Supporting Information

Content

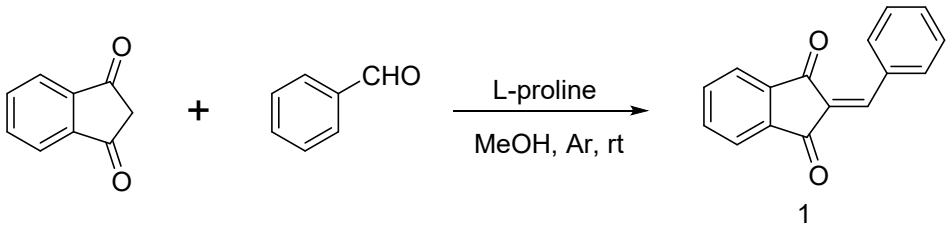
1 General information

All reactions were carried out under an Ar atmosphere in oven-dried glassware with magnetic stirring, unless otherwise specified. Dichloromethane was purified by passage through a bed of activated alumina. All other reagents and solvents were purchased from Energy Chemical or J&K Chemical Company and used without any further purification. Powdered 4 Å molecular sieves (MS 4Å) were dried at 400^{o}C under a vacuum prior to use. TLC information was recorded on GF 254 plates (Qingdao Haiyang Chemical Co. Ltd., P. R. China) and developed by staining with $KMnO_4$ or ceric ammonium molybdate (CAM). Purification of reaction products were carried out by flash chromatography with silica gel (200-300 mesh, Qingdao Haiyang Chemical Co. Ltd., P. R. China). Melting points were measured with X-4 digital display micro-melting point detector. ^{1}H NMR spectra were measured on Varian 400 (400 MHz) spectrometers and reported in ppm (s = singlet, d = doublet, t = triplet, q = quartet, m =

multiplet, br =broad; integration; coupling constant(s) in Hz), using TMS as an internal standard (TMS at 0.00 ppm) in $CDCl_3$. ^{13}C NMR spectra were recorded on V400 spectrometer and reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.16 ppm). High-resolution mass spectra were obtained using an Agilent 6230 TOF LC/MS with an (atmospheric pressure photo-ionization (APPI) or electrospray (ESI) source with purine and HP-0921 as an internal calibrants. HR-EI-MS were performed on an API-Qstar-Pulsar-1 spectrometer. HPLC was Agilent Technologies 1260 infinity II. IR spectra were obtained using a Perkin Elmer FT-IR spectrometer (Spectrum Two) with KBr pellets.

a) Preparation of 2-arylideneindane-1,3-dione 1[1]

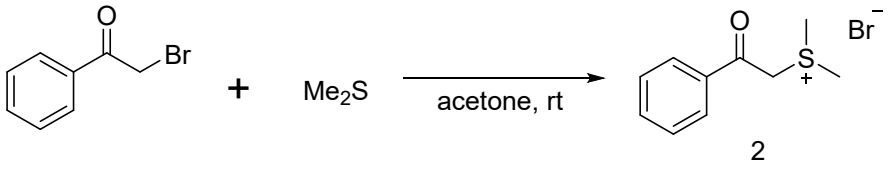
A 50 mL Schlenk flask, equipped with a magnetic stirring bar, was sequentially charged with a solution of 1,3-indanedione (1.5 g, 10 mmol), L-proline (349.0 mg, 0.3 equiv) and benzaldehyde (2.0 g, 1.1 equiv) in methanol (20 mL). The reaction mixture was stirred for 12 hours at room temperature. Then the resulting mixture was purified using vacuum-filtration and eluted by flash chromatography (petroleum ether/EtOAc = 5:1) furnished **1** as yellow solid.



1

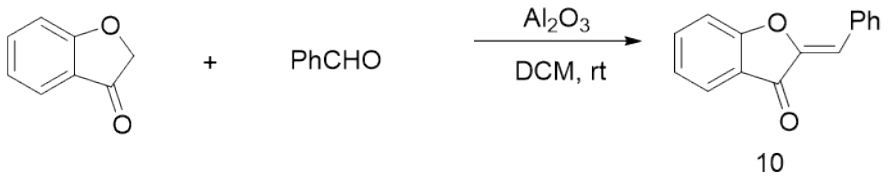
b) Preparation of Dimethyl(2-oxo-2-phenylethyl)sulfonium bromide 2

Dimethyl sulfide (0.34 mL, 4.6 mmol) was added to a rapidly stirred solution of the bromoacetophenone (0.92 g, 4.6 mmol) in acetone (3 mL) at rt and the mixture was stirred for 24 hours at room temperature. After reaction, filtration, the filter cake was washed several times with acetone, and then dried under vacuum for 4 hours at 40°C. The resulting colorless solid was the product **2**.



c) Preparation of 2-benzylidenebenzofuran-3(2H)-one 10 [2]

To a solution of benzofuran-3(2H)-one (1.0 mmol) and benzaldehyde (1.0 mmol) in dichloromethane (6 mL) was added aluminum oxide (30.0 mmol) at room temperature. After stirring for 6 h, the reaction mixture was filtered off. The filtrate was concentrated under vacuum and the residue was purified by flash chromatography on silica gel to give the desired compound **10**.

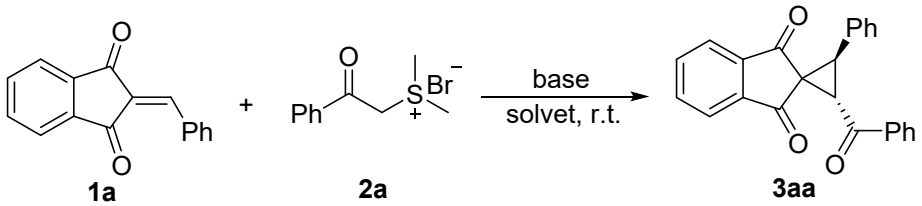


2 General procedure for the preparation of 3

Under Ar atmosphere, to a solution of 2-arylideneindane-1,3-dione **1** (0.22 mmol) and dimethyl(2-oxo-2-phenylethyl)sulfonium bromide **2** (0.26 mmol) in HFIP (2.0 mL) was added Et_3N (0.03 mL, 0.26 mmol). The resulting mixture was stirred at rt for a specified time. The reaction was monitored by TLC spectroscopy. After the reaction was completed, the solvent was then removed on a rotary evaporator at reduced pressure and the residue was subjected to column chromatographic isolation on silica gel (eluted with petroleum ether/EtOAc 20:1-5:1) to give the annulation product **3**.

3 The experimental results

Table 1. Optimization of Reaction Conditions. [a]

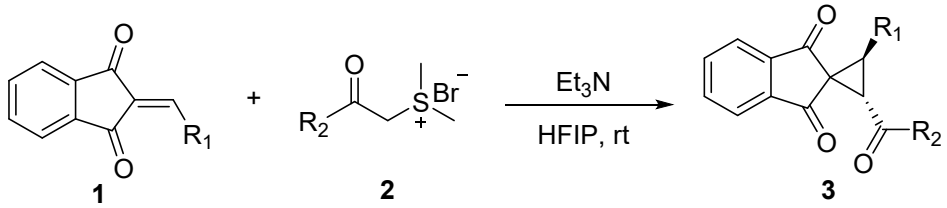


Entry	Base	Solvent	d.r. [b]	Yield (%) [c]
1	Cs_2CO_3	MeCN	20: 3	51

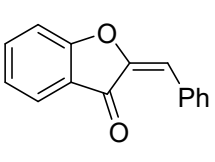
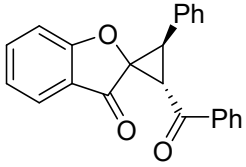
2	Cs_2CO_3	HFIP	20 : 4	72
3	Cs_2CO_3	DCM	20 : 6	52
4	Cs_2CO_3	DCE	20 : 6	48
5	Cs_2CO_3	EtOAc	20 : 3	52
6	Cs_2CO_3	MeOH	>20 :1	63
7	Cs_2CO_3	THF	20 : 2	60
8	Cs_2CO_3	EtOH	>20 : 1	54
9	Cs_2CO_3	1,4-Dioxane	20 : 4	59
10	Cs_2CO_3	TFE	>20 : 1	24
11	Cs_2CO_3	$CHCl_3$	20 : 5	63
12	Na_2CO_3	HFIP	20 : 6	37
13	K_2CO_3	HFIP	20 : 8	17
14	Et_3N	HFIP	>20 : 1	81[d]
15	$NaHCO_3$	HFIP	20 : 6	24
16	NaOH	HFIP	>20 : 1	63
17	NaOAc	HFIP	20 : 11	50
18	Pyridine	HFIP	20 : 4	32
19	Piperidine	HFIP	>20 : 1	46
20	DMAP	HFIP	20 : 2	50
21	DBU	HFIP	>20 : 1	38
22	Et_3N	MeCN	20 : 4	60
23	Et_3N	DCM	>20 : 1	51
24	Et_3N	DCE	20 : 8	43
25	Et_3N	EtOAc	>20 : 1	54
26	Et_3N	MeOH	>20 : 1	45
27	Et_3N	THF	>20 : 1	54
28	Et_3N	EtOH	>20 : 1	45
29	Et_3N	1,4-Dioxane	>20 : 1	70
30	Et_3N	TFE	4 : 20	24
31	Et_3N	$CHCl_3$	>20 : 1	42

[a] Reaction conditions: **1a** (0.22 mmol) with **2a** (0.26 mmol) and base (0.26 mmol) in 2 mL solvent. [b] Diastereomeric ratio (d.r.) was determined by ^{1}H NMR analysis. [c] NMR yield; they were determined by ^{1}H spectra using 1,3,5-trimethoxybenzene as an internal standard. [d] Yield of isolated product.

Table 2. Substrate Scope for Spiro-Cyclopropanation. [a]

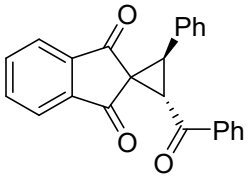


Entry	R_1	R_2	Product	d.r. [b]	Yield (%) [c]

1	Ph	Ph	**3aa**	>20:1	81
2	*o*-MePh	Ph	**3ab**	>20:1	79
3	*m*-MePh	Ph	**3ac**	>20:1	43
4	*p*-MePh	Ph	**3ad**	>20:1	59
5	*o*-MeOPh	Ph	**3ae**	>20:1	79
6	*m*-MeOPh	Ph	**3af**	>20:1	97
7	*p*-MeOPh	Ph	**3ag**	>20:1	59
8	2,5-MeOPh	Ph	**3ah**	>20:1	96
9	*p*-^{t}BuPh	Ph	**3ai**	>20:1	85
10	*p*-MeSPh	Ph	**3aj**	>20:1	59
11	*o*-ClPh	Ph	**3ak**	>20:1	94
12	*m*-ClPh	Ph	**3al**	>20:1	73
13	*p*-ClPh	Ph	**3am**	>20:1	61
14	2,4-ClPh	Ph	**3an**	>20:1	70
15	*m*-NO_2Ph	Ph	**3ao**	>20:1	60
16	*p*-NO_2Ph	Ph	**3ap**	>20:1	83
17	2-Furyl	Ph	**3aq**	>20:1	44
18	2-Thienyl	Ph	**3ar**	20:7	34
19	3-Pyridinyl	Ph	**3as**	20:4	76
20	1-Naphthyl	Ph	**3at**	20:4	42
21	3-Phenylpropynyl	Ph	**3au**	>20:1	71
22	3-Phenylpropenal	Ph	**3av**	>20:1	60
23	Cyclohexyl	Ph	**3aw**	20:3	88
24	Ph	*p*-MePh	**3ba**	20:2	94
25	Ph	*p*-MeOPh	**3ca**	>20:1	36
26	Ph	*m*-ClPh	**3da**	20:2	58
27	Ph	*p*-BrPh	**3ea**	>20:1	89
28	Ph	*o*-NO_2Ph	**3fa**	>20:1	31
29	Ph	*m*-NO_2Ph	**3ga**	>20:1	71
30	Ph	*p*-CNPh	**3ha**	>20:1	97
31	Ph	2-Thienyl	**3ia**	20:7	66
32	Ph	2-Naphthyl	**3ja**	20:2	95
33	Ph	Me	**3ka**	>20:1	67
34	Ph	Et	**3la**	>20:1	95
35	Ph	OEt	**3ma**	20:9	45
36			**3na**	20:18	31

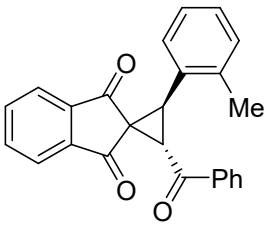
[a] Reaction conditions: **1** (0.22 mmol) with **2** (0.26 mmol) and Et_3N (0.26 mmol) in 2 mL HFIP. [b] Diastereomeric ratio (dr) was determined with the help of NMR. [c] Isolated yield after column chromatography purification.

4 Structural characterization



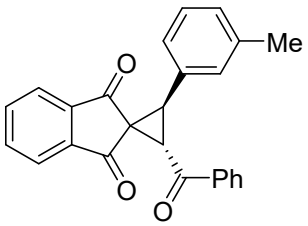
(2S,3R)-2-benzoyl-3-phenylspiro[cyclopropane-1,2'-indene]-1',3'-dione (**3aa**)

White solid, 81%, m.p. = 122-124°C, d.r.= >20:1; IR (KBr) ν_{max} = 3061, 1707, 1676, 1596, 1286, 1212, 749, 731, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96-7.94 (m, 2H), 7.91-7.87 (m, 2H), 7.80-7.76 (m, 2H), 7.56-7.53 (m, 1H), 7.42-7.31 (m, 7H), 4.30 (d, 1H, *J*= 9.5 Hz), 4.23 (d, 1H, *J*= 9.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.43, 194.19, 190.60, 142.03, 141.95, 136.09, 135.28, 135.18, 133.82, 132.31, 129.22, 128.89, 128.46, 128.40, 128.22, 123.08, 122.89, 47.38, 42.43, 40.73. HR-EI-MS (positive) *m/z* 375.0994 $[M+Na]^+$ (calcd for $C_{24}H_{16}O_3Na$ 375.0997).



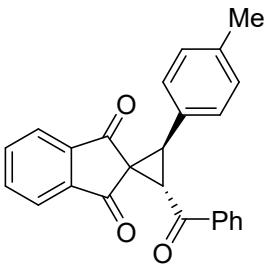
(2S,3R)-2-benzoyl-3-(o-tolyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3ab**)

White solid, 79%, m.p. = 106-107°C, d.r.= >20:1; IR (KBr) ν_{max} = 3056, 2924, 1707, 1692, 1594, 1273, 1219, 742 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96-7.92 (m, 2H), 7.90-7.87 (m, 2H), 7.81-7.78 (m, 2H), 7.55-7.51 (m, 1H), 7.42-7.37 (m, 3H), 7.25-7.24 (m, 2H), 7.13-7.11 (m, 1H), 4.28 (d, 1H, *J*= 9.5 Hz), 4.16 (d, 1H, *J*= 9.5 Hz), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.62, 193.89, 190.81, 141.84, 141.55, 138.03, 136.22, 135.36, 135.30, 133.82, 131.26, 130.10, 128.91, 128.73, 128.45, 128.37, 125.91, 123.09, 122.88, 46.73, 40.95, 40.71, 19.64. HR-EI-MS (positive) *m/z* 389.1159 $[M+Na]^+$ (calcd for $C_{24}H_{16}O_3Na$ 389.1154).



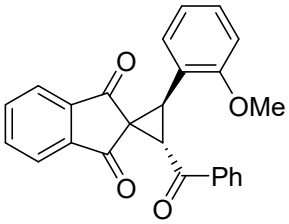
(2S,3R)-2-benzoyl-3-(m-tolyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3ac**)

White solid, 43%, m.p. = 125-127°C, d.r.= >20:1; IR (KBr) ν_{max} = 3018, 2919, 1706, 1677, 1594, 1285, 1223, 761, 741, 691 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96-7.94 (m, 2H), 7.90-7.87 (m, 2H), 7.80-7.76 (m, 2H), 7.55-7.52 (m, 1H), 7.42-7.38 (m, 2H), 7.25-7.21 (m, 1H), 7.17-7.11 (m, 3H), 4.28 (d, 1H, *J*= 9.5 Hz), 4.20 (d, 1H, *J*= 9.5 Hz), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.60, 194.33, 190.80, 142.17, 142.11, 138.17, 136.26, 135.33, 135.24, 133.88, 132.32, 130.12, 129.15, 128.99, 128.58, 128.35, 126.30, 123.17, 122.99, 47.55, 42.69, 40.91, 21.51. HR-EI-MS (positive) *m/z* 389.1157 $[M+Na]^+$ (calcd for $C_{24}H_{16}O_3Na$ 389.1154).



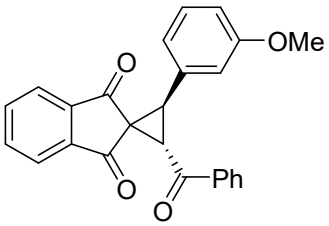
(2S,3R)-2-benzoyl-3-(p-tolyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3ad**)

White solid, 59%, m.p. = 109-110°C, d.r.= >20:1; IR (KBr) ν_{max} = 3029, 2923, 2856, 1704, 1594, 1282, 1225, 1085, 816, 731 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.96-7.94 (m, 2H), 7.90-7.87 (m, 2H), 7.79-7.75 (m, 2H), 7.55-7.52 (m, 1H), 7.42-7.38 (m, 2H), 7.25 (d, 2H, *J*= 8.2 Hz), 7.15 (d, 2H, *J*= 8.2 Hz), 4.28 (d, 1H, *J*= 9.5 Hz), 4.20 (d, 1H, *J*= 9.5 Hz), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.61, 194.40, 190.81, 142.18, 142.08, 138.14, 136.26, 135.31, 135.20, 133.87, 129.32, 129.24, 129.18, 128.98, 128.58, 123.14, 122.95, 47.65, 42.71, 40.94, 21.38. HR-EI-MS (positive) *m/z* 389.1157 $[M+Na]^+$ (calcd for $C_{24}H_{16}O_3Na$ 389.1154).



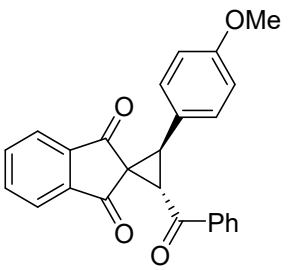
(2S,3R)-2-benzoyl-3-(2-methoxyphenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3ae**)

White solid, 79%, m.p. = 118-119°C, d.r.= >20:1; IR (KBr) ν_{max} = 3003, 2939, 2837, 1705, 1683, 1279, 1252, 754, 744 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96-7.95 (m, 2H), 7.91-7.86 (m, 2H), 7.79-7.77 (m, 2H), 7.54-7.50 (m, 1H), 7.41-7.37 (m, 3H), 7.32-7.27 (m, 1H), 7.02-6.96 (m, 1H), 6.76-6.74 (m, 1H), 4.11 (d, 1H, *J*= 9.5 Hz), 4.03 (d, 1H, *J*= 9.5 Hz), 3.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.19, 194.02, 191.33, 158.10, 142.07, 142.04, 136.41, 134.92, 134.88, 133.72, 130.04, 129.59, 128.89, 128.50, 122.98, 122.44, 121.99, 120.53, 110.08, 54.96, 46.44, 40.82, 37.81. HR-EI-MS (positive) *m/z* 405.1107 $[M+Na]^+$ (calcd for $C_{25}H_{18}O_4Na$ 405.1103).



(2S,3R)-2-benzoyl-3-(3-methoxyphenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3af**)

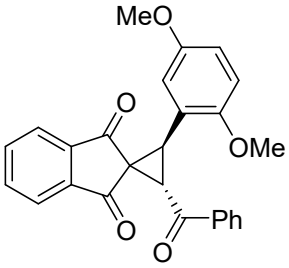
White solid, 97%, m.p. = 99-101°C, d.r.= >20:1; IR (KBr) ν_{max} = 3059, 2943, 2840, 1705, 1680, 1592, 1254, 1224, 1036, 764, 732, 689 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96-7.93 (m, 2H), 7.90-7.88 (m, 2H), 7.79-7.77 (m, 2H), 7.55-7.51 (m, 1H), 7.42-7.38 (m, 2H), 7.27-7.23 (m, 1H), 6.94-6.83 (m, 3H), 4.27 (d, 1H, *J*= 9.5 Hz), 4.20 (d, 1H, *J*= 9.5 Hz), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.48, 194.16, 190.64, 159.63, 142.11, 136.23, 135.34, 135.27, 133.99, 133.87, 129.46, 128.55, 123.15, 122.98, 121.61, 115.09, 113.76, 55.36, 47.49, 42.52, 41.01. HR-EI-MS (positive) *m/z* 405.1107 $[M+Na]^+$ (calcd for $C_{25}H_{18}O_4Na$ 405.1103).



(2S,3R)-2-benzoyl-3-(4-methoxyphenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3ag**)

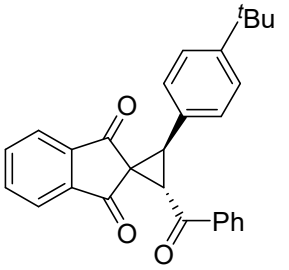
White solid, 59%, m.p. = 103-105°C, d.r.= >20:1; IR (KBr) ν_{max} = 3065, 2959, 2923, 1704, 1518, 1449, 1260, 1086, 1030, 804, 735 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96-7.94 (m, 2H), 7.89-7.86 (m, 2H), 7.79-

7.74 (m, 2H), 7.55-7.51 (m, 1H), 7.42-7.38 (m, 2H), 7.31-7.29 (m, 2H), 6.88-6.85 (m, 2H), 4.27 (d, 1H, *J*= 9.5 Hz), 4.16 (d, 1H, *J*= 9.5 Hz), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.59, 194.42, 190.82, 159.58, 142.21, 142.07, 136.26, 135.29, 135.19, 133.89, 130.46, 128.99, 128.58, 124.28, 123.13, 122.92, 113.92, 55.38, 47.85, 42.74, 41.06. HR-EI-MS (positive) *m/z* 405.1107 $[M+Na]^+$ (calcd for $C_{25}H_{18}O_4Na$ 405.1103).



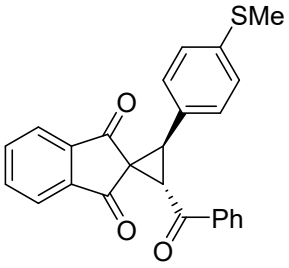
(2S,3R)-2-benzoyl-3-(2,5-dimethoxyphenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3ah**)

White solid, 96%, m.p. = 34-36°C, d.r.= >20:1; IR (KBr) ν_{max} = 3094, 2939, 2836, 1704, 1672, 1497, 1279, 1051, 801, 724 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 2H), 7.91-7.87 (m, 2H), 7.80-7.76 (m, 2H), 7.54-7.51 (m, 1H), 7.42-7.38 (m, 2H), 6.95-6.84 (m, 1H), 6.83-6.80 (m, 1H), 6.68-6.65 (m, 1H), 4.07 (d, 1H, *J*= 9.5 Hz), 4.00 (d, 1H, *J*= 9.5 Hz), 3.79 (s, 3H), 3.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.15, 194.00, 191.31, 153.53, 152.33, 142.20, 142.06, 136.42, 134.96, 134.89, 133.77, 128.94, 128.55, 123.06, 123.00, 122.48, 116.43, 114.02, 110.93, 55.94, 55.38, 46.46, 40.96, 37.67. HR-EI-MS (positive) *m/z* 435.1207 $[M+Na]^+$ (calcd for $C_{26}H_{20}O_5Na$ 435.1208).



(2S,3R)-2-benzoyl-3-(4-isopropylphenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3ai**)

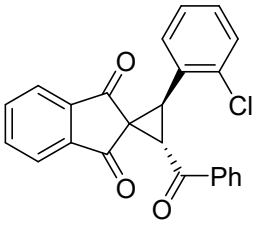
White solid, 85%, m.p. = 98-100°C, d.r.= >20:1; IR (KBr) ν_{max} = 3059, 2921, 2850, 1705, 1594, 1448, 1278, 1222, 1089, 743, 726 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.94 (m, 2H), 7.90-7.88 (m, 2H), 7.79-7.75 (m, 2H), 7.55-7.51 (m, 1H), 7.42-7.30 (m, 6H), 4.28 (d, 1H, *J*= 9.5 Hz), 4.16 (d, 1H, *J*= 9.5 Hz), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.61, 194.37, 190.80, 151.27, 142.17, 136.33, 135.28, 135.18, 133.84, 129.42, 128.98, 128.60, 125.47, 123.15, 122.96, 47.82, 42.90, 41.21, 34.75. HR-EI-MS (positive) *m/z* 431.1622 $[M+Na]^+$ (calcd for $C_{28}H_{24}O_3Na$ 431.1623).



(2S,3R)-2-benzoyl-3-(4-(methylthio)phenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3aj**)

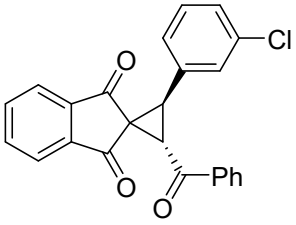
White solid, 59%, m.p. = 124-126°C, d.r.= >20:1; IR (KBr) ν_{max} = 3048, 2987, 2924, 2852, 1704, 1678, 1594, 1282, 1228, 1084, 817, 752, 736 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.93 (m, 2H), 7.90-7.87 (m, 2H), 7.80-7.75 (m, 2H), 7.55-7.51 (m, 1H), 7.42-7.38 (m, 2H), 7.30-7.26 (m, 2H), 7.21-7.19 (m, 2H), 4.26 (d, 1H, *J*= 9.5 Hz), 4.17 (d, 1H, *J*= 9.5 Hz), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.37, 194.25, 190.61, 142.18, 142.05, 138.93, 136.23, 135.37, 135.27,

133.91, 129.69, 128.99, 128.56, 126.28, 123.17, 122.95, 47.66, 42.40, 40.87, 15.67. HR-EI-MS (positive) *m/z* 421.0873 $[M+Na]^+$ (calcd for $C_{25}H_{18}O_3SNa$ 421.0874).



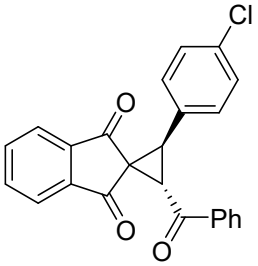
(2S,3S)-2-benzoyl-3-(2-chlorophenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3ak**)

White solid, 94%, m.p. = 83-85°C, d.r.= >20:1; IR (KBr) ν_{max} = 3065, 2922, 2850, 1706, 1688, 1449, 1280, 753, 737 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95-7.88 (m, 4H), 7.81-7.76 (m, 2H), 7.55-7.51 (m, 1H), 7.48-7.46 (m, 1H), 7.41-7.38 (m, 2H), 7.35-7.28 (m, 3H), 4.21-4.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.31, 194.01, 190.55, 142.08, 141.75, 136.14, 135.96, 135.37, 135.28, 133.94, 131.51, 130.66, 129.63, 129.33, 128.99, 128.47, 126.87, 123.18, 122.91, 46.33, 40.62, 39.36. HR-EI-MS (positive) *m/z* 409.0606 $[M+Na]^+$ (calcd for $C_{24}H_{15}O_3ClNa$ 409.0607).



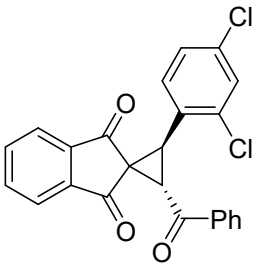
(2S,3R)-2-benzoyl-3-(3-chlorophenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3al**)

White solid, 73%, m.p. =103-105°C, d.r.= >20:1; IR (KBr) ν_{max} = 3068, 2925, 2856, 1707, 1686, 1595, 1277, 1216, 733, 689 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94-7.88 (m, 4H), 7.81-7.79 (m, 2H), 7.56-7.52 (m, 1H), 7.42-7.36 (m, 3H), 7.29-7.24 (m, 3H), 4.25 (d, 1H, *J*= 9.5 Hz), 4.18 (d, 1H, *J*= 9.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.10, 194.06, 190.26, 142.13, 142.00, 136.08, 135.56, 135.44, 134.54, 134.42, 134.01, 129.70, 129.53, 129.03, 128.53, 127.48, 123.29, 123.11, 47.16, 41.14, 40.63. HR-EI-MS (positive) *m/z* 409.0606 $[M+Na]^+$ (calcd for $C_{24}H_{15}O_3ClNa$ 409.0607).



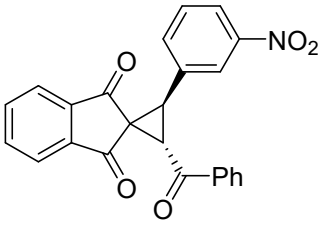
(2S,3R)-2-benzoyl-3-(4-chlorophenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3am**)

White solid, 61%, m.p. = 110-111°C, d.r.= >20:1; IR (KBr) ν_{max} = 3063, 2923, 2852, 1706, 1596, 1468, 1289, 1220, 734 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.93-7.89 (m, 4H), 7.80-7.78 (m, 2H), 7.56-7.52 (m, 1H), 7.42-7.33 (m, 2H), 7.30 (s, 4H), 4.25 (d, 1H, *J*= 9.5 Hz), 4.18 (d, 1H, *J*= 9.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.19, 194.17, 190.35, 142.13, 141.96, 136.09, 135.53, 135.40, 134.23, 134.00, 130.97, 130.64, 129.02, 128.72, 128.52, 123.26, 123.03, 47.31, 41.38, 40.76. HR-EI-MS (positive) *m/z* 409.0606 $[M+Na]^+$ (calcd for $C_{24}H_{15}O_3ClNa$ 409.0607).



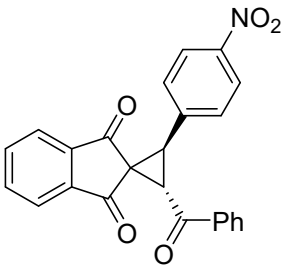
(2S,3S)-2-benzoyl-3-(2,4-dichlorophenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3an**)

White solid, 70%, m.p. = 120-121°C, d.r.= >20:1; IR (KBr) ν_{max} = 3074, 2920, 2848, 1705, 1684, 1291, 1205, 736, 695, 574 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92-7.89 (m, 4H), 7.83-7.78 (m, 2H), 7.55-7.52 (m, 1H), 7.42-7.38 (m, 3H), 7.32-7.29 (m, 2H), 4.15 (d, 1H, *J*= 9.5 Hz), 4.12 (d, 1H, *J*= 9.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.98, 193.94, 190.24, 142.06, 141.65, 136.58, 136.04, 135.55, 135.42, 134.89, 134.05, 131.47, 130.24, 129.31, 129.03, 128.46, 127.27, 123.28, 122.98, 46.18, 40.50, 38.42. HR-EI-MS (positive) *m/z* 443.0216 $[M+Na]^+$ (calcd for $C_{24}H_{14}O_3Cl_2Na$ 443.0218).



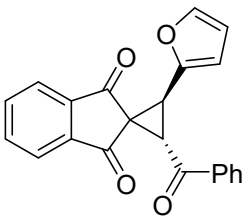
(2S,3R)-2-benzoyl-3-(3-nitrophenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3ao**)

White solid, 60%, m.p. = 119-121°C, d.r.= >20:1; IR (KBr) ν_{max} = 3067, 2918, 2850, 1700, 1677, 1530, 1351, 1281, 754, 742, 731 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.25-8.17 (m, 2H), 7.93-7.88 (m, 4H), 7.85-7.80 (m, 2H), 7.71-7.69 (m, 1H), 7.57-7.51 (m, 2H), 7.43-7.39 (m, 2H), 4.31 (d, 1H, *J*= 9.5 Hz), 4.28 (d, 1H, *J*= 9.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.05, 193.62, 189.81, 148.28, 142.16, 141.87, 135.95, 135.84, 135.64, 135.45, 134.78, 134.17, 129.47, 129.10, 128.52, 124.39, 123.45, 123.27, 123.18, 46.86, 40.54, 39.97. HR-EI-MS (positive) *m/z* 420.3758 $[M+Na]^+$ (calcd for $C_{24}H_{15}O_5NNa$ 420.3758).



(2S,3R)-2-benzoyl-3-(4-nitrophenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3ap**)

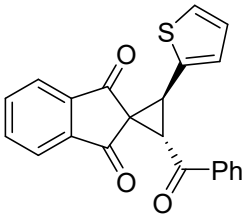
White solid, 83%, m.p. = 165-167°C, d.r.= >20:1; IR (KBr) ν_{max} = 3028, 2956, 2924, 2853, 1703, 1678, 1518, 1344, 1280, 1077, 792, 729 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.22-8.20 (m, 2H), 7.93-7.89 (m, 4H), 7.85-7.80 (m, 2H), 7.58-7.54 (m, 3H), 7.43-7.39 (m, 2H), 4.29 (d, 1H, *J*= 9.5 Hz), 4.27 (d, 1H, *J*= 9.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.97, 193.58, 189.79, 147.73, 142.14, 141.87, 140.08, 135.94, 135.89, 135.69, 134.22, 130.35, 129.13, 128.52, 123.71, 123.48, 123.22, 47.10, 40.68, 40.23. HR-EI-MS (positive) *m/z* 420.3758 $[M+Na]^+$ (calcd for $C_{24}H_{15}O_5NNa$ 420.3758).



(2S,3S)-2-benzoyl-3-(furan-2-yl)spiro[cyclopropane-1,2'-indene]-1',3'-dione（**3aq**）

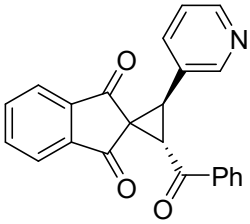
Yellow oil, 44%, d.r.= >20:1; IR (KBr) ν_{max} = 3068, 2926, 1710, 1595, 1448, 1278, 1225, 731, 693 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95-7.93 (m, 2H), 7.89-7.87 (m, 2H), 7.80-7.76 (m, 2H), 7.56-7.52 (m, 1H), 7.42-7.37 (m, 3H), 6.44-6.38 (m, 2H), 4.22 (d, 1H, *J*= 9.5 Hz), 4.07 (d, 1H, *J*= 9.5 Hz); ^{13}C NMR (100

MHz, $CDCl_3$) δ 193.80, 193.49, 189.96, 147.25, 142.98, 142.17, 142.03, 136.07, 135.41, 135.34, 133.98, 129.00, 128.58, 123.22, 123.06, 110.92, 110.04, 46.20, 40.01, 34.35. HR-EI-MS (positive) *m/z* 365.0792 $[M+Na]^+$ (calcd for $C_{22}H_{14}O_4Na$ 365.0790).



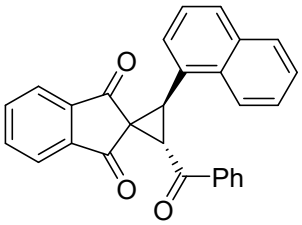
(2S,3S)-2-benzoyl-3-(thiophen-2-yl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3ar**)

Yellow solid, 34%, m.p. = 112-114°C, d.r.= 20:7; IR (KBr) ν_{max} = 3064, 2913, 1706, 1678, 1594, 1283, 1221, 1002, 734, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95-7.90 (m, 2H), 7.89-7.87 (m, 2H), 7.80-7.76 (m, 2H), 7.56-7.52 (m, 1H), 7.43-7.39 (m, 2H), 7.27-7.25 (m, 1H), 7.14-7.12 (m, 1H), 7.01-6.99 (m, 1H), 4.27 (d, 1H, *J*= 9.5 Hz), 4.23 (d, 1H, *J*= 9.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.94, 193.50, 190.06, 142.17, 142.01, 136.07, 135.42, 135.41, 135.35, 133.97, 129.00, 128.58, 128.04, 127.12, 126.11, 123.20, 123.05, 47.61, 42.33, 37.24. HR-EI-MS (positive) *m/z* 381.0560 $[M+Na]^+$ (calcd for $C_{22}H_{14}O_3SNa$ 381.0561).



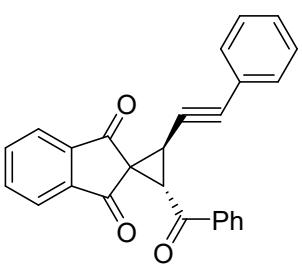
(2S,3R)-2-benzoyl-3-(pyridin-3-yl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3as**)

Yellow oil, 76%, d.r.= 20:4; IR (KBr) ν_{max} = 3065, 2907, 2850, 1707, 1541, 1231, 731 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.52-8.50 (m, 1H), 7.89-7.73 (m,7H), 7.52-7.48 (m, 1H), 7.38-7.27 (m, 3H), 4.26 (d, 1H, *J*= 9.5 Hz), 4.16 (d, 1H, *J*= 9.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.95, 193.73, 189.95, 150.35, 148.85, 142.05, 141.81, 136.81, 135.95, 135.64, 135.48, 134.00, 128.97, 128.41, 123.26, 123.04, 46.64, 40.08, 38.55. HR-EI-MS (positive) *m/z* 376.0952 $[M+Na]^+$ (calcd for $C_{23}H_{15}O_3NNa$ 376.0950).



(2S,3R)-2-benzoyl-3-(naphthalen-1-yl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3at**)

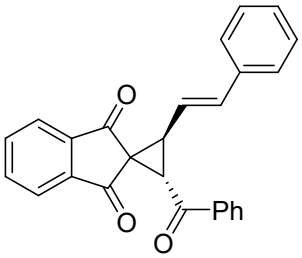
White solid, 42%, m.p. = 62-64°C, d.r.= 20:4; IR (KBr) ν_{max} = 3065, 1707, 1595, 1282, 1221, 776, 737 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.01-7.95 (m, 3H), 7.86-7.73 (m, 5H), 7.66-7.64 (m, 1H), 7.59-7.49 (m, 3H), 7.44-7.38 (m, 3H), 7.29-7.24 (m, 1H), 4.62 (d, 1H, *J*= 9.5 Hz), 4.41 (d, 1H, *J*= 9.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.98, 193.79, 190.95, 142.08, 141.83, 136.35, 135.37, 135.33, 133.95, 133.69, 132.92, 129.19, 129.07, 129.04, 128.87, 128.60, 126.88, 126.81, 125.99, 125.22, 123.19, 123.00, 47.02, 41.13, 39.83. HR-EI-MS (positive) *m/z* 425.1153 $[M+Na]^+$ (calcd for $C_{28}H_{18}O_3Na$ 425.1154).



(2S,3R)-2-benzoyl-3-(phenylethynyl)spiro[cyclopropane-1,2'-indene]-

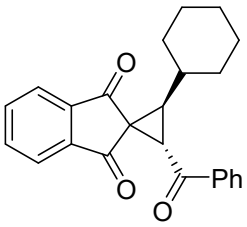
1',3'-dione (**3au**)

Yellow oil, 71%, d.r.= >20:1; IR (KBr) ν_{max} = 3060, 2919, 2850, 2183, 1695, 1690, 1353, 1219, 967, 734 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.07-8.05 (m, 1H), 7.94-7.78 (m, 5H), 7.56-7.52 (m, 1H), 7.49-7.47 (m, 2H), 7.43-7.39 (m, 2H), 7.32-7.29 (m, 3H), 3.98 (d, 1H, *J*= 9.5 Hz), 3.64 (d, 1H, *J*= 9.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.26, 192.62, 189.26, 142.12, 142.11, 135.82, 135.43, 135.40, 133.92, 131.99, 128.90, 128.57, 128.47, 128.30, 123.20, 123.13, 122.42, 84.22, 82.78, 45.42, 42.62, 25.95. HR-EI-MS (positive) *m/z* 399.0996 $[M+Na]^+$ (calcd for $C_{26}H_{16}O_3Na$ 399.0997).



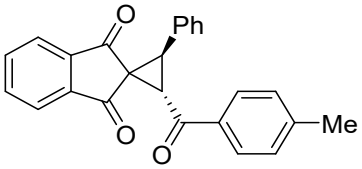
(2S,3S)-2-benzoyl-3-((E)-styryl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3av**)

Yellow oil, 60%, d.r.= >20:1; IR (KBr) ν_{max} = 2956, 2918, 2850, 1719, 1682, 1578, 1468, 977, 734 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.01-7.99 (m, 1H), 7.93-7.87 (m, 3H), 7.83-7.76 (m, 2H), 7.55-7.51 (m, 1H), 7.43-7.38(m, 4H), 7.34-7.30 (m, 2H), 7.25-7.23 (m, 2H), 6.81-6.77 (m, 1H), 6.56-6.49 (m, 1H), 3.92 (d, 1H, *J*= 9.5 Hz), 3.74 (dd, 1H, *J*= 9.5 Hz, *J*= 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.52, 194.22, 190.38, 142.52, 141.95, 136.43, 136.26, 135.48, 135.46, 135.24, 133.87, 128.97, 128.79, 128.62, 128.17, 126.58, 123.20, 122.96, 122.47, 47.11, 43.26, 42.11. HR-EI-MS (positive) *m/z* 401.1153 $[M+Na]^+$ (calcd for $C_{26}H_{18}O_3Na$ 401.1154).



(2S,3S)-2-benzoyl-3-cyclohexylspiro[cyclopropane-1,2'-indene]-1',3'-dione (**3aw**)

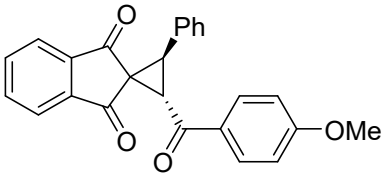
White solid, 88%, m.p. = 91-93°C, d.r. = 20:3; IR (KBr) ν_{max} = 3067, 2924, 2848, 1702, 1672, 1288, 1220, 757, 738 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.01-7.98 (m, 1H), 7.86-7.74 (m, 6H), 7.49-7.45 (m, 1H), 7.36-7.30 (m, 2H), 3.66 (d, 1H, *J*= 9.5 Hz), 2.86 (dd, 1H, *J*= 9.5 Hz, *J*= 8.5 Hz), 1.90-1.86 (m, 3H), 1.80-1.75 (m, 2H), 1.34-1.24 (3H), 1.21-1.03 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.61, 195.20, 191.09, 141.76, 136.36, 135.36, 135.06, 133.57, 128.79, 128.33, 123.06, 122.69, 45.65, 45.41, 43.36, 34.82, 33.31, 32.44, 26.12, 25.85, 25.66. HR-EI-MS (positive) *m/z* 381.1462 $[M+Na]^+$ (calcd for $C_{24}H_{22}O_3Na$ 381.1467).



(2S,3R)-2-(4-methylbenzoyl)-3-phenylspiro[cyclopropane-1,2'-indene]-1',3'-dione (**3ba**)

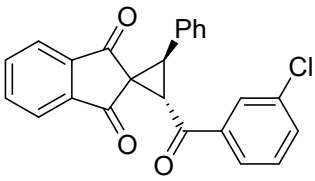
White solid, 94%, m.p. = 134-136°C, d.r.= 20:2; IR (KBr) ν_{max} = 3022, 2923, 2850, 1707, 1678, 1509, 1283, 1221, 1011, 826, 745, 697 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.90-7.86 (m, 4H), 7.80-7.75 (m, 2H), 7.37-7.30 (m, 5H),

7.20-7.18 (m, 2H), 4.28 (d, 1H, *J*= 9.5 Hz), 4.23 (d, 1H, *J*= 9.5 Hz), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.54, 194.41, 190.25, 144.88, 142.17, 142.07, 135.31, 135.21, 133.82, 132.55, 129.68, 129.34, 128.67, 128.48, 128.27, 123.16, 122.95, 47.49, 42.59, 40.99, 21.84. HR-EI-MS (positive) *m/z* 389.1150 $[M+Na]^+$ (calcd for $C_{25}H_{18}O_3Na$ 389.1154).



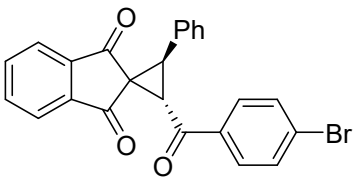
(2S,3R)-2-(4-methoxybenzoyl)-3-phenylspiro[cyclopropane-1,2'-indene]-1',3'-dione (**3ca**)

White solid, 36%, m.p. = 126-128°C, d.r.= >20:1; IR (KBr) ν_{max} = 3065, 2922, 2852, 1705, 1674, 1601, 1252, 1171, 1068, 842, 745 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.86 (m, 4H), 7.79-7.75 (m, 2H), 7.38-7.30 (m, 5H), 6.86-6.84 (m, 2H), 4.26 (d, 1H, *J*= 9.5 Hz), 4.22 (d, 1H, *J*= 9.5 Hz), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.57, 194.45, 189.08, 164.10, 142.15, 142.03, 135.29, 135.18, 132.57, 130.85, 129.40, 129.31, 128.45, 128.23, 123.12, 122.90, 114.16, 55.60, 47.46, 42.66, 41.00. HR-EI-MS (positive) *m/z* 405.1100 $[M+Na]^+$ (calcd for $C_{25}H_{18}O_4Na$ 405.1103).



