Electronic supplementary materials *Mendeleev Commun.*, 2025, **35**, 651–653

New phosphacoumarins containing aldehyde group: synthesis and properties

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1. Experimental section.

The IR spectra were recorded on a Vector 22 Fourier spectrometer by Bruker in the range of 400−4000 cm^{-1} from KBr pellets. ^{1}H, ^{13}C, and ^{31}P NMR spectra were acquired on Bruker Avance-400 (400, 101, and 162 MHz, respectively), Bruker Avance-600 (600, 151, and 243 MHz, respectively), and Bruker Avance-500 (500, 151, and 203 MHz, respectively) spectrometers in DMSO-d_6. The residual solvent signal (2.50 ppm for 1H nuclei and 39.5 ppm for 13C nuclei) was used as the internal standard. Elemental analysis was performed on a Carlo Erba EA-1108 elemental analyzer. The phosphorus content was determined by pyrolysis in a stream of oxygen. ESI-TOF-MS spectra were recorded on a Bruker AmazonX instrument. The melting points were determined in glass capillaries on a Stuart SMP 10 instrument.

X-ray diffraction study

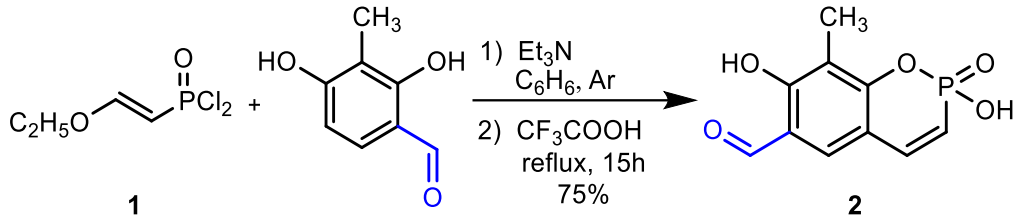
X-ray diffraction (XRD) study of the single crystal **2** were obtained on a Bruker D8 QUEST three-circle diffractometer with a PHOTON III area detector and an IμS DIAMOND microfocus X-ray tube at 150(2) K: λ(Mo *Kα*) = 0.71073 Å, ω/ϕ scanning mode with a step of 0.5°. Data collection and indexing, determination, and refinement of unit cell parameters were carried out using the *APEX*3 software package. Numerical absorption correction based on the crystal shape, additional spherical absorption correction, and systematic error correction were performed using the *SADABS*-2016/2 software.[S1] The structure were solved by the intrinsic phasing method using the *SHELXT*-2018/2 program[S2] and refined by full-matrix least-squares on F^2 using the *SHELXL*-2018/3 program.[S2] Nonhydrogen atoms were refined anisotropically. Positions of H(O) hydrogen atoms were determined from difference electron density maps and refined isotropically. The positions of hydrogen atoms of methyl group were inserted using the rotation of the group with idealized bond angles. The remaining hydrogen atoms were refined using a riding model. Most calculations were performed using the *WinGX*-2021.3 software package.[S3]

CCDC 2440419 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

General procedure for synthesis of phosphacoumarins 2, 3a,b

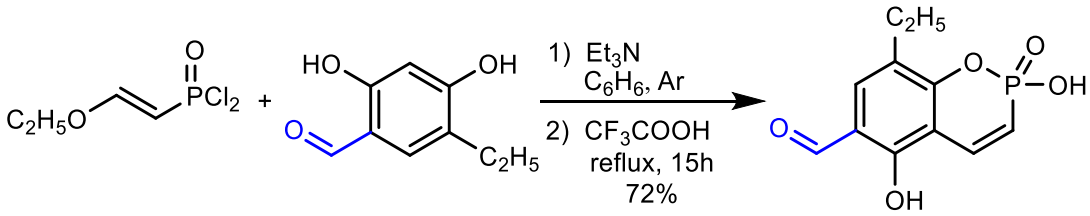
To a mixture of 5.3 mmol of the corresponding 2,4-dihydroxybenzaldehyde and 5.3 mmol triethylamine in 5 ml benzene, a solution of 5.3 mmol 2-ethoxy-vinylphosphonic dichloride **1** was added dropwise in 25 ml benzene in the argon flow and upon cooling in water bath. The reaction mixture was taken to room temperature and stirred for 5 h. Triethylamine hydrochloride precipitated was filtered. The 1 ml of trifluoroacetic acid was added to the filtrate, and the reaction

mixture was refluxed 15 h. The formed precipitate was filtered off, washed with 20 ml of acetone, and dried under vacuum to constant weight.



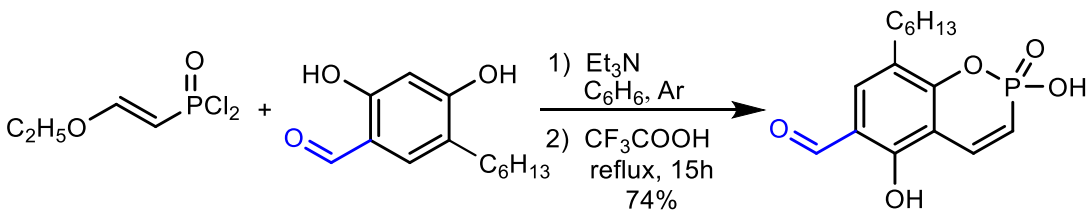
1 2

2,7-Dihydroxy-8-methylbenzo[*e*][1,2]oxaphosphinine-6-carbaldehyde 2-oxide (2). The target compound was prepared from 2-ethoxyvinylphosphonic dichloride and 2,4-dihydroxy-3-methylbenzaldehyde. Yield 0.94 g (75%), white powder, mp = 258-260 °C. IR (KBr), ν: 2842, 1663, 1616, 1231 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.13 (3H, s, CH_3), 6.26 (1H, dd, $^{2}J_{HP}$ 20.0, $^{3}J_{HH}$ 12.7 Hz, P-C*H*=), 7.41 (1H, dd, $^{3}J_{HP}$ 42.7, $^{3}J_{HH}$ 12.7 Hz, P-CH=C*H*), 7.80 (1H, s, CH_{Ar}), 9.97 (1H, s, -CHO), 11.45 (1H, br.s, OH). $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6): δ 190.5, 155.7, 150.6 (d, J_{CP} 8.1 Hz), 136.1, 127.7, 112.2, 109.6 (d, J_{CP} 6.3 Hz), 109.4 (d, J_{CP} 20.3 Hz), 109.1 (d, J_{CP} 168.2 Hz), 2.79. $^{31}P\{^{1}H\}$ NMR (162 MHz, DMSO-d_6): δ 4.94. Mass spectrum (ESI), *m*/*z*: 240.97 $[M+H]^+$, 272.97 $[M+K]^+$. Found, %: C, 49.93; H, 3.71; P, 12.84. $C_{10}H_9O_5P$. Calculated, (%): C, 50.01; H, 3.78; P, 12.90.



1 3a

8-Ethyl-2,5-dihydroxybenzo[*e*][1,2]oxaphosphinine-6-carbaldehyde 2-oxide (3a). The target compound was prepared from 2-ethoxyvinylphosphonic dichloride and 5-ethyl-2,4-dihydroxybenzaldehyde. Yield 0.96 g (72%), white powder, mp = 204-206 °C. IR (KBr), ν: 3435, 2971, 1653, 1619, 1232 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.18 (3H, t, $^{3}J_{HH}$ 7.2 Hz, CH_3), 2.59-2.65 (2H, m, -CH_2-), 6.39 (1H, dd, $^{2}J_{HP}$ 20.6, $^{3}J_{HH}$ 12.9 Hz, P-C*H*=), 7.62 (1H, dd, $^{3}J_{HP}$ 42.7, $^{3}J_{HH}$ 12.9 Hz, P-CH=C*H*), 7.69 (1H, s, CH_{Ar}), 9.97 (1H, s, -CHO), 11.58 (1H, br.s, OH). $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6): δ 190.3, 152.6 (d, J_{CP} 1.4 Hz), 150.7 (d, J_{CP} 9.2 Hz), 129.2, 128.9, 120.1 (d, J_{CP} 5.9 Hz), 111.7, 110.8 (d, J_{CP} 168.1 Hz), 105.1 (d, J_{CP} 18.9 Hz), 16.8, 9.1. $^{31}P\{^{1}H\}$ NMR (162 MHz, DMSO-d_6): δ 4.24. Mass spectrum (ESI), *m*/*z*: 255.94 $[M+H]^+$, 286.94 $[M+K]^+$. Found, %: C, 51.91; H, 4.28; P, 12.13. $C_{11}H_{11}O_5P$. Calculated, (%): C, 51.98; H, 4.36; P, 12.19.



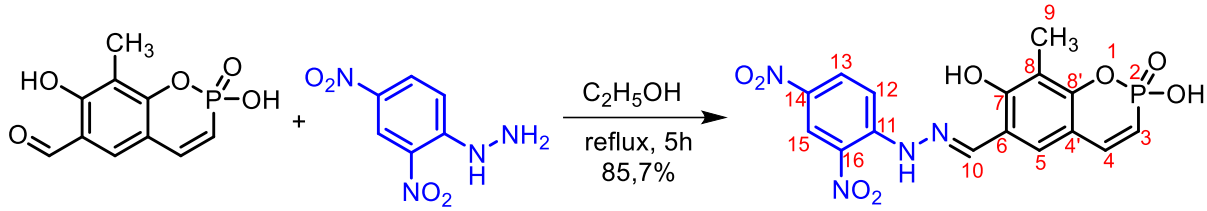
1 3b

8-Hexyl-2,5-dihydroxybenzo[*e*][1,2]oxaphosphinine-6-carbaldehyde 2-oxide (3b). The target compound was prepared from 2-ethoxyvinylphosphonic dichloride and 5-hexyl-2,4-

dihydroxybenzaldehyde. Yield 1.21 g (74%), white powder, mp =180-182 °C. IR (KBr), ν: 3410, 2926, 2856, 1665, 1620, 1229 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 0.85-0.88 (3H, m, CH_3), 1.30-1.34 (6H, m, -CH_2-), 1.53-1.58 (2H, m, -CH_2-), 2.50-2.61 (2H, m, -CH_2-Ar), 6.38 (1H, dd, $^2J_{HP}$ 20.6, $^3J_{HH}$ 12.9 Hz, P-C*H*=), 7.65 (1H, dd, $^3J_{HP}$ 42.7, $^3J_{HH}$ 12.9 Hz, P-CH=C*H*), 7.68 (1H, s, CH_{Ar}), 9.96 (1H, s, -CHO), 11.57 (1H, br.s, OH). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6): δ 195.2, 157.3, 155.5 (d, J_{CP} 9.1 Hz), 134.5, 134.0, 123.5 (d, J_{CP} 5.8 Hz), 116.4, 115.6 (d, J_{CP} 168.2 Hz), 109.9 (d, J_{CP} 18.9 Hz), 31.0, 29.0, 28.4, 28.3, 22.0, 13.9. $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6): δ 4.24. Mass spectrum (ESI), *m/z*: 311.03 $[M+H]^+$, 333.02 $[M+Na]^+$. Found, %: C, 57.99; H, 6.09; P, 9.92. $C_{15}H_{19}O_5P$. Calculated, (%): C, 58.06; H, 6.17; P, 9.98.

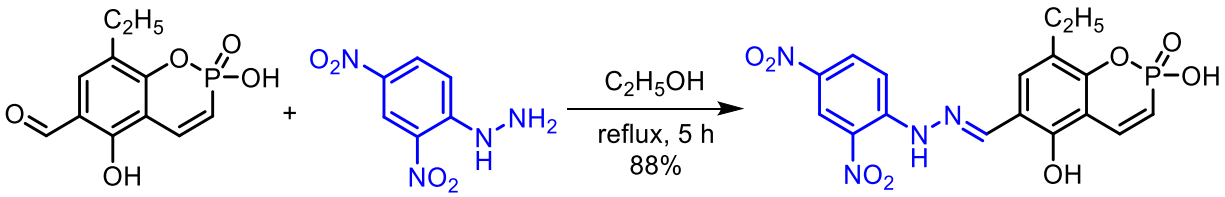
General procedure for synthesis of hydrazones 4, 5a,b

An equimolar mixture phosphacoumarin and (2,4-dinitrophenyl)hydrazine in 3 ml C_2H_5OH was refluxed 5 h, then cooled to the room temperature and filtered. The precipitate was washed C_2H_5OH.



