

CuBr₂-Mediated Dehydrogenative [4 + 2] Annulation of 1-Naphthyl-1,3-indandiones and Alkenes

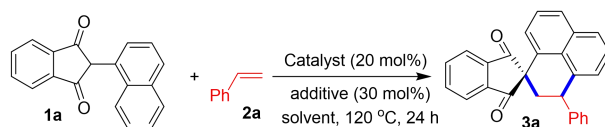
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General Methods and Materials

CuBr₂, CuBr, CuBr.SMe₂, CuCl₂, CuCl, CuI, Cu(OAc)₂, Cu(acac)₂, Cu(OTf)₂, CuOTf, Cu(TFA)₂, CuBr, Cs₂CO₃, NaOCH₃, KO^tBu, NaO^tBu, and LiO^tBu were purchased from Energy Chemical and used without further purification. Other chemicals were purchased from commercial suppliers, further dried and purified if necessary. The water used was re-distilled and ion-free. 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 spectra were measured on a Waters Micromass GCT facility. 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.

Screening of Reaction Conditions^a

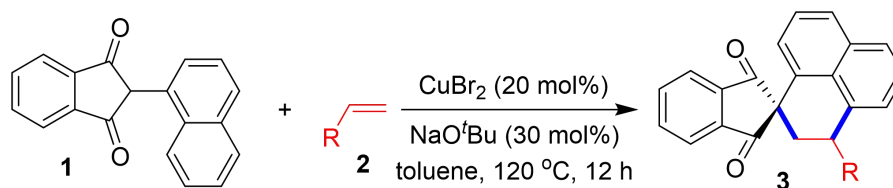


entry	catalyst	additive	solvent	yield (%) ^b
1	CuBr	K ₂ CO ₃	toluene	14
2	CuBr ₂	K ₂ CO ₃	toluene	21
3	CuBr.SMe ₂	K ₂ CO ₃	toluene	trace
4	CuCl ₂	K ₂ CO ₃	toluene	14
5	CuCl	K ₂ CO ₃	toluene	<5
6	CuI	K ₂ CO ₃	toluene	trace
7	Cu(OAc) ₂	K ₂ CO ₃	toluene	0
8	Cu(acac) ₂	K ₂ CO ₃	toluene	0
9	Cu(OTf) ₂	K ₂ CO ₃	toluene	0
10	CuOTf	K ₂ CO ₃	toluene	0
11	Cu(TFA) ₂	K ₂ CO ₃	toluene	0
12	CuBr ₂	Cs ₂ CO ₃	toluene	0
13	CuBr ₂	NaOCH ₃	toluene	0
14	CuBr ₂	KO ^t Bu	toluene	43
15	CuBr ₂	LiO ^t Bu	toluene	0
16	CuBr ₂	NaO ^t Bu	toluene	78
17	CuBr ₂	NaO ^t Bu	DMSO	0
18	CuBr ₂	NaO ^t Bu	DMF	0
19	CuBr ₂	NaO ^t Bu	MeOH	24
20	CuBr ₂	NaO ^t Bu	THF	17
21	CuBr ₂	NaO ^t Bu	1,4-dioxane	0
22	CuBr ₂	NaO ^t Bu	DCE	0
23	CuBr ₂	NaO ^t Bu	CH ₃ CN	0
24 ^c	CuBr ₂	NaO ^t Bu	toluene	trace
25 ^d		NaO ^t Bu	toluene	trace
26 ^e	CuBr ₂		toluene	trace

^aReaction conditions: 1-naphthyl-1,3-indandione **1a** (0.2 mmol), styrene **2a** (0.3 mmol), catalyst (20.0 mol%), additive (30.0 mol%), solvent (3 mL), 120 °C, 24 h, reaction under air; ^b Isolated yield after chromatography; ^c Reaction carried out in 1.0 equiv of NaO^tBu; ^d Reaction carried out in the absence of CuBr₂; ^e Reaction carried out in the absence of NaO^tBu.

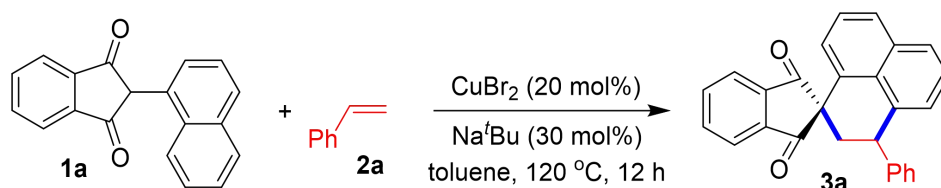
To examine the possibility of our proposed [4 + 2] cycloaddition for the formation of desired spirocyclic product **3a**, we commenced our investigations on the reaction of 1-naphthyl-1,3-indandione (**1a**) with styrene (**2a**), using CuBr (20 mol %) as the catalyst, and K₂CO₃ (30 mol %) as the base under air in toluene at 120 °C for 24 h. To our delight, the reaction proceeded smoothly and the desired cycloaddition product 3'-phenyl-2',3'-dihydrospiro[indene-2,1'-phenalene]-1,3-dione (**3a**) was observed in a 14% yield (Table 1, entry 1). Based on this finding, a variety of copper catalysts were examined, and the CuBr₂ was found to be the best choice (entries 2-11). Regarding additives (entries 12-16), NaO^tBu gave the highest yield (78%). Then, several solvents including DMSO, DMF, MeOH, THF, 1,4-dioxane, DCE, and CH₃CN were tested, and toluene proved to be the most appropriate solvent for this conversion (entries 17-23). The reaction obviously reduced yield or completely inhibited in the absence of either CuBr₂ or NaO^tBu, indicating that CuBr₂/NaO^tBu co-catalytic system was essential for the reaction outcome (entries 25-26).

General Catalytic Procedure for [4 + 2] Annulation of 1-Naphthyl-1,3-indandiones and Alkenes



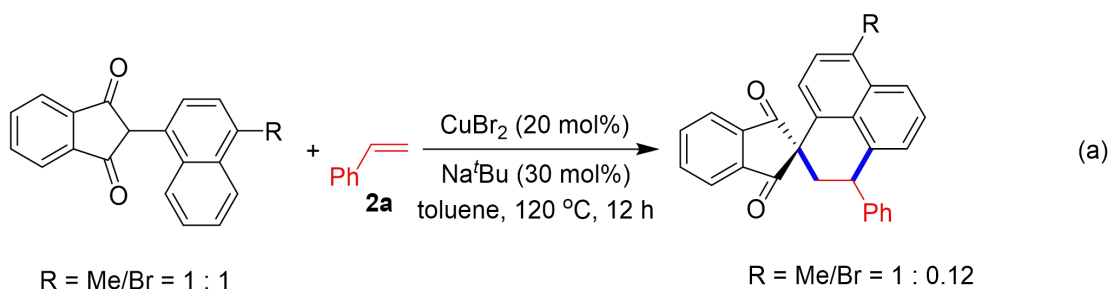
A reaction flask (25 mL) was charged with 1-naphthyl-1,3-indandione **1** (0.2 mmol, 1.0 equiv), alkene **2** (0.3 mmol, 1.5 equiv), CuBr₂ (8.9 mg, 20 mol%), NaO^tBu (5.8 mg, 30 mol%), then the toluene 3 mL was added. The mixture was stirred at 120 °C in the oil bath for 12 hours under an atmosphere 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 = 20 : 1) to yield product.

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

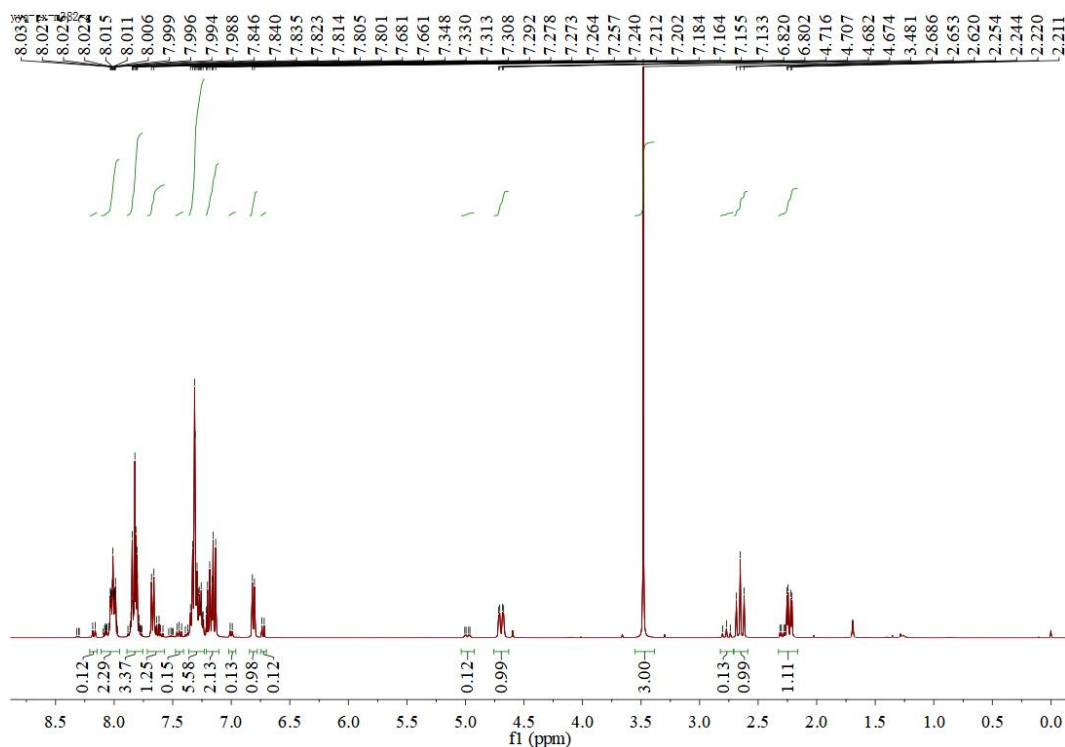


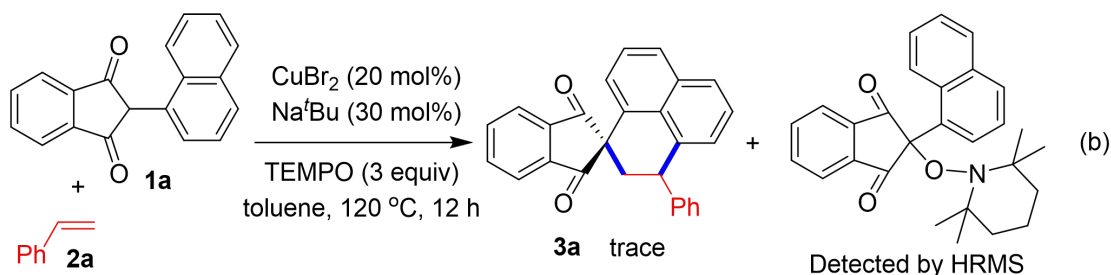
To a dry thick walled pressure resistant tube (250 mL) was charged with 1-naphthyl-1,3-indandione **1a** (5 mmol, 1.0 equiv), styrene **2a** (7.5 mmol, 1.5 equiv), CuBr_2 (223.0 mg, 20 mol%), NaO^tBu (145.0 mg, 30 mol%), then the toluene 75 mL was added. The tube was closed with a PTFE thread sealing cap. The mixture was stirred at 120 °C in oil bath for 12 hours under an atmosphere of air. After the reaction finished, the resulted mixtures were diluted with 50 mL of dichloromethane and washed with 100 mL of H_2O . The aqueous layer was extracted twice with dichloromethane (30 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 = 20 : 1) to yield product **3a** (61% yield, 1140.7 mg).

Mechanistic Study



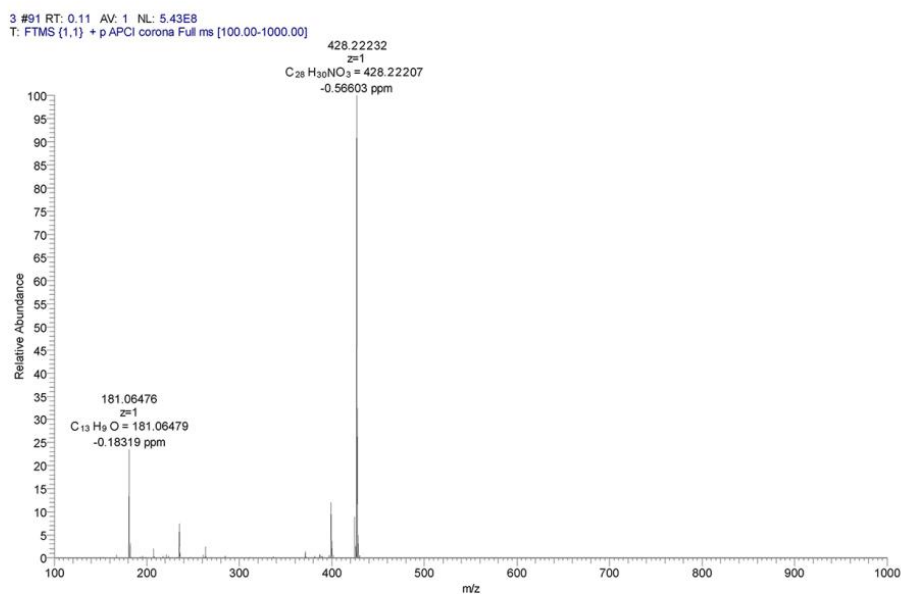
To a dry thick walled pressure resistant tube (25 mL) was charged with 2-(4-methylnaphthalen-1-yl)-1*H*-indene-1,3(2*H*)-dione (0.1 mmol, 1.0 equiv), 2-(4-bromonaphthalen-1-yl)-1*H*-indene-1,3(2*H*)-dione (0.1 mmol, 1.0 equiv), styrene (0.3 mmol, 1.5 equiv), CuBr₂ (8.9 mg, 20 mol%), NaO^tBu (5.8 mg, 30 mol%), then the toluene 3 mL was added. The mixture was stirred at 120 °C in the oil bath 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 = 20 : 1) to yield product.



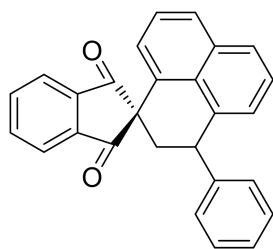


HRMS (ESI, m/z) calcd. for $\text{C}_{28}\text{H}_{30}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 428.2221, found 428.2223

To a dry thick walled pressure resistant tube (25 mL) was charged with 1-naphthyl-1,3-indandione **1a** (0.2 mmol, 1.0 equiv), styrene **2a** (0.3 mmol, 1.5 equiv), CuBr (8.9 mg, 20 mol%), NaO^tBu (5.8 mg, 30 mol%), TEMPO (0.6 mmol, 93.6 mg), then the toluene 3 mL was added. The mixture was stirred at 120 °C in the oil bath 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 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 = 20 : 1) to yield product.

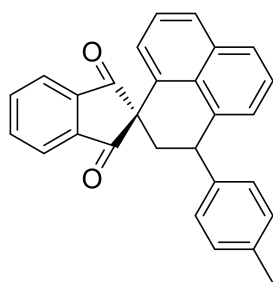


Characterization data for the products



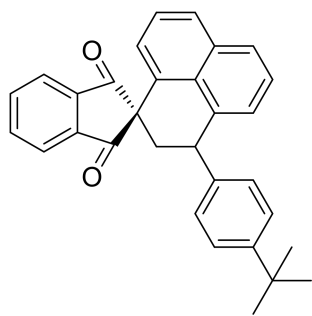
3'-Phenyl-2',3'-dihydrospiro[indene-2,1'-phenalene]-1,3-dione

(3a): Obtained as a pale yellow liquid (58.3 mg, 78% yield), eluting with 5% EtOAc in PE (elution gradient); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.11 (d, $J = 5.6$ Hz, 1H), 8.05 (d, $J = 4.4$ Hz, 1H), 7.87 - 7.89 (m, 2H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.29 - 7.36 (m, 7H), 6.93 (d, $J = 7.2$ Hz, 1H), 6.88 (d, $J = 6.8$ Hz, 1H), 5.00 - 5.04 (m, 1H), 2.76 - 2.83 (t, 1H), 2.27 - 2.31 (q, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 203.4, 200.3, 144.0, 142.1, 141.1, 138.1, 136.3, 136.0, 133.8, 131.1, 130.0, 129.1, 128.7, 128.5, 126.9, 126.8, 125.8, 125.7, 125.0, 124.6, 124.2, 123.6, 58.8, 41.8, 36.6; HRMS (ESI-TOF) m/z calcd for $\text{C}_{27}\text{H}_{19}\text{O}_2$ $[\text{M} + \text{H}]^+$ 375.1380, found 375.1378.



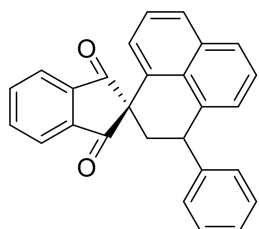
3'-(*p*-Tolyl)-2',3'-dihydrospiro[indene-2,1'-phenalene]-1,3-dione

(3b): Obtained as a pale yellow liquid (65.2 mg, 84% yield), eluting with 5% EtOAc in PE (elution gradient); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.10 - 8.17 (q, 2H), 7.94 - 7.96 (m, 2H), 7.85 (d, $J = 8.4$ Hz, 1H), 7.78 (d, $J = 8.0$ Hz, 1H), 7.35 - 7.42 (m, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 7.21 (d, $J = 7.6$ Hz, 2H), 7.01 (d, $J = 7.2$ Hz, 1H), 6.92 (d, $J = 7.2$ Hz, 1H), 5.00 - 5.05 (m, 1H), 2.80 - 2.87 (t, 1H), 2.40 (s, 3H), 2.30 - 2.34 (q, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 203.4, 200.4, 142.1, 141.1, 140.9, 138.3, 136.5, 136.3, 135.9, 133.9, 131.1, 130.0, 129.4, 129.0, 128.5, 126.7, 125.8, 125.7, 125.0, 124.6, 124.2, 123.6, 58.8, 41.4, 36.6, 21.1; HRMS (ESI-TOF) m/z calcd for $\text{C}_{28}\text{H}_{21}\text{O}_2$ $[\text{M} + \text{H}]^+$ 389.1536, found 389.1535.



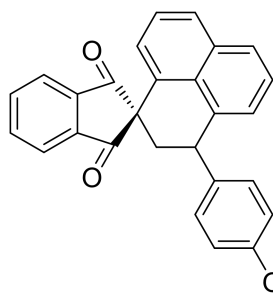
3'-(4-(*Tert*-butyl)phenyl)-2',3'-dihydrospiro[indene-2,1'-phenylene]-1,3-dione (**3c**):

Obtained as a pale yellow liquid (75.7 mg, 88% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 7.94 - 8.02 (m, 2H), 7.76 - 7.79 (m, 2H), 7.70 (d, $J = 8.4$ Hz, 1H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.20 - 7.28 (m, 4H), 7.15 (d, $J = 8.0$ Hz, 2H), 6.88 (d, $J = 7.6$ Hz, 1H), 6.78 (d, $J = 7.2$ Hz, 1H), 4.87 - 4.91 (q, 1H), 2.66 - 2.72 (t, 1H), 2.16 - 2.20 (q, 1H), 1.23 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 203.4, 200.4, 149.7, 142.1, 141.1, 140.8, 138.3, 136.3, 135.9, 133.8, 131.1, 130.1, 128.7, 128.5, 126.7, 125.8, 125.7, 125.6, 125.0, 124.5, 124.2, 123.6, 58.9, 41.3, 36.7, 34.4, 31.4; HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{27}\text{O}_2$ $[\text{M} + \text{H}]^+$ 431.2006, found 431.2008.

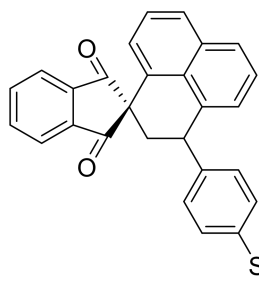


Ph 3'-([1,1'-Biphenyl]-4-yl)-2',3'-dihydrospiro[indene-2,1'-phenylene]-1,3-dione (**3d**):

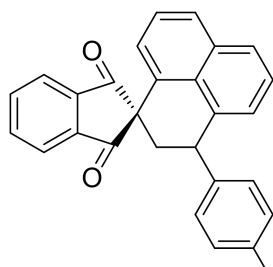
Obtained as a pale yellow liquid (65.7 mg, 73% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 8.12 - 8.15 (m, 1H), 8.07 - 8.09 (m, 1H), 7.91 - 7.93 (m, 2H), 7.81 (d, $J = 7.6$ Hz, 1H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.58 - 7.62 (m, 4H), 7.38 - 7.45 (m, 5H), 7.31 - 7.35 (m, 2H), 7.02 (d, $J = 6.8$ Hz, 1H), 6.89 (d, $J = 7.2$ Hz, 1H), 5.05 - 5.09 (m, 1H), 2.80 - 2.86 (t, 1H), 2.30 - 2.35 (q, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 203.4, 200.4, 143.1, 142.1, 141.1, 140.8, 139.8, 138.0, 136.4, 136.0, 135.3, 133.9, 131.0, 128.7, 128.6, 127.4, 127.2, 127.1, 127.0, 126.9, 125.8, 125.0, 124.6, 124.3, 123.7, 123.6, 58.8, 41.5, 36.6; HRMS (ESI-TOF) m/z calcd for $\text{C}_{33}\text{H}_{23}\text{O}_2$ $[\text{M} + \text{H}]^+$ 451.1693, found 451.1692.



3'-(4-Methoxyphenyl)-2',3'-dihydrospiro[indene-2,1'-phenylene]-1,3-dione (**3e**): Obtained as a pale yellow liquid (65.4 mg, 81% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 7.99 - 8.06 (m, 2H), 7.84 - 7.85 (m, 2H), 7.73 (d, $J = 8.4$ Hz, 1H), 7.65 (d, $J = 8.4$ Hz, 1H), 7.22 - 7.30 (m, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 6.88 (d, $J = 7.2$ Hz, 1H), 6.79 - 6.83 (m, 3H), 4.86 - 4.91 (q, 1H), 3.73 (s, 3H), 2.65 - 2.72 (t, 1H), 2.17 - 2.21 (q, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 203.5, 200.4, 158.5, 142.1, 141.1, 138.5, 136.3, 135.99, 135.97, 133.9, 131.1, 130.06, 130.07, 128.5, 126.7, 125.8, 125.7, 125.0, 124.6, 124.2, 123.6, 114.1, 58.9, 55.2, 41.0, 36.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{28}\text{H}_{21}\text{O}_3$ $[\text{M} + \text{H}]^+$ 405.1485, found 405.1483.

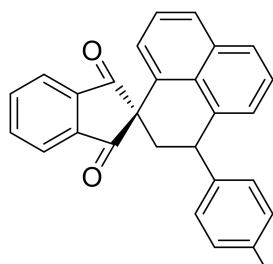


3'-(4-(Methylthio)phenyl)-2',3'-dihydrospiro[indene-2,1'-phenylene]-1,3-dione (**3f**): Obtained as a pale yellow liquid (62.2 mg, 74% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 8.10 - 8.11 (m, 1H), 8.03 - 8.05 (m, 1H), 7.87 - 7.89 (m, 2H), 7.76 - 7.80 (m, 2H), 7.72 (d, $J = 7.6$ Hz, 1H), 7.30 - 7.36 (m, 2H), 7.21 - 7.25 (m, 3H), 6.94 (d, $J = 6.8$ Hz, 1H), 6.87 (d, $J = 7.2$ Hz, 1H), 4.97 - 5.00 (m, 1H), 2.72 - 2.79 (t, 1H), 2.46 (s, 3H), 2.24 - 2.28 (q, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 203.3, 200.3, 142.0, 141.0, 140.8, 137.9, 136.8, 136.3, 136.0, 133.8, 131.0, 129.9, 129.6, 128.5, 126.8, 126.8, 125.7, 125.6, 125.0, 124.5, 124.2, 123.5, 58.6, 41.2, 36.4, 15.8; HRMS (ESI-TOF) m/z calcd for $\text{C}_{28}\text{H}_{21}\text{SO}_2$ $[\text{M} + \text{H}]^+$ 421.1257, found 421.1255.



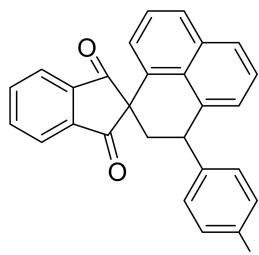
F 3'-(4-Fluorophenyl)-2',3'-dihydrospiro[indene-2,1'-phenalene]-1,

3-dione (**3g**): Obtained as a pale yellow liquid (58.0 mg, 74% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 8.10 - 8.18 (m, 2H), 7.94 - 7.98 (m, 2H), 7.85 (d, $J = 8.4$ Hz, 1H), 7.78 (d, $J = 8.0$ Hz, 1H), 7.29 - 7.42 (m, 4H), 7.06 - 7.11 (t, 2H), 6.92 - 6.96 (m, 2H), 5.05 - 5.09 (q, 1H), 2.76 - 2.83 (t, 1H), 2.30 - 2.34 (q, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 203.3, 200.3, 161.8 (d, $J = 243.5$ Hz), 142.1, 141.1, 139.7 (d, $J = 3.2$ Hz), 137.9, 136.4, 136.0, 133.9, 131.0, 130.6 (d, $J = 7.6$ Hz), 129.9, 128.5, 126.9, 125.8, 125.6, 125.1, 124.6, 124.3, 123.6, 115.6 (d, $J = 21.0$ Hz), 58.6, 41.1, 36.6; ^{19}F NMR (400 MHz, CDCl_3) δ -115.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{27}\text{H}_{18}\text{FO}_2$ $[\text{M} + \text{H}]^+$ 393.1285, found 393.1287.

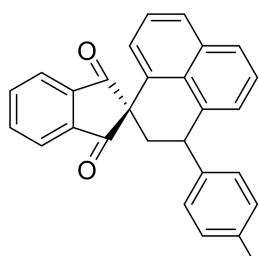


Cl 3'-(4-Chlorophenyl)-2',3'-dihydrospiro[indene-2,1'-phenalene]-

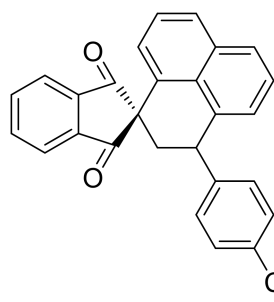
1,3-dione (**3h**): Obtained as a pale yellow liquid (57.9 mg, 71% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 7.98 - 8.06 (m, 2H), 7.82 - 7.87 (m, 2H), 7.73 (d, $J = 8.4$ Hz, 1H), 7.66 (d, $J = 8.0$ Hz, 1H), 7.17 - 7.30 (m, 6H), 6.78 - 6.83 (m, 2H), 4.92 - 4.96 (q, 1H), 2.63 - 2.70 (t, 1H), 2.16 - 2.20 (q, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 203.2, 200.3, 142.6, 142.1, 141.1, 137.6, 136.4, 136.1, 133.9, 132.7, 131.0, 130.5, 129.9, 128.9, 128.6, 127.0, 125.8, 125.7, 125.1, 124.6, 124.3, 123.7, 58.6, 41.2, 36.4; HRMS (ESI-TOF) m/z calcd for $\text{C}_{27}\text{H}_{18}\text{ClO}_2$ $[\text{M} + \text{H}]^+$ 409.0990, found 409.0988.



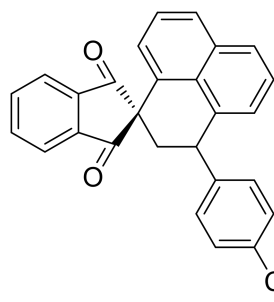
Br 3'--(4-Bromophenyl)-2',3'-dihydrospiro[indene-2,1'-phenalene]-1,3-dione (**3i**): Obtained as a pale yellow liquid (66.0 mg, 73% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 8.00 - 8.06 (m, 2H), 7.83 - 7.85 (m, 2H), 7.73 (d, $J = 8.4$ Hz, 1H), 7.67 (d, $J = 8.4$ Hz, 1H), 7.28 - 7.31 (t, 1H), 7.22 - 7.26 (t, 1H), 7.16 - 7.18 (m, 2H), 7.03 - 7.08 (m, 2H), 6.87 (d, $J = 7.2$ Hz, 1H), 6.80 (d, $J = 7.2$ Hz, 1H), 5.68 - 5.72 (q, 1H), 2.57 - 2.64 (t, 1H), 2.20 - 2.25 (q, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 203.4, 199.8, 143.5, 142.1, 141.2, 136.7, 136.4, 136.0, 134.0, 132.8, 131.1, 130.1, 129.9, 128.6, 128.4, 128.0, 126.9, 126.0, 125.8, 125.3, 125.1, 124.8, 124.3, 123.6, 58.5, 40.4, 35.4; HRMS (ESI-TOF) m/z calcd for $\text{C}_{27}\text{H}_{18}\text{BrO}_2$ $[\text{M} + \text{H}]^+$ 453.0458, found 453.0456.