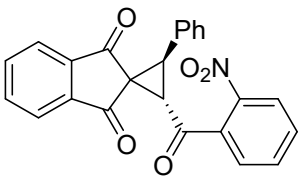
(2S,3R)-2-(3-chlorobenzoyl)-3-phenylspiro[cyclopropane-1,2'-indene]-1',3'-dione (**3da**)

White solid, 58%, m.p. = 112-114°C, d.r.= 20:2; IR (KBr) ν_{max} = 3065, 2920, 2853, 1704, 1602, 1435, 1277, 1096, 804, 740, 698 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.87 (m, 3H), 7.82-7.77 (m, 3H), 7.52-7.49 (m, 1H), 7.36-7.31 (m, 6H), 4.25 (d, 1H, *J*= 9.5 Hz), 4.21 (d, 1H, *J*= 9.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.42, 193.96, 189.65, 142.07, 142.04, 137.70, 135.48, 135.47, 135.42, 133.88, 132.14, 130.30, 129.29, 128.55, 128.42, 126.61, 123.23, 123.09, 47.44, 42.39, 40.40. HR-EI-MS (positive) *m/z* 409.0606 $[M+Na]^+$ (calcd for $C_{24}H_{15}O_3ClNa$ 409.0607).



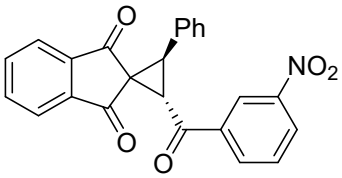
(2S,3R)-2-(4-bromobenzoyl)-3-phenylspiro[cyclopropane-1,2'-indene]-1',3'-dione (**3ea**)

White solid, 89%, m.p. = 156-158°C, d.r.= >20:1; IR (KBr) ν_{max} = 2923, 2853, 1703, 1684, 1584, 1282, 1213, 1066, 832, 792, 751 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.86 (m, 2H), 7.83-7.77 (m, 4H), 7.56-7.54 (m, 1H), 7.35-7.31 (m, 5H), 4.23 (d, 1H, *J*= 9.5 Hz), 4.19 (d, 1H, *J*= 9.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.44, 194.11, 189.90, 142.06, 135.49, 135.41, 134.95, 132.37, 132.20, 129.97, 129.29, 128.56, 128.42, 123.25, 123.06, 47.44, 42.50, 40.49. HR-EI-MS (positive) *m/z* 453.0100 $[M+Na]^+$ (calcd for $C_{24}H_{15}O_3BrNa$ 453.0102).



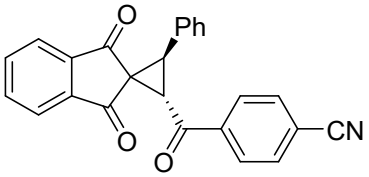
(2S,3R)-2-(2-nitrobenzoyl)-3-phenylspiro[cyclopropane-1,2'-indene]-1',3'-dione (**3fa**)

White solid, 31%, m.p. = 117-119°C, d.r.= >20:1; IR (KBr) ν_{max} = 3022, 2924, 2850, 1709, 1524, 1346, 1289, 792, 748, 711 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.15-8.12 (m, 1H), 8.00-7.98 (m, 1H), 7.85-7.74 (m, 4H), 7.65-7.61 (m, 2H), 7.32-7.22 (m, 5H), 4.13 (d, 1H, *J*= 9.5 Hz), 3.96 (d, 1H, *J*= 9.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.52, 193.98, 193.15, 146.00, 142.10, 141.99, 136.62, 135.57, 135.41, 134.85, 131.74, 131.34, 129.79, 129.18, 128.60, 128.45, 124.35, 123.18, 123.07, 48.23, 43.32, 42.22. HR-EI-MS (positive) *m/z* 420.0847 $[M+Na]^+$ (calcd for $C_{24}H_{15}O_5NNa$ 420.0848).



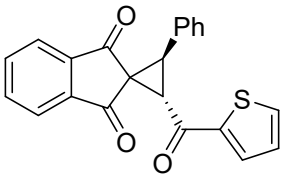
(2S,3R)-2-(3-nitrobenzoyl)-3-phenylspiro[cyclopropane-1,2'-indene]-1',3'-dione (**3ga**)

White solid, 71%, m.p. = 142-144°C, d.r.= >20:1; IR (KBr) ν_{max} = 3066, 2924, 1702, 1686, 1532, 1352, 1275, 745, 725, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.79-8.78 (m, 1H), 8.41-8.38 (m, 1H), 8.25-8.22 (m, 1H), 7.93-7.87 (m, 4H), 7.65-7.61 (m, 1H), 7.38-7.34 (m, 5H), 4.27 (d, 1H, *J*= 9.5 Hz), 4.21 (d, 1H, *J*= 9.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.30, 193.45, 189.00, 148.60, 141.97, 141.85, 137.37, 135.50, 135.47, 133.73, 131.70, 130.22, 129.14, 128.52, 128.46, 127.93, 123.24, 123.12, 47.32, 42.25, 39.99. HR-EI-MS (positive) *m/z* 420.0847 $[M+Na]^+$ (calcd for $C_{24}H_{15}O_5NNa$ 420.0848).



4-((2S,3R)-1',3'-dioxo-3-phenyl-1',3'-dihydrospiro[cyclopropane-1,2'-indene]-2-carbonyl)benzonitrile (**3ha**)

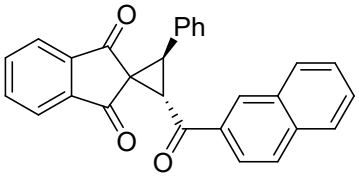
White solid, 97%, m.p. = 171-173°C, d.r.= >20:1; IR (KBr) ν_{max} = 3065, 2922, 2853, 2228, 1704, 1689, 1591, 1282, 1216, 1099, 840, 753 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.04-8.01 (m, 2H), 7.91-7.87 (m, 2H), 7.83-7.80 (m, 2H), 7.73-7.70 (m, 2H), 7.35 (m, 5H), 4.24 (d, 1H, *J*= 9.5 Hz), 4.19 (d, 1H, *J*= 9.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.35, 193.73, 189.87, 142.07, 141.98, 139.05, 135.63, 135.60, 132.90, 131.85, 129.25, 128.87, 128.58, 123.29, 123.18, 117.85, 117.12, 47.50, 42.44, 40.16. HR-EI-MS (positive) *m/z* 400.0952 $[M+Na]^+$ (calcd for $C_{25}H_{15}O_3NNa$ 400.0950).



(2S,3R)-2-phenyl-3-(thiophene-2-carbonyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**3ia**)

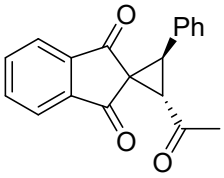
White solide, 66%, m.p. =120-121°C, d.r.= >20:1; IR (KBr) ν_{max} = 3084, 2962, 1703, 1660, 1411, 1236, 1054, 858, 764, 731, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94-7.92 (m, 2H), 7.89-7.78 (m, 2H), 7.68-7.62 (m, 2H), 7.37-7.28 (m, 6H),

7.06-7.04 (m, 1H), 4.23 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.42, 194.12, 183.38, 143.35, 142.17, 142.02, 135.38, 135.29, 134.72, 132.83, 132.28, 130.56, 129.28, 128.51, 128.45, 128.33, 127.97, 123.21, 122.99, 47.28, 42.27, 41.44. HR-EI-MS (positive) *m/z* 381.0566 $[M+Na]^+$ (calcd for $C_{22}H_{14}O_3SNa$ 381.0561).



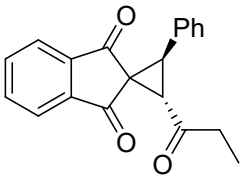
(2S,3R)-2-(2-naphthoyl)-3-phenylspiro[cyclopropane-1,2'-indene]-1',3'-dione (**3ja**)

White solid, 95%, m.p. =91-93°C, d.r.= 20:2; IR (KBr) ν_{max} = 3065, 2919, 1704, 1671, 1286, 757, 746, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.05-8.03 (m, 1H), 7.92-7.73 (m, 8H), 7.60-7.55 (m, 1H), 7.55-7.47 (m, 1H), 7.43-7.29 (m, 5H), 4.46 (d, 1H, *J*= 9.5 Hz), 4.31 (d, 1H, *J*= 9.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.51, 194.37, 190.62, 142.15, 142.04, 135.98, 135.36, 135.26, 133.65, 132.50, 130.49, 129.86, 129.36, 128.95, 128.52, 128.33, 127.91, 127.01, 123.96, 123.19, 122.97, 47.59, 42.61, 40.94. HR-EI-MS (positive) *m/z* 425.1154 $[M+Na]^+$ (calcd for $C_{28}H_{18}O_3Na$ 425.1154).



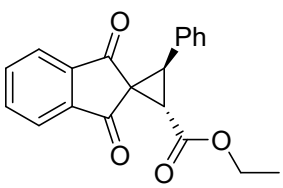
(2S,3R)-2-acetyl-3-phenylspiro[cyclopropane-1,2'-indene]-1',3'-dione (**3ka**)

White solid, 67%, m.p. = 131-133°C, d.r.= >20:1; IR (KBr) ν_{max} = 3050, 2920, 2850, 1711, 1597, 1292, 1170, 756, 698 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.97 (m, 1H), 7.85-7.76 (m, 3H), 7.33-7.28 (m, 5H), 4.04 (d, 1H, *J*= 9.5 Hz), 3.70 (d, 1H, *J*= 9.5 Hz), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.79, 195.12, 193.73, 142.07, 141.97, 135.42, 135.34, 132.20, 129.23, 128.44, 128.31, 123.09, 123.02, 47.19, 44.04, 42.63, 30.41. HR-EI-MS (positive) *m/z* 313.0844 $[M+Na]^+$ (calcd for $C_{19}H_{14}O_3Na$ 313.0841).



(2S,3R)-2-phenyl-3-propionylspiro[cyclopropane-1,2'-indene]-1',3'-dione (**3la**)

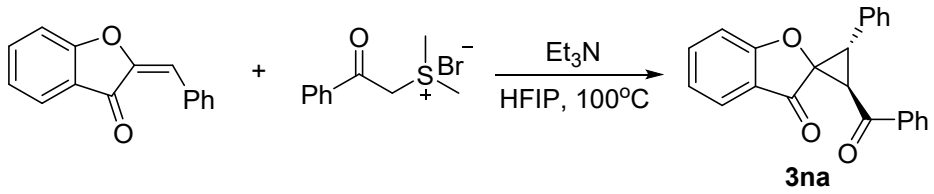
White solid, 95%, m.p. =131-133°C, d.r.= >20:1; IR (KBr) ν_{max} = 3062, 2944, 2928, 1719, 1702, 1594, 1287, 1099, 749 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.96 (m, 1H), 7.85-7.76 (m, 3H), 7.33-7.27 (m, 4H), 4.06 (d, 1H, *J*= 9.5 Hz), 3.69 (d, 1H, *J*= 9.5 Hz), 2.80-2.68 (m, 1H), 2.60-2.48 (m, 1H), 1.11 (t, 3H, *J*= 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.34, 195.17, 193.92, 142.04, 141.97, 135.35, 135.30, 132.33, 129.23, 128.41, 128.25, 123.05, 122.97, 47.10, 43.23, 42.26, 36.51, 7.73. HR-EI-MS (positive) *m/z* 327.0999 $[M+Na]^+$ (calcd for $C_{20}H_{16}O_3Na$ 327.0997).



Ethyl (2S,3R)-1',3'-dioxo-3-phenyl-1',3'-dihydrospiro[cyclopropane-1,2'-indene]-2-carboxylate (**3ma**)

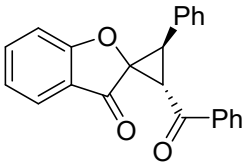
Yellow oil, 45%, d.r. = 20:9; IR (KBr) ν_{max} = 2955, 2924, 2850, 1732, 1709, 1595, 1464, 1288, 1195, 1021, 749, 695 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 6.5 Hz, 1H), 7.84-7.76 (m, 3H), 7.33-7.28 (m, 5H), 4.32-4.21 (m, 2H), 4.01 (d, *J* = 8.7 Hz, 1H), 3.59 (d, *J* = 8.7 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.79, 193.57, 166.49, 142.05, 135.16, 135.13, 132.00, 129.13, 128.29, 128.12, 122.89, 61.82, 45.77, 42.16, 36.73, 14.14. HR-EI-MS (positive) *m/z* 327.0999 $[M+Na]^+$ (calcd for $C_{20}H_{16}O_3Na$ 327.0997).

Preparation of compound 3na



3na

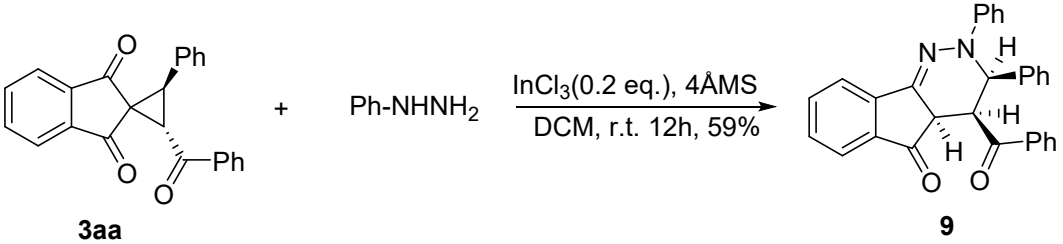
Under a Ar atmosphere, to a solution of 2-benzylidenebenzofuran-3(2H)-one (0.22 mmol) and dimethyl(2-oxo-2-phenylethyl)sulfonium bromide (0.26 mmol) in HFIP (2.0 mL) was added Et_3N (0.03 mL, 0.26 mmol). The resulting mixture was stirred at 100°C for a specified time. The reaction was monitored by TLC spectroscopy. After the reaction was completed, the solvent was then removed on a rotary evaporator at reduced pressure and the residue was subjected to column chromatographic isolation on silica gel (eluted with petroleum ether/EtOAc 50:1-20:1) to give the annulation product **3na**.



(2'S,3'R)-2'-benzoyl-3'-phenyl-3H-spiro[benzofuran-2,1'-cyclopropan]-3-one (**3na**)

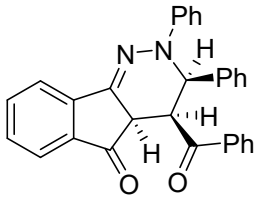
Yellow solid, 31%, m.p. = 103-104°C, d.r. = 20:18; IR (KBr) ν_{max} = 2959, 2922, 2852, 1710, 1460, 740 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95-7.93 (m, 2H), 7.64-7.51 (m, 3H), 7.42-7.33 (m, 8H), 7.19-7.10 (m, 2H), 3.97 (d, 1H, *J*= 9.5 Hz), 3.90 (d, 1H, *J*= 9.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.87, 189.90, 170.78, 137.13, 136.44, 133.75, 133.25, 128.93, 128.89, 128.71, 128.51, 127.86, 124.32, 122.79, 121.44, 113.54, 39.58, 35.97. HR-EI-MS (positive) *m/z* 363.0997 $[M+Na]^+$ (calcd for $C_{23}H_{16}O_3Na$ 363.0997).

Transformations of 3aa to Indeno[1,2-c]Pyridazine Derivatives



3aa **9**

A round-bottom flask equipped with a magnetic stir bar was charged with 4 Å MS (200 wt %) and $InCl_3$ (0.2 equiv) under Ar inert atmosphere. A DCM solution of 2-benzoyl-3-phenylspiro[cyclopropane-1,2'-indene]-1',3'-dione **3aa** (1 equiv) and aryl hydrazine (1 equiv) was added, and the mixture was stirred at room temperature until completion of the reaction (as monitored by TLC). The reaction mixture was filtered through a small pad of Celite that was subsequently washed with multiple small portions of DCM, and the solvent was evaporated on a rotary evaporator. The crude mixture was further purified by column chromatography on silica gel with ethyl acetate/hexane as an eluent.



4-benzoyl-2,3-diphenyl-2,3,4,4a-tetrahydro-5H-indeno[1,2-c]pyridazin-5-one (**9**)

Yellow oil, 57%; IR (KBr) ν_{max} = 3195, 2918, 2849, 1708, 1595, 1493, 1390, 1248, 747, 692 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.01-7.99 (m, 1H), 7.85-7.76 (m, 4H), 7.68-7.66 (m, 2H), 7.32-7.23 (m, 9H), 7.14-7.11 (m, 5H), 6.96-6.94 (m, 2H), 6.77-6.74 (m, 1H), 4.95 (d, 1H, *J*= 4.4 Hz), 4.00 (t, 1H, *J*= 3.9 Hz), 3.50 (d, 1H, *J*= 3.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.37, 196.74, 146.27, 143.72, 143.16, 142.53, 140.60, 136.16, 135.91, 131.80, 129.37, 129.02, 128.78, 128.08, 126.53, 125.72, 123.54, 123.30, 119.37, 113.31, 67.81, 54.59, 54.08. HR-EI-MS (positive) *m/z* 465.1577 $[M+Na]^+$ (calcd for $C_{30}H_{22}O_2N_2Na$ 465.1579).

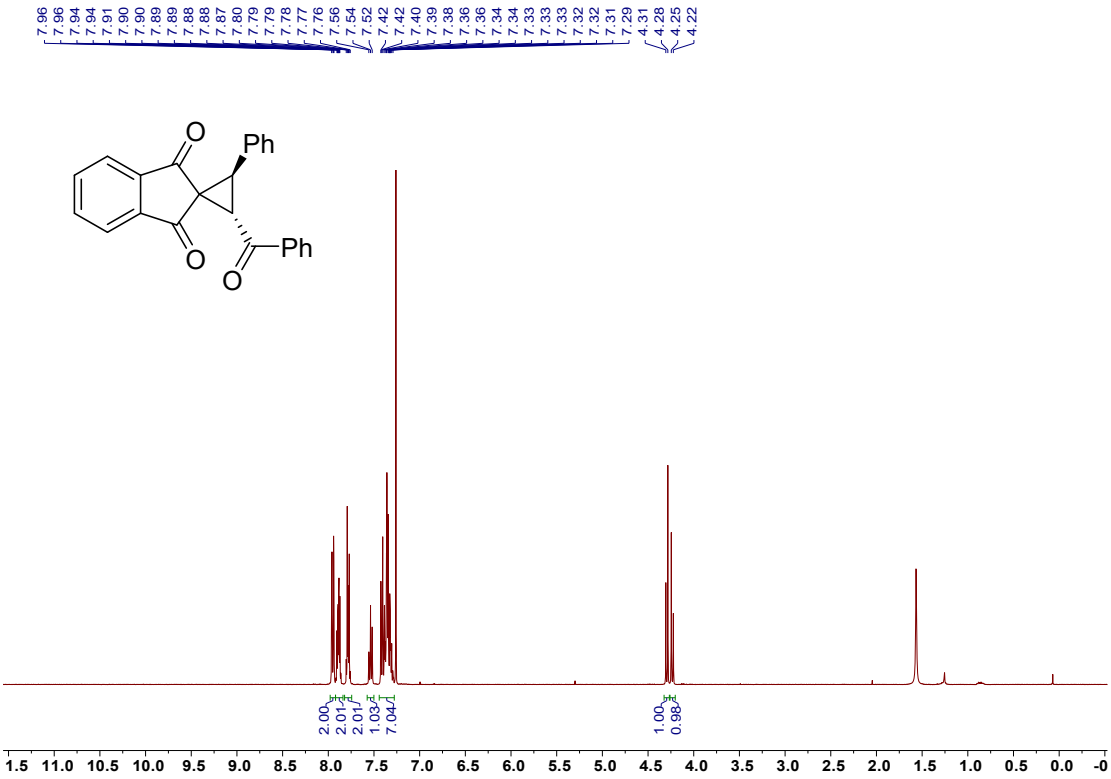
Reference

[1] (a) C. J. Lee, C. N. Sheu, C. C. Tsai, Z. Z. Wu, W. W. Lin, Chem. Commun. 2014, 50, 5304. (b) T. M. Kadayat, C. Park, K. Y. Jun, T. T. Magar, G. Bist, H. Y. Yoo, Y. Kwon, E. S. Lee, Bioorg. Med. Chem. 2015, 23, 3499.

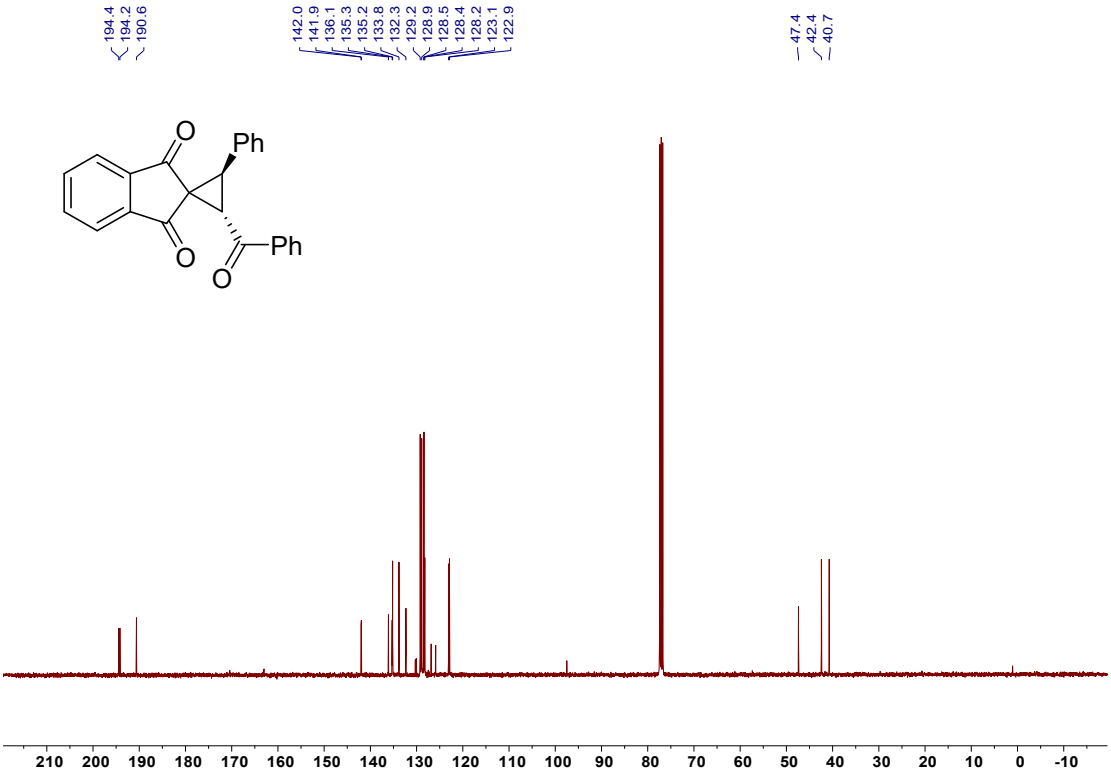
[2] S. Wang, L. Xu, Y. T. Lu, Y. F. Liu, B. Han, T. Liu, J. Tang, J. Li, J. P. Wu, J. Y. Li, L. F. Yu, F. Yang, Eur. J. Med. Chem. 2017, 130, 195.

[3] R. Dey, P. Kumar, P. Banerjee, J. Org. Chem. 2018, 83, 5438.

