Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

A Simple Approach to Indeno-Coumarins via Visible–Light–Induced Cyclization of Aryl Alkynoates with Diethyl Bromomalonate

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Experimental details and spectroscopic data

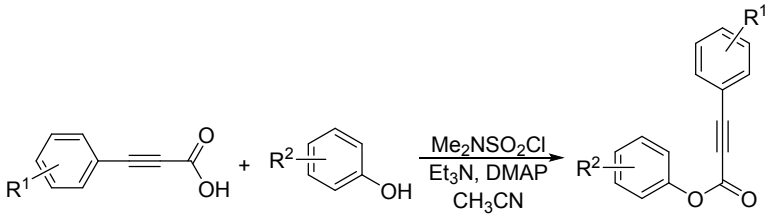
Contents:

1. General information

All reactions were performed using quartz tube. Solvents were dried and degassed by standard methods before they were used. Commercial grade reagents were used without further purification except as indicated below. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. The LCD Digital Hotplate Magnetic Stirrer MS-H-Pro^{+} was purchased from Dragon Laboratory Instruments Limited. ^{1}H NMR spectra was recorded on a Bruker DPX-400 (400 MHz) spectrometer with deuteraterated chloroform as solution, 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 $CHCl_3$ (δ_C = 77.00 ppm). ^{19}F NMR spectra was recorded at 376.5 MHz on Bruker DPX-400, the chemical shifts δ are reported relative to $CFCl_3$ (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 (HR-MS) 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 CHI660A. And the Luminescence Quenching Experiments were recorded using a F-4500 FL Spectrophotometer in DMF. All reactions were carried out with photoreactor (Serial No: D243V12) which was purchased from LUOYANG JINFENG ELECTROMECHANICAL EQUIPMENT CO., LTD.

2. Experimental Procedures

1) General Procedure **A** for the synthesis of the starting materials



Scheme S1. the synthesis of aryl 3- phenylpropionate

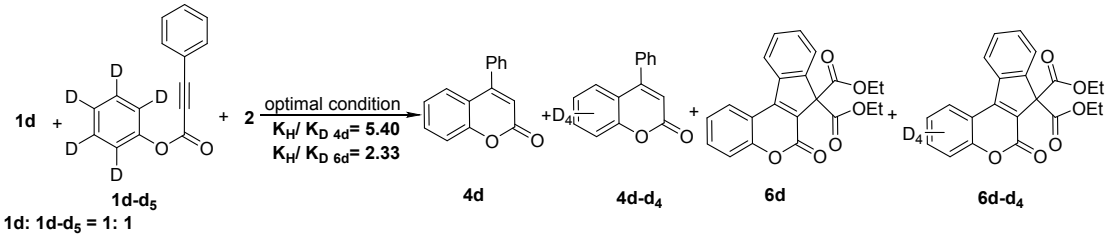
According to the method in the literature,[1, 2, 3, 4] typical procedure for the synthesis of aryl 3-phenylpropionate: $Me_3N{\cdot}HCl$ (258 mg, 2.7 mmol) was added to a stirred solution of phenylpropiolic acid (204.6 mg, 1.4 mmol), phenol (131.6 mg, 1.4 mmol), Et_3N (414.9 mg, 4.1 mmol), and DMAP (12.2 mg, 0.10 mmol) in CH_3CN (1.0 mL) at 0-5 ^oC under an nitrogen atmosphere, and the mixture was stirred for 10 min. Me_2NSO_2Cl (387.7 mg, 2.7 mmol) in CH_3CN (1.0 mL) was added to the mixture at 0-5 ^oC, and the mixture was stirred at that temperature for 3 h. The reaction was quenched with water and extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluant: petroleum ether/ethyl acetate = 5:1 to 7:1, V/V) to obtain the phenyl 3-phenylpropiolate as a colorless solid.

2) General Procedure **B** for the synthesis of the indeno-coumarins

P-tolyl 3-phenylpropiolate (23.6mg, 0.1mmol), diethyl bromomalonate (71.8 mg, 0.3 mmol), *fac*-Ir(ppy)$_3$ (0.005 mmol) and $K_2HPO_4{\cdot}3H_2O$ (0.2 mmol) were combined in DMF (1.0 mL) under Ar atmosphere. The mixture was stirred at room temperature under blue LED lamp (3 W). After 48 or 96 hours, the reaction mixture was extracted with ethyl acetate and saturated salt water, organic phase was purified by chromatography on silica gel (elute: ethyl acetate/petroleum ether = 1/5-1/7, v/v) to give the desired products.

3 Mechanistic investigations

3.1 Kinetic Isotope Effect (KIE) Measurement



Scheme S2. Kinetic Isotope Effect (KIE) Measurement

The representative procedure 2) was followed using **1d** (11.1mg, 0.05mmol), **1d-d$_5$** (11.4mg, 0.05mmol), diethyl bromomalonate (71.8 mg, 0.3 mmol), *fac*-Ir(ppy)$_3$ (0.005 mmol) and $K_2HPO_4{\cdot}3H_2O$ (0.2 mmol) were combined in DMF (1.0 mL) under Ar atmosphere. The mixture was stirred at room temperature under blue LED lamp (3 W). After 48 hours, the reaction mixture was extracted with ethyl acetate and saturated salt water, organic phase was purified by chromatography on silica gel (elute: ethyl acetate/petroleum ether 1/5-1/7, v/v). The deuterium content was determinded by NMR spectroscopy.

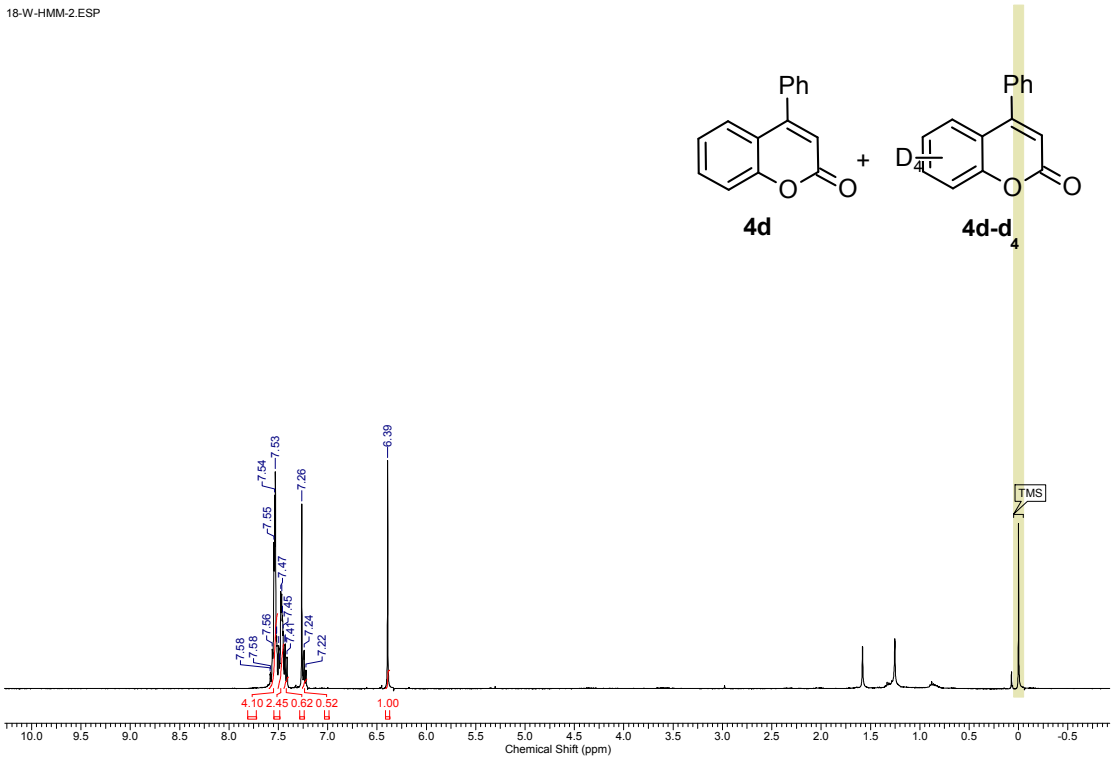


Figure S1. ^{1}H NMR spectrum of compound **4d/4d-d$_4$**

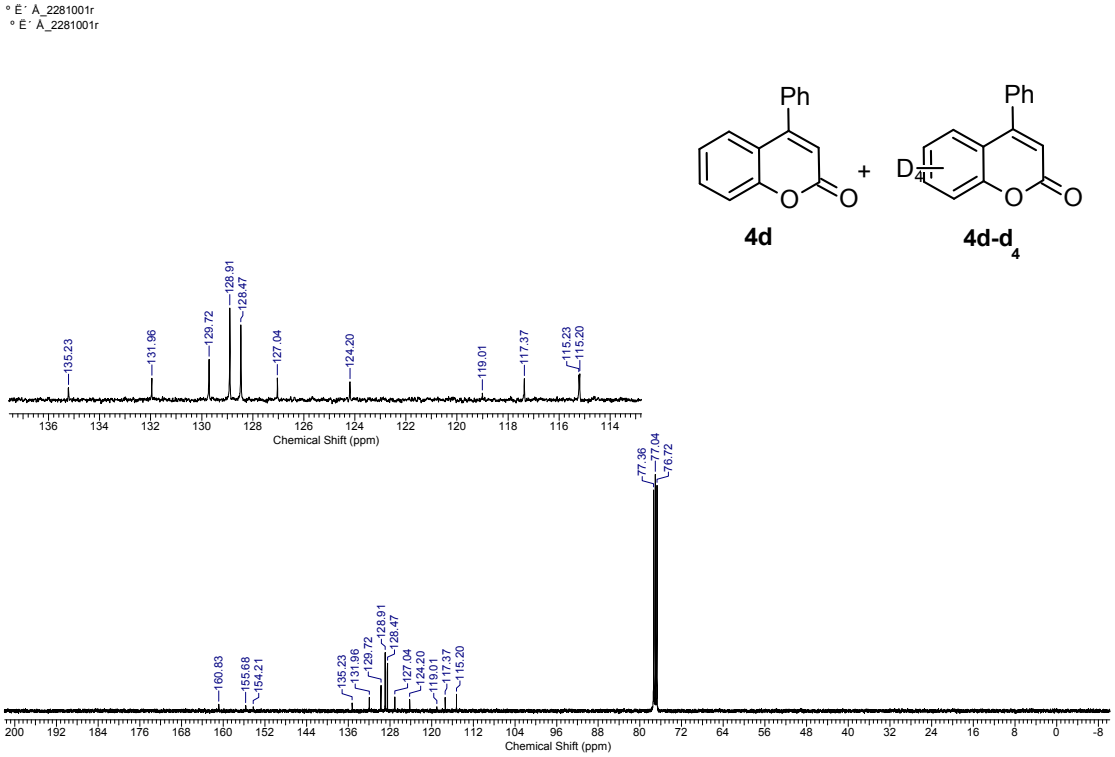


Figure S2. ^{13}C NMR spectrum of compound **4d/4d-d$_4$**

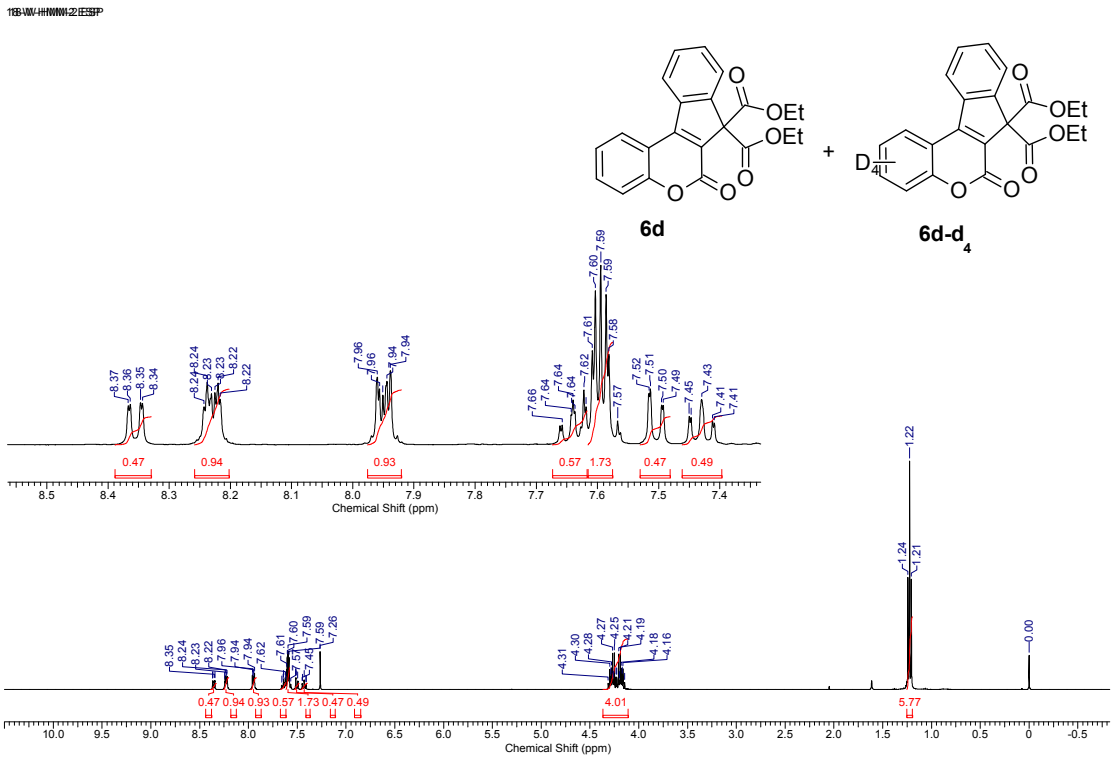


Figure S3. ^{1}H NMR spectrum of compound **6d/6d-d$_4$**

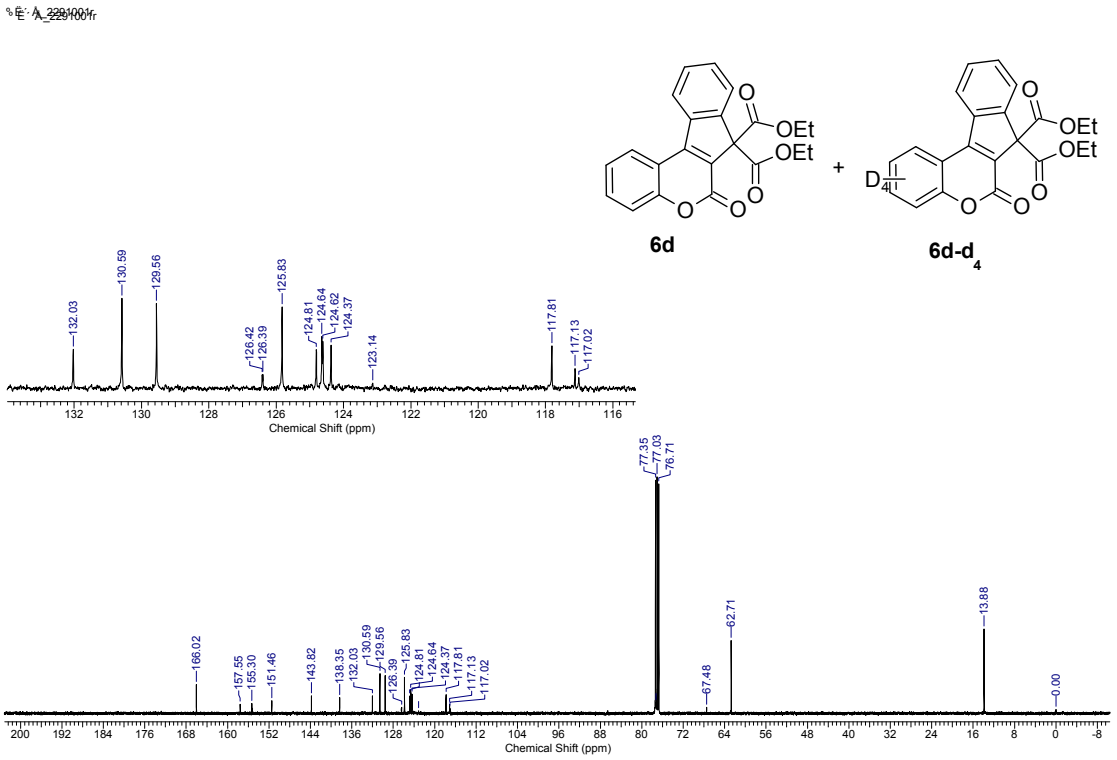
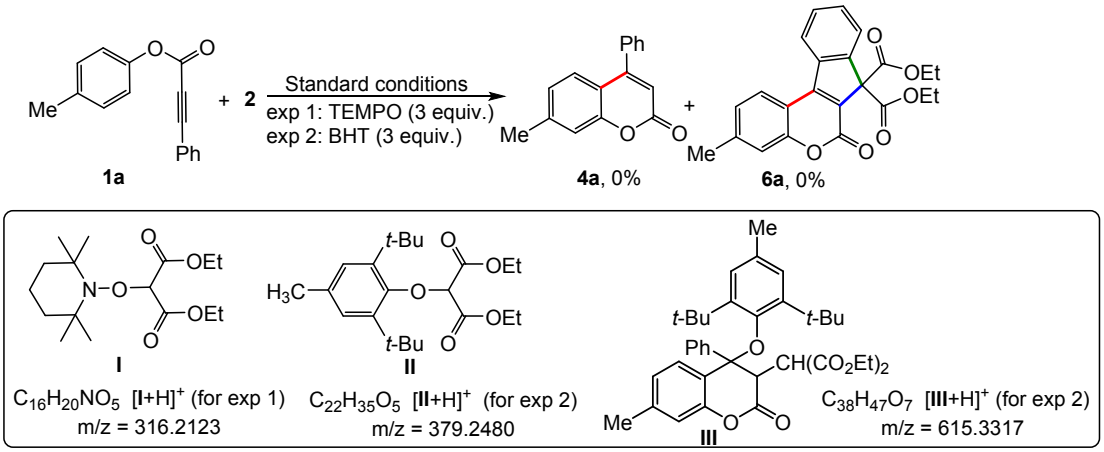


Figure S4. ^{13}C NMR spectrum of compound **6d/6d-d$_4$**

3.2 Radical scavenger experiments



Scheme S3. Radical scavenger experiments

P-tolyl 3-phenylpropiolate (23.6mg, 0.1mmol), diethyl bromomalonate (71.8 mg, 0.3 mmol), *fac*-Ir(ppy)$_3$ (0.005 mmol), $K_2HPO_4{\cdot}3H_2O$ (0.2 mmol) and TEMPO (0.3 mmol, 3 equiv., 46.8 mg) or BHT (0.3 mmol, 3 equiv., 55.7 mg) were combined in DMF (1.0 mL) under Ar atmosphere. The mixture was stirred at room temperature under blue LED lamp (3 W). After 12 hours, two strong molecular ion peaks (m/z = 316.2123 and 379.2480) were detected by ESI-MS (electrospray ionization mass spectrometry) and attributed to [**I** + H]$^+$ (exact mass: 316.2119) and [**II** + H]$^+$ (exact mass 379.2479). In addition, we found another one (m/z = 615.3317)

from the reaction with BHT, which could be attributed to [**III** + H]$^+$ (exact mass: 615.3316).

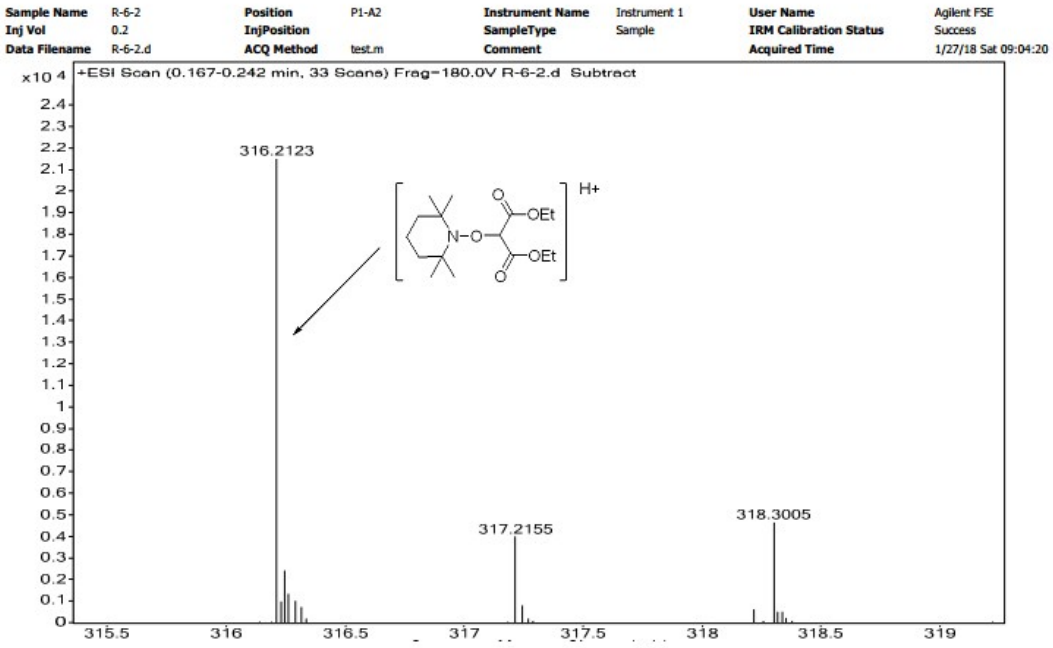


Figure S5. HRMS spectrum of compound [**I**+ H]$^+$ for exp 1

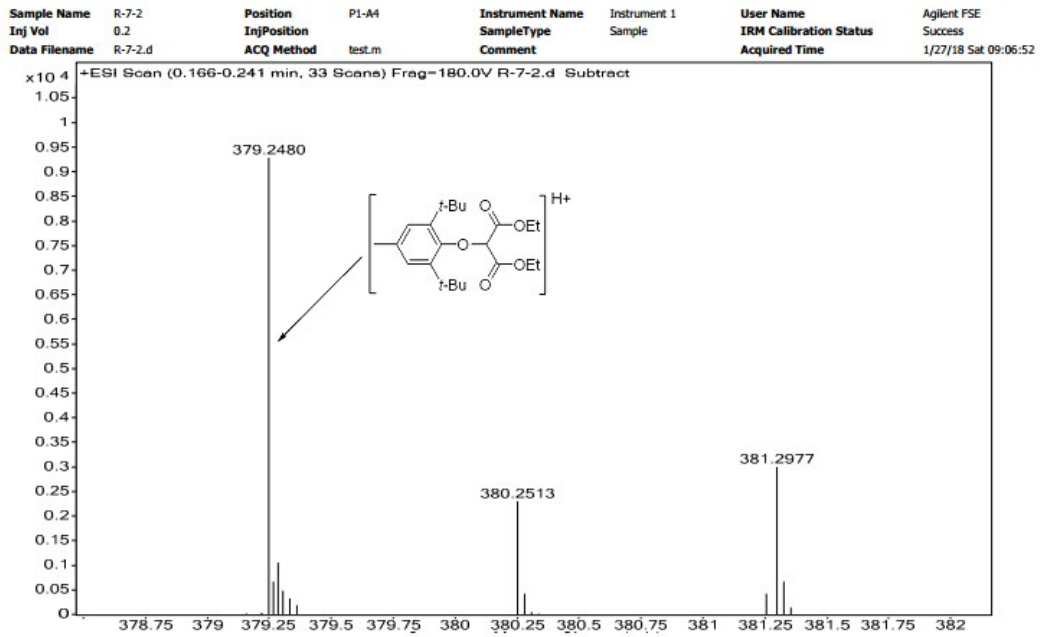


Figure S6. HRMS spectrum of compound [**II**+ H]$^+$ for exp 2

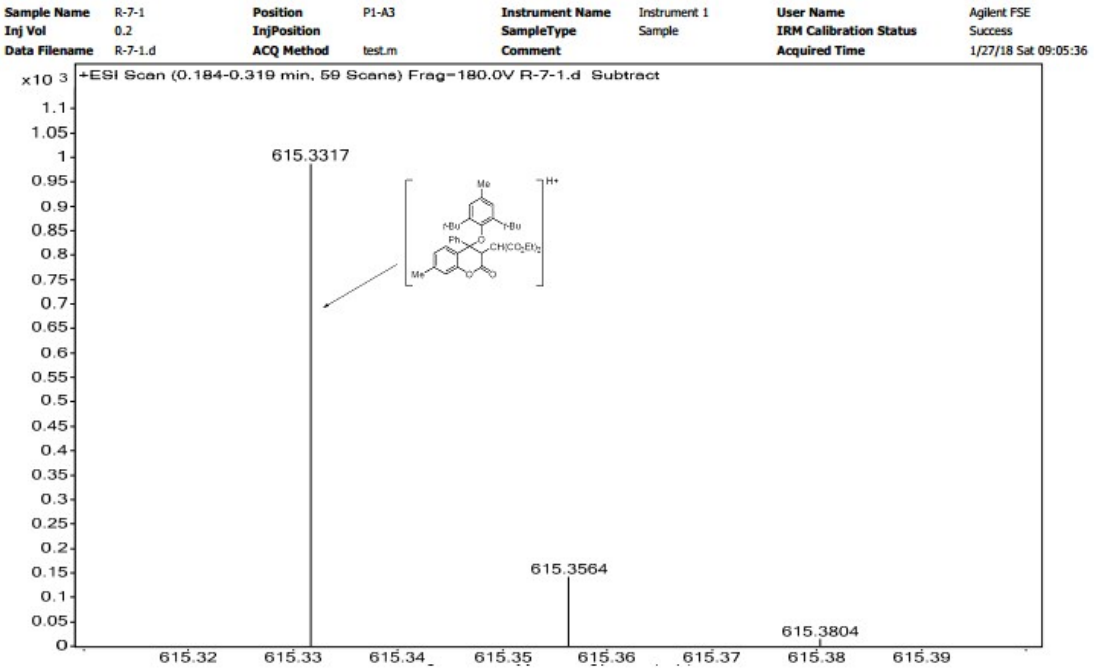


Figure S7. HRMS spectrum of compound [**III**+ H]$^+$ for exp 2

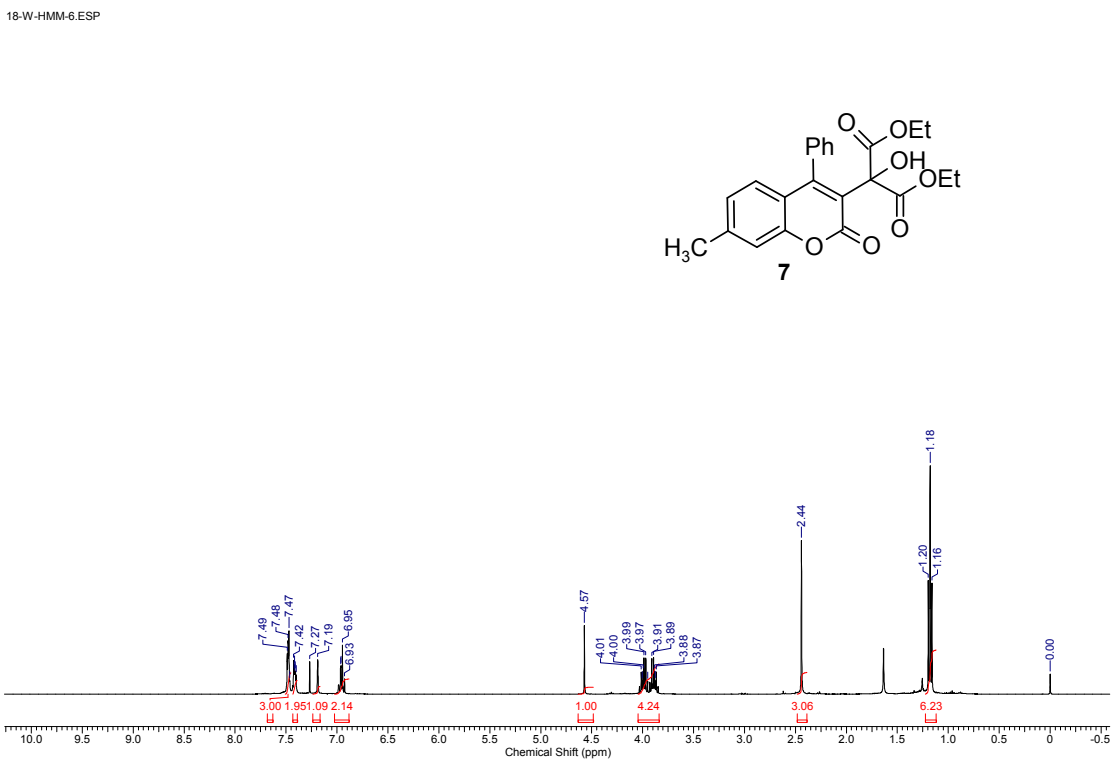


Figure S8. ^{1}H NMR spectrum of compound **7**

18-w-hmm-6.19_7301001r

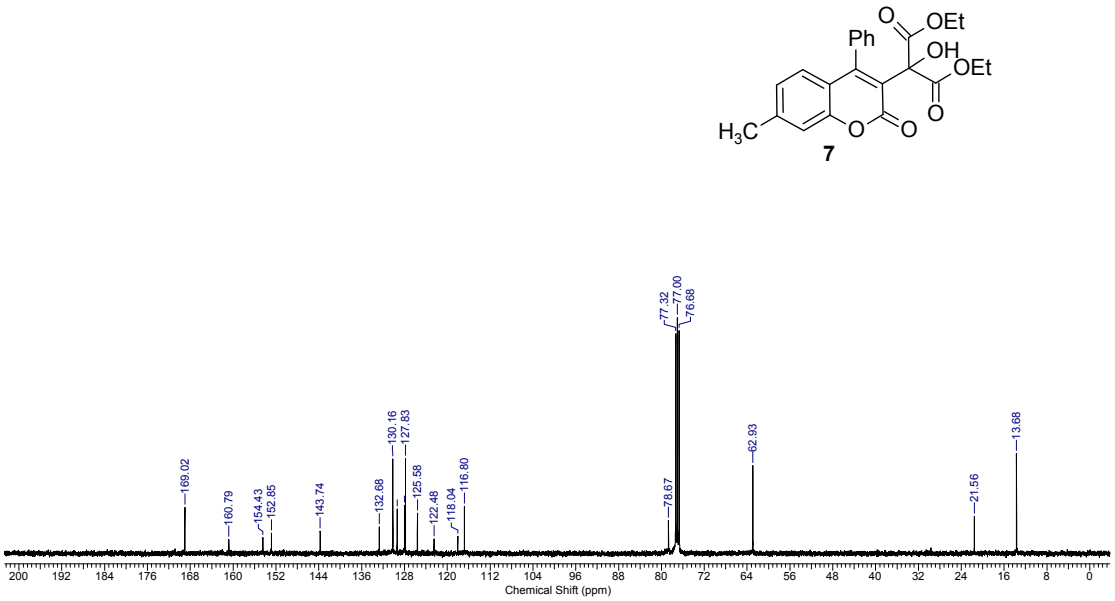


Figure S9. ^{13}C NMR spectrum of compound **7**

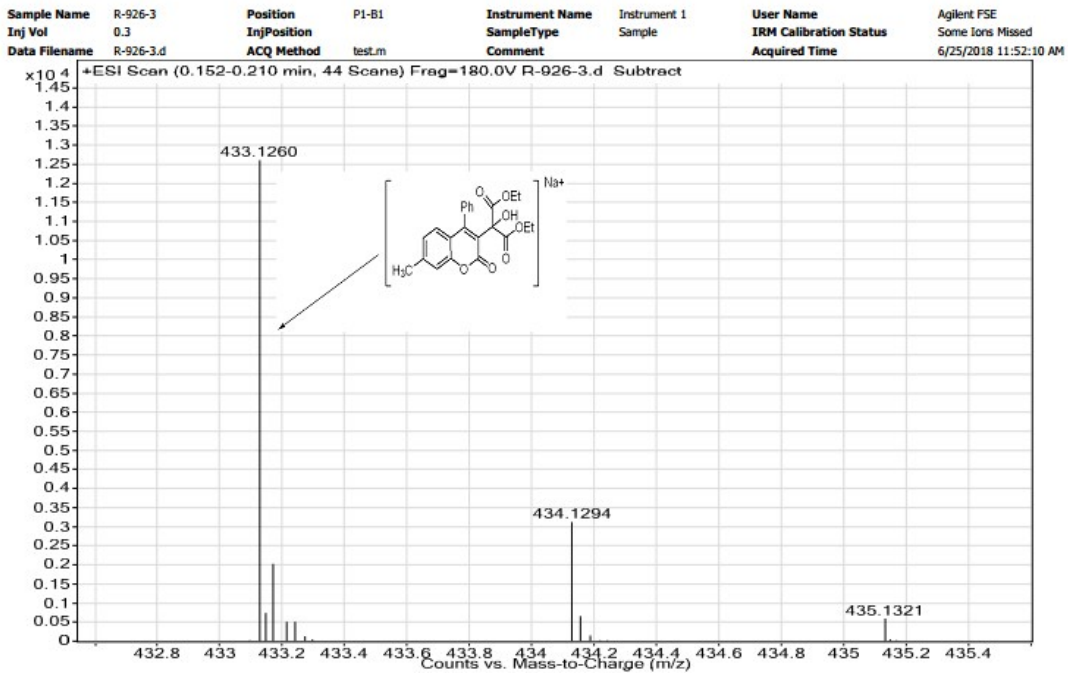


Figure S10. HRMS spectrum of compound [**7**+ Na]$^+$

4 Property test

4.1 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.

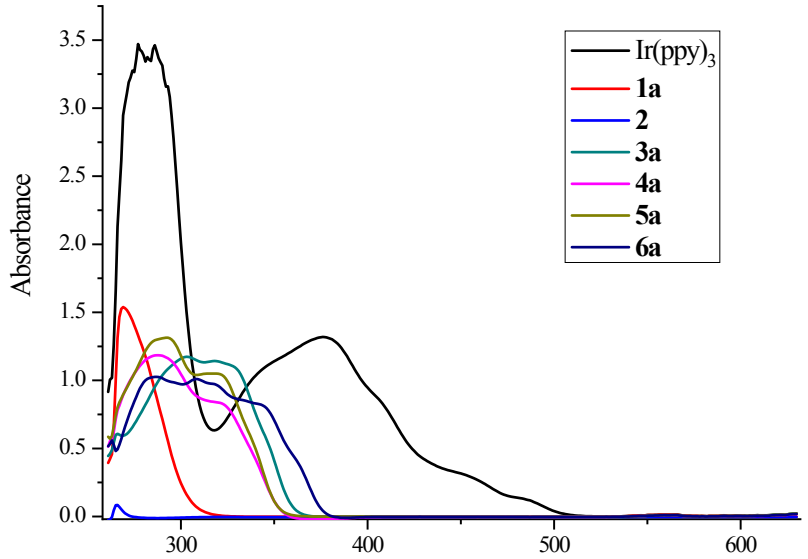


Figure S11. Absorption spectra of **Ir(ppy)$_3$** (λ_{max} = 505 nm), *p*-tolyl 3-phenylpropiolate **1a** (λ_{max} = 322 nm), diethyl bromomalonate **2** (λ_{max} = 274 nm), **3a** (λ_{max} = 367 nm), **4a** (λ_{max} = 357 nm), **5a** (λ_{max} = 357 nm), **6a** (λ_{max} = 383 nm) in DMF (0.1 mM).

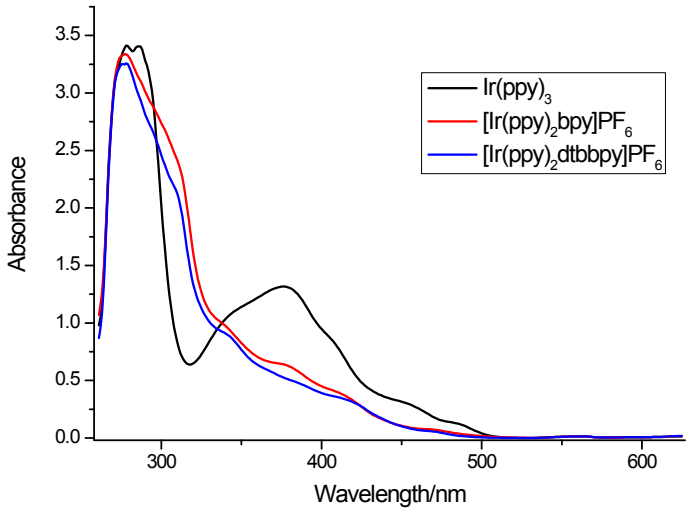


Figure S12. Absorption spectras of different catalysts: **Ir(ppy)$_3$** (λ_{max} = 505 nm), [**Ir(ppy)$_2$bpy]PF$_6$** (λ_{max} = 485 nm), [**Ir(ppy)$_2$dtbbpy]PF$_6$** (λ_{max} = 485 nm) in DMF (0.1 mM).

