Supporting Information

Asymmetric Catalytic Diverse Ring Opening/Cycloadditions of Cyclobutenones with (*E*)-Alkenyloxindoles and (*E*)-Dioxopyrrolidines

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Abstract: Highly enantioselective ring-opening/cycloaddition reactions of cyclobutenones were achieved by employing chiral *N,N'*-dioxide/metal complexes as the catalysts. The Diels–Alder type cycloaddition with (*E*)-alkenyloxindoles yielded spirocyclohexaneoxindoles with excellent results. Meanwhile, a hetero-Diels–Alder process occurred with (*E*)-dioxopyrrolidines to afford spiropyrrolidinone-dihydropyranone derivatives.

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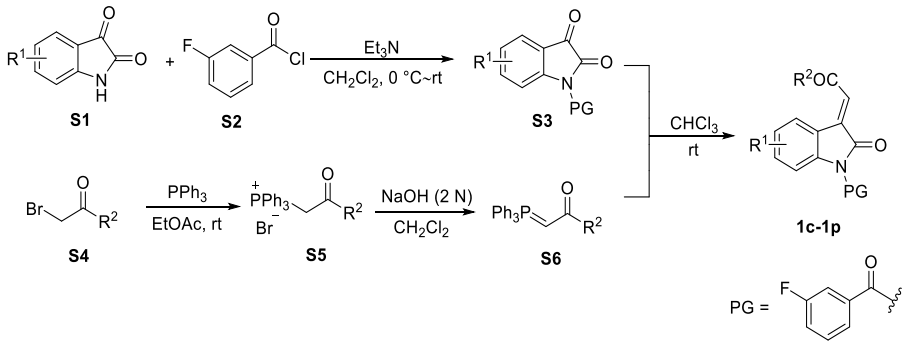
1 General remarks

^{1}H NMR (400M) spectra were recorded on bruker ASCEND™ 400M. Chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet), coupling constants (Hz), integration. ^{13}C{^{1}H} NMR data were collected on bruker ASCEND™ 400M (101M) with complete proton decoupling. Chemical shifts were reported in ppm relative to tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.16). ^{19}F{^{1}H} NMR spectra were collected on bruker ASCEND™ 400M (376 MHz) with complete proton decoupling. Enantiomeric excesses were determined by chiral HPLC analysis on Daicel Chiralcel IA, IB, ID at 23 °C with UV detector at 254 nm in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]_D^{25}$ (λ = 589 nm, *c*: g/100 mL, in CH_2Cl_2). HRMS was recorded on Thermo Q-Exactive Focus (FTMS+c ESI). IR was detected by Bruker Tensor II spectrometer with Plantium ATR accessory. All the solvents were purified by usual methods before use. Silica gel for thin-layer chromatography (HG/T2354-92) made in Qingdao Haiyang Chemical Co., Ltd. Chiral *N*,*N*′-dioxide ligands were prepared according to previously reported method.[1] (*E*)-Alkenyloxindoles and cyclobutenones were synthesized according to known procedures and purified by recrystallization prior to use.[2]

2 General procedures for the preparation of (*E*)-alkenyloxindoles



Procedure for the preparation of 1c:

To a solution of isatin **S1** (2.94 g, 20 mmol) in CH_2Cl_2 (50 mL) was added Et_3N (4.05 g, 40 mmol) at 0 °C, after stirring for 30 min at room temperature, benzoyl chloride **S2** (3.37 g, 24 mmol) was added, then stirred overnight. The CH_2Cl_2 was removed under reduced pressure, the crude product of **S3** was directly subjected into the next step without further purification.

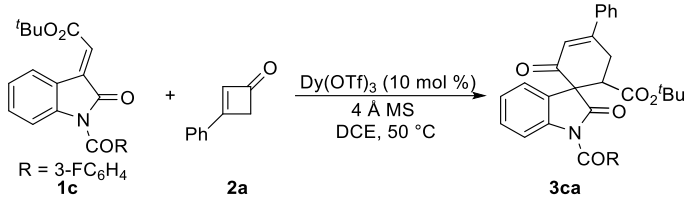
To a solution of triphenylphosphine (26.23 g, 100 mmol) in ethyl acetate (100 mL) was added ethyl bromoacetate **S4** (16.70 g, 100 mmol) at room temperature, and the mixture was stirred overnight. The resulting mixture was filtered (solvent: ethyl acetate), the crude product **S5** (white solid) was directly subjected to the next reaction without further purification. To a solution of **S5** in CH_2Cl_2 (50 mL) was added the NaOH (2 N) solution at room temperature until the PH value was 12. And the reaction mixture was stirred for another 30 minutes. Then, washed with saturated $NaHCO_3$ solution, the aqueous layer was extracted with CH_2Cl_2, the combined organic mixtures were washed with brine, dried over anhydrous Na_2SO_4, filtered (solvent: CH_2Cl_2), and concentrated under reduced pressure. The obtained product **S6** (white solid, 31.67 g, 91 mmol, two steps 91% yield) was used directly for the next step.

To a solution of crude product **S3** in $CHCl_3$ (50 mL) was added **S6** (3.76 g, 10 mmol) at room temperature. After stirring for 30 minutes, the solvent was removed under reduced pressure, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 9/1, v/v), the following recrystallization (CH_2Cl_2/PE = 5/1, v/v) was carried out to afford the product **1c** (ca. 2.20 g, 30% yield) as a yellow solid.

Other (*E*)-alkenyloxindoles **1d–1p** and **1a–1b** were prepared according to the procedure described for **1c**.

3 General procedures for the preparation of products

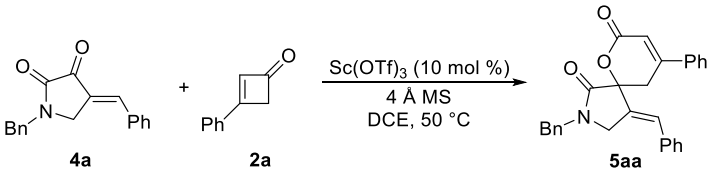
3.1 General procedure for the preparation of racemic products 3



An oven-dried test tube was charged with metal salt $Dy(OTf)_3$ (10 mol %), **1c** (0.10 mmol), **2a** (0.15 mmol), 4 Å MS (80 mg), DCE (0.5 mL) under N_2 atmosphere. The resulted solution was stirred at 50 °C in an oil bath for 48 h. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20/1 and 9/1, v/v) to afford the corresponding racemic product **3ca**.

Other racemic products **3** were prepared according to the procedure described for **3ca**.

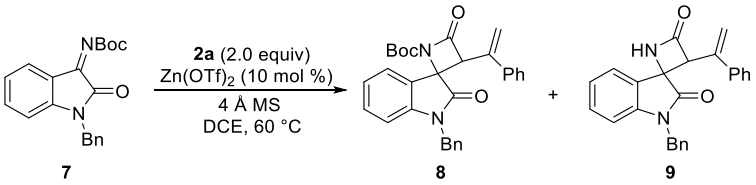
3.2 General procedure for the preparation of racemic products 5



An oven-dried test tube was charged with metal salt $Sc(OTf)_3$ (10 mol %), **4a** (0.10 mmol), **2a** (0.15 mmol), 4 Å MS (80 mg), DCE (0.5 mL) under N_2 atmosphere. The resulted solution was stirred at 50 °C in an oil bath for 72 h. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (4/1 and 2/1, v/v) to afford the desired racemic product **5aa**.

Other racemic products **5** were prepared according to the procedure described for **5aa**.

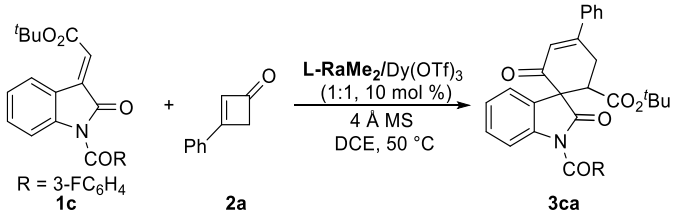
3.3 General procedure for the preparation of racemic products 8 and 9



An oven-dried test tube was charged with metal salt $Zn(OTf)_2$ (10 mol %), **7** (0.10 mmol), **2a** (0.20 mmol), 4 Å MS (30 mg), DCE (1.0 mL) under N_2 atmosphere. The resulted solution was stirred at 60 °C in an oil bath for 24 h. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20/1 and 2/1, v/v) to afford the expected racemic products **8** and **9**.

4 General procedures for the catalytic reactions

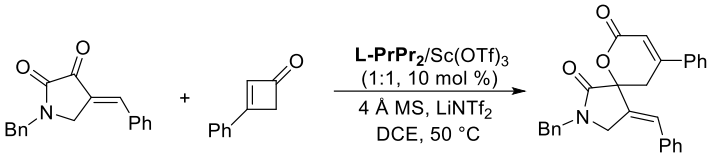
4.1 General procedure for the preparation of products 3



An oven-dried test tube was charged with catalyst **L-RaMe$_2$**/$Dy(OTf)_3$ (1:1, 10 mol %), **1c** (0.10 mmol), **2a** (0.15 mmol), 4 Å MS (80 mg), DCE (0.5 mL) under N_2 atmosphere. The resulted solution was stirred at 50 °C in an oil bath for 48 h. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20/1 and 9/1, v/v) to afford the corresponding product **3ca**.

Other products **3** were prepared according to the procedure described for **3ca**.

4.2 General procedure for the preparation of products 5

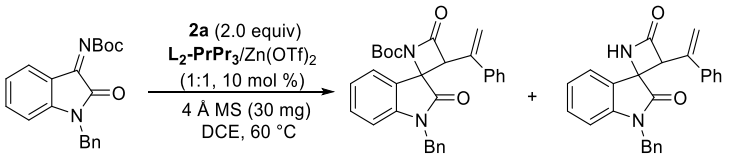


4a **2a** **5aa**

An oven-dried test tube was charged with catalyst **L-PrPr$_2$**/Sc(OTf)$_3$ (1:1, 10 mol %), LiNTf$_2$ (30 mol %), **4a** (0.10 mmol), **2a** (0.15 mmol), 4 Å MS (80 mg), DCE (0.5 mL) under N_2 atmosphere. The resulted solution was stirred at 50 °C in an oil bath for 72 h. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (4/1 and 2/1, v/v) to afford the desired product **5aa**.

Other products **5** were prepared according to the procedure described for **5aa**.

4.3 General procedure for the preparation of products 8 and 9



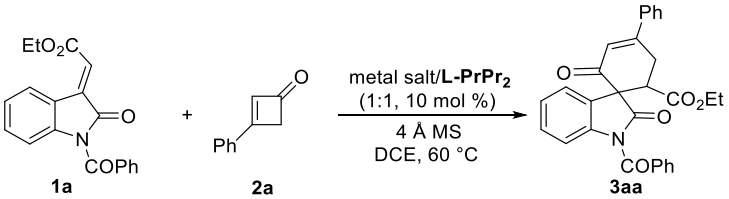
7 **8** **9**

An oven-dried test tube was charged with catalyst **L$_2$-PrPr$_3$**/Zn(OTf)$_2$ (1:1, 10 mol %), **7** (0.10 mmol), **2a** (0.20 mmol), 4 Å MS (30 mg), DCE (1.0 mL) under N_2 atmosphere. The resulted solution was stirred at 60 °C in an oil bath for 24 h and 36 h. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20/1 and 2/1, v/v) to afford the expected products **8** and **9**.

5 Optimization of the reaction conditions

5.1 Optimization of the reaction conditions of [4+2] cycloaddition between cyclobutenones with (*E*)-alkenyloxindoles

Table S1. Screening of metal salts.



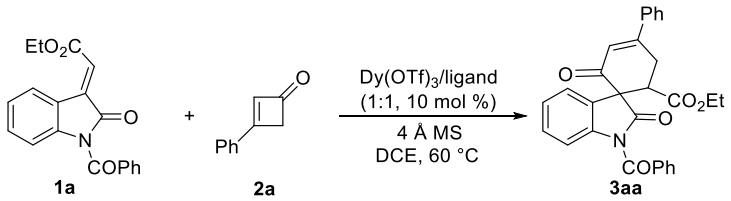
1a **2a** **3aa**

entry[a]	metal salts	ligand	yield[b] (%)	ee[c] (%)	dr[d]
1	Mg(OTf)$_2$	**L-PrPr$_2$**	35	race	>19:1
2	Sc(OTf)$_3$	**L-PrPr$_2$**	32	race	84:16
3	Cu(OTf)$_2$	**L-PrPr$_2$**	32	race	19:1
4	Y(OTf)$_3$	**L-PrPr$_2$**	48	−31	84:16
5	In(OTf)$_3$	**L-PrPr$_2$**	32	race	>19:1
6	Nd(OTf)$_3$	**L-PrPr$_2$**	55	−30	84:16
7	Eu(OTf)$_3$	**L-PrPr$_2$**	56	−33	89:11

8	$Gd(OTf)_3$	**L-PrPr$_2$**	47	–33	84:16
9	$Tb(OTf)_3$	**L-PrPr$_2$**	68	–25	87:13
10	$Dy(OTf)_3$	**L-PrPr$_2$**	55	–39	85:15
11	$Ho(OTf)_3$	**L-PrPr$_2$**	73	–17	91:9
12	$Er(OTf)_3$	**L-PrPr$_2$**	51	–25	87:13
13	$Tm(OTf)_3$	**L-PrPr$_2$**	63	–21	85:15
14	$Yb(OTf)_3$	**L-PrPr$_2$**	62	–28	83:17
15	$Lu(OTf)_3$	**L-PrPr$_2$**	26	–17	92:8

[a]The reactions were performed with **1a** (0.10 mmol), **2a** (0.10 mmol), 4 Å MS (50 mg) and metal salt/**L-PrPr$_2$** (1:1, 10 mol %) in DCE (0.1 M) at 60 °C for 16 h. [b]Yield of the isolated product. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Determined by ^{1}H NMR analysis.

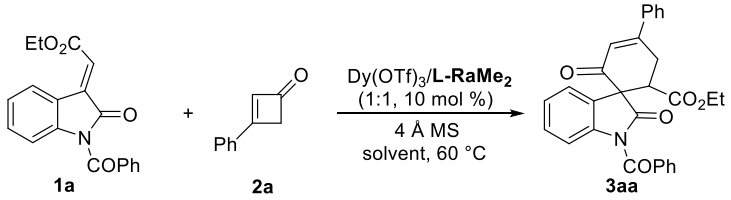
Table S2. Screening of the ligands.



entry[a]	ligand	yield[b] (%)	ee[c] (%)	dr[d]
1	**L-PrPr$_2$**	55	–39	85:15
2	**L-PiPr$_2$**	50	–34	>19:1
3	**L-RaPr$_2$**	32	–48	92:8
4	**L-RaEt$_2$**	56	61	>19:1
5	**L-RaMe$_2$**	59	72	94:6
6	**L-RaPh**	76	race	92:8
7	**L-RaMe$_3$**	56	62	91:9
8	**L$_2$-RaMe$_2$**	50	43	>19:1
9	**L-RaPr$_3$**	30	–34	84:16
10	**L-Ra^{t}Bu**	45	6	88:12
11	**L-RaAd**	60	–16	94:6

[a]The reactions were performed with **1a** (0.10 mmol), **2a** (0.10 mmol), 4 Å MS (50 mg) and $Dy(OTf)_3$/ligand (1:1, 10 mol %) in DCE (0.1 M) at 60 °C for 16 h. [b]Yield of the isolated product. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Determined by ^{1}H NMR analysis.

Table S3. Screening of the solvents.

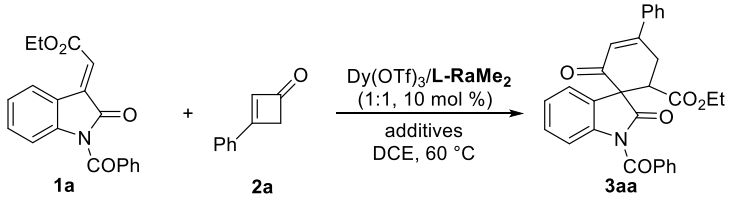


entry[a]	solvent	yield[b] (%)	ee[c] (%)	dr[d]
1	DCE	59	72	94:6
2	EtOAc	n.d.[e]	11	19:1
3	Toluene	n.d.[e]	17	92:8

4	THF	n.d.[e]	59	>19:1
5	MeCN	n.d.[e]	–31	91:9
6	$CHCl_3$	n.d.[e]	53	94:6
7	CCl_2HCClH_2	8	44	>19:1
8	CCl_2HCCl_2H	28	30	86:14

[a]The reactions were performed with **1a** (0.10 mmol), **2a** (0.10 mmol), 4 Å MS (50 mg) and $Dy(OTf)_3$/**L-RaMe$_2$** (1:1, 10 mol %) in solvent (0.1 M) at 60 °C for 16 h. [b]Yield of the isolated product. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Determined by ^{1}H NMR analysis. [e]Not determined.

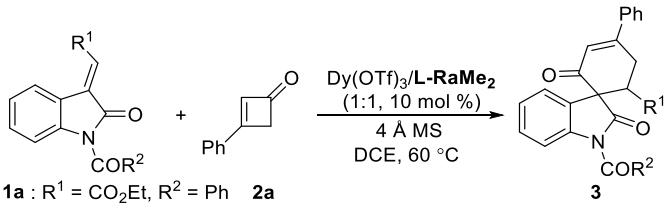
Table S4. Screening of the additives.



entry[a]	additives	yield[b] (%)	ee[c] (%)	dr[d]
1	4 Å MS (50 mg)	59	72	94:6
2	3 Å MS (50 mg)	57	64	90:10
3	5 Å MS (50 mg)	52	68	93:7
4	4 Å MS (40 mg)	49	73	93:7
5	4 Å MS (60 mg)	52	70	94:6
6	4 Å MS (80 mg)	64	73	94:6
7	4 Å MS (100 mg)	66	68	92:8
8	4 Å MS (80 mg), $LiNTf_2$ (10 mol %)	66	72	19:1
9	4 Å MS (80 mg), $NaBAr^F$ (10 mol %)	65	65	93:7

[a]The reactions were performed with **1a** (0.10 mmol), **2a** (0.10 mmol), additives and $Dy(OTf)_3$/**L-RaMe$_2$** (1:1, 10 mol %) in DCE (0.1 M) at 60 °C for 16 h. [b]Yield of the isolated product. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Determined by ^{1}H NMR analysis.

Table S5. Screening of the substrates **1**.

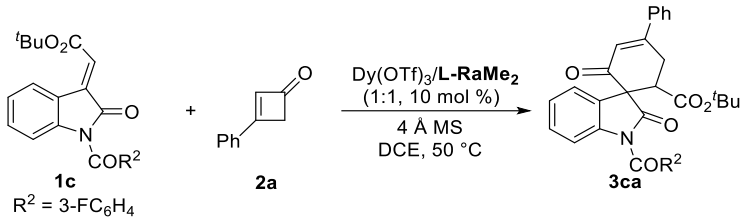


1a : $R^1 = CO_2Et$, R^2 = Ph **2a**
1b : $R^1 = CO_2{}^tBu$, R^2 = Ph
1c : $R^1 = CO_2{}^tBu$, R^2 = 3-FC_6H_4

entry[a]	substrates **1**	yield[b] (%)	ee[c] (%)	dr[d]
1	**1a**	59	72	94:6
2[e]	**1a**	52	75	19:1
3[e]	**1b**	75	87	>19:1
4[e]	**1c**	72	92	>19:1

[a]The reactions were performed with **1** (0.10 mmol), **2a** (0.10 mmol), 4 Å MS (80 mg) and $Dy(OTf)_3$/**L-RaMe$_2$** (1:1, 10 mol %) in DCE (0.1 M) at 60 °C for 16 h. [b]Yield of the isolated product. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Determined by ^{1}H NMR analysis. [e]At 50 °C for 48 h.

Table S6. Screening of the ratio of substrates.

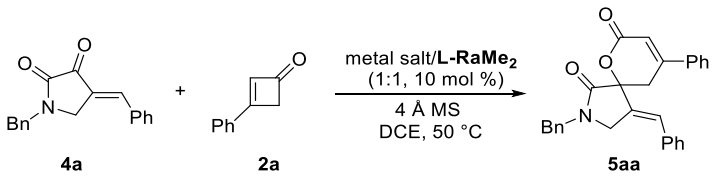


entry[a]	**1c** (mmol)/**2a** (mmol)	yield[b] (%)	ee[c] (%)	dr[d]
1	0.10/0.10(**1:1**)	73	93	>19:1
2	0.10/0.12 (**1:1.2**)	79	92	>19:1
3	0.10/0.14 (**1:1.4**)	93	92	>19:1
4	0.10/0.15 (**1:1.5**)	99	93	>19:1
5	0.10/0.16 (**1:1.6**)	99	93	>19:1
6	0.10/0.18 (**1:1.8**)	97	92	>19:1
7	0.10/0.20 (**1:2.0**)	94	91	>19:1

[a]The reactions were performed with **1c** (0.10 mmol), **2a** (x mmol), 4 Å MS (80 mg) and $Dy(OTf)_3$/**L-RaMe$_2$** (1:1, 10 mol %) in DCE (0.2 M) at 50 °C for 48 h. [b]Yield of the isolated product. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Determined by ^{1}H NMR analysis.

5.2 Optimization of the reaction conditions of [4+2] cycloaddition between cyclobutenones and (*E*)-dioxopyrrolidines

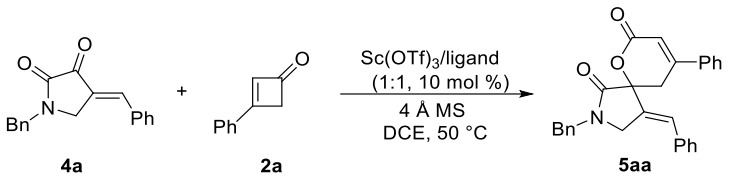
Table S7. Screening of metal salts.



entry[a]	metal salt	ligand	yield[b] (%)	ee[c] (%)
1	$Dy(OTf)_3$	**L-RaMe$_2$**	62	23
2	$Ho(OTf)_3$	**L-RaMe$_2$**	67	20
3	$Er(OTf)_3$	**L-RaMe$_2$**	68	21
4	$Tm(OTf)_3$	**L-RaMe$_2$**	64	17
5	$Gd(OTf)_3$	**L-RaMe$_2$**	63	21
6	$Eu(OTf)_3$	**L-RaMe$_2$**	64	14
7	$Sm(OTf)_3$	**L-RaMe$_2$**	65	9
8	$Nd(OTf)_3$	**L-RaMe$_2$**	73	race
9	$Pr(OTf)_3$	**L-RaMe$_2$**	70	6
10	$Sc(OTf)_3$	**L-RaMe$_2$**	53	68
11	$Y(OTf)_3$	**L-RaMe$_2$**	66	14
12	$Ni(OTf)_2$	**L-RaMe$_2$**	38	7
13	$Cu(OTf)_2$	**L-RaMe$_2$**	48	5
14	$Zn(OTf)_2$	**L-RaMe$_2$**	56	race
15	$Mg(OTf)_2$	**L-RaMe$_2$**	46	5

[a]The reactions were performed with **4a** (0.1 mmol), **2a** (0.15 mmol), 4 Å MS (80 mg) and metal salt/**L-RaMe$_2$** (1:1, 10 mol %) in DCE (0.2 M) at 50 °C for 48 h. [b]Yield of the isolated product. [c]Determined by HPLC analysis on a chiral stationary phase.

Table S8. Screening of the ligands.

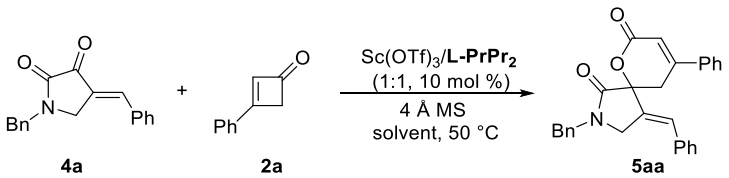


4a **2a** **5aa**

entry[a]	ligand	yield[b] (%)	ee[c] (%)
1	**L-RaMe$_2$**	53	68
2	**L-RaPr$_2$**	48	71
3	**L-PiPr$_2$**	65	80
4	**L-PrPr$_2$**	67	83
5	**L-PrEt$_2$**	n.d.[d]	64
6	**L-PrMe$_2$**	n.d.[d]	47
7	**L-PrPr$_3$**	n.d.[d]	73
8	**L-PrEt$_2$Me**	n.d.[d]	57
9	**L-PrCy**	n.d.[d]	51

[a]The reactions were performed with **4a** (0.1 mmol), **2a** (0.15 mmol), 4 Å MS (80 mg) and Sc(OTf)$_3$/ligand (1:1, 10 mol %) in DCE (0.2 M) at 50 °C for 48 h. [b]Yield of the isolated product. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Not Determined.

Table S9. Screening of the solvents.

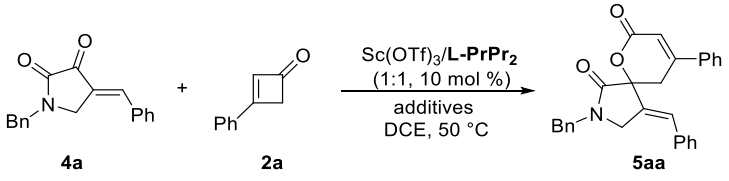


4a **2a** **5aa**

entry[a]	solvents	yield[b] (%)	ee[c] (%)
1	DCE	48	83
2	$CHCl_3$	46	83
3	EtOAc	36	65
4	Toluene	17	70
5	THF	23	69

[a]The reactions were performed with **4a** (0.1 mmol), **2a** (0.15 mmol), 4 Å MS (80 mg) and Sc(OTf)$_3$/**L-PrPr$_2$** (1:1, 10 mol %) in solvent (0.2 M) at 50 °C for 48 h. [b]Yield of the isolated product. [c]Determined by HPLC analysis on a chiral stationary phase.

Table S10. Screening of additives and other conditions.



4a **2a** **5aa**

entry[a]	additives	yield[b] (%)	ee[c] (%)

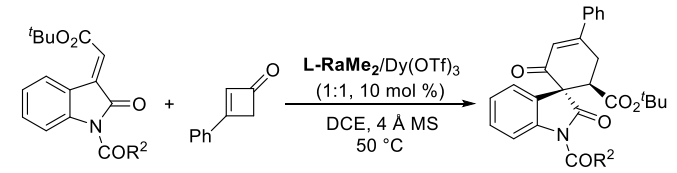
1	4 Å MS (80 mg)	55	83
2	3 Å MS (80 mg)	54	82
3	5 Å MS (80 mg)	43	77
4	No additives	14	40
5	4 Å MS (80 mg), $NaBAr^F$ (10 mol %)	78	84
6	4 Å MS (80 mg), $LiNTf_2$ (10 mol %)	66	86
7	4 Å MS (80 mg), $LiNTf_2$ (20 mol %)	68	89
8[d]	4 Å MS (80 mg), $LiNTf_2$ (30 mol %)	84	89

[a]The reactions were performed with **4a** (0.1 mmol), **2a** (0.15 mmol), additives and $Sc(OTf)_3$/**L-PrPr$_2$** (1:1, 10 mol %) in DCE (0.2 M) at 50 °C for 48 h. [b]Yield of the isolated product. [c]Determined by HPLC analysis on a chiral stationary phase. [d]For 72 h.

$LiNTf_2$ was beneficial to activate cyclobutenone to generate the vinylketene intermediate under mild conditions presumably through coordinating with the oxygen of cyclobutenone. On the other hand, a counter ion exchange between $^-NTf_2$ and ^-OTf might occur, the larger steric hindrance of the $^-NTf_2$ ion would make the catalyst space more compact. As a result, the enantioselectivities of the reactions with (*E*)-dioxopyrrolidines were increased. As for the more bulky (*E*)-alkenyloxindoles, the addition of $LiNTf_2$ as the additive did not show any obvious effect on the chiral control (Table S4, entry 8).

6 General procedures for the scale-up versions

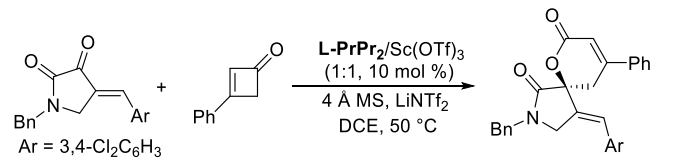
6.1 General procedure for the gram-scale synthesis of product 3ca



1c R^2 = 3-FC_6H_4 3.0 mmol, 1.10 g | **2a** 4.5 mmol, 0.65 g | **3ca** 1.53 g, 99% yield, 93% ee, >19:1 dr

An oven-dried round-bottom flask was charged with catalyst **L-RaMe$_2$**/$Dy(OTf)_3$ (1:1, 10 mol %), **1c** (3.0 mmol), **2a** (4.5 mmol), 4 Å MS (2.40 g), DCE (15 mL) under N_2 atmosphere. The resulted solution was stirred at 50 °C in an oil bath for 48 h. The reaction mixture was filtered (solvent: CH_2Cl_2), and concentrated under reduced pressure, the crude product was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20/1 and 9/1, v/v) to afford the corresponding product **3ca** (1.53 g, 99% yield, 93% ee).

6.2 General procedure for the gram-scale synthesis of product 5da

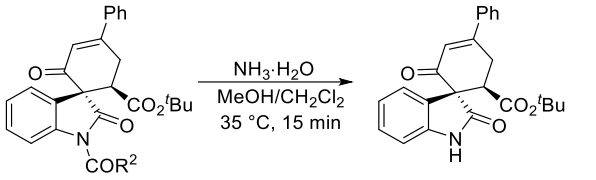


Ar = 3,4-$Cl_2C_6H_3$

4d 2.5 mmol, 0.87 g | **2a** 3.75 mmol, 0.54 g | **5da** 1.03 g, 84% yield, 87% ee

An oven-dried round-bottom flask was charged with catalyst **L-PrPr$_2$**/$Sc(OTf)_3$ (1:1, 10 mol %), $LiNTf_2$ (30 mol %), **4d** (2.5 mmol), **2a** (3.75 mmol), 4 Å MS (2.0 g), DCE (12.5 mL) under N_2 atmosphere. The resulted solution was stirred at 50 °C in an oil bath for 72 h. The reaction mixture was filtered (solvent: CH_2Cl_2), and concentrated under reduced pressure, the crude product was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (4/1 and 2/1, v/v) to afford the desired product **5da** (1.03 g, 84% yield, 87% ee).

7 General procedure for the synthesis of compound 11

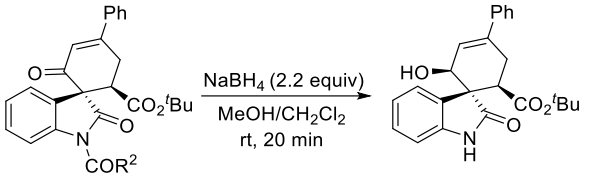


3ca R^2 = 3-FC_6H_4
93% ee, >19:1 dr

11
88% yield, 93% ee, >19:1 dr

To a solution of **3ca** (51.1 mg, 0.1 mmol, 93% ee, >19:1 dr) in CH_2Cl_2 (0.5 mL) and MeOH (0.5 mL) was added $NH_3{\cdot}H_2O$ (0.2 mL) at room temperature and stirred for 15 minutes at 35 °C. Then, the mixture was concentrated under reduced pressure, the crude product was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1 and 1/1, v/v) to afford the desired product **11** (34.3 mg, 88% yield, 93% ee, >19:1 dr).

8 General procedure for the synthesis of compound 12

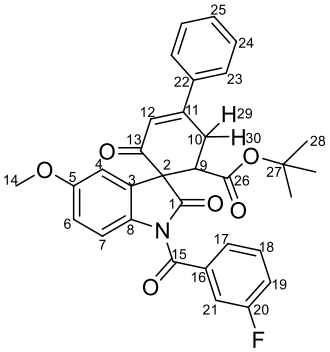


3ca R^2 = 3-FC_6H_4
93% ee, >19:1 dr

12
44% yield, 90% ee, >19:1 dr

To a solution of **3ca** (51.1 mg, 0.1 mmol, 93% ee, >19:1 dr) in CH_2Cl_2 (0.5 mL) and MeOH (0.5 mL) was added $NaBH_4$ (8.4 mg) at room temperature and stirred for 20 minutes. Then, the mixture was quenched with H_2O, extracted with CH_2Cl_2, dried over Na_2SO_4, concentrated, the residue was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate = 2/1 and 1/1, v/v) to afford the desired product **12** (17.2 mg, 44% yield, 90% ee, >19:1 dr).

9 Analysis results of 2D NMR spectra of the product 3ja



HSQC-Correlation Peak: (3,43, 27.0); (3.95, 44.4); (3.77, 55.8); (7.77, 119.6); (7.64, 116.2); (7.47, 129.7); (7.28, 125.2); (7.71, 129.1); (7.49, 126.4); (6.79, 110.6); (6.60, 122.7); (8.02, 112.6); (6.91, 116.4).
HMBC-Correlation Peak: (1.16, 83.1); (1.16, 27.4); (3.95, 168.8); (3.95, 176.7); (7.75, 167.9); (3.76, 157.1); (6.60, 137.1); (8.00, 157.0); (6.90, 157.1); 6.75, 157.2); (6.75, 61.0); (7.50, 137.1); (7.68, 158.7); (6.76, 112.7); (6.76, 134.6); (7.99, 134.6).

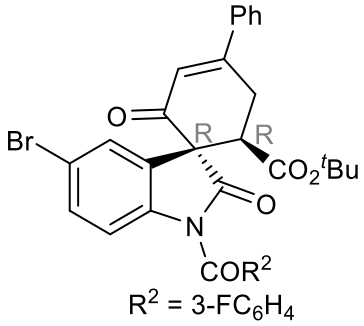
Number of Atom	H	C	Number of Atom	H	C
1	--	168.9	16	--	136.4 ($J_{C\text{-}F}$ = 7.1 Hz)
2	--	61.1	17	7.28 (ddd)	125.3 ($J_{C\text{-}F}$ = 3.0 Hz)
3	--	128.3	18	7.54-7.43 (m)	130.0 ($J_{C\text{-}F}$ = 8.1 Hz)
4	6.76 (d)	110.8	19	7.64 (ddd)	116.4 ($J_{C\text{-}F}$ = 23.2 Hz)
5	--	157.2	20	--	162.4 ($J_{C\text{-}F}$ = 247.5 Hz)
6	8.01 (d)	112.8	21	7.76 (dt)	119.8 ($J_{C\text{-}F}$ = 21.2 Hz)

7	6.90 (dd)	116.5	22	--	137.2
8	--	134.7	23	7.72-7.68 (m)	129.3
9	3.95 (dd)	44.5	24	7.54-7.43 (m)	126.5
10	--	27.2	25	7.54-7.43 (m)	131.4
11	--	158.8	26	--	175.8
12	6.60-6.58 (m)	122.8	27	--	83.2
13	--	192.7	28	1.16	27.5
14	3.76	55.9	29	3.50-3.36 (m)	--
15	--	168.0 ($J_{C\text{-}F}$ = 3.0 Hz)	30	3.50-3.36 (m)	--

10 Determination of absolute configurations of compound 3fa, 5da and 12

10.1 The X-ray structure of product 3fa

The crystals of product **3fa** were obtained from its solution in CH_2Cl_2 and petroleum ether. The absolute configuration of the product **3fa** was determined as (1*R*,2*R*) by its X-ray crystal structure. CCDC **1956580** contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



R^2 = 3-FC_6H_4

3fa

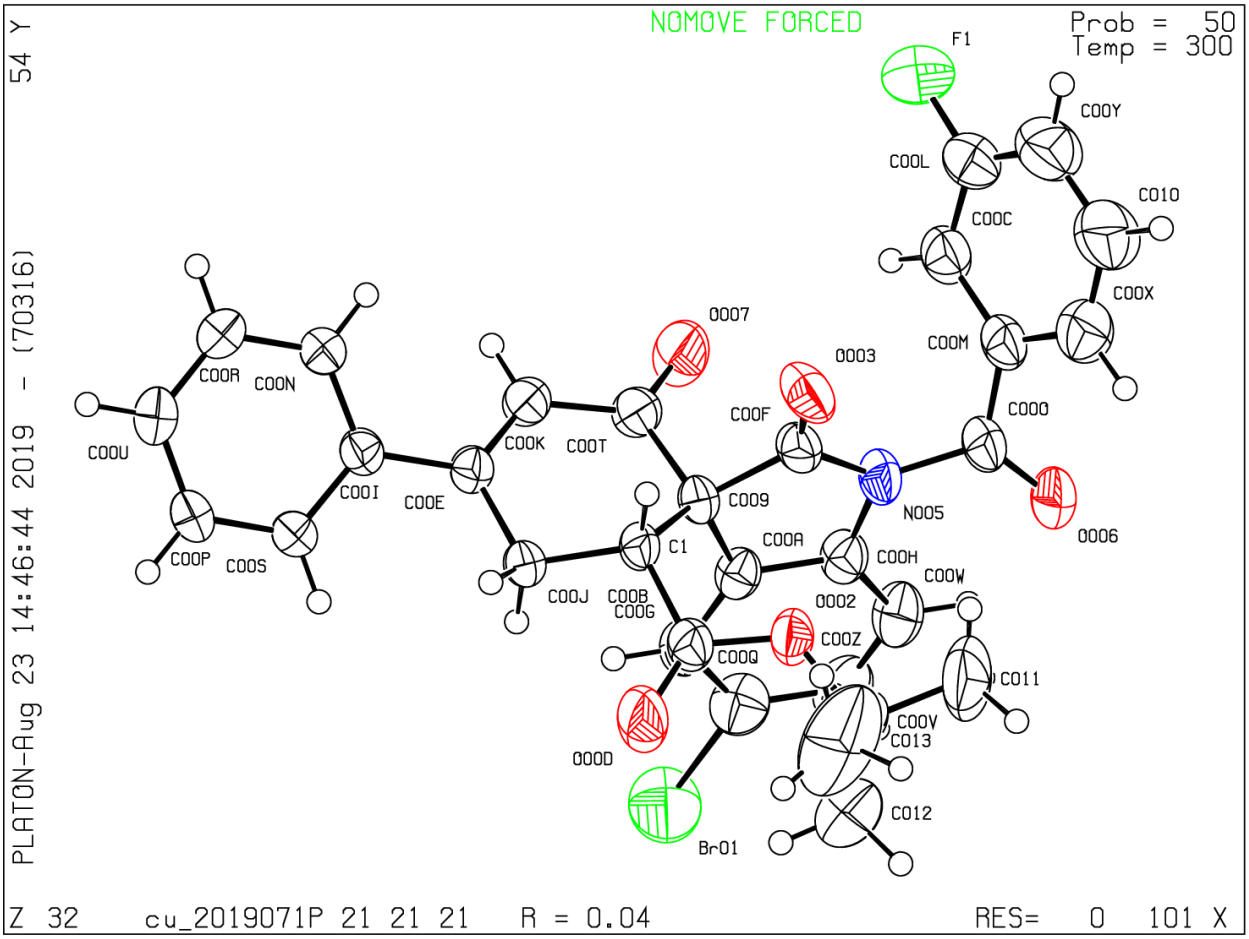
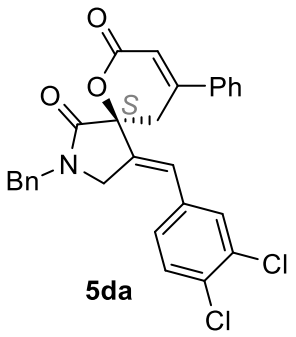


Figure 1. the thermal ellipsoid figure of **3fa** with 50% probablities

10.2 The X-ray structure of product 5da

The crystals of product **5da** were obtained from its solution in CH_2Cl_2, toluene and ethyl acetate. The absolute configuration of the product **5da** was determined as (*S*) by its X-ray crystal structure. CCDC **1989600** contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



5da

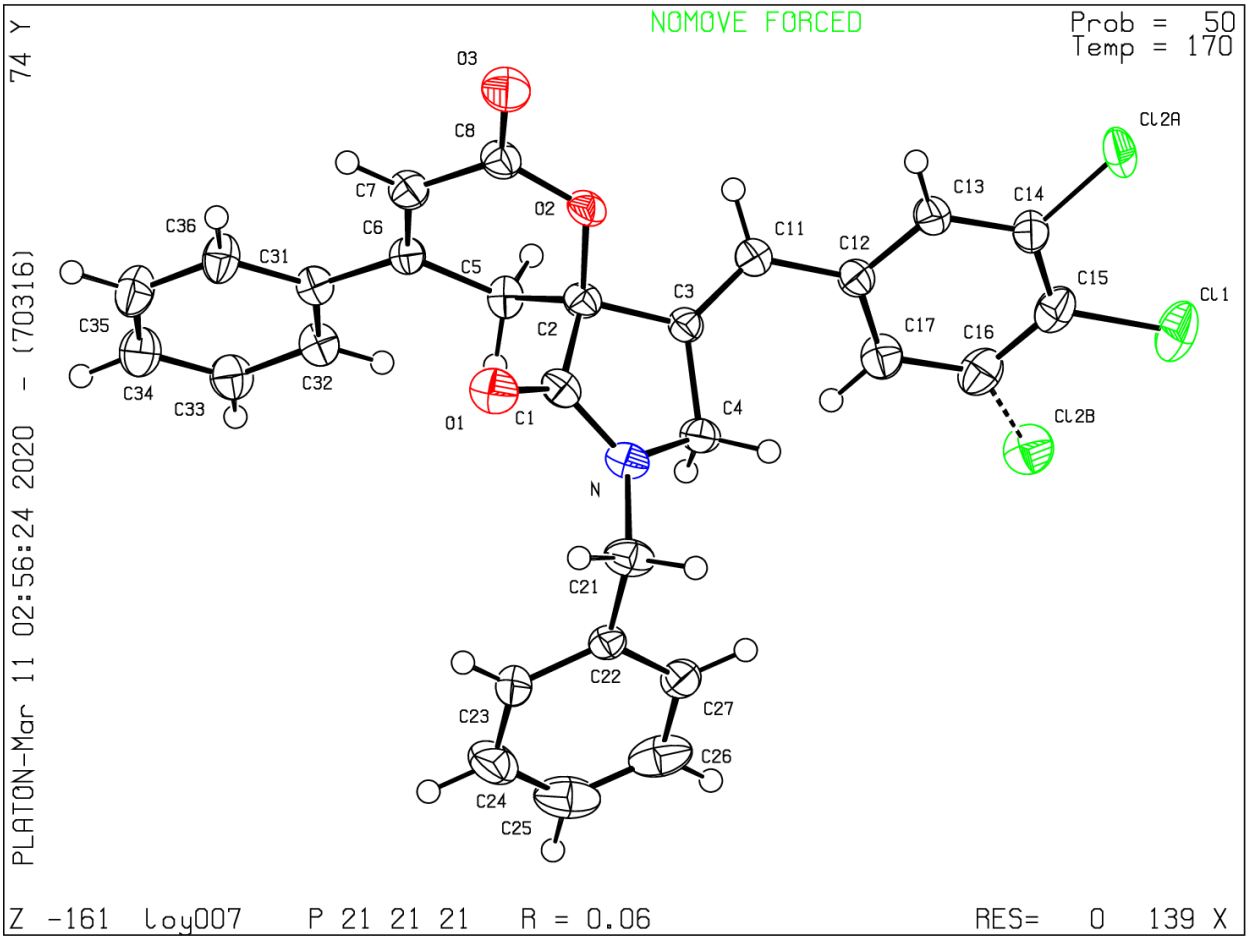
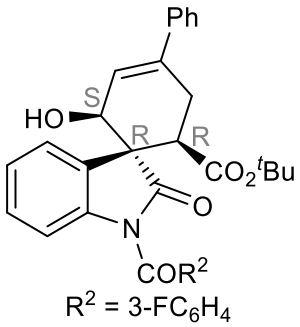


Figure 2. the thermal ellipsoid figure of **5da** with 50% probablities

10.3 The X-ray structure of product 12

The crystals of product **12** were obtained from its solution in CH_2Cl_2 and petroleum ether. The absolute configuration of the product **12** was determined as (1*R*,2*R*,3*S*) by its X-ray crystal structure. CCDC **1956579** contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



R^2 = 3-FC_6H_4

12

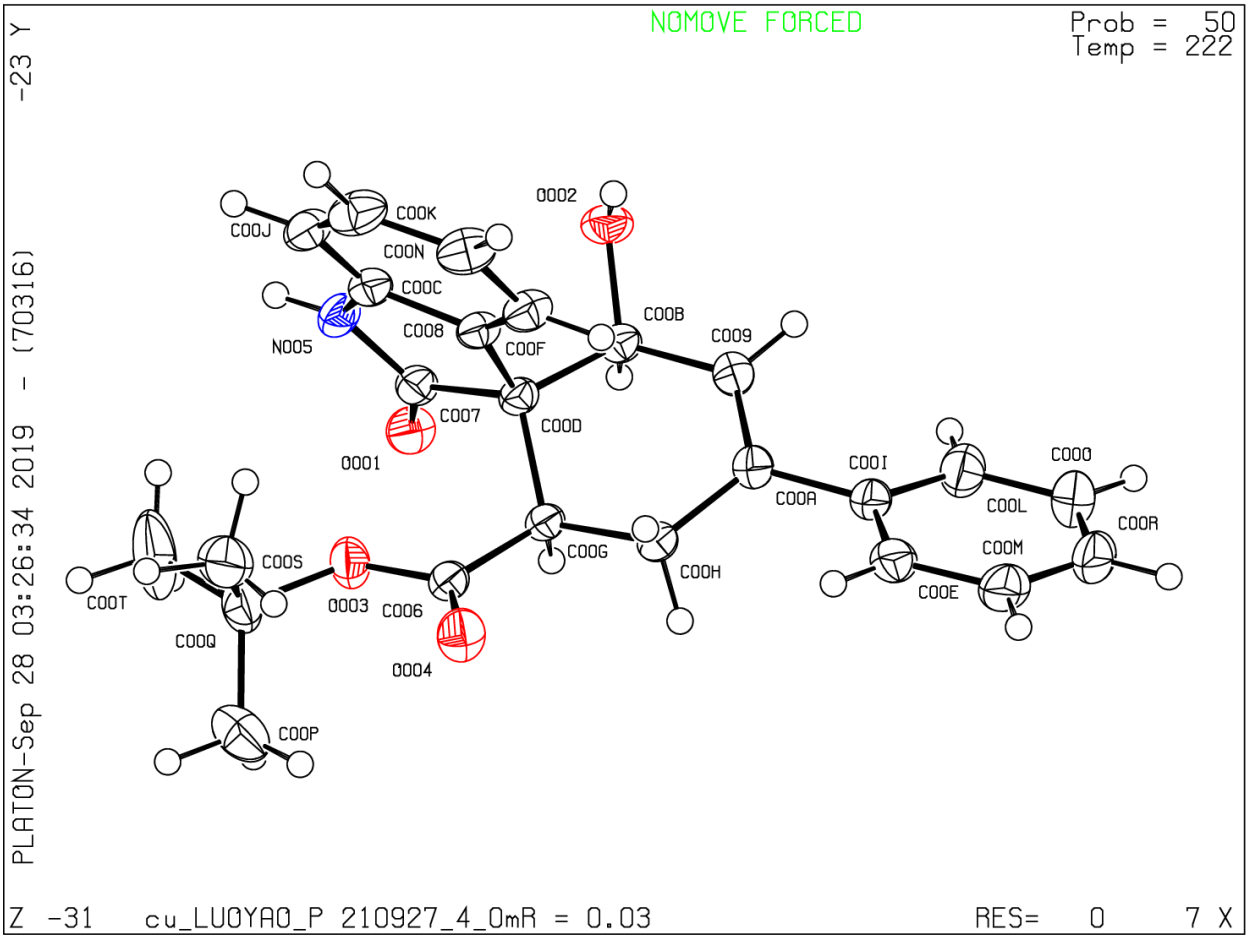
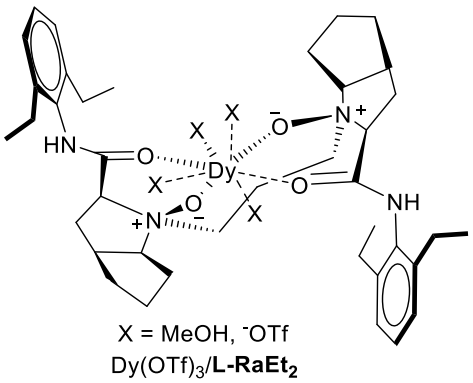


Figure 3. the thermal ellipsoid figure of **12** with 50% probablities

11 The X-ray structure of catalyst Dy(OTf)$_3$/L-RaEt$_2$ and working modes

The crystals of complex Dy(OTf)$_3$/**L-RaEt$_2$** were obtained from its solution in MeOH and ether. The coordination mode of catalyst Dy(OTf)$_3$/**L-RaEt$_2$** was determined by its X-ray crystal structure. CCDC **1977127** contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



X = MeOH, $^-$OTf
Dy(OTf)$_3$/**L-RaEt$_2$**

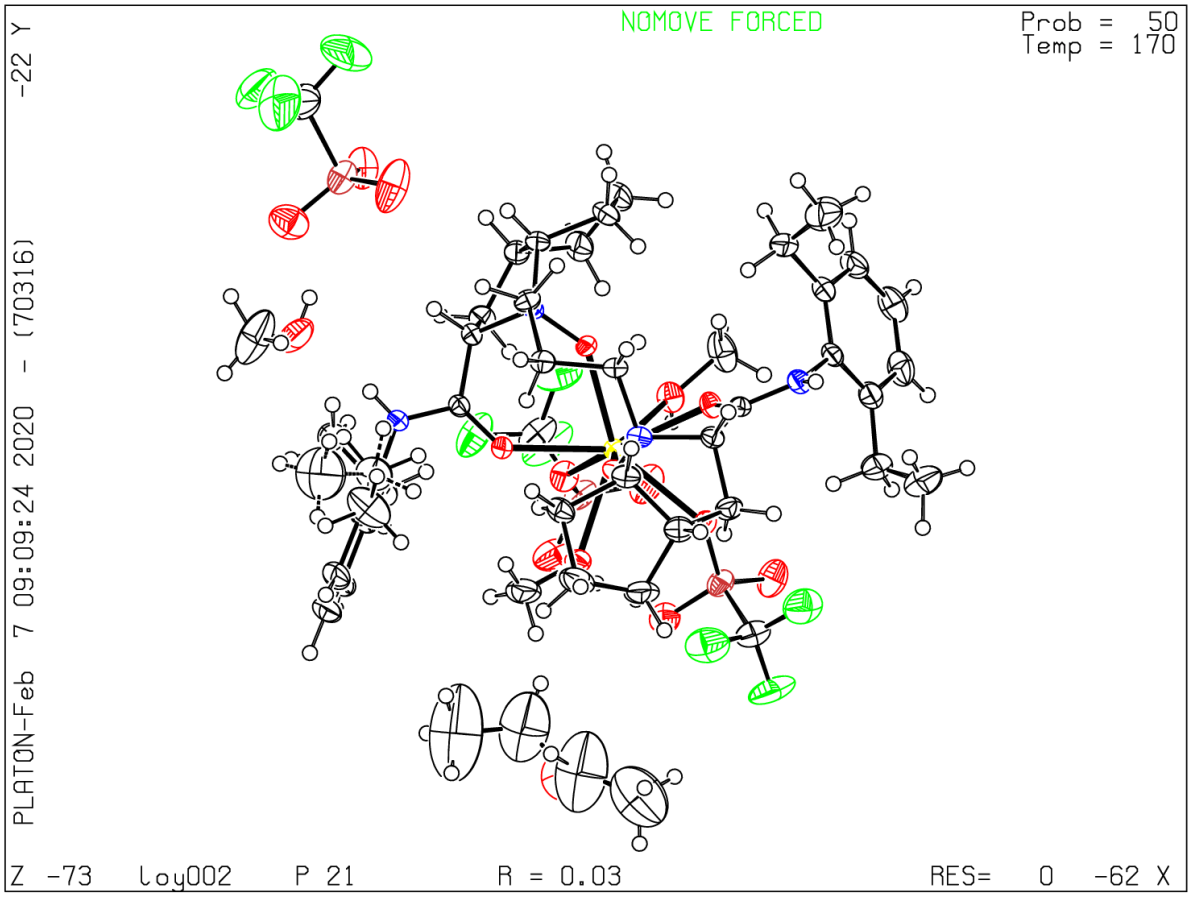


Figure 4. the thermal ellipsoid figure of catalyst **Dy(OTf)$_3$/L-RaEt$_2$** with 50% probablities

At the current stage, we do not have a clear-cut explanation on this interesting reverse (ref.11 in manuscript), and we assumed that steric hindrance or coordination form played an important role in chiral control. As shown in Figure 5, when **L-RaMe$_2$** or **L-RaEt$_2$** was used, the vinylketene intermediate would attack (*E*)-alkenyloxindole from its β-*Re* face (Mode I), delivering the observed (1*R*,2*R*)-**3aa** as the major enantiomer. However, when **L-RaPr$_2$** was used, arising from the steric repulsion between 2,6-diisopropyl group and oxindole moiety of substrate **1a** (Mode I'), the vinylketene intermediate preferred to attack (*E*)-alkenyloxindole from its β-*Si* face to afforded (1*S*,2*S*)-**3aa** as the main product (Mode II). Further studies on the reaction mechanism are undergoing in our laboratory.