2 **4**

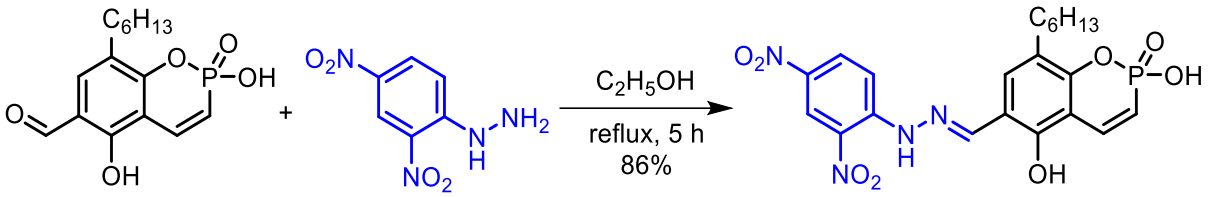
(*E*)-6-((2-(2,4-Dinitrophenyl)hydrazono)methyl)-2,5-dihydroxy-8-methyl-benzo[*e*][1,2]oxaphosphinine 2-oxide (4). Yield 0.075 g (85%), orange powder, mp >300 °C. IR (KBr), ν: 3436, 3266, 1615, 1515, 1339, 1174, 1150 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 2.17 (3H, s, CH_3), 6.19 (1H, dd, $^2J_{PH}$ 20.0 Hz, $^3J_{HH}$ 12.6 Hz, P-C*H*=), 7.39 (1H, dd, $^3J_{PH}$ 42.6 Hz, $^3J_{HH}$ 12.6 Hz, P-CH=C*H*), 7.60 (1H, s, CH_{Ar}), 7.83 (1H, d, $^3J_{HH}$ 9.6 Hz, CH_{Ar}), 8.39 (1H, dd, $^3J_{HH}$ 9.6 Hz, $^4J_{HH}$ 2.7 Hz, CH_{Ar}), 8.85 (1H, d, $^4J_{HH}$ 2.7 Hz, CH_{Ar}), 8.90 (1H, s, -N=C*H*), 10.56 (1H, br.s, OH), 11.68 (1H, s, -NH-).$^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 156.9 (C7), 152.2 (d, J_{CP} 8.2 Hz, C8a), 149.8 (C10), 143.6 (C16), 141.3 (C4), 137.0 (C11), 130.0 (C13), 129.5 (C14), 127.9 (C5), 123.0 (C15), 116.0 (C12), 114.7 (C6), 114.3 (d, J_{CP} 4.2 Hz, C8), 114.2 (d, J_{CP} 9.5 Hz, C4a), 113.3 (d, J_{CP} = 168.4 Hz, C3), 8.3 (C9). $^{31}P\{H\}$ NMR (162 MHz, DMSO-d_6): δ 5.49. Mass spectrum (ESI), *m/z*: 421.03 $[M+H]^+$, 443.02 $[M+Na]^+$. Found, %: C, 45.78; H, 3.18; N, 13.35; P, 7.35. $C_{16}H_{13}N_4O_8P$. Calculated, (%): C, 45.73; H, 3.12; N, 13.33; P, 7.37.



3a **5a**

(*E*)-6-((2-(2,4-Dinitrophenyl)hydrazono)methyl)-8-ethyl-2,5-dihydroxy-benzo[*e*][1,2]oxaphosphinine 2-oxide (5a). Yield 0.096 g (88%), orange powder, mp > 300 °C. IR (KBr), ν: 3434, 3277, 1619, 1512, 1335, 1175, 1121 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 1.19 (3H, t, $^3J_{HH}$ 7.5 Hz, CH_3), 2.60-2.65 (2H, m, -CH_2-), 6.35 (1H, dd, $^2J_{HP}$ 20.4, $^3J_{HH}$ 12.9 Hz, P-C*H*=), 7.56 (1H, s, CH_{Ar}), 7.67 (1H, dd, $^3J_{HP}$ 42.5, $^3J_{HH}$ 12.9 Hz, P-CH=C*H*), 7.84 (1H, d, $^3J_{HH}$ 9.6 Hz, CH_{Ar}), 8.39 (1H, dd, $^3J_{HH}$ 9.6 Hz, $^4J_{HH}$ 2.6 Hz, CH_{Ar}), 8.84 (1H, d, $^4J_{HH}$ 2.7 Hz, CH_{Ar}),

8.88 (1H, s, -N=C*H*), 10.57 (1H, br.s, OH), 11.67 (1H, s, -NH-). $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6): δ 153.1, 151.9 (d, J_{CP} 9.0 Hz), 149.5, 143.6, 137.0, 135.2, 130.8, 130.0, 129.5, 123.5, 123.0, 116.0, 115.1 (d, J_{CP} 167.8 Hz), 114.2 (d, J_{CP} 3.0 Hz), 110.7 (d, J_{CP} 12.0 Hz), 31.0, 29.3, 28.5, 28.3, 22.0, 13.9. $^{31}P\{^{1}H\}$ NMR (162 MHz, DMSO-d_6): δ 4.46. Mass spectrum (ESI), *m*/*z*: 435.04 $[M+H]^+$, 457.05 $[M+Na]^+$. Found, %: C, 46.94; H, 3.39; N, 12.84; P, 7.08. $C_{17}H_{15}N_4O_8P$. Calculated, (%): C, 47.02; H, 3.48; N, 12.9; P, 7.13.



3b **5b**

(*E*)-6-((2-(2,4-Dinitrophenyl)hydrazono)methyl)-8-hexyl-2,5-dihydroxy-methylbenzo[*e*][1,2]oxaphosphinine 2-oxide (5b). Yield 0.068 g (86%), orange powder, mp > 300 °C. IR (KBr), ν: 3445, 3288, 1617, 1518, 1334, 1174, 1128 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.87 (s, 3H, CH_3), 1.17-1.31 (m, 6H, -CH_2-), 1.58 (m, 2H, -CH_2-), 2.59 (m, 2H, -C*H*$_2$-Ar), 6.33 (m, 1H, P-C*H*=), 7.51 (s, 1H, CH_{Ar}), 7.57-7.71 (m, 1H, P-CH=C*H*), 7.81 (d, 1H, $^{3}J_{HH}$ 9.6 Hz, CH_{Ar}), 8.38 (d, 1H, $^{3}J_{HH}$ 8.7 Hz, CH_{Ar}), 8.86 (1H, d, $^{4}J_{HH}$ 2.7 Hz, CH_{Ar}), 8.87 (1H, s, -N=C*H*), 10.59 (1H, br.s, OH), 11.64 (1H, s, -NH-). $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6): δ 153.1, 152.2 (d, J_{CP} 8.2 Hz), 149.9, 143.6, 137.0, 134.8, 130.8, 130.0, 129.5, 123.5, 123.0, 116.0, 115.1 (d, J_{CP} 167.8 Hz), 114.2 (d, J_{CP} 3.0 Hz), 110.7 (d, J_{CP} 12.0 Hz), 31.0, 29.3, 28.5, 28.3, 22.0, 13.9. $^{31}P\{^{1}H\}$ NMR (162 MHz, DMSO-d_6): δ 4.15. Mass spectrum (ESI), *m*/*z*: 491.17 $[M+H]^+$, 513.17 $[M+Na]^+$. Found, %: C, 51.40; H, 4.70; N, 11.41; P, 6.31. $C_{21}H_{23}N_4O_8P$. Calculated, (%): C, 51.43; H, 4.73; N, 11.42; P, 6.32.

Crystal data for compounds 2

A single crystal of compound **2** was studied by single crystal X-ray diffraction analysis (Figure S1). The crystal structure of **2** was solved in the triclinic space group $P\bar{1}$, the asymmetric part of the unit cell is represented by a single molecule (Z' = 1). In the crystal of **2**, a dimer is formed by O–H···O=C interactions. The dimers are linked to each other by O–H···O=P contacts, forming an infinite stack of molecules along the 0*a* axis (Figure S2).

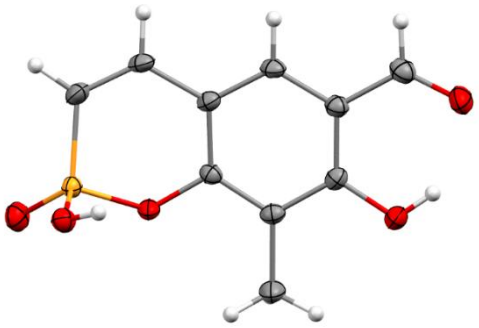


Figure S1. ORTEP view of the molecule in the crystal of **2**. Displacement ellipsoids are drawn at the 50% probability level.

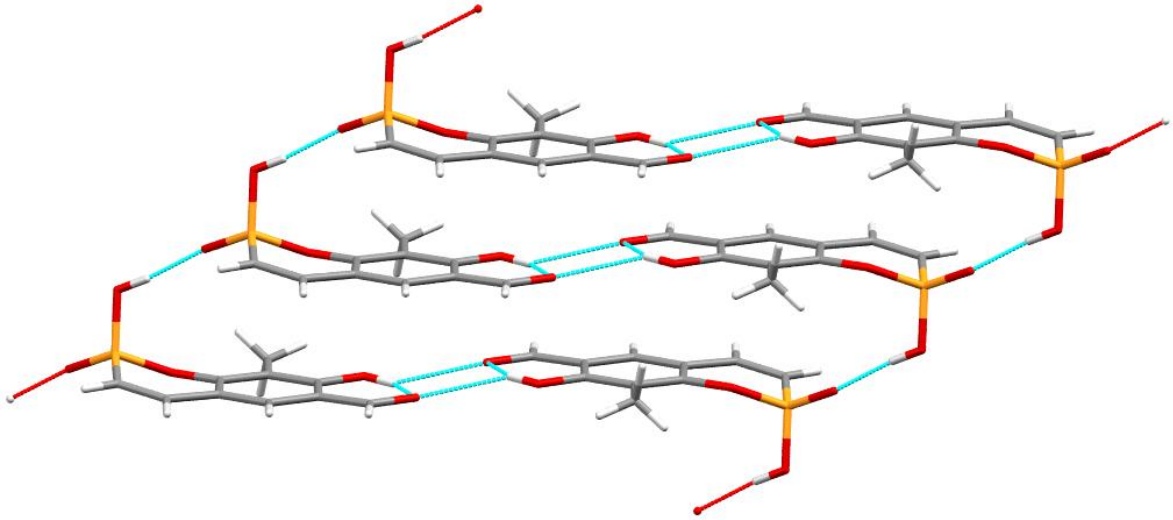


Figure S2. Intermolecular interactions in the crystal **2.**

Crystallographic data for **2**. $C_{10}H_9O_5P$ (M = 240.14), colorless plate crystal, triclinic, $P\bar{1}$, a = 4.7873(10), b = 6.8584(15) and c = 14.831(3) Å, α = 90.842(6)°, β = 98.581(6)°, γ = 92.956(6)°, V = 480.73(18) Å^3, Z' = 1, d_{calc} = 1.659 g·cm^{-3}, μ(Mo $K\alpha$) = 0.288 mm^{-1}. F(000) = 248, reflections collected = 11938, unique = 2094, R_{int} = 0.0651, full-matrix least-squares on F^2, parameters = 154, restraints = 2. Final indices R_1 = 0.0678, wR_2 = 0.1620 for 1937 reflections with $I > 2\sigma(I)$, goodness-of-fit on F^2 = 1.255, largest difference in peak and hole (0.838 and –0.376 e Å^{-3}), data completeness 0.999.