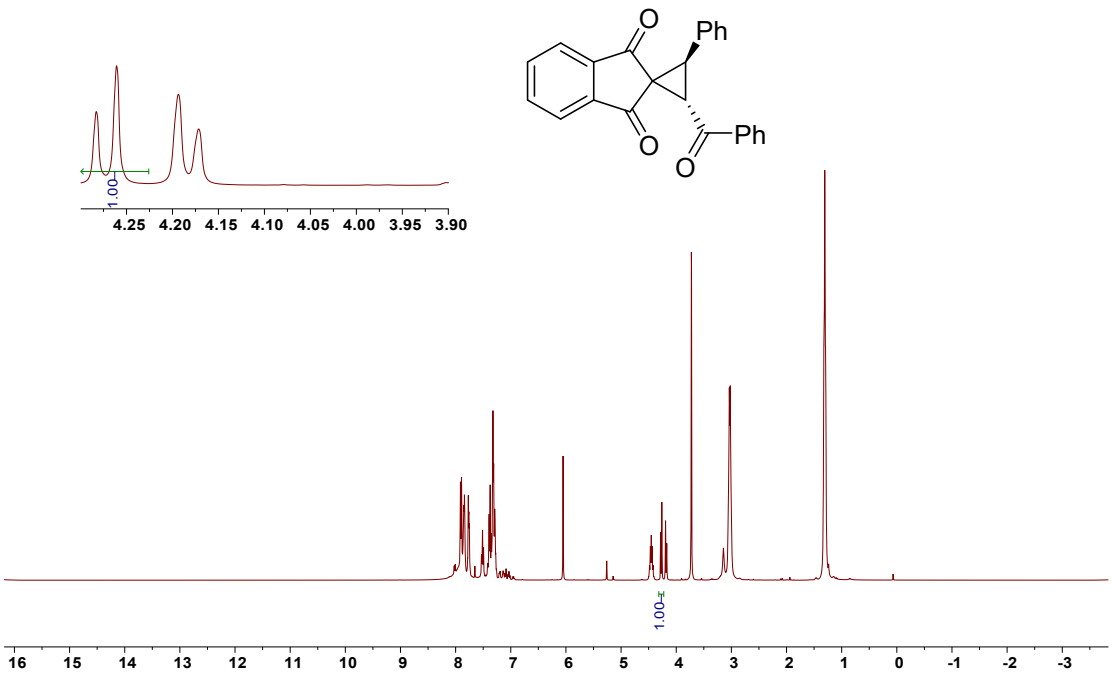
5 Original spectrogram



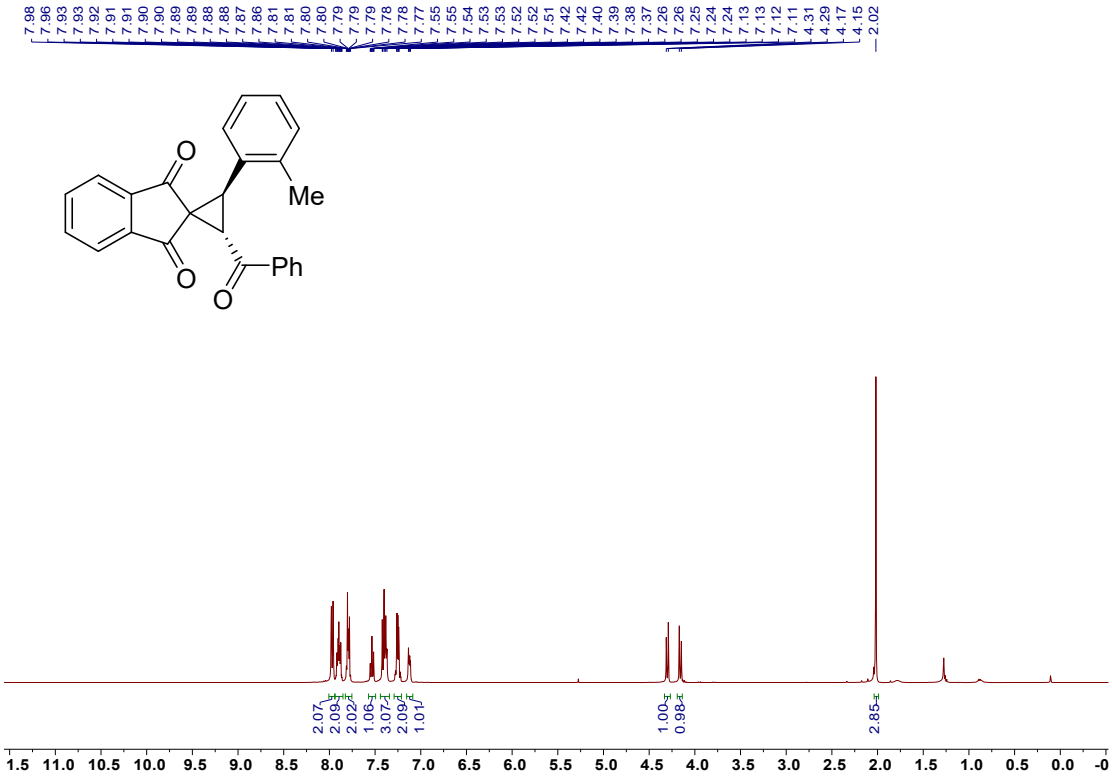
^{1}H NMR of compound **3aa**



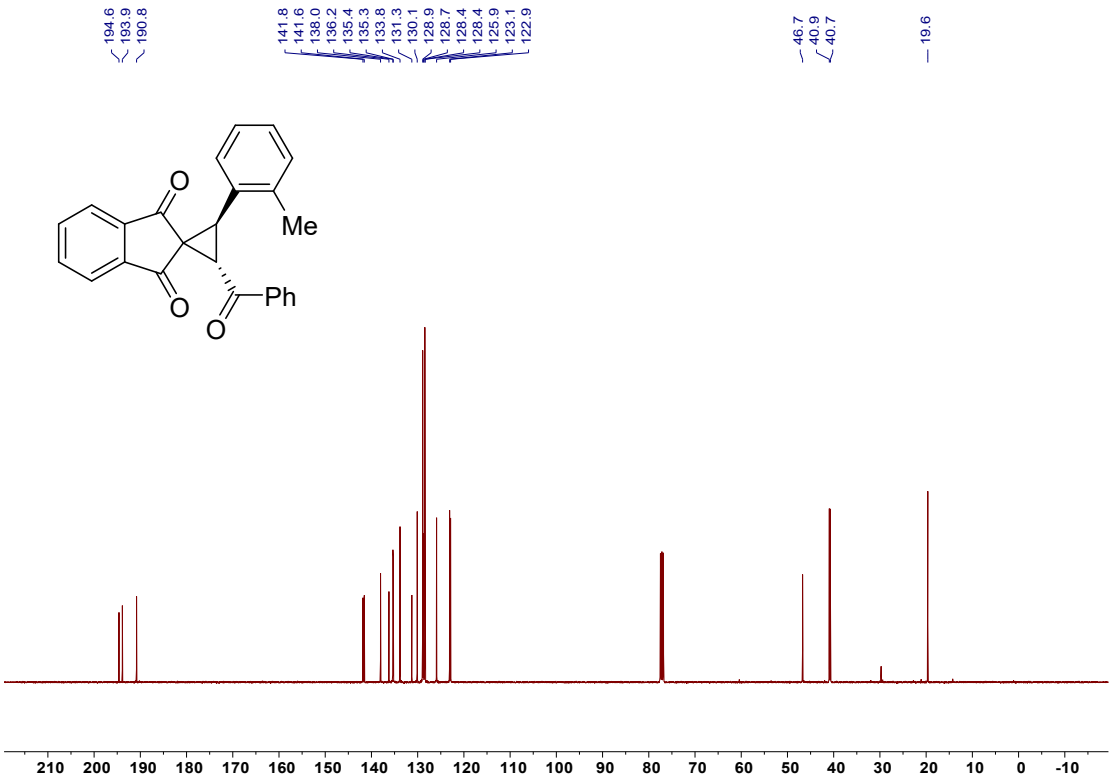
^{13}C NMR of compound **3aa**



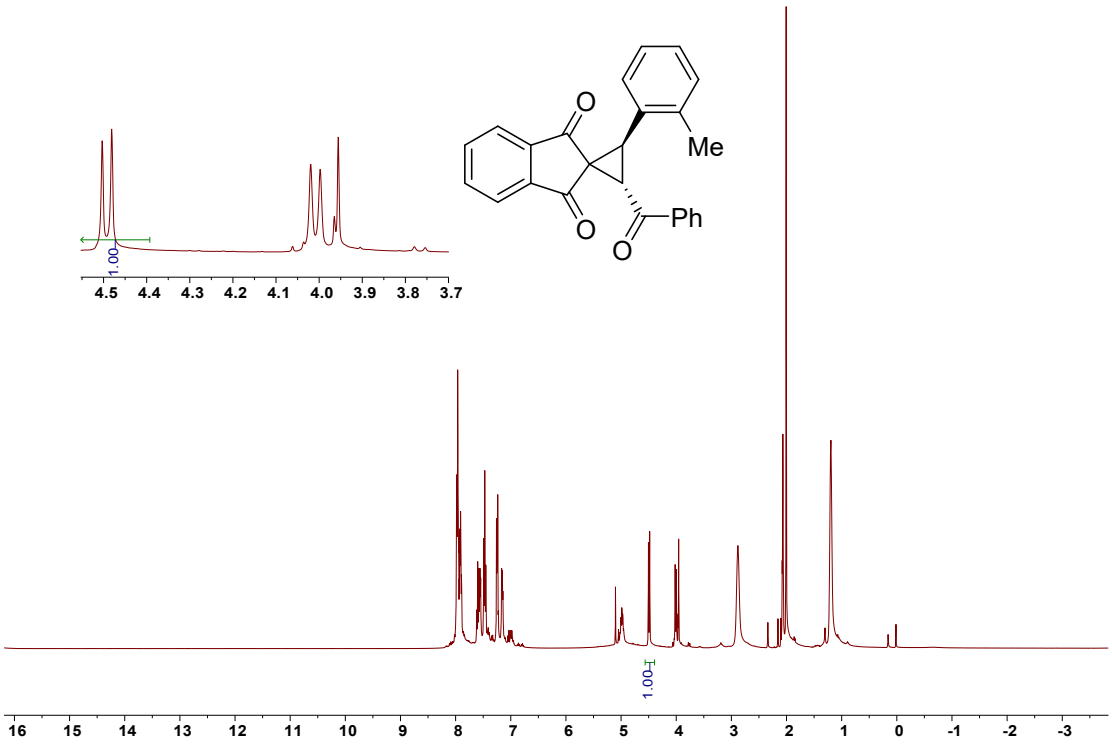
^{1}H NMR of reaction mixture **3aa**



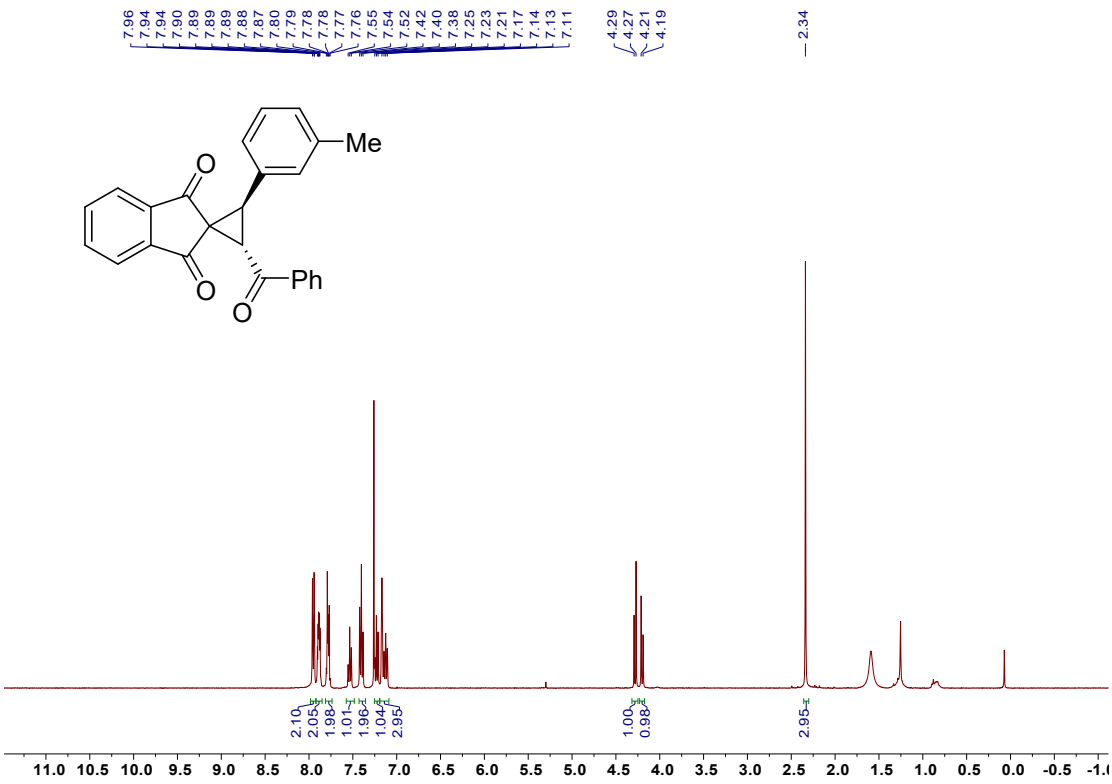
^{1}H NMR of compound **3ab**



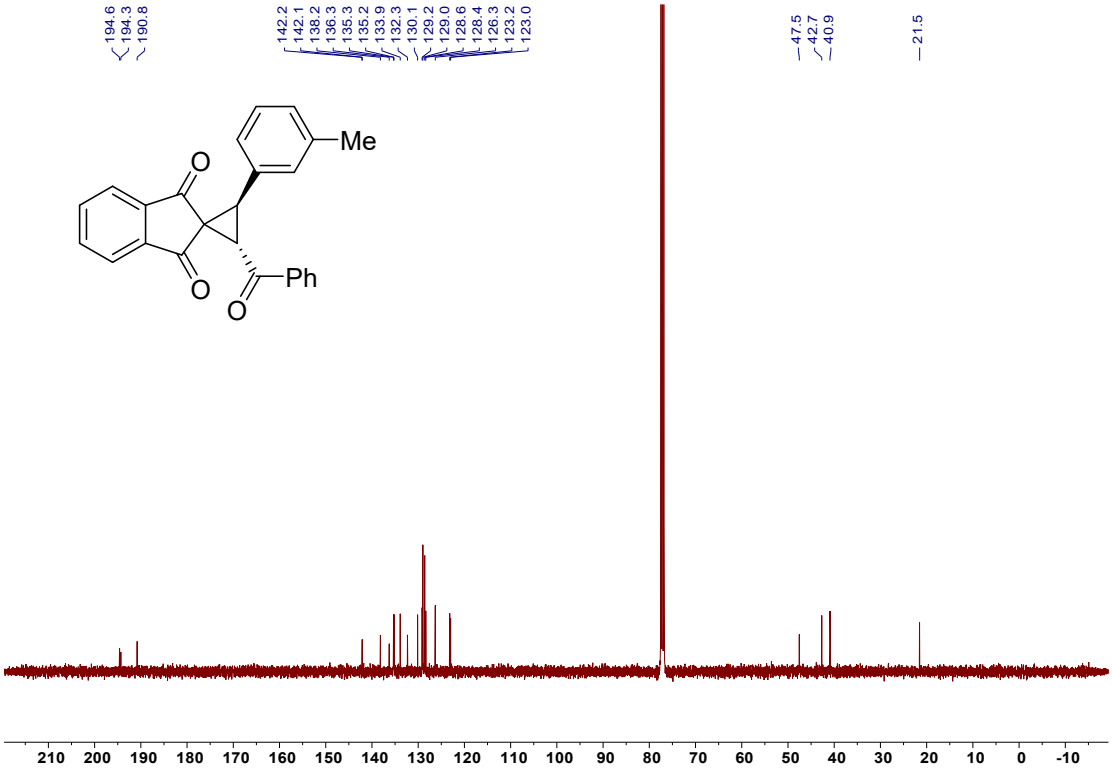
^{13}C NMR of compound **3ab**



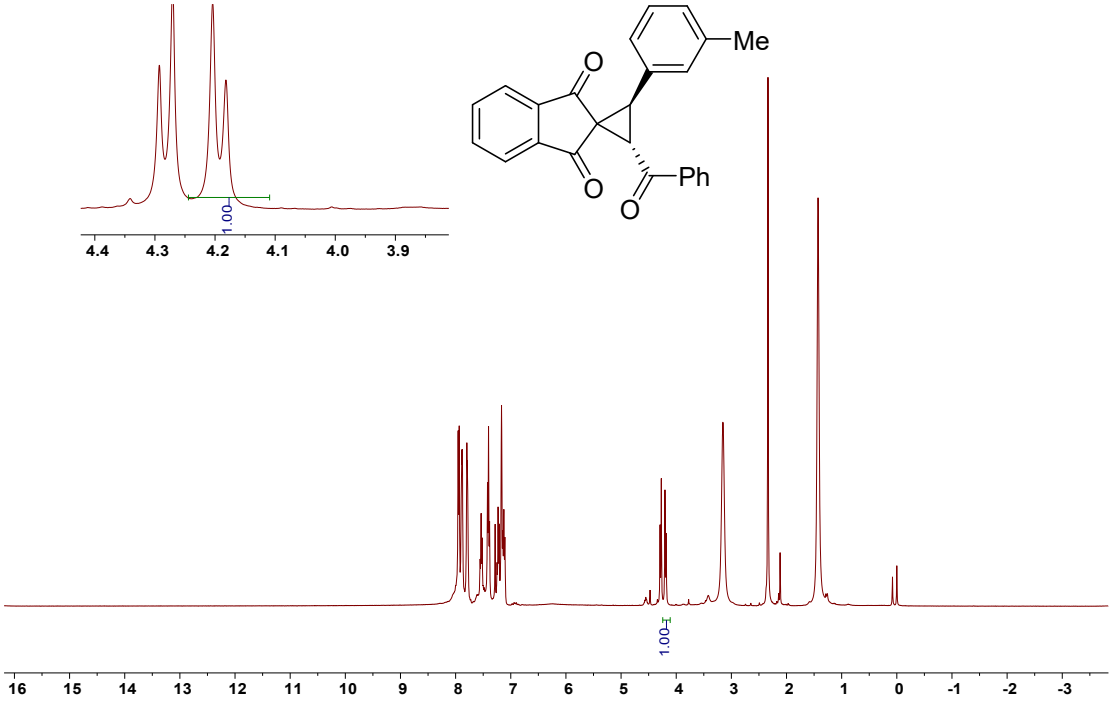
^{1}H NMR of reaction mixture **3ab**



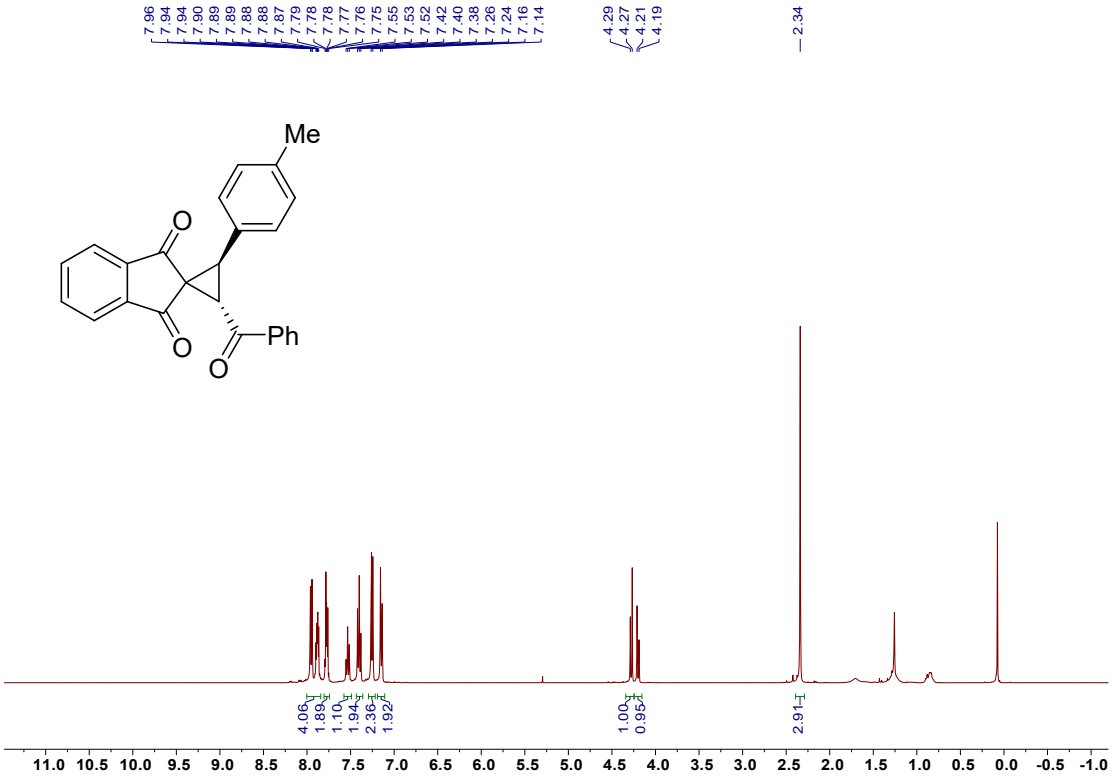
^{1}H NMR of compound **3ac**



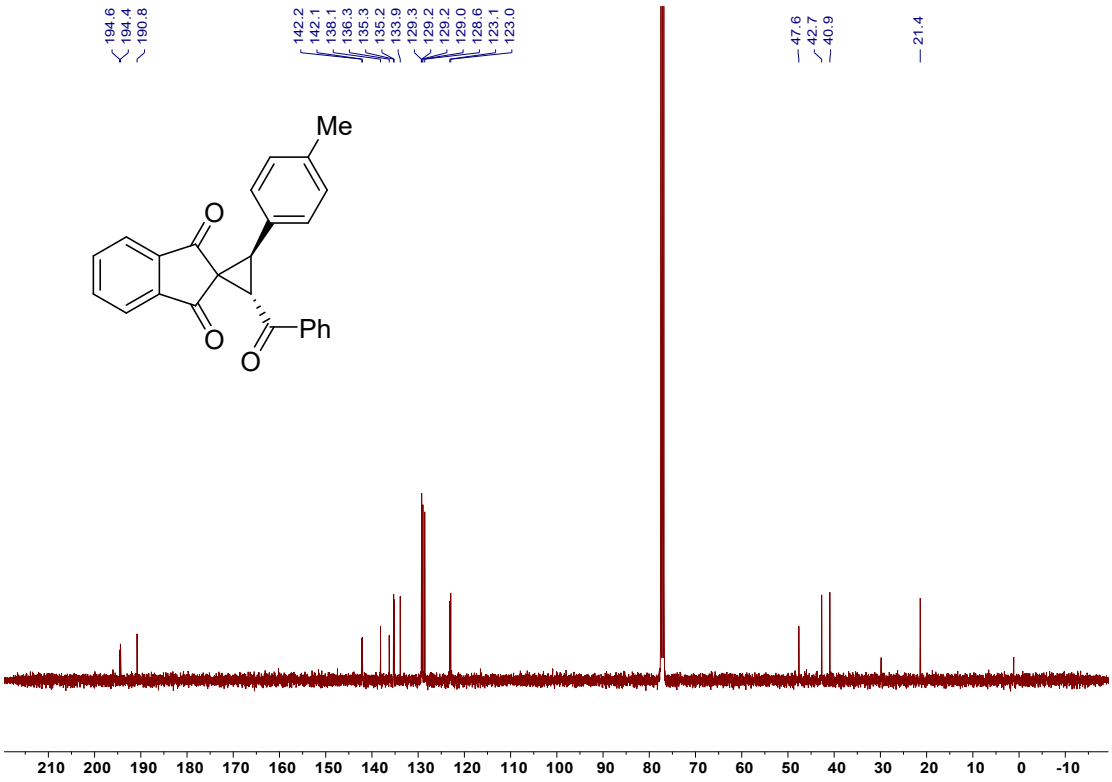
^{13}C NMR of compound **3ac**



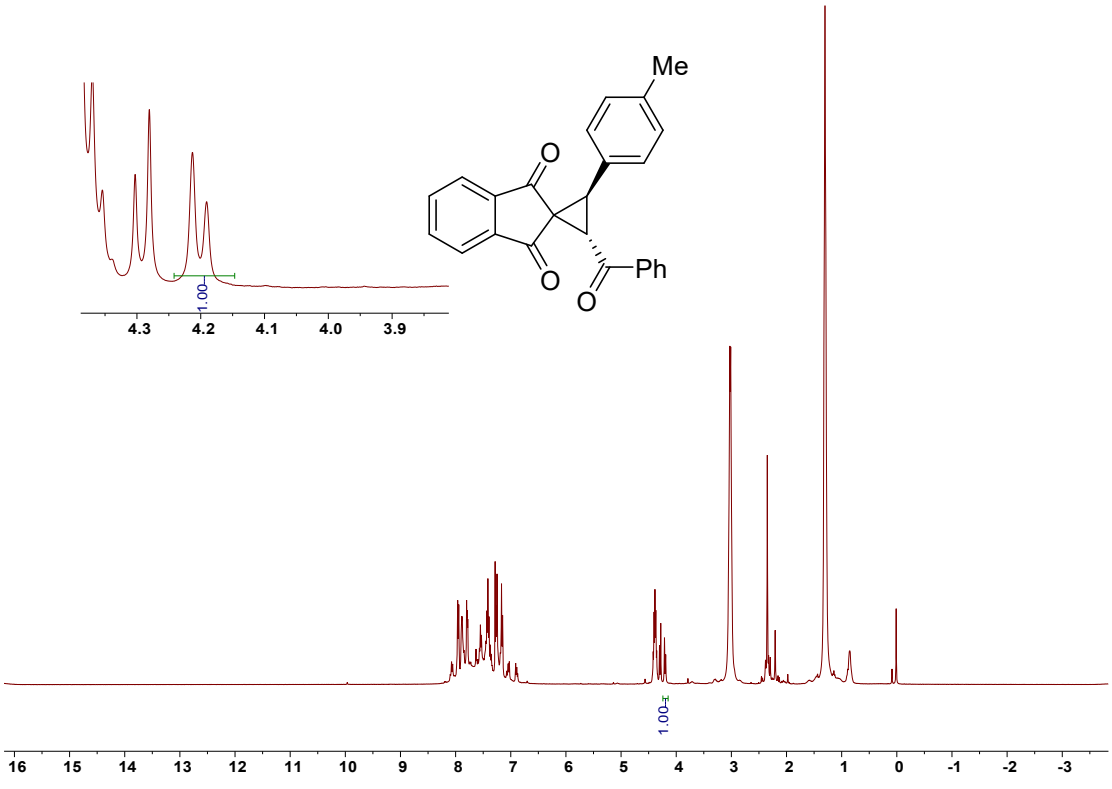
^{1}H NMR of reaction mixture **3ac**



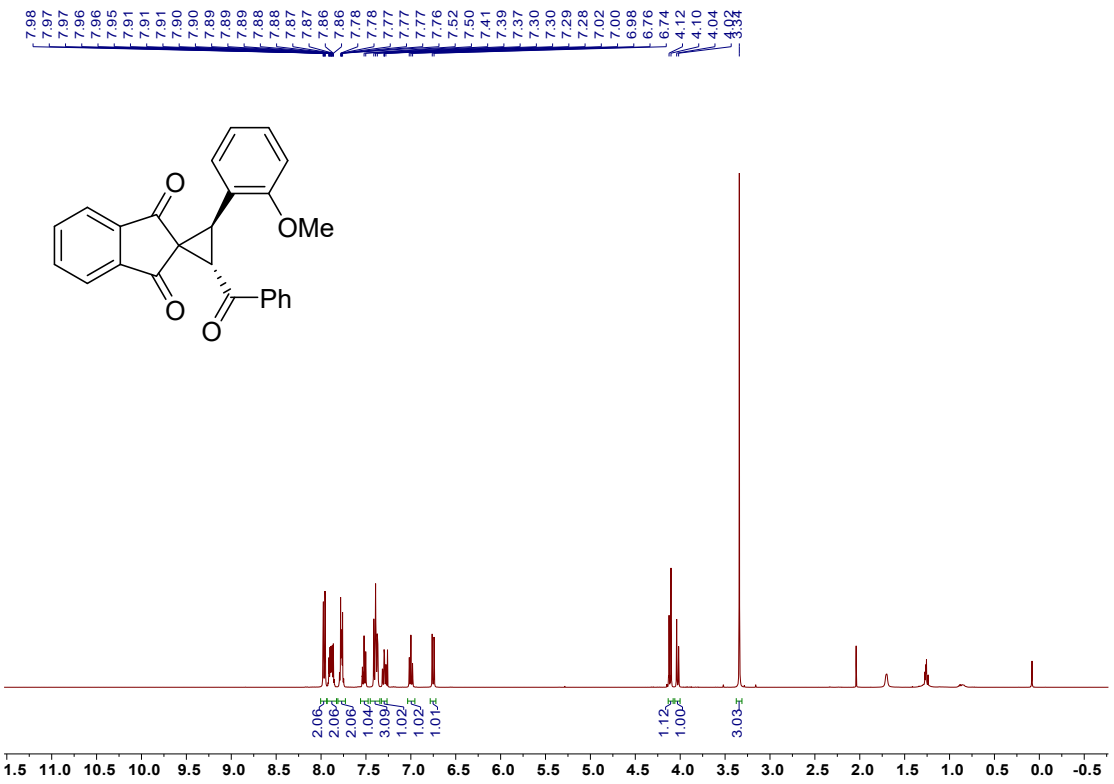
^{1}H NMR of compound **3ad**



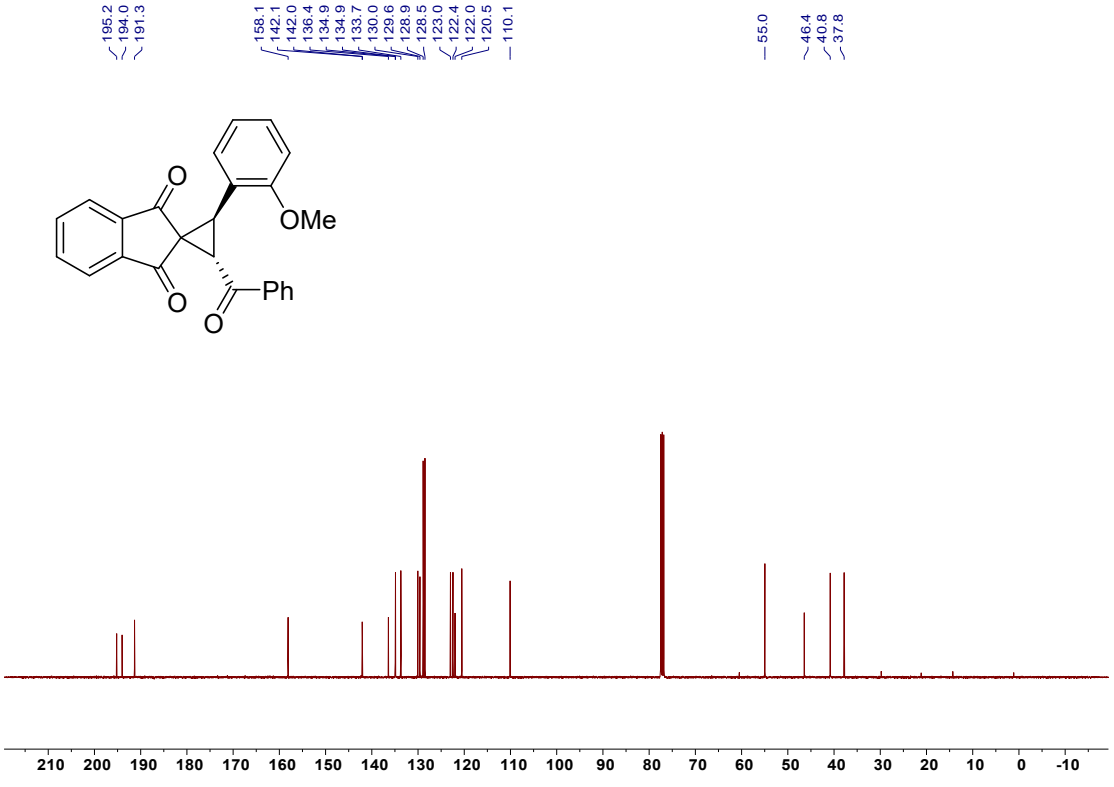
^{13}C NMR of compound **3ad**



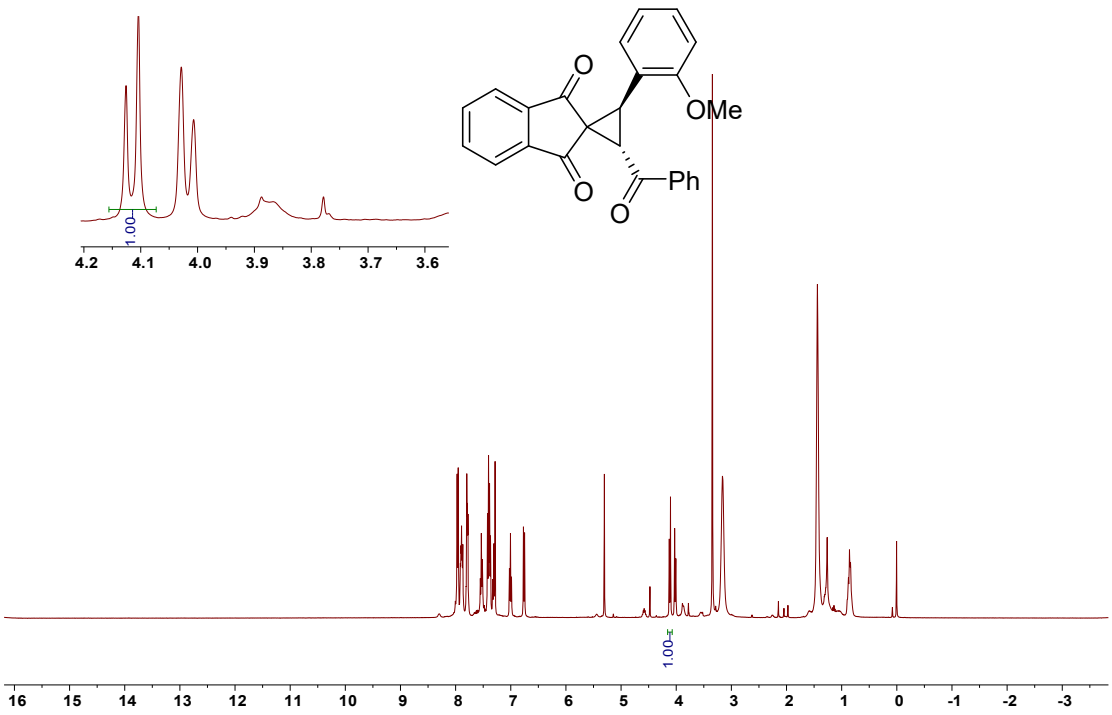
^{1}H NMR of reaction mixture **3ad**



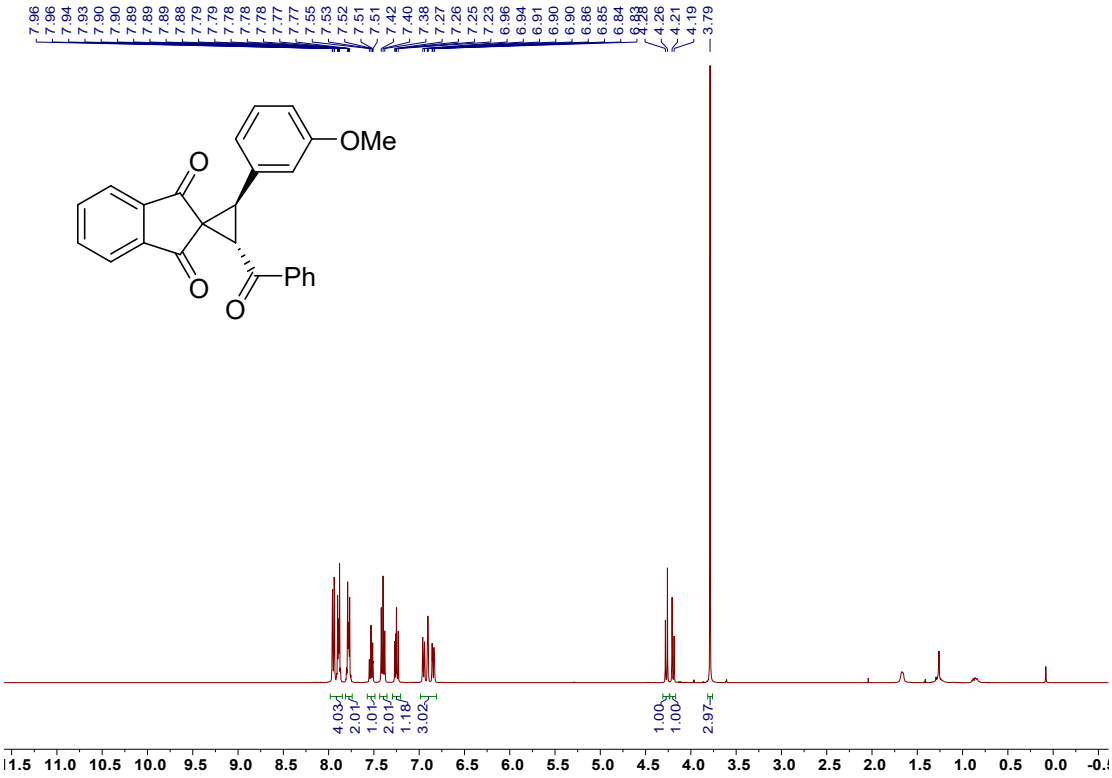
^{1}H NMR of compound **3ae**



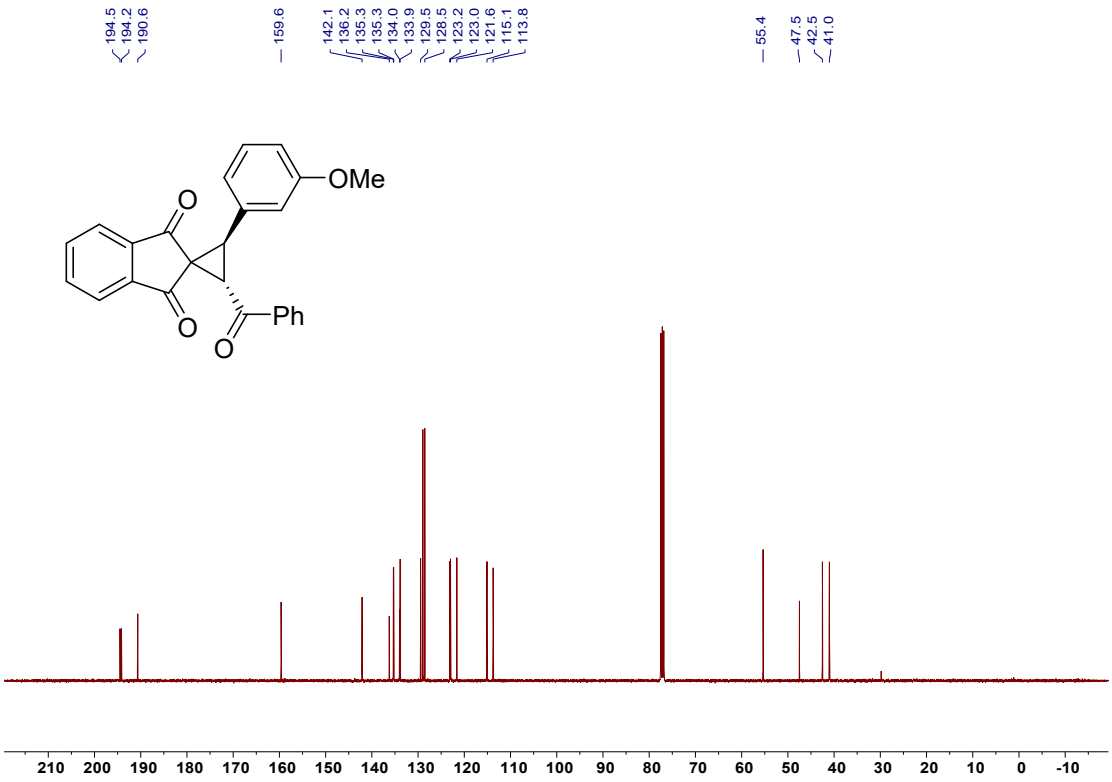
^{13}C NMR of compound **3ae**



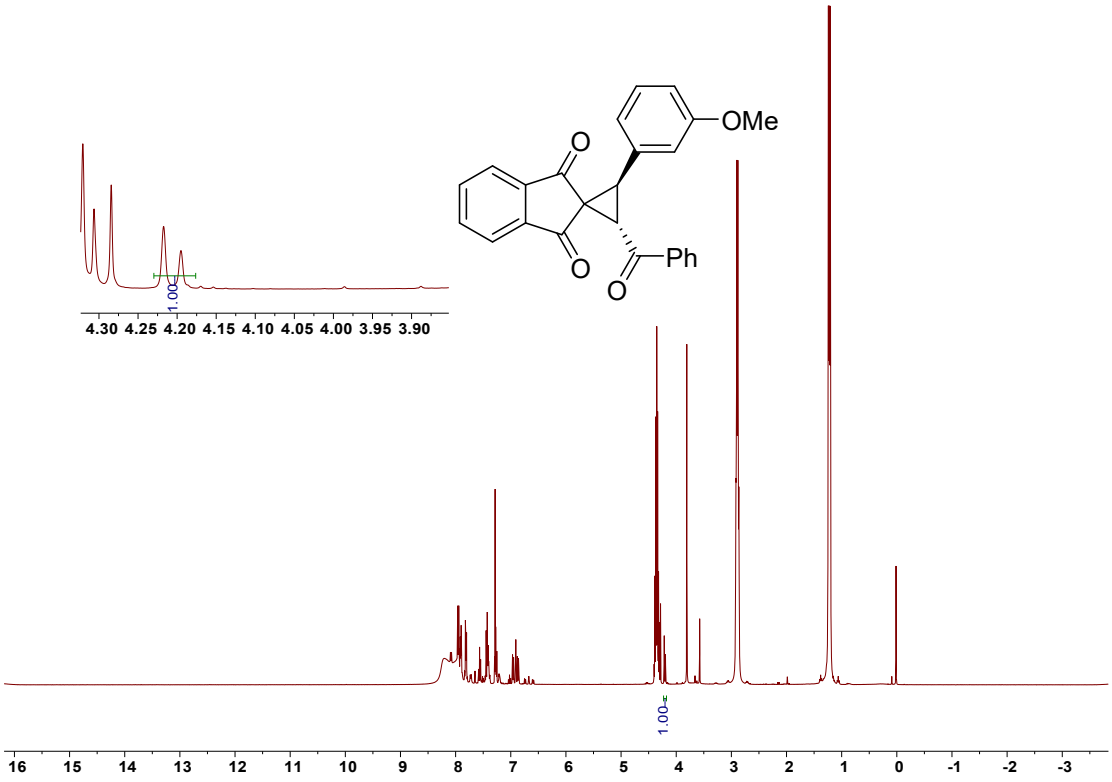
^{1}H NMR of reaction mixture **3ae**



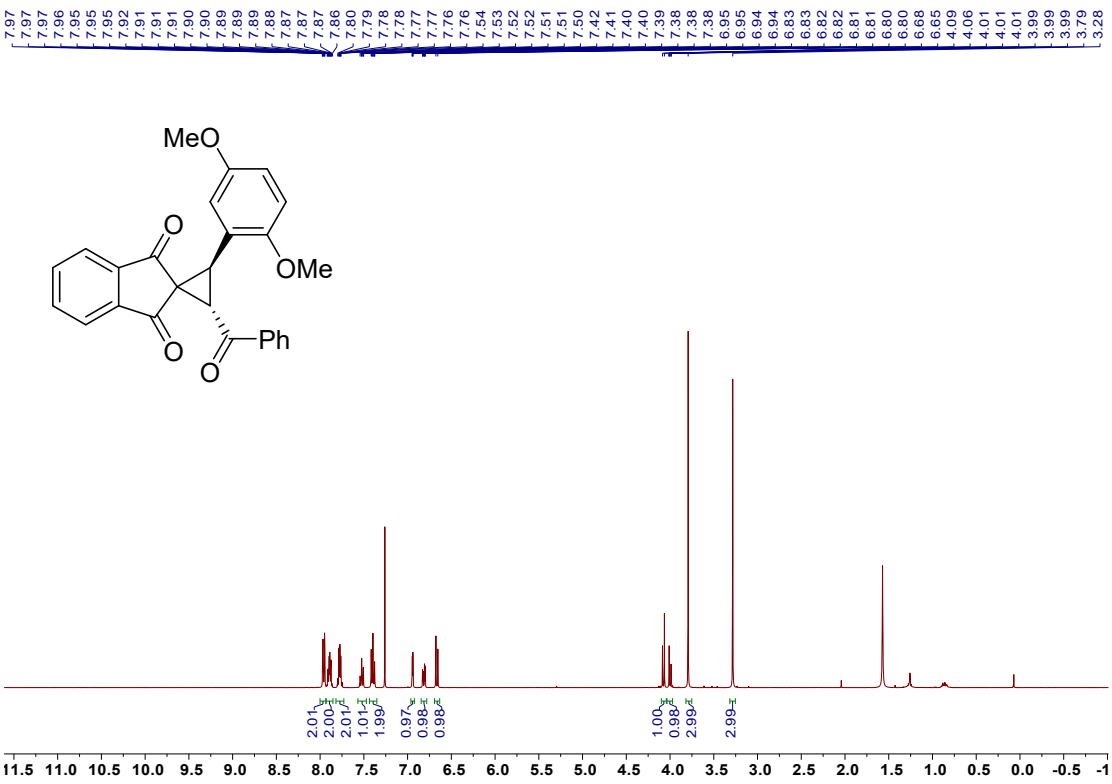
^{1}H NMR of compound **3af**



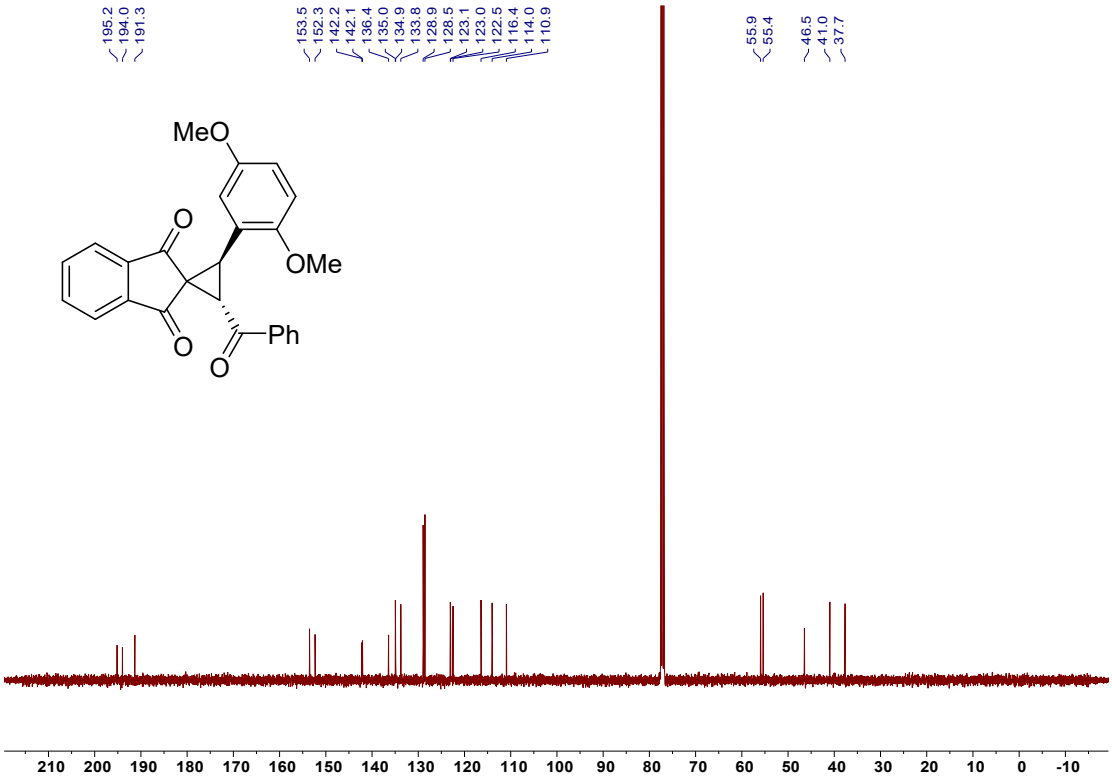
^{13}C NMR of compound **3af**



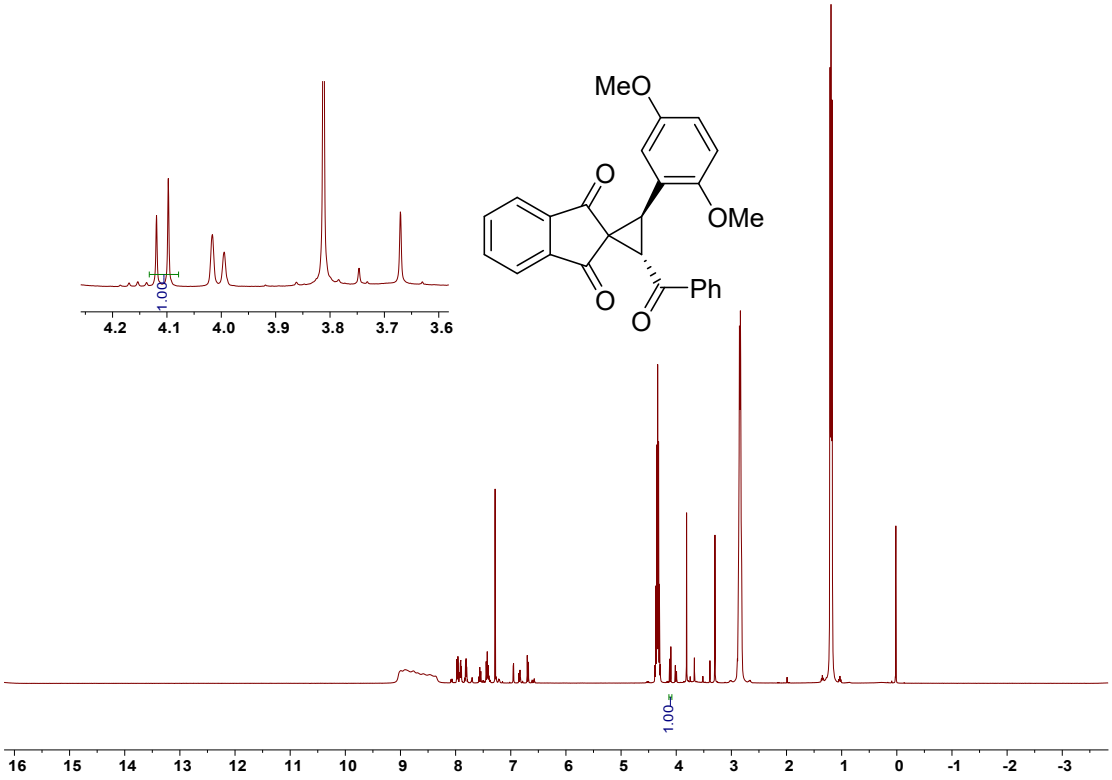
^{1}H NMR of reaction mixture **3af**



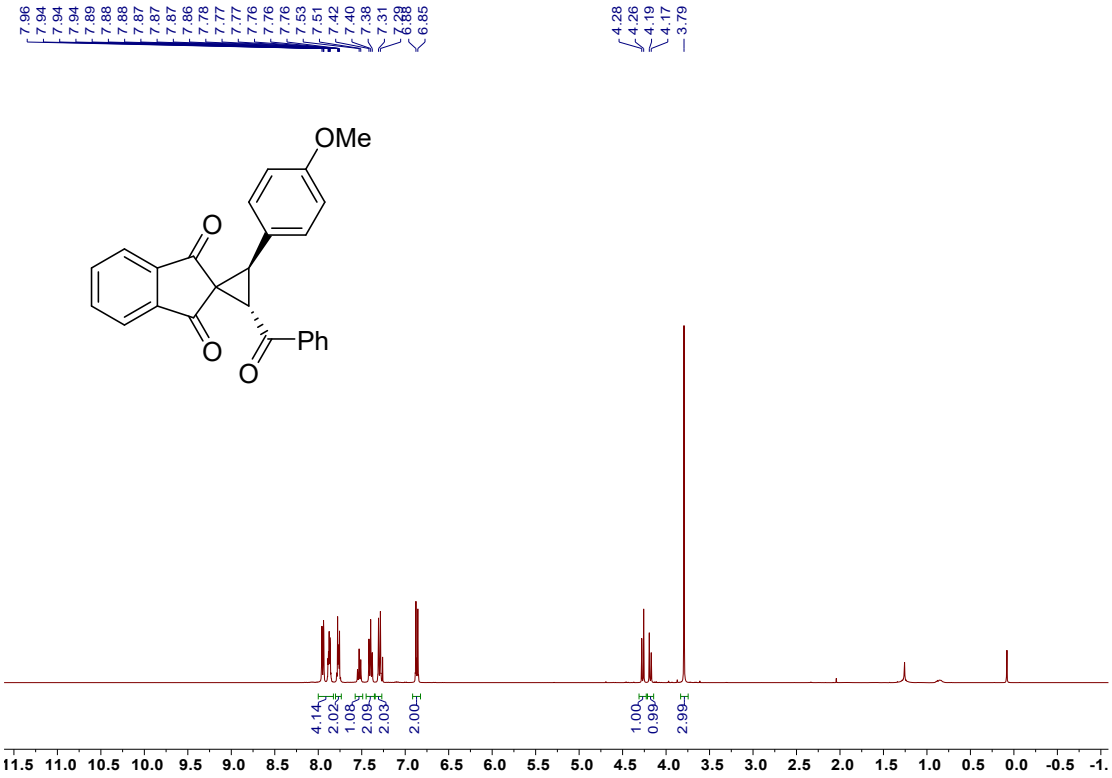
^{1}H NMR of compound **3ah**



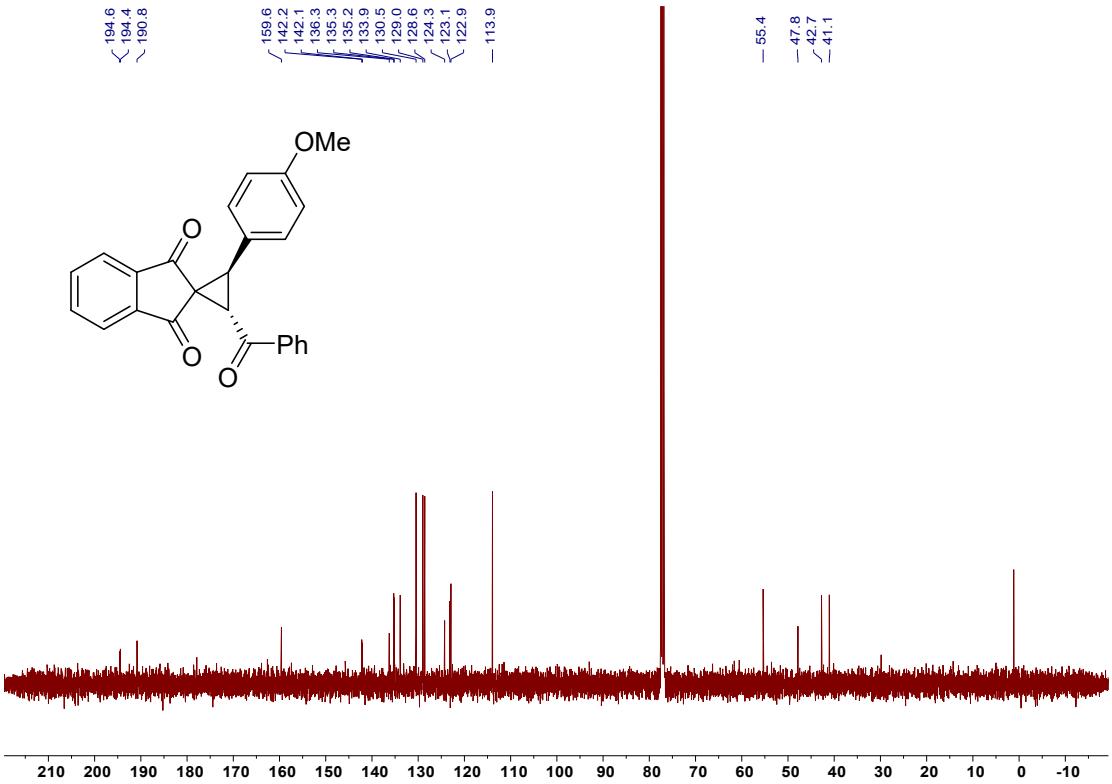
