

(91 pages)
Supporting Information For

**Cp*Co(III)-Catalyzed C-H Functionalization/Spiroannulations Synthesis of
Spiroindenes from 1,3-indandione with Alkenes**

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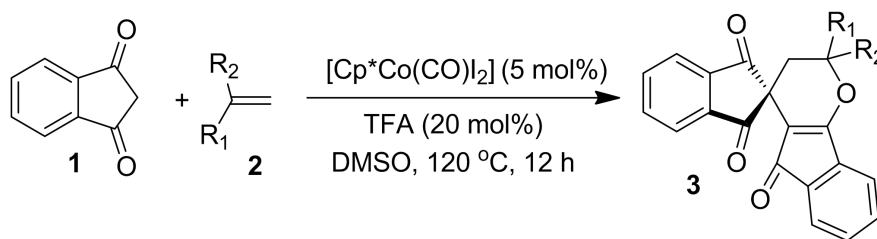
Table of Contents

General methods and materials.....	2
General catalytic procedure for Co(III)-catalyzed Synthesis of Spiroindenes from 1,3-indandione with Alkenes.....	3
Procedure Gram-scale for the Synthesis of 3a	4
Procedure Gram-scale for the Synthesis of 4a	5
Control experiments.....	6-13
X-Ray Crystallographic Data.....	14
Characterization data for the products.....	15-37
References.....	38
Copies of ¹ H and ¹³ C NMR spectra of products.....	39-91

General Methods and Materials

Co(acac)₃, Co(acac)₂, Co(OAc)₂·4H₂O, CoI₂, [Cp*RhCl₂]₂, [Ru(*p*-cymene)Cl₂]₂, [IrCp*Cl₂]₂ and Pd(OAc)₂ were purchased from Energy Chemical and used without further purification. The cobalt catalyst Cp*CoI₂(CO) was synthesized according to previously described methods^[1]. Other chemicals were purchased from commercial suppliers, further dried and purified if necessary. ¹H and ¹³C NMR spectra were achieved on a Bruker AVANCE 400 MHz spectrometer (¹H 400 MHz; ¹³C 100 MHz) in CDCl₃. Abbreviations for data quoted are *s*-singlet; *brs*-broad singlet; *d*-doublet; *t*-triplet; *dd*-doublet of doublets; *m*-multiplet. High-resolution mass spectrometry (HRMS) was performed with a TOF MS instrument with an ESI source. Thin-layer chromatographies were done on pre-coated silica gel 60F254 plates (Merck). Silica gel 60H (200-300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China) was used for general chromatography.

General catalytic procedure for Co(III)-catalyzed Synthesis of Spiroindenes from 1,3-indandione with Alkenes.



A reaction flask (25 mL) was charged with 1,3-indandione **1** (0.2 mmol, 1.0 equiv), alkenes **2** (0.2 mmol, 2.0 equiv), [Cp*CoI₂(CO)] (4.8 mg, 5.0 mol %), TFA (0.02 mmol), then the DMSO (3 mL) was added. The mixture was stirred at 120 °C for 12 hours under an atmosphere of air. After the reaction finished, the resulted mixtures were diluted with 20 mL of dichloromethane and washed with 20 mL of H₂O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na₂SO₄. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 10 : 1 - 5 : 1) to yield product.

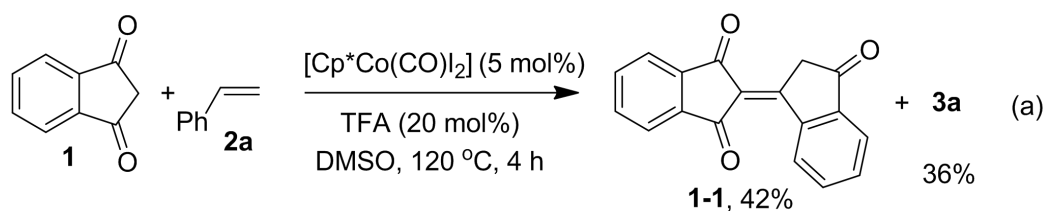
Procedure Gram-scale for the Synthesis of **3a**

A reaction flask (250 mL) was charged with 1,3-indandione **1** (10.0 mmol, 1.0 equiv), styrene **2** (10.0 mmol, 2.0 equiv), [Cp*CoI₂(CO)] (240.0 mg, 5.0 mol %), TFA (1.0 mmol), then the DMSO (100 mL) was added. The mixture was stirred at 120 °C for 12 hours under an atmosphere of air. After the reaction finished, the resulted mixtures were diluted with 100 mL of dichloromethane and washed with 100 mL of H₂O. The aqueous layer was extracted twice with dichloromethane (50 mL) and the combined organic phase was dried over Na₂SO₄. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 10 : 1) to yield product of **3a** (79% yield, 1548.2 mg).

Procedure Gram-scale for the Synthesis of **4a**

A reaction flask (250 mL) was charged with 1,3-indandione **1** (10.0 mmol, 1.0 equiv), prop-1-en-2-ylbenzene **2** (10.0 mmol, 2.0 equiv), [Cp*CoI₂(CO)] (240.0 mg, 5.0 mol %), TFA (1.0 mmol), then the DMSO (100 mL) was added. The mixture was stirred at 120 °C for 12 hours under an atmosphere of air. After the reaction finished, the resulted mixtures were diluted with 100 mL of dichloromethane and washed with 100 mL of H₂O. The aqueous layer was extracted twice with dichloromethane (50 mL) and the combined organic phase was dried over Na₂SO₄. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 10 : 1) to yield product of **4a** (74% yield, 1502.2 mg).

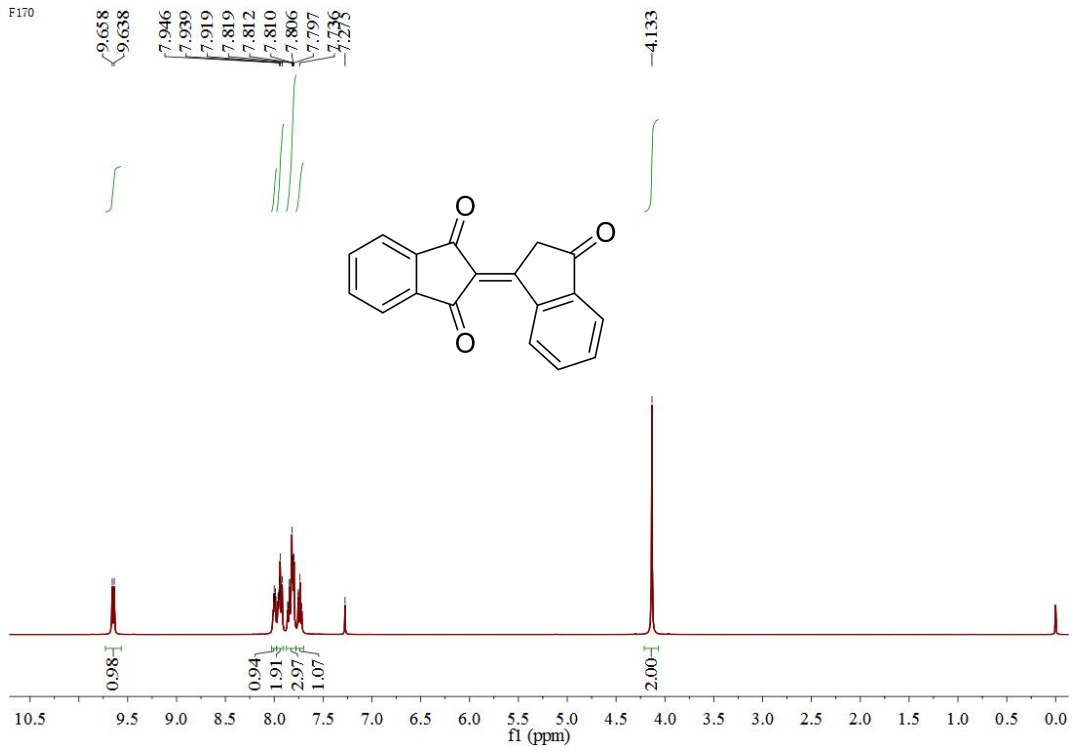
Control Experiments



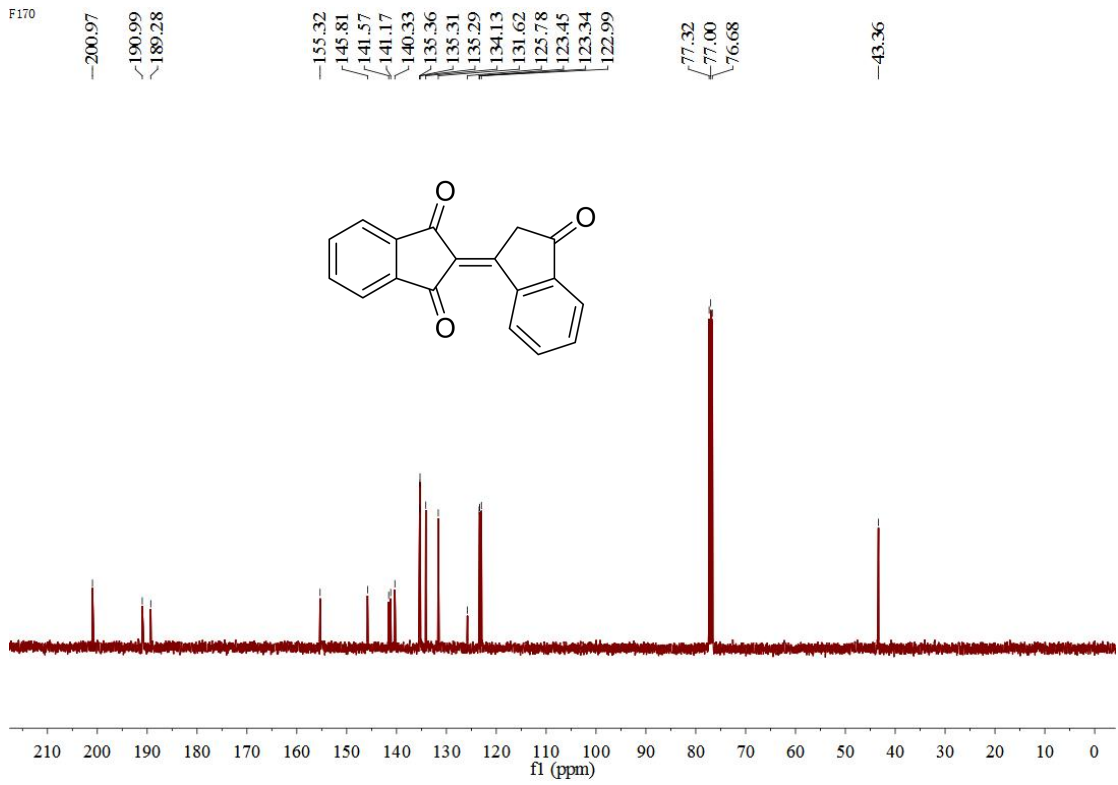
A reaction flask (25 mL) was charged with 1,3-indandione **1** (0.5 mmol, 1.0 equiv), alkenes **2** (0.5 mmol, 2.0 equiv), $[\text{Cp}^*\text{CoI}_2(\text{CO})]$ (12.0 mg, 5.0 mol %), TFA (0.05 mmol), then the DMSO (6 mL) was added. The mixture was stirred at 120 °C for 4 hours under an atmosphere of air. After the reaction finished, the resulted mixtures were diluted with 20 mL of dichloromethane and washed with 20 mL of H_2O . The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na_2SO_4 . After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 5 : 1 - 2 : 1) to yield product **3a** and **1-1** in 36%, and 42% yield, respectively.

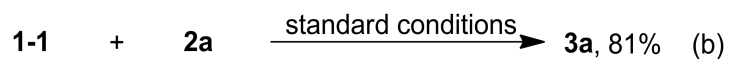
[1,2'-biindenylidene]-1',3,3'(2H)-trione (**1-1**): Obtained as a light yellow solid (57.5 mg, 42% yield); Melting point: 65 - 67 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ ppm: 9.65 (d, $J = 8.0$ Hz, 1H), 7.99 - 8.01 (m, 1H), 7.92 - 7.96 (m, 2H), 7.80 - 7.86 (m, 3H), 7.72 - 7.76 (m, 1H), 4.13 (s, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ ppm: 201.0, 191.0, 189.3, 155.3, 145.8, 141.6, 141.2, 140.3, 135.4, 135.31, 135.29, 134.1, 131.6, 125.8, 123.5, 123.3, 123.0, 43.4; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{18}\text{H}_{11}\text{O}_3$ $[\text{M} + \text{H}]^+$ 275.0703, found 275.0706.

F170

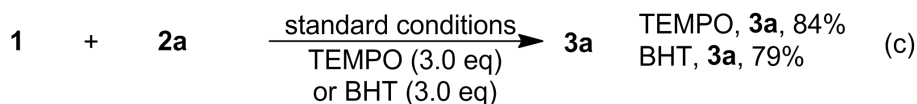


F170



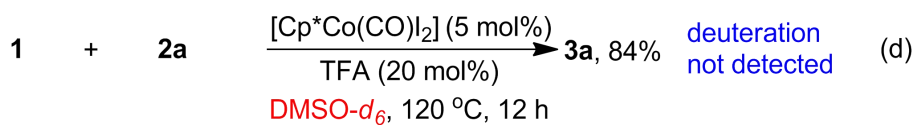


A reaction flask (25 mL) was charged with **1-1** (0.1 mmol, 1.0 equiv), styrene **2a** (0.2 mmol, 2.0 equiv), [Cp*CoI₂(CO)] (4.8 mg, 5.0 mol %), TFA (0.02 mmol), then the DMSO (3 mL) was added. The mixture was stirred at 120 °C for 12 hours under an atmosphere of air. After the reaction finished, the resulted mixtures were diluted with 20 mL of dichloromethane and washed with 20 mL of H₂O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na₂SO₄. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 5 : 1) to yield product **3a** in 81% yield.

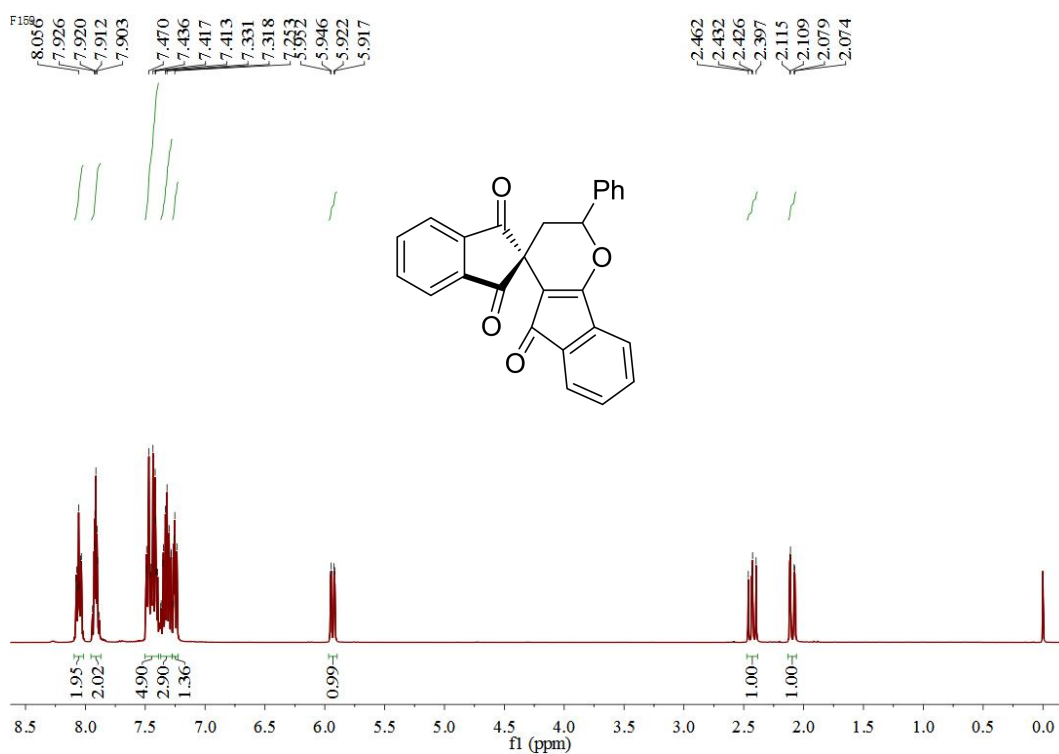


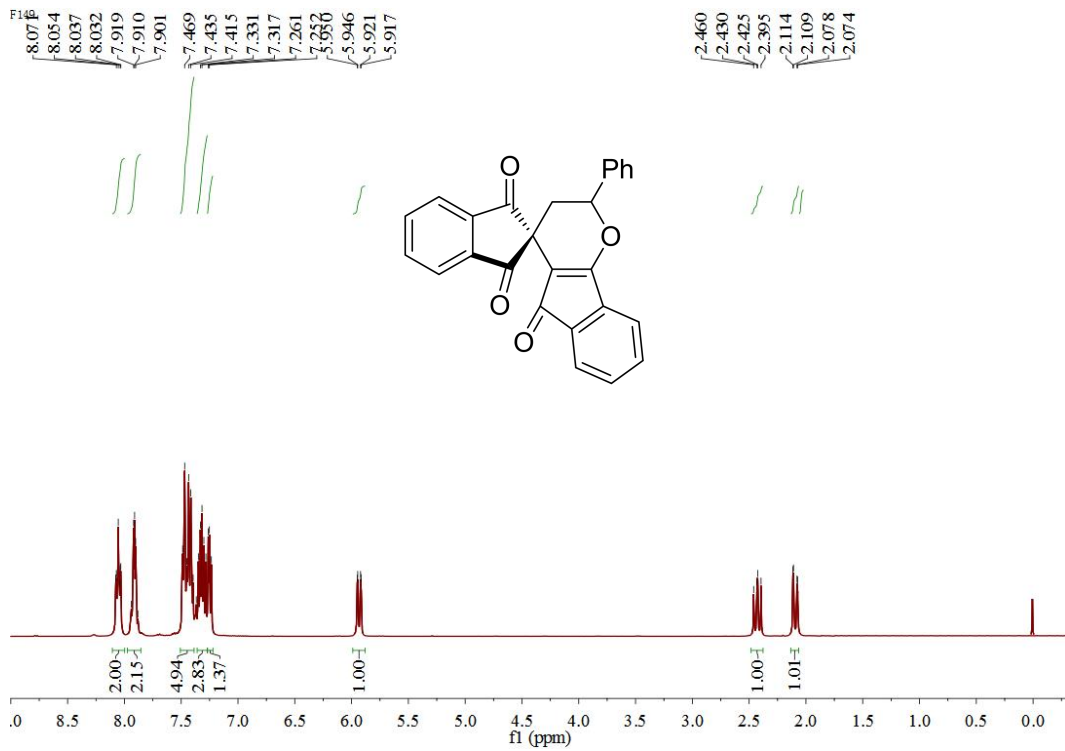
A reaction flask (25 mL) was charged with 1,3-indandione **1** (0.2 mmol, 1.0 equiv), styrene **2a** (0.2 mmol, 2.0 equiv), [Cp*CoI₂(CO)] (4.8 mg, 5.0 mol %), TFA (0.02 mmol), TEMPO (0.3 mmol, 3.0 equiv), then the DMSO (3 mL) was added. The mixture was stirred at 120 °C for 12 hours under an atmosphere of air. After the reaction finished, the resulted mixtures were diluted with 20 mL of dichloromethane and washed with 20 mL of H₂O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na₂SO₄. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 5 : 1) to yield product **3a** in 84% yield.

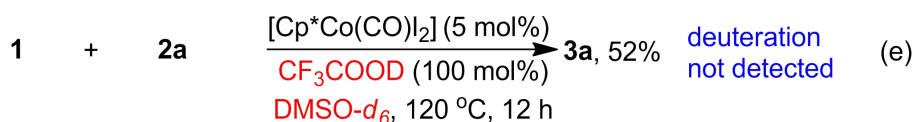
A reaction flask (25 mL) was charged with 1,3-indandione **1** (0.2 mmol, 1.0 equiv), styrene **2a** (0.2 mmol, 2.0 equiv), [Cp*CoI₂(CO)] (4.8 mg, 5.0 mol %), TFA (0.02 mmol), BHT (0.3 mmol, 3.0 equiv), then the DMSO (3 mL) was added. The mixture was stirred at 120 °C for 12 hours under an atmosphere of air. After the reaction finished, the resulted mixtures were diluted with 20 mL of dichloromethane and washed with 20 mL of H₂O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na₂SO₄. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 5 : 1) to yield product **3a** in 79% yield.



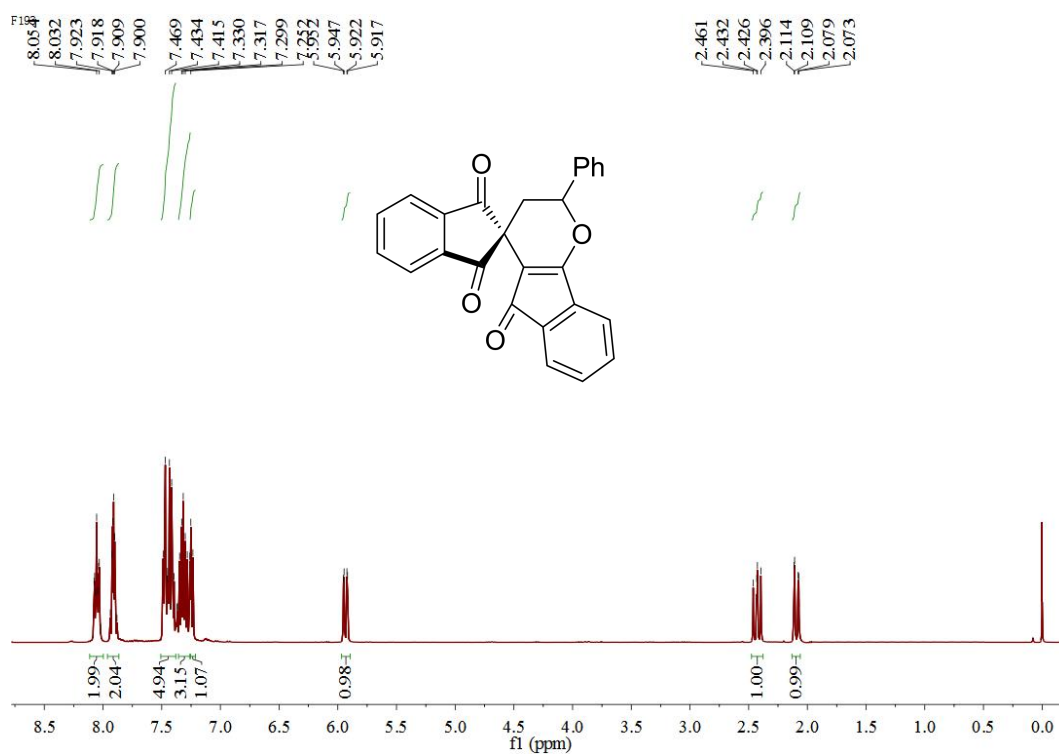
A reaction flask (25 mL) was charged with 1,3-indandione **1** (0.2 mmol, 1.0 equiv), styrene **2a** (0.2 mmol, 2.0 equiv), [Cp*CoI₂(CO)] (4.8 mg, 5.0 mol %), TFA (0.02 mmol), then the DMSO-*d*₆ (3 mL) was added. The mixture was stirred at 120 °C for 12 hours under an atmosphere of air. After the reaction finished, the resulted mixtures were diluted with 20 mL of dichloromethane and washed with 20 mL of H₂O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na₂SO₄. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 5 : 1) to yield product **3a** in 84% yield.

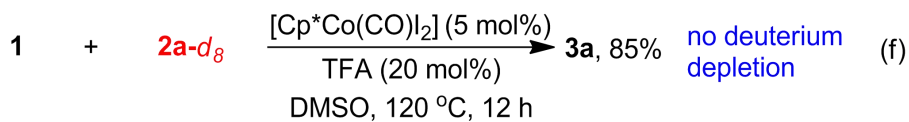




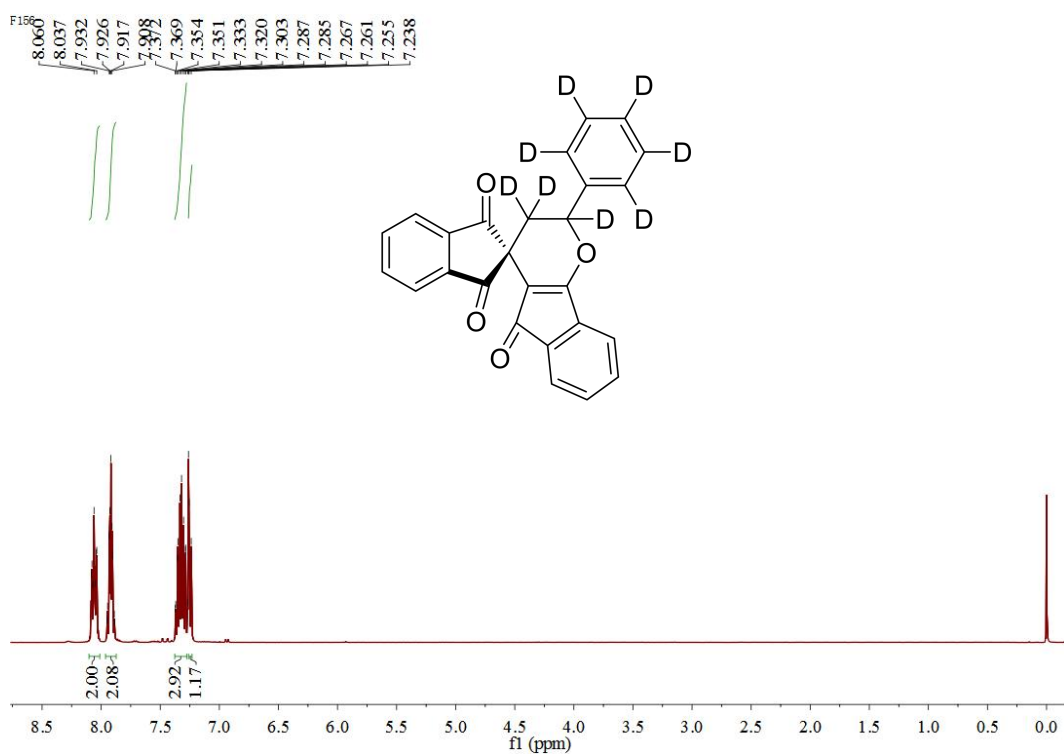


A reaction flask (25 mL) was charged with 1,3-indandione **1** (0.2 mmol, 1.0 equiv), styrene **2a** (0.2 mmol, 2.0 equiv), [Cp*CoI₂(CO)] (4.8 mg, 5.0 mol %), CF₃COOD (0.1 mmol), then the DMSO-*d*₆ (3 mL) was added. The mixture was stirred at 120 °C for 12 hours under an atmosphere of air. After the reaction finished, the resulted mixtures were diluted with 20 mL of dichloromethane and washed with 20 mL of H₂O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na₂SO₄. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 5 : 1) to yield product **3a** in 52% yield.



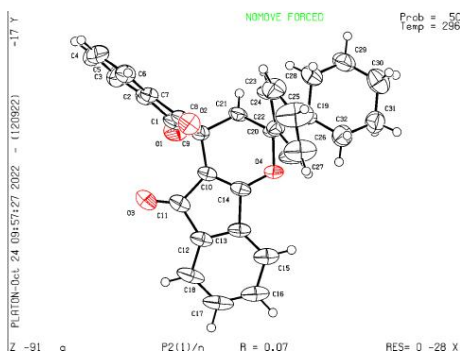


A reaction flask (25 mL) was charged with 1,3-indandione **1** (0.2 mmol, 1.0 equiv), styrene-*d*₈ **2a** (0.2 mmol, 2.0 equiv), [Cp*CoI₂(CO)] (4.8 mg, 5.0 mol %), TFA (0.02 mmol), then the DMSO (3 mL) was added. The mixture was stirred at 120 °C for 12 hours under an atmosphere of air. After the reaction finished, the resulted mixtures were diluted with 20 mL of dichloromethane and washed with 20 mL of H₂O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na₂SO₄. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 5 : 1) to yield product **3a** in 85% yield.



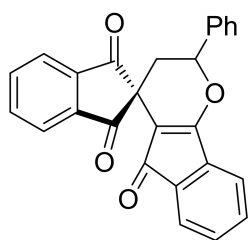
X-Ray Crystallographic Data

Crystal structure details for Product 4x (CCDC:2225895).

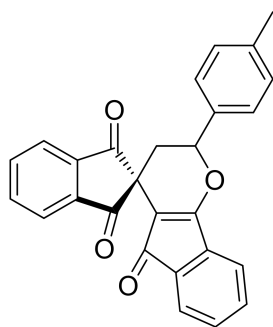


Identification code	A
Empirical formula	C ₃₂ H ₂₆ O ₄
Formula weight	474.53
Temperature/K	296.15
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	10.225(4)
b/Å	12.421(5)
c/Å	18.911(8)
α/°	90
β/°	99.081(7)
γ/°	90
Volume/Å ³	2371.9(16)
Z	4
ρ _{calc} /cm ³	1.329
μ/mm ⁻¹	0.087
F(000)	1000.0
Crystal size/mm ³	0.36 × 0.32 × 0.25
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.938 to 49.996
Index ranges	-11 ≤ h ≤ 12, -9 ≤ k ≤ 14, -22 ≤ l ≤ 22
Reflections collected	11065
Independent reflections	4157 [R _{int} = 0.0858, R _{sigma} = 0.1093]
Data/restraints/parameters	4157/0/338
Goodness-of-fit on F ²	0.883
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0634, wR ₂ = 0.1549
Final R indexes [all data]	R ₁ = 0.1377, wR ₂ = 0.1808
Largest diff. peak/hole / e Å ⁻³	0.23/-0.24

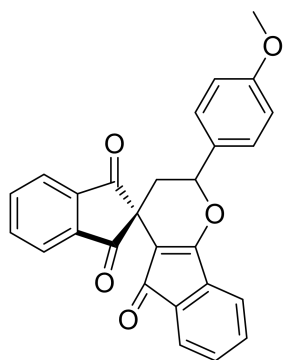
Characterization data for the products



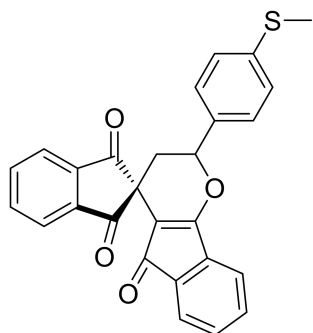
22'-Phenyl-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**3a**): Obtained as a yellow solid (33.7 mg, 86% yield); Melting point: 91 - 92 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ ppm: 8.03 - 8.08 (m, 2H), 7.88 - 7.94 (m, 2H), 7.40 - 7.49 (m, 5H), 7.28 - 7.37 (m, 3H), 7.24 - 7.26 (m, 1H), 5.92 - 5.95 (q, 1H), 2.40 - 2.46 (q, 1H), 2.07 - 2.12 (q, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ ppm: 201.1, 200.1, 190.5, 177.5, 141.8, 140.2, 137.8, 137.4, 136.3, 136.1, 132.5, 132.3, 130.7, 129.1, 128.9, 126.6, 124.0, 123.6, 121.5, 118.6, 105.1, 79.0, 50.2, 35.6; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{26}\text{H}_{17}\text{O}_4$ [$\text{M} + \text{H}$] $^+$ 393.1121, found 393.1120.



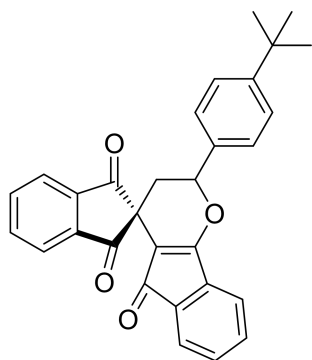
2'-(*p*-Tolyl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**3b**): Obtained as a yellow solid (35.7 mg, 88% yield); Melting point: 95 - 96 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ ppm: 8.03 - 8.08 (m, 2H), 7.89 - 7.94 (m, 2H), 7.31 - 7.38 (m, 4H), 7.22 - 7.29 (m, 4H), 5.88 - 5.92 (q, 1H), 2.43 - 2.47 (q, 1H), 2.38 (s, 3H), 2.05 - 2.09 (q, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ ppm: 201.1, 200.1, 190.5, 177.6, 141.8, 140.2, 139.1, 137.5, 136.3, 136.0, 134.9, 132.5, 132.3, 130.6, 129.5, 126.6, 124.0, 123.6, 121.5, 118.6, 105.0, 79.0, 50.3, 35.5, 21.2; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{27}\text{H}_{19}\text{O}_4$ [$\text{M} + \text{H}$] $^+$ 407.12779, found 407.12781.



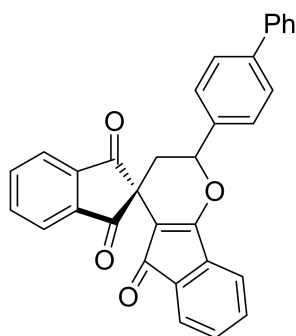
2'-(4-Methoxyphenyl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**3c**): Obtained as a yellow solid (35.5 mg, 84% yield); Melting point: 110 - 111 °C; **¹H NMR** (400 MHz, CDCl₃) δ ppm: 8.03 - 8.08 (m, 2H), 7.88 - 7.94 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.26 - 7.36 (m, 3H), 7.22 (d, *J* = 6.8 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 2H), 5.89 (d, *J* = 10.8 Hz, 1H), 3.83 (s, 3H), 2.42 - 2.48 (q, 1H), 2.04 - 2.08 (q, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ ppm: 201.2, 200.2, 190.6, 177.6, 160.2, 141.8, 140.2, 137.5, 136.3, 136.1, 132.5, 132.3, 130.6, 129.8, 128.2, 124.0, 123.6, 121.5, 118.6, 114.2, 105.0, 78.8, 55.3, 50.3, 35.3; **HRMS** (ESI-TOF) *m/z* calcd for C₂₇H₁₉O₅ [M + H]⁺ 423.1227, found 423.1228.



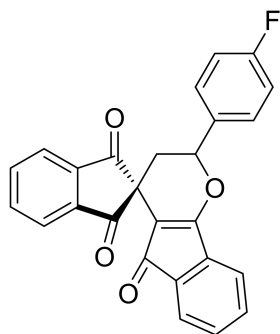
2'-(4-(Methylthio)phenyl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**3d**): Obtained as a yellow solid (38.1 mg, 87% yield); Melting point: 99 - 100 °C; **¹H NMR** (400 MHz, CDCl₃) δ ppm: 8.03 - 8.08 (m, 2H), 7.88 - 7.94 (m, 2H), 7.29 - 7.40 (m, 7H), 7.23 (d, *J* = 6.8 Hz, 1H), 5.89 (d, *J* = 11.2 Hz, 1H), 2.50 (s, 3H), 2.38 - 2.45 (t, *J* = 14.0, 12.4 Hz, 1H), 2.06 (d, *J* = 16.0 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ ppm: 201.1, 200.0, 190.5, 177.4, 152.3, 141.8, 140.2, 140.0, 137.4, 136.4, 136.1, 134.4, 132.5, 132.3, 130.7, 127.1, 126.5, 124.0, 123.6, 121.5, 118.6, 105.1, 78.7, 50.2, 35.3, 15.5; **HRMS** (ESI-TOF) *m/z* calcd for C₂₇H₁₉O₄S [M + H]⁺ 439.0999, found 439.0997.



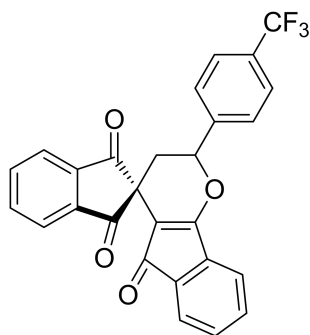
2'-(4-(Tert-butyl)phenyl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**3e**): Obtained as a yellow solid (38.1 mg, 85% yield); Melting point: 102 - 104 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.03 - 8.08 (m, 2H), 7.88 - 7.94 (m, 2H), 7.40 - 7.47 (q, 4H), 7.22 - 7.36 (m, 4H), 5.89 - 5.93 (q, 1H), 2.42 - 2.48 (q, 1H), 2.04 - 2.10 (q, 1H), 1.34 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 201.2, 200.2, 190.6, 177.6, 152.3, 141.8, 140.2, 137.5, 136.3, 136.0, 134.5, 132.5, 132.3, 130.6, 126.4, 125.8, 124.0, 123.6, 121.5, 118.6, 105.0, 78.9, 50.2, 35.4, 34.7, 31.3; HRMS (ESI-TOF) m/z calcd for C₃₀H₂₅O₄ [M + H]⁺ 449.1747, found 449.1748.



2'-([1,1'-Biphenyl]-4-yl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**3f**): Obtained as a yellow solid (43.1 mg, 92% yield); Melting point: 133 - 134 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.04 - 8.08 (m, 2H), 7.88 - 7.94 (m, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.43 - 7.47 (t, d, *J* = 7.6, 7.2 Hz, 2H), 7.25 - 7.38 (m, 5H), 5.98 (d, *J* = 11.2 Hz, 1H), 2.44 - 2.51 (q, 1H), 2.11 - 2.15 (q, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 201.1, 200.1, 190.5, 177.5, 142.1, 141.8, 140.3, 140.2, 137.4, 136.8, 136.4, 136.1, 132.5, 132.3, 130.7, 128.8, 127.63, 127.57, 127.11, 127.08, 124.0, 123.6, 121.5, 118.7, 105.1, 78.8, 50.2, 35.5; HRMS (ESI-TOF) m/z calcd for C₃₂H₂₁O₄ [M + H]⁺ 469.1434, found 469.1437.

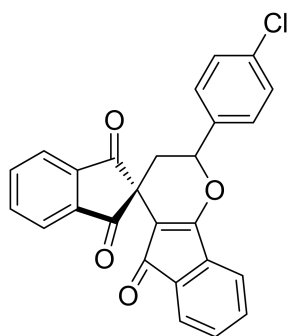


2'-(4-Fluorophenyl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**3g**): Obtained as a yellow solid (33.2 mg, 81% yield); Melting point: 112 - 113 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.04 - 8.07 (m, 2H), 7.90 - 7.96 (m, 2H), 7.45 - 7.49 (m, 2H), 7.23 - 7.38 (m, 4H), 7.11 - 7.15 (t, *J* = 8.8, 8.4 Hz, 2H), 5.91 - 5.94 (q, 1H), 2.38 - 2.44 (q, 1H), 2.05 - 2.10 (q, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 201.1, 200.0, 190.5, 177.3, 164.2, 161.8, 141.8, 140.2, 137.3, 136.4, 136.1, 133.7 (d, *J* = 3.2 Hz), 132.4 (d, *J* = 2.1 Hz), 130.7, 128.5 (d, *J* = 8.3 Hz), 124.0, 123.6, 121.6, 118.8, 118.6, 115.9 (d, *J* = 21.6 Hz), 105.1, 78.3, 50.1, 35.5; ¹⁹F NMR (400 MHz, CDCl₃) δ ppm: -104.0; HRMS (ESI-TOF) *m/z* calcd for C₂₆H₁₆FO₄ [M + H]⁺ 411.1027, found 411.1029.



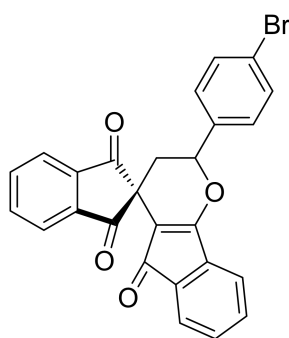
2'-(4-(Trifluoromethyl)phenyl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**3h**): Obtained as a yellow solid (34.5 mg, 75% yield); Melting point: 107 - 108 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.04 - 8.09 (m, 2H), 7.90 - 7.96 (m, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.28 - 7.39 (m, 3H), 7.24 - 7.26 (m, 1H), 6.00 - 6.03 (q, 1H), 2.36 - 2.43 (q, 1H), 2.09 - 2.13 (q, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 200.9, 199.7, 190.4, 177.0, 141.8 (d, *J* = 2.0 Hz), 140.2, 137.2, 136.5, 136.2, 132.4, 132.3, 131.2 (d, *J* = 22.6 Hz), 130.8, 126.9, 125.9 (q, *J* = 3.6, 7.3 Hz), 124.1, 123.8 (d, *J* = 270.7 Hz), 123.7, 121.7, 118.6, 105.2, 78.1, 49.9, 35.5; ¹⁹F NMR (400 MHz, CDCl₃) δ ppm: -62.7; HRMS (ESI-TOF) *m/z* calcd

for C₂₇H₁₆O₄F₃ [M + H]⁺ 461.0995, found 461.0996.



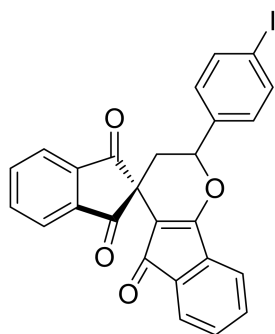
2'-(4-Chlorophenyl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-

1,3,5'(3'H)-trione (**3i**): Obtained as a yellow solid (34.1 mg, 80% yield); Melting point: 120 - 121 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.03 - 8.08 (m, 2H), 7.89 - 7.95 (m, 2H), 7.42 (s, 4H), 7.23 - 7.38 (m, 4H), 5.91 - 5.94 (t, *J* = 10.0, 1.6 Hz, 1H), 2.35 - 2.42 (q, 1H), 2.05 - 2.09 (q, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 201.0, 199.9, 190.4, 177.2, 141.8, 140.2, 137.3, 136.43, 136.39, 136.1, 135.0, 132.4, 130.7, 129.1, 128.0, 124.0, 123.7, 121.6, 118.6, 105.2, 78.2, 50.0, 35.4; HRMS (ESI-TOF) *m/z* calcd for C₂₆H₁₆O₄Cl [M + H]⁺ 427.0732, found 427.0733.

