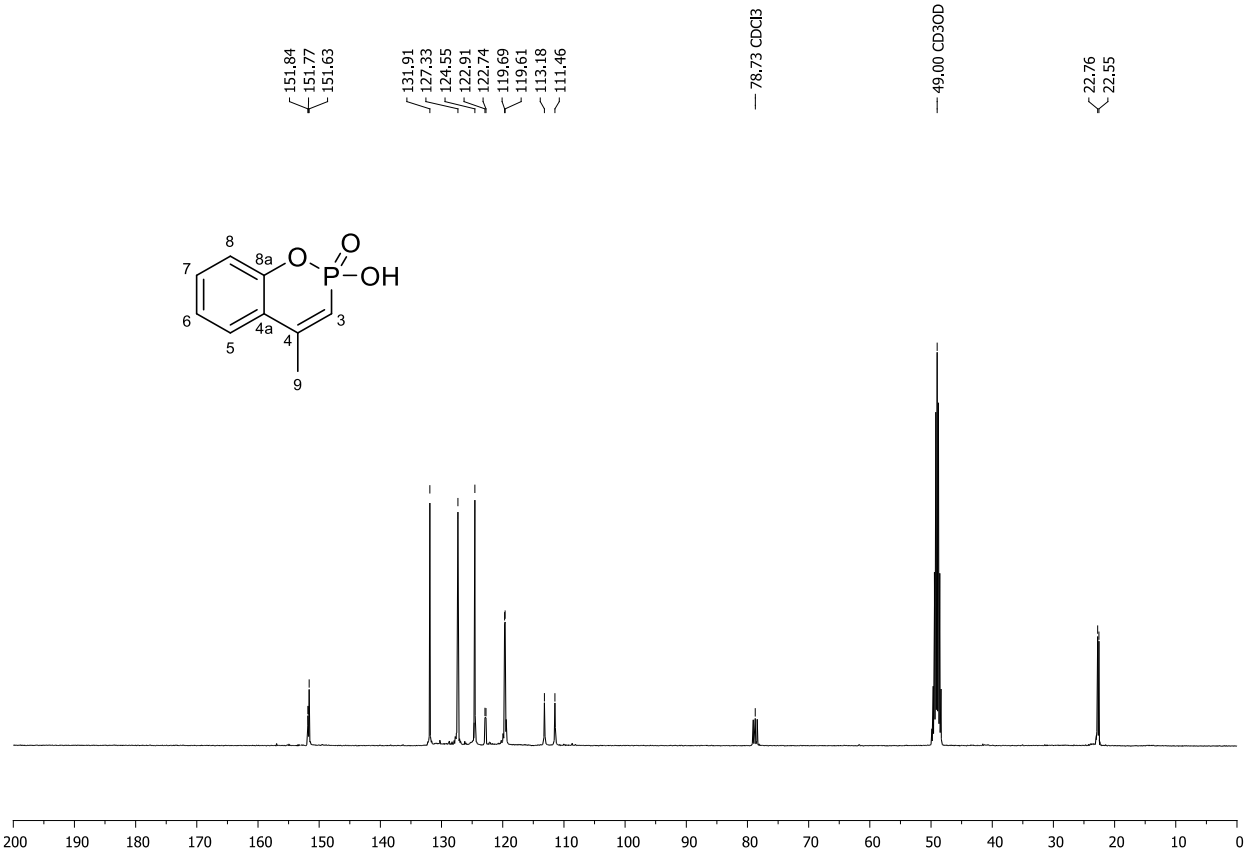
^{31}P NMR (243 MHz, $CDCl_3$) of compound **(3f)**



^{1}H NMR (400 MHz, MeOH-d_4) of compound **(3f)**

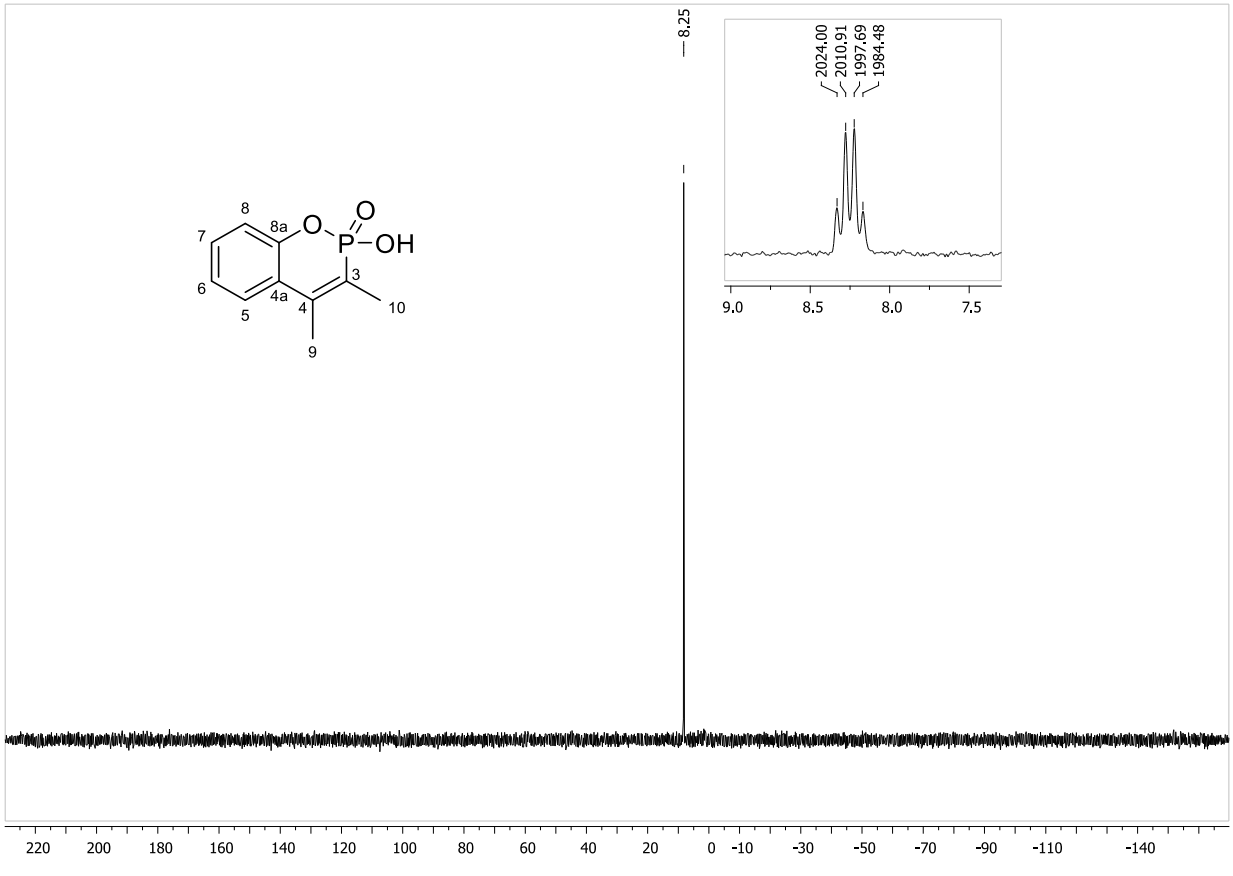


^{13}C NMR (101 MHz, MeOH-d$_4$) of compound **(3f)**

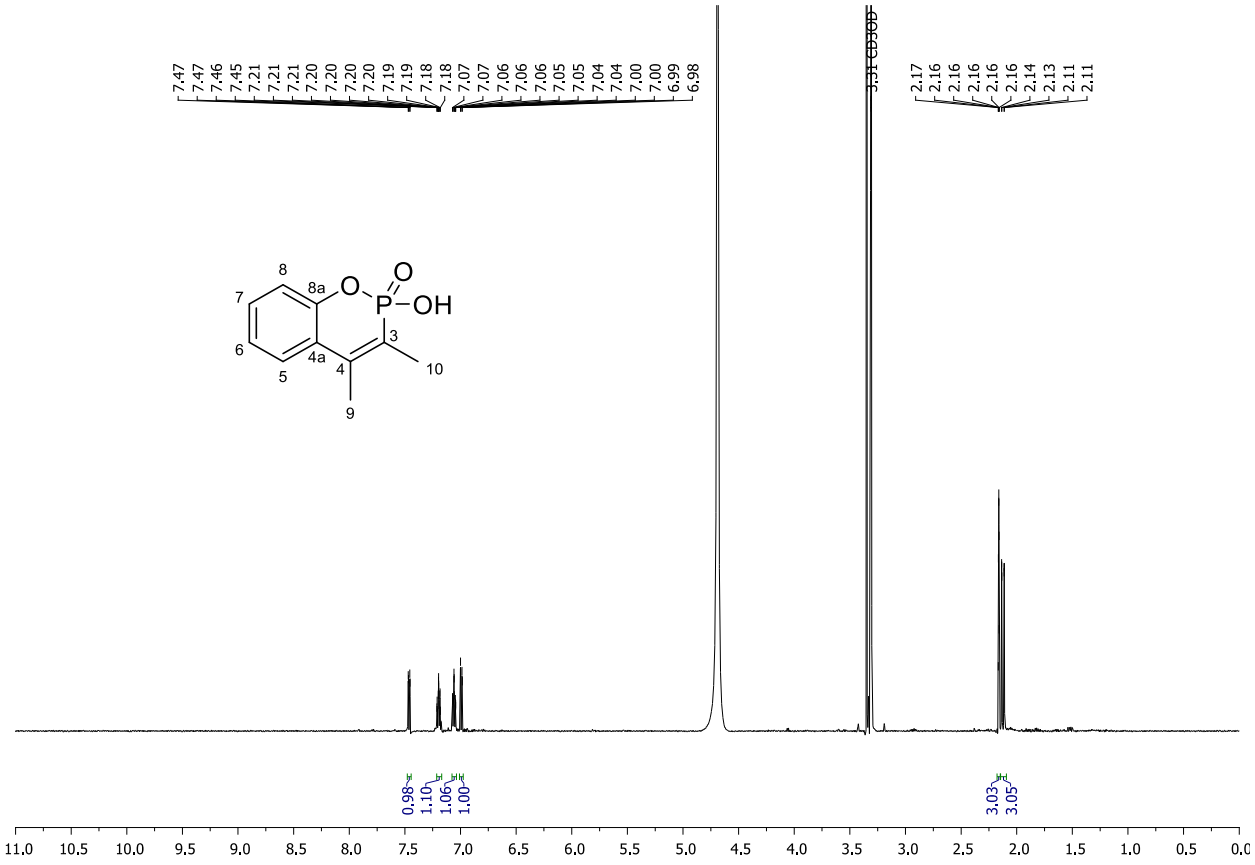


2-hydroxy-3,4-dimethylbenzo[*e*][1,2]oxaphosphinine 2-oxide (3g)

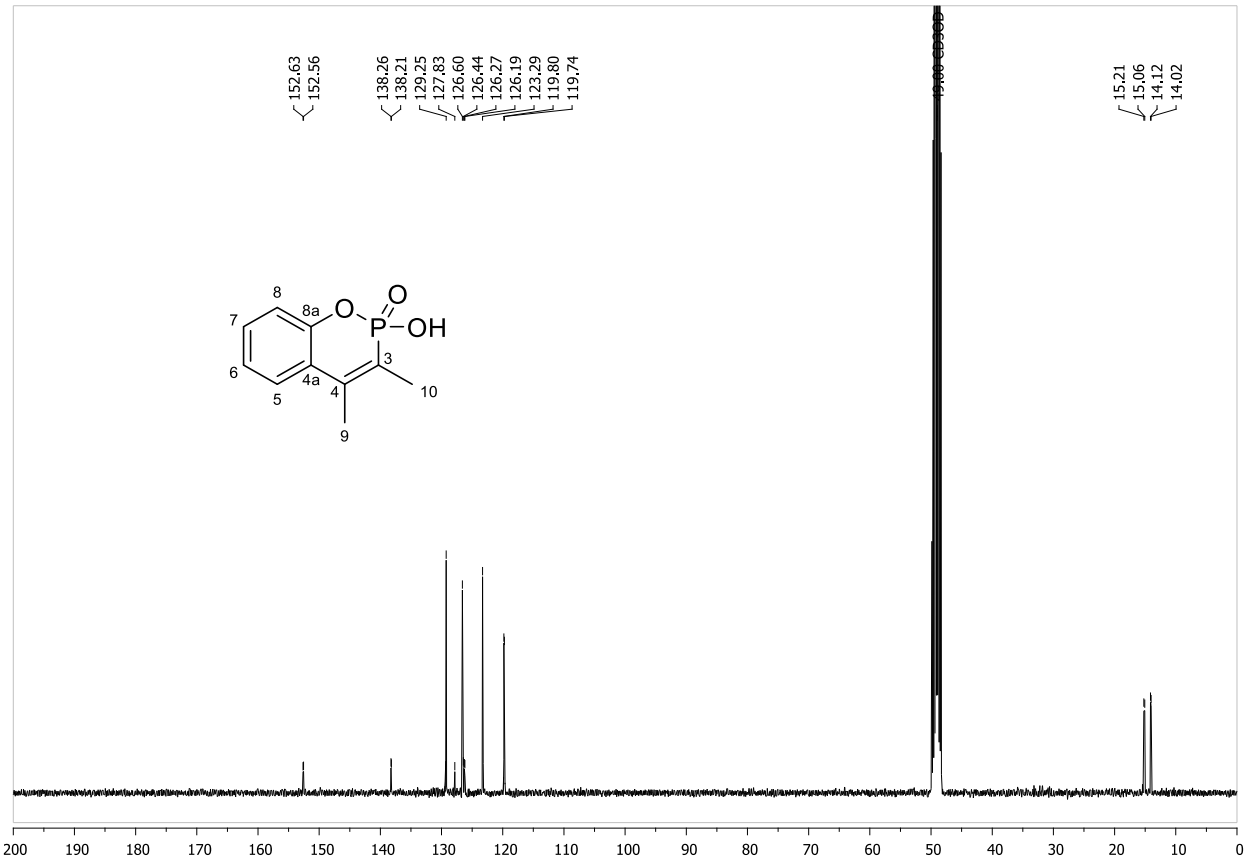
^{31}P NMR (243 MHz, MeOH-d$_4$) of compound **(3g)**



^{1}H NMR (600 MHz, MeOH-d$_4$) of compound **(3g)**

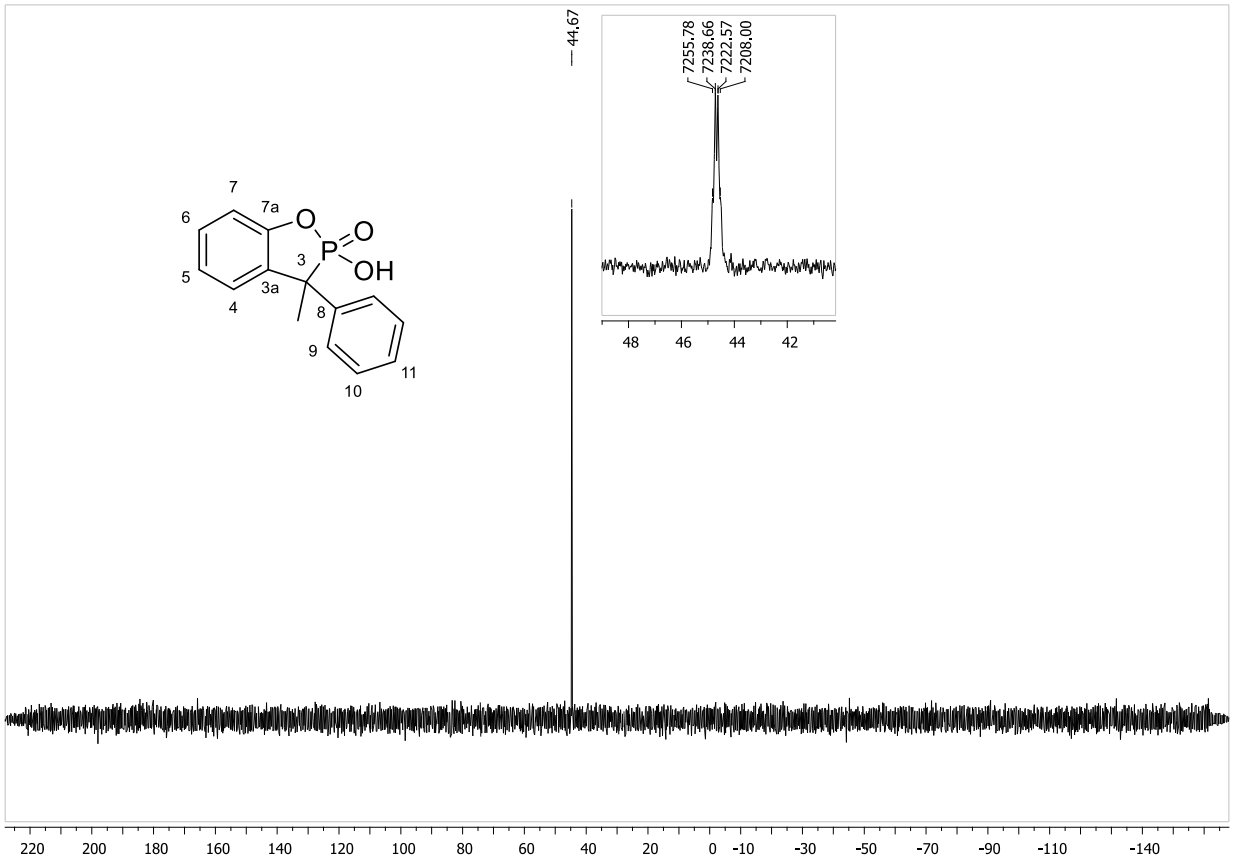


^{13}C NMR (101 MHz, MeOH-d$_4$) of compound **(3g)**

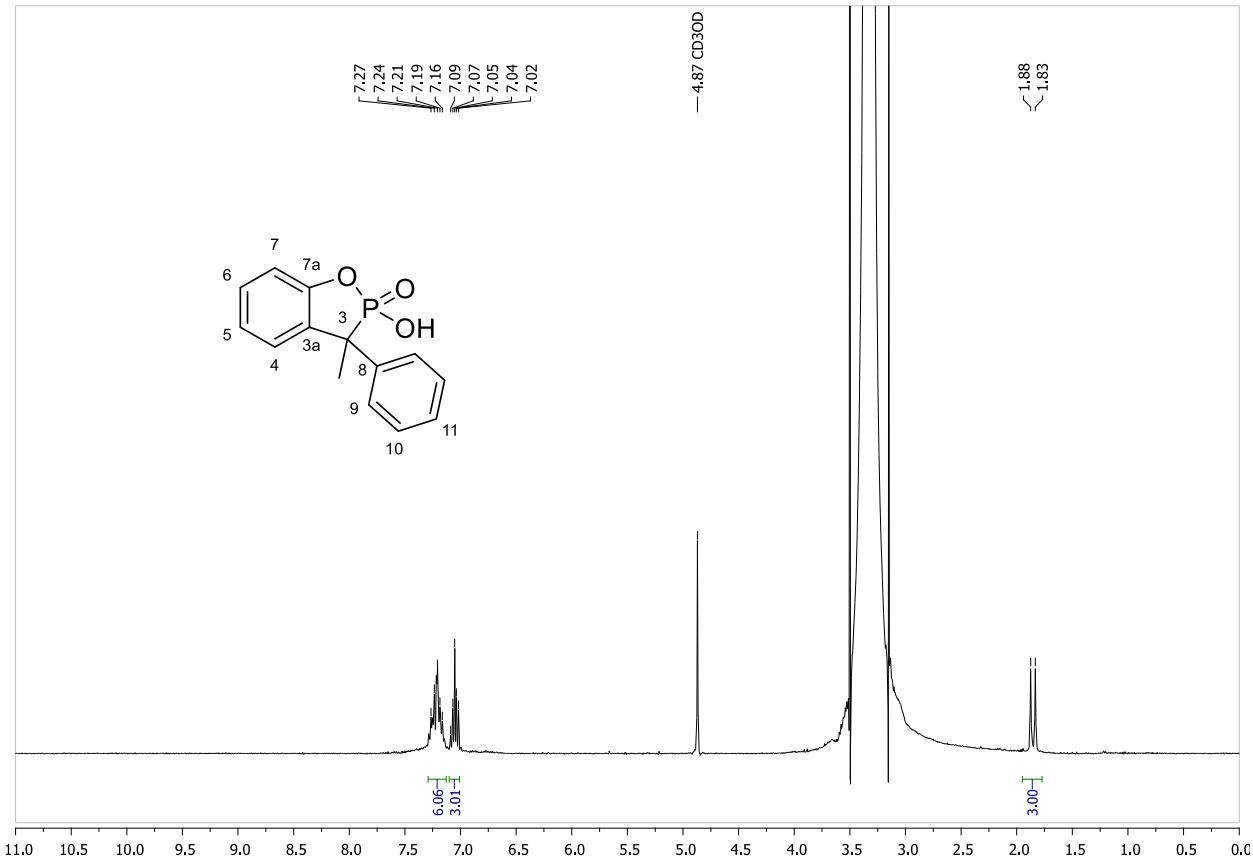


2-hydroxy-3-methyl-3-phenyl-3*H*-benzo[*d*][1,2]oxaphosphole 2-oxide (9a)