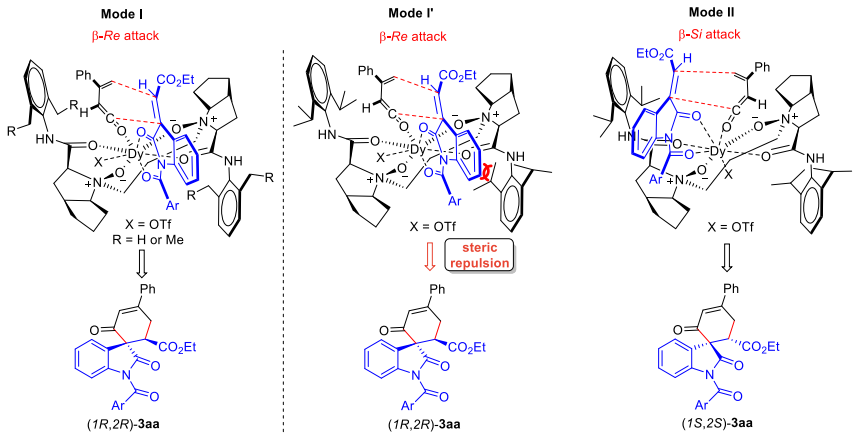


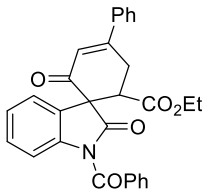
Figure 5. Working modes with different catalysts

12 Reference

(1) Wen, Y. H.; Huang, X.; Huang, J. L.; Xiong, Y.; Qin, B.; Feng, X. M. *Synlett* **2005**, 2445.
(2) Sugimoto, K.; Hayashi, R.; Nemoto, H. Toyooka, N.; Matsuya, Y. *Org. Lett.* **2012**, *14*, 3510.

13 Characterization of the products

Ethyl 1'-benzoyl-4-phenyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3aa

Oil; 29.8 mg, 64% yield, 73% ee; $[\alpha]^{25}_{D}$ = +84.90 (*c* = 0.40 in CH_2Cl_2).

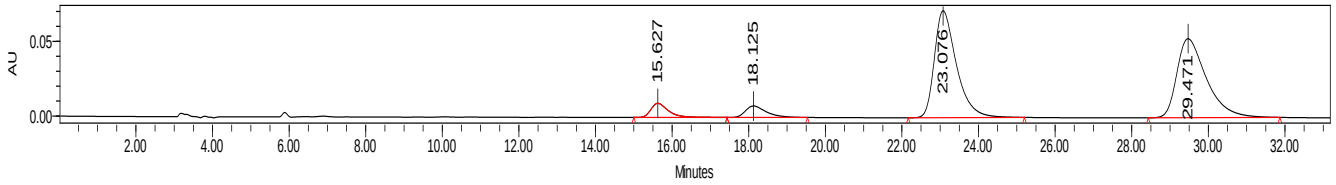
HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 30.60 min, t_R (minor) = 24.51 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 – 8.00 (m, 2H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.75 – 7.68 (m, 2H), 7.65 – 7.58 (m, 1H), 7.57 – 7.48 (m, 5H), 7.38 (td, *J* = 7.9, 1.4 Hz, 1H), 7.15 (ddd, *J* = 21.1, 7.6, 1.3 Hz, 2H), 6.62 (t, *J* = 1.5 Hz, 1H), 4.08 – 3.98 (m, 2H), 3.91 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.53 – 3.45 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H);

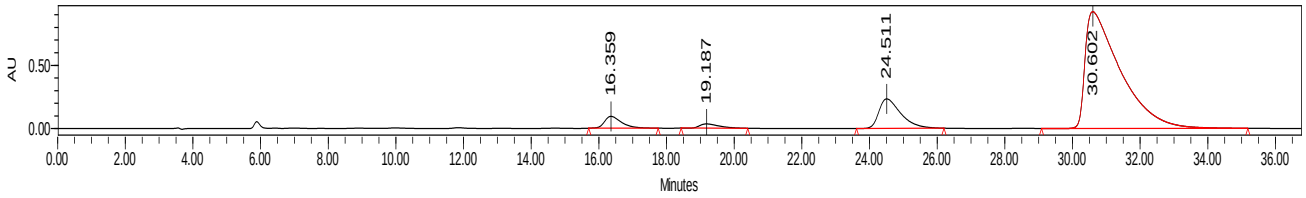
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 192.3, 175.4, 169.6, 169.0, 158.2, 141.4, 136.8, 133.6, 133.0, 131.1, 129.7, 129.3, 129.0, 128.1, 126.3, 124.5, 122.9, 122.7, 115.3, 61.6, 60.7, 44.1, 27.0, 13.4.

IR: 3061, 2982, 1765, 1733, 1691, 1658, 1606, 1472, 1343, 1286, 1249, 1167, 1075, 753, 695 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{29}H_{23}NO_5Na^+$ 488.1468; Found 488.1480.

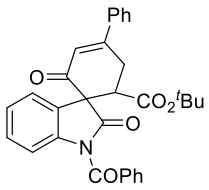


	Retention Time	Area	% Area
1	15.627	303915	4.84
2	18.125	292016	4.65
3	23.076	2859565	45.51
4	29.471	2828392	45.01



	Retention Time	Area	% Area
1	16.359	3281966	3.99
2	19.187	1320088	1.61
3	24.511	10541159	12.82
4	30.602	67054782	81.58

Tert-butyl 1'-benzoyl-4-phenyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3ba

Oil; 37.0 mg, 75% yield, 87% ee; $[\alpha]^{25}_{D}$ = +123.89 (*c* = 0.54 in CH_2Cl_2).

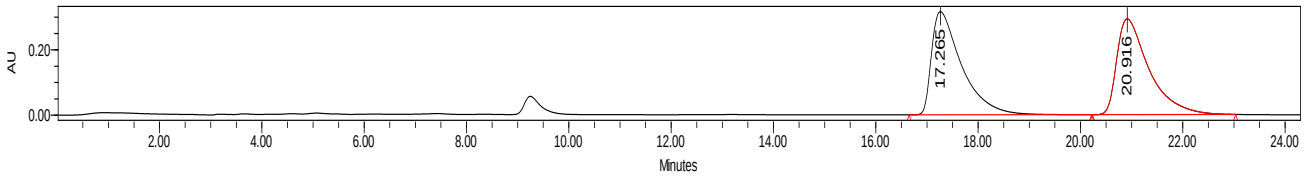
HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 18.99 min, t_R (minor) = 21.57 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.09 – 7.93 (m, 3H), 7.76 – 7.67 (m, 2H), 7.64 – 7.57 (m, 1H), 7.51 (qd, *J* = 4.9, 1.7 Hz, 5H), 7.39 (td, *J* = 7.9, 1.4 Hz, 1H), 7.24 – 7.08 (m, 2H), 6.64 – 6.56 (m, 1H), 3.97 (dd, *J* = 11.1, 6.8 Hz, 1H), 3.58 – 3.33 (m, 2H), 1.14 (s, 9H).

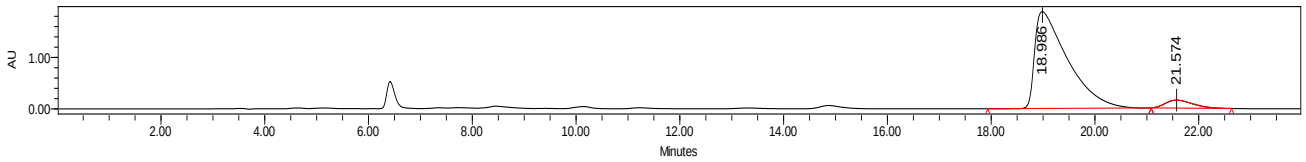
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 192.7, 175.6, 169.1, 168.8, 158.4, 141.4, 136.9, 133.8, 132.8, 131.1, 129.5, 129.3, 128.9, 128.1, 126.8, 126.2, 124.6, 122.6, 122.5, 115.3, 82.9, 60.8, 44.2, 27.1, 26.9.

IR: 3062, 2978, 1768, 1227, 1690, 1656, 1607, 1472, 1368, 1343, 1286, 1247, 1162, 754, 695 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{27}NO_5Na^+$ 516.1781; Found 516.1788.

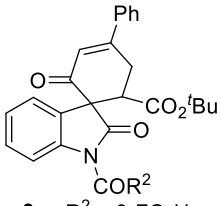


	Retention Time	Area	% Area
1	17.265	12917246	50.17
2	20.916	12830478	49.83



	Retention Time	Area	% Area
1	18.986	83008814	93.52
2	21.574	5749222	6.48

Tert-butyl 1'-(3-fluorobenzoyl)-4-phenyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3ca R^2 = 3-FC_6H_4

White solid; melting point: 76–78 °C; 50.9 mg, 99% yield, 93% ee; $[\alpha]^{25}_D$ = +122.77 (*c* = 0.94 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 14.17 min, t_R (minor) = 20.66 min.

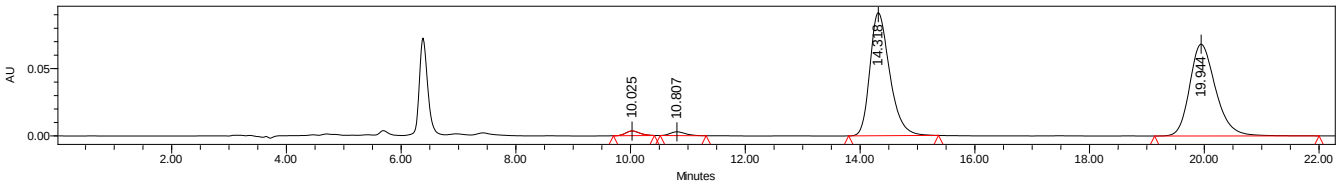
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 – 7.97 (m, 1H), 7.81 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.75 – 7.65 (m, 3H), 7.53 – 7.44 (m, 4H), 7.43 – 7.36 (m, 1H), 7.33 – 7.27 (m, 1H), 7.24 – 7.18 (m, 1H), 7.14 (td, *J* = 7.6, 1.1 Hz, 1H), 6.63 – 6.55 (m, 1H), 3.97 (dd, *J* = 11.0, 6.9 Hz, 1H), 3.56 – 3.34 (m, 2H), 1.14 (s, 9H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 192.6, 175.6, 168.7, 167.9 ($J_{C\text{-}F}$ = 3.0 Hz), 162.2 ($J_{C\text{-}F}$ = 248.5 Hz), 158.5, 141.0, 136.9, 135.8 ($J_{C\text{-}F}$ = 7.1 Hz), 131.1, 129.7 ($J_{C\text{-}F}$ = 7.1 Hz), 129.3, 129.0, 126.8, 126.2, 125.2 ($J_{C\text{-}F}$ = 3.0 Hz), 124.8, 122.7, 122.5, 119.7 ($J_{C\text{-}F}$ = 21.2 Hz), 116.3 ($J_{C\text{-}F}$ = 24.2 Hz), 115.3, 82.9, 60.7, 44.1, 27.1, 26.9;

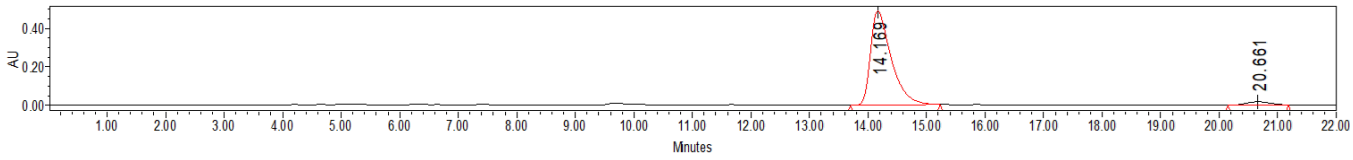
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –112. 2.

IR: 2977, 2362, 1767, 1726, 1691, 1651, 1607, 1471, 1442, 1342, 1244, 1153, 754 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{26}FNO_5Na^+$ 534.1687; Found 534.1686.

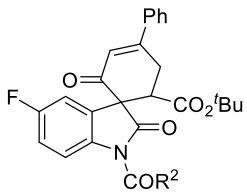


	Retention Time	Area	% Area
1	10.025	59861	1.35
2	10.807	52606	1.19
3	14.318	2185114	49.28
4	19.944	2136876	48.19



	Retention Time	Area	% Area
1	14.169	11968218	96.52
2	20.661	509023	3.48

Tert-butyl 5'-fluoro-1'-(3-fluorobenzoyl)-4-phenyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3da R^2 = 3-FC_6H_4

White solid; melting point: 81–84 °C; 52.5 mg, 99% yield, 91% ee; $[\alpha]^{25}_D$ = +129.12 (*c* = 0.89 in CH_2Cl_2). HPLC DAIC EL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 9.82 min, t_R (minor) = 14.96 min.

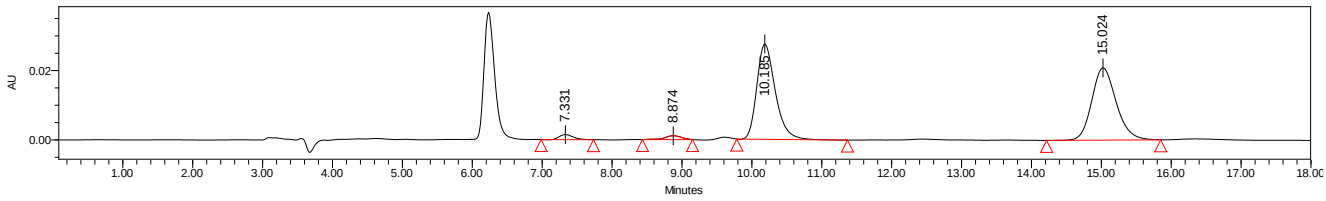
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (dd, *J* = 9.0, 4.6 Hz, 1H), 7.77 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.73 – 7.69 (m, 2H), 7.65 (ddd, *J* = 9.1, 2.6, 1.5 Hz, 1H), 7.53 – 7.44 (m, 4H), 7.29 (tdd, *J* = 8.4, 2.6, 1.0 Hz, 1H), 7.11 (td, *J* = 8.9, 2.6 Hz, 1H), 6.92 (dd, *J* = 7.7, 2.7 Hz, 1H), 6.61 (t, *J* = 1.5 Hz, 1H), 3.97 (dd, *J* = 10.4, 7.5 Hz, 1H), 3.44 – 3.41 (m, 2H), 1.17 (s, 9H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 192.2, 175.5, 168.7, 168.0 ($J_{C\text{-}F}$ = 3.0 Hz), 162.5 ($J_{C\text{-}F}$ = 248.5 Hz), 159.9 ($J_{C\text{-}F}$ = 246.4 Hz), 159.0, 137.4 ($J_{C\text{-}F}$ = 2.0 Hz), 137.0, 136.0 ($J_{C\text{-}F}$ = 8.1 Hz), 131.6, 130.0 ($J_{C\text{-}F}$ = 8.1 Hz), 129.3, 128.5 ($J_{C\text{-}F}$ = 8.1 Hz), 126.6, 125.4 ($J_{C\text{-}F}$ = 3.0 Hz), 122.7, 120.1 ($J_{C\text{-}F}$ = 21.2 Hz), 116.9 ($J_{C\text{-}F}$ = 8.1 Hz), 116.5 ($J_{C\text{-}F}$ = 24.2 Hz), 116.0 ($J_{C\text{-}F}$ = 22.2 Hz), 110.8 ($J_{C\text{-}F}$ = 25.3 Hz), 83.4, 61.07, 44.5, 27.5, 27.1;

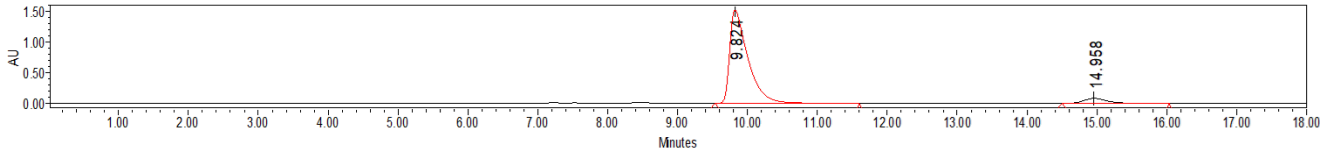
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –112.2, –115.9.

IR: 2964, 2362, 1770, 1726, 1691, 1650, 1609, 1479, 1443, 1343, 1257, 1151, 1086, 760 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{25}F_2NO_5Na^+$ 552.1593; Found 552.1590.

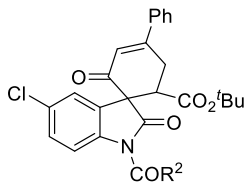


	Retention Time	Area	% Area
1	7.331	20347	1.94
2	8.874	18259	1.74
3	10.185	504209	48.13
4	15.024	504731	48.18



	Retention Time	Area	% Area
1	9.824	27493964	95.43
2	14.958	1316845	4.57

Tert-butyl 5'-chloro-1'-(3-fluorobenzoyl)-4-phenyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3ea R^2 = 3-FC_6H_4

Oil; 54.1 mg, 99% yield, 91% ee; $[\alpha]^{25}_D$ = +154.54 (*c* = 0.97 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 9.75 min, t_R (minor) = 12.36 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 8.8 Hz, 1H), 7.78 (dt, *J* = 7.9, 1.2 Hz, 1H), 7.74 – 7.70 (m, 2H), 7.66 (ddd, *J* = 9.2, 2.4, 1.6 Hz, 1H), 7.54 – 7.44 (m, 4H), 7.38 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.30 (tdd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 7.14 (d, *J* = 2.1 Hz, 1H), 6.61 (t, *J* = 1.5 Hz, 1H), 3.96 (dd, *J* = 10.4, 7.6 Hz, 1H), 3.48 – 3.37 (m, 2H), 1.18 (s, 9H);

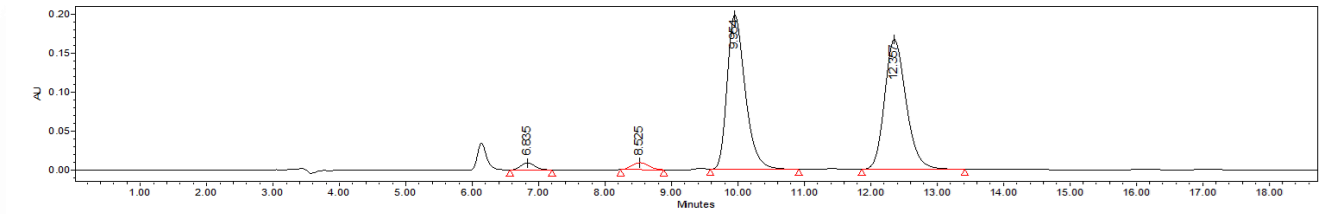
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 192.2, 175.3, 168.7, 167.9 ($J_{C\text{-}F}$ = 3.0 Hz), 162.5 ($J_{C\text{-}F}$ = 248.5 Hz), 159.1, 140.0, 137.0,135.8 ($J_{C\text{-}F}$ = 8.1 Hz), 131.6, 130.4, 130.1 ($J_{C\text{-}F}$ = 8.1 Hz), 129.6, 129.3, 128.7, 126.6, 125.5 ($J_{C\text{-}F}$ = 3.0 Hz), 123.2, 122.7, 120.2 ($J_{C\text{-}F}$ = 21.2 Hz), 116.7, 116.6 ($J_{C\text{-}F}$ = 24.2 Hz), 83.5, 60.9, 44.5, 27.6, 27.1;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –112.1.

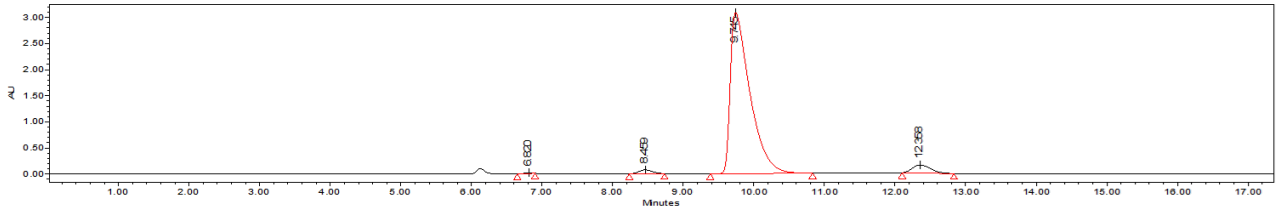
IR: 2361, 1770, 1729, 1695, 1652, 1609, 1471, 1426, 1332, 1234, 1153, 757 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{25}{}^{34.9689}ClFNO_5Na^+$ 568.1297; Found 568.1293.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{25}{}^{36.9659}ClFNO_5Na^+$ 570.1267; Found 570.1264.

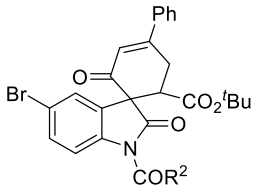


	Retention Time	Area	% Area
1	6.835	134327	1.73
2	8.525	156381	2.02
3	9.954	3727156	48.08
4	12.357	3733573	48.17



	Retention Time	Area	% Area
1	6.820	102974	0.16
2	8.459	1019293	1.60
3	9.745	59584095	93.74
4	12.358	2859235	4.50

Tert-butyl 5'-bromo-1'-(3-fluorobenzoyl)-4-phenyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3fa R^2 = 3-FC_6H_4

White solid; melting point: 198–200 °C; 58.7 mg, 99% yield, 90% ee; $[\alpha]^{25}_D$ = +154.03 (*c* = 0.94 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 10.13 min, t_R (minor) = 11.81 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 8.7 Hz, 1H), 7.78 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.74 – 7.70 (m, 2H), 7.66 (ddd, *J* = 9.0, 2.6, 1.5 Hz, 1H), 7.56 – 7.44 (m, 5H), 7.30 (tdd, *J* = 8.0, 2.4, 1.2 Hz, 2H), 6.61 (t, *J* = 1.6 Hz, 1H), 3.96 (dd, *J* = 10.6, 7.4 Hz, 1H), 3.50 – 3.36 (m, 2H), 1.18 (s, 9H);

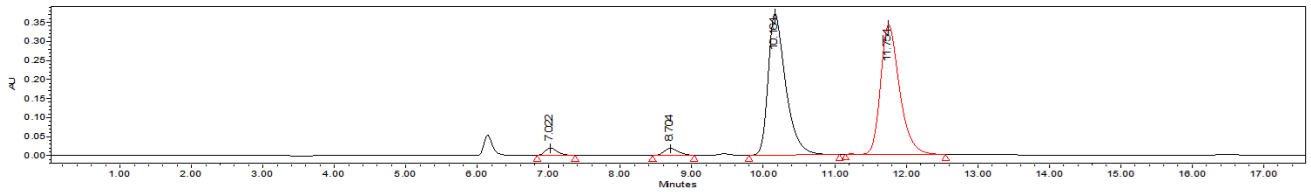
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 192.1, 175.2, 168.7,167.9 ($J_{C\text{-}F}$ = 3.0 Hz),162.5 ($J_{C\text{-}F}$ = 248.5 Hz), 159.1, 140.5, 137.0, 135.81 ($J_{C\text{-}F}$ = 7.1 Hz), 132.6, 131.6, 130.1 ($J_{C\text{-}F}$ = 8.1 Hz), 129.3, 129.1, 126.6, 126.0, 125.5 ($J_{C\text{-}F}$ = 4.0 Hz), 122.7, 120.2 ($J_{C\text{-}F}$ = 21.2 Hz), 117.9, 117.1, 116.6 ($J_{C\text{-}F}$ = 24.2 Hz), 83.5, 60.9, 44.6, 27.6, 27.1;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –112.1.

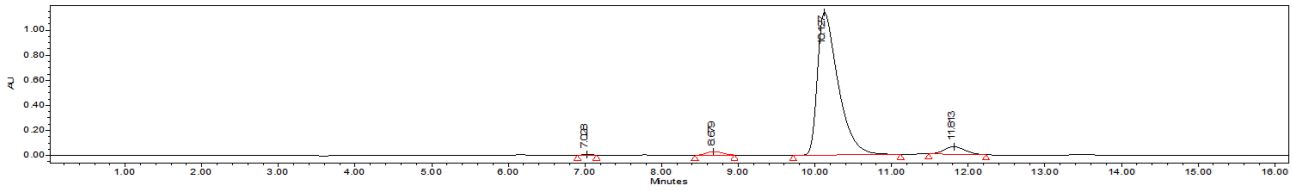
IR: 2972, 2362, 1776, 1731, 1690, 1650, 1609, 1464, 1368, 1240, 1156, 754 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{25}{}^{78.9183}BrFNO_5Na^+$ 612.0792; Found 612.0793.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{25}{}^{80.9163}BrFNO_5Na^+$ 614.0772; Found 614.0775.

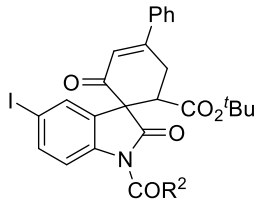


	Retention Time	Area	% Area
1	7.022	233866	1.78
2	8.704	264629	2.02
3	10.164	6343013	48.40
4	11.754	6264889	47.80



	Retention Time	Area	% Area
1	7.028	40791	0.18
2	8.679	433350	1.89
3	10.127	21279025	92.92
4	11.813	1146618	5.01

Tert-butyl 5'-iodo-1'-(3-fluorobenzoyl)-4-phenyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3ga R^2 = 3-FC_6H_4

White solid; melting point: 200–202 °C; 61.4 mg, 96% yield, 84% ee; $[\alpha]^{25}_D$ = +148.50 (*c* = 0.80 in CH_2Cl_2)

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 10.62 min, t_R (minor) = 11.62 min.

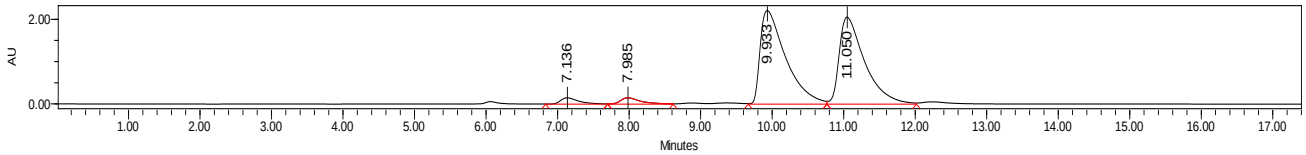
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82 – 7.75 (m, 2H), 7.75 – 7.70 (m, 3H), 7.66 (ddd, *J* = 9.0, 2.6, 1.6 Hz, 1H), 7.54 – 7.42 (m, 5H), 7.33 – 7.27 (m, 1H), 6.63 – 6.57 (m, 1H), 3.95 (dd, *J* = 10.7, 7.3 Hz, 1H), 3.49 – 3.36 (m, 2H), 1.17 (s, 9H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 191.9, 174.8, 168.4, 167.6 ($J_{C\text{-}F}$ = 3.0 Hz), 162.2 ($J_{C\text{-}F}$ = 248.5 Hz), 158.8, 140.9, 138.3, 136.7, 135.5 (J = 7.1 Hz), 131.3, 131.2,129.8 (J = 8.1 Hz), 129.2 , 129.0, 126.3, 125.2 ($J_{C\text{-}F}$ = 3.0 Hz), 122.4, 119.9 ($J_{C\text{-}F}$ = 22.2 Hz), 116.3 ($J_{C\text{-}F}$ = 23.2 Hz), 116.2, 87.8, 83.2, 60.4, 44.3, 27.2, 26.76;

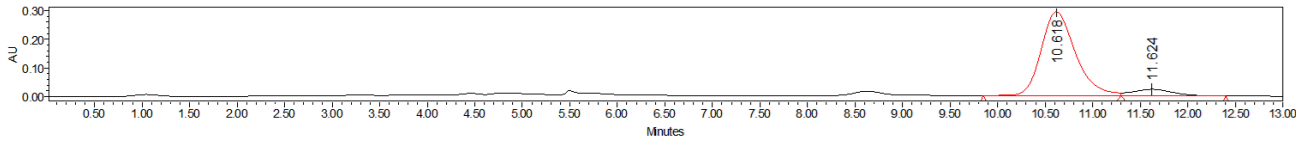
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –112.0.

IR: 2967, 2362, 1776, 1728, 1680, 1649, 1610, 1463, 1368, 1329, 1240, 1156, 751 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{25}IFNO_5Na^+$ 660.0654; Found 660.0654.

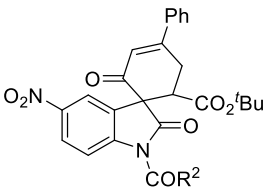


	Retention Time	Area	% Area
1	7.136	2641881	2.37
2	7.985	2931024	2.63
3	9.933	54981136	49.25
4	11.050	51085412	45.76



	Retention Time	Area	% Area
1	10.618	7322133	91.78
2	11.624	655452	8.22

Tert-butyl 1'-(3-fluorobenzoyl)-5'-nitro-4-phenyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3ha R^2 = 3-FC_6H_4

White solid; melting point: 101–103 °C; 51.2 mg, 92% yield, 79% ee; $[\alpha]^{25}_D$ = +182.66 (*c* = 0.74 in CH_2Cl_2)

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 22.44 min, t_R (minor) = 18.80 min.

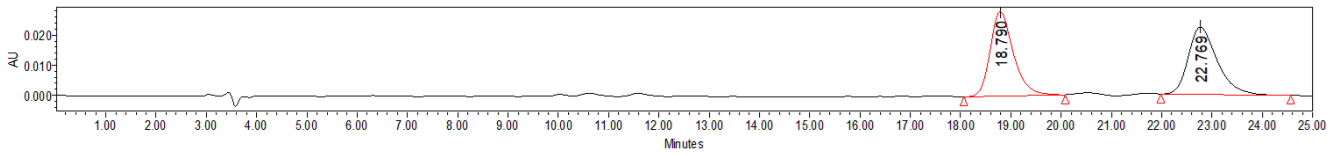
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.35 (dd, *J* = 9.0, 2.3 Hz, 1H), 8.11 (d, *J* = 9.0 Hz, 1H), 8.02 (d, *J* = 2.3 Hz, 1H), 7.82 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.72 (tdd, *J* = 8.9, 2.9, 1.6 Hz, 3H), 7.58 – 7.47 (m, 4H), 7.34 (tdd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 6.63 (dd, *J* = 2.1, 1.0 Hz, 1H), 4.02 (dd, *J* = 11.1, 6.8 Hz, 1H), 3.57 – 3.42 (m, 2H), 1.19 (s, 9H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 191.5, 175.1, 168.4, 167.8 ($J_{C\text{-}F}$ = 3.0 Hz), 162.5 ($J_{C\text{-}F}$ = 248.5 Hz), 159.8, 146.7, 144.6, 136.8, 135.1 ($J_{C\text{-}F}$ = 7.1 Hz), 131.8, 130.3 ($J_{C\text{-}F}$ = 8.1 Hz), 129.4, 128.3, 126.7, 126.0, 125.8 ($J_{C\text{-}F}$ = 3.0 Hz), 122.6, 120.9 ($J_{C\text{-}F}$ = 21.2 Hz), 118.5, 116.9 ($J_{C\text{-}F}$ = 23.2 Hz), 115.3, 83.8, 60.8, 44.8, 27.7, 27.2;

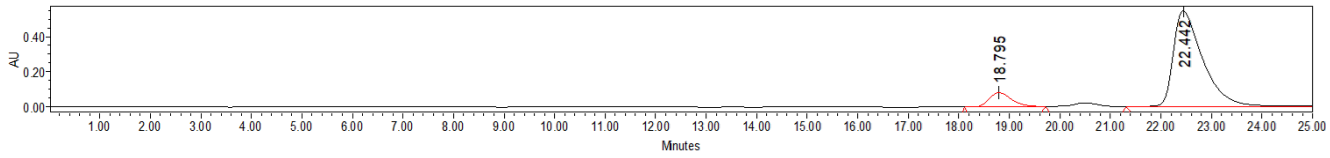
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –111.7.

IR: 2362, 1772, 1701, 1654, 1607, 1524, 1470, 1441, 1341, 1297, 1244, 1152, 1079, 736 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{25}FN_2O_7Na^+$ 579.1538; Found 579.1538.

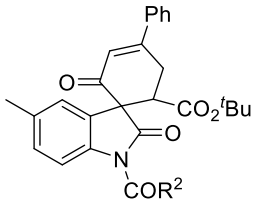


	Retention Time	Area	% Area
1	18.790	900135	50.22
2	22.769	892127	49.78



	Retention Time	Area	% Area
1	18.795	2658315	10.50
2	22.442	22647476	89.50

Tert-butyl 1'-(3-fluorobenzoyl)-5'-methyl-4-phenyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3ia R^2 = 3-FC_6H_4

White solid; melting point: 198–200 °C; 49.5 mg, 94% yield, 85% ee; $[\alpha]^{25}_D$ = +154.29 (*c* = 0.79 in CH_2Cl_2)

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 8.86 min, t_R (minor) = 23.17 min.

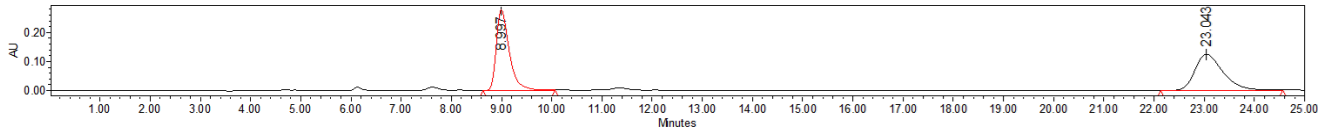
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 8.3 Hz, 1H), 7.78 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.73 (m, 2H), 7.66 (ddd, *J* = 9.1, 2.6, 1.5 Hz, 1H), 7.53 – 7.43 (m, 4H), 7.29 (ddd, *J* = 8.4, 2.6, 1.0 Hz, 1H), 7.19 (ddd, *J* = 8.3, 1.8, 0.8 Hz, 1H), 6.98 (d, *J* = 1.6 Hz, 1H), 6.60 (dd, *J* = 2.4, 1.2 Hz, 1H), 3.96 (dd, *J* = 11.2, 6.7 Hz, 1H), 3.53 – 3.36 (m, 2H), 2.30 (s, 3H), 1.14 (s, 9H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 193.1, 176.0, 169.1, 168.1 ($J_{C\text{-}F}$ = 3.0 Hz), 162.5 ($J_{C\text{-}F}$ = 248.5 Hz), 158.7, 139.0, 137.3, 136.3 ($J_{C\text{-}F}$ = 7.1 Hz), 135.0, 131.4, 130.1, 130.0 ($J_{C\text{-}F}$ = 7.1 Hz), 129.3, 127.1, 126.6, 125.4 ($J_{C\text{-}F}$ = 3.0 Hz), 123.5, 122.9, 119.9 ($J_{C\text{-}F}$ = 22.2 Hz), 116.5 ($J_{C\text{-}F}$ = 23.2 Hz), 115.4, 83.2, 61.1, 44.5, 27.5, 27.1, 21.4;

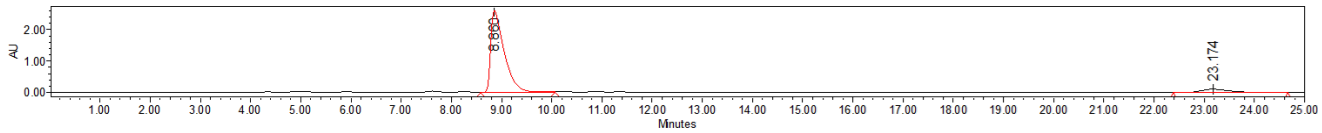
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –112.3.

IR: 2967, 2361, 1767, 1726, 1691, 1651, 1604, 1473, 1435, 1342, 1244, 1154, 753 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{32}H_{28}FNO_5Na^+$ 548.1844; Found 548.1838.

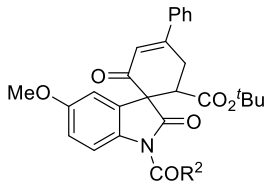


	Retention Time	Area	% Area
1	8.997	4942876	50.60
2	23.043	4825898	49.40



	Retention Time	Area	% Area
1	8.860	48766724	92.52
2	23.174	3940671	7.48

Tert-butyl 1'-(3-fluorobenzoyl)-5'-methoxy-4-phenyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3ja R^2 = 3-FC_6H_4

White solid; melting point: 201–203 °C; 46.7 mg, 86% yield; 90% ee; $[\alpha]^{25}_D$ = +104.30 (*c* = 0.70 in CH_2Cl_2)

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 10.80 min, t_R (minor) = 26.95 min.

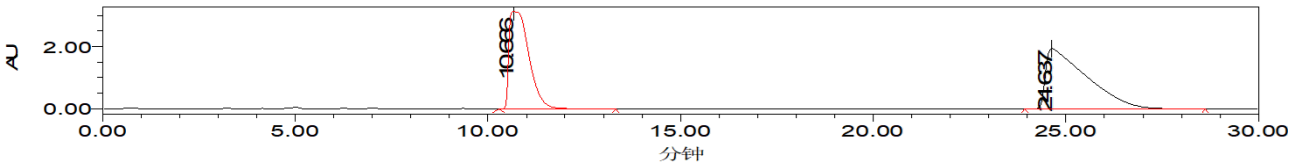
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (d, *J* = 8.9 Hz, 1H), 7.76 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.72 -7.68 (m, 2H), 7.64 (ddd, *J* = 9.1, 2.6, 1.5 Hz, 1H), 7.54 – 7.43 (m, 4H), 7.28 (ddd, *J* = 8.4, 2.6, 1.0 Hz, 1H), 6.90 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.76 (d, *J* = 2.6 Hz, 1H), 6.60 – 6.58 (m, 1H), 3.95 (dd, *J* = 10.5, 7.4 Hz, 1H), 3.76 (s, 3H), 3.50 – 3.36 (m, 2H), 1.16 (s, 9H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 192.8, 175.8, 168.9, 168.0 ($J_{C\text{-}F}$ = 3.0 Hz), 162.4 ($J_{C\text{-}F}$ = 247.5 Hz), 158.8, 157.2, 137.2, 136.4 ($J_{C\text{-}F}$ = 7.1 Hz), 134.7, 131.4, 130.0 ($J_{C\text{-}F}$ = 8.1 Hz), 129.3, 128.3, 126.5, 125.3 ($J_{C\text{-}F}$ = 3.0 Hz), 122.8, 119.8 ($J_{C\text{-}F}$ = 21.2 Hz), 116.4 ($J_{C\text{-}F}$ = 23.2 Hz), 116.5, 112.7, 110.8, 83.2, 61.1, 55.9, 44.5, 27.5, 27.1;

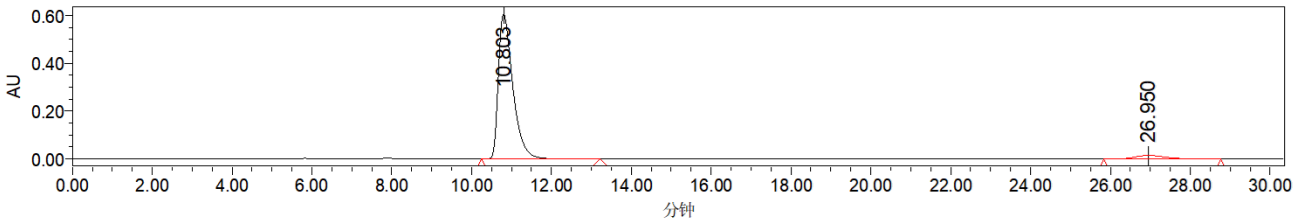
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –112.3.

IR: 2964, 2362, 1775, 1727, 1680, 1648, 1613, 1482, 1348, 1302, 1273, 1238, 1153, 752 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{32}H_{28}FNO_6Na^+$ 564.1793; Found 564.1790.

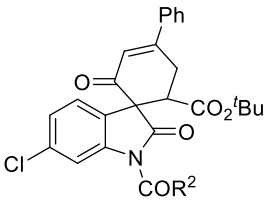


	Retention Time	Area	% Area
1	10.666	112497129	48.86
2	24.637	117754550	51.14



	Retention Time	Area	% Area
1	10.803	15278026	94.97
2	26.950	809121	5.03

Tert-butyl 6'-chloro-1'-(3-fluorobenzoyl)- 4-phenyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3ka R^2 = 3-FC_6H_4

White solid; melting point: 99–101 °C; 54.3 mg, 99% yield, 92% ee; $[\alpha]^{25}_D$ = +157.62 (*c* = 0.89 in CH_2Cl_2)

HPLC DAICEL CHIRALCEL ·IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 9.82 min, t_R (minor) = 14.45 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (d, *J* = 1.7 Hz, 1H), 7.79 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.69 (dddd, *J* = 11.5, 9.1, 3.0, 1.6 Hz, 3H), 7.53 – 7.43 (m, 4H), 7.30 (tdd, *J* = 8.4, 2.6, 1.0 Hz, 1H), 7.15 – 7.07 (m, 2H), 6.59 (t, *J* = 1.5 Hz, 1H), 3.95 (dd, *J* = 9.9, 7.9 Hz, 1H), 3.46 – 3.36 (m, 2H), 1.18 (s, 9H);

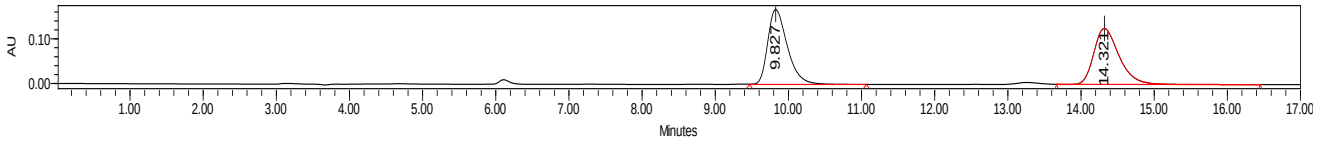
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 192.0, 175.2, 168.5, 167.6 ($J_{C\text{-}F}$ = 3.0 Hz), 162.2 ($J_{C\text{-}F}$ = 248.5 Hz), 158.6, 142.0, 136.7, 135.4 ($J_{C\text{-}F}$ = 8.1 Hz), 135.2, 131.3, 129.7 ($J_{C\text{-}F}$ = 8.1 Hz), 129.0, 126.2, 125.2 ($J_{C\text{-}F}$ = 3.0 Hz), 125.1, 124.8, 123.5, 122.4, 120.0 ($J_{C\text{-}F}$ = 21.2 Hz), 116.3 ($J_{C\text{-}F}$ = 23.2 Hz), 115.9, 83.1, 60.4, 44.2, 27.3, 26.9;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –112.1.

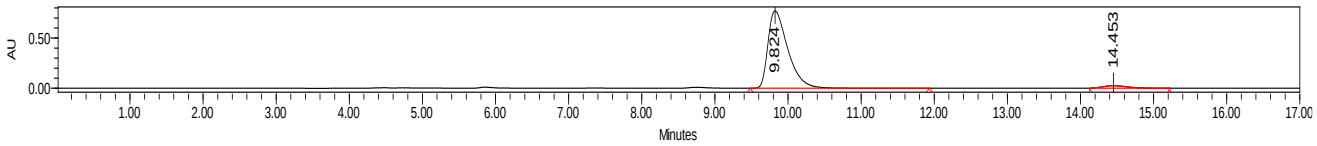
IR: 2979, 1770, 1695, 1653, 1596, 1477, 1442, 1338, 1243, 1155, 1072, 759 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{25}{}^{34.9689}ClFNO_5Na^+$ 568.1297; Found 568.1294.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{25}{}^{36.9659}ClFNO_5Na^+$ 570.1267; Found 570.1275.

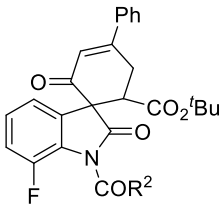


	Retention Time	Area	% Area
1	9.827	3048735	50.44
2	14.321	2994948	49.56



	Retention Time	Area	% Area
1	9.824	14545605	96.28
2	14.453	562244	3.72

Tert-butyl 7'-fluoro-1'-(3-fluorobenzoyl)- 4-phenyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3la R^2 = 3-FC_6H_4

White solid; melting point: 84–86 °C; 49.8 mg, 94% yield, 48% ee; $[\alpha]^{25}_D$ = +73.86 (*c* = 0.75 in CH_2Cl_2) HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 14.00 min, t_R (minor) = 32.71 min.

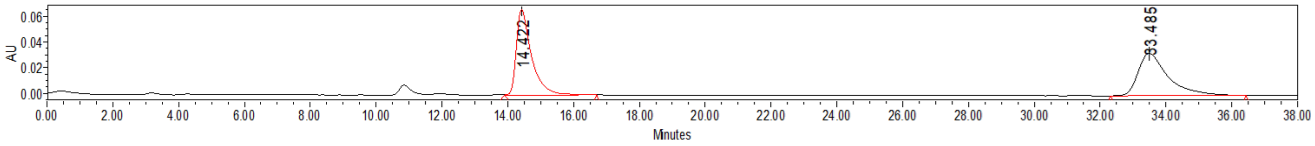
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 (dt, *J* = 7.9, 1.2 Hz, 1H), 7.84 (ddd, *J* = 9.1, 2.6, 1.6 Hz, 1H), 7.72 – 7.68 (m, 2H), 7.53 – 7.47 (m, 4H), 7.36 – 7.31 (m, 1H), 7.14 – 7.07 (m, 2H), 7.03 – 6.95 (m, 1H), 6.60 – 6.56 (m, 1H), 4.00 (dd, *J* = 11.0, 6.8 Hz, 1H), 3.51 – 3.35 (m, 2H), 1.23 (s, 9H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 191.6, 174.5, 168.7, 165.9 (J = 3.0 Hz), 162.4 ($J_{C\text{-}F}$ = 248.5 Hz), 158.6, 148.7 ($J_{C\text{-}F}$ = 253.5 Hz), 136.8, 134.7 ($J_{C\text{-}F}$ = 7.1 Hz), 131.2, 130.0 ($J_{C\text{-}F}$ = 8.1 Hz), 129.7 ($J_{C\text{-}F}$ = 2.0 Hz), 129.0, 128.4 ($J_{C\text{-}F}$ = 10.1 Hz), 126.5 ($J_{C\text{-}F}$ = 3.0 Hz), 126.2, 125.6 ($J_{C\text{-}F}$ = 7.1 Hz), 122.4, 120.9 ($J_{C\text{-}F}$ = 21.2 Hz), 118.6 (J = 3.0 Hz), 117.8 ($J_{C\text{-}F}$ = 20.2 Hz), 117.2 ($J_{C\text{-}F}$ = 20.2 Hz), 83.2, 61.6, 44.5, 27.4, 27.0;

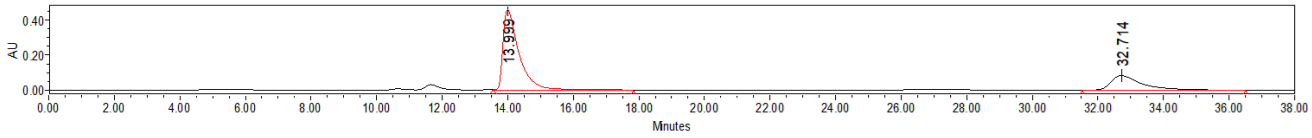
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –112.0, –116.1.

IR: 2971, 2362, 1765, 1713, 1654, 1608, 1484, 1443, 1346, 1243, 1150, 744 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{25}F_2NO_5Na^+$ 552.1593; Found 552.1599.