2. Spectra of compounds.

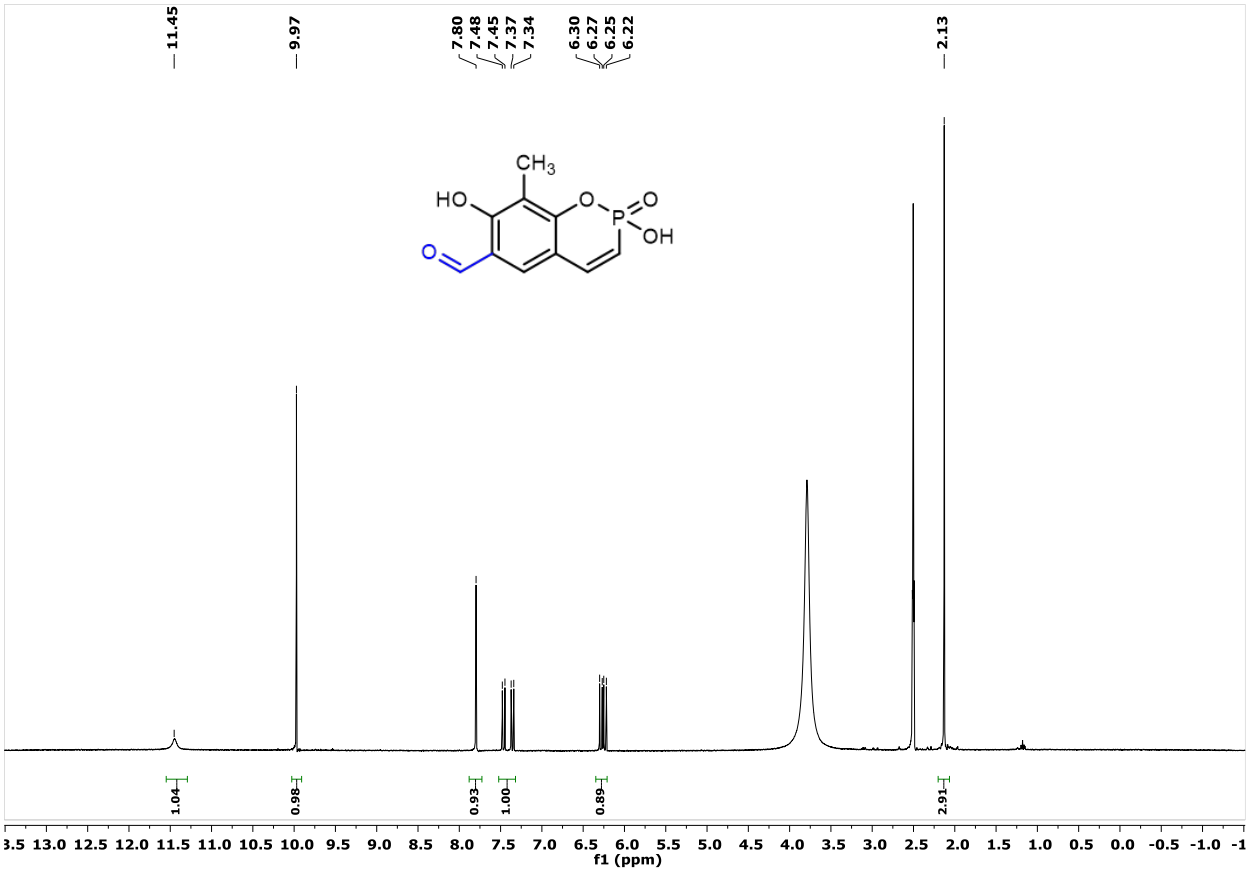


Figure S3. ^{1}H NMR (400 MHz, DMSO-d6) spectrum of compound **2.**

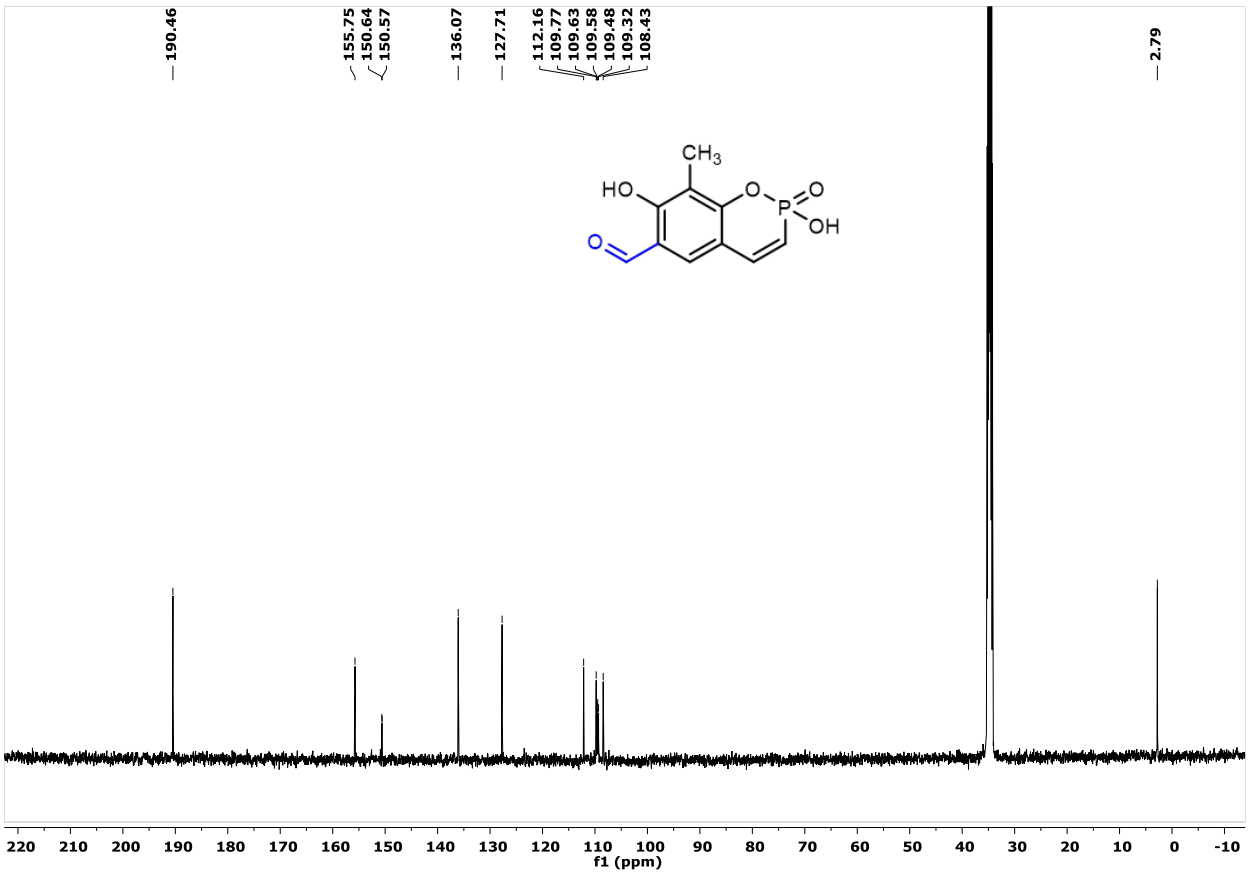


Figure S4. $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6) spectrum of compound **2.**

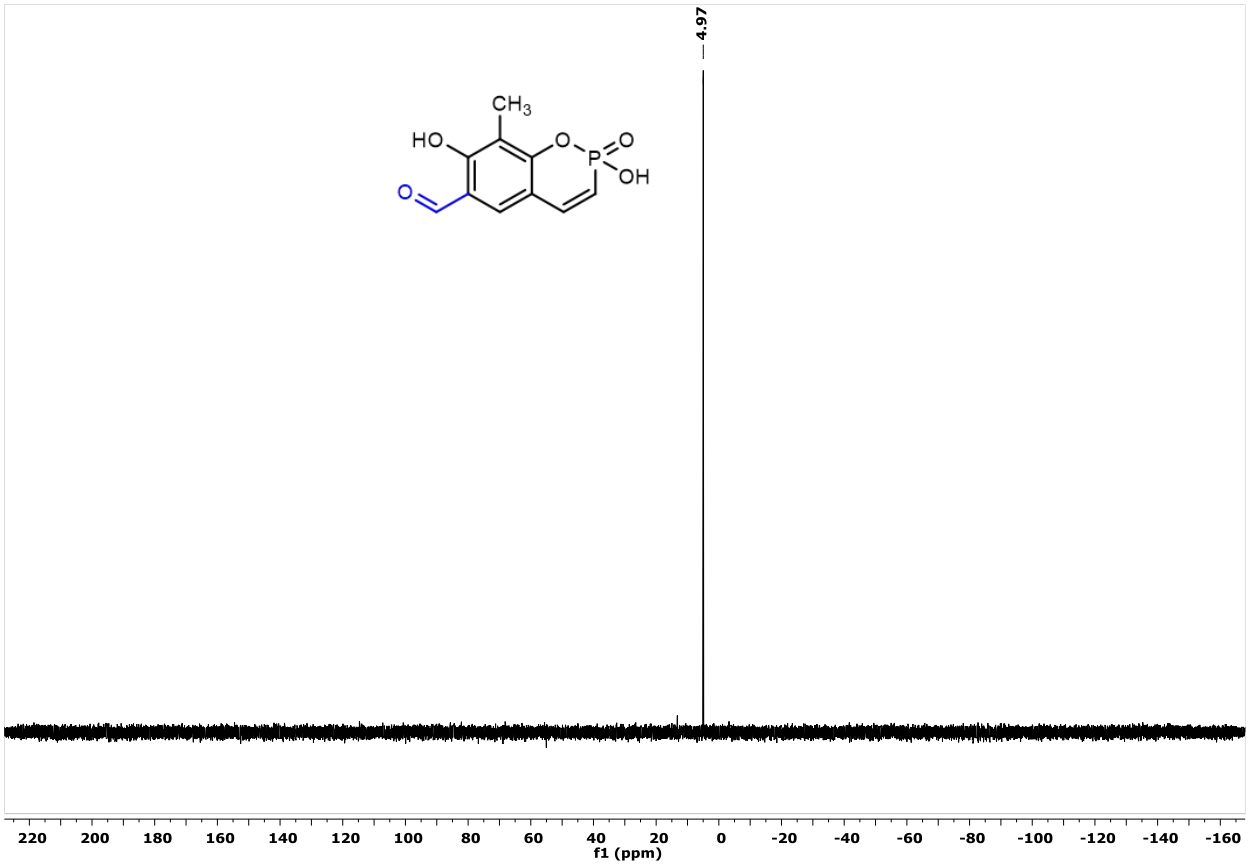


Figure S5. $^{31}P\{^{1}H\}$ NMR (162 MHz, DMSO-d_6) spectrum of compound **2.**

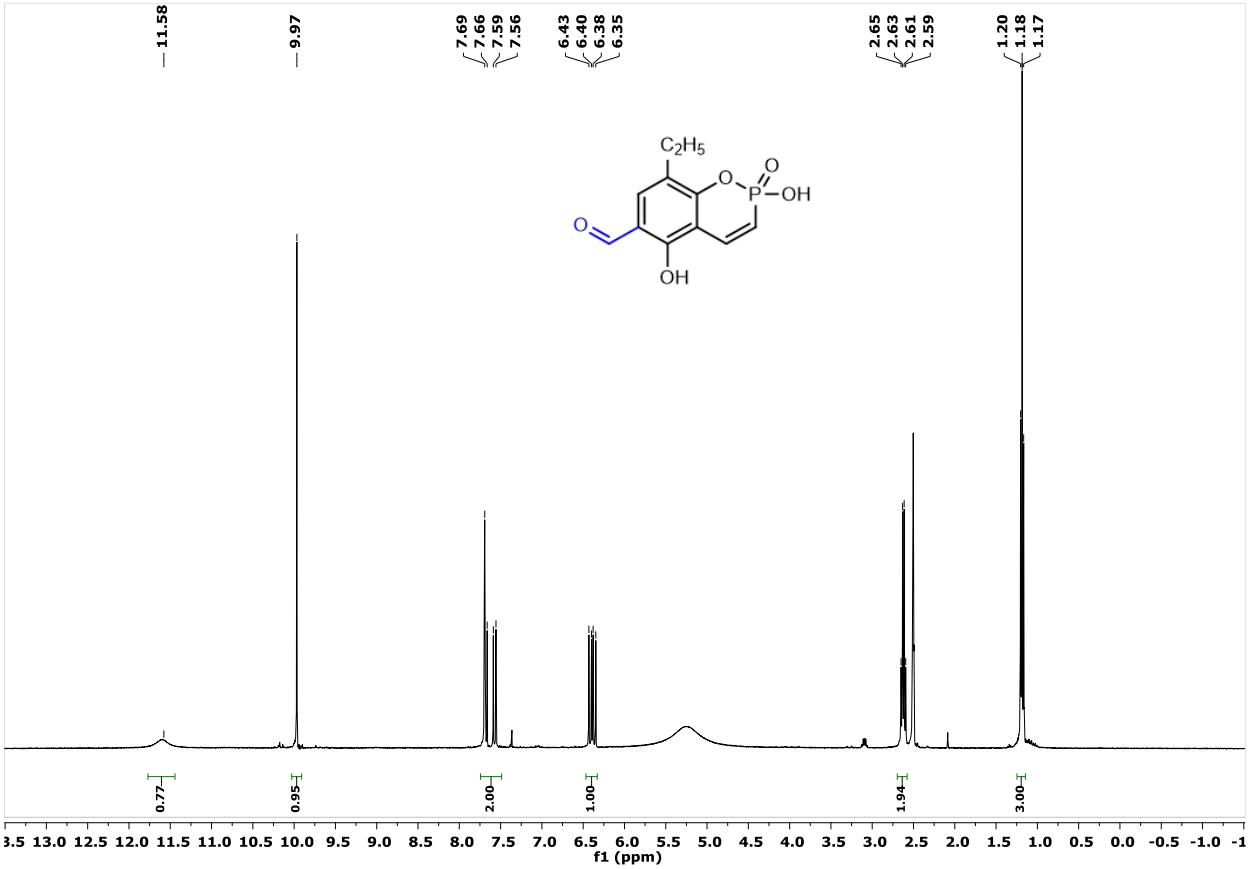


Figure S6. ^{1}H NMR (400 MHz, DMSO-d6) spectrum of compound **3a** .