4.2 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.

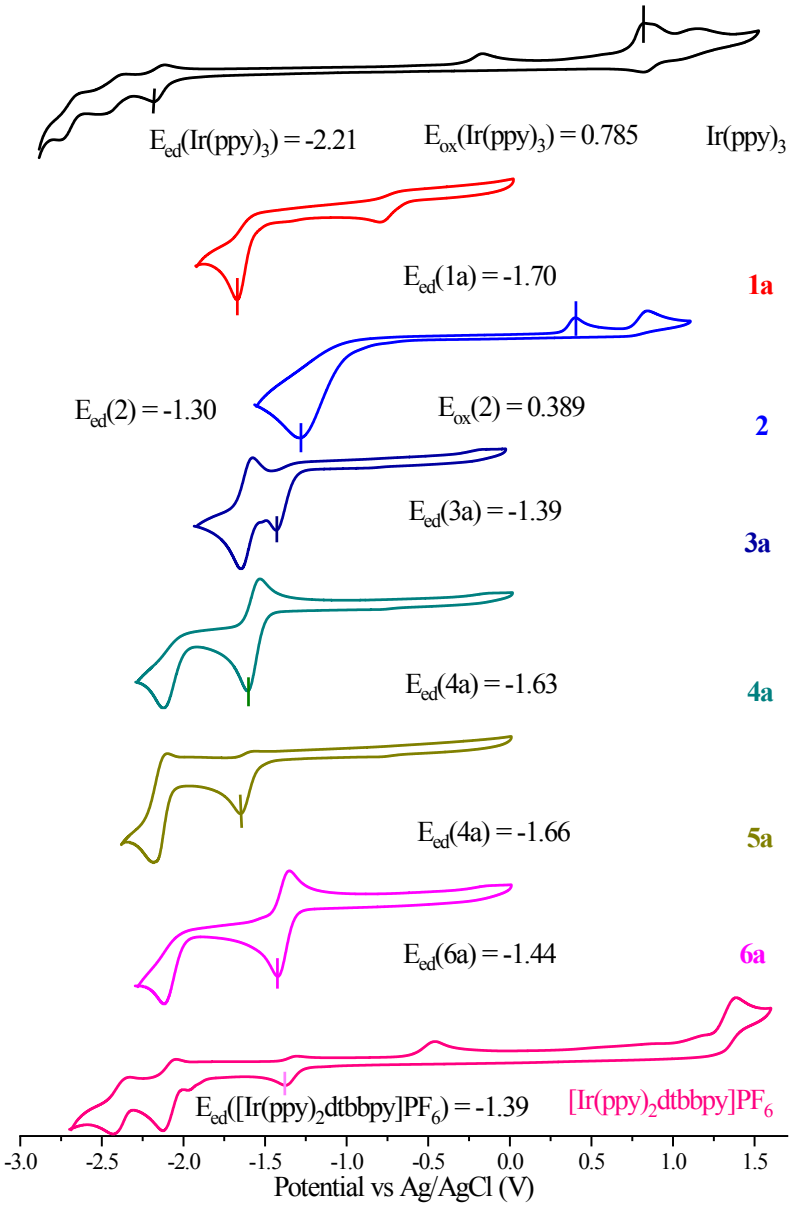


Figure S13. CV of Reaction reagents (1 mM in DMF)

4.3 Luminescence Quenching Experiments

Emission intensities were recorded using a F-4500 FL Spectrophotometer. First, all $Ir(ppy)_3$ solutions were excited at 381 nm and the emission /intensity at 370 nm was observed. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of $Ir(ppy)_3$ and different concentration of *p*-tolyl 3-phenylpropiolate **1a**, diethyl bromomalonate **2** and **6a** in DMF in 10 mm path length quartz cuvette was collected. Next, the product **5a** solution was excited at 377 nm and the emission intensity at 300 nm was observed. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of **5a** and different concentration of diethyl bromomalonate **2** in DMF in 10 mm path length quartz cuvette was collected. The product **6a** solution was excited at 309 nm and the emission intensity at 300 nm was observed. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of **6a** and different concentration of diethyl bromomalonate **2** in DMF in 10 mm path length quartz cuvette was

collected.

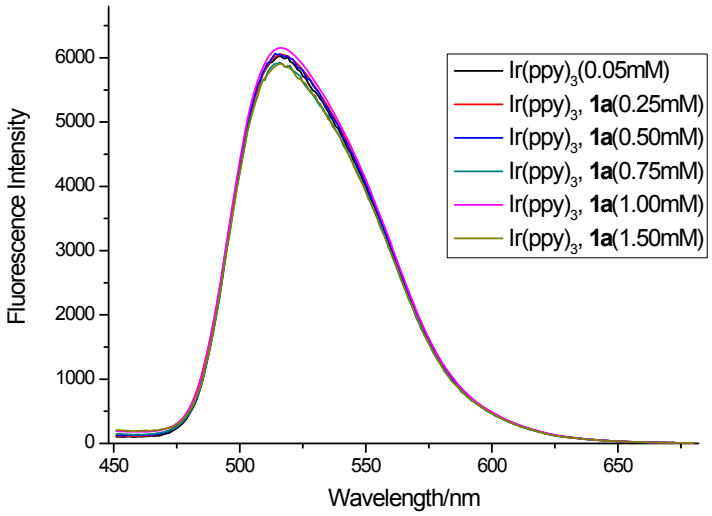


Figure S14. Luminescence quenching experiments of $Ir(ppy)_3$ with **1a**

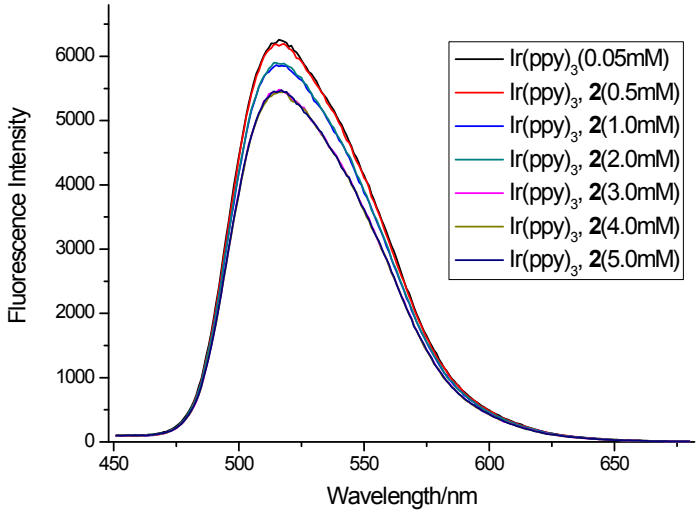


Figure S15. Luminescence quenching experiments of $Ir(ppy)_3$ with **2**

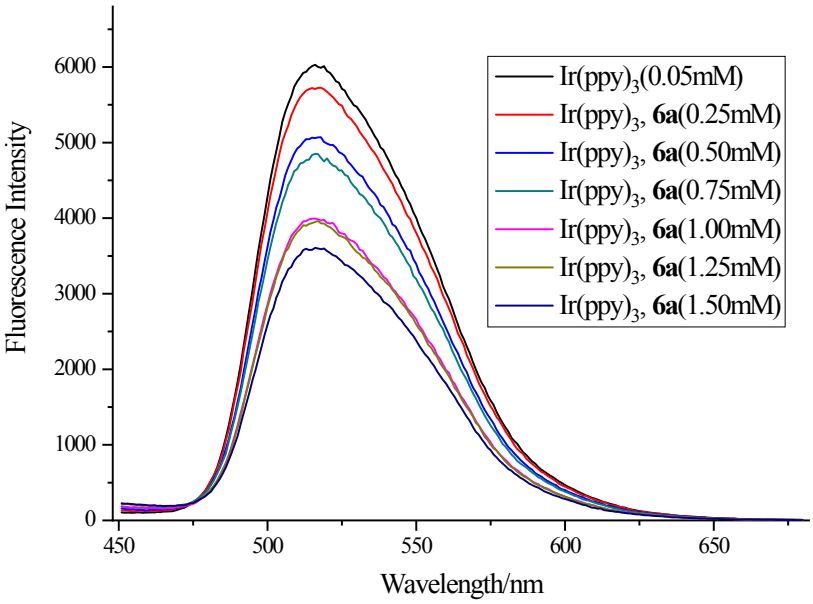


Figure S16. Luminescence quenching experiments of $Ir(ppy)_3$ with **6a**

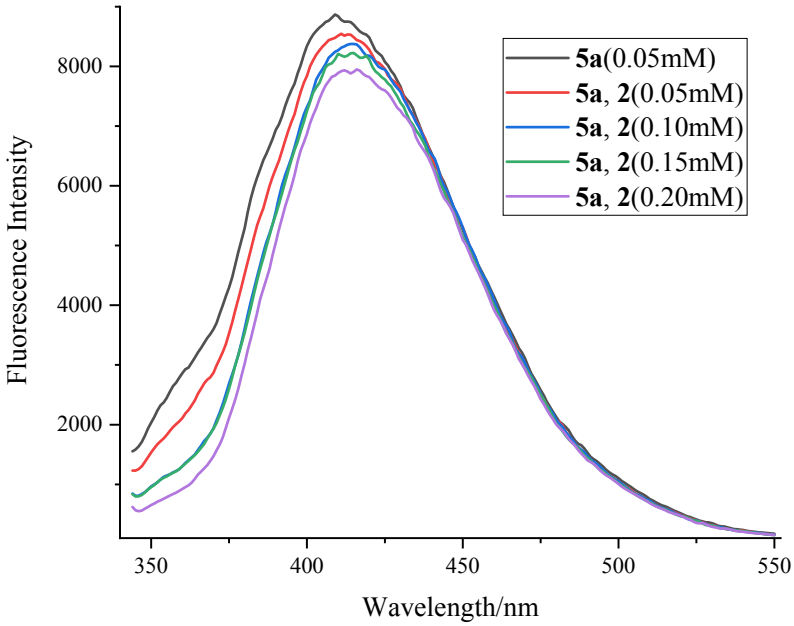


Figure S17. Luminescence quenching experiments of **5a** with **2**

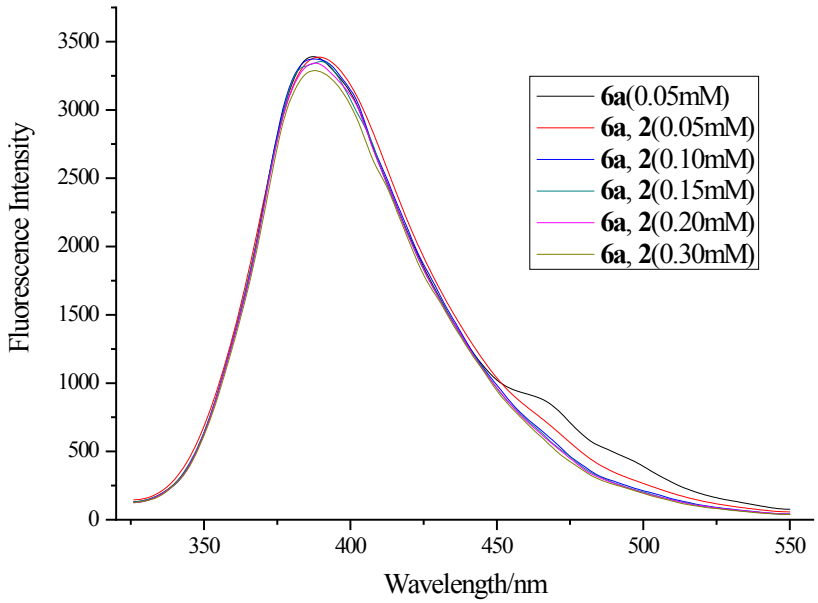


Figure S18. Luminescence quenching experiments of **6a** with **2**

4.4 Measurement and calculation of fluorescence quantum yield

The quantum yields of the different samples was calculated using quinine sulfate (QY = 0.542) as the standard (in 0.1 M H_2SO_4).[7] Emission spectra of solutions were recorded from 310 to 600 nm and 345 nm as the excitation wavelength as reference For calculation of quantum yield, various concentrations of each samples were made, all of which had absorbance less than 0.05 at 345 nm. And absorbance (optical density, OD) of all the samples was recorded at 345 nm.

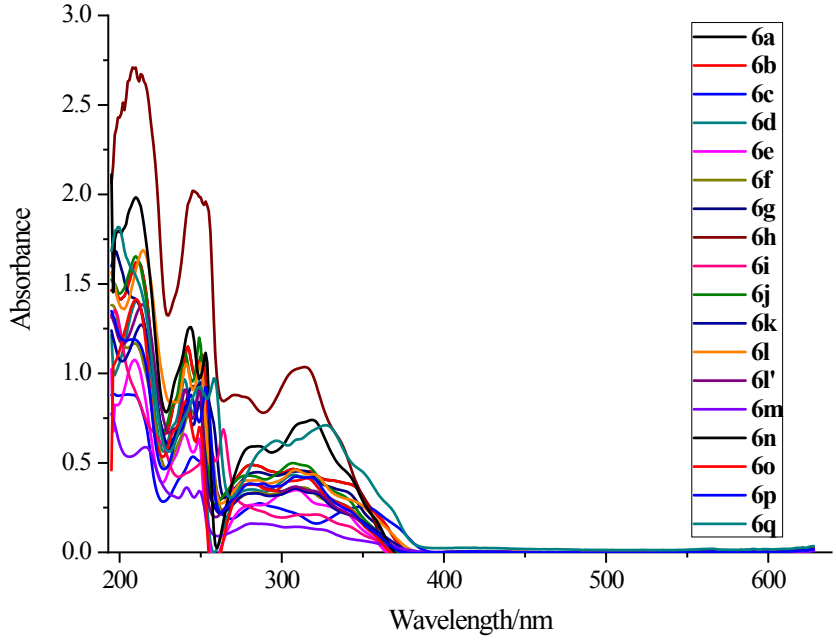


Figure S19. Absorption spectra of prodct **6** in CH_3CN (0.05 mM).

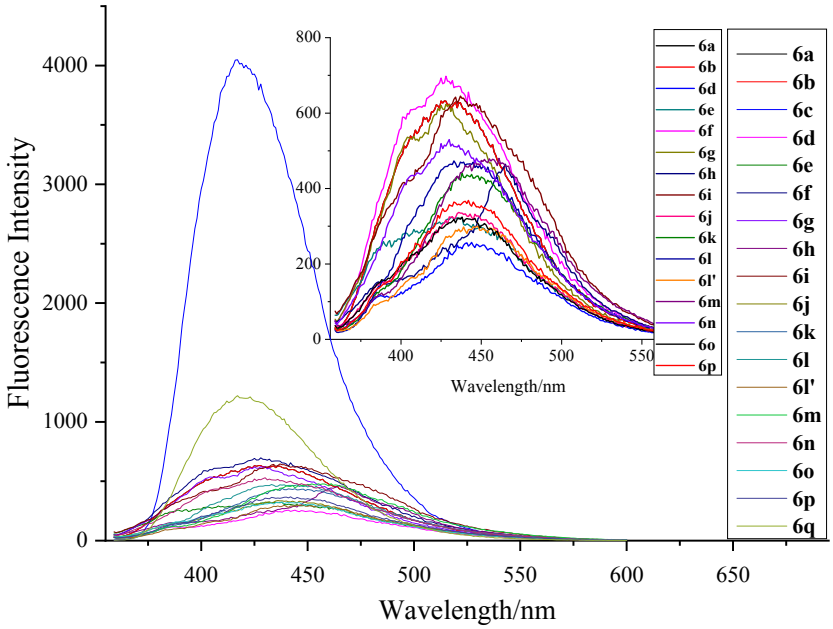


Figure S20. Fluorescence experiments of **6** in CH_3CN (0.05 mM).

Table S1. Fluorescence quantum yield of product **6**

Product **6**	Absorbance	Fluorescence area	Φ_F (%)
6a	0.010849	9623.145	**1.04**
6b	0.010595	9623.145	**1.06**
6c	0.010812	211114.5	**22.79**
6d	0.005415	9472.53	**2.04**
6e	0.004289	7999.405	**2.18**
6f	0.006968	9396.07	**1.57**
6g	0.023081	11751.78	**0.59**
6h	0.022783	8769.94	**0.45**
6i	0.005449	11889.6	**2.55**
6j	0.007292	9089.995	**1.45**
6k	0.020544	15708.41	**0.89**
6l	0.013975	10939.06	**0.91**
6l'	0.009899	10477.38	**1.24**
6m	0.005199	15448.07	**3.47**
6n	0.038741	14649.24	**0.44**
6o	0.018062	12934.98	**0.84**
6p	0.012191	12154.05	**1.16**
6q	0.031577	136246.5	**5.04**

4.5 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 CV and UV absorption spectrometry theory [**S19**].

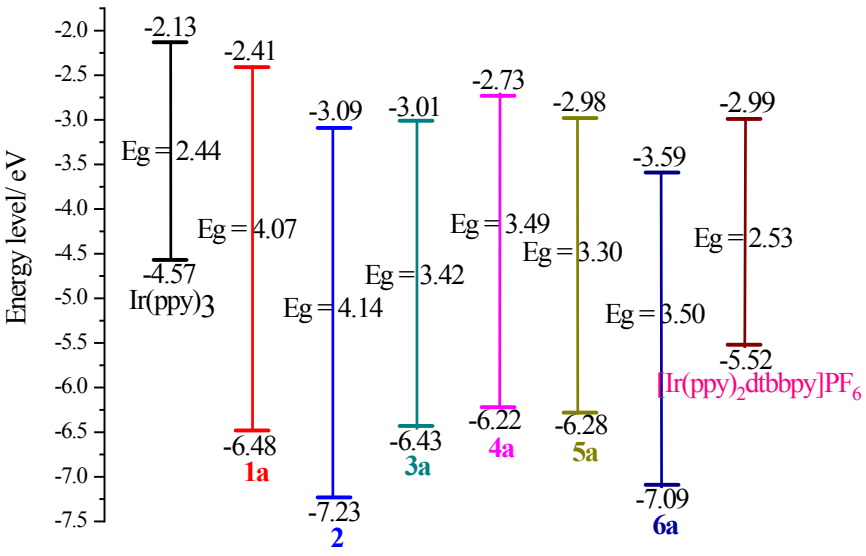
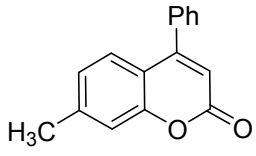
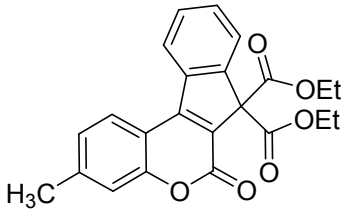


Figure S21. The E_{HOMO}, E_{LUMO} and Eg of different reagents

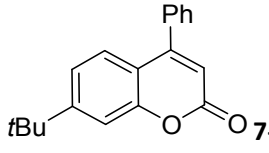
5. Characterization data



7-methyl-4-phenyl-*2H*-chromen-2-one (4a): This compound was synthesized from *p*-tolyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:5) as the eluting solvent to give the product as a white solid (7.3 mg, 31%), mp. 84.7-89.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.51 (m, 3H), 7.46-7.44 (m, 2H), 7.38-7.36 (m, 1H), 7.22 (s, 1H), 7.06-7.03 (m, 1H), 6.32 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.13, 155.72, 154.30, 143.23, 135.42, 129.63, 128.86, 128.45, 126.71, 125.39, 117.49, 116.57, 114.06, 21.65. HRMS (ESI) calcd. for $C_{16}H_{13}O_2$ $(M+H)^+$: 237.0910, found: 237.0914.

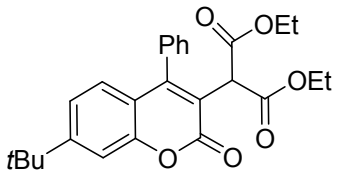


diethyl 3-methyl-6-oxoindeno[2,1-*c*]chromene-7,7(*6H*)-dicarboxylate (6a): This compound was synthesized from *p*-tolyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:7) as the eluting solvent to give the product as a white solid (21.0 mg, 54%). mp. 165.2-166.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22-8.19 (m, 4H), 7.95-7.92 (m, 1H), 7.61-7.55 (m, 2H), 7.30 (s, 1H), 7.23 (d, J = 8.1Hz, 1H), 4.31-4.14 (m, 4H), 2.51 (s, 3H), 1.22 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.20, 157.79, 155.48, 151.57, 143.89, 143.37, 138.51, 130.52, 129.51, 125.81, 125.59, 125.24, 124.63, 124.46, 117.93, 114.64, 67.45, 62.68, 21.81, 13.91. HRMS (ESI) calcd. for $C_{23}H_{21}O_6$ $(M+H)^+$: 393.1333, found: 393.1332.

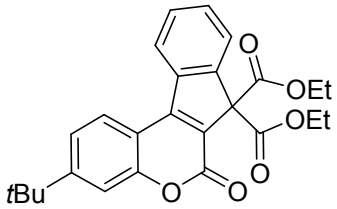


7-(*tert*-butyl)-4-phenyl-*2H*-chromen-2-one (4b): This compound was synthesized from 4-(*tert*-butyl)phenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:5) as

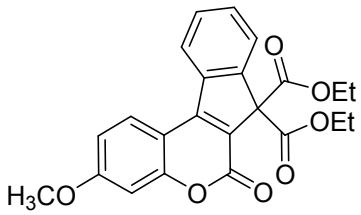
the eluting solvent to give the product as a yellow oil (3.2 mg, 12%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.51 (m, 3H), 7.47-7.42 (m, 4H), 7.28-7.26 (m, 1H), 6.33 (s, 1H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.20, 156.45, 155.54, 154.23, 135.40, 129.60, 128.82, 128.41, 126.52, 121.70, 116.46, 114.22, 35.19, 31.02. HRMS (ESI) calcd. for $C_{19}H_{19}O_2$ $(M+H)^+$: 279.1380, found: 279.1383.



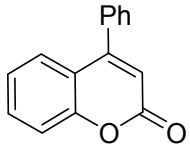
diethyl 2-(7-(*tert*-butyl)-2-oxo-4-phenyl-*2H*-chromen-3-yl)malonate (5b): This compound was synthesized from 4-(*tert*-butyl)phenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:7) as the eluting solvent to give the product as a yellow oil (7.0 mg, 16%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.47 (m, 3H), 7.43-7.39 (m, 3H), 7.21 (d, J = 8.6 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 4.57 (s, 1H), 4.01-3.85 (m, 4H), 1.33 (s, 9H), 1.18 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.05, 160.93, 156.97, 154.27, 152.79, 132.69, 130.15, 129.40, 127.85, 122.67, 121.96, 117.93, 113.47, 78.64, 62.94, 35.20, 30.95, 13.71. HRMS (ESI) calcd. for $C_{26}H_{29}O_6$ $(M+H)^+$: 437.1959, found: 437.1958.



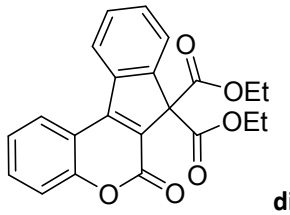
diethyl 3-(*tert*-butyl)-6-oxoindeno[2,1-*c*]chromene-7,7(*6H*)-dicarboxylate (6b): This compound was synthesized from 4-(*tert*-butyl)phenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:5) as the eluting solvent to give the product as a white solid (27.4 mg, 63%), mp. 165.3-165.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 8.4 Hz, 1H), 8.22-8.20 (m, 1H), 7.95-7.93 (m, 1H), 7.61-7.55 (m, 2H), 7.51 (d, J = 1.8 Hz, 1H), 7.46 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 4.29-4.15 (m, 4H), 1.40(s, 9H), 1.21(t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.18, 157.87, 156.54, 155.45, 151.44, 143.89, 138.52, 130.50, 129.53, 125.79, 125.50, 124.58, 124.34, 121.96, 114.59, 114.55, 67.42, 62.66, 35.32, 31.04, 13.91. HRMS (ESI) calcd. for $C_{26}H_{27}O_6$ $(M+H)^+$: 435.1802, found: 435.1804.



diethyl 3-methoxy-6-oxoindeno[2,1-c]chromene-7,7(6H)-dicarboxylate (6c): This compound was synthesized from 4-methoxyphenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:7) as the eluting solvent to give the product as a white solid (30.2 mg, 74%), mp. 178.9-180.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25-8.22 (m, 1H), 8.19-8.17 (m, 1H), 7.94-7.92 (m, 1H), 7.59-7.56 (m, 2H), 7.00-6.98 (m, 2H), 4.31-4.15 (m, 4H), 3.93 (s, 3H), 1.22 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.32, 162.84, 157.81, 157.42, 151.68, 144.03, 138.54, 130.50, 129.45, 125.88, 125.73, 124.50, 122.97, 112.78, 110.59, 101.48, 67.41, 62.63, 55.83, 13.89. HRMS (ESI) calcd. for $C_{23}H_{231}O_7$ $(M+H)^+$: 409.1282, found: 409.1285.

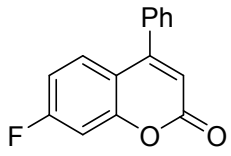


4-phenyl-*2H*-chromen-2-one (4d)[5, 6, 7, 8]**:** This compound was synthesized from phenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:5) as the eluting solvent to give the product as a white solid (3.9 mg, 18%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.56 (m, 1H), 7.55-7.53 (m, 3H), 7.51 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H), 7.48-7.45 (m, 2H), 7.44-7.41 (m, 1H), 7.24-7.22 (m, 1H), 6.39 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.82, 155.71, 154.21, 153.22, 131.96, 129.72, 128.91, 128.48, 127.04, 124.20, 119.01, 117.37, 115.23. HRMS (ESI) calcd. for $C_{15}H_{11}O_2$ $(M+H)^+$: 223.0754, found: 223.0755.

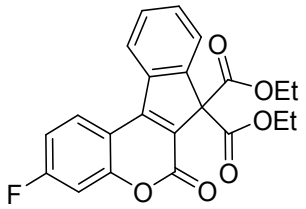


diethyl 6-oxoindeno[2,1-*c*]chromene-7,7(*6H*)-dicarboxylate (6d): This compound was synthesized from phenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:7) as the eluting solvent to give the product as a white solid (30.1 mg, 80%), mp. 133.1-134.9 °C.. ^{1}H

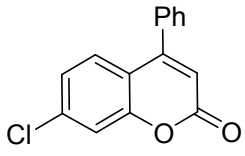
NMR (400 MHz, $CDCl_3$): δ 8.36 (dd, J_1 = 8.1 Hz, J_2 = 1.3 Hz, 1H), 8.24-8.22 (m, 1H), 7.96-7.94 (m, 1H), 7.66-7.58 (m, 3H), 7.51-7.49 (m, 1H), 7.45-7.41 (m, 1H), 4.31-4.14 (m, 4H), 1.22 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.02, 157.55, 155.30, 151.47, 143.81, 138.34, 132.04, 130.59, 129.56, 126.41, 125.83, 124.81, 124.64, 124.38, 117.81, 117.12, 67.47, 62.71, 13.88. HRMS (ESI) calcd. for $C_{22}H_{19}O_6$ $(M+H)^+$: 379.1176, found: 379.1177.



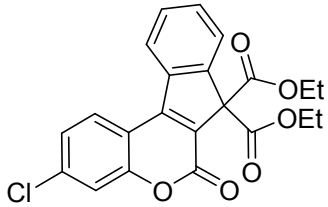
7-fluoro-4-phenyl-*2H*-chromen-2-one (4e): This compound was synthesized from 4-fluorophenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:5) as the eluting solvent to give the product as a white solid (5.8 mg, 24%), mp. 119.1-120.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.52 (m, 3H), 7.50 (dd, J_1 = 8.9 Hz, J_2 = 6.1 Hz, 1H), 7.45-7.43 (m, 2H), 7.14 (dd, J_1 = 8.9 Hz, J_2 = 2.5 Hz, 1H), 7.00-6.95 (m, 1H), 6.34 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.78, 161.85 (d, J = 282.4 Hz), 155.32, 135.07, 129.91, 129.03, 128.81 (d, J = 10.3 Hz), 128.38, 115.80 (d, J = 2.9 Hz), 113.98 (d, J = 2.9 Hz), 112.38, 112.16, 104.82 (d, J = 25.7). ^{19}F NMR (376.5 MHz, $CDCl_3$): δ -105.35. HRMS (ESI) calcd. for $C_{15}H_{10}FO_2$ $(M+H)^+$: 241.0659, found: 241.0660.



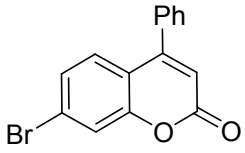
diethyl 3-fluoro-6-oxoindeno[2,1-*c*]chromene-7,7(*6H*)-dicarboxylate (6e): This compound was synthesized from 4-fluorophenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:7) as the eluting solvent to give the product as an oil (22.0 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (dd, J_1 = 8.9 Hz, J_2 = 5.9 Hz, 1H), 8.18-8.16 (m, 1H), 7.96-7.94 (m, 1H), 7.62-7.57 (m, 2H), 7.23-7.15 (m, 2H), 4.32-4.15 (m, 4H), 1.23 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.93, 165.73, 163.20, 157.13, 156.77, 156.65, 151.09, 143.87, 138.03, 130.21 (d, J = 118.8 Hz), 126.50, 126.39, 125.97, 124.43, 113.89 (d, J = 2.9 Hz), 112.53 (d, J = 22.7 Hz), 105.30 (d, J = 25.7 Hz), 67.50, 62.79, 13.88. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ -104.49. HRMS (ESI) calcd. for $C_{22}H_{19}FO_6$ $(M+H)^+$: 397.1082, found: 397.1081.



7-chloro-4-phenyl-*2H*-chromen-2-one (4f): This compound was synthesized from 4-chlorophenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:5) as the eluting solvent to give the product as a white solid (5.1 mg, 20%), mp. 86.5-88.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.53 (m, 3H), 7.44-7.42 (m, 4H), 7.22-7.20 (m, 1H), 6.37 (d, J = 0.98 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.12, 155.10, 154.48, 137.91, 134.82, 129.96, 129.04, 128.37, 127.96, 124.76, 117.68, 117.58, 115.03. HRMS (ESI) calcd. for $C_{15}H_{10}ClO_2$ $(M+H)^+$: 257.0364, found: 257.0364.

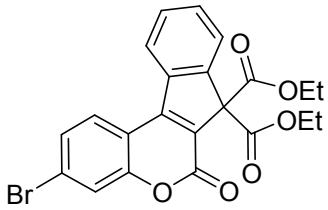


diethyl 3-chloro-6-oxoindeno[2,1-*c*]chromene-7,7(*6H*)-dicarboxylate (6f): This compound was synthesized from 4-chlorophenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:7) as the eluting solvent to give the product as a white solid (16.5 mg, 40%), mp. 182.9-184.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 8.6 Hz, 1H), 8.18-8.16 (m, 1H), 7.96-7.94 (m, 1H), 7.61-7.59 (m, 2H), 7.51 (d, J = 2.1 Hz, 1H), 7.41 (dd, J_1 = 8.6 Hz, J_2 = 2.0 Hz, 1H), 4.30-4.16 (m, 4H), 1.23 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.83, 156.90, 155.66, 150.93, 143.81, 138.06, 137.93, 130.85, 129.66, 126.20, 125.98, 124.95, 124.47, 118.08, 115.72, 67.56, 62.84, 13.90. HRMS (ESI) calcd. for $C_{22}H_{18}ClO_6$ $(M+H)^+$: 413.0786, found: 413.0791.

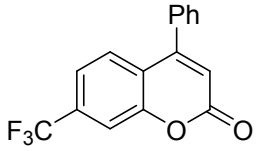


7-bromo-4-phenyl-*2H*-chromen-2-one (4g): This compound was synthesized from 4-bromophenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:5) as the eluting solvent to give the product as a yellow oil (6.3 mg, 21%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.58 (m, 1H), 7.55-7.53 (m, 3H), 7.45-7.42 (m, 2H), 7.36 (d, J = 1.0 Hz, 2H), 6.39 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.00, 155.15, 154.39, 134.74, 129.95, 129.03, 128.35, 127.81 (d, J =

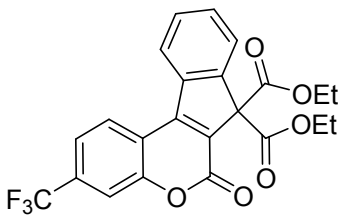
46.2 Hz), 125.93, 120.52, 118.02, 115.24. HRMS (ESI) calcd. for $C_{15}H_{10}BrO_2$ $(M+H)^+$: 300.9859, found: 300.9860.



diethyl 3-bromo-6-oxoindeno[2,1-*c*]chromene-7,7(*6H*)-dicarboxylate (6g): This compound was synthesized from 4-bromophenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:7) as the eluting solvent to give the product as a white solid (17.4 mg, 38%), mp. 172.0-172.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 8.6 Hz 1H), 8.18-8.15 (m, 1H), 7.96-7.94 (m, 1H), 7.68 (d, J = 2.0 Hz, 1H), 7.61-7.53 (m, 3H), 4.34-4.14 (m, 4H), 1.22 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.63, 165.76, 156.87, 155.52, 143.78, 137.90, 130.84, 129.65, 129.25, 128.06, 127.75, 126.07, 125.96, 125.71, 124.44, 121.03, 119.88, 116.06, 62.82, 62.03, 13.88. HRMS (ESI) calcd. for $C_{22}H_{20}BrO_6$ $(M+H)^+$: 459.0438, found: 459.0440.

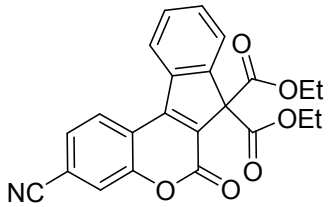


4-phenyl-7-(trifluoromethyl)-*2H*-chromen-2-one (4h): This compound was synthesized from 4-(trifluoromethyl)phenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:5) as the eluting solvent to give the product as a white solid (16.6 mg, 57%), mp. 70.9-71.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.63 (m, 2H), 7.58-7.55 (m, 3H), 7.49-7.44 (m, 3H), 6.50 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.74, 154.64, 153.81, 134.39, 133.69, 133.25, 129.13, 129.01 (d, J = 223.0 Hz), 128.36, 121.64, 120.67 (d, J = 3.7 Hz), 117.06, 114.72 (d, J = 4.4 Hz). ^{19}F NMR (376.5 MHz, $CDCl_3$): δ -62.90. HRMS (ESI) calcd. for $C_{16}H_{10}F_3O_2$ $(M+H)^+$: 291.0627, found: 291.0630.

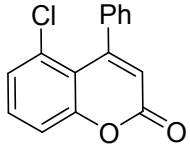


diethyl 6-oxo-3-(trifluoromethyl)indeno[2,1-*c*]chromene-7,7(*6H*)-dicarboxylate (6h): This compound was synthesized from 4-(trifluoromethyl)phenyl 3-phenylpropiolate following general

procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:7) as the eluting solvent to give the product as a white solid (16.0 mg, 36%), mp. 84.7-85.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J = 8.3 Hz, 1H), 8.22-8.20 (m, 1H), 7.98-7.96 (m, 1H), 7.75 (s, 1H), 7.68-7.66 (m, 1H), 7.64-7.55 (m, 2H), 4.32-4.15 (m, 4H), 1.23 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.56, 156.64, 154.92, 150.42, 143.70, 137.66, 133.53 (d, J = 33.8 Hz), 130.39 (d, J = 122.5 Hz), 129.36, 128.68, 128.22 (d, J = 36.0 Hz), 125.83 (d, J = 36.7 Hz), 124.49, 120.86 (d, J = 3.7 Hz), 119.75, 1115.14 (d, J = 3.7 Hz), 67.63, 62.92, 13.87. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ -62.98. HRMS (ESI) calcd. for $C_{23}H_{18}F_3O_6$ $(M+H)^+$: 447.1050, found: 447.1053.

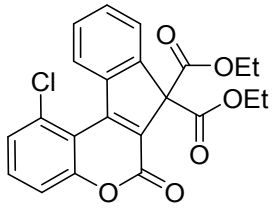


diethyl 3-cyano-6-oxoindeno[2,1-*c*]chromene-7,7(*6H*)-dicarboxylate (6i): This compound was synthesized from 4-cyanophenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:7) as the eluting solvent to give the product as an oil (11.3 mg, 28%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, J = 8.2 Hz, 1H), 8.19-8.17 (m, 1H), 7.99-7.96 (m, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.69 (dd, J_1 = 8.2 Hz, J_2 = 1.6 Hz, 1H), 7.64-7.62 (m, 2H), 4.30-4.17 (m, 4H), 1.23 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.02, 165.36, 156.14, 154.69, 150.10, 143.63, 137.31, 131.17, 129.85, 128.99, 127.33, 126.09, 125.83, 124.43, 121.47, 120.72, 117.30, 114.97, 67.73, 63.01, 13.86. HRMS (ESI) calcd. for $C_{23}H_{18}NO_6$ $(M+H)^+$: 404.1129, found: 404.1131.