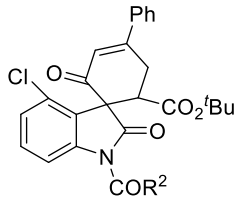


	Retention Time	Area	% Area
1	14.422	2129030	50.41
2	33.485	2094709	49.59



	Retention Time	Area	% Area
1	13.999	15441028	74.21
2	32.714	5364803	25.79

Tert-butyl 4'-chloro-1'-(3-fluorobenzoyl)- 4-phenyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3ma R^2 = 3-FC_6H_4

White solid; melting point: 72–75 °C; 50.4 mg, 92% yield; 79% ee; $[\alpha]^{25}_D$ = –64.68 (*c* = 0.50 in CH_2Cl_2) HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 17.58 min, t_R (minor) = 14.35 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.63 – 7.53 (m, 4H), 7.46 – 7.36 (m, 5H), 7.25 – 7.22 (m, 2H), 6.61 (d, *J* = 2.2 Hz, 1H), 4.50 (dd, *J* = 12.0, 5.0 Hz, 1H), 3.72 (ddd, *J* = 18.0, 12.0, 2.4 Hz, 1H), 3.14 (dd, *J* = 18.0, 6.0 Hz, 1H), 1.25 (s, 9H);

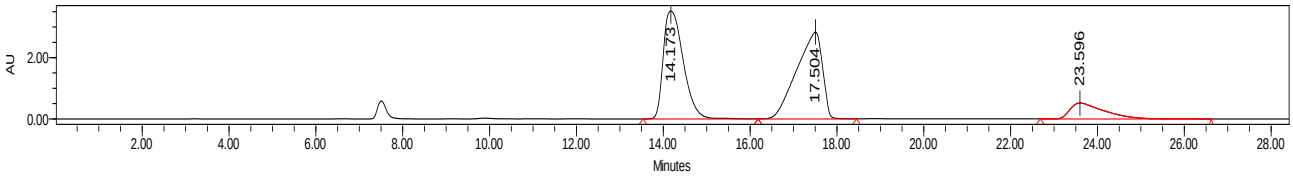
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 189.1, 170.7, 169.7, 167.4 ($J_{C\text{-}F}$ = 3.0 Hz), 162.1 ($J_{C\text{-}F}$ = 248.5 Hz), 159.8, 142.7, 137.1, 135.9 ($J_{C\text{-}F}$ = 8.1 Hz), 130.7, 130.4, 130.2, 129.7 ($J_{C\text{-}F}$ = 8.1 Hz), 128.7, 126.2, 125.8, 125.3, 124.8 ($J_{C\text{-}F}$ = 3.0 Hz), 122.4, 119.7 ($J_{C\text{-}F}$ = 21.2 Hz), 116.1 ($J_{C\text{-}F}$ = 23.2 Hz), 113.2, 82.5, 61.0, 46.1, 27.5, 27.4;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –112.1.

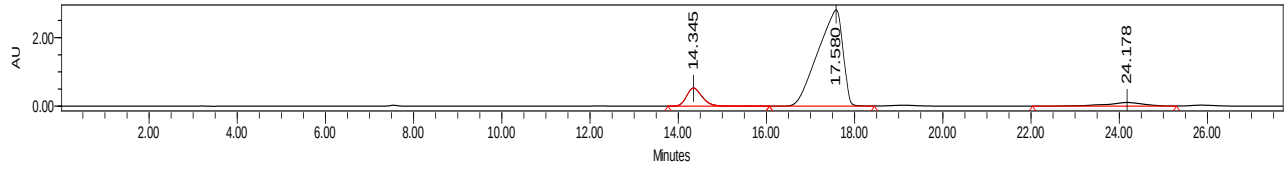
IR: 2977, 2362, 1772, 1699, 1661, 1594, 1444, 1341, 1256, 1133, 748 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{25}{}^{34.9689}ClFNO_5Na^+$ 568.1297; Found 568.1295.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{25}{}^{36.9659}ClFNO_5Na^+$ 570.1267; Found 570.1270.

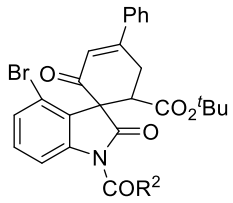


	Retention Time	Area	% Area
1	14.173	112787886	43.75
2	17.504	116782472	45.30
3	23.596	28248854	10.96



	Retention Time	Area	% Area
1	14.345	13034303	10.01
2	17.580	110614134	84.92
3	24.178	6607526	5.07

Tert-butyl 4'-bromo-1'-(3-fluorobenzoyl)- 4-phenyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3na R^2 = 3-FC_6H_4

White solid; melting point: 158–160 °C; 52.0 mg, 88% yield; 55% ee; $[\alpha]^{25}_D$ = –74.39 (*c* = 0.58 in CH_2Cl_2) HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 19.08 min, t_R (minor) = 15.67 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.65 – 7.51 (m, 4H), 7.47 – 7.37 (m, 5H), 7.31 (t, *J* = 8.1 Hz, 1H), 7.24 (ddd, *J* = 8.3, 2.6, 1.1 Hz, 1H), 6.62 (d, *J* = 2.2 Hz, 1H), 4.64 (dd, *J* = 12.0, 5.0 Hz, 1H), 3.73 (ddd, *J* = 18.0, 12.0, 2.4 Hz, 1H), 3.16 (dd, J = 20.0, 4.0 Hz, 1H), 1.25 (s, 9H);

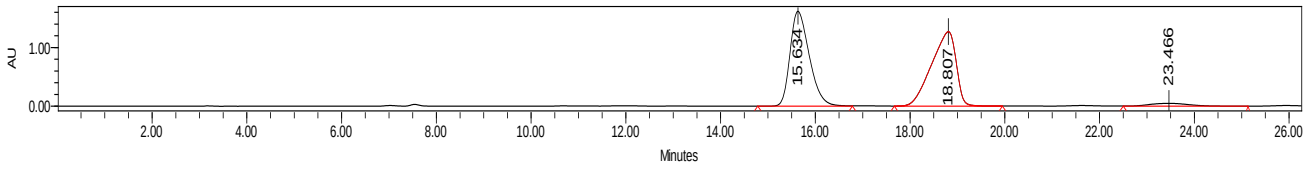
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 189.1, 170.7, 169.7, 167.3 ($J_{C\text{-}F}$ = 3.0 Hz), 162.1 ($J_{C\text{-}F}$ = 258.6 Hz), 159.6, 142.9, 137.1, 135.9 ($J_{C\text{-}F}$ = 7.1 Hz), 130.7, 130.6, 129.7 ($J_{C\text{-}F}$ = 8.1 Hz), 129.0, 128.7, 127.0, 126.2 , 124.8 ($J_{C\text{-}F}$ = 3.0 Hz), 122.6, 119.7 ($J_{C\text{-}F}$ = 21.2 Hz), 118.6, 116.1 ($J_{C\text{-}F}$ = 23.2 Hz), 113.7, 82.4, 61.7, 45.9, 29.5, 27.4;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –112.1.

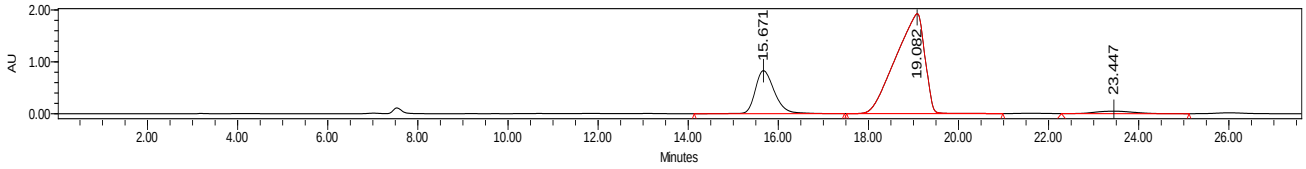
IR: 2975, 2362, 1759, 1663, 1588, 1444, 1339, 1259, 1124, 755 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{25}{}^{78.9183}BrFNO_5Na^+$ 612.0792; Found 612.0792.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{25}{}^{80.9163}BrFNO_5Na^+$ 614.0772; Found 614.0770.

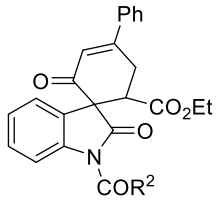


	Retention Time	Area	% Area
1	15.634	45783165	48.50
2	18.807	45906716	48.64
3	23.466	2699414	2.86



	Retention Time	Area	% Area
1	15.671	24440360	21.59
2	19.082	85937622	75.92
3	23.447	2810369	2.48

Ethyl 1'-(3-fluorobenzoyl)- 4-phenyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3oa R^2 = 3-FC_6H_4

White solid; melting point: 209–211 °C; 42.6 mg, 88% yield, 86% ee; $[\alpha]^{25}_D$ = +132.28 (*c* = 0.63 in CH_2Cl_2)

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 23.26 min, t_R (minor) = 19.12 min.

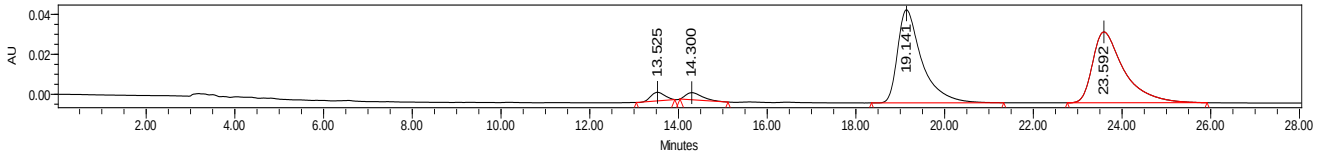
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 8.1 Hz, 1H), 7.81 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.74 – 7.68 (m, 3H), 7.55 – 7.45 (m, 4H), 7.39 (td, *J* = 7.8, 1.5 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.20 – 7.11 (m, 2H), 6.62 (t, *J* = 1.5 Hz, 1H), 4.08 – 3.98 (m, 2H), 3.93 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.58 – 3.39 (m, 2H), 1.00 (t, *J* = 7.1 Hz, 3H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 192.2, 175.5, 169.5, 167.7 ($J_{C\text{-}F}$ = 3.0 Hz), 162.2 ($J_{C\text{-}F}$ = 247.5 Hz), 158.2, 141.1, 136.8, 135.7 ($J_{C\text{-}F}$ = 7.1 Hz), 131.2, 129.7 ($J_{C\text{-}F}$ = 8.1 Hz), 129.4, 129.0, 126.2, 126.2 , 125.4 ($J_{C\text{-}F}$ = 3.0 Hz), 124.8, 122.8, 122.7, 119.8 ($J_{C\text{-}F}$ = 21.2 Hz), 116.5 ($J_{C\text{-}F}$ = 23.2 Hz), 115.3, 61.6, 60.7, 44.1, 27.0, 13.4;

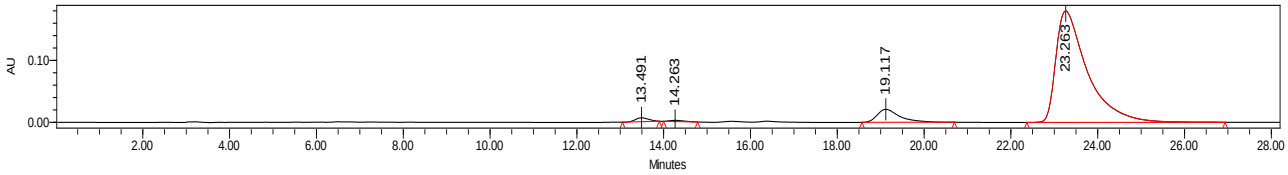
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –112.3.

IR: 2921, 2362, 1762, 1735, 1690, 1643, 1602, 1443, 1345, 1295, 1251, 1159, 754 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{29}H_{22}FNO_5Na^+$ 506.1374; Found 506.1370.

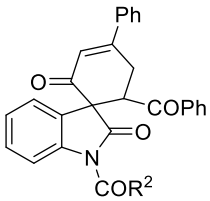


	Retention Time	Area	% Area
1	13.525	93595	2.54
2	14.300	90730	2.46
3	19.141	1768403	47.92
4	23.592	1737862	47.09



	Retention Time	Area	% Area
1	13.491	137205	1.38
2	14.263	43556	0.44
3	19.117	760545	7.63
4	23.263	9031908	90.56

6-Benzoyl-1'-(3-fluorobenzoyl)-4-phenyl[cyclohexane-1,3'-indolin]-3-ene-2,2'-dione



3pa R^2 = 3-FC_6H_4

White solid; melting point: 95–97 °C; 51.2 mg, 99% yield, 91% ee; $[\alpha]^{25}_D$ = +56.70 (*c* = 0.84 in CH_2Cl_2)

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 39.79 min, t_R (minor) = 27.17 min.

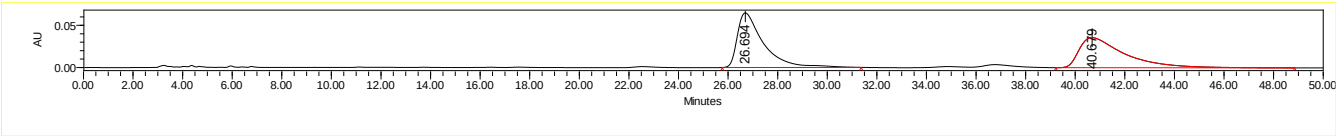
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 – 7.98 (m, 1H), 7.81 – 7.79 (m, 2H), 7.66 – 7.35 (m, 12H), 7.26 – 7.13 (m, 3H), 6.68 (d, *J* = 1.7 Hz, 1H), 4.92 (dd, *J* = 10.5, 6.8 Hz, 1H), 3.54 – 3.37 (m, 2H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 197.7, 191.8, 175.1, 167.3 ($J_{C\text{-}F}$ = 2.0 Hz), 162.0 ($J_{C\text{-}F}$ = 248.5 Hz), 157.9, 140.6, 136.6, 135.8 ($J_{C\text{-}F}$ = 7.1 Hz), 135.2, 133.6, 131.1, 129.6 ($J_{C\text{-}F}$ = 8.1 Hz), 129.0, 128.9, 128.7, 128.4, 126.1, 126.1, 125.1 ($J_{C\text{-}F}$ = 3.0 Hz), 124.7, 123.2, 123.03, 119.5 ($J_{C\text{-}F}$ = 21.2 Hz) , 116.2 ($J_{C\text{-}F}$ = 24.2 Hz), 115.4, 61.2, 47.6, 29.1;

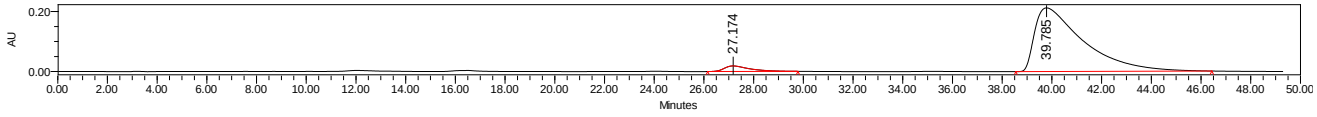
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –112.3.

IR: 2362, 1758, 1658, 1594, 1441, 1341, 1257, 1161, 752 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{33}H_{22}FNO_4Na^+$ 538.1425; Found 538.1432.

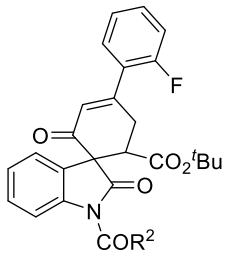


	Retention Time	Area	% Area
1	26.694	4633754	50.58
2	40.679	4527869	49.42



	Retention Time	Area	% Area
1	27.174	1306499	4.34
2	39.785	28789887	95.66

Tert-butyl 1'-(3-fluorobenzoyl)- 4-(2-flurophenyl)-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3cb R^2 = 3-FC_6H_4

Oil; 36.7 mg, 69% yield, 66% ee; $[\alpha]^{25}_D$ = +96.6 (*c* = 0.71 in CH_2Cl_2);

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 9.05 min, t_R (minor) = 13.74 min.

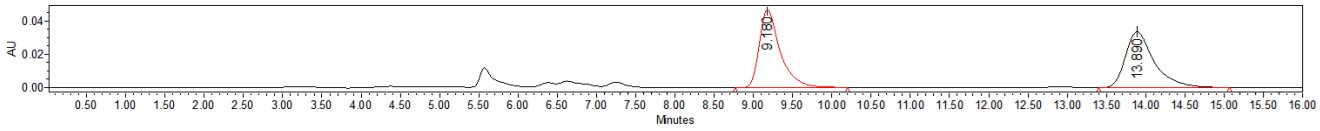
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.80 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.68 (ddd, *J* = 9.1, 2.7, 1.6 Hz, 1H), 7.46 (dddd, *J* = 9.1, 6.7, 4.5, 1.4 Hz, 3H), 7.40 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.23 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.20 – 7.16 (m, 2H), 6.46 (d, *J* = 2.3 Hz, 1H), 3.97 (dd, *J* = 11.6, 6.3 Hz, 1H), 3.56 (ddt, *J* = 20.0, 11.7, 2.3 Hz, 1H), 3.32 – 3.25 (m, 1H), 1.13 (s, 9H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 192.6, 175.8, 168.8, 168.2 ($J_{C\text{-}F}$ = 3.0 Hz), 162.5 ($J_{C\text{-}F}$ = 248.5 Hz), 161.1 ($J_{C\text{-}F}$ = 252.5 Hz), 156.2 ($J_{C\text{-}F}$ = 2.0 Hz), 141.4, 136.2 ($J_{C\text{-}F}$ = 8.1 Hz), 132.2 ($J_{C\text{-}F}$ = 8.1 Hz), 130.0 ($J_{C\text{-}F}$ = 8.1 Hz), 129.7, 129.0 ($J_{C\text{-}F}$ = 3.0 Hz), 126.8 ($J_{C\text{-}F}$ = 22.2 Hz),126.7, 126.6, 126.4, 125.5 ($J_{C\text{-}F}$ = 3.0 Hz), 125.3, 124.9 ($J_{C\text{-}F}$ = 3.0 Hz), 123.1, 120.0 ($J_{C\text{-}F}$ = 22.2 Hz), 116.9 ($J_{C\text{-}F}$ = 23.2 Hz), 116.6 ($J_{C\text{-}F}$ = 24.2 Hz), 115.60 , 83.2, 61.1, 44.7, 28.6 ($J_{C\text{-}F}$ = 5.1 Hz), 27.5;

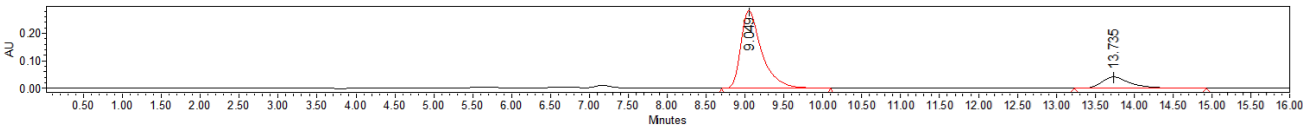
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –111.7, –112.3.

IR: 2925, 2362, 1767, 1726, 1692, 1658, 1609, 1481, 1342, 1242, 1153, 754 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{25}F_2NO_5Na^+$ 552.1593; Found 552.1595.

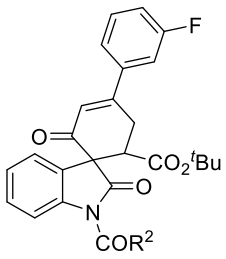


	Retention Time	Area	% Area
1	9.180	861943	50.31
2	13.890	851461	49.69



	Retention Time	Area	% Area
1	9.049	5215367	82.88
2	13.735	1077139	17.12

Tert-butyl 1'-(3-fluorobenzoyl)- 4-(3-flurophenyl)-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3cc R^2 = 3-FC_6H_4

Oil; 52.5 mg, 99% yield, 92% ee; $[\alpha]^{25}_D$ = +140.68 (*c* = 1.03 in CH_2Cl_2)

HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 8.43 min, t_R (minor) = 11.93 min.

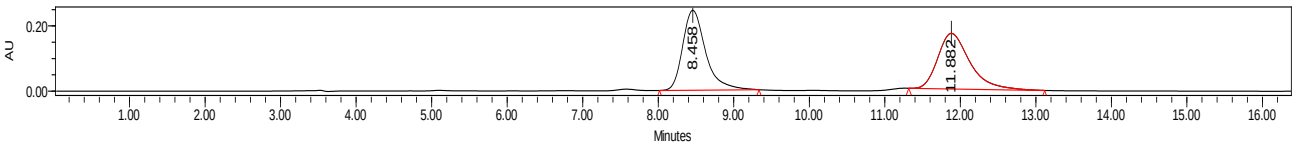
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 8.1 Hz, 1H), 7.80 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.68 (ddd, *J* = 9.1, 2.6, 1.6 Hz, 1H), 7.50 – 7.44 (m, 3H), 7.42 – 7.38 (m, 2H), 7.32 – 7.27 (m, 1H), 7.24 – 7.17 (m, 2H), 7.14 (td, *J* = 7.5, 1.0 Hz, 1H), 6.57 (d, *J* = 2.1 Hz, 1H), 3.97 (dd, *J* = 11.2, 6.6 Hz, 1H), 3.51 – 3.32 (m, 2H), 1.13 (s, 9H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 192.4, 175.4, 168.5, 167.8 ($J_{C\text{-}F}$ = 2.0 Hz), 162.8 ($J_{C\text{-}F}$ = 248.5 Hz), 162.2 ($J_{C\text{-}F}$ = 247.5 Hz), 156.9 ($J_{C\text{-}F}$ = 2.0 Hz), 141.0, 139.1 ($J_{C\text{-}F}$ = 7.1 Hz), 135.8 ($J_{C\text{-}F}$ = 8.1 Hz), 130.6 ($J_{C\text{-}F}$ = 8.1 Hz), 129.7 ($J_{C\text{-}F}$ = 7.1 Hz), 129.4, 126.6, 125.2 ($J_{C\text{-}F}$ = 3.0 Hz), 124.9, 123.3, 122.6, 121.9 ($J_{C\text{-}F}$ = 3.0 Hz), 119.8 ($J_{C\text{-}F}$ = 21.2 Hz), 117.9 ($J_{C\text{-}F}$ = 21.2 Hz), 116.3 ($J_{C\text{-}F}$ = 23.2 Hz), 115.3, 113.3 ($J_{C\text{-}F}$ = 23.2 Hz), 83.0, 60.7, 44.0, 27.1, 26.9;

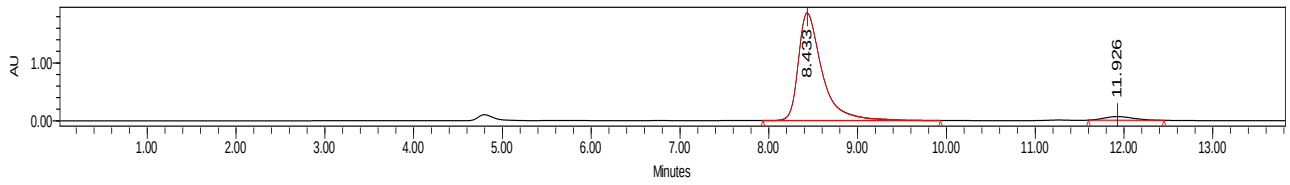
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –111.2, –112.2.

IR: 2924, 2362, 1767, 1726, 1692, 1656, 1584, 1440, 1342, 1244, 1154, 754 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{25}F_2NO_5Na^+$ 552.1593; Found 552.1594.

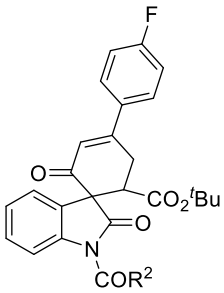


	Retention Time	Area	% Area
1	8.458	5165189	50.66
2	11.882	5031269	49.34



	Retention Time	Area	% Area
1	8.433	34412872	96.03
2	11.926	1423158	3.97

Tert-butyl 1'-(3-fluorobenzoyl)- 4-(4-flurophenyl)-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3cd R^2 = 3-FC_6H_4

Oil; 52.5 mg, 99% yield, 87% ee; $[\alpha]^{25}_D$ = +134.42 (*c* = 0.89 in CH_2Cl_2)

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 16.06 min, t_R (minor) = 29.27 min.

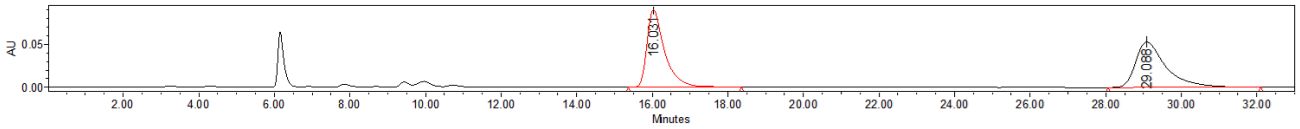
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 8.0 Hz, 1H), 7.80 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.74 – 7.66 (m, 3H), 7.46 (td, *J* = 8.0, 5.4 Hz, 1H), 7.40 (ddd, *J* = 8.1, 7.3, 1.6 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.22 – 7.15 (m, 3H), 7.13 (td, *J* = 7.5, 1.0 Hz, 1H), 6.54 (d, *J* = 2.0 Hz, 1H), 3.96 (dd, *J* = 11.1, 6.8 Hz, 1H), 3.50 – 3.33 (m, 2H), 1.13 (s, 9H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 192.4, 175.6, 168.6, 167.8 ($J_{C\text{-}F}$ = 3.0 Hz), 164.3 ($J_{C\text{-}F}$ = 254.5 Hz), 162.2 ($J_{C\text{-}F}$ = 247.5 Hz), 157.1, 141.0, 135.8 ($J_{C\text{-}F}$ = 7.1 Hz), 133.0 ($J_{C\text{-}F}$ = 4.0 Hz), 131.0 ($J_{C\text{-}F}$ =9.1 Hz), 129.7 ($J_{C\text{-}F}$ = 7.1 Hz), 129.4, 128.3 ($J_{C\text{-}F}$ = 9.1 Hz), 126.7, 125.2 ($J_{C\text{-}F}$ = 3.0 Hz), 124.8, 122.4 ($J_{C\text{-}F}$ = 29.3 Hz), 119.7 ($J_{C\text{-}F}$ = 21.2 Hz), 116.3 ($J_{C\text{-}F}$ = 23.2 Hz), 116.1 ($J_{C\text{-}F}$ = 22.2 Hz), 115.3, 83.0, 60.6, 44.1, 27.1, 26.9.;

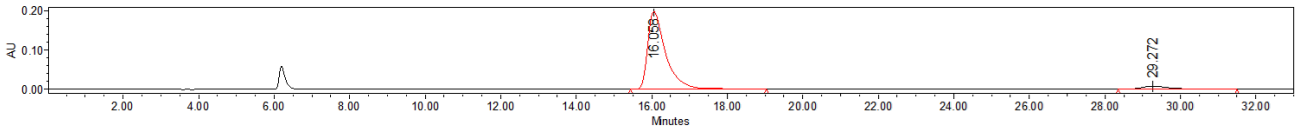
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –108.1, –112.2.

IR: 2362, 1763, 1726, 1692, 1652, 1594, 1508, 1471, 1342, 1293, 1231, 1154, 755 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{25}F_2NO_5Na^+$ 552.1593; Found 552.1592.

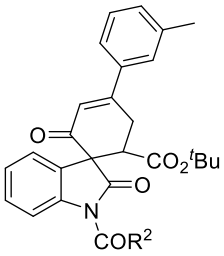


	Retention Time	Area	% Area
1	16.031	2943136	49.97
2	29.088	2946867	50.03



	Retention Time	Area	% Area
1	16.058	6592312	93.62
2	29.272	449033	6.38

Tert-butyl 1'-(3-fluorobenzoyl)- 4-(3-methylphenyl)-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3ce R^2 = 3-FC_6H_4

Oil; 52.3 mg, 99% yield, 90% ee; $[\alpha]^{25}_D$ = +142.58 (*c* = 0.88 in CH_2Cl_2)

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 12.48 min, t_R (minor) = 15.33 min.

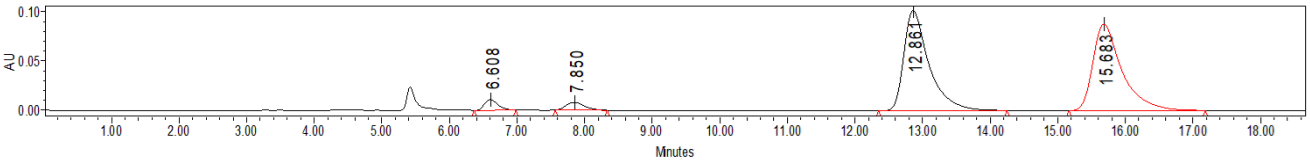
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 8.0 Hz, 1H), 7.81 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.69 (ddd, *J* = 9.1, 2.6, 1.6 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.42 – 7.37 (m, 2H), 7.34 – 7.27 (m, 2H), 7.21 – 7.19 (m, 1H), 7.14 (td, *J* = 7.5, 1.1 Hz, 1H), 6.59 – 6.58 (m, 1H), 3.96 (dd, *J* = 10.9, 7.0 Hz, 1H), 3.2 – 3.37 (m, 2H), 2.44 (s, 3H), 1.14 (s, 9H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 192.6, 175.7, 168.8, 167.9 ($J_{C\text{-}F}$ = 3.0 Hz), 162.2 ($J_{C\text{-}F}$ = 248.5 Hz), 158.7, 141.0, 138.7, 136.9, 135.8 ($J_{C\text{-}F}$ = 8.1 Hz), 131.9, 129.7 ($J_{C\text{-}F}$ = 8.1 Hz), 129.3, 128.8, 126.9 , 126.8, 125.2 ($J_{C\text{-}F}$ = 4.1 Hz) , 124.8, 123.4, 122.7, 122.4, 119.7 ($J_{C\text{-}F}$ = 22.2 Hz), 116.3 ($J_{C\text{-}F}$ = 23.2 Hz), 115.2, 82.9, 60.7, 44.1, 27.1, 26.9, 21.3;

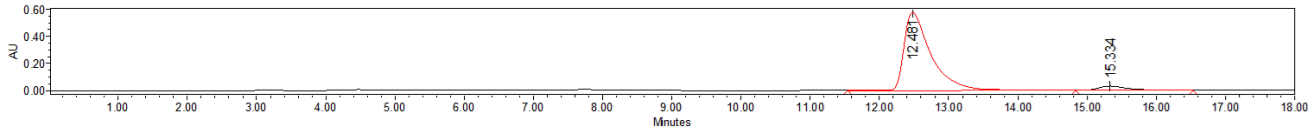
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –112.2.

IR: 2976, 1767, 1726, 1691, 1652, 1592, 1471, 1343, 1293, 1243, 1156, 754 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{32}H_{28}FNO_5Na^+$ 548.1844; Found 548.1841.

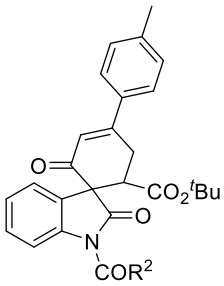


	Retention Time	Area	% Area
1	6.608	150841	2.73
2	7.850	147805	2.68
3	12.861	2604332	47.19
4	15.683	2615779	47.40



	Retention Time	Area	% Area
1	12.481	15696010	94.94
2	15.334	1013333	5.06

Tert-butyl 1'-(3-fluorobenzoyl)- 4-(4-methylphenyl)-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3cf R^2 = 3-FC_6H_4

Oil, 41.7 mg, 79% yield, 88% ee; $[\alpha]^{25}_D$ = +131.29 (*c* = 0.59 in CH_2Cl_2)

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 12.91 min, t_R (minor) = 33.31 min.

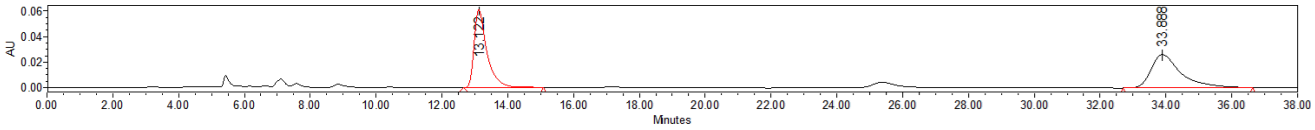
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.81 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.69 (ddd, *J* = 9.2, 2.6, 1.5 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.47 (td, *J* = 8.0, 5.4 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.34 – 7.27 (m, 3H), 7.19 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.13 (td, *J* = 7.5, 1.1 Hz, 1H), 6.60 – 6.57 (m, 1H), 3.96 (dd, *J* = 10.4, 7.5 Hz, 1H), 3.50 – 3.37 (m, 2H), 2.43 (s, 3H), 1.13 (s, 9H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 192.6, 175.7, 168.8, 167.9 ($J_{C\text{-}F}$ = 3.1 Hz), 162.2 ($J_{C\text{-}F}$ = 248.5 Hz), 158.3, 141.8, 141.0, 135.9 ($J_{C\text{-}F}$ = 7.1 Hz), 133.9, 129.7 ($J_{C\text{-}F}$ = 7.1 Hz), 129.6, 129.3, 126.9, 126.2, 125.2 ($J_{C\text{-}F}$ = 3.1 Hz), 124.8, 122.7, 121.6, 119.7 ($J_{C\text{-}F}$ = 21.2 Hz), 116.3 ($J_{C\text{-}F}$ = 24.2 Hz), 115.2, 82.9, 60.7, 44.1, 27.1, 26.7, 21.3;

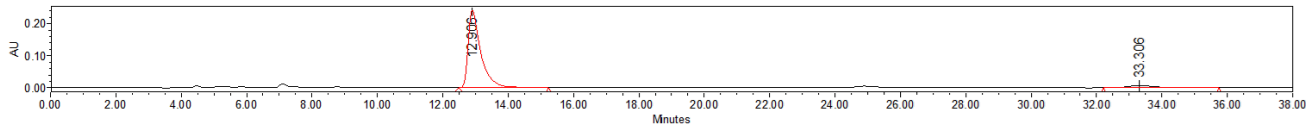
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –112.3.

IR: 2362, 1767, 1726, 1691, 1649, 1598, 1471, 1343, 1245, 1154, 754 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{32}H_{28}FNO_5Na^+$ 548.1844; Found 548.1848.

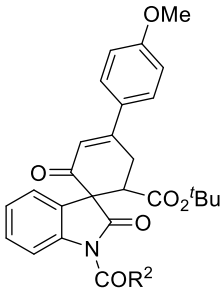


	Retention Time	Area	% Area
1	13.122	1652336	50.09
2	33.888	1646382	49.91



	Retention Time	Area	% Area
1	12.906	6480819	93.69
2	33.306	436510	6.31

Tert-butyl 1'-(3-fluorobenzoyl)- 4-(4-methoxyphenyl)-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3cg R^2 = 3-FC_6H_4

Oil; 53.7 mg, 99% yield, 87% ee; $[\alpha]^{25}_D$ = +149.90 (*c* = 0.92 in CH_2Cl_2)

HPLC DAICEL CHIRALCEL ID, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 24.86 min, t_R (minor) = 44.07 min.

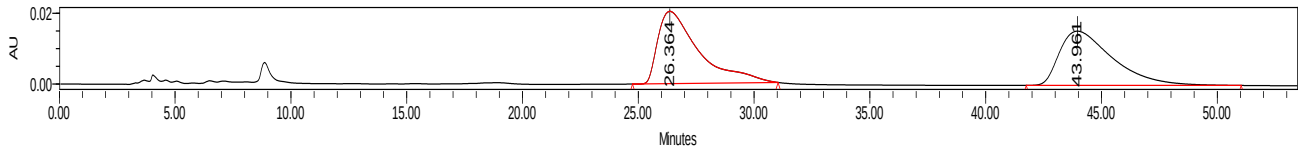
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.81 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.72 – 7.67 (m, 3H), 7.46 (td, *J* = 8.0, 5.5 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.32 – 7.27 (m, 1H), 7.19 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.12 (td, *J* = 7.5, 1.1 Hz, 1H), 7.02 – 6.98 (m, 2H), 6.56 (d, *J* = 1.6 Hz, 1H), 3.95 (dd, *J* = 9.6, 8.4 Hz, 1H), 3.88 (s, 3H), 3.43 – 3.41 (m, 2H), 1.13 (s, 9H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 192.5, 175.8, 168.8, 167.9 ($J_{C\text{-}F}$ = 3.0 Hz), 162.2 ($J_{C\text{-}F}$ = 247.5 Hz), 162.1, 157.7, 141.0, 135.9 ($J_{C\text{-}F}$ = 8.1 Hz), 129.7 ($J_{C\text{-}F}$ = 7.1 Hz), 129.2, 128.8, 128.0, 127.0, 125.2 ($J_{C\text{-}F}$ = 3.0 Hz), 124.8, 122.7, 120.5, 119.7 ($J_{C\text{-}F}$ = 21.2 Hz), 116.3 ($J_{C\text{-}F}$ = 24.2 Hz), 115.2, 114.3, 82.8, 60.6, 55.3, 44.1, 29.5, 27.1;

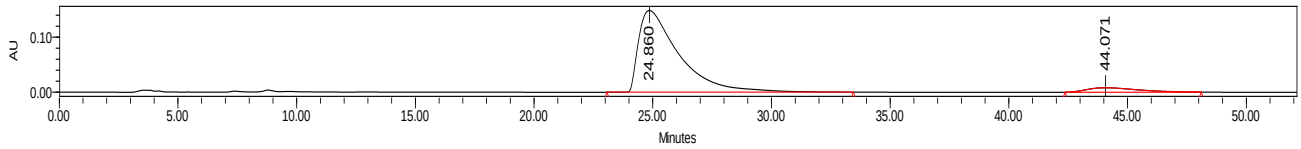
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –112.3.

IR: 2921, 2361, 1767, 1726, 1691, 1646, 1593, 1513, 1468, 1343, 1239, 1155, 1028, 755 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{32}H_{28}FNO_6Na^+$ 564.1793; Found 564.1793.

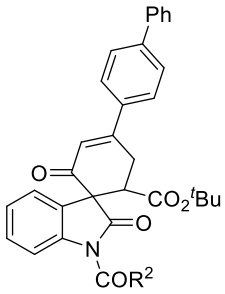


	Retention Time	Area	% Area
1	26.364	2519765	50.69
2	43.961	2451328	49.31



	Retention Time	Area	% Area
1	24.860	17581717	93.68
2	44.071	1187066	6.32

Tert-butyl 1'-(3-fluorobenzoyl)- 4-(4-phenylphenyl)-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3ch R^2 = 3-FC_6H_4

Oil; 58.5 mg, 99% yield, 99% ee; $[\alpha]^{25}_D$ = +149.15 (*c* = 1.06 in CH_2Cl_2)

HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 20.42 min, t_R (minor) = 32.96 min.

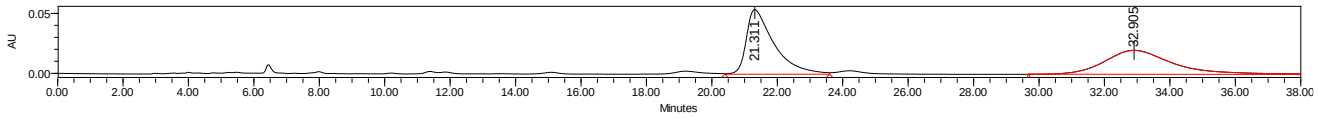
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.84 – 7.79 (m, 3H), 7.76 – 7.69 (m, 3H), 7.68 – 7.64 (m, 2H), 7.52 – 7.47 (m, 3H), 7.44 – 7.39 (m, 2H), 7.30 (tdd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 7.23 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.15 (td, *J* = 7.6, 1.1 Hz, 1H), 6.69 – 6.64 (m, 1H), 4.00 (dd, *J* = 10.6, 7.3 Hz, 1H), 3.57 – 3.47 (m, 2H), 1.15 (s, 9H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 192.5, 175.6, 168.7, 167.9 ($J_{C\text{-}F}$ = 3.0 Hz), 162.2 ($J_{C\text{-}F}$ = 248.5 Hz), 157.8, 143.9, 141.0, 139.5, 135.8 ($J_{C\text{-}F}$ = 7.1 Hz), 135.5, 129.7 ($J_{C\text{-}F}$ = 7.1 Hz), 129.3, 128.8, 128.0, 127.5, 126.9, 126.8, 126.7, 125.2 ($J_{C\text{-}F}$ = 3.0 Hz), 124.8, 122.7, 122.1, 119.7 ($J_{C\text{-}F}$ = 21.2 Hz), 116.3 ($J_{C\text{-}F}$ = 23.2 Hz), 115.3, 82.9, 60.7, 44.1, 27.1, 26.7;

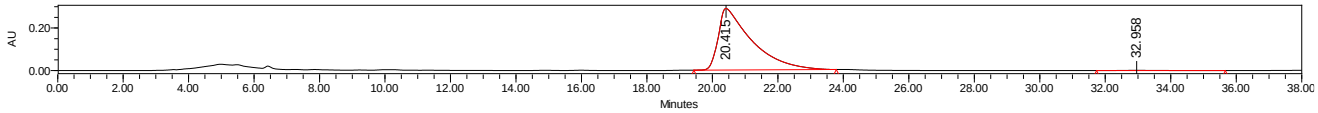
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –112.2.

IR: 2921, 2362, 1767, 1726, 1692, 1650, 1597, 1458, 1343, 1293, 1245, 1155, 757 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{37}H_{30}FNO_5Na^+$ 610.2000; Found 610.2000.

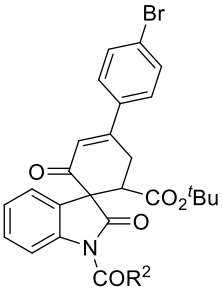


	Retention Time	Area	% Area
1	21.311	2910076	50.09
2	32.905	2899585	49.91



	Retention Time	Area	% Area
1	20.415	20514202	99.50
2	32.958	102460	0.50

Tert-butyl 1'-(3-fluorobenzoyl)- 4-(4-bromophenyl)-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



3ci R^2 = 3-FC_6H_4

Oil; 58.6 mg, 99% yield, 87% ee; $[\alpha]^{25}_D$ = +114.88 (*c* = 1.10 in CH_2Cl_2)

HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 21.11 min, t_R (minor) = 38.87 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.79 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.68 (ddd, *J* = 9.1, 2.7, 1.6 Hz, 1H), 7.64 – 7.61 (m, 2H), 7.58 – 7.54 (m, 2H), 7.48 – 7.45 (m, 1H), 7.40 (ddd, *J* = 8.1, 7.3, 1.7 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.18 – 7.11 (m, 2H), 6.59 – 6.54 (m, 1H), 3.96 (dd, *J* = 11.2, 6.6 Hz, 1H), 3.49 – 3.31 (m, 2H), 1.12 (s, 9H);

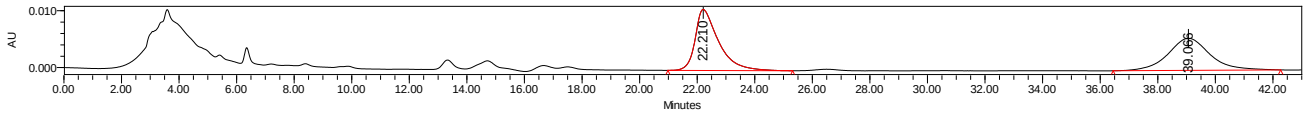
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 192.4, 175.5, 168.5, 167.8 ($J_{C\text{-}F}$ = 3.0 Hz), 162.2 ($J_{C\text{-}F}$ = 248.5 Hz), 157.0, 141.0, 135.7, 132.2, 132.1, 130.0, 129.7 ($J_{C\text{-}F}$ = 8.1 Hz), 129.4, 127.7, 126.6, 125.7, 125.1 ($J_{C\text{-}F}$ = 3.0 Hz), 124.8, 122.6 ($J_{C\text{-}F}$ = 11.1 Hz), 119.8 ($J_{C\text{-}F}$ = 21.2 Hz), 116.3 ($J_{C\text{-}F}$ = 24.2 Hz), 115.3, 83.0, 60.6, 44.0, 27.1, 26.7;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –112.2.

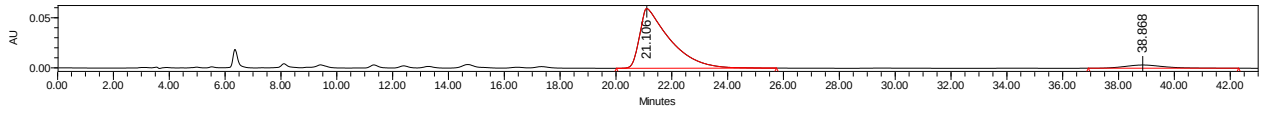
IR: 2923, 2362, 1764, 1725, 1692, 1652, 1587, 1479, 1342, 1292, 1245, 1154, 1073, 755 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{25}{}^{78.9183}BrFNO_5Na^+$ 612.0792; Found 612.0793.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{25}{}^{80.9163}BrFNO_5Na^+$ 614.0772; Found 614.0774.

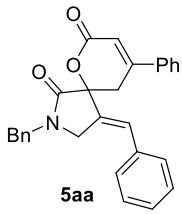


	Retention Time	Area	% Area
1	22.210	591006	50.78
2	39.066	572743	49.22



	Retention Time	Area	% Area
1	21.106	4467222	93.44
2	38.868	313760	6.56

(*E*)-2-Benzyl-4-benzylidene-9-phenyl-6-oxa-2-azaspiro[4.5]dec-8-ene-1,7-dione



5aa

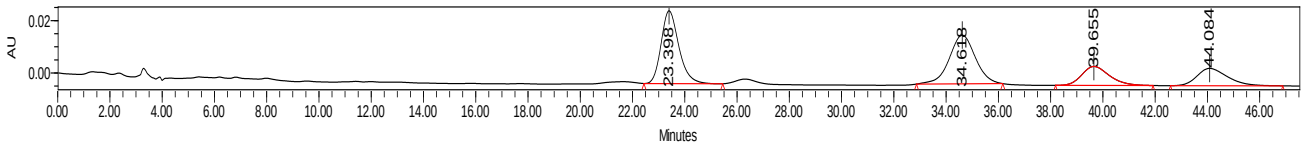
White solid; melting point: 197–198 °C; 35.5 mg, 84% yield, 89% ee; $[\alpha]^{25}_{D}$ = –5.07 (*c* = 0.41 in CH_2Cl_2) HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 37.27 min, t_R (minor) = 24.37 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 – 7.56 (m, 2H), 7.47 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.37 – 7.27 (m, 7H), 7.25 (d, *J* = 1.4 Hz, 1H), 7.16 – 7.14 (m, 2H), 6.91 (t, *J* = 2.4 Hz, 1H), 6.53 (t, *J* = 1.5 Hz, 1H), 4.57 (d, *J* = 1.7 Hz, 2H), 4.29 – 4.13 (m, 2H), 3.28 (ddd, *J* = 101.3, 18.0, 1.6 Hz, 2H);

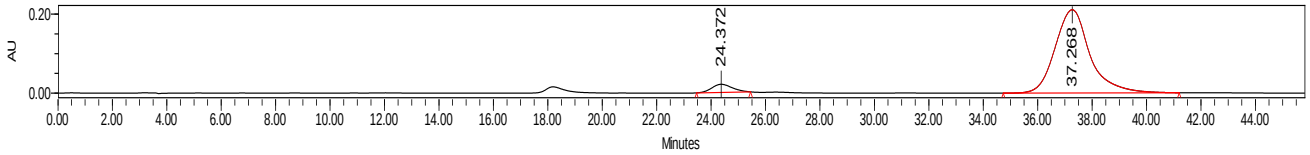
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.0, 163.3, 151.0, 135.9, 134.8, 134.4, 132.3, 130.6, 128.9, 128.8, 128.6, 128.5, 128.3, 127.9, 127.8, 125.9, 114.7, 99.8, 81.7, 48.0, 46.8, 33.2.

IR: 2362, 1697, 1489, 1447, 1365, 1270, 1242, 1110, 1071, 1025, 875, 752, 688 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{28}H_{24}NO_3^+$ 422.1756; Found 422.1767.

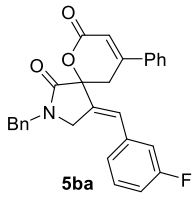


	Retention Time	Area	% Area
1	23.398	1306096	35.62
2	34.618	1289057	35.16
3	39.655	533919	14.56
4	44.084	537614	14.66



	Retention Time	Area	% Area
1	24.372	1080102	5.46
2	37.268	18690572	94.54

(*E*)-2-Benzyl-4-(3-fluorobenzylidene)-9-phenyl-6-oxa-2-azaspiro[4.5]dec-8-ene-1,7-dione



5ba

White solid; melting point: 181–183 °C; 33.0 mg, 75% yield, 88% ee; $[\alpha]^{25}_{D}$ = –11.69 (*c* = 0.40 in CH_2Cl_2) HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 21.87 min, t_R (minor) = 16.07 min.

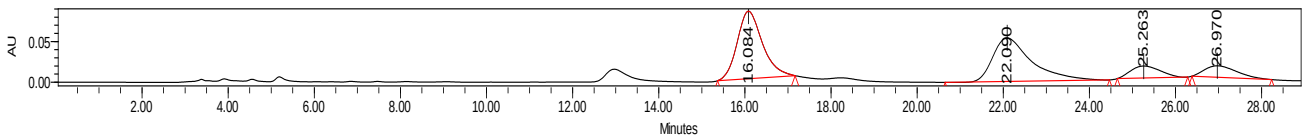
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 (dd, *J* = 6.8, 2.9 Hz, 2H), 7.47 (dd, *J* = 5.2, 1.9 Hz, 3H), 7.38 – 7.29 (m, 4H), 7.28 – 7.25 (m, 2H), 6.99 (td, *J* = 8.4, 2.4 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 2.4 Hz, 1H), 6.84 (dt, *J* = 9.9, 2.0 Hz, 1H), 6.53 (s, 1H), 4.57 (s, 2H), 4.26 – 4.11 (m, 2H), 3.40 – 3.11 (m, 2H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 168.9, 162.6 ($J_{C\text{-}F}$ = 247.5 Hz), 163.2, 150.8, 136.4 ($J_{C\text{-}F}$ = 7.1 Hz), 135.8, 134.7, 133.9, 130.7, 130.2 ($J_{C\text{-}F}$ = 8.1 Hz), 128.9, 128.8, 128.0 ($J_{C\text{-}F}$ = 2.0 Hz), 127.3, 125.9, 124.4 ($J_{C\text{-}F}$ = 3.0 Hz), 115.2 ($J_{C\text{-}F}$ = 21.2 Hz), 115.1 ($J_{C\text{-}F}$ = 21.2 Hz), 114.7, 81.5, 47.9, 46.8, 33.3;

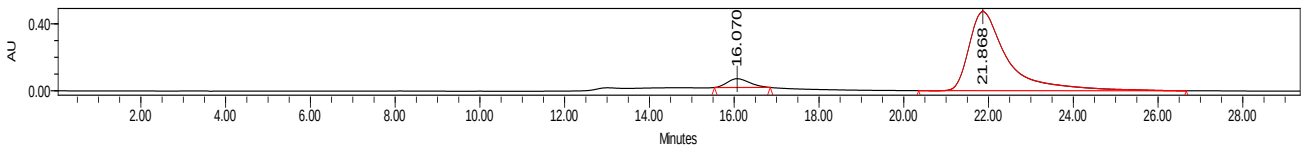
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –112.1.

IR: 2362, 1696, 1579, 1447, 1363, 1271, 1237, 1106, 1077, 875, 763, 680 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{28}H_{23}FNO_3^+$ 440.1662; Found 440.1651.

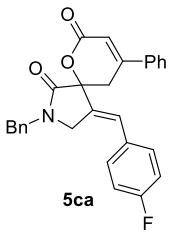


	Retention Time	Area	% Area
1	16.084	3377335	41.38
2	22.090	3344029	40.97
3	25.263	700980	8.59
4	26.970	740067	9.07



	Retention Time	Area	% Area
1	16.070	1913097	6.04
2	21.868	29780570	93.96

(*E*)-2-Benzyl-4-(4-fluorobenzylidene)-9-phenyl-6-oxa-2-azaspiro[4.5]dec-8-ene-1,7-dione



5ca

White solid; melting point: 183–185 °C; 32.1 mg, 73% yield, 90% ee; $[\alpha]^{25}_{D}$ = –7.88 (*c* = 0.37 in CH_2Cl_2) HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 22.45 min, t_R (minor) = 19.51 min.