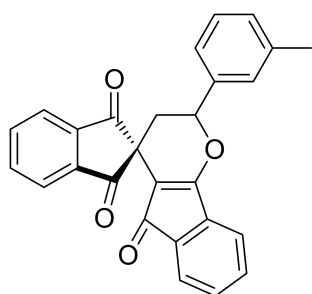


2'-(4-Bromophenyl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]

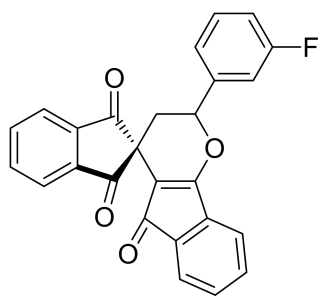
-1,3,5'(3'H)-trione (**3j**): Obtained as a yellow solid (39.0 mg, 83% yield); Melting point: 114 - 116 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.03 - 8.08 (m, 2H), 7.89 - 7.95 (m, 2H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.29 - 7.37 (m, 5H), 7.23 - 7.24 (d, *J* = 7.2 Hz, 1H), 5.91 (d, *J* = 11.6 Hz, 1H), 2.35 - 2.41 (t, *J* = 13.2, 12.8 Hz, 1H), 2.07 (d, *J* = 14.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 201.0, 199.9, 190.4, 177.1, 141.9, 140.2, 137.3, 136.9, 136.4, 136.1, 132.4, 132.1, 130.7, 128.3, 124.0, 123.7, 123.1, 121.6, 118.6, 105.2, 78.3, 50.0, 35.4; HRMS (ESI-TOF) *m/z* calcd for C₂₆H₁₆BrO₄ [M + H]⁺ 471.0227, found 471.0228.



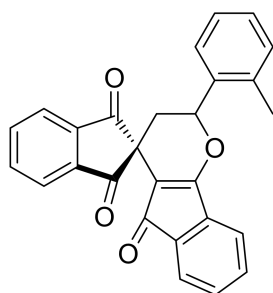
2'-(4-Iodophenyl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**3k**): Obtained as a yellow solid (44.0 mg, 85% yield); Melting point: 115 - 117 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.03 - 8.08 (m, 2H), 7.90 - 7.96 (m, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.22 - 7.38 (m, 6H), 5.87 - 5.90 (q, 1H), 2.34 - 2.40 (q, 1H), 2.05 - 2.09 (q, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 201.0, 199.9, 190.4, 177.2, 141.7, 140.1, 138.0, 137.5, 137.2, 136.5, 136.2, 132.4, 132.2, 130.8, 128.4, 124.0, 123.7, 121.6, 118.6, 105.1, 94.9, 78.3, 50.0, 35.3; HRMS (ESI-TOF) *m/z* calcd for C₂₆H₁₆IO₄ [M + H]⁺ 519.0088, found 519.0085.



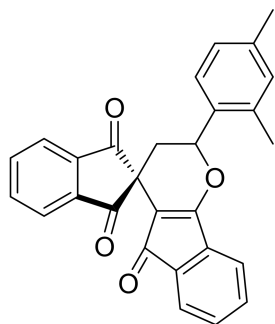
2'-(*m*-Tolyl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**3l**): Obtained as a yellow solid (35.7 mg, 88% yield); Melting point: 98 - 99 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.03 - 8.08 (m, 2H), 7.88 - 7.94 (m, 2H), 7.20 - 7.37 (m, 8H), 5.90 (d, *J* = 11.2 Hz, 1H), 2.42 - 2.46 (t, *J* = 12.4, 2.0 Hz, 1H), 2.39 (s, 3H), 2.06 - 2.10 (q, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 201.1, 200.1, 190.5, 177.5, 141.8, 140.2, 138.6, 137.8, 137.4, 136.3, 136.0, 132.5, 132.3, 130.6, 129.8, 128.8, 127.3, 124.0, 123.7, 123.6, 121.5, 118.7, 105.1, 79.1, 50.2, 35.6, 21.4; HRMS (ESI-TOF) *m/z* calcd for C₂₇H₁₉O₄ [M + H]⁺ 407.1278, found 407.1280.



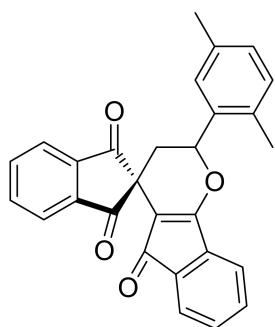
2'-(3-Fluorophenyl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**3m**): Obtained as a yellow solid (32.4 mg, 79% yield); Melting point: 105 - 106 °C; **¹H NMR** (400 MHz, CDCl₃) δ ppm: 8.05 - 8.09 (m, 2H), 7.90 - 7.96 (m, 2H), 7.20 - 7.44 (m, 7H), 7.08 - 7.12 (m, 1H), 5.94 (d, *J* = 10.0 Hz, 1H), 2.35 - 2.42 (m, 1H), 2.05 - 2.13 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ ppm: 201.1, 199.9, 190.5, 177.1, 164.1, 161.7, 141.8, 140.3 (d, *J* = 7.4 Hz), 140.2, 137.2, 136.4 (d, *J* = 30.4 Hz), 135.9, 132.4, 132.3, 130.8, 130.5 (d, *J* = 8.3 Hz), 124.1, 123.7, 122.1 (d, *J* = 2.8 Hz), 121.6, 118.6, 116.0 (d, *J* = 20.9 Hz), 113.6 (d, *J* = 22.5 Hz), 105.1, 78.1, 50.0, 35.5; **¹⁹F NMR** (400 MHz, CDCl₃) δ ppm: -117.7; **HRMS** (ESI-TOF) *m/z* calcd for C₂₆H₁₆FO₄ [M + H]⁺ 411.1027, found 411.1028.



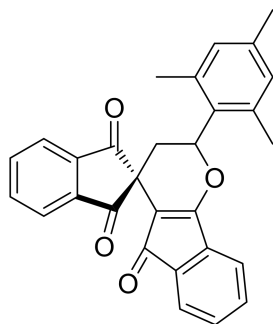
2'-(*o*-Tolyl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**3n**): Obtained as a yellow solid (34.5 mg, 85% yield); Melting point: 97 - 99 °C; **¹H NMR** (400 MHz, CDCl₃) δ ppm: 7.97 - 8.01 (m, 2H), 7.82 - 7.88 (m, 2H), 7.45 - 7.48 (m, 1H), 7.14 - 7.30 (m, 6H), 6.15 - 6.18 (q, 1H), 2.33 (s, 3H), 2.26 - 2.30 (t, *J* = 11.6, 2.4 Hz, 1H), 1.96 - 2.00 (q, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ ppm: 201.2, 200.1, 190.6, 177.7, 141.9, 140.2, 137.4, 136.4, 136.1, 135.1, 132.4, 132.3, 130.7, 128.7, 126.6, 125.9, 124.0, 123.6, 121.5, 118.6, 105.2, 76.0, 50.3, 34.5, 19.0; **HRMS** (ESI-TOF) *m/z* calcd for C₂₇H₁₉O₄ [M + H]⁺ 407.1278, found 407.1280.



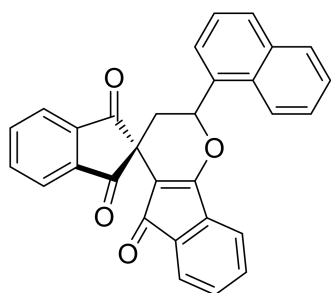
2'-(2,4-Dimethylphenyl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**3o**): Obtained as a yellow solid (32.8 mg, 78% yield); Melting point: 114 - 115 °C; **¹H NMR** (400 MHz, CDCl₃) δ ppm: 7.95 - 8.00 (m, 2H), 7.808 - 7.86 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.14 - 7.28 (m, 4H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.96 (s, 1H), 6.11 - 6.14 (q, 1H), 2.22 - 2.33 (m, 7H), 1.93 - 1.96 (q, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ ppm: 201.2, 200.1, 190.5, 177.8, 141.9, 140.2, 138.6, 137.4, 136.3, 136.0, 135.2, 133.0, 132.5, 132.3, 131.4, 130.6, 127.2, 125.9, 124.0, 123.6, 121.4, 118.6, 105.1, 76.01, 50.3, 34.4, 21.1, 18.9; **HRMS** (ESI-TOF) *m/z* calcd for C₂₈H₂₁O₄ [M + H]⁺ 421.1434, found 421.1436.



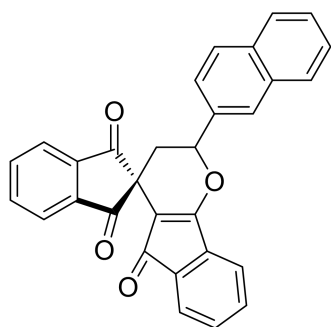
2'-(2,5-Dimethylphenyl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**3p**): Obtained as a yellow solid (36.5 mg, 87% yield); Melting point: 117 - 118 °C; **¹H NMR** (400 MHz, CDCl₃) δ ppm: 8.04 - 8.08 (m, 2H), 7.88 - 7.94 (m, 2H), 7.26 - 7.37 (m, 5H), 7.10 (s, 2H), 6.20 (d, *J* = 11.6 Hz, 1H), 2.34 - 2.41 (m, 7H), 2.01 - 2.04 (q, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ ppm: 201.2, 200.1, 190.6, 177.8, 141.9, 140.3, 137.5, 136.3, 136.2, 136.0, 135.8, 132.5, 132.3, 132.0, 130.7, 129.5, 126.6, 124.0, 123.6, 121.5, 118.7, 105.2, 76.2, 50.3, 34.6, 21.1, 18.5; **HRMS** (ESI-TOF) *m/z* calcd for C₂₈H₂₁O₄ [M + H]⁺ 421.1434, found 421.1437.



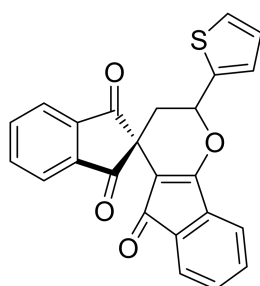
2'-Mesityl-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**3q**): Obtained as a yellow solid (33.9 mg, 78% yield); Melting point: 95 - 96 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ ppm: 8.02 - 8.07 (m, 2H), 7.87 - 7.93 (m, 2H), 7.21 - 7.36 (m, 4H), 6.89 (s, 2H), 6.40 - 6.43 (q, 1H), 2.62 - 2.69 (q, 1H), 2.41 (s, 6H), 2.27 (s, 3H), 1.88 - 1.92 (q, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ ppm: 201.4, 200.0, 190.5, 177.0, 141.9, 140.2, 138.3, 137.4, 136.6, 136.3, 135.9, 132.6, 132.3, 130.6, 130.3, 123.9, 123.5, 121.4, 118.4, 105.1, 76.8, 50.1, 31.8, 20.8, 20.4; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{29}\text{H}_{23}\text{O}_4$ [$\text{M} + \text{H}$] $^+$ 435.1591, found 435.1593.



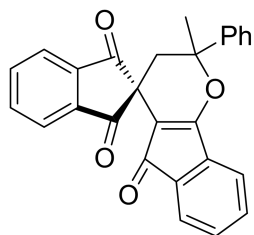
2'-(Naphthalen-1-yl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**3r**): Obtained as a yellow solid (36.7 mg, 83% yield); Melting point: 121 - 123 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ ppm: 8.06 - 8.12 (m, 2H), 8.01 (d, $J = 7.6$ Hz, 1H), 7.88 - 7.94 (m, 4H), 7.79 (d, $J = 7.2$ Hz, 1H), 7.50 - 7.58 (m, 3H), 7.29 - 7.39 (m, 4H), 6.82 (d, $J = 10.0$ Hz, 1H), 2.47 - 2.53 (q, 1H), 2.29 - 2.33 (q, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ ppm: 201.5, 200.0, 190.6, 177.7, 142.0, 140.3, 137.4, 136.4, 136.1, 133.6, 132.43, 132.39, 130.7, 130.0, 129.3, 129.1, 127.0, 126.0, 125.4, 124.1, 123.8, 123.6, 122.3, 121.6, 118.7, 105.5, 76.0, 50.3, 35.1; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{30}\text{H}_{19}\text{O}_4$ [$\text{M} + \text{H}$] $^+$ 443.1278, found 443.1276.



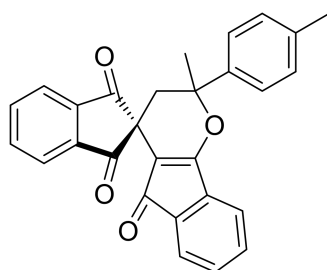
2'-(Naphthalen-2-yl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**3s**): Obtained as a yellow solid (40.2 mg, 91% yield); Melting point: 139 - 140 °C; **¹H NMR** (400 MHz, CDCl₃) δ ppm: 8.04 - 8.10 (m, 2H), 7.86 - 7.94 (m, 6H), 7.50 - 7.56 (m, 3H), 7.24 - 7.35 (m, 4H), 6.10 (d, *J* = 11.2 Hz, 1H), 2.49 - 2.55 (q, 1H), 2.13 - 2.17 (q, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ ppm: 201.1, 200.1, 190.5, 177.4, 141.8, 140.2, 137.3, 136.3, 136.0, 135.1, 133.4, 133.0, 132.4, 132.3, 130.6, 128.8, 128.1, 127.7, 126.64, 126.56, 126.1, 124.0, 123.8, 123.6, 121.5, 118.6, 105.1, 79.1, 50.2, 35.5; **HRMS** (ESI-TOF) *m/z* calcd for C₃₀H₁₉O₄ [M + H]⁺ 443.1278, found 443.1279.



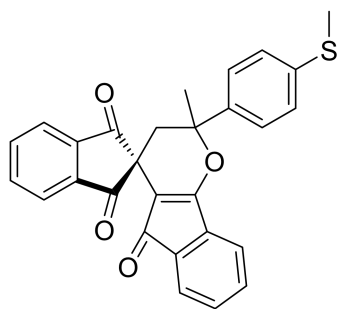
2'-(Thiophen-2-yl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**3t**): Obtained as a yellow solid (29.5 mg, 74% yield); Melting point: 86 - 87 °C; **¹H NMR** (400 MHz, CDCl₃) δ ppm: 7.95 - 8.03 (m, 2H), 7.82 - 7.89 (m, 2H), 7.33 - 7.34 (q, 1H), 7.15 - 7.29 (m, 5H), 6.98 - 7.00 (q, 1H), 6.12 - 6.16 (q, 1H), 2.47 - 2.54 (q, 1H), 2.15 - 2.19 (q, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ ppm: 201.0, 199.8, 190.4, 177.0, 141.8, 140.2, 140.1, 137.3, 136.4, 136.1, 132.47, 132.35, 130.7, 126.9, 126.8, 126.7, 124.0, 123.7, 121.5, 118.8, 105.0, 74.5, 50.1, 35.2; **HRMS** (ESI-TOF) *m/z* calcd for C₂₄H₁₅O₄S [M + H]⁺ 399.0686, found 399.0687.



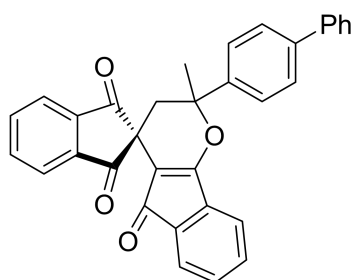
2'-Methyl-2'-phenyl-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4a**): Obtained as a yellow solid (33.3 mg, 82% yield); Melting point: 122 - 124 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.02 (d, *J* = 6.8 Hz, 1H), 7.93 (d, *J* = 6.8 Hz, 1H), 7.84 - 7.88 (m, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.25 - 7.41 (m, 7H), 2.48 (d, *J* = 14.4 Hz, 1H), 2.33 (d, *J* = 14.8 Hz, 1H), 2.03 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 199.6, 190.8, 175.6, 140.0, 141.2, 141.1, 137.8, 135.93, 135.88, 132.6, 132.2, 130.6, 132.2, 130.6, 128.5, 127.8, 124.3, 123.9, 123.5, 121.4, 118.5, 105.1, 84.4, 51.1, 40.6, 26.7; HRMS (ESI-TOF) *m/z* calcd for C₂₇H₁₉O₄ [M + H]⁺ 407.1278, found 407.1276.



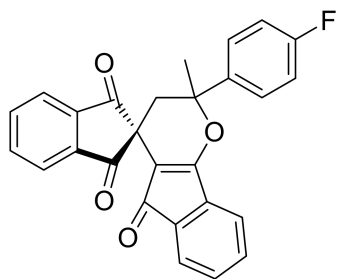
2'-Methyl-2'-(p-tolyl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4b**): Obtained as a yellow solid (34.9 mg, 83% yield); Melting point: 127 - 128 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.03 (d, *J* = 6.8 Hz, 1H), 7.95 (d, *J* = 6.4 Hz, 1H), 7.83 - 7.89 (q, 2H), 7.30 - 6.40 (m, 6H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.48 (d, *J* = 14.4 Hz, 1H), 2.36 (s, 3H), 2.29 (d, *J* = 14.4 Hz, 1H), 2.02 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 199.8, 199.7, 190.9, 175.9, 141.2, 137.9, 137.6, 135.94, 135.87, 132.7, 132.2, 130.6, 129.2, 124.4, 123.9, 123.6, 121.3, 118.5, 105.0, 84.4, 51.2, 40.7, 26.5, 21.0; HRMS (ESI-TOF) *m/z* calcd for C₂₈H₂₁O₄ [M + H]⁺ 421.1434, found 421.1433.



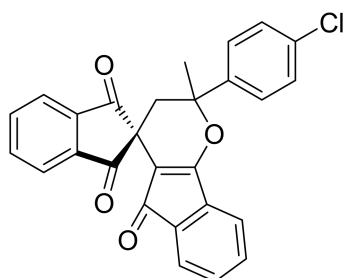
2'-methyl-2'-(4-(methylthio)phenyl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4c**): Obtained as a yellow solid (35.7 mg, 79% yield); Melting point: 131 - 132 °C; **¹H NMR** (400 MHz, CDCl₃) δ ppm: 8.04 (d, *J* = 7.2 Hz, 1H), 7.96 (d, *J* = 6.8 Hz, 1H), 7.85 - 7.91 (m, 2H), 7.31 - 7.39 (m, 6H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.47 (d, *J* = 14.8 Hz, 4H), 2.29 (d, *J* = 14.8 Hz, 1H), 2.02 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ ppm: 199.8, 199.7, 190.9, 175.8, 141.28, 141.25, 141.0, 138.5, 137.9, 136.0, 135.9, 132.7, 132.3, 130.7, 126.5, 125.0, 124.0, 123.6, 121.4, 118.5, 105.1, 84.2, 51.2, 40.6, 26.5, 15.7; **HRMS** (ESI-TOF) *m/z* calcd for C₂₈H₂₁SO₄ [M + H]⁺ 453.1155, found 453.1158.



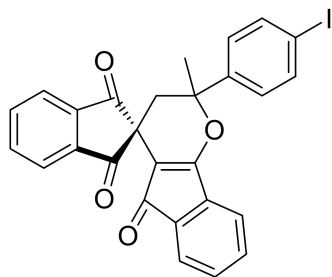
2'-([1,1'-Biphenyl]-4-yl)-2'-methyl-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4d**): Obtained as a yellow solid (42.4 mg, 88% yield); Melting point: 164 - 165 °C; **¹H NMR** (400 MHz, CDCl₃) δ ppm: 8.04 (d, *J* = 7.2 Hz, 1H), 7.96 (d, *J* = 7.2 Hz, 1H), 7.84 - 7.90 (m, 2H), 7.59 - 7.63 (t, *J* = 9.6, 8.8 Hz, 4H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.42 - 7.46 (t, *J* = 7.6 Hz, 2H), 7.30 - 7.40 (m, 5H), 2.53 (d, *J* = 14.8 Hz, 1H), 2.34 (d, *J* = 14.4 Hz, 1H), 2.08 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ ppm: 199.8, 199.7, 191.0, 175.9, 143.2, 141.27, 141.25, 140.8, 140.3, 137.9, 136.0, 135.9, 132.7, 132.3, 130.7, 128.8, 127.5, 127.2, 127.1, 125.0, 124.0, 123.6, 121.4, 118.6, 105.1, 84.4, 51.2, 40.6, 26.4; **HRMS** (ESI-TOF) *m/z* calcd for C₃₃H₂₃O₄ [M + H]⁺ 483.1591, found 483.1594.



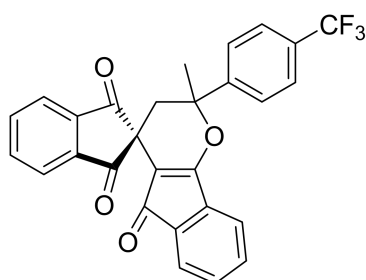
2'-(4-Fluorophenyl)-2'-methyl-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4e**): Obtained as a yellow solid (31.4 mg, 74% yield); Melting point: 144 - 145 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.04 (d, *J* = 7.2 Hz, 1H), 7.96 (d, *J* = 7.2 Hz, 1H), 7.85 - 7.92 (m, 2H), 7.39 - 7.45 (m, 3H), 7.30 - 7.35 (m, 3H), 7.06 - 7.10 (t, *J* = 8.4 Hz, 2H), 2.47 (d, *J* = 14.8 Hz, 1H), 2.31 (d, *J* = 14.8 Hz, 1H), 2.02 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 199.6, 190.8, 175.7, 163.5, 161.0, 141.3 (d, *J* = 3.1 Hz), 140.0 (d, *J* = 3.2 Hz), 137.8, 136.0 (d, *J* = 4.5 Hz), 132.6, 132.3, 130.7, 126.4 (d, *J* = 8.1 Hz), 124.0, 123.7, 121.5, 118.5, 115.5, 115.3, 105.2, 84.0, 51.1, 40.7, 26.9; ¹⁹F NMR (400 MHz, CDCl₃) δ ppm: -114.6; HRMS (ESI-TOF) *m/z* calcd for C₂₇H₁₈FO₄ [M + H]⁺ 425.1184, found 425.1185.



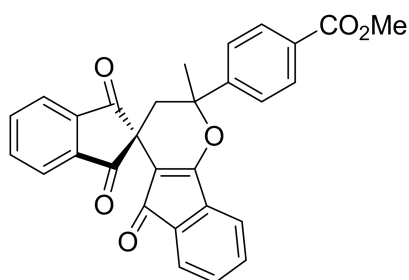
2'-(4-Chlorophenyl)-2'-methyl-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4f**): Obtained as a yellow solid (33.9 mg, 77% yield); Melting point: 139 - 141 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.03 (d, *J* = 7.2 Hz, 1H), 7.94 - 7.96 (t, *J* = 7.2 Hz, 1H), 7.85 - 7.91 (m, 2H), 7.30 - 7.42 (m, 8H), 2.45 (d, *J* = 14.8 Hz, 1H), 2.31 (d, *J* = 14.8 Hz, 1H), 2.01 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 199.6, 190.8, 175.6, 142.6, 141.23, 141.21, 137.7, 136.04, 136.00, 133.8, 132.6, 132.3, 130.7, 128.7, 126.0, 124.0, 123.7, 121.5, 118.5, 105.2, 83.9, 51.1, 40.4, 26.9; HRMS (ESI-TOF) *m/z* calcd for C₂₇H₁₈O₄Cl [M + H]⁺ 441.0888, found 441.0891.



2'-(4-Iodophenyl)-2'-methyl-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4g**): Obtained as a yellow solid (38.3 mg, 72% yield); Melting point: 151 - 153 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.03 (d, *J* = 6.8 Hz, 1H), 7.95 (d, *J* = 6.8 Hz, 1H), 7.84 - 7.90 (m, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.38 - 7.41 (t, *J* = 7.2 Hz, 1H), 7.29 - 7.34 (q, 3H), 7.17 - 7.21 (t, *J* = 8.0 Hz, 2H), 7.02 - 7.06 (m, 1H), 2.44 (d, *J* = 14.8 Hz, 1H), 2.30 (d, *J* = 14.4 Hz, 1H), 1.99 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 199.5, 190.7, 175.5, 143.9, 141.23, 141.20, 137.6, 136.03, 135.99, 132.5, 132.3, 130.7, 126.5, 124.0, 123.7, 121.5, 118.5, 105.2, 93.6, 84.0, 51.0, 40.2, 26.8; HRMS (ESI-TOF) *m/z* calcd for C₂₇H₁₈IO₄ [M + H]⁺ 533.0244, found 533.0247.

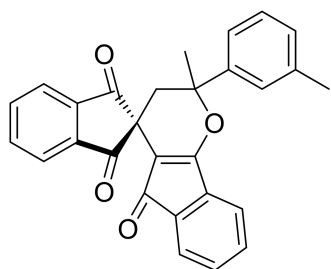


2'-Methyl-2'-(4-(trifluoromethyl)phenyl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4h**): Obtained as a yellow solid (31.2 mg, 67% yield); Melting point: 155 - 157 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.05 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 7.2 Hz, 1H), 7.86 - 7.92 (m, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.04 Hz, 2H), 7.40 - 7.44 (t, *J* = 7.2 Hz, 1H), 7.31 - 7.37 (m, 3H), 2.48 (d, *J* = 14.8 Hz, 1H), 2.36 (d, *J* = 14.4 Hz, 1H), 2.04 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 199.5, 199.4, 190.7, 175.4, 147.9, 141.2 (d, *J* = 3.1 Hz), 137.7, 136.1 (d, *J* = 3.0 Hz), 132.5, 132.4, 130.8, 125.6 (q, *J* = 3.5, 10.9 Hz), 124.9, 123.9 (d, *J* = 27.6 Hz), 121.6, 118.5, 105.3, 83.9, 51.0, 40.1, 27.1; ¹⁹F NMR (400 MHz, CDCl₃) δ ppm: -62.1; HRMS (ESI-TOF) *m/z* calcd for C₂₈H₁₈F₃O₄ [M + H]⁺ 475.1152, found 475.1155.

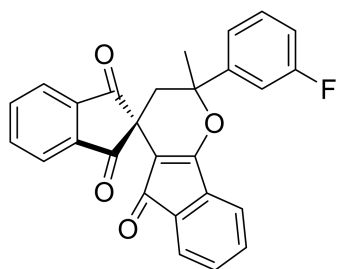


Methyl

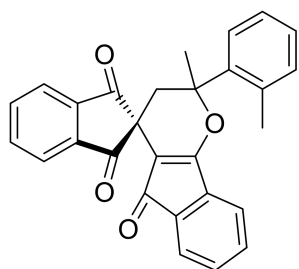
4-(2'-methyl-1,3,5'-trioxo-1,3,3',5'-tetrahydro-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-2'-yl)benzoate (**4i**): Obtained as a yellow solid (28.8 mg, 62% yield); Melting point: 129 - 130 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.04 - 8.08 (t, *J* = 8.4, 7.62 Hz, 3H), 7.85 - 7.96 (m, 3H), 7.51 - 7.53 (d, *J* = 8.4 Hz, 2H), 7.31 - 7.44 (m, 4H), 3.93 (s, 3H), 2.49 (d, *J* = 14.8 Hz, 1H), 2.37 (d, *J* = 14.4 Hz, 1H), 2.03 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 199.6, 199.4, 190.8, 175.5, 166.6, 148.8, 141.2, 137.7, 136.0, 132.6, 132.4, 130.8, 129.9, 129.7, 124.5, 124.0, 123.7, 121.6, 118.6, 105.3, 84.1, 52.2, 51.0, 40.1, 27.2; HRMS (ESI-TOF) *m/z* calcd for C₂₉H₂₁O₆ [M + H]⁺ 465.1333, found 465.1335.



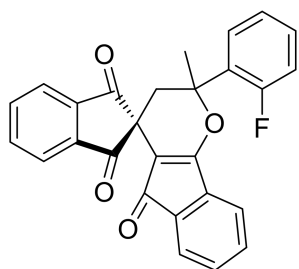
2'-Methyl-2'-(m-tolyl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4j**): Obtained as a yellow solid (34.0 mg, 81% yield); Melting point: 133 - 134 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.04 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.84 - 7.91 (m, 2H), 7.26 - 7.42 (m, 7H), 7.14 - 7.16 (m, 1H), 2.48 (d, *J* = 14.8 Hz, 1H), 2.38 (s, 3H), 2.29 (d, *J* = 14.4 Hz, 1H), 2.03 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 199.9, 199.7, 190.9, 175.9, 144.2, 141.29, 141.27, 138.3, 138.0, 136.0, 135.9, 132.7, 132.2, 130.7, 128.6, 128.5, 125.1, 124.0, 123.6, 121.5, 121.4, 118.6, 105.0, 100.0, 84.5, 51.3, 40.8, 26.4, 21.6; HRMS (ESI-TOF) *m/z* calcd for C₂₈H₂₁O₄ [M + H]⁺ 421.1434, found 421.1436.



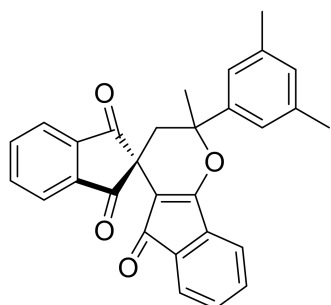
2'-(3-Fluorophenyl)-2'-methyl-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4k**): Obtained as a yellow solid (30.1 mg, 71% yield); Melting point: 124 - 125 °C; **¹H NMR** (400 MHz, CDCl₃) δ ppm: 8.04 - 8.05 (m, 1H), 7.95 - 7.97 (m, 1H), 7.86 - 7.92 (m, 2H), 7.31 - 7.44 (m, 5H), 7.17 - 7.22 (t, *J* = 9.6, 7.6 Hz, 2H), 7.02 - 7.06 (m, 1H), 2.47 (d, *J* = 14.8 Hz, 1H), 2.34 (d, *J* = 14.4 Hz, 1H), 2.02 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ ppm: 199.7, 199.6, 190.9, 175.6, 164.1, 161.7, 141.7 (d, *J* = 6.9 Hz), 141.3 (d, *J* = 3.9 Hz), 137.8, 136.1 (d, *J* = 2.6 Hz), 132.6, 132.4, 130.8, 130.3 (d, *J* = 8.2 Hz), 124.0, 123.8, 121.6, 120.1, 118.6, 114.8 (d, *J* = 20.9 Hz), 114.6 (d, *J* = 23.4 Hz), 105.2, 83.8, 51.0, 40.3, 27.1; **¹⁹F NMR** (400 MHz, CDCl₃) δ ppm: -113.0; **HRMS** (ESI-TOF) *m/z* calcd for C₂₇H₁₈FO₄ [M + H]⁺ 425.1184, found 425.1185.



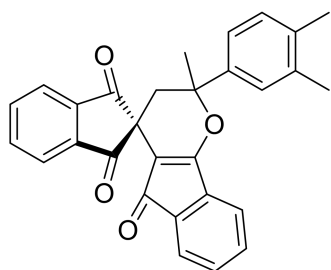
2'-Methyl-2'-(o-tolyl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4l**): Obtained as a yellow solid (31.9 mg, 76% yield); Melting point: 118 - 119 °C; **¹H NMR** (400 MHz, CDCl₃) δ ppm: 8.03 - 8.05 (m, 1H), 7.98 - 8.00 (m, 1H), 7.85 - 7.91 (q, 2H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.31 - 7.39 (m, 3H), 7.20 - 7.28 (m, 4H), 2.70 (d, *J* = 14.8 Hz, 1H), 2.53 (s, 3H), 2.15 (s, 3H), 2.13 (d, *J* = 14.4 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ ppm: 200.4, 199.8, 190.9, 175.0, 141.3, 141.2, 137.8, 136.1, 136.0, 135.9, 133.2, 132.8, 132.3, 130.7, 128.5, 126.1, 125.8, 124.0, 123.6, 121.4, 118.5, 104.8, 85.6, 50.8, 38.4, 26.1, 22.0; **HRMS** (ESI-TOF) *m/z* calcd for C₂₈H₂₁O₄ [M + H]⁺ 421.1434, found 421.1436.



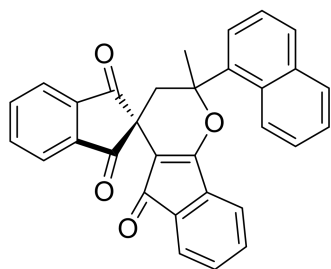
2'-(2-Fluorophenyl)-2'-methyl-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4m**): Obtained as a yellow solid (27.3 mg, 67% yield); Melting point: 132 - 133 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.04 (d, *J* = 6.8 Hz, 1H), 7.84 - 7.93 (m, 3H), 7.50 - 7.54 (t, *J* = 14.4 Hz, 1H), 7.32 - 7.42 (m, 6H), 7.19 - 7.23 (t, *J* = 8.0 Hz, 1H), 7.04 - 7.09 (m, 1H), 2.75 (d, *J* = 14.4 Hz, 1H), 2.59 (d, *J* = 14.8 Hz, 1H), 2.02 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 200.0, 199.1, 190.8, 175.2, 160.4, 160.0, 141.2, 137.6, 135.9 (d, *J* = 11.7 Hz), 132.6, 132.3, 130.7, 130.1, 129.7 (d, *J* = 8.6 Hz), 126.0 (d, *J* = 3.5 Hz), 124.5 (d, *J* = 3.2 Hz), 123.8 (d, *J* = 2.2 Hz), 121.6, 118.4, 116.3 (d, *J* = 23.3 Hz), 109.4, 105.6, 82.7, 50.7, 37.5, 27.4; ¹⁹F NMR (400 MHz, CDCl₃) δ ppm: -110.6; HRMS (ESI-TOF) *m/z* calcd for C₂₇H₁₈FO₄ [M + H]⁺ 425.1184, found 425.1186.



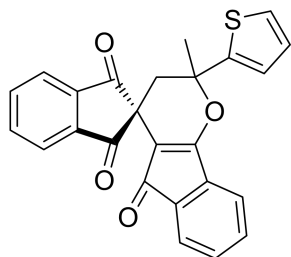
2'-(3,5-Dimethylphenyl)-2'-methyl-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4n**): Obtained as a yellow solid (37.8 mg, 87% yield); Melting point: 125 - 126 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.03 - 8.05 (m, 1H), 7.98 - 8.00 (m, 1H), 7.85 - 7.91 (m, 2H), 7.28 - 6.38 (m, 4H), 7.23 - 7.26 (m, 1H), 7.06 (s, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 2.69 (d, *J* = 15.2 Hz, 1H), 2.49 (s, 3H), 2.32 (s, 3H), 2.13 (s, 3H), 2.09 (d, *J* = 15.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 200.5, 199.8, 191.0, 175.1, 141.3, 138.30, 138.25, 137.81, 136.0, 135.9, 133.9, 132.8, 132.2, 130.6, 126.6, 125.8, 124.0, 123.5, 121.4, 118.4, 104.7, 85.5, 50.7, 38.4, 26.0, 21.8, 20.8; HRMS (ESI-TOF) *m/z* calcd for C₂₉H₂₃O₄ [M + H]⁺ 435.1591, found 435.1595.



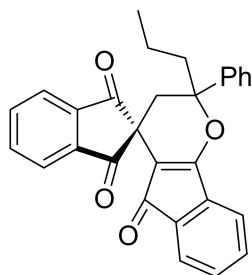
2'-(3,4-Dimethylphenyl)-2'-methyl-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4o**): Obtained as a yellow solid (36.9 mg, 85% yield); Melting point: 144 - 145 °C; **¹H NMR** (400 MHz, CDCl₃) δ ppm: 8.04 (d, *J* = 7.2 Hz, 1H), 7.97 (d, *J* = 7.2 Hz, 1H), 7.85 - 7.91 (m, 2H), 7.30 - 7.39 (m, 4H), 7.20 - 7.24 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 2.48 (d, *J* = 14.8 Hz, 1H), 2.25 - 2.29 (m, 7H), 2.02 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ ppm: 200.0, 199.7, 191.0, 176.1, 141.8, 141.3, 138.0, 136.8, 136.4, 136.0, 135.9, 132.8, 132.2, 130.6, 129.7, 125.8, 124.0, 123.6, 121.9, 121.4, 118.6, 105.0, 84.5, 51.3, 40.8, 26.2, 20.0, 19.4; **HRMS** (ESI-TOF) *m/z* calcd for C₂₉H₂₃O₄ [M + H]⁺ 435.1591, found 435.1592.



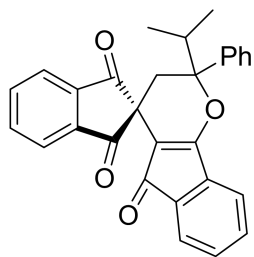
2'-Methyl-2'-(naphthalen-1-yl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4p**): Obtained as a yellow solid (36.0 mg, 79% yield); Melting point: 153 - 155 °C; **¹H NMR** (400 MHz, CDCl₃) δ ppm: 8.23 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.83 - 7.96 (m, 5H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.56 - 7.60 (t, *J* = 8.4, 7.2 Hz, 1H), 7.44 - 7.52 (m, 2H), 7.30 - 7.40 (m, 3H), 7.23 - 7.26 (d, *J* = 6.8 Hz, 1H), 3.16 (d, *J* = 15.2 Hz, 1H), 2.28 - 2.33 (m, 4H); **¹³C NMR** (100 MHz, CDCl₃) δ ppm: 200.2, 199.8, 191.1, 175.2, 141.4, 138.2, 137.9, 136.0, 135.9, 134.9, 132.8, 132.3, 130.7, 130.3, 130.2, 129.5, 126.6, 125.6, 125.5, 124.7, 124.3, 124.1, 123.6, 121.5, 118.7, 105.3, 85.8, 51.0, 38.7, 26.4; **HRMS** (ESI-TOF) *m/z* calcd for C₃₁H₂₁O₄ [M + H]⁺ 457.1434, found 457.1435.



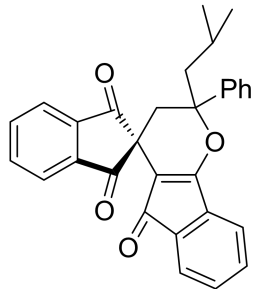
2'-methyl-2'-(thiophen-2-yl)-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4q**): Obtained as a yellow solid (28.0 mg, 68% yield); Melting point: 118 - 119 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.03 - 8.05 (m, 1H), 7.95 - 7.97 (m, 1H), 7.84 - 7.90 (m, 2H), 7.37 - 7.40 (m, 3H), 7.30 - 7.35 (m, 2H), 7.22 - 7.26 (t, *J* = 8.0, 7.6 Hz, 2H), 2.48 (d, *J* = 14.8 Hz, 1H), 2.29 (d, *J* = 14.8 Hz, 1H), 2.03 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 199.8, 199.7, 190.9, 175.9, 141.5, 141.3, 138.0, 136.0, 135.9, 133.0, 132.7, 132.3, 130.7, 128.5, 128.3, 127.6, 126.5, 126.4, 124.0, 123.7, 123.3, 122.7, 121.5, 118.6, 105.1, 84.5, 51.2, 40.6, 26.4; HRMS (ESI-TOF) *m/z* calcd for C₂₅H₁₇SO₄ [M + H]⁺ 413.0842, found 413.0846.



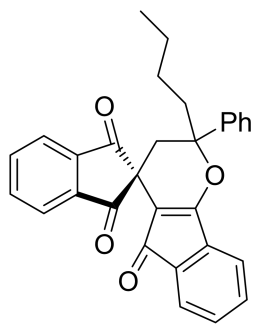
2'-Phenyl-2'-propyl-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4r**): Obtained as a yellow solid (33.1 mg, 76% yield); Melting point: 138 - 139 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.04 (d, *J* = 7.2 Hz, 1H), 7.90 - 7.93 (t, *J* = 7.2, 5.6 Hz, 1H), 7.83 - 7.88 (m, 2H), 7.30 - 7.43 (m, 9H), 2.62 - 2.70 (m, 1H), 2.42 - 2.51 (m, 2H), 1.93 - 2.01 (m, 1H), 1.34 - 1.41 (m, 1H), 1.05 - 1.14 (m, 1H), 0.87 - 0.90 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 200.0, 199.3, 190.8, 175.6, 141.8, 141.2, 137.8, 135.9, 135.8, 132.8, 132.3, 130.7, 128.5, 127.6, 124.7, 123.9, 123.7, 121.5, 118.4, 105.5, 86.8, 51.0, 41.5, 39.7, 17.2, 14.1; HRMS (ESI-TOF) *m/z* calcd for C₂₉H₂₃O₄ [M + H]⁺ 435.1591, found 435.1593.



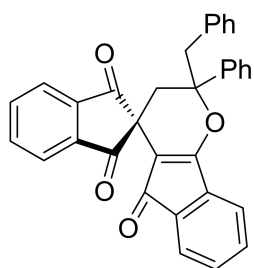
2'-Isopropyl-2'-phenyl-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4s**): Obtained as a yellow solid (30.8 mg, 71% yield); Melting point: 133 - 134 °C; **¹H NMR** (400 MHz, CDCl₃) δ ppm: 8.02 - 8.04 (m, 1H), 7.82 - 7.89 (m, 3H), 7.42 - 7.44 (q, 2H), 7.36 - 7.37 (m, 3H), 7.31 - 7.34 (m, 2H), 7.25 - 7.26 (m, 2H), 2.77 (d, *J* = 14.8 Hz, 1H), 2.55 - 2.61 (m, 2H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ ppm: 200.3, 198.4, 190.6, 175.4, 141.2, 141.0, 139.6, 137.8, 136.0, 135.7, 132.9, 132.2, 130.7, 127.9, 127.5, 125.7, 123.8, 123.7, 121.5, 118.2, 105.6, 100.0, 88.5, 50.7, 46.8, 35.5, 27.8, 27.1, 26.13, 26.07; **HRMS** (ESI-TOF) *m/z* calcd for C₂₉H₂₃O₄ [M + H]⁺ 435.1591, found 435.1588.



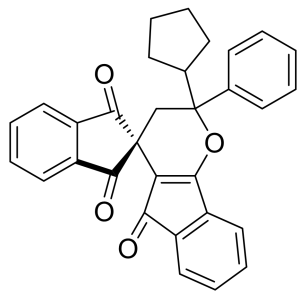
2'-Isobutyl-2'-phenyl-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4t**): Obtained as a yellow solid (35.4 mg, 79% yield); Melting point: 136 - 137 °C; **¹H NMR** (400 MHz, CDCl₃) δ ppm: 8.03 (d, *J* = 7.2 Hz, 1H), 7.82 - 7.91 (m, 3H), 7.30 - 7.43 (m, 9H), 2.61 - 2.67 (q, 1H), 2.35 - 2.43 (q, 2H), 1.88 - 1.93 (m, 1H), 1.50 - 1.65 (m, 1H), 0.95 (d, *J* = 6.4 Hz, 3H), 0.80 (d, *J* = 6.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ ppm: 199.9, 199.3, 190.8, 175.5, 141.8, 141.2, 137.7, 135.90, 135.88, 132.8, 132.3, 130.7, 128.5, 127.5, 124.7, 123.9, 123.7, 121.5, 118.4, 105.6, 87.4, 51.1, 47.4, 41.1, 24.6, 24.5, 23.4; **HRMS** (ESI-TOF) *m/z* calcd for C₃₀H₂₅O₄ [M + H]⁺ 449.1747, found 449.1749.



