Supporting information for

Regioselective Phosphinylation of Coumarins under Green LED Irradiation and Mechanism Study

Qingrui Li, Xiuli Zhao, Yabo Li, Mengmeng Huang*, Jung Keun Kim and Yangjie Wu*

College of Chemistry and Molecular Engineering, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Zhengzhou 450052, P.R. China.

Experimental details and spectroscopic data

Contents:

1. General information

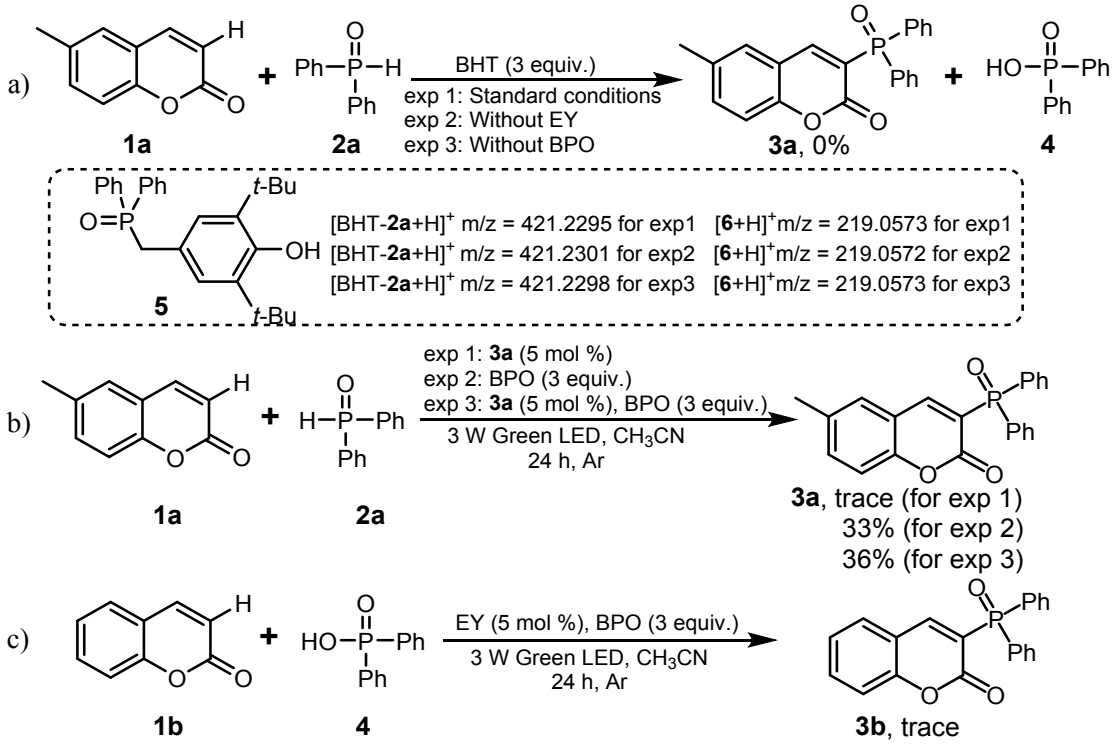
All reactions were performed under Ar atmosphere using quartz tube. Solvents were dried and degassed by standard methods before they were used. Coumarins were purchased from commercial suppliers and used without further purification. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. ^{1}H NMR spectra was recorded on a Bruker DPX-400 (400 MHz) spectrometer with deuteraterated chloroform or Dimethylsulfoxid-d6 as solutions, the chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. ^{13}C NMR spectra was recorded at 100 MHz on Bruker DPX-400. The chemical shifts δ are reported relative to residual $CHCl_3$ (δc = 77.00 ppm) or DMSO-d6 (δc = 39.52 ppm). ^{31}P NMR spectra was recorded at 160 MHz on Bruker DPX-400, the chemical shifts δ are reported relative to H_3PO_4 (δ = 0 ppm) as internal standard. The multiplicity of signals is designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd = doublet of doublet. Coupling constants *J* are reported in Hertz (Hz). High resolution mass spectra (HRMS) were obtained on an Agilent LC-MSD-Trap-XCT spectrometer with micromass MS software using electrospray ionisation (ESI). The UV/VIS Absorption spectra was recorded in DMF on a Perkin Elmer Lambda 35 Spectrometer. The Cyclic voltammetry (CV) was recorded in DMF by CHI650A. And the Luminescence Quenching Experiments were recorded using a F-4500 FL Spectrophotometer in CH_3CN.

2. Experimental Procedure

6-Methylcoumarin (32.4mg, 0.2mmol), diphenylphosphine oxide (122.5 mg, 0.6 mmol), EY (6.5mg, 0.01 mmol) and benzoyl peroxide (wetted with ca. 25% H_2O, 193.8mg, 0.6 mmol) were combined in CH_3CN (2.0 mL) under Ar atmosphere. The mixture was stirred at room temperature under green LED lamp (3 W). After 24 hours, the reaction mixture was purified by chromatography on silica gel (elute: EtOAc/Petroleum ether 1/1-2/1, v/v) to give the desired product.

3. Control Experiments

Scheme S1. Control experiments.



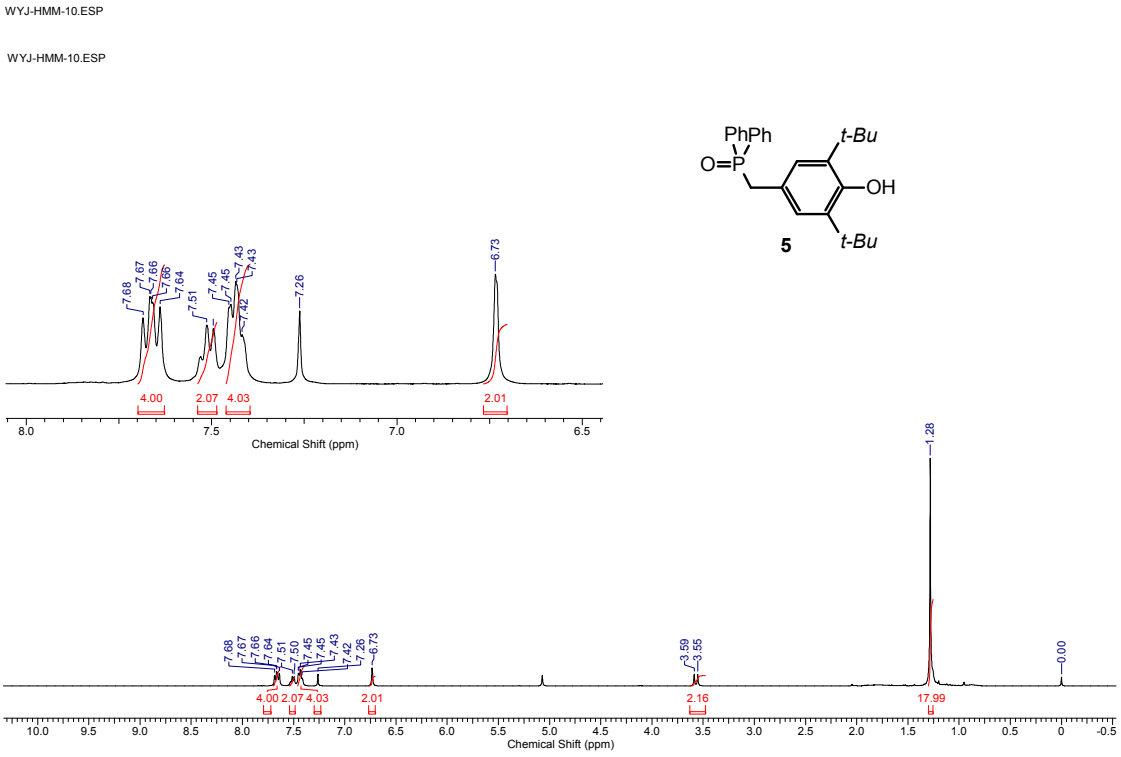


Figure S1. ^{1}H NMR spectrum of compound **5**

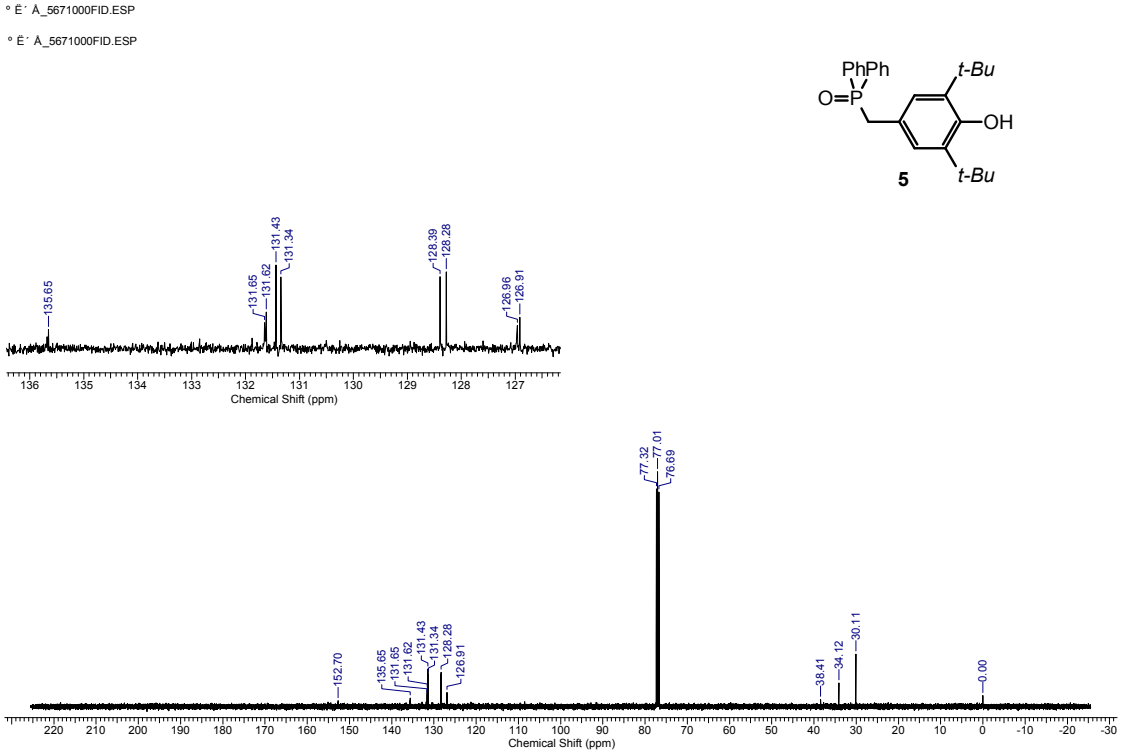


Figure S2. ^{13}C NMR spectrum of compound **5**

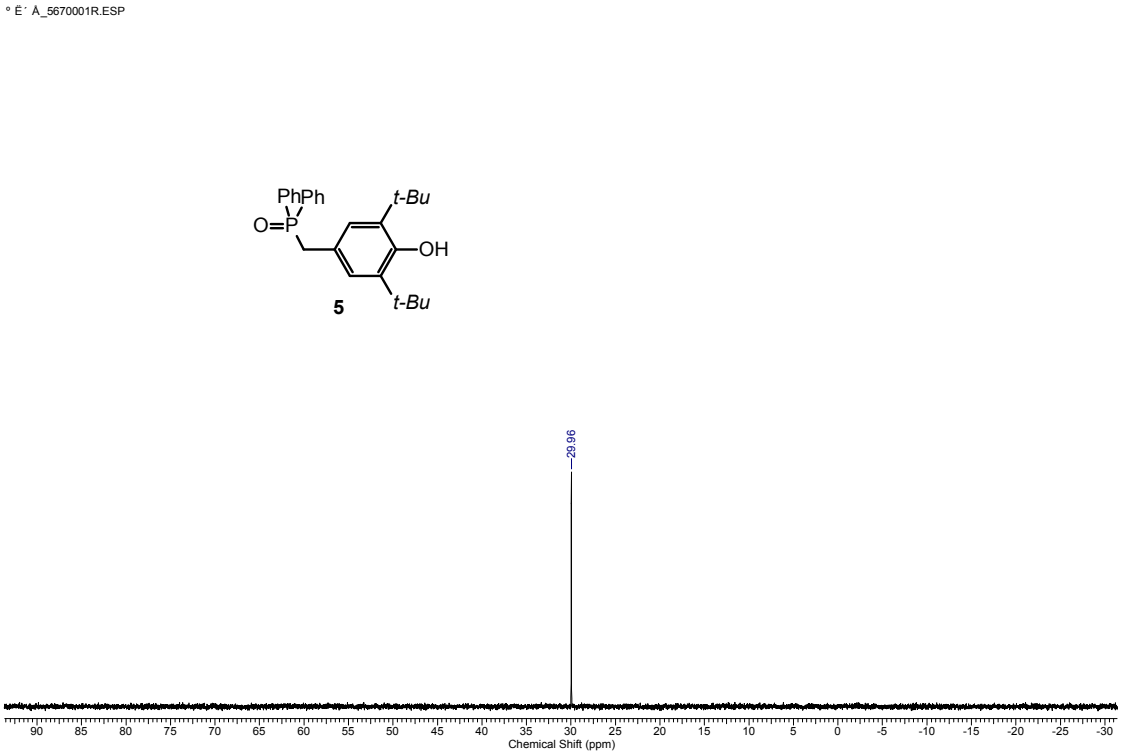


Figure S3. ^{31}P NMR spectrum of compound **5**

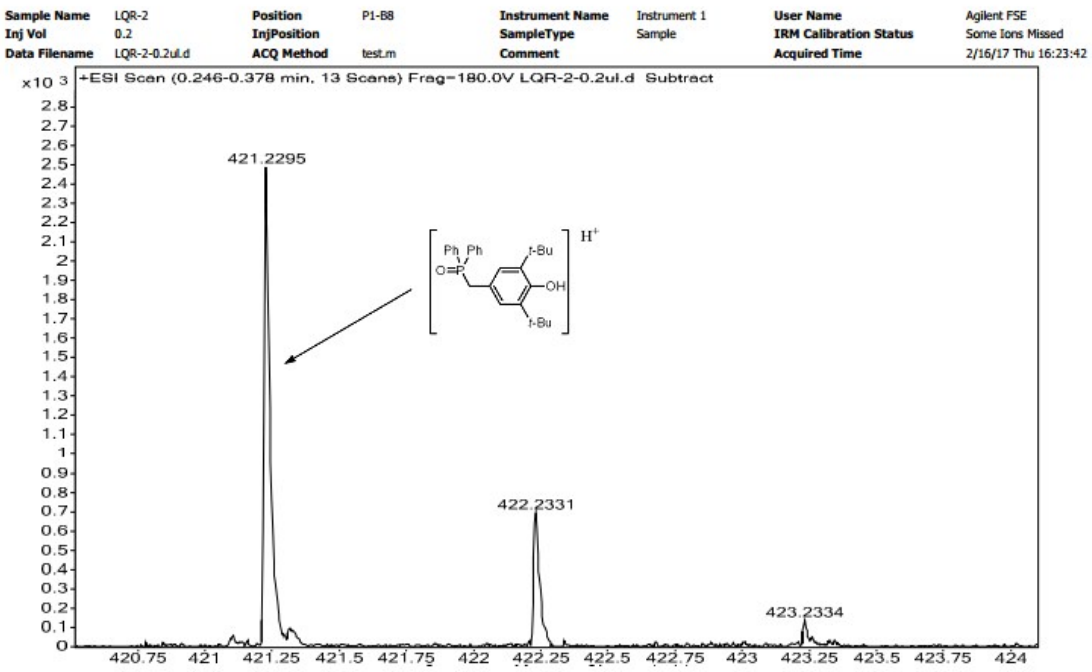


Figure S4. HRMS spectrum of compound [BHT-**2a**+H]$^+$ for exp 1

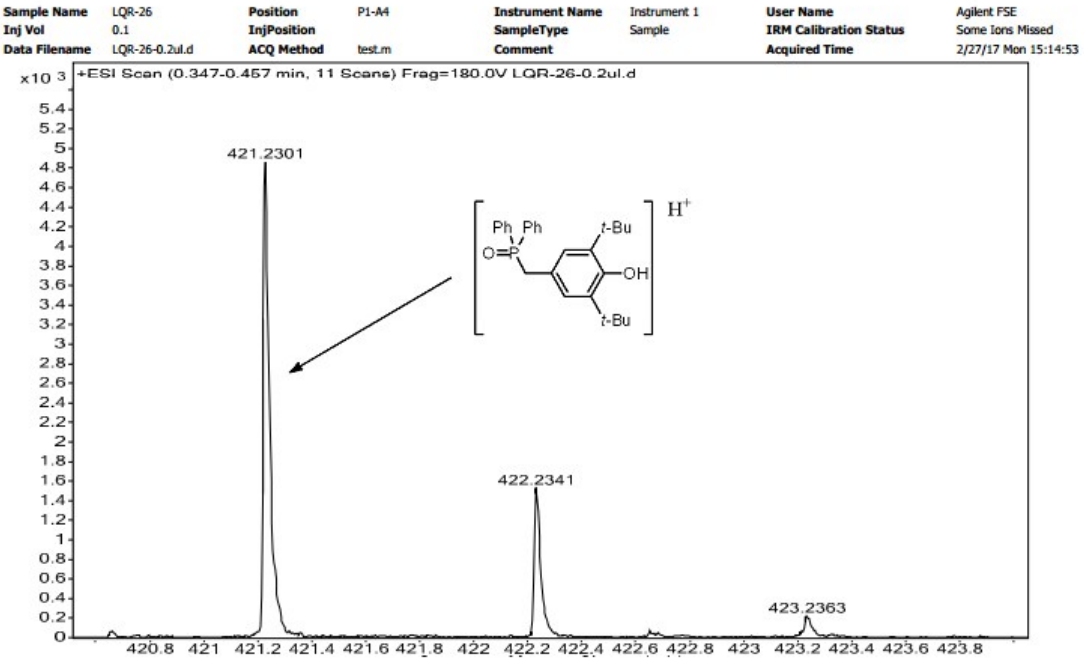


Figure S5. HRMS spectrum of compound [BHT-**2a**+H]$^+$ for exp 2

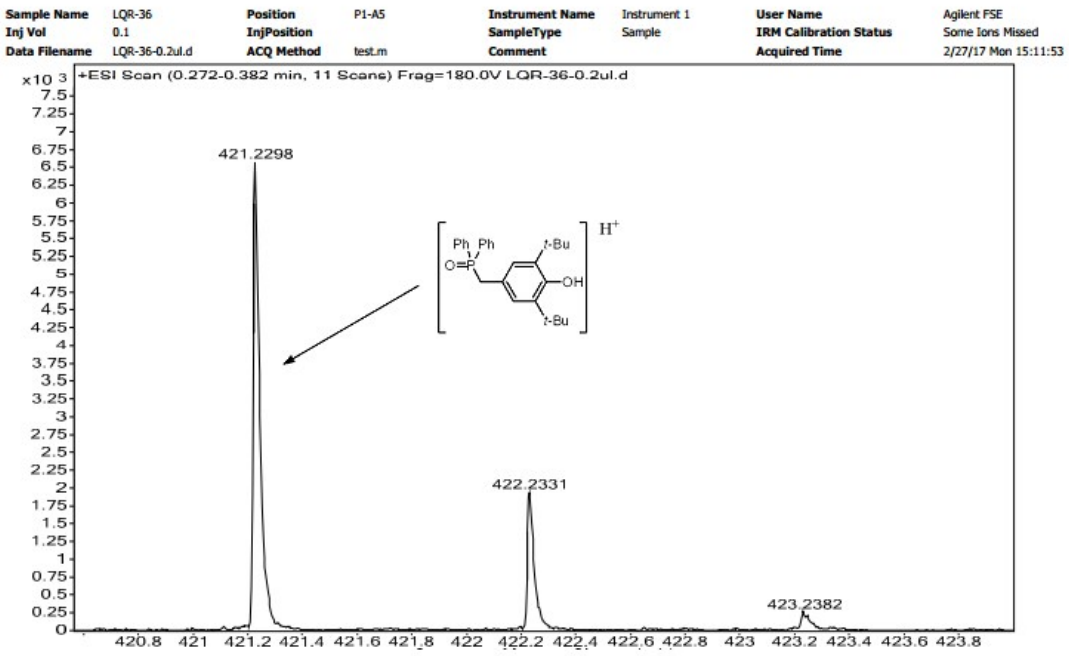


Figure S6. HRMS spectrum of compound [BHT-**2a**+H]$^+$ for exp 3

At the same time, we got another substrate **4** in the control experiments a) (**Scheme S1**).

