Supporting Information

Divergent Synthesis of Indenoisoquinolines and Indenoisochromenes by Rhodium-Catalyzed Cyclocondensation of *N*-Substituted Benazamides with 2-Diazoindenediones

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1. General information

NMR spectra were recorded on a JEOL JNM-ECZ400s/L1 spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C using $CDCl_3$ as the solvent. For some products that were insoluble in $CDCl_3$, a few drops of CF_3COOD were added to $CDCl_3$ to obtain the corresponding NMR spectra. ESI-HRMS were obtained with Thermo Scientific Exactive Plus. Crude reaction mixtures were purified by column chromatography on silica gel 60N (40–50 μm, Kanto Chemical Co., Inc.). *N*-Substituted benzamides were synthesized from the corresponding benzoic acids or benzoyl chlorides and amines according to a reported procedure.[1] 2-Azido-1,3-indandione was prepared from indandione following a literature method.[2] Unless otherwise stated, all commercially available reagents and solvents were used without further purification.

2. Reaction procedure

2.1 General procedure for the synthesis of products 3

A reaction tube equipped with a magnetic stir bar was charged with *N*-alkoxybenzamide **1** (0.20 mmol), 2-diazo-1,3-indandione **2** (0.24 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), and AgOAc (10 mol%) in MeOH (4.0 mL). The reaction was carried out in a closed system equipped with a reflux condenser under air (1 atm, balloon), and the resulting mixture was stirred at 60 °C for 1 h. Upon completion of the reaction, the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel 60N (40–50 μm) using hexane/ethyl acetate (10:1 to 10:3) as the eluent to afford the desired product **3** as an orange solid.

2.2 General procedure for the synthesis of products 5

A reaction tube equipped with a magnetic stir bar was charged with *N*-arylbenzamide **4** (0.20 mmol), 2-diazo-1,3-indandione **2** (0.24 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $Cu(OAc)_2 \cdot H_2O$ (10 mol%), and CsOAc (2.0 equiv) in DCE (4.0 mL). The reaction was carried out in a closed system equipped with a reflux condenser under air (1 atm, balloon), and the mixture was stirred at 80 °C for 3 h. For *ortho*- and *meta*-substituted *N*-arylbenzamides, the reaction mixture was cooled to room temperature and the crude product was purified by column chromatography on silica gel 60N (40–50 μm) using hexane/ethyl acetate (10:1 to 10:3) as the eluent. For para-substituted substrates, after the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure. The crude residue was treated with MeOH (1–2 mL) followed by the addition of water to induce precipitation. The solidified indenoisoquinoline was

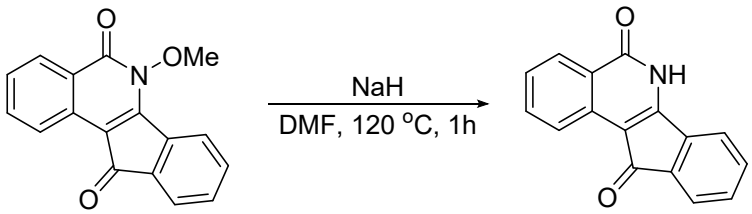
collected by filtration, washed with MeOH (1–2 mL), and dried to afford the desired product **5** as an orange solid.

2.3 General procedure for the synthesis of products 7

A reaction tube equipped with a magnetic stir bar was charged with *N*-*tert*-butylbenzamide **6** (0.20 mmol), 2-diazo-1,3-indandione **2** (0.24 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (10 mol%), and $Cu(OAc)_2 \cdot H_2O$ (20 mol%) in DCE (4.0 mL). The reaction was carried out in a closed system equipped with a reflux condenser under air (1 atm, balloon), and the resulting mixture was stirred at 110 °C for 2 h. After completion of the reaction, the mixture was cooled to room temperature, and the crude product was purified by column chromatography on silica gel 60N (40–50 μm) using hexane/ethyl acetate (20:1 to 10:1) as the eluent to afford the desired product 7 as a yellow solid.

3. Synthetic application

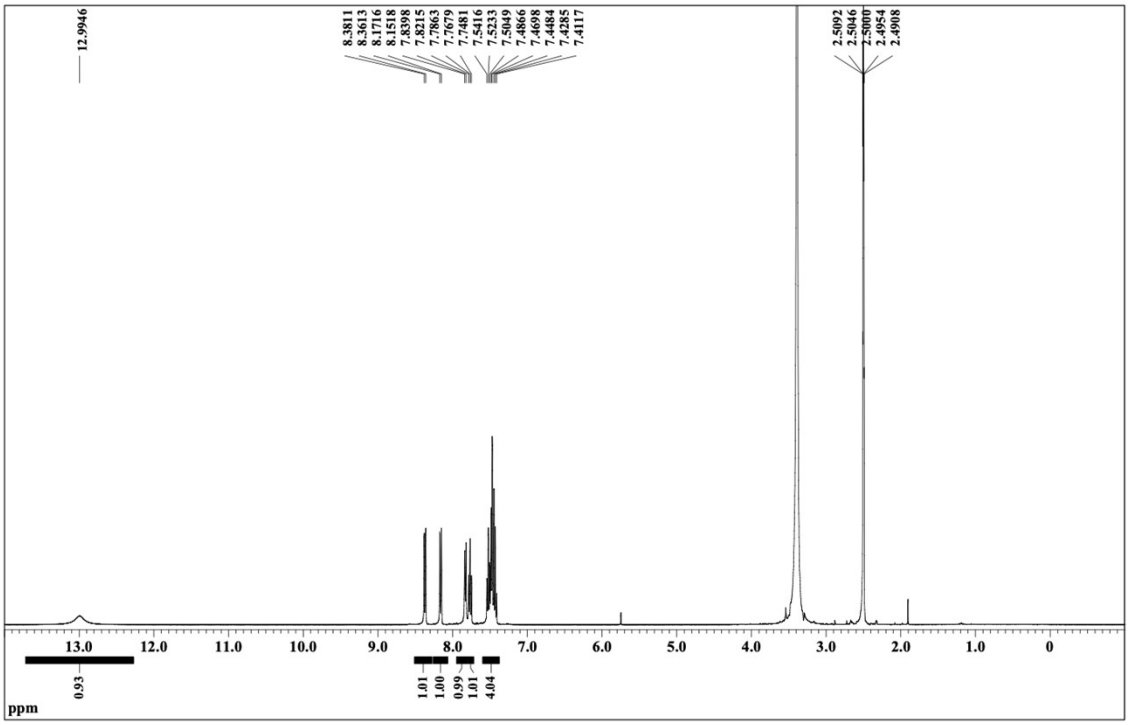
3.1 Deprotection of 3a[1a]



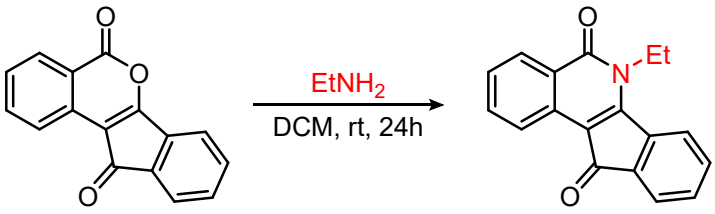
3a **8**, 72%

NaH (0.30 mmol) was added to a stirred solution of *N*-methoxyindeno[1,2-*c*]isoquinoline-5,11-dione **3a** (0.10 mmol) in DMF (0.5 mL). The reaction mixture was heated at 120 °C for 1 h under N_2 (1 atm, balloon) in a closed system equipped with a condenser, and then cooled to room temperature. Water (8 mL) was added, and the resulting mixture was extracted with DCM (3 × 5 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel 60N (40–50 μm) using hexane/ethyl acetate (10:1) as the eluent to afford the desired product **8** as a white solid (18 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.99 (s, 1H), 8.37 (d, J = 7.9 Hz, 1H), 8.16 (d, J = 7.9 Hz, 1H), 7.83 (d, J = 7.3 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.48 (m, 4H).



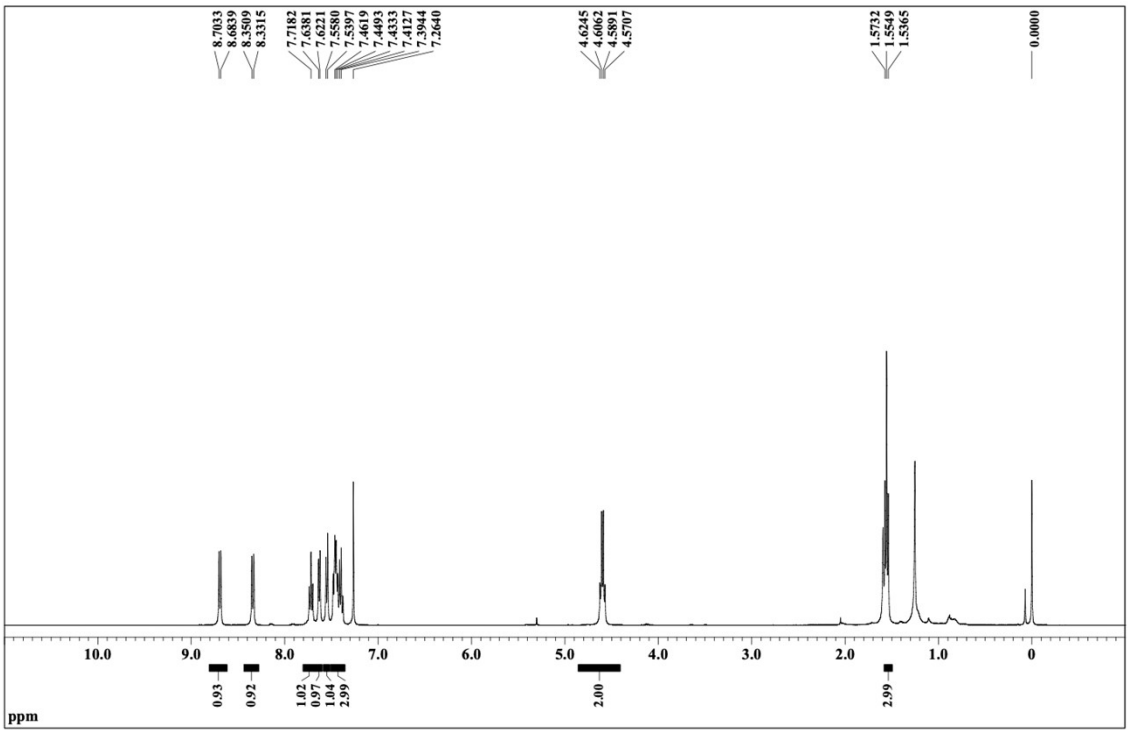
3.2 Transformation of 3a[3]



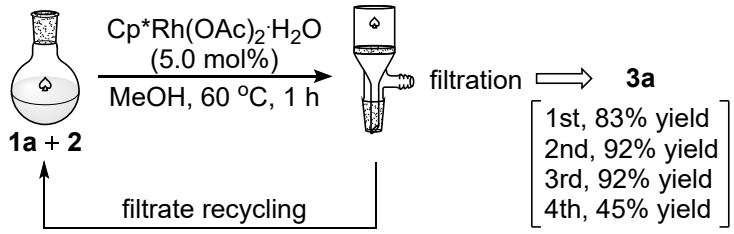
7a **9**, 69%

A reaction tube equipped with a magnetic stir bar was charged with indeno[1,2-*c*]isochromene-5,11-dione **7a** (0.10 mmol), ethylamine (0.11 mmol), and DCM (1.0 mL). The resulting mixture was stirred at room temperature for 24 h under air (1 atm, balloon). Upon completion of the reaction, the mixture was purified by column chromatography on silica gel 60N (40–50 μm) using hexane/ethyl acetate (10:1) as the eluent to afford the desired product **9** as an orange solid (19 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 7.8 Hz, 1H), 8.34 (d, J = 7.8 Hz, 1H), 7.72 (t, J = 7.3 Hz, 1H), 7.63 (d, J = 6.4 Hz, 1H), 7.55 (d, J = 7.3 Hz, 1H), 7.48-7.38 (m, 3H), 4.60 (q, J = 7.2 Hz, 2H), 1.56 (t, J = 7.2 Hz, 3H).



3.3 Recycling study of rhodium catalyst[4]



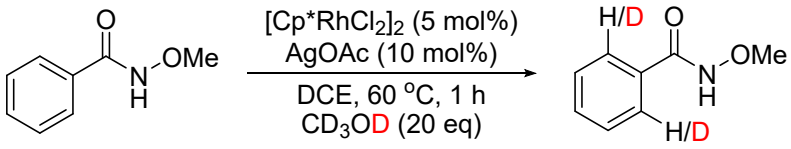
A reaction tube equipped with a magnetic stir bar was charged with **1a** (0.20 mmol), **2** (2-diazo-1,3-indandione, 0.24 mmol), Cp*Rh(OAc)$_2$·H$_2$O (5 mol%), and MeOH (2.0 mL). The reaction was carried out in a closed system equipped with a reflux condenser under air (1 atm, balloon), and the mixture was stirred at 60 °C for 1 h and then cooled to room temperature. The precipitated product **3a** was collected by filtration and washed with a minimal amount of cold MeOH. The methanolic filtrate containing the active rhodium species was retained.

For recycling runs, the retained filtrate was returned to the reaction tube, and **1a** (0.20 mmol) and **2** (0.24 mmol) were added. The reaction was repeated at 60 °C for 1 h under air (1 atm, balloon), followed by isolation of **3a** as above. This sequence was repeated without additional catalyst. The isolated yields of **3a** over successive cycles were 83%

(1st), 92% (2nd), 92% (3rd), and 45% (4th), demonstrating that Cp*Rh(OAc)$_2$·H$_2$O can be effectively reused for at least three cycles before a noticeable decline in activity.

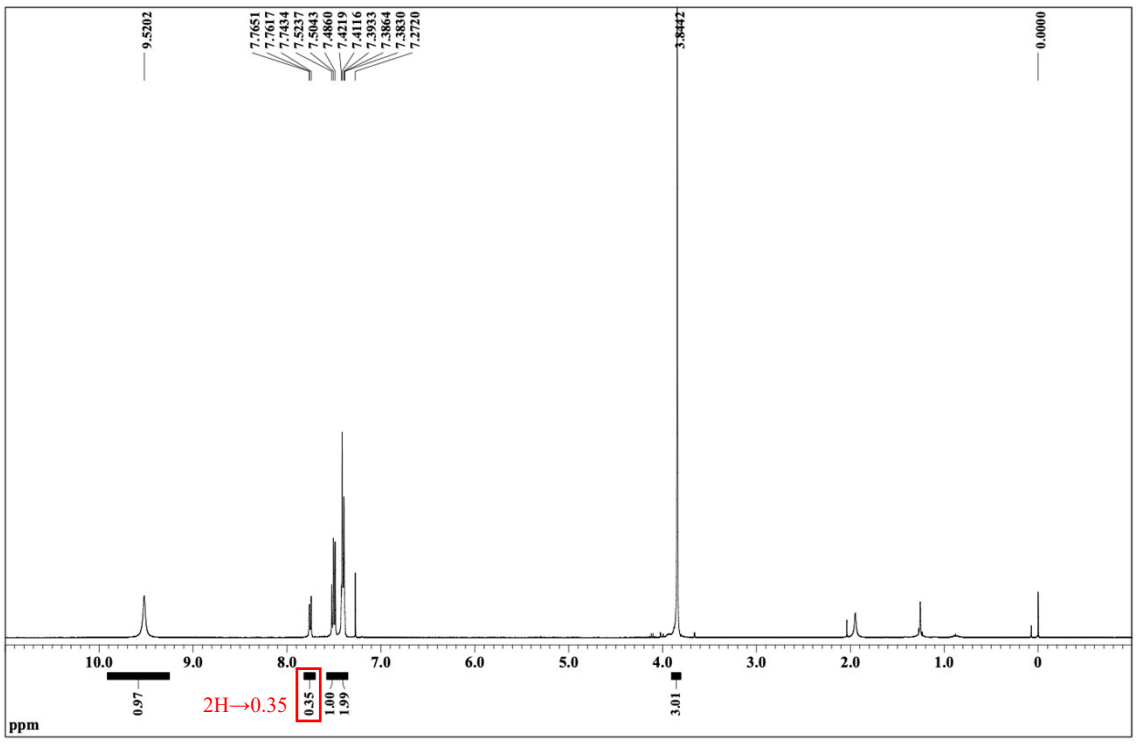
4. Mechanistic study

4.1 H/D exchange experiment

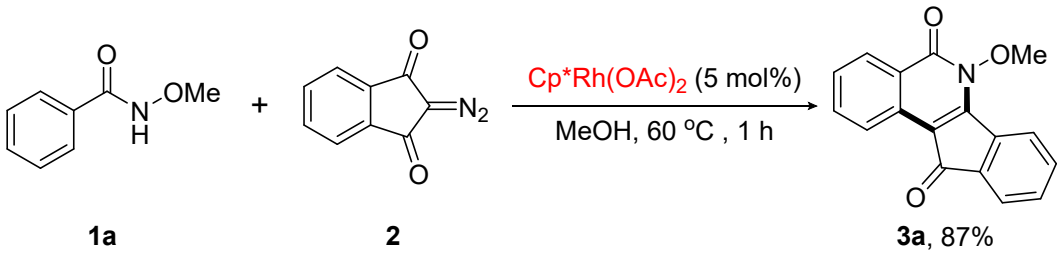


1a **H_D = 83%**

A reaction tube equipped with a magnetic stir bar was charged with *N*-methoxybenzamide **1a** (0.20 mmol), [Cp*RhCl$_2$]$_2$ (5 mol%), AgOAc (10 mol%), 1,2-dichloroethane (4.0 mL), and CD$_3$OD (4.0 mmol, 20 equiv). The resulting mixture was stirred at 60 °C for 1 h under air (1 atm, balloon) using a reflux condenser. Upon completion of the reaction, the mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel 60N (40–50 μm) using hexane/ethyl acetate (10:1 to 10:3) as the eluent to afford the deuterated product as a white solid.



4.2 Activity of a rhodium catalyst precusor closer to the real catalyst species

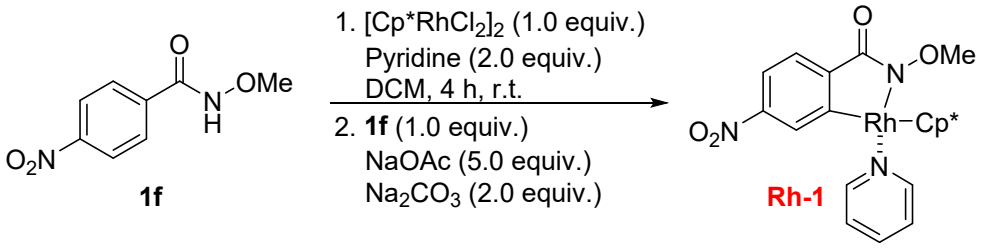


1a **2** **3a**, 87%

A reaction tube was charged with *N*-alkoxy benzamides **1a** (0.2 mmol), 2-diazo-1,3-indandione **2** (0.24 mmol), Cp*Rh(OAc)$_2$ (5 mol%), and MeOH (4 mL) with a magnetic stir bar. After that, the mixture was stirred at 60 ℃ for 1 h under air (1 atm, balloon) using a reflux condenser. After the reaction completed, the reaction mixture was cooled to room temperature, which were purified by column chromatograph (silica gel 60N, 40-50 μm), eluting with hexane/ethyl acetate (10:1 to 10:3). The product **3a** was obtained as white solids in 87% yields.

4.3 Reaction with rhodacyclic intermediates[5]

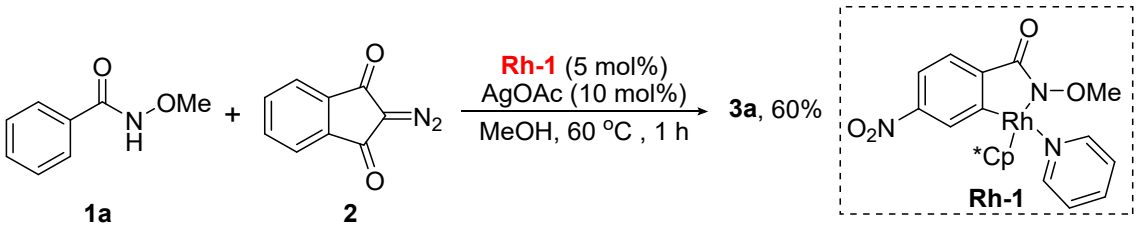
4.3.1 Preparation of rhodacyclic intermediates Rh-1



1f

A solution of [Cp*RhCl$_2$]$_2$ (0.20 mmol) in CH_2Cl_2 (2.0 mL) was placed in a reaction tube, and pyridine (0.40 mmol) was added. The mixture was stirred at room temperature for 4 h under air (1 atm, balloon) using a reflux condenser. Subsequently, *N*-methoxy-4-nitrobenzamide (**1f**, 0.20 mmol), NaOAc (1.0 mmol), and Na_2CO_3 (0.40 mmol) were added, and stirring was continued for 12 h. After completion of the reaction, the mixture was purified by column chromatography on silica gel 60N (40–50 μm) using CH_2Cl_2/MeOH (10:1) as the eluent. The desired rhodacyclic complex **Rh-1** was isolated as a red solid.

4.3.2 Reaction with rhodacyclic intermediates Rh-1

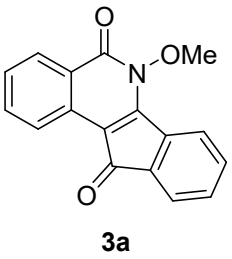


A reaction tube equipped with a magnetic stir bar was charged with *N*-methoxybenzamide **1a** (0.20 mmol), 2-diazo-1,3-indandione **2** (0.24 mmol), Rh-1 (5 mol%), AgOAc (10 mol%), and MeOH (4.0 mL). The resulting mixture was stirred at 60 °C for 1 h under air (1 atm, balloon) using a reflux condenser. Upon completion of the reaction, the mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel 60N (40–50 μm) using hexane/ethyl acetate (10:1 to 10:3) as the eluent to afford **3a** as a orange solid in 60% yield.

5. Analytic data and copies of NMR spectra

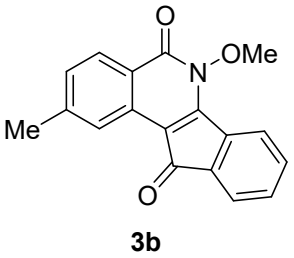
5.1 Analytic data for products

6-methoxy-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**3a**).



Yield: 92% (51 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 7.8 Hz, 1H), 8.32 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.73-7.68 (m, 2H), 7.57-7.55 (m, 1H), 7.46-7.42 (m, 2H), 7.40-7.34 (m, 1H), 4.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 159.4, 152.7, 135.3, 134.6, 133.9, 133.6, 131.8, 131.5, 128.2, 127.0, 125.1, 123.6, 123.2, 123.2, 106.8, 64.7. HRMS(ESI) m/z calcd for $C_{17}H_{12}NO_3$ $[M+H]^+$: 278.0812, found 278.0816.

6-methoxy-2-methyl-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**3b**).

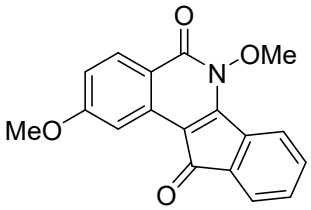


Yield: 93% (54 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (t, *J* = 0.9 Hz, 1H), 8.23 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 7.3 Hz, 1H), 7.59 (dd, *J* = 6.9, 0.9 Hz, 1H), 7.45 (td, *J* = 7.5, 1.4 Hz, 1H), 7.41-7.37 (m, 1H), 7.27 (dd, *J* = 7.8, 1.8 Hz, 1H), 4.27 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 159.4, 152.9, 145.1, 135.5, 134.7, 133.6, 131.9, 131.5,

128.7, 128.2, 123.4, 123.2, 123.2, 122.9, 106.8, 64.7, 22.1. HRMS(ESI) *m/z* calcd for $C_{18}H_{14}NO_3$ $[M+H]^+$: 292.0968, found 292.0970.

2,6-dimethoxy-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (3c).

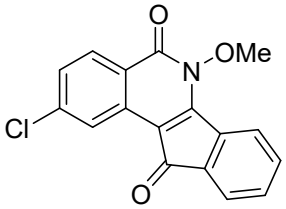
Yield: 93% (57 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 9.1 Hz, 1H), 8.00 (d, *J* = 2.7 Hz, 1H), 7.74 (d, *J* = 7.3 Hz, 1H), 7.58 (d, *J* = 6.9 Hz, 1H), 7.46 (t, *J* = 7.1 Hz, 1H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.00 (dd, *J* = 9.1, 2.3 Hz, 1H), 4.27 (s, 3H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 164.2, 159.0, 153.3, 135.3, 134.8, 134.0, 133.6, 131.6, 130.2, 123.3, 123.1, 118.7, 117.2, 106.4, 104.0, 64.8, 55.7. HRMS(ESI) *m/z* calcd for $C_{18}H_{14}NO_4$ $[M+H]^+$: 308.0917, found 308.0919.



3c

2-chloro-6-methoxy-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**3d**).

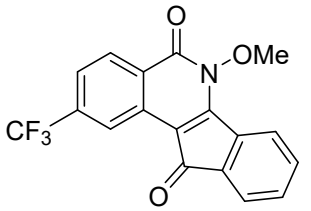
Yield: 82% (51 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 1.8 Hz, 1H), 8.27 (d, *J* = 8.7 Hz, 1H), 7.76 (d, *J* = 6.9 Hz, 1H), 7.62 (d, *J* = 6.4 Hz, 1H), 7.49-7.38 (m, 3H), 4.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 159.0, 153.7, 141.1, 135.0, 134.6, 133.8, 132.9, 132.0, 130.0, 127.6, 123.6, 123.5, 123.3, 123.1, 105.8, 64.8. HRMS(ESI) *m/z* calcd for $C_{17}H_{11}ClNO_3$ $[M+H]^+$: 312.0422, found 312.0424.



3d

6-methoxy-2-(trifluoromethyl)-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**3e**).

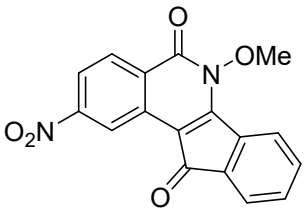
Yield: 92% (63 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.45 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 7.3 Hz, 1H), 7.64 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.61-7.58 (m, 1H), 7.49 (td, *J* = 7.5, 1.4 Hz, 1H), 7.44-7.40 (m, 1H), 4.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 158.8, 153.9, 135.6(q, $^2J_{C\text{-}F}$ = 32.6 Hz, 1C), 134.9, 134.5, 133.9, 132.1, 132.0, 129.4, 127.1, 123.7, 123.66, 123.5 (q, $^1J_{C\text{-}F}$ = 272.2 Hz, 1C), 123.0 (q, $^3J_{C\text{-}F}$ = 3.8 Hz, 1C), 121.1 (q, $^3J_{C\text{-}F}$ = 3.8 Hz, 1C), 106.3, 64.8. HRMS(ESI) *m/z* calcd for $C_{18}H_{11}F_3NO_3$ $[M+H]^+$: 346.0686, found 346.0688.



3e

6-methoxy-2-nitro-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (3f).

Yield: 85% (55 mg). Orange solid. ^{1}H NMR (400 MHz,

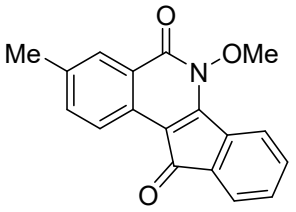


3f

$CDCl_3$, CF_3COOD) δ 9.39 (d, *J* = 2.3 Hz, 1H), 8.55 (d, *J* = 8.7 Hz, 1H), 8.24 (dd, *J* = 9.1, 2.3 Hz, 1H), 7.82 (d, *J* = 6.9 Hz, 1H), 7.69 (dd, *J* = 6.9, 0.9 Hz, 1H), 7.59-7.50 (m, 2H), 4.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, CF_3COOD) δ 189.7, 159.8, 154.3, 151.7, 134.8, 134.4, 134.0, 133.0, 132.6, 130.6, 127.7, 124.6, 124.3, 121.2, 119.2, 107.6, 65.4. HRMS(ESI) *m/z* calcd for $C_{17}H_{10}N_2NaO_5$ $[M+Na]^+$: 345.0482, found 345.0485.

6-methoxy-3-methyl-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**3ga**).

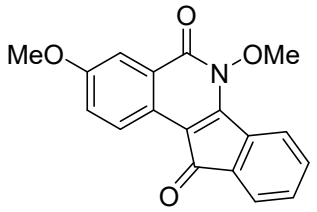
Yield: 80% (46 mg). Orange solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.2 Hz, 1H), 8.16 (d, *J* = 0.9 Hz, 1H), 7.72-7.71 (m, 1H), 7.58 (dd, *J* = 6.6, 1.1 Hz, 1H), 7.55 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.45 (td, *J* = 7.4, 1.2 Hz, 1H), 7.40-7.36 (m, 1H), 4.27 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 159.5, 152.0, 137.4, 135.7, 135.5, 134.6, 133.6, 131.3, 129.5, 127.9, 125.2, 123.6, 123.3, 123.0, 107.2, 64.7, 21.5. HRMS(ESI) *m/z* calcd for $C_{18}H_{14}NO_3$ $[M+H]^+$: 292.0968, found 292.0969.



3ga

3,6-dimethoxy-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**3ha**).

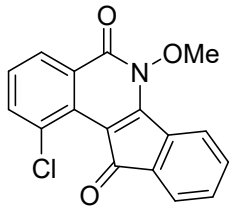
Yield: 61% (37 mg). Orange solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.7 Hz, 1H), 7.74 (d, *J* = 2.7 Hz, 1H), 7.68 (d, *J* = 7.3 Hz, 1H), 7.56 (dd, *J* = 6.4, 0.9 Hz, 1H), 7.43 (td, *J* = 7.5, 1.2 Hz, 1H), 7.37-7.32 (m, 2H), 4.27 (s, 3H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 159.2, 158.8, 150.5, 135.8, 134.5, 133.7, 131.1, 126.7, 125.9, 125.3, 124.5, 123.3, 122.7, 108.3, 107.3, 64.7, 55.7. HRMS(ESI) *m/z* calcd for $C_{18}H_{14}NO_4$ $[M+H]^+$: 308.0917, found 308.0919.



3ha

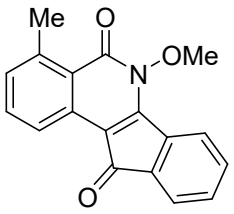
1-chloro-6-methoxy-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**3ib**).

Yield: 78% (49 mg). Orange solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.82 (dd, *J* = 6.6, 1.1 Hz, 1H), 7.77 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.65-7.63 (m, 1H), 7.52-7.44 (m, 2H), 7.39 (t, *J* = 7.8 Hz, 1H), 4.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 158.6, 154.3, 136.6, 134.2, 134.0, 133.5, 132.1, 131.1, 130.3, 127.9, 127.5, 127.4, 123.5, 123.5, 107.5, 64.7. HRMS(ESI) *m/z* calcd for $C_{17}H_{11}ClNO_3$ $[M+H]^+$: 312.0422, found 312.0424.



3ib

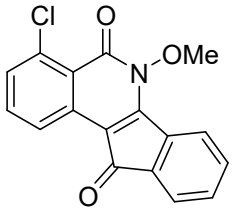
6-methoxy-4-methyl-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**3j**).



3j

Yield: 69% (40 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.0 Hz, 1H), 7.71-7.69 (m, 1H), 7.56-7.51 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 4.25 (s, 3H), 2.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 159.8, 152.8, 142.6, 135.2, 135.0, 133.5, 133.5, 133.3, 131.5, 130.2, 123.3, 123.2, 123.1, 121.6, 106.4, 64.5, 23.7. HRMS(ESI) *m/z* calcd for $C_{18}H_{14}NO_3$ $[M+H]^+$: 292.0968, found 292.0969.

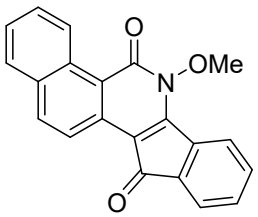
4-chloro-6-methoxy-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**3k**).



3k

Yield: 66% (41 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.75 (d, *J* = 6.9 Hz, 1H), 7.61 (dd, *J* = 6.7, 1.0 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.51-7.42 (m, 3H), 4.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 157.5, 153.5, 136.1, 135.0, 134.8, 134.8, 133.8, 133.7, 132.0, 130.2, 123.6, 123.5, 122.5, 121.2, 105.5, 64.7. HRMS(ESI) *m/z* calcd for $C_{17}H_{11}ClNO_3$ $[M+H]^+$: 312.0422, found 312.0423.

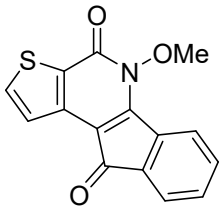
8-methoxy-7*H*-benzo[*h*]indeno[1,2-*c*]isoquinoline-7,13(8*H*)-dione (**3l**).



3l

Yield: 68% (45 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (d, *J* = 8.7 Hz, 1H), 8.77 (d, *J* = 9.1 Hz, 1H), 8.07 (d, *J* = 9.1 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.3 Hz, 1H), 7.75-7.71 (m, 1H), 7.64-7.57 (m, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 7.3 Hz, 1H), 4.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 159.4, 153.0, 135.7, 135.3, 135.0, 134.5, 133.8, 132.1, 131.9, 131.9, 129.1, 128.7, 126.8, 126.5, 123.5, 123.5, 120.7, 118.1, 106.5, 64.7. HRMS(ESI) *m/z* calcd for $C_{21}H_{13}NNaO_3$ $[M+Na]^+$: 350.0788, found 350.0787.

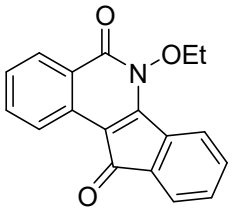
5-methoxy-4*H*-indeno[1,2-*b*]thieno[3,2-*d*]pyridine-4,10(5*H*)-dione (**3m**).



3m

Yield: 88% (50 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 6.9, 5.0 Hz, 2H), 7.75 (d, *J* = 6.9 Hz, 1H), 7.61 (d, *J* = 7.3 Hz, 1H), 7.50-7.46 (m, 1H), 7.41 (t, *J* = 7.3 Hz, 1H), 4.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9, 155.5, 153.0, 139.4, 136.7, 135.8, 134.2, 133.9, 131.6, 129.3, 123.7, 123.1, 122.7, 107.5, 65.0. HRMS(ESI) *m/z* calcd for $C_{15}H_{10}NO_3S$ $[M+H]^+$: 284.0376, found 284.0377.