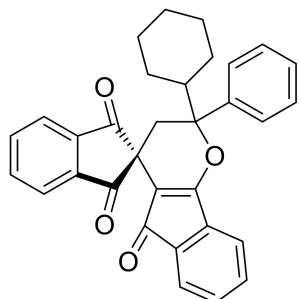
2'-Butyl-2'-phenyl-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4u**): Obtained as a yellow solid (36.3 mg, 81% yield); Melting point: 149 - 151 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.03 (d, *J* = 7.2 Hz, 1H), 7.89 - 7.93 (t, *J* = 7.2, 6.0 Hz, 1H), 7.83 - 7.88 (m, 2H), 7.30 - 7.43 (m, 9H), 2.65 - 2.72 (m, 1H), 2.42 - 2.51 (q, 2H), 1.95 - 2.01 (m, 1H), 1.26 - 1.34 (m, 3H), 1.01 - 1.10 (m, 1H), 0.81 - 0.85 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 200.0, 199.3, 190.8, 175.6, 141.9, 141.3, 137.9, 135.92, 135.87, 132.8, 132.3, 130.7, 128.5, 127.6, 124.7, 123.9, 123.7, 121.5, 118.4, 105.5, 86.8, 51.0, 39.7, 39.2, 26.0, 22.6, 13.9; HRMS (ESI-TOF) *m/z* calcd for C₃₀H₂₅O₄ [M + H]⁺ 449.1747, found 449.1746.



2'-Benzyl-2'-phenyl-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4v**): Obtained as a yellow solid (34.7 mg, 72% yield); Melting point: 168 - 169 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.06 (d, *J* = 7.6 Hz, 1H), 7.84 - 7.94 (m, 3H), 7.41 - 7.44 (t, *J* = 7.2, 6.8 Hz, 1H), 7.28 - 7.36 (m, 6H), 7.20 - 7.22 (m, 2H), 7.08 - 7.15 (m, 3H), 6.83 (d, *J* = 7.2 Hz, 1H), 4.02 (d, *J* = 14.4 Hz, 1H), 3.20 (d, *J* = 14.4 Hz, 1H), 2.62 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 200.2, 198.9, 190.7, 175.2, 141.3, 141.2, 141.0, 137.6, 136.0, 135.9, 135.1, 132.7, 132.4, 130.79, 130.76, 128.2, 127.6, 127.6, 126.5, 124.9, 123.9, 123.8, 121.6, 118.5, 105.9, 85.9, 50.9, 46.5, 38.9; HRMS (ESI-TOF) *m/z* calcd for C₃₃H₂₃O₄ [M + H]⁺ 483.1591, found 483.1595.

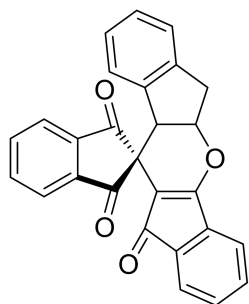


2'-cyclopentyl-2'-phenyl-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4w**): Obtained as a yellow solid (30.4 mg, 66% yield); Melting point: 146 - 147 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 7.98 - 8.01 (m, 1H), 7.80 - 7.85 (m, 3H), 7.41 - 7.43 (q, 2H), 7.31 - 7.37 (m, 5H), 7.21 - 7.23 (m, 2H), 2.73 (d, *J* = 14.4 Hz, 1H), 2.61 - 2.69 (m, 1H), 2.56 (d, *J* = 14.4 Hz, 1H), 1.81 - 1.91 (m, 1H), 1.46 - 1.62 (m, 6H), 1.30 - 1.34 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 200.5, 197.7, 190.5, 175.9, 141.2, 140.9, 140.7, 137.6, 135.9, 135.5, 132.8, 132.2, 130.7, 128.1, 127.4, 125.2, 123.8, 123.5, 121.5, 118.1, 105.9, 87.8, 50.6, 50.4, 37.6, 27.3, 27.02, 25.69, 25.4; HRMS (ESI-TOF) *m/z* calcd for C₃₁H₂₅O₄ [M + H]⁺ 461.1747, found 461.1745.



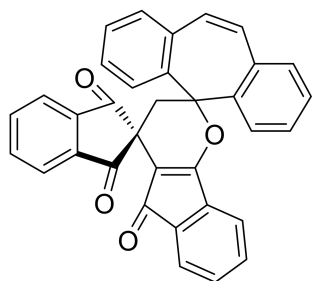
2'-cyclohexyl-2'-phenyl-2'H-spiro[indene-2,4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4x**): Obtained as a yellow solid (30.3 mg, 64% yield); Melting point: 153 - 154 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.02 - 8.04 (m, 1H), 7.84 - 7.90 (m, 3H), 7.42 - 7.44 (q, 2H), 7.31 - 7.38 (m, 5H), 7.24 - 7.26 (q, 2H), 2.81 (d, *J* = 14.4 Hz, 1H), 2.57 (d, *J* = 14.8 Hz, 1H), 2.22 - 2.28 (t, *J* = 12.0, 11.6 Hz, 1H), 2.05 - 2.10 (m, 1H), 1.69 - 1.76 (t, *J* = 13.2, 12.8 Hz, 2H), 1.58 - 1.64 (t, *J* = 13.2, 9.6 Hz, 1H), 1.51 - 1.55 (m, 1H), 1.24 - 1.32 (m, 2H), 0.98 - 1.92 (m, 2H), 0.86 - 0.93 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 200.3, 198.4, 190.6, 175.4, 141.2, 141.0, 139.6, 137.8, 136.0, 135.7, 132.9, 132.2, 130.7, 127.9, 127.5, 125.7, 123.8, 123.7, 121.5, 118.2, 105.6, 100.0, 88.5, 50.7, 46.8, 35.5, 27.8, 27.1, 26.13, 26.07; HRMS (ESI-TOF)

m/z calcd for C₃₂H₂₇O₄ [M + H]⁺ 475.1904, found 459.1956.



5a,6-Dihydrospiro[diindeno[1,2-b:1',2'-e]pyran-11,2'-indene]-1',3',

12(10bH)-trione (**4y**): Obtained as a yellow solid (32.7 mg, 81% yield); Melting point: 172 - 173 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.13 (d, *J* = 7.2 Hz, 1H), 8.03 (d, *J* = 7.2 Hz, 1H), 7.88 - 7.96 (m, 2H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.23 - 7.39 (m, 6H), 7.15 (d, *J* = 6.8 Hz, 1H), 5.99 (d, *J* = 4.4 Hz, 1H), 3.44 - 3.50 (q, 1H), 2.81 - 2.87 (q, 1H), 2.66 - 2.71 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 201.0, 199.0, 190.8, 177.5, 143.6, 142.3, 140.0, 138.8, 137.4, 136.3, 135.9, 132.7, 132.0, 130.5, 130.3, 127.1, 125.7, 125.2, 124.1, 123.6, 121.3, 118.7, 102.2, 83.6, 51.4, 43.4, 33.0; HRMS (ESI-TOF) m/z calcd for C₂₇H₁₇O₄ [M + H]⁺ 405.1121, found 405.1124.



2',-2'-5H-dibenzo[a,d][7]annulene-phenyl-2'H-spiro[indene-2,

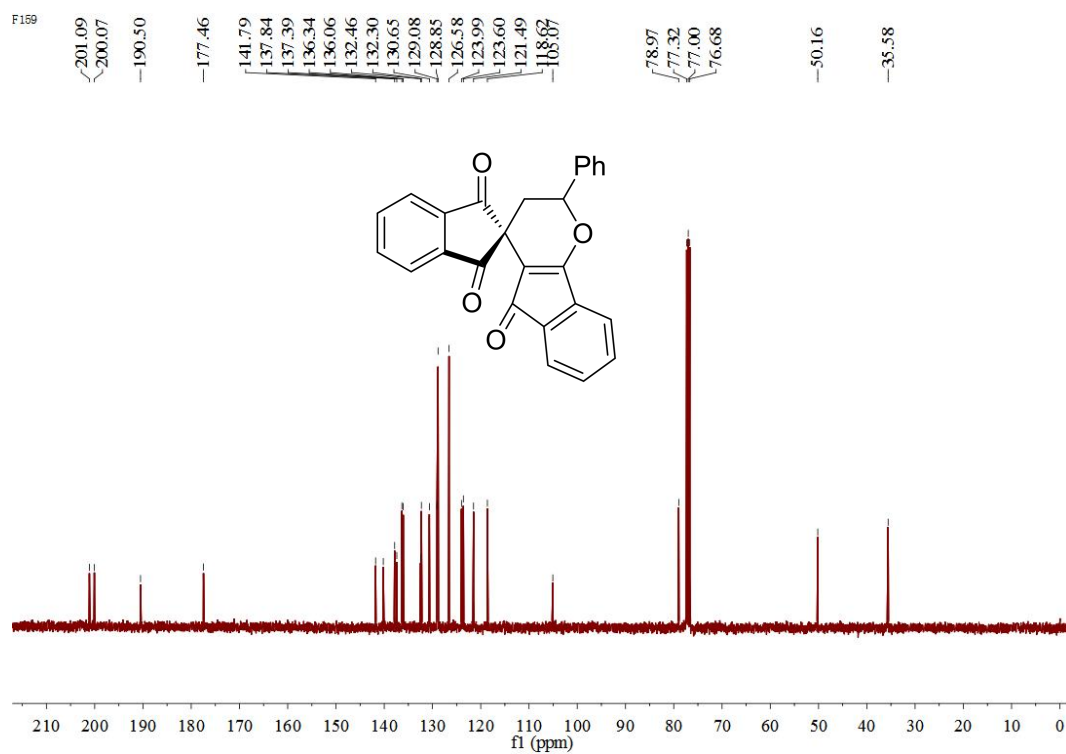
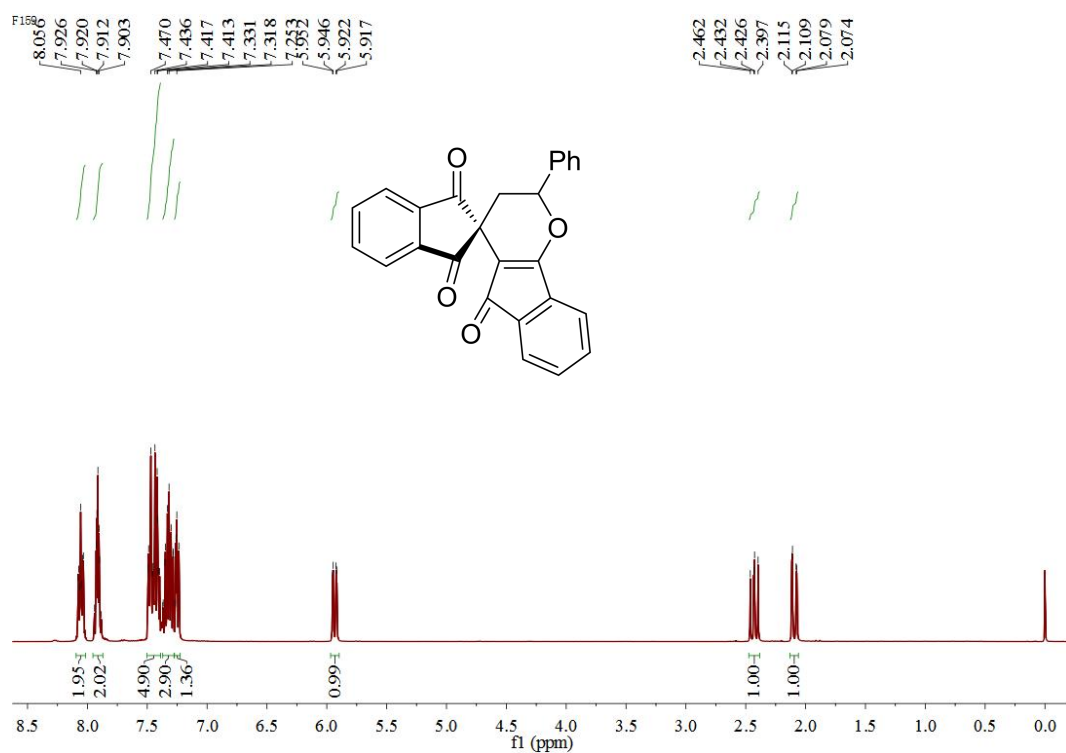
4'-indeno[1,2-b]pyran]-1,3,5'(3'H)-trione (**4z**): Obtained as a yellow solid (41.3 mg, 84% yield); Melting point: 186 - 187 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm: 7.77 - 7.86 (m, 6H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.47 - 7.54 (m, 3H), 7.38 - 7.41 (m, 6H), 6.94 (s, 2H), 2.75 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 198.6, 190.5, 175.1, 141.0, 137.6, 137.5, 135.7, 132.7, 132.5, 132.2, 131.5, 130.9, 130.0, 129.4, 127.5, 123.6, 123.4, 121.8, 118.4, 106.3, 85.1, 50.6, 31.0; HRMS (ESI-TOF) m/z calcd for C₃₄H₂₁O₄ [M + H]⁺ 493.1434, found 493.1436.

References:

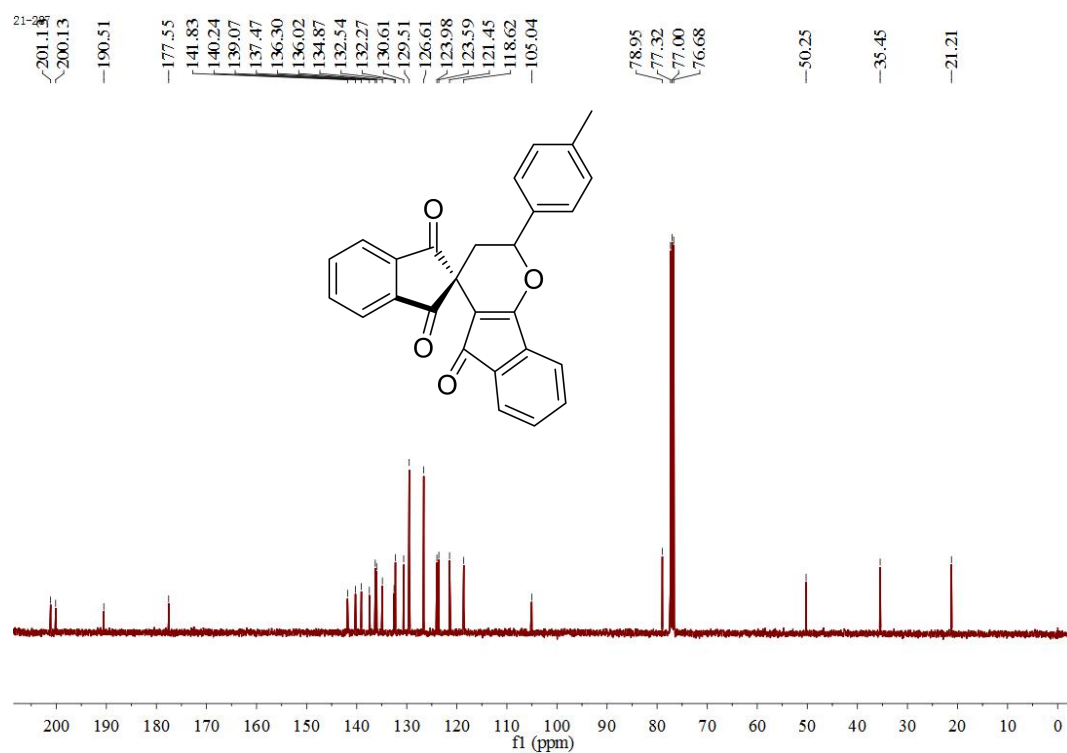
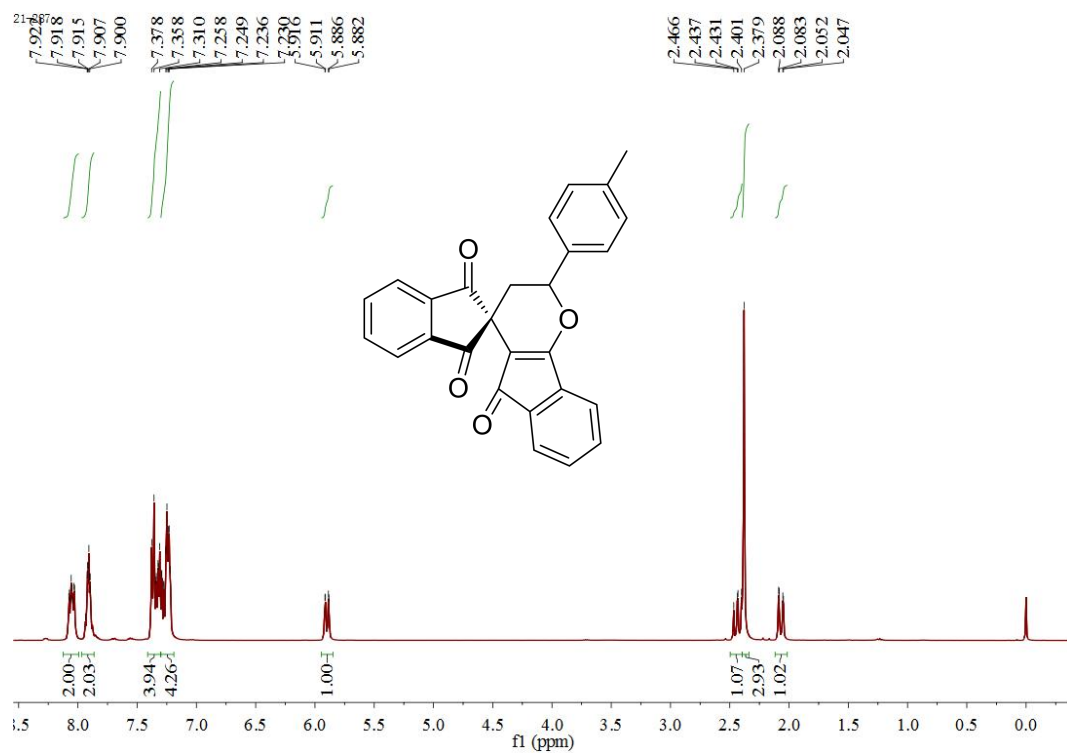
- (1) (a) Li, W.; Weng, L.; Jin, G. *Inorg. Chem. Commun.*, **2004**, 7, 1174; b) Sun, B.; Yoshino, T.; Matsunaga, S.; Kanai, M. *Adv. Synth. Catal.* **2014**, 356, 1491.

Copies of ^1H and ^{13}C NMR spectra of products

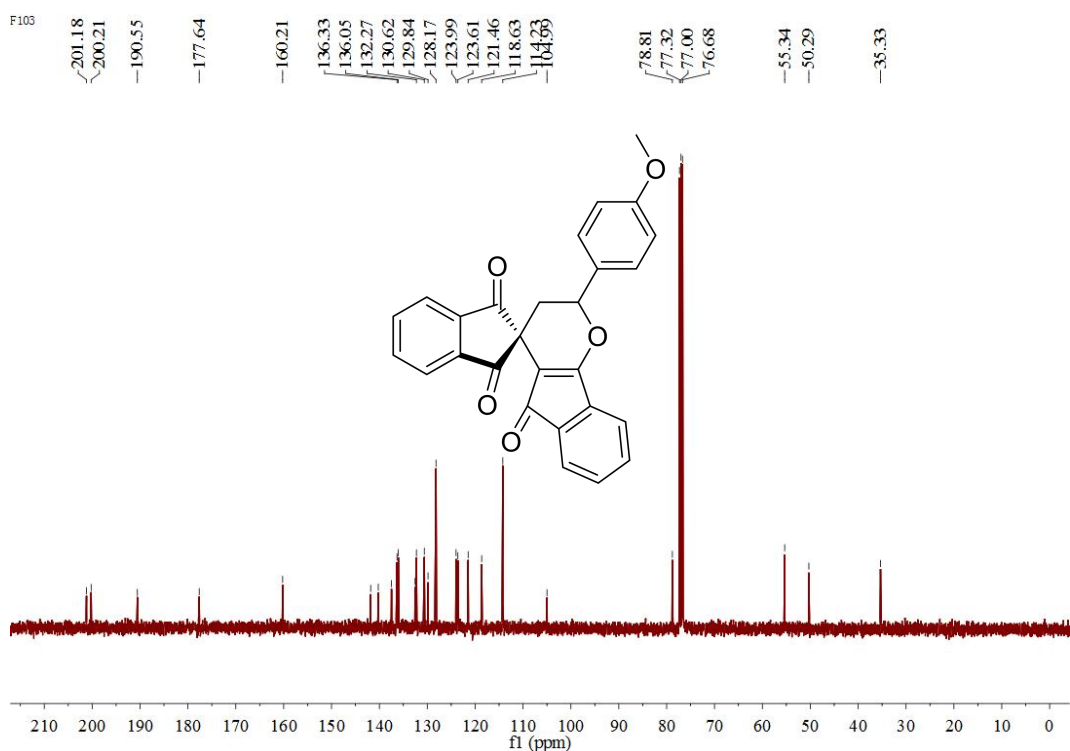
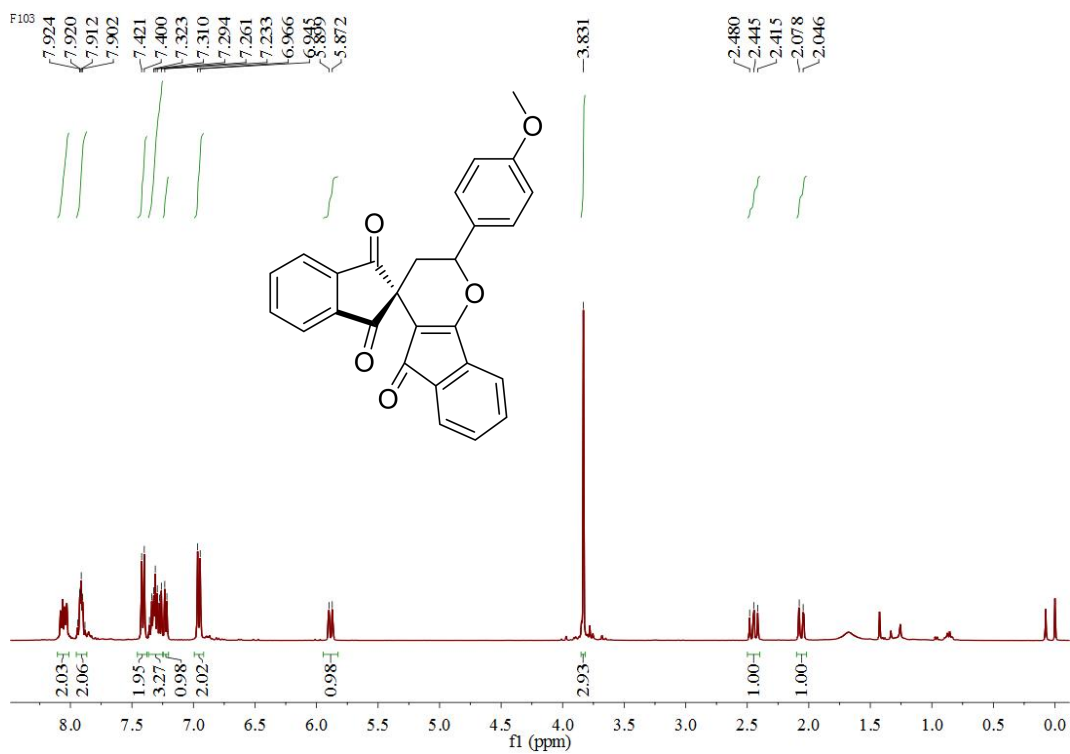
^1H NMR and ^{13}C NMR of 3a



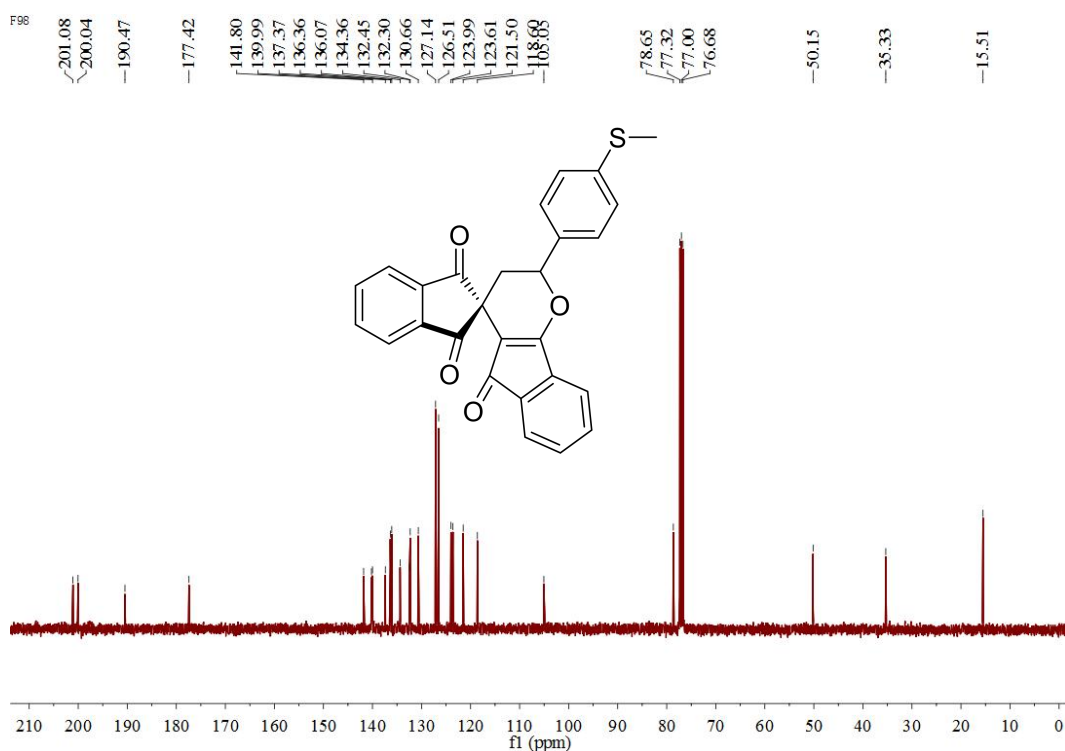
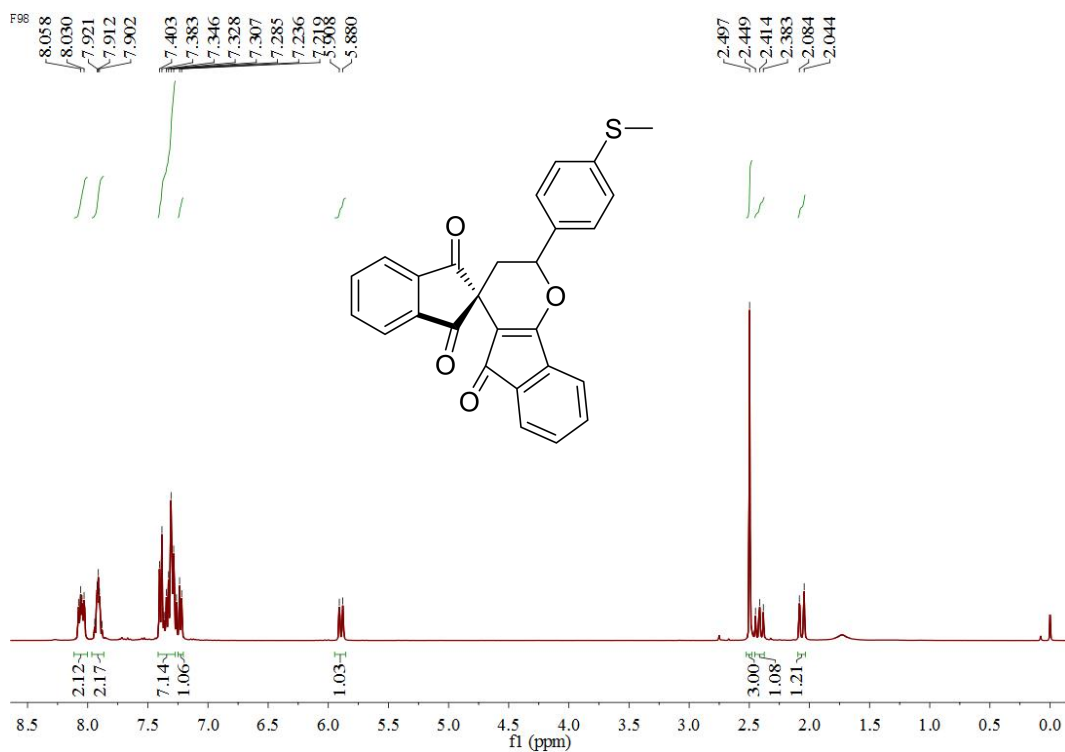
¹H NMR and ¹³C NMR of 3b



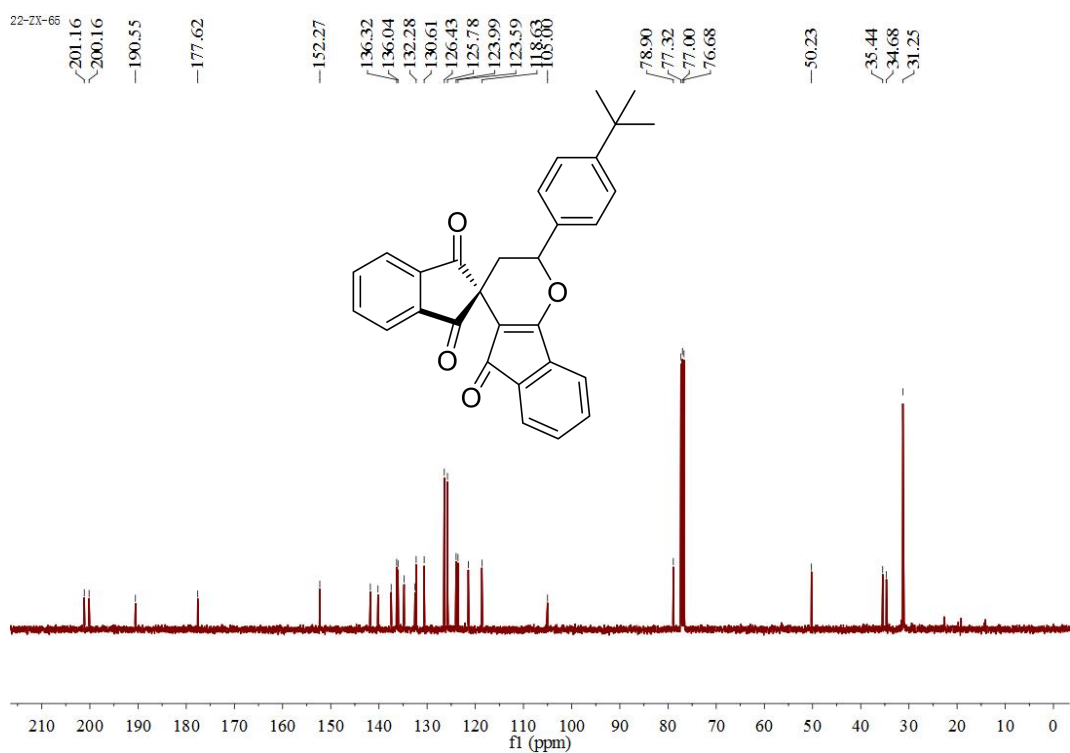
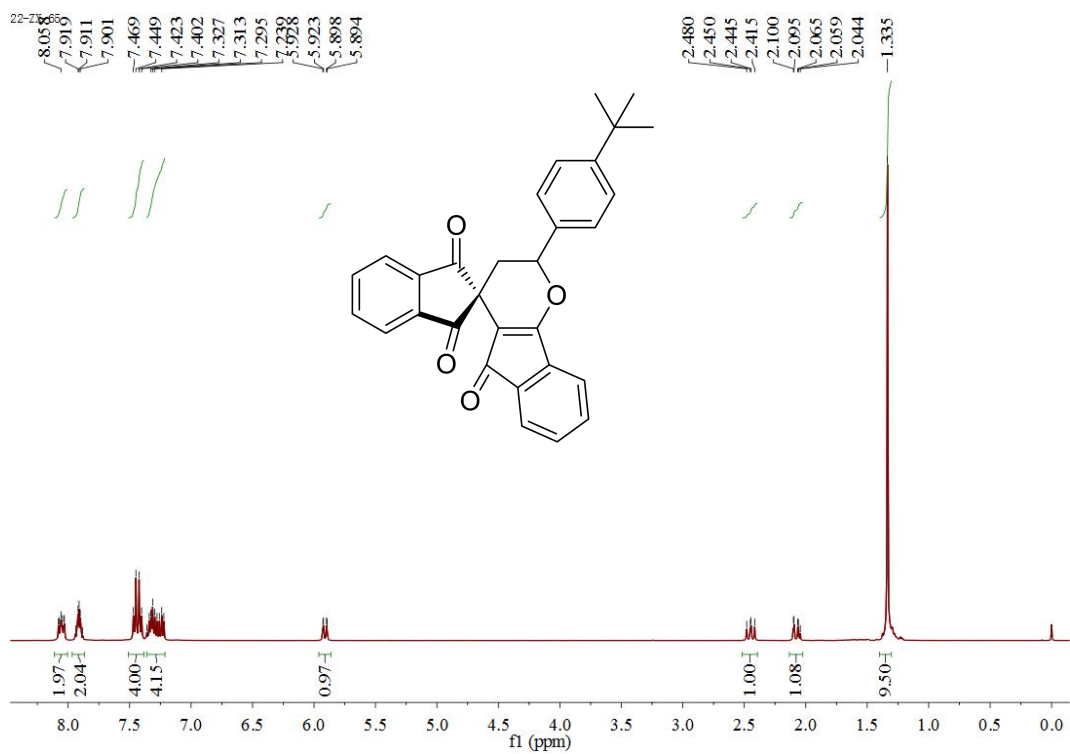
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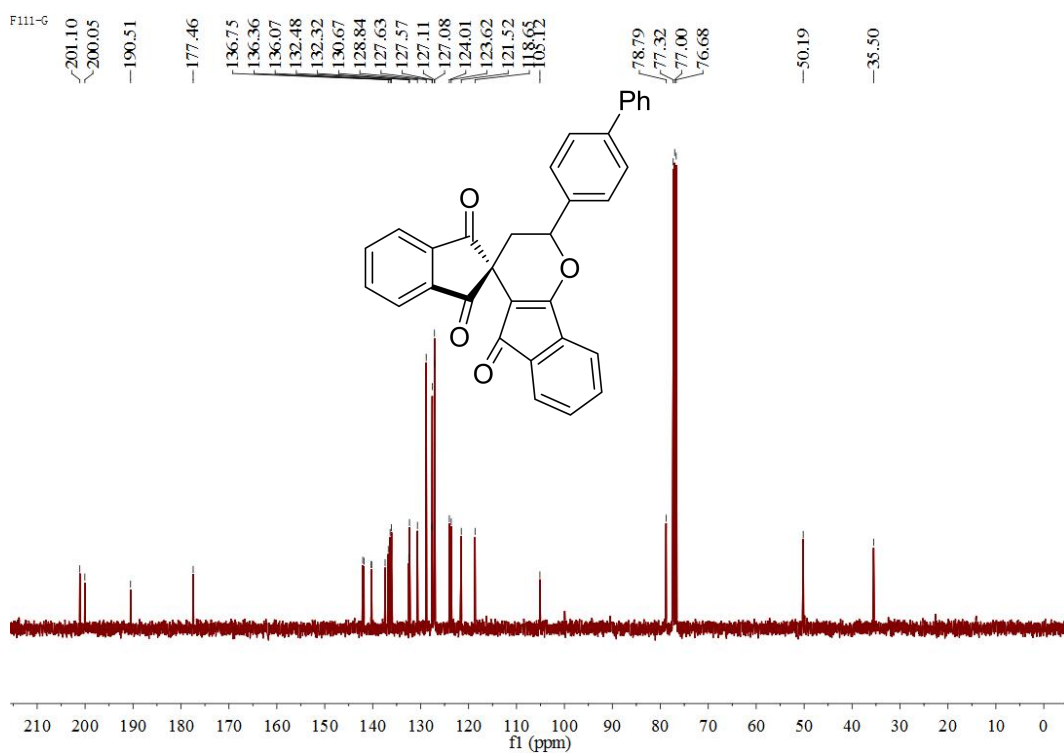
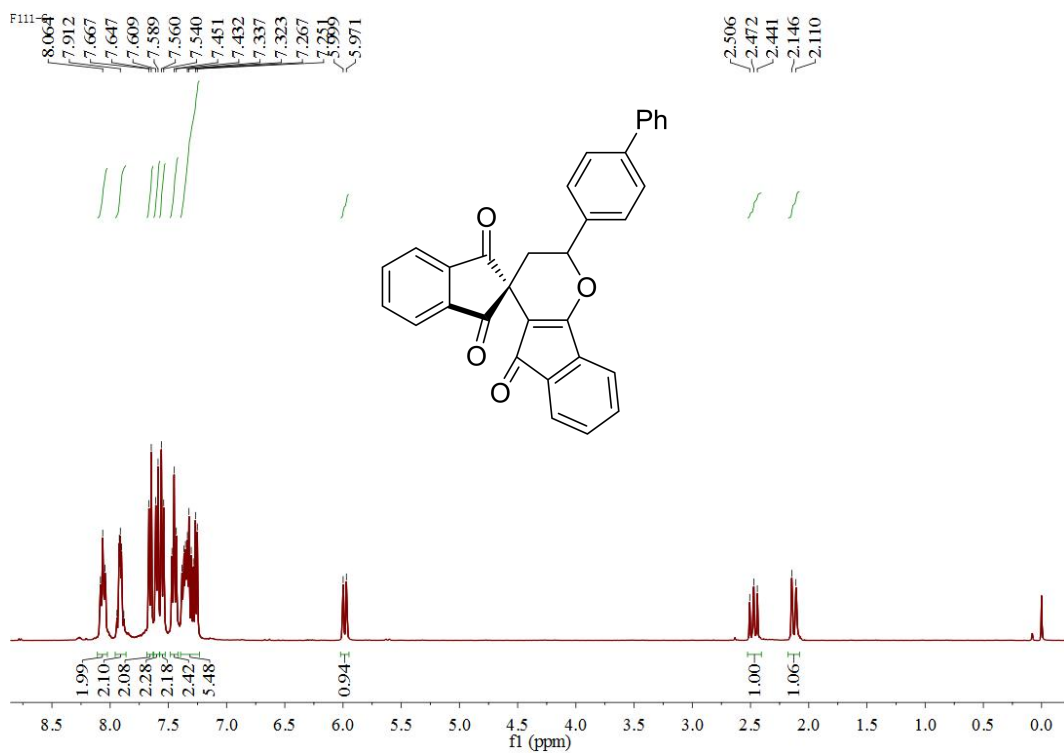
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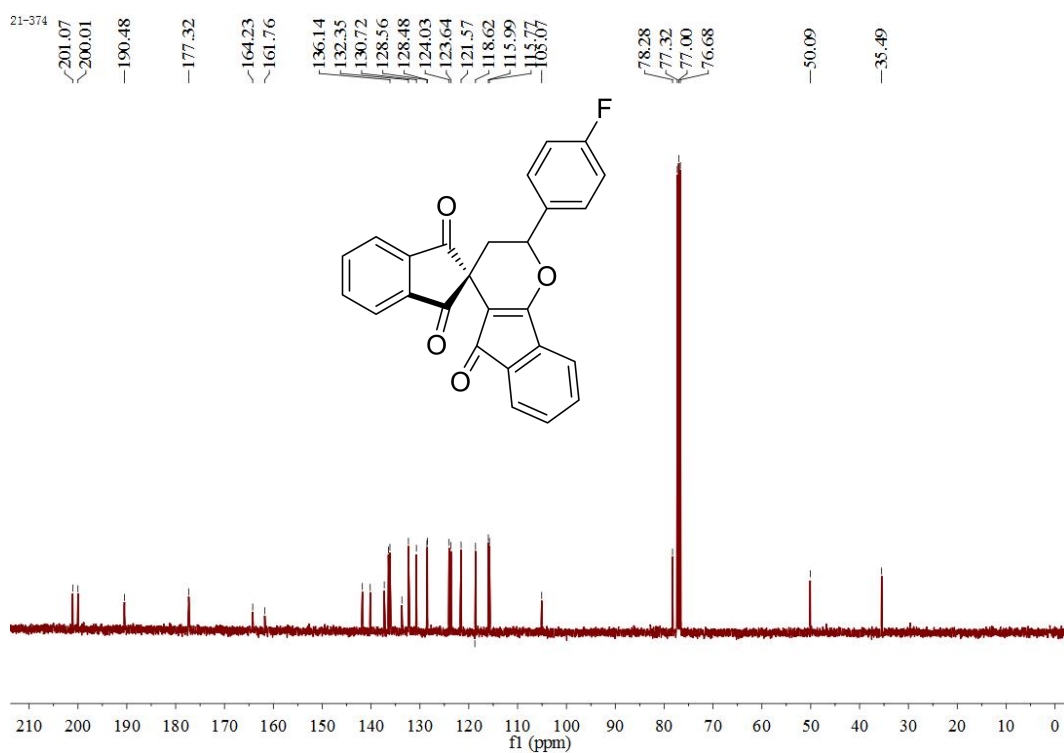
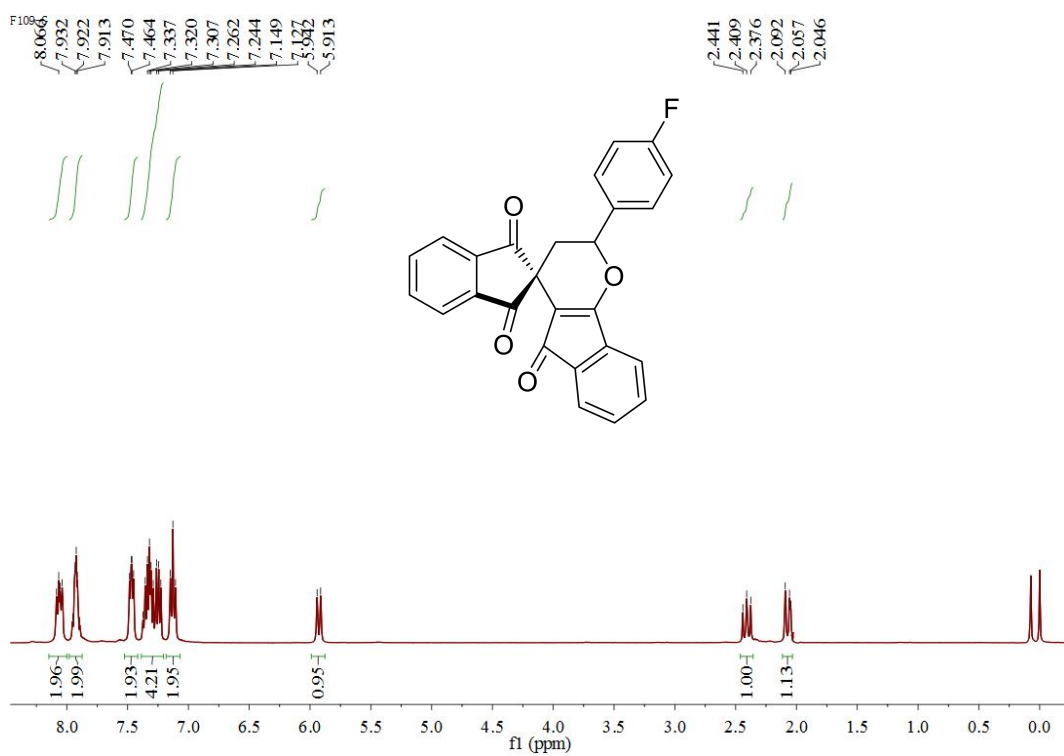
¹H NMR and ¹³C NMR of 3e