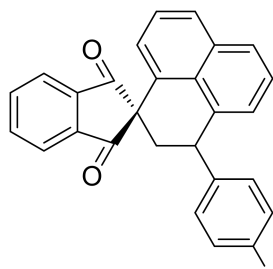
I 3'--(4-Iodophenyl)-2',3'-dihydrospiro[indene-2,1'-phenalene]-1,3-dione (**3j**): Obtained as a pale yellow liquid (73.0 mg, 73% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 8.12 - 8.14 (m, 1H), 8.05 - 8.07 (m, 1H), 7.91 - 7.93 (m, 2H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.74 (d, $J = 8.8$ Hz, 1H), 7.67 (d, $J = 8.4$ Hz, 2H), 7.30 - 7.37 (m, 2H), 7.08 (d, $J = 8.0$ Hz, 2H), 6.86 - 6.92 (q, 2H), 4.96 - 5.01 (q, 1H), 2.70 - 2.76 (t, 1H), 2.24 - 2.28 (q, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 203.2, 200.3, 143.8, 142.1, 141.1, 137.8, 137.4, 136.4, 136.1, 133.8, 131.2, 130.9, 129.8, 128.6, 127.0, 125.8, 125.7, 125.1, 124.6, 124.3, 123.6, 92.3, 58.5, 41.4, 36.2; HRMS (ESI-TOF) m/z calcd for $\text{C}_{27}\text{H}_{18}\text{IO}_2$ $[\text{M} + \text{H}]^+$ 501.0346, found 501.0344.



3'-(4-(Trifluoromethyl)phenyl)-2',3'-dihydrospiro[indene-2,1'-phenalene]-1,3-dione (**3k**): Obtained as a pale yellow liquid (60.1 mg, 68% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 7.99 - 8.07 (m, 2H), 7.83 - 7.88 (m, 2H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.54 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.23 - 7.30 (m, 2H), 6.78 - 6.82 (m, 2H), 5.03 - 5.07 (q, 1H), 2.67 - 2.74 (t, 1H), 2.18 - 2.22 (q, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 203.1, 200.2, 148.3, 142.2, 141.1, 137.1, 136.5, 136.1, 133.9, 130.9, 129.5 (q, $J = 25.4, 35.6$ Hz), 128.6, 127.2, 125.7 (q, $J = 3.9, 7.1$ Hz), 125.2, 124.7, 124.4, 123.7, 58.4, 41.7, 36.3; ^{19}F NMR (400 MHz, CDCl_3) δ -62.4; HRMS (ESI-TOF) m/z calcd for $\text{C}_{28}\text{H}_{18}\text{F}_3\text{O}_2$ $[\text{M} + \text{H}]^+$ 443.1253, found 443.1251.

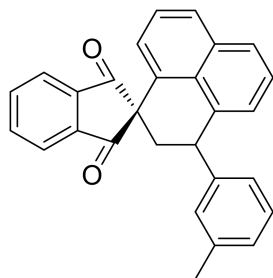


4-(1,3-Dioxo-1,2',3,3'-tetrahydrospiro[indene-2,1'-phenalene]-3'-yl)benzonitrile (**3l**): Obtained as a pale yellow liquid (49.5 mg, 62% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 7.99 - 8.08 (m, 2H), 7.84 - 7.90 (m, 2H), 7.74 (d, $J = 8.4$ Hz, 1H), 7.69 (d, $J = 8.4$ Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.24 - 7.31 (m, 2H), 6.81 (d, $J = 7.2$ Hz, 1H), 6.75 (d, $J = 7.2$ Hz, 1H), 5.04 - 5.08 (q, 1H), 2.64 - 2.71 (t, 1H), 2.17 - 2.22 (q, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 202.9, 200.1, 149.9, 142.1, 141.1, 136.6, 136.5, 136.2, 133.9, 132.6, 130.8, 130.0, 129.7, 128.7, 127.4, 125.7, 125.6, 125.3, 124.7, 124.4, 123.7, 118.8, 110.9, 58.2, 42.0, 36.0; HRMS (ESI-TOF) m/z calcd for $\text{C}_{28}\text{H}_{18}\text{NO}_2$ $[\text{M} + \text{H}]^+$ 400.1332, found 400.1331.



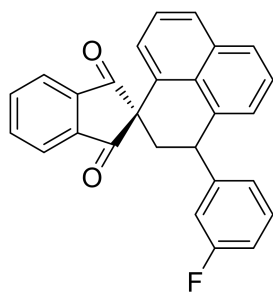
NO₂ 3'-(4-Nitrophenyl)-2',3'-dihydrospiro[indene-2,1'-phenalene]-

1,3-dione (**3m**): Obtained as a pale yellow liquid (53.6 mg, 64% yield), eluting with 5% EtOAc in PE (elution gradient); ¹H NMR (400 MHz, CDCl₃) δ 8.01 - 8.08 (m, 2H), 7.86 - 7.88 (m, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.22 - 7.31 (m, 6H), 6.87 (d, *J* = 6.8 Hz, 1H), 6.81 (d, *J* = 6.8 Hz, 1H), 4.92 - 4.96 (q, 1H), 2.70 - 2.76 (t, 1H), 2.20 - 2.25 (q, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 200.4, 197.2, 144.0, 142.2, 141.2, 138.1, 136.4, 136.0, 133.9, 131.1, 129.3, 129.2, 128.8, 128.6, 127.0, 126.8, 125.8, 125.8, 125.0, 124.6, 124.3, 123.7, 58.8, 41.8, 36.6; HRMS (ESI-TOF) *m/z* calcd for C₂₇H₁₈NO₄ [M + H]⁺ 420.1230, found 420.1231.



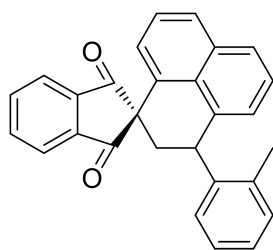
3'-(*m*-Tolyl)-2',3'-dihydrospiro[indene-2,1'-phenalene]-1,3-dione

(**3n**): Obtained as a pale yellow liquid (59.8 mg, 77% yield), eluting with 5% EtOAc in PE (elution gradient); ¹H NMR (400 MHz, CDCl₃) δ 7.99 - 8.07 (q, 2H), 7.85 - 7.86 (m, 2H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.23 - 7.31 (m, 2H), 7.15 - 7.19 (t, 1H), 7.02 - 7.08 (m, 3H), 6.89 (d, *J* = 7.2 Hz, 1H), 6.80 (d, *J* = 7.2 Hz, 1H), 4.87 - 4.92 (m, 1H), 2.69 - 2.75 (t, 1H), 2.26 (s, 3H), 2.18 - 2.23 (q, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 203.5, 200.4, 143.9, 142.1, 141.1, 138.3, 138.2, 136.3, 136.0, 133.9, 131.1, 130.0, 128.6, 128.5, 127.7, 126.7, 125.8, 125.8, 125.0, 124.6, 124.3, 123.6, 58.9, 41.8, 36.6, 21.4; HRMS (ESI-TOF) *m/z* calcd for C₂₈H₂₁O₂ [M + H]⁺ 389.1536, found 389.1538.



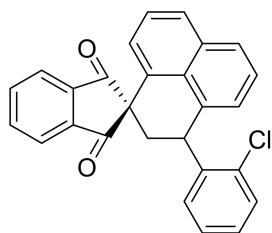
3'-(3-Fluorophenyl)-2',3'-dihydrospiro[indene-2,1'-phenalene]-1,

3-dione (**3o**): Obtained as a pale yellow liquid (54.9 mg, 70% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 7.99 - 8.08 (q, 2H), 7.85 - 7.89 (m, 2H), 7.74 (d, $J = 8.4$ Hz, 1H), 7.68 (d, $J = 8.0$ Hz, 1H), 7.22 - 7.32 (m, 3H), 7.05 (d, $J = 7.6$ Hz, 1H), 6.86 - 6.98 (m, 3H), 6.80 (d, $J = 7.2$ Hz, 1H), 4.95 - 4.99 (m, 1H), 2.65 - 2.72 (t, 1H), 2.20 - 2.24 (q, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 203.2, 200.3, 163.1 (d, $J = 244.5$ Hz), 146.7 (d, $J = 6.9$ Hz), 142.2, 141.1, 137.3, 136.4, 136.1, 133.9, 130.9, 130.2 (d, $J = 8.1$ Hz), 129.9, 128.6, 127.1, 125.7 (d, $J = 13.0$ Hz), 125.1, 124.9, 124.7, 124.3, 123.7, 116.0 (d, $J = 21.0$ Hz), 113.9 (d, $J = 20.9$ Hz), 58.6, 41.7, 36.3; ^{19}F NMR (400 MHz, CDCl_3) δ -112.8; HRMS (ESI-TOF) m/z calcd for $\text{C}_{27}\text{H}_{18}\text{FO}_2$ $[\text{M} + \text{H}]^+$ 393.1285, found 393.1286.

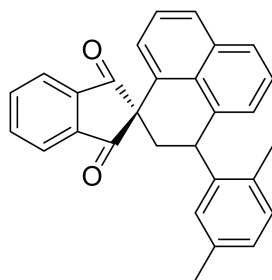


3'-(*o*-Tolyl)-2',3'-dihydrospiro[indene-2,1'-phenalene]-1,3-dione

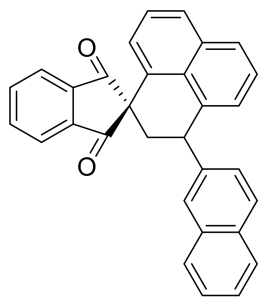
(**3p**): Obtained as a pale yellow liquid (56.6 mg, 73% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 8.00 - 8.06 (m, 2H), 7.84 - 7.86 (m, 2H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.23 - 7.29 (m, 2H), 7.11 - 7.17 (m, 4H), 6.77 - 7.80 (m, 2H), 5.33 - 5.37 (q, 1H), 2.70 - 2.77 (t, 1H), 2.39 (s, 3H), 2.14 - 2.18 (q, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 203.5, 200.6, 142.2, 142.1, 141.2, 137.9, 137.1, 136.3, 136.0, 134.0, 131.2, 130.2, 128.6, 127.9, 126.7, 126.6, 125.8, 125.1, 124.6, 124.3, 123.6, 58.8, 36.1, 35.7, 19.6; HRMS (ESI-TOF) m/z calcd for $\text{C}_{28}\text{H}_{21}\text{O}_2$ $[\text{M} + \text{H}]^+$ 389.1536, found 389.1535.



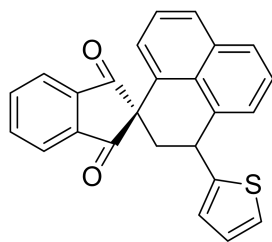
3'-(2-Chlorophenyl)-2',3'-dihydrospiro[indene-2,1'-phenalene]-1,3-dione (**3q**): Obtained as a pale yellow liquid (53.9 mg, 66% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 8.14 - 8.16 (m, 1H), 8.09 - 8.12 (m, 1H), 7.93 - 7.97 (m, 2H), 7.82 (d, $J = 8.4$ Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.44 - 7.47 (m, 1H), 7.31 - 7.41 (m, 3H), 7.25 - 7.29 (m, 1H), 7.22 - 7.24 (m, 1H), 6.95 (d, $J = 7.2$ Hz, 1H), 6.88 (d, $J = 7.2$ Hz, 1H), 5.78 - 5.82 (m, 1H), 2.68 - 2.74 (t, 1H), 2.28 - 2.32 (q, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 203.5, 199.9, 142.1, 141.7, 141.2, 136.7, 136.4, 136.0, 135.1, 134.0, 131.0, 130.1, 129.8, 129.4, 128.6, 128.1, 127.3, 126.9, 125.8, 125.3, 125.1, 124.8, 124.3, 123.6, 58.5, 37.3, 35.4; HRMS (ESI-TOF) m/z calcd for $\text{C}_{27}\text{H}_{18}\text{ClO}_2$ $[\text{M} + \text{H}]^+$ 409.0990, found 409.0993.



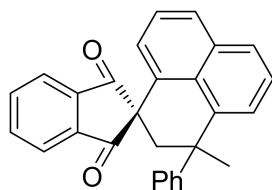
3'-(2,5-Dimethylphenyl)-2',3'-dihydrospiro[indene-2,1'-phenalene]-1,3-dione (**3r**): Obtained as a pale yellow liquid (66.7 mg, 83% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 7.99 - 8.07 (m, 2H), 7.84 - 7.86 (m, 2H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.66 (d, $J = 8.0$ Hz, 1H), 7.25 - 7.30 (m, 2H), 7.05 (d, $J = 7.6$ Hz, 1H), 6.91 - 6.94 (m, 2H), 6.79 - 6.83 (t, 2H), 5.28 - 5.32 (q, 1H), 2.71 - 2.77 (t, 1H), 2.34 (s, 3H), 2.13 - 2.17 (q, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 203.6, 200.5, 142.2, 141.8, 141.2, 138.0, 136.3, 136.0, 133.9, 133.9, 131.2, 130.2, 130.1, 128.5, 128.4, 127.4, 126.6, 125.9, 125.1, 125.0, 124.6, 124.3, 123.6, 58.9, 36.1, 35.7, 21.0, 19.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{29}\text{H}_{23}\text{O}_2$ $[\text{M} + \text{H}]^+$ 403.1693, found 403.1692.



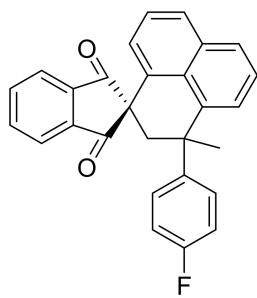
3'-(Naphthalen-2-yl)-2',3'-dihydrospiro[indene-2,1'-phenalene]-1,3-dione (**3s**): Obtained as a pale yellow liquid (76.3 mg, 90% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 8.11 - 8.14 (m, 1H), 8.07 - 8.09 (m, 1H), 7.78 - 7.90 (m, 8H), 7.45 - 7.47 (m, 2H), 7.30 - 7.38 (m, 3H), 6.90 - 6.95 (m, 2H), 5.21 (d, $J = 13.2$ Hz, 1H), 2.88 - 2.95 (m, 1H), 2.32 - 2.36 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 203.4, 200.4, 142.1, 141.5, 141.3, 141.1, 137.9, 136.4, 136.0, 135.3, 133.9, 133.6, 132.6, 128.5, 128.5, 127.7, 127.6, 126.9, 126.6, 126.1, 126.0, 125.8, 125.7, 125.0, 124.6, 124.3, 123.7, 123.6, 58.7, 41.9, 36.4; HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{21}\text{O}_2$ $[\text{M} + \text{H}]^+$ 425.1536, found 425.1534.



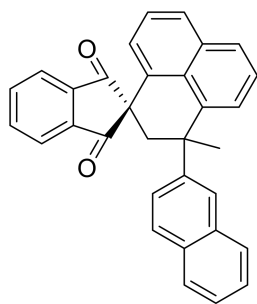
3'-(Thiophen-2-yl)-2',3'-dihydrospiro[indene-2,1'-phenalene]-1,3-dione (**3t**): Obtained as a pale yellow liquid (62.3 mg, 82% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 8.05 - 8.07 (t, 1H), 7.98 - 8.00 (m, 1H), 7.83 - 7.87 (m, 2H), 6.73 (d, $J = 8.0$ Hz, 1H), 6.67 (d, $J = 8.4$ Hz, 1H), 7.30 - 7.34 (t, 1H), 7.22 - 7.26 (t, 1H), 7.17 (d, $J = 4.2$ Hz, 1H), 7.07 (d, $J = 7.2$ Hz, 1H), 7.01 (d, $J = 3.2$ Hz, 1H), 6.93 - 6.95 (t, 1H), 6.79 (d, $J = 7.2$ Hz, 1H), 5.31 - 5.35 (m, 1H), 2.72 - 2.79 (t, 1H), 2.33 - 2.37 (q, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 203.0, 200.3, 146.8, 142.2, 141.1, 137.4, 136.4, 136.1, 133.8, 130.8, 129.5, 128.5, 127.2, 126.6, 126.4, 125.9, 125.3, 125.1, 124.6, 124.4, 124.3, 123.7, 58.6, 37.2, 37.0; HRMS (ESI-TOF) m/z calcd for $\text{C}_{25}\text{H}_{17}\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 381.0944, found 381.0946.



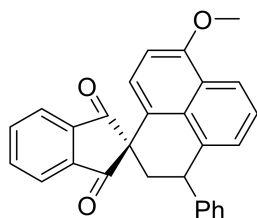
3'-Methyl-3'-phenyl-2',3'-dihydrospiro[indene-2,1'-phenalene]-1,3-dione (**3u**): Obtained as a pale yellow liquid (54.3 mg, 70% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, $J = 7.2$ Hz, 1H), 7.91 (d, $J = 6.8$ Hz, 1H), 7.76 - 7.85 (m, 3H), 7.71 (d, $J = 8.0$ Hz, 1H), 7.35 - 7.39 (t, 1H), 7.25 - 7.29 (t, 1H), 7.11 - 7.19 (m, 6H), 6.74 (d, $J = 7.2$ Hz, 1H), 2.85 (d, $J = 10.0$ Hz, 1H), 2.32 (d, $J = 14.0$ Hz, 1H), 1.89 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 201.8, 201.3, 150.2, 142.1, 141.9, 135.9, 135.9, 134.0, 131.0, 129.9, 128.7, 127.9, 127.7, 126.9, 126.2, 126.2, 125.8, 125.2, 125.1, 124.4, 123.9, 60.3, 44.6, 43.1, 30.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{28}\text{H}_{21}\text{O}_2$ $[\text{M} + \text{H}]^+$ 389.1536, found 389.1535.



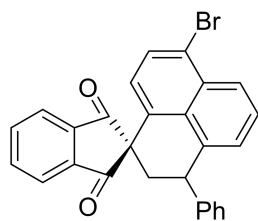
3'-(4-Fluorophenyl)-3'-methyl-2',3'-dihydrospiro[indene-2,1'-phenalene]-1,3-dione (**3v**): Obtained as a pale yellow liquid (50.3 mg, 62% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 8.08 - 8.10 (m, 1H), 7.97 - 7.99 (m, 1H), 7.83 - 7.91 (m, 3H), 7.79 (d, $J = 8.0$ Hz, 1H), 7.43 - 7.47 (t, 1H), 7.32 - 7.36 (m, 1H), 7.18 - 7.22 (m, 3H), 6.90 - 6.96 (m, 2H), 6.80 - 6.82 (q, 1H), 2.86 (d, $J = 14.4$ Hz, 1H), 2.40 (d, $J = 14.4$ Hz, 1H), 1.94 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 201.7, 201.2, 161.2 (d, $J = 243.6$ Hz), 145.8 (d, $J = 3.2$ Hz), 141.9 (d, $J = 10.5$ Hz), 141.7, 135.9 (d, $J = 4.5$ Hz), 134.0, 130.9, 129.7, 129.3, 129.2, 128.7, 127.0, 126.1, 125.8, 125.3, 125.2, 124.3, 124.0, 114.7, 114.5, 60.1, 44.6, 42.6, 31.0; ^{19}F NMR (400 MHz, CDCl_3) δ -117.0; HRMS (ESI-TOF) m/z calcd for $\text{C}_{28}\text{H}_{20}\text{FO}_2$ $[\text{M} + \text{H}]^+$ 407.1442, found 407.1445.



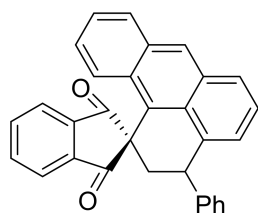
3'-Methyl-3'-(naphthalen-2-yl)-2',3'-dihydrospiro[indene-2,1'-phenalene]-1,3-dione (**3w**): Obtained as a pale yellow liquid (57.8 mg, 66% yield), eluting with 5% EtOAc in PE (elution gradient); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.09 (d, $J = 7.2$ Hz, 1H), 7.98 (d, $J = 6.8$ Hz, 1H), 7.83 - 7.88 (m, 4H), 7.76 - 7.78 (m, 3H), 7.69 (d, $J = 8.8$ Hz, 1H), 7.41 - 7.45 (m, 2H), 7.34 - 7.39 (m, 2H), 7.28 - 7.30 (m, 1H), 7.11 (d, $J = 7.2$ Hz, 1H), 6.84 (d, $J = 6.8$ Hz, 1H), 3.06 (d, $J = 14.4$ Hz, 1H), 2.35 (d, $J = 14.4$ Hz, 1H), 2.09 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 202.4, 201.0, 147.6, 142.2, 142.1, 141.8, 136.1, 135.8, 134.0, 132.9, 131.9, 130.9, 129.7, 128.7, 128.0, 127.7, 127.4, 127.1, 126.8, 126.4, 125.9, 125.9, 125.7, 125.5, 125.2, 125.1, 124.4, 123.9, 60.1, 44.1, 43.3, 26.9; HRMS (ESI-TOF) m/z calcd for $\text{C}_{32}\text{H}_{23}\text{O}_2$ [$\text{M} + \text{H}$] $^+$ 439.1693, found 439.1692.



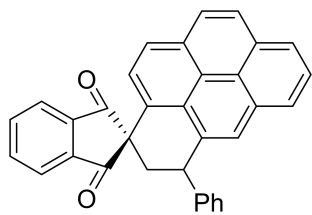
7'-Methoxy-3'-phenyl-2',3'-dihydrospiro[indene-2,1'-phenalene]-1,3-dione (**3x**): Obtained as a pale yellow liquid (73.5 mg, 91% yield), eluting with 5% EtOAc in PE (elution gradient); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.97 - 8.02 (m, 2H), 7.78 - 7.83 (m, 3H), 7.66 (d, $J = 8.0$ Hz, 1H), 7.23 - 7.34 (m, 5H), 7.12 - 7.19 (m, 2H), 6.81 (d, $J = 6.8$ Hz, 1H), 4.69 - 4.72 (m, 1H), 3.46 (s, 3H), 2.62 - 2.69 (t, 1H), 2.21 - 2.25 (q, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 203.4, 202.9, 152.7, 143.2, 140.7, 138.8, 136.7, 135.4, 135.2, 131.6, 130.1, 129.2, 129.0, 128.6, 126.9, 126.6, 125.3, 123.5, 123.4, 122.8, 116.5, 112.9, 56.9, 55.8, 41.6, 37.1; HRMS (ESI-TOF) m/z calcd for $\text{C}_{28}\text{H}_{21}\text{O}_3$ [$\text{M} + \text{H}$] $^+$ 405.1485, found 405.1484.



7'-Bromo-3'-phenyl-2',3'-dihydrospiro[indene-2,1'-phenalene]-1,3-dione (**3y**): Obtained as a pale yellow liquid (48.8 mg, 54% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 8.4$ Hz, 1H), 8.08 - 8.10 (m, 1H), 8.03 - 8.05 (m, 1H), 7.86 - 7.89 (m, 2H), 7.62 (d, $J = 7.6$ Hz, 1H), 7.42 - 7.46 (m, 1H), 7.27 - 7.37 (m, 5H), 7.00 (d, $J = 7.6$ Hz, 1H), 6.73 (d, $J = 8.0$ Hz, 1H), 4.96 - 5.01 (m, 1H), 2.73 - 2.80 (t, 1H), 2.26 - 2.31 (q, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 202.9, 200.0, 143.8, 142.0, 141.0, 138.8, 136.6, 136.3, 135.6, 132.4, 131.4, 131.2, 129.2, 129.0, 128.8, 128.4, 127.2, 127.0, 126.3, 124.7, 123.8, 123.5, 58.8, 41.9, 36.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{27}\text{H}_{18}\text{BrO}_2$ $[\text{M} + \text{H}]^+$ 453.0485, found 453.0488.

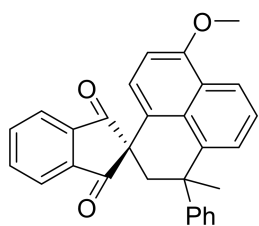


3-Phenyl-2,3-dihydrospiro[benzo[de]anthracene-1,2'-indene]-1',3'-dione (**3z**): Obtained as a pale yellow liquid (73.8 mg, 87% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 8.53 (s, 1H), 8.13 - 8.17 (m, 2H), 7.91 - 8.04 (m, 4H), 7.28 - 7.40 (m, 7H), 7.16 - 7.21 (m, 2H), 6.79 (d, $J = 6.8$ Hz, 1H), 4.70 (d, $J = 13.2$ Hz, 1H), 2.84 - 2.91 (t, 1H), 2.42 - 2.47 (q, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 203.1, 202.0, 142.7, 140.1, 138.8, 138.1, 136.3, 136.2, 131.7, 131.6, 131.0, 129.7, 129.1, 128.8, 128.7, 127.6, 127.2, 126.4, 125.7, 124.7, 124.6, 124.4, 124.2, 124.2, 61.5, 42.0, 40.3; HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{21}\text{O}_2$ $[\text{M} + \text{H}]^+$ 425.1536, found 425.1537.



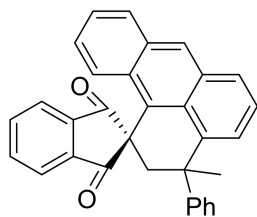
5-Phenyl-4,5-dihydrospiro[benzo[cd]pyrene-3,2'-indene]-1',3'

-dione (**3aa**): Obtained as a pale yellow liquid (78.8 mg, 88% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 8.15 - 8.17 (m, 1H), 8.03 - 8.12 (m, 5H), 7.98 - 8.01 (m, 1H), 7.90 - 7.96 (m, 4H), 7.44 - 7.50 (m, 3H), 7.36 - 7.43 (m, 3H), 5.17 - 5.21 (m, 1H), 2.94 - 3.01 (t, 1H), 2.40 - 2.45 (q, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 203.7, 200.7, 143.6, 142.1, 141.1, 136.8, 136.4, 136.1, 131.1, 131.0, 130.6, 129.4, 128.9, 128.8, 128.6, 128.4, 127.7, 127.2, 127.1, 126.4, 126.1, 125.2, 124.9, 124.8, 124.7, 124.6, 124.4, 123.8, 123.7, 123.6, 59.6, 42.1, 37.1; HRMS (ESI-TOF) m/z calcd for $\text{C}_{33}\text{H}_{21}\text{O}_2$ $[\text{M} + \text{H}]^+$ 449.1536, found 449.1535.



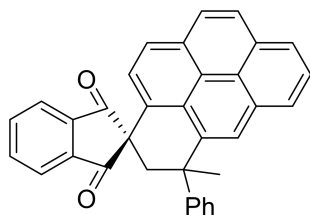
7'-Methoxy-3'-methyl-3'-phenyl-2',3'-dihydrospiro[indene-2,1'-ph

enalene]-1,3-dione(**3ab**): Obtained as a pale yellow liquid (70.2 mg, 84% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 8.02 - 8.03 (m, 1H), 7.89 - 7.91 (m, 2H), 7.79 - 7.86 (m, 2H), 7.73 (d, $J = 8.4$ Hz, 1H), 7.23 - 7.29 (m, 5H), 7.17 - 7.21 (m, 2H), 7.08 (d, $J = 7.2$ Hz, 1H), 3.47 (s, 3H), 2.75 (d, $J = 14.4$ Hz, 1H), 2.25 (d, $J = 14.0$ Hz, 1H), 1.84 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 203.1, 202.6, 152.8, 149.5, 140.9, 140.03, 140.02, 135.2, 135.1, 131.2, 130.4, 129.5, 127.9, 127.7, 126.7, 126.2, 126.0, 123.6, 123.5, 123.1, 116.2, 112.8, 58.4, 55.9, 44.8, 43.4, 29.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{29}\text{H}_{23}\text{O}_3$ $[\text{M} + \text{H}]^+$ 419.1642, found 419.1643.



