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Supporting Information

Synthesis and Photophysical Properties of Donor-substituted Phenyl-phosphachromones as Potential TADF Material.

Shuangshuang Xu, Haiyang Huang, Chengxiong Yuan, Fen Liu, Haixin Ding, Qiang Xiao**

Key Laboratory of Organic Chemistry in Jiangxi Province, Institute of Organic Chemistry, Jiangxi Science & Technology Normal University, Nanchang 330013, China

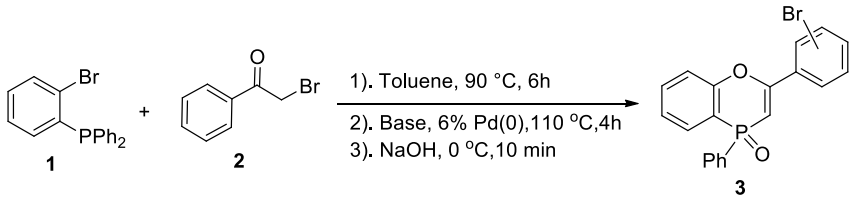
huanghaiyang1209@163.com; xiaoqiang@tsinghua.org.cn

Contents

1. Materials and Instruments

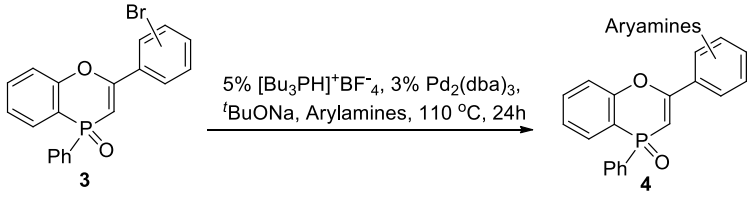
All reactions were routinely performed under an inert atmosphere of nitrogen by using standard Schlenk techniques and dry deoxygenated solvents. Dry toluene was obtained by distillation from P_4O_{10}. Aluminum oxide neutral for TLC (100 - 200 mesh) were purchased from Kermel Co. Ltd. And silica gel (200 - 300 mesh) purchased from Qingdao Hai Yang Chemical Industry Co. Ltd. was used for chromatographic separations. NMR spectra (400 MHz/100 MHz) were recorded on an Advance DPX spectrometer (Bruker,Billerica, MA, USA) at room temperature with Chloroform-*d* or DMSO-*d* as solvent. Tetramethylsilane (TMS) was used as an internal reference. Fuorescence data were measured with an Agilent F-4600. The sample film were measured Edinburgh FLS980 spectrometer.

2. Detailed syntheses of (di)bromphenyl phosphachromones.



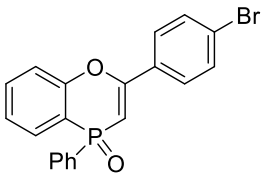
Compounds **1** (2 mmol) and **2** (2.1 mmol) were dissolved in toluene (8 mL) in a Schlenk bottle under argon gas atmosphere. After stirring at 90 ^{o}C in oil bath for 6 h, washed twice with Et_2O. To dissolve the solid in CH_2Cl_2 (5 mL), ^{t}BuOK (2.5 mmol) was added and the mixture was stirred at room temperature for 5 min , and then corresponding phosphonium ylides were obtained. The crude product is filtered through column chromatography (petroleum ether : ethyl acetate = 1 : 1 (v/v)) to remove impurities, and the product is obtained by column chromatography(CH_2Cl_2 : CH_3OH = 15 : 1 (v/v)) to afford the corresponding phosphonium ylides. The phosphonium ylides were dissolved in toluene (8 mL) in a Schlenk bottle under argon gas atmosphere. While $Pd(Ph_3P)_4$ (0.12 mmol) as catalyst added directly at room temperature, heterocyclic phosphoniums were precipitated from mixture under reflux at 110 ^{o}C for 4 h. To a toluene solution of heterocyclic phosphoniums, aqueous solution of NaOH (10M, 2.0 mL) was added at -10 – 0 ^{o}C. After the reaction mixture was stirred for 20 min at this temperature, water (20 mL) was added to the resulting mixture. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (5 mL × 2). All combined organic solutions were dried with anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (petroleum ether : ethyl acetate = 1 : 2 (v/v)) to afford the corresponding products **3**.[1]

3. Detailed synthesis of amino substituted phenyl-phosphachromones.



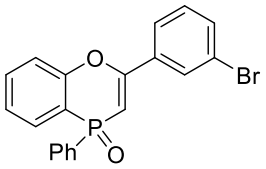
Compounds **3** (1 mmol), Aryamines (1.1 mmol), ^{t}BuONa (1.15 mmol), $[Bu_3PH]^+BF_4^-$ (0.05 mmol) and $Pd_2(dba)_3$ (0.03 mmol) were dissolved in toluene (2 mL) in a Schlenk bottle under argon gas atmosphere. The reaction was refluxed at 110 ^{o}C for 24 h. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (5 mL × 2). All combined organic solutions were dried with anhydrous Mg_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (CH_2Cl_2 : ethyl acetate = 20 : 1 (v/v)) to afford the corresponding products **4**.

4. The analytical and spectral characterization data.



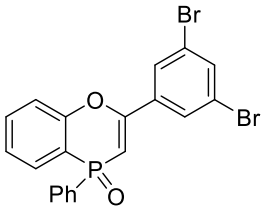
4′-bromphenyl phosphachromones

Reaction condition as general procedure for synthesis of compounds **3**: The reaction of compounds **1** (2 mmol) and 2-bromo-1-(3,5-dibromophenyl)ethanone (2.1 mmol), then a flash columnchromatography (petroleum ether : ethyl acetate = 1 : 2 (v/v)) to afford the corresponding products 4′-bromphenyl phosphachromone (651 mg, 82% yield).[1]



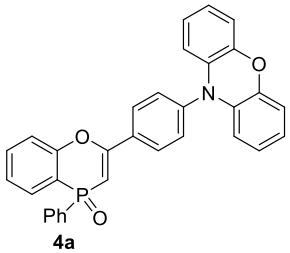
3′-bromphenyl phosphachromones

Reaction condition as general procedure for synthesis of compounds **3**: The reaction of compounds **1** (2 mmol) and 2-bromo-1-(3,5-dibromophenyl)ethanone (2.1 mmol), then a flash columnchromatography (petroleum ether : ethyl acetate = 1 : 2 (v/v)) to afford the corresponding products 3′-bromphenyl phosphachromone (635 mg, 80% yield).[1]



3′,5′-dibromphenyl phosphachromones

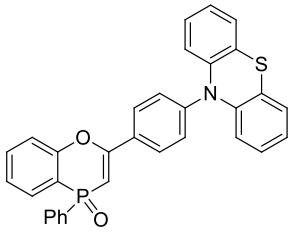
Reaction condition as general procedure for synthesis of compounds **3**: The reaction of compounds **1** (2 mmol) and 2-bromo-1-(3,5-dibromophenyl)ethanone (2.1 mmol), then a flash columnchromatography (petroleum ether : ethyl acetate = 1 : 2 (v/v)) to afford the corresponding products 3′,5′-dibromphenyl phosphachromone (809 mg, 85% yield); ^{31}P NMR (162 MHz, $CDCl_3$) δ -1.95 (s) ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 1.1 Hz, 2H), 7.76 (s, 1H), 7.72- 7.67 (m, 2H), 7.65 – 7.59 (m, 2H), 7.52 – 7.42 (m, 4H), 7.29 (t, *J* = 7.5 Hz, 1H), 6.07 (d, *J* = 1.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.34 (s, C), 155.37 (d, $J_{C\text{-}P}$ = 3.4 Hz, C), 136.86 (d, $J_{C\text{-}P}$ = 10.2 Hz, C), 136.17 (s, CH), 133.78 (d, $J_{C\text{-}P}$ = 60.6 Hz, C), 133.61 (s, CH), 132.03 (d, $J_{C\text{-}P}$ = 2.0 Hz, CH), 131.92 (d, $J_{C\text{-}P}$ = 11.0 Hz, 2CH), 131.09 (d, $J_{C\text{-}P}$ = 5.7 Hz, CH), 128.60 (d, $J_{C\text{-}P}$ = 13.3 Hz, 2CH), 128.08 (s, 2CH), 125.58 (d, $J_{C\text{-}P}$ = 10.6 Hz, CH), 123.45 (s, 2C), 118.50 (d, $J_{C\text{-}P}$ = 5.3 Hz, CH), 115.87 (d, $J_{C\text{-}P}$ = 103.9 Hz, C), 93.90 (d, $J_{C\text{-}P}$ = 103.1 Hz, CH). HRMS Calcd. For $C_{20}H_{14}Br_2O_2P^+$ $[M+H^+]^+$, 474.9093. Found: 474.9090.



4a

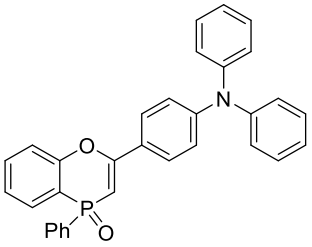
Reaction condition as general procedure for synthesis of compounds **4**: The reaction of compound **3** (396 mg, 1 mmol) and Phenoxazine(PO) (219 mg, 1.1 mmol), then a flash columnchromatography (CH_2Cl_2 : ethyl acetate = 20 : 1 (v/v)) afforded Yellow solid **4a** (424 mg, 85% yield); ^{31}P NMR (162 MHz, Chloroform-*d*) δ -1.45; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.2 Hz, 2H), 7.79 – 7.73 (m, 2H), 7.72– 7.67 (m, 1H), 7.65 – 7.60 (m, 1H), 7.54 – 7.44 (m, 6H), 7.31 (t, *J* = 7.5 Hz, 1H), 6.73 – 6.65 (m, 4H), 6.63– 6.59 (m, 2H), 6.16 (d, *J* = 2.0 Hz, 1H), 5.96 (dd, *J* = 7.9, 1.5 Hz, 2H); ^{13}C

NMR (101 MHz, Chloroform-*d*) δ 160.49 (s, C), 155.60 (d, J_{C-P} = 3.2 Hz, C), 143.95 (s, 2C), 141.60 (s, C), 134.79 (d, J_{C-P} = 15.2 Hz, C), 133.86 (s, 2C), 133.73 (s, C), 133.50 (s, CH), 131.98 (d, J_{C-P} = 4.0 Hz, 2CH), 131.88 (s, CH), 131.35 (s, 2CH), 131.10 (d, J_{C-P} = 3.0 Hz, CH), 129.04 (s, 2CH), 128.55 (d, J_{C-P} = 13.1 Hz, 2CH), 125.38 (d, J_{C-P} = 10.6 Hz, CH), 123.32 (s, 2CH), 121.76 (s, 2CH), 118.45 (d, J_{C-P} = 5.5 Hz, CH), 116.54 (d, J_{C-P} = 51.5 Hz, C), 115.68 (s, 2CH), 113.27 (s, 2CH), 92.71 (d, J_{C-P} = 104.5 Hz, CH). HRMS Calcd. For $C_{32}H_{23}NO_3P^+$ $[M + H^+]^+$, 500.1410. Found: 500.1411.



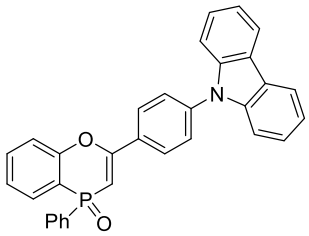
4b

Reaction condition as general procedure for synthesis of compounds **4**: The reaction of compound **3** (396 mg, 1 mmol) and Phenothiazine(PT) (237 mg, 1.1 mmol), then a flash columnchromatography (CH_2Cl_2 : ethyl acetate = 20 : 1 (v/v)) afforded Red solid **4b** (412 mg, 80% yield); ^{31}P NMR (162 MHz, Chloroform-*d*) δ -1.32; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.94 (m, 2H), 7.78– 7.72 (m, 2H), 7.70 – 7.65 (m, 1H), 7.59 (t, *J* = 8.7 Hz, 1H), 7.50 – 7.39 (m, 4H), 7.37 – 7.35 (m, 2H), 7.28 (t, *J* = 40.4 Hz, 1H), 7.20 – 7.17 (m, 2H), 7.06 – 7.01 (m, 2H), 6.98– 6.94 (m, 2H), 6.66 (dd, *J* = 8.1, 1.4 Hz, 2H), 6.08 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.89 (s, C), 155.61 (d, J_{C-P} = 3.0 Hz, C), 145.25 (s, C), 142.95 (s, 2C), 134.54 (d, J_{C-P} = 120.1 Hz, C), 133.37 (s, CH), 131.92 (d, J_{C-P} = 10.1 Hz, 2CH), 131.78 (d, J_{C-P} = 3.0 Hz, CH), 131.05 (d, J_{C-P} = 5.1 Hz, CH), 130.64 (d, J_{C-P} = 10.1 Hz, C), 128.51 (d, J_{C-P} = 13.1 Hz, 2CH), 128.29 (s, 2CH), 127.62 (s, 2CH), 127.07 (s, 2CH), 125.52 (s, 2CH), 125.50 (s, 2C), 125.22 (d, J_{C-P} = 10.1 Hz, CH), 124.05 (s, 2CH), 120.03 (s, 2CH), 118.43 (d, J_{C-P} = 5.5 Hz, CH), 116.10 (d, J_{C-P} = 104.0 Hz, C), 91.32 (d, J_{C-P} = 105.6 Hz, CH). HRMS Calcd. For $C_{32}H_{23}NO_2PS^+$ $[M + H^+]^+$, 516.1182. Found: 516.1182.



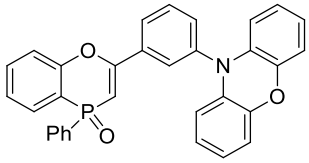
4c

Reaction condition as general procedure for synthesis of compounds **4**: The reaction of compound **3** (396 mg, 1 mmol) and Diphenylamine(DPA) (201 mg, 1.1 mmol), then a flash columnchromatography (CH_2Cl_2 : ethyl acetate = 20 : 1 (v/v)) afforded Yellow solid **4c** (407 mg, 84% yield); ^{31}P NMR (162 MHz, Chloroform-*d*) δ -0.92; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.69 (m, 4H), 7.67 – 7.62 (m, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.51 – 7.42 (m, 3H), 7.39 – 7.36 (m, 1H), 7.33 – 7.23 (m, 7H), 7.16 – 7.07 (m, 6H), 5.94 (d, *J* = 2.0 Hz, 1H);^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.43 (s, C), 155.64 (d, J_{C-P} = 3.0 Hz, C), 150.40 (s, C), 146.83 (s, 2C), 134.86 (d, J_{C-P} = 120.3 Hz, C), 133.15 (s, CH), 131.93 (d, J_{C-P} = 10.8 Hz, 2CH), 131.58 (d, J_{C-P} = 3.0 Hz, CH), 130.98 (d, J_{C-P} = 5.4 Hz, CH), 129.53 (s, 4CH), 128.39 (d, J_{C-P} = 13.1 Hz, 2CH), 127.24 (s, 2CH), 125.85 (d, J_{C-P} = 10.1 Hz, C), 125.47 (s, 4CH), 124.97 (d, J_{C-P} = 10.5 Hz, CH), 124.15 (s, 2CH), 121.25 (s, 2CH), 118.35 (d, J_{C-P} = 6.1 Hz, CH), 116.21 (d, J_{C-P} = 102.3 Hz, C), 89.29 (d, J_{C-P} = 107.1 Hz, CH). HRMS Calcd. For $C_{32}H_{24}NO_2PNa^+$ $[M + Na^+]^+$, 508.1437. Found: 508.1432.



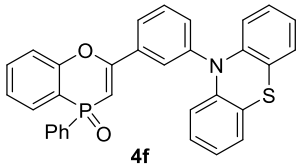
4d

Reaction condition as general procedure for synthesis of compounds **4**: The reaction of compound **3** (396 mg, 1 mmol) and Carbazole(CZ) (199 mg, 1.1 mmol), then a flash columnchromatography (CH_2Cl_2 : ethyl acetate = 20 : 1 (v/v)) afforded Yellow solid **4d** (396 mg, 82% yield); ^{31}P NMR (162 MHz, Chloroform-*d*) δ -1.32; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 – 8.10 (m, 4H), 7.82 – 7.77 (m, 2H), 7.72 (d, *J* = 8.4 Hz, 3H), 7.63 (t, *J* = 7.9 Hz, 1H), 7.51 – 7.41 (m, 8H), 7.32 (t, *J* = 7.2 Hz, 3H), 6.19 (s, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.67 (s, C), 155.64 (d, $J_{C\text{-}P}$ = 3.0 Hz, C), 140.39 (s, 2C), 140.24 (s, C), 134.44 (d, $J_{C\text{-}P}$ = 120.3 Hz, C), 133.46 (s, CH), 132.24 (d, $J_{C\text{-}P}$ = 9.1 Hz, C), 131.95 (d, $J_{C\text{-}P}$ = 11.0 Hz, 2CH), 131.86 (d, $J_{C\text{-}P}$ = 2.9 Hz, CH), 131.12 (d, $J_{C\text{-}P}$ = 5.5 Hz, CH), 128.56 (d, $J_{C\text{-}P}$ = 13.2 Hz, 2CH), 127.91 (s, 2CH), 126.96 (s, 2CH), 126.19 (s, 2CH), 125.34 (d, $J_{C\text{-}P}$ = 10.5 Hz, CH), 123.73 (s, 2C), 120.50 (s, 2CH), 120.48 (s, 2CH), 118.47 (d, $J_{C\text{-}P}$ = 2.0 Hz, CH), 116.11 (d, $J_{C\text{-}P}$ = 104.0 Hz, C), 109.74 (s, 2CH), 92.15 (d, $J_{C\text{-}P}$ = 105.1 Hz, CH). HRMS Calcd. For $C_{32}H_{23}NO_2P^+$ $[M + H^+]^+$, 484.1461. Found: 484.1460.



4e

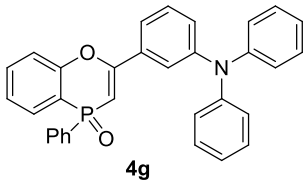
Reaction condition as general procedure for synthesis of compounds **4**: The reaction of compound **3** (396 mg, 1 mmol) and Phenoxazine(PO) (219 mg, 1.1 mmol), then a flash columnchromatography (CH_2Cl_2 : ethyl acetate = 20 : 1 (v/v)) afforded Yellow solid **4e** (404 mg, 81% yield); ^{31}P NMR (162 MHz, Chloroform-*d*) δ -1.64; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 2.1 Hz, 1H), 7.55 – 7.41 (m, 4H), 7.38 – 7.34 (m, 1H), 7.30 – 7.18 (m, 5H), 7.07 – 7.03 (m, 1H), 6.50 – 6.37 (m, 6H), 5.93 (d, *J* = 1.9 Hz, 1H), 5.72 – 5.70 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.04 (s, C), 155.54 (d, $J_{C\text{-}P}$ = 3.0 Hz, C), 143.94 (s, 2C), 139.76 (s, C), 136.89 (d, $J_{C\text{-}P}$ = 10.1 Hz, C), 134.43 (d, $J_{C\text{-}P}$ = 78.8 Hz, C), 134.04 (s, 2C), 133.62 (s, CH), 133.47 (s, CH), 131.95 (d, $J_{C\text{-}P}$ = 10.1 Hz, 2CH), 131.90 (s, CH)，131.66 (s, CH), 131.05 (d, $J_{C\text{-}P}$ = 5.1 Hz, CH), 128.87 (s, CH), 128.56 (d, $J_{C\text{-}P}$ = 13.1 Hz, 2CH), 126.26 (s, CH), 125.38 (d, $J_{C\text{-}P}$ = 10.1 Hz, CH), 123.37 (s, 2CH), 121.71 (s, 2CH), 118.56 (d, $J_{C\text{-}P}$ = 5.1 Hz, CH), 116.02 (d, $J_{C\text{-}P}$ = 104.0 Hz, C), 115.66 (s, 2CH), 113.23 (s, 2CH), 92.76 (d, $J_{C\text{-}P}$ = 104.3 Hz, CH). HRMS Calcd. For $C_{32}H_{23}NO_3P^+$ $[M + H^+]^+$, 500.1410. Found: 500.1413.



4f

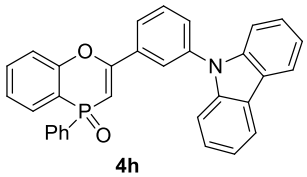
Reaction condition as general procedure for synthesis of compounds **4**: The reaction of compound **3** (396 mg, 1 mmol) and Phenothiazine(PT) (237 mg, 1.1 mmol), then a flash columnchromatography (CH_2Cl_2 : ethyl acetate = 20 : 1 (v/v)) afforded Red solid **4f** (391 mg, 76% yield); ^{31}P NMR (162 MHz, Chloroform-*d*) δ -1.59; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.92 (m, 2H), 7.77 – 7.63 (m, 4H), 7.61 – 7.56 (m, 1H), 7.54 – 7.39 (m, 5H), 7.29 – 7.25 (m, 1H), 7.09 – 7.06 (m, 2H), 6.93 – 6.84 (m, 4H), 6.30 – 6.28 (m, 2H), 6.14 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.26 (s, C), 155.56 (d, $J_{C\text{-}P}$ = 3.1 Hz, C), 143.81 (s, C), 142.03 (s, C), 136.54 (d, $J_{C\text{-}P}$ = 10.4 Hz, C), 134.28 (d, $J_{C\text{-}P}$ = 120.0 Hz, C), 133.44 (s, CH), 132.67 (s, CH), 131.95 (d, $J_{C\text{-}P}$ = 11.1 Hz, 2CH), 131.87 (s, CH) , 131.84 (s, C), 131.09 (s, CH), 131.05 (d, $J_{C\text{-}P}$ = 5.9 Hz, CH), 128.54 (d, $J_{C\text{-}P}$ = 13.1 Hz, 2CH), 127.79 (s, CH), 127.06(s, 2CH), 127.01(s, 2CH) , 125.52 (s, CH), 125.34 (d, $J_{C\text{-}P}$ = 10.5 Hz, CH), 123.04(s, 2CH),

121.38 (s, 2C), 118.54 (d, J_{C-P} = 5.4 Hz, CH), 116.77(s, 2CH),116.04 (d, J_{C-P} = 103.5 Hz, C), 92.66 (d, J_{C-P} = 104.2 Hz, CH). HRMS Calcd. For $C_{32}H_{23}NO_2PS^+$ $[M + H^+]^+$, 516.1182. Found: 516.1180.



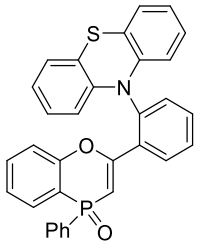
4g

Reaction condition as general procedure for synthesis of compounds **4**: The reaction of compound **3** (396 mg, 1 mmol) and Diphenylamine(DPA) (201 mg, 1.1 mmol), then a flash columnchromatography (CH_2Cl_2 : ethyl acetate = 20 : 1 (v/v)) afforded White solid **4g** (388 mg, 80% yield); ^{31}P NMR (162 MHz, Chloroform-*d*) δ -1.17; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.48 (m, 2H), 7.45 – 7.40 (m, 1H), 7.37 – 7.32 (m, 2H), 7.31 – 7.21 (m, 4H), 7.14 – 7.02 (m, 7H), 6.98 (dd, *J* = 7.9, 2.3 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 4H), 6.86 (t, *J* = 7.4 Hz, 2H), 5.73 (d, *J* = 2.3 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.43 (s, C), 155.55 (d, J_{C-P} = 3.0 Hz, C), 148.50 (s, C), 147.33 (s, 2C), 135.01 (d, J_{C-P} = 17.2 Hz, C), 134.35 (d, J_{C-P} = 92.9 Hz, C), 133.24 (s, CH), 131.96 (d, J_{C-P} = 10.8 Hz, 2CH), 131.71 (d, J_{C-P} = 3.1 Hz, CH), 130.96 (d, J_{C-P} = 6.1 Hz, CH), 129.61 (s, CH), 129.48 (s, 4CH), 128.46 (d, J_{C-P} = 13.1 Hz, 2CH), 125.79 (s, CH), 125.11 (d, J_{C-P} = 10.1 Hz, CH), 124.55 (s, 4CH), 123.46 (s, 2CH), 120.98 (s, CH), 120.05 (s, CH), 118.47 (d, J_{C-P} = 6.1 Hz, CH), 116.04 (d, J_{C-P} = 102.9 Hz, C), 91.70 (d, J_{C-P} = 105.3 Hz, CH). HRMS Calcd. For $C_{32}H_{24}NO_2PNa^+$ $[M + Na^+]^+$, 508.1437. Found: 508.1434.



4h

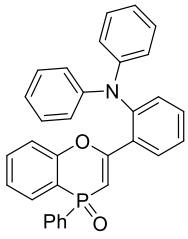
Reaction condition as general procedure for synthesis of compounds **4**: The reaction of compound **3** (396 mg, 1 mmol) and Carbazole(CZ) (199 mg, 1.1 mmol), then a flash columnchromatography (CH_2Cl_2 : ethyl acetate = 20 : 1 (v/v)) afforded Yellow solid **4h** (377 mg, 78% yield); ^{31}P NMR (162 MHz, Chloroform-*d*) δ -1.42; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.94 (m, 3H), 7.77 – 7.75 (m, 1H), 7.61 – 7.56 (m, 2H), 7.54 – 7.47 (m, 3H), 7.38 – 7.23 (m, 8H), 7.20 – 7.16 (m, 1H), 7.15 – 7.11 (m, 2H), 7.09 – 7.05 (m, 1H), 6.02 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.46 (s, C), 155.58 (d, J_{C-P} = 3.3 Hz, C), 140.71 (s, 2C), 138.50 (s, C), 135.69 (d, J_{C-P} = 10.1 Hz, C), 134.25 (d, J_{C-P} = 120.3 Hz, C), 133.53 (s, CH), 131.99 (d, J_{C-P} =5.6 Hz, 2CH), 131.96 (s, CH), 131.08 (d, J_{C-P} = 5.6 Hz, CH), 130.54 (s, CH), 129.49 (s, CH), 128.59 (d, J_{C-P} = 4.0 Hz, 2CH), 126.27 (s, 2CH), 125.43 (d, J_{C-P} = 10.6 Hz, CH), 125.06 (d, J_{C-P} = 29.6 Hz, 2CH), 123.60 (s, 2C), 120.53 (s, 2CH), 120.41 (s, 2CH), 118.57 (d, J_{C-P} = 5.3 Hz, CH), 116.05 (d, J_{C-P} = 103.3 Hz, C) ,109.62 (s, 2CH), 92.78 (d, J_{C-P} = 104.3 Hz, CH). HRMS Calcd. For $C_{32}H_{23}NO_2P^+$ $[M + H^+]^+$, 484.1461. Found: 484.1460.