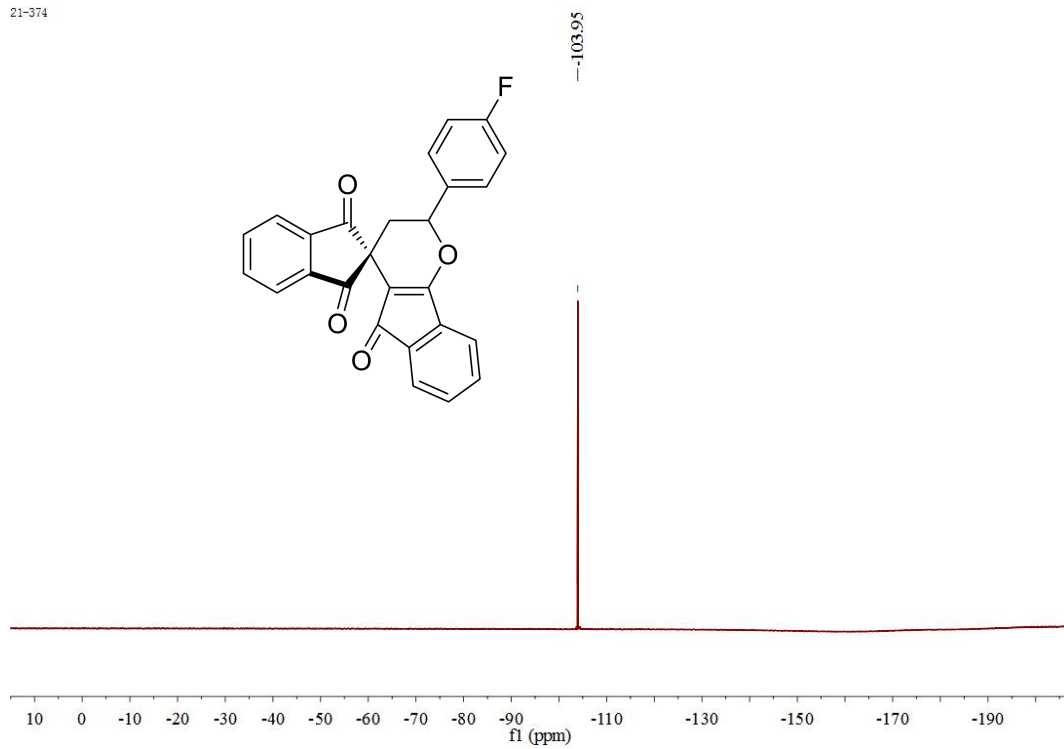
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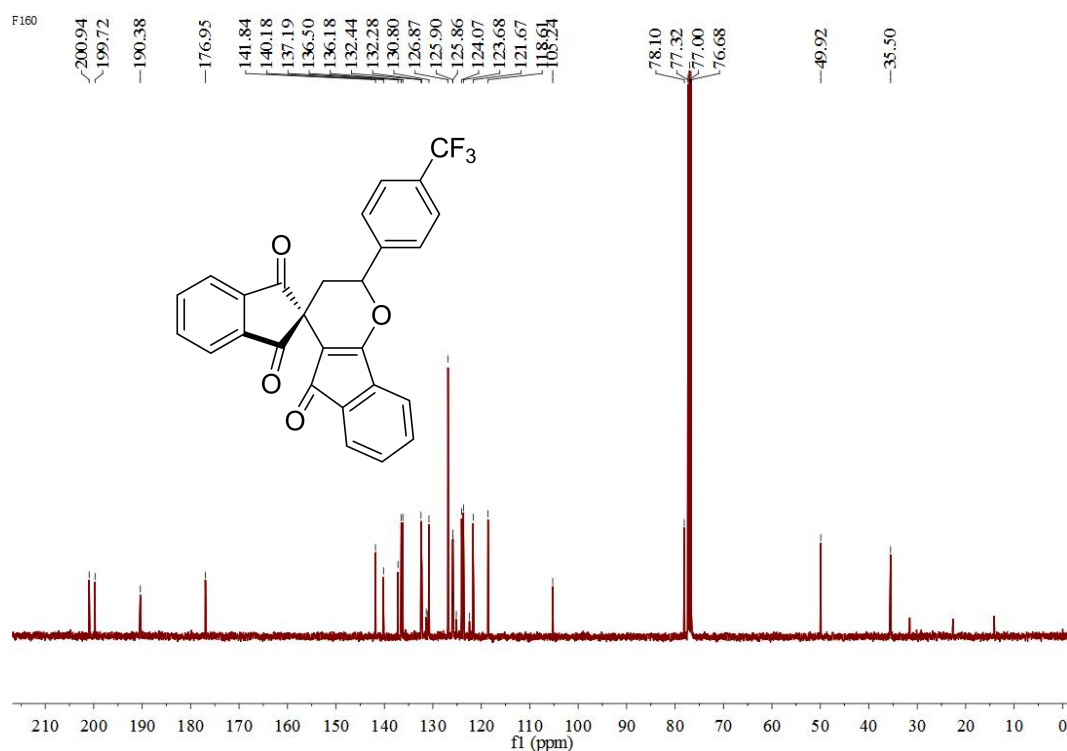
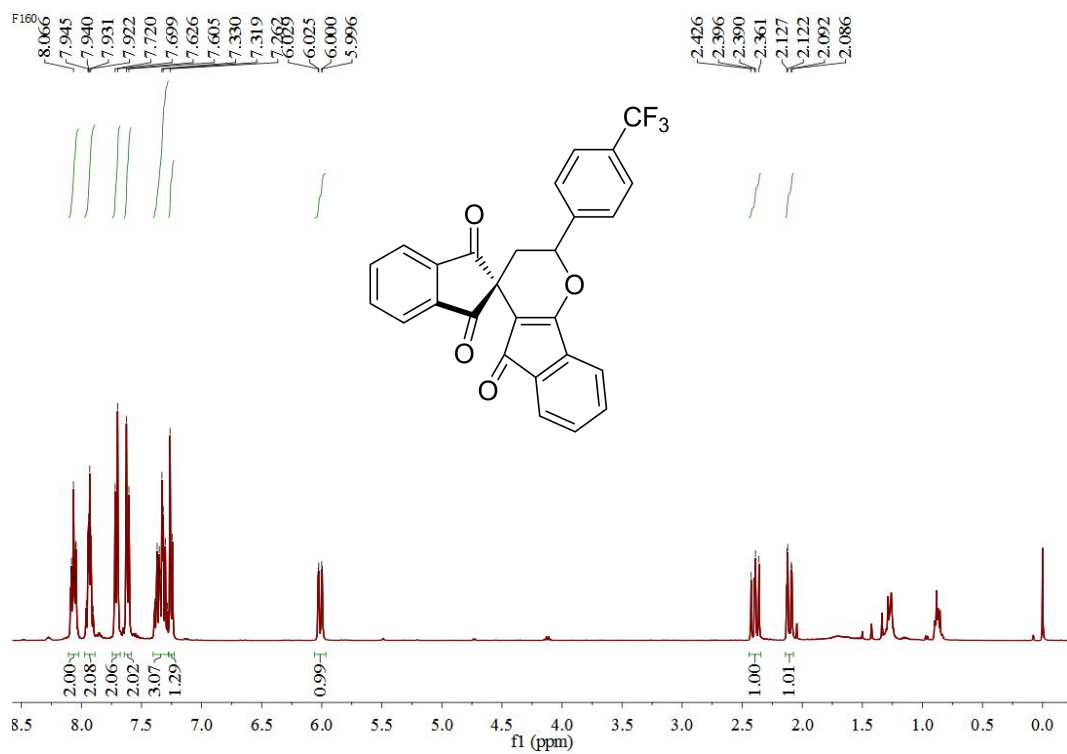
¹H NMR, ¹³C NMR and ¹⁹F NMR of 3g



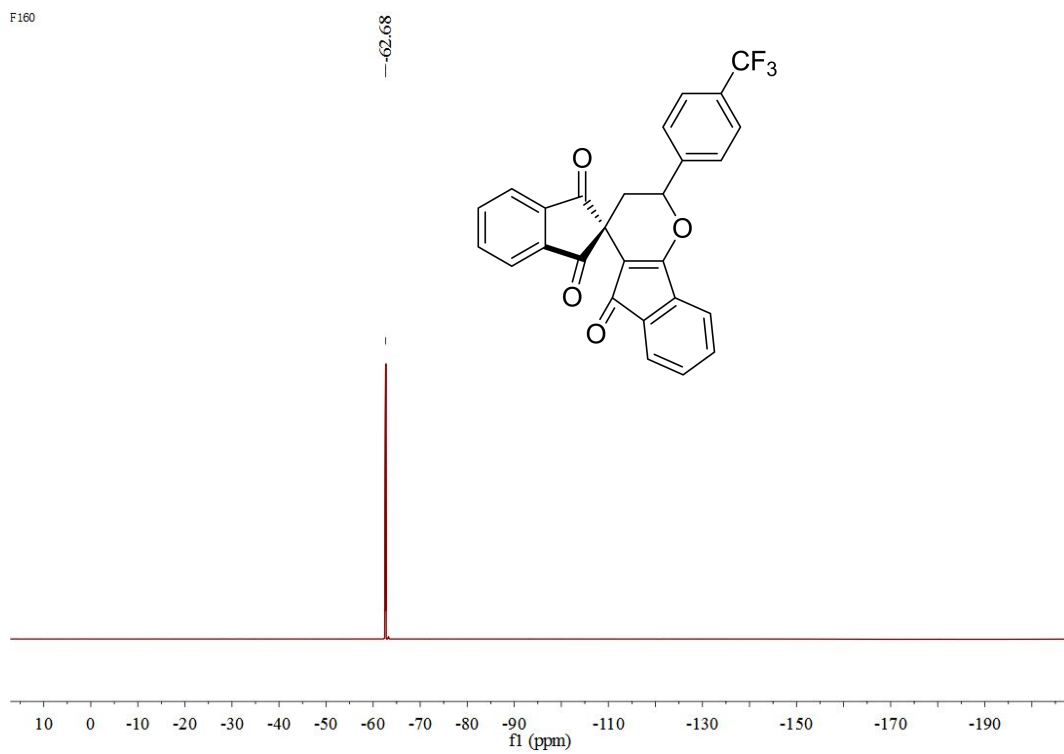
21-374



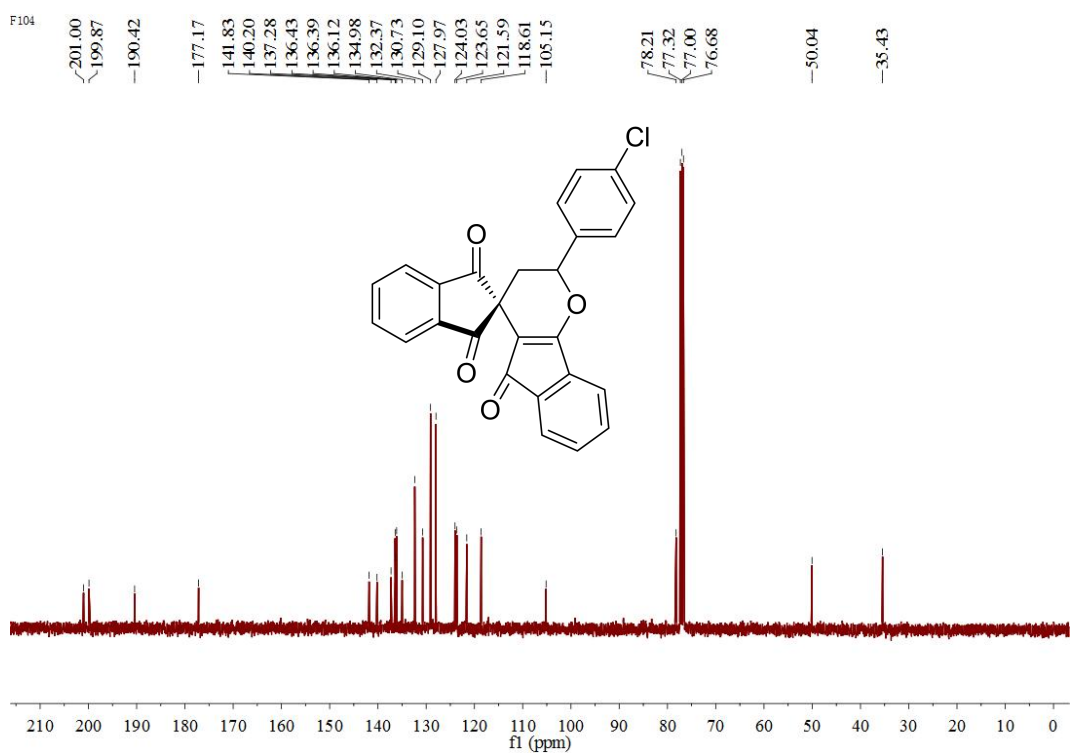
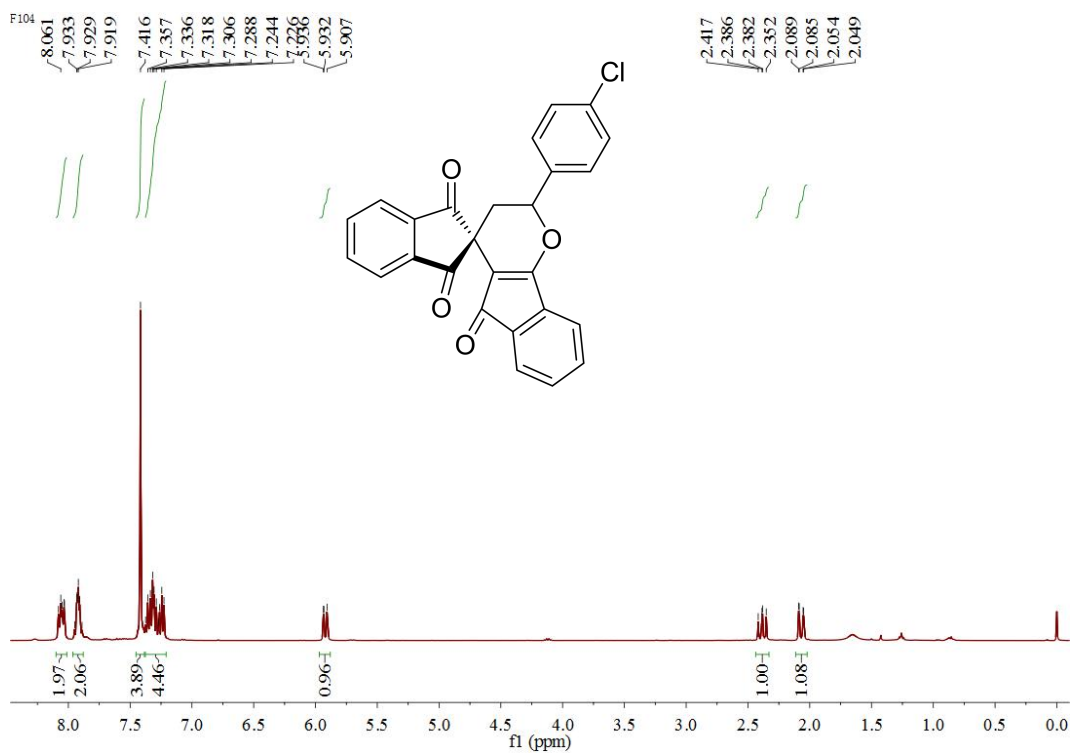
¹H NMR, ¹³C NMR and ¹⁹F NMR of 3h



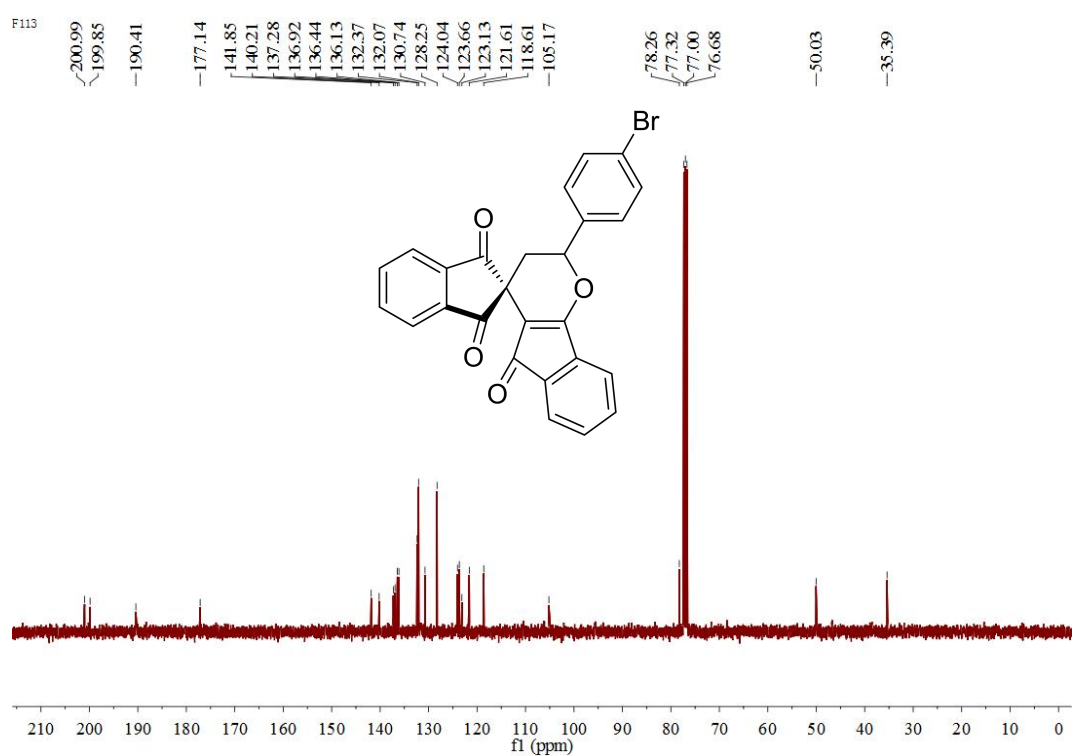
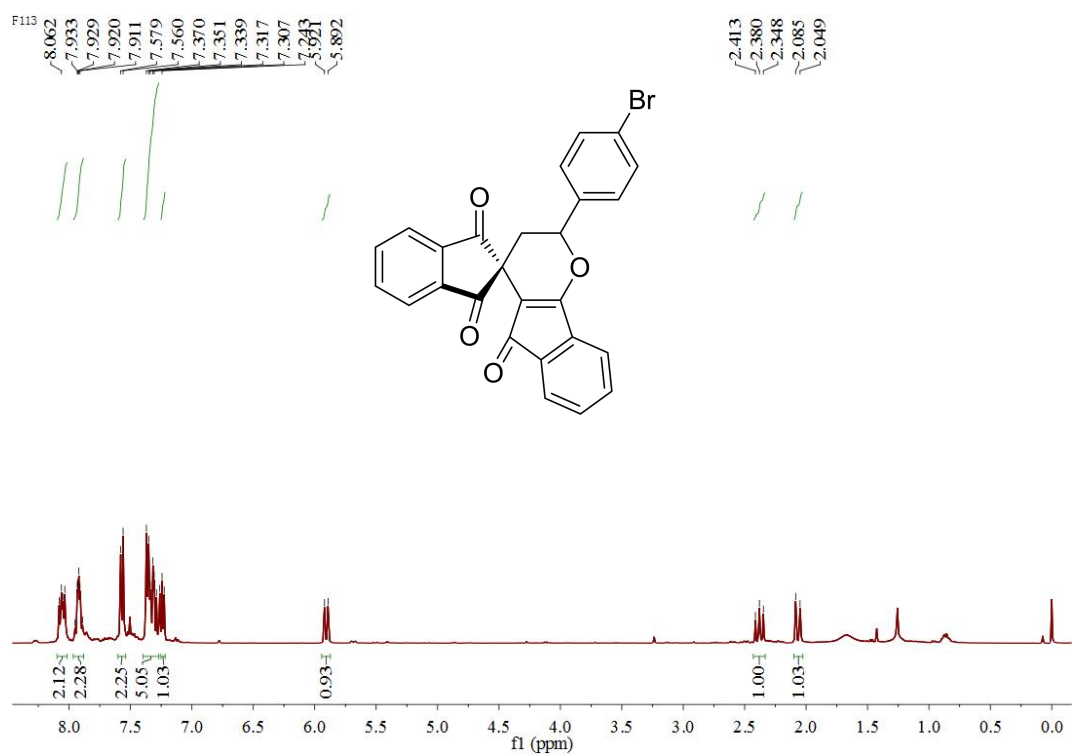
F160



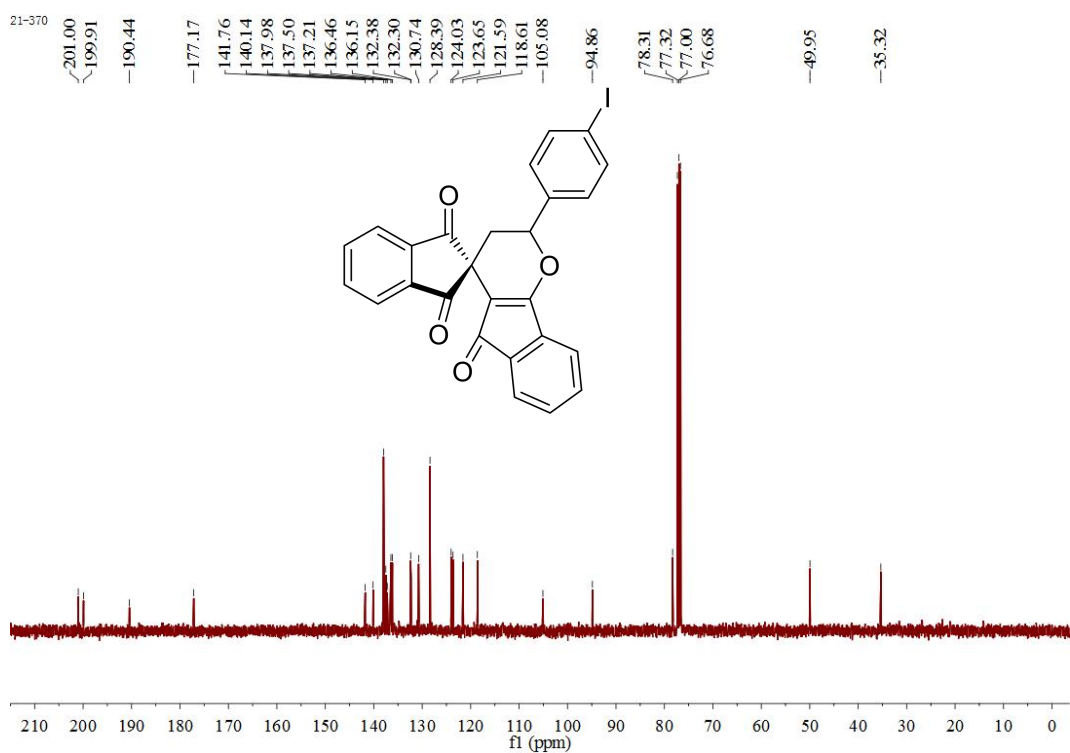
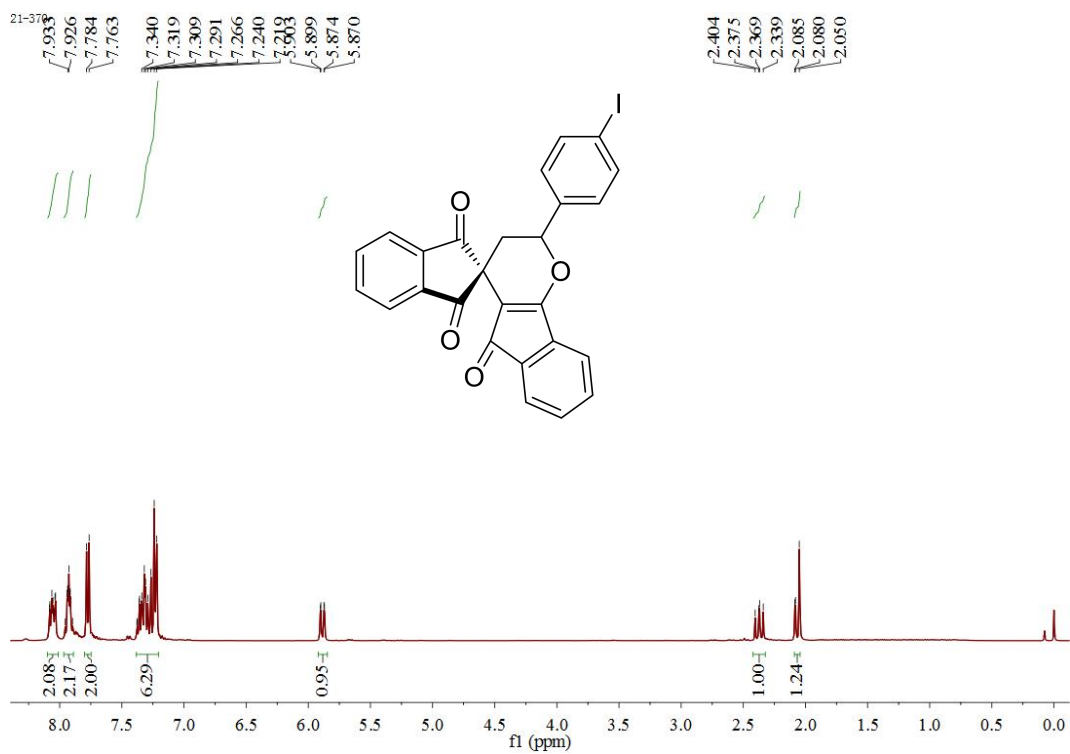
¹H NMR and ¹³C NMR of 3i



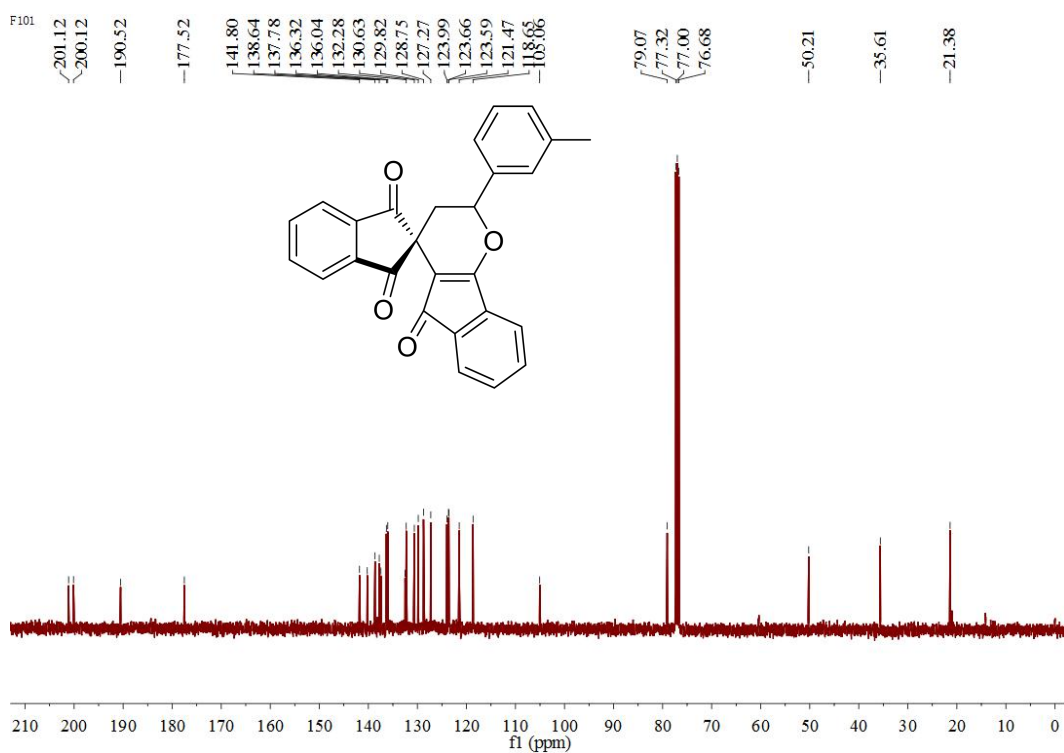
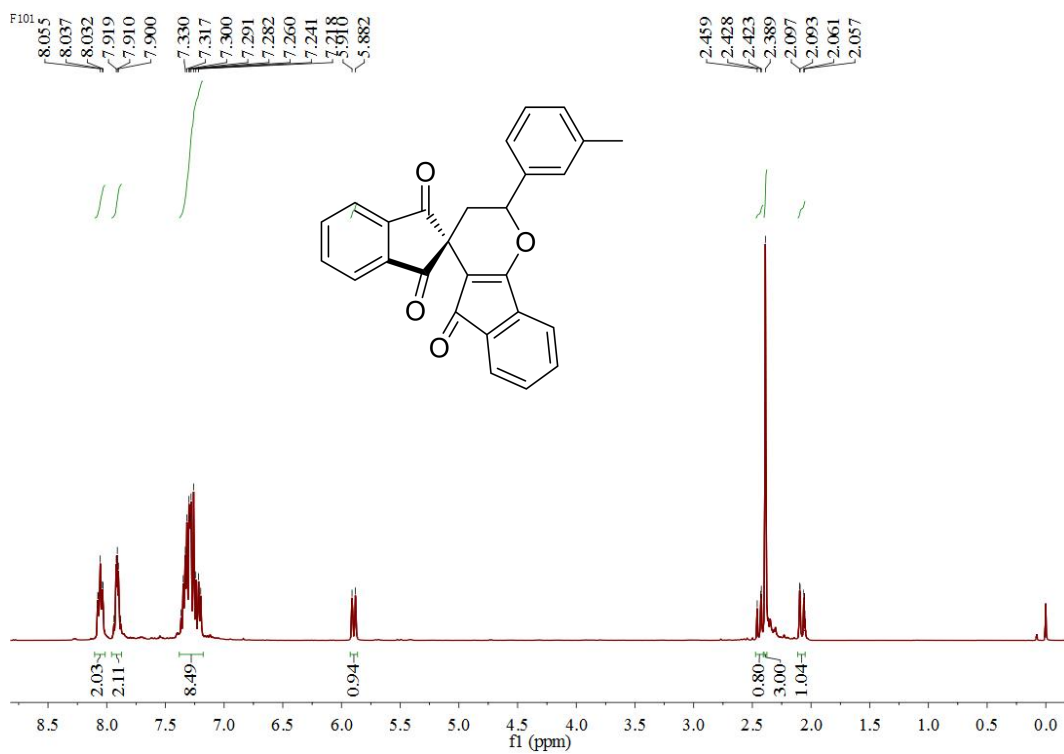
¹H NMR and ¹³C NMR of 3j



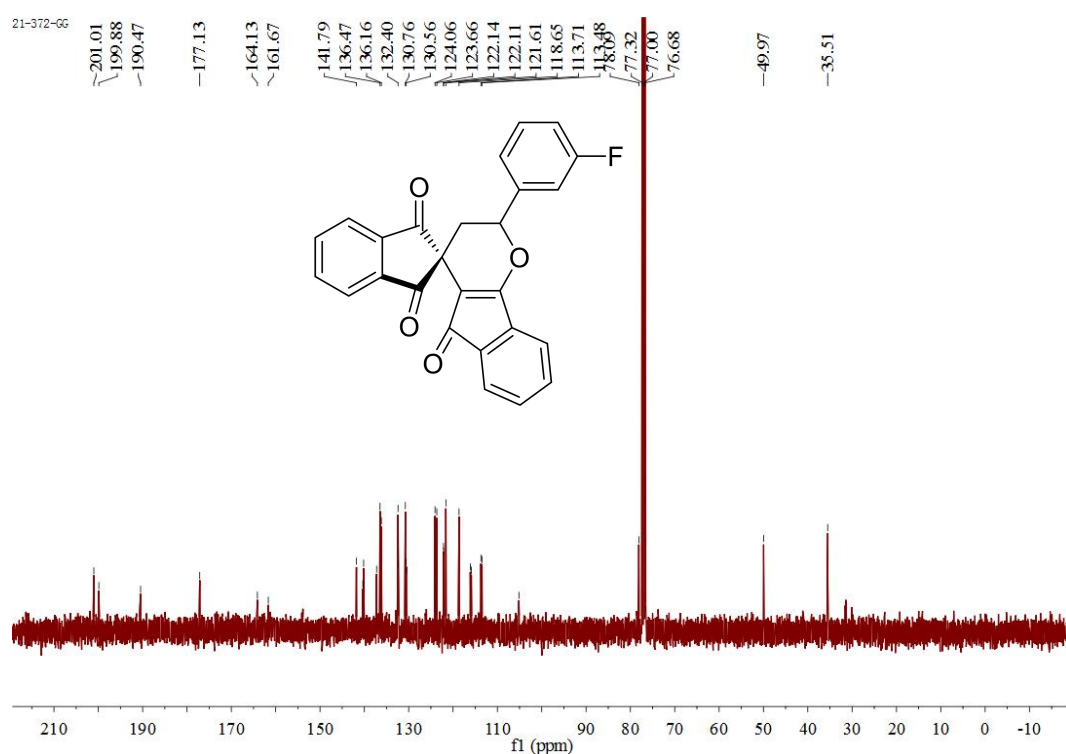
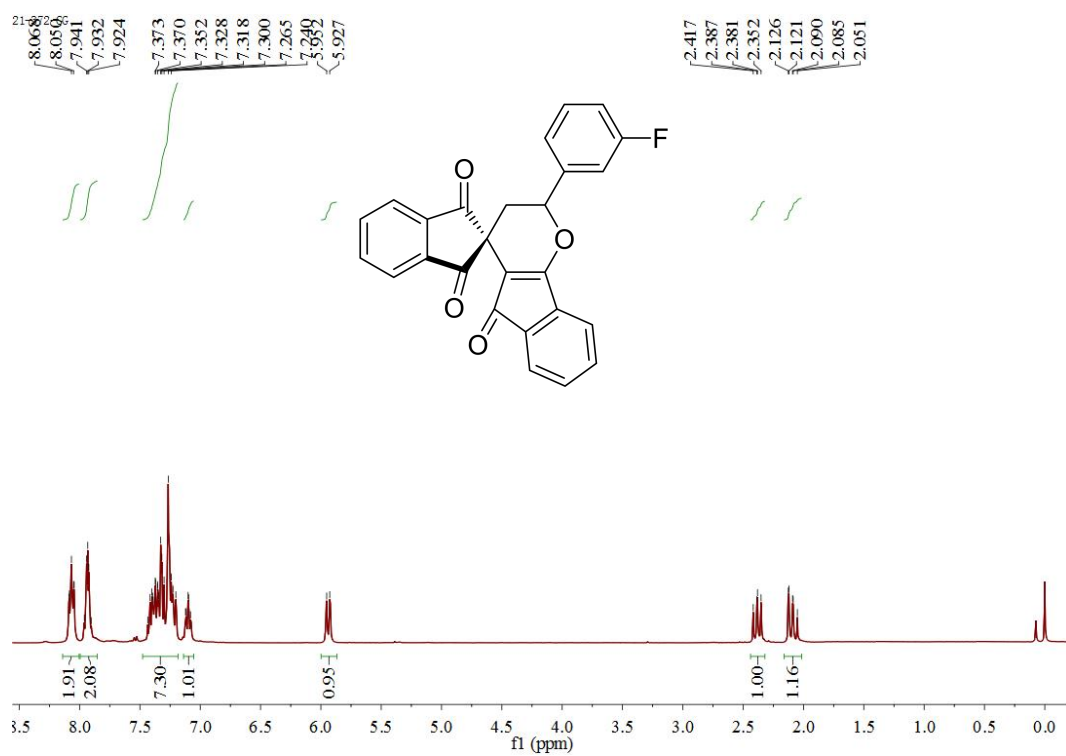
¹H NMR and ¹³C NMR of 3k



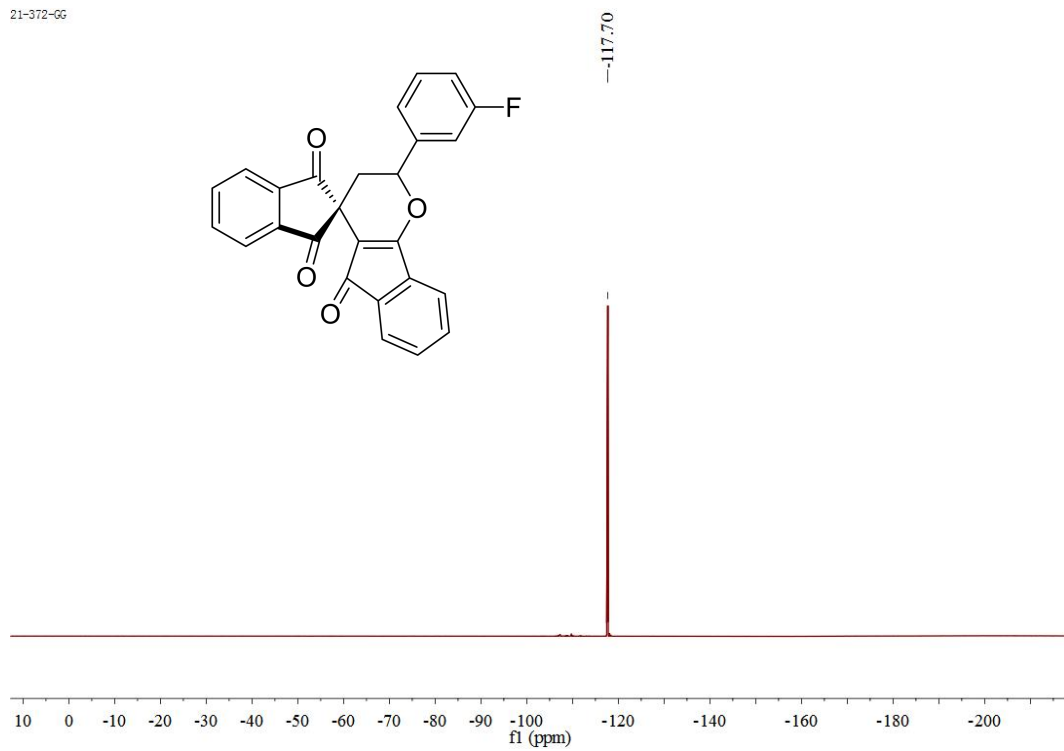
¹H NMR and ¹³C NMR of 31



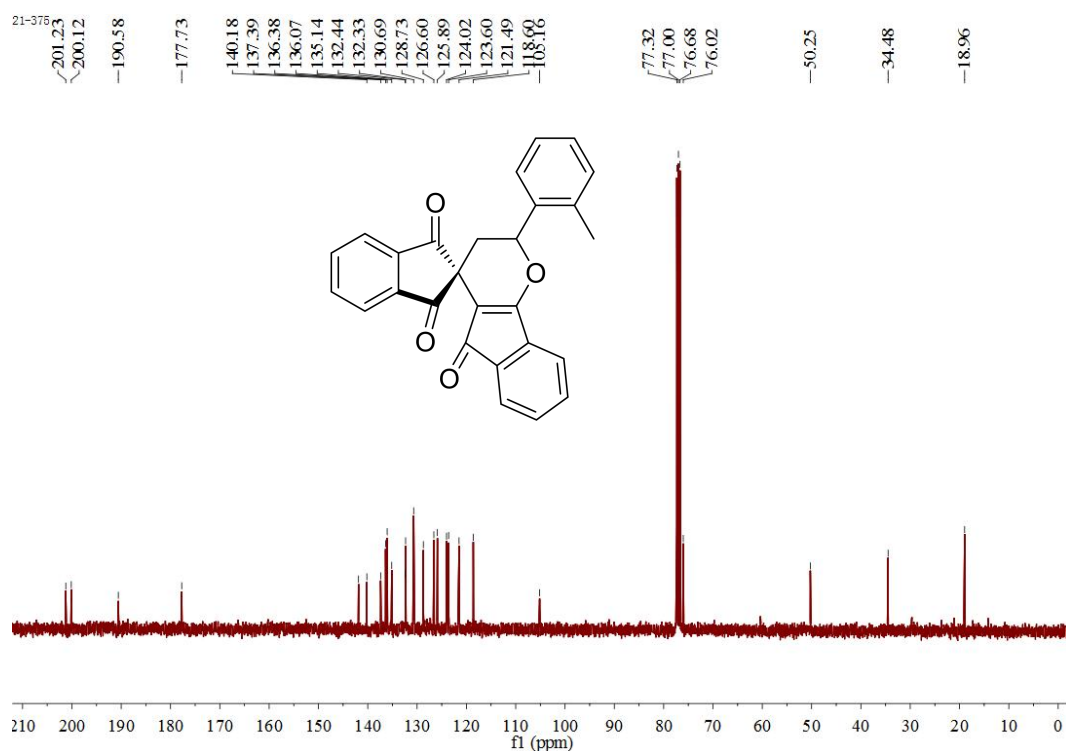
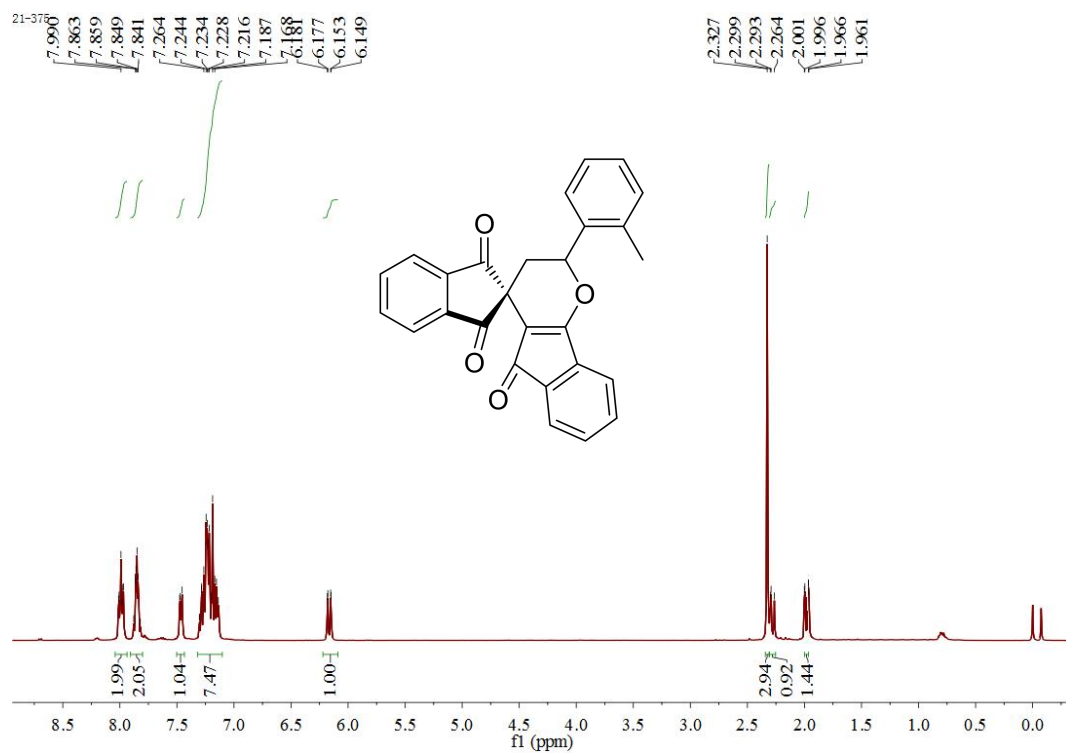
¹H NMR, ¹³C NMR and ¹⁹F NMR of 3m