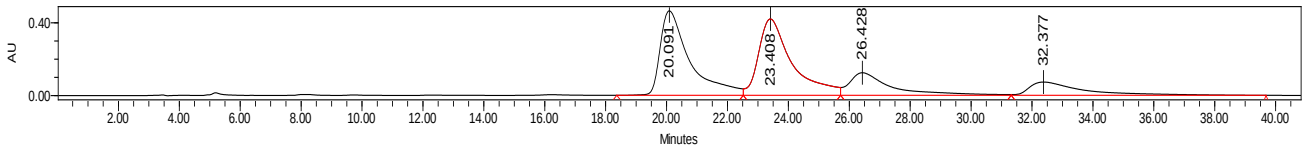
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 (dd, *J* = 6.8, 2.9 Hz, 2H), 7.47 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.34 (qd, *J* = 7.7, 6.9, 3.7 Hz, 3H), 7.26 (t, *J* = 4.4 Hz, 2H), 7.12 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.03 (t, *J* = 8.6 Hz, 2H), 6.87 (s, 1H), 6.52 (d, *J* = 2.0 Hz, 1H), 4.57 (s, 2H), 4.24 – 4.08 (m, 2H), 3.41 – 3.11 (m, 2H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.0, 163.3, 162.3 ($J_{C\text{-}F}$ = 250.5 Hz), 150.9, 135.8, 134.8, 132.1, 130.6, 130.5 ($J_{C\text{-}F}$ = 3.0 Hz), 130.3 ($J_{C\text{-}F}$ = 8.1 Hz), 128.9, 128.8, 128.0, 127.9, 127.3, 125.9, 115.7 ($J_{C\text{-}F}$ = 21.2 Hz), 114.7, 81.6, 47.90 , 46.8, 33.2;

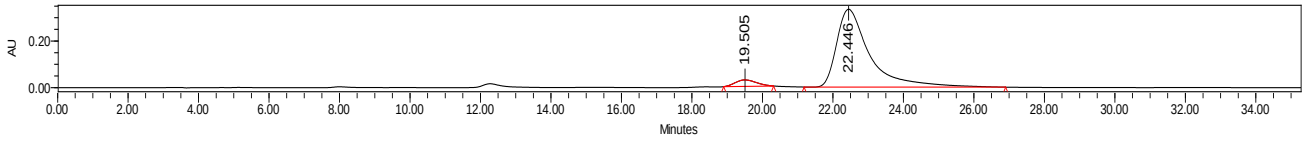
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –111.9.

IR: 2362, 1691, 1505, 1416, 1273, 1225, 1102, 1072, 1020, 822, 761, 679 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{28}H_{23}FNO_3^+$ 440.1662; Found 440.1661.

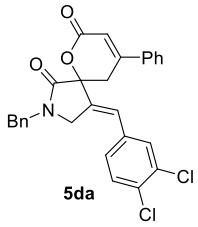


	Retention Time	Area	% Area
1	20.091	31273692	37.14
2	23.408	31951373	37.95
3	26.428	11978837	14.23
4	32.377	8991032	10.68



	Retention Time	Area	% Area
1	19.505	1151873	5.01
2	22.446	21850892	94.99

(*E*)-2-Benzyl-4-(3,4-dichlorobenzylidene)-9-phenyl-6-oxa-2-azaspiro[4.5]dec-8-ene-1,7-dione



5da

White solid; melting point: 178–180 °C; 41.8 mg, 85% yield, 87% ee; $[\alpha]^{25}_{D}$ = –5.02 (*c* = 0.46 in CH_2Cl_2) HPLC DAICEL CHIRALCEL IB , *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 36.34 min, t_R (minor) = 31.94 min.

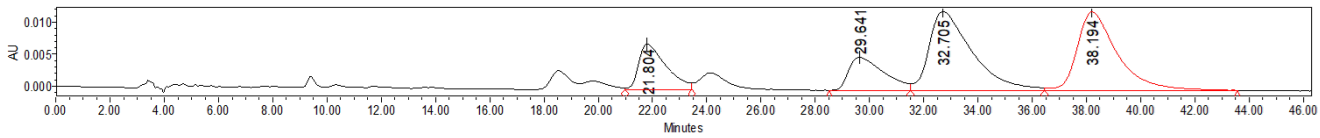
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 – 7.56 (m, 2H), 7.47 (dd, *J* = 5.3, 1.9 Hz, 3H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.26 – 7.22 (m, 3H), 6.98 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.81 (s, 1H), 6.52 (s, 1H), 4.56 (s, 2H), 4.22 – 4.08 (m, 2H), 3.39 – 3.09 (m, 2H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 168.8, 163.1, 150.6, 135.7, 134.7, 134.6, 134.3, 132.8, 132.4, 130.7, 130.6, 130.1, 128.9, 128.9, 128.0, 127.9, 127.5, 126.1, 125.9, 114.6, 81.38, 47.69, 46.76, 33.29.

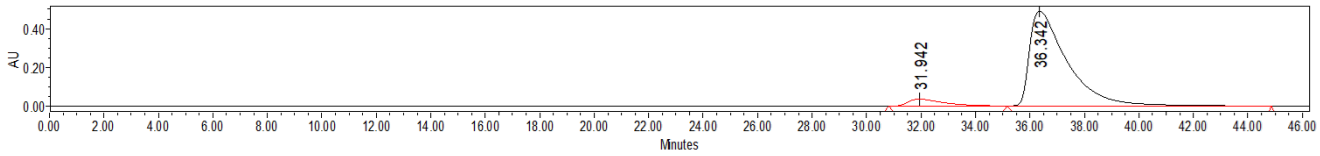
IR: 2362, 1708, 1475, 1446, 1364, 1245, 1109, 765, 698 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{28}H_{22}{}^{34.9689}Cl_2NO_3^+$ 490.0971; Found 490.0968.

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{28}H_{22}{}^{36.9659}Cl_2NO_3^+$ 494.0911; Found 494.0910.

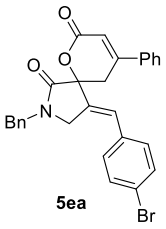


	Retention Time	Area	% Area
1	21.804	500458	13.95
2	29.641	469707	13.09
3	32.705	1355148	37.77
4	38.194	1263033	35.20



	Retention Time	Area	% Area
1	31.942	3360317	6.67
2	36.342	47043512	93.33

(*E*)-2-Benzyl-4-(4-bromobenzylidene)-9-phenyl-6-oxa-2-azaspiro[4.5]dec-8-ene-1,7-dione



5ea

White solid; melting point: 164–166 °C; 35.6 mg, 71% yield, 87% ee; $[\alpha]^{25}_{D}$ = –1.43 (*c* = 0.63 in CH_2Cl_2) HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 41.38 min, t_R (minor) = 32.09 min.

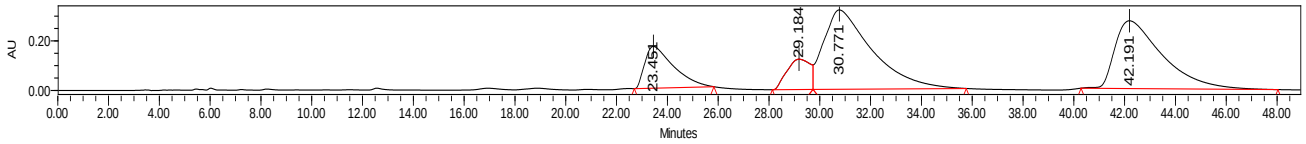
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (dt, *J* = 6.8, 2.2 Hz, 2H), 7.48 – 7.43 (m, 5H), 7.37 – 7.30 (m, 3H), 7.27 – 7.24 (m, 2H), 7.02 – 6.98 (m, 2H), 6.84 (d, *J* = 2.4 Hz, 1H), 6.52 (d, *J* = 1.6 Hz, 1H), 4.56 (s, 2H), 4.22 – 4.07 (m, 2H), 3.25 (ddd, *J* = 100.3, 18.0, 1.6 Hz, 2H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 168.9, 163.2, 150.8, 135.8, 134.7, 133.3, 133.2, 131.8, 130.6, 129.9, 128.9, 128.8, 128.0, 127.3, 125.9, 122.4, 114.7, 81.5, 47.9 , 46.8, 33.3.

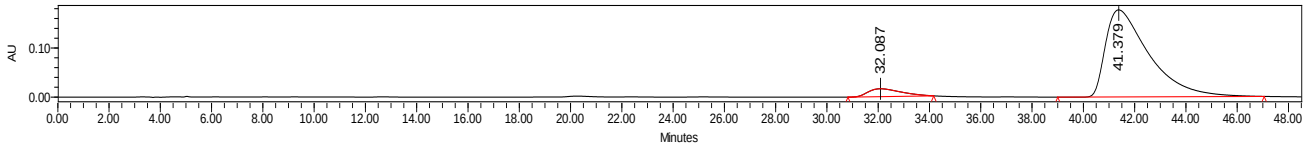
IR: 2362, 1694, 1485, 1364, 1268, 1238, 1006, 874, 763, 695 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{28}H_{23}{}^{78.9183}BrNO_3{}^+$ 500.0856; Found 500.0883.

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{28}H_{23}{}^{80.9163}BrNO_3{}^+$ 502.0835; Found 502.0863.

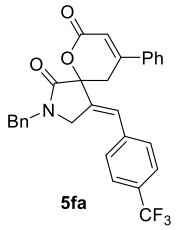


	Retention Time	Area	% Area
1	23.451	13209034	13.36
2	29.184	7745921	7.83
3	30.771	42413489	42.88
4	42.191	35537941	35.93



	Retention Time	Area	% Area
1	32.087	1447576	6.48
2	41.379	20907090	93.52

(*E*)-2-Benzyl-4-(4-(trifluoromethyl)benzylidene)-9-phenyl-6-oxa-2-azaspiro[4.5]dec-8-ene-1,7-dione



5fa

White solid; melting point: 153–156 °C; 35.4 mg, 72% yield, 83% ee; $[\alpha]^{25}_{D}$ = –11.35 (*c* =0.65 in CH_2Cl_2)

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 39.31 min, t_R (minor) = 26.59 min.

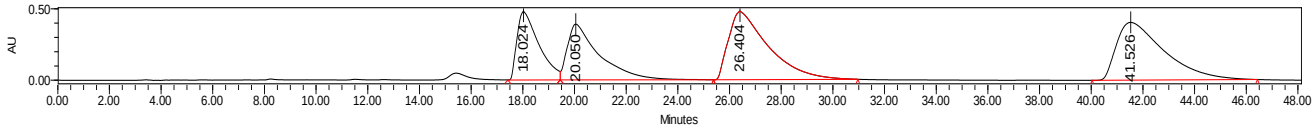
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 – 7.54 (m, 4H), 7.46 (dd, *J* = 5.2, 2.0 Hz, 3H), 7.36 – 7.30 (m, 3H), 7.26 – 7.24 (m, 4H), 6.94 (s, 1H), 6.52 (d, *J* = 1.6 Hz, 1H), 4.56 (s, 2H), 4.24 – 4.11 (m, 2H), 3.26 (ddd, *J* = 95.4, 18.0, 1.6 Hz, 2H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 168.8, 163.1, 150.6, 137.8, 135.7, 135.2, 134.7, 130.7, 130.0 ($J_{C\text{-}F}$ = 33.3 Hz), 128.9, 128.8, 128.7, 128.0, 127.0, 125.9, 125.5 ($J_{C\text{-}F}$ = 4.0 Hz), 123.6 ($J_{C\text{-}F}$ = 272.7 Hz), 114.7, 81.4, 47.8, 46.8, 33.4;

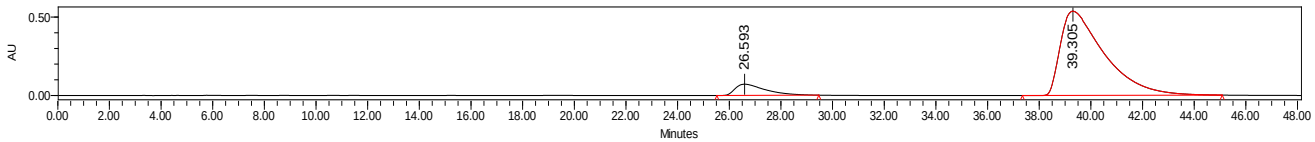
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –62.7.

IR: 2362, 1698, 1617, 1448, 1363, 1321, 1264, 1112, 1067, 1013, 828, 761, 695 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{29}H_{23}F_3NO_3^+$ 490.1625; Found 490.1632.

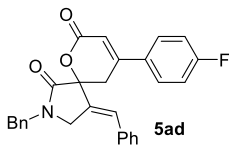


	Retention Time	Area	% Area
1	18.024	28191909	17.12
2	20.050	33589480	20.39
3	26.404	50983837	30.95
4	41.526	51952279	31.54



	Retention Time	Area	% Area
1	26.593	5847883	8.44
2	39.305	63453571	91.56

(*E*)-2-Benzyl-4-benzylidene-9-(4-fluorophenyl)-6-oxa-2-azaspiro[4.5]dec-8-ene-1,7-dione



5ad

White solid; melting point: 141–144°C; 36.2 mg, 82% yield, 97% ee; $[\alpha]^{25}_{D}$ = –8.13 (*c* = 0.41 in CH_2Cl_2) HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 23.23 min, t_R (minor) = 33.82 min.

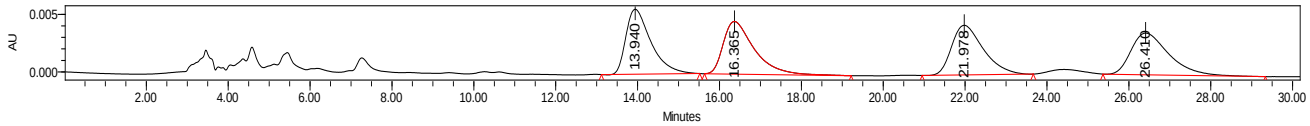
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 (dd, *J* = 8.6, 5.2 Hz, 2H), 7.32 (dq, *J* = 12.3, 6.7 Hz, 6H), 7.27 – 7.25 (m, 2H), 7.15 (dt, *J* = 8.6, 4.8 Hz, 4H), 6.90 (s, 1H), 6.48 (s, 1H), 4.56 (s, 2H), 4.21 (ddd, *J* = 48.4, 14.3, 2.3 Hz, 2H), 3.36 – 3.10 (m, 2H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.0, 164.0 ($J_{C\text{-}F}$ = 253.5 Hz), 163.2, 149.6, 134.8, 134.3, 132.2, 132.0 ($J_{C\text{-}F}$ = 3.0 Hz), 128.8, 128.6, 128.5, 128.3, 128.0,128.0, 127.9, 127.9, 116.1 ($J_{C\text{-}F}$ = 21.2 Hz), 114.5, 81.5, 48.1, 46.8, 33.4;

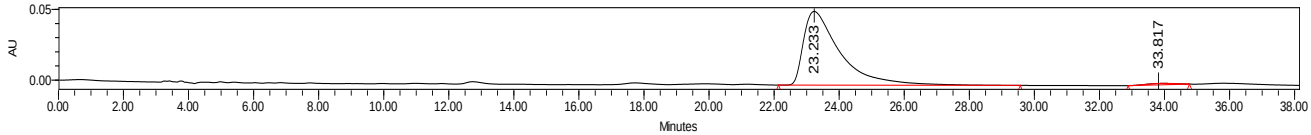
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = –108.9.

IR: 2360, 1699, 1599, 1510, 1413, 1358, 1232, 1162, 1073, 1017, 832, 753, 696 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{28}H_{22}FNO_3Na^+$ 462.1476; Found 462.1480.

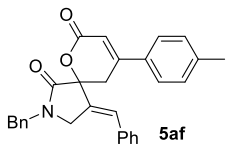


	Retention Time	Area	% Area
1	13.940	240447	25.39
2	16.365	240954	25.44
3	21.978	232033	24.50
4	26.410	233599	24.67



	Retention Time	Area	% Area
1	23.233	4069565	98.56
2	33.817	59271	1.44

(*E*)-2-Benzyl-4-benzylidene-9-(4-methylphenyl)-6-oxa-2-azaspiro[4.5]dec-8-ene-1,7-dione



5af

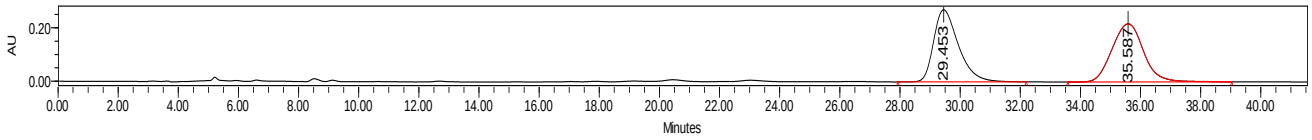
White solid; melting point: 134–137 °C; 29.3 mg, 67% yield, 86% ee; $[\alpha]^{25}_{D}$ = +13.39 (*c* =0.34 in CH_2Cl_2) HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 35.40 min, t_R (minor) = 29.06 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 (d, *J* = 8.0 Hz, 2H), 7.33 (dt, *J* = 12.1, 6.1 Hz, 5H), 7.28 (m, 5H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.89 (s, 1H), 6.50 (s, 1H), 4.57 (s, 2H), 4.20 (ddd, *J* = 56.6, 14.2, 2.3 Hz, 2H), 3.26 (ddd, *J* = 114.5, 18.0, 1.5 Hz, 2H), 2.41 (s, 3H);

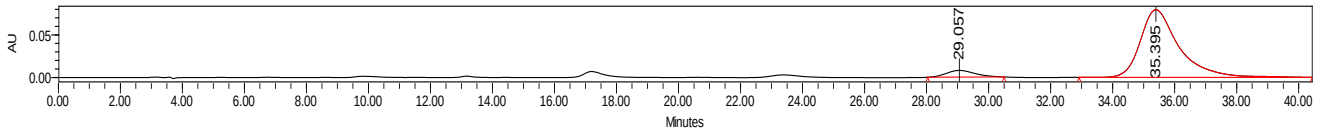
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.1, 163.5, 151.0, 141.2, 134.9, 134.4, 132.9, 132.5, 129.6, 128.8, 128.6, 128.5, 128.4, 128.2, 128.0, 127.9, 125.8, 113.7, 81.7, 48.1, 46.8, 33.0, 21.2.

IR: 2362, 1693, 1610, 1447, 1360, 1270, 1022, 947, 815, 759, 694 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{29}H_{26}NO_3^+$ 436.1913; Found 436.1911.

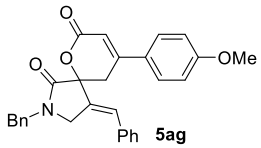


	Retention Time	Area	% Area
1	29.453	15484044	49.41
2	35.587	15850731	50.59



	Retention Time	Area	% Area
1	29.057	504832	6.85
2	35.395	6870310	93.15

(*E*)-2-Benzyl-4-benzylidene-9-(4-methoxyphenyl)-6-oxa-2-azaspiro[4.5]dec-8-ene-1,7-dione



5ag

White solid; melting point: 147–150 °C; 28.1 mg, 62% yield, 78% ee; $[\alpha]^{25}_{D}$ = +27.8 (*c* =0.32 in CH_2Cl_2)

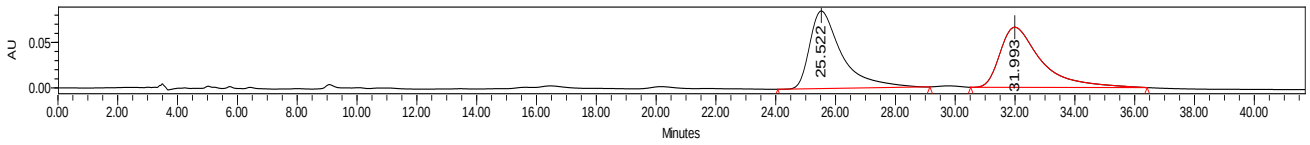
HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 31.97 min, t_R (minor) = 25.68 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.29 (m, 5H), 7.27 (d, *J* = 6.5 Hz, 3H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.89 (s, 1H), 6.45 (d, *J* = 1.7 Hz, 1H), 4.57 (s, 2H), 4.20 (ddd, *J* = 58.4, 14.2, 2.3 Hz, 2H), 3.87 (s, 3H), 3.25 (ddd, *J* = 117.6, 17.9, 1.6 Hz, 2H);

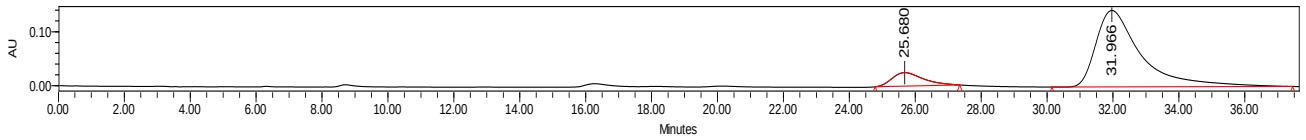
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.1, 163.6, 161.6, 150.5, 134.9, 134.4, 132.5, 128.8, 128.6, 128.5, 128.4, 128.2, 128.0, 127.9, 127.5, 114.3, 112.4, 81.6, 55.3, 48.1, 46.8, 32.8.

IR: 2362, 1694, 1602, 1516, 1421, 1362, 1245, 1182, 1115, 1023, 829, 753, 691 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{29}H_{26}NO_4^+$ 452.1862; Found 452.1843.

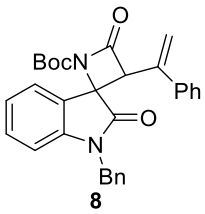


	Retention Time	Area	% Area
1	25.522	6341578	49.99
2	31.993	6343205	50.01



	Retention Time	Area	% Area
1	25.680	1664538	11.00
2	31.966	13461984	89.00

Tert-butyl 1'-benzyl-2',4-dioxo-3-(1-phenylvinyl)spiro[azetidine-2,3'-indoline]-1-carboxylate



8

Oil.

Reacted for 24 h: 27.0 mg, 56% yield, 50% ee; $[\alpha]^{25}_{D}$ = +36.8 (*c* = 0.59 in CH_2Cl_2)

HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 9.57 min, t_R (minor) = 18.78 min.

Reacted for 36 h: 31.4 mg, 65% yield, 60% ee; $[\alpha]^{25}_{D}$ = +57.5 (*c* =0.35 in CH_2Cl_2)

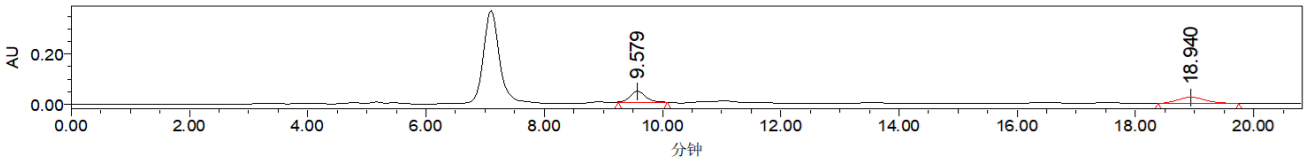
HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 9.56 min, t_R (minor) = 18.80 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.23 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.14 (dd, *J* = 6.7, 2.8 Hz, 2H), 7.09 – 7.02 (m, 2H), 6.92 (td, *J* = 7.6, 5.3 Hz, 3H), 6.81 (dd, *J* = 7.6, 1.6 Hz, 2H), 6.45 (d, *J* = 7.8 Hz, 1H), 5.80 (d, *J* = 1.8 Hz, 1H), 5.62 (d, *J* = 1.2 Hz, 1H), 5.05 – 4.95 (m, 2H), 4.64 (d, *J* = 15.7 Hz, 1H), 1.28 (s, 9H);

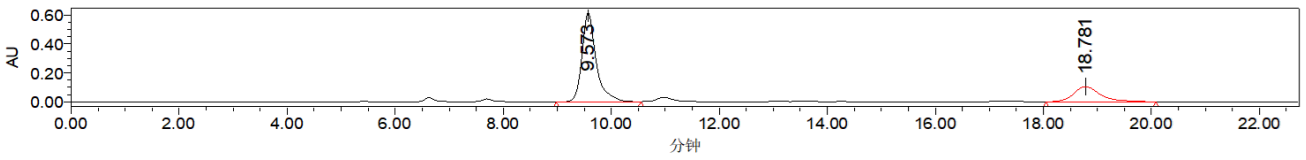
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.1, 163.6, 161.6, 150.5, 134.9, 134.4, 132.5, 128.8, 128.6, 128.5, 128.4, 128.2, 128.0, 127.9, 127.5, 114.3, 112.4, 81.6, 55.3, 48.1, 46.8, 32.8.

IR: 2979, 2362, 1813, 1721, 1613, 1490, 1465, 1311, 1261, 1183, 1152, 1080, 908, 733, 697 cm^{-1}.

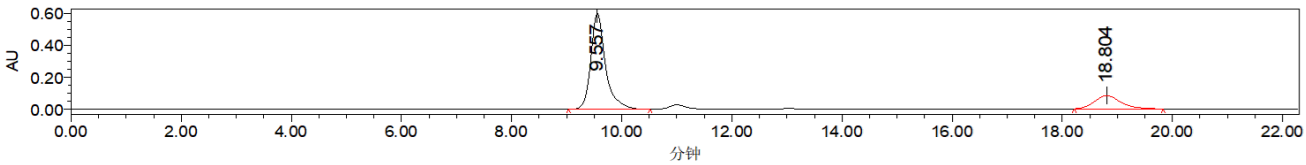
HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{30}H_{28}N_2O_4Na^+$ 503.1941; Found 503.1941.



	Retention Time	Area	% Area
1	9.579	788597	49.50
2	18.940	804432	50.50

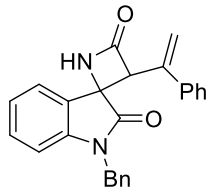


	Retention Time	Area	% Area
1	9.573	11210468	75.22
2	18.781	3692847	24.78



	Retention Time	Area	% Area
1	9.557	11106545	79.98
2	18.804	2779806	20.02

1'-Benzyl-3-(1-phenylvinyl)spiro[azetidine-2,3'-indoline]-2',4-dione



9

Oil.

Reacted for 24 h: 10.4 mg, 27% yield, 70% ee; $[\alpha]^{25}_{D}$ = –140.4 (*c* = 0.17 in CH_2Cl_2)

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 9.62 min, t_R (minor) = 15.63 min.

Reacted for 36 h: 11.4 mg, 30% yield, 63% ee; $[\alpha]^{25}_{D}$ = –128.7 (*c* = 0.18 in CH_2Cl_2)

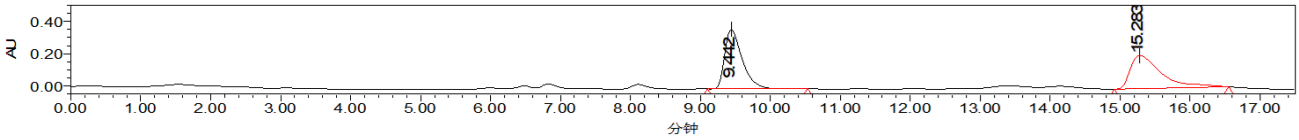
HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 9.65 min, t_R (minor) = 15.68 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 – 7.27 (m, 4H), 7.10 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.07 – 7.01 (m, 2H), 6.97 – 6.90 (m, 3H), 6.78 (dd, *J* = 8.1, 1.4 Hz, 2H), 6.45 (d, *J* = 7.8 Hz, 1H), 6.30 (s, 1H), 5.79 (d, *J* = 1.8 Hz, 1H), 5.59 (s, 1H), 5.00 – 4.93 (m, 2H), 4.62 (dd, *J* = 15.7, 3.5 Hz, 1H);

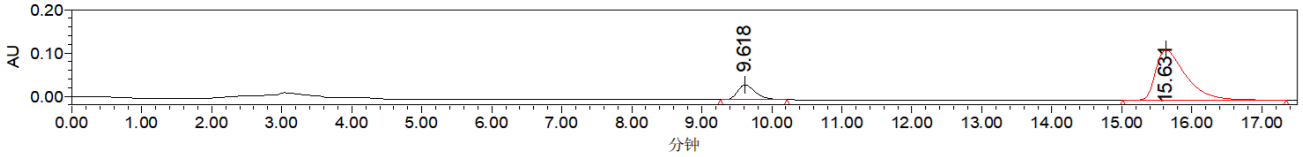
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 175.2, 167.0, 142.6, 139.5, 137.9, 135.0, 129.9, 128.7, 127.9, 127.6, 127.5, 127.1, 125.1, 124.8, 123.6, 122.4, 116.4, 108.9, 66.0, 60.4, 44.1.

IR: 3279, 2977, 2362, 1814, 1770, 1723, 1613, 1490, 1466, 1184, 1153, 1079, 914, 732, 697 cm^{-1}.

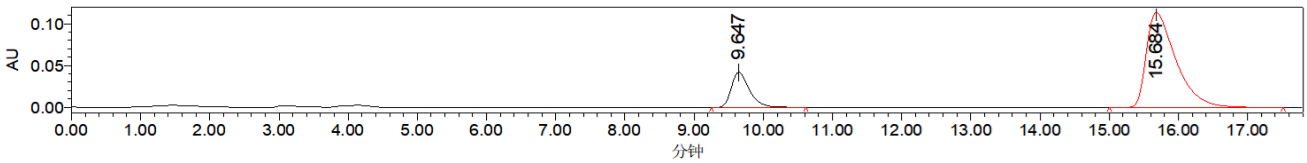
HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{25}H_{20}N_2O_2Na^+$ 403.1417; Found 403.1432.



	Retention Time	Area	% Area
1	9.442	6325132	50.20
2	15.283	6275960	49.80

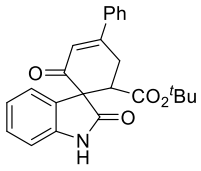


	Retention Time	Area	% Area
1	9.618	612286	15.19
2	15.631	3417276	84.81



	Retention Time	Area	% Area
1	9.647	770727	18.56
2	15.684	3380815	81.44

Tert-butyl 4-phenyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



11

White solid; melting point: 199–202 °C; 34.3 mg, 88% yield, 93% ee; $[\alpha]^{25}_{D}$ = +346.05 (*c* = 0.54 in CH_2Cl_2).

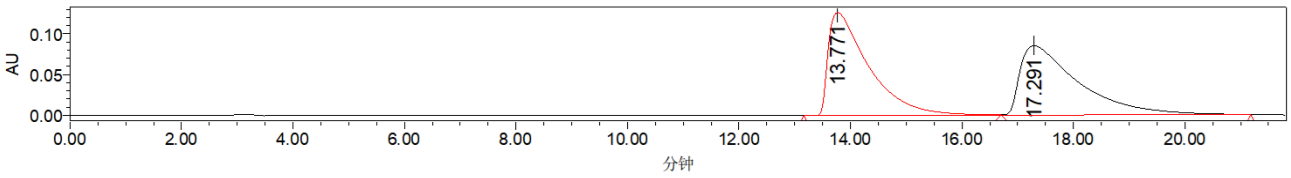
HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 13.53 min, t_R (minor) = 18.24 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.56 (s, 1H), 7.70 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.49 (hept, *J* = 4.4 Hz, 3H), 7.23 (d, *J* = 15.3 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.97 – 6.90 (m, 2H), 6.61 (s, 1H), 3.96 (dd, *J* = 11.1, 6.4 Hz, 1H), 3.56 – 3.29 (m, 2H), 1.19 (s, 9H);

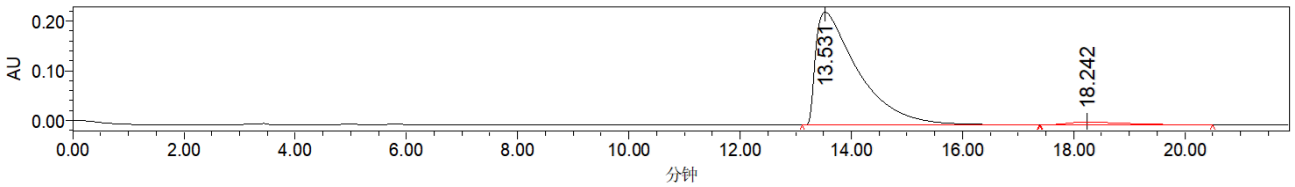
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 193.0, 177.7, 169.5, 157.9, 142.4, 137.5, 131.1, 129.4, 129.2, 127.8, 126.5, 123.6, 123.5, 122.5, 110.7, 82.72, 61.25, 44.78, 27.57, 27.36.

IR: 3273, 2979, 1726, 1656, 1615, 1472, 1333, 1248, 1156, 751, 695 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{24}H_{23}O_4Na^+$ 412.1519; Found 412.1517.

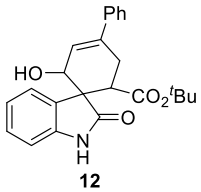


	Retention Time	Area	% Area
1	13.771	6350249	50.61
2	17.291	6196340	49.39



	Retention Time	Area	% Area
1	13.531	12097113	96.50
2	18.242	438731	3.50

Tert-butyl 2-hydroxy-4-phenyl-2'-oxospiro[cyclohexane-1,3'-indolin]-3-ene-6-carboxylate



12

White solid; melting point: 102–106 °C; 17.2 mg, 44% yield, 90% ee; $[\alpha]^{25}_D$ = +147.6 (*c* = 0.13 in CH_2Cl_2).

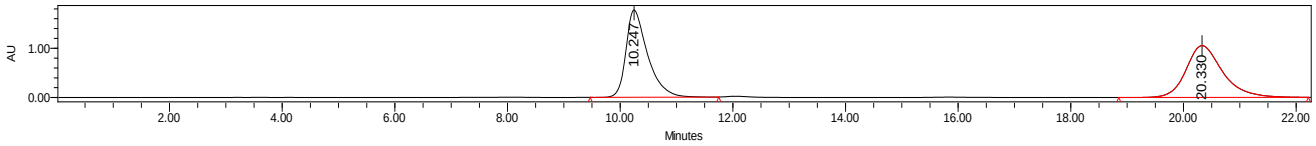
HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 20.55 min, t_R (minor) = 10.44 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.25 (s, 1H), 7.57 – 7.54 (m, 2H), 7.44 – 7.33 (m, 3H), 7.25 – 7.21 (m, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.96 – 6.90 (m, 2H), 6.13 (q, *J* = 1.9 Hz, 1H), 4.90 – 4.86 (m, 1H), 3.44 (dd, *J* = 10.6,)7.1 Hz, 1H), 3.13 – 2.97 (m, 2H), 2.10 – 2.08 (m, 1H), 1.23 (s, 9H);

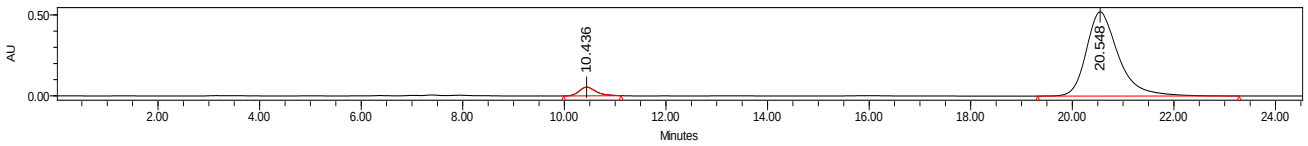
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 180.4, 169.9, 142.5, 138.9, 136.9, 128.6, 128.5, 128.0, 126.5, 126.5, 125.3, 125.1, 122.2, 109.7, 81.64, 73.2, 54.6, 44.6, 27.5.

IR: 2964, 2362, 1707, 1619, 1468, 1259, 1153, 1020, 796, 752, 688 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{24}H_{25}NO_4Na^+$ 414.1676; Found 414.1676.

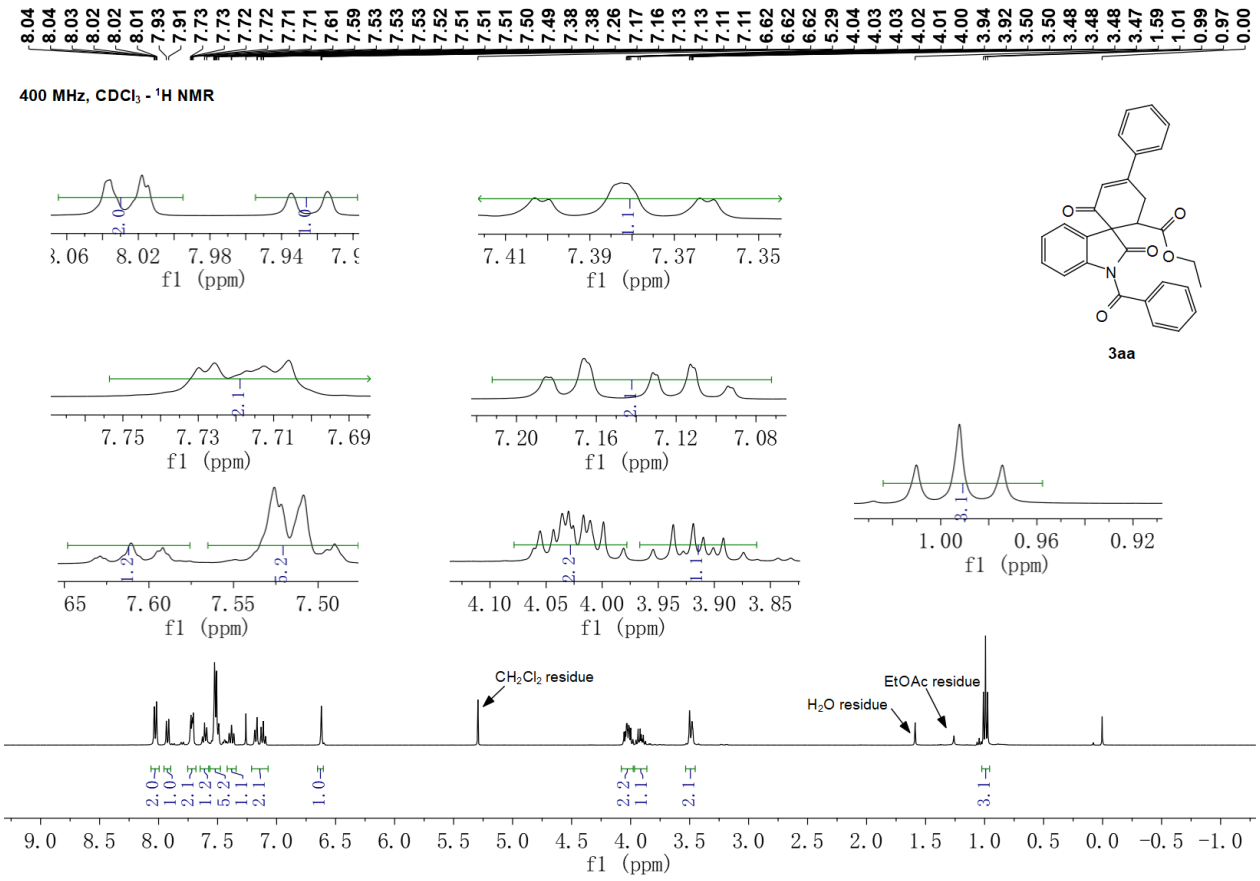


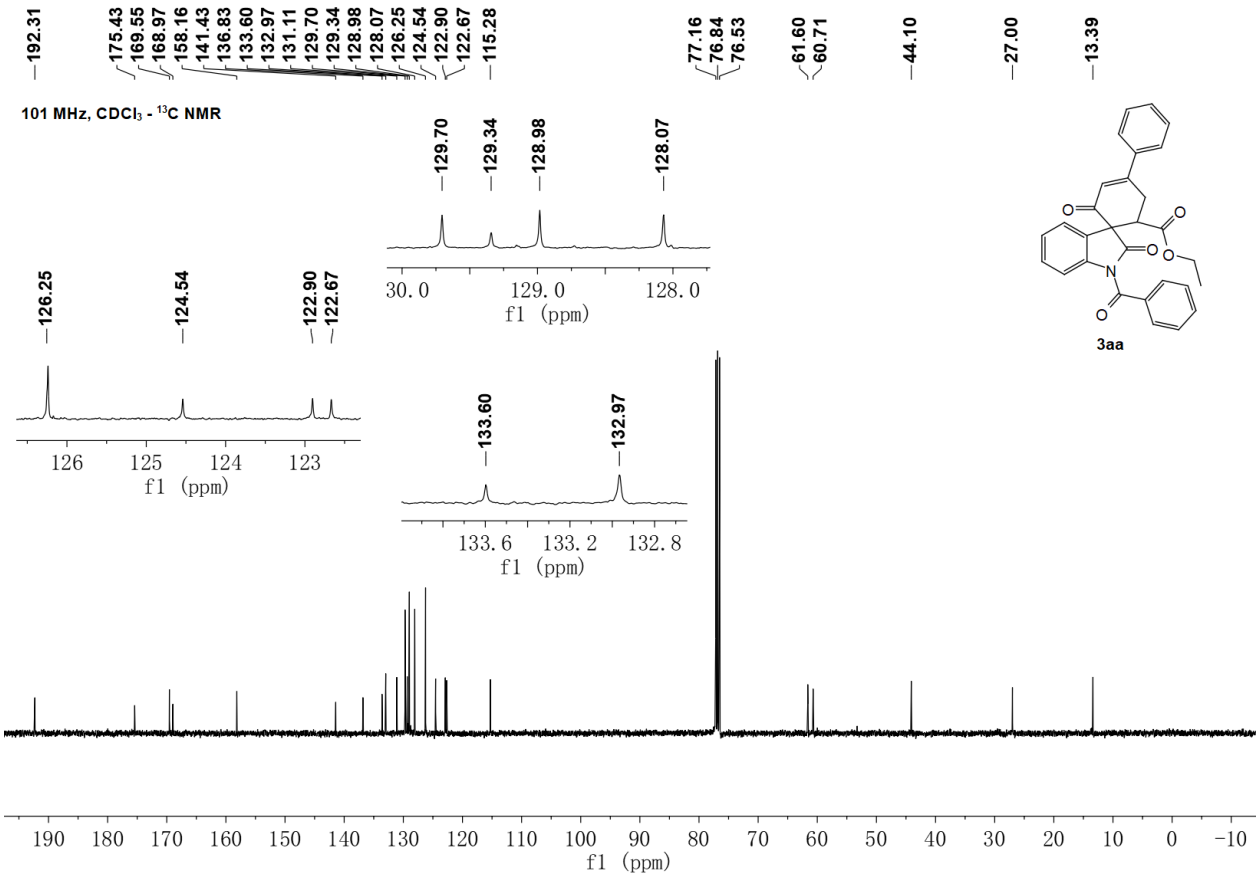
	Retention Time	Area	% Area
1	10.247	47209353	49.82
2	20.330	47555912	50.18



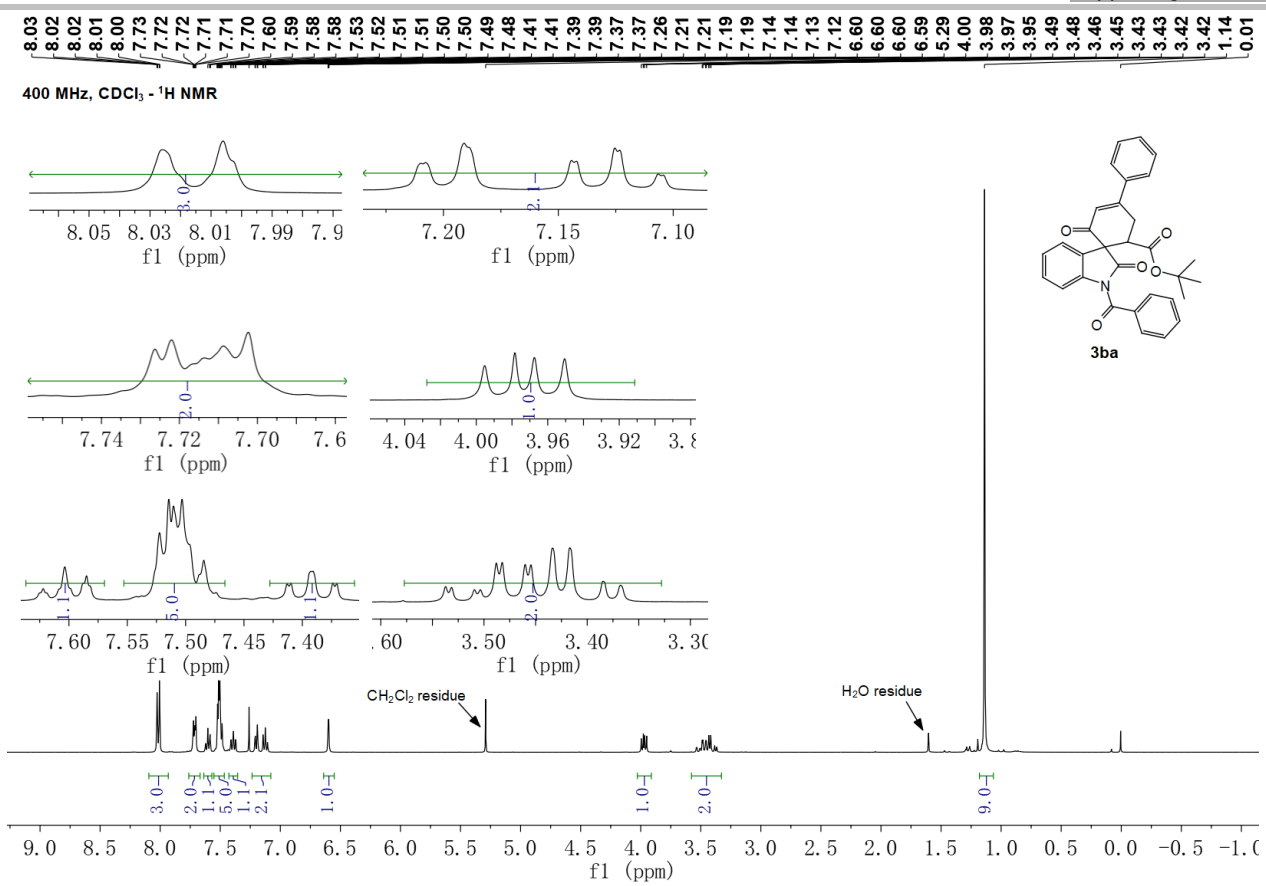
	Retention Time	Area	% Area
1	10.436	1234086	5.15
2	20.548	22736543	94.85