^{13}C NMR of compound **3ah**



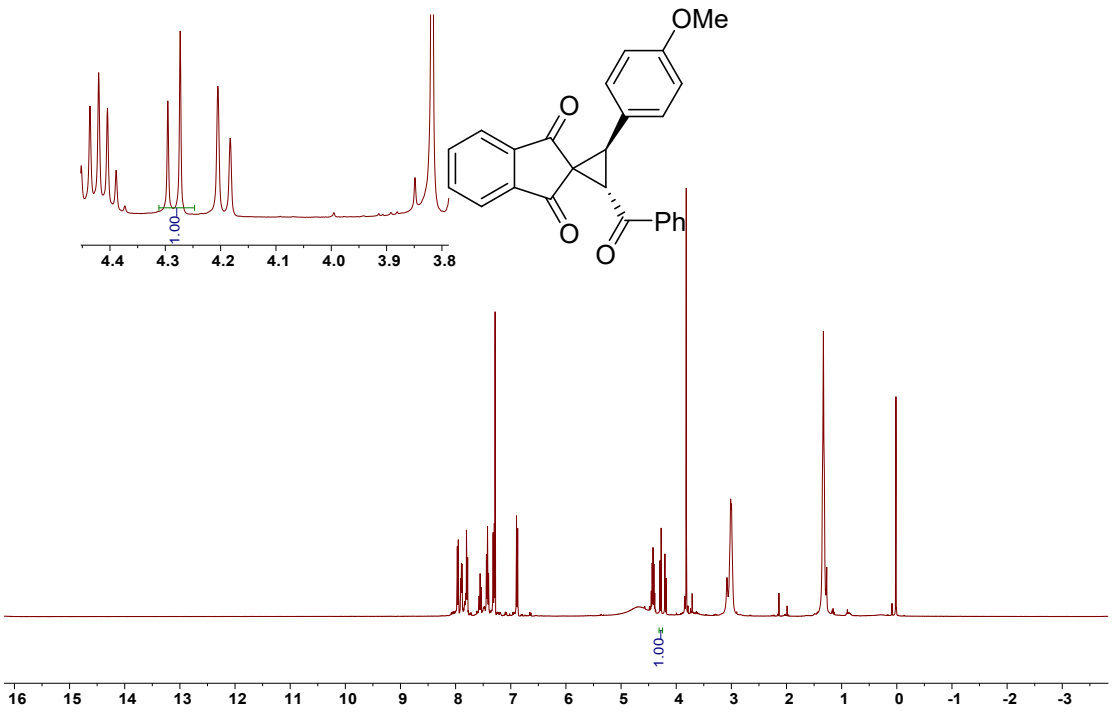
^{1}H NMR of reaction mixture **3ah**



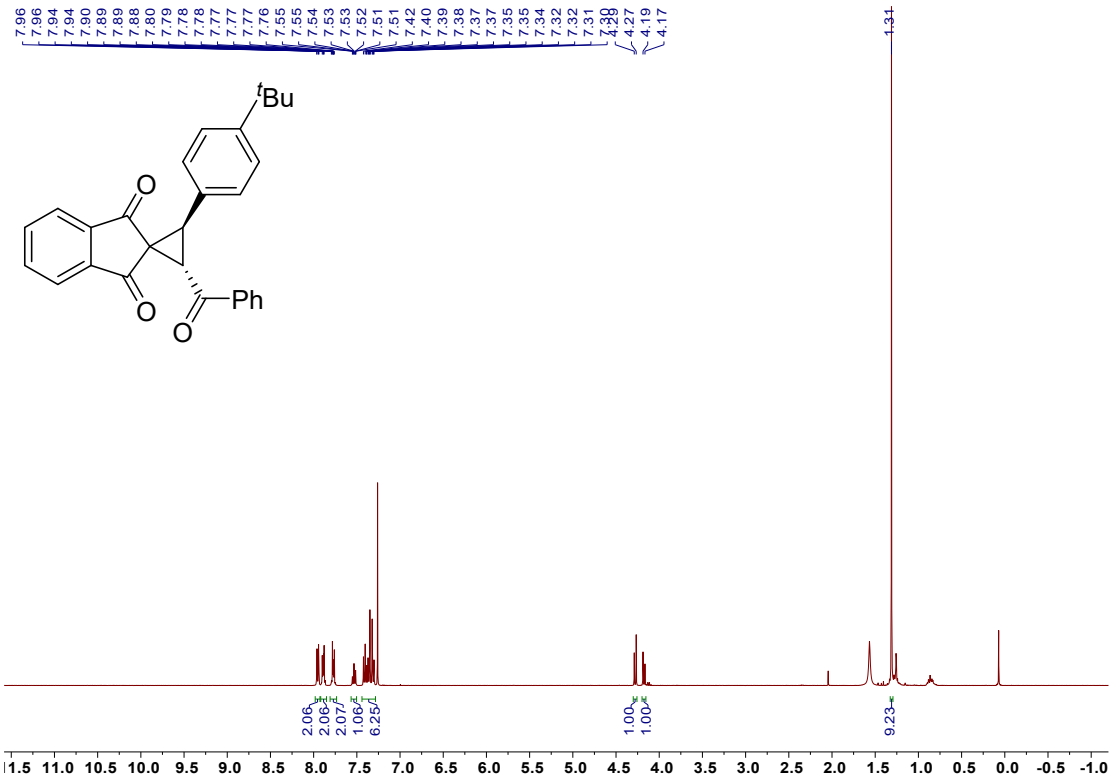
^{1}H NMR of compound **3ag**



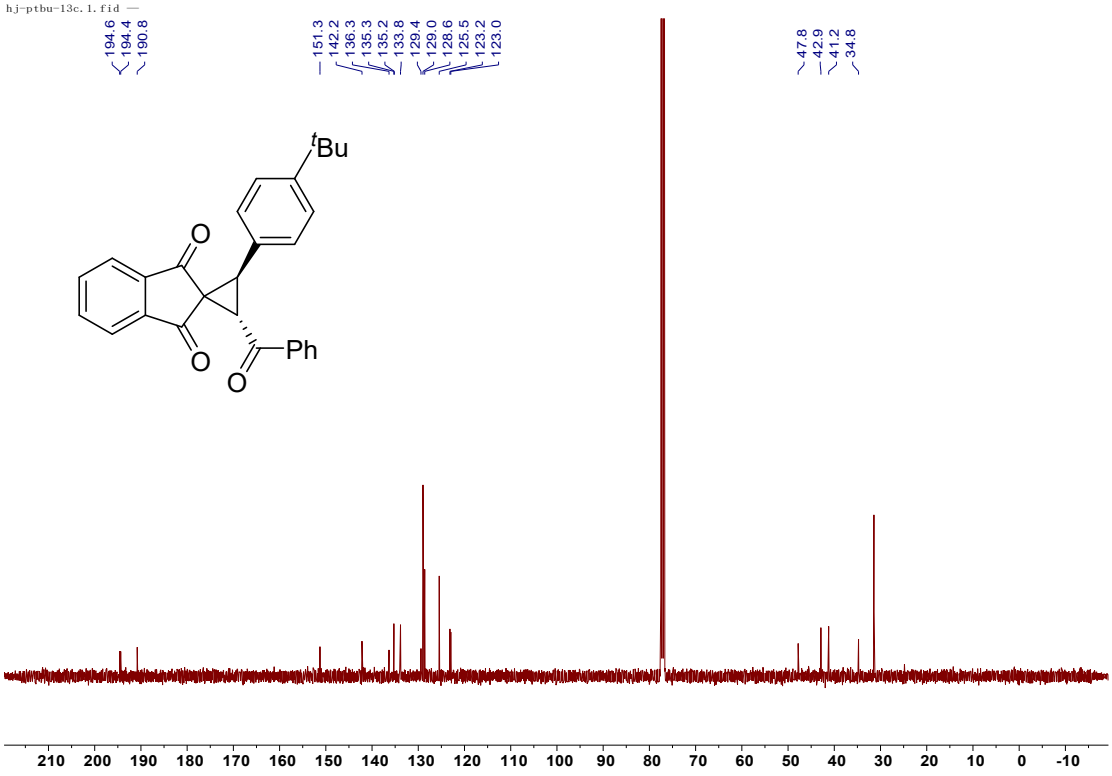
^{13}C NMR of compound **3ag**



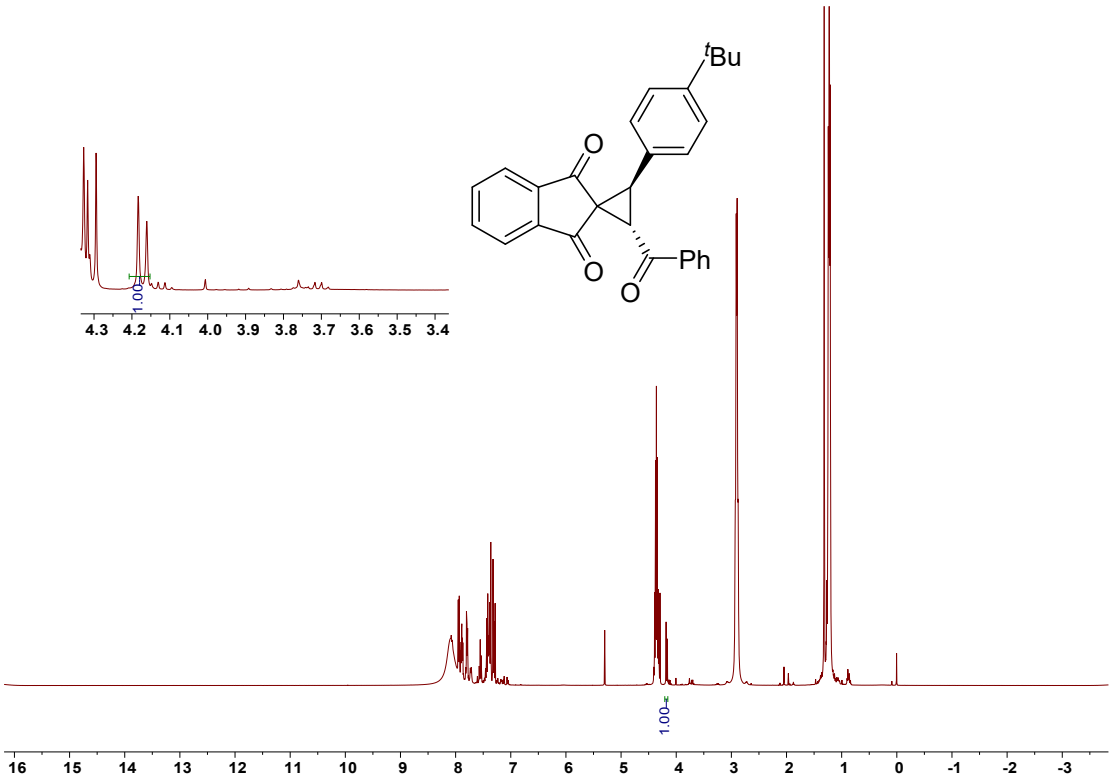
^{1}H NMR of reaction mixture **3ag**



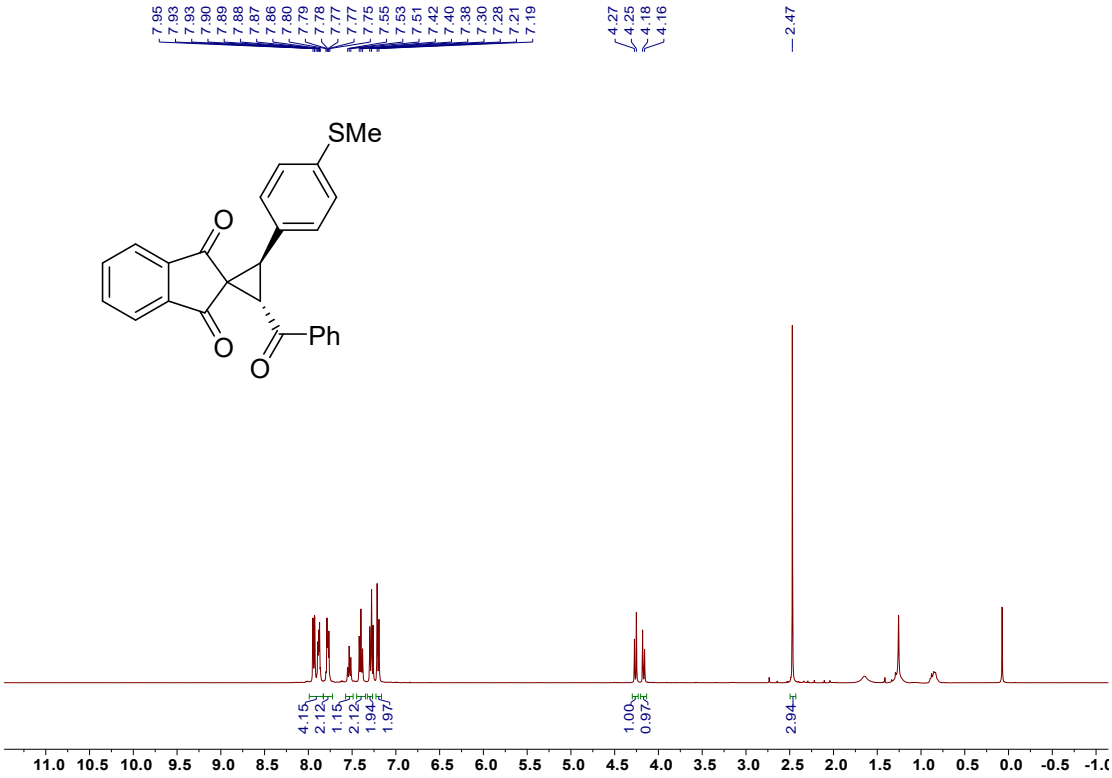
^{1}H NMR of compound **3ai**



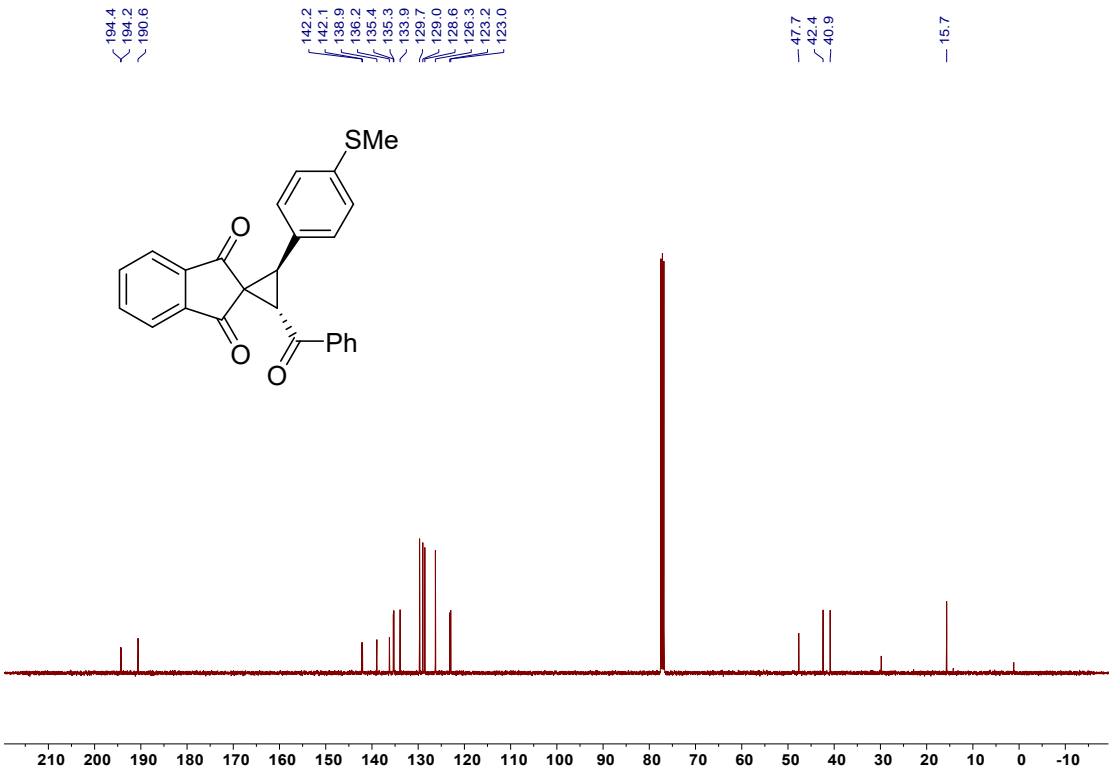
^{13}C NMR of compound **3ai**



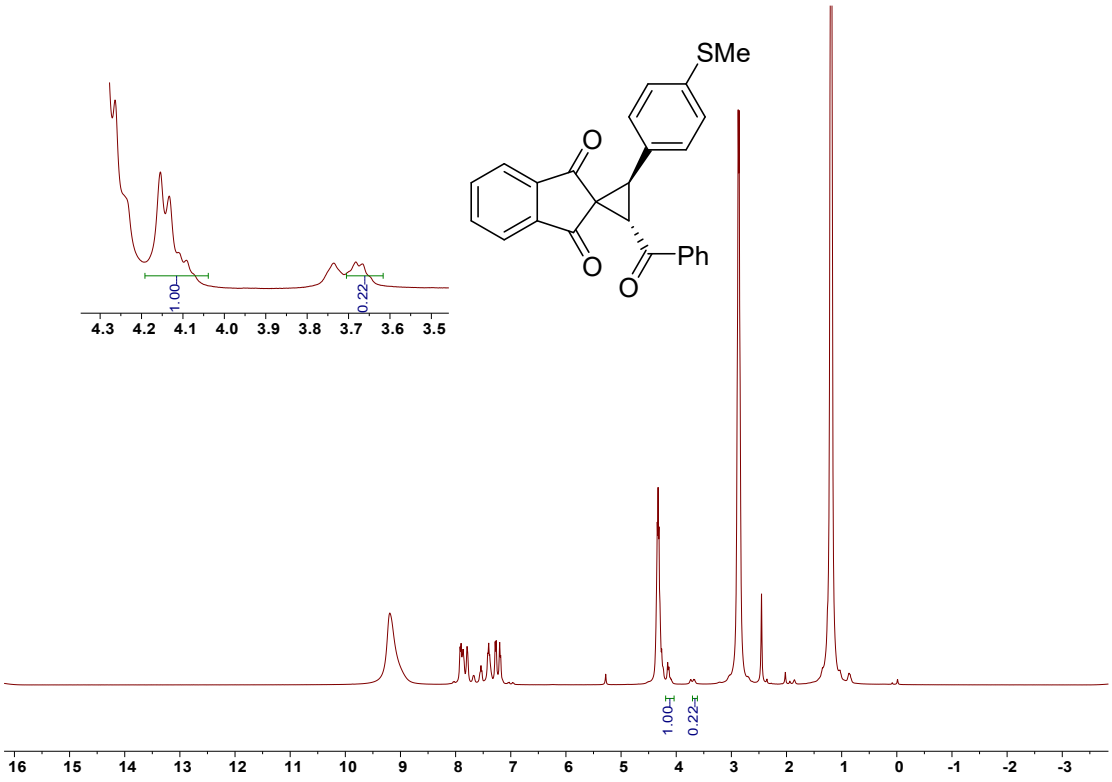
^{1}H NMR of reaction mixture **3ai**



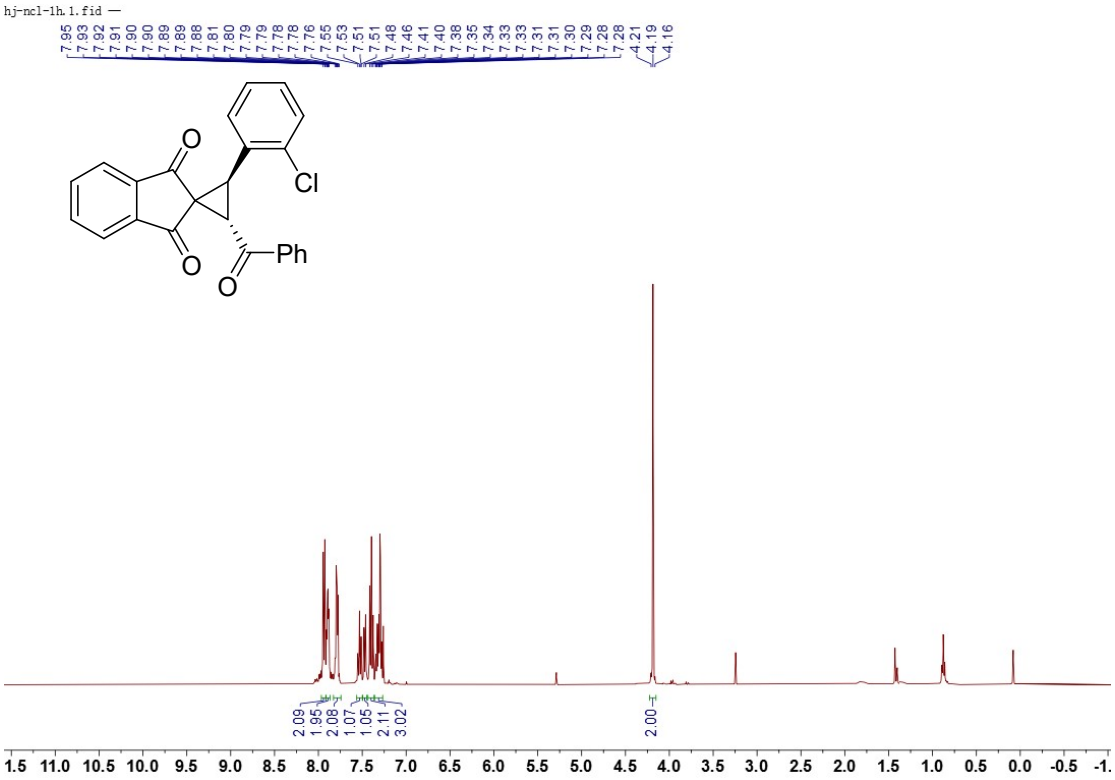
^{1}H NMR of compound **3aj**



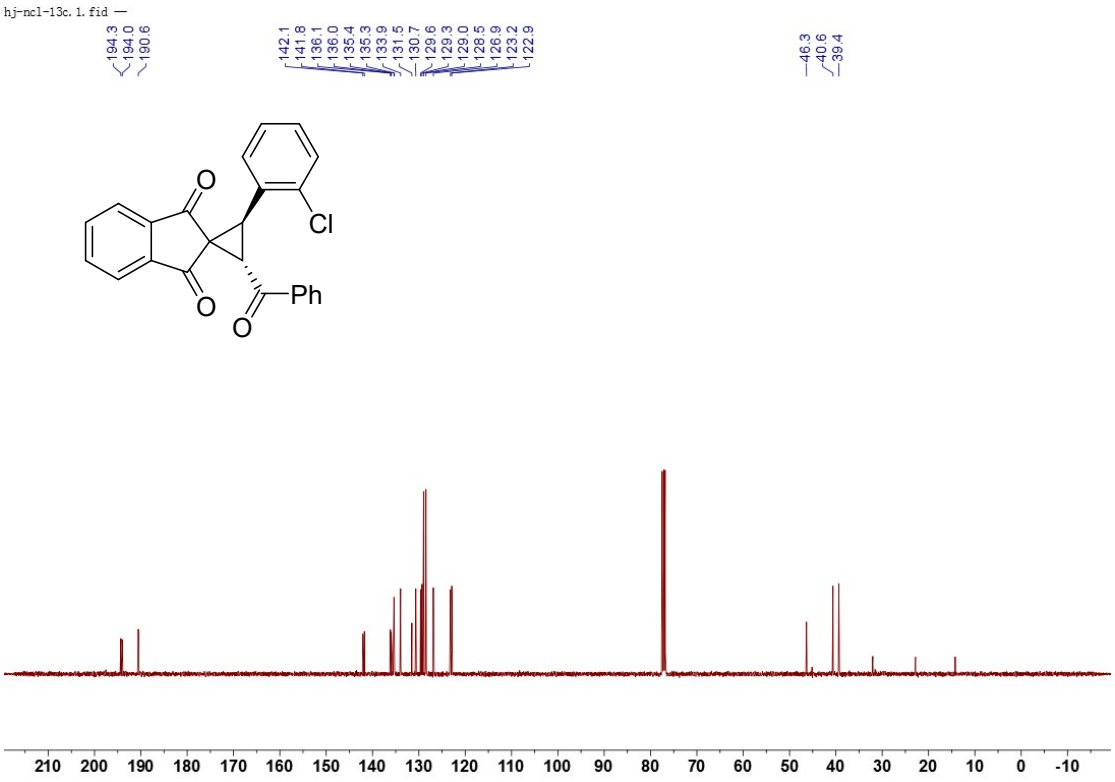
^{13}C NMR of compound **3aj**



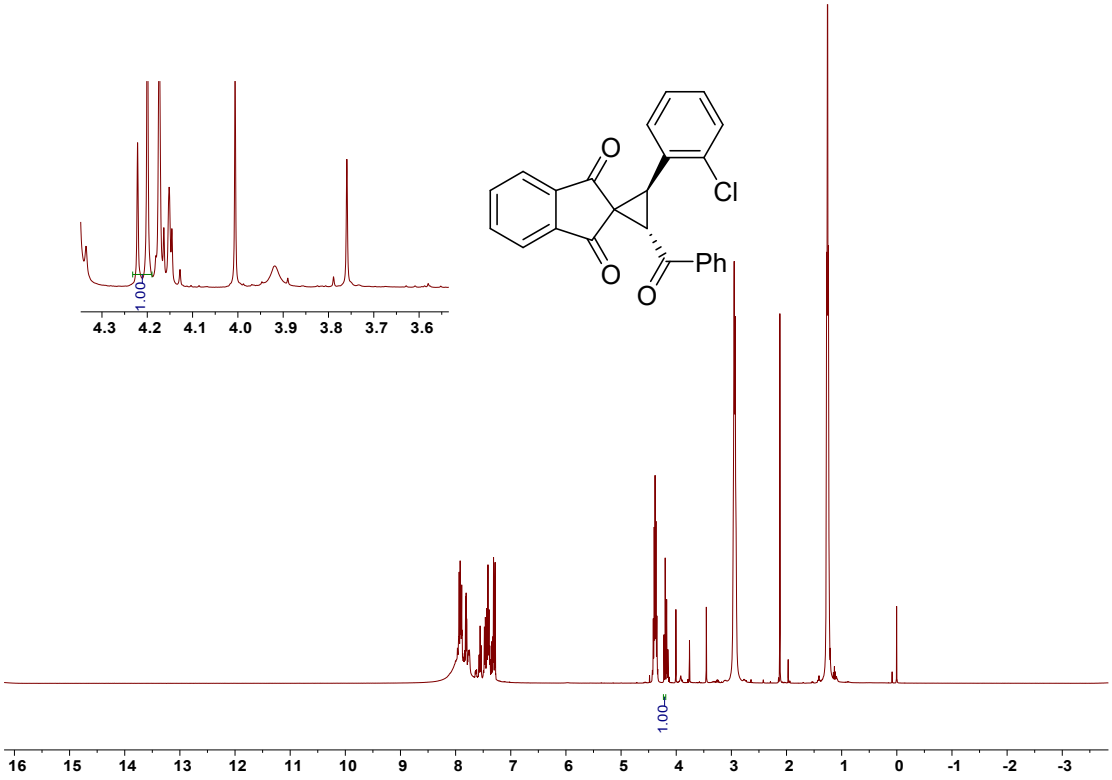
^{1}H NMR of reaction mixture **3aj**



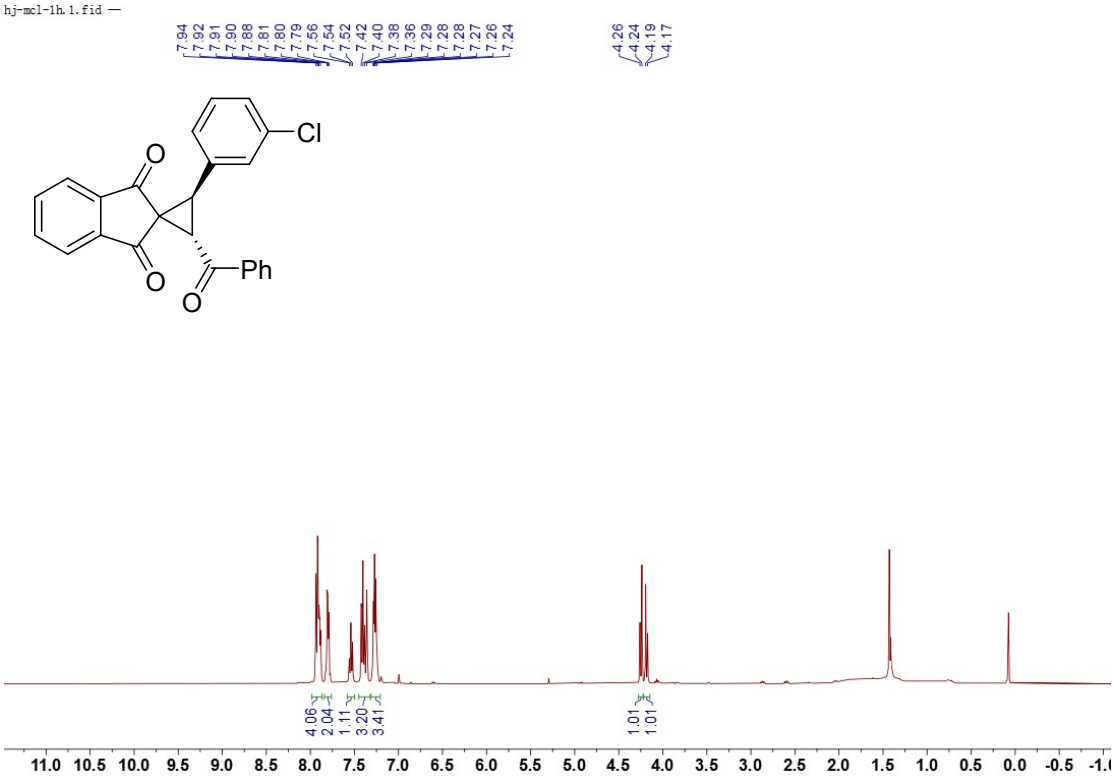
^{1}H NMR of compound **3ak**



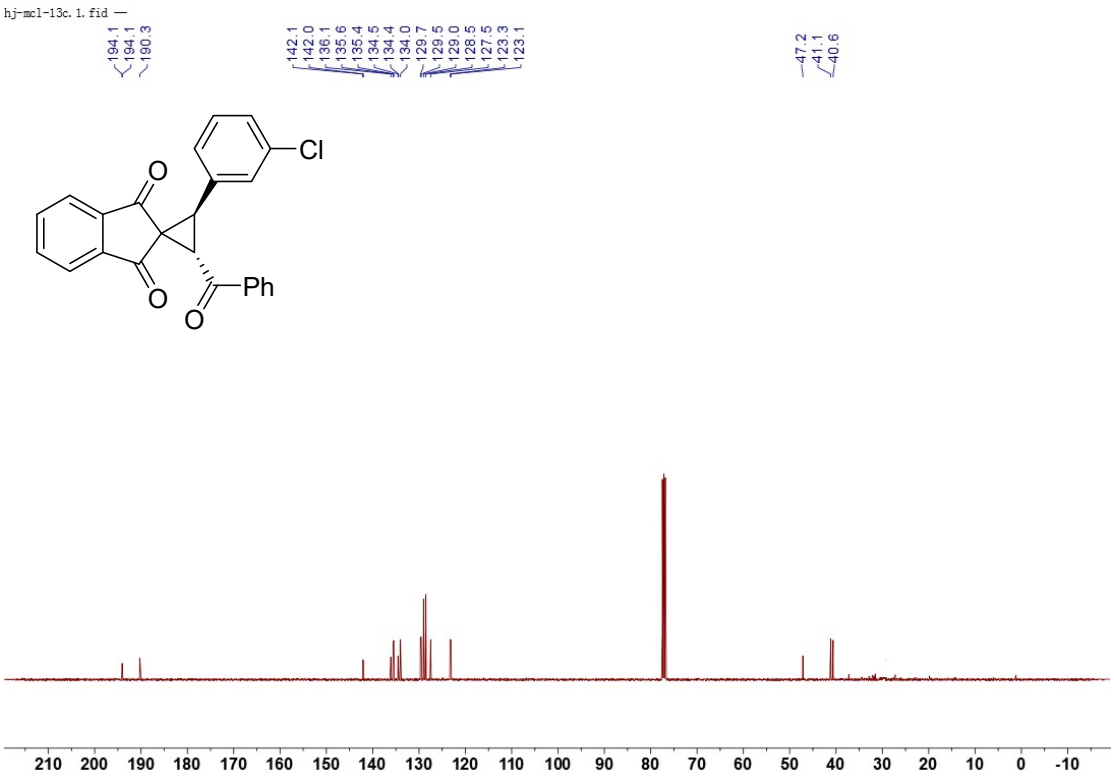
^{13}C NMR of compound **3ak**



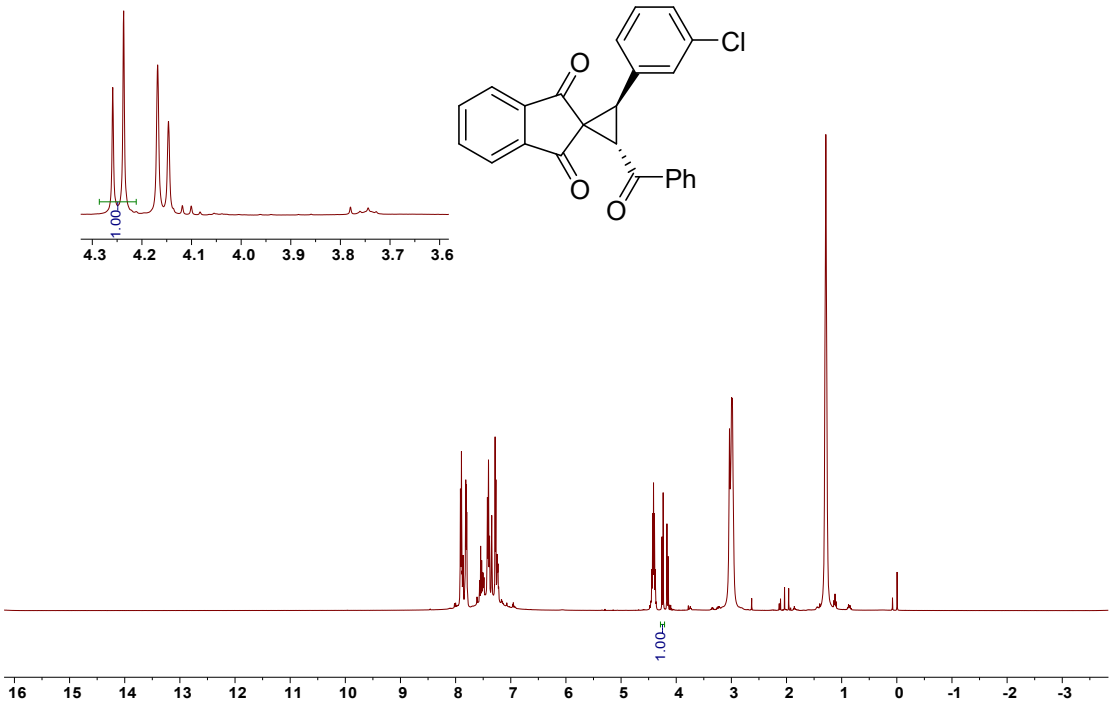
^{1}H NMR of reaction mixture **3ak**



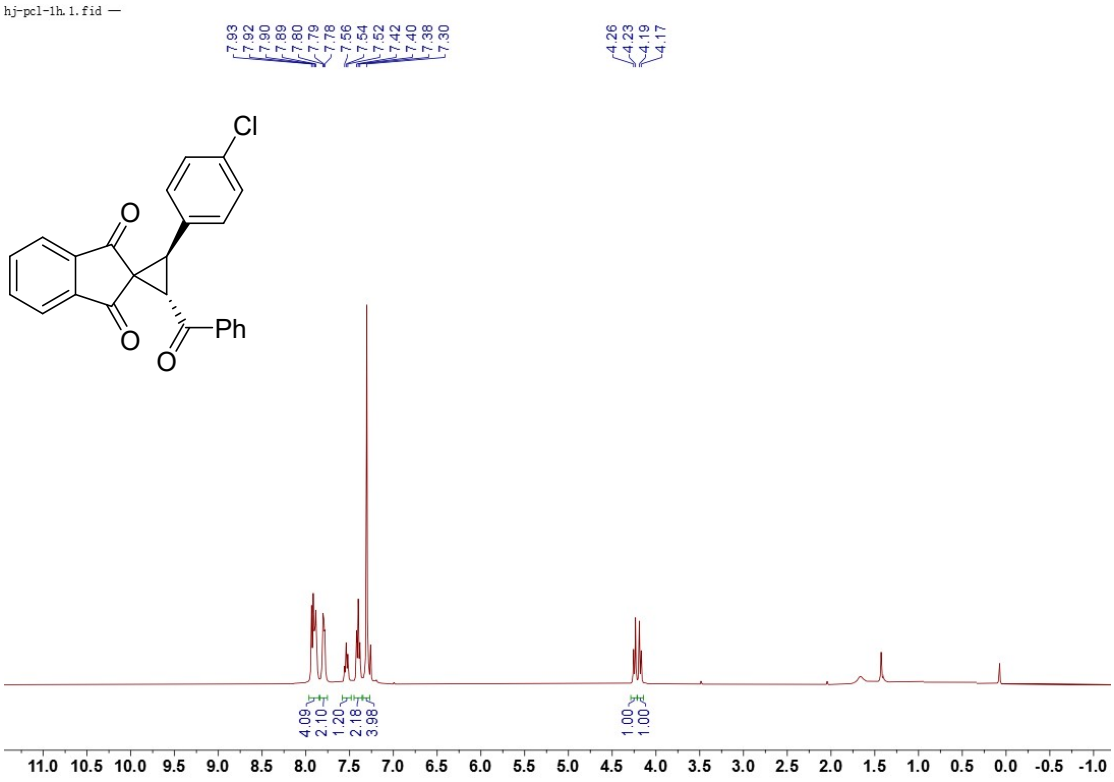
^{1}H NMR of compound **3al**



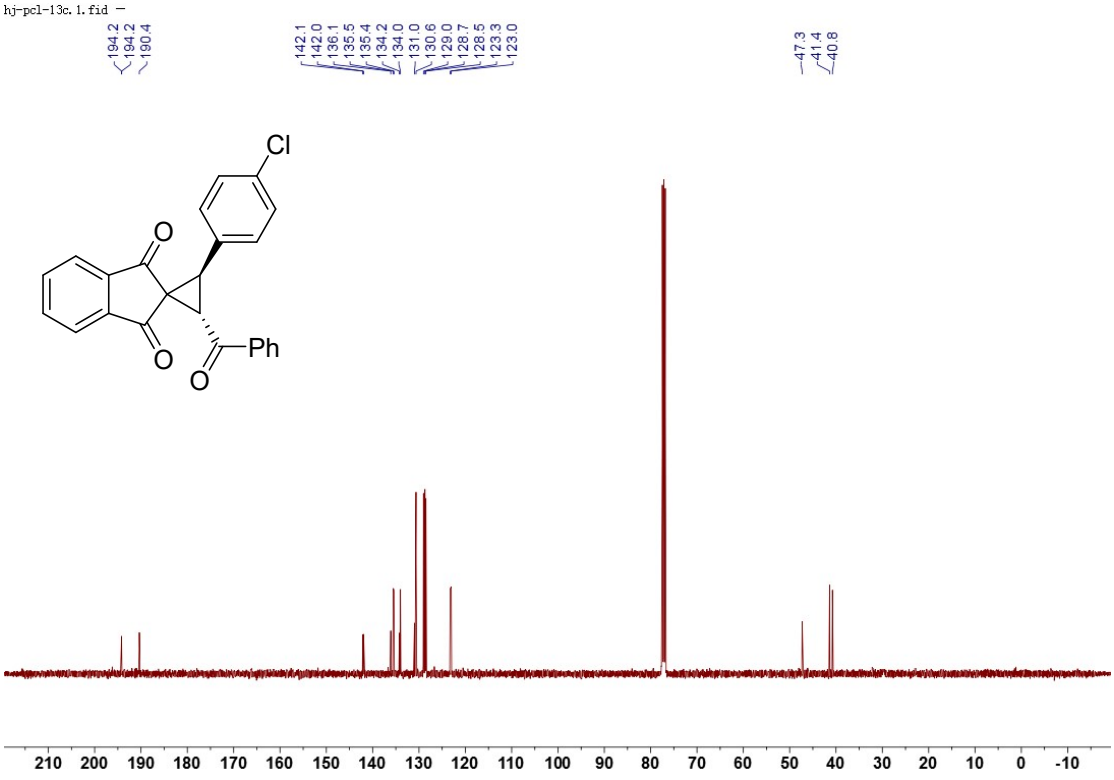
^{13}C NMR of compound **3al**



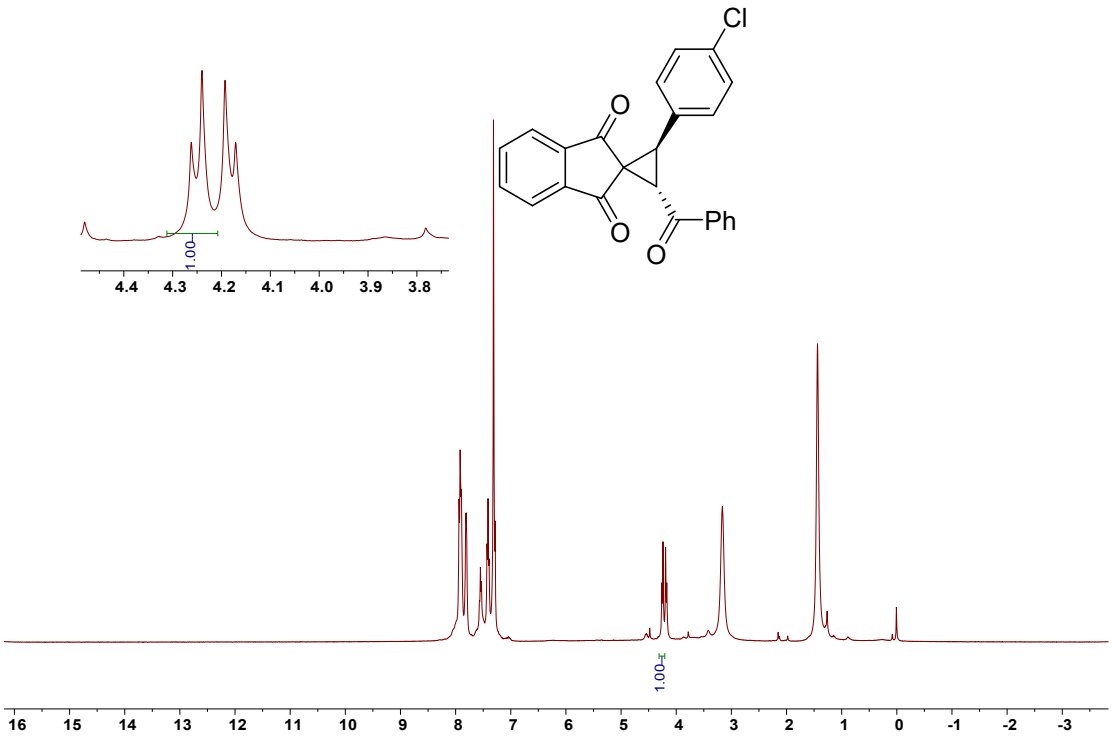
^{1}H NMR of reaction mixture **3al**



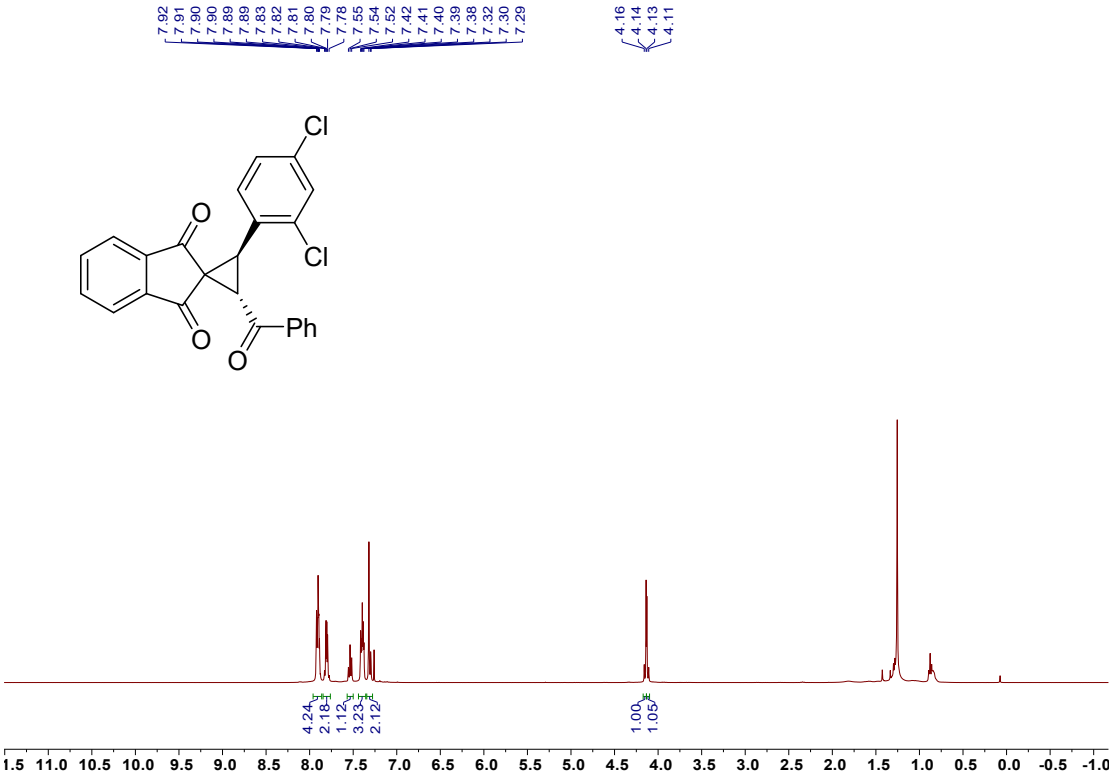
^{1}H NMR of compound **3am**



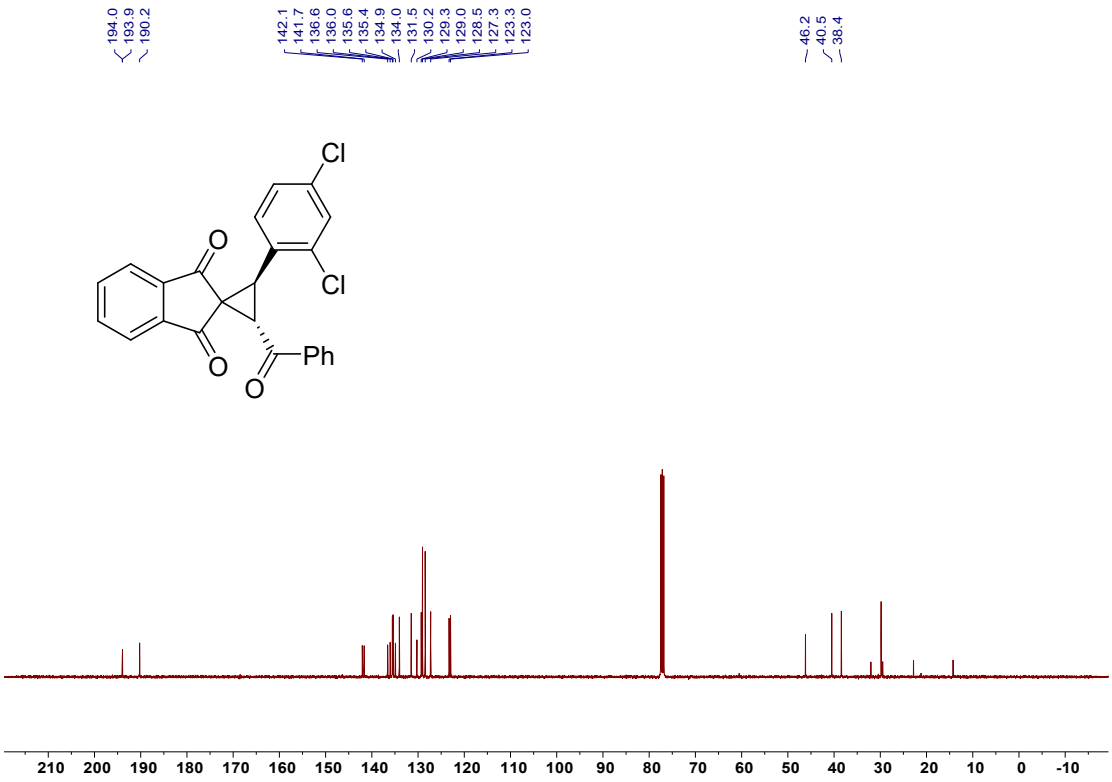
^{13}C NMR of compound **3am**



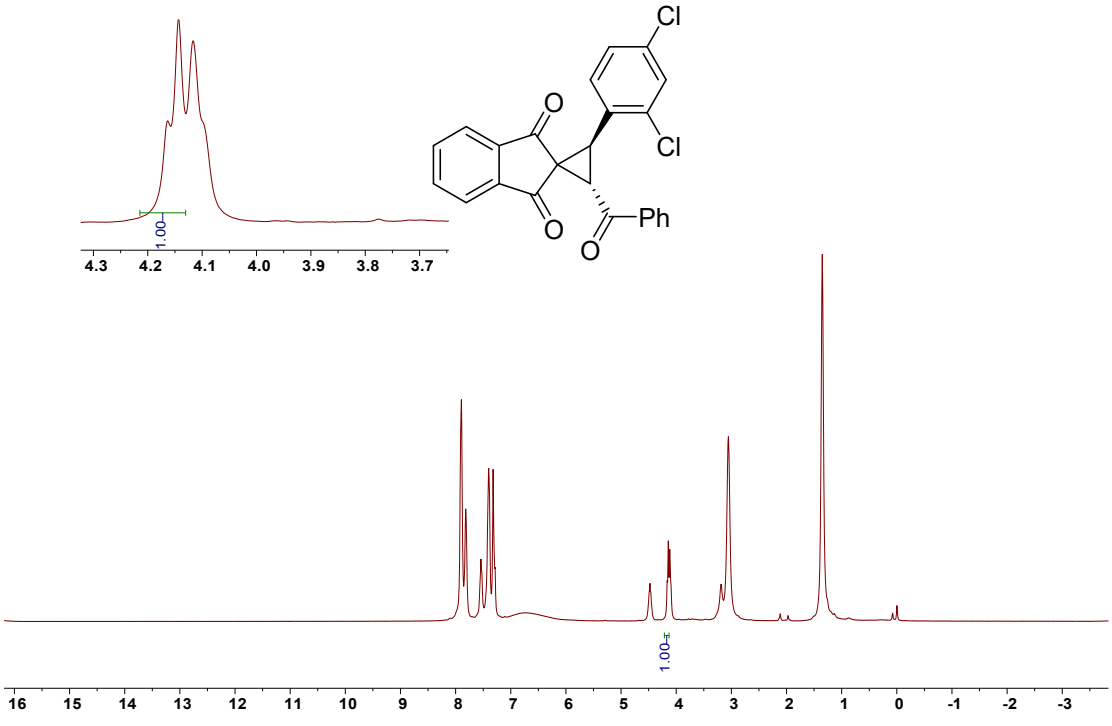
^{1}H NMR of reaction mixture **3am**



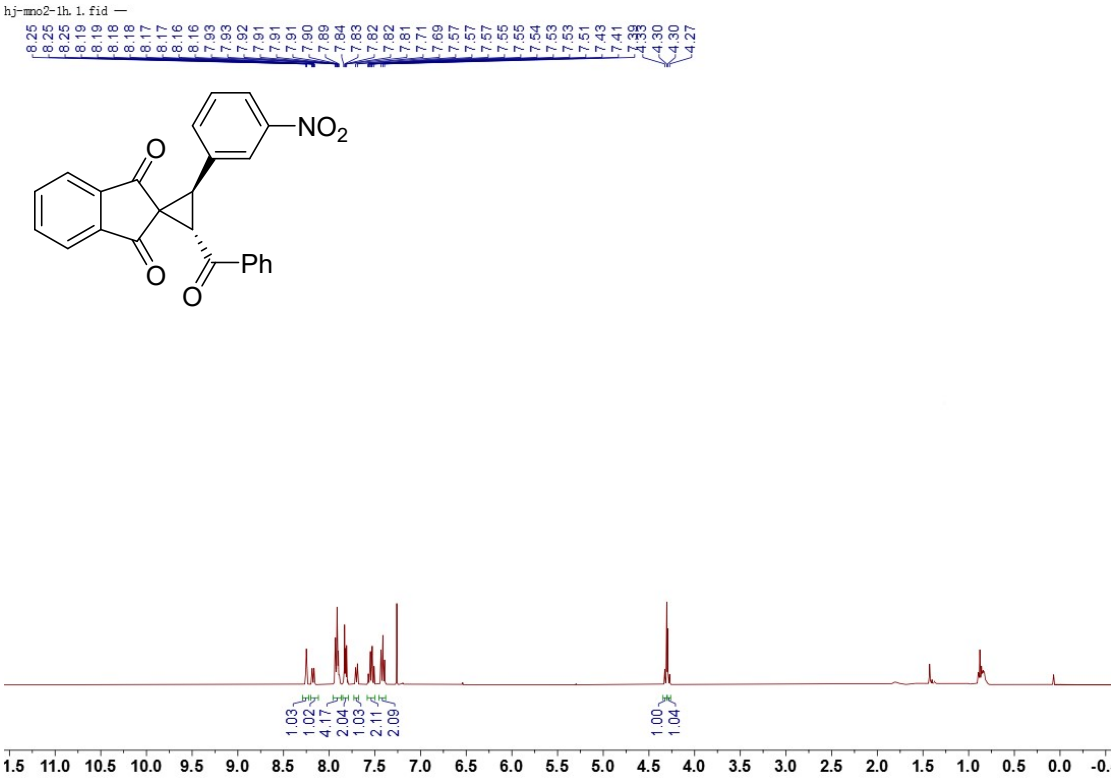