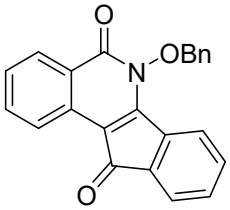
6-ethoxy-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**3n**).



3n

Yield: 90% (52 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.2 Hz, 1H), 8.30 (d, *J* = 7.3 Hz, 1H), 7.73-7.67 (m, 2H), 7.54 (d, *J* = 6.9 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.38-7.34 (m, 1H), 4.51 (q, *J* = 7.0 Hz, 2H), 1.55 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.5, 159.6, 153.2, 135.6, 134.7, 133.9, 133.5, 131.8, 131.4, 128.3, 126.9, 125.1, 123.6, 123.2, 123.2, 106.8, 73.0, 13.4. HRMS(ESI) *m/z* calcd for $C_{18}H_{14}NO_3$ $[M+H]^+$: 292.0968, found 292.0971.

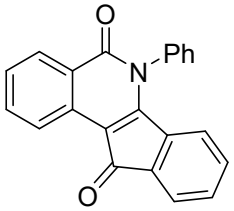
6-(benzyloxy)-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**3o**).



3o

Yield: 93% (65 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 7.8 Hz, 1H), 8.37-8.35 (m, 1H), 7.73-7.71 (m, 1H), 7.70-7.67 (m, 1H), 7.62-7.59 (m, 2H), 7.54-7.52 (m, 1H), 7.46 (td, *J* = 7.7, 1.1 Hz, 1H), 7.43-7.41 (m, 3H), 7.37-7.31 (m, 2H), 5.42 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.5, 159.6, 153.2, 135.5, 134.6, 134.0, 133.4, 132.9, 131.9, 131.4, 130.1, 130.1, 129.7, 128.9, 128.9, 128.3, 127.0, 125.1, 123.7, 123.5, 123.1, 106.8, 79.0. HRMS(ESI) *m/z* calcd for $C_{23}H_{16}NO_3$ $[M+H]^+$: 354.1125, found 354.1125.

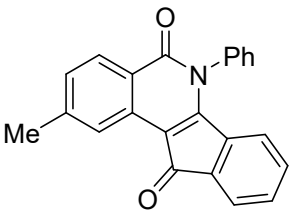
6-phenyl-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**5a**).



5a

Yield: 90% (58 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 7.8 Hz, 1H), 8.35 (d, *J* = 8.2 Hz, 1H), 7.78-7.74 (m, 1H), 7.67-7.62 (m, 3H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.50-7.43 (m, 3H), 7.24-7.20 (m, 1H), 7.00-6.97 (m, 1H), 5.48 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 163.6, 155.3, 137.4, 137.1, 134.7, 134.2, 132.7, 132.7, 130.7, 130.1, 128.7, 128.6, 127.3, 124.0, 123.7, 122.7, 122.4, 108.2. HRMS(ESI) *m/z* calcd for $C_{22}H_{14}NO_2$ $[M+H]^+$: 324.1025, found 324.1026.

2-methyl-6-phenyl-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**5b**).

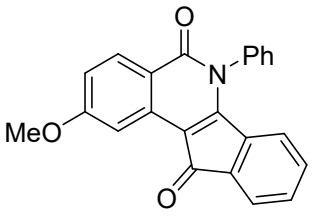


5b

Yield: 92% (62 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 7.66-7.60 (m, 3H), 7.54 (dd, *J* = 6.4, 1.4 Hz, 1H), 7.47-7.41 (m, 2H), 7.30 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.22 (td, *J* = 7.5, 0.9 Hz, 1H), 6.98 (td, *J* = 7.7, 1.2 Hz, 1H), 5.47 (d, *J* = 7.3 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 163.5, 155.5, 145.3, 137.5,

137.2, 134.8, 132.8, 132.6, 130.6, 130.0, 128.9, 128.7, 123.4, 122.7, 122.3, 121.8, 108.1, 22.2. HRMS(ESI) *m/z* calcd for $C_{23}H_{16}NO_2$ $[M+H]^+$: 338.1176, found 338.1179.

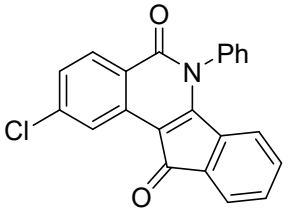
2-methoxy-6-phenyl-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**5c**).



5c

Yield: 92% (65 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.7 Hz, 1H), 8.13 (d, *J* = 2.7 Hz, 1H), 7.67-7.60 (m, 3H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.47-7.42 (m, 2H), 7.24-7.20 (m, 1H), 7.03-6.97 (m, 2H), 5.49 (d, *J* = 7.3 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 164.4, 163.1, 156.0, 137.5, 137.0, 134.9, 134.9, 132.6, 130.7, 130.7, 130.0, 128.7, 122.6, 122.5, 117.6, 117.3, 107.8, 104.1, 55.7. HRMS(ESI) *m/z* calcd for $C_{23}H_{16}NO_3$ $[M+H]^+$: 354.1125, found 354.1125.

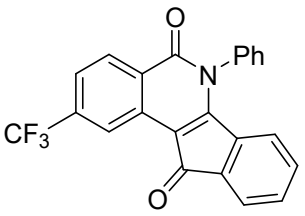
2-chloro-6-phenyl-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (5d).



5d

Yield: 91% (65 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 2.3 Hz, 1H), 8.28 (d, *J* = 8.7 Hz, 1H), 7.68-7.63 (m, 3H), 7.57 (d, *J* = 6.9 Hz, 1H), 7.46-7.41 (m, 3H), 7.28-7.24 (m, 1H), 7.01 (td, *J* = 7.7, 1.2 Hz, 1H), 5.51 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 163.1, 156.3, 141.2, 137.2, 136.7, 134.7, 133.8, 132.8, 131.1, 130.4, 130.3, 130.2, 128.6, 127.8, 123.1, 123.0, 122.7, 122.3, 107.1. HRMS(ESI) *m/z* calcd for $C_{22}H_{12}ClNNaO_2$ $[M+Na]^+$: 380.0449, found 380.0453.

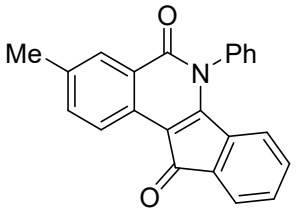
6-phenyl-2-(trifluoromethyl)-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**5e**).



5e

Yield: 89% (70 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.45 (d, *J* = 8.2 Hz, 1H), 7.70-7.64 (m, 4H), 7.53 (d, *J* = 6.9 Hz, 1H), 7.50-7.44 (m, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.00 (td, *J* = 7.8, 0.9 Hz, 1H), 5.52 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 162.9, 156.4, 137.0, 136.6, 135.6 (q, $^2J_{C\text{-}F}$ = 32.6 Hz, 1C), 134.5, 132.9, 132.9, 131.2, 130.4, 130.3, 129.7, 128.5, 126.0, 123.6 (q, $^1J_{C\text{-}F}$ = 272.2 Hz, 1C), 123.1 (q, $^3J_{C\text{-}F}$ = 3.8 Hz, 1C), 123.0, 122.8, 121.0 (q, $^3J_{C\text{-}F}$ = 3.8 Hz, 1C), 107.5. HRMS(ESI) *m/z* calcd for $C_{23}H_{13}F_3NO_2$ $[M+H]^+$: 392.0893, found 392.0897.

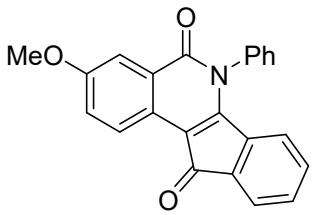
3-methyl-6-phenyl-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**5f**).



5f

Yield: 73% (50 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.2 Hz, 1H), 8.13 (s, 1H), 7.65-7.62 (m, 3H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 7.3 Hz, 1H), 7.46-7.43 (m, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 5.44 (d, *J* = 7.8 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 163.5, 154.5, 137.6, 137.5, 137.3, 135.6, 134.7, 132.6, 130.4, 130.3, 130.0, 128.7, 128.3, 124.0, 123.6, 122.6, 122.1, 108.4, 21.6. HRMS(ESI) *m/z* calcd for $C_{23}H_{16}NO_2$ $[M+H]^+$: 338.1176, found 338.1177.

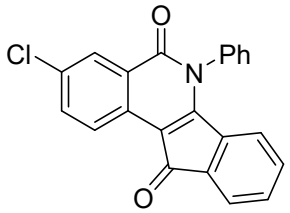
3-methoxy-6-phenyl-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**5g**).



5g

Yield: 31% (22 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.7 Hz, 1H), 7.75 (d, *J* = 2.7 Hz, 1H), 7.66-7.61 (m, 3H), 7.49 (d, *J* = 7.3 Hz, 1H), 7.46-7.44 (m, 2H), 7.37 (dd, *J* = 8.7, 2.7 Hz, 1H), 7.19-7.15 (m, 1H), 6.96 (td, *J* = 7.7, 1.1 Hz, 1H), 5.43 (d, *J* = 7.3 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 163.3, 159.0, 153.1, 137.6, 137.5, 134.6, 132.7, 130.2, 130.0, 128.6, 126.7, 125.5, 125.3, 124.3, 122.7, 121.9, 108.9, 108.6, 55.6. HRMS(ESI) *m/z* calcd for $C_{23}H_{16}NO_3$ $[M+H]^+$: 354.1125, found 354.1126.

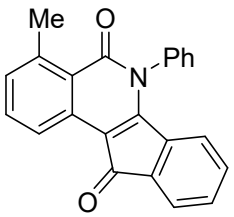
3-chloro-6-phenyl-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**5h**).



5h

Yield: 71% (51 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.7 Hz, 1H), 8.28 (d, *J* = 1.8 Hz, 1H), 7.70-7.63 (m, 4H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.47-7.44 (m, 2H), 7.23-7.19 (m, 1H), 6.99 (td, *J* = 7.8, 1.4 Hz, 1H), 5.47 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 162.5, 155.3, 137.2, 136.8, 134.5, 133.2, 132.8, 131.0, 130.9, 130.3, 130.2, 128.5, 128.1, 125.2, 122.9, 122.5, 107.6. HRMS(ESI) *m/z* calcd for $C_{22}H_{12}ClNNaO_2$ $[M+Na]^+$: 380.0449, found 380.0455.

4-methyl-6-phenyl-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**5i**).

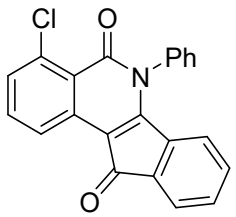


5i

Yield: 71% (48 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 7.8 Hz, 1H), 7.67-7.63 (m, 3H), 7.62-7.58 (m, 1H), 7.52 (d, *J* = 6.9 Hz, 1H), 7.47-7.42 (m, 2H), 7.25-7.19 (m, 2H), 6.98 (td,

J = 7.7, 1.2 Hz, 1H), 5.46 (d, *J* = 7.8 Hz, 1H), 2.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 164.1, 155.4, 142.8, 137.7, 136.8, 135.1, 134.5, 133.5, 132.5, 130.7, 130.5, 130.1, 129.9, 128.8, 122.7, 122.3, 122.2, 121.7, 108.0, 24.0. HRMS(ESI) *m/z* calcd for $C_{23}H_{16}NO_2$ $[M+H]^+$: 338.1176, found 338.1179.

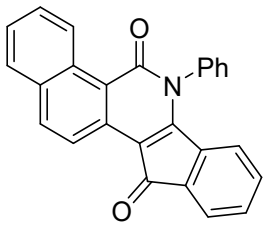
4-chloro-6-phenyl-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**5j**).



5j

Yield: 65% (47 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 7.3 Hz, 1H), 7.67-7.62 (m, 3H), 7.61-7.56 (m, 1H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.46-7.44 (m, 3H), 7.26-7.21 (m, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 5.49 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 161.6, 156.0, 137.2, 136.4, 135.9, 134.9, 134.0, 132.8, 131.1, 130.4, 130.1, 130.1, 128.7, 122.9, 122.7, 122.5, 120.3, 107.0. HRMS(ESI) *m/z* calcd for $C_{22}H_{13}ClNO_2$ $[M+H]^+$: 358.0629, found 358.0633.

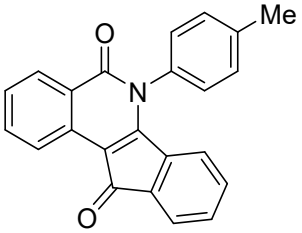
8-phenyl-7*H*-benzo[*h*]indeno[1,2-*c*]isoquinoline-7,13(8*H*)-dione (5k).



5k

Yield: 72% (54 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (d, *J* = 8.7 Hz, 1H), 8.90 (d, *J* = 8.7 Hz, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.71-7.68 (m, 3H), 7.67-7.63 (m, 1H), 7.58-7.51 (m, 2H), 7.52-7.49 (m, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.01 (td, *J* = 7.7, 1.1 Hz, 1H), 5.53 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 163.6, 155.8, 137.9, 136.6, 136.0, 135.6, 135.3, 132.8, 132.4, 131.9, 131.1, 130.2, 130.1, 129.0, 128.7, 128.6, 126.7, 126.6, 123.0, 122.5, 120.8, 117.0, 108.0. HRMS(ESI) *m/z* calcd for $C_{26}H_{16}NO_2$ $[M+H]^+$: 374.1176, found 374.1178.

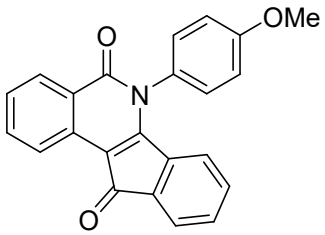
6-(*p*-tolyl)-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (5l).



5l

Yield: 81% (55 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.2 Hz, 1H), 8.33 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.75-7.71 (m, 1H), 7.51 (d, *J* = 6.4 Hz, 1H), 7.47-7.42 (m, 3H), 7.33- 7.30 (m, 2H), 7.23-7.19 (m, 1H), 7.00 (td, *J* = 7.7, 1.2 Hz, 1H), 5.58 (d, *J* = 7.8 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 163.7, 155.5, 140.2, 137.2, 134.8, 134.7, 134.1, 132.7, 132.6, 130.7, 130.6, 128.7, 128.3, 127.1, 124.0, 123.6, 122.7, 122.5, 108.0, 21.5. HRMS(ESI) *m/z* calcd for $C_{23}H_{16}NO_2$ $[M+H]^+$: 338.1176, found 338.1178.

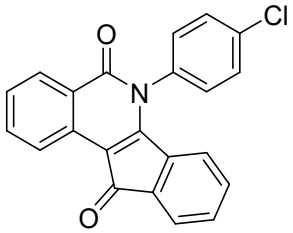
6-(4-methoxyphenyl)-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**5m**).



5m

Yield: 88% (62 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 7.8 Hz, 1H), 8.35-8.33 (m, 1H), 7.75 (td, *J* = 7.5, 1.4 Hz, 1H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.49-7.44 (m, 1H), 7.36-7.35 (m, 1H), 7.34-7.32 (m, 1H), 7.25-7.21 (m, 1H), 7.15-7.13 (m, 1H), 7.12-7.11 (m, 1H), 7.04 (td, *J* = 7.7, 1.2 Hz, 1H), 5.65 (d, *J* = 7.3 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 163.9, 160.5, 155.7, 137.2, 134.8, 134.1, 132.7, 130.7, 129.9, 129.6, 128.7, 127.2, 124.0, 123.6, 122.7, 122.5, 115.2, 108.1, 55.7. HRMS(ESI) *m/z* calcd for $C_{23}H_{16}NO_3$ $[M+H]^+$: 354.1125, found 354.1127.

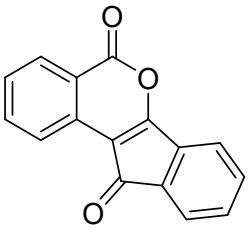
6-(4-chlorophenyl)-5*H*-indeno[1,2-*c*]isoquinoline-5,11(6*H*)-dione (**5n**).



5n

Yield: 89% (64 mg). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 7.8 Hz, 1H), 8.32 (d, *J* = 8.7 Hz, 1H), 7.77-7.73 (m, 1H), 7.64-7.63 (m, 1H), 7.62-7.60 (m, 1H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.47 (td, *J* = 7.7, 1.1 Hz, 1H), 7.42-7.41 (m, 1H), 7.40-7.39 (m, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.06 (td, *J* = 7.7, 1.1 Hz, 1H), 5.65 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 163.5, 154.9, 136.9, 136.2, 135.9, 134.6, 134.3, 132.8, 132.6, 130.9, 130.3, 130.1, 128.7, 127.4, 123.9, 123.7, 122.9, 122.2, 108.4; HRMS(ESI) *m/z* calcd for $C_{22}H_{13}ClNO_2$ $[M+H]^+$ 358.0629, found 358.0633.

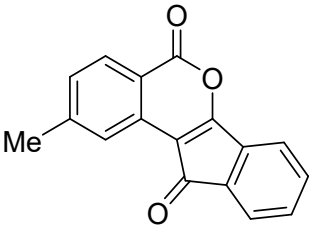
Indeno[1,2-*c*]isochromene-5,11-dione (7a)



7a

Yield: 82% (41 mg). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.8 Hz, 1H), 8.29 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.80 (td, *J* = 7.5, 1.4 Hz, 1H), 7.58 (dd, *J* = 5.9, 0.9 Hz, 1H), 7.53-7.44 (m, 3H), 7.41 (td, *J* = 6.9, 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 170.6, 160.8, 136.3, 136.0, 133.7, 132.8, 132.6, 131.6, 130.9, 128.4, 123.3, 123.1, 119.8, 118.9, 107.7. HRMS(ESI) *m/z* calcd for $C_{16}H_9O_3$ $[M+H]^+$: 249.0546, found 249.0549.

2-methylindeno[1,2-*c*]isochromene-5,11-dione (7b)

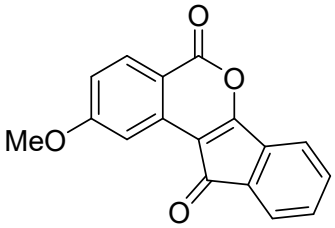


7b

Yield: 76% (40 mg). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.7 Hz, 2H), 7.57 (d, *J* = 6.9 Hz, 1H), 7.47-7.37 (m, 3H), 7.31 (dd, *J* = 8.2, 1.4 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 170.7, 160.8,

147.6, 136.4, 133.6, 132.8, 132.6, 131.5, 130.8, 129.7, 123.2, 123.1, 119.7, 116.4, 107.6, 22.2. HRMS(ESI) *m/z* calcd for $C_{17}H_{11}O_3$ $[M+H]^+$: 263.0703, found 263.0705.

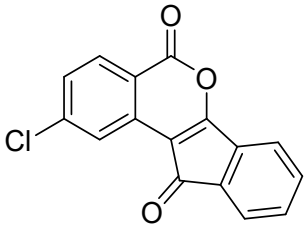
2-methoxyindeno[1,2-*c*]isochromene-5,11-dione (7c)



7c

Yield: 70% (39 mg). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.7 Hz, 1H), 7.76 (d, *J* = 2.7 Hz, 1H), 7.57 (d, *J* = 6.9 Hz, 1H), 7.50-7.39 (m, 3H), 7.01 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 171.4, 165.7, 160.5, 136.3, 135.0, 133.6, 133.0, 132.9, 131.7, 123.0, 119.9, 117.3, 111.6, 107.5, 105.0, 55.9. HRMS(ESI) *m/z* calcd for $C_{17}H_{11}O_4$ $[M+H]^+$: 279.0652, found 279.0653.

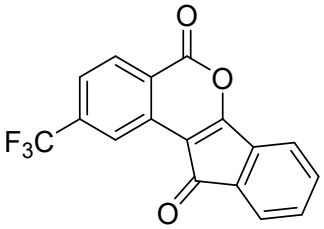
2-chloroindeno[1,2-*c*]isochromene-5,11-dione (7d)



7d

Yield: 66% (37 mg). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, CF_3COOD) δ 8.33 (d, *J* = 1.8 Hz, 1H), 8.25 (d, *J* = 8.7 Hz, 1H), 7.65-7.63 (m, 1H), 7.57-7.52 (m, 2H), 7.50-7.46 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, CF_3COOD) δ 191.9, 172.2, 162.6, 144.7, 135.8, 134.9, 134.0, 132.9, 132.8, 132.4, 129.8, 124.4, 123.3, 121.0, 116.6, 107.6. HRMS(ESI) *m/z* calcd for $C_{16}H_8ClO_3$ $[M+H]^+$: 283.0156, found 283.0157.

2-(trifluoromethyl)indeno[1,2-*c*]isochromene-5,11-dione (7e)

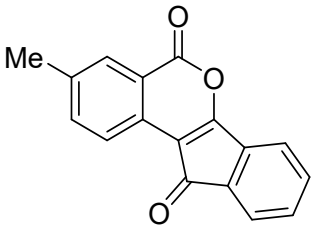


7e

Yield: 55% (35 mg). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.40 (d, *J* = 8.2 Hz, 1H), 7.72 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.63 (d, *J* = 6.9 Hz, 1H), 7.54-7.44 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 171.5, 159.7, 137.4 (q, $^2J_{C\text{-}F}$ = 32.6 Hz, 1C), 135.8, 133.9, 133.1, 132.6, 132.3, 131.7, 124.5 (q, $^3J_{C\text{-}F}$ = 3.8 Hz, 1C), 123.5, 123.1 (q, $^1J_{C\text{-}F}$ = 272.2 Hz, 1C), 121.3, 120.5 (q, $^3J_{C\text{-}F}$ = 3.8 Hz, 1C), 120.3, 106.9. HRMS(ESI) *m/z* calcd for $C_{17}H_7F_3NaO_3$ $[M+Na]^+$: 339.0239, found 339.0239.

3-methylindeno[1,2-*c*]isochromene-5,11-dione (7f)

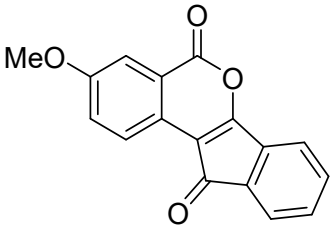
Yield: 71% (37 mg). yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, CF_3COOD) δ 8.23 (d, *J* = 8.2 Hz, 1H), 8.11 (s, 1H), 7.67 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.49 (td, *J* = 7.4, 1.1 Hz, 1H), 7.43-7.39 (m, 2H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, CF_3COOD) δ 191.8, 170.1, 162.8, 139.5, 138.1, 136.2, 134.3, 132.4, 131.9, 130.8, 130.1, 123.8, 123.3, 120.1, 118.4, 108.4, 21.6. HRMS(ESI) *m/z* calcd for $C_{17}H_{11}O_3$ $[M+H]^+$: 263.0703, found 263.0706.



7f

3-methoxyindeno[1,2-*c*]isochromene-5,11-dione (7g)

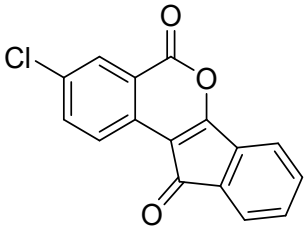
Yield: 15% (8 mg). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 9.1 Hz, 1H), 7.70 (d, *J* = 2.7 Hz, 1H), 7.55 (d, *J* = 7.3 Hz, 1H), 7.47-7.34 (m, 4H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 168.4, 161.0, 159.6, 136.7, 133.7, 132.6, 131.1, 126.3, 125.3, 124.9, 123.1, 120.4, 119.3, 111.8, 108.0, 55.8. HRMS(ESI) *m/z* calcd for $C_{17}H_{11}O_4$ $[M+H]^+$: 279.0652, found 279.0656.



7g

3-chloroindeno[1,2-*c*]isochromene-5,11-dione (7h)

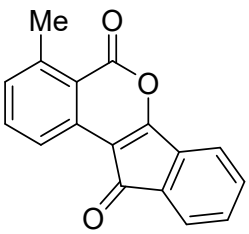
Yield: 31% (18 mg). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, CF_3COOD) δ 8.30 (d, *J* = 8.7 Hz, 1H), 8.28 (d, *J* = 2.3 Hz, 1H), 7.81 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.61 (dd, *J* = 6.6, 1.6 Hz, 1H), 7.55-7.51 (m, 1H), 7.47-7.43 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, CF_3COOD) δ 191.7, 171.1, 161.5, 137.3, 135.9, 135.0, 134.7, 132.5, 132.3, 131.0, 130.6, 124.9, 124.2, 120.6, 119.8, 107.8. HRMS(ESI) *m/z* calcd for $C_{16}H_8ClO_3$ $[M+H]^+$: 283.0156, found 283.0159.



7h

4-methylindeno[1,2-*c*]isochromene-5,11-dione (7i)

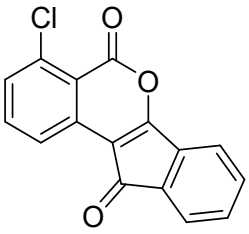
Yield: 46% (24 mg). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 6.9 Hz, 1H), 7.48-7.37 (m, 3H), 7.30 (d, *J* = 7.3 Hz, 1H), 2.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 170.6, 159.8, 144.7, 136.2, 135.2, 134.0, 133.5, 133.1, 131.5, 131.4, 123.0, 121.2, 119.7, 117.1, 107.6, 23.5. HRMS(ESI) *m/z* calcd for $C_{17}H_{11}O_3$ $[M+H]^+$:



7i

263.0703, found 263.0706.

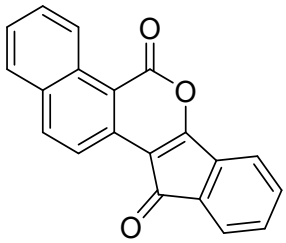
4-chloroindeno[1,2-*c*]isochromene-5,11-dione (7j)



7j

Yield: 48% (27 mg). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, CF_3COOD) δ 8.34 (d, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.60-7.54 (m, 2H), 7.51-7.43 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, CF_3COOD) δ 191.6, 171.7, 158.9, 138.7, 136.7, 135.6, 135.5, 134.6, 132.7, 132.6, 131.9, 124.1, 122.0, 120.8, 115.5, 107.4. HRMS(ESI) *m/z* calcd for $C_{16}H_8ClO_3$ $[M+H]^+$: 283.0156, found 283.0160.

Benzo[h]indeno[1,2-*c*]isochromene-7,13-dione (7k)

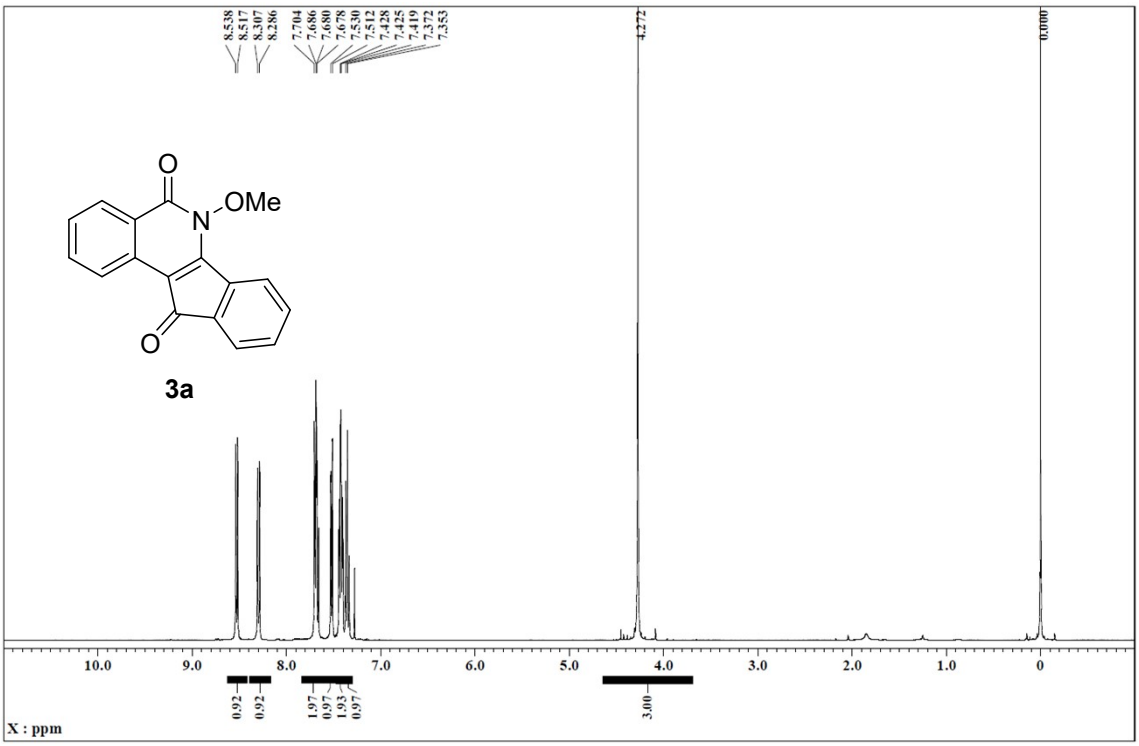


7k

Yield: 15% (9 mg). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, CF_3COOD) δ 9.47 (d, *J* = 8.7 Hz, 1H), 8.45 (d, *J* = 8.7 Hz, 1H), 8.23 (d, *J* = 8.7 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.80-7.76 (m, 1H), 7.65-7.61 (m, 2H), 7.56-7.44 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, CF_3COOD) δ 191.7, 172.3, 162.0, 139.1, 136.4, 135.7, 134.7, 133.1, 133.0, 132.7, 131.8, 130.6, 129.6, 127.7, 126.0, 124.1, 120.7, 119.9, 111.5, 108.6. HRMS(ESI) *m/z* calcd for $C_{20}H_{11}O_3$ $[M+H]^+$: 299.0703, found 299.0704.