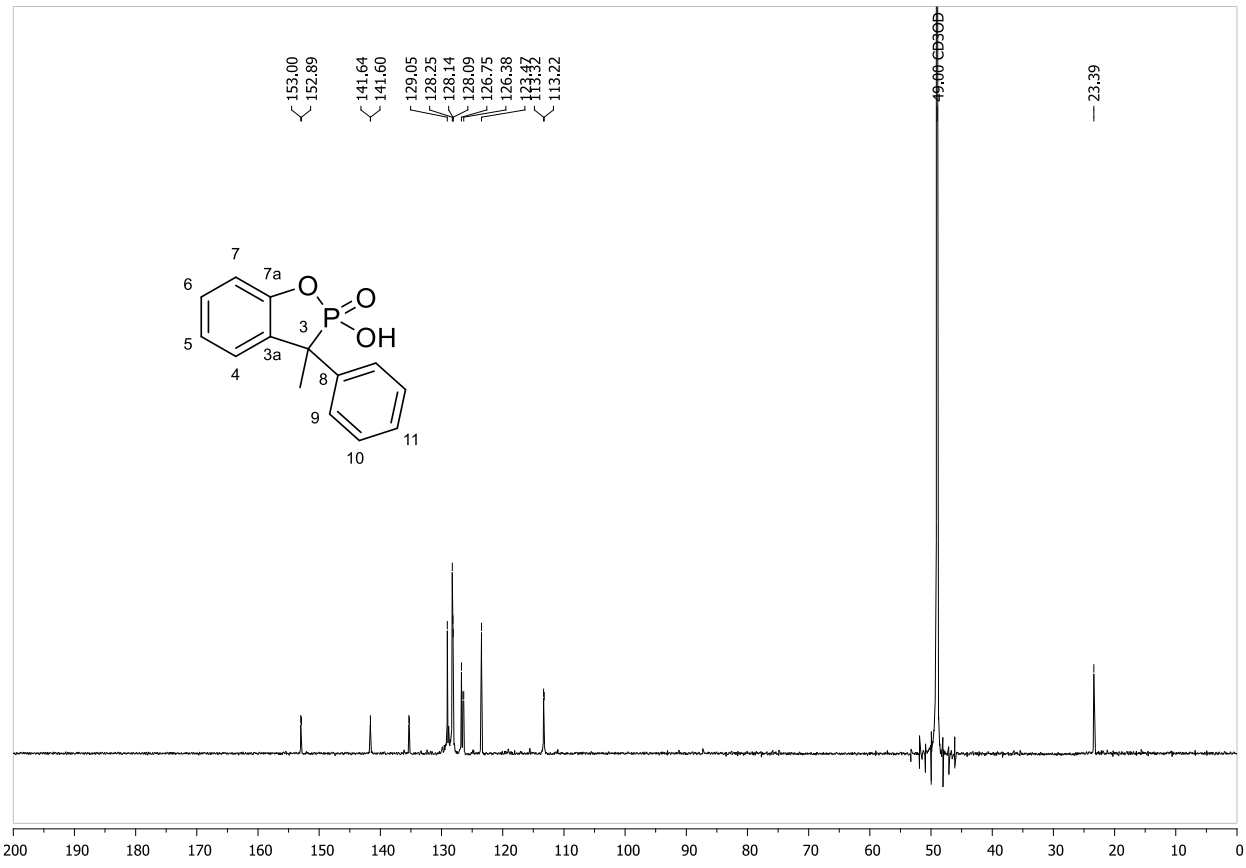
^{31}P NMR (162 MHz, $CDCl_3$) of compound **(9a)**



^{1}H NMR (400 MHz, MeOH-d_4) of compound **(9a)**

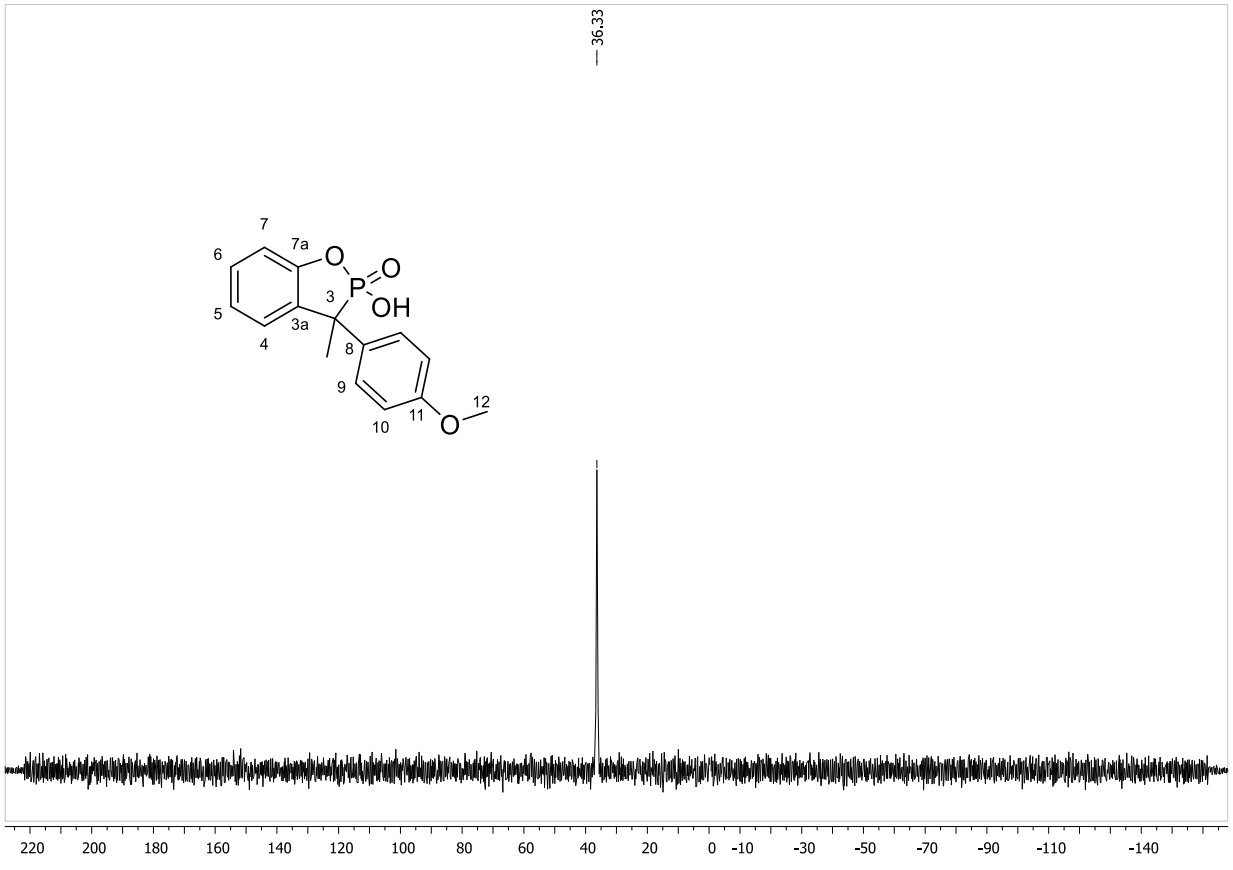


^{13}C NMR (101 MHz, MeOH-d$_4$) of compound **(9a)**

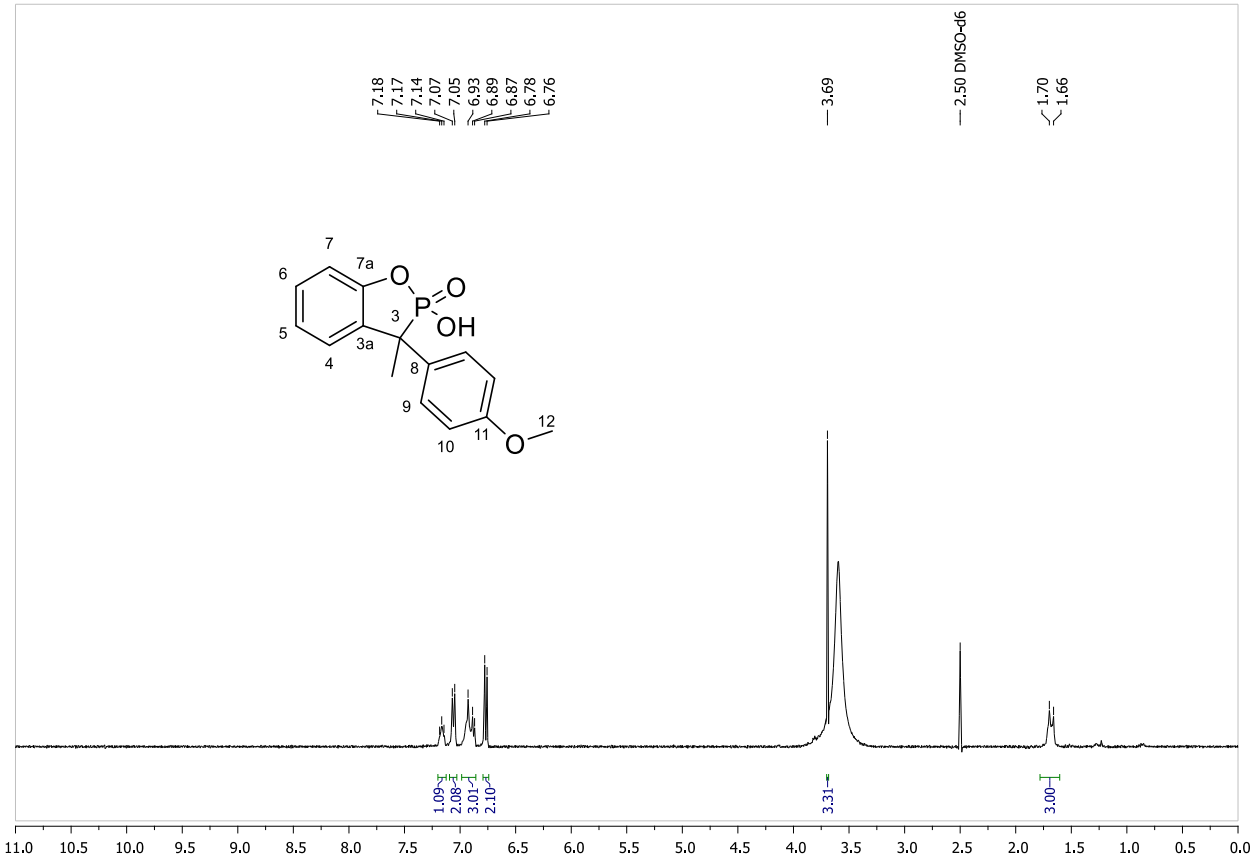


2-hydroxy-3-(4-methoxyphenyl)-3-methyl-3*H*-benzo[*d*][1,2]oxaphosphole 2-oxide (9b)

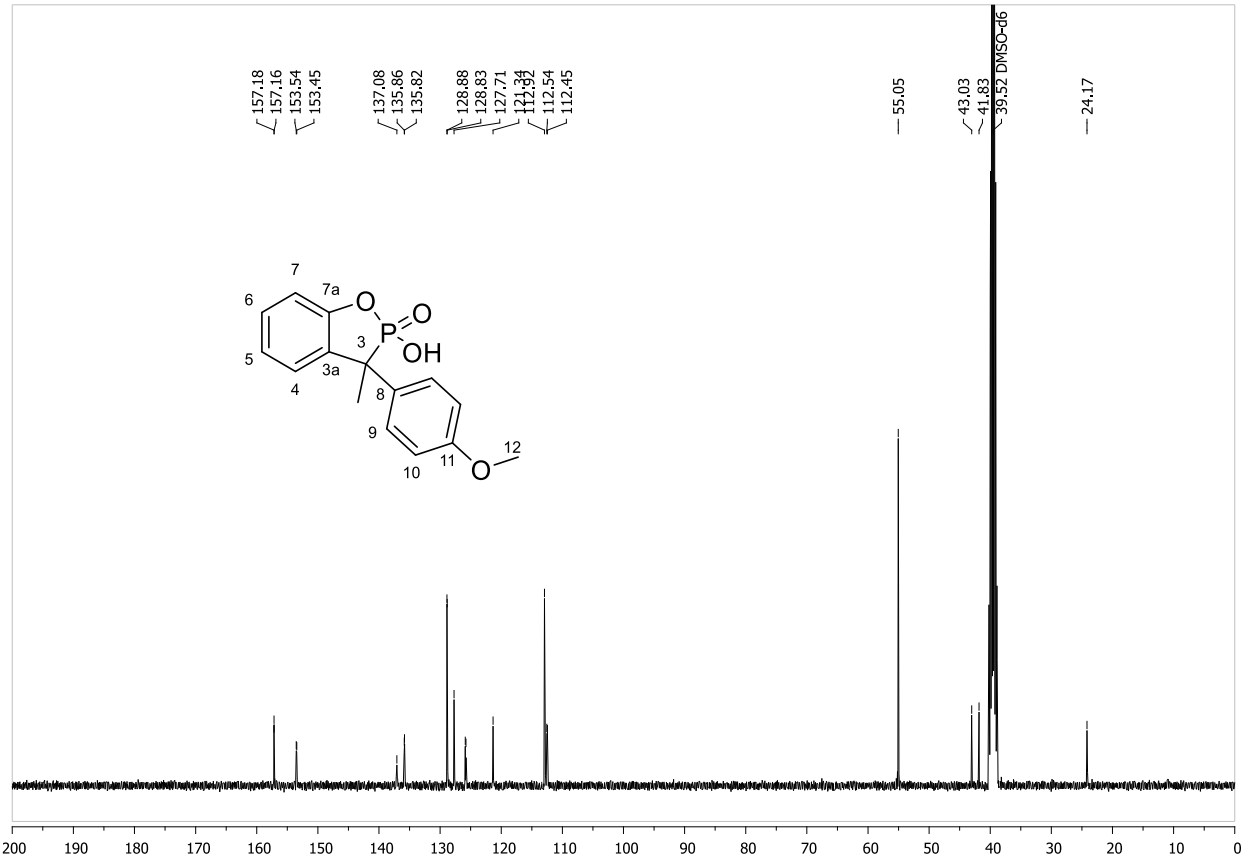
^{31}P NMR (162 MHz, DMSO-d$_6$) of compound **(9b)**



^{1}H NMR (400 MHz, DMSO-d$_6$) of compound **(9b)**

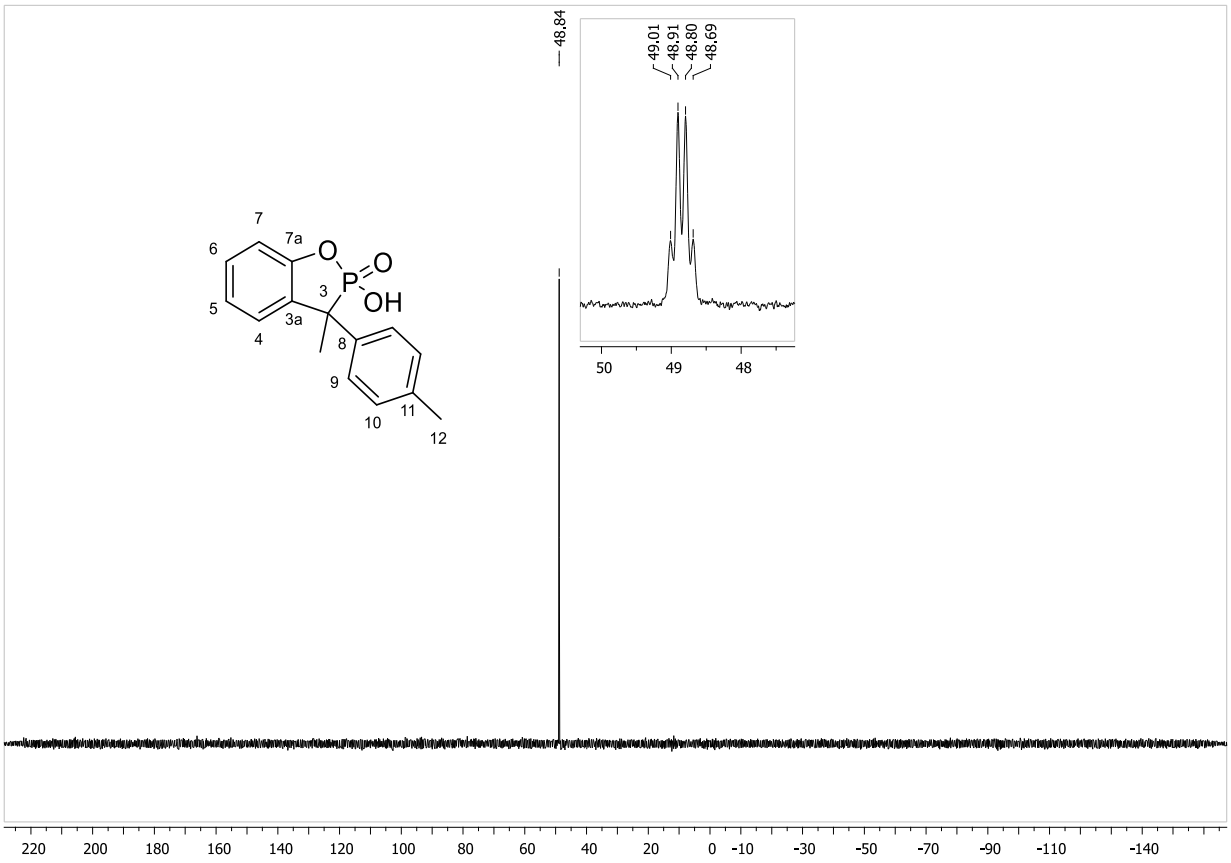


^{13}C NMR (101 MHz, DMSO-d$_6$) of compound **(9b)**

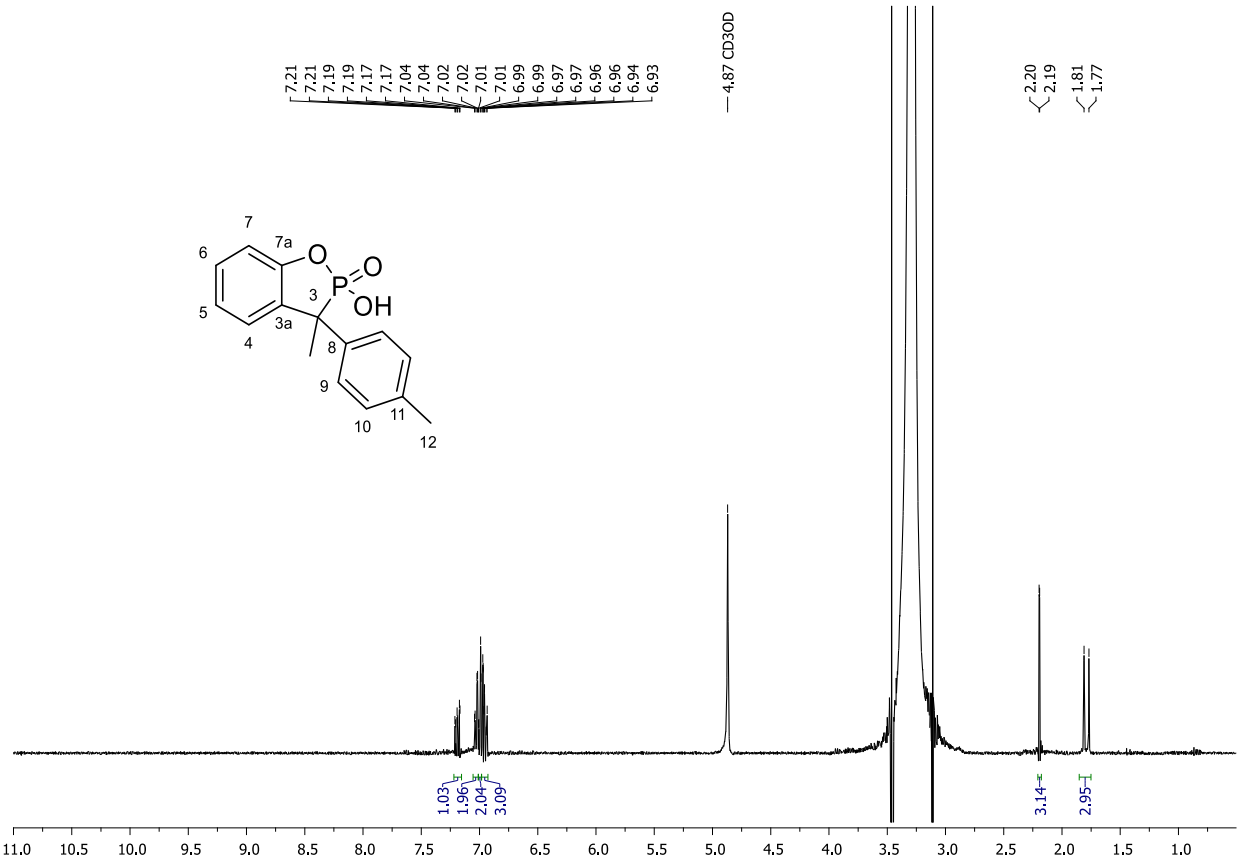


2-hydroxy-3-methyl-3-(p-tolyl)-3*H*-benzo[*d*][1,2]oxaphosphole 2-oxide (9c)

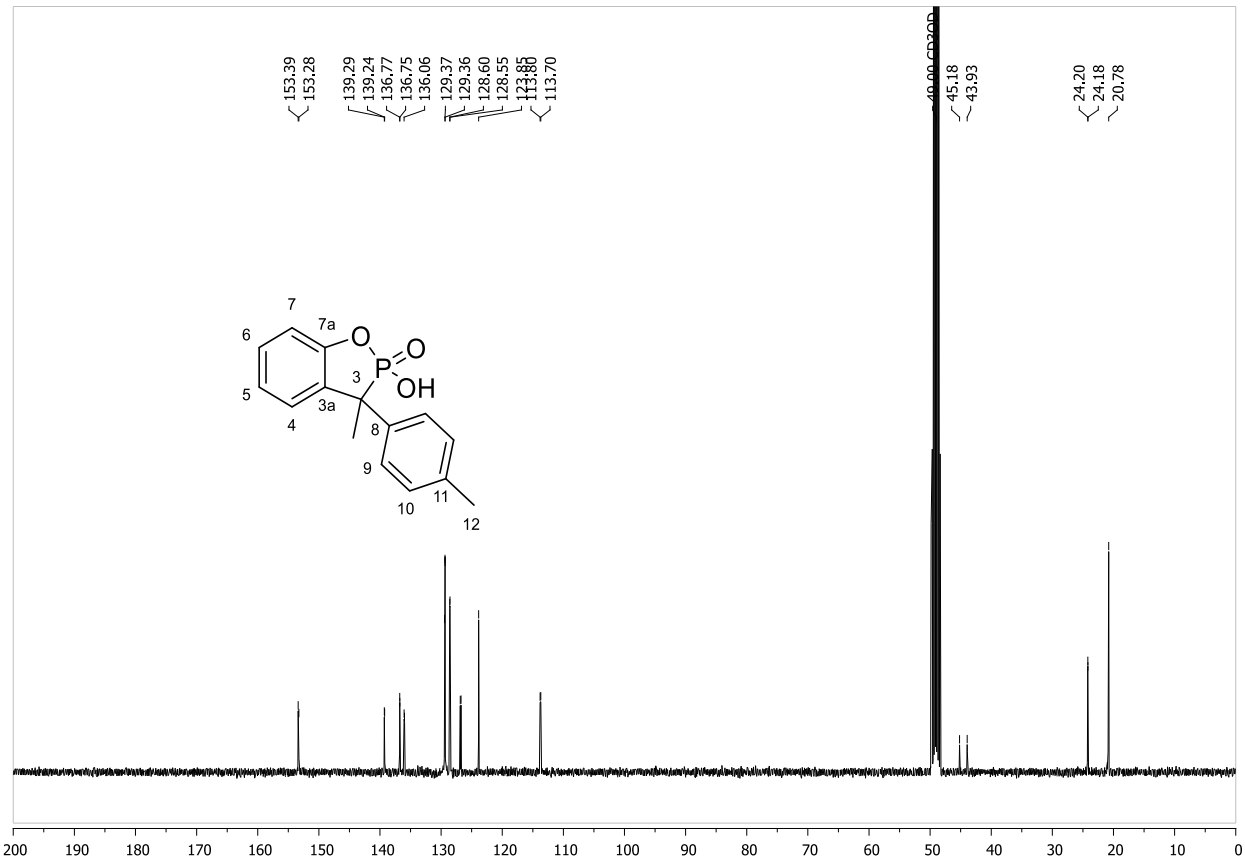
^{31}P NMR (162 MHz, $CDCl_3$) of compound **(9c)**