14 Copies of NMR spectra for products

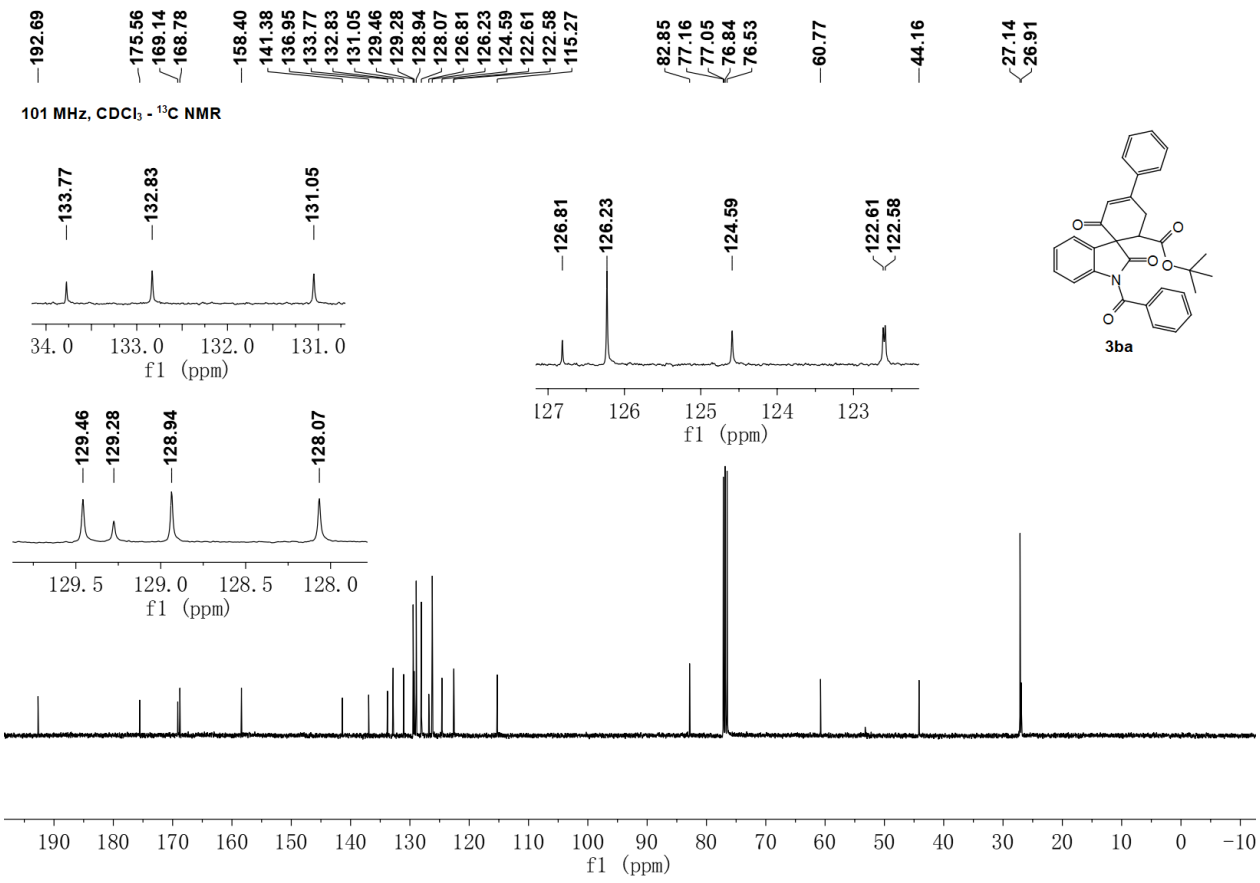


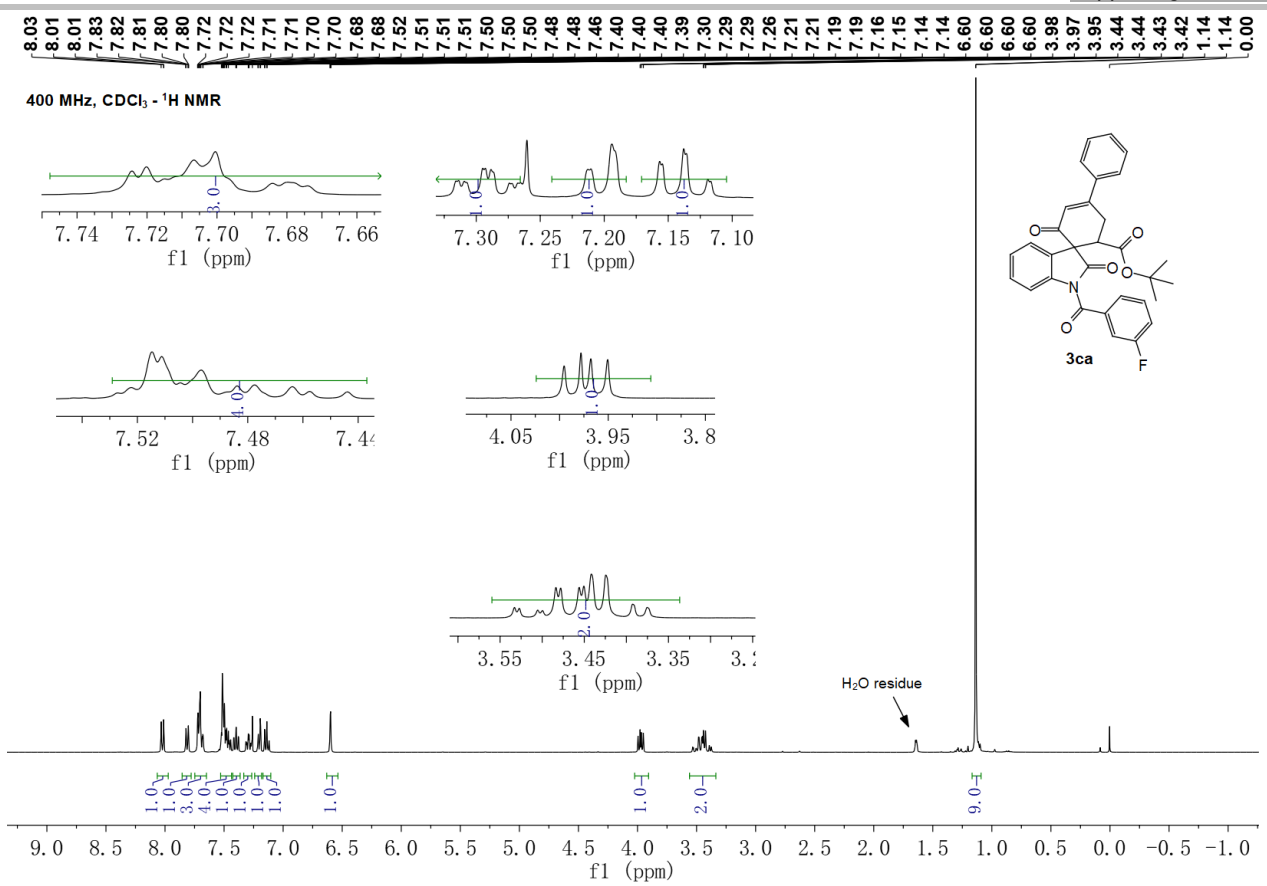


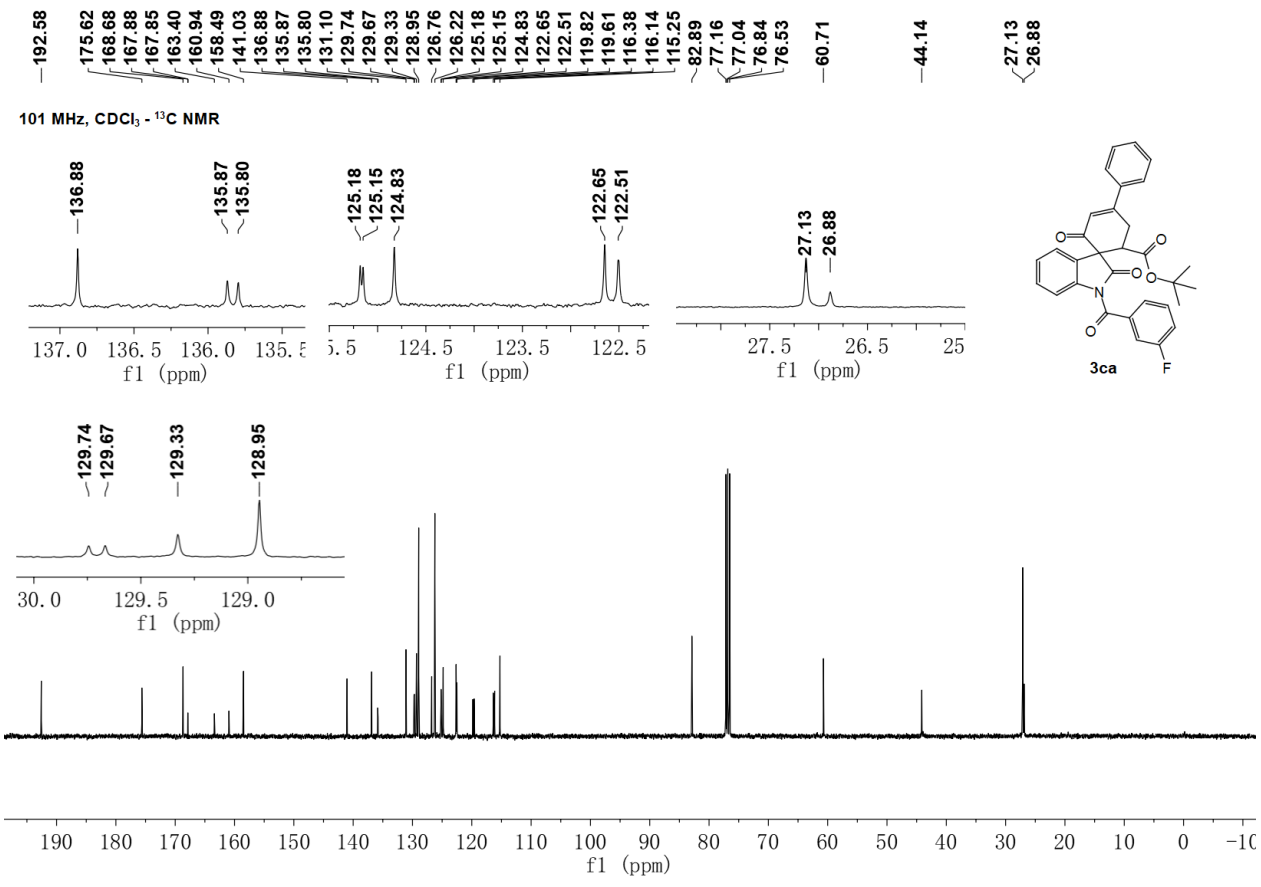
400 MHz, $CDCl_3$ - ^1H NMR



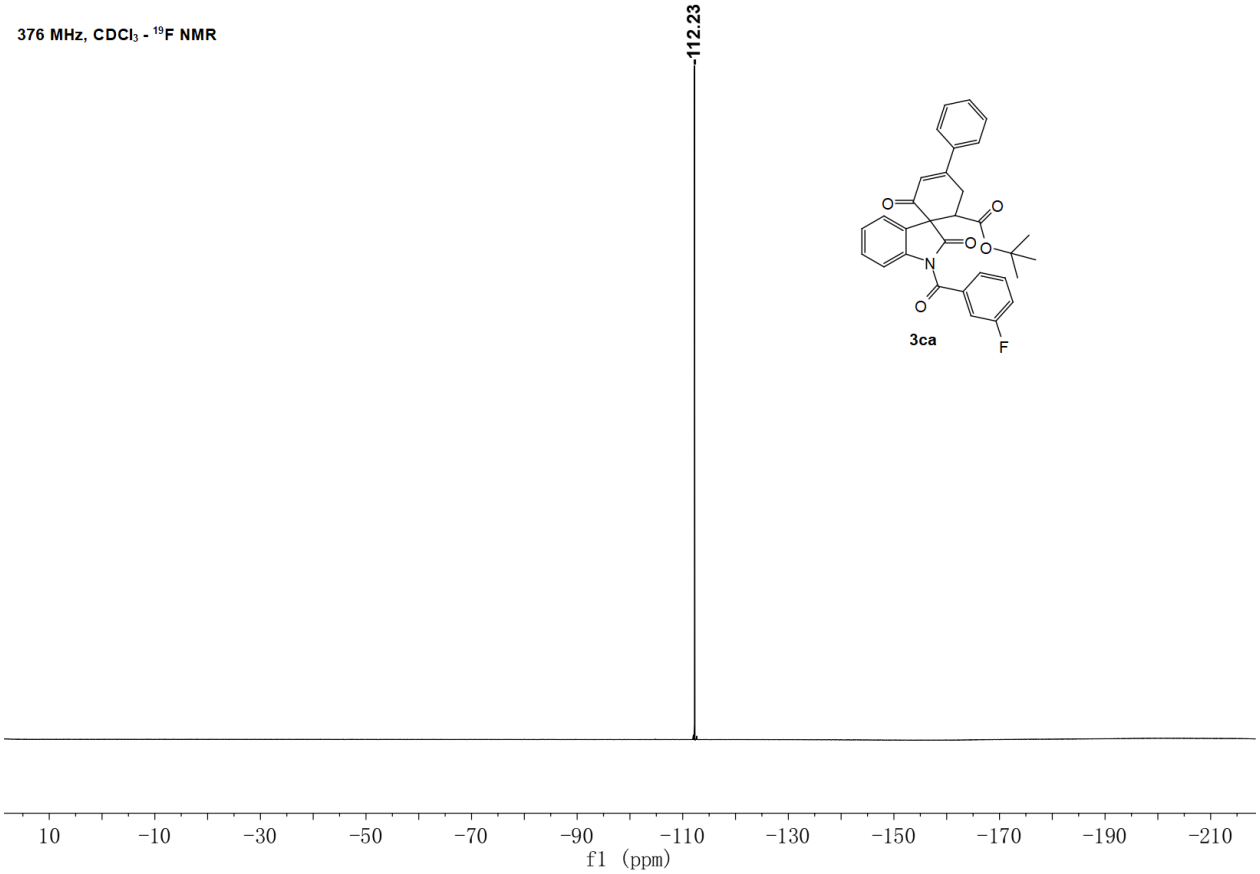
101 MHz, $CDCl_3$ - ^{13}C NMR



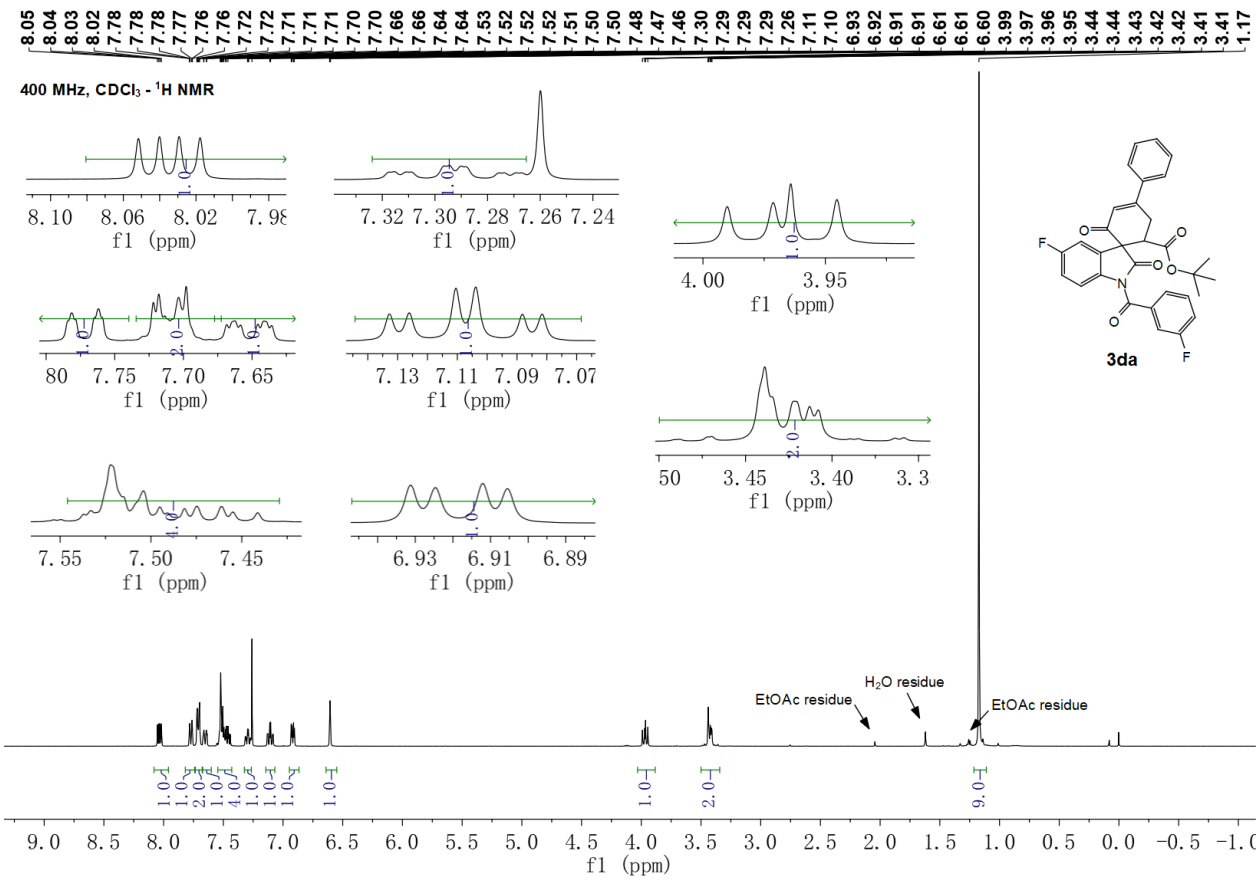

400 MHz, CDCl3 - 1H NMR
3ca
F
H2O residue
f1 (ppm)

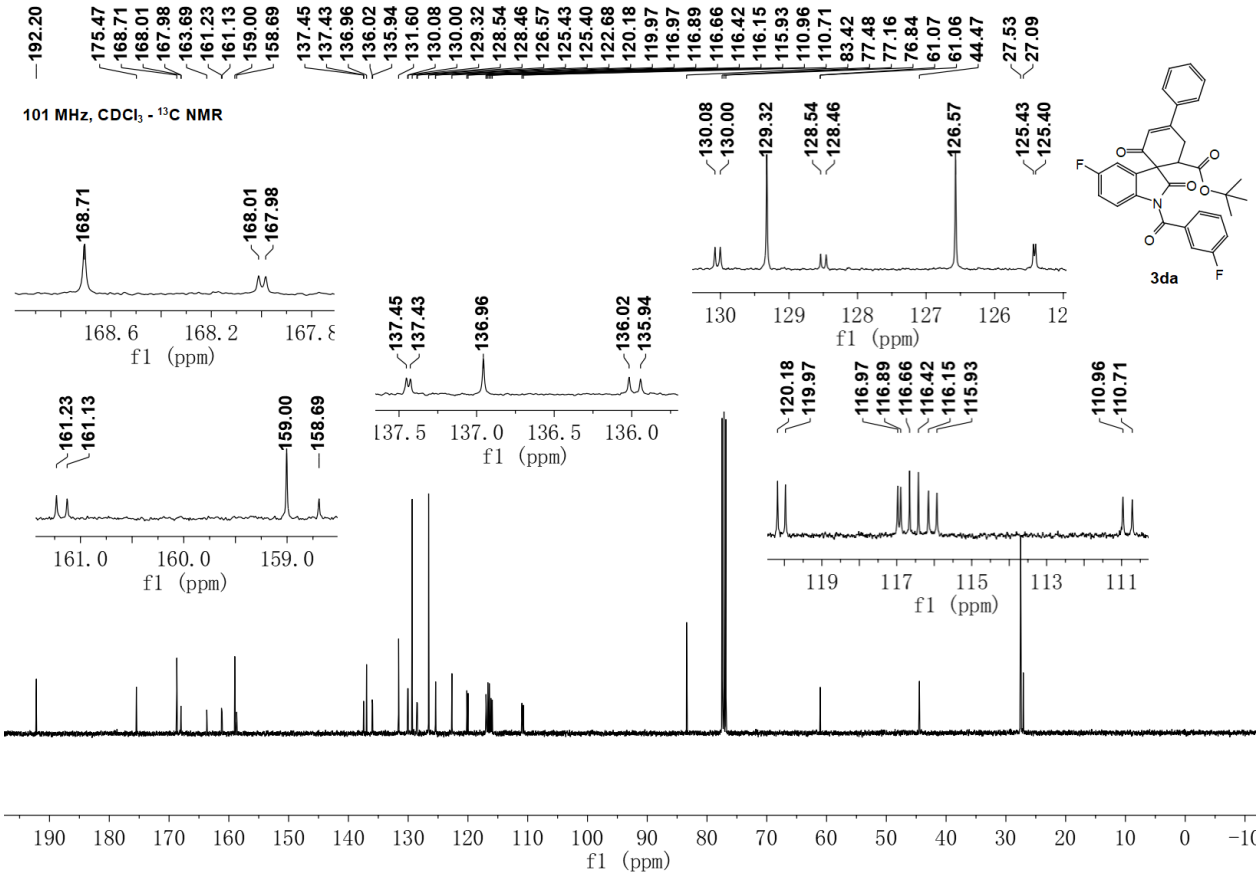

101 MHz, CDCl3 - 13C NMR
3ca
F
f1 (ppm)

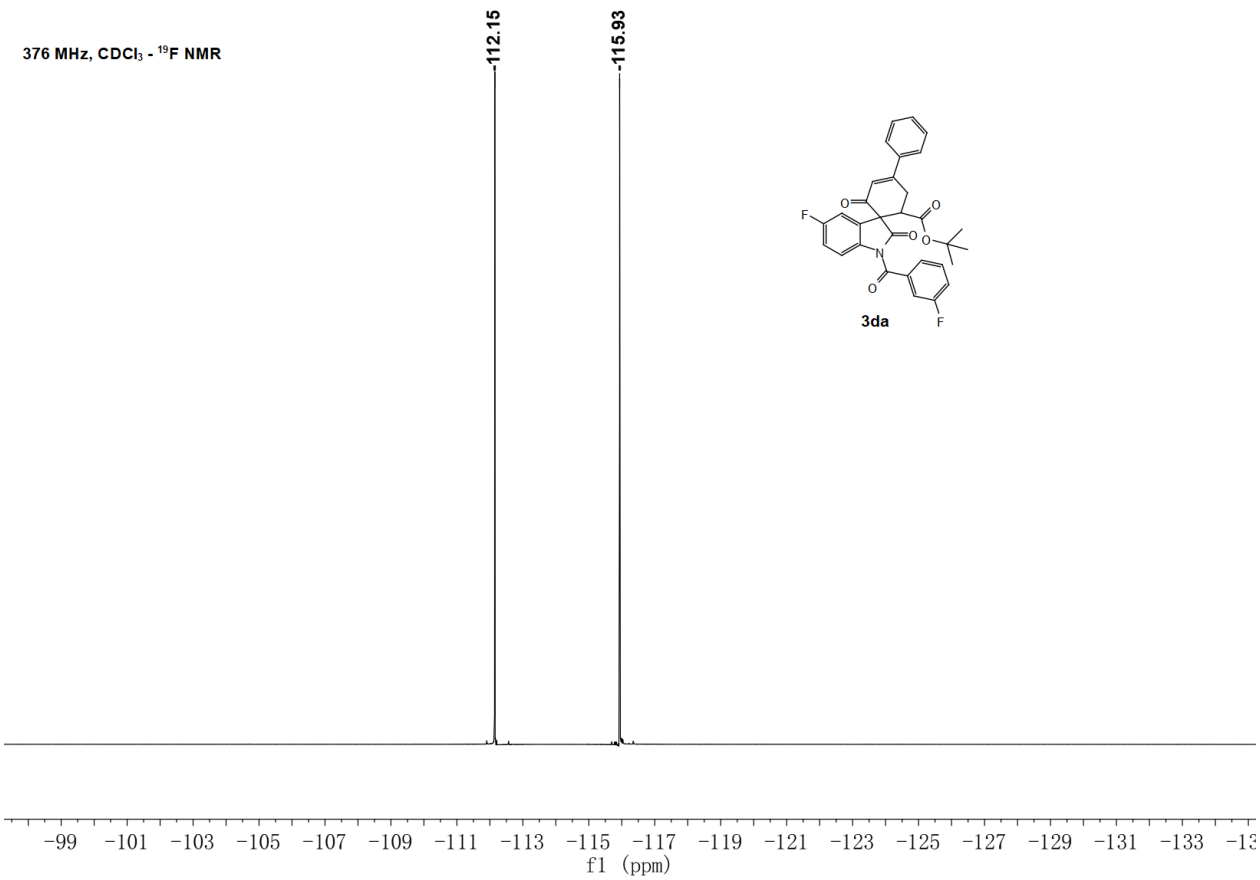
376 MHz, $CDCl_3$ - ^{19}F NMR

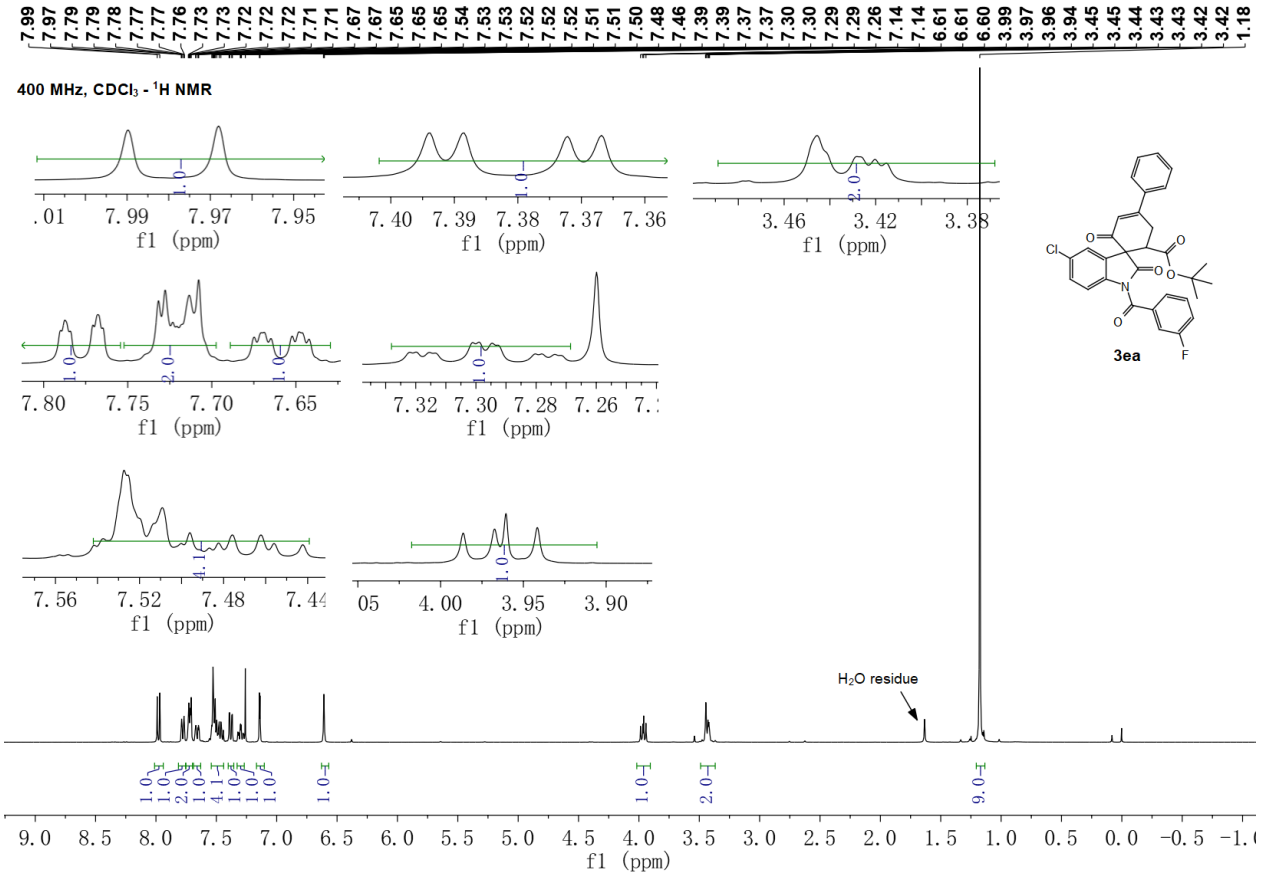


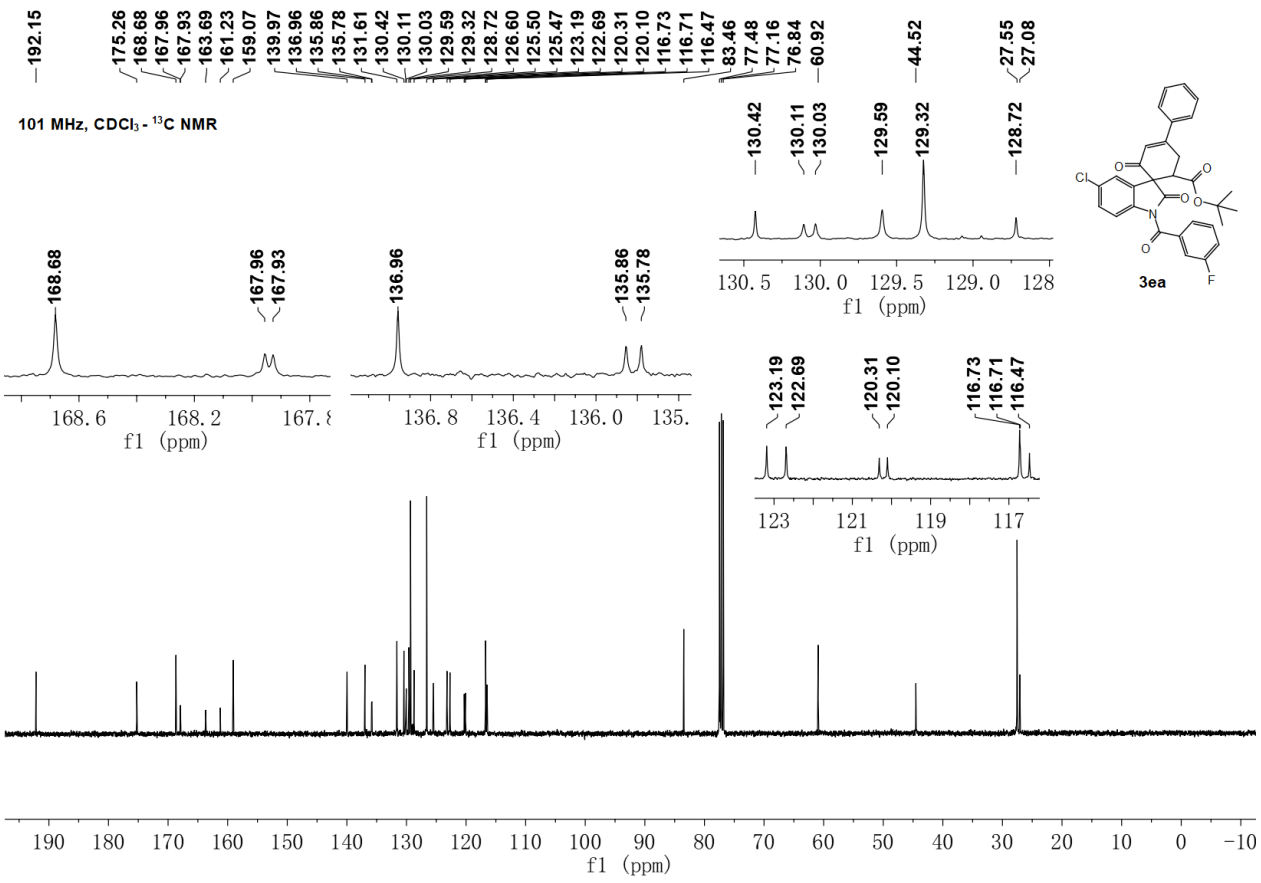
400 MHz, $CDCl_3$ - ^{1}H NMR



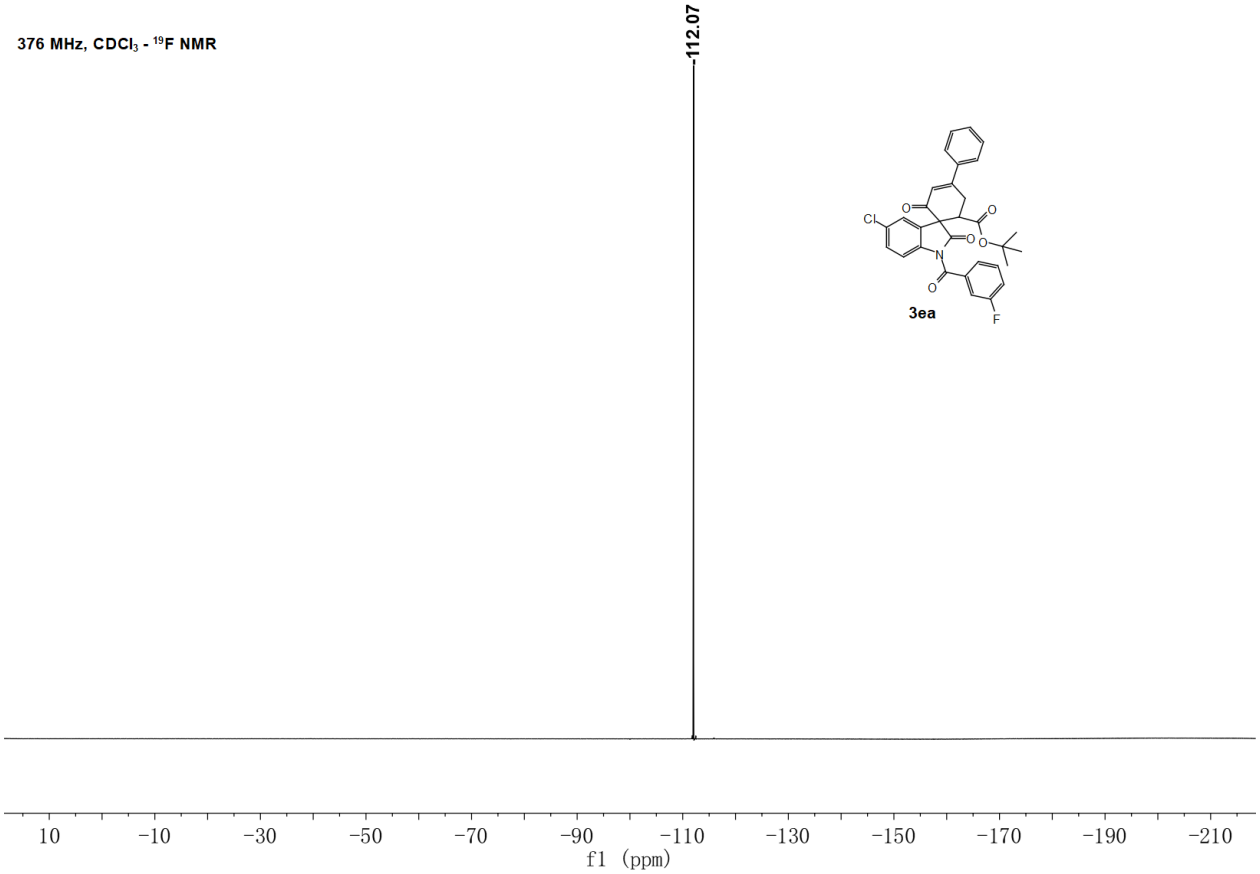

101 MHz, CDCl3 - 13C NMR
192.20
175.47
168.71
168.01
167.98
163.69
161.23
161.13
159.00
158.69
137.45
137.43
136.96
136.02
135.94
131.60
130.08
130.00
129.32
128.54
128.46
126.57
125.43
125.40
122.68
120.18
119.97
116.97
116.89
116.66
116.42
116.15
115.93
110.96
110.71
83.42
77.48
77.16
76.84
61.07
61.06
44.47
27.53
27.09
3da
f1 (ppm)


376 MHz, CDCl3 - 19F NMR
112.15
115.93
3da
f1 (ppm)


400 MHz, CDCl3 - 1H NMR
H2O residue
3ea
f1 (ppm)

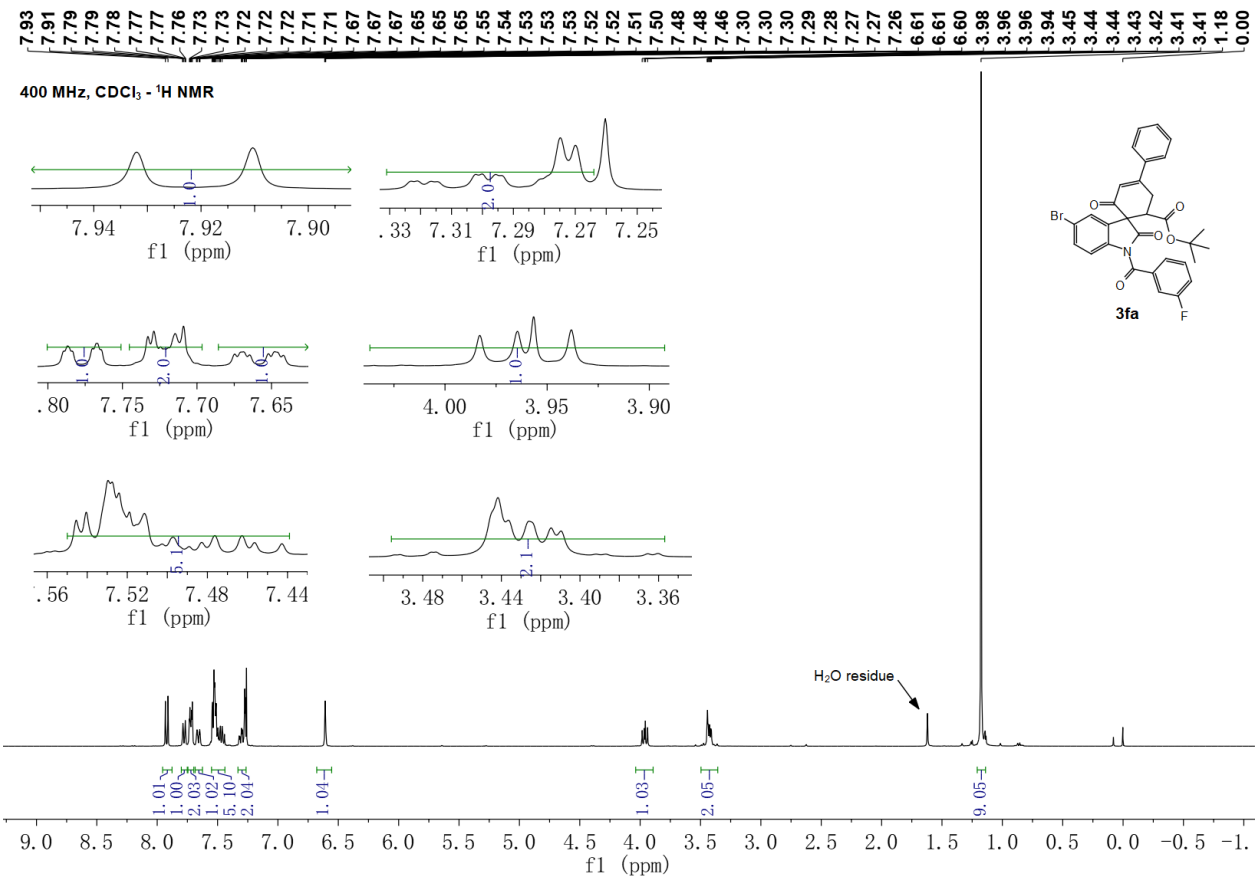

101 MHz, CDCl3 - 13C NMR
3ea
f1 (ppm)

376 MHz, $CDCl_3$ - ^{19}F NMR

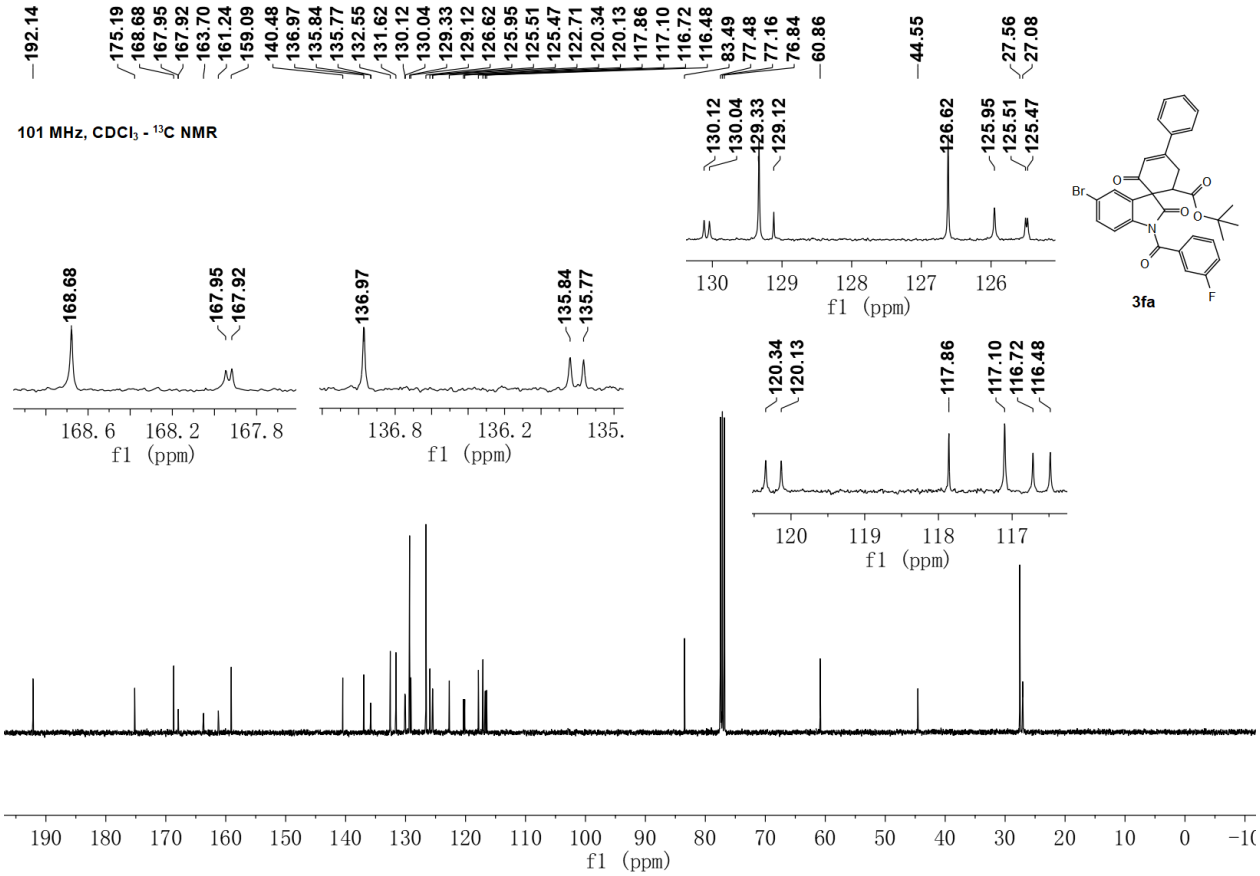


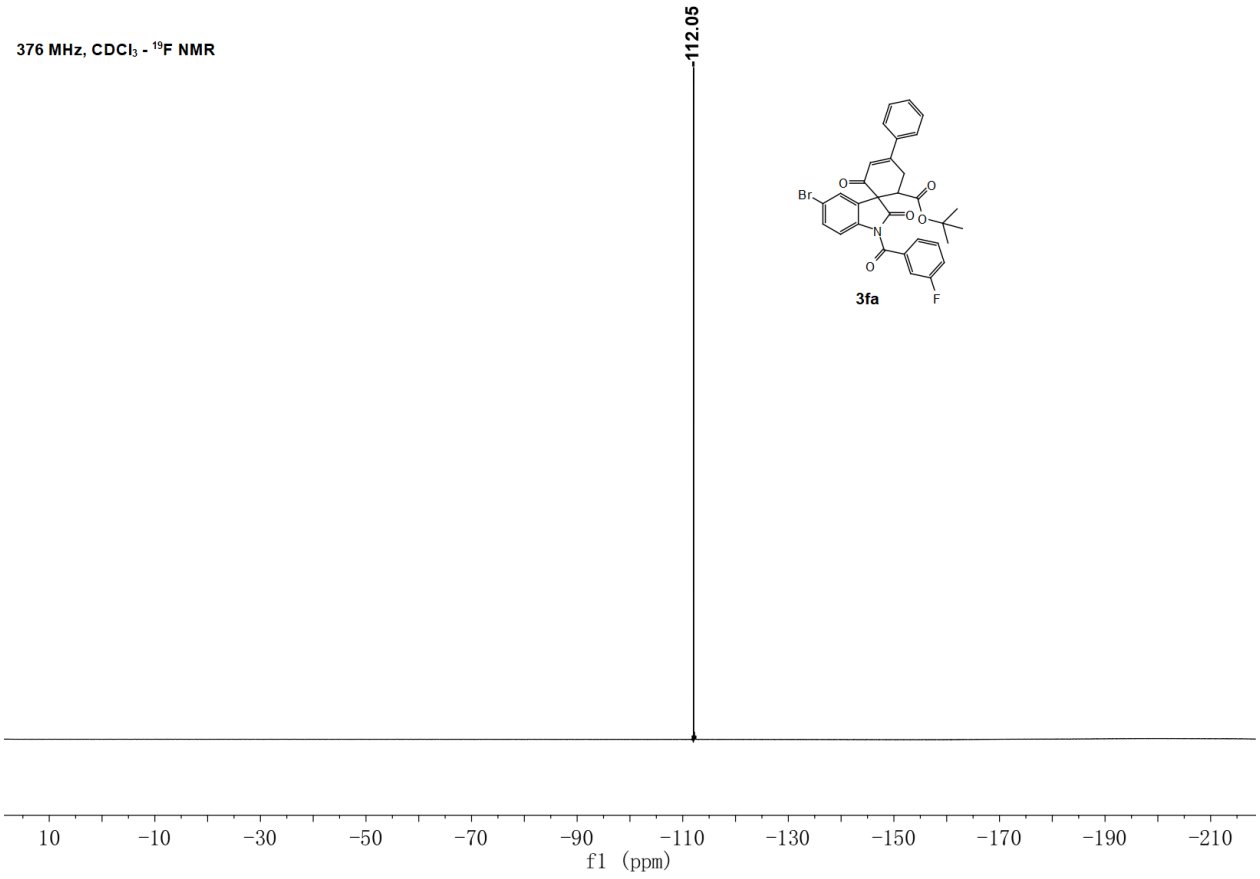
3ea

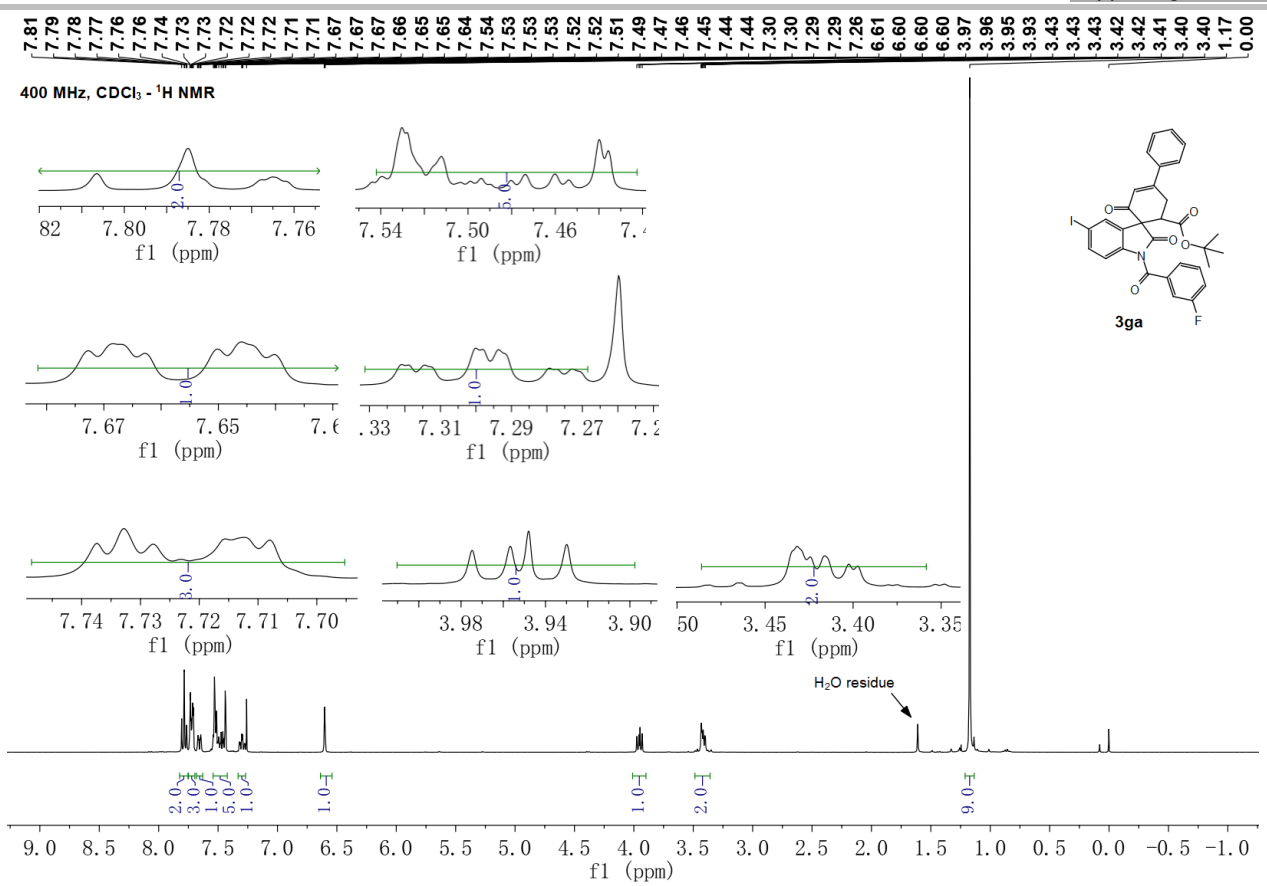
400 MHz, $CDCl_3$ - ^{1}H NMR

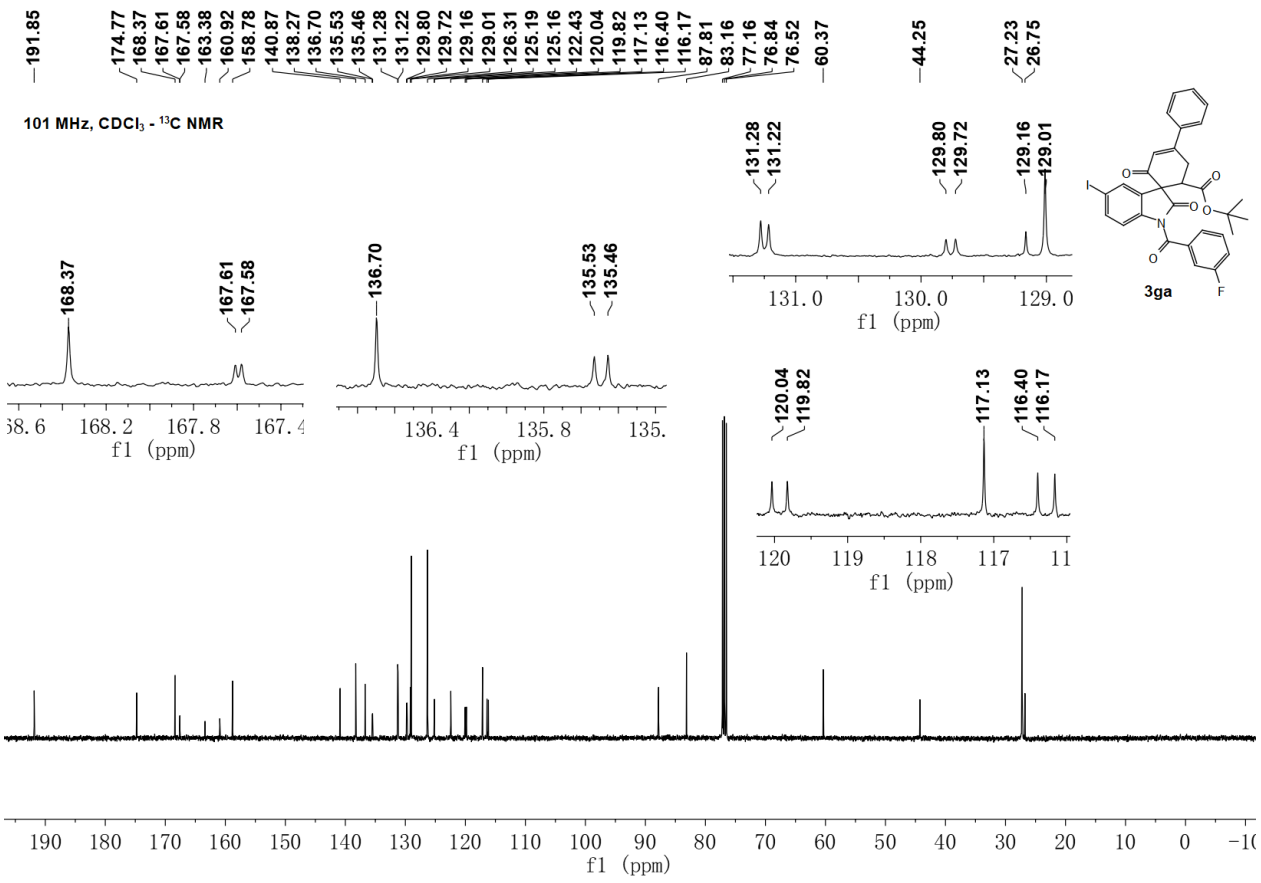


3fa

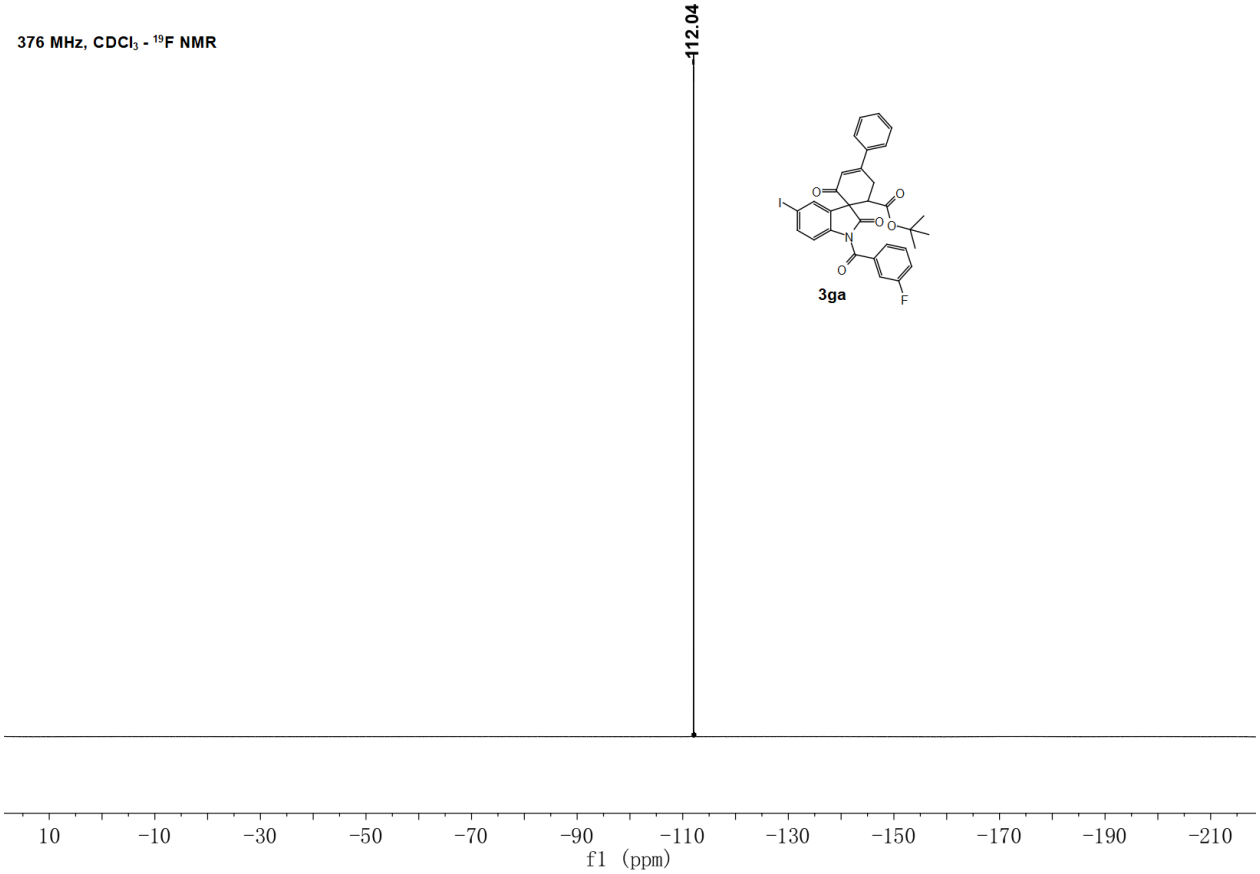

192.14
175.19
168.68
167.95
167.92
163.70
161.24
159.09
140.48
136.97
135.84
135.77
132.55
131.62
130.12
130.04
129.33
129.12
126.62
125.95
125.51
125.47
122.71
120.34
120.13
117.86
117.10
116.72
116.48
83.49
77.48
77.16
76.84
60.86
44.55
27.56
27.08
101 MHz, CDCl3 - 13C NMR
130.12
130.04
129.33
129.12
126.62
125.95
125.51
125.47
130
129
128
127
126
f1 (ppm)
Br
O
O
O
O
N
O
F
3fa
168.68
167.95
167.92
168.6
168.2
167.8
f1 (ppm)
136.97
135.84
135.77
136.8
136.2
135.
f1 (ppm)
120.34
120.13
117.86
117.10
116.72
116.48
120
119
118
117
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