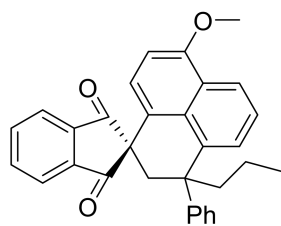
3-Methyl-3-phenyl-2,3-dihydrospiro[benzo[de]anthracene-1,2'-in

dene]-1',3'-dione (**3ac**): Obtained as a pale yellow liquid (70.1 mg, 80% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 8.57 (s, 1H), 8.14 - 8.16 (m, 1H), 7.90 - 8.04 (m, 5H), 7.40 - 7.43 (q, 1H), 7.33 - 7.37 (m, 1H), 7.19 - 7.27 (m, 6H), 7.12 - 7.16 (m, 1H), 6.98 (d, $J = 8.8$ Hz, 1H), 2.98 (d, $J = 14.0$ Hz, 1H), 2.52 (d, $J = 14.0$ Hz, 1H), 1.87 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 201.8, 201.5, 148.8, 141.6, 140.0, 139.9, 136.0, 135.9, 132.0, 131.6, 130.5, 129.7, 129.6, 128.7, 128.0, 127.9, 127.5, 126.5, 125.4, 125.3, 124.7, 124.6, 124.5, 124.2, 124.1, 62.6, 47.4, 43.5, 29.9; HRMS (ESI-TOF) m/z calcd for $\text{C}_{32}\text{H}_{23}\text{O}_2$ [$\text{M} + \text{H}$] $^+$ 439.1693, found 439.1695.



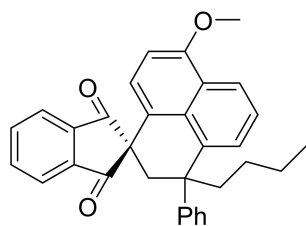
5-Methyl-5-phenyl-4,5-dihydrospiro[benzo[cd]pyrene-3,2'-in

dene]-1',3'-dione (**3ad**): Obtained as a pale yellow liquid (70.2 mg, 76% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 7.95 - 8.17 (m, 8H), 7.87 - 7.93 (m, 2H), 7.78 (s, 1H), 6.42 (d, $J = 7.6$ Hz, 2H), 7.24 - 7.33 (m, 4H), 3.08 (d, $J = 14.4$ Hz, 1H), 2.53 (d, $J = 14.4$ Hz, 1H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 202.0, 201.4, 149.6, 142.2, 142.0, 140.9, 136.0, 135.9, 131.2, 131.1, 130.7, 128.6, 128.4, 128.1, 127.8, 127.6, 127.4, 126.8, 126.4, 126.1, 125.3, 125.3, 125.0, 124.8, 124.4, 124.0, 123.6, 61.1, 44.9, 43.6, 30.6; HRMS (ESI-TOF) m/z calcd for $\text{C}_{34}\text{H}_{23}\text{O}_2$ [$\text{M} + \text{H}$] $^+$ 463.1693, found 463.1695.



7'-Methoxy-3'-phenyl-3'-propyl-2',3'-dihydrospiro[indene-2,1'-p

henalene]-1,3-dione (**3ae**): Obtained as a pale yellow liquid (63.3 mg, 71% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 7.2$ Hz, 1H), 7.79 - 7.92 (m, 4H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.29 - 7.33 (t, 1H), 7.14 - 7.31 (m, 7H), 3.46 (s, 3H), 2.68 (d, $J = 14.0$ Hz, 1H), 2.40 (d, $J = 14.0$ Hz, 1H), 2.24 - 2.32 (m, 1H), 2.07 - 2.14 (m, 1H), 1.28 - 1.38 (m, 1H), 1.06 - 1.17 (m, 1H), 0.85 - 0.89 (t, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 202.8, 152.8, 147.7, 140.1, 140.0, 137.6, 135.1, 131.8, 130.4, 129.8, 128.0, 127.9, 127.0, 126.9, 126.1, 123.6, 123.1, 122.9, 116.3, 112.8, 58.5, 56.0, 47.2, 42.8, 41.8, 18.5, 14.3; HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{27}\text{O}_3$ $[\text{M} + \text{H}]^+$ 447.1955, found 447.1954.

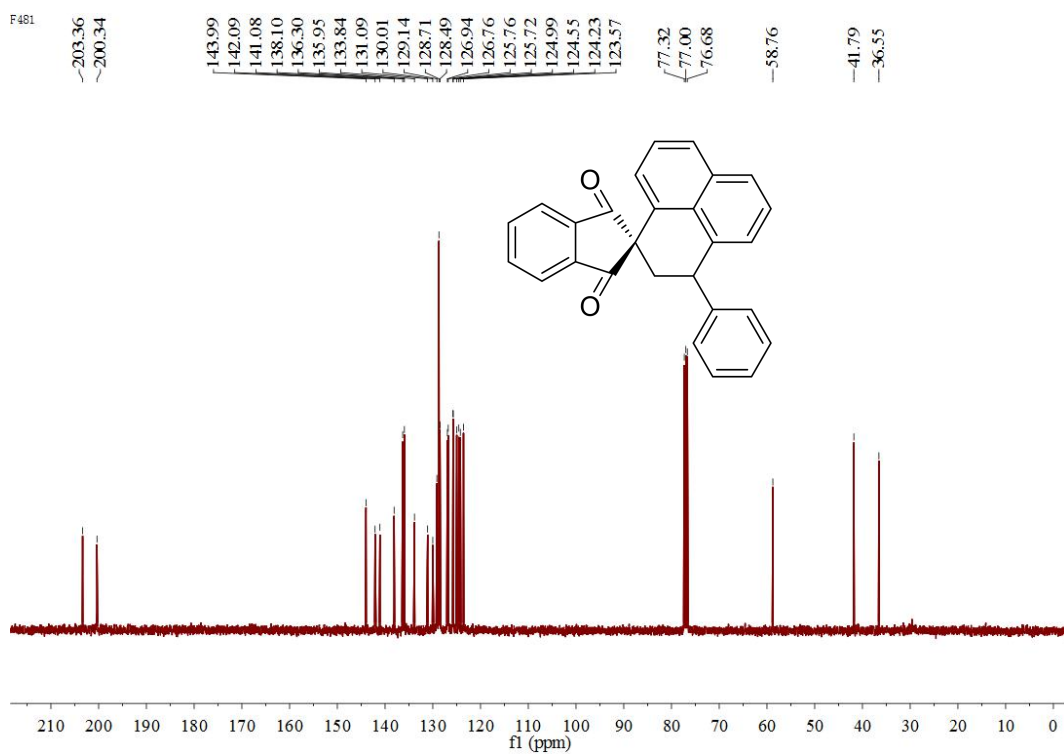
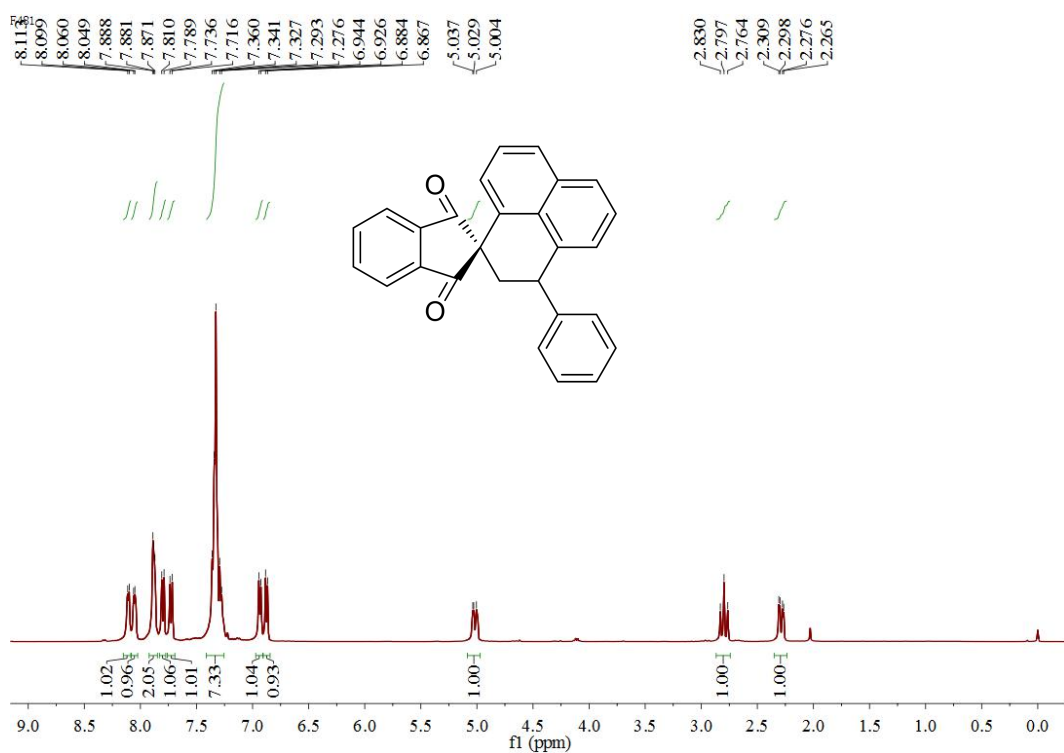


3'-Butyl-7'-methoxy-3'-phenyl-2',3'-dihydrospiro[indene-2,1'-p

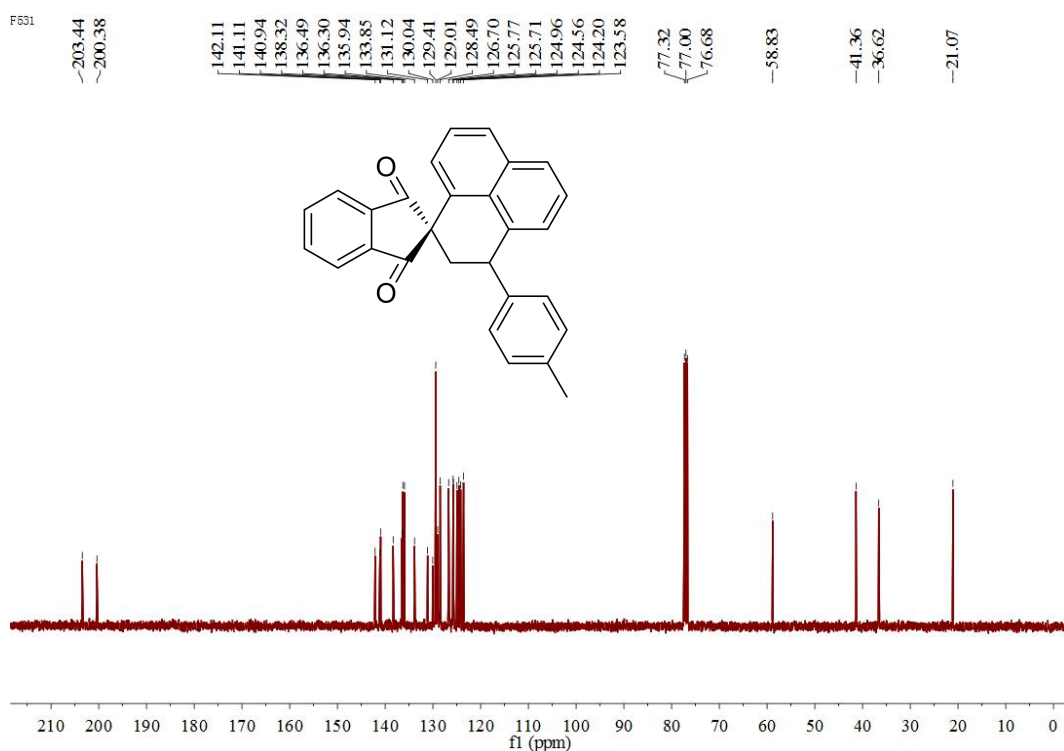
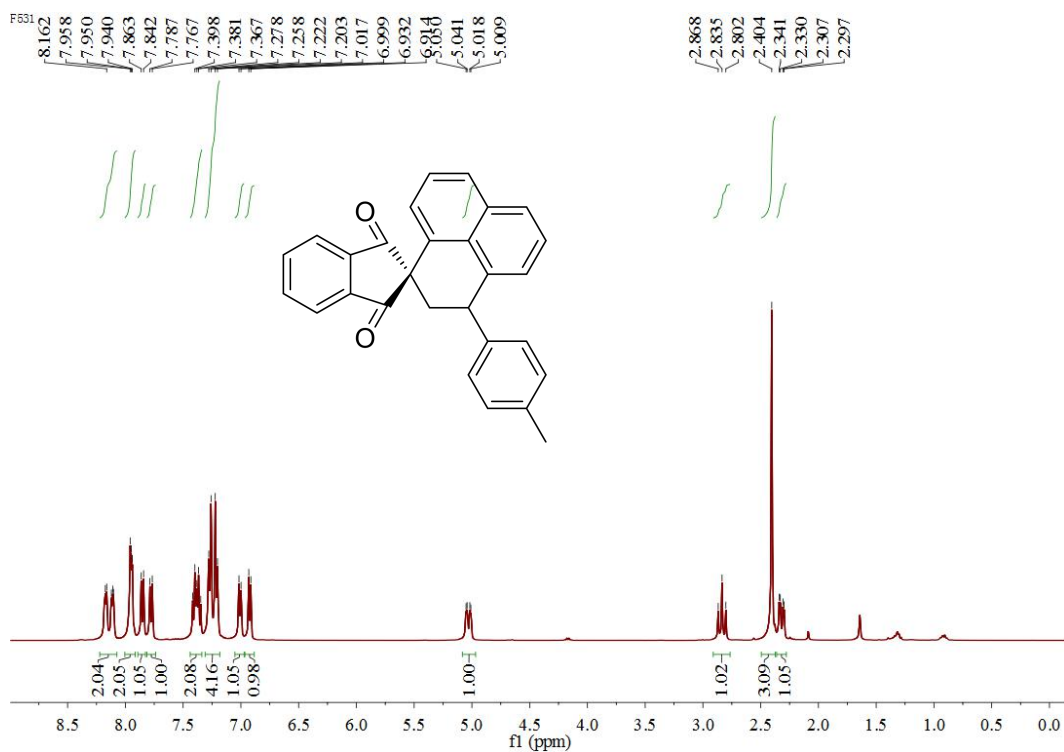
henalene]-1,3-dione (**3af**): Obtained as a pale yellow liquid (57.0 mg, 62% yield), eluting with 5% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 6.8$ Hz, 1H), 7.75 - 7.91 (m, 5H), 7.31 - 7.34 (t, 1H), 7.17 - 7.26 (m, 7H), 6.74 (d, $J = 7.2$ Hz, 1H), 3.46 (s, 3H), 2.67 (d, $J = 14.4$ Hz, 1H), 2.43 (d, $J = 14.4$ Hz, 1H), 2.25 - 2.32 (m, 1H), 2.10 - 2.17 (m, 1H), 1.21 - 1.34 (m, 4H), 0.81 - 0.84 (t, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 202.8, 202.6, 152.8, 147.8, 140.1, 140.0, 137.4, 135.1, 131.8, 130.4, 129.7, 128.0, 127.9, 127.0, 126.9, 126.1, 123.6, 123.2, 122.9, 116.3, 112.8, 58.5, 56.0, 47.1, 42.7, 39.6, 27.4, 23.1, 14.1; HRMS (ESI-TOF) m/z calcd for $\text{C}_{32}\text{H}_{29}\text{O}_3$ $[\text{M} + \text{H}]^+$ 461.2111, found 461.2108.

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

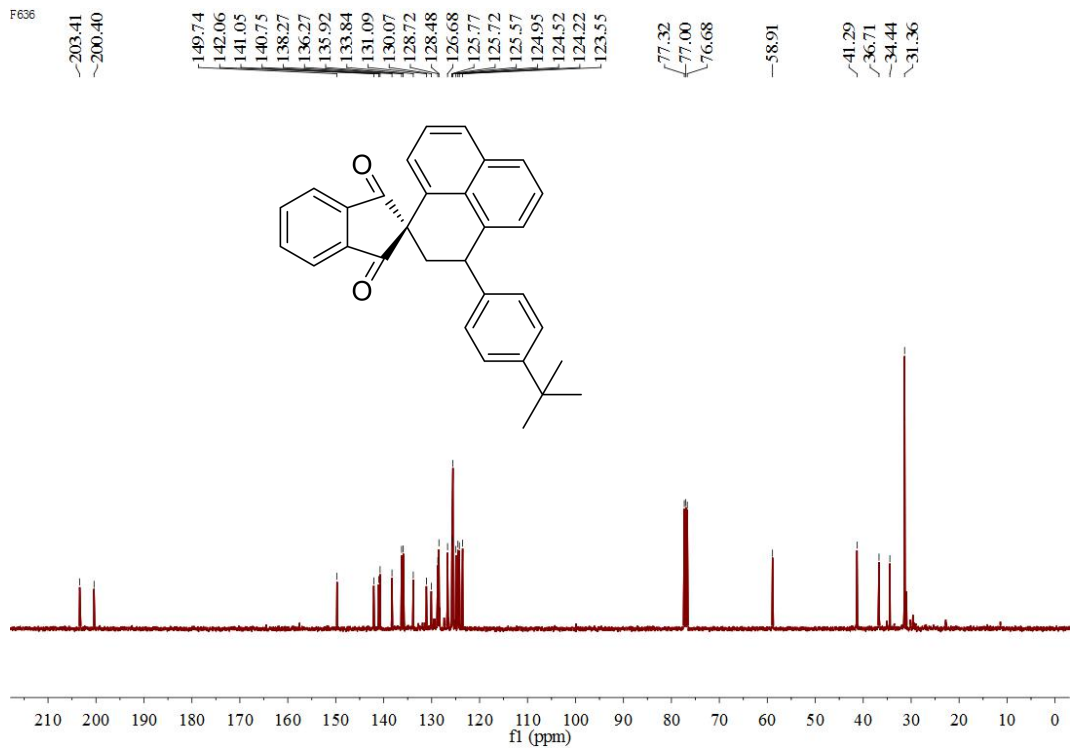
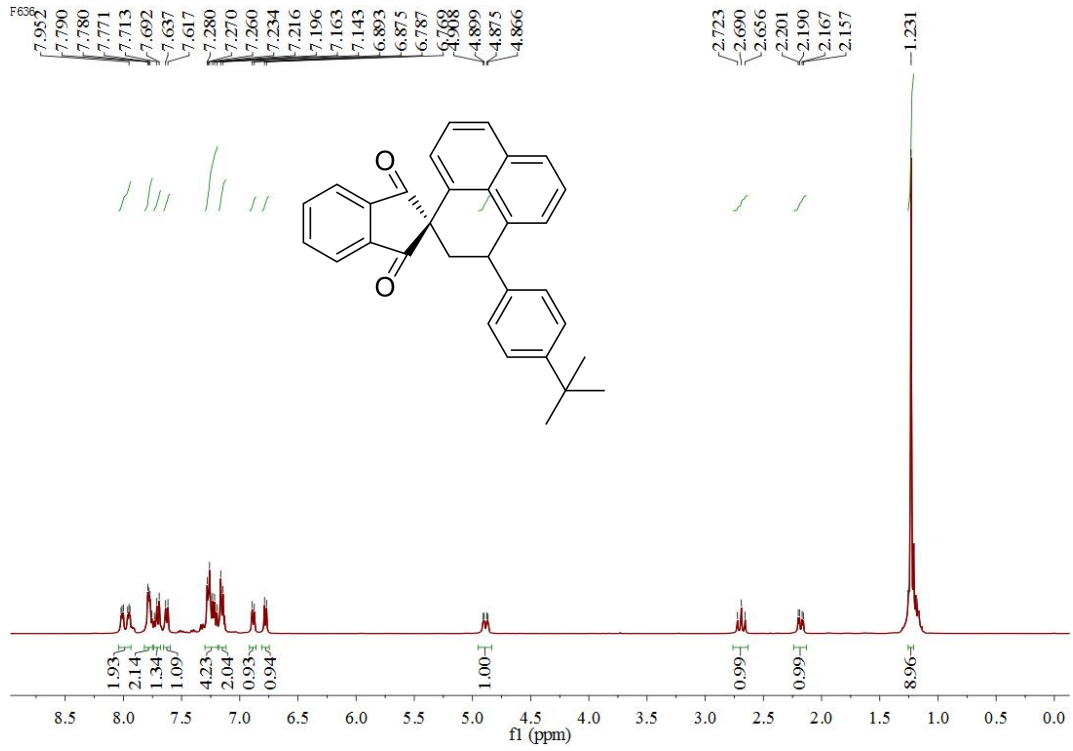
^1H NMR and ^{13}C NMR of 3a



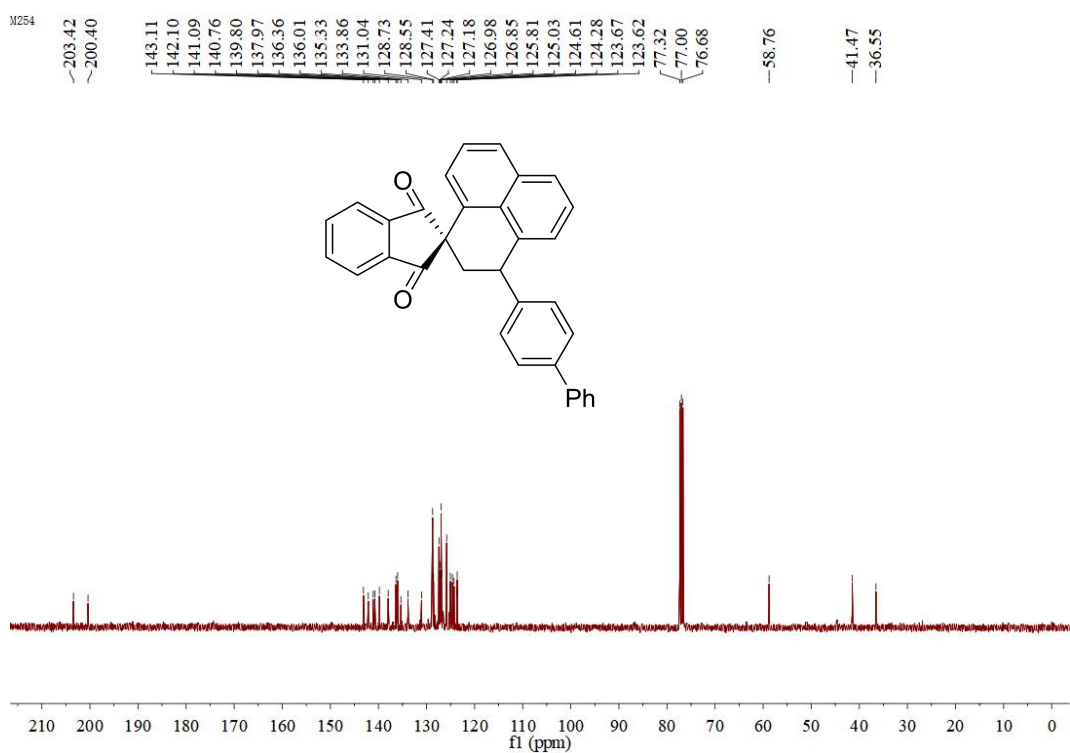
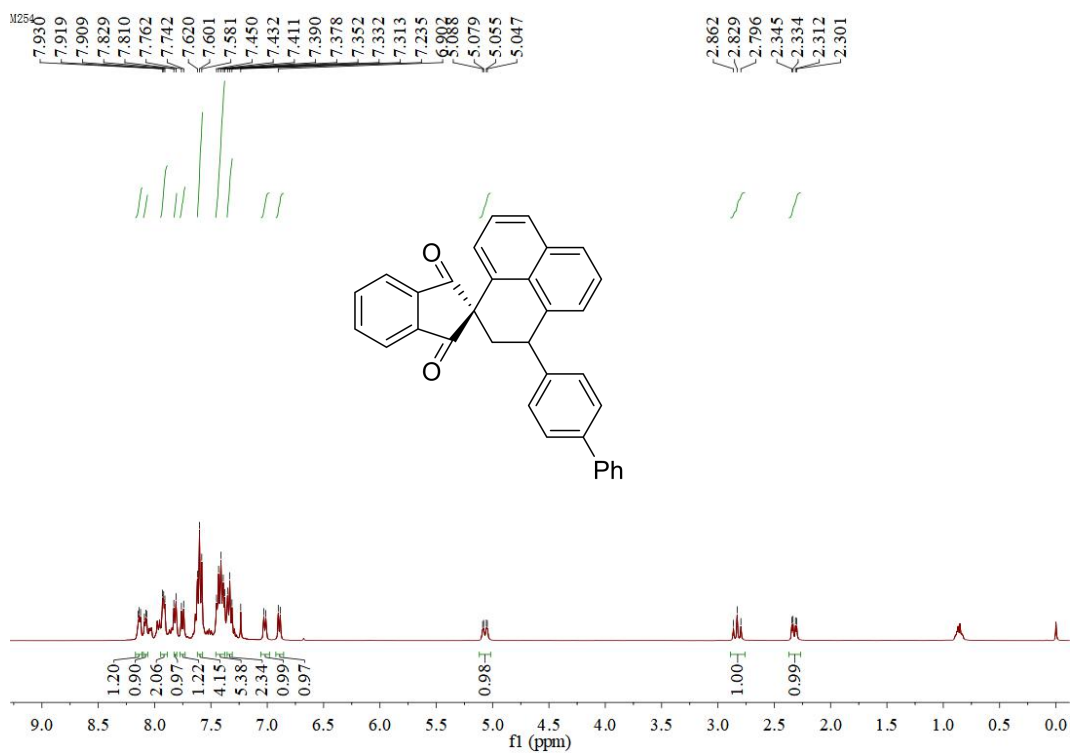
¹H NMR and ¹³C NMR of 3b



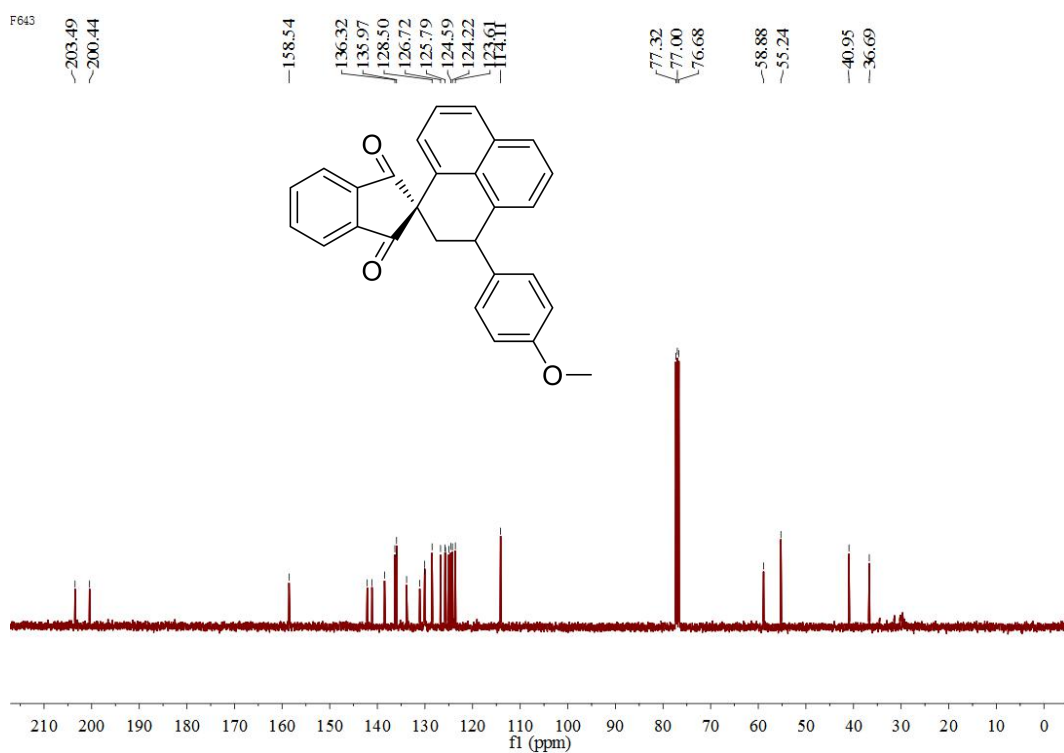
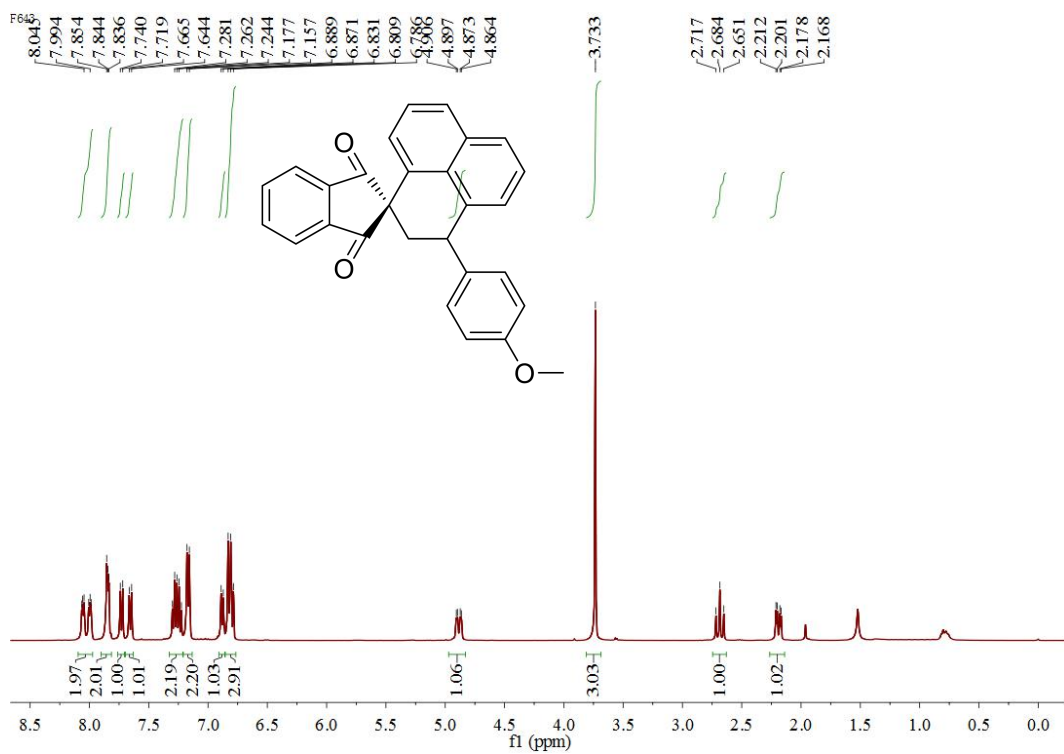
¹H NMR and ¹³C NMR of 3c