^{1}H NMR (400 MHz, MeOH-d_4) of compound **(9c)**

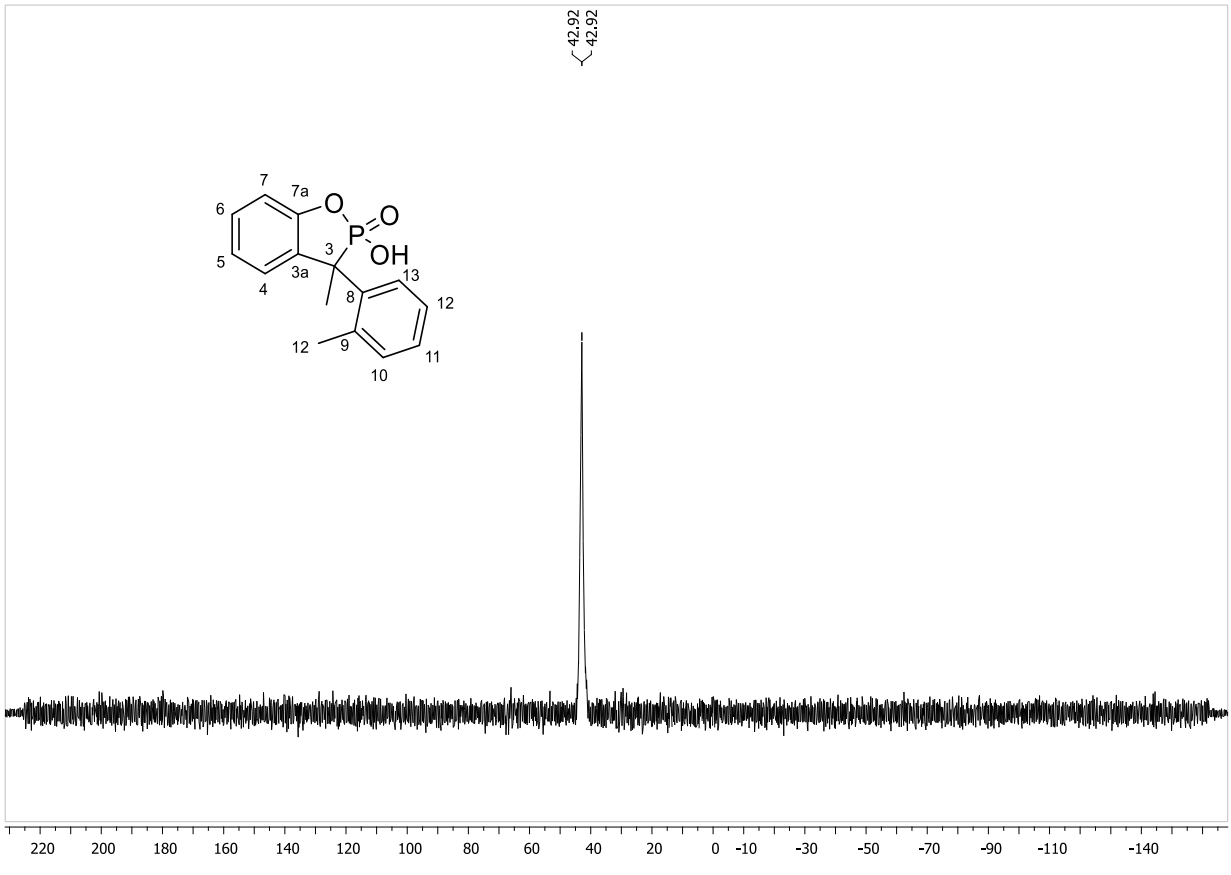


^{13}C NMR (101 MHz, MeOH-d_4) of compound **(9c)**

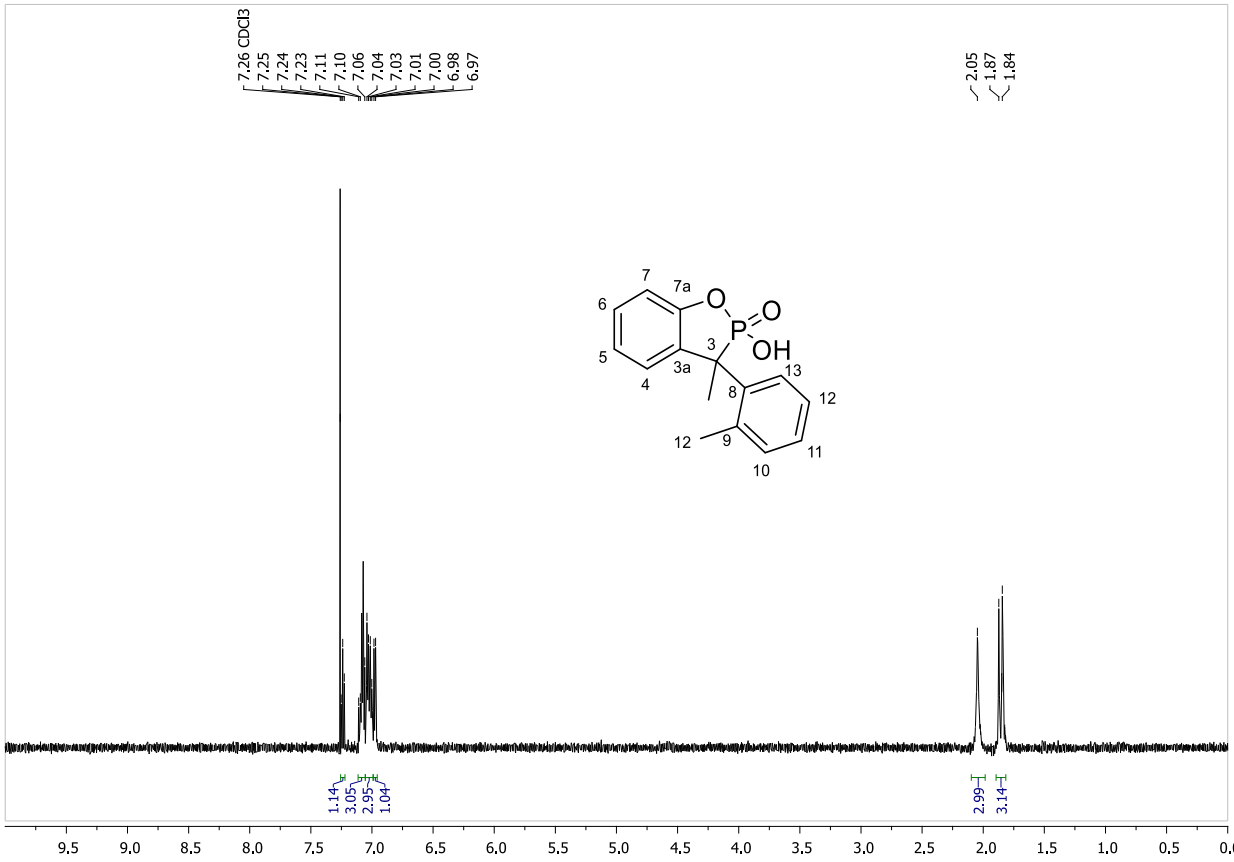


2-hydroxy-3-methyl-3-(o-tolyl)-3*H*-benzo[*d*][1,2]oxaphosphole 2-oxide (9d)

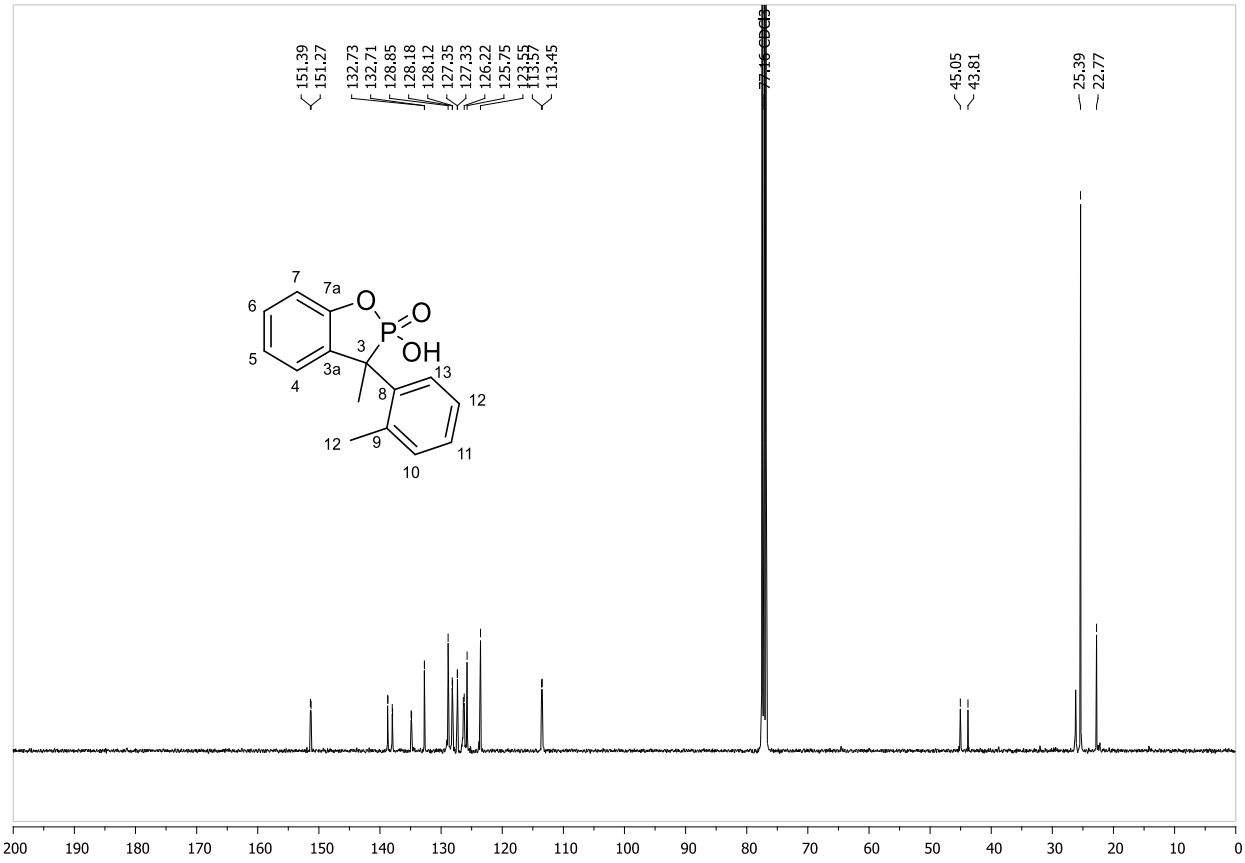
^{31}P NMR (243 MHz, D_2O) of compound **(9d)**



^{1}H NMR (600 MHz, $CDCl_3$) of compound **(9d)**

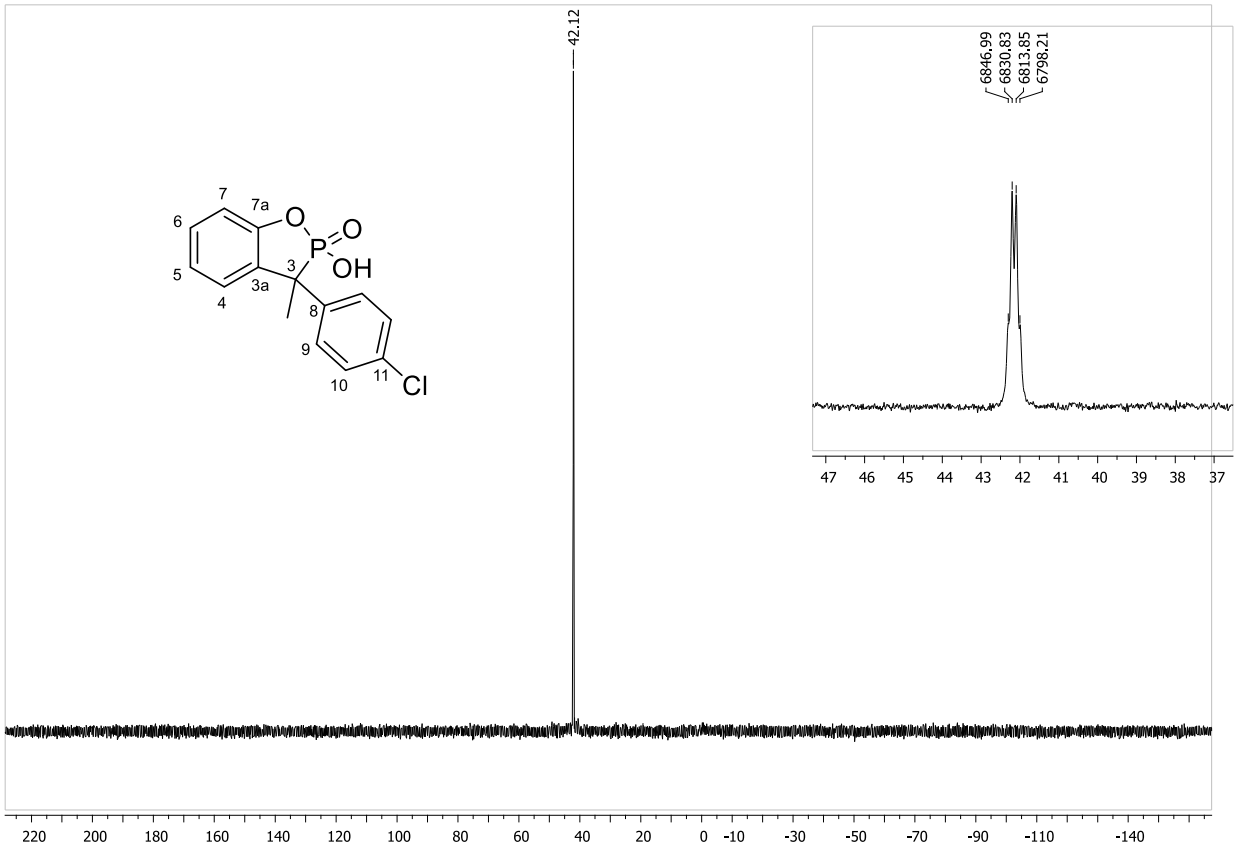


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(9d)**

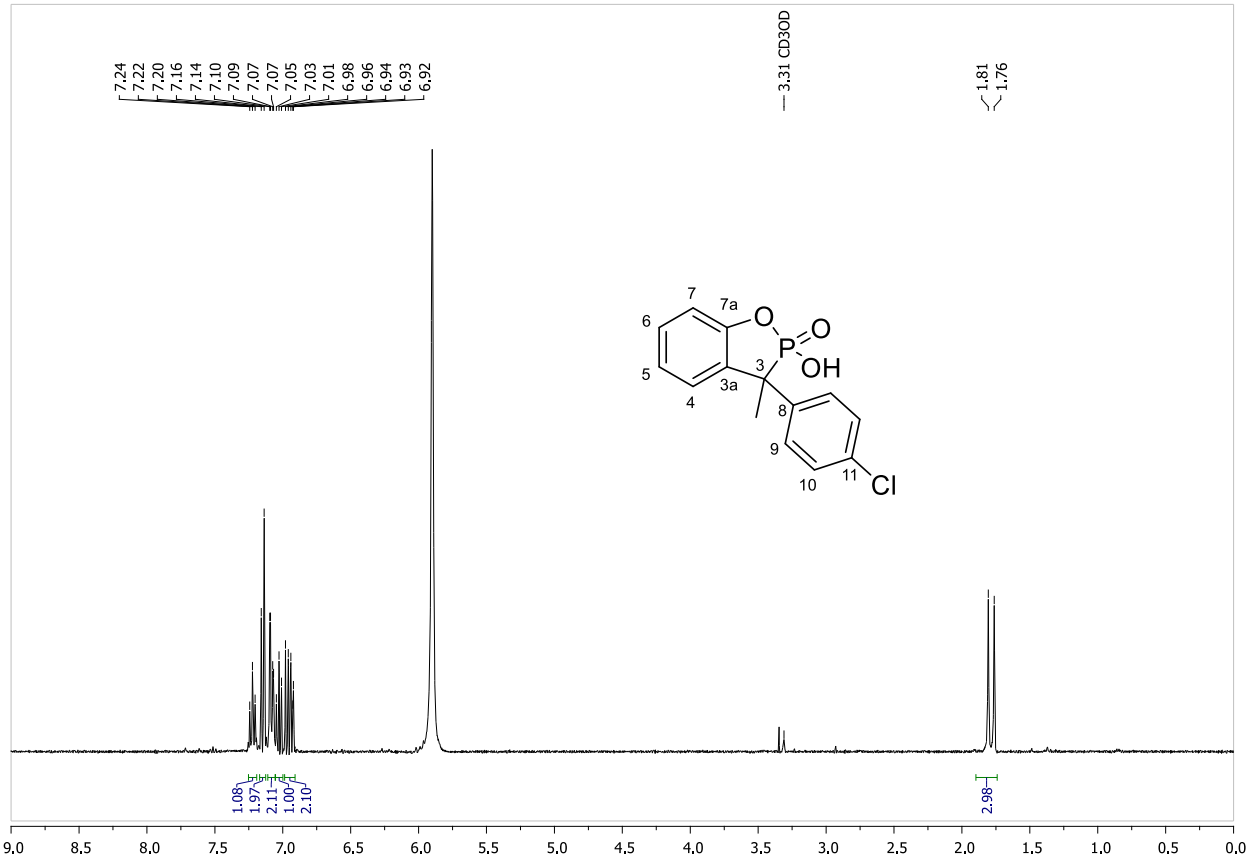


3-(4-chlorophenyl)-2-hydroxy-3-methyl-3*H*-benzo[*d*][1,2]oxaphosphole 2-oxide (9e)

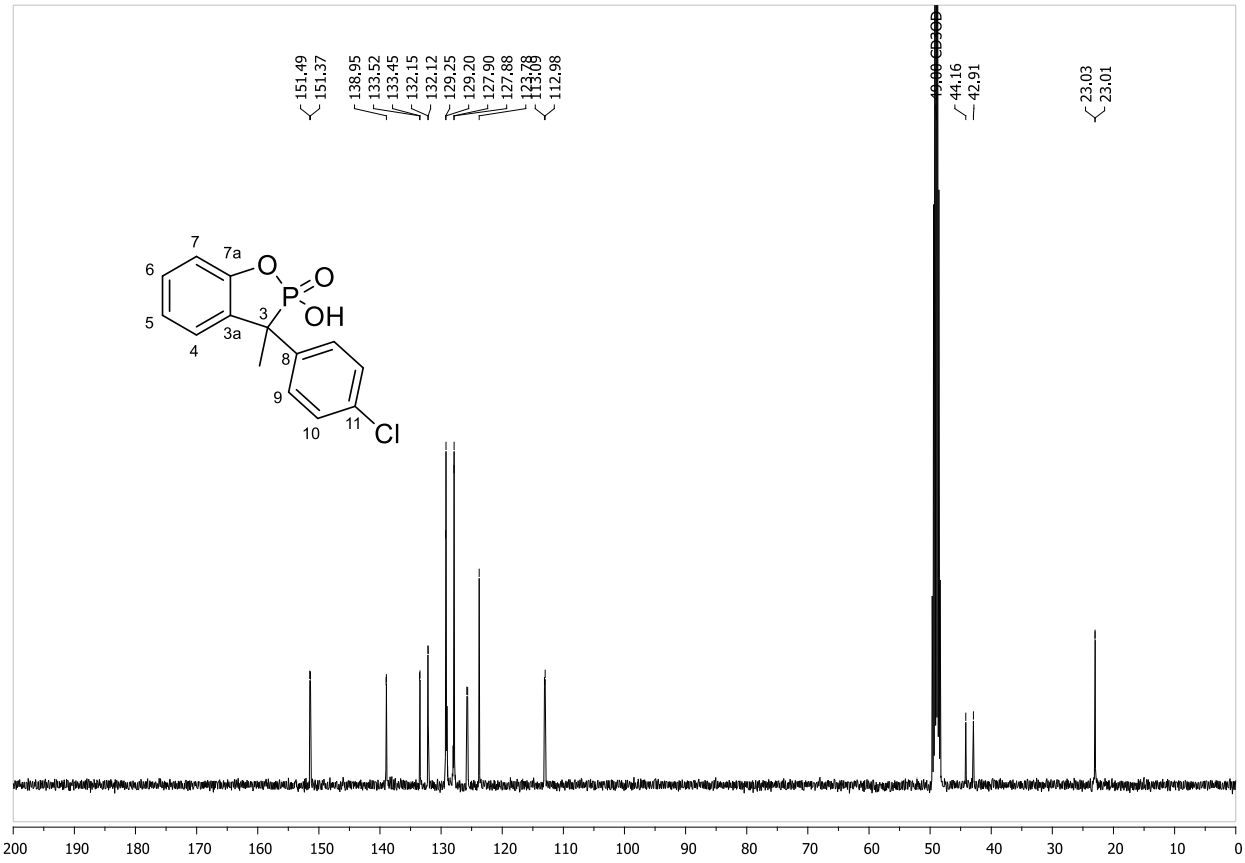
^{31}P NMR (162 MHz, $CDCl_3$) of compound **(9e)**