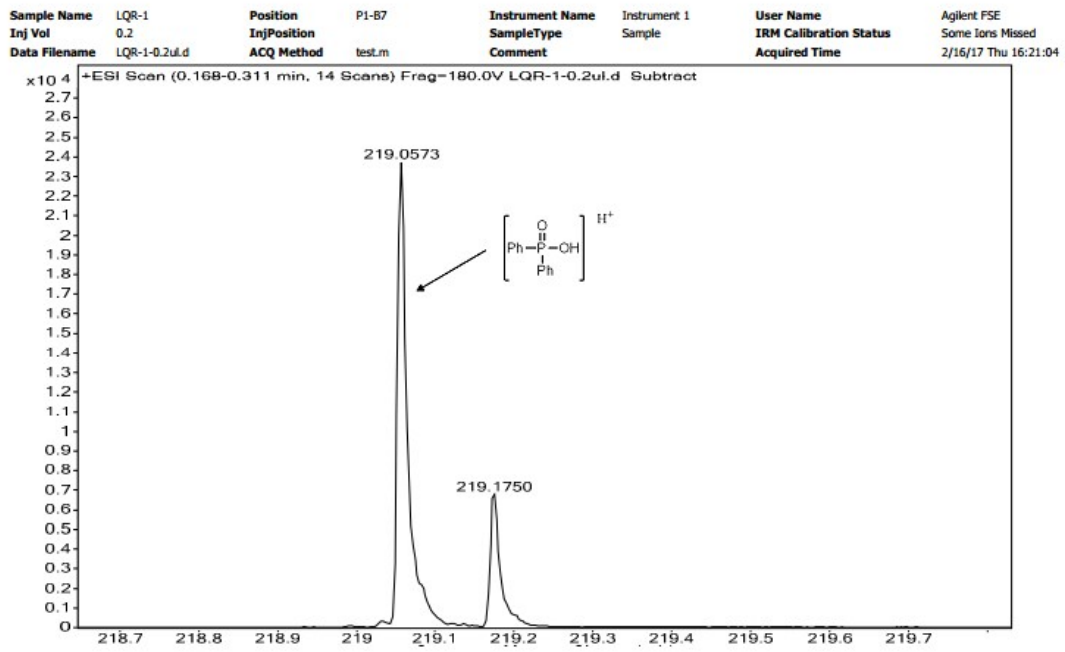


Figure S7. HRMS spectrum of compound [**4**+H]$^+$ for exp 1

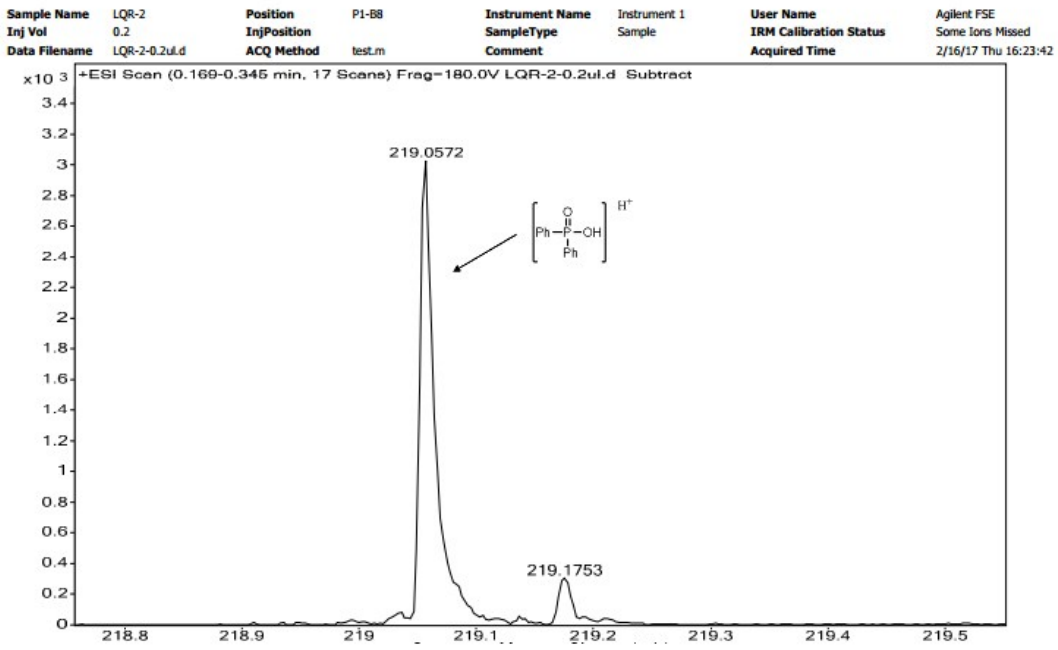


Figure S8. HRMS spectrum of compound $[4+H]^+$ for exp 2

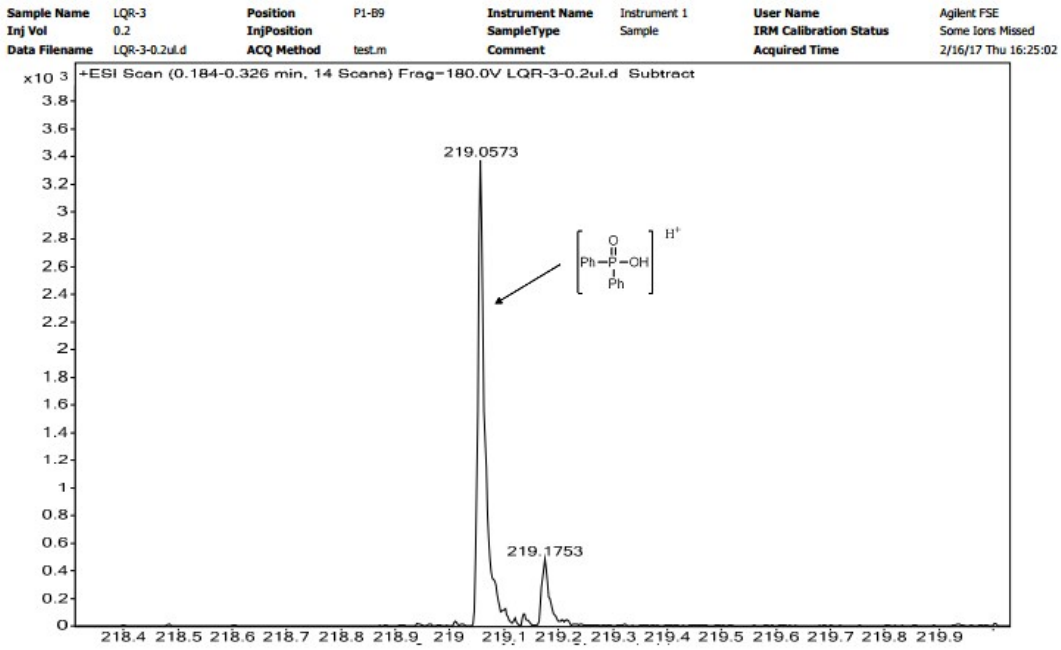
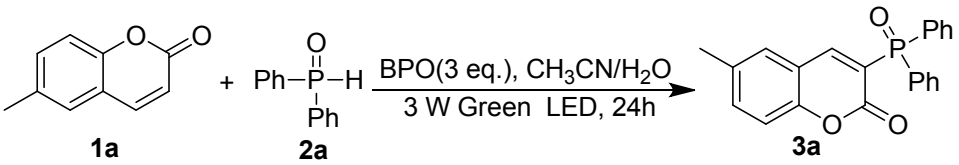


Figure S9. HRMS spectrum of compound $[4+H]^+$ for exp 3

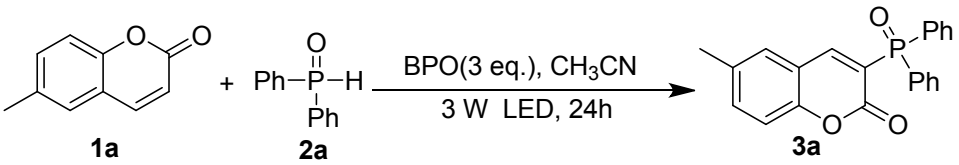
From the results, we guessed that the substrate **4** may be gotten by **2a** with the water in Benzoyl peroxide. Next, we changed the source of **2a** which is pure and doesn't include the substrate **4** to do the experiments to confirm our guess.

Scheme S3.



entry	Solvent	Yield (%)
1	CH_3CN (2 mL)	31
2	CH_3CN/H_2O (1.98 mL +0.02 mL)	58
3	CH_3CN/H_2O (1.96 mL +0.04 mL)	61
4	CH_3CN/H_2O (1.90 mL +0.10 mL)	64
5	CH_3CN/H_2O (1.87 mL +0.13 mL)	62
6	CH_3CN/H_2O (1.80 mL +0.20 mL)	57

Scheme S4. Photocatalytic activity of BPO



entry	Light Source	Yield (%)
1	3 W blue LED (470 nm)	36
2	3 W green LED (530 nm)	33
3	3 W yellow-green LED (550 nm)	29
4	3 W orange LED (610 nm)	9
5	18 W CFL (compact fluorescent light bulb)	trace

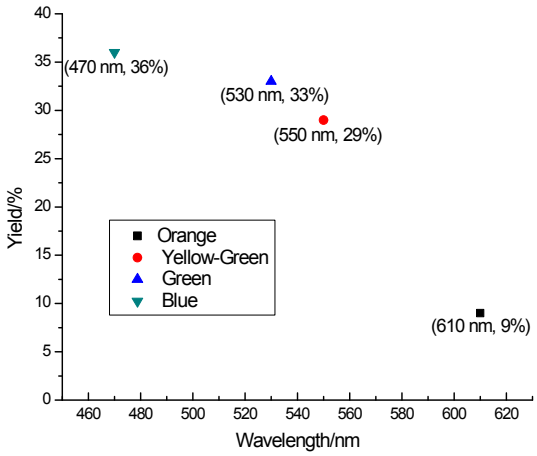


Figure S10. Photocatalytic activity of BPO

4. UV/VIS Absorption spectra, Cyclic Voltammetry Luminescence Quenching Experiments and Data processing

1) UV/VIS Absorption spectra

The UV/VIS Absorption spectra was recorded in DMF of a 0.1 mM solution in 10 mm path length quartz cuvette on a Perkin Elmer Lambda 35 Spectrometer.

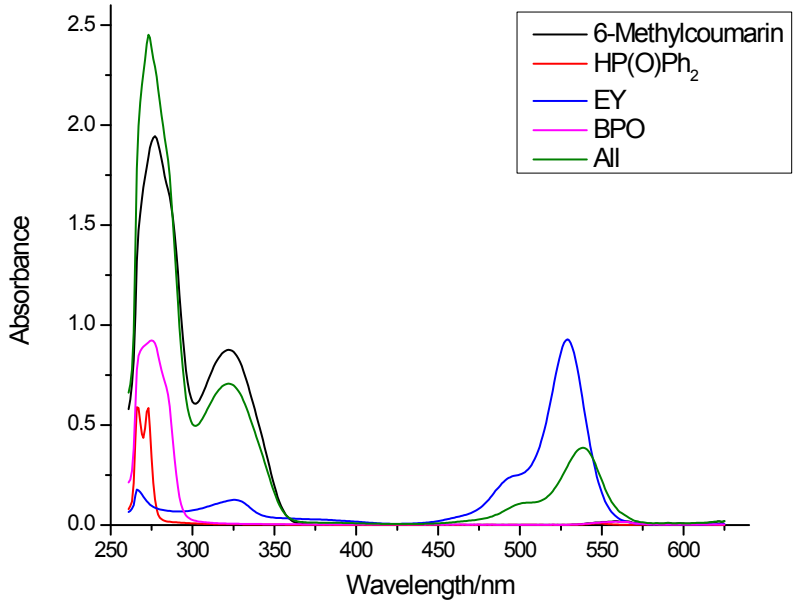


Figure S11. Absorption spectra of 6-methyl coumarin **1a** (λ_{max} = 357 nm), diphenylphosphine oxide **2a** (λ_{max} = 278 nm), **EY** (λ_{max} = 553 nm), **BPO** (λ_{max} = 294 nm) in DMF(0.1 mM) and **All** in a mixture (Reaction ratio) of DMF.

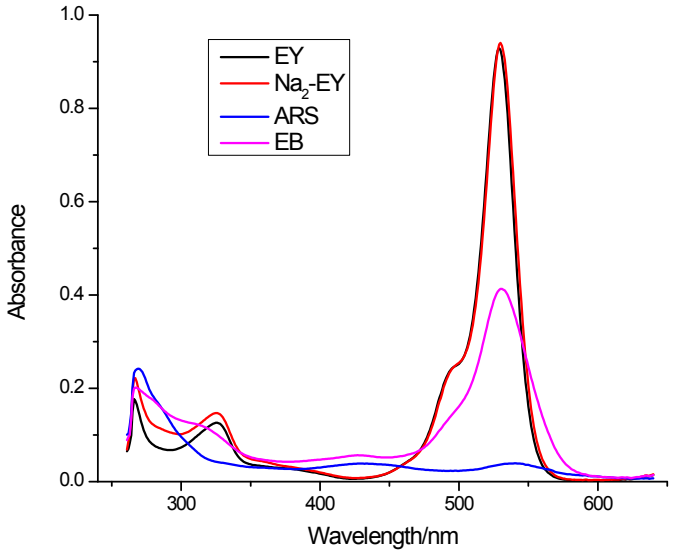


Figure S12. Absorption spectras of different catalysts: **EY** (λ_{max} = 553 nm), **Na_2-EY** (λ_{max} = 556 nm), **ARS** (λ_{max} = 503 nm), **EB** (λ_{max} = 573 nm) in DMF (0.1 mM).

2) Cyclic Voltammetry

Cyclic voltammetry was measured under Ar balloon protection with conventional three−electrode system (Reference electrode: Ag/AgCl, working electrode: Glassy carbon, counter electrode: Pt wire, Supporting electrolyte: 0.1 M $TBAPF_6$ in DMF) at 50 mV/sec of scan rate.

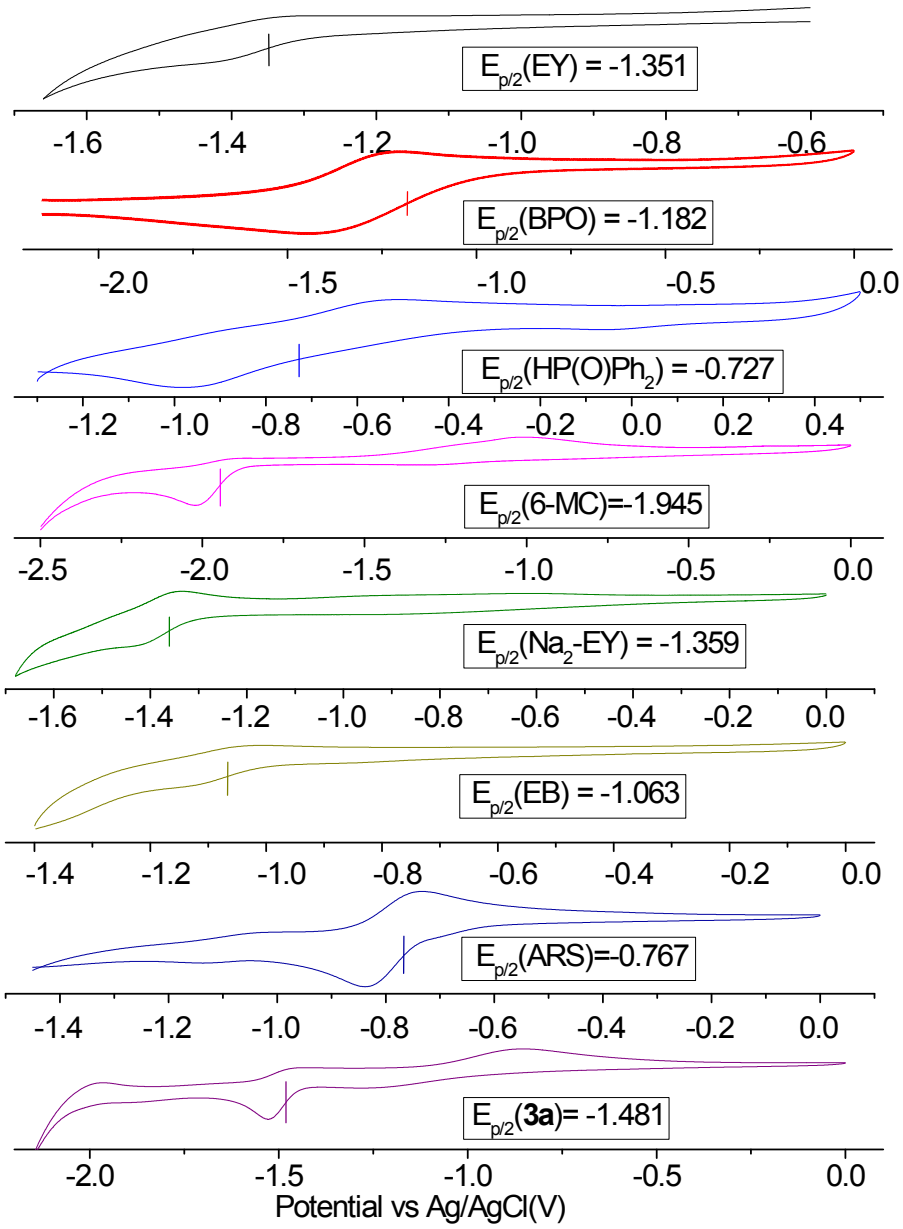


Figure S13. CV of Reaction reagents (1 mM in DMF)

3) Luminescence Quenching Experiments

Emission intensities were recorded using a F-4500 FL Spectrophotometer. First, all EY solutions were excited at 520 nm and the emission intensity at 560 nm was observed. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of EY and different concentration of 6-methyl coumarin **1a**, diphenylphosphine oxide **2a** and BPO in anhydrous CH_3CN in 10 mm path length quartz cuvette was collected. Next, the BPO solution was excited at 280 nm and the emission intensity at 310 nm was observed. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of BPO and different concentration (0.025~0.100 mM) of diphenylphosphine oxide **2a** in anhydrous CH_3CN in 10 mm path length quartz cuvette was collected.

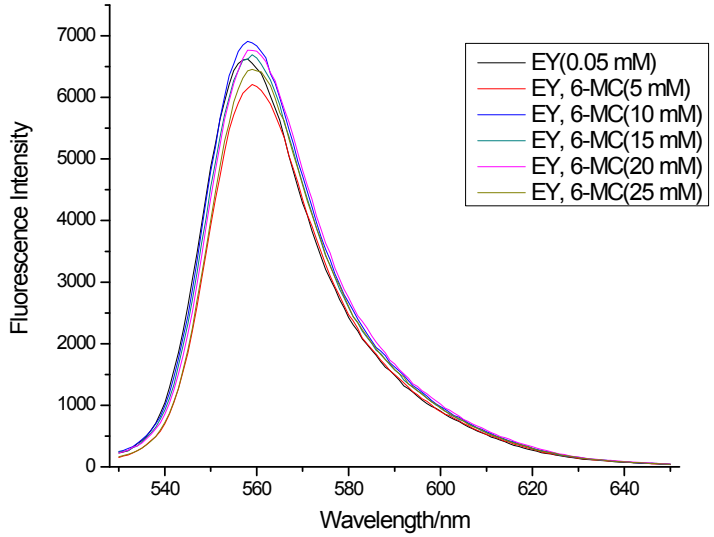


Figure S14. Luminescence quenching experiments of EY with **1a**

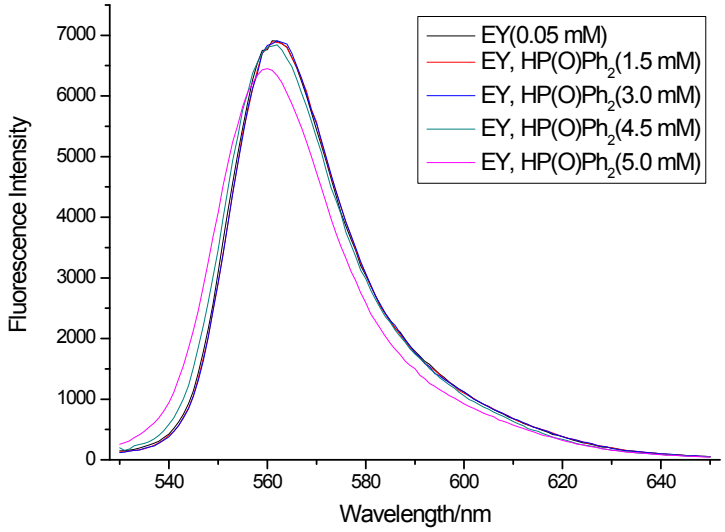


Figure S15. Luminescence quenching experiments of EY with **2a**

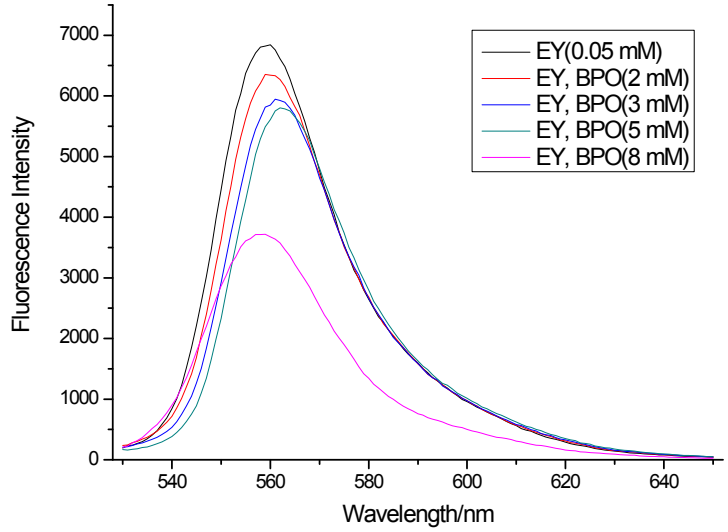


Figure S16. Luminescence quenching experiments of EY with **BPO**

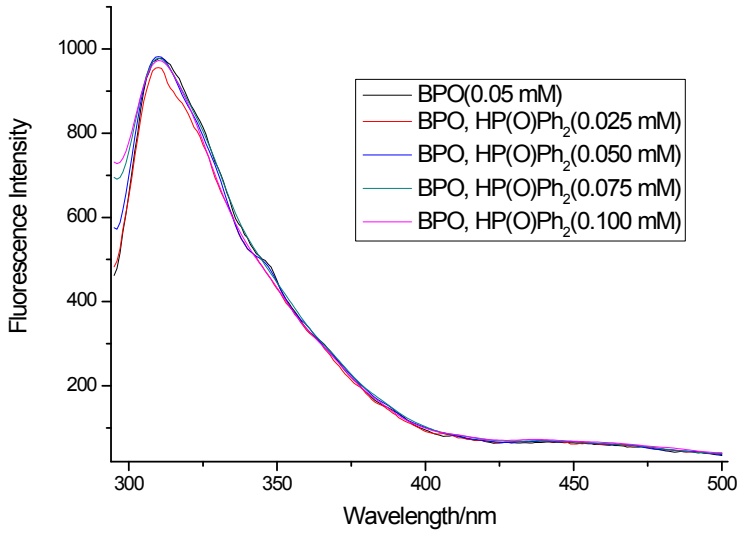


Figure S17. Luminescence quenching experiments of BPO with **2a**

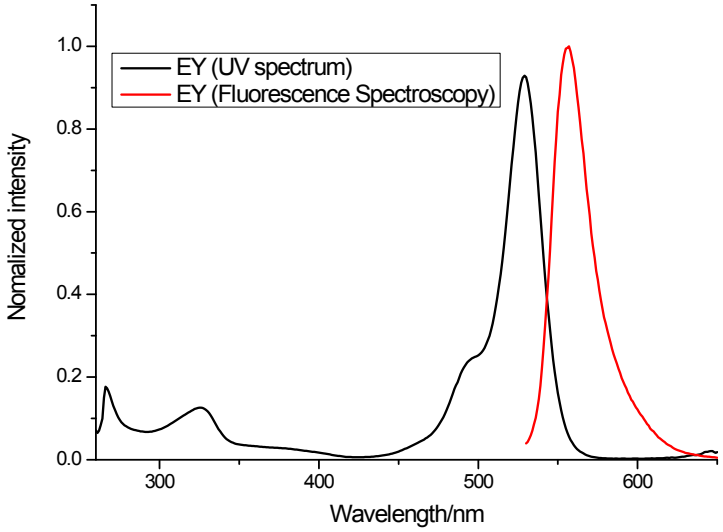


Figure S18. Nomalized experiments of UV spectrum and Fluorescence Spectroscopy about EY

4) Data processing

We could see the Reversible reduction waves of all the reagents. With these datas in hand we calculated the excited redox potential, Eg by the IFO theory [**S19**].

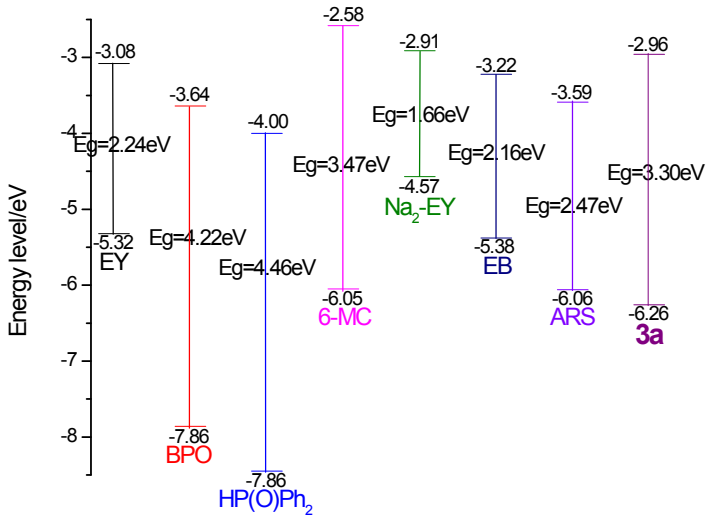
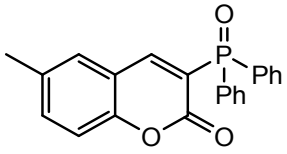


Figure S19. The E_{HOMO}, E_{LUMO} and Eg of different reagents

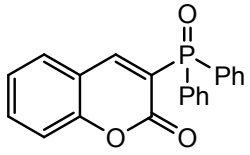
5. Characterization data

3-(diphenylphosphoryl)-6-methyl-2H-chromen-2-one (3a)[1,2]:



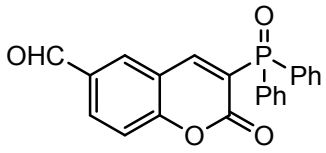
White solid (56.9 mg, 79%). mp. 235.5-237.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (d, J = 14.1 Hz, 1H), 7.91 (dd, J = 12.7 Hz, J = 7.3 Hz, 4H), 7.58-7.44 (m, 8H), 7.24 (t, J = 4.2 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.37 (d, J = 13.2 Hz), 154.00 (d, J = 4.4 Hz), 153.59, 135.27, 134.85, 132.43 (d, J = 2.9 Hz), 132.08 (d, J = 10.3 Hz), 131.19, 130.09, 129.08, 128.50 (d, J = 13.2 Hz), 121.31 (d, J = 102.7 Hz), 118.30 (d, J = 10.3 Hz), 116.53, 20.78. ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.39. HRMS (ESI) calcd. for $C_{22}H_{18}O_3P$ $(M+H)^+$: 361.0988, found: 361.0994.