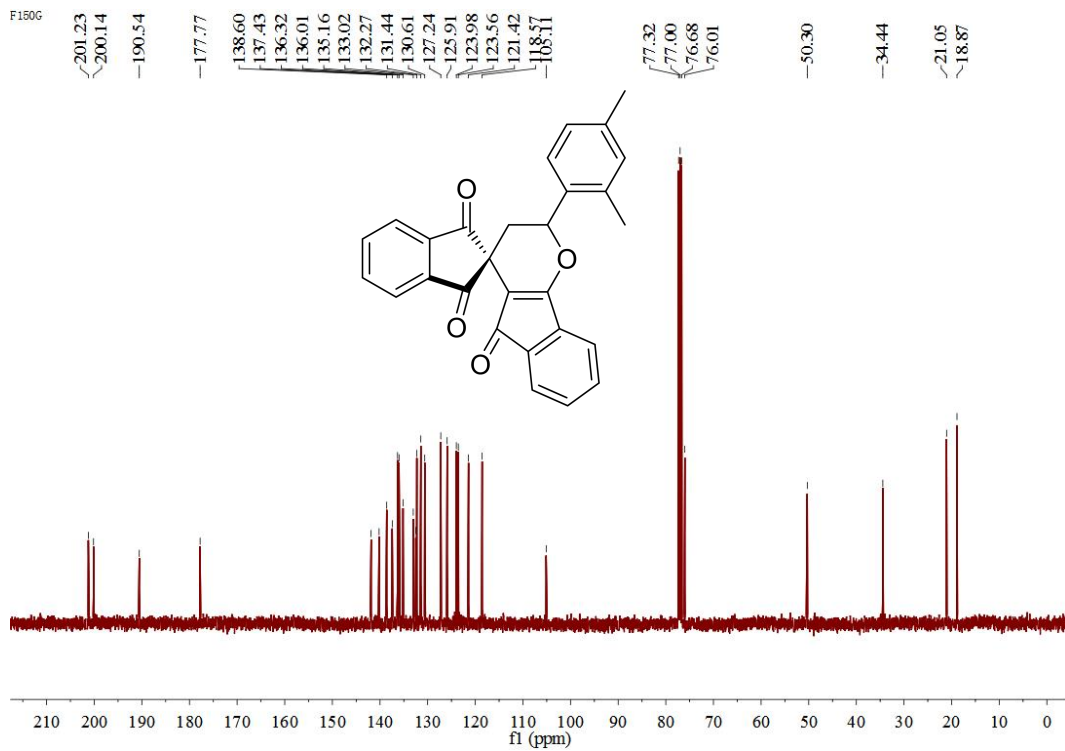
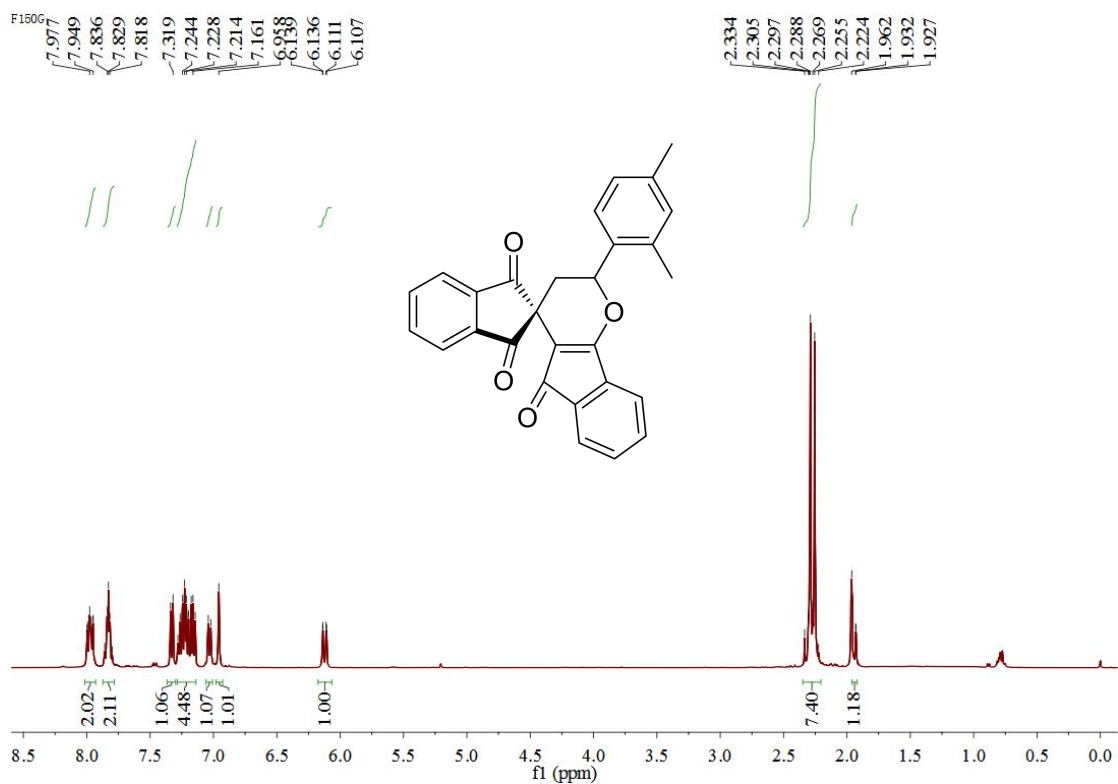
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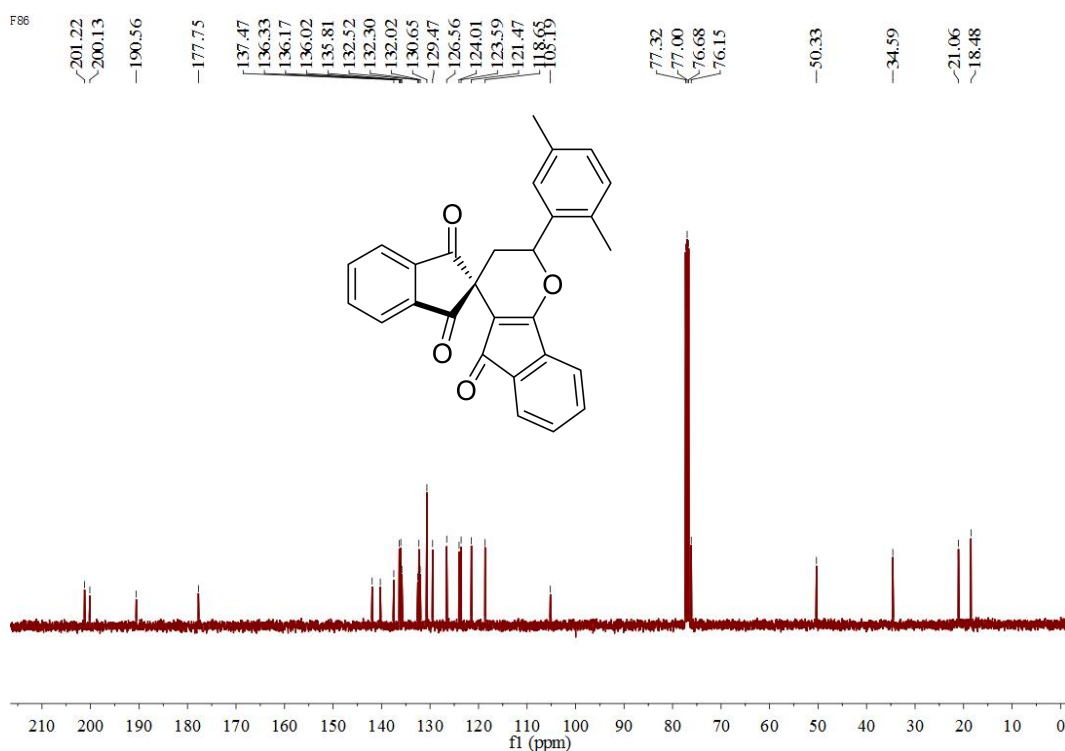
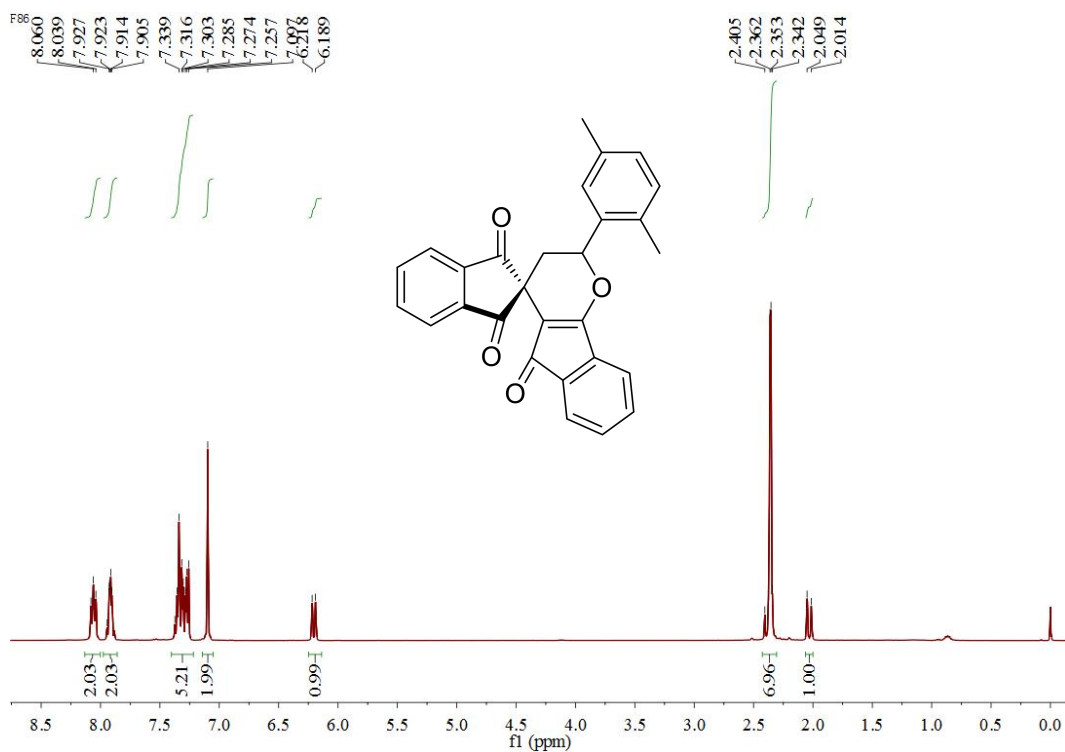
¹H NMR and ¹³C NMR of 3n



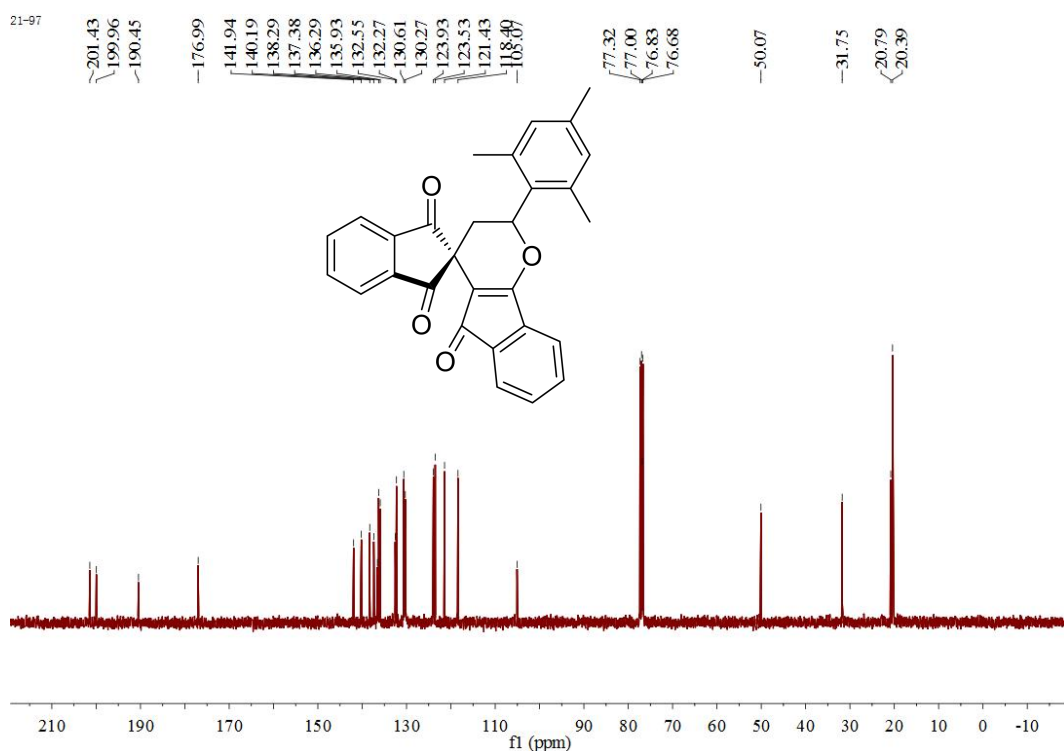
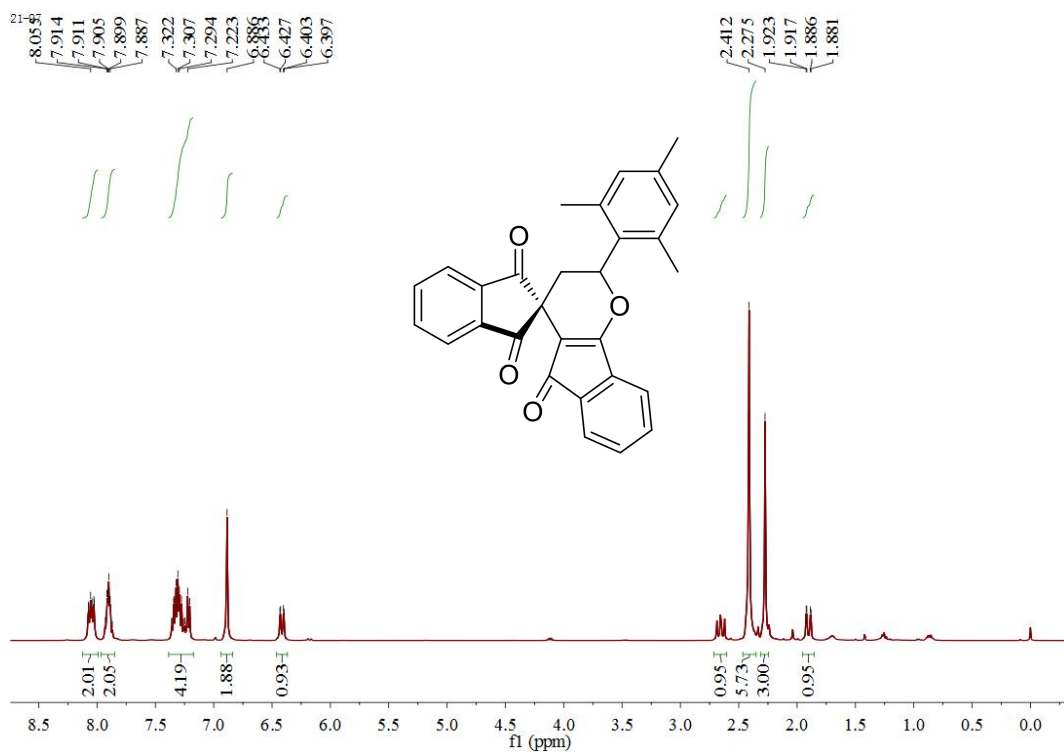
¹H NMR and ¹³C NMR of 3o



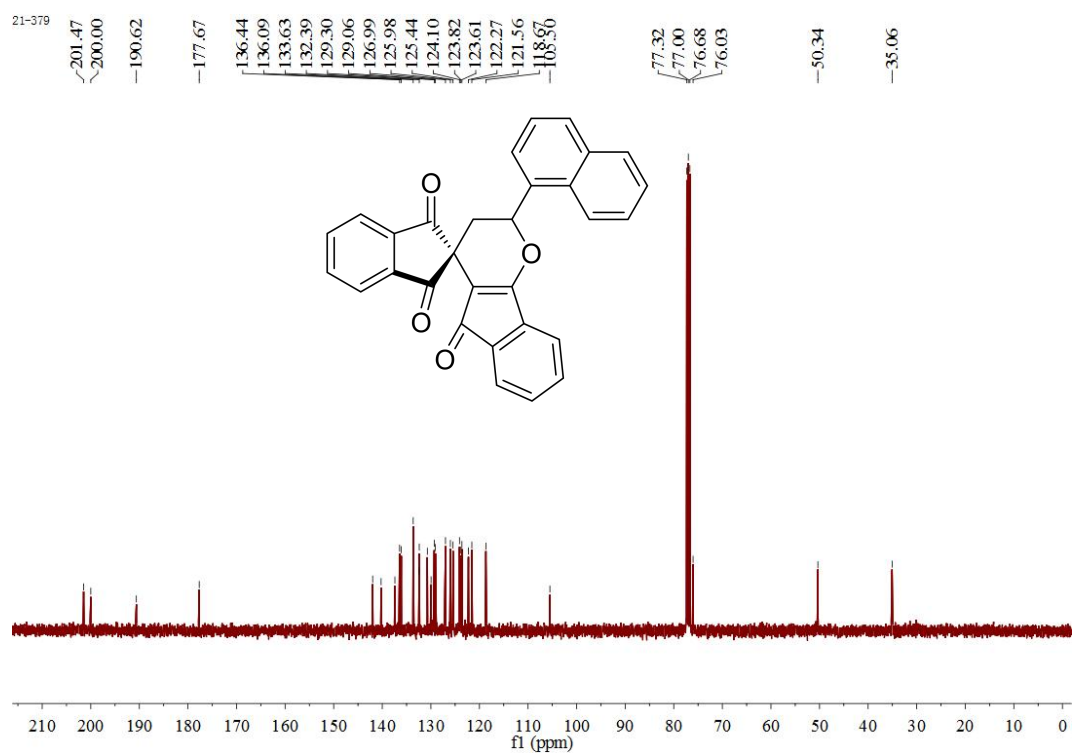
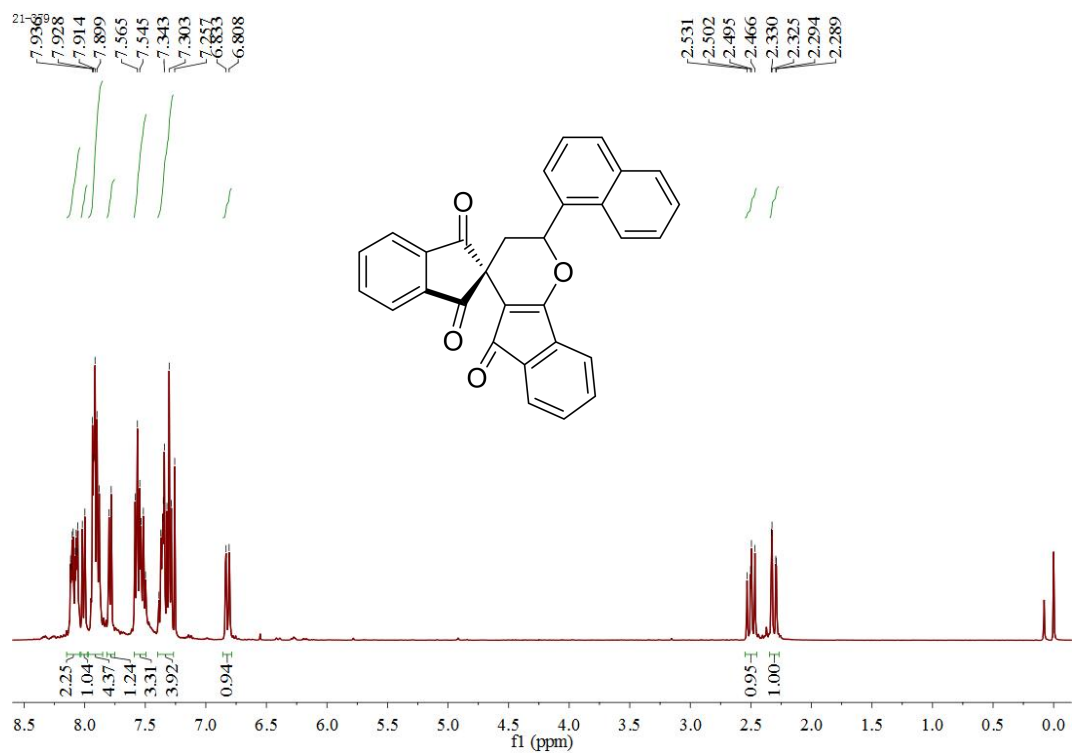
¹H NMR and ¹³C NMR of 3p



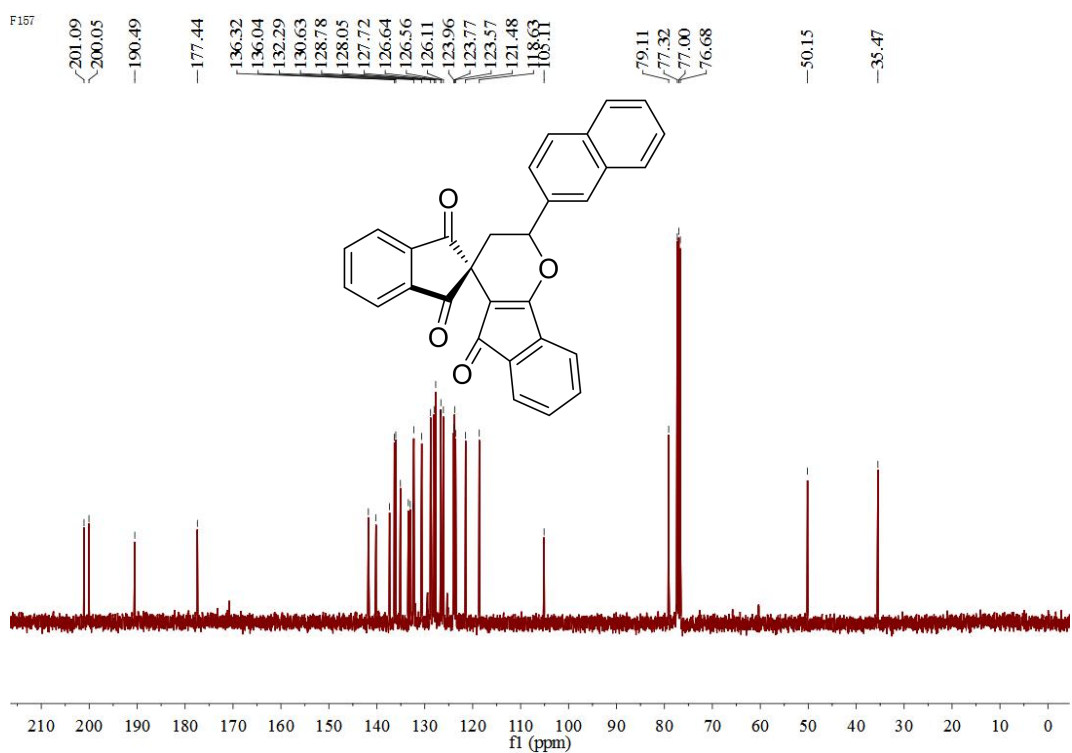
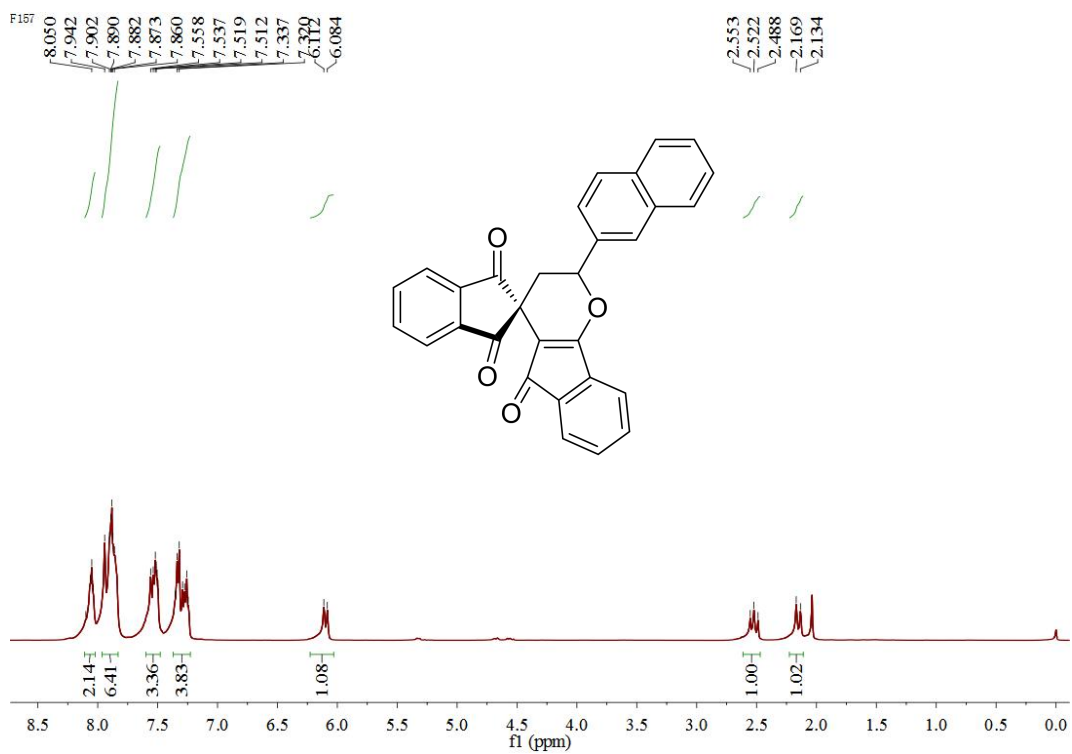
¹H NMR and ¹³C NMR of 3q



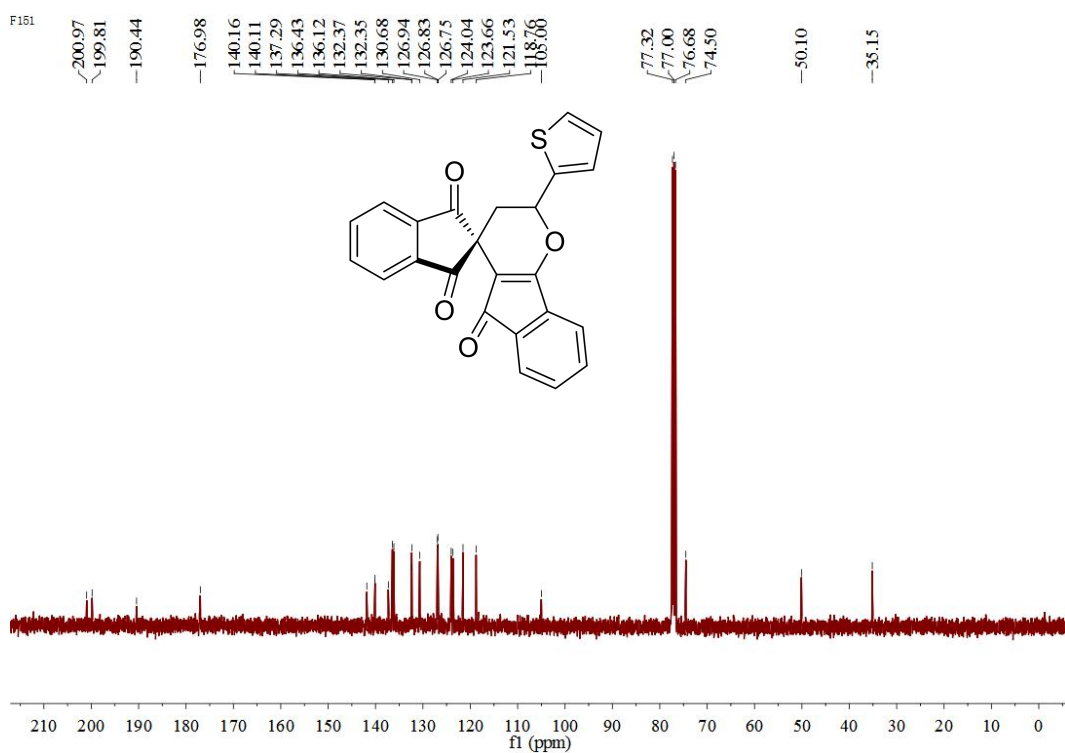
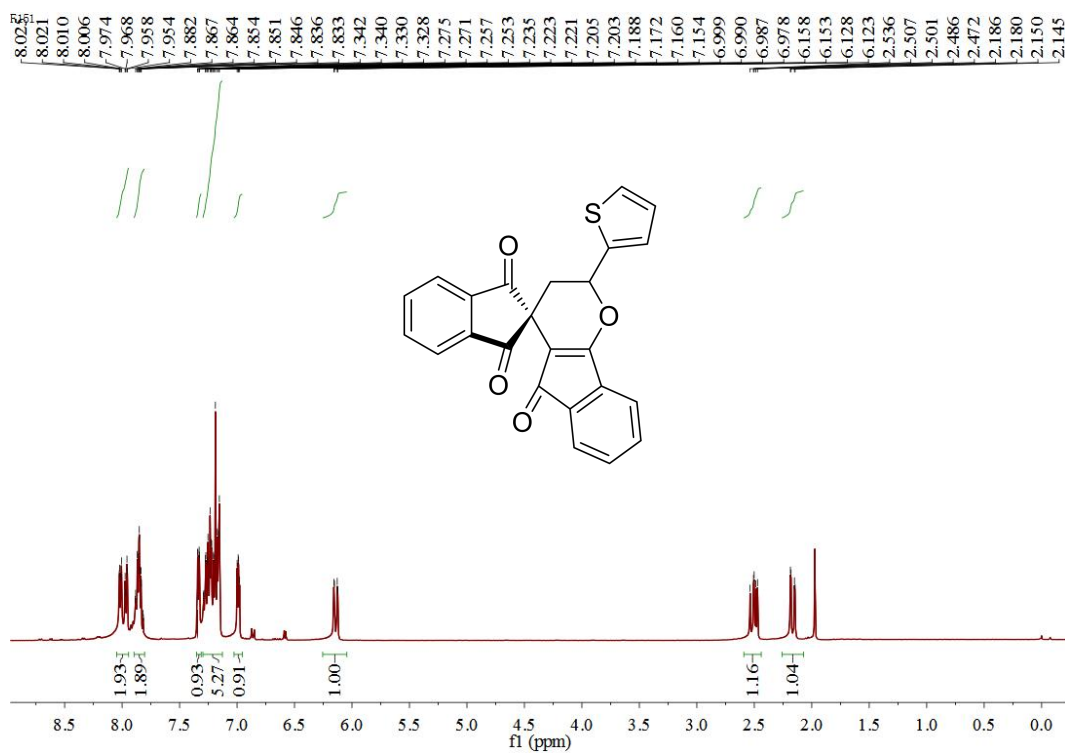
¹H NMR and ¹³C NMR of 3r



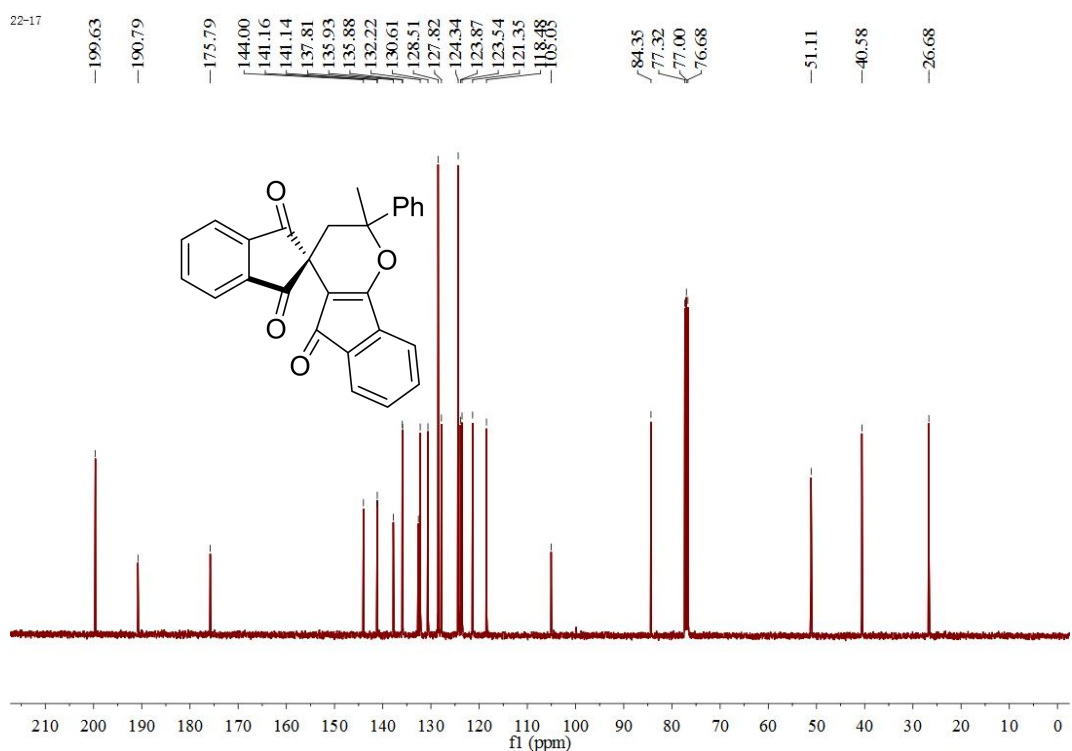
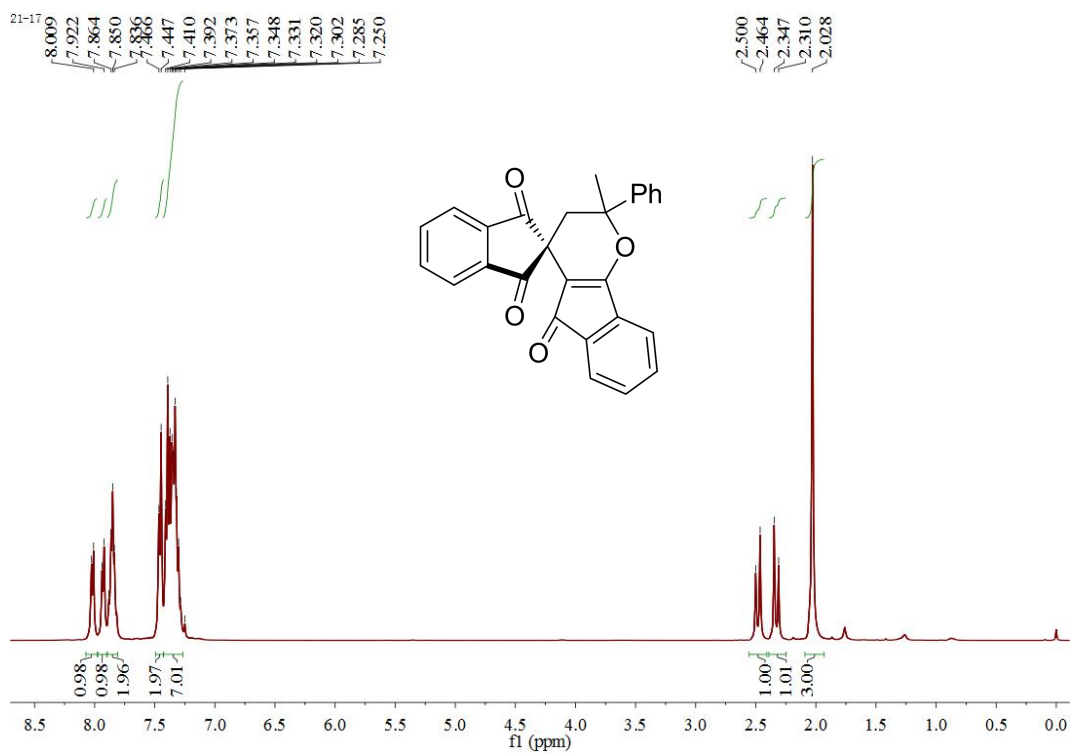
¹H NMR and ¹³C NMR of 3s



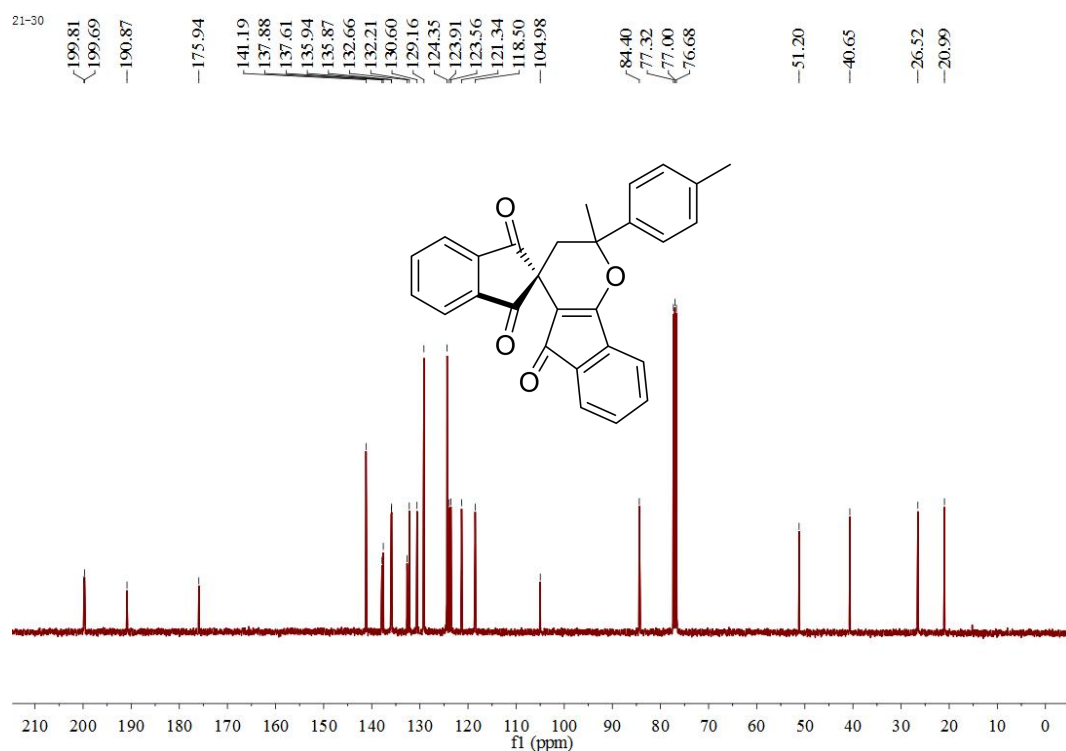
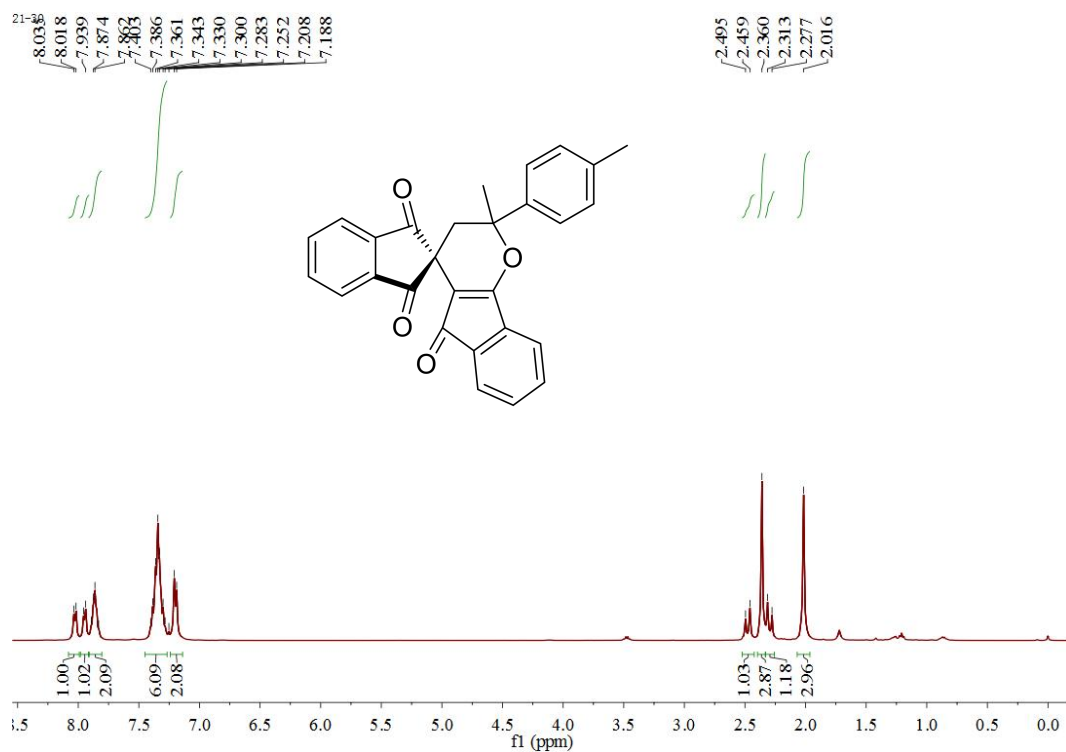
¹H NMR and ¹³C NMR of 3t