^{1}H NMR (400 MHz, MeOH-d_4) of compound **(9e)**

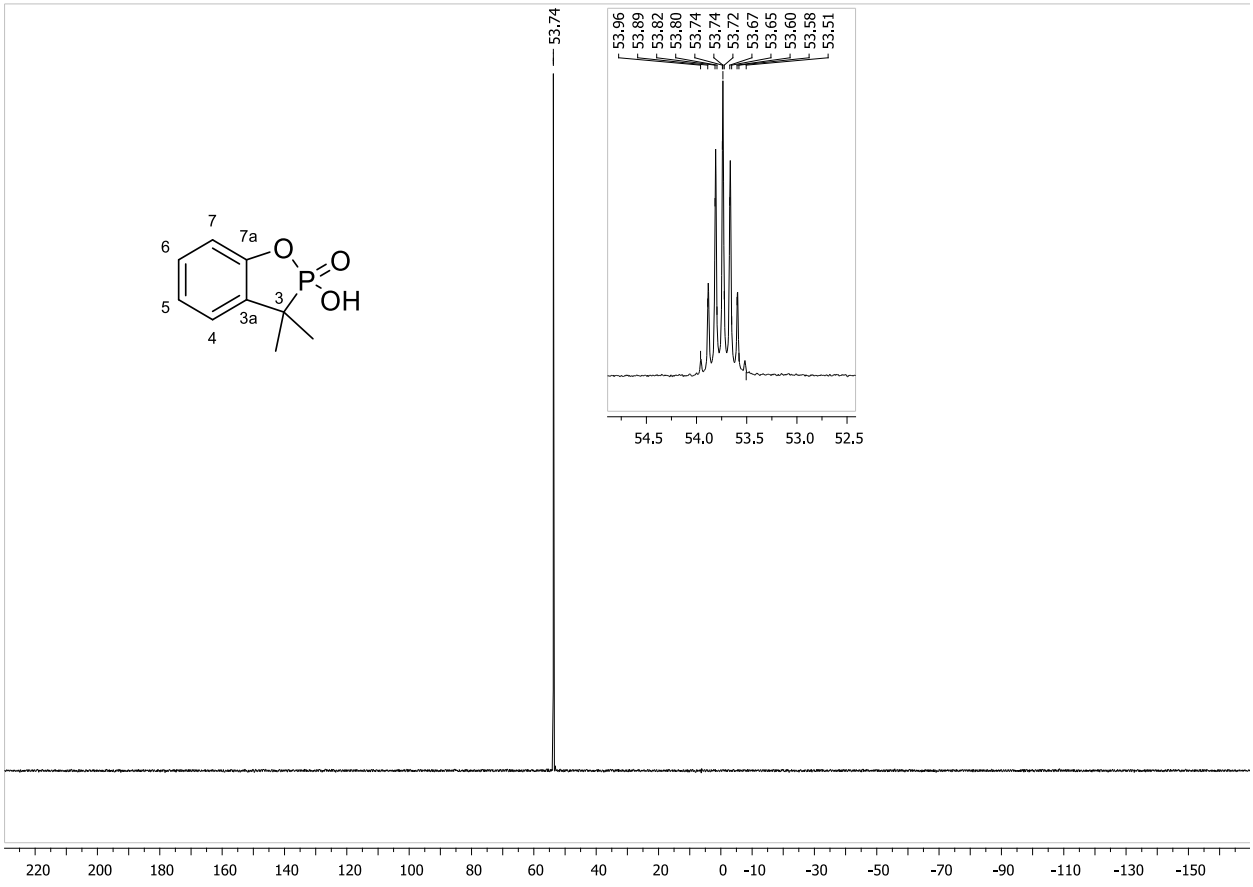


^{13}C NMR (101 MHz, MeOH-d_4) of compound **(9e)**

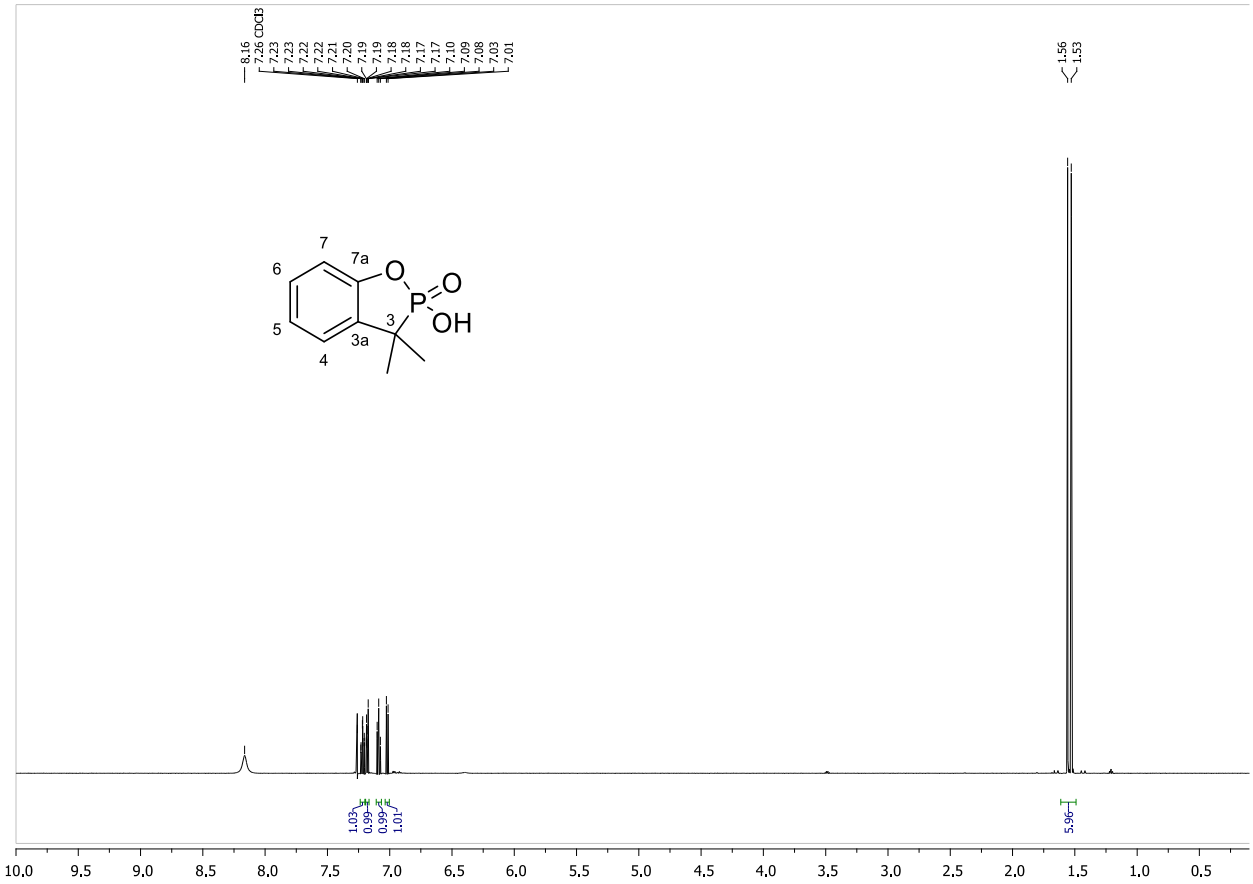


2-hydroxy-3,3-dimethyl-3*H*-benzo[*d*][1,2]oxaphosphole 2-oxide (9f)

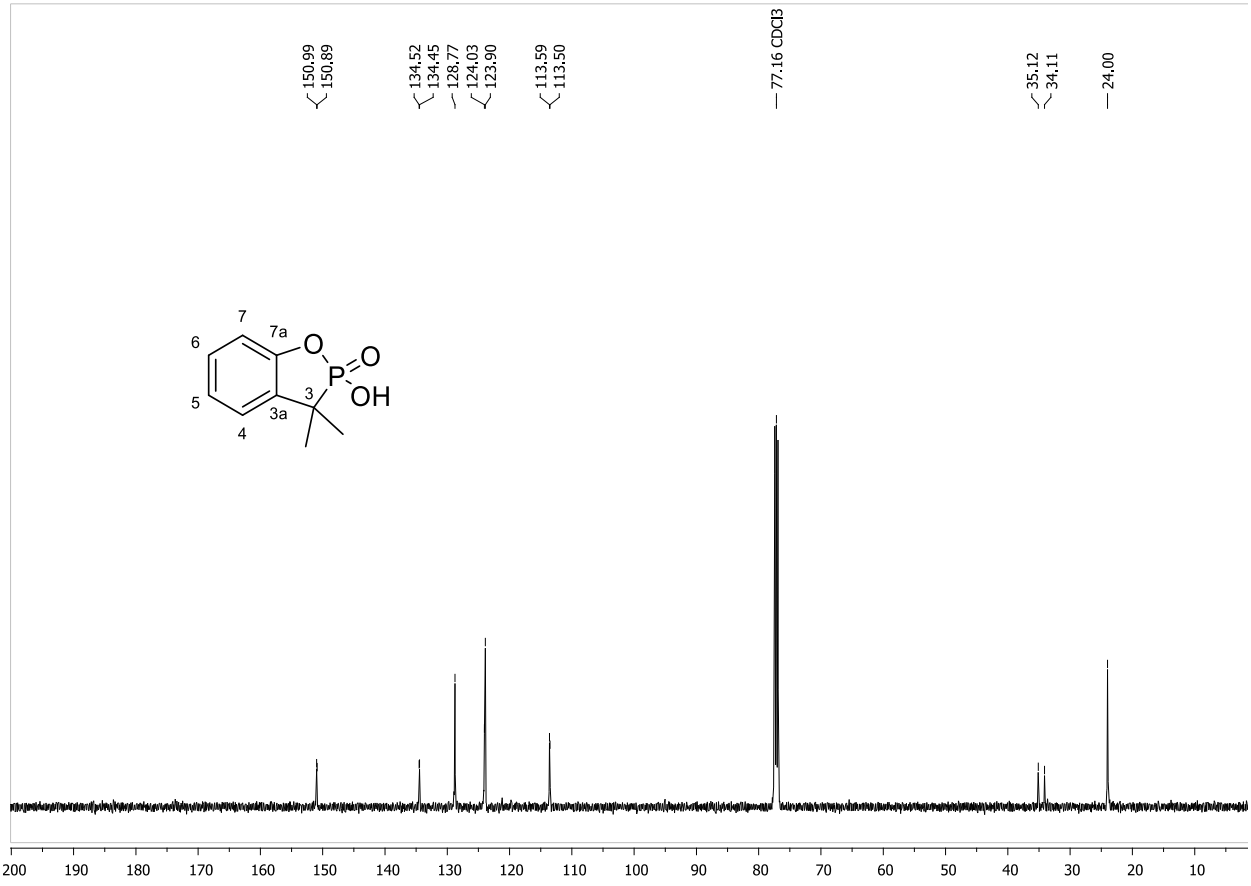
^{31}P NMR (243 MHz, $CDCl_3$) of compound **(9f)**



^{1}H NMR (600 MHz, $CDCl_3$) of compound **(9f)**

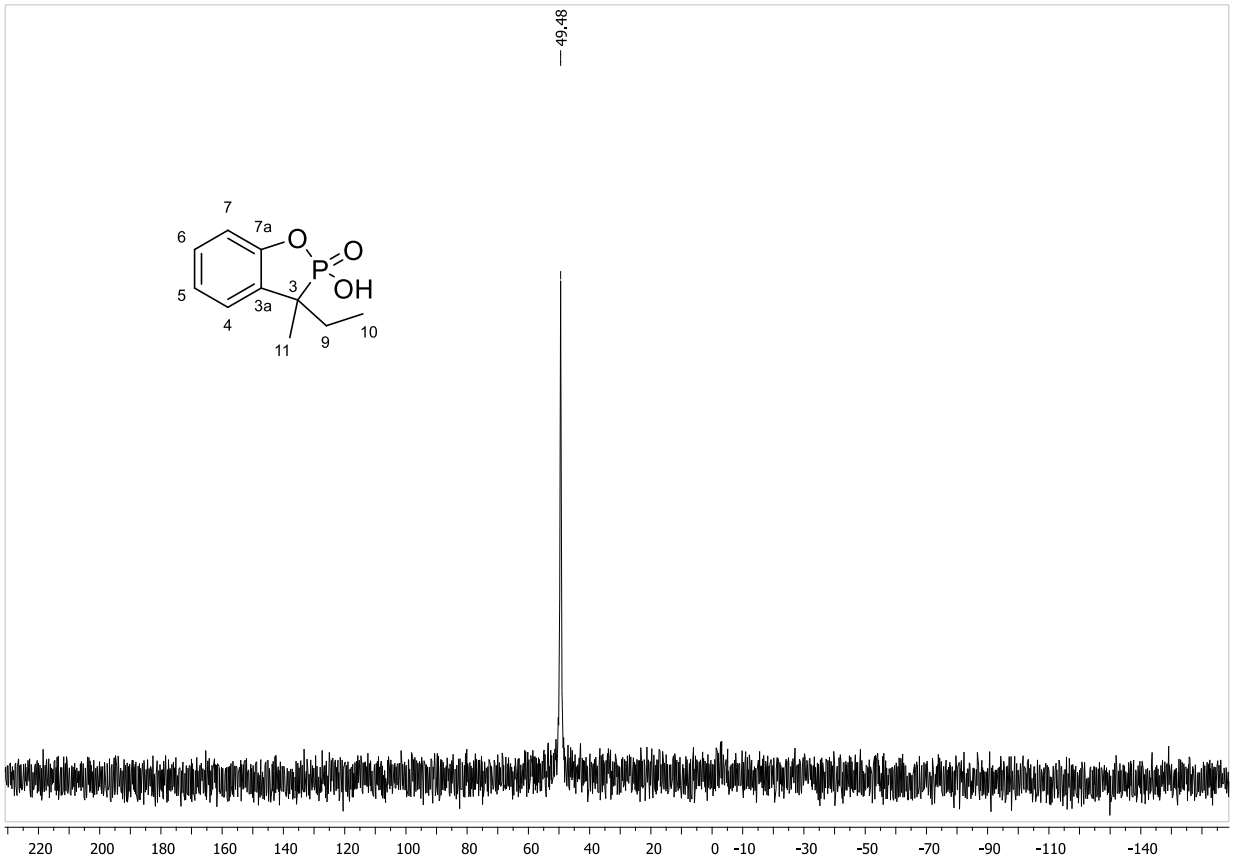


^{13}C NMR (126 MHz, $CDCl_3$) of compound **(9f)**

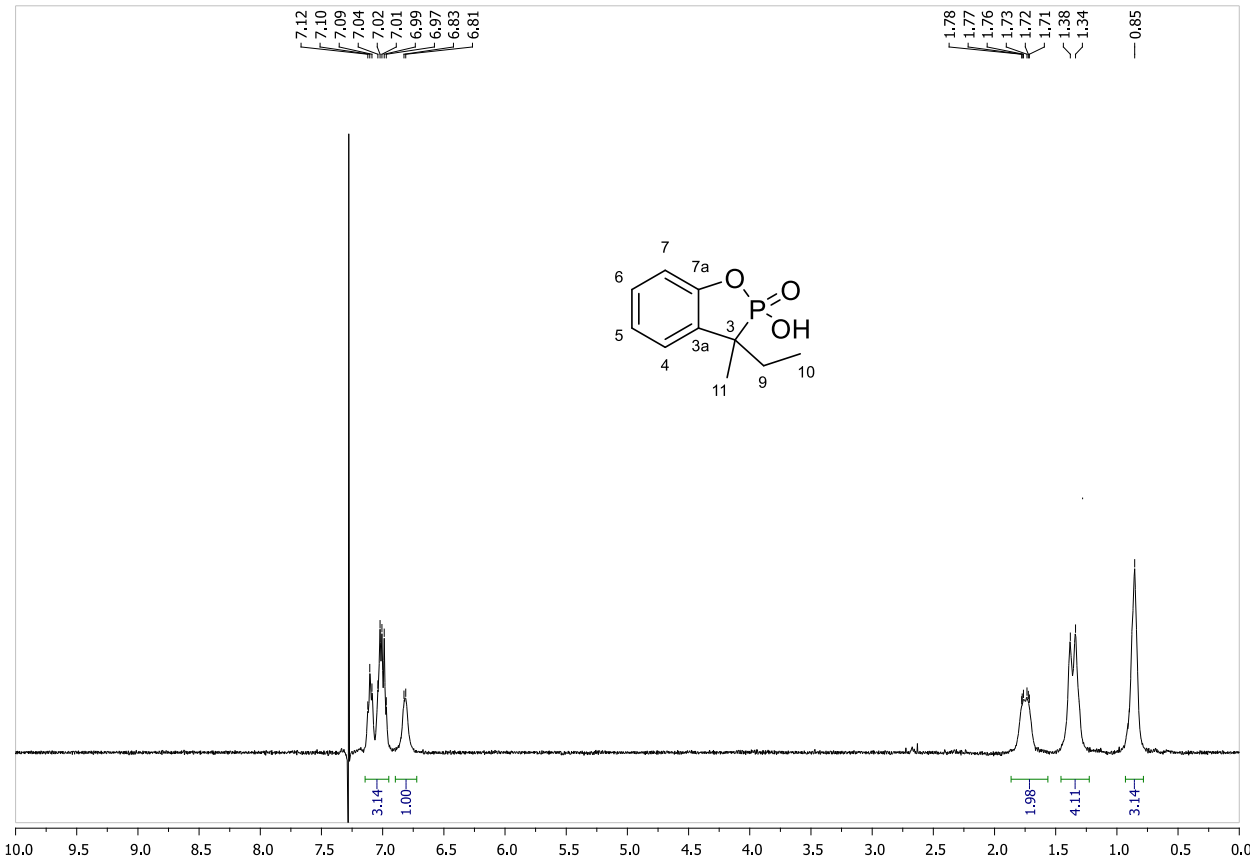


3-ethyl-2-hydroxy-3-methyl-3*H*-benzo[*d*][1,2]oxaphosphole 2-oxide (9g)

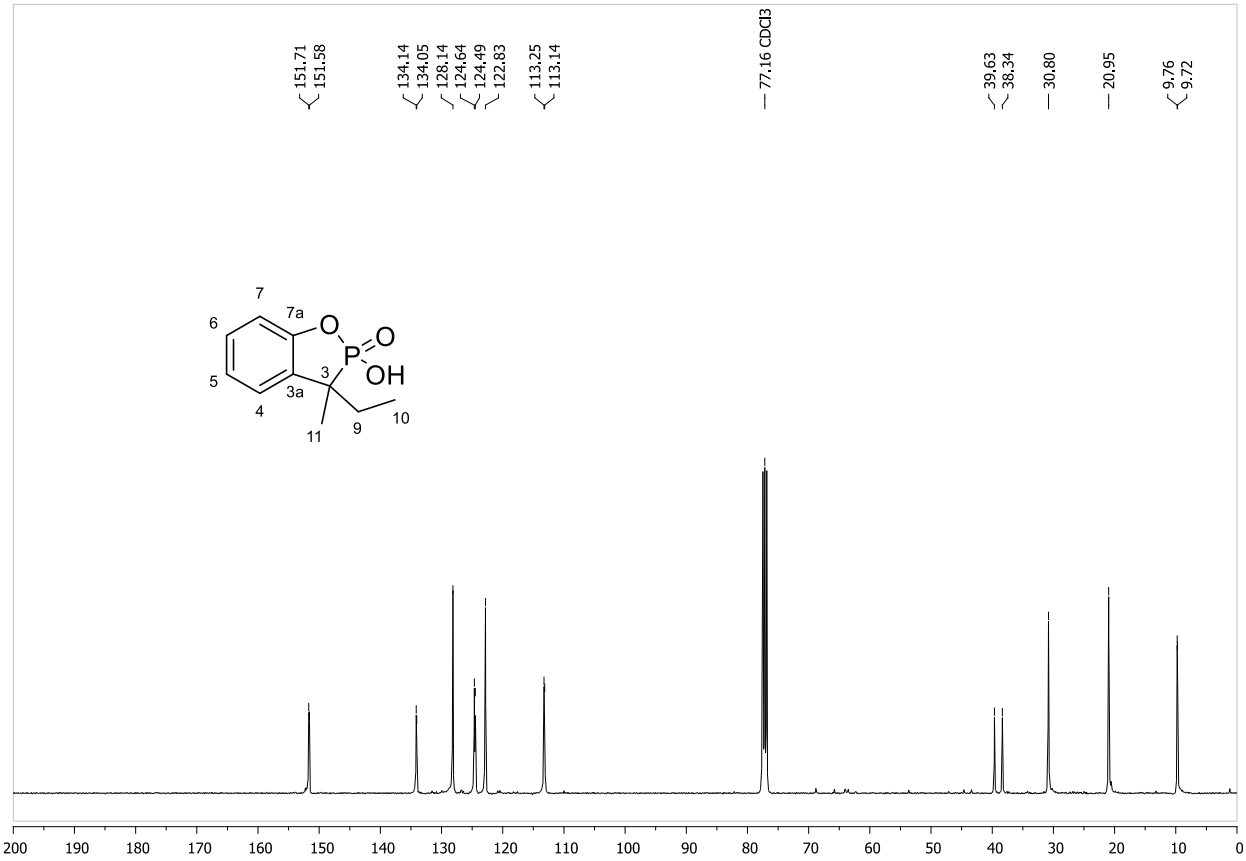
^{31}P NMR (243 MHz, $CDCl_3$) of compound **(9g)**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(9g)**