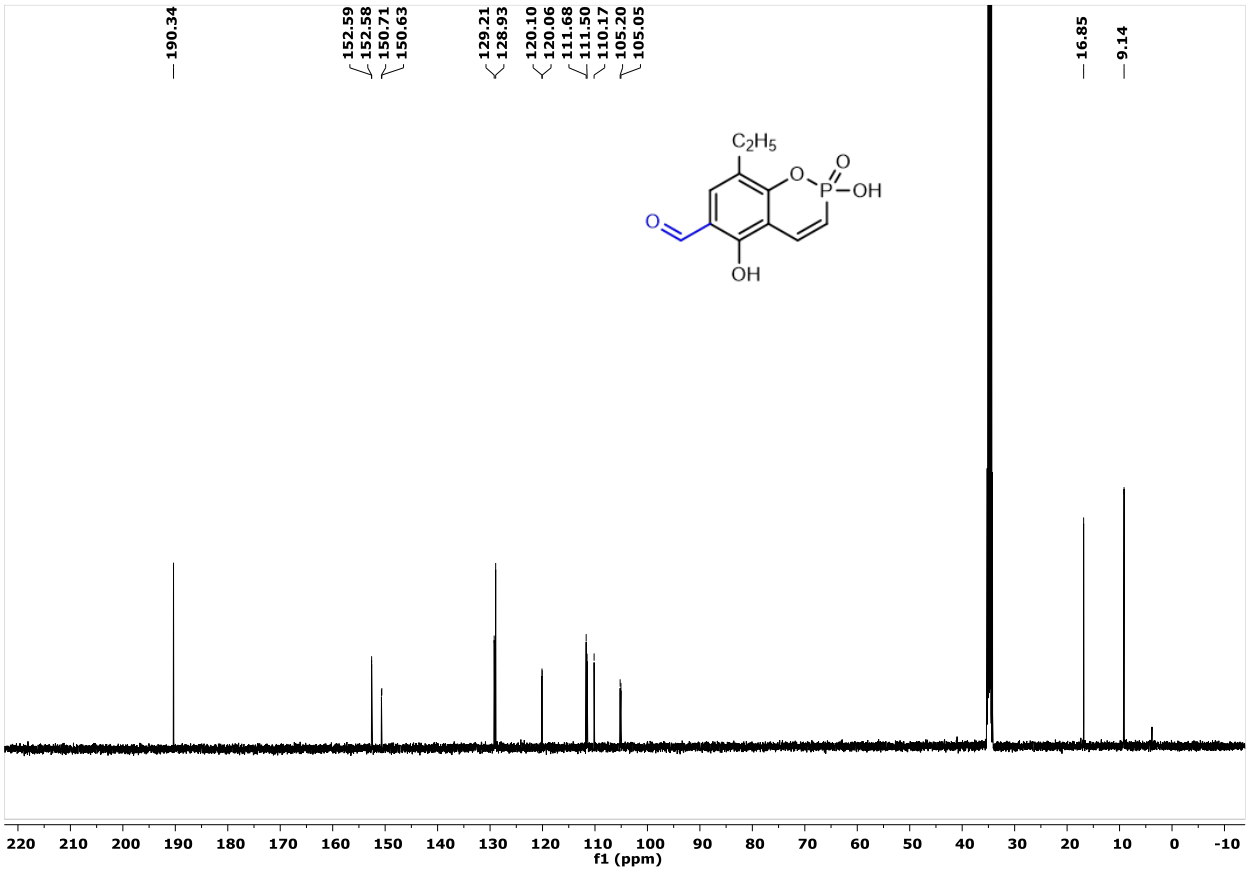


Figure S7. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) spectrum of compound **3a**.

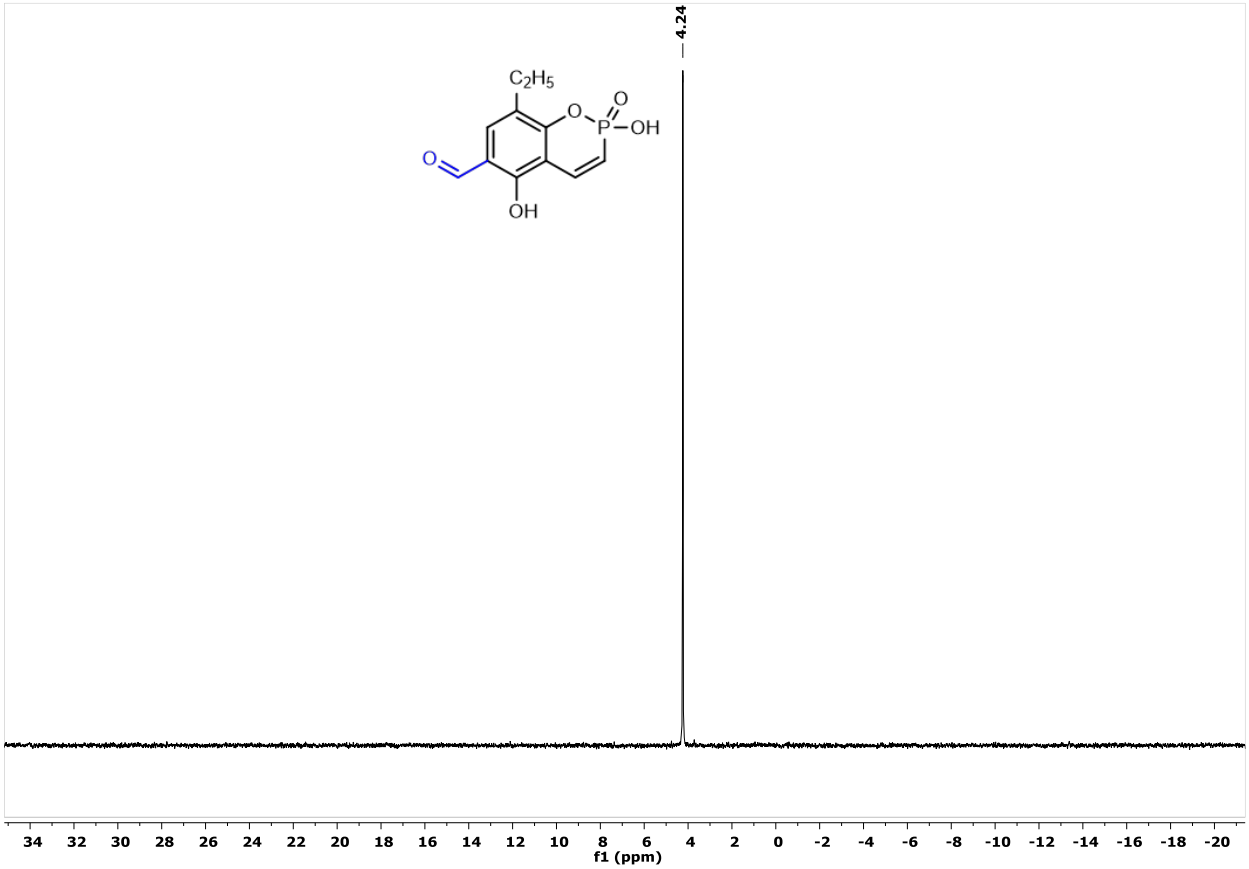


Figure S8. $^{31}P\{^{1}H\}$ NMR (162 MHz, DMSO-d_6) spectrum of compound **3a** .

