Electronic Supplementary Material (ESI) for Chemical Science.

Asymmetric catalytic synthesis of spirocyclobutyl oxindoles and beyond *via* [2+2] cycloaddition and sequential transformations

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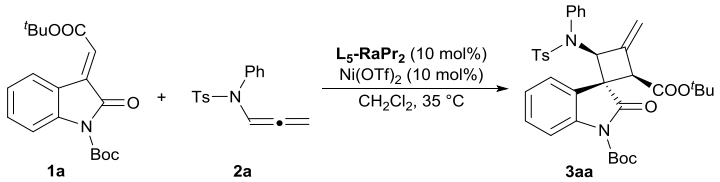
(A) General Information

CH_2Cl_2, $CHCl_3$, $CHCl_2CHCl_2$, CH_2ClCH_2Cl, EtOAc, MeCN were freshly distilled from CaH_2 prior to use; THF, toluene, Et_2O were freshly distilled from sodium metal prior to use. ^1H NMR spectra were recorded on bruker ASCEND^{TM} operating at 400 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet), coupling constants (Hz), integration. $^{13}C\{^1H\}$ NMR data were collected bruker ASCEND^{TM} operating at 101 MHz with complete proton decoupling. $^{19}F\{^1H\}$ NMR was collected bruker ASCEND^{TM} operating at 376 M Hz with complete proton decoupling. Metal salts obtained from commercial sources were used without further purification. Enantiomeric excesses were determined by HPLC analysis on Daicel Chiralcel IA/IB/IE/ADH in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]^T_D$ = (*c* = g/100 mL, in solvent). HRMS was recorded on Thermo Q-Exactive Focus (FTMS+c ESI) and data were reported as (m/z). The chiral *N,N′*-dioxide ligands were synthesized by the same procedure in the literature.[1] The substrates 1 and *N*-allenamides 2 were prepared according to the literature.[2,3] Unless noted, other commercial reagents were used without further purification.

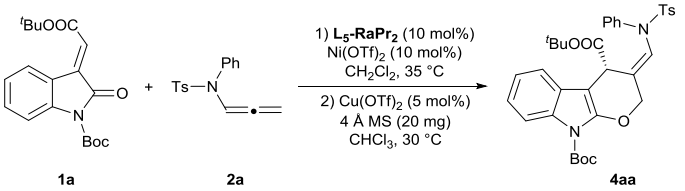
(B) General Procedure for the Synthesis of Products

1. Typical procedure for the chiral product 3aa



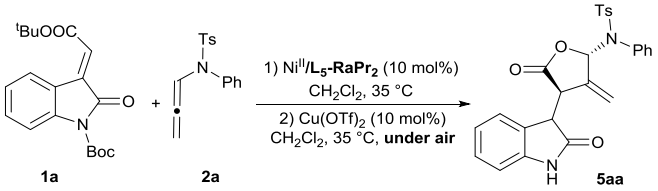
The reaction was conducted with $Ni(OTf)_2$ (3.6 mg, 10 mol%), **L_5-RaPr$_2$** (7.4 mg, 10 mol%), **1a** (34.5 mg, 0.10 mmol) under N_2, CH_2Cl_2 (1.0 mL) was added and the mixture was stirred at 30 °C for 15 min. Removed the solvent and **2a** (34.2 mg, 0.12 mmol) was added. The resulting mixture was dissolved with CH_2Cl_2 (0.5 mL) and stirred at 35 °C for 15 hours. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether, dichloromethane and ethyl acetate (from 16/1/1 to 9/1/1,v/v) to afford the corresponding product **3aa**.

2. Typical procedure for the chiral product 4aa



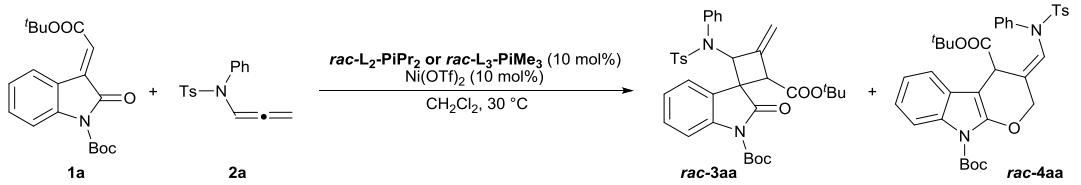
The reaction was conducted with $Ni(OTf)_2$ (3.6 mg, 10 mol%), **L_5-RaPr$_2$** (7.4 mg, 10 mol%), **1a** (34.5 mg, 0.10 mmol) under N_2, CH_2Cl_2 (1.0 mL) was added and the mixture was stirred at 30 °C for 15 min. Removed the solvent in vacuo and **2a** (34.2 mg, 0.12 mmol) was added. The resulting mixture was dissolve with CH_2Cl_2 (0.5 mL) and stirred at 35 °C for 15 hours.
$Cu(OTf)_2$ (1.8 mg, 5 mol%) and 4 Å MS (20.0 mg) were added after removed the solvent in vacuo. The resulting mixture was dissolve with $CHCl_3$ (2.0 mL) and stirred at 30 °C for 4 hours. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether, dichloromethane and ethyl acetate (from 16/1/1 to 9/1/1,v/v) to afford the corresponding product **4aa**.

3. Typical procedure for the chiral product 5aa



The reaction was conducted with $Ni(OTf)_2$ (3.6 mg, 10 mol%), **L_5-RaPr$_2$** (7.4 mg, 10 mol%), **1a** (34.5 mg, 0.10 mmol) under N_2, CH_2Cl_2 (1.0 mL) was added and the mixture was stirred at 30 °C for 15 min. Removed the solvent in vacuo and **2a** (34.2 mg, 0.12 mmol) was added. The resulting mixture was dissolve with CH_2Cl_2 (0.5 mL) and stirred at 35 °C for 15 hours. The reaction mixture was subjected to column chromatography on silica gel to afford the corresponding product **3aa**. The isolated **3aa** was then dissolved in CH_2Cl_2 (1.0 mL) with $Cu(OTf)_2$ (3.6 mg, 10 mol%) at 35 °C for 4 hours. The reaction mixture was subjected to column chromatography on silica gel and eluted with dichloromethane and ethyl acetate 9/1,v/v) to afford the corresponding product **5aa**.

4. Typical procedure for transformation of the racemic product

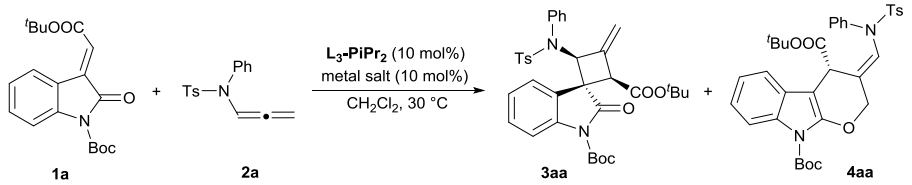


The reaction was conducted with $Ni(OTf)_2$ (3.6 mg, 10 mol%), ***rac*-L$_2$-PiPr$_2$** or ***rac*-L$_3$-PiMe$_3$** (10 mol%), **1a** (34.5 mg, 0.10 mmol) under N_2, CH_2Cl_2 (1.0 mL) was added and the mixture was stirred at 30 °C for 15 min. Removed the solvent and **2a** (34.2 mg, 0.10 mmol) was added. The resulting mixture was dissolve with CH_2Cl_2 (1.0 mL) and stirred at 30 °C for 15 hours. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether, dichloromethane and ethyl acetate (from 16/1/1 to 9/1/1,v/v) to afford the corresponding product ***rac*-3aa** and ***rac*-4aa**.

(C) Optimization of Conditions

1. Optimizing the conditions of the [2+2] cycloaddition reaction

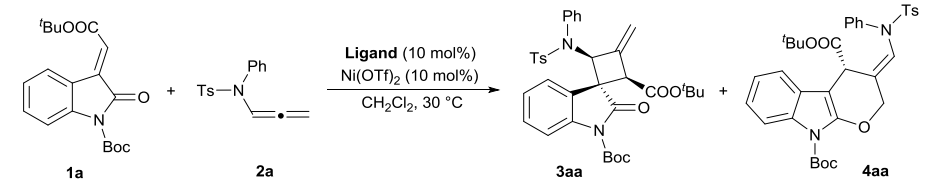
Table S1. Screening of metal salts[a]

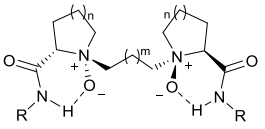


Entry	Metal salt	Yield of **3aa** and **4aa** (%)[b]	Ratio of **3aa**:**4aa**[c]	ee (%) of **3aa**/**4aa**[c]
1	$Zn(OTf)_2$	52	87:13	89/81
2	$Mg(OTf)_2$	69	70:30	89/40
3	**$Ni(OTf)_2$**	**58**	**89:11**	**91/51**
4	$Cu(OTf)_2$	40	90:10	74/--
5	$Yb(OTf)_3$	36	94:6	-38/--
6	$Fe(OTf)_3$	11	95:5	59/--
7	$Sc(OTf)_3$	< 3	34:66	0/0
8[d]	$Zn(OTf)_2$	42	1:99	--/59
9[id]	$Mg(OTf)_2$	48	46:54	82/28
10[id]	$Ni(OTf)_2$	39	1:99	--/60
11	$Ni(acac)_2$	No reaction		
12	$Ni(BF_4)_2{\cdot}6H_2O$	14	89:11	38/50
13	$Ni(ClO_4)_2{\cdot}6H_2O$	35	95:5	84/--
14[e]	$Ni(OTf)_2$	13	1:99	--/race
15[e,f]	$Ni(OTf)_2$	16	70:30	race/race

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.05 mmol), **2a** (0.05 mmol), **L$_3$-PiPr$_2$** (10 mol%) and metal salt (10 mol%) in CH_2Cl_2 (0.1 M) at 30 °C for 16 h. [b]Isolated yield of **3aa** and **4aa** based on **1a**. [c]Determined by HPLC on a chiral stationary phase (λ = 224 nm). [d]Metal salt (15 mol%) was used. [e]Without **L$_3$-PiPr$_2$**. [f]The reaction was carried out with $Ni(OTf)_2$ (2.5 mol%) at 20 °C.

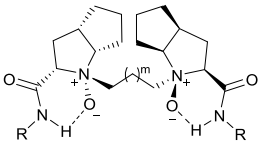
Table S2. Screening of ligands[a]





L_3-PrPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 1, m = 1
L_4-PrPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 1, m = 2
L_3-PiPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 2, m = 1
L_3-PiPr$_3$: R = 2,4,6-^{i}Pr$_3$C$_6$H$_2$, n = 2, m = 1
L_3-PiEt$_2$: R = 2,6-Et$_2$C$_6$H$_3$, n = 2, m = 1
L_3-PiEt$_2$Me: R = 2,6-Et$_2$-4-MeC$_6$H$_2$, n = 2, m = 1
L_3-PiEt$_3$: R = 2,4,6-Et$_3$C$_6$H$_2$, n = 2, m = 1

L_3-PiMe$_2$: R = 2,6-Me$_2$C$_6$H$_3$, n = 2, m = 1
L_3-Pi(O^{t}Bu)$_2$: R = 2,6-(O^{t}Bu)$_2$C$_6$H$_3$, n = 2, m = 1
L_3-Pi(O^{i}Pr)$_2$: R = 2,6-(O^{i}Pr)$_2$C$_6$H$_3$, n = 2, m = 1
L_3-Pi(OMe)$_2$: R = 2,6-(OMe)$_2$C$_6$H$_3$, n = 2, m = 1
L_3-Pi^{t}Bu: R = *tert*-butyl, n = 2, m = 1
L_3-PiCHPh$_2$: R = CH(C$_6$H$_5$)$_2$, n = 2, m = 1
L_3-PiCy: R = C$_6$H$_{11}$, n = 2, m = 1
L_3-Pi$_m$^{t}Bu$_2$: R = 3,5-^{t}Bu$_2$C$_6$H$_3$, n = 2, m = 1
L_2-PiPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 2, m = 0
L_4-PiPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 2, m = 2
L_5-PiPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 2, m = 3

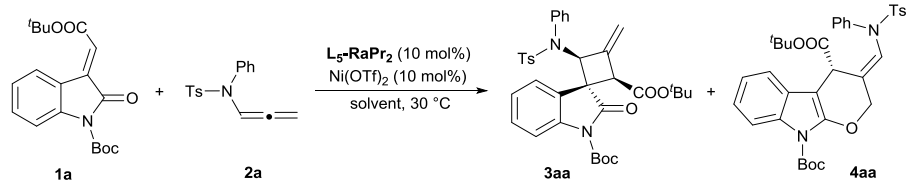


L_3-RaPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, m = 1
L_4-RaPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, m = 2
L_5-RaPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, m = 3

Entry	**Ligand**	Yield of **3aa** and **4aa** (%)[b]	Ratio of **3aa**:**4aa**[c]	ee (%) of **3aa**/**4aa**[c]
1	**L_3-PrPr$_2$**	58	74:26	55/79
2	**L_3-PiPr$_2$**	58	89:11	91/51
3	**L_3-RaPr$_2$**	72	80:20	60/80
4	**L_3-PiPr$_3$**	65	90:10	90/--
5	**L_3-PiEt$_2$**	56	87:13	88/40
6	**L_3-PiEt$_2$Me**	58	95:5	89/--
7	**L_3-PiEt$_3$**	63	95:5	89/--
8	**L_3-PiMe$_2$**	61	90:10	79/--
9	**L_3-Pi(O^{i}Bu)$_2$**	53	89:11	90/33
10	**L_3-Pi(O^{i}Pr)$_2$**	45	87:13	88/63
11	**L_3-Pi(OMe)$_2$**	52	93:7	70/--
12	**L_3-Pi^{t}Bu**	44	95:5	20/--
13	**L_3-PiCHPh$_2$**	38	93:7	25/--
14	**L_3-PiCy**	40	89:11	35/34
15	**L_3-Pi$_m$^{t}Bu$_2$**	52	98:2	8/--
16	**L_2-PiPr$_2$**	59	60:40	58/83
17	**L_4-PiPr$_2$**	55	97:3	95/--
18	**L_4-PrPr$_2$**	55	98:2	79/--
19	**L_4-RaPr$_2$**	75	97:3	90/--
20	**L_5-PiPr$_2$**	49	98:2	90/--
21	**L_5-RaPr$_2$**	**74**	**98:2**	**95/--**

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.05 mmol), **2a** (0.05 mmol), **Ligand** (10 mol%) and Ni(OTf)$_2$ (10 mol%) in CH_2Cl_2 (0.1 M) at 30 °C for 16 h. [b]Isolated yield of **3aa** and **4aa** based on **1a**. [c]Determined by HPLC on a chiral stationary phase (λ = 224 nm).

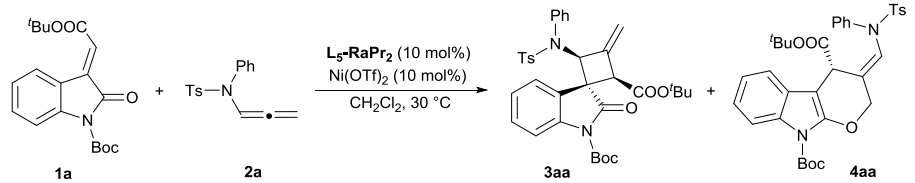
Table S3. Screening of solvent[a]



Entry	Solvent	Yield of **3aa** and **4aa** (%)[b]	Ratio of **3aa**:**4aa**[c]	ee (%) of **3aa**/**4aa**[c]
1	THF	6	90:10	51/--
2	toluene	14	99:1	7/--
3	Et_2O	36	88:12	40/46
4	EtOAc	9	89:11	33/3
5	CH_2Cl_2	74	98:2	95/--
6	$CHCl_3$	31	95:5	79/--
7	CH_2ClCH_2Cl	66	98:2	95/--
8	$CHCl_2CHCl_2$	62	98:2	93/--
9[d]	**CH_2Cl_2**	**84**	**98:2**	**95/--**
10[e]	CH_2Cl_2	55	98:2	97/--

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.05 mmol), **2a** (0.05 mmol), **L_5-RaPr$_2$** (10 mol%) and $Ni(OTf)_2$ (10 mol%) in solvent (0.1 M) at 30 °C for 16 h. [b]Isolated yield of **3aa** and **4aa** based on **1a**. [c]Determined by HPLC on a chiral stationary phase (λ = 224 nm). [d]CH_2Cl_2 (0.2 M) was used. [e]CH_2Cl_2 (0.05 M) was used.

Table S4. Screening of ratio of 1a and 2a[a]

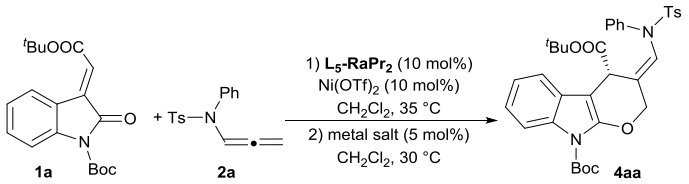


Entry	Ratio of **1a** and **2a**	Yield of **3aa** and **4aa** (%)[b]	Ratio of **3aa**:**4aa**[c]	ee (%) of **3aa**/**4aa**[c]
1	1:1	84	98:2	95/--
2	1.2:1	85	98:2	95/--
3	1.5:1	83	98:2	95/--
4	1:1.2	88	98:2	95/--
5	1:1.5	91	98:2	95/--
6[d]	1:1.2	81	98:2	95/--
7[e]	**1:1.2**	**94**	**98:2**	**95/--**
8[e,f]	1:1.2	80	98:2	95/--
9[e,g]	**1:1.2**	**93**	**98:2**	**95/--**

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.050 mmol), **2a**, **L_5-RaPr$_2$** (10 mol%) and $Ni(OTf)_2$ (10 mol%) in CH_2Cl_2 (0.2 M) at 30 °C for 16 h. [b]Isolated yield of **3aa** and **4aa** based on **1a**. [c]Determined by HPLC on a chiral stationary phase (λ = 224 nm). [d]The reaction was carried out at 20°C for 40 h. [e]The reaction was carried out at 35°C for 16 h. [f]**L_5-RaPr$_2$** (5 mol%) and $Ni(OTf)_2$ (5 mol%) were used. [g]The reaction was carried out with **1a** (0.10 mmol), **2a** (0.12 mmol), **L_5-RaPr$_2$** (10 mol%) and $Ni(OTf)_2$ (10 mol%) in CH_2Cl_2 (0.2 M) at 35 °C for 16 h.

2. Optimizing the conditions of the transformation

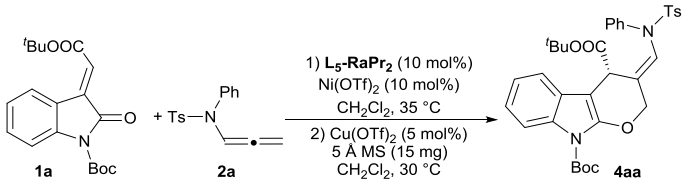
Table S5. Screening of metal salts[a]



Entry	Metal salt	Yield of **3aa** and **4aa** (%)[b]	Ratio of **3aa**:**4aa**[c]	ee (%) of **3aa**/**4aa**[c]
1	$Ni(OTf)_2$	76	82:18	95/92
2[d]	$Ni(OTf)_2$	37	3:97	--/92
3[e]	$Ni(OTf)_2$	56	1:99	--/92
4	$Zn(OTf)_2$	54	6:94	--/91
5	$Mg(OTf)_2$	52	34:66	94/91
6	$Cu(OTf)_2$	49	1:99	--/93
7[e]	$Cu(OTf)_2$	46	1:99	--/92
8[f]	**$Cu(OTf)_2$**	**58**	**1:99**	**--/92**

[a]Unless otherwise noted, all reactions were carried out with 1) **1a** (0.05 mmol), **2a** (0.06 mmol), **L_5-RaPr$_2$** (10 mol%) and $Ni(OTf)_2$ (10 mol%) in CH_2Cl_2 (0.2 M) at 35 °C for 16 h. 2) Metal salt (5 mol%) was then added in CH_2Cl_2 (0.1 M) at 30°C for 16 h under air. [b]Isolated yield of **3aa** and **4aa** based on **1a**. [c]Determined by HPLC on a chiral stationary phase (λ = 224 nm). [d]**3aa** was isolated and treated with $Ni(OTf)_2$ (10 mol%) in CH_2Cl_2, **5aa** was found in 18% yield, 65:35 dr and 95% ee for each diastereoisomer. [e]Metal salt (10 mol%) was used. [f]5 Å MS (15 mg) was added.

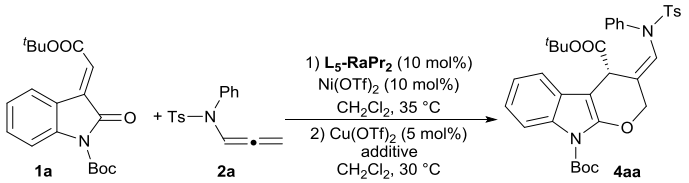
Table S6. Screening of solvent[a]



Entry	Solvent	Yield of **3aa** and **4aa** (%)[b]	Ratio of **3aa**:**4aa**[c]	ee (%) of **3aa**/**4aa**[c]
1	CH_2Cl_2	58	1:99	--/92
2	**$CHCl_3$**	**63**	**2:98**	**--/92**
3[d]	$CHCl_3$	60	45:55	95/91
4	CH_2ClCH_2Cl	52	1:99	--/91
5	$CHCl_2CHCl_2$	52	1:99	--/91
6	Et_2O	64	85:15	95/93
7	THF	48	22:78	96/91
8	EtOAc	83	93:7	94/92

[a]Unless otherwise noted, all reactions were carried out with 1) **1a** (0.05 mmol), **2a** (0.06 mmol), **L_5-RaPr$_2$** (10 mol%) and $Ni(OTf)_2$ (10 mol%) in CH_2Cl_2 (0.2 M) at 35 °C for 16 h. 2) $Cu(OTf)_2$ (5 mol%) and 5 Å MS (15 mg) were then added in solvent (0.1 M) at 30°C for 16 h under air. [b]Isolated yield of **3aa** and **4aa** based on **1a**. [c]Determined by HPLC on a chiral stationary phase (λ = 224 nm). [d]Without 5 Å MS.

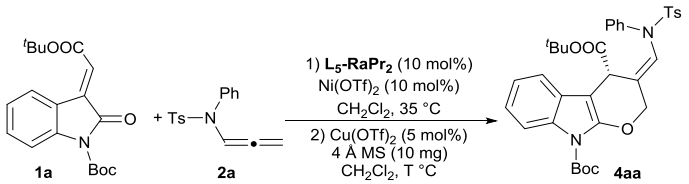
Table S7. Screening of additives[a]



Entry	Additive	Yield of **3aa** and **4aa** (%)[b]	Ratio of **3aa**:**4aa**[c]	ee (%) of **3aa**/**4aa**[c]
1	5 Å MS (15 mg)	63	2:98	--/92
2	3 Å MS (15 mg)	63	1:99	--/93
3	4 Å MS (15 mg)	65	1:99	--/93
4	4 Å MS (5 mg)	57	1:99	--/93
5	**4 Å MS (10 mg)**	**65**	**1:99**	**--/93**
6	$TsOH·H_2O$ (20 mol%)	26	1:99	--/91
7	$MgSO_4$ (10 mg)	87	97:3	94/--
8[d]	$TsOH·H_2O$ (50 mol%)	Decomposed		
9[d]	$TsOH·H_2O$ (100 mol%)	Decomposed		

[a]Unless otherwise noted, all reactions were carried out with 1) **1a** (0.05 mmol), **2a** (0.06 mmol), **L_5-RaPr$_2$** (10 mol%) and $Ni(OTf)_2$ (10 mol%) in CH_2Cl_2 (0.2 M) at 35 °C for 16 h. 2) $Cu(OTf)_2$ (5 mol%) and additive were then added in $CHCl_3$ (0.1 M) at 30°C for 16 h under air. [b]Isolated yield of **3aa** and **4aa** based on **1a**. [c]Determined by HPLC on a chiral stationary phase (λ = 224 nm). [d]Without $Cu(OTf)_2$.

Table S8. Screening of temperature[a]

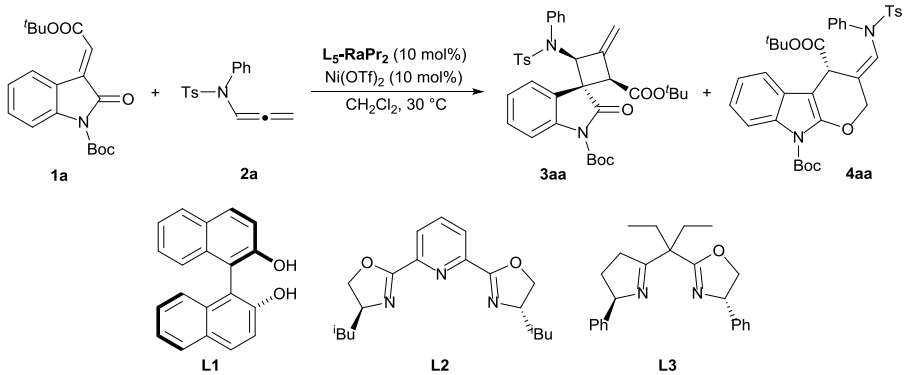


Entry	Temperature (°C)	Yield of **3aa** and **4aa** (%)[b]	Ratio of **3aa**:**4aa**[c]	ee (%) of **3aa**/**4aa**[c]
1	0	87	83:17	95/93
2	10	86	87:13	95/93
3	20	65	1:99	--/93
4	25	65	1:99	--/93
5	30	65	1:99	--/93
6	35	65	1:99	--/93
7[d]	30	68	1:99	--/93
8[e]	30	74	59:41	95/93
9[d,f]	30	83	94:6	95/--
10[d,g]	30	96	97:3	94/--
11[d,h]	30	75	85:15	95/92
12[d,i]	30	43	1:99	--/93
13[d,j]	**30**	**70**	**1:99**	**--/93**
14[k]	30	72	1:99	--/93

14[l]	**30**	**70**	**1:99**	**--/93**

[a]Unless otherwise noted, all reactions were carried out with 1) **1a** (0.050 mmol), **2a** (0.060 mmol), **L_5-RaPr$_2$** (10 mol%) and $Ni(OTf)_2$ (10 mol%) in CH_2Cl_2 (0.2 M) at 35 °C for 16 h. 2) $Cu(OTf)_2$ (5 mol%) and 4 Å MS (10 mg) were then added in $CHCl_3$ (0.1 M) at 30°C for 16 h under air. [b]Isolated yield of **3aa** and **4aa** based on **1a**. [c]Determined by HPLC on a chiral stationary phase (λ = 224 nm). [d]The reaction was carried out with $CHCl_3$ (0.05 M). [e]The reaction was carried out with $CHCl_3$ (0.025 M). [f]$Cu(OTf)_2$ was replaced by $Cu(acac)_2$. [g]$Cu(OTf)_2$ was replaced by $Cu(OAc)_2$. [h]$Cu(OTf)_2$ was replaced by $Cu(BF_4)_2{\cdot}6H_2O$. [i]$Cu(OTf)_2$ was replaced by $Cu(ClO_4)_2{\cdot}6H_2O$. [j]The reaction was carried out for 3 h. [k]In N_2. [l]The reaction was carried out with 1) **1a** (0.10 mmol), **2a** (0.12 mmol), **L_5-RaPr$_2$** (10 mol%) and $Ni(OTf)_2$ (10 mol%) in CH_2Cl_2 (0.1 M) at 35 °C for 16 h. 2) $Cu(OTf)_2$ (5 mol%) and 4 Å MS (20 mg) were then added in $CHCl_3$ (0.05 M) at 30°C for 3 h under air.

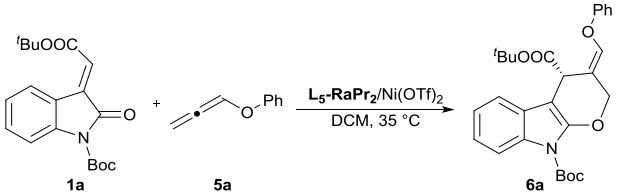
Table S9. Screening of ligands[a]



Entry	**Ligand**	Yield of **3aa** and **4aa** (%)[b]	Ratio of **3aa**:**4aa**[c]	ee (%) of **3aa**/**4aa**[c]
1	**L1**	29	1:99	--/0
2	**L2**	33	1:99	--/–11
3	**L3**	27	6:94	--/36

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.05 mmol), **2a** (0.05 mmol), **Ligand** (10 mol%) and $Ni(OTf)_2$ (10 mol%) in CH_2Cl_2 (0.1 M) at 30 °C for 16 h. [b]Isolated yield of **3aa** and **4aa** based on **1a**. [c]Determined by HPLC on a chiral stationary phase (λ = 224 nm).

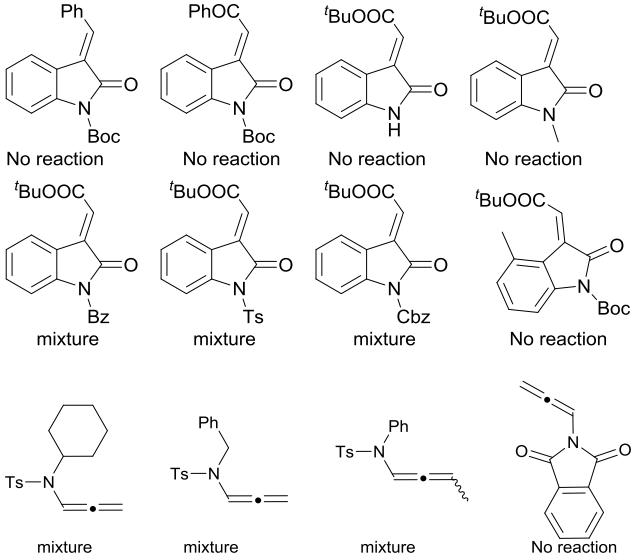
Table S10. Optimization of the conditions of reaction with alkoxyallene[a]



Entry	Ratio of **L_5-RaPr$_2$** and $Ni(OTf)_2$	Yield (%)[b]	ee (%)[c]
1	**1:1**	**60**	**97**
2	1:1.5	56	97
3	1.5:1	50	97
4[d]	1:1	59	97
5[e]	1:1	8	97

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.1 mmol), **5a** (0.6 mmol), **L_5-RaPr$_2$**/$Ni(OTf)_2$ (x:y, 10 mol%) in solvent (0.2 M) at 30 °C for 16 h. [b]Isolated yield of **3aa** and **4aa** based on **1a**. [c]Determined by HPLC on a chiral stationary phase. [d]The reaction was carried out at 20 °C. [e]The reaction was carried out at 0 °C.

Table S11. Faild examples



(D) X-ray Crystal Structure of Product 3aa, *rac*-4ka and *rac*-5aa

The colourless crystal in block-shape, with approximate dimensions of 0.298 × 0.219 × 0.131 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 148(2)K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) program package. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested.

The crystal of product **3aa** was obtained in the solvents of ethyl acetate and *n*-hexane. CCDC 2042864 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* https://www.ccdc.cam.ac.uk/.

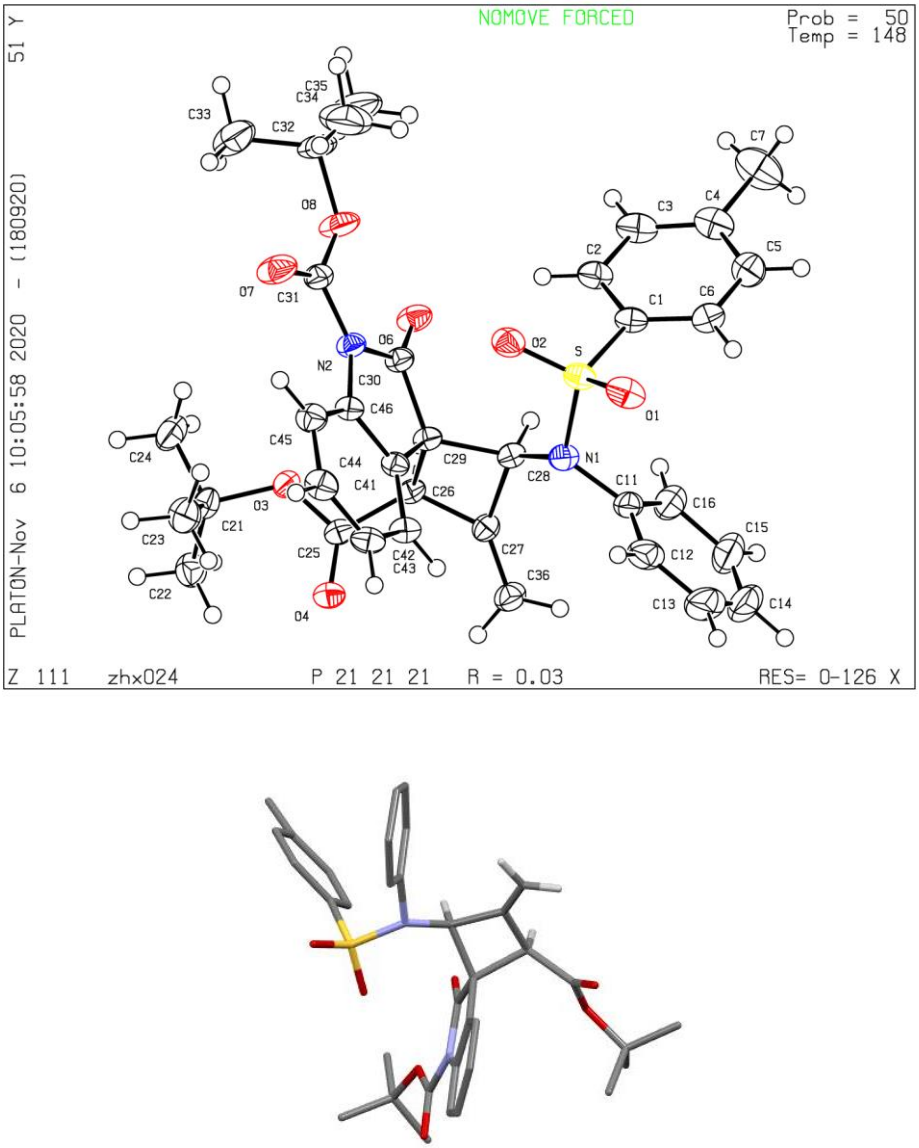


Figure S1. X-ray Crystal Structure of Product **3aa**

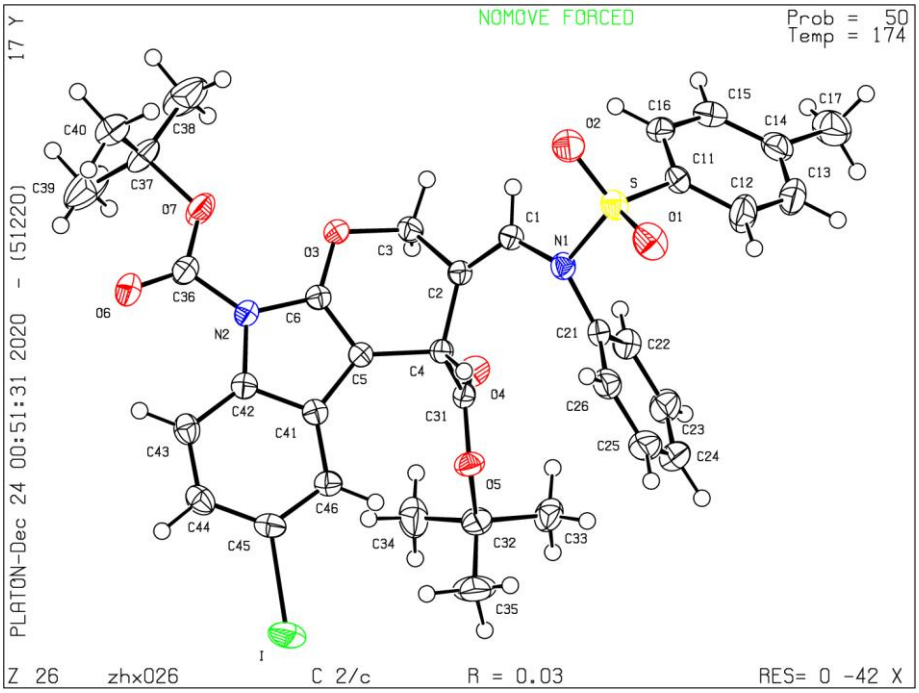
Crystallographic Data for $C_{35}H_{38}N_2O_7S$.

Formula	$C_{35}H_{38}N_2O_7S$
Formula mass (amu)	630.73
Space group	P 21 21 21
a (Å)	9.6132(4)
b (Å)	17.1589(7)

c (Å)	20.1048(9)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	3316.3(2)
Z	4
λ (Å)	1.54178
T (K)	148 K
r_{calcd} (g cm^{-3})	1.263
m (mm^{-1})	1.280
Transmission factors	0.736, 0.895
$2q_{max}$ (deg)	80.721
No. of unique data, including $F_o^2 < 0$	7224
No. of unique data, with $F_o^2 > 2s(F_o^2)$	7063
No. of variables	413
$R(F)$ for $F_o^2 > 2s(F_o^2)$ [a]	0.0275
$R_w(F_o^2)$ [b]	0.0710
Goodness of fit	1.058
Flack Parameter	**0.014(3)**

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$. [b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

The crystal of product ***rac*-4ka** was obtained in the solvents of ethyl acetate and *n*-hexane. CCDC 2052253 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* https://www.ccdc.cam.ac.uk/.



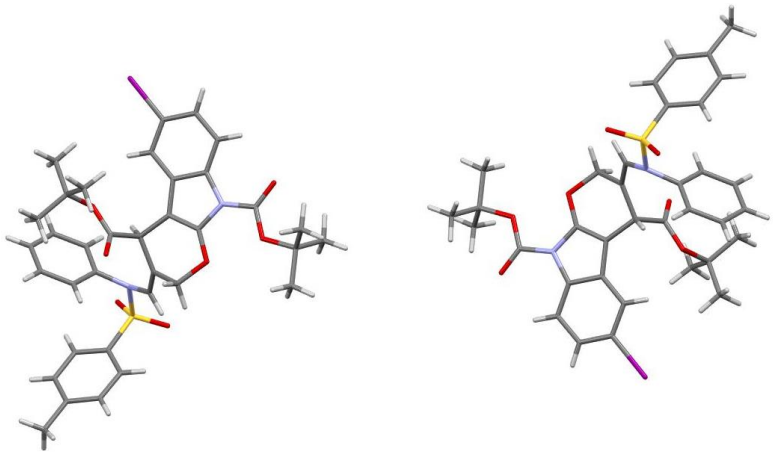


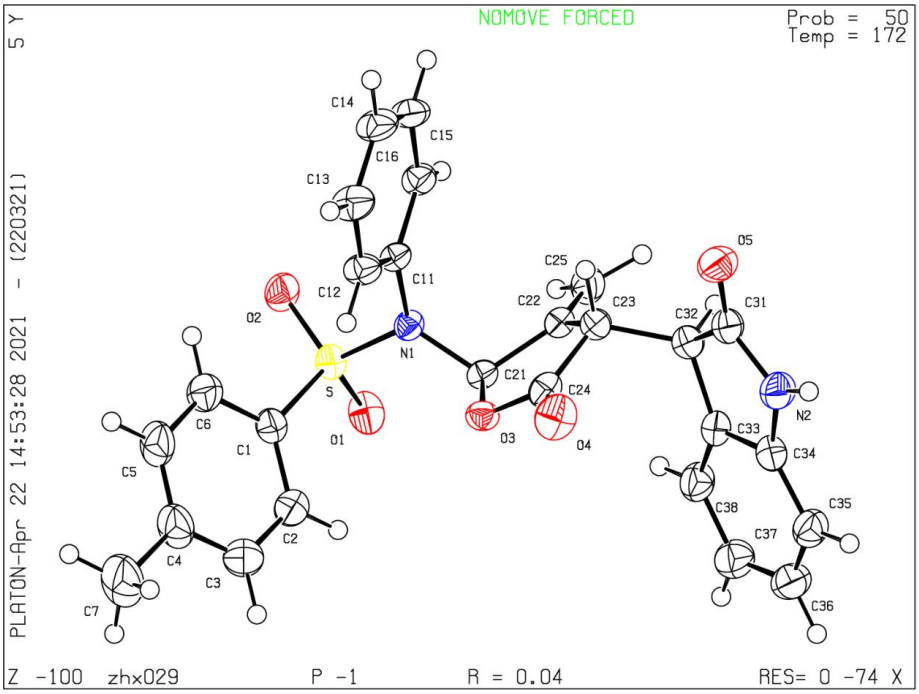
Figure S2. X-ray Crystal Structure of Product ***rac*-4ka**

Crystallographic Data for $C_{35}H_{37}IN_2O_7S$.

Formula	$C_{35}H_{37}IN_2O_7S$
Formula mass (amu)	756.62
Space group	C 2/c
a (Å)	26.3668(7)
b (Å)	12.0985(3)
c (Å)	22.1997(6)
α (deg)	90
β (deg)	101.169(1)
γ (deg)	90
V (Å^3)	6947.5(3)
Z	8
λ (Å)	1.54178
T (K)	174 K
r_{calcd} (g cm^{-3})	1.447
m (mm^{-1})	8.212
Transmission factors	0.180, 0.719
$2q_{max}$ (deg)	68.379
No. of unique data, including $F_o^2 < 0$	6388
No. of unique data, with $F_o^2 > 2s(F_o^2)$	6318
No. of variables	422
$R(F)$ for $F_o^2 > 2s(F_o^2)$ [a]	0.0259
$R_w(F_o^2)$ [b]	0.0651
Goodness of fit	1.036

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$. [b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

The crystal of product ***rac*-5aa** was obtained in the solvents of ethyl acetate and *n*-hexane. CCDC 2079315 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* https://www.ccdc.cam.ac.uk/.



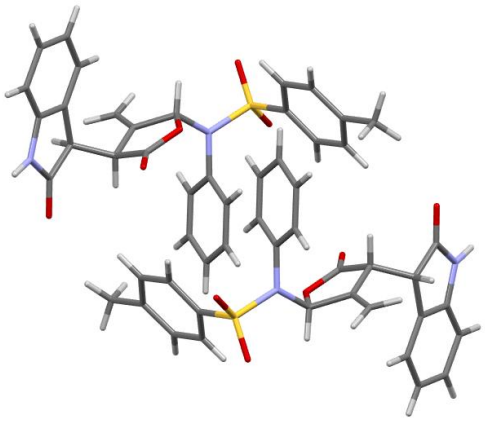


Figure S3. X-ray Crystal Structure of Product ***rac*-5aa**

Crystallographic Data for $C_{26}H_{22}IN_2O_5S$.

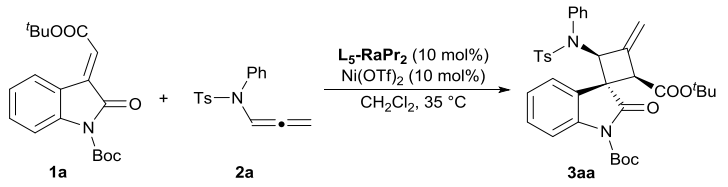
Formula	$C_{26}H_{22}IN_2O_5S$
Formula mass (amu)	474.51
Space group	P –1
a (Å)	8.3490(2)
b (Å)	11.8120(3)
c (Å)	14.8662(4)
α (deg)	96.220(1)
β (deg)	95.738(1)
γ (deg)	105.762(1)
V (Å^3)	1389.76(6)
Z	2
λ (Å)	1.54178
T (K)	172 K

r_{calcd} (g cm^{-3})	1.134
m (mm^{-1})	1.322
Transmission factors	0.717, 0.951
$2q_{max}$ (deg)	68.323
No. of unique data, including $F_o^2 < 0$	4998
No. of unique data, with $F_o^2 > 2s(F_o^2)$	4334
No. of variables	318
$R(F)$ for $F_o^2 > 2s(F_o^2)$ [a]	0.0429
$R_w(F_o^2)$ [b]	0.1110
Goodness of fit	1.037

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$. [b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

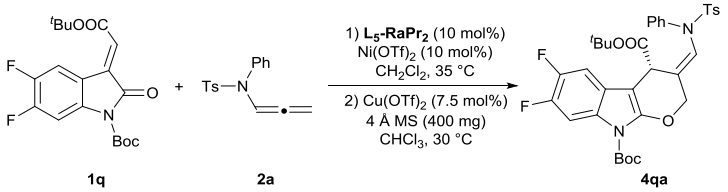
(E) Experimental Procedure for the Scale-up Reaction and Product Derivation

1. Scale-up reaction procedure for the chiral product 3aa



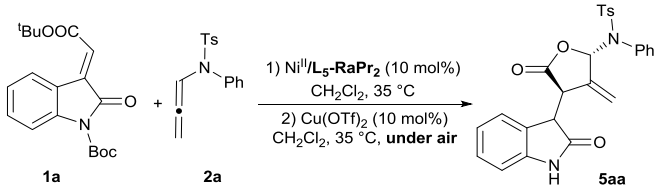
The reaction was conducted with $Ni(OTf)_2$ (72.0 mg, 10 mol%), **L_5-RaPr$_2$** (148.0 mg, 10 mol%), **1a** (690.0 mg, 2.0 mmol) under N_2, CH_2Cl_2 (20.0 mL) was added and the mixture was stirred at 30 °C for 30 min. Removed the solvent and **2a** (684.0 mg, 2.4 mmol) was added. The resulting mixture was dissolve with CH_2Cl_2 (10.0 mL) and stirred at 35 °C for 15 hours. The reaction mixture was subjected to column chromatography on silica gel to afford the product **3aa** (petroleum ether/ethyl acetate/dichloromethane = 16/1/1 to petroleum ether/ethyl acetate/dichloromethane = 9/1/1 as eluent) as a white soild (1.124 g, 89% yield, **3aa**:**4aa** > 19:1, 90% ee).

2. Scale-up reaction procedure for the chiral product 4qa



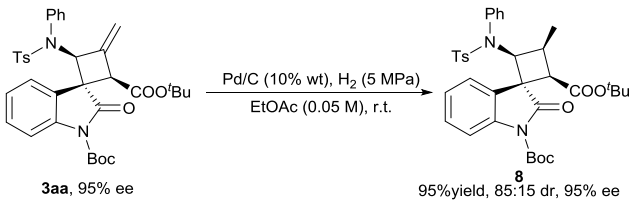
The reaction was conducted with $Ni(OTf)_2$ (57.6 mg, 10 mol%), **L_5-RaPr$_2$** (116.8 mg, 10 mol%), **1q** (609.0 mg, 1.60 mmol) under N_2, CH_2Cl_2 (16.0 mL) was added and the mixture was stirred at 30 °C for 30 min. Removed the solvent in vacuo and **2a** (547.2 mg, 1.92 mmol) was added. The resulting mixture was dissolve with CH_2Cl_2 (8.0 mL) and stirred at 35 °C for 15 hours.
The solvent removed in vacuo. Then $Cu(OTf)_2$ (36.0 mg, 7.5 mol%) and 4 Å MS (400.0 mg) were added. The resulting mixture was dissolve with $CHCl_3$ (24.0 mL) and stirred at 30 °C for 4 hours. The reaction mixture was subjected to column chromatography on silica gel to afford the product **3qa** (petroleum ether/ethyl acetate/dichloromethane = 16/1/1 to petroleum ether/ethyl acetate/dichloromethane = 9/1/1 as eluent) as white soild (0.618 g, 58% yield, **3qa**:**4qa** > 19:1, 88% ee).

3. Scale-up reaction procedure for the chiral product 5ba



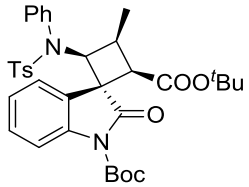
The reaction was conducted with **3ba** (1.74 mg, 2.5 mol) and $Cu(OTf)_2$ (90.0 mg, 10 mol%), CH_2Cl_2 (25.0 mL) was added and the mixture was stirred at 35 °C for 6 hours under air. The reaction mixture was subjected to column chromatography on silica gel to afford the product **5ab** (ethyl acetate/dichloromethane = 1/12 to ethyl acetate/dichloromethane = 1/9 as eluent) as yellow soild (0.72 g, 63% yield, 66:34 dr, 94/94% *ee*).

4. Hydrogrnation of 3aa

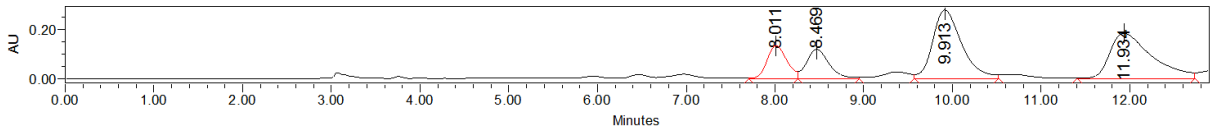


In a 10 mL tube equipped with a magnetic stirring bar, **3aa** (0.1 mmol) was dissolved in 2.0 mL MeOH, the mixture was then hydrogenated at 50 atm with Pd/C (10% wt) at 25 ºC for 24 h, The reaction was determined by TLC, after the substrate was consumed, the reaction mixture were filtered over Celite, evaporated under reduced pressure, and was subjected to column chromatography on silica gel.

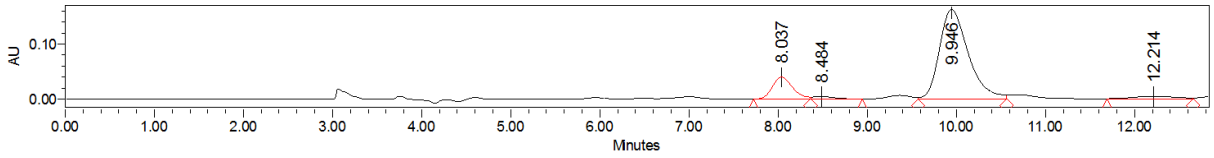
Di-*tert*-butyl (1*R*,2*R*,3*S*,4*S*)-3-methyl-4-[(4-methyl-*N*-phenylphenyl)sulfonamido]-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (8)



97% yield, Pale yellow oil; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IB, hexane/^{i}PrOH = 95/5, flow rate 1.0 mL/min, λ = 224 nm), major isomer: t_r (major) = 9.95 min, t_r (minor) = 12.21 min, ee = 95%; minor isomer: t_r (major) = 8.04 min, t_r (minor) = 8.48 min, ee = 84%. dr = 85:15, determined by ^{1}H NMR. $[\alpha]^{22}_D$ = –55.2 (*c* = 0.47, in dichloromethane). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.64 – 7.59 (m, 2H), 7.23 – 7.08 (m, 8H), 6.97 – 6.93 (m, 1H), 6.90 – 6.79 (m, 1H), 6.48 – 6.46 (m, 1H), 4.78 (d, *J* = 8.4 Hz, 1H), 3.54 (d, *J* = 9.6 Hz, 1H), 3.12 (dt, *J* = 15.6, 7.8 Hz, 1H), 2.38 (s, 3H), 1.63 (s, 9H), 1.34 (d, *J* = 7.2 Hz, 3H), 0.94 (s, 9H) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ 177.2, 167.4, 148.7, 144.1, 140.9, 138.8, 131.4, 129.4, 129.1, 128.9, 128.7, 128.4, 128.3, 128.23, 128.16, 127.7, 127.5, 126.6, 125.9, 125.4, 123.7, 114.6, 84.2, 81.0, 58.0, 57.2, 45.4, 35.3, 28.1, 27.2, 21.6, 11.0 ppm; **IR (neat) ν (cm^{-1}):** 2979, 1730, 1601, 1481, 1359, 1299, 1248, 1157, 841, 750, 702, 601; **HRMS** (ESI-FT) calcd for $C_{35}H_{40}N_2O_7SNa^+$ ([M]+Na$^+$) = 655.2448, found 655.2450. Relative configuration of **8** was determined by COSY and NOESY NMR spectra.

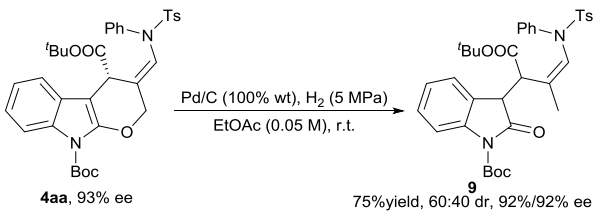


	Retention Time	Area	% Area
1	8.011	2104986	12.65
2	8.469	2124459	12.76
3	9.913	6371820	38.28
4	11.934	6043936	36.31



	Retention Time	Area	% Area
1	8.037	626664	13.97
2	8.484	72473	1.62
3	9.946	3646280	81.27
4	12.214	140988	3.14

5. Hydrogrnation of 4aa



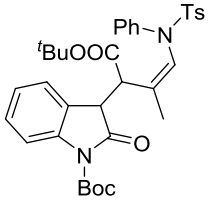
4aa, 93% ee

9
75%yield, 60:40 dr, 92%/92% ee

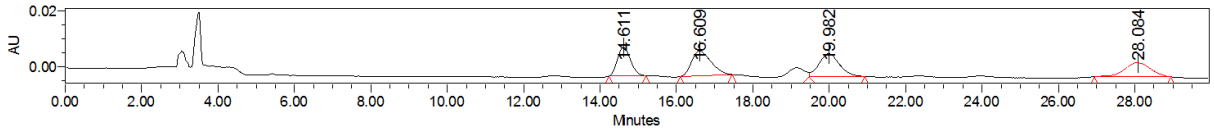
In a 10 mL tube equipped with a magnetic stirring bar, **4aa** (0.1 mmol) was dissolved in 2.0 mL MeOH, the mixture was then hydrogenated at 50 atm with Pd/C (100% wt) at 25 ºC for 24 h, The reaction was determined by TLC, after the substrate was consumed, the reaction mixture were filtered over Celite, evaporated under reduced pressure, and was subjected to column

chromatography on silica gel.

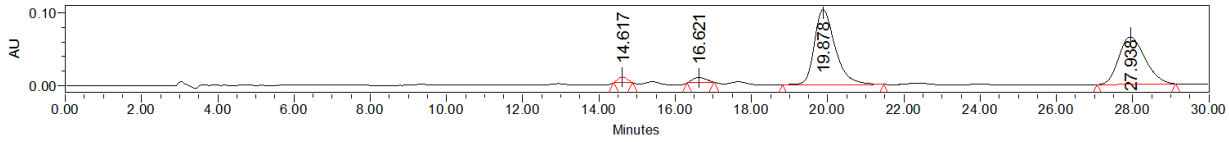
***Tert*-butyl (*Z*)-3-{1-(*tert*-butoxy)-3-methyl-4-[(4-methyl-*N*-phenylphenyl)sulfonamido]-1-oxobut-3-en-2-yl}-2-oxoindoline-1-carboxylate (9)**



75% yield, White solid; **m.p.**: 71.8 – 94.0 °C; R_f = 0.5 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IF, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 224 nm), major isomer: t_r (major) = 19.88 min, t_r (minor) = 16.62 min, ee = 92%; minor isomer: t_r (major) = 27.94 min, t_r (minor) = 14.62 min, ee = 92%. dr = 60:40, determined by ^{1}H NMR. $[\alpha]^{23}_D$ = +46.1 (*c* = 0.43, in dichloromethane). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.78 – 7.75 (m, 1H), 7.48 – 7.44 (m, 2H), 7.30 – 7.27 (m, 1H), 7.25 – 7.18 (m, 6H), 7.13 – 7.06 (m, 3H), 5.96 (d, *J* = 1.8 Hz, 1H), 4.32 (d, *J* = 8.4 Hz, 1H), 4.12 (d, *J* = 9.0 Hz, 1H), 2.41 (s, 3H), 1.85 (d, *J* = 1.2 Hz, 3H), 1.59 (s, 9H), 1.31 (s, 9H) ppm. **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ 173.1, 169.5, 149.1, 143.8, 141.2, 140.0, 136.3, 134.3, 134.1, 129.4, 128.9, 128.2, 128.0, 127.3, 126.7, 126.2, 125.5, 124.2, 123.5, 114.9, 83.8, 81.9, 48.7, 45.0, 28.1, 27.7, 21.6, 18.1 ppm. **IR (neat) ν (cm^{-1}):** 2978, 1767, 1727, 1484, 1357, 1297, 1251, 1157, 1093, 754, 697, 611; **HRMS** (ESI-FT) calcd for $C_{35}H_{40}N_2O_7SNa^+$ ([M]+Na^+) = 655.2448, found 655.2450.



	Retention Time	Area	% Area
1	14.611	243168	21.95
2	16.609	314264	28.37
3	19.982	310119	28.00
4	28.084	240156	21.68



	Retention Time	Area	% Area
1	14.617	127255	1.73
2	16.621	171952	2.34
3	19.878	3928772	53.41
4	27.938	3127308	42.52

(F) Control Experiments and React IR Experiment

1. Control experiments

1.1

When the transformation of **3aa** to **4aa** is carried out in glove box, the yield of **4aa** increased to 70% (Figure S4a). However, **4aa** could converted into **3aa** under the same condition (Figure S4b, condition 2), which indicates that the transformation from **3aa** to **4aa** is irreversible.

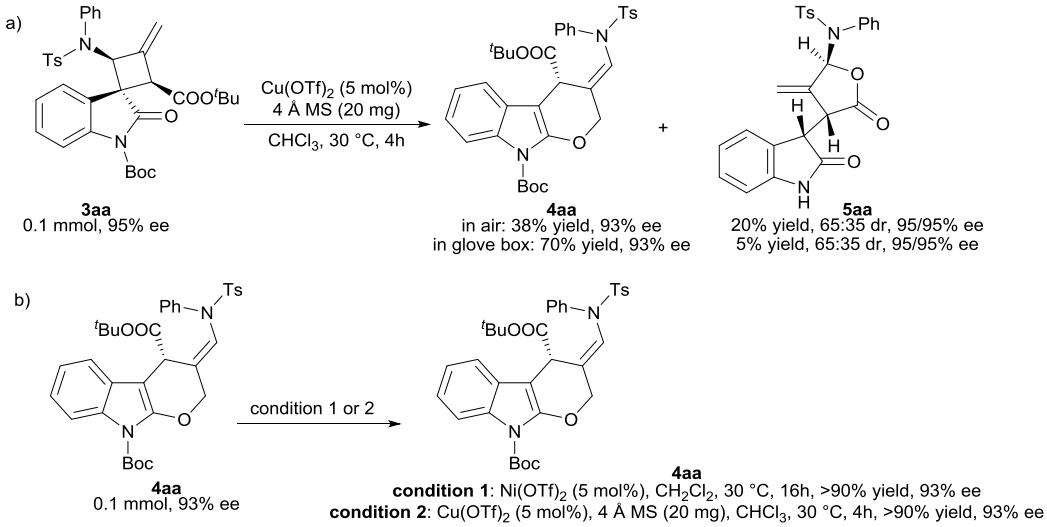


Figure S4

1.2

When **3aa** (95% ee) was heated in $CHCl_2CHCl_2$ at 80 ℃ under N_2 atmosphere for 24 h, compound **4aa** was isolated in 40% yield with 94% ee. It is indicated that **4aa** could be obtained through thermal conversion of **3aa**. (Figure S5).

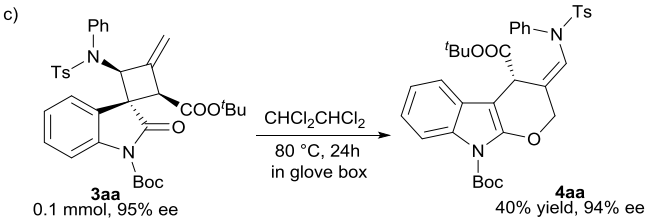


Figure S5

1.3

Treatment **4aa** with TFA led to the formation of **5aa** in 59% yield, 65:35 dr and 93%/93% ee (Figure S6). Moreover, treatment of product **4aa** with TFA gave rise to intermediate **V**, which underwent ring-open and proton transfer to produce **5aa**.

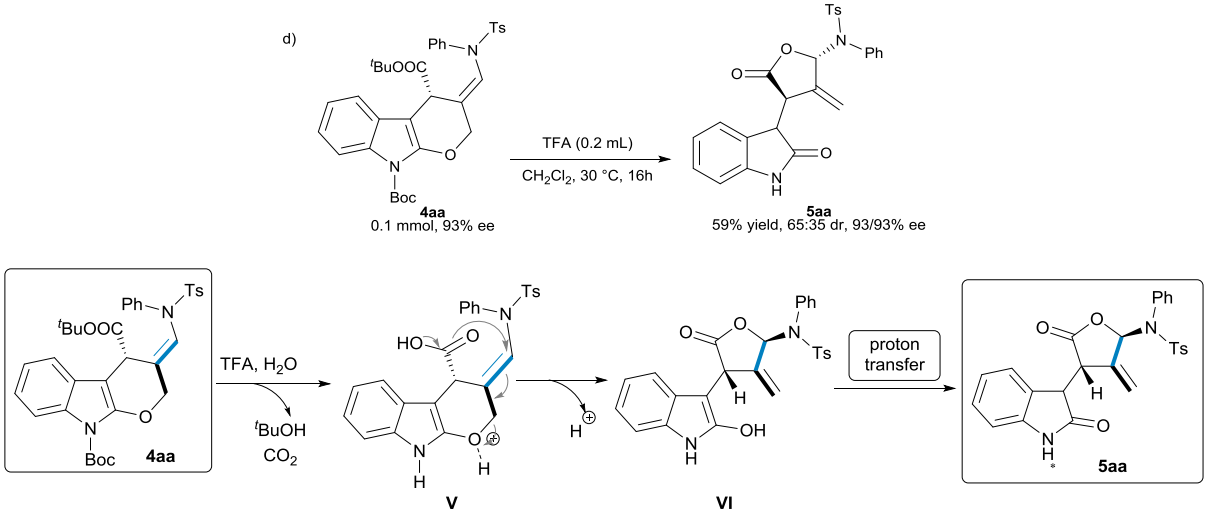
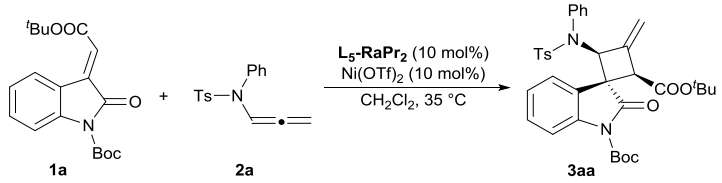


Figure S6

2. React IR experiments

2.1. React IR experiment of the [2+2] cycloaddition reaction

Kinetic analyses were performed using in situ attenuated total reflectance Fouriertransform infrared (ATR FTIR) spectroscopy to track the formation of product **3aa** under synthetically relevant conditions. A Mettler Toledo ReactIR 701L was treated as main experiment equipment. All of the kinetic experiments on each plot were performed using a single batch of reagents.



A three-necked reaction tube was charge with $Ni(OTf)_2$ (10 mol%), **L_5-RaPr$_2$** (10 mol%), **1a** (0.8 mmol) under N_2, CH_2Cl_2 (8.0 mL) was added and the mixture was stirred at 30 °C for 30 min. Removed the solvent in vacuo and **2a** (0.96 mmol) was added. The resulting mixture was dissolve with CH_2Cl_2 (4.0 mL) and stirred at 35 °C and the IR data collection was started. The React IR spectra were recorded over the process of the reaction. ConcIRT Spectrum of the **1a** with peak at 1484 cm^{-1} and **3aa** with peak at 1461 cm^{-1} was selected to acquire kinetic data.

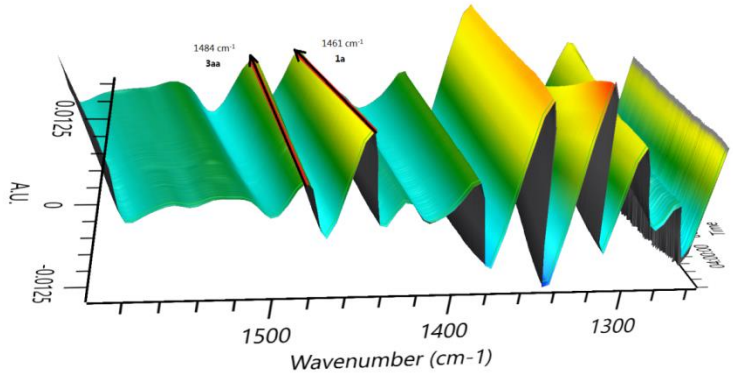


Figure S7. 3D ATR-FTIR Profile of the Recorded over the Reaction of **1a** and **3aa**

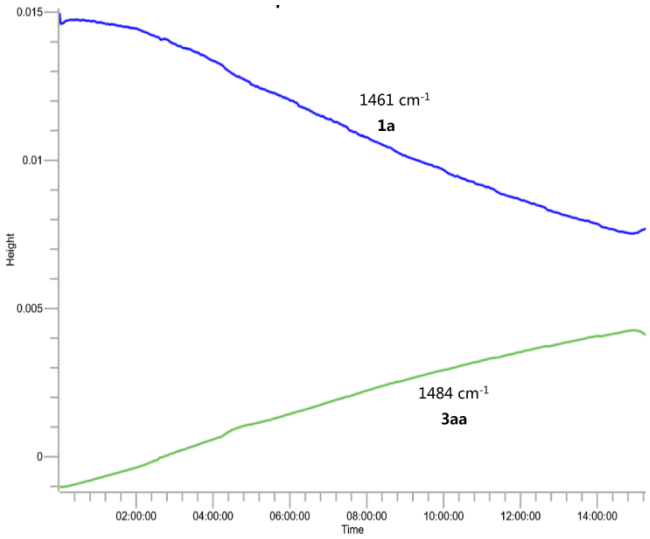
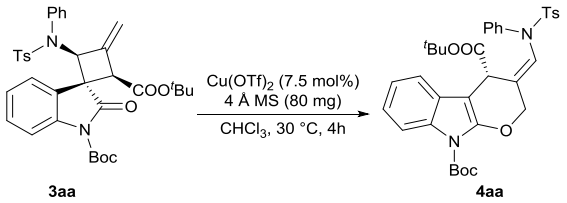


Figure S8. The trend of each component (X axes: reaction time; Y axes: absorbance unit). **1a**: peak at 1461 cm^{-1} ; **3aa**: peak at 1484 cm^{-1}

2.2. React IR experiment of the transformation

Kinetic analyses were performed using in situ attenuated total reflectance Fouriertransform infrared (ATR FTIR) spectroscopy to track the formation of product **4aa** under synthetically relevant conditions. A Mettler Toledo ReactIR 701L was treated as main experiment equipment. All of the kinetic experiments on each plot were performed using a single batch of reagents.



3aa **4aa**

A three-necked reaction tube was charge with $Cu(OTf)_2$ (7.5 mol%) and 4 Å MS (80 mg), **3aa** (0.4 mmol) was added and the resulting mixture was dissolve with $CHCl_3$ (8.0 mL) and stirred at 30 °C and the IR data collection was started. The React IR spectra were recorded over the process of the reaction. ConcIRT Spectrum of the **4aa** with peak at 1252 cm^{-1} and intermediate **int.** with peak at 1420 cm^{-1} was selected to acquire kinetic data.

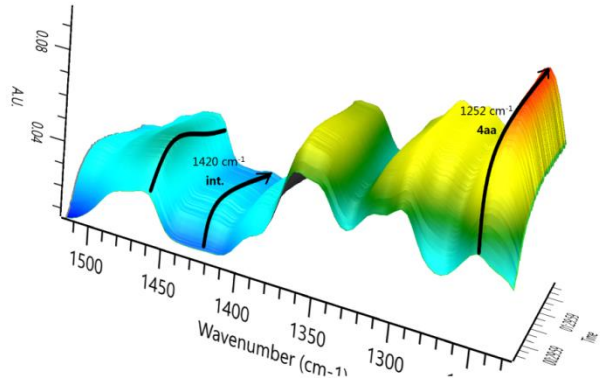


Figure S9. 3D ATR-FTIR Profile of the Recorded over the Reaction of **4aa** and **int.**

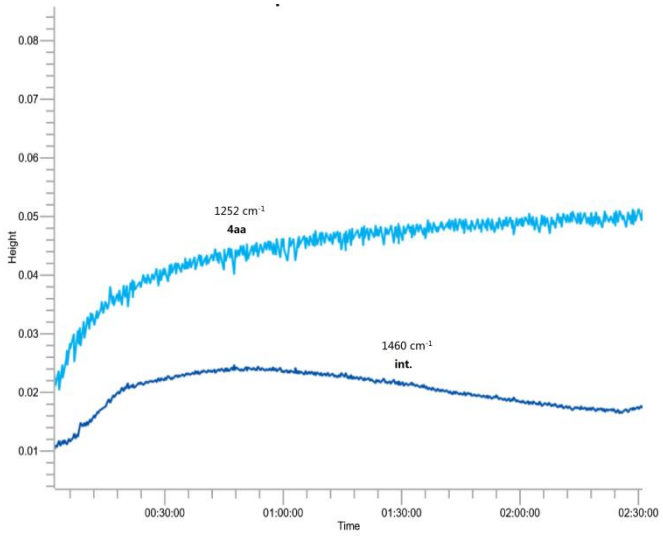


Figure S10. The trend of each component (X axes: reaction time; Y axes: absorbance unit). **4aa**: peak at 1252 cm^{-1}; intermediate **int.**: peak at 1420 cm^{-1}.

(G) Computational Details

All calculations were performed using Gaussian 09 program package.[4] The geometries of **3aa** and **4aa** were optimized at the M062X-D3/6-31G(d,p)(SMD, dichloromethane) theoretical level, and characterized by frequency analysis at 303 K. In the $Cu(OTf)_2$-catalyzed isomerization reaction from **3aa** to **4aa**, the M06 density functional with the 6-31G(d,p) basis set was employed. The self-consistent reaction field (SCRF) method based on the universal solvation model SMD[5] was adopted to evaluate the effect of solvent. The intrinsic reaction coordinate (IRC) path was traced to check the energy profiles connecting each transition state to two associated minima of the proposed mechanism.[6] The stability of wavefunction was checked at the same theoretical level.

The optimized geometries of **3aa** and **4aa** obtained at the M062X-D3/6-31G(d,p)(SMD, dichloromethane) theoretical level were shown in Figure S11. The calculations indicated that ***E*-4aa** was stable than **3aa** by 1.2 kcal mol^{-1}. Moreover, the ΔG of ***Z*-4aa** was higher than that of ***E*-4aa** by 2.3 kcal mol^{-1}.

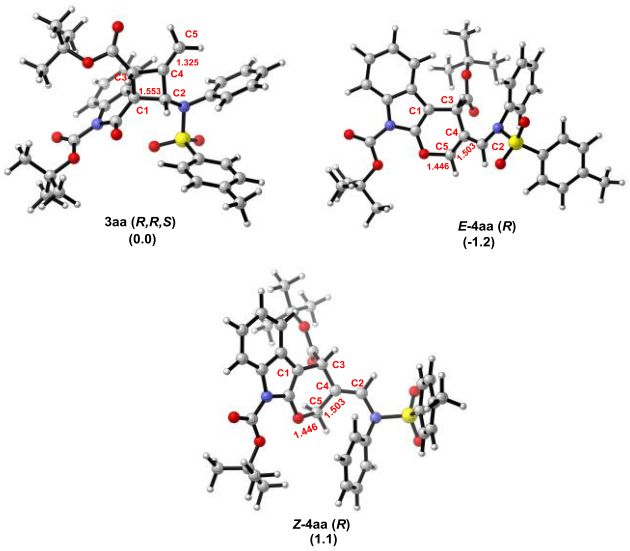


Figure S11 Optimized geometries of **3aa** and **4aa** at the M062X-D3/6-31G(d,p)(SMD, dichloromethane) theoretical level. The relative Gibbs free energy (in kcal mol^{-1}) of **3aa** was set to zero.

The $Cu(OTf)_2$-catalyzed isomerizations from **3aa** to ***E*-4aa** or ***Z*-4aa** were studied at the M06-D3/6-31G(d,p)(SMD, dichloromethane) theoretical level, and the energy profiles were shown in Figure S12. **3aa** coordinated to $Cu(OTf)_2$ in bidentate fashion, forming an intermediate **IM1**. This process was exothermic by 25.5 kcal mol^{-1}. Then, it underwent an open-ring process via transition state **TS1**, generating **I**. Suffering from the steric repulsion from OTf^- anion in the catalyst, the relative Gibbs free energy of intermediate **II** with *cis*-unsaturated imine **II** was slightly higher than that with *trans*-one by 0.8 kcal mol^{-1}. In the following step, the C-O bond in ***E*-IM2** was constructed *via* transition state ***E*-TS2**, with $\Delta G^{\neq}$ of 12.3 kcal mol^{-1}. In contrast, the activation barrier associated with the formation of ***Z*-IM2** *via* ***Z*-TS2** was 14.3 kcal mol^{-1}. In addition, the ***Z*-IM2** was less stable than ***E*-IM2** by 5.0 kcal mol^{-1}. These results indicated that the ***E*-4aa** was predominantly formed in the presence of $Cu(OTf)_2$.

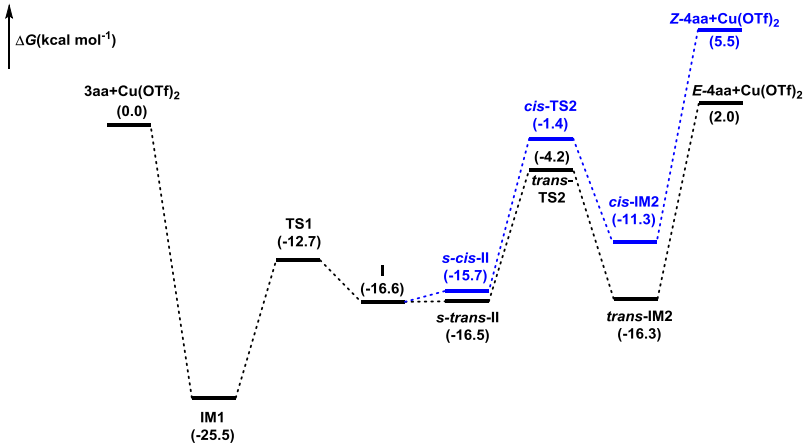
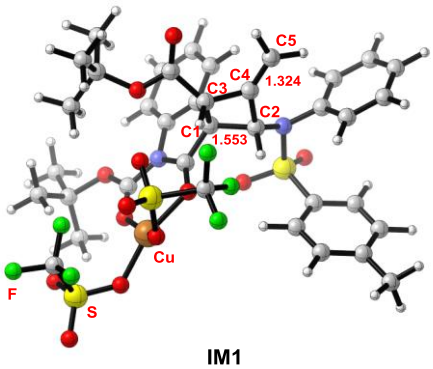
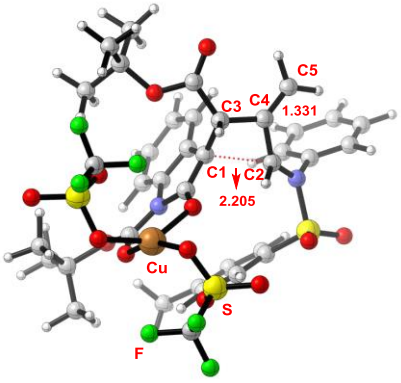


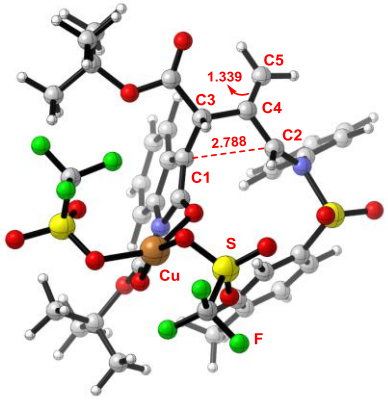
Figure S12 Energy profiles for the isomerization from **3aa** to ***E*-4aa** or ***Z*-4aa** catalyzed by $Cu(OTf)_2$. The relative Gibbs free energies (in kcal mol^{-1}) were obtained at the M06-D3/6-31G(d,p)(SMD, dichloromethane) theoretical level at 303 K.



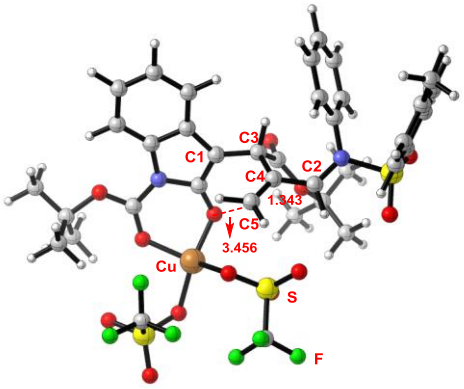
IM1
(-25.5)



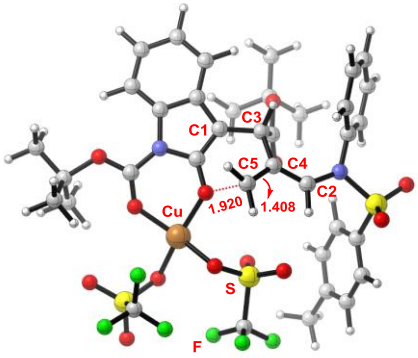
TS1
(-12.7)



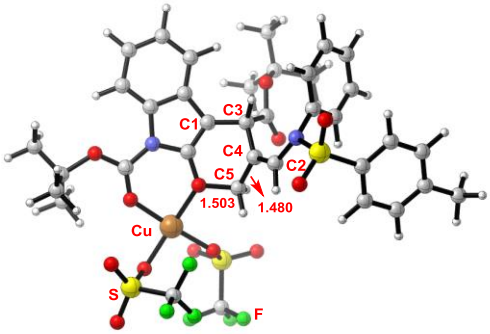
I
(-16.6)



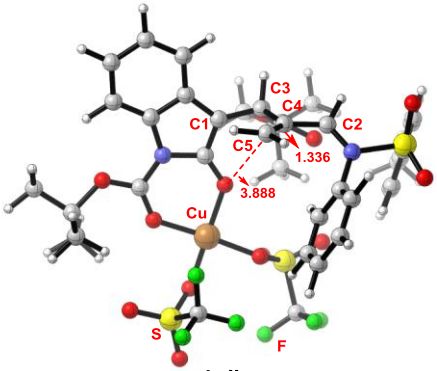
***s-trans*-II**
(-16.5)



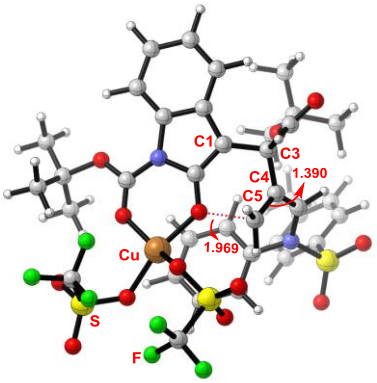
***E*-TS2**
(-4.2)



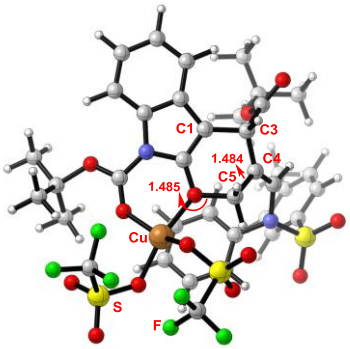
***E*-IM2**
(-16.3)



***s-cis*-II**
(-15.7)



***Z*-TS2**
(-1.4)



***Z*-IM2**
(-11.3)

Figure S13 Optimized geometries of intermediates and transition states in the isomerizations from **3aa** to ***E*-4aa** or ***Z*-4aa** catalyzed by $Cu(OTf)_2$. The relative Gibbs free energies (in kcal mol^{-1}) were obtained at the M06-D3/6-31G(d,p)(SMD, dichloromethane) theoretical level at 303 K.

Cartesian coordinates and the corresponding energies of all stationary points in this work.

3aa (M062X-D3)

Zero-point correction = 0.67791 a.u.
Thermal correction to Gibbs Free Energy = 0.60021 a.u.
Sum of electronic and zero-point Energies = -2389.41999 a.u.
Sum of electronic and thermal Free Energies = -2389.49770 a.u.
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates(Angstroms) X	Y	Z
1	16	0	2.183483	0.488726	1.439518
2	8	0	2.954405	0.123126	2.616243
3	8	0	0.823353	0.999302	1.566235
4	8	0	-2.825618	-1.700250	-1.428472
5	8	0	-1.720724	-3.632091	-1.890919
6	8	0	-0.762965	1.531002	-1.257055
7	8	0	-3.898803	1.557889	1.529626
8	8	0	-2.745372	2.756433	-0.007340
9	7	0	2.057693	-0.912179	0.496997
10	7	0	-1.998702	0.719578	0.572595
11	6	0	3.117907	1.654522	0.488042
12	6	0	2.447141	2.484451	-0.407691
13	6	0	3.193147	3.350818	-1.201520
14	6	0	4.586798	3.396179	-1.106616
15	6	0	5.230991	2.552855	-0.191764
16	6	0	4.508163	1.677168	0.607068
17	6	0	5.391540	4.343911	-1.953603
18	6	0	3.318905	-1.564721	0.243676
19	6	0	3.786965	-2.492604	1.171808
20	6	0	4.990979	-3.150323	0.934604
21	6	0	5.717329	-2.886185	-0.225792
22	6	0	5.246231	-1.952851	-1.147636
23	6	0	4.049928	-1.281558	-0.912033
24	6	0	-4.147014	-2.292550	-1.212030
25	6	0	-4.639769	-2.918015	-2.510732
26	6	0	-4.081489	-3.292453	-0.064350
27	6	0	-4.991125	-1.085690	-0.823494
28	6	0	-1.748579	-2.440766	-1.692183
29	6	0	-0.552991	-1.523824	-1.691789
30	6	0	0.854180	-2.030728	-1.483161
31	6	0	1.159703	-0.793600	-0.647443
32	6	0	-0.366832	-0.686956	-0.383108
33	6	0	-1.017701	0.681325	-0.439068
34	6	0	-2.977794	1.707142	0.756420
35	6	0	-3.694190	3.875737	-0.050242
36	6	0	-5.044780	3.386807	-0.558367

37	6	0	-3.783509	4.533427	1.320999
38	6	0	-3.043202	4.811996	-1.058676
39	6	0	1.431972	-3.196421	-1.735761
40	6	0	-0.936444	-1.309653	0.851380
41	6	0	-0.653613	-2.518667	1.467132
42	6	0	-1.359572	-2.865243	2.623178
43	6	0	-2.327274	-2.006580	3.135831
44	6	0	-2.628049	-0.788569	2.517524
45	6	0	-1.920215	-0.459484	1.369129
46	1	0	1.363068	2.459943	-0.478081
47	1	0	2.682666	4.004887	-1.902425
48	1	0	6.313613	2.586199	-0.106205
49	1	0	5.006571	1.026167	1.318499
50	1	0	6.210390	3.820052	-2.455020
51	1	0	5.838253	5.127887	-1.333615
52	1	0	4.770193	4.823404	-2.712741
53	1	0	3.197911	-2.691645	2.061052
54	1	0	5.357400	-3.876768	1.652715
55	1	0	6.650646	-3.408106	-0.412027
56	1	0	5.811071	-1.741572	-2.049895
57	1	0	3.680230	-0.550009	-1.625753
58	1	0	-4.611872	-2.180717	-3.318658
59	1	0	-5.674321	-3.249851	-2.383657
60	1	0	-4.029750	-3.778277	-2.791431
61	1	0	-3.648552	-2.816453	0.821397
62	1	0	-3.487117	-4.169029	-0.326299
63	1	0	-5.096954	-3.617147	0.181724
64	1	0	-4.970066	-0.332403	-1.616890
65	1	0	-4.612494	-0.634808	0.100020
66	1	0	-6.027644	-1.393069	-0.660505
67	1	0	-0.621843	-0.836107	-2.544587
68	1	0	1.430737	0.039716	-1.317382
69	1	0	-5.527168	2.721416	0.158935
70	1	0	-4.920789	2.862103	-1.510505
71	1	0	-5.694603	4.250427	-0.726193
72	1	0	-4.279995	3.885861	2.044258
73	1	0	-4.351459	5.464136	1.233161
74	1	0	-2.781512	4.777369	1.686384
75	1	0	-2.928092	4.312884	-2.024620
76	1	0	-2.056465	5.126155	-0.707485
77	1	0	-3.666310	5.700033	-1.192902
78	1	0	0.880093	-3.953202	-2.284033
79	1	0	2.435281	-3.436384	-1.402012
80	1	0	0.108332	-3.177351	1.060832
81	1	0	-1.148580	-3.804967	3.122631
82	1	0	-2.868922	-2.280425	4.035692
83	1	0	-3.381243	-0.128423	2.921229

3aa

Zero-point correction = 0.67005 a.u.
Thermal correction to Gibbs Free Energy = 0.59415 a.u.
Sum of electronic and zero-point Energies = -2388.96551 a.u.
Sum of electronic and thermal Free Energies = -2389.04141 a.u.
Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	16	0	2.225451	0.588648	1.437642
2	8	0	2.975361	0.208690	2.624717
3	8	0	0.886715	1.156821	1.547689
4	8	0	-2.833037	-1.693791	-1.448404
5	8	0	-1.673410	-3.601815	-1.881349
6	8	0	-0.832518	1.574722	-1.223934
7	8	0	-3.976860	1.512753	1.545106
8	8	0	-2.791235	2.773856	0.081900

9	7	0	2.053152	-0.823758	0.511194
10	7	0	-2.025938	0.741916	0.626621
11	6	0	3.213632	1.692198	0.472253
12	6	0	2.593771	2.485090	-0.491975
13	6	0	3.383919	3.266924	-1.325073
14	6	0	4.775641	3.270062	-1.204615
15	6	0	5.369091	2.474273	-0.217225
16	6	0	4.600442	1.680891	0.620044
17	6	0	5.625783	4.114661	-2.100052
18	6	0	3.276187	-1.550775	0.300247
19	6	0	3.606266	-2.563873	1.196424
20	6	0	4.763284	-3.307752	0.994553
21	6	0	5.583170	-3.040034	-0.099396
22	6	0	5.252084	-2.022028	-0.990044
23	6	0	4.100052	-1.269491	-0.790441
24	6	0	-4.164555	-2.300284	-1.303124
25	6	0	-4.575741	-2.931768	-2.619379
26	6	0	-4.163260	-3.287706	-0.151556
27	6	0	-5.034656	-1.102392	-0.973486
28	6	0	-1.735259	-2.409658	-1.682865
29	6	0	-0.562445	-1.470260	-1.657656
30	6	0	0.849659	-1.953484	-1.464590
31	6	0	1.143851	-0.723160	-0.623344
32	6	0	-0.381822	-0.632522	-0.348065
33	6	0	-1.054731	0.721670	-0.398664
34	6	0	-3.033760	1.703555	0.807323
35	6	0	-3.769827	3.870551	-0.014772
36	6	0	-5.073654	3.345435	-0.585329
37	6	0	-3.940878	4.530289	1.339761
38	6	0	-3.093680	4.810906	-0.993393
39	6	0	1.445037	-3.102249	-1.752185
40	6	0	-0.936041	-1.272821	0.875701
41	6	0	-0.639672	-2.489356	1.467977
42	6	0	-1.348073	-2.872194	2.607282
43	6	0	-2.333009	-2.040148	3.129301
44	6	0	-2.644767	-0.814381	2.536438
45	6	0	-1.932492	-0.447868	1.403943
46	1	0	1.509638	2.494620	-0.586169
47	1	0	2.911883	3.890237	-2.082142
48	1	0	6.452626	2.478184	-0.110276
49	1	0	5.064073	1.059501	1.382288
50	1	0	6.418123	3.519836	-2.569237
51	1	0	6.122397	4.912089	-1.533387
52	1	0	5.034612	4.584197	-2.892211
53	1	0	2.940361	-2.760125	2.033556
54	1	0	5.021155	-4.104700	1.687609
55	1	0	6.483742	-3.628017	-0.259988
56	1	0	5.891079	-1.811268	-1.844002
57	1	0	3.830572	-0.477214	-1.487777
58	1	0	-4.506810	-2.199267	-3.432411
59	1	0	-5.617010	-3.268239	-2.552339
60	1	0	-3.949156	-3.793561	-2.865703
61	1	0	-3.821479	-2.800782	0.770423
62	1	0	-3.527239	-4.153306	-0.352740
63	1	0	-5.187768	-3.642312	0.012701
64	1	0	-4.975319	-0.350224	-1.768958
65	1	0	-4.717415	-0.642323	-0.029105
66	1	0	-6.079655	-1.414961	-0.869886
67	1	0	-0.644580	-0.772513	-2.505435
68	1	0	1.401316	0.115860	-1.297936
69	1	0	-5.583168	2.671538	0.108806
70	1	0	-4.892037	2.815192	-1.527940
71	1	0	-5.738516	4.191138	-0.795754
72	1	0	-4.447588	3.874761	2.052373

73	1	0	-4.538420	5.441636	1.219964
74	1	0	-2.965620	4.816600	1.750429
75	1	0	-2.909192	4.306293	-1.948538
76	1	0	-2.134075	5.160687	-0.596274
77	1	0	-3.732663	5.681954	-1.175710
78	1	0	0.899528	-3.859563	-2.309188
79	1	0	2.458562	-3.337089	-1.439544
80	1	0	0.133375	-3.130705	1.047352
81	1	0	-1.128101	-3.821875	3.088239
82	1	0	-2.880102	-2.343389	4.018881
83	1	0	-3.416249	-0.172059	2.943151

***E*-4aa (M062X-D3)**

Zero-point correction = 0.68024 a.u.
Thermal correction to Gibbs Free Energy = 0.60063 a.u.
Sum of electronic and zero-point Energies = -2389.42005 a.u.
Sum of electronic and thermal Free Energies = -2389.49966 a.u.
Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	16	0	3.319698	-1.640502	1.878690
2	8	0	3.871276	-0.874669	2.983675
3	8	0	2.633828	-2.902851	2.109369
4	8	0	-2.096707	-1.641106	-0.629611
5	8	0	0.137254	1.344134	-2.174022
6	8	0	-0.139540	2.920525	-0.572996
7	8	0	-6.116222	-0.968579	0.334450
8	8	0	-4.541527	-2.411682	-0.422183
9	7	0	2.178005	-0.634960	1.124352
10	7	0	-3.915813	-0.360656	0.238676
11	6	0	1.231763	-1.286021	0.295763
12	1	0	1.437381	-2.332776	0.089914
13	6	0	0.133936	-0.713017	-0.203448
14	6	0	-0.749761	-1.492729	-1.135473
15	1	0	-0.384945	-2.508756	-1.287886
16	1	0	-0.818114	-0.974708	-2.099068
17	6	0	-0.353768	0.680499	0.107558
18	1	0	0.089007	1.067639	1.029844
19	6	0	-1.850704	0.593017	0.267336
20	6	0	-2.557086	-0.517458	-0.079431
21	6	0	4.594040	-1.885997	0.676178
22	6	0	5.599607	-0.926376	0.548488
23	1	0	5.629724	-0.071047	1.216455
24	6	0	6.559233	-1.096257	-0.439754
25	1	0	7.349117	-0.358524	-0.549547
26	6	0	6.528799	-2.205388	-1.295551
27	6	0	5.510174	-3.149867	-1.139984
28	1	0	5.482049	-4.018495	-1.791133
29	6	0	4.534645	-2.997640	-0.159161
30	1	0	3.752862	-3.739144	-0.030382
31	6	0	7.591812	-2.375585	-2.346469
32	1	0	7.663332	-1.483714	-2.976074
33	1	0	8.571215	-2.524582	-1.881024
34	1	0	7.382839	-3.235311	-2.986180
35	6	0	2.641194	0.690409	0.801630
36	6	0	3.008541	0.997870	-0.509960
37	1	0	2.905914	0.247099	-1.288112
38	6	0	3.492075	2.269200	-0.802379
39	1	0	3.776926	2.512504	-1.821188
40	6	0	3.615928	3.222336	0.208135
41	1	0	3.997923	4.211866	-0.023880
42	6	0	3.242064	2.908171	1.513512
43	1	0	3.329941	3.650908	2.299797
44	6	0	2.751144	1.641065	1.815778

45	1	0	2.454575	1.375208	2.824382
46	6	0	-0.058823	1.669838	-1.024531
47	6	0	-0.276068	4.054839	-1.494090
48	6	0	0.974299	4.218596	-2.348770
49	1	0	1.853097	4.354002	-1.712722
50	1	0	1.130023	3.356606	-2.998250
51	1	0	0.859397	5.112525	-2.969400
52	6	0	-1.531962	3.861016	-2.334968
53	1	0	-1.418186	3.037611	-3.042187
54	1	0	-2.389409	3.660274	-1.684735
55	1	0	-1.733874	4.777450	-2.896979
56	6	0	-0.433679	5.240982	-0.552460
57	1	0	0.415357	5.292905	0.135854
58	1	0	-0.473001	6.168748	-1.129577
59	1	0	-1.356046	5.154143	0.028811
60	6	0	-4.974713	-1.262362	0.060056
61	6	0	-5.473732	-3.509638	-0.702001
62	6	0	-4.543344	-4.596075	-1.223344
63	1	0	-3.805696	-4.864578	-0.462052
64	1	0	-5.122412	-5.486140	-1.481973
65	1	0	-4.014931	-4.249324	-2.115755
66	6	0	-6.464808	-3.082894	-1.777301
67	1	0	-7.144814	-2.311968	-1.413057
68	1	0	-5.930134	-2.706450	-2.654524
69	1	0	-7.054172	-3.952348	-2.082478
70	6	0	-6.155826	-3.951586	0.586248
71	1	0	-5.407220	-4.161663	1.356133
72	1	0	-6.845891	-3.192335	0.955775
73	1	0	-6.716121	-4.871125	0.393419
74	6	0	-2.786437	1.522211	0.848562
75	6	0	-4.062694	0.918168	0.820800
76	6	0	-5.188524	1.561390	1.331480
77	1	0	-6.161831	1.092524	1.307764
78	6	0	-5.010684	2.832028	1.874314
79	1	0	-5.872828	3.354142	2.277066
80	6	0	-3.750659	3.441949	1.915229
81	6	0	-2.631288	2.795377	1.405941
82	1	0	-1.649684	3.257129	1.433325
83	1	0	-3.646955	4.430431	2.352328

***E*-4aa**

Zero-point correction = 0.67244 a.u.
Thermal correction to Gibbs Free Energy = 0.59368 a.u.
Sum of electronic and zero-point Energies = -2388.95952 a.u.
Sum of electronic and thermal Free Energies = -2389.03827 a.u.
Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	16	0	3.274124	1.671496	-1.891287
2	8	0	3.743478	0.885253	-3.020834
3	8	0	2.600178	2.945766	-2.094472
4	8	0	-2.179912	1.648183	0.601318
5	8	0	-0.013250	-1.300908	2.195349
6	8	0	-0.050997	-2.854728	0.542911
7	8	0	-6.163380	0.882599	-0.473011
8	8	0	-4.673175	2.289494	0.496499
9	7	0	2.160598	0.686346	-1.047719
10	7	0	-3.948324	0.334437	-0.318209
11	6	0	1.186850	1.351094	-0.269672
12	1	0	1.375009	2.406526	-0.075467
13	6	0	0.079385	0.773901	0.208038
14	6	0	-0.827818	1.547658	1.107722
15	1	0	-0.490122	2.578279	1.242118
16	1	0	-0.888287	1.056573	2.088861

17	6	0	-0.373064	-0.625812	-0.103417
18	1	0	0.102049	-1.003474	-1.017759
19	6	0	-1.860431	-0.569996	-0.301489
20	6	0	-2.603121	0.519693	0.041960
21	6	0	4.614741	1.885650	-0.760765
22	6	0	5.626100	0.925971	-0.714973
23	1	0	5.628549	0.096755	-1.418643
24	6	0	6.618314	1.047859	0.244543
25	1	0	7.413369	0.305621	0.294170
26	6	0	6.617133	2.111744	1.154288
27	6	0	5.591312	3.058007	1.083274
28	1	0	5.585355	3.892041	1.782572
29	6	0	4.583176	2.951226	0.134233
30	1	0	3.789761	3.692899	0.076906
31	6	0	7.707975	2.232937	2.170118
32	1	0	7.842578	1.295494	2.722193
33	1	0	8.667533	2.456330	1.687262
34	1	0	7.501537	3.030163	2.890393
35	6	0	2.679916	-0.586957	-0.627529
36	6	0	3.104481	-0.759721	0.691235
37	1	0	3.001568	0.059172	1.401752
38	6	0	3.652253	-1.975222	1.080640
39	1	0	3.977748	-2.113975	2.108963
40	6	0	3.794803	-3.006275	0.154004
41	1	0	4.231756	-3.954168	0.460277
42	6	0	3.369796	-2.827800	-1.159622
43	1	0	3.470307	-3.634413	-1.881515
44	6	0	2.806194	-1.619474	-1.554645
45	1	0	2.461027	-1.464107	-2.573257
46	6	0	-0.096514	-1.615018	1.027347
47	6	0	-0.212844	-4.029191	1.418651
48	6	0	0.957749	-4.150952	2.374711
49	1	0	1.897185	-4.221358	1.815276
50	1	0	1.012622	-3.300894	3.059317
51	1	0	0.843923	-5.070015	2.962105
52	6	0	-1.545888	-3.931858	2.138135
53	1	0	-1.559655	-3.114006	2.863722
54	1	0	-2.361556	-3.783529	1.419304
55	1	0	-1.733383	-4.869003	2.675272
56	6	0	-0.215774	-5.185763	0.437214
57	1	0	0.711233	-5.198040	-0.148761
58	1	0	-0.290919	-6.133654	0.982098
59	1	0	-1.065656	-5.117781	-0.252566
60	6	0	-5.046261	1.183364	-0.114720
61	6	0	-5.639486	3.349538	0.829328
62	6	0	-4.753447	4.382357	1.499074
63	1	0	-3.972165	4.726118	0.811552
64	1	0	-5.352033	5.247254	1.805823
65	1	0	-4.270856	3.959650	2.387723
66	6	0	-6.675551	2.814615	1.798617
67	1	0	-7.325020	2.070849	1.329856
68	1	0	-6.187963	2.362953	2.670611
69	1	0	-7.297946	3.645782	2.150252
70	6	0	-6.251122	3.904684	-0.442394
71	1	0	-5.465117	4.210688	-1.142898
72	1	0	-6.900716	3.176137	-0.933865
73	1	0	-6.848652	4.790001	-0.195280
74	6	0	-2.748486	-1.507797	-0.926559
75	6	0	-4.040424	-0.938468	-0.930295
76	6	0	-5.128351	-1.604957	-1.482150
77	1	0	-6.115766	-1.160289	-1.481846
78	6	0	-4.901712	-2.862112	-2.038070
79	1	0	-5.738612	-3.401300	-2.475856
80	6	0	-3.626524	-3.435880	-2.048313

81	6	0	-2.542766	-2.765995	-1.495631
82	1	0	-1.545992	-3.202799	-1.492886
83	1	0	-3.481704	-4.417472	-2.495125

***Z*-4aa (M062X-D3)**

Zero-point correction = 0.67975 a.u.
Thermal correction to Gibbs Free Energy = 0.60107 a.u.
Sum of electronic and zero-point Energies = -2389.41731 a.u.
Sum of electronic and thermal Free Energies = -2389.49599 a.u.
Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	16	0	2.887557	-1.696170	-1.277650
2	8	0	3.605606	-2.944561	-1.483235
3	8	0	1.862241	-1.269873	-2.217464
4	8	0	-1.937069	-1.281745	-0.410054
5	8	0	0.343801	1.952035	-1.429084
6	8	0	-0.093586	3.304038	0.330956
7	8	0	-6.066256	-0.741016	0.035437
8	8	0	-4.372745	-2.096625	-0.617714
9	7	0	2.117658	-1.845534	0.237946
10	7	0	-3.887024	-0.118221	0.325245
11	6	0	1.414955	-0.686833	0.686630
12	1	0	1.916123	-0.084984	1.443738
13	6	0	0.224289	-0.311094	0.217534
14	6	0	-0.566254	-1.067020	-0.814196
15	1	0	-0.157907	-2.060523	-0.985427
16	1	0	-0.570488	-0.505199	-1.754108
17	6	0	-0.375513	0.998362	0.681327
18	1	0	-0.005571	1.260269	1.678938
19	6	0	-1.872278	0.870318	0.687557
20	6	0	-2.496369	-0.220035	0.167307
21	6	0	4.055718	-0.378841	-1.099412
22	6	0	5.365964	-0.675823	-0.725264
23	1	0	5.677880	-1.707898	-0.600414
24	6	0	6.255574	0.372498	-0.529831
25	1	0	7.282132	0.158032	-0.245453
26	6	0	5.852038	1.703226	-0.699468
27	6	0	4.530925	1.966394	-1.074778
28	1	0	4.211367	2.994829	-1.218267
29	6	0	3.620373	0.933107	-1.275092
30	1	0	2.594504	1.136668	-1.572511
31	6	0	6.838227	2.821726	-0.498574
32	1	0	7.342489	2.728747	0.467578
33	1	0	7.611694	2.795139	-1.273061
34	1	0	6.347117	3.795946	-0.542016
35	6	0	2.894002	-2.543776	1.237665
36	6	0	3.806583	-1.869218	2.049985
37	1	0	3.954211	-0.798843	1.937081
38	6	0	4.531078	-2.580729	3.002953
39	1	0	5.240338	-2.058333	3.636947
40	6	0	4.351027	-3.955797	3.136615
41	1	0	4.917592	-4.506708	3.880647
42	6	0	3.442846	-4.623632	2.316922
43	1	0	3.300725	-5.694713	2.418992
44	6	0	2.710482	-3.918565	1.366347
45	1	0	1.996516	-4.416793	0.718621
46	6	0	0.016436	2.126192	-0.275893
47	6	0	0.098820	4.559123	-0.405033
48	6	0	1.532923	4.639674	-0.916619
49	1	0	2.234254	4.471161	-0.093237
50	1	0	1.715644	3.906120	-1.703182
51	1	0	1.713147	5.639945	-1.321001
52	6	0	-0.933279	4.659247	-1.521305

53	1	0	-0.747613	3.925391	-2.306213
54	1	0	-1.937818	4.504225	-1.115232
55	1	0	-0.889500	5.660644	-1.959264
56	6	0	-0.154551	5.619129	0.658318
57	1	0	0.538987	5.495845	1.495072
58	1	0	-0.010695	6.613976	0.228816
59	1	0	-1.179220	5.548216	1.034765
60	6	0	-4.892022	-1.001672	-0.096333
61	6	0	-5.234274	-3.147452	-1.172149
62	6	0	-4.219261	-4.164267	-1.675562
63	1	0	-3.595639	-4.521183	-0.851337
64	1	0	-4.739684	-5.017505	-2.118090
65	1	0	-3.572087	-3.715288	-2.434124
66	6	0	-6.056929	-2.586934	-2.325411
67	1	0	-6.803588	-1.872713	-1.976601
68	1	0	-5.401523	-2.096779	-3.051573
69	1	0	-6.569393	-3.411414	-2.829251
70	6	0	-6.098696	-3.742489	-0.068245
71	1	0	-5.472167	-4.075071	0.764706
72	1	0	-6.829997	-3.021891	0.299627
73	1	0	-6.631084	-4.611951	-0.464573
74	6	0	-2.898528	1.736016	1.213203
75	6	0	-4.142417	1.107509	0.979017
76	6	0	-5.343911	1.684712	1.384105
77	1	0	-6.290262	1.197303	1.199189
78	6	0	-5.278477	2.914058	2.034854
79	1	0	-6.201093	3.385416	2.358276
80	6	0	-4.053912	3.547575	2.281105
81	6	0	-2.858332	2.967164	1.875878
82	1	0	-1.905370	3.452428	2.060347
83	1	0	-4.038843	4.503344	2.795974

***Z*-4aa**

Zero-point correction = 0.67220 a.u.
Thermal correction to Gibbs Free Energy = 0.59441 a.u.
Sum of electronic and zero-point Energies = -2388.95479 a.u.
Sum of electronic and thermal Free Energies = -2389.03258 a.u.
Standard orientation:

Center	**Atomic**	**Atomic**	**Coordinates (Angstroms)**		
Number	Number	Type	X	Y	Z
1	16	0	2.844277	-1.716331	-1.305772
2	8	0	3.533281	-2.978899	-1.528024
3	8	0	1.827389	-1.249853	-2.236334
4	8	0	-2.014042	-1.275233	-0.372799
5	8	0	0.278191	1.935639	-1.441186
6	8	0	0.139585	3.237346	0.409442
7	8	0	-6.132254	-0.564688	-0.072052
8	8	0	-4.467757	-2.040512	-0.513268
9	7	0	2.068157	-1.870880	0.218177
10	7	0	-3.937110	-0.015890	0.270519
11	6	0	1.373437	-0.716454	0.669296
12	1	0	1.890136	-0.091923	1.402518
13	6	0	0.169449	-0.347127	0.225711
14	6	0	-0.636168	-1.110503	-0.774274
15	1	0	-0.252937	-2.121904	-0.917914
16	1	0	-0.626193	-0.584327	-1.737869
17	6	0	-0.398760	0.975357	0.677252
18	1	0	-0.037848	1.216444	1.687316
19	6	0	-1.893095	0.906493	0.649605
20	6	0	-2.547964	-0.179398	0.155034
21	6	0	4.041626	-0.428959	-1.109508
22	6	0	5.341017	-0.756045	-0.722918
23	1	0	5.627619	-1.797107	-0.595796
24	6	0	6.254996	0.266408	-0.520470

25	1	0	7.274923	0.025880	-0.224544
26	6	0	5.891012	1.606048	-0.700877
27	6	0	4.581771	1.901924	-1.089688
28	1	0	4.295177	2.941021	-1.245012
29	6	0	3.646436	0.894960	-1.291531
30	1	0	2.628512	1.128716	-1.601755
31	6	0	6.900440	2.691521	-0.498563
32	1	0	7.401314	2.592017	0.471468
33	1	0	7.683589	2.644563	-1.265581
34	1	0	6.441787	3.683683	-0.549264
35	6	0	2.812367	-2.601592	1.213072
36	6	0	3.709822	-1.962892	2.069398
37	1	0	3.877880	-0.890365	1.988333
38	6	0	4.393539	-2.707083	3.024921
39	1	0	5.091912	-2.210442	3.694109
40	6	0	4.189863	-4.080725	3.119771
41	1	0	4.726333	-4.658605	3.868559
42	6	0	3.298502	-4.714121	2.257606
43	1	0	3.137360	-5.786946	2.329468
44	6	0	2.606462	-3.975784	1.305298
45	1	0	1.902442	-4.447537	0.624142
46	6	0	0.060298	2.090889	-0.258256
47	6	0	0.387773	4.516618	-0.276753
48	6	0	1.759079	4.492067	-0.926798
49	1	0	2.514218	4.170691	-0.198326
50	1	0	1.788836	3.822691	-1.791044
51	1	0	2.019107	5.503445	-1.260901
52	6	0	-0.733696	4.784747	-1.262376
53	1	0	-0.719330	4.078960	-2.097139
54	1	0	-1.706201	4.716705	-0.758558
55	1	0	-0.627156	5.799096	-1.664471
56	6	0	0.352720	5.516978	0.862254
57	1	0	1.125910	5.289719	1.605218
58	1	0	0.529052	6.526957	0.475791
59	1	0	-0.624159	5.506163	1.360659
60	6	0	-4.965986	-0.886181	-0.121484
61	6	0	-5.318922	-3.111680	-1.054309
62	6	0	-4.296374	-4.175565	-1.405695
63	1	0	-3.741057	-4.488220	-0.514065
64	1	0	-4.798934	-5.052367	-1.828570
65	1	0	-3.579902	-3.793303	-2.141974
66	6	0	-6.037372	-2.621413	-2.296610
67	1	0	-6.787894	-1.862636	-2.061454
68	1	0	-5.320300	-2.203455	-3.013017
69	1	0	-6.540800	-3.468810	-2.776520
70	6	0	-6.267797	-3.603644	0.021115
71	1	0	-5.710685	-3.887330	0.921726
72	1	0	-7.009820	-2.845801	0.285379
73	1	0	-6.794596	-4.492366	-0.345585
74	6	0	-2.891229	1.833091	1.106440
75	6	0	-4.154465	1.250266	0.861077
76	6	0	-5.337282	1.899169	1.194065
77	1	0	-6.299524	1.442249	0.995831
78	6	0	-5.238813	3.155192	1.787617
79	1	0	-6.150738	3.685406	2.052168
80	6	0	-3.996727	3.742820	2.046649
81	6	0	-2.817444	3.088895	1.714215
82	1	0	-1.846910	3.538408	1.913957
83	1	0	-3.953131	4.723243	2.516246

$Cu(OTf)_2$

Zero-point correction = 0.06059 a.u.