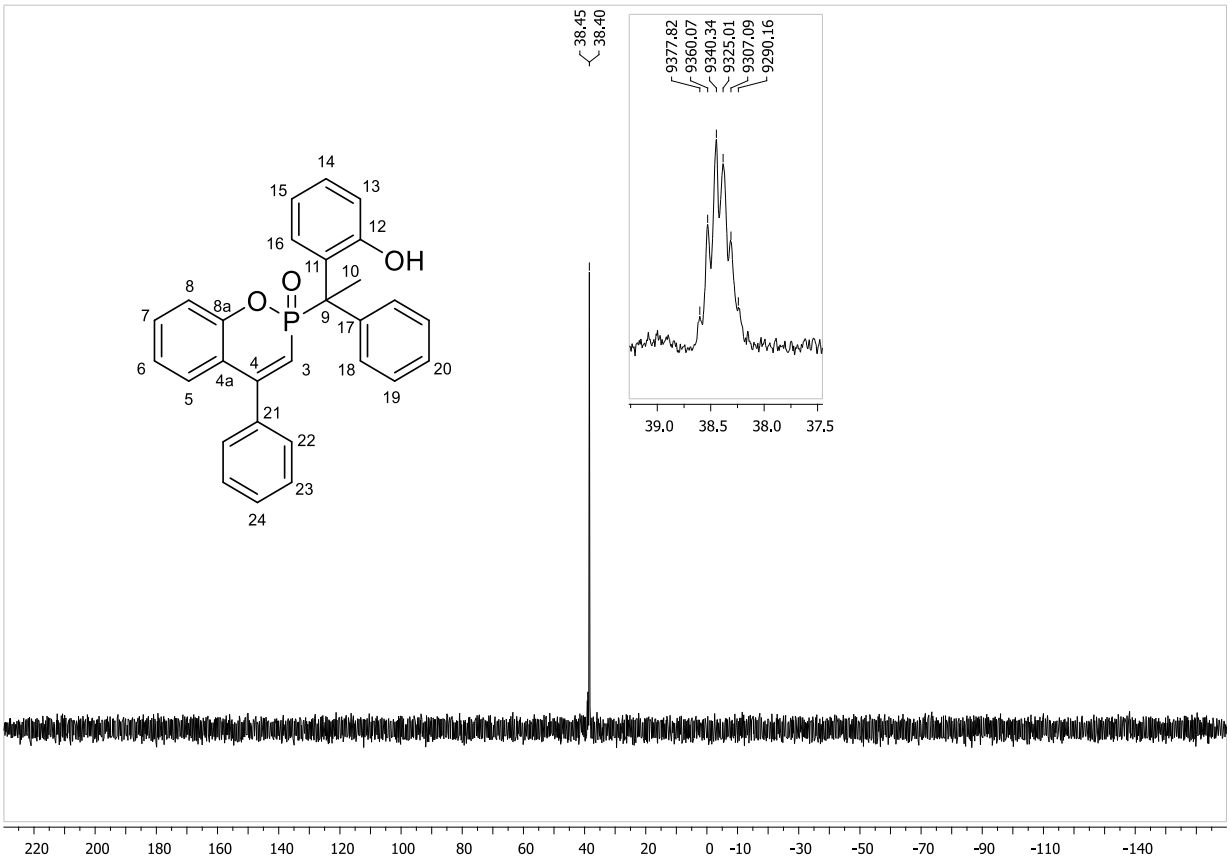


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(9g)**

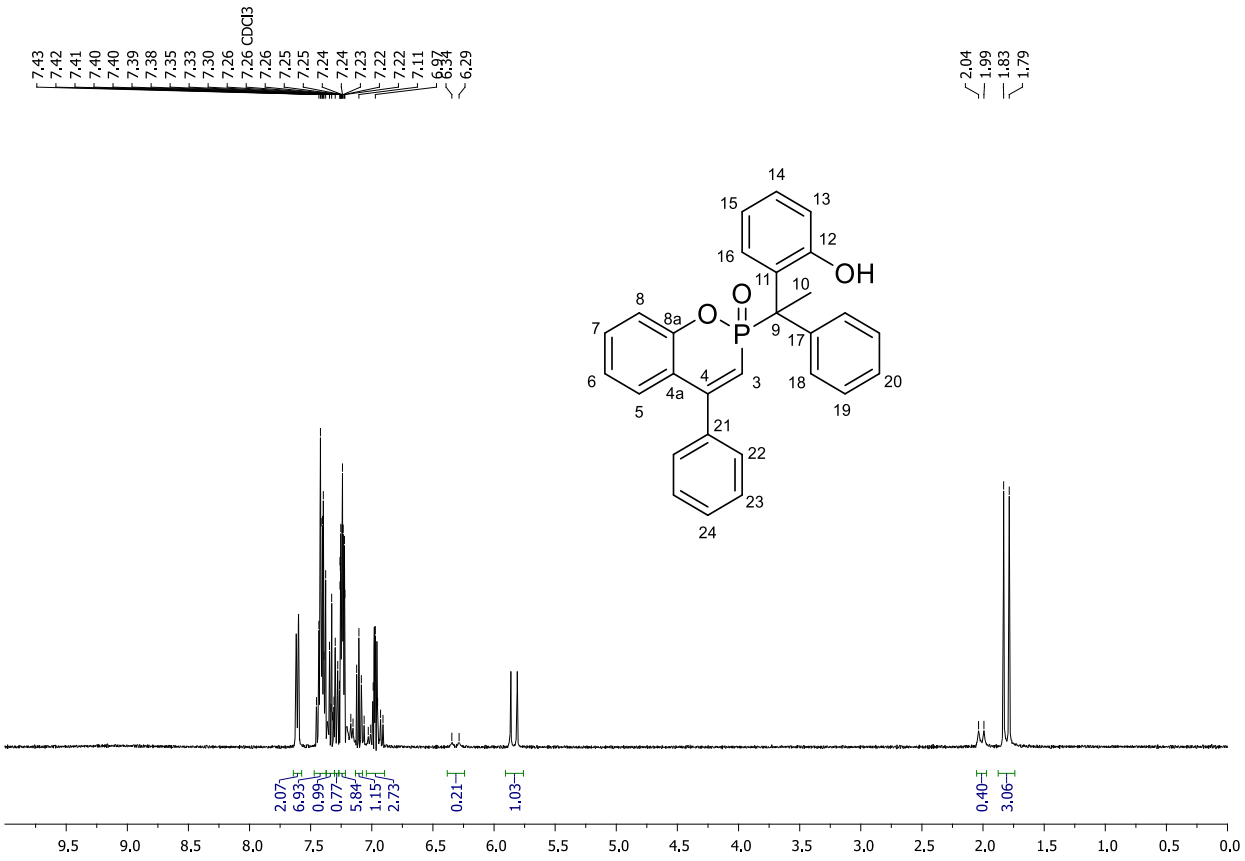


2-(1-(2-hydroxyphenyl)-1-phenylethyl)-4-phenylbenzo[*e*][1,2]oxaphosphinine 2-oxide (10a)

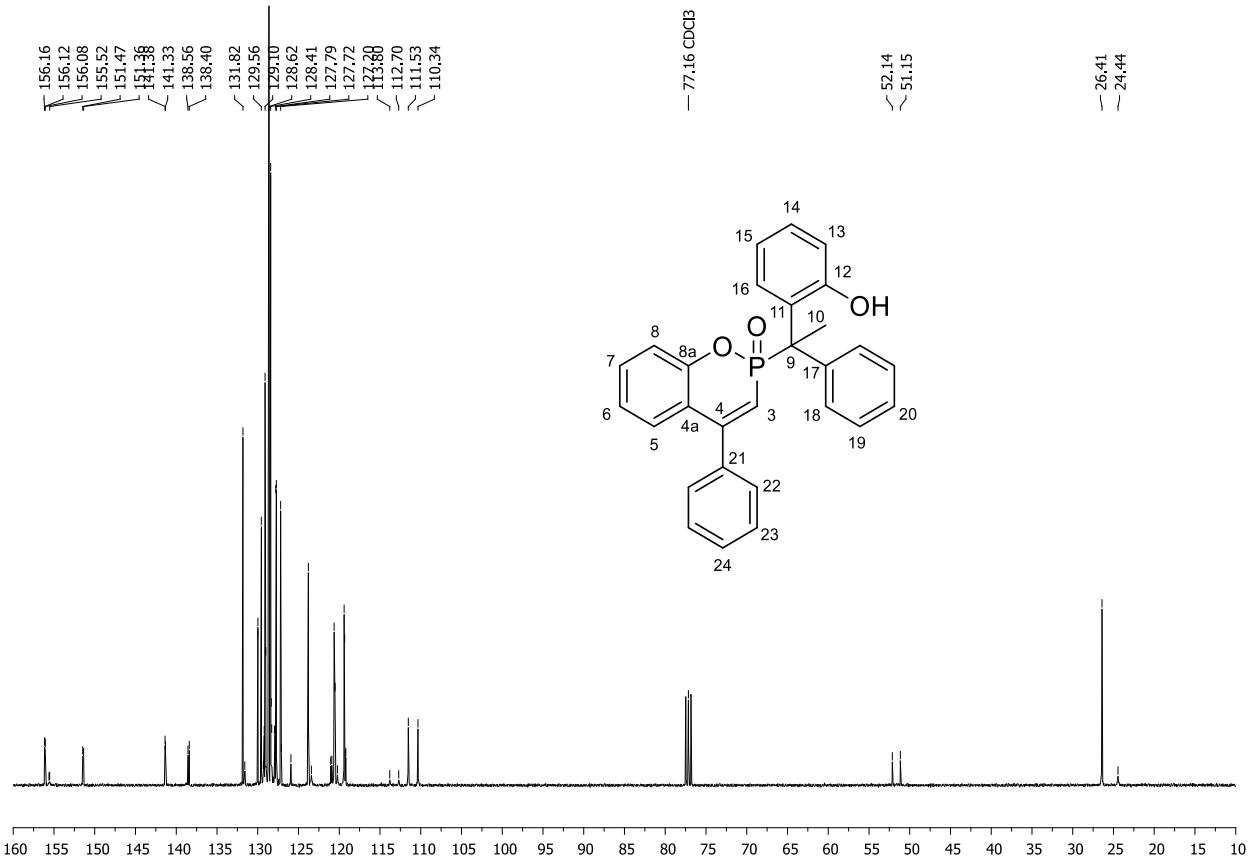
^{31}P NMR (243 MHz, $CDCl_3$) of compound **(10a)**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(10a)**

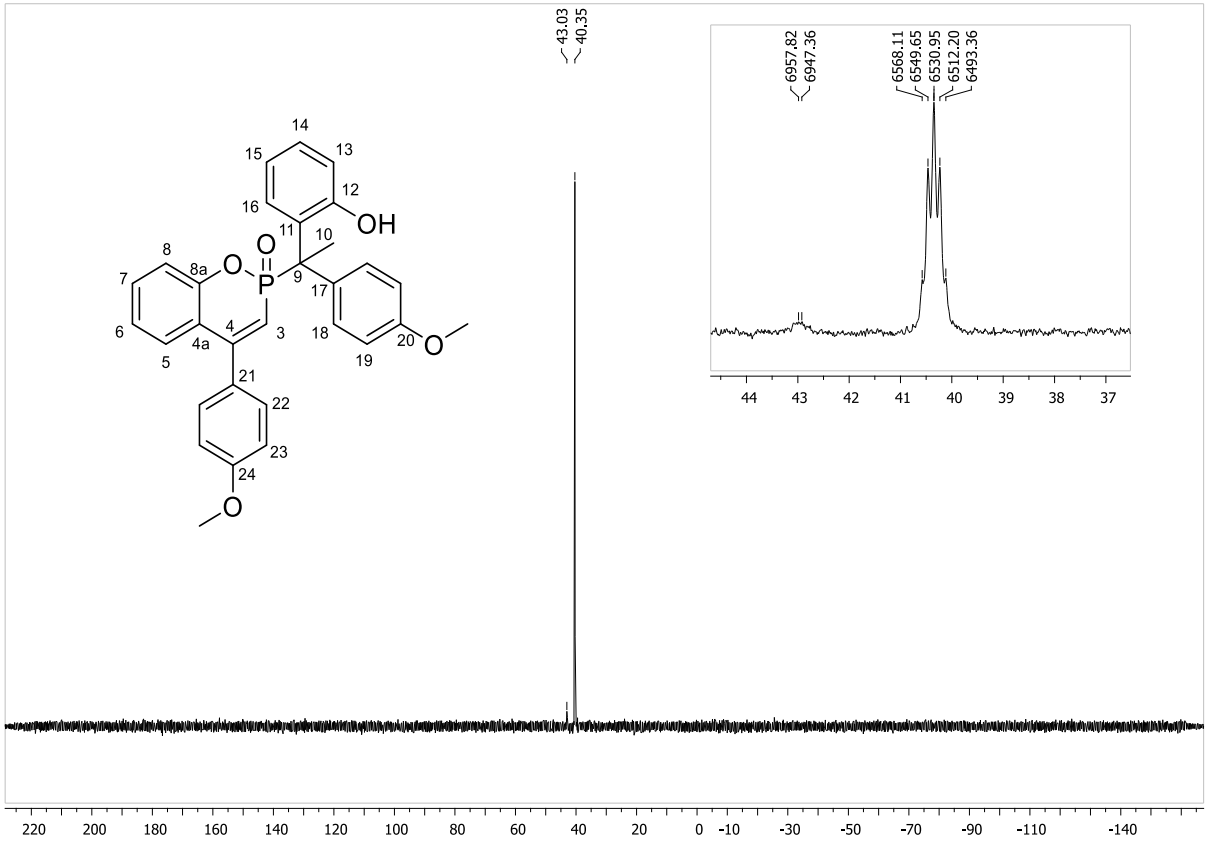


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(10a)**

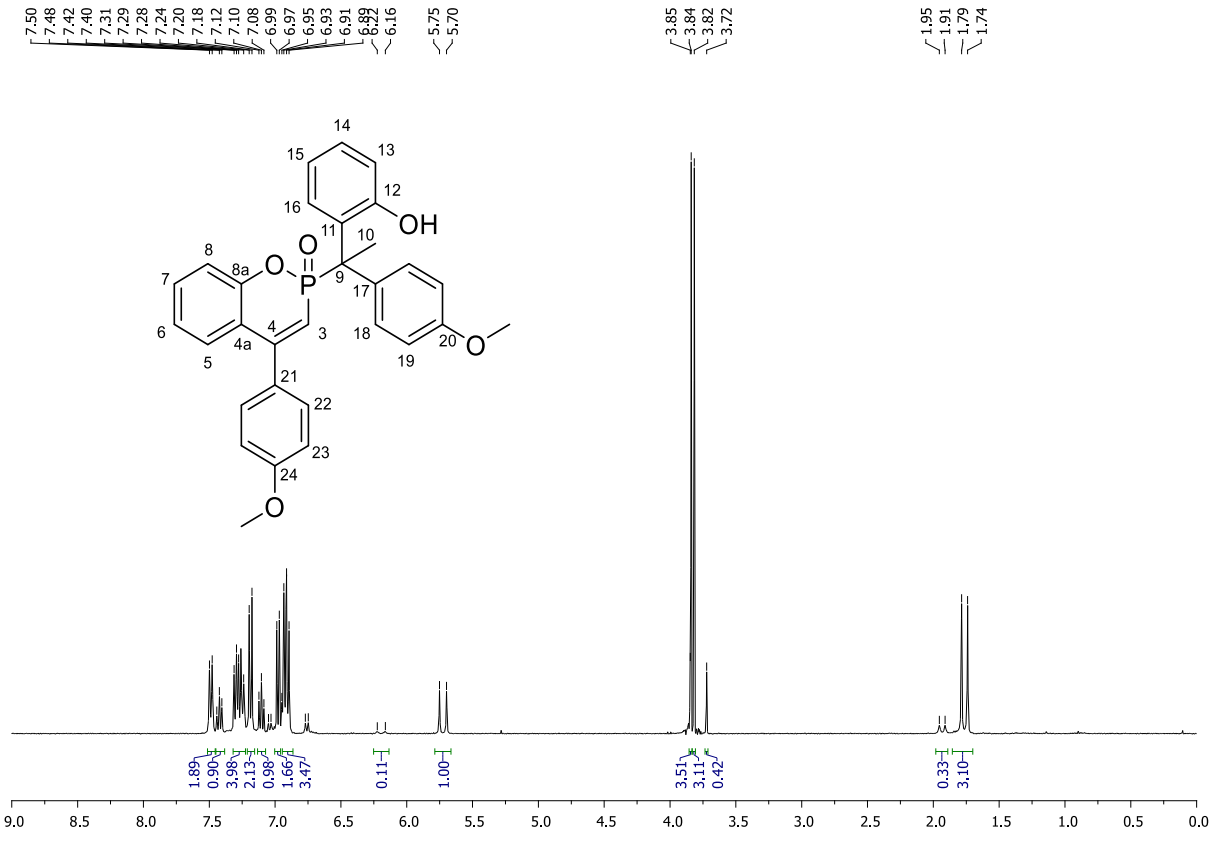


2-(1-(2-hydroxyphenyl)-1-(4-methoxyphenyl)ethyl)-4-(4-methoxyphenyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (10b)

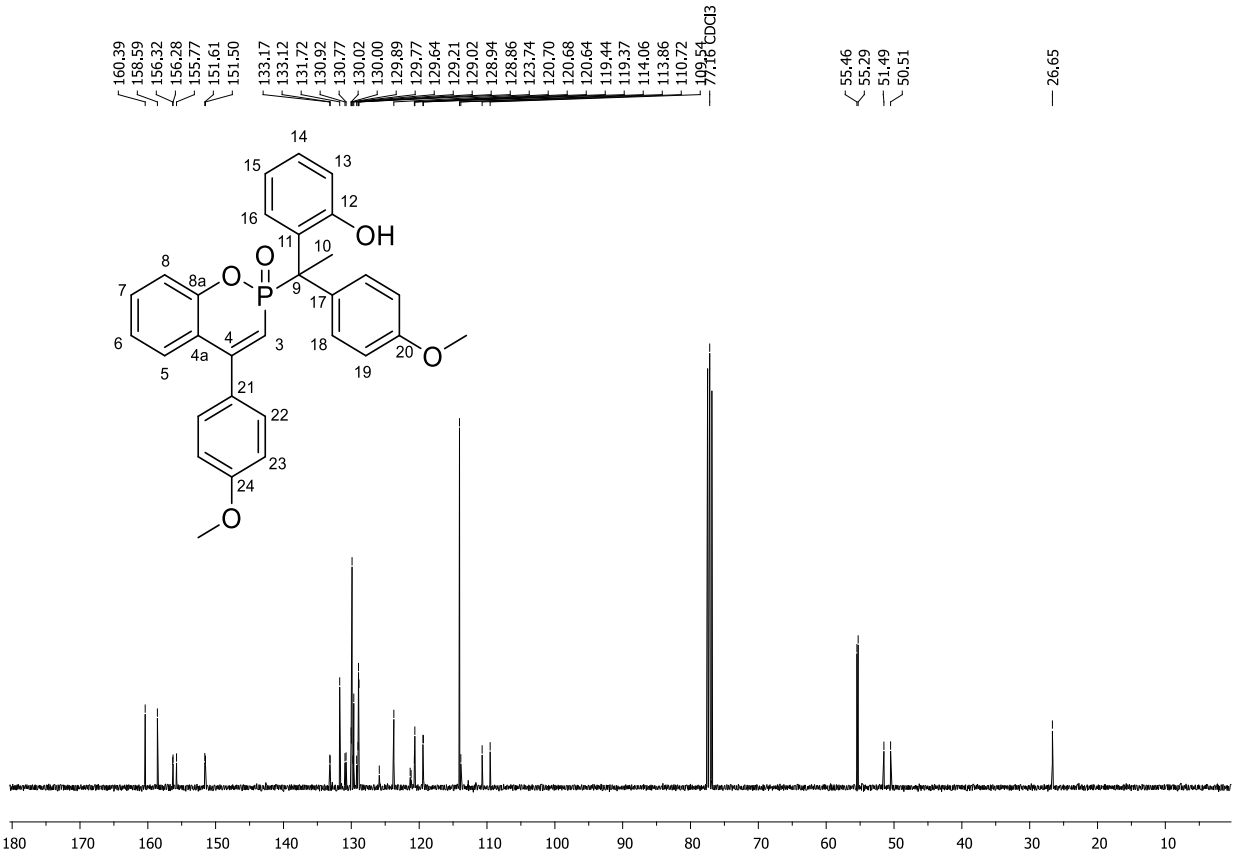
^{31}P NMR (162 MHz, $CDCl_3$) of compound **(10b)**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(10b)**