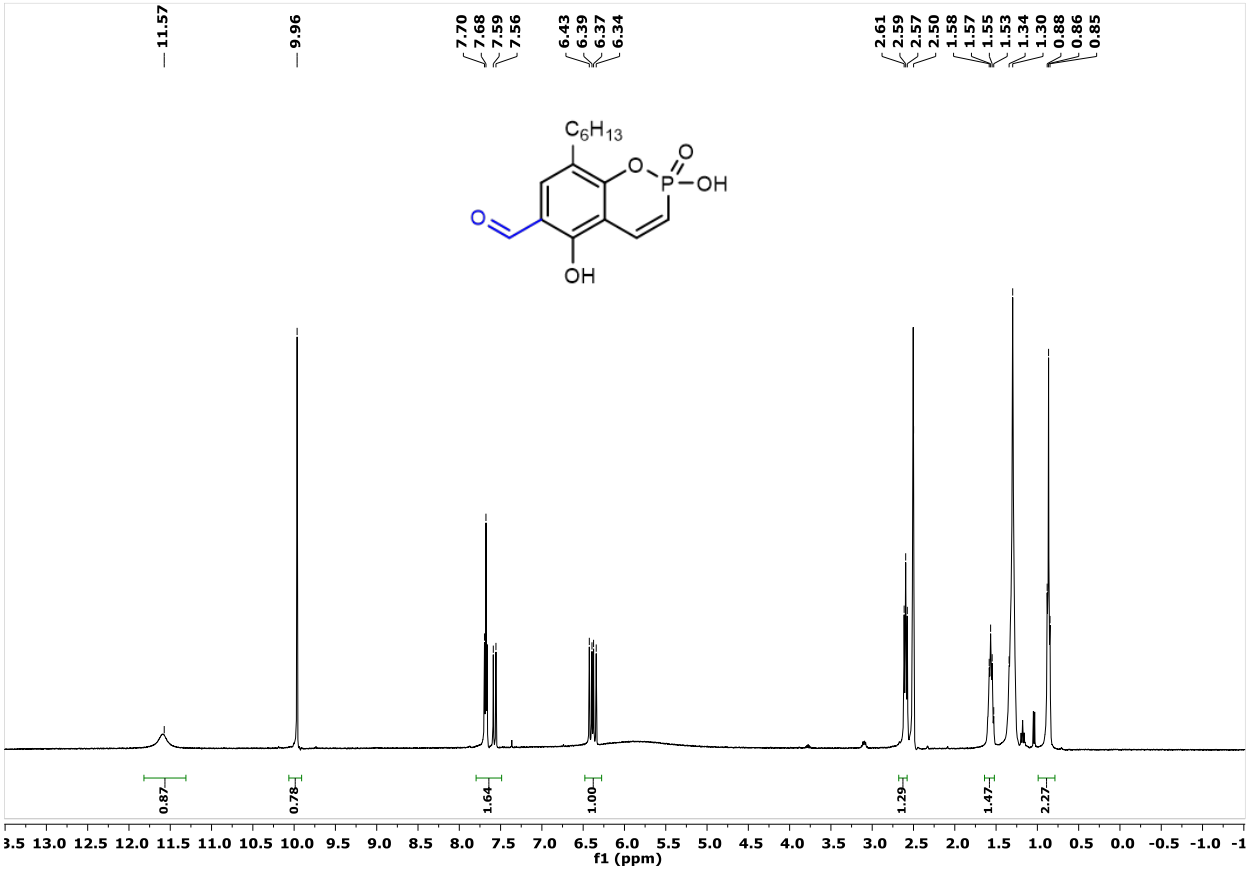


Figure S9. ^{1}H NMR (400 MHz, DMSO-d6) spectrum of compound **3b.**

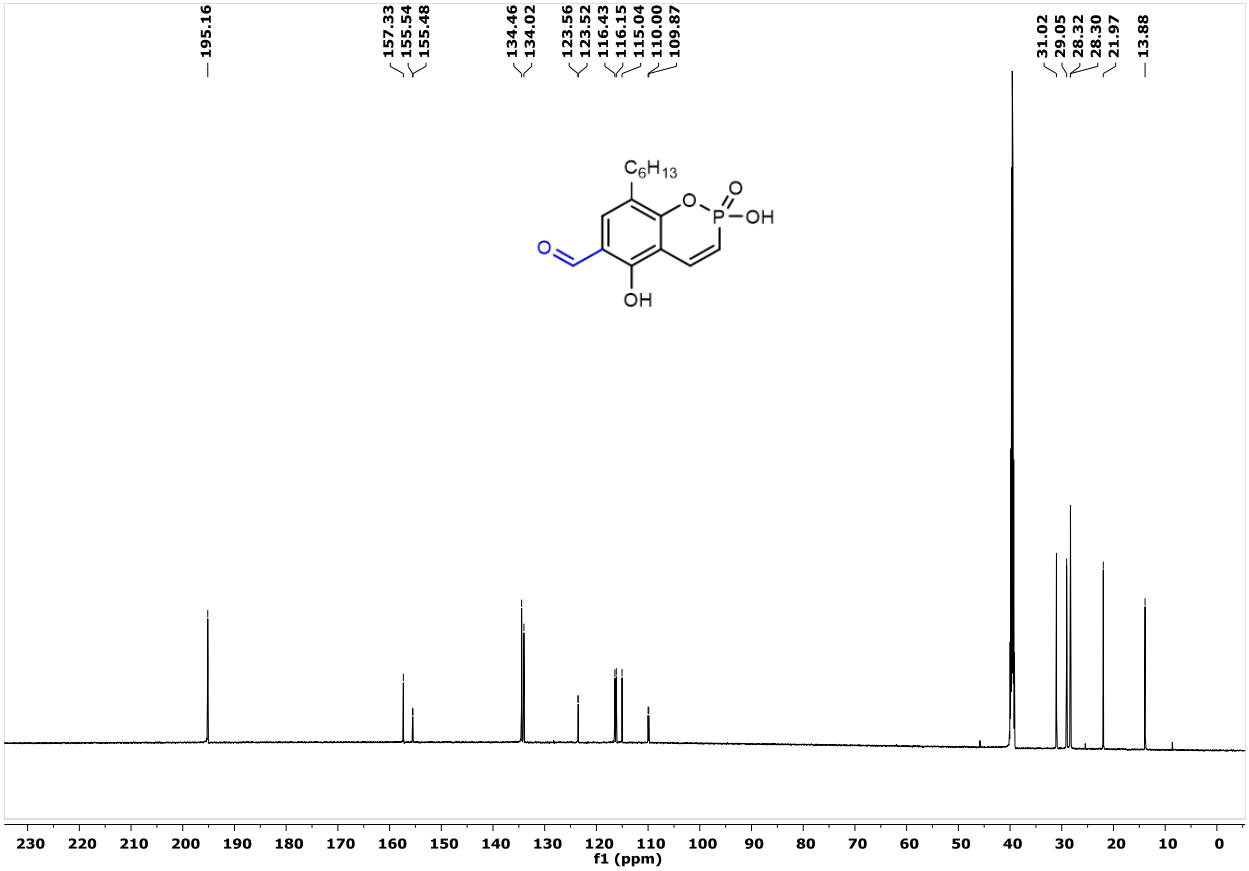


Figure S10. $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6) of compound **3b.**

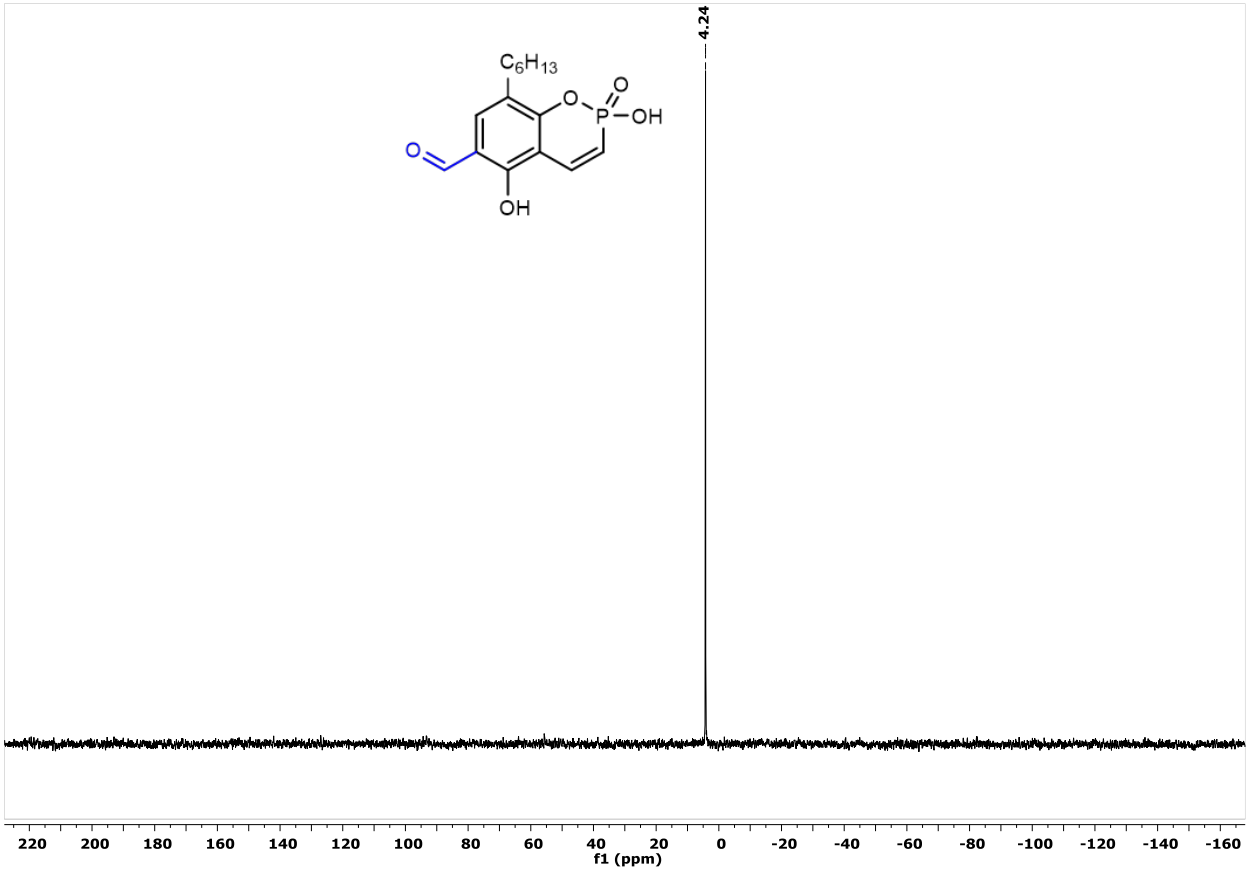


Figure S11. $^{31}P\{^{1}H\}$ NMR (162 MHz, DMSO-d_6) spectrum of compound **3b.**