5.2 Copies of NMR spectra

Figure S1. The ^{1}H and ^{13}C NMR Spectra of **3a**



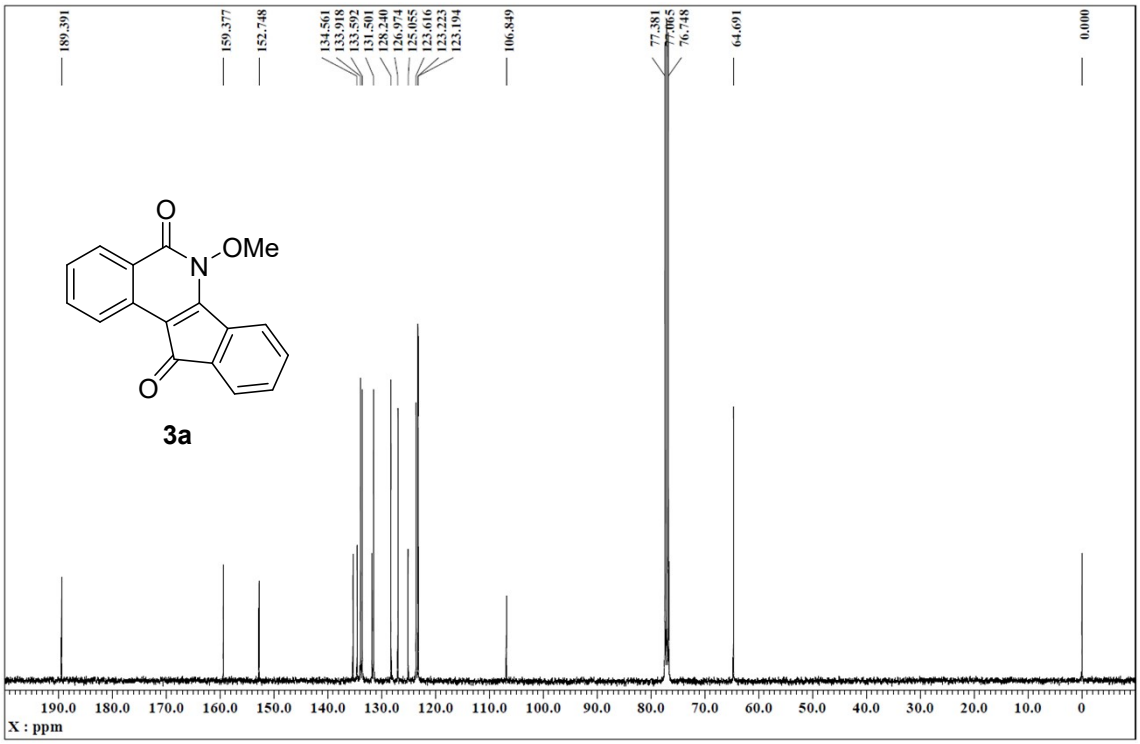
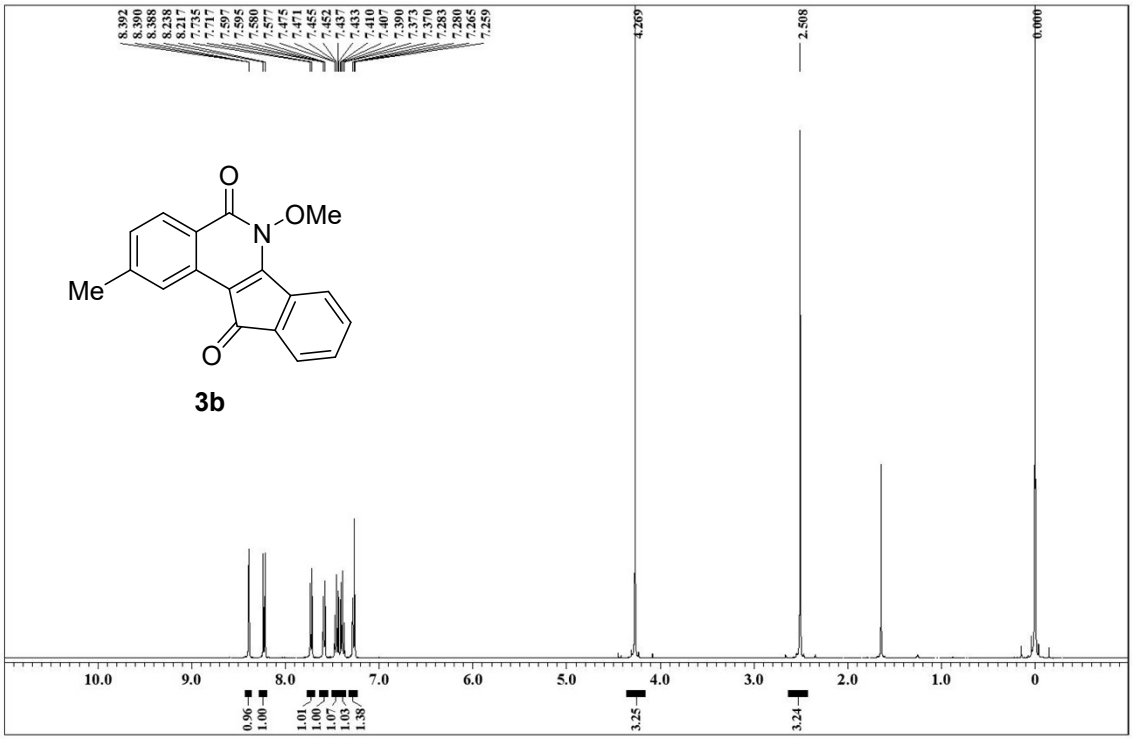


Figure S2. The ^{1}H and ^{13}C NMR Spectra of **3b**



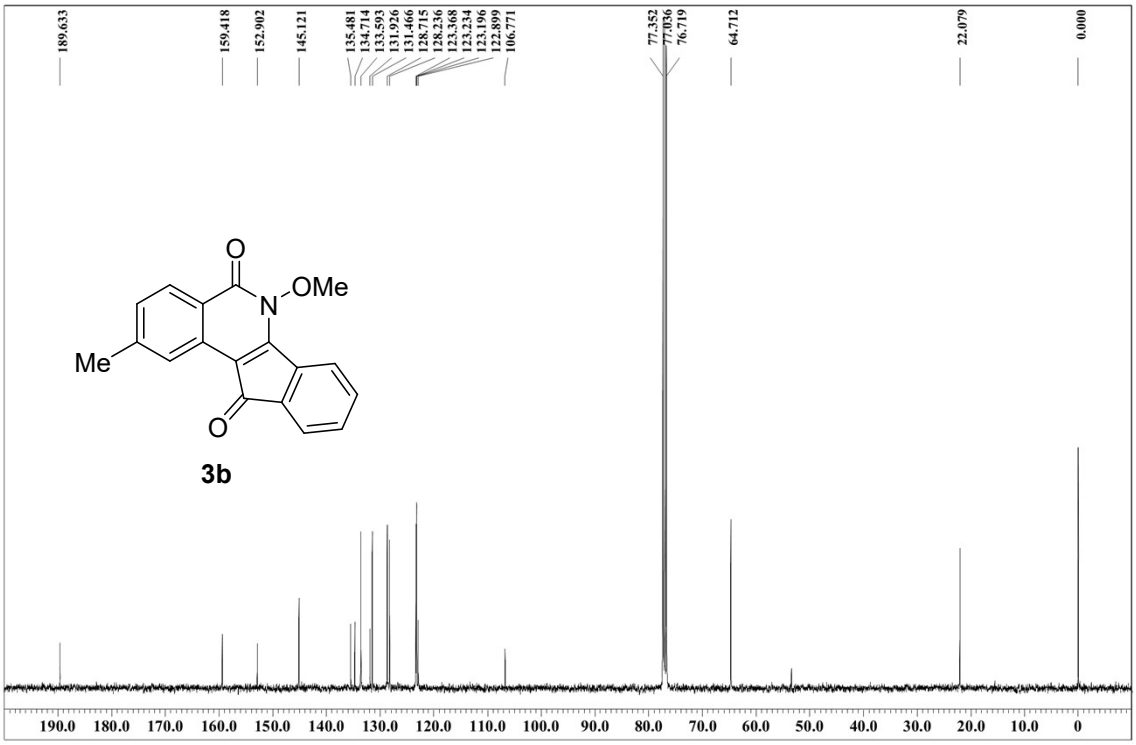
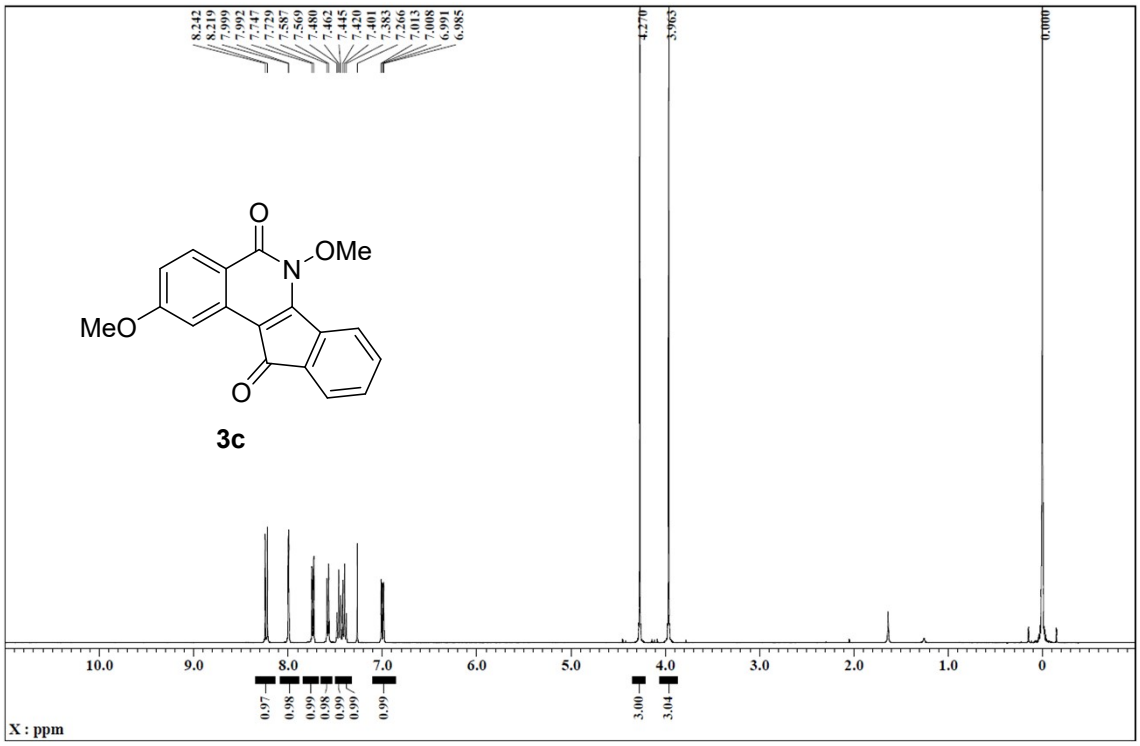


Figure S3. The ^{1}H and ^{13}C NMR Spectra of **3c**



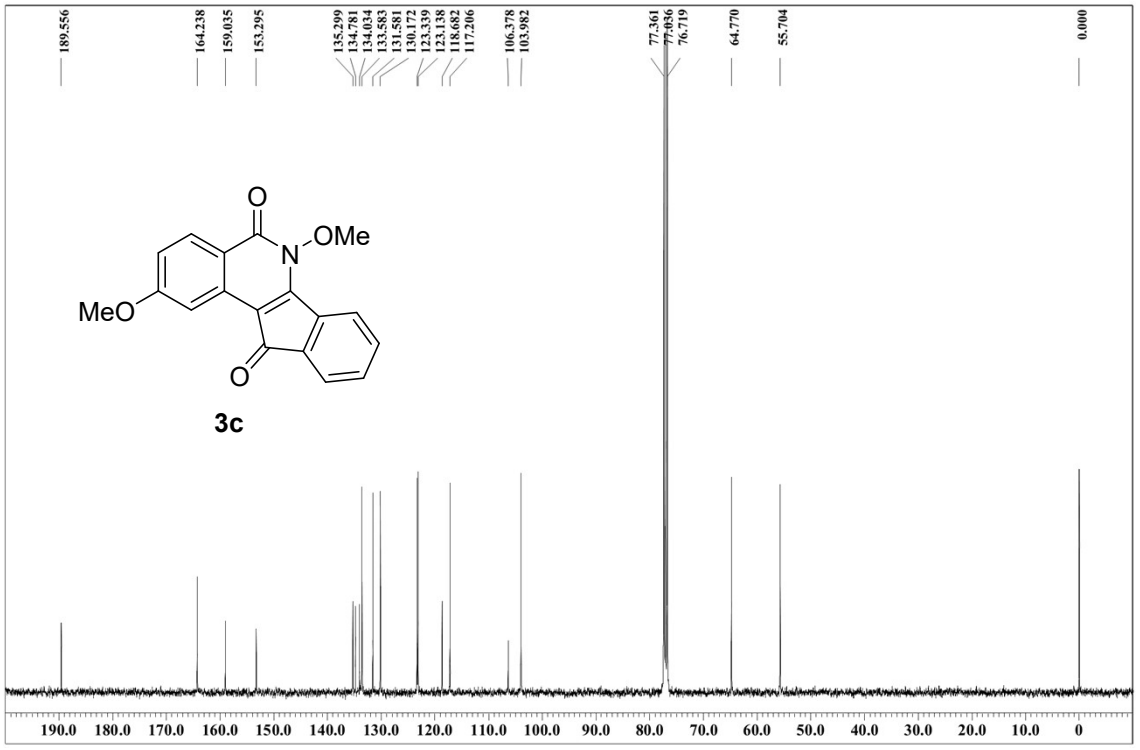
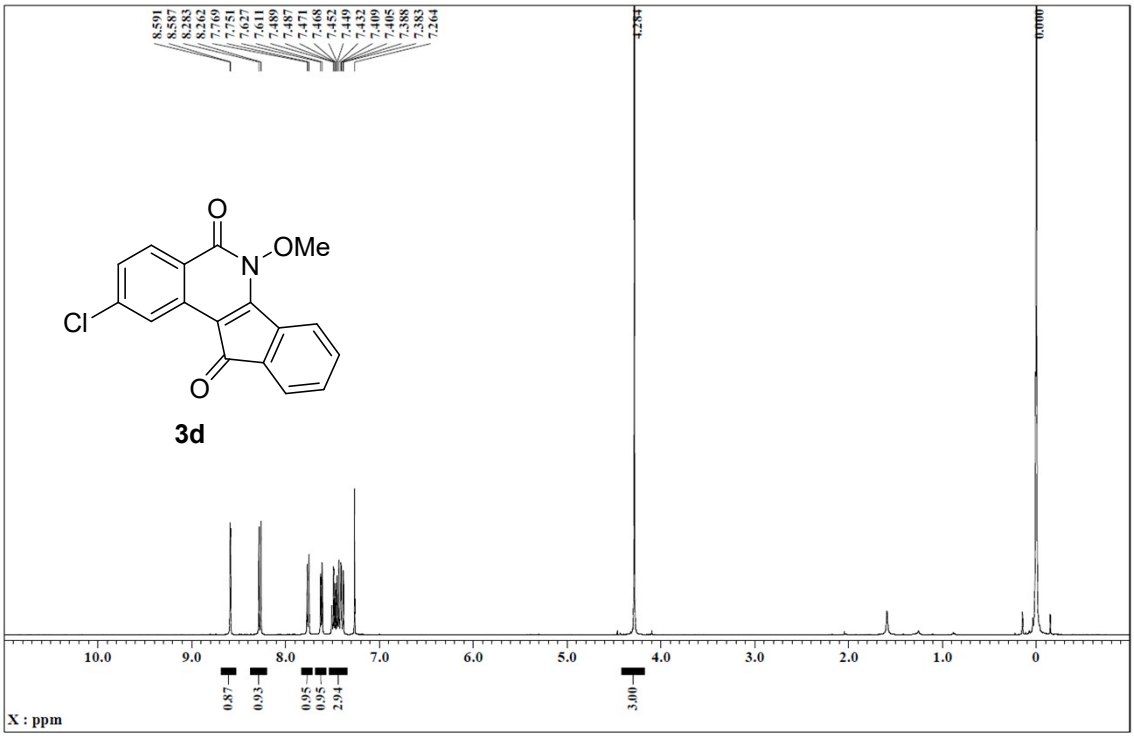


Figure S4. The ^{1}H and ^{13}C NMR Spectra of **3d**



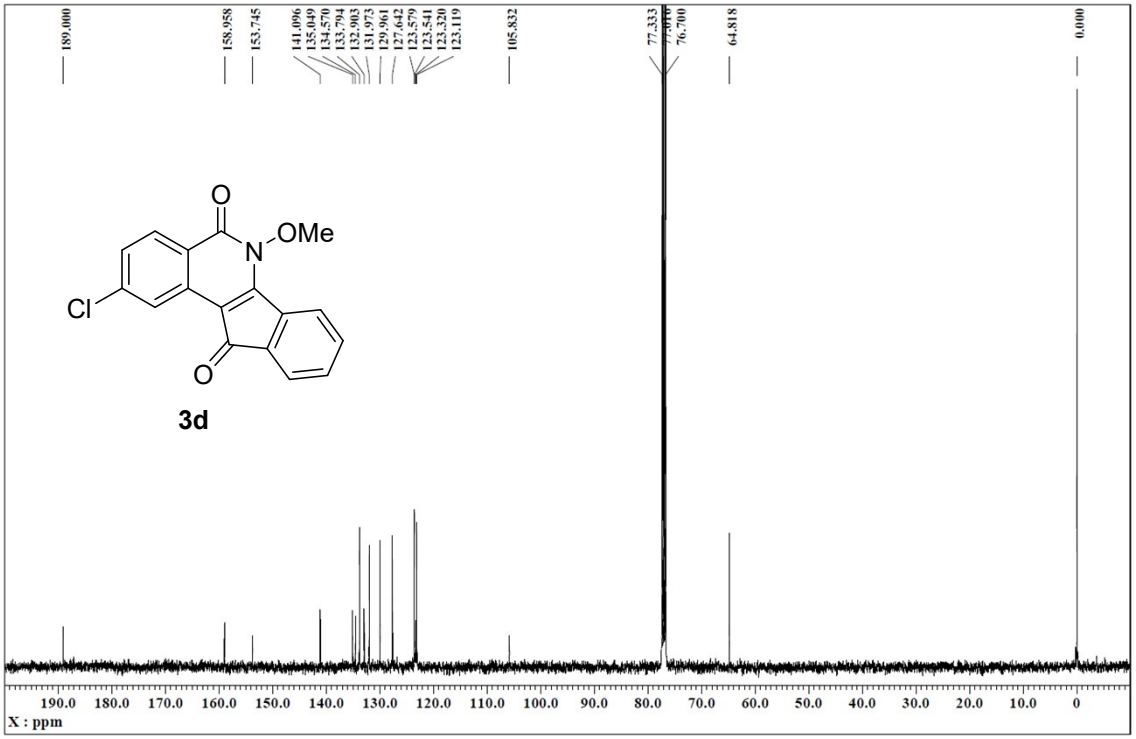
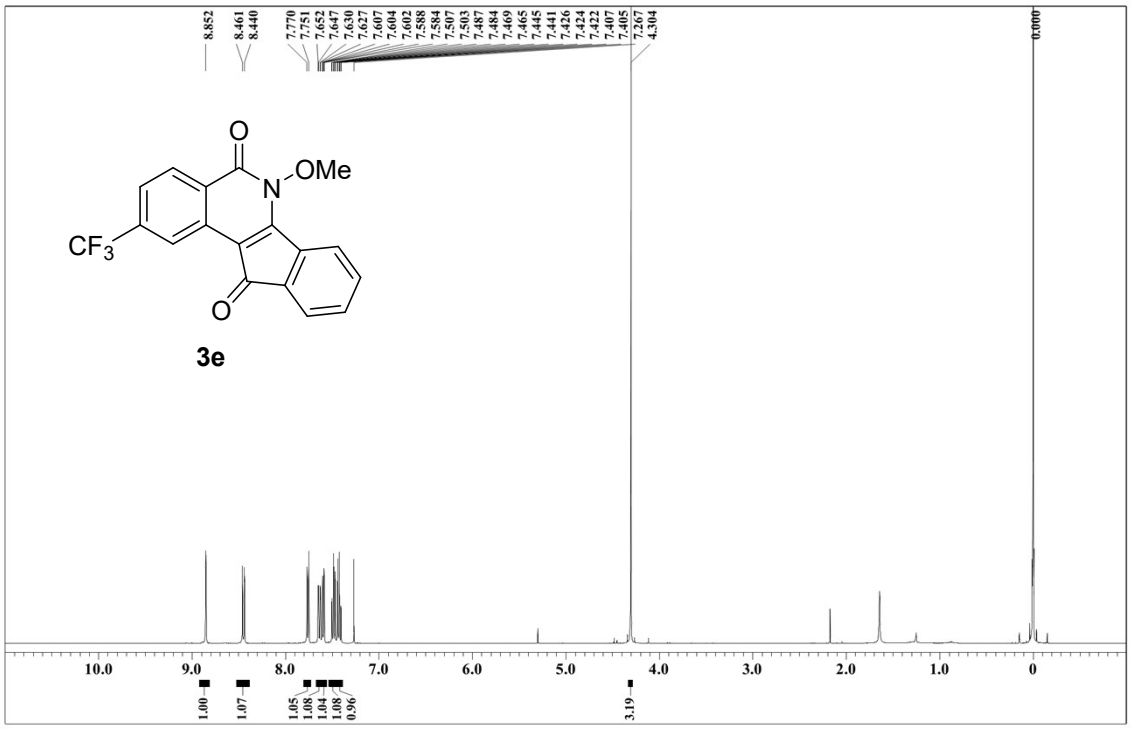


Figure S5. The ^{1}H and ^{13}C NMR Spectra of **3e**



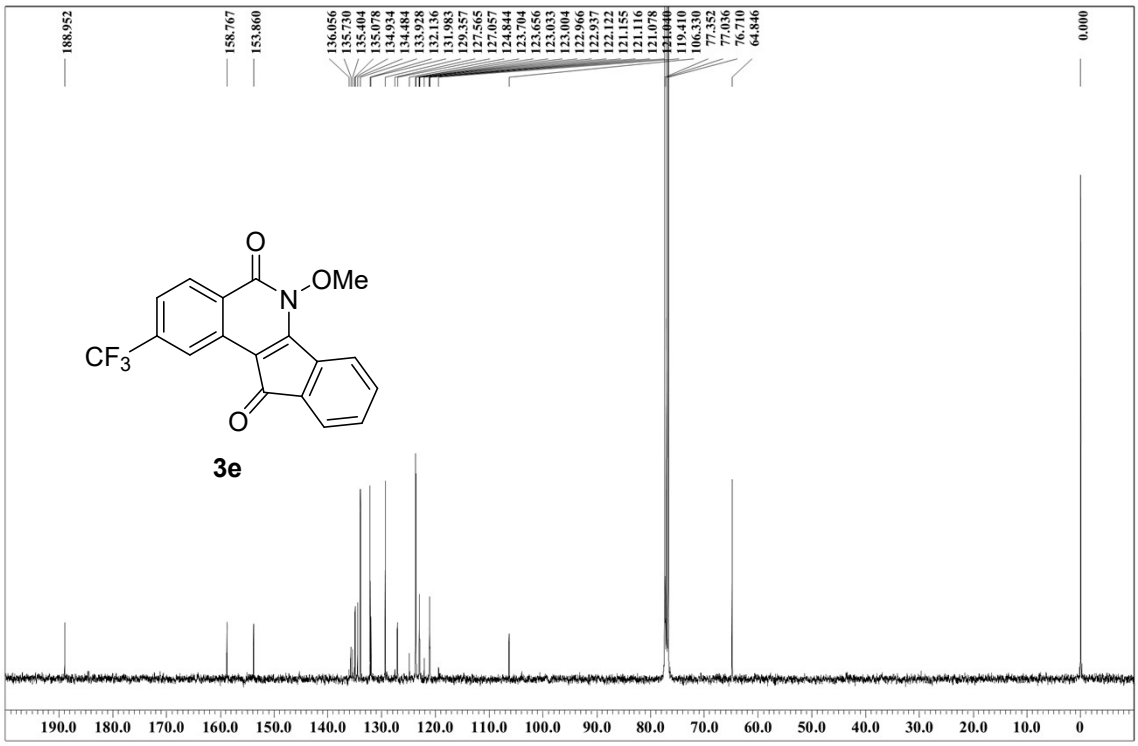
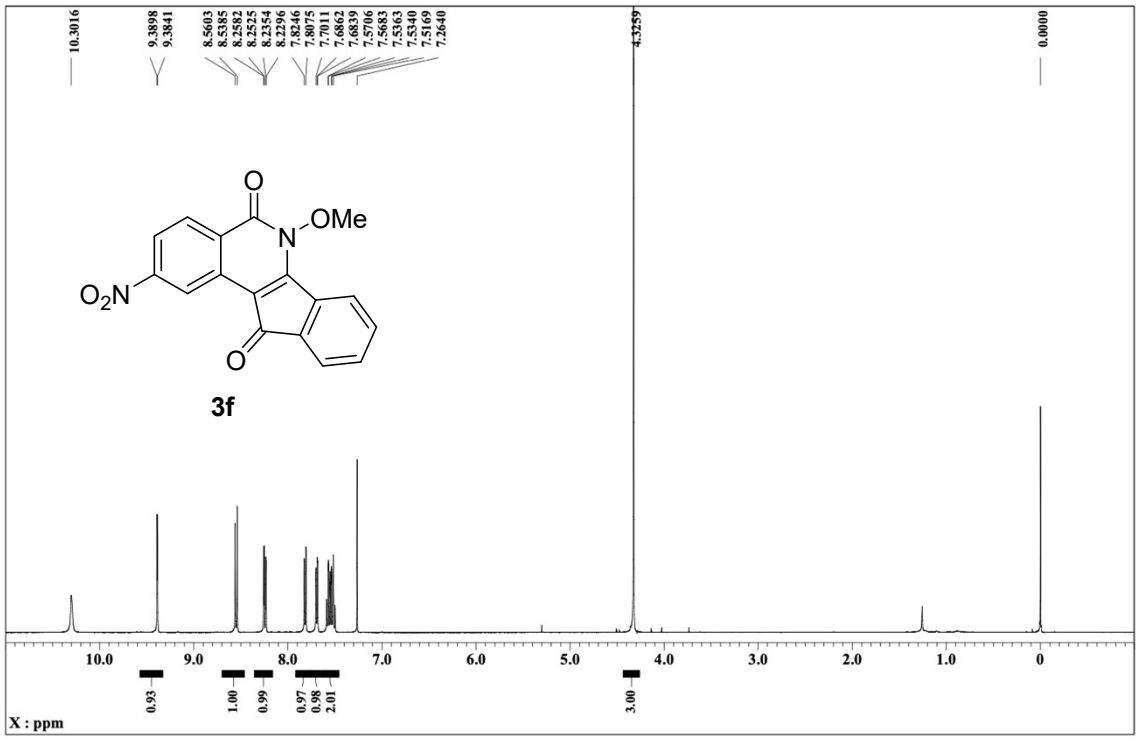


Figure S6. The ^{1}H and ^{13}C NMR Spectra of **3f**



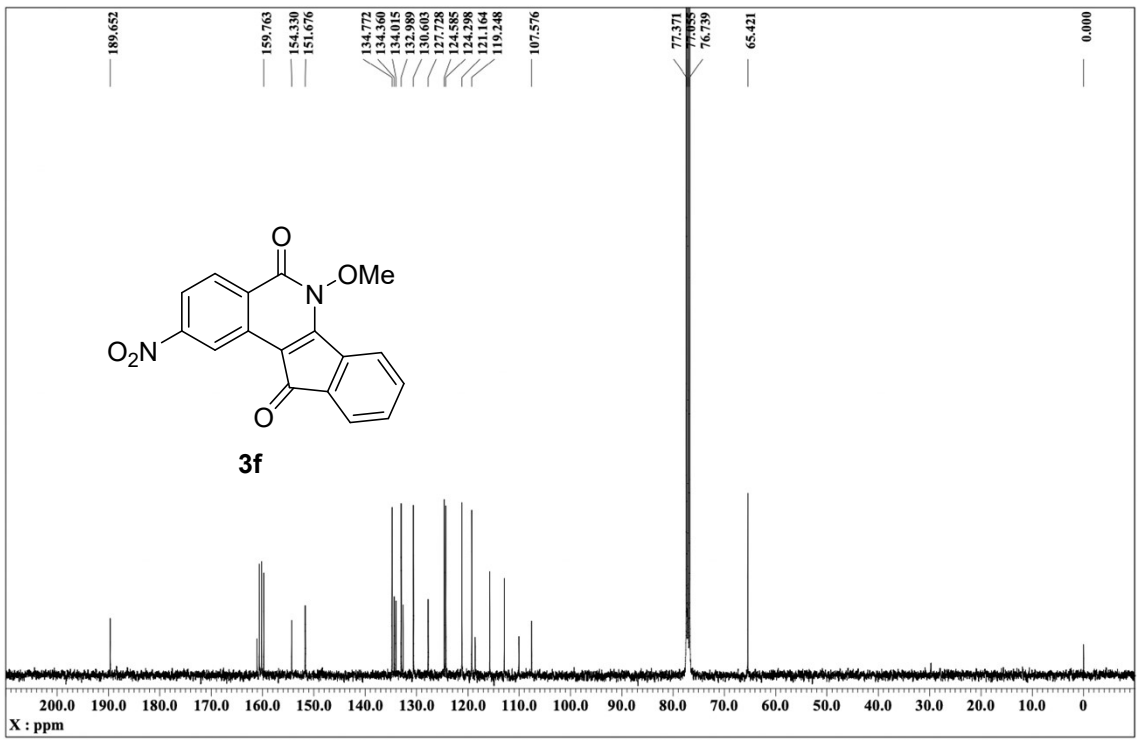
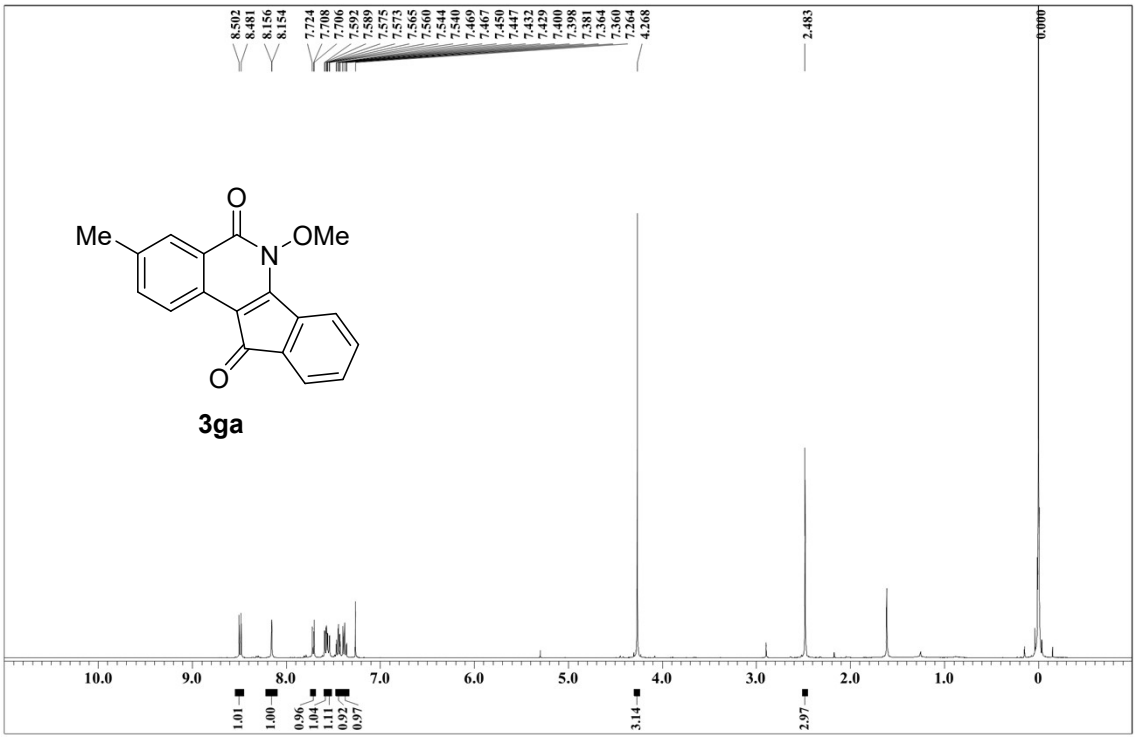


Figure S7. The ^{1}H and ^{13}C NMR Spectra of **3ga**



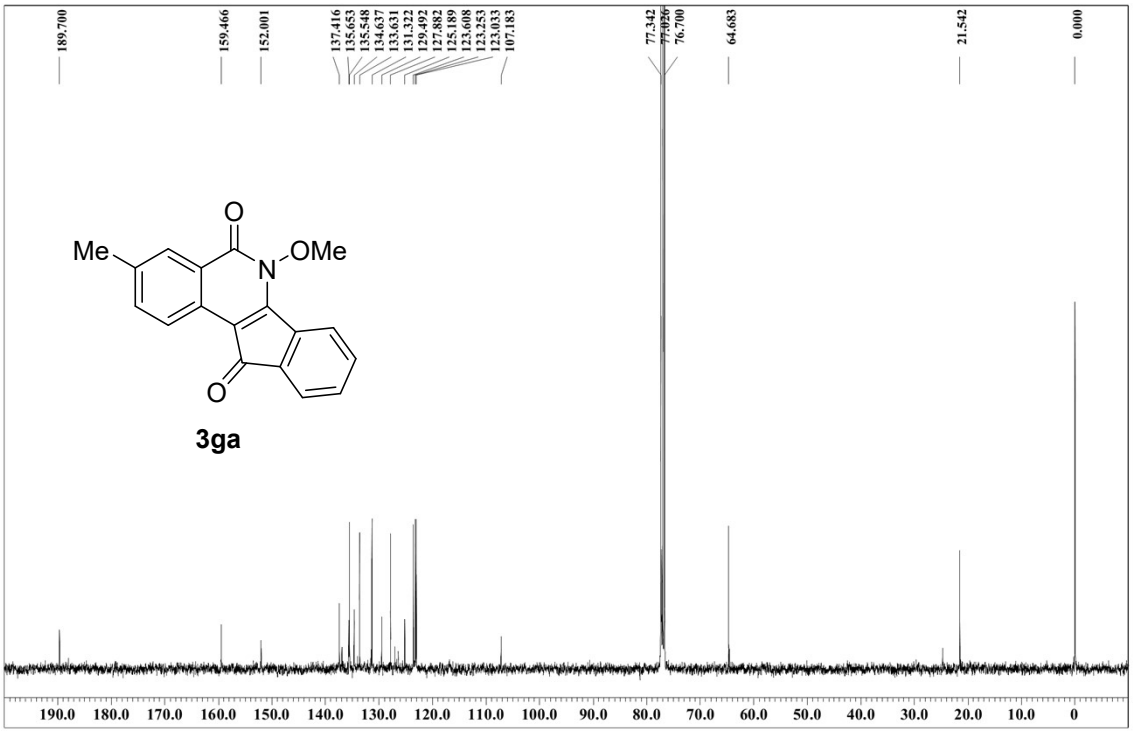
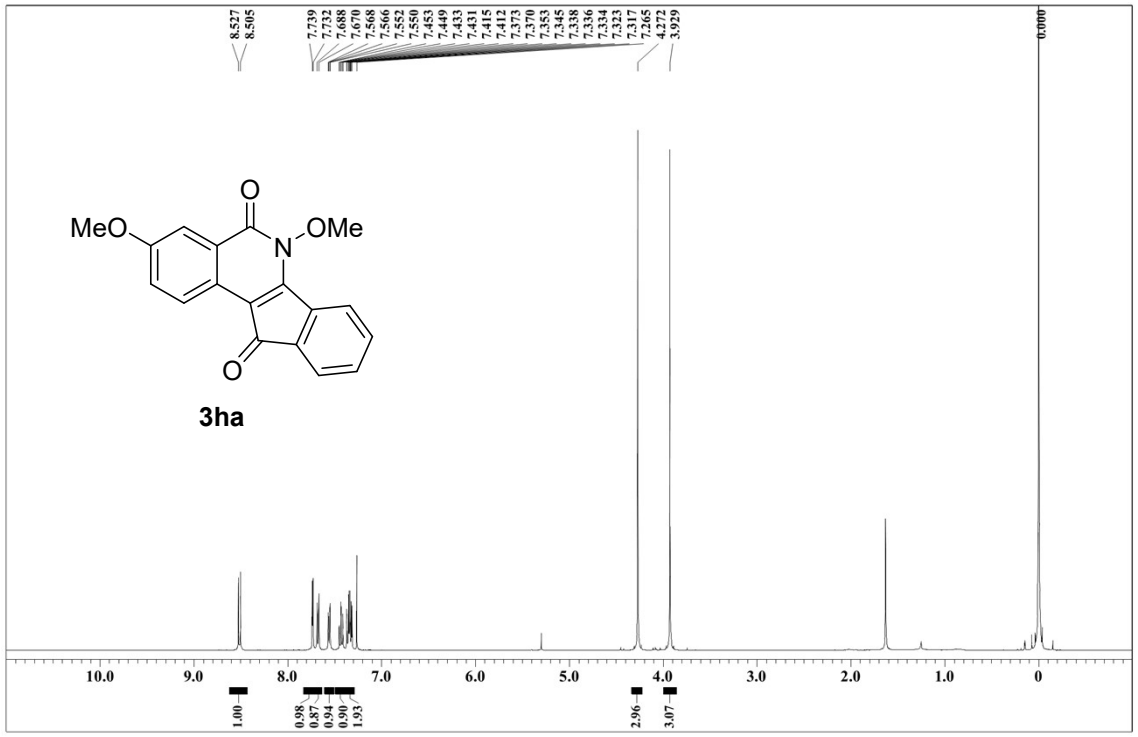