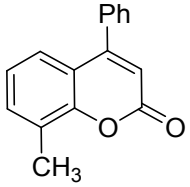


5-chloro-4-phenyl-*2H*-chromen-2-one (4j): This compound was synthesized from 2-chlorophenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:5) as the eluting solvent to give the product as a white solid (3.9 mg, 15%), mp. 86.3-87.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.56 (m, 1H), 7.55-7.53 (m, 2H), 7.52-7.50 (m, 1H), 7.48-7.45 (m, 2H), 7.44-7.41 (m, 1H), 7.24-7.22 (m, 1H), 6.40 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.83, 155.69, 154.15, 135.17, 131.95, 129.70, 128.88, 128.45, 127.01, 124.19, 118.96, 117.35, 115.18. HRMS (ESI) calcd. for

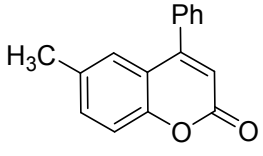
$C_{15}H_{10}ClO_2$ $(M+H)^+$: 257.0364, found: 257.0366.



diethyl 1-chloro-6-oxoindeno[2,1-*c*]chromene-7,7(*6H*)-dicarboxylate (6j): This compound was synthesized from 2-chlorophenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:7) as the eluting solvent to give the product as a yellow oil (6.4 mg, 17%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (dd, J_1 = 8.0 Hz, J_2 = 1.4 Hz, 1H), 8.24-8.22 (m, 1H), 7.96-7.94 (m, 1H), 7.66-7.56 (m, 3H), 7.52-7.49 (m, 1H), 7.45-7.41 (m, 1H), 4.37 (s, 1H), 4.31-4.14 (m, 4H), 1.22 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.03, 157.55, 155.35, 151.45, 143.88, 138.38, 132.03, 130.58, 129.56, 126.49, 125.87, 124.82, 124.64, 124.37, 117.85, 117.17, 67.52, 62.72, 13.89. HRMS (ESI) calcd. for $C_{22}H_{18}ClO_6$ $(M+H)^+$: 413.0786, found: 413.0796.

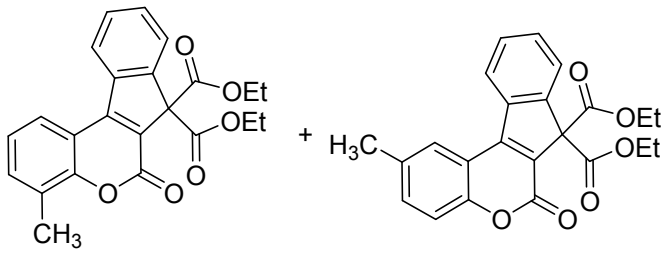


8-methyl-4-phenyl-*2H*-chromen-2-one (4k): This compound was synthesized from *m*-tolyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:5) as the eluting solvent to give the product as a yellow oil (3.6 mg, 15%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.50 (m, 4H), 7.46-7.43 (m, 2H), 7.41 (d, J = 7.5 Hz, 1H), 7.33-7.31 (m, 1H), 7.13 (t, J = 7.7 Hz, 1H), 6.37 (s, 1H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.93, 156.07, 152.48, 135.56, 133.23, 129.53, 128.78, 128.46, 126.69, 124.77, 123.60, 118.73, 114.89, 15.80. HRMS (ESI) calcd. for $C_{16}H_{13}O_2$ $(M+H)^+$: 237.0910, found: 237.0911.

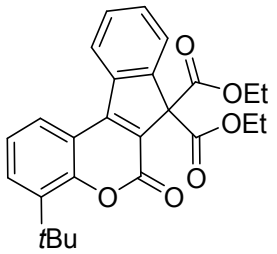


6-methyl-4-phenyl-*2H*-chromen-2-one (4k'): This compound was synthesized from *m*-tolyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:5) as the eluting solvent to give the product as a yellow oil (2.4 mg, 10%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.53

(m, 3H), 7.46-7.44 (m, 2H), 7.37-7.35 (m, 1H), 7.32-7.30 (m, 1H), 7.25 (s, 1H), 6.35 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.01, 155.63, 152.31, 135.37, 133.88, 132.93, 129.60, 128.86, 128.43, 126.70, 118.67, 117.06, 115.18, 20.95. HRMS (ESI) calcd. for $C_{16}H_{13}O_2$ $(M+H)^+$: 237.0910, found: 237.0911.

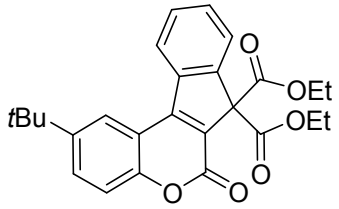


diethyl 4-methyl-6-oxoindeno[2,1-*c*]chromene-7,7(*6H*)-dicarboxylate (6k) and diethyl 2-methyl-6-oxoindeno[2,1-*c*]chromene-7,7(*6H*)-dicarboxylate (6k'): This compound was synthesized from *m*-tolyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:7) as the eluting solvent to give the product as a white solid (15.7 mg, 40%), mp. 85.9-87.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25-8.19 (m, 2.7H), 8.12 (s, 1.1H), 7.95-7.93 (m, 1.9H), 7.62-7.56 (m, 4.0H), 7.50-7.38 (m, 3.5H), 7.32 (t, J = 7.7 Hz, 0.8H), 4.31-4.14 (m, 8.1H), 2.55 (s, 2.0H), 2.53 (s, 3.0H), 1.24-1.20 (m, 12.3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.14, 166.09, 157.76, 157.62, 153.69, 153.45, 151.76, 151.36, 143.82, 138.56, 138.47, 134.02, 133.34, 133.03, 130.49, 130.45, 129.49, 127.27, 126.35, 126.20, 125.77, 124.70, 124.60, 123.88, 122.43, 117.48, 116.88, 116.84, 67.42, 67.37, 62.67, 21.20, 16.33, 13.90, 13.88. HRMS (ESI) calcd. for $C_{23}H_{21}O_6$ $(M+H)^+$: 393.1333, found: 393.1334.

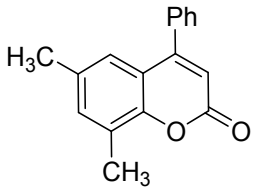


diethyl 4-(*tert*-butyl)-6-oxoindeno[2,1-*c*]chromene-7,7(*6H*)-dicarboxylate (6l): This compound was synthesized from 3-(*tert*-butyl)phenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:7) as the eluting solvent to give the product as an oil (7.8 mg, 18%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26-8.22 (m, 2H), 7.95-7.92 (m, 1H), 7.64 (dd, J_1 = 7.8 Hz, J_2 = 1.3 Hz, 1H), 7.59-7.56 (m, 2H), 7.35 (t, J

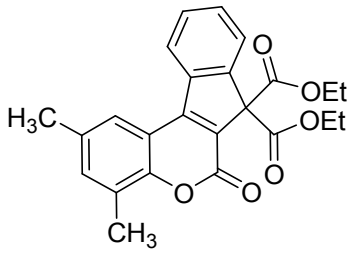
= 7.8 Hz, 1H), 4.32-4.17 (m, 4H), 1.57 (s, 9H), 1.24 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 166.25, 156.86, 154.09, 152.07, 143.83, 138.83, 138.77, 130.93, 130.33, 129.62, 129.49, 125.83, 125.72, 124.70, 123.81, 122.96, 117.58, 67.42, 65.58, 62.65, 35.36, 30.01, 13.88. HRMS (ESI) calcd. for $C_{26}H_{27}O_6$ $(M+H)^+$: 435.1802, found: 435.1800.



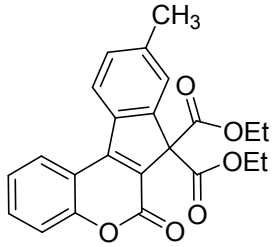
diethyl 2-(*tert*-butyl)-6-oxoindeno[2,1-*c*]chromene-7,7(*6H*)-dicarboxylate (6l'): This compound was synthesized from 3-(*tert*-butyl)phenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:7) as the eluting solvent to give the product as an oil (19.5 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.34 (d, *J* = 2.2 Hz, 1H), 8.21 (d, *J* = 7.0 Hz, 1H), 7.96-7.94 (m, 1H), 7.69 (dd, J_1 = 8.8 Hz, J_2 = 2.2 Hz, 1H), 7.65-7.57 (m, 2H), 7.44 (d, *J* = 8.8 Hz, 1H), 4.31-4.11 (m, 4H), 1.45 (s, 9H), 1.21 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 166.09, 157.86, 153.31, 151.70, 147.36, 143.94, 138.53, 130.52, 129.77, 129.57, 126.28, 125.82, 124.61, 120.90, 117.31, 116.58, 67.42, 62.65, 34.79, 31.47, 13.88. HRMS (ESI) calcd. for $C_{26}H_{27}O_6$ $(M+H)^+$: 435.1802, found: 435.1797.



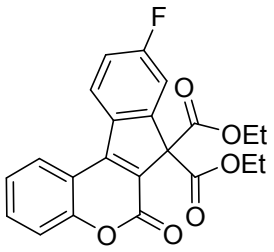
6,8-dimethyl-4-phenyl-*2H*-chromen-2-one (4m): This compound was synthesized from 3,5-dimethylphenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:5) as the eluting solvent to give the product as a yellow oil (7.3 mg, 29%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.54-7.51 (m, 3H), 7.45-7.42 (m, 2H), 7.23 (s, 1H), 7.07 (s, 1H), 6.34 (s, 1H), 2.47 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 161.15, 156.03, 150.65, 135.74, 133.19, 129.45, 128.77, 126.33, 124.45, 118.48, 114.90, 20.87, 15.71. HRMS (ESI) calcd. for $C_{17}H_{15}O_2$ $(M+H)^+$: 251.1067, found: 251.1068.



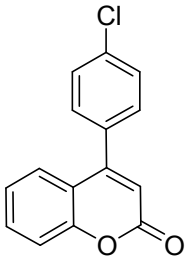
diethyl 2,4-dimethyl-6-oxoindeno[2,1-*c*]chromene-7,7(*6H*)-dicarboxylate (6m): This compound was synthesized from 3,5-dimethylphenyl 3-phenylpropiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:7) as the eluting solvent to give the product as a white solid (9.3 mg, 23%), mp. 198.3-201.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25-8.23 (m, 1H), 7.97-7.92 (m, 2H), 7.62-7.55 (m, 2H), 7.31 (s, 1H), 4.28-4.16 (m, 4H), 2.51 (s, 3H), 2.49 (s, 3H), 1.22 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.20, 159.93, 152.81, 149.90, 143.86, 143.17, 134.49, 133.40, 130.37, 129.43, 126.87, 125.75, 124.76, 122.20, 116.66, 114.67, 66.84, 62.63, 21.14, 16.25, 13.90. HRMS (ESI) calcd. for $C_{24}H_{23}O_6$ $(M+H)^+$: 407.1489, found: 407.1492.



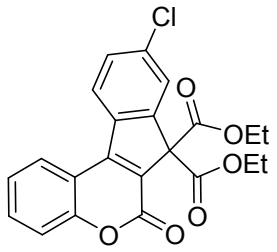
diethyl 9-methyl-6-oxoindeno[2,1-*c*]chromene-7,7(*6H*)-dicarboxylate (6n): This compound was synthesized from phenyl 3-(*p*-tolyl)propiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:7) as the eluting solvent to give the product as a white solid (24.3 mg, 62%), mp. 132.7-135.2 °C.. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.75 (s, 1H), 7.65-7.60 (m, 1H), 7.50-7.48 (m, 1H), 7.43-7.38 (m, 2H), 4.32-4.13 (m, 4H), 2.50 (s, 3H), 1.22 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.23, 157.63, 155.35, 151.56, 144.14, 141.47, 135.63, 131.93, 130.40, 126.50, 125.73, 124.87, 124.32, 124.28, 117.79, 117.22, 67.24, 62.67, 21.92, 13.89. HRMS (ESI) calcd. for $C_{23}H_{21}O_6$ $(M+H)^+$: 393.1333, found: 393.1336.



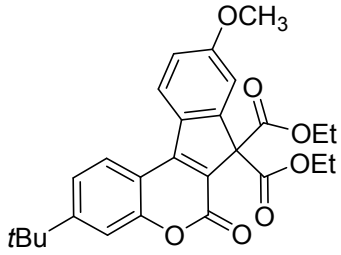
diethyl 9-fluoro-6-oxoindeno[2,1-*c*]chromene-7,7(*6H*)-dicarboxylate (6o): This compound was synthesized from phenyl 3-(4-fluorophenyl)propiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:7) as the eluting solvent to give the product as a white solid (20.0 mg, 51%), mp. 153.4-154.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (dd, J_1 = 8.1 Hz, J_2 = 1.2 Hz, 1H), 8.19 (dd, J_1 = 8.7 Hz, J_2 = 4.8 Hz, 1H), 7.67-7.62 (m, 2H), 7.51-7.48 (m, 1H), 7.44-7.40 (m, 1H), 7.32-7.27 (m, 1H), 4.33-4.17 (m, 4H), 1.25 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.57, 165.25, 162.73, 157.20, 155.36, 150.71, 146.43 (d, J = 9.5 Hz), 134.39 (d, J = 2.9 Hz), 132.33, 126.18 (d, J = 2.9 Hz), 125.96 (d, J = 8.8 Hz), 124.59, 124.44, 117.37 (d, J = 109.31 Hz), 117.04, 114.01 (d, J = 24.2 Hz), 67.51, 62.98, 13.88. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ -107.23. HRMS (ESI) calcd. for $C_{22}H_{18}FO_6$ $(M+H)^+$: 397.1082, found: 397.1084.



4-(4-chlorophenyl)-*2H*-chromen-2-one (4p)[6, 7]**:** This compound was synthesized from phenyl 3-(4-chlorophenyl)propiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:5) as the eluting solvent to give the product as a white solid (6.8 mg, 27%), mp. 180.3-181.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.55 (m, 1H), 7.54-7.51 (m, 2H), 7.45-7.40 (m, 4H), 7.25-7.23 (m, 1H), 6.37 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.49, 154.45, 154.20, 136.01, 133.58, 132.17, 129.81, 129.25, 126.69, 124.31, 118.71, 117.49, 115.42. HRMS (ESI) calcd. for $C_{15}H_{10}ClO_2$ $(M+H)^+$: 257.0364, found: 257.0365.



diethyl 9-chloro-6-oxoindeno[2,1-*c*]chromene-7,7(*6H*)-dicarboxylate (6p): This compound was synthesized from phenyl 3-(4-chlorophenyl)propiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:7) as the eluting solvent to give the product as an oil (19.8 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 1.8 Hz, 1H), 7.66-7.62 (m, 1H), 7.57 (dd, J_1 = 8.3 Hz, J_2 = 2.1 Hz, 1H), 7.51-7.48 (m, 1H), 7.44-7.40 (m, 1H), 4.32-4.18 (m, 4H), 1.23 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.49, 157.23, 155.33, 150.55, 145.33, 136.96, 136.82, 132.27, 129.92, 126.47, 126.43, 125.36, 124.60, 124.48, 117.90, 116.77, 67.47, 63.02, 13.89. HRMS (ESI) calcd. for $C_{22}H_{18}ClO_6$ $(M+H)^+$: 413.0786, found: 413.0787.



diethyl 3-(*tert*-butyl)-9-methoxy-6-oxoindeno[2,1-*c*]chromene-7,7(*6H*)-dicarboxylate (6q): This compound was synthesized from phenyl 4-(*tert*-butyl)phenyl 3-(4-methoxyphenyl)propiolate following general procedure **B** and purified by flash silica gel column chromatography using ethyl acetate/petroleum ether (1:7) as the eluting solvent to give the product as an oil (17.6 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 8.7 Hz, 1H), 7.48 (dd, J_1 = 9.5 Hz, J_2 = 2.5 Hz, 2H), 7.44 (dd, J_1 = 6.7 Hz, J_2 = 1.7 Hz, 1H), 7.09 (dd, J_1 = 8.6 Hz, J_2 = 2.5 Hz, 1H), 4.32-4.13 (m, 4H), 3.92 (s, 3H), 1.39 (s, 9H), 1.22 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.33, 161.80, 157.82, 156.42, 155.51, 151.52, 146.38, 130.85, 125.46, 124.31, 123.66, 121.78, 115.90, 114.54, 111.16, 67.24, 62.63, 55.79, 35.29, 31.04, 13.91. HRMS (ESI) calcd. for $C_{27}H_{29}O_7$ $(M+H)^+$: 465.1908, found: 465.1910.