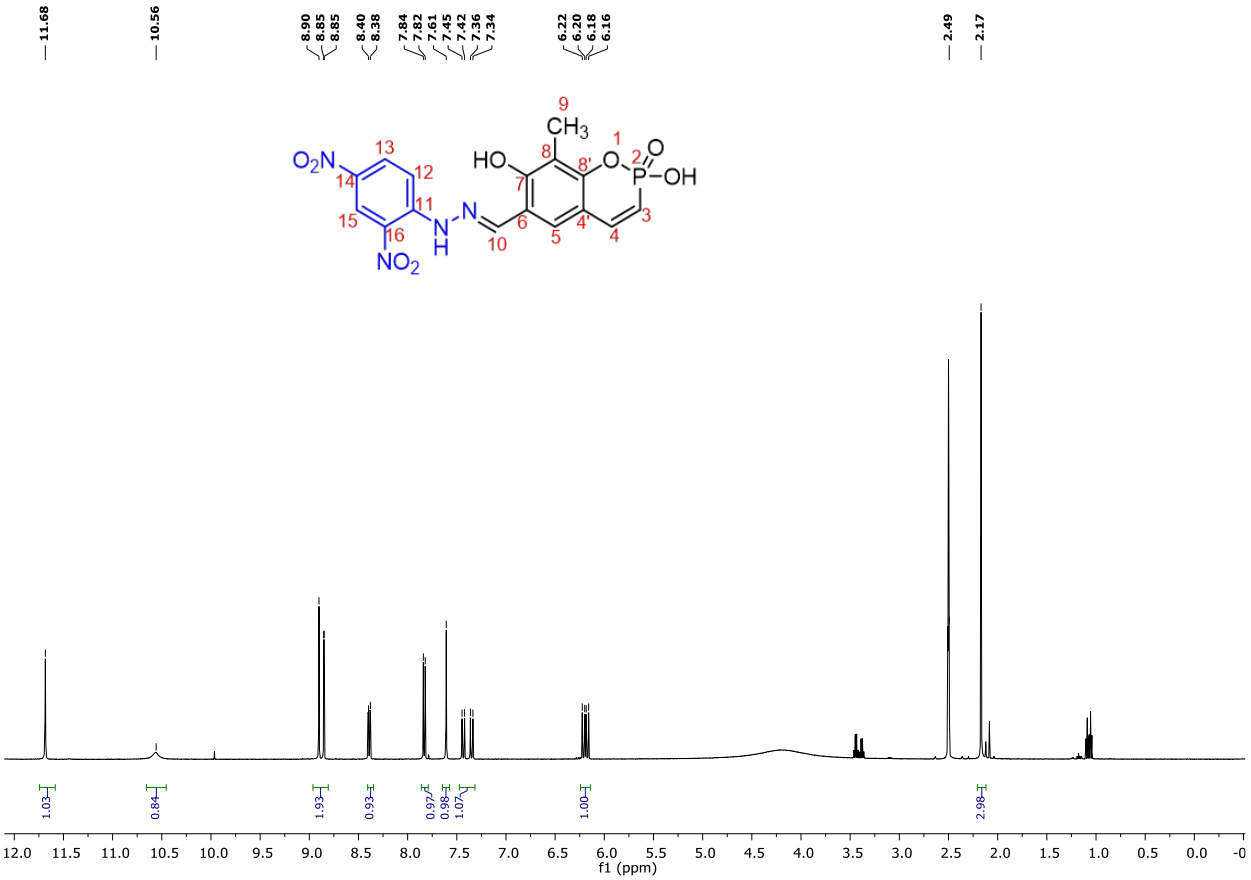


Figure S12. ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **4.**

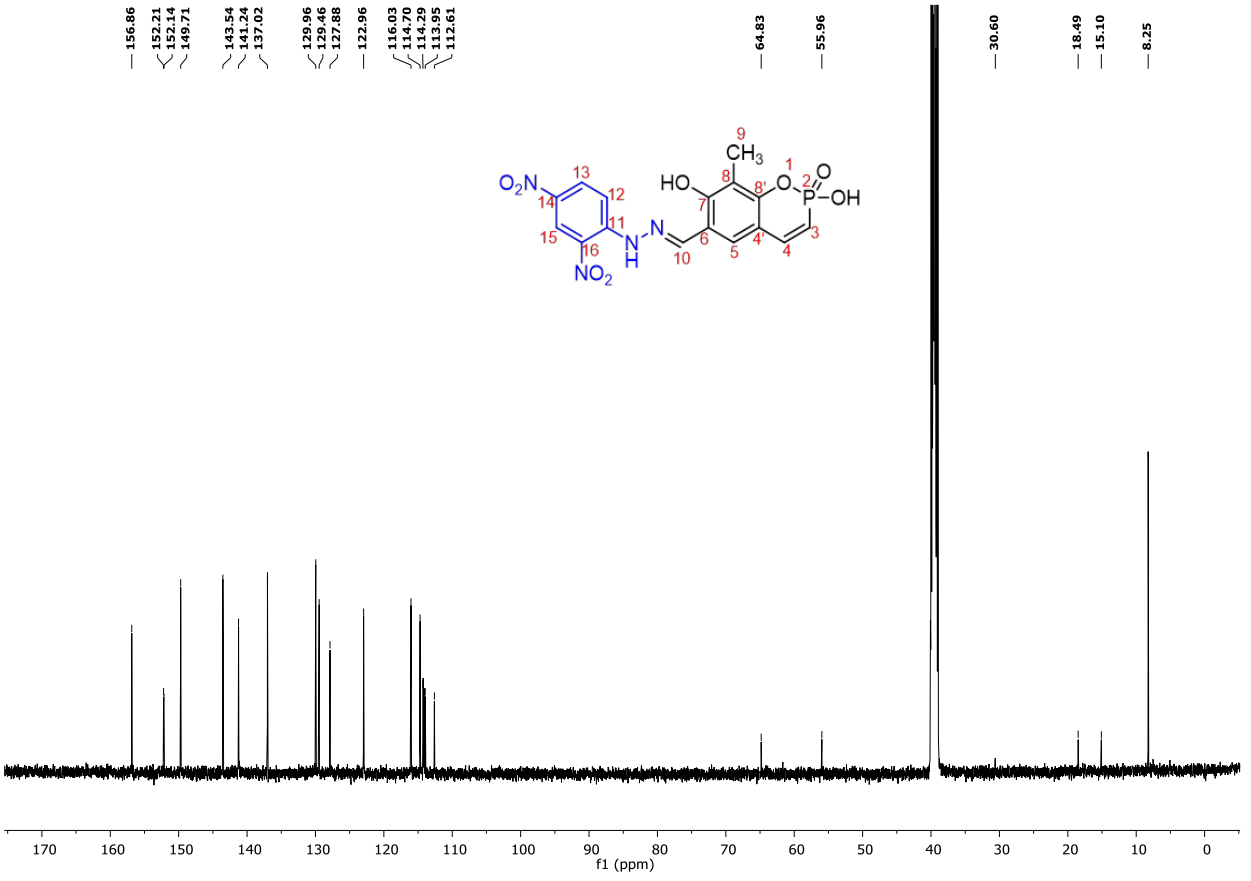


Figure S13. ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) spectrum of compound **4.**