Figure S8. The ^{1}H and ^{13}C NMR Spectra of **3ha**



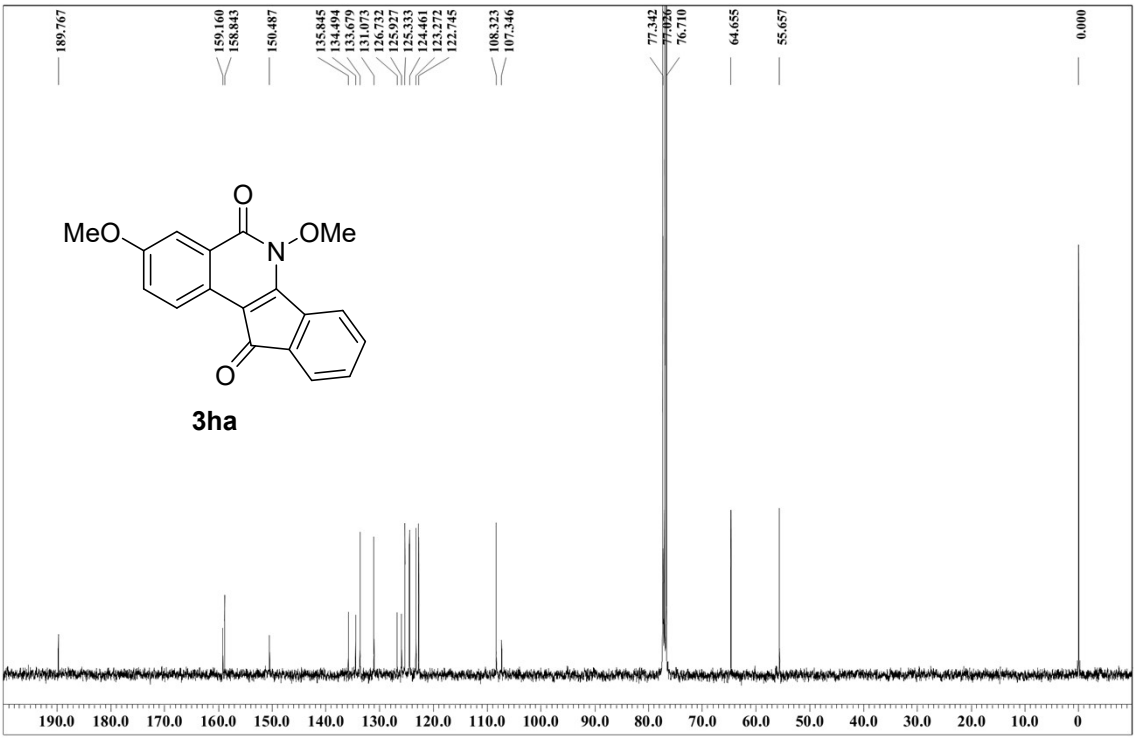
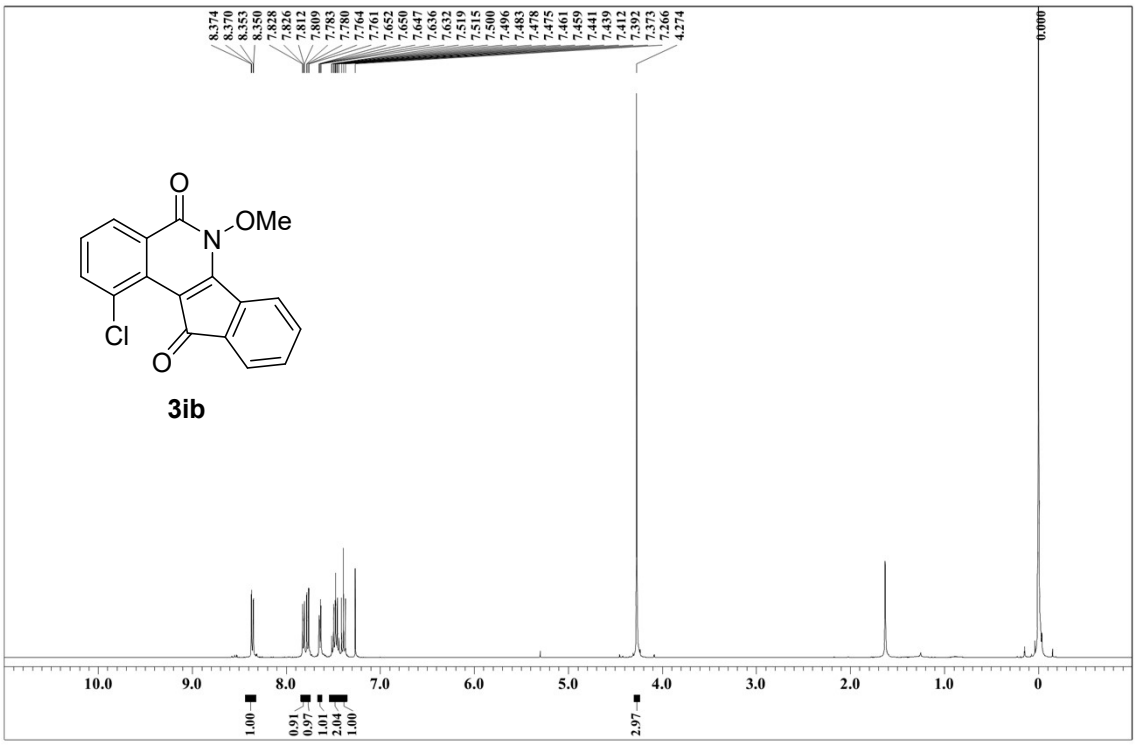


Figure S9. The ^{1}H and ^{13}C NMR Spectra of **3ib**



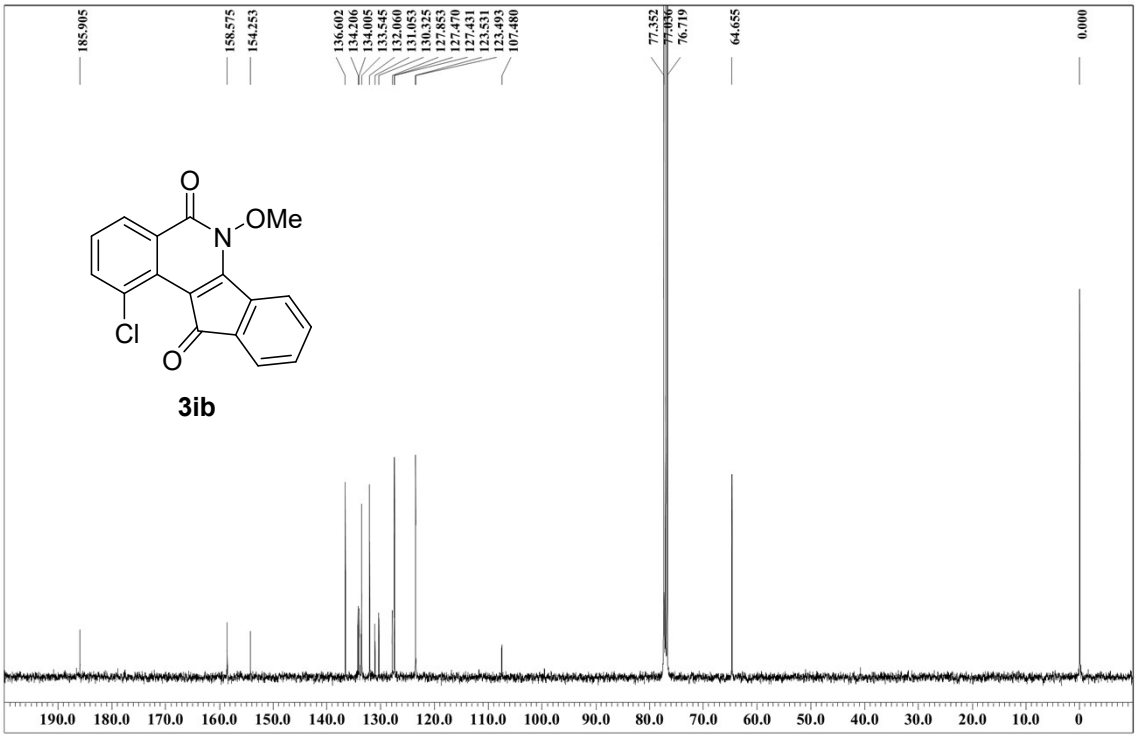
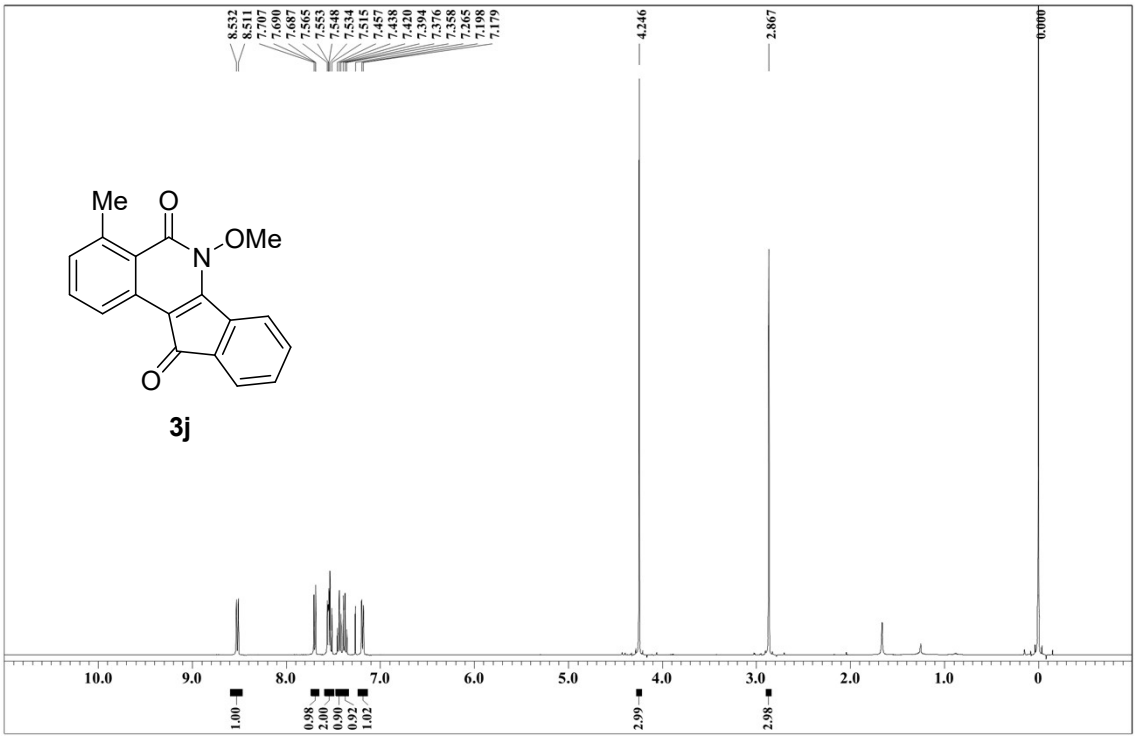


Figure S10. The ^{1}H and ^{13}C NMR Spectra of **3j**



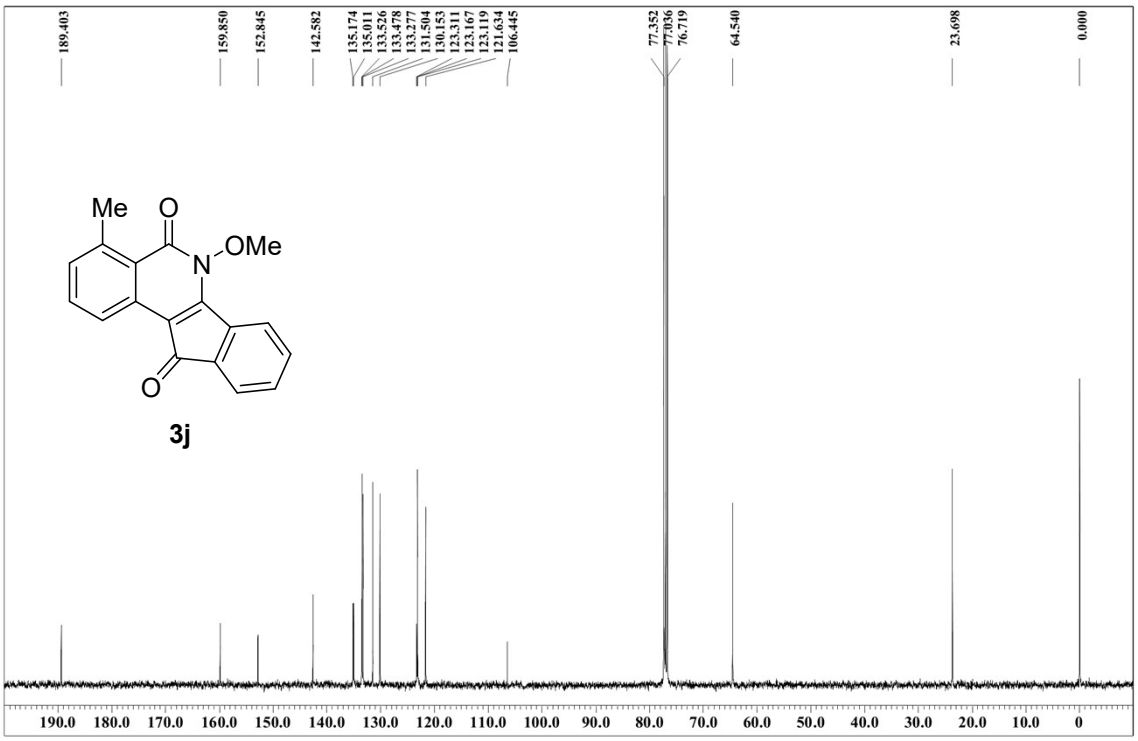
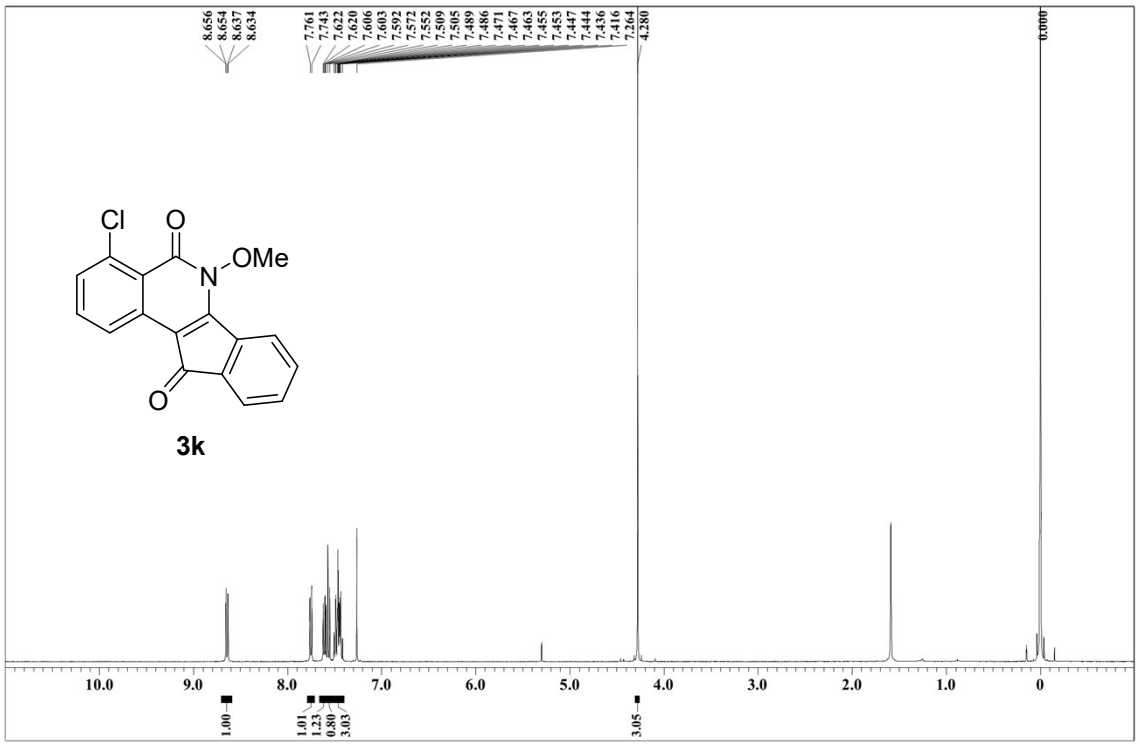


Figure S11. The ^{1}H and ^{13}C NMR Spectra of **3k**



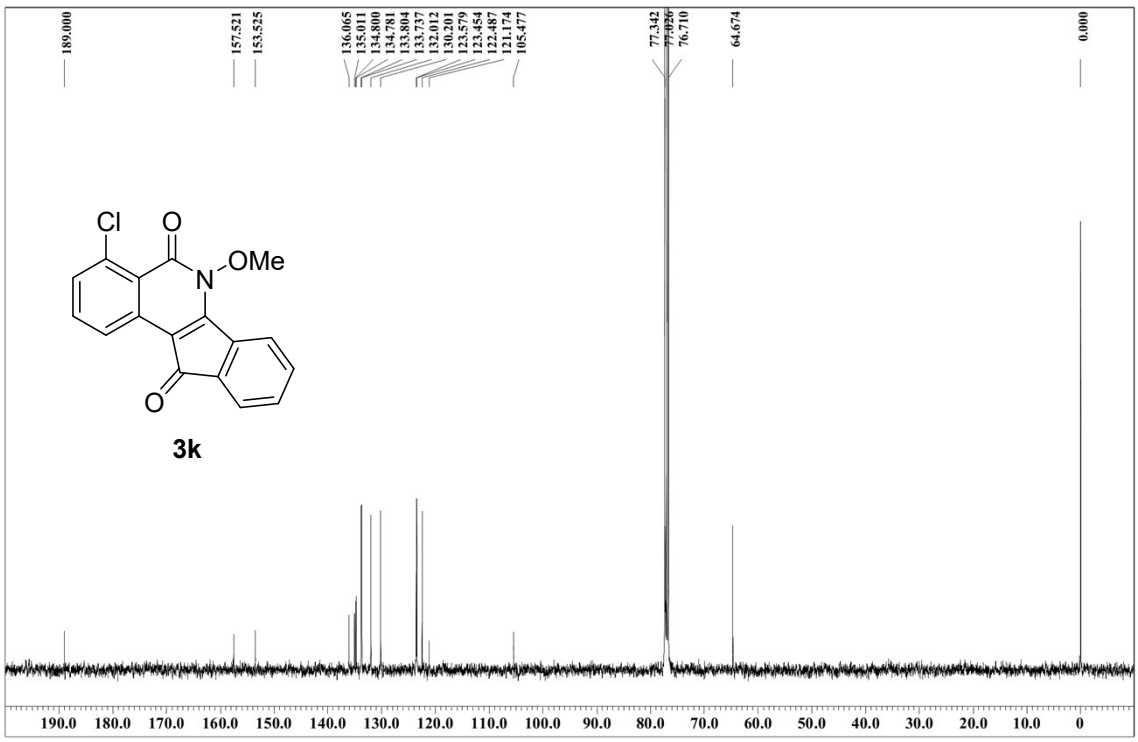
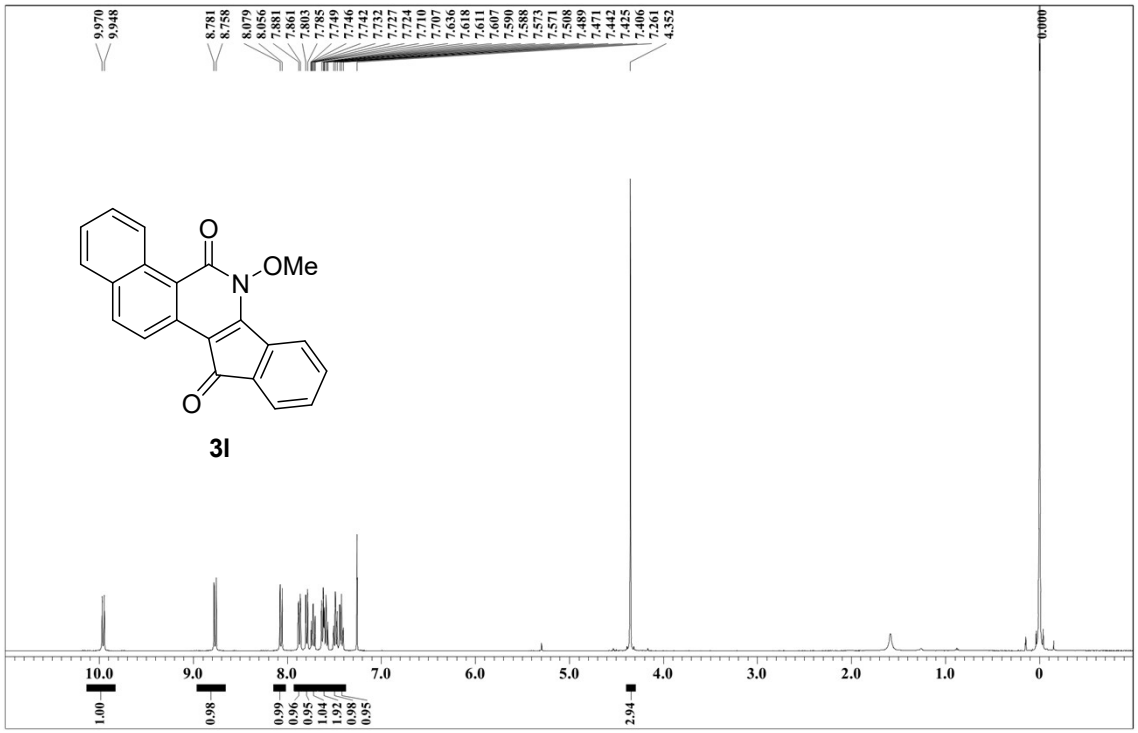


Figure S12. The ^{1}H and ^{13}C NMR Spectra of **3l**



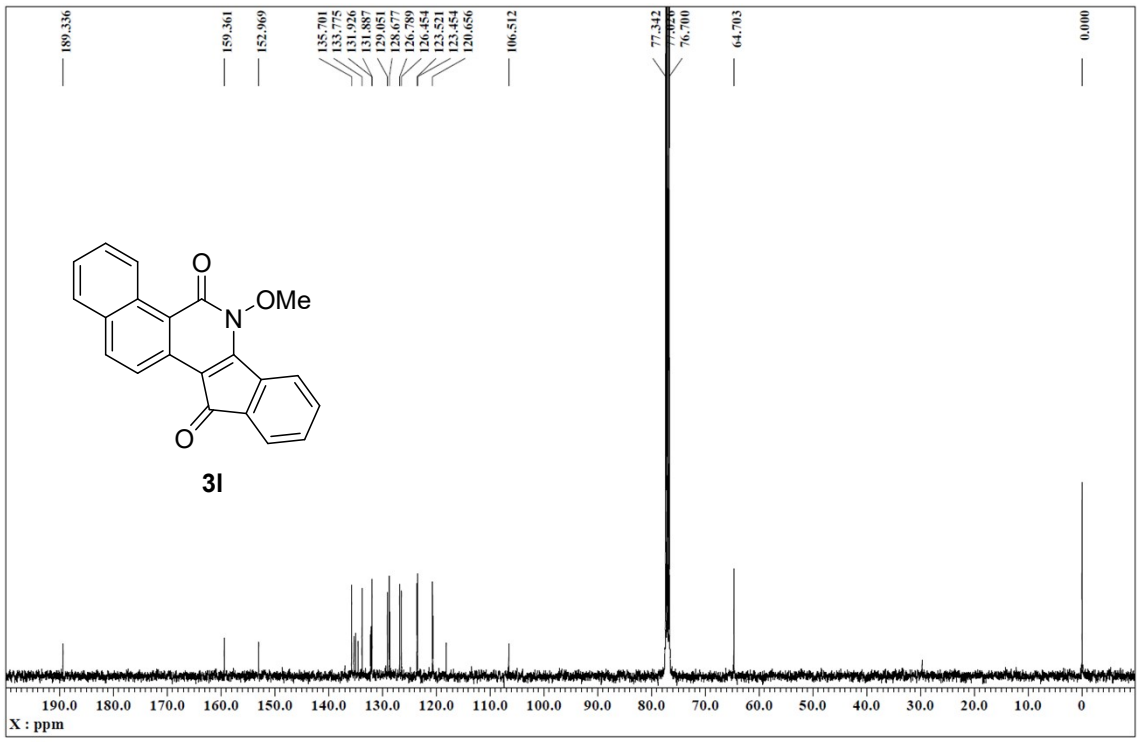
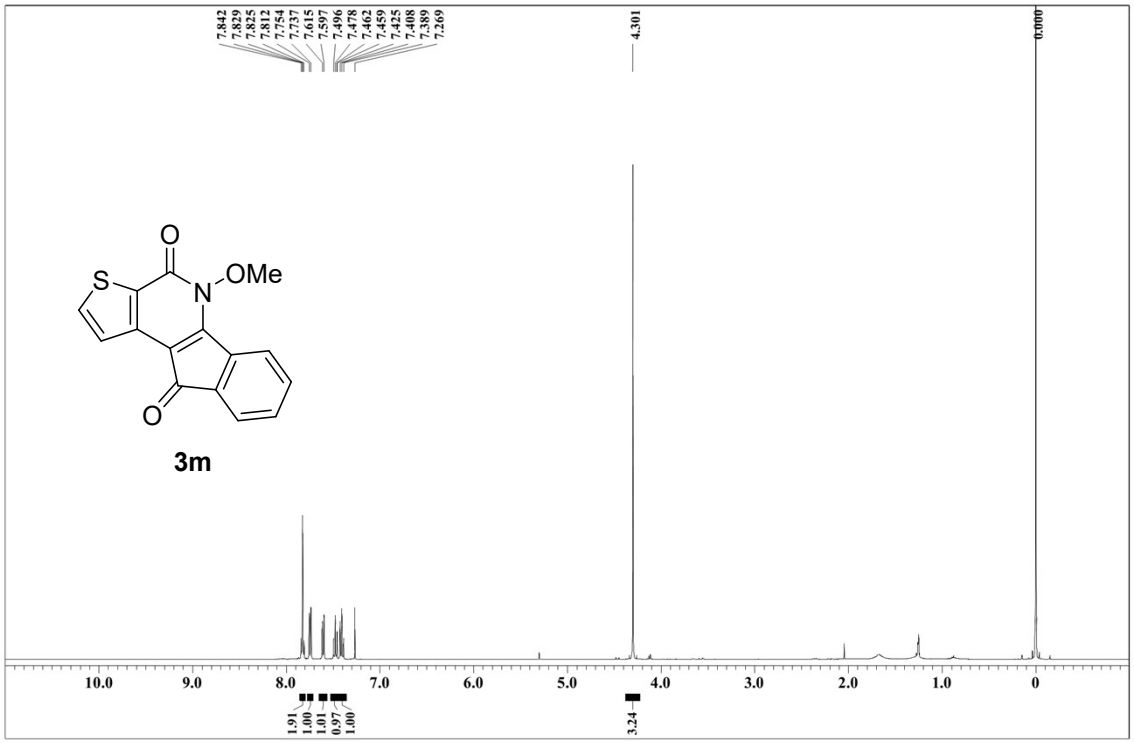


Figure S13. The ^{1}H and ^{13}C NMR Spectra of **3m**



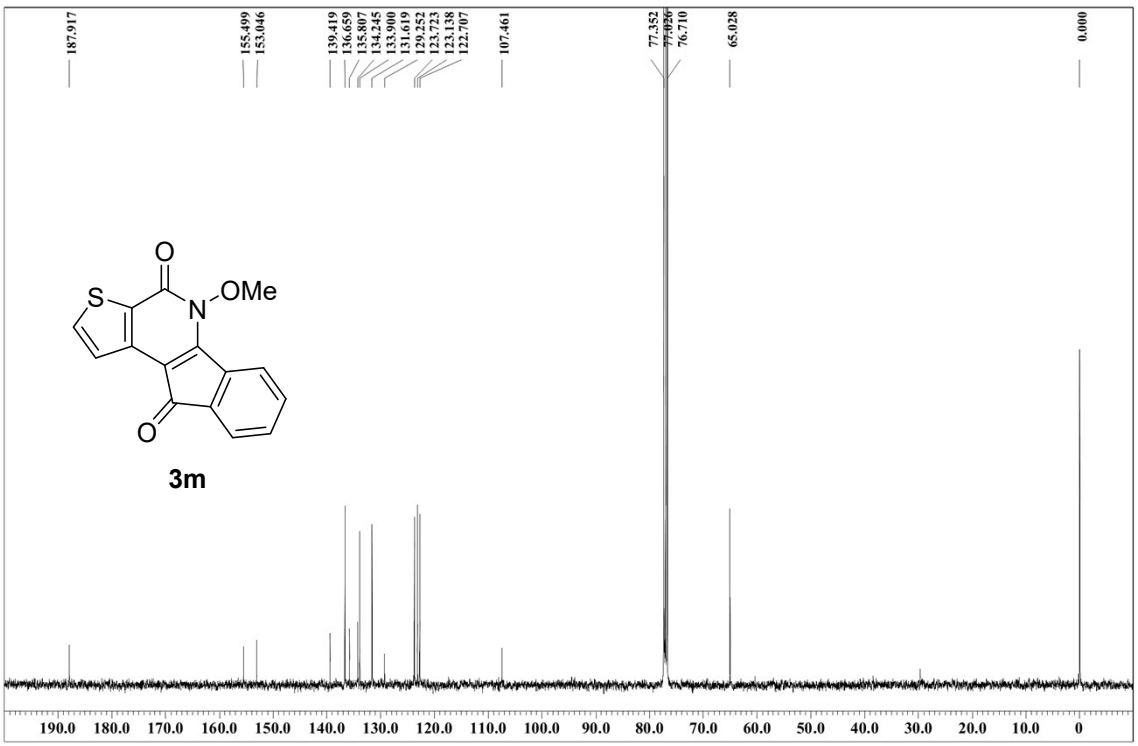
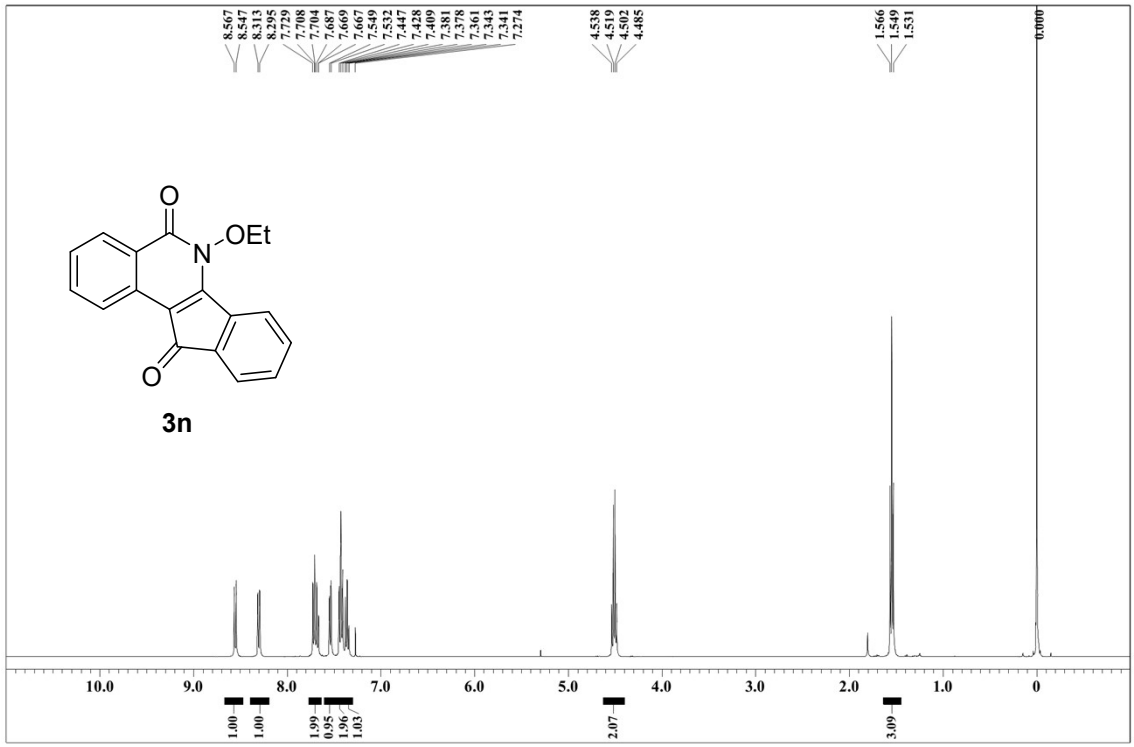


Figure S14. The ^{1}H and ^{13}C NMR Spectra of **3n**



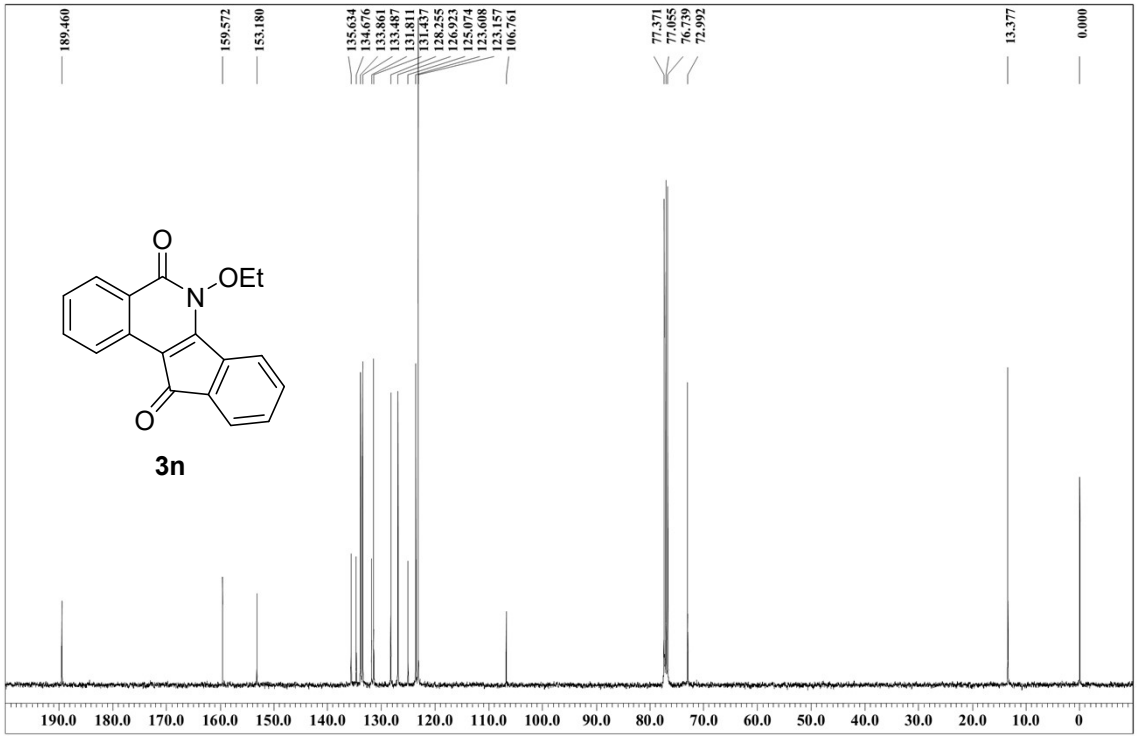
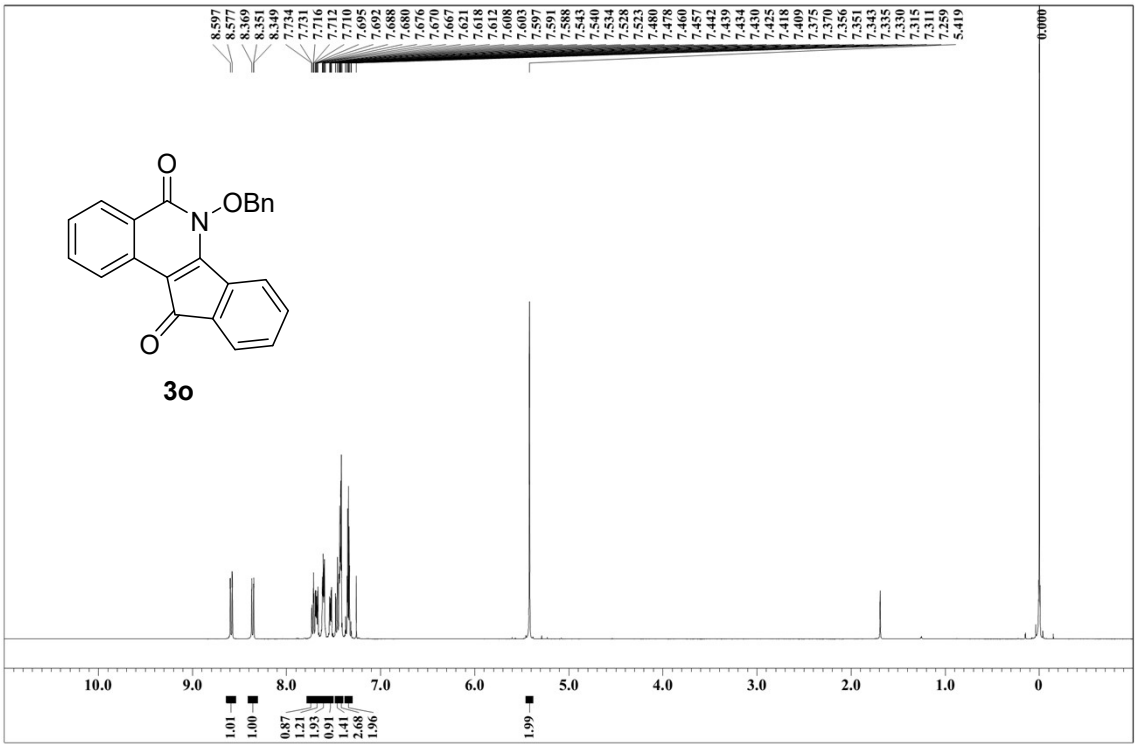