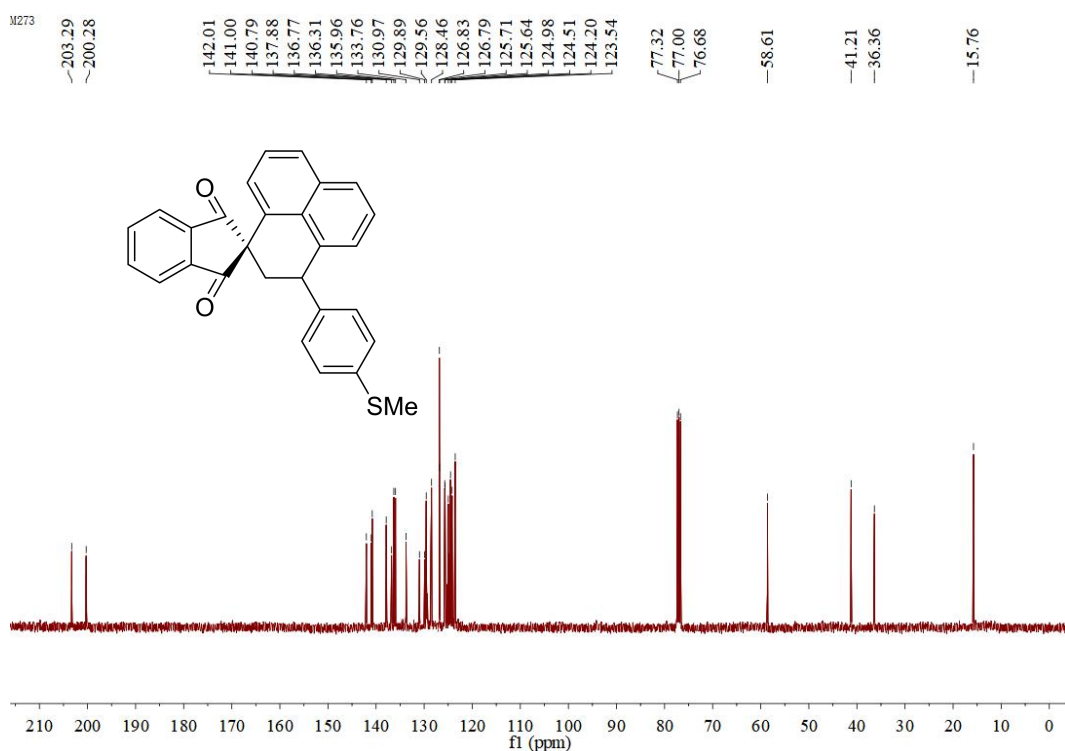
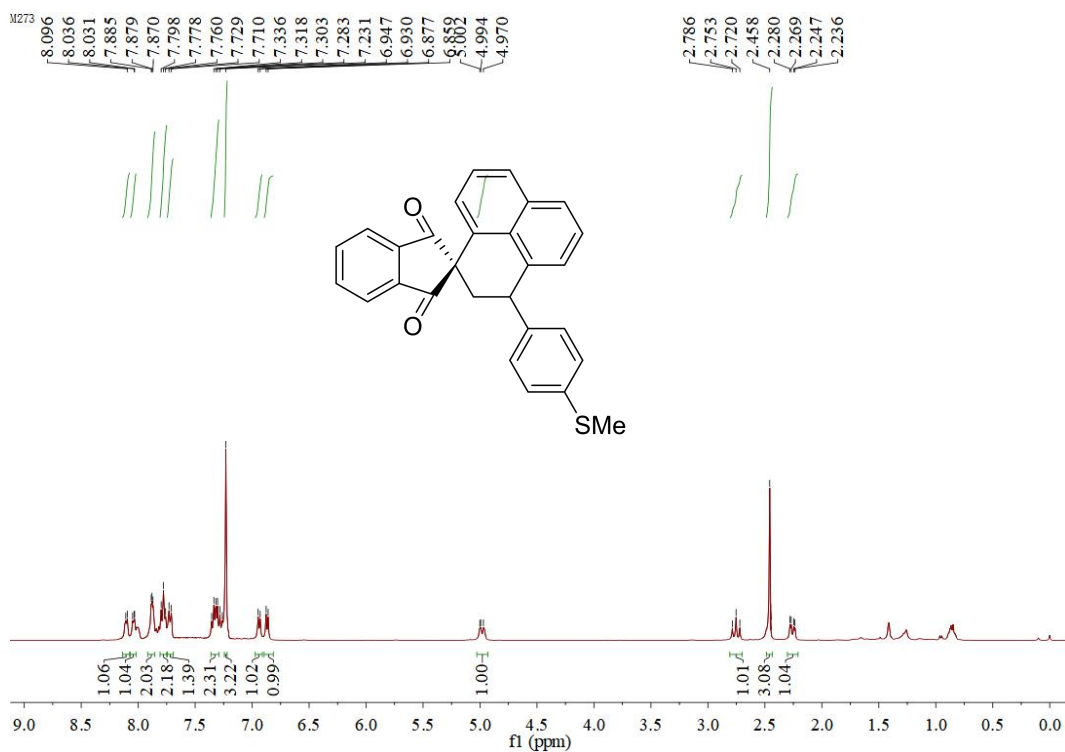
¹H NMR and ¹³C NMR of 3d



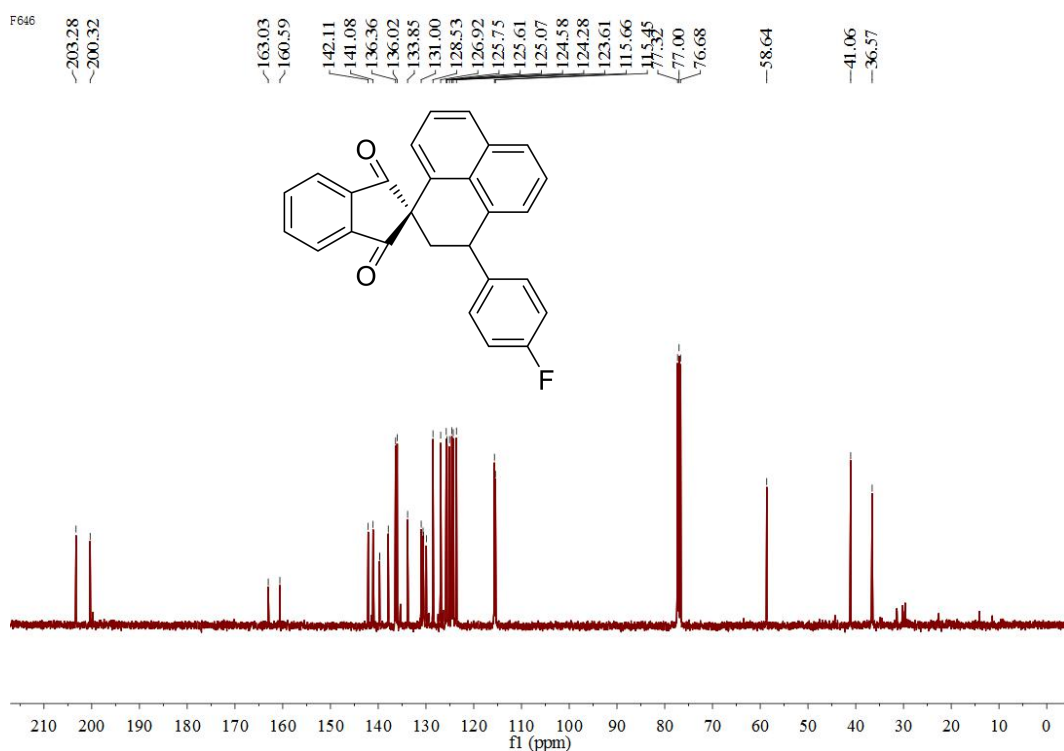
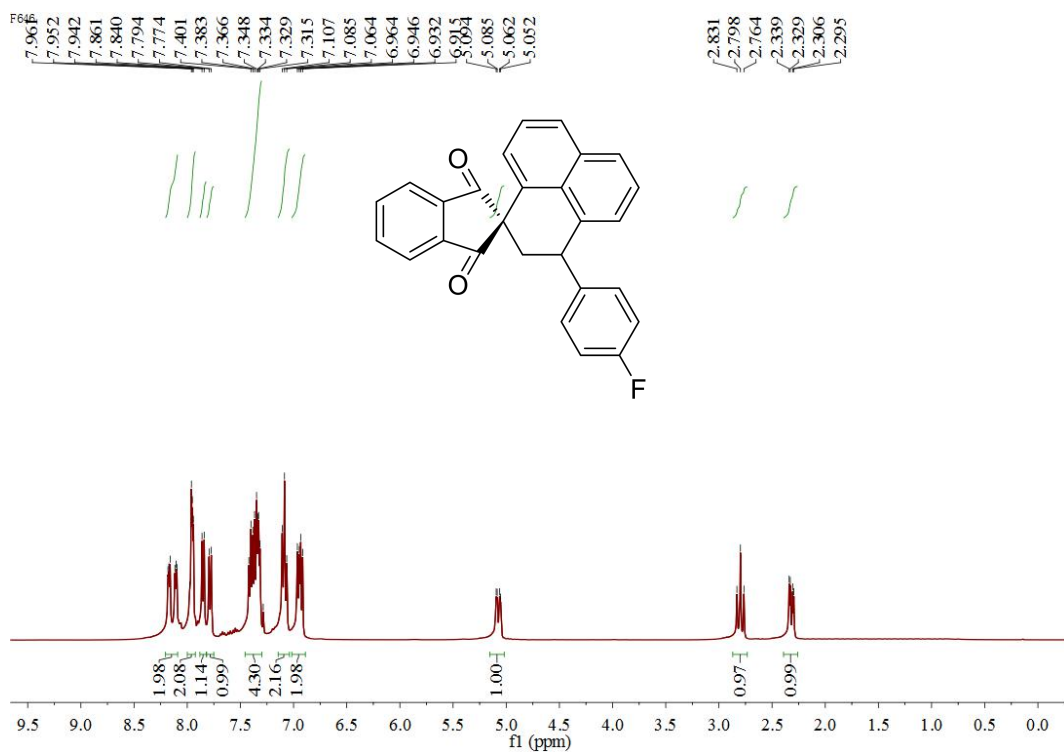
¹H NMR and ¹³C NMR of 3e



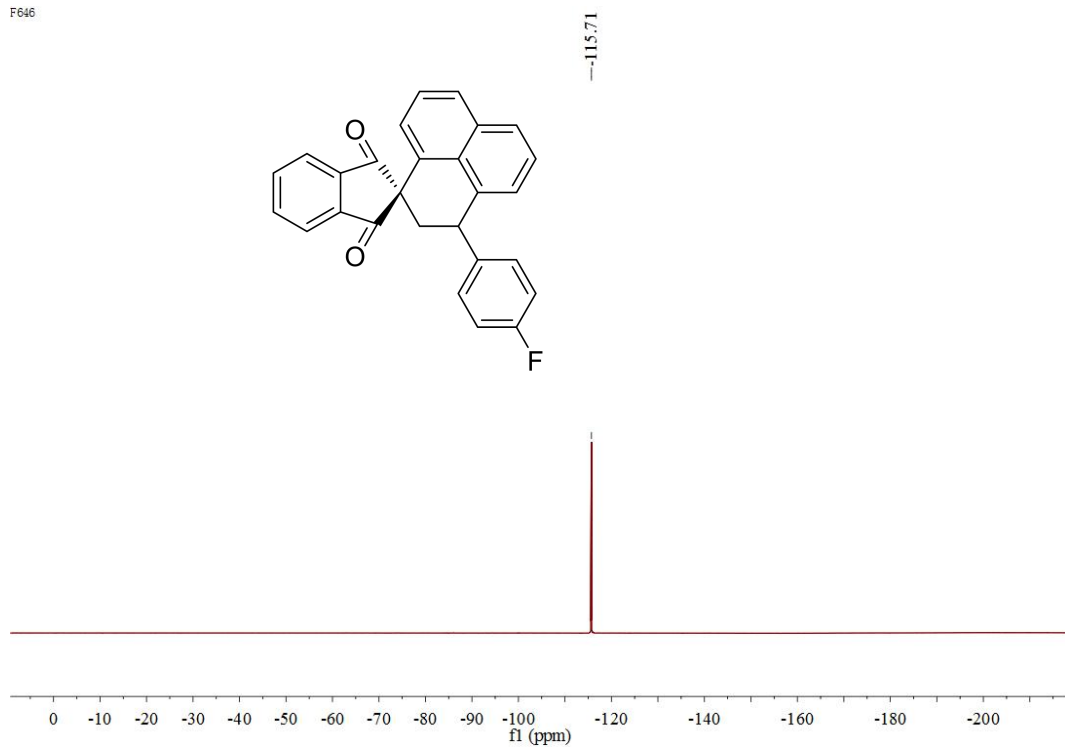
¹H NMR and ¹³C NMR of 3f



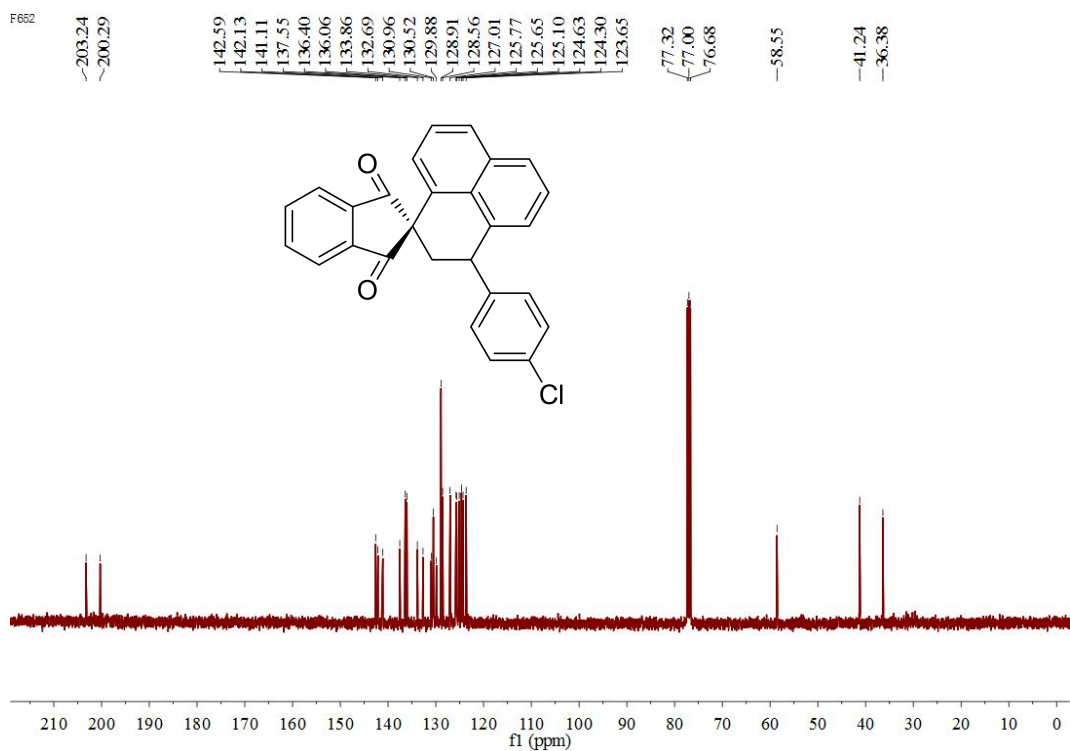
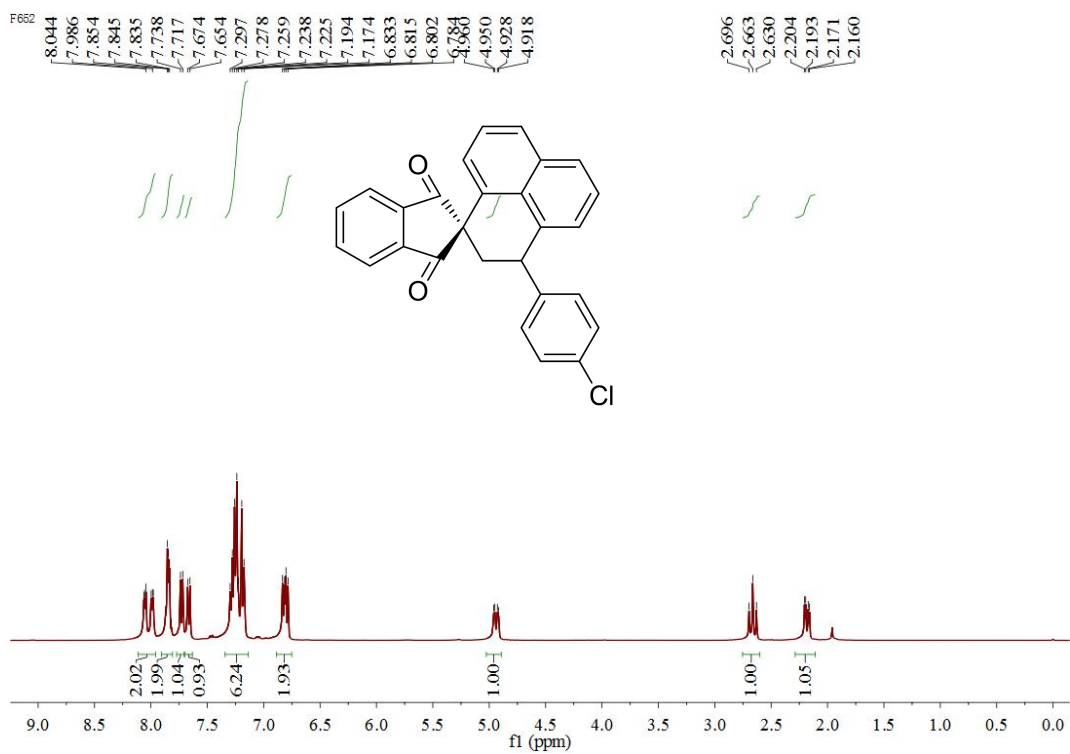
¹H NMR, ¹³C NMR and ¹⁹F NMR of 3g



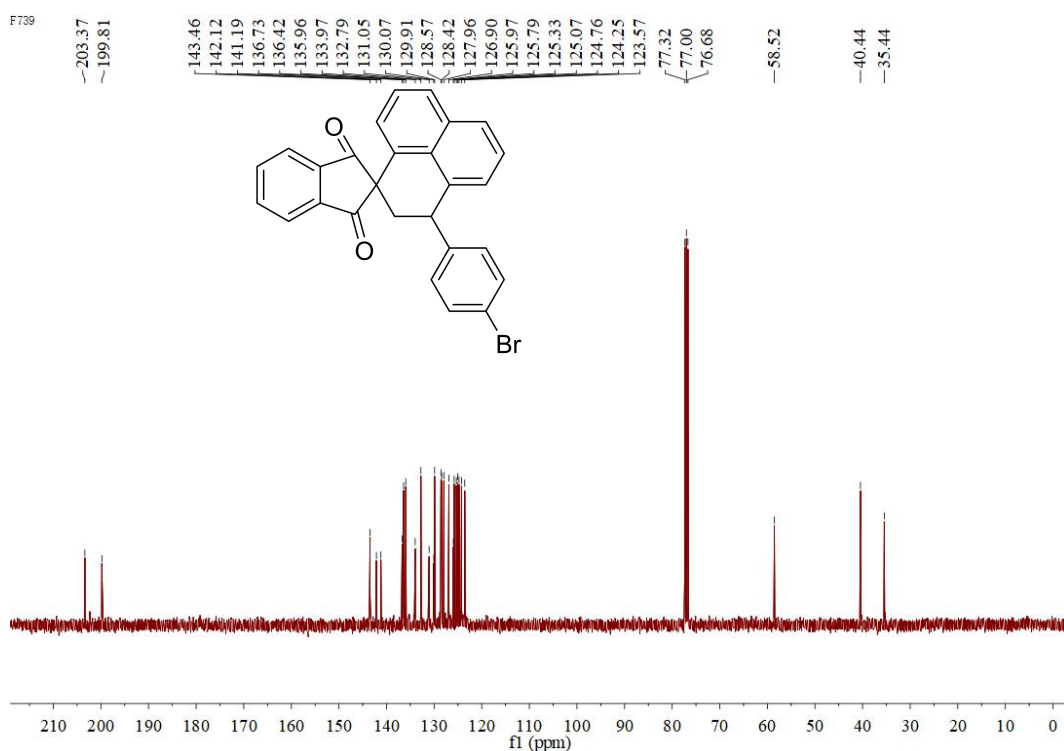
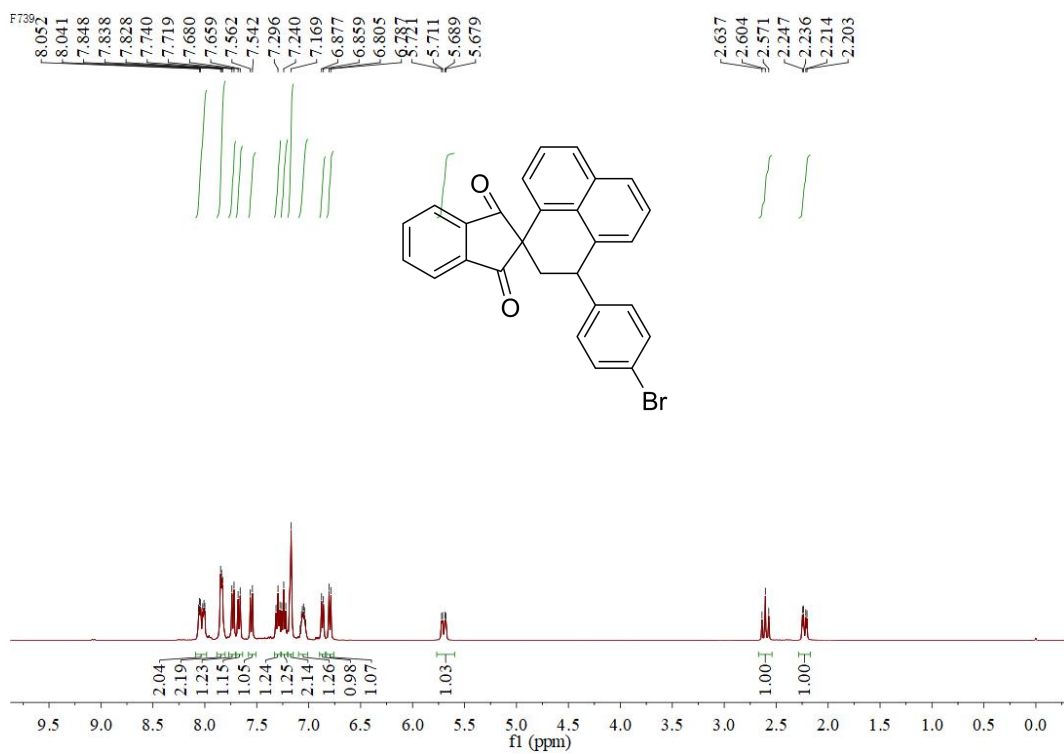
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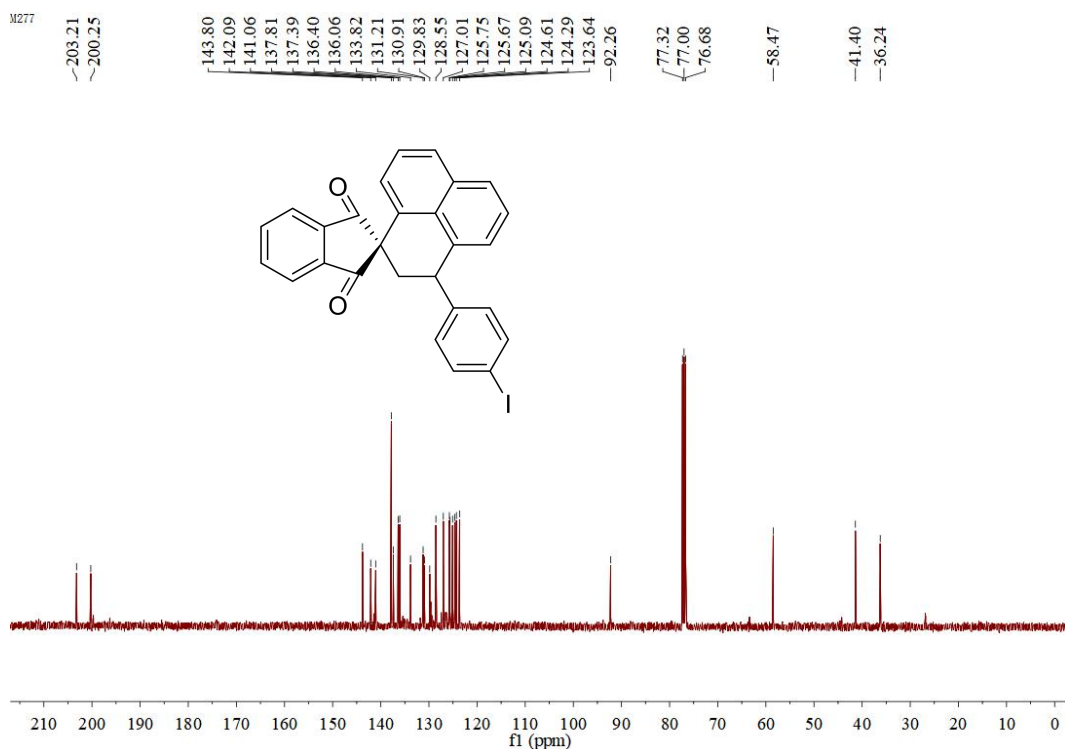
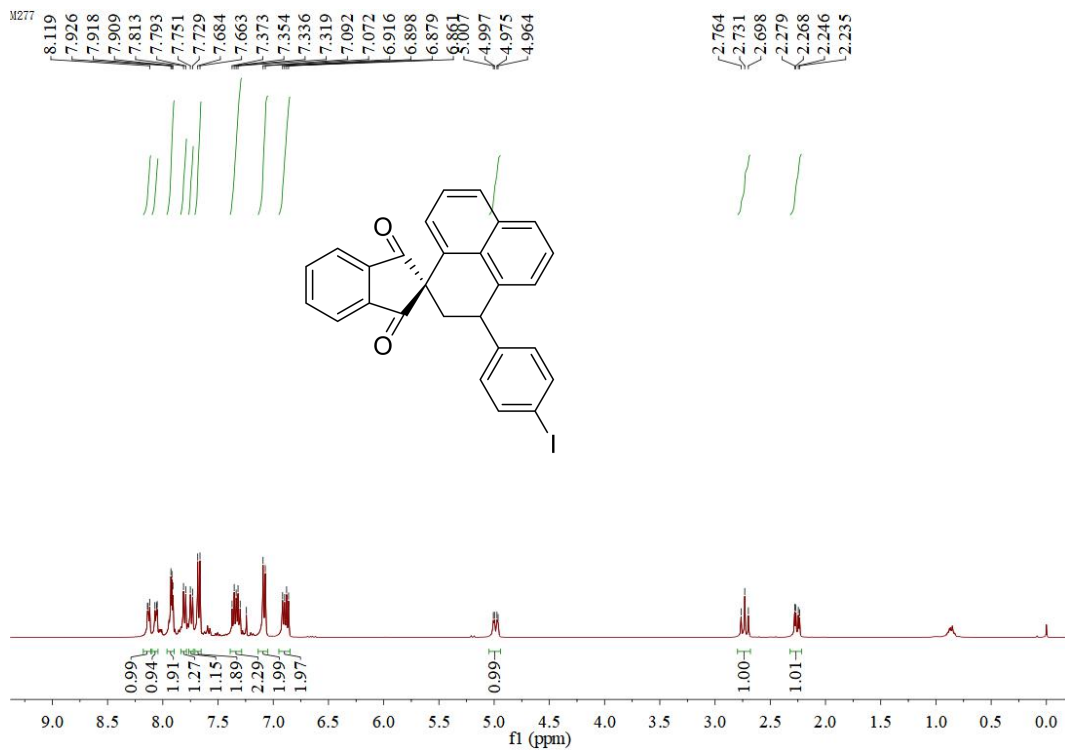
¹H NMR and ¹³C NMR of 3h