Thermal correction to Gibbs Free Energy = 0.01228 a.u.

Sum of electronic and zero-point Energies = -3562.62744 a.u.

Sum of electronic and thermal Free Energies = -3562.67575 a.u.
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	0.122689	-0.982900	-0.464843
2	8	0	-1.334604	-0.822734	0.703286
3	16	0	-2.788077	-0.720854	0.233116
4	8	0	-2.960389	-1.240980	-1.117475
5	6	0	-2.942151	1.102959	0.074767
6	9	0	-4.132165	1.407116	-0.415456
7	9	0	-2.792868	1.674327	1.256032
8	8	0	-3.708493	-1.118177	1.280469
9	9	0	-2.002620	1.549491	-0.750300
10	8	0	0.955695	0.748376	0.093988
11	16	0	2.247667	0.445740	-0.621326
12	8	0	1.966501	-0.891569	-1.268320
13	6	0	3.443490	0.056802	0.725530
14	9	0	4.576429	-0.343105	0.186224
15	9	0	3.638797	1.139071	1.448693
16	8	0	2.839411	1.479647	-1.432980
17	9	0	2.936380	-0.903470	1.476837

IM1

Zero-point correction = 0.73514 a.u.
Thermal correction to Gibbs Free Energy = 0.63962 a.u.
Sum of electronic and zero-point Energies = -5951.66221 a.u.
Sum of electronic and thermal Free Energies = -5951.75773 a.u.
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	1.951305	1.288000	-0.599187
2	8	0	3.389927	2.282303	-1.357509
3	16	0	4.879801	2.016374	-1.419432
4	8	0	5.226207	0.771560	-2.093327
5	6	0	5.284291	1.708613	0.348082
6	9	0	6.570247	1.417554	0.463215
7	9	0	5.008401	2.771387	1.079565
8	8	0	5.610136	3.222188	-1.775364
9	9	0	4.572587	0.671623	0.801852
10	8	0	1.962849	2.465836	0.927639
11	16	0	1.780862	1.904210	2.323877
12	8	0	1.572029	0.456158	2.322233
13	6	0	0.153089	2.633860	2.781308
14	9	0	-0.224808	2.159580	3.959904
15	9	0	0.248408	3.950836	2.850056
16	8	0	2.716473	2.469004	3.281130
17	9	0	-0.773504	2.319268	1.880002
18	16	0	-3.391673	-0.050445	-2.040221
19	8	0	-4.357387	-0.697484	-2.912210
20	8	0	-1.956750	-0.247048	-2.243074
21	8	0	0.571414	-2.366429	2.042846
22	8	0	-1.027859	-2.770934	3.612441
23	8	0	0.201907	0.595973	-0.208844
24	8	0	2.269342	-0.297832	-1.680512
25	8	0	2.158176	-2.482178	-2.165735
26	7	0	-3.704600	-0.613874	-0.467121
27	7	0	0.464650	-1.575531	-1.036413
28	6	0	-3.722538	1.682748	-2.003489
29	6	0	-2.732266	2.560671	-1.564428
30	6	0	-3.047717	3.904152	-1.413298
31	6	0	-4.331641	4.379447	-1.696185
32	6	0	-5.303201	3.475780	-2.142414
33	6	0	-5.011720	2.129708	-2.294100
34	6	0	-4.664746	5.830024	-1.551397

35	6	0	-5.070391	-0.481664	-0.037628
36	6	0	-5.944533	-1.536502	-0.285322
37	6	0	-7.264605	-1.446082	0.140777
38	6	0	-7.703179	-0.309054	0.815030
39	6	0	-6.826619	0.746156	1.054978
40	6	0	-5.507634	0.668300	0.622201
41	6	0	1.584416	-3.328055	2.487213
42	6	0	2.039590	-2.971953	3.888367
43	6	0	1.021400	-4.731511	2.383346
44	6	0	2.699297	-3.104962	1.480325
45	6	0	-0.590497	-2.173582	2.656297
46	6	0	-1.272508	-1.036243	1.948345
47	6	0	-2.762531	-0.823135	1.934777
48	6	0	-2.661118	-0.325011	0.500760
49	6	0	-1.345561	-1.143977	0.387573
50	6	0	-0.165775	-0.575218	-0.323385
51	6	0	1.699667	-1.394578	-1.652323
52	6	0	3.536829	-2.604609	-2.778743
53	6	0	3.660475	-1.632623	-3.929994
54	6	0	4.553558	-2.392943	-1.680841
55	6	0	3.521297	-4.039722	-3.254791
56	6	0	-3.718890	-1.142982	2.793270
57	6	0	-1.419838	-2.537701	-0.136078
58	6	0	-2.342102	-3.539280	0.116760
59	6	0	-2.148719	-4.789775	-0.467347
60	6	0	-1.047797	-5.021533	-1.284437
61	6	0	-0.107357	-4.022419	-1.542726
62	6	0	-0.317514	-2.786587	-0.953680
63	1	0	-1.726972	2.202901	-1.352991
64	1	0	-2.283856	4.600427	-1.072240
65	1	0	-6.304516	3.837734	-2.369659
66	1	0	-5.769930	1.428078	-2.633301
67	1	0	-5.614453	5.968428	-1.022322
68	1	0	-4.777517	6.302856	-2.535292
69	1	0	-3.883422	6.371490	-1.009620
70	1	0	-5.570085	-2.416025	-0.804461
71	1	0	-7.950200	-2.268723	-0.045810
72	1	0	-8.733925	-0.244872	1.155230
73	1	0	-7.169818	1.634640	1.579025
74	1	0	-4.815160	1.488779	0.807960
75	1	0	2.382291	-1.931511	3.923995
76	1	0	2.878526	-3.618198	4.171455
77	1	0	1.238126	-3.106333	4.619605
78	1	0	0.634423	-4.912986	1.372036
79	1	0	0.215067	-4.895843	3.103507
80	1	0	1.817262	-5.459517	2.579362
81	1	0	2.997823	-2.046537	1.469758
82	1	0	2.372604	-3.395222	0.472061
83	1	0	3.573643	-3.711203	1.743263
84	1	0	-0.728191	-0.114973	2.207619
85	1	0	-2.384303	0.745186	0.523097
86	1	0	3.756343	-0.598453	-3.592247
87	1	0	2.805116	-1.725528	-4.609092
88	1	0	4.564407	-1.890314	-4.493725
89	1	0	4.502656	-1.385975	-1.259857
90	1	0	5.553498	-2.516049	-2.112777
91	1	0	4.431100	-3.139589	-0.887926
92	1	0	2.755565	-4.193428	-4.023618
93	1	0	3.336846	-4.726222	-2.419920
94	1	0	4.497223	-4.281714	-3.688678
95	1	0	-3.449120	-1.574762	3.753687
96	1	0	-4.775243	-1.005169	2.579716
97	1	0	-3.197479	-3.349656	0.761105
98	1	0	-2.864937	-5.585882	-0.283376

99	1	0	-0.907545	-5.998902	-1.738654
100	1	0	0.740935	-4.223023	-2.183225

TS1

Zero-point correction = 0.73356 a.u.
Thermal correction to Gibbs Free Energy = 0.63737 a.u.
Sum of electronic and zero-point Energies = -5951.64114 a.u.
Sum of electronic and thermal Free Energies = -5951.73733 a.u.
Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	16	0	-3.062571	-2.951744	-1.011661
2	8	0	-1.932202	-3.276296	-1.861427
3	8	0	-4.310769	-3.685172	-1.072335
4	8	0	-0.608272	3.449965	-1.042924
5	8	0	-1.854096	3.705268	-2.924972
6	8	0	0.547793	-0.369188	-0.762565
7	8	0	1.856582	-0.388552	1.640535
8	8	0	0.669275	0.407630	3.353670
9	7	0	-3.517084	-1.293419	-1.464964
10	7	0	-0.274301	0.419454	1.323413
11	6	0	-2.530132	-2.769249	0.653152
12	6	0	-3.490377	-2.561640	1.644146
13	6	0	-3.061696	-2.379031	2.948668
14	6	0	-1.701473	-2.430206	3.274840
15	6	0	-0.769904	-2.683883	2.260852
16	6	0	-1.168774	-2.840719	0.940975
17	6	0	-1.253174	-2.190025	4.679110
18	6	0	-4.874814	-0.886924	-1.219052
19	6	0	-5.174690	-0.155794	-0.074413
20	6	0	-6.485113	0.256066	0.140287
21	6	0	-7.480311	-0.084155	-0.770989
22	6	0	-7.171352	-0.840952	-1.899415
23	6	0	-5.864074	-1.250277	-2.129066
24	6	0	-0.303026	4.861753	-0.777214
25	6	0	0.712052	5.326985	-1.801314
26	6	0	-1.568311	5.699709	-0.777112
27	6	0	0.293458	4.804106	0.617581
28	6	0	-1.352587	3.028403	-2.053823
29	6	0	-1.445200	1.517525	-1.991834
30	6	0	-2.675467	0.829892	-2.516054
31	6	0	-2.531839	-0.478369	-1.855857
32	6	0	-1.423659	0.950924	-0.595350
33	6	0	-0.289464	0.280504	-0.089082
34	6	0	0.820813	0.114077	2.099026
35	6	0	1.833123	0.476410	4.308982
36	6	0	2.354884	-0.918575	4.570308
37	6	0	2.884675	1.409235	3.743913
38	6	0	1.180047	1.071390	5.538190
39	6	0	-3.693024	1.281358	-3.245919
40	6	0	-2.106857	1.538256	0.539800
41	6	0	-3.219413	2.371386	0.616247
42	6	0	-3.672727	2.773250	1.869128
43	6	0	-3.022352	2.348572	3.027451
44	6	0	-1.883652	1.543852	2.969091
45	6	0	-1.428145	1.171380	1.713437
46	1	0	-4.549874	-2.548325	1.400252
47	1	0	-3.793318	-2.207746	3.735375
48	1	0	0.288877	-2.767017	2.509057
49	1	0	-0.432985	-3.026642	0.160453
50	1	0	-0.872818	-1.162810	4.779323
51	1	0	-0.440249	-2.867557	4.962686
52	1	0	-2.073921	-2.310398	5.392451
53	1	0	-4.386173	0.084253	0.634011

54	1	0	-6.723840	0.841926	1.024771
55	1	0	-8.504331	0.238493	-0.600381
56	1	0	-7.951099	-1.111138	-2.606410
57	1	0	-5.598522	-1.835115	-3.006651
58	1	0	1.606386	4.693675	-1.769293
59	1	0	1.013968	6.357297	-1.579455
60	1	0	0.296999	5.301710	-2.814322
61	1	0	-2.322745	5.248298	-0.120310
62	1	0	-1.993623	5.812131	-1.777067
63	1	0	-1.330861	6.694409	-0.381738
64	1	0	1.141054	4.108505	0.648510
65	1	0	-0.461243	4.466774	1.340474
66	1	0	0.639420	5.799422	0.919228
67	1	0	-0.554523	1.141997	-2.524412
68	1	0	-1.573615	-0.981184	-2.015831
69	1	0	2.797758	-1.366429	3.677206
70	1	0	1.562418	-1.573157	4.948864
71	1	0	3.133085	-0.854263	5.339803
72	1	0	3.470774	0.941844	2.948895
73	1	0	3.574016	1.676905	4.552173
74	1	0	2.428675	2.333883	3.370121
75	1	0	0.367348	0.433223	5.904356
76	1	0	0.780836	2.069407	5.324437
77	1	0	1.926799	1.162088	6.333822
78	1	0	-3.646092	2.278282	-3.673773
79	1	0	-4.574789	0.678270	-3.441879
80	1	0	-3.728860	2.685901	-0.294257
81	1	0	-4.544843	3.418338	1.944273
82	1	0	-3.395251	2.658294	4.000292
83	1	0	-1.379234	1.238439	3.878038
84	29	0	2.349449	-0.629199	-0.189628
85	8	0	4.063015	0.291131	0.016245
86	16	0	3.823049	1.786993	-0.021526
87	8	0	2.395965	2.099066	0.124870
88	6	0	4.176842	2.164531	-1.781715
89	9	0	4.003691	3.460356	-2.003095
90	9	0	5.420985	1.835094	-2.084156
91	8	0	4.788951	2.545085	0.754681
92	9	0	3.343037	1.477805	-2.553046
93	8	0	2.857704	-1.561127	-1.826794
94	16	0	2.495126	-3.006178	-1.553893
95	8	0	1.849751	-3.095691	-0.232437
96	6	0	4.148041	-3.760564	-1.294700
97	9	0	4.003917	-5.027996	-0.941247
98	9	0	4.860231	-3.692625	-2.406048
99	8	0	1.903850	-3.706666	-2.677584
100	9	0	4.782147	-3.109460	-0.328527

I

Zero-point correction = 0.73455 a.u.
Thermal correction to Gibbs Free Energy = 0.63803 a.u.
Sum of electronic and zero-point Energies = -5951.64704 a.u.
Sum of electronic and thermal Free Energies = -5951.74357 a.u.
Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	16	0	-3.223452	-2.584220	-1.880404
2	8	0	-2.008704	-2.744702	-2.652819
3	8	0	-4.497817	-3.123132	-2.301340
4	8	0	-0.009221	3.812658	-1.051080
5	8	0	-1.275056	4.062075	-2.912989
6	8	0	0.489539	-0.394037	-0.666603
7	8	0	1.556240	-0.949993	1.771190
8	8	0	0.298955	-0.324606	3.510777

9	7	0	-3.502994	-0.764264	-1.885389
10	7	0	-0.340999	0.303879	1.462429
11	6	0	-2.944274	-2.818106	-0.173801
12	6	0	-4.037845	-2.974901	0.677835
13	6	0	-3.803493	-2.993077	2.044351
14	6	0	-2.508836	-2.865169	2.557063
15	6	0	-1.433220	-2.748623	1.665846
16	6	0	-1.636194	-2.699411	0.297929
17	6	0	-2.267405	-2.853119	4.030792
18	6	0	-4.715589	-0.321014	-1.251360
19	6	0	-4.635888	0.136316	0.063062
20	6	0	-5.808779	0.499031	0.711789
21	6	0	-7.031358	0.389705	0.054185
22	6	0	-7.091770	-0.079687	-1.255842
23	6	0	-5.928147	-0.446120	-1.921116
24	6	0	0.506576	5.186346	-0.974021
25	6	0	1.398537	5.447347	-2.171796
26	6	0	-0.638967	6.175146	-0.864048
27	6	0	1.305042	5.153466	0.314620
28	6	0	-0.838749	3.400953	-1.994739
29	6	0	-1.126425	1.919010	-1.803911
30	6	0	-2.463809	1.436854	-2.319509
31	6	0	-2.502361	-0.012891	-2.237618
32	6	0	-1.017253	1.450386	-0.386168
33	6	0	-0.211529	0.421359	0.032429
34	6	0	0.569425	-0.356119	2.236974
35	6	0	1.303990	-0.717785	4.550777
36	6	0	1.521546	-2.214629	4.506684
37	6	0	2.578762	0.075247	4.345903
38	6	0	0.601212	-0.298056	5.824773
39	6	0	-3.512614	2.153381	-2.743582
40	6	0	-1.726406	1.962615	0.752622
41	6	0	-2.690933	2.962223	0.876858
42	6	0	-3.254661	3.200423	2.126610
43	6	0	-2.866690	2.452522	3.238514
44	6	0	-1.890172	1.458628	3.138292
45	6	0	-1.322067	1.237842	1.893790
46	1	0	-5.046475	-3.067073	0.281917
47	1	0	-4.640691	-3.100713	2.730222
48	1	0	-0.415431	-2.702801	2.052549
49	1	0	-0.797778	-2.572699	-0.385928
50	1	0	-1.741636	-1.935455	4.328870
51	1	0	-1.635296	-3.698018	4.331346
52	1	0	-3.203099	-2.910327	4.593908
53	1	0	-3.667973	0.192533	0.562527
54	1	0	-5.763274	0.860749	1.735728
55	1	0	-7.946713	0.669337	0.569546
56	1	0	-8.048981	-0.164261	-1.762846
57	1	0	-5.948476	-0.821290	-2.940785
58	1	0	2.182798	4.683837	-2.236200
59	1	0	1.883087	6.424311	-2.059268
60	1	0	0.827147	5.449429	-3.104779
61	1	0	-1.296312	5.905763	-0.028369
62	1	0	-1.230338	6.229600	-1.781044
63	1	0	-0.227268	7.170519	-0.659099
64	1	0	2.093544	4.394765	0.264130
65	1	0	0.652544	4.909964	1.162397
66	1	0	1.766604	6.130500	0.496153
67	1	0	-0.331345	1.408205	-2.375032
68	1	0	-1.585279	-0.552597	-2.503691
69	1	0	1.986010	-2.535572	3.570878
70	1	0	0.577493	-2.752915	4.647392
71	1	0	2.190521	-2.490364	5.330039
72	1	0	3.164081	-0.287408	3.496906

73	1	0	3.193270	-0.023435	5.247697
74	1	0	2.356848	1.138765	4.200331
75	1	0	-0.368862	-0.800786	5.922430
76	1	0	0.442287	0.786111	5.845005
77	1	0	1.217435	-0.572220	6.687654
78	1	0	-3.428341	3.227373	-2.878105
79	1	0	-4.450902	1.677846	-3.016959
80	1	0	-3.009452	3.528761	0.002857
81	1	0	-4.014522	3.970879	2.235575
82	1	0	-3.326459	2.641484	4.205357
83	1	0	-1.595602	0.886295	4.010190
84	29	0	2.208758	-0.788241	-0.029289
85	8	0	3.986328	-0.162631	0.523274
86	16	0	3.933542	1.318353	0.824310
87	8	0	2.578904	1.757211	1.173159
88	6	0	4.204262	2.033976	-0.847862
89	9	0	4.327344	3.352253	-0.761589
90	9	0	5.298784	1.534426	-1.397429
91	8	0	5.048427	1.776163	1.636456
92	9	0	3.161672	1.753118	-1.625103
93	8	0	2.826210	-1.355124	-1.797700
94	16	0	2.391552	-2.790536	-1.991364
95	8	0	1.640439	-3.263075	-0.820276
96	6	0	4.002905	-3.661931	-1.873230
97	9	0	3.806029	-4.971080	-1.930288
98	9	0	4.798315	-3.297875	-2.866374
99	8	0	1.877944	-3.083796	-3.318510
100	9	0	4.585198	-3.362384	-0.718876

***s-trans*-II**

Zero-point correction = 0.73433 a.u.

Thermal correction to Gibbs Free Energy = 0.63634 a.u.

Sum of electronic and zero-point Energies = -5951.64545 a.u.

Sum of electronic and thermal Free Energies = -5951.74344 a.u.

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	16	0	-5.116358	-1.504857	0.457586
2	8	0	-5.661903	-1.221083	1.768764
3	8	0	-4.379407	-2.720831	0.176534
4	8	0	1.393761	0.561159	1.242130
5	8	0	-1.279102	1.922748	2.899106
6	8	0	-1.637569	-0.179883	2.133885
7	8	0	3.943421	1.064316	0.530095
8	8	0	4.331318	3.233487	0.081539
9	7	0	-3.898519	-0.186619	0.187685
10	7	0	2.218623	2.537136	0.187189
11	6	0	-2.697115	-0.521064	-0.201485
12	6	0	-1.583014	0.372082	-0.406793
13	6	0	-0.760292	0.002687	-1.402285
14	6	0	-1.336427	1.547364	0.524865
15	6	0	-0.030793	2.218657	0.269159
16	6	0	1.170826	1.649448	0.598793
17	6	0	-6.263840	-1.124760	-0.804794
18	6	0	-7.374534	-0.343137	-0.496934
19	6	0	-8.212715	0.040985	-1.533446
20	6	0	-7.947762	-0.335227	-2.853026
21	6	0	-6.818660	-1.121837	-3.125042
22	6	0	-5.968121	-1.522345	-2.110901
23	6	0	-8.847533	0.086894	-3.968144
24	6	0	-4.378687	1.166834	0.292985
25	6	0	-4.562658	1.880161	-0.890753
26	6	0	-5.002988	3.194504	-0.816615
27	6	0	-5.255971	3.775824	0.424211

28	6	0	-5.084292	3.042999	1.595164
29	6	0	-4.650872	1.723295	1.539261
30	6	0	-1.404577	1.122078	2.001931
31	6	0	-1.699055	-0.852771	3.446834
32	6	0	-2.846865	-0.290702	4.263315
33	6	0	-0.350693	-0.717337	4.125586
34	6	0	-1.974497	-2.295522	3.074051
35	6	0	3.547635	2.211794	0.278567
36	6	0	5.813530	3.118090	-0.058019
37	6	0	6.215320	4.565905	-0.248908
38	6	0	6.412025	2.544776	1.209472
39	6	0	6.115229	2.294059	-1.290064
40	6	0	0.223165	3.482912	-0.354927
41	6	0	1.622971	3.684268	-0.396400
42	6	0	2.182892	4.818446	-0.964704
43	6	0	1.315290	5.773000	-1.494992
44	6	0	-0.069453	5.592624	-1.459779
45	6	0	-0.624944	4.451893	-0.893474
46	1	0	-2.527693	-1.586150	-0.391201
47	1	0	-0.928393	-0.912882	-1.962422
48	1	0	0.078469	0.626437	-1.700665
49	1	0	-2.127954	2.304148	0.419976
50	1	0	-7.571684	-0.038962	0.527817
51	1	0	-9.087577	0.649510	-1.316066
52	1	0	-6.610523	-1.419385	-4.150855
53	1	0	-5.090614	-2.128520	-2.325660
54	1	0	-9.328892	-0.783407	-4.430756
55	1	0	-8.281446	0.592147	-4.759434
56	1	0	-9.632768	0.763663	-3.619275
57	1	0	-4.353085	1.405626	-1.847739
58	1	0	-5.147323	3.765181	-1.729863
59	1	0	-5.592584	4.807793	0.477841
60	1	0	-5.281459	3.500005	2.560850
61	1	0	-4.503324	1.144619	2.447611
62	1	0	-3.798447	-0.439787	3.734796
63	1	0	-2.713279	0.770394	4.488707
64	1	0	-2.909063	-0.840124	5.210234
65	1	0	-0.132327	0.321568	4.387466
66	1	0	0.436908	-1.095431	3.462583
67	1	0	-0.347883	-1.316989	5.043532
68	1	0	-2.920614	-2.387704	2.523916
69	1	0	-2.055028	-2.900092	3.984597
70	1	0	-1.167412	-2.696643	2.454009
71	1	0	5.749079	4.987498	-1.147362
72	1	0	7.302353	4.628849	-0.366428
73	1	0	5.925089	5.171091	0.617444
74	1	0	6.199833	1.478782	1.321279
75	1	0	6.043422	3.084961	2.089548
76	1	0	7.499508	2.675028	1.166465
77	1	0	5.602632	2.709180	-2.166081
78	1	0	5.834169	1.247214	-1.154357
79	1	0	7.194454	2.328019	-1.479123
80	1	0	3.256078	4.970224	-0.990117
81	1	0	1.731800	6.674517	-1.937688
82	1	0	-1.704486	4.307730	-0.866807
83	1	0	-0.720892	6.355806	-1.879865
84	29	0	2.758687	-0.525115	0.590059
85	8	0	4.151557	-1.852472	0.543902
86	16	0	5.375906	-1.936421	-0.333632
87	8	0	6.323126	-0.844726	-0.139977
88	6	0	4.633646	-1.624543	-1.987501
89	9	0	5.581393	-1.560886	-2.910384
90	9	0	3.777535	-2.581029	-2.304689
91	8	0	5.905862	-3.289761	-0.402408

92	9	0	3.976507	-0.458773	-1.976195
93	8	0	1.516792	-1.640509	-0.458010
94	16	0	0.783119	-2.749211	0.251755
95	8	0	1.133601	-2.836008	1.667561
96	6	0	1.520605	-4.243718	-0.523932
97	9	0	0.973938	-5.328697	0.012173
98	9	0	1.274412	-4.241419	-1.828656
99	8	0	-0.628633	-2.831655	-0.114977
100	9	0	2.826478	-4.277122	-0.329683

***E*-TS2**

Zero-point correction = 0.73611 a.u.
Thermal correction to Gibbs Free Energy = 0.64350 a.u.
Sum of electronic and zero-point Energies = -5951.63131 a.u.
Sum of electronic and thermal Free Energies = -5951.72392 a.u.
Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	16	0	-4.409864	2.716979	0.974285
2	8	0	-4.072548	3.373160	2.227990
3	8	0	-5.796609	2.611346	0.557123
4	8	0	0.690519	-0.703893	0.911808
5	8	0	-2.326091	-0.624471	-1.231822
6	8	0	-3.371808	-2.590404	-0.800822
7	8	0	3.057626	-1.626819	0.044461
8	8	0	3.271049	-3.852868	0.041728
9	7	0	-3.854962	1.050062	1.078254
10	7	0	1.247032	-2.983286	0.407265
11	6	0	-2.560197	0.888467	1.439399
12	6	0	-1.833154	-0.274417	1.545211
13	6	0	-0.599659	-0.115634	2.206011
14	6	0	-2.175337	-1.631821	0.971192
15	6	0	-0.932501	-2.469403	0.821075
16	6	0	0.318503	-1.946581	0.679495
17	6	0	-3.373249	3.338339	-0.305648
18	6	0	-3.139998	2.567113	-1.444111
19	6	0	-2.319366	3.080572	-2.431487
20	6	0	-1.737208	4.347827	-2.299796
21	6	0	-2.010928	5.102355	-1.157601
22	6	0	-2.820965	4.603817	-0.146975
23	6	0	-0.798374	4.849831	-3.349029
24	6	0	-4.831305	-0.001782	1.081172
25	6	0	-5.017501	-0.736217	2.252153
26	6	0	-5.945735	-1.770190	2.267746
27	6	0	-6.707992	-2.040568	1.134513
28	6	0	-6.539326	-1.278027	-0.017831
29	6	0	-5.594555	-0.260196	-0.054251
30	6	0	-2.658542	-1.515678	-0.480839
31	6	0	-3.570787	-2.990124	-2.206635
32	6	0	-2.214018	-3.272350	-2.826958
33	6	0	-4.349442	-1.940299	-2.977598
34	6	0	-4.383637	-4.263131	-2.077994
35	6	0	2.575466	-2.765208	0.153394
36	6	0	4.735229	-3.848280	-0.300259
37	6	0	5.032858	-5.331658	-0.354802
38	6	0	4.928316	-3.198423	-1.653747
39	6	0	5.501638	-3.173400	0.817257
40	6	0	-0.826827	-3.893132	0.634080
41	6	0	0.522021	-4.205255	0.366799
42	6	0	0.938115	-5.501117	0.093572
43	6	0	-0.027818	-6.503815	0.117802
44	6	0	-1.365029	-6.217574	0.404991
45	6	0	-1.775694	-4.915861	0.662927
46	1	0	-2.044651	1.815950	1.701566

47	1	0	-0.244011	0.887934	2.437860
48	1	0	-0.231605	-0.901727	2.861815
49	1	0	-2.934825	-2.176502	1.550054
50	1	0	-3.550704	1.563773	-1.533865
51	1	0	-2.094259	2.477657	-3.309473
52	1	0	-1.553180	6.082945	-1.043064
53	1	0	-3.001943	5.175164	0.759392
54	1	0	0.063997	4.177652	-3.444974
55	1	0	-0.424354	5.850469	-3.111575
56	1	0	-1.281649	4.887427	-4.332613
57	1	0	-4.426219	-0.499627	3.134431
58	1	0	-6.083245	-2.354255	3.173930
59	1	0	-7.440877	-2.843381	1.151760
60	1	0	-7.141005	-1.483839	-0.900187
61	1	0	-5.446018	0.330505	-0.955022
62	1	0	-1.689681	-4.062165	-2.274085
63	1	0	-1.585106	-2.376540	-2.852489
64	1	0	-2.353132	-3.618071	-3.858033
65	1	0	-3.777814	-1.018545	-3.109355
66	1	0	-5.290441	-1.708177	-2.466555
67	1	0	-4.594951	-2.342329	-3.967763
68	1	0	-3.833567	-5.021857	-1.508915
69	1	0	-4.600743	-4.668804	-3.072492
70	1	0	-5.334420	-4.064969	-1.568344
71	1	0	4.807149	-5.812974	0.603657
72	1	0	6.096190	-5.478291	-0.572091
73	1	0	4.451003	-5.820599	-1.144715
74	1	0	4.778792	-2.116025	-1.623842
75	1	0	4.257263	-3.649128	-2.394289
76	1	0	5.959186	-3.384126	-1.977002
77	1	0	5.255708	-3.629443	1.783180
78	1	0	5.319687	-2.096464	0.857003
79	1	0	6.572366	-3.323446	0.636489
80	1	0	1.973730	-5.734557	-0.123270
81	1	0	0.272633	-7.528180	-0.087540
82	1	0	-2.819400	-4.685508	0.864252
83	1	0	-2.095406	-7.023454	0.421573
84	29	0	2.255999	0.107417	0.192703
85	8	0	3.558923	0.960494	-0.936562
86	16	0	5.038891	1.133174	-0.673388
87	8	0	5.786703	-0.118744	-0.654548
88	6	0	5.027516	1.664674	1.084068
89	9	0	6.265025	1.735956	1.544906
90	9	0	4.441447	2.839413	1.225595
91	8	0	5.590331	2.252640	-1.419655
92	9	0	4.356285	0.756776	1.806132
93	8	0	1.757023	1.760360	1.051538
94	16	0	0.786183	2.641160	0.288986
95	8	0	0.433785	2.070138	-1.006946
96	6	0	1.838821	4.104145	-0.071039
97	9	0	1.119634	5.020232	-0.706231
98	9	0	2.288281	4.620222	1.063171
99	8	0	-0.278799	3.145832	1.150585
100	9	0	2.862312	3.755602	-0.829921

***E*-IM2**

Zero-point correction = 0.73379 a.u.
Thermal correction to Gibbs Free Energy = 0.63114 a.u.
Sum of electronic and zero-point Energies = -5951.64052 a.u.
Sum of electronic and thermal Free Energies = -5951.74317 a.u.
Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	16	0	-4.191636	-1.491400	-2.819622

2	8	0	-5.090868	-0.743230	-3.681304
3	8	0	-3.076399	-2.245968	-3.372017
4	8	0	0.968796	0.353280	-0.244637
5	8	0	-2.121677	0.888341	2.261734
6	8	0	-2.874299	2.899027	1.527852
7	8	0	3.503318	1.140495	-0.637052
8	8	0	3.802238	3.319140	-1.023880
9	7	0	-3.486860	-0.335710	-1.754880
10	7	0	1.762507	2.619516	-0.451301
11	6	0	-2.230659	-0.641461	-1.229016
12	1	0	-1.836712	-1.608928	-1.535614
13	6	0	-1.486589	0.137303	-0.428053
14	6	0	-0.248498	-0.437324	0.144683
15	1	0	-0.036703	-1.447352	-0.207402
16	1	0	-0.260343	-0.415905	1.240807
17	6	0	-1.769604	1.561662	-0.038633
18	1	0	-2.491529	2.030529	-0.717645
19	6	0	-0.471674	2.303850	-0.147270
20	6	0	0.727183	1.687727	-0.248528
21	6	0	-5.144270	-2.522842	-1.749699
22	6	0	-6.483644	-2.213212	-1.518071
23	1	0	-6.961574	-1.401516	-2.061445
24	6	0	-7.184479	-2.950925	-0.577043
25	1	0	-8.231079	-2.720956	-0.384639
26	6	0	-6.566560	-3.982715	0.138732
27	6	0	-5.223290	-4.271936	-0.118801
28	1	0	-4.735955	-5.077746	0.426507
29	6	0	-4.502607	-3.547425	-1.058021
30	1	0	-3.458183	-3.778701	-1.253902
31	6	0	-7.341677	-4.757851	1.156509
32	1	0	-7.766792	-4.092748	1.917701
33	1	0	-8.183527	-5.284713	0.691115
34	1	0	-6.716219	-5.499485	1.662306
35	6	0	-4.433179	0.457049	-1.015723
36	6	0	-4.791542	0.071059	0.276857
37	1	0	-4.332754	-0.808903	0.725479
38	6	0	-5.737750	0.814148	0.971518
39	1	0	-6.024597	0.512418	1.976075
40	6	0	-6.320436	1.932627	0.380069
41	1	0	-7.060381	2.511794	0.928408
42	6	0	-5.955541	2.312494	-0.908836
43	1	0	-6.407274	3.187367	-1.369421
44	6	0	-5.013042	1.572497	-1.614737
45	1	0	-4.715661	1.848901	-2.622917
46	6	0	-2.292003	1.713181	1.391621
47	6	0	-3.162959	3.476479	2.854643
48	6	0	-4.203886	2.650552	3.584364
49	1	0	-5.131902	2.602093	3.002829
50	1	0	-3.851585	1.634863	3.781313
51	1	0	-4.429541	3.133364	4.542648
52	6	0	-1.864248	3.597707	3.628906
53	1	0	-1.467810	2.620340	3.917830
54	1	0	-1.111504	4.125936	3.030043
55	1	0	-2.041529	4.179577	4.540766
56	6	0	-3.716822	4.844997	2.509593
57	1	0	-4.585572	4.751382	1.846830
58	1	0	-4.032422	5.359391	3.424141
59	1	0	-2.960158	5.462259	2.010815
60	6	0	3.073343	2.303260	-0.701795
61	6	0	5.260175	3.194751	-1.390495
62	6	0	5.646138	4.647012	-1.568288
63	1	0	5.536472	5.200384	-0.628621
64	1	0	6.693980	4.703745	-1.880951
65	1	0	5.029993	5.124159	-2.338718

66	6	0	5.353573	2.426275	-2.689133
67	1	0	5.065604	1.376878	-2.572854
68	1	0	4.732828	2.895471	-3.460795
69	1	0	6.394833	2.453986	-3.030179
70	6	0	6.026084	2.557358	-0.251380
71	1	0	5.788329	3.048056	0.699580
72	1	0	5.835443	1.484689	-0.164822
73	1	0	7.095942	2.698335	-0.442078
74	6	0	-0.225537	3.718447	-0.273806
75	6	0	1.156310	3.909630	-0.456890
76	6	0	1.709732	5.176544	-0.592796
77	1	0	2.773668	5.329621	-0.724390
78	6	0	0.837165	6.260257	-0.557316
79	1	0	1.244635	7.262469	-0.662043
80	6	0	-0.540041	6.086668	-0.395831
81	6	0	-1.083515	4.817727	-0.251749
82	1	0	-2.152059	4.669796	-0.115159
83	1	0	-1.193062	6.955994	-0.379993
84	29	0	2.787438	-0.381042	0.243623
85	8	0	4.476054	-1.290929	0.141553
86	16	0	4.921050	-1.926086	-1.161127
87	8	0	4.892819	-1.006709	-2.291761
88	6	0	3.529872	-3.081120	-1.504363
89	9	0	3.728029	-3.692151	-2.659462
90	9	0	3.409228	-3.982762	-0.547606
91	8	0	6.088352	-2.769356	-0.967039
92	9	0	2.386767	-2.384509	-1.583796
93	8	0	1.989700	-1.838205	1.163222
94	16	0	2.220177	-2.027857	2.656543
95	8	0	3.145792	-1.037535	3.196546
96	6	0	3.125579	-3.627487	2.679633
97	9	0	3.322206	-3.982701	3.941990
98	9	0	2.403633	-4.558652	2.074480
99	8	0	0.974897	-2.289039	3.360724
100	9	0	4.293428	-3.516340	2.074088

***s-cis*-II**

Zero-point correction = 0.73586 a.u.
Thermal correction to Gibbs Free Energy = 0.64278 a.u.
Sum of electronic and zero-point Energies = -5951.64912 a.u.
Sum of electronic and thermal Free Energies = -5951.74221 a.u.
Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	8	0	-0.730053	0.834940	-0.460616
2	8	0	-3.414933	0.462696	-0.549495
3	8	0	-4.652909	2.310987	-0.321320
4	7	0	-2.440570	2.482881	-0.079667
5	6	0	-0.274622	3.053185	0.297763
6	6	0	-1.082371	2.013528	-0.092464
7	6	0	-3.516098	1.680262	-0.330121
8	6	0	-5.976783	1.610034	-0.329716
9	6	0	-6.935264	2.779566	-0.417324
10	6	0	-6.108813	0.708025	-1.540735
11	6	0	-6.113494	0.876899	0.986762
12	6	0	-1.096121	4.190293	0.585217
13	6	0	-2.442220	3.841352	0.342462
14	6	0	-3.477349	4.745398	0.528637
15	6	0	-3.149700	6.023884	0.980918
16	6	0	-1.825528	6.380989	1.240599
17	6	0	-0.792133	5.471697	1.047861
18	1	0	-6.792861	3.469971	0.422090
19	1	0	-7.964786	2.407694	-0.383779
20	1	0	-6.796496	3.328978	-1.355642

21	1	0	-5.578345	-0.239605	-1.417818
22	1	0	-5.752967	1.218627	-2.443380
23	1	0	-7.173132	0.486348	-1.682874
24	1	0	-6.028528	1.575493	1.827055
25	1	0	-5.371286	0.080436	1.089037
26	1	0	-7.103695	0.408062	1.028168
27	1	0	-4.508512	4.480578	0.328326
28	1	0	-3.945444	6.749401	1.130595
29	1	0	0.240852	5.748262	1.254470
30	1	0	-1.599711	7.383429	1.597798
31	29	0	-1.856944	-0.658024	-0.605720
32	8	0	-2.966031	-2.191365	-1.030841
33	16	0	-3.948583	-2.901451	-0.135363
34	8	0	-5.171727	-2.146475	0.115138
35	6	0	-3.076172	-2.869434	1.486747
36	9	0	-3.864611	-3.348837	2.434559
37	9	0	-1.962810	-3.582574	1.448248
38	8	0	-4.077265	-4.311476	-0.470646
39	9	0	-2.758613	-1.604487	1.801182
40	8	0	-0.376857	-1.859524	-0.254884
41	16	0	0.459835	-2.379122	-1.398063
42	8	0	-0.110986	-2.071209	-2.705917
43	6	0	0.271050	-4.195450	-1.193260
44	9	0	1.041373	-4.808728	-2.084173
45	9	0	0.657633	-4.553157	0.026002
46	8	0	1.886962	-2.151855	-1.188212
47	9	0	-0.981609	-4.570999	-1.379050
48	16	0	5.247404	0.328069	2.040650
49	8	0	5.434623	-0.886620	2.804070
50	8	0	5.890762	1.577124	2.402215
51	8	0	2.684560	1.347534	-0.596859
52	8	0	1.399494	2.662987	-1.911082
53	7	0	3.466309	0.668146	2.237366
54	6	0	3.025780	1.766302	1.680614
55	6	0	1.655384	2.250547	1.698235
56	6	0	0.902618	2.184747	2.799985
57	6	0	1.201701	2.936320	0.417310
58	6	0	5.374715	0.046799	0.316116
59	6	0	4.679686	-1.021898	-0.250510
60	6	0	4.766560	-1.206808	-1.618441
61	6	0	5.536739	-0.352147	-2.415784
62	6	0	6.221233	0.707939	-1.813061
63	6	0	6.137656	0.927801	-0.446169
64	6	0	5.597283	-0.562388	-3.893813
65	6	0	2.639152	-0.374290	2.787284
66	6	0	1.765599	-1.059134	1.948874
67	6	0	0.977230	-2.063663	2.498520
68	6	0	1.069969	-2.368200	3.853998
69	6	0	1.951491	-1.670468	4.675658
70	6	0	2.748637	-0.665294	4.143256
71	6	0	1.830654	2.207203	-0.762022
72	6	0	1.835971	2.093962	-3.206648
73	6	0	1.509337	0.616730	-3.239048
74	6	0	3.307268	2.392728	-3.414533
75	6	0	0.981516	2.861832	-4.195191
76	1	0	3.790593	2.419979	1.254619
77	1	0	1.261805	1.742863	3.725212
78	1	0	-0.092653	2.622853	2.807185
79	1	0	1.640559	3.949315	0.390165
80	1	0	4.056885	-1.682034	0.350197
81	1	0	4.198551	-2.011702	-2.079886
82	1	0	6.814878	1.379591	-2.430290
83	1	0	6.654082	1.761027	0.022512
84	1	0	6.142016	-1.482950	-4.137727

85	1	0	6.097084	0.269347	-4.400352
86	1	0	4.589557	-0.671028	-4.313458
87	1	0	1.700436	-0.807447	0.890140
88	1	0	0.292237	-2.603807	1.852597
89	1	0	0.447625	-3.155565	4.272272
90	1	0	2.020482	-1.908311	5.733754
91	1	0	3.442042	-0.103899	4.764933
92	1	0	0.463283	0.455197	-2.954750
93	1	0	2.138715	0.031056	-2.561728
94	1	0	1.645201	0.237535	-4.258978
95	1	0	3.938763	1.843365	-2.709392
96	1	0	3.501901	3.466602	-3.307469
97	1	0	3.590551	2.100569	-4.433220
98	1	0	-0.083064	2.673376	-4.015079
99	1	0	1.221602	2.546316	-5.216395
100	1	0	1.163732	3.939621	-4.113660

***Z*-TS2**

Zero-point correction = 0.73491 a.u.
Thermal correction to Gibbs Free Energy = 0.64078 a.u.
Sum of electronic and zero-point Energies = -5951.62533 a.u.
Sum of electronic and thermal Free Energies = -5951.71946 a.u.
Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	8	0	0.500206	0.152545	-0.962780
2	8	0	1.899884	1.640977	0.776945
3	8	0	1.148068	3.741198	0.986068
4	7	0	0.313396	2.502182	-0.657036
5	6	0	-1.135009	1.523982	-2.125302
6	6	0	-0.093213	1.282192	-1.268548
7	6	0	1.179530	2.579668	0.405860
8	6	0	2.051338	4.134536	2.112840
9	6	0	1.579261	5.543966	2.402592
10	6	0	1.807548	3.219367	3.293418
11	6	0	3.479245	4.127359	1.614171
12	6	0	-1.357465	2.948083	-2.127727
13	6	0	-0.473618	3.547657	-1.210257
14	6	0	-0.437946	4.921468	-1.013852
15	6	0	-1.325689	5.702036	-1.751042
16	6	0	-2.210149	5.126075	-2.664707
17	6	0	-2.229486	3.751491	-2.865104
18	1	0	1.740838	6.198070	1.537947
19	1	0	2.146729	5.948261	3.247582
20	1	0	0.514852	5.555450	2.662667
21	1	0	2.138189	2.197745	3.092589
22	1	0	0.745928	3.222368	3.568235
23	1	0	2.377597	3.598458	4.149302
24	1	0	3.571464	4.744564	0.712934
25	1	0	3.838383	3.116909	1.410528
26	1	0	4.121821	4.560506	2.389315
27	1	0	0.251006	5.380873	-0.315340
28	1	0	-1.318139	6.780090	-1.611433
29	1	0	-2.903063	3.309796	-3.596772
30	1	0	-2.885183	5.760324	-3.234493
31	29	0	2.151496	-0.097586	-0.055885
32	8	0	3.420538	-0.756965	1.218643
33	16	0	4.651556	-0.093432	1.792645
34	8	0	4.359724	1.075574	2.613342
35	6	0	5.414300	0.579675	0.259191
36	9	0	6.439372	1.359594	0.557747
37	9	0	5.819021	-0.400520	-0.529088
38	8	0	5.600513	-1.067212	2.308517
39	9	0	4.505561	1.309273	-0.402469

40	8	0	2.898826	-1.152799	-1.502796
41	16	0	2.783288	-2.646014	-1.712317
42	8	0	1.979887	-3.300895	-0.681735
43	6	0	4.508300	-3.210227	-1.419419
44	9	0	4.587524	-4.506048	-1.695759
45	9	0	5.341677	-2.549087	-2.210071
46	8	0	2.515760	-2.979012	-3.105270
47	9	0	4.855304	-3.017270	-0.159858
48	16	0	-3.583703	-3.418350	0.252680
49	8	0	-2.794031	-4.444861	0.904186
50	8	0	-4.377816	-3.689824	-0.932719
51	8	0	-4.201400	0.965699	-3.675544
52	8	0	-3.806597	1.063485	-1.444916
53	7	0	-2.404693	-2.227852	-0.280299
54	6	0	-2.657203	-1.532098	-1.410339
55	6	0	-1.699164	-0.824635	-2.123229
56	6	0	-0.365656	-1.214051	-2.085948
57	6	0	-1.990974	0.489922	-2.824804
58	6	0	-4.551750	-2.554814	1.440636
59	6	0	-4.005872	-2.256826	2.689526
60	6	0	-4.771776	-1.526026	3.586613
61	6	0	-6.068974	-1.114823	3.263709
62	6	0	-6.599234	-1.462666	2.015953
63	6	0	-5.848397	-2.174735	1.095149
64	6	0	-6.889031	-0.318877	4.226896
65	6	0	-1.446759	-1.755630	0.689407
66	6	0	-1.632356	-0.472973	1.210742
67	6	0	-0.737032	0.010494	2.153293
68	6	0	0.333273	-0.782908	2.566378
69	6	0	0.514651	-2.054969	2.028585
70	6	0	-0.384610	-2.555339	1.091116
71	6	0	-3.466475	0.872353	-2.718710
72	6	0	-5.178728	1.405392	-1.032316
73	6	0	-6.138072	0.316737	-1.474534
74	6	0	-5.545519	2.771136	-1.577402
75	6	0	-5.061088	1.440410	0.479359
76	1	0	-3.689703	-1.562213	-1.766452
77	1	0	-0.055439	-2.089948	-1.518931
78	1	0	0.275061	-0.930843	-2.919279
79	1	0	-1.767360	0.431831	-3.899838
80	1	0	-3.006273	-2.590155	2.958862
81	1	0	-4.358039	-1.273038	4.560396
82	1	0	-7.614126	-1.159431	1.763123
83	1	0	-6.259494	-2.447473	0.126791
84	1	0	-6.322081	-0.061546	5.126325
85	1	0	-7.782424	-0.875700	4.534497
86	1	0	-7.240159	0.611533	3.763731
87	1	0	-2.457243	0.140559	0.849176
88	1	0	-0.868892	1.011036	2.560686
89	1	0	1.038676	-0.403886	3.302958
90	1	0	1.367805	-2.659144	2.325388
91	1	0	-0.250949	-3.540226	0.653914
92	1	0	-5.774988	-0.665679	-1.144898
93	1	0	-6.271610	0.300269	-2.558757
94	1	0	-7.115192	0.484760	-1.005292
95	1	0	-5.614292	2.766553	-2.668658
96	1	0	-4.801814	3.516102	-1.269651
97	1	0	-6.518542	3.071556	-1.171189
98	1	0	-4.752084	0.459794	0.865688
99	1	0	-6.029695	1.693848	0.926789
100	1	0	-4.325947	2.191286	0.792245

***Z*-IM2**

Zero-point correction = 0.73757 a.u.

Thermal correction to Gibbs Free Energy = 0.64309 a.u.
Sum of electronic and zero-point Energies = -5951.64076 a.u.
Sum of electronic and thermal Free Energies = -5951.73524 a.u.
Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	8	0	0.346716	0.151162	-0.896878
2	8	0	1.867479	1.519878	0.841407
3	8	0	1.274168	3.666310	1.107885
4	7	0	0.328823	2.521827	-0.542455
5	6	0	-1.195261	1.656048	-2.006349
6	6	0	-0.168338	1.373326	-1.174096
7	6	0	1.217241	2.522316	0.509761
8	6	0	2.229787	3.987357	2.225129
9	6	0	1.802857	5.392796	2.590274
10	6	0	2.007302	3.029334	3.375169
11	6	0	3.632814	3.963044	1.663496
12	6	0	-1.354646	3.090252	-1.972210
13	6	0	-0.421854	3.617417	-1.057994
14	6	0	-0.319121	4.980967	-0.816066
15	6	0	-1.189960	5.818245	-1.506870
16	6	0	-2.124983	5.312999	-2.414148
17	6	0	-2.212873	3.949493	-2.658652
18	1	0	1.914196	6.073372	1.738503
19	1	0	2.436526	5.758715	3.405061
20	1	0	0.760426	5.411767	2.927161
21	1	0	2.382849	2.027166	3.158528
22	1	0	0.943279	2.985055	3.637728
23	1	0	2.549836	3.412919	4.246759
24	1	0	3.725432	4.667081	0.828745
25	1	0	3.930149	2.964738	1.336531
26	1	0	4.328229	4.274286	2.451309
27	1	0	0.404242	5.386009	-0.118314
28	1	0	-1.132975	6.889810	-1.334186
29	1	0	-2.927239	3.554484	-3.378686
30	1	0	-2.786551	5.996588	-2.940322
31	29	0	2.127327	-0.170806	-0.056996
32	8	0	3.453820	-0.861347	1.120971
33	16	0	4.717468	-0.219579	1.657753
34	8	0	4.469159	0.875119	2.586066
35	6	0	5.365349	0.579208	0.130506
36	9	0	6.388698	1.361963	0.421147
37	9	0	5.737799	-0.335195	-0.745234
38	8	0	5.708469	-1.218517	2.019436
39	9	0	4.402930	1.328572	-0.427409
40	8	0	2.780622	-1.138067	-1.568187
41	16	0	2.709605	-2.640338	-1.801928
42	8	0	1.951378	-3.325618	-0.760258
43	6	0	4.460182	-3.146509	-1.552656
44	9	0	4.562200	-4.447411	-1.788451
45	9	0	5.242130	-2.490200	-2.396804
46	8	0	2.419715	-2.943757	-3.194776
47	9	0	4.843081	-2.897811	-0.314575
48	16	0	-3.284641	-3.500840	0.276996
49	8	0	-2.539374	-4.419653	1.120318
50	8	0	-3.865753	-3.923781	-0.987513
51	8	0	-4.201973	1.111062	-3.603008
52	8	0	-3.903404	1.231047	-1.359595
53	7	0	-2.195225	-2.252671	-0.131972
54	6	0	-2.600754	-1.377387	-1.160777
55	6	0	-1.721394	-0.663253	-1.876981
56	6	0	-0.258515	-0.889436	-1.766069
57	6	0	-2.049897	0.593971	-2.654863
58	6	0	-4.536917	-2.719495	1.250868

59	6	0	-4.271840	-2.415554	2.585326
60	6	0	-5.244346	-1.757618	3.326326
61	6	0	-6.473678	-1.410120	2.758614
62	6	0	-6.713995	-1.735993	1.419021
63	6	0	-5.754096	-2.387077	0.658127
64	6	0	-7.523961	-0.709816	3.561002
65	6	0	-1.362726	-1.716243	0.915395
66	6	0	-1.651631	-0.458746	1.452970
67	6	0	-0.785203	0.103772	2.381819
68	6	0	0.353320	-0.591606	2.788529
69	6	0	0.613401	-1.861628	2.278761
70	6	0	-0.243682	-2.427364	1.338200
71	6	0	-3.518777	1.001891	-2.610022
72	6	0	-5.281521	1.618182	-1.013921
73	6	0	-6.271551	0.600900	-1.550312
74	6	0	-5.549341	3.017362	-1.531400
75	6	0	-5.251800	1.589940	0.502226
76	1	0	-3.675378	-1.255681	-1.302255
77	1	0	-0.000283	-1.839626	-1.296079
78	1	0	0.239059	-0.798588	-2.739103
79	1	0	-1.798702	0.478486	-3.718937
80	1	0	-3.326396	-2.699158	3.041141
81	1	0	-5.051840	-1.515849	4.369731
82	1	0	-7.671380	-1.476621	0.968697
83	1	0	-5.946202	-2.654650	-0.378458
84	1	0	-7.187886	-0.516045	4.583933
85	1	0	-8.442961	-1.306304	3.611685
86	1	0	-7.797011	0.249196	3.104095
87	1	0	-2.532964	0.083768	1.109220
88	1	0	-0.997790	1.091172	2.787410
89	1	0	1.045191	-0.142210	3.498517
90	1	0	1.498208	-2.410007	2.591122
91	1	0	-0.029483	-3.396121	0.897402
92	1	0	-5.956343	-0.416463	-1.286220
93	1	0	-6.384550	0.663256	-2.634689
94	1	0	-7.249588	0.779678	-1.087617
95	1	0	-5.544099	3.047558	-2.625045
96	1	0	-4.798847	3.720979	-1.150938
97	1	0	-6.535260	3.349337	-1.184850
98	1	0	-5.016129	0.581102	0.868206
99	1	0	-6.231571	1.878336	0.900322
100	1	0	-4.500044	2.288030	0.888848

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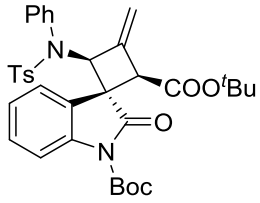
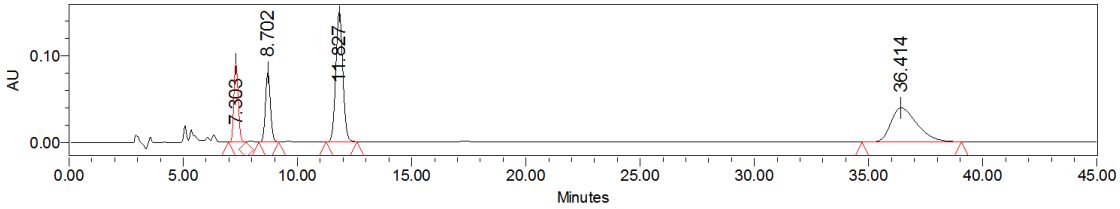
(H) The Analytical and Spectral Characterization Data of the Products

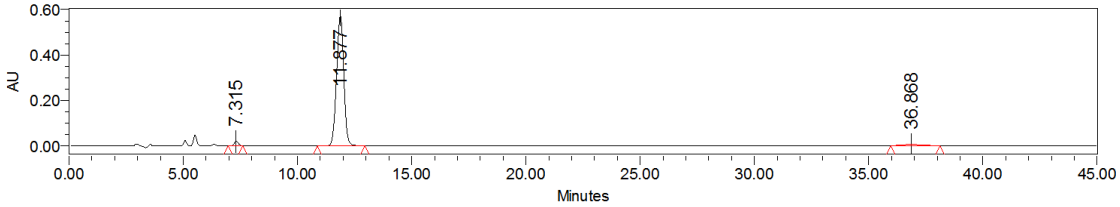
Di-*tert*-butyl (1*R*,2*R*,4*S*)-4-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3aa)



93% yield, White solid; **m.p.**: 138.4 – 143.5 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 224 nm), t_r (major) = 11.88 min, t_r (minor) = 36.87 min, ee = 95%. **3aa**:**4aa** > 19:1, determined by ^{1}H NMR. $[\alpha]^{18}_D$ = –24.3 (*c* = 0.46, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.86 – 7.83 (m, 1H), 7.41 – 7.15 (m, 12H), 5.34 – 5.31 (m, 1H), 5.26 – 5.24 (m, 1H), 3.98 – 3.96 (m, 1H), 3.93 – 3.91 (m, 1H), 2.40 (s, 3H), 1.67 (s, 9H), 0.94 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 174.9, 166.2, 149.1, 144.1, 141.4, 138.1, 137.9, 132.5, 129.2, 128.9, 128.8, 128.7, 128.6, 125.5, 123.8, 115.0, 110.7, 84.1, 81.5, 61.0, 56.0, 51.9, 28.1, 27.2, 21.6 ppm; **IR (neat) ν (cm^{-1}):** 2979, 1766, 1732, 1601, 1483, 1366, 1299, 1251, 1156, 1087, 1007, 890, 857, 816, 755, 700, 670; **HRMS** (ESI-FT) calcd for $C_{35}H_{38}N_2O_7SNa^+$ ([M+Na$^+$]) = 653.2292, found 653.2294.

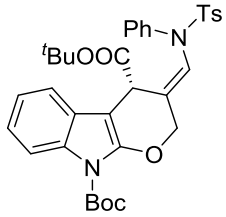


	Retention Time	Area	% Area
1	7.303	1214165	13.85
2	8.702	1206313	13.76
3	11.827	3210591	36.63
4	36.414	3134577	35.76



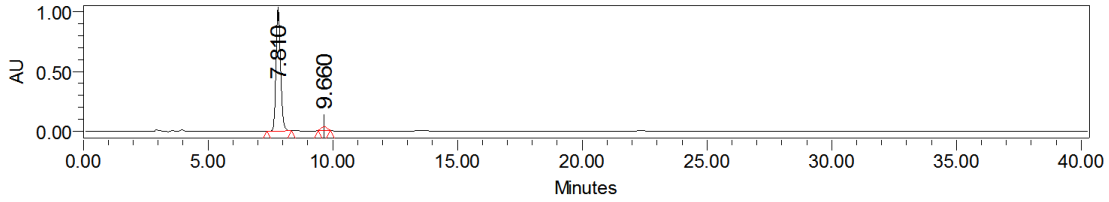
	Retention Time	Area	% Area
1	7.315	250492	1.91
2	11.877	12519879	95.40
3	36.868	352879	2.69

Di-*tert*-butyl (*R*,*E*)-3-{[(4-methyl-*N*-phenylphenyl)sulfonamido]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4aa)



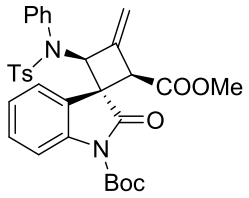
70% yield for two steps, White solid; **m.p.**: 189.7 – 197.4 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 224 nm), t_r (major) = 7.81 min, t_r (minor) = 9.66 min, ee = 93%. **3aa**:**4aa** < 1:19, determined by ^{1}H NMR. $[\alpha]^{23}_D$ = +154.8 (*c* = 0.37, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.90 – 7.85 (m, 1H), 7.49 – 7.44 (m, 2H), 7.33 – 7.25 (m, 4H), 7.22 – 7.20 (m, 2H), 7.14 – 7.07 (m, 4H), 6.83 (s, 1H),

5.14 (d, *J* = 11.6 Hz, 1H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.02 (s, 1H), 2.37 (s, 3H), 1.66 (s, 9H), 1.24 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 169.4, 149.0, 148.4, 144.3, 139.3, 134.3, 131.0, 129.6, 129.4, 128.5, 128.2, 127.81, 127.75, 126.9, 122.7, 121.7, 119.4, 117.6, 114.7, 89.6, 84.1, 81.7, 71.3, 38.5, 28.2, 27.9, 21.5 ppm; **IR (neat) ν (cm^{-1}):** 2979, 1730, 1625, 1599, 1464, 1415, 1351, 1327, 1302, 1254, 1146, 1116, 1091, 1001, 951, 839, 747, 696, 663; **HRMS** (ESI-FT) calcd for $C_{35}H_{38}N_2O_7SNa^+$ ([M+Na$^+$]) = 653.2292, found 653.2294.

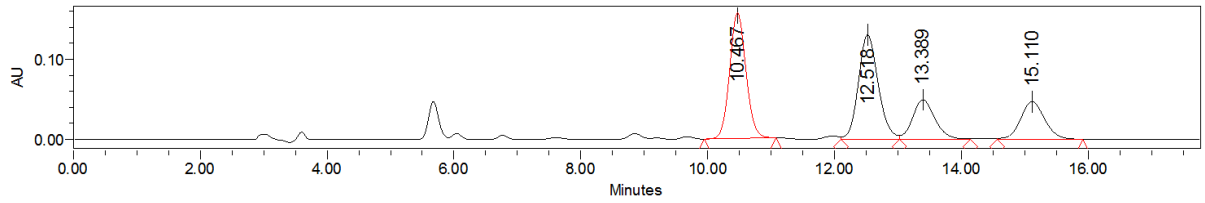


	Retention Time	Area	% Area
1	7.810	13140958	96.57
2	9.660	466675	3.43

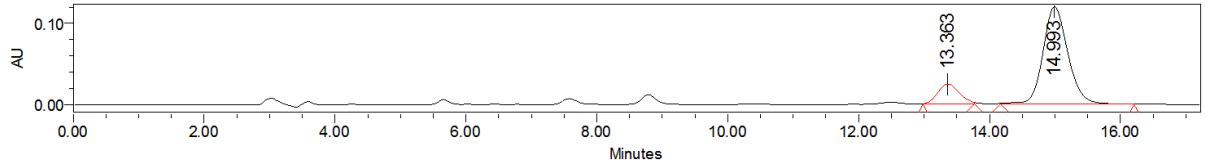
1'-(*tert*-Butyl) 2-methyl (1*R*,2*R*,4*S*)-4-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3ba)



85% yield, White solid; **m.p.**: 91.3 – 102.9 °C; R_f = 0.3 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 224 nm), t_r (major) = 14.99 min, t_r (minor) = 13.36 min, ee = 70%. **3ba**:**4ba** > 19:1, determined by ^{1}H NMR. $[\alpha]^{21}_{\lambda}$ = –16.256 (*c* = 0.41, in dichloromethane, λ = 405 nm). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.85 – 7.83 (m, 1H), 7.35 – 7.15 (m, 12H), 5.33 – 5.30 (m, 1H), 5.29 – 5.26 (m, 1H), 4.12 – 4.09 (m, 1H), 4.07 – 4.04 (m, 1H), 3.22 (s, 3H), 2.40 (s, 3H), 1.68 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 174.8, 167.6, 149.1, 144.1, 141.1, 137.7, 137.6, 132.7, 129.6, 129.3, 129.2, 128.9, 128.84, 128.80, 128.6, 127.2, 125.4, 124.8, 123.7, 121.7, 115.1, 111.5, 84.2, 62.1, 56.0, 51.5, 51.0, 28.2, 21.6 ppm; **IR (neat) ν (cm^{-1}):** 2981, 1734, 1600, 1483, 1349, 1287, 1252, 1211, 1155, 1089, 1029, 916, 845, 816, 755, 700, 669; **HRMS** (ESI-FT) calcd for $C_{32}H_{32}N_2O_7SNa^+$ ([M+Na$^+$]) = 611.1822, found 611.1828.

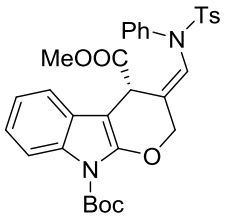


	Retention Time	Area	% Area
1	10.467	2795959	34.57
2	12.518	2830060	34.99
3	13.389	1215315	15.03
4	15.110	1246567	15.41

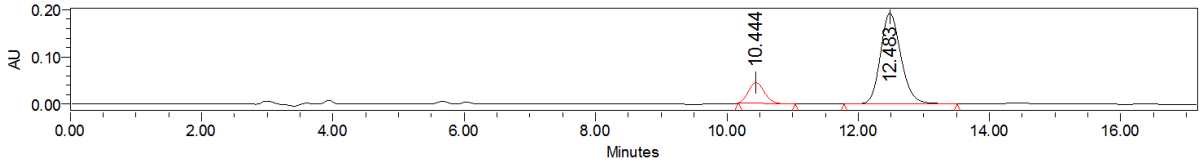


	Retention Time	Area	% Area
1	13.363	556358	14.94
2	14.993	3167204	85.06

9-(*tert*-Butyl) 4-methyl (*R*,*E*)-3-{[(4-methyl-*N*-phenylphenyl)sulfonamide]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4ba)

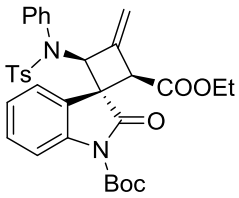


73% yield for two steps, Yellow oil; R_f = 0.3 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 224 nm), t_r (major) = 12.48 min, t_r (minor) = 10.44 min, ee = 70%. **3ba**:**4ba** < 1:19, determined by ^{1}H NMR. $[\alpha]^{21}_D$ = +105.8 (*c* = 0.27, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.90 – 7.84 (m, 1H), 7.48 – 7.43 (m, 2H), 7.34 – 7.29 (m, 3H), 7.25 – 7.21 (m, 3H), 7.13 – 7.07 (m, 4H), 6.88 (d, *J* = 1.2 Hz, 1H), 5.11 (d, *J* = 11.6 Hz, 1H), 4.78 (d, *J* = 11.6 Hz, 1H), 4.11 (s, 1H), 3.35 (s, 3H), 2.39 (s, 3H), 1.65 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 170.6, 148.9, 148.5, 144.5, 139.2, 134.2, 131.0, 129.6, 129.3, 128.8, 128.3, 128.2, 127.7, 126.7, 123.0, 121.9, 117.6, 117.3, 114.7, 88.8, 84.2, 71.2, 52.0, 37.4, 28.2, 21.6 ppm; **IR (neat) ν (cm^{-1}):** 2979, 1733, 1625, 1599, 1463, 1416, 1349, 1326, 1302, 1254, 1223, 1165, 1145, 1115, 1091, 1000, 946, 913, 841, 817, 747, 697, 663, 633; **HRMS** (ESI-FT) calcd for $C_{32}H_{32}N_2O_7SNa^+$ ([M]+Na$^+$) = 611.1822, found 611.1831.

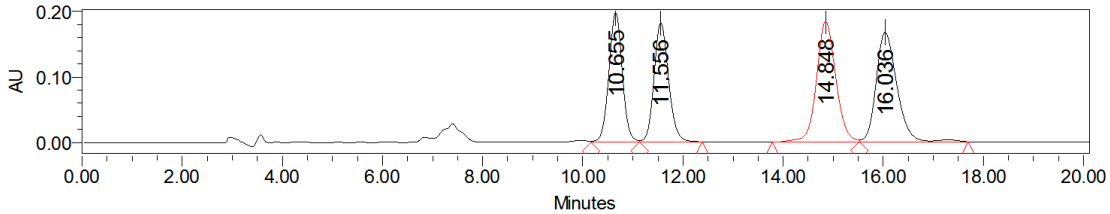


	Retention Time	Area	% Area
1	10.444	739428	14.97
2	12.483	4200147	85.03

1'-(*tert*-Butyl) 2-ethyl (1*R*,2*R*,4*S*)-4-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3ca)

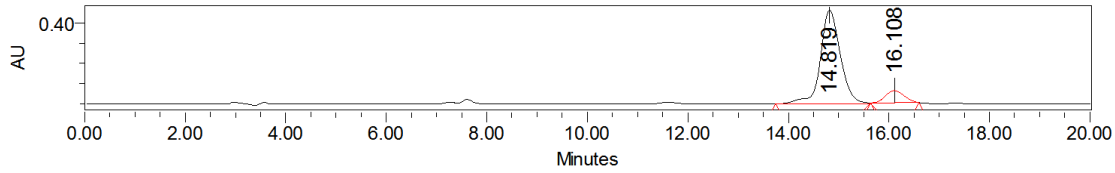


86% yield, White solid; **m.p.**: 121.9 – 126.5 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 224 nm), t_r (major) = 14.82 min, t_r (minor) = 16.11 min, ee = 78%. **3ca**:**4ca** > 19:1, determined by ^{1}H NMR. $[\alpha]^{22}_\lambda$ = –17.5 (*c* = 0.41, in dichloromethane, λ = 405 nm). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.84 – 7.81 (m, 1H), 7.38 – 7.26 (m, 4H), 7.25 – 7.12 (m, 8H), 5.35 – 5.32 (m, 1H), 5.29 – 5.26 (m, 1H), 4.08 – 4.05 (m, 1H), 4.03 – 4.01 (m, 1H), 3.78 – 3.71 (m, 1H), 3.66 – 3.58 (m, 1H), 2.40 (s, 3H), 1.68 (s, 9H), 0.66 (t, *J* = 7.2 Hz, 3H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 174.9, 167.1, 149.1, 144.1, 141.2, 137.8, 137.7, 132.6, 129.6, 129.2, 128.9, 128.82, 128.79, 128.6, 127.2, 125.0, 123.7, 123.6, 121.7, 115.1, 111.3, 84.2, 61.7, 60.4, 56.0, 51.1, 28.1, 21.6, 13.4 ppm; **IR (neat) ν (cm^{-1}):** 2981, 1764, 1734, 1600, 1483, 1354, 1298, 1252, 1206, 1156, 1088, 1034, 891, 846, 816, 755, 700, 670; **HRMS** (ESI-FT) calcd for $C_{33}H_{34}N_2O_7SNa^+$ ([M]+Na$^+$) = 625.1979, found 625.1986.



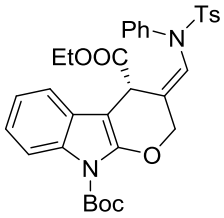
	Retention Time	Area	% Area
1	10.655	3682167	21.49
2	11.556	3662427	21.37

3	14.848	4951832	28.90
4	16.036	4839294	28.24

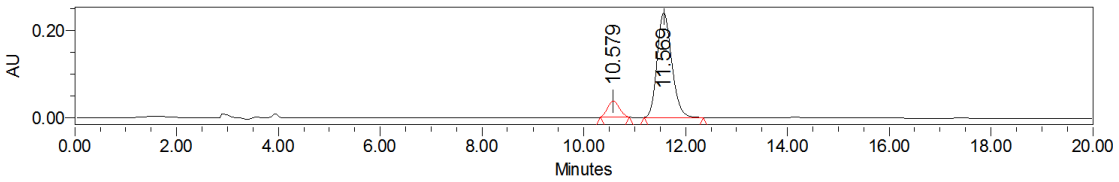


	Retention Time	Area	% Area
1	14.819	12732374	89.15
2	16.108	1534100	10.85

9-(*tert*-Butyl) 4-ethyl (*R*,*E*)-3-{[(4-methyl-*N*-phenylphenyl)sulfonamide]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4ca)

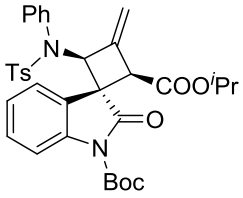


83% yield for two steps, Colorless oil; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 224 nm), t_r (major) = 11.57 min, t_r (minor) = 10.58 min, ee = 78%. **3ca**:**4ca** < 1:19, determined by ^{1}H NMR. $[\alpha]^{22}_{D}$ = +104.6 (*c* = 0.30, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.90 – 7.86 (m, 1H), 7.48 – 7.44 (m, 2H), 7.34 – 7.27 (m, 4H), 7.24 – 7.20 (m, 2H), 7.13 – 7.08 (m, 4H), 5.12 (d, *J* = 12.0 Hz, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.10 (s, 1H), 3.87 – 3.80 (m, 1H), 3.74 – 3.67 (m, 1H), 2.39 (s, 3H), 1.66 (s, 9H), 1.08 (t, *J* = 7.2 Hz, 3H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 170.1, 148.9, 148.5, 144.4, 139.2, 134.2, 131.0, 129.62, 129.56, 129.2, 128.7, 128.2, 128.1, 127.7, 127.2, 126.7, 122.8, 121.9, 121.7, 117.8, 117.4, 114.7, 89.0, 84.2, 71.3, 61.1, 37.6, 28.2, 21.6, 13.9 ppm; **IR (neat) ν (cm^{-1}):** 2982, 1733, 1625, 1600, 1465, 1416, 1351, 1328, 1301, 1255, 1223, 1166, 1147, 1116, 1091, 1002, 951, 922, 841, 749, 698, 663; **HRMS** (ESI-FT) calcd for $C_{33}H_{35}N_2O_7S^+$ ([M]+H$^+$) = 603.2159, found 603.2158.



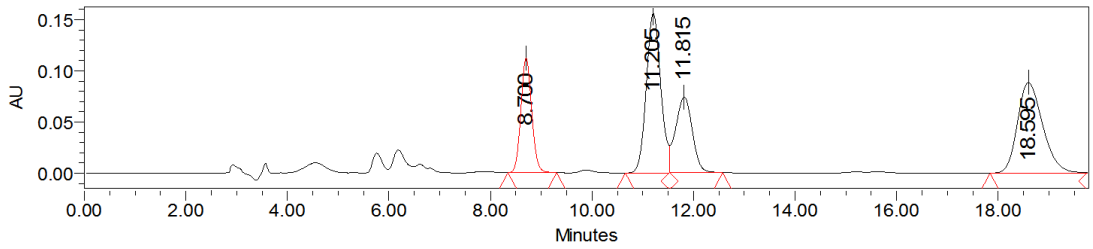
	Retention Time	Area	% Area
1	10.579	584614	10.90
2	11.569	4777921	89.10

1'-(*tert*-Butyl) 2-isopropyl (1*R*,2*R*,4*S*)-4-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3da)

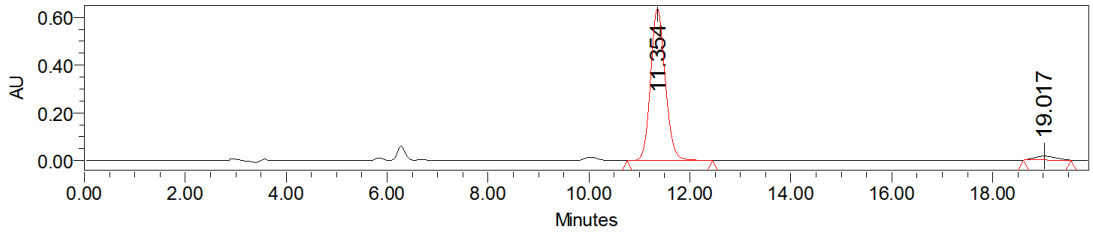


93% yield, White solid; **m.p.**: 70.1 – 76.4 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 224 nm), t_r (major) = 11.35 min, t_r (minor) = 19.02 min, ee = 93%. **3da**:**4da** > 19:1, determined by ^{1}H NMR. $[\alpha]^{22}_{\lambda}$ = –38.1 (*c* = 0.46, in dichloromethane, λ = 436 nm). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.84 – 7.81 (m, 1H), 7.40 – 7.26 (m, 4H), 7.25 – 7.11 (m, 8H), 5.34 – 5.32 (m, 1H), 5.28 – 5.26 (m, 1H), 4.55 (hept, *J* = 6.4 Hz, 1H), 4.04 – 4.01 (m, 1H), 4.00 – 3.97 (m, 1H), 2.40 (s, 3H), 1.68 (s, 9H), 0.97 (d, *J* = 6.0 Hz, 3H), 0.45 (d, *J* = 6.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 175.0, 166.6, 149.1, 144.1, 141.3, 137.8, 137.7, 132.5, 129.6, 129.3, 129.2, 128.8, 128.7, 128.6, 127.2, 125.0, 123.7, 121.7, 115.1, 111.1, 84.1, 68.2, 61.5, 56.0, 51.2, 28.1, 21.6, 21.5, 20.4 ppm; **IR (neat) ν (cm^{-1}):** 2981, 1765, 1732, 1600, 1484,

1352, 1298, 1251, 1210, 1155, 1107, 1008, 909, 857, 816, 755, 700, 669; **HRMS** (ESI-FT) calcd for $C_{34}H_{36}N_2O_7SNa^+$ ([M+Na$^+$]) = 639.2135, found 639.2148.

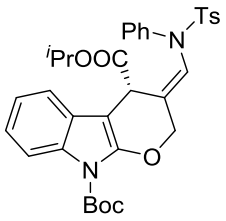


	Retention Time	Area	% Area
1	8.700	1658599	17.45
2	11.205	3094561	32.55
3	11.815	1700367	17.88
4	18.595	3053754	32.12

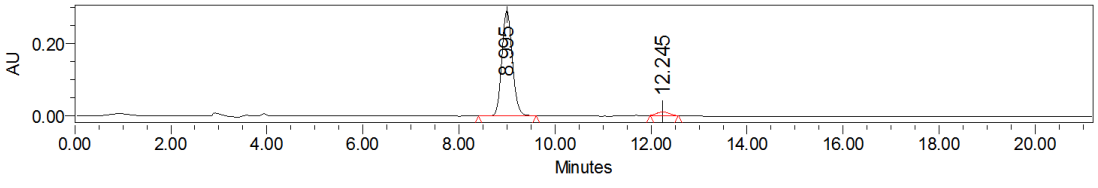


	Retention Time	Area	% Area
1	11.354	12820456	96.43
2	19.017	475228	3.57

9-(*tert*-Butyl) 4-isopropyl (*R*,*E*)-3-{[(4-methyl-*N*-phenylphenyl)sulfonamide]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4da)



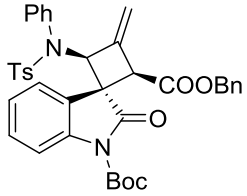
71% yield for two steps, White solid; **m.p.**: 167.3 – 174.7 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 224 nm), t_r (major) = 9.00 min, t_r (minor) = 12.25 min, ee = 92%. **3da**:**4da** < 1:19, determined by ^{1}H NMR. $[\alpha]^{23}_D$ = +125.6 (*c* = 0.31, in dichloromethane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 – 7.85 (m, 1H), 7.48 – 7.44 (m, 2H), 7.33 – 7.27 (m, 4H), 7.23 – 7.20 (m, 2H), 7.12 – 7.07 (m, 4H), 6.86 (s, 1H), 5.13 (d, *J* = 12.0 Hz, 1H), 4.78 (d, *J* = 11.6 Hz, 1H), 4.63 (hept, *J* = 6.0 Hz, 1H), 4.06 (s, 1H), 2.38 (s, 3H), 1.66 (s, 9H), 1.09 (d, *J* = 6.4 Hz, 3H), 0.99 (d, *J* = 6.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 169.6, 148.9, 148.4, 144.4, 139.1, 134.2, 131.0, 129.6, 129.3, 128.6, 128.3, 128.0, 127.7, 127.2, 126.8, 122.7, 121.8, 118.5, 117.7, 114.6, 89.2, 84.1, 71.3, 68.9, 37.8, 28.2, 21.64, 21.55, 21.5 ppm; **IR (neat) ν (cm^{-1}):** 2980, 1728, 1625, 1599, 1463, 1415m 1349, 1326, 1298, 1253, 1224, 1166, 1146, 1108, 1000, 952, 838, 748, 697, 663, 632; **HRMS** (ESI-FT) calcd for $C_{34}H_{36}N_2O_7SNa^+$ ([M+Na$^+$]) = 639.2135, found 639.2140.



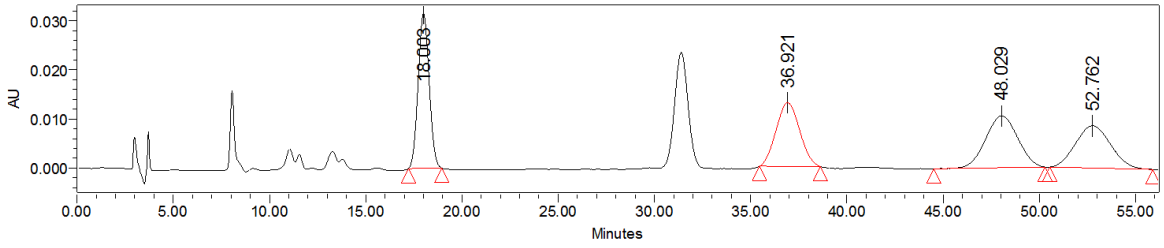
	Retention Time	Area	% Area

1	8.995	4414515	96.04
2	12.245	181978	3.96

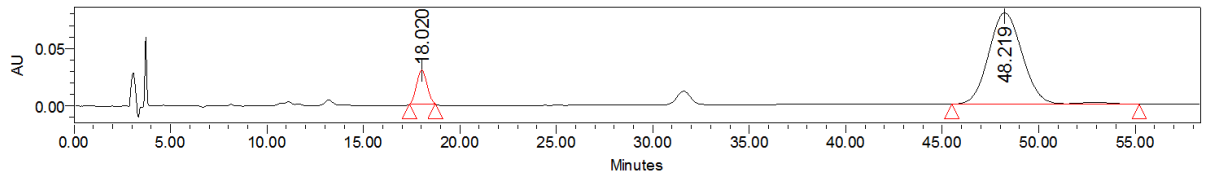
2-Benzyl 1'-(*tert*-butyl) (1*R*,2*R*,4*S*)-4-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3ea)



93% yield, White solid; **m.p.**: 70.1 – 78.6 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel AD-H, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm), t_r (major) = 48.22 min, t_r (minor) = 18.02 min, ee = 81%. **3ea**:**4ea** > 19:1, determined by ^{1}H NMR. $[\alpha]^{22}_{\lambda}$ = –15.1 (*c* = 0.48, in dichloromethane, λ = 405 nm). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 – 7.76 (m, 1H), 7.33 – 7.07 (m, 15H), 6.84 – 6.81 (m, 2H), 5.37 – 5.35 (m, 1H), 5.30 – 5.27 (m, 1H), 4.62 (q, *J* = 12.0 Hz, 2H), 4.11 – 4.07 (m, 2H), 2.39 (s, 3H), 1.63 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 174.7, 167.1, 148.9, 144.1, 141.1, 137.7, 137.5, 134.6, 132.6, 129.6, 129.2, 128.91, 128.85, 128.78, 128.6, 128.3, 128.2, 128.0, 127.2, 124.6, 123.8, 123.6, 121.7, 115.2, 111.5, 84.1, 66.6, 62.0, 56.0, 50.9, 28.1, 21.6 ppm; **IR (neat) ν (cm^{-1}):** 2980, 1764, 1734, 1600, 1483, 1361, 1298, 1252, 1156, 1087, 1023, 910, 845, 817, 752, 699, 670; **HRMS** (ESI-FT) calcd for $C_{38}H_{36}N_2O_7SNa^+$ ([M]+Na^+) = 687.2135, found 687.2135.

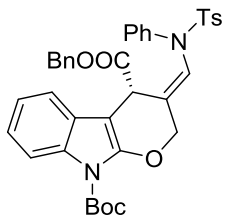


	Retention Time	Area	% Area
1	18.003	1253572	26.83
2	36.921	1102822	23.61
3	48.029	1223706	26.19
4	52.762	1091826	23.37



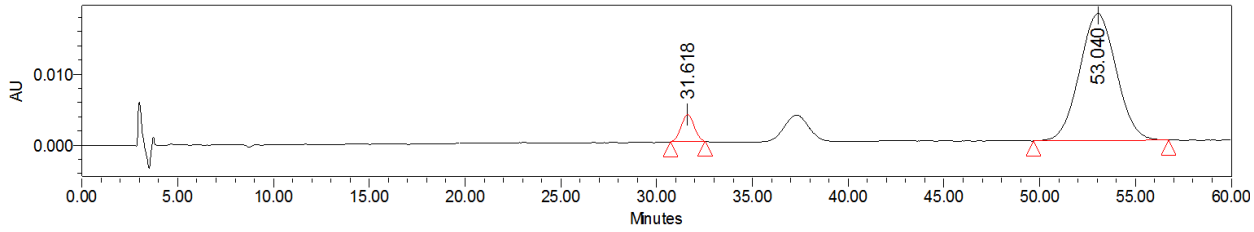
	Retention Time	Area	% Area
1	18.020	1006662	9.49
2	48.219	9600950	90.51

4-Benzyl 9-(*tert*-butyl) (*R*,*E*)-3-{[(4-methyl-*N*-phenylphenyl)sulfonamide]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4ea)



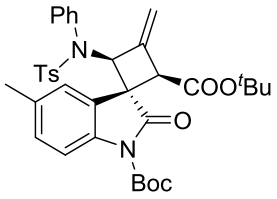
64% yield for two steps, White solid; **m.p.**: 161.9 – 170.9 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel AD-H, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm), t_r (major) = 53.04 min, t_r (minor) = 31.62 min, ee = 83%. **3ea**:**4ea** < 1:19, determined by ^{1}H NMR. $[\alpha]^{23}_{D}$ = +127.5 (*c* = 0.35, in dichloromethane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.88 – 7.83 (m, 1H), 7.48 – 7.43 (m, 2H), 7.34 – 7.30 (m, 3H), 7.25 – 7.15 (m, 8H), 7.09 – 7.00 (m, 4H), 6.91 (s, 1H),

5.12 (d, *J* = 11.6 Hz, 1H), 4.84 – 4.76 (m, 2H), 4.70 (d, *J* = 12.0 Hz, 1H), 4.12 (s, 1H), 2.39 (s, 3H), 1.66 (s, 9H) ppm; **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)** δ 169.9, 148.9, 148.6, 144.4, 139.0, 135.1, 134.2, 130.9, 129.63, 129.57, 129.3, 128.8, 128.40, 128.35, 128.3, 128.2, 127.7, 127.2, 126.6, 125.4, 122.8, 121.9, 121.7, 117.6, 117.1, 114.6, 88.8, 84.2, 71.3, 67.1, 37.6, 28.2, 21.6 ppm; **IR (neat) ν (cm^{-1}):** 2979, 1733, 1625, 1600, 1463, 1416, 1351, 1327, 1299, 1165, 1147, 1116, 1091, 1000, 953, 842, 817, 748, 697, 664; **HRMS** (ESI-FT) calcd for $C_{38}H_{36}N_2O_7SNa^+$ ([M]+Na^+) = 687.2135, found 687.2147.

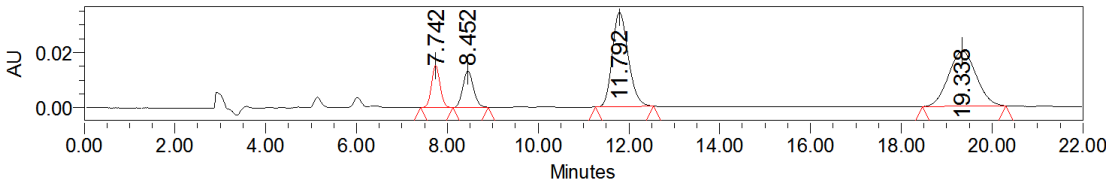


	Retention Time	Area	% Area
1	31.618	199933	8.50
2	53.040	2151836	91.50

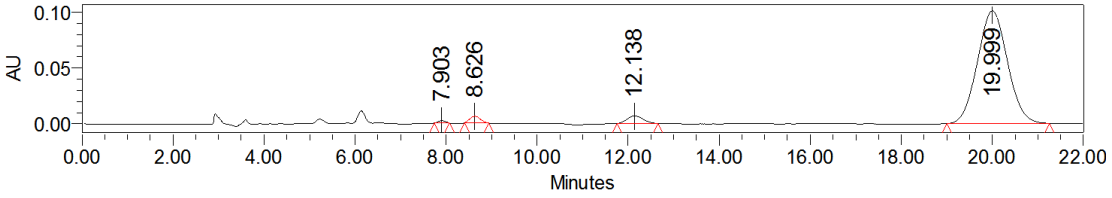
Di-*tert*-butyl (1*R*,2*R*,4*S*)-5'-methyl-4-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3fa)



91% yield, White solid; **m.p.**: 80.5 –88.6 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 227 nm), t_r (major) = 20.00 min, t_r (minor) = 12.14 min, ee = 93%. **3fa**:**4fa** > 19:1, determined by ^{1}H NMR. $[\alpha]^{22}_{\lambda}$ = –85.2 (*c* = 0.49, in dichloromethane, λ = 436 nm). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 – 7.69 (m, 1H), 7.34 – 7.26 (m, 2H), 7.26 – 7.14 (m, 8H), 5.34 – 5.32 (m, 1H), 5.26 – 5.24 (m, 1H), 4.04 – 4.00 (m, 1H), 3.92 – 3.89 (m, 1H), 2.40 (s, 3H), 2.34 (s, 3H), 1.66 (s, 9H), 0.94 (s, 9H) ppm; **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)** δ 175.1, 166.3, 149.1, 144.1, 139.0, 138.3, 137.8, 133.3, 132.7, 129.2, 129.1, 128.8, 128.6, 125.4, 124.4, 114.8, 110.9, 83.9, 81.4, 61.1, 56.1, 51.7, 28.1, 27.1, 21.6, 21.1 ppm; **IR (neat) ν (cm^{-1}):** 2978, 1766, 1732, 1596, 1489, 1365, 1339, 1308, 1251, 1158, 1088, 1009, 878, 816, 700, 669; **HRMS** (ESI-FT) calcd for $C_{36}H_{40}N_2O_7SNa^+$ ([M]+Na^+) = 667.2445, found 667.2448.