4j

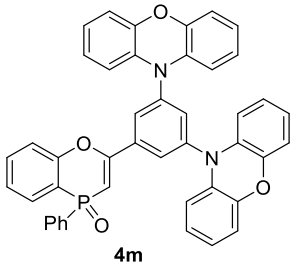
Reaction condition as general procedure for synthesis of compounds **4**: The reaction of compound **3** (396 mg, 1 mmol) and Phenothiazine(PT) (237 mg, 1.1 mmol), then a flash columnchromatography (CH_2Cl_2 : ethyl acetate = 20 : 1 (v/v)) afforded Yellow solid **4j** (160 mg, 30% yield);^{31}P NMR (162 MHz, Chloroform-*d*) δ -1.38; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.39 – 7.20 (m, 7H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.88 – 6.79 (m, 5H), 6.25 – 6.16 (m, 3H), 5.68 (d, *J* = 3.8 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.97 (s, C), 155.58 (d, J_{C-P} = 1.5 Hz, C), 143.44 (s, 2C), 138.42 (s, C), 136.72 (d, J_{C-P} = 10.0 Hz, C), 134.24 (d, J_{C-P} = 60.10 Hz, C), 133.77 (s, CH), 132.84 (s, CH), 132.02 (s, CH), 131.87 (s, CH), 131.79 (d, J_{C-P} = 5.1 Hz, 2CH), 131.42 (d, J_{C-P} = 1.5 Hz, CH), 130.56 (d, J_{C-P} = 5.6 Hz, CH), 129.39 (s, CH),

128.32 (d, $J_{C\text{-}P}$ = 13.2 Hz, 2CH), 126.99 (s, 2CH), 126.46 (s, 2CH), 124.91 (d, $J_{C\text{-}P}$ = 10.5 Hz, CH), 122.50 (s, 2CH), 119.64 (s, 2C), 118.25 (d, $J_{C\text{-}P}$ = 5.2 Hz, CH), 115.66 (d, $J_{C\text{-}P}$ = 51.51 Hz, C), 115.49 (s, 2CH), 96.28 (d, $J_{C\text{-}P}$ = 101.6 Hz, CH). HRMS Calcd. For $C_{32}H_{23}NO_2PS^+$ $[M + H^+]^+$, 516.1182. Found: 516.1181.



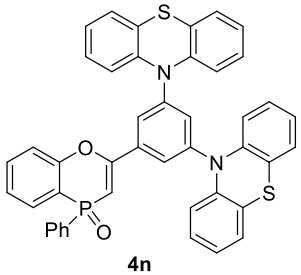
4k

Reaction condition as general procedure for synthesis of compounds **4**: The reaction of compound **3** (396 mg, 1 mmol) and Diphenylamine(DPA) (201 mg, 1.1 mmol), then a flash columnchromatography (CH_2Cl_2 : ethyl acetate = 20 : 1 (v/v)) afforded White solid **4k** (184 mg, 38% yield); ^{31}P NMR (162 MHz, Chloroform-*d*) δ -1.30; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.49 – 7.37 (m, 4H), 7.36 – 7.29 (m, 3H), 7.24 – 7.10 (m, 8H), 6.98 – 6.93 (m, 7H), 5.63 (d, *J* = 3.9 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.89 (s, C), 155.74 (d, $J_{C\text{-}P}$ = 3.3 Hz, C), 147.26 (s, 2C), 145.32 (s, C), 133.83 (d, $J_{C\text{-}P}$ = 65.7 Hz, C), 133.28 (s, CH), 132.83 (s, C), 132.21 (d, $J_{C\text{-}P}$ = 11.2 Hz, 2CH), 131.86 (d, $J_{C\text{-}P}$ = 20.5 Hz, 2CH), 131.43 (d, $J_{C\text{-}P}$ = 2.9 Hz, CH), 130.77 (d, $J_{C\text{-}P}$ = 5.8 Hz, CH), 130.45 (s, CH), 129.02 (s, 4CH), 128.16 (d, $J_{C\text{-}P}$ = 13.1 Hz, 2CH), 125.72 (s, CH), 124.60 (d, $J_{C\text{-}P}$ = 10.5 Hz, CH), 122.47 (s, 4CH), 121.97 (s, 2CH), 118.77 (d, $J_{C\text{-}P}$ = 5.4 Hz, CH), 115.74 (d, $J_{C\text{-}P}$ = 102.9 Hz, C), 94.93 (d, $J_{C\text{-}P}$ = 102.7 Hz, CH). HRMS Calcd. For $C_{32}H_{24}NO_2PNa^+$ $[M + Na^+]^+$, 508.1437. Found: 508.1432.



4m

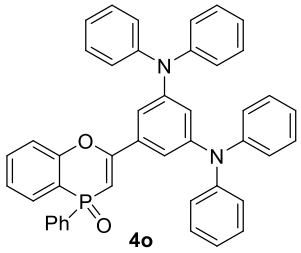
Reaction condition as general procedure for synthesis of compounds **4**: The reaction of compound **3** (476 mg, 1 mmol) and Phenoxazine(PO) (438 mg, 2.2 mmol), then a flash columnchromatography (CH_2Cl_2 : ethyl acetate = 20 : 1 (v/v)) afforded Yellow solid **4m** (551 mg, 81% yield); ^{31}P NMR (162 MHz, Chloroform-*d*) δ -1.84; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 2.0 Hz, 2H), 7.75 – 7.69 (m, 2H), 7.67 – 7.57 (m, 3H), 7.54 – 7.42 (m, 4H), 7.28 (t, *J* = 8 Hz, 1H), 6.75 – 6.66 (m, 12H), 6.18 (s, 1H), 6.05 – 6.03 (m, 4H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.77 (s, C), 155.44 (d, $J_{C\text{-}P}$ = 3.3 Hz, C), 144.01 (s, 4C), 142.68 (s, 2C), 139.70 (d, $J_{C\text{-}P}$ = 10.1 Hz, C), 136.46 (s, CH), 133.82 (d, $J_{C\text{-}P}$ = 60.1 Hz, C), 133.64 (s, CH), 133.59 (s, 4C), 132.05 (s, CH), 131.97 (d, $J_{C\text{-}P}$ = 11.0 Hz, 2CH), 131.11 (d, $J_{C\text{-}P}$ = 5.6 Hz, CH), 129.03 (s, 2CH), 128.61 (d, $J_{C\text{-}P}$ = 13.3 Hz, 2CH), 125.60 (d, $J_{C\text{-}P}$ = 10.6 Hz, CH), 123.48 (s, 4CH), 122.18 (s, 4CH), 118.60 (d, $J_{C\text{-}P}$ = 5.4 Hz, CH), 115.97 (s, 4CH), 115.88 (d, $J_{C\text{-}P}$ = 52.0 Hz, C), 113.14 (s, 4CH), 93.77 (d, $J_{C\text{-}P}$ = 103.1 Hz, CH). HRMS Calcd. For $C_{44}H_{29}N_2O_4PNa^+$ $[M + Na^+]^+$, 703.1757. Found: 703.1760.



4n

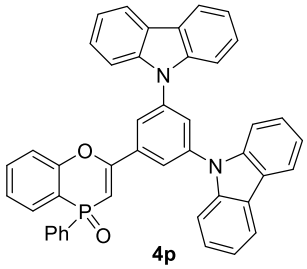
Reaction condition as general procedure for synthesis of compounds **4**: The reaction of compound **3** (476 mg, 1 mmol) and Phenothiazine(PT) (474 mg, 2.2 mmol), then a flash columnchromatography

(CH_2Cl_2 : ethyl acetate = 20 : 1 (v/v)) afforded Red solid **4n** (527 mg, 74% yield); ^{31}P NMR (162 MHz, Chloroform-*d*) δ -1.39; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 2.1 Hz, 2H), 7.72 (dd, *J* = 13.5, 7.3 Hz, 2H), 7.65 (dd, *J* = 12.8, 7.7 Hz, 1H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.36 – 7.33 (m, 2H), 7.28 (t, *J* = 0.51 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 4H), 7.06 (t, *J* = 7.8 Hz, 4H), 6.97 (t, *J* = 7.5 Hz, 4H), 6.65 (d, *J* = 8.1 Hz, 4H), 6.08 (s, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.75 (s, C), 155.44 (d, J_{C-P} = 3.2 Hz, C), 145.08 (s, 2C), 143.07 (s, 4C), 137.76 (d, J_{C-P} = 10.2 Hz, C), 134.08 (d, J_{C-P} = 59.1 Hz, C), 133.49 (s, CH), 131.97 (d, J_{C-P} = 5.6 Hz, 2CH), 131.91 (s, CH), 131.04 (d, J_{C-P} = 5.4 Hz, CH), 128.55 (d, J_{C-P} = 13.2 Hz, 2CH), 127.63 (s, 4CH), 127.24 (s, 4CH), 126.95 (s, CH), 125.41 (d, J_{C-P} = 10.6 Hz, CH), 124.60 (s, 4C), 123.98 (s, 4CH), 121.87 (s, 2CH), 119.14 (s, 4CH), 118.51 (d, J_{C-P} = 5.2 Hz, CH), 115.95 (d, J_{C-P} = 103.2 Hz, C), 92.95 (d, J_{C-P} = 104.1 Hz, CH). HRMS Calcd. For $C_{44}H_{30}N_2O_2PS_2^+$ $[M + H^+]^+$, 713.1481. Found: 713.1480.



4o

Reaction condition as general procedure for synthesis of compounds **4**: The reaction of compound **3** (476 mg, 1 mmol) and Diphenylamine(DPA) (402 mg, 2.2 mmol), then a flash columnchromatography (CH_2Cl_2 : ethyl acetate = 20 : 1 (v/v)) afforded White solid **4o** (522 mg, 80% yield); ^{31}P NMR (162 MHz, Chloroform-*d*) δ -1.14; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.61 (m, 2H), 7.58 – 7.53 (m, 1H), 7.49 – 7.39 (m, 4H), 7.23 – 7.19 (m, 10H), 7.16 – 7.11 (m, 1H), 7.07 – 7.05 (m, 9H), 6.98 (t, *J* = 7.2 Hz, 4H), 6.89 (d, *J* = 2.2 Hz, 1H), 5.74 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.39 (s, C), 155.43 (d, J_{C-P} = 3.4 Hz, C), 149.07 (s, 2C), 147.06 (s, 4C), 135.71 (d, J_{C-P} = 10.3 Hz, C), 134.43 (d, J_{C-P} = 120.0 Hz, C), 133.19 (s, CH), 131.96 (d, J_{C-P} = 10.8 Hz, 2CH), 131.70 (d, J_{C-P} = 2.9 Hz, CH), 130.90 (d, J_{C-P} = 5.5 Hz, CH), 129.35 (s, 8CH), 128.43 (d, J_{C-P} = 13.1 Hz, 2CH), 125.08 (d, J_{C-P} = 10.5 Hz, CH), 124.39 (s, 8CH), 123.35 (s, 4CH), 120.67 (s, CH), 118.49 (d, J_{C-P} = 5.3 Hz, CH), 115.91 (d, J_{C-P} = 103.0 Hz, C), 115.06 (s, 2CH), 91.67 (d, J_{C-P} = 104.9 Hz, CH). HRMS Calcd. For $C_{44}H_{34}N_2O_2P^+$ $[M + H^+]^+$, 653.2352. Found: 653.2350.



4p

Reaction condition as general procedure for synthesis of compounds **4**: The reaction of compound **3** (476 mg, 1 mmol) and Carbazole(CZ) (398 mg, 2.2 mmol), then a flash columnchromatography (CH_2Cl_2 : ethyl acetate = 20 : 1 (v/v)) afforded Yellow solid **4p** (521 mg, 77% yield); ^{31}P NMR (162 MHz, Chloroform-*d*) δ -1.49; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 – 8.17 (m, 6H), 7.98 (d, *J* = 2.0 Hz, 1H), 7.79 – 7.67 (m, 4H), 7.62 – 7.57 (m, 5H), 7.52 – 7.47 (m, 6H), 7.41 – 7.29 (m, 6H), 6.28 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.52 (s, C), 155.49 (d, J_{C-P} = 3.3 Hz, C), 140.42 (s, 4C), 140.16 (s, 2C), 137.33 (d, J_{C-P} = 10.2 Hz, C), 133.87 (d, J_{C-P} = 60.60 Hz, C), 133.66 (s, CH), 132.04 (d, J_{C-P} = 4.0 Hz, 2CH), 131.91 (s, CH), 131.12 (d, J_{C-P} = 5.5 Hz, CH), 128.64 (d, J_{C-P} = 13.3 Hz, 2CH), 127.31 (s, CH), 126.46 (s, 4C), 125.61 (d, J_{C-P} = 10.6 Hz, CH), 123.82 (s, 4C), 123.37 (s, 2CH), 120.78 (s, 4C), 120.65 (s, 4C), 118.58 (d, J_{C-P} = 5.5 Hz, CH), 115.91 (d, J_{C-P} = 103.6 Hz, C), 109.54 (s, 4C), 93.74 (d, J_{C-P} = 103.5 Hz, CH). HRMS Calcd. For $C_{44}H_{30}N_2O_2P^+$ $[M + H^+]^+$, 649.2039. Found: 649.2040.

[1] S. Xu, H. Huang, Z. Yan, Q. Xiao, *Org. Lett.* **2019**, *21*, 10018-10022.

5. The photoelectric properties.

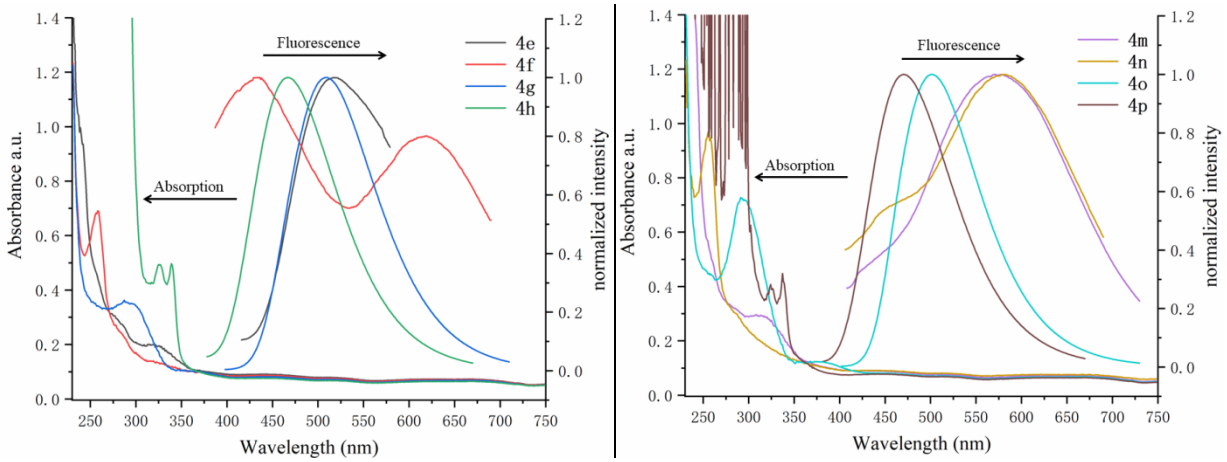


Figure s1. UV−vis absorption spectra and fluorescence spectra of the amino-substituted phenyl-phosphachromones **4e – h** and **4m - p** in CH_2Cl_2 (1×10^{-5} M) at rt.

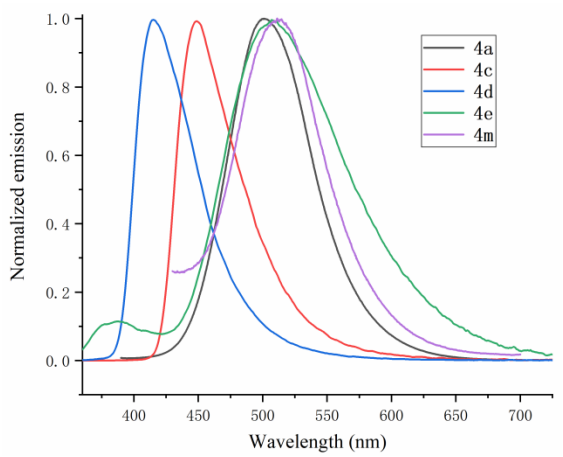


Figure s2. Fluorescence spectra of compound **4c - 4e** in film (The sample film was a host-guest system composed of **4e** (mass fraction 0.3%) as the guest and β-estradiol as the host matrix on a glass substrate).

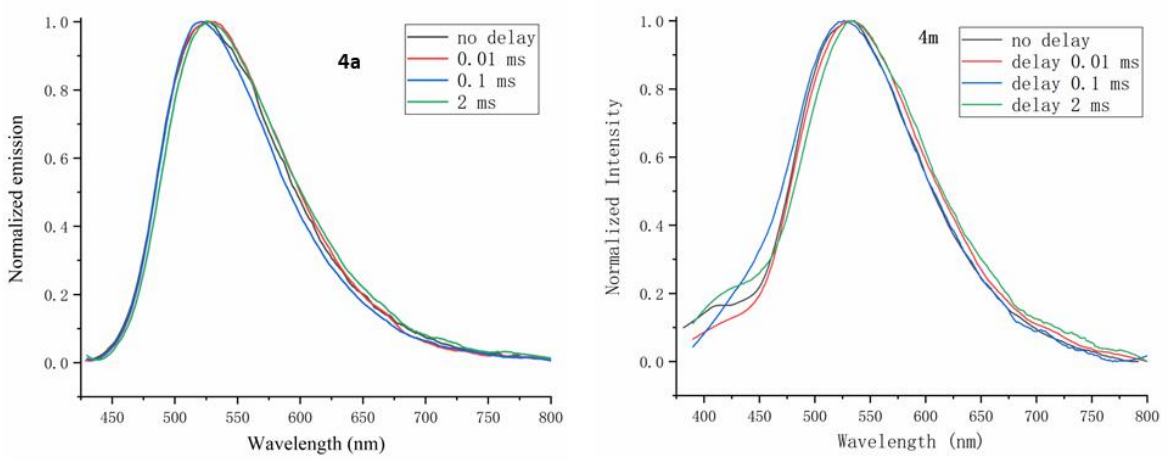


Figure s3. Prompt and delayed emission spectra **4a (**left**)** and **4m (**right**)** in the film (The sample film was a host-guest system composed of **4e** (mass fraction 0.3%) as the guest and β-estradiol as the host matrix on a glass substrate).

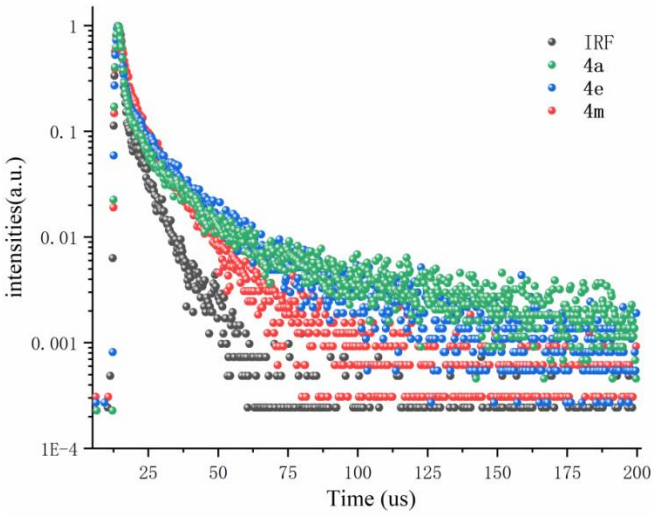


Figure s4. Fluorescence lifetime of **4a**, **4e**, and **4m** in the film at room temperature. prompt fluorescence (**4a**: τ_1 = 3.6 ns, τ_2 = 21.0 ns; **4e**: τ_1 = 5.7 ns, τ_2 = 48 ns; **4m**: τ_1 = 2.7 ns, τ_2 = 26.1 ns, lifetime) and delayed fluorescence (**4a**: τ_1 = 1.5 μs, τ_2 = 17.1 μs; **4e**: τ_1 = 1.5 μs, τ_2 = 8.7 μs, τ_3 = 25.7 μs; **4m**: τ_1 = 1.1 μs, τ_2 = 17.9 μs, lifetime)

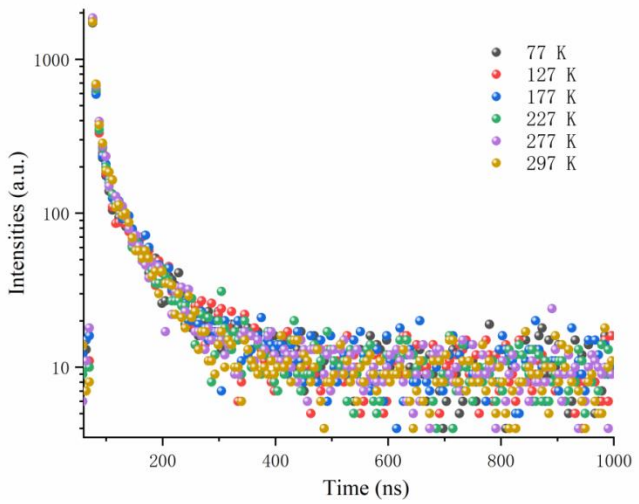


Figure s5. Temperature-dependent luminescence prompt decayed curves of 4e in the film at 525 nm.

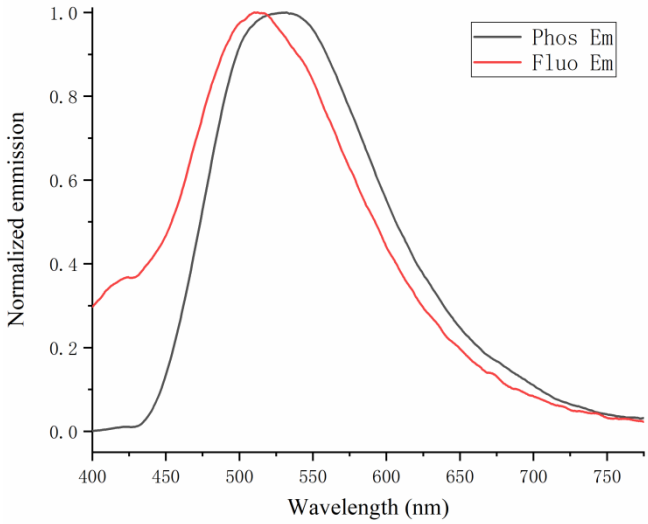


Figure s6. Phosphorescence spectra at 77 K and fluorescence spectra at room temperture**.**

6. The calculation data.

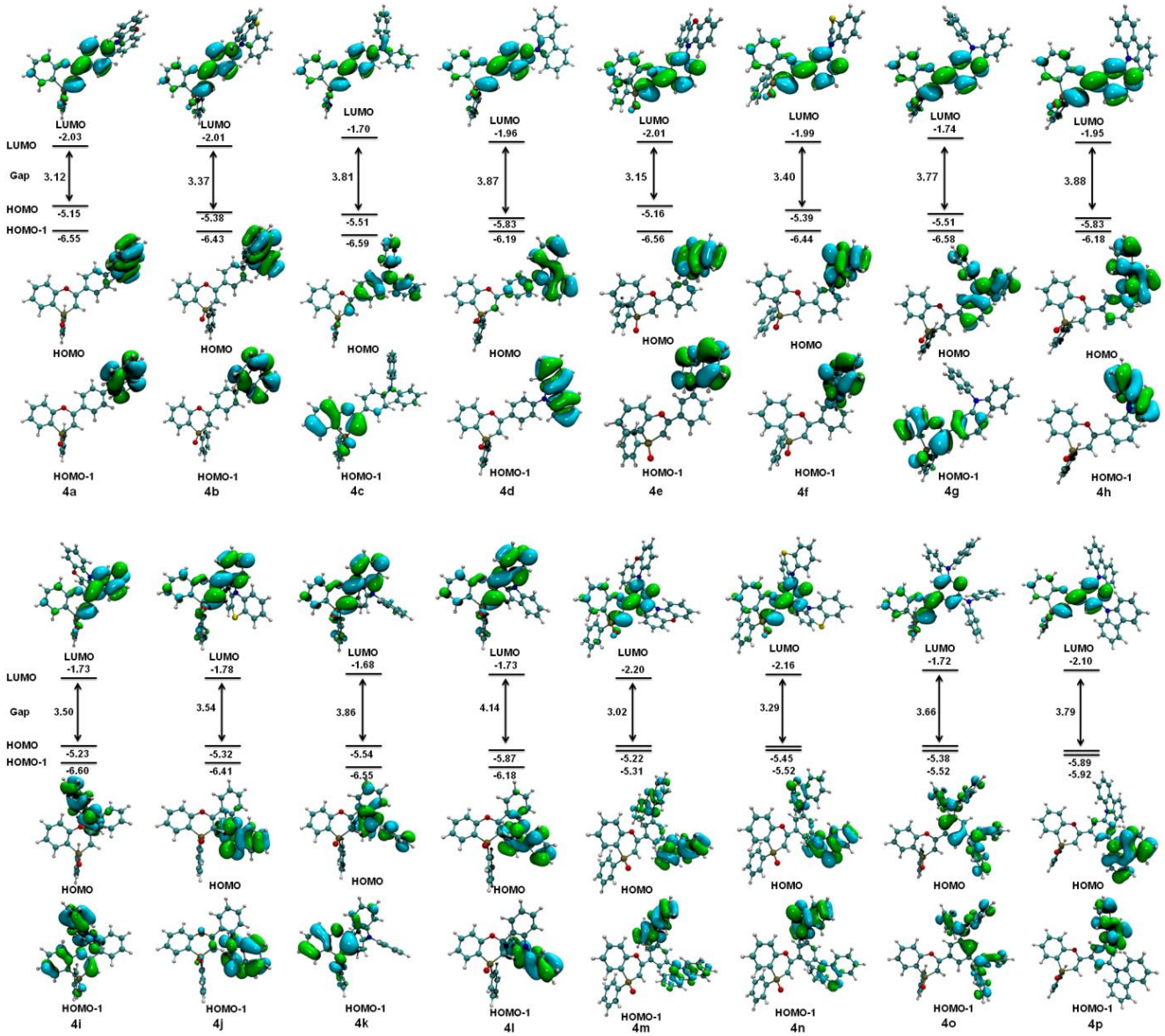


Figure s7. Frontier orbital distributions and LUMO/HOMO gaps of the compounds **4a** - **4n** based on DFT/B3LYP/6-311G+(d, p); orbital energies in eV.

Table s1. The energy difference ($\triangle E_{ST}$) between the first singlet excited state (S1) and first triplet excited state (T1) gotten by TD-DFT calculation at b3lyp/6-311G+(d,p) level.[a]

compd	**4a**	**4b**	**4c**	**4d**	**4e**	**4f**	**4g**	**4h**	**4i**	**4j**	**4k**	**4l**	**4m**	**4n**	**4o**	**4p**
$\triangle E_{ST}$ (eV)	0.01	0.02	0.74	0.48	0.04	0.06	0.44	0.33	0.08	0.06	0.32	0.31	0.03	0.05	0.34	0.30

[a] the calculation of excited states based on the optimized structures of their ground states.