3-(diphenylphosphoryl)-2H-chromen-2-one (3b)[3,4]:



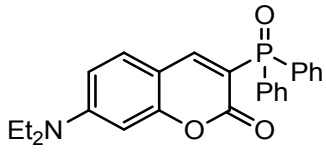
White solid (51.9 mg, 75%). mp. 202.7-204.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (d, J = 14.1 Hz, 1H), 7.92 (dd, J = 12.5 Hz, J = 7.7 Hz, 4H), 7.69-7.56 (m, 4H), 7.50-7.48 (m, 4H), 7.36-7.34 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.15 (d, J = 13.1 Hz), 155.42, 154.02 (d, J = 4.6 Hz), 134.15, 132.48 (d, J = 2.3 Hz), 132.08 (d, J = 10.8 Hz), 131.06, 129.96, 128.53 (d, J = 12.3 Hz), 125.01, 121.62 (d, J = 102.5 Hz), 118.55 (d, J = 10.8 Hz), 116.83. ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.23. HRMS (ESI) calcd. for $C_{21}H_{16}O_3P$ $(M+H)^+$: 347.0832, found: 347.0839.

3-(diphenylphosphoryl)-2-oxo-2H-chromene-6-carbaldehyde (3c):



Yellow oil (44.9 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.07 (s, 1H), 8.99 (d, J = 13.9 Hz, 1H), 8.18-8.16 (m, 2H), 7.91 (dd, J = 13.0 Hz, J = 7.2 Hz, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.62, 158.85, 153.22 (d, J = 4.6 Hz), 133.74, 133.18, 132.73 (d, J = 2.3 Hz), 132.07 (d, J = 10.8 Hz), 130.54, 129.44, 128.66 (d, J = 13.1 Hz), 124.04, 123.06, 118.72 (d, J = 10.0 Hz), 118.01. ^{31}P NMR (162 MHz, $CDCl_3$): δ 22.83. HRMS (ESI) calcd. for $C_{22}H_{16}O_4P$ $(M+H)^+$: 375.0781, found: 375.0785.

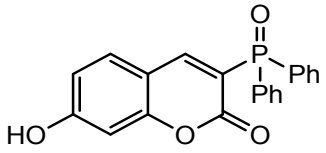
7-(diethylamino)-3-(diphenylphosphoryl)-2H-chromen-2-one (3e):



Yellow solid (56.8 mg, 68%). mp. 170.2-174.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, J = 13.8 Hz, 1H), 7.90 (dd, J = 12.7 Hz, J = 7.2 Hz, 4H), 7.55-7.40 (m, 7H), 6.62-6.59 (m, 1H), 6.45 (s, 1H), 3.44 (q, J = 7.1 Hz, 4H), 1.22 (t, J = 7.1 Hz, 6H). ^{13}C NMR

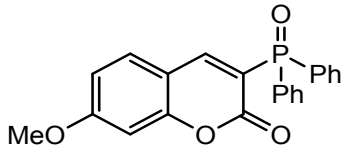
(100 MHz, $CDCl_3$): δ 160.52, 160.38, 158.54, 153.35 (d, J = 5.9 Hz), 152.49, 132.28, 132.06, 132.00, 131.95, 131.19, 130.80, 129.76, 128.31 (d, J = 12.5 Hz), 110.41 (d, J = 110.8 Hz), 109.36, 108.47 (d, J = 10.3 Hz), 96.79, 45.08, 12.42. ^{31}P NMR (162 MHz, $CDCl_3$): δ 24.72. HRMS (ESI) calcd. for $C_{25}H_{25}NO_3P$ $(M+H)^+$: 418.1567, found: 418.1569.

3-(diphenylphosphoryl)-7-hydroxy-2H-chromen-2-one (3f):



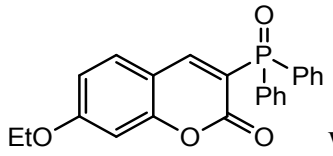
Yellow solid (53.6 mg, 74%). mp. 294.6-295.6 °C. ^{1}H NMR (400 MHz, DMSO-d6): δ 11.07 (s, 1H), 8.69 (d, J = 14.2 Hz, 1H), 7.84 (d, J = 8.9 Hz, 1H), 7.76 (dd, J = 12.1 Hz, J = 7.5 Hz, 4H), 7.64-7.61 (m, 2H), 7.55-7.54 (m, 4H), 6.86 (d, J = 6.9 Hz, 1H), 6.76 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d6): δ 164.23, 159.52 (d, J = 13.1 Hz), 157.71, 154.35 (d, J = 6.2 Hz), 132.59 (d, J = 2.3 Hz), 132.38, 132.14 (d, J = 108.7 Hz), 131.95 (d, J = 10.8 Hz), 129.00 (d, J = 12.3 Hz), 115.06 (d, J = 107.1 Hz), 114.39, 119.90 (d, J = 108.7 Hz), 111.66 (d, J = 10.8 Hz), 102.41. ^{31}P NMR (162 MHz, DMSO-d6): δ 22.12. HRMS (ESI) calcd. for $C_{21}H_{16}O_4P$ $(M+H)^+$: 363.0781, found: 363.0789.

3-(diphenylphosphoryl)-7-methoxy-2H-chromen-2-one (3g)[2]:



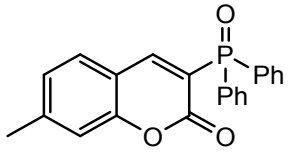
White solid (61.0 mg, 81%). mp. 172.4-174.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, J = 13.8 Hz, 1H), 7.91 (dd, J = 12.6 Hz, J = 7.7 Hz, 4H), 7.58-7.55 (m, 3H), 7.50-7.46 (m, 4H), 6.91 (d, J = 8.6 Hz, 1H), 6.82 (s, 1H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.84, 159.51 (d, J = 14.6 Hz), 157.66, 153.77 (d, J = 5.4 Hz), 132.33 (d, J = 3.1 Hz), 132.03 (d, J = 10.0 Hz), 131.47, 130.63, 130.38, 128.46 (d, J = 13.1 Hz), 116.71 (d, J = 105.6 Hz), 113.46, 112.45 (d, J = 10.0 Hz), 100.54, 56.03. ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.68. HRMS (ESI) calcd. for $C_{22}H_{18}O_4P$ $(M+H)^+$: 377.0937, found: 377.0944.

3-(diphenylphosphoryl)-7-ethoxy-2H-chromen-2-one (3h)[2]:



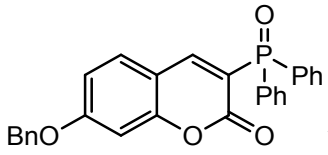
White solid (55.2 mg, 71%). mp. 154.1-156.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, J = 13.9 Hz, 1H), 7.90 (dd, J = 12.7 Hz, J = 7.3 Hz, 4H), 7.58-7.46 (m, 7H), 6.90-6.88 (m, 1H), 6.79 (s, 1H), 4.11 (q, J = 7.0 Hz, 2H), 1.46 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.26, 159.59 (d, J = 13.9 Hz), 157.68, 153.81 (d, J = 5.4 Hz), 132.31 (d, J = 2.3 Hz), 132.04 (d, J = 10.8 Hz), 131.49, 130.61, 130.39, 128.46 (d, J = 12.3 Hz), 116.45 (d, J = 105.6 Hz), 113.83, 112.32 (d, J = 10.8 Hz), 100.93, 64.53, 14.50. ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.75. HRMS (ESI) calcd. for $C_{23}H_{20}O_4P$ $(M+H)^+$: 391.1094, found: 391.1098.

3-(diphenylphosphoryl)-7-methyl-2H-chromen-2-one (3i)[2]:



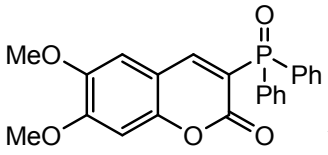
White solid (54.1 mg, 75%). mp. 190.0-191.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (d, J = 14.1 Hz, 1H), 7.91 (dd, J = 12.7 Hz, J = 7.3 Hz, 4H), 7.58-7.46 (m, 7H), 7.17-7.15 (m, 2H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.41 (d, J = 13.8 Hz), 155.59, 153.93 (d, J = 4.6 Hz), 146.07, 132.40 (d, J = 2.3 Hz), 132.06 (d, J = 10.8 Hz), 131.27, 130.16, 129.15, 128.49 (d, J = 13.1 Hz), 126.27, 119.88 (d, J = 104.0 Hz) 116.92, 116.27 (d, J = 10.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.41. HRMS (ESI) calcd. for $C_{22}H_{18}O_3P$ $(M+H)^+$: 361.0988, found: 361.0995.

7-(benzyloxy)-3-(diphenylphosphoryl)-2H-chromen-2-one (3j):



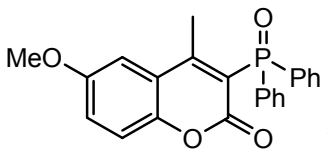
Yellow oil (67.0 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, J = 13.9 Hz, 1H), 7.90 (dd, J = 12.7 Hz, J = 7.6 Hz, 4H), 7.57-7.54 (m, 3H), 7.49-7.34 (m, 9H), 6.98-6.96 (m, 1H), 6.87 (s, 1H), 5.14 (s, 2H). ^{13}C NMR (100 MHz, CDCl3): δ 163.83, 159.50 (d, J = 13.9 Hz), 157.55, 153.75 (d, J = 4.6 Hz), 135.34, 132.35 (d, J = 3.1 Hz), 132.00 (d, J = 10.8 Hz), 131.42, 130.68, 130.32, 128.85, 128.48 (d, J = 13.1 Hz), 127.52, 116.85 (d, J = 104.8 Hz), 114.12, 112.63 (d, J = 10.0 Hz), 101.56, 70.73. ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.68. HRMS (ESI) calcd. for $C_{28}H_{22}O_4P$ $(M+H)^+$: 453.1250, found: 453.1259.

3-(diphenylphosphoryl)-6,7-dimethoxy-2H-chromen-2-one (3k):



Yellow solid (69.0 mg, 85%). mp. 264.5-267.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, J = 13.9 Hz, 1H), 7.91 (dd, J = 12.7 Hz, J = 7.2 Hz, 4H), 7.58-7.46 (m, 6H), 7.00 (s, 1H), 6.84 (s, 1H), 3.95 (d, J = 13.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.67 (d, J = 13.9 Hz), 155.05, 153. 55 (d, J = 5.1 Hz), 152.20, 146.78, 132.31 (d, J = 2.9 Hz), 132.04 (d, J = 11.0 Hz), 131.51, 130.42, 128.45 (d, J = 12.5 Hz), 117.98 (d, J = 105.6 Hz), 111.45 (d, J = 11.0 Hz), 108.64, 99.57, 56.53 (d, J = 24.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.70. HRMS (ESI) calcd. for $C_{23}H_{20}O_5P$ $(M+H)^+$: 407.1043, found: 407.1048.

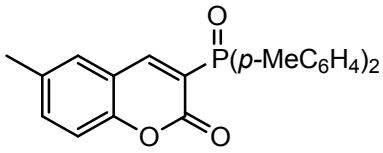
3-(diphenylphosphoryl)-6-methoxy-4-methyl-2H-chromen-2-one (3l):



White solid (30.3 mg, 39%). mp. 213.0-215.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, J = 12.7 Hz, J = 7.3 Hz, 4H), 7.56-7.45 (m, 6H), 7.25-7.17 (m, 3H), 3.89 (s, 3H), 3.18 (d, J = 1.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.10 (d, J = 5.9 Hz), 159.76 (d, J = 14.7 Hz), 156.17, 148.32, 133.23, 132.13, 131.90 (d, J = 2.9 Hz), 131.72 (d, J = 10.3 Hz), 121.24, 121.13 (d, J = 10.3 Hz), 118.01, 117.94 (d, J = 103.4 Hz), 107.98, 55.96, 15.78 (d, J = 3.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.28. HRMS (ESI) calcd. for $C_{23}H_{20}O_4P$ $(M+H)^+$:

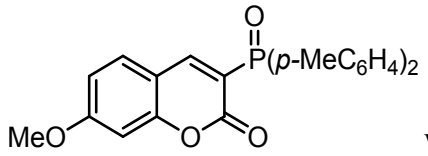
391.1094, found: 391.1094.

3-(di-*p*-tolylphosphoryl)-6-methyl-2H-chromen-2-one (3m):



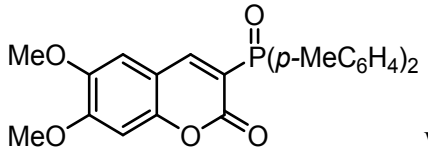
Yellow oil (44.2 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (d, J = 14.1 Hz, 1H), 7.78 (dd, J = 12.6 Hz, J = 8.0 Hz, 4H), 7.43-7.41 (m, 2H), 7.29-7.27 (m, 4H), 7.23 (d, J = 9.1 Hz, 1H), 2.42 (s, 3H), 2.40 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.39 (d, J = 13.9 Hz), 153.64 (d, J = 4.6 Hz), 153.53, 142.91 (d, J = 3.1 Hz), 135.10, 134.74, 132.08 (d, J = 10.8 Hz), 129.24 (d, J = 13.1 Hz), 129.03, 128.03, 126.91, 121.20 (d, J = 102.5 Hz), 118.34 (d, J = 10.2 Hz), 116.48, 21.70, 20.79. ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.50. HRMS (ESI) calcd. for $C_{24}H_{22}O_3P$ $(M+H)^+$: 389.1301, found: 389.1306.

3-(di-*p*-tolylphosphoryl)-7-methoxy-2H-chromen-2-one (3n):



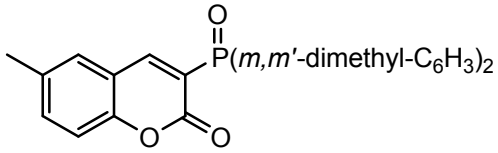
White solid (64.7 mg, 84%). mp. 157.7-160.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (d, J = 13.9 Hz, 1H), 7.78 (dd, J = 12.6 Hz, J = 8.0 Hz, 4H), 7.55 (d, J = 8.7 Hz, 1H), 7.28-7.27 (m, 4H), 6.90 (dd, J = 8.6 Hz, J = 2.2 Hz, 1H), 6.80 (s, 1H), 3.88 (s, 3H), 2.40 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.70, 159.54 (d, J = 13.9 Hz), 157.60, 153.45 (d, J = 5.1 Hz), 142.79 (d, J = 2.2 Hz), 132.05 (d, J = 11.0 Hz), 130.58, 129.20 (d, J = 13.2 Hz), 128.31, 127.19, 117.17 (d, J = 105.6 Hz), 113.36, 112.51 (d, J = 10.3 Hz), 100.50, 56.00, 21.68. ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.78. HRMS (ESI) calcd. for $C_{24}H_{22}O_4P$ $(M+H)^+$: 405.1250, found: 405.1250.

3-(di-*p*-tolylphosphoryl)-6,7-dimethoxy-2H-chromen-2-one (3o):



White powder (78.1 mg, 90%). mp. 243.1-245.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (d, J = 13.9 Hz, 1H), 7.78 (dd, J = 12.5 Hz, J = 8.1 Hz, 4H), 7.28-7.27 (m, 4H), 6.99 (s, 1H), 6.83 (s, 1H), 3.95 (d, J = 13.8 Hz, 6H), 2.40 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.68 (d, J = 13.9 Hz), 154.90, 153.23 (d, J = 5.4 Hz), 152.11, 146.72, 142.71 (d, J = 3.1 Hz), 132.05 (d, J = 11.6 Hz), 129.18 (d, J = 13.1 Hz), 128.36, 127.25, 117.47 (d, J = 104.8 Hz), 111.49 (d, J = 10.8 Hz), 108.64, 99.55, 56.51 (d, J = 22.4 Hz), 21.68. ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.78. HRMS (ESI) calcd. for $C_{25}H_{24}O_5P$ $(M+H)^+$: 435.1356, found: 435.1365.

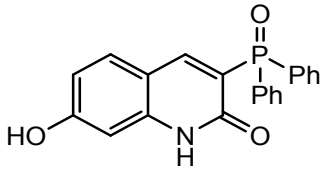
3-(bis(3,5-dimethylphenyl)phosphoryl)-6-methyl-2H-chromen-2-one (3p):



Yellow oil (32.5 mg, 39%). ^{1}H NMR (400 MHz,

$CDCl_3$): δ 8.80 (d, J = 13.9 Hz, 1H), 7.50 (d, J = 13.1 Hz, 4H), 7.42 (s, 2H), 7.25-7.23 (m, 1H), 7.18 (s, 2H), 2.43 (s, 3H), 2.33 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.37 (d, J = 13.2 Hz), 153.68 (d, J = 5.1 Hz), 153.54, 138.19 (d, J = 13.2 Hz), 135.07, 134.74, 134.20 (d, J = 2.9 Hz), 130.94, 129.85, 129.49 (d, J = 11.0 Hz), 129.02, 121.73 (d, J = 101.2 Hz), 118.39 (d, J = 10.3 Hz), 116.50, 21.36, 20.78. ^{31}P NMR (162 MHz, $CDCl_3$): δ 24.13. HRMS (ESI) calcd. for $C_{26}H_{26}O_3P$ $(M+H)^+$: 417.1614, found: 417.1620.

3-(diphenylphosphoryl)-7-hydroxyquinolin-2(1H)-one (3q):



White powder (61.9 mg, 86%). mp. 297.3-298.9 °C. ^{1}H NMR (400 MHz, DMSO-d6): δ 12.90 (s, 1H), 11.78 (s, 1H), 10.61 (s, 1H), 8.56 (d, J = 14.3 Hz, 1H), 7.96 (d, J = 6.4 Hz, 1H), 7.78-7.73 (m, 4H), 7.58 (d, J = 5.6 Hz, 2H), 7.51 (s, 4H), 6.74 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d6): δ 167.79, 162.39, 161.36 (d, J = 11.6 Hz), 149.78 (d, J = 6.2 Hz), 143.45, 133.90, 133.35, 132.83, 132.11 (d, J = 2.3 Hz), 131.88 (d, J = 10.8 Hz), 131.86, 131.19, 129.73, 129.05, 128.71 (d, J = 12.3 Hz), 119.90 (d, J = 108.7 Hz), 113.14, 112.56 (d, J = 12.3 Hz), 99.99. ^{31}P NMR (162 MHz, DMSO-d6): δ 23.10. HRMS (ESI) calcd. for $C_{21}H_{17}NO_3P$ $(M+H)^+$: 362.0941, found: 362.0946.

References:

1. J.-W., Yuan, Y.-Z., Li, L.-R., Yang, W.-P., Mai, P., Mao, Y.-M., Xiao, L.-B., Qu, *Tetrahedron*, 2015, **71**, 8178.
2. I., Kim, M., Min, D., Kang, K., Kim, S.-W., Hong, *Org. Lett.*, 2017, **19**, 1394.
3. P., Bouyssou, J., ChenauIt, *Tetrahedron Letters*, 1991, **32**, 5341.
4. L.-R., Yang, X.-C., Zhang, J.-W., Yuan, Y.-M., Xiao, P., Mao, *Journal of Organometallic Chemistry*, 2016, **818**, 179.

6. ^{1}H, ^{13}C and ^{31}P NMR spectra

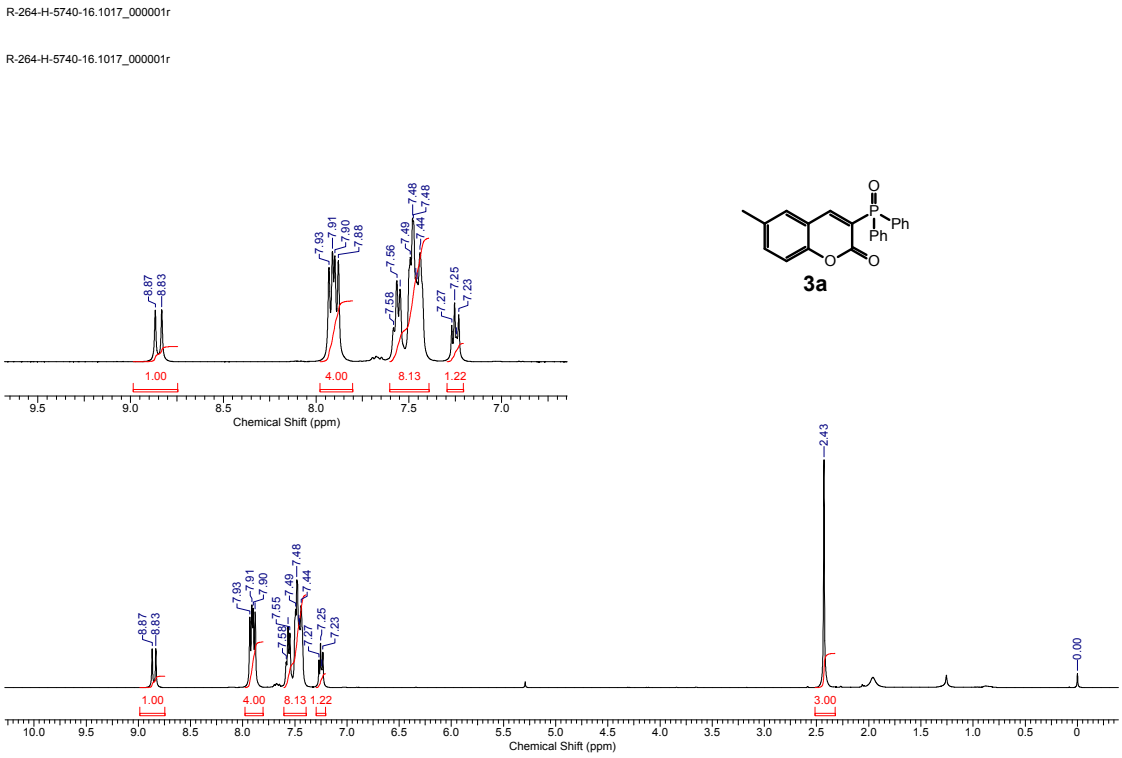


Figure S20. ^{1}H NMR spectrum of compound **3a**

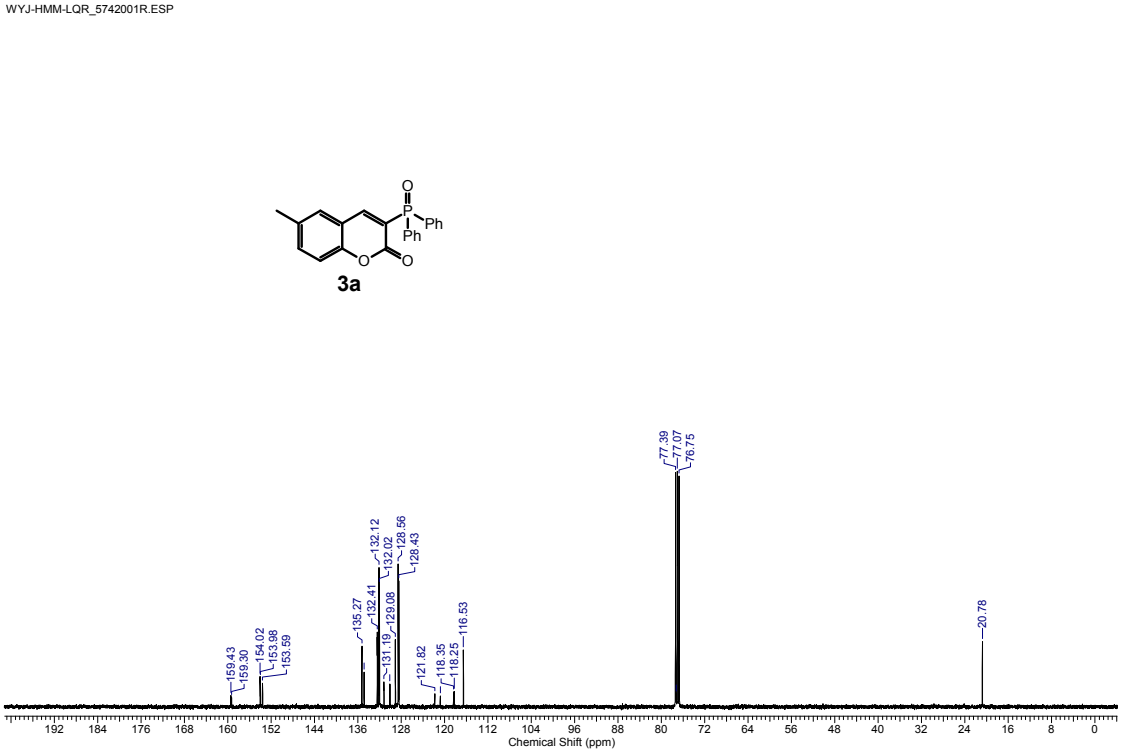
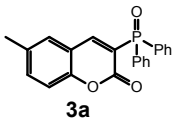