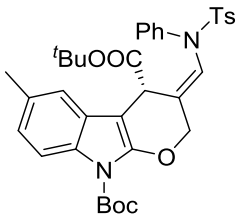
	Retention Time	Area	% Area
1	7.742	199733	9.52
2	8.452	214903	10.24
3	11.792	836474	39.87
4	19.338	846966	40.37



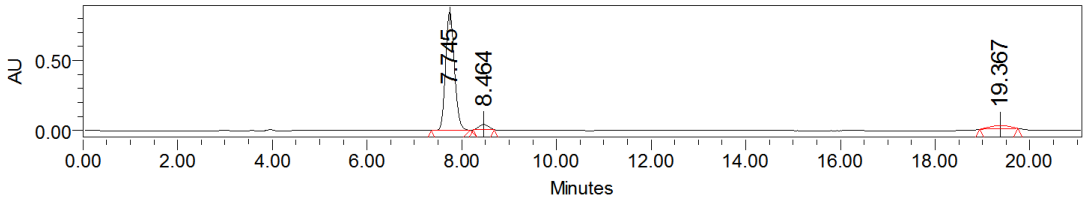
	Retention Time	Area	% Area
1	7.903	23086	0.47
2	8.626	96174	1.96
3	12.138	166052	3.38

4	19.999	4625464	94.19

Di-*tert*-butyl (*R*,*E*)-6-methyl-3-{[(4-methyl-*N*-phenylphenyl)sulfonamide]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4fa)

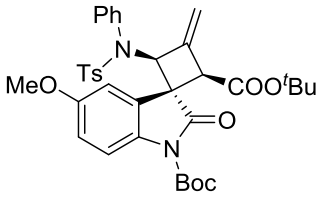


72% yield for two steps, White solid; **m.p.**: 160.6 – 168.5 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 227 nm), t_r (major) = 7.75 min, t_r (minor) = 8.46 min, ee = 91%. **3fa**:**4fa** = 1:19, determined by ^{1}H NMR. $[\alpha]^{24}_D$ = +132.7 (*c* = 0.28, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.74 – 7.72 (m, 1H), 7.49 – 7.45 (m, 2H), 7.34 – 7.30 (m, 3H), 7.22 – 7.19 (m, 3H), 7.11 – 7.09 (m, 2H), 6.92 – 6.90 (m, 1H), 6.79 (s, 1H), 5.13 (d, *J* = 11.6 Hz, 1H), 4.74 (d, *J* = 11.6 Hz, 1H), 4.06 (s, 1H), 2.38 – 2.36 (m, 6H), 1.65 (s, 9H), 1.24 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 169.4, 149.0, 148.4, 144.3, 139.4, 134.3, 132.1, 129.6, 129.4, 129.2, 129.1, 128.8, 128.4, 128.2, 127.8, 127.0, 122.8, 120.3, 118.0, 114.8, 114.3, 89.4, 83.9, 81.6, 71.1, 38.6, 28.2, 27.8, 21.5, 21.3 ppm; **IR (neat) ν (cm^{-1}):** 2978, 1729, 1607, 1477, 1413, 1394, 1354, 1320, 1254, 1223, 1169, 1141, 1091, 1005, 959, 841, 766, 696, 665; **HRMS** (ESI-FT) calcd for $C_{36}H_{40}N_2O_7SNa^+$ ([M]+Na$^+$) = 667.2445, found 667.2445.

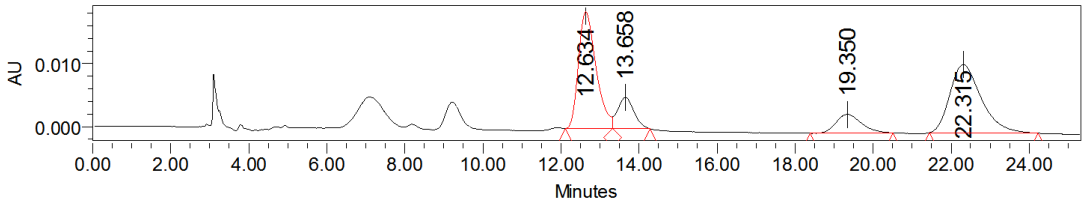


	Retention Time	Area	% Area
1	7.745	11061525	90.75
2	8.464	520643	4.27
3	19.367	605994	4.97

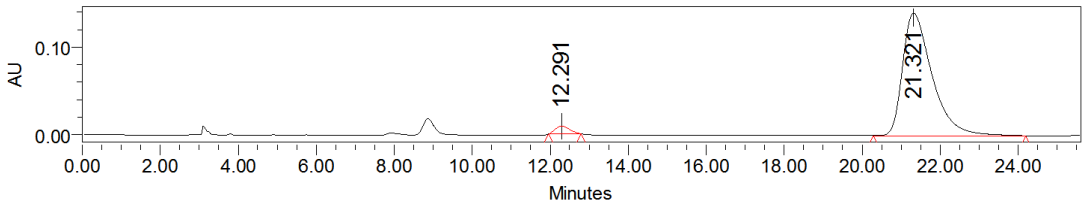
Di-*tert*-butyl (1*R*,2*R*,4*S*)-5'-methoxy-4-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3ga)



94% yield, White solid; **m.p.**: 83.0 – 92.8 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IB, hexane/^{i}PrOH = 95/5, flow rate 1.0 mL/min, λ = 231 nm), t_r (major) = 21.32 min, t_r (minor) = 12.29 min, ee = 94%. **3ga**:**4ga** > 19:1, determined by ^{1}H NMR. $[\alpha]^{23}_\lambda$ = –88.2 (*c* = 0.45, in dichloromethane, λ = 436 nm). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.76 – 7.73 (m, 1H), 7.33 – 7.29 (m, 1H), 7.26 – 7.15 (m, 7H), 6.97 – 6.96 (m, 1H), 6.92 – 6.85 (m, 2H), 5.35 – 5.33 (m, 1H), 5.24 – 5.23 (m, 1H), 4.00 – 3.99 (m, 1H), 3.92 – 3.90 (m, 1H), 3.78 (s, 3H), 2.40 (s, 3H), 1.66 (s, 9H), 0.98 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 175.0, 166.1, 156.4, 149.1, 144.1, 138.3, 138.0, 134.9, 132.5, 129.2, 128.9, 128.8, 128.6, 126.7, 115.7, 113.5, 110.6, 110.3, 83.9, 81.4, 61.1, 56.2, 55.7, 51.9, 28.2, 27.2, 21.6 ppm; **IR (neat) ν (cm^{-1}):** 2979, 1764, 1731, 1598, 1489, 1364, 1304, 1239, 1158, 1087, 1007, 877, 817, 700, 669; **HRMS** (ESI-FT) calcd for $C_{36}H_{40}N_2O_8SNa^+$ ([M]+Na$^+$) = 683.2398, found 683.2401.

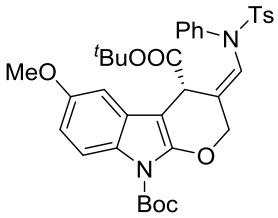


	Retention Time	Area	% Area
1	12.634	584007	39.74
2	13.658	144442	9.83
3	19.350	134652	9.16
4	22.315	606307	41.26

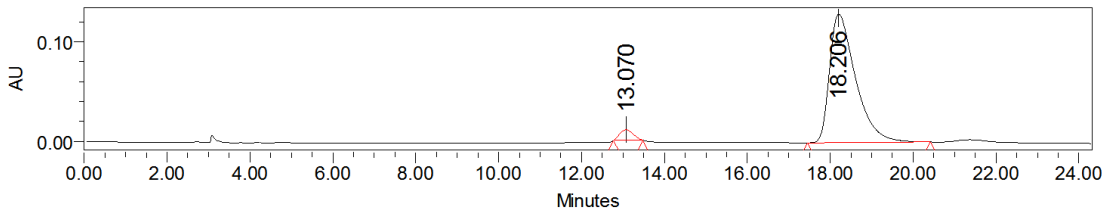


	Retention Time	Area	% Area
1	12.291	229442	2.99
2	21.321	7388676	97.01

Di-*tert*-butyl (*R*,*E*)-6-methoxy-3-{[(4-methyl-*N*-phenylphenyl)sulfonamide]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4ga)

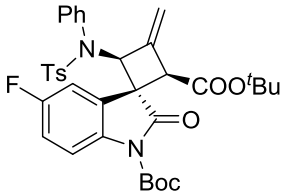


79% yield for two steps, yellow oil; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IB, hexane/^{i}PrOH = 95/5, flow rate 1.0 mL/min, λ = 231 nm), t_r (major) = 18.21 min, t_r (minor) = 13.07 min, ee = 92%. **3ga**:**4ga** < 1:19, determined by ^{1}H NMR. $[\alpha]^{24}_D$ = +146.0 (*c* = 0.30, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.77 – 7.74 (m, 1H), 7.48 – 7.43 (m, 2H), 7.33 – 7.28 (m, 3H), 7.22 – 7.20 (m, 2H), 7.12 – 7.07 (m, 2H), 6.79 (s, 1H), 6.78 – 6.77 (m, 1H), 6.70 – 6.67 (m, 1H), 5.16 (d, *J* = 11.6 Hz, 1H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.02 (s, 1H), 3.81 (s, 3H), 2.38 (s, 3H), 1.65 (s, 9H), 1.26 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 169.4, 155.9, 148.91, 148.89, 144.4, 139.3, 134.3, 129.6, 129.4, 129.3, 128.4, 128.2, 127.9, 127.8, 127.2, 125.5, 121.7, 120.1, 115.4, 109.0, 101.8, 89.7, 84.0, 81.7, 71.2, 55.6, 38.5, 28.2, 27.9, 21.5 ppm; **IR (neat) ν (cm^{-1}):** 2978, 1728, 1604, 1479, 1416, 1394, 1362, 1322, 1305, 1257, 1221, 1169, 1143, 1091, 1027, 1003, 962, 841, 696, 665; **HRMS** (ESI-FT) calcd for $C_{36}H_{40}N_2O_8SNa^+$ ([M]+Na$^+$) = 683.2398, found 683.2397.

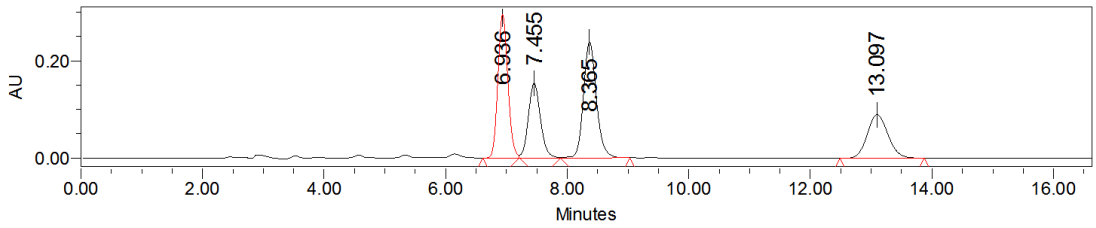


	Retention Time	Area	% Area
1	13.070	237437	4.06
2	18.206	5615593	95.94

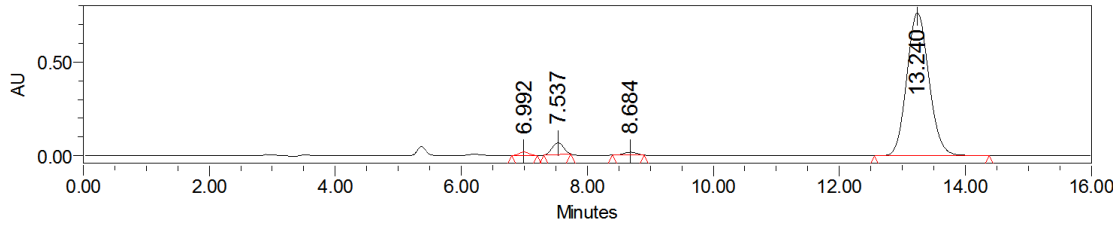
Di-*tert*-butyl (1*R*,2*R*,4*S*)-5'-fluoro-4-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3ha)



77% yield, White solid; **m.p.**: 89.1 – 95.6 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 226 nm), t_r (major) = 13.24 min, t_r (minor) = 7.54 min, ee = 92%. **3ha**:**4ha** > 19:1, determined by ^{1}H NMR. $[\alpha]^{23}_{\lambda}$ = –69.9 (*c* = 0.44, in dichloromethane, λ = 436 nm). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.85 – 7.82 (m, 1H), 7.35 – 7.27 (m, 2H), 7.25 – 7.18 (m, 6H), 7.18 – 6.99 (m, 3H), 5.35 – 5.33 (m, 1H), 5.23 – 5.22 (m, 1H), 3.96 – 3.91 (m, 2H), 2.41 (s, 3H), 1.66 (s, 9H), 1.00 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 174.5, 159.4 (d, *J* = 244.2 Hz), 158.2, 149.0, 144.3, 137.8 (d, *J* = 7.5 Hz), 137.5, 132.3, 129.3, 129.0, 128.9, 128.7, 127.4 (d, *J* = 8.6 Hz), 116.1 (d, *J* = 8.0 Hz), 116.0, 115.0 (d, *J* = 23.0 Hz), 111.4 (d, *J* = 25.0 Hz), 111.0, 84.3, 81.7, 61.1, 51.9, 28.1, 27.2, 21.6 ppm; **^{19}F NMR (376 MHz, CDCl$_3$)** δ–118.7 ppm; **IR (neat) ν (cm^{-1}):** 2979, 1768, 1733. 1598, 1484, 1364, 1303, 1230, 1154, 1084, 1010, 910, 883, 819, 700, 669; **HRMS** (ESI-FT) calcd for $C_{35}H_{37}FN_2O_7SNa^+$ ([M]+Na$^+$) = 671.2198, found 671.2203.

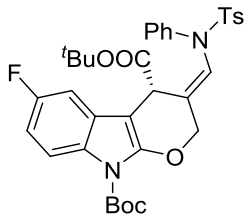


	Retention Time	Area	% Area
1	6.936	3351144	30.11
2	7.455	2127154	19.11
3	8.365	3523107	31.65
4	13.097	2129623	19.13

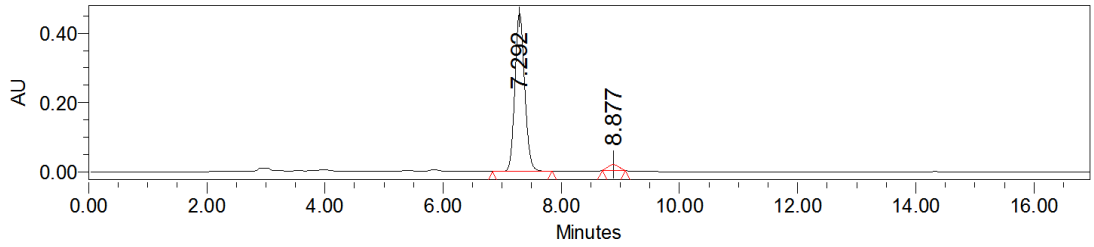


	Retention Time	Area	% Area
1	6.992	205374	1.03
2	7.537	789359	3.96
3	8.684	218925	1.10
4	13.240	18655176	93.90

Di-*tert*-butyl (*R*,*E*)-6-fluoro-3-{[(4-methyl-*N*-phenylphenyl)sulfonamide]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4ha)

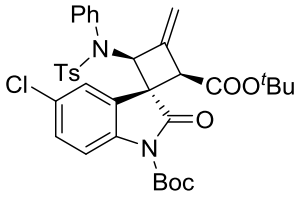


67% yield for two steps, White solid; **m.p.**: 168.7 – 178.5 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 226 nm), t_r (major) = 7.29 min, t_r (minor) = 8.88 min, ee = 92%. **3ha**:**4ha** < 1:19, determined by ^{1}H NMR. $[\alpha]^{21}_{D}$ = +148.7 (*c* = 0.38, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.83 – 7.80 (m, 1H), 7.48 – 7.43 (m, 2H), 7.36 – 7.29 (m, 3H), 7.22 – 7.20 (m, 2H), 7.10 – 7.08 (m, 2H), 6.93 – 6.90 (m, 1H), 6.87 (s, 1H), 6.82 – 6.76 (m, 1H), 5.12 (d, *J* = 11.6 Hz, 1H), 4.75 (d, *J* = 11.6 Hz, 1H), 3.93 (s, 1H), 2.38 (s, 3H), 1.65 (s, 9H), 1.24 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 169.2, 159.4 (d, *J* = 239.3 Hz), 149.5, 148.7, 144.4, 139.1, 134.3, 129.6, 129.5, 128.6, 128.4, 128.1, 128.0, 127.8, 127.2, 118.2, 115.7, 115.6, 108.8 (d, *J* = 24.2 Hz), 103.8 (d, *J* = 25.4 Hz), 89.6, 84.3, 81.9, 71.5, 38.4, 28.2, 27.8, 21.5 ppm; **^{19}F NMR (376 MHz, CDCl$_3$)** δ–120.46 ppm; **IR (neat) ν (cm^{-1}):** 2980, 1729, 1599, 1473, 1417, 1364, 1324, 1300, 1255, 1167, 1140, 1114, 1091, 1004, 967, 896, 843, 813, 766, 736, 696, 664; **HRMS** (ESI-FT) calcd for $C_{35}H_{37}FN_2O_7SNa^+$ ([M]+Na$^+$) = 671.2198, found 671.2198.

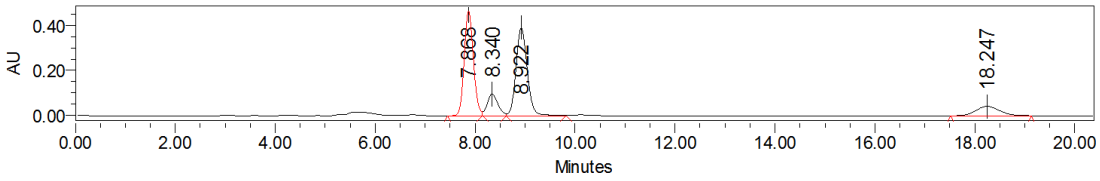


	Retention Time	Area	% Area
1	7.292	5255238	96.02
2	8.877	217622	3.98

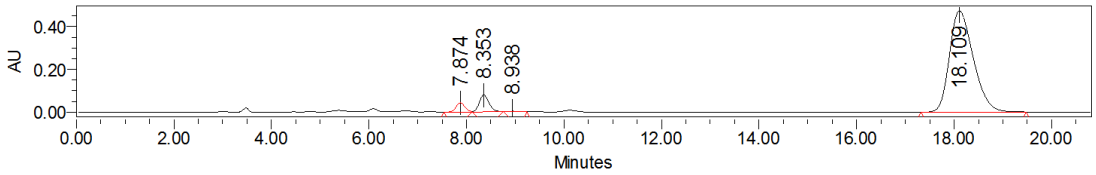
Di-*tert*-butyl (1*R*,2*R*,4*S*)-5'-chloro-4-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3ia)



72% yield, White solid; **m.p.**: 87.2 – 94.0 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 232 nm), t_r (major) = 18.11 min, t_r (minor) = 8.35 min, ee = 88%. **3ia**:**4ia** > 19:1, determined by ^{1}H NMR. $[\alpha]^{21}_{\lambda}$ = –60.9 (*c* = 0.40, in dichloromethane, λ = 436 nm). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.85 – 7.81 (m, 1H), 7.39 – 7.31 (m, 4H), 7.29 – 7.18 (m, 7H), 5.35 (p, *J* = 1.4 Hz, 1H), 5.26 – 5.21 (m, 1H), 3.98 – 3.96 (m, 1H), 3.94 – 3.91 (m, 1H), 2.41 (s, 3H), 1.66 (s, 9H), 1.00 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 174.3, 165.9, 148.9, 144.3, 140.0, 137.7, 137.6, 132.4, 129.3, 129.2, 129.0, 128.8, 128.6, 127.5, 123.9, 116.2, 111.3, 84.5, 81.8, 61.1, 56.1, 51.8, 28.1, 27.2, 21.6 ppm; **IR (neat) ν (cm^{-1}):** 2979, 1769, 1732, 1595, 1475, 1395, 1364, 1336, 1302, 1276, 1251, 1155, 1093, 1008, 862, 818, 739, 700, 667; **HRMS** (ESI-FT) calcd for $C_{35}H_{38}{}^{35}ClN_2O_7S^+$ ([M]+H$^+$) = 665.2083, found 665.2089; $C_{35}H_{38}{}^{37}ClN_2O_7S^+$ ([M]+H$^+$) = 667.2053, found 6667.2065.

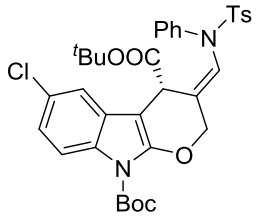


	Retention Time	Area	% Area
1	7.868	5929310	39.98
2	8.340	1431309	9.65
3	8.922	6094501	41.09
4	18.247	1376113	9.28

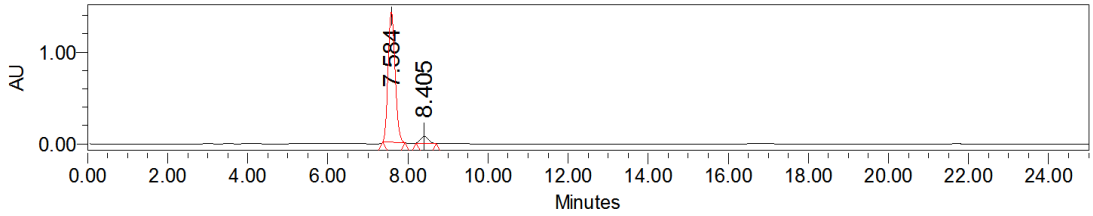


	Retention Time	Area	% Area
1	7.874	532722	3.01
2	8.353	1099930	6.22
3	8.938	29965	0.17
4	18.109	16019696	90.60

Di-*tert*-butyl (*R*,*E*)-6-chloro-3-{[(4-methyl-*N*-phenylphenyl)sulfonamide]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4ia)

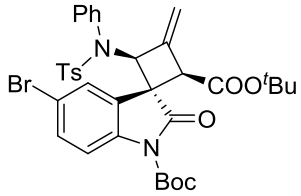


55% yield for two steps, White solid; **m.p.**: 171.4 – 179.4 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 232 nm), t_r (major) = 7.58 min, t_r (minor) = 8.41 min, ee = 89%. **3ia**:**4ia** < 1:19, determined by ^{1}H NMR. $[\alpha]^{22}_D$ = +132.4 (*c* = 0.41, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.82 – 7.79 (m, 1H), 7.48 – 7.44 (m, 2H), 7.37 – 7.31 (m, 3H), 7.25 – 7.24 (m, 1H), 7.23 – 7.19 (m, 2H), 7.10 – 7.02 (m, 3H), 6.86 (s, 1H), 5.11 (d, *J* = 11.6 Hz, 1H), 4.76 (d, *J* = 11.6 Hz, 1H), 3.98 (s, 1H), 2.38 (s, 3H), 1.65 (s, 9H), 1.24 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 169.2, 149.2, 148.6, 144.4, 139.2, 134.3, 129.6, 129.5, 129.4, 128.5, 128.34, 128.26, 128.2, 127.8, 121.6, 118.5, 117.5, 115.7, 89.2, 84.5, 82.0, 71.5, 38.4, 28.1, 27.8, 21.5 ppm; **IR (neat) ν (cm^{-1}):** 2979, 1732, 1624, 1594, 1469, 1412, 1351, 1297, 1147, 1091, 1003, 955, 840, 766, 697, 665; **HRMS** (ESI-FT) calcd for $C_{35}H_{37}{}^{35}ClN_2O_7SNa^+$ ([M]+Na$^+$) = 687.1902, found 687.1902; $C_{35}H_{37}{}^{37}ClN_2O_7SNa^+$ ([M]+Na$^+$) = 687.1873 found 687.1881.

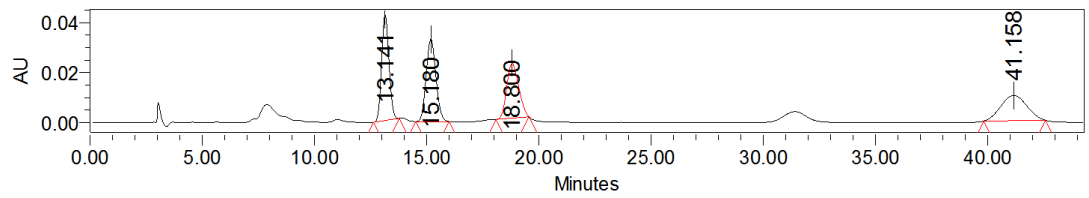


	Retention Time	Area	% Area
1	7.584	17292958	94.54
2	8.405	999010	5.46

Di-*tert*-butyl (1*R*,2*R*,4*S*)-5'-bromo-4-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3ja)

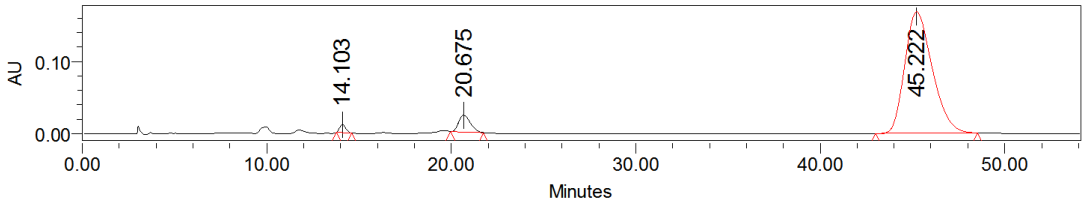


81% yield, White solid; **m.p.**: 81.8 – 88.7 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 95/5, flow rate 1.0 mL/min, λ = 231 nm), t_r (major) = 45.22 min, t_r (minor) = 20.68 min, ee = 88%. **3ja**:**4ja** > 19:1, determined by ^{1}H NMR. $[\alpha]^{23}_\lambda$ = –75.0 (*c* = 0.44, in dichloromethane, λ = 436 nm). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.79 – 7.77 (m, 1H), 7.52 – 7.50 (m, 1H), 7.47 – 7.46 (m, 1H), 7.43 – 7.26 (m, 3H), 7.25 – 7.08 (m, 6H), 5.36 – 5.33 (m, 1H), 5.25 – 5.22 (m, 1H), 3.99 – 3.96 (m, 1H), 3.94 – 3.91 (m, 1H), 2.41 (s, 3H), 1.66 (s, 9H), 1.01 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 174.1, 165.9, 148.9, 144.3, 140.4, 137.6, 132.6, 131.5 129.3, 129.0, 128.8, 127.9, 126.8, 116.69, 116.66, 111.4, 84.5, 81.8, 61.2, 56.0, 51.8, 28.1, 27.2, 21.6 ppm; **IR (neat) ν (cm^{-1}):** 2979, 1770, 1733, 1596, 1473, 1395, 1365, 1336, 1301, 1276, 1251, 1156, 1091, 1007, 890, 860, 817, 700, 666; **HRMS** (ESI-FT) calcd for $C_{35}H_{37}{}^{79}BrN_2O_7SNa^+$ ([M]+Na$^+$) = 731.1397, found 731.1393; $C_{35}H_{37}{}^{81}BrN_2O_7SNa^+$ ([M]+Na$^+$) = 733.1377, found 733.1375.



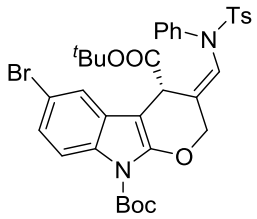
	Retention Time	Area	% Area
1	13.141	962051	26.91

2	15.180	992375	27.75
3	18.800	813267	22.75
4	41.158	807835	22.59

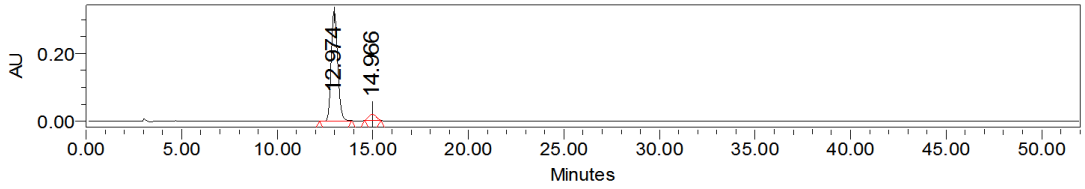


	Retention Time	Area	% Area
1	14.103	259446	1.39
2	20.675	1034993	5.53
3	45.222	17419146	93.08

Di-*tert*-butyl (*R*,*E*)-6-bromo-3-{[(4-methyl-*N*-phenylphenyl)sulfonamide]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4ja)

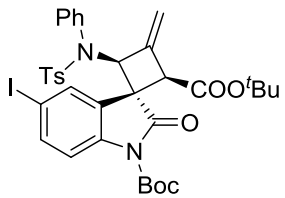


61% yield for two steps, White solid; **m.p.**: 173.4 – 179.4 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 95/5, flow rate 1.0 mL/min, λ = 231 nm), t_r (major) = 12.97 min, t_r (minor) = 14.97 min, ee = 88%. **3ja**:**4ja** < 1:19, determined by ^{1}H NMR. $[\alpha]^{23}_D$ = +106.5 (*c* = 0.41, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.77 – 7.75 (m, 1H), 7.47 – 7.43 (m, 2H), 7.42 – 7.40 (m, 1H), 7.36 – 7.31 (m, 3H), 7.23 – 7.16 (m, 3H), 7.12 – 7.06 (m, 2H), 6.85 (s, 1H), 5.10 (d, *J* = 11.6 Hz, 1H), 4.75 (d, *J* = 11.6 Hz, 1H), 3.98 (s, 1H), 2.38 (s, 3H), 1.65 (s, 9H), 1.23 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 169.1, 149.0, 148.6, 144.4, 139.2, 134.2, 129.8, 129.6, 129.5, 128.6, 128.5, 128.33, 128.29, 127.7, 124.4, 120.5, 118.5, 116.1, 116.1, 89.0, 84.5, 82.0, 71.5, 38.4, 28.1, 27.8, 21.6 ppm; **IR (neat) ν (cm^{-1}):** 2978, 1732, 1624, 1592, 1468, 1350, 1296, 1168, 1147, 1091, 1063, 1002, 953, 839, 697, 664; **HRMS** (ESI-FT) calcd for $C_{35}H_{37}{}^{79}BrN_2O_7SNa^+$ ([M]+Na$^+$) = 731.1397, found 731.1398; $C_{35}H_{37}{}^{81}BrN_2O_7SNa^+$ ([M]+Na$^+$) = 733.1377, found 733.1378.



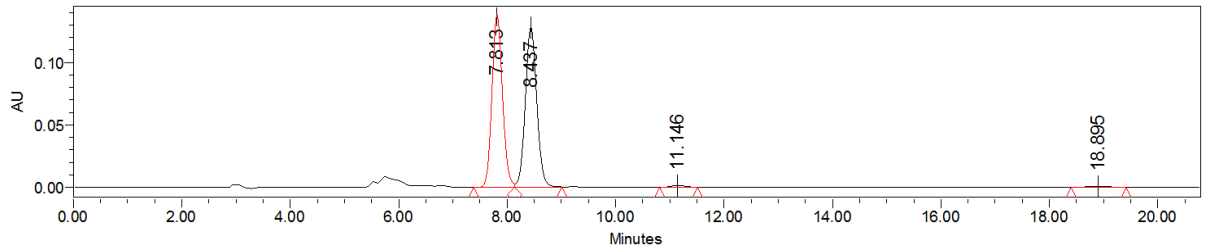
	Retention Time	Area	% Area
1	12.974	7607795	94.05
2	14.966	481060	5.95

Di-*tert*-butyl (1*R*,2*R*,4*S*)-5'-iodo-4-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3ka)

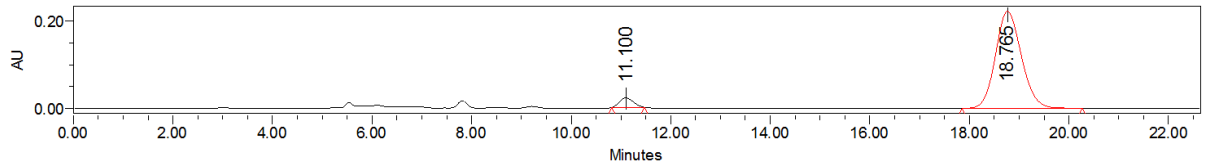


83% yield, White solid; **m.p.**: 88.6 – 95.3 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 237 nm), t_r (major) = 18.77 min, t_r (minor) = 11.10 min, ee = 90%. **3ka**:**4ka** > 19:1, determined by ^{1}H NMR. $[\alpha]^{22}_\lambda$ = –78.4 (*c* = 0.50, in dichloromethane, λ = 436 nm). **^{1}H NMR (400 MHz, CDCl$_3$)**

δ 7.73 – 7.26 (m, 8H), 7.24 – 7.12 (m, 4H), 5.35 – 5.32 (m, 1H), 5.25 – 5.22 (m, 1H), 3.97 – 3.95 (m, 1H), 3.93 – 3.91 (m, 1H), 2.41 (s, 3H), 1.66 (s, 9H), 1.00 (s, 9H). ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 174.0, 165.9, 148.8, 144.283 141.2, 137.53, 137.50, 137.47, 132.5, 132.4, 129.3, 129.1, 128.8, 128.1, 117.1, 111.5, 87.0, 84.5, 81.8 61.2, 55.9, 51.7, 28.1, 27.2, 21.7 ppm; **IR (neat) ν (cm^{-1}):** 2978, 1770, 1732, 1597, 1472, 1395, 1365, 1334, 1302, 1276, 1252, 1157, 1090, 1006, 890, 859, 817, 740, 700, 666; **HRMS** (ESI-FT) calcd for $C_{35}H_{37}IN_2O_7SNa^+$ ([M]+Na$^+$) = 779.1258, found 779.1259.

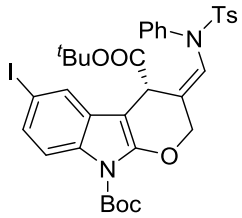


	Retention Time	Area	% Area
1	7.813	1864821	49.23
2	8.437	1871843	49.41
3	11.146	26652	0.70
4	18.895	24715	0.65

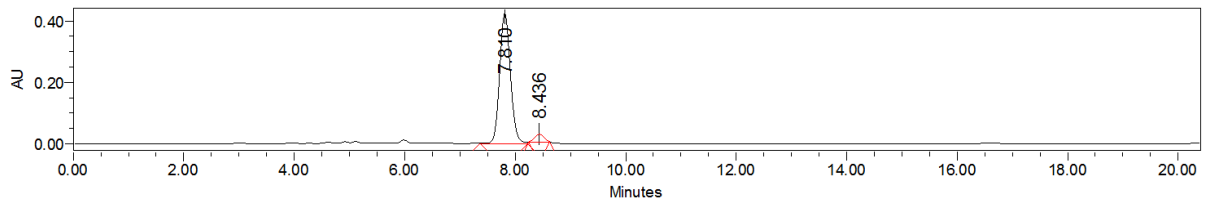


	Retention Time	Area	% Area
1	11.100	421564	5.00
2	18.765	8010895	95.00

Di-*tert*-butyl (*R*,*E*)-6-iodo-3-{[(4-methyl-*N*-phenylphenyl)sulfonamide]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4ka)

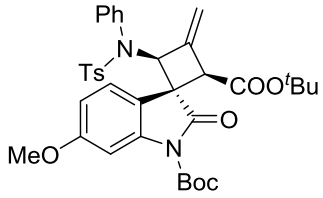


57% yield for two steps, White solid; **m.p.**: 147.1 – 153.8 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 237 nm), t_r (major) = 7.81 min, t_r (minor) = 8.44 min, ee = 90%. **3ka**:**4ka** < 1:19, determined by ^{1}H NMR. $[\alpha]^{22}_D$ = +83.2 (*c* = 0.19, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.68 – 7.61 (m, 2H), 7.48 – 7.44 (m, 2H), 7.39 – 7.29 (m, 4H), 7.22 – 7.20 (m, 2H), 7.11 – 7.06 (m, 2H), 6.84 (s, 1H), 5.11 (d, *J* = 11.6 Hz, 1H), 4.75 (d, *J* = 11.6 Hz, 1H), 3.99 (s, 1H), 2.38 (s, 3H), 1.64 (s, 9H), 1.24 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 169.1, 148.7, 144.4, 139.2, 134.3, 130.4, 130.2, 129.6, 129.5, 129.1, 128.5, 128.3, 127.8, 126.5, 118.9, 116.6, 88.7, 86.8, 84.6, 82.1, 71.5, 38.4, 28.2, 27.9, 21.6 ppm; **IR (neat) ν (cm^{-1}):** 2971, 1732, 1622, 1588, 1468, 1347, 1296 1146 1092, 1000 952, 892, 797,762, 696 669; **HRMS** (ESI-FT) calcd for $C_{35}H_{37}IN_2O_7SNa^+$ ([M]+Na$^+$) = 779.1258, found 779.1259.

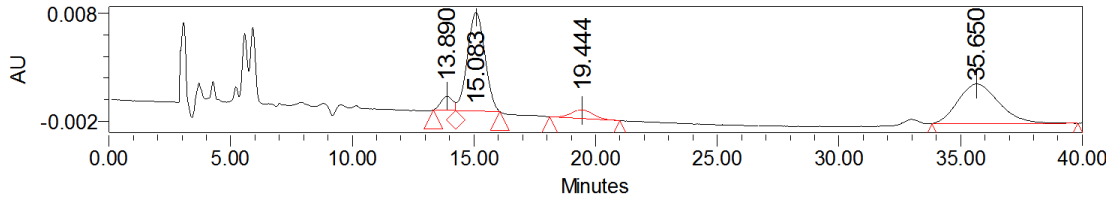


	Retention Time	Area	% Area
1	7.810	5742252	94.99
2	8.436	302920	5.01

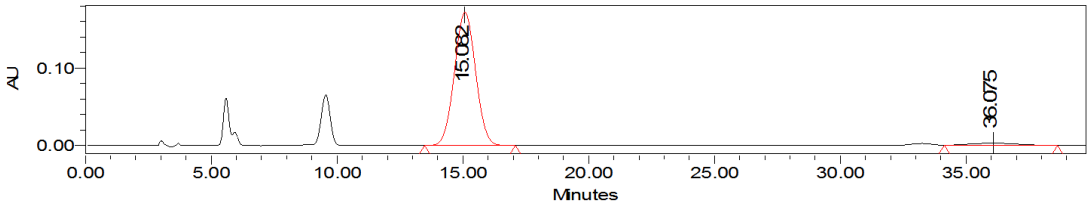
Di-*tert*-butyl (1*R*,2*R*,4*S*)-6'-methoxy-4-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3la)



84% yield, White solid; **m.p.**: 88.4 – 93.1 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel AD-H, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 226 nm), t_r (major) = 15.08 min, t_r (minor) = 36.08 min, ee = 93%. **3la**:**4la** > 19:1, determined by ^{1}H NMR. $[\alpha]^{22}_{\lambda}$ = –74.7 (*c* = 0.95, in dichloromethane, λ = 436 nm). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.53 – 7.51 (m, 1H), 7.33 – 7.28 (m, 2H), 7.25 – 7.12 (m, 8H), 6.72 – 6.69 (m, 1H), 5.30 – 5.28 (m, 1H), 5.22 – 5.19 (m, 1H), 3.95 – 3.93 (m, 1H), 3.90 – 3.88 (m, 1H), 3.85 (s, 3H), 2.40 (s, 3H), 1.66 (s, 9H), 0.98 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 175.3, 166.3, 160.3, 149.0, 144.1, 142.4, 138.2, 137.9, 132.5, 129.9, 129.6, 129.20, 129.17, 129.0, 128.84, 128.77, 128.6, 127.6, 124.3, 117.2, 110.6, 109.1, 102.2, 84.0, 81.3, 61.1, 55.7, 55.5, 51.9, 28.1, 27.3, 21.6 ppm; **IR (neat) ν (cm^{-1}):** 2978, 1793, 1767, 1731, 1618, 1495, 1452, 1366, 1307, 1254, 1207, 1154, 1090, 1022, 903, 851, 819, 700, 671; **HRMS** (ESI-FT) calcd for $C_{36}H_{40}N_2O_8SNa^+$ ([M]+Na$^+$) = 683.2398, found 683.2402.

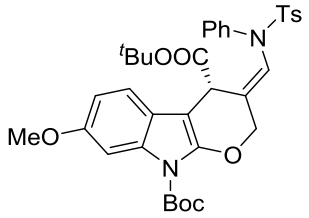


	Retention Time	Area	% Area
1	13.890	44169	4.50
2	15.083	456195	46.50
3	19.444	50752	5.17
4	35.650	429978	43.83



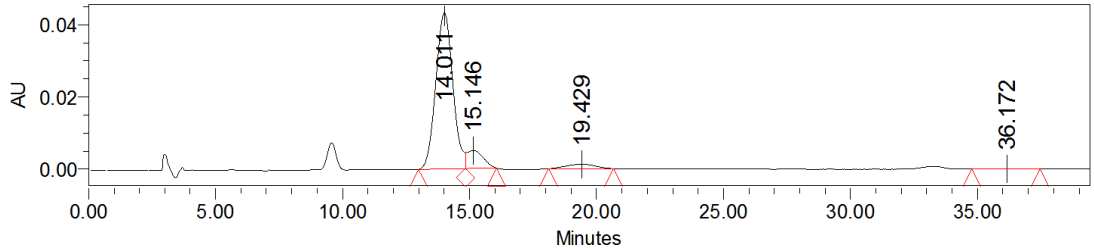
	Retention Time	Area	% Area
1	15.082	10048453	96.51
2	36.075	363375	3.49

Di-*tert*-butyl (*R*,*E*)-7-methoxy-3-{[(4-methyl-*N*-phenylphenyl)sulfonamide]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4la)



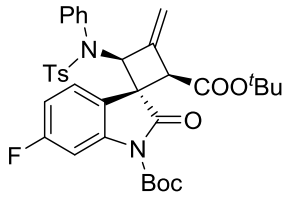
33% yield for two steps, Yellow oil; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel AD-H, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 226 nm), t_r (major) = 14.01 min, t_r (minor) = 19.43 min, ee = 91%. **3la**:**4la** = 1:9, determined by ^{1}H NMR. $[\alpha]^{23}_{D}$ = +73.8 (*c* = 0.26, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.55 – 7.53 (m, 1H), 7.48 – 7.44 (m, 2H), 7.33 – 7.28 (m, 3H), 7.24 – 7.18 (m, 2H), 7.15 – 7.13 (m, 1H), 7.10 – 7.07 (m, 2H), 6.80 (s, 1H), 6.77 – 6.74 (m, 1H), 5.10 (d, *J* = 11.6 Hz, 1H), 4.71 (d, *J* = 11.6 Hz, 1H), 3.99 (s, 1H), 3.81 (s, 3H), 2.38 (s, 3H), 1.66 (s, 9H), 1.23 (s, 9H) ppm;

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.5, 155.9, 149.0, 147.4, 144.3, 139.3, 134.4, 131.8, 129.6, 129.4, 129.2, 128.9, 128.5, 128.2, 127.8, 127.7, 121.8, 120.6, 119.8, 118.1, 110.7, 100.5, 89.3, 84.0, 81.6, 71.1, 55.7, 38.6, 28.2, 27.9, 21.5 ppm; **IR (neat) ν (cm^{-1}):** 2978, 1731, 1627, 1486, 1453, 1352, 1301, 1256, 1147, 1113, 1016, 939, 845, 771, 695, 665; **HRMS** (ESI-FT) calcd for $C_{36}H_{40}N_2O_8SNa^+$ ([M]+Na^+) = 683.2398, found 683.2402.

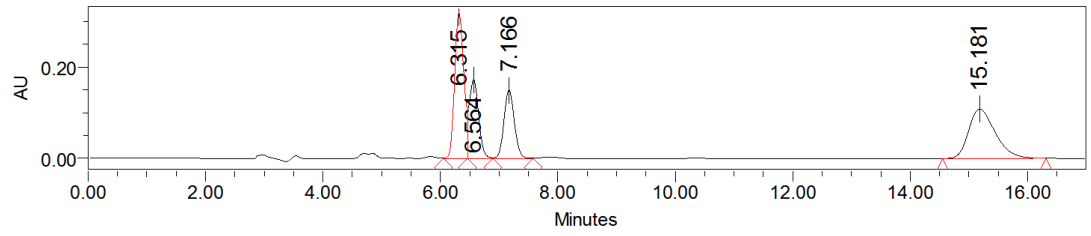


	Retention Time	Area	% Area
1	14.011	2023372	86.26
2	15.146	221600	9.45
3	19.429	97213	4.14
4	36.172	3446	0.15

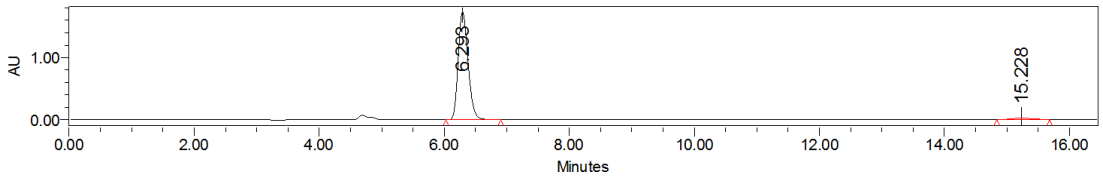
Di-*tert*-butyl (1*R*,2*R*,4*S*)-6'-fluoro-4-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3ma)



90% yield, White solid; **m.p.**: 87.2 – 93.5 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 224 nm), t_r (major) = 6.29 min, t_r (minor) = 15.23 min, ee = 93%. **3ma**:**4ma** > 19:1, determined by ^{1}H NMR. $[\alpha]^{22}_{\lambda}$ = –76.5 (*c* = 0.49, in dichloromethane, λ = 436 nm). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 – 7.63 (m, 1H), 7.42 – 7.26 (m, 4H), 7.25 – 7.16 (m, 6H), 6.91 – 6.87 (m, 1H), 5.33 – 5.30 (m, 1H), 5.22 – 5.20 (m, 1H), 3.96 – 3.93 (m, 1H), 3.92 – 3.90 (m, 1H), 2.41 (s, 3H), 1.67 (s, 9H), 0.99 (s, 9H) ppm; **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)** δ 74.8, 166.1, 163.0 (d, *J* = 245.4 Hz), 148.8, 144.3, 142.6, 142.5, 137.8, 137.82, 132.2, 129.3, 129.0, 128.9, 128.7, 124.7 (d, *J* = 9.6 Hz), 121.0 (d, *J* = 2.9 Hz), 111.0, 110.4 (d, *J* = 22.5 Hz), 104.0 (d, *J* = 29.8 Hz), 84.7, 81.7, 61.1, 55.7, 52.0, 28.1, 27.3, 21.7 ppm; **^{19}F NMR (376 MHz, $CDCl_3$)** δ –110.7 ppm; **IR (neat) ν (cm^{-1}):** 2981, 1771, 1734, 1611, 1493, 1445, 1368, 1303, 1255, 1153, 1089, 1011, 907, 851, 701, 672; **HRMS** (ESI-FT) calcd for $C_{35}H_{37}FN_2O_7SNa^+$ ([M]+Na^+) = 671.2198, found 671.2194.

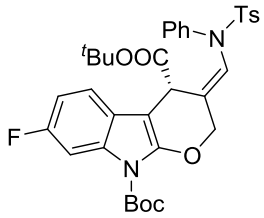


	Retention Time	Area	% Area
1	6.315	3480574	32.68
2	6.564	1906987	17.91
3	7.166	1856195	17.43
4	15.181	3405589	31.98

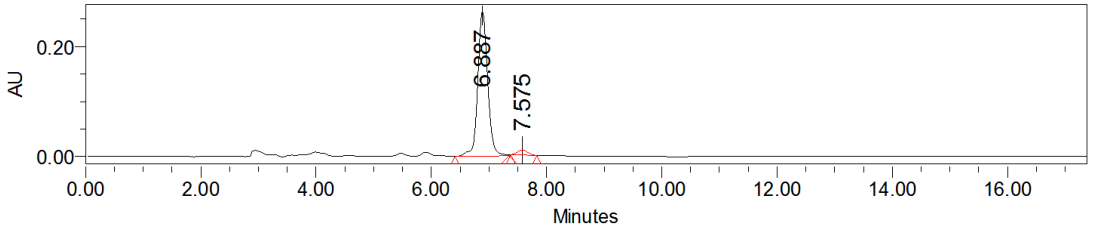


	Retention Time	Area	% Area
1	6.293	19093306	96.69
2	15.228	653124	3.31

Di-*tert*-butyl (*R*,*E*)-7-fluoro-3-{[(4-methyl-*N*-phenylphenyl)sulfonamide]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4ma)

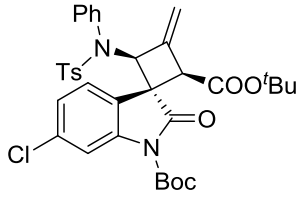


62% yield for two steps, White solid; **m.p.**: 185.7 – 195.1 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 224 nm), t_r (major) = 6.89 min, t_r (minor) = 7.58 min, ee = 93%. **3ma**:**4ma** < 1:19, determined by ^{1}H NMR. $[\alpha]^{23}_D$ = +129.1 (*c* = 0.37, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.66 – 7.62 (m, 1H), 7.47 – 7,45 (m, 2H), 7.34 – 7.28 (m, 3H), 7.22 – 7.20 (m, 2H), 7.17 – 7.14 (m, 1H), 7.11 – 7.07 (m, 2H), 6.90 – 6.84 (m, 1H), 6.82 (s, 1H), 5.10 (d, *J* = 10.8 Hz, 1H), 4.73 (d, *J* = 11.2 Hz, 1H), 4.00 (s, 1H), 2.38 (s, 3H), 1.66 (s, 9H), 1.23 (s, 9H). ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 148.7, 148.3, 144.4, 139.2, 134.3, 131.1 (d, *J* = 12.9 Hz), 129.6, 129.5, 128.5, 128.3, 128.0, 127.8, 123.0, 119.1, 118.0, 117.9, 110.2 (d, *J* = 23.4 Hz), 102.7 (d, *J* = 29.7 Hz), 89.2, 84.6, 81.8, 71.3, 38.5, 28.1, 27.8, 21.5 ppm; **^{19}F NMR (376 MHz, CDCl$_3$)** δ –120.3 ppm; **IR (neat) ν (cm^{-1}):** 2979, 1731, 1627, 1486, 1453, 1352, 1301, 1256, 1147, 1113, 1016, 939, 845, 814, 769, 697, 668; **HRMS** (ESI-FT) calcd for $C_{35}H_{37}FN_2O_7SNa^+$ ([M]+Na$^+$) = 671.2198, found 671.2196.

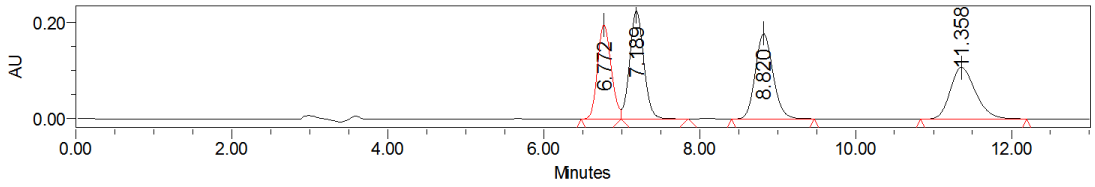


	Retention Time	Area	% Area
1	6.887	3147124	96.45
2	7.575	115803	3.55

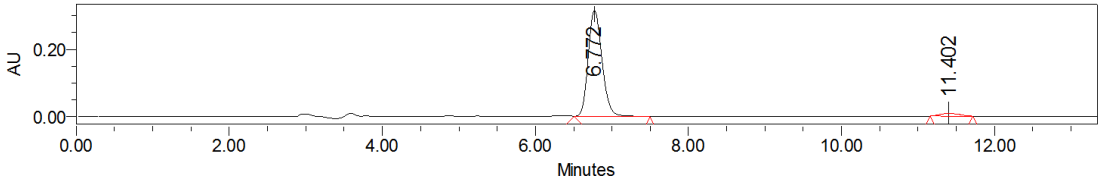
Di-*tert*-butyl (1*R*,2*R*,4*S*)-6'-chloro-4-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3na)



81% yield, White solid; **m.p.**: 91.1 – 97.4 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 225 nm), t_r (major) = 6.77 min, t_r (minor) = 11.40 min, ee = 93%. **3na**:**4na** > 19:1, determined by ^{1}H NMR. $[\alpha]^{20}_\lambda$ = –40.5 (*c* = 0.37, in dichloromethane, λ = 436 nm). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.95 – 7.94 (m, 1H), 7.36 – 7.16 (m, 11H), 5.32 – 5.30 (m, 1H), 5.23 – 5.21 (m, 1H), 3.95 – 3.89 (m, 2H), 2.41 (s, 3H), 1.67 (s, 9H), 1.00 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 174.4, 166.0, 148.8, 144.3, 142.3, 137.8, 137.7, 134.5, 132.3, 129.2, 129.0, 128.8, 128.7, 124.5, 124.0, 123.7, 115.8, 111.0, 84.7, 81.7, 61.0, 55.8, 51.9, 28.1, 27.3, 21.6 ppm; **IR (neat) ν (cm^{-1}):** 2927, 1770, 1733, 1606, 1483, 1425, 1366, 1341, 1298, 1246, 1154, 1089, 1013, 845, 816, 700, 670, 602; **HRMS** (ESI-FT) calcd for $C_{35}H_{37}{}^{35}ClN_2O_7SNa^+$ ([M]+Na$^+$) = 687.1902, found 687.1896; $C_{35}H_{37}{}^{37}ClN_2O_7SNa^+$ ([M]+Na$^+$) = 687.1873 found 687.1874.

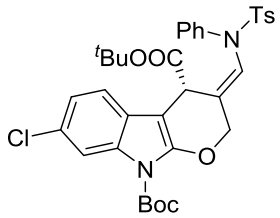


	Retention Time	Area	% Area
1	6.772	2370812	22.81
2	7.189	2816261	27.10
3	8.820	2797732	26.92
4	11.358	2408980	23.18

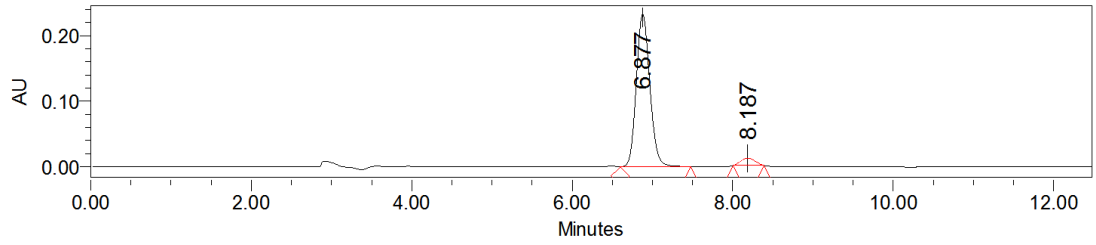


	Retention Time	Area	% Area
1	6.772	3965455	96.59
2	11.402	140115	3.41

Di-*tert*-butyl (*R*,*E*)-7-chloro-3-{[(4-methyl-*N*-phenylphenyl)sulfonamide]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4na)

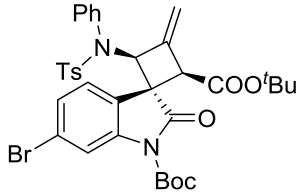


54% yield for two steps, White solid; **m.p.**: 191.5 – 197.4 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 225 nm), t_r (major) = 6.88 min, t_r (minor) = 8.19 min, ee = 90%. **3na**:**4na** < 1:19, determined by ^{1}H NMR. $[\alpha]^{23}_{D}$ = +90.6 (*c* = 0.35, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.94 – 7.92 (m, 1H), 7.46 – 7.44 (m, 2H), 7.35 – 7.28 (m, 3H), 7.22 – 7.20 (m, 2H), 7.15 – 7.10 (m, 1H), 7.10 – 7.07 (m, 3H), 5.11 (d, *J* = 11.2 Hz, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 3.97 (s, 1H), 2.38 (s, 3H), 1.66 (s, 9H), 1.22 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 169.2, 148.6, 144.4, 139.2, 134.3, 131.4, 129.6, 129.5, 128.6, 128.3, 128.1, 127.8, 127.3, 125.4, 123.0, 118.6, 118.3, 115.2, 89.4, 84.7, 81.9, 71.4, 38.4, 28.1, 27.8, 21.6 ppm; **IR (neat) ν (cm^{-1}):** 2979, 1731, 1624, 1597, 1470, 1410, 1347, 1295, 1249, 1149, 1123, 1091, 1013, 926, 841, 816, 764, 697, 663; **HRMS** (ESI-FT) calcd for $C_{35}H_{37}{}^{35}ClN_2O_7SNa^+$ ([M]+Na$^+$) = 687.1902, found 687.1891; $C_{35}H_{37}{}^{37}ClN_2O_7SNa^+$ ([M]+Na$^+$) = 687.1873 found 687.1874.

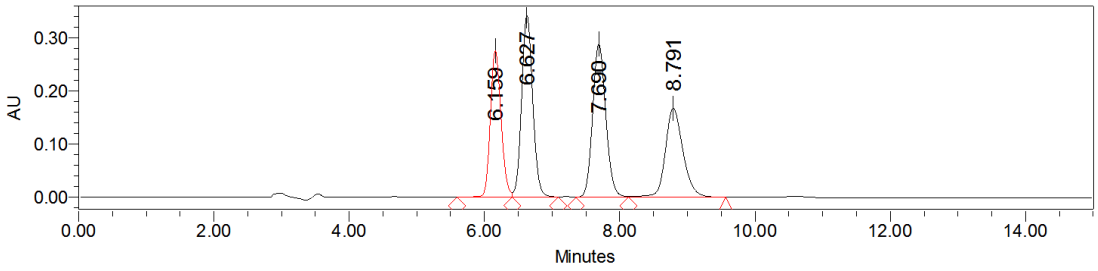


	Retention Time	Area	% Area
1	6.877	2714192	95.17
2	8.187	137647	4.83

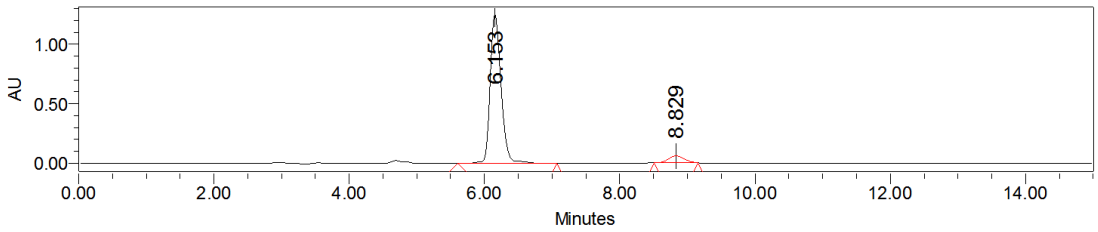
Di-*tert*-butyl (1*R*,2*R*,4*S*)-6'-bromo-4-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3oa)



86% yield, White solid; **m.p.**: 98.1 – 107.4 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 225 nm), t_r (major) = 6.15 min, t_r (minor) = 8.83 min, ee = 87%. **3oa**:**4oa** > 19:1, determined by ^{1}H NMR. $[\alpha]^{22}_{\lambda}$ = –29.1 (*c* = 0.48, in dichloromethane, λ = 436 nm). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.11 – 8.10 (m, 1H), 7.35 – 7.19 (m, 11H), 5.32 – 5.29 (m, 1H), 5.23 – 5.21 (m, 1H), 3.92 – 3.90 (m, 2H), 2.41 (s, 3H), 1.67 (s, 9H), 0.99 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 174.3, 166.0, 148.7, 144.3, 142.5, 137.72, 137.66, 132.2, 129.3, 129.0, 128.8, 126.7, 124.9, 124.6, 122.4, 118.6, 111.1, 84.7, 81.8, 60.9, 55.9, 51.8, 28.1, 27.2, 21.6 ppm; **IR (neat) ν (cm^{-1}):** 2978, 1771, 1733, 1602, 1478, 1420, 1366, 1340, 1297, 1245, 1154, 1090, 1012, 859, 816, 760, 700, 668; **HRMS** (ESI-FT) calcd for $C_{35}H_{37}{}^{79}BrN_2O_7SNa^+$ ([M]+Na$^+$) = 731.1397, found 731.1392; $C_{35}H_{37}{}^{81}BrN_2O_7SNa^+$ ([M]+Na$^+$) = 733.1377, found 733.1376.

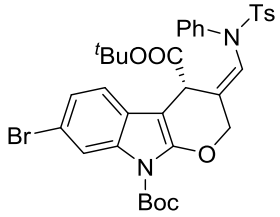


	Retention Time	Area	% Area
1	6.159	3039289	21.85
2	6.627	3918016	28.17
3	7.690	3906263	28.09
4	8.791	3043275	21.88



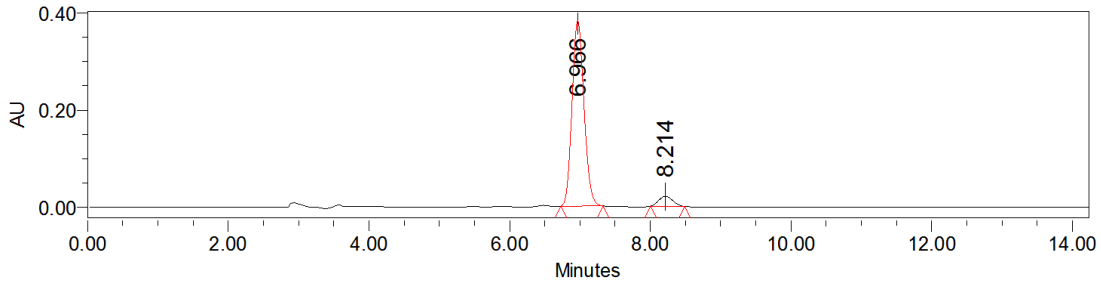
	Retention Time	Area	% Area
1	6.153	13980721	93.66
2	8.829	946714	6.34

Di-*tert*-butyl (*R*,*E*)-7-bromo-3-{[(4-methyl-*N*-phenylphenyl)sulfonamide]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4oa)



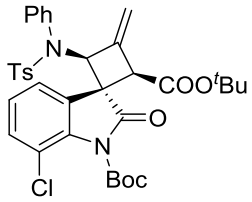
57% yield for two steps, White solid; **m.p.**: 192.5 – 199.7 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 225 nm), t_r (major) = 6.97 min, t_r (minor) = 8.21 min, ee = 88%. **3oa**:**4oa** < 1:19, determined by ^{1}H NMR. $[\alpha]^{23}_{D}$ = +87.4 (*c* = 0.36, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.10 – 8.08 (m, 1H), 7.46 – 7.44 (m, 2H), 7.35 – 7.28 (m, 3H), 7.24 – 7.20 (m, 3H), 7.11 – 7.06 (m, 3H), 6.85 (s, 1H), 5.11 (d, *J* = 11.6 Hz, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 3.97 (s, 1H), 2.38 (s, 3H), 1.66 (s, 9H), 1.22 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz,**

$CDCl_3$) δ 169.2, 148.6, 148.5, 144.4, 139.2, 134.3, 131.7, 129.6, 129.5, 128.6, 128.3, 128.1, 127.8, 125.8, 118.7, 118.5, 117.9, 114.8, 89.4, 84.7, 81.9, 71.4, 38.4, 28.1, 27.8, 21.6 ppm; **IR (neat) ν (cm^{-1}):** 2978, 1731, 1623, 1597, 1470, 1410, 1347, 1295, 1249, 1149, 1123, 1091, 1013, 926, 841, 816, 764, 697, 663; **HRMS** (ESI-FT) calcd for $C_{35}H_{37}{}^{79}BrN_2O_7SNa^+$ ([M+Na^+]) = 731.1397, found 731.1397; $C_{35}H_{37}{}^{81}BrN_2O_7SNa^+$ ([M+Na^+]) = 733.1377, found 733.1377.

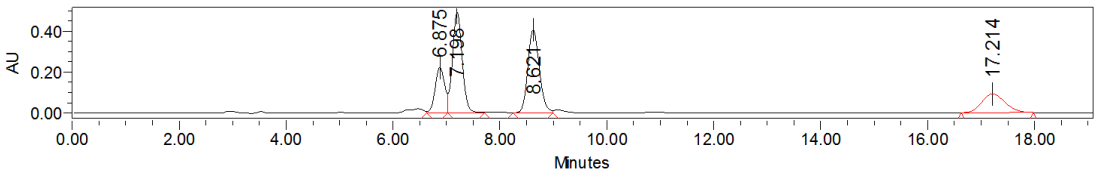


	Retention Time	Area	% Area
1	6.966	4504465	94.00
2	8.214	287326	6.00

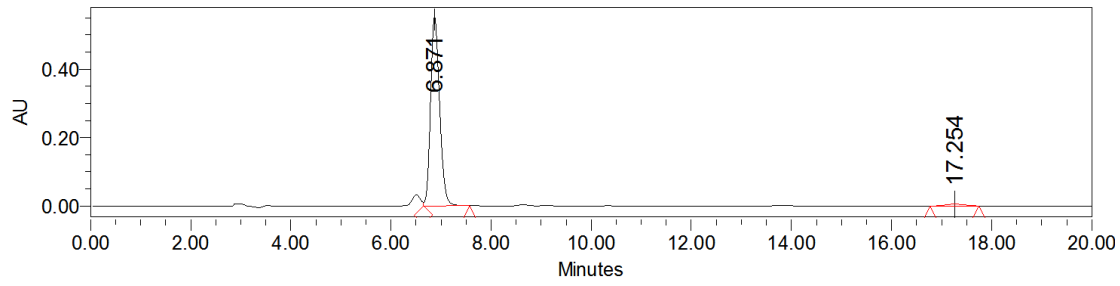
Di-*tert*-butyl (1*R*,2*R*,4*S*)-7'-chloro-4-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3pa)



83% yield, White solid; **m.p.**: 89.5 – 95.8 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 225 nm), t_r (major) = 6.87 min, t_r (minor) = 17.25 min, ee = 96%. **3pa**:**4pa** > 19:1, determined by ^{1}H NMR. $[\alpha]^{23}_{\lambda}$ = –27.5 (*c* = 0.45, in dichloromethane, λ = 405 nm). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 – 7.26 (m, 4H), 7.26 – 7.17 (m, 7H), 7.11 – 7.07 (m, 1H), 5.35 – 5.34 (m, 1H), 5.23 – 5.21 (m, 1H), 4.03 – 4.01 (m, 1H), 3.95 – 3.93 (m, 1H), 2.40 (s, 3H), 1.62 (s, 9H), 1.00 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 174.8, 166.0, 147.5, 144.2, 138.8, 137.9, 137.8, 132.7, 130.4, 129.3, 128.90, 128.86, 128.8, 128.7, 124.6, 122.2, 119.4, 111.0, 84.8, 81.8, 61.7, 56.6, 51.2, 27.7, 27.4, 21.6 ppm; **IR (neat) ν (cm^{-1}):** 2980, 1737, 1598, 1451, 1366, 1253, 1152, 1010, 894, 857, 815, 701, 669; **HRMS** (ESI-FT) calcd for $C_{35}H_{37}{}^{35}ClN_2O_7SNa^+$ ([M+Na^+]) = 687.1902, found 687.1902; $C_{35}H_{37}{}^{37}ClN_2O_7SNa^+$ ([M+Na^+]) = 687.1873 found 687.1882.

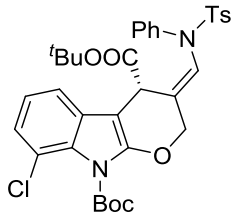


	Retention Time	Area	% Area
1	6.875	2756507	15.50
2	7.198	6224354	35.01
3	8.621	6037310	33.96
4	17.214	2760812	15.53

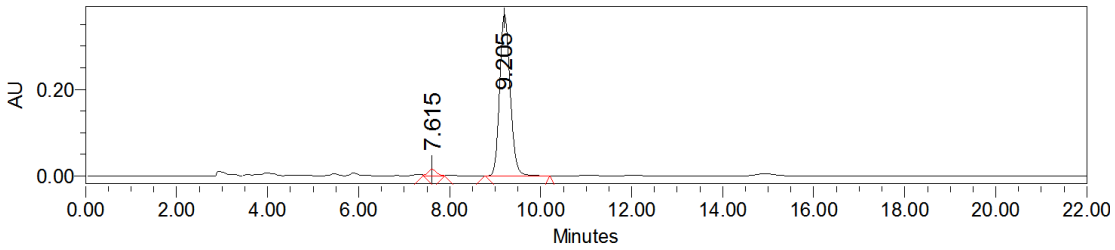


	Retention Time	Area	% Area
1	6.871	6968158	97.96
2	17.254	145009	2.04

Di-*tert*-butyl (*R*,*E*)-8-chloro-3-{[(4-methyl-*N*-phenylphenyl)sulfonamide]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4pa)

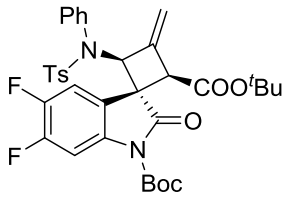


61% yield for two steps, White solid; **m.p.**: 173.6 – 181.3 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 225 nm), t_r (major) = 9.21 min, t_r (minor) = 7.62 min, ee = 94%. **3pa**:**4pa** < 1:19, determined by ^{1}H NMR. $[\alpha]^{23}_D$ = +99.7 (*c* = 0.30, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.50 – 7.43 (m, 2H), 7.35 – 7.29 (m, 3H), 7.22 – 7.18 (m, 2H), 7.16 – 7.14 (m, 1H), 7.11 – 7.07 (m, 2H), 7.07 – 6.98 (m, 2H), 5.11 (d, *J* = 11.6 Hz, 1H), 4.73 (d, *J* = 12.0 Hz, 1H), 3.98 (s, 1H), 2.36 (s, 3H), 1.63 (s, 9H), 1.23 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 169.4, 149.0, 147.8, 144.4, 139.2, 134.3, 130.0, 129.6, 129.5, 128.6, 128.3, 128.2, 127.8, 123.2, 123.0, 119.0, 116.3, 87.7, 85.0, 81.8, 71.6, 38.4, 27.9, 27.8, 21.5 ppm; **IR (neat) ν (cm^{-1}):** 2980, 1753, 1727, 1628, 1598, 1460, 1366, 1335, 1303, 1250, 1143, 1091, 999, 952, 841, 775, 731, 697, 662; **HRMS** (ESI-FT) calcd for $C_{35}H_{37}{}^{35}ClN_2O_7SNa^+$ ([M]+Na$^+$) = 687.1902, found 687.1902; $C_{35}H_{37}{}^{37}ClN_2O_7SNa^+$ ([M]+Na$^+$) = 687.1873 found 687.1878.

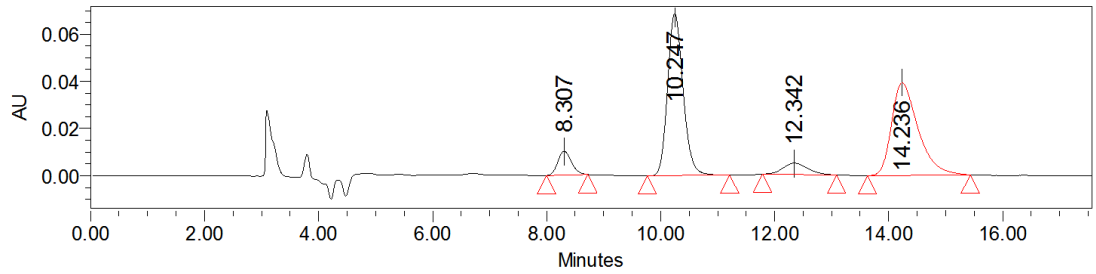


	Retention Time	Area	% Area
1	7.615	189635	3.07
2	9.205	5991758	96.93

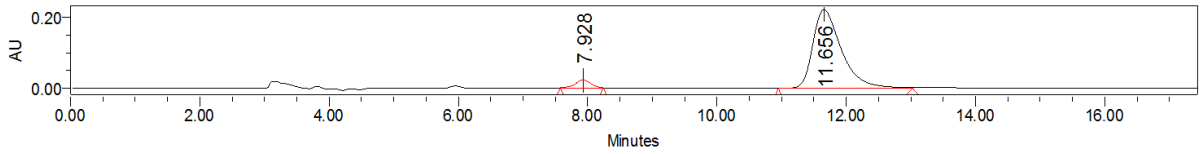
Di-*tert*-butyl (1*R*,2*R*,4*S*)-5',6'-difluoro-4-[(4-methyl-*N*-phenylphenyl)sulfonamide]-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3qa)



76% yield, White solid; **m.p.**: 82.6 – 89.1 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IB, hexane/^{i}PrOH = 95/5, flow rate 1.0 mL/min, λ = 224 nm), t_r (major) = 11.66 min, t_r (minor) = 7.93 min, ee = 92%. **3qa**:**4qa** > 19:1, determined by ^{1}H NMR. $[\alpha]^{23}_\lambda$ = –62.2 (*c* = 0.47, in dichloromethane, λ = 436 nm). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.83 – 7.78 (m, 1H), 7.37 – 7.29 (m, 2H), 7.27 – 7.21 (m, 8H), 5.34 – 5.31 (m, 1H), 5.20 – 5.17 (m, 1H), 3.94 – 3.90 (m, 2H), 2.42 (s, 3H), 1.67 (s, 9H), 1.04 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 174.1, 165.8 149.0 (d, *J* = 13.6 Hz), 148.6, 148.3 (d, *J* = 13.6 Hz), 144.5, 137.7, 137.4, 131.9, 129.4, 129.0, 128.9, 121.3 (dd, *J* = 7.0, 3.9 Hz), 112.8 (d, *J* = 20.5 Hz), 111.2, 105.7 (d, *J* = 25.1 Hz), 84.8, 81.8, 61.0, 55.8, 51.9, 28.1, 27.3, 21.6 ppm; **^{19}F NMR (376 MHz, CDCl$_3$)** δ –135.4 (d, *J* = 20.7 Hz, 1F), –143.3 (d, *J* = 20.7 Hz, 1F) ppm; **IR (neat) ν (cm^{-1}):** 2979, 1773, 1734, 1623, 1597, 1496, 1454, 1391, 1301, 1254, 1149, 1088, 1011, 883, 851, 816, 792, 700, 671; **HRMS** (ESI-FT) calcd for $C_{35}H_{36}F_2N_2O_7SNa^+$ ([M]+Na$^+$) = 689.2103, found 689.2091.

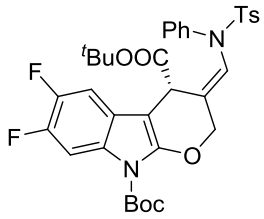


	Retention Time	Area	% Area
1	8.307	169404	5.87
2	10.247	1299542	45.04
3	12.342	144599	5.01
4	14.236	1271520	44.07

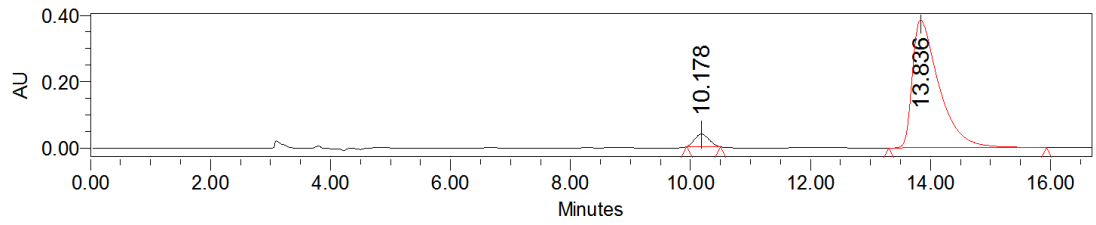


	Retention Time	Area	% Area
1	7.928	270984	3.97
2	11.656	6553496	96.03

Di-*tert*-butyl (*R*,*E*)-6,7-difluoro-3-{[(4-methyl-*N*-phenylphenyl)sulfonamido]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4qa)

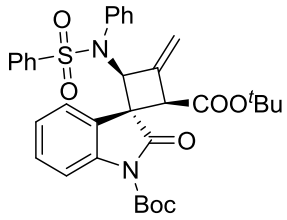


57% yield for two steps, White solid; **m.p.**: 200.2 – 206.8 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IB, hexane/^{i}PrOH = 95/5, flow rate 1.0 mL/min, λ = 224 nm), t_r (major) = 13.84 min, t_r (minor) = 10.18 min, ee = 90%. **3qa**:**4qa** < 1:19, determined by ^{1}H NMR. $[\alpha]^{23}_D$ = +125.6 (*c* = 0.46, in dichloromethane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 – 7.74 (m, 1H), 7.48 – 7.43 (m, 2H), 7.37 – 7.30 (m, 3H), 7.23 – 7.21 (m, 2H), 7.09 – 7.07 (m, 2H), 7.03 – 6.98 (m, 1H), 6.86 (s, 1H), 5.07 (d, *J* = 11.6 Hz, 1H), 4.74 (d, *J* = 11.6 Hz, 1H), 3.91 (s, 1H), 2.39 (s, 3H), 1.65 (s, 9H), 1.24 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 169.1, 148.9, 148.4, 144.4, 139.1, 134.2, 129.6, 129.5, 128.6, 128.4, 128.3, 127.8, 126.0 (d, *J* = 11.5 Hz), 122.7 (d, *J* = 9.7 Hz), 117.9, 105.1 (d, *J* = 20.7 Hz), 104.5 (d, *J* = 24.8 Hz), 89.1, 84.8, 82.0, 71.5, 38.4, 28.1, 27.8, 21.6 ppm; **^{19}F NMR (376 MHz, $CDCl_3$)** δ –144.31 (d, *J* = 21.1 Hz, 1F), –144.61 (d, *J* = 20.7 Hz, 1F) ppm; **IR (neat) ν (cm^{-1}):** 2980, 1731, 1612, 1481, 1362, 1301, 1169, 1141, 1091, 1013, 940, 841, 777, 697, 667; **HRMS** (ESI-FT) calcd for $C_{35}H_{36}F_2N_2O_7SNa^+$ ([M]+Na^+) = 689.2103, found 689.2098.

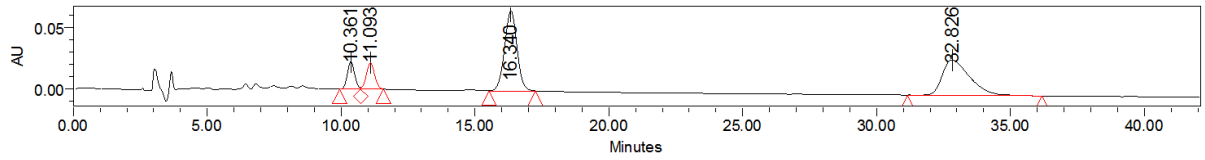


	Retention Time	Area	% Area
1	10.178	624196	5.00
2	13.836	11855878	95.00

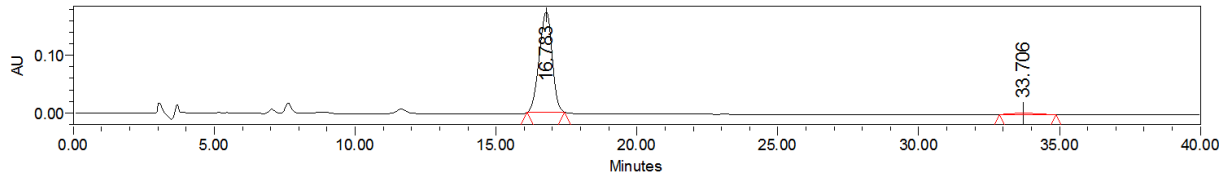
Di-*tert*-butyl (1*R*,2*R*,4*S*)-3-methylene-2'-oxo-4-(*N*-phenylphenylsulfonamido)spiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3ab)



94% yield, White solid; **m.p.**: 167.4 – 174.1 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 95/5, flow rate 1.0 mL/min, λ = 220 nm), t_r (major) = 16.78 min, t_r (minor) = 33.71 min, ee = 95%. **3ab**:**4ab** > 19:1, determined by ^{1}H NMR. $[\alpha]^{22}_{\lambda}$ = –88.6 (*c* = 0.47, in dichloromethane, λ = 436 nm). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.88 – 7.85 (m, 1H), 7.58 – 7.54 (m, 1H), 7.42 – 7.26 (m, 9H), 7.25 – 7.14 (m, 3H), 5.34 – 5.31 (m, 1H), 5.29 – 5.26 (, 1H), 3.96 – 3.92 (m, 2H), 1.67 (s, 9H), 0.94 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 174.9, 166.2, 149.0, 141.4, 138.0, 137.7, 135.4, 133.2, 128.9, 128.8, 128.7, 128.6, 125.4, 123.81, 123.77, 115.0, 110.8, 84.1, 81.5, 61.0, 56.0, 51.9, 28.1, 27.2 ppm; **IR (neat) ν (cm^{-1}):** 2978, 1794, 1766, 1733, 1609, 1482, 1366, 1299, 1251, 1155, 1088, 1007, 891, 858, 757, 696; **HRMS** (ESI-FT) calcd for $C_{34}H_{36}N_2O_7SNa^+$ ([M]+Na$^+$) = 639.2135, found 639.2135.

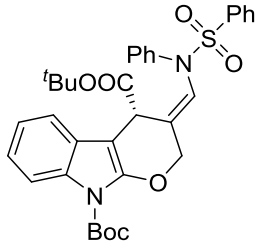


	Retention Time	Area	% Area
1	10.361	417343	8.26
2	11.093	454217	8.99
3	16.340	2106283	41.68
4	32.826	2075949	41.08

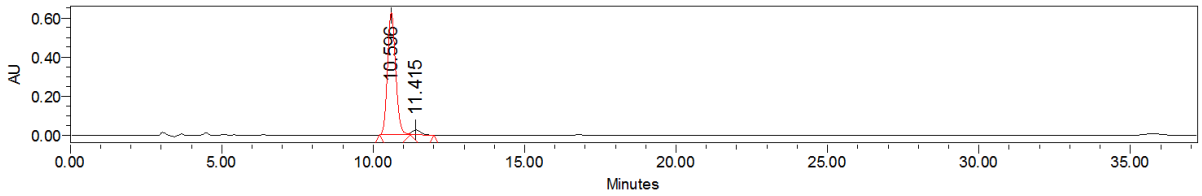


	Retention Time	Area	% Area
1	16.783	5520674	97.03
2	33.706	168892	2.97

Di-*tert*-butyl (*R*,*E*)-3-[(*N*-phenylphenylsulfonamido)methylene]-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4ab)

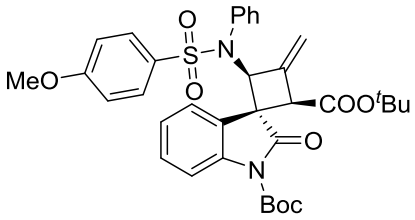


71% yield for two steps, White solid; **m.p.**: 180.2 – 188.2 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm), t_r (major) = 10.60 min, t_r (minor) = 11.42 min, ee = 92%. **3ab**:**4ab** < 1:19, determined by ^{1}H NMR. $[\alpha]^{24}_{D}$ = +138.6 (*c* = 0.31, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.90 – 7.86 (m, 1H), 7.60 – 7.55 (m, 3H), 7.45 – 7.41 (m, 2H), 7.33 – 7.27 (m, 3H), 7.12 – 7.07 (m, 4H), 6.84 (s, 1H), 5.15 (d, *J* = 11.6 Hz, 1H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.04 (s, 1H), 1.66 (s, 9H), 1.24 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 169.5, 149.0, 148.4, 139.1, 137.2, 133.4, 131.1, 129.5, 129.0, 128.6, 128.4, 127.8, 127.7, 127.2, 126.9, 122.7, 121.8, 119.5, 117.7, 114.7, 89.6, 84.2, 81.8, 71.3, 38.6, 28.2, 27.9 ppm; **IR (neat) ν (cm^{-1}):** 2978, 1729, 1625, 1600, 1464, 1415, 1351, 1327, 1253, 1145, 1115, 1092, 1000, 952, 838, 746, 693; **HRMS** (ESI-FT) calcd for $C_{34}H_{36}N_2O_7SNa^+$ ([M]+Na$^+$) = 639.2135, found 639.2137.

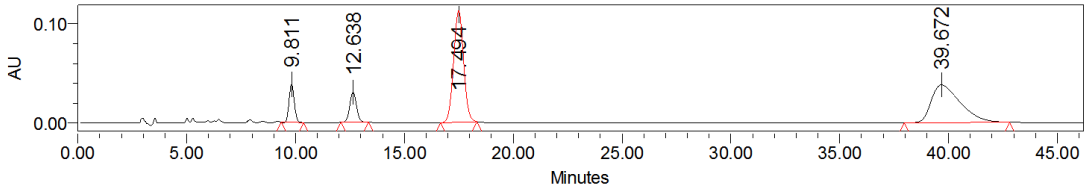


	Retention Time	Area	% Area
1	10.596	11680596	96.03
2	11.415	483255	3.97

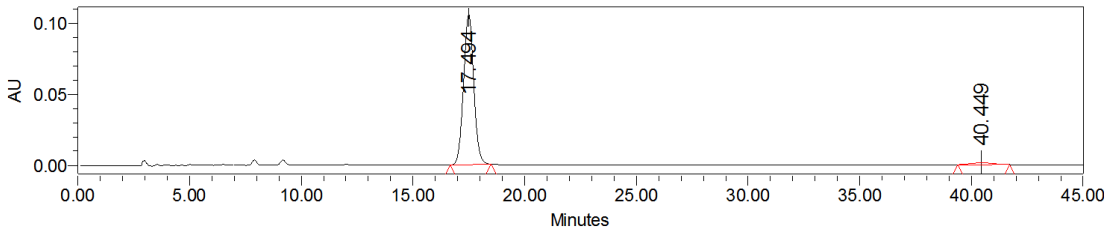
Di-*tert*-butyl (1*R*,2*R*,4*S*)-4-[(4-methoxy-*N*-phenylphenyl)sulfonamide]-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3ac)



88% yield, White solid; **m.p.**: 89.1 – 96.2 °C; R_f = 0.3 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 227 nm), t_r (major) = 17.49 min, t_r (minor) = 40.45 min, ee = 95%. **3ac**:**4ac** > 19:1, determined by ^{1}H NMR. $[\alpha]^{23}_{\lambda}$ = –82.1 (*c* = 0.25, in dichloromethane, λ = 436 nm). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 – 7.84 (m, 1H), 7.46 – 7.27 (m, 5H), 7.26 – 7.08 (m, 11H), 6.86 – 6.82 (m, 2H), 5.34 – 5.31 (m, 1H), 5.25 – 5.23 (m, 1H), 3.95 – 3.91 (m, 2H), 3.85 (s, 3H), 1.67 (s, 9H), 0.94 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 175.0, 166.2, 163.3, 149.0, 141.3, 138.1, 138.0, 131.0, 128.8, 128.6, 127.0, 125.5, 123.8, 115.0, 113.7, 110.7, 84.1, 81.4, 60.9, 55.9, 55.5, 51.9, 28.1, 27.1 ppm; **IR (neat) ν (cm^{-1}):** 2980, 1766, 1733, 1596, 1496, 1366, 1300, 1258, 1156, 1089, 1023, 840, 757, 698, 675; **HRMS** (ESI-FT) calcd for $C_{35}H_{38}N_2O_8SNa^+$ ([M]+Na^+) = 669.2241, found 669.2230.

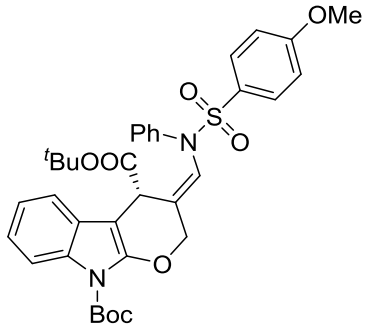


	Retention Time	Area	% Area
1	9.811	639617	7.63
2	12.638	645653	7.70
3	17.494	3579269	42.70
4	39.672	3517245	41.96

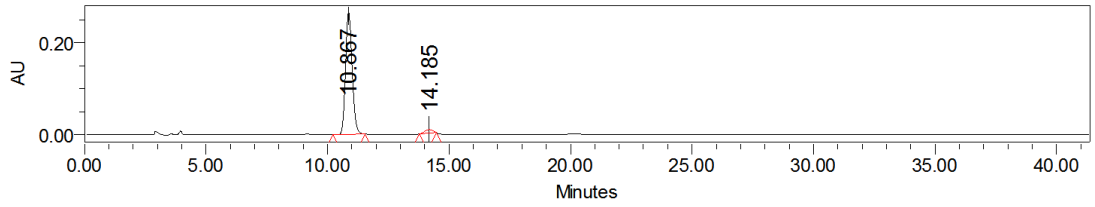


	Retention Time	Area	% Area
1	17.494	3367720	97.61
2	40.449	82604	2.39

Di-*tert*-butyl (*R*,*E*)-3-{[(4-methoxy-*N*-phenylphenyl)sulfonamide]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4ac)

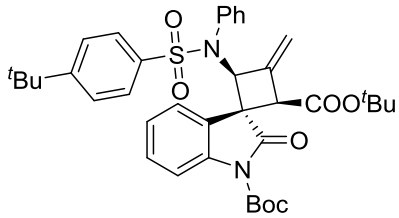


63% yield for two steps, White solid; **m.p.**: 181.7 – 187.6 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 227 nm), t_r (major) = 10.87 min, t_r (minor) = 14.19 min, ee = 93%. **3ac**:**4ac** < 1:19, determined by ^{1}H NMR. $[\alpha]^{24}_D$ = +137.5 (*c* = 0.17, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.89 – 7.85 (m, 1H), 7.53 – 7.49 (m, 2H), 7.34 – 7.29 (m, 3H), 7.26 – 7.25 (m, 1H), 7.13 – 7.07 (m, 4H), 6.90 – 6.86 (m, 2H), 6.83 (s, 1H), 5.14 (d, *J* = 12.0 Hz, 1H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.02 (s, 1H), 3.82 (s, 3H), 1.66 (s, 9H), 1.24 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 169.5, 163.4, 149.0, 148.4, 139.3, 131.0, 129.9, 129.4, 128.9, 128.6, 128.2, 127.9, 126.9, 122.7, 121.7, 119.1, 117.6, 114.7, 114.1, 100.0, 89.6, 84.1, 81.7, 71.4, 55.6, 38.5, 28.2, 27.9 ppm; **IR (neat) ν (cm^{-1}):** 2979, 1729, 1625, 1600, 1464, 1415, 1351, 1327, 1253, 1145, 1115, 1092, 1000, 952, 838, 746, 693; **HRMS** (ESI-FT) calcd for $C_{35}H_{38}N_2O_8SNa^+$ ([M]+Na$^+$) = 669.2241, found 669.2244.

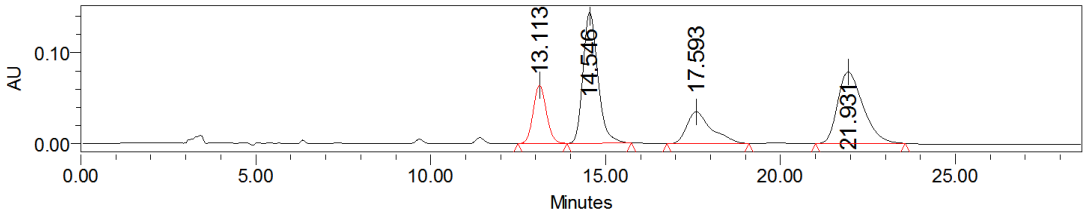


	Retention Time	Area	% Area
1	10.867	4998169	96.54
2	14.185	179311	3.46

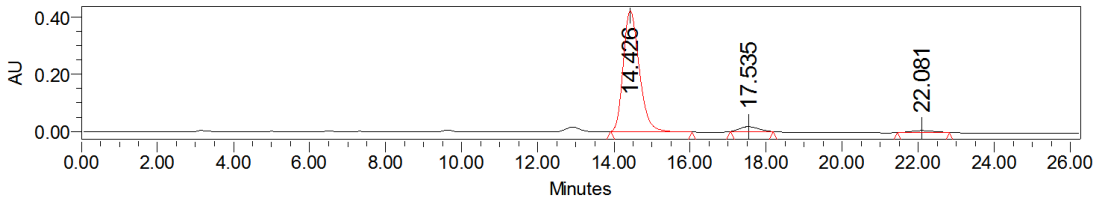
Di-*tert*-butyl (1*R*,2*S*,4*R*)-2-{[4-(*tert*-butyl)-*N*-phenylphenyl]sulfonamide}-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',4-dicarboxylate (3ad)



85% yield, White solid; **m.p.**: 100.3 – 108.1 °C; R_f = 0.5 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IE, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 224 nm), t_r (major) = 14.43 min, t_r (minor) = 22.08 min, ee = 95%. **3ad**:**4ad** > 19:1, determined by ^{1}H NMR. $[\alpha]^{22}_\lambda$ = –58.7 (*c* = 0.48, in dichloromethane, λ = 436 nm). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.87 – 7.83 (m, 1H), 7.42 – 7.16 (m, 12H), 5.34 – 5.31 (m, 1H), 5.26 – 5.23 (m, 1H), 3.97 – 3.95 (m, 1H), 3.93 – 3.91 (m, 1H), 1.67 (s, 9H), 1.32 (s, 9H), 0.94 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 175.0, 166.3, 157.1, 149.0, 141.3, 138.1, 137.9, 132.3, 128.8, 128.72, 128.69, 125.6, 125.5, 123.8, 123.7, 115.0, 110.7, 84.1, 81.5, 60.9, 56.0, 51.9, 35.2, 31.0, 28.13, 27.2 ppm; **IR (neat) ν (cm^{-1}):** 2973, 1795, 1766, 1732, 1595, 1481, 1466, 1395, 1367, 1299, 1251, 1154, 1113, 1085, 1005, 890, 858, 841, 814, 758, 698, 670, 630; **HRMS** (ESI-FT) calcd for $C_{38}H_{44}N_2O_7SNa^+$ ([M]+Na$^+$) = 695.2761, found 695.2764.

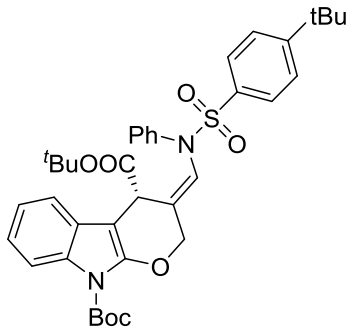


	Retention Time	Area	% Area
1	13.113	1683996	14.45
2	14.546	4253729	36.51
3	17.593	1735078	14.89
4	21.931	3977866	34.14

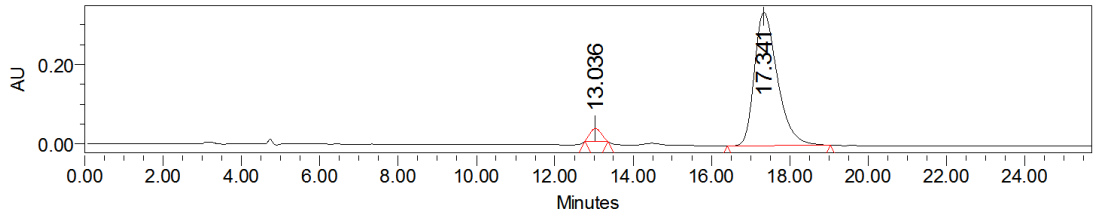


	Retention Time	Area	% Area
1	14.426	12306433	93.21
2	17.535	584173	4.42
3	22.081	311949	2.36

Di-*tert*-butyl (*R*,*E*)-3-{[(4-(*tert*-butyl)-*N*-phenylphenyl)sulfonamide]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4ad)

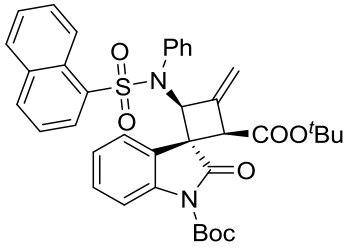


75% yield for two steps, White solid; **m.p.**: 195.1 – 202.4 °C; R_f = 0.5 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IE, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 224 nm), t_r (major) = 17.34 min, t_r (minor) = 13.04 min, ee = 91%. **3ad**:**4ad** < 1:19, determined by ^{1}H NMR. $[\alpha]^{24}_D$ = +128.1 (*c* = 0.39, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.91 – 7.85 (m, 1H), 7.51 – 7.49 (m, 2H), 7.45 – 7.43 (m, 2H), 7.36 – 7.29 (m, 3H), 7.26 – 7.23 (m, 1H), 7.13 – 7.08 (m, 4H), 6.85 (s, 1H), 5.14 (d, *J* = 11.6 Hz, 1H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.00 (s, 1H), 1.66 (s, 9H), 1.31 (s, 9H), 1.24 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 169.5, 157.3, 149.0, 148.4, 139.2, 134.3, 131.0, 129.4, 128.7, 128.3, 127.9, 127.6, 126.9, 126.0, 122.7, 121.7, 118.4, 117.6, 114.7, 89.6, 84.1, 81.7, 71.4, 38.5, 35.2, 31.0, 28.2, 27.8 ppm; **IR (neat) ν (cm^{-1}):** 2973, 1730, 1625, 1600, 1508, 1464, 1416, 1351, 1327, 1302, 1254, 1147, 1116, 1091, 912, 840, 748, 707, 664; **HRMS** (ESI-FT) calcd for $C_{38}H_{45}N_2O_7S^+$ ([M]+H$^+$) = 673.2942, found 673.2946.