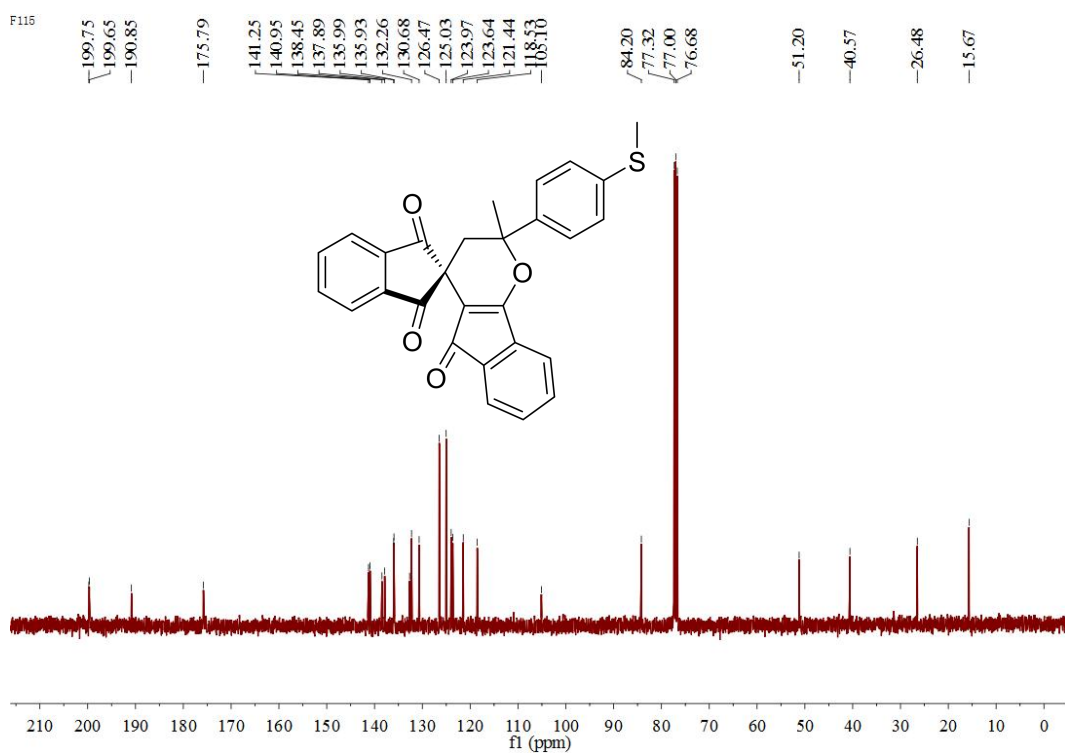
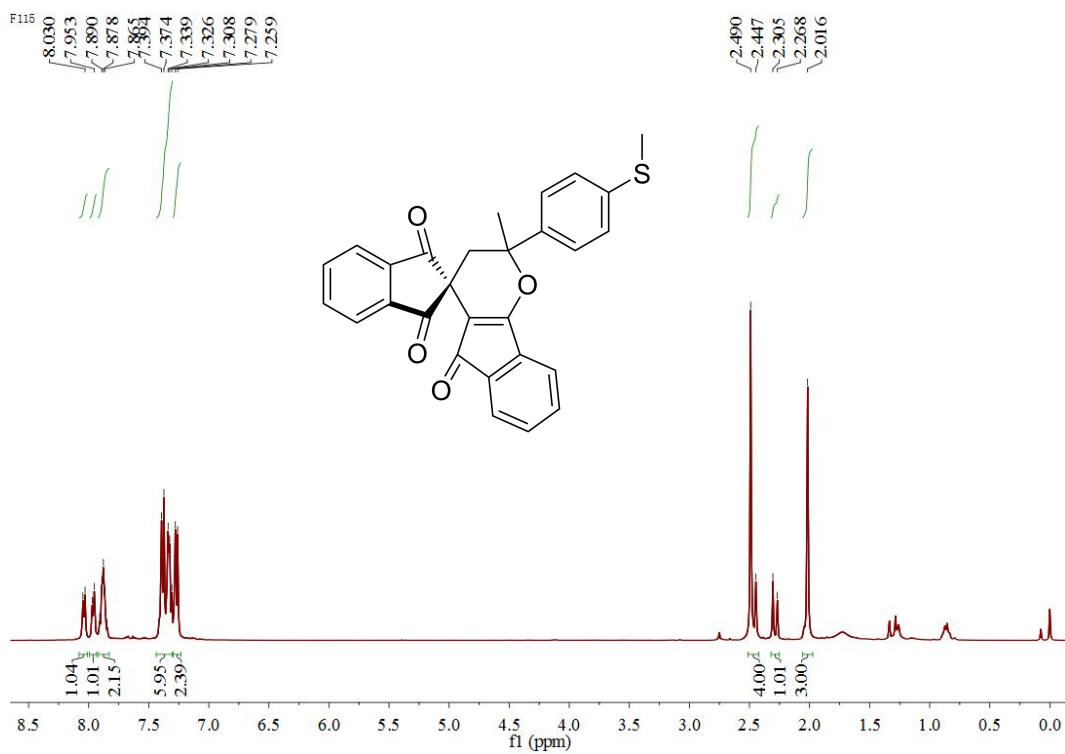
¹H NMR and ¹³C NMR of 4a



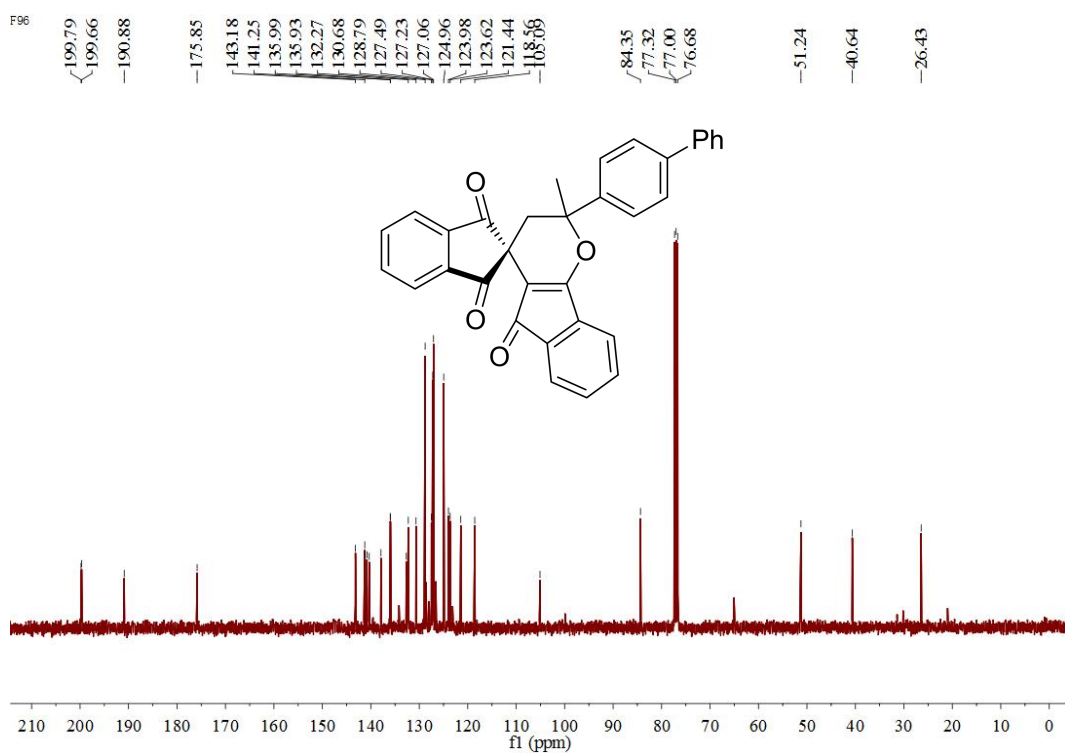
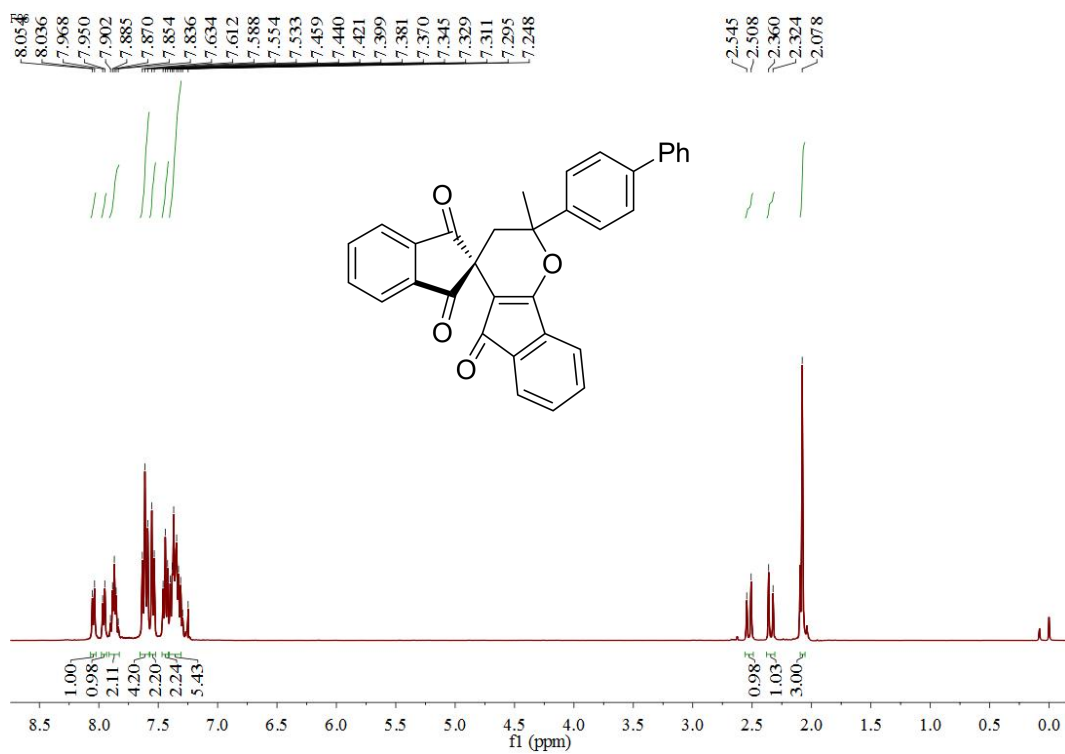
¹H NMR and ¹³C NMR of 4b



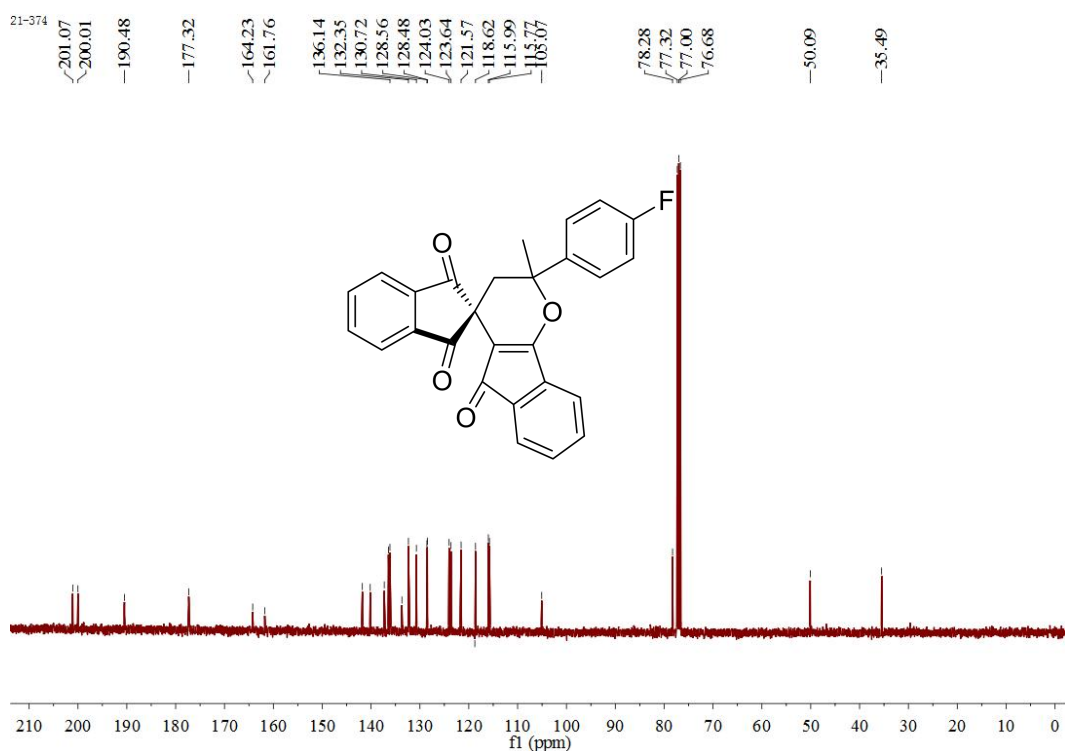
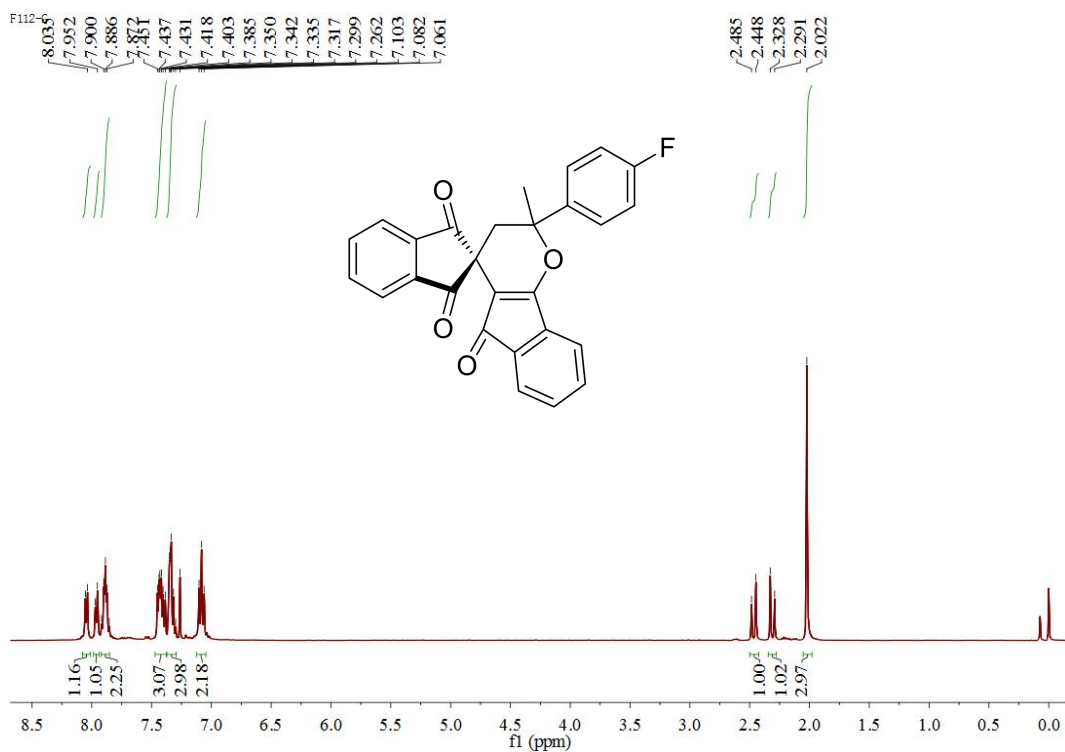
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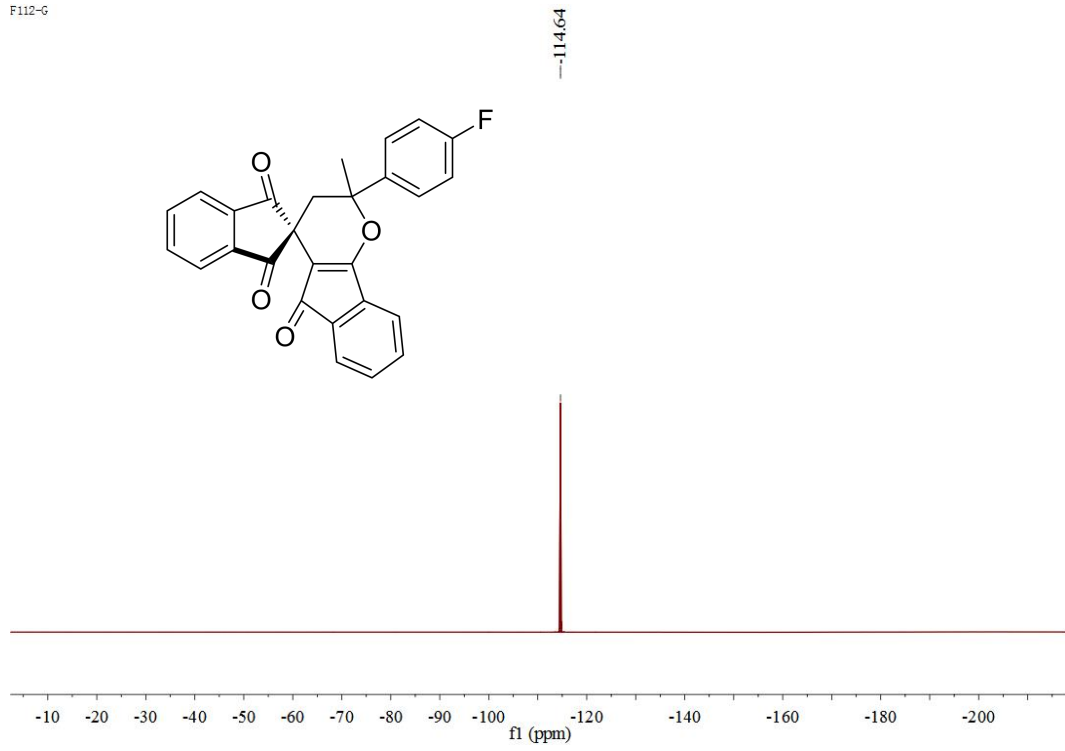
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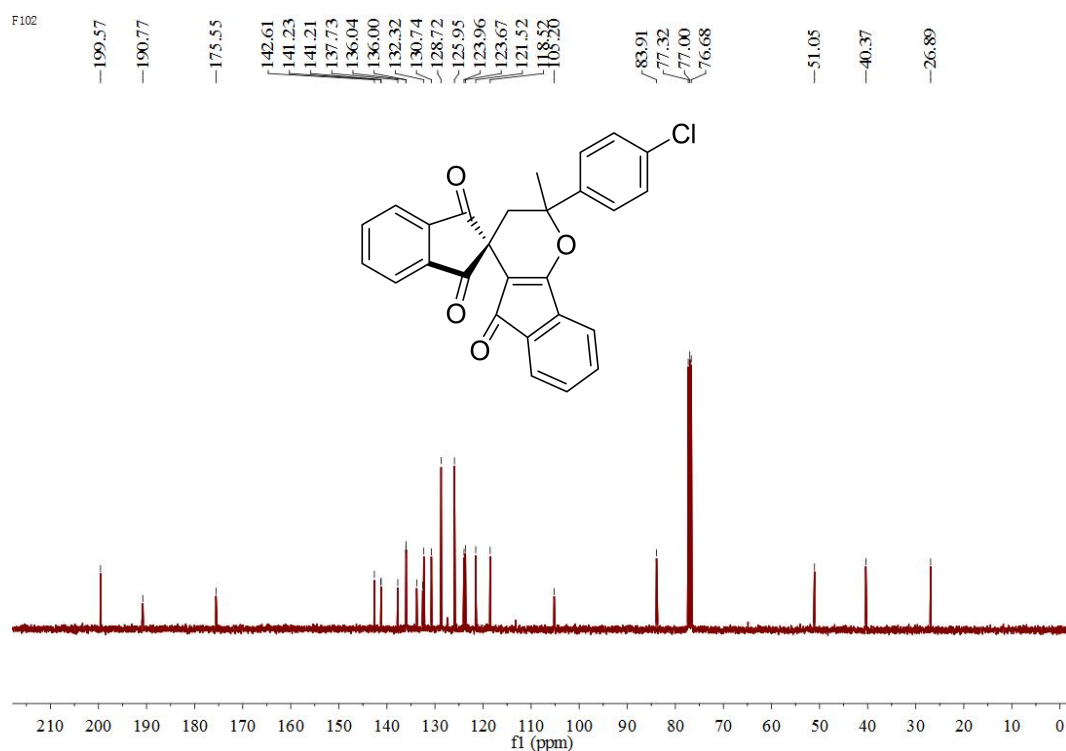
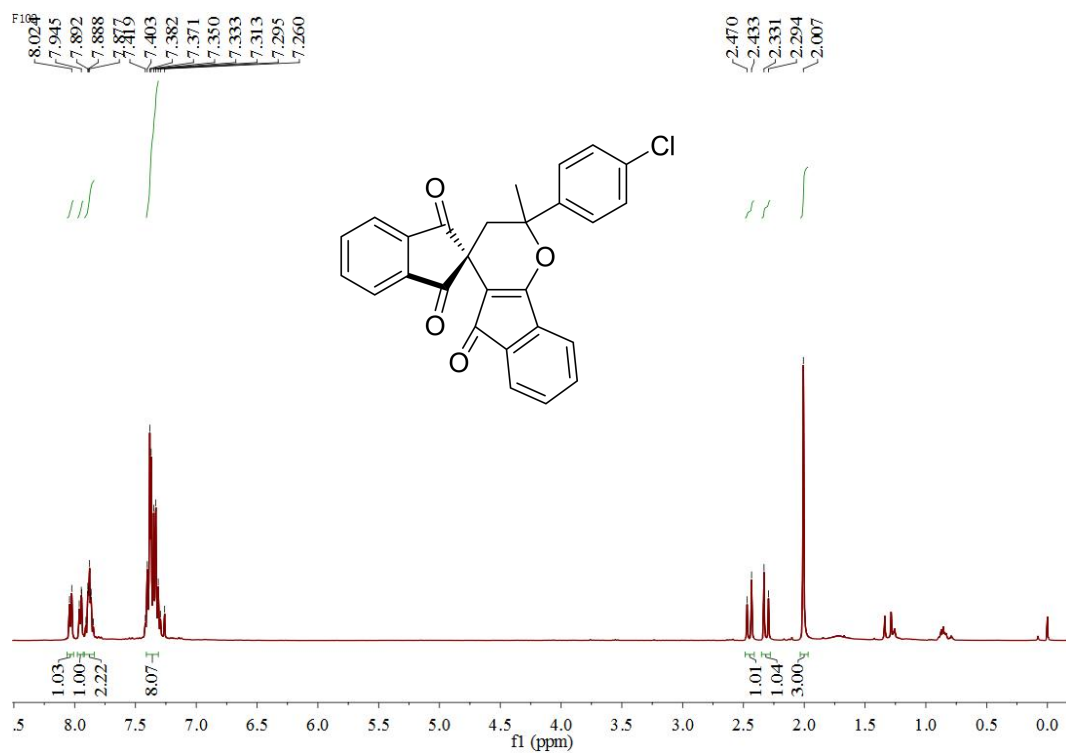
¹H NMR, ¹³C NMR and ¹⁹F NMR of 4e



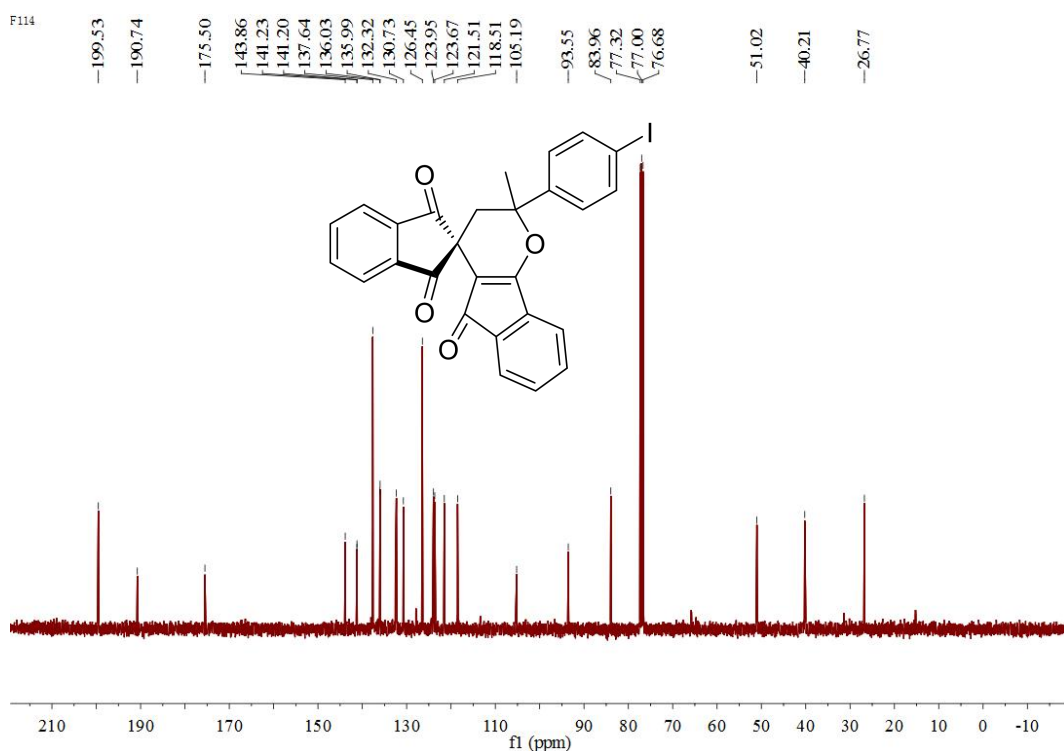
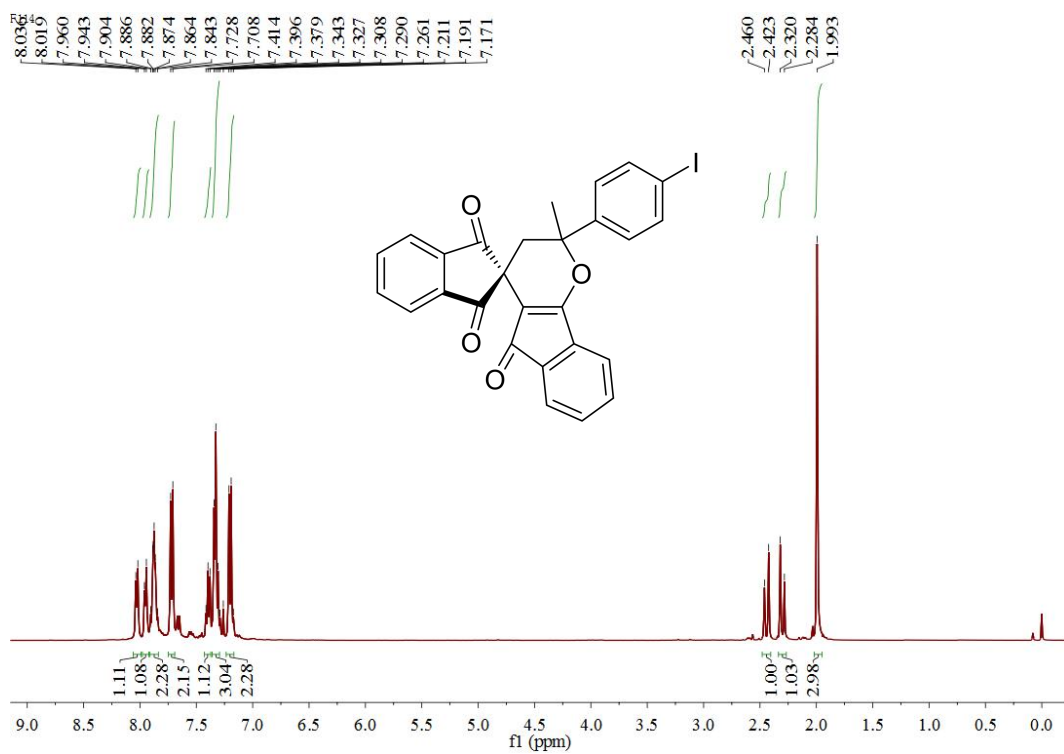
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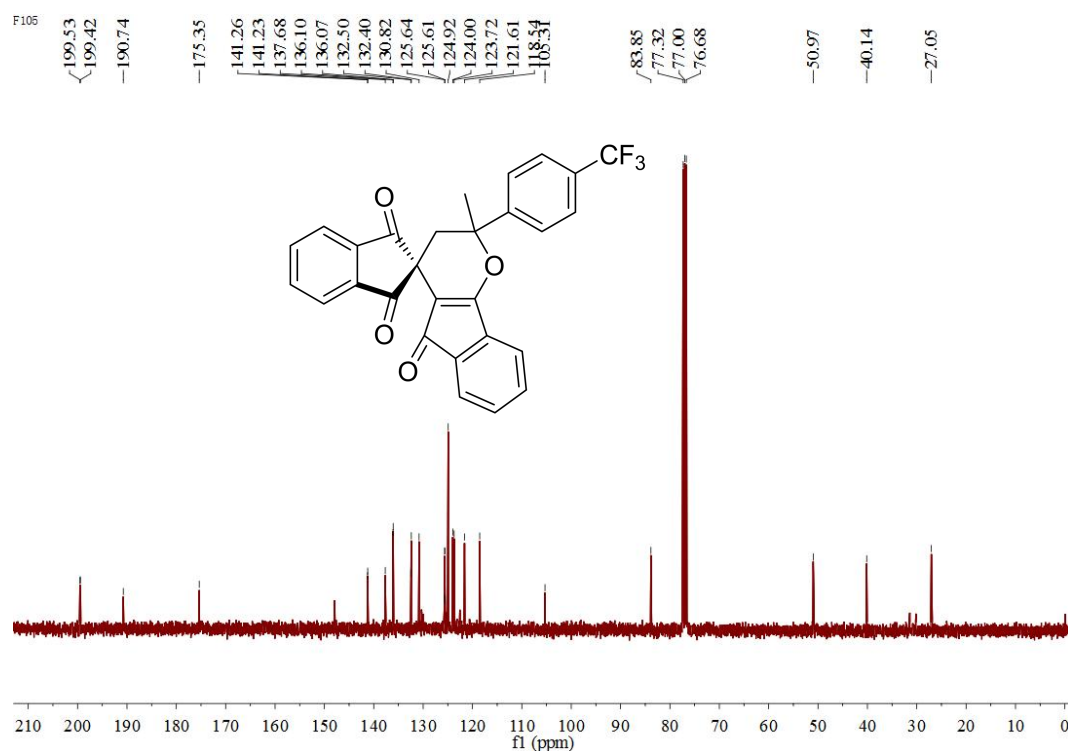
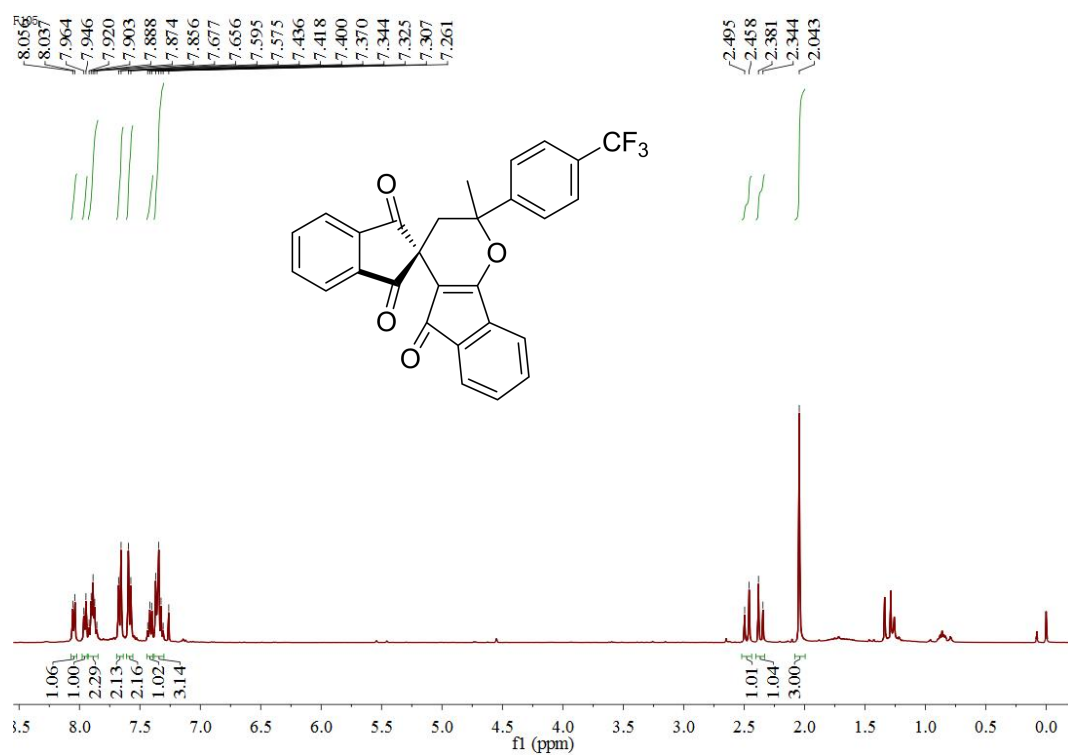
¹H NMR and ¹³C NMR of 4f



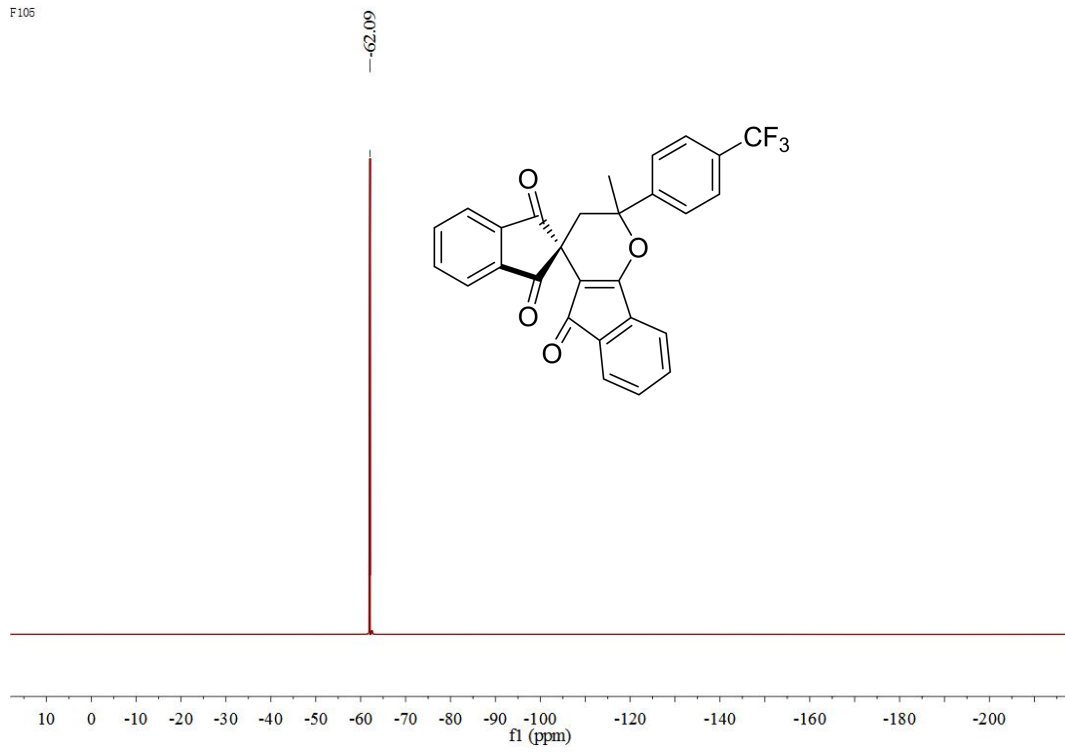
¹H NMR and ¹³C NMR of 4g



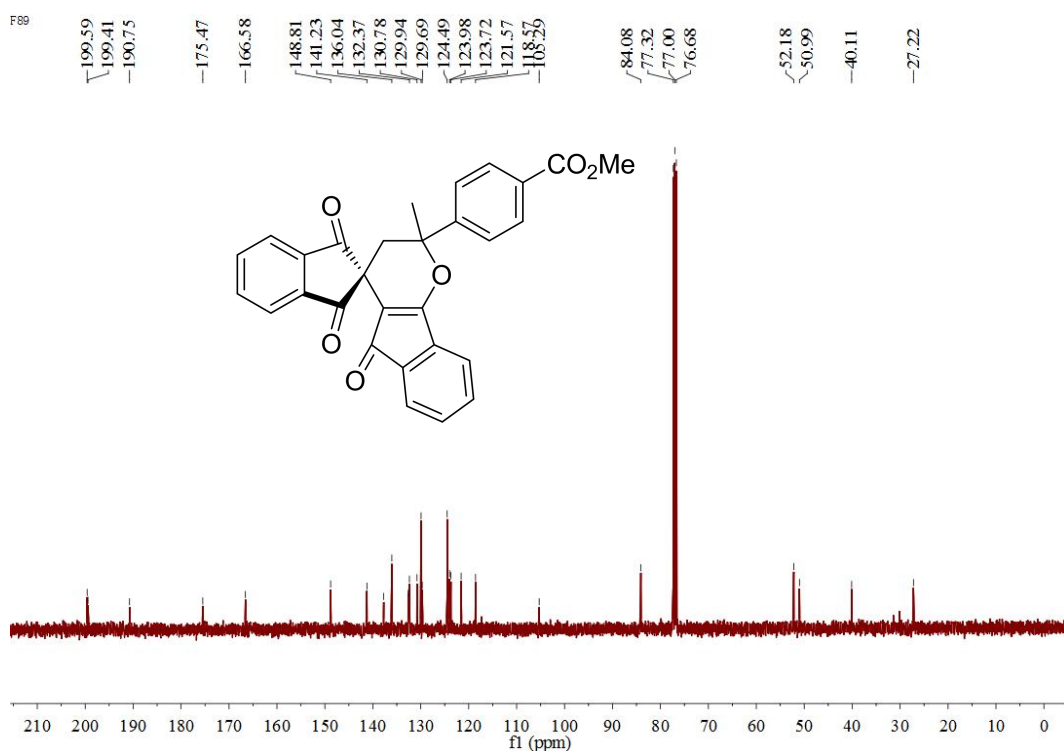
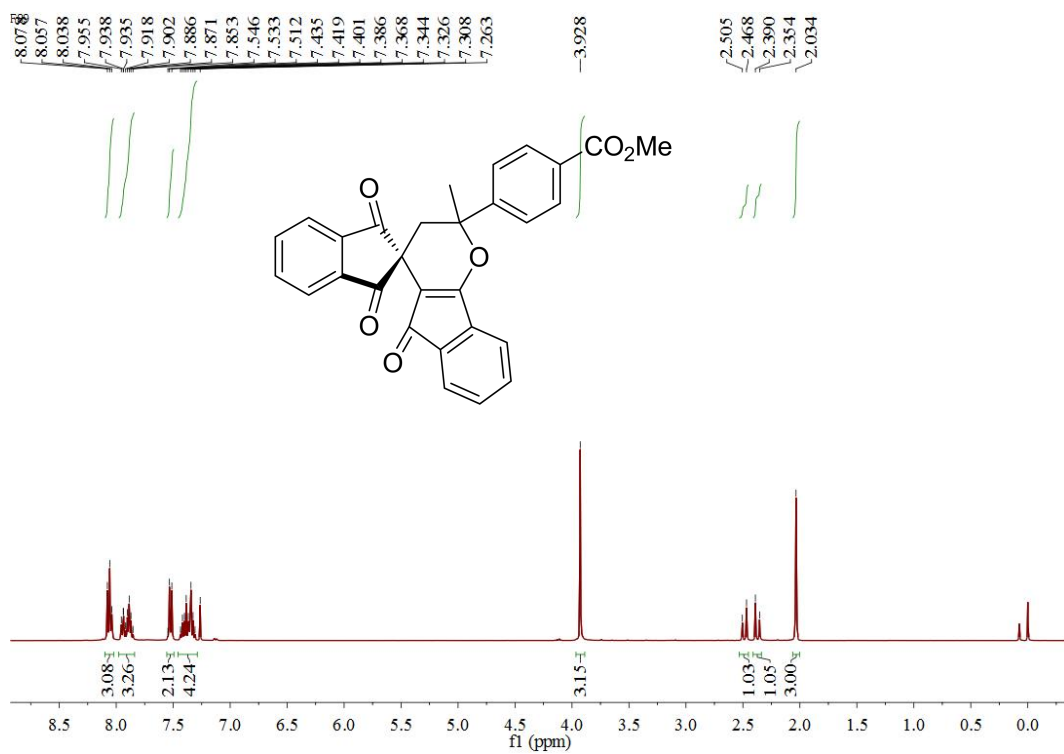
¹H NMR, ¹³C NMR and ¹⁹F NMR of 4h