Figure S21. ^{13}C NMR spectrum of compound **3a**

R-264-P-5741-16.10.17_000001r



3a

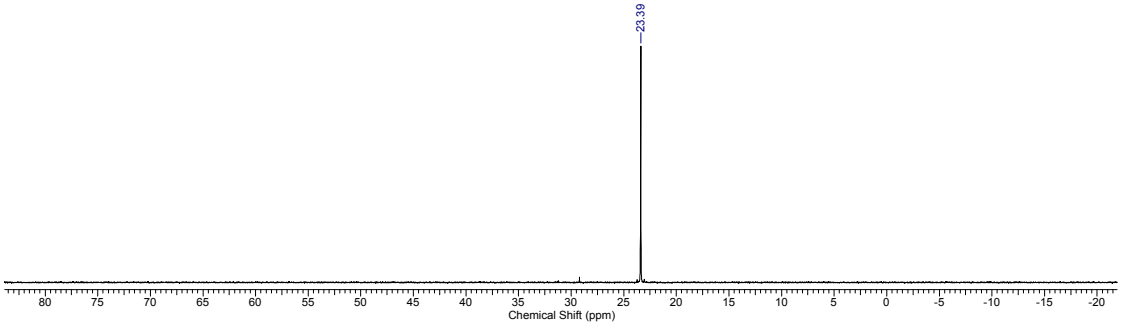
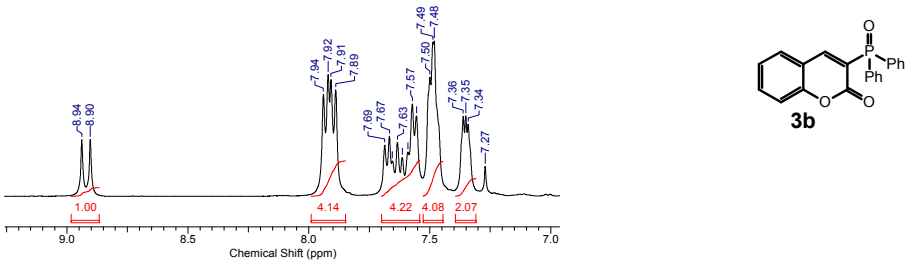