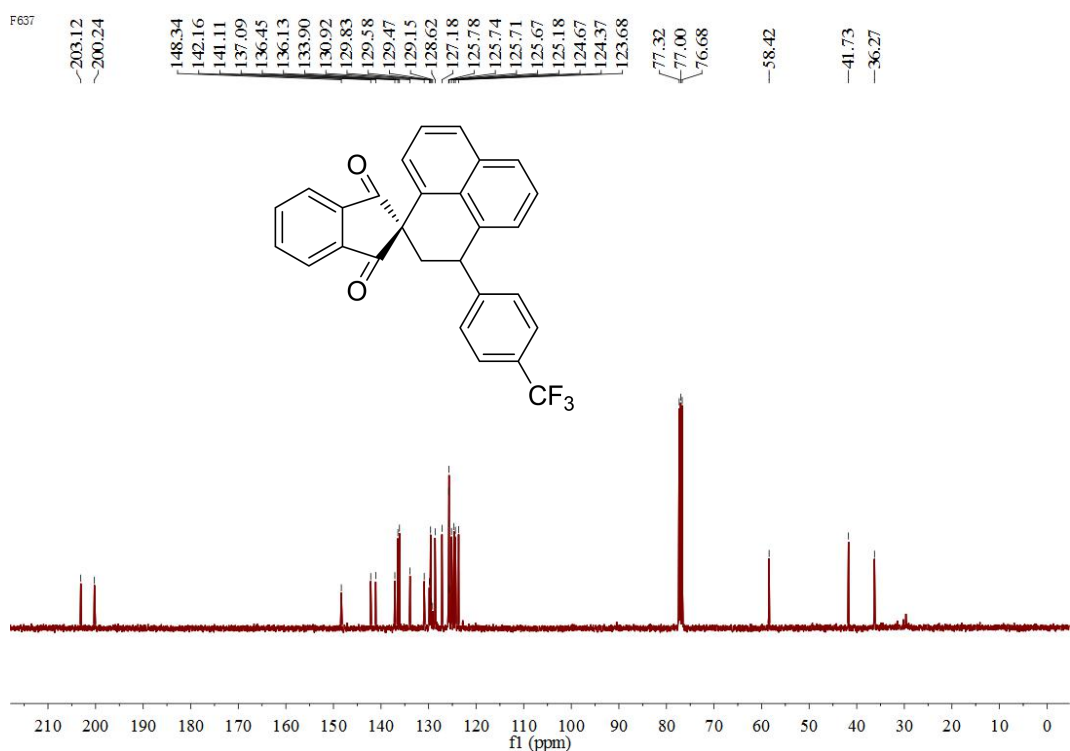
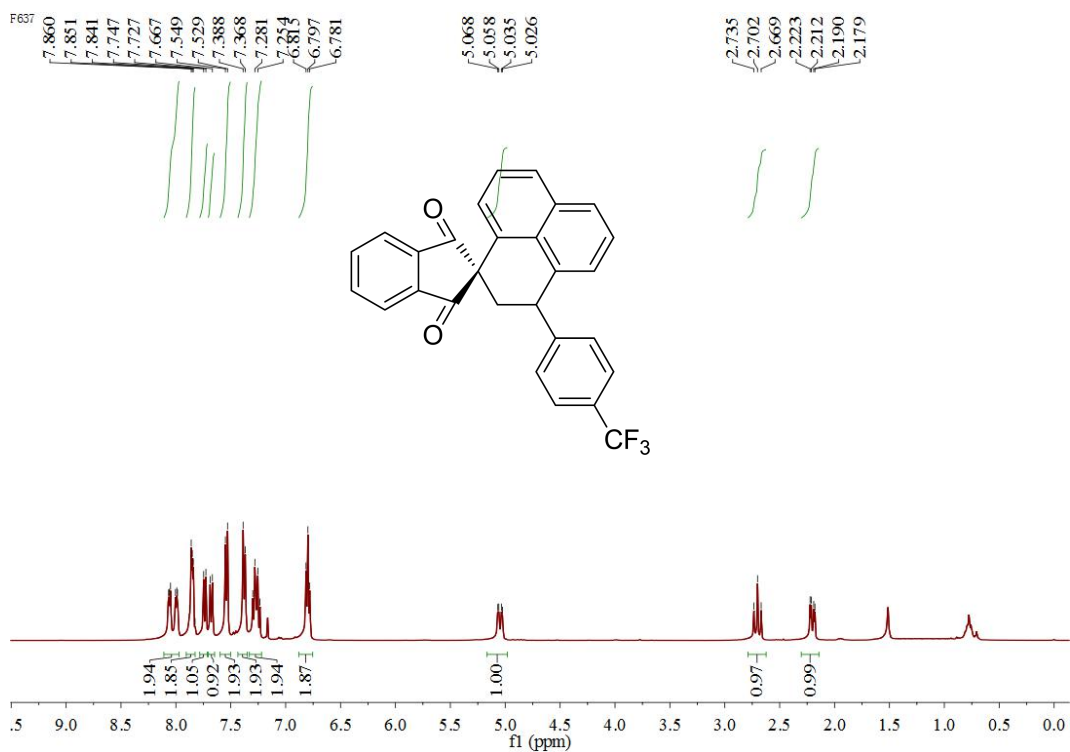
¹H NMR and ¹³C NMR of 3i



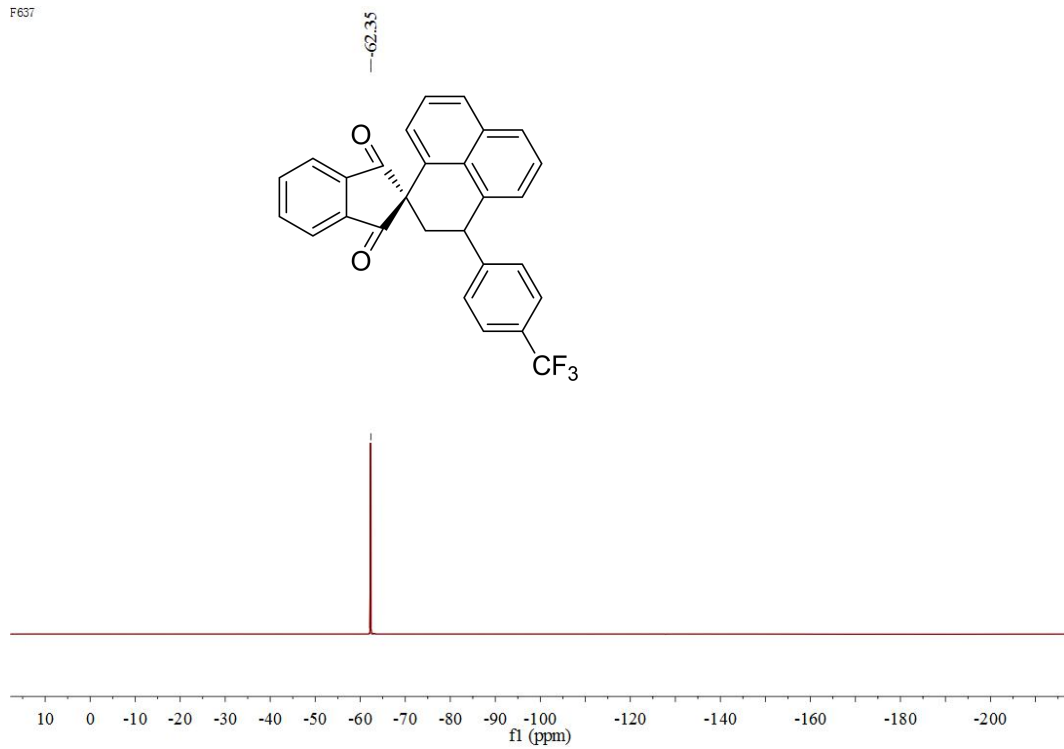
¹H NMR and ¹³C NMR of 3j



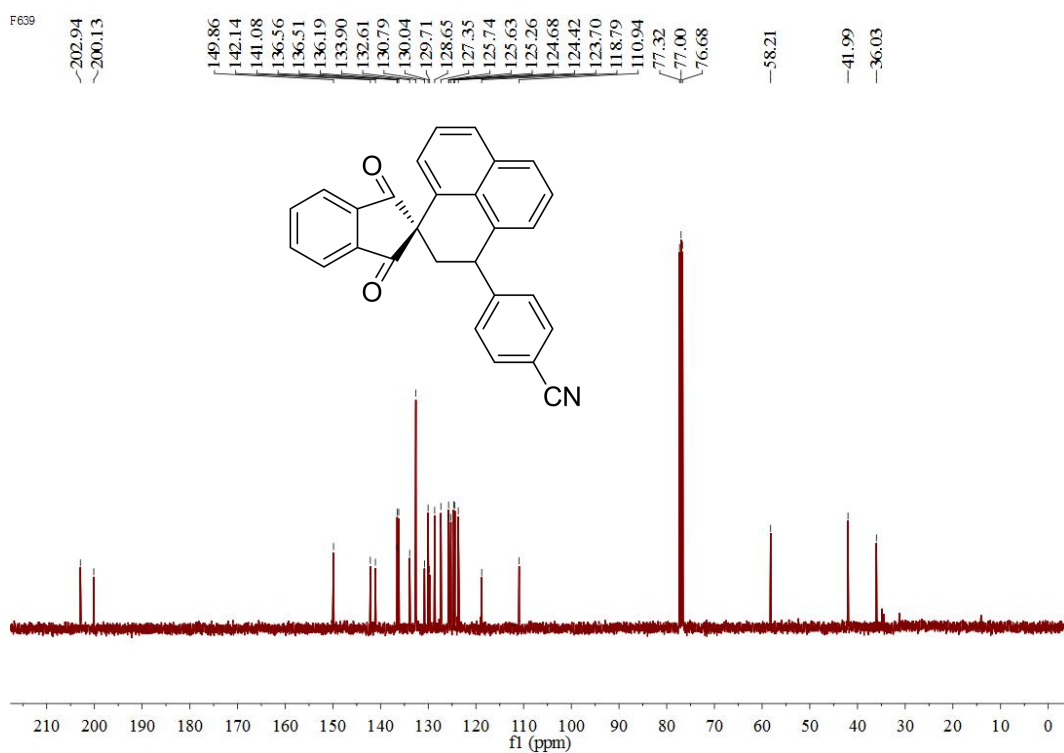
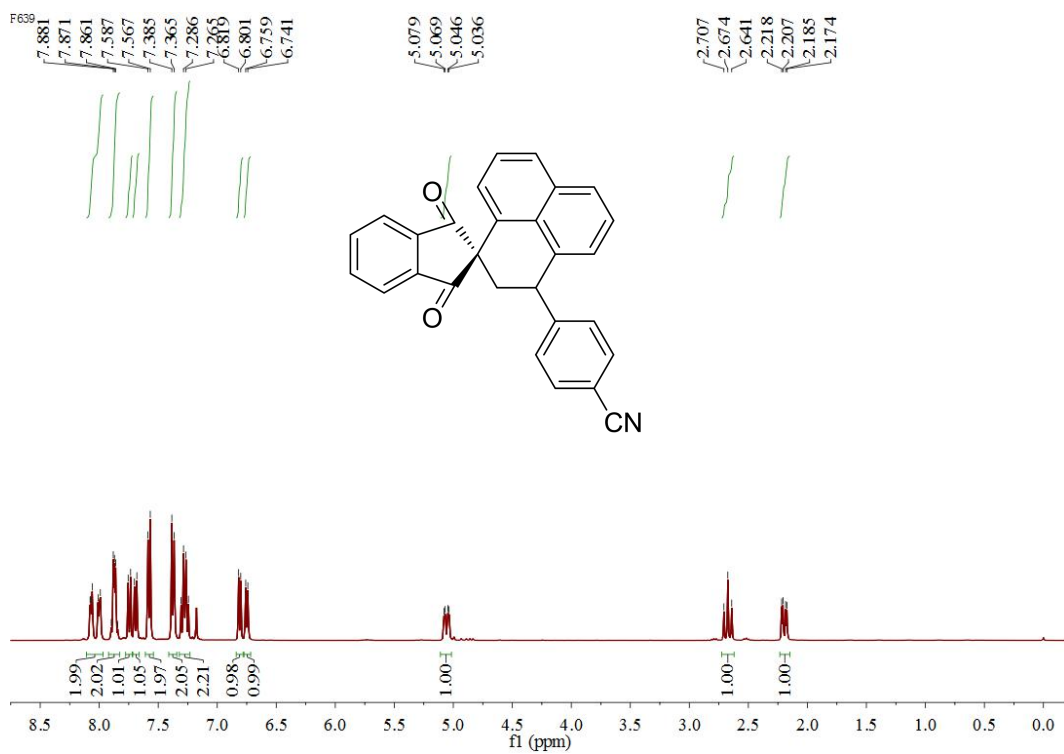
¹H NMR, ¹³C NMR and ¹⁹F NMR of 3k



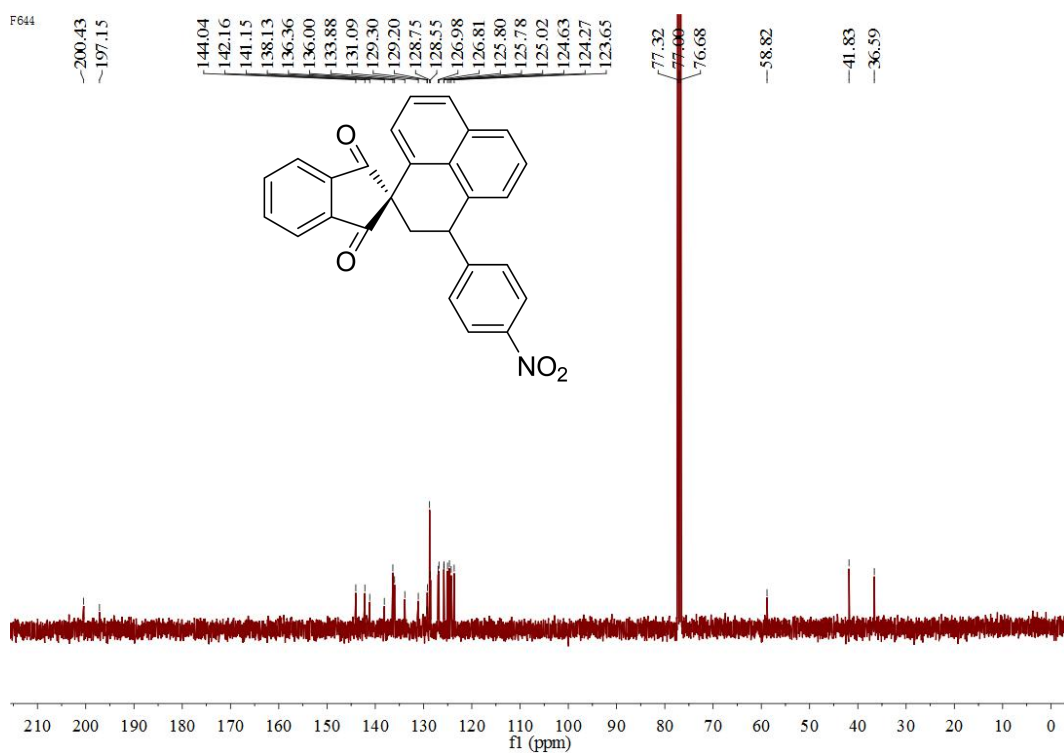
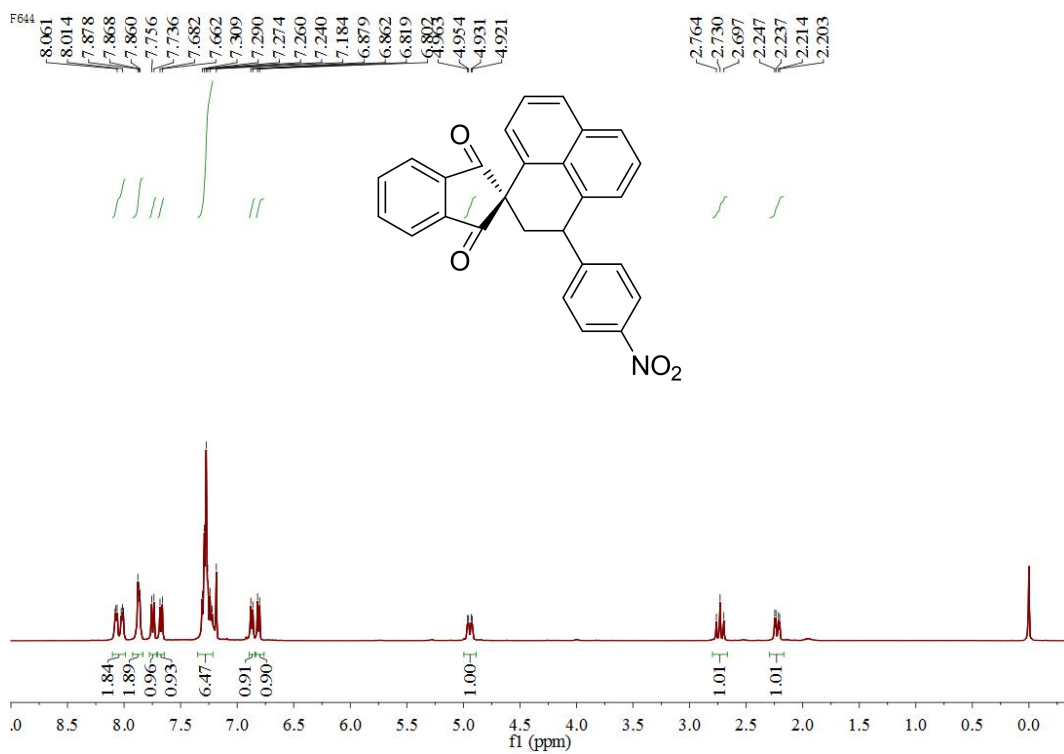
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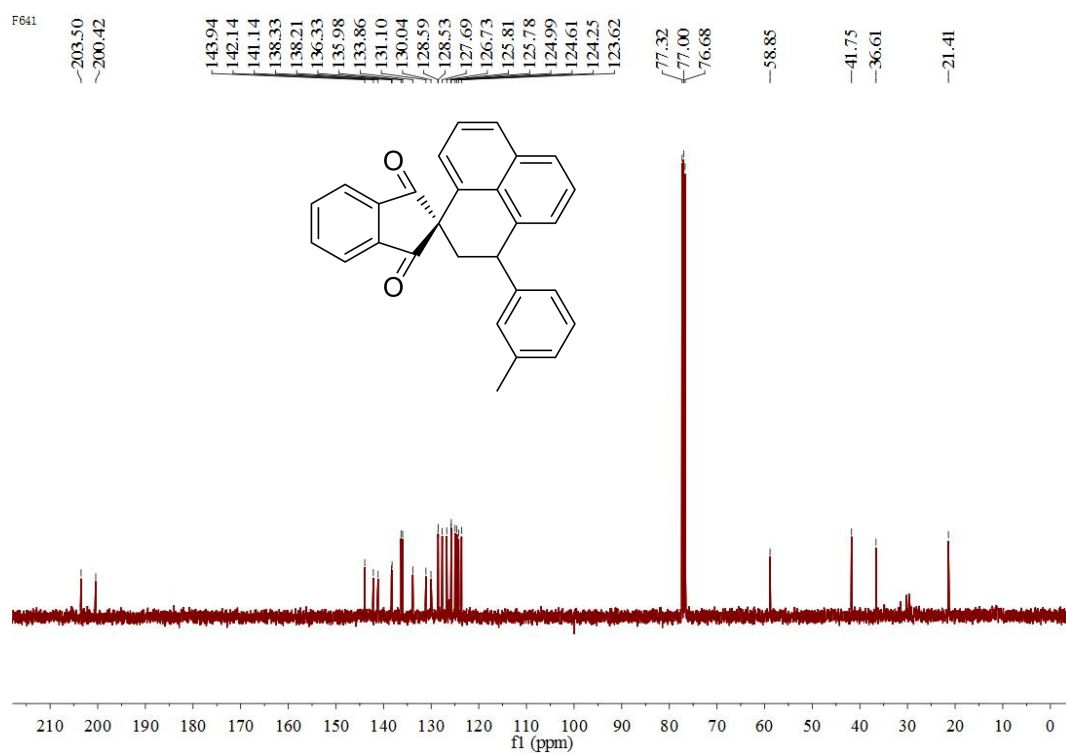
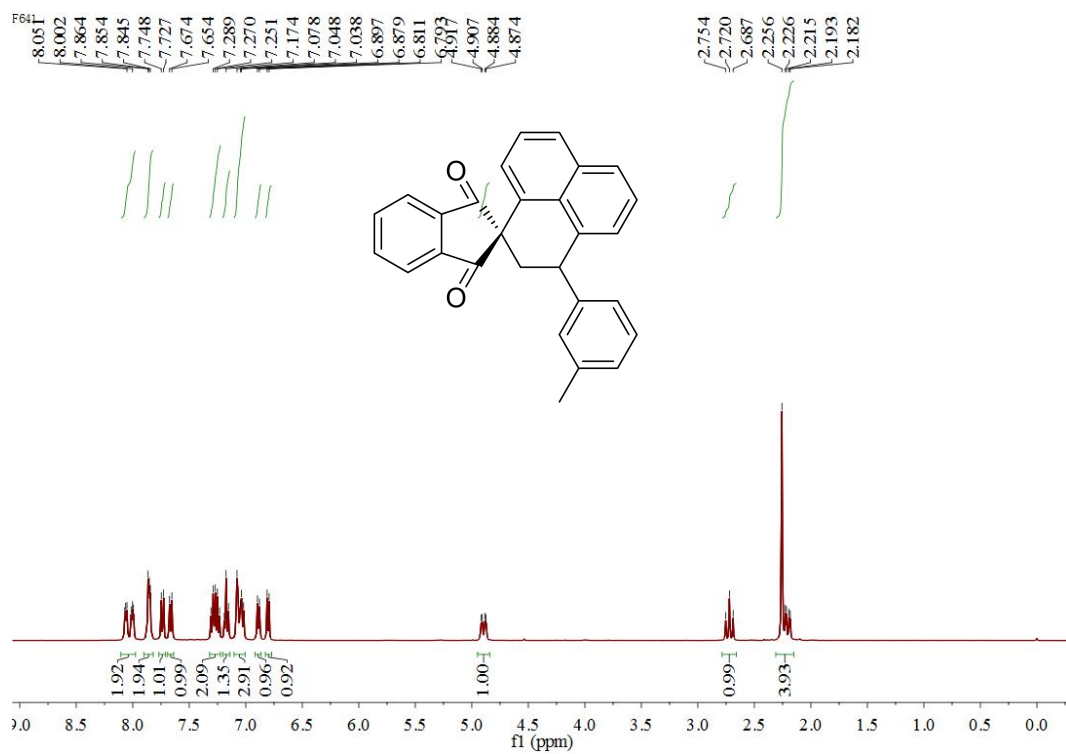
¹H NMR and ¹³C NMR of 3l



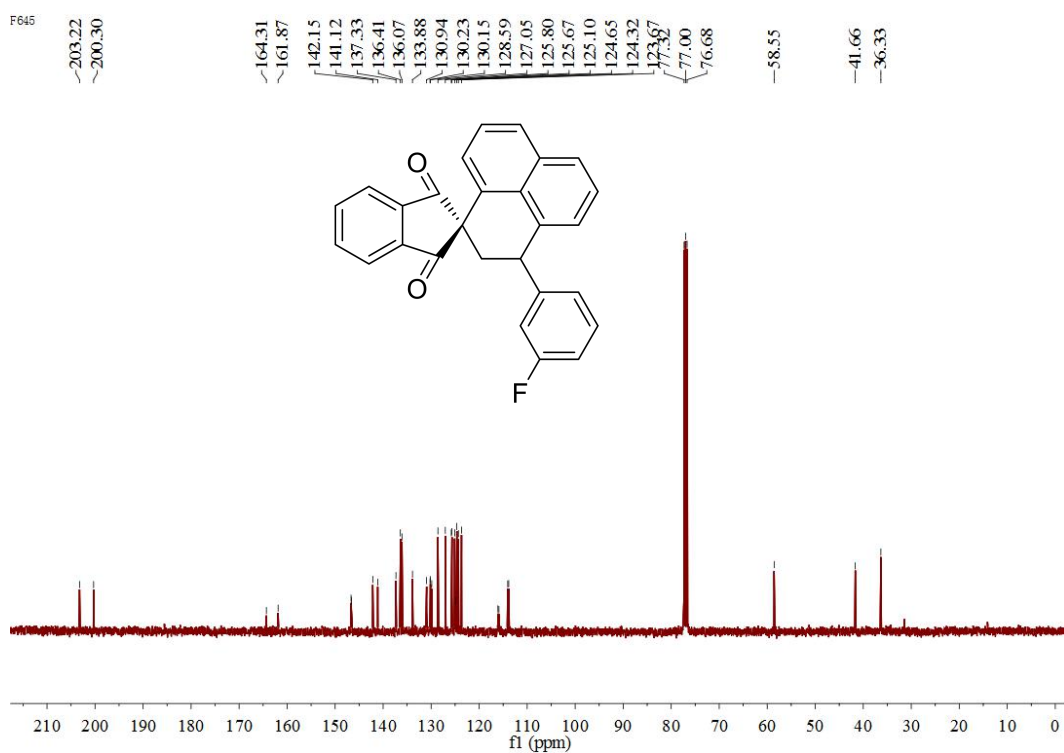
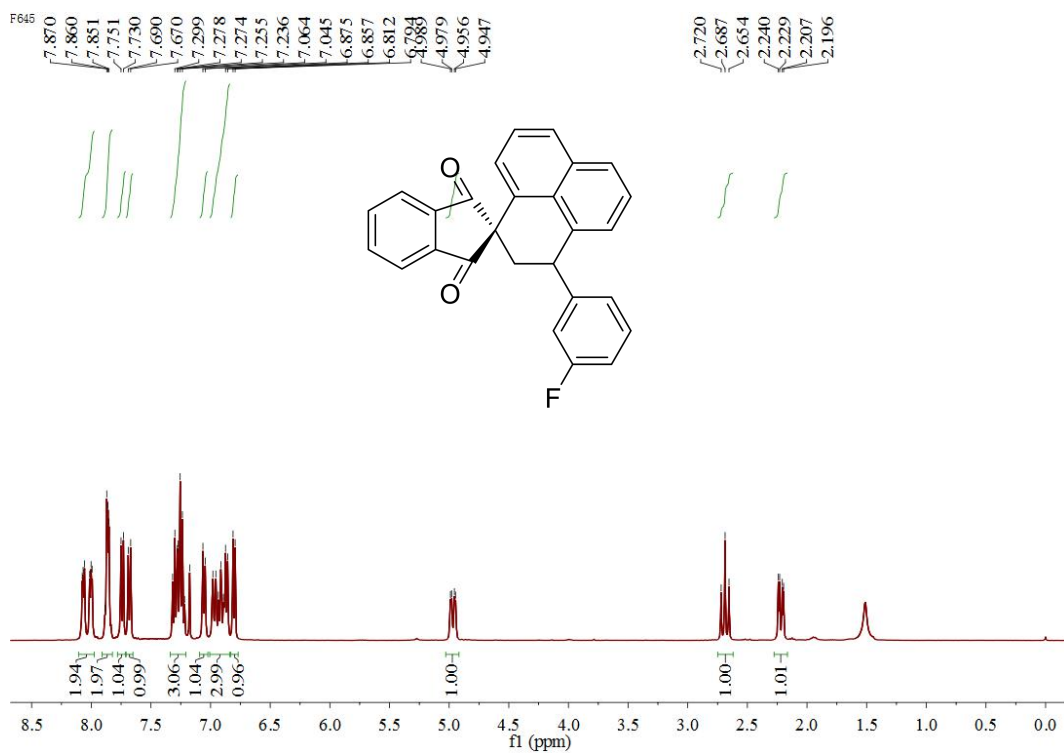
¹H NMR and ¹³C NMR of 3m