376 MHz, CDCl3 - 19F NMR
112.05
Br
O
O
O
O
N
O
F
3fa
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

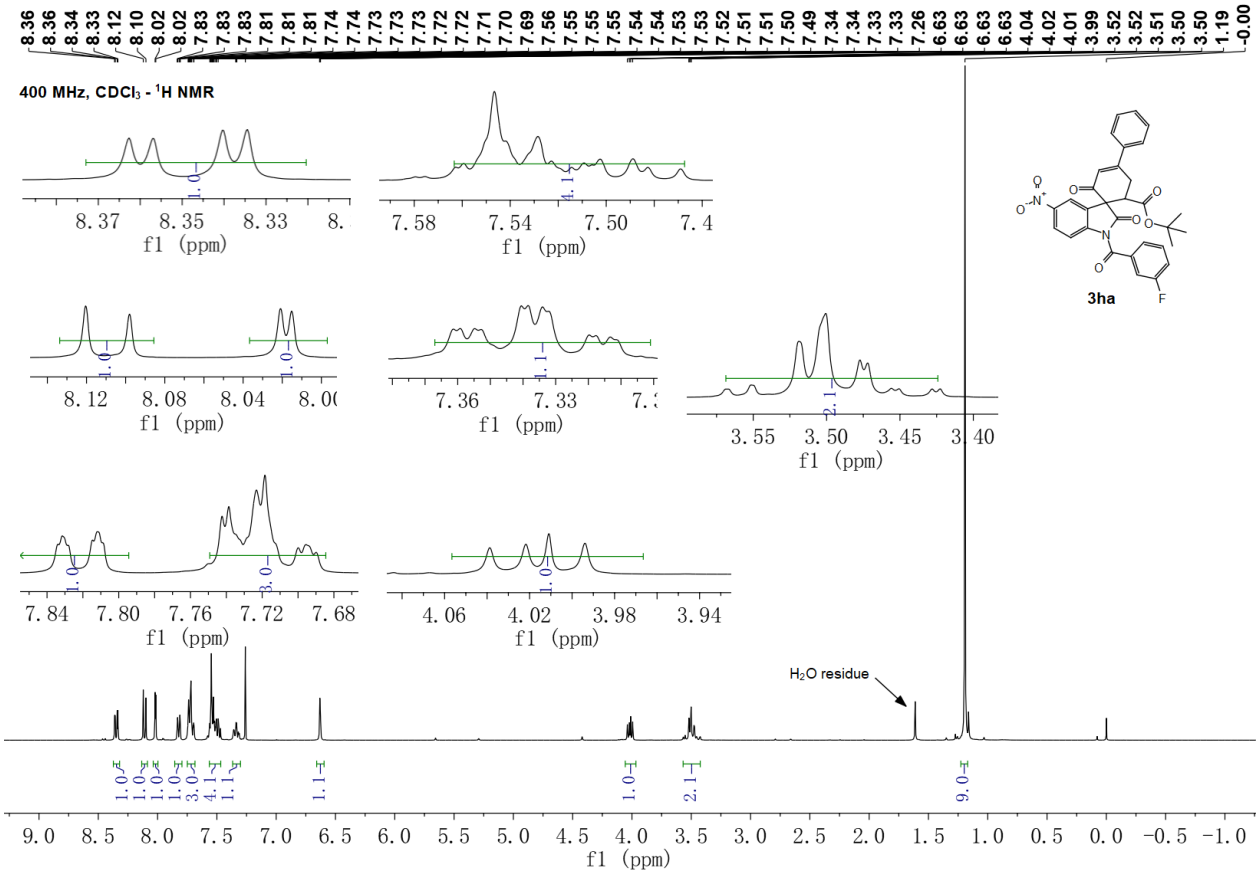

400 MHz, CDCl3 - 1H NMR
H2O residue
3ga

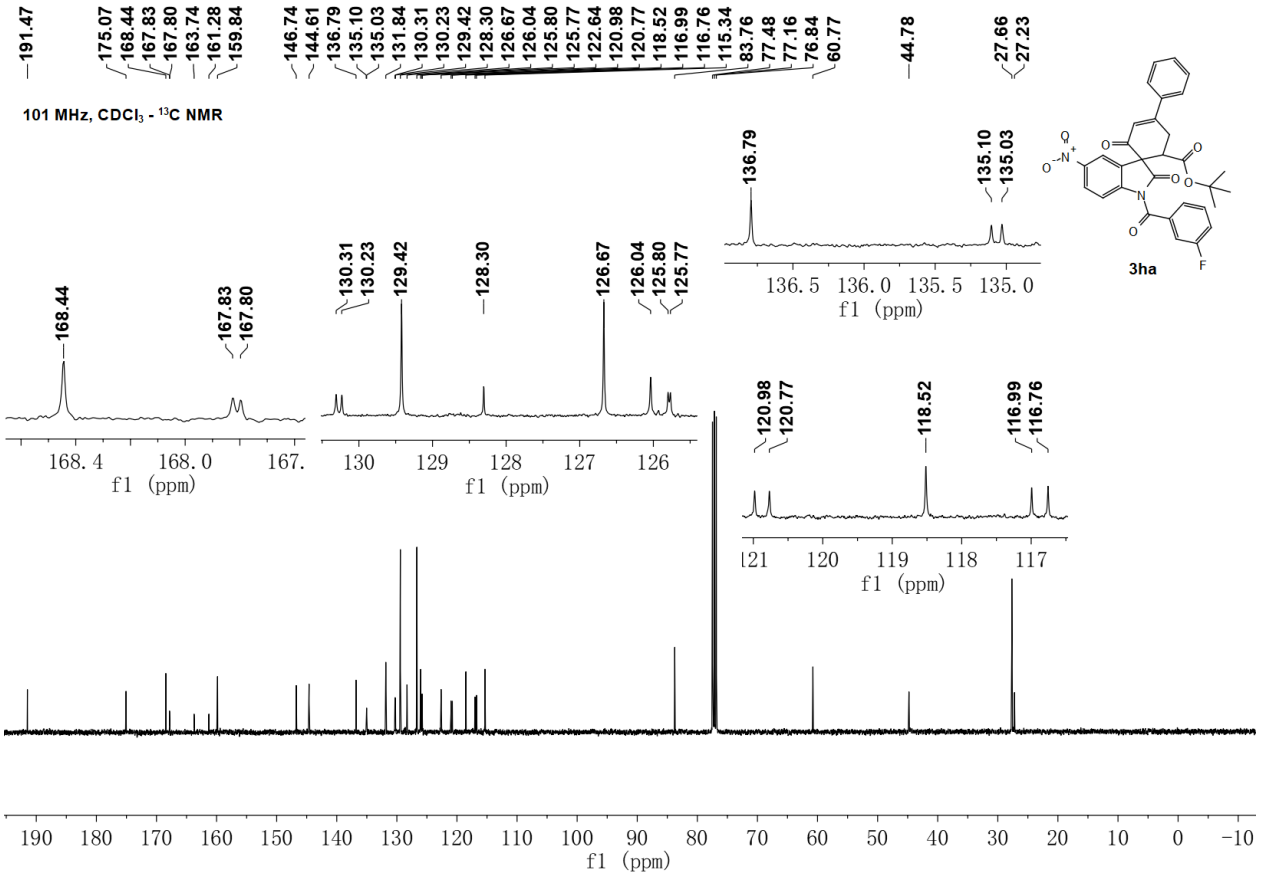

101 MHz, CDCl3 - 13C NMR
3ga

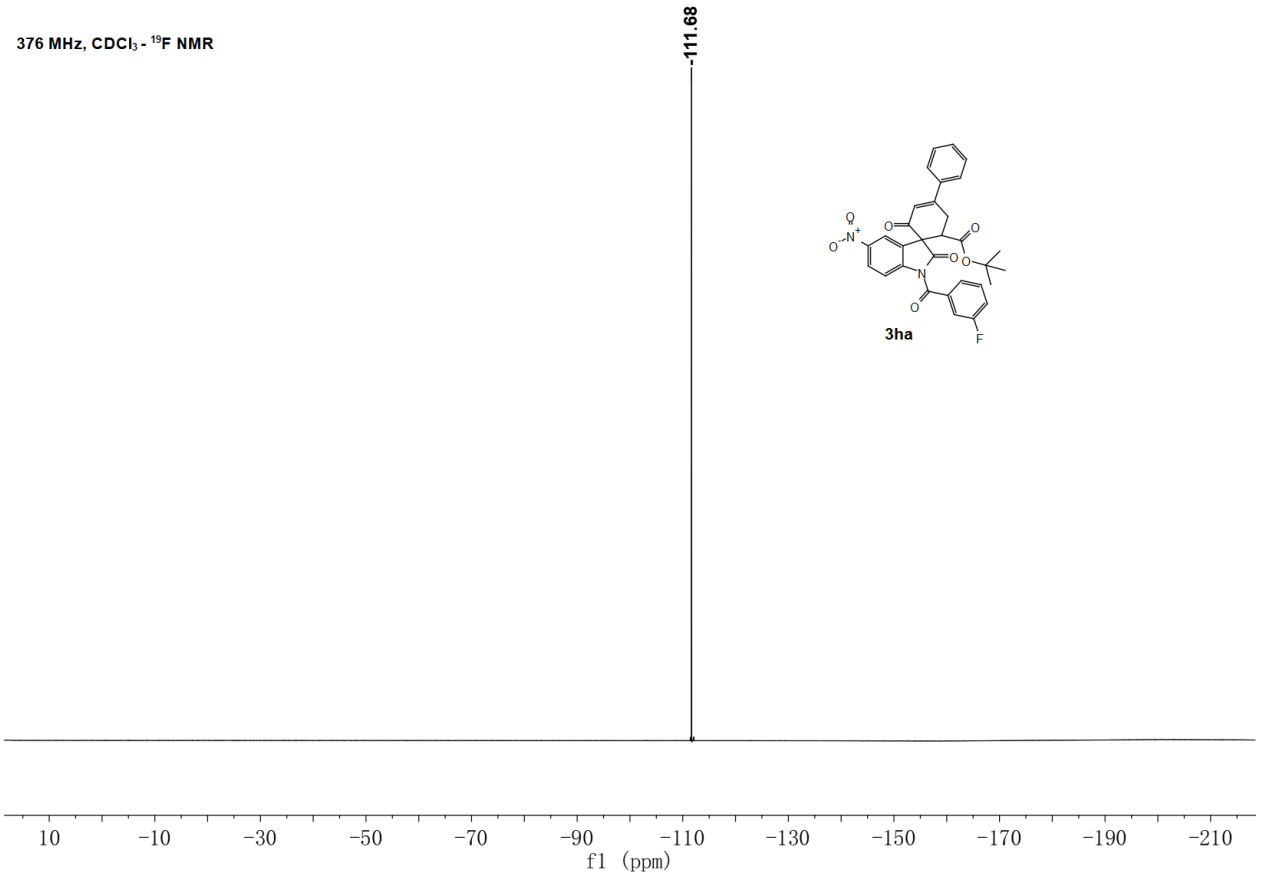
376 MHz, $CDCl_3$ - ^{19}F NMR

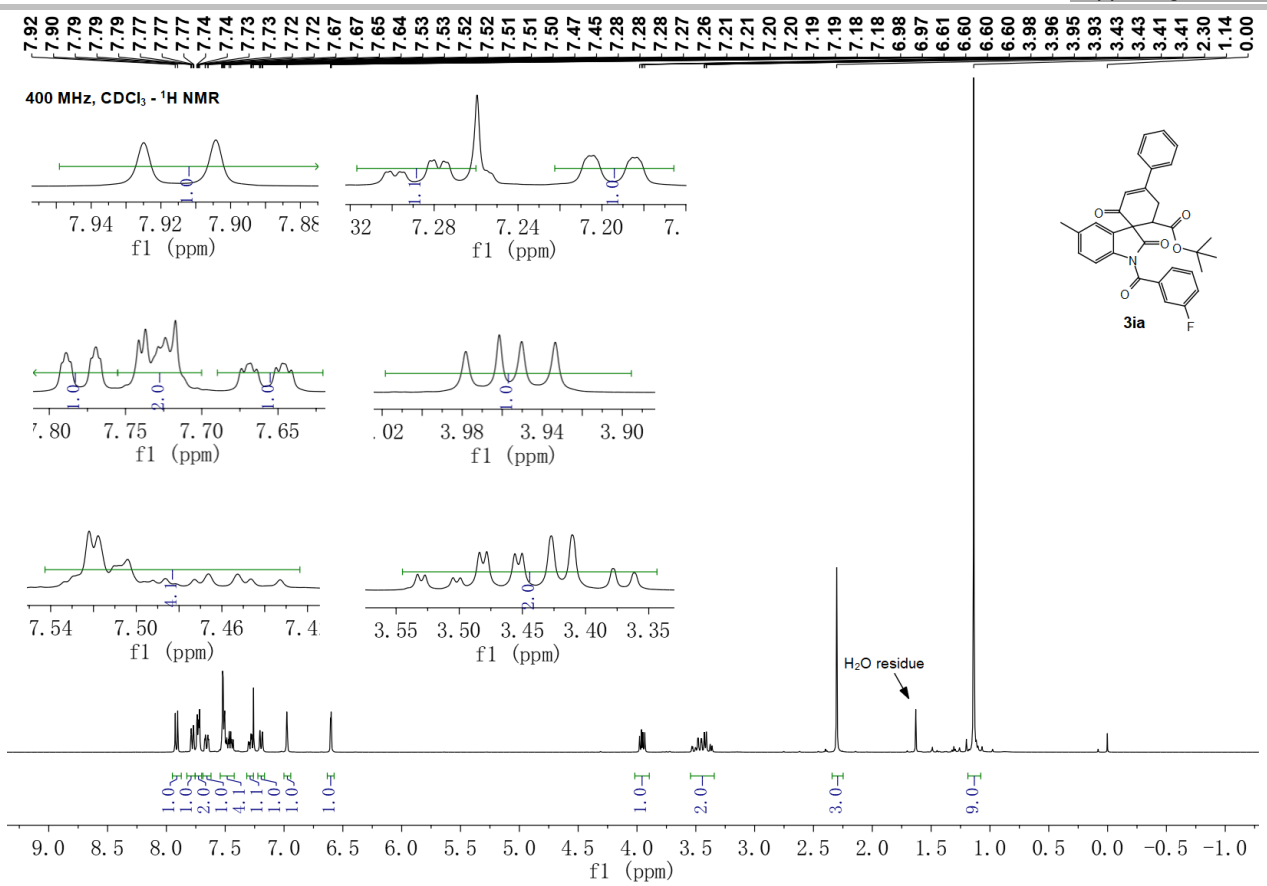


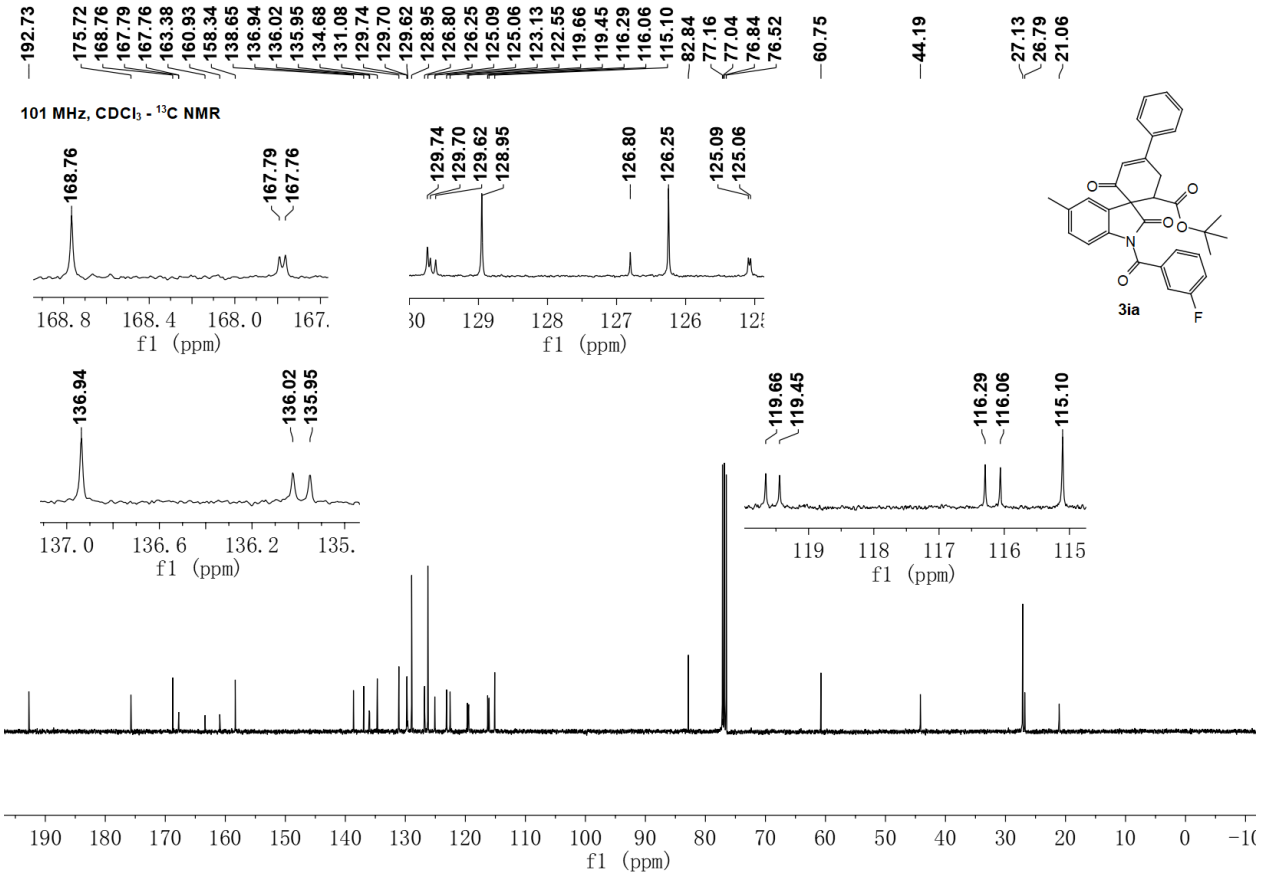
400 MHz, $CDCl_3$ - ^{1}H NMR



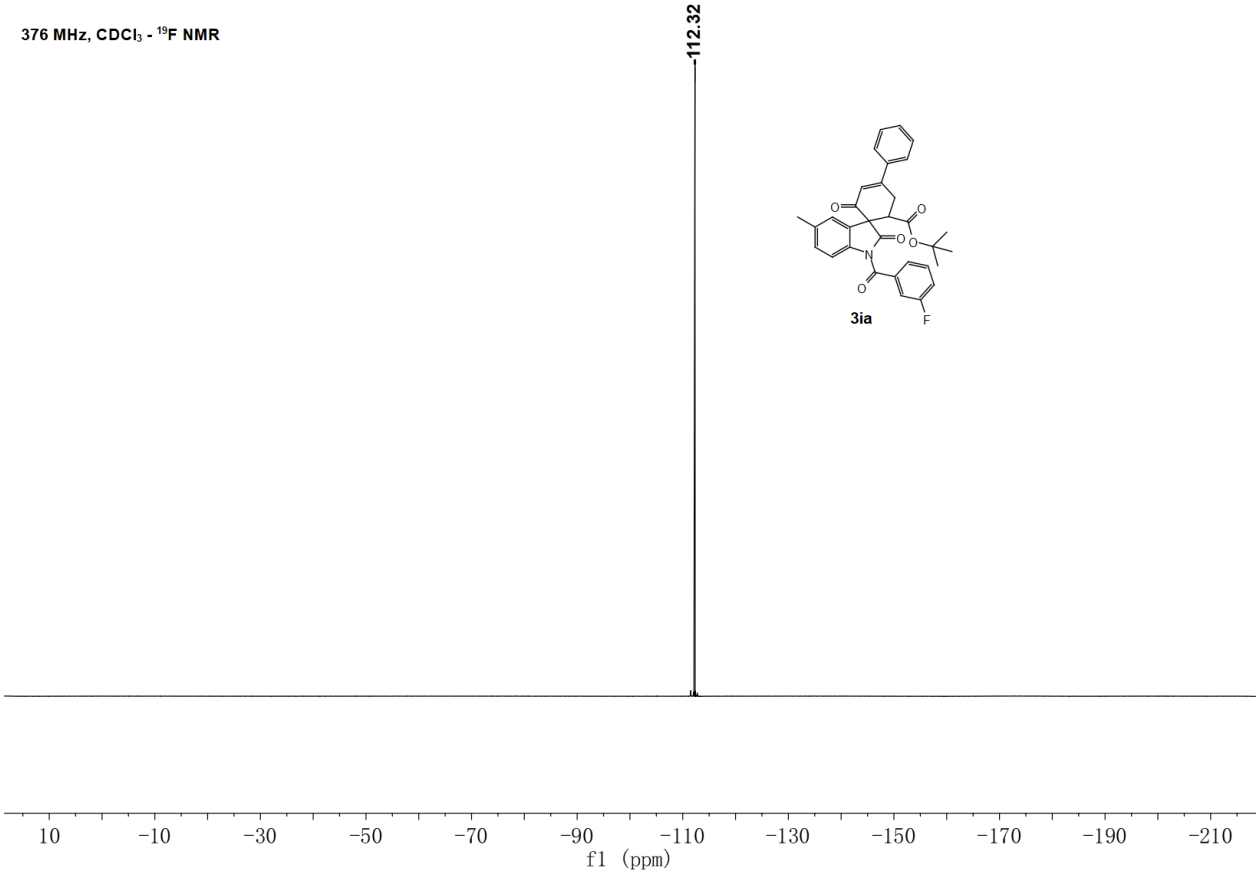

191.47
175.07
168.44
167.83
167.80
163.74
161.28
159.84
146.74
144.61
136.79
135.10
135.03
131.84
130.31
130.23
129.42
128.30
126.67
126.04
125.80
125.77
122.64
120.98
120.77
118.52
116.99
116.76
115.34
83.76
77.48
77.16
76.84
60.77
44.78
27.66
27.23
101 MHz, CDCl3 - 13C NMR
3ha
f1 (ppm)


376 MHz, CDCl3 - 19F NMR
-111.68
3ha
f1 (ppm)

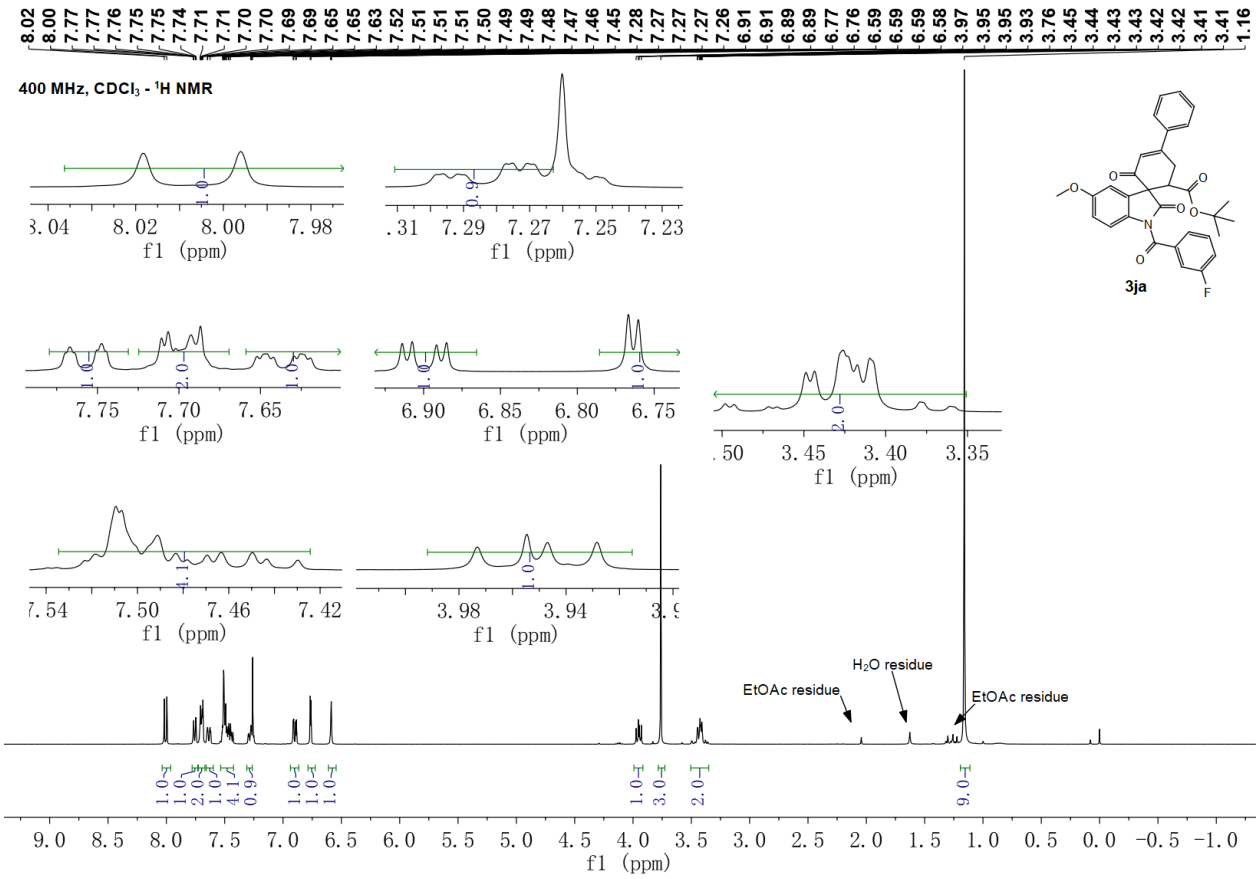

400 MHz, CDCl3 - 1H NMR
3ia
H2O residue
f1 (ppm)

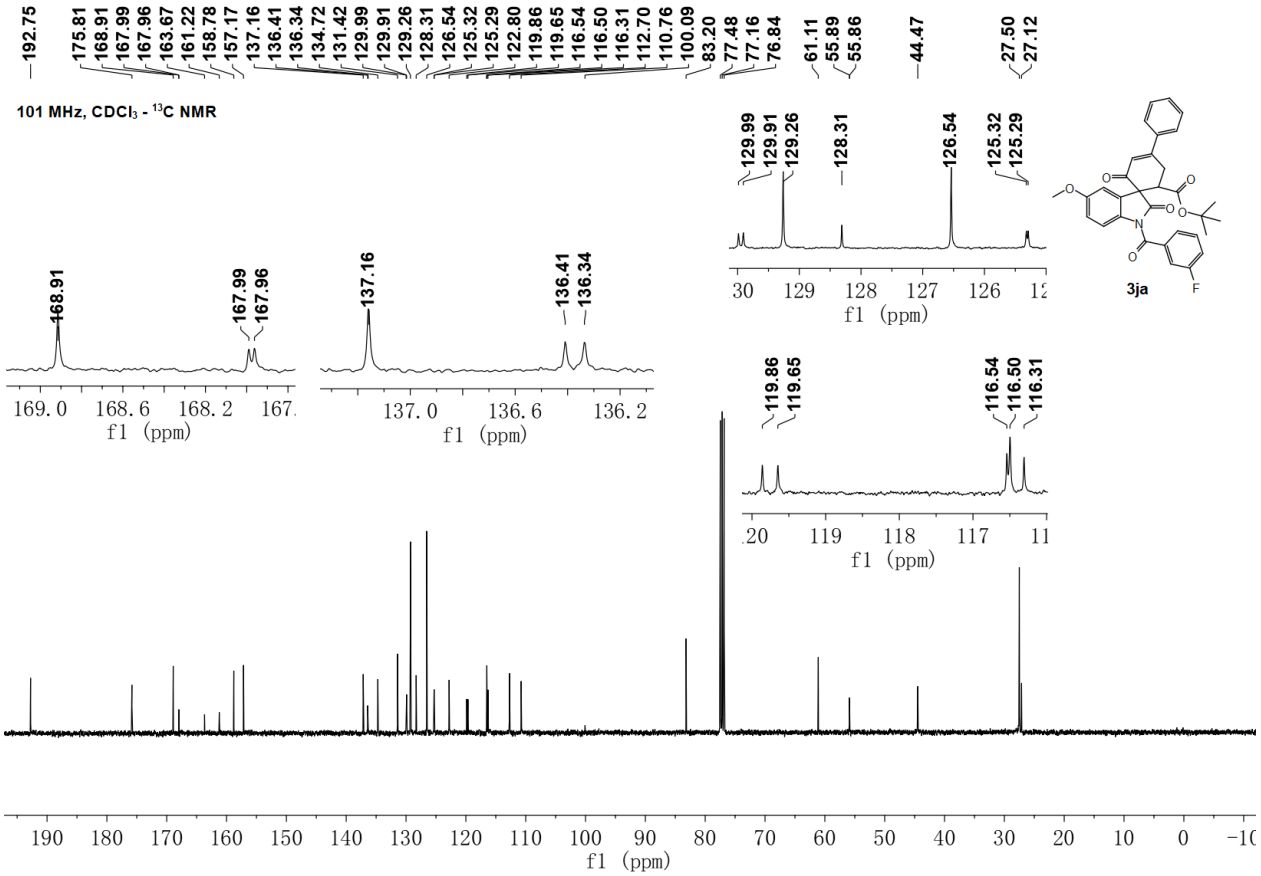

101 MHz, CDCl3 - 13C NMR
3ia
f1 (ppm)

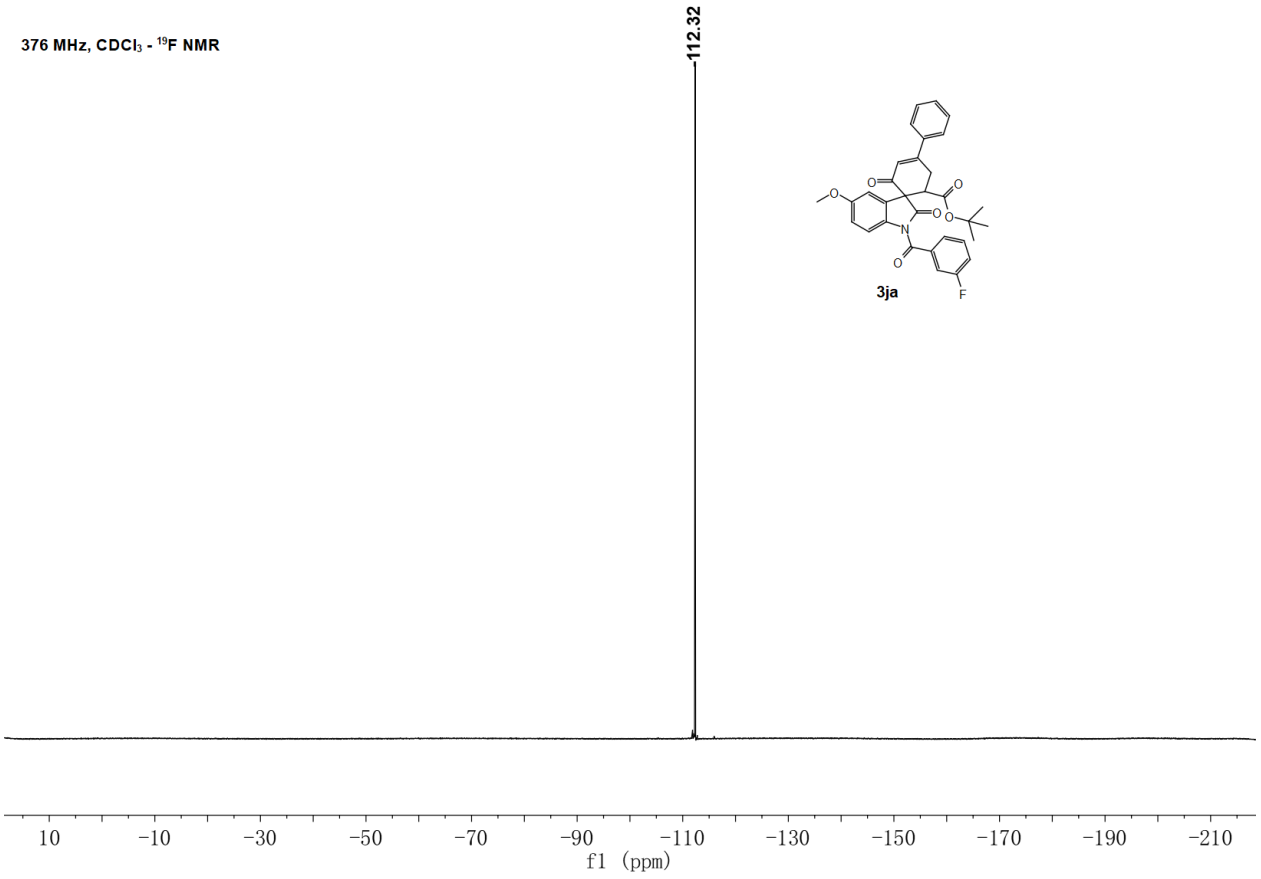
376 MHz, $CDCl_3$ - ^{19}F NMR

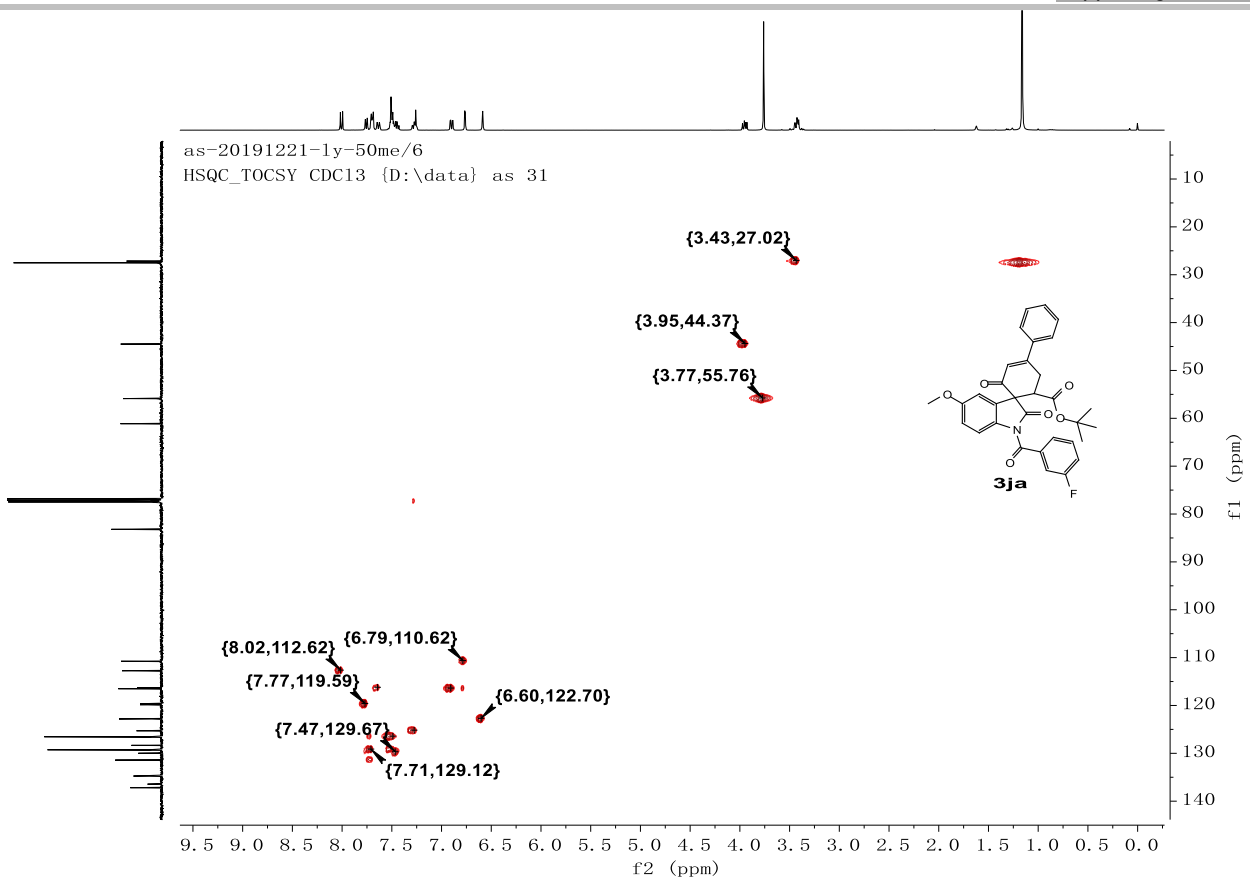


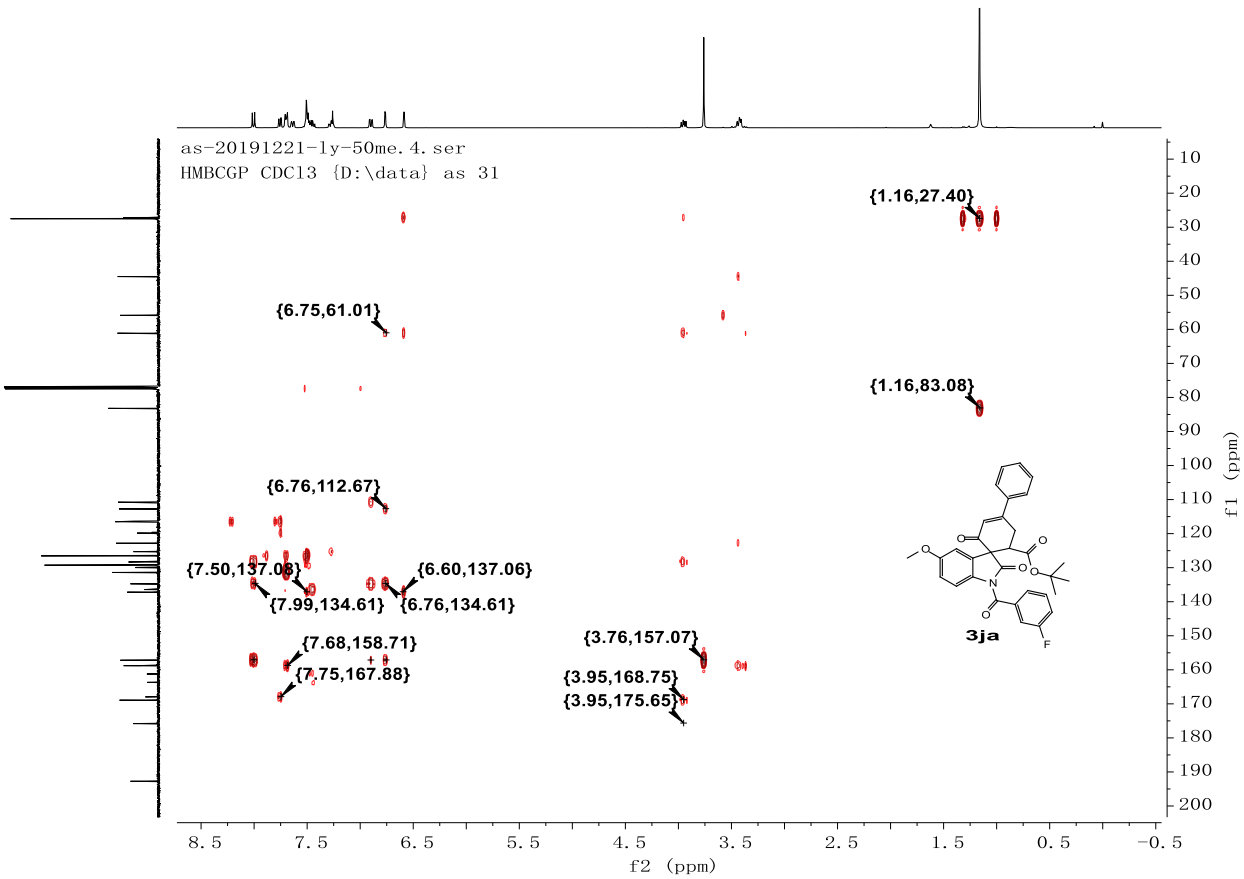
400 MHz, $CDCl_3$ - ^{1}H NMR




192.75
175.81
168.91
167.99
167.96
163.67
161.22
158.78
157.17
137.16
136.41
136.34
134.72
131.42
129.99
129.91
129.26
128.31
126.54
125.32
125.29
122.80
119.86
119.65
116.54
116.50
116.31
112.70
110.76
100.09
83.20
77.48
77.16
76.84
61.11
55.89
55.86
44.47
27.50
27.12
101 MHz, CDCl3 - 13C NMR
3ja
f1 (ppm)


112.32
376 MHz, CDCl3 - 19F NMR
3ja
f1 (ppm)


as-20191221-1y-50me/6
HSQC_TOCSY CDCl3 {D:\data} as 31
{3.43,27.02}
{3.95,44.37}
{3.77,55.76}
3ja
{8.02,112.62}
{6.79,110.62}
{7.77,119.59}
{6.60,122.70}
{7.47,129.67}
{7.71,129.12}
f2 (ppm)
f1 (ppm)


as-20191221-1y-50me.4.ser
HMBCGP CDCl3 {D:\data} as 31
{1.16,27.40}
{6.75,61.01}
{1.16,83.08}
3ja
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{7.50,137.08}
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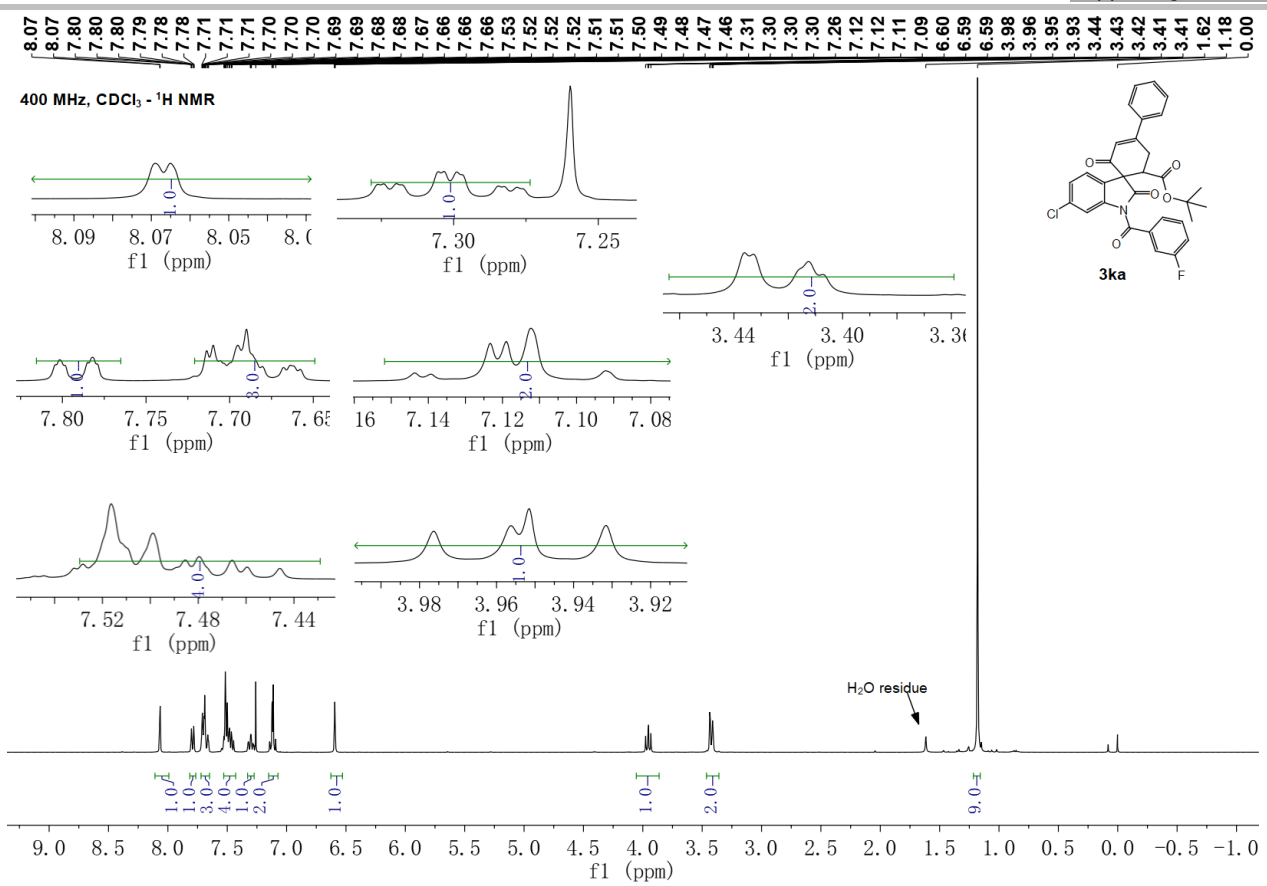
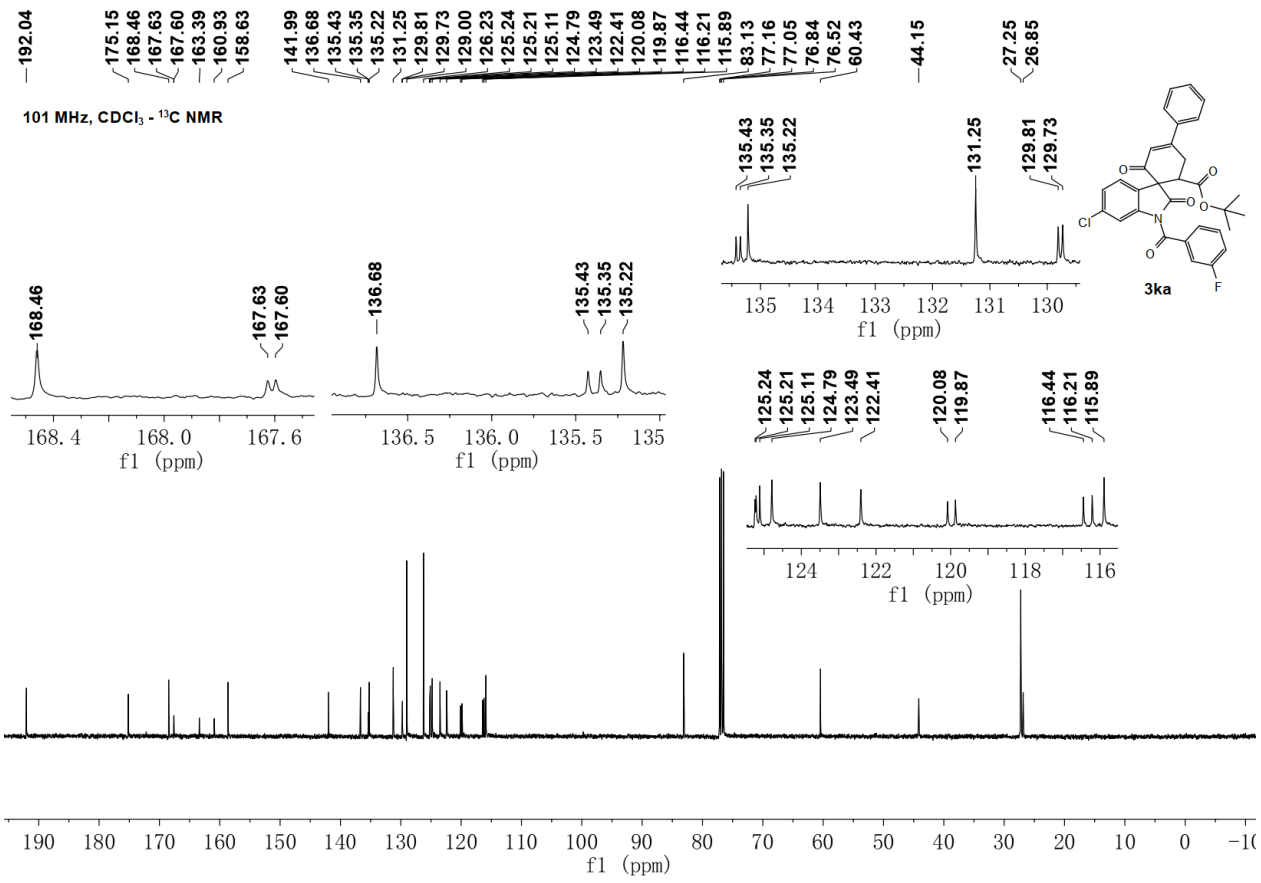
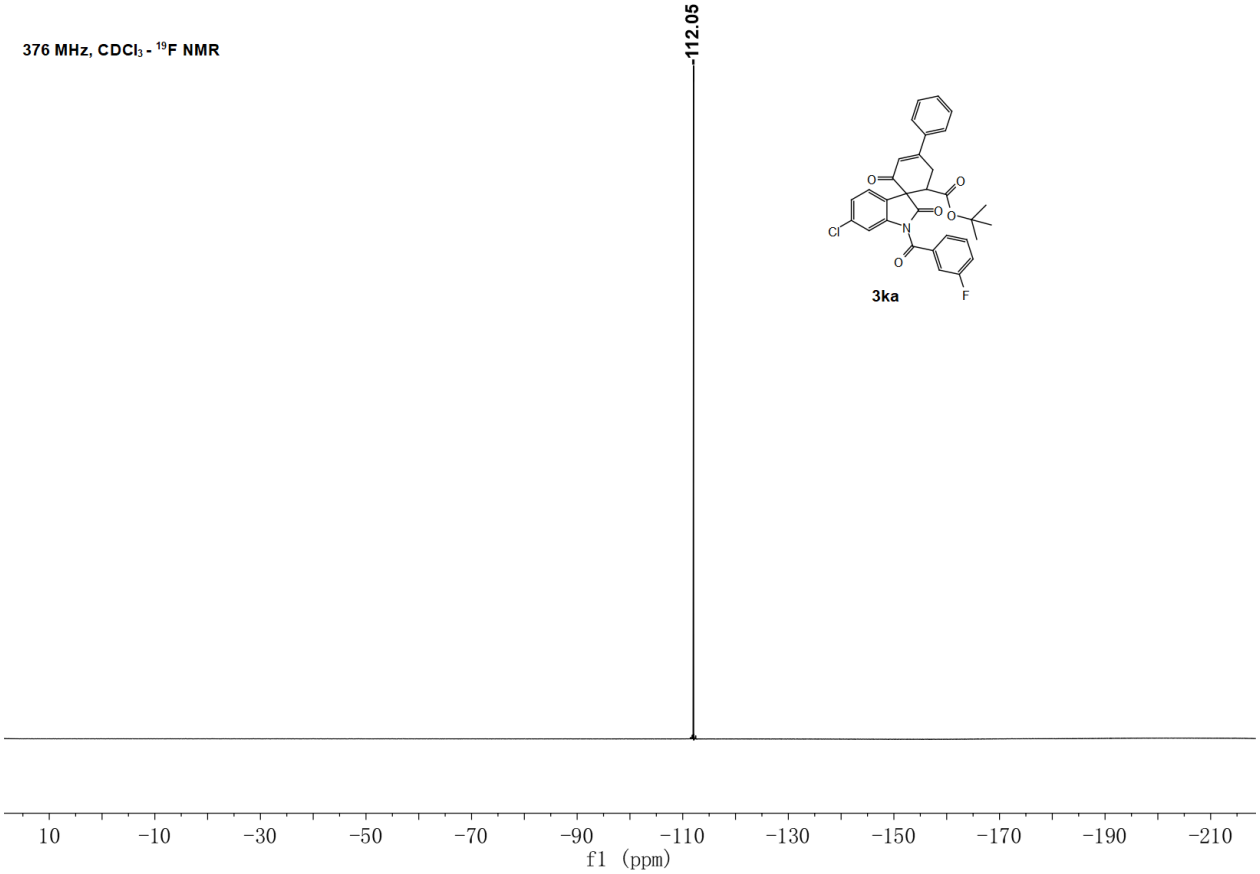
{3.95,175.65}
f2 (ppm)
f1 (ppm)