Figure S22. ^{31}P NMR spectrum of compound **3a**

LQR-4 1770_000001R.ESP

LQR-4 1770_000001R.ESP



3b

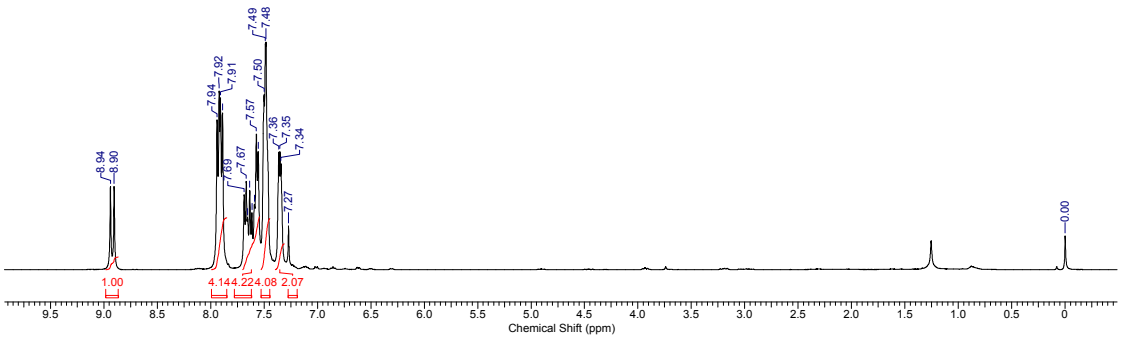


Figure S23. ^{1}H NMR spectrum of compound **3b**

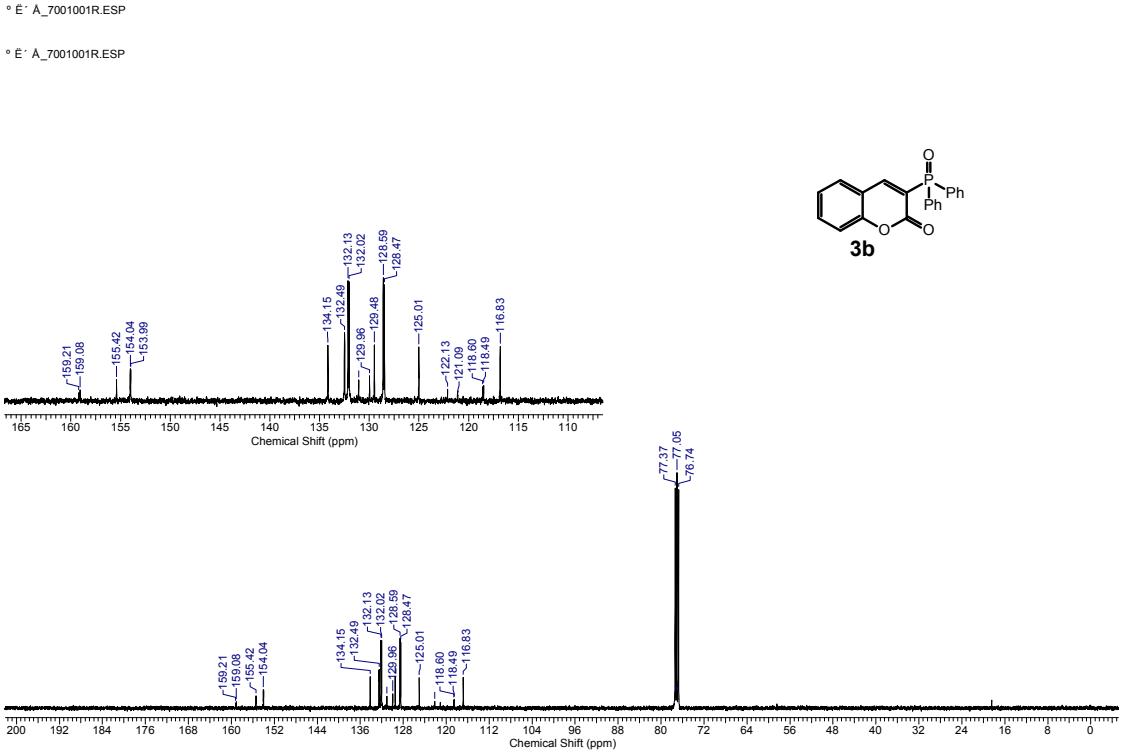


Figure S24. ^{13}C NMR spectrum of compound **3b**

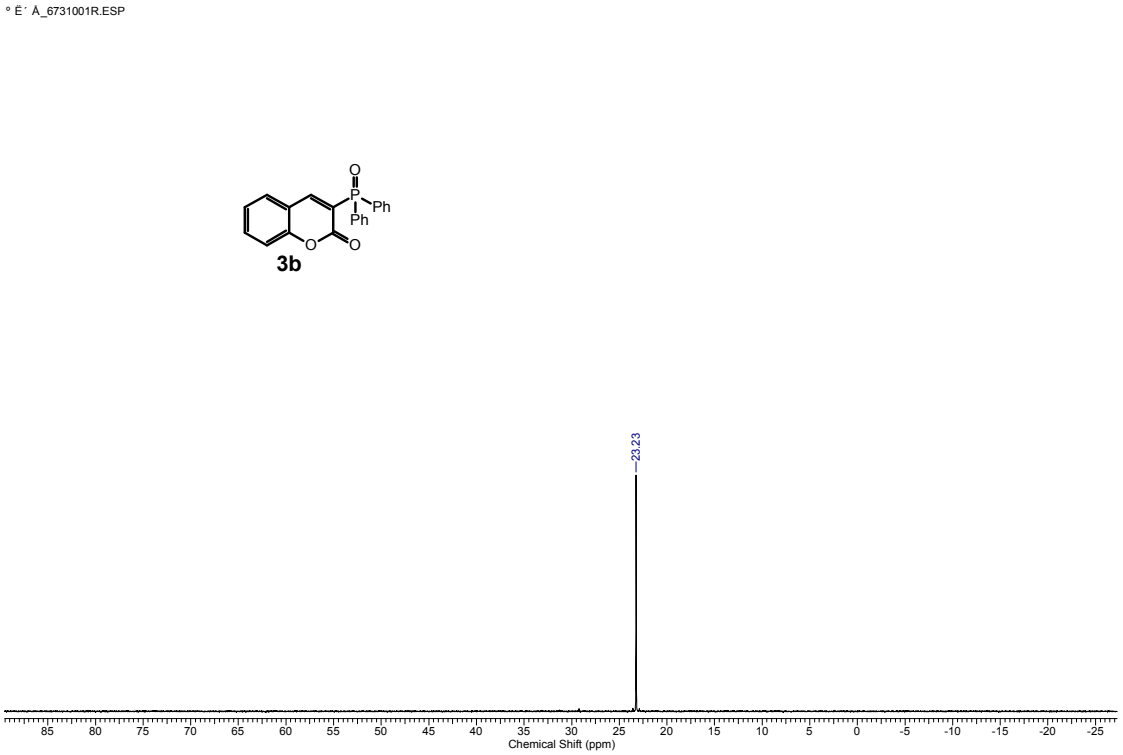


Figure S25. ^{31}P NMR spectrum of compound **3b**

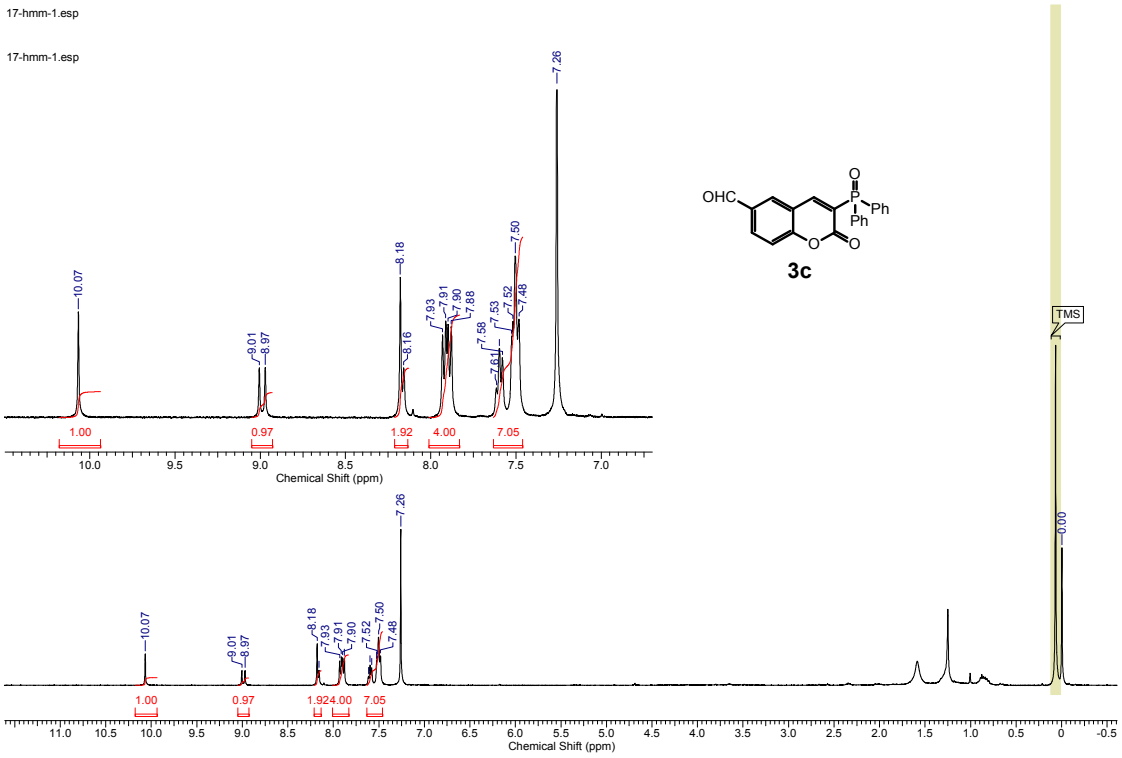


Figure S26. ^{1}H NMR spectrum of compound **3c**

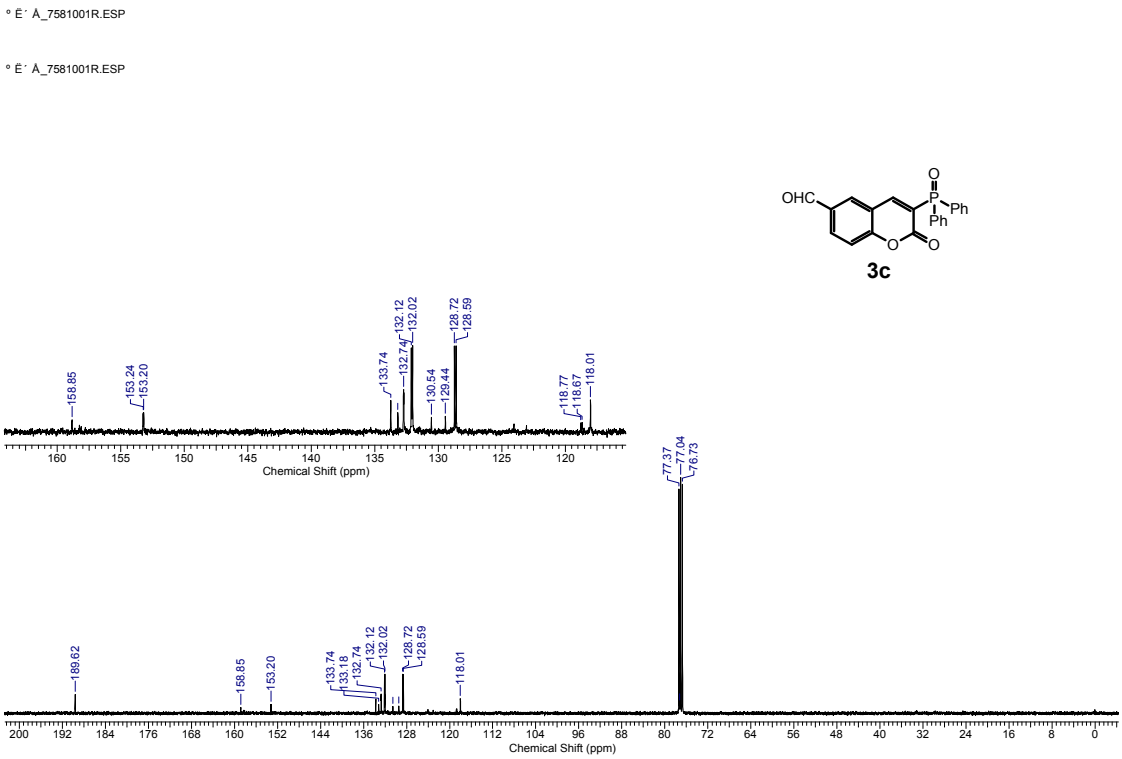


Figure S27. ^{13}C NMR spectrum of compound **3c**

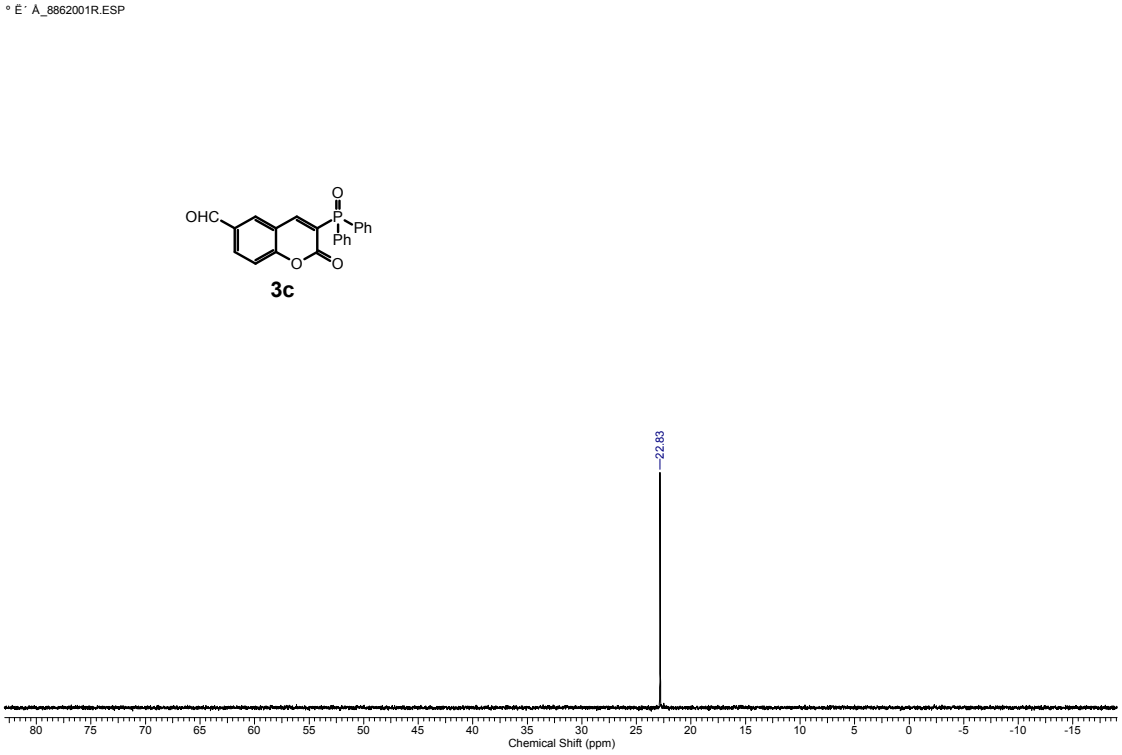


Figure S28. ^{31}P NMR spectrum of compound **3c**

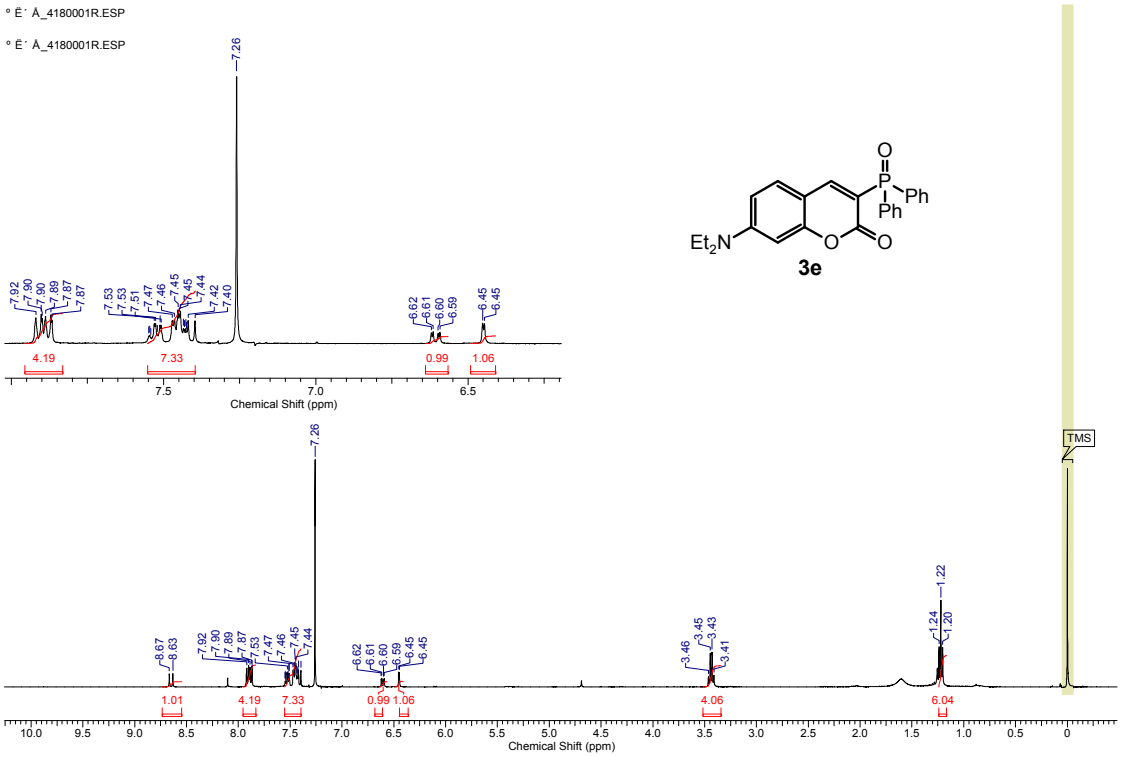


Figure S29. ^{1}H NMR spectrum of compound **3e**

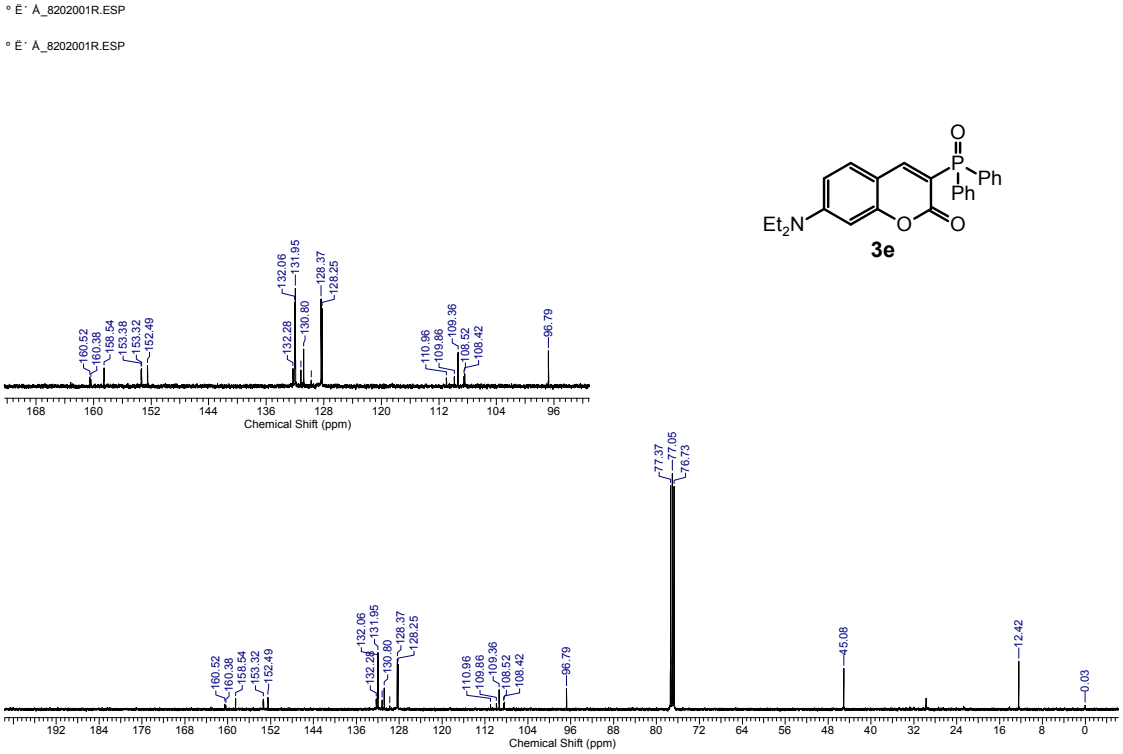


Figure S30. ^{13}C NMR spectrum of compound **3e**

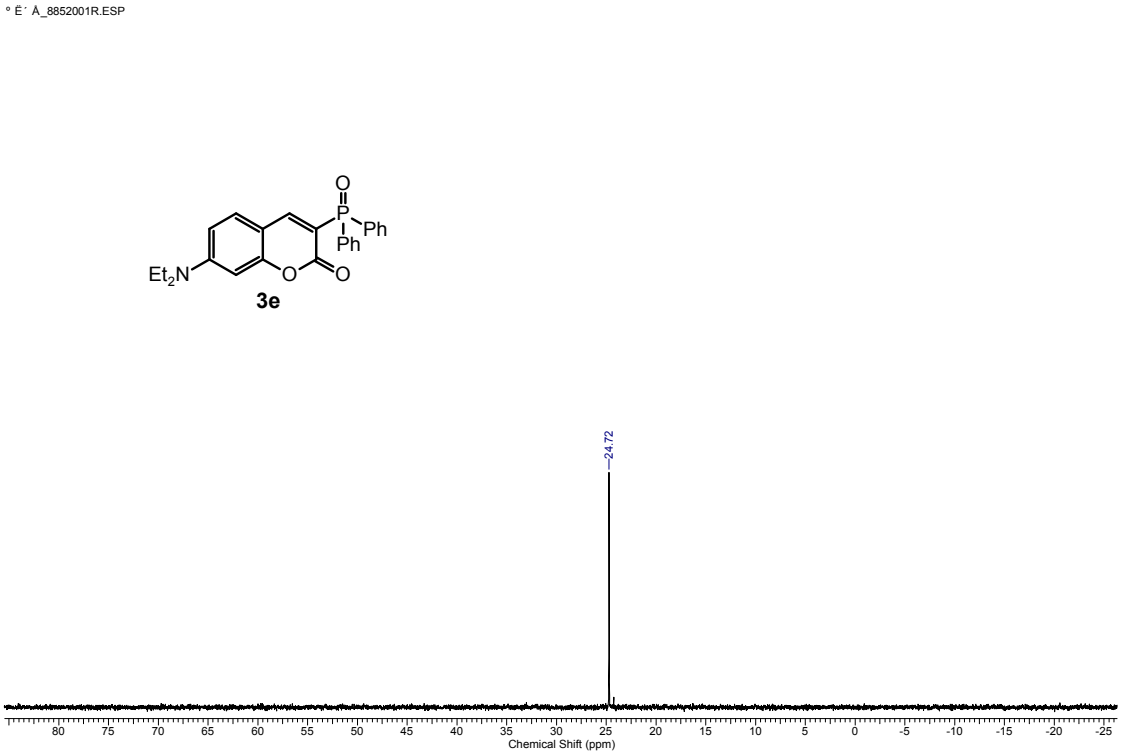


Figure S31. ^{31}P NMR spectrum of compound **3e**

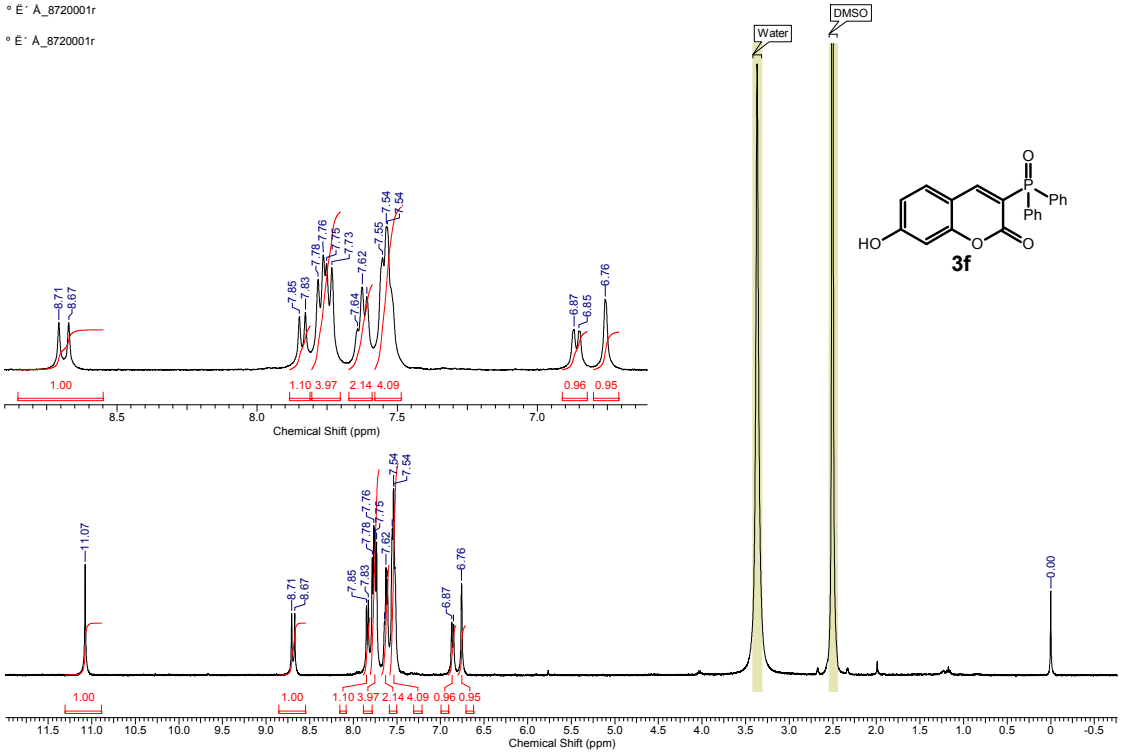


Figure S32. ^{1}H NMR spectrum of compound **3f**

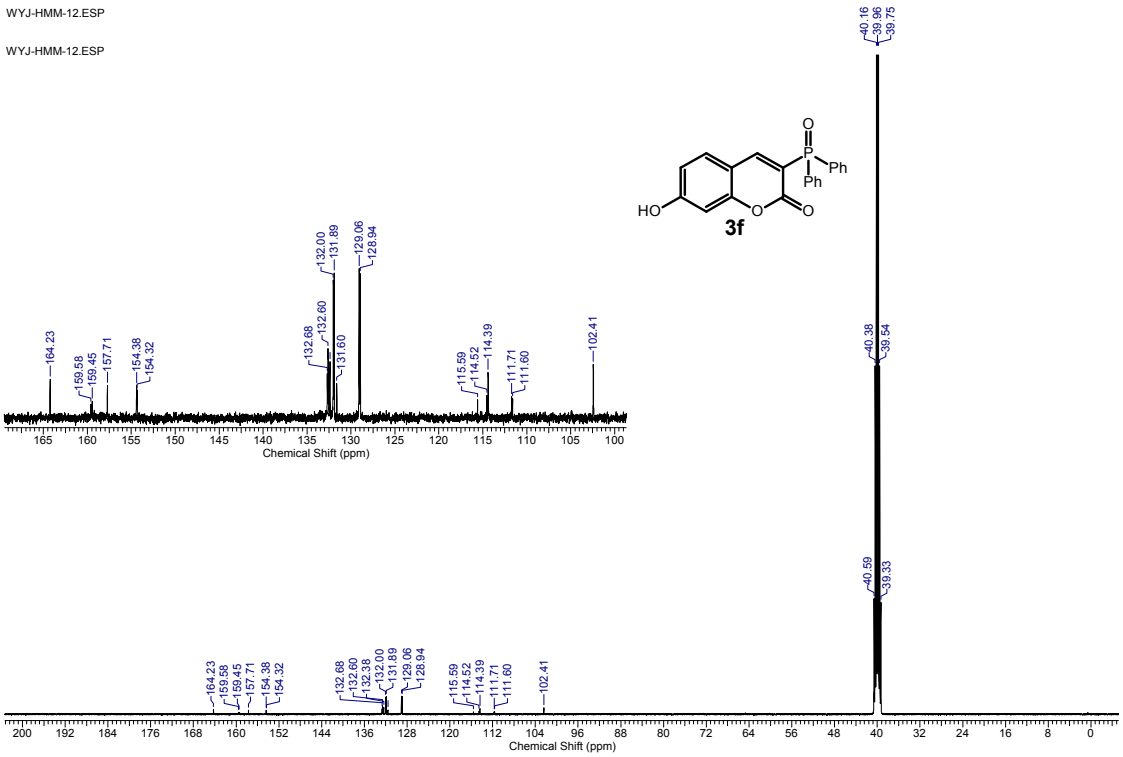
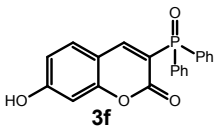


Figure S33. ^{13}C NMR spectrum of compound **3f**

° Ê´ À_8721001R.ESP



3f

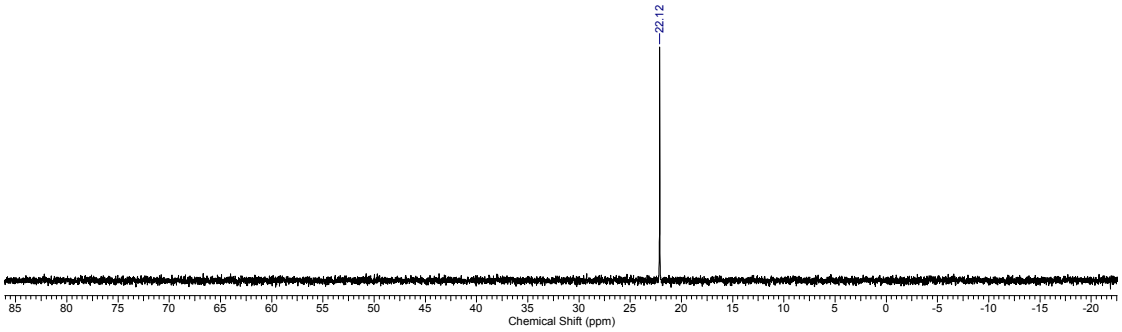
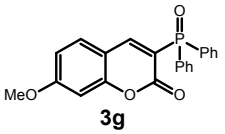


Figure S34. ^{31}P NMR spectrum of compound **3f**

R-280-7310_000001r

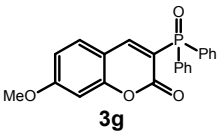
R-280-7310_000001r



3g

Figure S35. ^{1}H NMR spectrum of compound **3g**

° Ë´ Ä_7471001R.ESP



3g

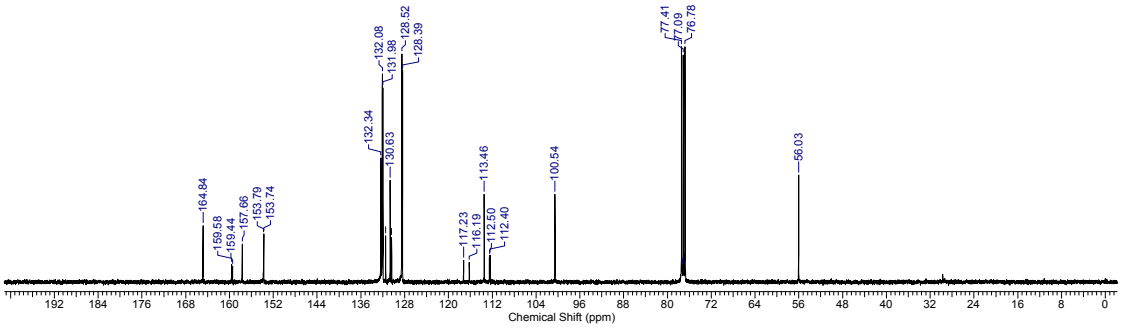
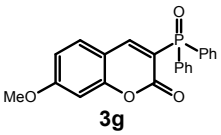