6. References

1 K. Park, J. M, You, S. Jeon and S. Lee, *Eur. J. Org. Chem.*, 2013, **2013**, 1973-1978.

2 J. Lim, J. Choi, H. S. Kim, I. S. Kim, K. C. Nam, J. Kim and S. Lee, *J. Org. Chem.*, 2016, **81**, 303-308.

3 C. E. Song, D. Jung, S. Y. Choung, E. J. Roh and S. Lee, *Angew. Chem. Int. Ed.*, 2004, **43**, 6183-6185.

4 Y. Zhou, M. X. Zhou, M. Chen, J. H. Su, J. F. Du and Q. L. Song, *RSC Adv.*, 2015, **5**, 103977-103981.

5 A. Dikova, N. P. Cheval, A. Blanc, J. M. Weibel and P. Palea, *Adv. Synth. Catal.*, 2015, **357**, 4093-4100.

6 M. L. N. Rao, V. Venkatesh and D. N. Jadhav, *Eur. J. Org. Chem.*, 2010, 3945-3955.

7 J. M. Pérez, R. Cano, G. P. McGlacken and D. J. Ramón, *RSC Adv.*, 2016, **6**, 36932-36941.

8 F. X. Zhu and X. F. Wu, *Org. Lett.*, 2018, **20**, 3422-3425.

7. ^{1}H, ^{13}C and ^{19}F NMR spectra

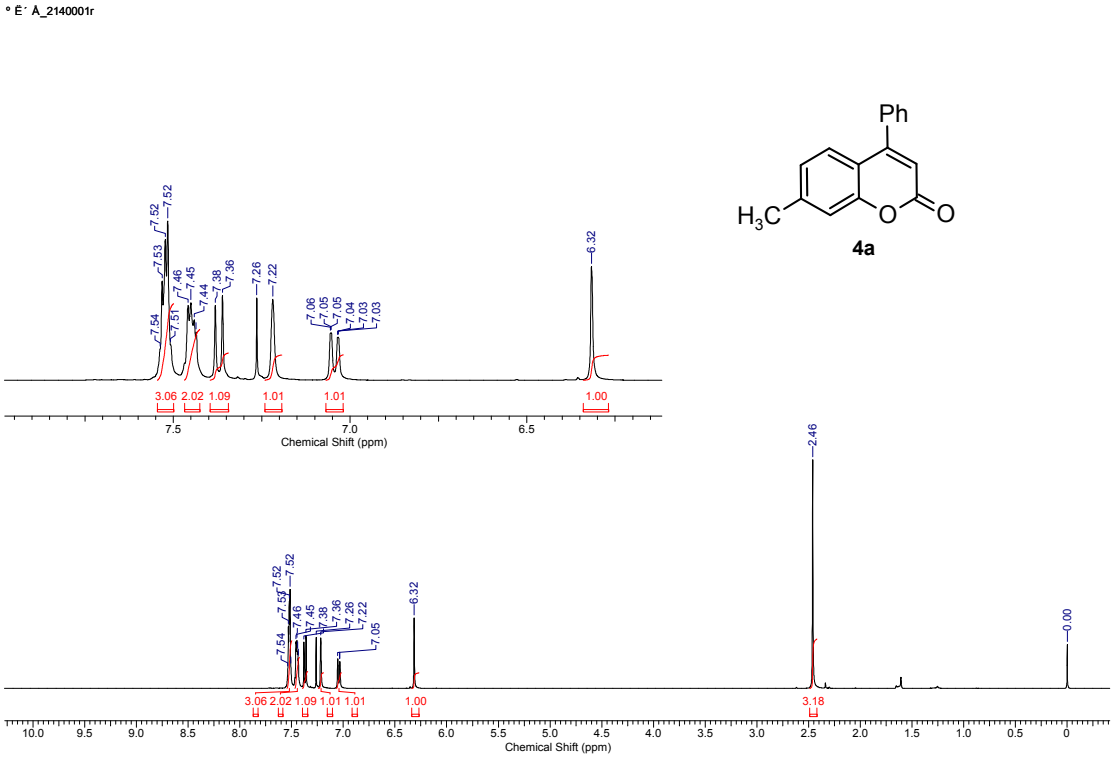


Figure S22. ^{1}H NMR spectrum of compound **4a**

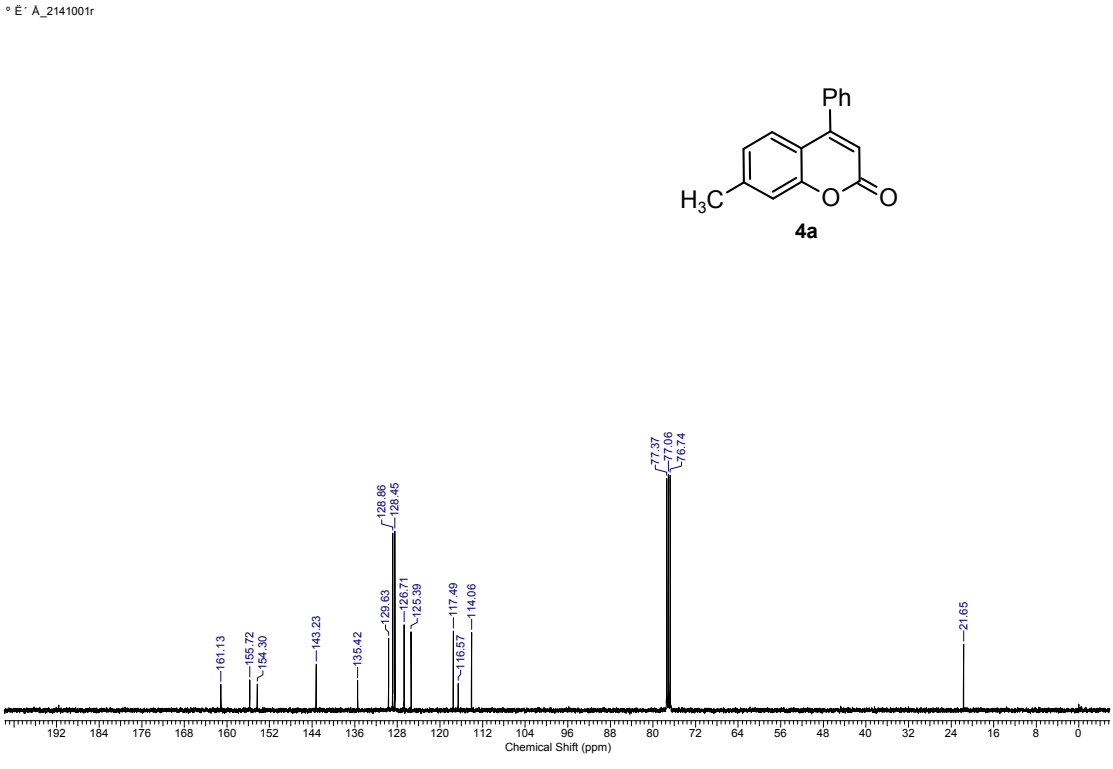


Figure S23. ^{13}C NMR spectrum of compound **4a**

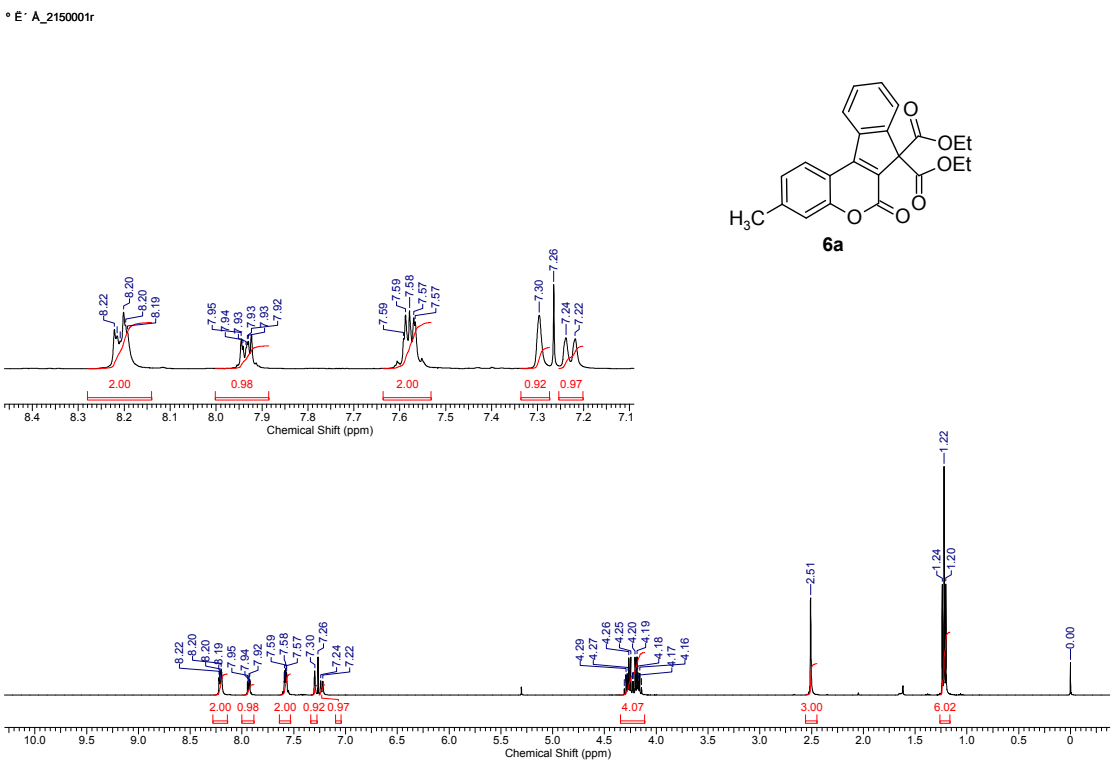


Figure S24. ^{1}H NMR spectrum of compound **6a**

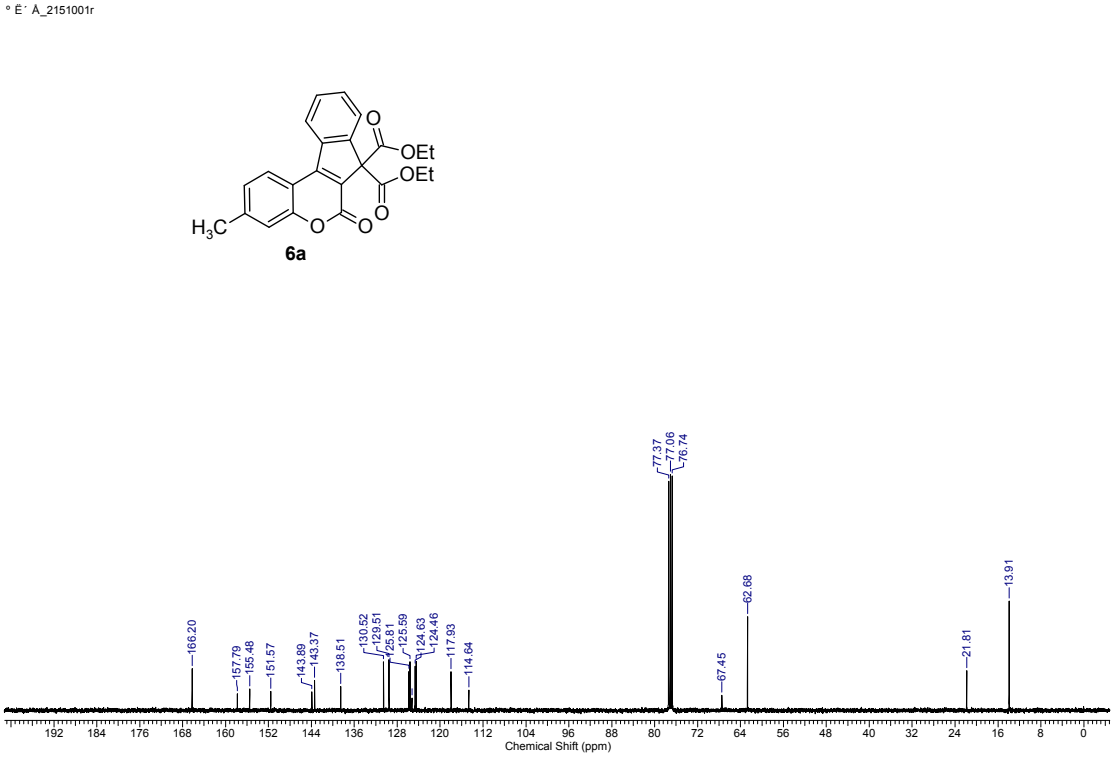


Figure S25. ^{13}C NMR spectrum of compound **6a**

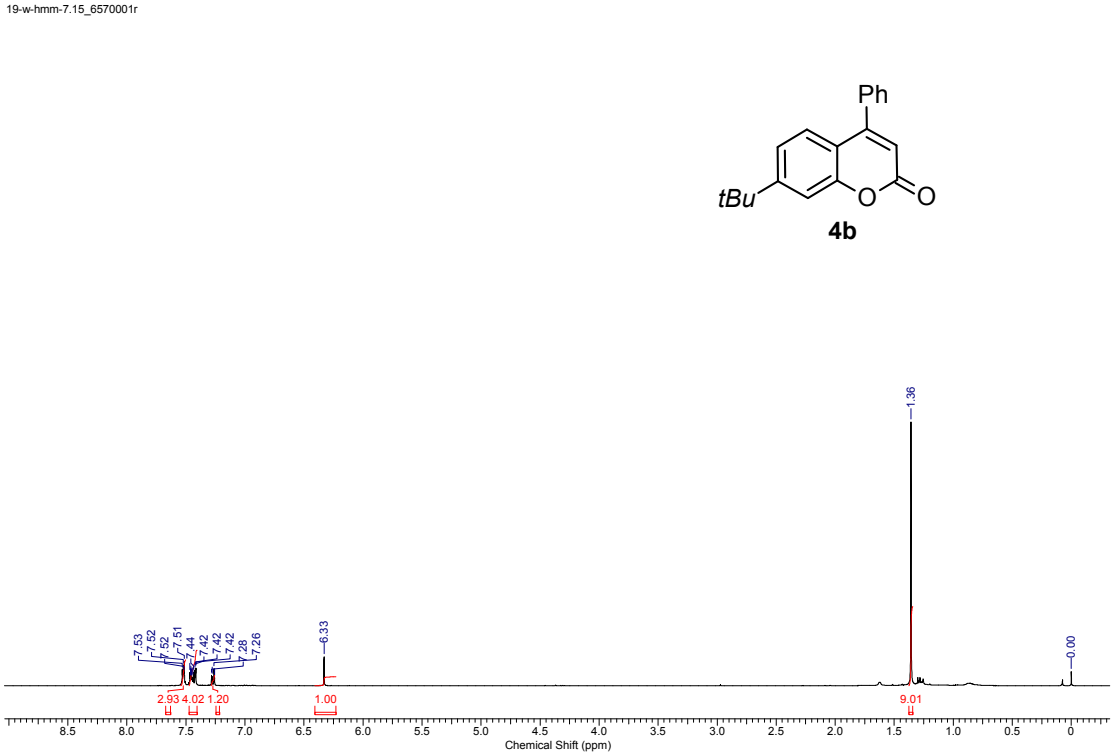


Figure S26. ^{1}H NMR spectrum of compound **4b**

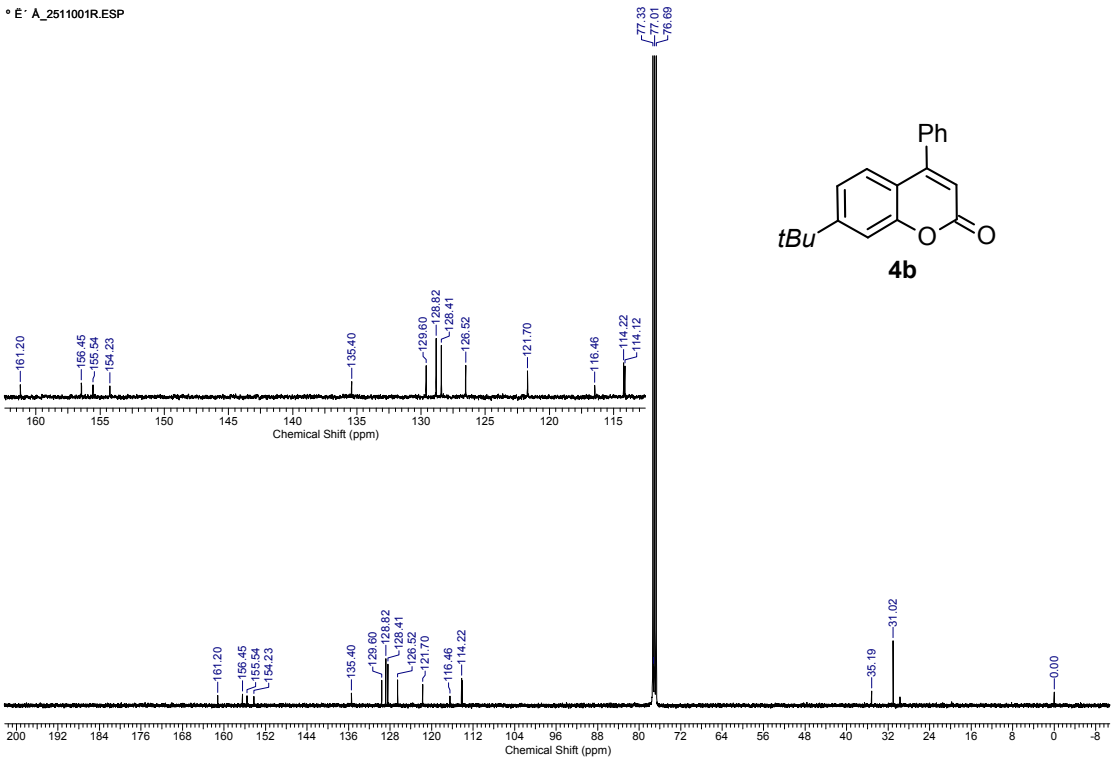


Figure S27. ^{13}C NMR spectrum of compound **4b**

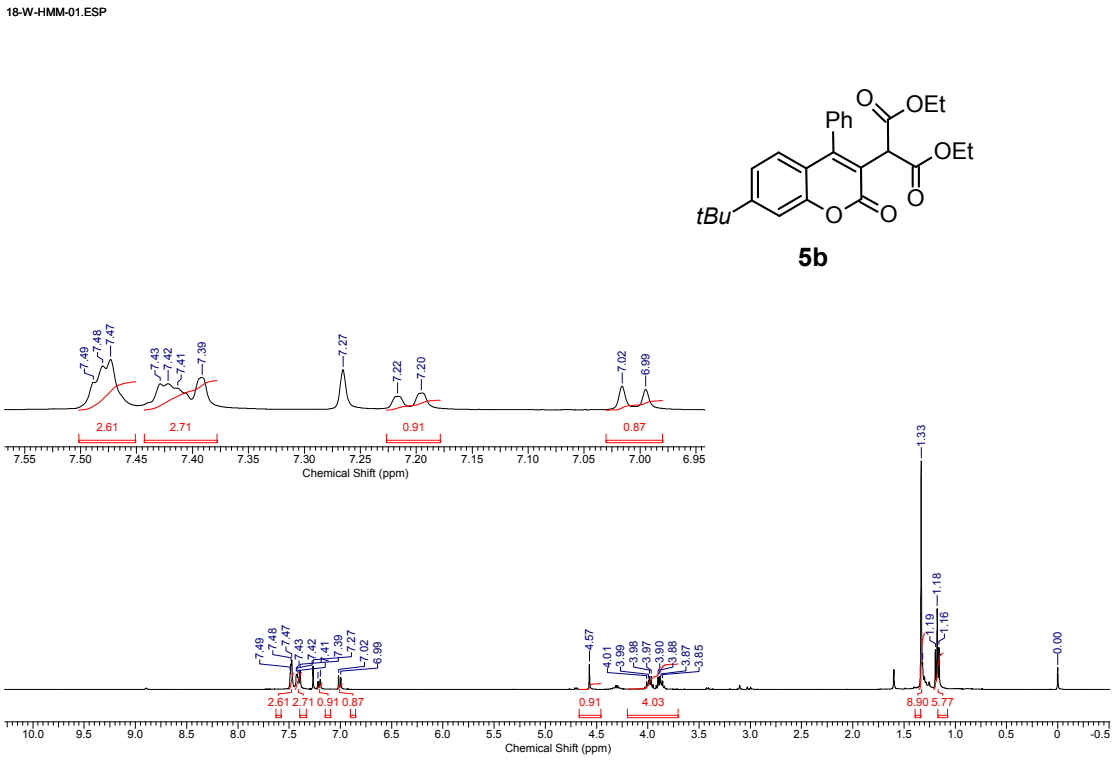


Figure S28. ^{1}H NMR spectrum of compound **5b**

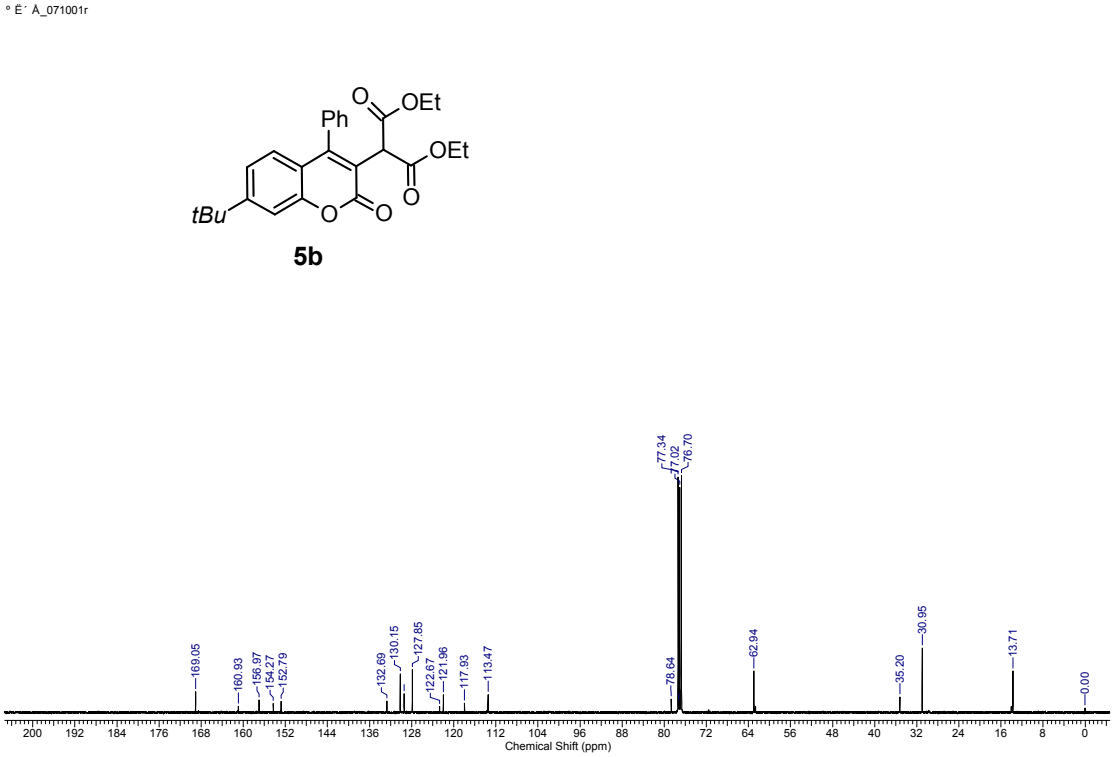


Figure S29. ^{13}C NMR spectrum of compound **5b**

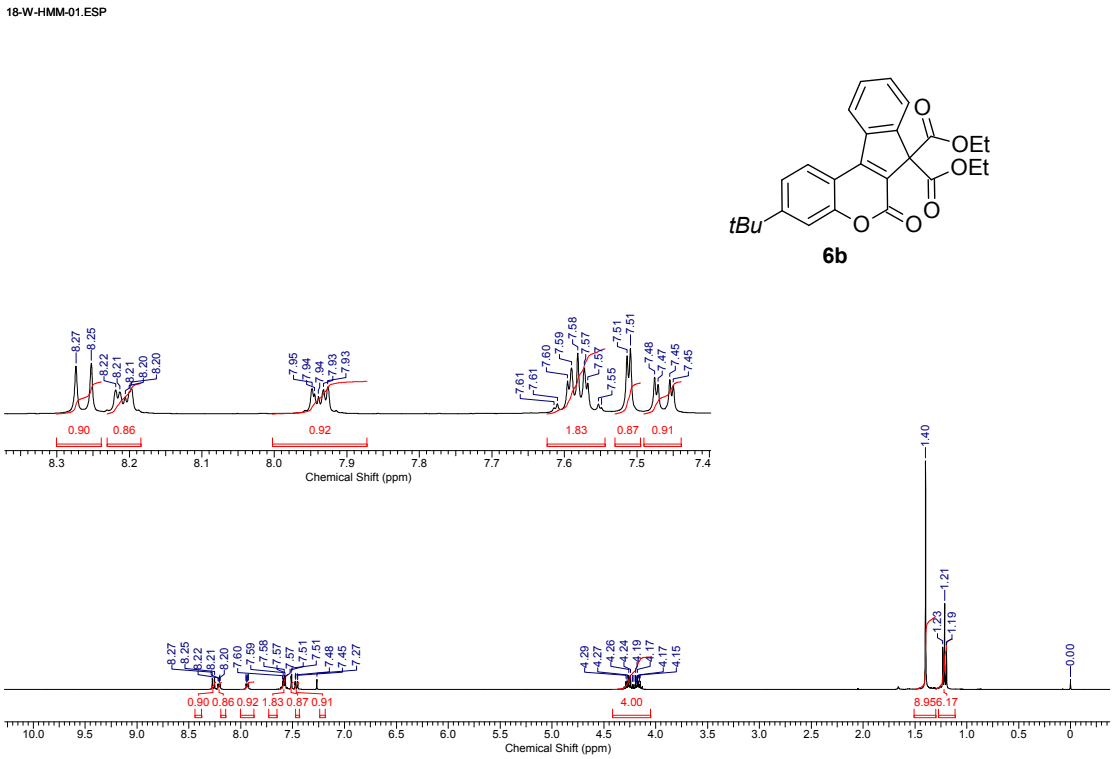


Figure S30. ^{1}H NMR spectrum of compound **6b**

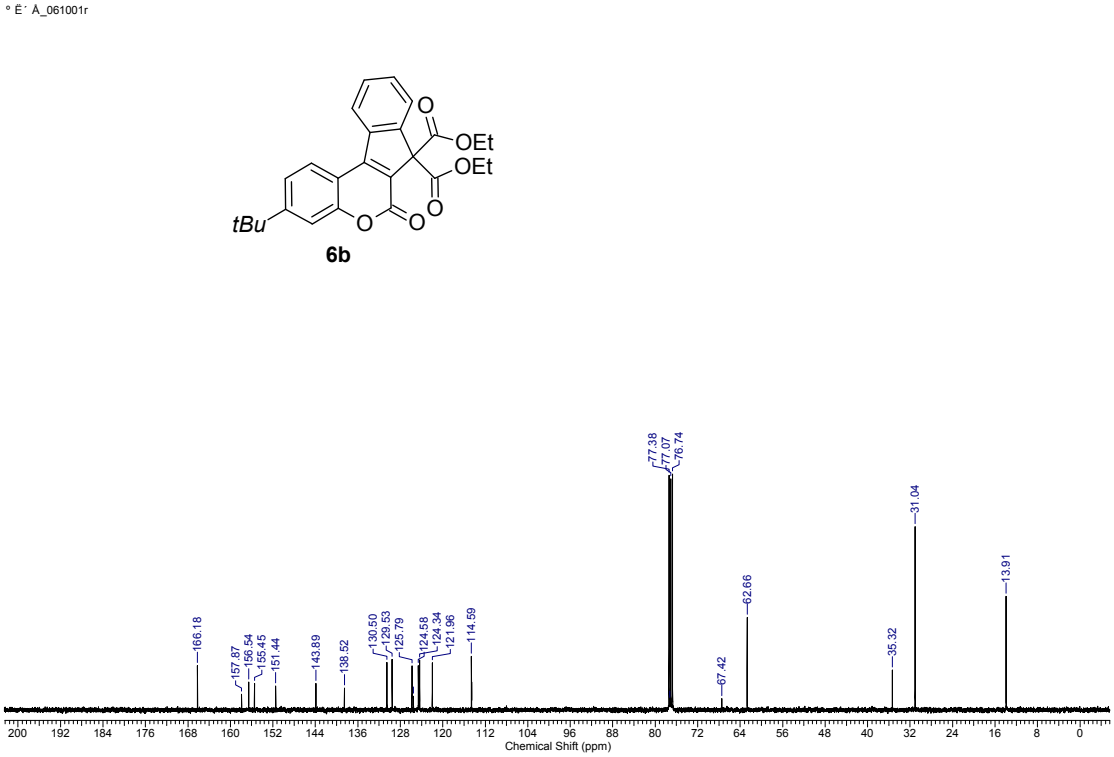


Figure S31. ^{13}C NMR spectrum of compound **6b**

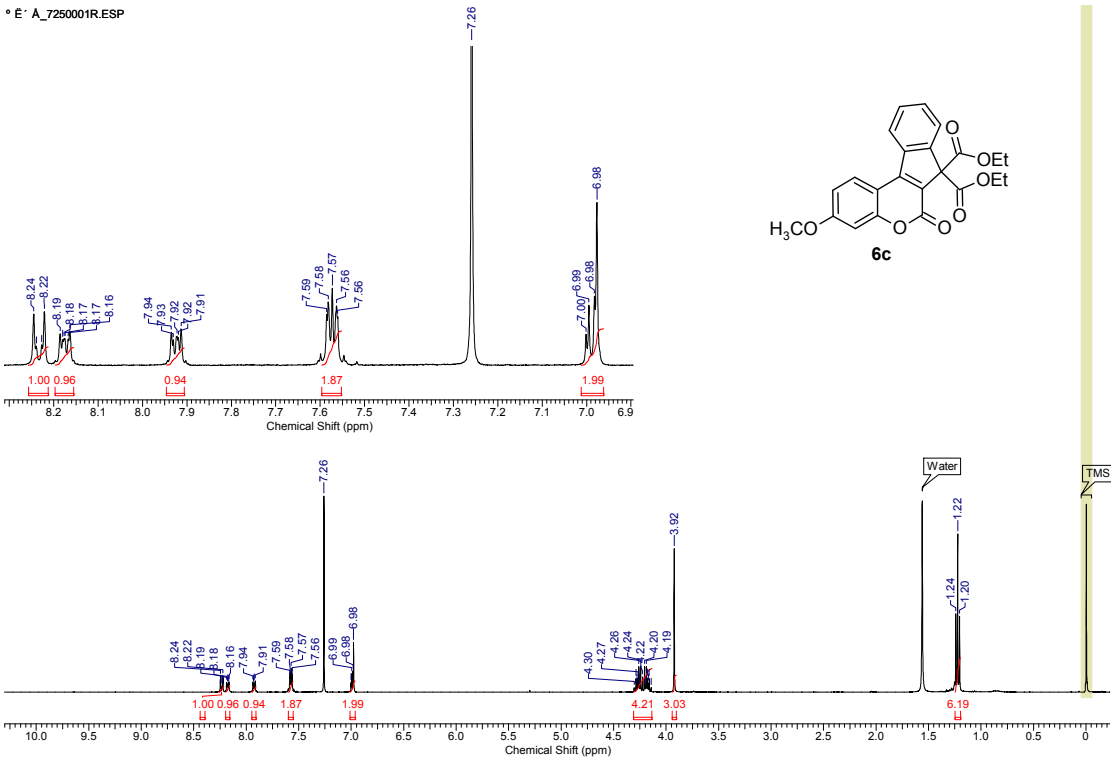


Figure S32. ^{1}H NMR spectrum of compound **6c**

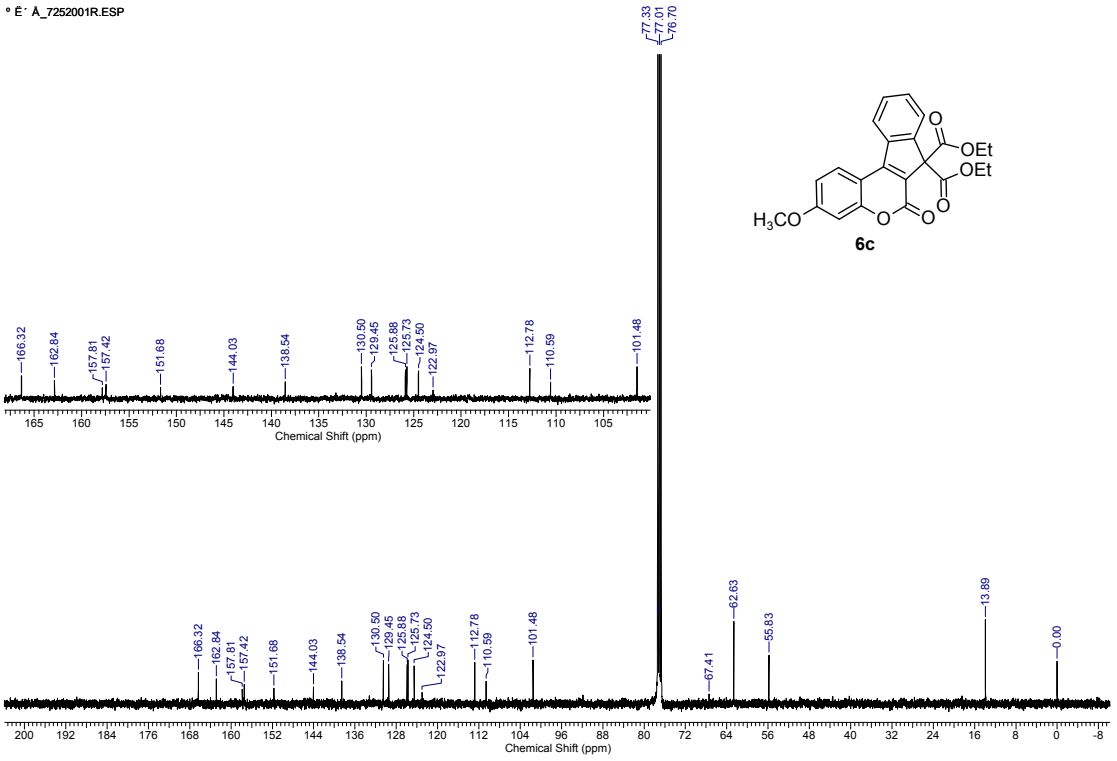


Figure S33. ^{13}C NMR spectrum of compound **6c**

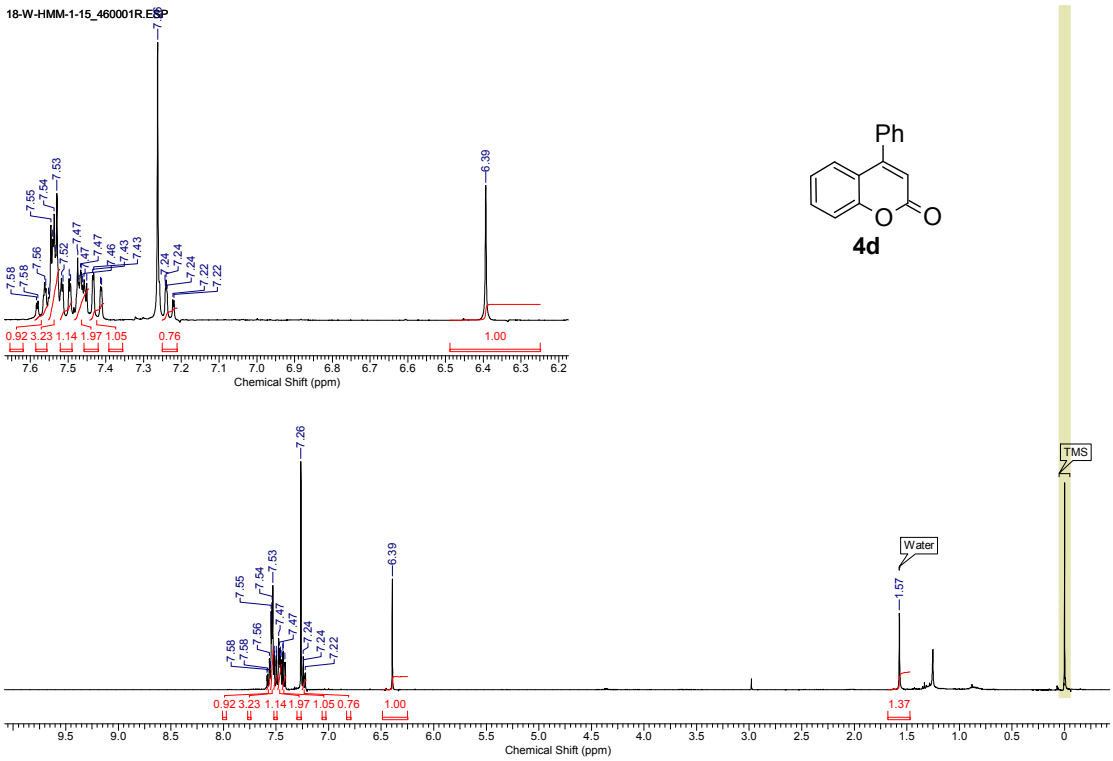


Figure S34. ^{1}H NMR spectrum of compound **4d**

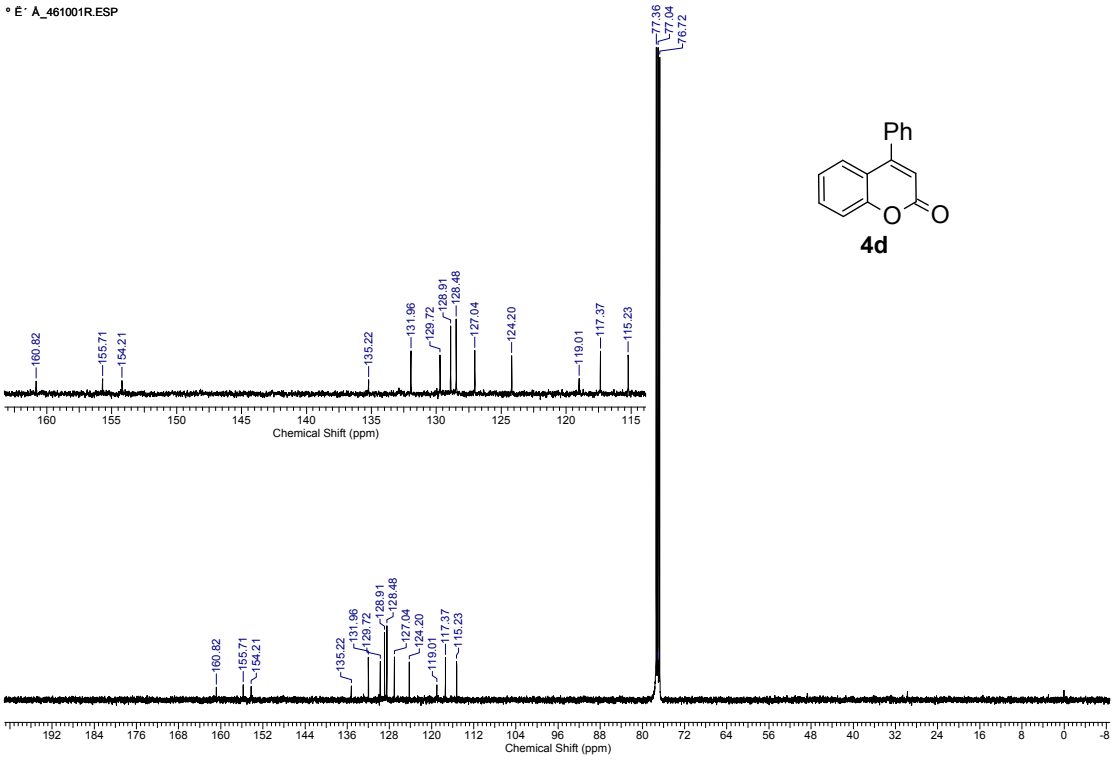


Figure S35. ^{13}C NMR spectrum of compound **4d**

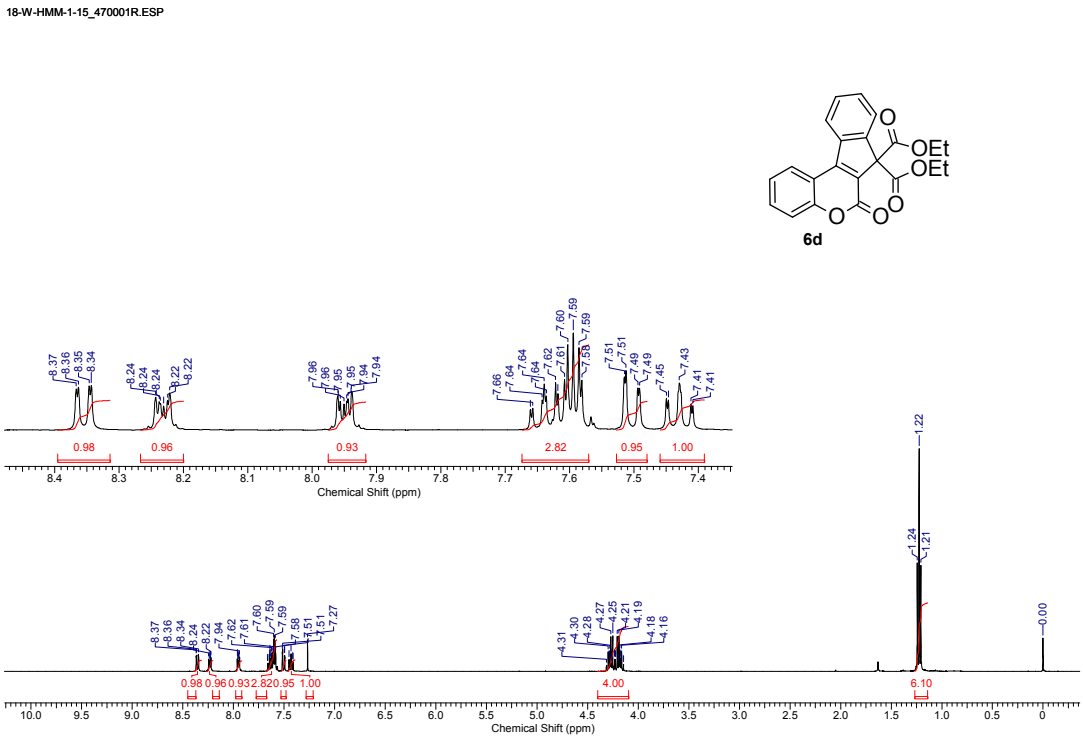


Figure S36. ^{1}H NMR spectrum of compound **6d**

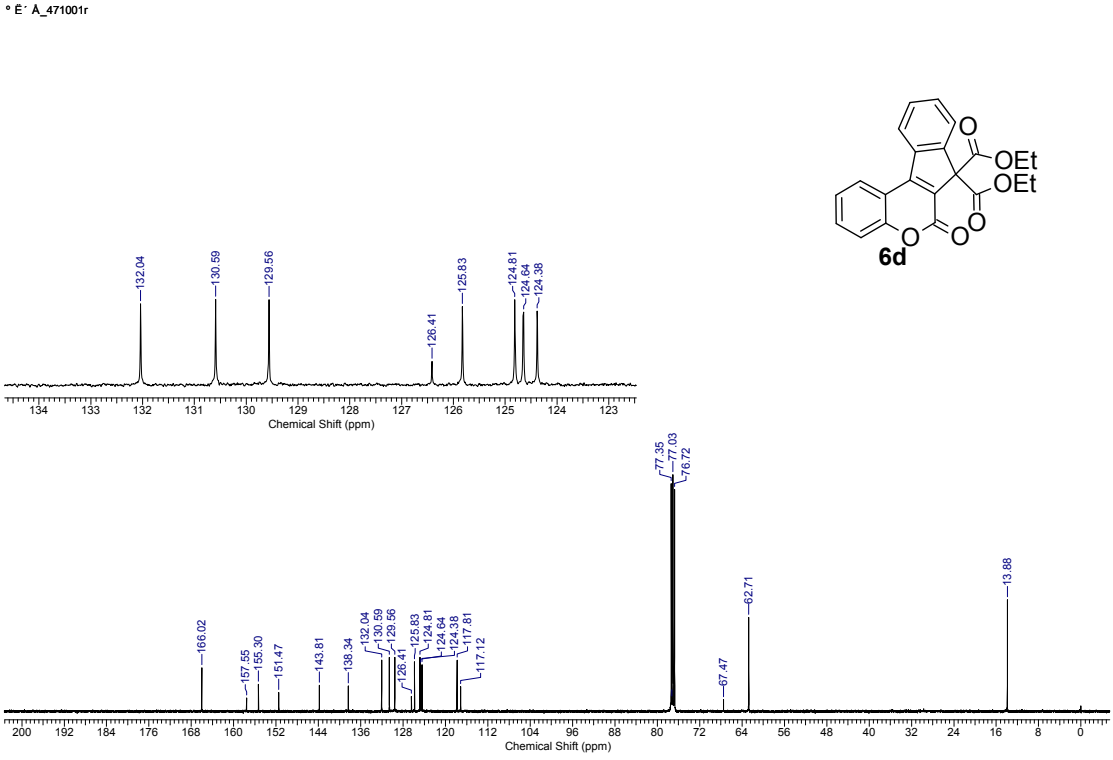


Figure S37. ^{13}C NMR spectrum of compound **6d**

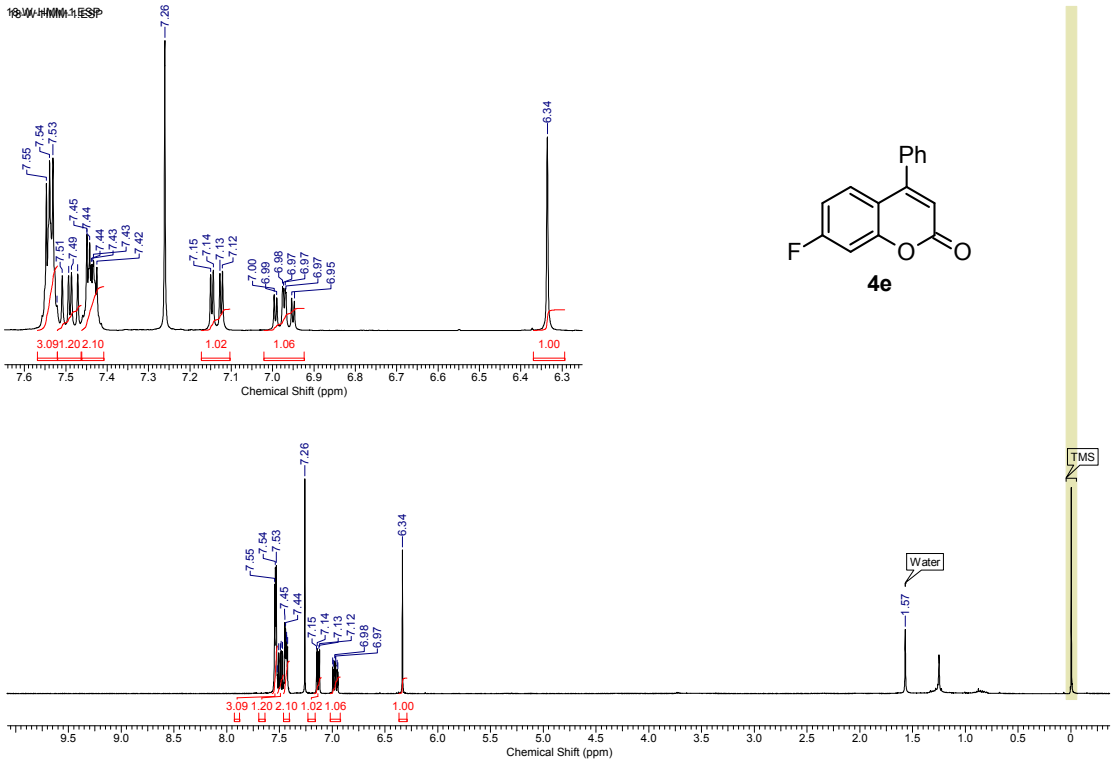


Figure S38. ^{1}H NMR spectrum of compound **4e**