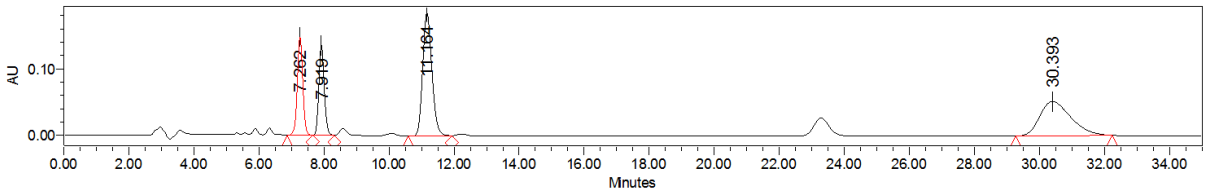


	Retention Time	Area	% Area
1	13.036	641673	4.47
2	17.341	13714721	95.53

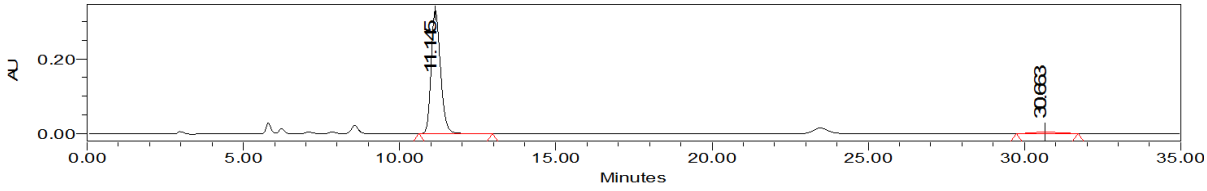
Di-*tert*-butyl (1*R*,2*R*,4*S*)-3-methylene-2'-oxo-4-(*N*-phenylnaphthalene-1-sulfonamido)spiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3ae)



96% yield, White solid; **m.p.**: 88.8 – 94.9 °C; R_f = 0.5 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 226 nm), t_r (major) = 11.15 min, t_r (minor) = 30.66 min, ee = 94%. **3ae**:**4ae** > 19:1, determined by ^{1}H NMR. $[\alpha]^{24}_D$ = –85.4 (*c* = 0.51, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.00 – 7.98 (m, 1H), 7.92 – 7.85 (m, 3H), 7.80 – 7.78 (m, 1H), 7.45 – 7.35 (m, 4H), 7.25 – 7.09 (m, 4H), 7.02 – 7.01 (m, 2H), 6.81 – 6.80 (m, 1H), 5.49 – 5.48 (m, 1H), 5.36 – 5.33 (m, 1H), 4.08 – 4.07 (m, 1H), 3.97 – 3.93 (m, 1H), 1.68 (s, 9H), 0.94 (s, 9H) ppm. **^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$)** δ 174.7, 166.2, 149.1, 141.3, 138.5, 137.3, 134.8, 133.6, 131.7, 131.6, 129.5, 128.8, 128.5, 128.2, 127.7, 126.5, 125.3, 125.2, 124.1, 123.9, 123.8, 121.8, 115.0, 110.8, 84.1, 81.5, 61.2, 56.3, 51.8, 28.1, 27.2 ppm. **IR (neat) ν (cm^{-1}):** 2982, 2362, 2179, 2026, 1968, 1732, 1477, 1359, 1299, 1251, 1155, 1009, 766, 695, 595; **HRMS** (ESI-FT) calcd for $C_{38}H_{38}N_2O_7SNa^+$ ([M]+Na$^+$) = 689.2292, found 689.2297.

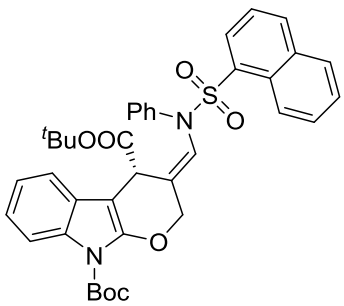


	Retention Time	Area	% Area
1	7.262	1727117	16.64
2	7.919	1580111	15.22
3	11.164	3646138	35.12
4	30.393	3427155	33.02

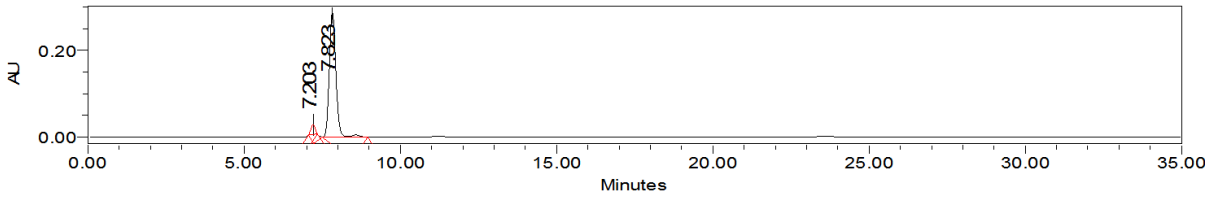


	Retention Time	Area	% Area
1	11.145	6889017	96.85
2	30.663	224280	3.15

Di-*tert*-butyl (*R*,*E*)-3-[(*N*-phenylnaphthalene-1-sulfonamido)methylene]-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4ae)

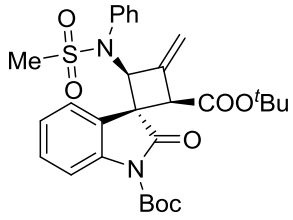


83% yield for two steps, White solid; **m.p.**: 90.7 – 96.1 °C; R_f = 0.5 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 226 nm), t_r (major) = 7.82 min, t_r (minor) = 7.20 min, ee = 90%. **3ae**:**4ae** < 19:1, determined by ^{1}H NMR. $[\alpha]^{21}_D$ = +136.0 (*c* = 0.47, in dichloromethane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.37 – 8.34 (m, 1H), 8.08 – 8.06 (m, 1H), 8.00 – 7.98 (m, 1H), 7.90 – 7.87 (m, 1H), 7.83 – 7.81 (m, 1H), 7.45 – 7.41 (m, 2H), 7.36 – 7.32 (m, 1H), 7.25 – 7.21 (m, 1H), 7.21 – 7.19 (m, 1H), 7.19 – 7.13 (m, 2H), 7.12 – 7.08 (m, 2H), 7.01 – 6.98 (m, 3H), 5.14 (d, *J* = 11.6 Hz, 1H), 4.77 (d, *J* = 11.6 Hz, 1H), 4.01 (s, 1H), 1.67 (s, 9H), 1.19 (s, 9H) ppm. **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ 169.3, 149.0, 148.3, 139.1, 135.0, 134.1, 133.0, 131.2, 131.0, 129.4, 128.73, 128.67, 128.3, 127.7, 126.9, 124.7, 123.9, 122.7, 121.8, 121.0, 117.7, 114.6, 89.5, 84.1, 81.7, 71.1, 38.6, 28.2, 27.8 ppm. **IR (neat) ν (cm^{-1}):** 2979, 1731, 1599, 1464, 1352, 1117, 1003, 836, 769, 694; **HRMS** (ESI-FT) calcd for $C_{38}H_{38}N_2O_7SNa^+$ ([M]+Na^+) = 689.2292, found 689.2301.

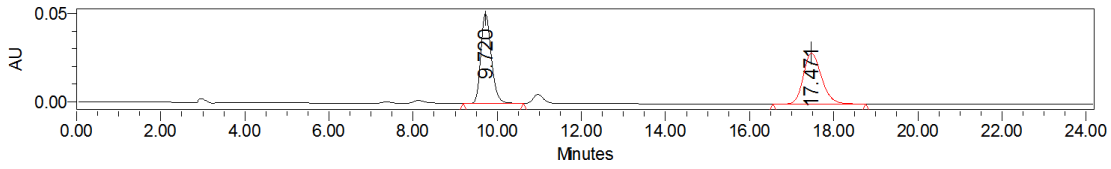


	Retention Time	Area	% Area
1	7.203	207408	4.68
2	7.823	4219988	95.32

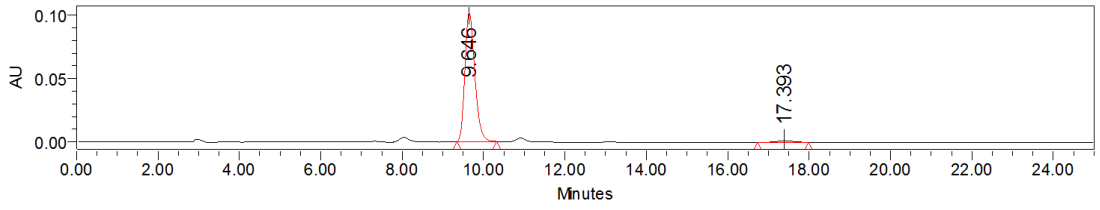
Di-*tert*-butyl (1*R*,2*R*,4*S*)-3-methylene-2'-oxo-4-(*N*-phenylmethylsulfonamido)spiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3af)



69% yield, White solid; **m.p.**: 85.1 – 93.9 °C; R_f = 0.2 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 240 nm), t_r (major) = min, t_r (minor) = min, ee = 96%. **3af**:**4af** > 19:1, determined by ^{1}H NMR. $[\alpha]^{22}_\lambda$ = +57.9 (*c* = 0.32, in dichloromethane, λ = 436 nm). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 – 7.88 (m, 1H), 7.43 – 7.39 (m, 4H), 7.36 – 7.31 (m, 3H), 7.22 – 7.15 (m, 1H), 5.46 – 5.43 (m, 1H), 5.38 – 5.35 (m, 1H), 4.00 – 3.97 (m, 2H), 2.39 (s, 3H), 1.65 (s, 9H), 0.94 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 174.6, 166.2, 149.2, 141.5, 137.9, 137.7, 130.6, 129.7, 129.4, 129.3, 129.0, 125.2, 123.9, 123.5, 120.7, 115.2, 111.2, 84.2, 81.5, 62.1, 55.8, 51.3, 37.4, 28.1, 27.2 ppm; **IR (neat) ν (cm^{-1}):** 2979, 1770, 1732, 1604, 1482, 1347, 1299, 1251, 1153, 1082, 1007, 969, 894, 842, 756, 699; **HRMS** (ESI-FT) calcd for $C_{29}H_{34}N_2O_7SNa^+$ ([M]+Na^+) = 577.1979, found 577.1980.

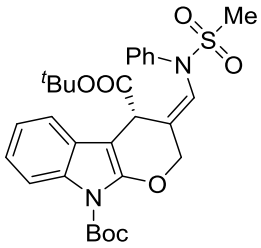


	Retention Time	Area	% Area
1	9.720	870799	50.36
2	17.471	858199	49.64

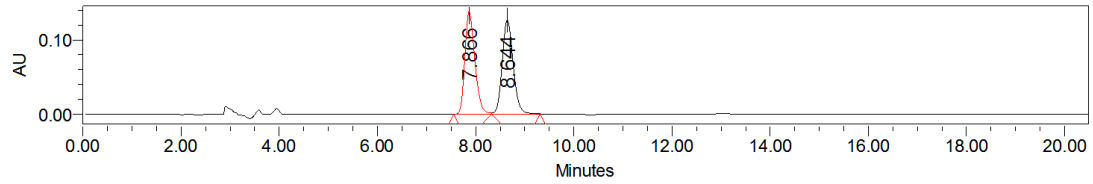


	Retention Time	Area	% Area
1	9.646	1716114	98.31
2	17.393	29434	1.69

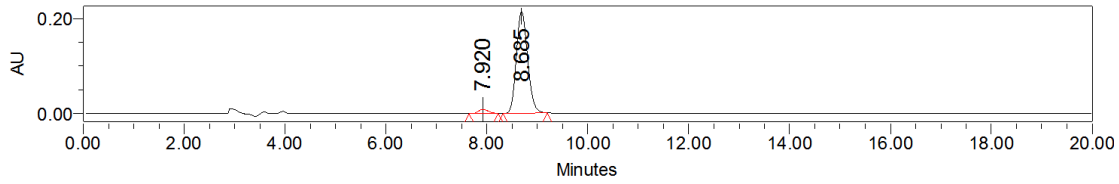
Di-*tert*-butyl (*R*,*E*)-3-[(*N*-phenylmethylsulfonamido)methylene]-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4af)



40% yield for two steps, Colorless oil; R_f = 0.2 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 240 nm), t_r (major) = 8.69 min, t_r (minor) = 7.92 min, ee = 93%. **3af**:**4af** < 1:19, determined by ^{1}H NMR. $[\alpha]^{24}_D$ = +92.4 (*c* = 0.13, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.93 – 7.86 (m, 1H), 7.45 – 7.37 (m, 5H), 7.29 – 7.27 (m, 1H), 7.15 – 7.08 (m, 2H), 6.91 (s, 1H), 5.18 (d, *J* = 11.6 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.01 (s, 1H), 2.96 (s, 3H), 1.66 (s, 9H), 1.27 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 169.4, 149.0, 148.4, 138.9, 131.0, 130.0, 128.5, 128.1, 127.3, 126.8, 122.7, 121.8, 118.8, 117.6, 114.7, 89.4, 84.2, 81.9, 71.3, 38.5, 37.9, 28.2, 27.9 ppm; **IR (neat)** ν **(cm^{-1}):** 2979, 1729, 1626, 1600, 1464, 1415, 1350, 1301, 1253, 1149, 1116, 1000, 963, 841, 750, 696; **HRMS** (ESI-FT) calcd for $C_{29}H_{34}N_2O_7SNa^+$ ([M+Na$^+$]) = 577.1979, found 577.1979.

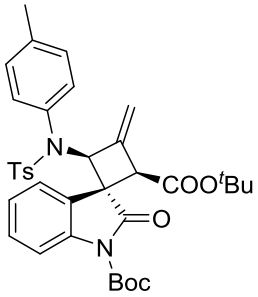


	Retention Time	Area	% Area
1	7.866	1942713	49.85
2	8.644	1954078	50.15



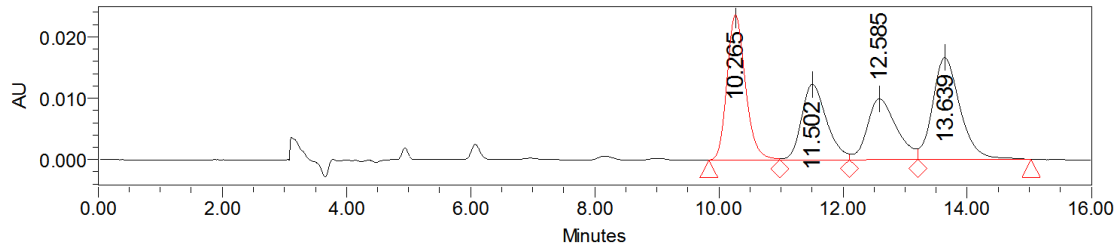
	Retention Time	Area	% Area
1	7.920	119571	3.46
2	8.685	3335276	96.54

Di-*tert*-butyl (1*R*,2*R*,4*S*)-4-((4-methyl-*N*-(*p*-tolyl)phenyl)sulfonamido)-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1',2-dicarboxylate (3ag)

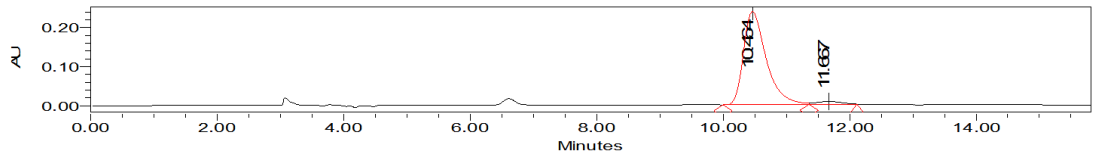


97% yield, White solid; **m.p.**: 90.1 – 97.8 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IB, hexane/^{i}PrOH = 95/5, flow rate 1.0 mL/min, λ = 224 nm), t_r (major) = 10.46 min, t_r (minor) = 11.67 min, ee = %. **3ag**:**4ag** > 19:1, determined by ^{1}H NMR. $[\alpha]^{23}_D$ = –30.0 (*c* = 0.59, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ .86 – 7.83 (m,

1H), 7.48 – 7.28 (m, 3H), 7.25 – 7.00 (m, 8H), 5.34 – 5.30 (m, 1H), 5.23 – 5.21 (m, 1H), 4.01 – 3.98 (m, 1H), 3.92 – 3.90 (m, 1H), 2.40 (s, 3H), 2.34 (s, 3H), 1.67 (s, 9H), 0.94 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 175.0, 166.3, 149.1, 144.0, 141.3, 138.9, 138.1, 135.1, 132.5, 129.2, 128.9, 128.6, 125.5, 123.8, 115.0, 110.7, 84.1, 81.4, 61.0, 56.0, 51.9, 28.1, 27.1, 21.6, 21.2 ppm; **IR (neat) ν (cm^{-1}):** 2979, 1766, 1732, 1603, 1508, 1480, 1365, 1299, 1251, 1156, 1087, 1009, 893, 863, 757, 712, 669; **HRMS** (ESI-FT) calcd for $C_{36}H_{40}N_2O_7SNa^+$ ([M]+Na$^+$) = 667.2448, found 667.2450.

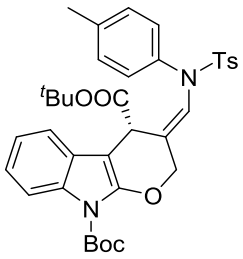


	Retention Time	Area	% Area
1	10.265	488039	29.23
2	11.502	344119	20.61
3	12.585	325237	19.48
4	13.639	512060	30.67

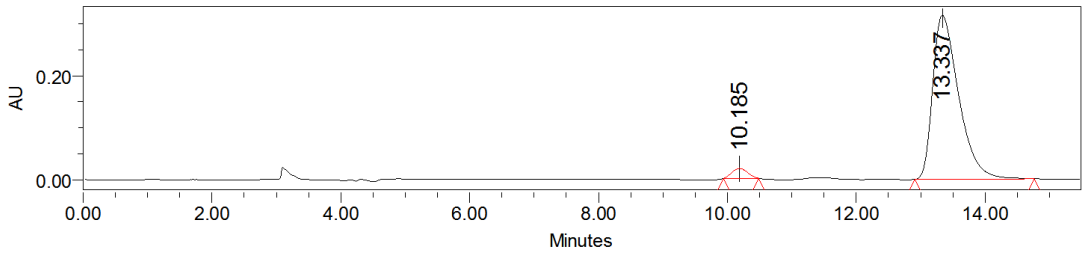


	Retention Time	Area	% Area
1	10.464	5937102	96.83
2	11.667	194171	3.17

Di-*tert*-butyl (*R*,*E*)-3-{[(4-methyl-*N*-(*p*-tolyl)phenyl)sulfonamido]methylene}-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (4ag)

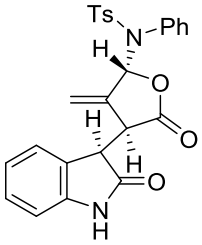


71% yield for two steps, White solid; **m.p.**: 183.0 – 186.6 °C; R_f = 0.4 (petroleum ether/ethyl acetate/dichloromethane = 9/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IB, hexane/^{i}PrOH = 95/5, flow rate 1.0 mL/min, λ = 224 nm), t_r (major) = 13.34 min, t_r (minor) = 10.19 min, ee = 93%. **3ag**:**4ag** < 1:19, determined by ^{1}H NMR. $[\alpha]^{24}_D$ = +90.3 (*c* = 0.39, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.91 – 7.86 (m, 1H), 7.50 – 7.45 (m, 2H), 7.25 – 7.19 (m, 3H), 7.14 – 7.07 (m, 4H), 6.97 – 6.94 (m, 2H), 6.83 (s, 1H), 5.13 (d, *J* = 11.6 Hz, 1H), 4.74 (d, *J* = 11.6 Hz, 1H), 4.00 (s, 1H), 2.38 (s, 3H), 2.36 (s, 3H), 1.66 (s, 9H), 1.24 (s, 9H) ppm; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 169.5, 149.0, 148.4, 144.2, 138.2, 136.5, 134.4, 131.0, 130.1, 129.8, 129.6, 129.5, 128.5, 128.0, 127.8, 127.2, 126.9, 122.6, 122.5, 121.7, 118.2, 117.6, 114.6, 89.6, 84.1, 81.6, 71.4, 38.4, 28.2, 27.8, 21.5, 21.2 ppm; **IR (neat) ν (cm^{-1}):** 2979, 1730, 1625, 1600, 1508, 1464, 1416, 1351, 1327, 1302, 1254, 1147, 1116, 1091, 912, 840, 748, 707, 664; **HRMS** (ESI-FT) calcd for $C_{36}H_{40}N_2O_7SNa^+$ ([M]+Na$^+$) = 667.2448, found 667.2446.

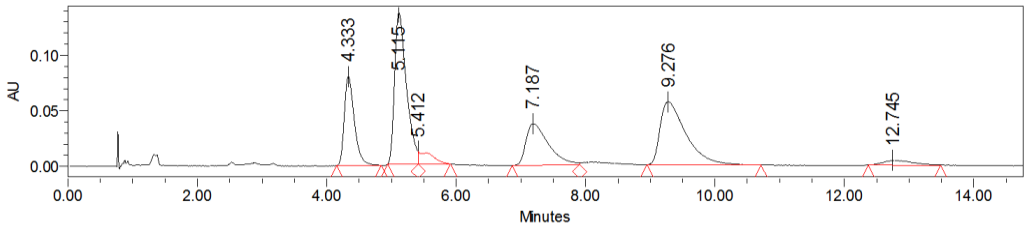


	Retention Time	Area	% Area
1	10.185	324372	3.55
2	13.337	8818720	96.45

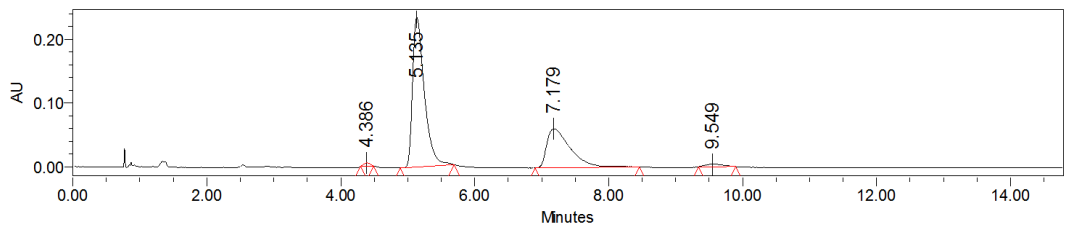
4-Methyl-*N*-{(2*R*,4*S*)-3-methylene-5-oxo-4-[(*R*)-2-oxoindolin-3-yl]tetrahydrofuran-2-yl}-*N*-phenylbenzenesulfonamide (5aa)



70% yield, Yellow solid; **m.p.**: 107.7 – 126.7 °C; R_f = 0.4 (ethyl acetate/dichloromethane = 1/9); Dissolved in ^{i}PrOH for SFC; **SFC** (Chiralcel IA-3, MeOH/CO_2 = 80/20, flow rate 1.5 mL/min, λ = 230 nm), major isomer: t_r (major) = 5.14 min, t_r (minor) = 9.55 min, ee = 95%; minor isomer: t_r (major) = 7.18 min, t_r (minor) = 4.39 min, ee = 95%. dr = 65:35, determined by ^{1}H NMR. $[\alpha]^{25}_D$ = –178.2 (*c* = 0.25, in dichloromethane). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.43 (s, 1H), 7.58 – 7.55 (m, 2H), 7.36 – 7.32 (m, 1H), 7.28 – 7.23 (m, 6H), 7.10 – 7.03 (m, 2H), 7.02 – 6.98 (m, 1H), 6.95 – 6.90 (m, 2H), 6.89 – 6.86 (m, 1H), 5.53 – 5.51 (m, 1H), 4.92 – 4.90 (m, 1H), 3.92 (d, *J* = 3.6 Hz, 1H), 3.10 (p, *J* = 3.0 Hz, 1H), 2.42 (s, 3H) ppm. **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ 176.6, 173.6, 144.3, 142.0, 139.3, 135.3, 134.2, 131.8, 129.5, 129.4, 129.28, 129.26, 129.2, 128.2 125.6, 123.6, 122.8, 115.4, 110.4, 90.3, 46.7, 43.6, 21.6 ppm. **IR (neat) ν (cm^{-1}):** 1786, 1713, 1621, 1521, 1480, 1349, 1232, 1166, 1094, 975, 809, 752, 660, 572; **HRMS** (ESI-FT) calcd for $C_{26}H_{22}N_2O_5SNa^+$ ([M]+Na^+) = 497.1142, found 497.1145.



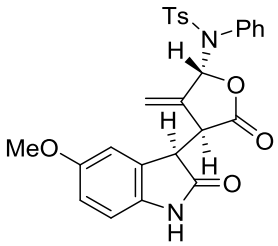
	Retention Time	Area	% Area
1	4.333	857765	15.97
2	5.115	1731596	32.25
3	5.412	167281	3.12
4	7.187	901502	16.79
5	9.276	1572356	29.28
6	12.745	139075	2.59



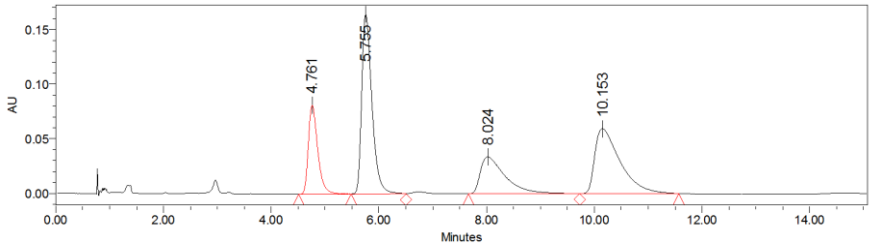
	Retention Time	Area	% Area

1	4.386	35607	0.80
2	5.135	2865814	64.06
3	7.179	1499080	33.51
4	9.549	73394	1.64

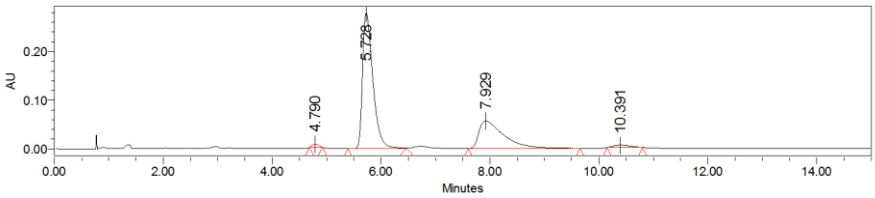
***N*-{(2*R*,4*S*)-4-[(*R*)-5-Methoxy-2-oxoindolin-3-yl]-3-methylene-5-oxotetrahydrofuran-2-yl}-4-methyl-*N*-phenylbenzenesulfonamide (5ga)**



56% yield, Red solid; **m.p.**: 111.9 – 128.2°C; R_f = 0.5 (ethyl acetate/dichloromethane = 1/9); Dissolved in ^{i}PrOH for SFC; **SFC** (Chiralcel IA-3, MeOH/CO_2 = 80/20, flow rate 1.5 mL/min, λ = 230 nm), major isomer: t_r (major) = 5.73 min, t_r (minor) = 10.39 min, ee = 94%; minor isomer: t_r (major) = 7.93 min, t_r (minor) = 4.79 min, ee = 94%. dr = 69:31, determined by ^{1}H NMR. $[\alpha]^{26}_D$ = –158.8 (*c* = 0.31, in dichloromethane). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.19 (s, 1H), 7.59 – 7.56 (m, 2H), 7.37 – 7.31 (m, 1H), 7.27 – 7.24 (m, 4H), 7.04 (d, *J* = 1.2 Hz, 1H), 6.97 – 6.93 (m, 2H), 6.81 – 6.76 (m, 2H), 6.70 – 6.68 (m, 1H), 5.51 (s, 1H), 4.89 (s, 1H), 3.92 – 3,90 (m, 1H), 3.75 (s, 3H), 3.05 (p, *J* = 3.0 Hz, 1H), 2.42 (s, 3H) ppm. **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ 176.3, 173.6, 155.9, 144.3, 139.2, 135.33, 135.28, 131.8, 129.6, 129.4, 129.30, 129.27, 128.3, 127.0, 115.4, 113.1, 111.2, 110.6, 90.3, 55.8, 47.1, 43.6, 21.6 ppm. **IR (neat) ν (cm^{-1}):** 1787, 1713, 1602, 1490, 1448, 1351, 1314, 1208, 1164, 1092, 1031, 972, 813, 689, 663, 571; **HRMS** (ESI-FT) calcd for $C_{26}H_{21}{}^{35}ClN_2O_5SNa^+$ ([M]+Na^+) = 531.0752, found 531.0756; $C_{27}H_{24}N_2O_6SNa^+$ ([M]+Na^+) = 527.1247 found 527.1246.

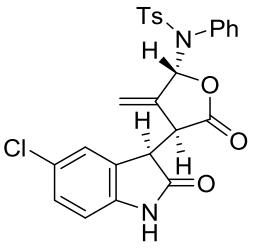


	Retention Time	Area	% Area
1	4.761	994763	16.06
2	5.755	2174586	35.11
3	8.024	1083716	17.50
4	10.153	1941223	31.34

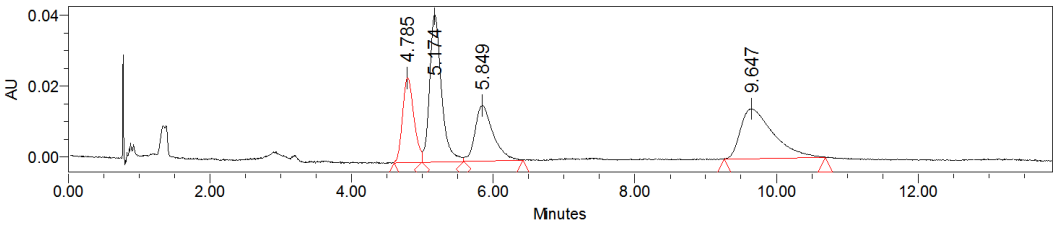


	Retention Time	Area	% Area
1	4.790	54791	0.98
2	5.728	3663492	65.49
3	7.929	1764489	31.54
4	10.391	111213	1.99

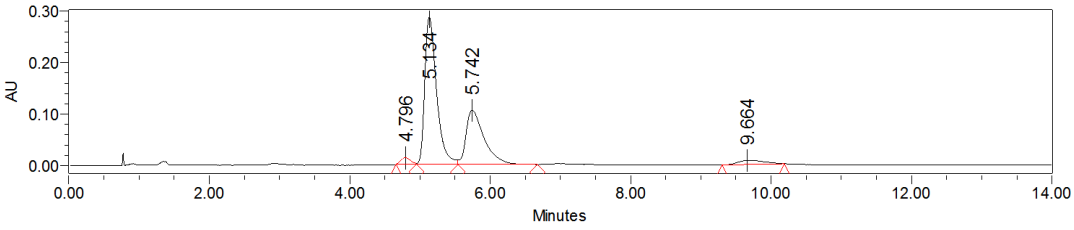
***N*-{(2*R*,4*S*)-4-[(*R*)-5-Chloro-2-oxoindolin-3-yl))-3-methylene-5-oxotetrahydrofuran-2-yl}-4-methyl-*N*-phenylbenzenesulfonamide (5ia)**



52% yield, Yellow solid; **m.p.**: 115.7 – 131.6°C; R_f = 0.5 (ethyl acetate/dichloromethane = 1/9); Dissolved in ^{i}PrOH for SFC; **SFC** (Chiralcel IA-3, MeOH/CO_2 = 80/20, flow rate 1.5 mL/min, λ = 230 nm), major isomer: t_r (major) = 5.13 min, t_r (minor) = 9.66 min, ee = 88%; minor isomer: t_r (major) = 5.74 min, t_r (minor) = 4.80 min, *ee* = 88%. dr = 68:32, determined by ^{1}H NMR. $[\alpha]^{25}_D$ = –138.4 (*c* = 0.32, in dichloromethane). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.49 (s, 1H), 7.58 – 7.56 (m, 2H), 7.38 – 7.33 (m, 1H), 7.29 – 7.22 (m, 6H), 7.07 (s, 1H), 7.06 – 7.04 (m, 1H), 6.96 – 6.92 (m, 2H), 6.84 – 6.81 (m, 1H), 5.56 (s, 1H), 4.95 (s, 1H), 3.93 – 3.91 (m, 1H), 3.06 (s, 1H), 2.43 (s, 3H) ppm. **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ 176.1, 173.3, 144.4, 140.6, 139.0, 135.2, 134.2, 131.8, 129.6, 129.5, 129.4, 129.3, 129.2, 128.3, 127.3, 124.0, 115.6, 111.4, 90.3, 46.6, 43.6, 21.6 ppm. **IR (neat) ν (cm^{-1}):** 1785, 1716, 1620, 1481, 1442, 1351, 1317, 1235, 1165, 1094, 971, 819, 755, 699, 660, 572; **HRMS** (ESI-FT) calcd for $C_{26}H_{21}{}^{35}ClN_2O_5SNa^+$ ([M+Na$^+$]) = 531.0752, found 531.0756; $C_{26}H_{21}{}^{37}ClN_2O_5SNa^+$ ([M+Na$^+$]) = 533.0722 found 533.0721.

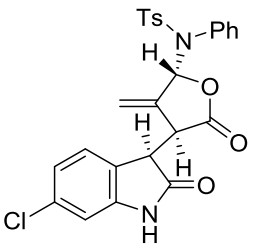


	Retention Time	Area	% Area
1	4.785	265843	17.99
2	5.174	483760	32.73
3	5.849	277555	18.78
4	9.647	450943	30.51



	Retention Time	Area	% Area
1	4.796	122271	2.21
2	5.134	3324737	60.09
3	5.742	1876637	33.92
4	9.664	209015	3.78

***N*-{(2*R*,4*S*)-4-[(*R*)-6-Chloro-2-oxoindolin-3-yl]-3-methylene-5-oxotetrahydrofuran-2-yl}-4-methyl-*N*-phenylbenzenesulfonamide (5na)**

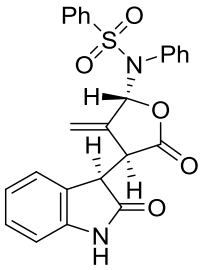


44% yield, Yellow solid; **m.p.**: 135.4 – 148.6°C; R_f = 0.5 (ethyl acetate/dichloromethane = 1/9); Dissolved in ^{i}PrOH for SFC; **SFC** (Chiralcel IA-3, MeOH/CO_2 = 80/20, flow rate 1.5 mL/min, λ = 230 nm), major isomer: t_r (major) = 5.97 min, t_r (minor) = 12.90 min, ee = 93%; minor isomer: t_r (major) = 6.64 min, t_r (minor) = 4.72 min, ee = 93%. dr = 67:32, determined by ^{1}H NMR. $[\alpha]^{26}_D$ = –139.4 (*c* = 0.29, in dichloromethane). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.23 (s, 1H), 7.57 – 7.54 (m, 2H), 7.36 – 7.33 (m, 1H), 7.28 – 7.23 (m, 4H), 7.06 – 7.01 (m, 2H), 7.00 – 6.99 (m, 1H), 6.96 – 6.92 (m, 2H), 6.89 – 6.88 (m, 1H), 5.59 (s, 1H), 5.02 (s, 1H), 3.86 (d, *J* = 3.0 Hz, 1H), 3.08 (s, 1H), 2.42 (s, 2H) ppm. **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ 176.2, 173.2, 144.5, 143.0, 139.3, 135.2, 135.0, 131.8, 129.6, 129.5, 129.3, 128.3, 124.6, 123.9, 122.9, 115.6, 111.0, 90.3, 46.1, 43.7, 21.6 ppm. **IR (neat) ν (cm^{-1}):** 1784, 1723, 1618, 1487, 1453, 1349, 1165, 1093, 972, 756, 696, 658, 571; **HRMS** (ESI-FT) calcd for $C_{26}H_{21}{}^{35}ClN_2O_5SNa^+$ ([M+Na$^+$]) = 531.0752, found 531.0762; $C_{26}H_{21}{}^{37}ClN_2O_5SNa^+$ ([M+Na$^+$]) = 533.0722 found 533.0732.

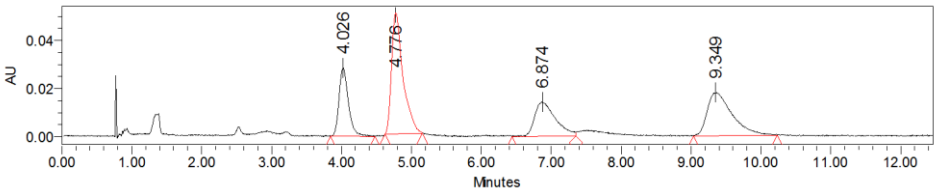
	Retention Time	Area	% Area
1	4.710	776588	17.49
2	6.012	1503128	33.86
3	6.745	743163	16.74
4	12.754	1416108	31.90

	Retention Time	Area	% Area
1	4.730	67236	1.39
2	5.974	3011795	62.25
3	6.636	1691182	34.95
4	12.861	68322	1.41

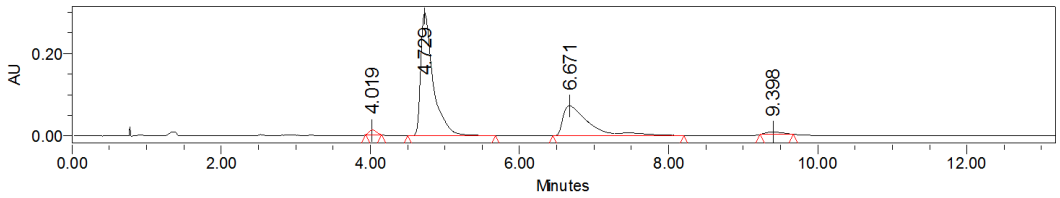
***N*-{(2*R*,4*S*)-3-Methylene-5-oxo-4-[(*R*)-2-oxoindolin-3-yl]tetrahydrofuran-2-yl}-*N*-phenylbenzenesulfonamide (5ba)**



60% yield, Yellow solid; **m.p.**: 114.0 – 130.6°C; R_f = 0.4 (ethyl acetate/dichloromethane = 1/9); Dissolved in ^{i}PrOH for SFC; **SFC** (Chiralcel IA-3, MeOH/CO_2 = 80/20, flow rate 1.5 mL/min, λ = 230 nm), major isomer: t_r (major) = 4.73 min, t_r (minor) = 9.40 min, ee = 95%; minor isomer: t_r (major) = 6.67 min, t_r (minor) = 4.02 min, ee = 95%. dr = 66:34, determined by ^{1}H NMR. $[\alpha]^{26}_D$ = –132.2 (*c* = 0.62, in dichloromethane). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.43 (s, 1H), 7.71 – 7.66 (m, 2H), 7.62 – 7.58 (m, 1H), 7.50 – 7.44 (m, 2H), 7.36 – 7.32 (m, 1H), 7.27 – 7.24 (m, 3H), 7.11 – 7.04 (m, 2H), 7.02 – 6.99 (m, 1H), 6.95 – 6.93 (m, 2H), 6.88 – 6.87 (m, 1H), 5.52 (s, 1H), 4.92 (s, 1H), 3.95 – 3.92 (m, 1H), 3.11 (s, 1H) ppm. **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ 176.6, 173.5, 142.0, 139.3, 138.2, 134.1, 133.4, 131.8, 129.5, 129.3, 129.2, 128.9, 128.2, 125.5, 123.6, 122.9, 115.5, 110.4, 90.2, 46.7, 43.6 ppm. **IR (neat) ν (cm^{-1}):** 1785, 1715, 1621, 1478, 1349, 1234, 1167, 1094, 973, 792, 755, 693, 589, 562; **HRMS** (ESI-FT) calcd for $C_{25}H_{20}N_2O_5SNa^+$ ([M+Na$^+$]) = 483.0985, found 483.0988.

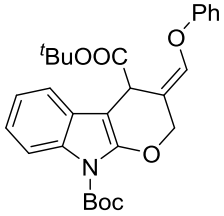


	Retention Time	Area	% Area
1	4.026	266570	18.30
2	4.776	459352	31.54
3	6.874	288541	19.81
4	9.349	442064	30.35

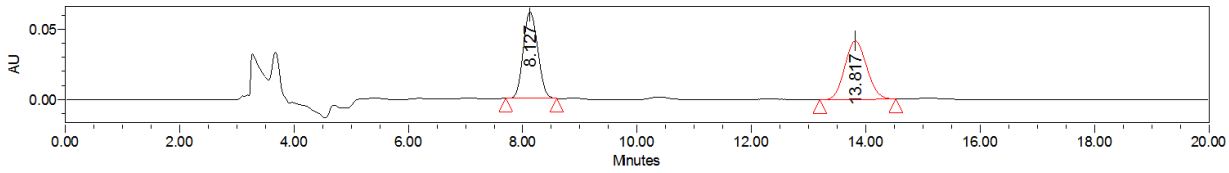


	Retention Time	Area	% Area
1	4.019	78208	1.45
2	4.729	3471660	64.29
3	6.671	1758754	32.57
4	9.398	91266	1.69

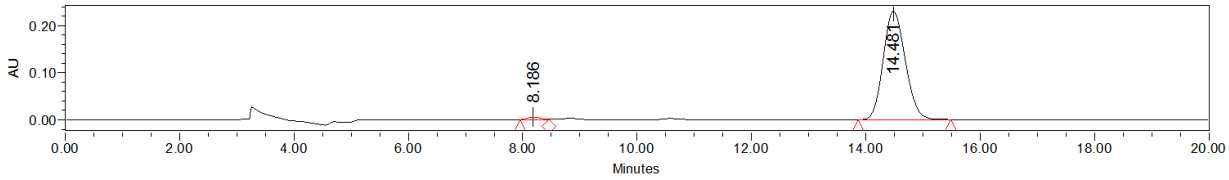
Di-*tert*-butyl (*E*)-3-(phenoxymethylene)-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (7aa)



60% yield, White solid; **m.p.**: 43.4 – 50.5 °C; R_f = 0.5 (petroleum ether/ethyl acetate/dichloromethane = 16/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IB, hexane/^{i}PrOH = 98/2, flow rate 1.0 mL/min, λ = 226 nm), t_r (major) = 14.48 min, t_r (minor) = 8.19 min, ee = 97%. $[\alpha]^{24}_{D}$ = +189.7 (*c* = 0.14, in dichloromethane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.94 – 7.92 (m, 1H), 7.57 – 7.55 (mz, 1H), 7.35 – 7.31 (m, 2H), 7.22 – 7.07 (m, 4H), 7.04 – 7.01 (m, 2H), 6.77 (s, 1H), 5.16 (d, *J* = 12.0 Hz, 1H), 4.81 (d, *J* = 12.0 Hz, 1H), 4.78 (s, 1H), 1.68 (s, 9H), 1.45 (s, 9H) ppm. **^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$)** δ 170.7, 156.8, 149.1, 148.9, 141.1, 131.1, 129.7, 127.4, 123.6, 122.9, 121.9, 117.7, 116.8, 114.8, 111.2, 90.4, 84.1, 81.8, 68.8, 37.4, 28.2, 28.0 ppm. **IR (neat) ν (cm^{-1}):** 2978, 1731, 1596, 1465, 1354, 1254, 1217, 1118, 999, 752; **HRMS** (ESI-FT) calcd for $C_{28}H_{31}NO_6Na^+$ ([M]+Na$^+$) = 500.2044, found 500.2048.

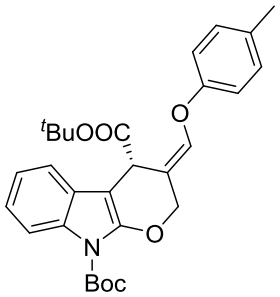


	Retention Time	Area	% Area
1	8.127	1080491	49.29
2	13.817	1111702	50.71

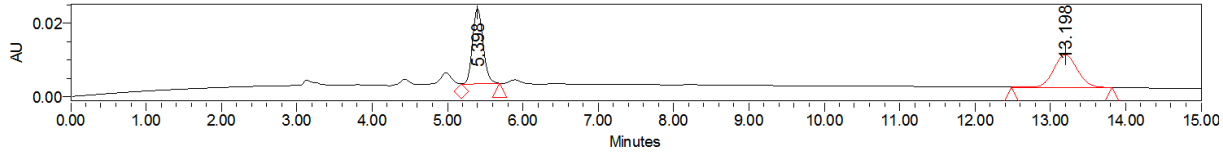


	Retention Time	Area	% Area
1	8.186	92223	1.47
2	14.481	6196244	98.53

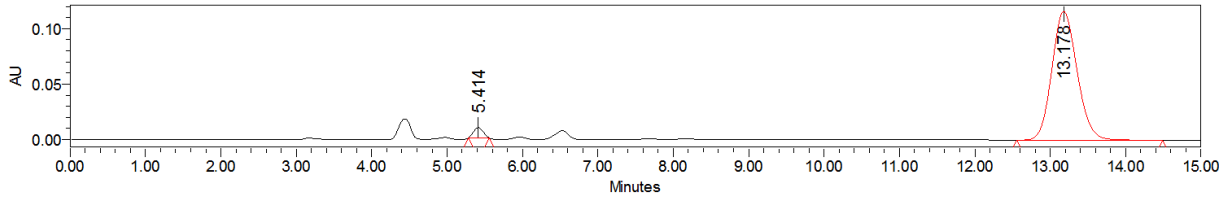
Di-*tert*-butyl (*R*,*E*)-3-[(*p*-tolyloxy)methylene]-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (7ab)



50% yield, Pure yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate/dichloromethane = 16/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IB, hexane/^{i}PrOH = 95/5, flow rate 1.0 mL/min, λ = 272 nm), t_r (major) = 13.18 min, t_r (minor) = 5.41 min, ee = 94%. $[\alpha]^{24}_{D}$ = +159.1 (*c* = 0.25, in dichloromethane). **^{1}H NMR (600 MHz, CD_2Cl_2)** δ 7.97 – 7.96 (m, 1H), 7.54 – 7.52 (m, 1H), 7.21 – 7.18 (m, 1H), 7.16 – 7.14 (m, 3H), 6.96 – 6.94 (m, 2H), 6.80 (s, 1H), 5.08 (d, *J* = 12.0 Hz, 1H), 4.79 – 4.75 (m, 2H), 2.32 (s, 3H), 1.66 (s, 9H), 1.44 (s, 9H) ppm. **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ 171.1, 155.2, 149.3, 141.9, 133.6, 131.6, 130.6, 130.3, 127.7, 123.2, 122.1, 117.9, 117.0, 115.1, 115.1, 111.1, 90.6, 84.2, 81.9, 69.1, 37.9, 28.3, 28.1, 20.7 ppm. **IR (neat) ν (cm^{-1}):** 2978, 1731, 1603, 1508, 1465, 1354, 1252, 1218, 1148, 998, 922, 842, 751; **HRMS** (ESI-FT) calcd for $C_{29}H_{33}NO_6Na^+$ ([M]+Na$^+$) = 514.2200, found 514.2206.

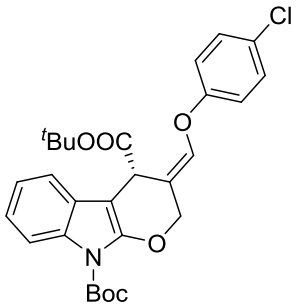


	Retention Time	Area	% Area
1	5.398	199144	50.78
2	13.198	193022	49.22

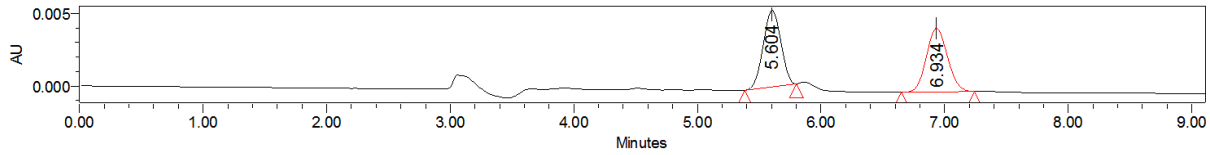


	Retention Time	Area	% Area
1	5.414	82004	2.95
2	13.178	2693910	97.05

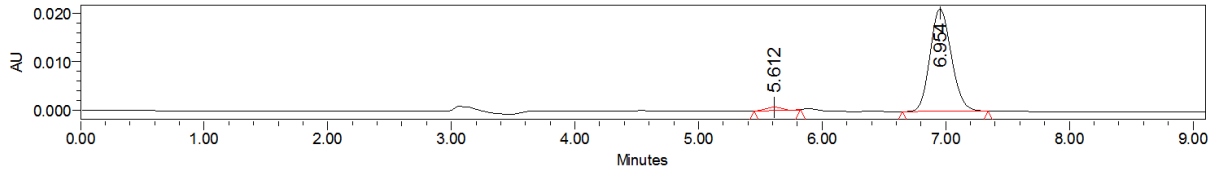
Di-*tert*-butyl (*R*,*E*)-3-[(4-chlorophenoxy)methylene]-3,4-dihydropyrano[2,3-*b*]indole-4,9(2*H*)-dicarboxylate (7ac)



48% yield, White solid; **m.p.**: 51.7 – 60.9 °C; R_f = 0.5 (petroleum ether/ethyl acetate/dichloromethane = 16/1/1); Dissolved in ^{i}PrOH for HPLC; **HPLC** (Chiralcel IA, hexane/^{i}PrOH = 95/5, flow rate 1.0 mL/min, λ = 271 nm), t_r (major) = 6.95 min, t_r (minor) = 5.61 min, ee = 95%. $[\alpha]^{23}_{D}$ = +165.5 (*c* = 0.26, in dichloromethane). **^{1}H NMR (600 MHz, CD_2Cl_2)** δ 7.97 – 7.76 (m, 1H), 7.53 – 7.50 (m, 1H), 7.34 – 7.32 (m, 2H), 7.21 – 7.18 (m, 1H), 7.16 – 7.14 (m, 1H), 7.03 – 7.00 (m, 2H), 6.78 (s, 1H), 5.08 (d, *J* = 12.0 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.76 (s, 1H), 1.66 (s, 9H), 1.43 (s, 9H) ppm. **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ 170.4, 148.8, 140.5, 131.2, 129.6, 122.7, 121.8, 118.0, 117.5, 114.6, 112.3, 90.0, 83.8, 81.6, 68.4, 37.5, 27.9, 27.7 ppm. **IR (neat) ν (cm^{-1}):** 2979, 1731, 1597, 1485, 1354, 1251, 1219, 1148, 1001, 833, 750; **HRMS** (ESI-FT) calcd for $C_{28}H_{30}{}^{35}ClNO_6Na^+$ ([M]+Na$^+$) = 534.1654, found 534.1652; $C_{28}H_{30}{}^{37}ClNO_6Na^+$ ([M]+Na$^+$) = 536.1624, found 536.1623.



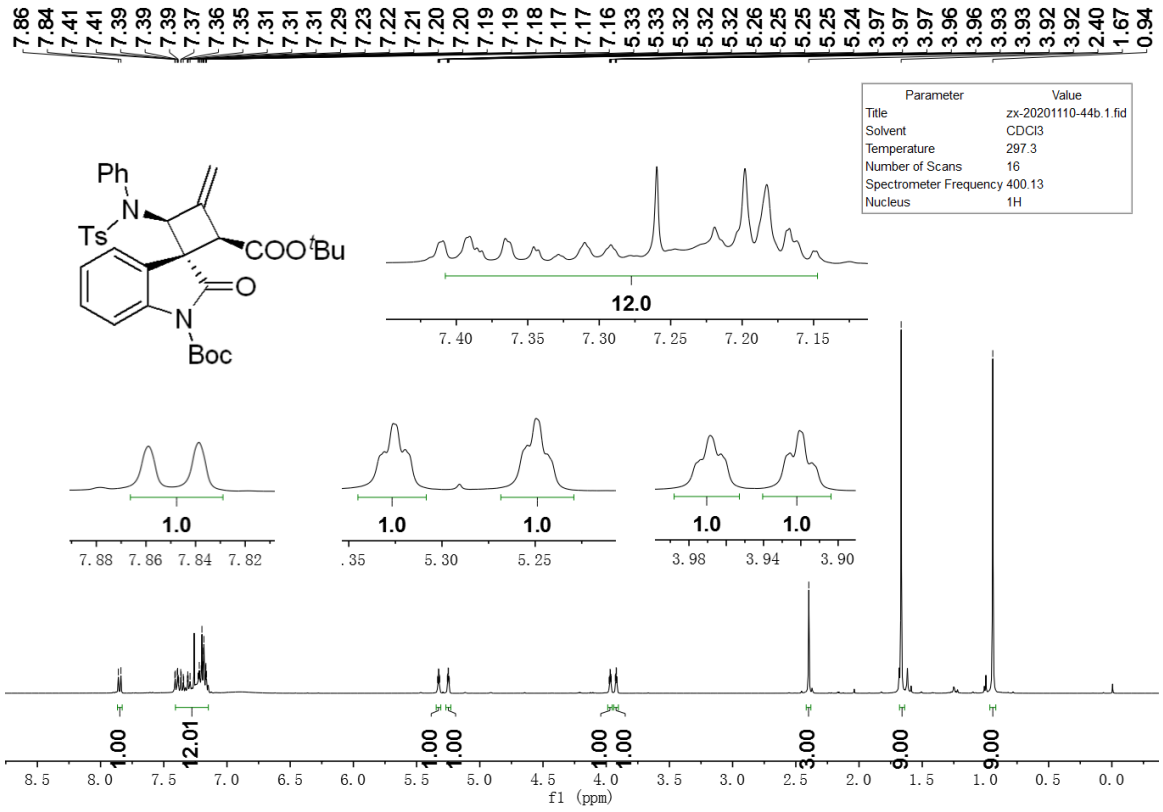
	Retention Time	Area	% Area
1	5.604	52602	50.35
2	6.934	51875	49.65

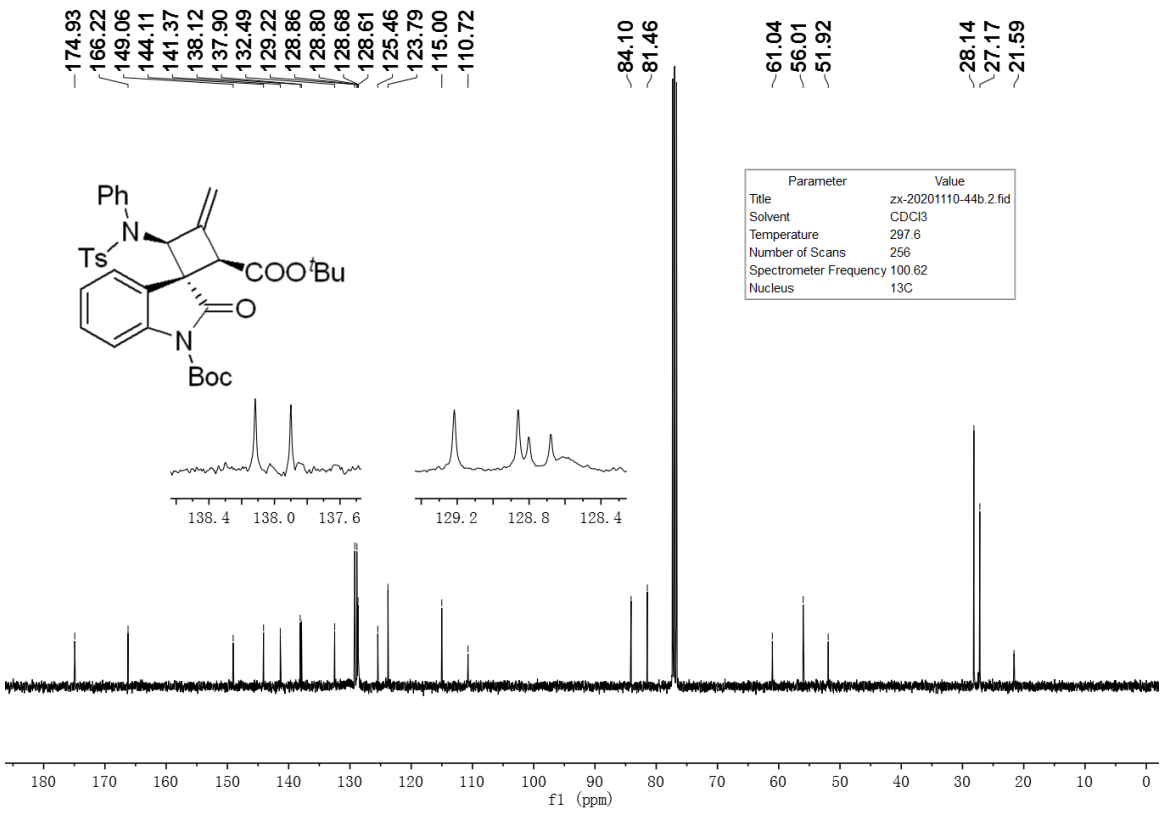


	Retention Time	Area	% Area
1	5.612	6525	2.53
2	6.954	251451	97.47

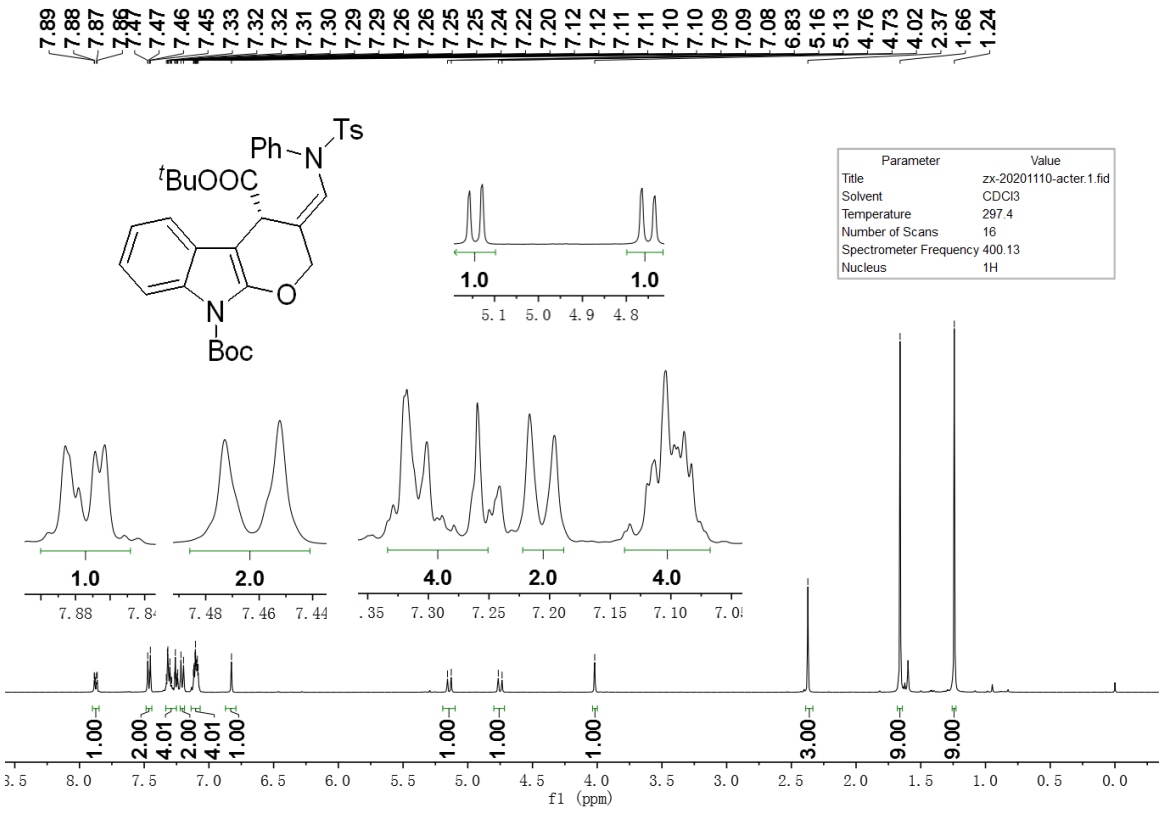
(I) Copies of NMR Spectra

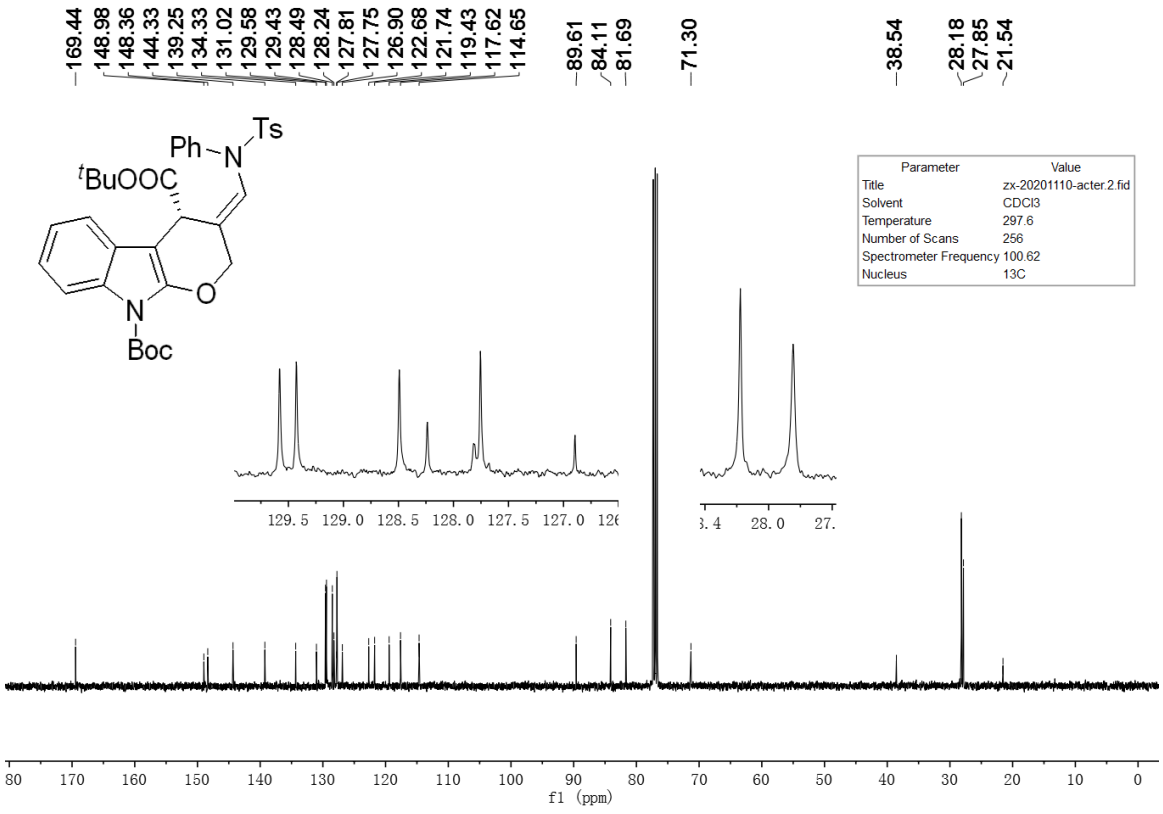
^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of compound **3aa** in $CDCl_3$



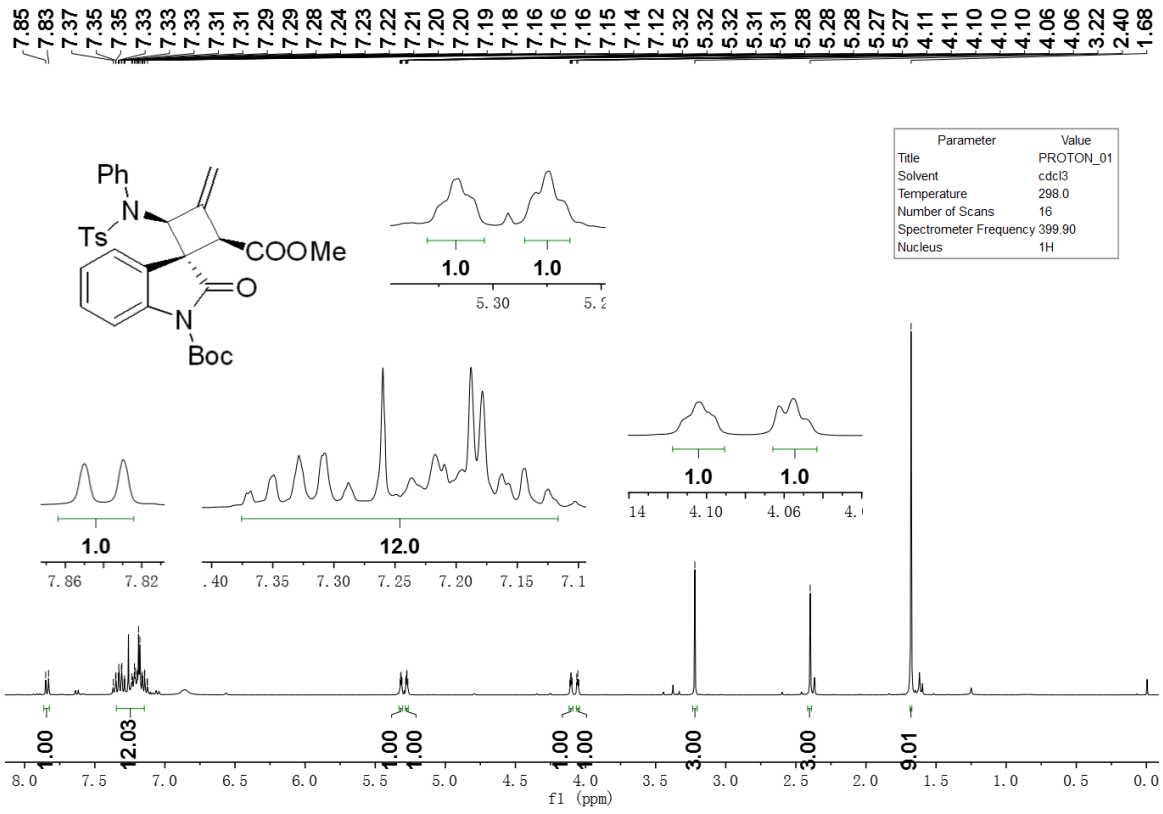


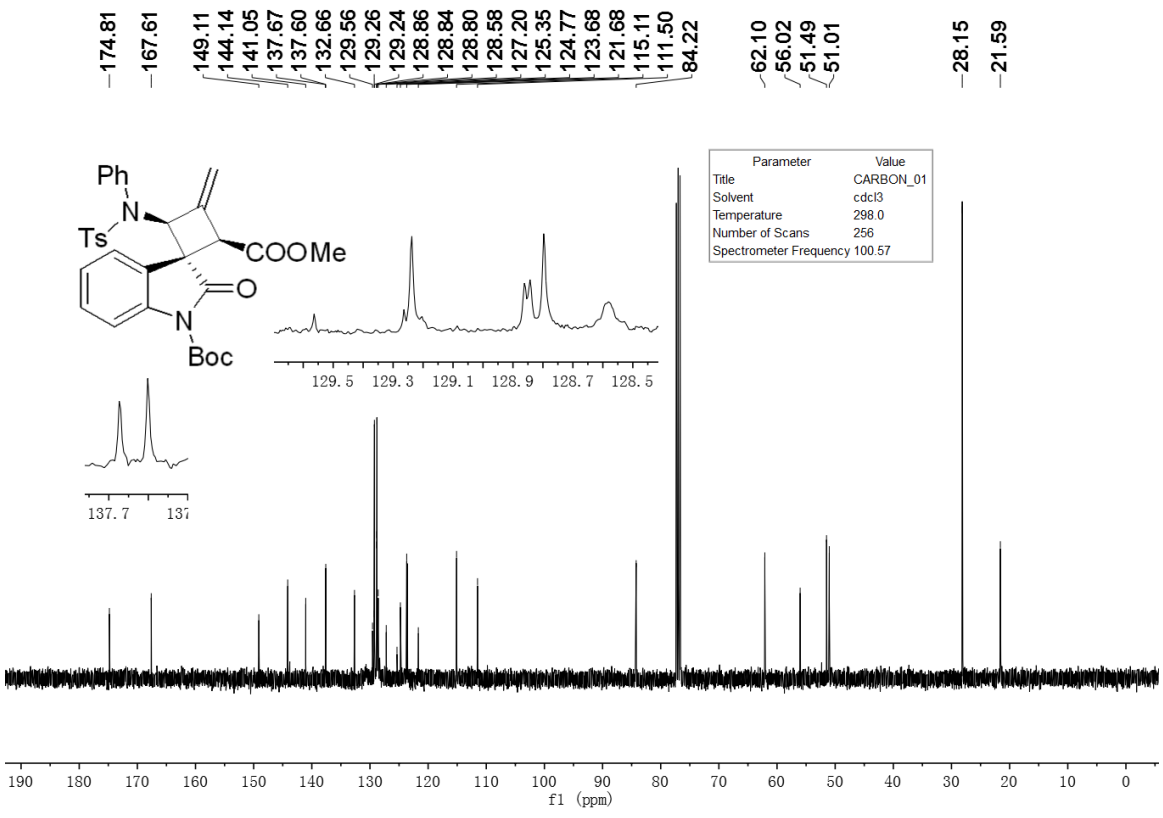
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4aa** in $CDCl_3$



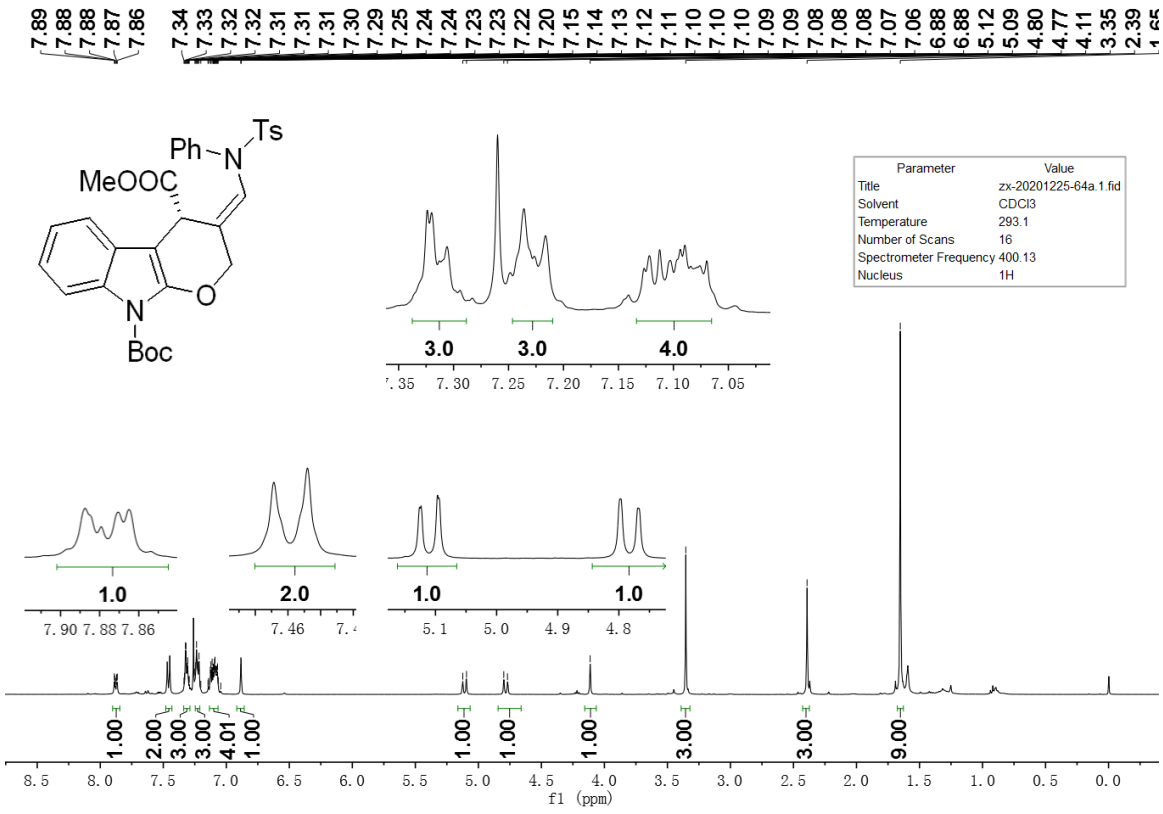


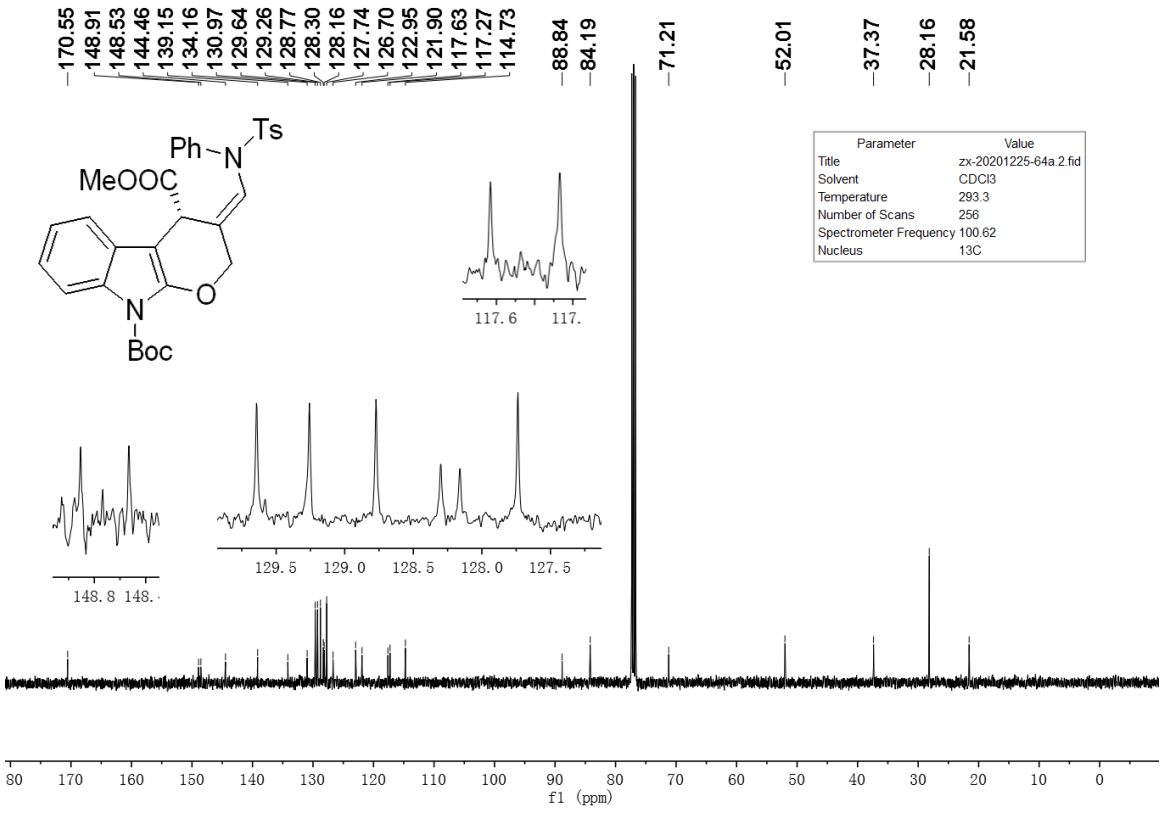
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3ba** in $CDCl_3$



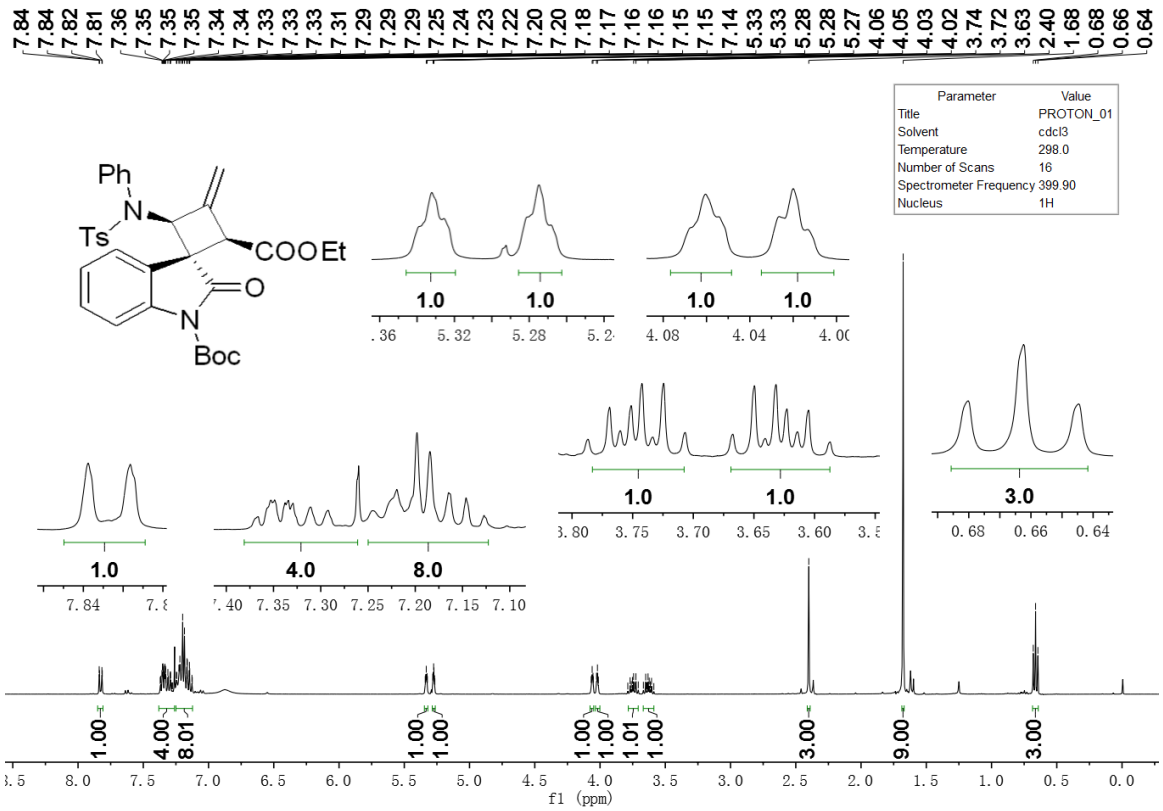


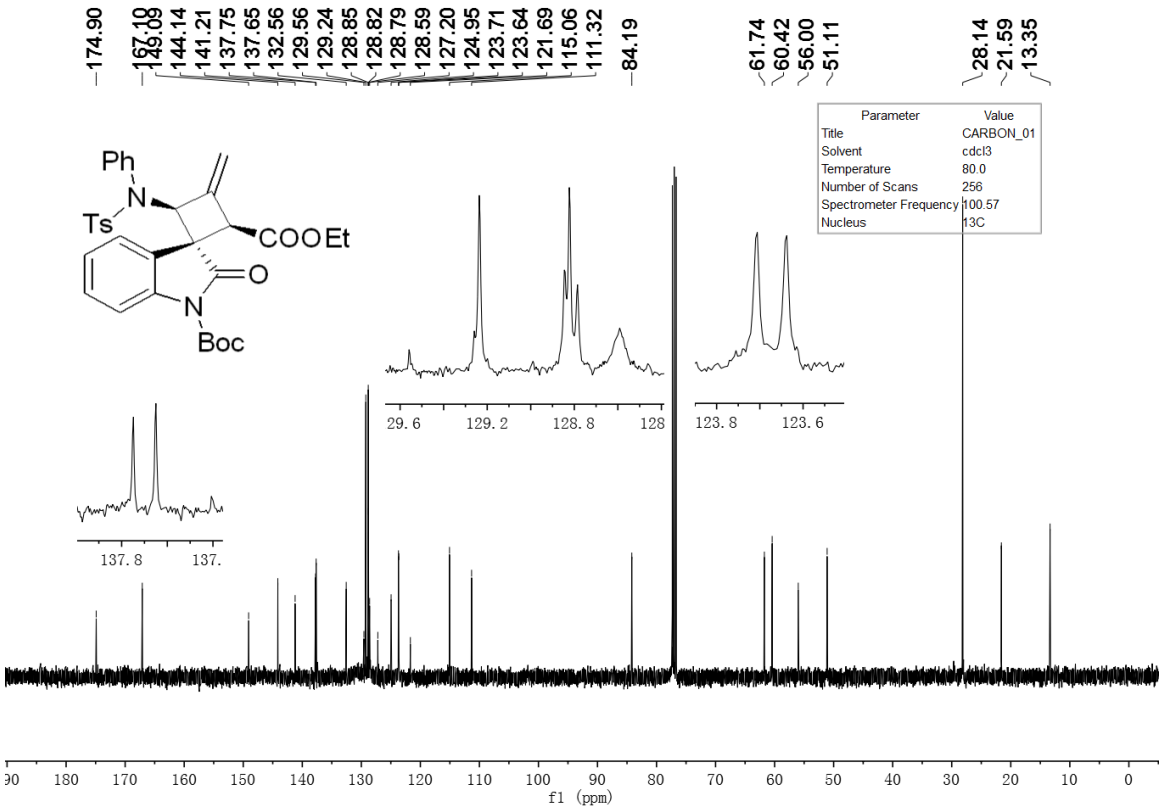
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4ba** in $CDCl_3$



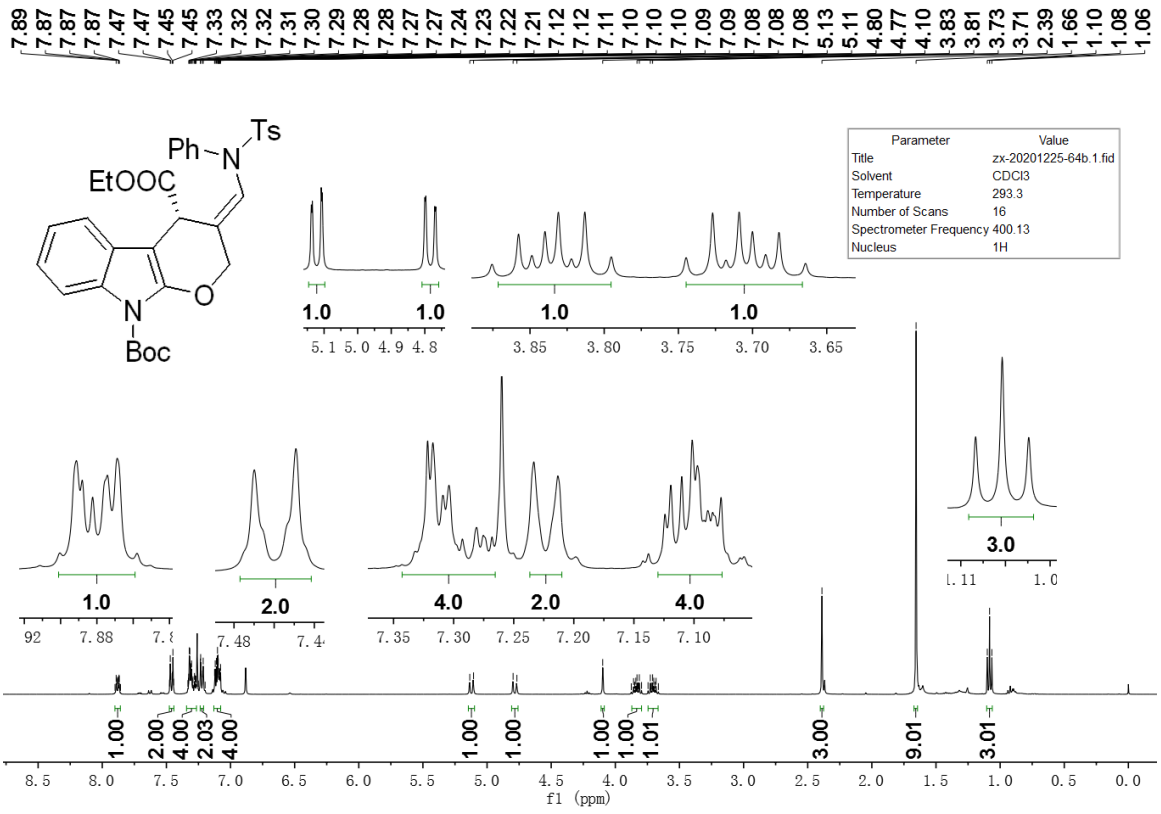


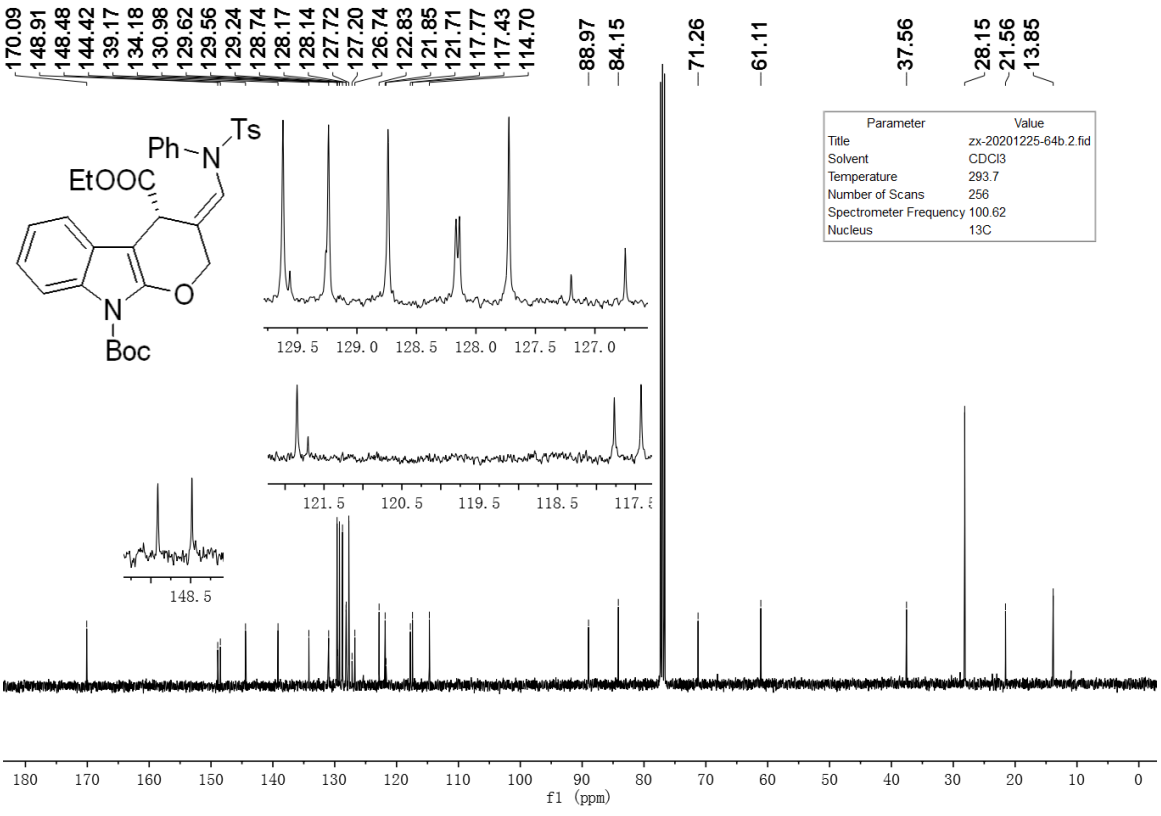
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3ca** in $CDCl_3$



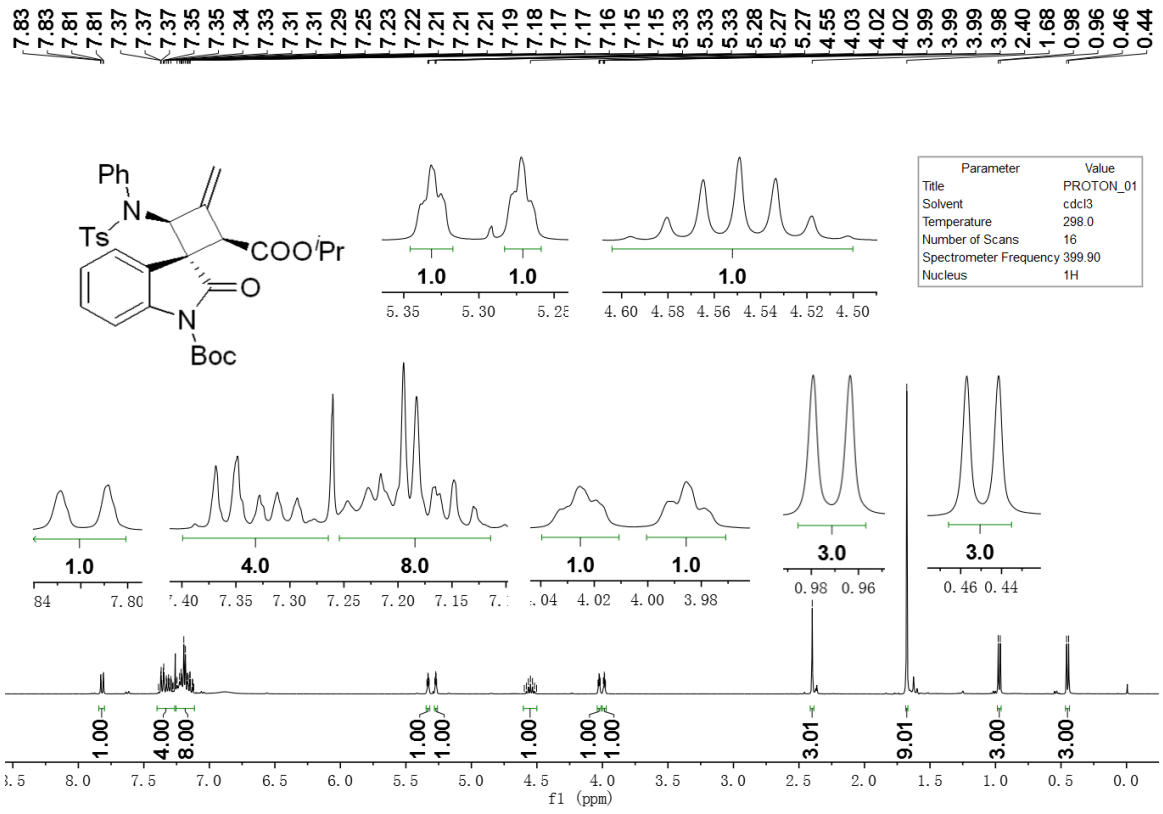


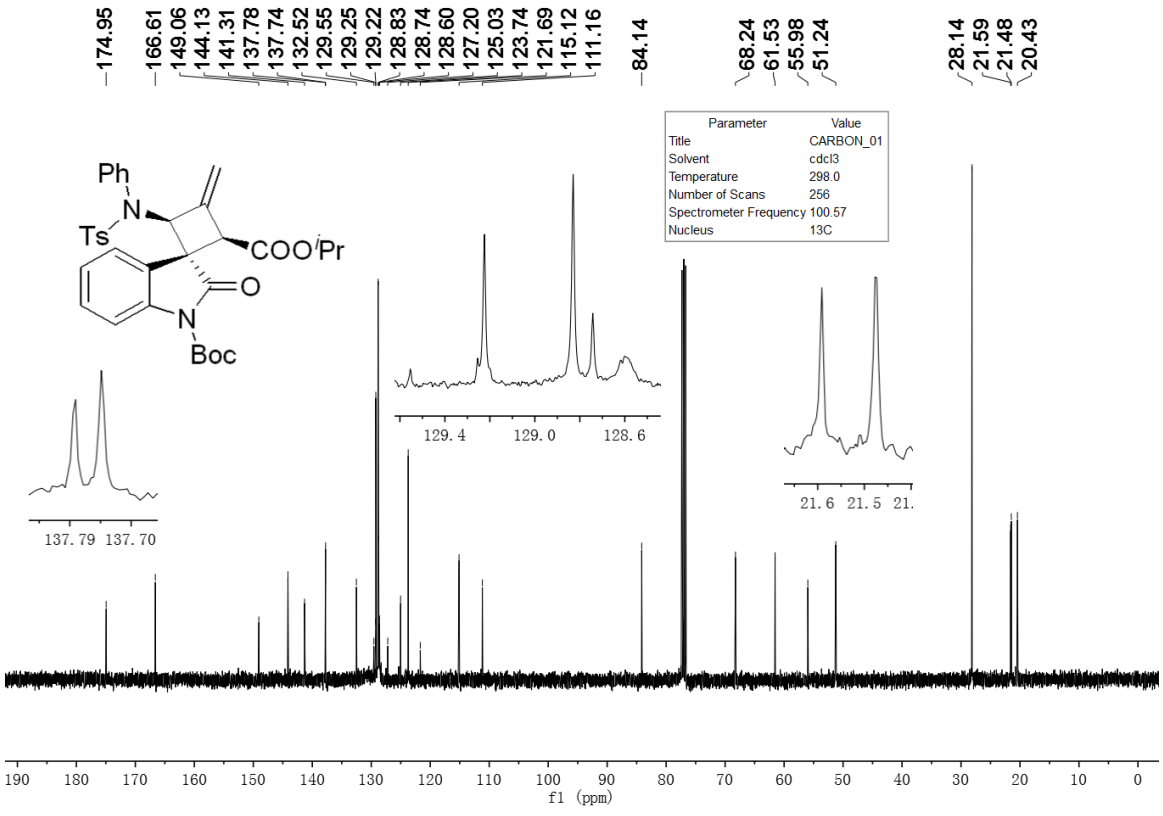
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4ca** in $CDCl_3$



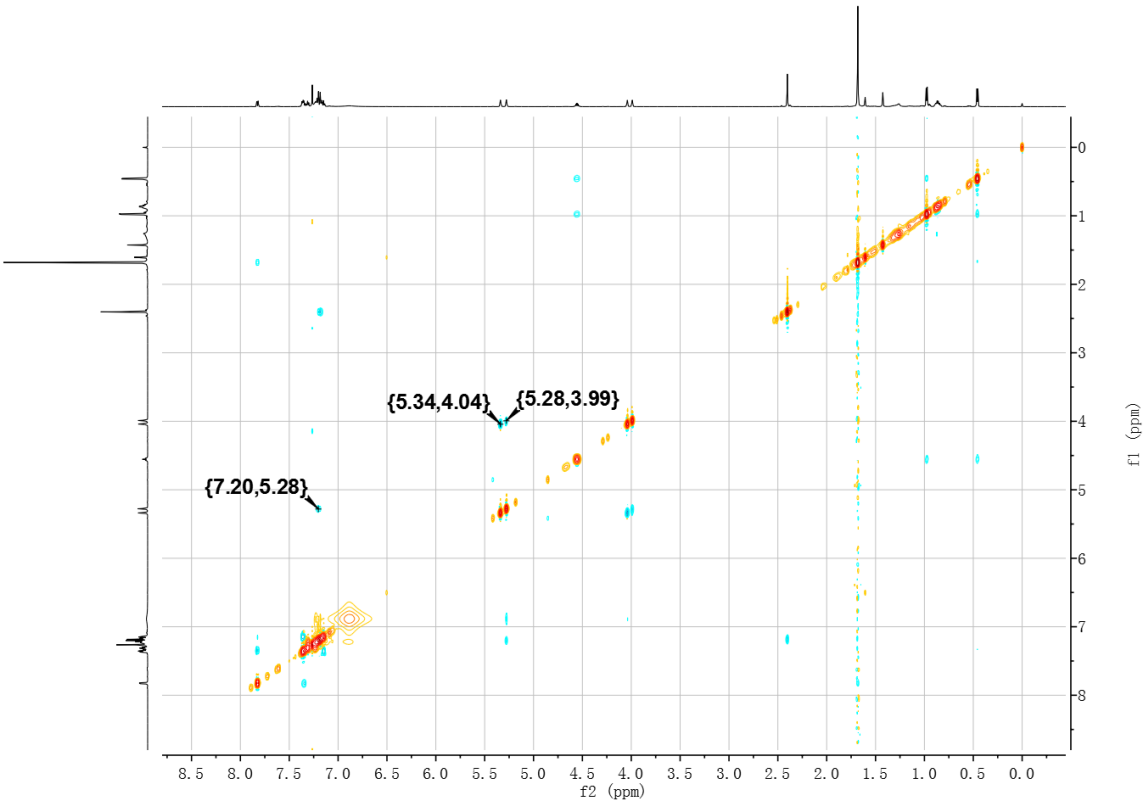


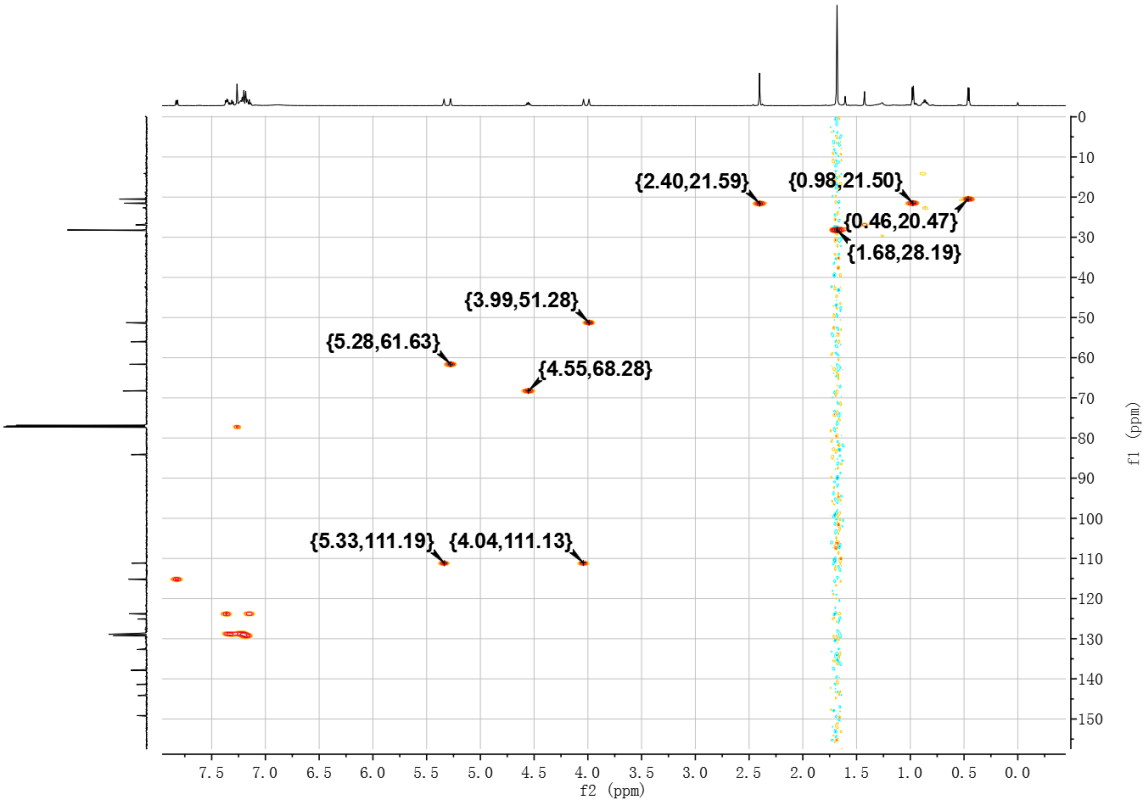
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3da** in $CDCl_3$