¹H NMR and ¹³C NMR of 3n

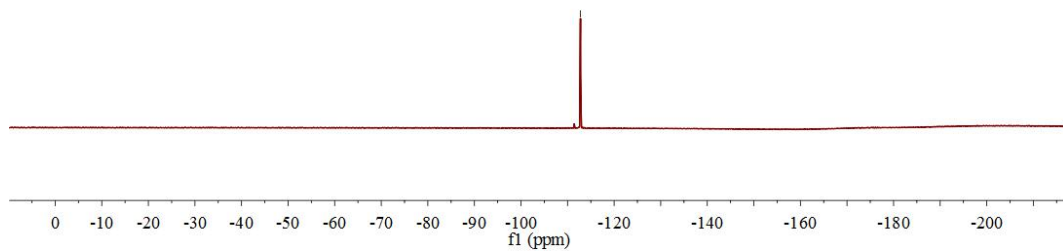
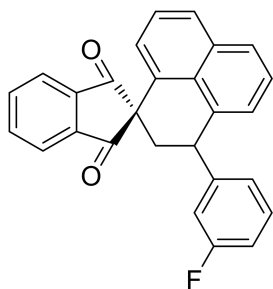


¹H NMR, ¹³C NMR and ¹⁹F NMR of 3o

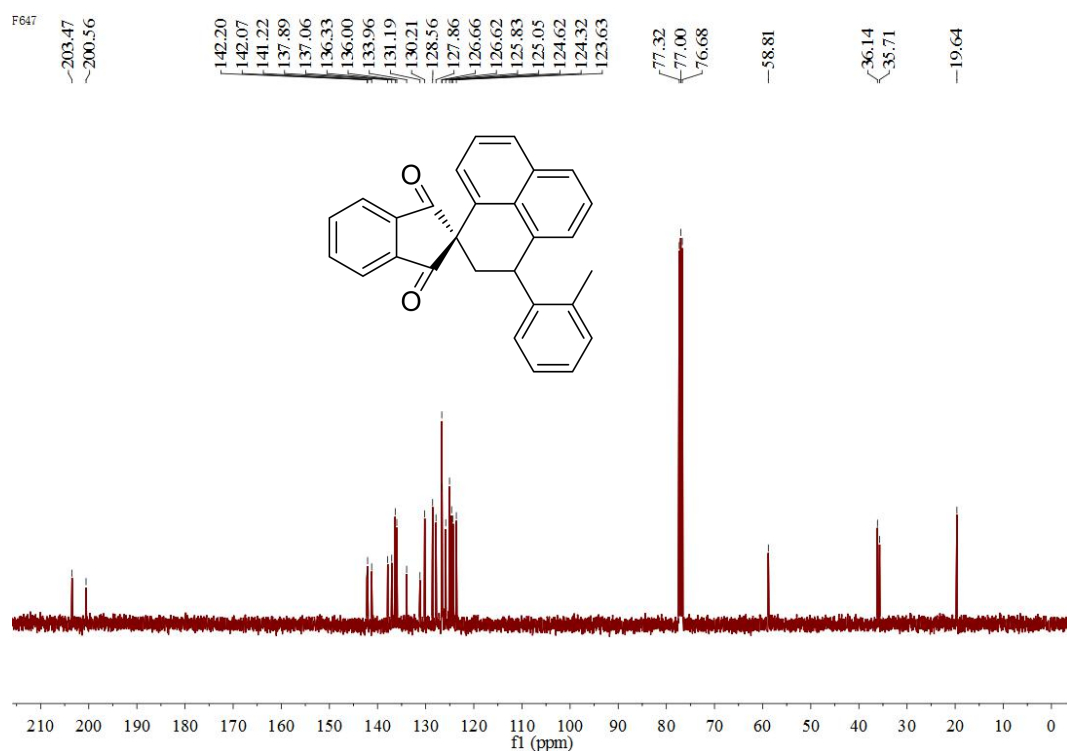
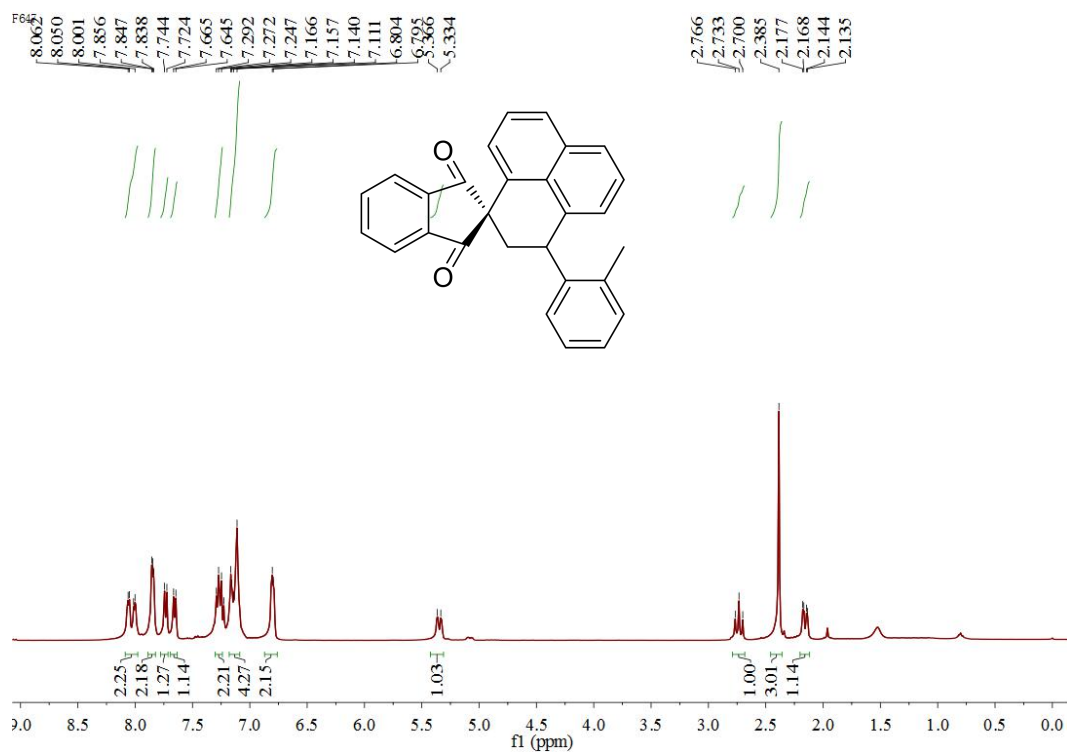


F645

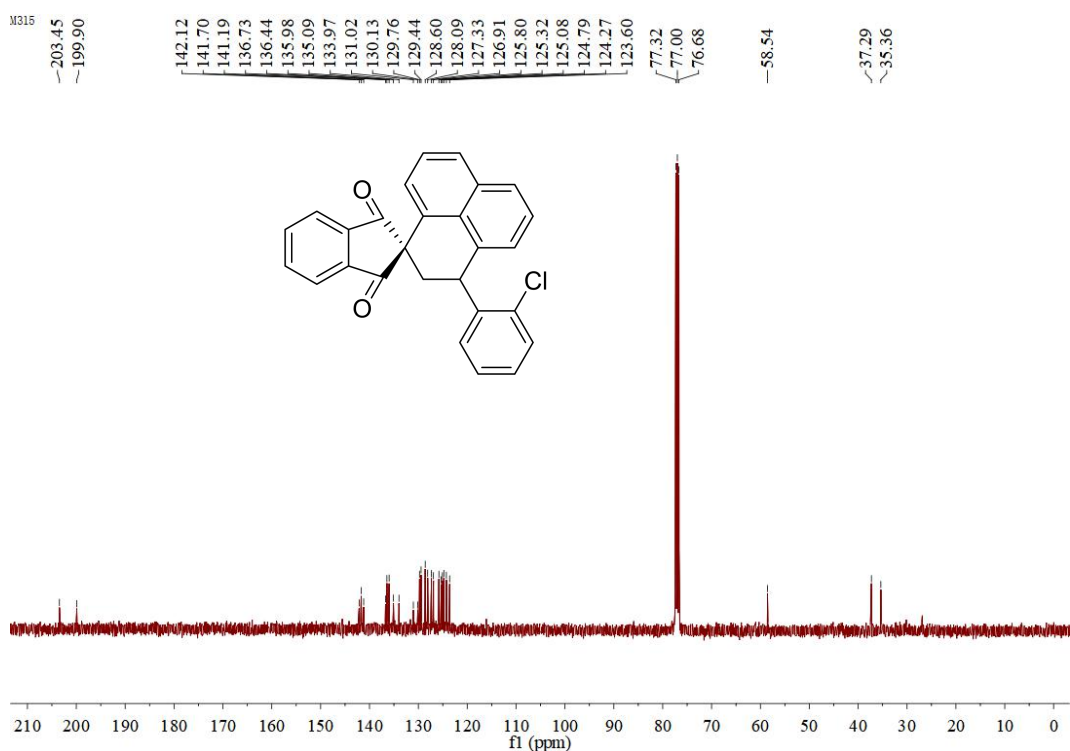
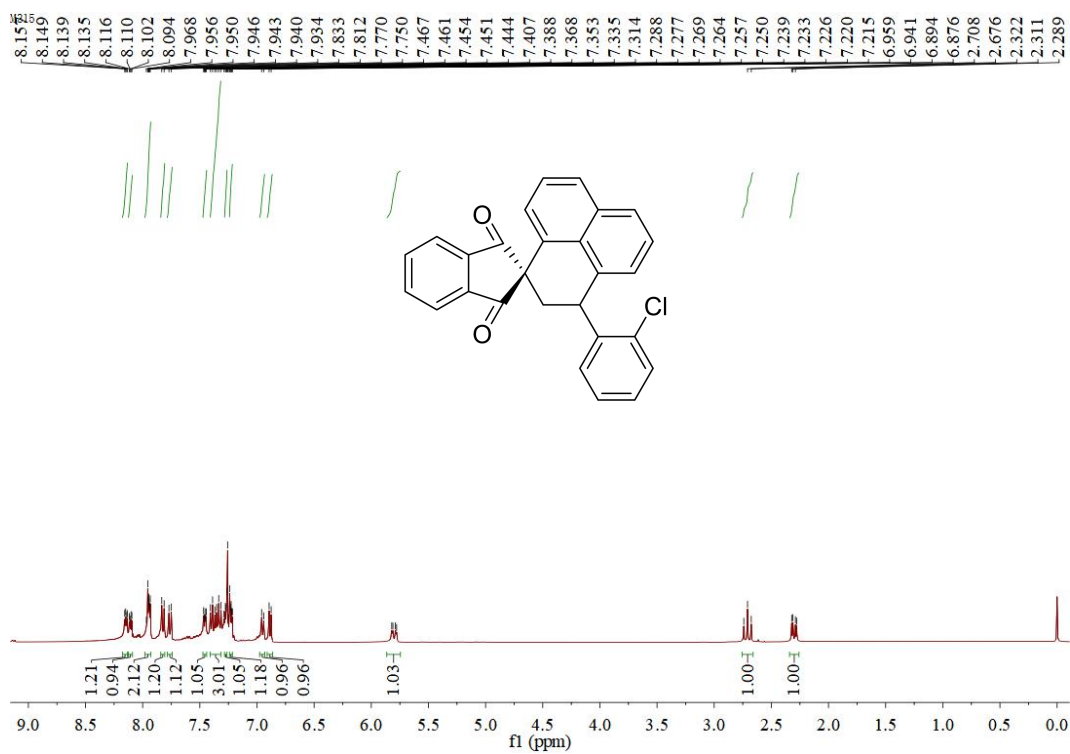
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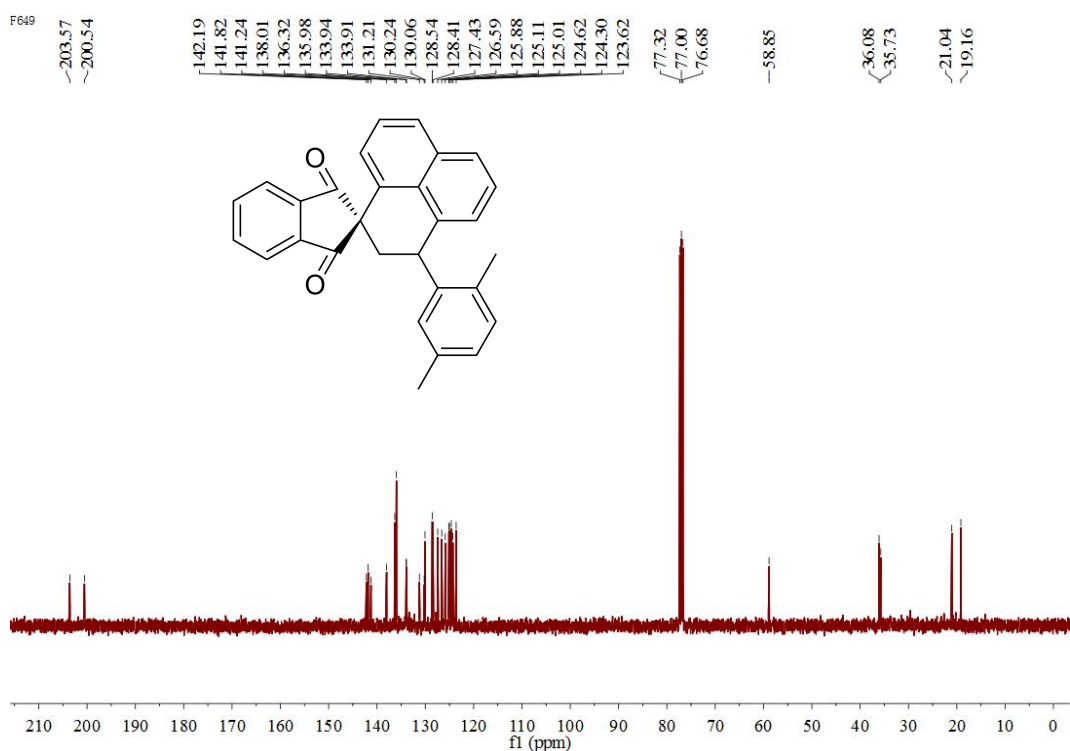
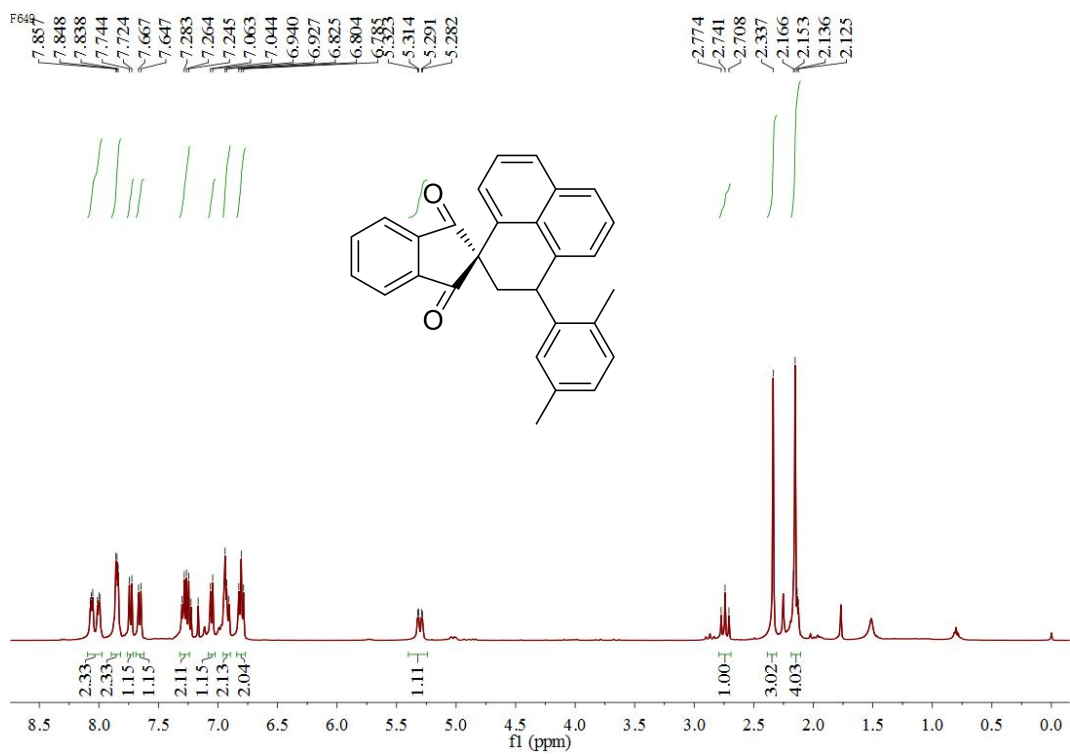
¹H NMR and ¹³C NMR of 3p



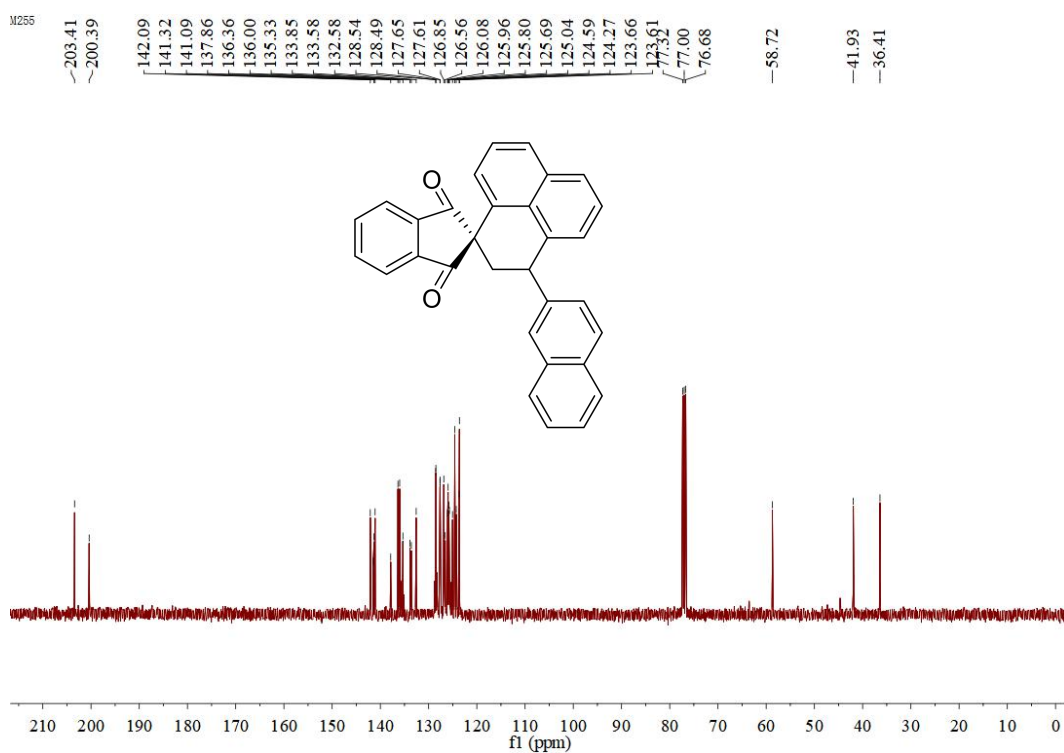
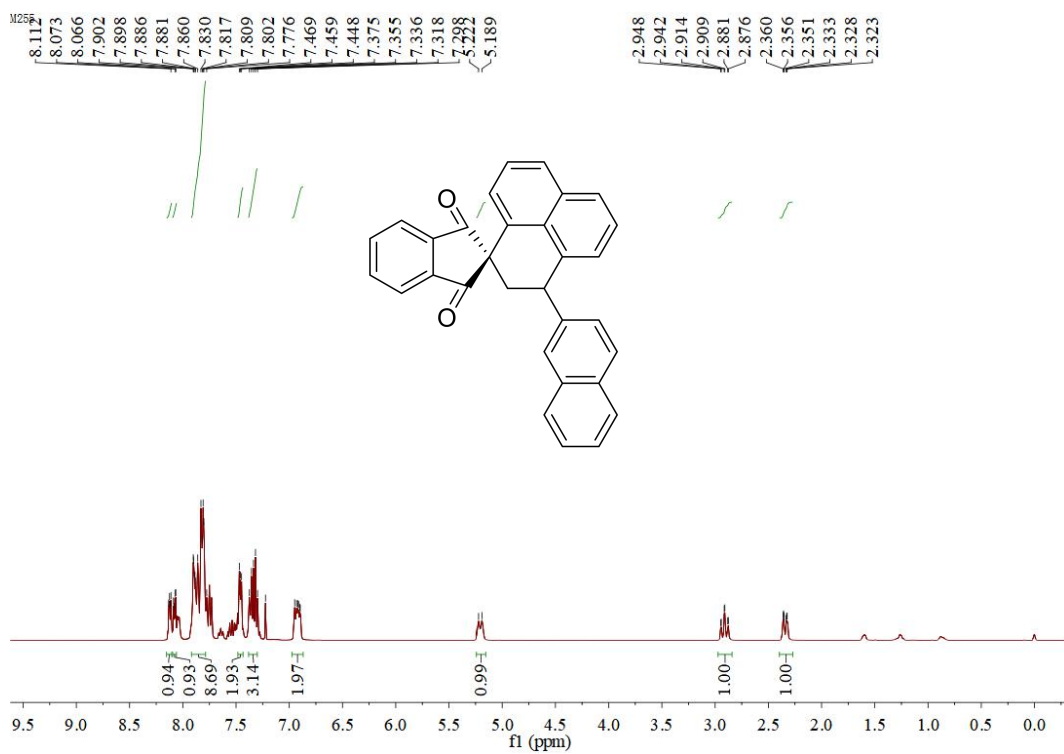
¹H NMR and ¹³C NMR of 3q



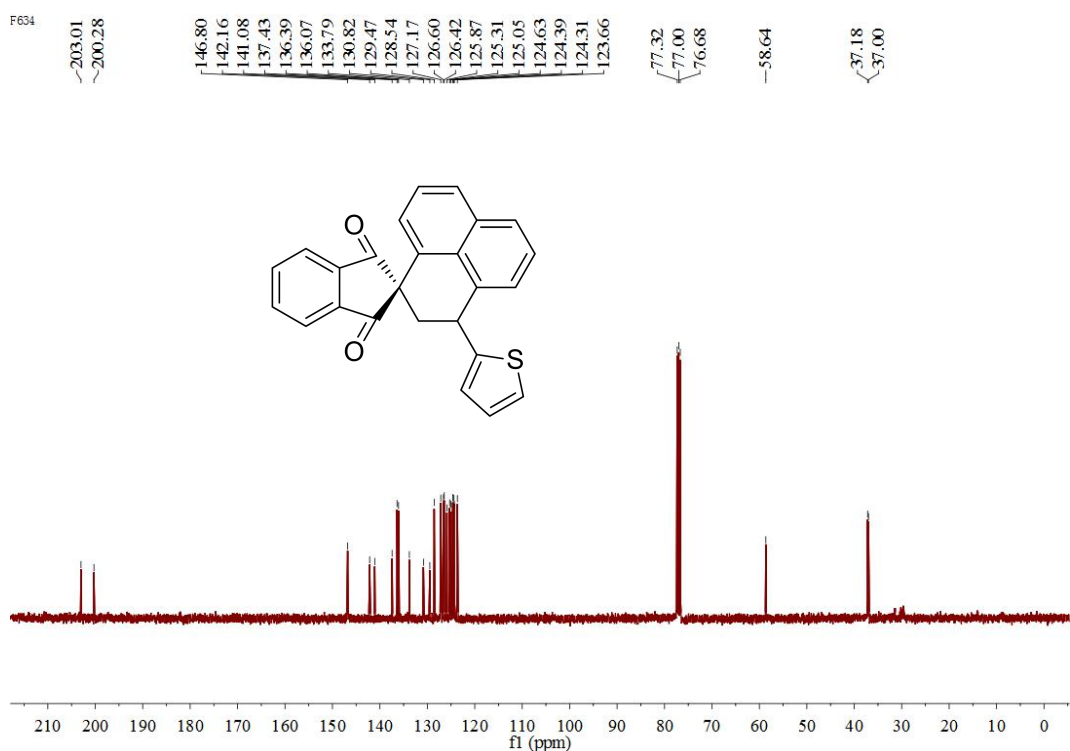
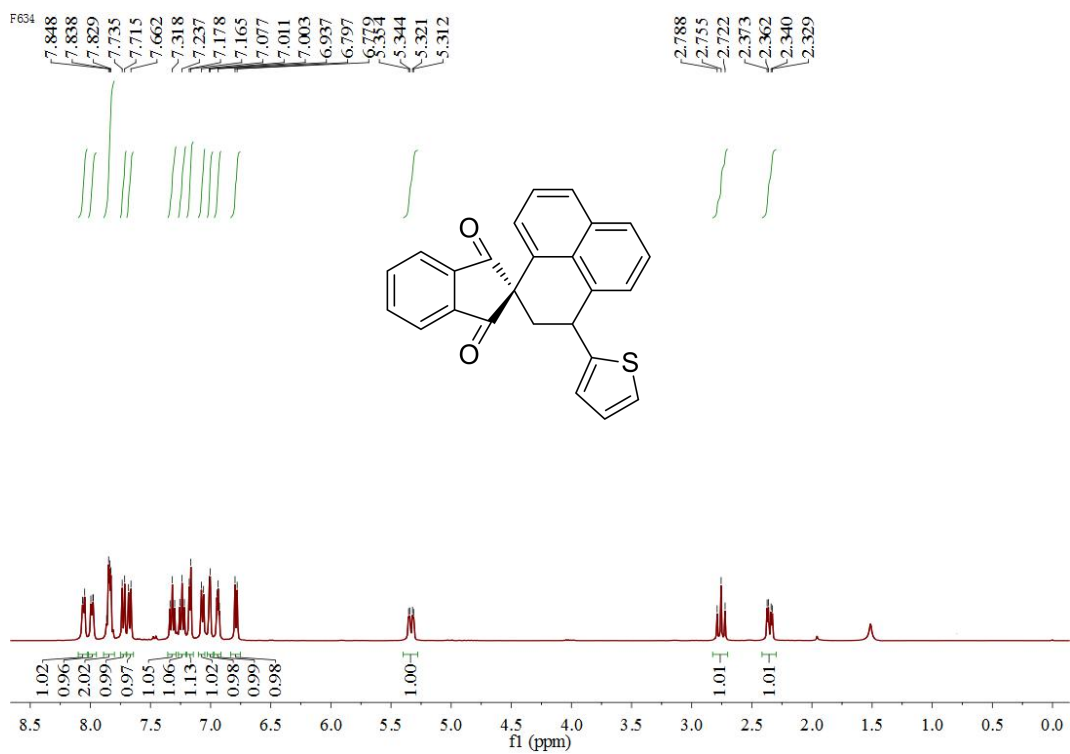
¹H NMR and ¹³C NMR of 3r