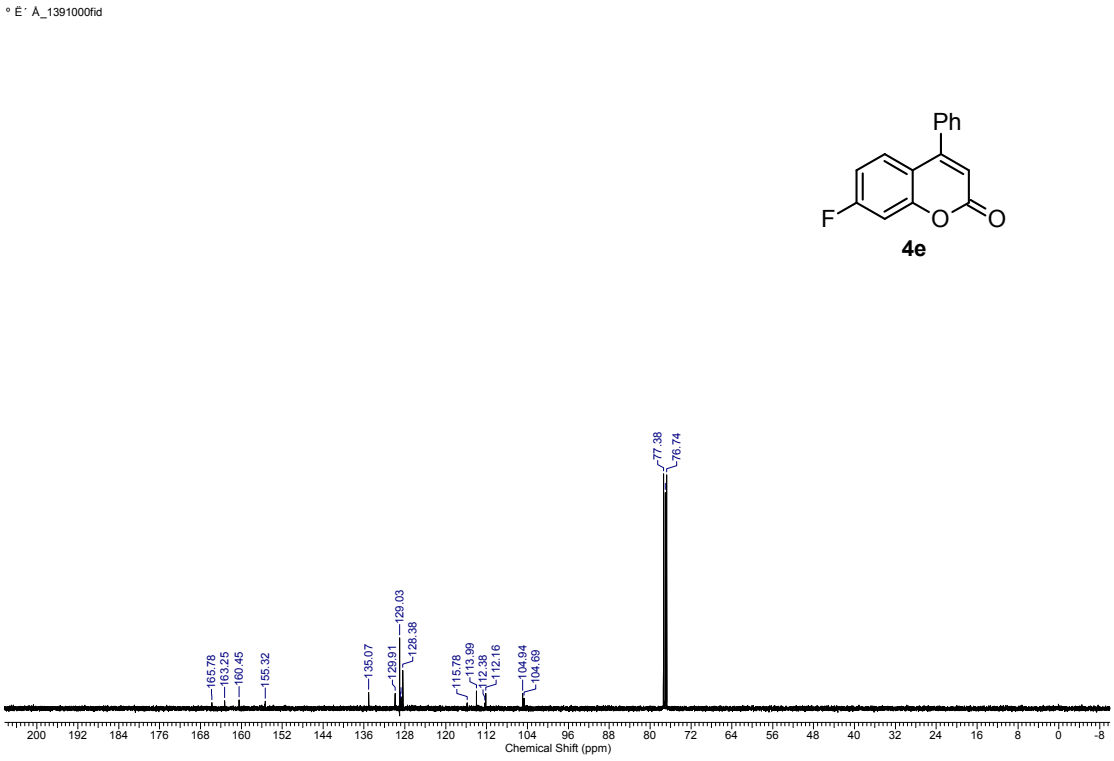


Figure S39. ^{13}C NMR spectrum of compound **4e**

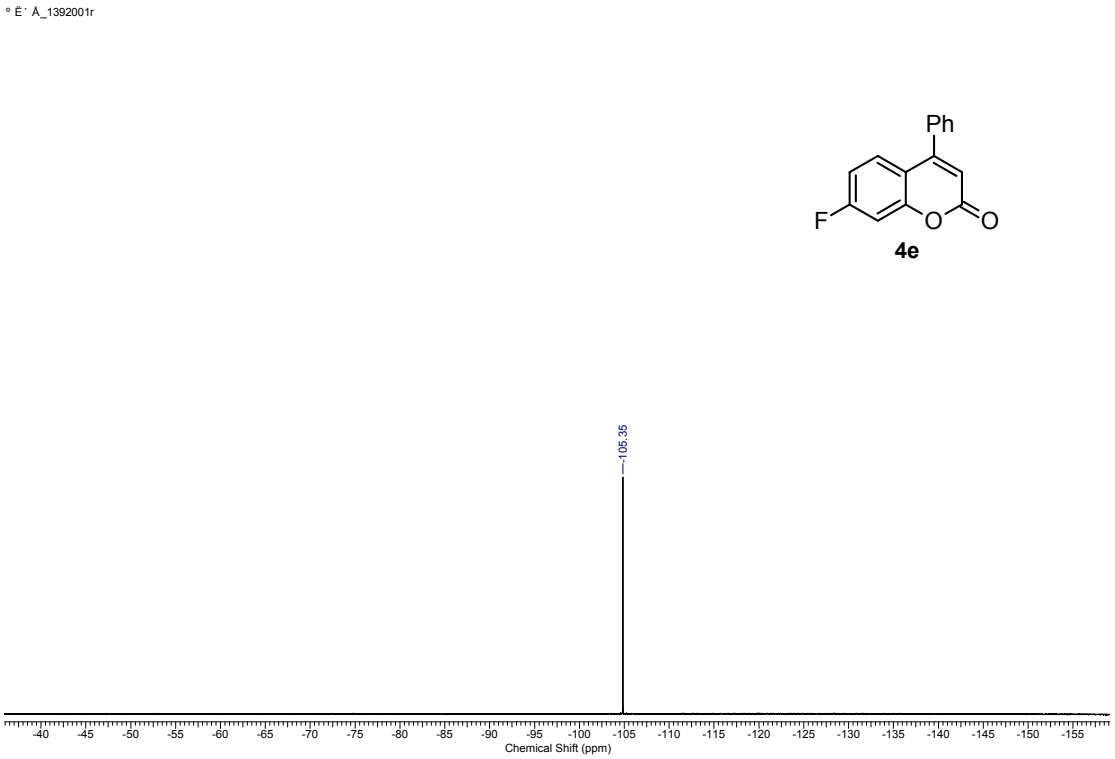


Figure S40. ^{19}F NMR spectrum of compound **4e**

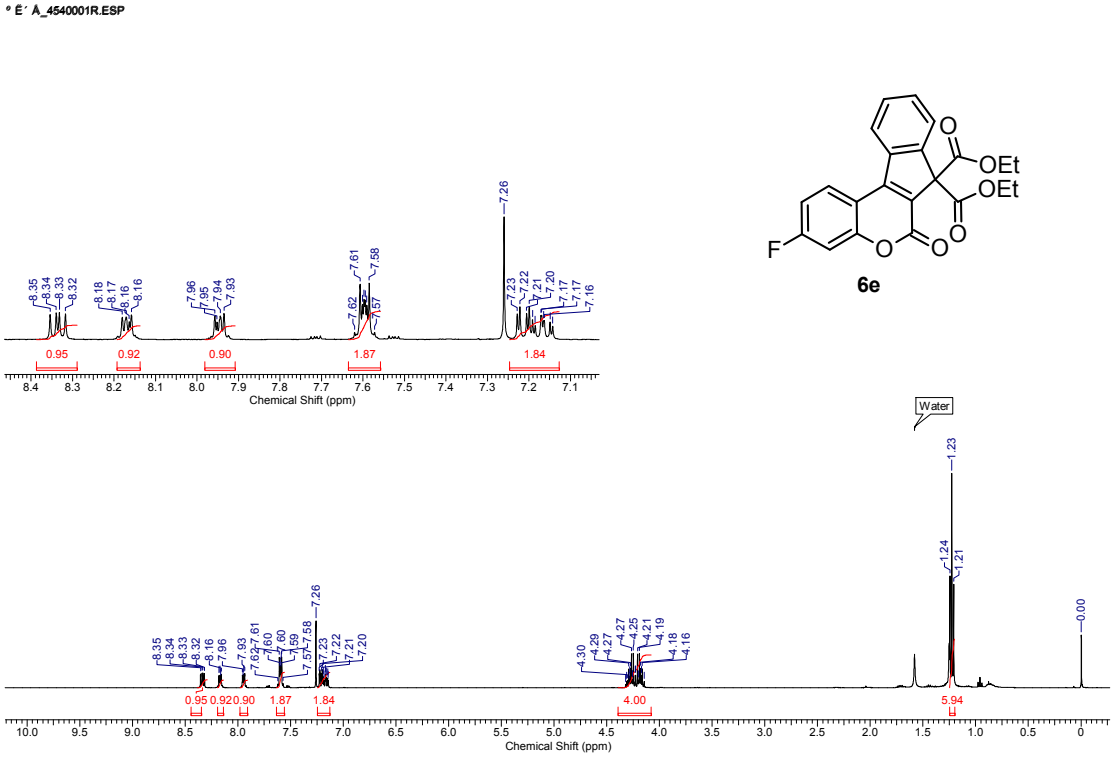


Figure S41. ^{1}H NMR spectrum of compound **6e**

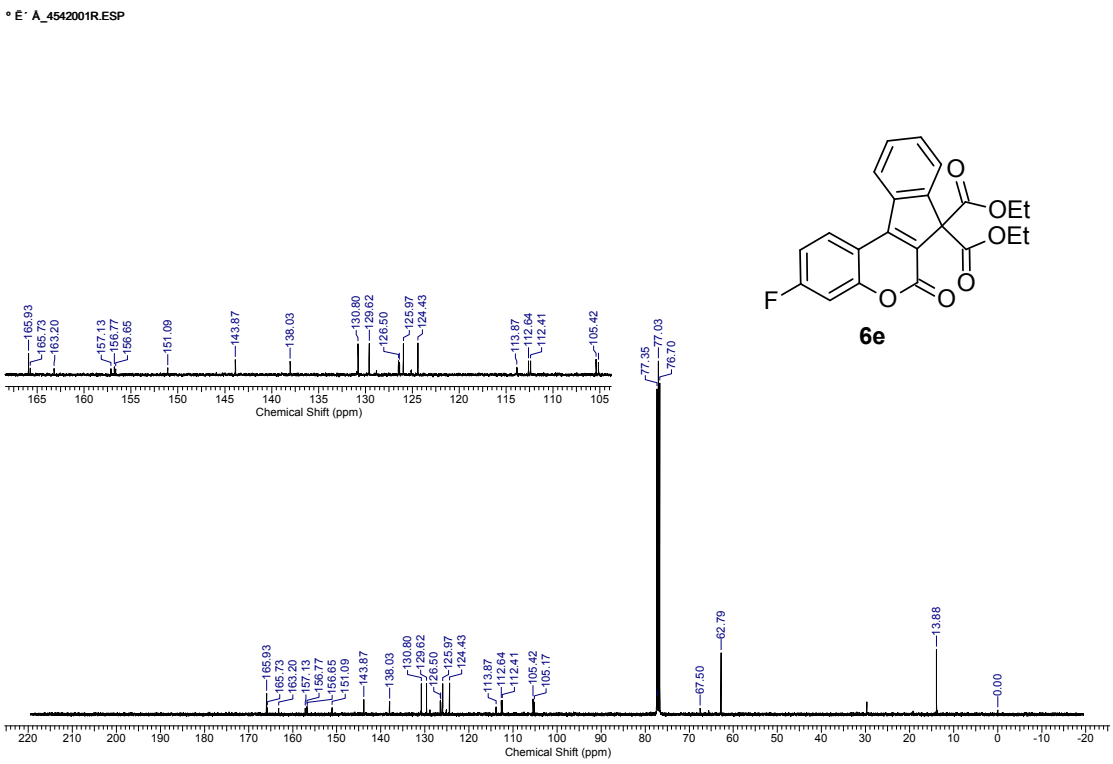


Figure S42. ^{13}C NMR spectrum of compound **6e**

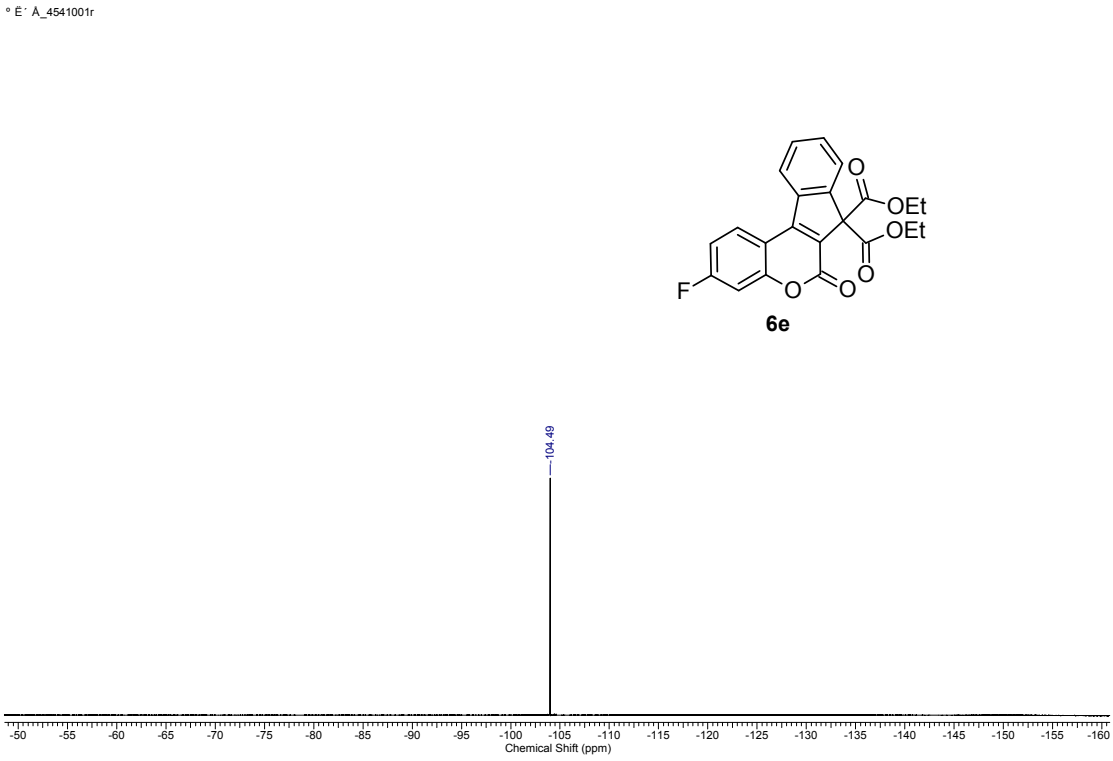


Figure S43. ^{19}F NMR spectrum of compound **6e**

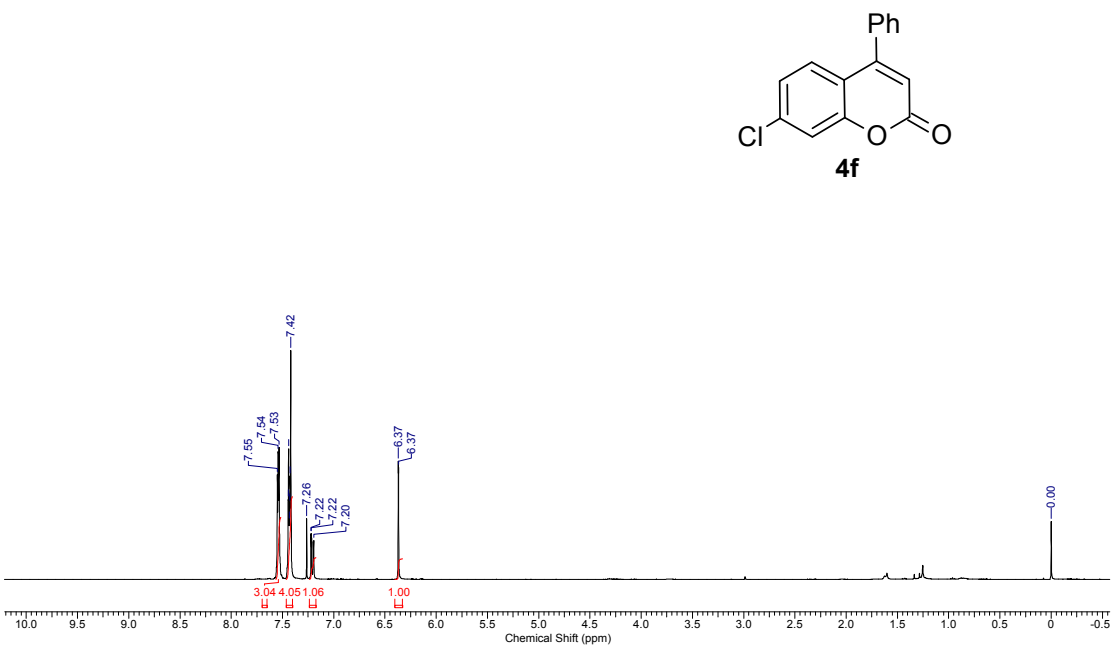


Figure S44. ^{1}H NMR spectrum of compound **4f**

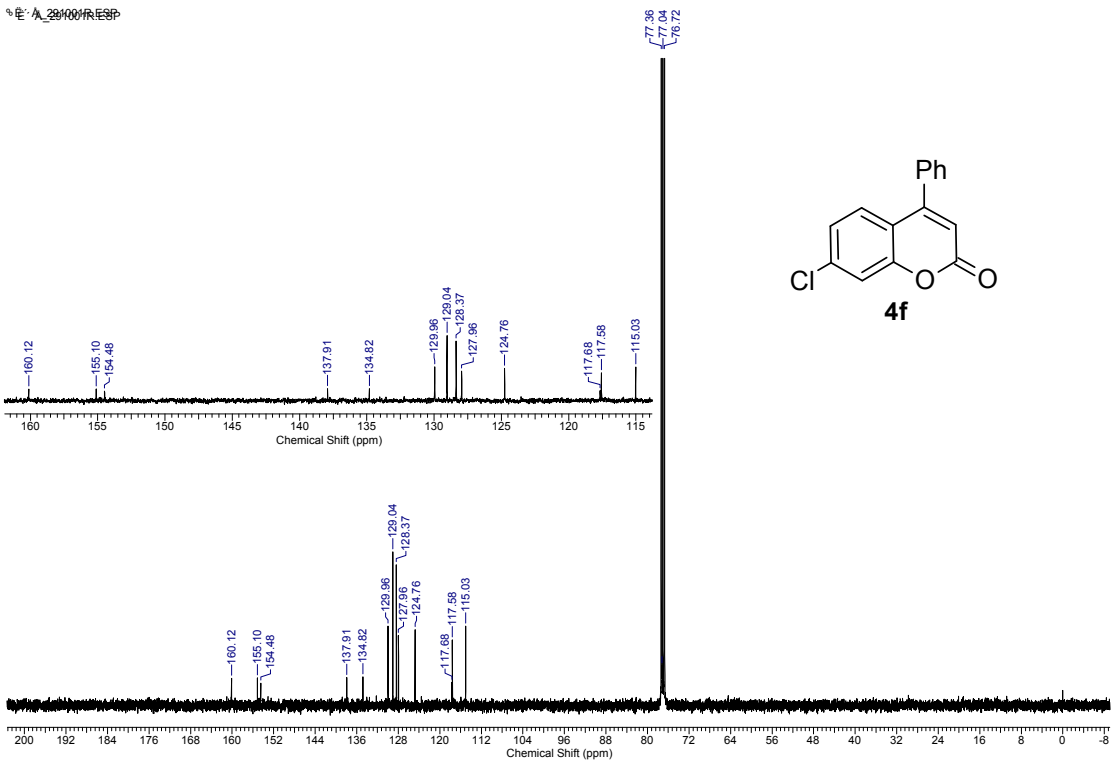


Figure S45. ^{13}C NMR spectrum of compound **4f**

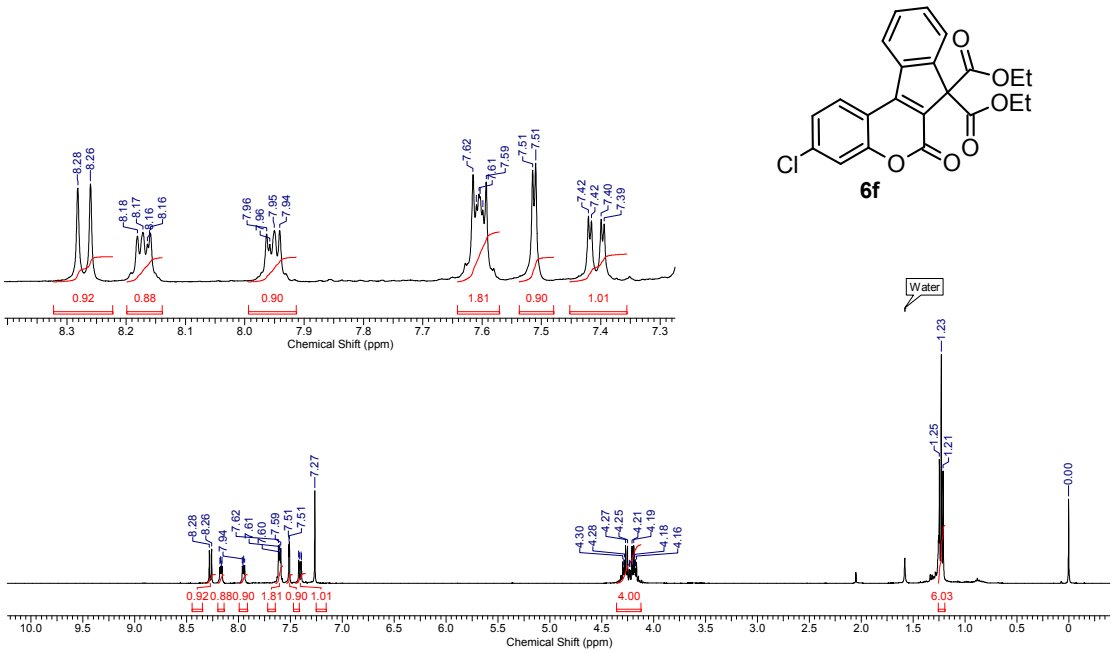


Figure S46. ^{1}H NMR spectrum of compound **6f**

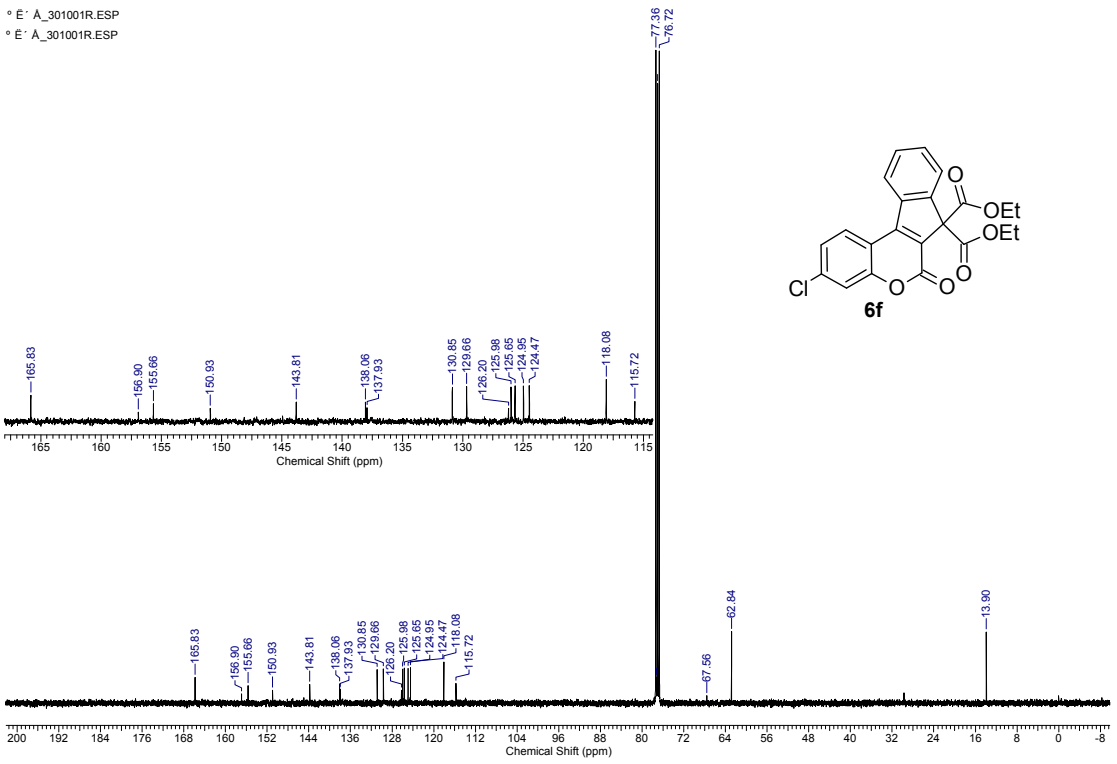


Figure S47. ^{13}C NMR spectrum of compound **6f**

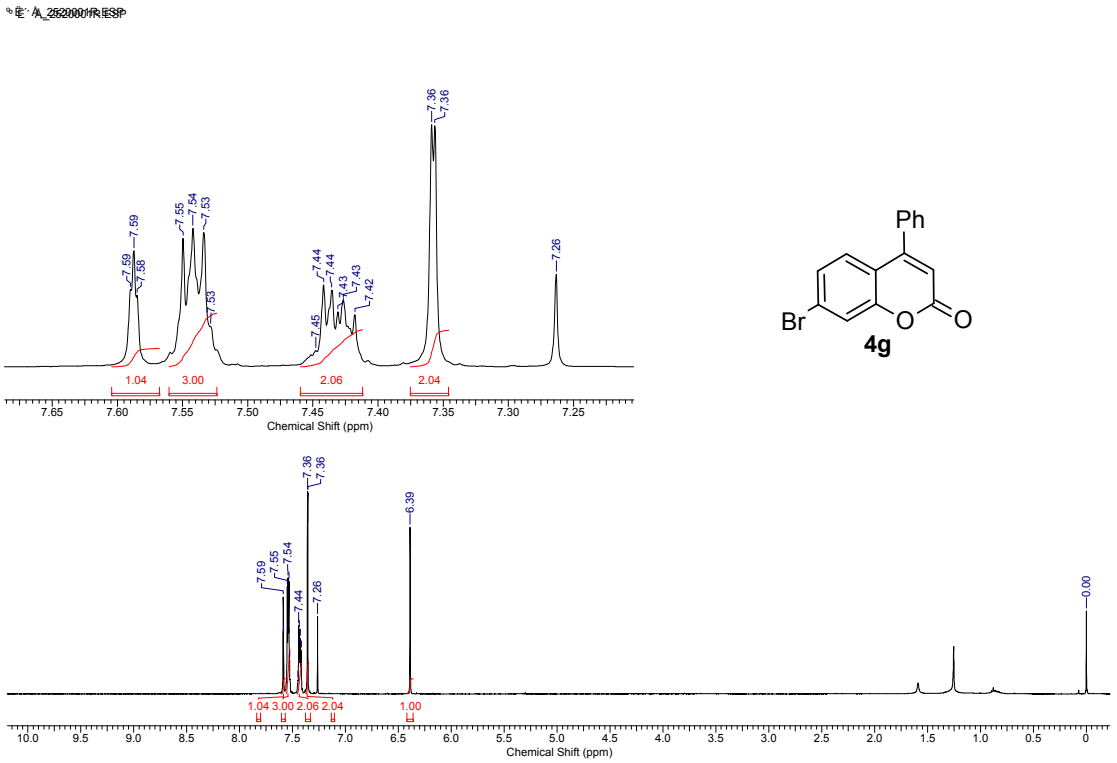


Figure S48. ^{1}H NMR spectrum of compound **4g**

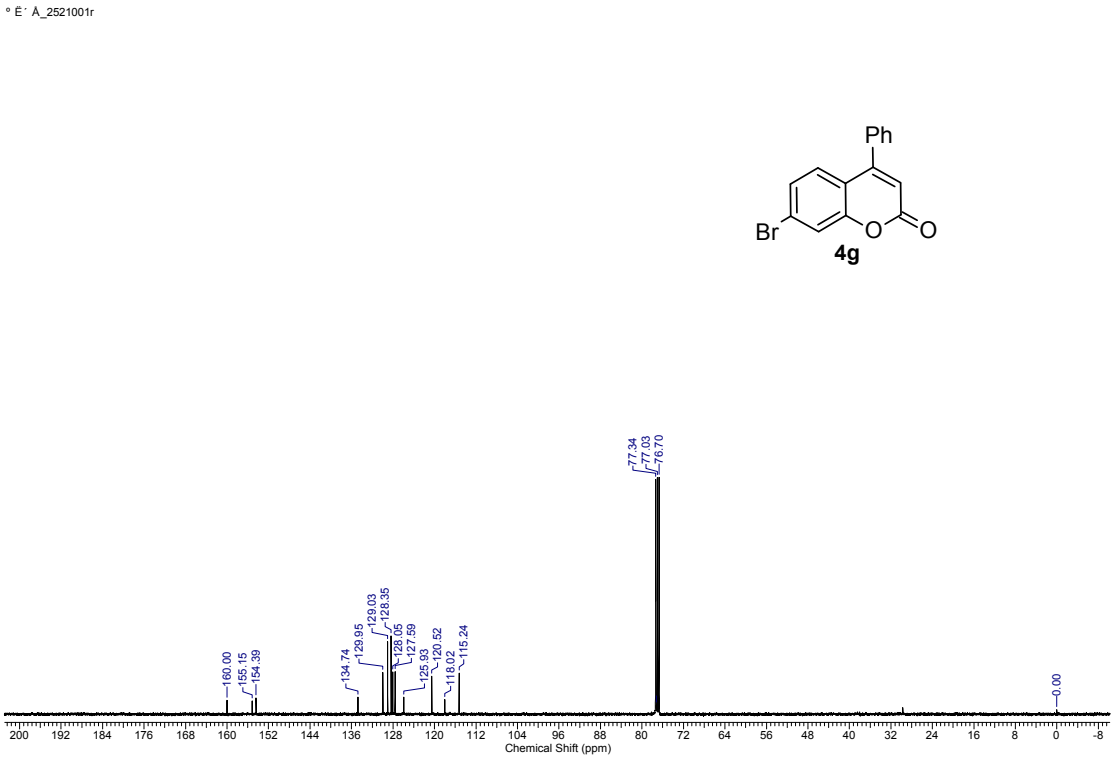


Figure S49. ^{13}C NMR spectrum of compound **4g**

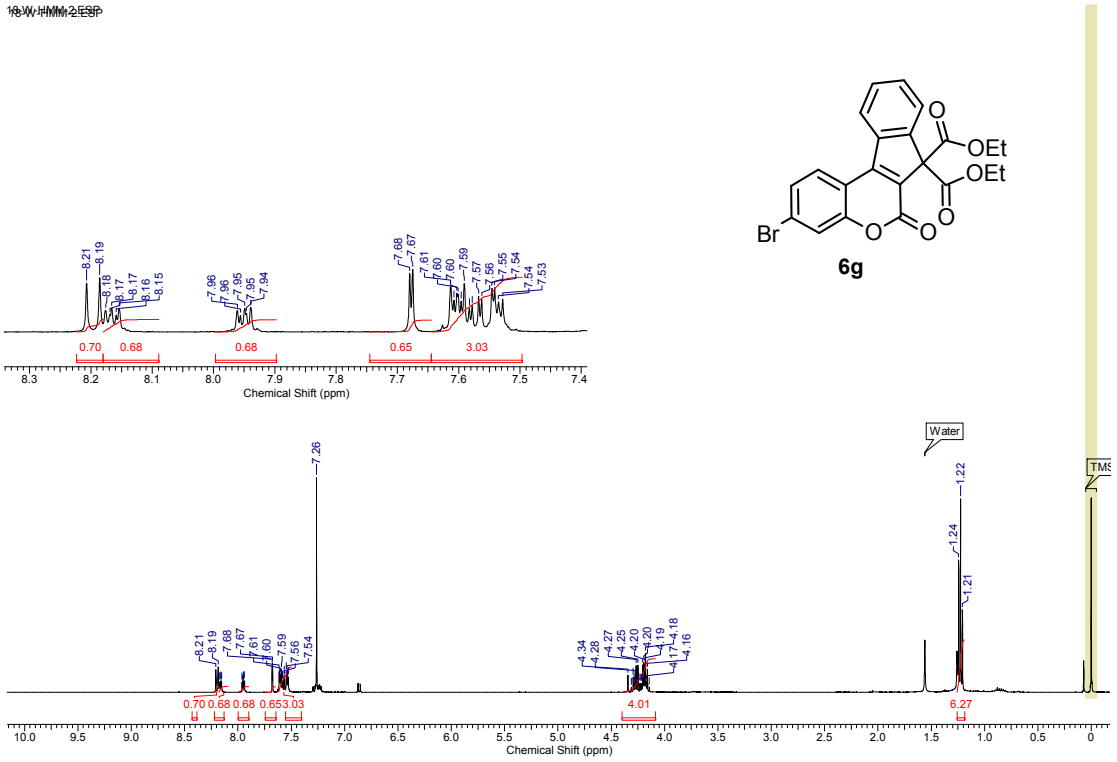


Figure S50. ^{1}H NMR spectrum of compound **6g**

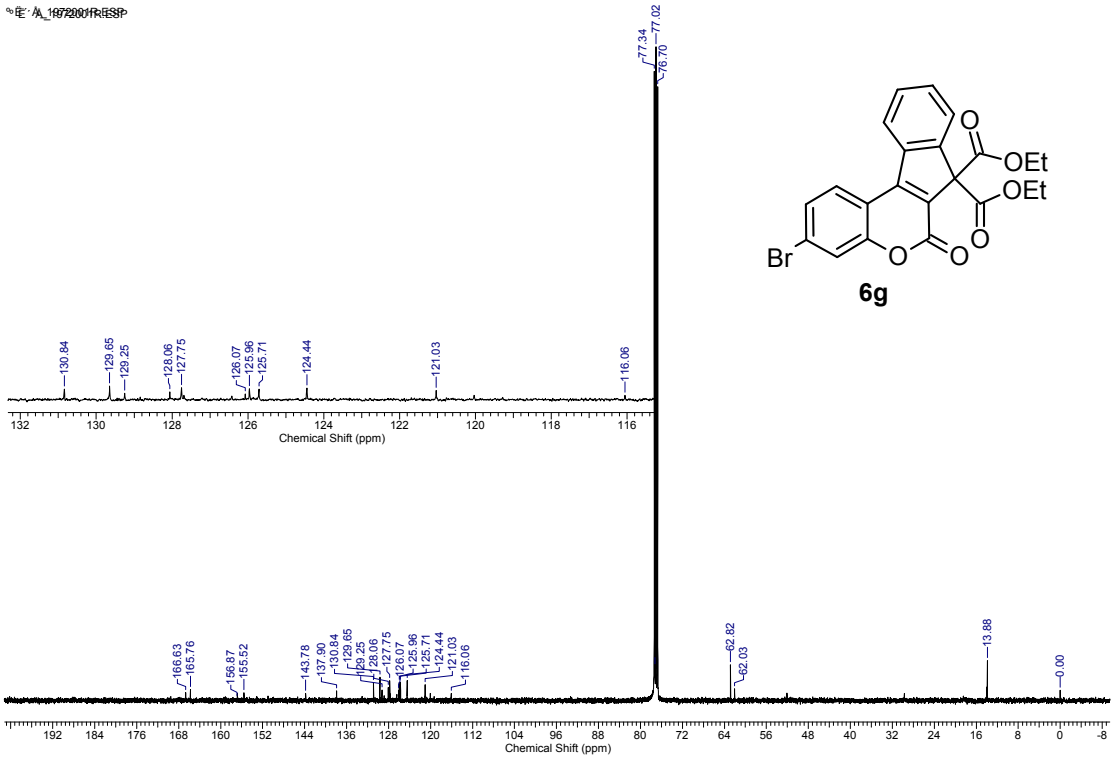


Figure S51. ^{13}C NMR spectrum of compound **6g**

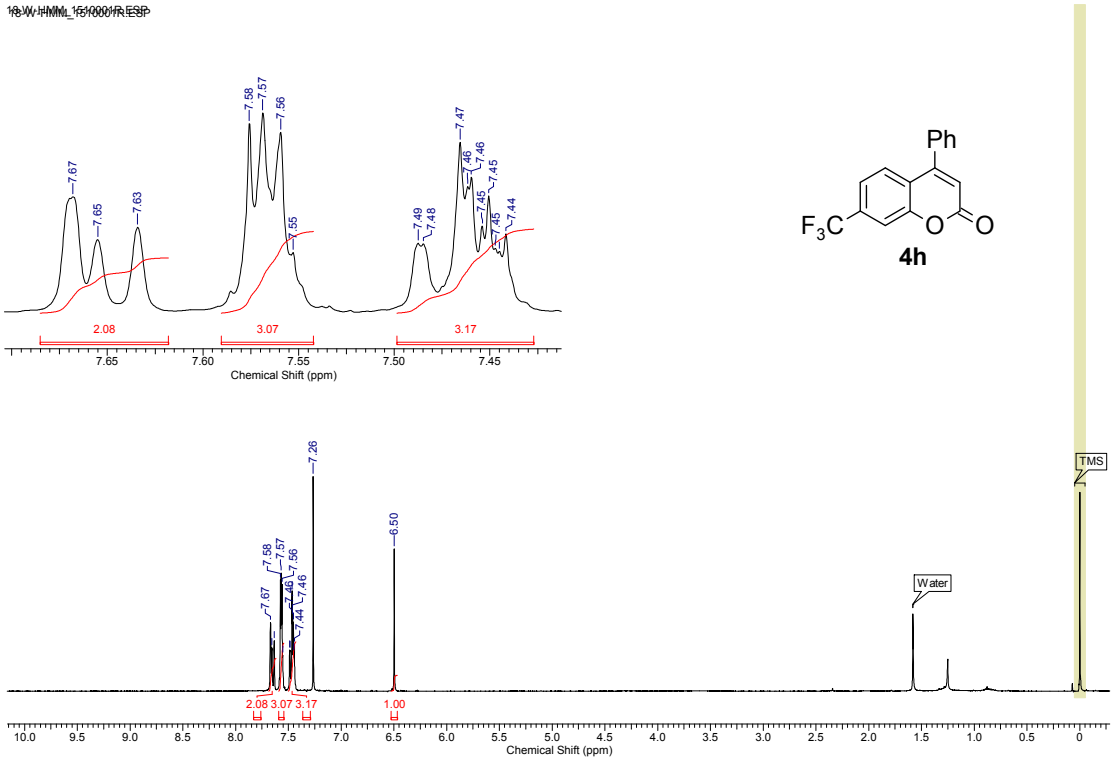


Figure S52. ^{1}H NMR spectrum of compound **4h**

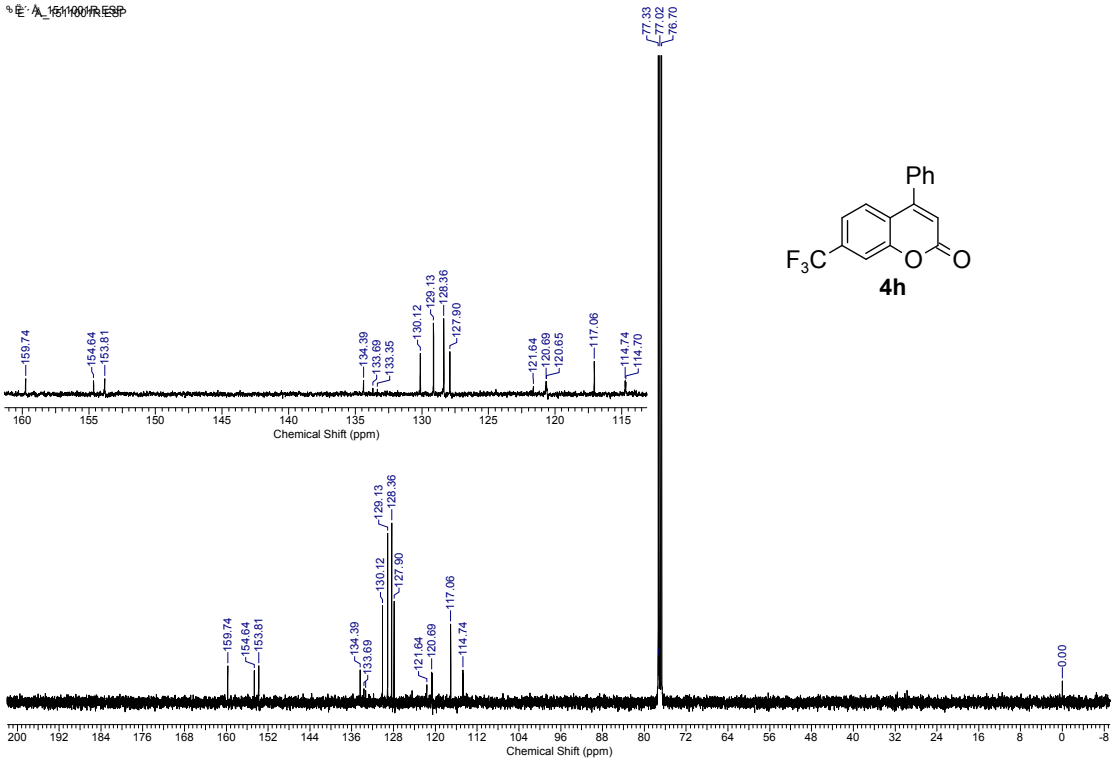


Figure S53. ^{13}C NMR spectrum of compound **4h**

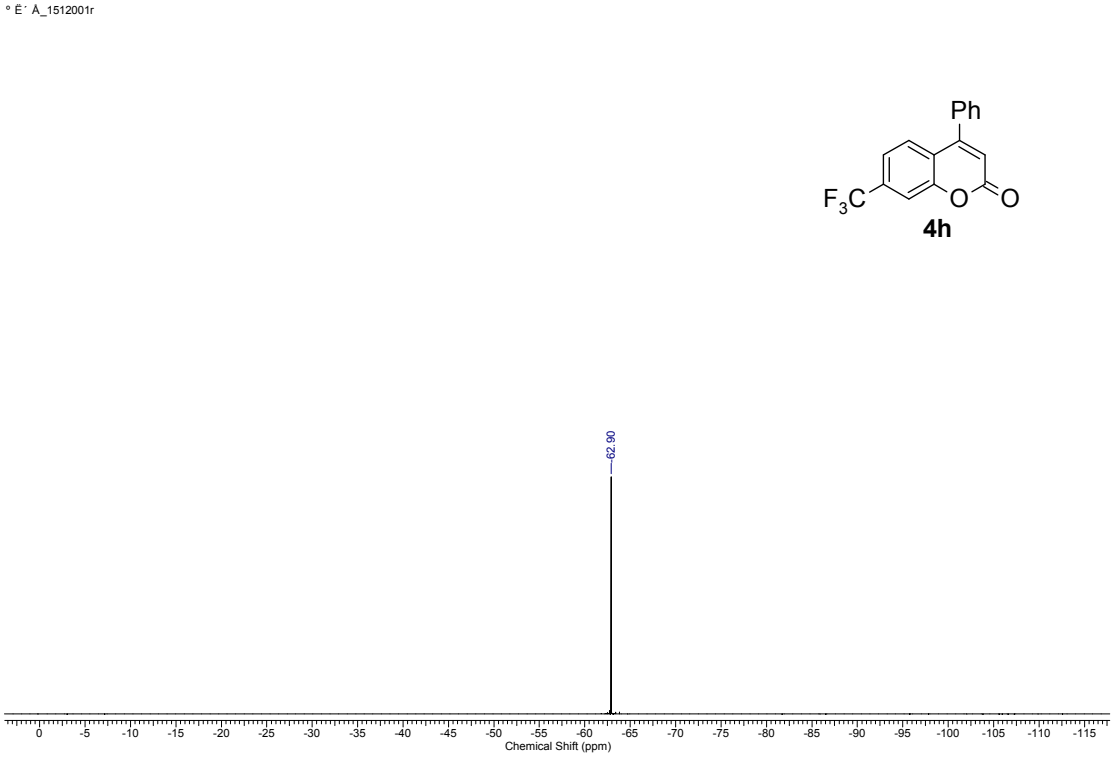


Figure S54. ^{19}F NMR spectrum of compound **4h**

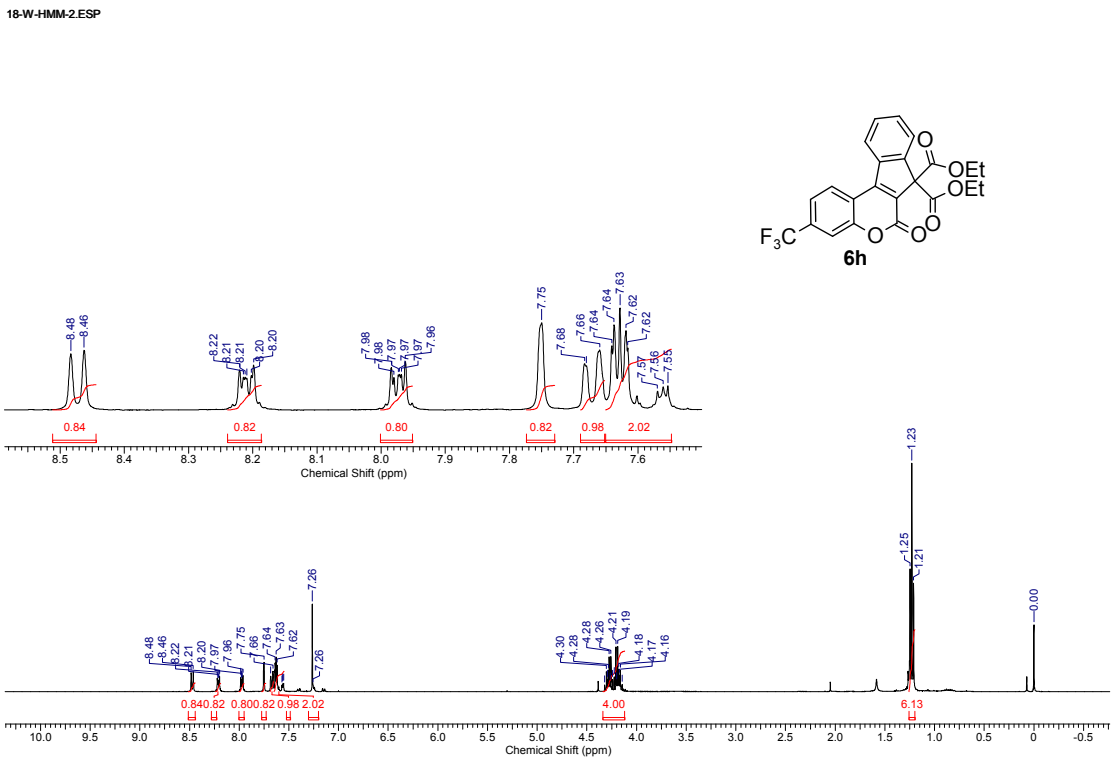


Figure S55. ^{1}H NMR spectrum of compound **6h**

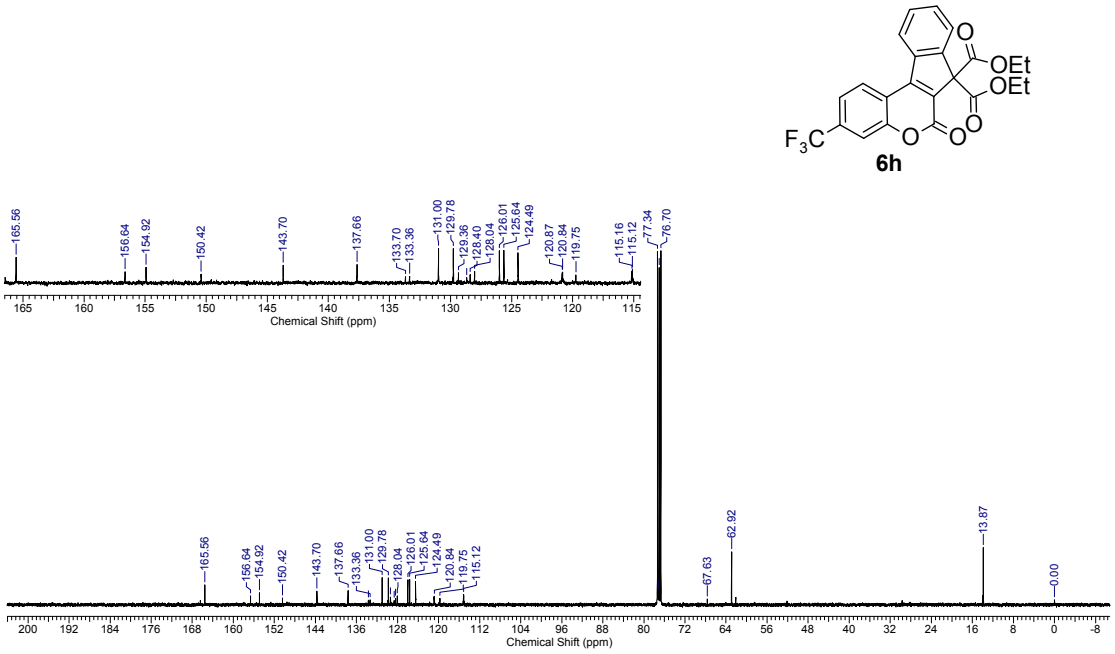


Figure S56. ^{13}C NMR spectrum of compound **6h**

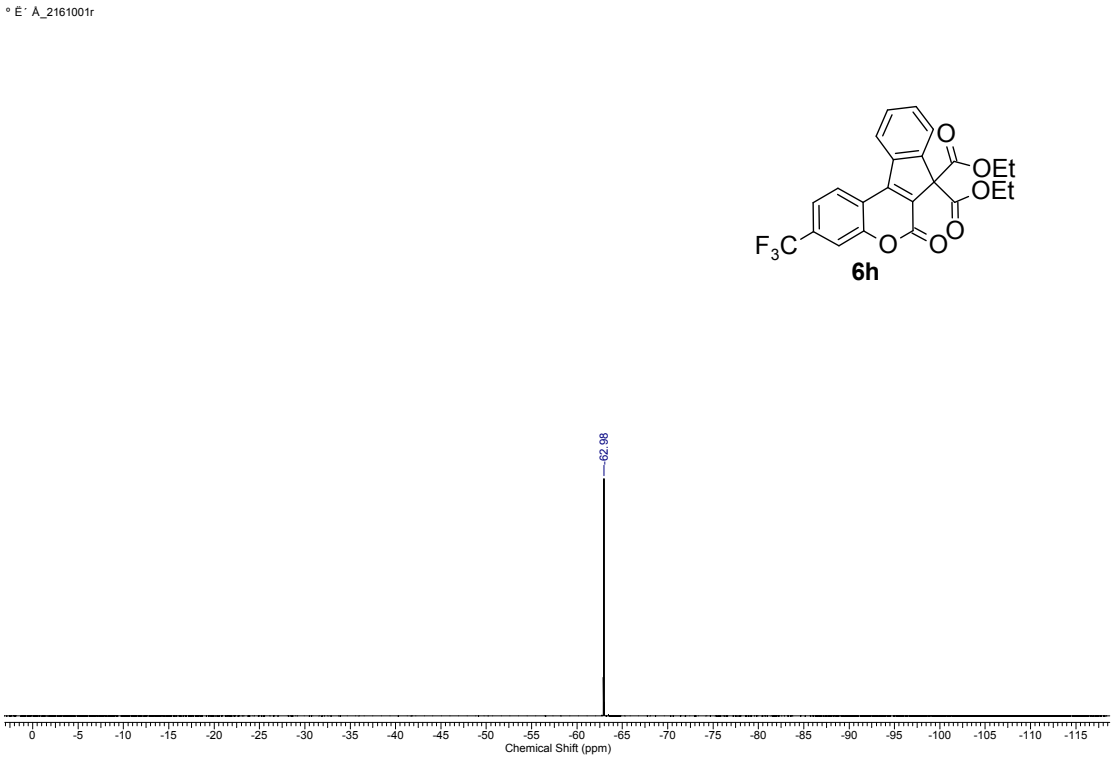


Figure S57. ^{19}F NMR spectrum of compound **6h**

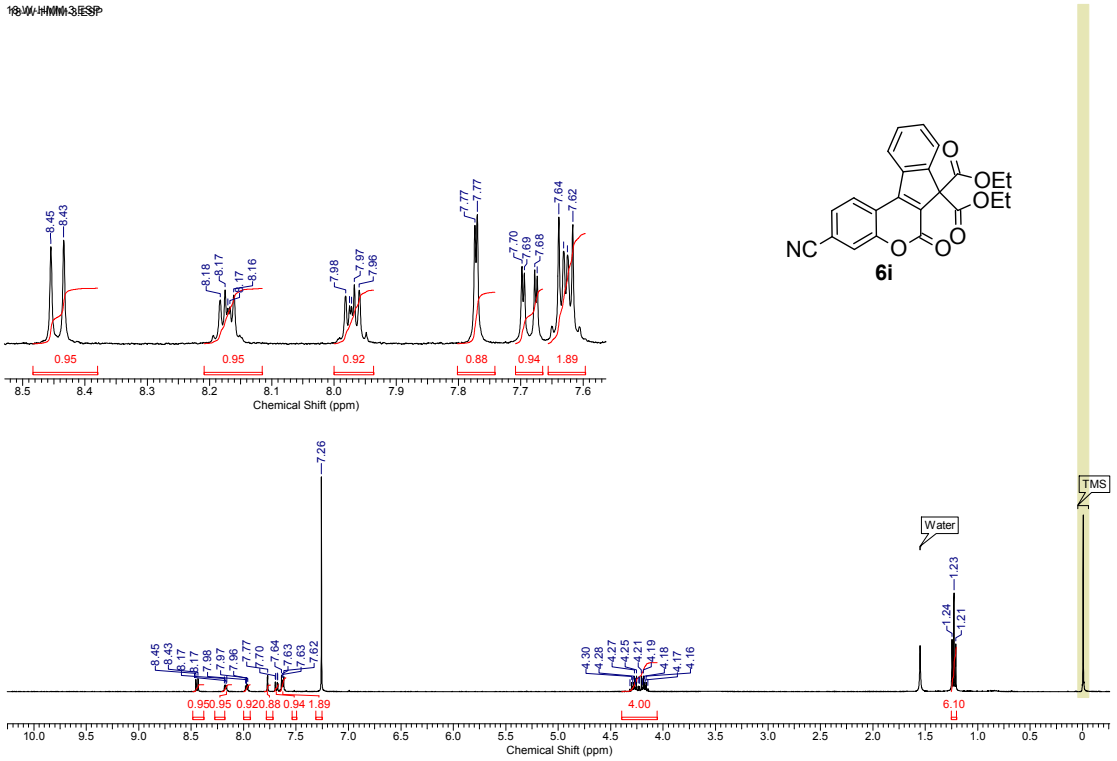


Figure S58. ^{1}H NMR spectrum of compound **6i**

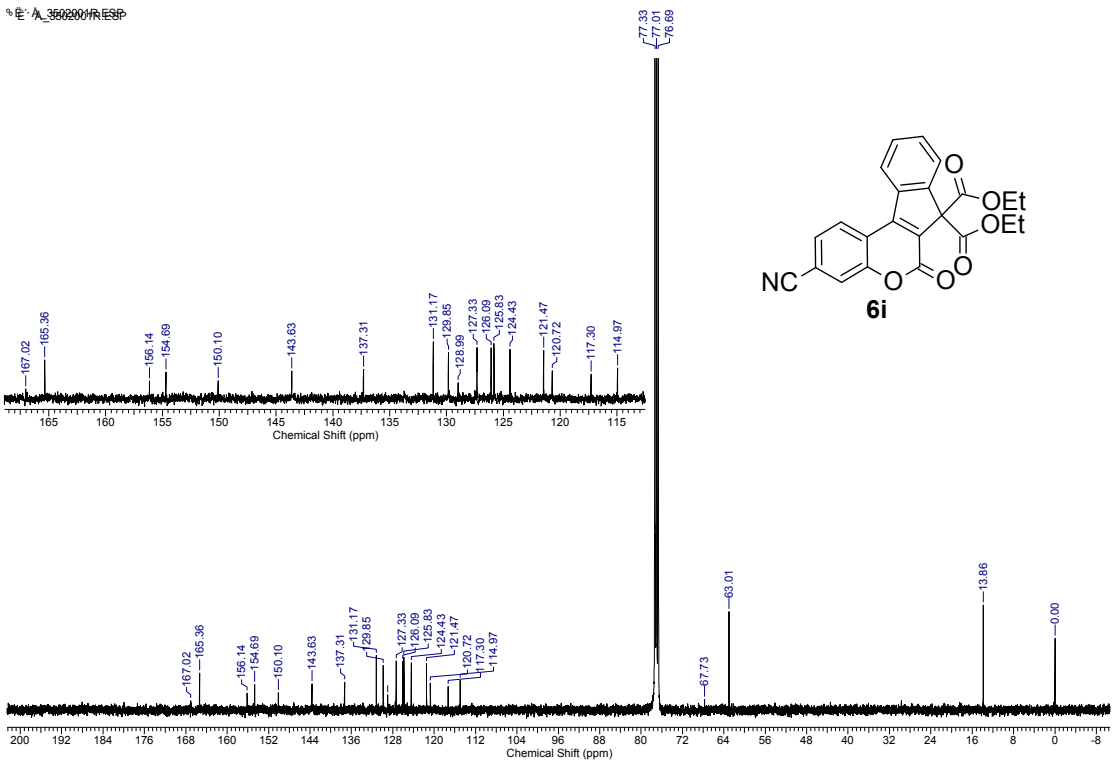


Figure S59. ^{13}C NMR spectrum of compound **6i**

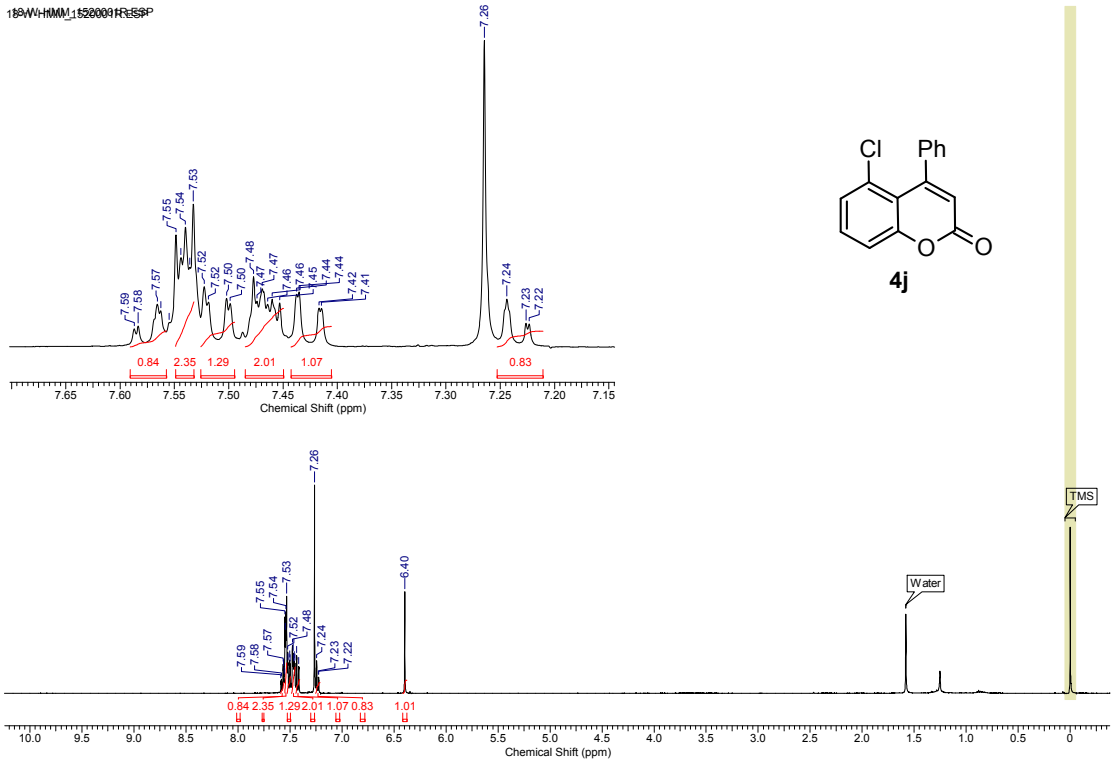


Figure S60. ^{1}H NMR spectrum of compound **4j**

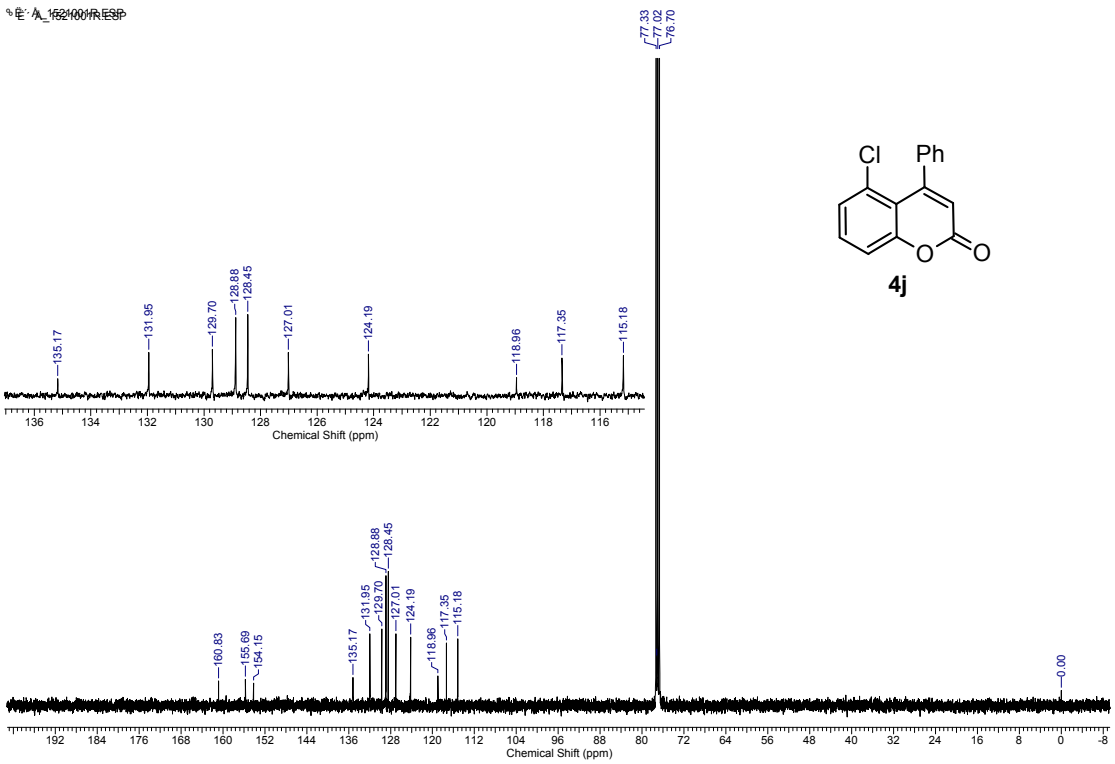


Figure S61. ^{13}C NMR spectrum of compound **4j**

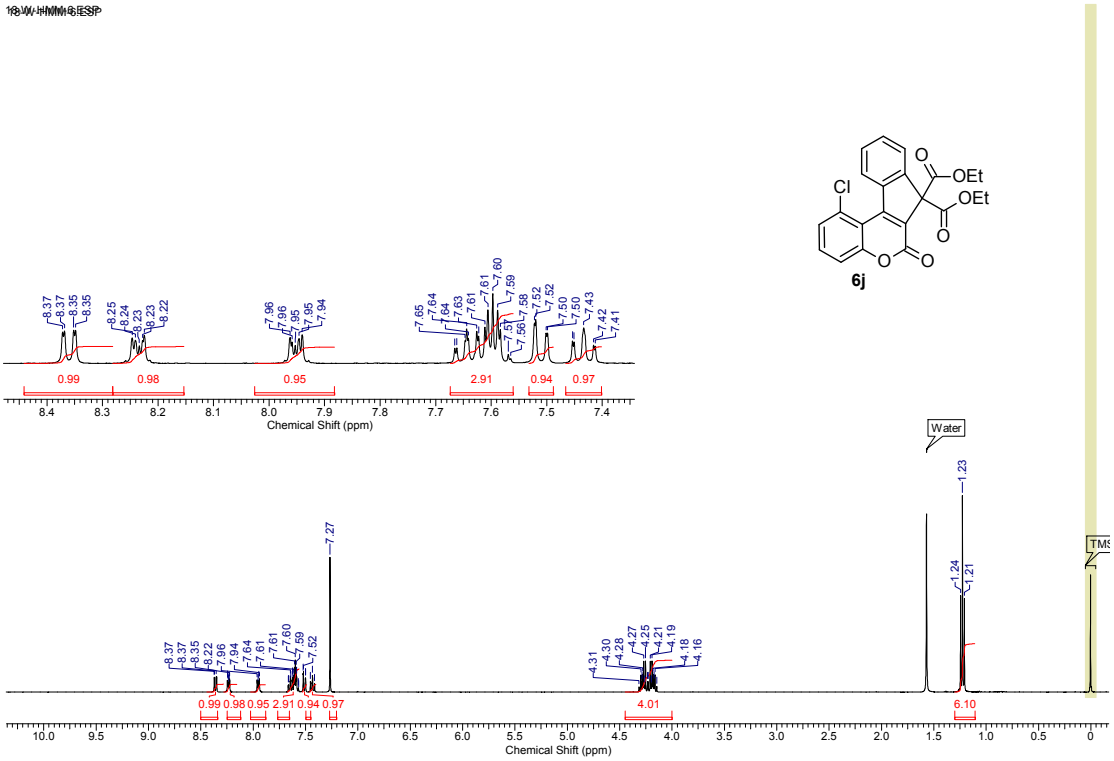


Figure S62. ^{1}H NMR spectrum of compound **6j**

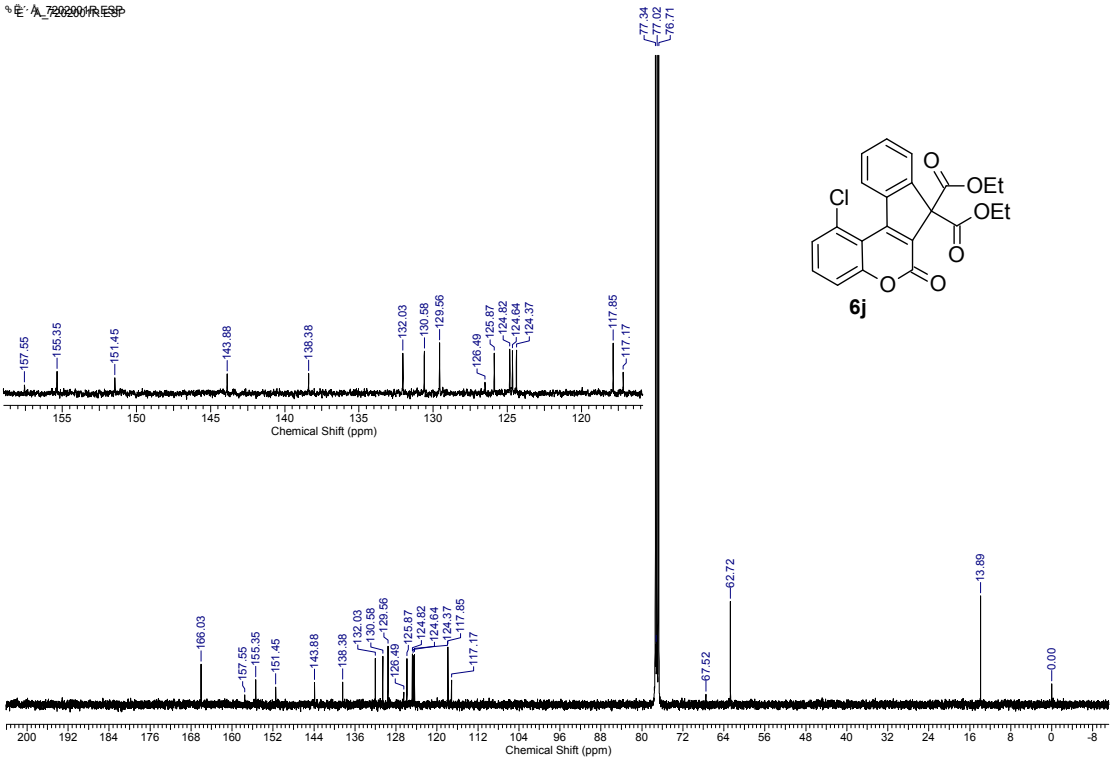


Figure S63. ^{13}C NMR spectrum of compound **6j**

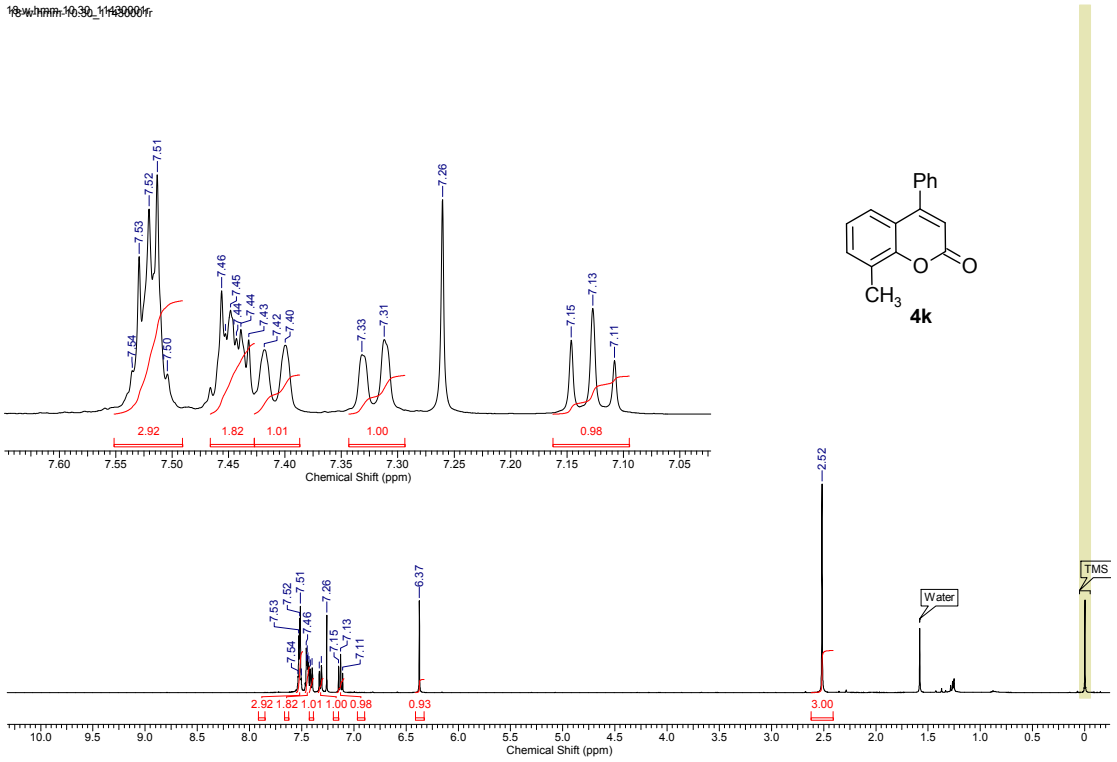


Figure S64. ^{1}H NMR spectrum of compound **4k**