Figure S15. The ^{1}H and ^{13}C NMR Spectra of **3o**



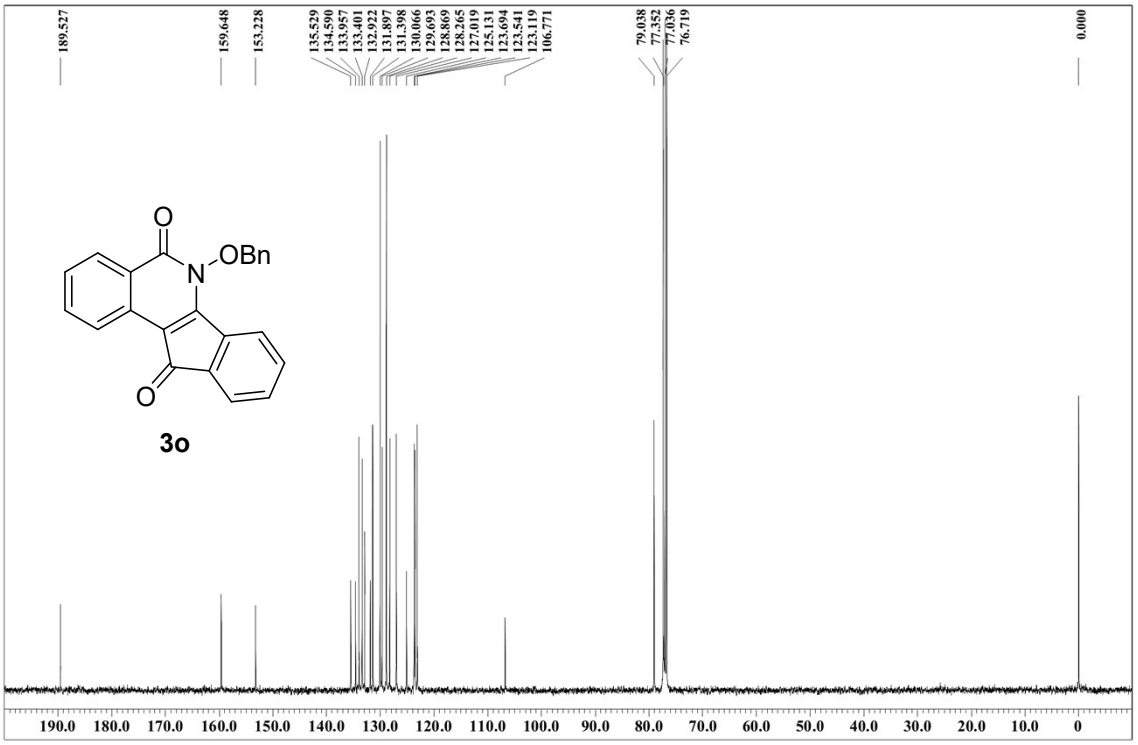
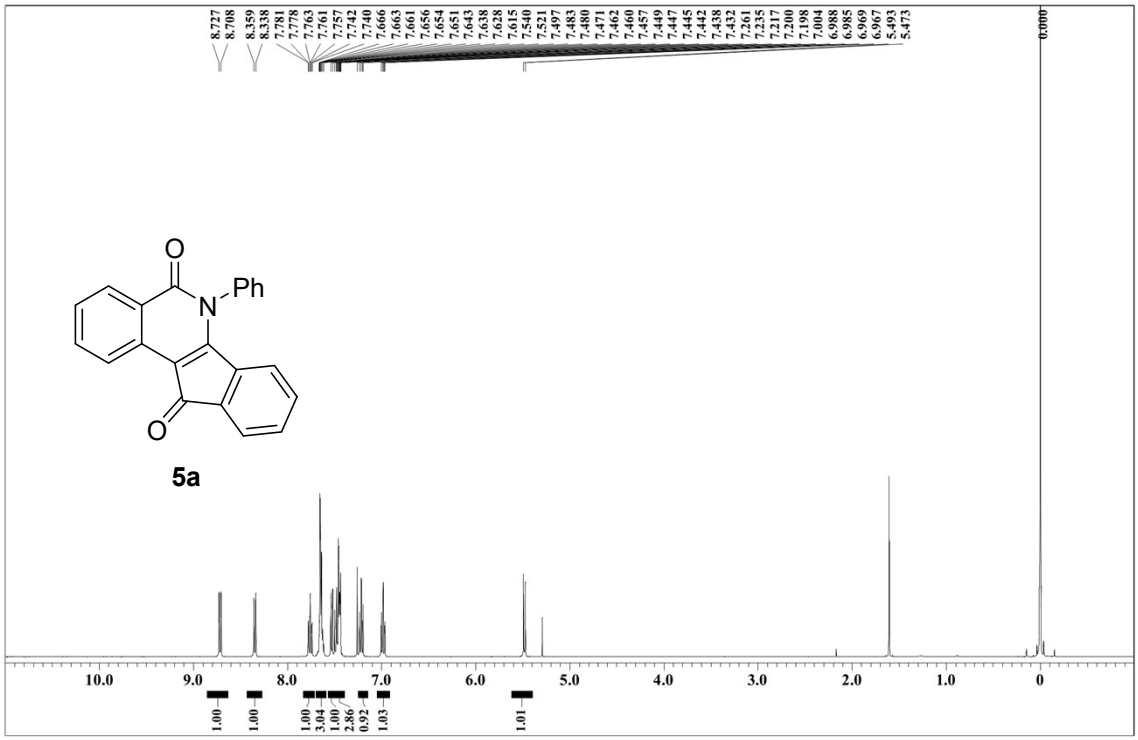


Figure S16. The ^{1}H and ^{13}C NMR Spectra of **5a**



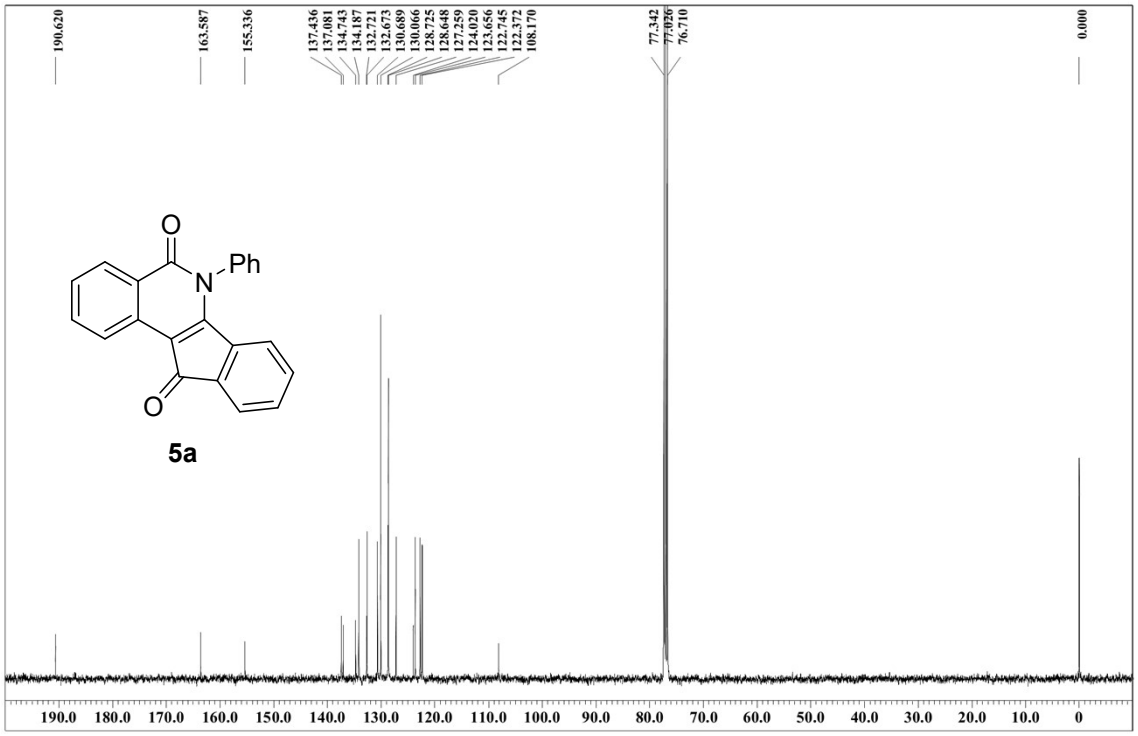
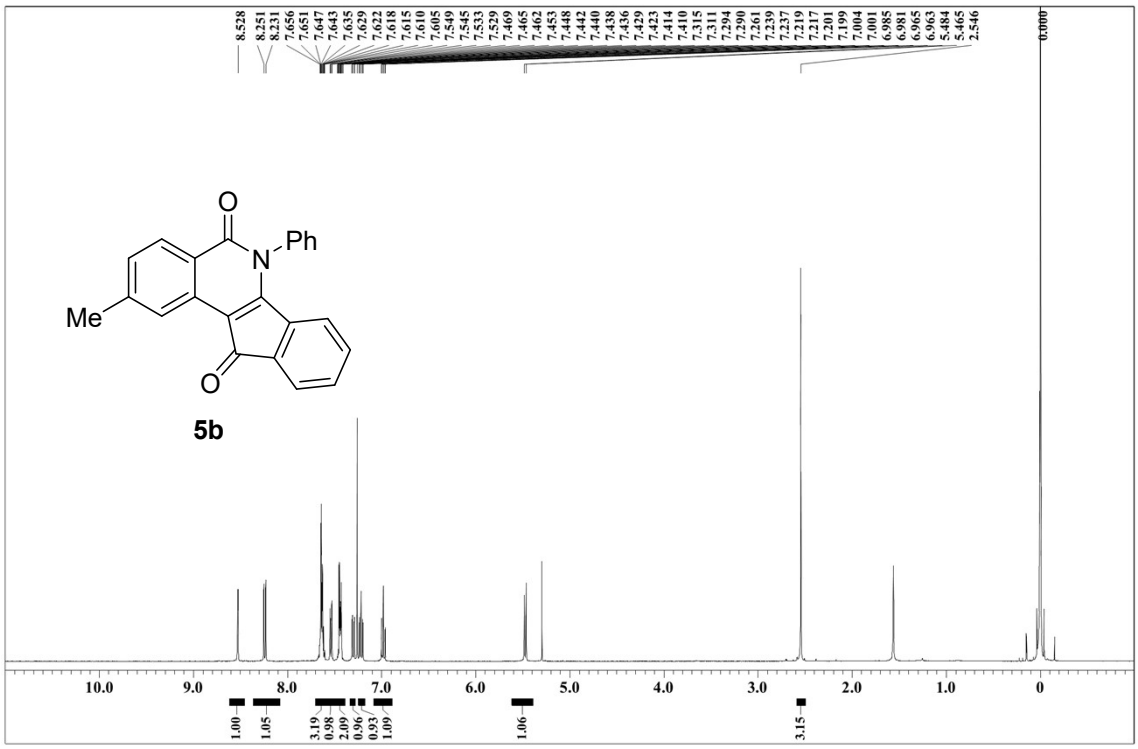


Figure S17. The ^{1}H and ^{13}C NMR Spectra of **5b**



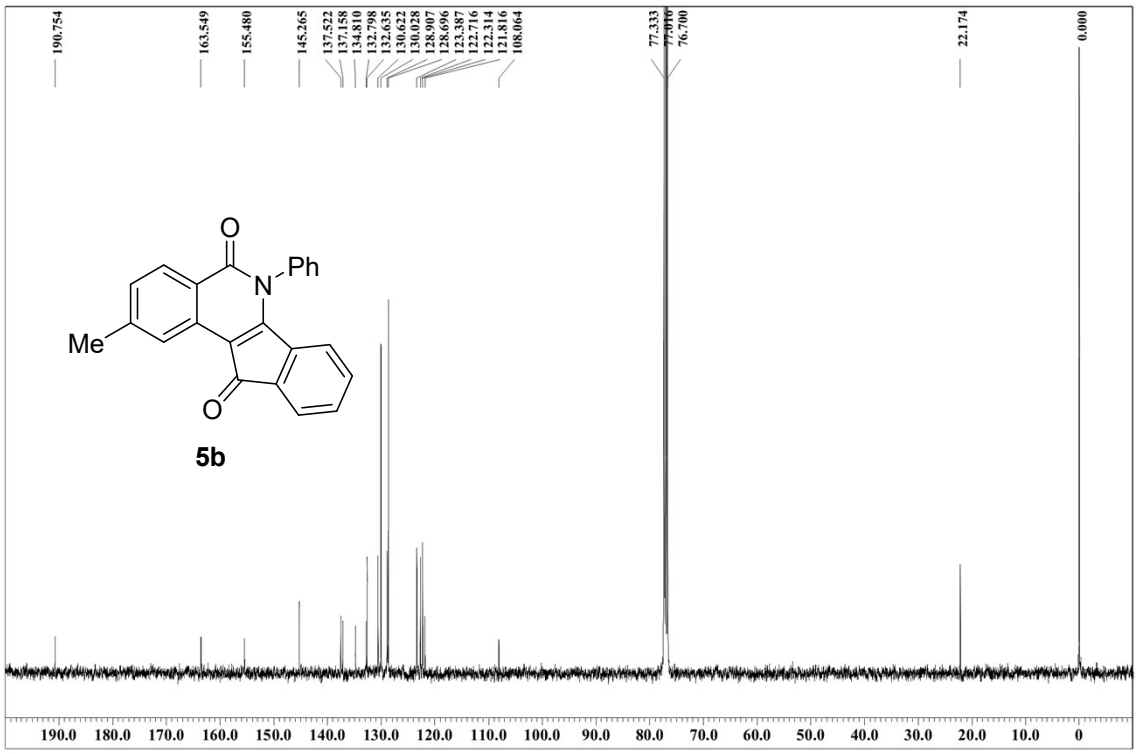
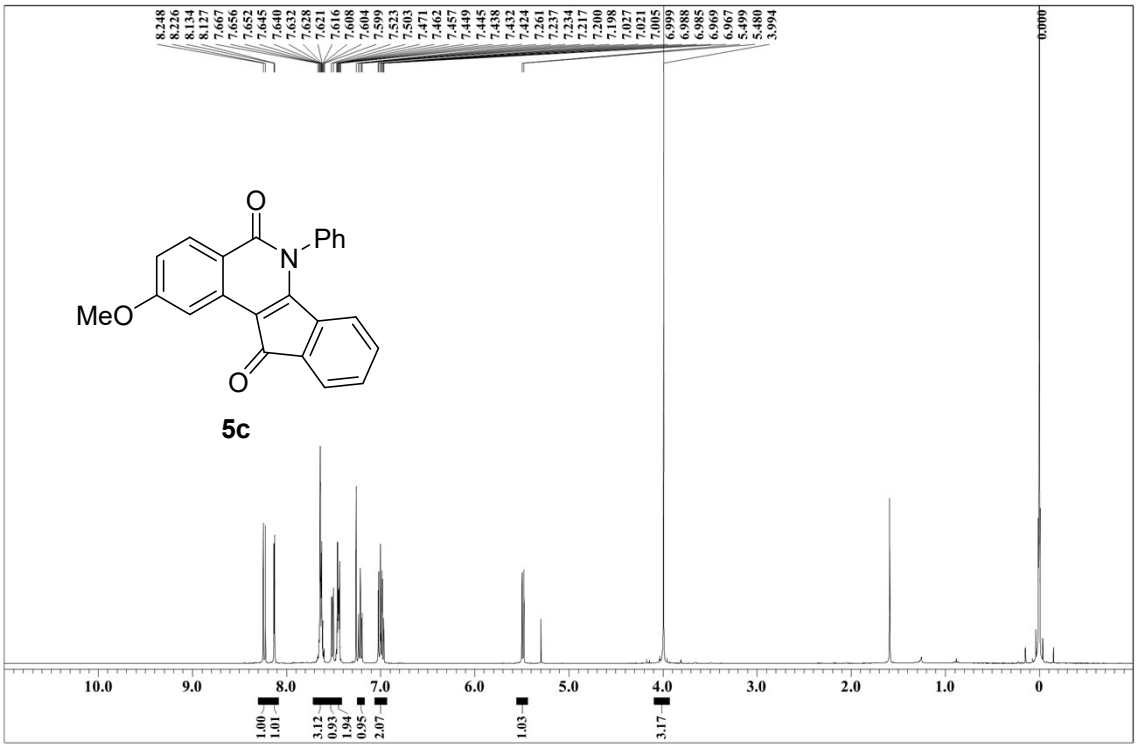


Figure S18. The ^{1}H and ^{13}C NMR Spectra of **5c**



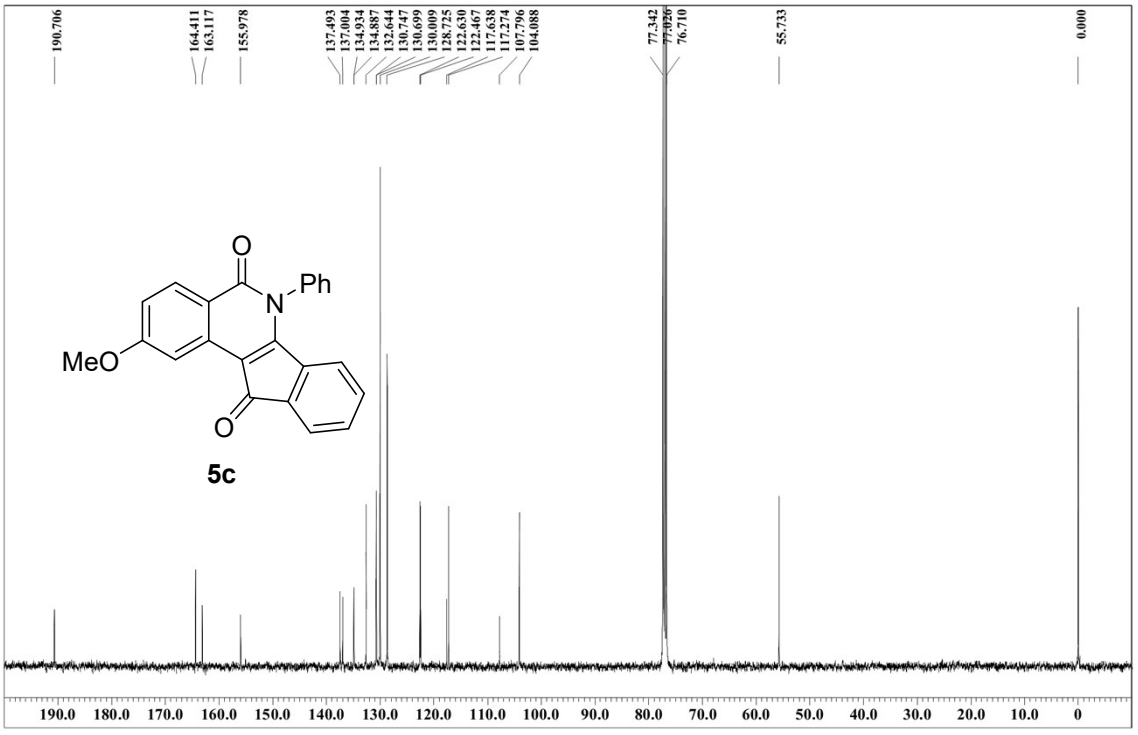
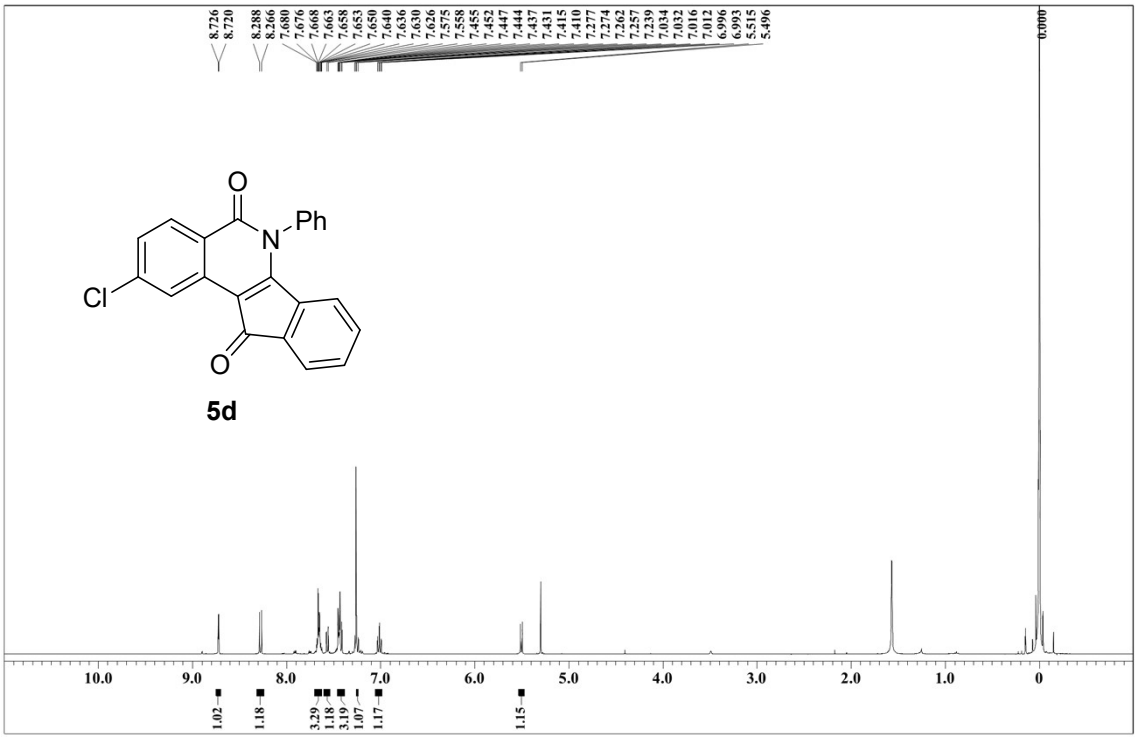


Figure S19. The ^{1}H and ^{13}C NMR Spectra of **5d**



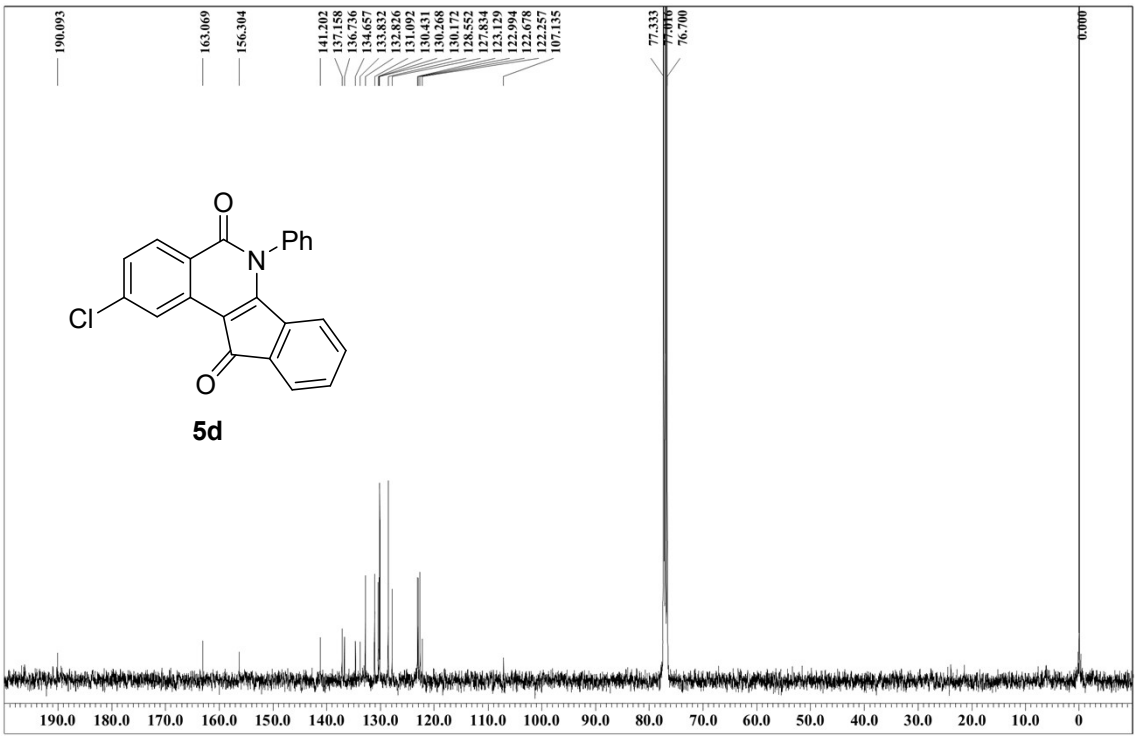
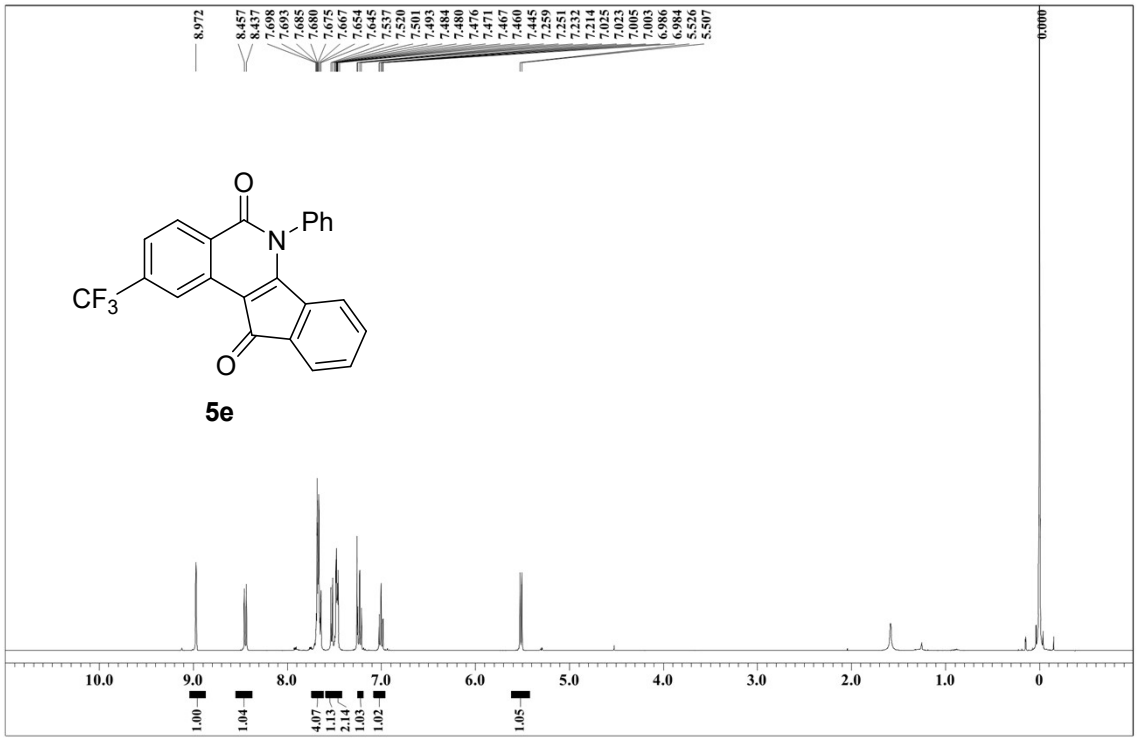


Figure S20. The ^{1}H and ^{13}C NMR Spectra of **5e**



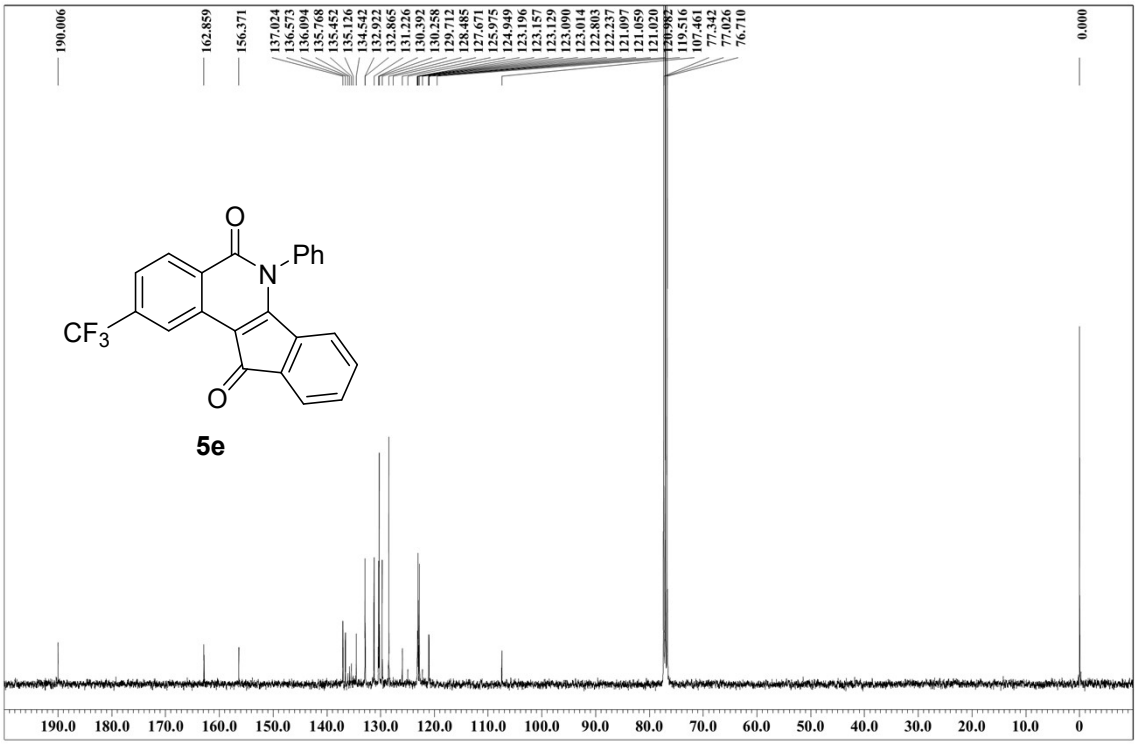
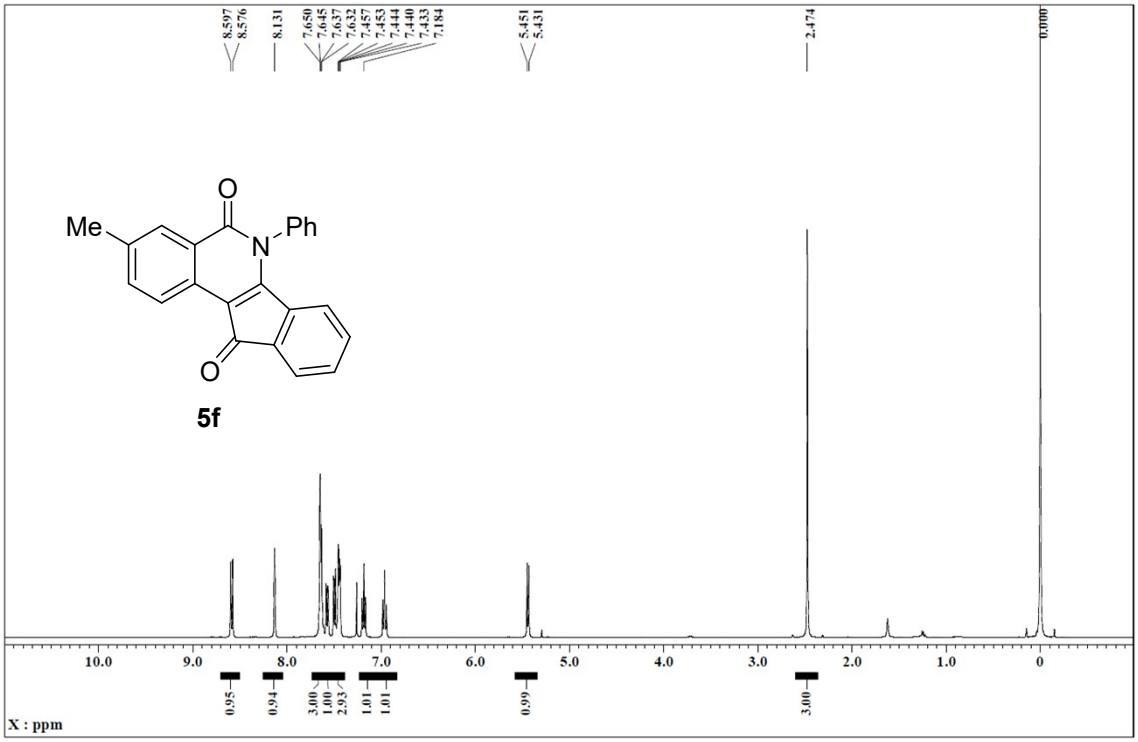