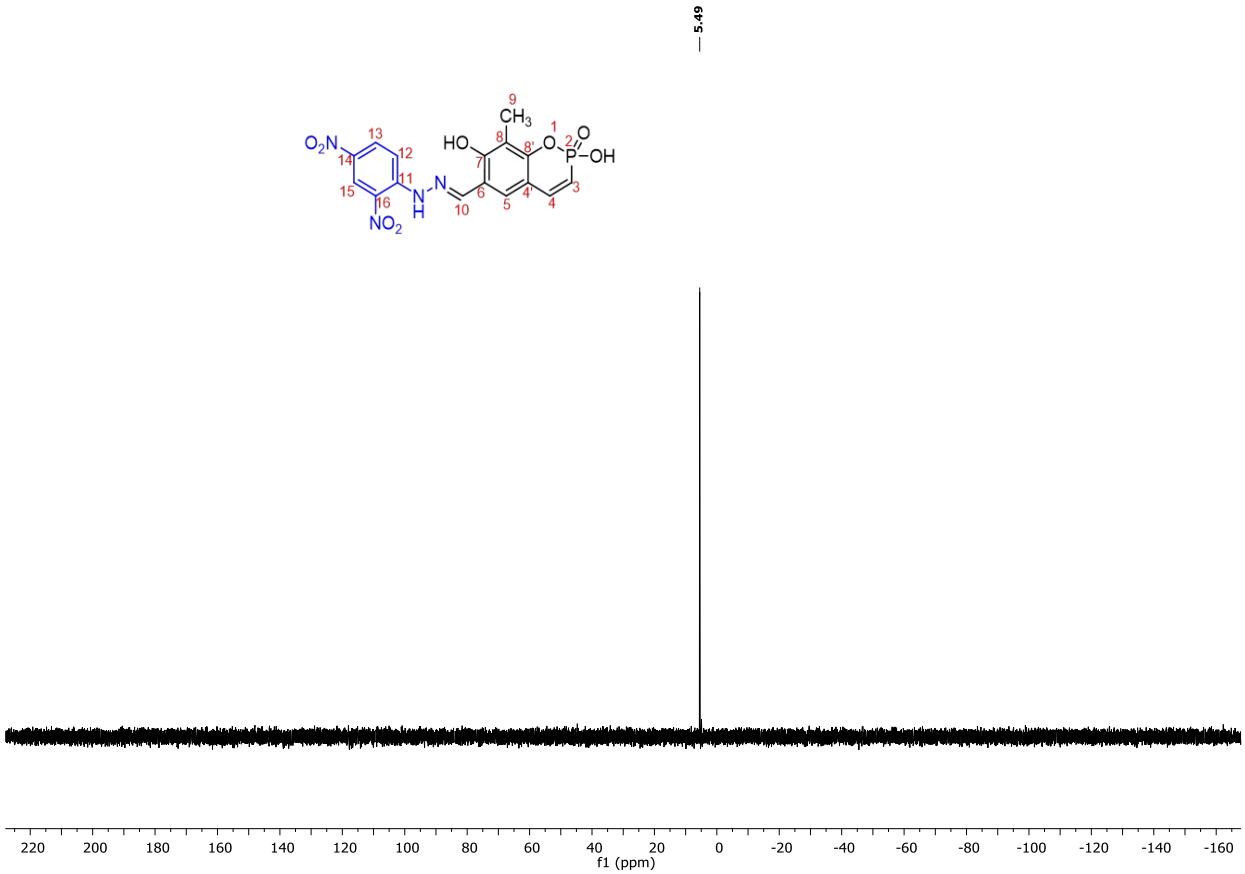


Figure S14. $^{31}P\{H\}$ NMR (162 MHz, DMSO-d_6) spectrum of compound **4.**

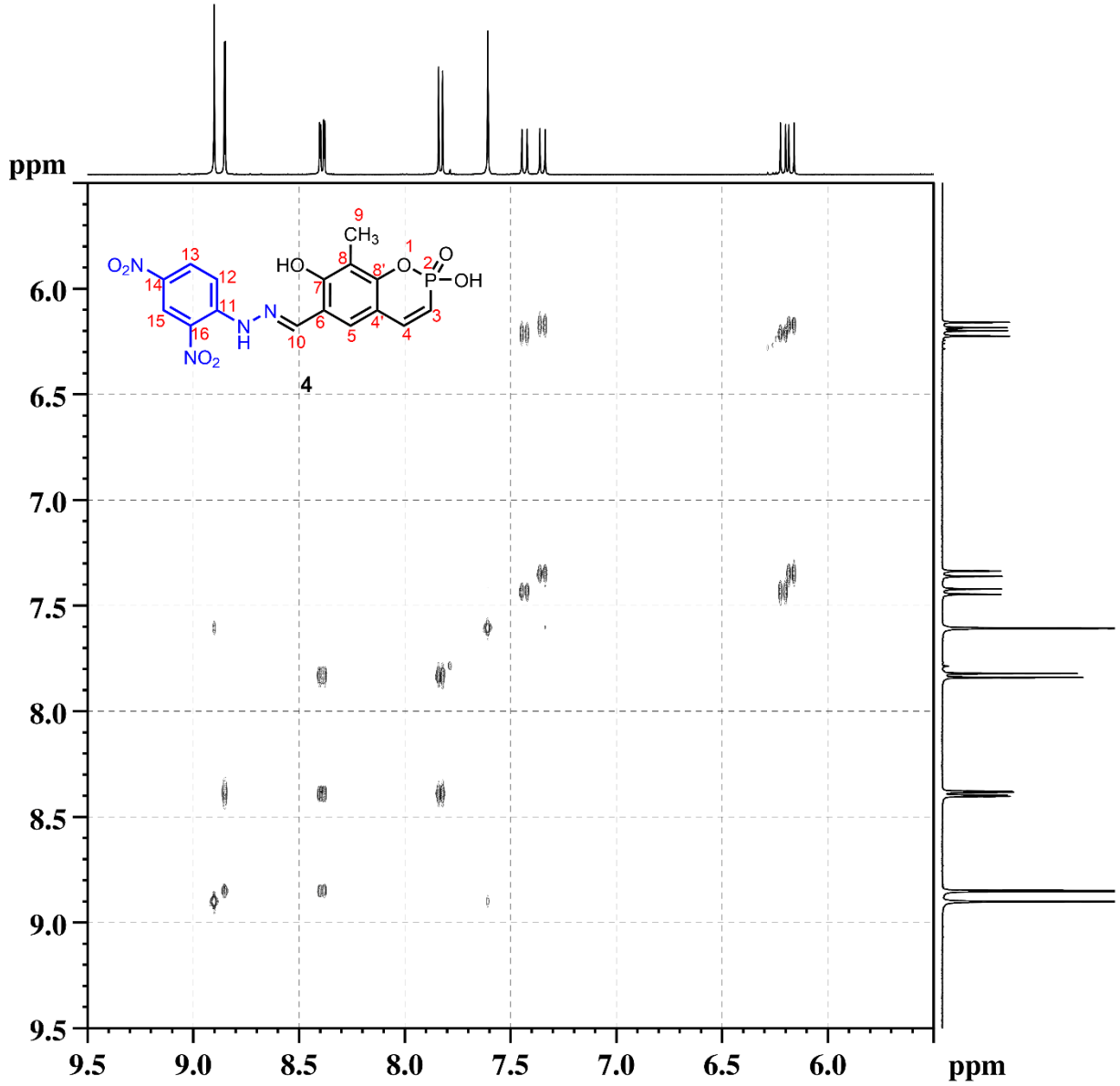


Figure S15. ^{1}H-^{1}H COSY spectrum of compound **4** in DMSO-d_6

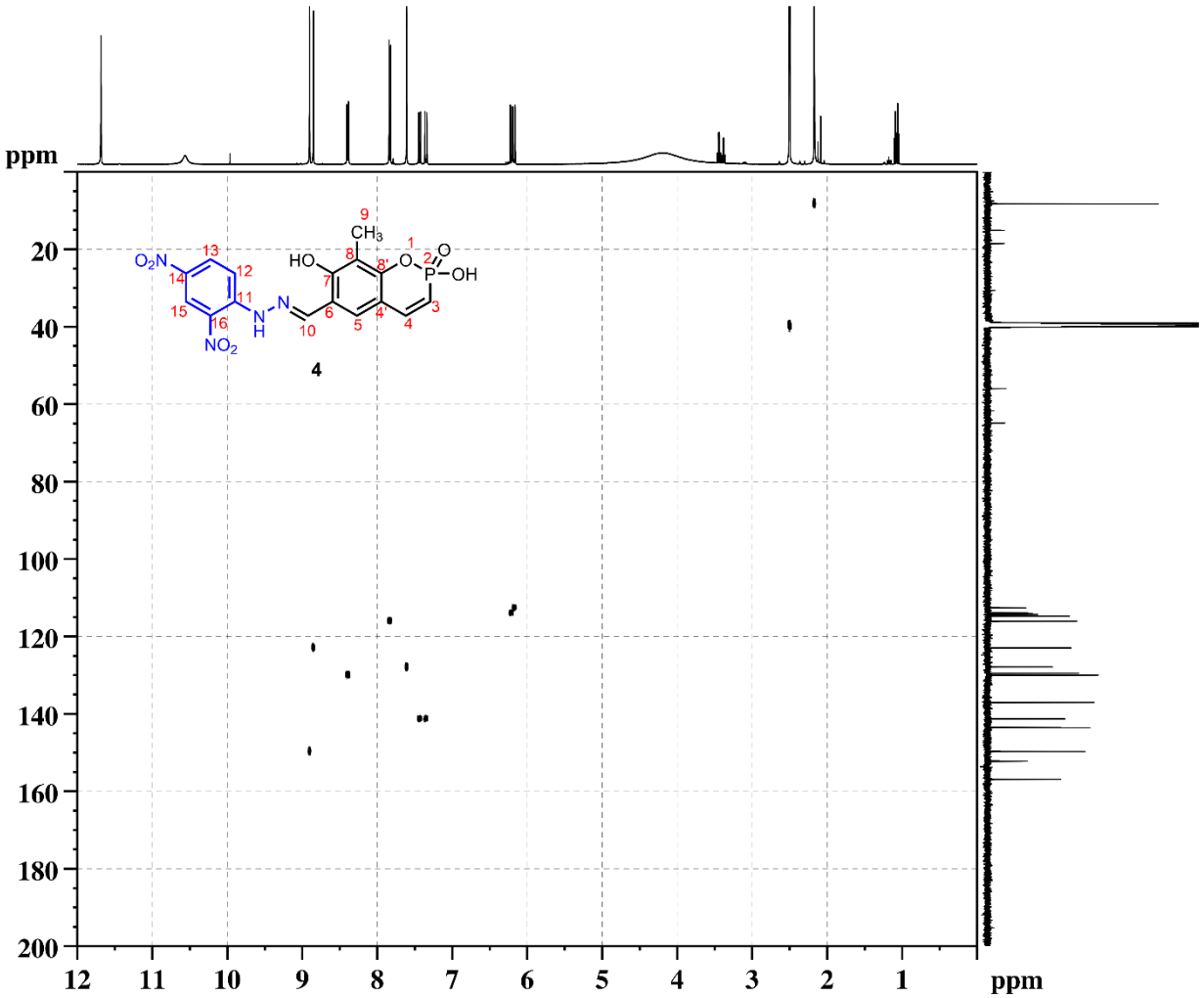


Figure S16. ^{1}H-^{13}C HSQC spectrum of compound **4** in DMSO-d_6

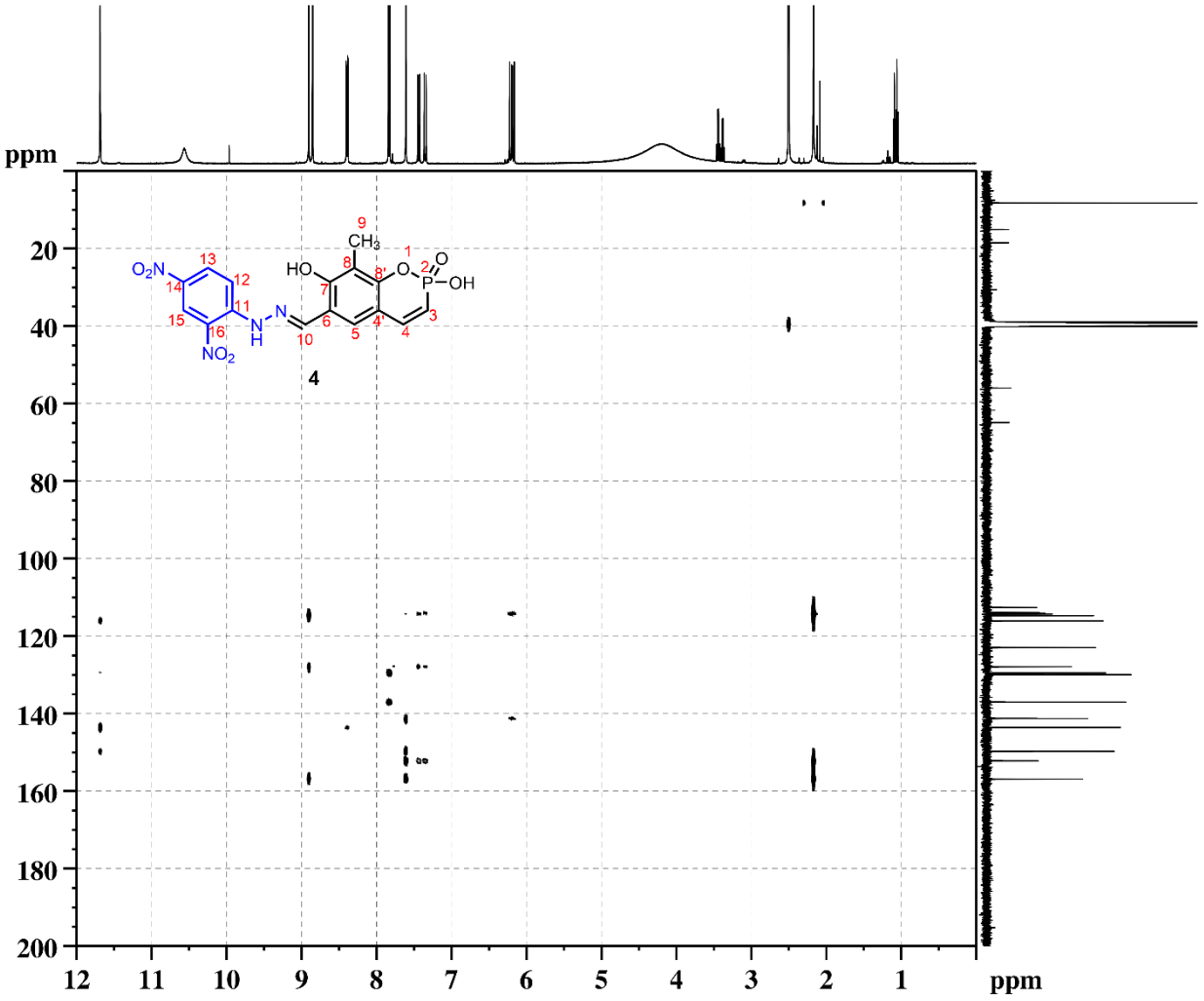


Figure S17. ^{1}H-^{13}C HMBC spectrum of compound **4** in DMSO-d_6

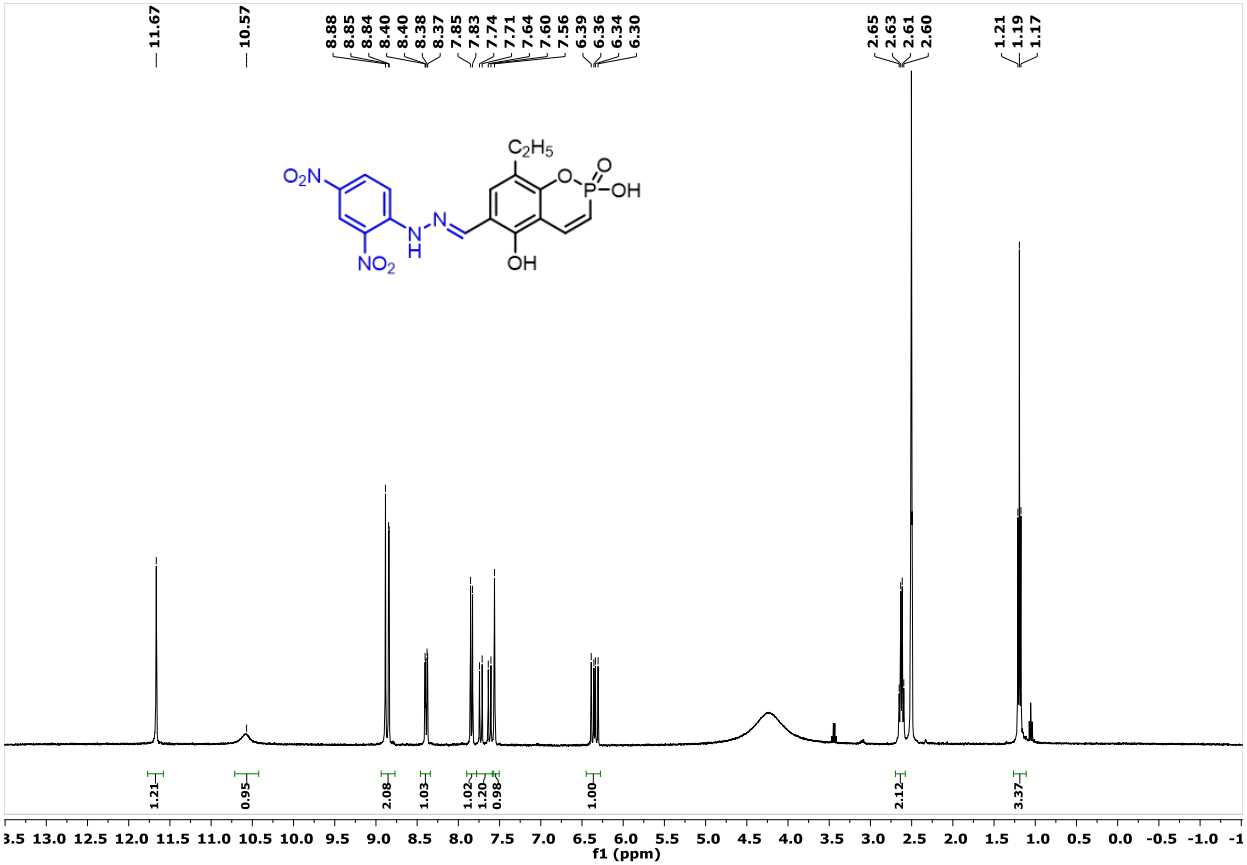


Figure S18. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound **5a.**

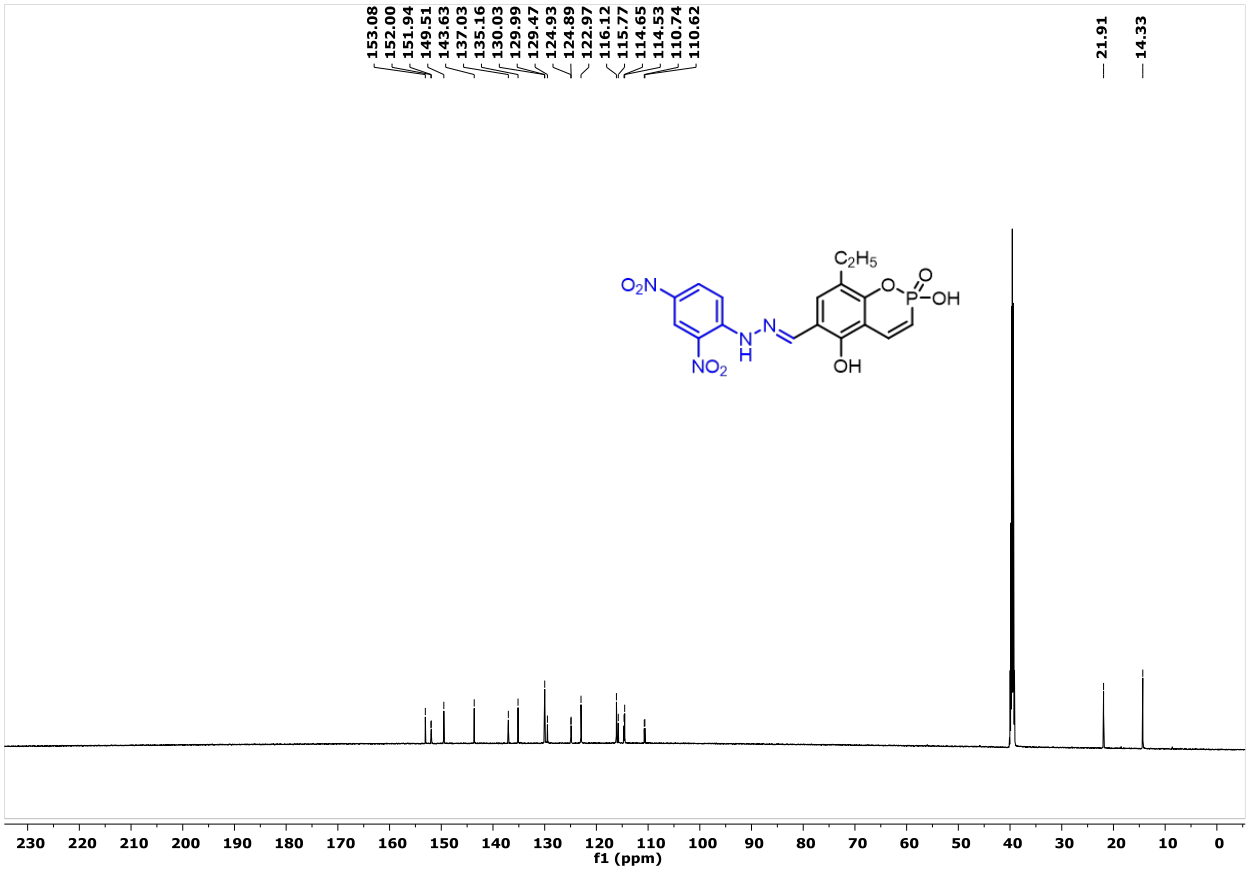


Figure S19. ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) spectrum of compound **5a.**