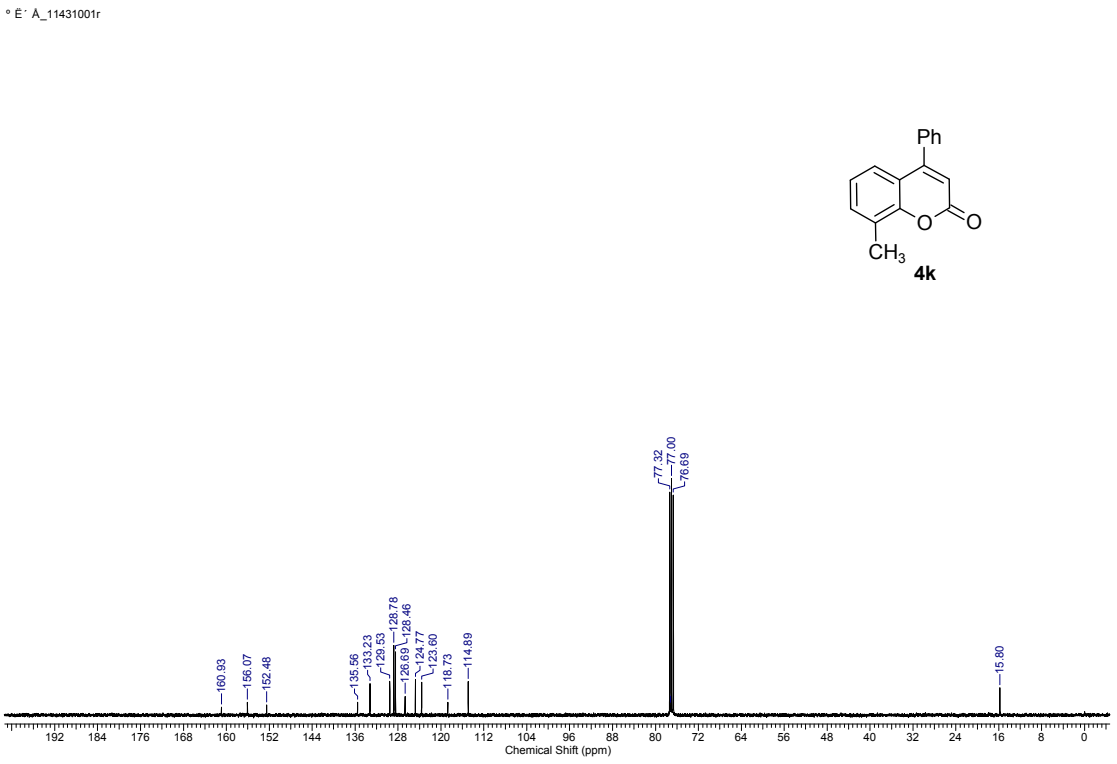


Figure S65. ^{13}C NMR spectrum of compound **4k**

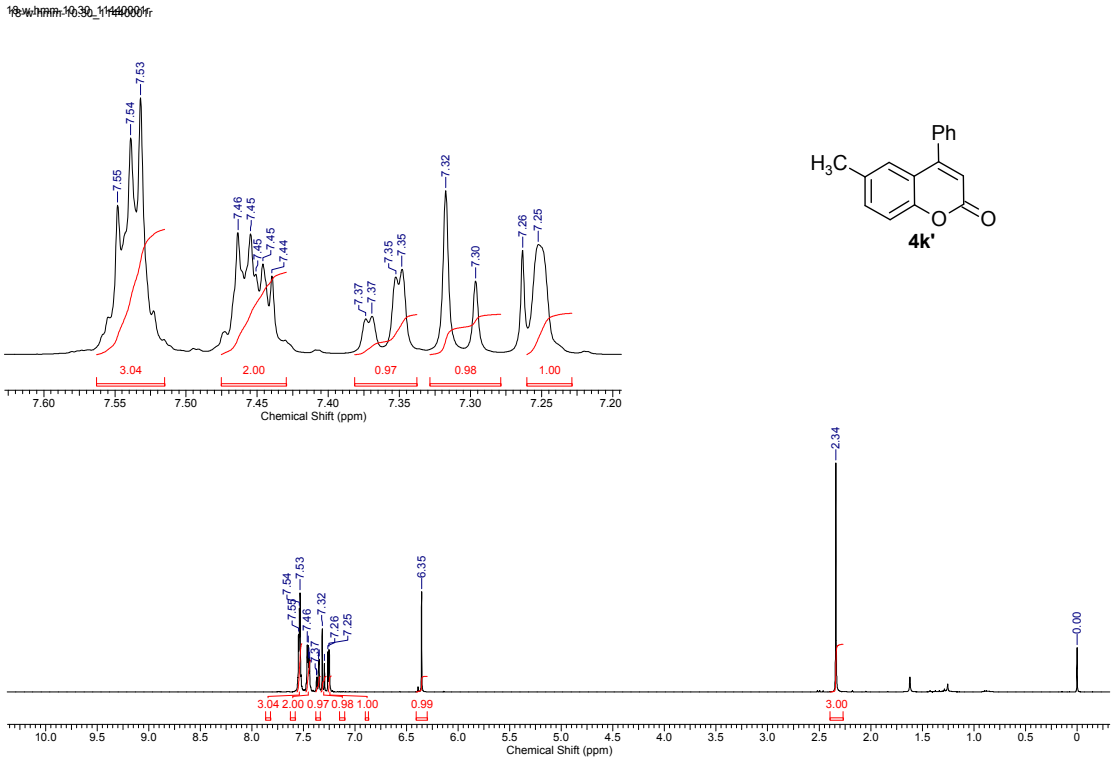


Figure S66. ^{1}H NMR spectrum of compound **4k'**

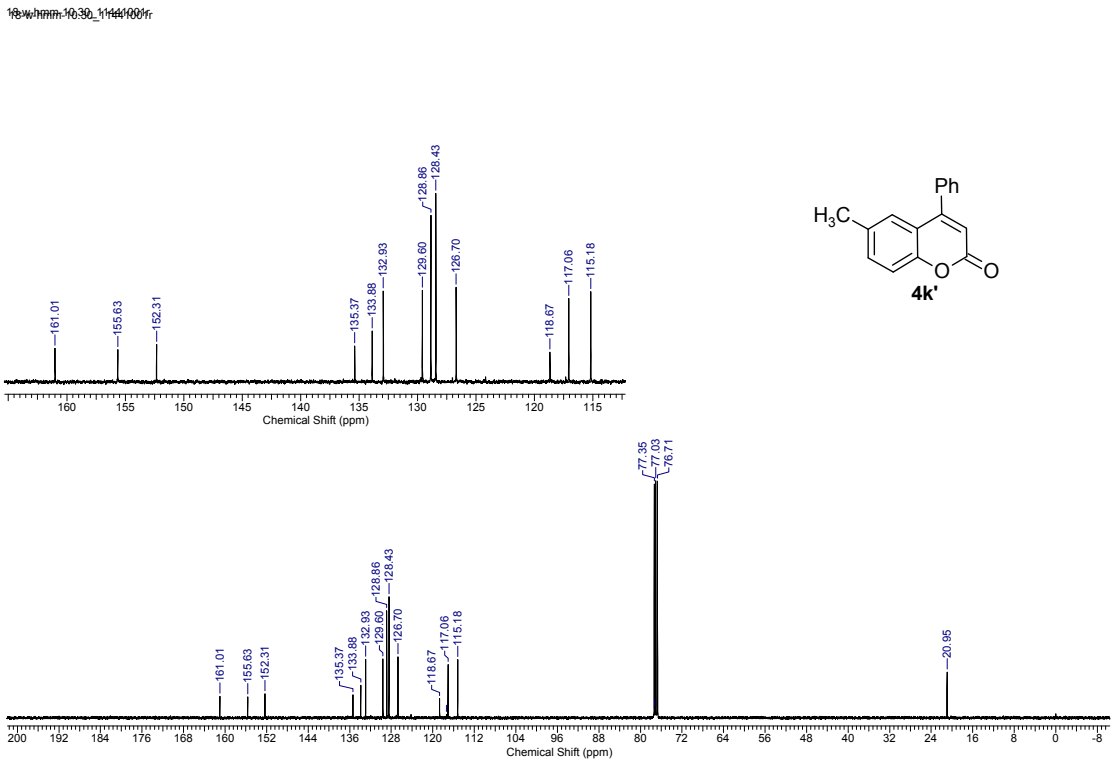


Figure S67. ^{13}C NMR spectrum of compound **4k'**

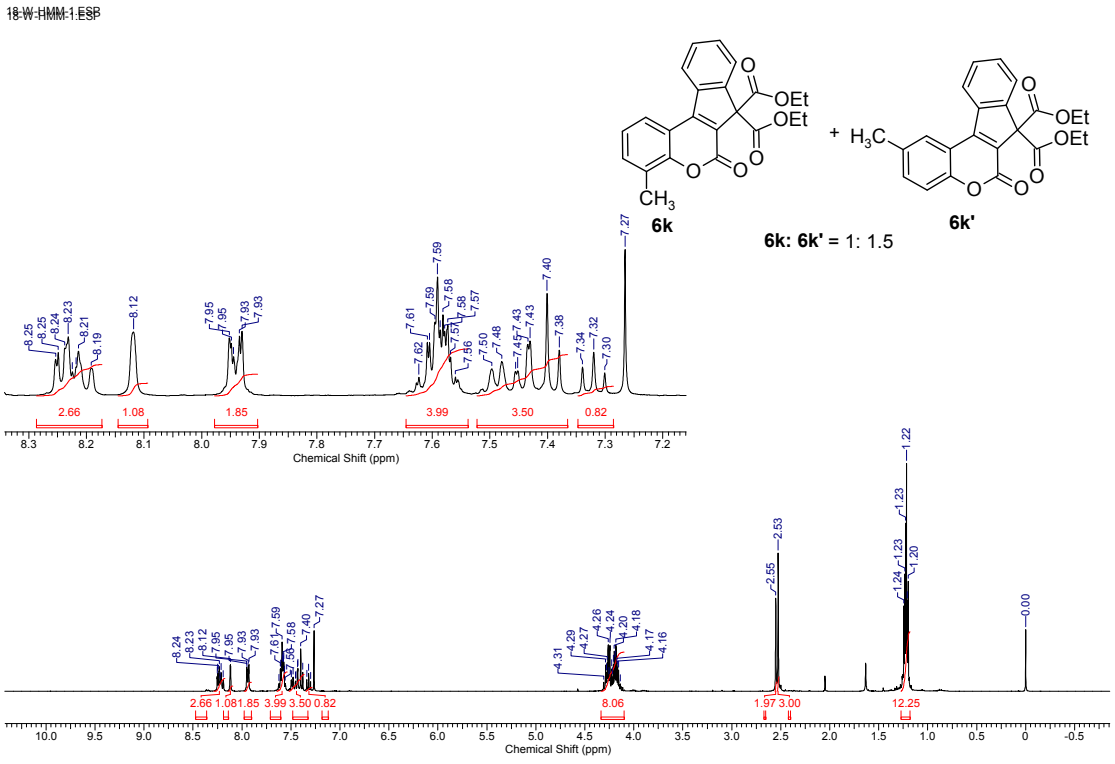


Figure S68. ^{1}H NMR spectrum of compound **6k** and **6k'**

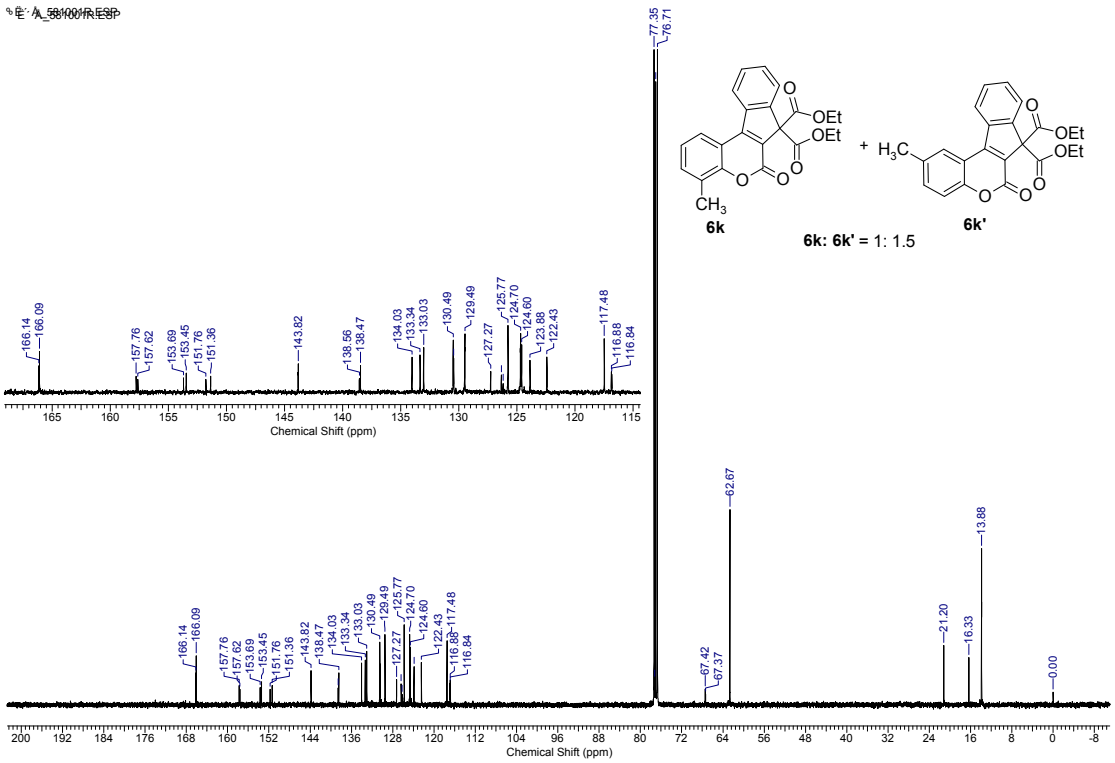


Figure S69. ^{13}C NMR spectrum of compound **6k** and **6k'**

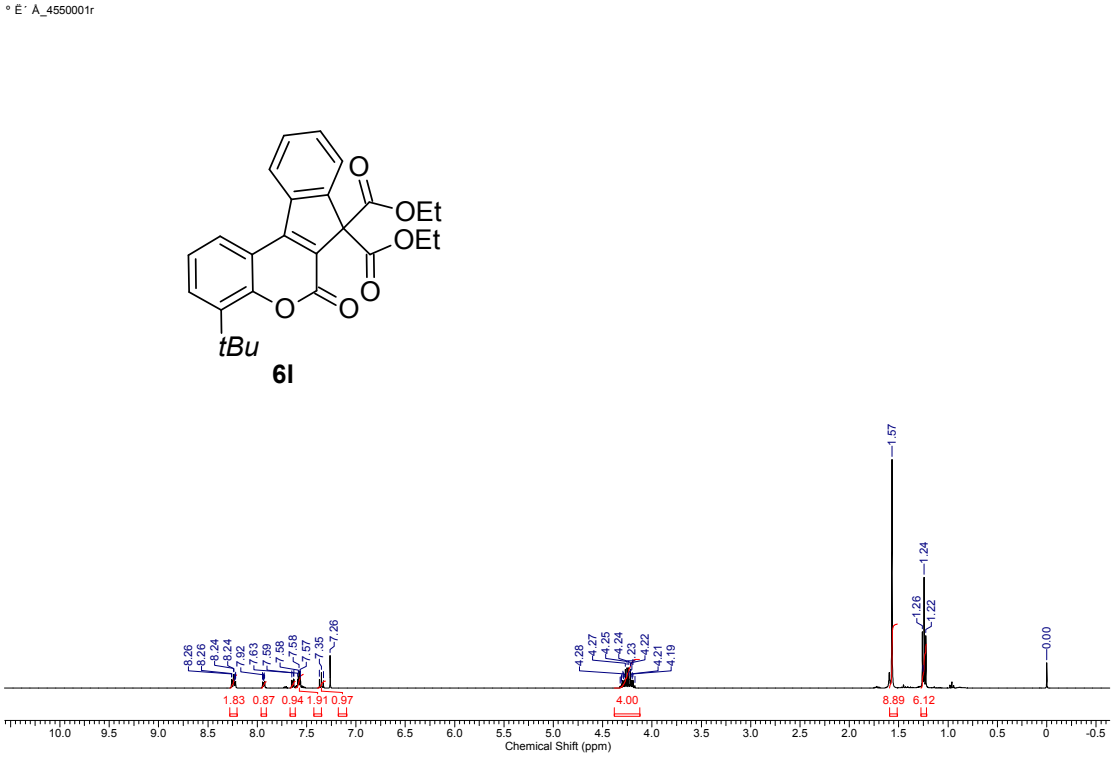


Figure S70. ^{1}H NMR spectrum of compound **6l**

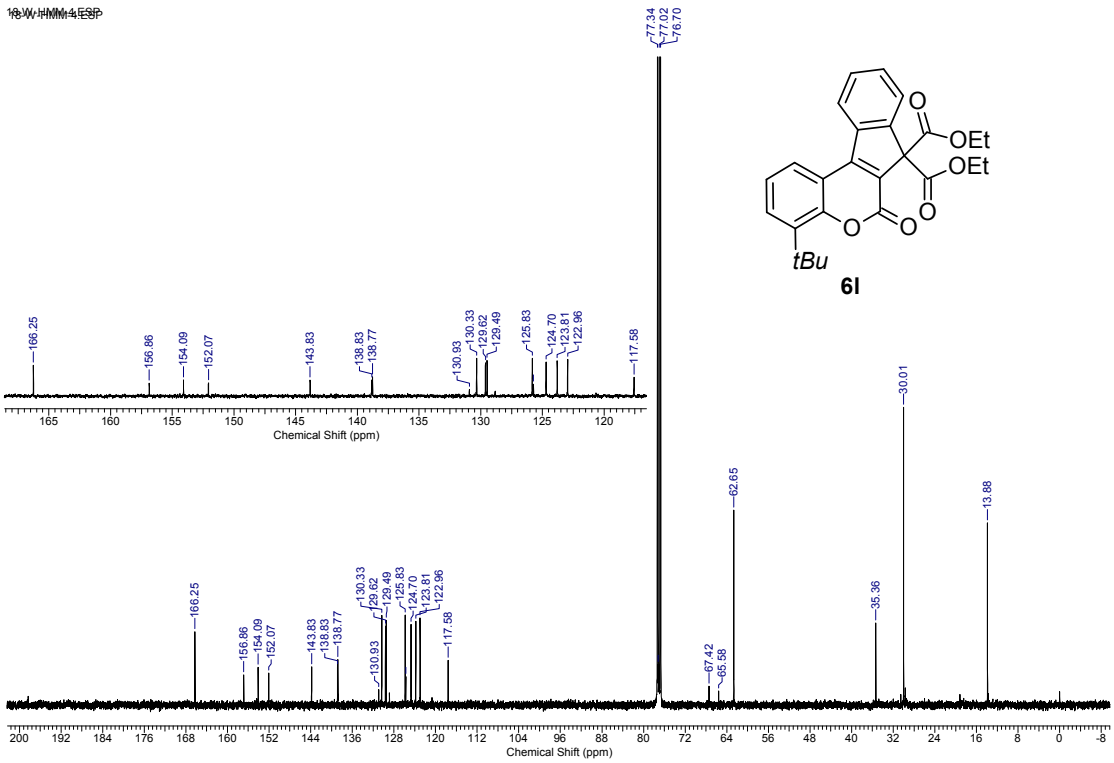


Figure S71. ^{13}C NMR spectrum of compound **6l**

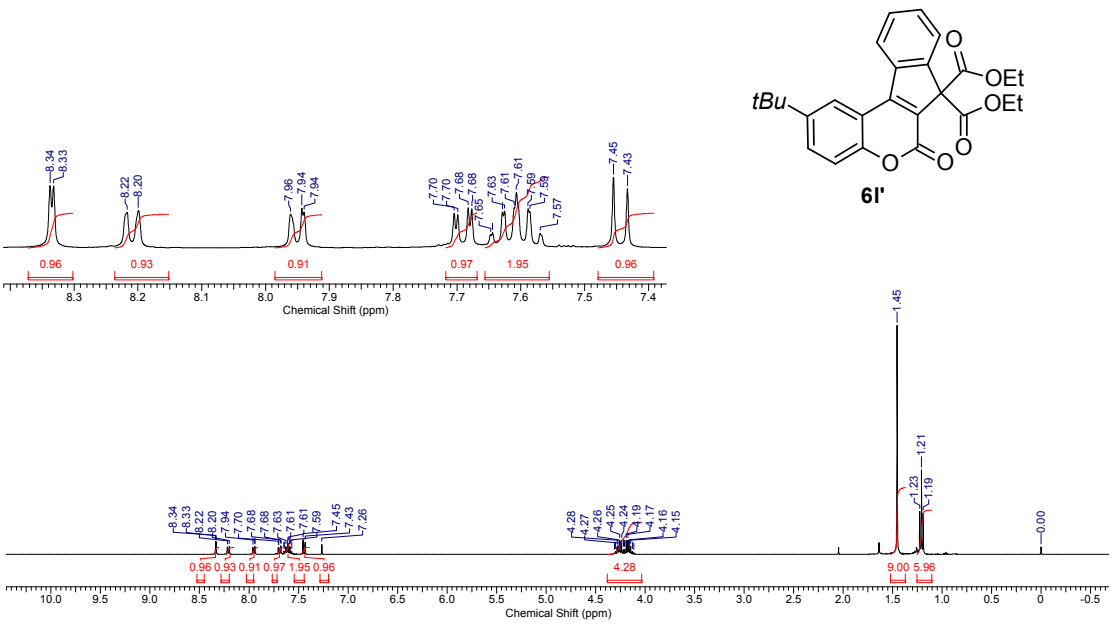


Figure S72. ^{1}H NMR spectrum of compound **6l'**

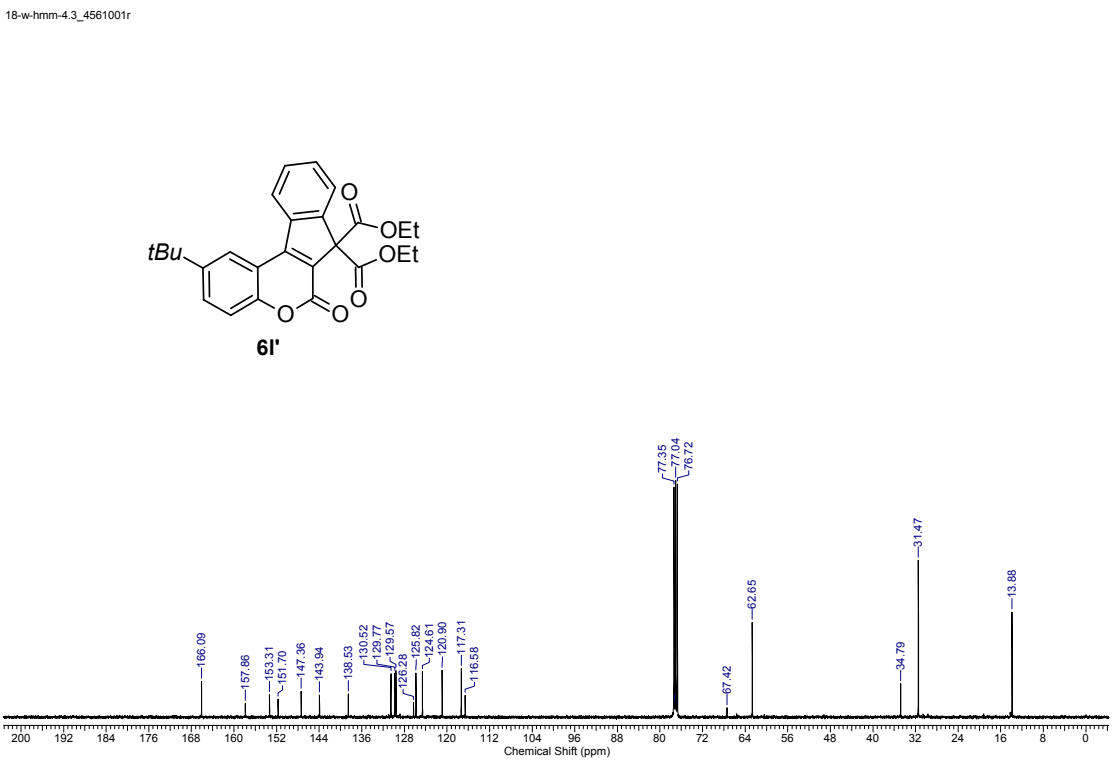


Figure S73. ^{13}C NMR spectrum of compound **6l'**

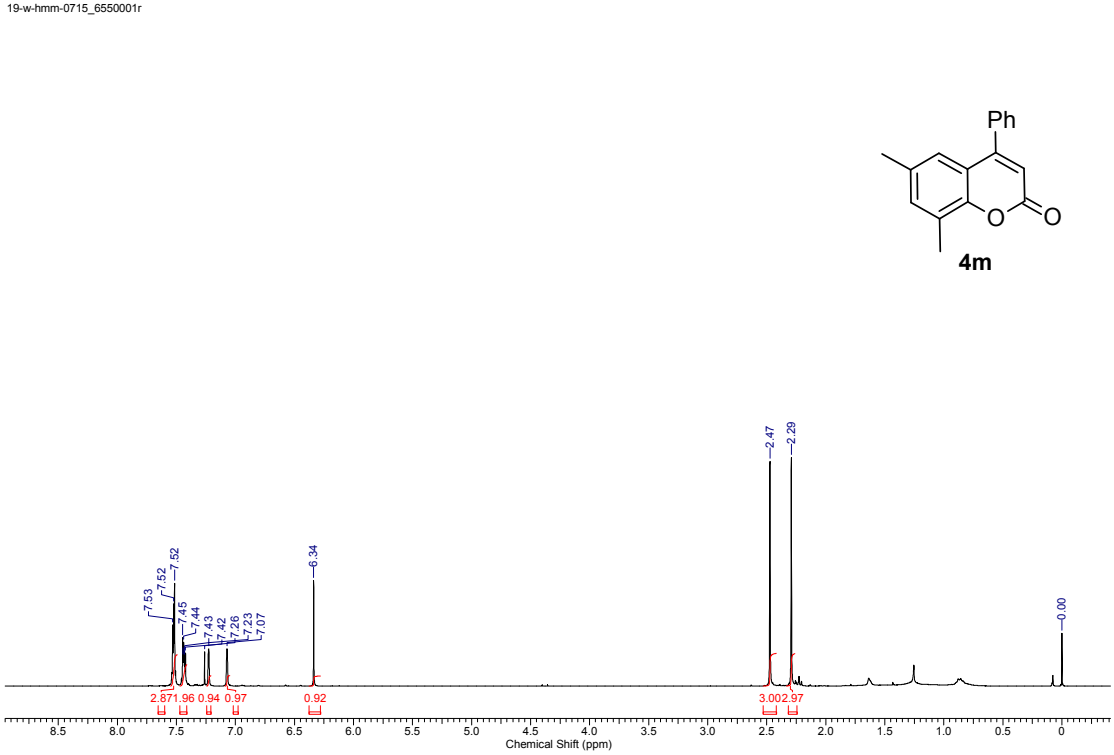


Figure S74. ^{1}H NMR spectrum of compound **4m**

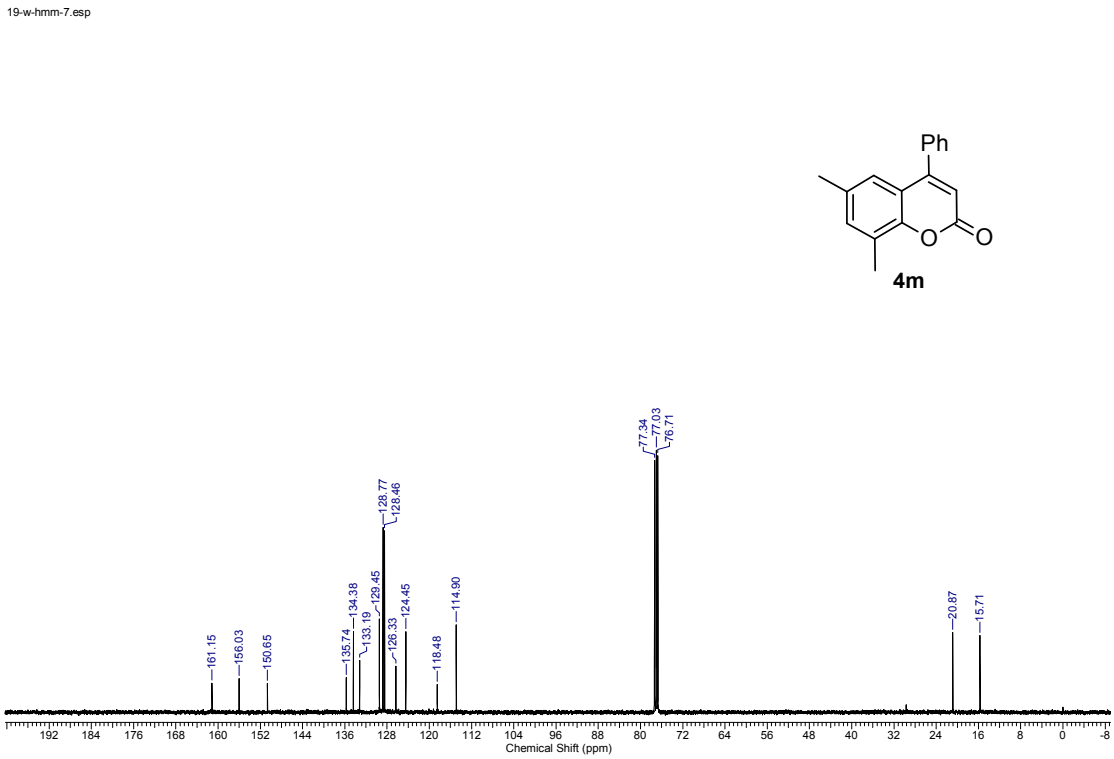


Figure S75. ^{13}C NMR spectrum of compound **4m**

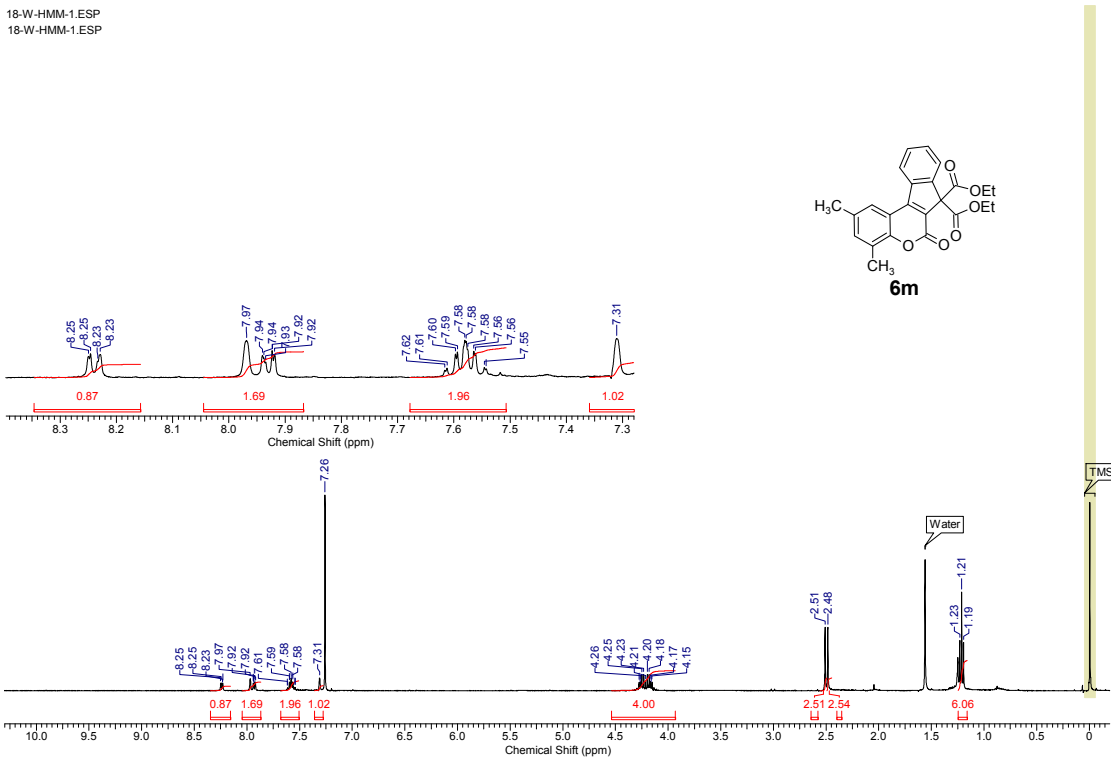


Figure S76. ^{1}H NMR spectrum of compound **6m**

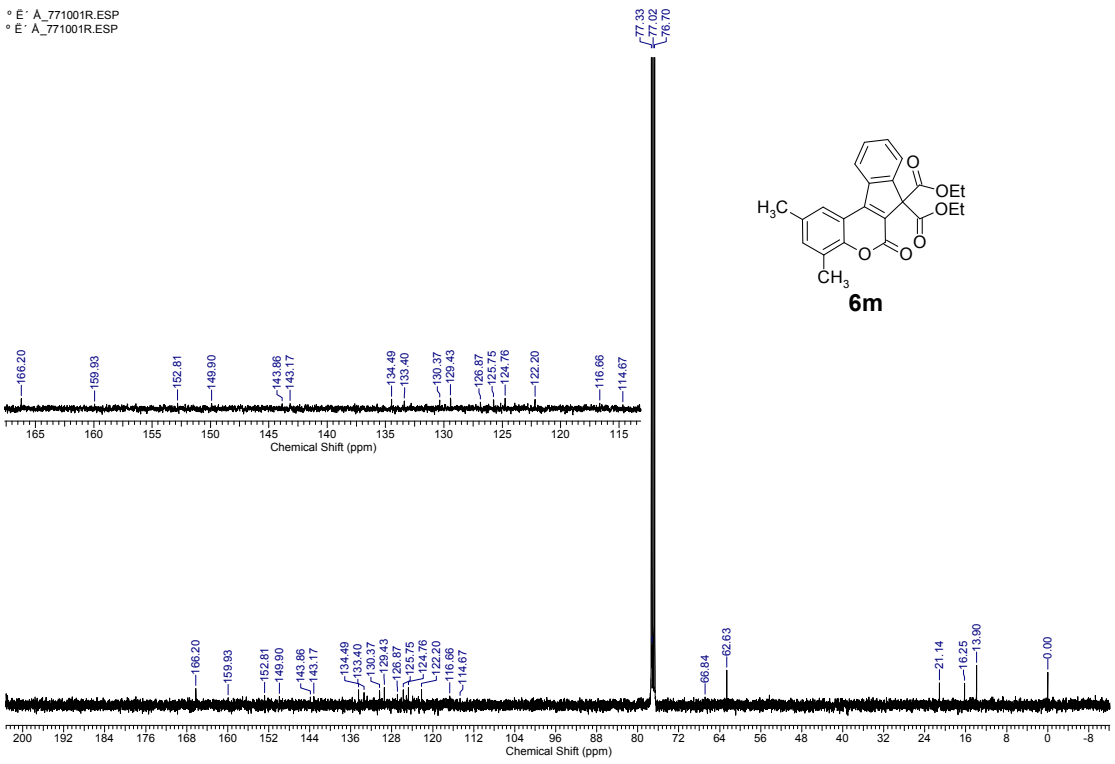


Figure S77. ^{13}C NMR spectrum of compound **6m**

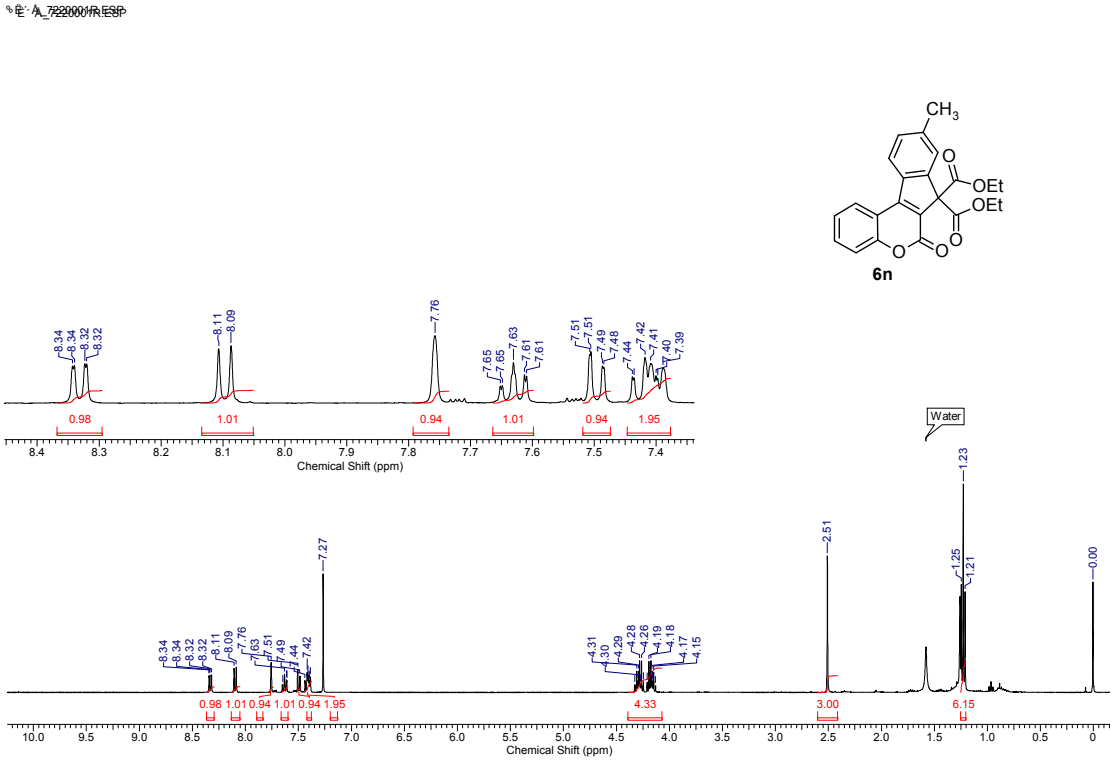


Figure S78. ^{1}H NMR spectrum of compound **6n**

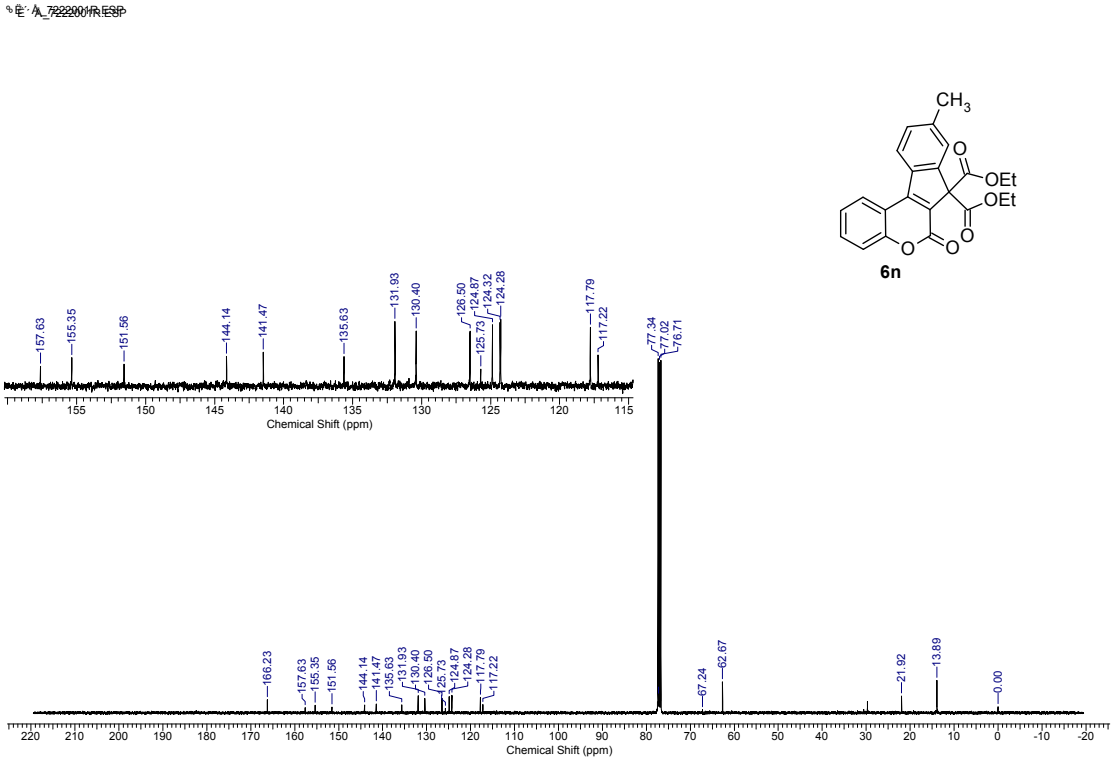


Figure S79. ^{13}C NMR spectrum of compound **6n**

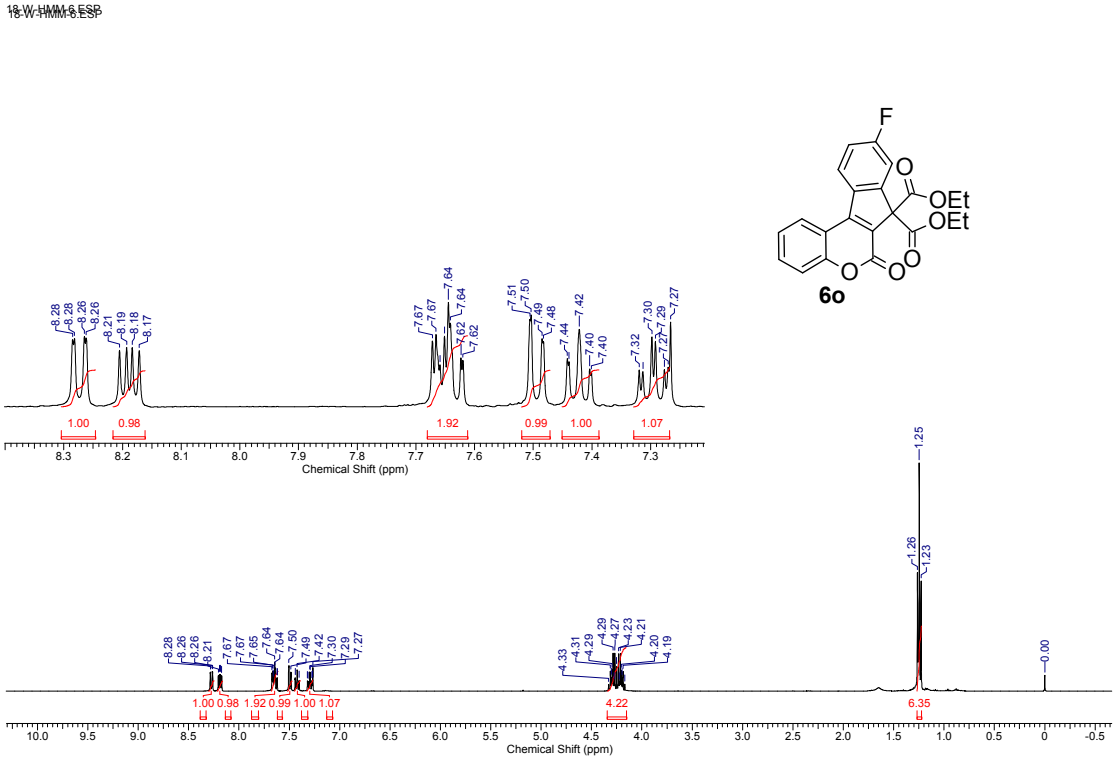


Figure S80. ^{1}H NMR spectrum of compound **6o**

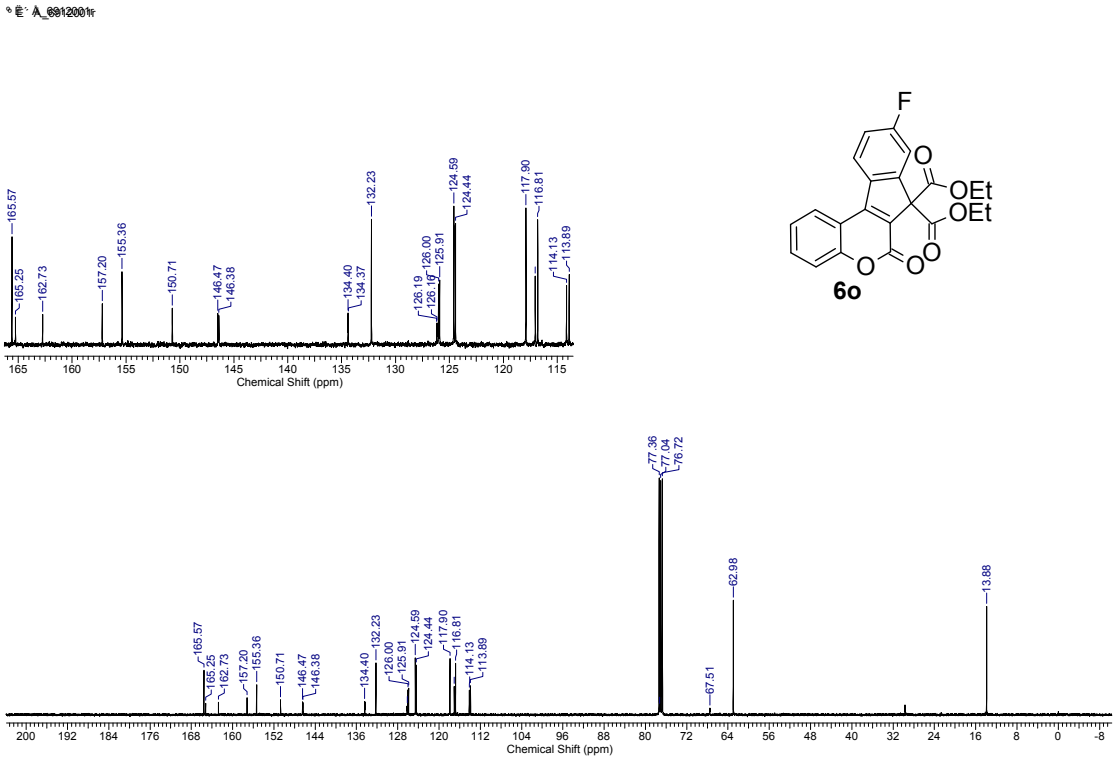


Figure S81. ^{13}C NMR spectrum of compound **6o**

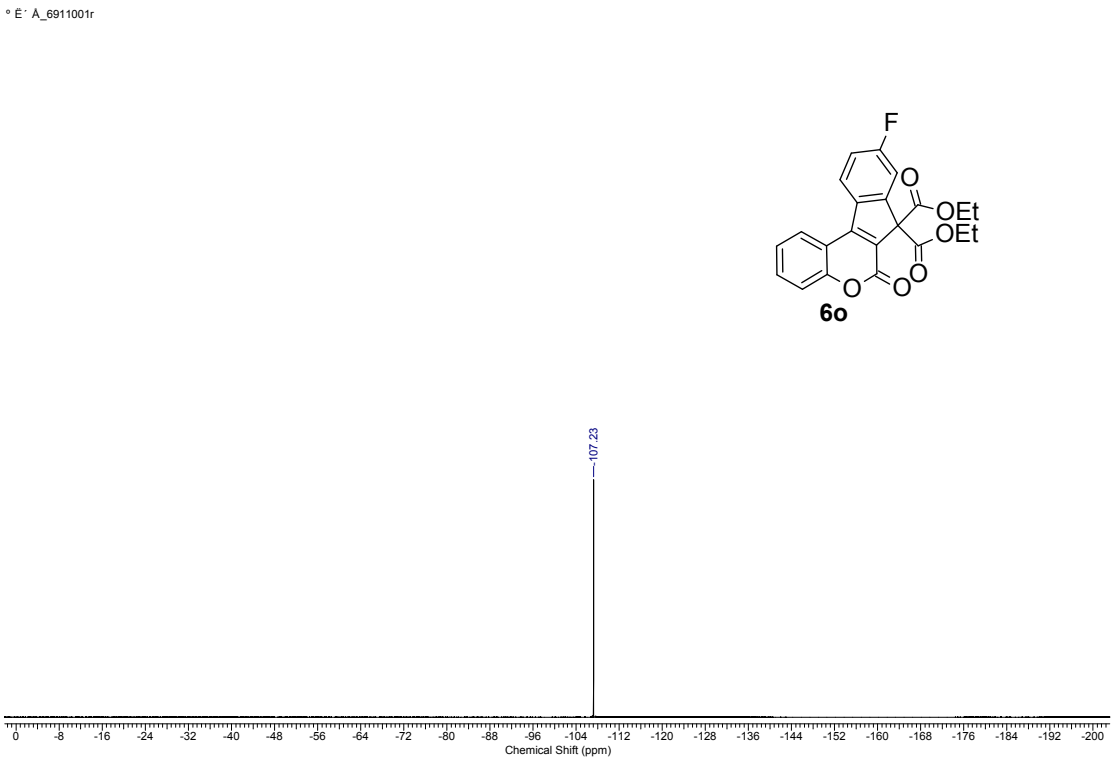


Figure S82. ^{19}F NMR spectrum of compound **6o**

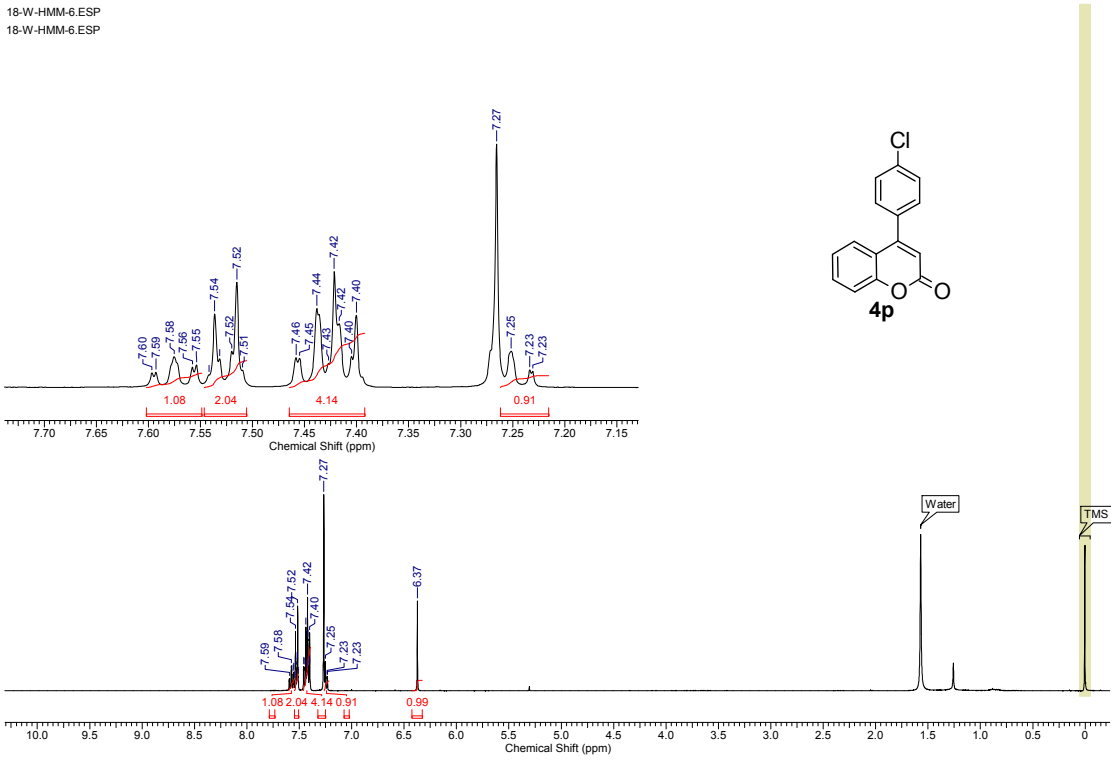


Figure S83. ^{1}H NMR spectrum of compound **4p**

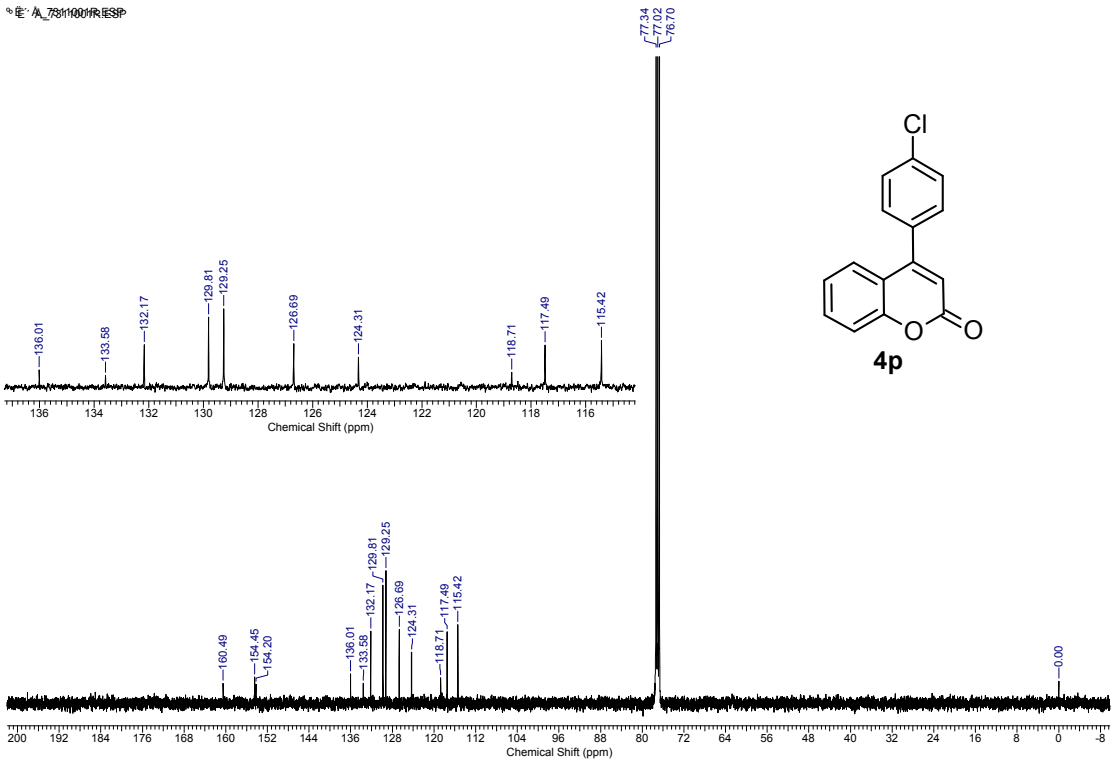


Figure S84. ^{13}C NMR spectrum of compound **4p**

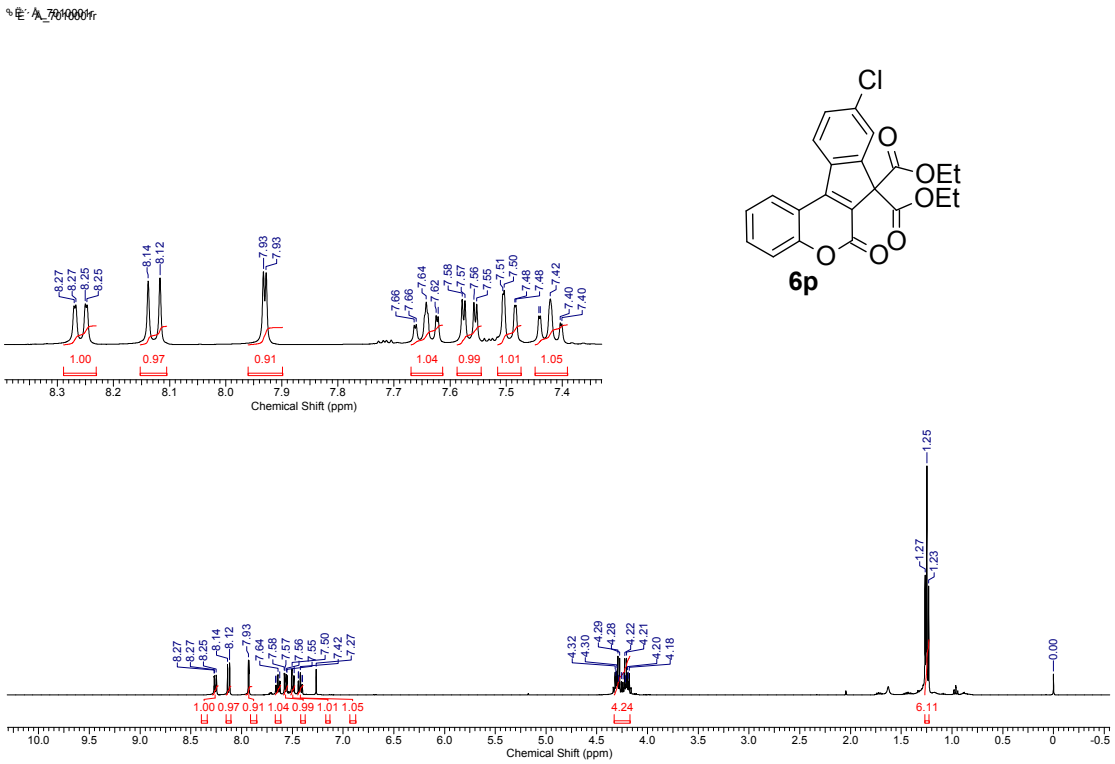


Figure S85. ^{1}H NMR spectrum of compound **6p**

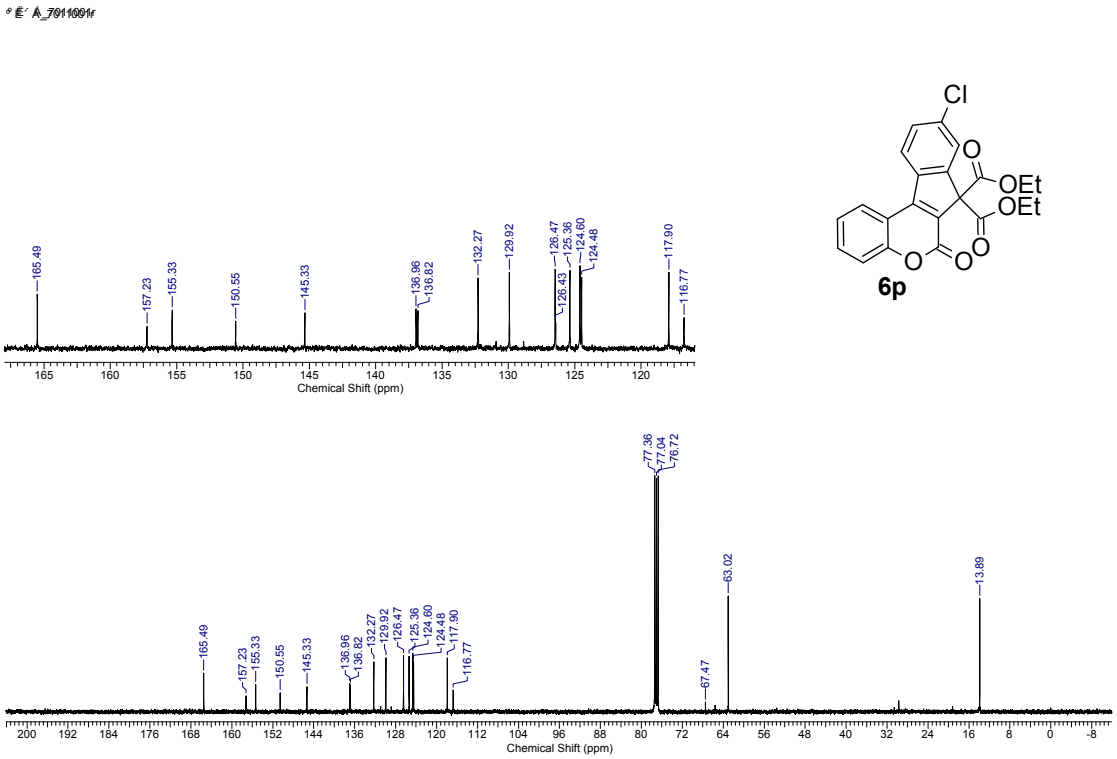


Figure S86. ^{13}C NMR spectrum of compound **6p**

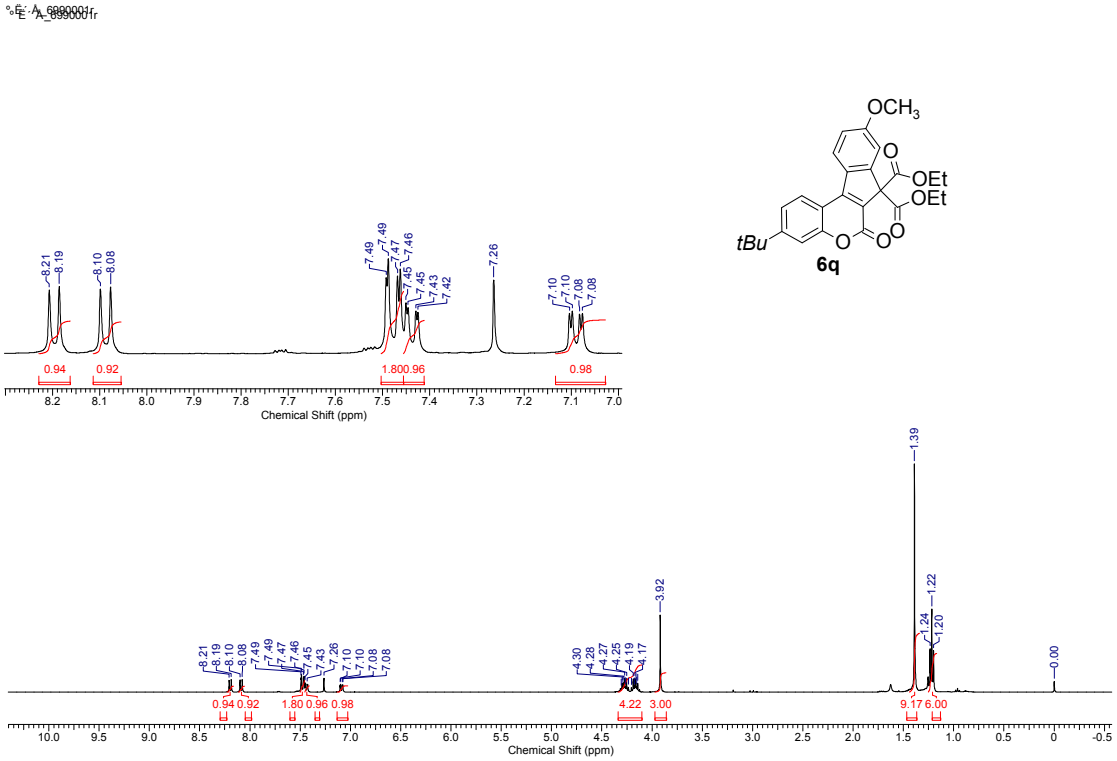


Figure S87. ^{1}H NMR spectrum of compound **6q**

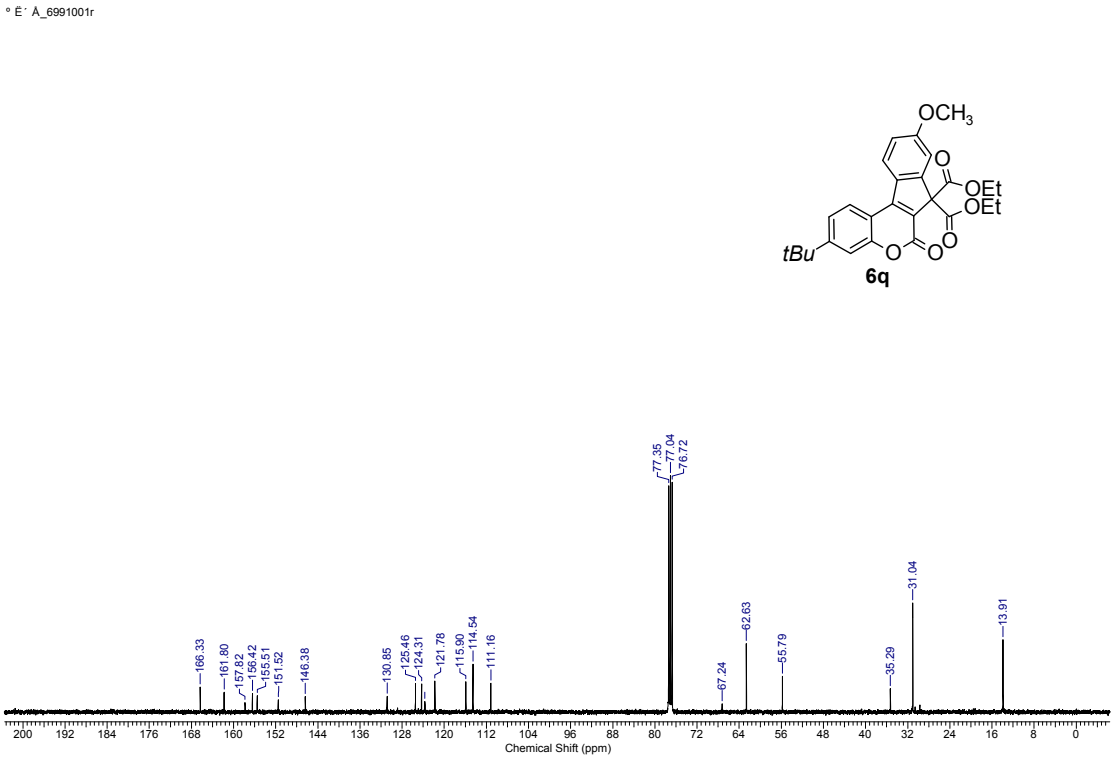


Figure S88. ^{13}C NMR spectrum of compound **6q**

7. Determination of Structures of 3a, 4a, 5a, 6a, 6p

The adducts **3a**, **4a**, **5a**, **6a**, **6p** were readily crystallized from mixtures of ethyl EtOH and dichloromethane.