^{1}H NMR of compound **3an**



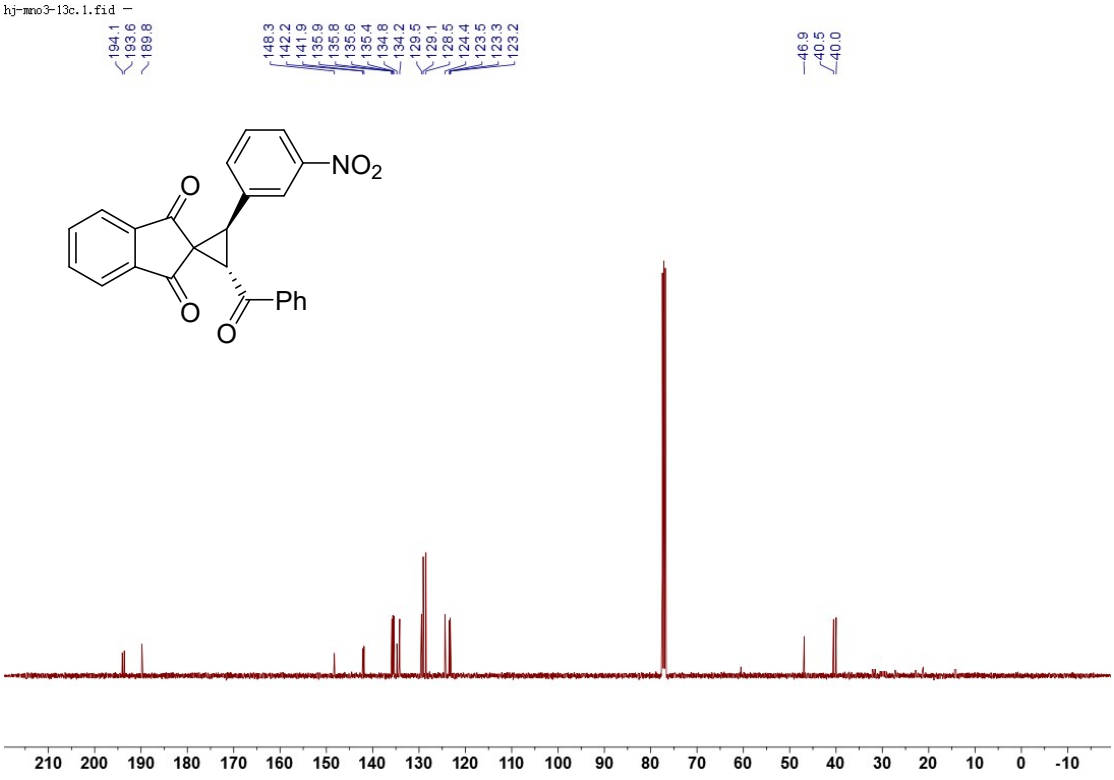
^{13}C NMR of compound **3an**



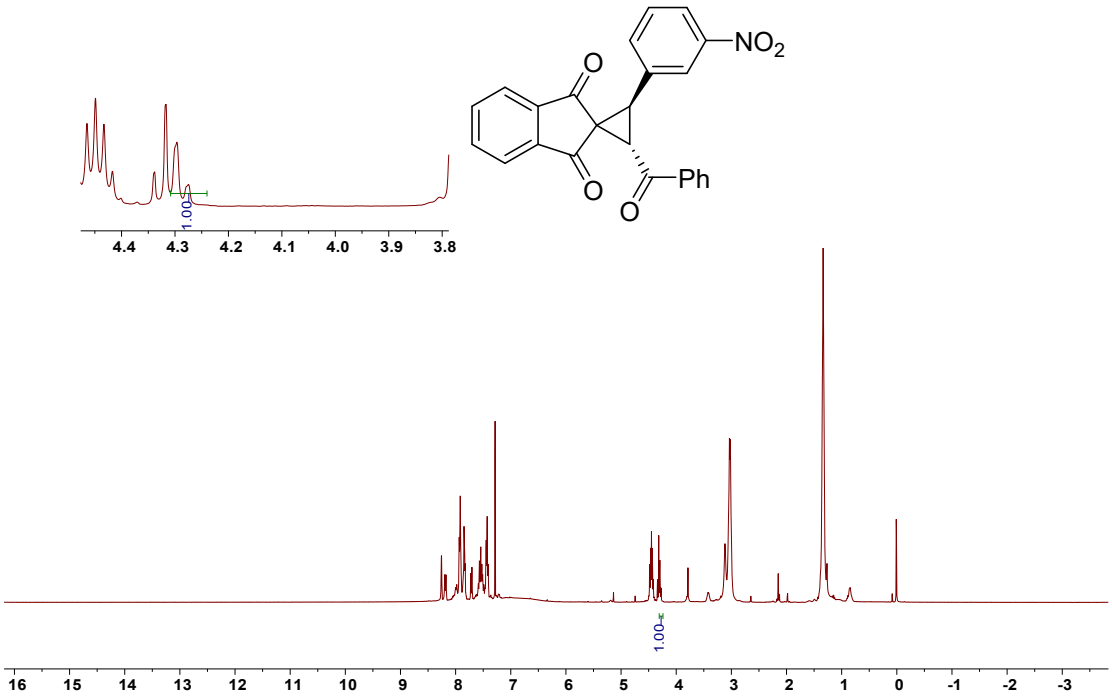
^{1}H NMR of reaction mixture **3an**



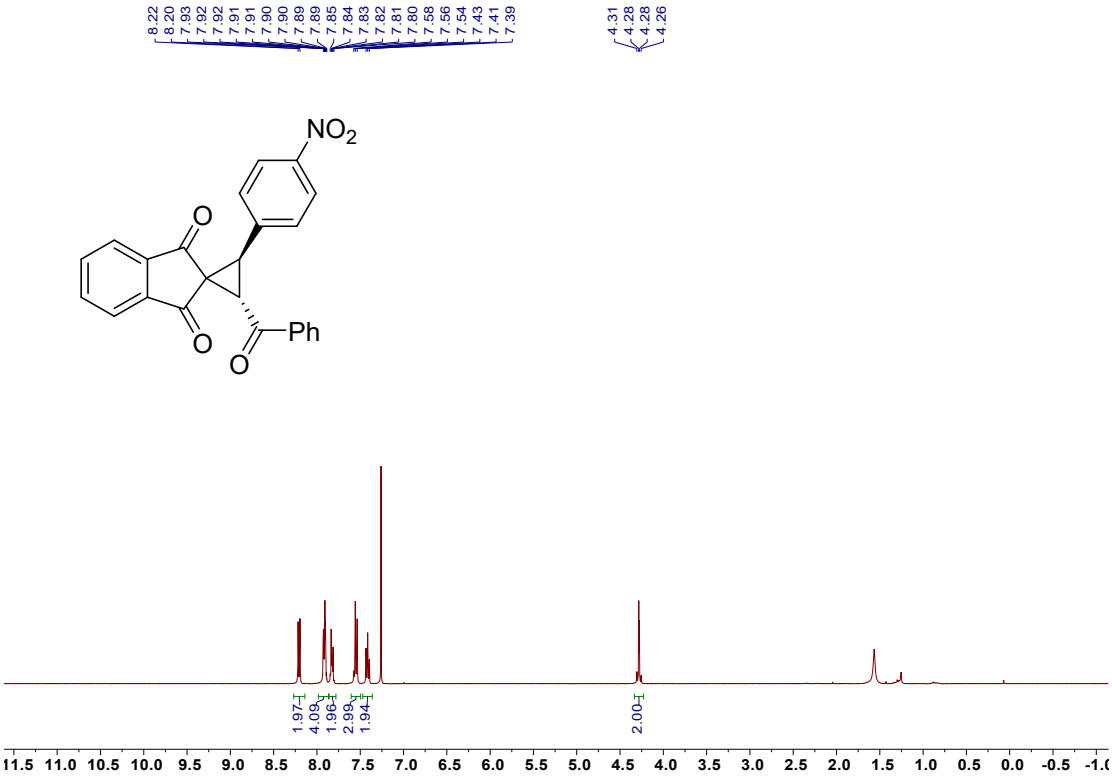
^{1}H NMR of compound **3ao**



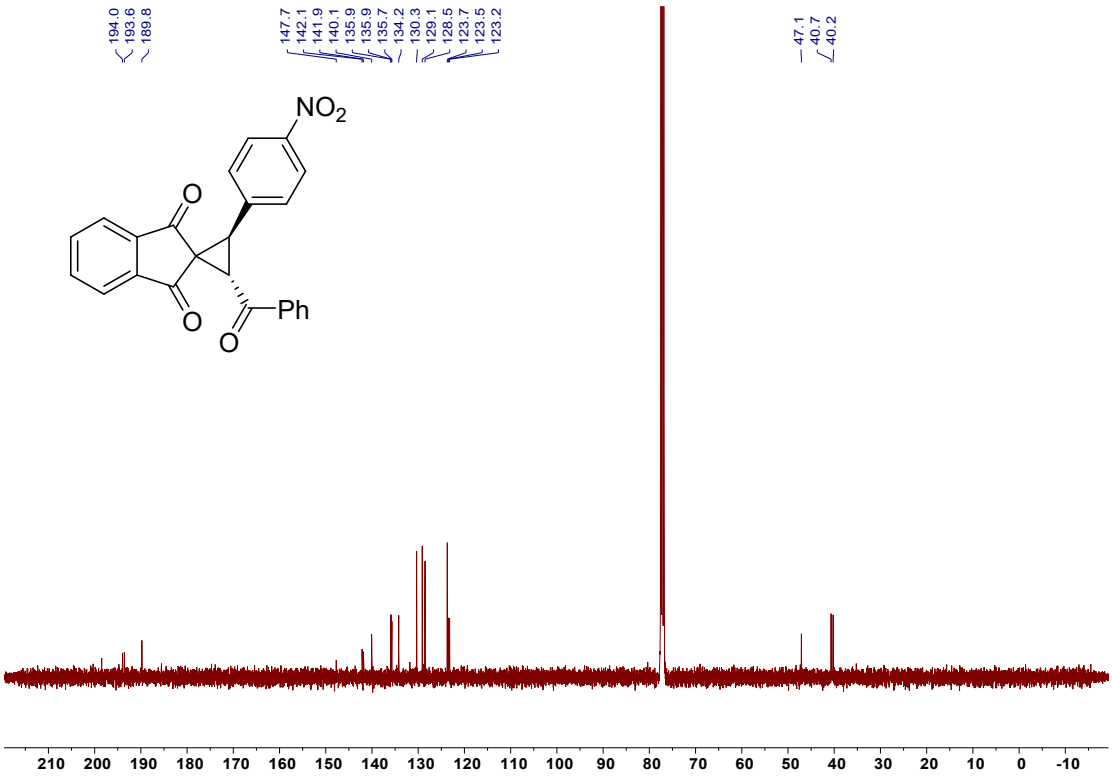
^{13}C NMR of compound **3ao**



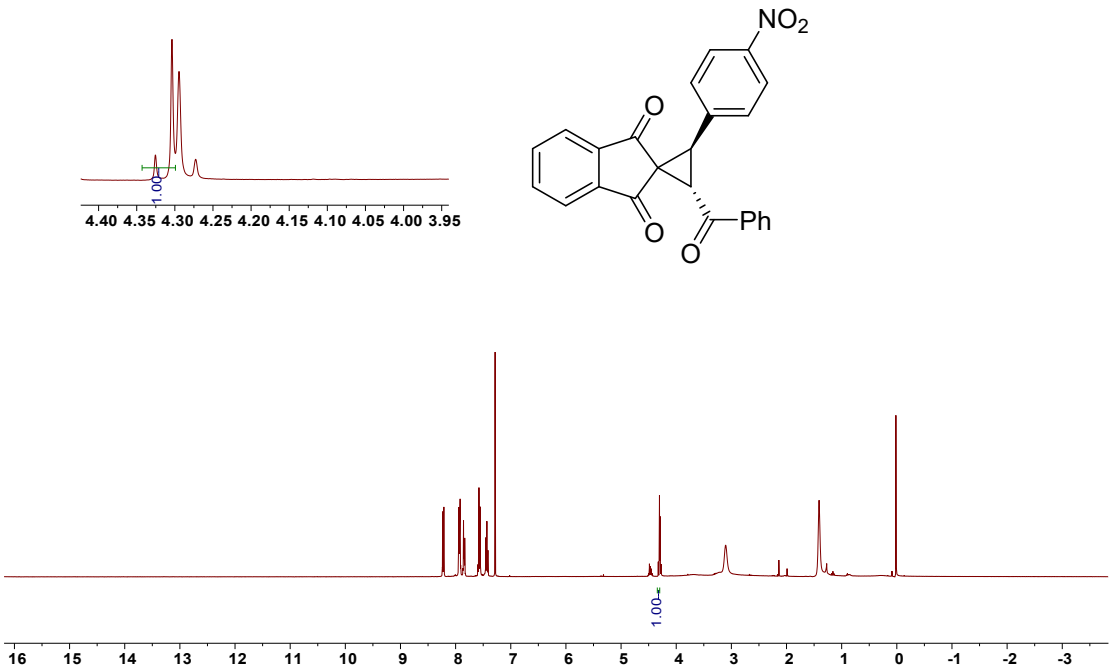
^{1}H NMR of reaction mixture **3ao**



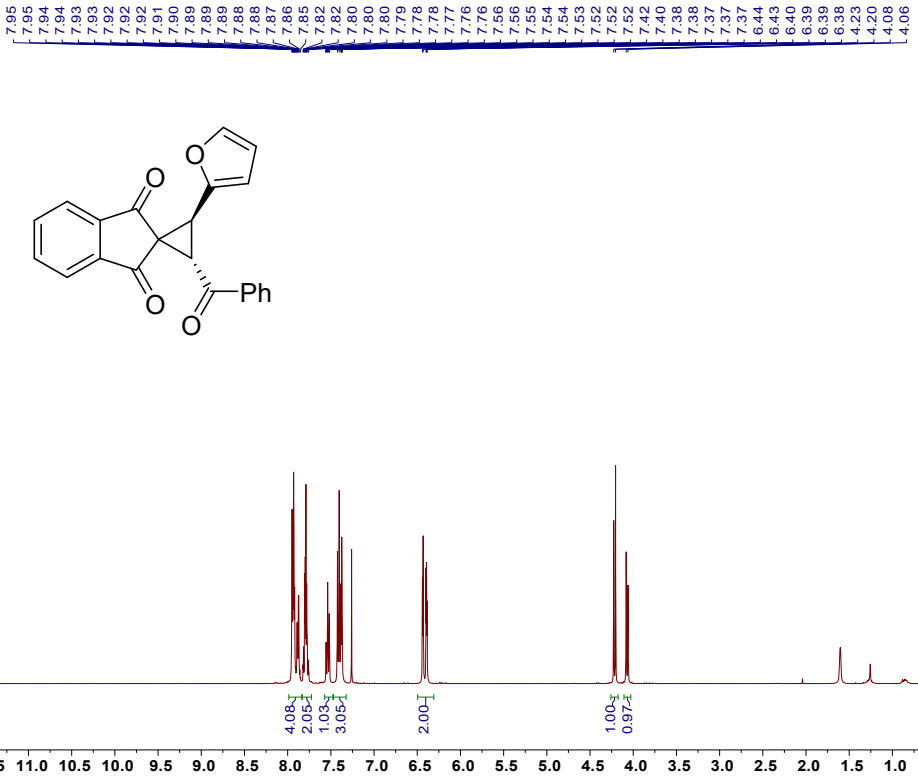
^{1}H NMR of compound **3ap**



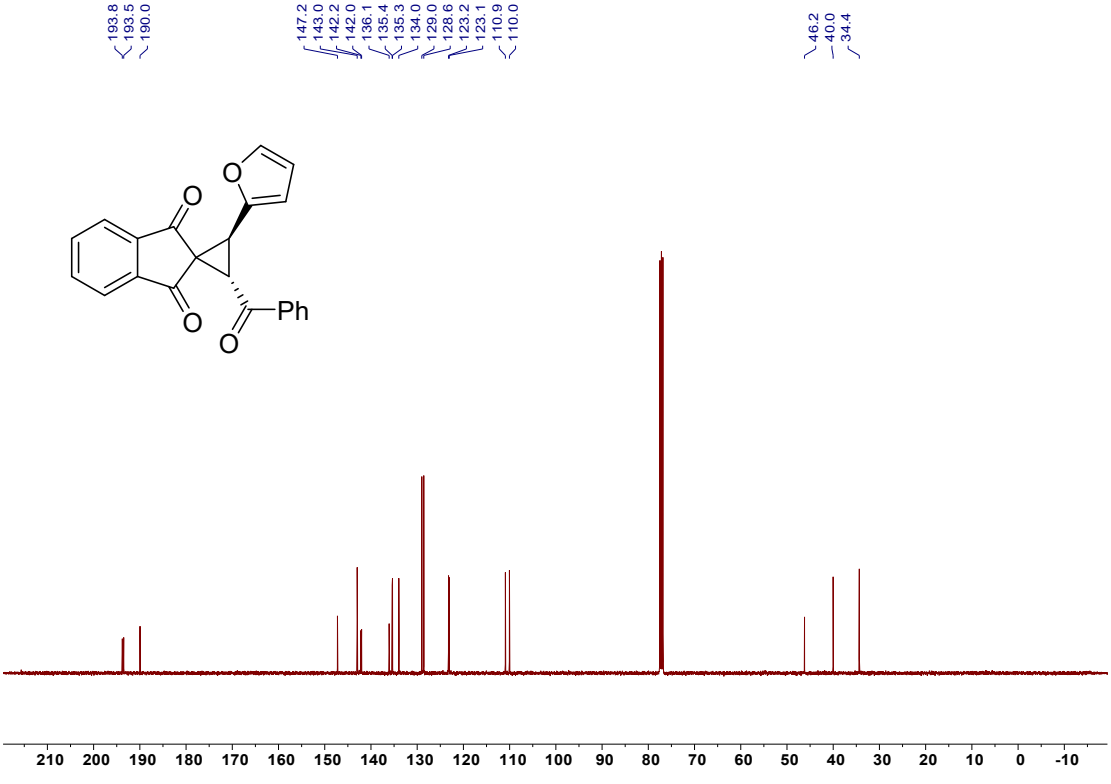
^{13}C NMR of compound **3ap**



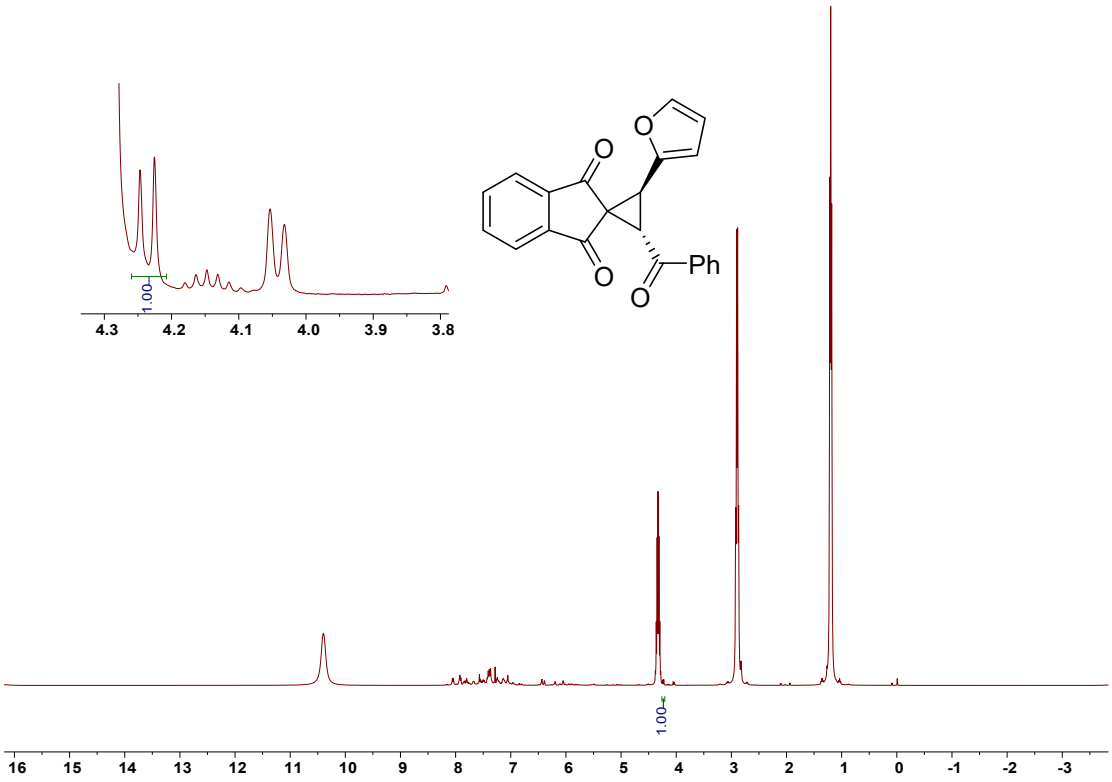
^{1}H NMR of reaction mixture **3ap**



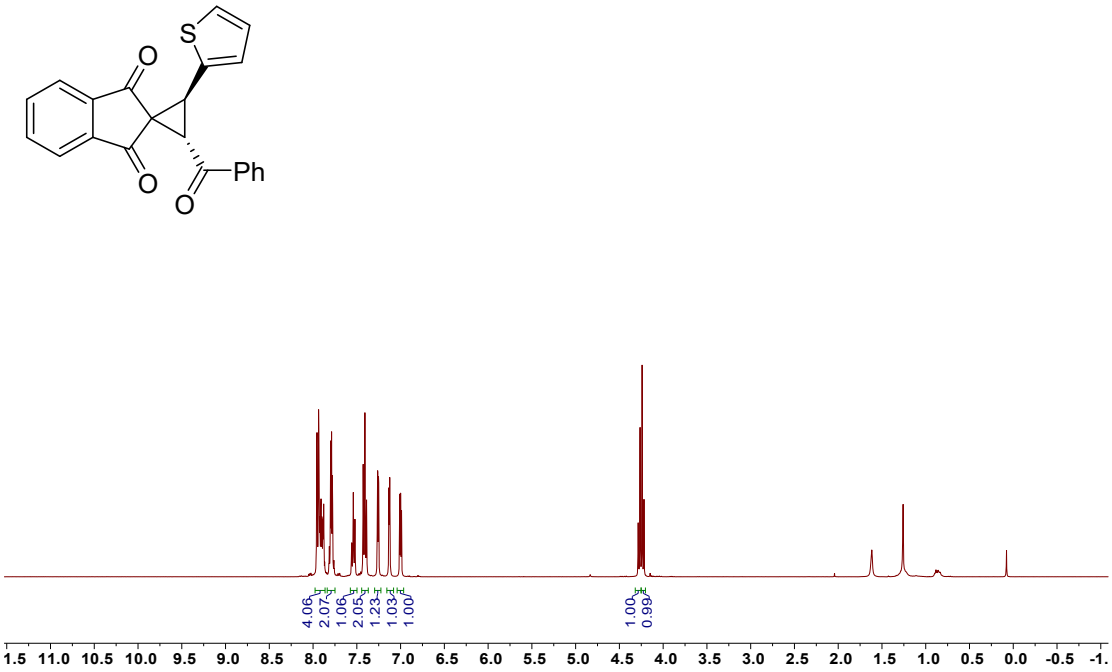
^{1}H NMR of compound **3aq**



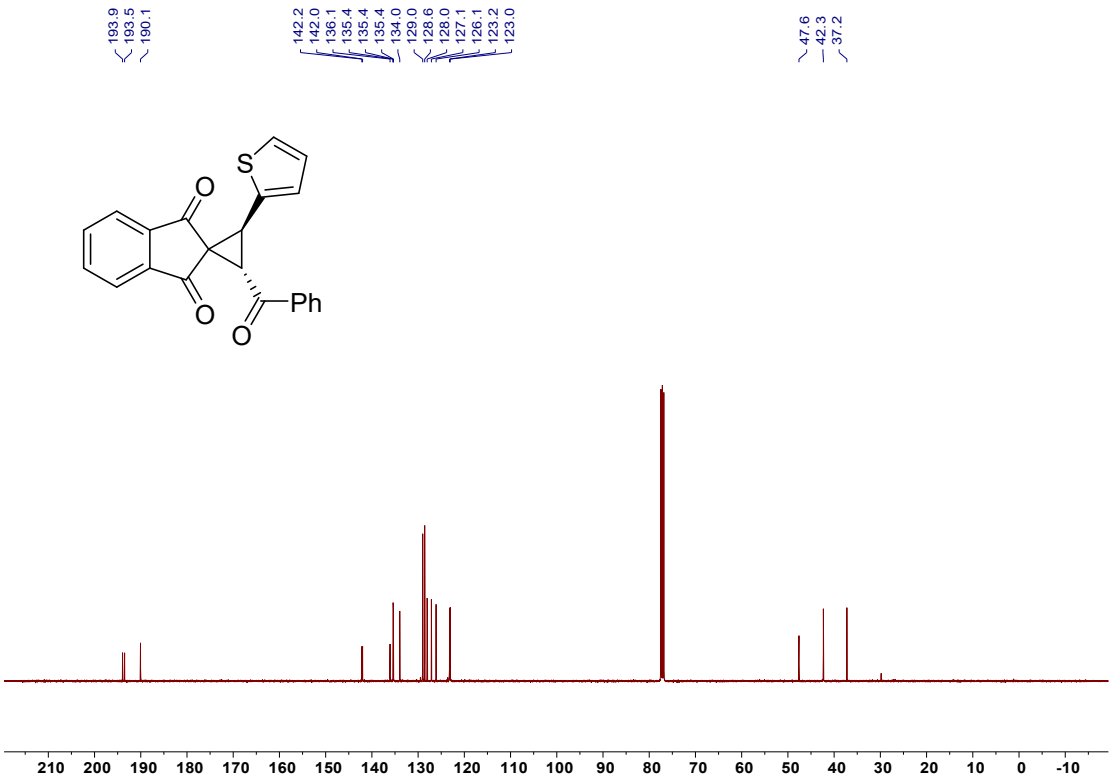
^{13}C NMR of compound **3aq**



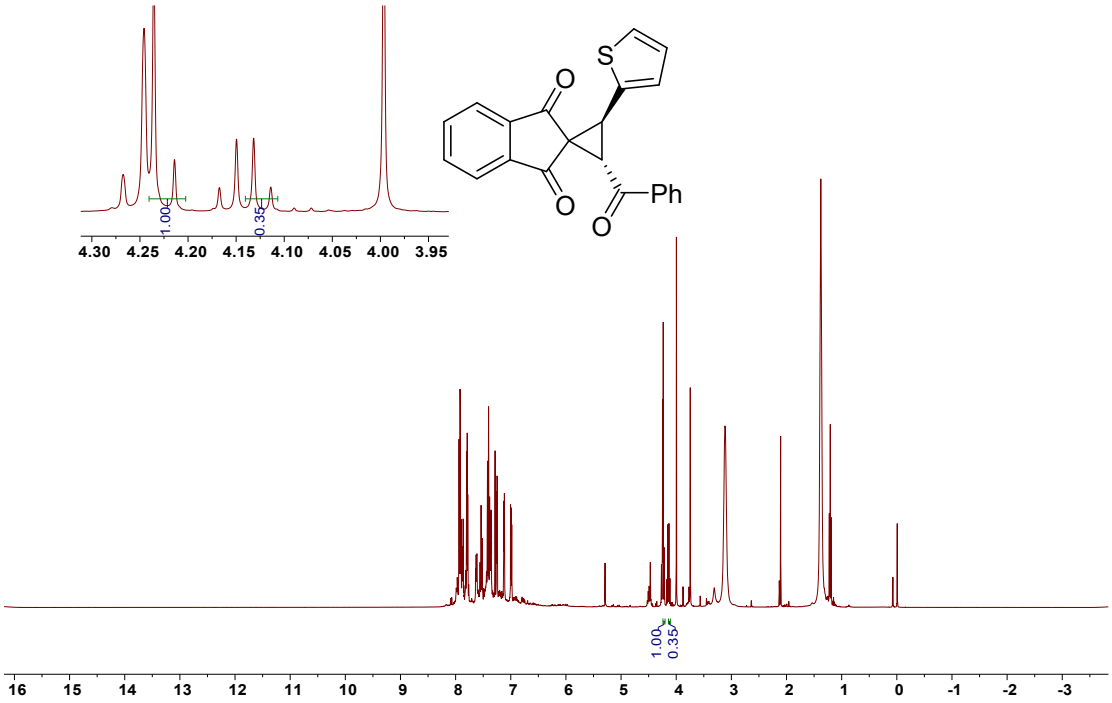
^{1}H NMR of reaction mixture **3aq**



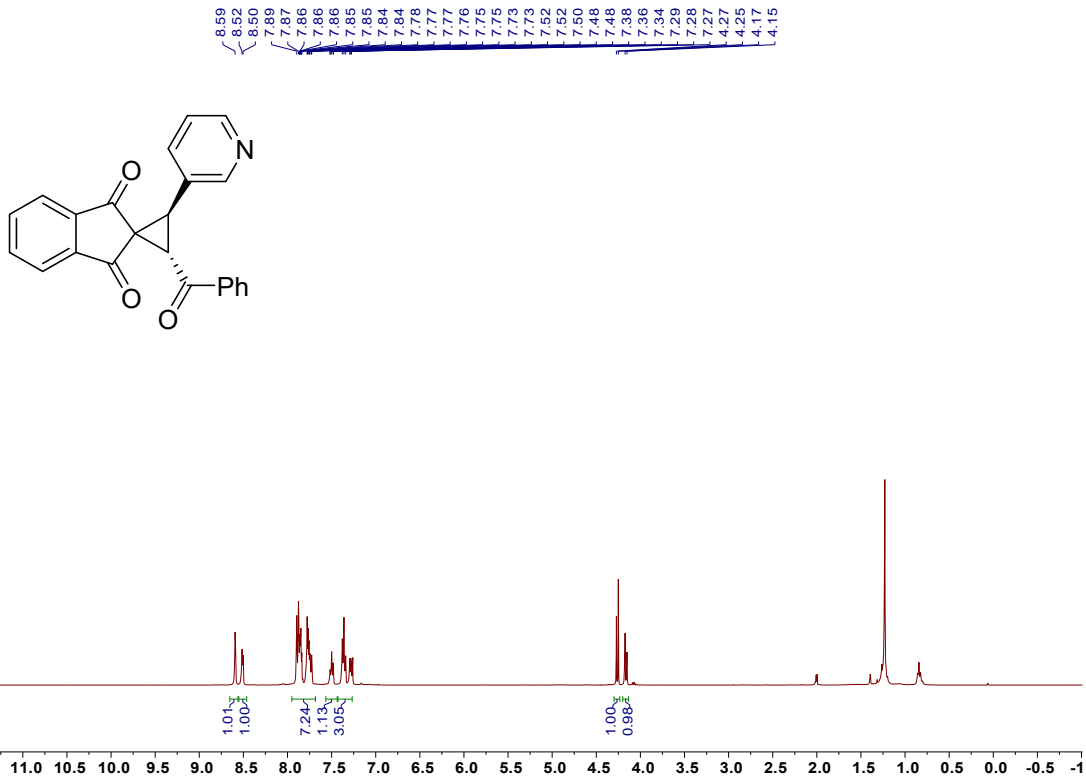
^{1}H NMR of compound **3ar**



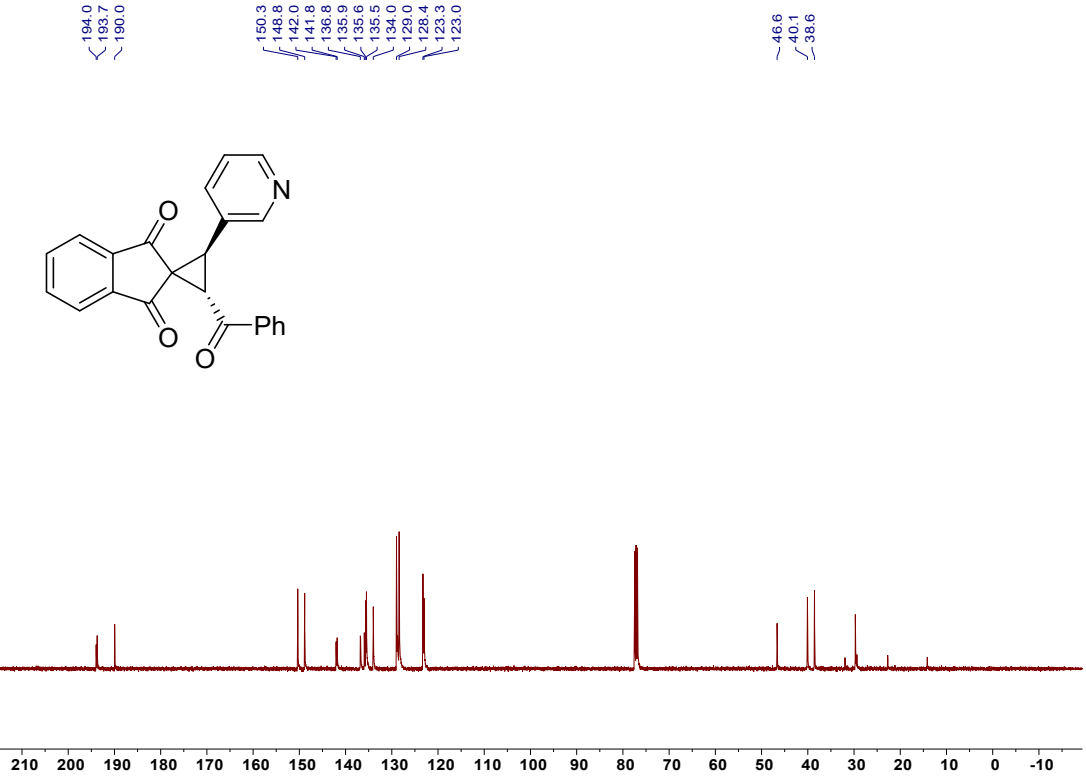
^{13}C NMR of compound **3ar**



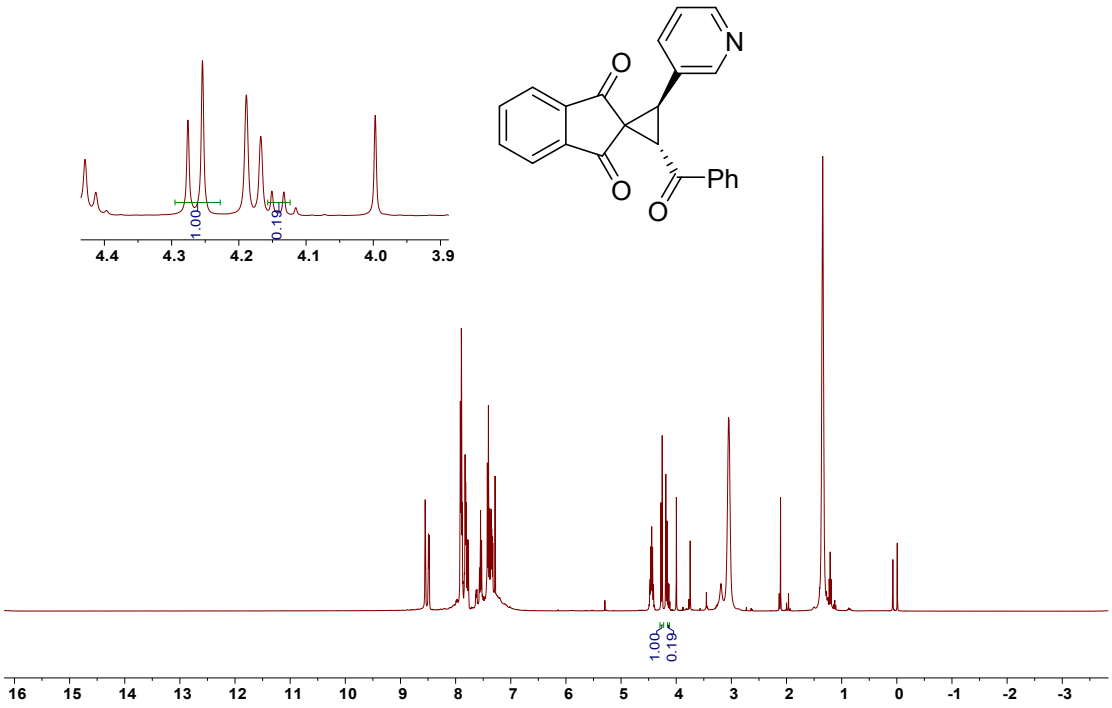
^{1}H NMR of reaction mixture **3ar**



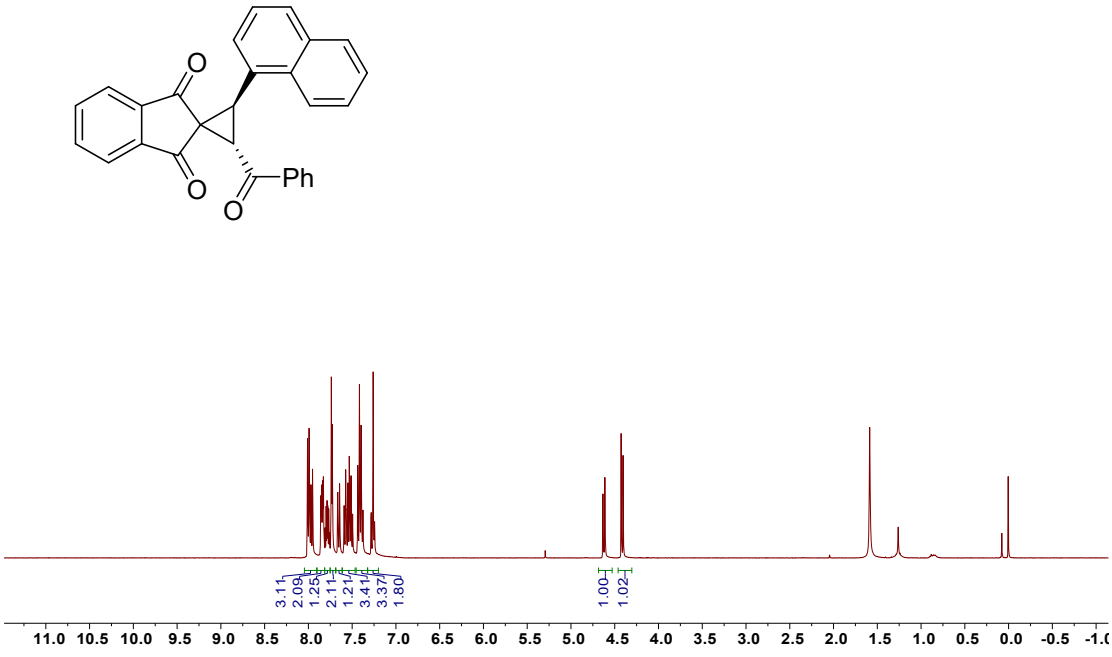
^{1}H NMR of compound **3as**



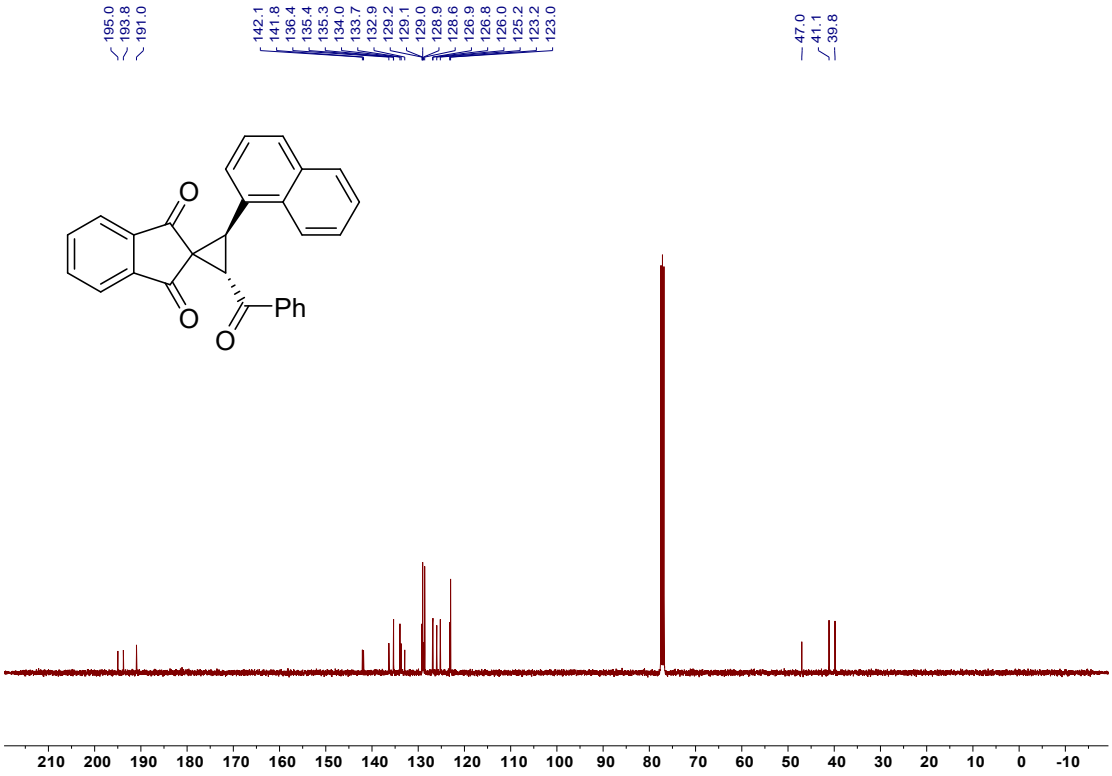
^{13}C NMR of compound **3as**



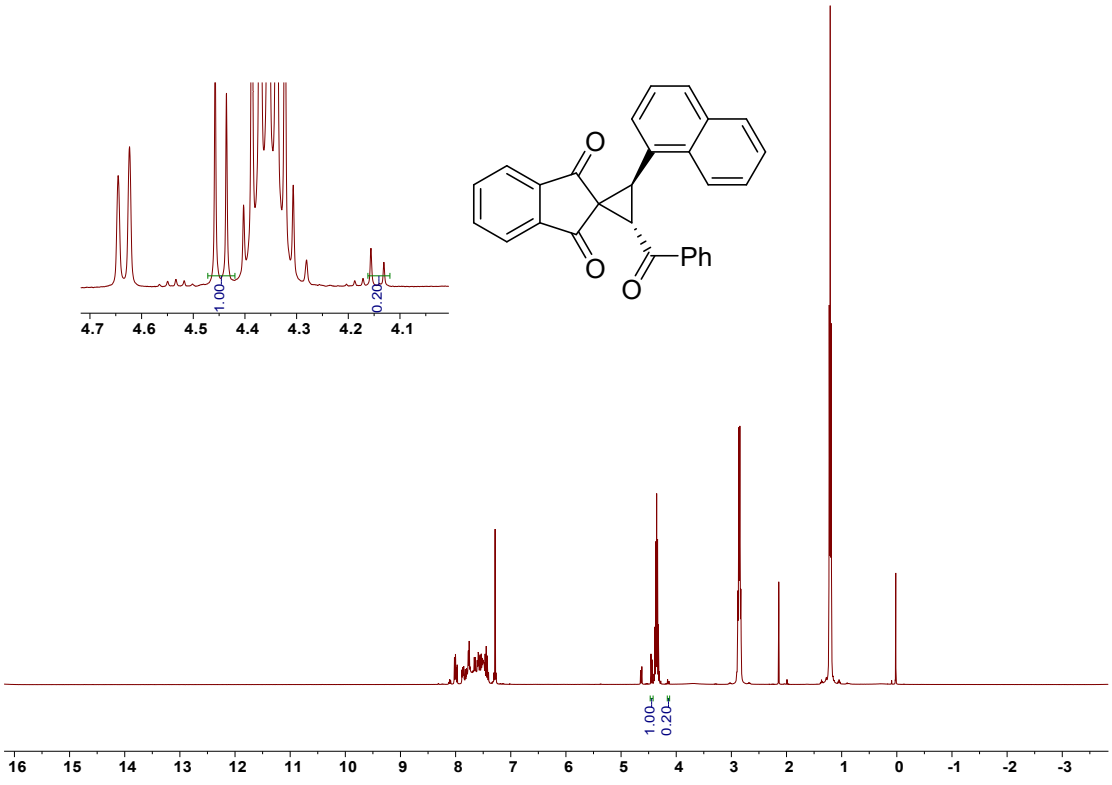
^{1}H NMR of reaction mixture **3as**



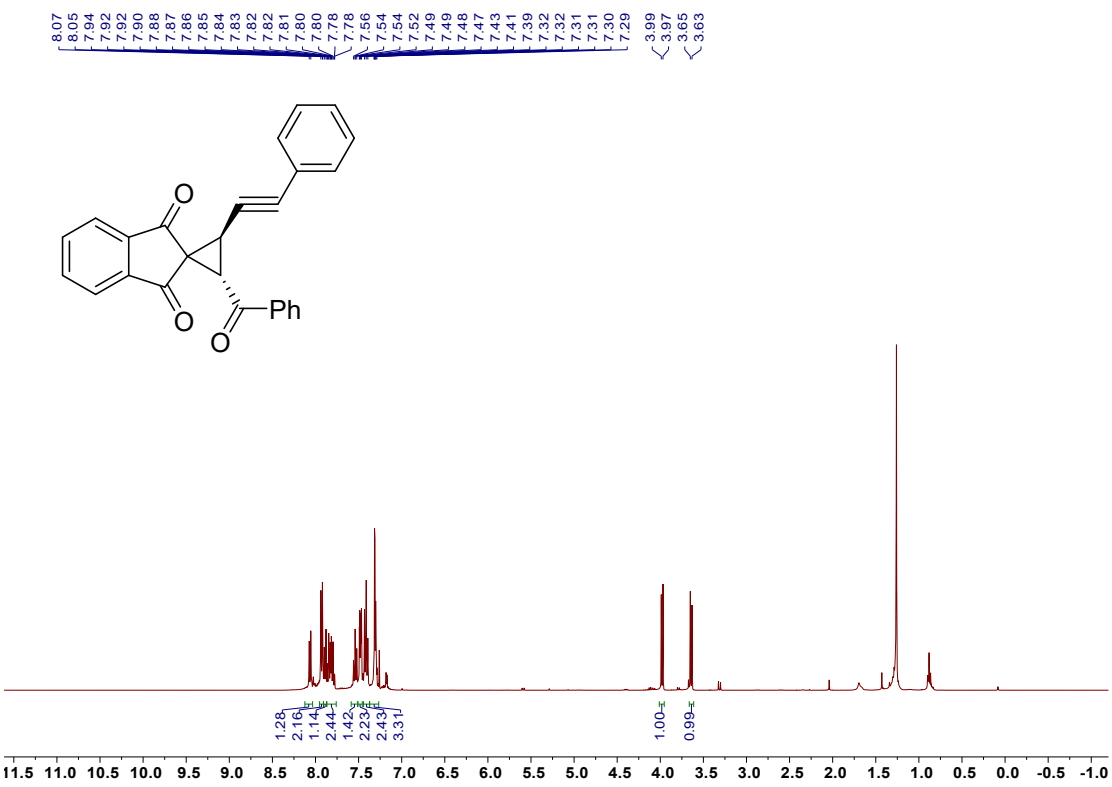
^{1}H NMR of compound **3at**



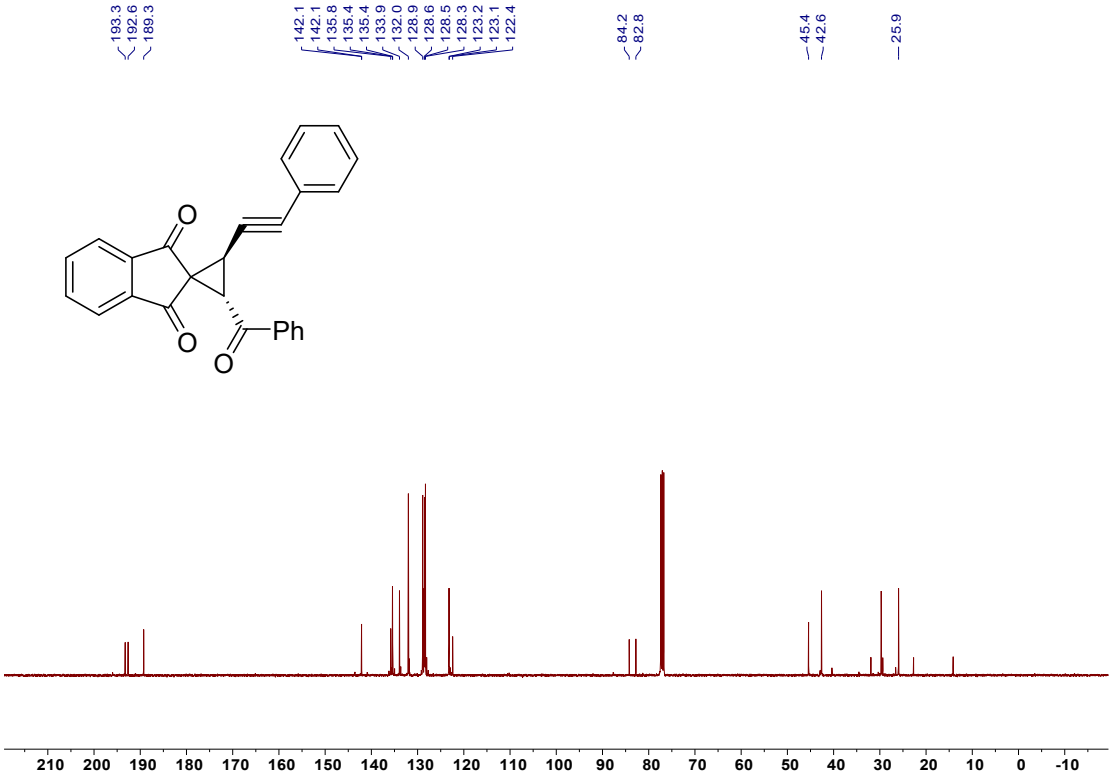
^{13}C NMR of compound **3at**



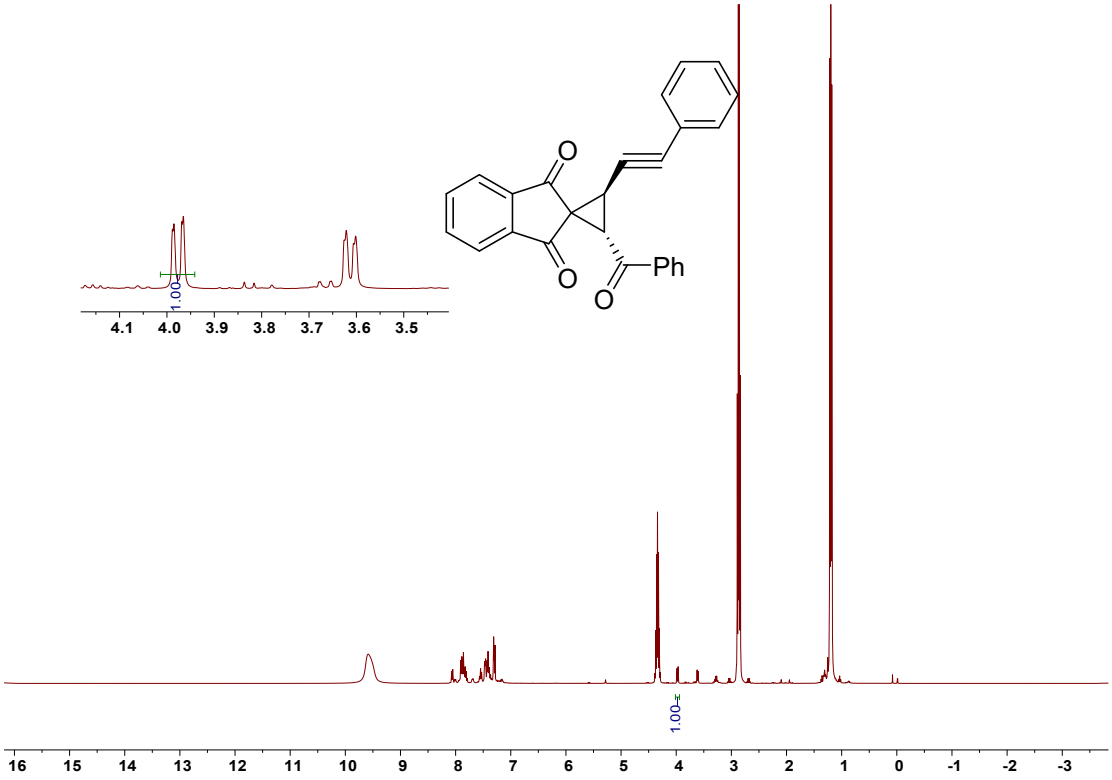
^{1}H NMR of reaction mixture **3at**