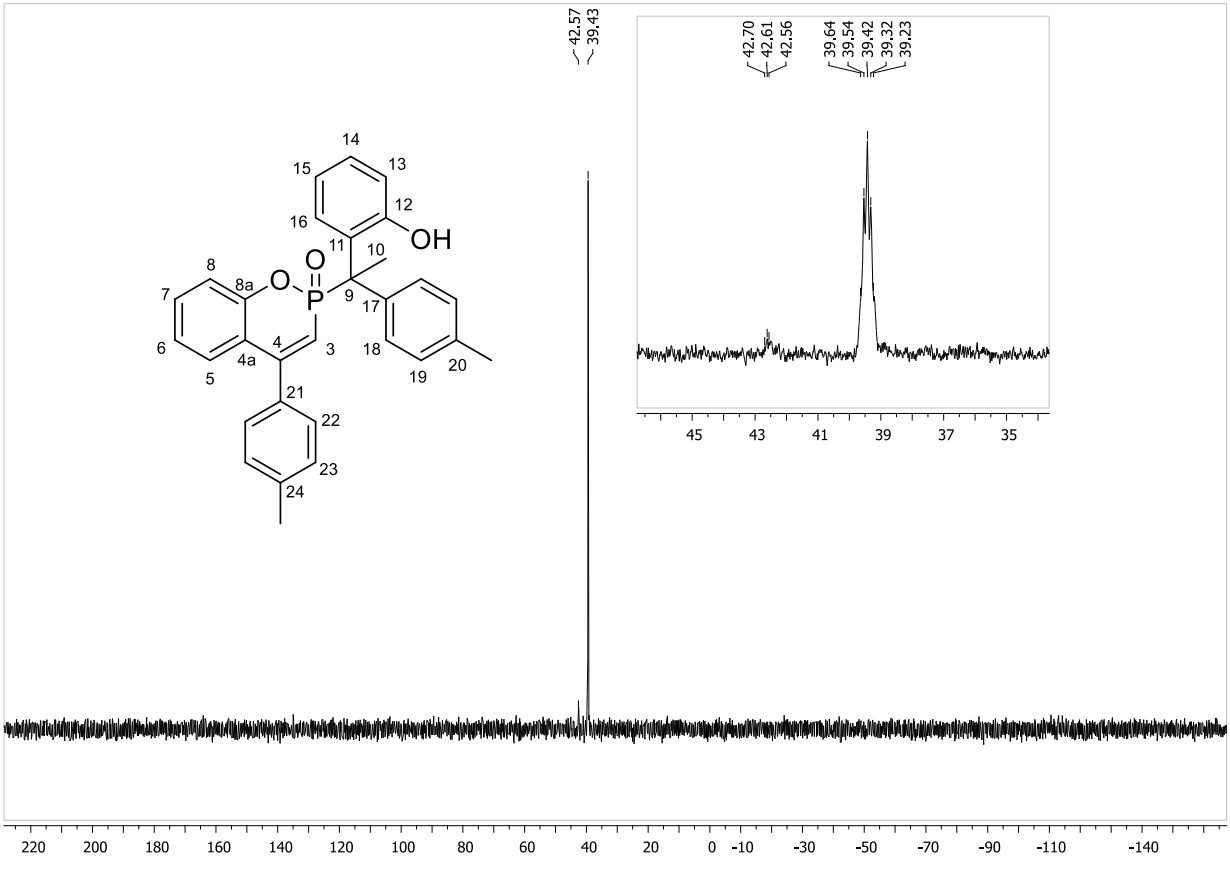


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(10b)**

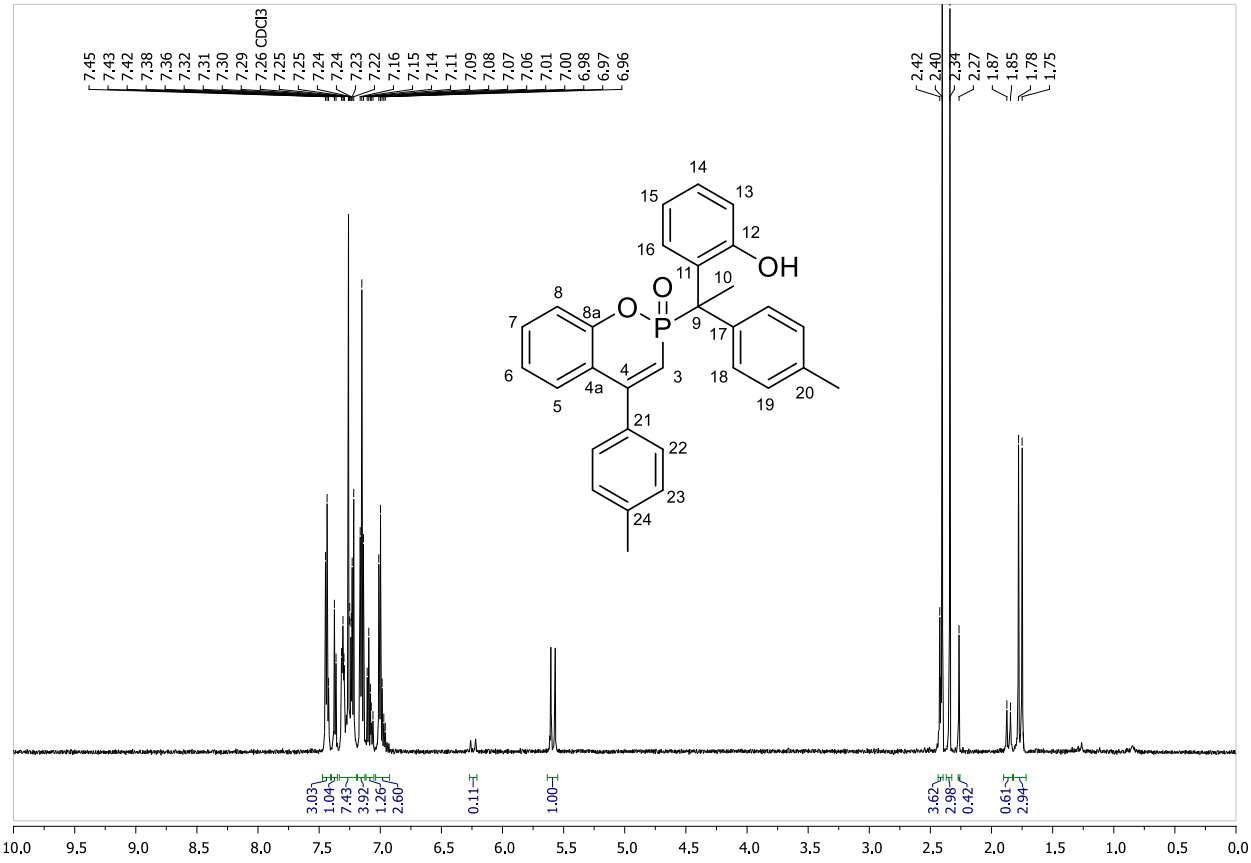


2-(1-(2-hydroxyphenyl)-1-(p-tolyl)ethyl)-4-(p-tolyl)benzo[*e*][1,2]oxaphosphinine-2-oxide (10c)

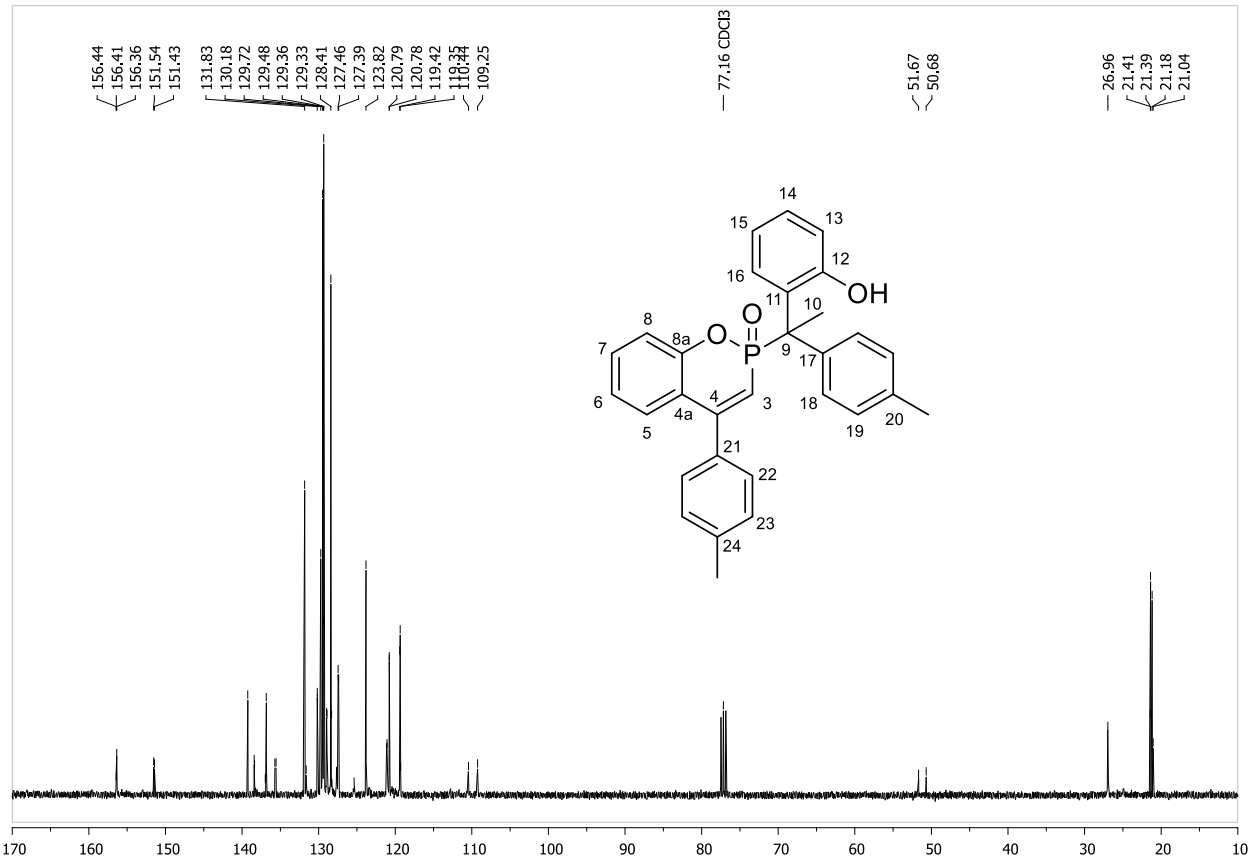
^{31}P NMR (162 MHz, $CDCl_3$) of compound **(10c)**



^{1}H NMR (600 MHz, $CDCl_3$) of compound **(10c)**

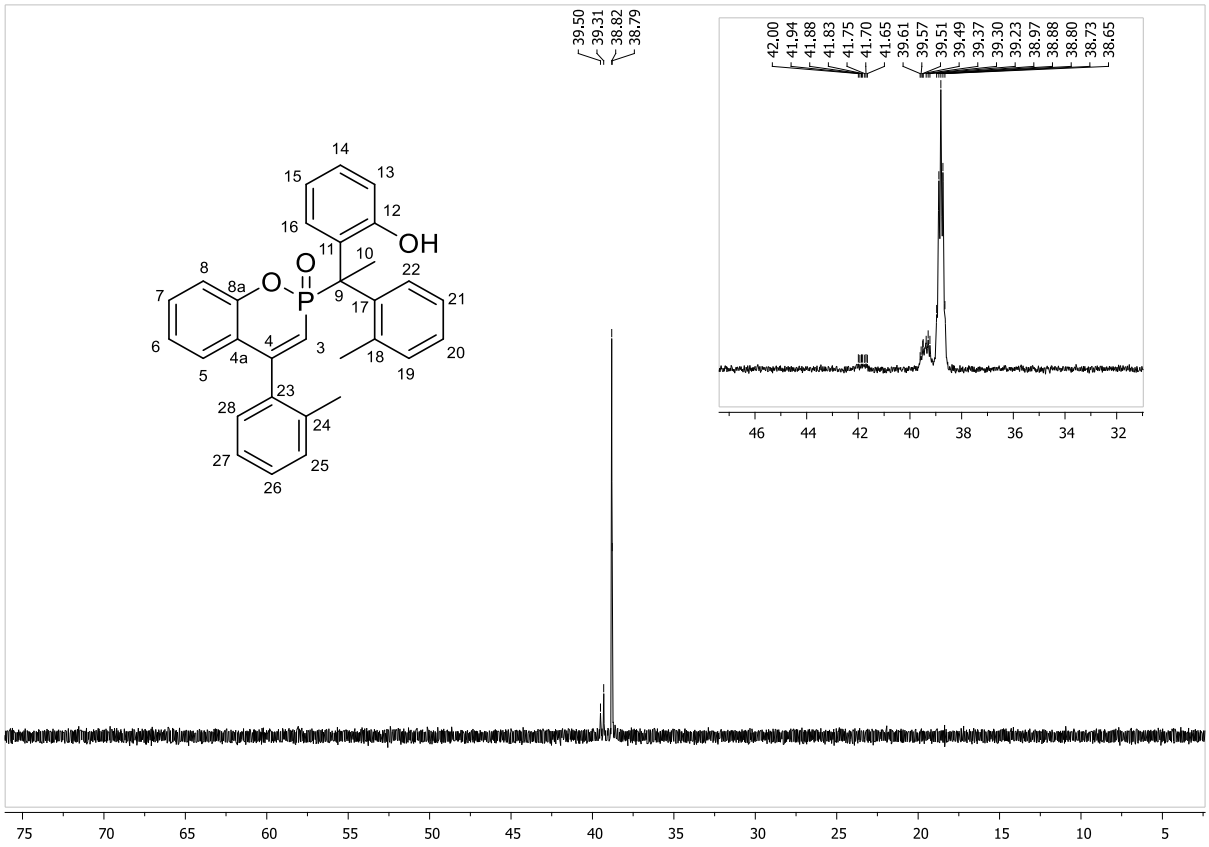


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(10c)**

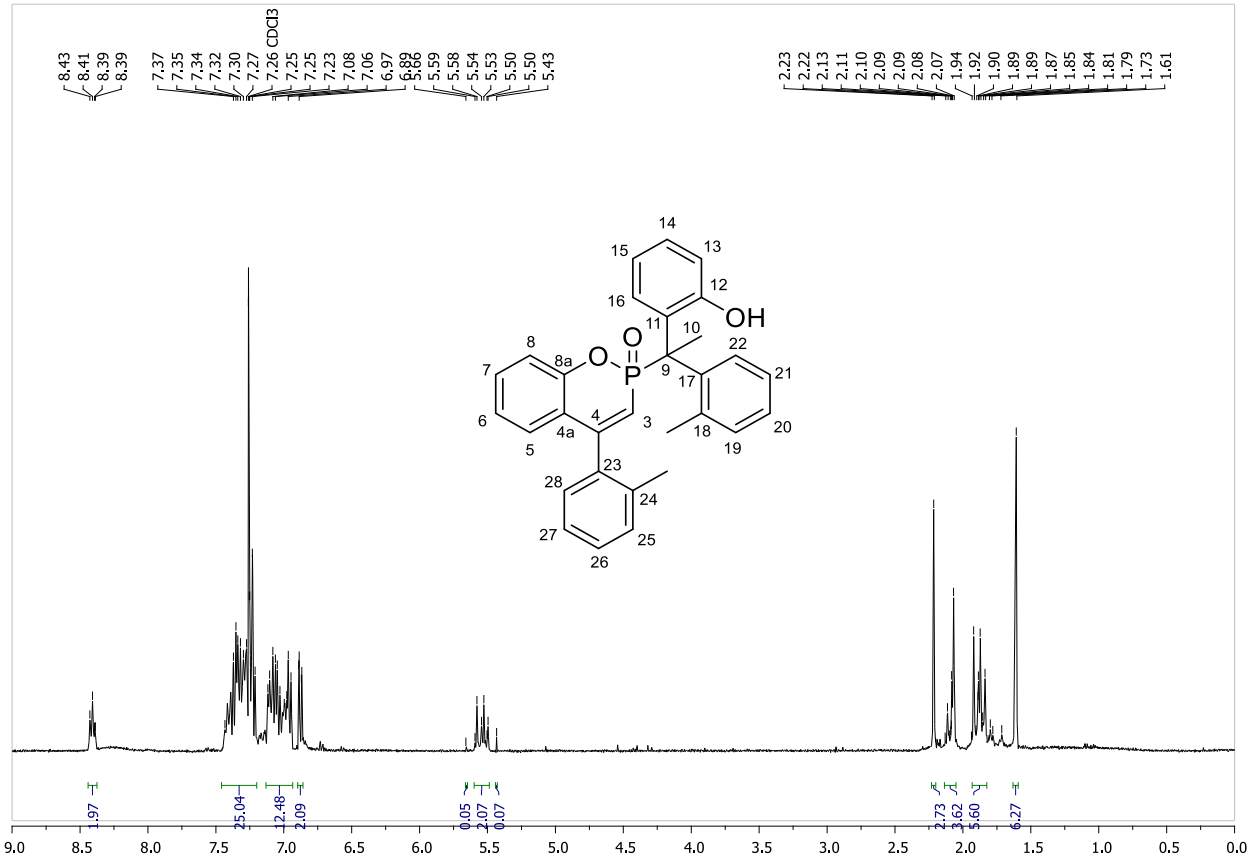


2-(1-(2-hydroxyphenyl)-1-(o-tolyl)ethyl)-4-(o-tolyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (10d)

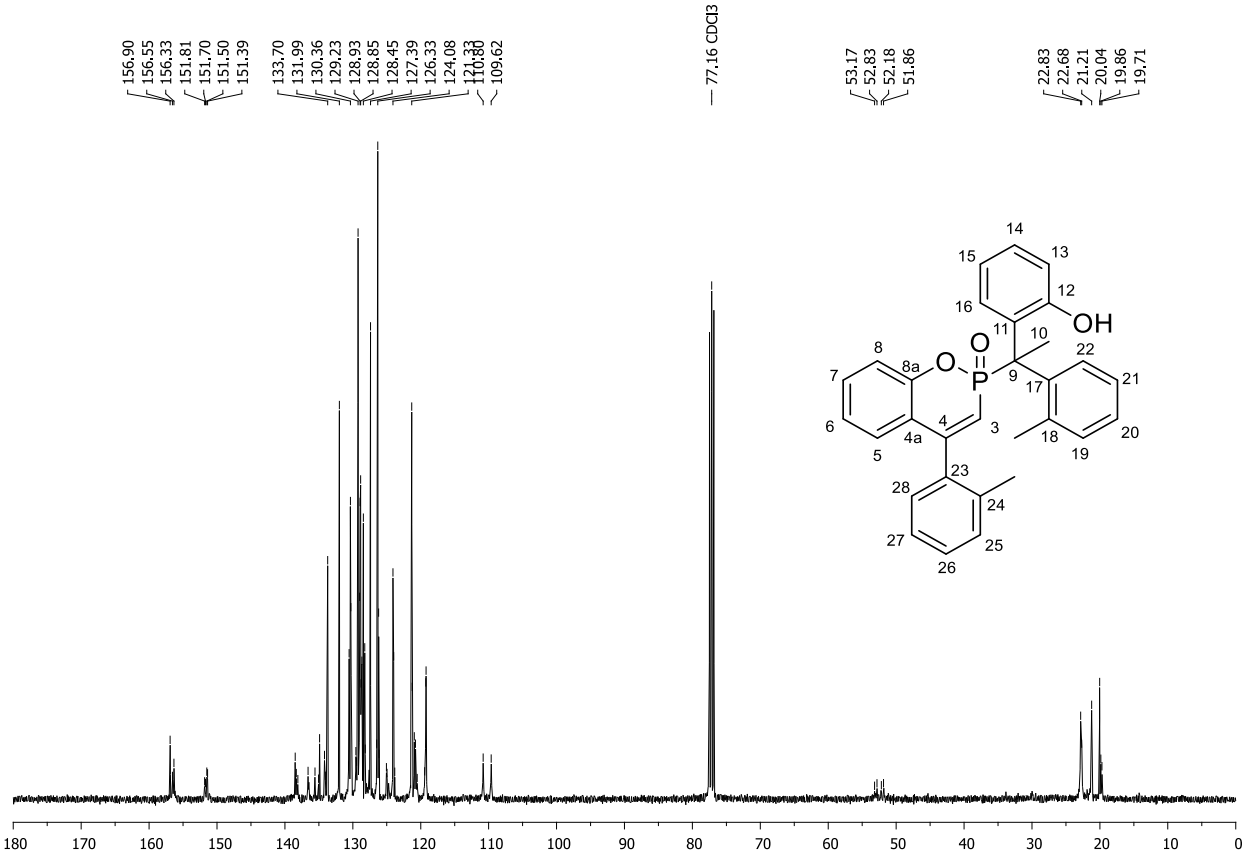
^{31}P NMR (243 MHz, $CDCl_3$) of compound **(10d)**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(10d)**

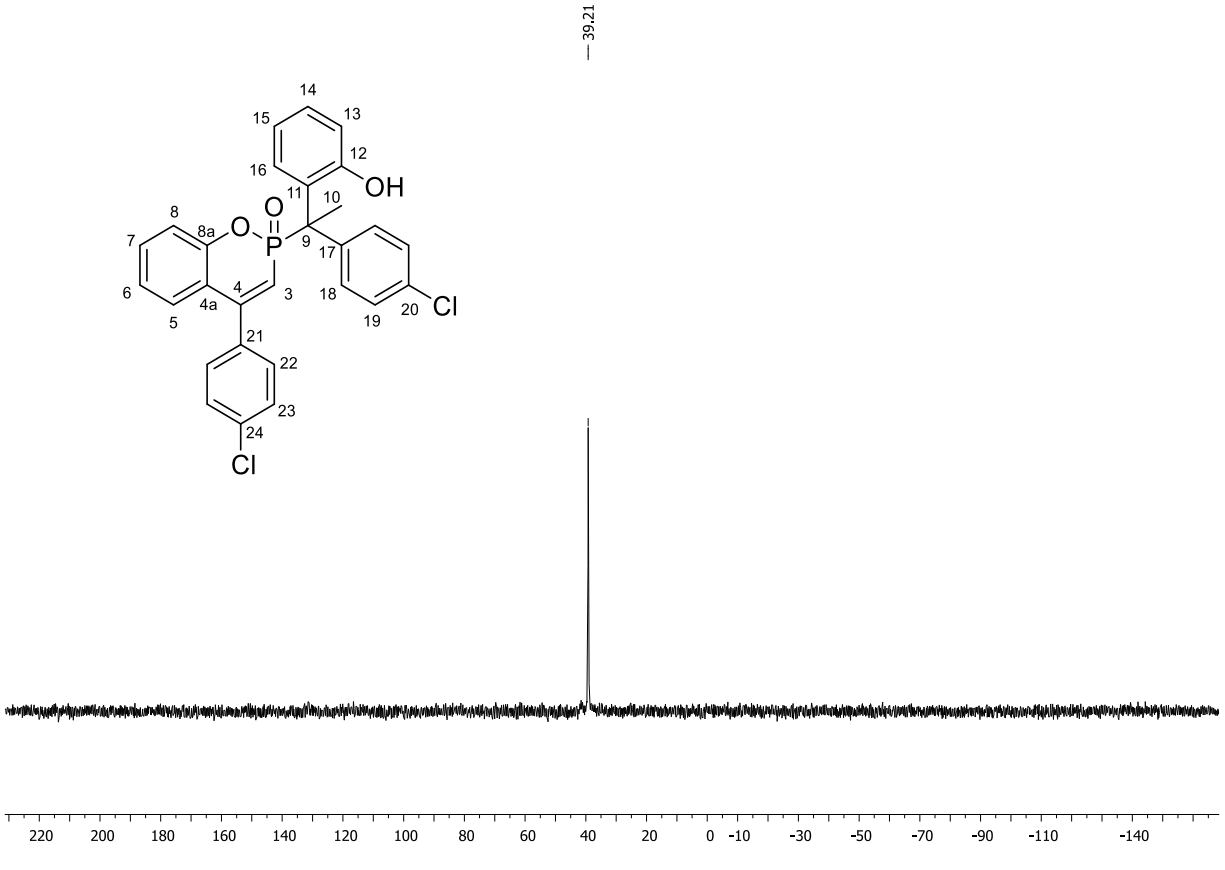


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(10d)**

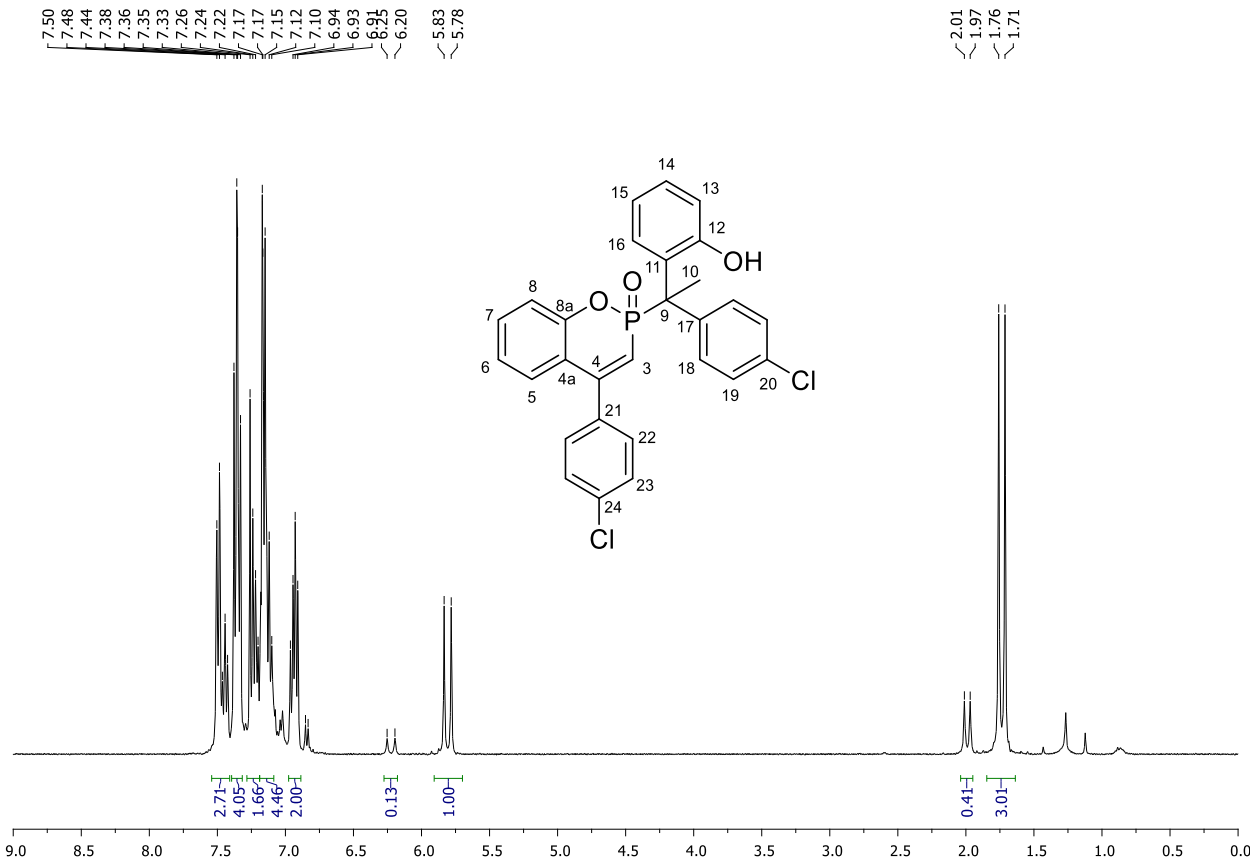


4-(4-chlorophenyl)-2-(1-(4-chlorophenyl)-1-(2-hydroxyphenyl)ethyl)benzo[*e*][1,2]oxaphosphinine 2-oxide (10e)