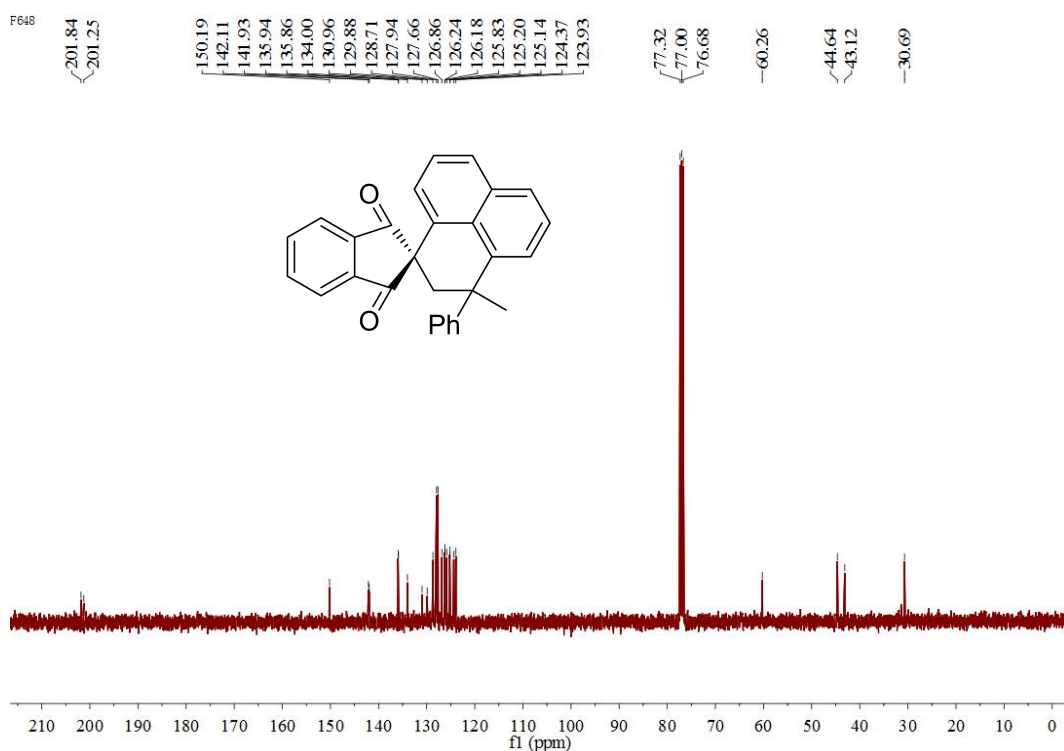
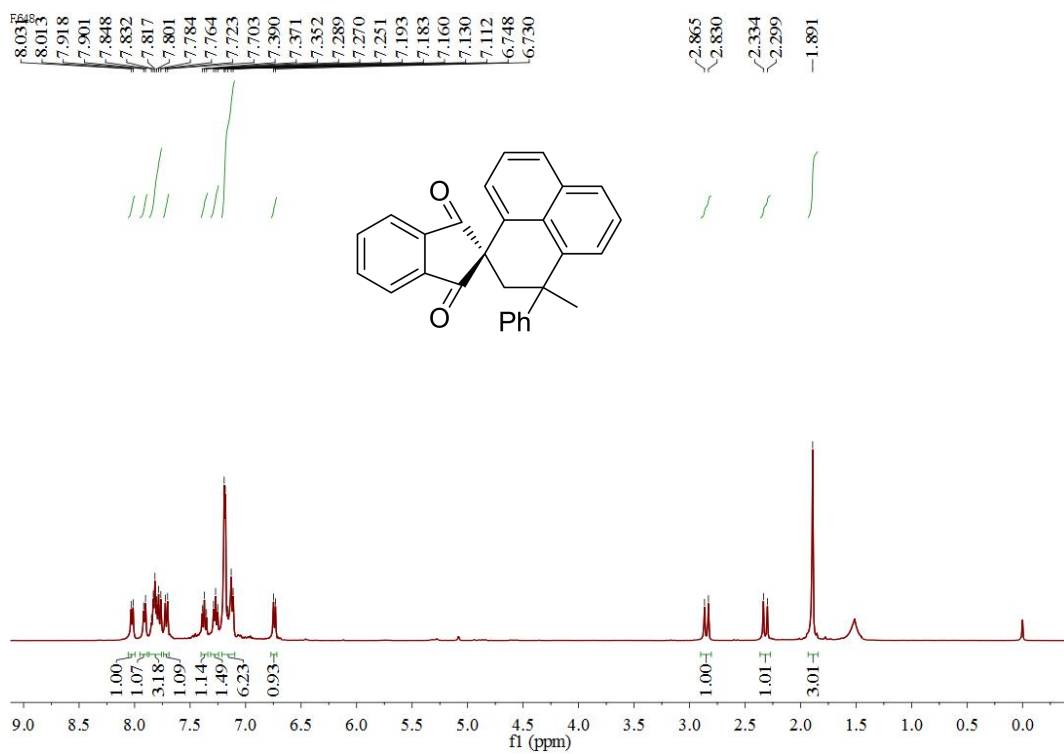
¹H NMR and ¹³C NMR of 3s



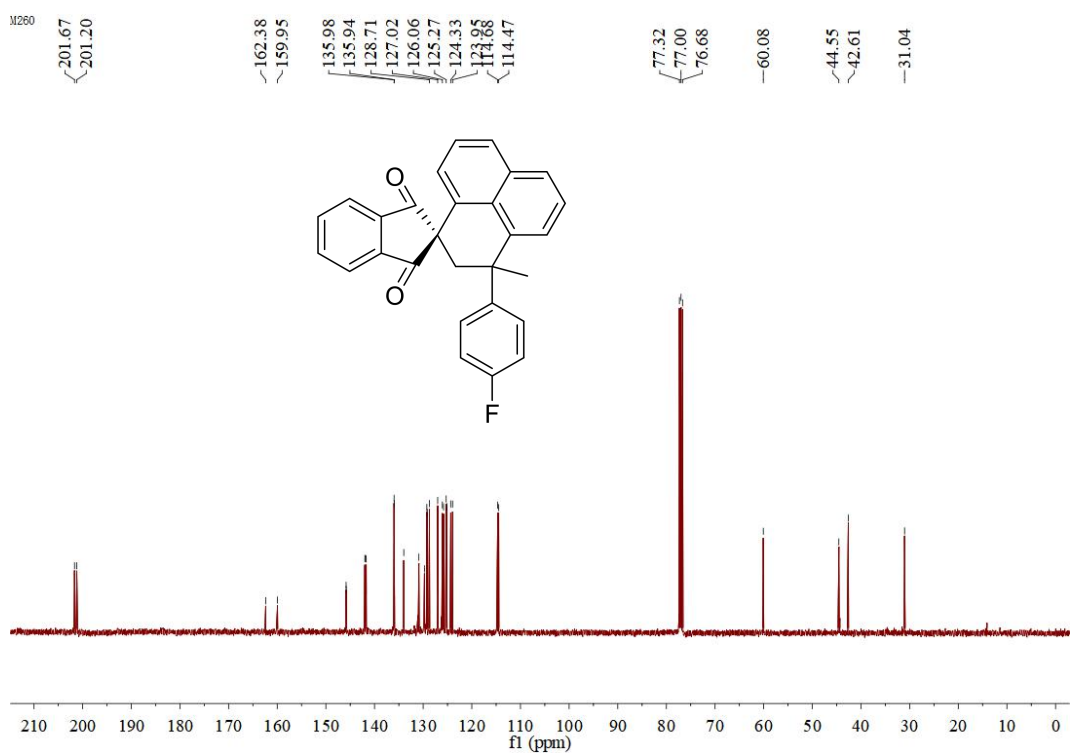
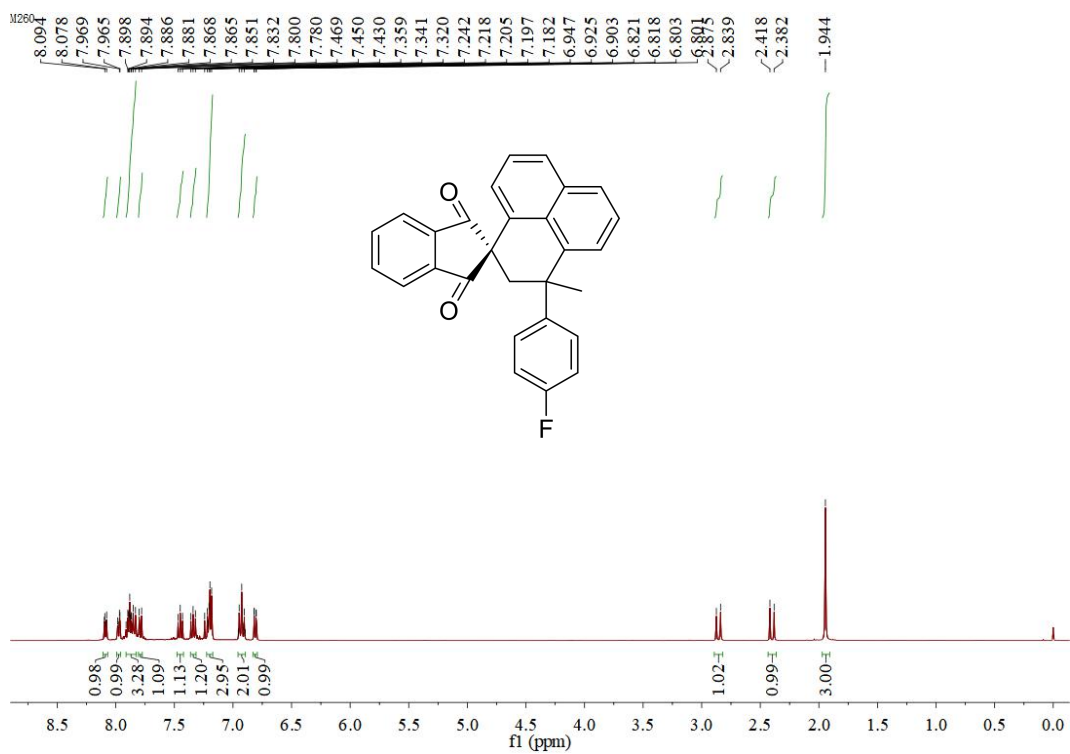
¹H NMR and ¹³C NMR of 3t



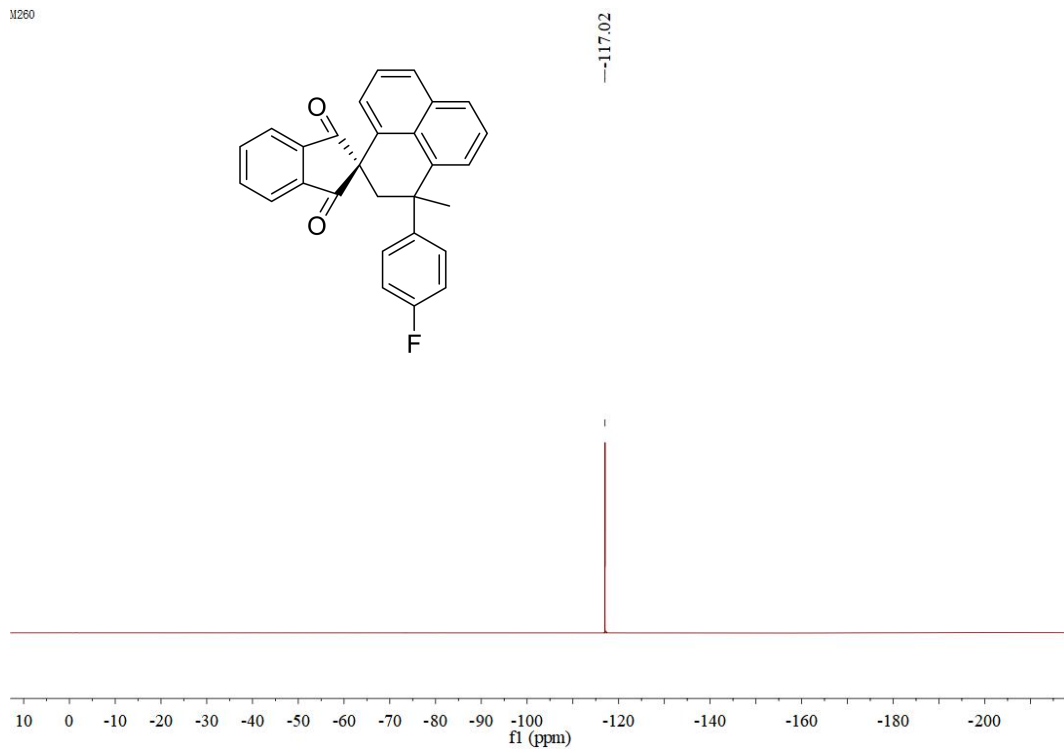
¹H NMR and ¹³C NMR of 3u



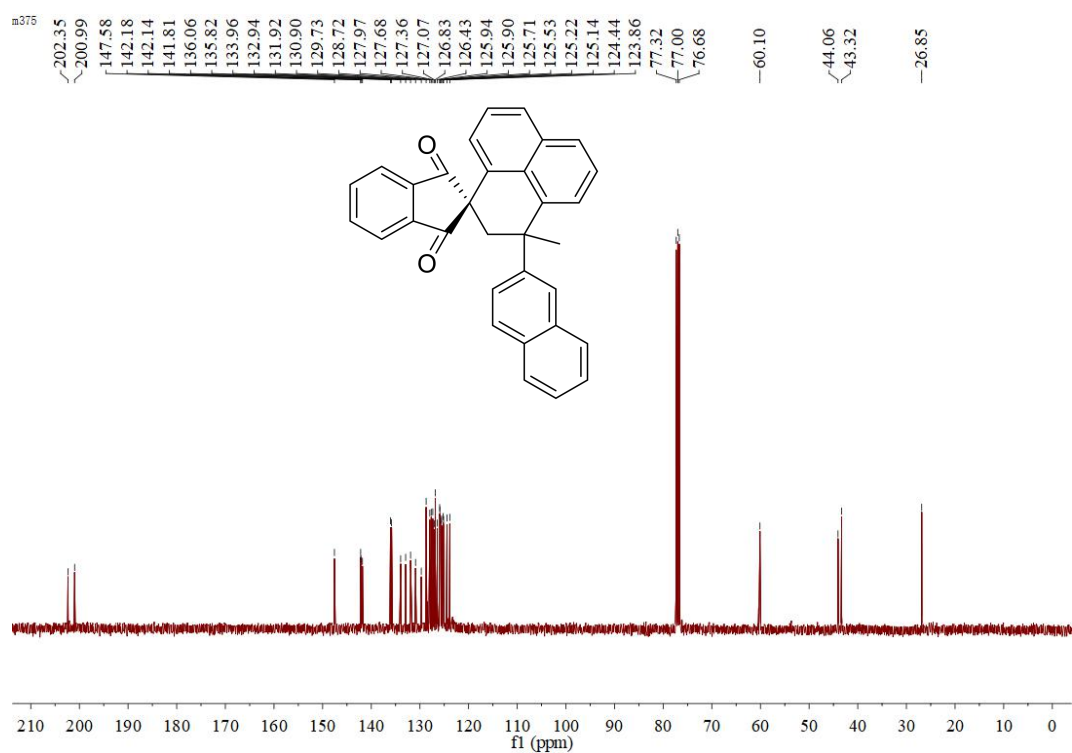
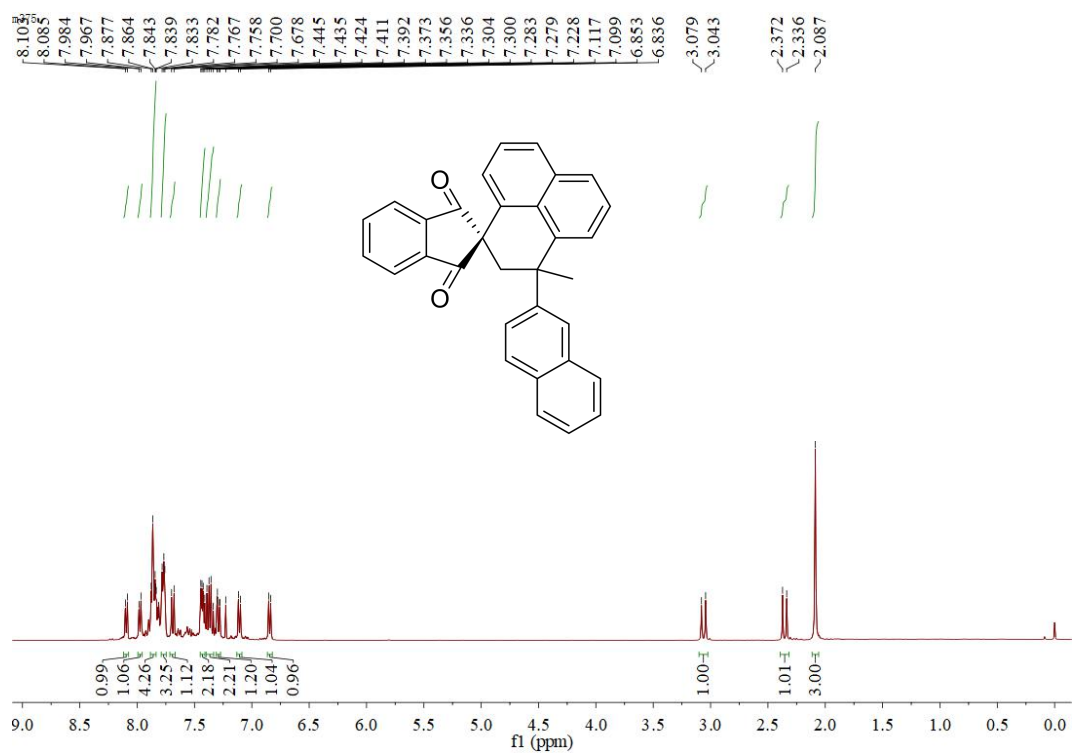
¹H NMR, ¹³C NMR and ¹⁹F NMR of 3v



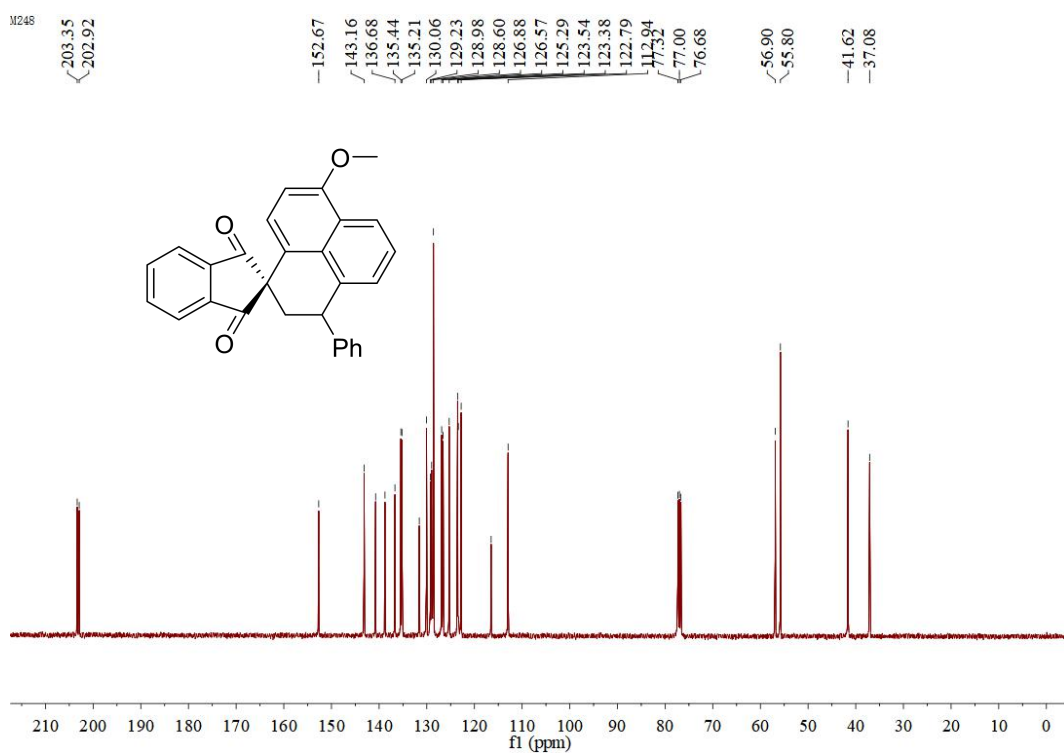
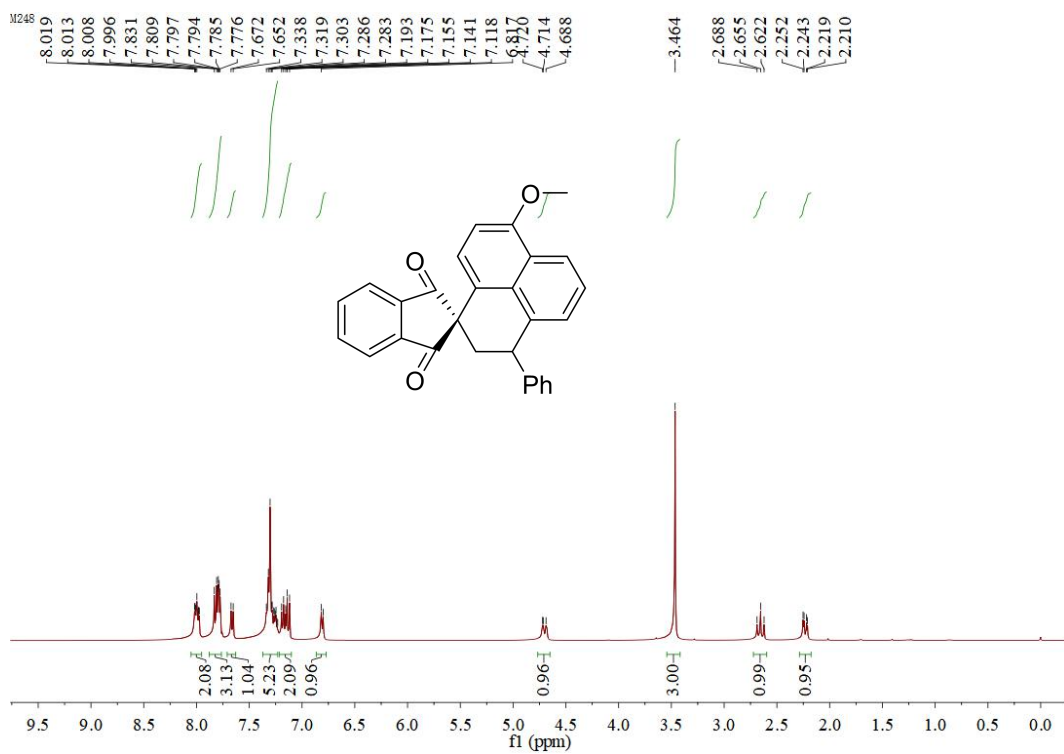
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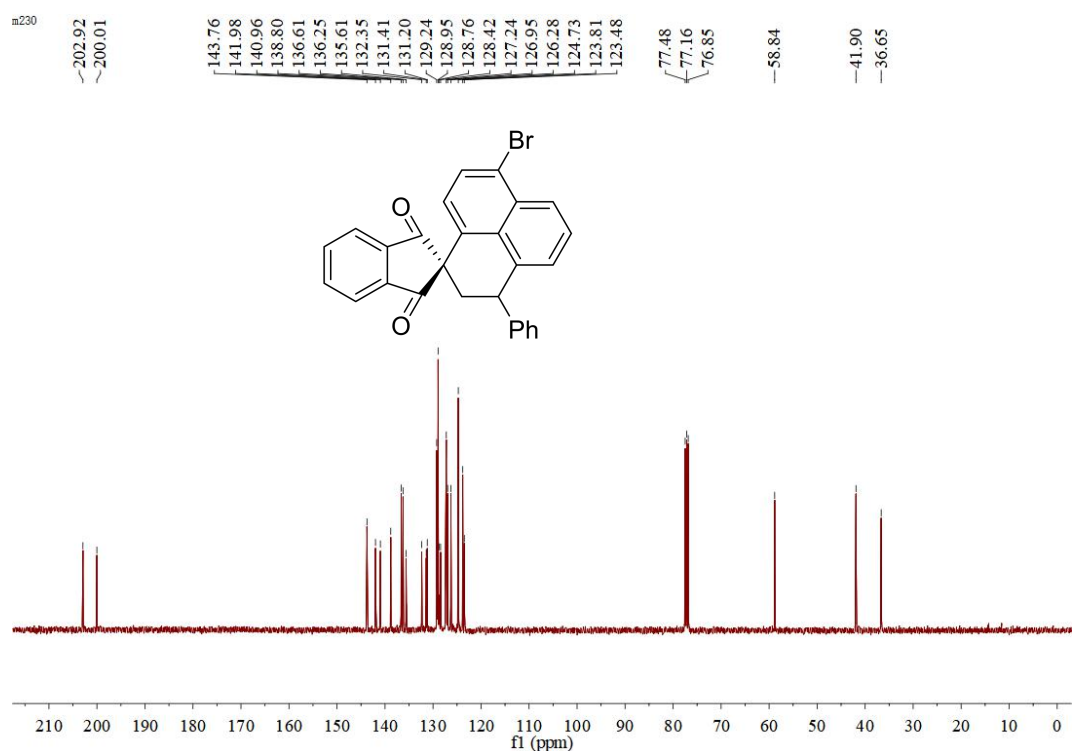
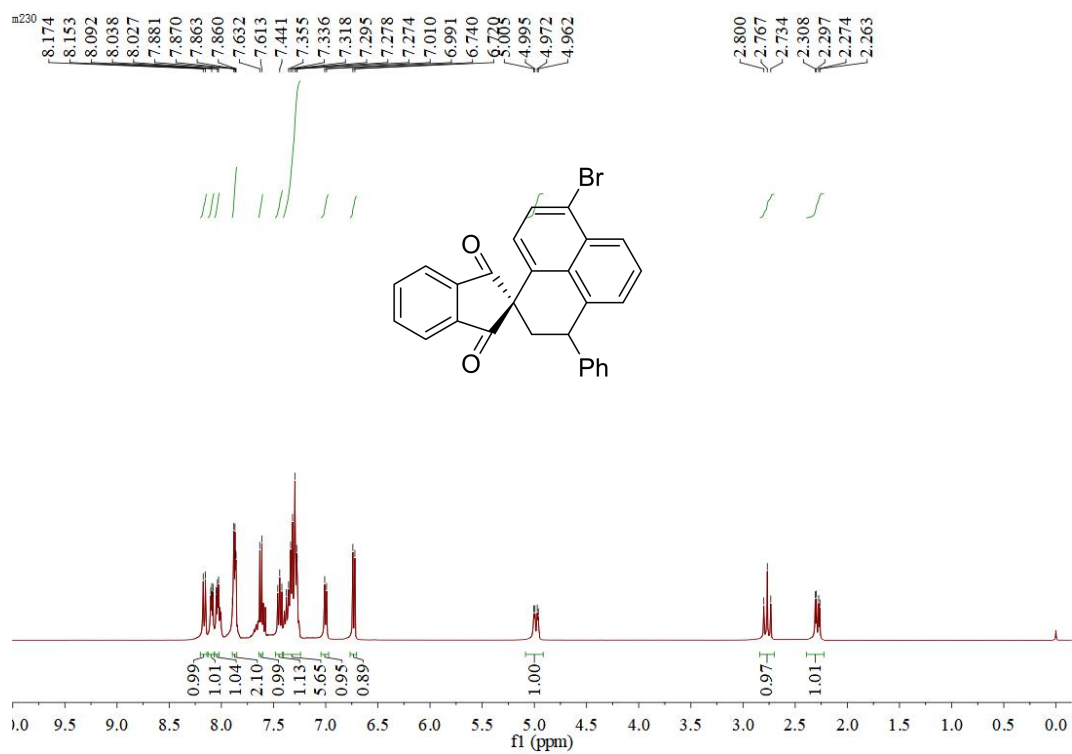
^1H NMR and ^{13}C NMR of 3w