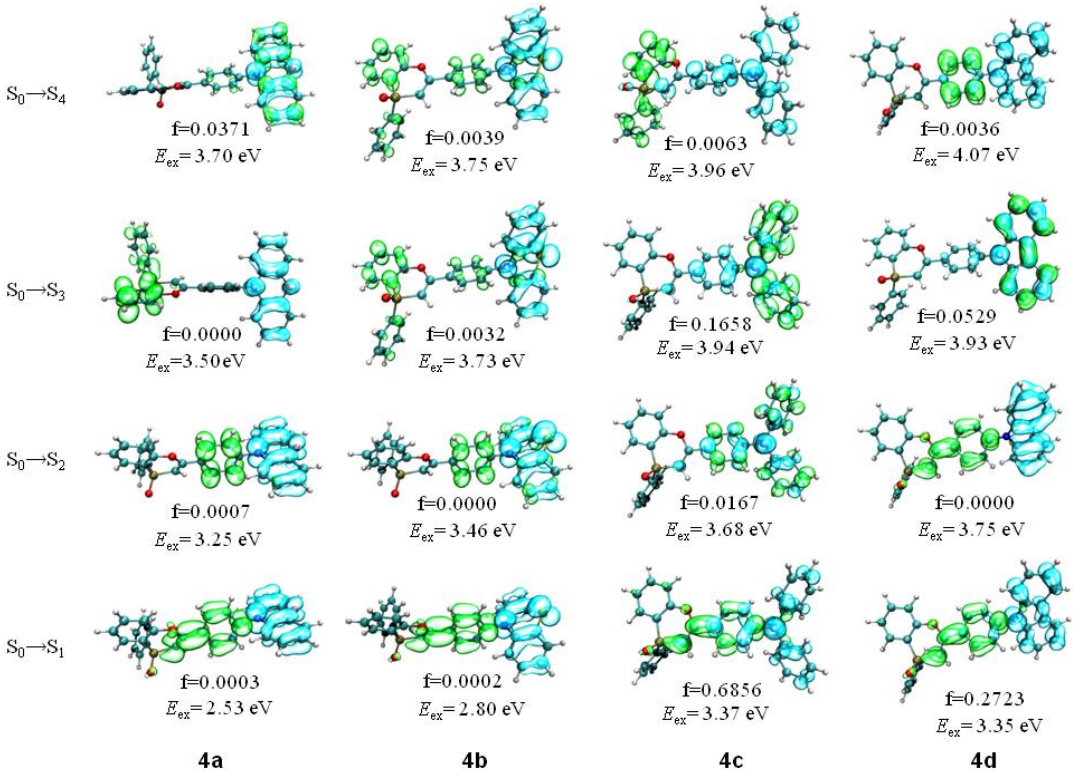


Figure s8. Electrons and holes of the vertical excitation process for **4a**–**4d** based on DFT/B3LYP/6-311G+(d, p); electrons in green and holes in blue transparent isosurface; energies in eV.

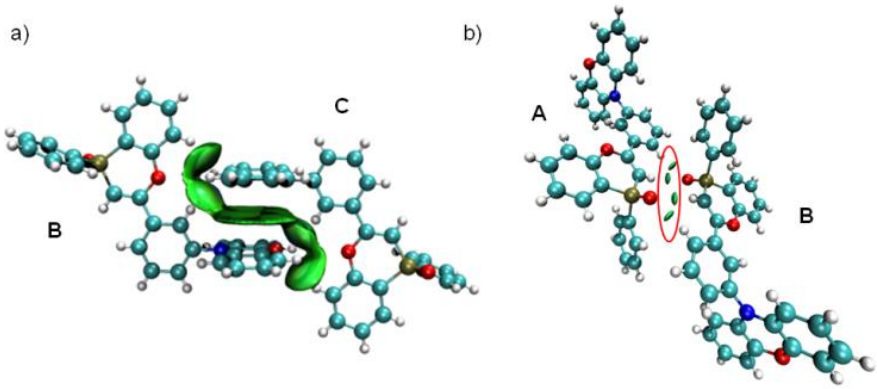
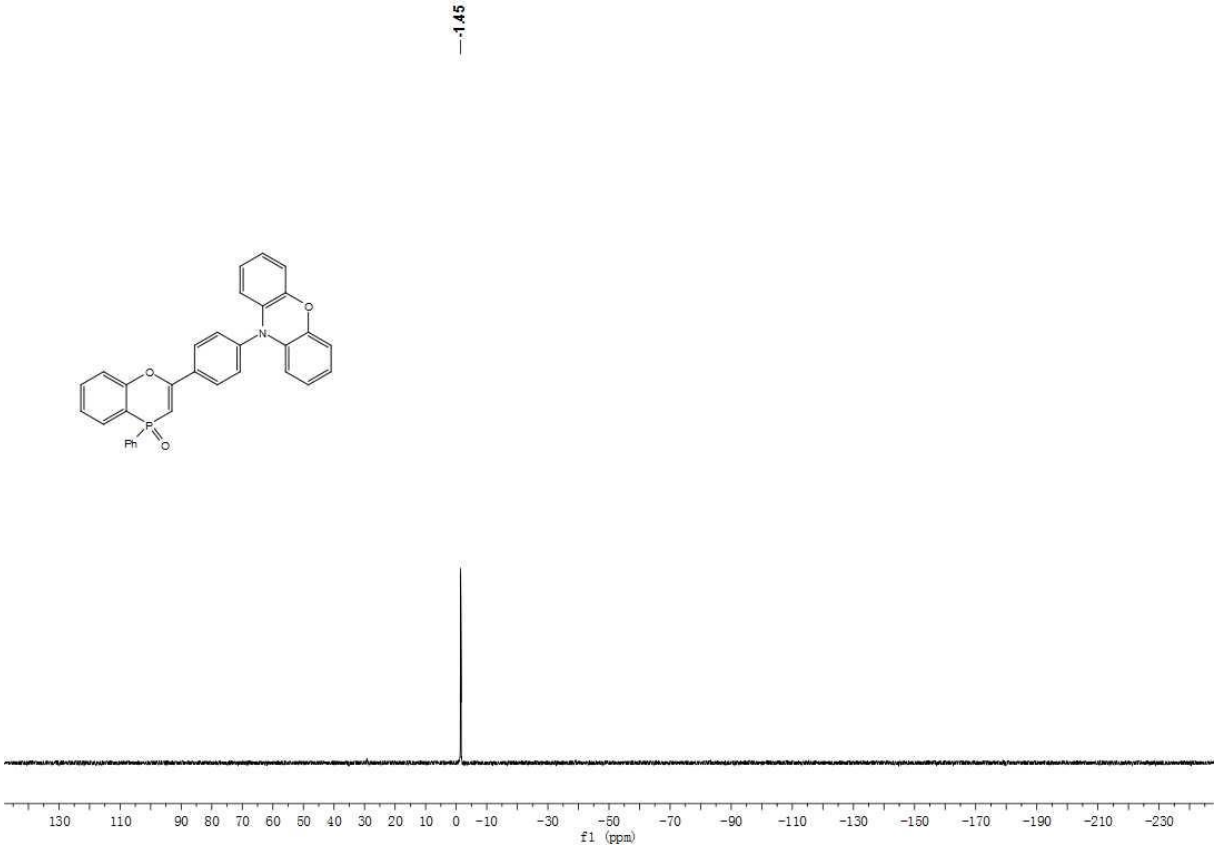
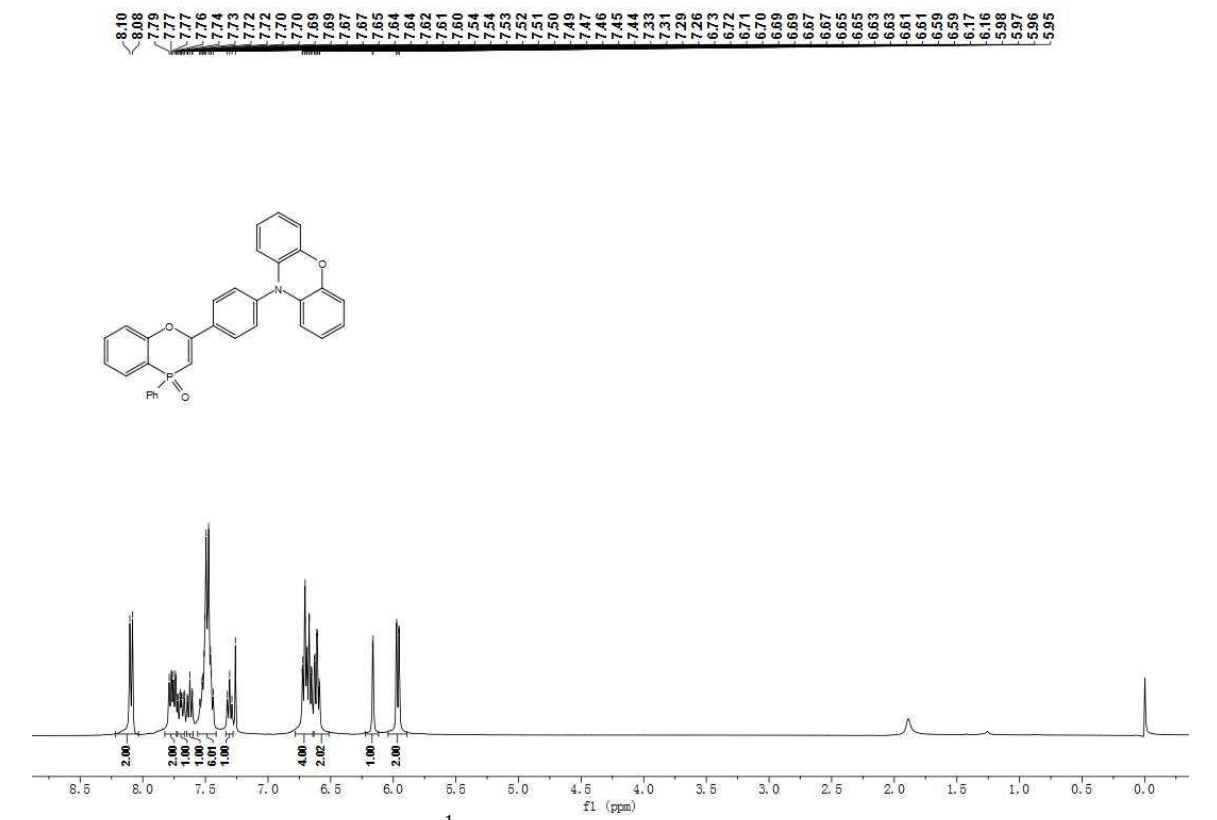


Figure s9. (a) Visualization of intermolecular π-π stacking interaction by IGM (isovalue = 0.002); (b) Visualization of intermolecular H-bond interaction by IGM (isovalue = 0.014).

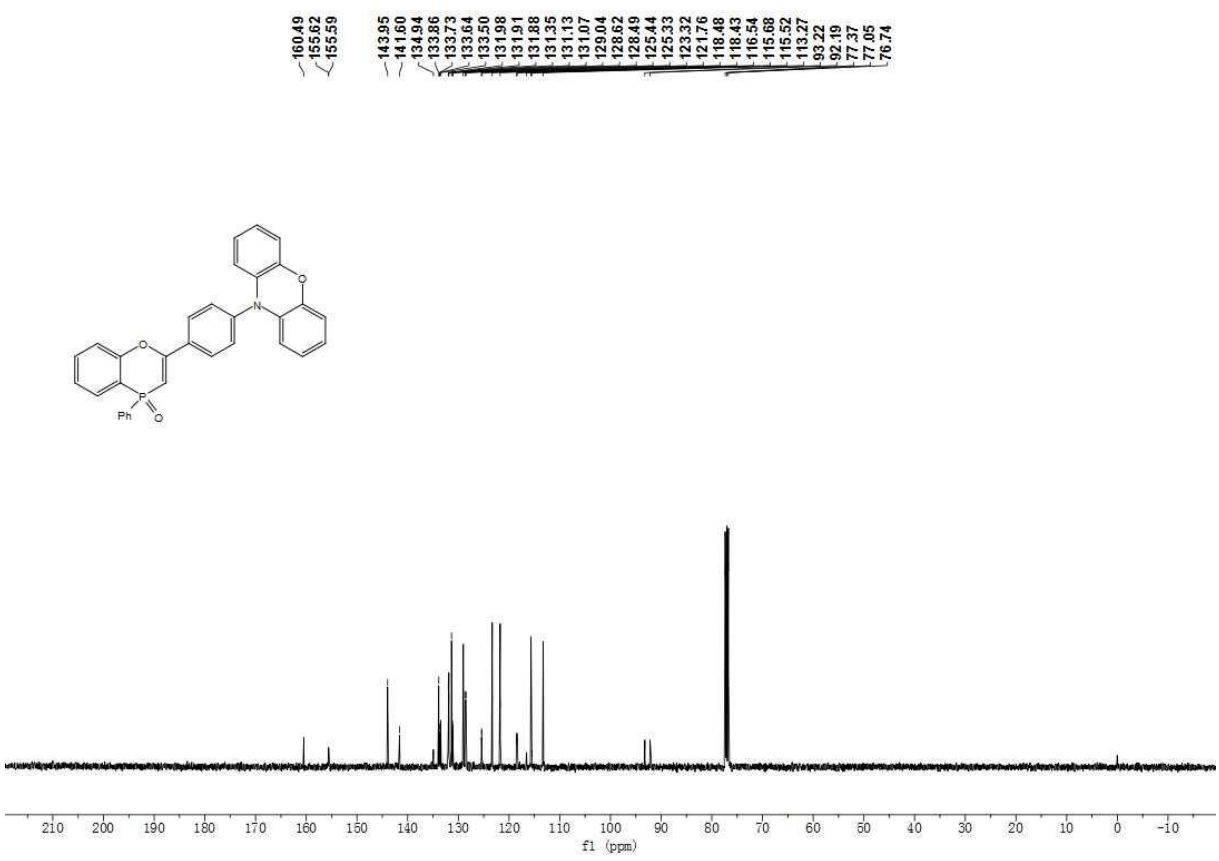
7. Copies of ^{31}P NMR, ^{1}H NMR, ^{13}C NMR Spectra.