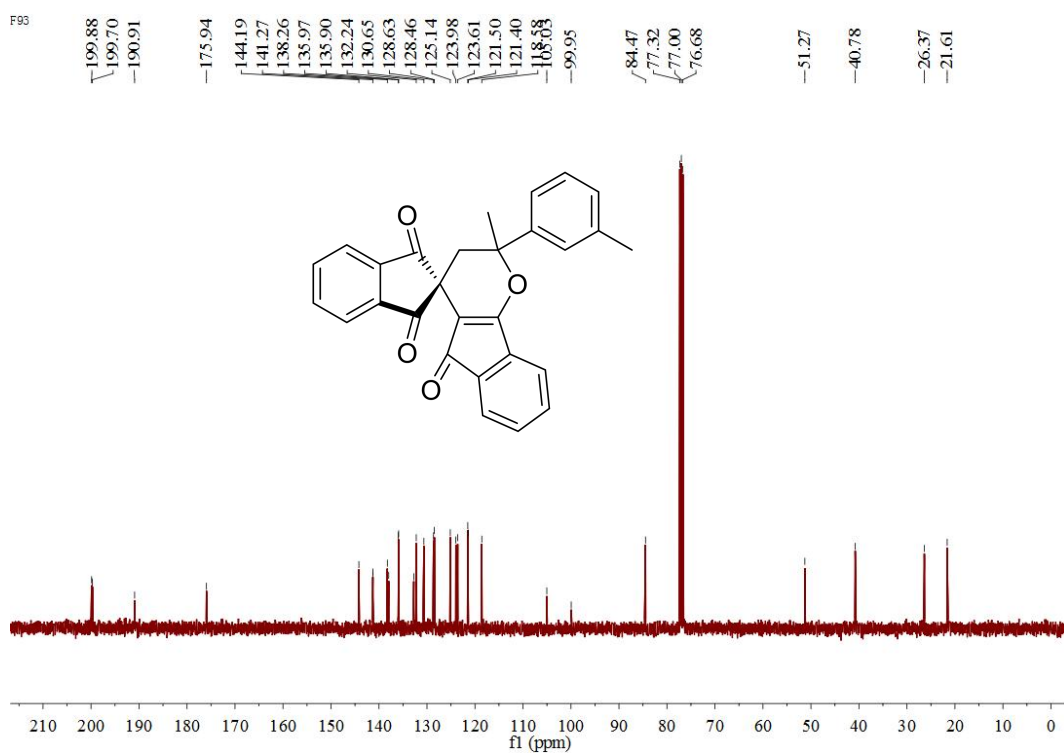
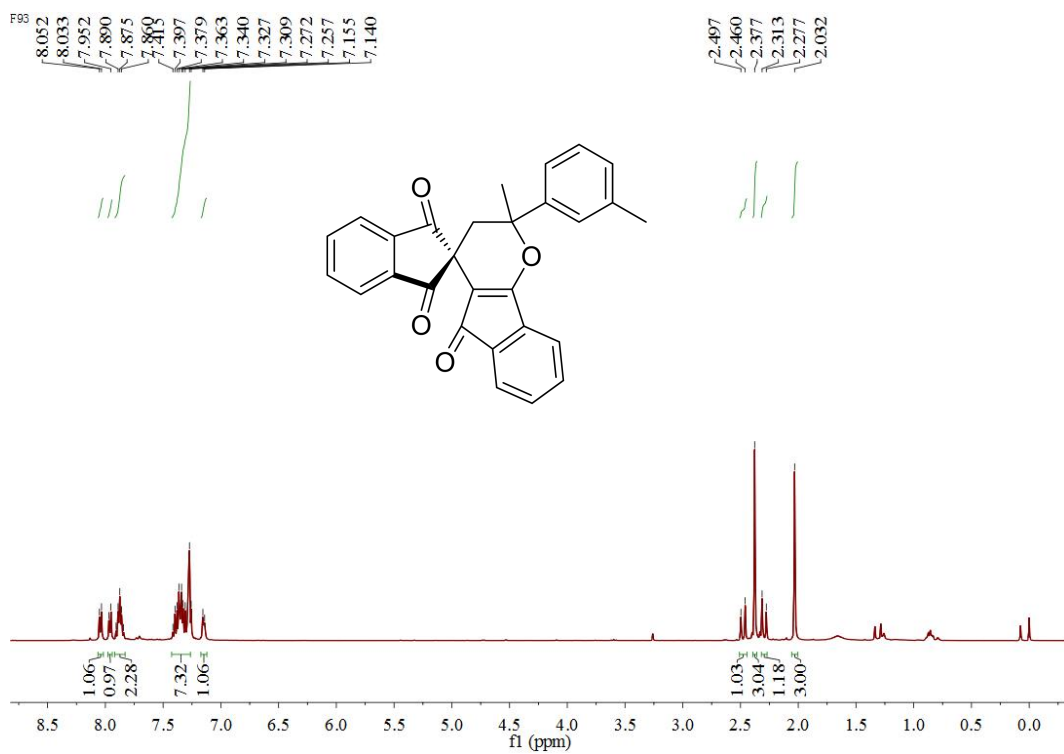
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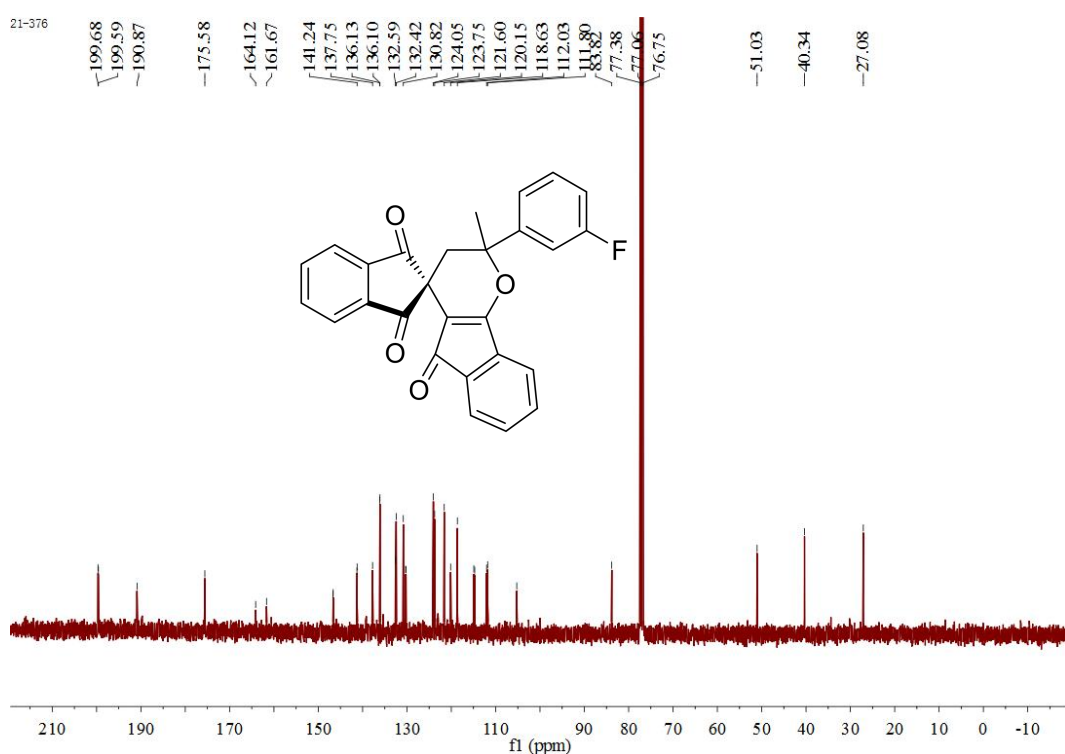
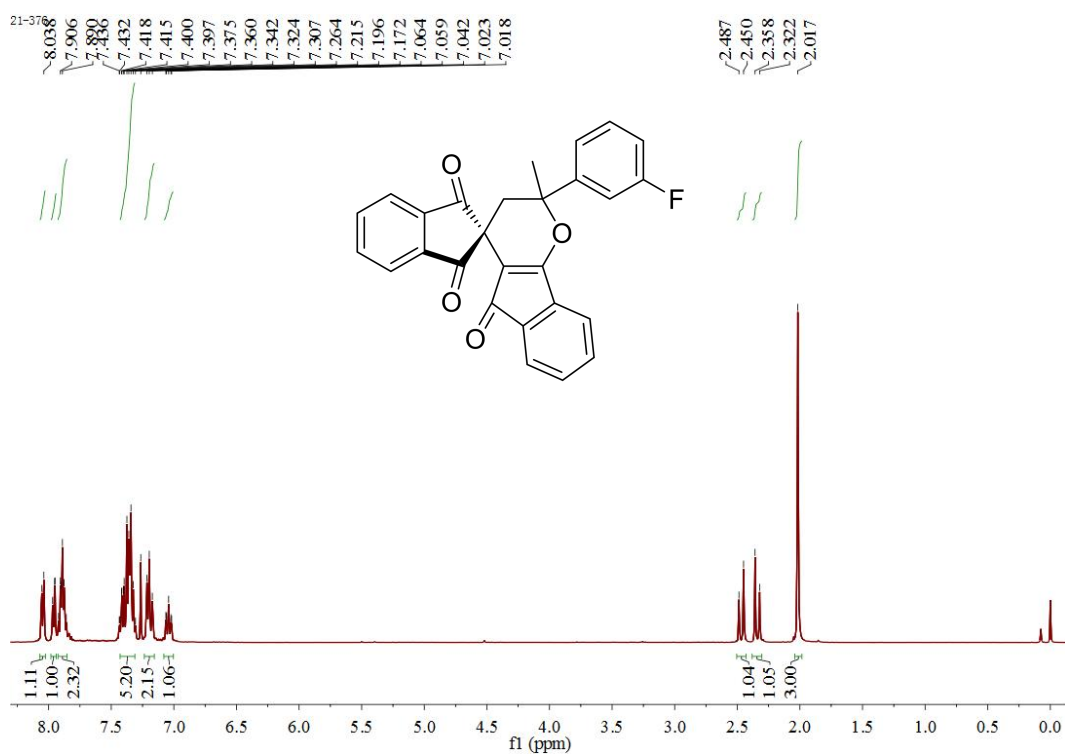
¹H NMR and ¹³C NMR of 4i



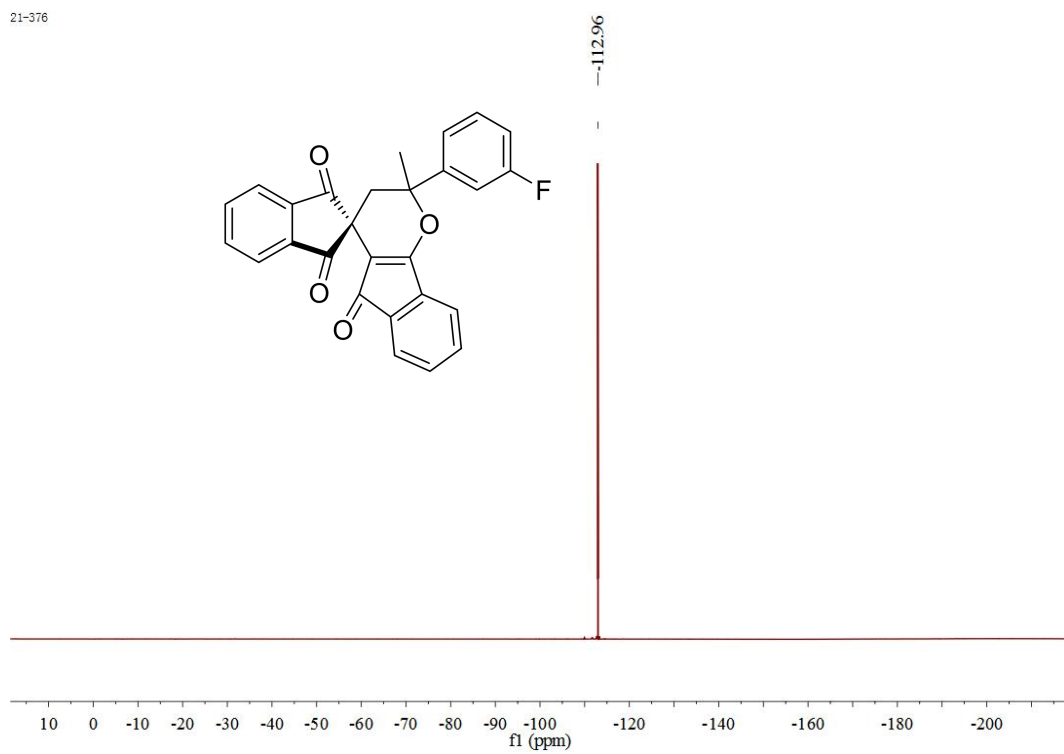
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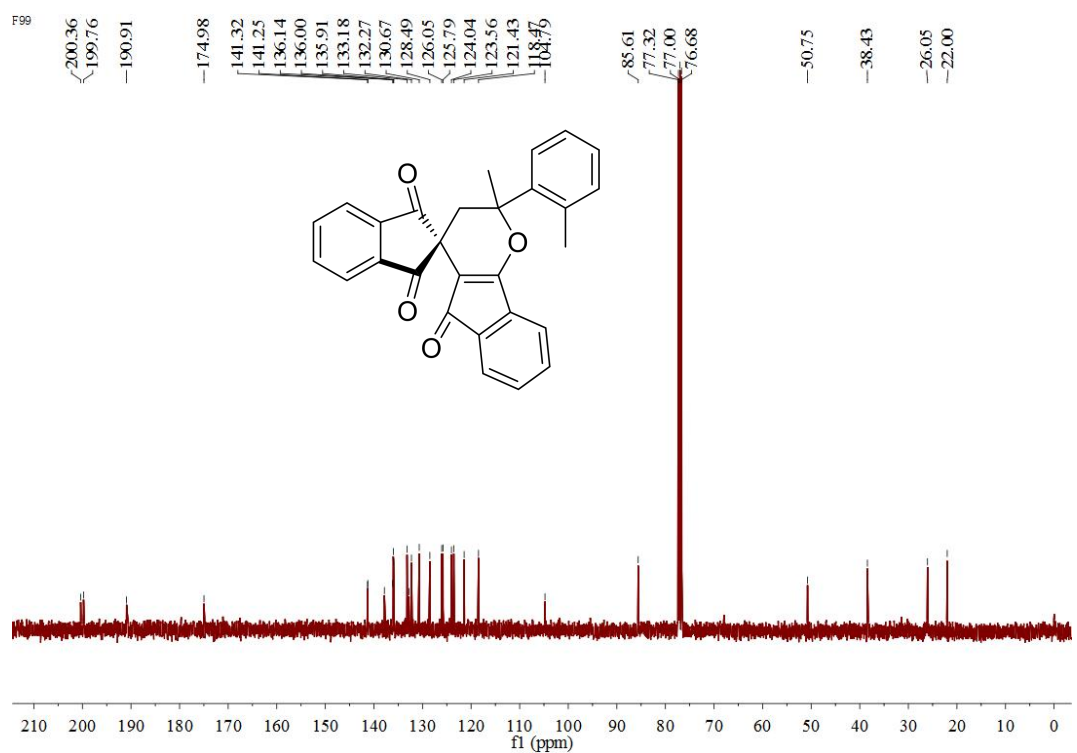
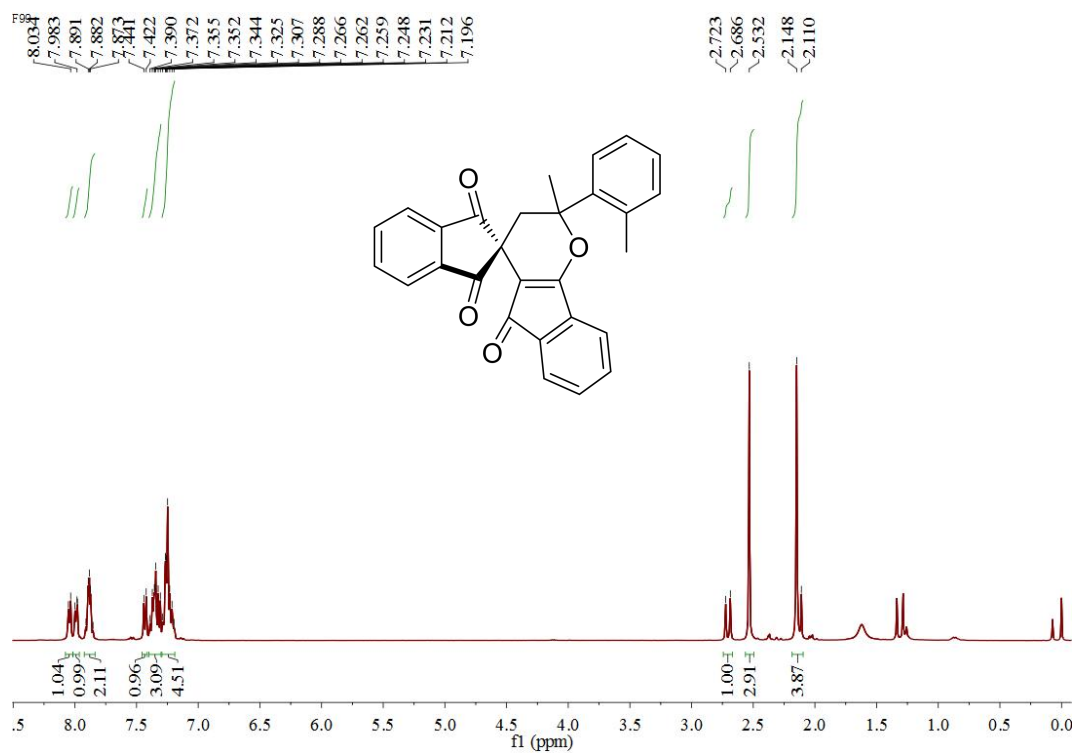
¹H NMR, ¹³C NMR and ¹⁹F NMR of 4k



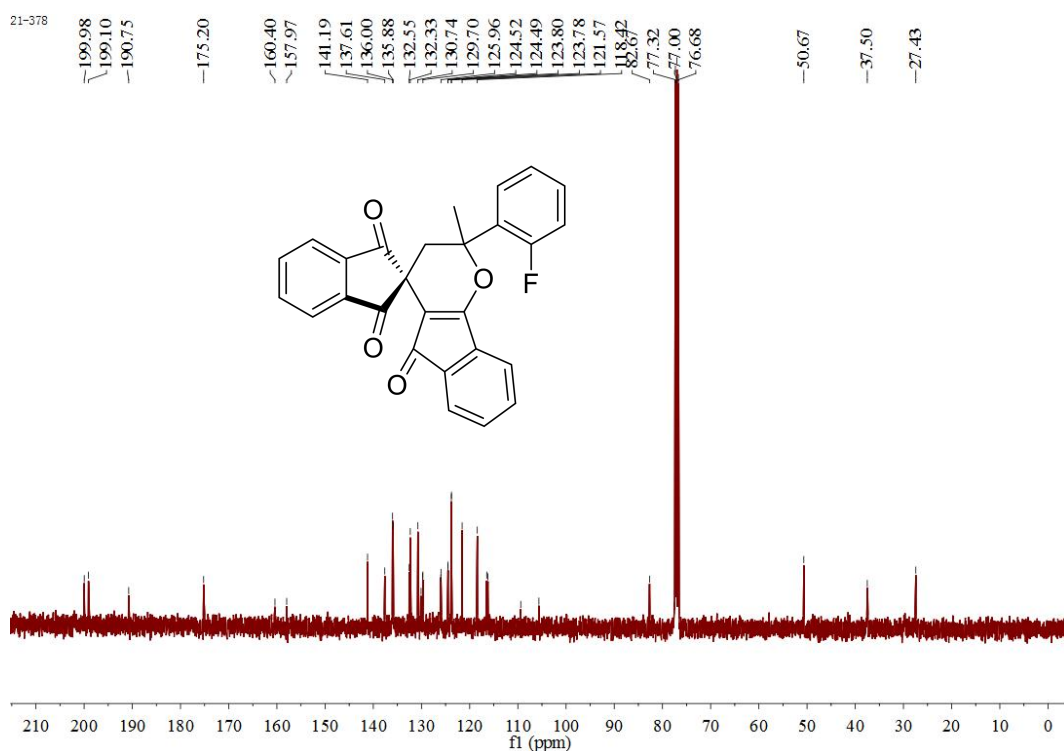
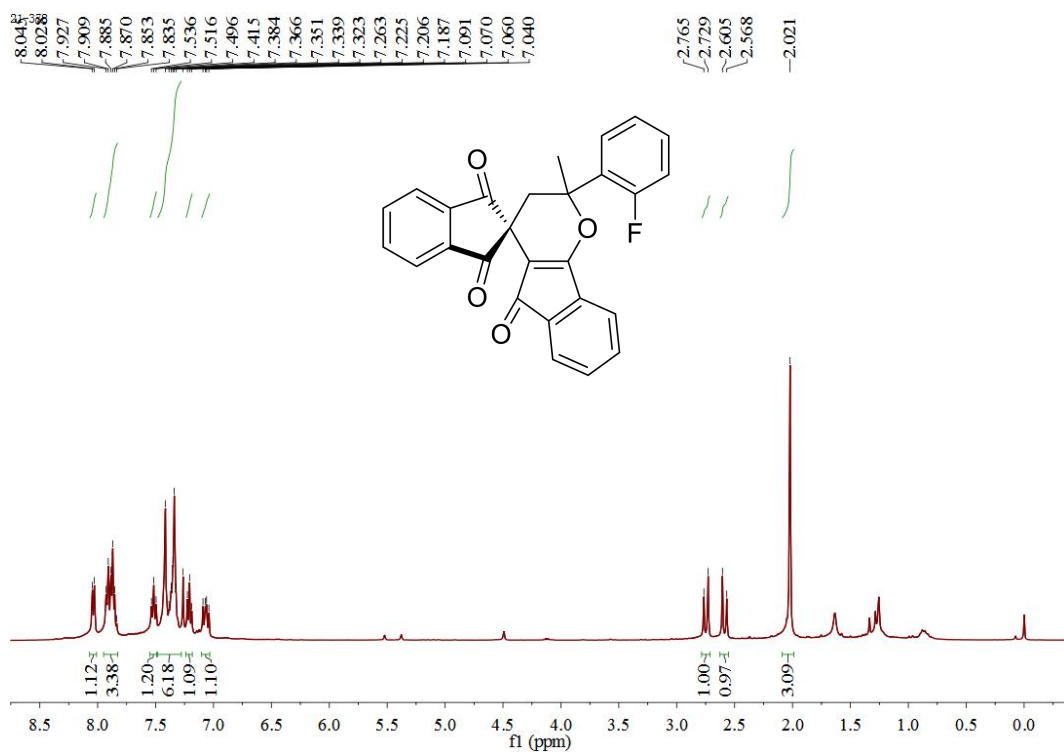
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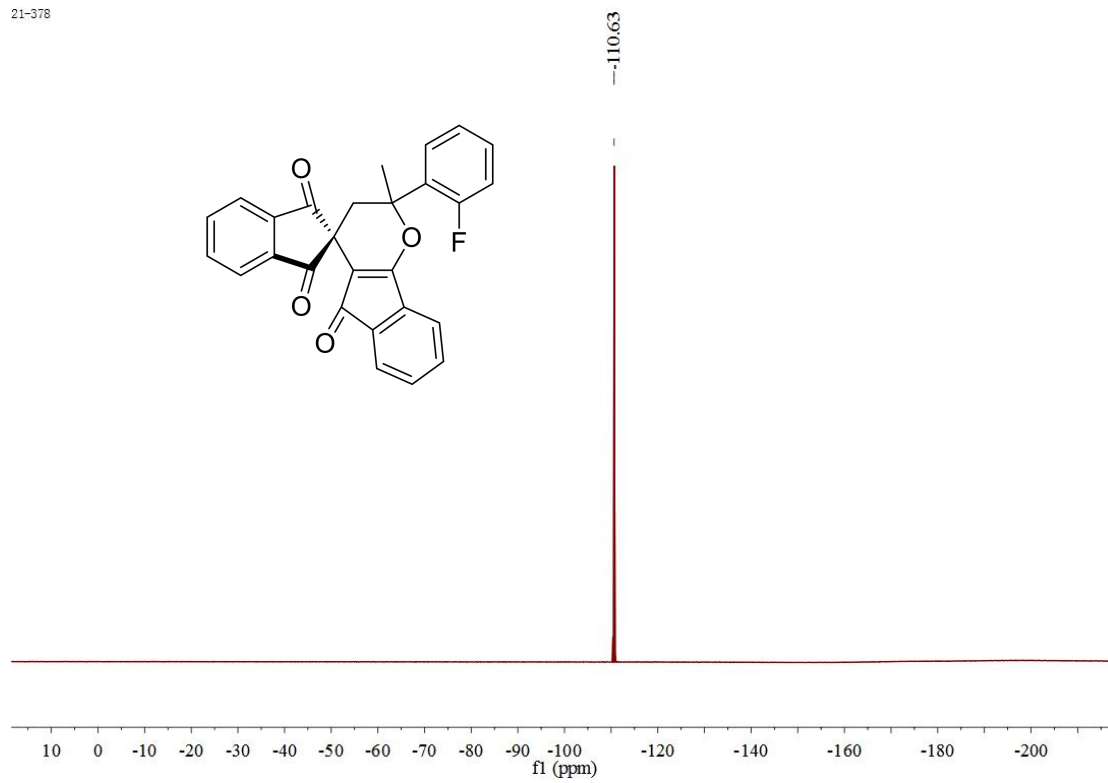
¹H NMR and ¹³C NMR of 4l



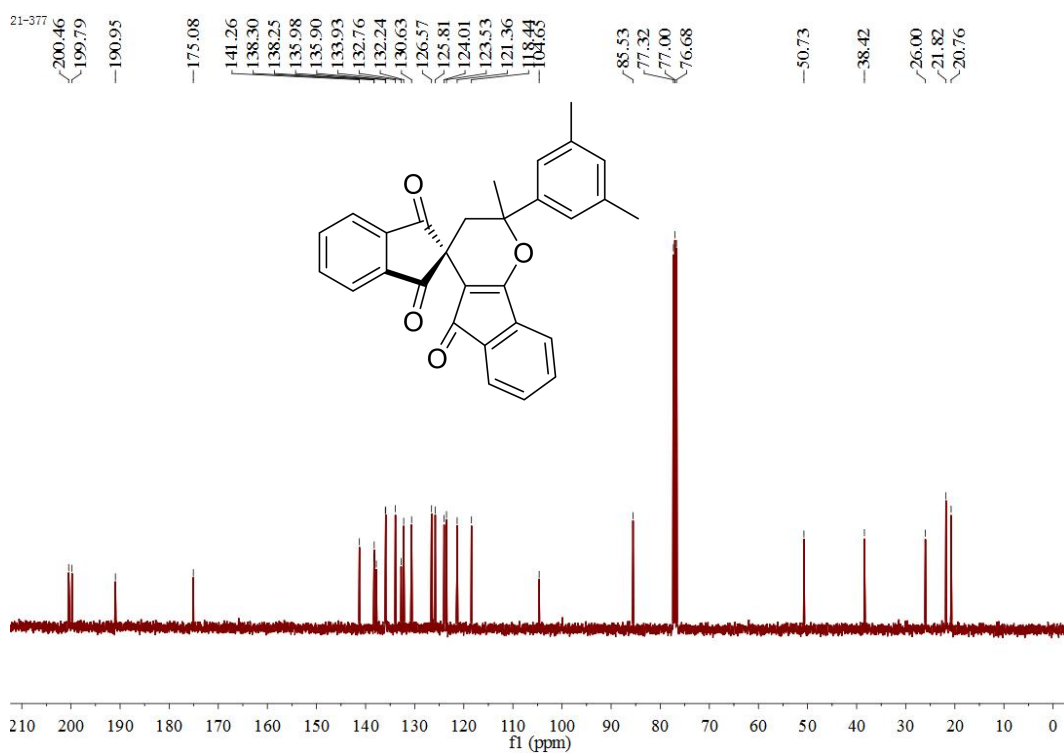
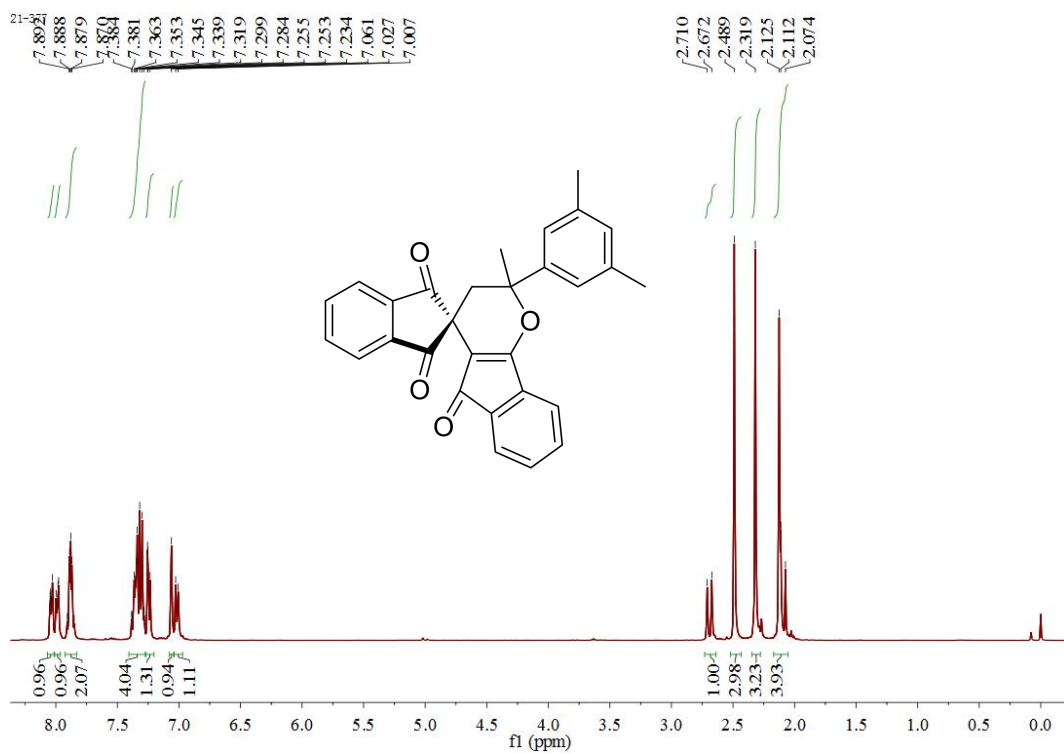
¹H NMR, ¹³C NMR and ¹⁹F NMR of 4m



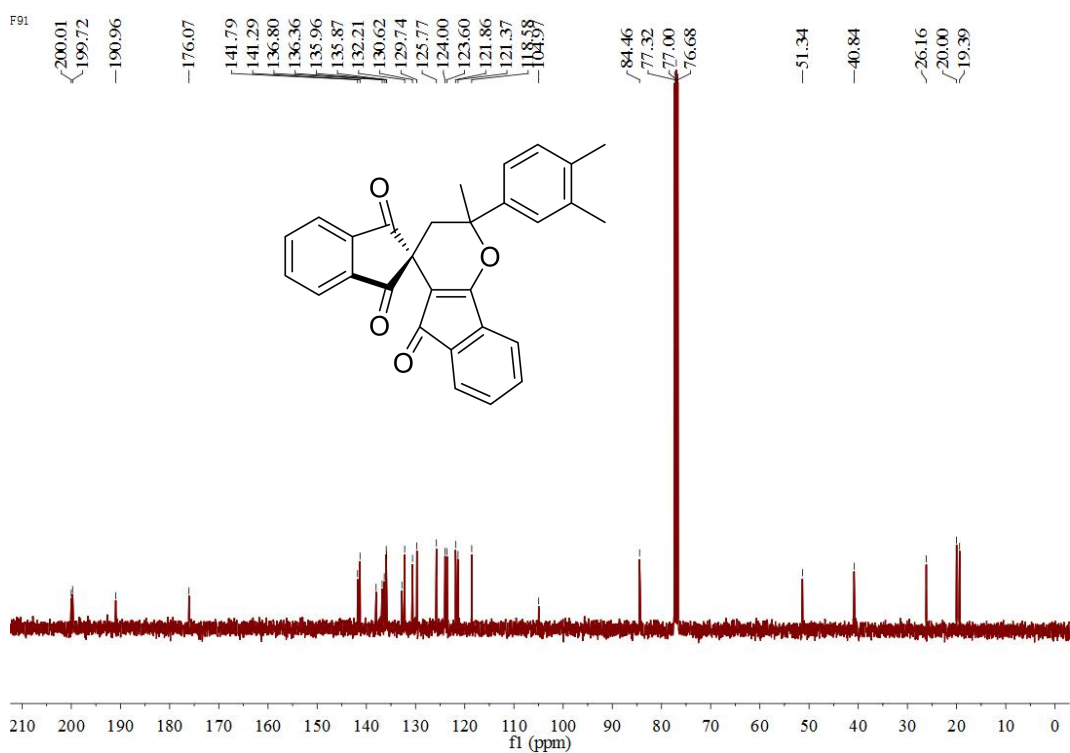
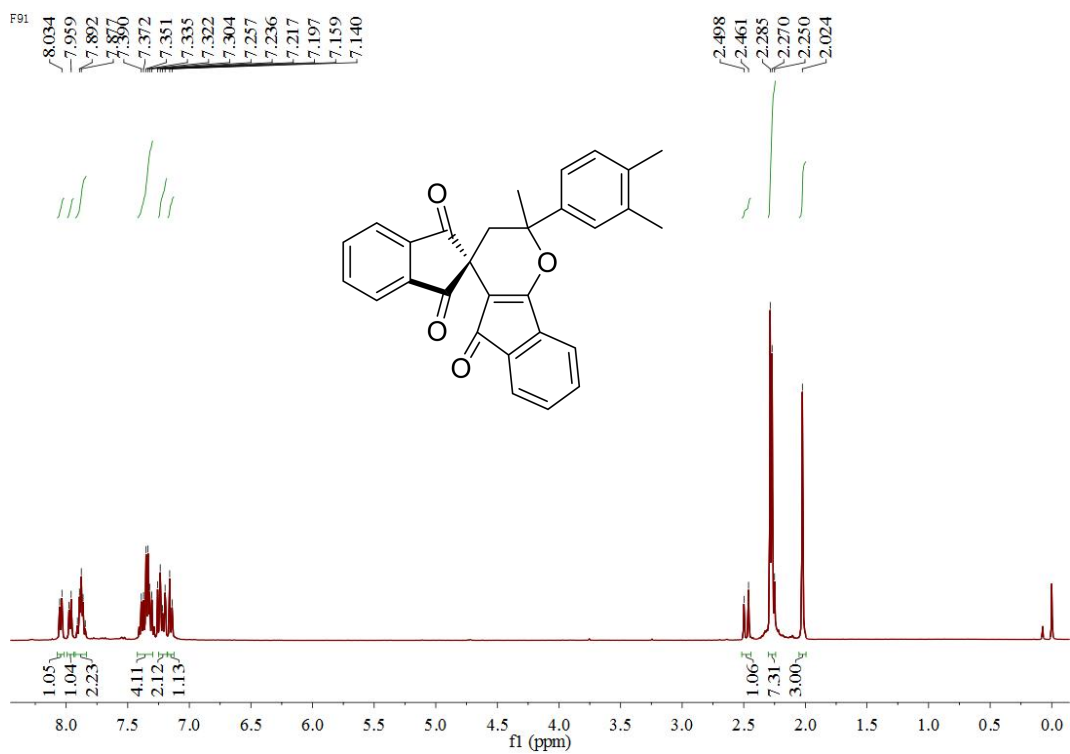
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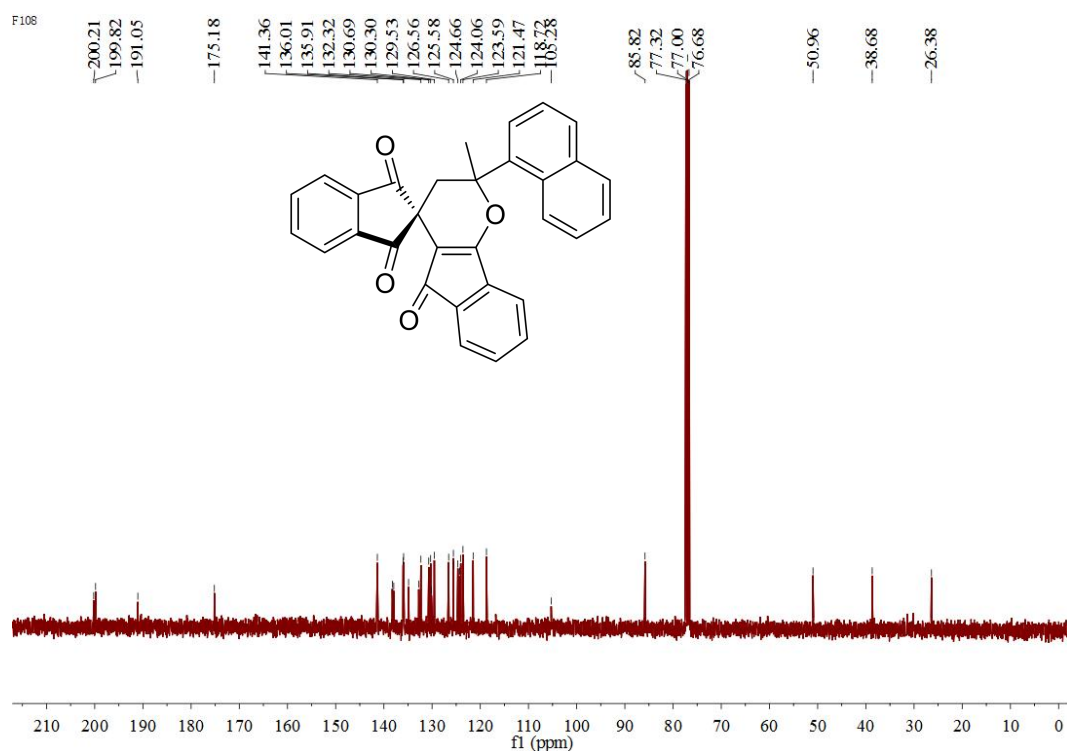
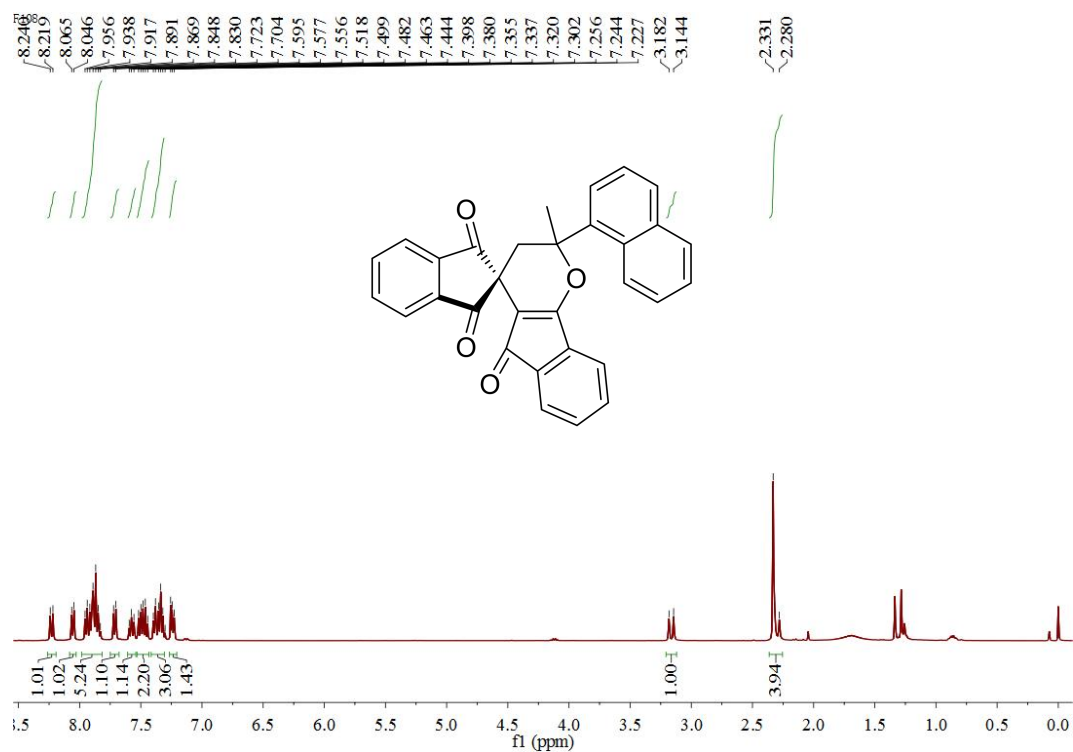
¹H NMR and ¹³C NMR of 4n



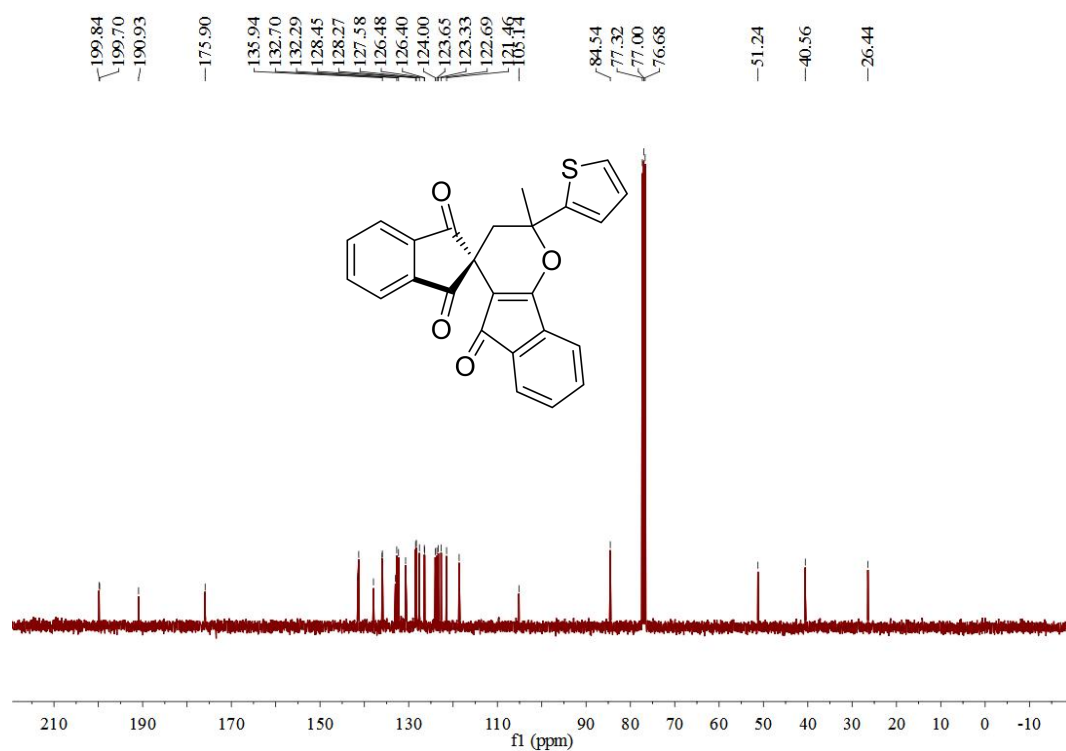
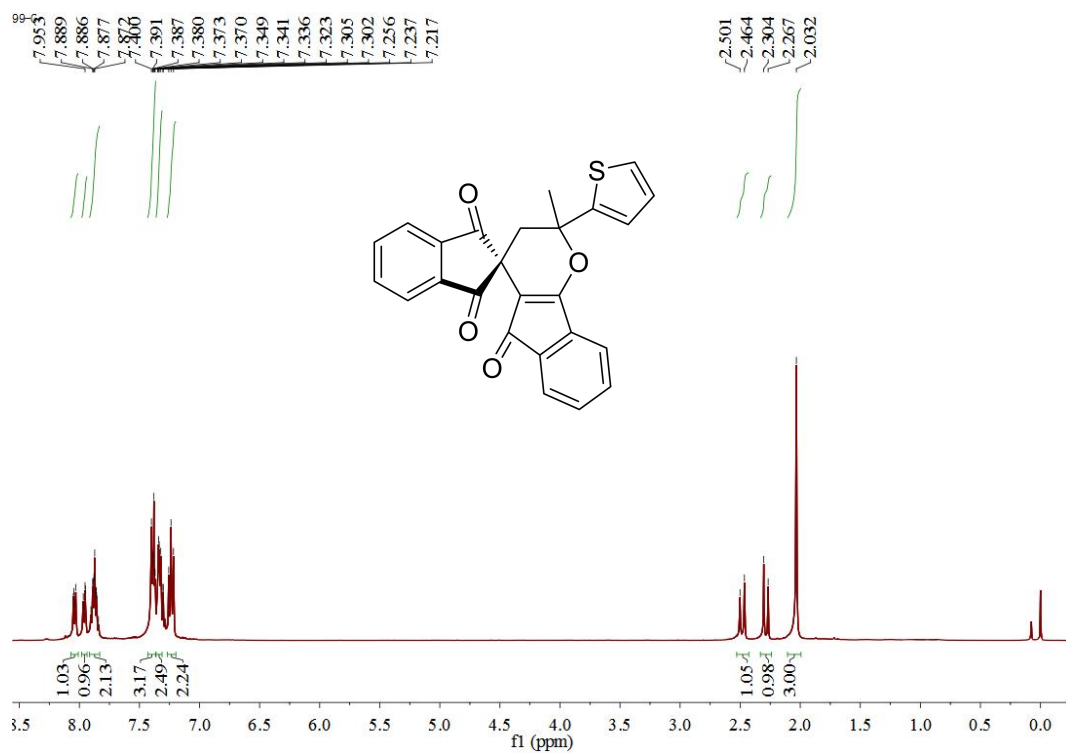
¹H NMR and ¹³C NMR of 4o