Figure S21. The ^{1}H and ^{13}C NMR Spectra of **5f**



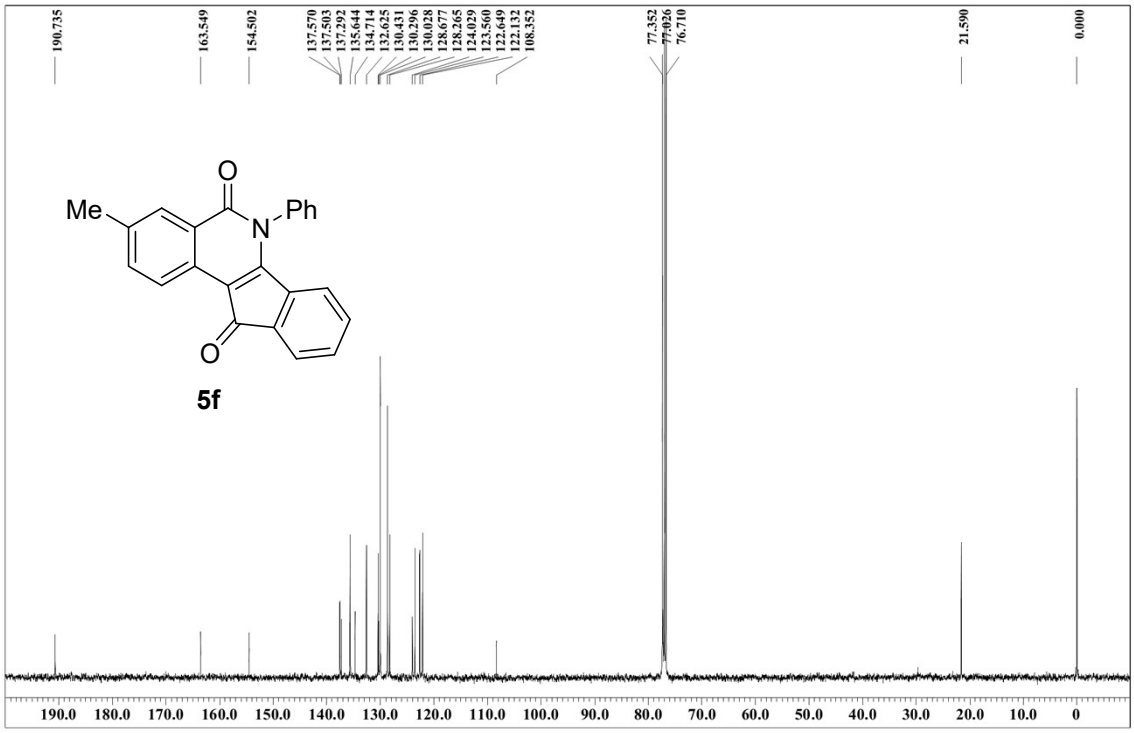
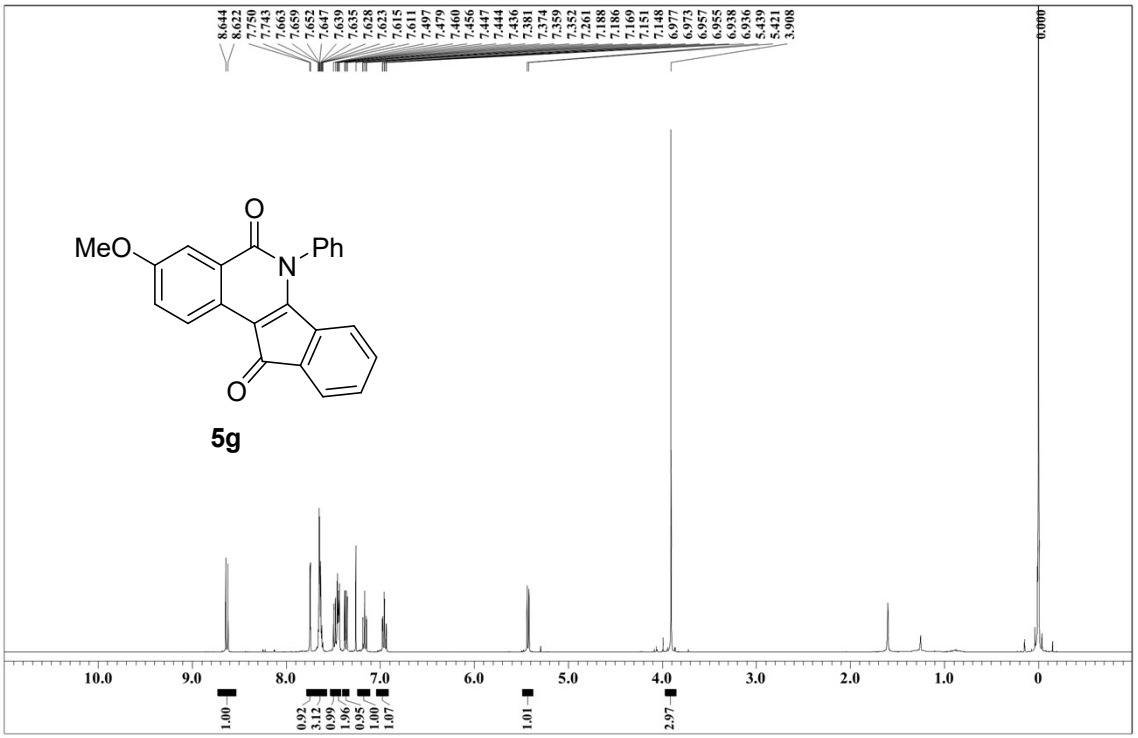


Figure S22. The ^{1}H and ^{13}C NMR Spectra of **5g**



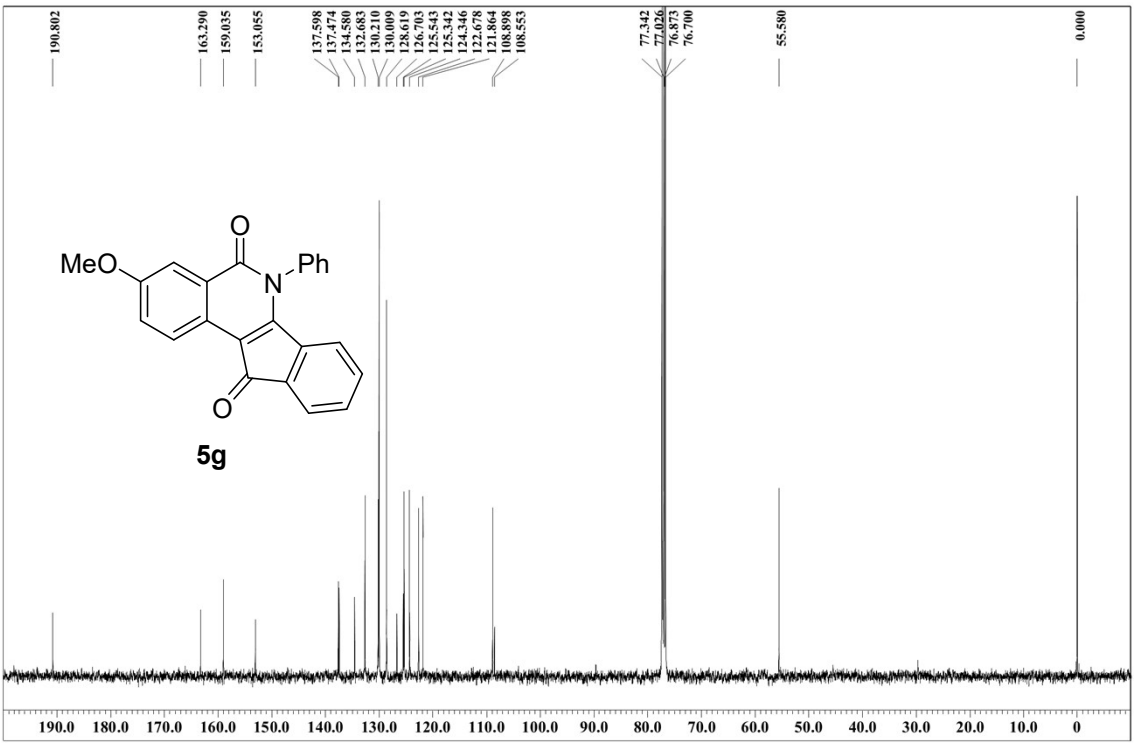
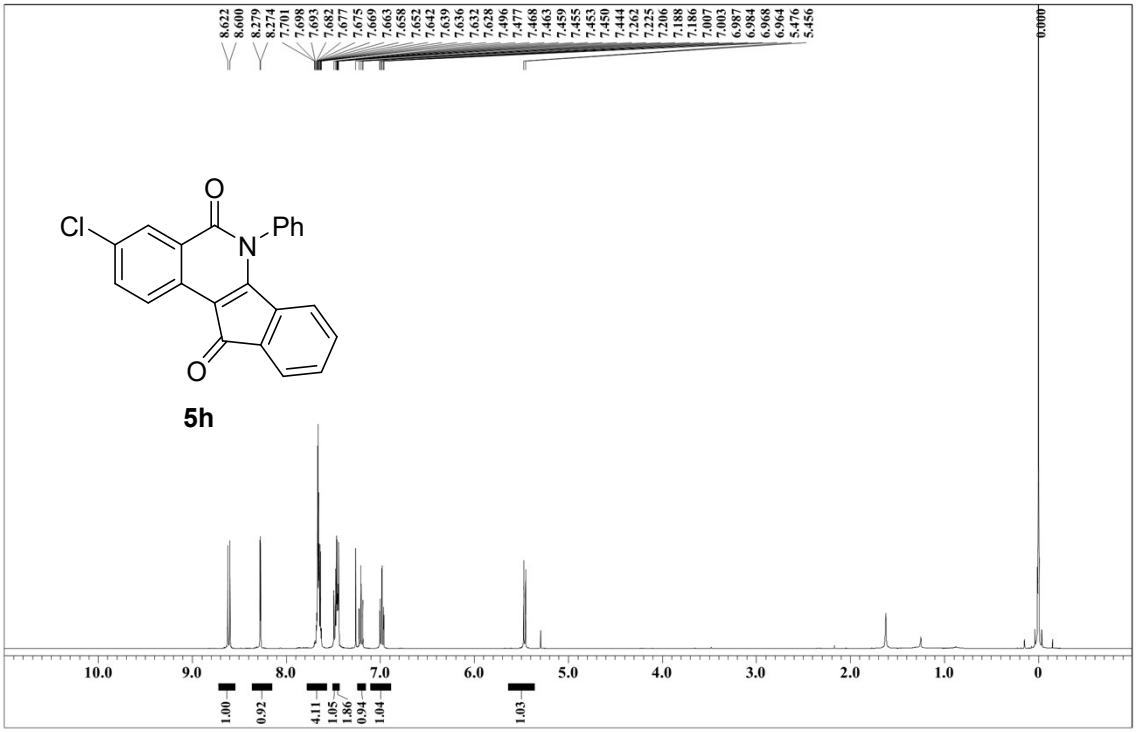


Figure S23. The ^{1}H and ^{13}C NMR Spectra of **5h**



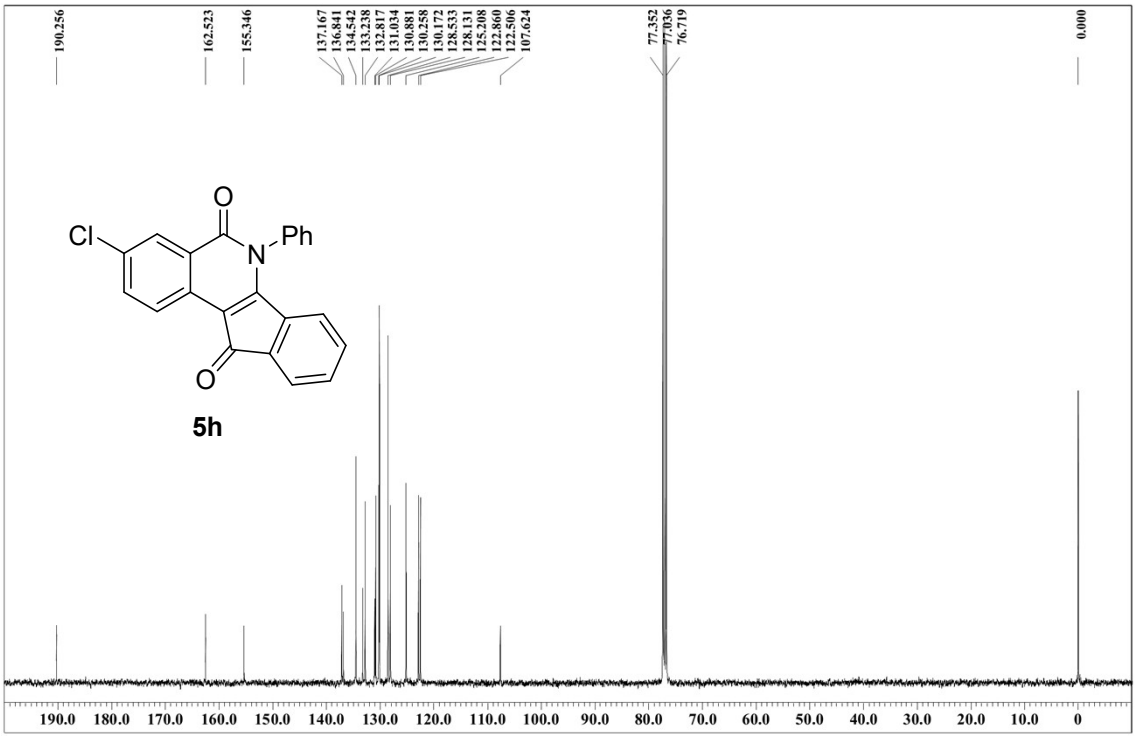
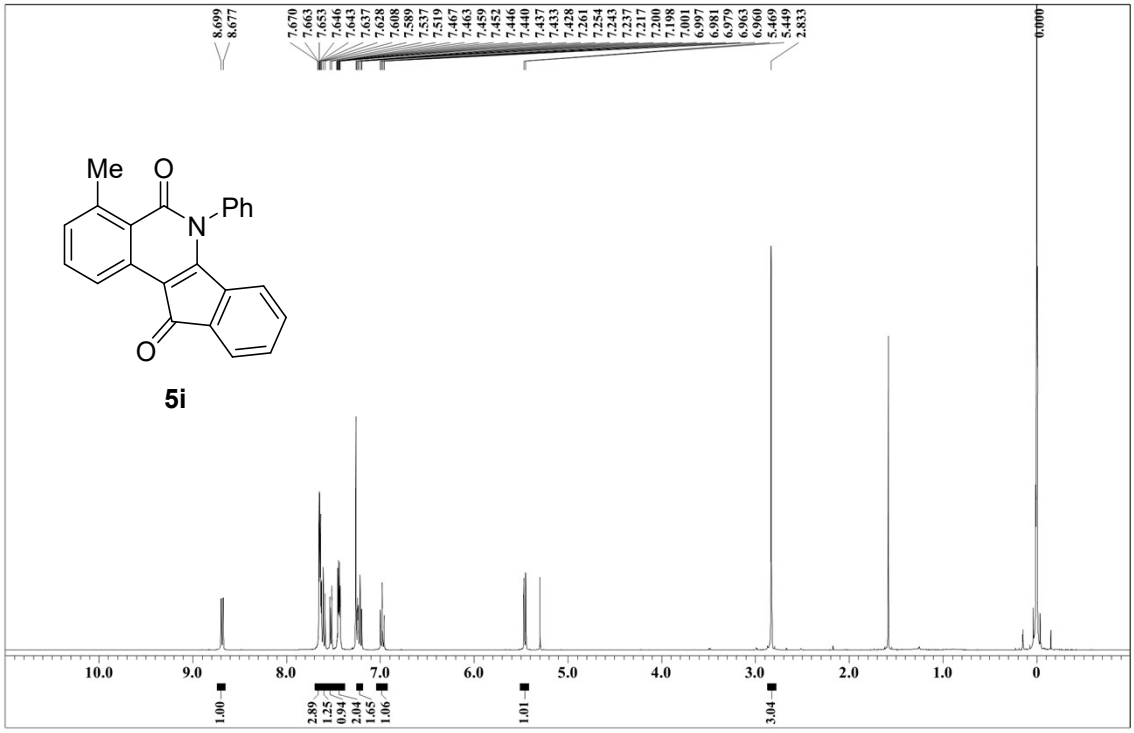


Figure S24. The ^{1}H and ^{13}C NMR Spectra of **5i**



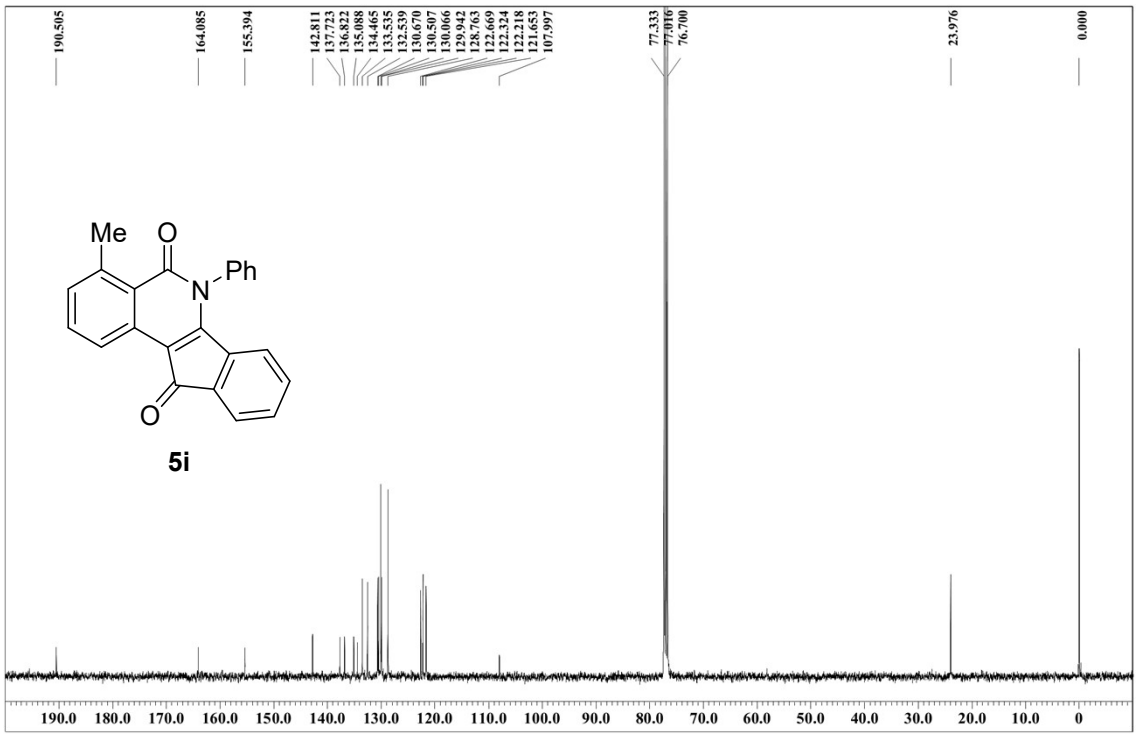
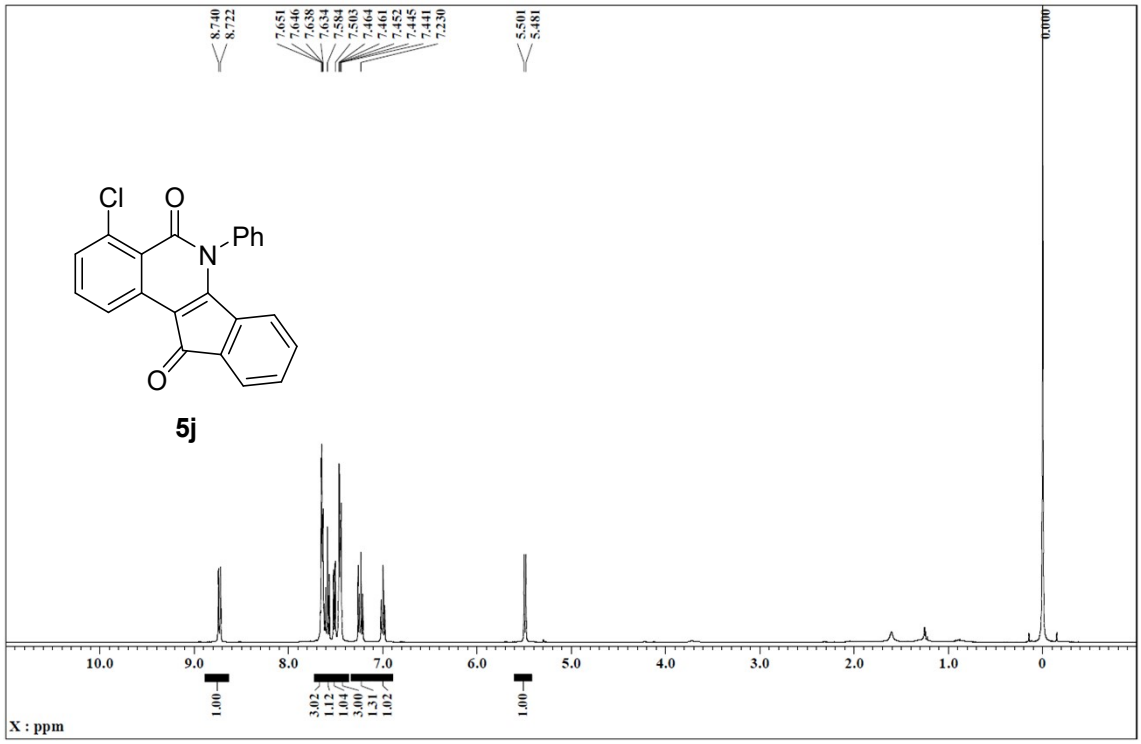


Figure S25. The ^{1}H and ^{13}C NMR Spectra of **5j**



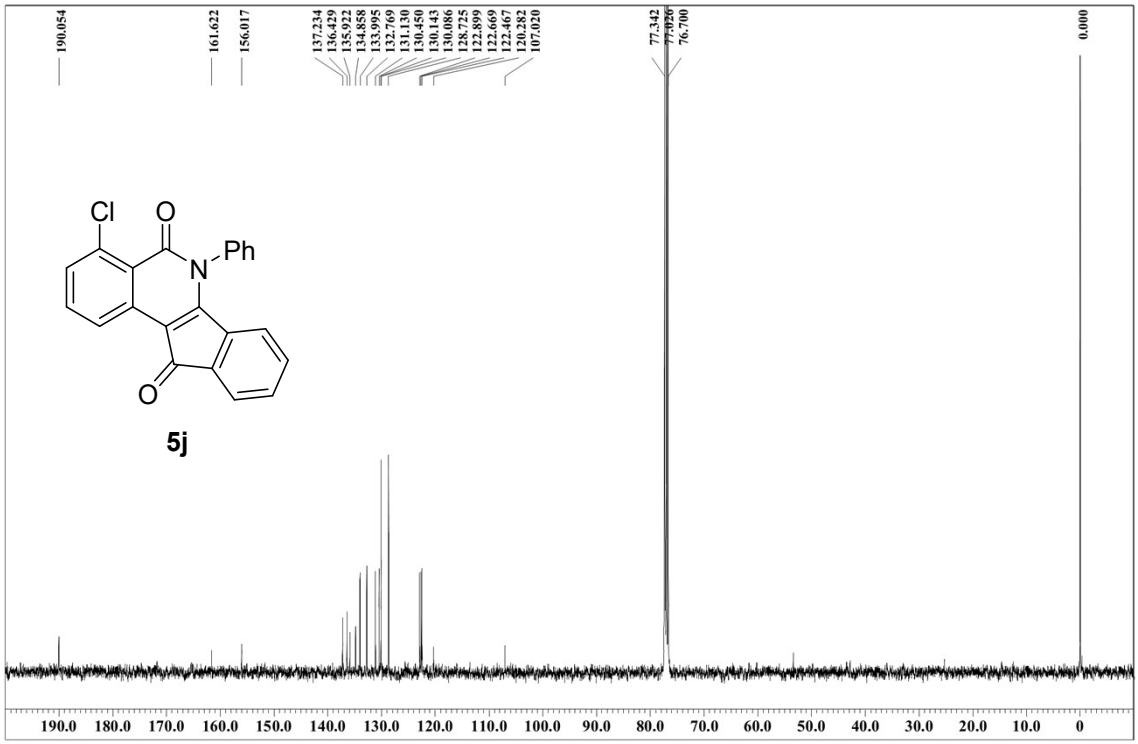
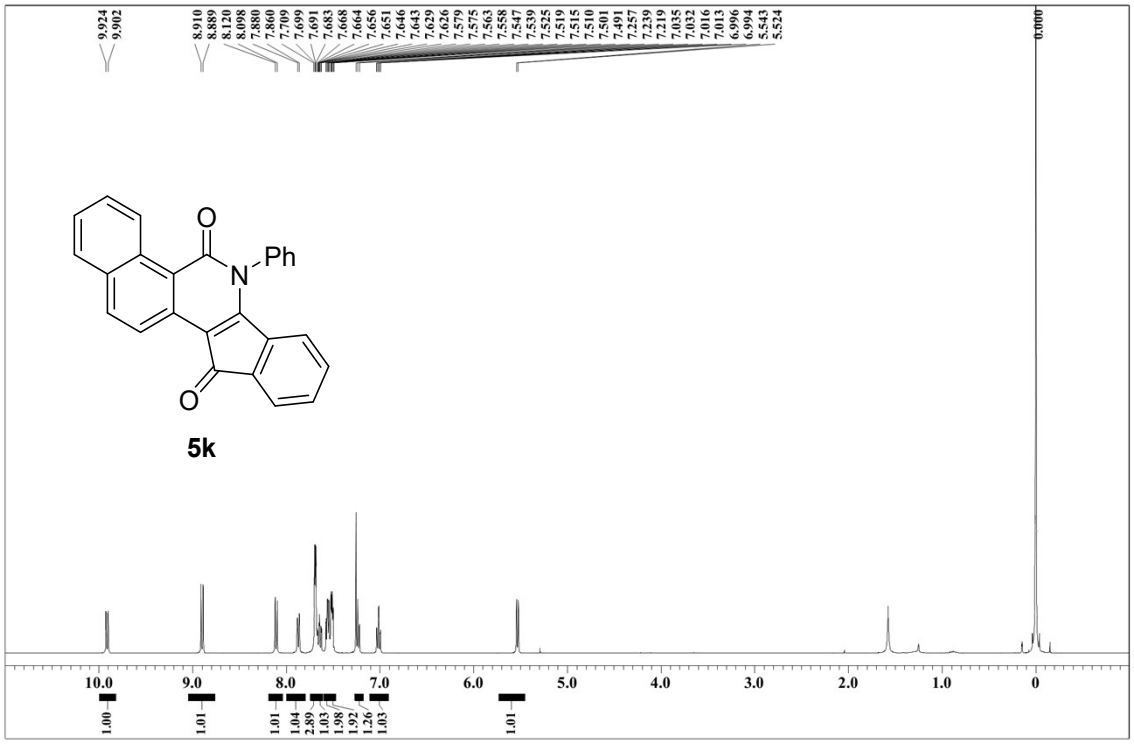


Figure S26. The ^{1}H and ^{13}C NMR Spectra of **5k**



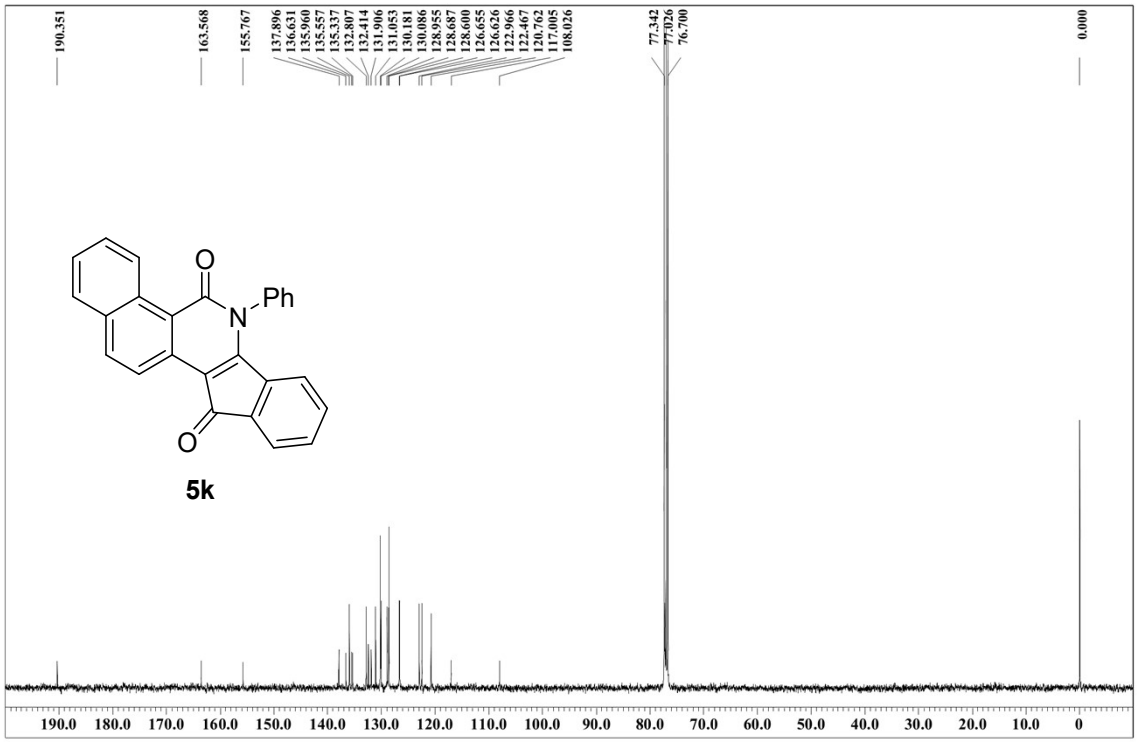
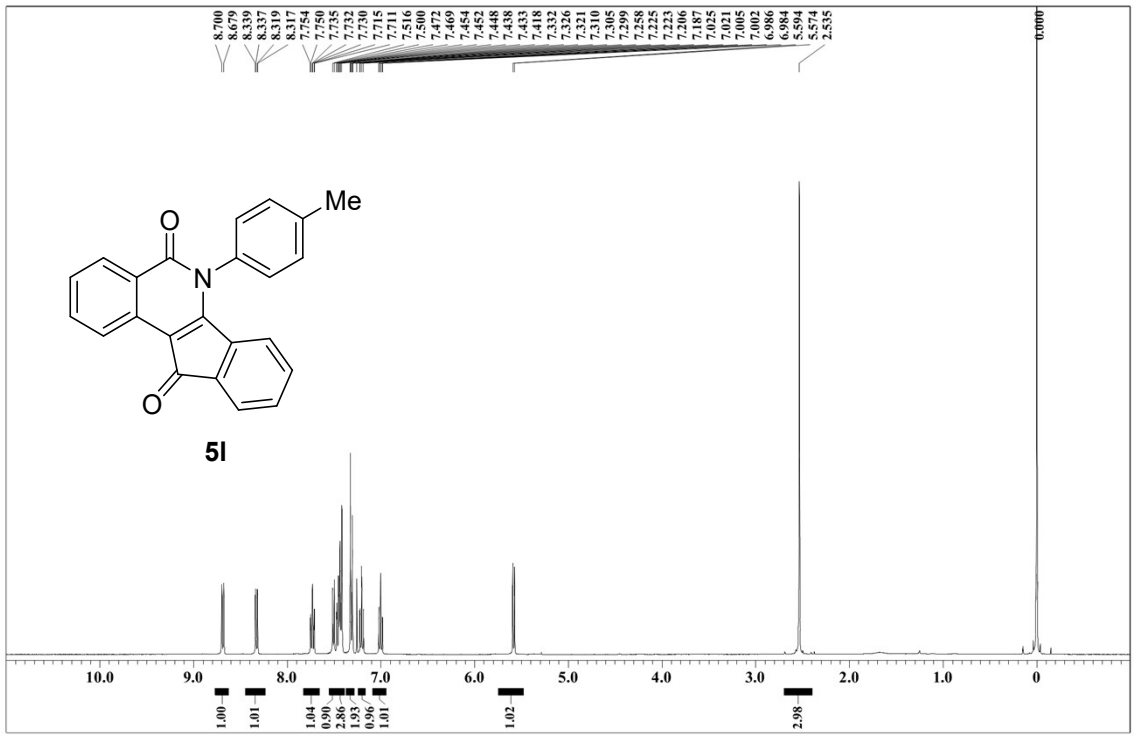