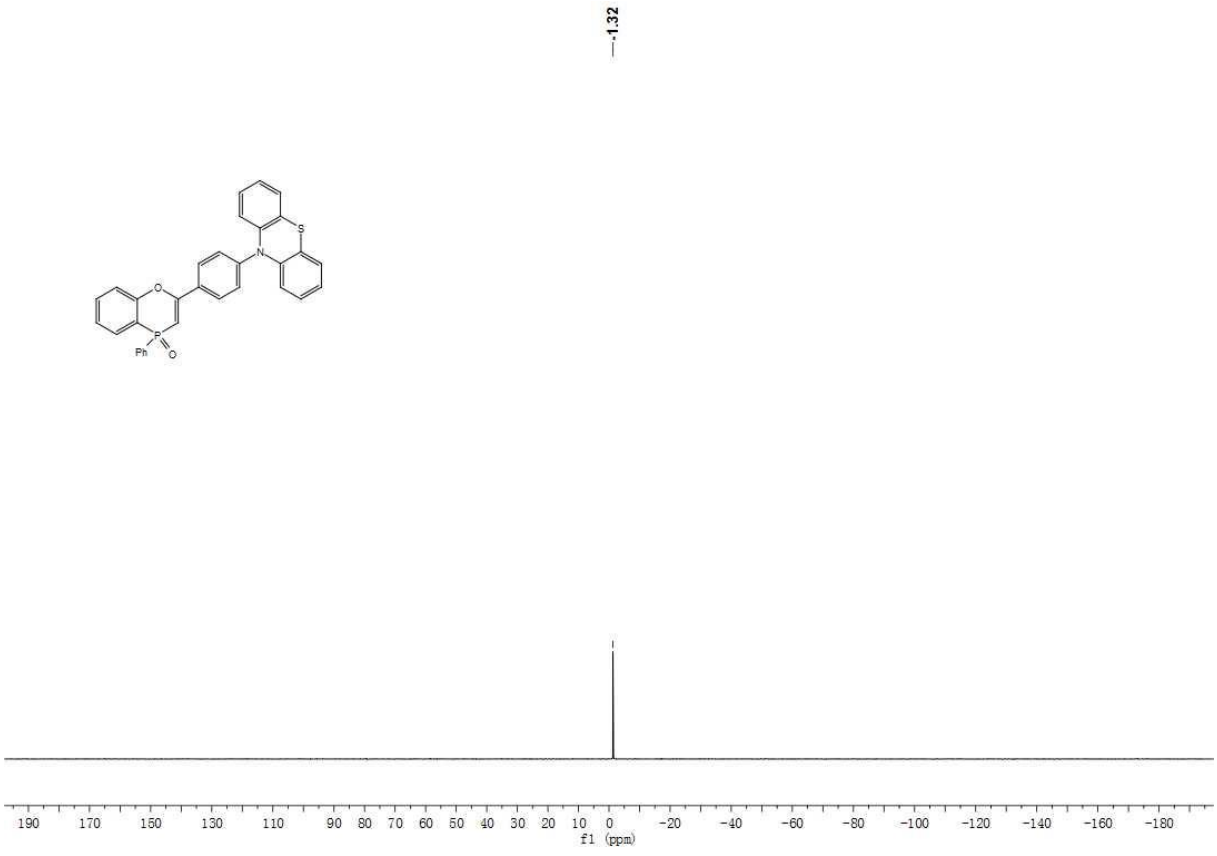
^{31}P NMR ($CDCl_3$-*d*) of 4**a**



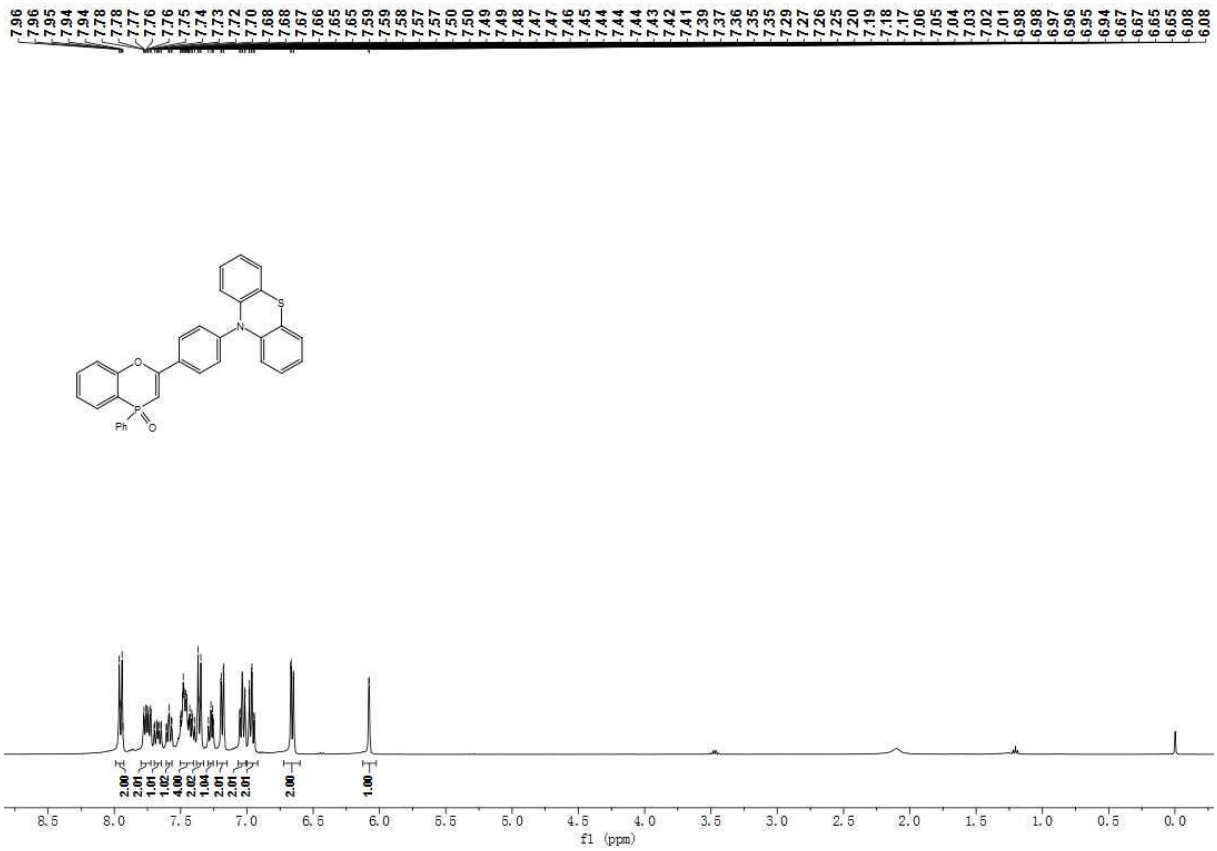
^{1}H NMR ($CDCl_3$-*d*) of 4**a**



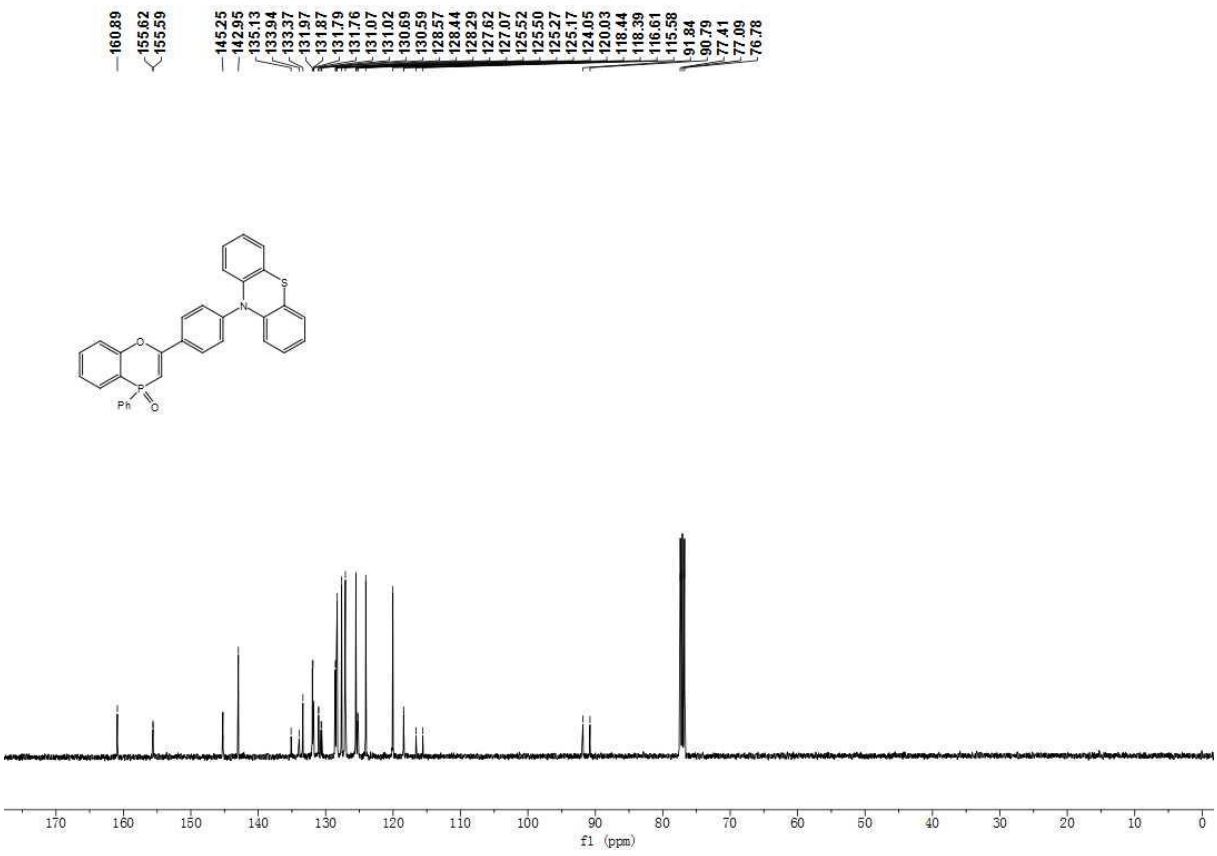
^{13}C NMR ($CDCl_3$-*d*) of 4**a**



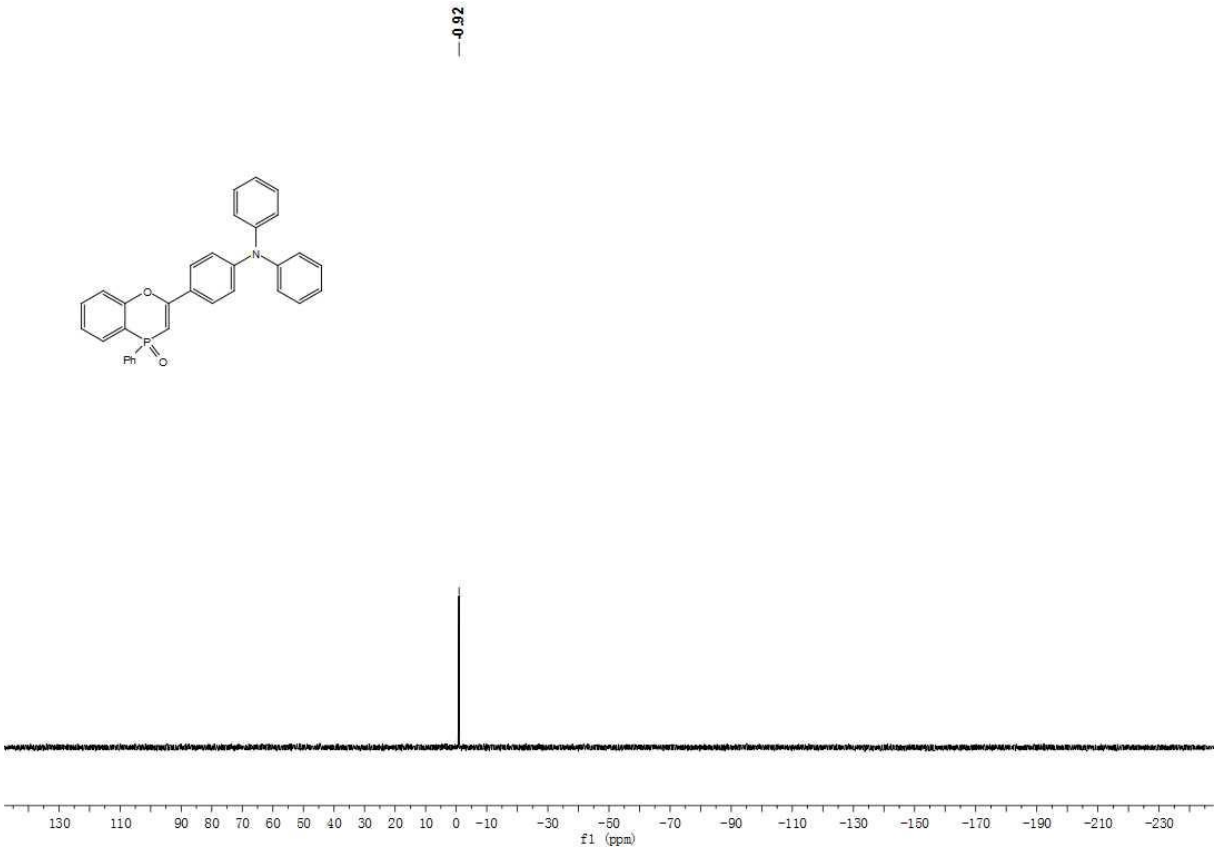
^{31}P NMR ($CDCl_3$-*d*) of 4**b**



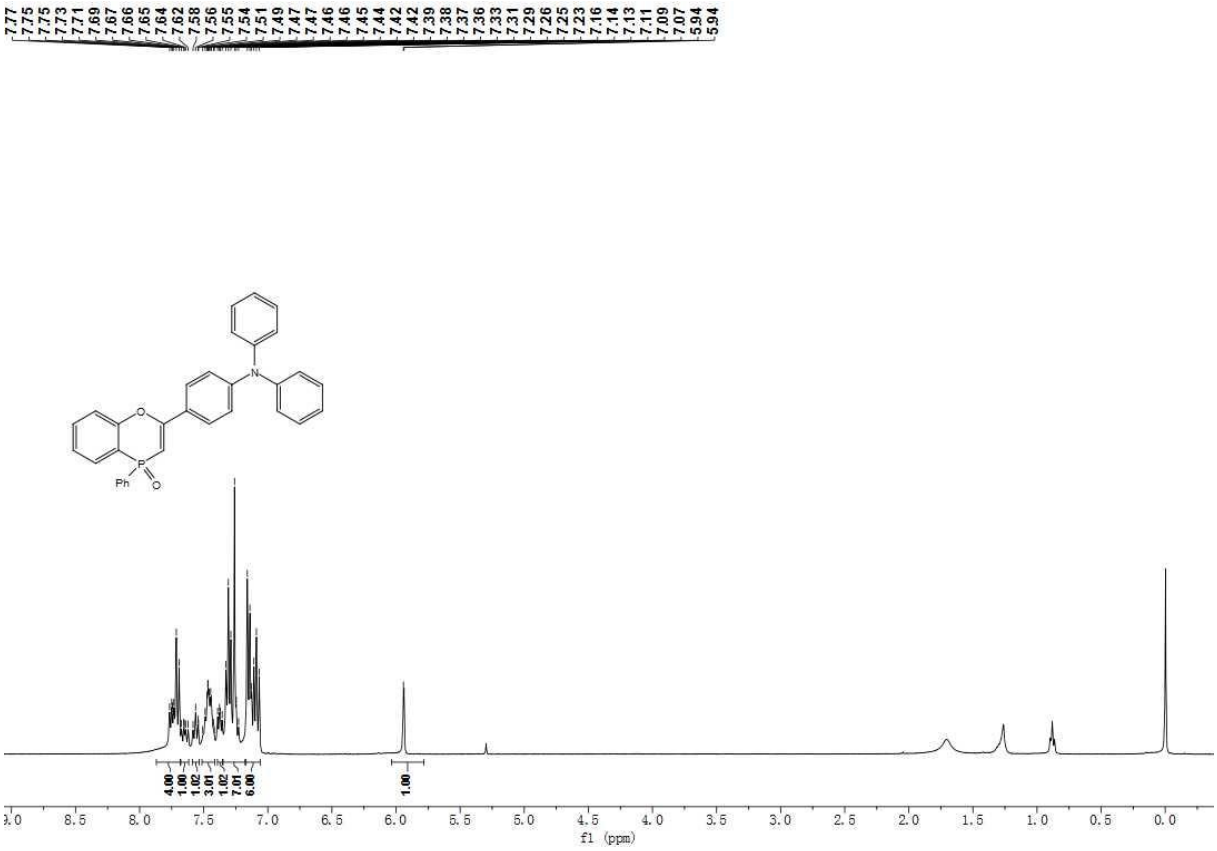
^{1}H NMR ($CDCl_3$-*d*) of 4**b**



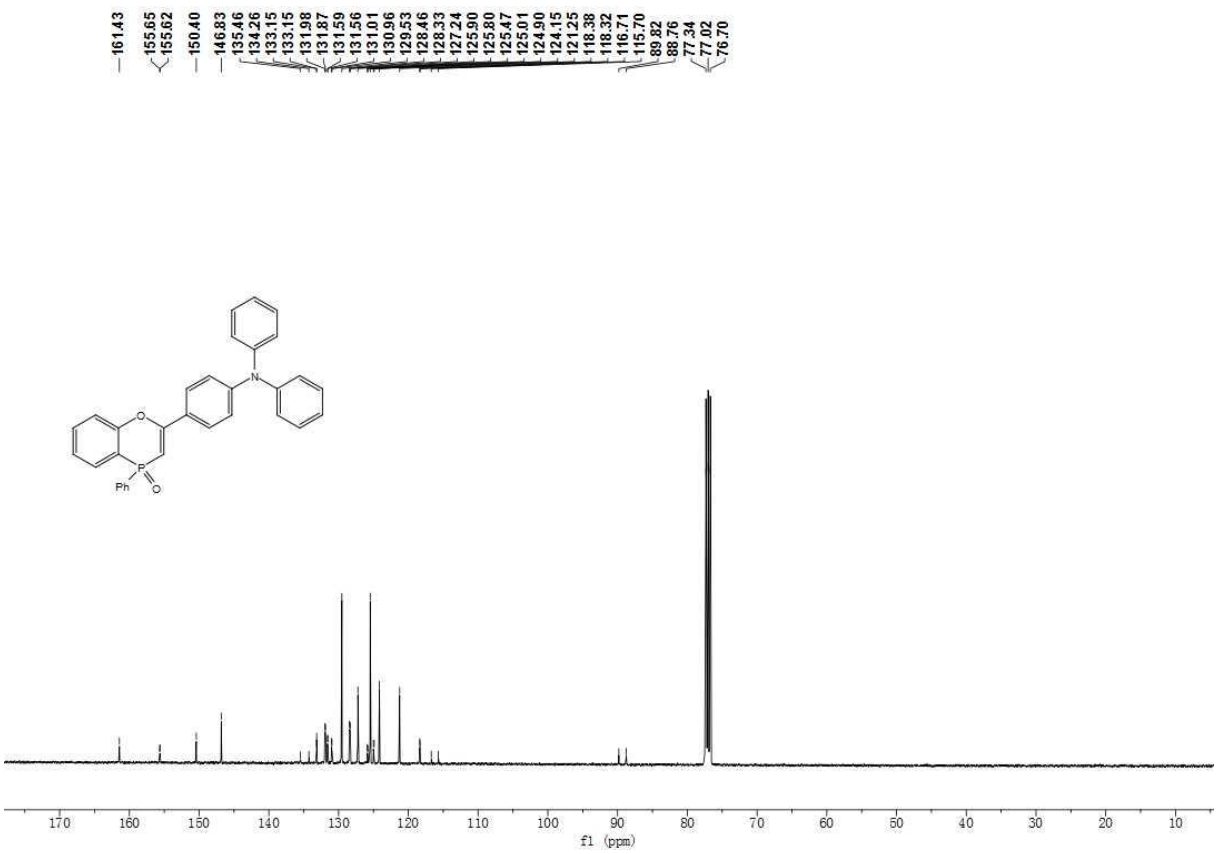
^{13}C NMR ($CDCl_3$-*d*) of 4**b**



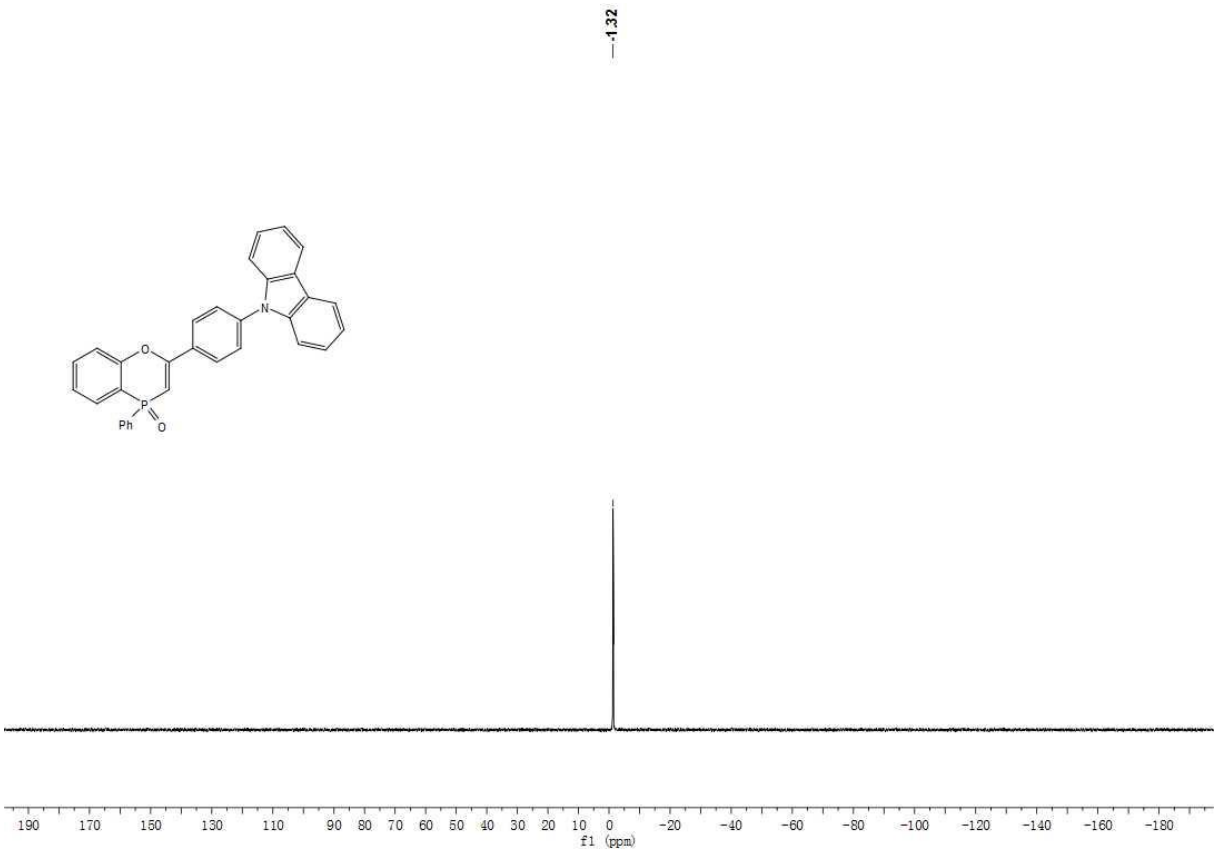
^{31}P NMR ($CDCl_3$-*d*) of 4**c**



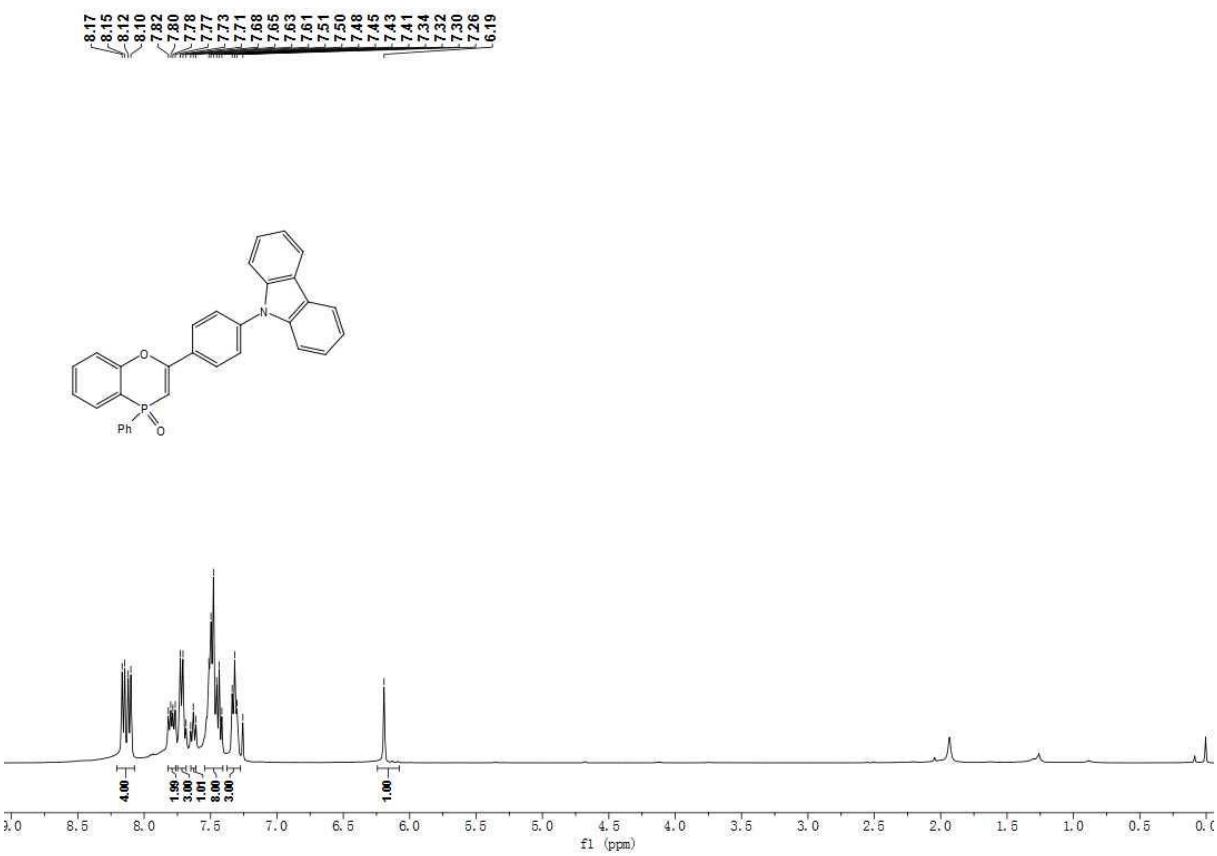
^{1}H NMR ($CDCl_3$-*d*) of 4**c**



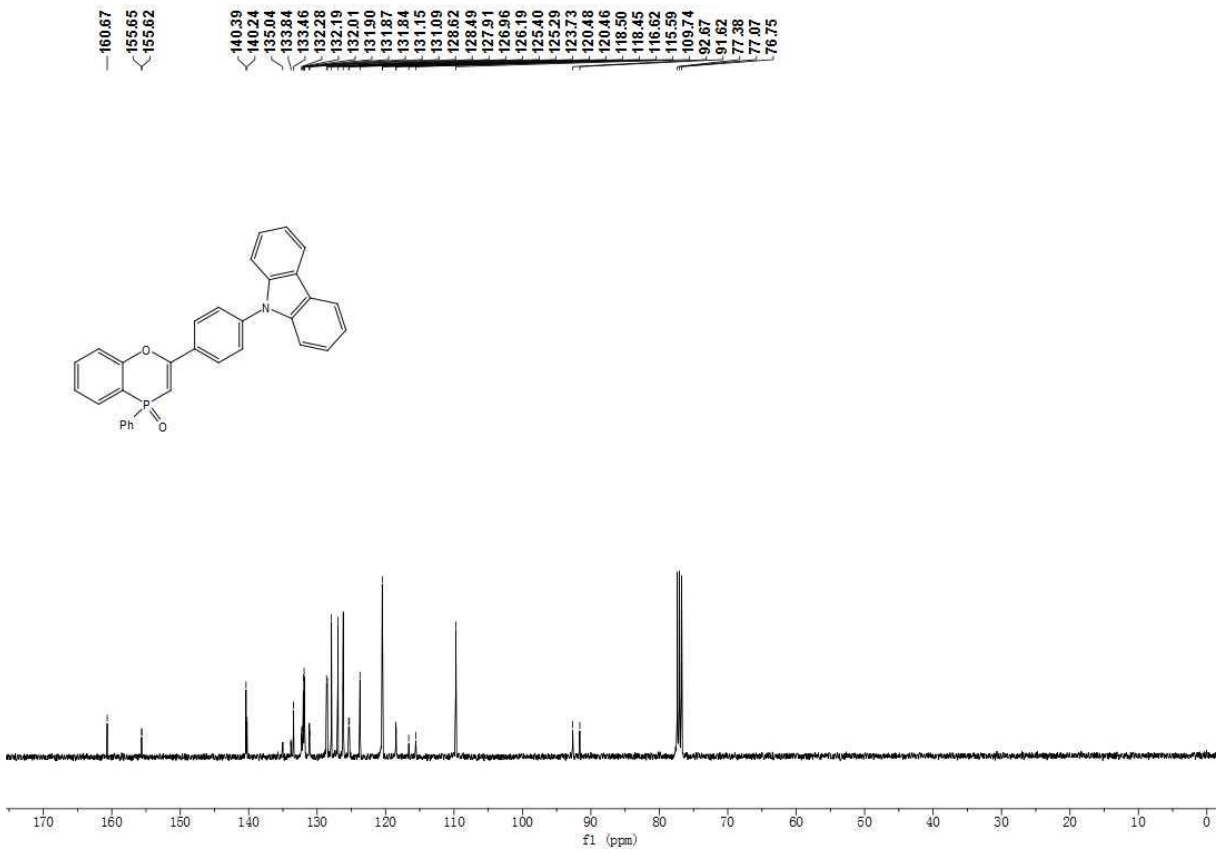
^{13}C NMR ($CDCl_3$-*d*) of 4**c**



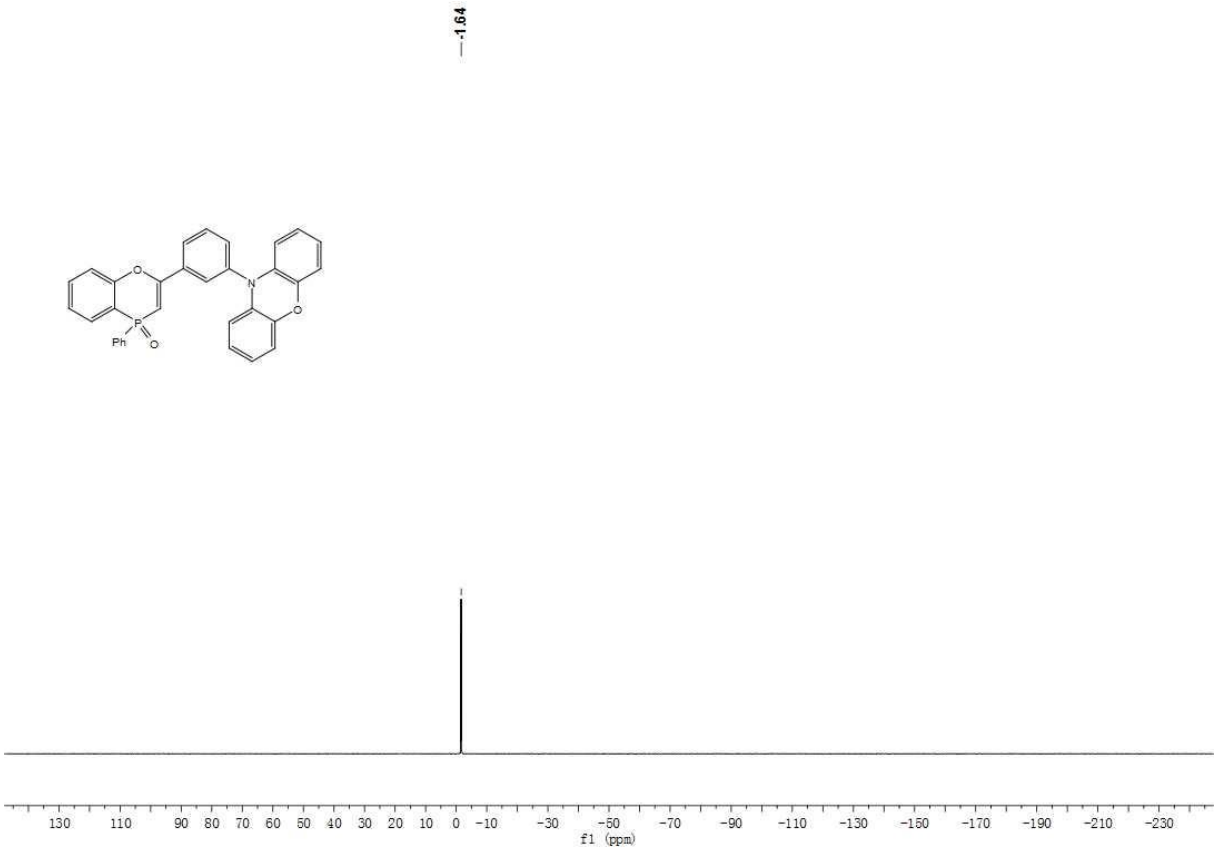
^{31}P NMR ($CDCl_3$-*d*) of 4**d**



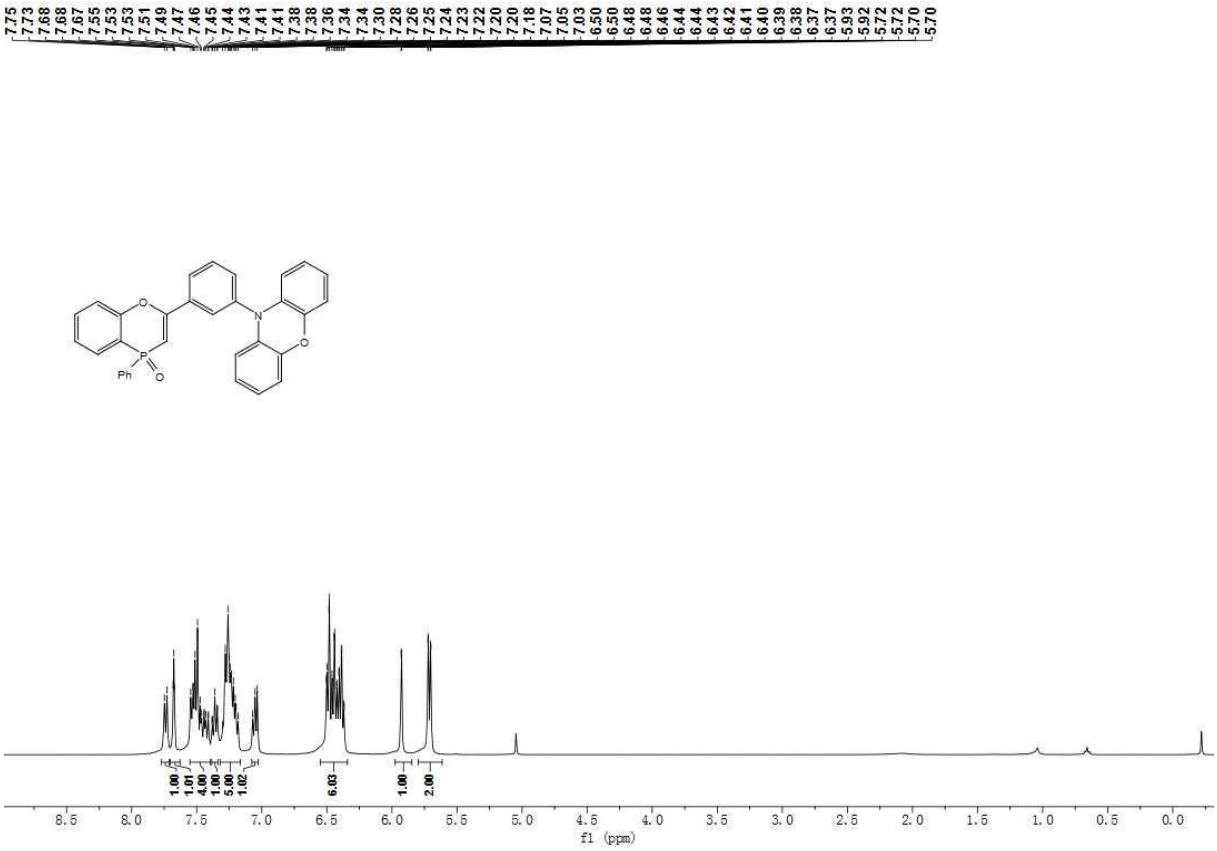
^{1}H NMR ($CDCl_3$-*d*) of 4**d**



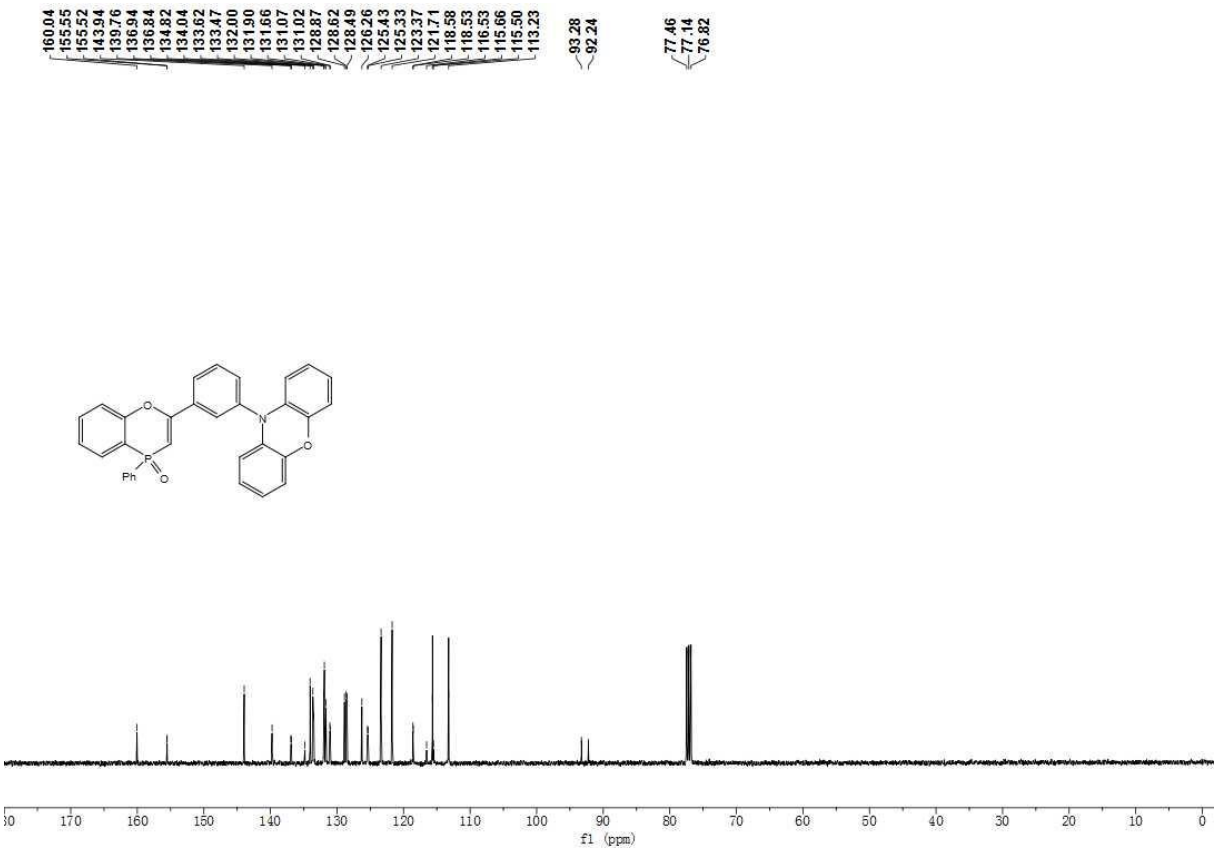
^{13}C NMR ($CDCl_3$-*d*) of 4**d**



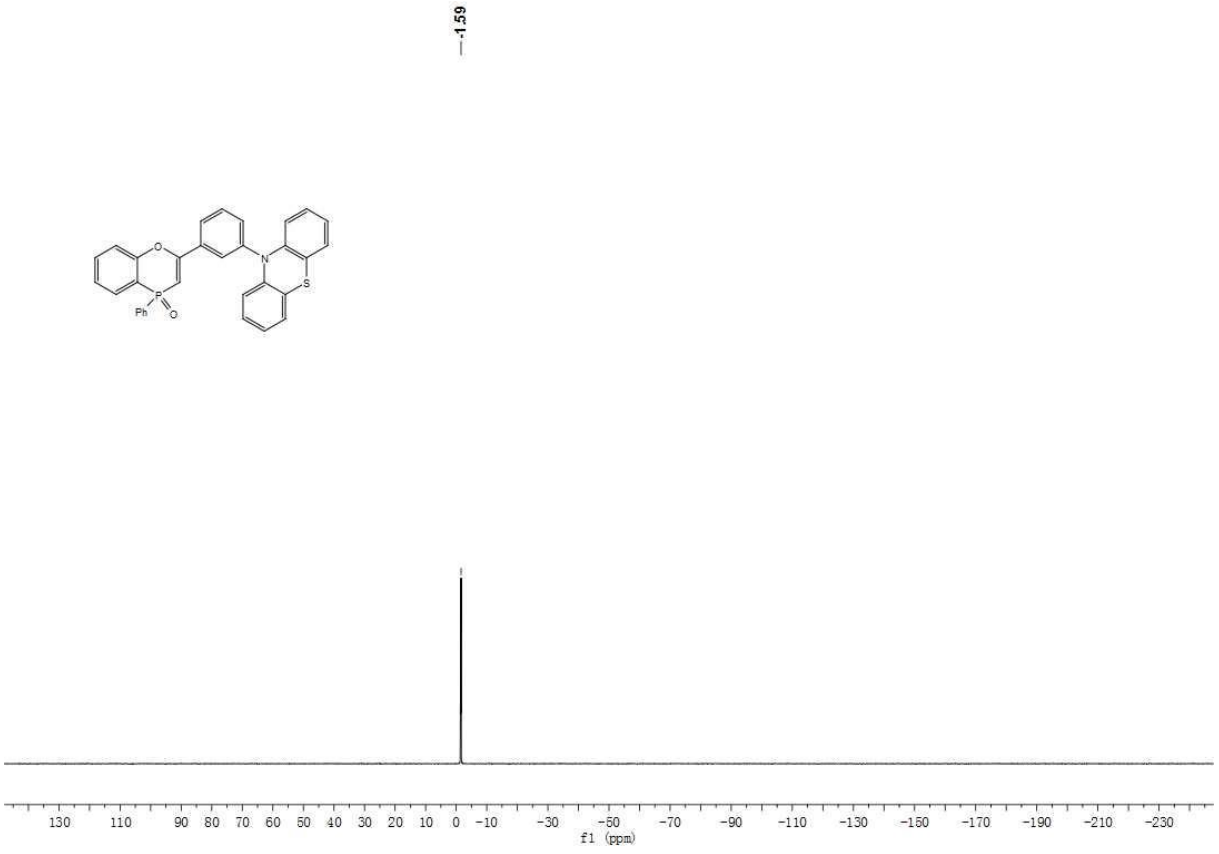
^{31}P NMR ($CDCl_3$-*d*) of 4**e**



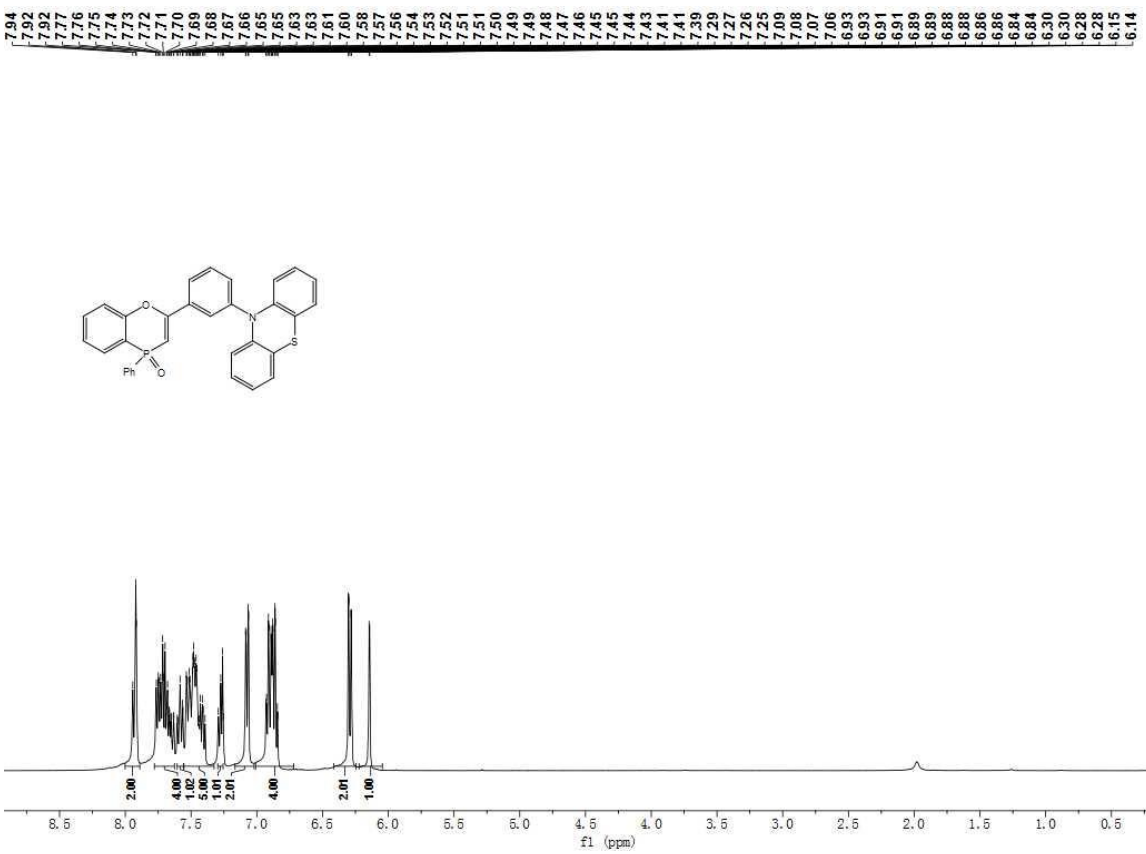
^{1}H NMR ($CDCl_3$-*d*) of 4**e**



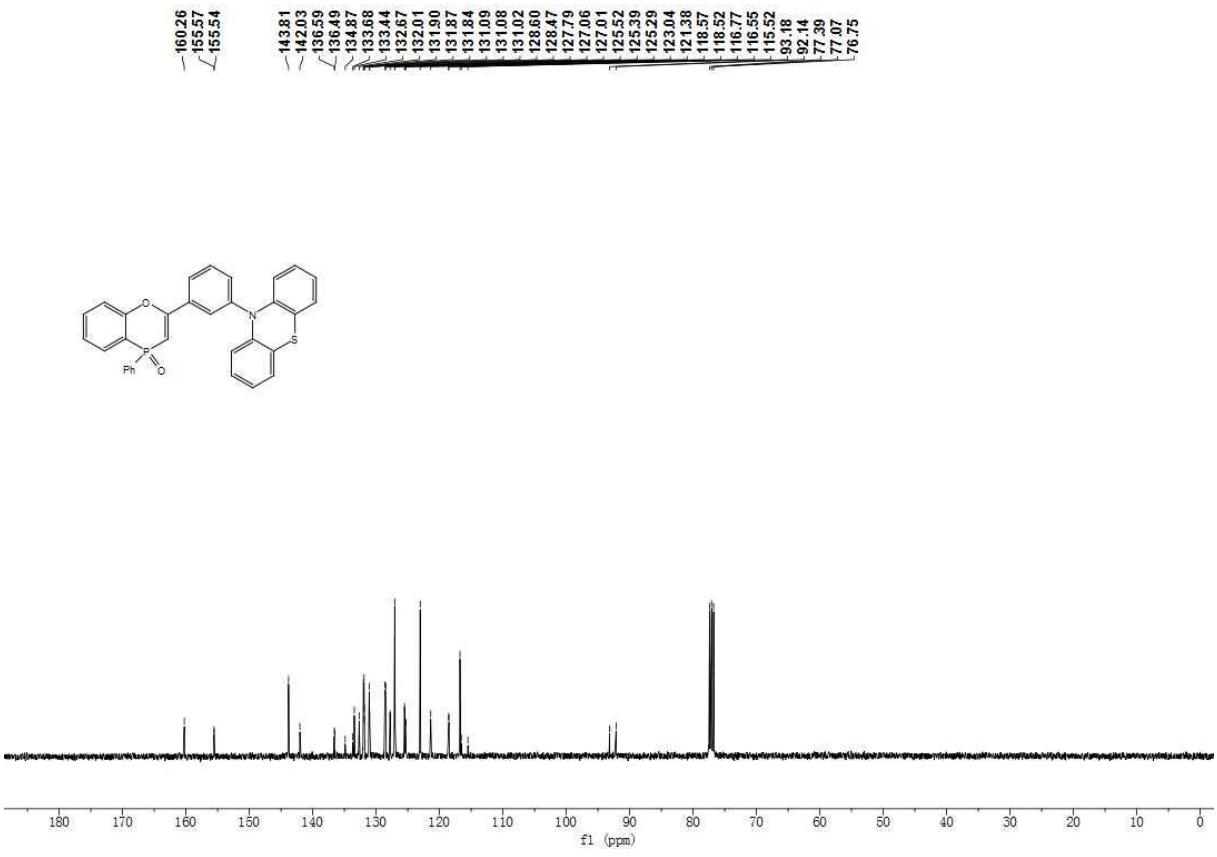
^{13}C NMR ($CDCl_3$-*d*) of 4**e**



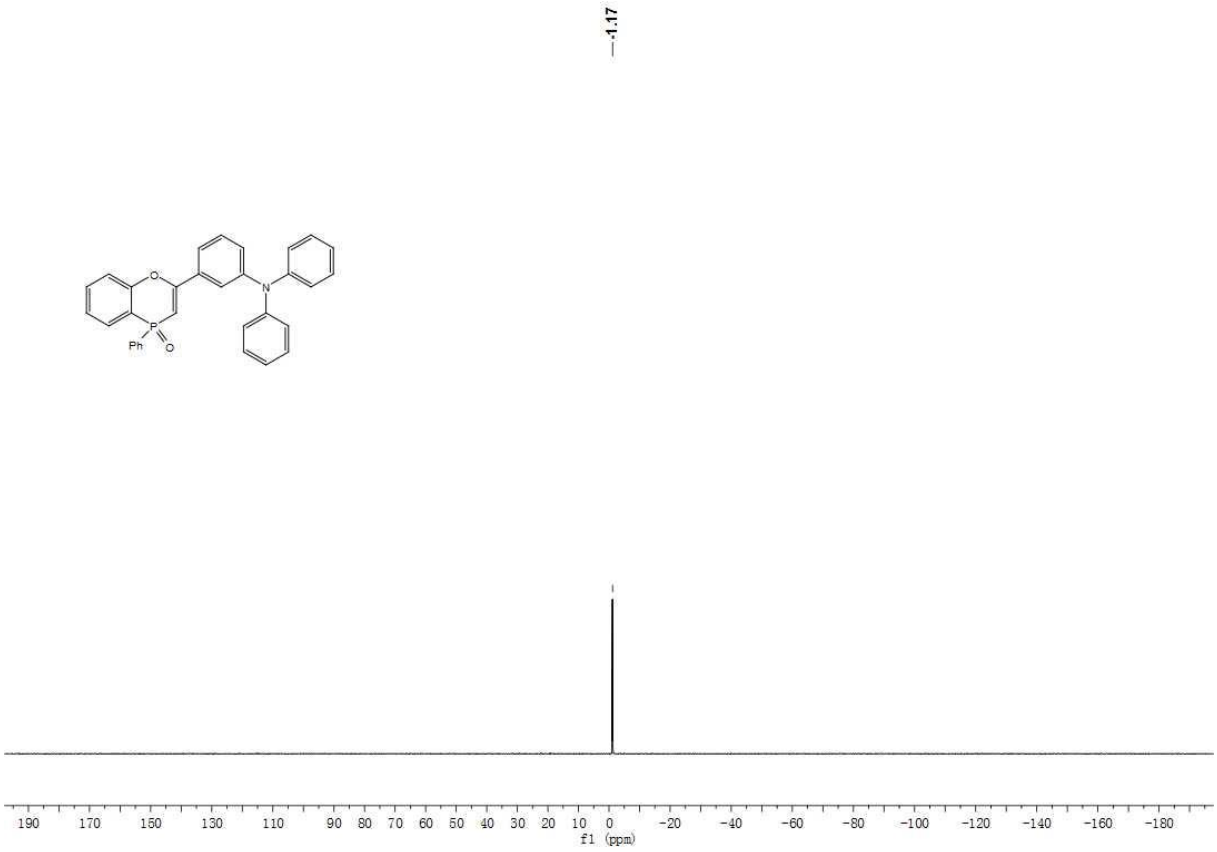
^{31}P NMR ($CDCl_3$-*d*) of **4f**



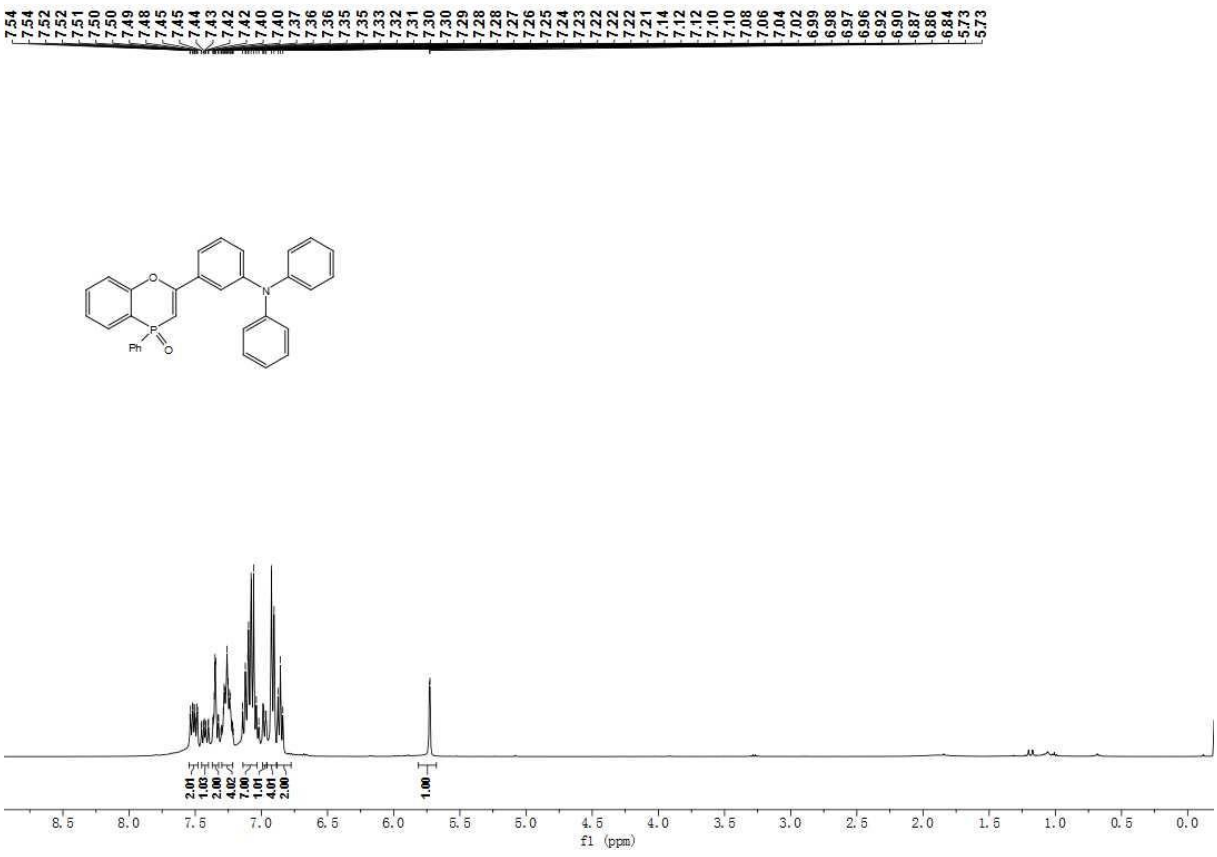
^{1}H NMR ($CDCl_3$-*d*) of 4**f**



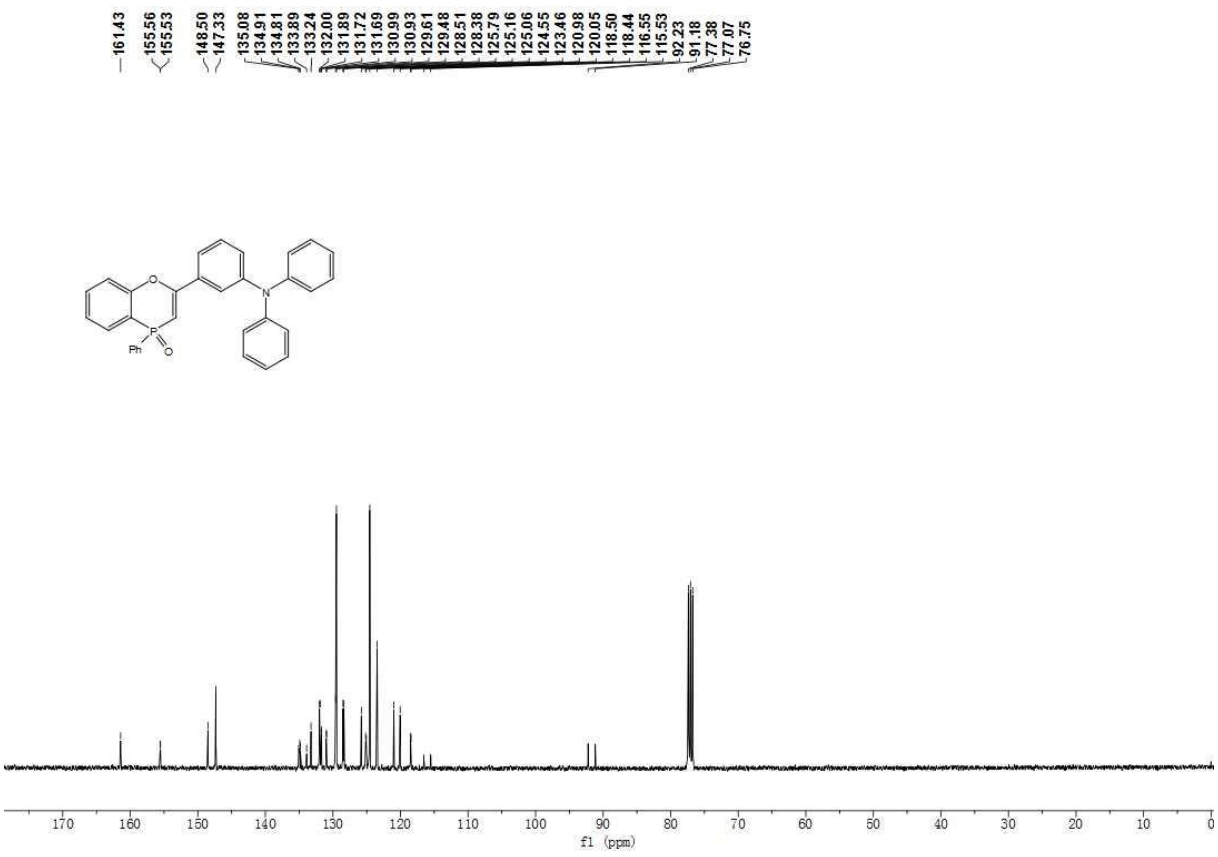
^{13}C NMR ($CDCl_3$-*d*) of 4**f**



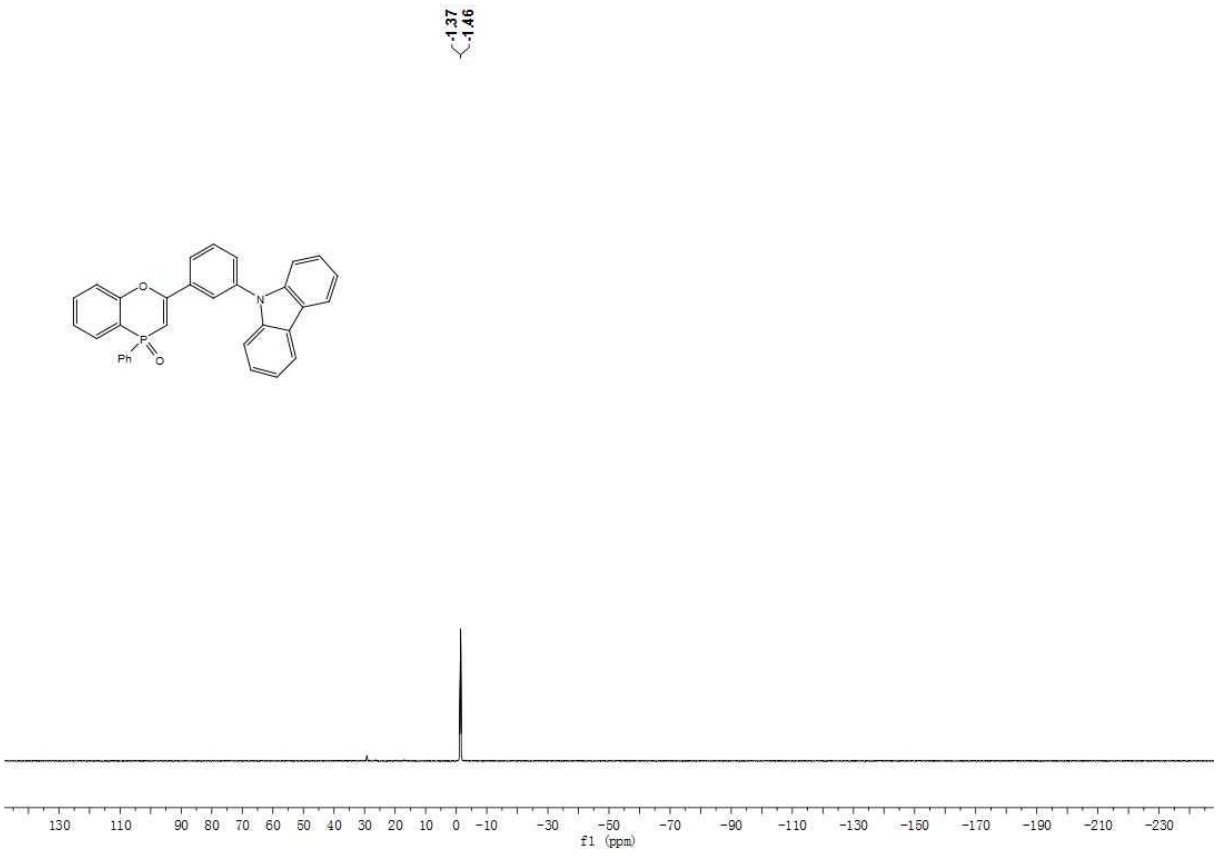
^{31}P NMR ($CDCl_3$-*d*) of **4g**



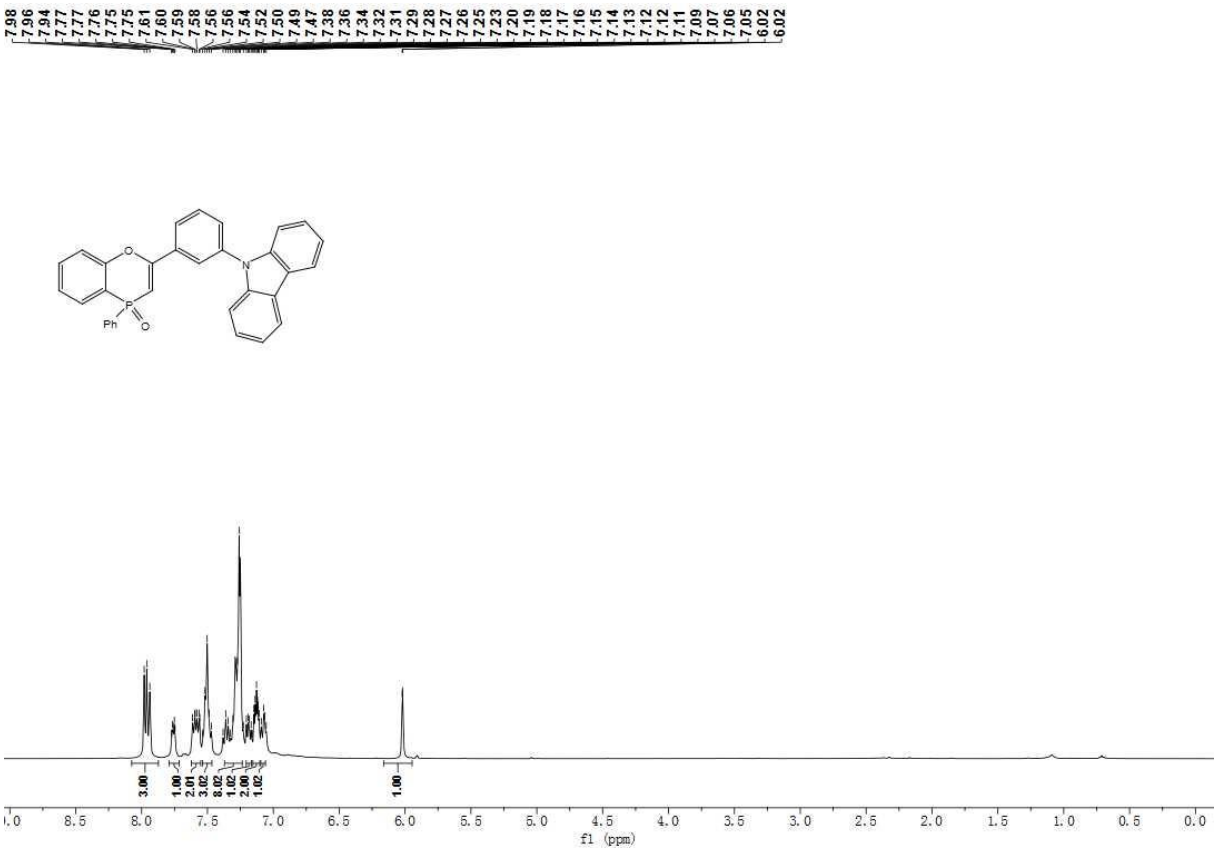
^{1}H NMR ($CDCl_3$-*d*) of 4**g**



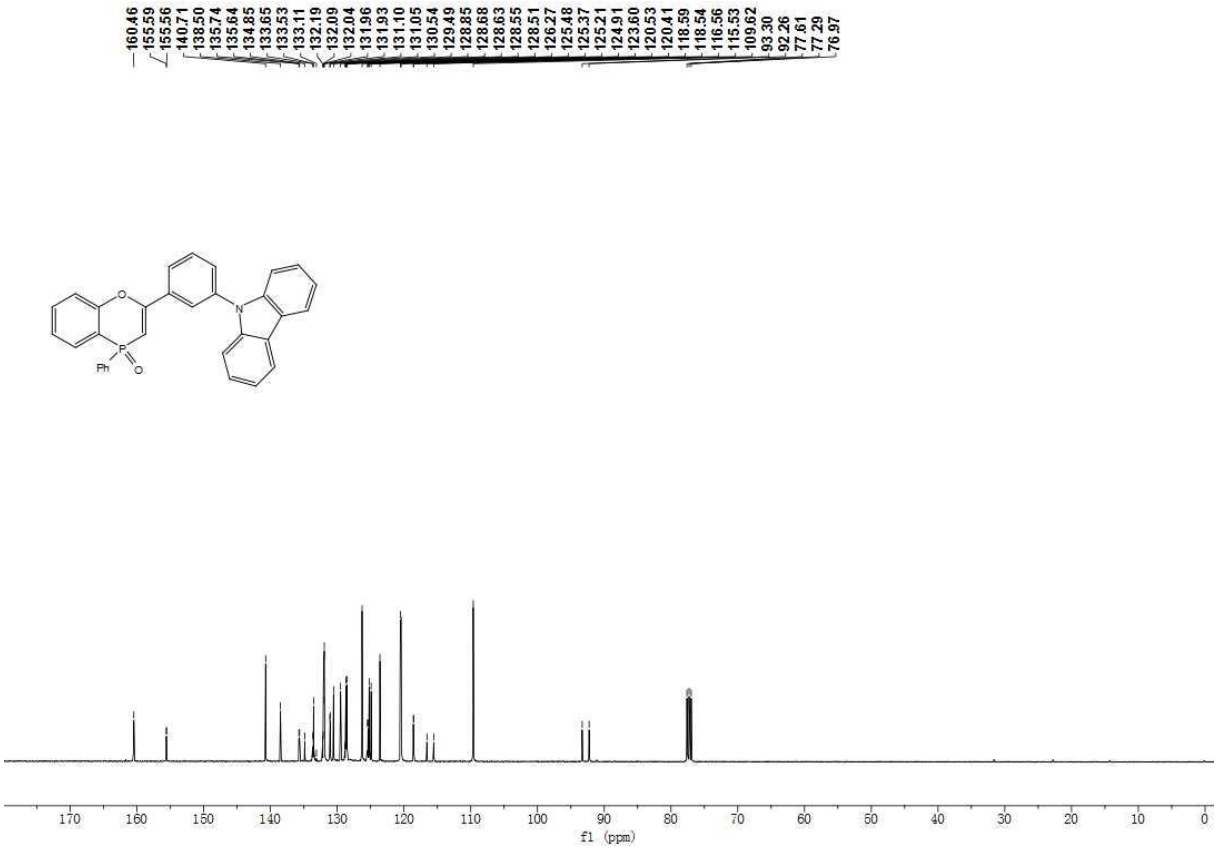
^{13}C NMR ($CDCl_3$-*d*) of 4**g**



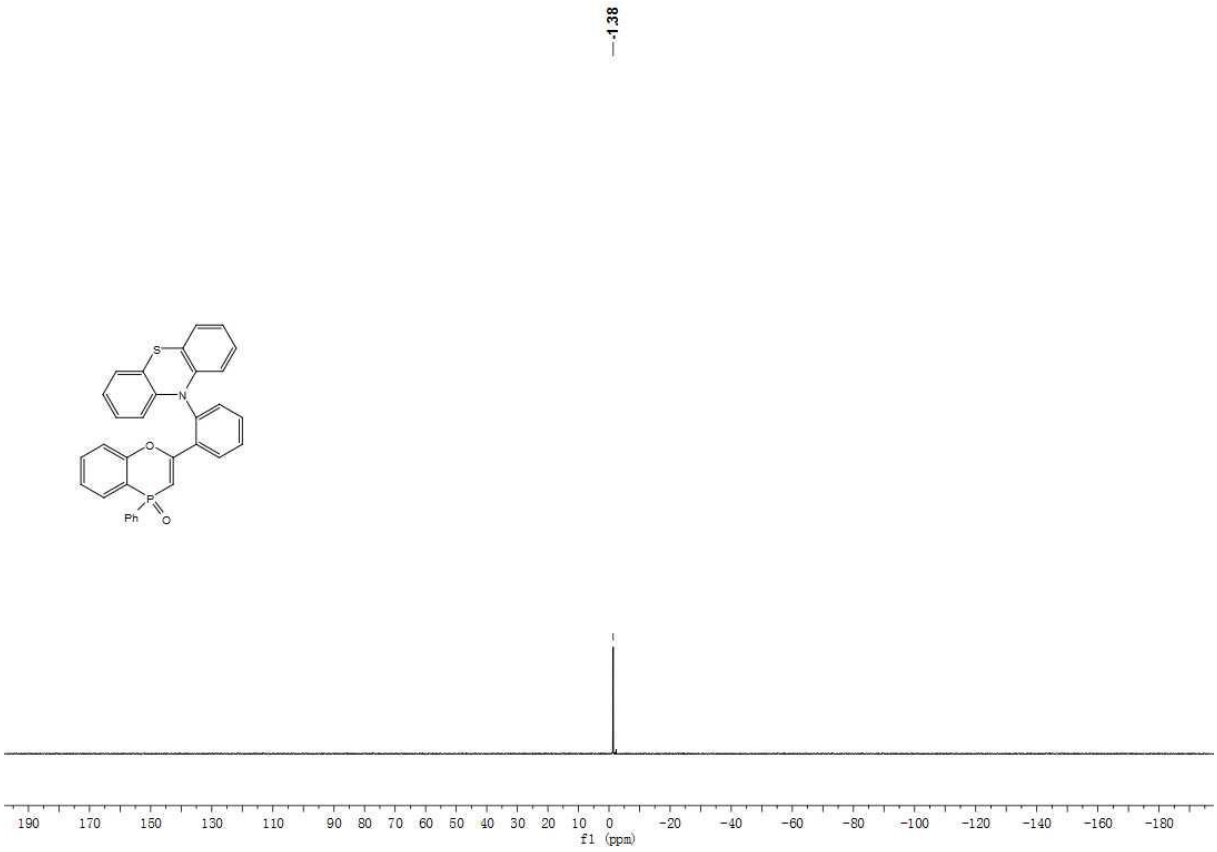
^{31}P NMR ($CDCl_3$-*d*) of **4h**



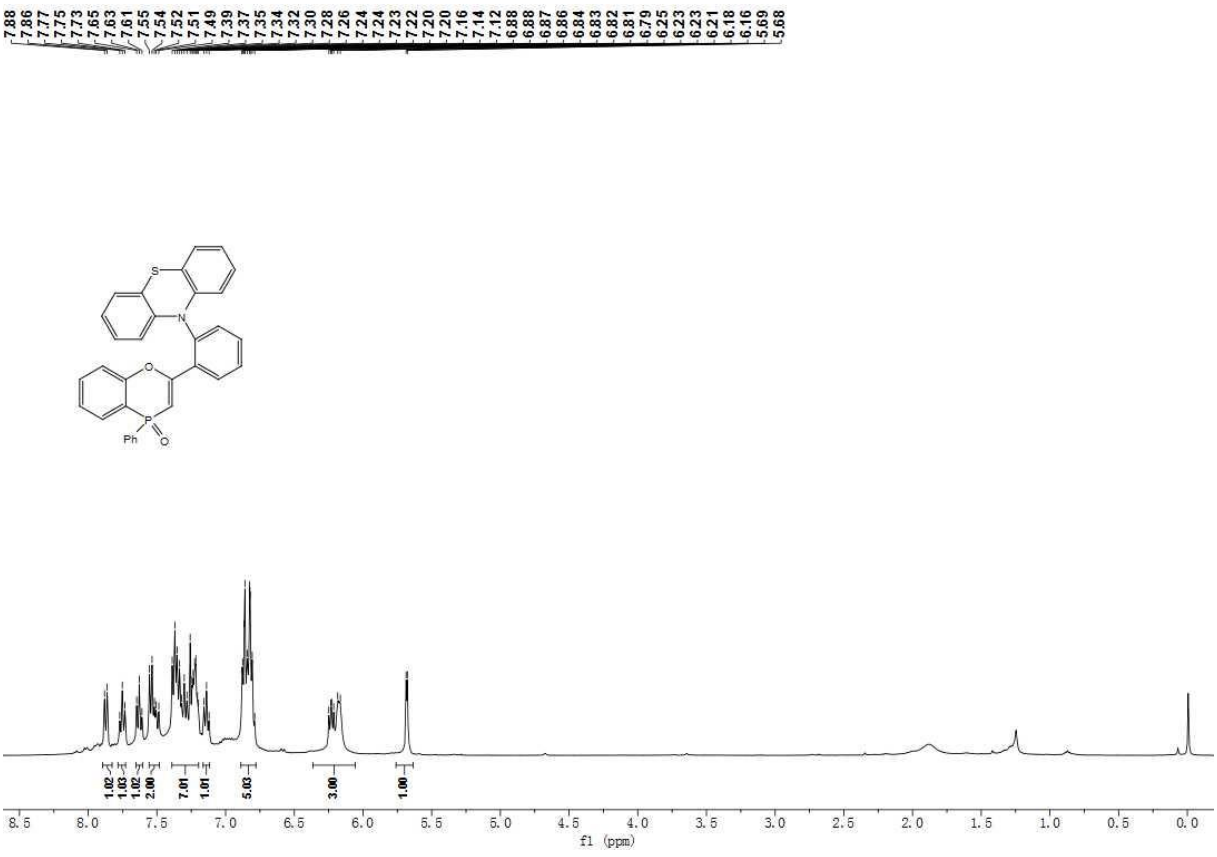
^{1}H NMR ($CDCl_3$-*d*) of 4**h**



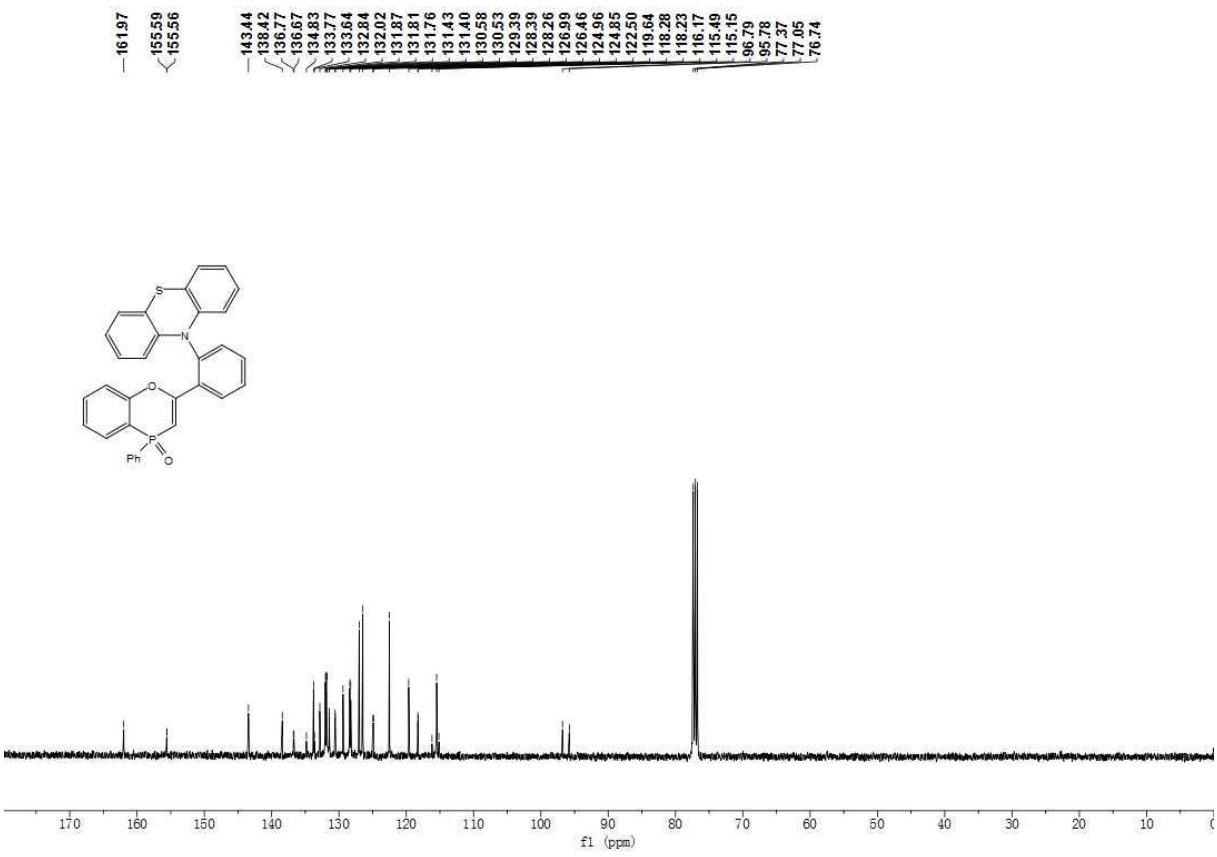
^{13}C NMR ($CDCl_3$-*d*) of 4**h**



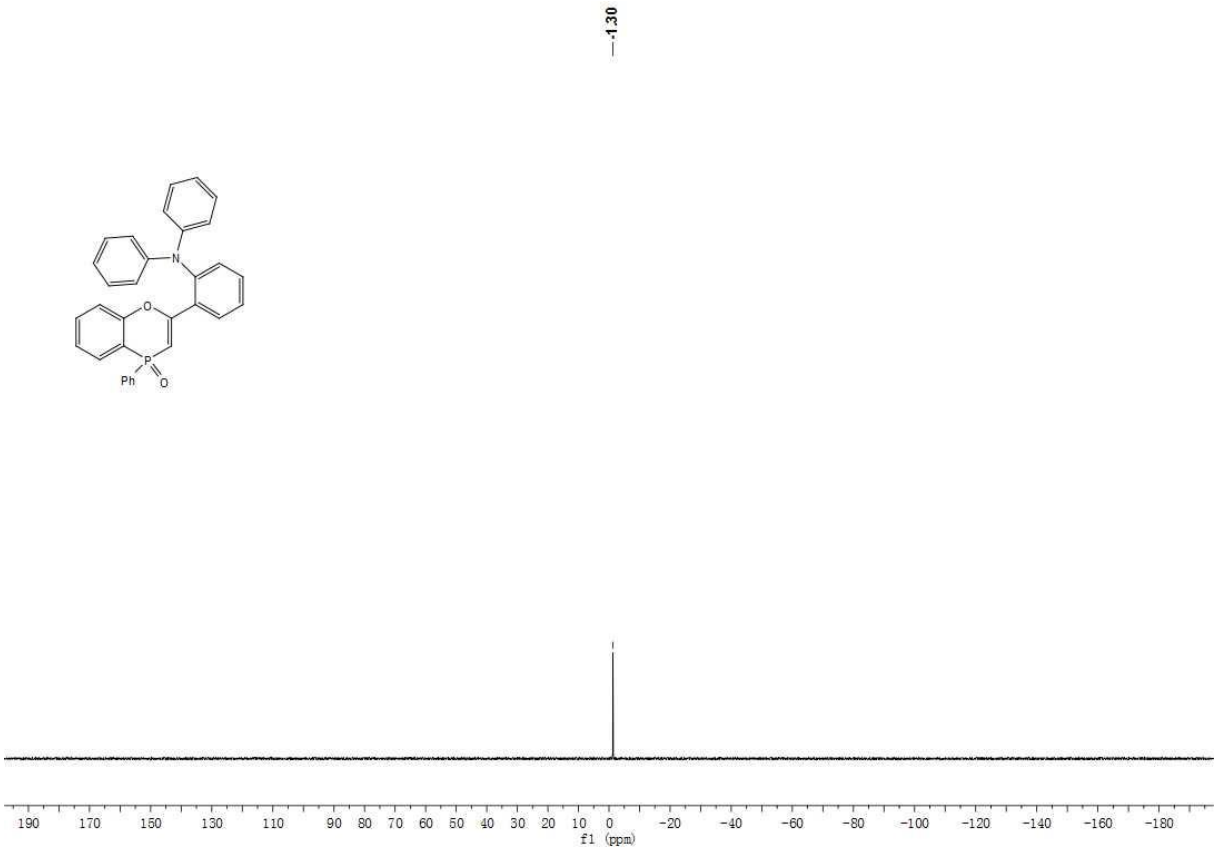
^{31}P NMR ($CDCl_3$-*d*) of **4j**



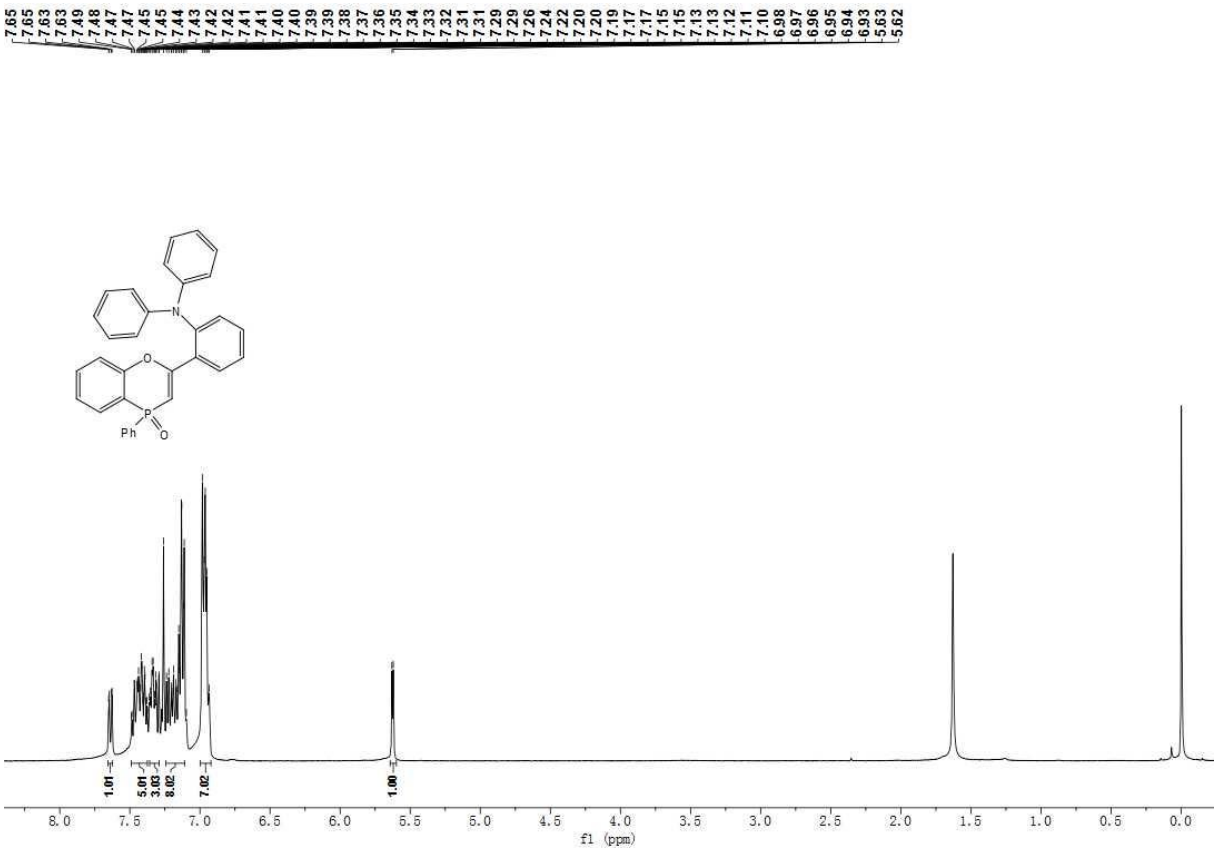
^{1}H NMR ($CDCl_3$-*d*) of 4**j**



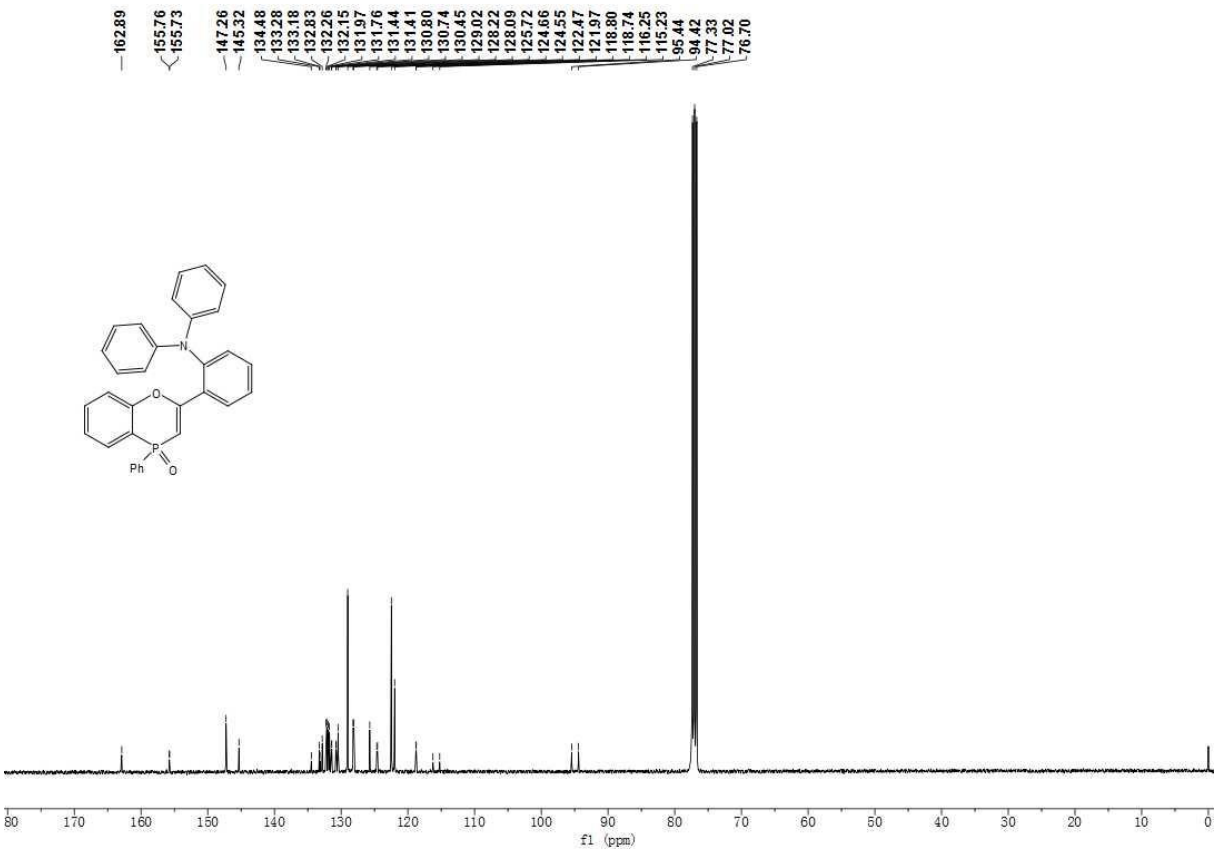
^{13}C NMR ($CDCl_3$-*d*) of 4**j**



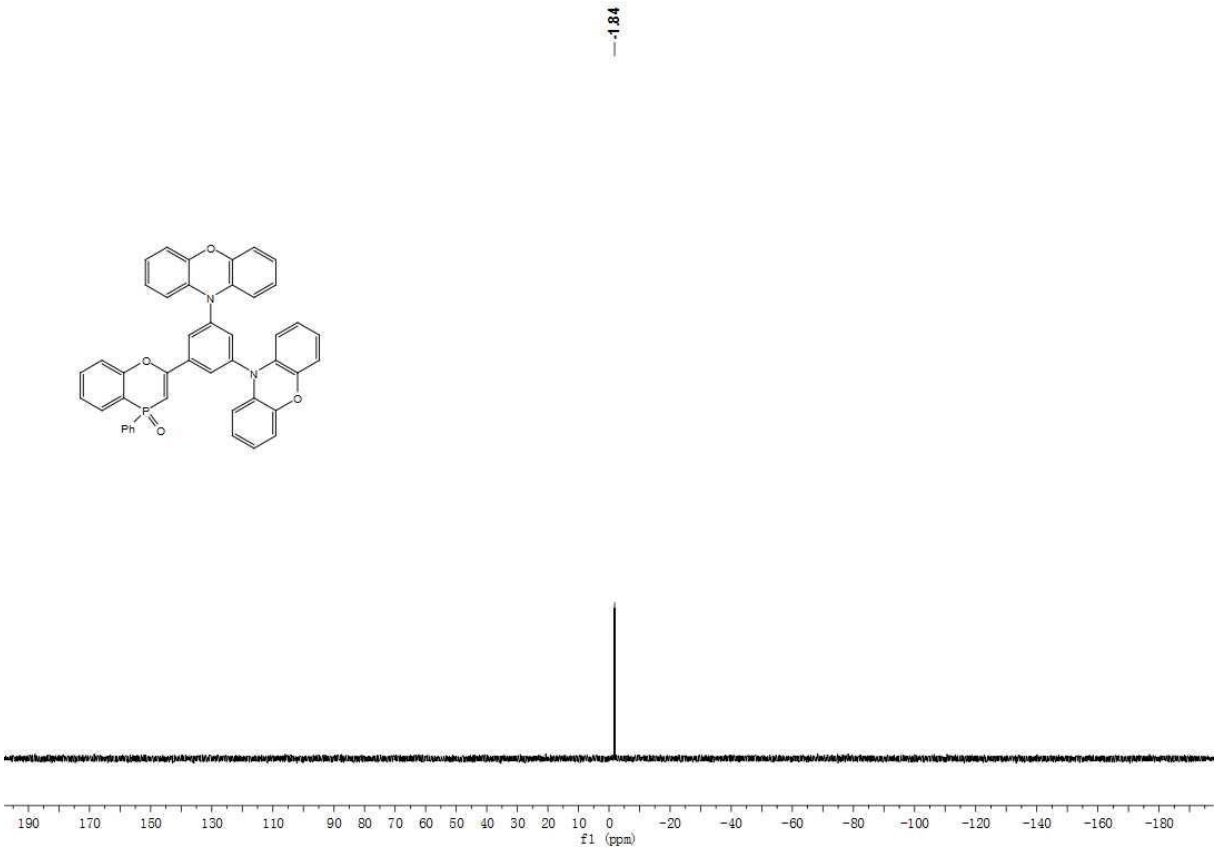
^{31}P NMR ($CDCl_3$-*d*) of **4k**



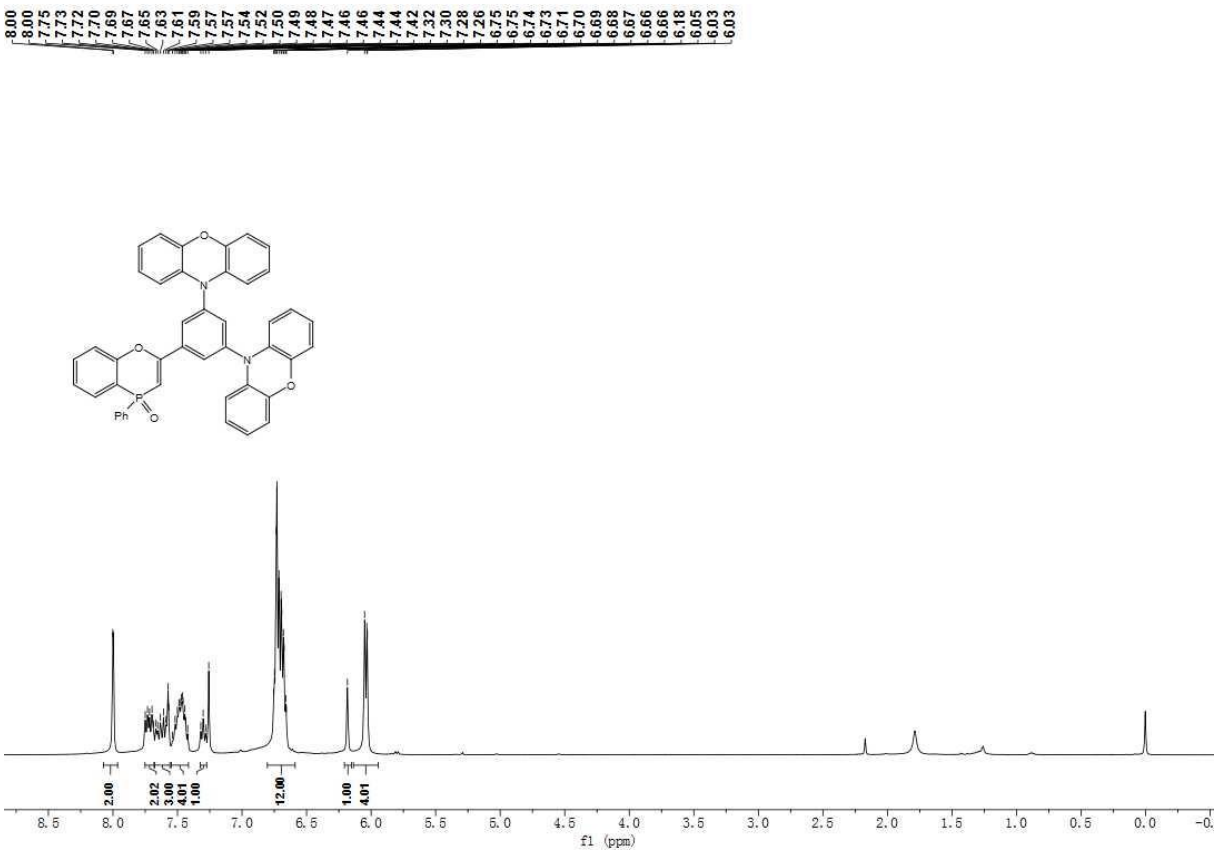
^{1}H NMR ($CDCl_3$-*d*) of 4**k**



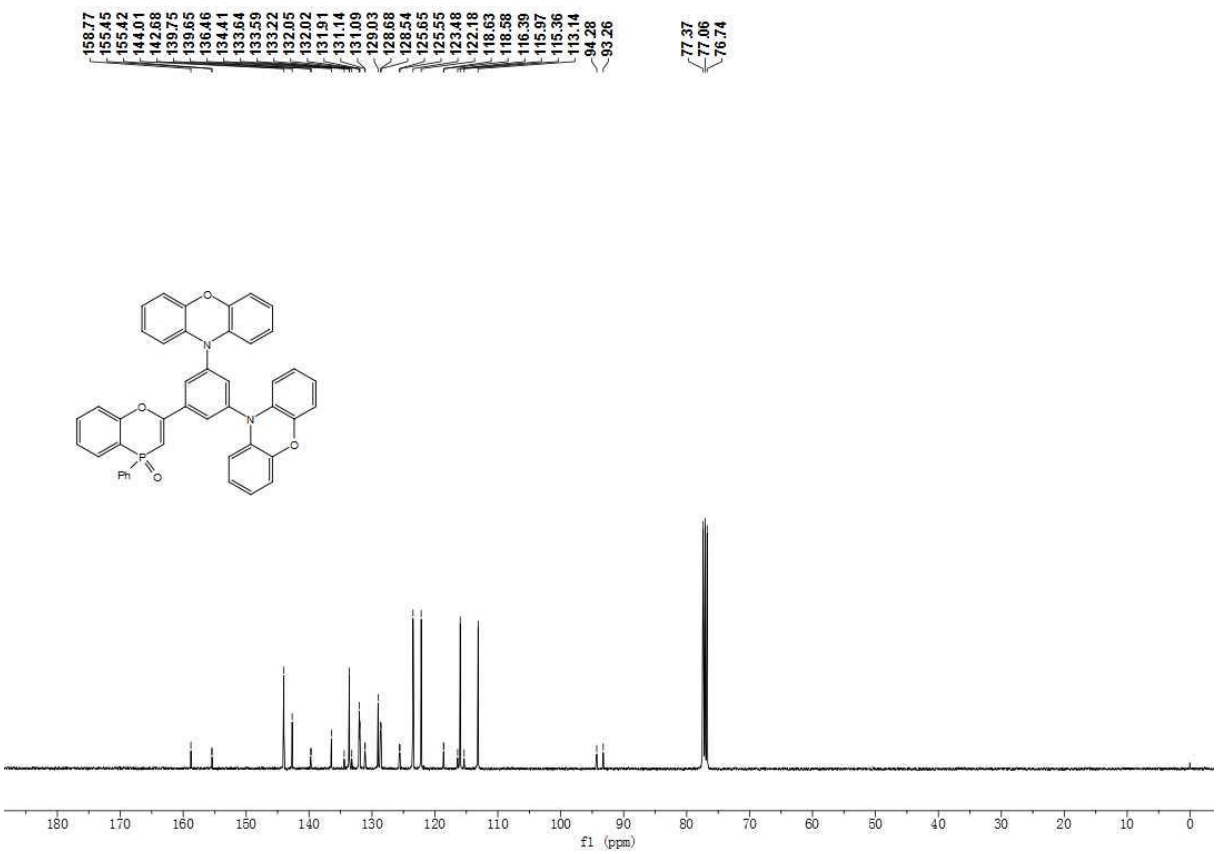
^{13}C NMR ($CDCl_3$-*d*) of 4**k**



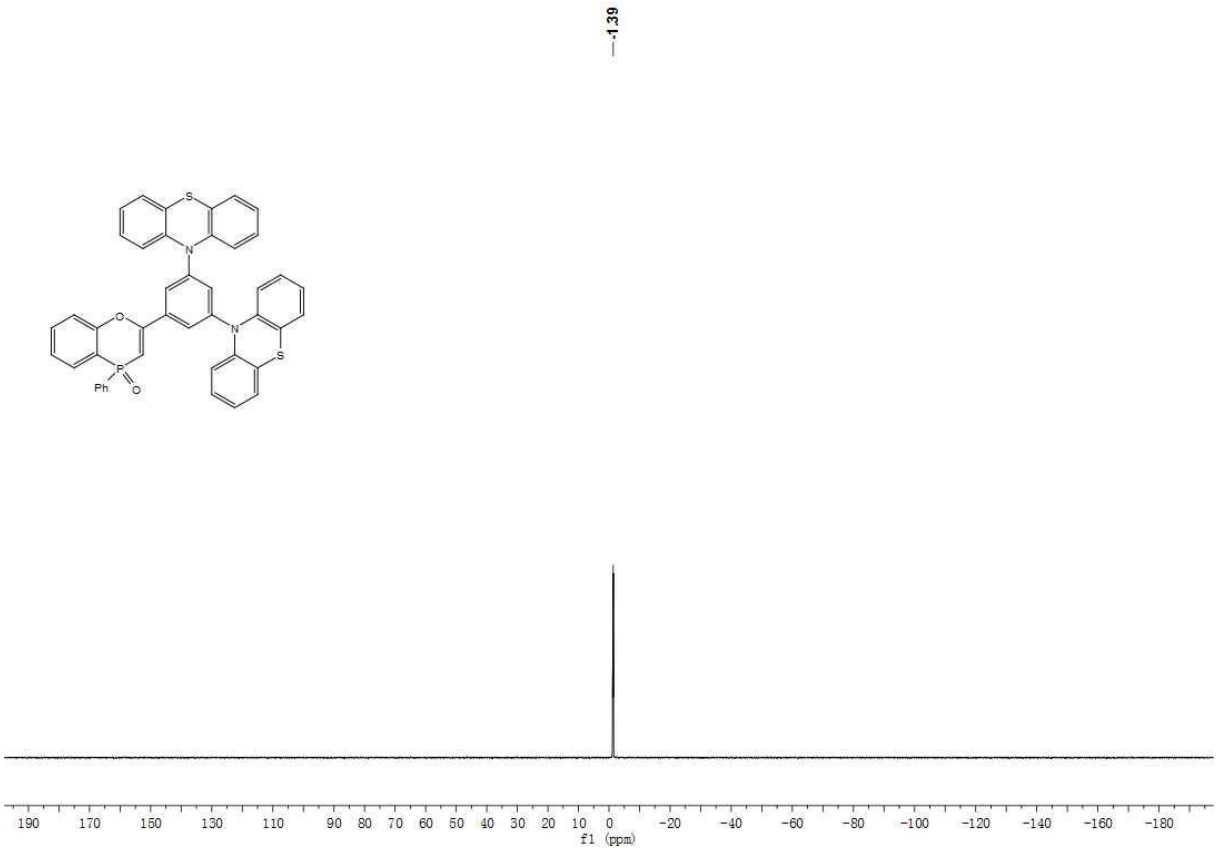
^{31}P NMR ($CDCl_3$-*d*) of **4m**



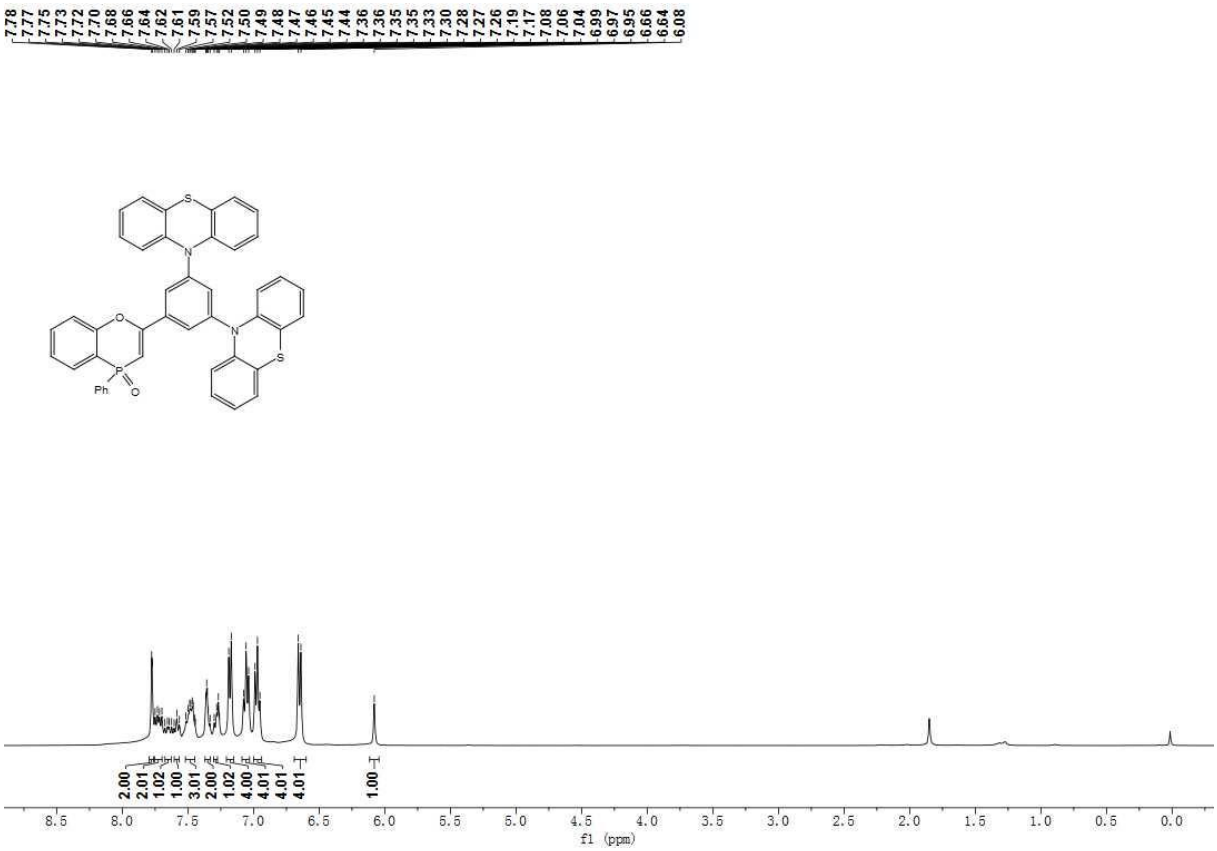
^{1}H NMR ($CDCl_3$-*d*) of 4**m**



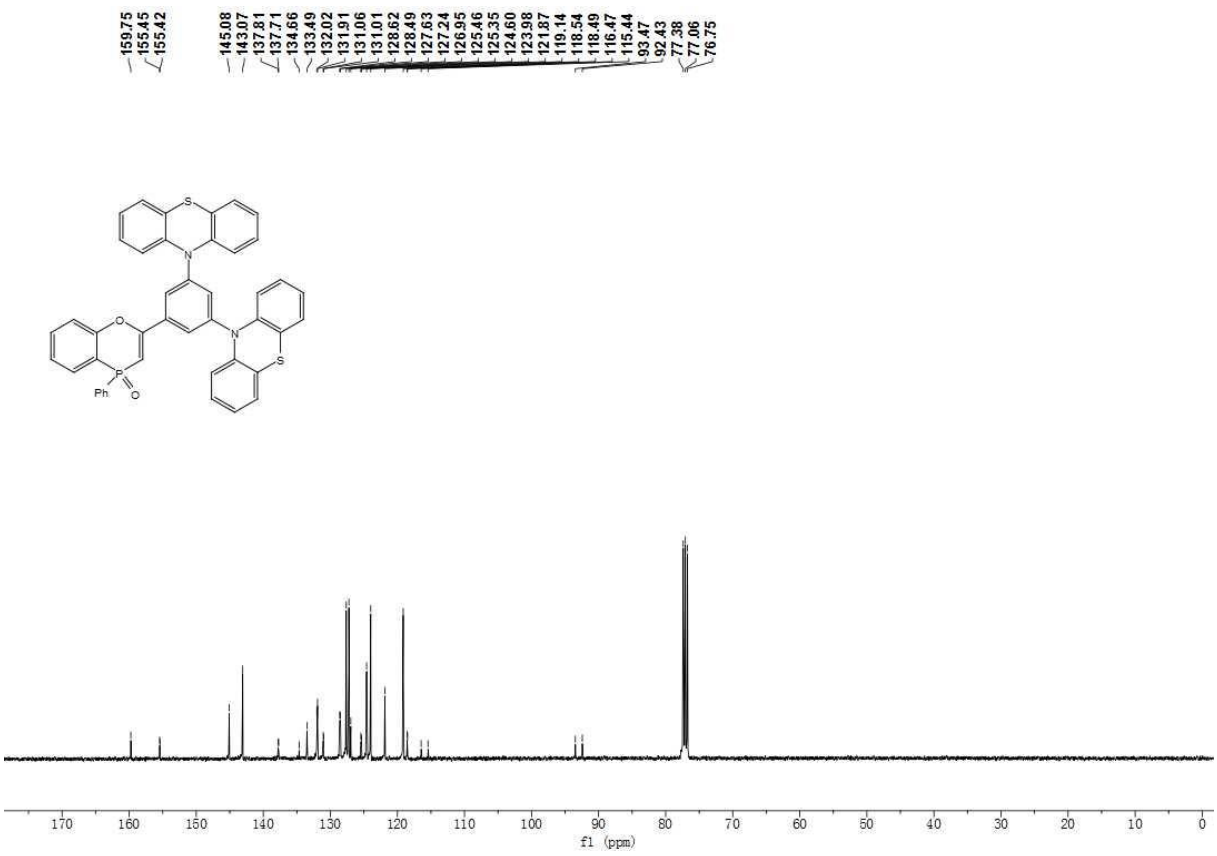
^{13}C NMR ($CDCl_3$-*d*) of 4**m**



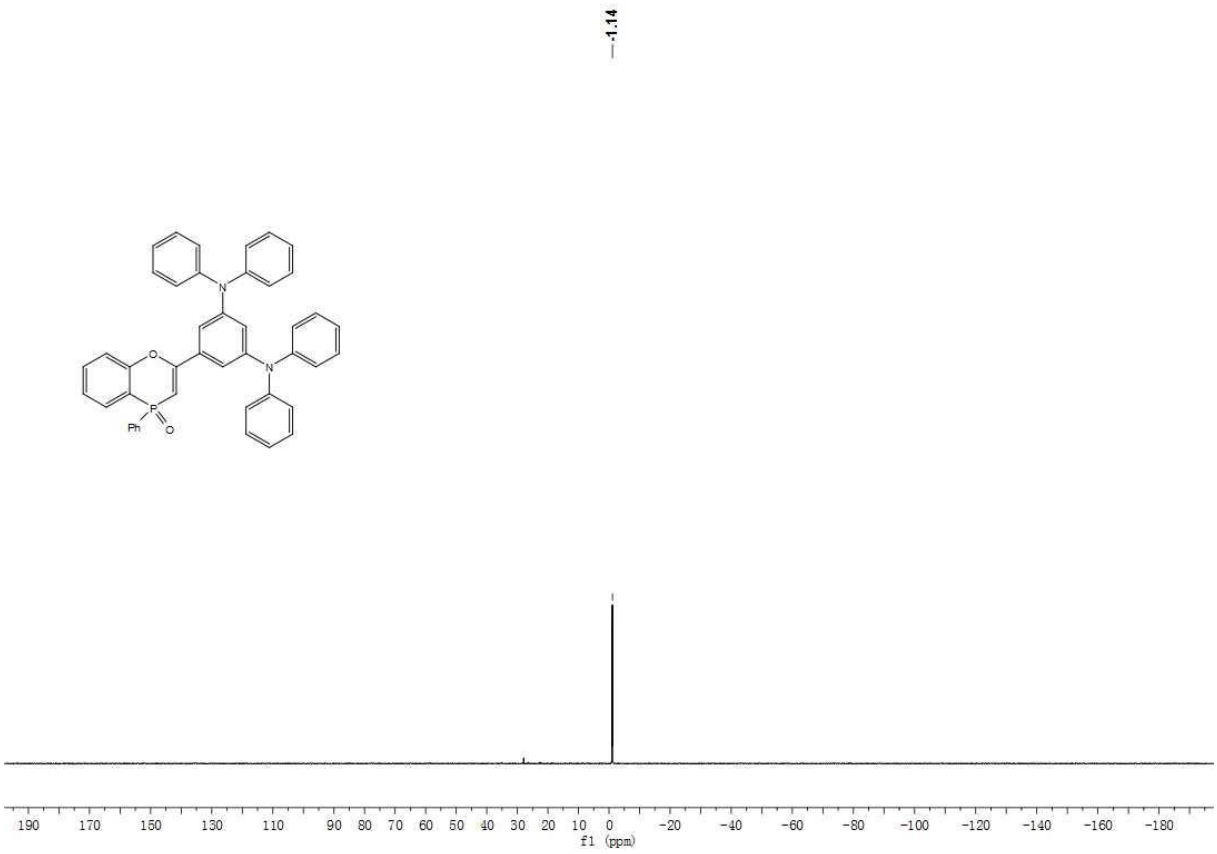
^{31}P NMR ($CDCl_3$-*d*) of **4n**