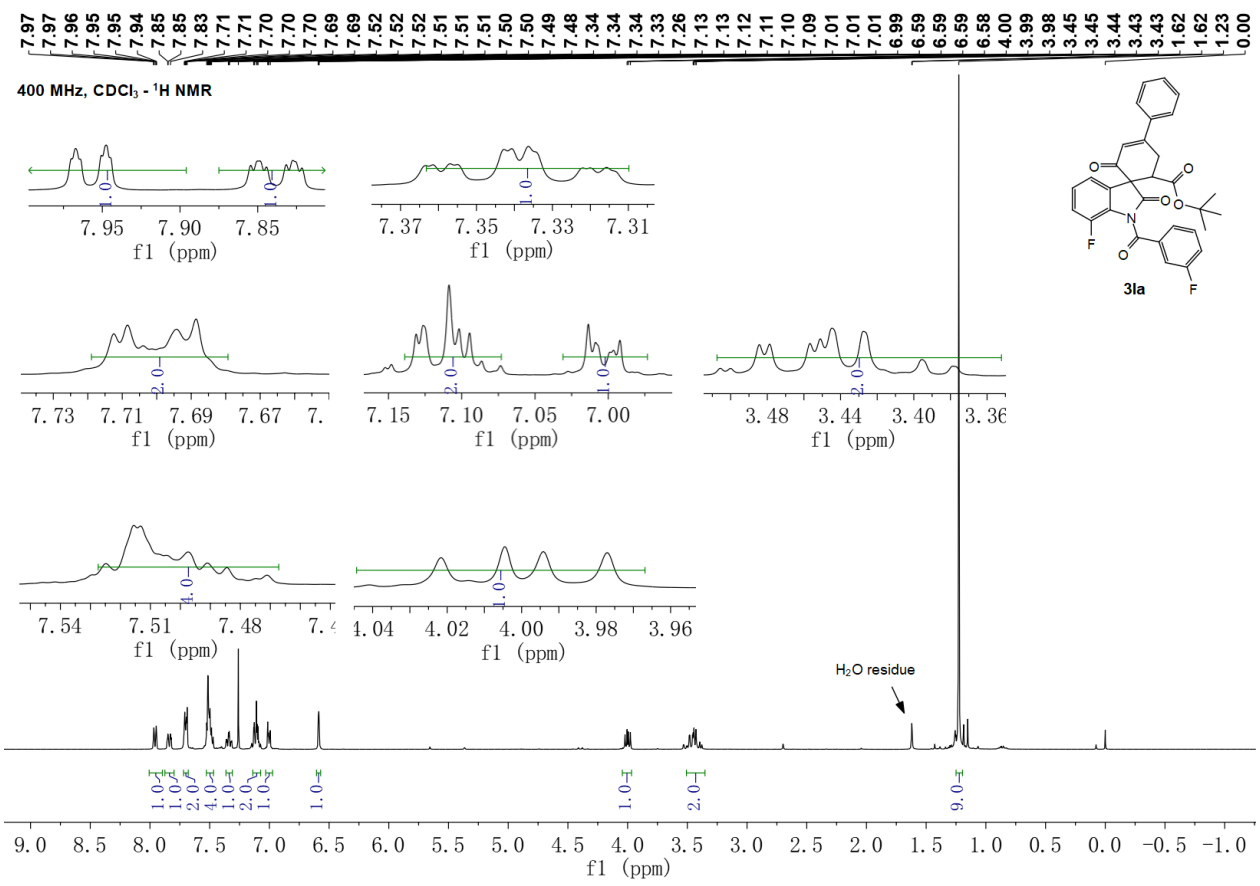

400 MHz, CDCl3 - 1H NMR
3ka
H2O residue
f1 (ppm)

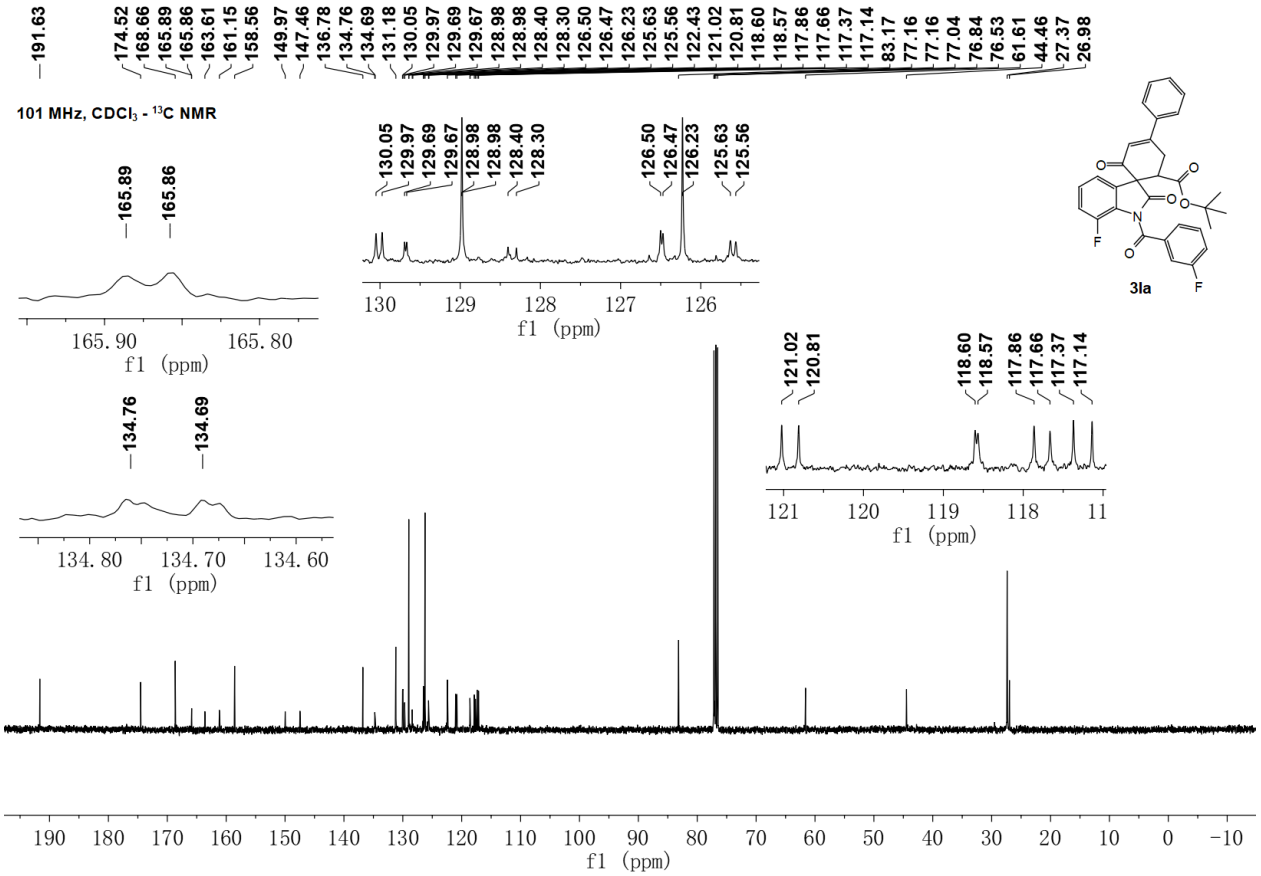

101 MHz, CDCl3 - 13C NMR
3ka
f1 (ppm)

376 MHz, $CDCl_3$ - ^{19}F NMR



400 MHz, $CDCl_3$ - ^{1}H NMR

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158.56
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134.69
131.18
130.05
129.97
129.69
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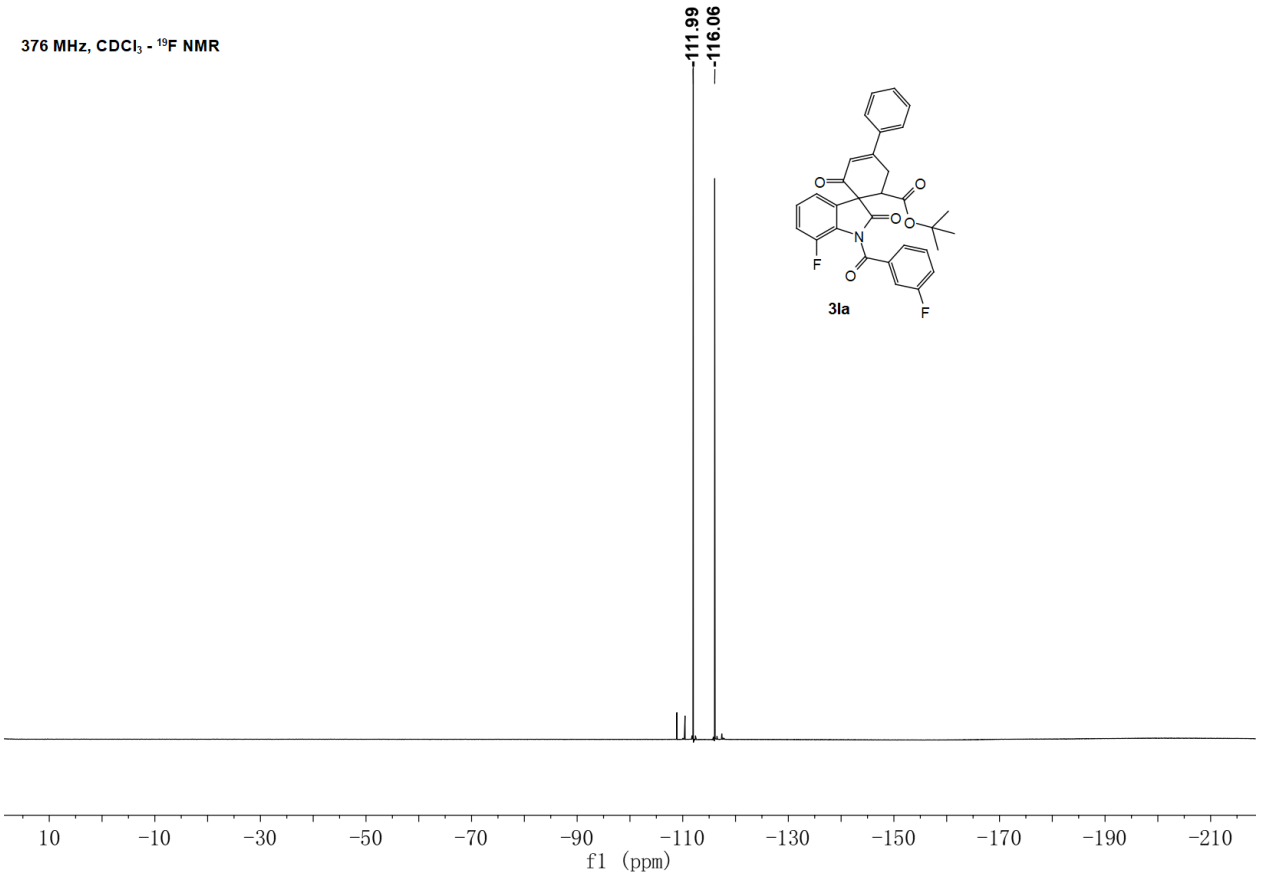
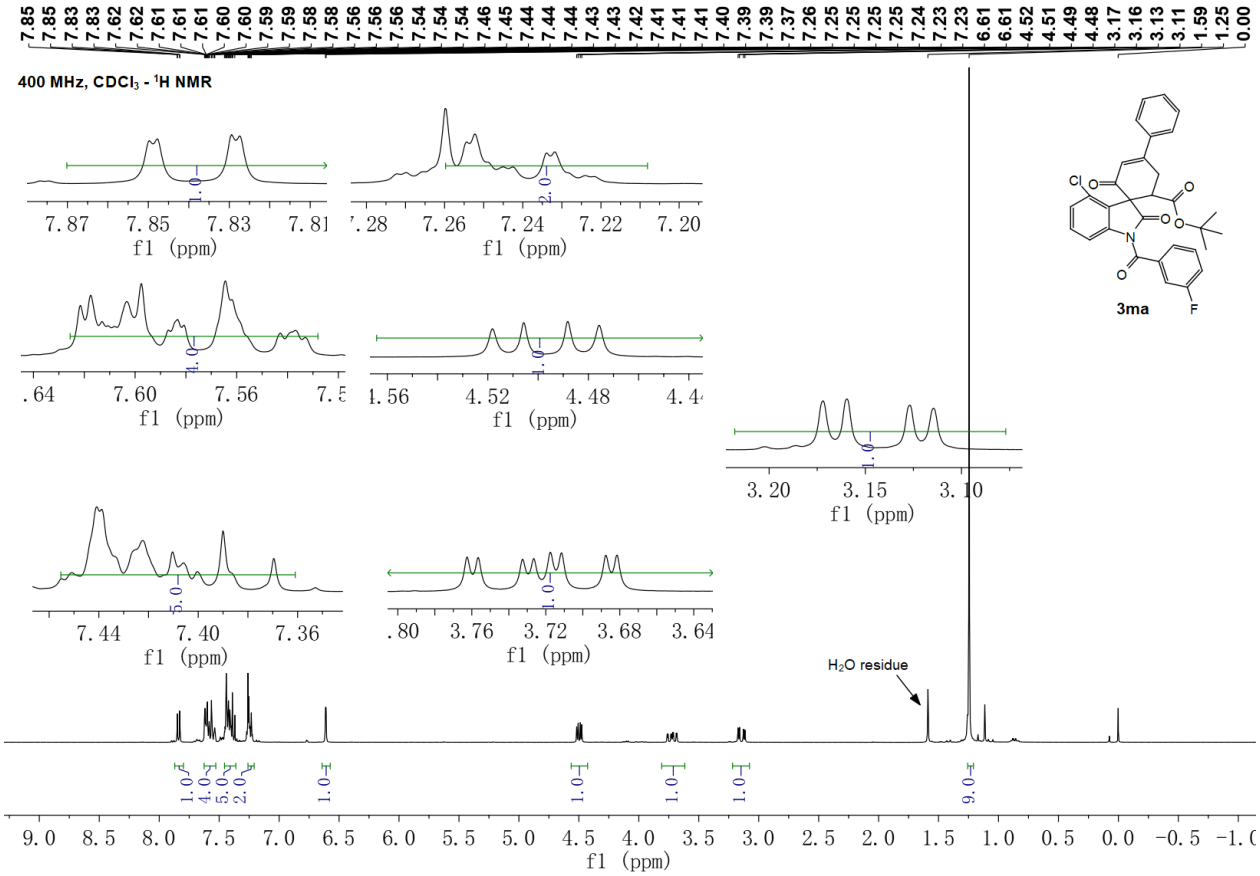
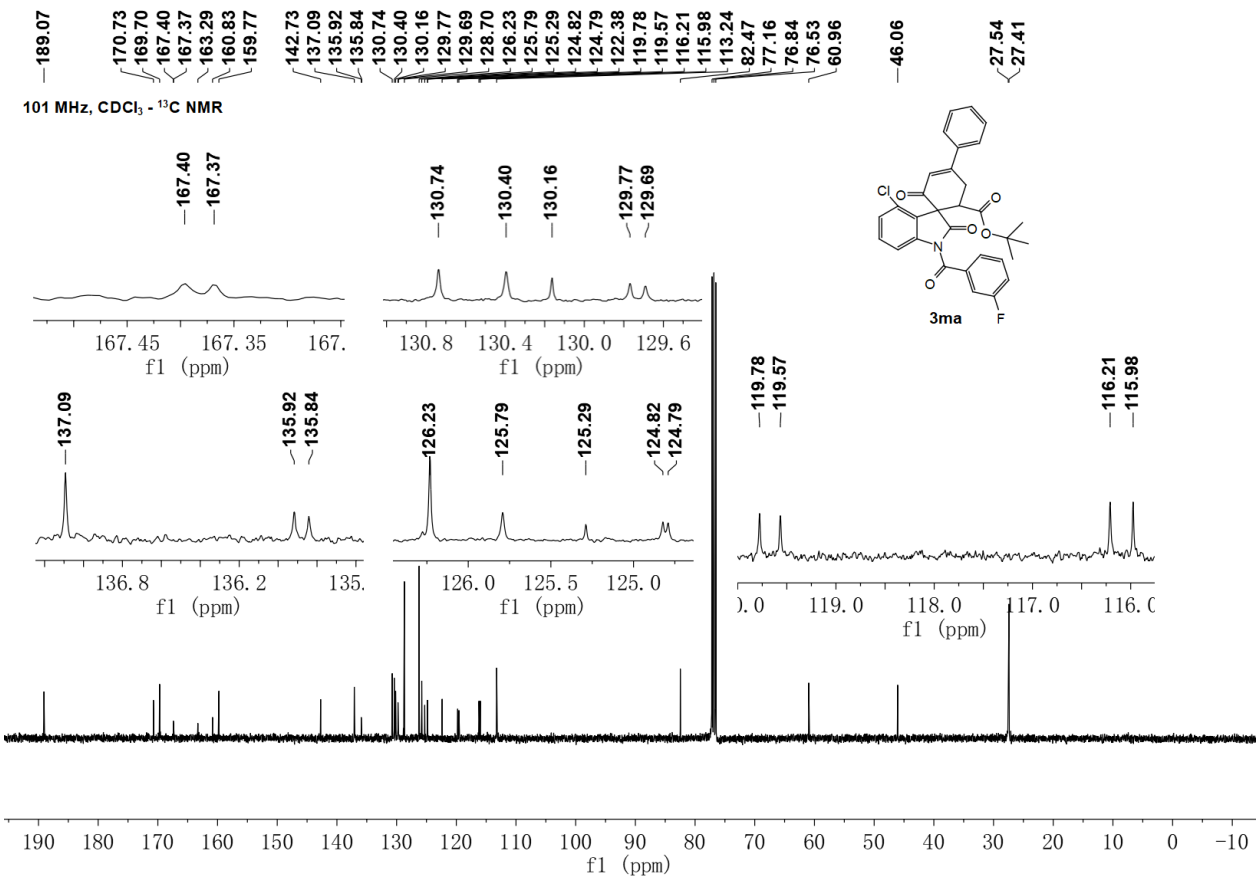
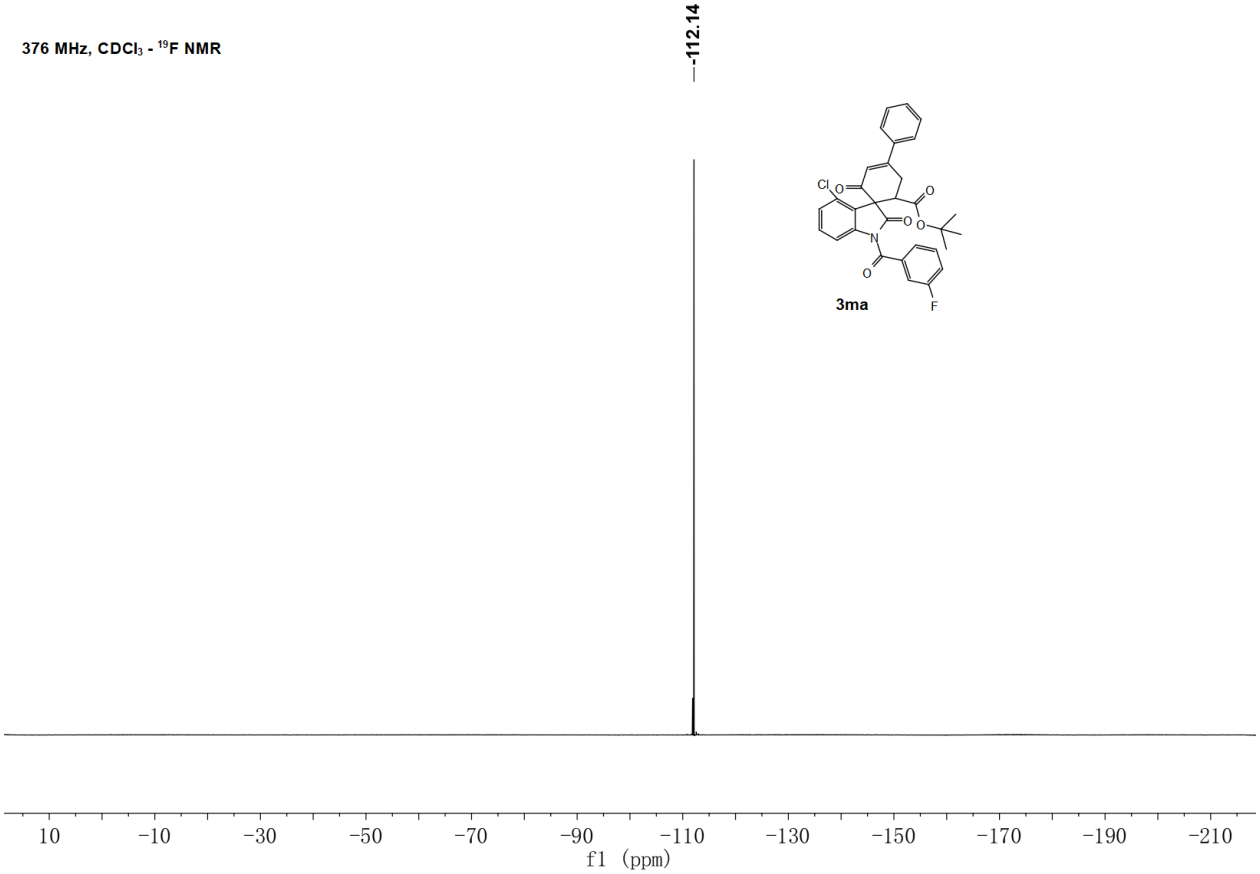
128.98
128.98
128.40
128.30
126.50
126.47
126.23
125.63
125.56
122.43
121.02
120.81
118.60
118.57
117.86
117.66
117.37
117.14
83.17
77.16
77.16
77.04
76.84
76.53
61.61
44.46
27.37
26.98
101 MHz, CDCl3 - 13C NMR
3la
f1 (ppm)


376 MHz, CDCl3 - 19F NMR
-111.99
-116.06
3la
f1 (ppm)

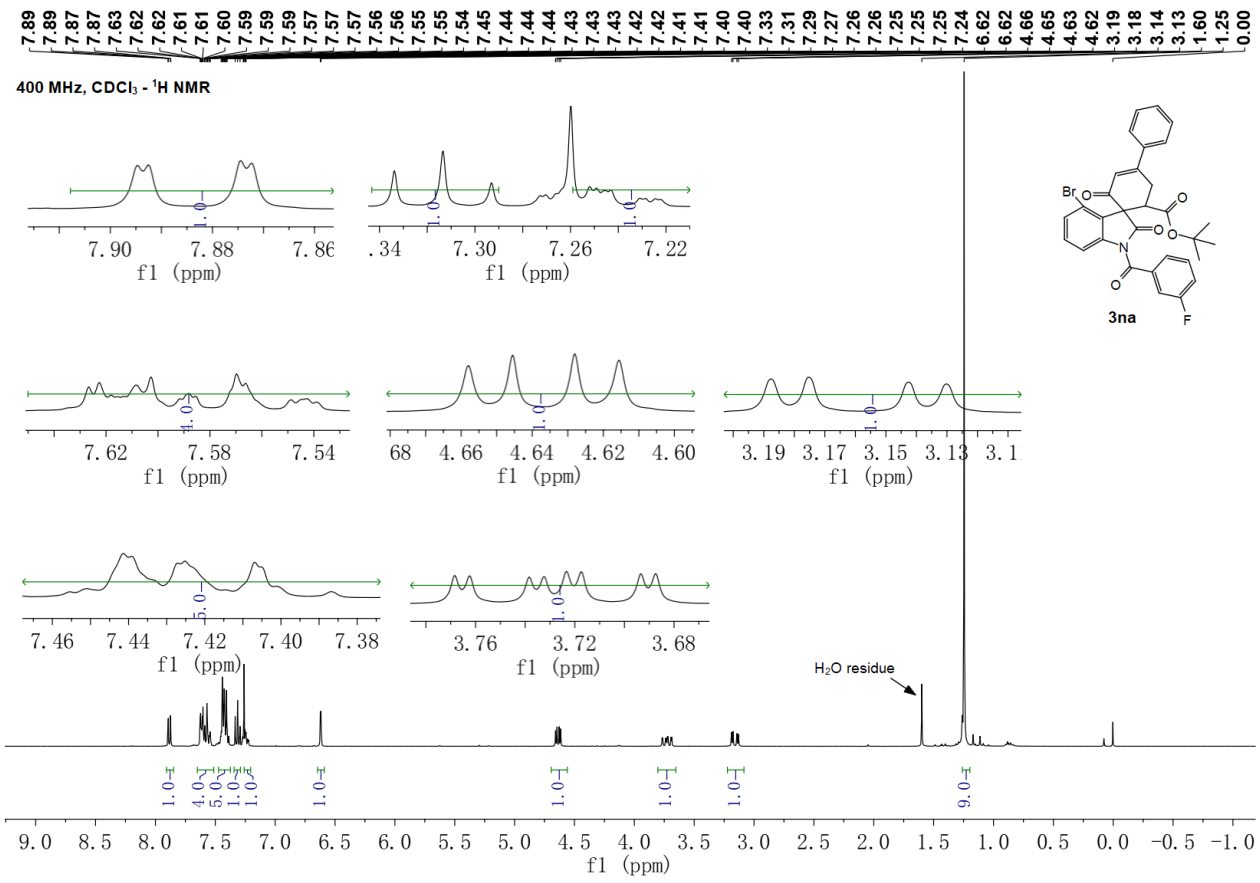

400 MHz, CDCl3 - 1H NMR
3ma
H2O residue
f1 (ppm)

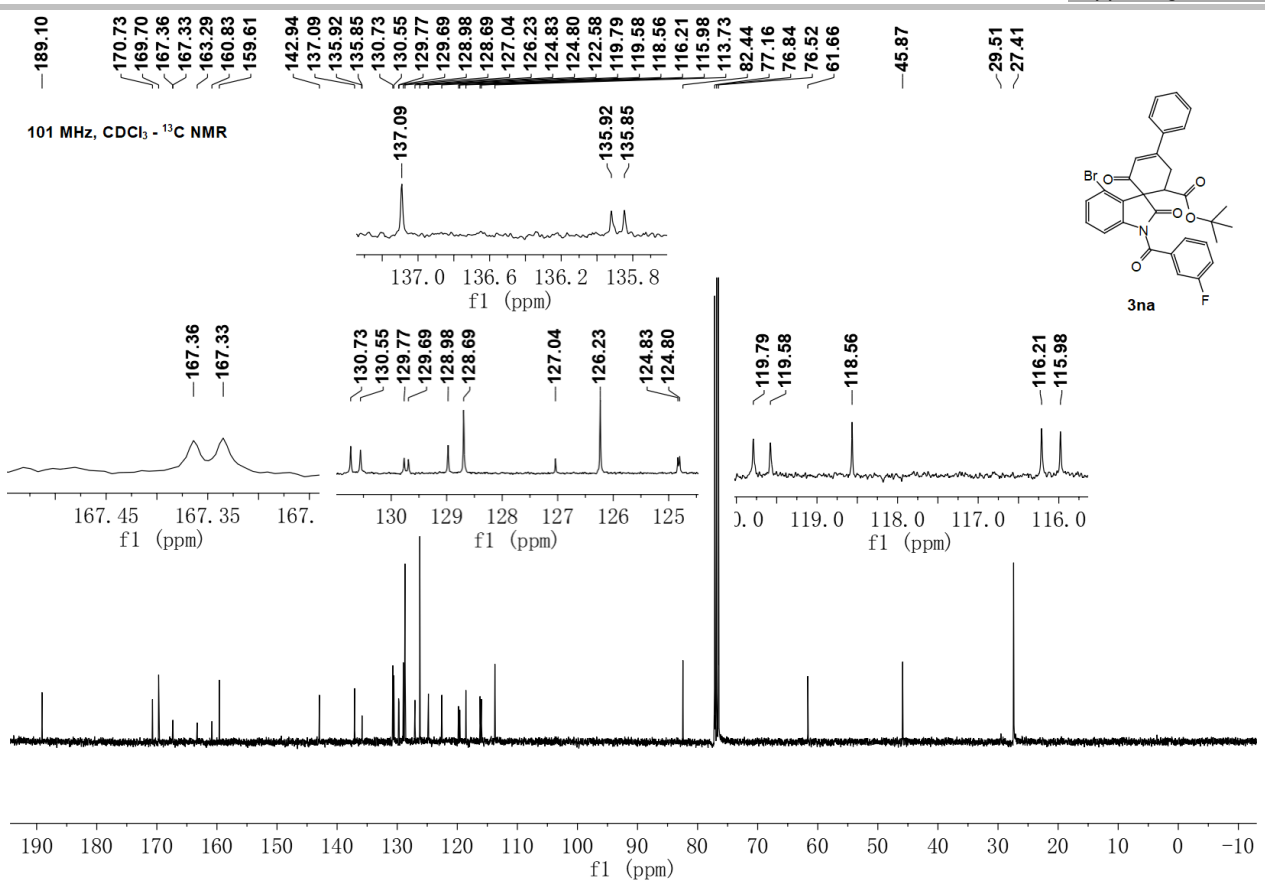

101 MHz, CDCl3 - 13C NMR
3ma
f1 (ppm)

376 MHz, $CDCl_3$ - ^{19}F NMR



400 MHz, $CDCl_3$ - ^{1}H NMR

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167.33
163.29
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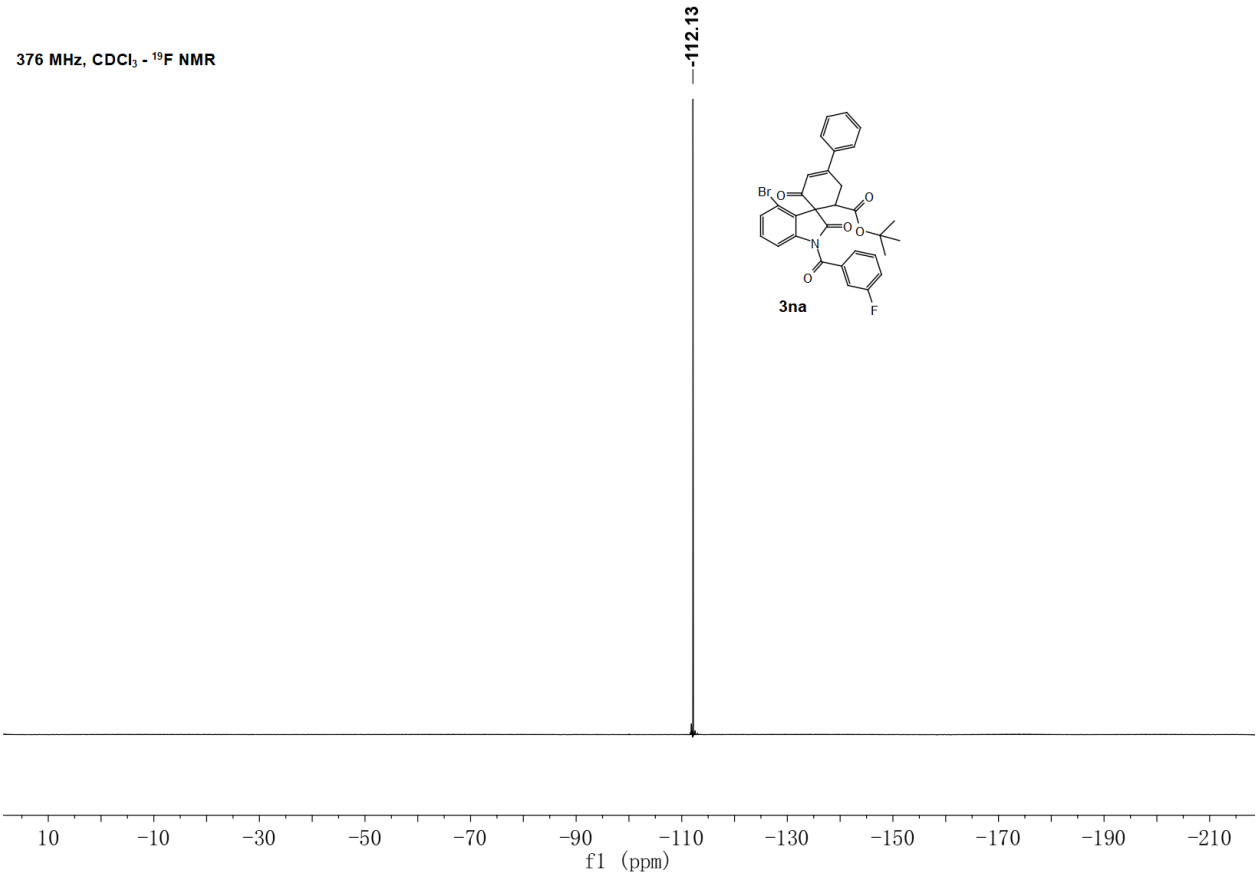
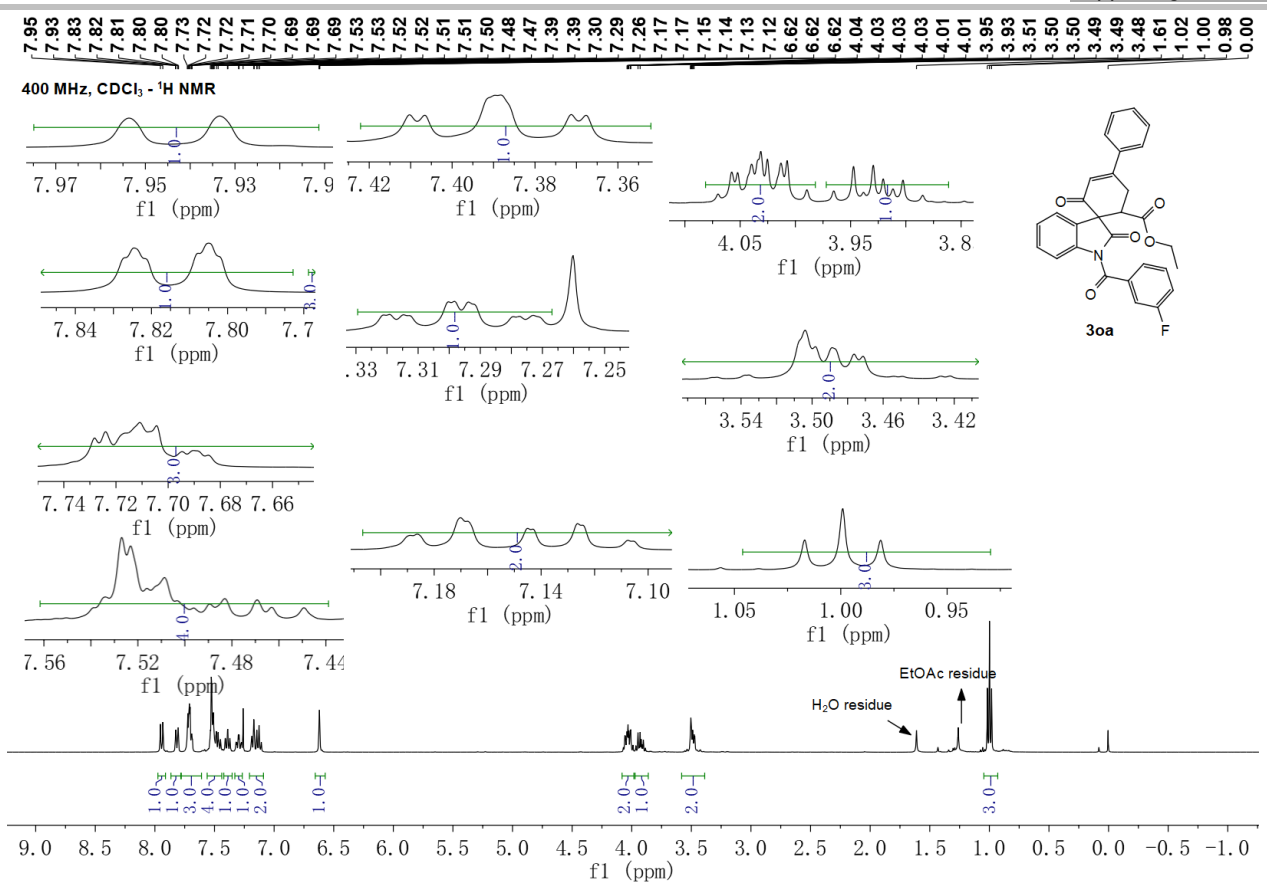
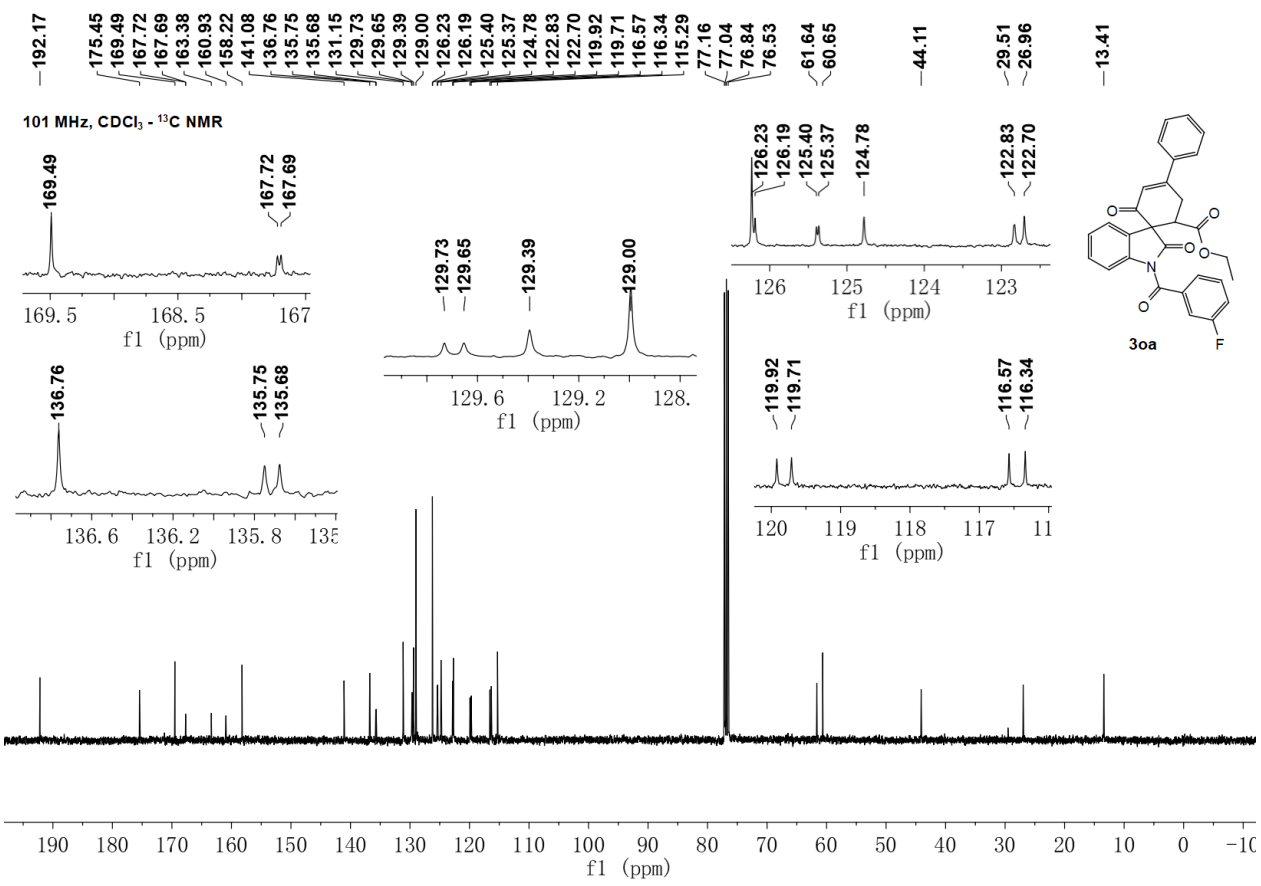
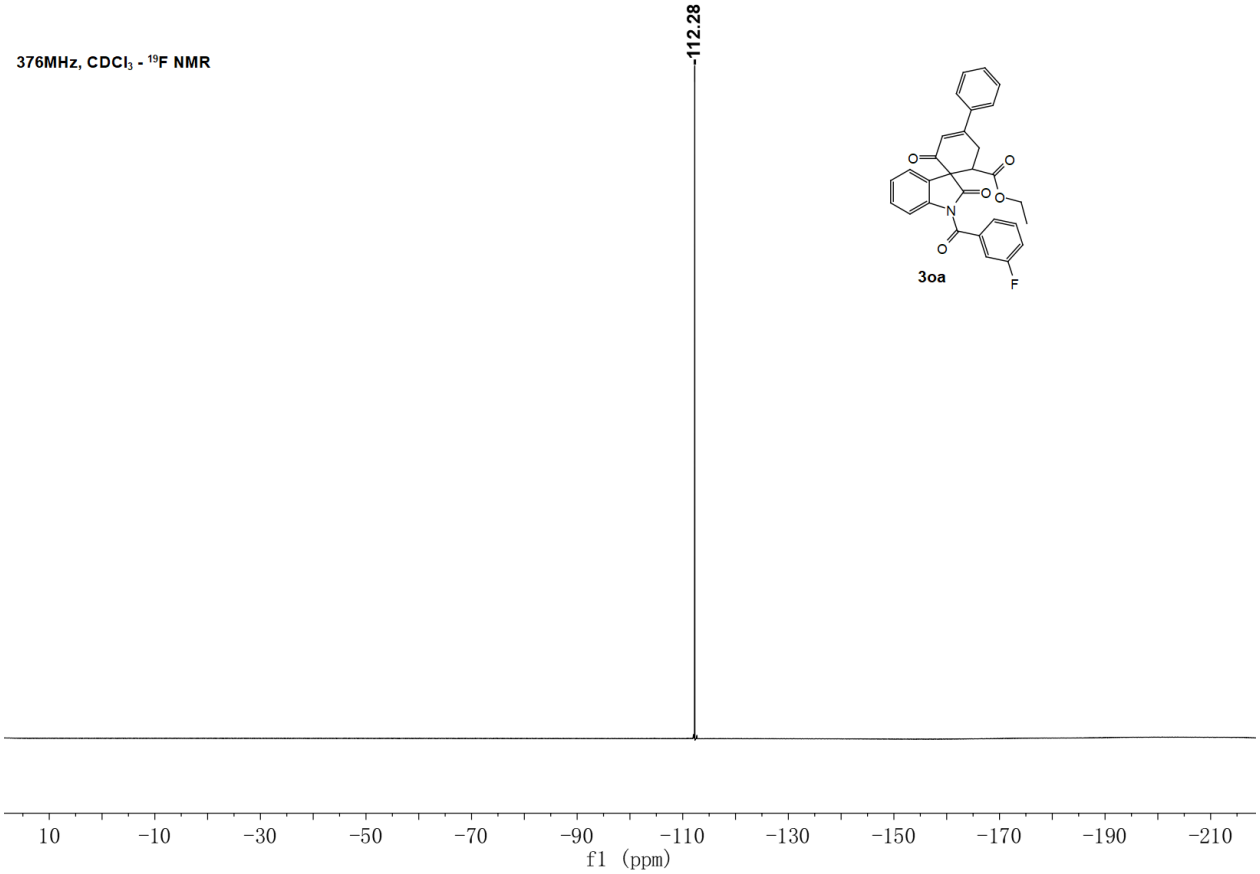
137.09
135.92
135.85
130.73
130.55
129.77
129.69
128.98
128.69
127.04
126.23
124.83
124.80
122.58
119.79
119.58
118.56
116.21
115.98
113.73
82.44
77.16
76.84
76.52
61.66
45.87
29.51
27.41
101 MHz, CDCl3 - 13C NMR
3na
f1 (ppm)


-112.13
376 MHz, CDCl3 - 19F NMR
3na
f1 (ppm)