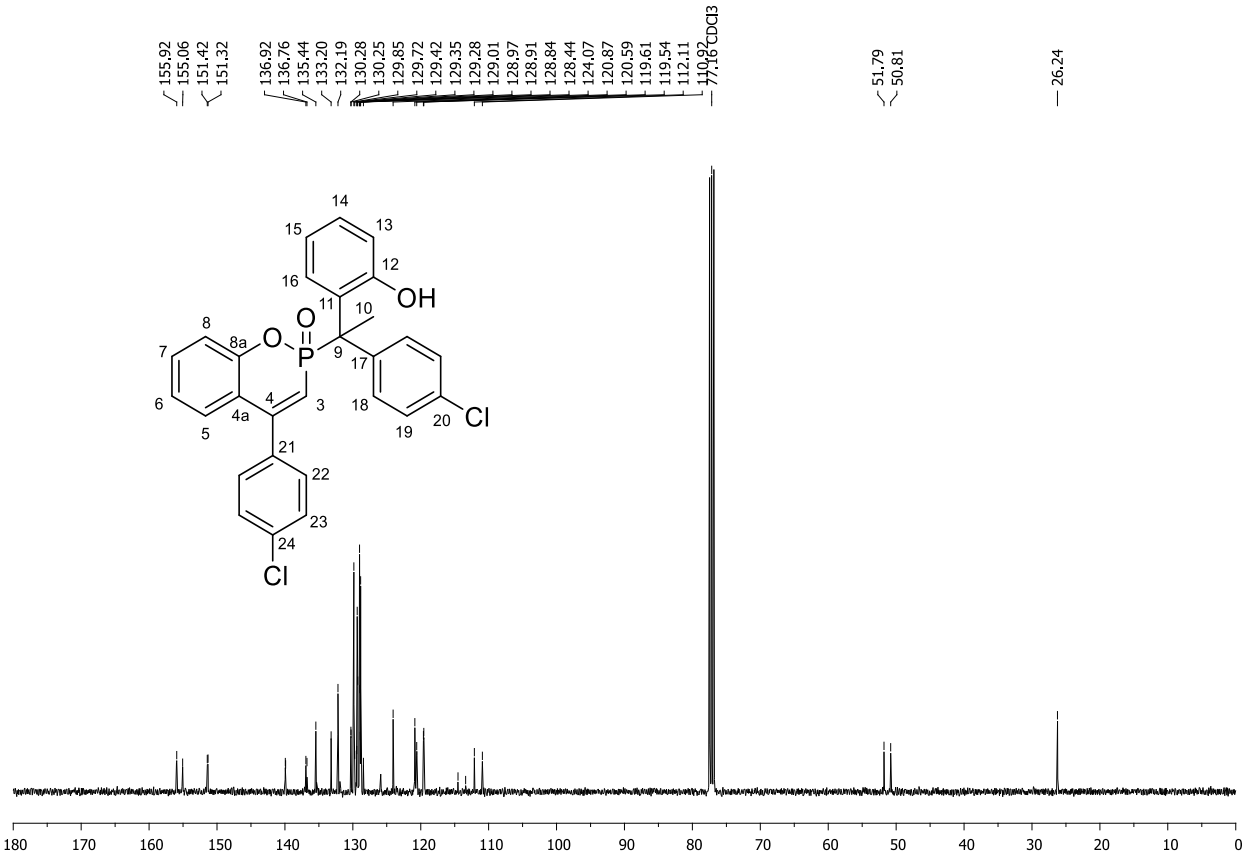
^{31}P NMR (243 MHz, $CDCl_3$) of compound **(10e)**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(10e)**

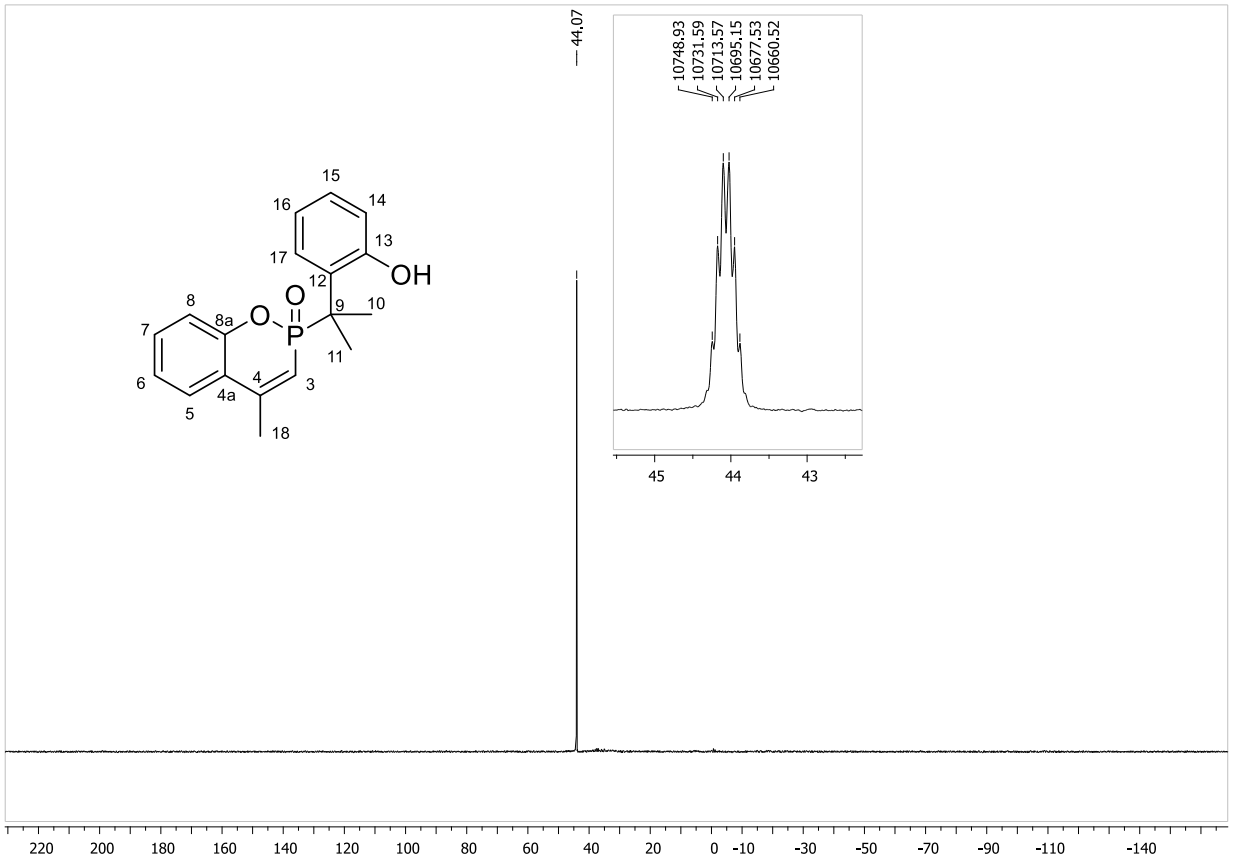


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(10e)**

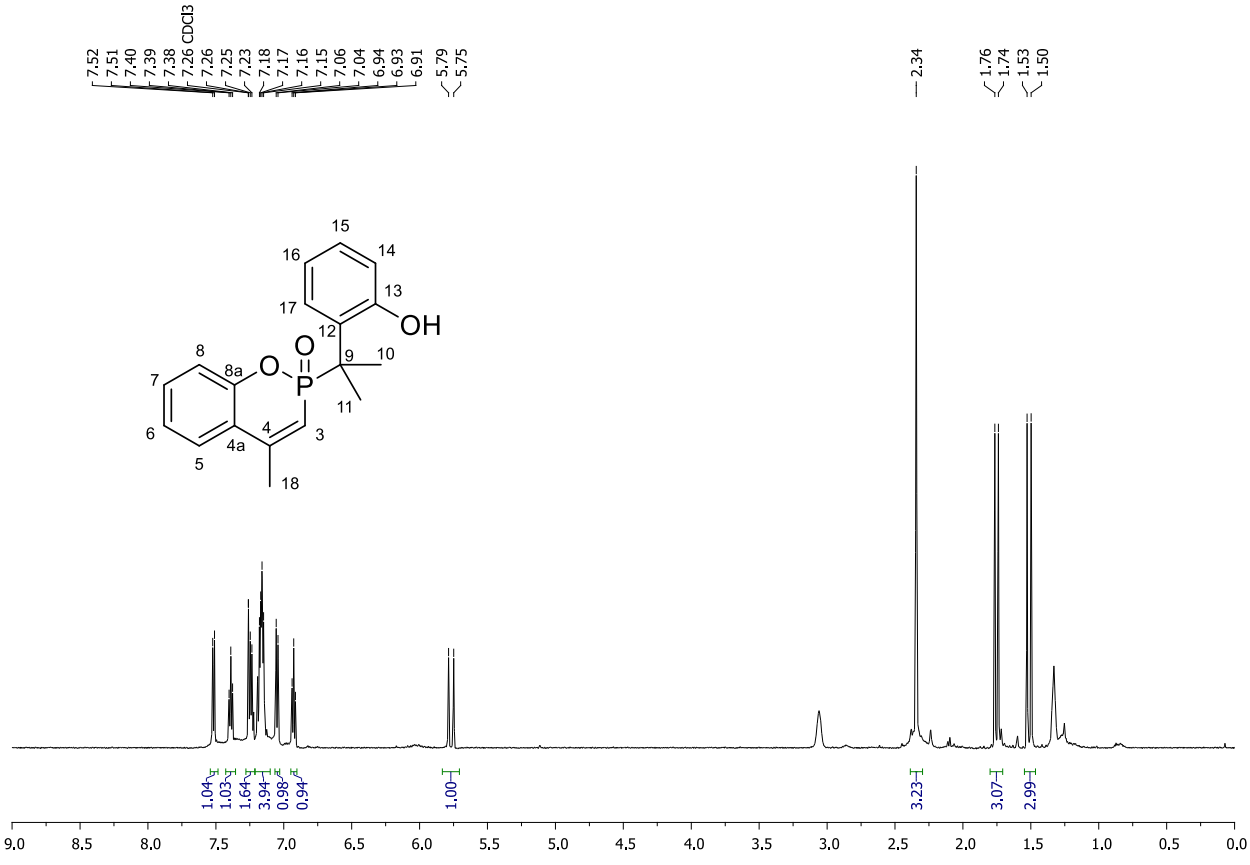


2-(2-(2-hydroxyphenyl)propan-2-yl)-4-methylbenzo[*e*][1,2]oxaphosphinine 2-oxide (10f)

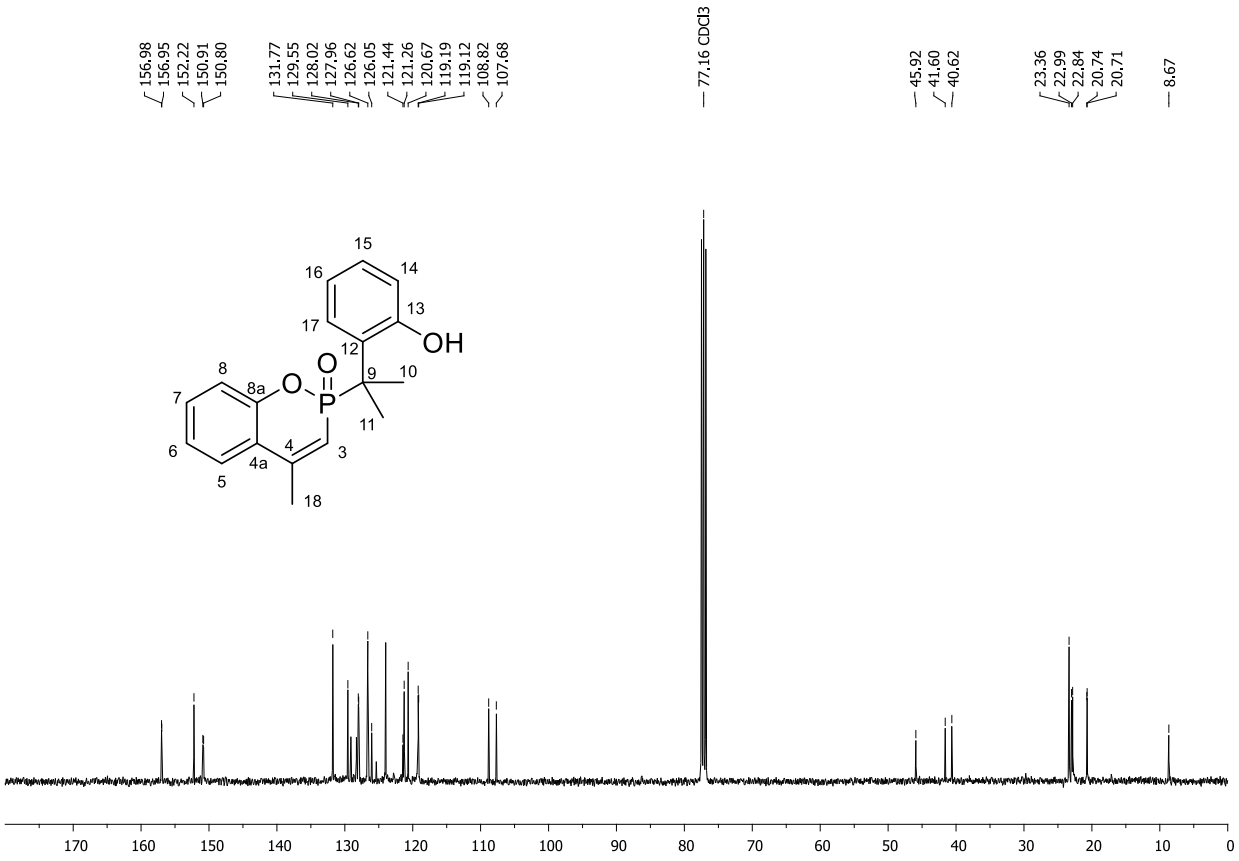
^{31}P NMR (243 MHz, $CDCl_3$) of compound **(10f)**



^{1}H NMR (600 MHz, $CDCl_3$) of compound **(10f)**

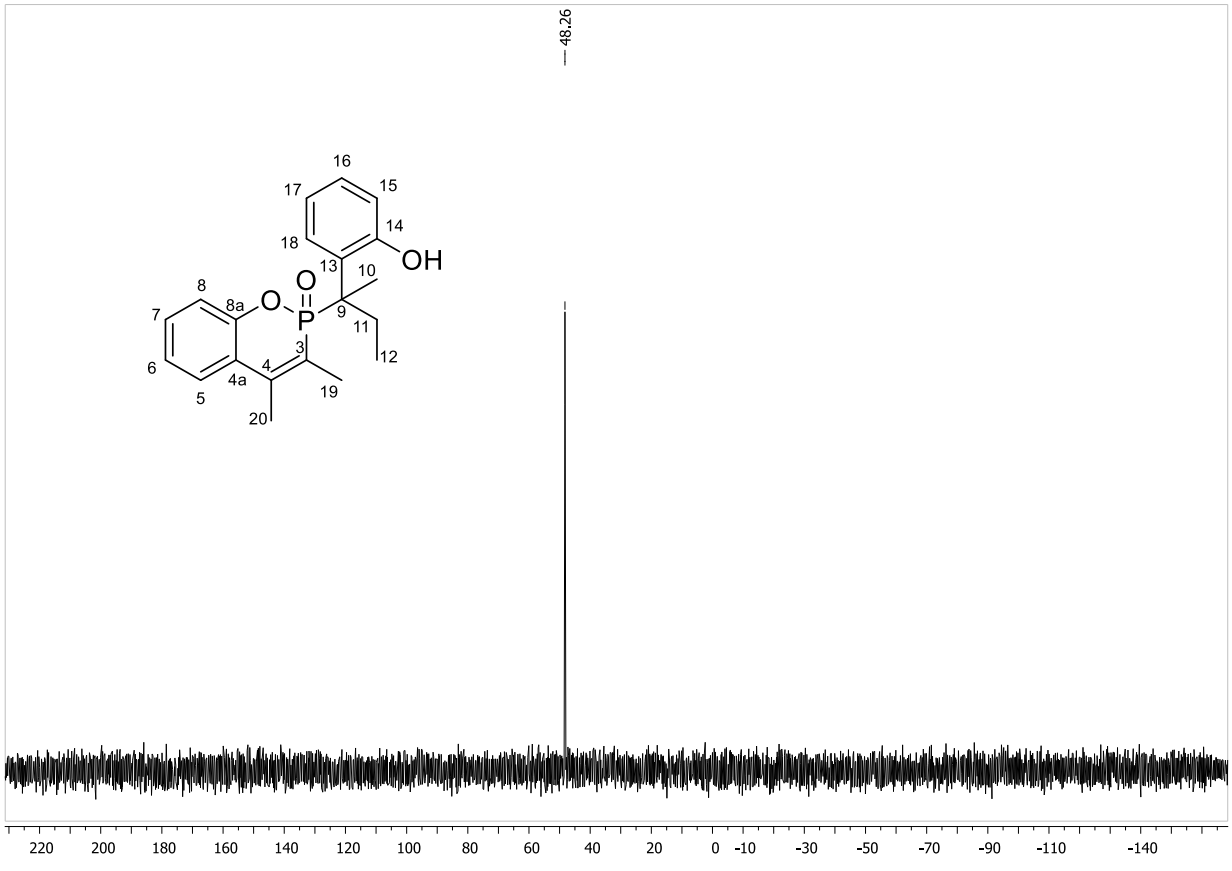


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(10f)**

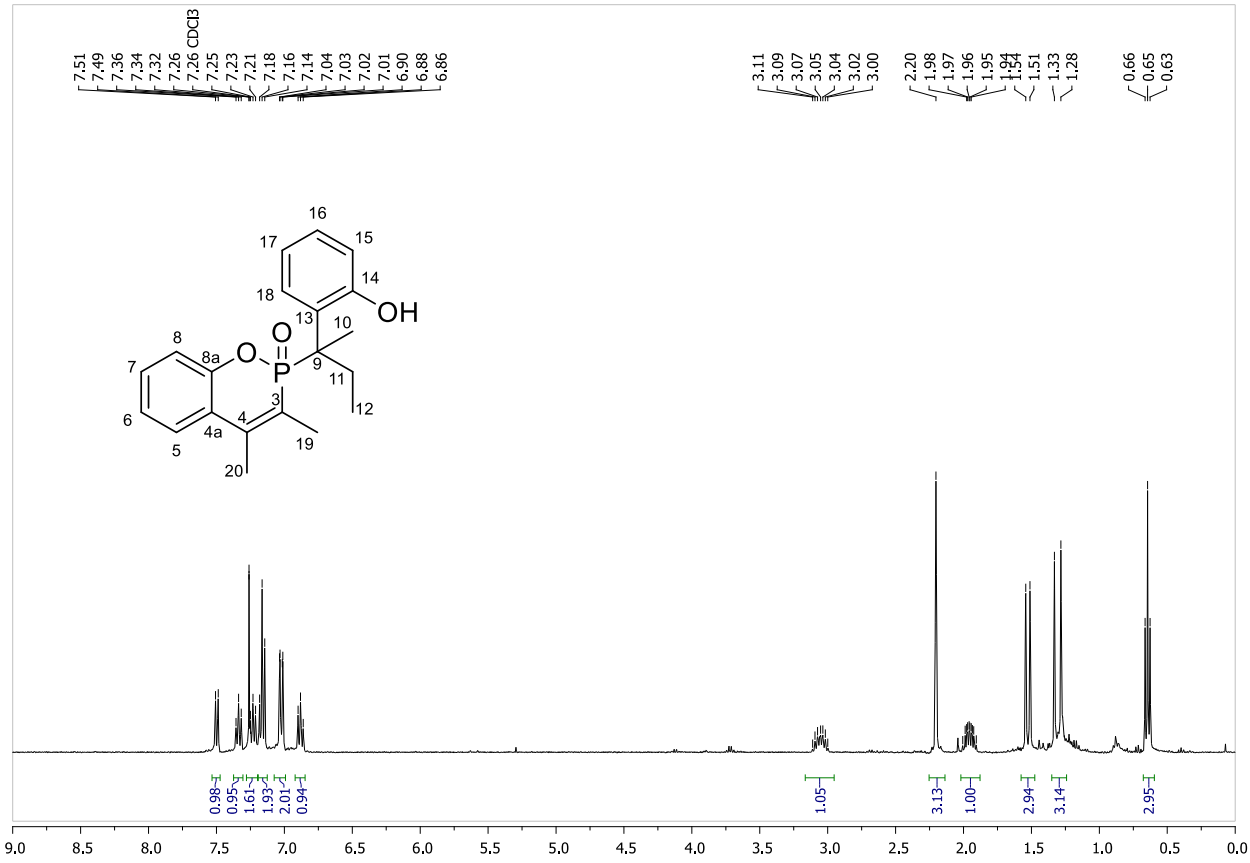


2-(2-(2-hydroxyphenyl)butan-2-yl)-3,4-dimethylbenzo[*e*][1,2]oxaphosphinine 2-oxide (10g)