Figure S36. ^{13}C NMR spectrum of compound **3g**

° Ë´ Ä_6751001R.ESP



3g

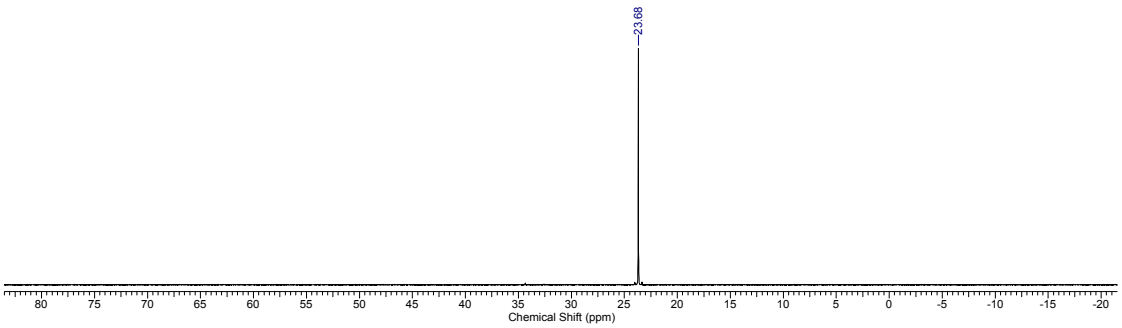


Figure S37. ^{31}P NMR spectrum of compound **3g**

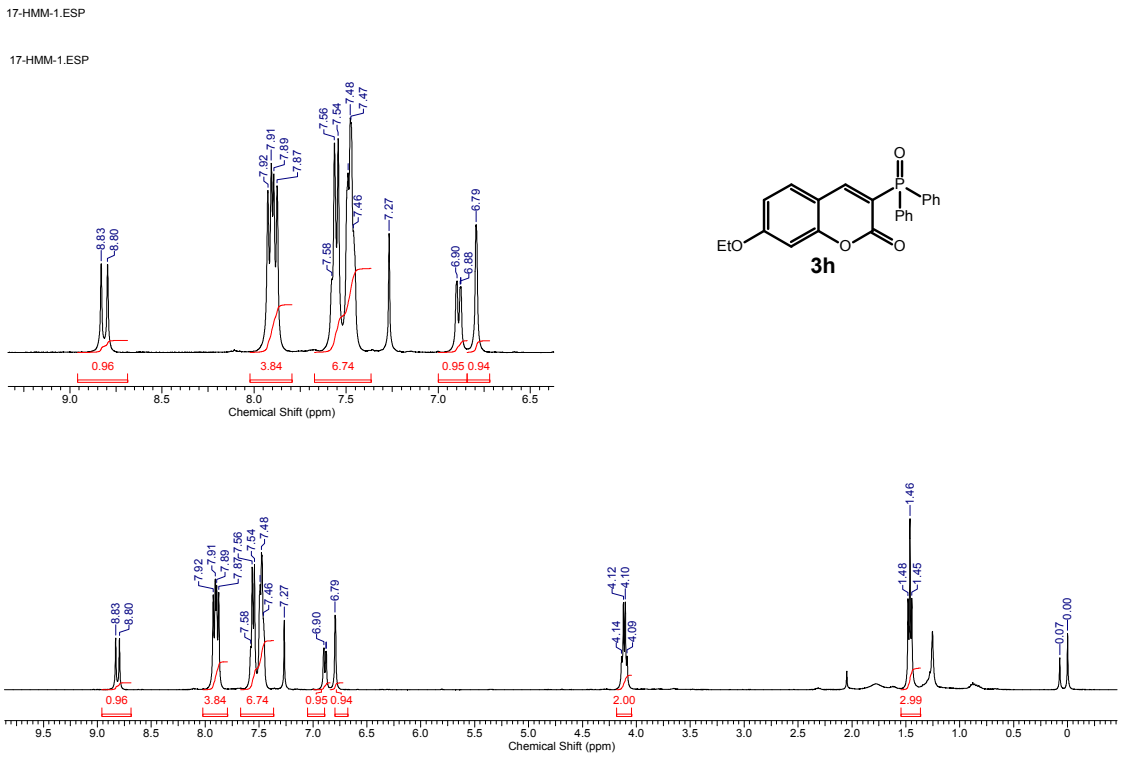


Figure S38. ^{1}H NMR spectrum of compound **3h**

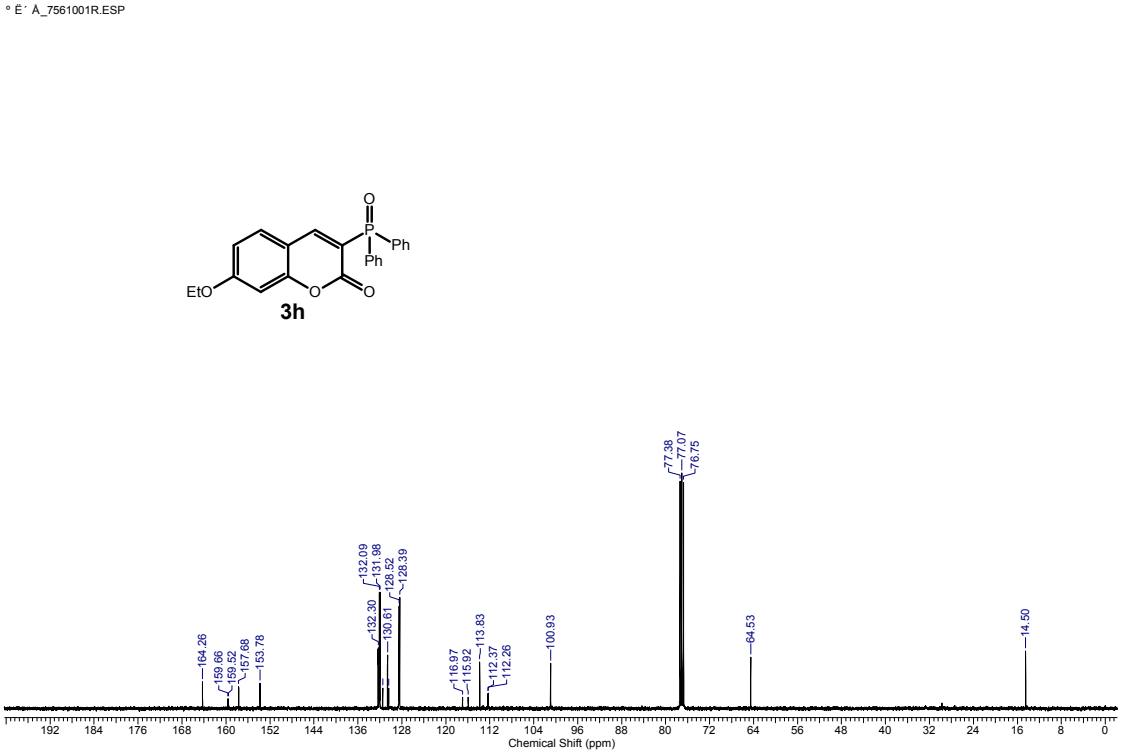


Figure S39. ^{13}C NMR spectrum of compound **3h**

° Ê´ Â_6761001R.ESP

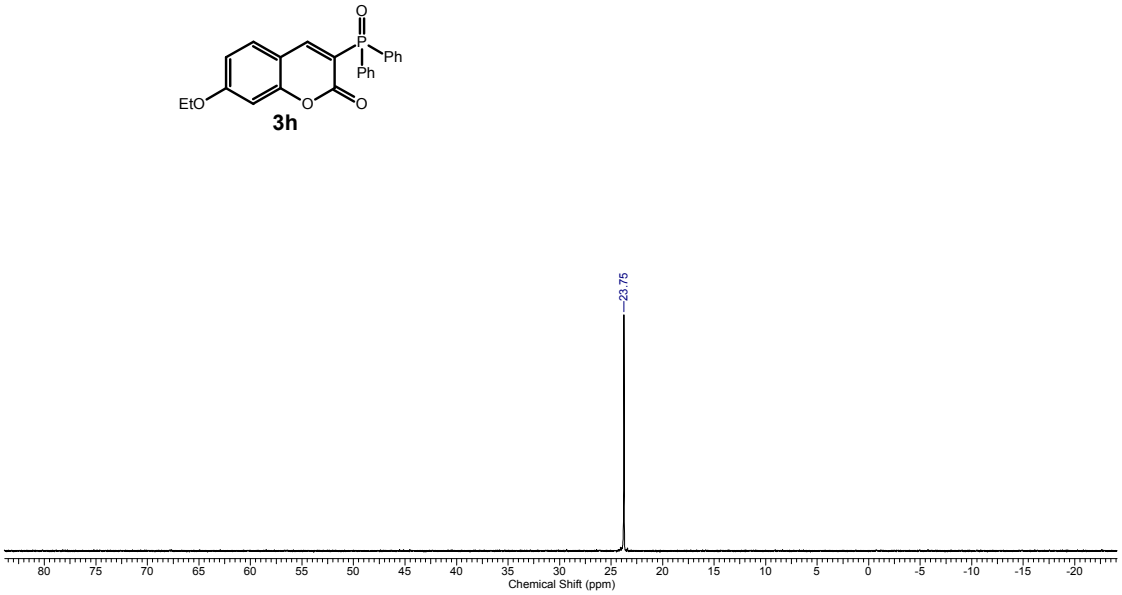


Figure S40. ^{31}P NMR spectrum of compound **3h**

R-279-7300_000001R.ESP

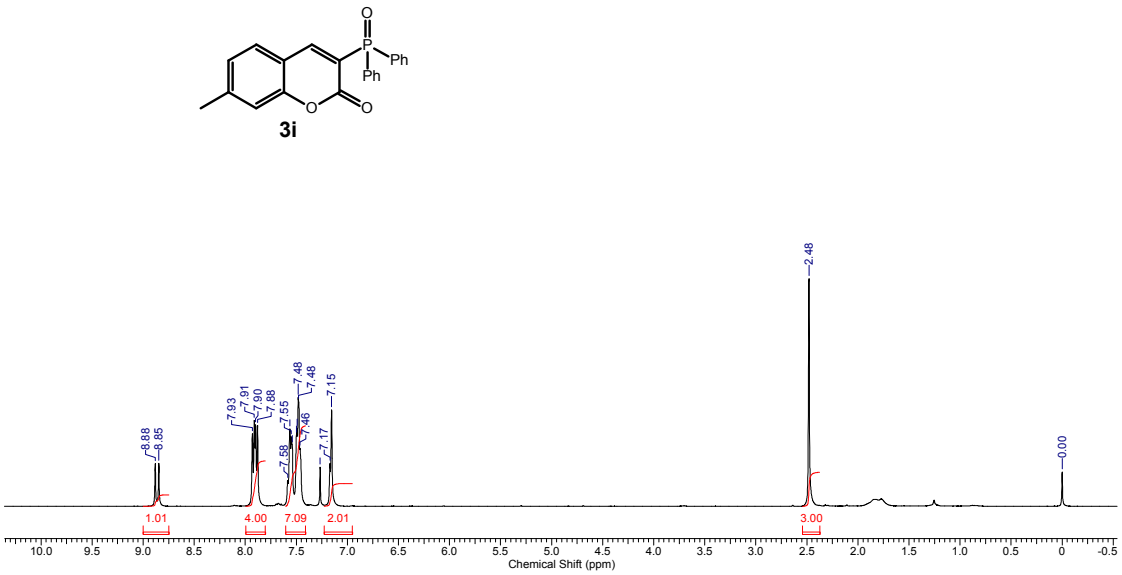


Figure S41. ^{1}H NMR spectrum of compound **3i**

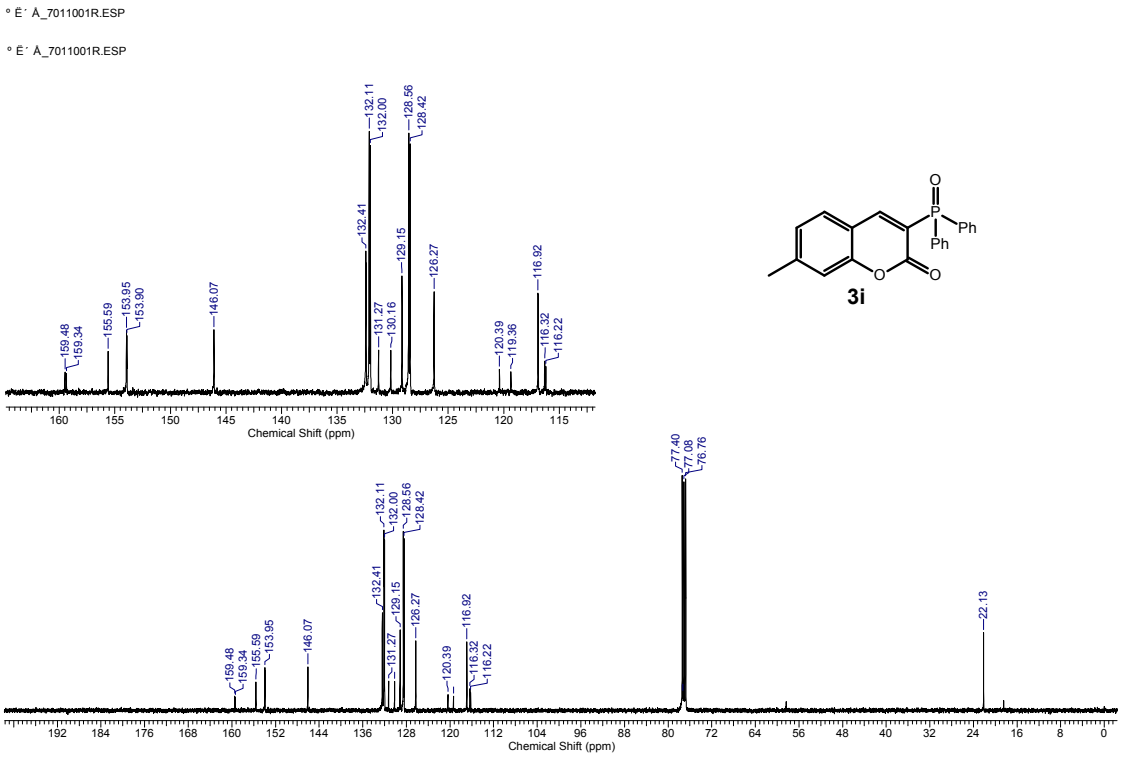


Figure S42. ^{13}C NMR spectrum of compound **3i**

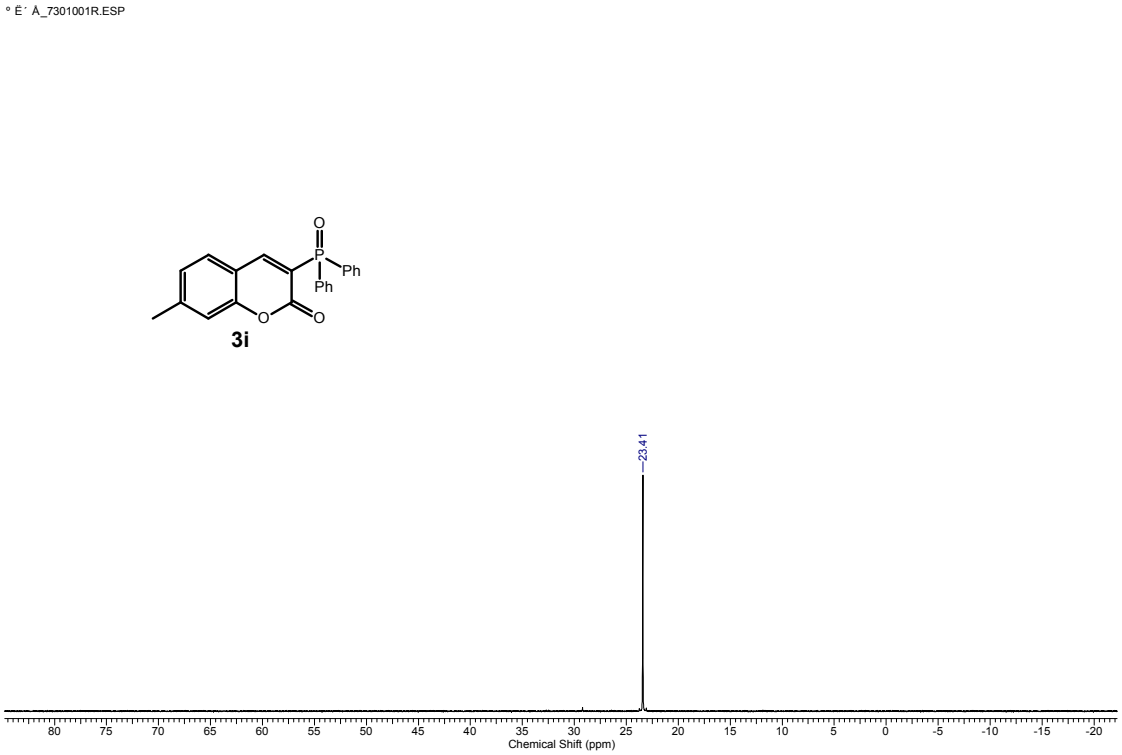


Figure S43. ^{31}P NMR spectrum of compound **3i**

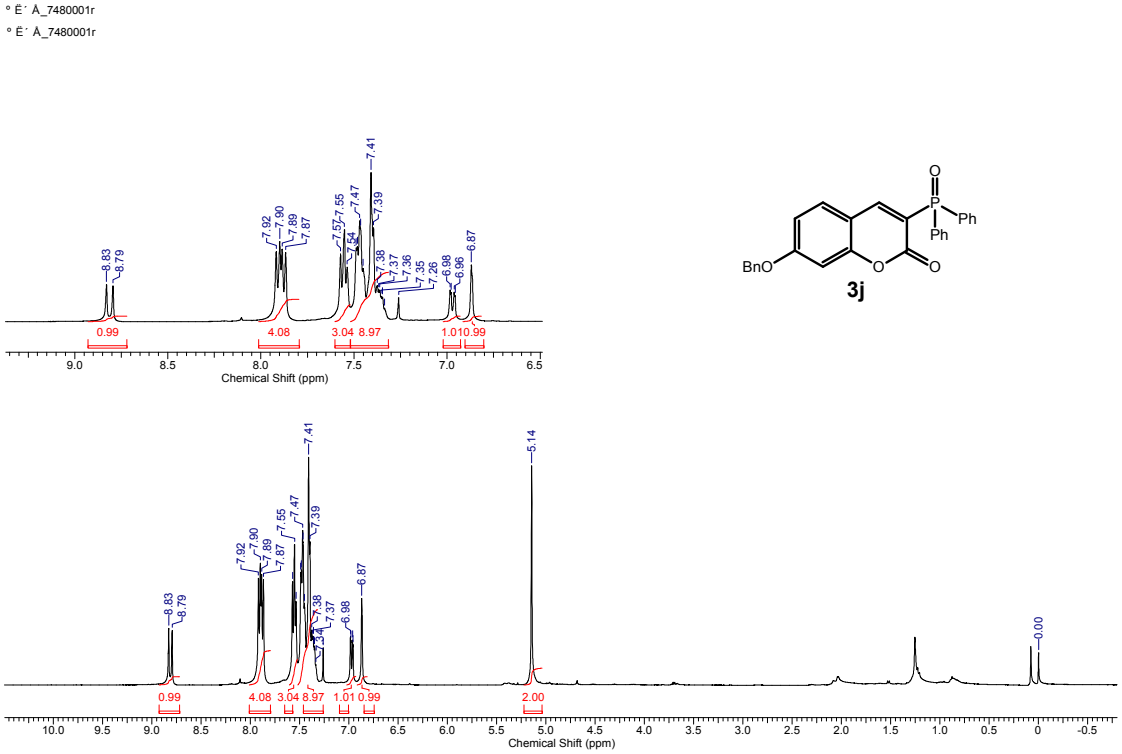


Figure S44. ^{1}H NMR spectrum of compound **3j**

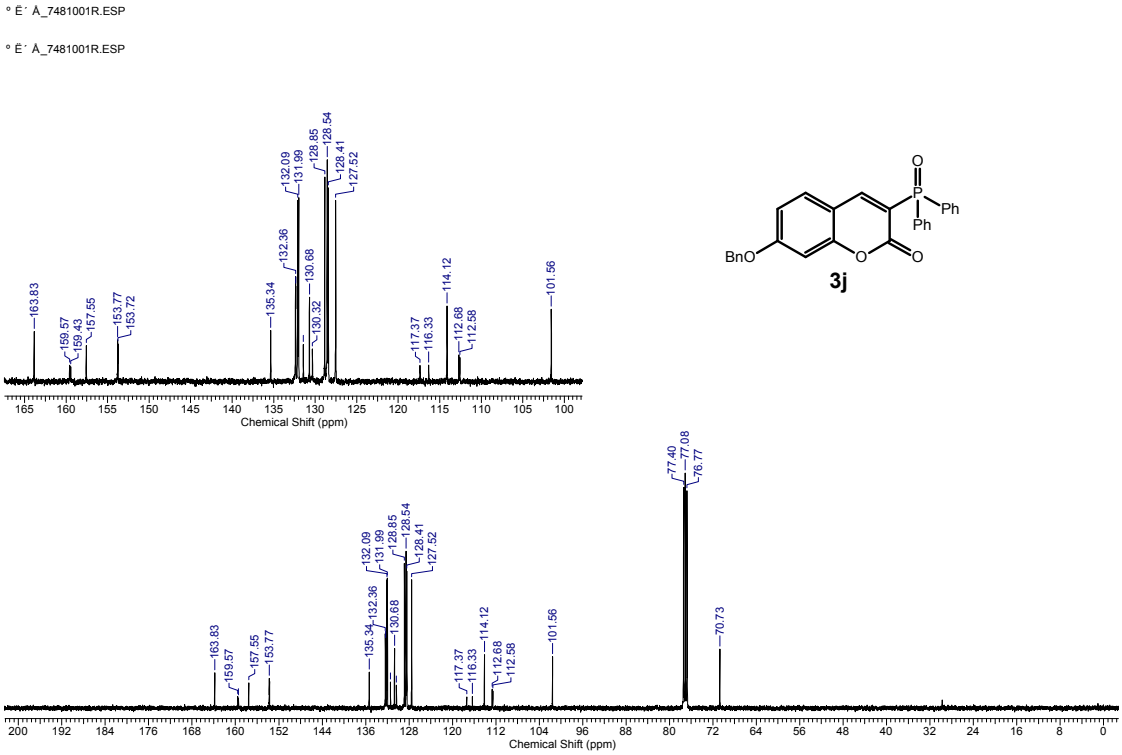
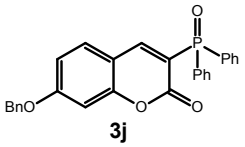


Figure S45. ^{13}C NMR spectrum of compound **3j**

P_8961001R.ESP



3j

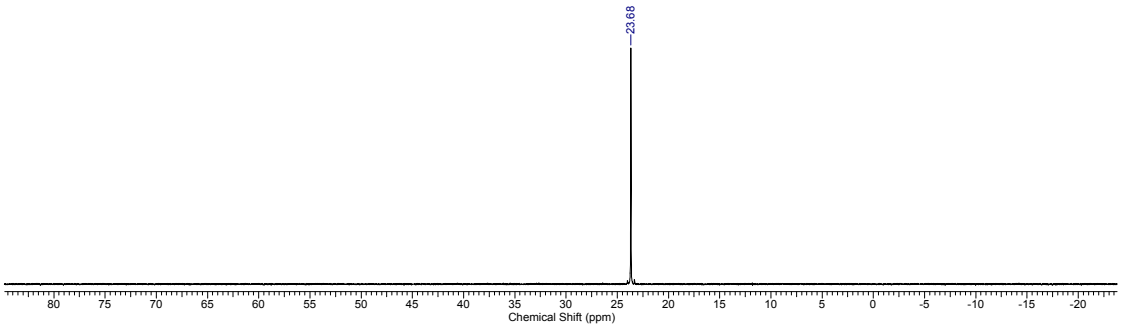
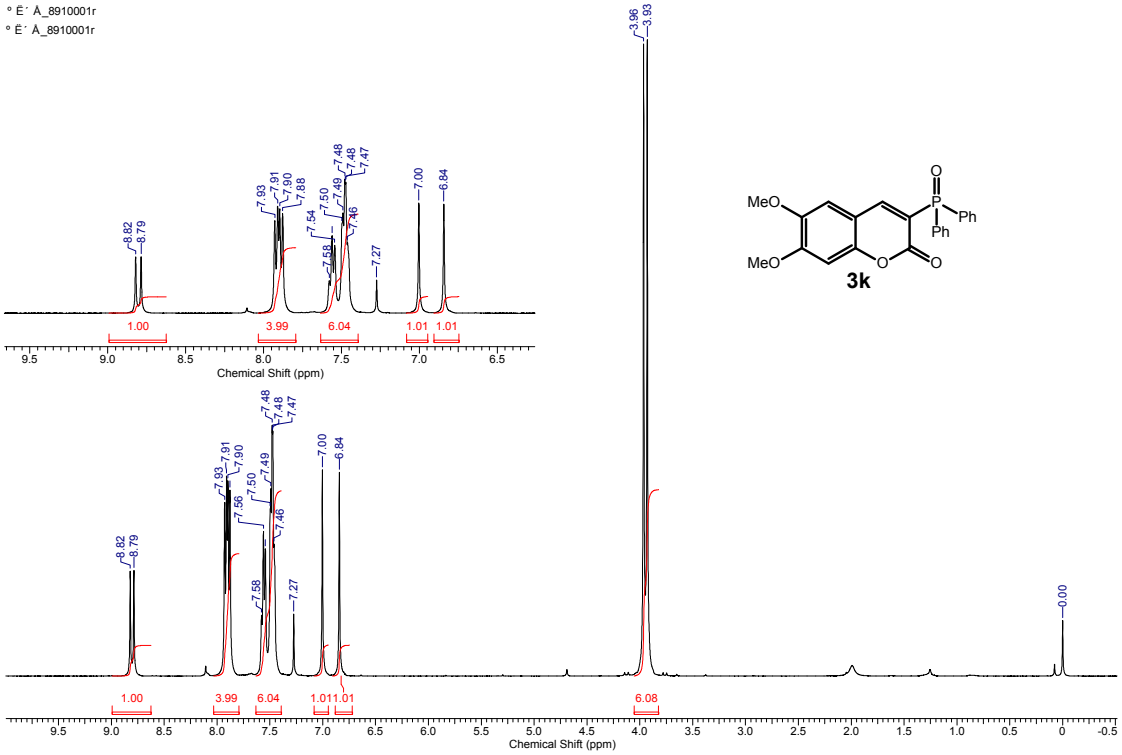