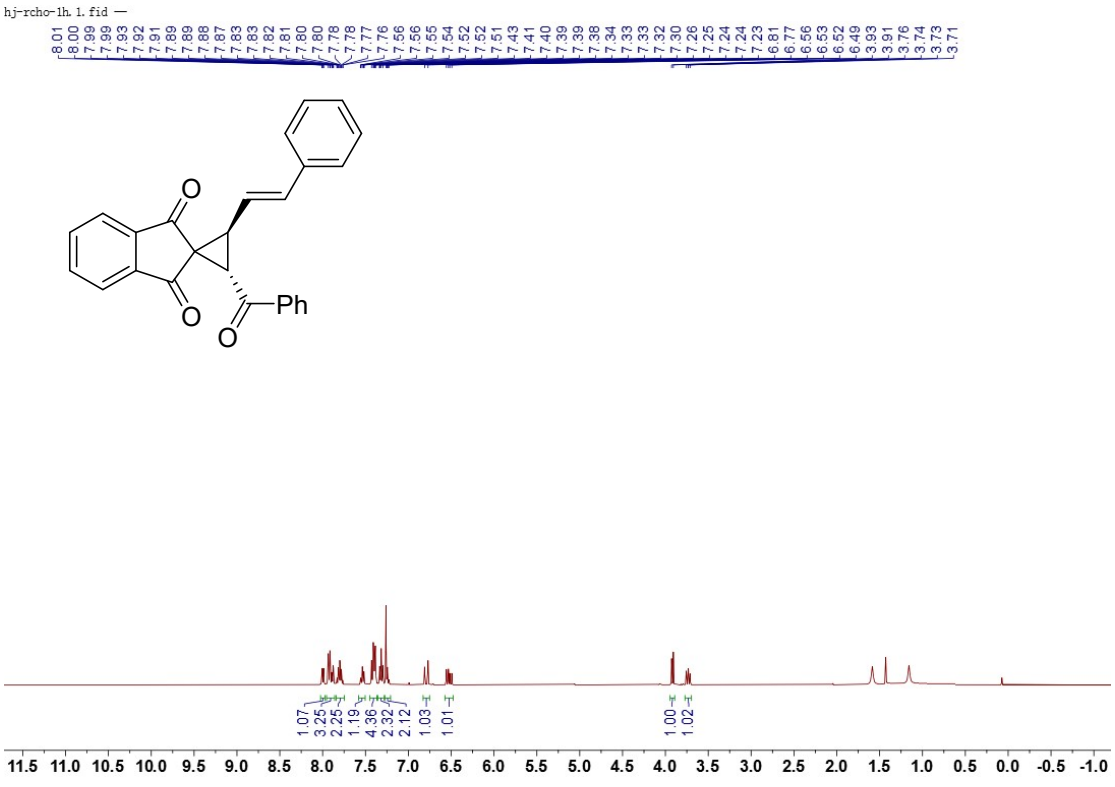
^{1}H NMR of compound **3au**



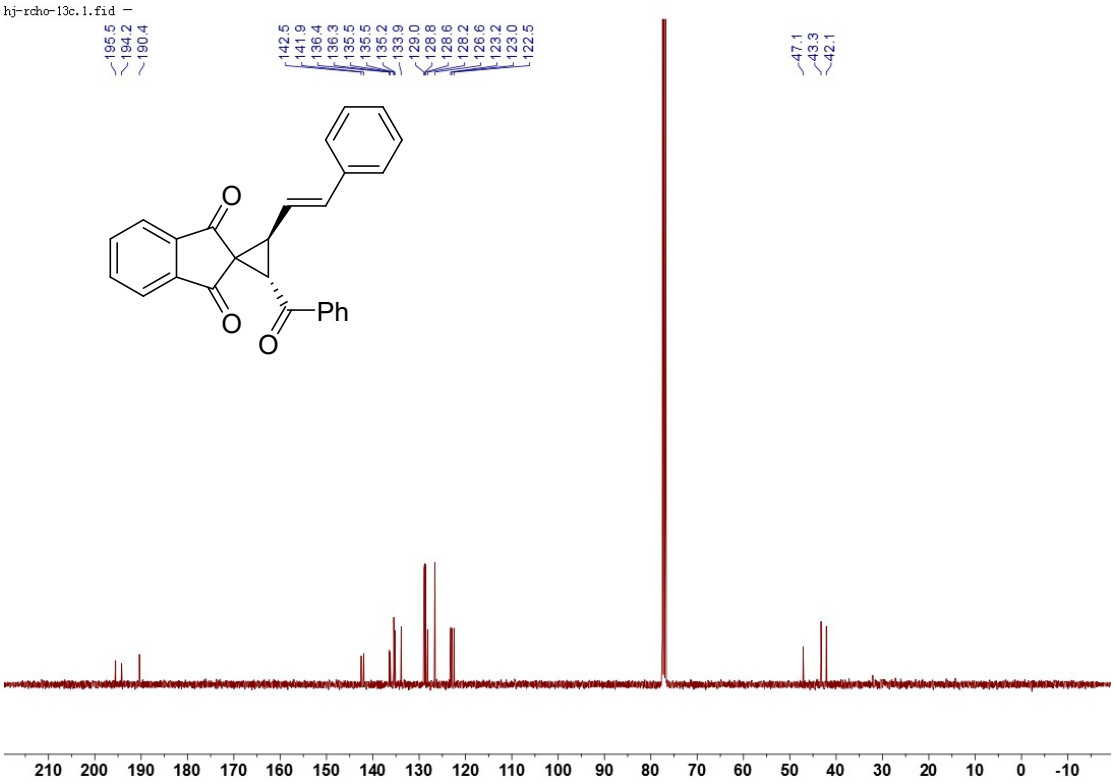
^{13}C NMR of compound **3au**



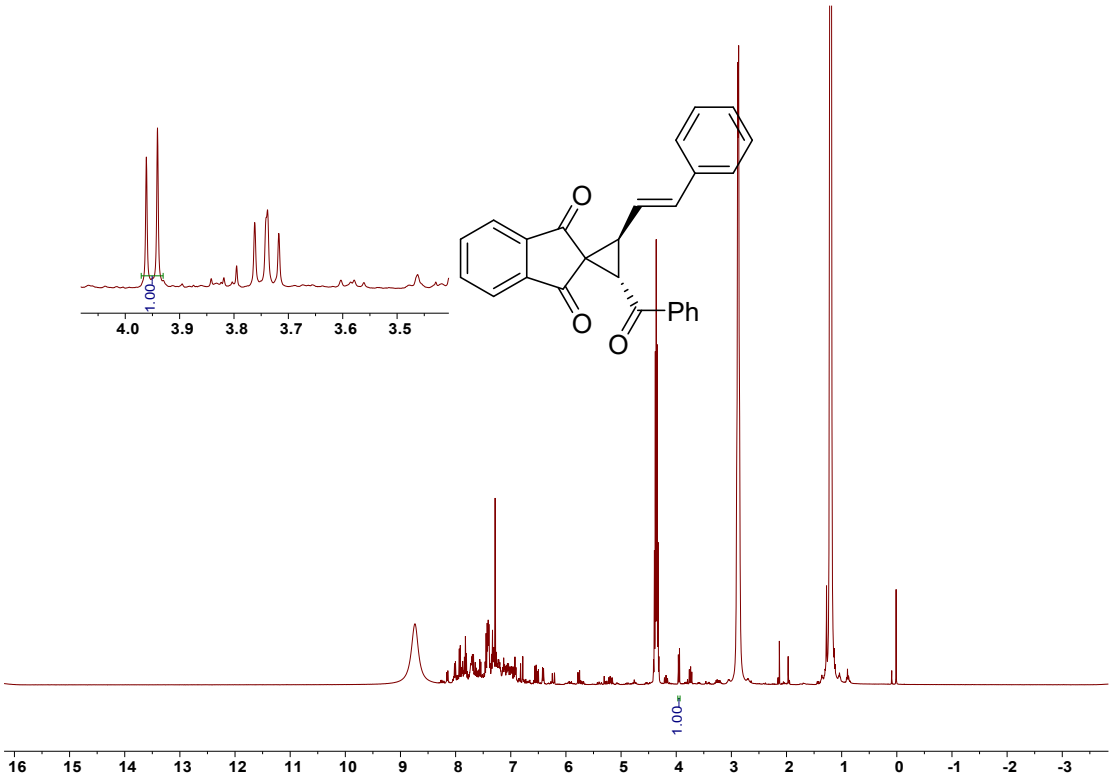
^{1}H NMR of reaction mixture **3au**



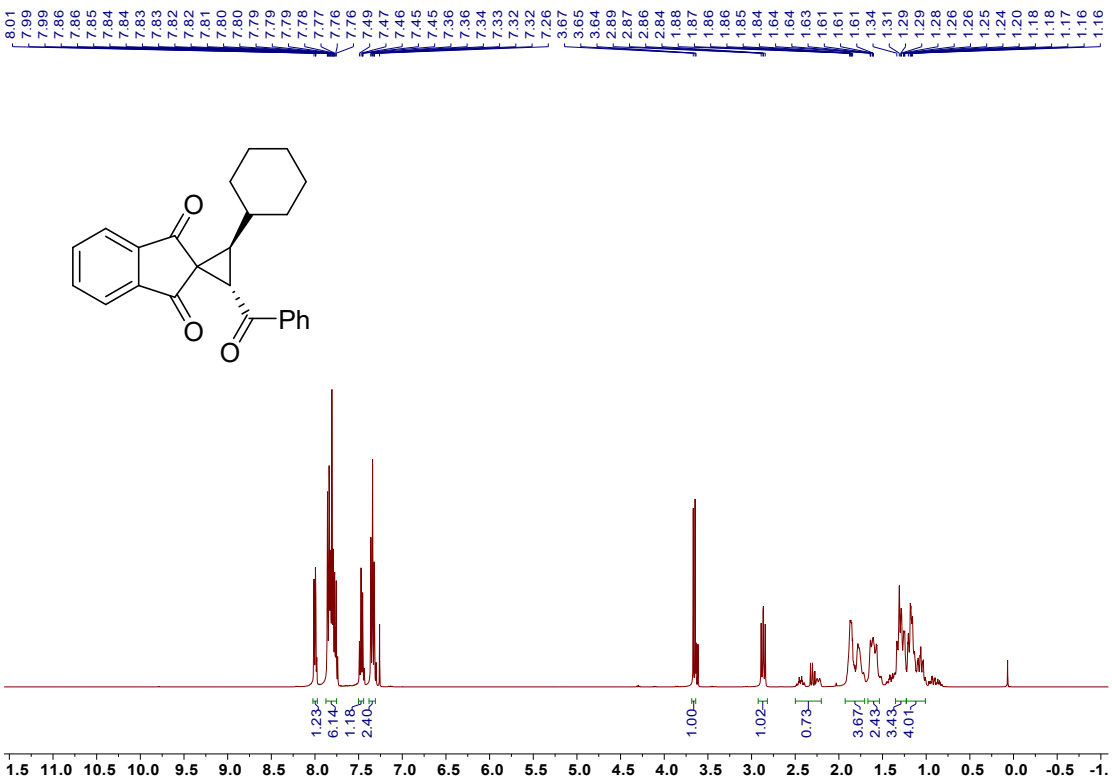
^{1}H NMR of compound **3av**



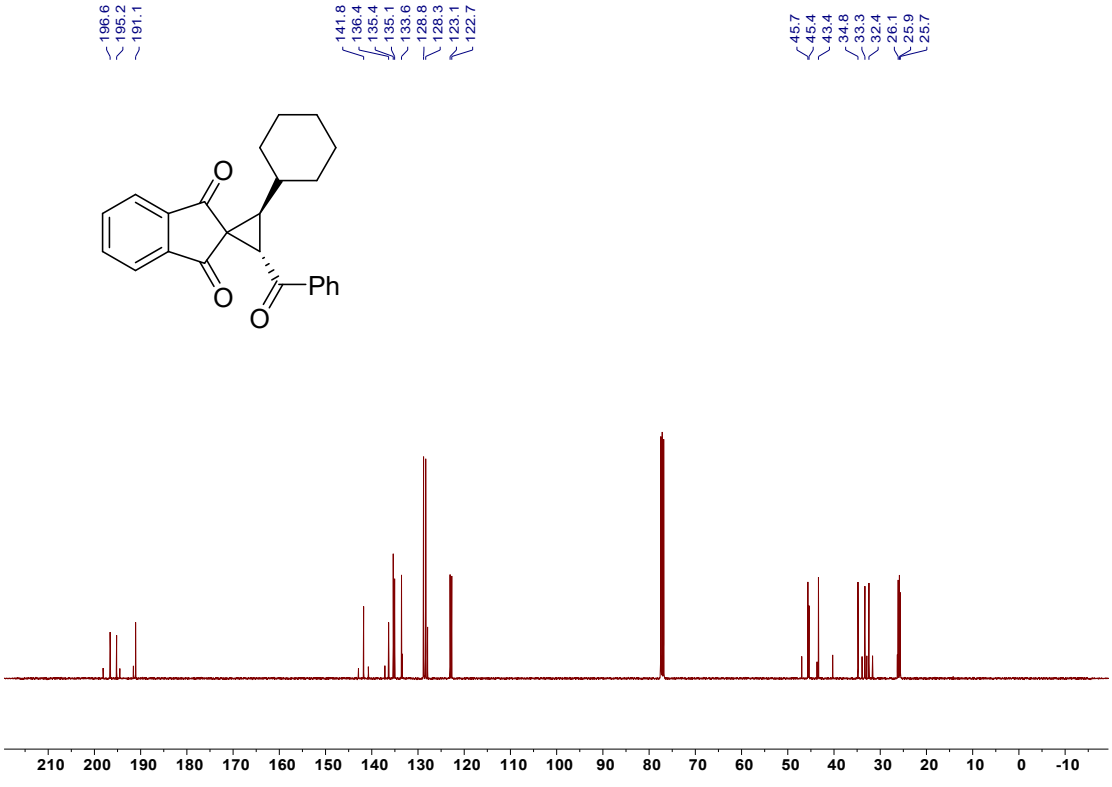
^{13}C NMR of compound **3av**



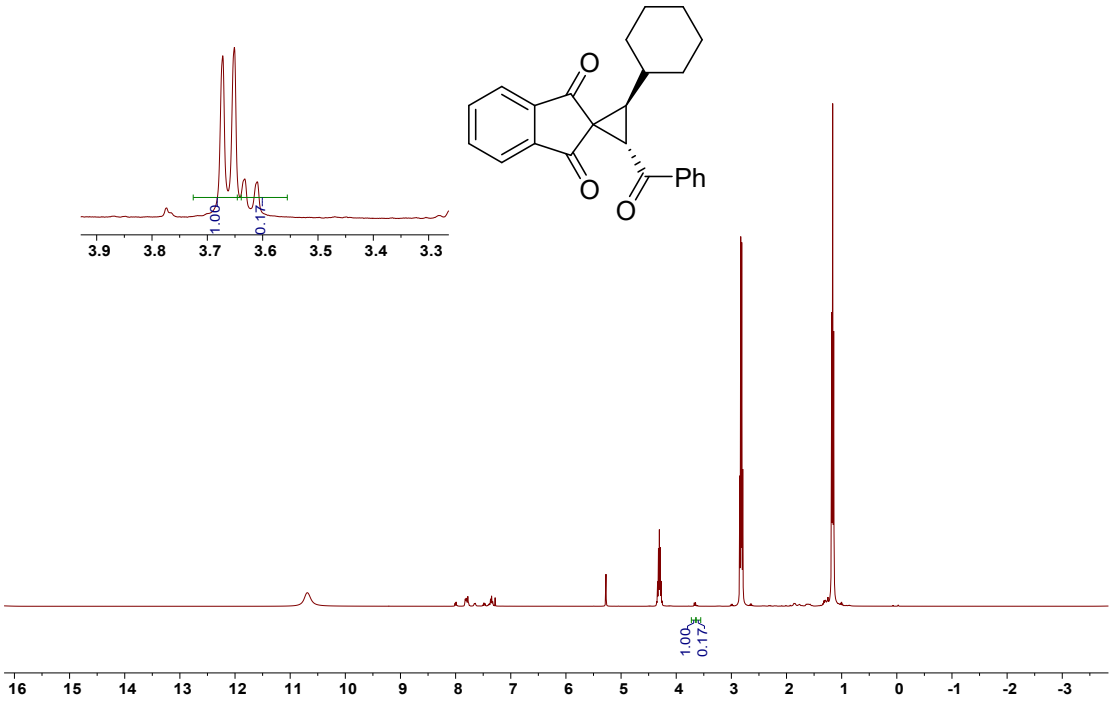
^{1}H NMR of reaction mixture **3av**



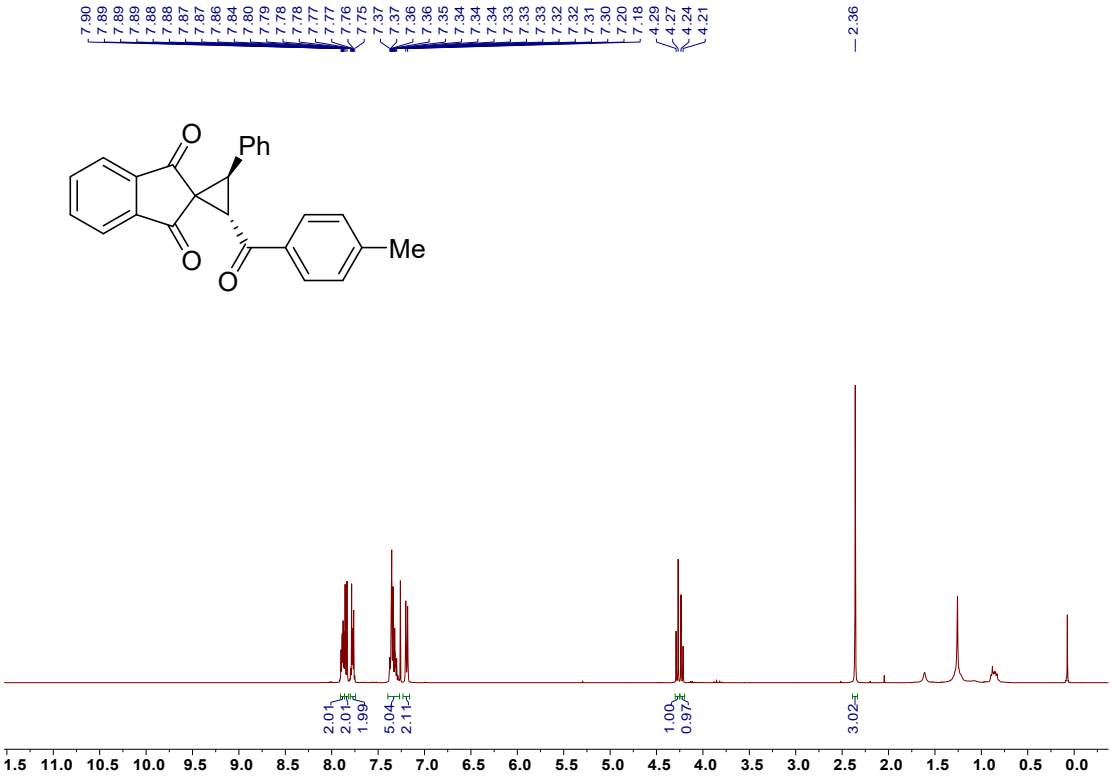
^{1}H NMR of compound **3aw**



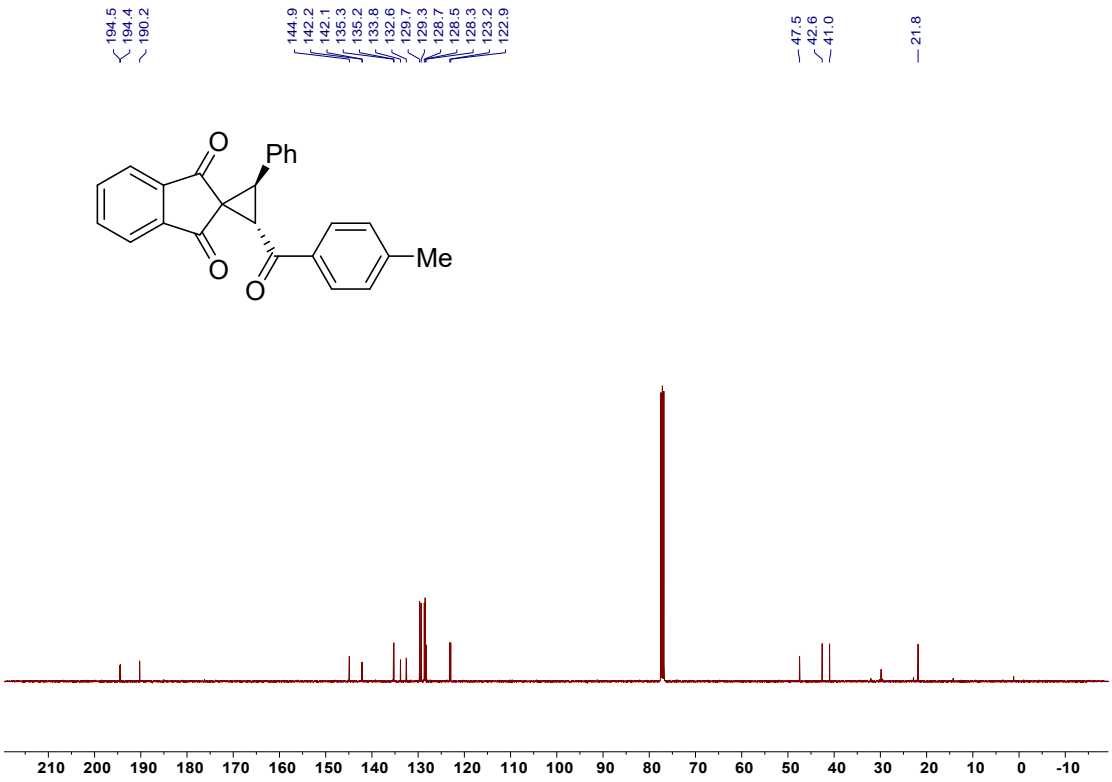
^{13}C NMR of compound **3aw**



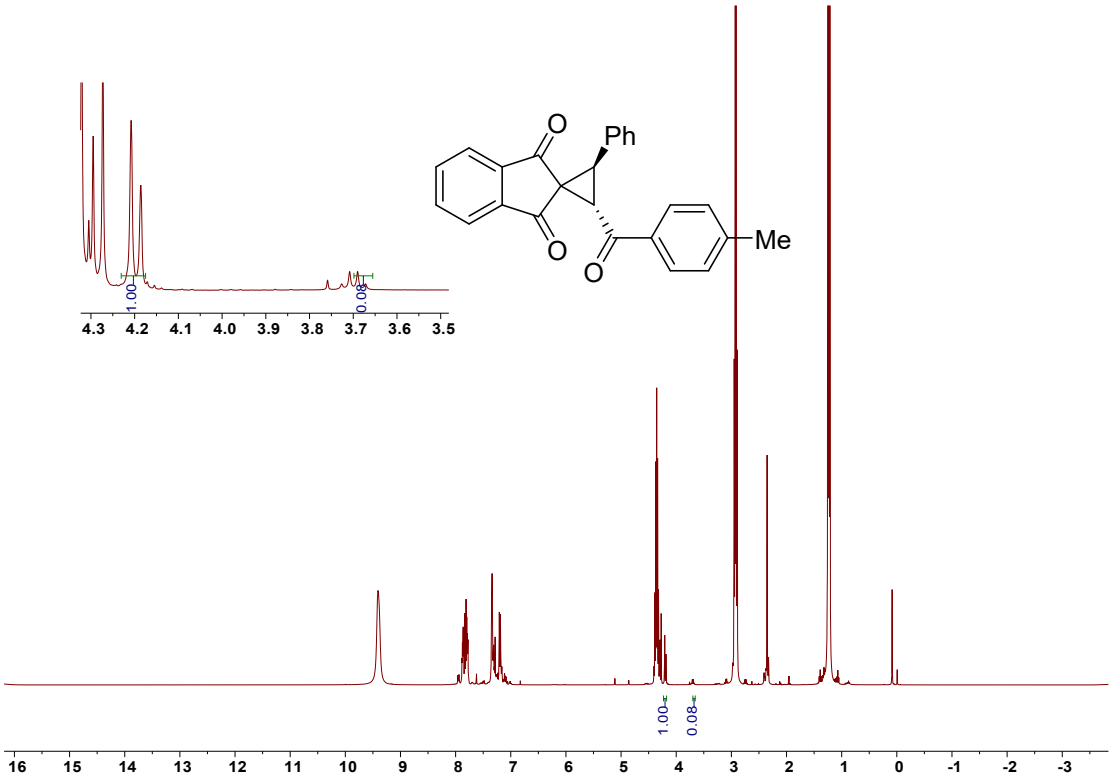
^{1}H NMR of reaction mixture **3aw**



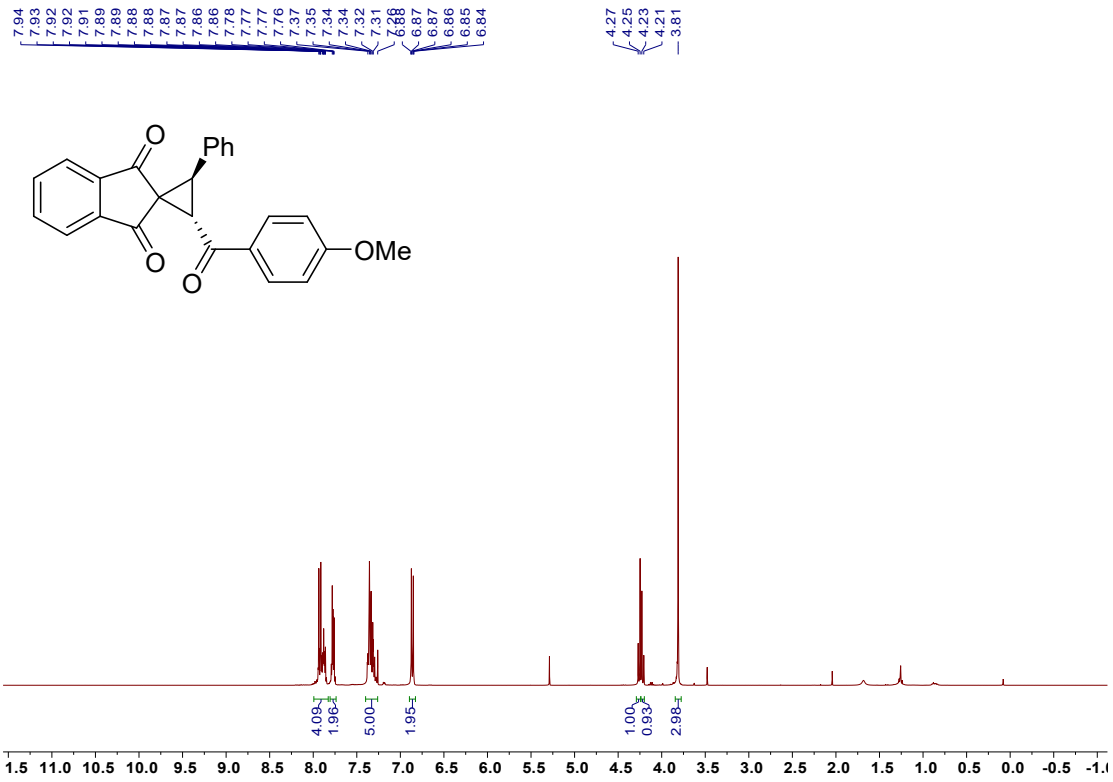
^{1}H NMR of compound **3ba**



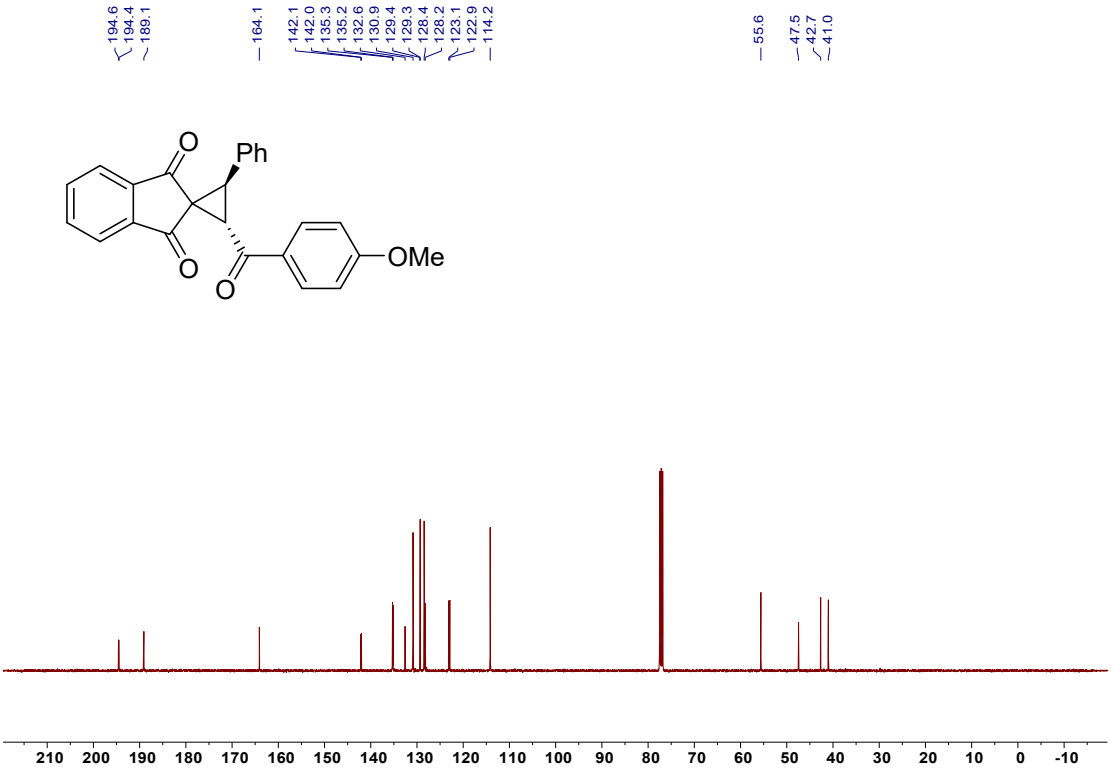
^{13}C NMR of compound **3ba**



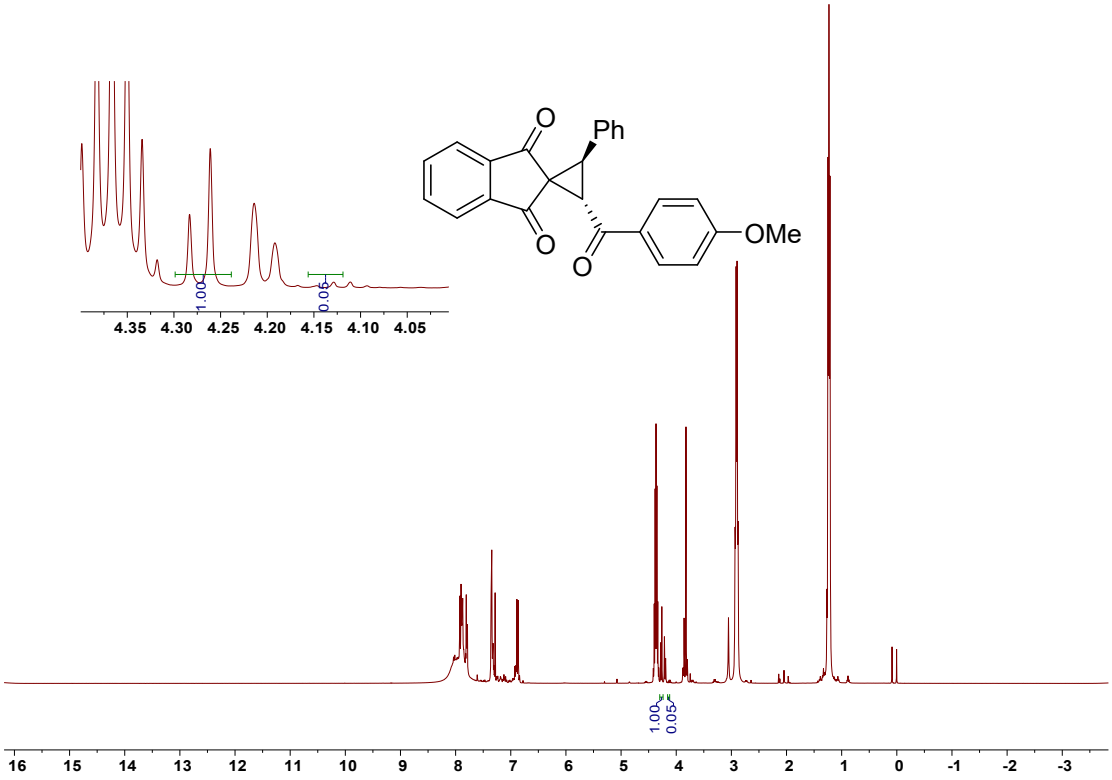
^{1}H NMR of reaction mixture **3ba**



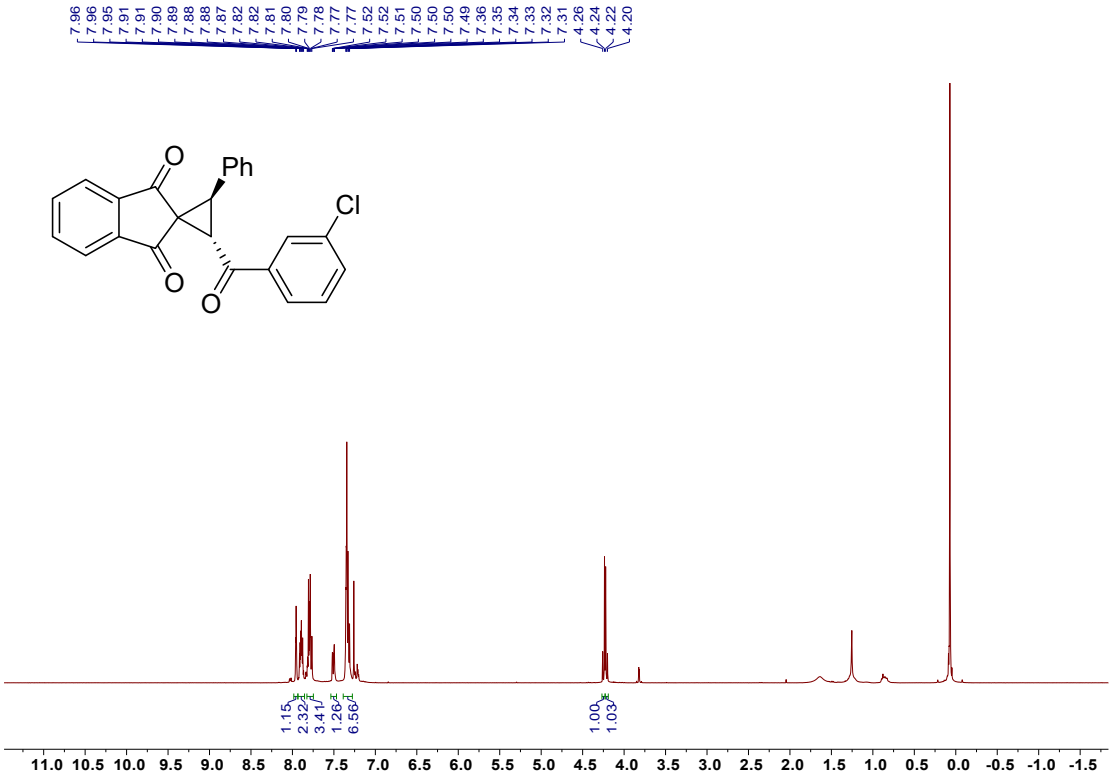
^{1}H NMR of compound **3ca**



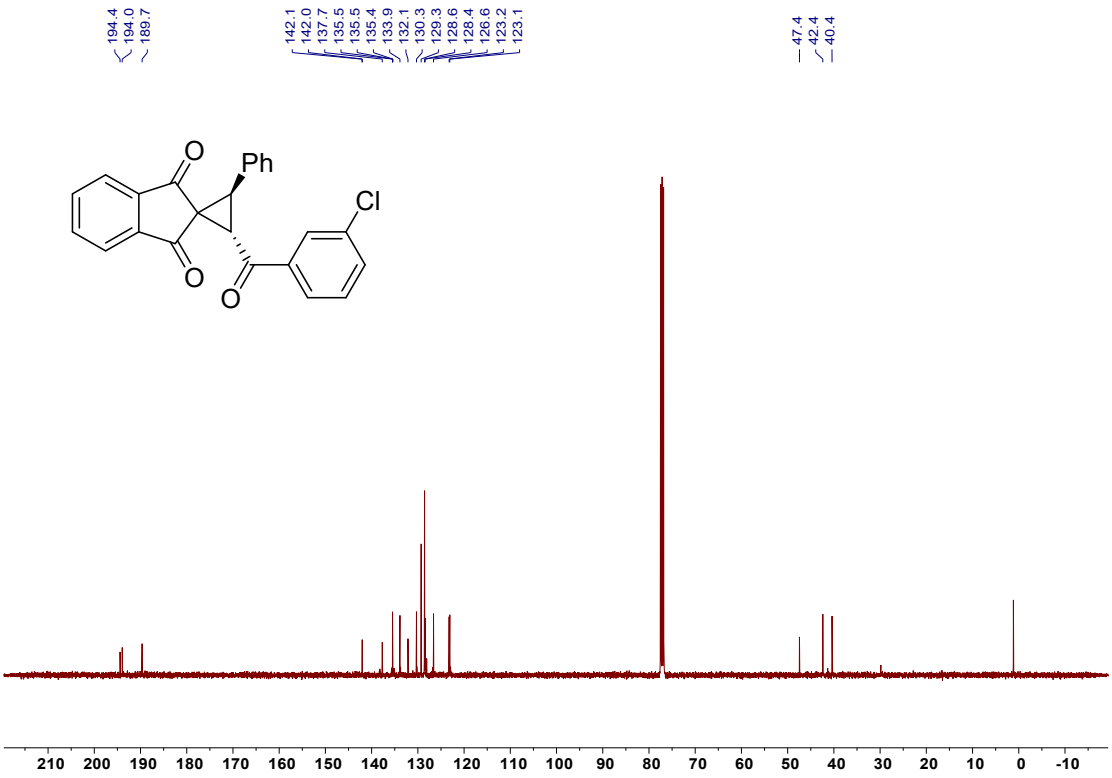
^{13}C NMR of compound **3ca**



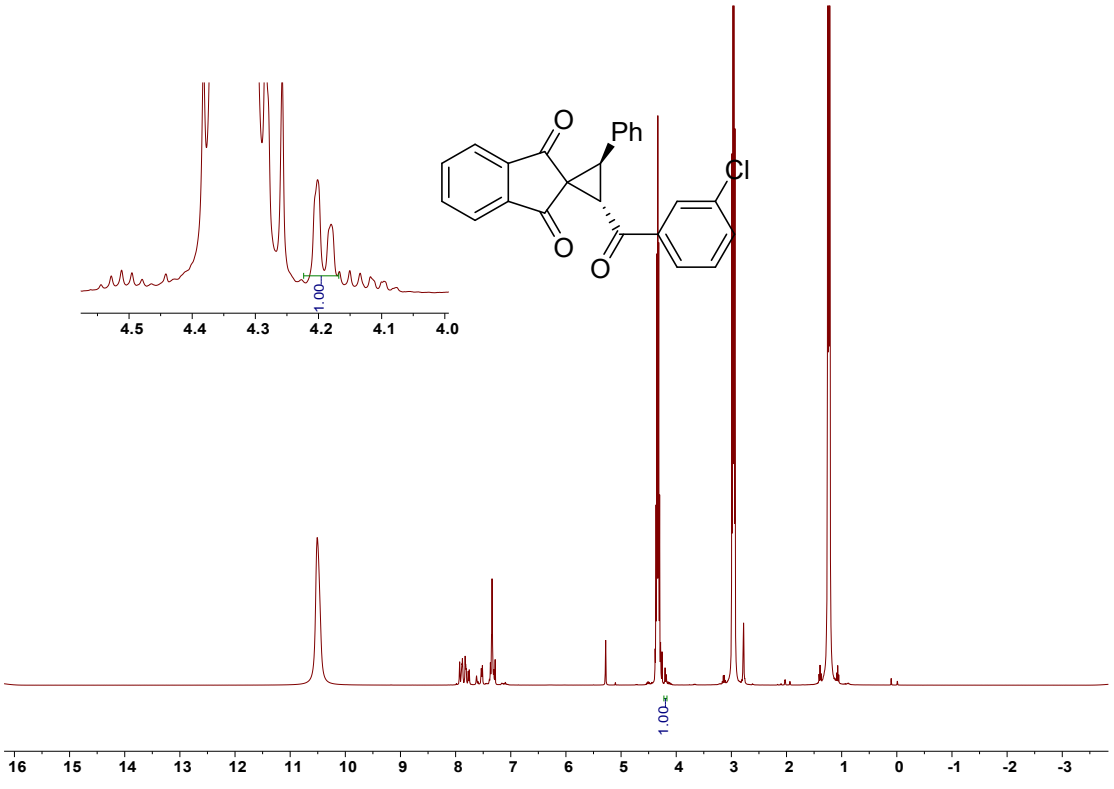
^{1}H NMR of reaction mixture **3ca**



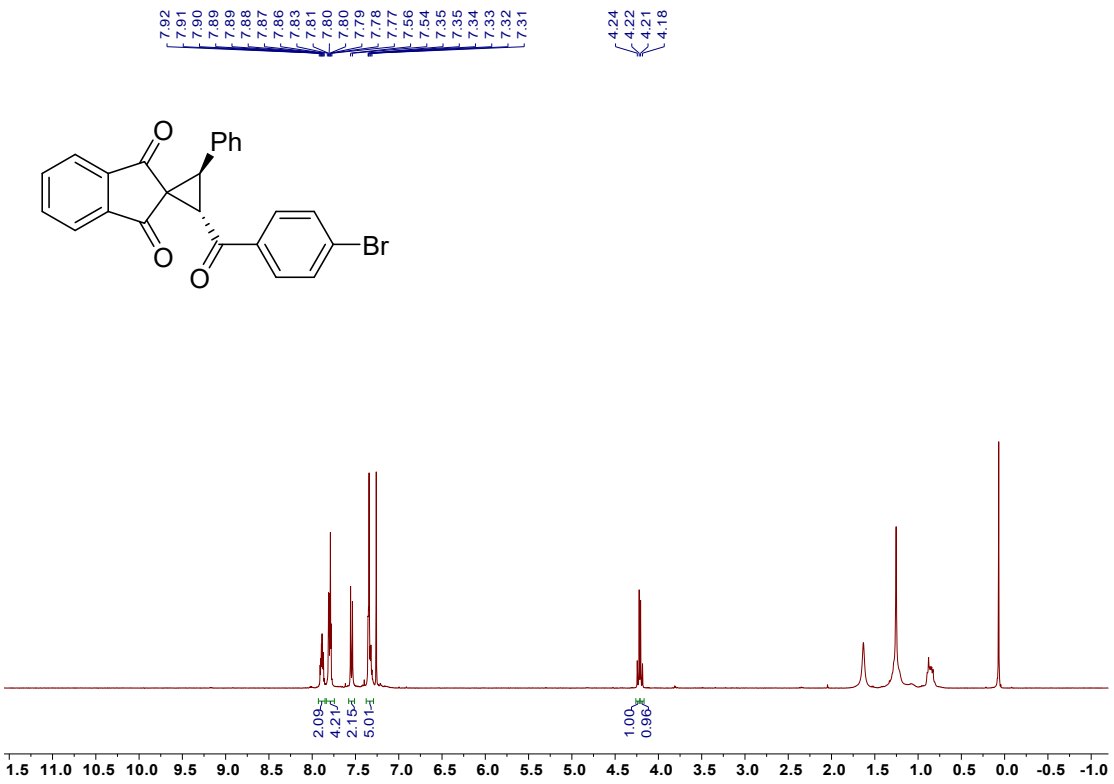
^{1}H NMR of compound **3da**



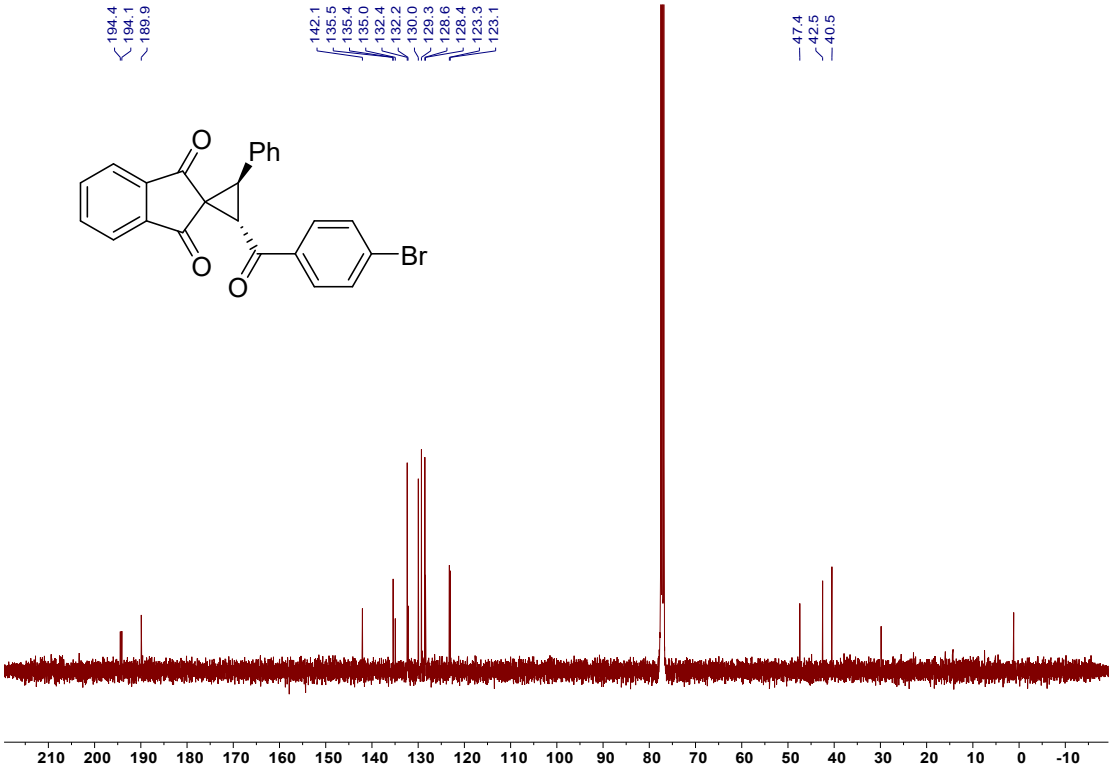
^{13}C NMR of compound **3da**



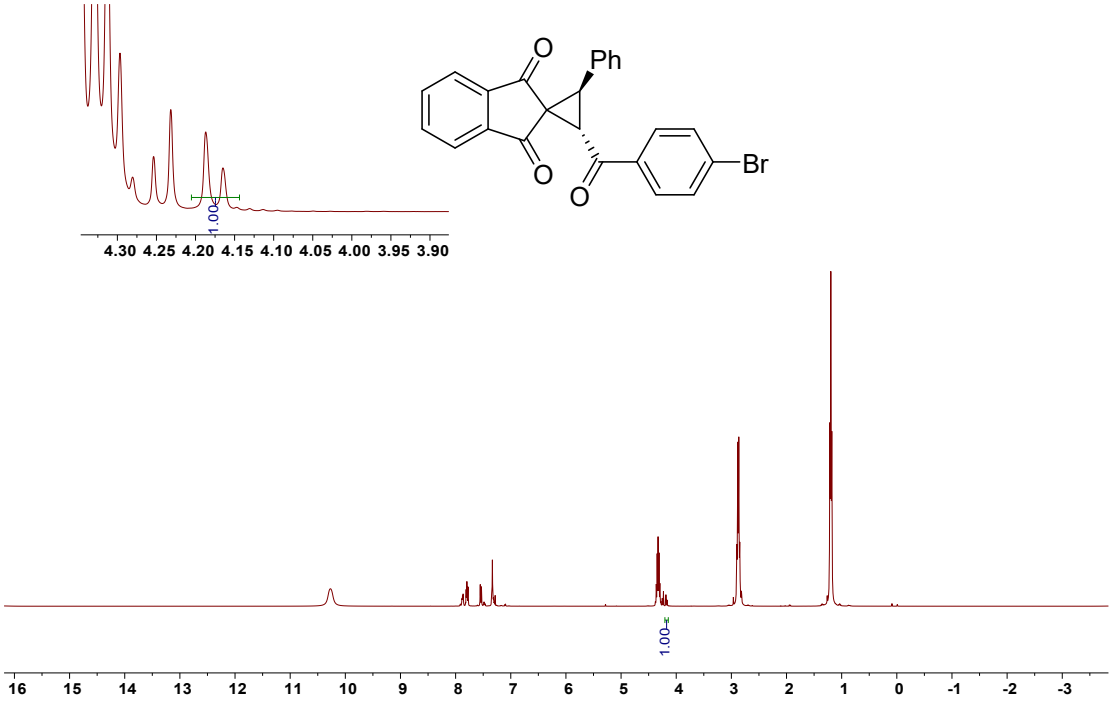
^{1}H NMR of reaction mixture **3da**



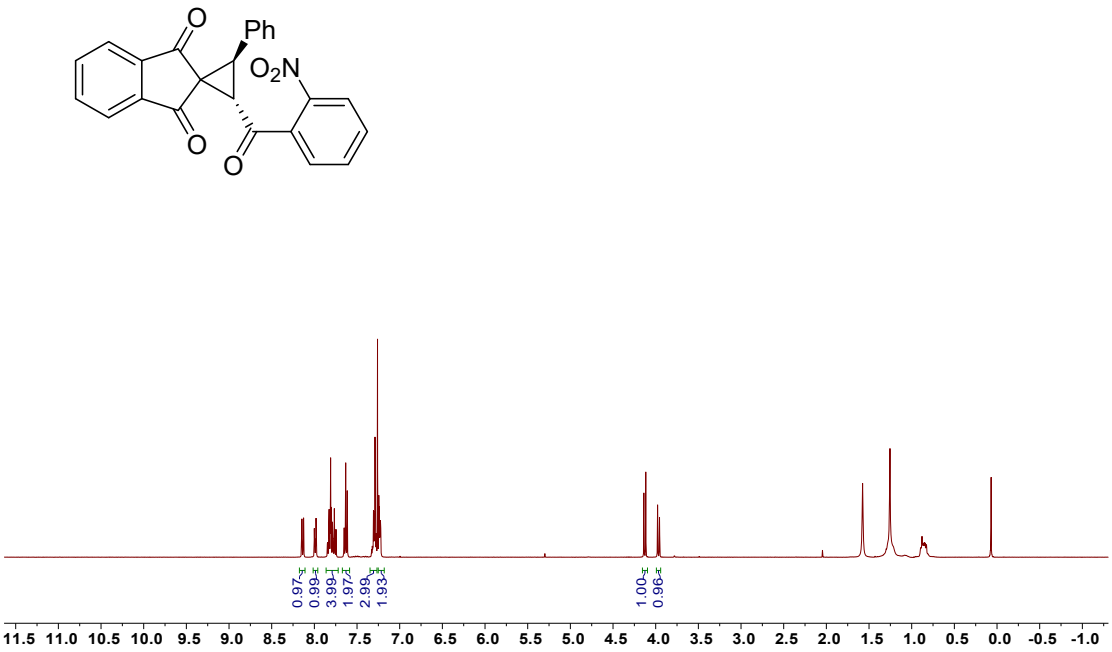
^{1}H NMR of compound **3ea**



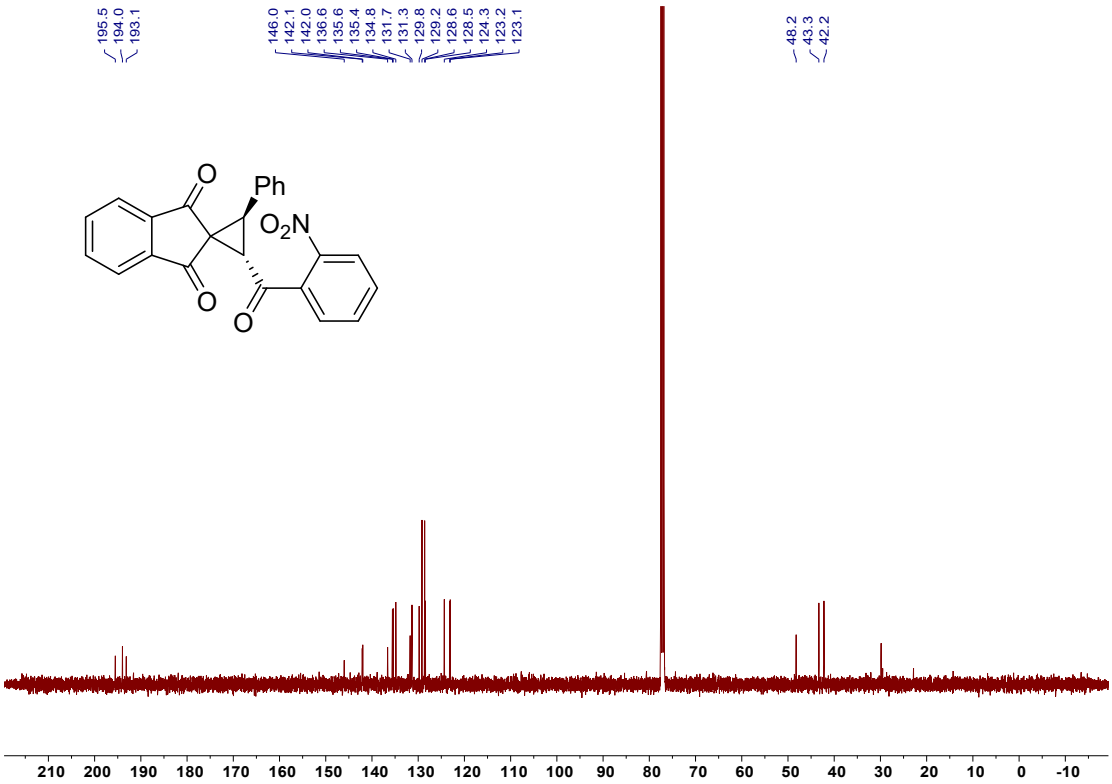
^{13}C NMR of compound **3ea**