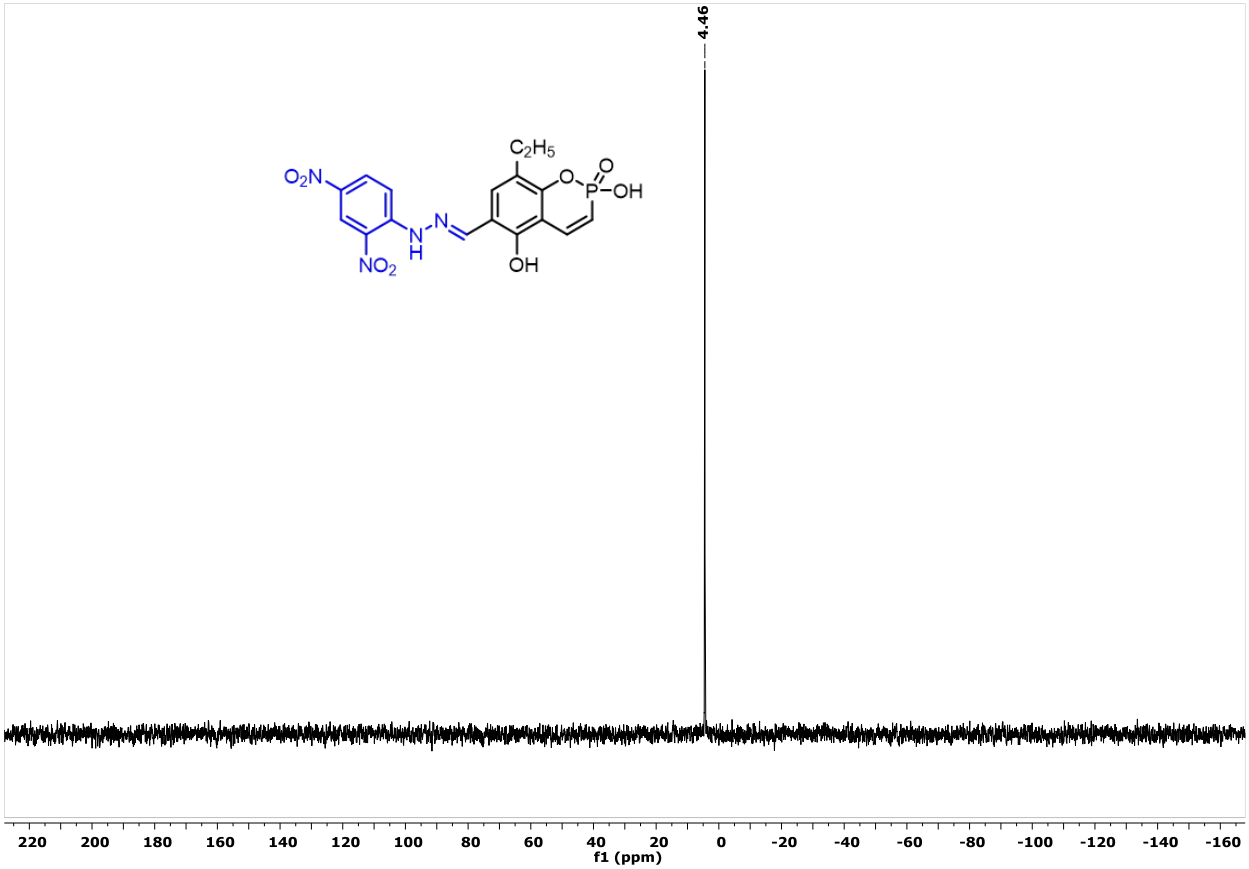


Figure S20. $^{31}P\{^{1}H\}$ NMR (162 MHz, DMSO-d_6) spectrum of compound **5a.**

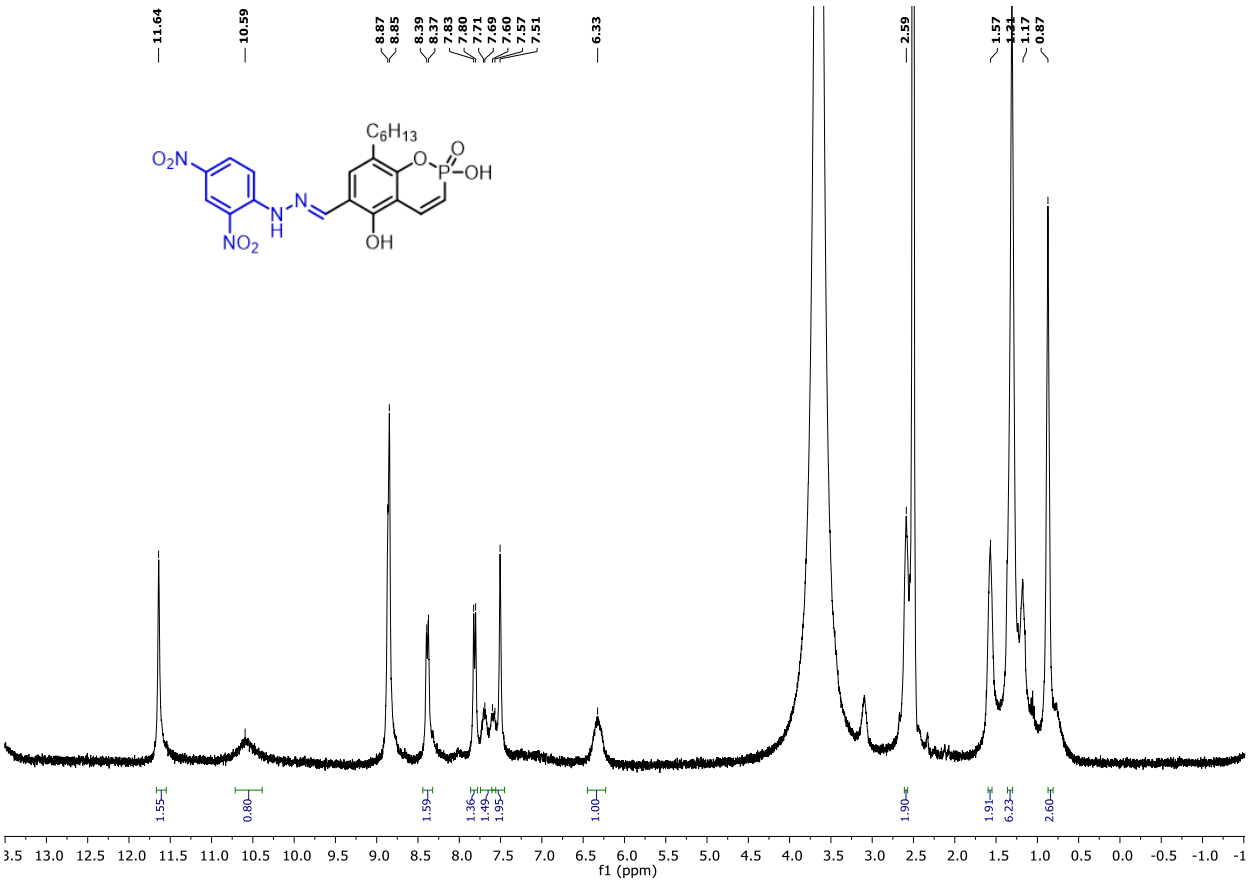


Figure S21. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound **5b.**

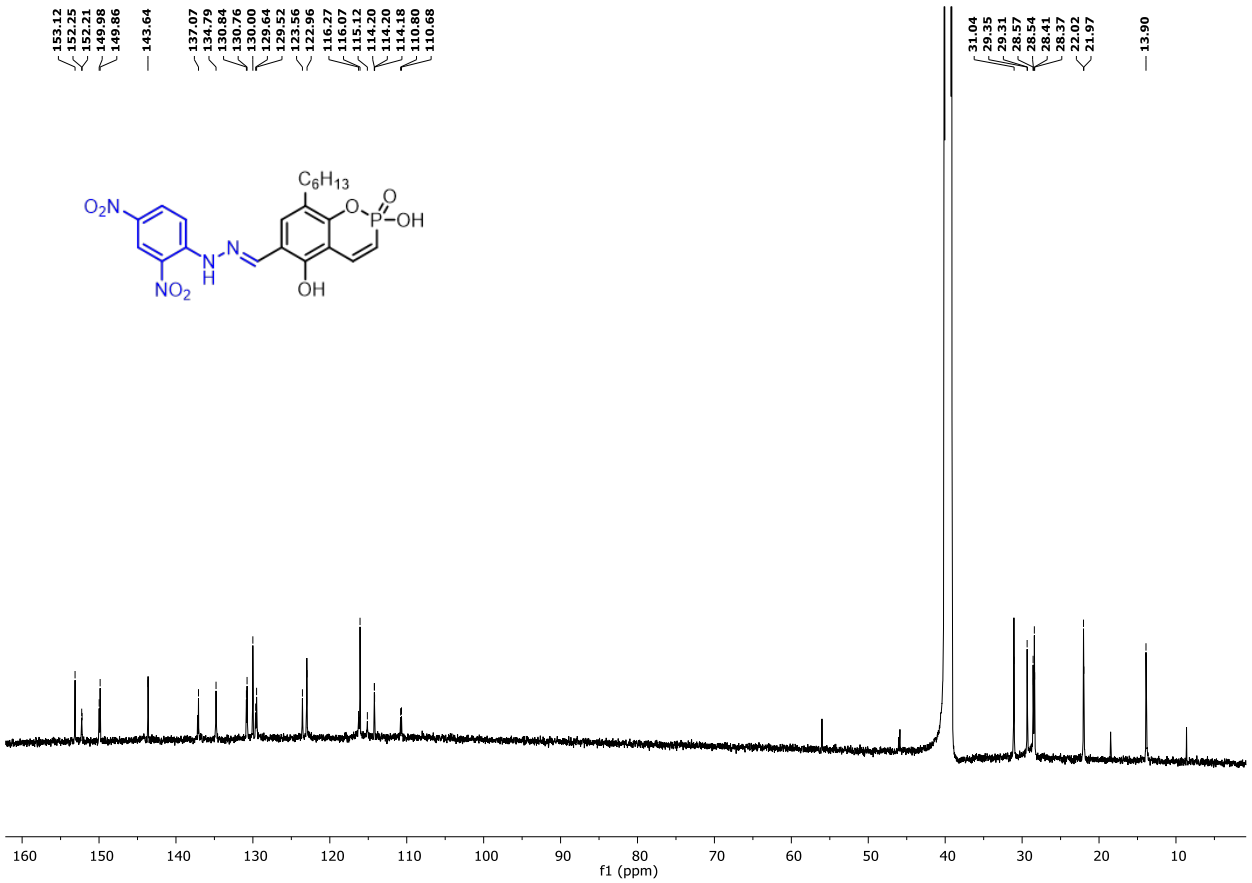


Figure S22. $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6) spectrum of compound **5b** in DMSO- d_6

References.

S1. L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3; https://doi.org/10.1107/S1600576714022985

S2. G. M. Sheldrick, *Acta Crystallogr.*, 2015, **A71**, 3; https://doi.org/10.1107/S2053273314026370G.

S3. L. J. Farrugia, *J. Appl. Crystallogr.*, 2012, **45**, 849; http://dx.doi.org/10.1107/S0021889812029111