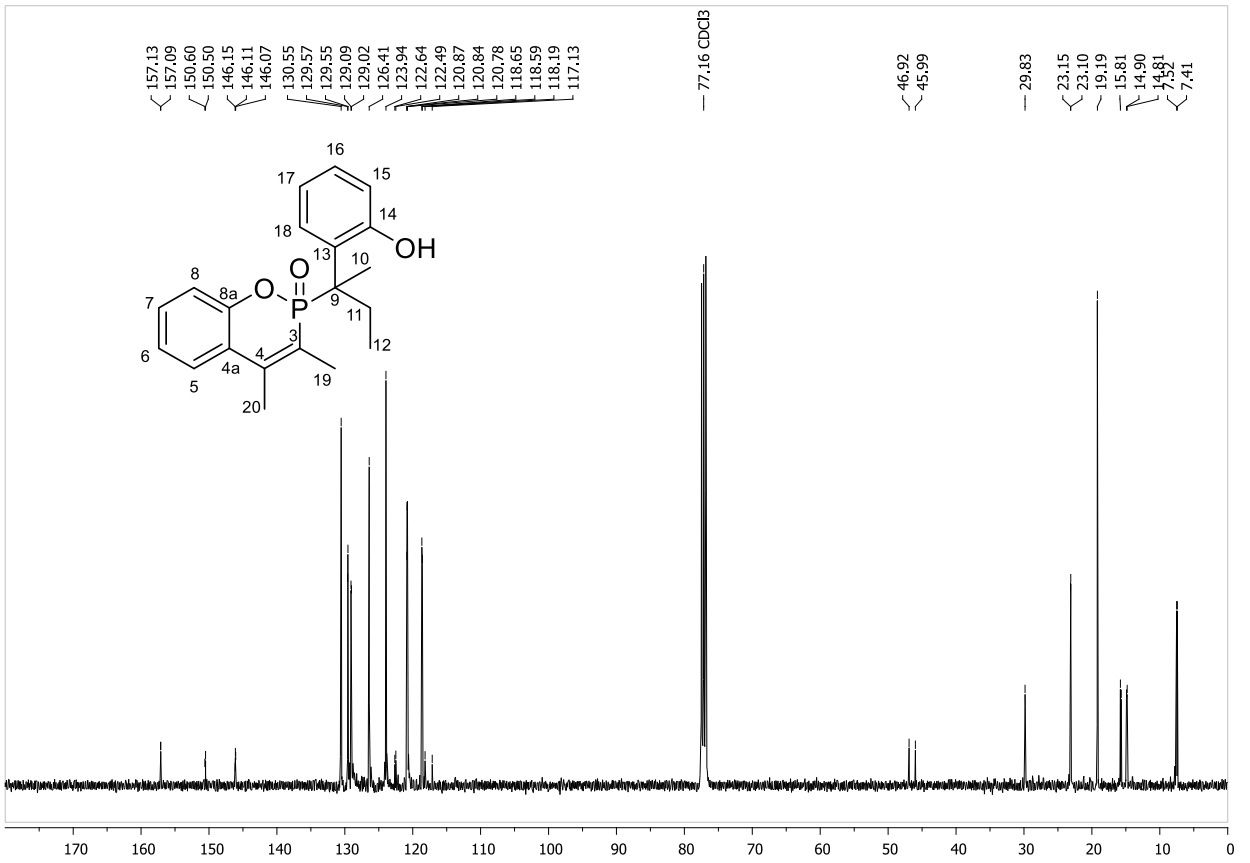
^{31}P NMR (243 MHz, $CDCl_3$) of compound **(10g)**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(10g)**

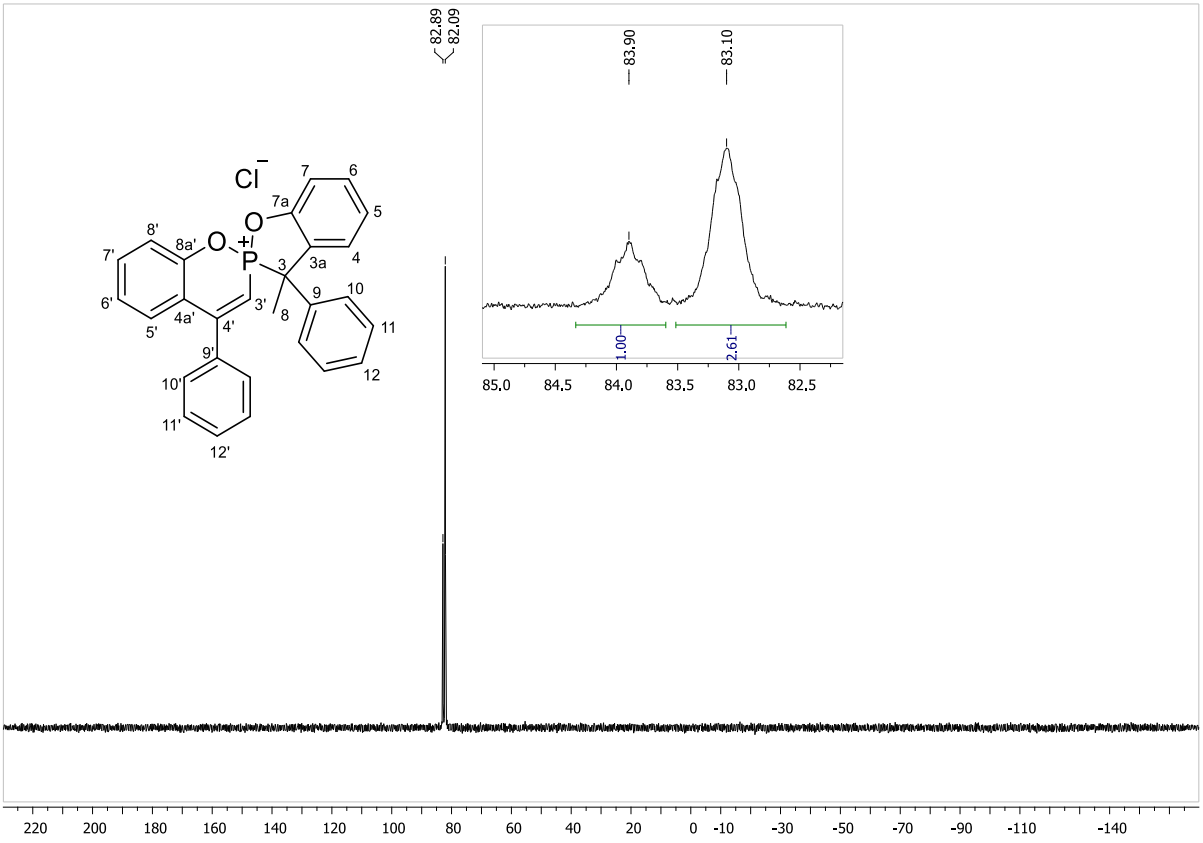


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(10g)**

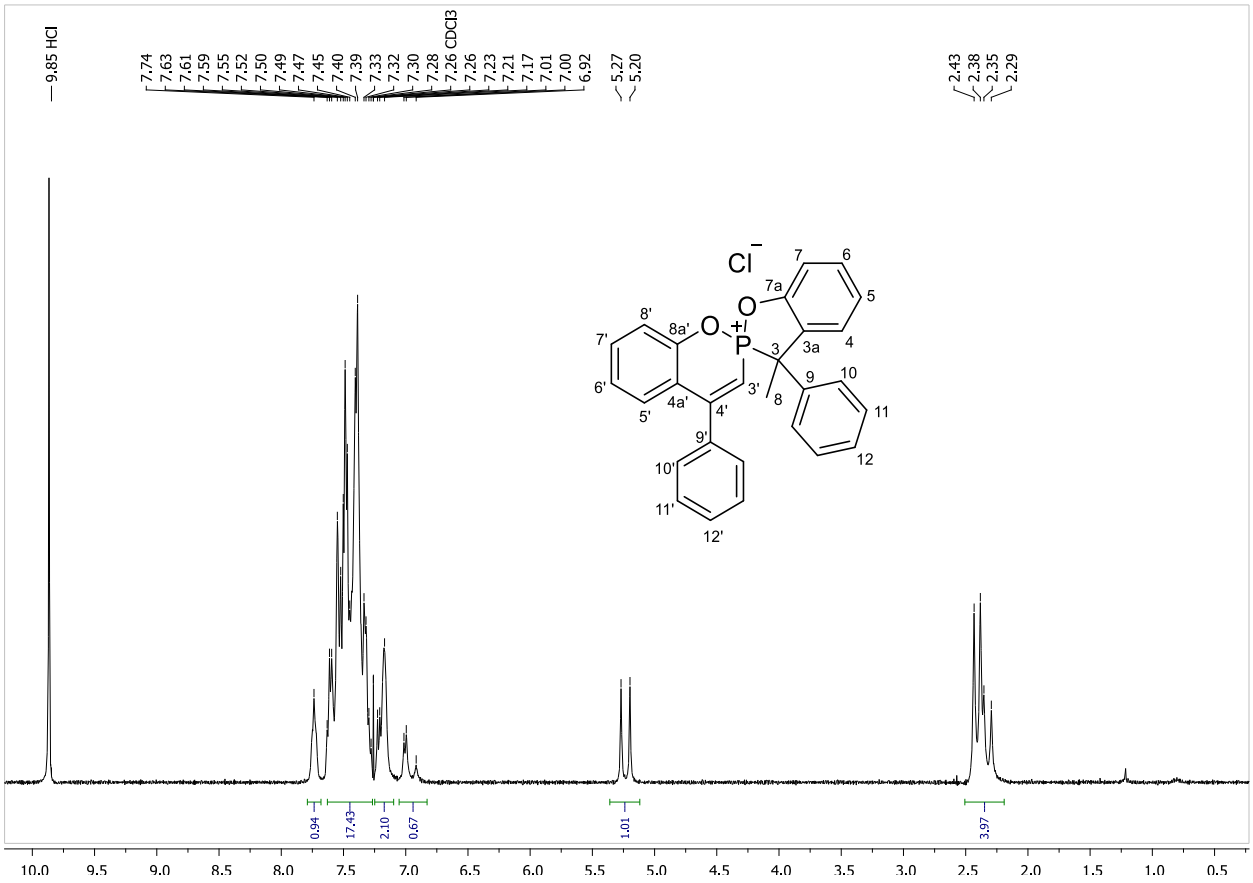


3-methyl-3,4'-diphenyl-3*H*-spiro[benzo[*d*][1,2]oxaphosphole-2,2'-benzo[*e*][1,2]oxaphosphinin]-2-ium chloride (8a)

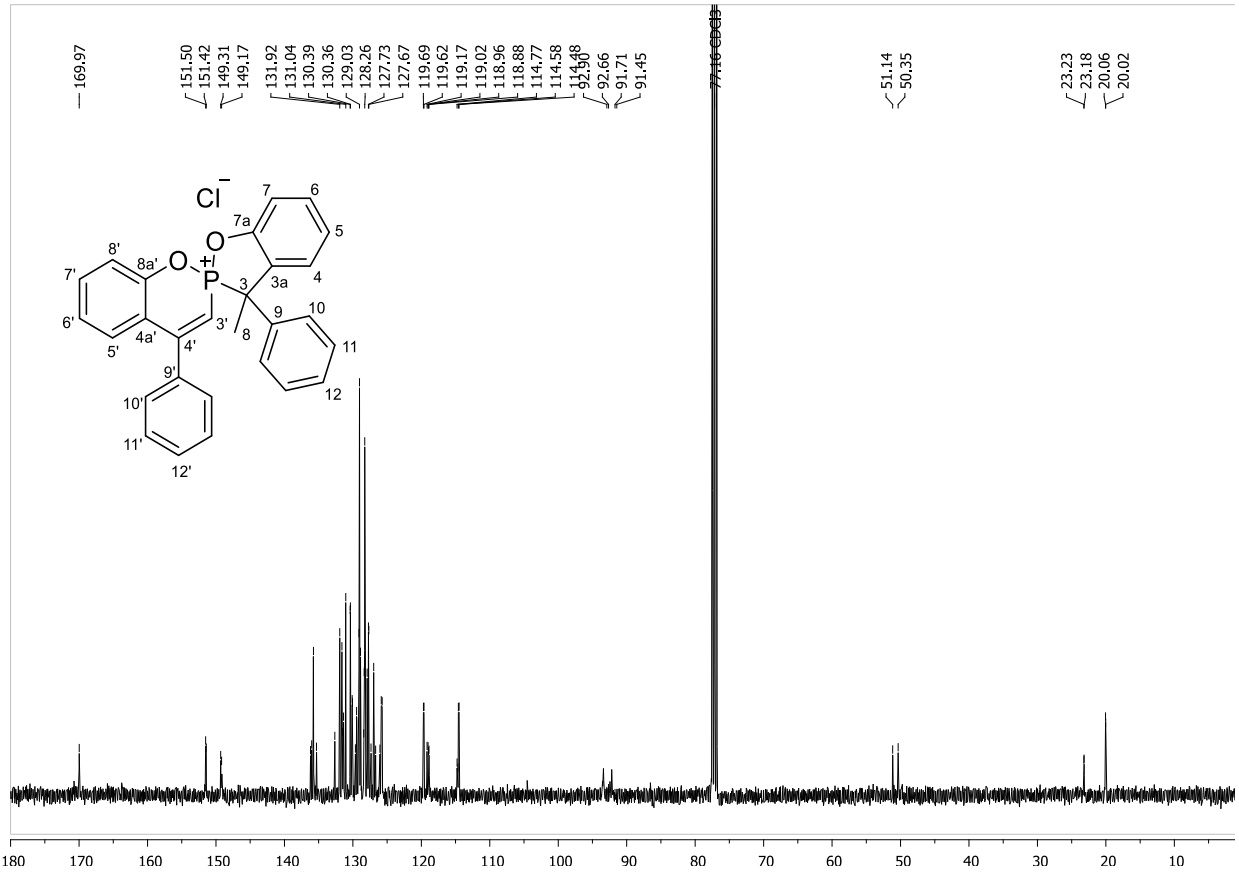
^{31}P NMR (243 MHz, $CDCl_3$) of compound **(8a)**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(8a)**

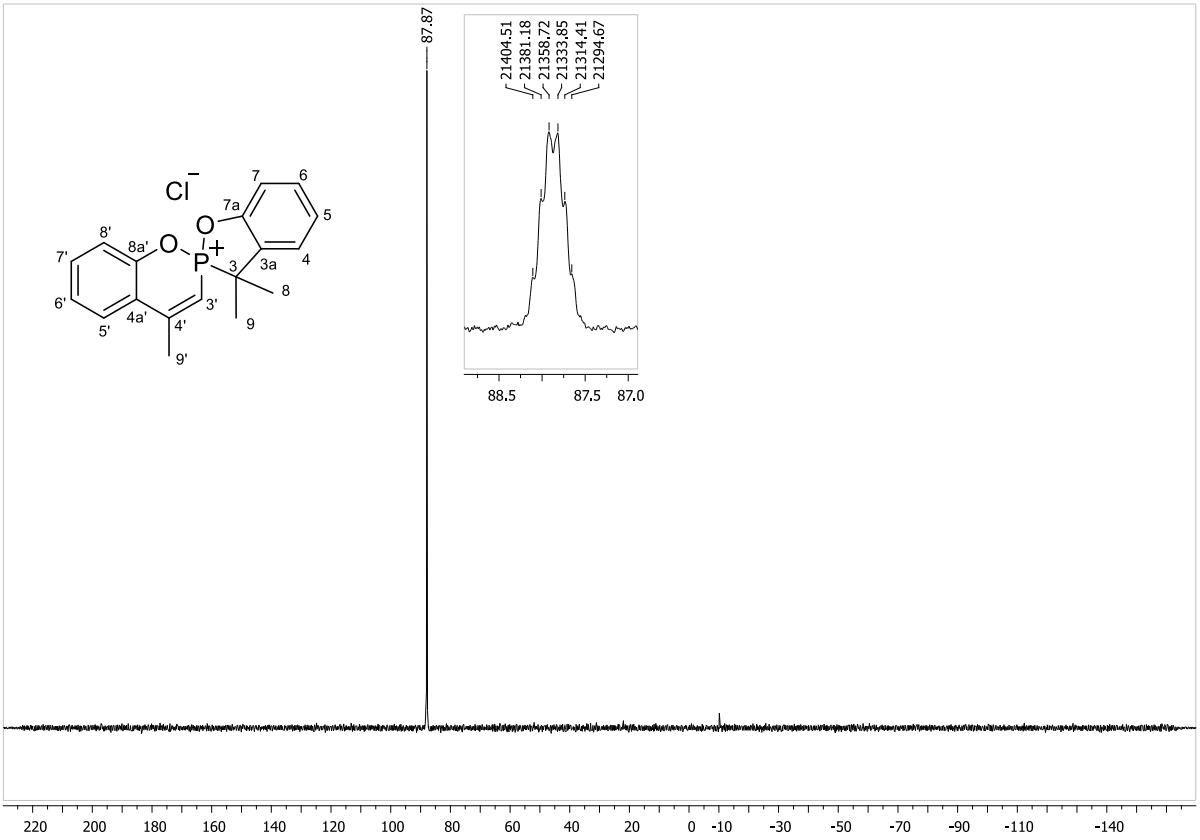


^{13}C NMR (101 MHz, $CDCl_3$) of compound **(8a)**

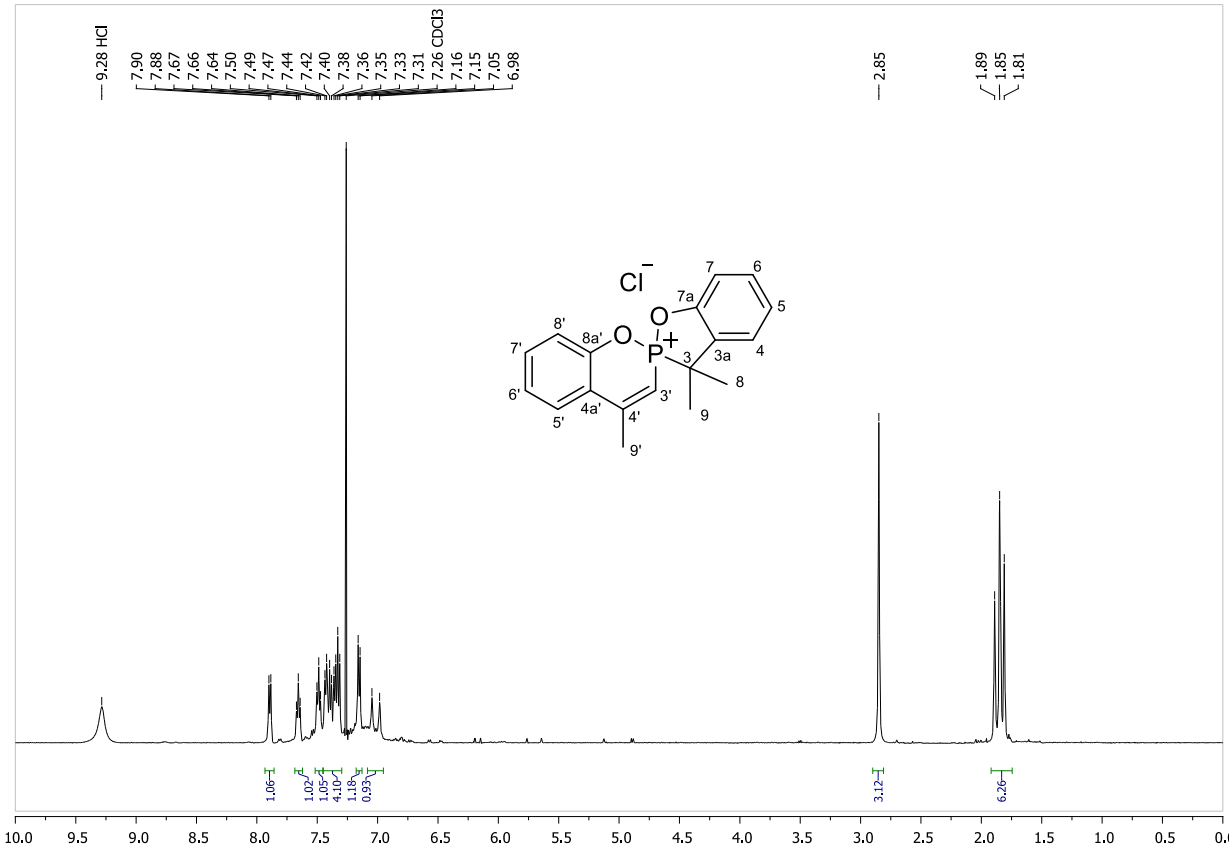


3,3,4'-trimethyl-3*H*-spiro[benzo[*d*][1,2]oxaphosphole-2,2'-benzo[*e*][1,2]oxaphosphinin]-2-ium chloride (8f)

^{31}P NMR (243 MHz, $CDCl_3$) of compound **(8f)**



^{1}H NMR (500 MHz, $CDCl_3$) of compound **(8f)**



^{13}C NMR (101 MHz, $CDCl_3$) of compound **(8f)**