Figure S27. The ^{1}H and ^{13}C NMR Spectra of **5l**



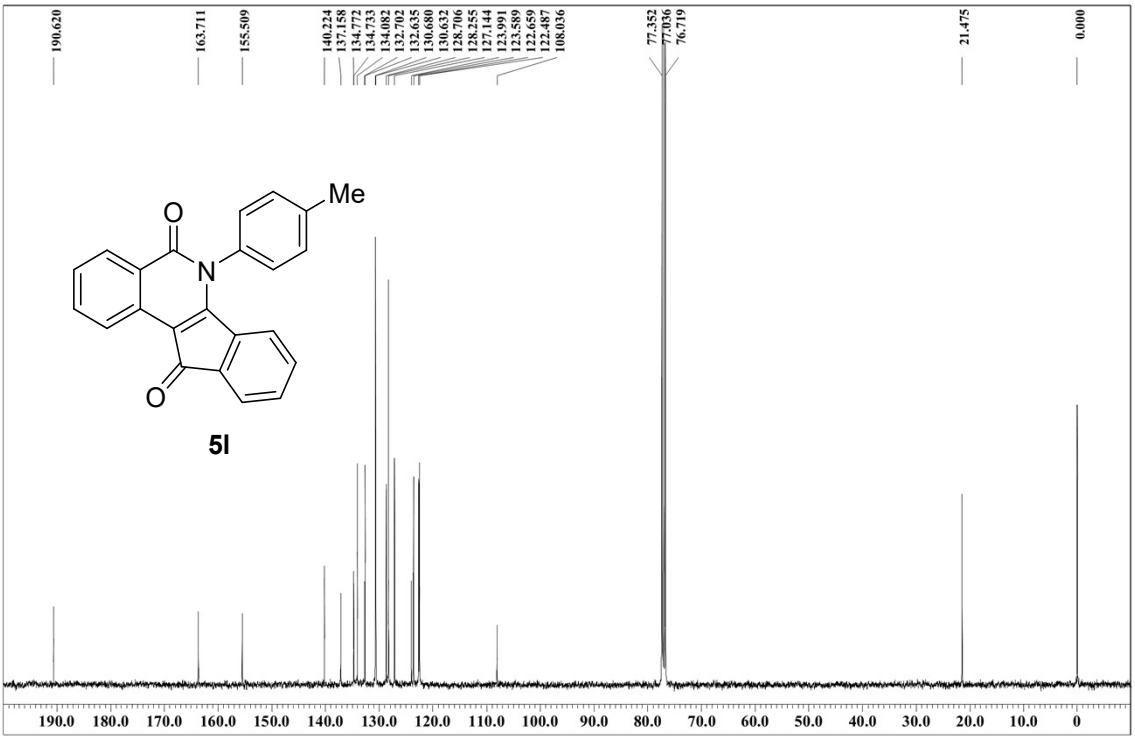


Figure S28. The ^{1}H and ^{13}C NMR Spectra of **5m**

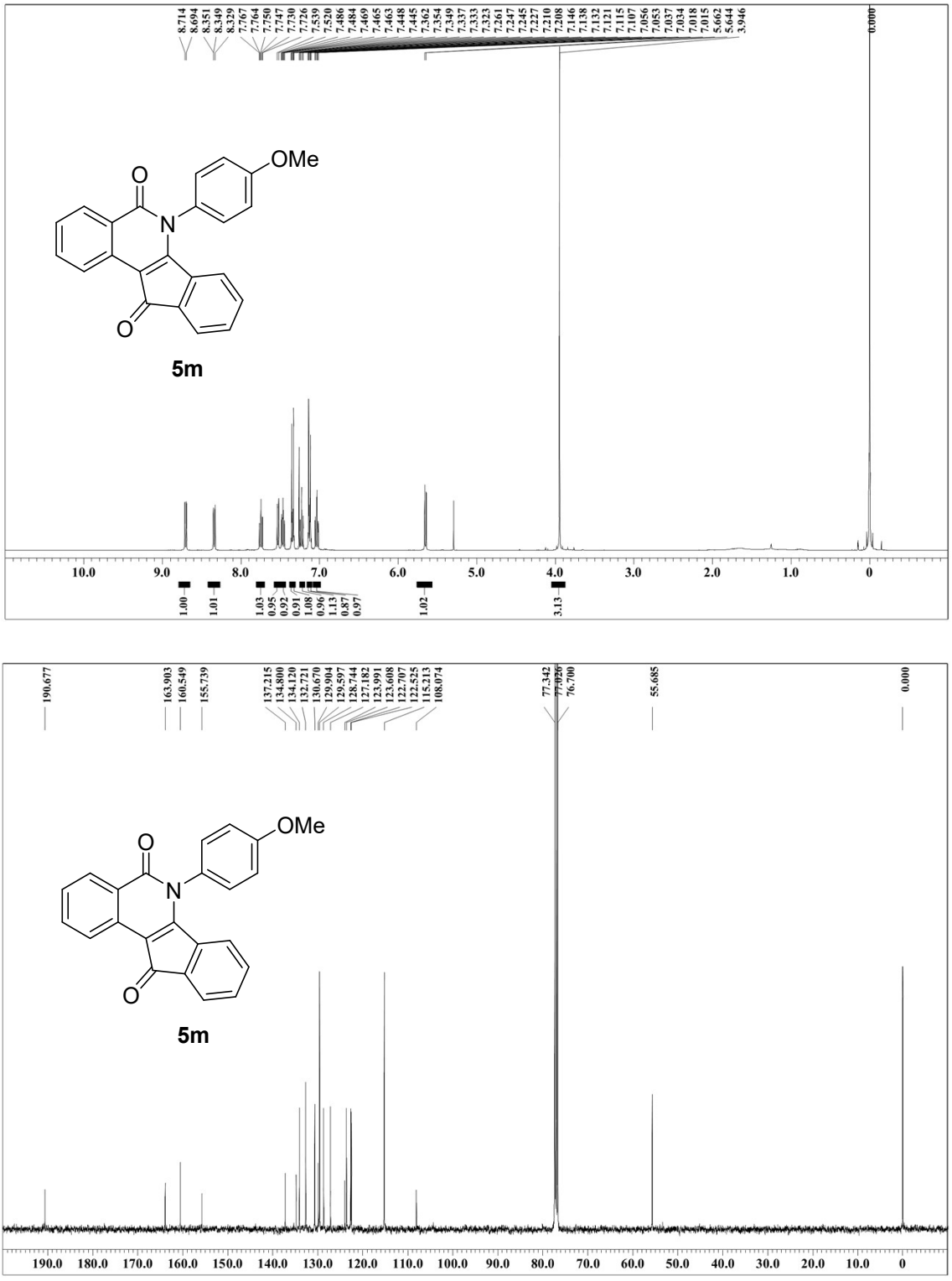
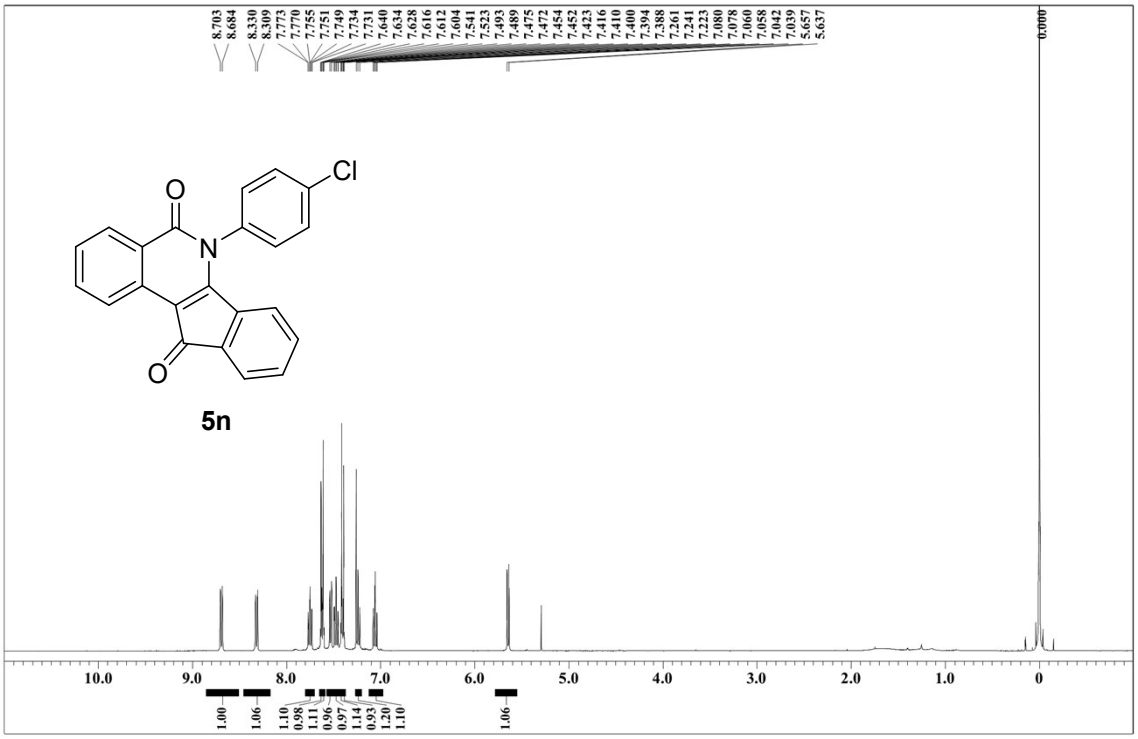


Figure S29. The ^{1}H and ^{13}C NMR Spectra of **5n**



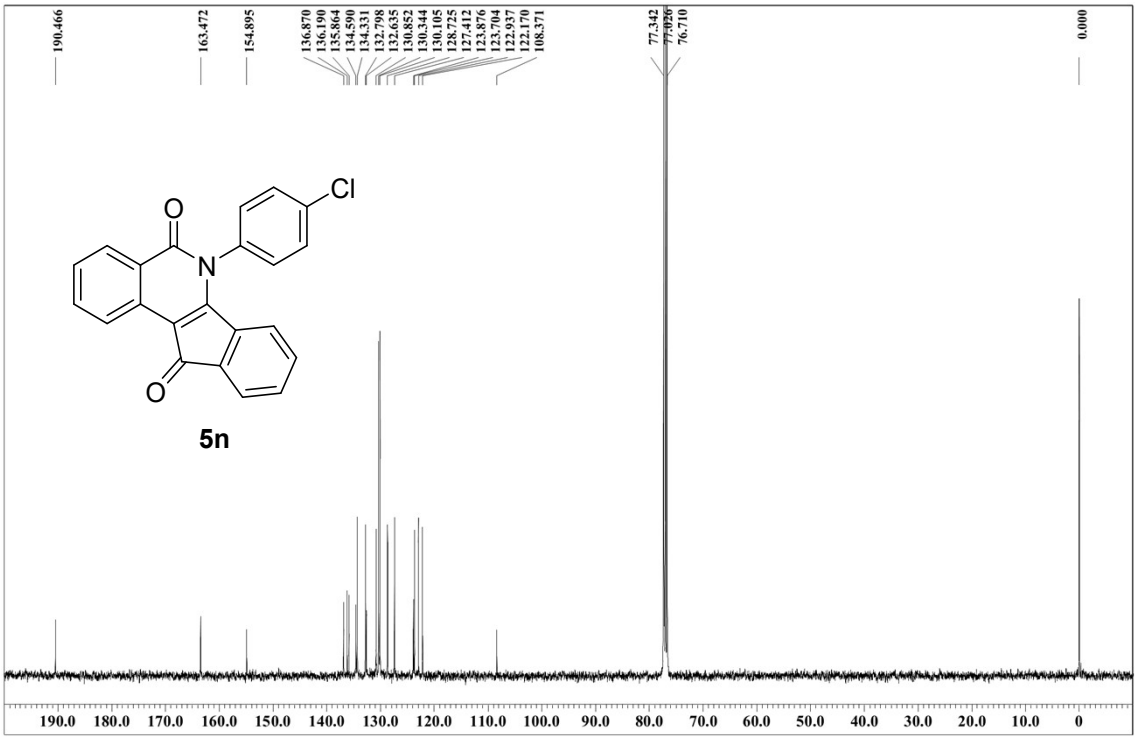
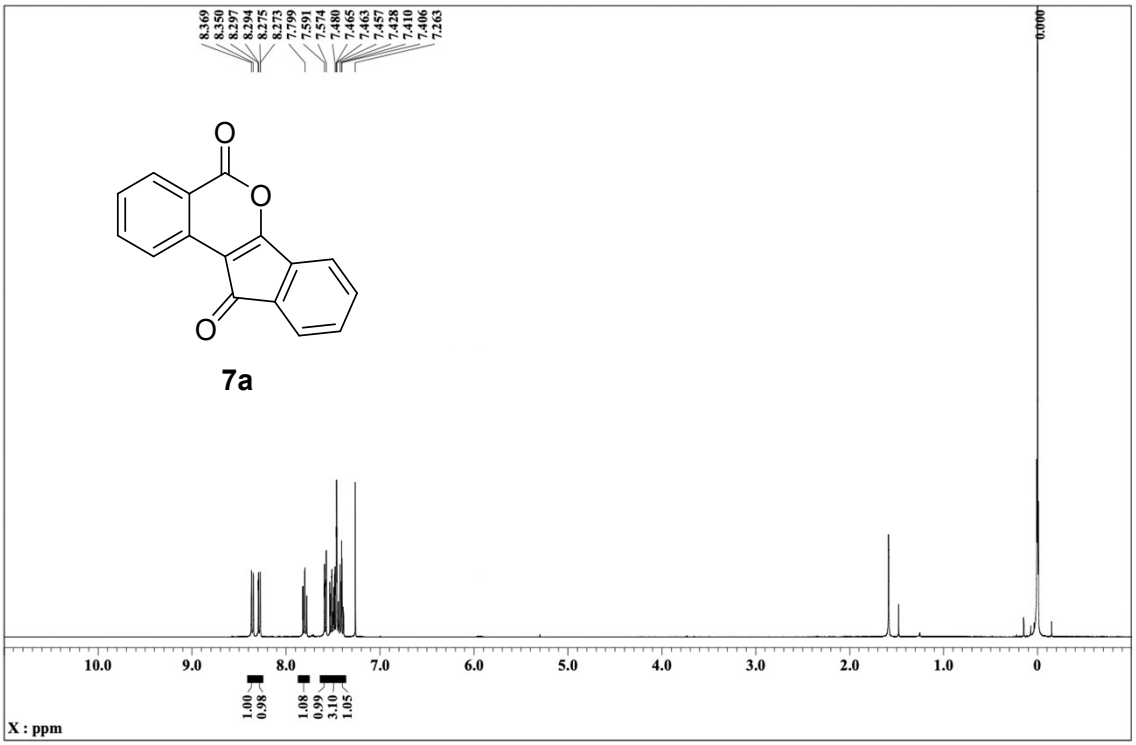


Figure S30. The ^{1}H and ^{13}C NMR Spectra of **7a**



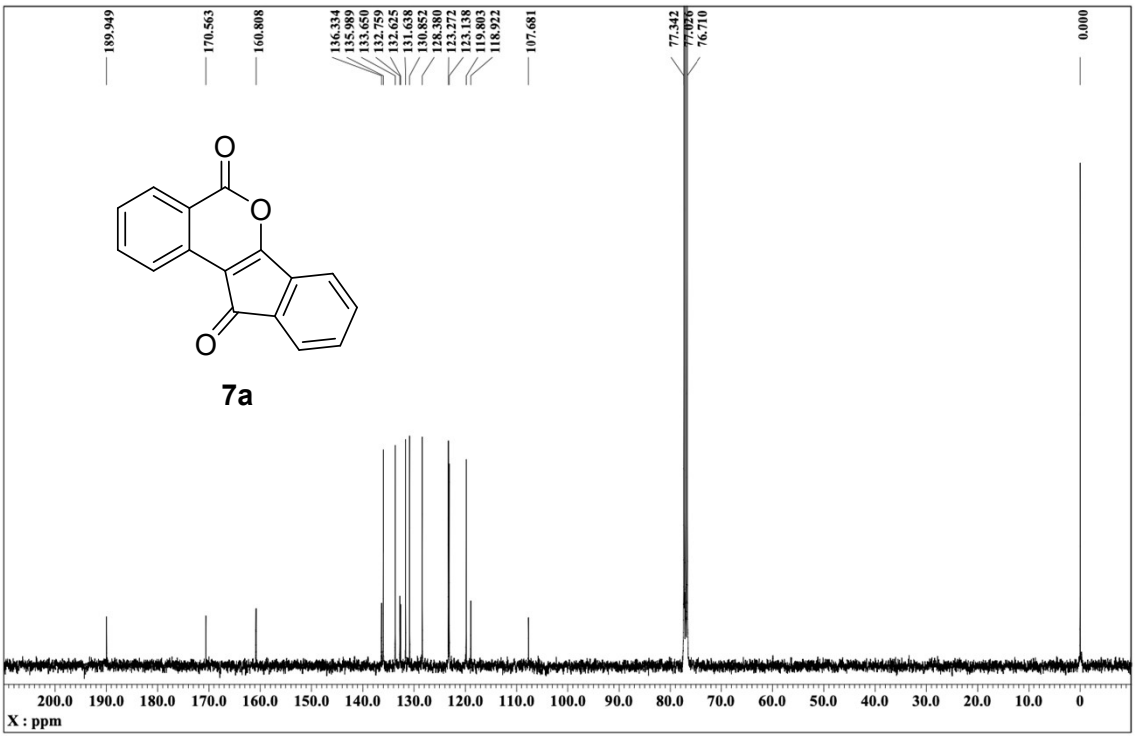
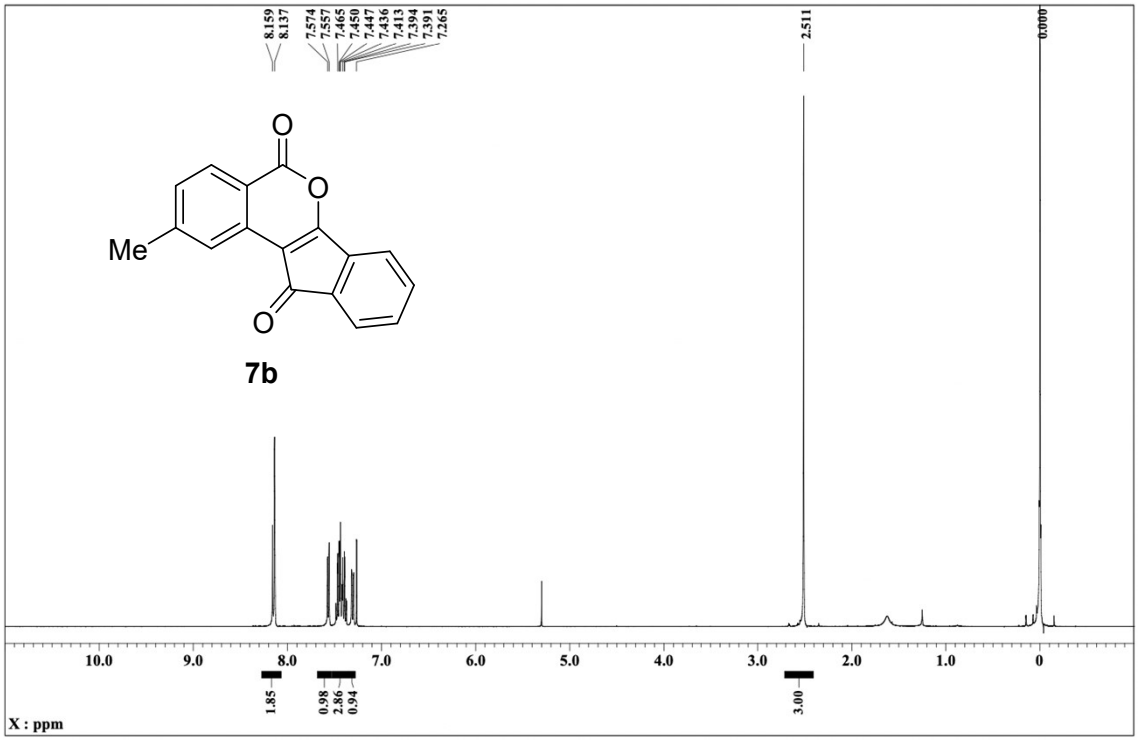


Figure S31. The ^{1}H and ^{13}C NMR Spectra of **7b**



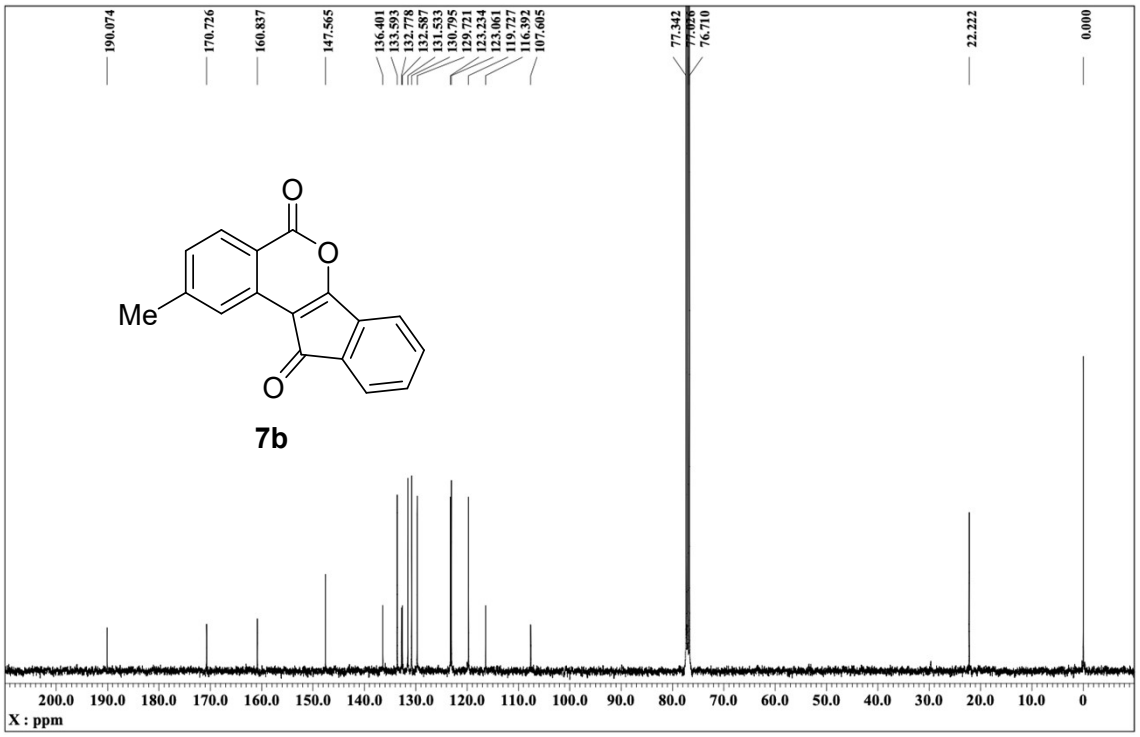
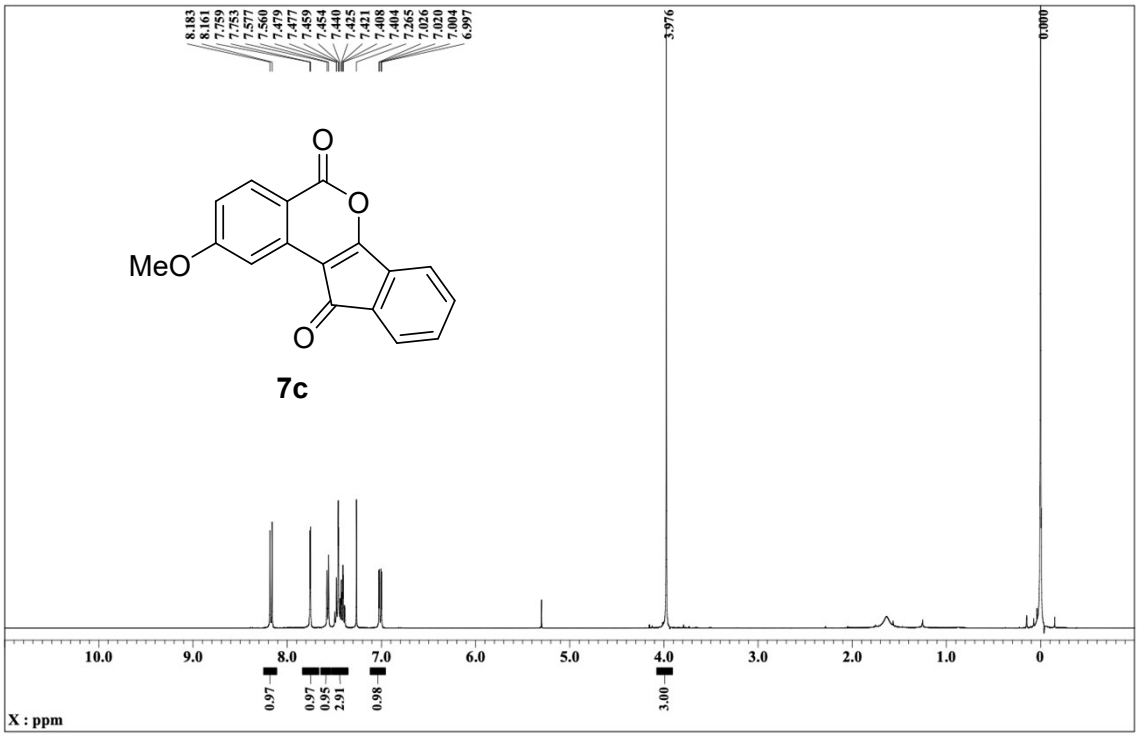


Figure S32. The ^{1}H and ^{13}C NMR Spectra of **7c**



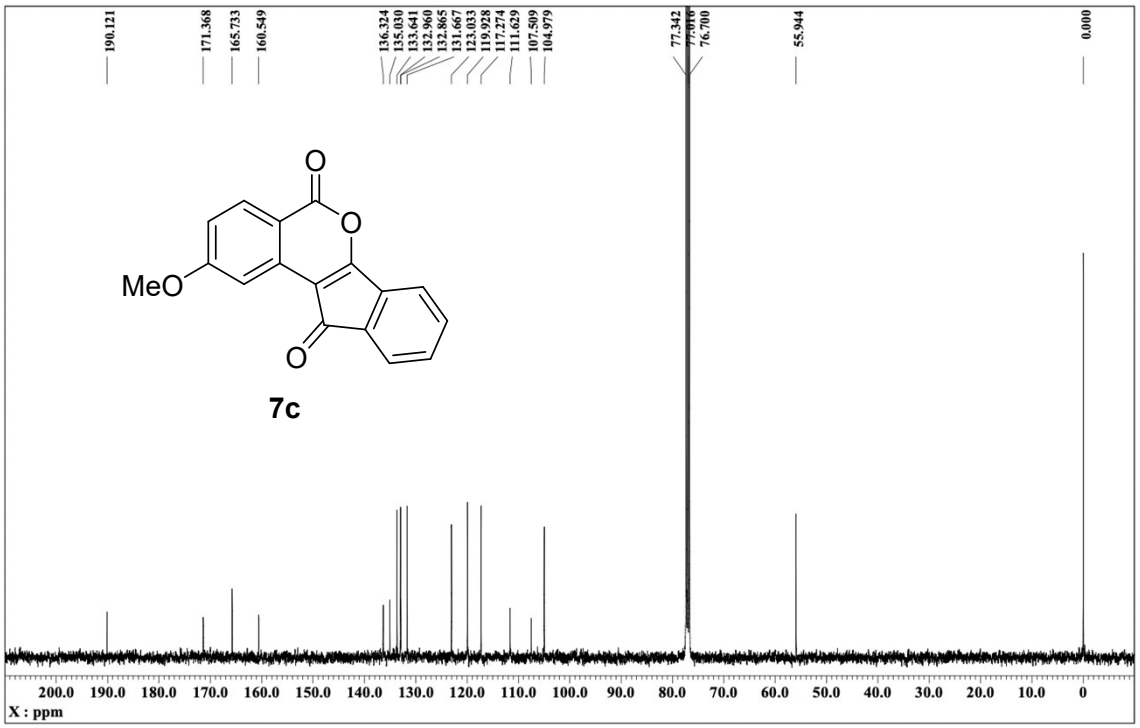
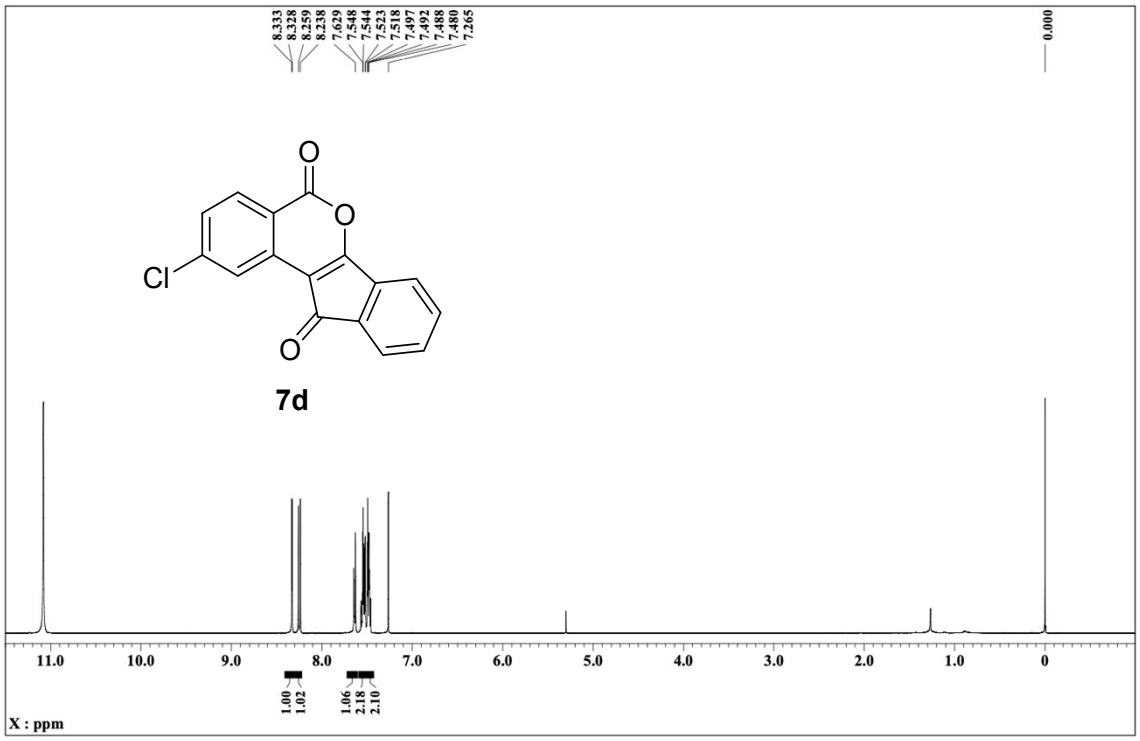


Figure S33. The ^{1}H and ^{13}C NMR Spectra of **7d**



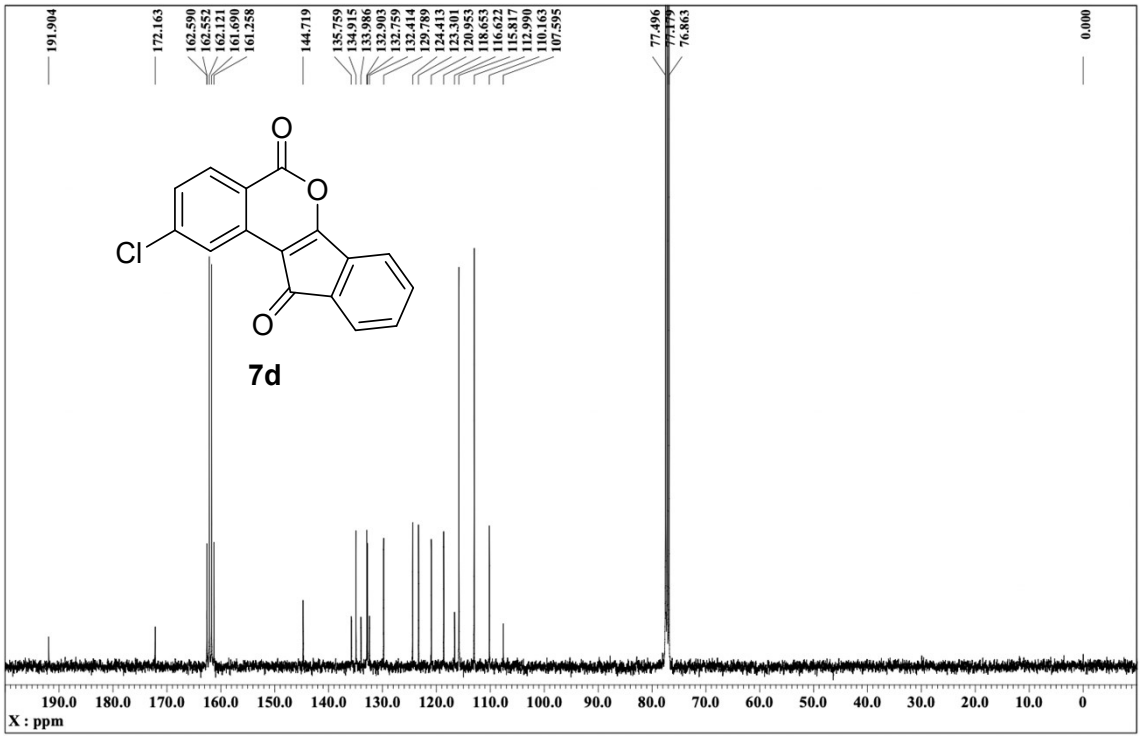
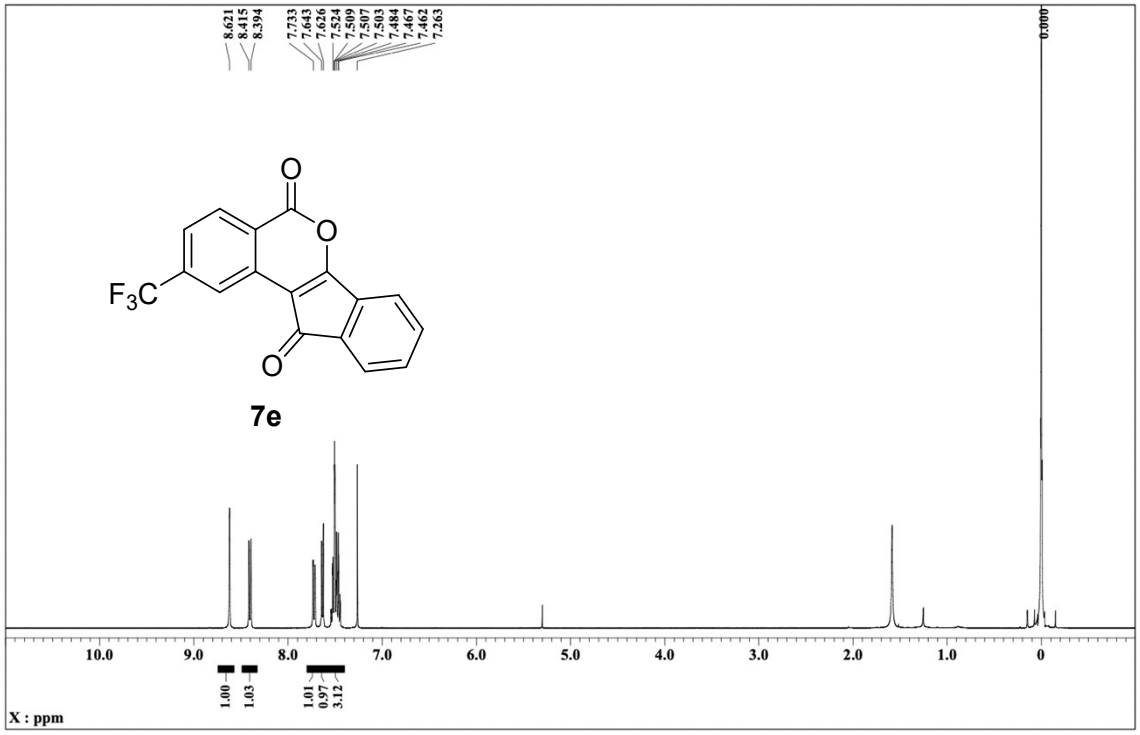