7.1 3a (CCDC **1858970**)

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 **1858970**.

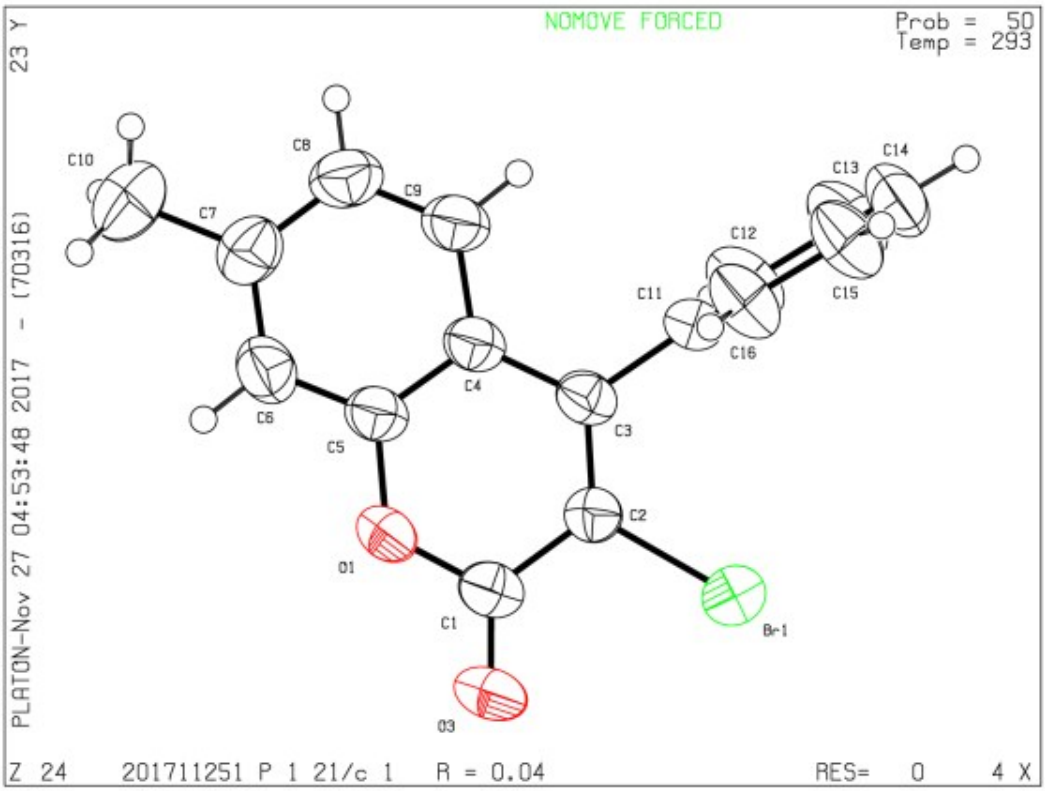


Table 5 Crystal data and structure refinement for 3a.

Identification code	201711251
Empirical formula	$C_{16}H_{11}BrO_2$
Formula weight	315.16
Temperature/K	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	10.0036(11)
b/Å	15.5670(13)
c/Å	8.7599(11)
α/°	90
β/°	100.953(11)
γ/°	90

Volume/Å^3	1339.3(3)
Z	4
ρ_{calc}g/cm^3	1.563
μ/mm^{-1}	4.138
F(000)	632.0
Crystal size/mm^3	0.17 × 0.15 × 0.13
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.004 to 134.176
Index ranges	-11 ≤ h ≤ 11, -17 ≤ k ≤ 18, -10 ≤ l ≤ 7
Reflections collected	5202
Independent reflections	2381 [R_{int} = 0.0295, R_{sigma} = 0.0413]
Data/restraints/parameters	2381/0/173
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0403, wR_2 = 0.0957
Final R indexes [all data]	R_1 = 0.0661, wR_2 = 0.1132
Largest diff. peak/hole / e Å^{-3}	0.35/-0.36

7.2 4a (CCDC **1858972**)

The structure of **4a** 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 **1858972**.

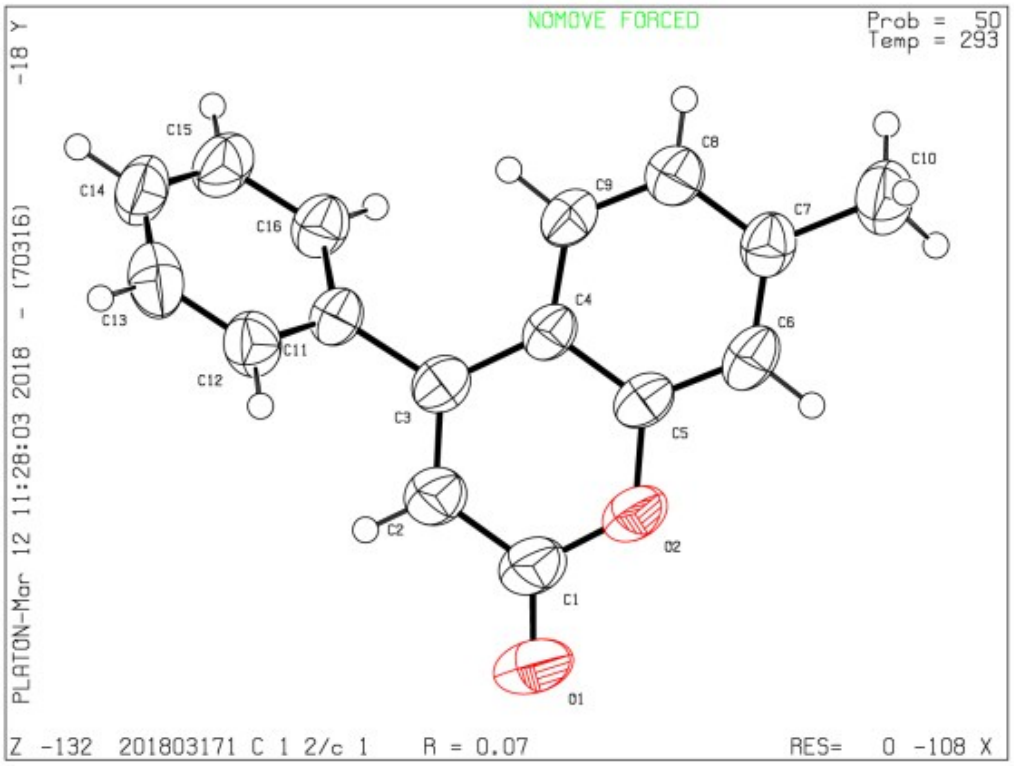


Table 1 Crystal data and structure refinement for 4a.

Identification code	201803171
Empirical formula	$C_{16}H_{12}O_2$
Formula weight	236.26
Temperature/K	293(2)
Crystal system	Monoclinic
Space group	C2/c
a/Å	25.676(2)
b/Å	4.1792(4)
c/Å	24.335(3)
α/°	90
β/°	112.380(14)
γ/°	90
Volume/Å^3	2414.6(5)
Z	8
ρ_{calc}g/cm^3	1.300
μ/mm^{-1}	0.085
F(000)	992.0
Crystal size/mm^3	0.2 × 0.14 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.732 to 52.744
Index ranges	-32 ≤ h ≤ 32, -4 ≤ k ≤ 5, -30 ≤ l ≤ 20
Reflections collected	5181
Independent reflections	2469 [R_{int} = 0.0439, R_{sigma} = 0.0596]
Data/restraints/parameters	2469/0/164
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0687, wR_2 = 0.1635
Final R indexes [all data]	R_1 = 0.1134, wR_2 = 0.2052
Largest diff. peak/hole / e Å^{-3}	0.19/-0.25

7.3 5a (CCDC **1858971**)

The structure of **5a** 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 **1858971**.

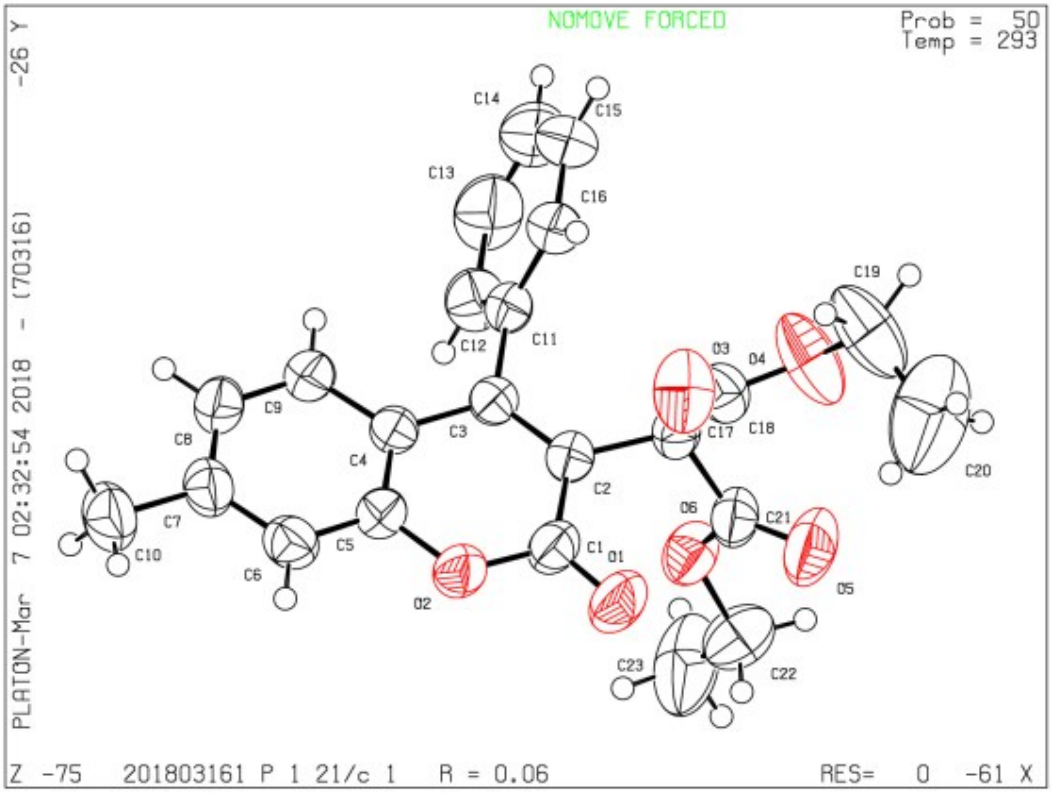


Table 2 Crystal data and structure refinement for 5a.

Identification code	201803161
Empirical formula	$C_{23}H_{22}O_6$
Formula weight	394.40
Temperature/K	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	14.7414(4)
b/Å	8.7416(3)
c/Å	16.4090(5)
α/°	90
β/°	104.242(3)
γ/°	90
Volume/Å^3	2049.53(11)
Z	4
ρ_{calc}g/cm^3	1.278
μ/mm^{-1}	0.762