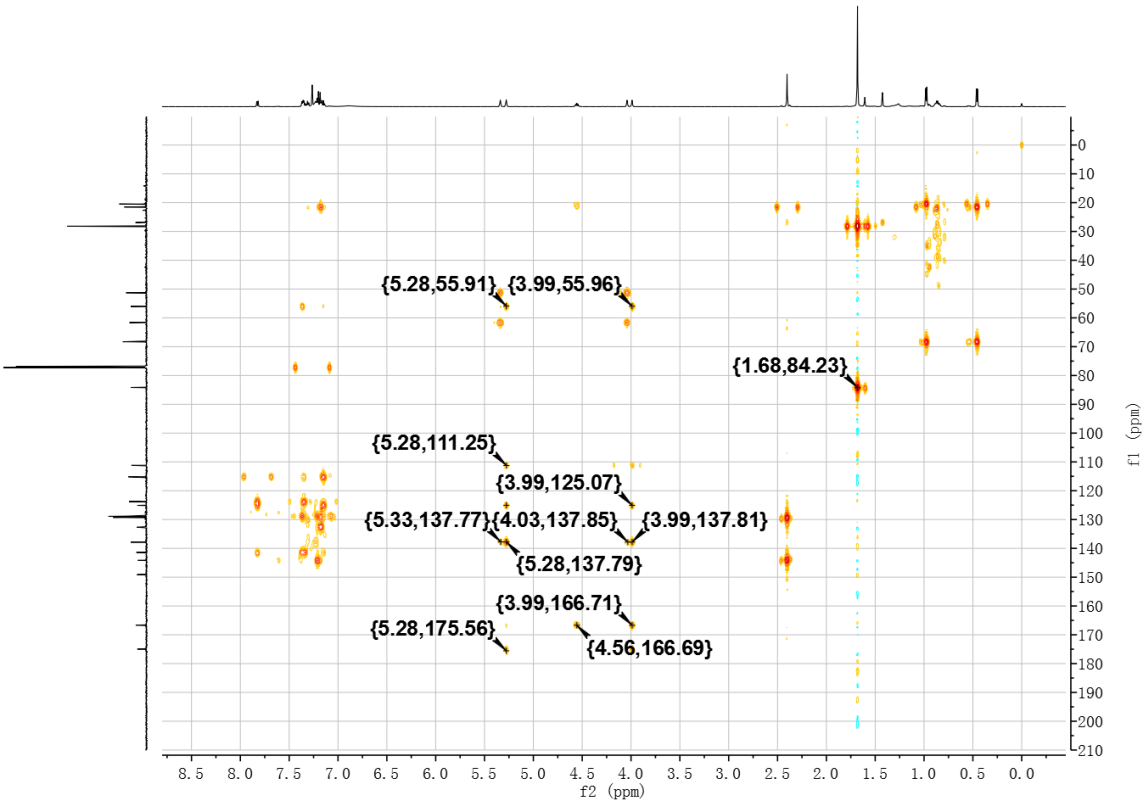


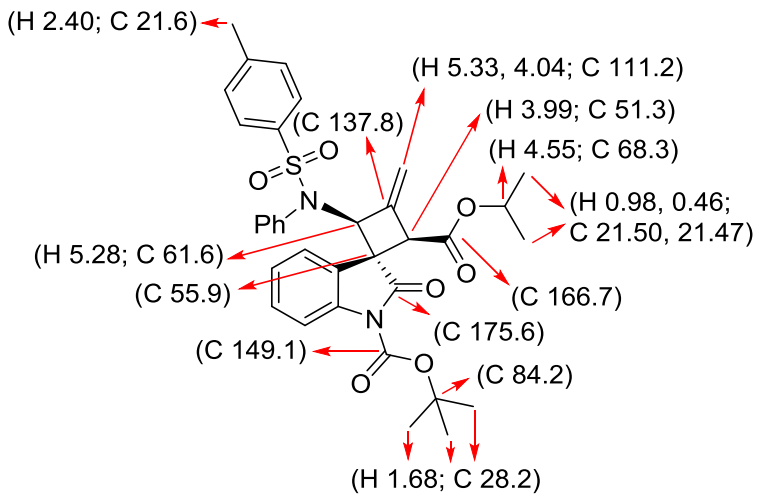
NOESY and HSQC spectra of compound **3da** in $CDCl_3$



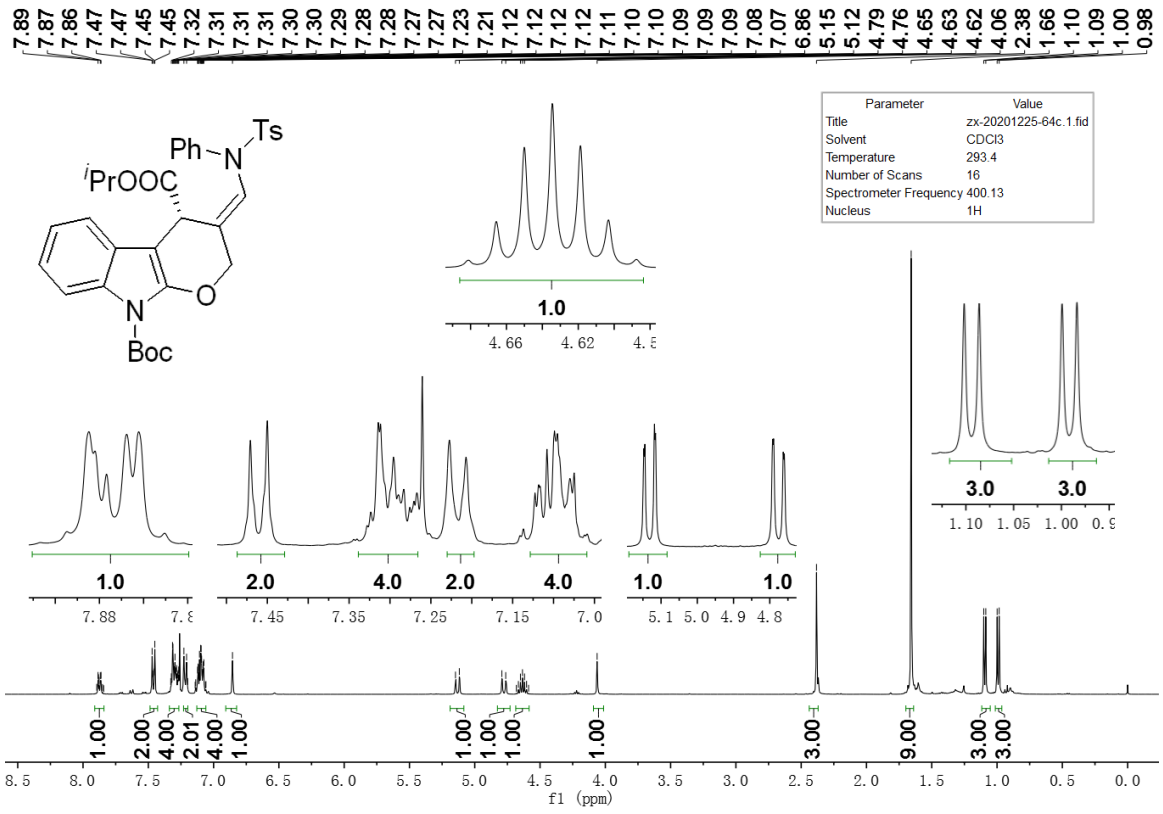


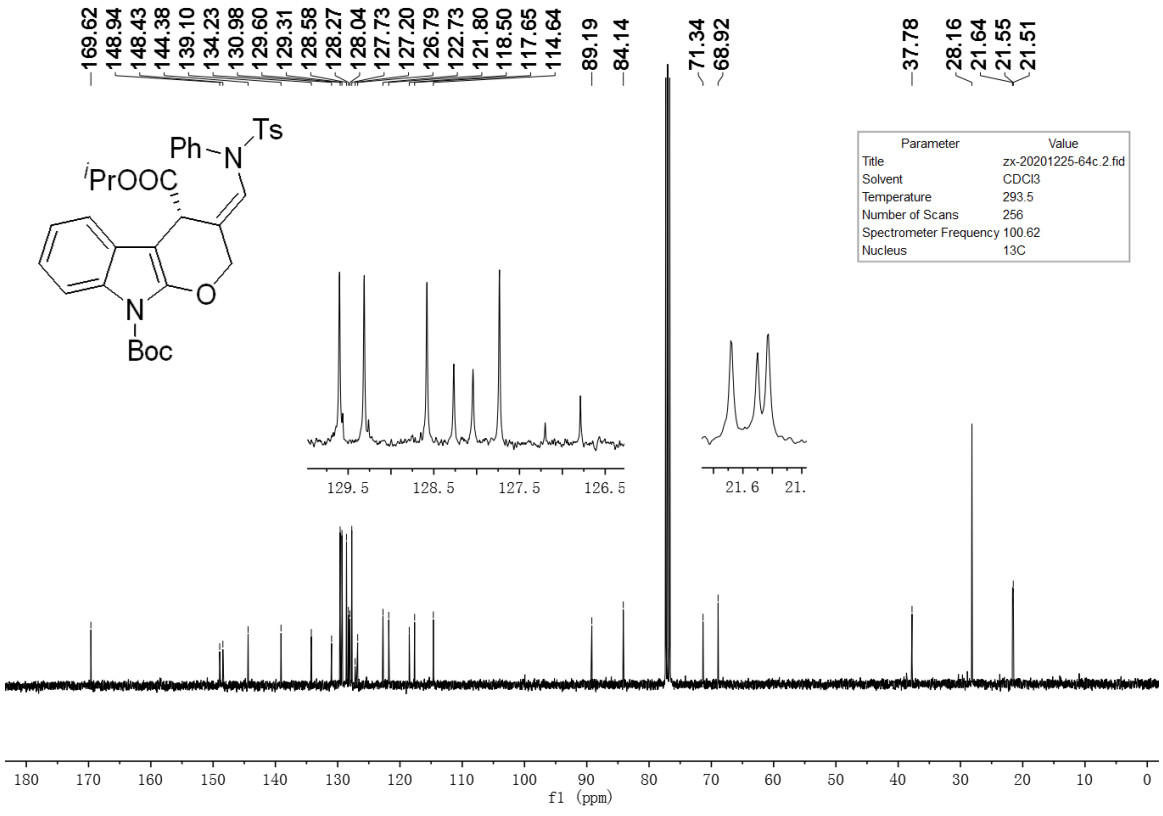
HMBC spectra of compound **3da** in $CDCl_3$



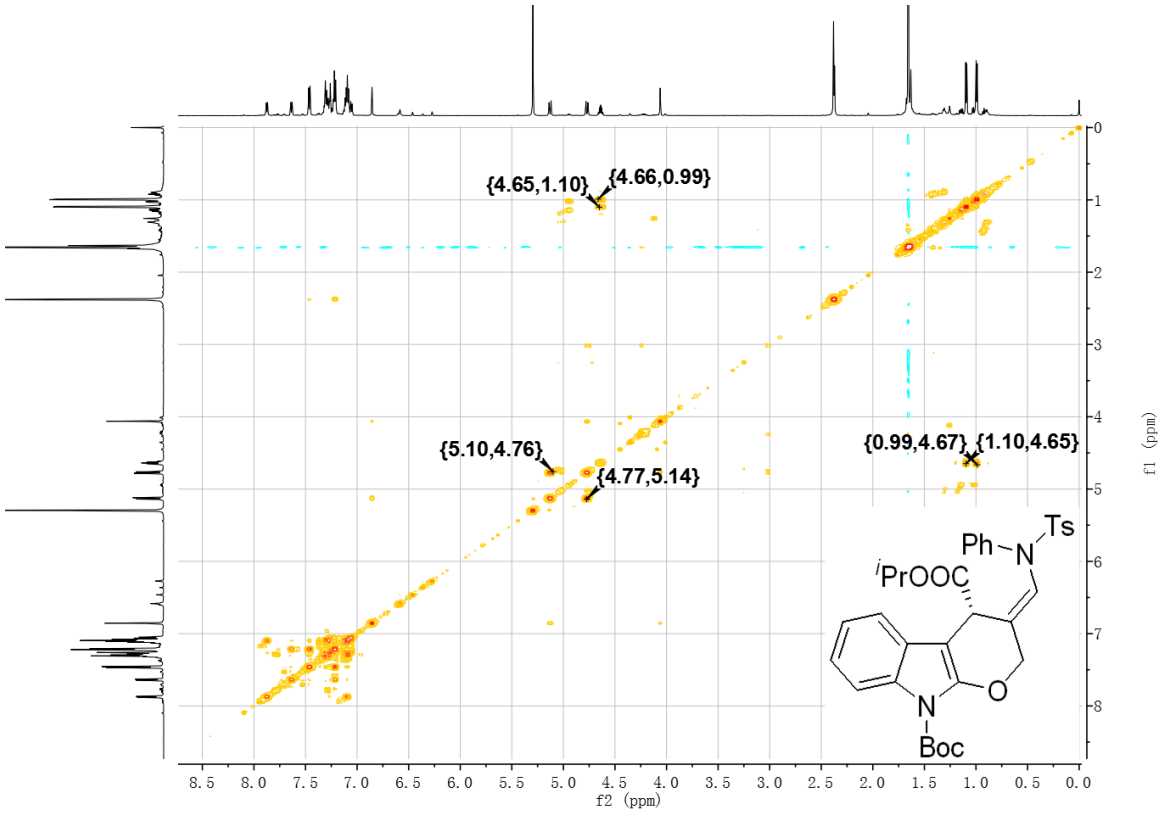


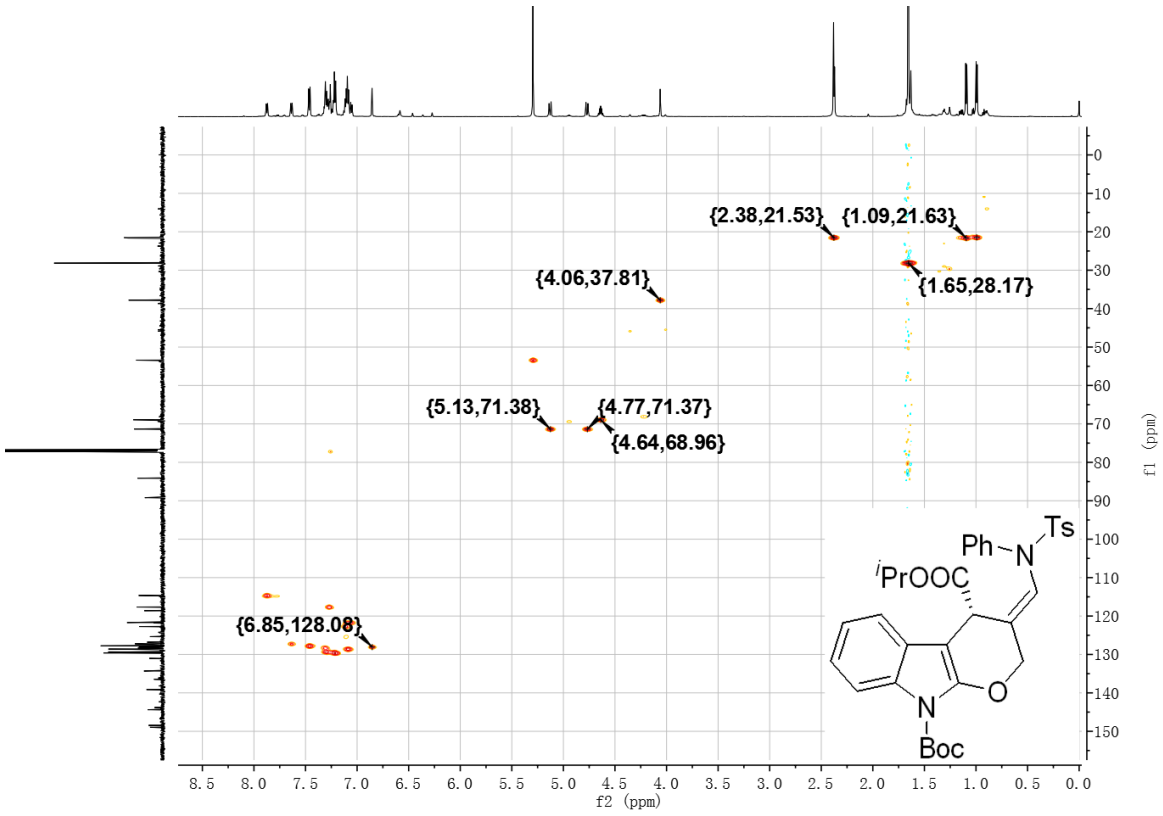
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4da** in $CDCl_3$



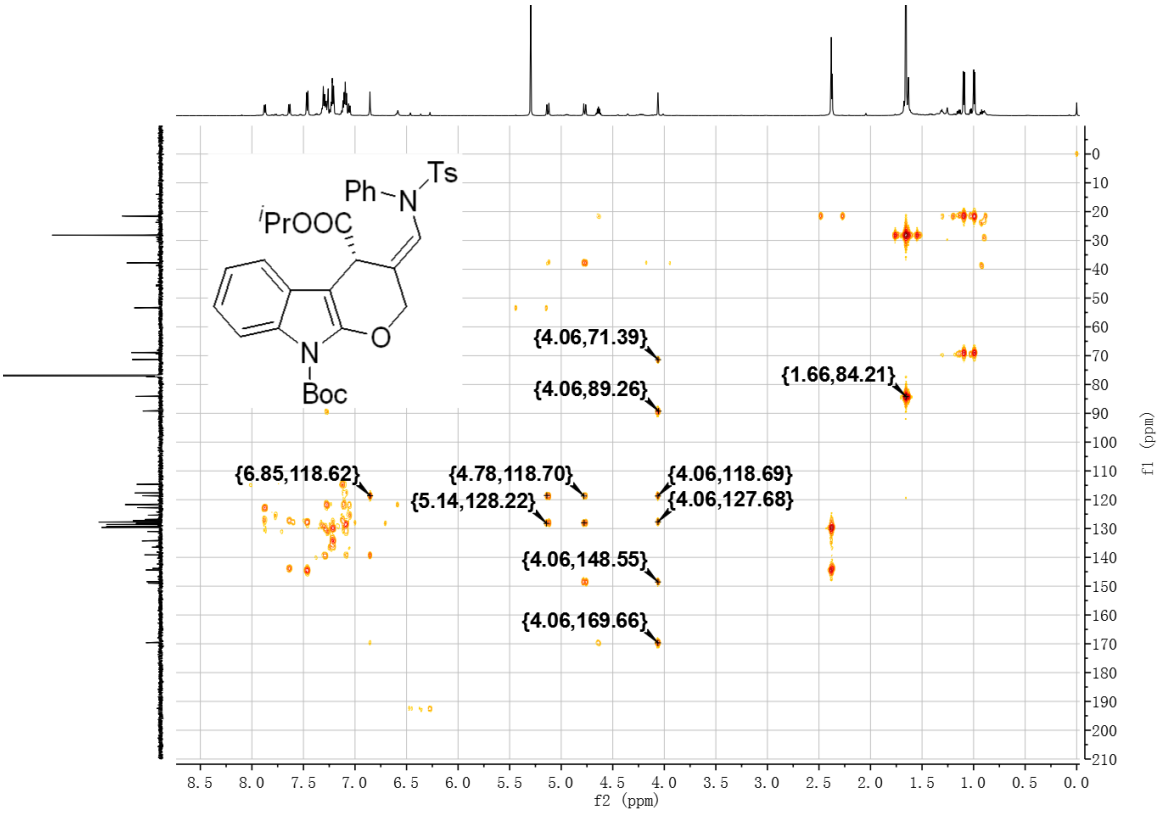


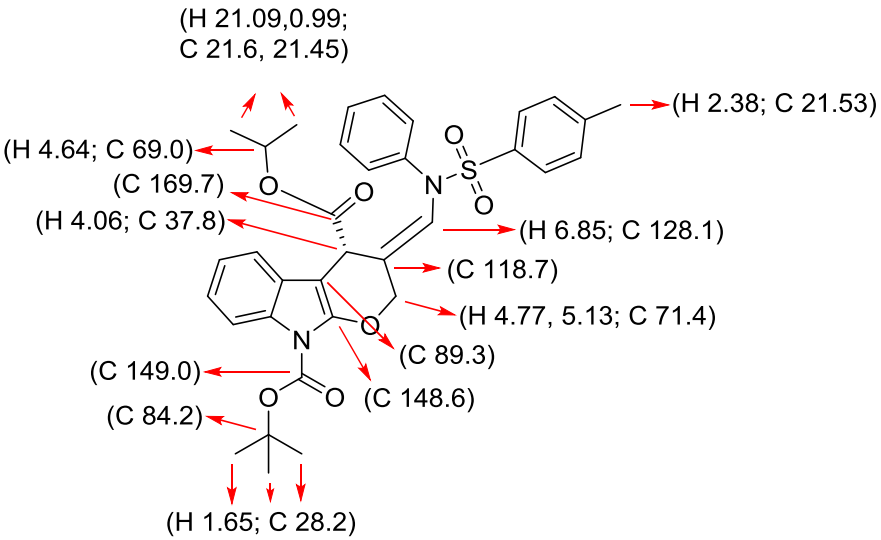
COSY and HSQC spectra of compound **4da** in $CDCl_3$



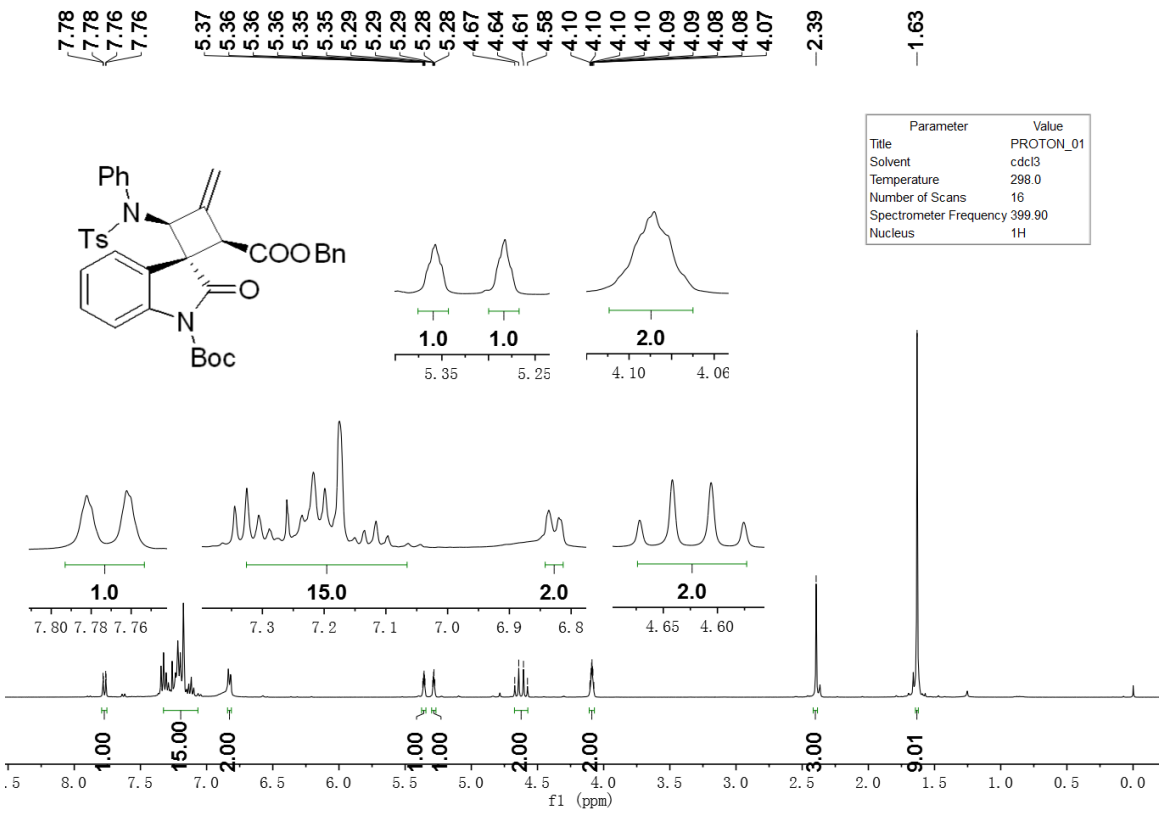


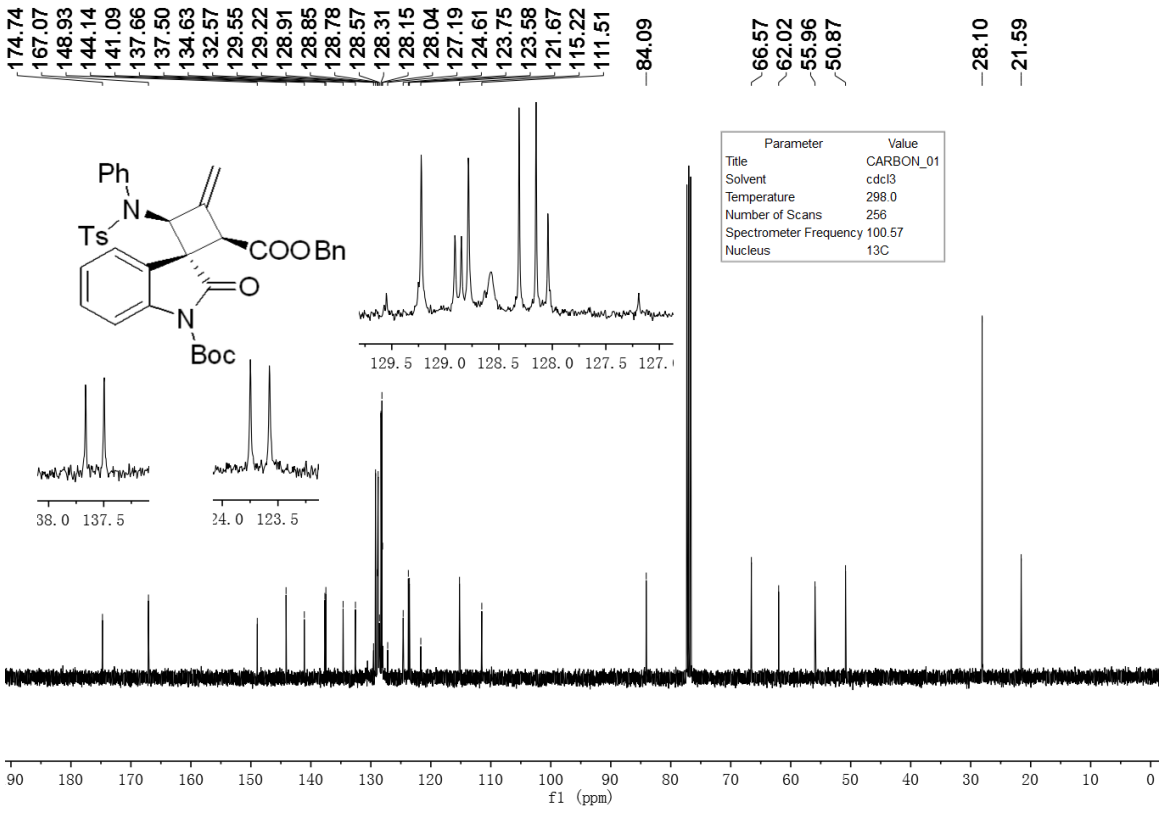
HMBC spectra of compound **4da** in $CDCl_3$



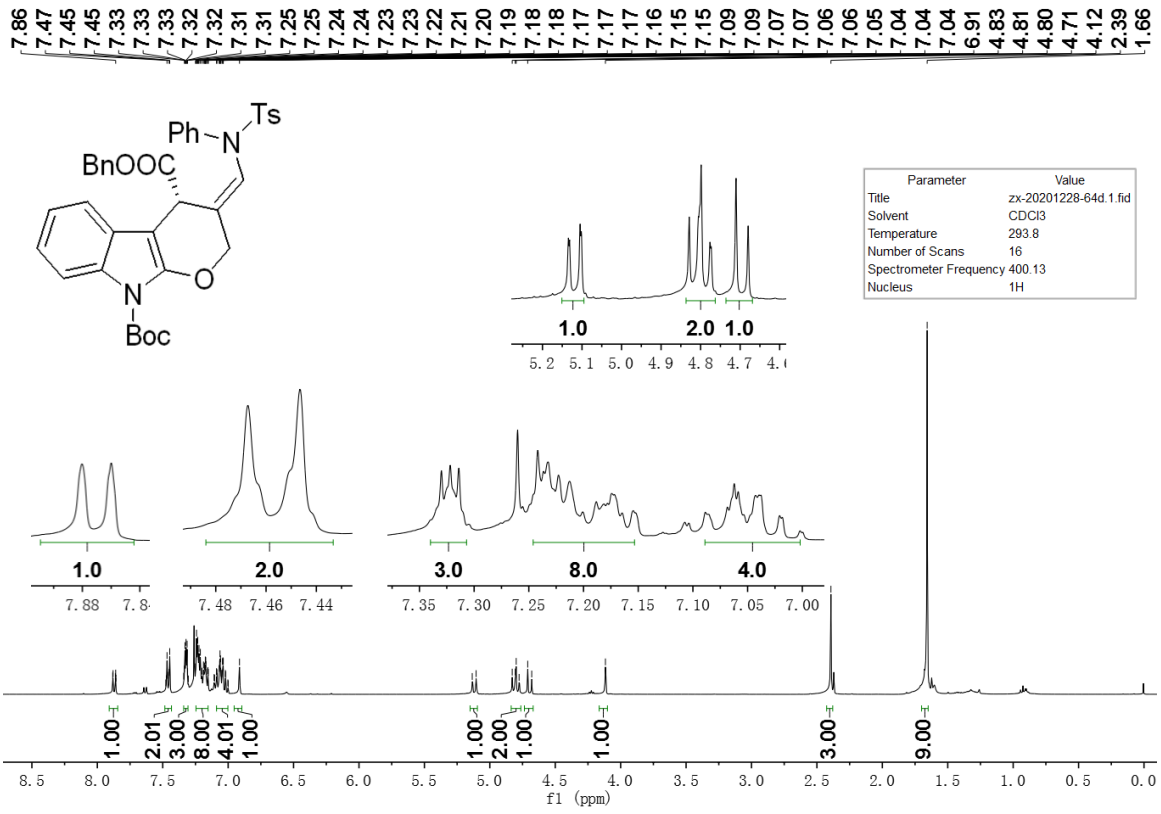


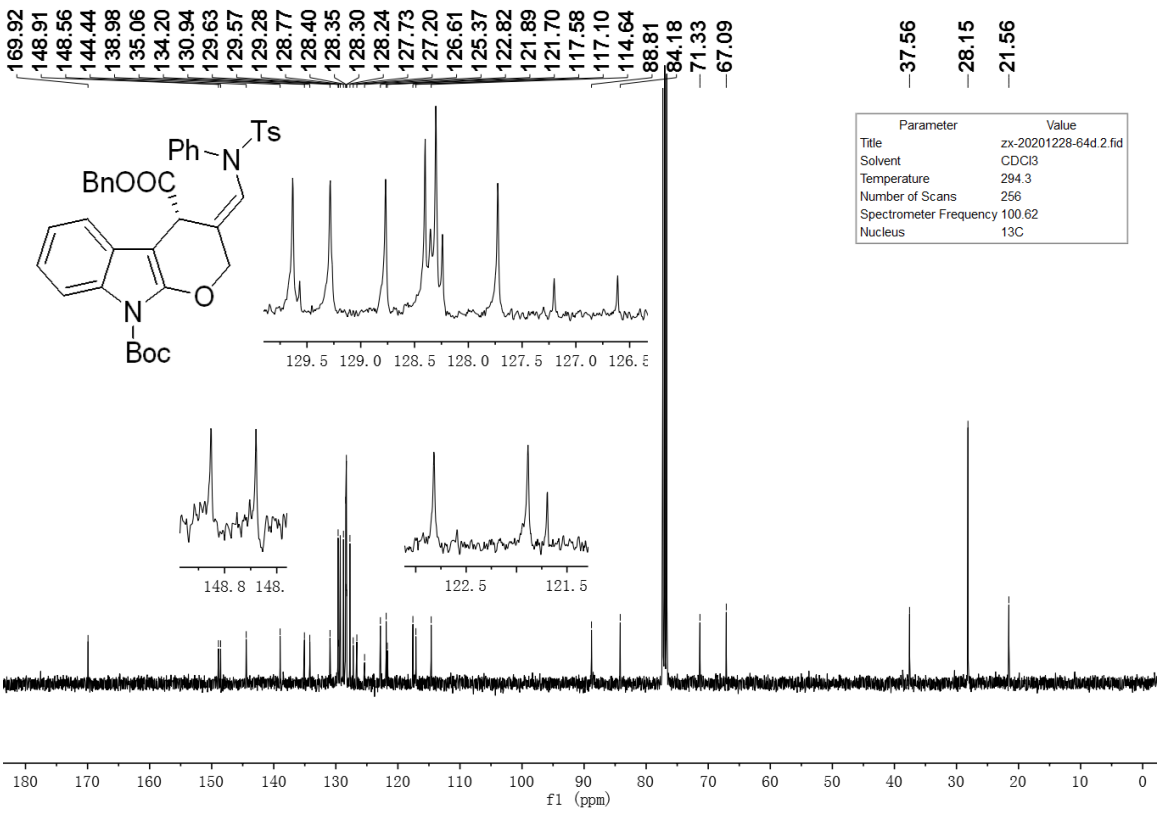
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3ea** in $CDCl_3$



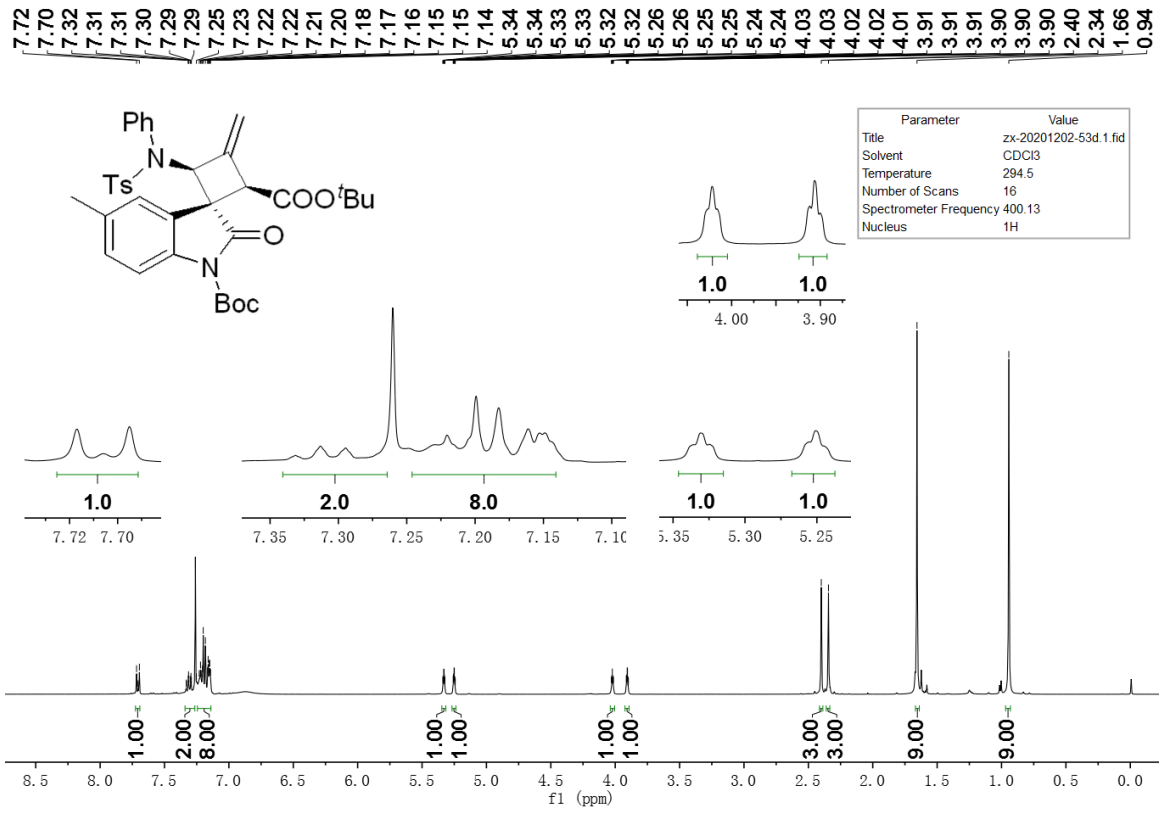


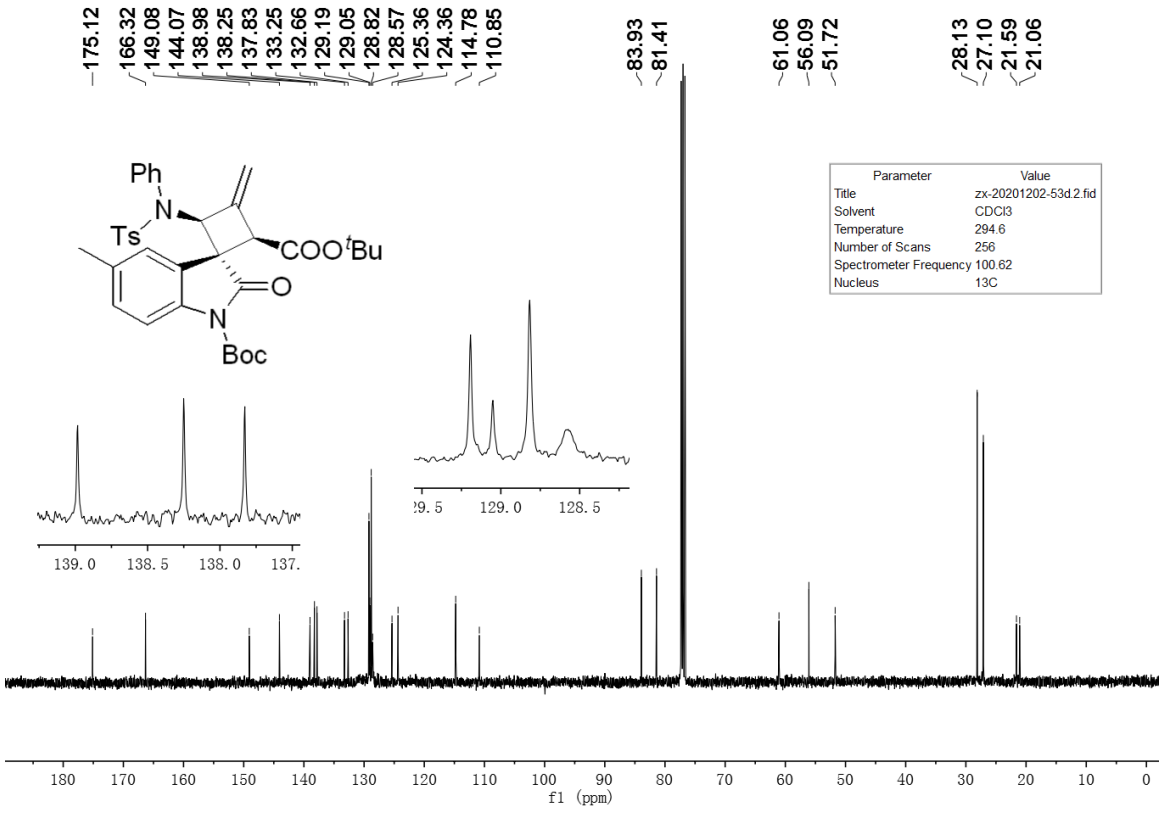
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4ea** in $CDCl_3$



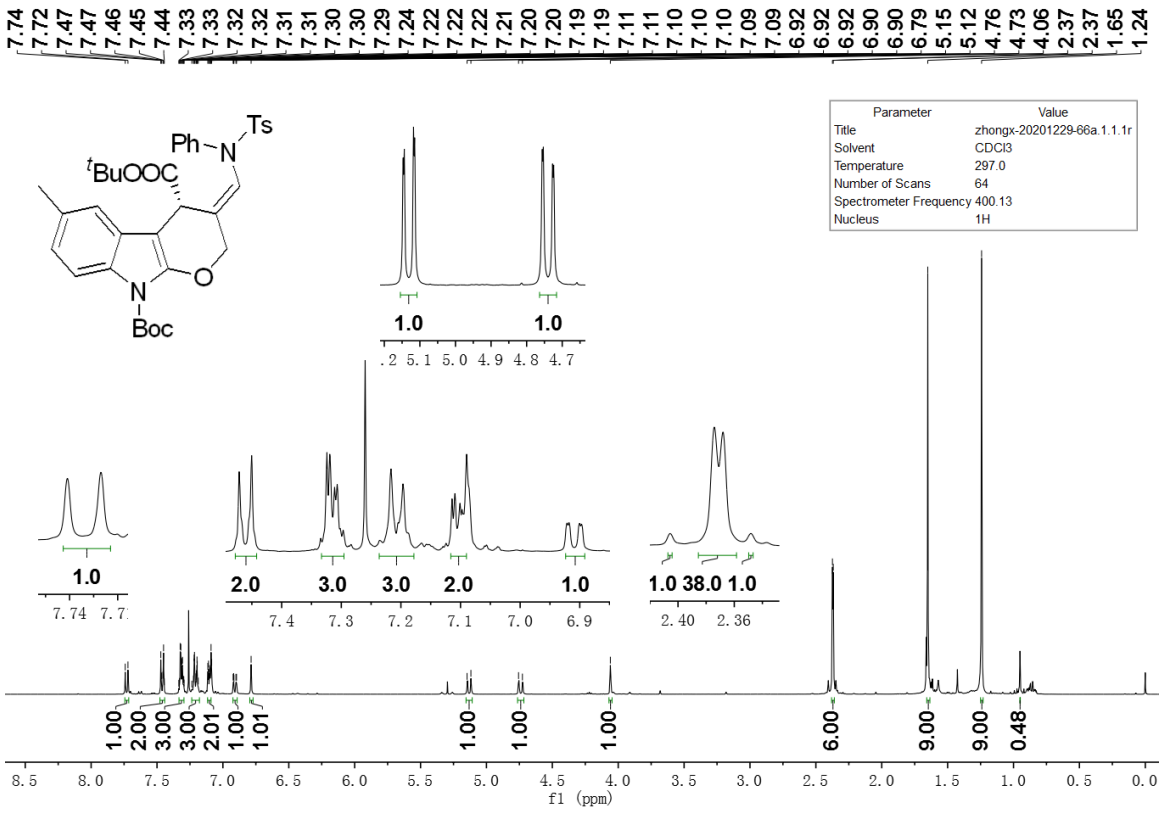


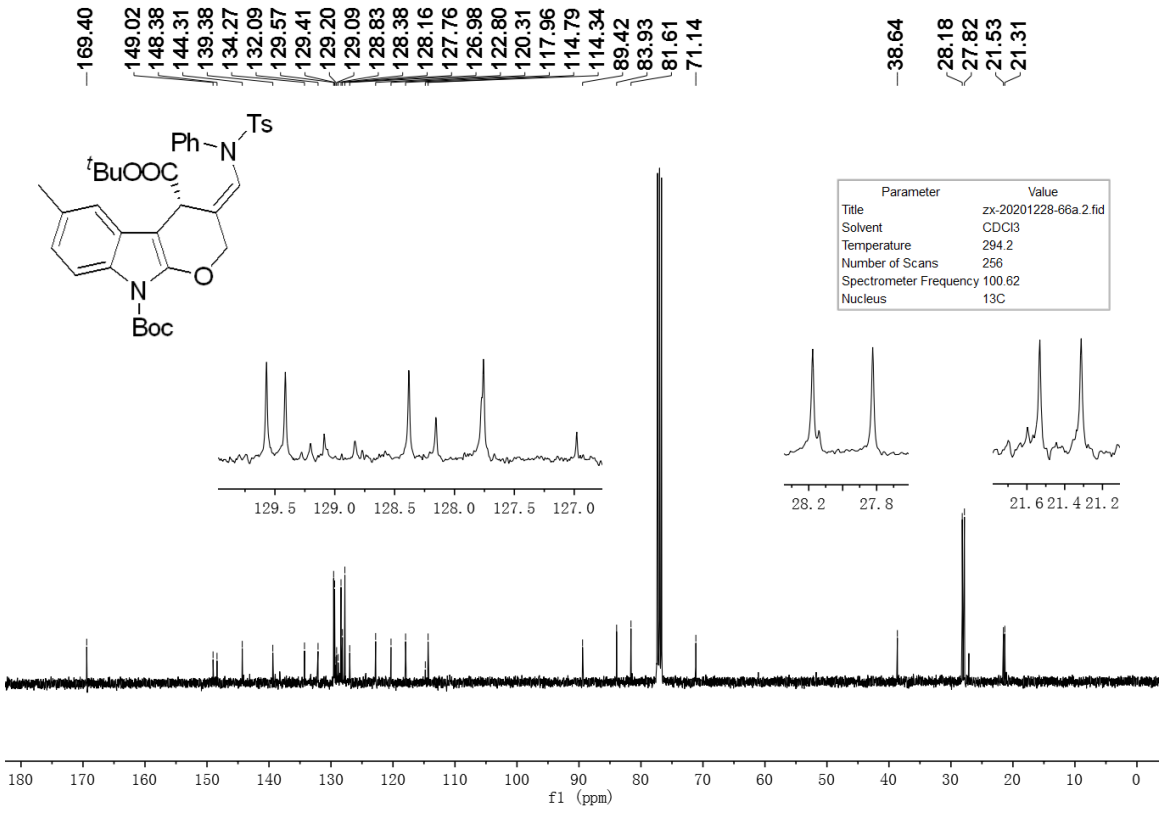
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3fa** in $CDCl_3$



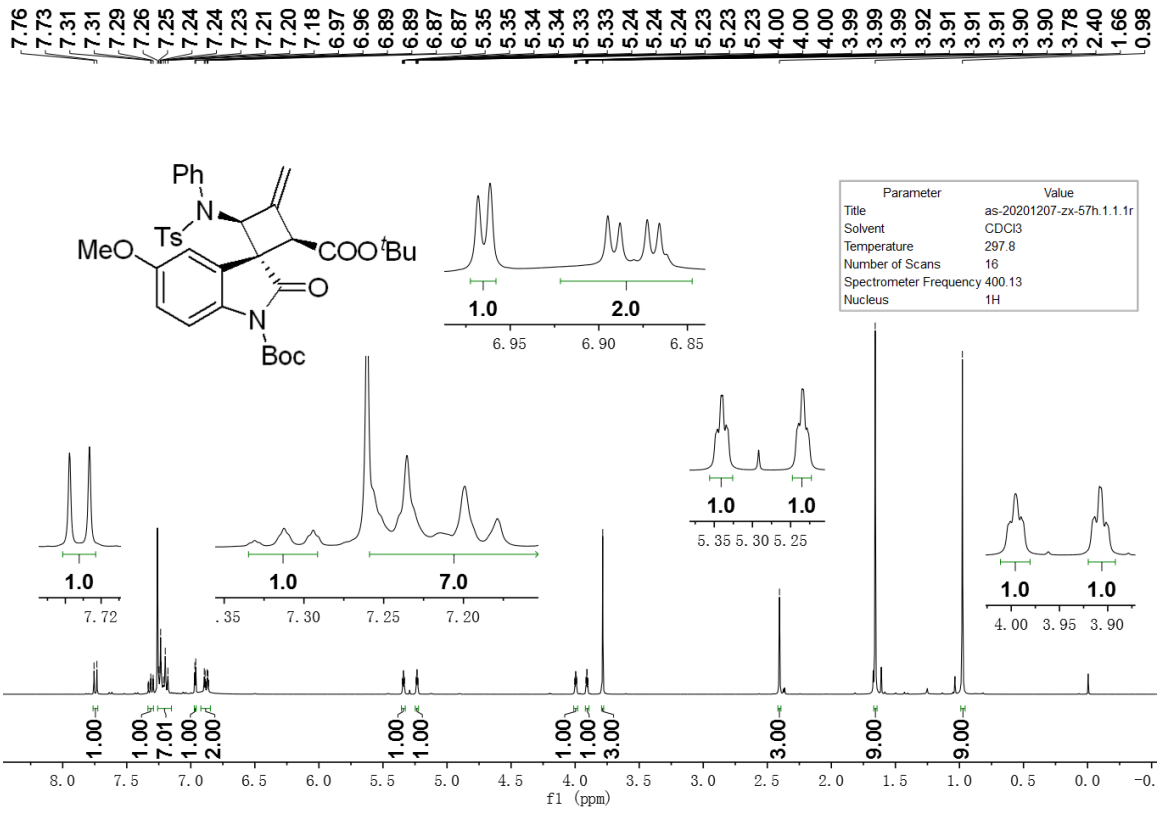


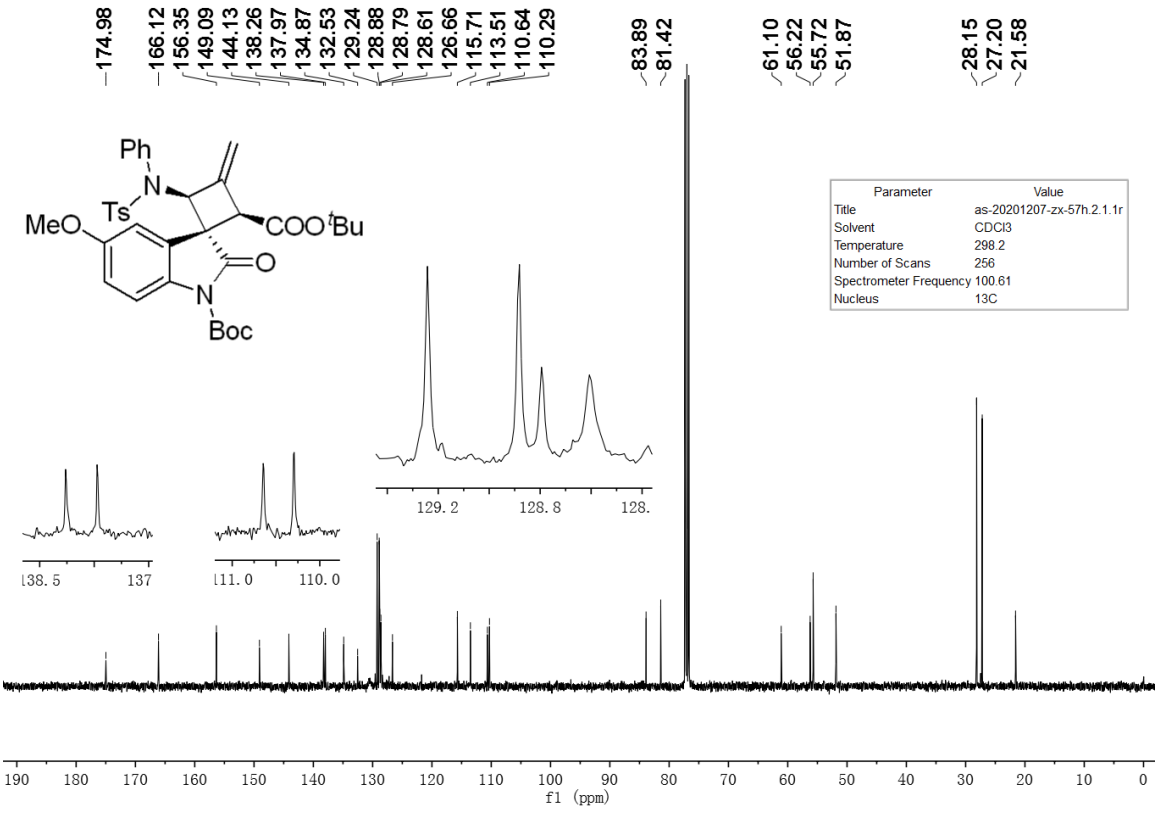
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4fa** in $CDCl_3$



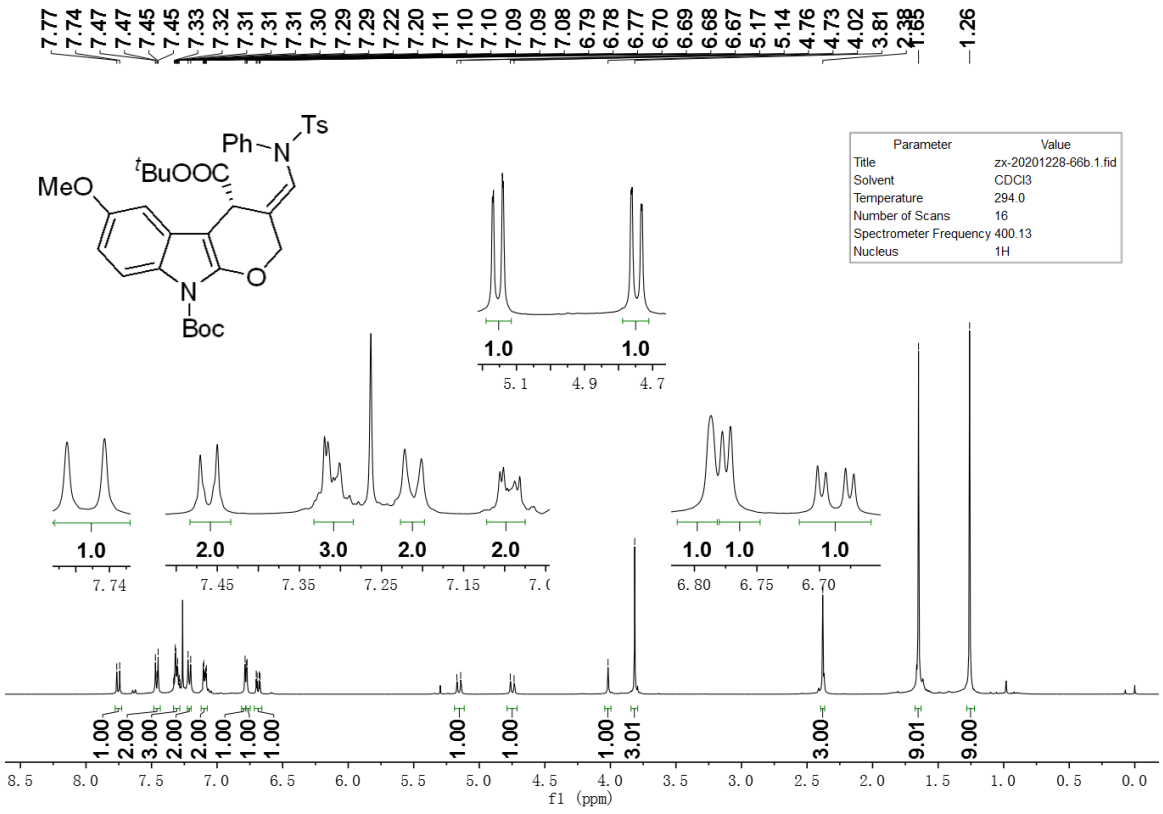


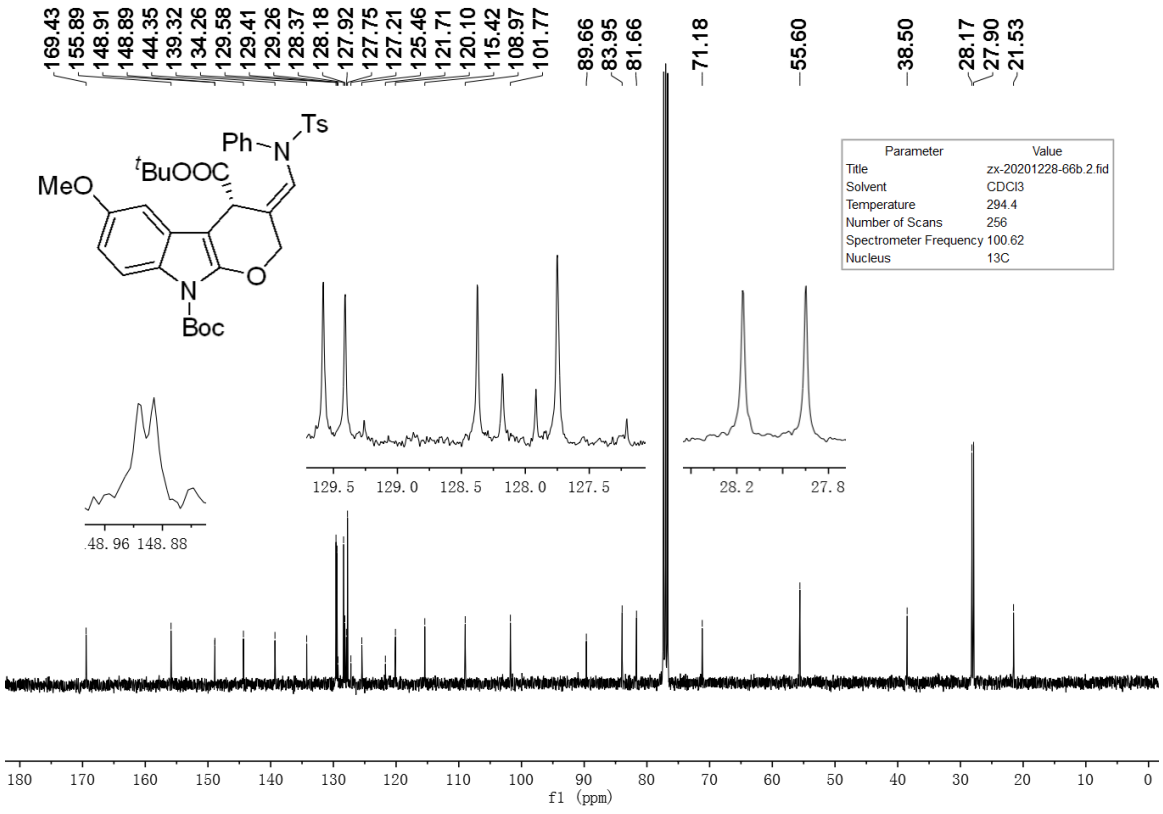
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3ga** in $CDCl_3$



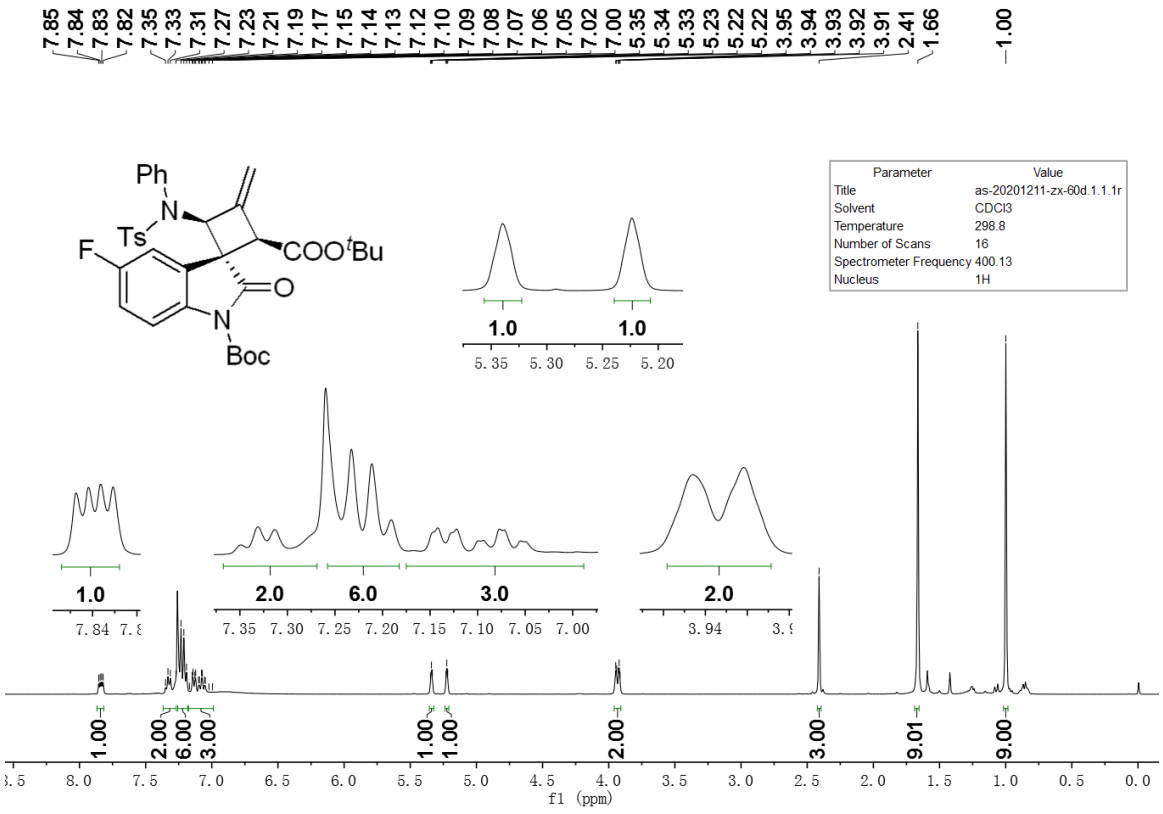


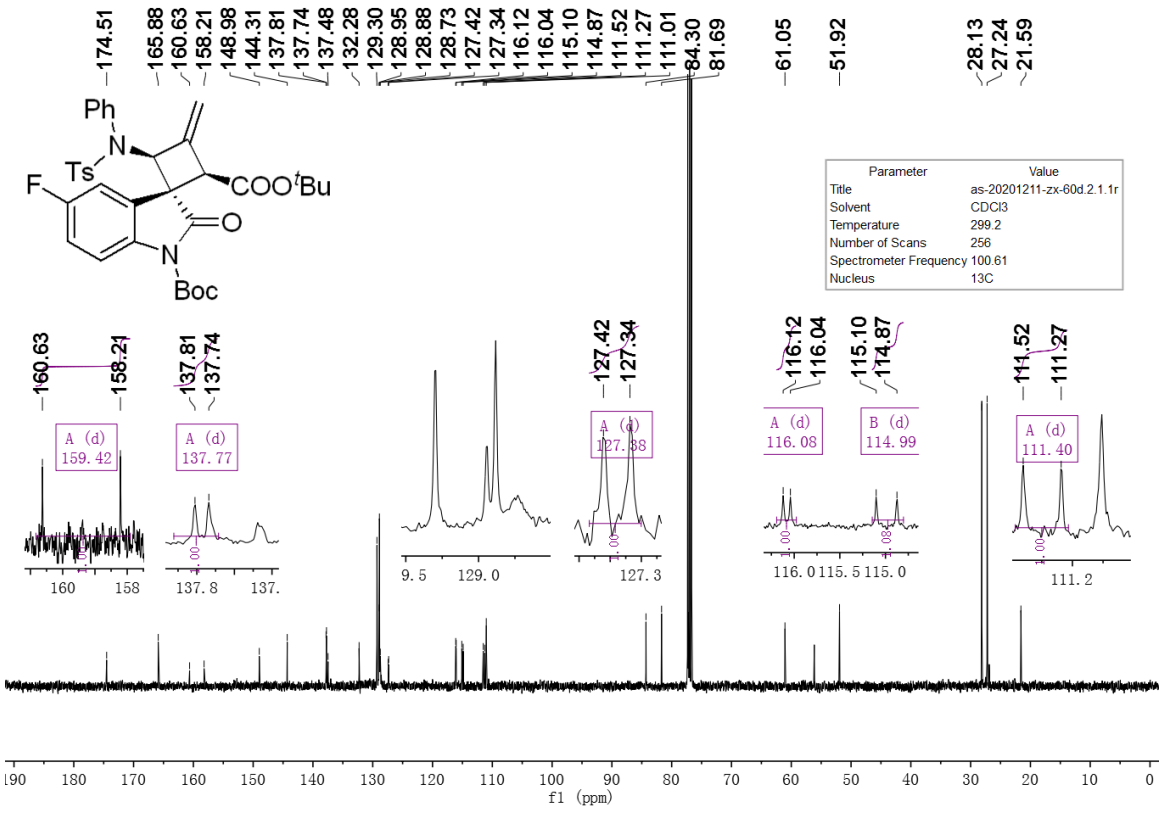
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4ga** in $CDCl_3$



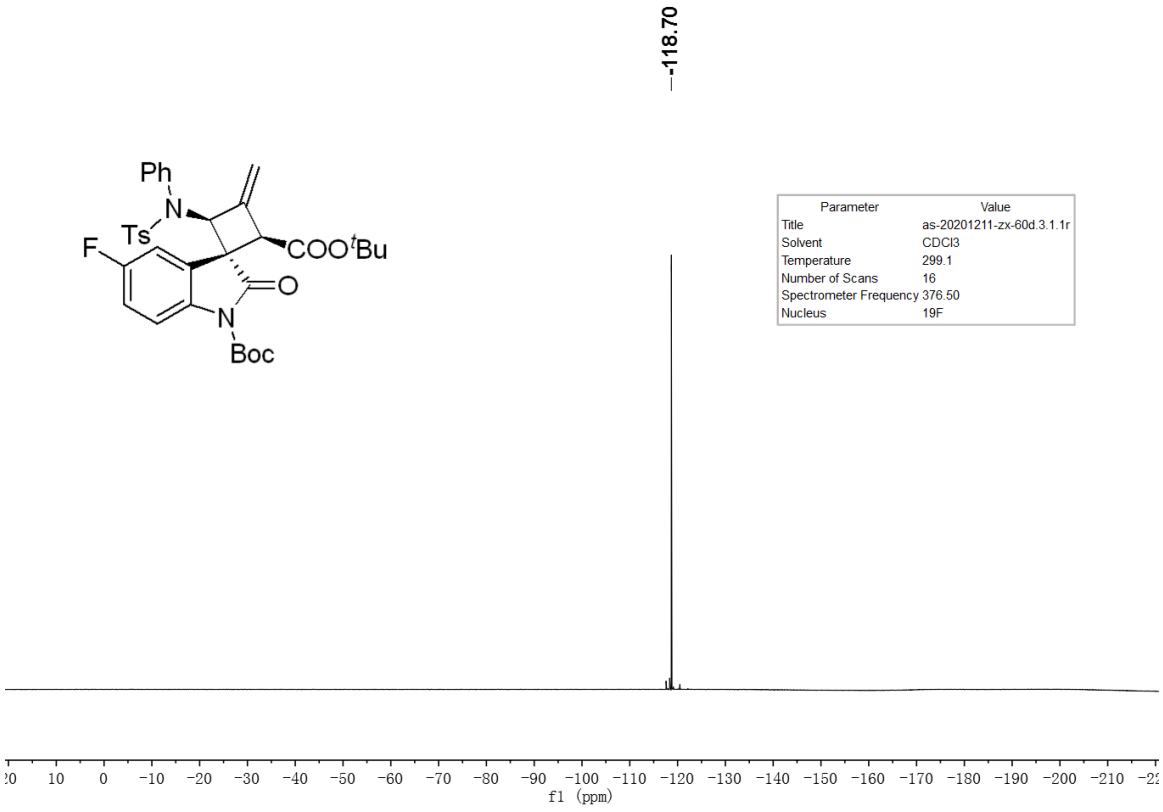


^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3ha** in $CDCl_3$

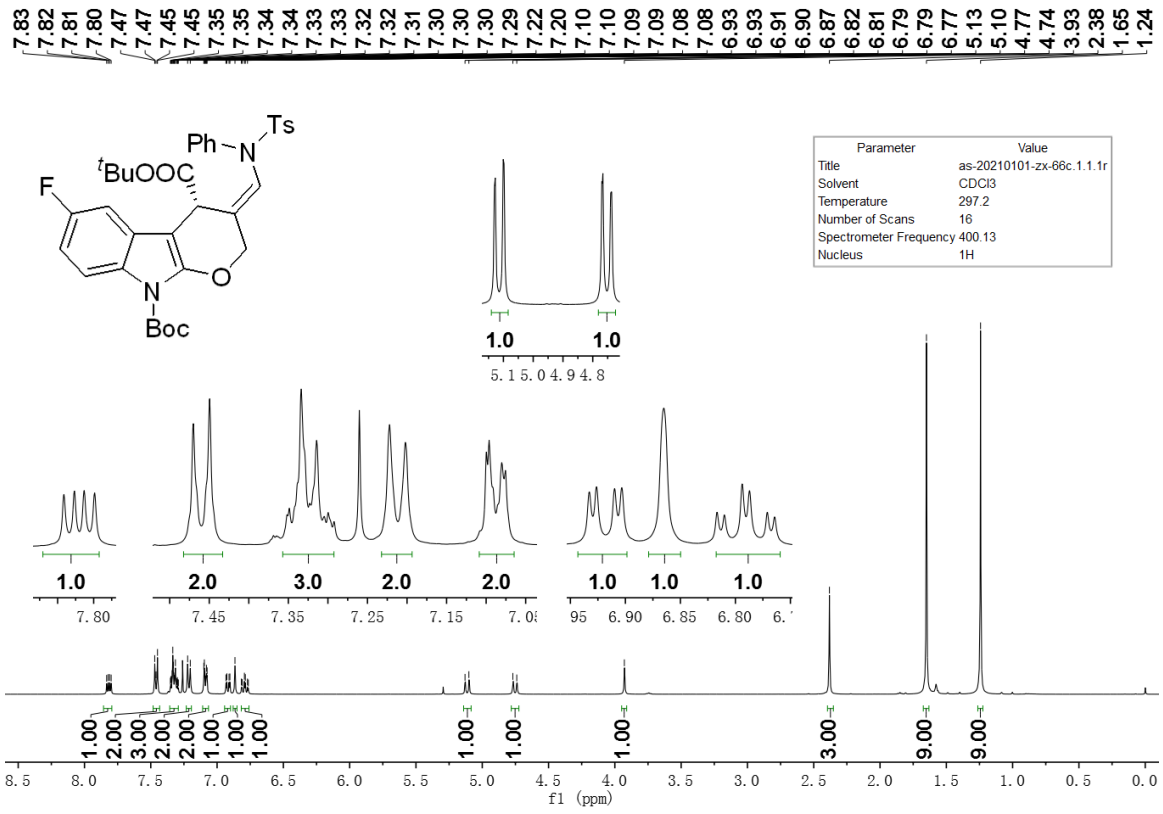


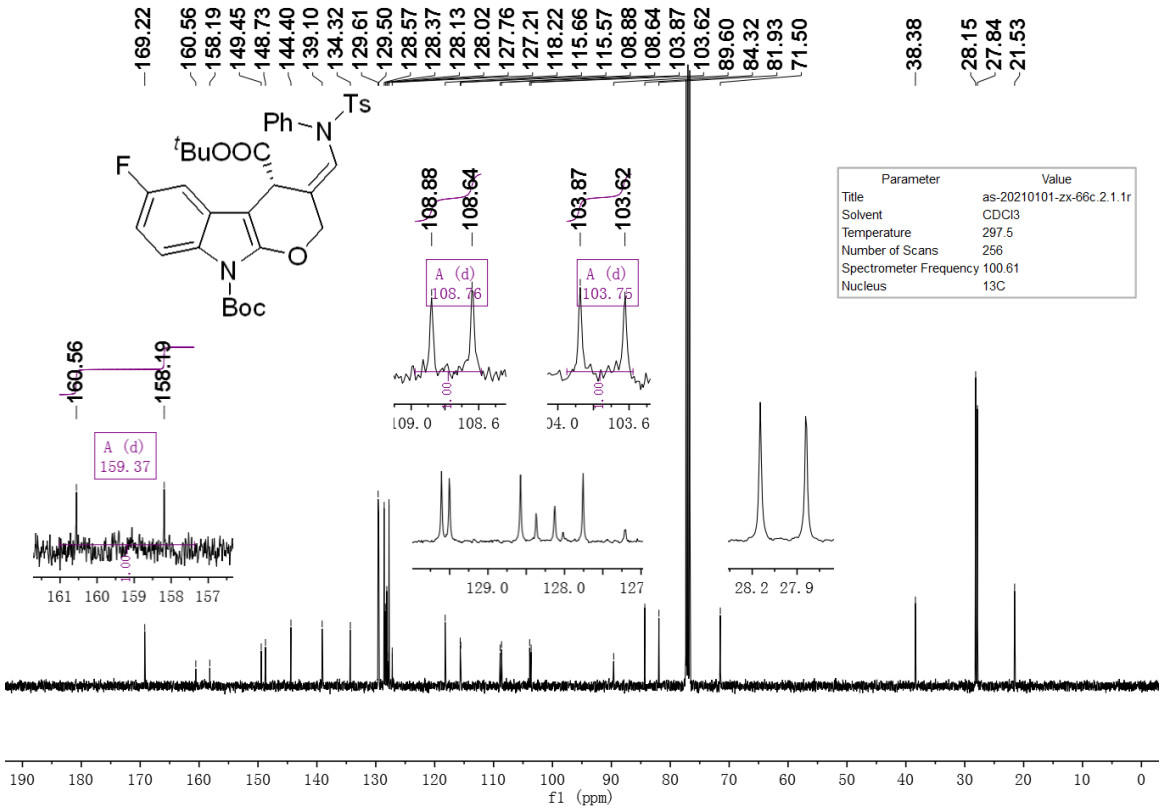


^{19}F NMR spectra of compound **3ha** in $CDCl_3$



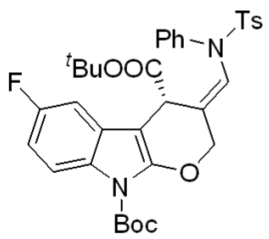
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4ha** in $CDCl_3$



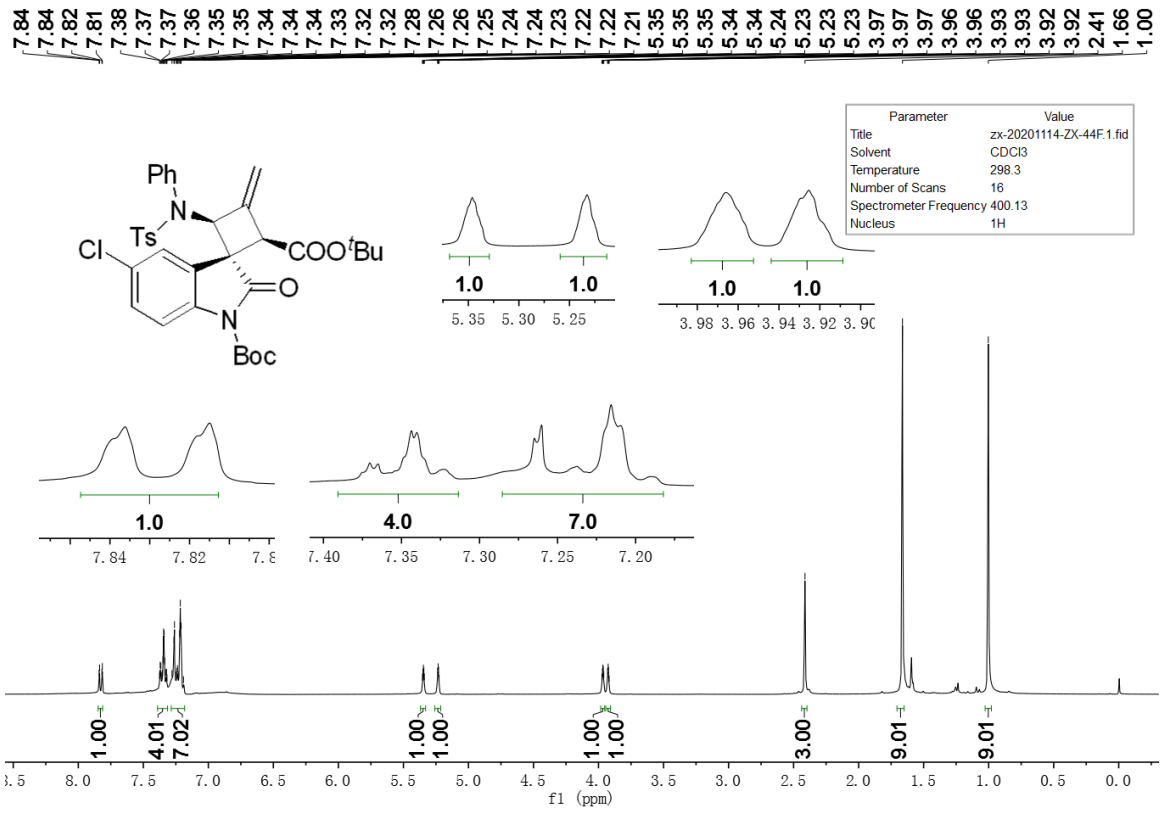


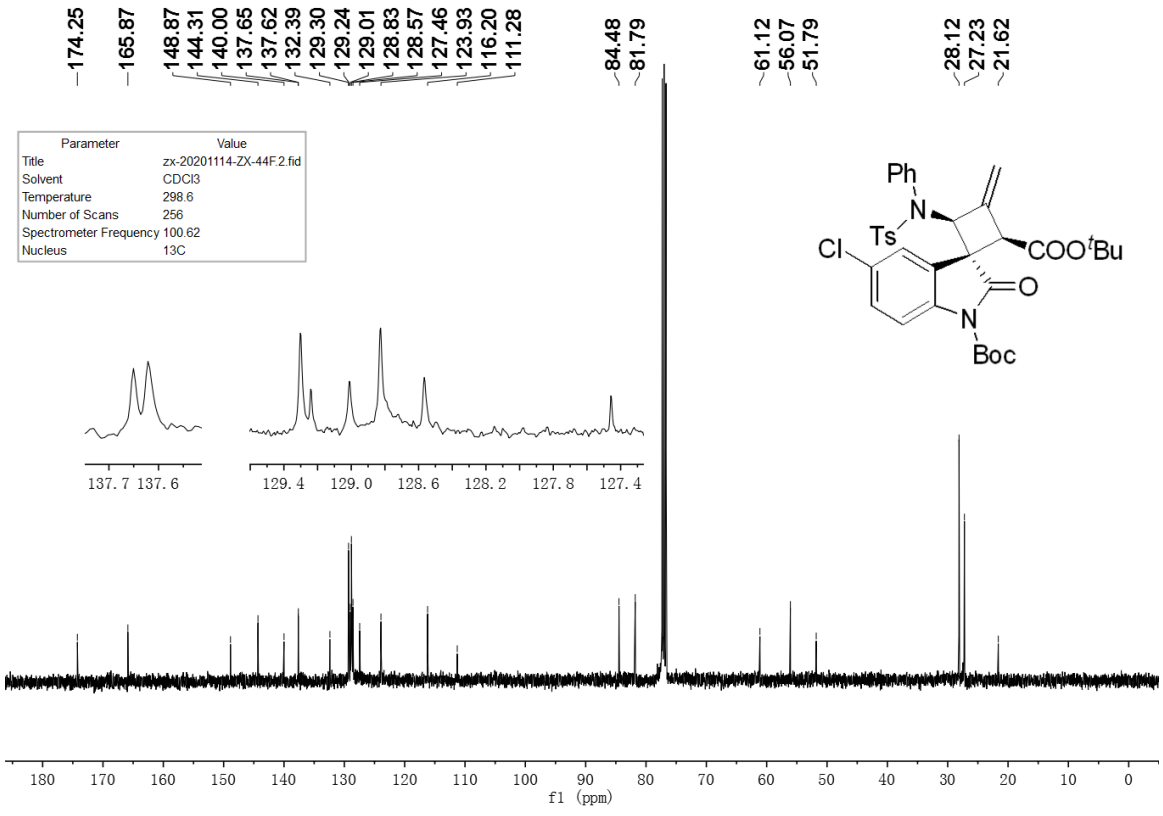
^{19}F NMR spectra of compound **4ha** in $CDCl_3$

Parameter	Value
Title	as-20210101-zx-66c.3.1.1r
Solvent	CDCl3
Temperature	297.3
Number of Scans	16
Spectrometer Frequency	376.50
Nucleus	19F

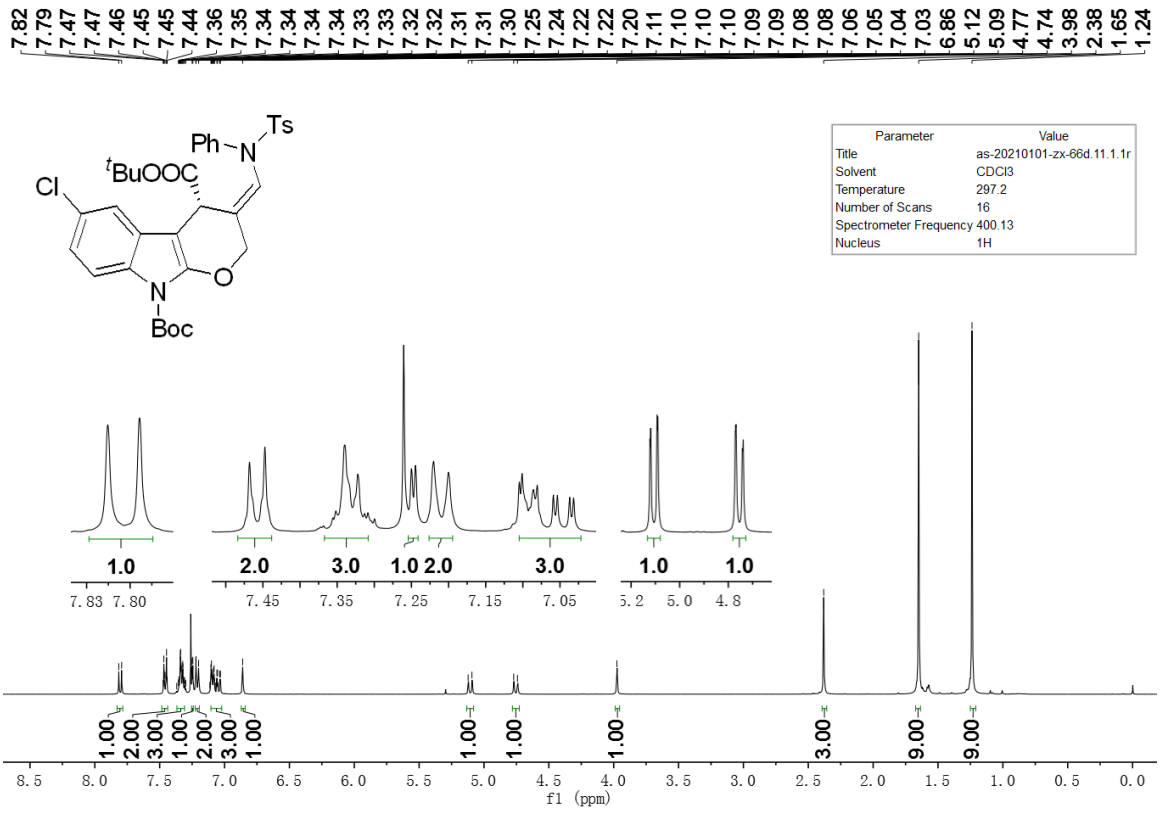


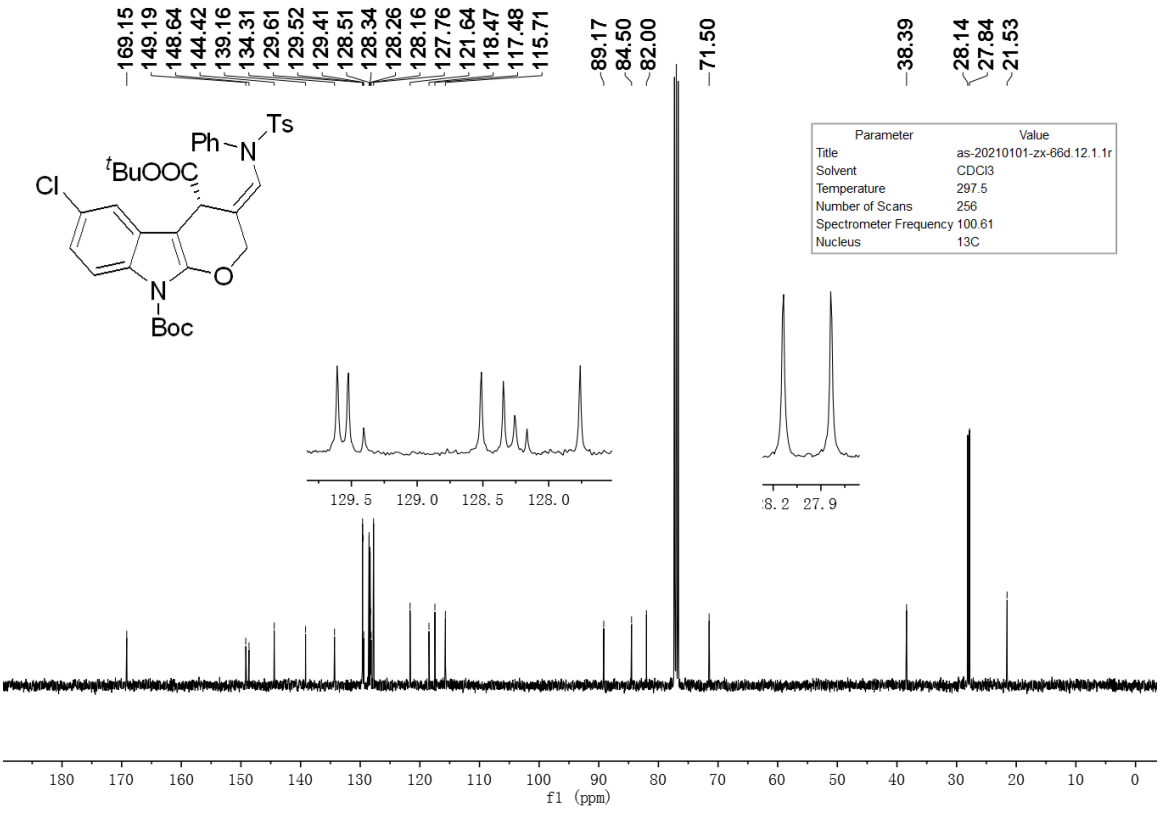
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3ia** in $CDCl_3$



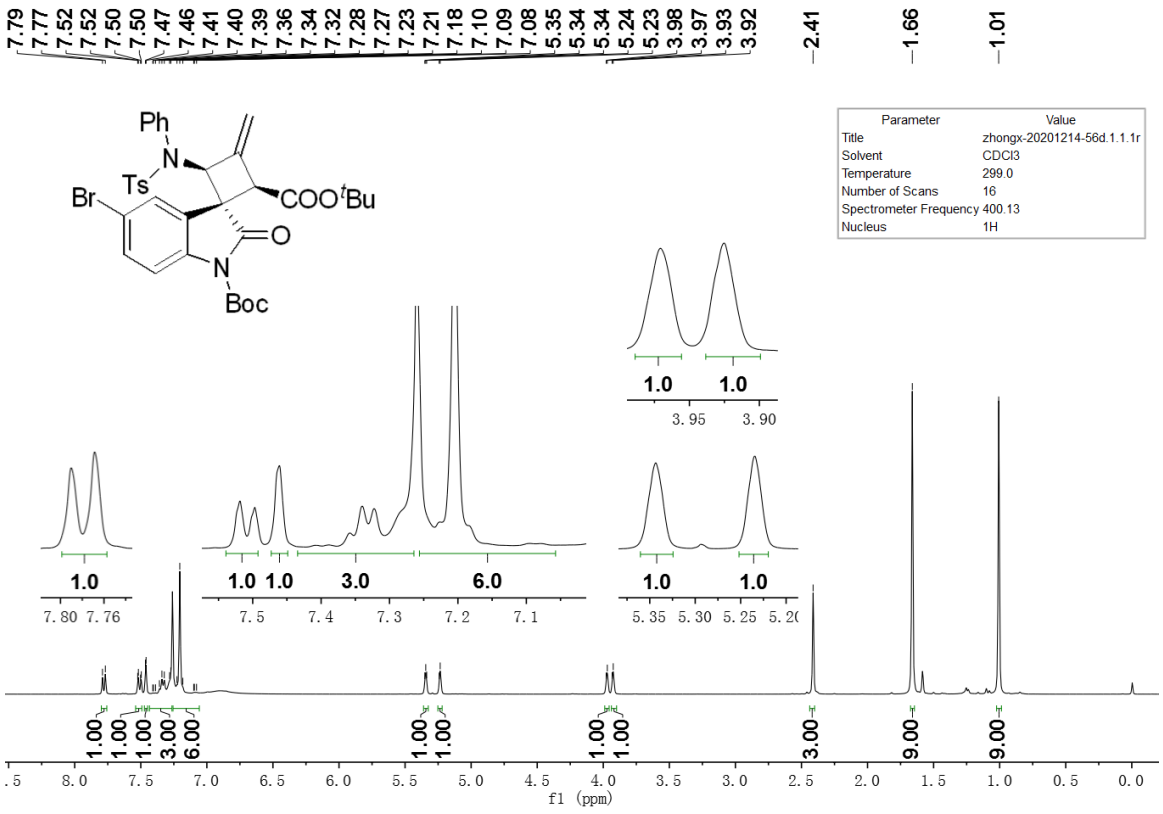


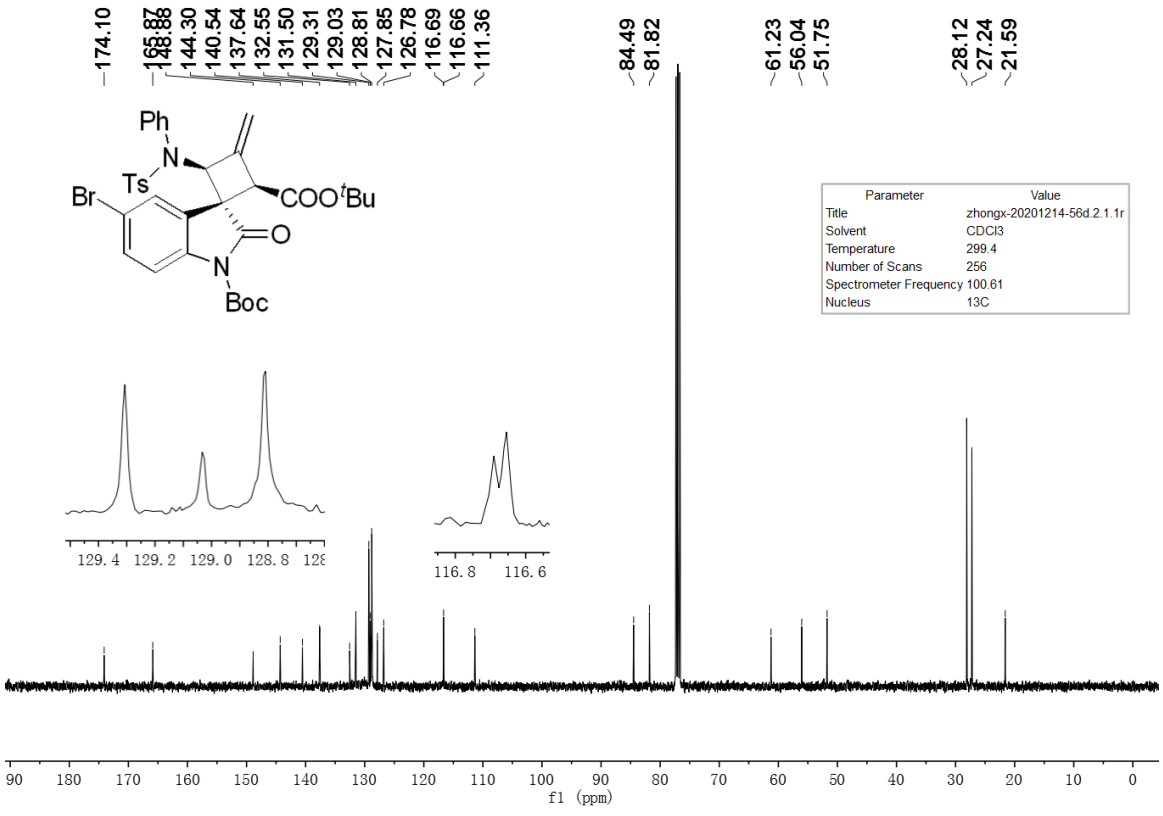
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4ia** in $CDCl_3$



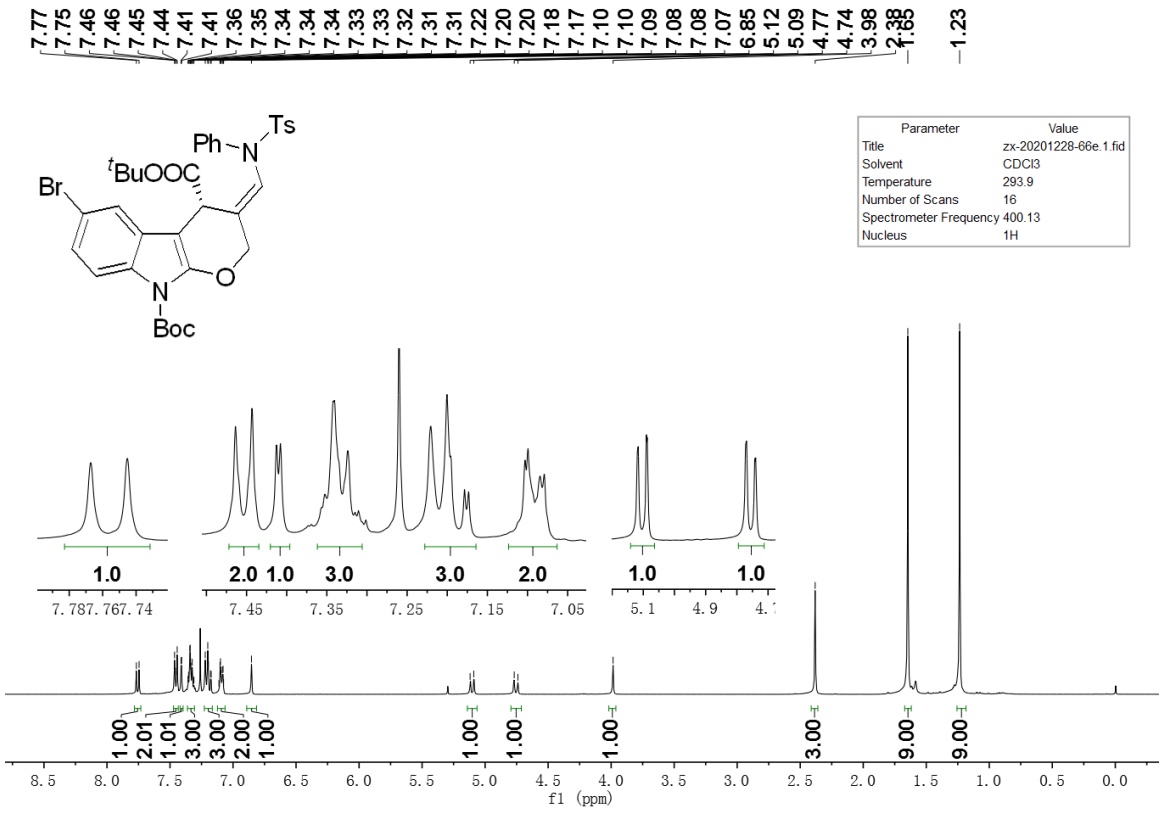


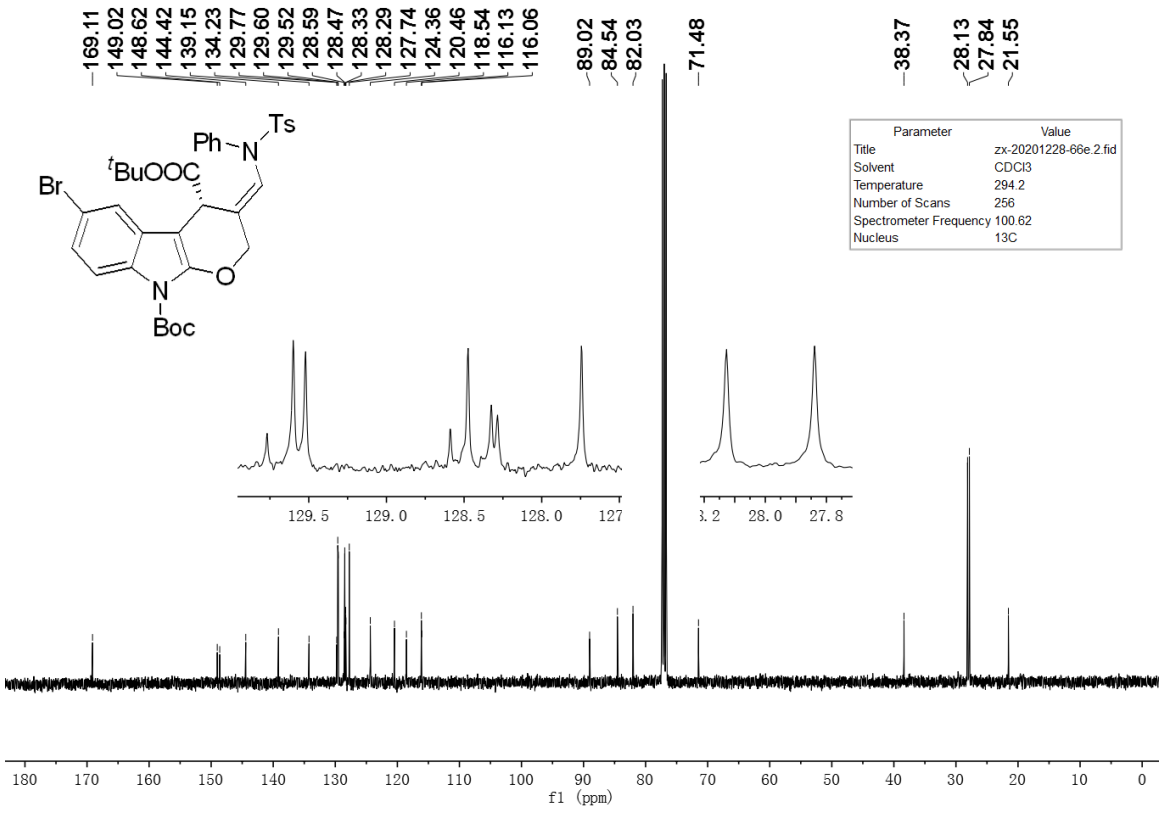
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3ja** in $CDCl_3$