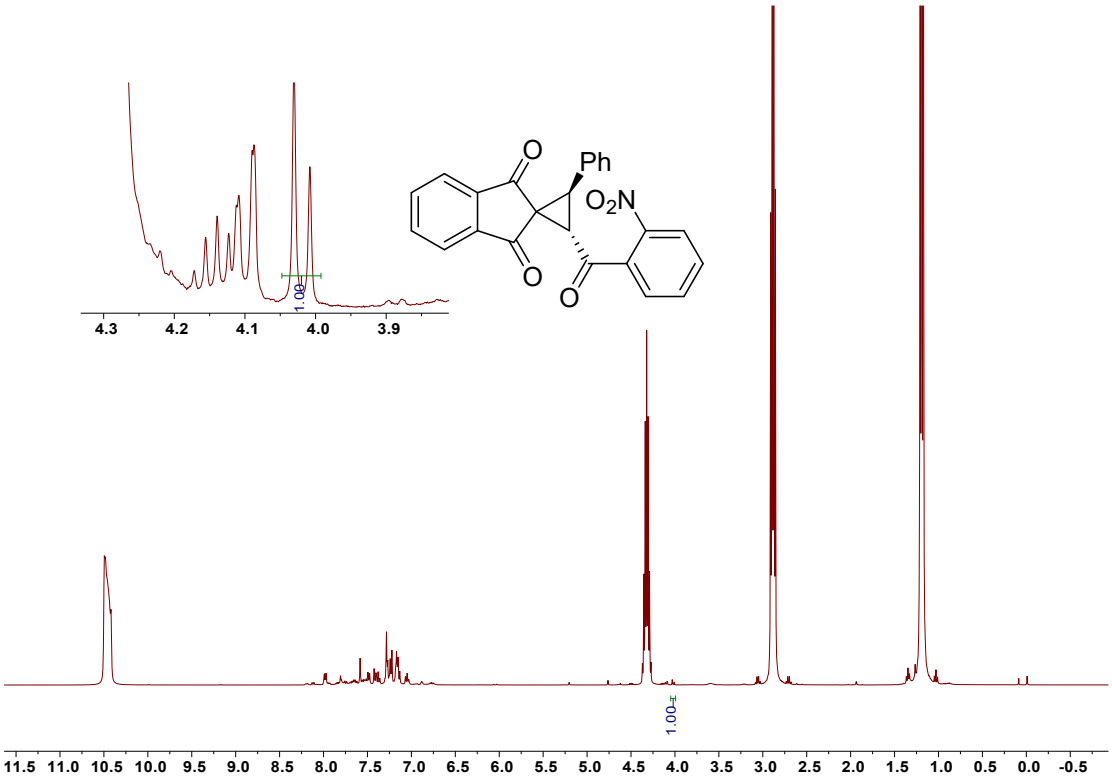
^{1}H NMR of reaction mixture **3ea**



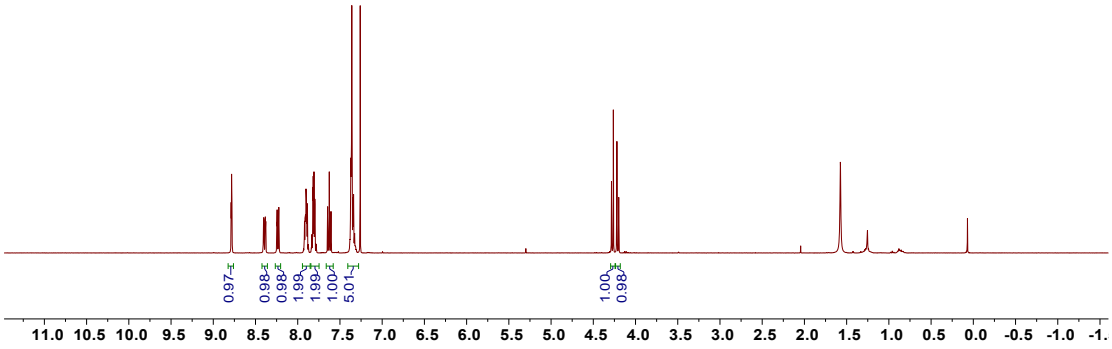
^{1}H NMR of compound **3fa**



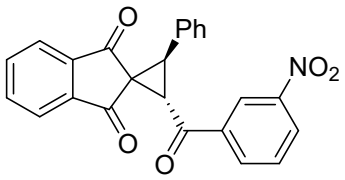
^{13}C NMR of compound **3fa**



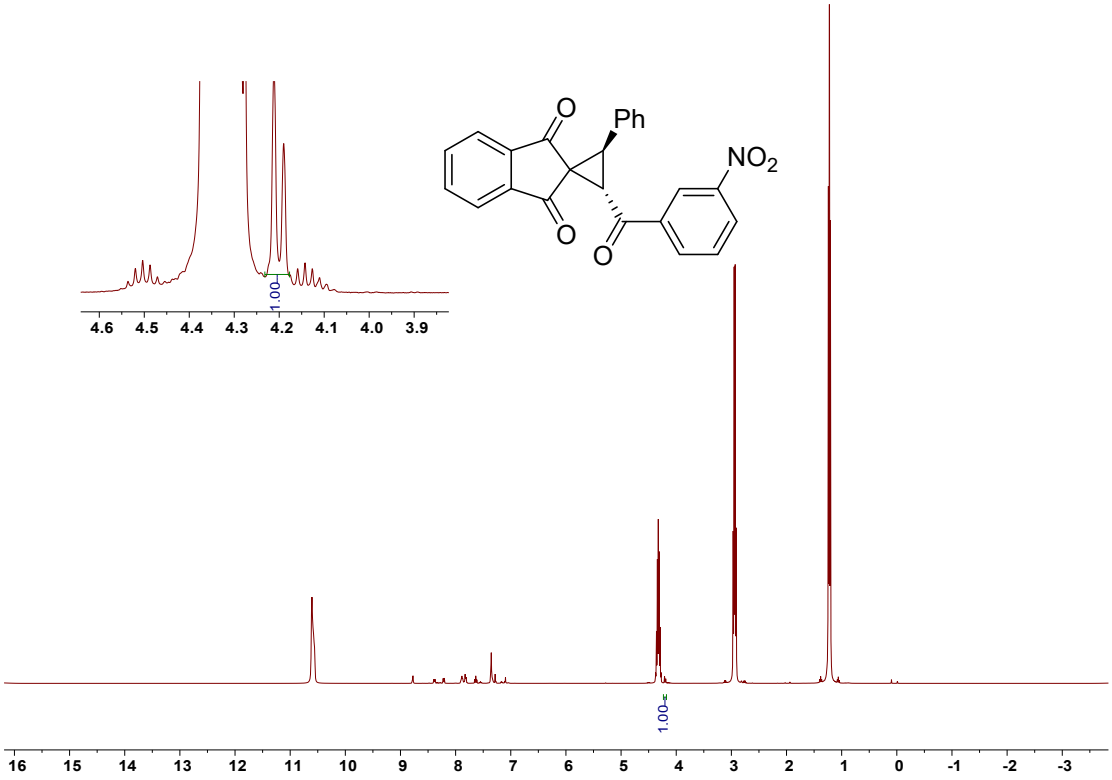
^{1}H NMR of reaction mixture **3fa**



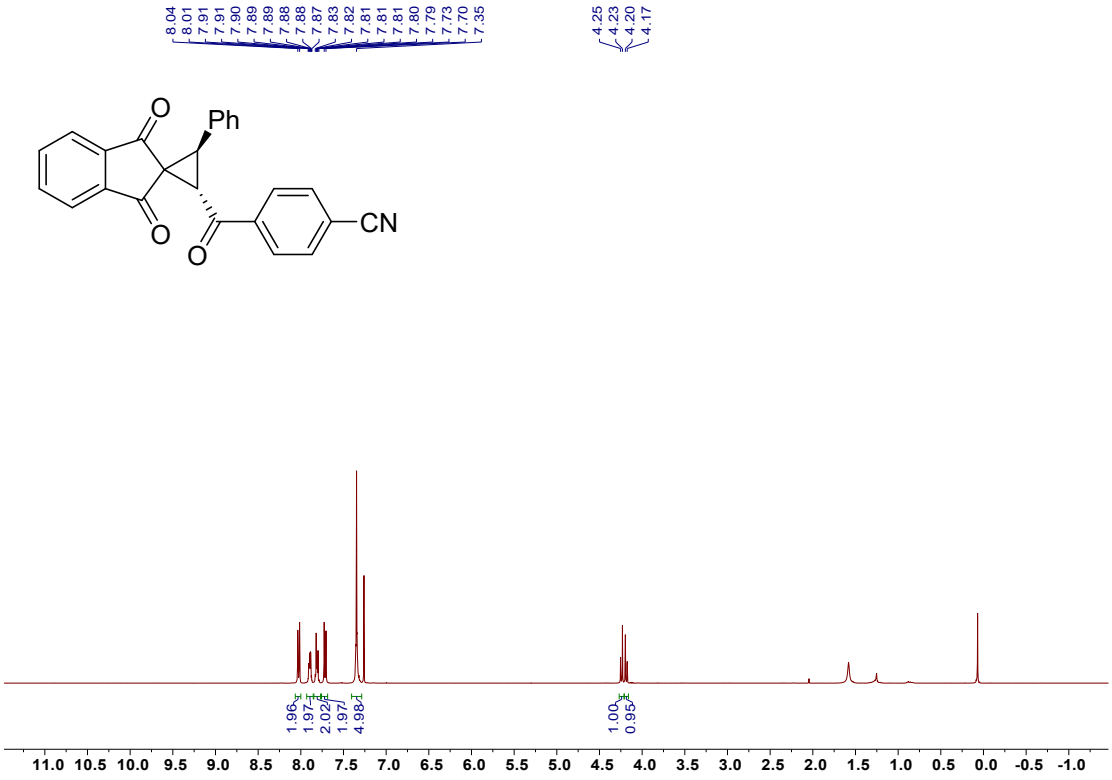
^{1}H NMR of compound **3ga**



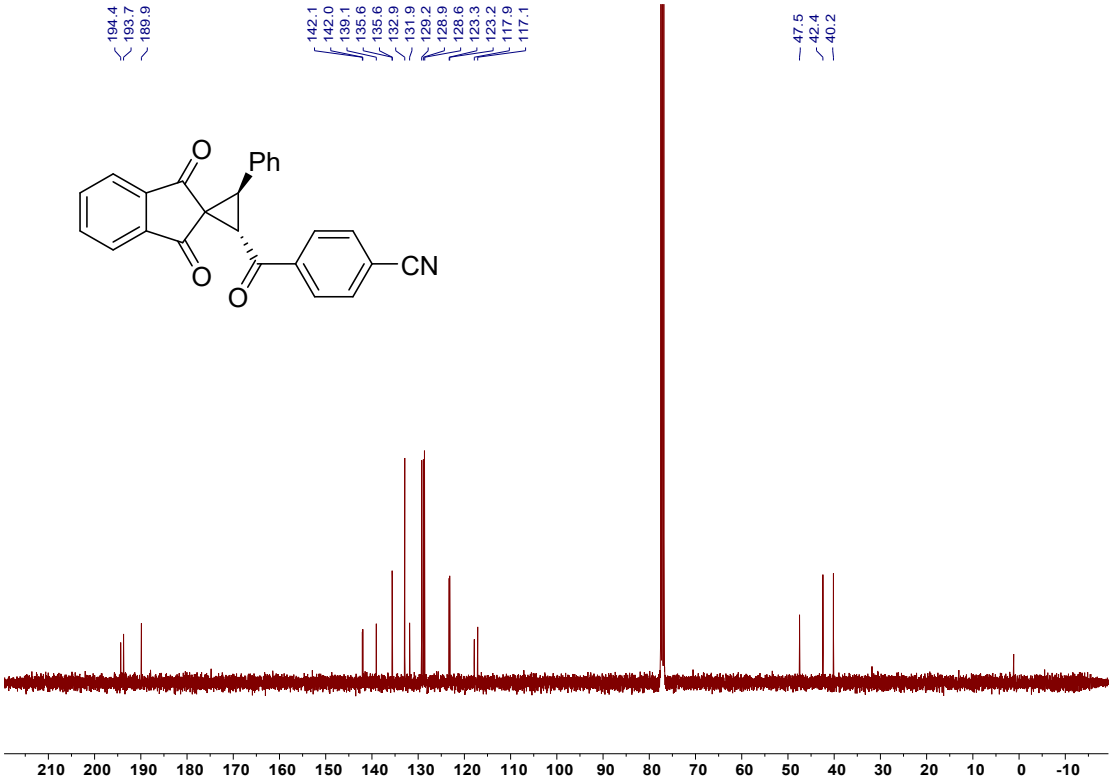
^{13}C NMR of compound **3ga**



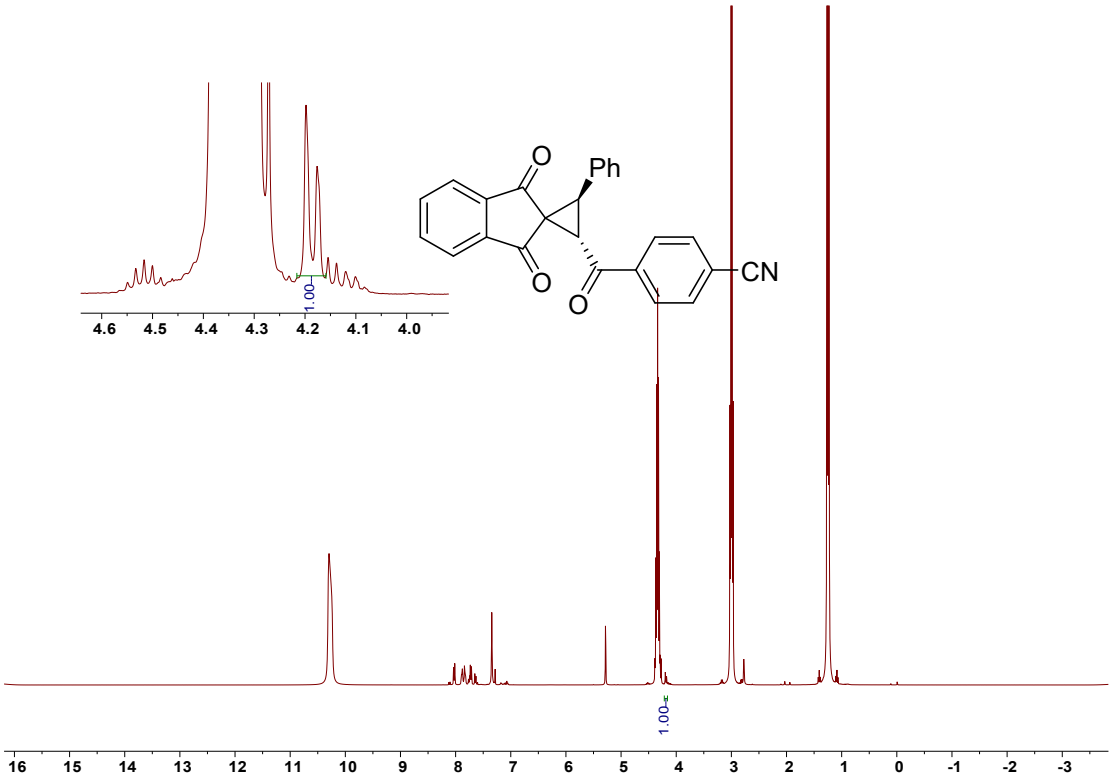
^{1}H NMR of reaction mixture **3ga**



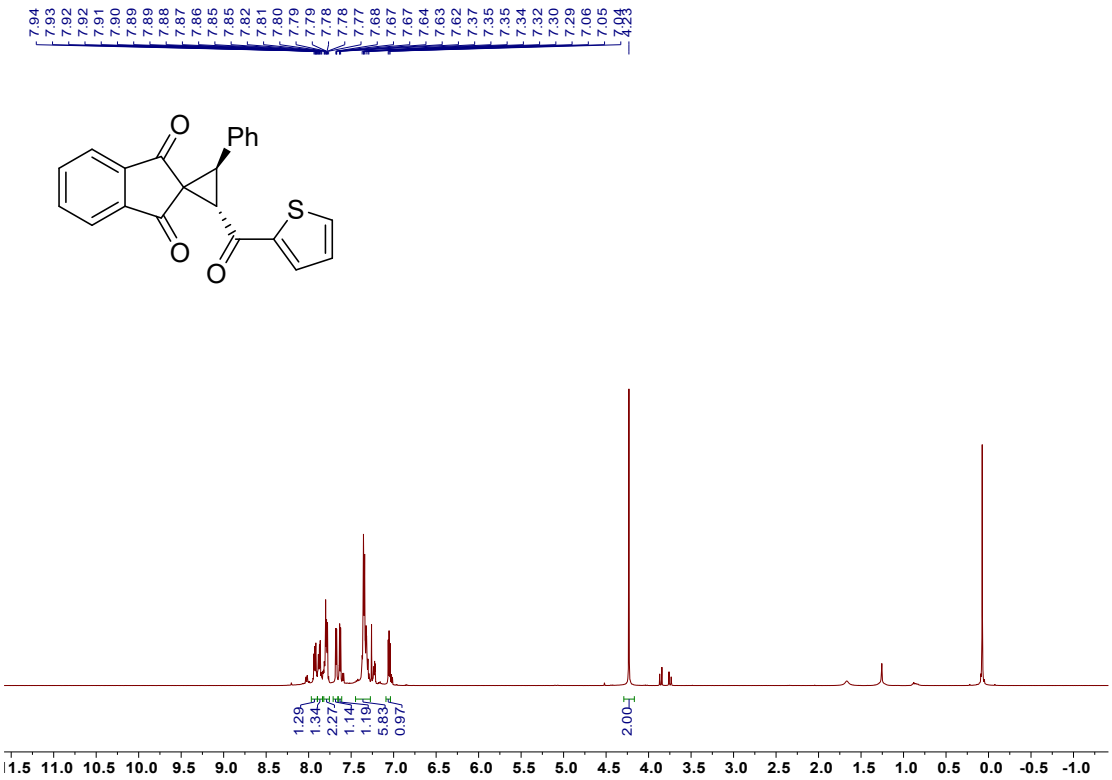
^{1}H NMR of compound **3ha**



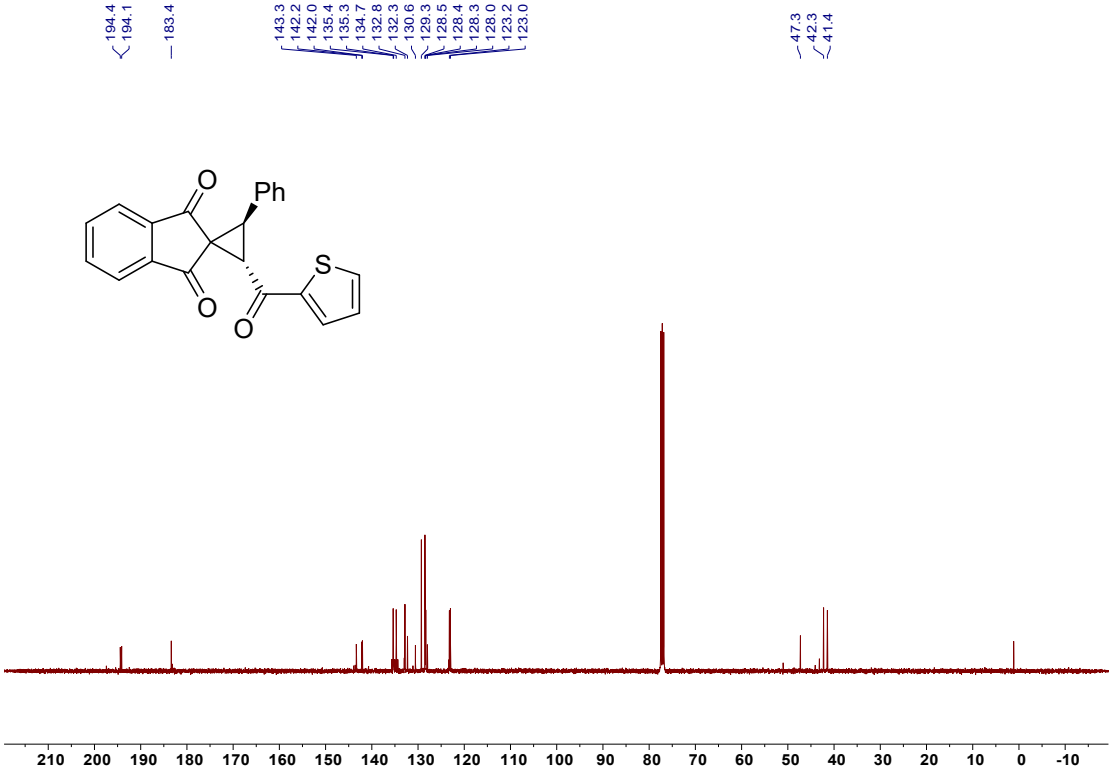
^{13}C NMR of compound **3ha**



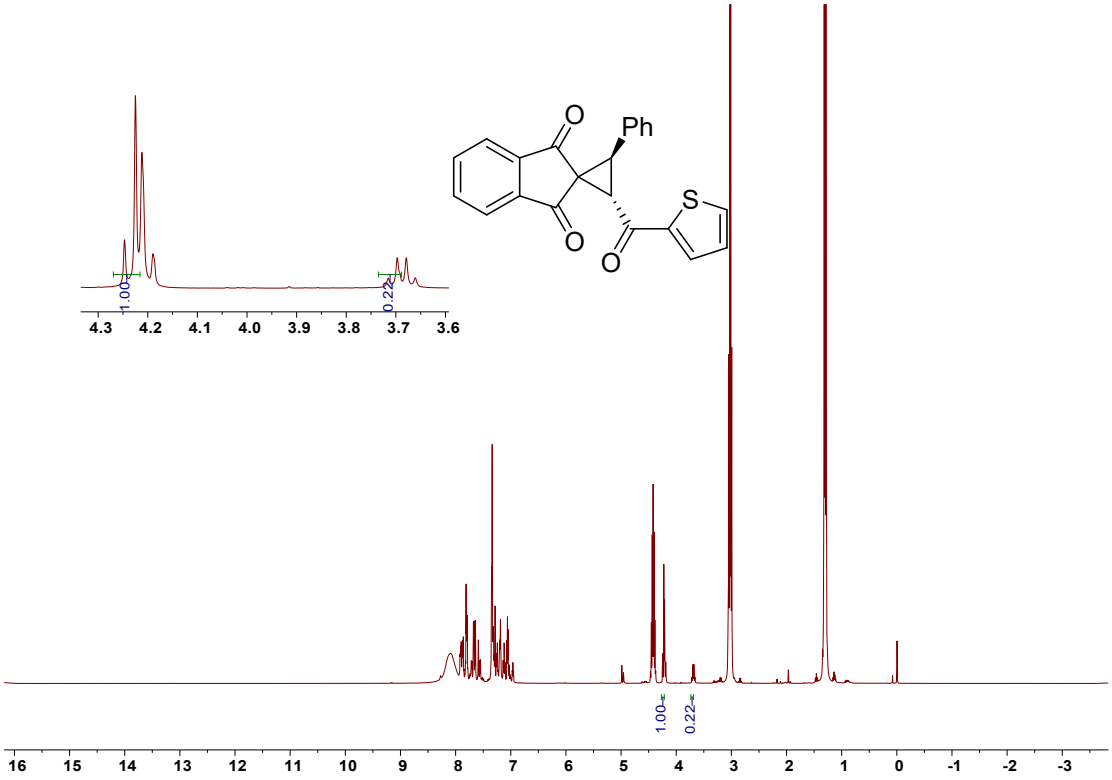
^{1}H NMR of reaction mixture **3ha**



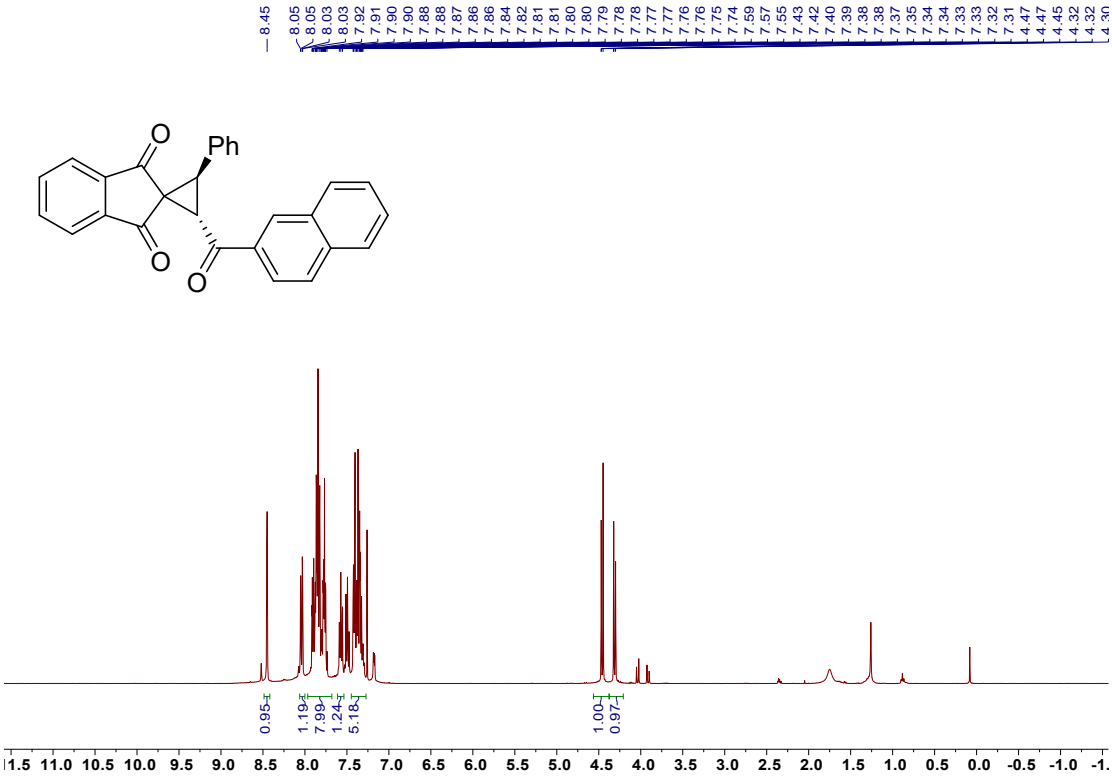
^{1}H NMR of compound **3ia**



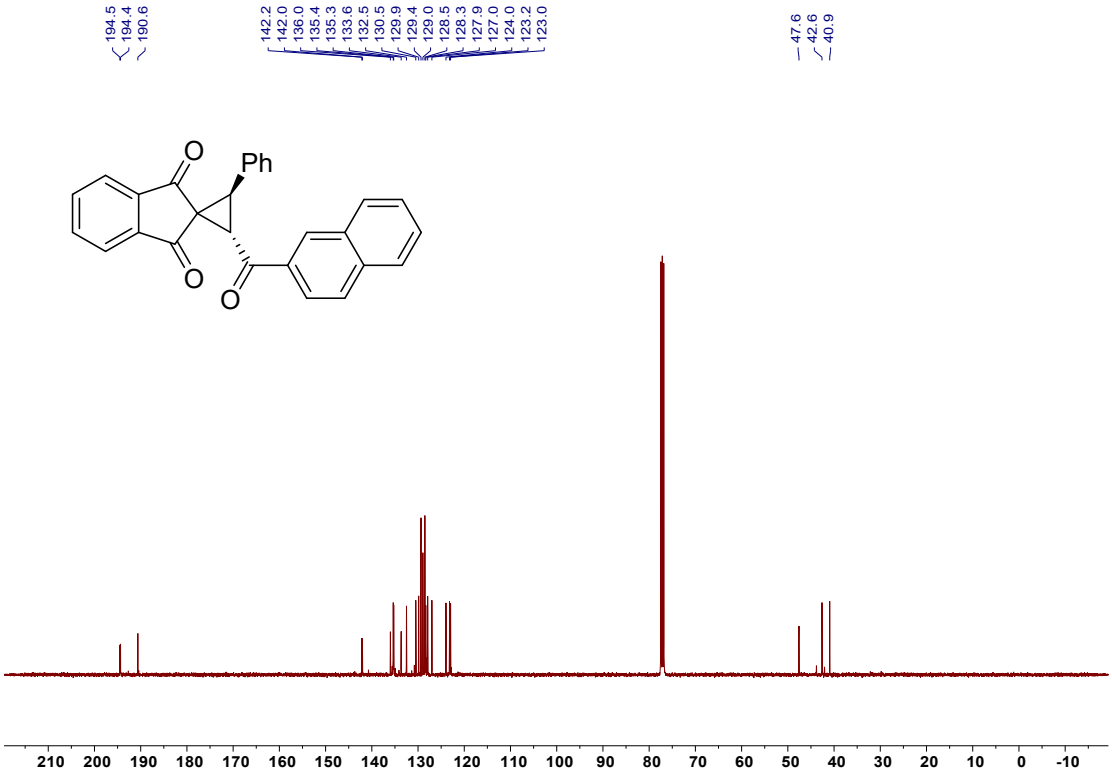
^{13}C NMR of compound **3ia**



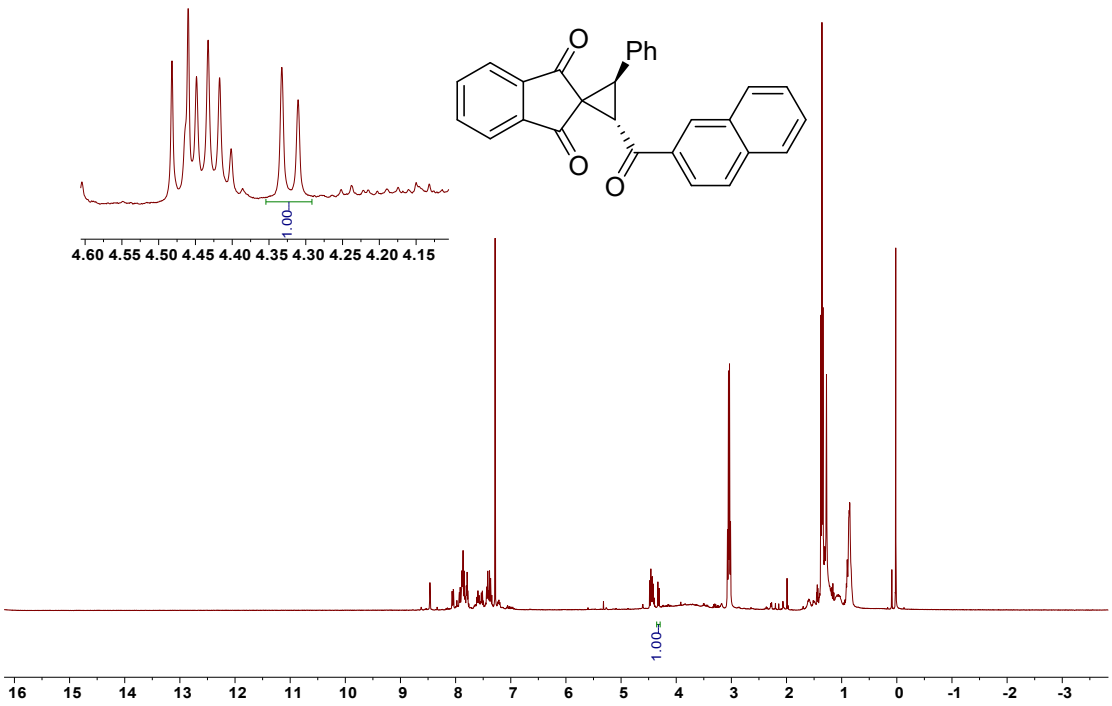
^{1}H NMR of reaction mixture **3ia**



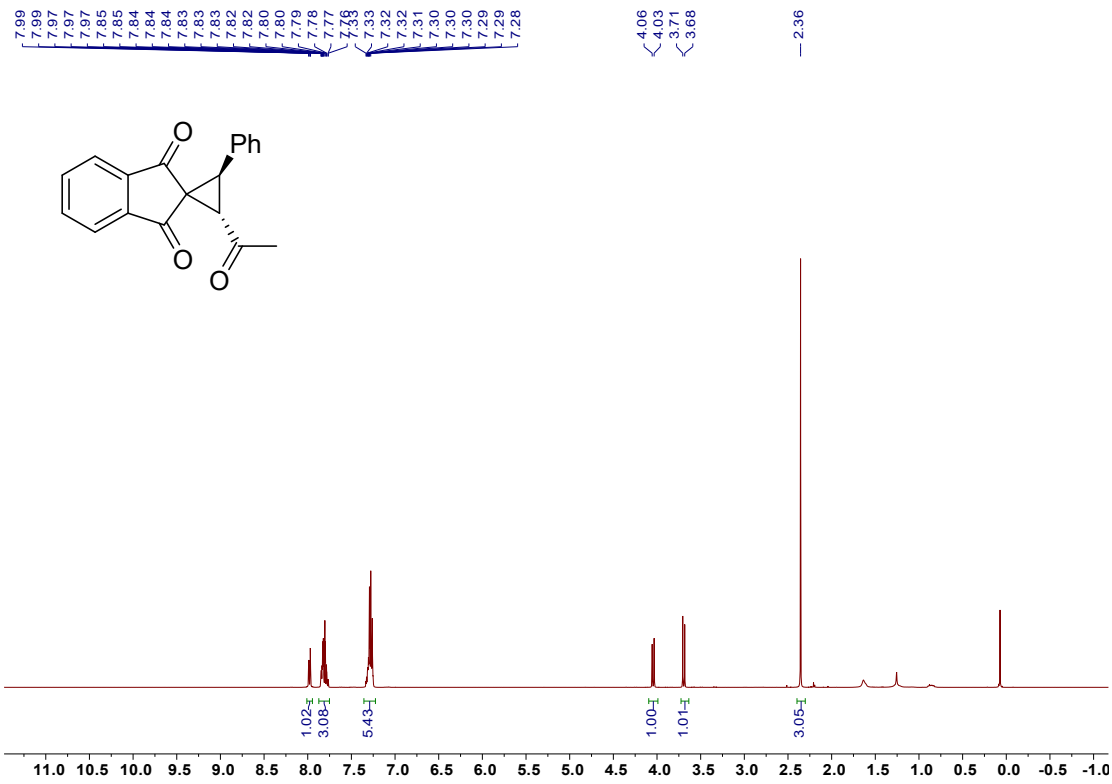
^{1}H NMR of compound **3ja**



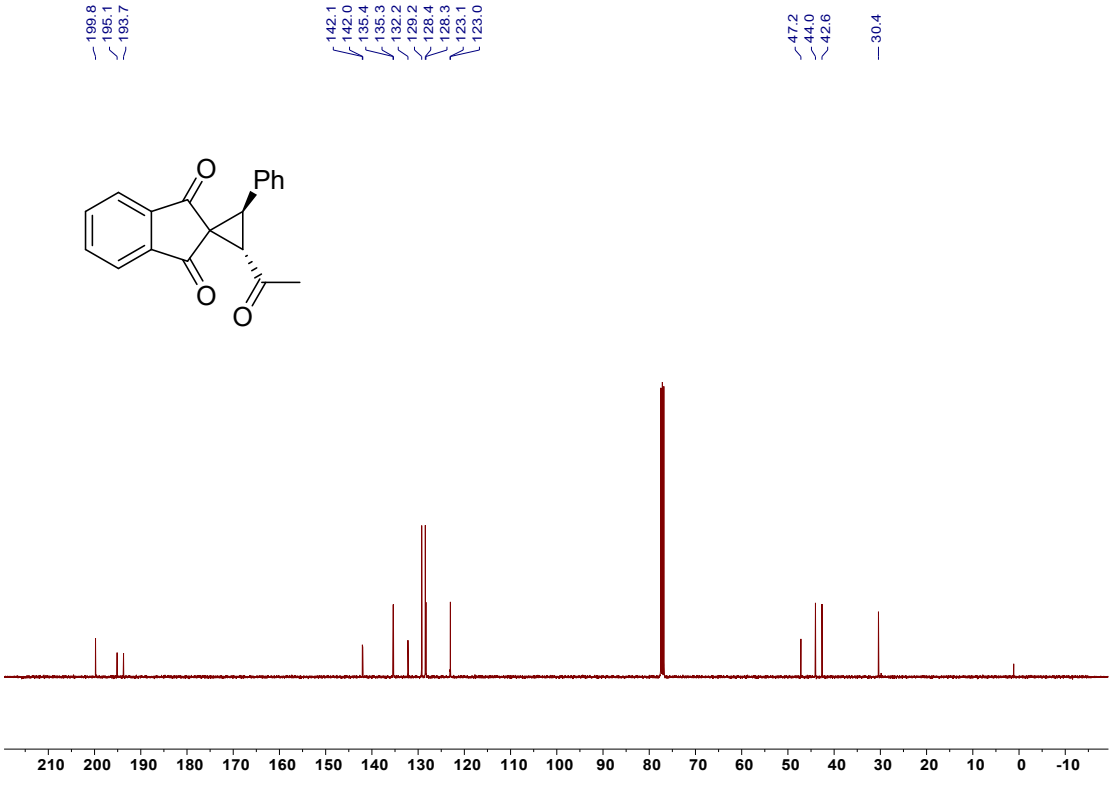
^{13}C NMR of compound **3ja**



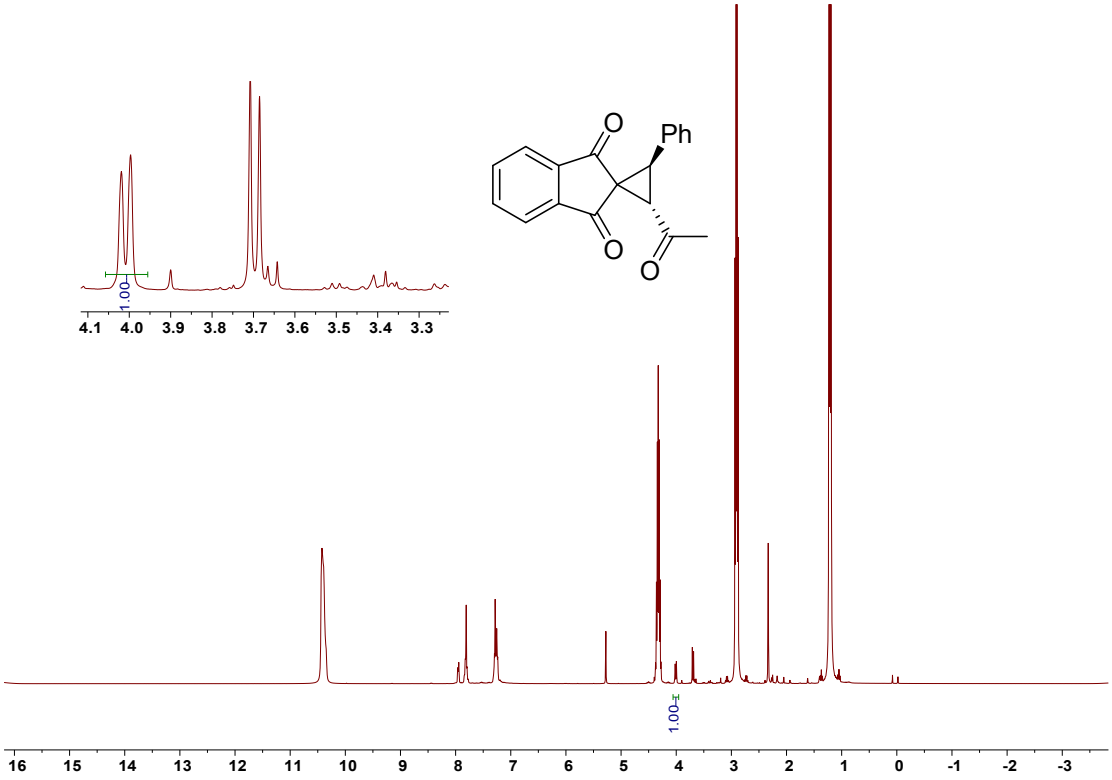
^{1}H NMR of reaction mixture **3ja**



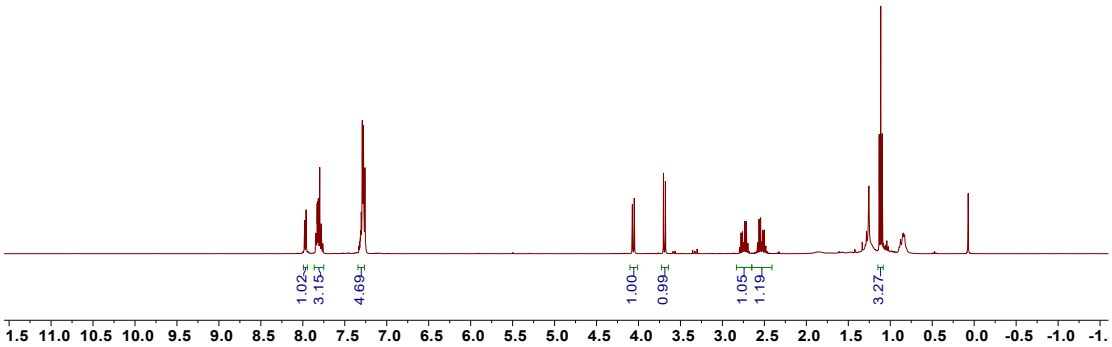
^{1}H NMR of compound **3ka**



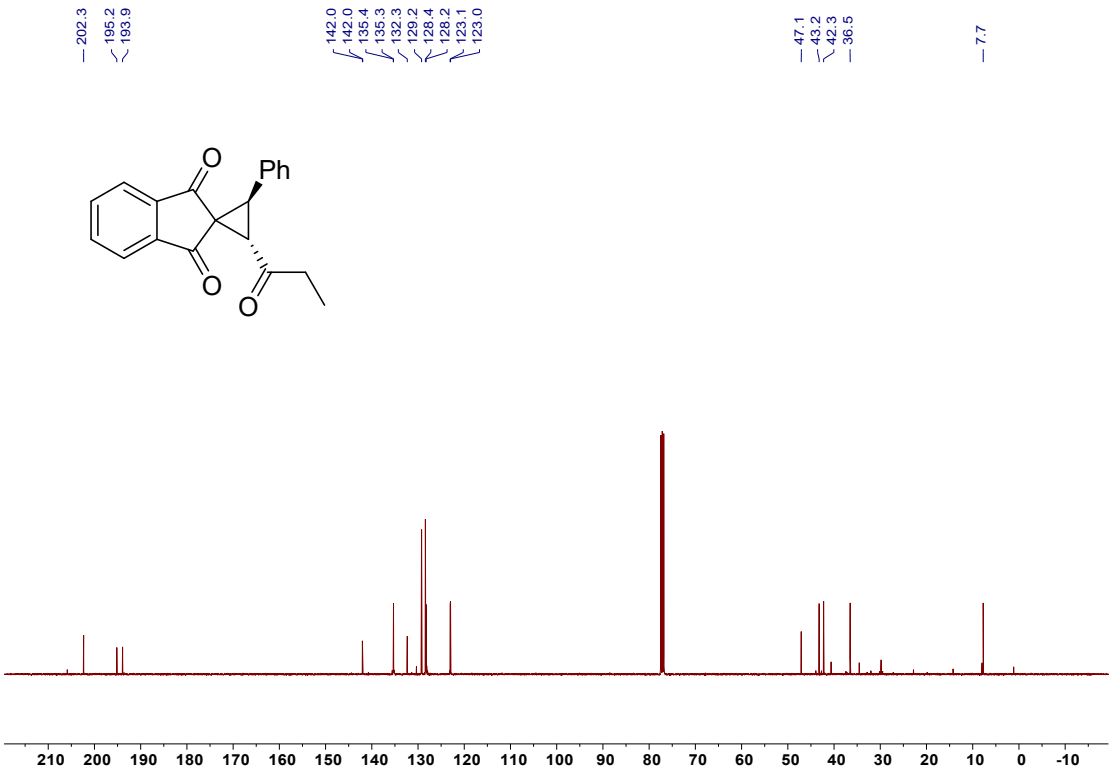
^{13}C NMR of compound **3ka**



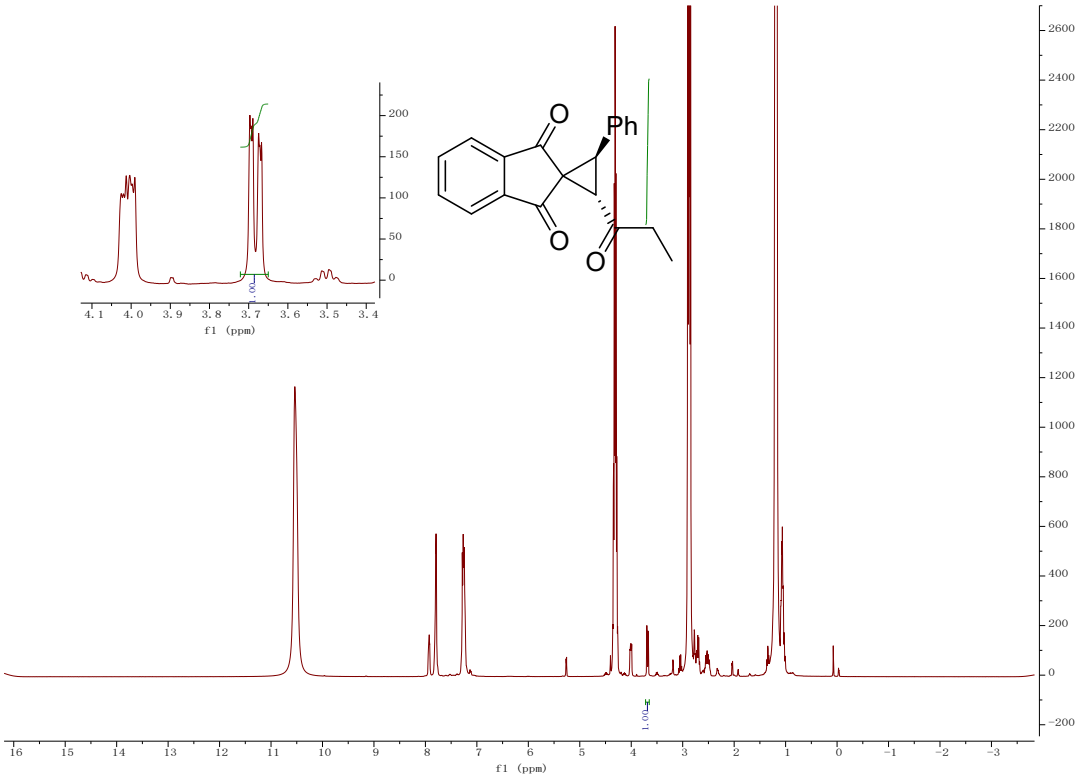
^{1}H NMR of reaction mixture **3ka**



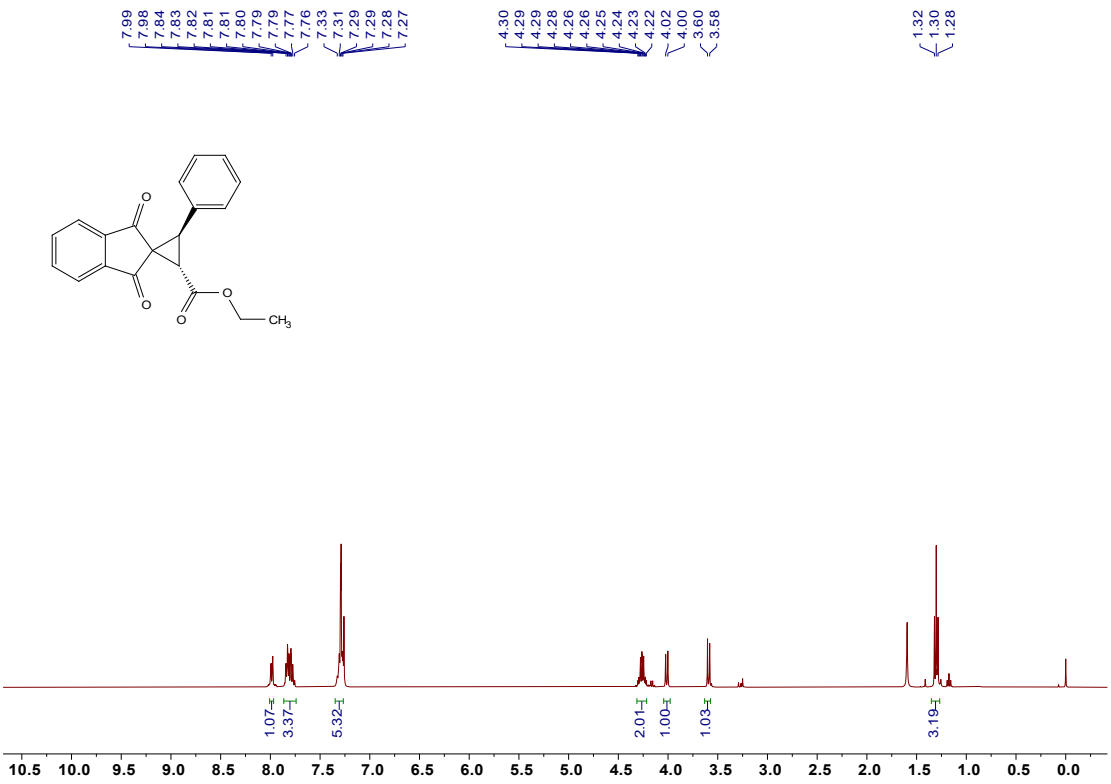
^{1}H NMR of compound **3la**



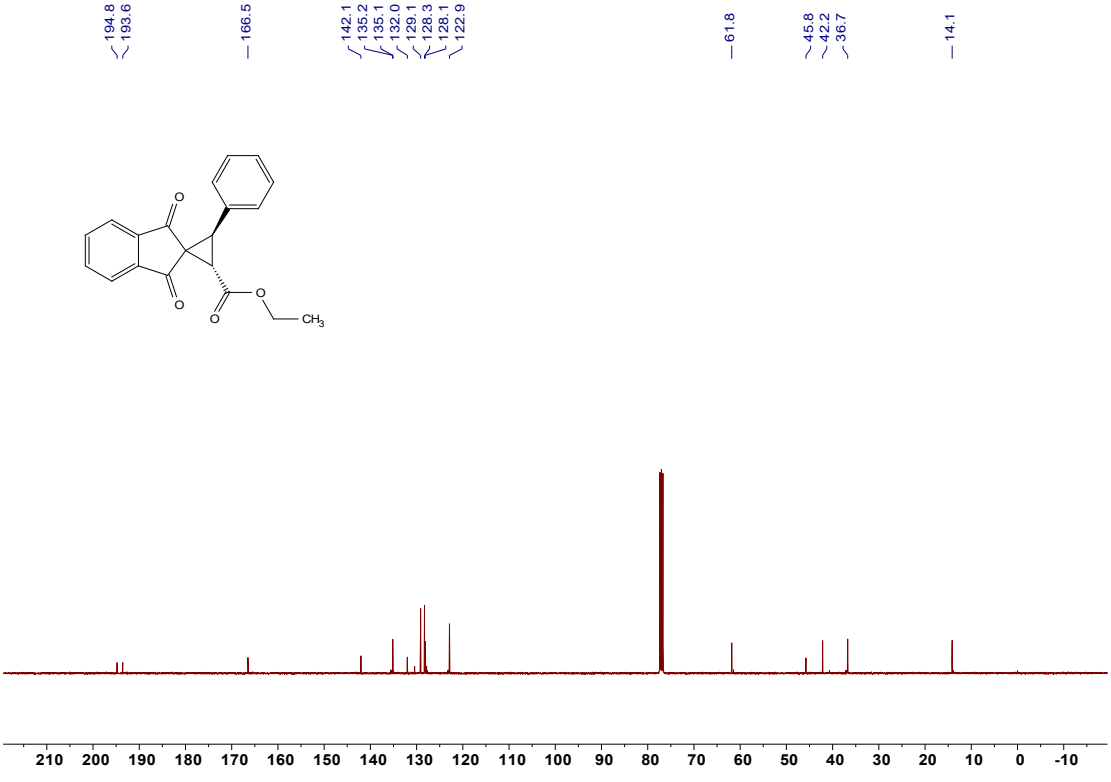