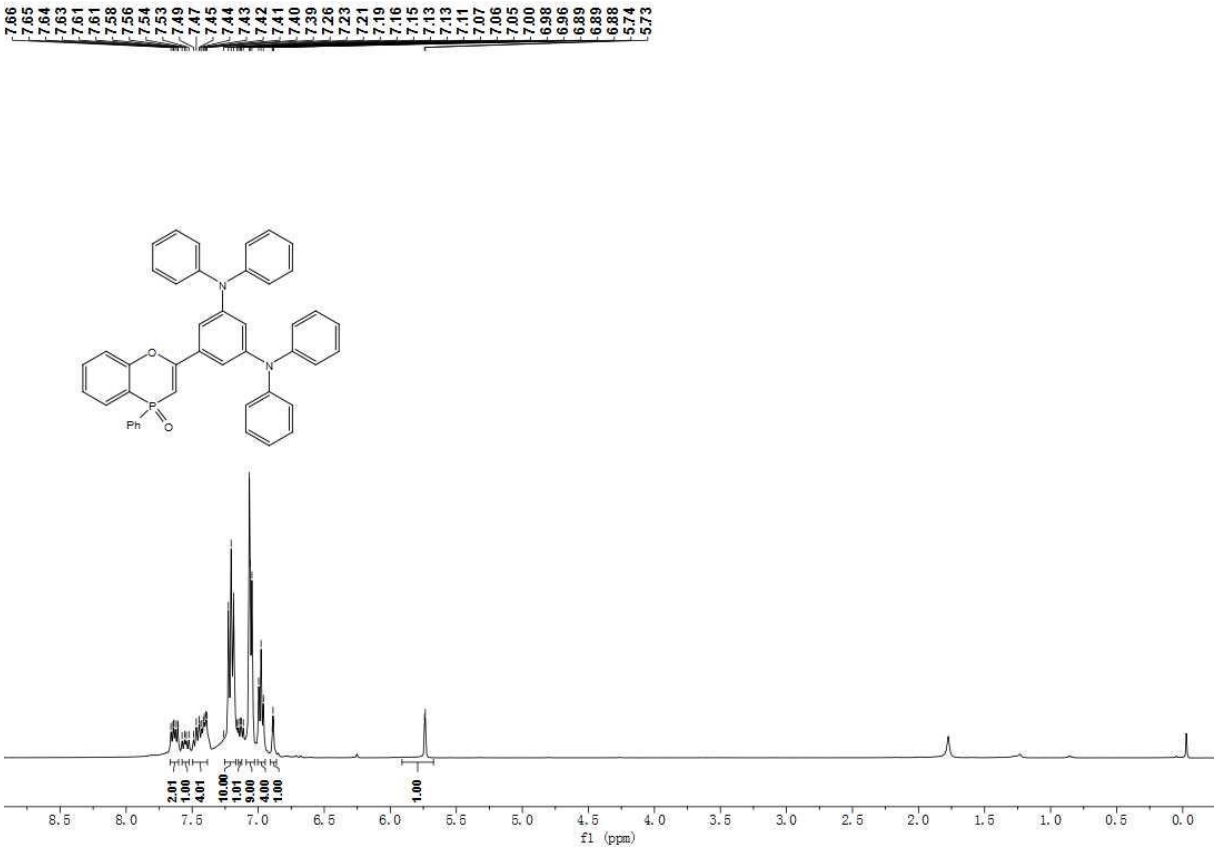
^{1}H NMR ($CDCl_3$-*d*) of 4**n**



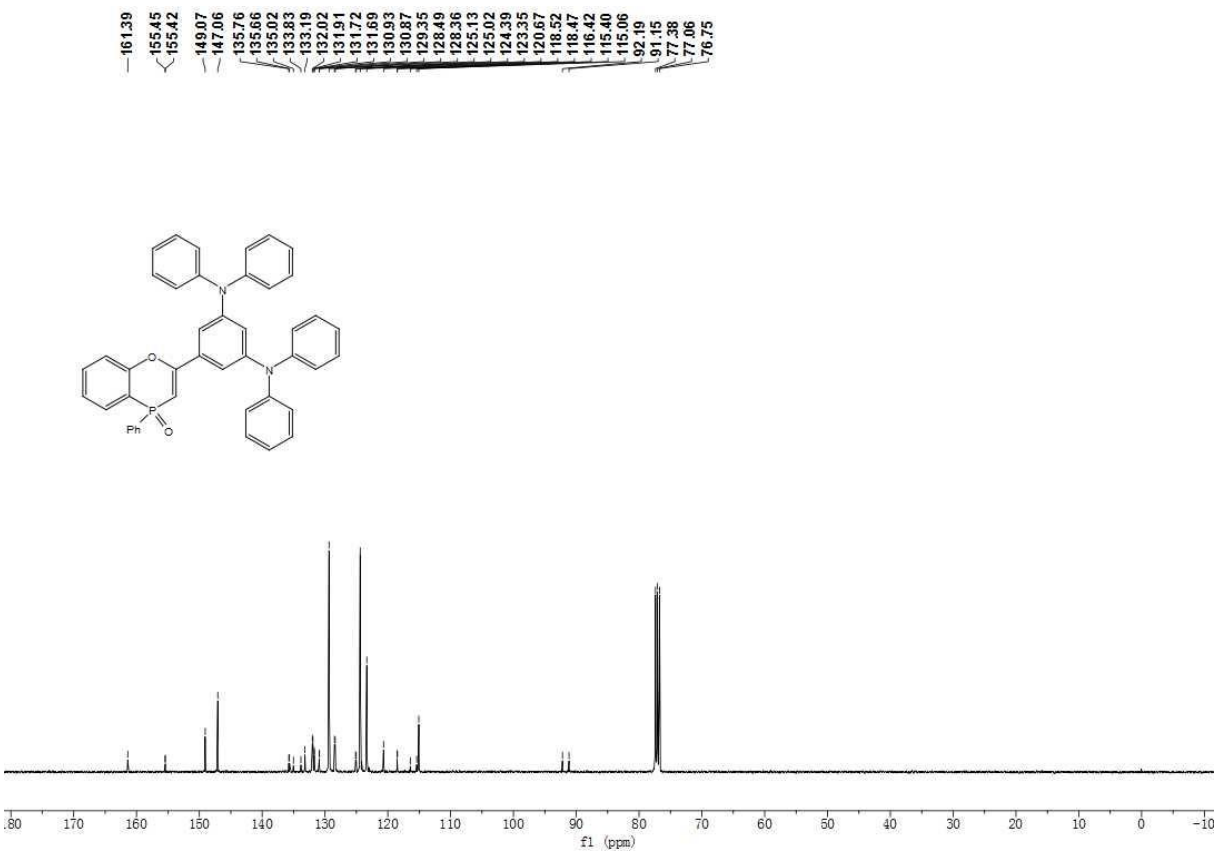
^{13}C NMR ($CDCl_3$-*d*) of 4**n**



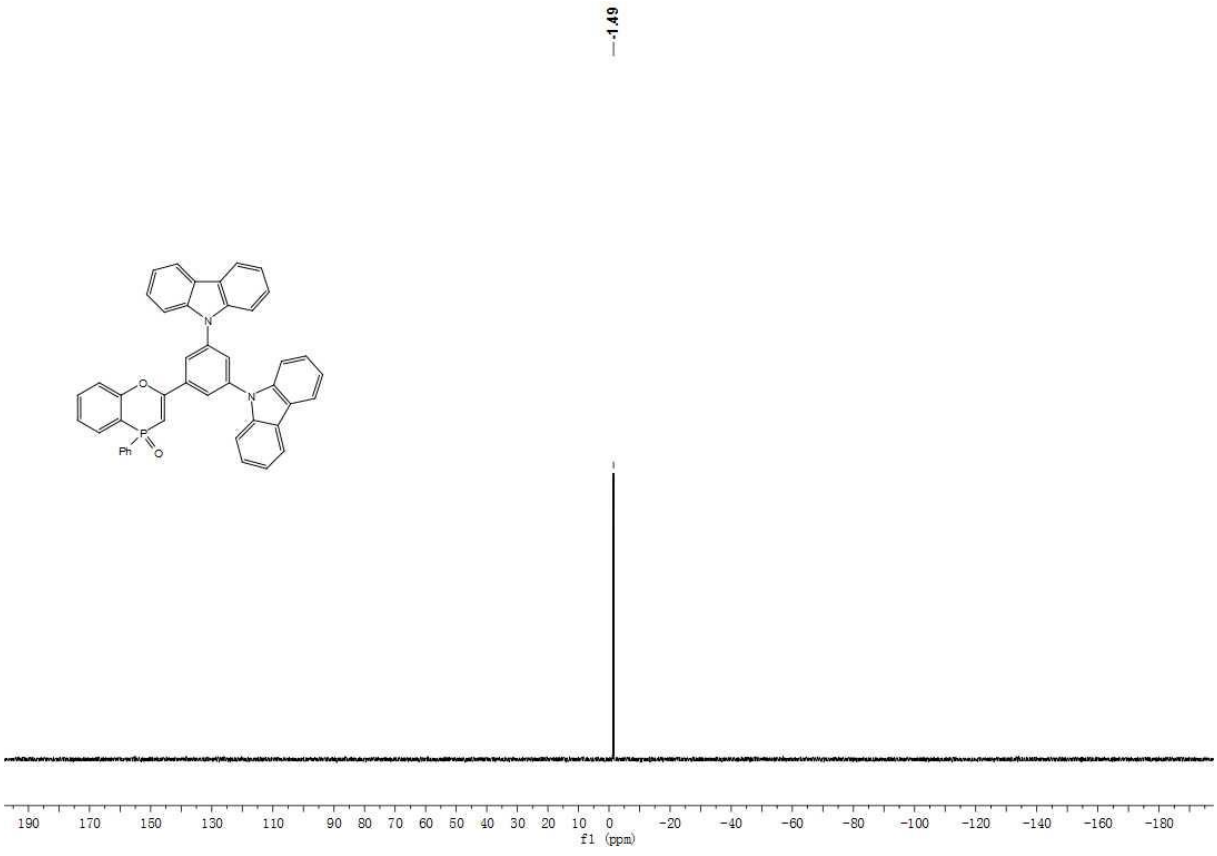
^{31}P NMR ($CDCl_3$-*d*) of **4o**



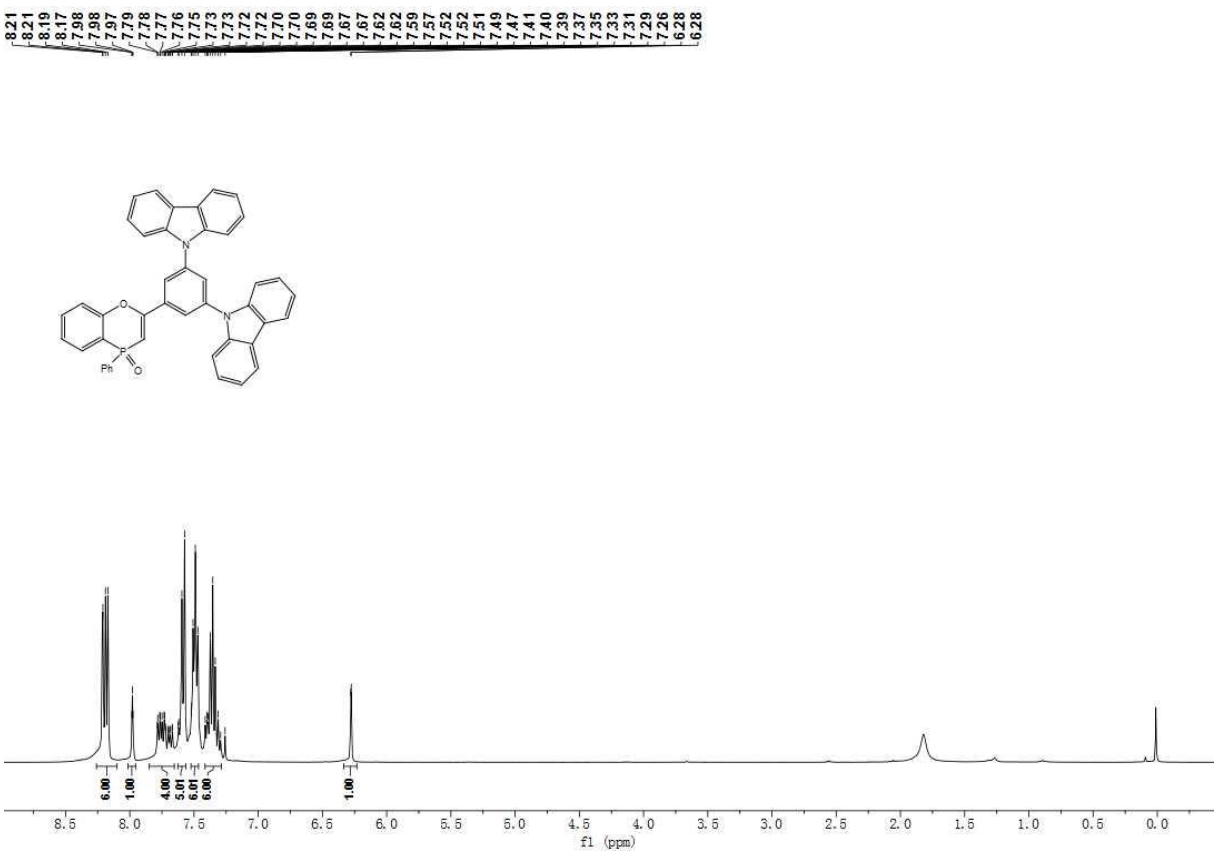
^{1}H NMR ($CDCl_3$-*d*) of 4**o**



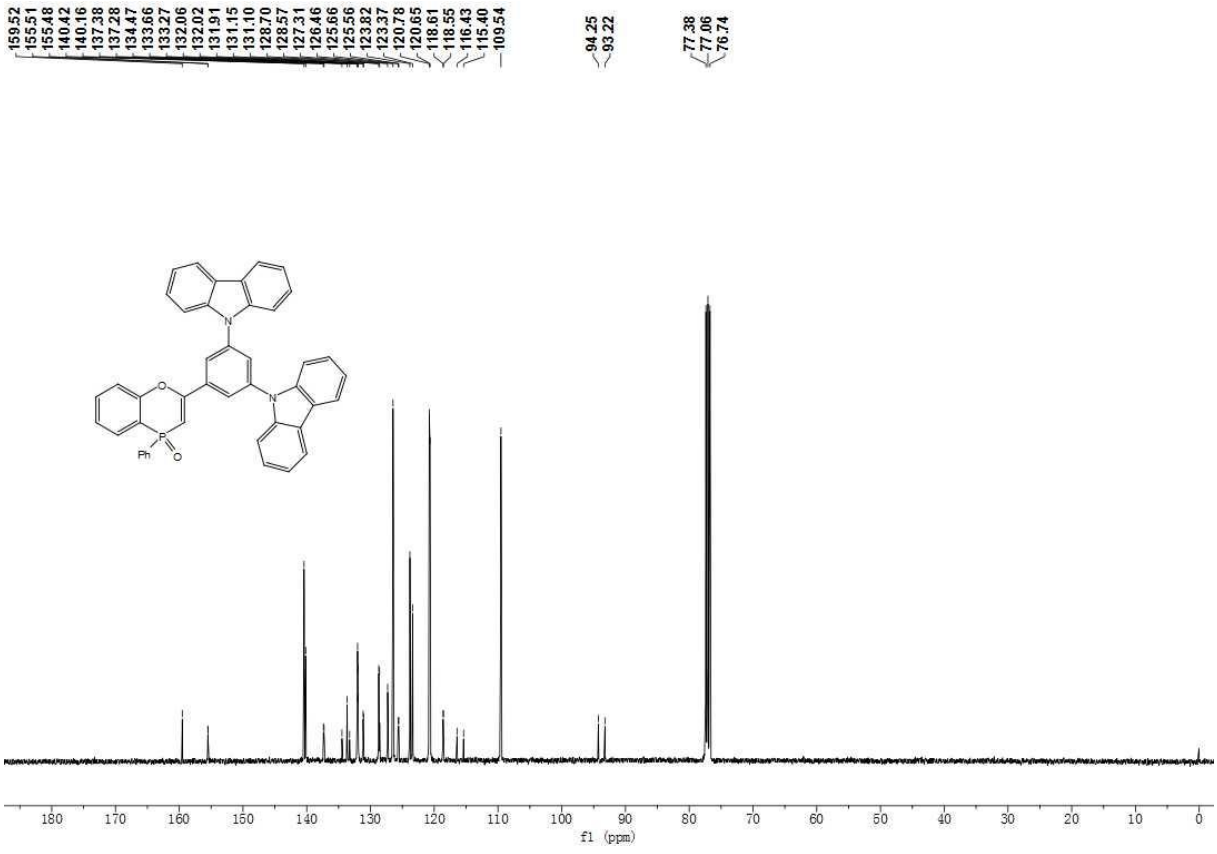
^{13}C NMR ($CDCl_3$-*d*) of 4**o**



^{31}P NMR ($CDCl_3$-*d*) of **4p**



^{1}H NMR ($CDCl_3$-*d*) of 4**p**



^{13}C NMR ($CDCl_3$-*d*) of 4**p**

8. X-ray crystal structures of **4e**, **4i** and **4k**.

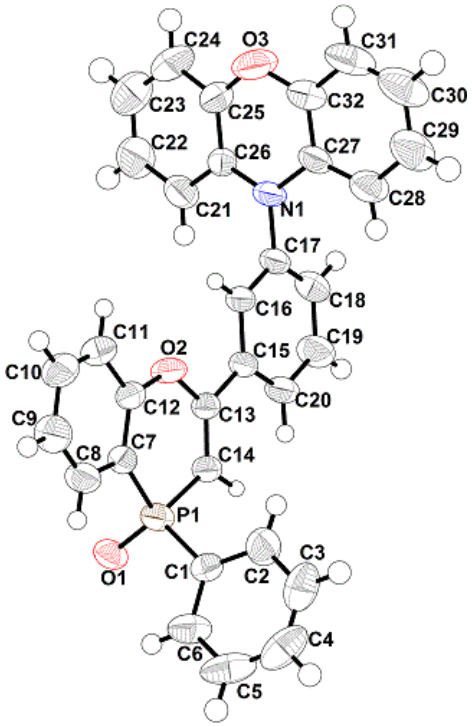


Figure s10. Crystal data and structure refinement for **4e**. CCDC reference number: 2014047

Table s2 Crystal data and structure refinement for 4e.

Identification code	4e
Empirical formula	$C_{33}H_{23}Cl_2NO_3P$
Formula weight	583.39
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	8.8411(17)
b/Å	12.359(2)
c/Å	14.778(3)
α/°	97.562(4)
β/°	107.094(3)
γ/°	107.232(3)
Volume/Å^3	1431.3(5)
Z	2
ρ_{calc}g/cm^3	1.354
μ/mm^{-1}	0.318
F(000)	602.0
Crystal size/mm^3	0.02 × 0.02 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.962 to 55.234
Index ranges	-11 ≤ h ≤ 11, -15 ≤ k ≤ 16, -15 ≤ l ≤ 18
Reflections collected	8694

Independent reflections	6224 [R_{int} = 0.0208, R_{sigma} = 0.0507]
Data/restraints/parameters	6224/26/379
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0673, wR_2 = 0.1745
Final R indexes [all data]	R_1 = 0.1078, wR_2 = 0.2039
Largest diff. peak/hole / e $Å^{-3}$	0.48/-0.56

Table s3 Bond Lengths for 4e.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	C14	1.753(3)	C1	C2	1.389(5)
P1	C7	1.787(3)	O3	C25	1.385(4)
P1	O1	1.483(2)	O3	C32	1.373(4)
P1	C1	1.798(3)	C25	C26	1.390(4)
O2	C13	1.366(3)	C25	C24	1.361(5)
O2	C12	1.381(3)	C21	C26	1.379(4)
C13	C14	1.334(4)	C21	C22	1.389(5)
C13	C15	1.489(4)	C27	C32	1.393(4)
C12	C7	1.388(4)	C27	C28	1.381(5)
C12	C11	1.393(4)	C32	C31	1.377(5)
C7	C8	1.399(4)	C28	C29	1.385(5)
C20	C15	1.392(4)	C31	C30	1.374(6)
C20	C19	1.372(4)	C29	C30	1.365(6)
C16	C17	1.375(4)	C24	C23	1.373(6)
C16	C15	1.393(4)	C22	C23	1.373(6)
C17	C18	1.375(5)	C6	C5	1.388(5)
C17	N1	1.437(4)	C2	C3	1.385(5)
C19	C18	1.387(5)	C5	C4	1.355(7)
C11	C10	1.361(5)	C3	C4	1.356(7)
C8	C9	1.360(5)	Cl1	C9BA	1.692(11)
C10	C9	1.384(5)	Cl2	C9BA	1.816(12)
N1	C26	1.402(4)	C1	C6	1.376(4)
N1	C27	1.394(4)			

Table s4 Bond Angles for 4e.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C14	P1	C7	100.32(13)	C27	N1	C26	119.4(2)
C14	P1	C1	107.36(14)	C6	C1	P1	120.2(3)
C7	P1	C1	108.26(13)	C6	C1	C2	117.7(3)
O1	P1	C14	115.32(13)	C2	C1	P1	122.1(2)
O1	P1	C7	113.79(13)	C32	O3	C25	117.8(3)

O1	P1	C1	111.04(13)	O3	C25	C26	121.4(3)