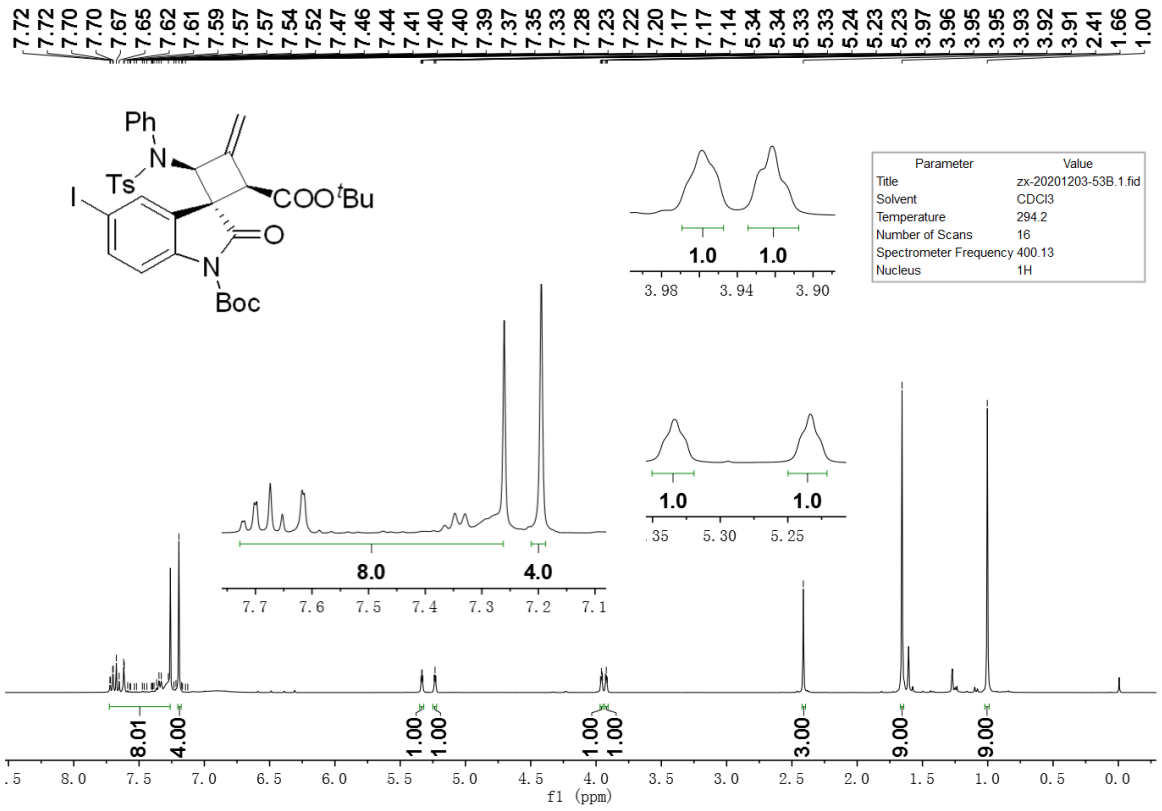


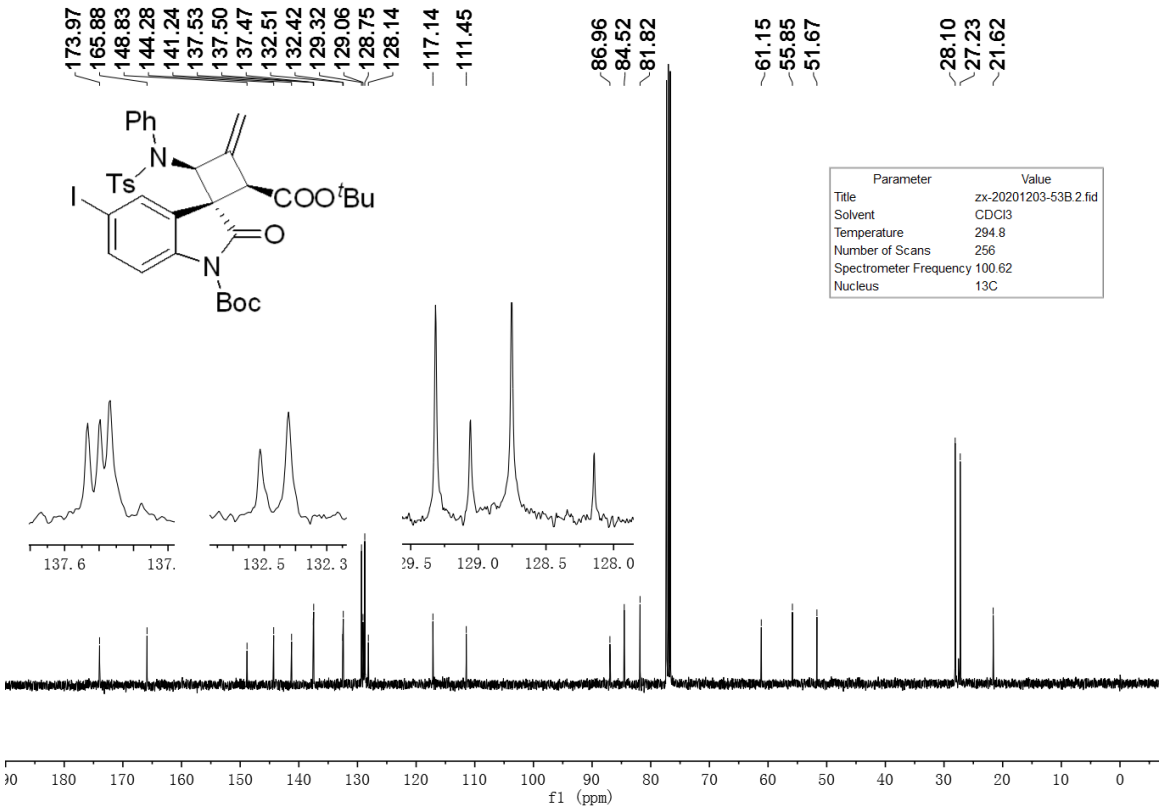
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4ja** in $CDCl_3$



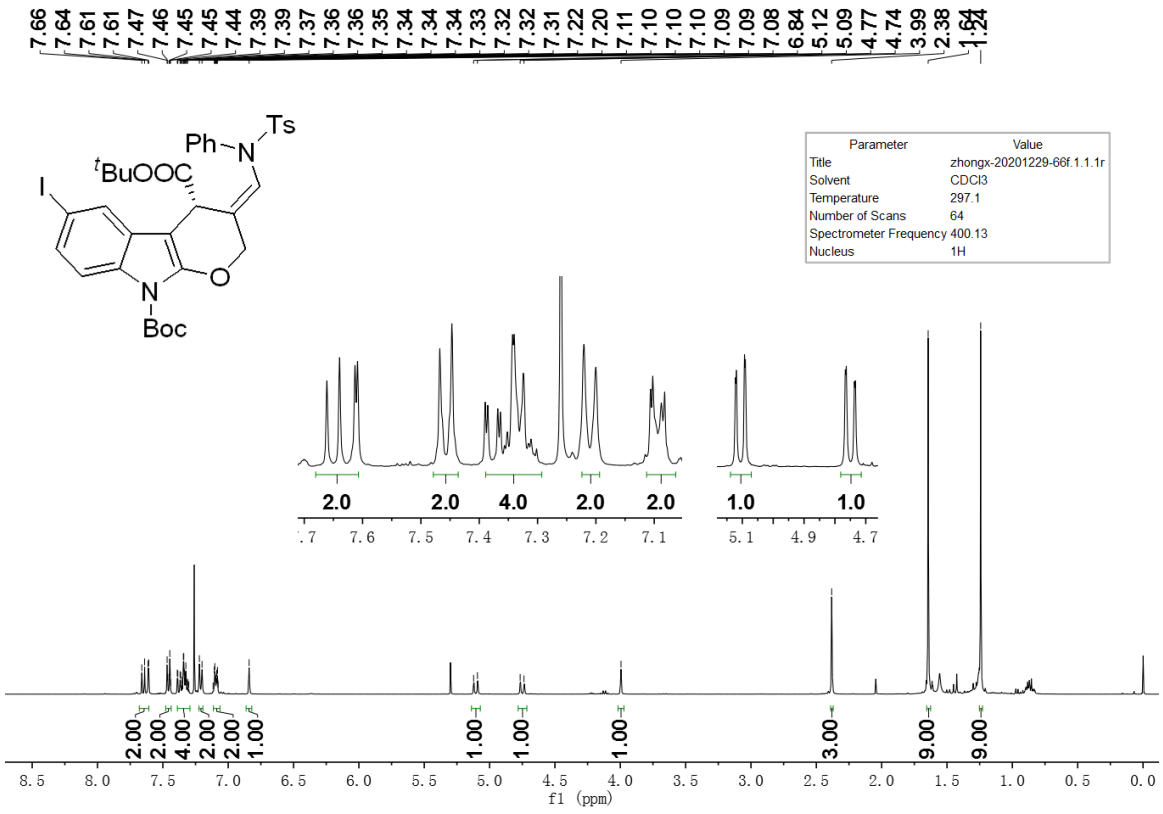


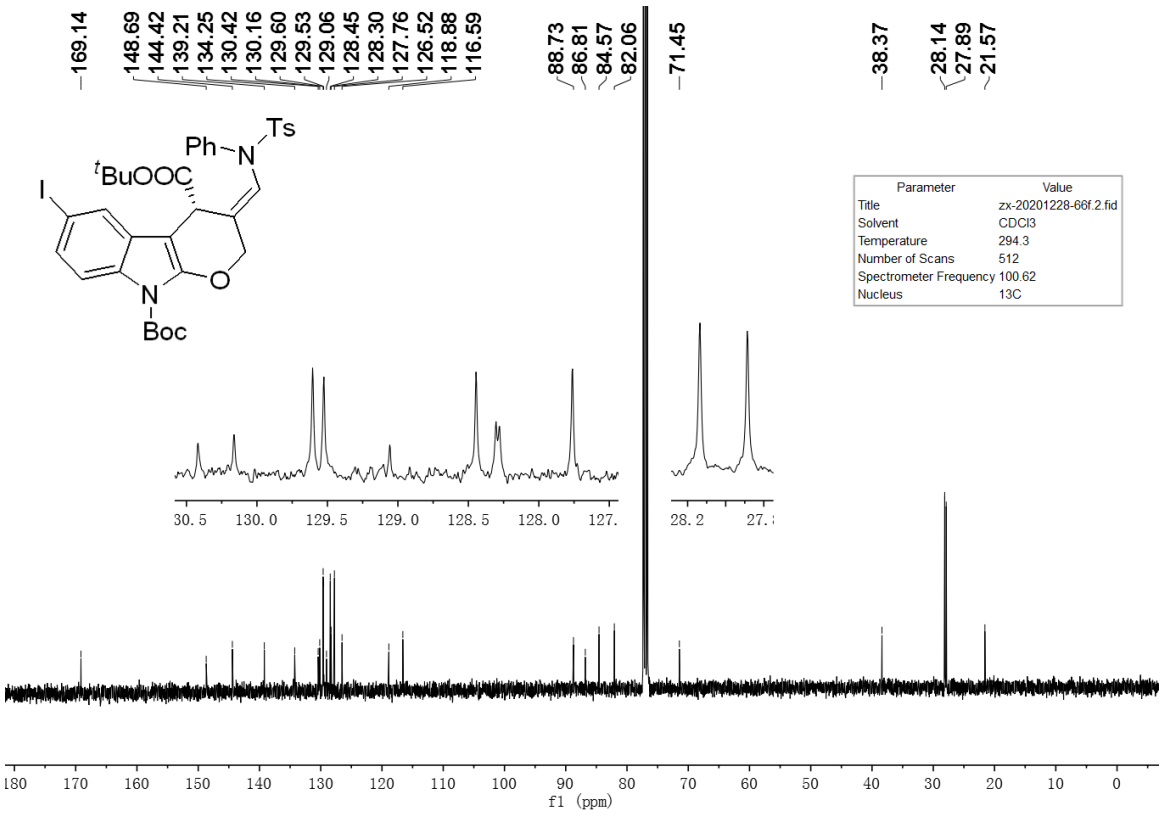
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3ka** in $CDCl_3$



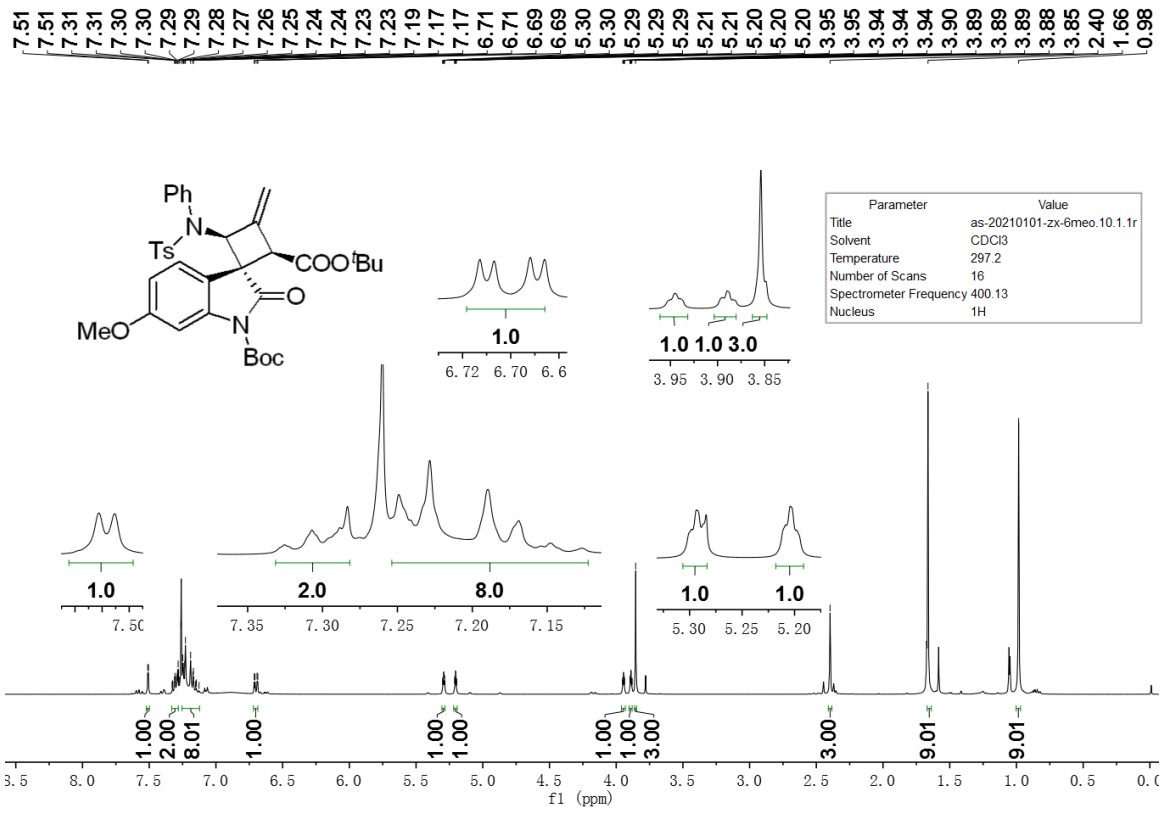


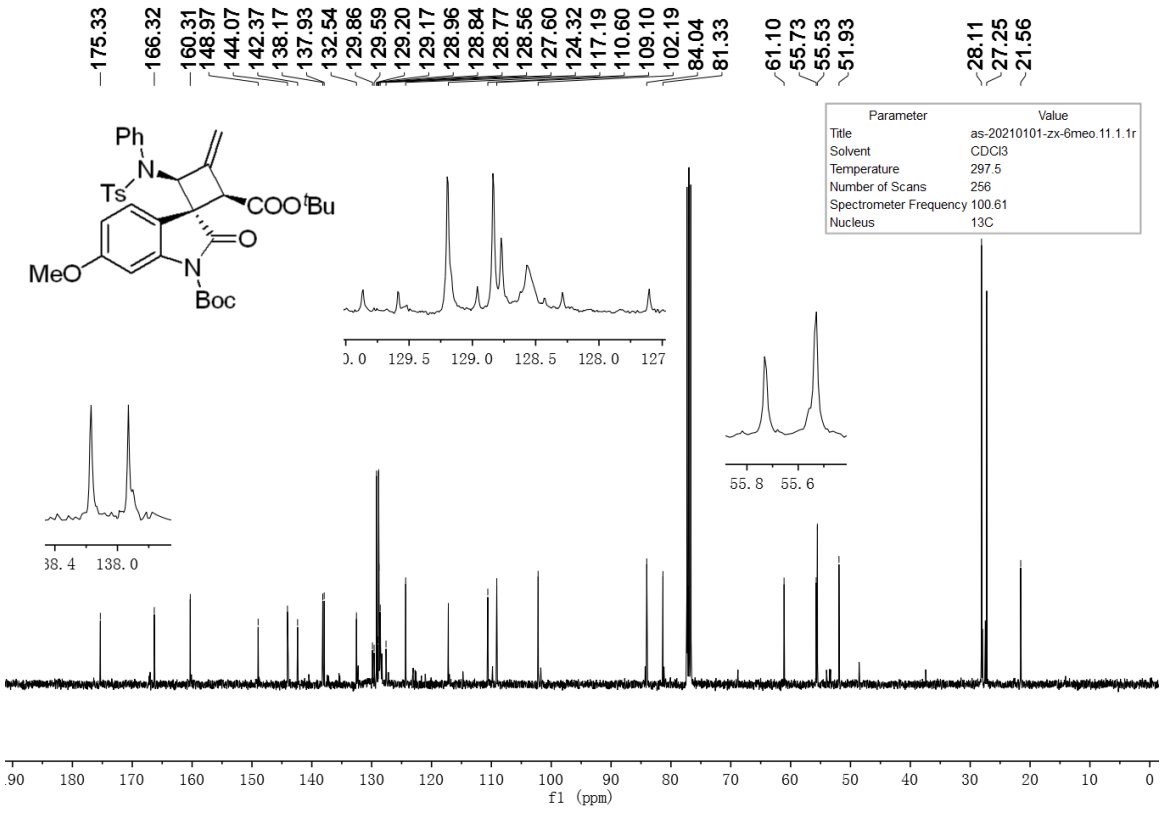
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4ka** in $CDCl_3$



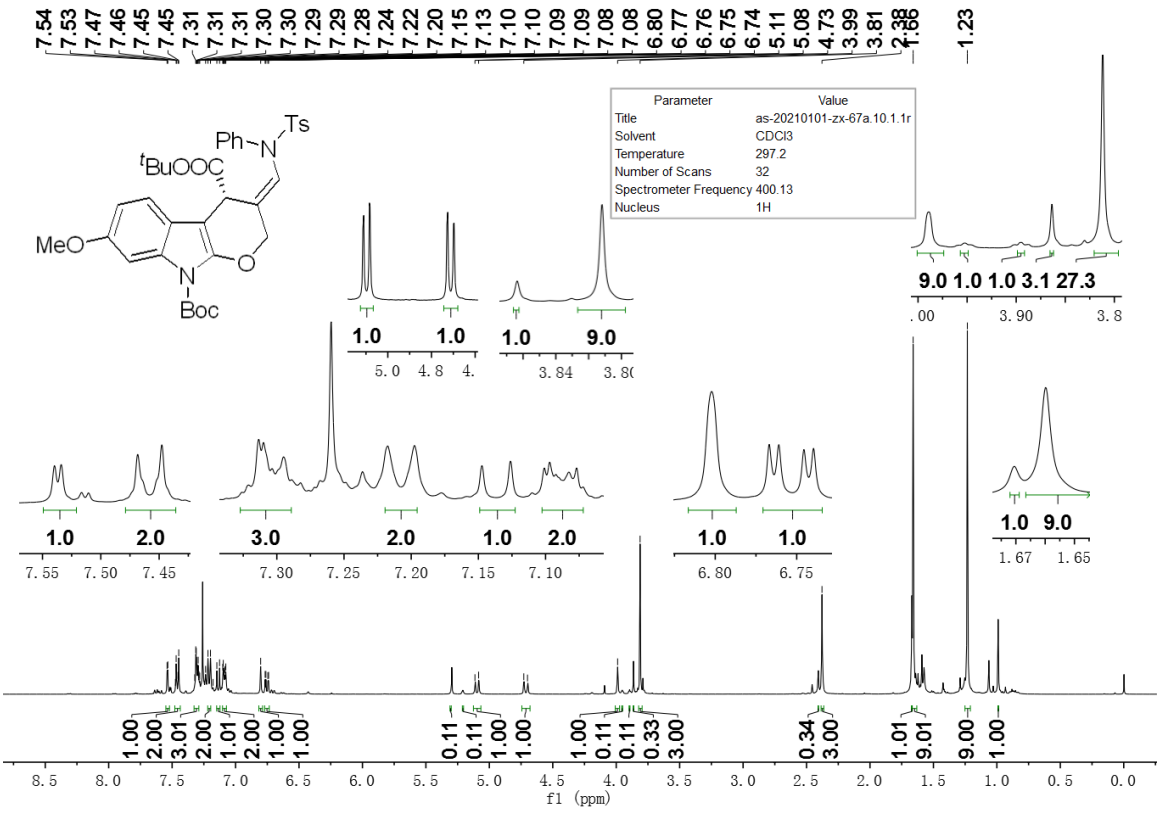


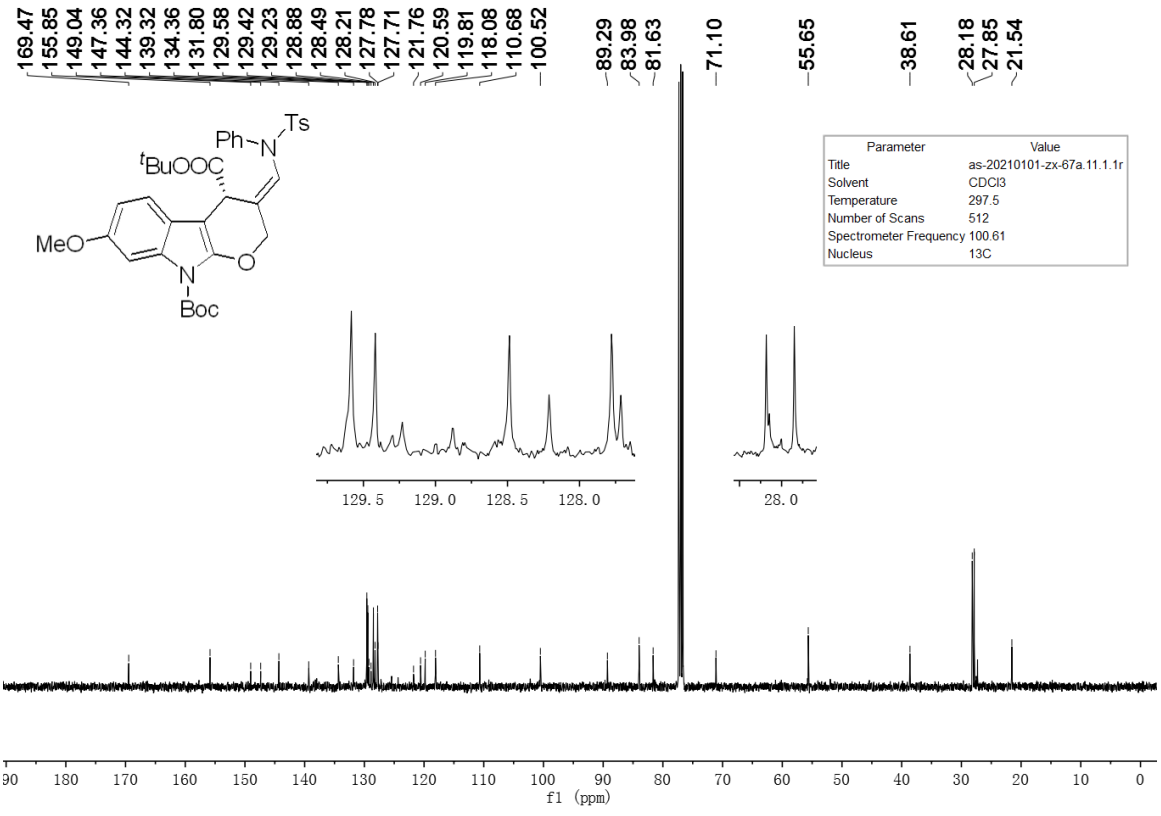
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3la** in $CDCl_3$



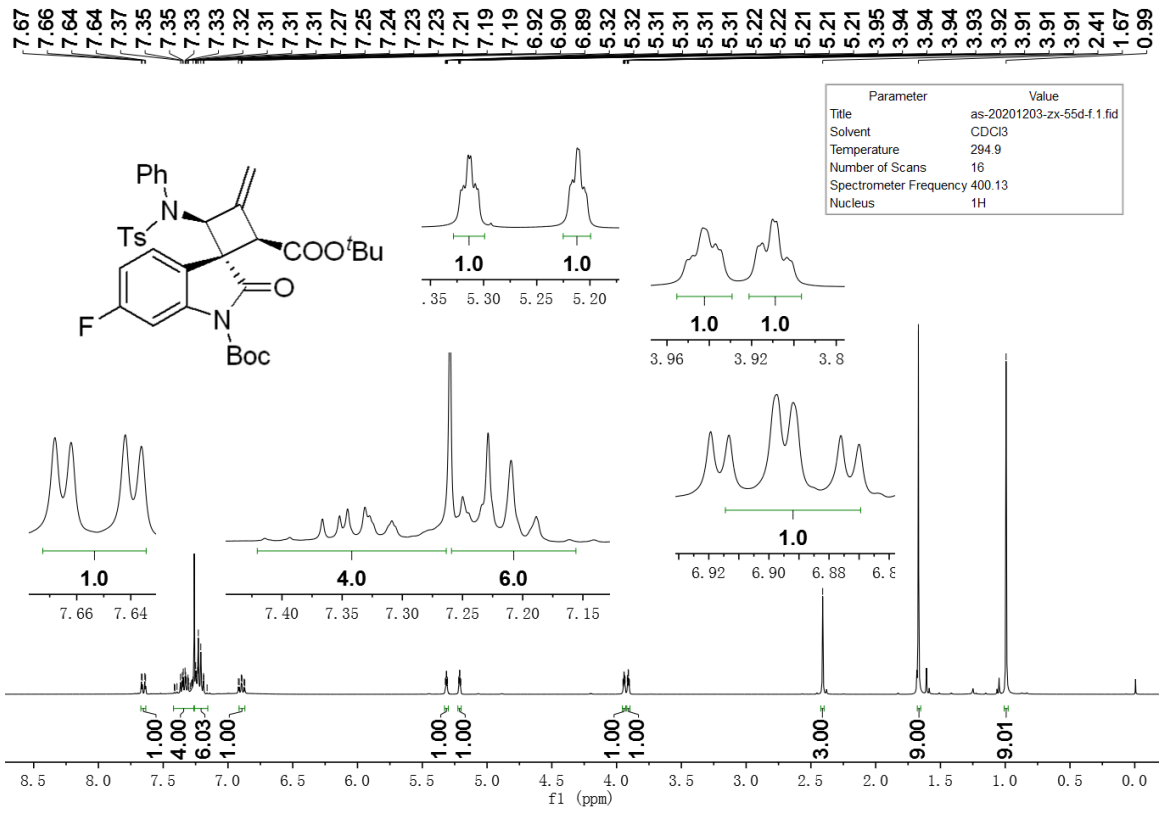


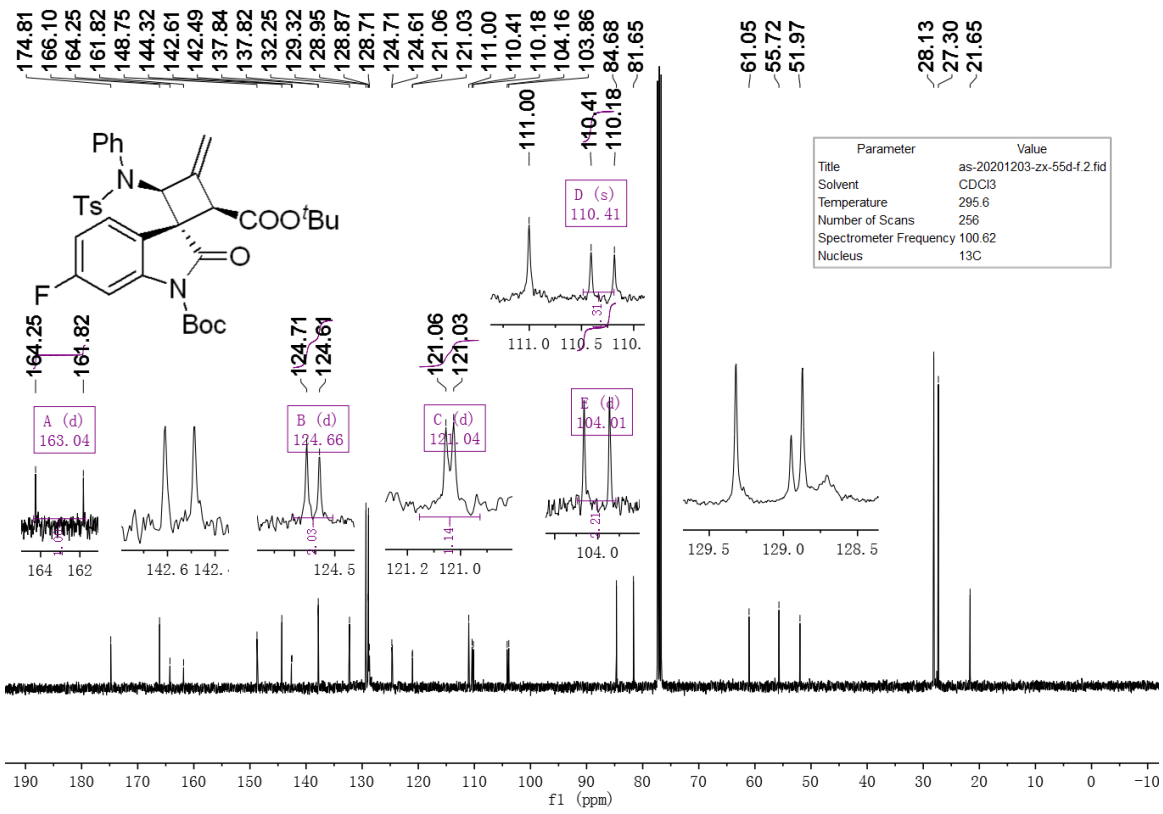
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4la** in $CDCl_3$



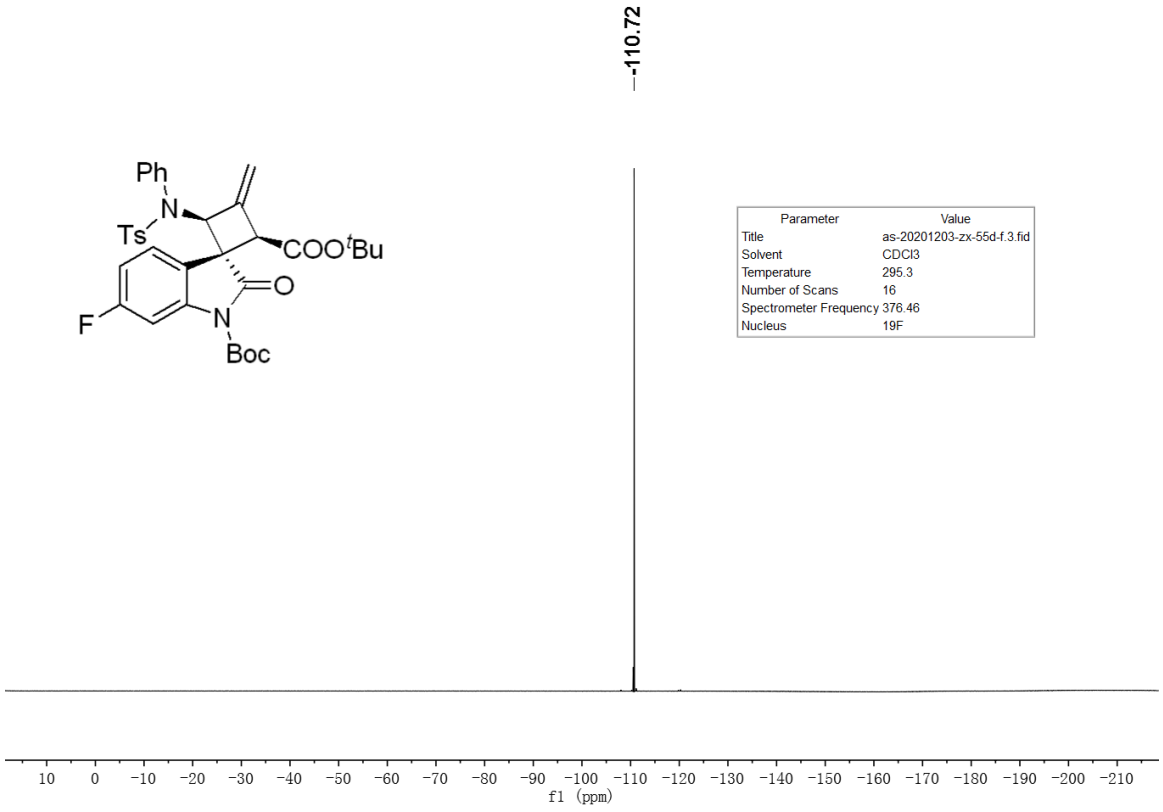


^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3ma** in $CDCl_3$

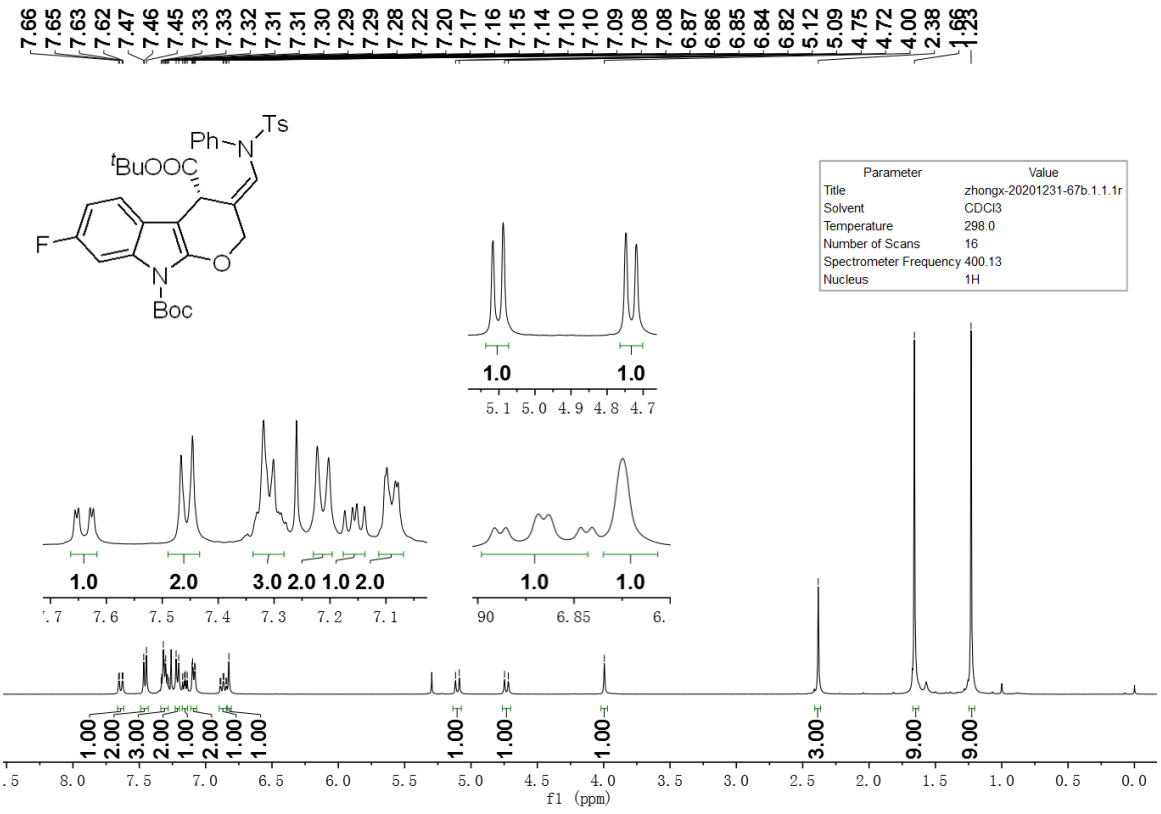


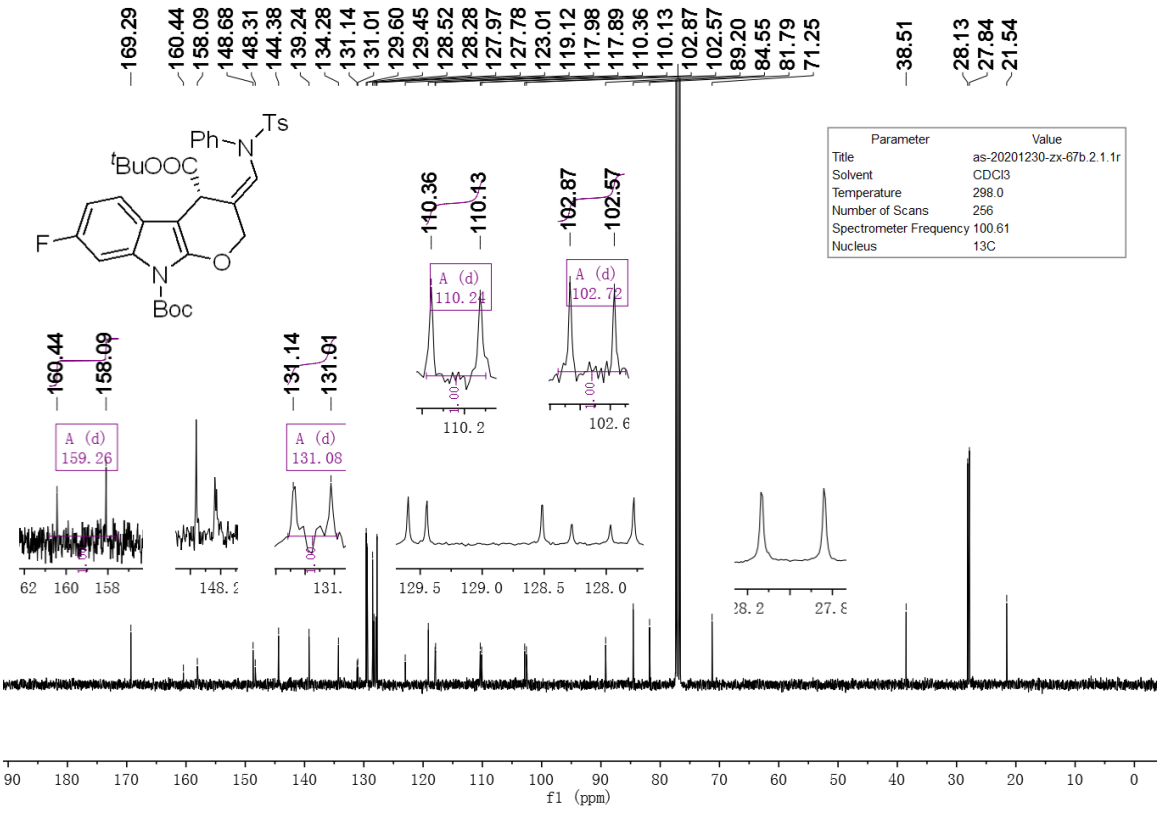


^{19}F NMR spectra of compound **3ma** in $CDCl_3$

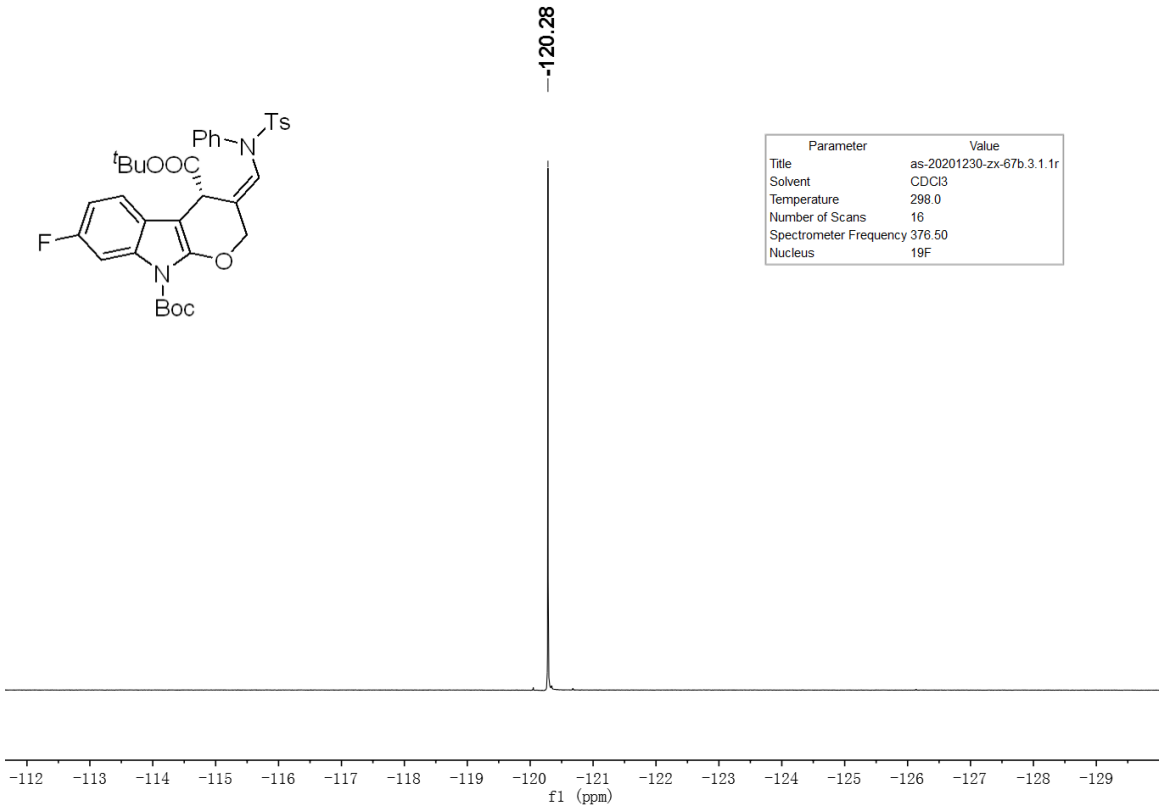


^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4ma** in $CDCl_3$

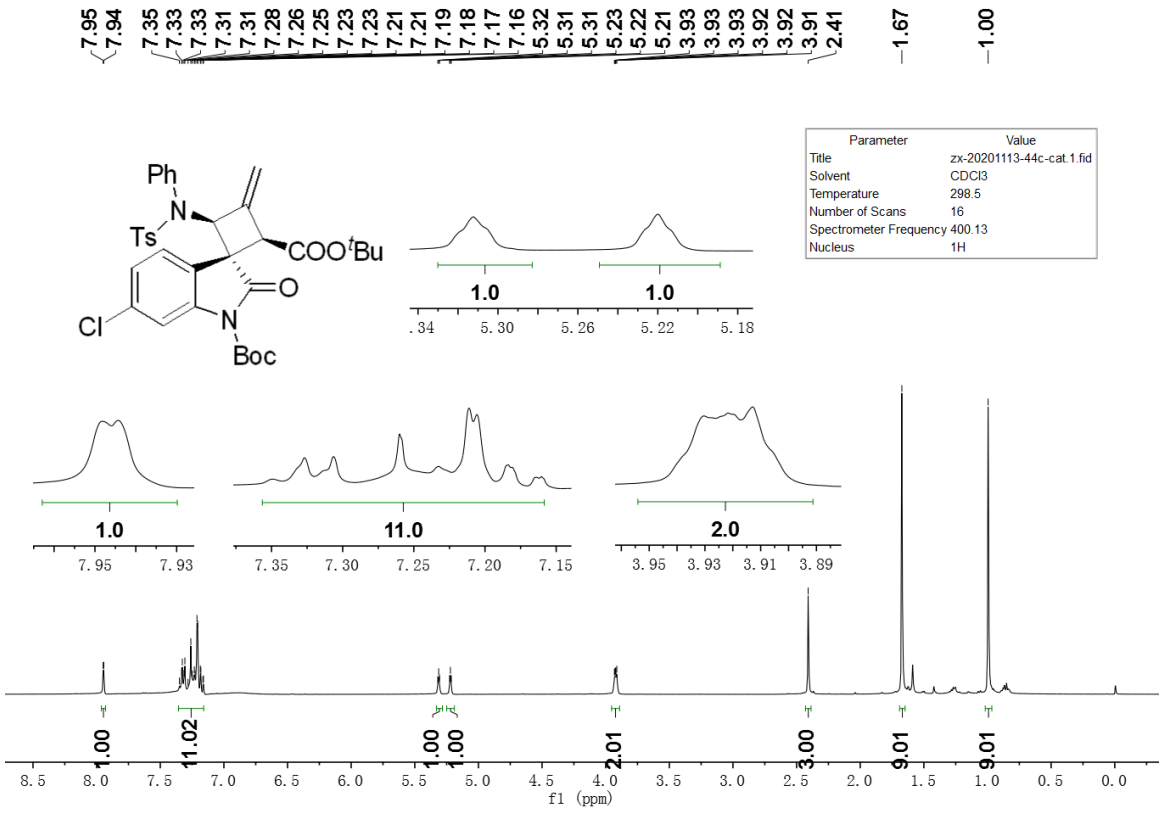


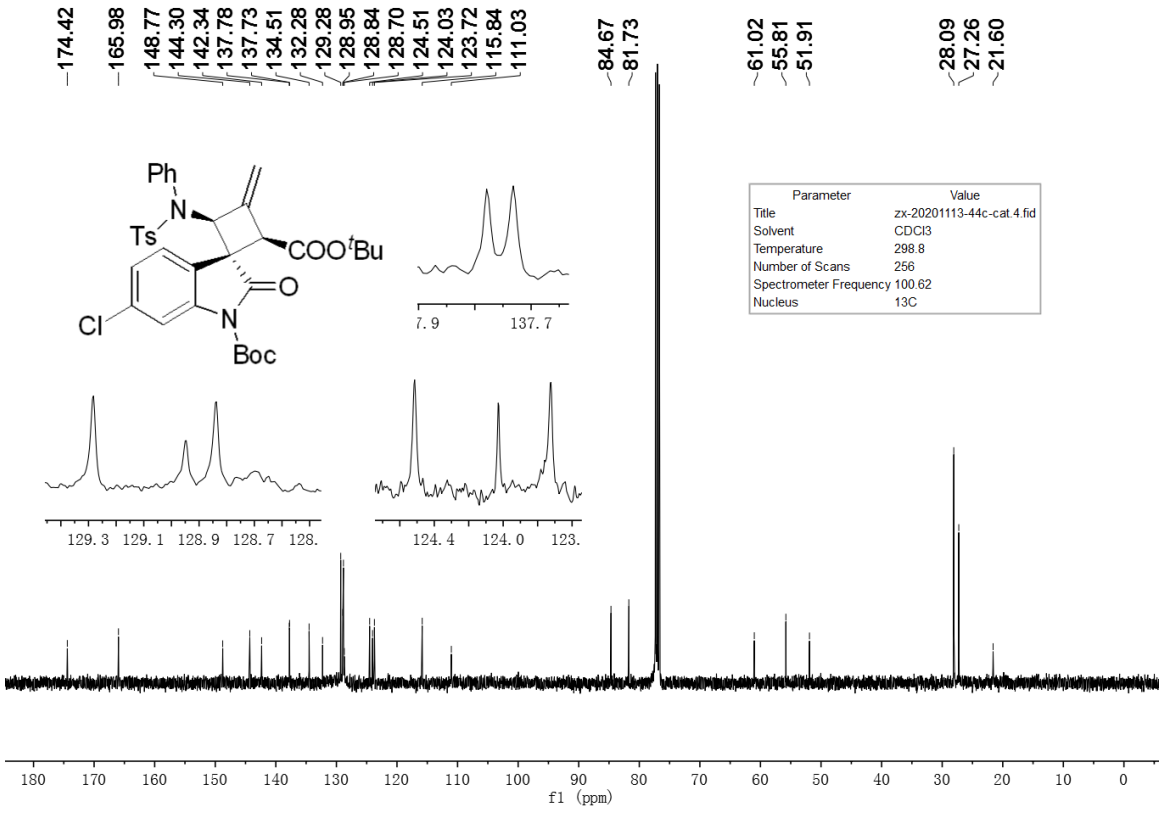


^{19}F NMR spectra of compound **4ma** in $CDCl_3$

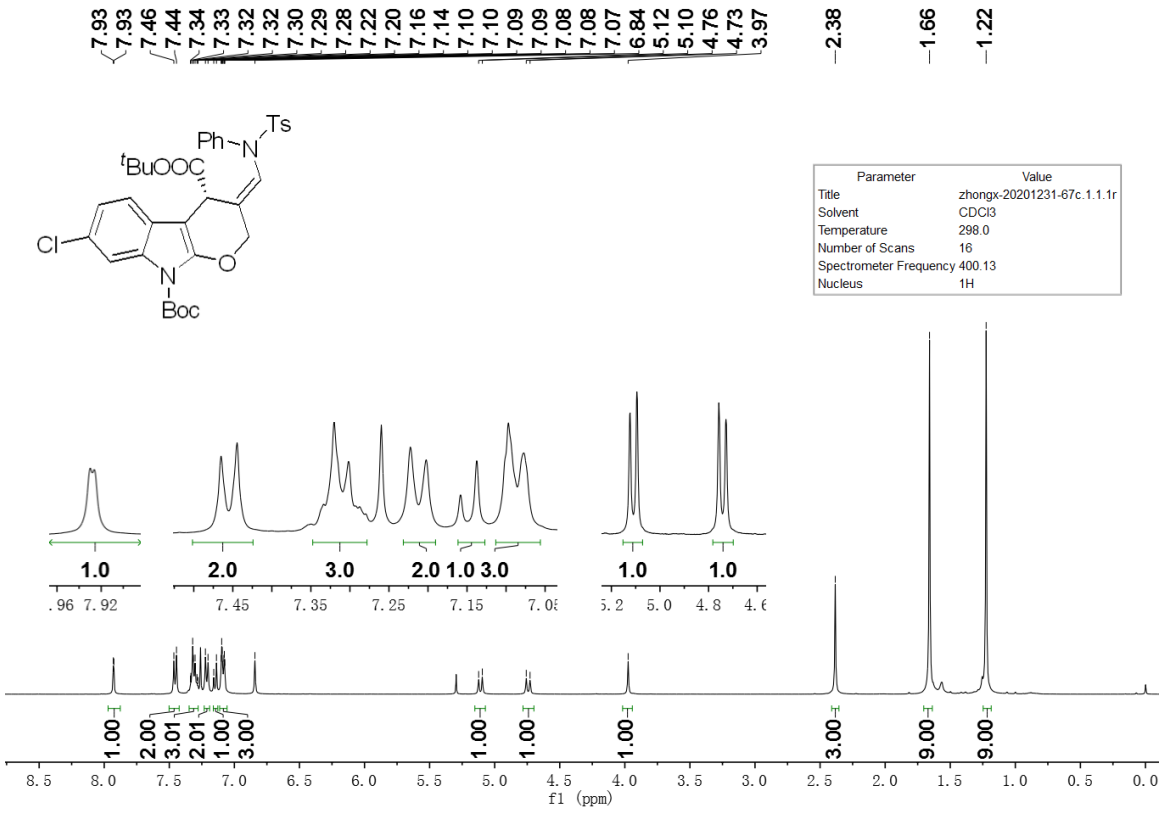


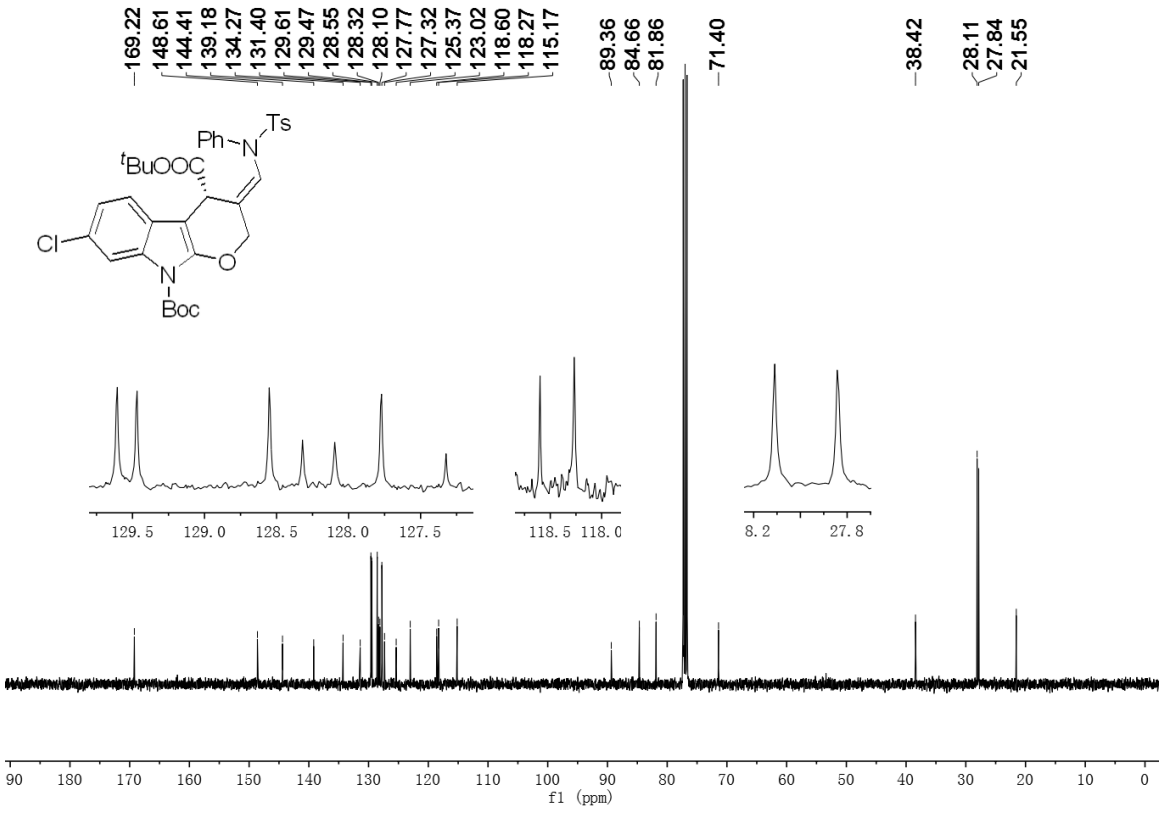
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3na** in $CDCl_3$



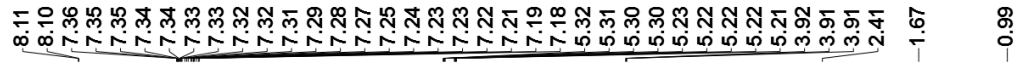


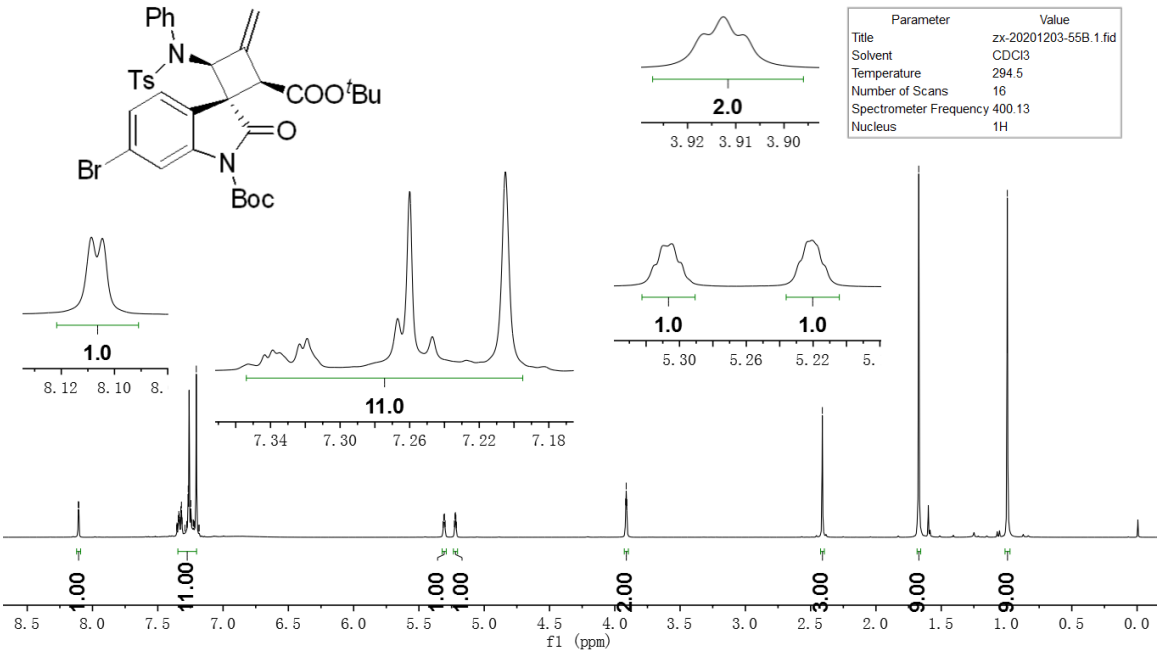
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4na** in $CDCl_3$

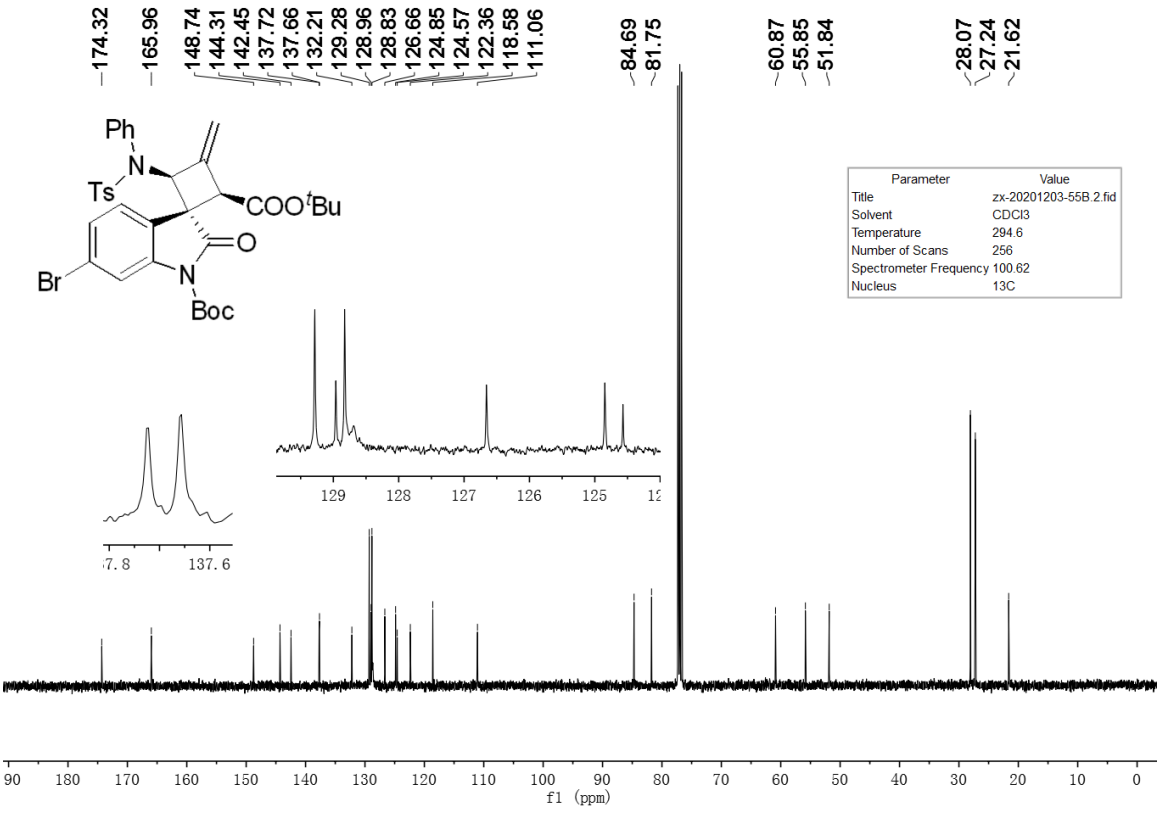




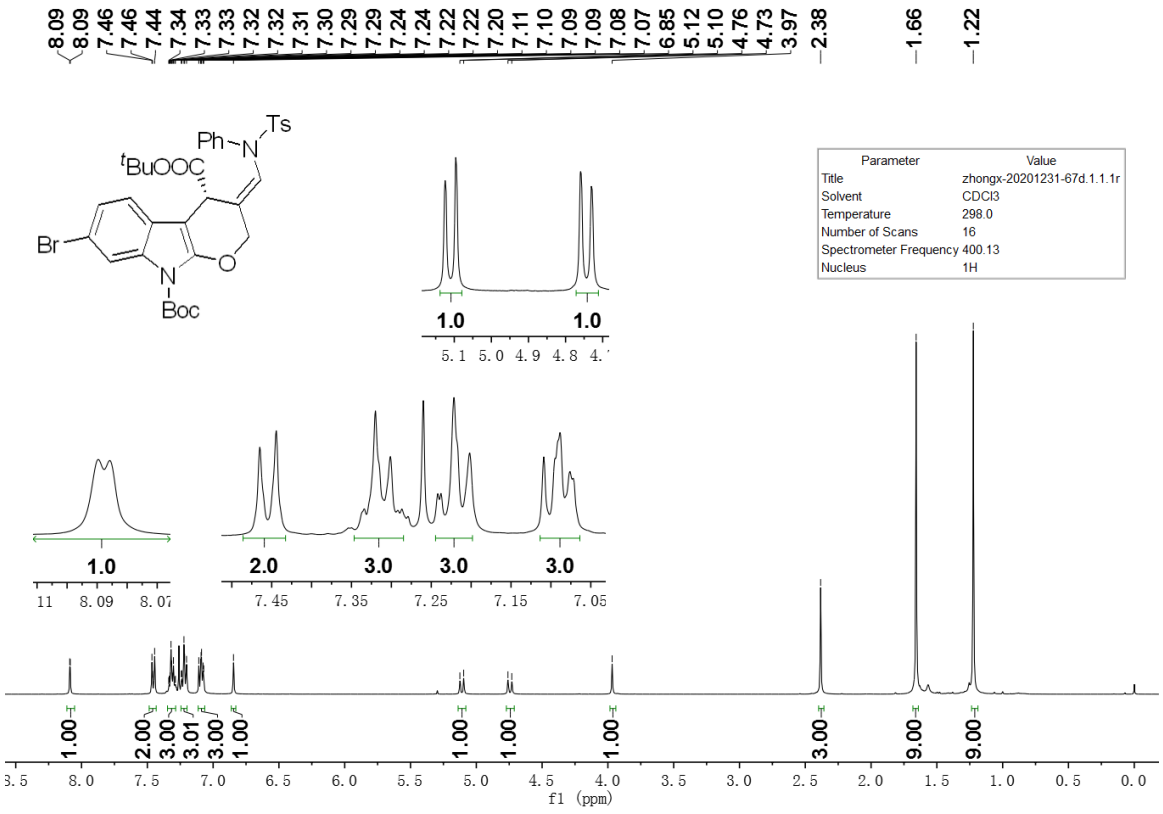
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3oa** in $CDCl_3$

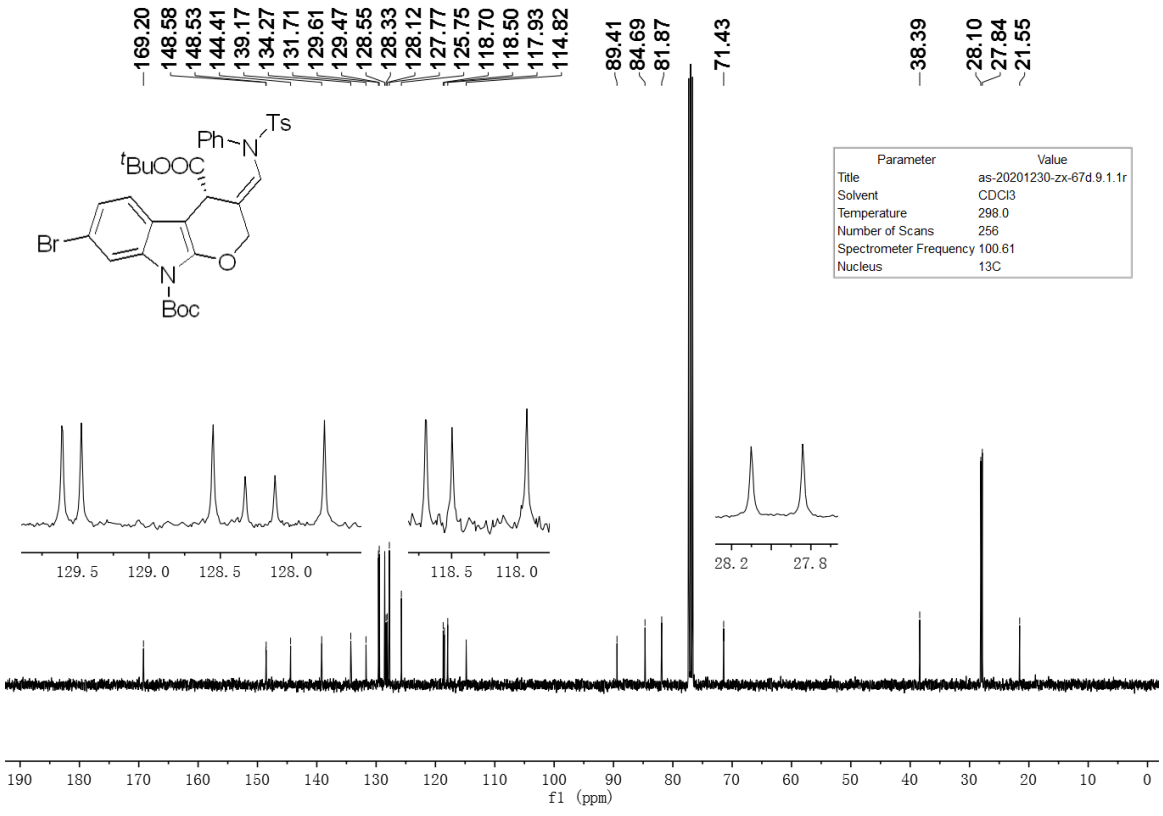




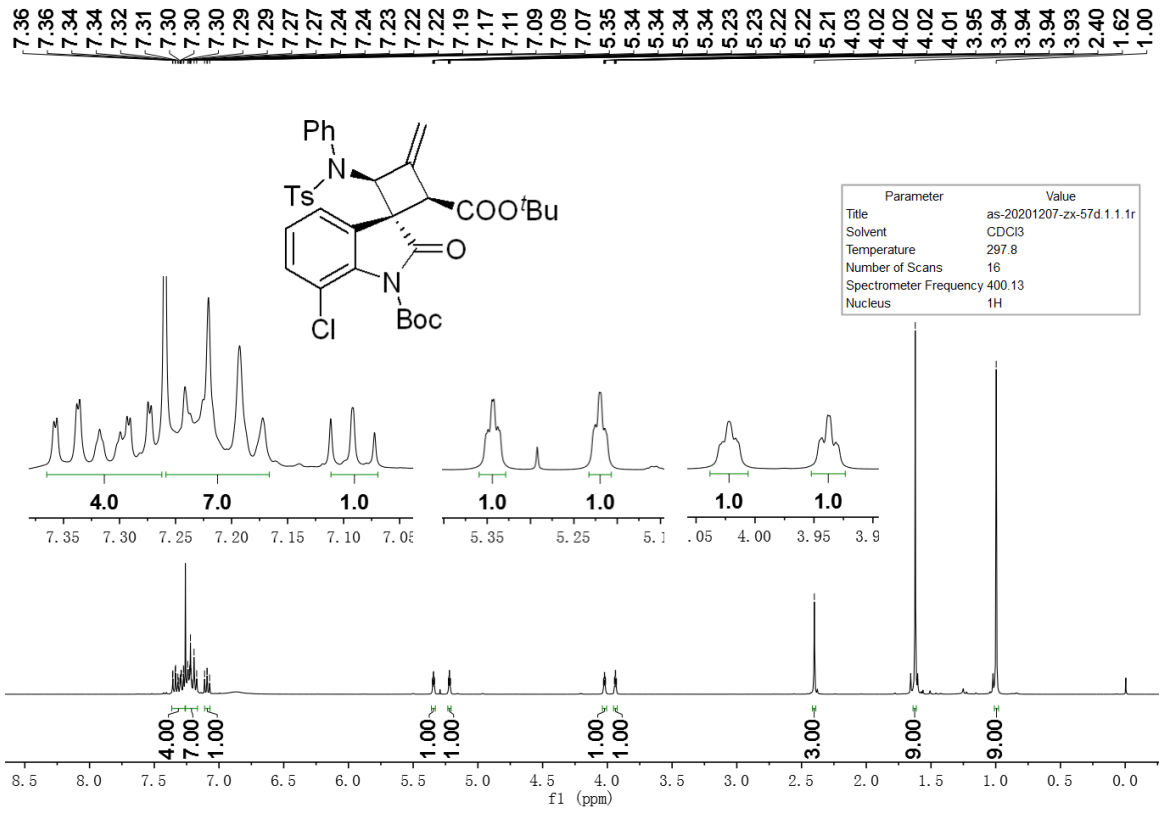


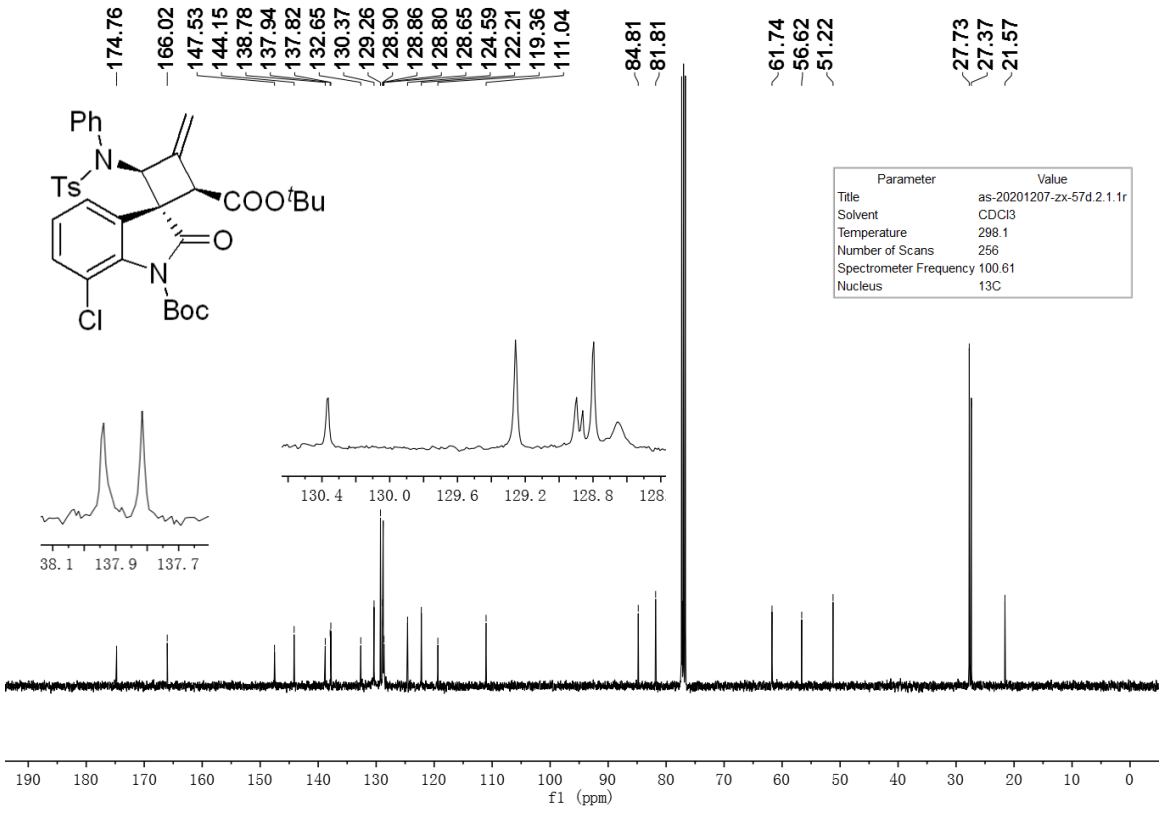
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4oa** in $CDCl_3$



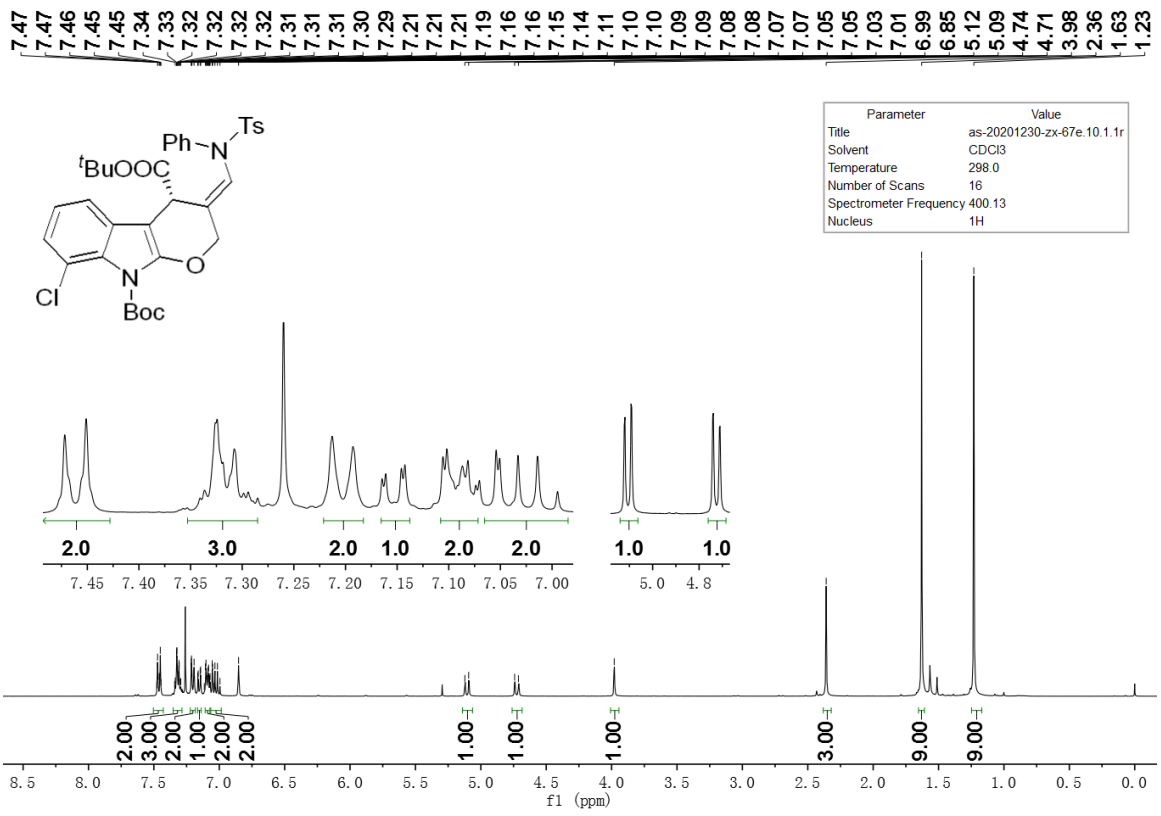


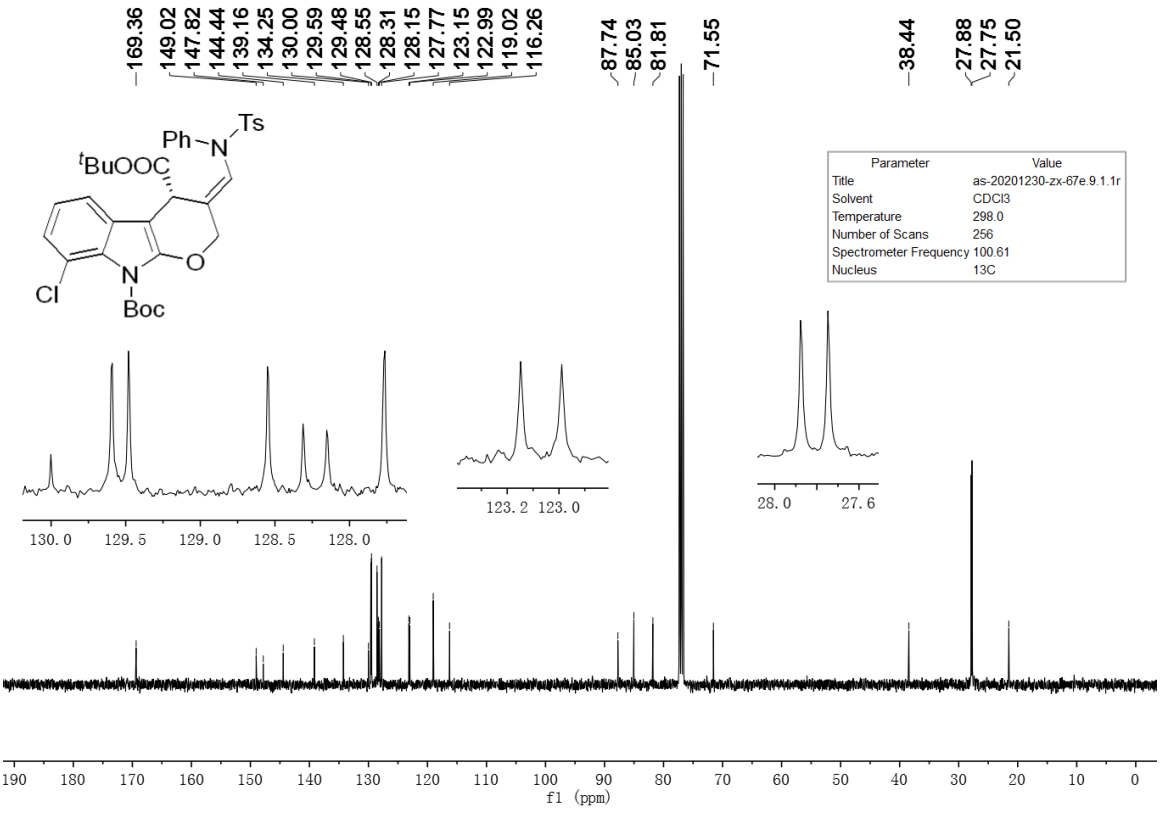
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3pa** in $CDCl_3$



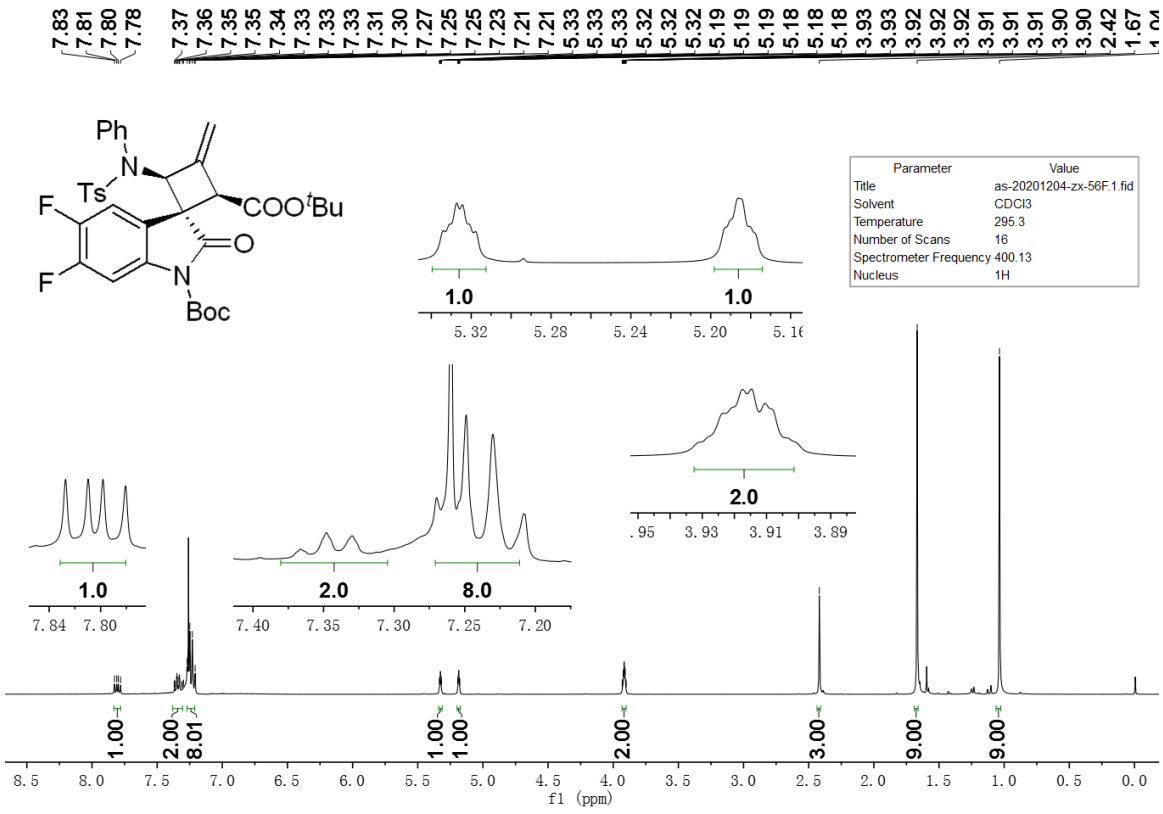


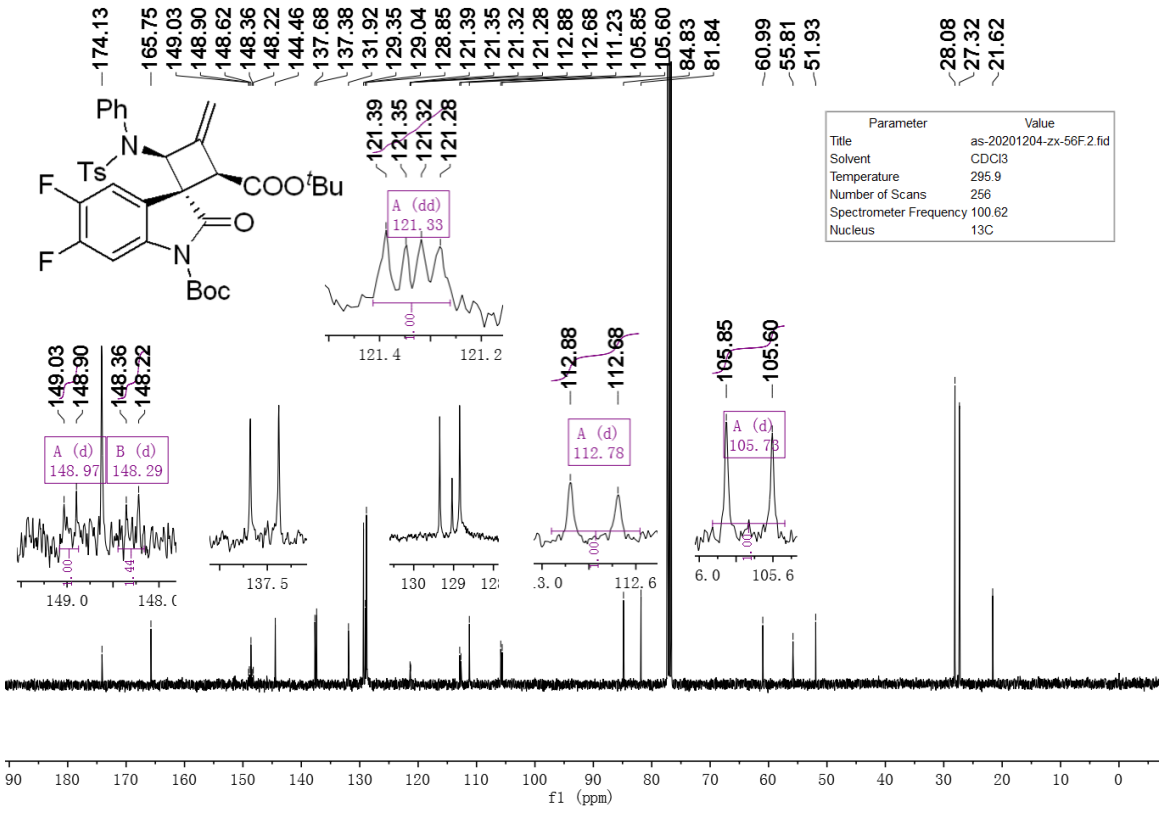
^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of compound **4pa** in $CDCl_3$