Figure S46. ^{31}P NMR spectrum of compound **3j**



3k

Figure S47. ^{1}H NMR spectrum of compound **3k**

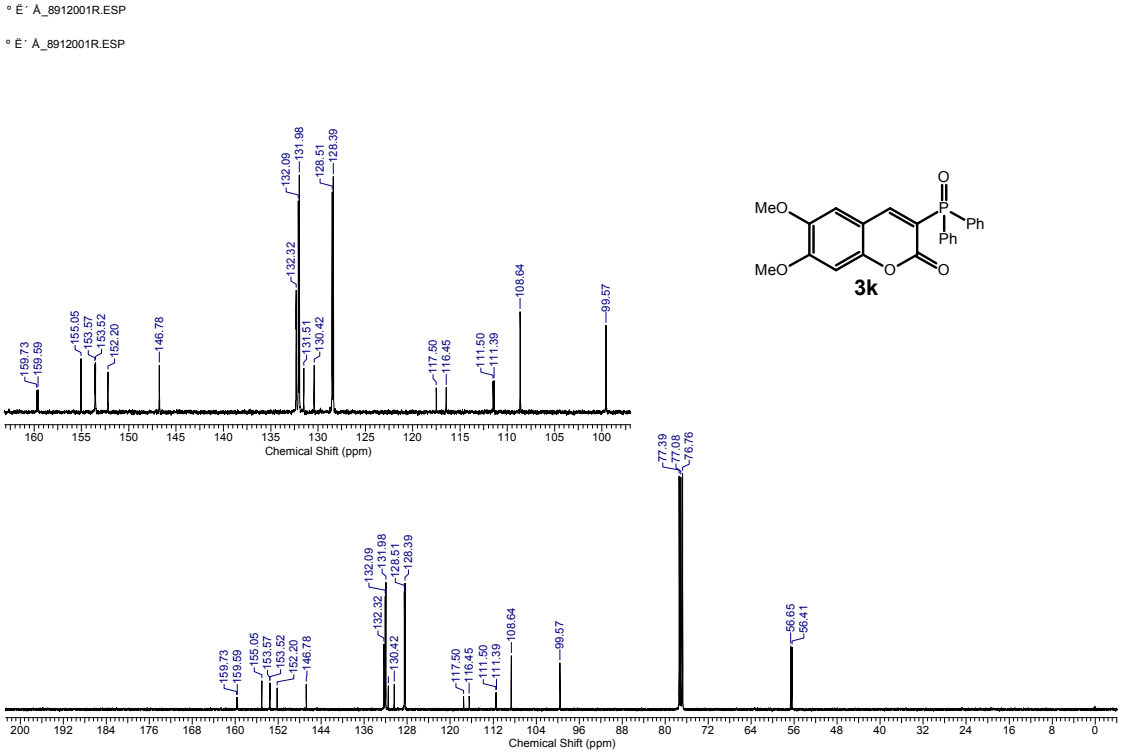


Figure S48. ^{13}C NMR spectrum of compound **3k**

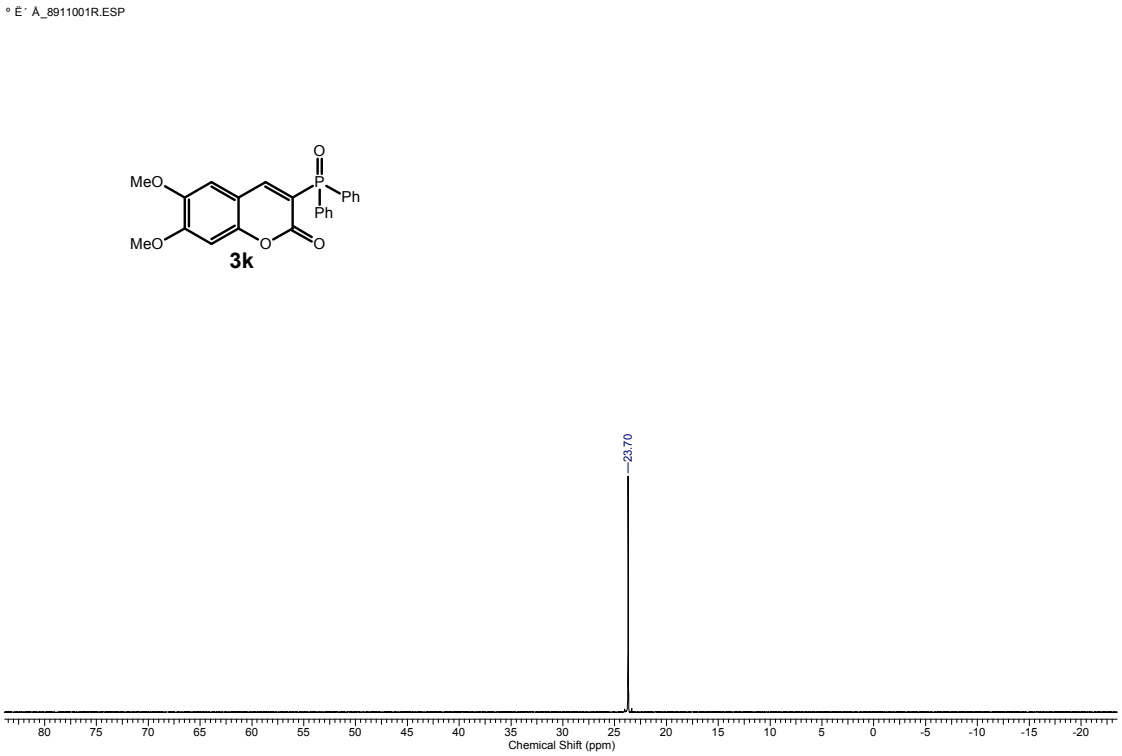


Figure S49. ^{31}P NMR spectrum of compound **3k**

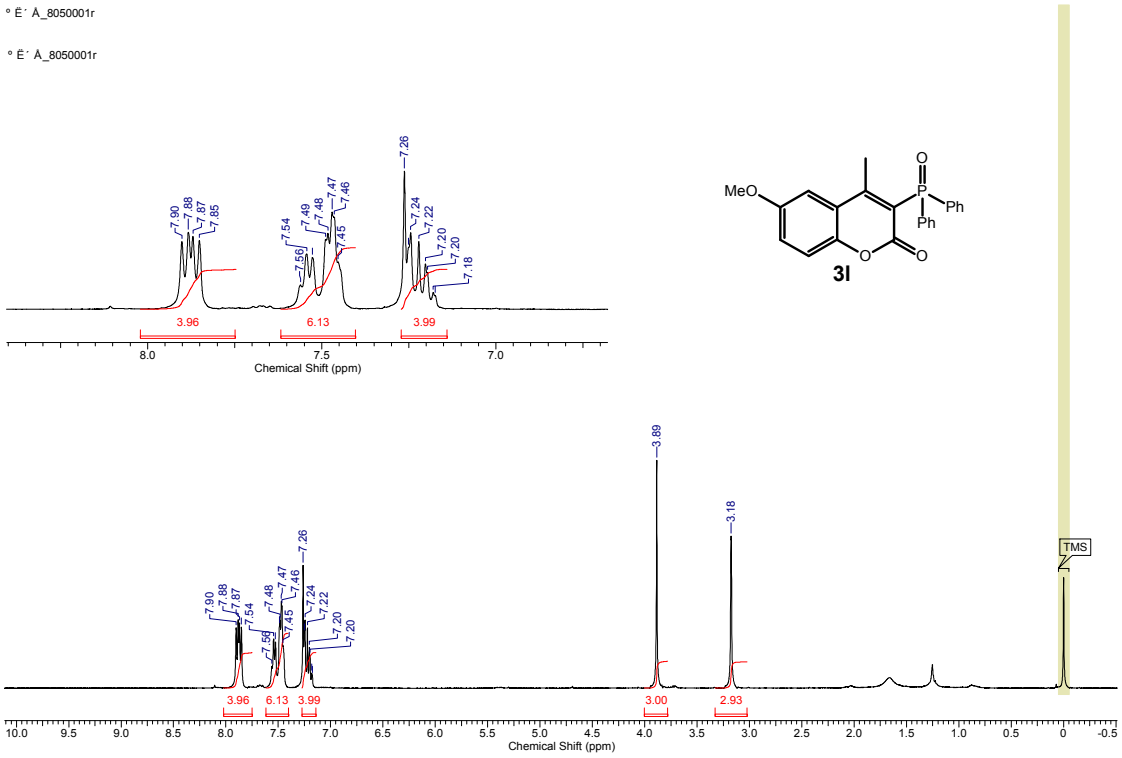


Figure S50. ^{1}H NMR spectrum of compound **3l**

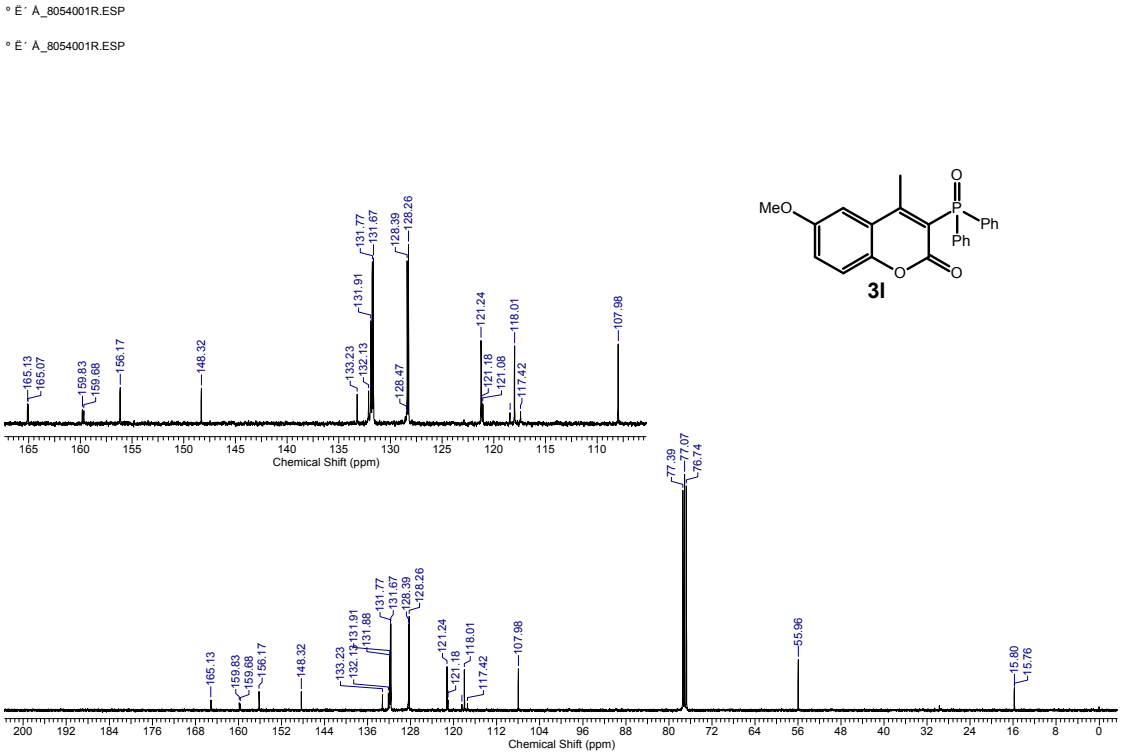


Figure S51. ^{13}C NMR spectrum of compound **3l**

° Ë´ Ä_8052001R.ESP

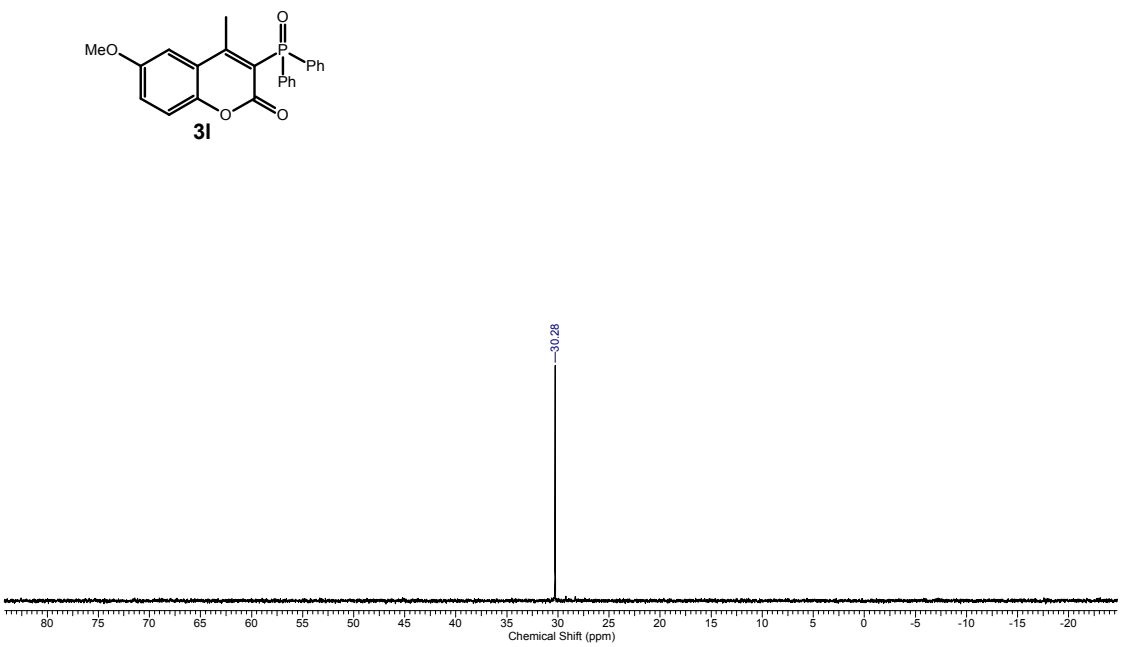


Figure S52. ^{31}P NMR spectrum of compound **3l**

° Ë´ Ä_7490001R.ESP

° Ë´ Ä_7490001R.ESP

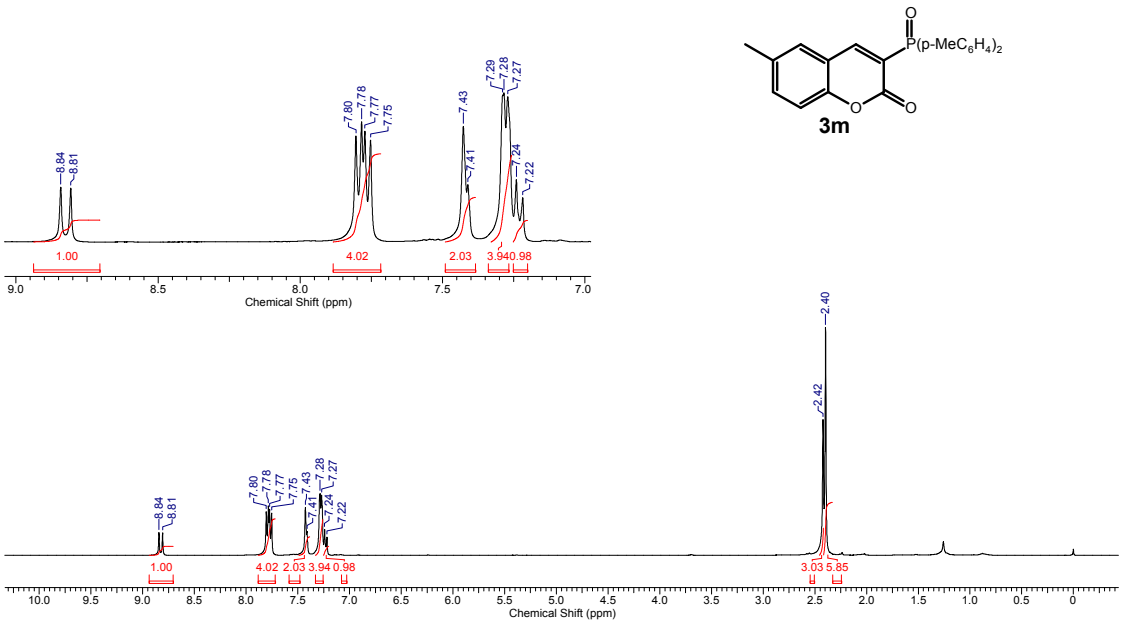


Figure S53. ^{1}H NMR spectrum of compound **3m**

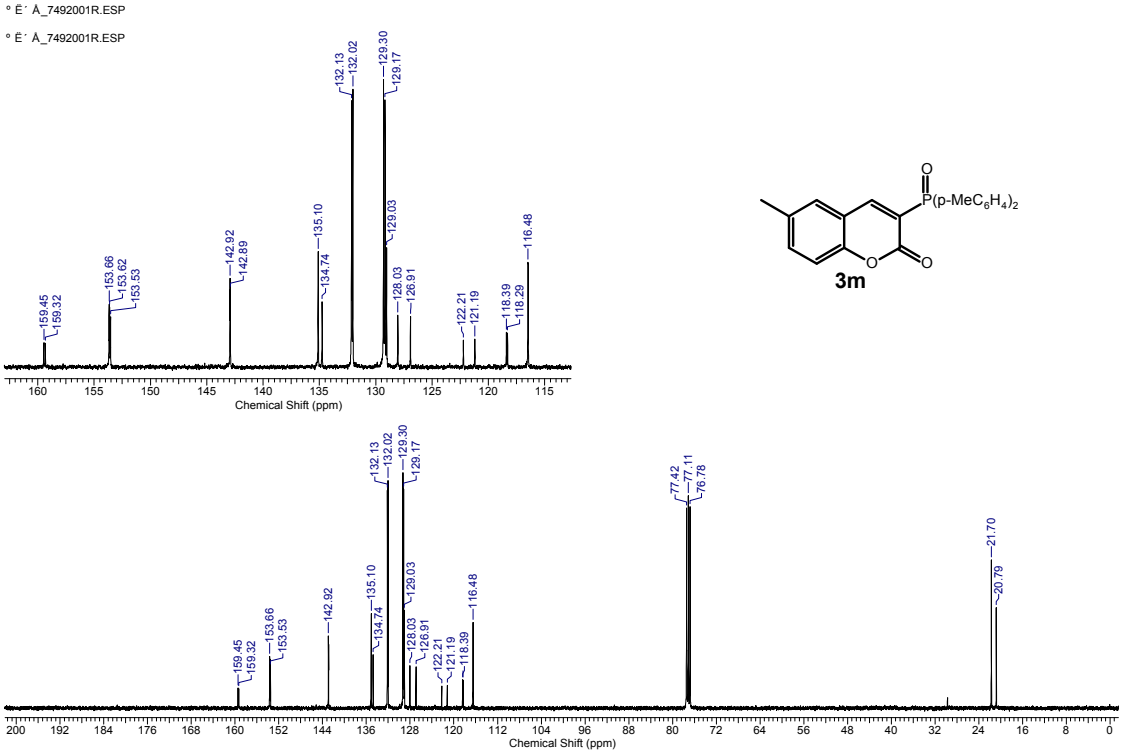


Figure S54. ^{13}C NMR spectrum of compound **3m**

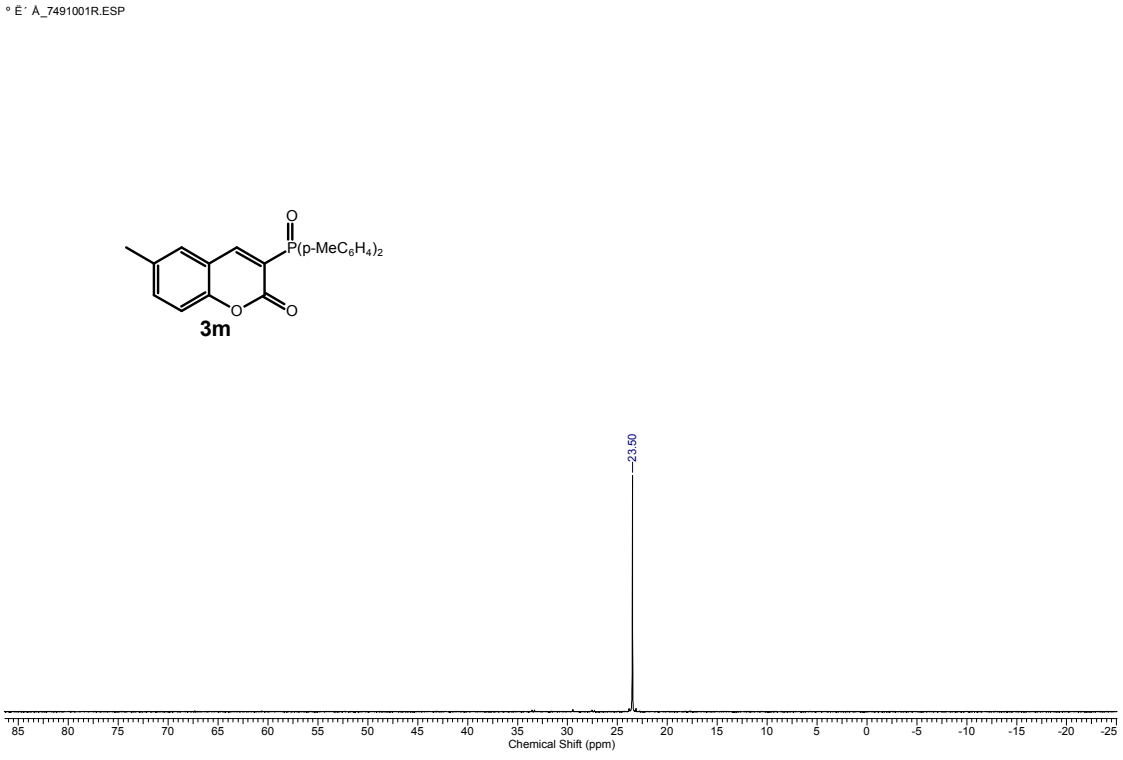


Figure S55. ^{31}P NMR spectrum of compound **3m**

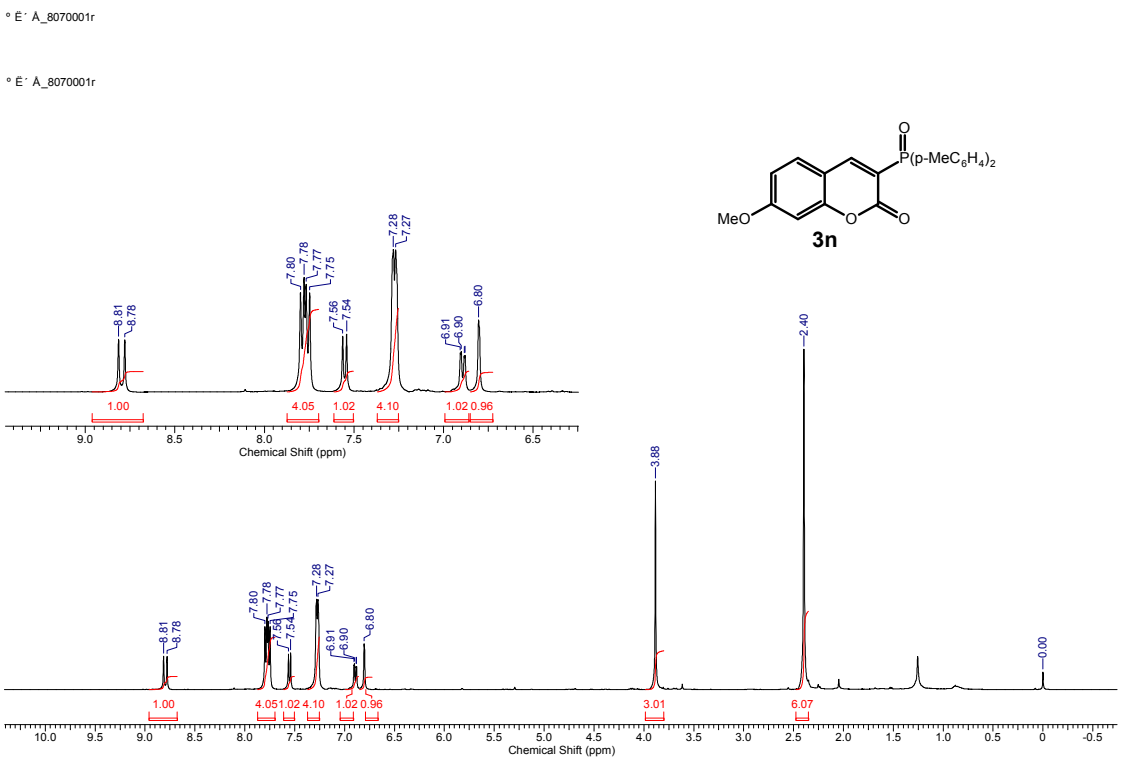


Figure S56. ^{1}H NMR spectrum of compound **3n**

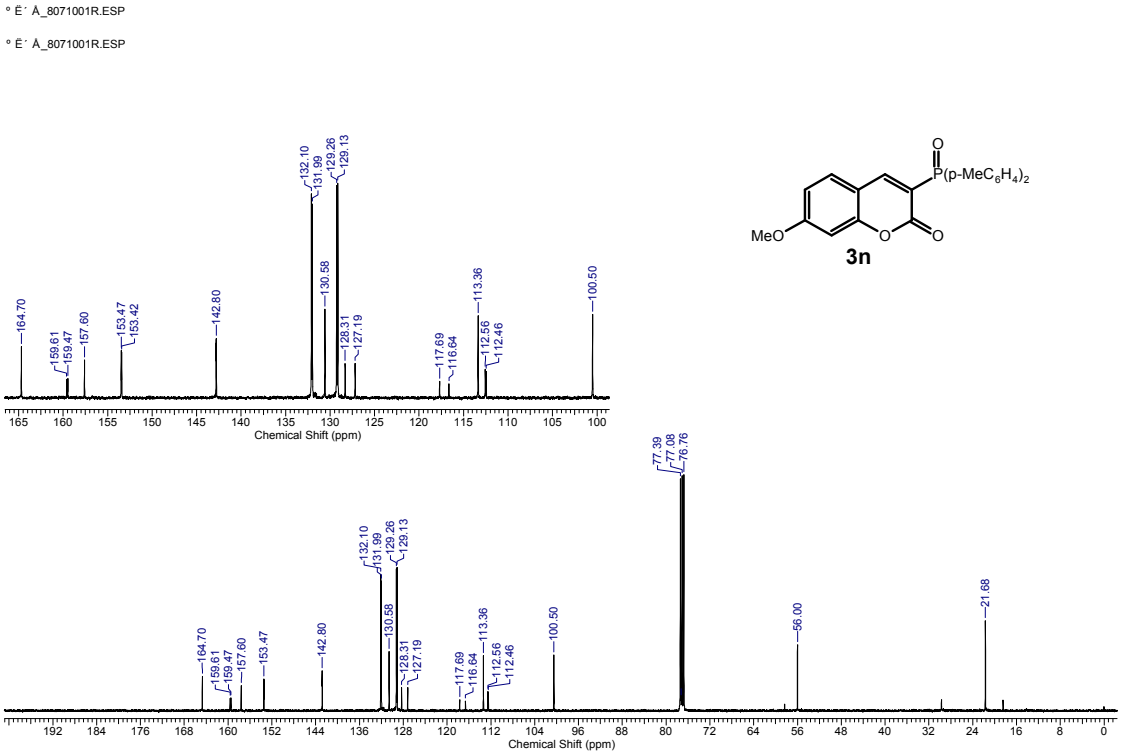
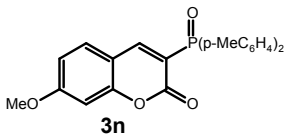


Figure S57. ^{13}C NMR spectrum of compound **3n**

° Ë˙ Ä_8072001R.ESP



3n

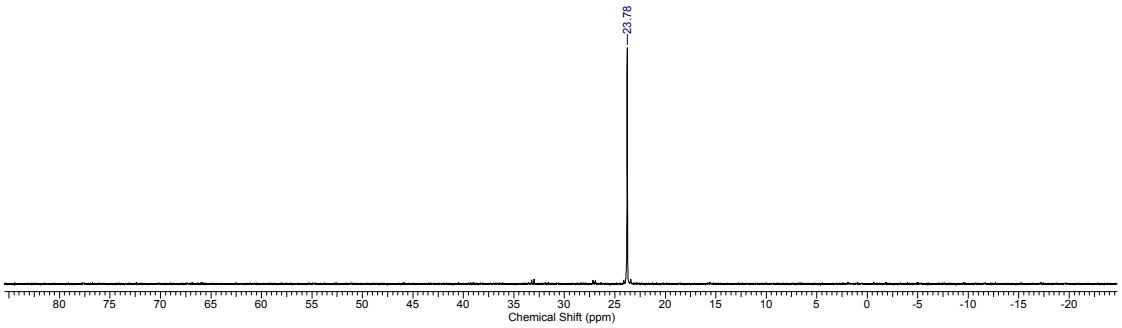
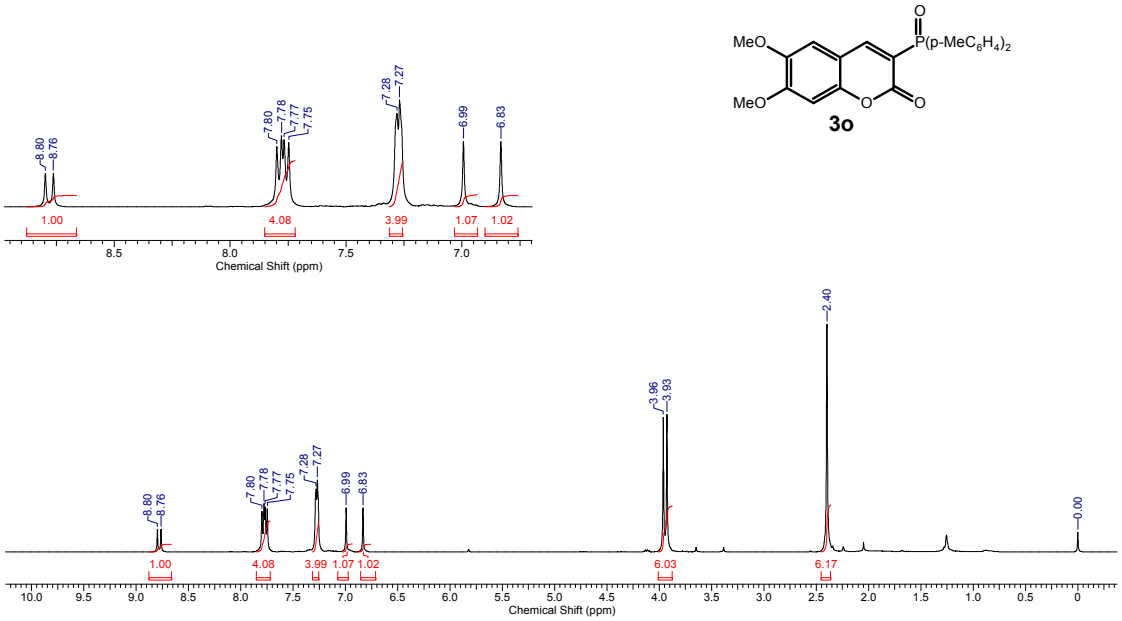