Figure S34. The ^{1}H and ^{13}C NMR Spectra of **7e**



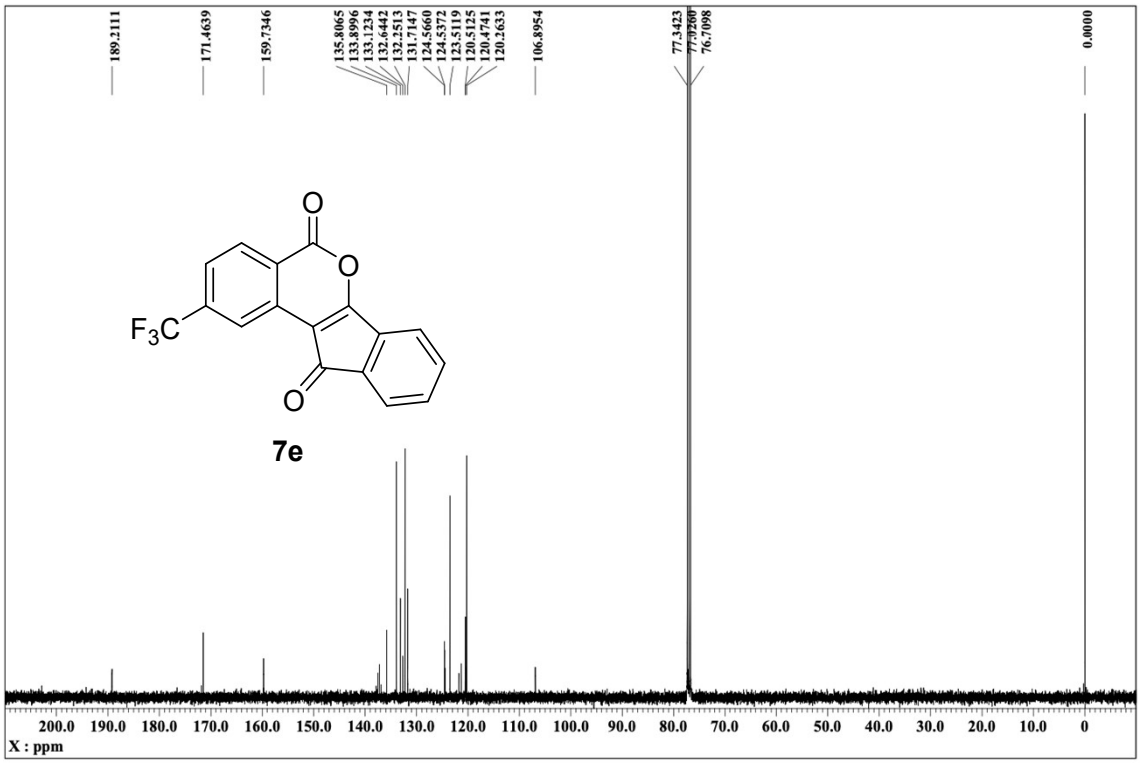
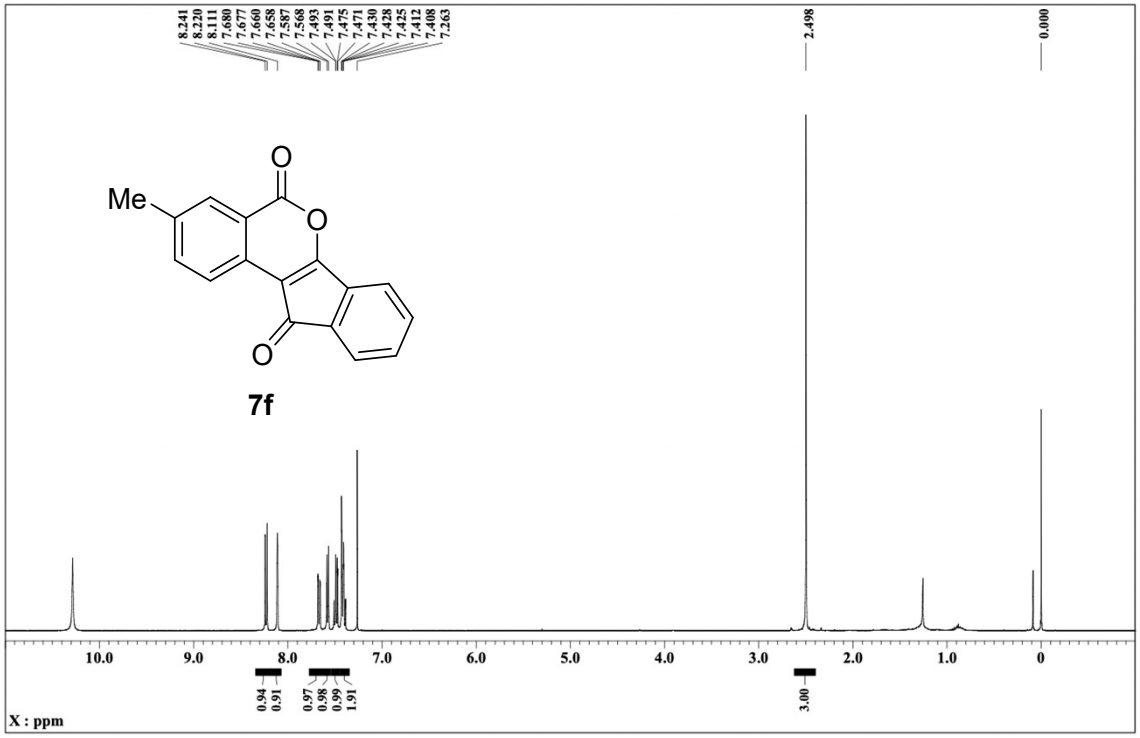


Figure S35. The ^{1}H and ^{13}C NMR Spectra of **7f**



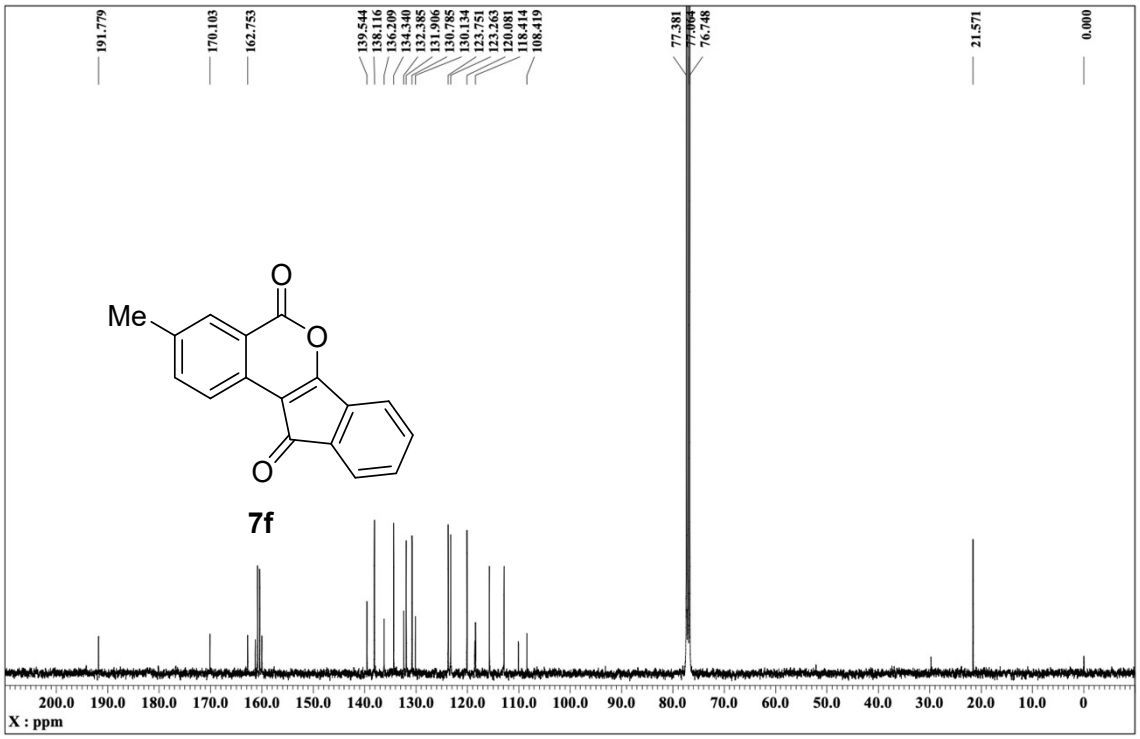
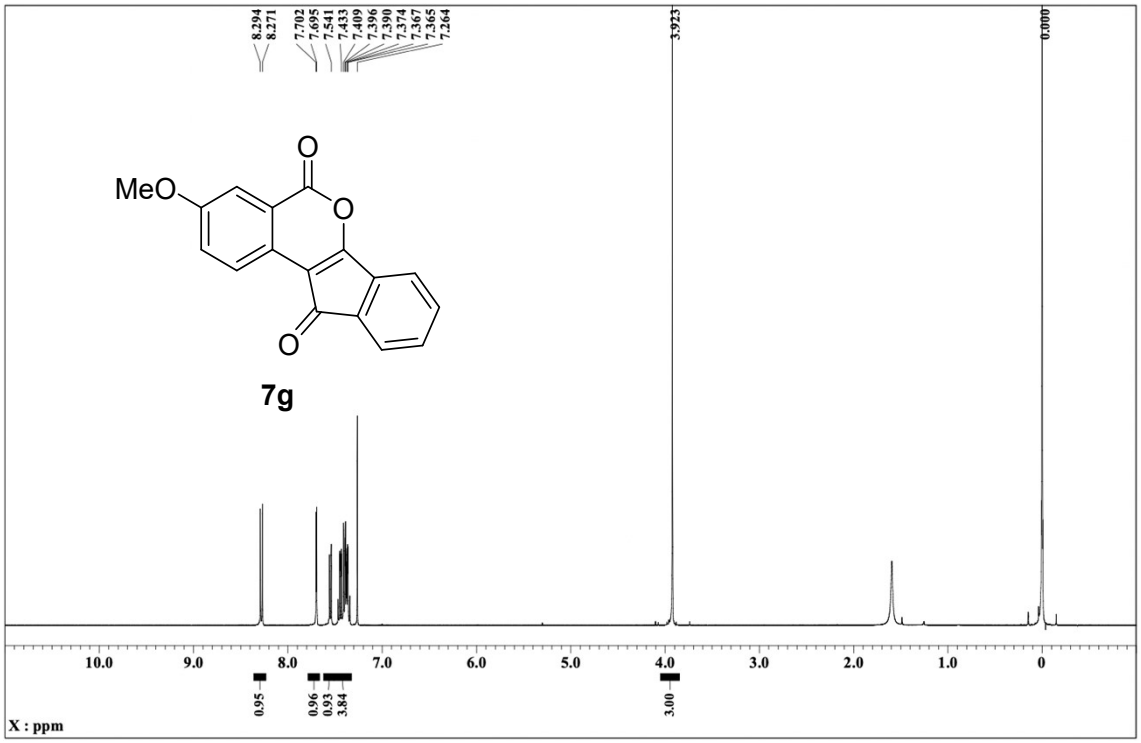


Figure S36. The ^{1}H and ^{13}C NMR Spectra of **7g**



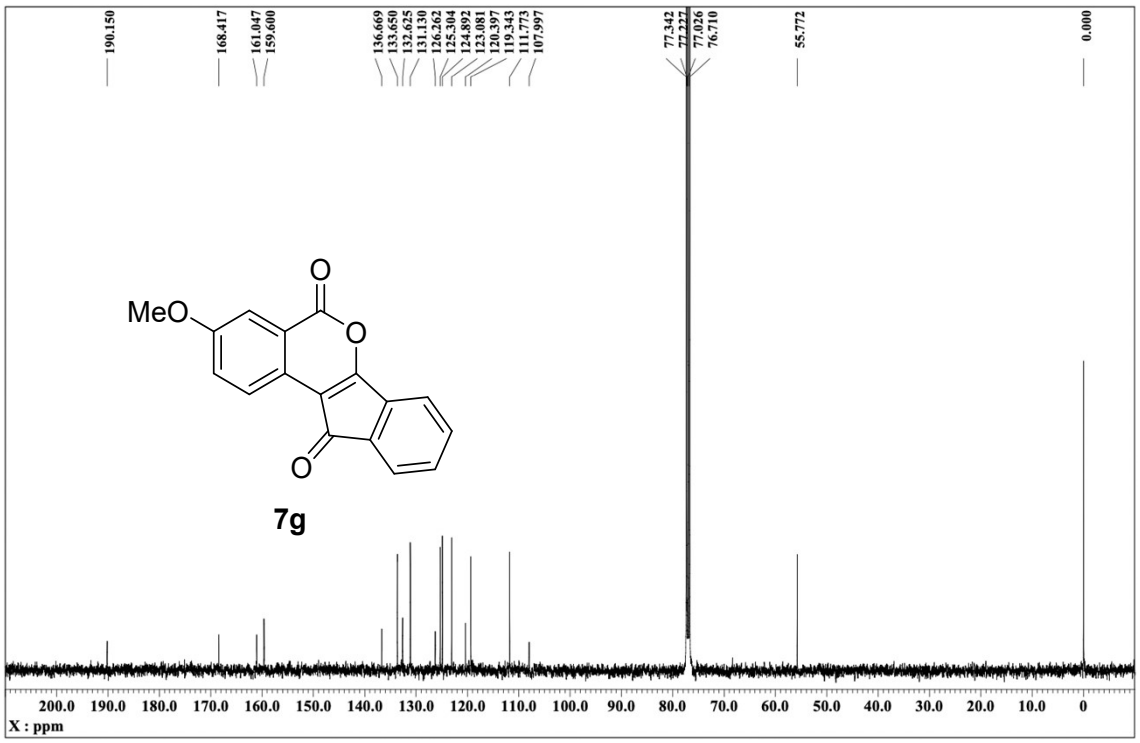
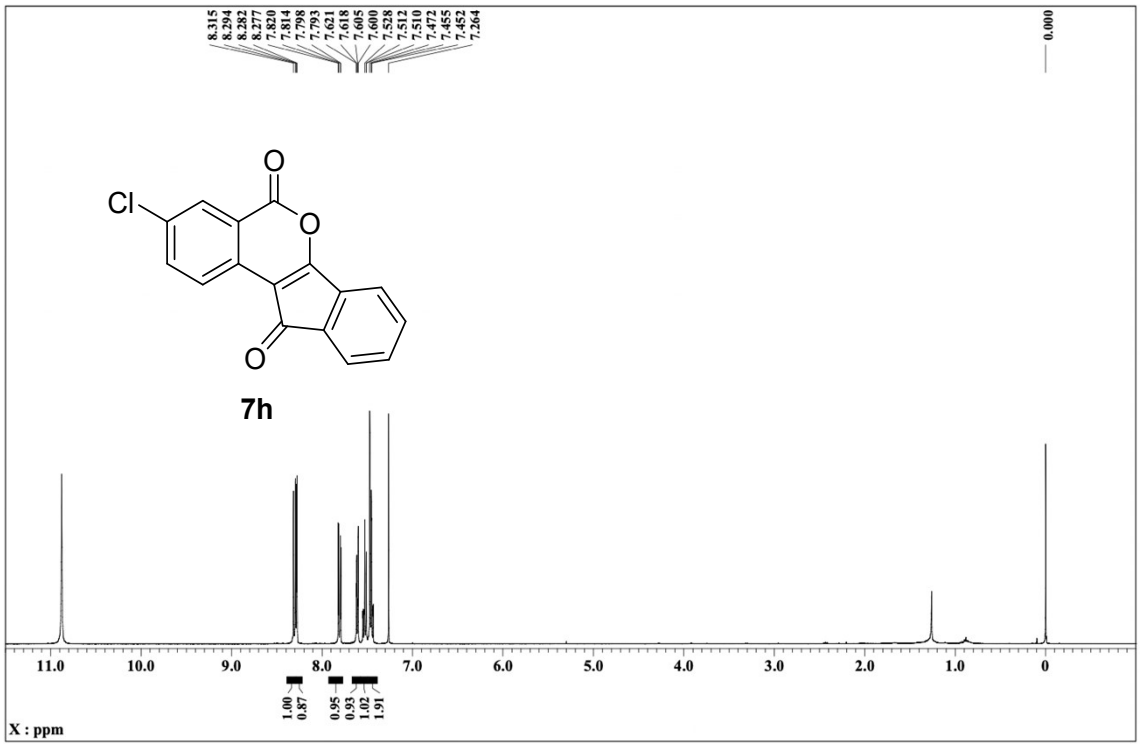


Figure S37. The ^{1}H and ^{13}C NMR Spectra of **7h**



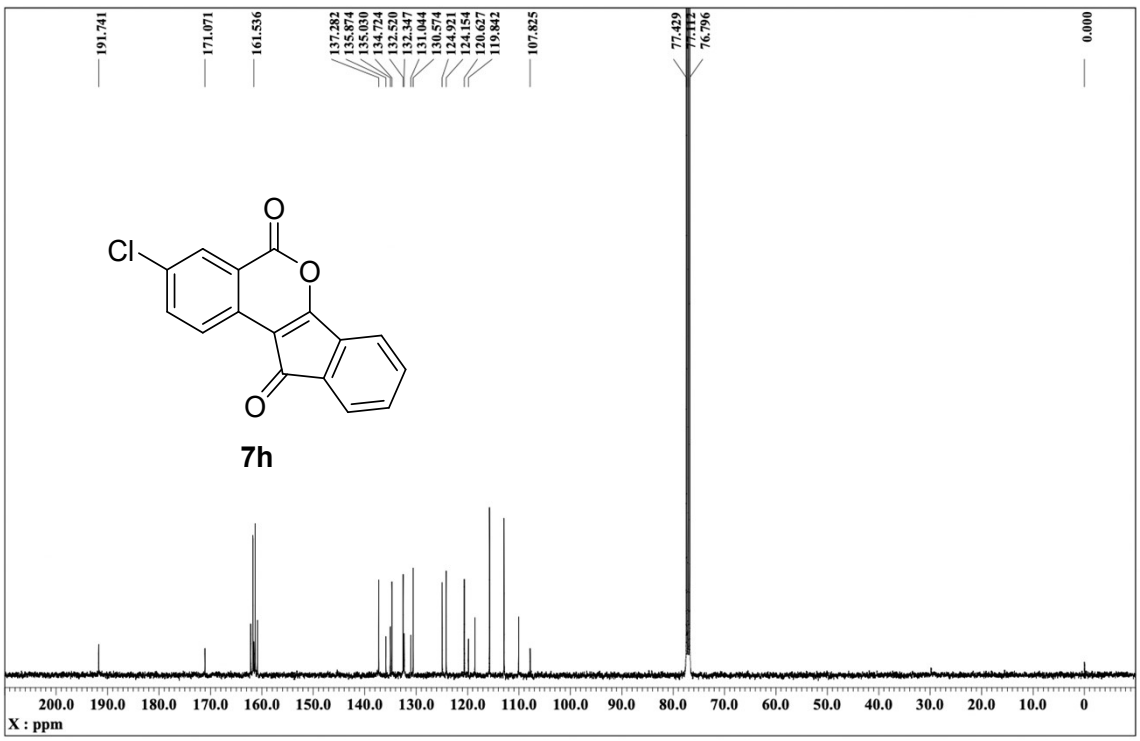
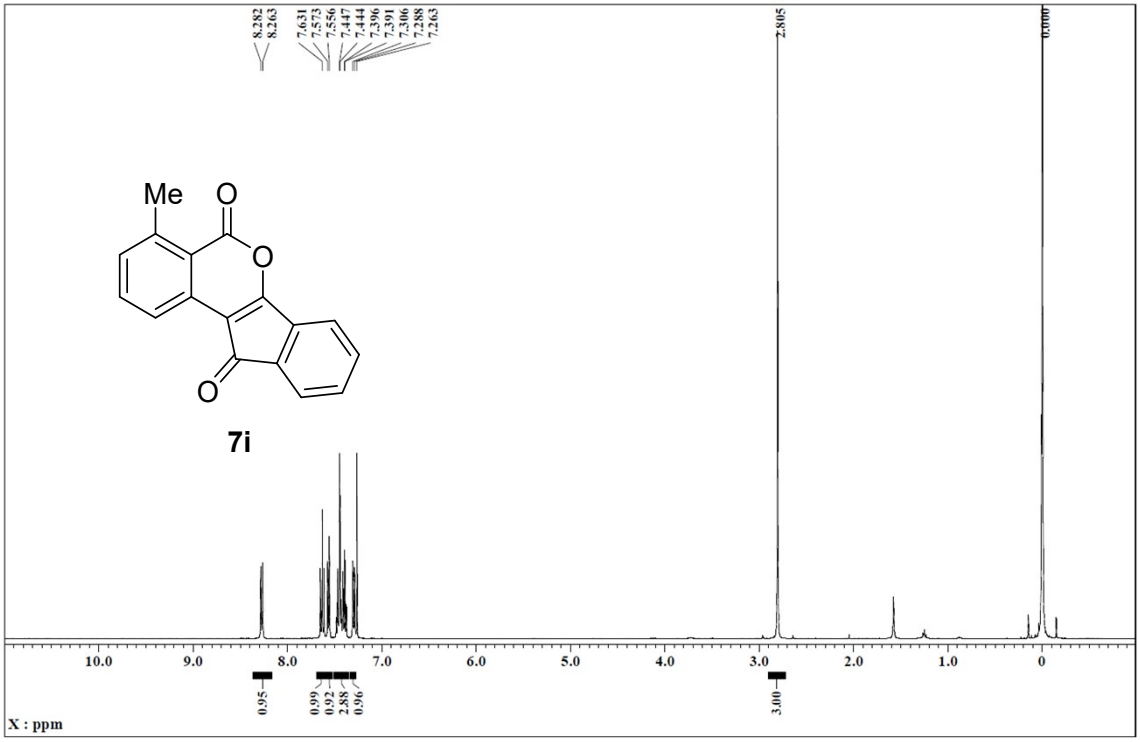


Figure S38. The ^{1}H and ^{13}C NMR Spectra of **7i**



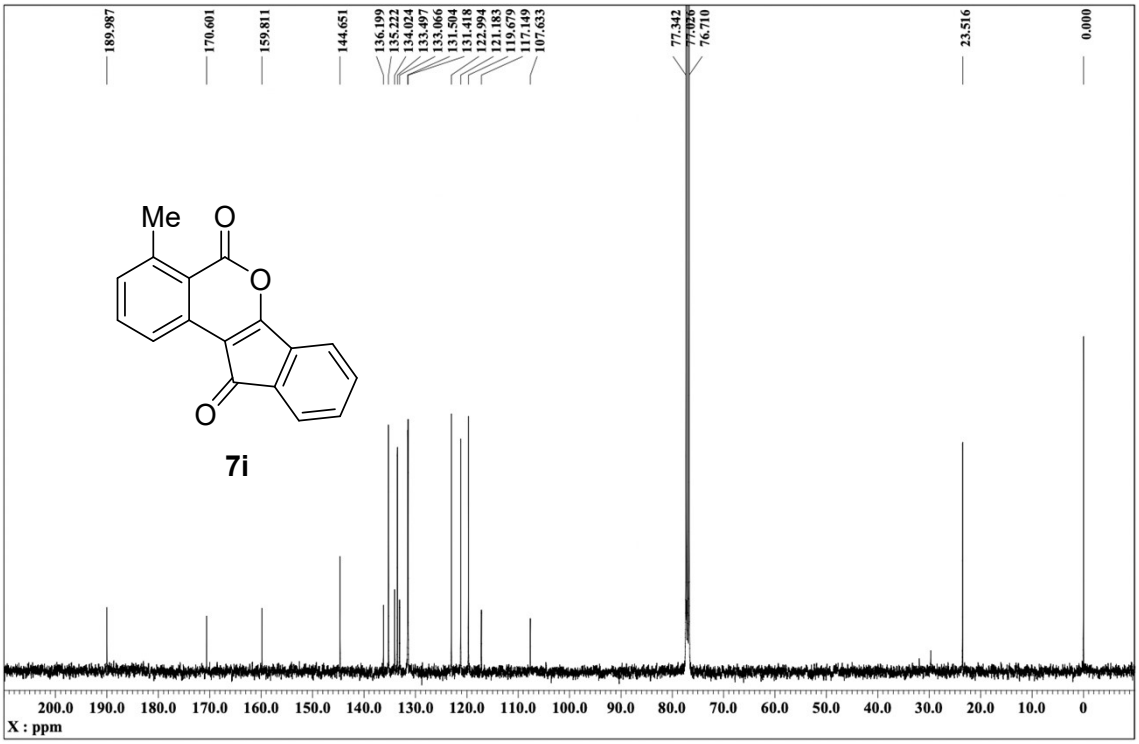
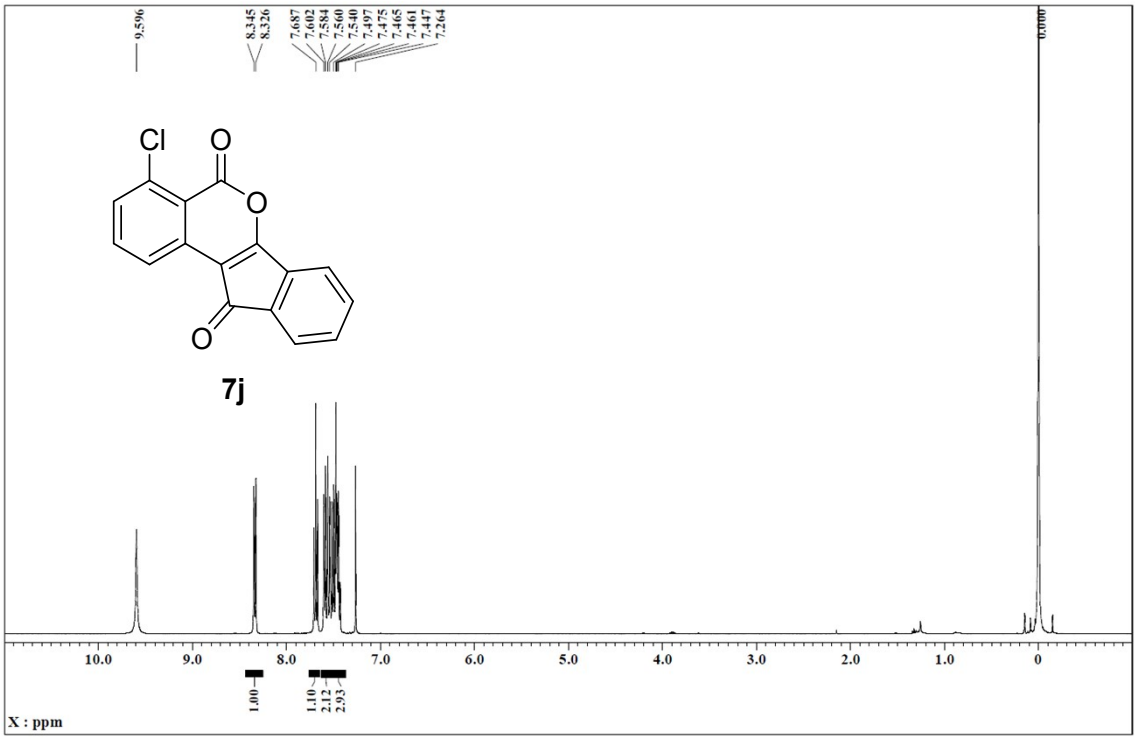


Figure S39. The ^{1}H and ^{13}C NMR Spectra of **7j**



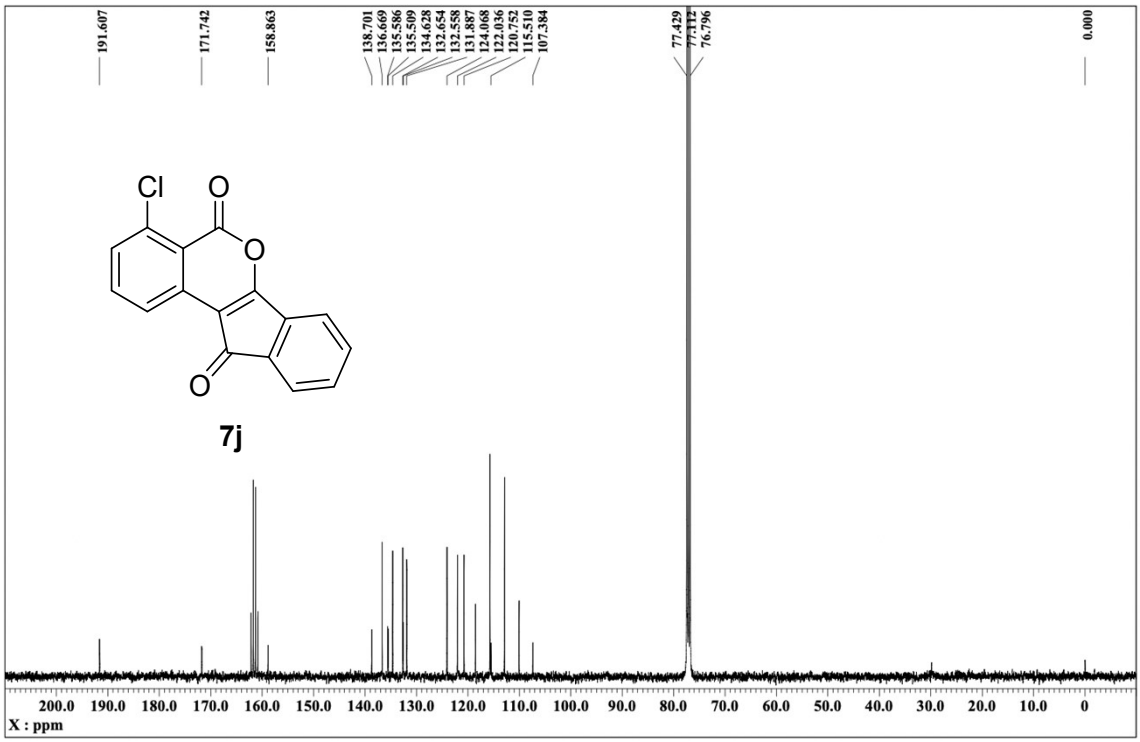
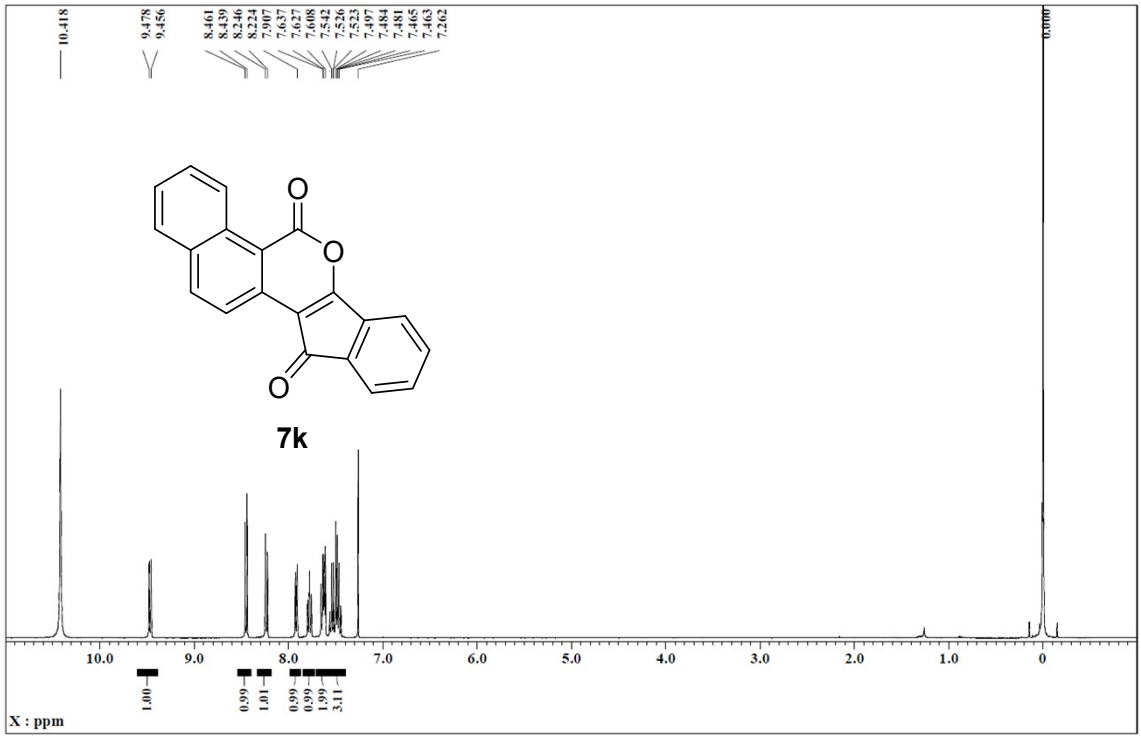
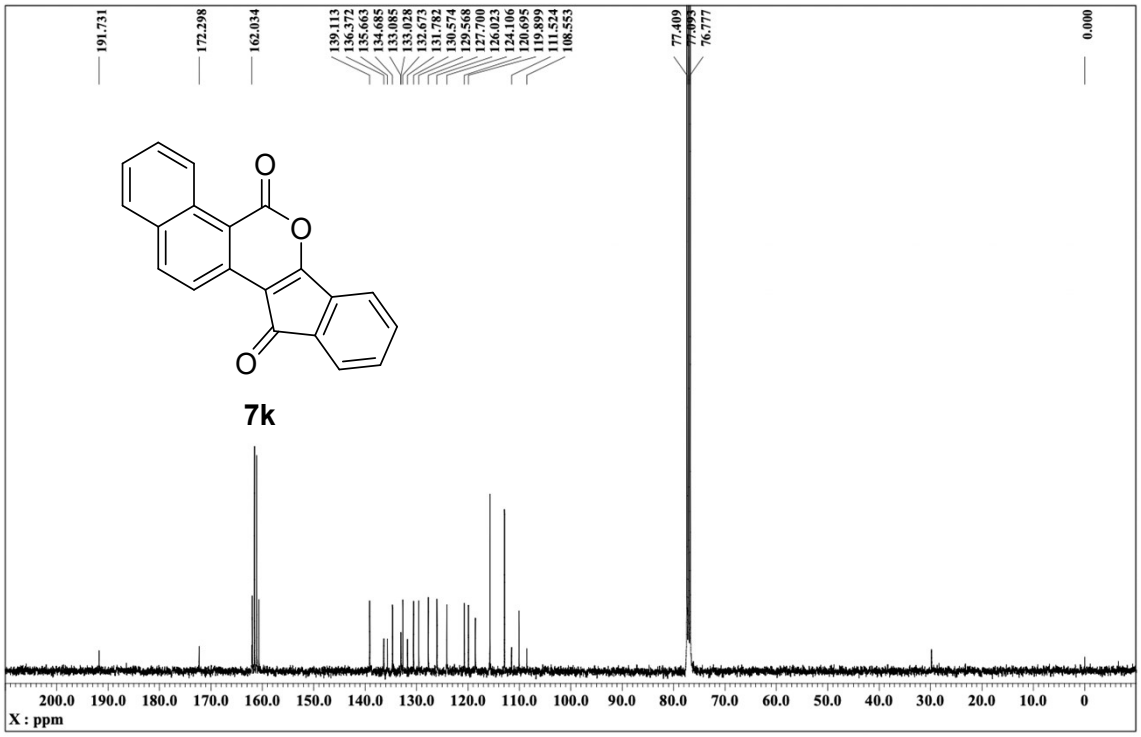


Figure S40. The ^{1}H and ^{13}C NMR Spectra of **7k**





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