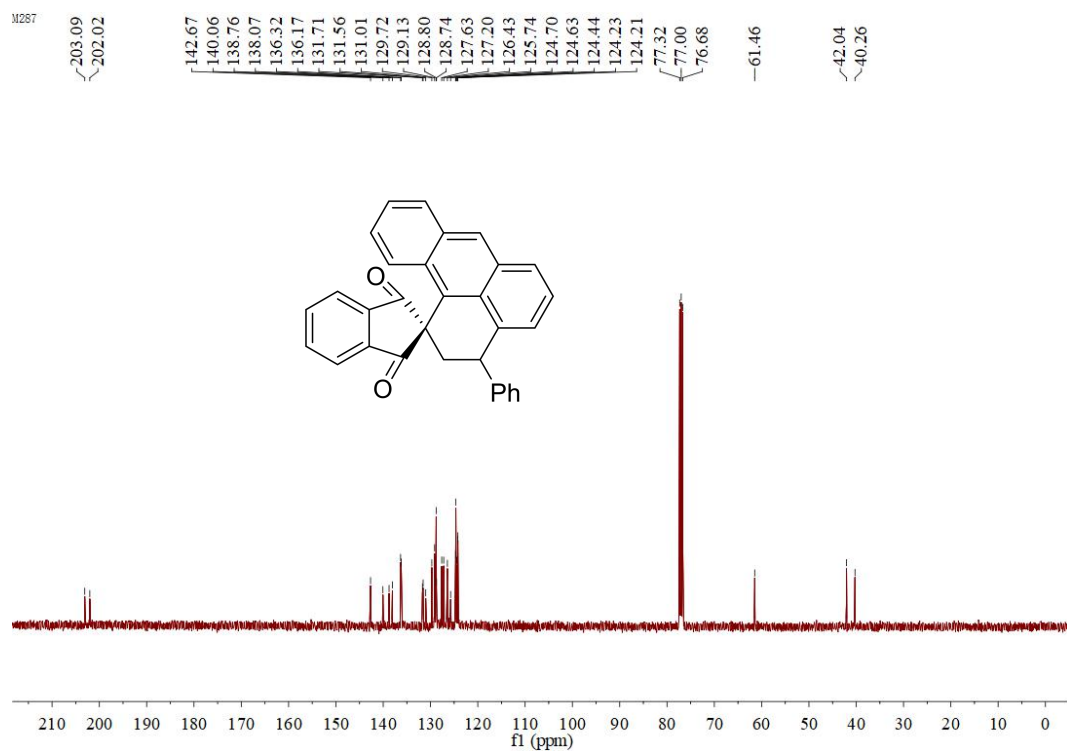
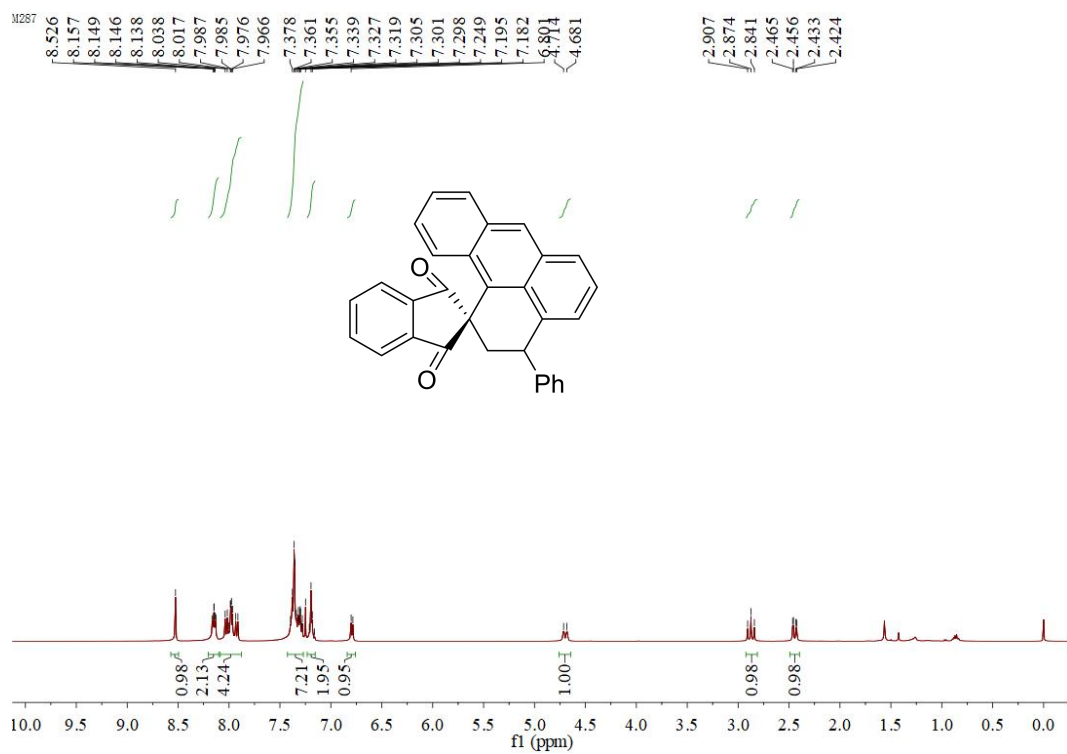
¹H NMR and ¹³C NMR of 3x



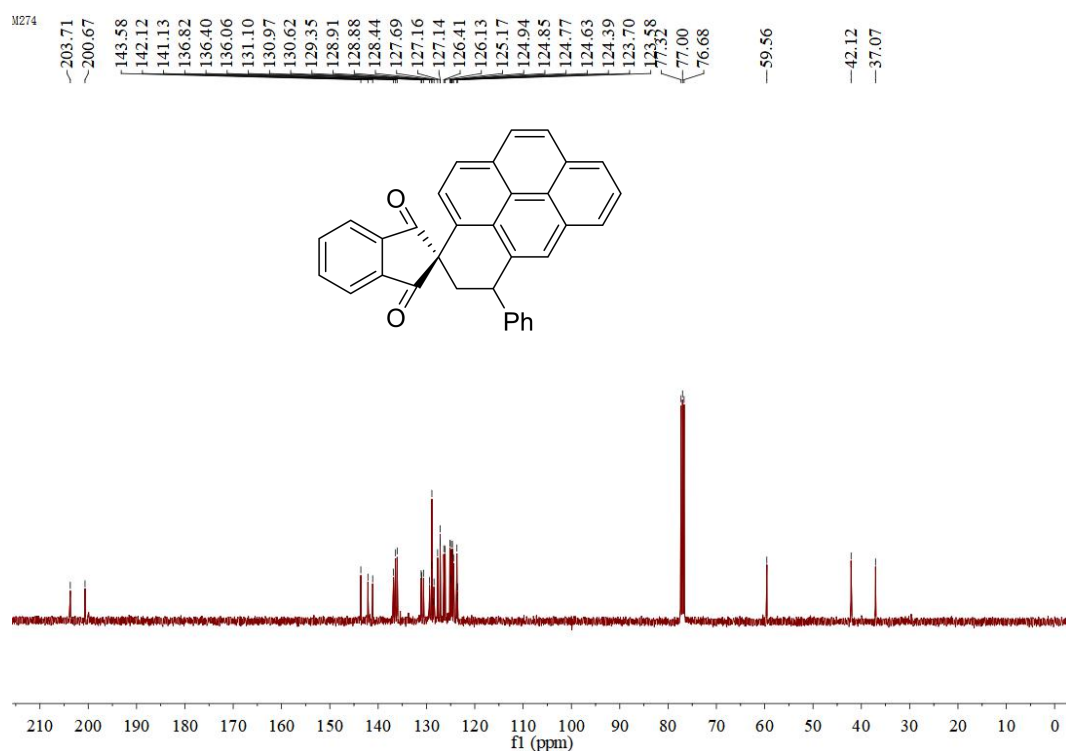
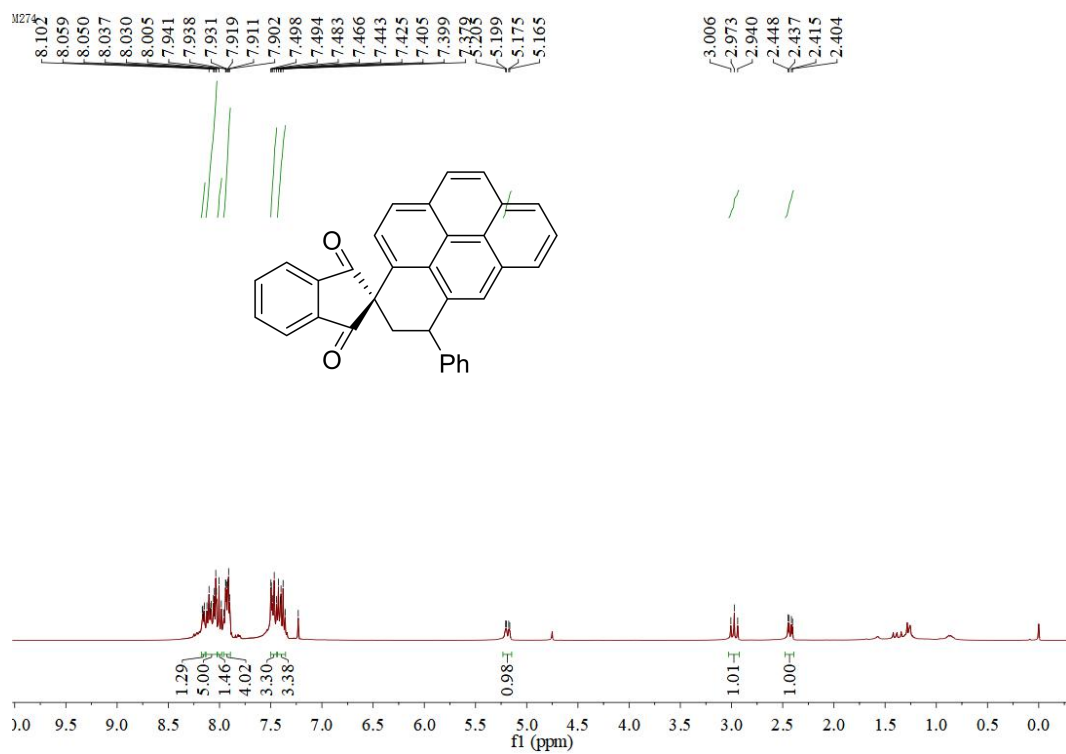
¹H NMR and ¹³C NMR of 3y



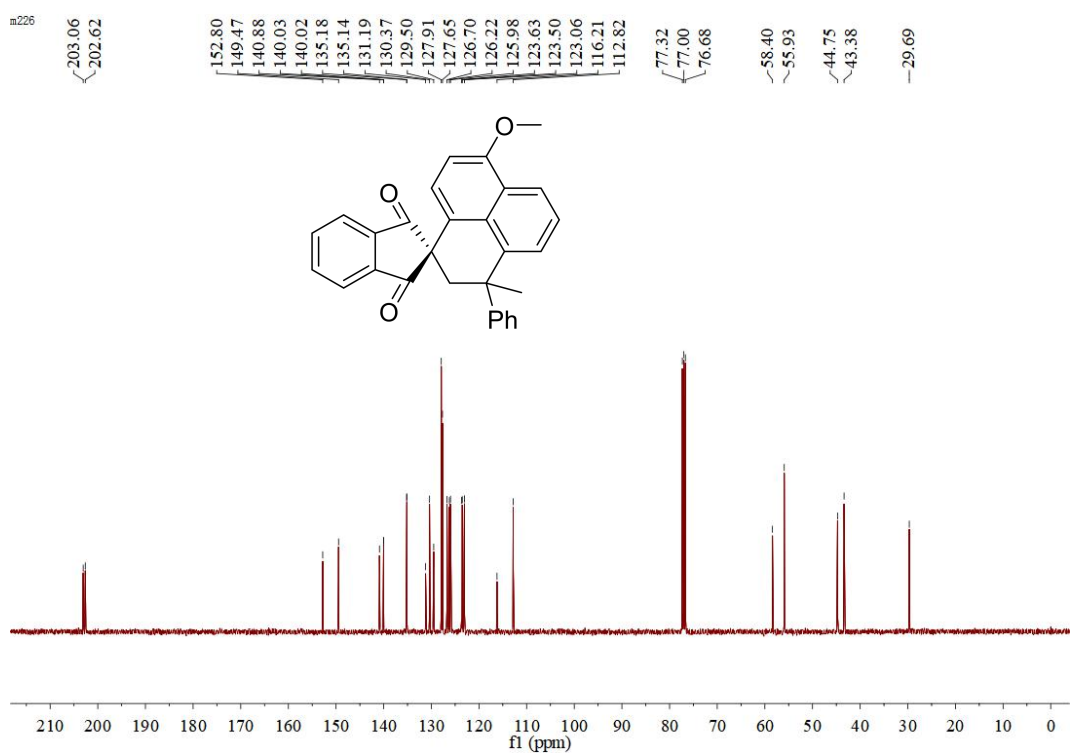
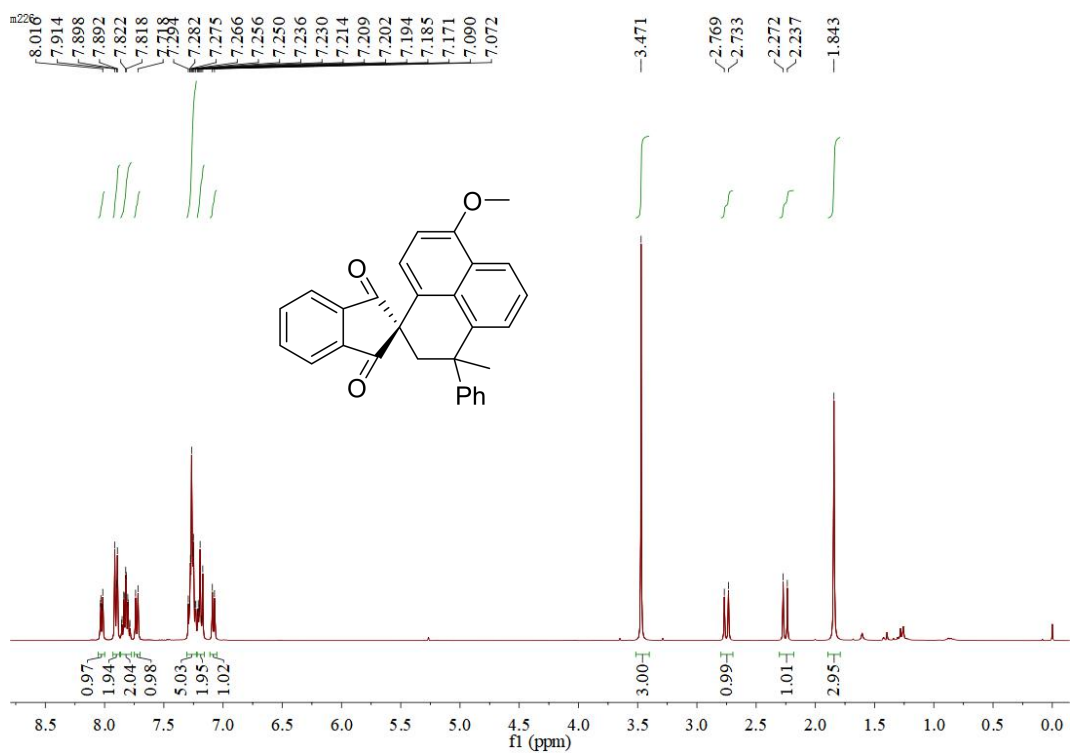
¹H NMR and ¹³C NMR of 3z



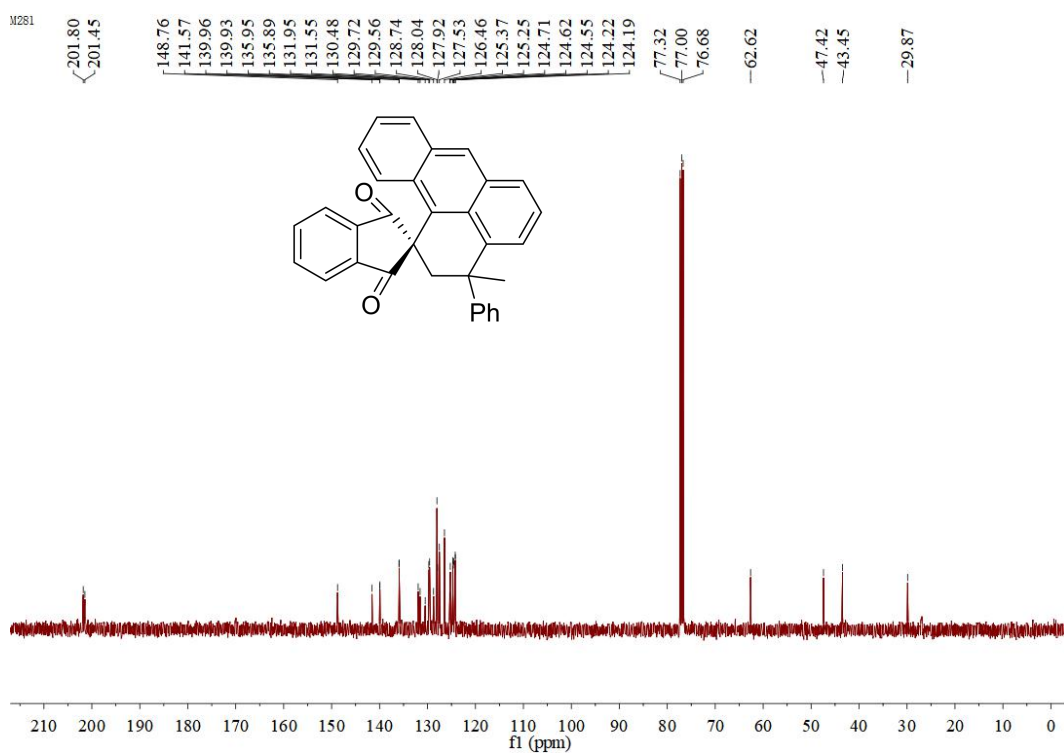
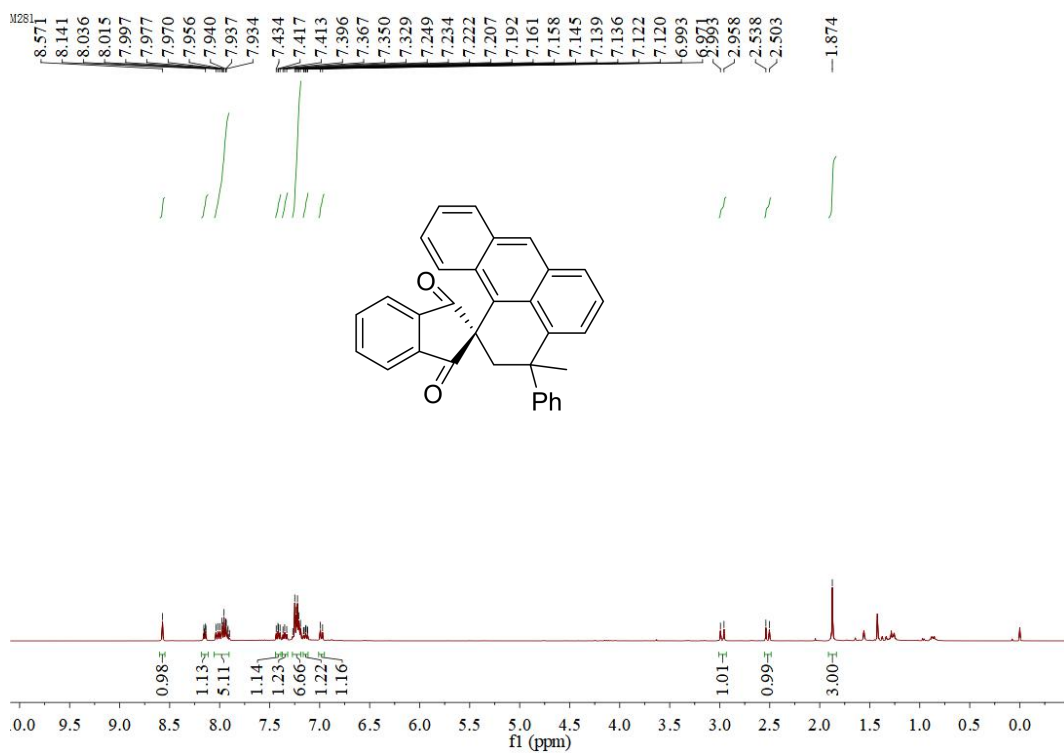
¹H NMR and ¹³C NMR of 3aa



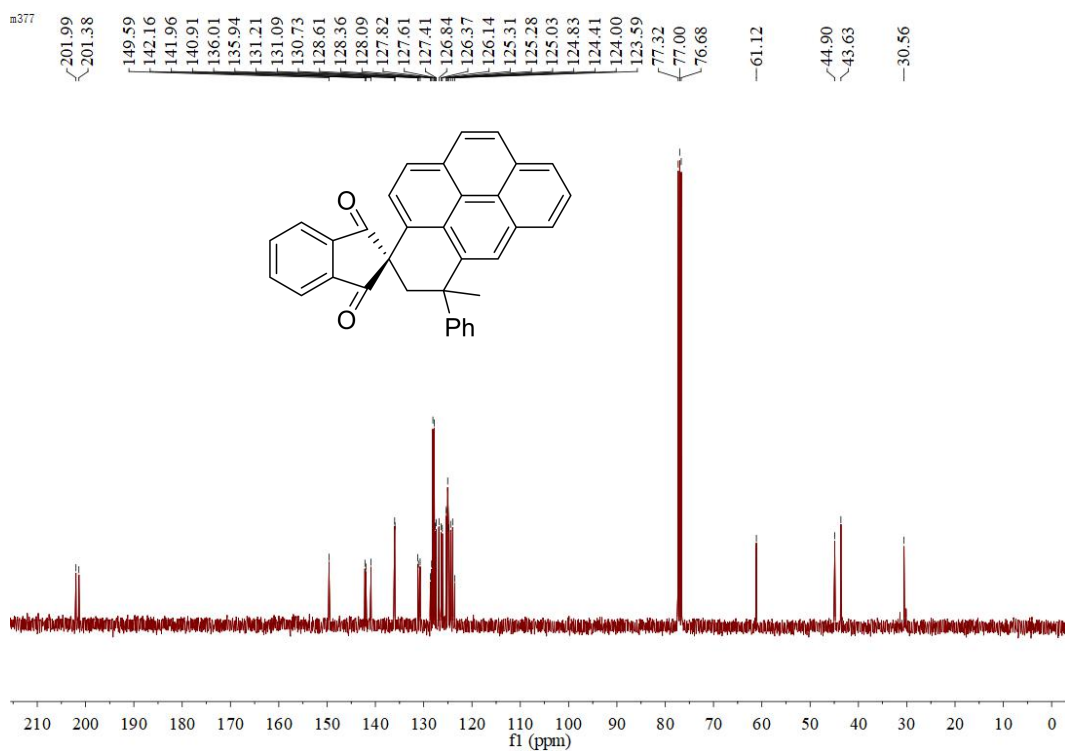
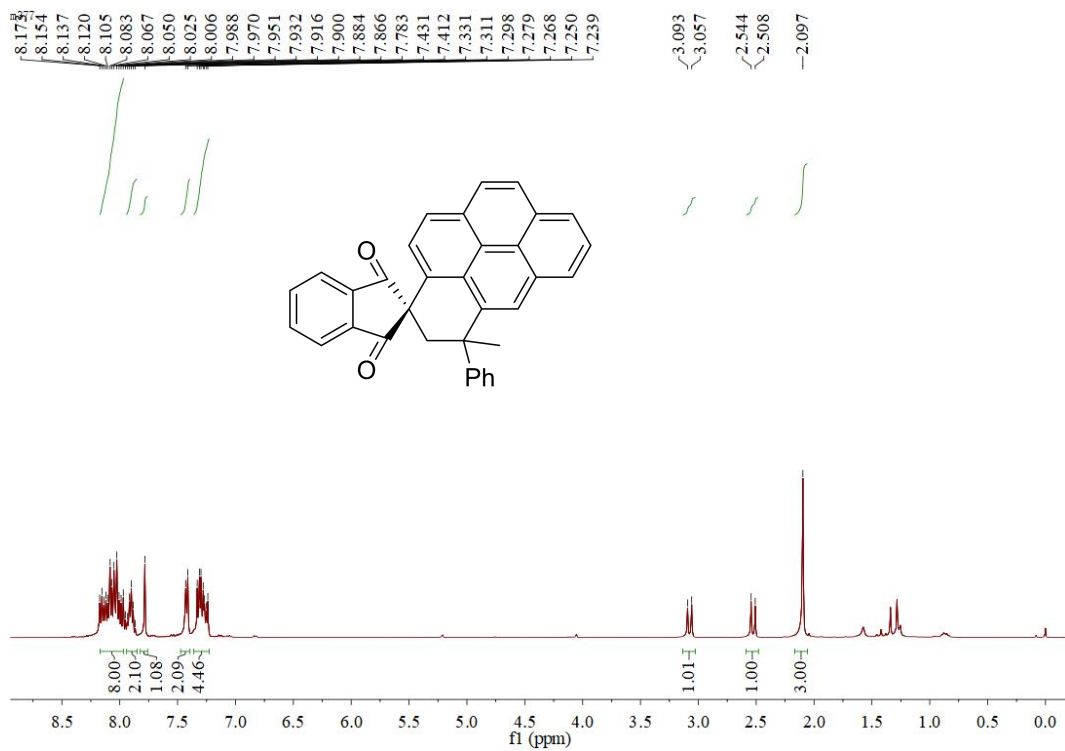
¹H NMR and ¹³C NMR of 3ab



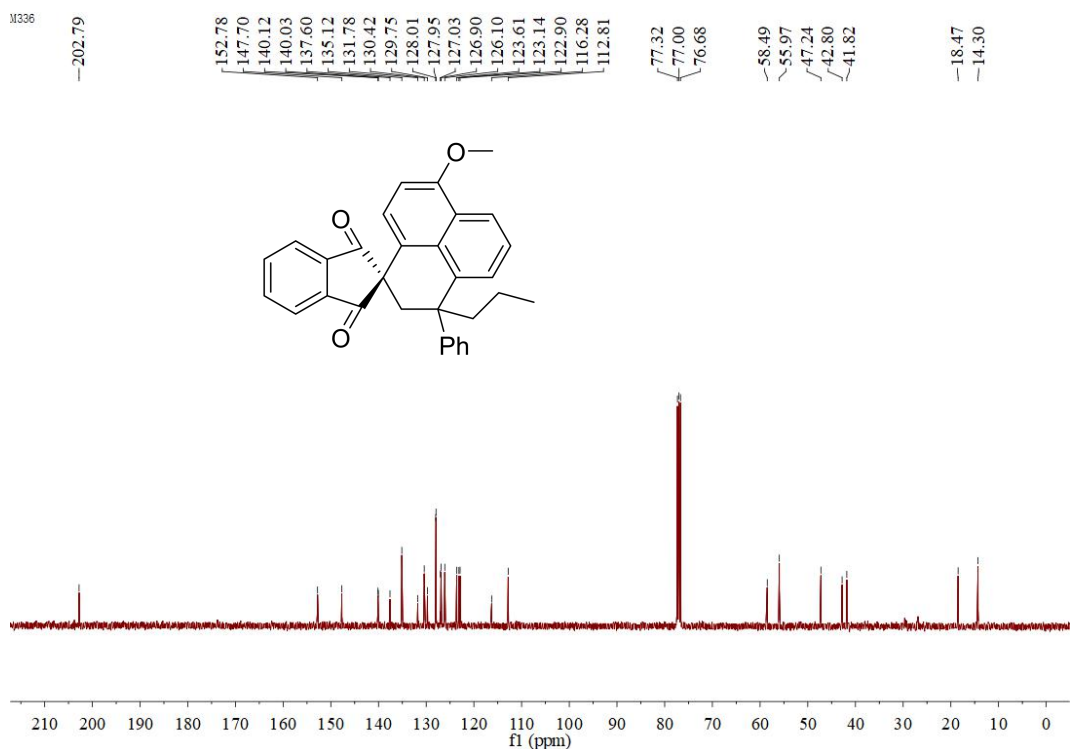
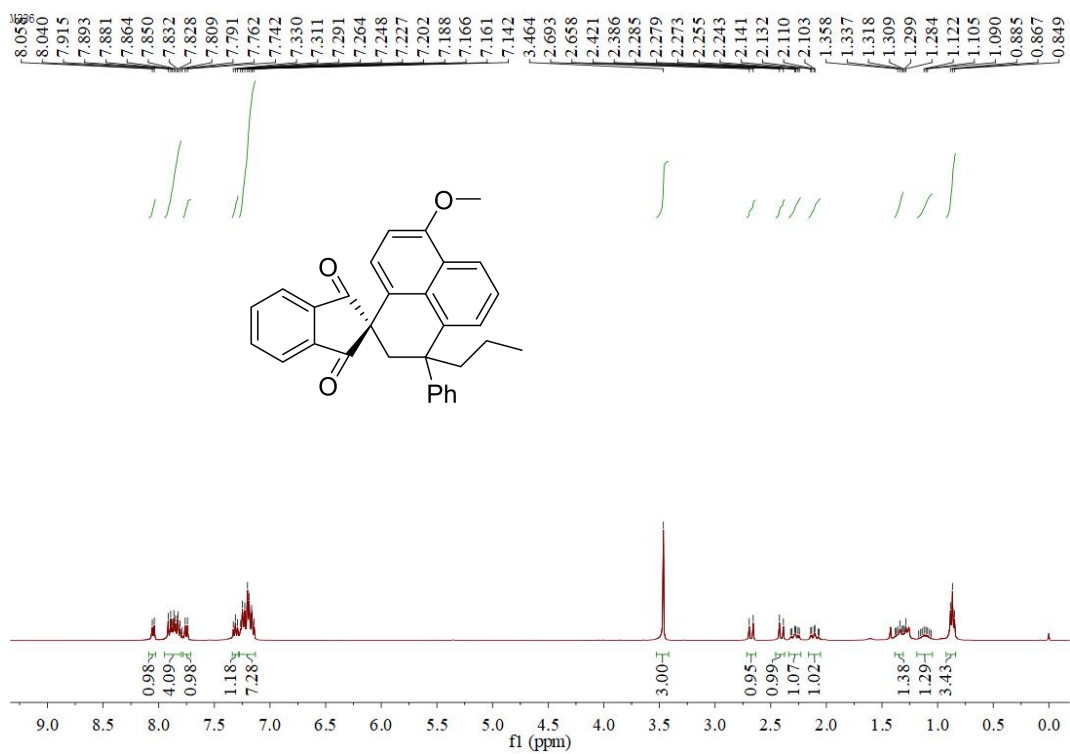
¹H NMR and ¹³C NMR of 3ac



¹H NMR and ¹³C NMR of 3ad



¹H NMR and ¹³C NMR of 3ae



¹H NMR and ¹³C NMR of 3f