Figure S58. ^{31}P NMR spectrum of compound **3n**

° Ë˙ Ä_8190001R.ESP

° Ë˙ Ä_8190001R.ESP



3o

Figure S59. ^{1}H NMR spectrum of compound **3o**

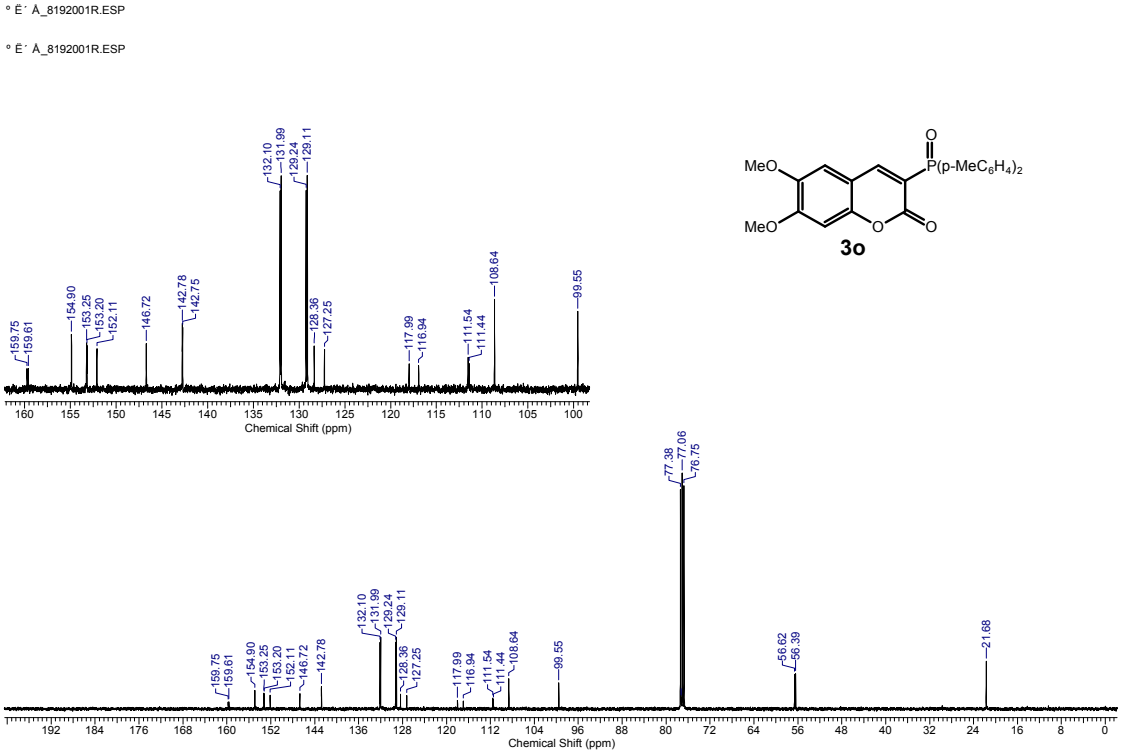


Figure S60. ^{13}C NMR spectrum of compound **3o**

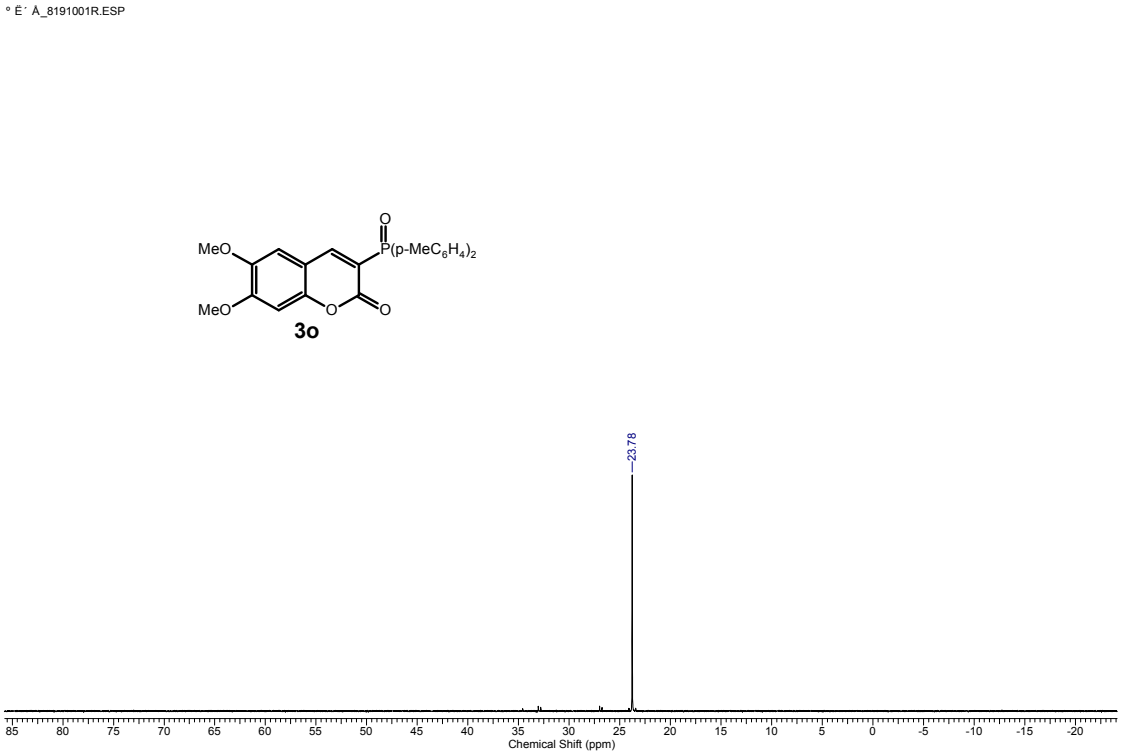


Figure S61. ^{31}P NMR spectrum of compound **3o**

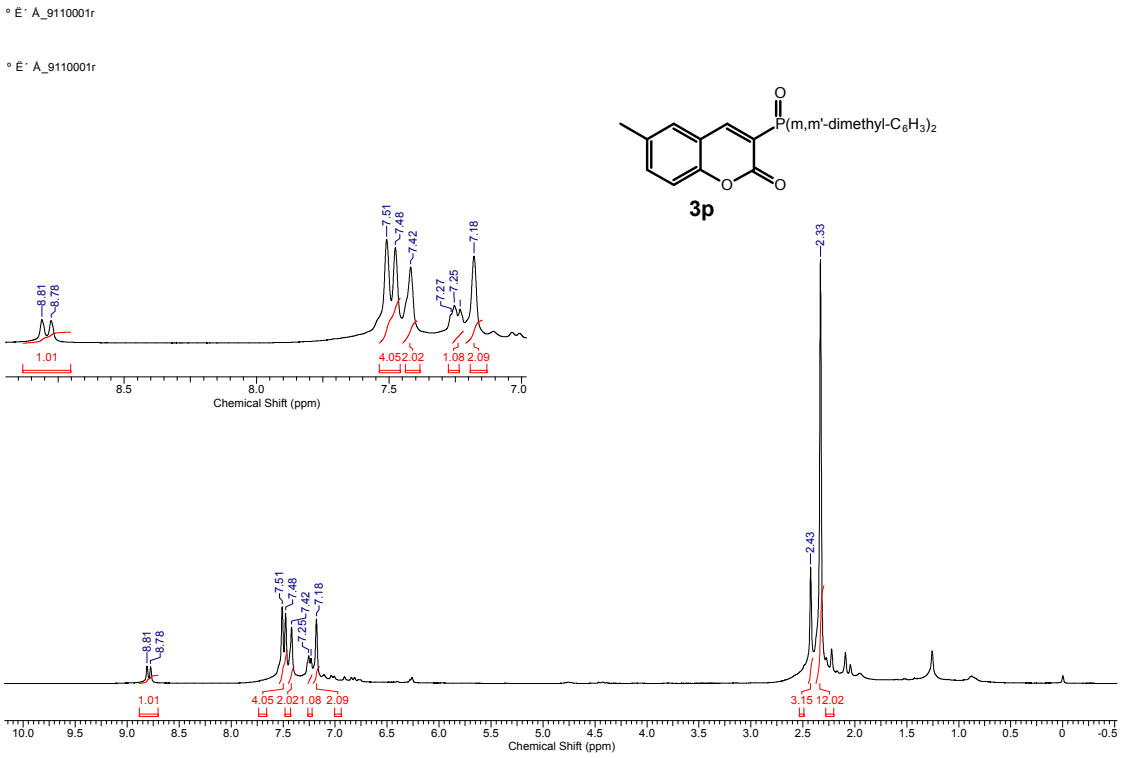


Figure S62. ^{1}H NMR spectrum of compound **3p**

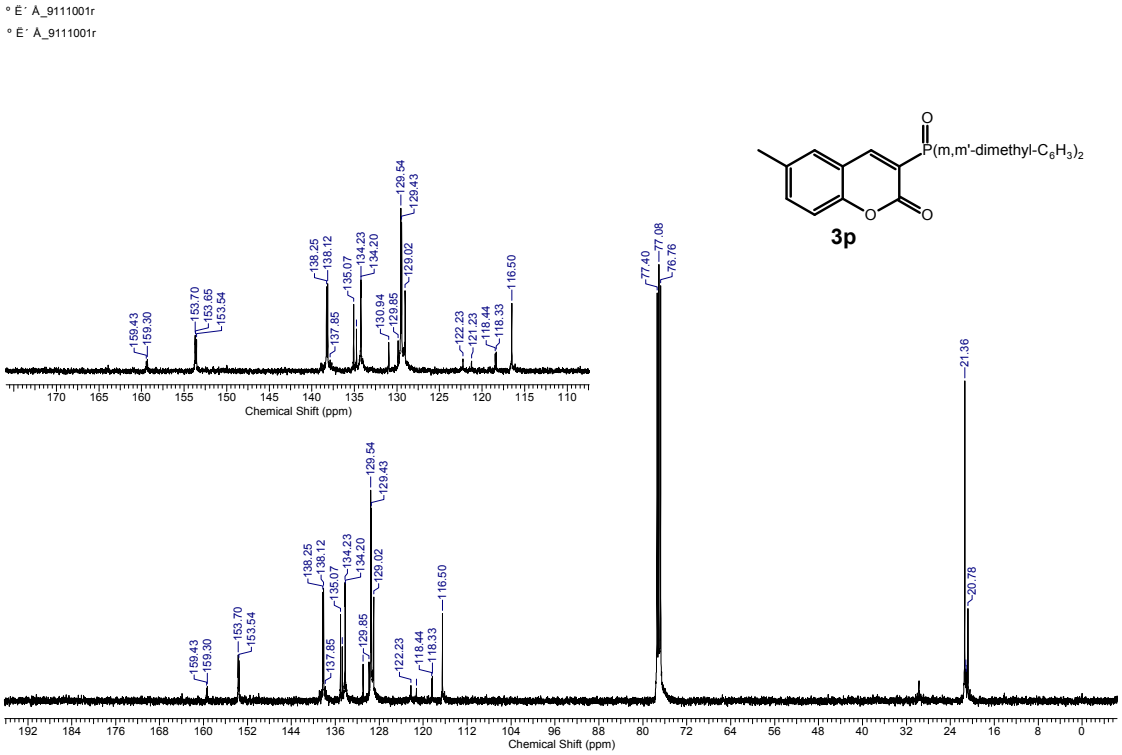


Figure S63. ^{13}C NMR spectrum of compound **3p**

° Ê´ À_8231001R.ESP

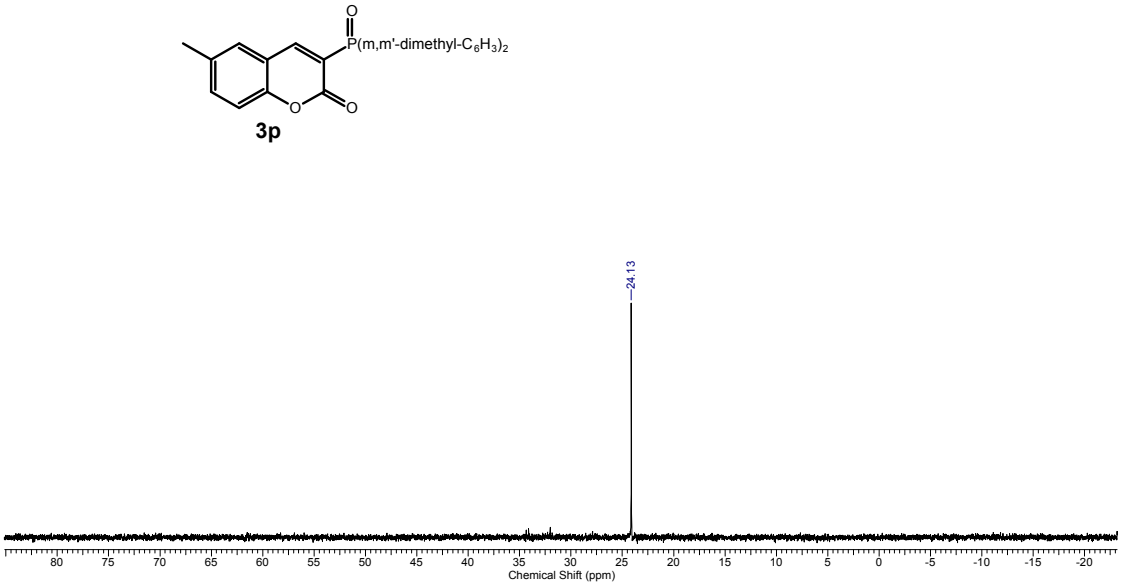


Figure S64. ^{31}P NMR spectrum of compound **3p**

× ÀÃæ_7700001R.ESP

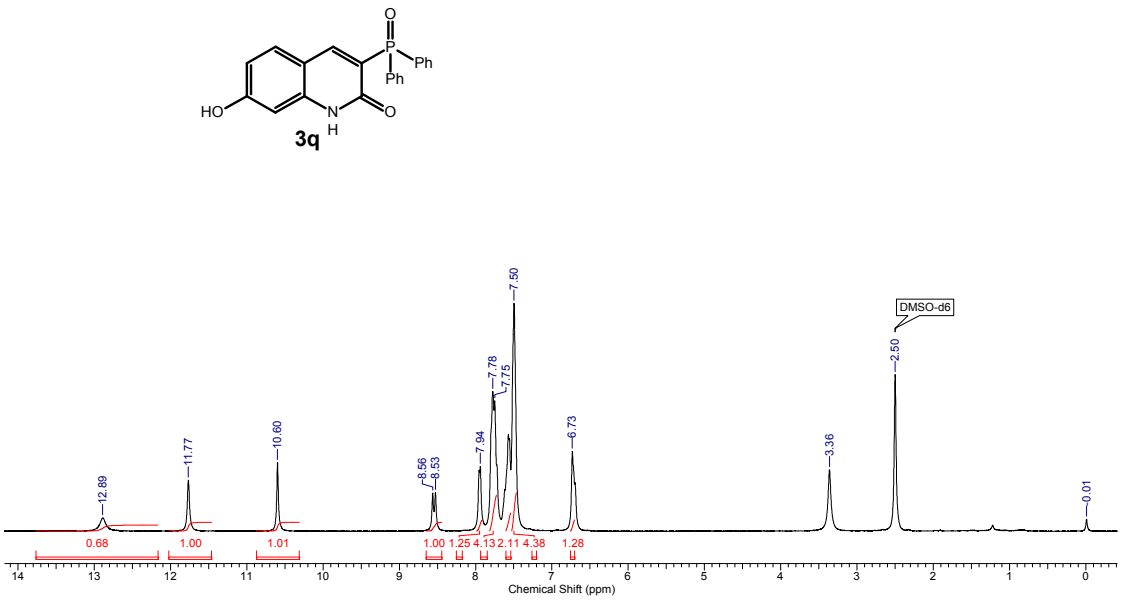


Figure S65. ^{1}H NMR spectrum of compound **3q**

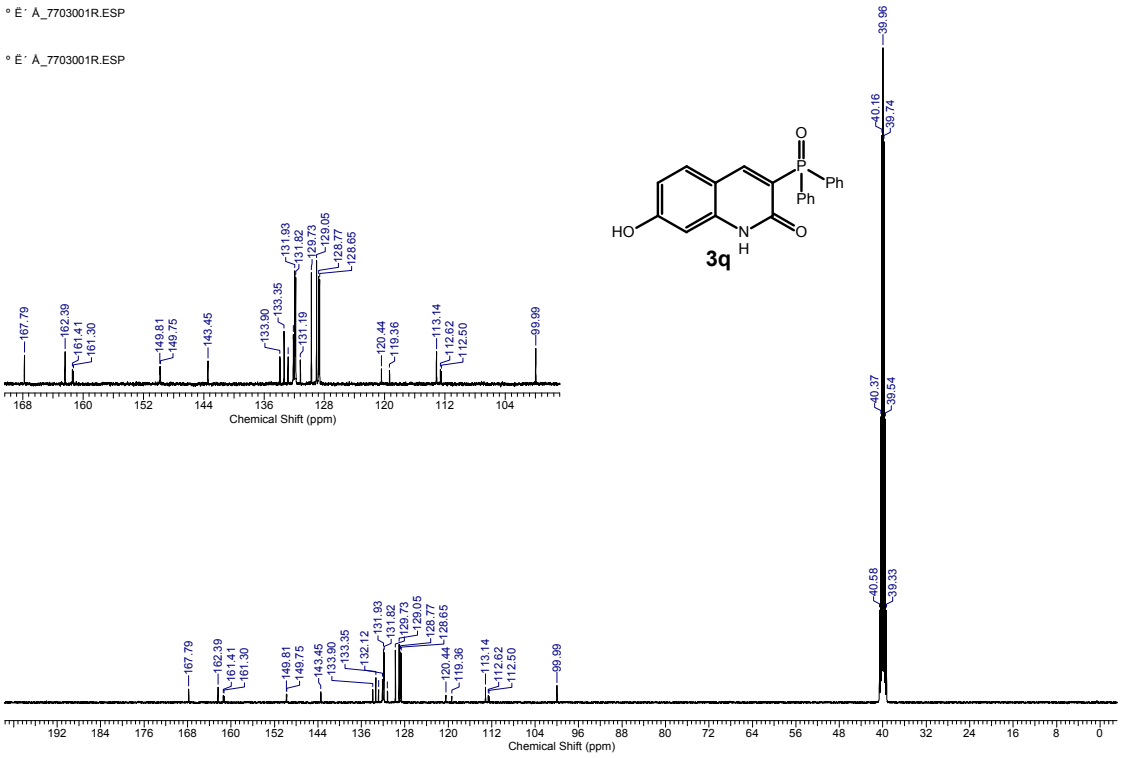


Figure S66. ^{13}C NMR spectrum of compound **3q**

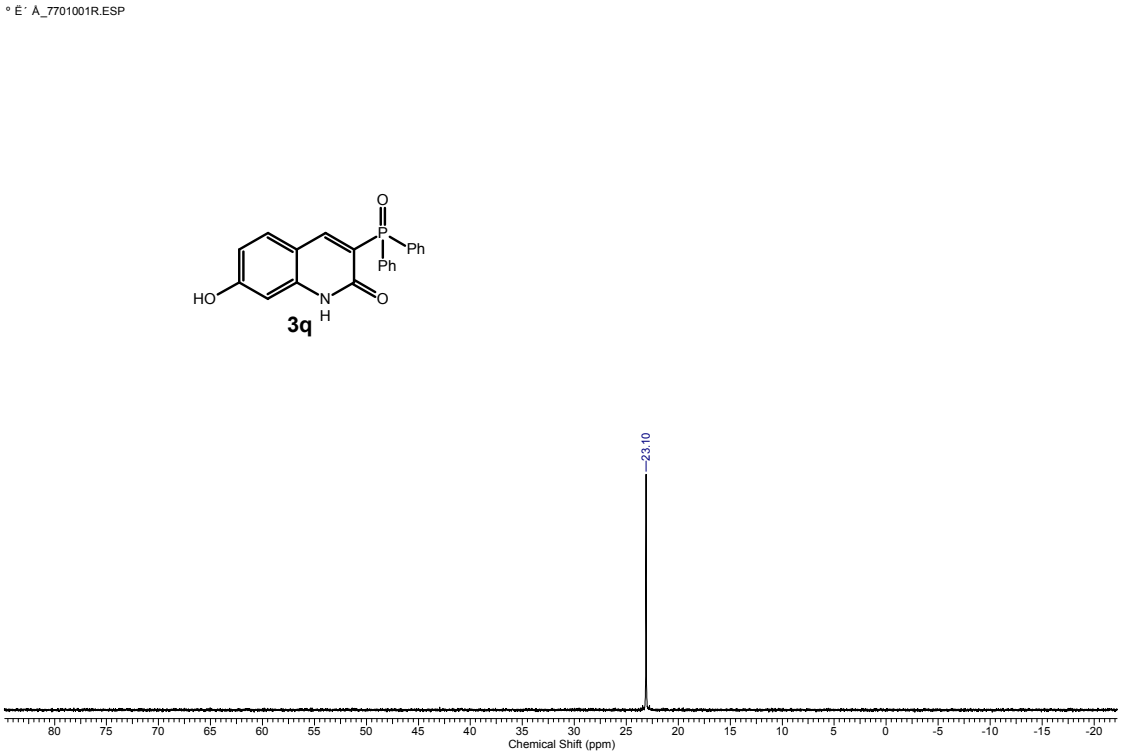


Figure S67. ^{31}P NMR spectrum of compound **3q**

7. Determination of Structure of 3a

The structure of **3a** was determined by the X-ray diffraction. Recrystallized from EtOH/dichloromethane. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC **1521144**.

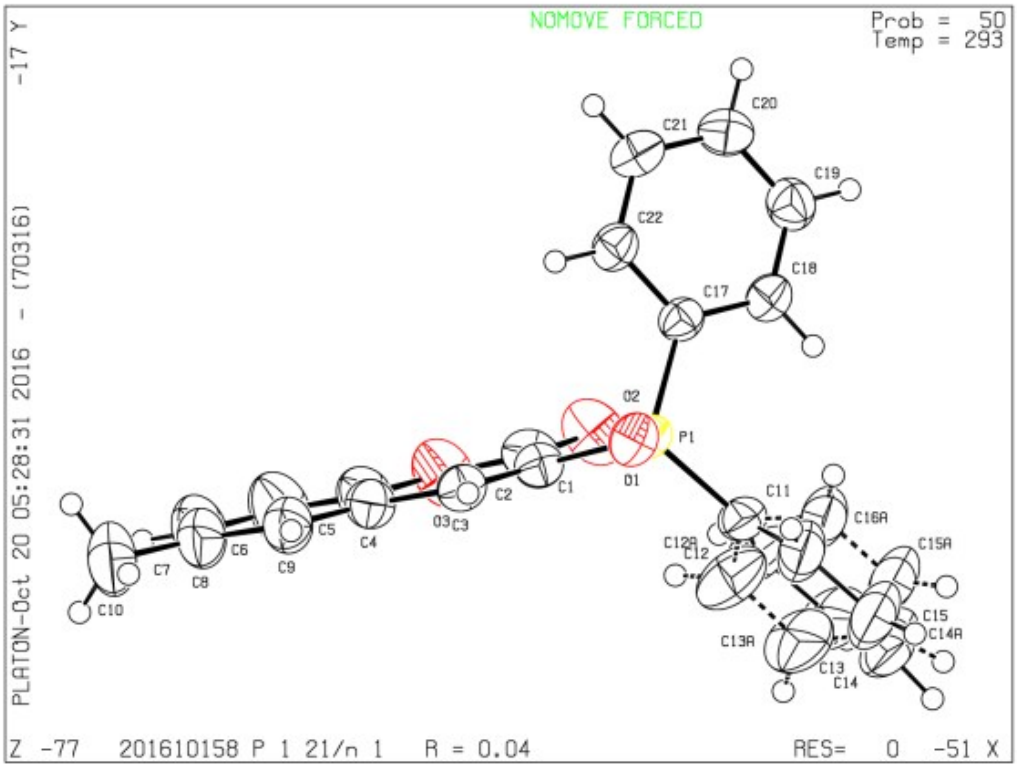


Table 1 Crystal data and structure refinement for 3a.

Identification code	201610158
Empirical formula	$C_{22}H_{17}O_3P$
Formula weight	360.32
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.6045(3)
b/Å	21.7424(7)
c/Å	10.3736(4)
α/°	90
β/°	109.450(4)
γ/°	90
Volume/Å^3	1829.96(12)
Z	4
ρ_{calc}g/cm^3	1.308

μ/mm^{-1}	1.482
F(000)	752.0
Crystal size/mm^3	0.21 × 0.18 × 0.16
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.132 to 141.596
Index ranges	-10 ≤ h ≤ 6, -16 ≤ k ≤ 26, -6 ≤ l ≤ 12
Reflections collected	6869
Independent reflections	3406 [R_{int} = 0.0236, R_{sigma} = 0.0319]
Data/restraints/parameters	3406/5/252
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ(I)]	R_1 = 0.0432, wR_2 = 0.1132
Final R indexes [all data]	R_1 = 0.0531, wR_2 = 0.1228
Largest diff. peak/hole / e Å^{-3}	0.35/-0.21