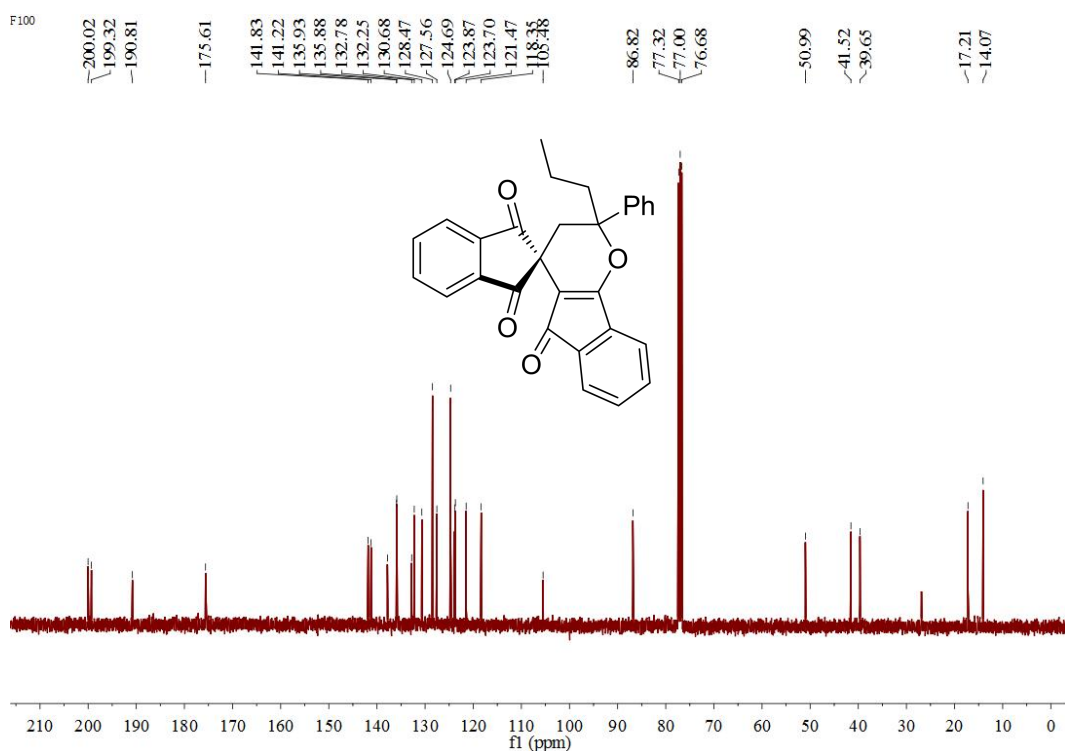
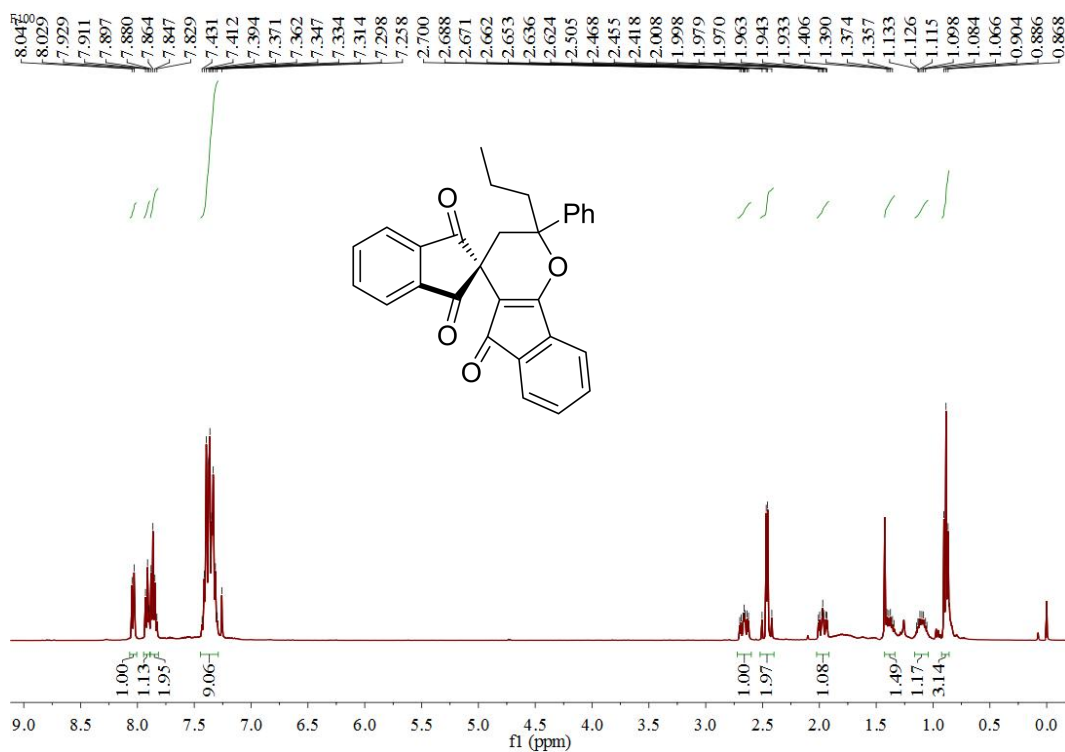
¹H NMR and ¹³C NMR of 4p



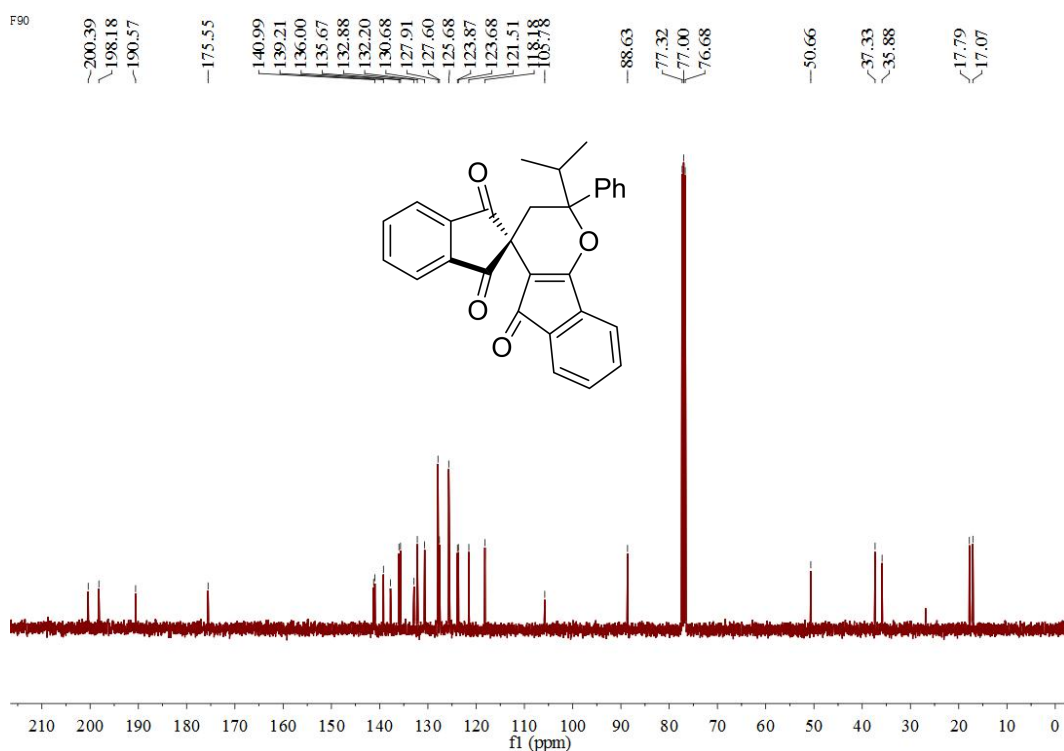
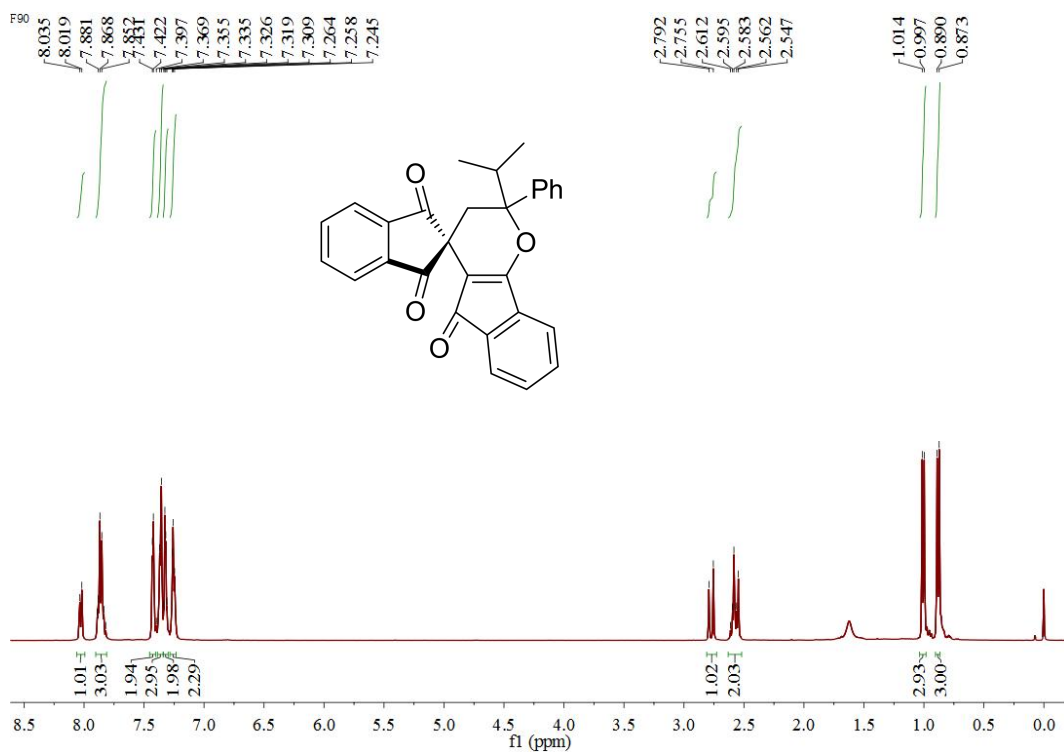
¹H NMR and ¹³C NMR of 4q



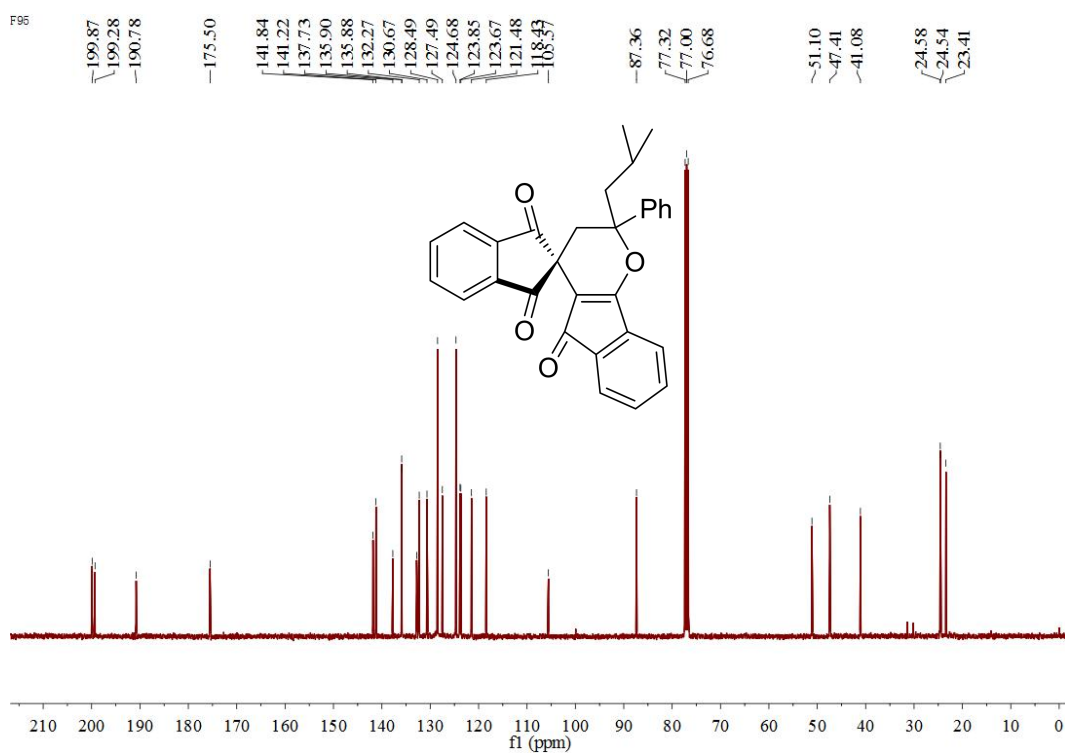
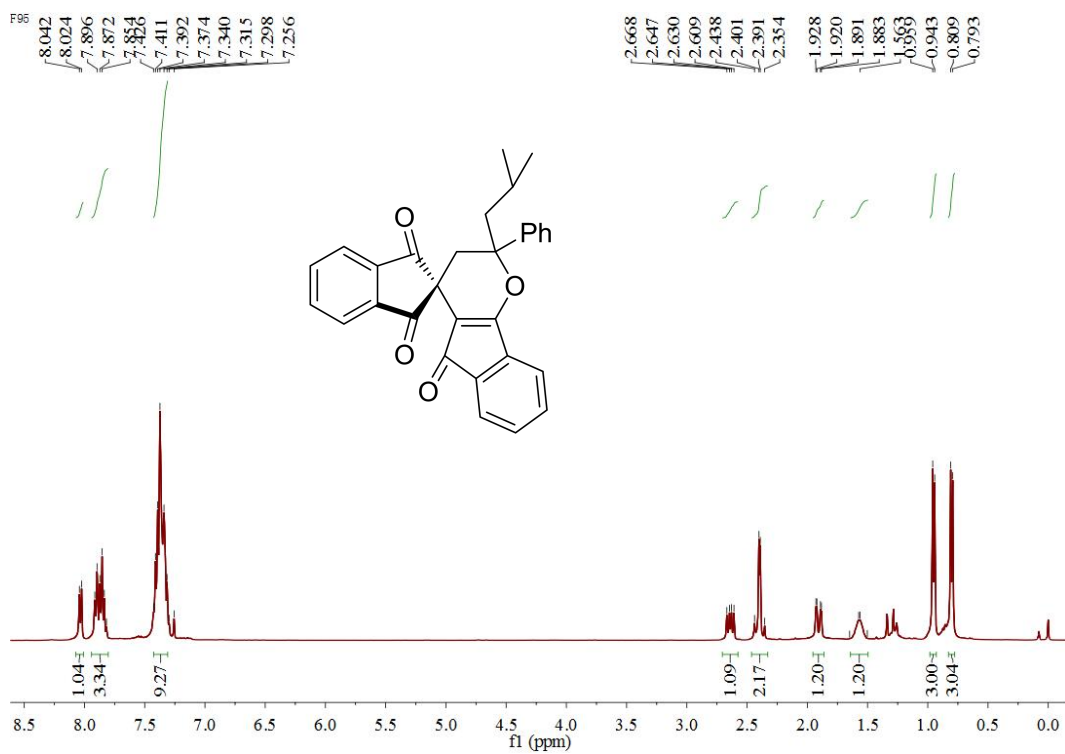
¹H NMR and ¹³C NMR of 4r



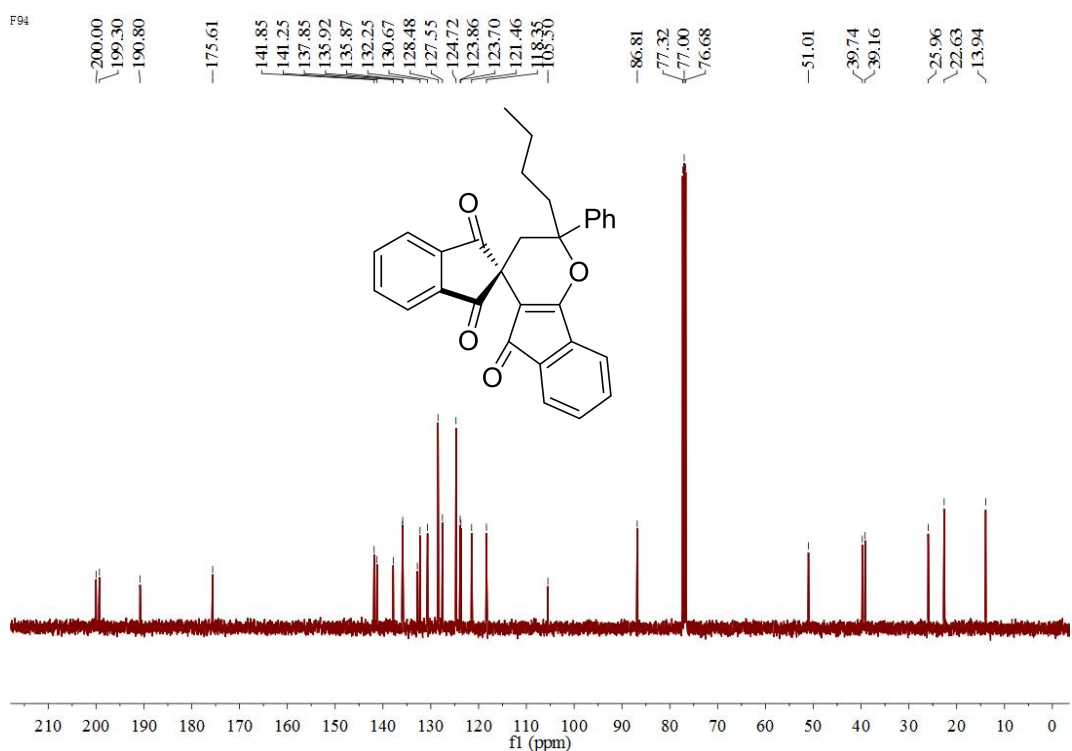
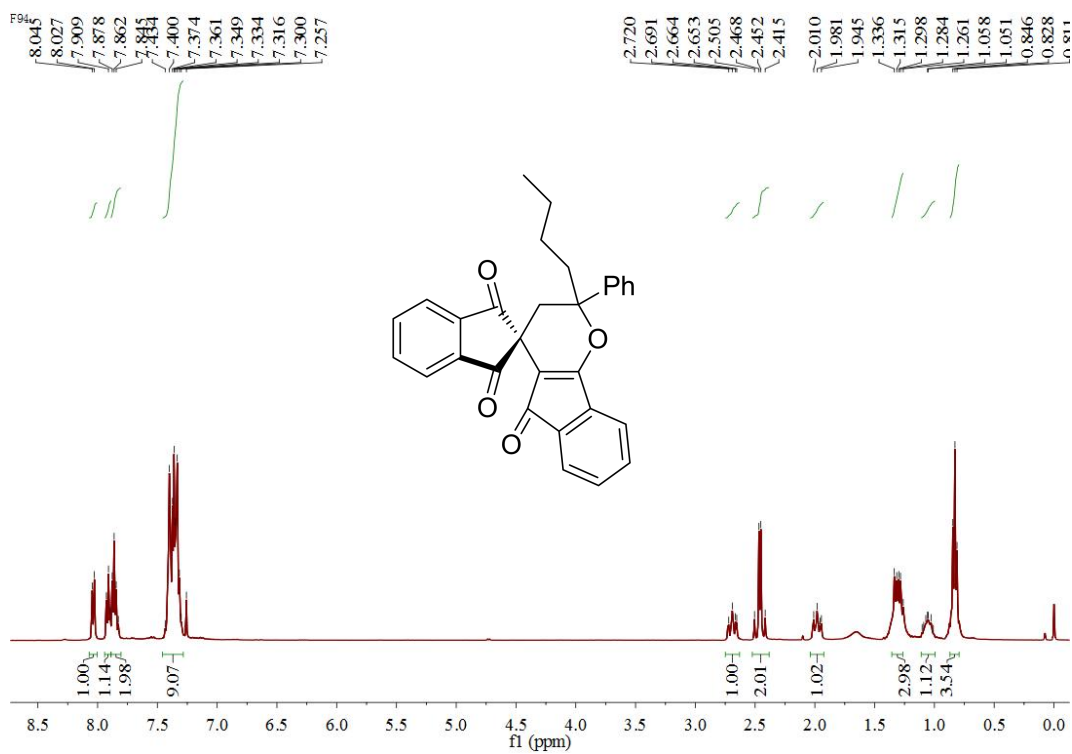
¹H NMR and ¹³C NMR of 4s



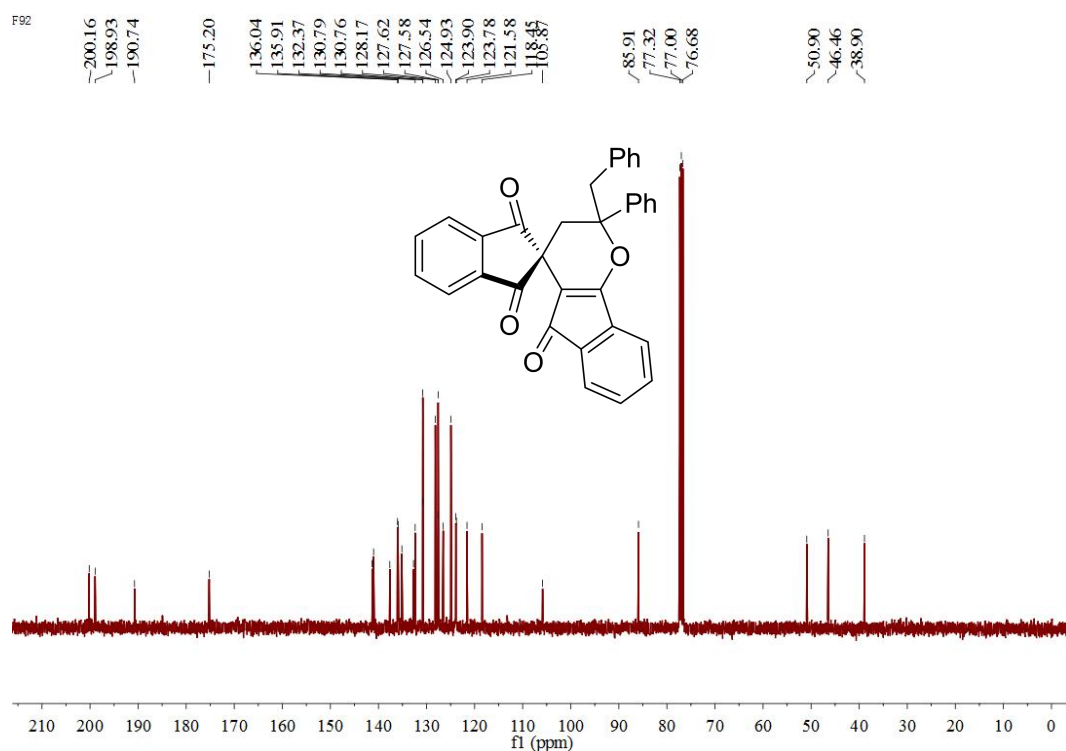
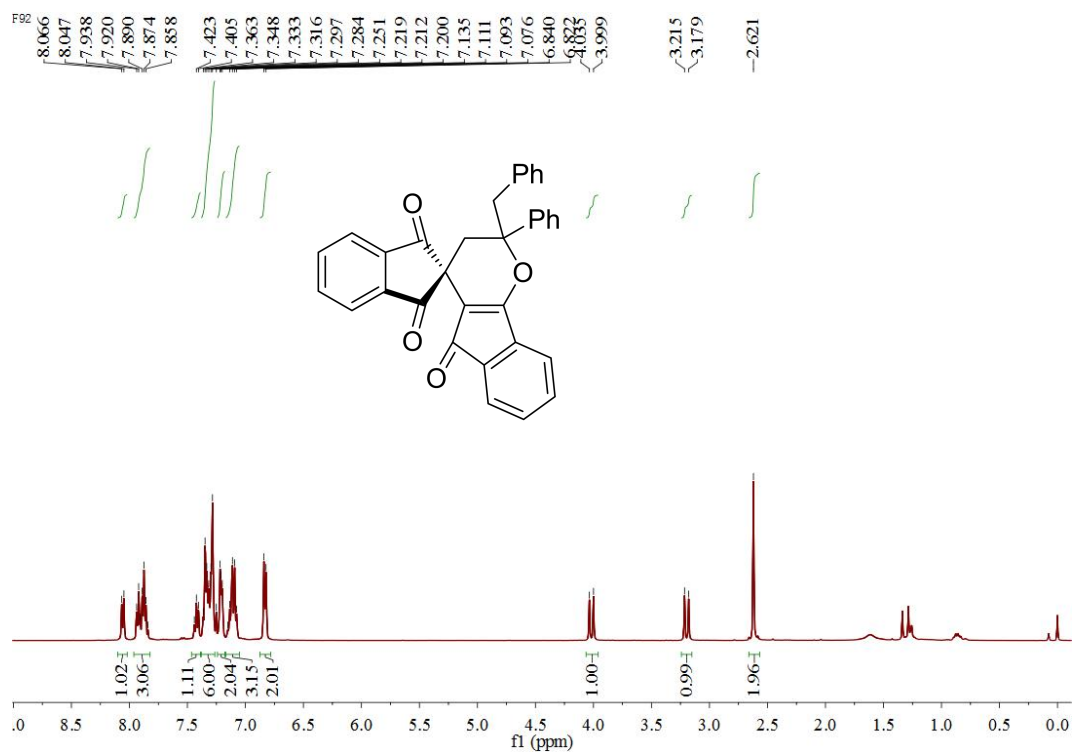
¹H NMR and ¹³C NMR of 4t



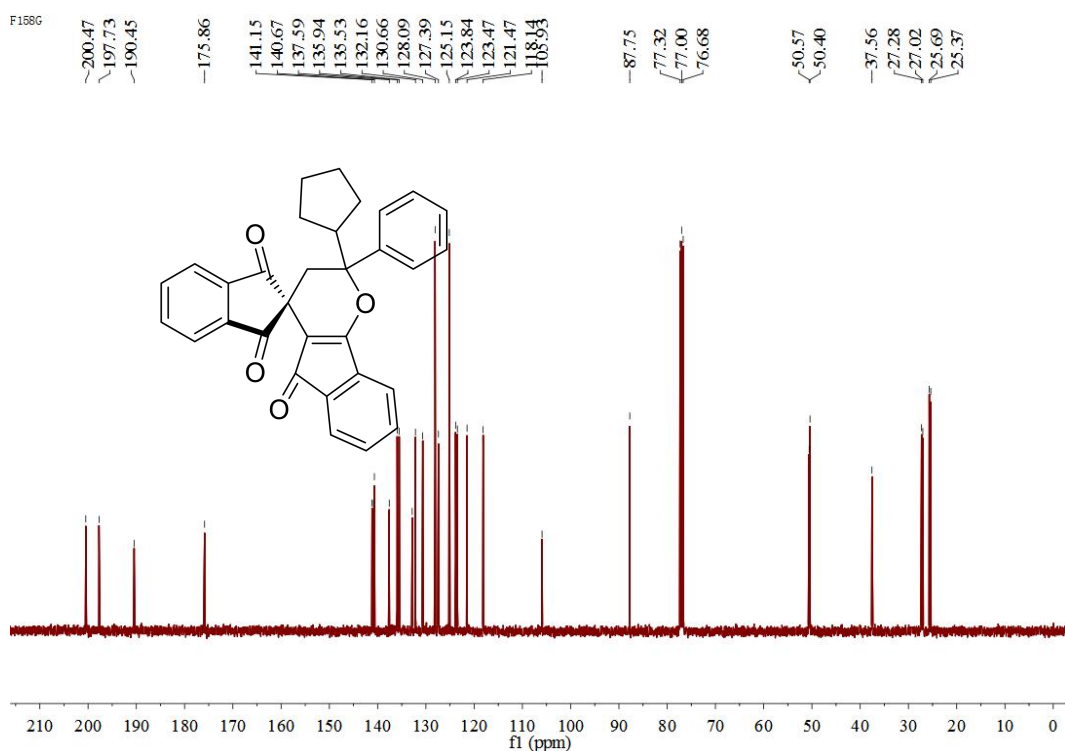
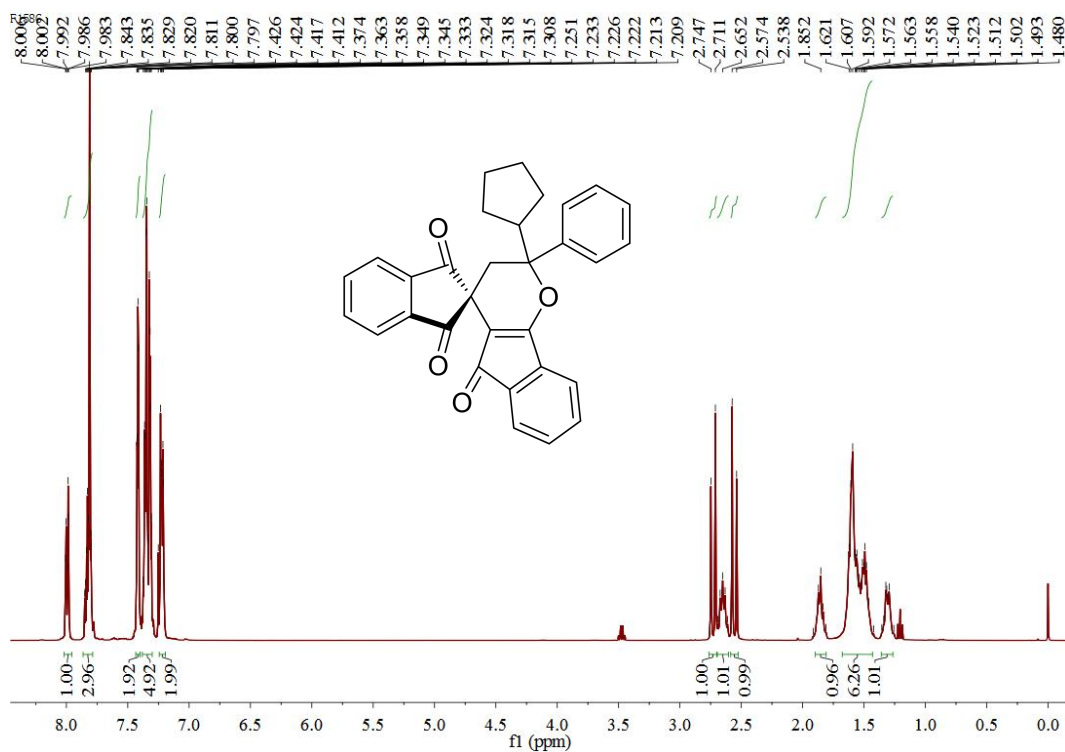
¹H NMR and ¹³C NMR of 4u



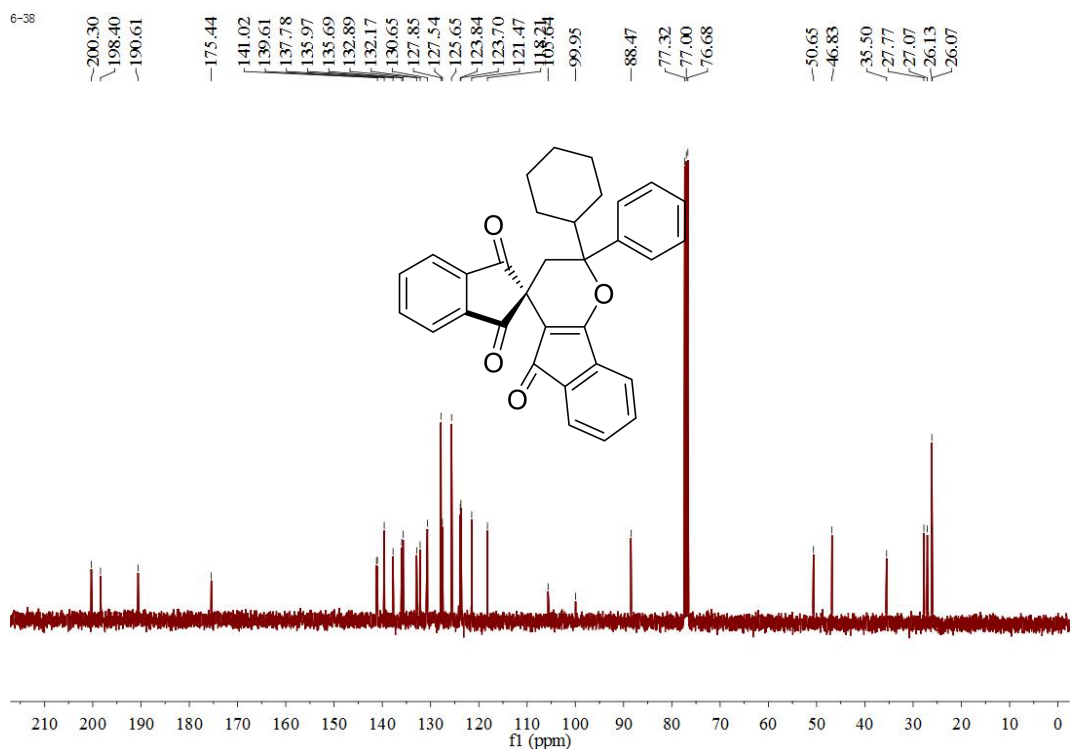
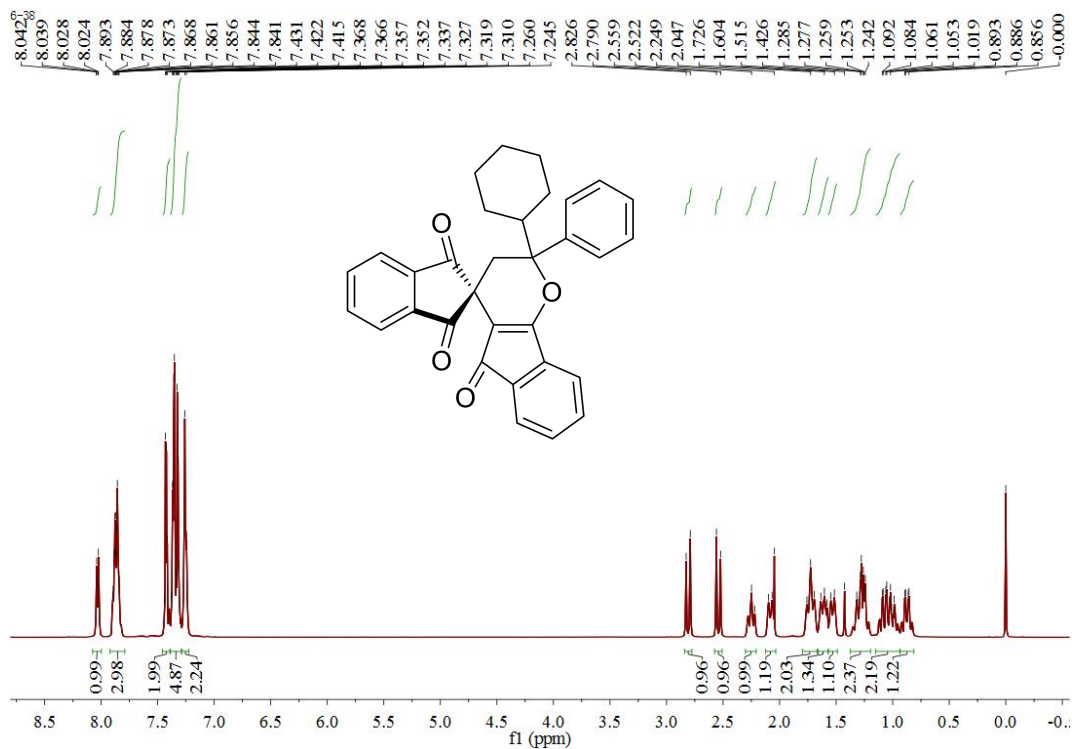
¹H NMR and ¹³C NMR of 4v



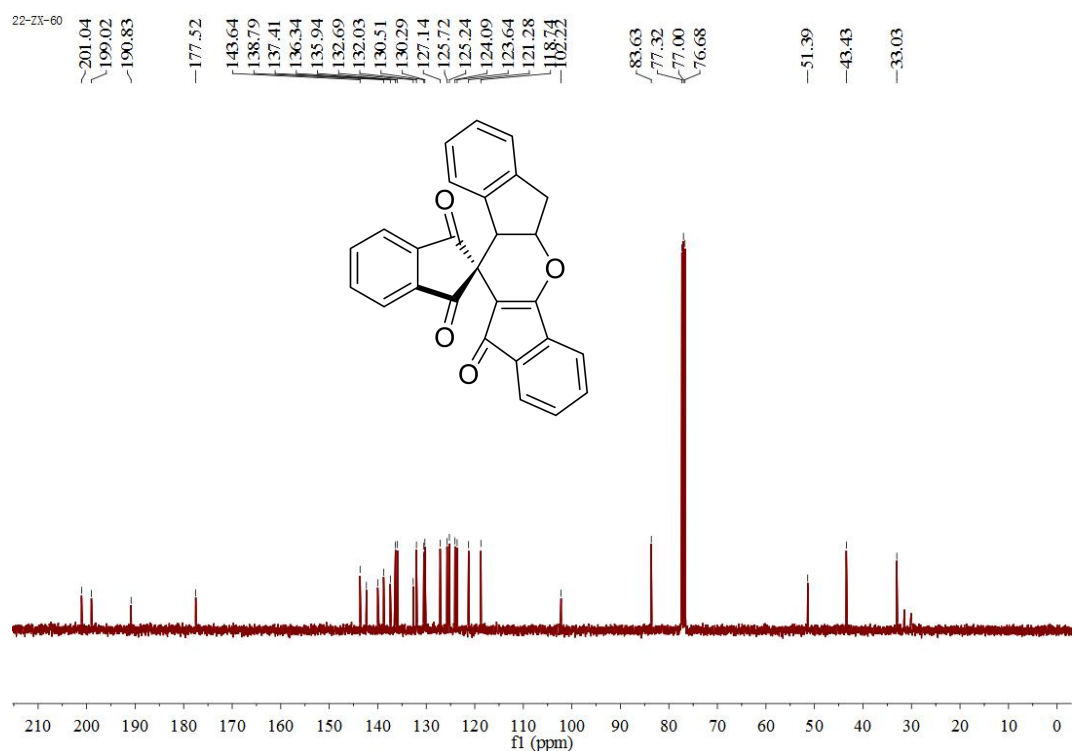
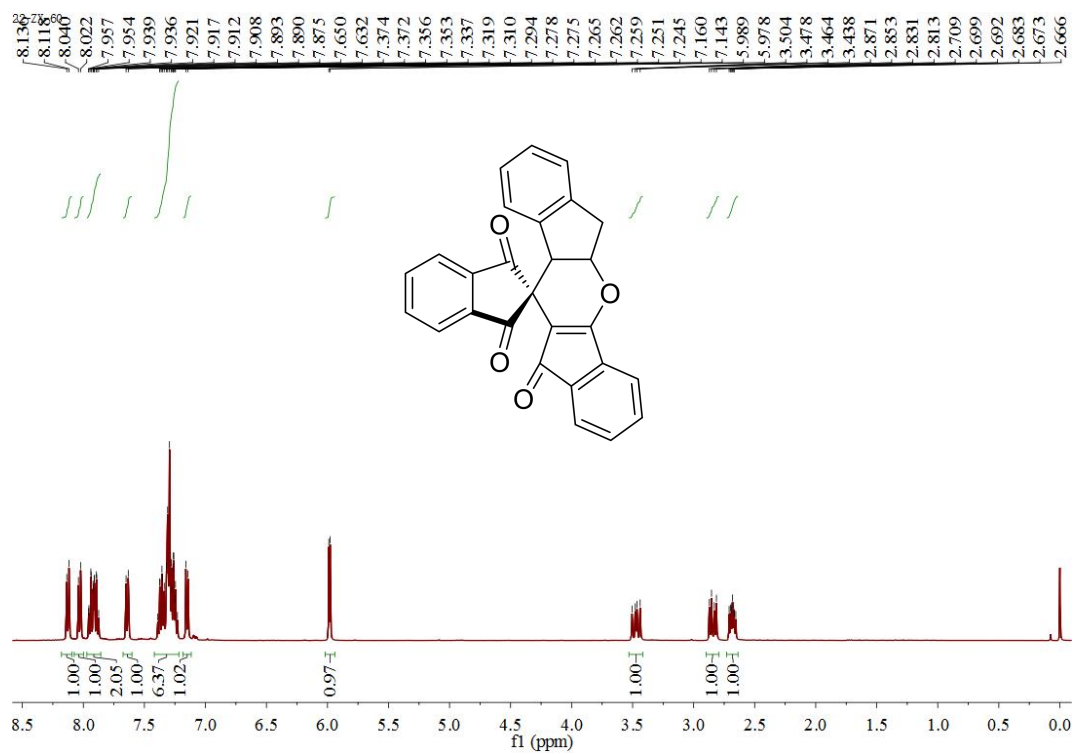
¹H NMR and ¹³C NMR of 4w



¹H NMR and ¹³C NMR of 4x



¹H NMR and ¹³C NMR of 4y



¹H NMR and ¹³C NMR of 4z