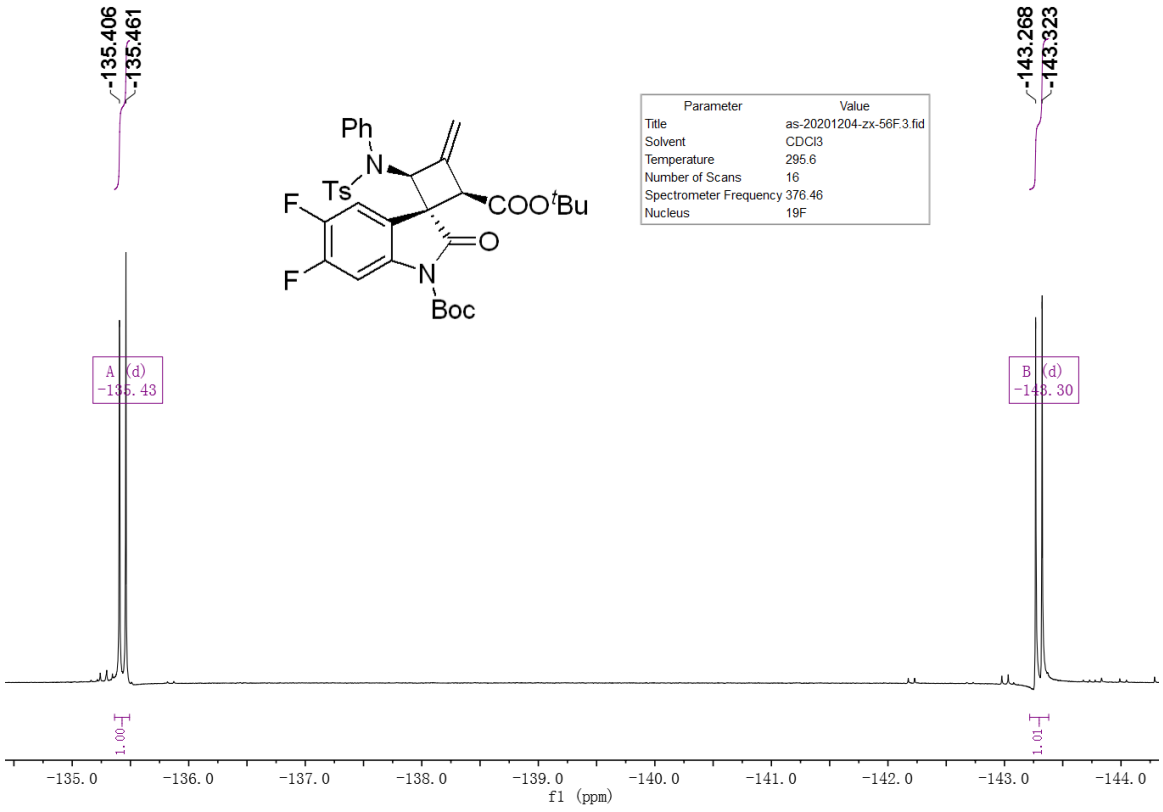


^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3qa** in $CDCl_3$

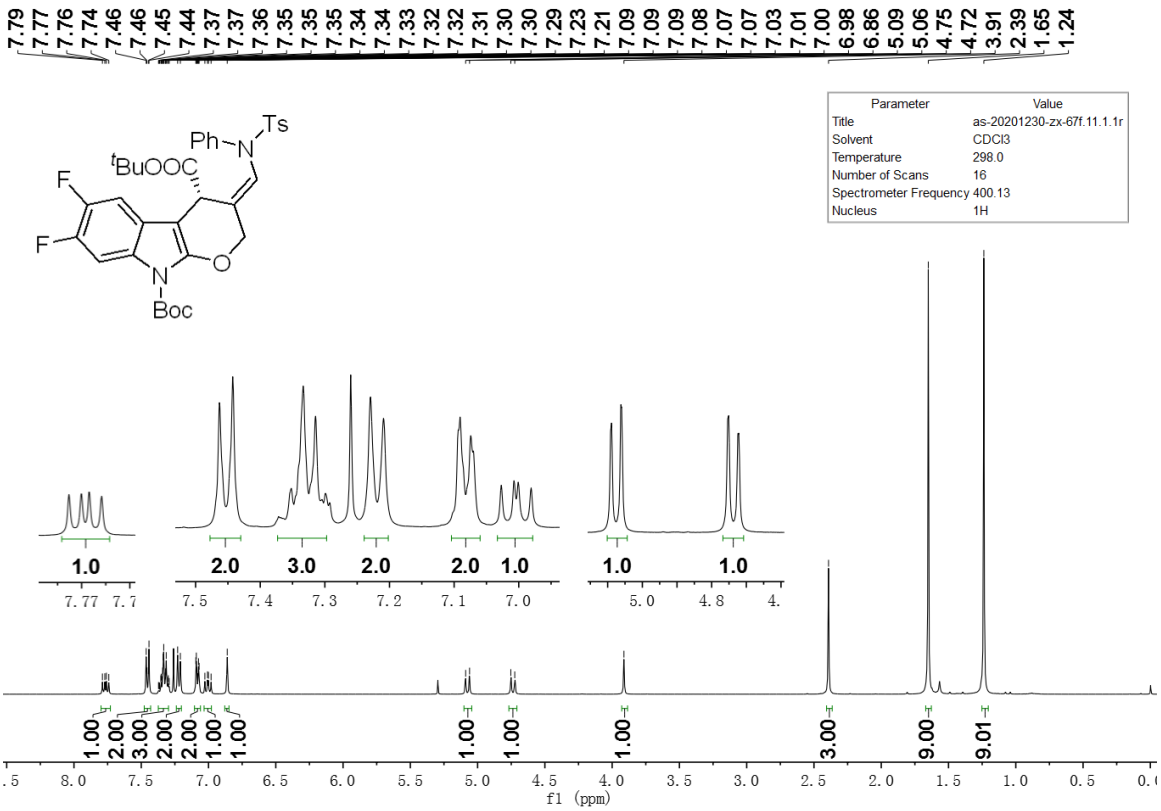


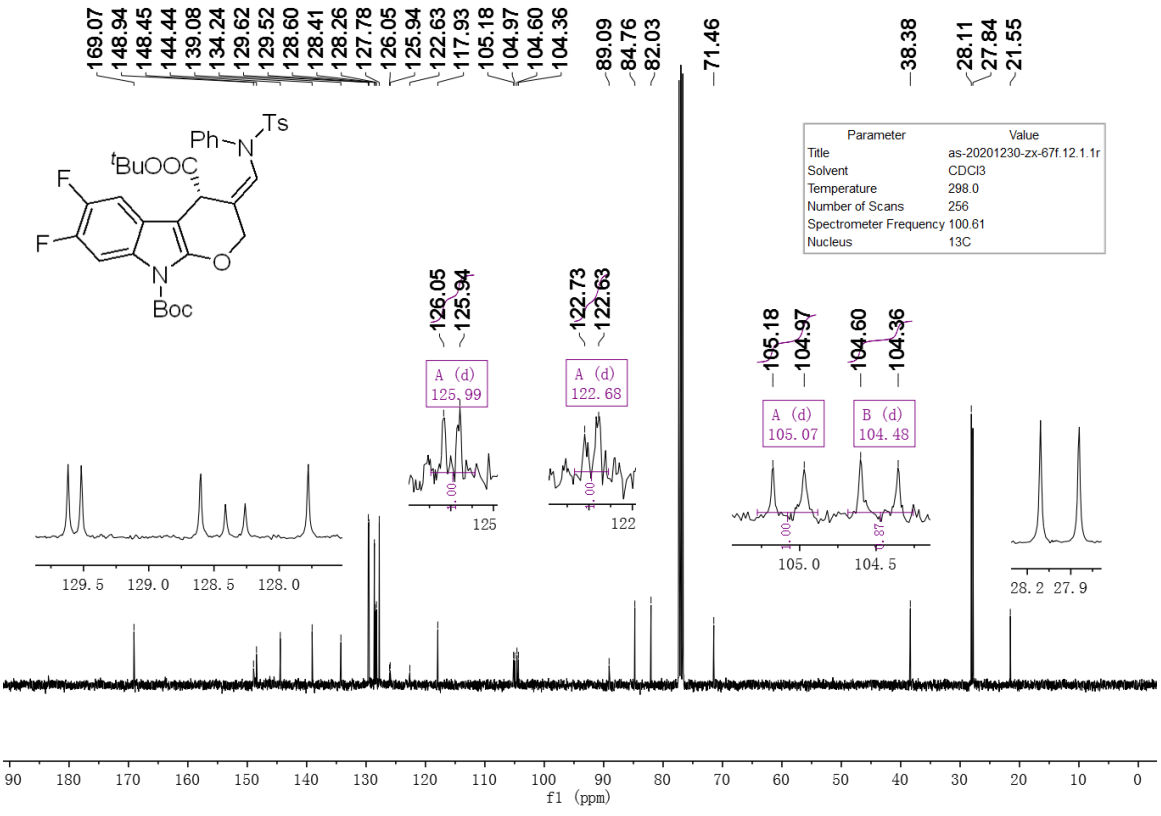


^{19}F NMR spectra of compound **3qa** in $CDCl_3$

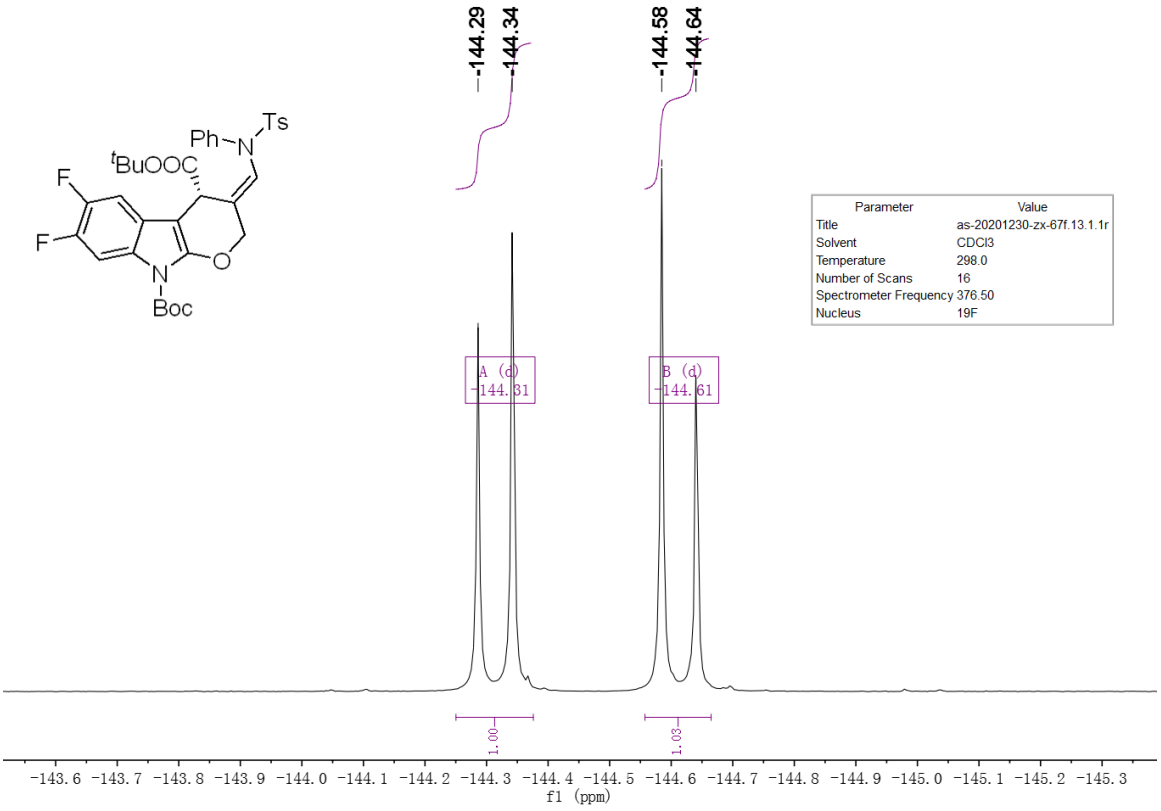


^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4qa** in $CDCl_3$

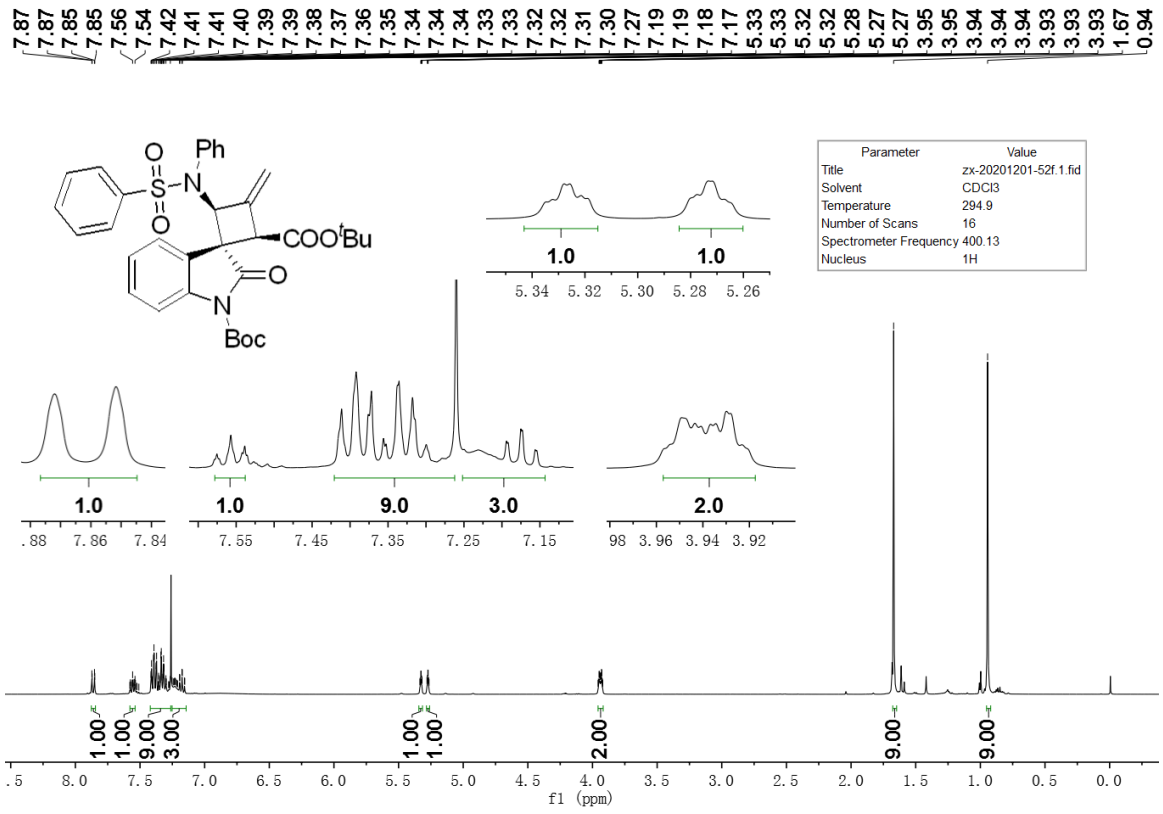


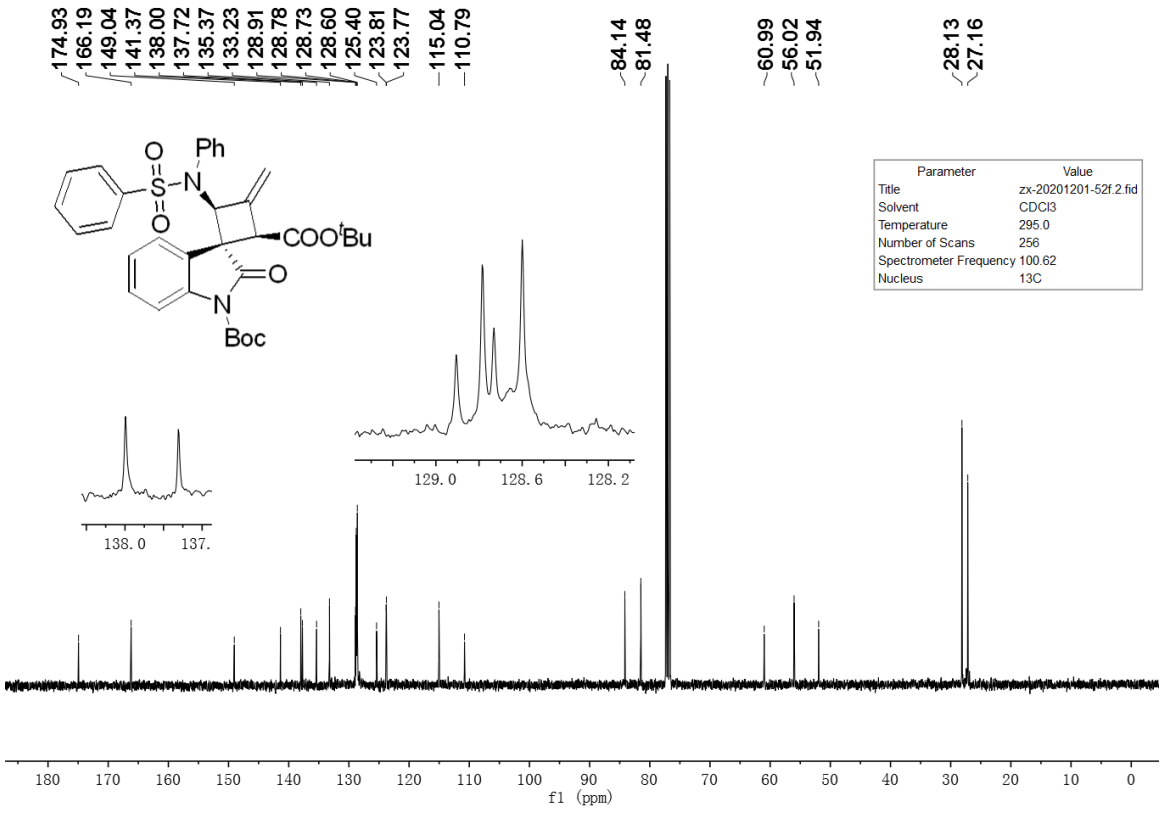


^{19}F NMR spectra of compound **4qa** in $CDCl_3$

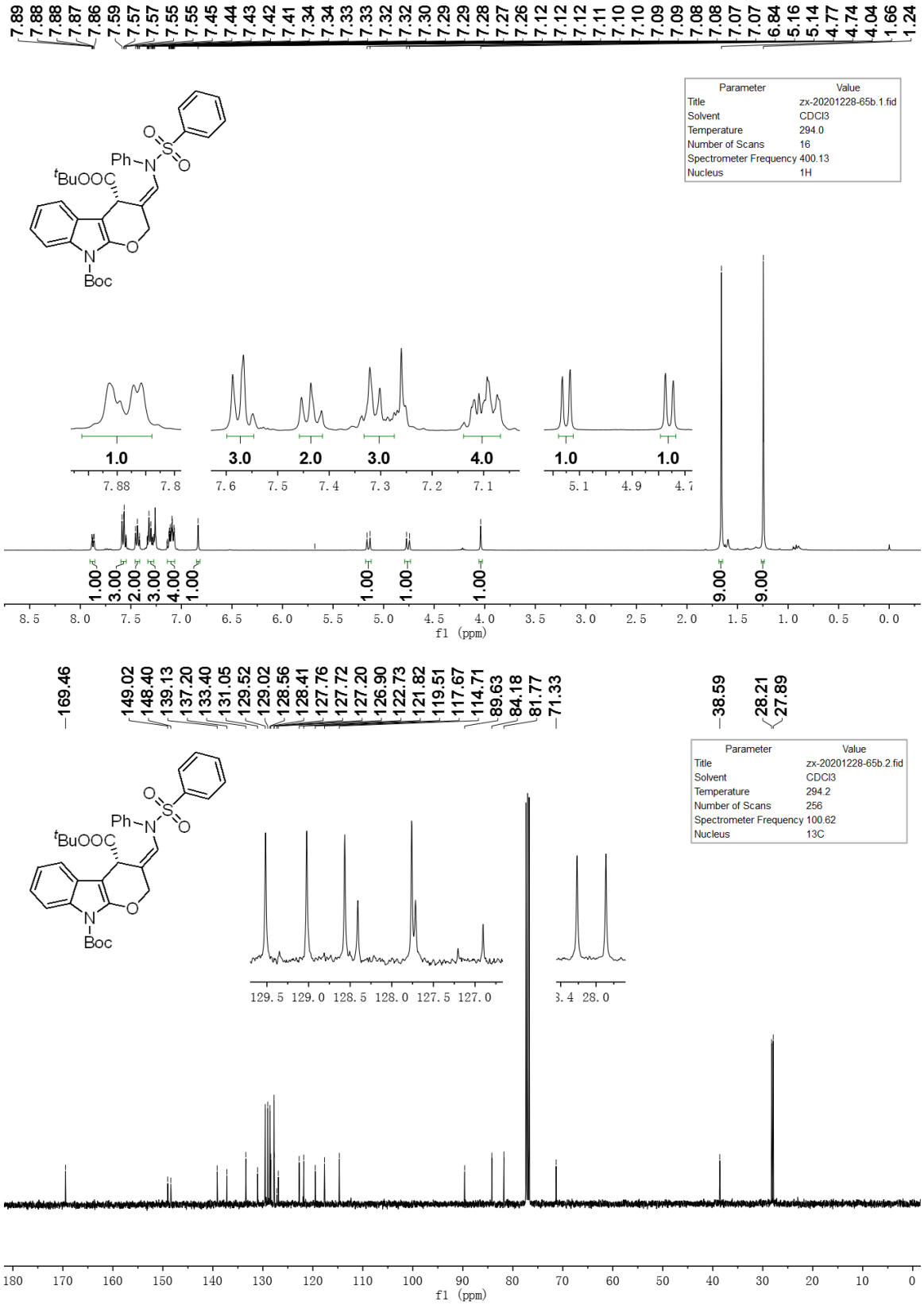


^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3ab** in $CDCl_3$

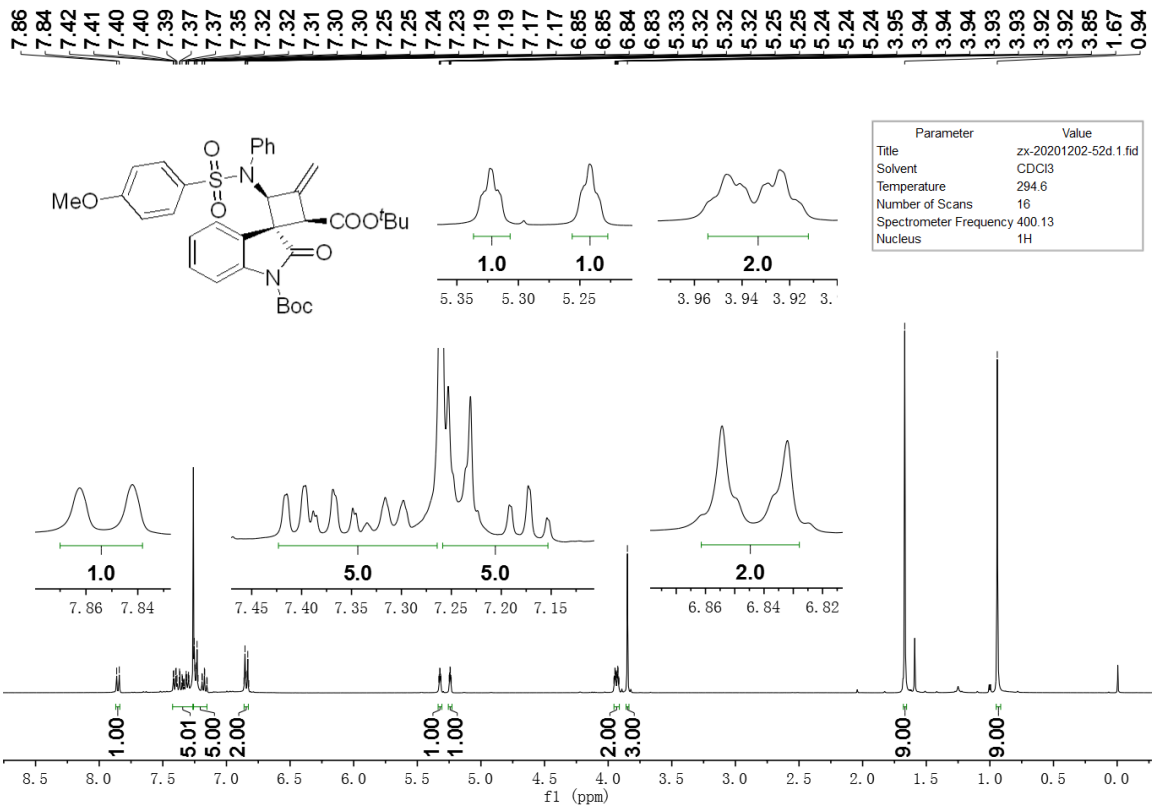


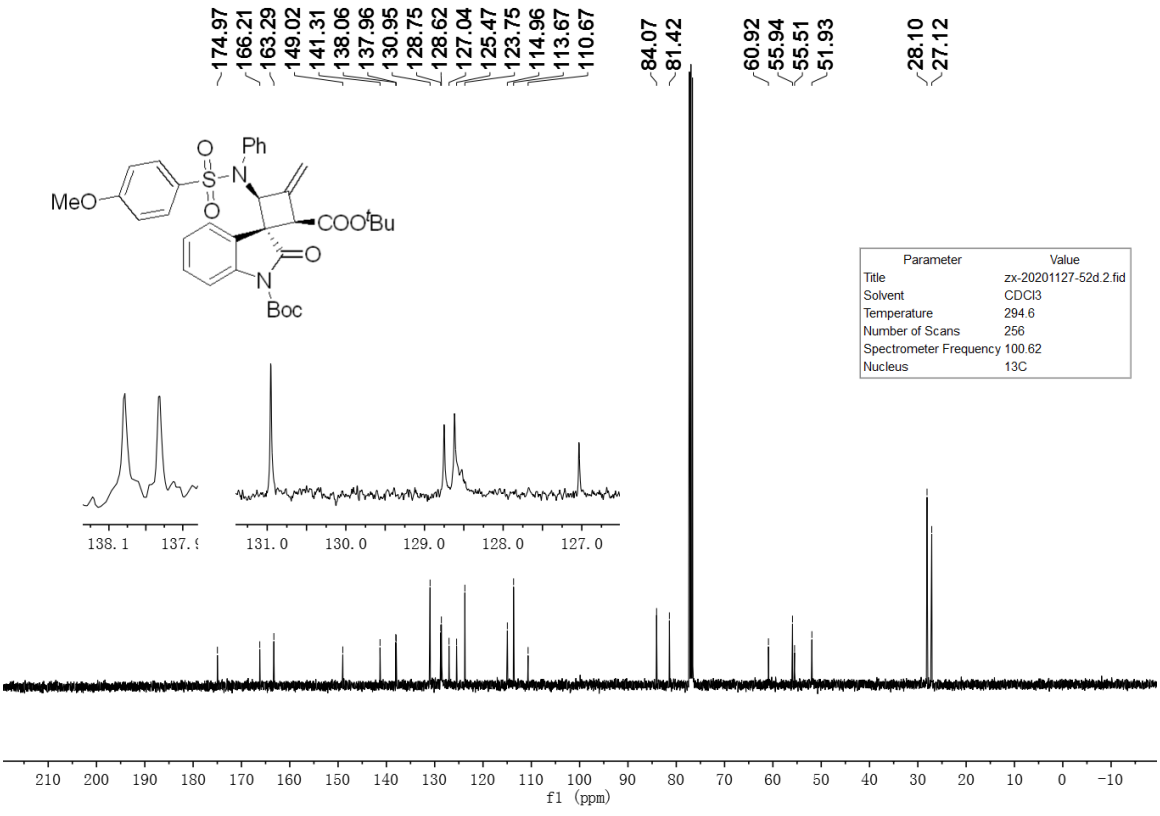


^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4ab** in $CDCl_3$

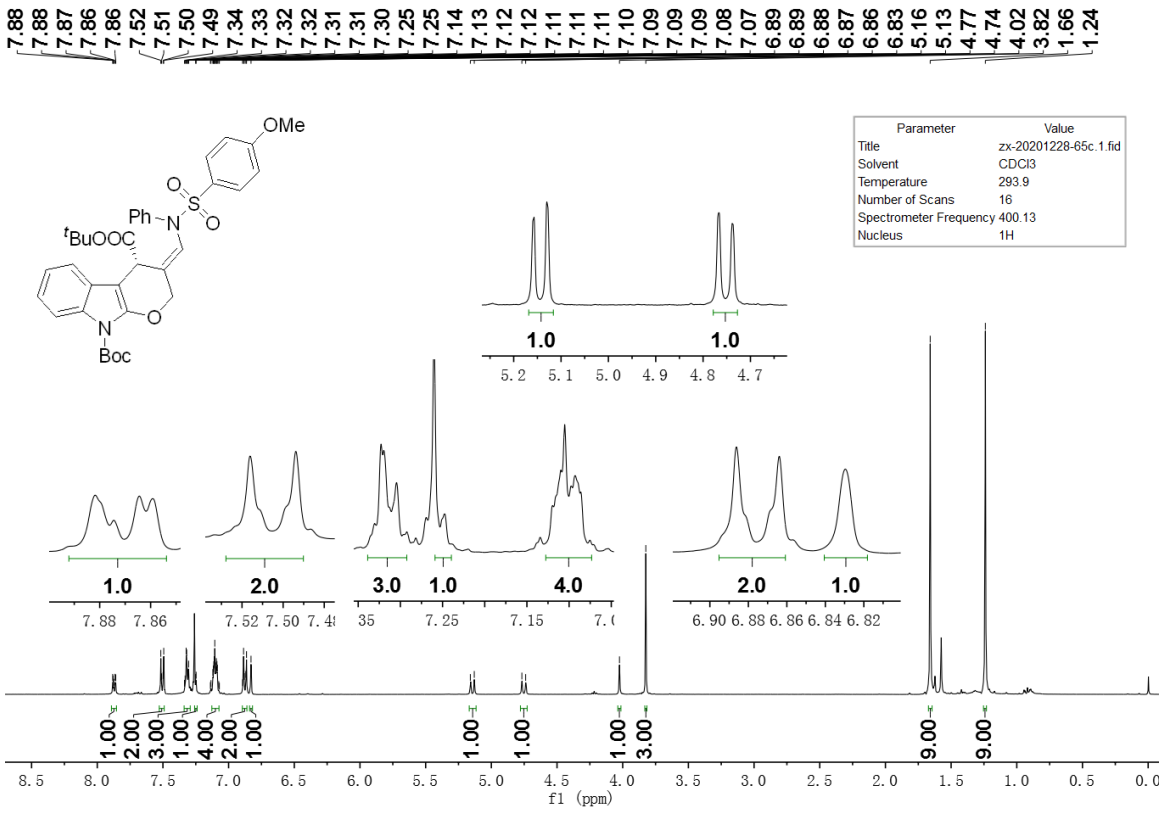


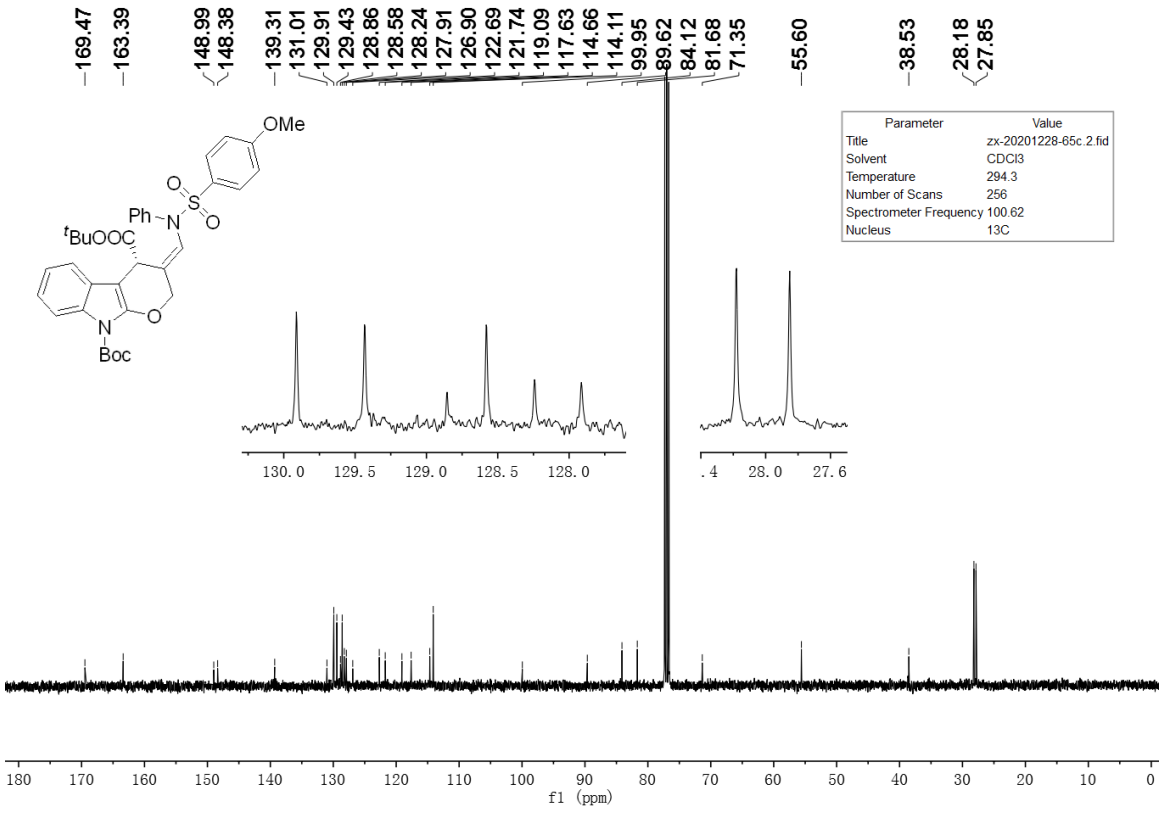
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3ac** in $CDCl_3$



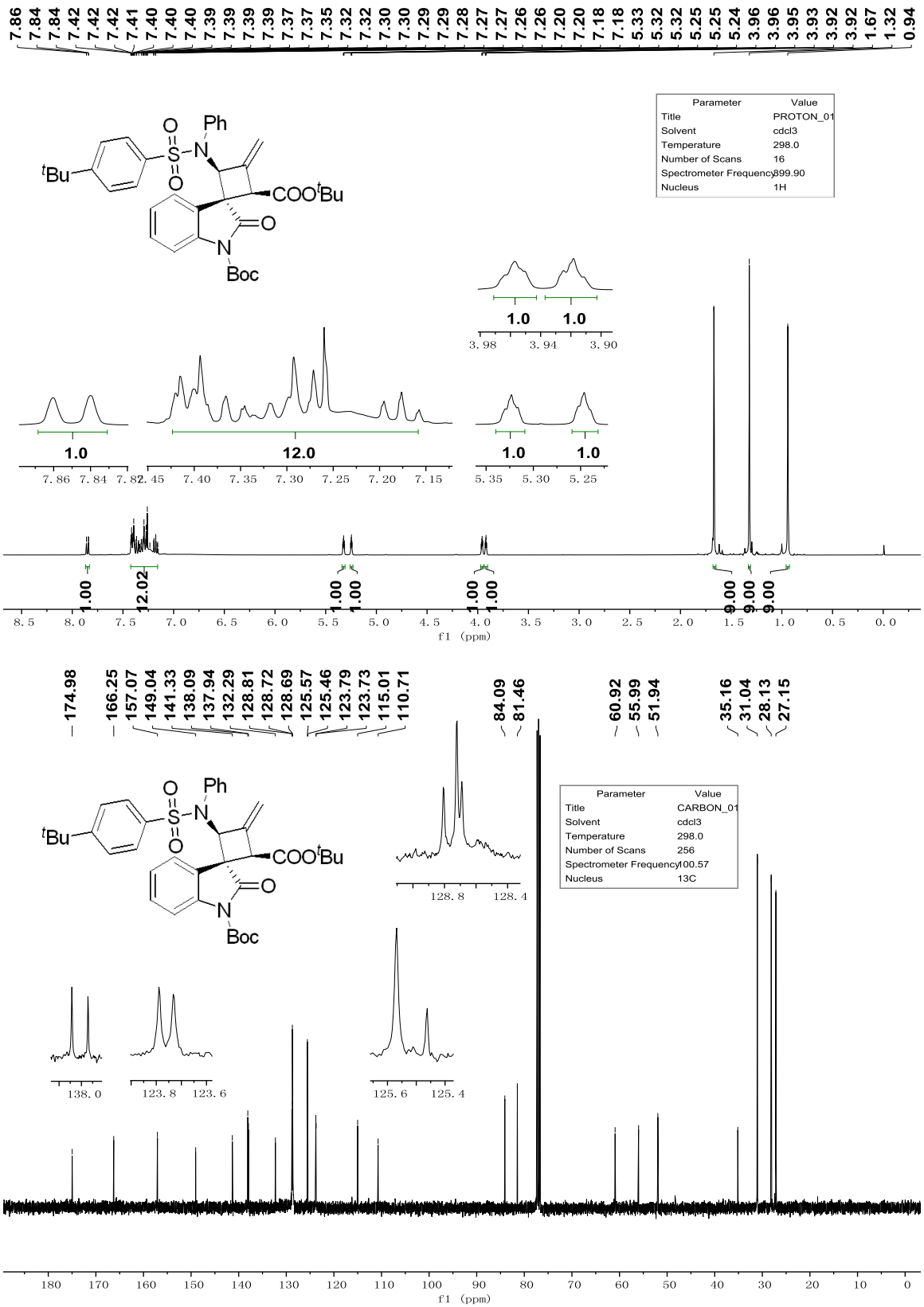


^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4ac** in $CDCl_3$

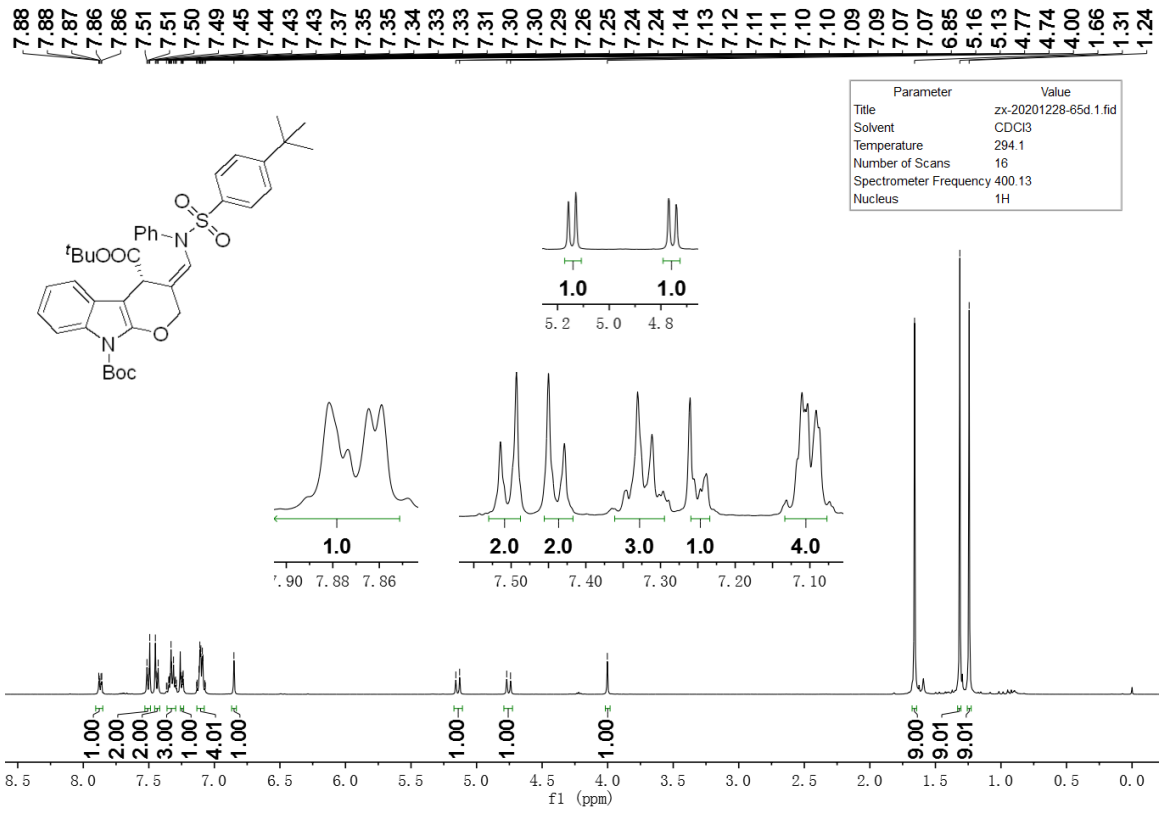


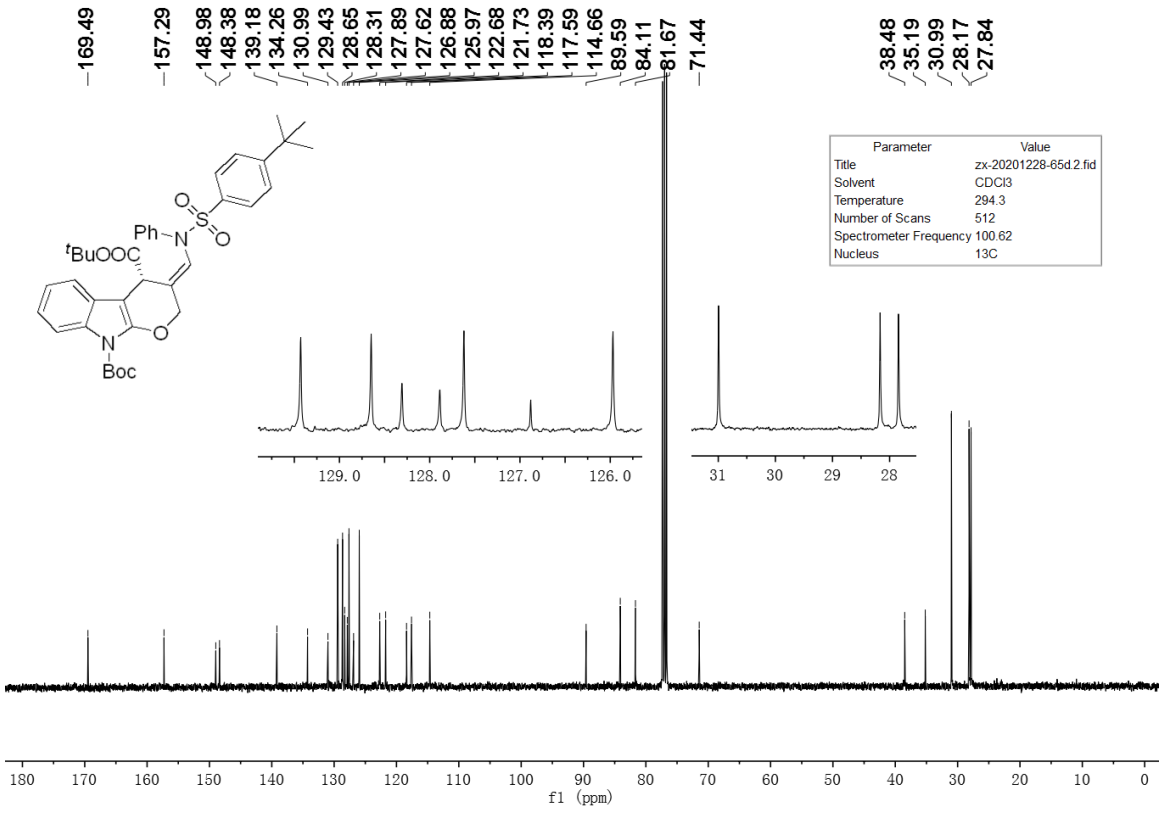


^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of compound **3ad** in $CDCl_3$

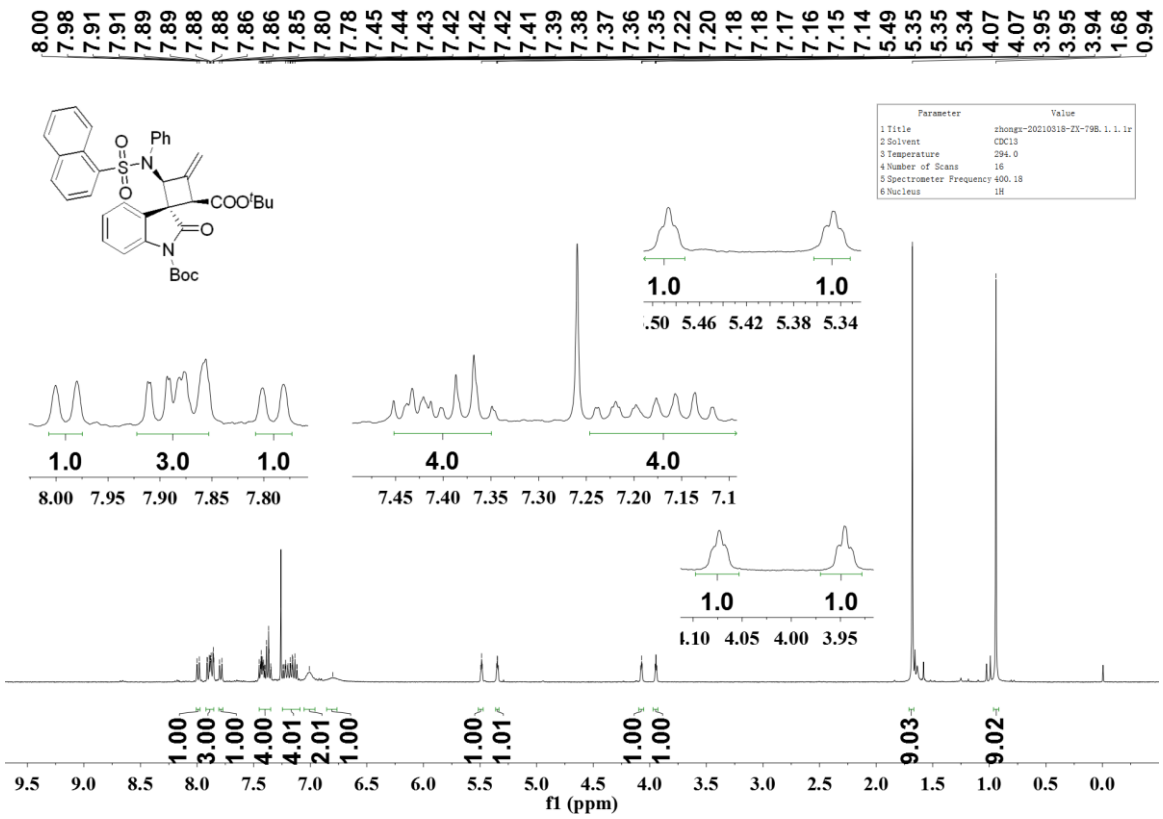


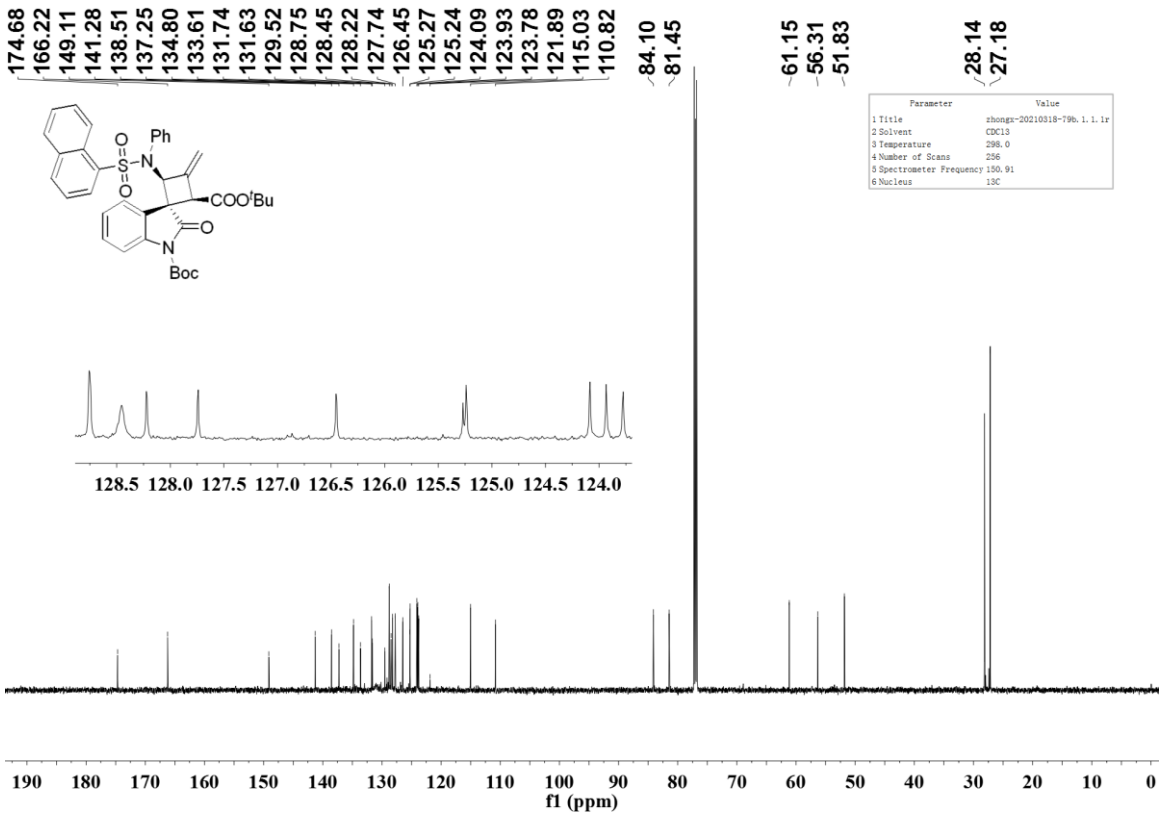
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4ad** in $CDCl_3$



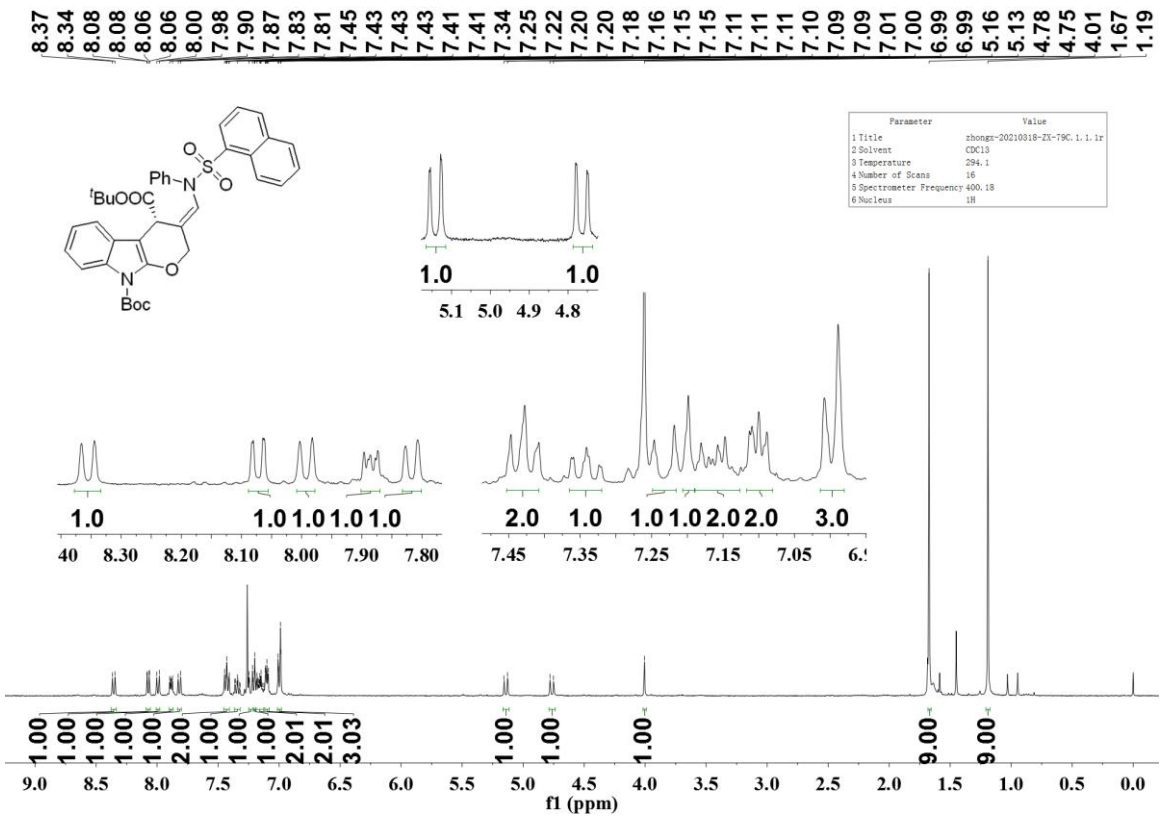


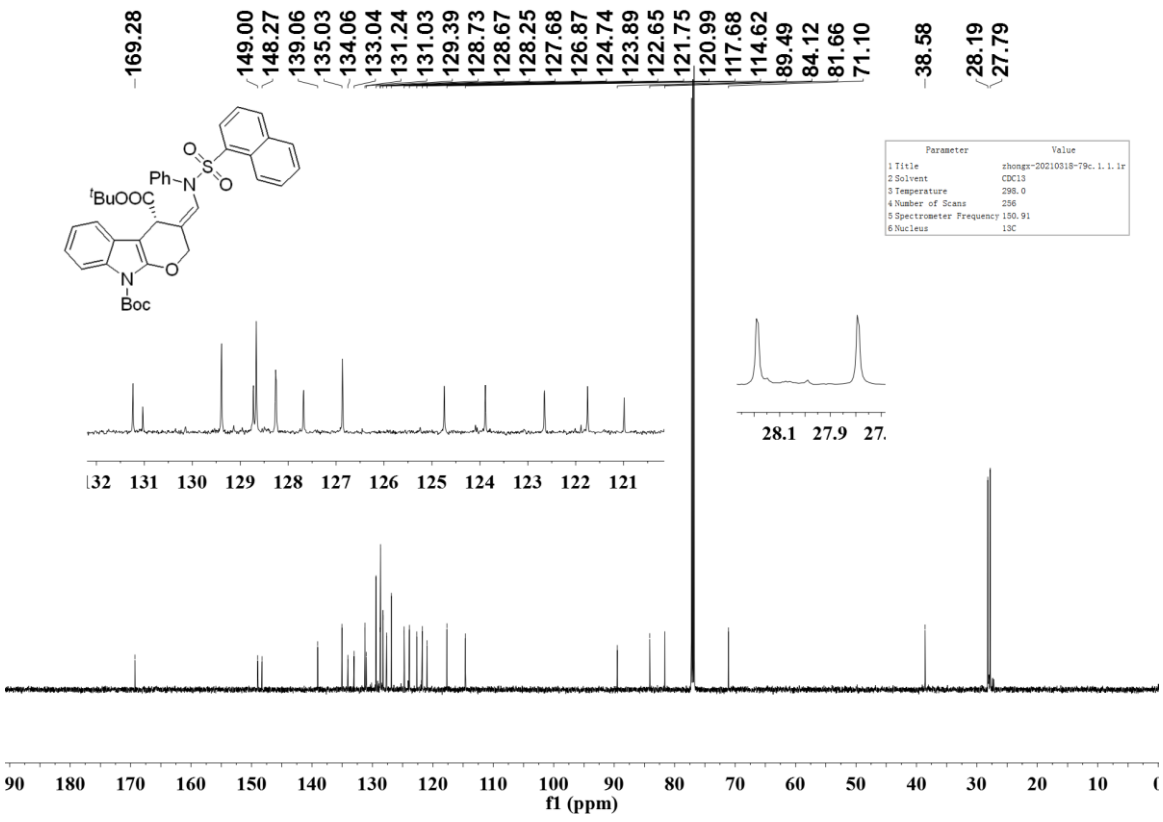
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3ae** in $CDCl_3$



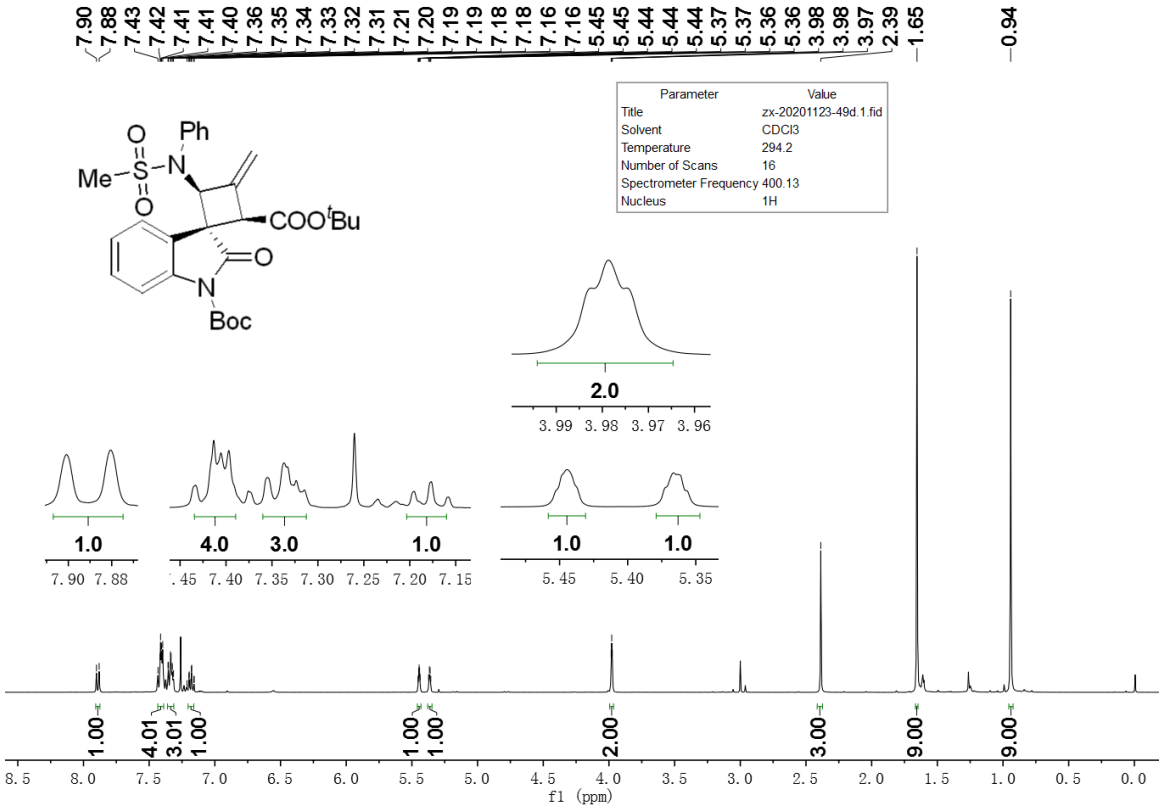


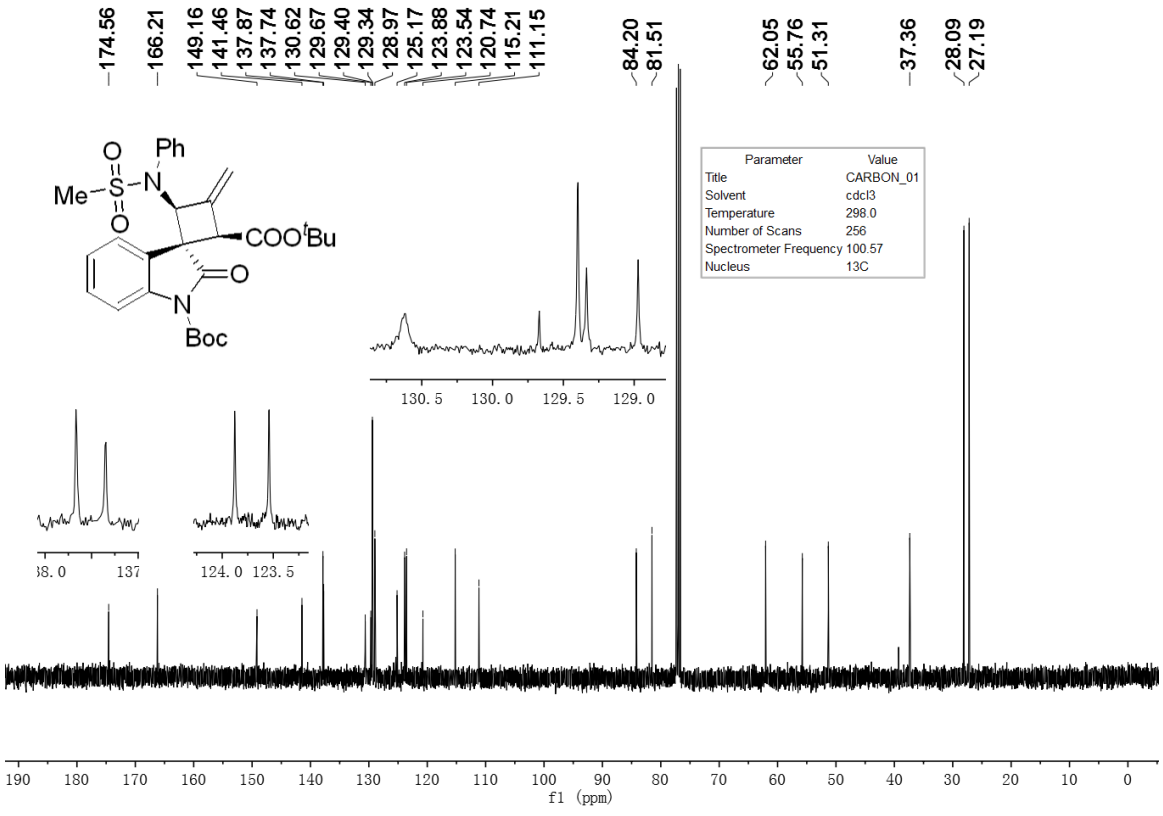
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4ae** in $CDCl_3$



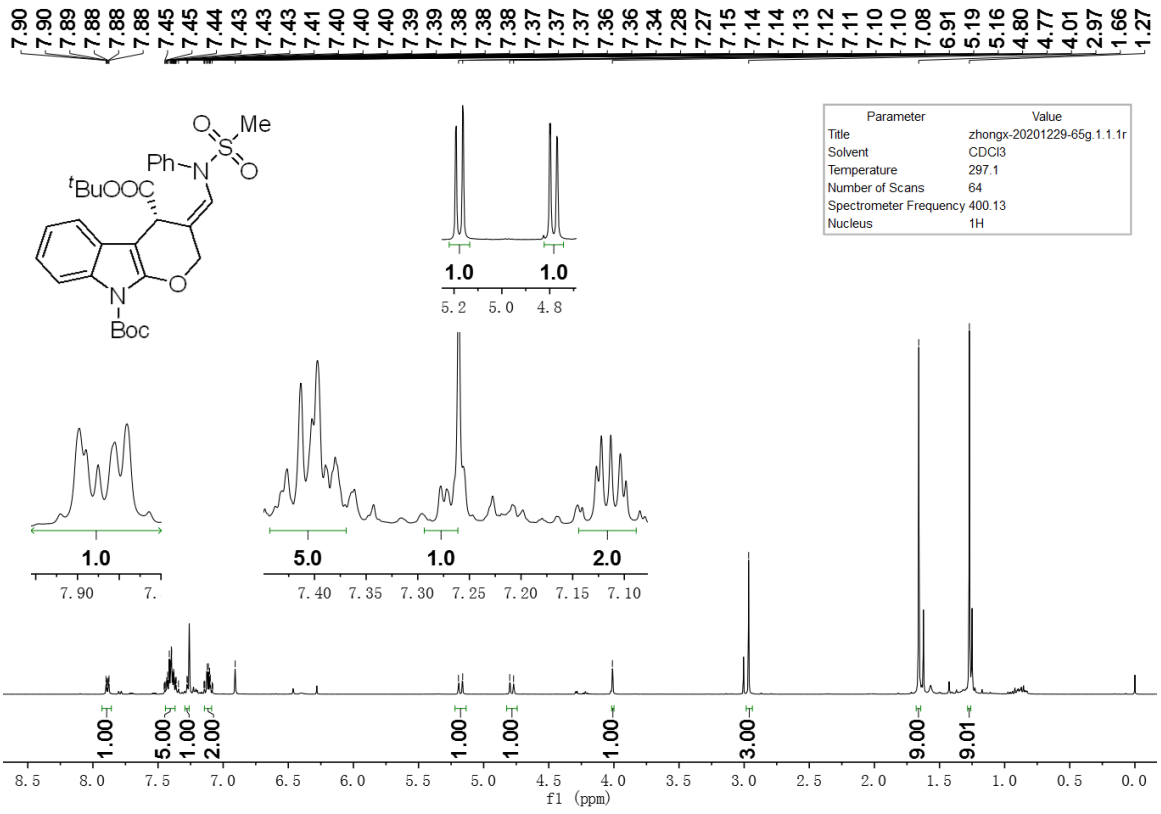


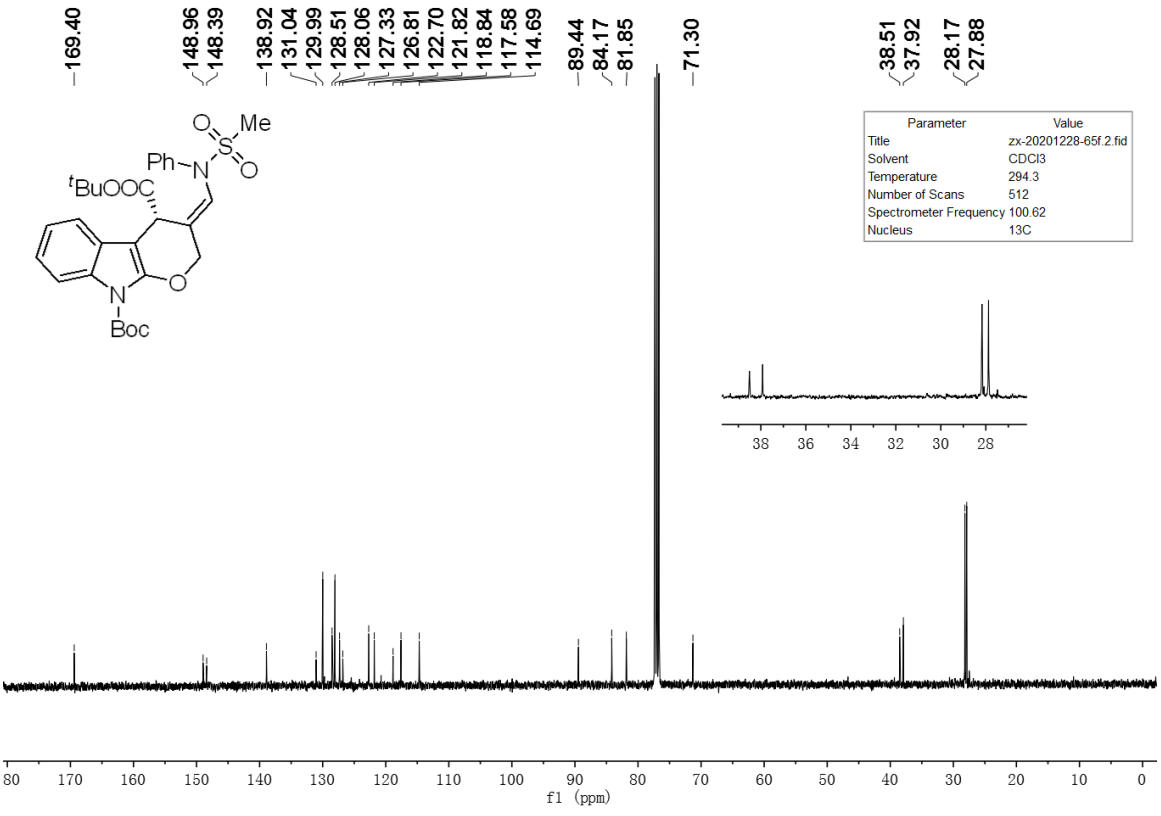
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3af** in $CDCl_3$



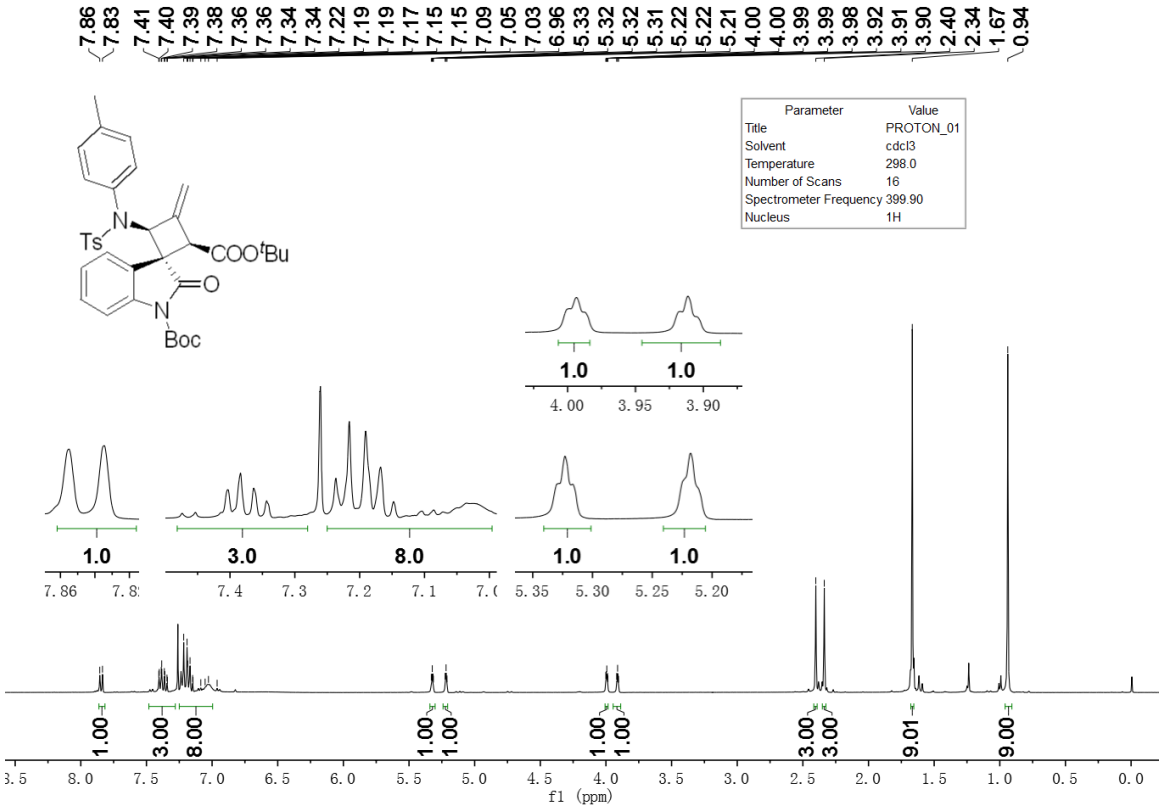


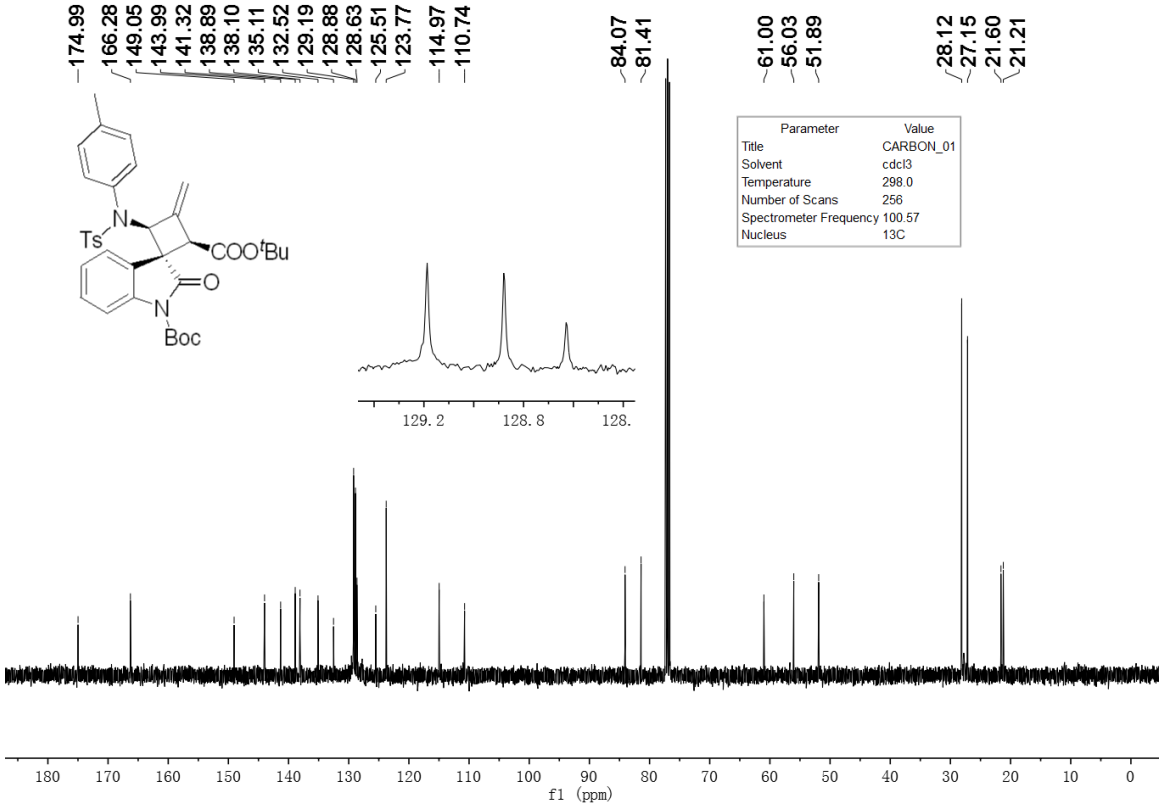
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4af** in $CDCl_3$



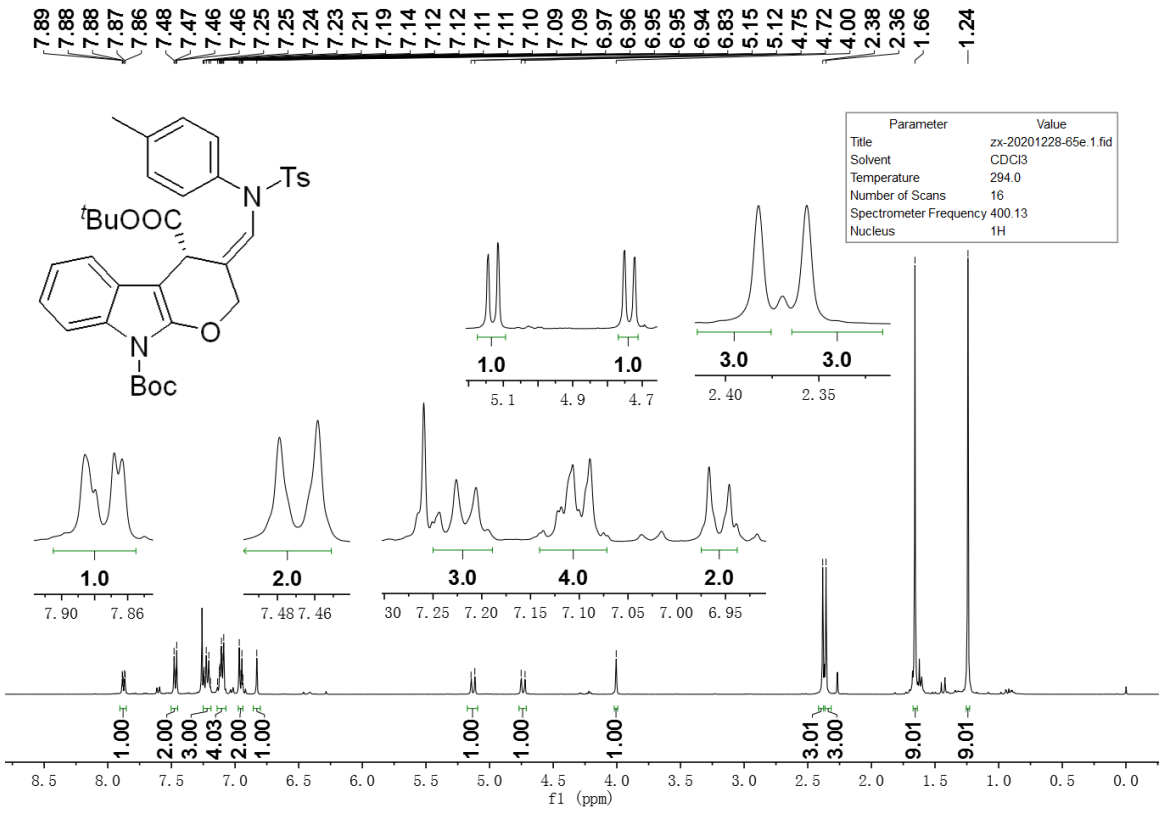


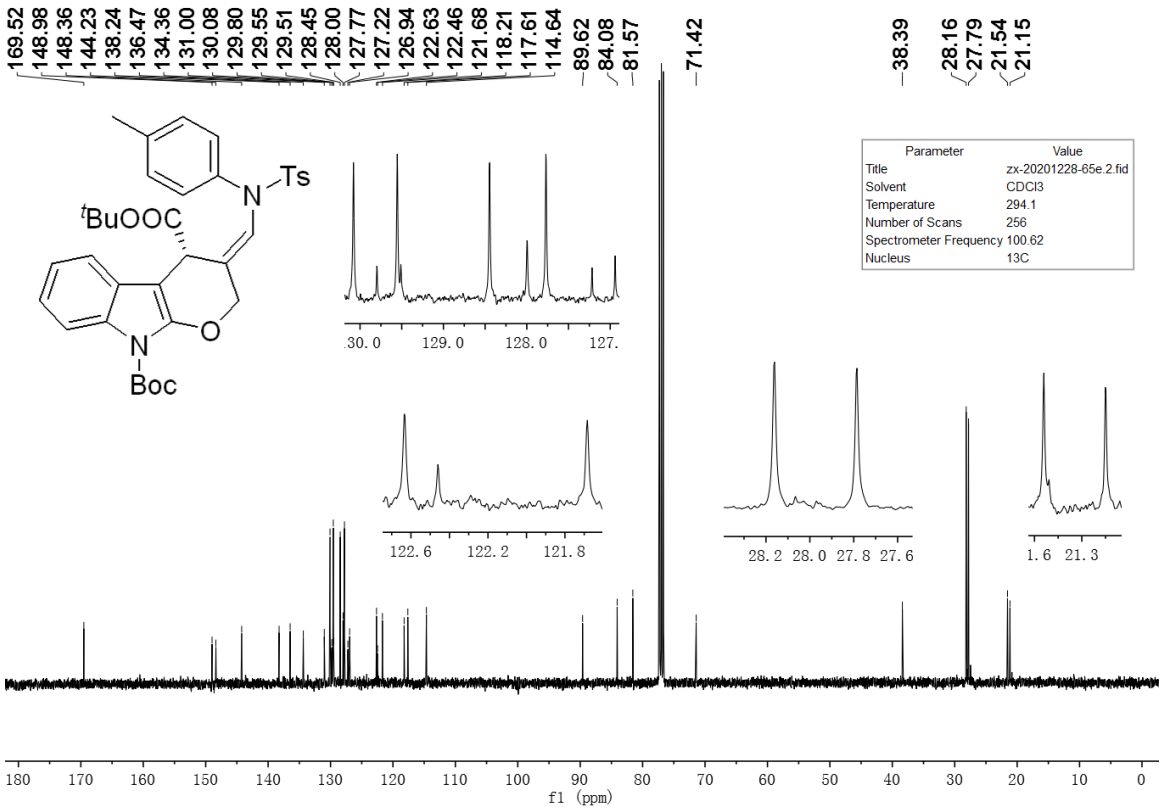
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **3ag** in $CDCl_3$



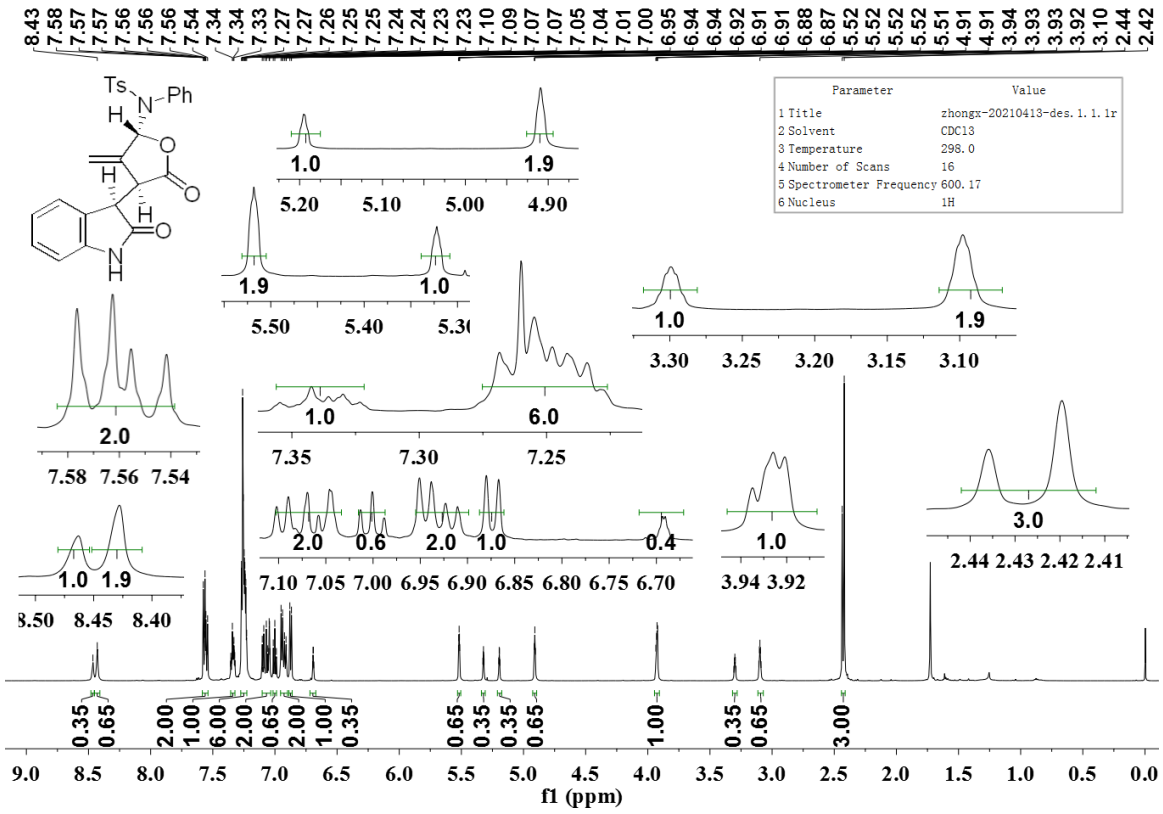


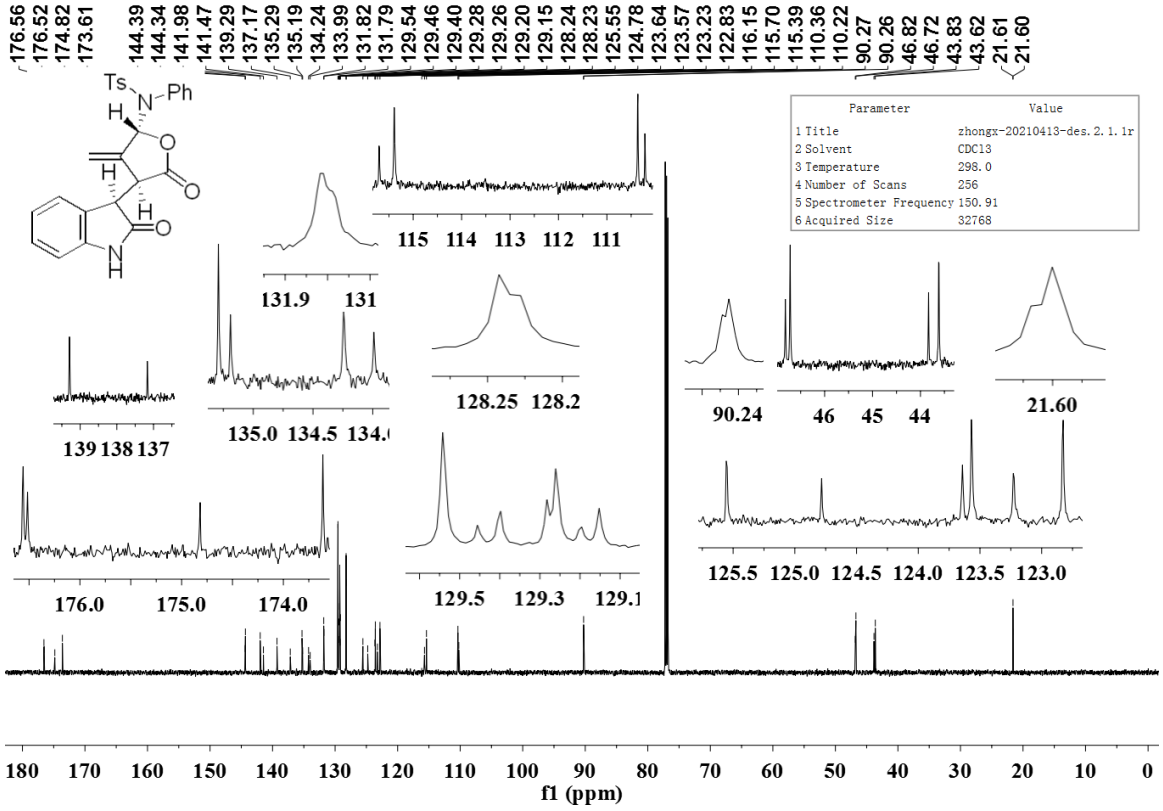
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **4ag** in $CDCl_3$



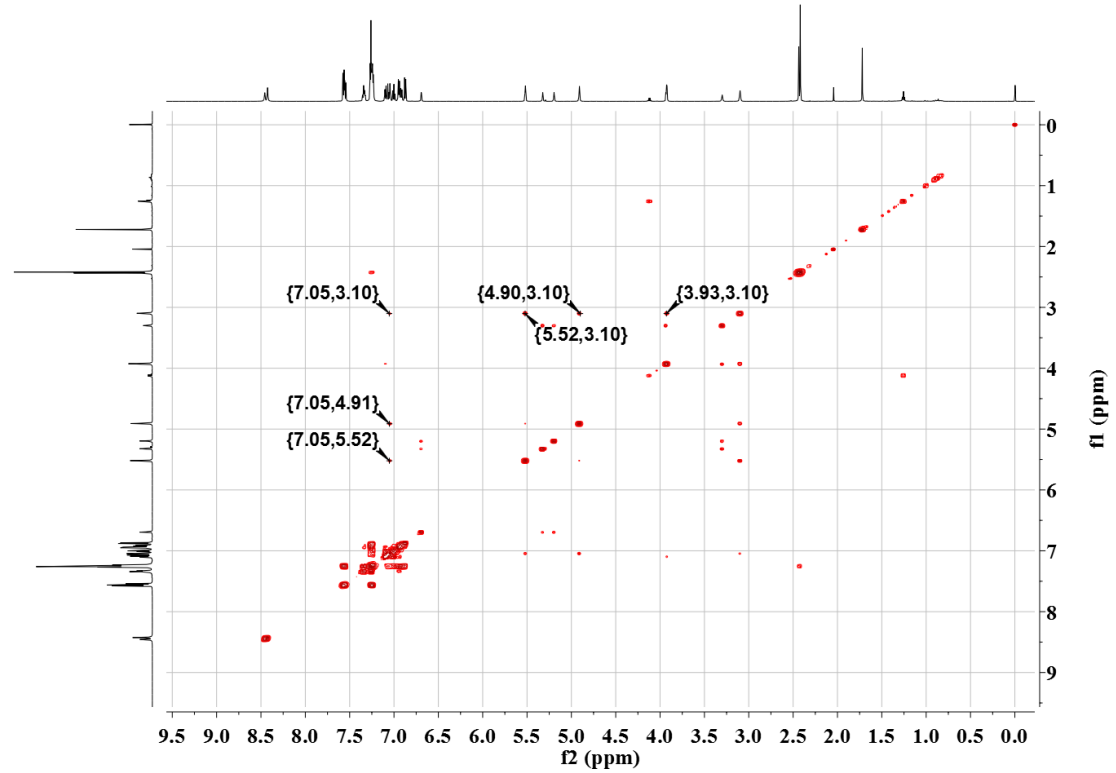


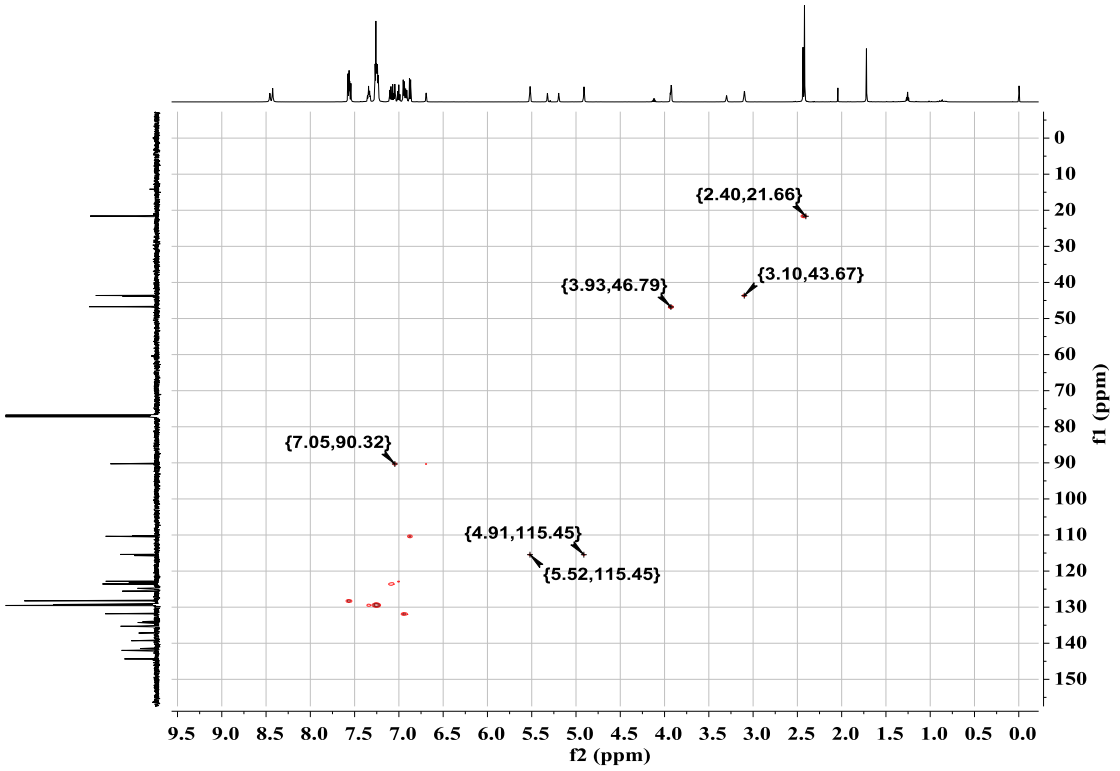
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **5aa** in $CDCl_3$



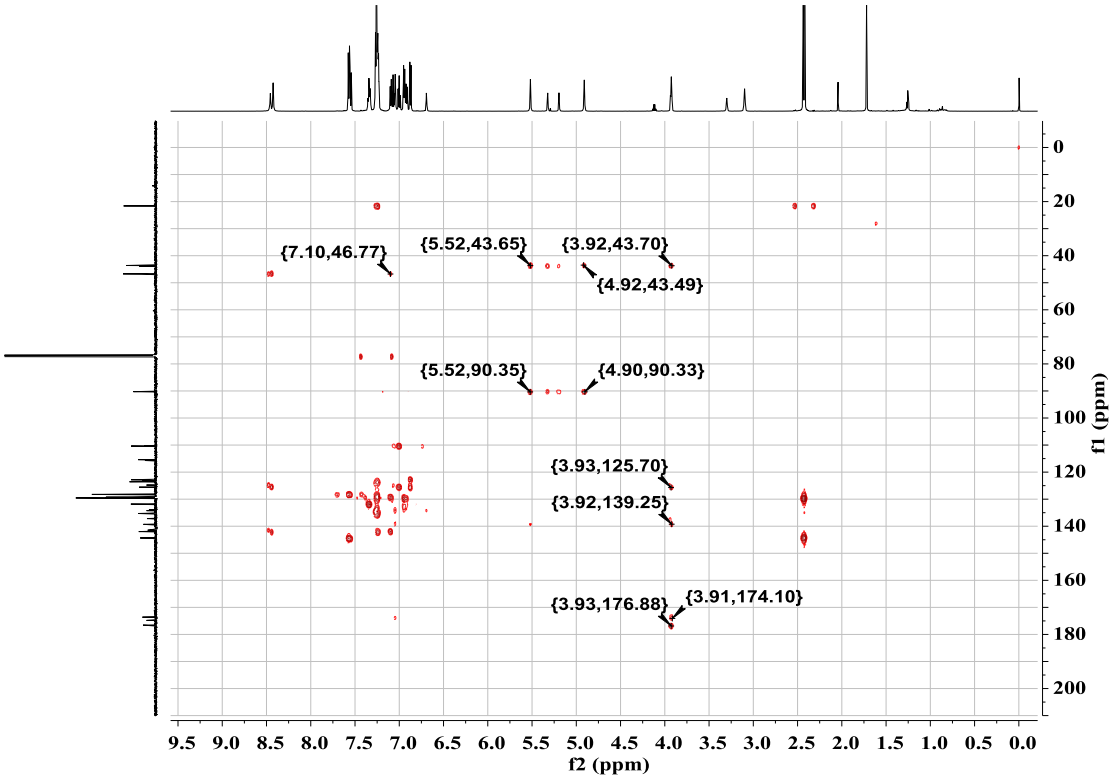


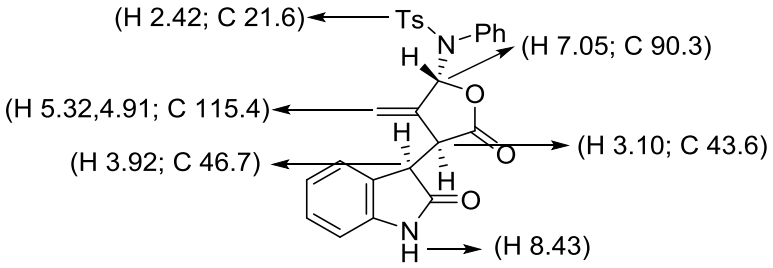
NOESY and HSQC spectra of compound **5aa** in $CDCl_3$



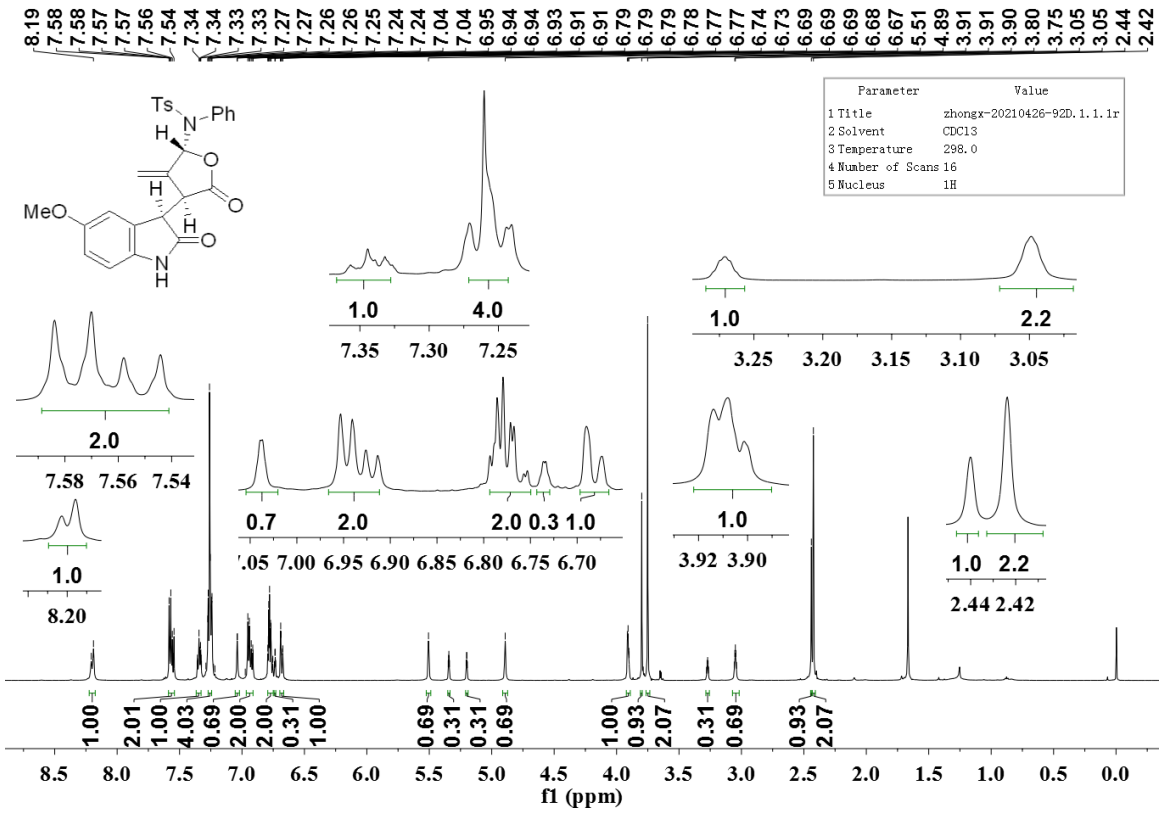


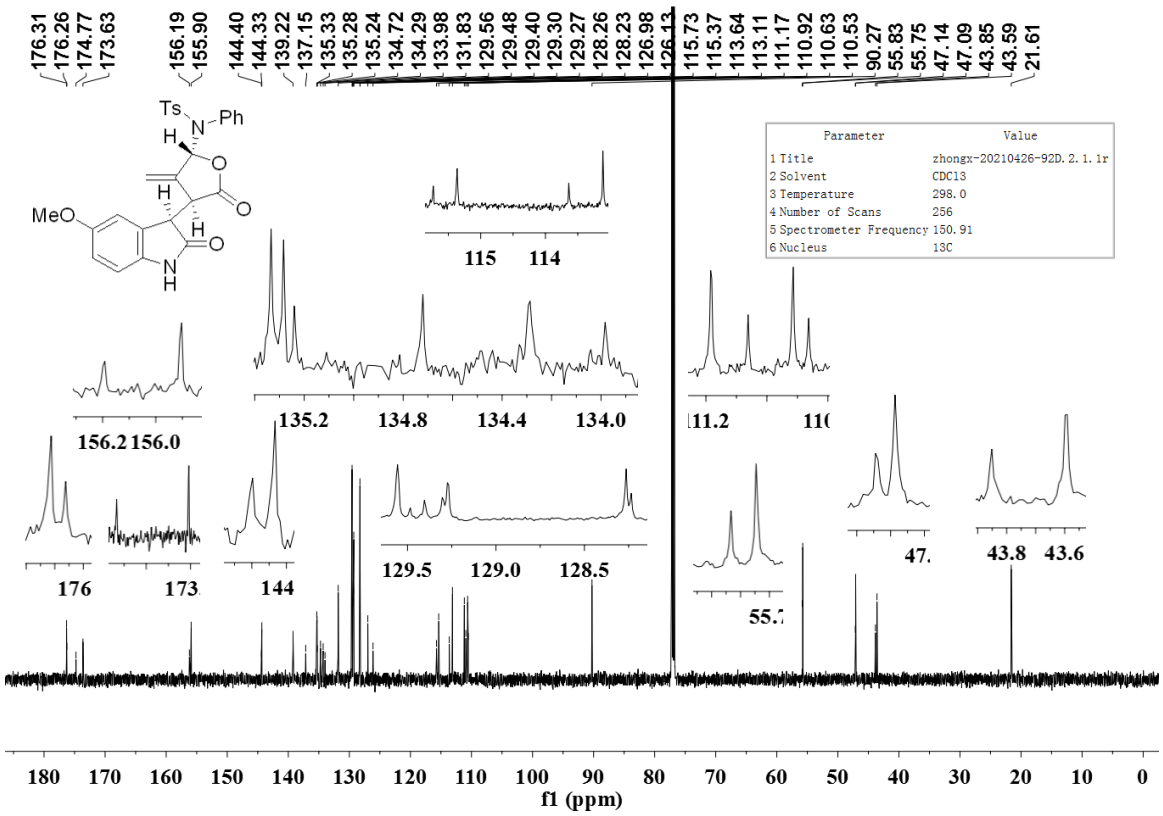
HMBC spectra of compound **5aa** in $CDCl_3$



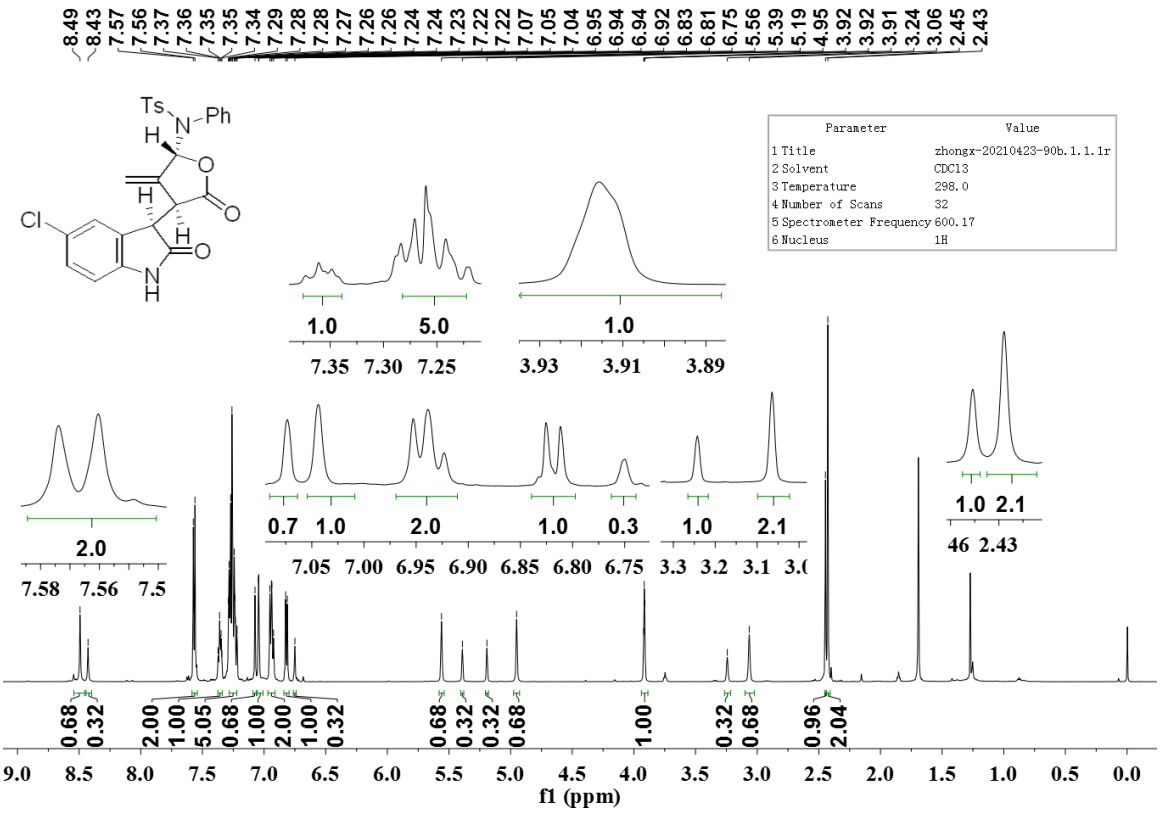


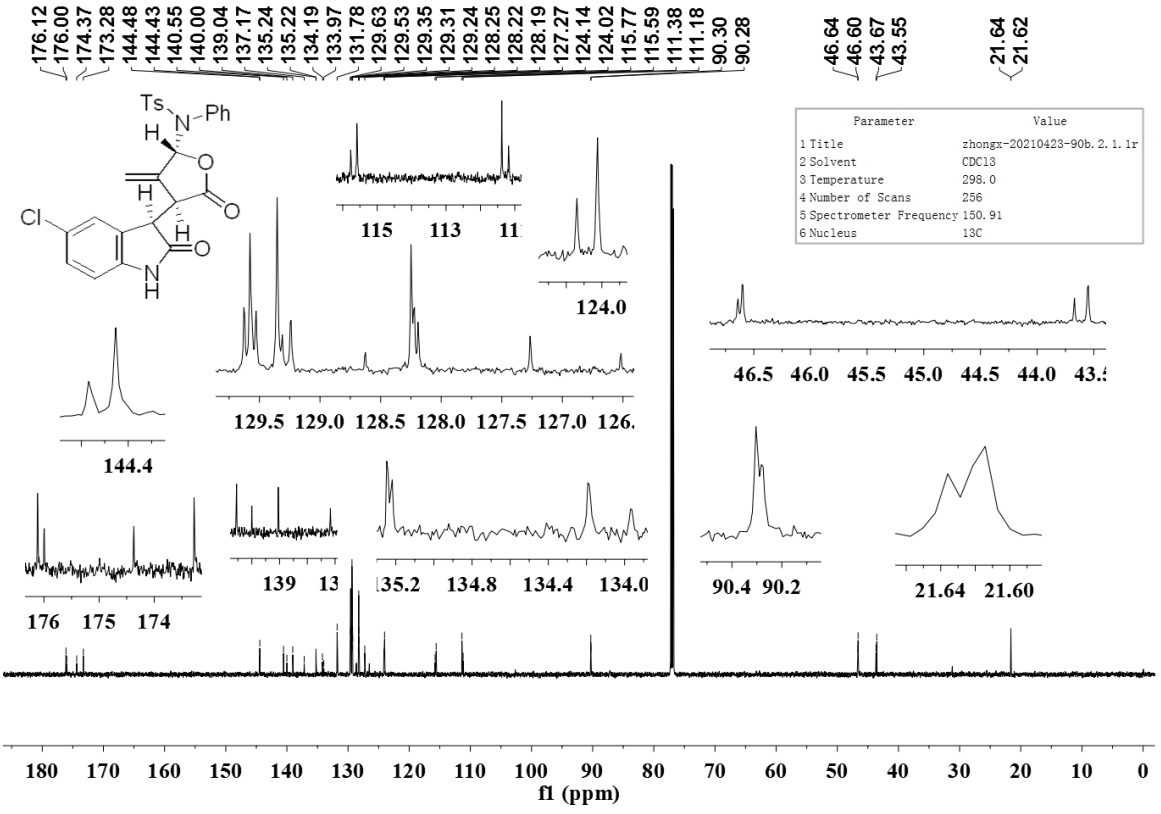
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **5ga** in $CDCl_3$



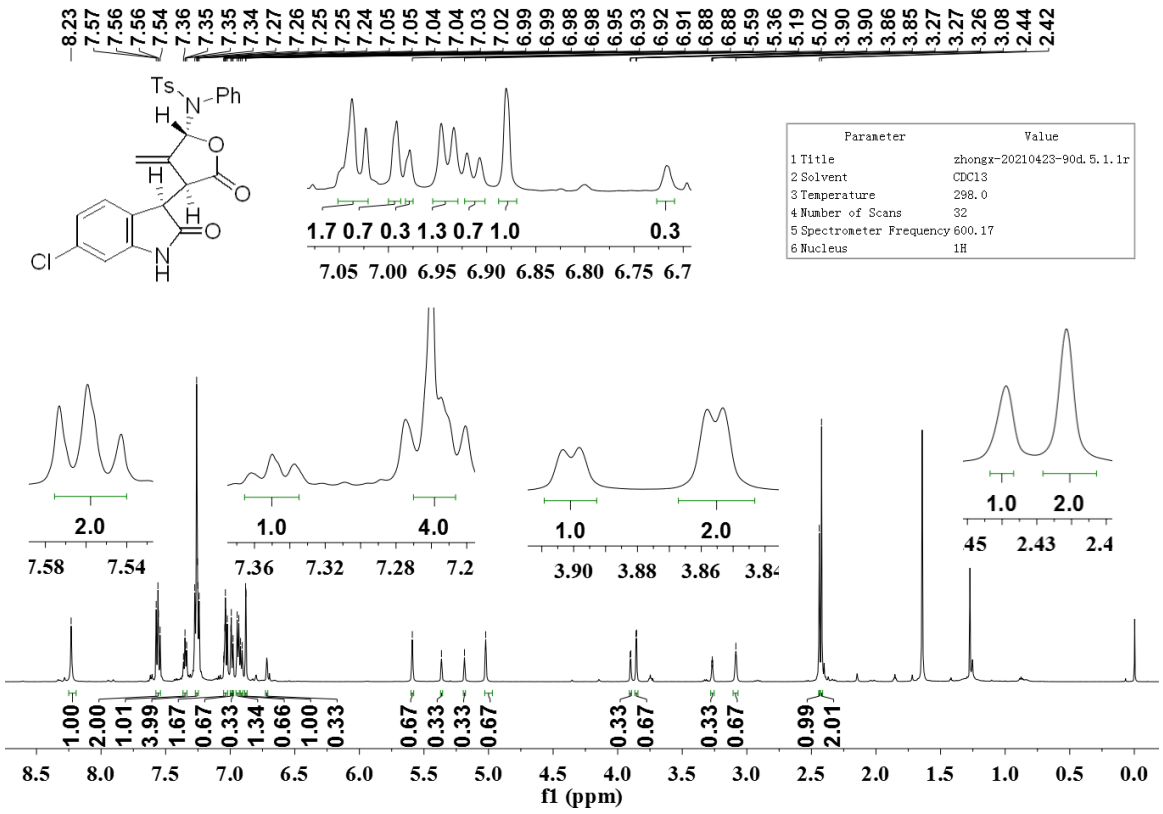


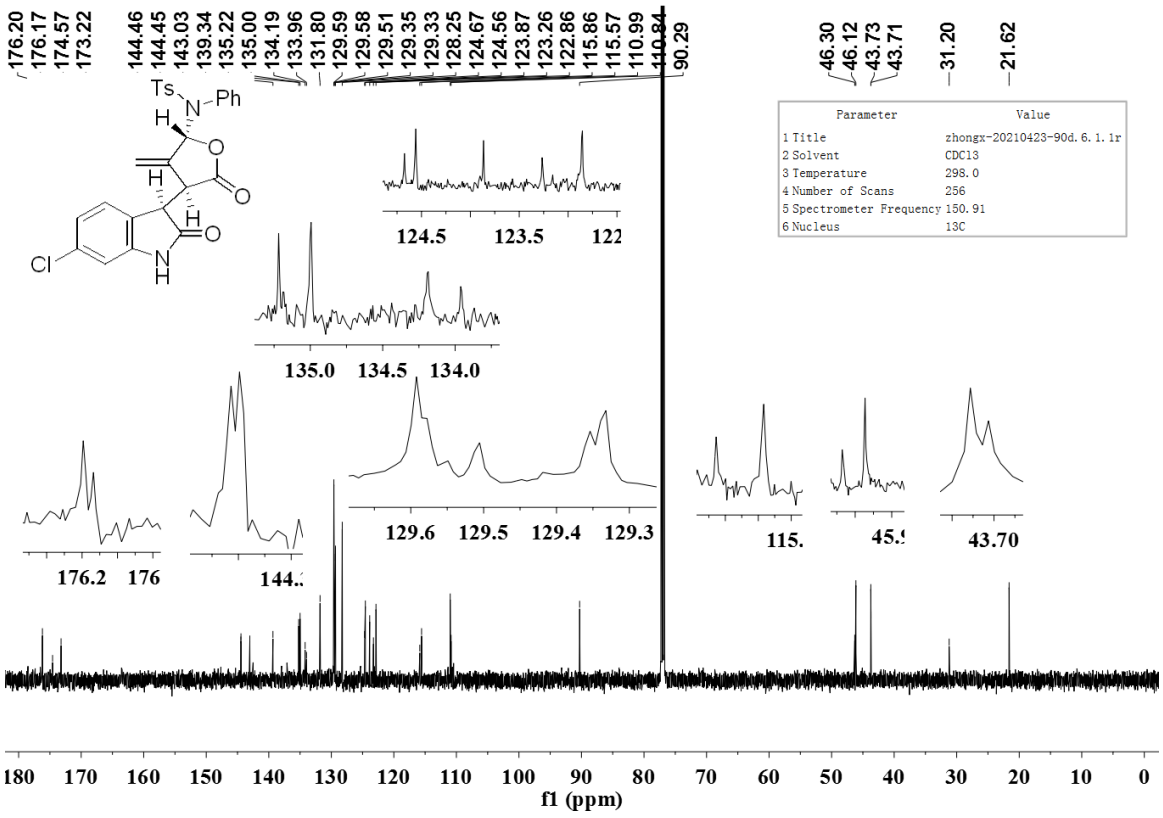
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **5ia** in $CDCl_3$