^{13}C NMR of compound **3la**



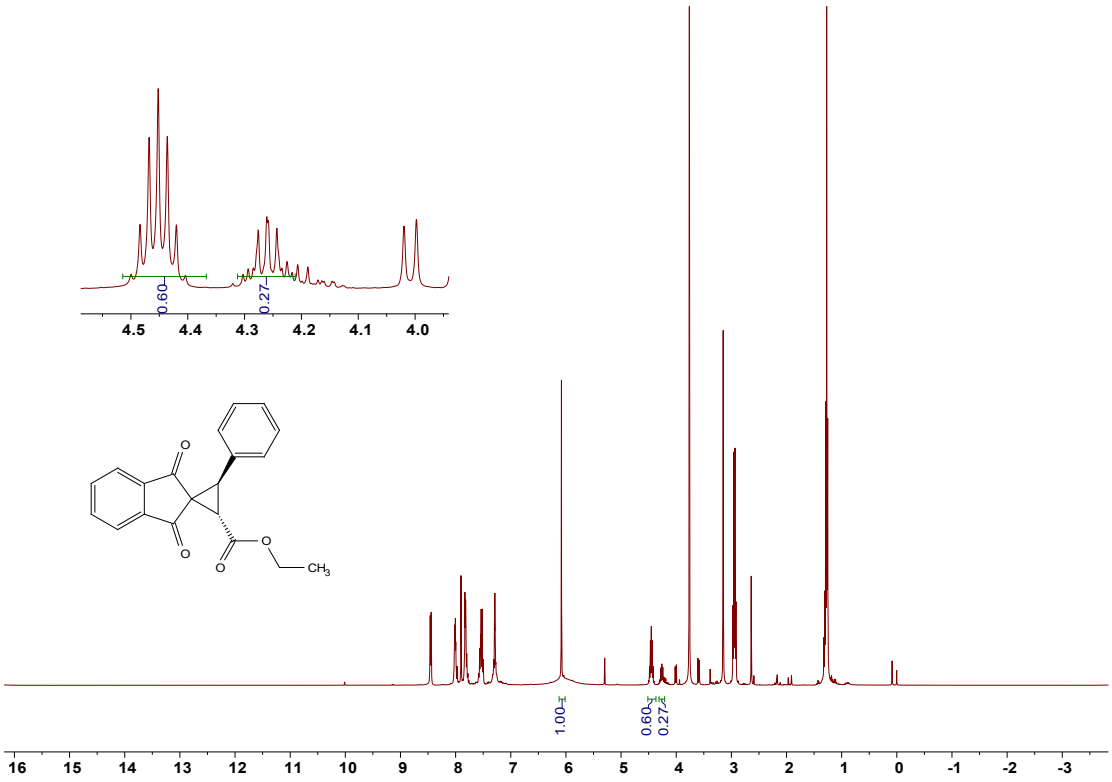
^{1}H NMR of reaction mixture **3la**



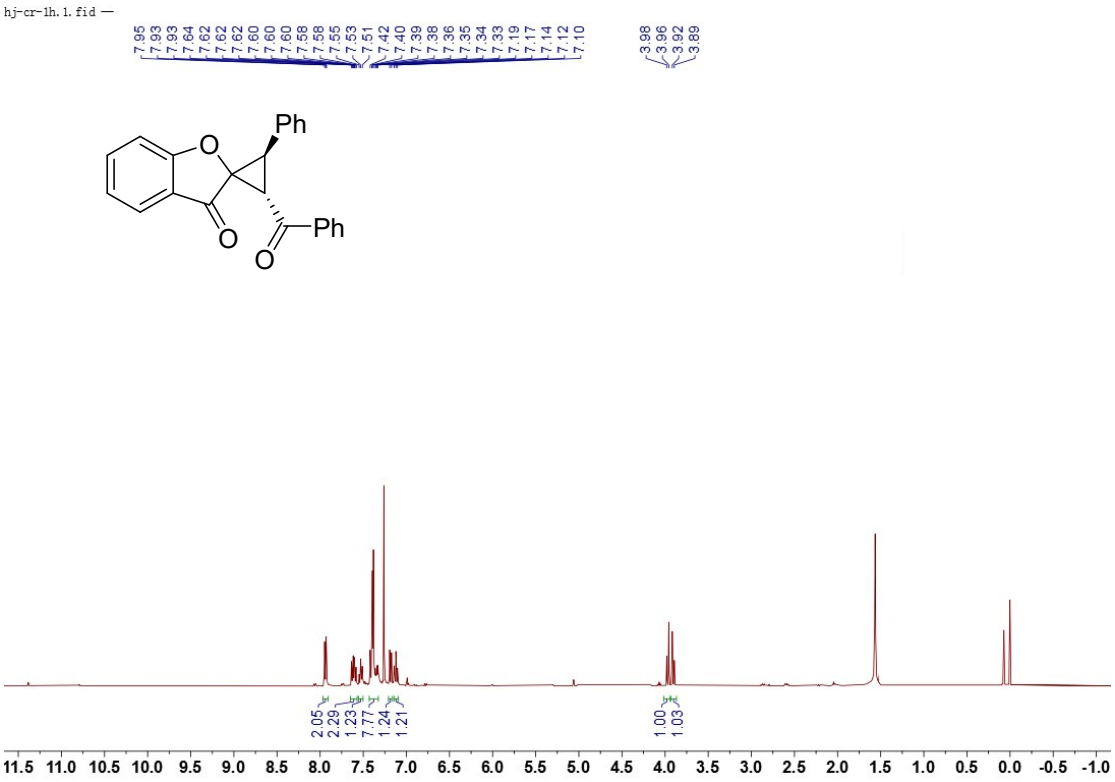
^{1}H NMR of compound **3ma**



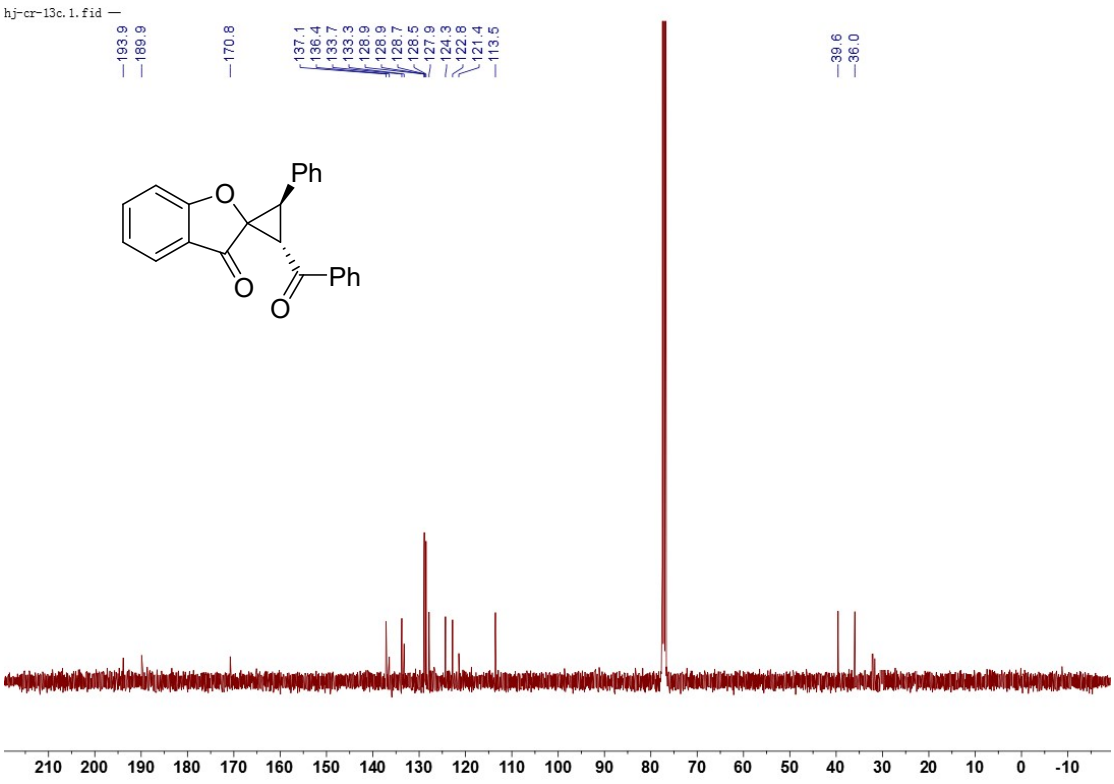
^{13}C NMR of compound **3ma**



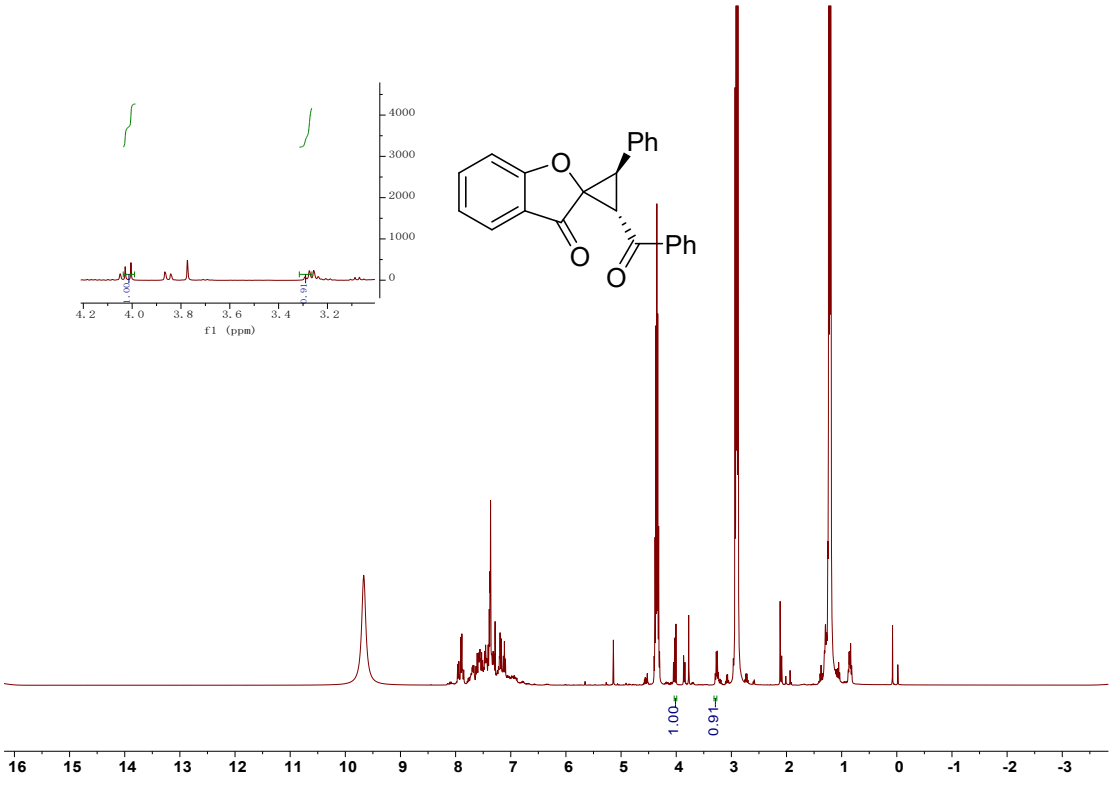
^{1}H NMR of reaction mixture **3ma**



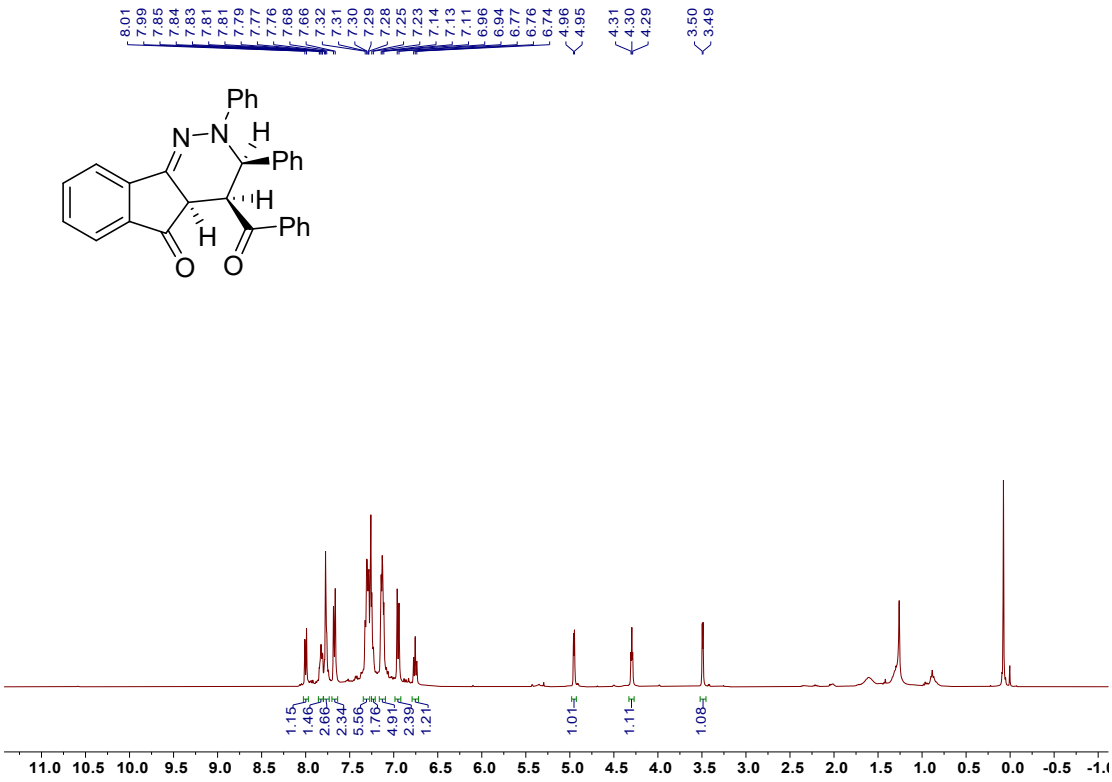
^{1}H NMR of compound **3na**



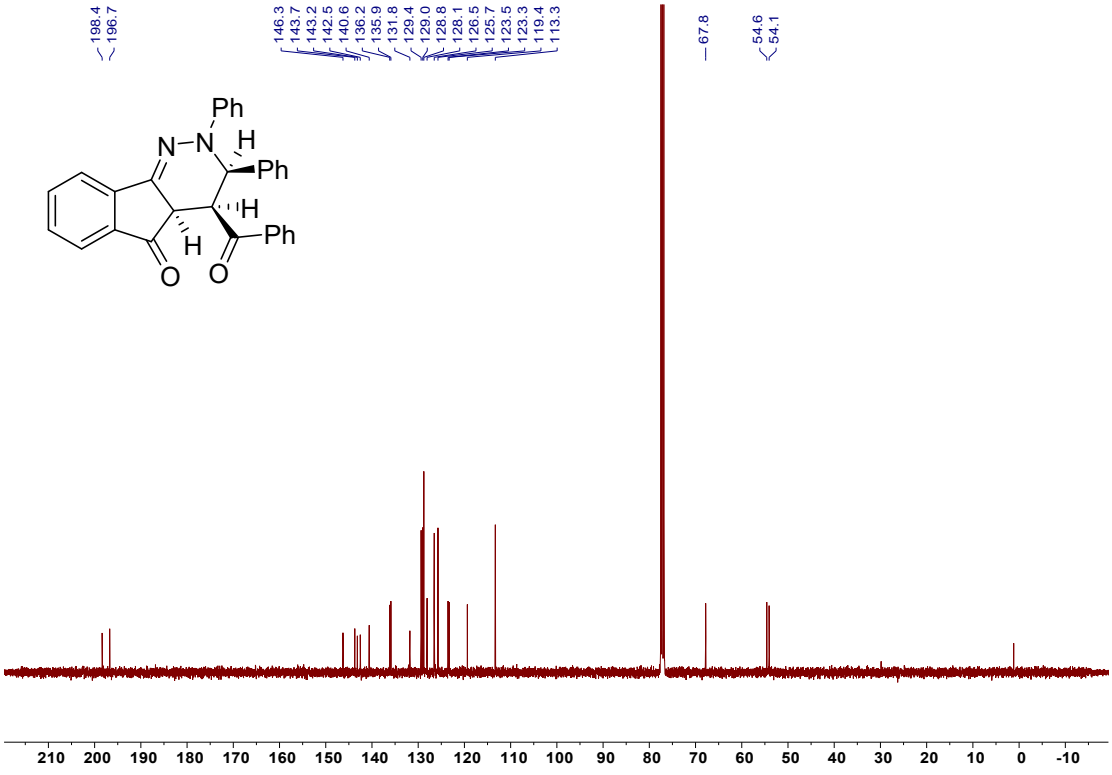
^{13}C NMR of compound **3na**



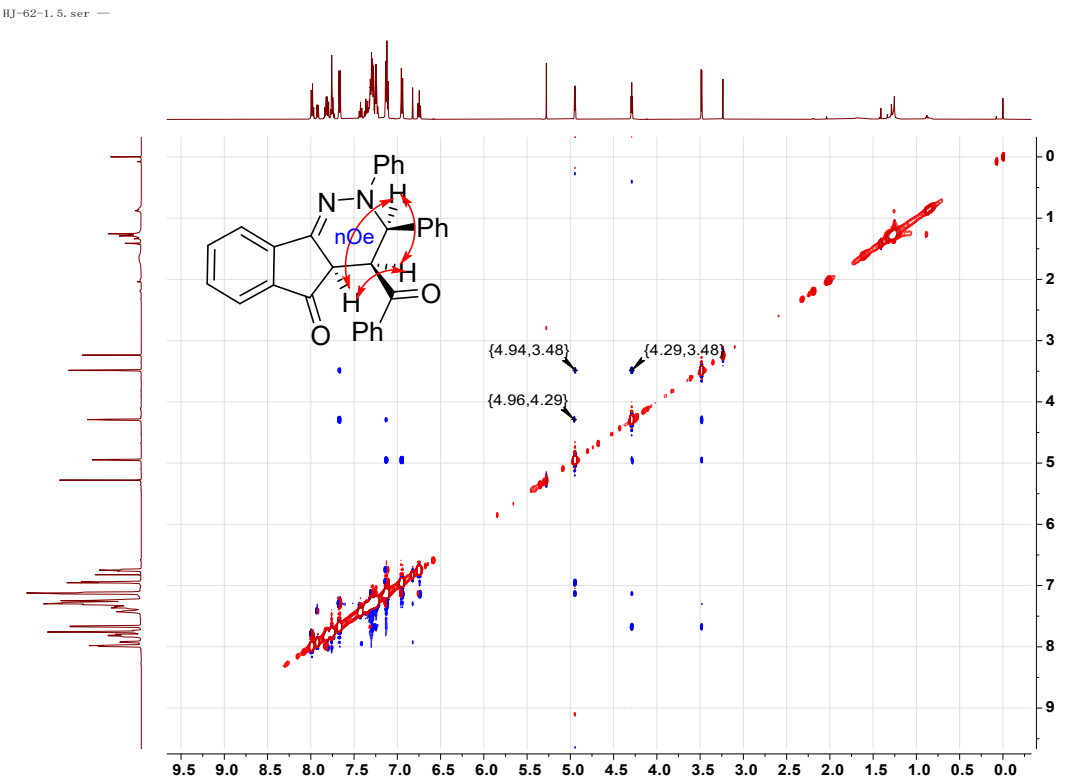
^{1}H NMR of reaction mixture **3na**



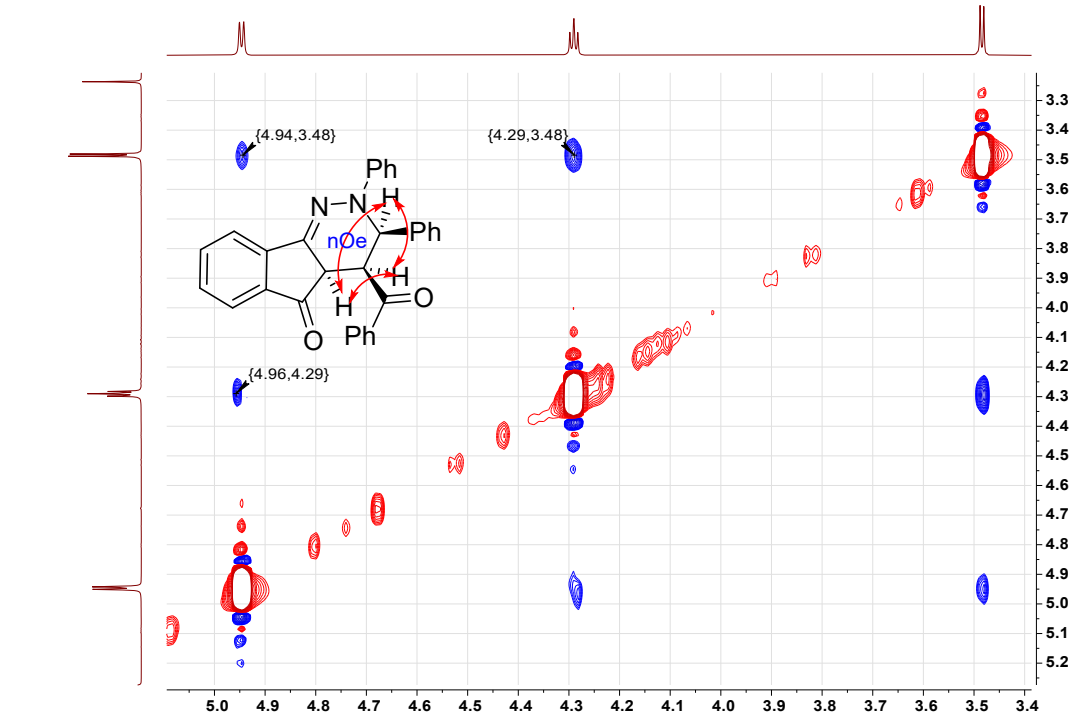
^{1}H NMR of compound **9**



^{13}C NMR of compound **9**

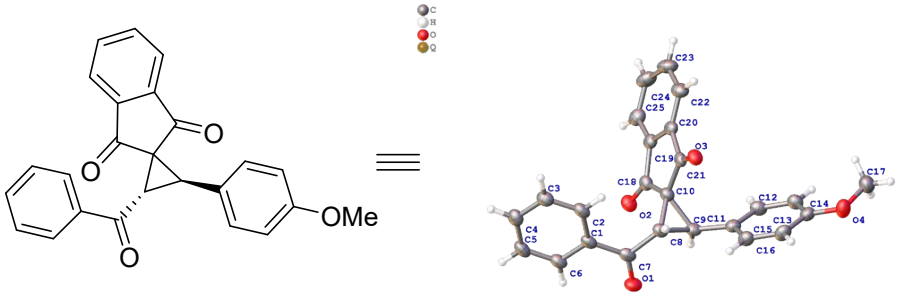


ROESY of compound **9**



ROESY of compound **9**

6 X-ray crystallographic data of 3ag



Crystal data and structure refinement

Empirical formula	C25H18O4
Formula weight	382.39
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	P21/c
a/Å	10.0932(6)
b/Å	17.3340(10)
c/Å	11.3690(7)
α/°	90
β/°	104.954(6)
γ/°	90
Volume/Å3	1921.7(2)
Z	4
ρcalcg/cm3	1.322
μ/mm-1	0.089
F(000)	800.0
Crystal size/mm3	0.13 × 0.12 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.176 to 50
Index ranges	-11 ≤ h ≤ 11, -20 ≤ k ≤ 20, -11 ≤ l ≤ 13
Reflections collected	8529
Independent reflections	3382 [Rint = 0.0264, Rsigma = 0.0334]
Data/restraints/parameters	3382/0/263
Goodness-of-fit on F2	1.076
Final R indexes [I>=2σ (I)]	R1 = 0.0414, wR2 = 0.0931
Final R indexes [all data]	R1 = 0.0508, wR2 = 0.0989
Largest diff. peak/hole / e Å-3	0.16/-0.22