C13	O2	C12	123.7(2)	C24	C25	O3	116.8(3)
O2	C13	C15	110.0(2)	C24	C25	C26	121.8(4)
C14	C13	O2	124.2(3)	C26	C21	C22	120.4(4)
C14	C13	C15	125.7(3)	C25	C26	N1	118.9(3)
O2	C12	C7	124.5(3)	C21	C26	N1	123.0(3)
O2	C12	C11	114.3(3)	C21	C26	C25	118.1(3)
C7	C12	C11	121.2(3)	C32	C27	N1	118.8(3)
C13	C14	P1	124.9(2)	C28	C27	N1	122.9(3)
C12	C7	P1	121.3(2)	C28	C27	C32	118.2(3)
C12	C7	C8	117.7(3)	O3	C32	C27	121.8(3)
C8	C7	P1	120.9(2)	O3	C32	C31	117.5(3)
C19	C20	C15	120.5(3)	C31	C32	C27	120.6(4)
C17	C16	C15	120.3(3)	C27	C28	C29	120.6(4)
C16	C17	C18	120.7(3)	C30	C31	C32	120.3(4)
C16	C17	N1	118.9(3)	C30	C29	C28	120.5(4)
C18	C17	N1	120.3(3)	C25	C24	C23	119.6(4)
C20	C15	C13	120.7(2)	C29	C30	C31	119.7(4)
C20	C15	C16	118.6(3)	C23	C22	C21	119.9(4)
C16	C15	C13	120.7(3)	C22	C23	C24	120.2(4)
C20	C19	C18	120.4(3)	C1	C6	C5	120.5(4)
C17	C18	C19	119.3(3)	C3	C2	C1	120.8(4)
C10	C11	C12	119.2(3)	C4	C5	C6	120.9(4)
C9	C8	C7	121.0(3)	C4	C3	C2	120.5(4)
C11	C10	C9	120.6(3)	C5	C4	C3	119.6(4)
C8	C9	C10	120.2(3)	Cl1	C9BA	Cl2	72.2(7)
C26	N1	C17	119.3(2)	Cl2A	C9BA	Cl1A	126.0(10)
C27	N1	C17	120.9(2)				

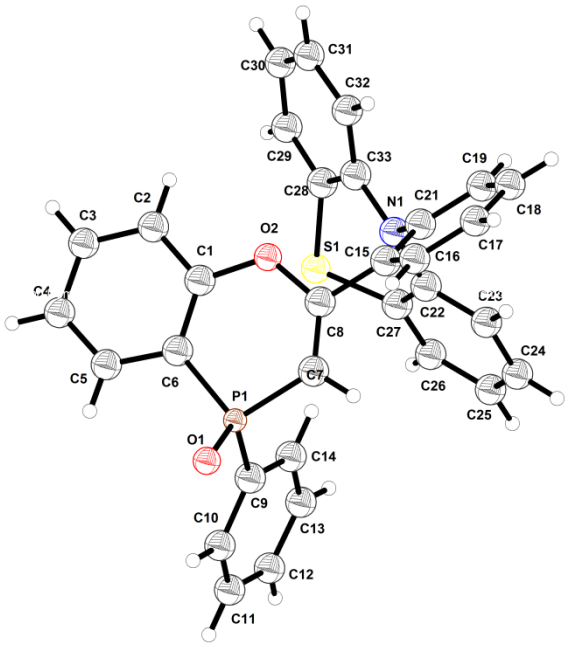


Figure s11. Crystal data and structure refinement for **4j**. CCDC reference number: 2014049

Table s5 Crystal data and structure refinement for 4j.

Identification code	200104HUANGHY_0m
Empirical formula	$C_{32}H_{22}NO_2PS$
Formula weight	515.577
Temperature/K	296.15
Crystal system	orthorhombic
Space group	Pbca
a/Å	21.166(4)
b/Å	16.659(3)
c/Å	14.675(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5174.7(17)
Z	8
ρ_{calc}g/cm^3	1.324
μ/mm^{-1}	0.218
F(000)	2146.7
Crystal size/mm^3	0.03 × 0.025 × 0.02
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.16 to 55.04
Index ranges	-26 ≤ h ≤ 25, -19 ≤ k ≤ 21, -18 ≤ l ≤ 19
Reflections collected	29589
Independent reflections	5903 [R_{int} = 0.0668, R_{sigma} = 0.0580]
Data/restraints/parameters	5903/0/334
Goodness-of-fit on F^2	1.095
Final R indexes [I>=2σ (I)]	R_1 = 0.0551, wR_2 = 0.1224
Final R indexes [all data]	R_1 = 0.1163, wR_2 = 0.1603
Largest diff. peak/hole / e Å^{-3}	0.59/-0.58

Table s6 Bond Lengths for 4j.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	O1	1.480(2)	C1	C2	1.393(4)
P1	C6	1.786(3)	C9	C14	1.392(4)
P1	C7	1.764(3)	C9	C10	1.388(4)
P1	C9	1.800(3)	C16	C17	1.383(4)
S1	C28	1.775(3)	C28	C29	1.374(5)
S1	C27	1.751(4)	C3	C2	1.372(5)
O2	C8	1.374(3)	C3	C4	1.385(5)
O2	C1	1.382(4)	C17	C18	1.370(4)
N1	C22	1.425(4)	C5	C4	1.377(5)
N1	C21	1.439(3)	C27	C26	1.384(5)
N1	C33	1.415(4)	C18	C19	1.382(4)
C8	C15	1.480(4)	C14	C13	1.391(5)
C8	C7	1.324(4)	C10	C11	1.382(5)
C15	C21	1.395(4)	C23	C24	1.377(5)
C15	C16	1.384(4)	C32	C31	1.381(5)
C6	C1	1.392(4)	C13	C12	1.365(5)
C6	C5	1.395(4)	C29	C30	1.386(5)
C22	C27	1.401(4)	C31	C30	1.368(5)