F(000)	832.0
Crystal size/mm^3	0.23 × 0.18 × 0.15
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	11.126 to 141.79
Index ranges	-17 ≤ h ≤ 12, -10 ≤ k ≤ 10, -19 ≤ l ≤ 20

Reflections collected	8150
Independent reflections	3871 [R_{int} = 0.0250, R_{sigma} = 0.0307]
Data/restraints/parameters	3871/0/266
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0626, wR_2 = 0.1809
Final R indexes [all data]	R_1 = 0.0794, wR_2 = 0.2038
Largest diff. peak/hole / e Å^{-3}	0.43/-0.25

7.4 **6a** (CCDC **1858969**)

The structure of **6a** 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 **1858969**.

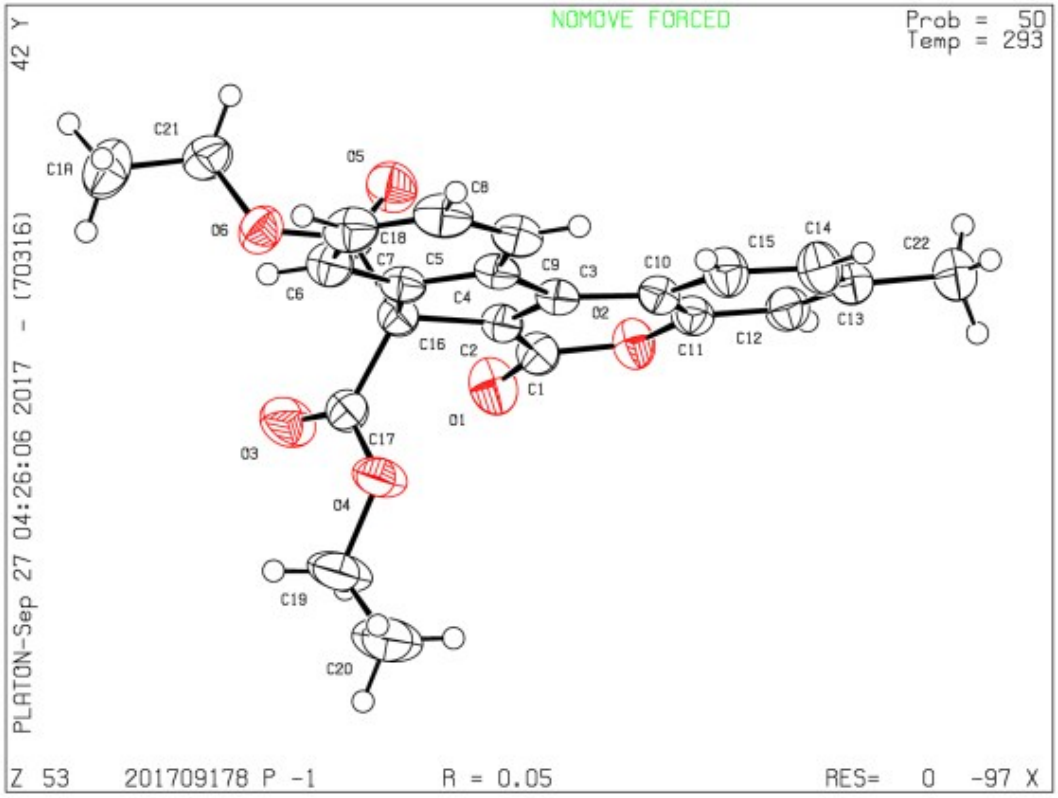


Table 3 Crystal data and structure refinement for 6a.

Identification code	201709178
Empirical formula	$C_{23}H_{20}O_6$
Formula weight	392.39
Temperature/K	293(2)
Crystal system	Triclinic
Space group	P-1
a/Å	7.7957(7)
b/Å	10.1827(6)
c/Å	12.7574(8)

α/°	79.033(5)
β/°	76.634(7)
γ/°	77.369(6)
Volume/Å^3	950.95(13)
Z	2
ρ_{calc}g/cm^3	1.370
μ/mm^{-1}	0.099
F(000)	412.0
Crystal size/mm^3	0.18 × 0.16 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.638 to 52.744
Index ranges	-9 ≤ h ≤ 9, -12 ≤ k ≤ 12, -13 ≤ l ≤ 15
Reflections collected	7725
Independent reflections	3885 [R_{int} = 0.0289, R_{sigma} = 0.0508]
Data/restraints/parameters	3885/0/265
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0530, wR_2 = 0.1189
Final R indexes [all data]	R_1 = 0.0829, wR_2 = 0.1395
Largest diff. peak/hole / e Å^{-3}	0.21/-0.21

7.5 6p (CCDC **1858974**)

The structure of **6p** 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 **1858974**.

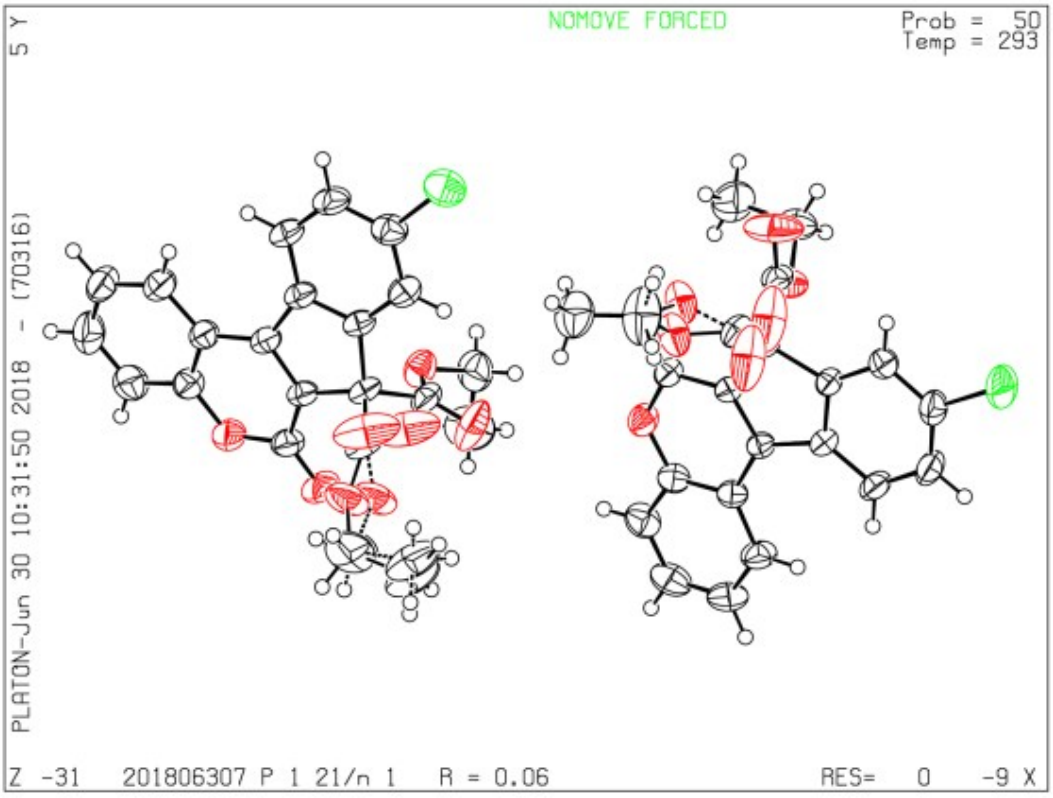


Table 4 Crystal data and structure refinement for 6p.

Identification code	201806307
Empirical formula	$C_{22}H_{17}ClO_6$
Formula weight	412.80
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.6483(3)
b/Å	17.4042(4)
c/Å	15.2455(4)
α/°	90
β/°	94.817(2)
γ/°	90
Volume/Å^3	3872.98(15)
Z	8
ρ_{calc}g/cm^3	1.416
μ/mm^{-1}	2.077
F(000)	1712.0
Crystal size/mm^3	0.17 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.724 to 134.156

Index ranges	$-17 \leq h \leq 12$, $-20 \leq k \leq 20$, $-18 \leq l \leq 18$
Reflections collected	16152
Independent reflections	6898 [R_{int} = 0.0232, R_{sigma} = 0.0267]
Data/restraints/parameters	6898/29/548
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0613, wR_2 = 0.1690
Final R indexes [all data]	R_1 = 0.0746, wR_2 = 0.1846
Largest diff. peak/hole / e $Å^{-3}$	0.47/-0.28