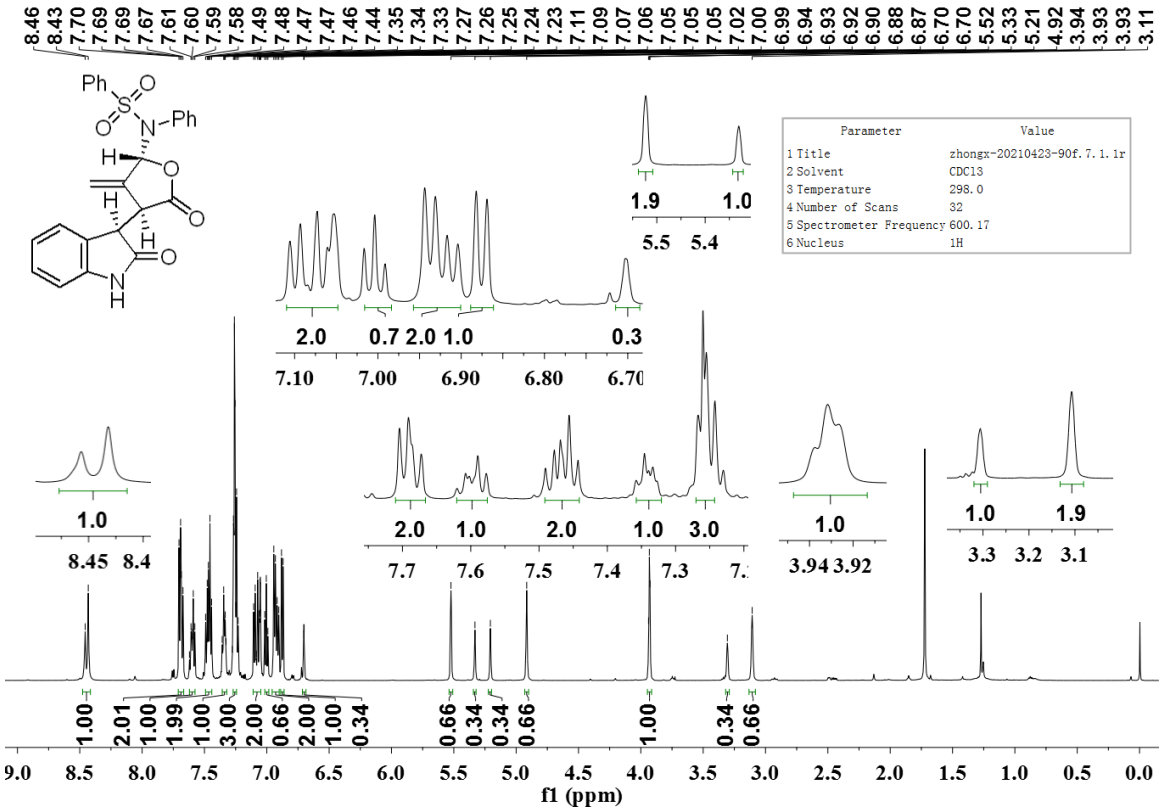


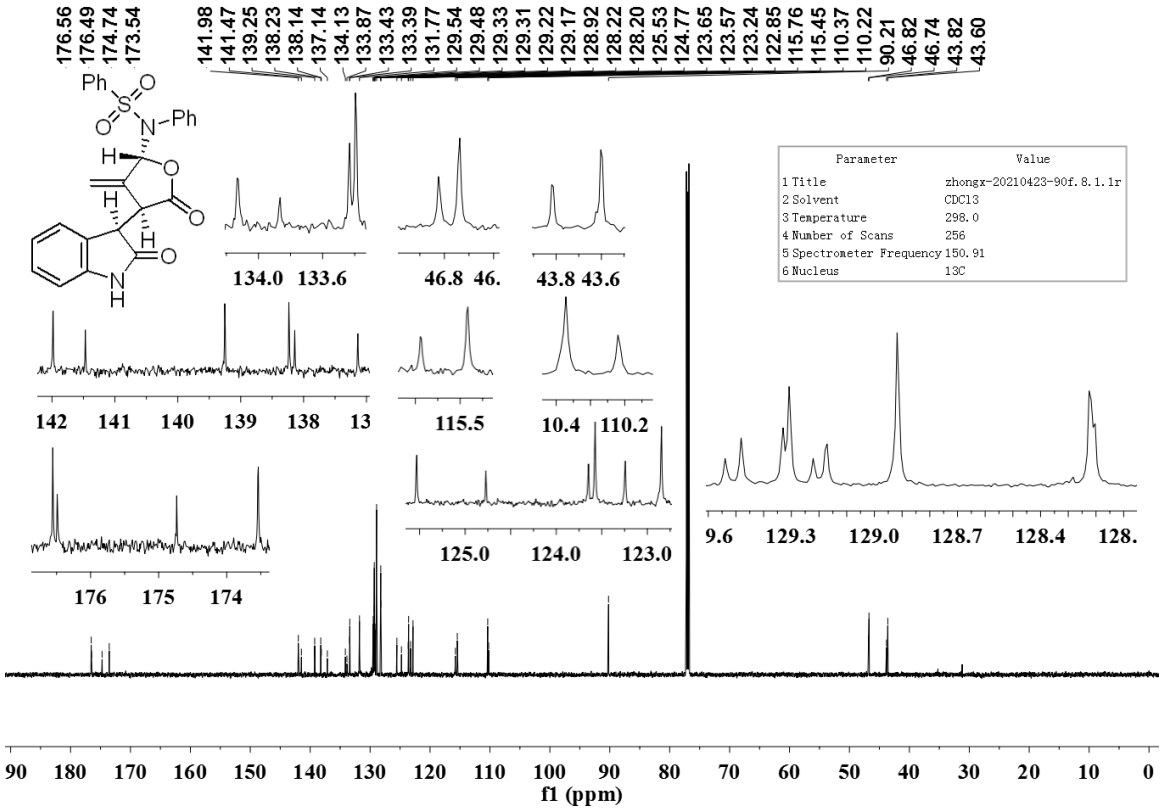
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **5na** in $CDCl_3$



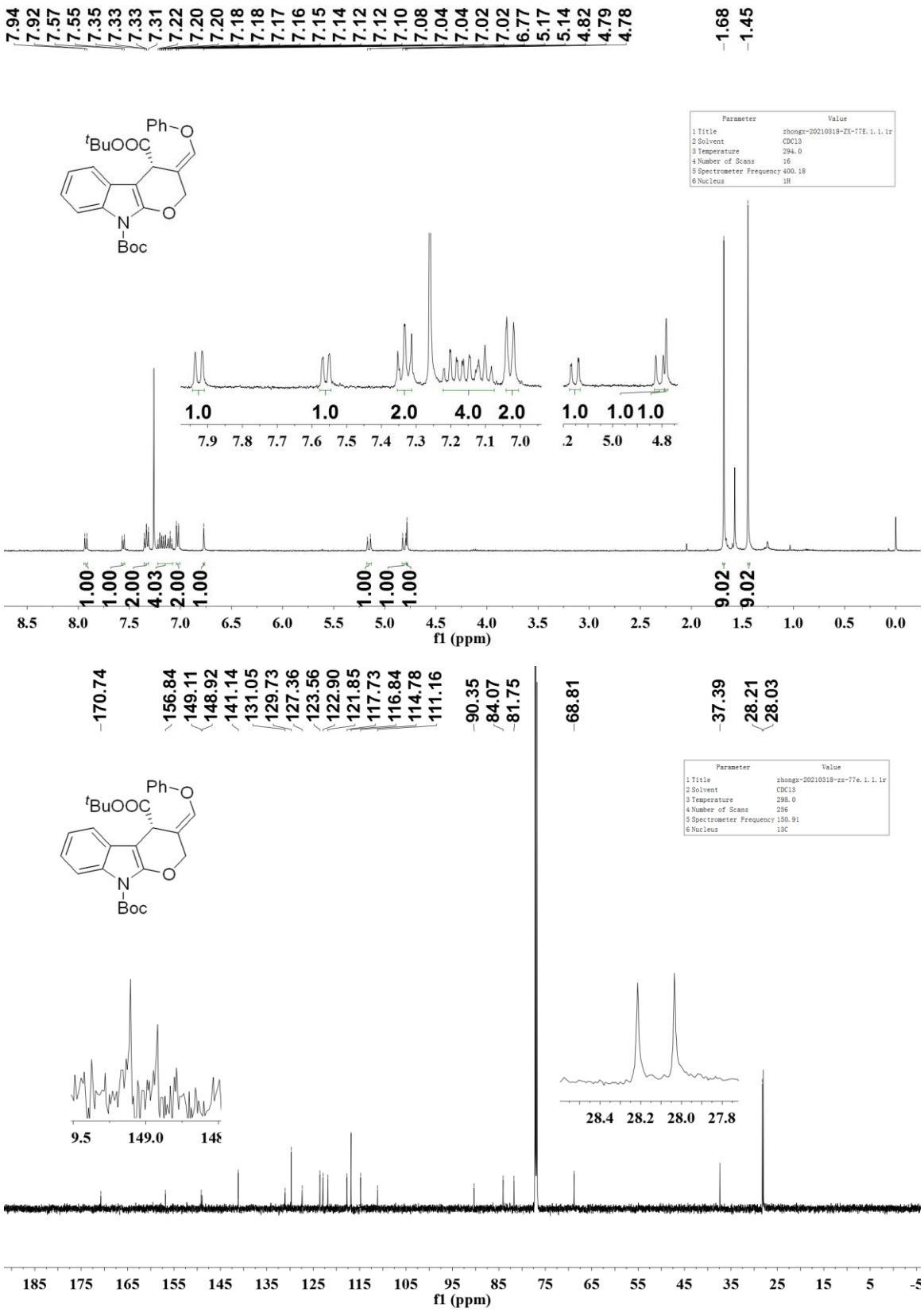


^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **5ab** in $CDCl_3$

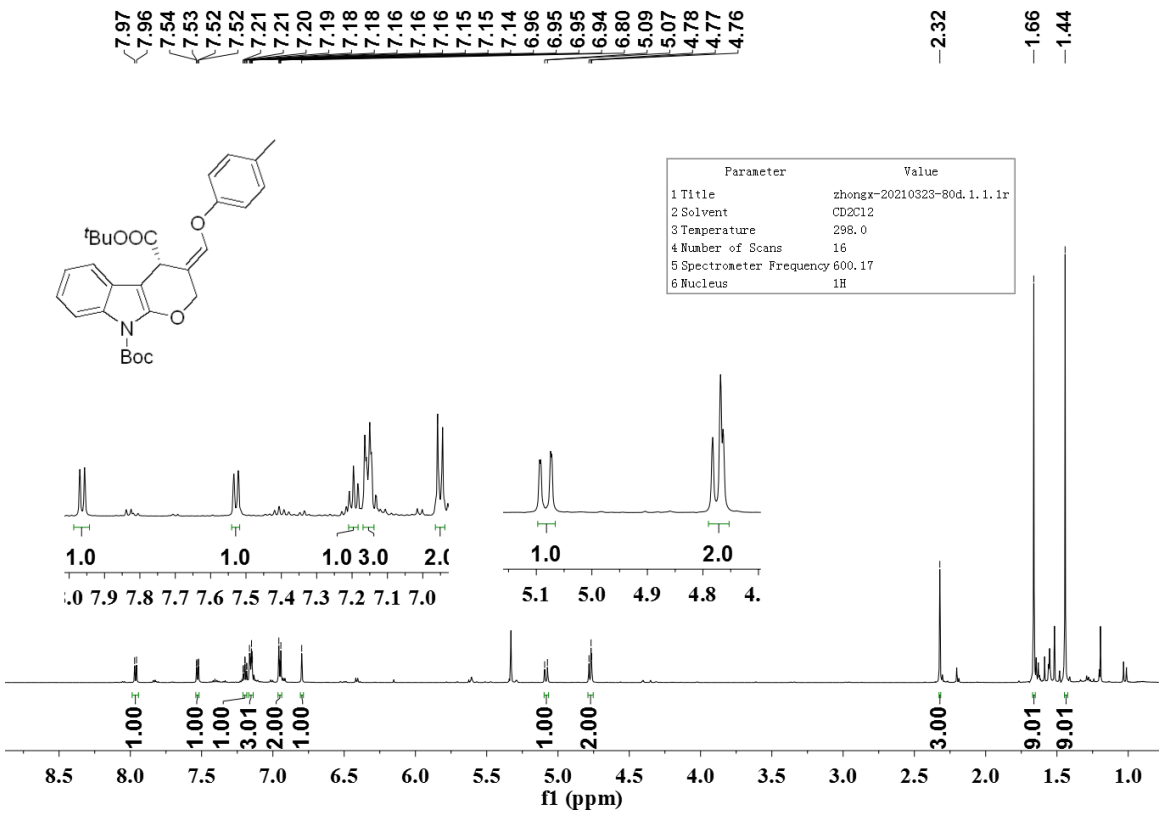


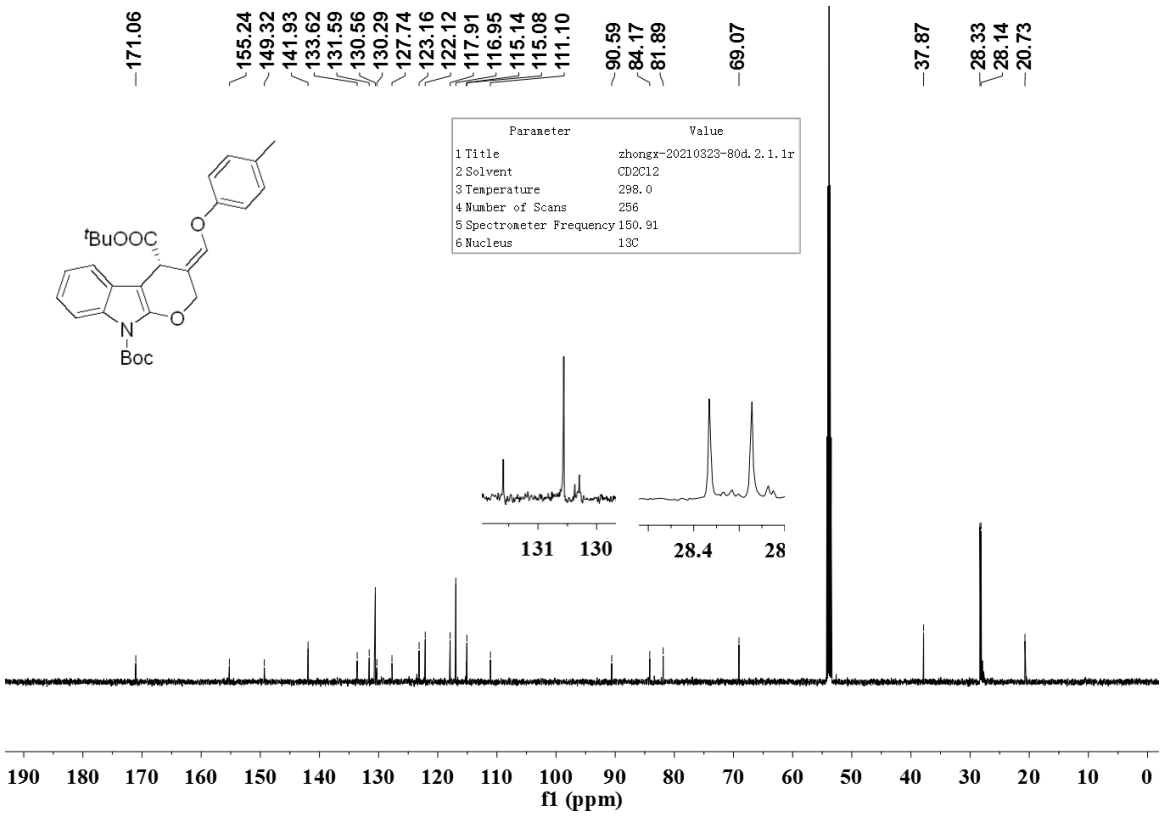


^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **7aa** in $CDCl_3$

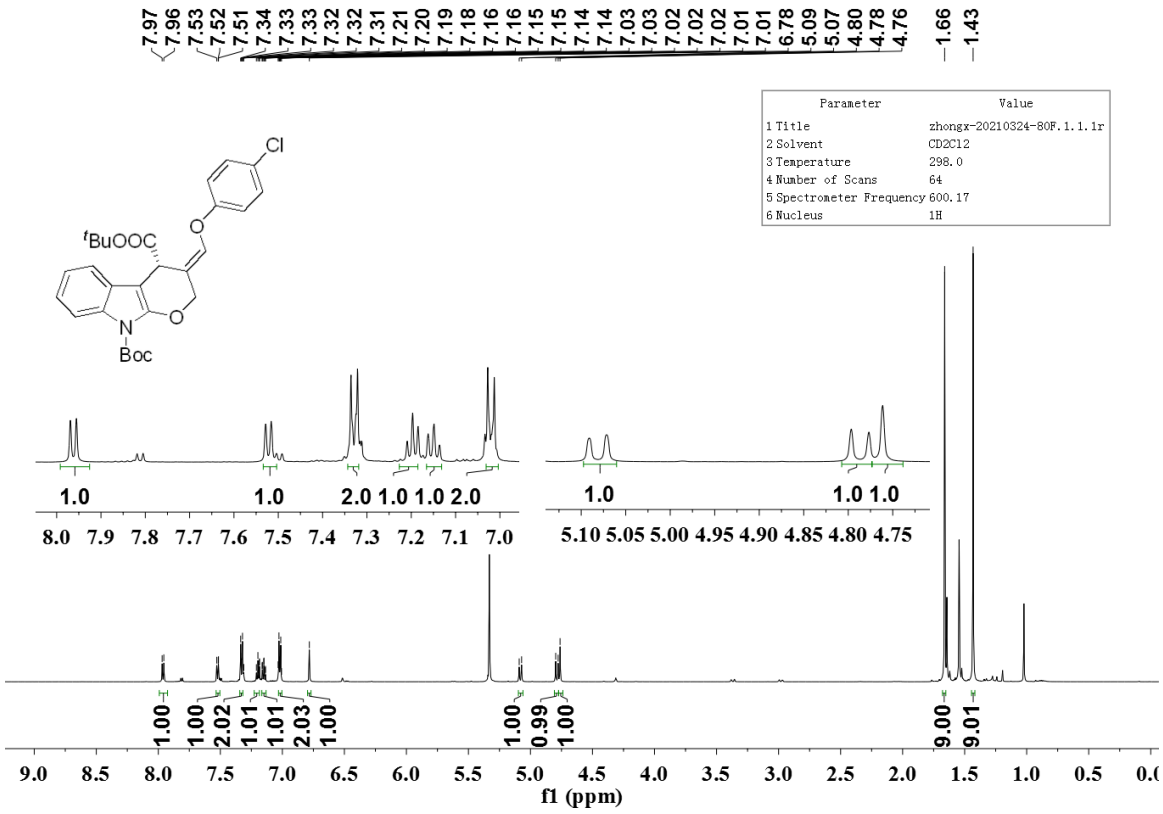


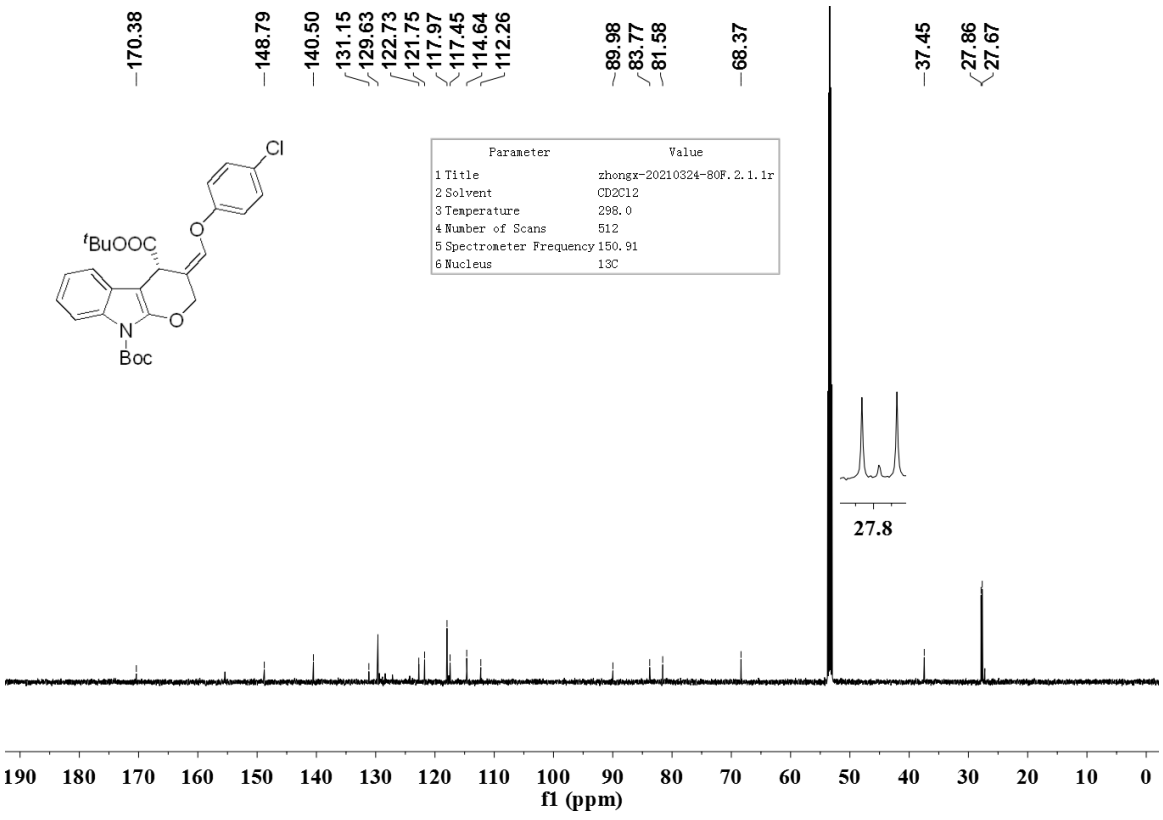
^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of compound **7ab** in CD_2Cl_2



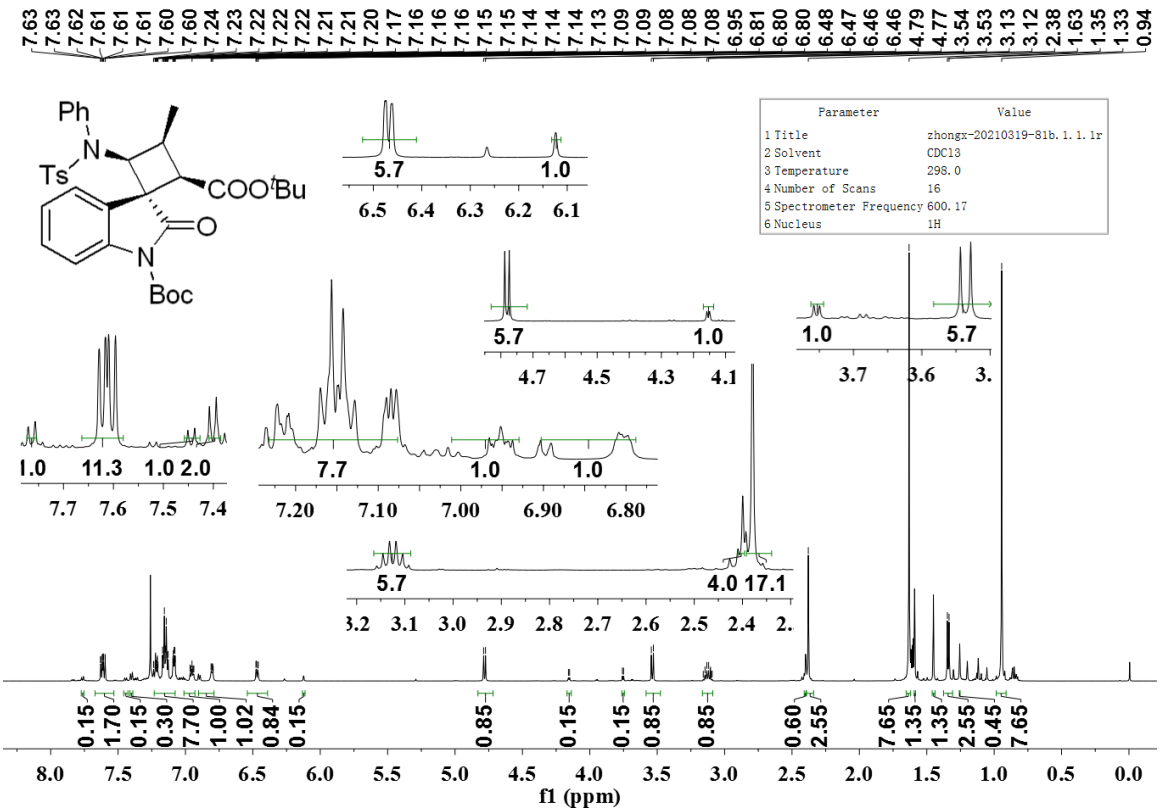


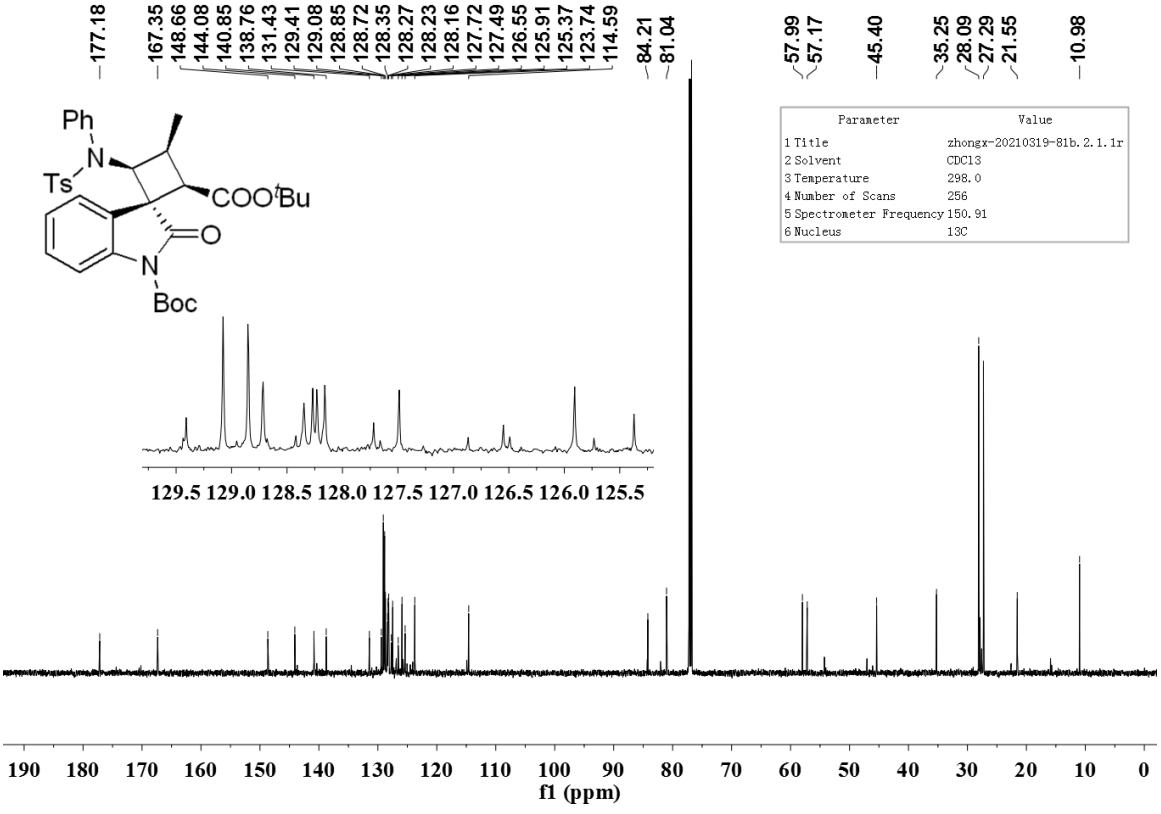
^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of compound **7ac** in CD_2Cl_2



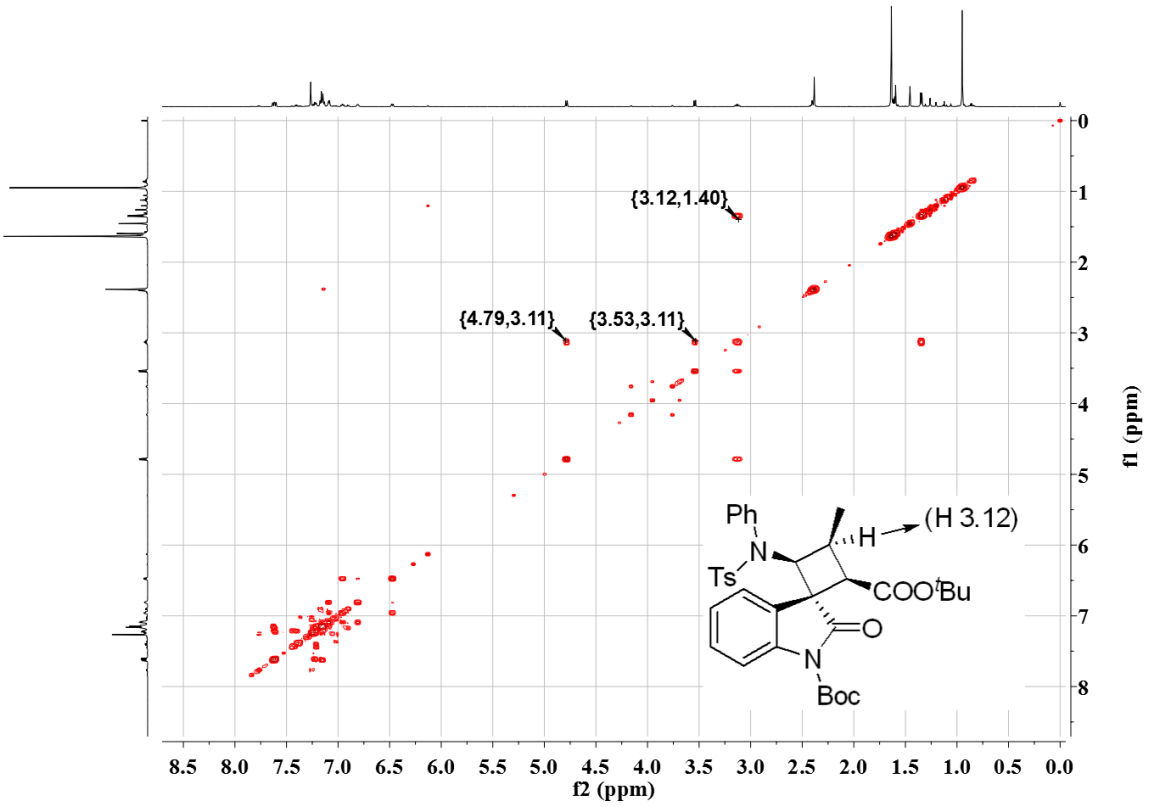


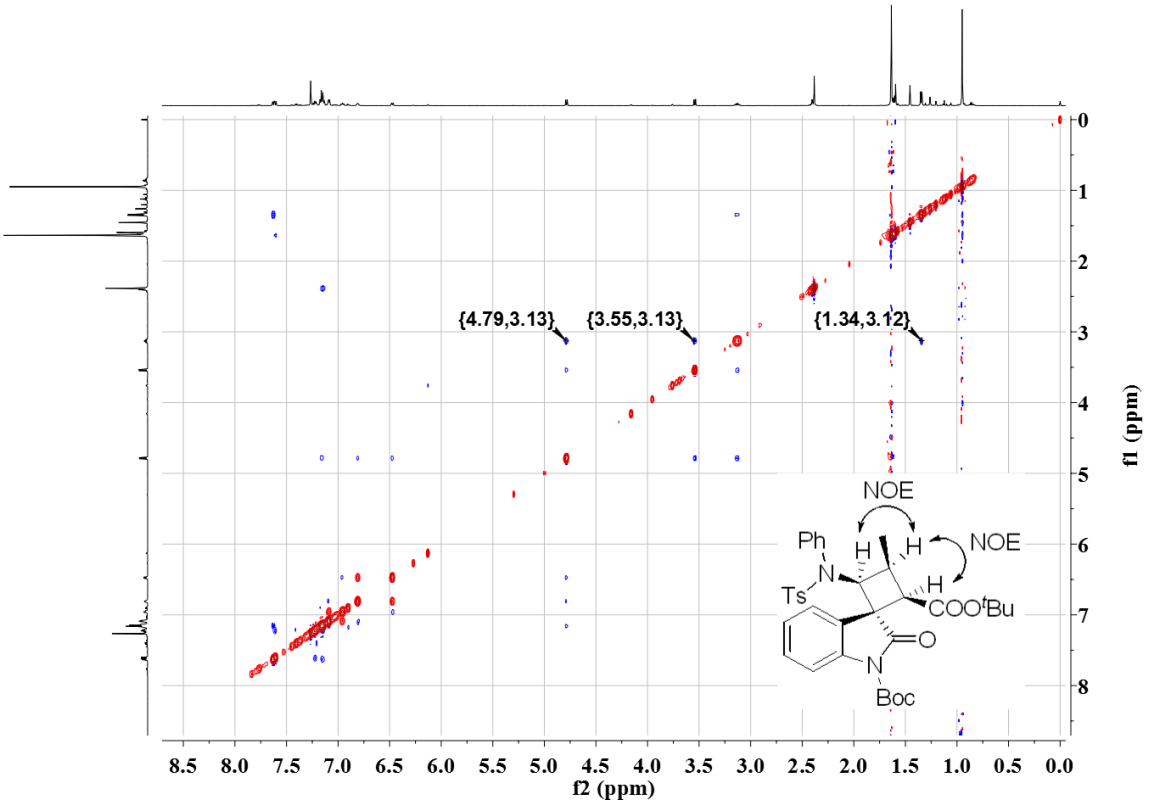
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **8** in $CDCl_3$



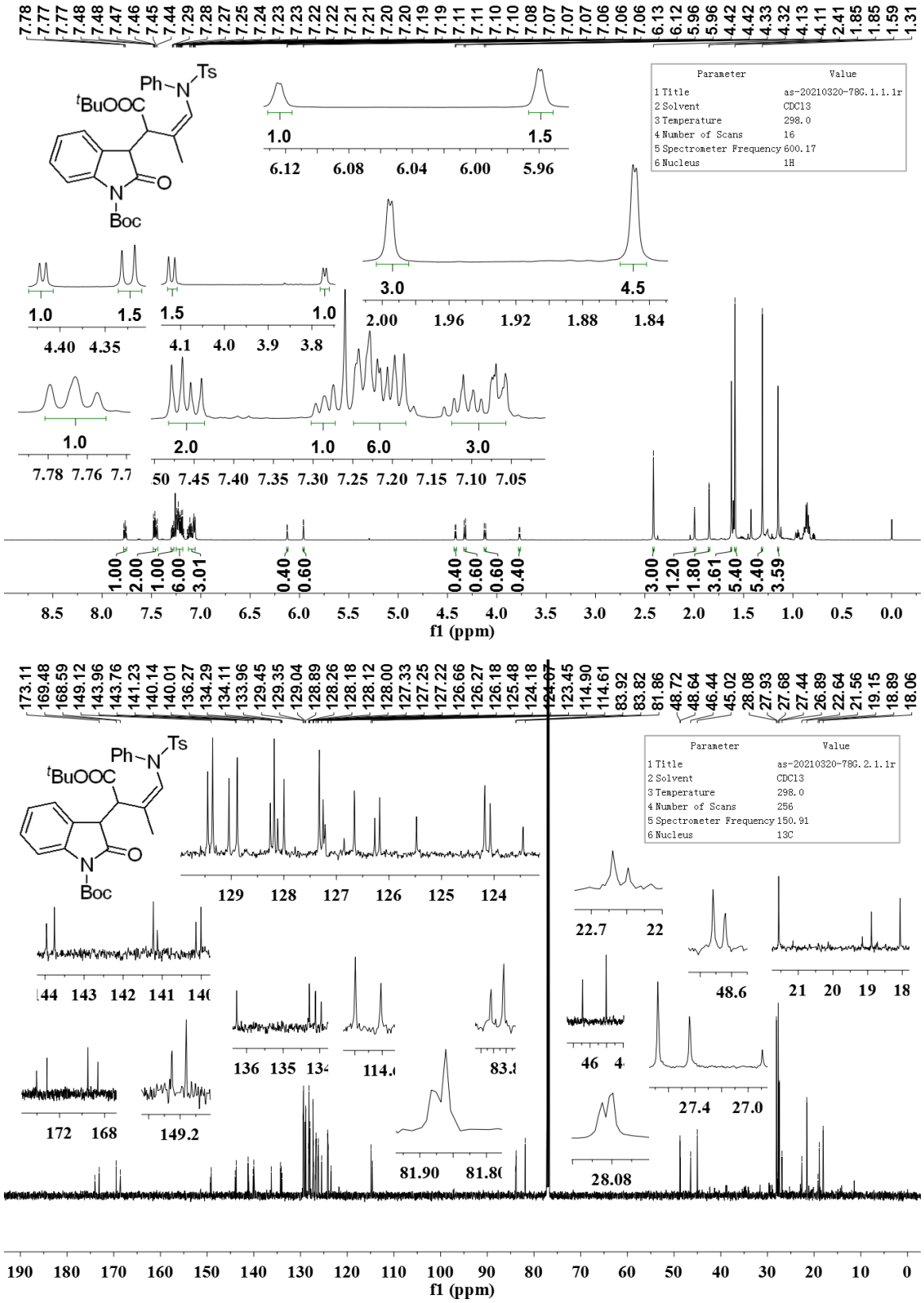


COSY and NOESY NMR spectra of compound **8** in $CDCl_3$

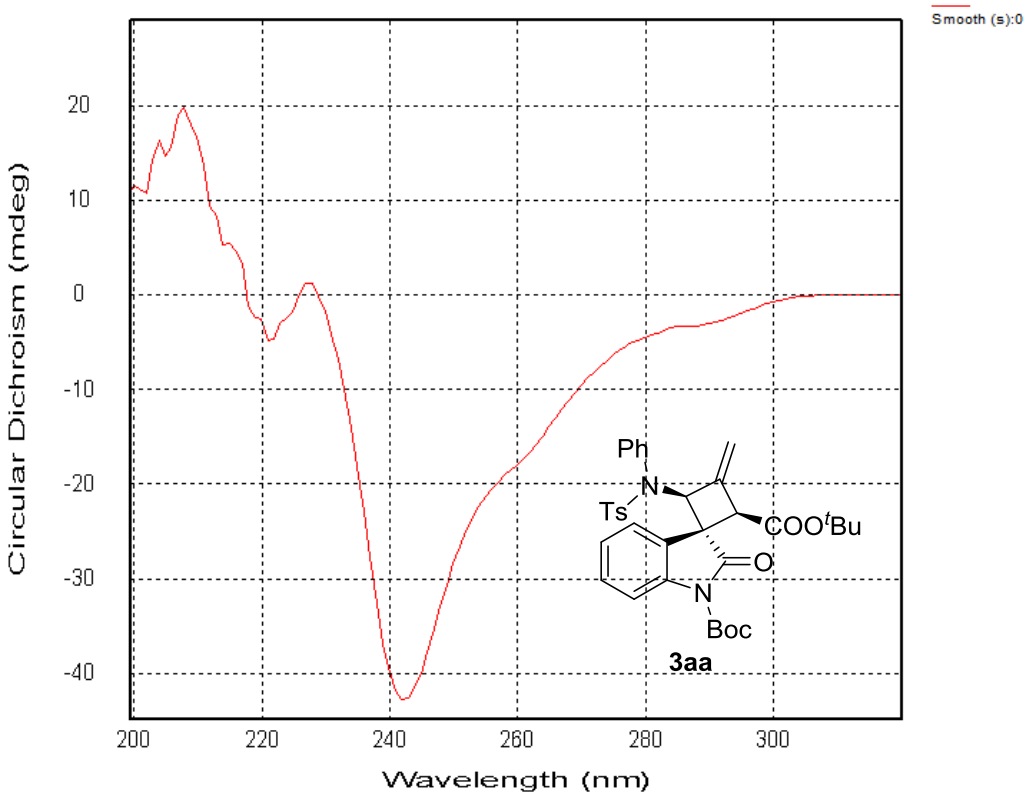


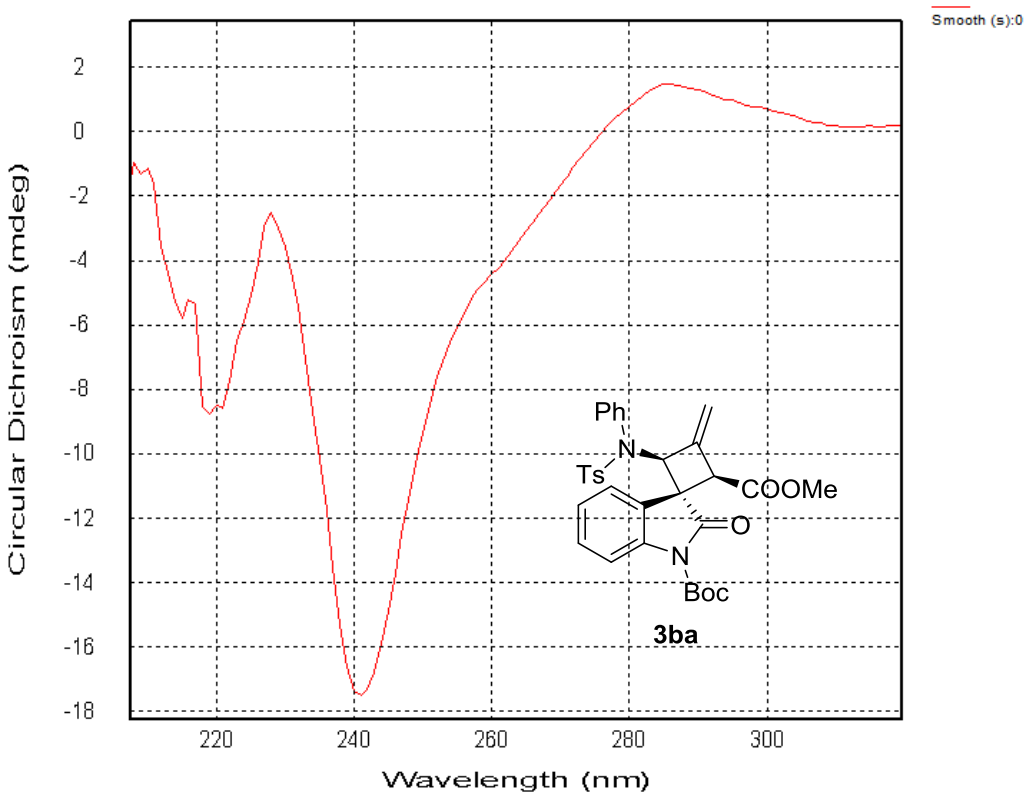


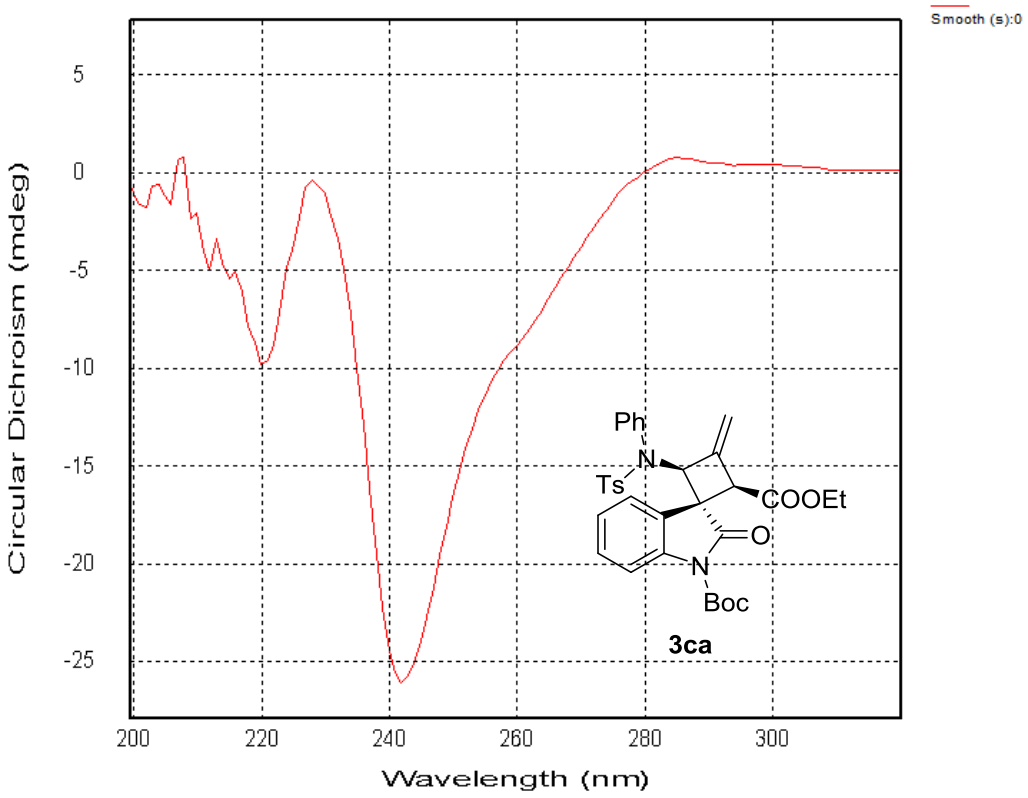
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **9** in $CDCl_3$



(J) Copies of CD Spectra in CH_2Cl_2



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300
Wavelength (nm)
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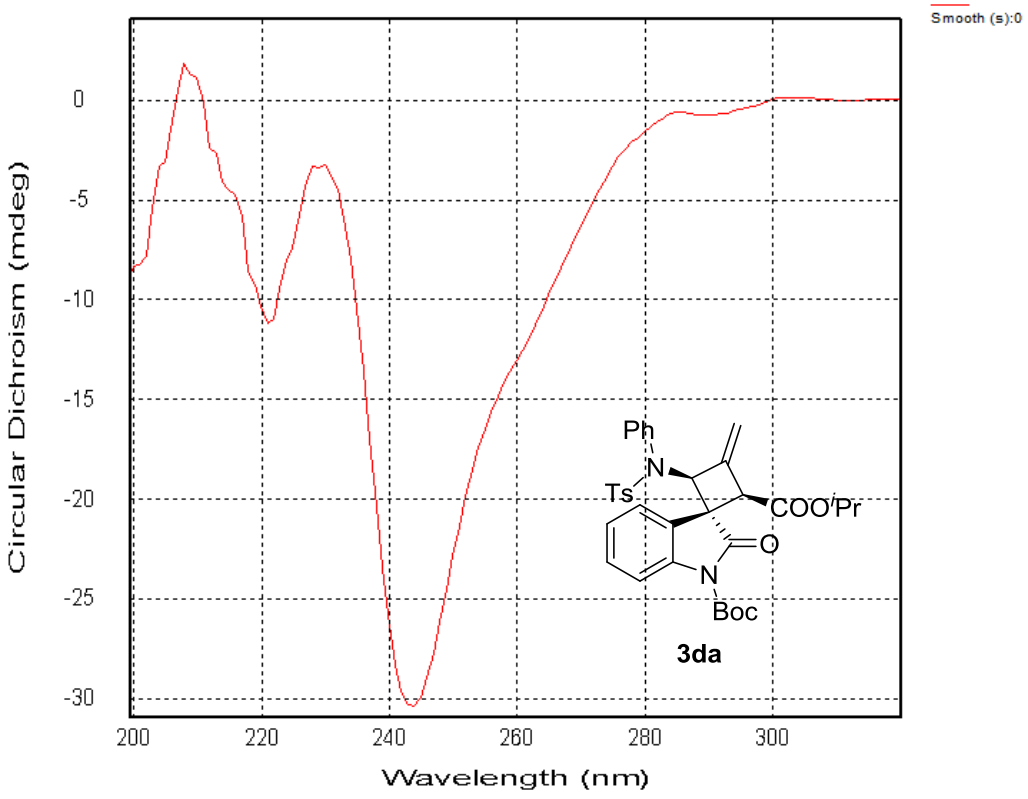
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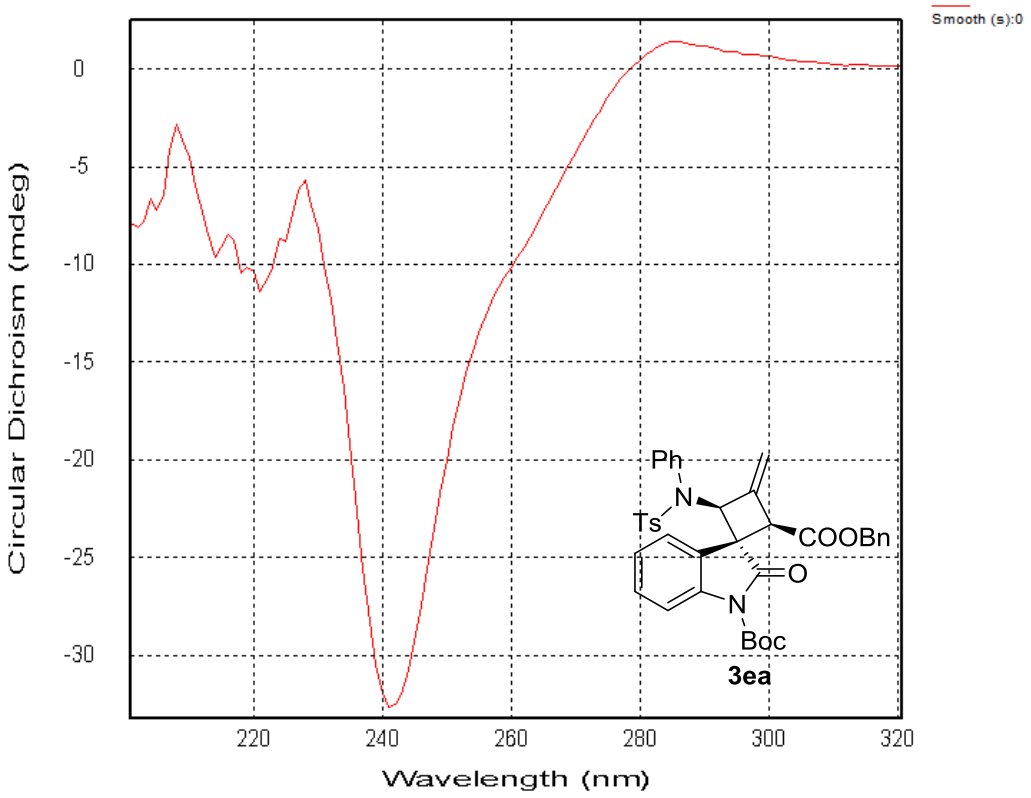
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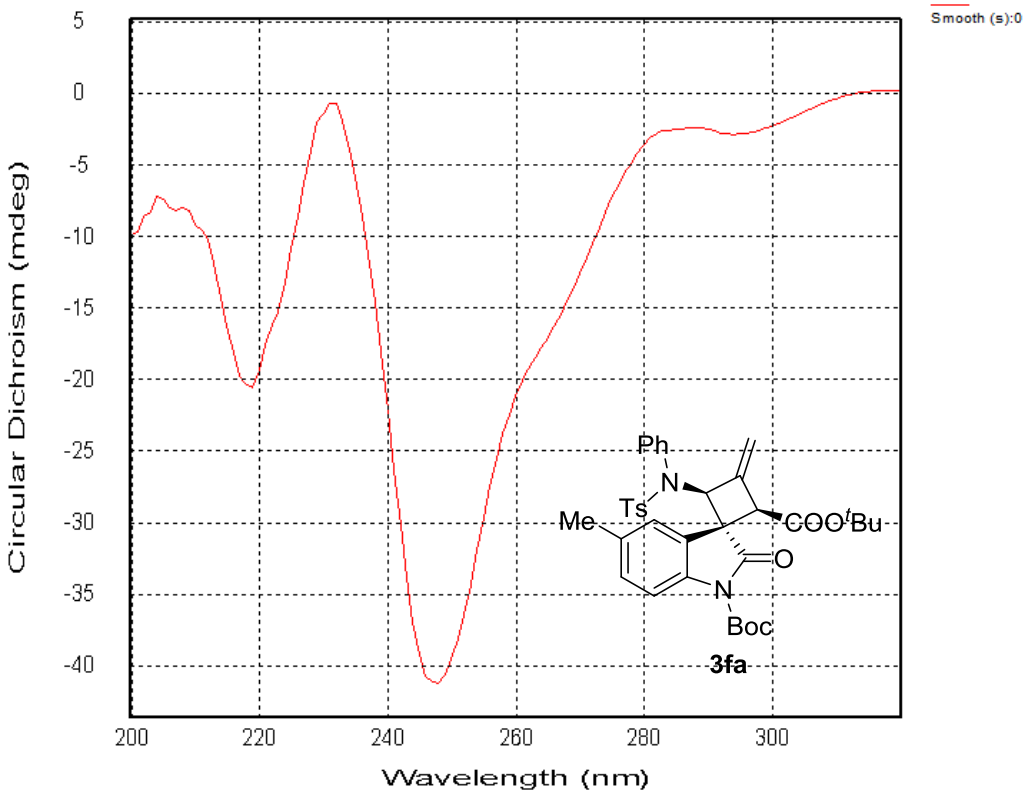
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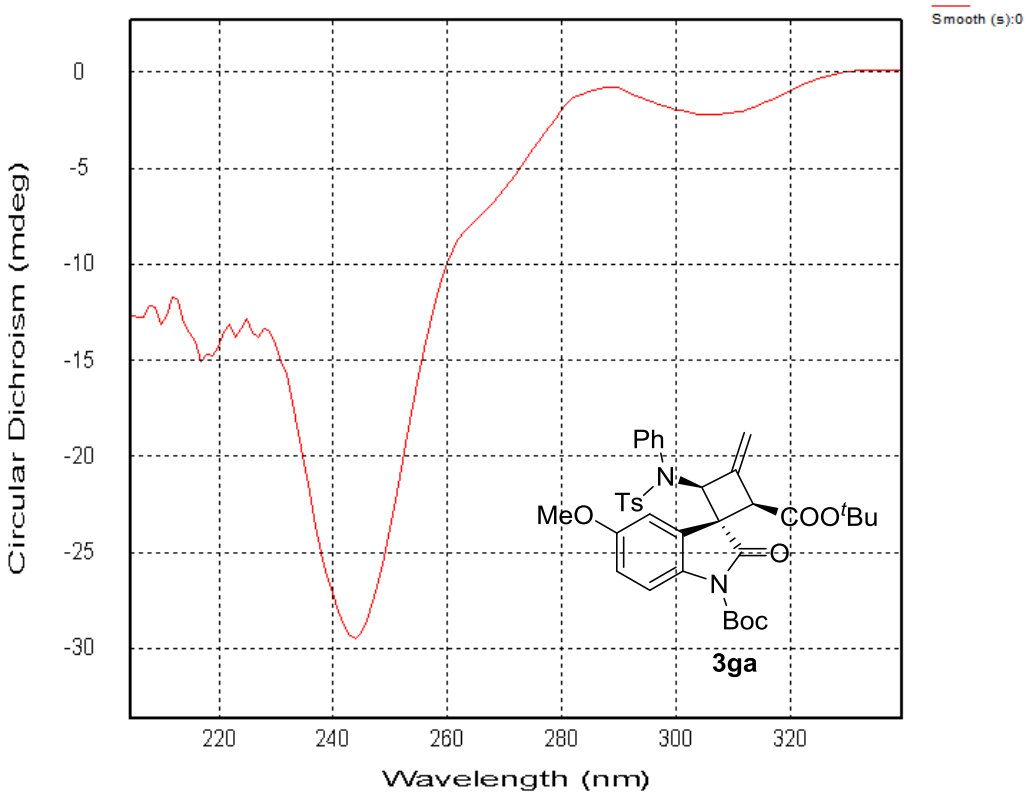
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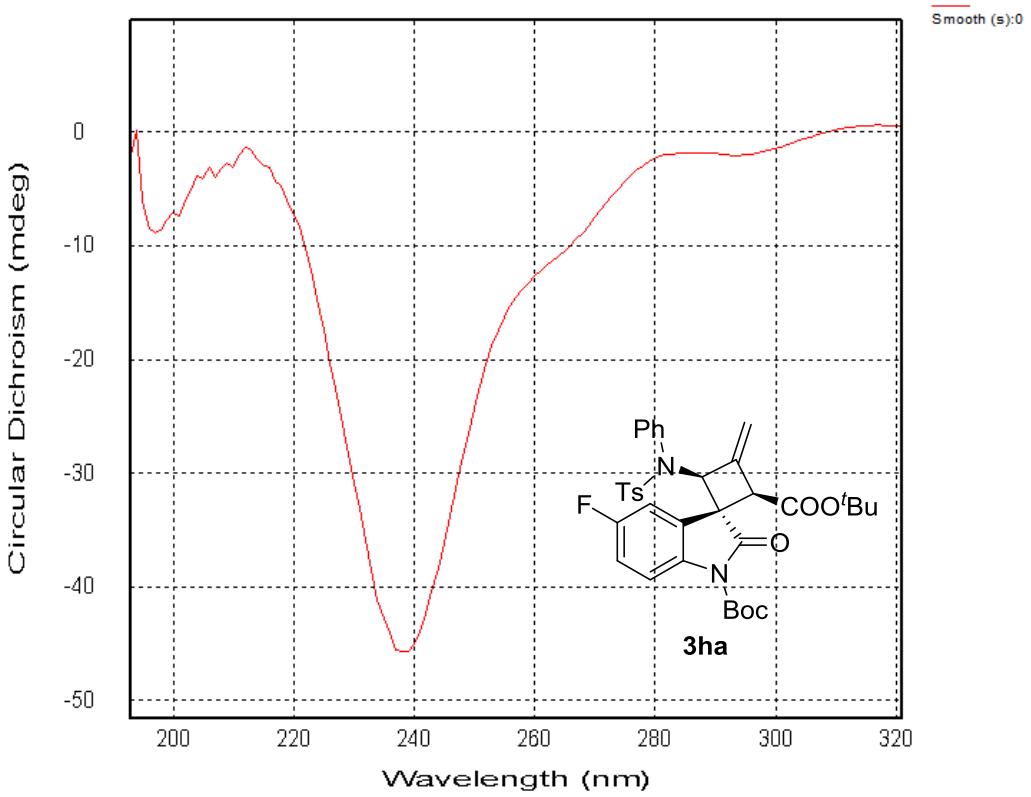
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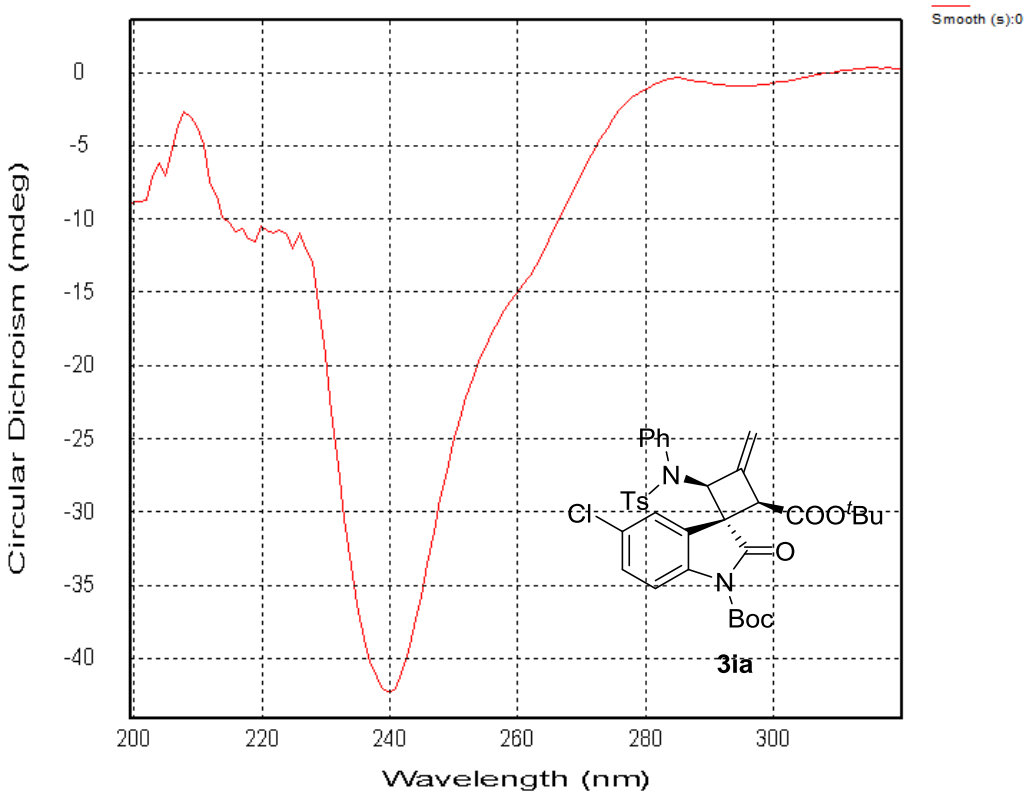
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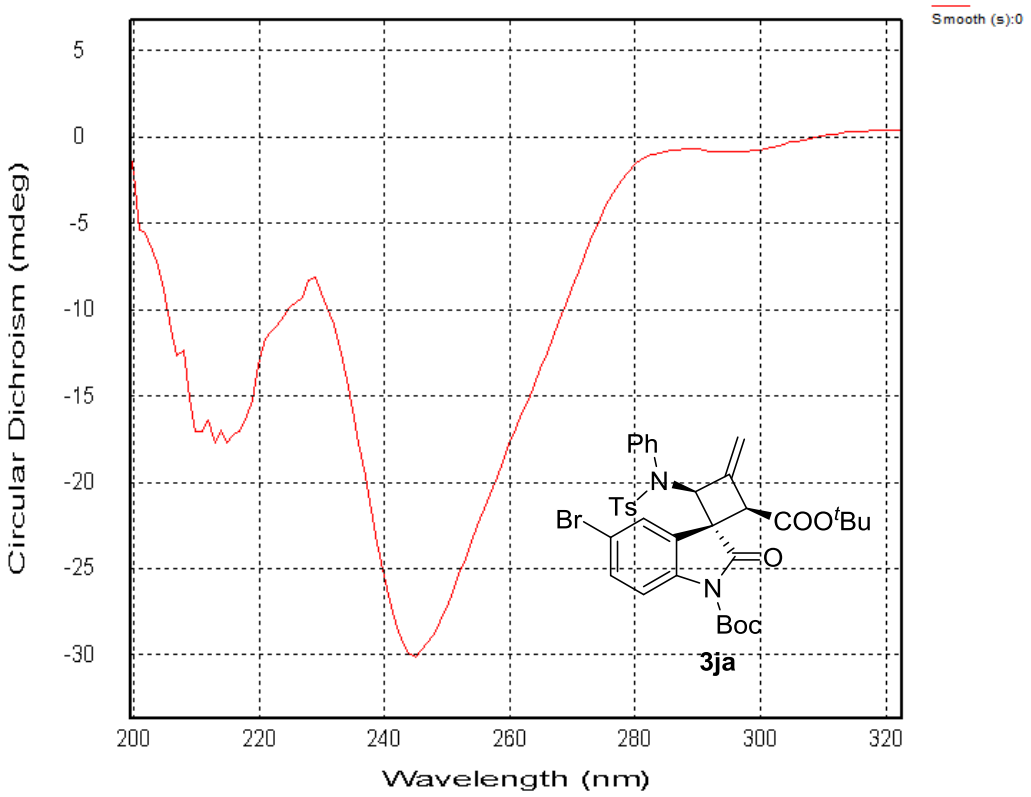
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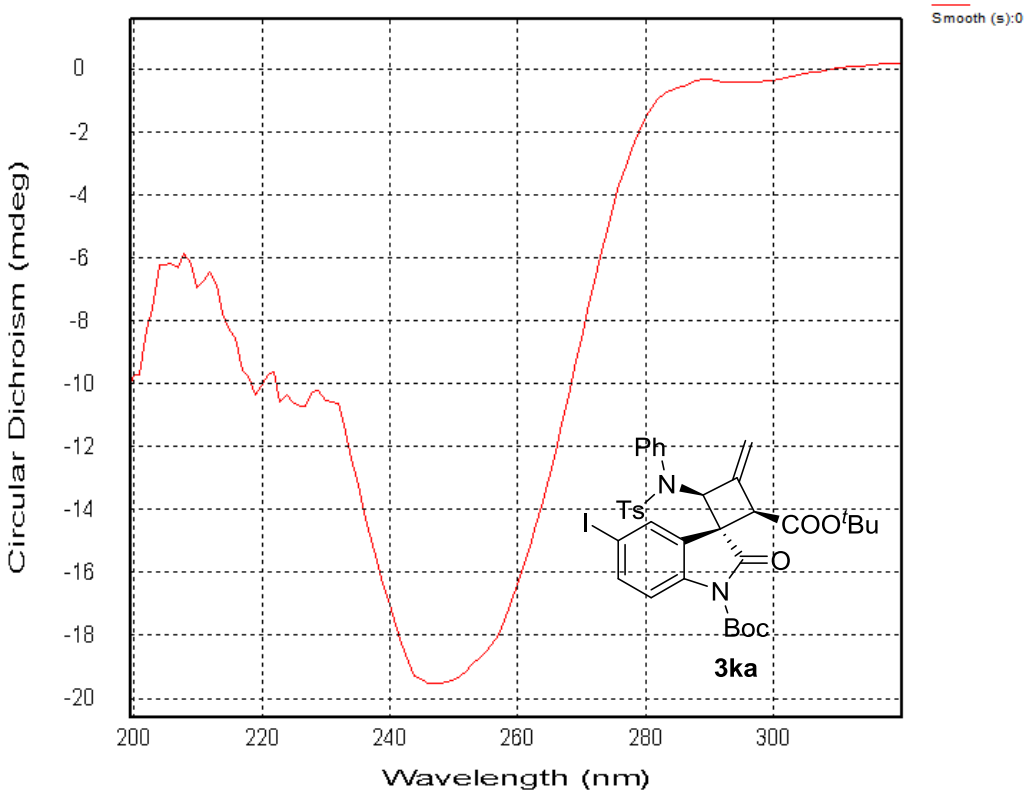
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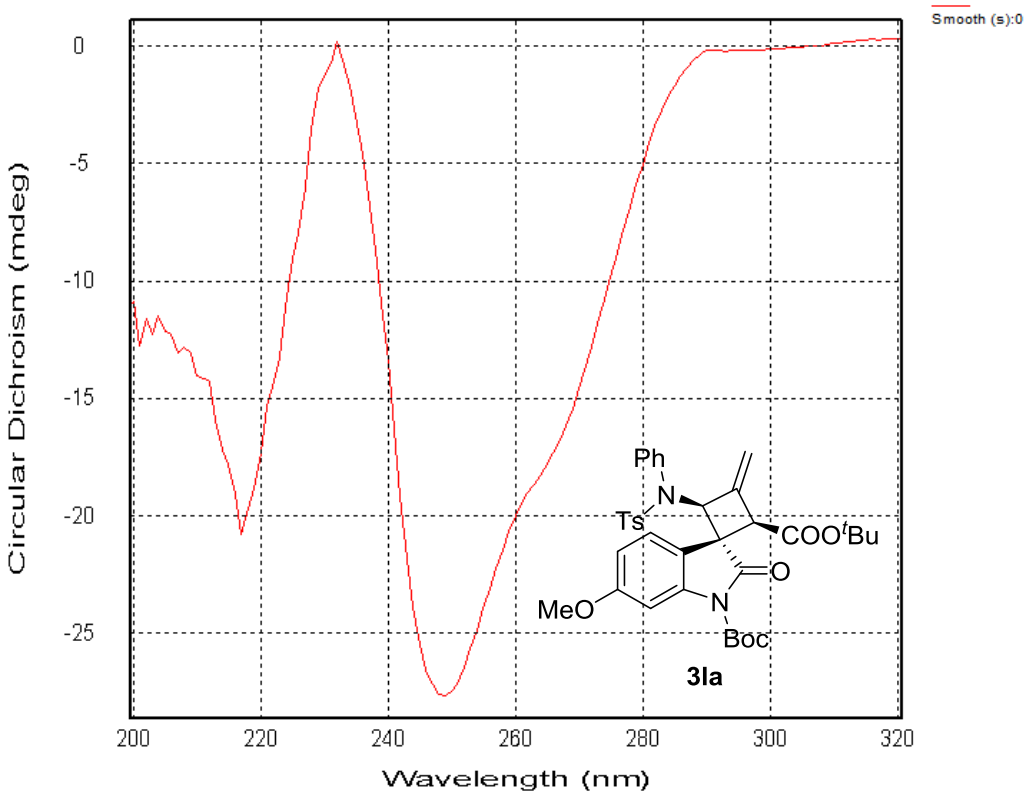
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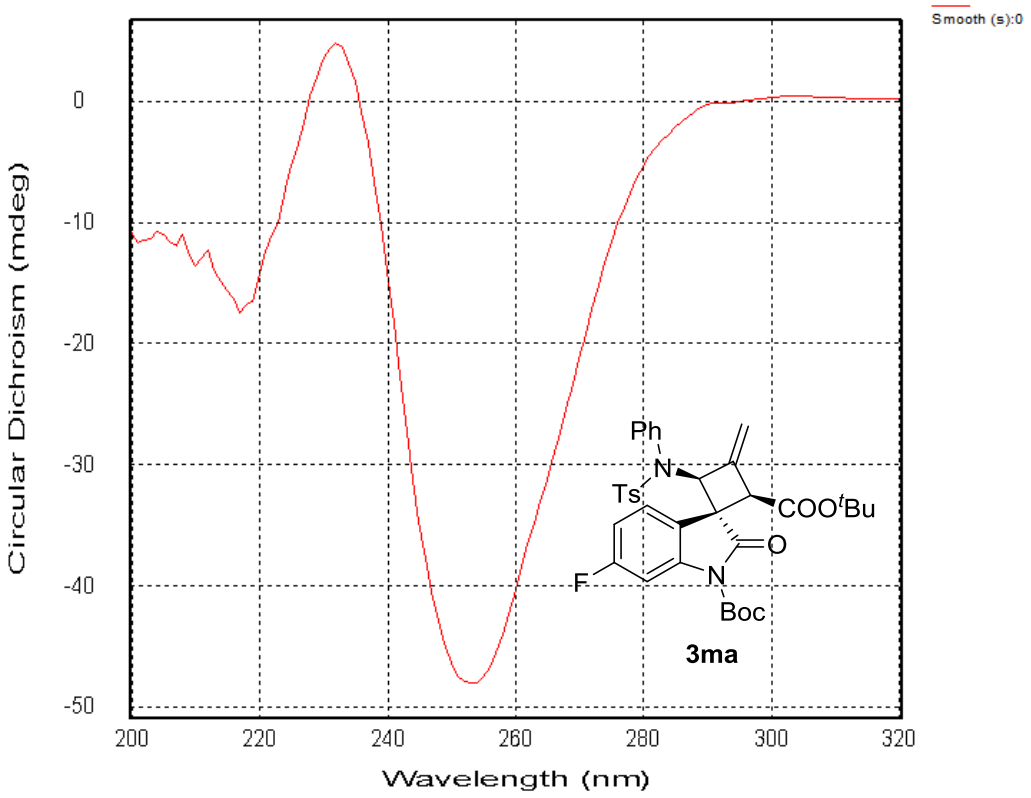
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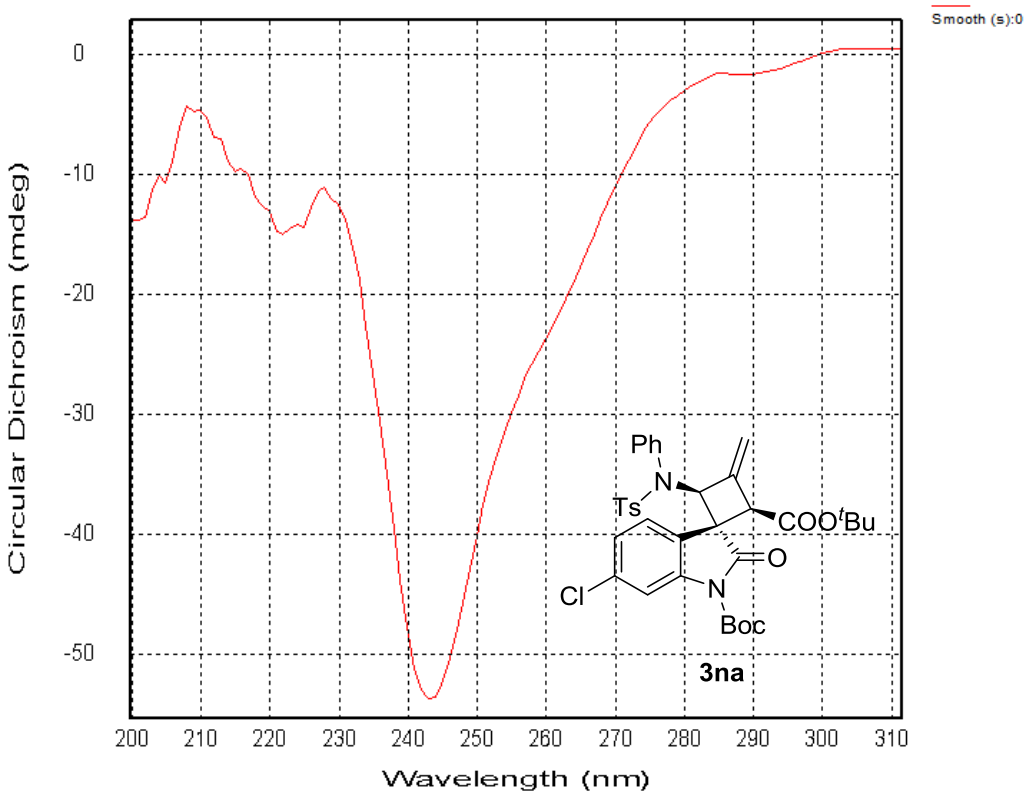
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Wavelength (nm)
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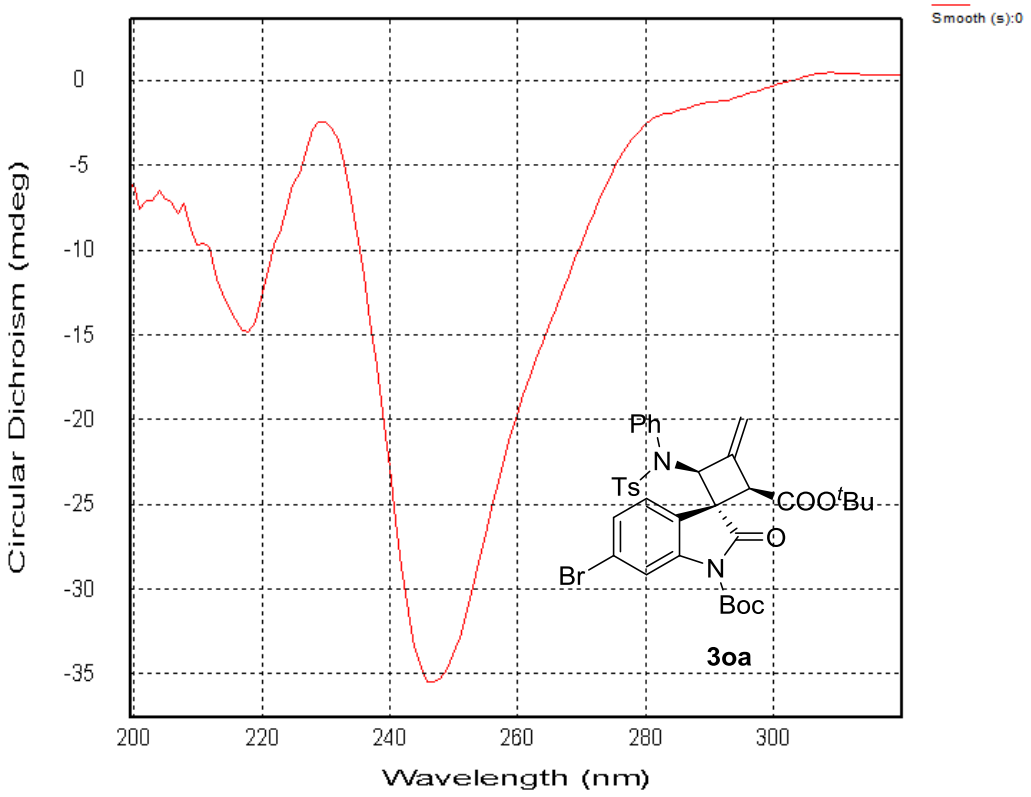
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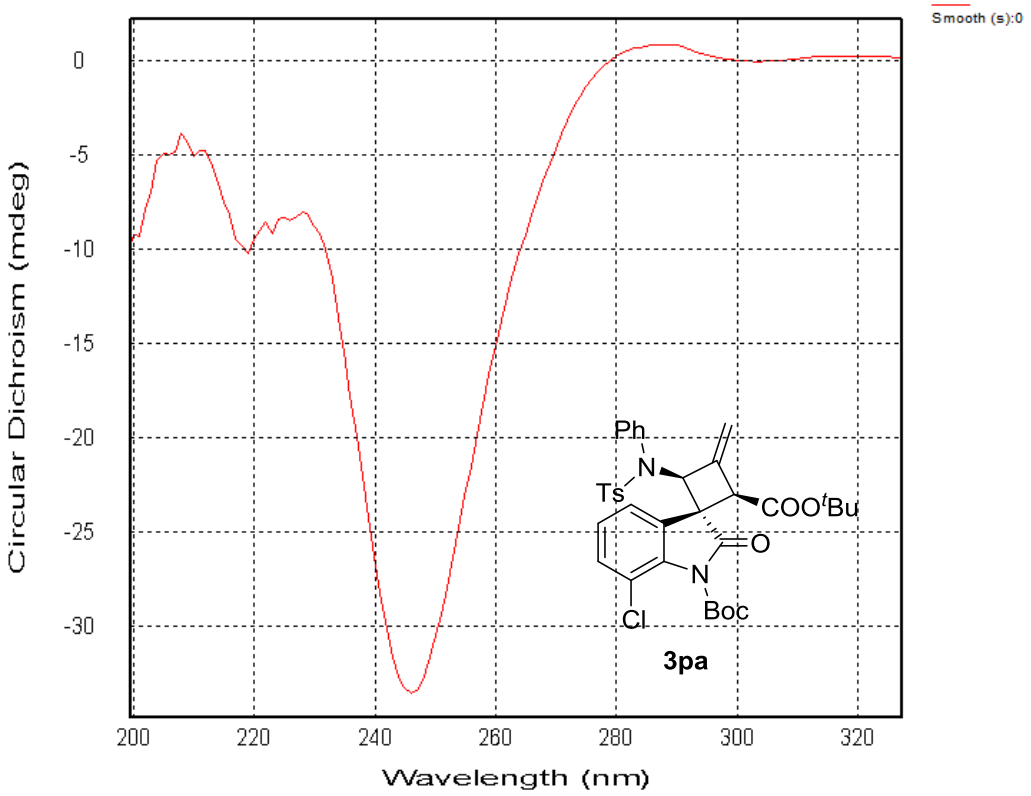
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Cl
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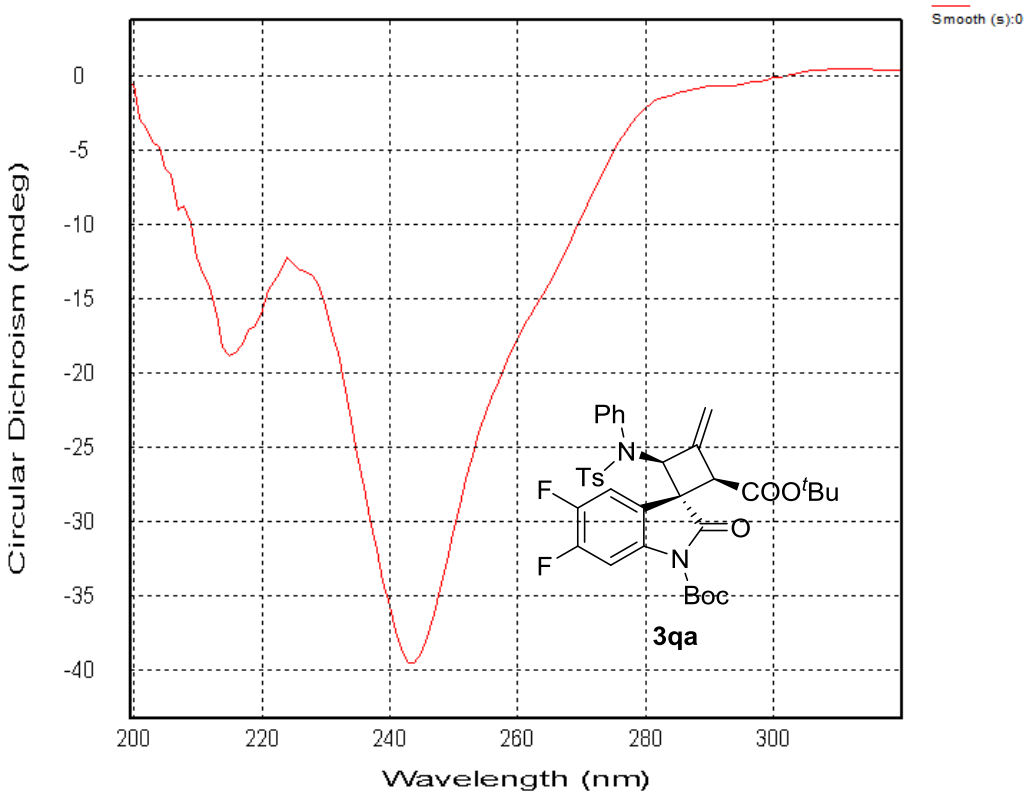
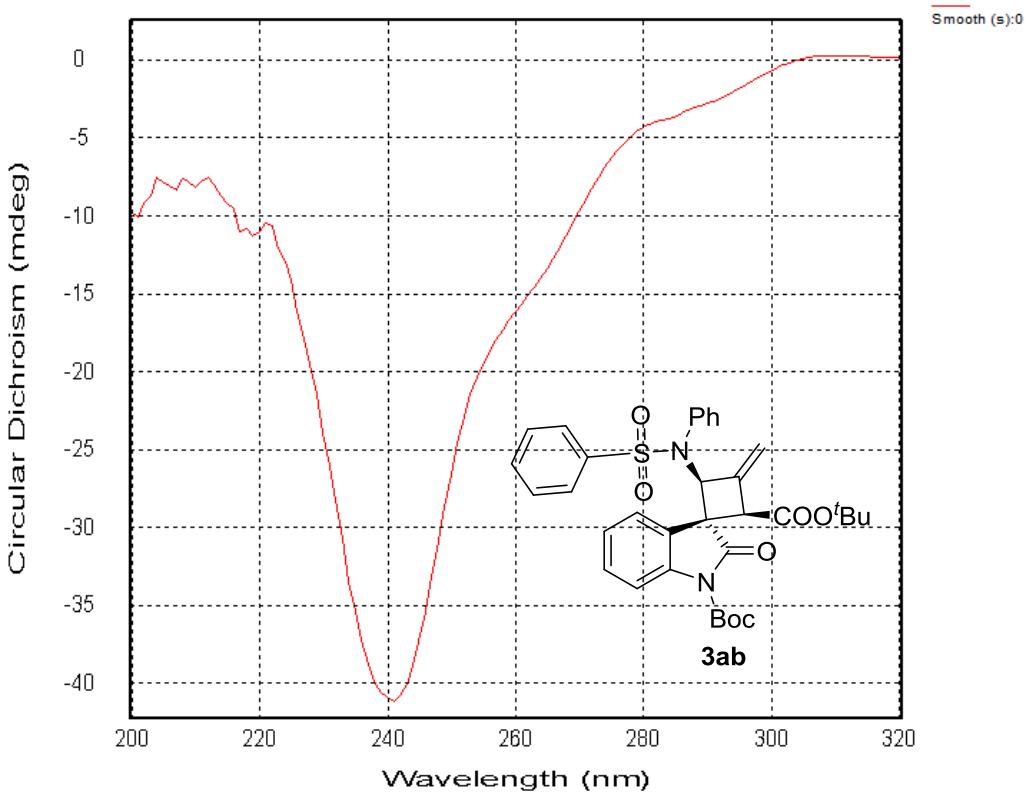
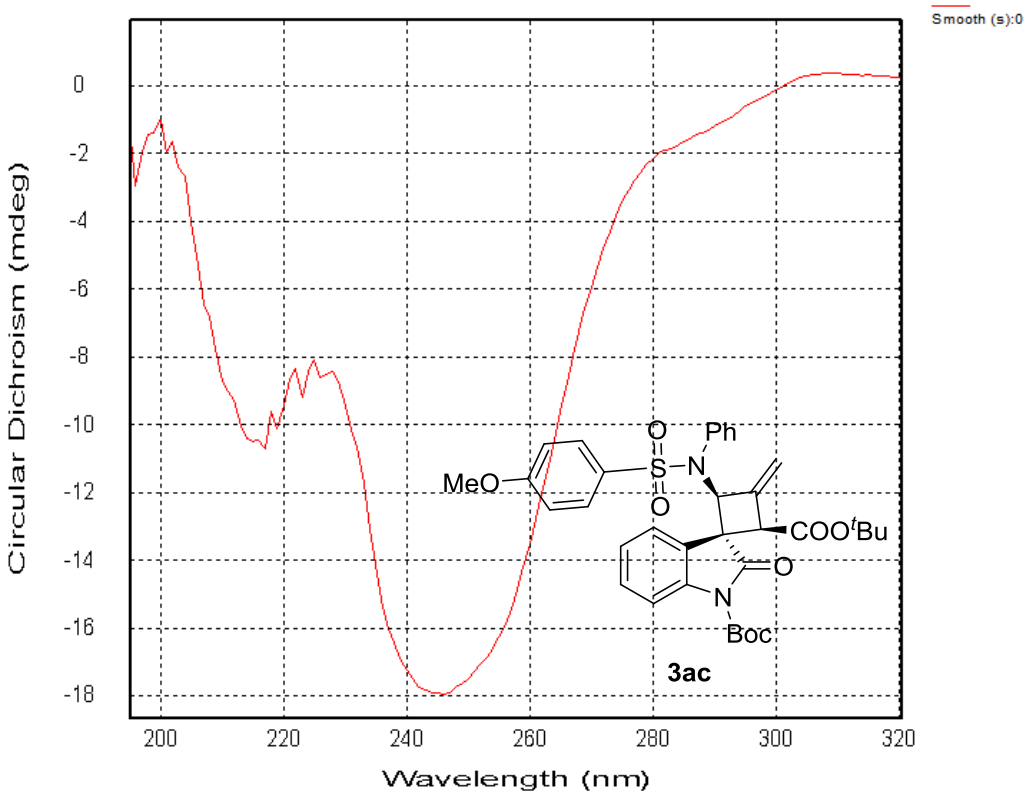
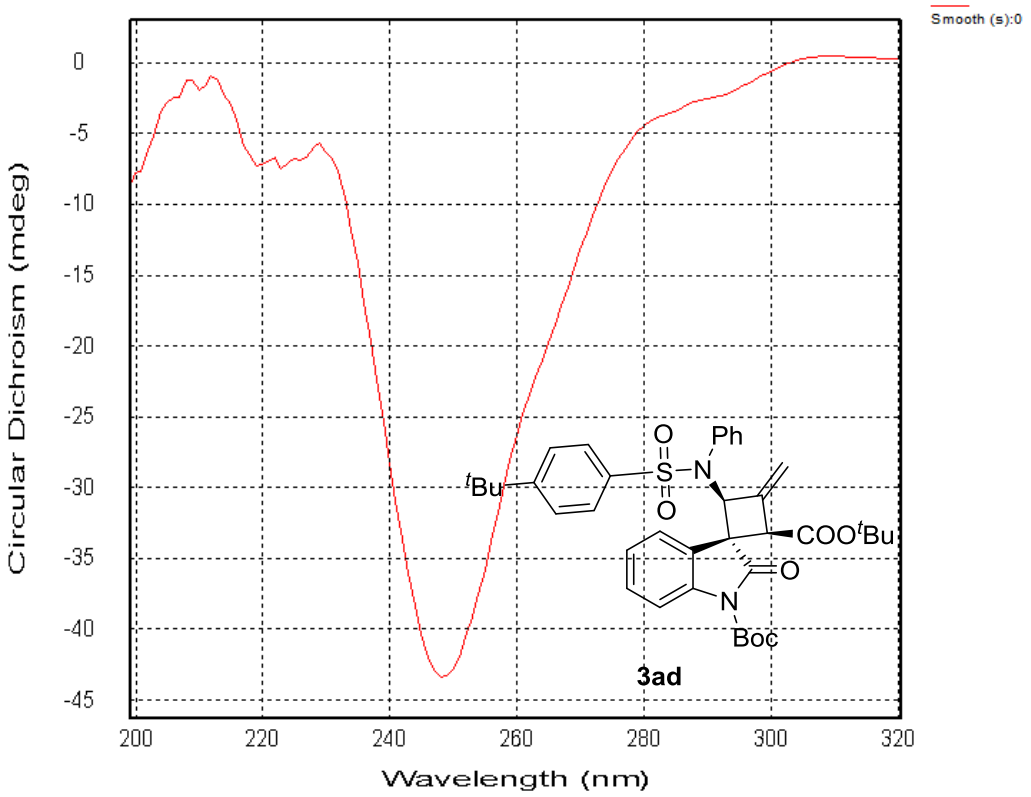
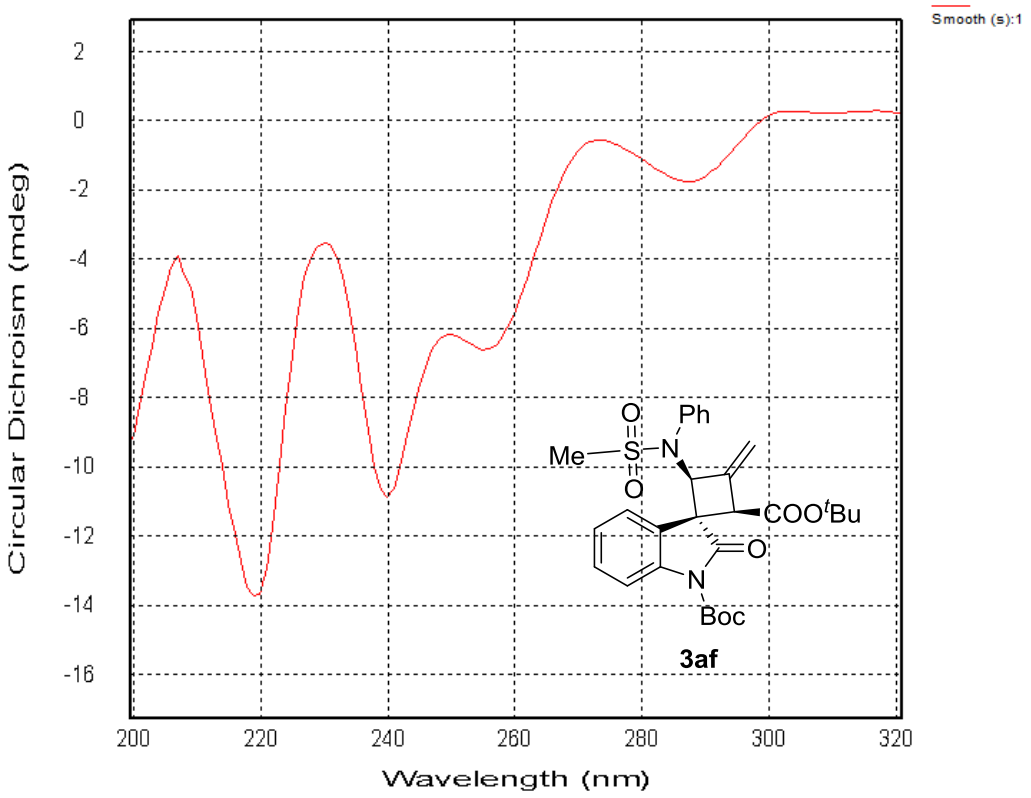
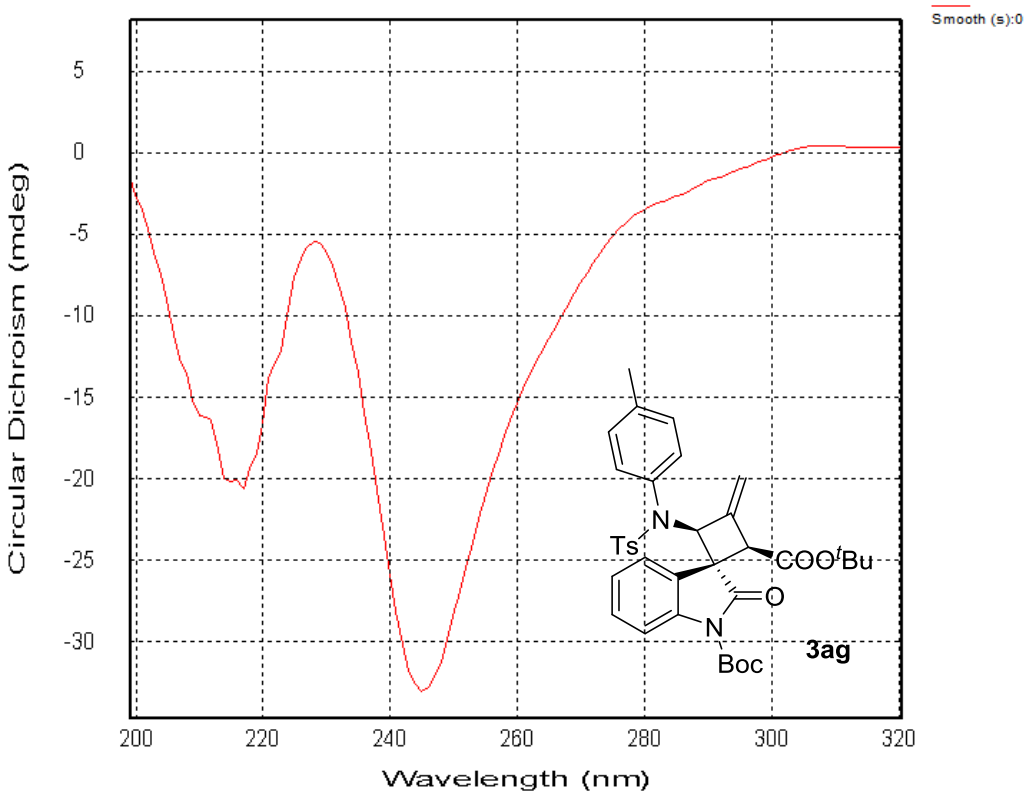

Smooth (s):0
Circular Dichroism (mdeg)
0
-5
-10
-15
-20
-25
-30
-35
-40
200
220
240
260
280
300
Wavelength (nm)
Ph
N
Ts
F
F
COO^{t}Bu
O
N
Boc
3qa


Smooth (s):0
Circular Dichroism (mdeg)
0
-5
-10
-15
-20
-25
-30
-35
-40
200
220
240
260
280
300
320
Wavelength (nm)
O
Ph
S
N
O
COO^{t}Bu
O
N
Boc
3ab


Smooth (s):0
Circular Dichroism (mdeg)
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
200
220
240
260
280
300
320
Wavelength (nm)
MeO
O
S
O
N
Ph
COO^{t}Bu
O
N
Boc
3ac


Smooth (s):0
Circular Dichroism (mdeg)
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
200
220
240
260
280
300
320
Wavelength (nm)
^{t}Bu
O
S
O
N
Ph
COO^{t}Bu
O
N
Boc
3ad


Smooth (s):1
Circular Dichroism (mdeg)
2
0
-2
-4
-6
-8
-10
-12
-14
-16
200
220
240
260
280
300
320
Wavelength (nm)
O
Ph
Me
S
N
O
COO^{t}Bu
O
N
Boc
3af


Smooth (s):0
Circular Dichroism (mdeg)
5
0
-5
-10
-15
-20
-25
-30
200
220
240
260
280
300
320
Wavelength (nm)
N
Ts
COO^{t}Bu
O
N
Boc
3ag