C22	C23	1.390(4)	C12	C11	1.375(6)
C21	C19	1.389(4)	C26	C25	1.372(5)
C33	C28	1.403(4)	C24	C25	1.367(5)
C33	C32	1.382(4)			

Table s7 Bond Angles for 4j.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O1	P1	C6	114.25(14)	O2	C1	C6	124.2(3)
O1	P1	C7	116.67(14)	O2	C1	C2	114.2(3)
O1	P1	C9	110.97(14)	C6	C1	C2	121.6(3)
C6	P1	C9	106.71(14)	C8	C7	P1	125.1(2)
C7	P1	C6	99.67(15)	C14	C9	P1	121.7(2)
C7	P1	C9	107.59(14)	C10	C9	P1	119.2(2)
C27	S1	C28	99.23(15)	C10	C9	C14	119.1(3)
C8	O2	C1	122.6(2)	C17	C16	C15	120.7(3)
C22	N1	C21	116.3(2)	C33	C28	S1	119.9(3)
C33	N1	C22	122.1(2)	C29	C28	S1	118.4(3)
C33	N1	C21	119.0(2)	C29	C28	C33	121.2(3)
O2	C8	C15	110.1(2)	C2	C3	C4	120.4(3)

C7	C8	O2	125.6(3)	C18	C17	C16	120.2(3)
C7	C8	C15	124.3(3)	C4	C5	C6	122.1(3)
C21	C15	C8	120.0(2)	C22	C27	S1	120.8(3)
C16	C15	C8	120.9(3)	C26	C27	S1	119.2(3)
C16	C15	C21	119.1(3)	C26	C27	C22	119.8(3)
C1	C6	P1	122.7(2)	C17	C18	C19	120.0(3)
C1	C6	C5	117.0(3)	C18	C19	C21	120.4(3)
C5	C6	P1	120.2(2)	C3	C2	C1	119.5(3)
C27	C22	N1	120.4(3)	C13	C14	C9	119.8(3)
C23	C22	N1	121.5(3)	C5	C4	C3	119.4(3)
C23	C22	C27	118.1(3)	C11	C10	C9	120.3(3)
C15	C21	N1	118.6(2)	C24	C23	C22	120.8(3)
C19	C21	N1	121.5(3)	C31	C32	C33	120.7(3)
C19	C21	C15	119.7(3)	C12	C13	C14	120.3(4)
C28	C33	N1	120.6(3)	C28	C29	C30	120.2(3)
C32	C33	N1	121.8(3)	C30	C31	C32	121.4(4)
C32	C33	C28	117.6(3)	C13	C12	C11	120.5(4)
C12	C11	C10	120.0(4)	C31	C30	C29	118.8(4)
C24	C25	C26	119.3(4)	C25	C26	C27	121.0(4)
C25	C24	C23	120.8(4)				

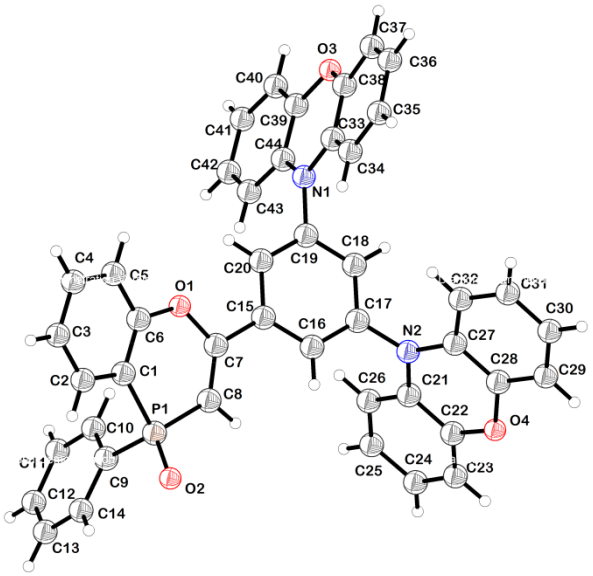


Figure s12. Crystal data and structure refinement for **4m**. CCDC reference number: 2014048

Table s8 Crystal data and structure refinement for 4m.

Identification code	4m
Empirical formula	$C_{44}H_{29}N_2O_4P$
Formula weight	680.66
Temperature/K	296.15
Crystal system	monoclinic

Space group	C2/c
a/Å	27.765(7)
b/Å	11.840(3)
c/Å	25.681(7)
α/°	90
β/°	126.333(4)
γ/°	90
Volume/Å^3	6801(3)
Z	8
ρ_{calc}g/cm^3	1.330
μ/mm^{-1}	0.130
F(000)	2832.0
Crystal size/mm^3	0.02 ×0.02 ×0.015
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.708 to 55.294
Index ranges	-18 ≤ h ≤ 36, -14 ≤ k ≤ 14, -33 ≤ l ≤ 32
Reflections collected	20206
Independent reflections	7554 [R_{int} = 0.0602, R_{sigma} = 0.0808]
Data/restraints/parameters	7554/0/460
Goodness-of-fit on F^2	0.991
Final R indexes [I>=2σ (I)]	R_1 = 0.0551, wR_2 = 0.1120
Final R indexes [all data]	R_1 = 0.1290, wR_2 = 0.1406
Largest diff. peak/hole / e Å^{-3}	0.24/-0.28

Table s9 Bond Lengths for 4m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	O2	1.4818(16)	C19	C20	1.378(3)
P1	C1	1.782(2)	C19	C18	1.379(3)
P1	C8	1.752(2)	C14	C13	1.370(4)
P1	C9	1.795(2)	C38	C33	1.400(3)
O1	C6	1.382(3)	C38	C37	1.372(4)
O1	C7	1.375(3)	C33	C34	1.372(3)
O3	C39	1.380(3)	C2	C3	1.372(4)
O3	C38	1.378(3)	C27	C28	1.389(4)
N1	C44	1.401(3)	C27	C32	1.375(4)
N1	C19	1.441(3)	C21	C22	1.392(4)
N1	C33	1.405(3)	C21	C26	1.371(4)
N2	C17	1.435(3)	C5	C4	1.369(3)
N2	C27	1.405(3)	C10	C11	1.382(4)
N2	C21	1.402(3)	C3	C4	1.383(4)
C6	C1	1.390(3)	C40	C41	1.373(4)

C6	C5	1.383(3)	C43	C42	1.381(4)
C7	C15	1.479(3)	C22	C23	1.358(5)
C7	C8	1.336(3)	C12	C13	1.365(4)
O4	C22	1.377(4)	C12	C11	1.374(4)
O4	C28	1.382(4)	C34	C35	1.385(4)
C1	C2	1.393(3)	C37	C36	1.375(4)
C15	C16	1.388(3)	C35	C36	1.377(4)
C15	C20	1.405(3)	C28	C29	1.391(5)
C9	C14	1.391(3)	C26	C25	1.389(4)
C9	C10	1.382(3)	C32	C31	1.393(5)
C44	C39	1.399(3)	C23	C24	1.360(6)
C44	C43	1.374(3)	C41	C42	1.375(4)
C16	C17	1.380(3)	C24	C25	1.383(6)
C39	C40	1.369(4)	C29	C30	1.363(6)
C17	C18	1.383(3)	C31	C30	1.361(6)

Table s10 Bond Angles for 4m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	P1	C1	114.68(10)	C19	C18	C17	119.5(2)
O2	P1	C8	116.66(10)	C13	C14	C9	120.6(3)
O2	P1	C9	110.47(10)	O3	C38	C33	121.7(2)
C1	P1	C9	107.50(11)	C37	C38	O3	117.6(2)
C8	P1	C1	99.80(11)	C37	C38	C33	120.8(3)
C8	P1	C9	106.83(11)	C38	C33	N1	118.9(2)
C7	O1	C6	122.57(17)	C34	C33	N1	123.0(2)
C38	O3	C39	118.22(18)	C34	C33	C38	118.1(2)
C44	N1	C19	120.7(2)	C3	C2	C1	121.7(3)
C44	N1	C33	119.58(19)	C28	C27	N2	118.9(3)
C33	N1	C19	118.6(2)	C32	C27	N2	123.8(3)
C27	N2	C17	120.8(2)	C32	C27	C28	117.3(3)
C21	N2	C17	119.6(2)	C22	C21	N2	119.1(3)
C21	N2	C27	119.2(2)	C26	C21	N2	122.8(3)
O1	C6	C1	123.9(2)	C26	C21	C22	118.1(3)
O1	C6	C5	114.5(2)	C4	C5	C6	119.6(2)
C5	C6	C1	121.5(2)	C11	C10	C9	120.1(3)
O1	C7	C15	110.23(18)	C2	C3	C4	119.5(3)
C8	C7	O1	124.4(2)	C39	C40	C41	121.0(3)
C8	C7	C15	125.4(2)	C5	C4	C3	120.5(3)
C22	O4	C28	118.0(3)	C44	C43	C42	121.1(3)
C6	C1	P1	122.32(18)	O4	C22	C21	121.6(3)
C6	C1	C2	117.2(2)	C23	C22	O4	117.1(4)

C2	C1	P1	120.43(18)	C23	C22	C21	121.3(4)
C16	C15	C7	120.05(19)	C13	C12	C11	120.7(3)
C16	C15	C20	118.9(2)	C33	C34	C35	121.2(3)
C20	C15	C7	121.0(2)	C12	C13	C14	119.9(3)
C7	C8	P1	125.12(19)	C38	C37	C36	120.3(3)
C14	C9	P1	118.8(2)	C12	C11	C10	119.8(3)
C10	C9	P1	122.24(19)	C36	C35	C34	120.0(3)
C10	C9	C14	118.9(2)	O4	C28	C27	121.7(3)
C39	C44	N1	118.9(2)	O4	C28	C29	116.6(4)
C43	C44	N1	123.3(2)	C27	C28	C29	121.6(4)
C43	C44	C39	117.8(2)	C21	C26	C25	120.3(4)
C17	C16	C15	120.3(2)	C37	C36	C35	119.6(3)
O3	C39	C44	121.8(2)	C27	C32	C31	121.6(4)
C40	C39	O3	117.5(2)	C22	C23	C24	120.9(4)
C40	C39	C44	120.7(3)	C40	C41	C42	118.8(3)
C16	C17	N2	119.2(2)	C41	C42	C43	120.6(3)
C16	C17	C18	120.5(2)	C23	C24	C25	119.0(4)
C18	C17	N2	120.2(2)	C30	C29	C28	119.1(4)
C20	C19	N1	120.0(2)	C30	C31	C32	119.4(5)
C20	C19	C18	120.7(2)	C24	C25	C26	120.3(4)
C18	C19	N1	119.3(2)	C31	C30	C29	121.1(5)
C19	C20	C15	120.0(2)				