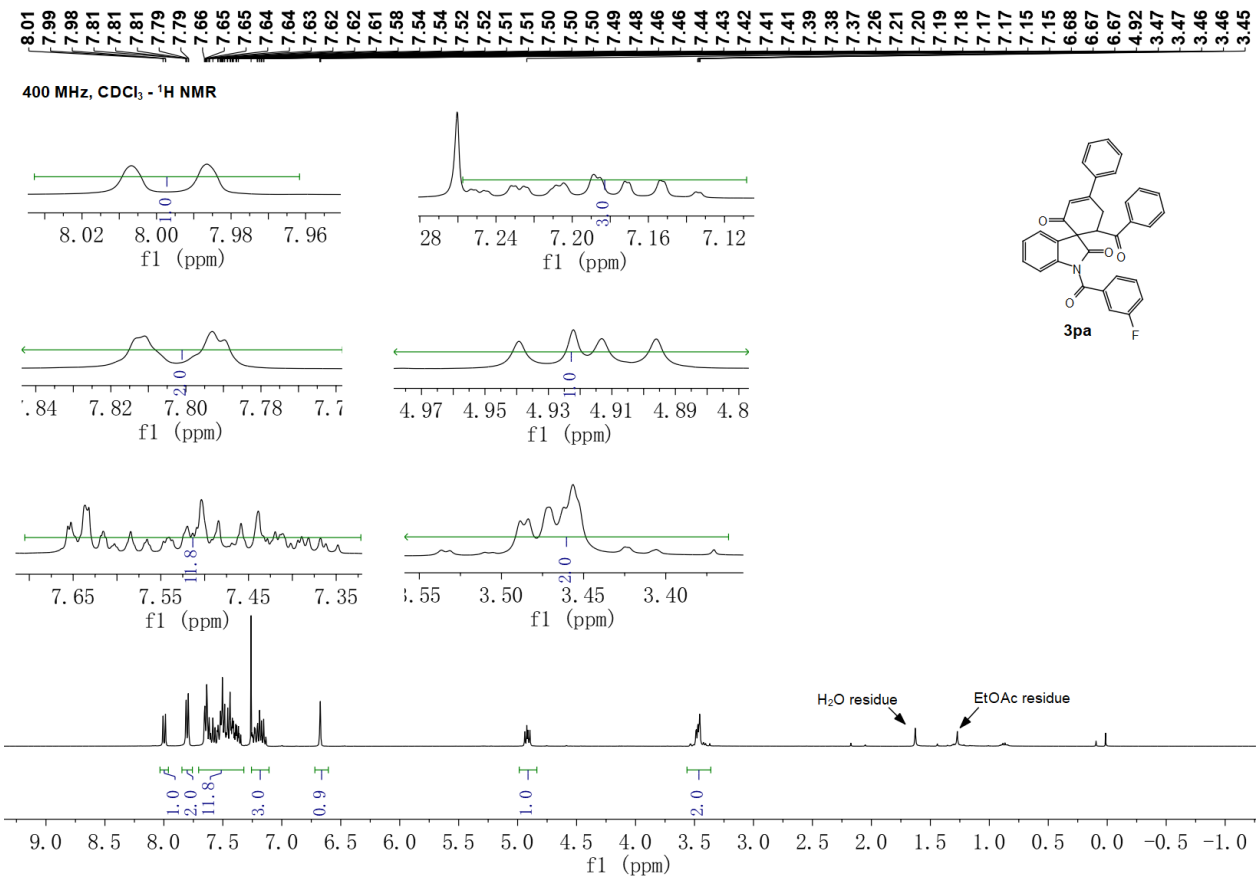

400 MHz, CDCl3 - 1H NMR
EtOAc residue
H2O residue
3oa
F
f1 (ppm)

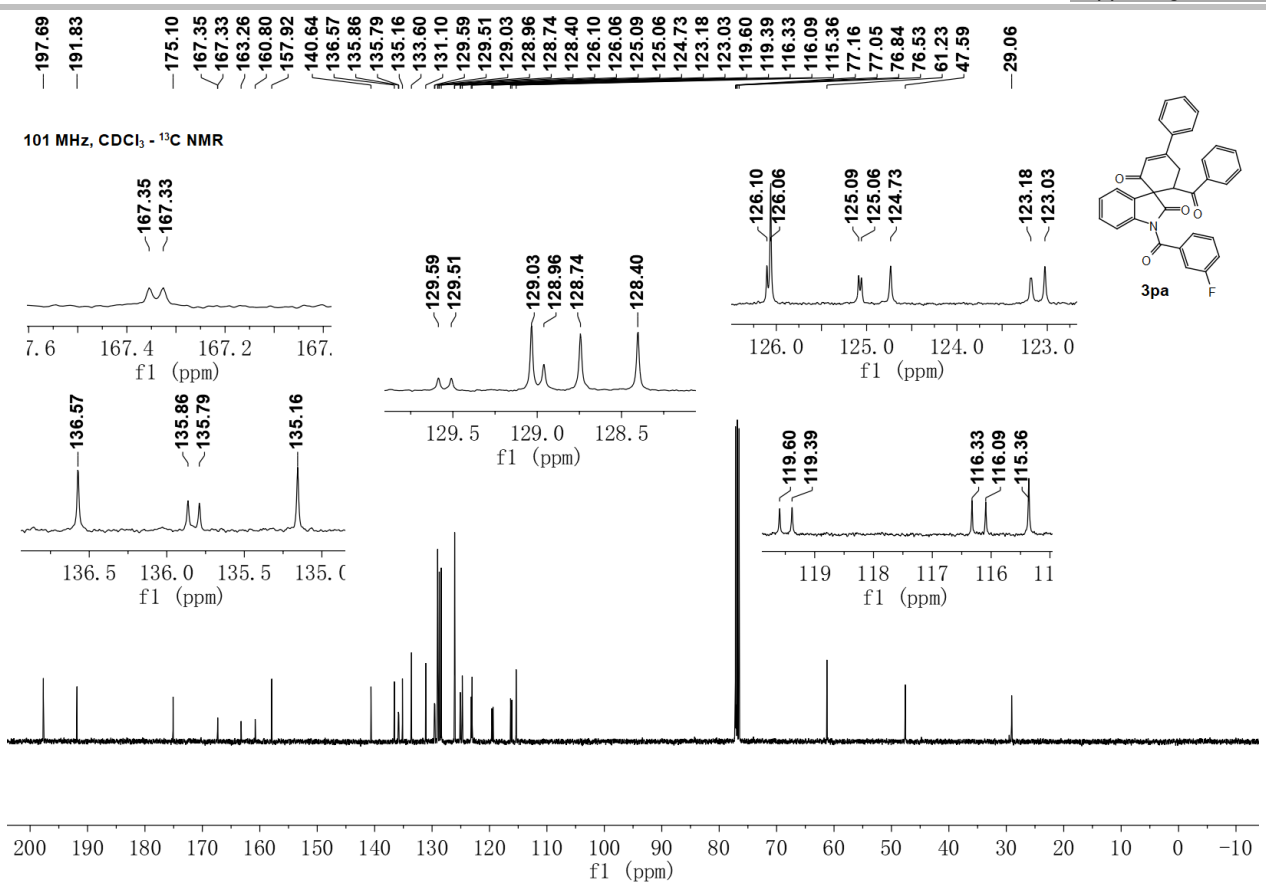

101 MHz, CDCl3 - 13C NMR
3oa
F
f1 (ppm)

376MHz, $CDCl_3$ - ^{19}F NMR



400 MHz, $CDCl_3$ - ^1H NMR

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191.83
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167.35
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157.92
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136.57
135.86
135.79
135.16
133.60
131.10
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129.51
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126.06
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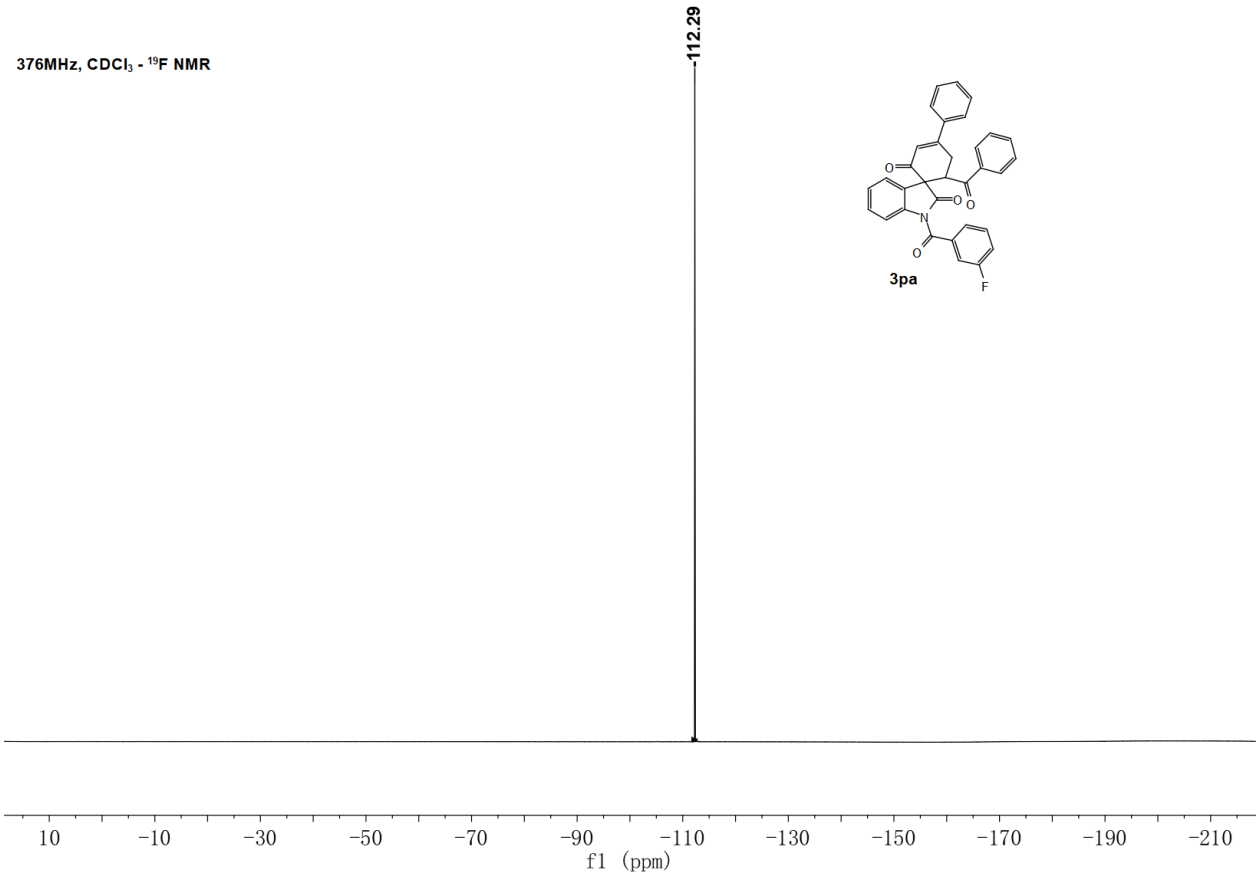
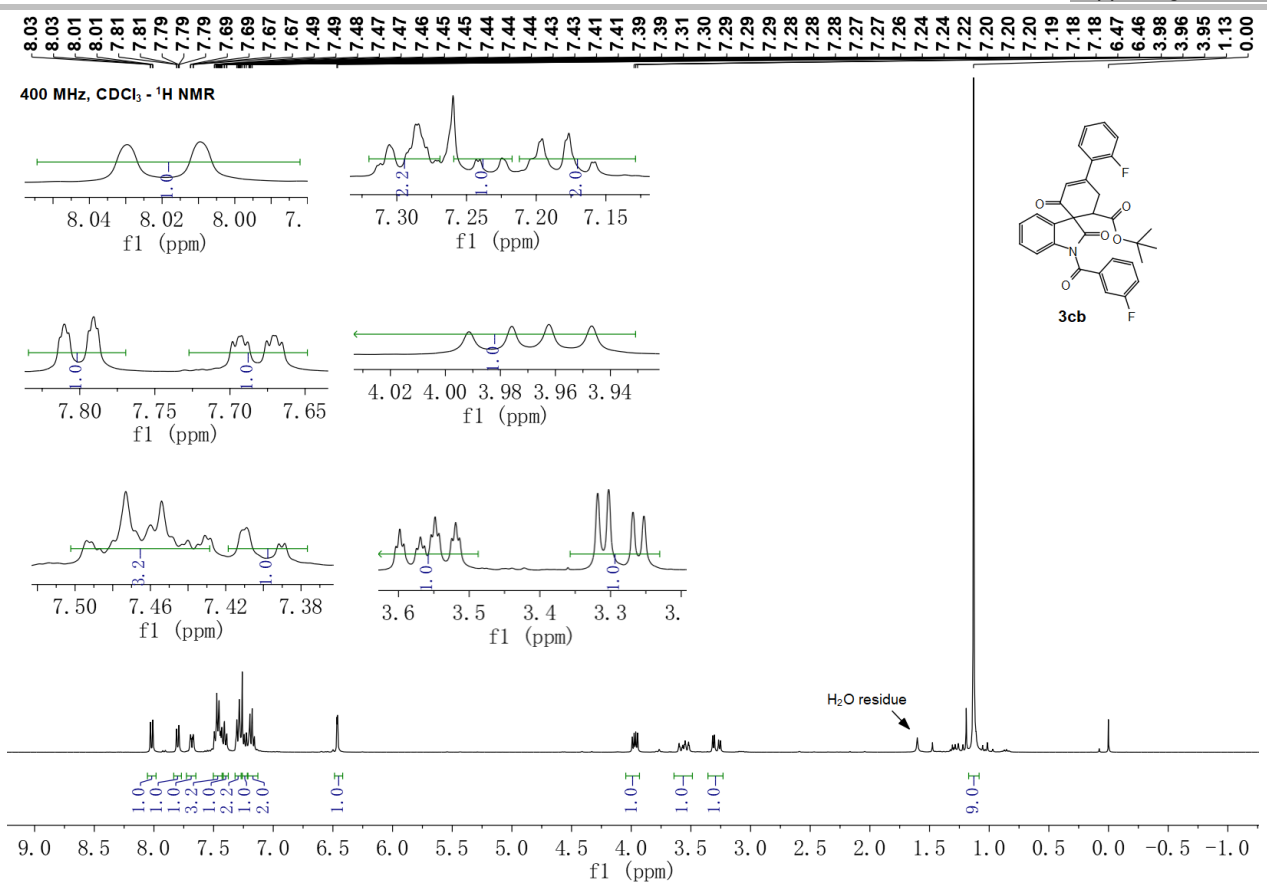
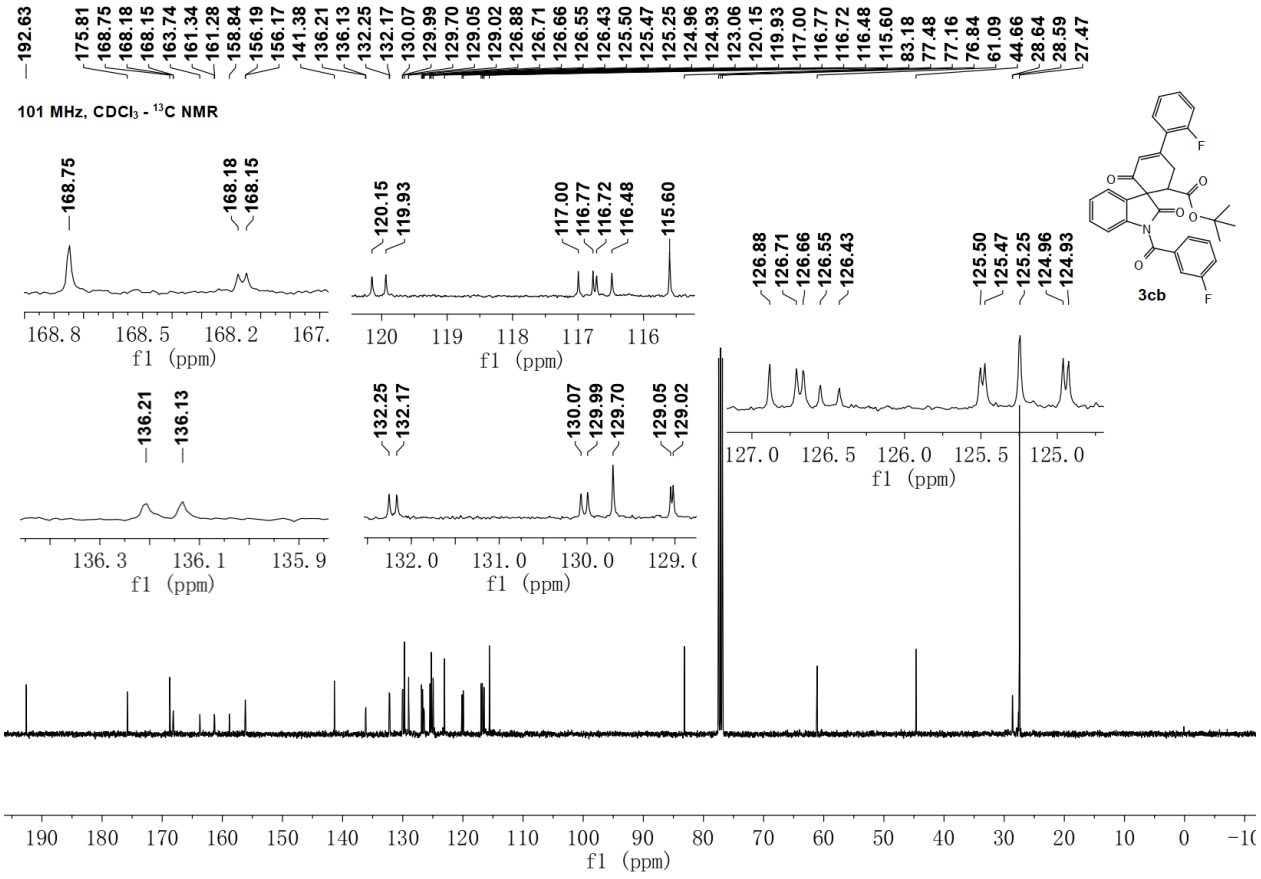
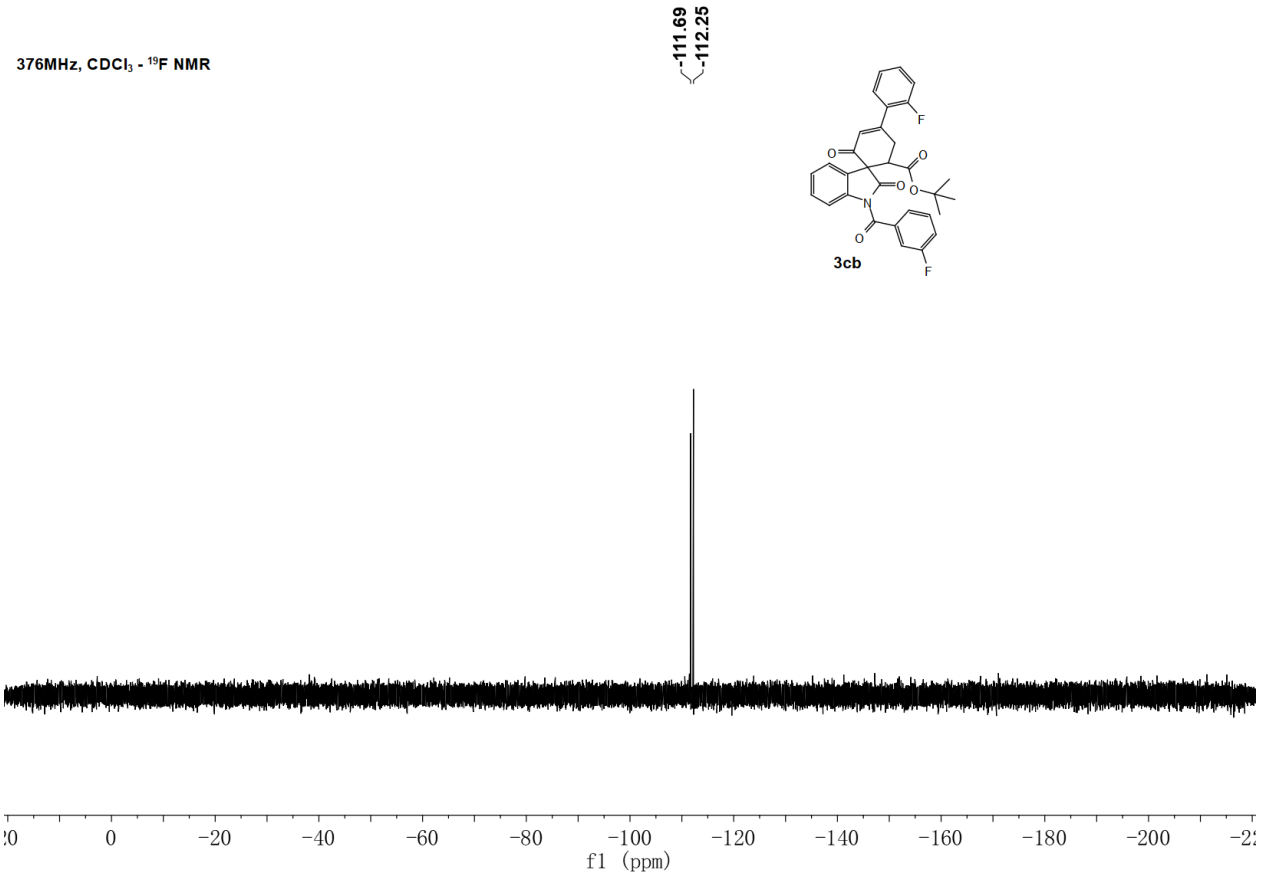
123.18
123.03
119.60
119.39
116.33
116.09
115.36
77.16
77.05
76.84
76.53
61.23
47.59
29.06
101 MHz, CDCl3 - 13C NMR
3pa
f1 (ppm)


376MHz, CDCl3 - 19F NMR
-112.29
3pa
f1 (ppm)

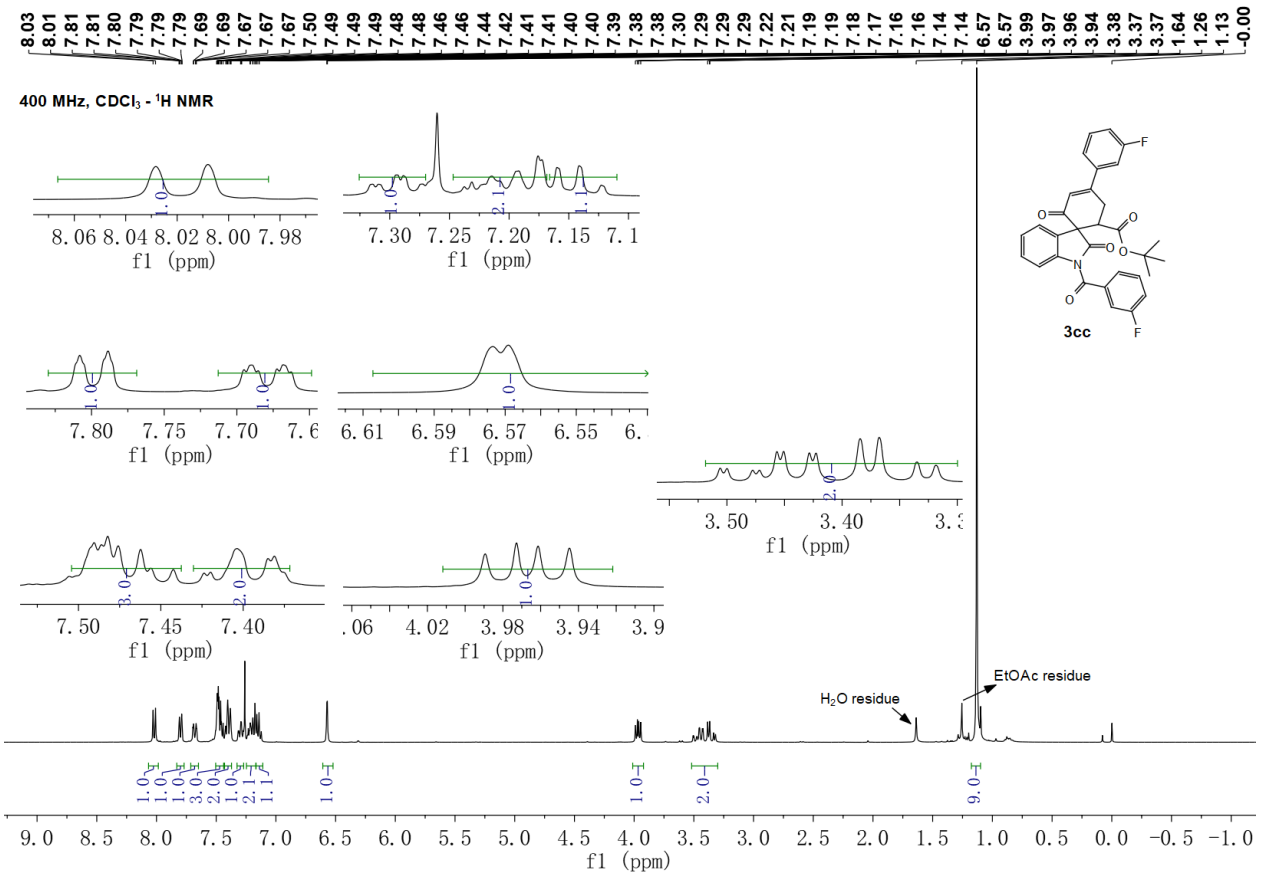

400 MHz, CDCl3 - 1H NMR
3cb
H2O residue
f1 (ppm)

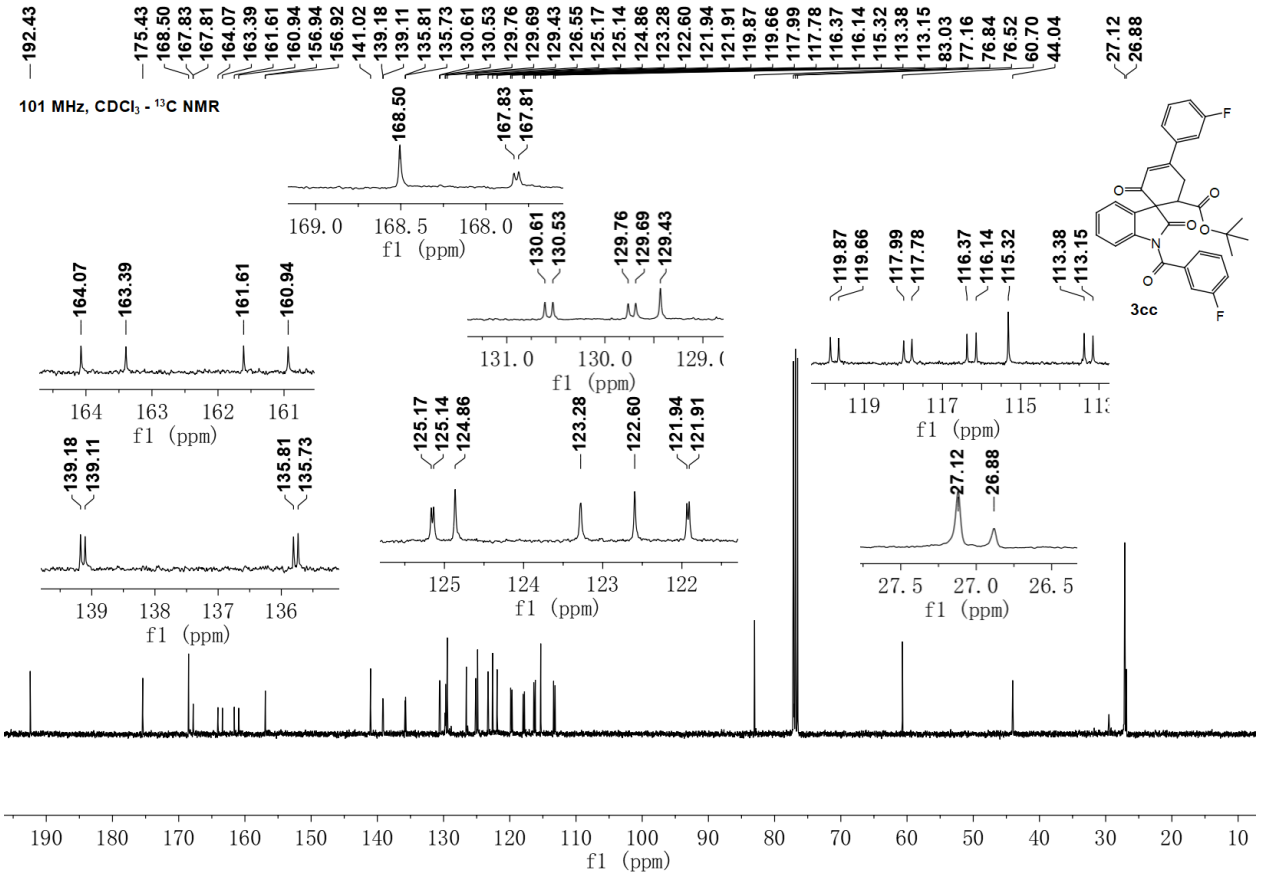

101 MHz, CDCl3 - 13C NMR
3cb
f1 (ppm)

376MHz, $CDCl_3$ - ^{19}F NMR



400 MHz, $CDCl_3$ - ^{1}H NMR

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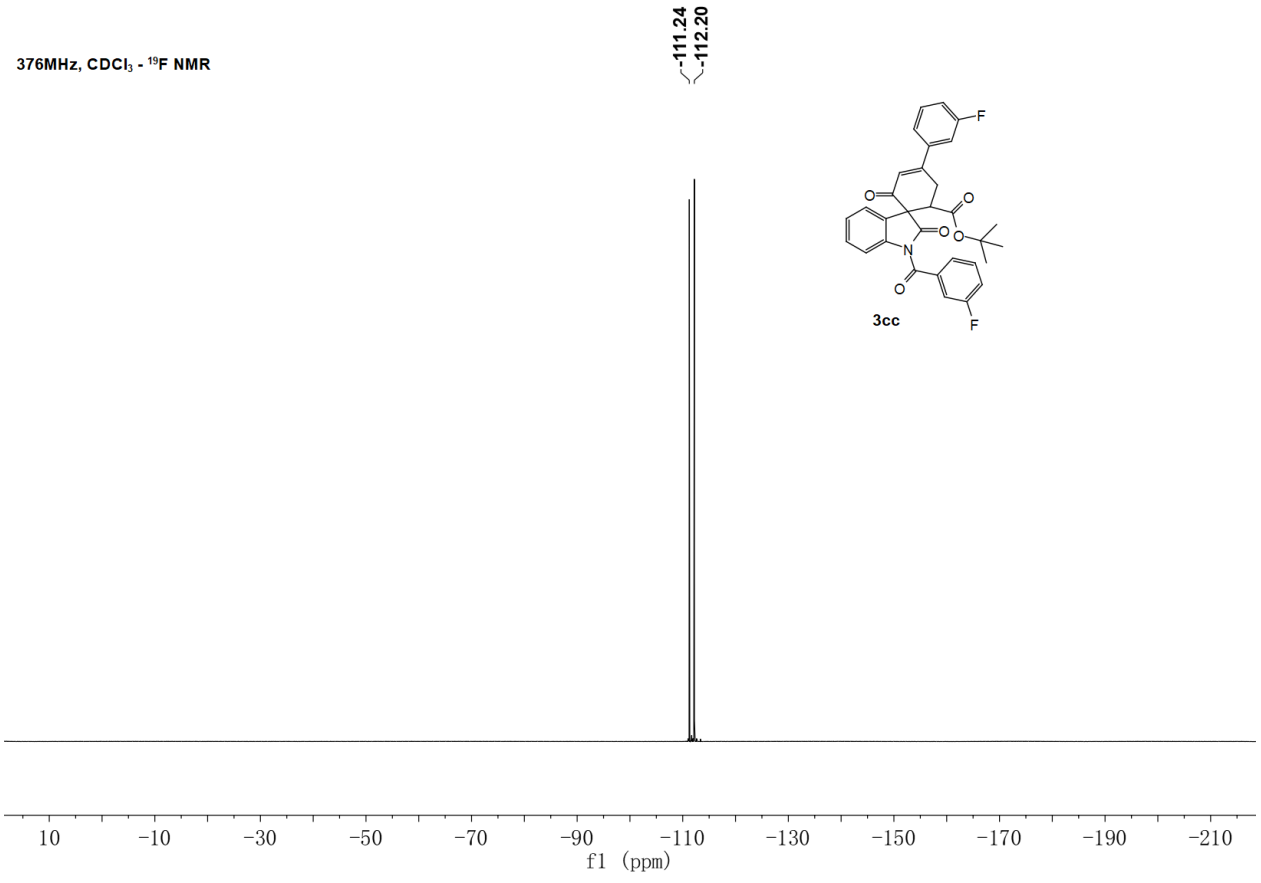
116.37
116.14
115.32
113.38
113.15
83.03
77.16
76.84
76.52
60.70
44.04
27.12
26.88
101 MHz, CDCl3 - 13C NMR
3cc
f1 (ppm)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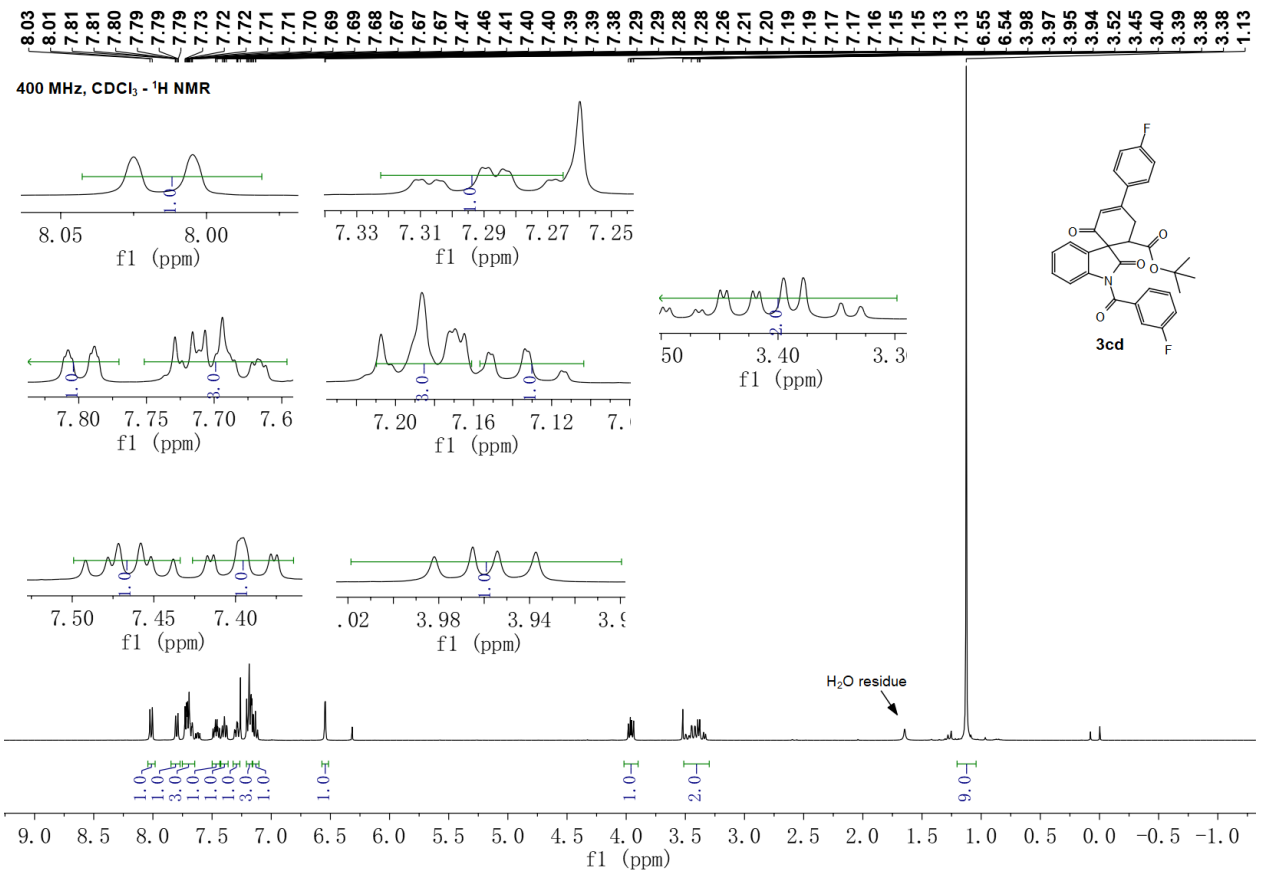
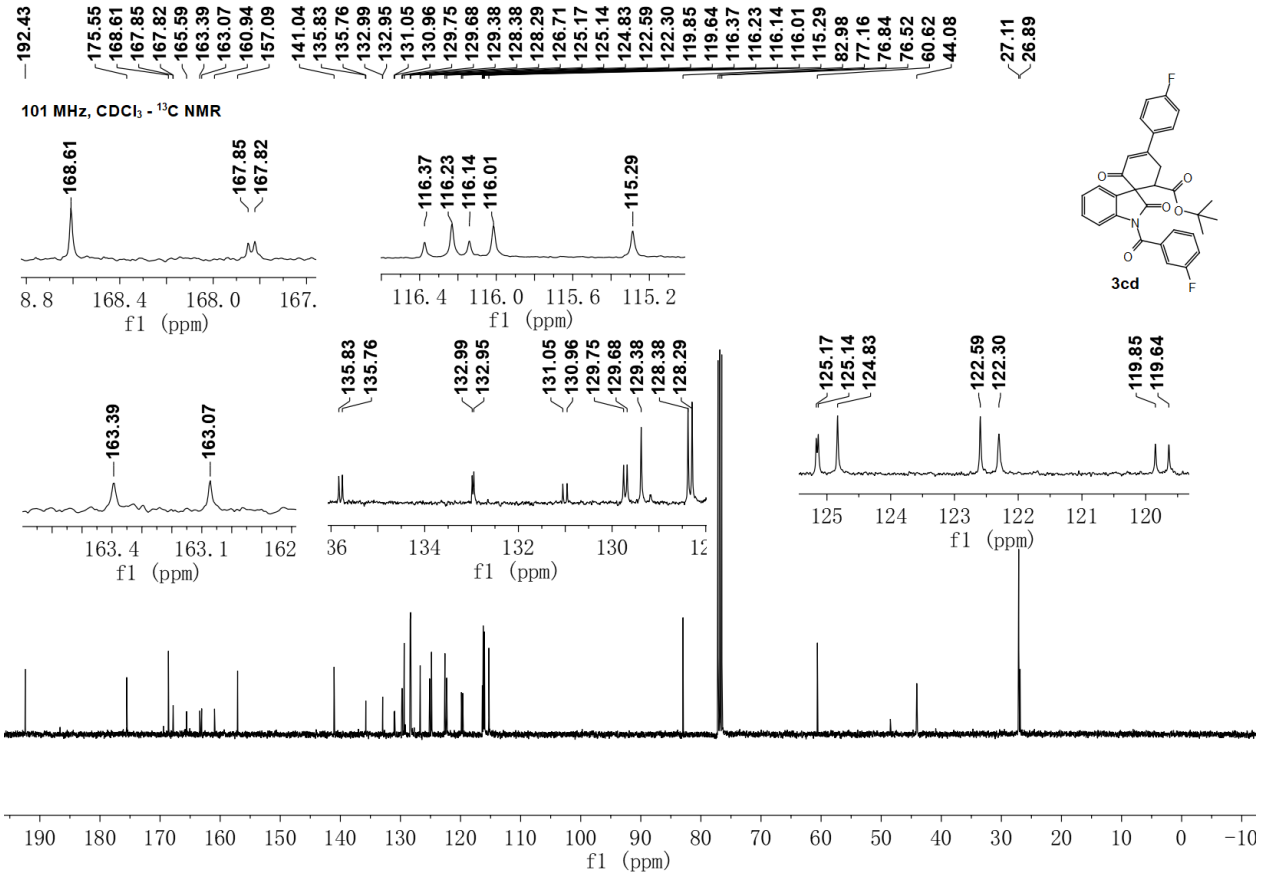
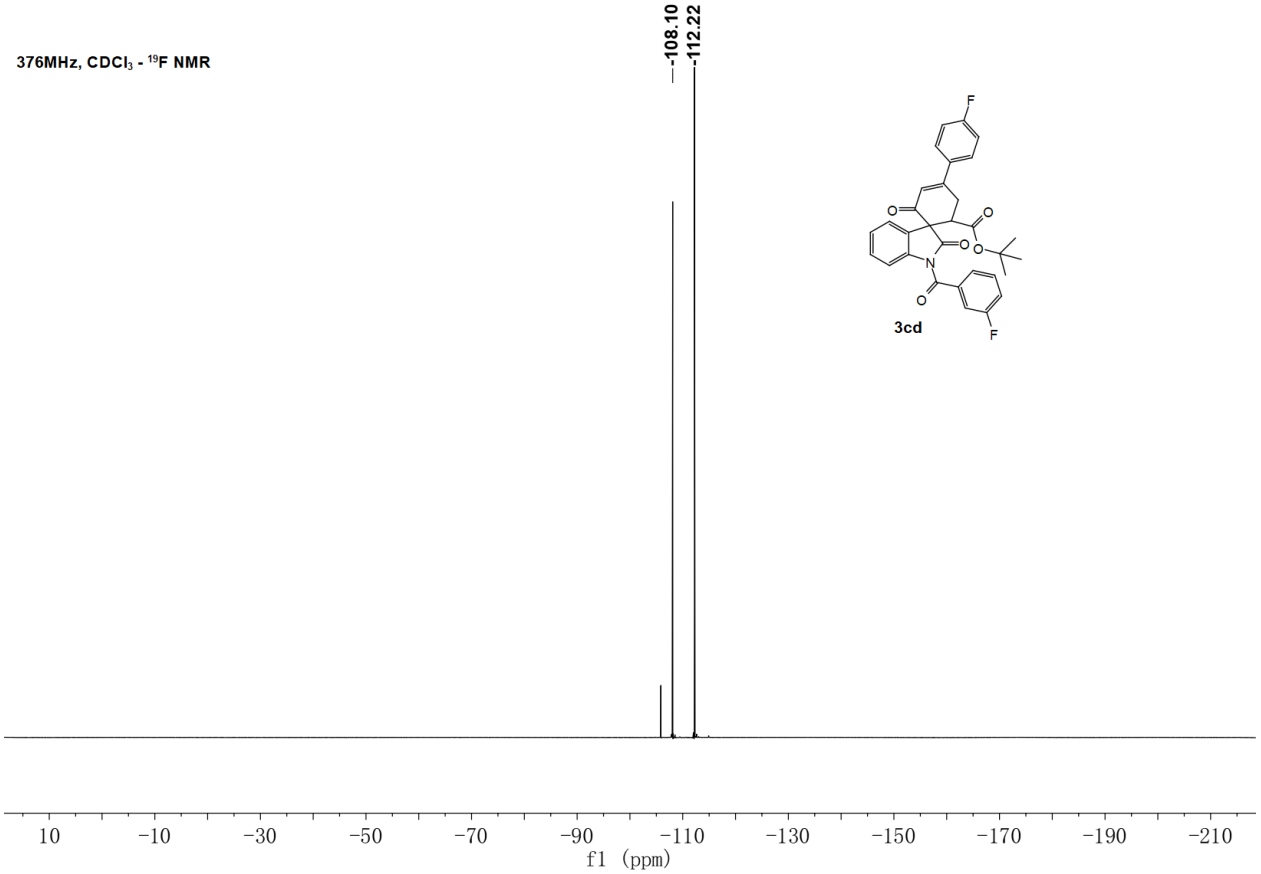
-112.20
376MHz, CDCl3 - 19F NMR
3cc
f1 (ppm)


400 MHz, CDCl3 - 1H NMR
3cd
H2O residue
f1 (ppm)

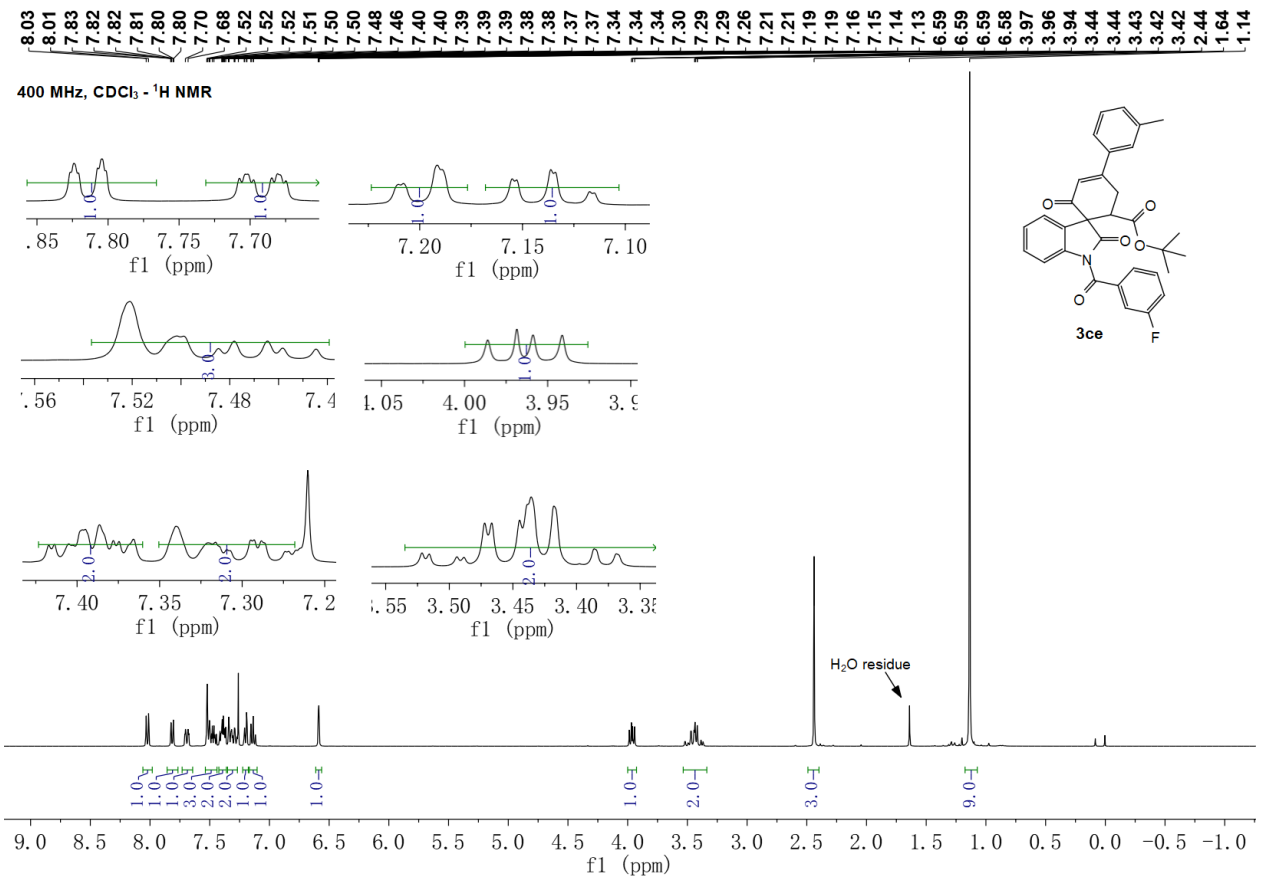

101 MHz, CDCl3 - 13C NMR
3cd
f1 (ppm)

376MHz, $CDCl_3$ - ^{19}F NMR

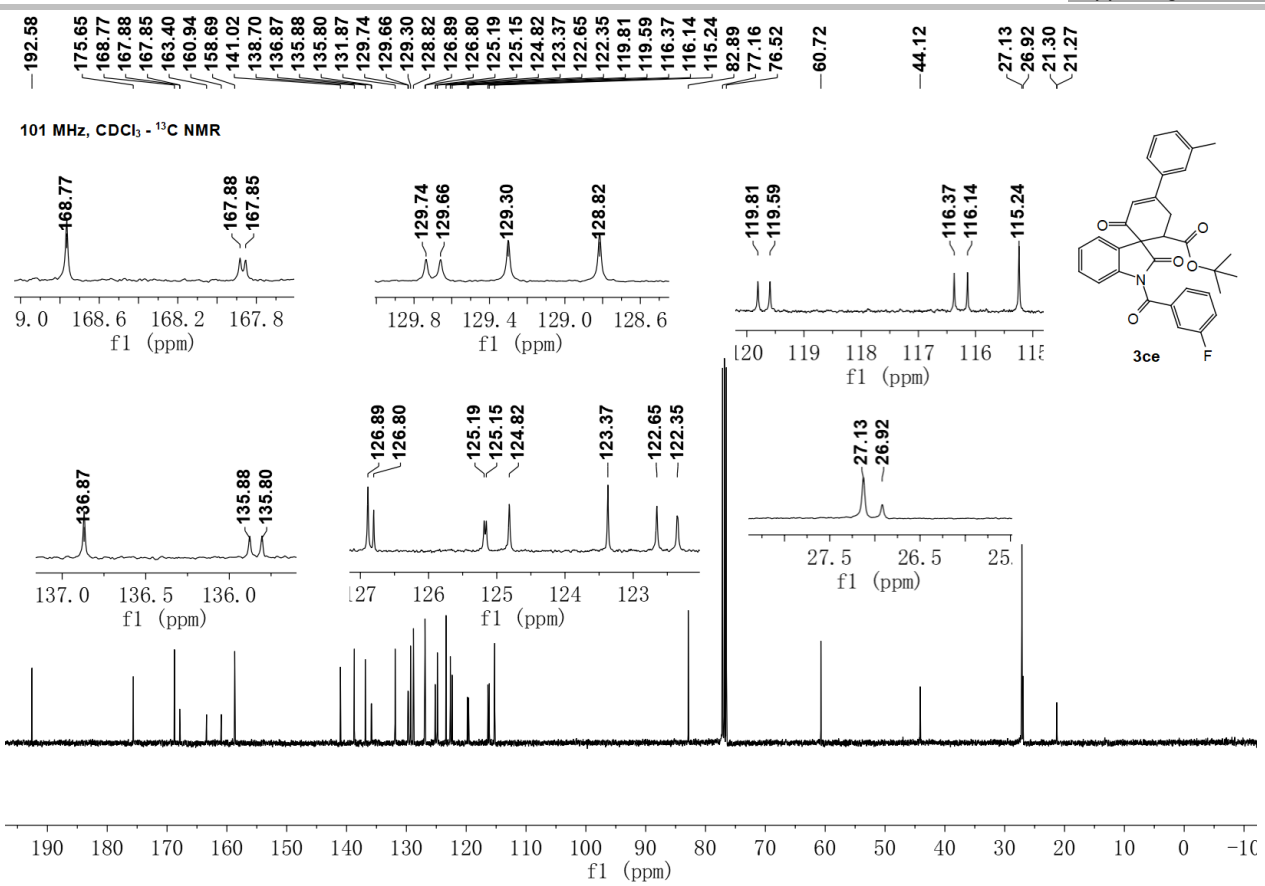


3cd

400 MHz, $CDCl_3$ - ^{1}H NMR



3ce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116.37
116.14
115.24
82.89
77.16
76.52
60.72
44.12
27.13
26.92
21.30
21.27
101 MHz, CDCl3 - 13C NMR
168.77
167.88
167.85
129.74
129.66
129.30
128.82
119.81
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124.82
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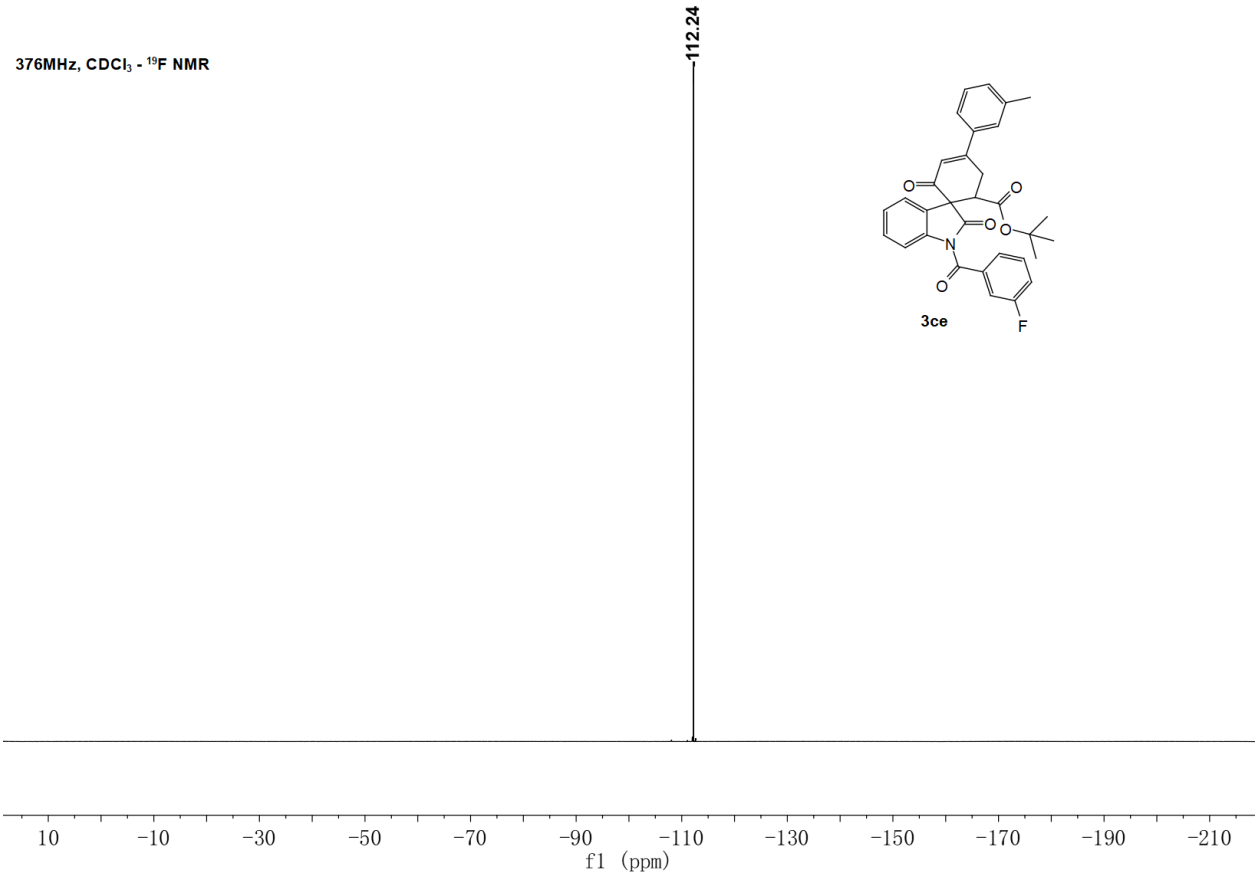
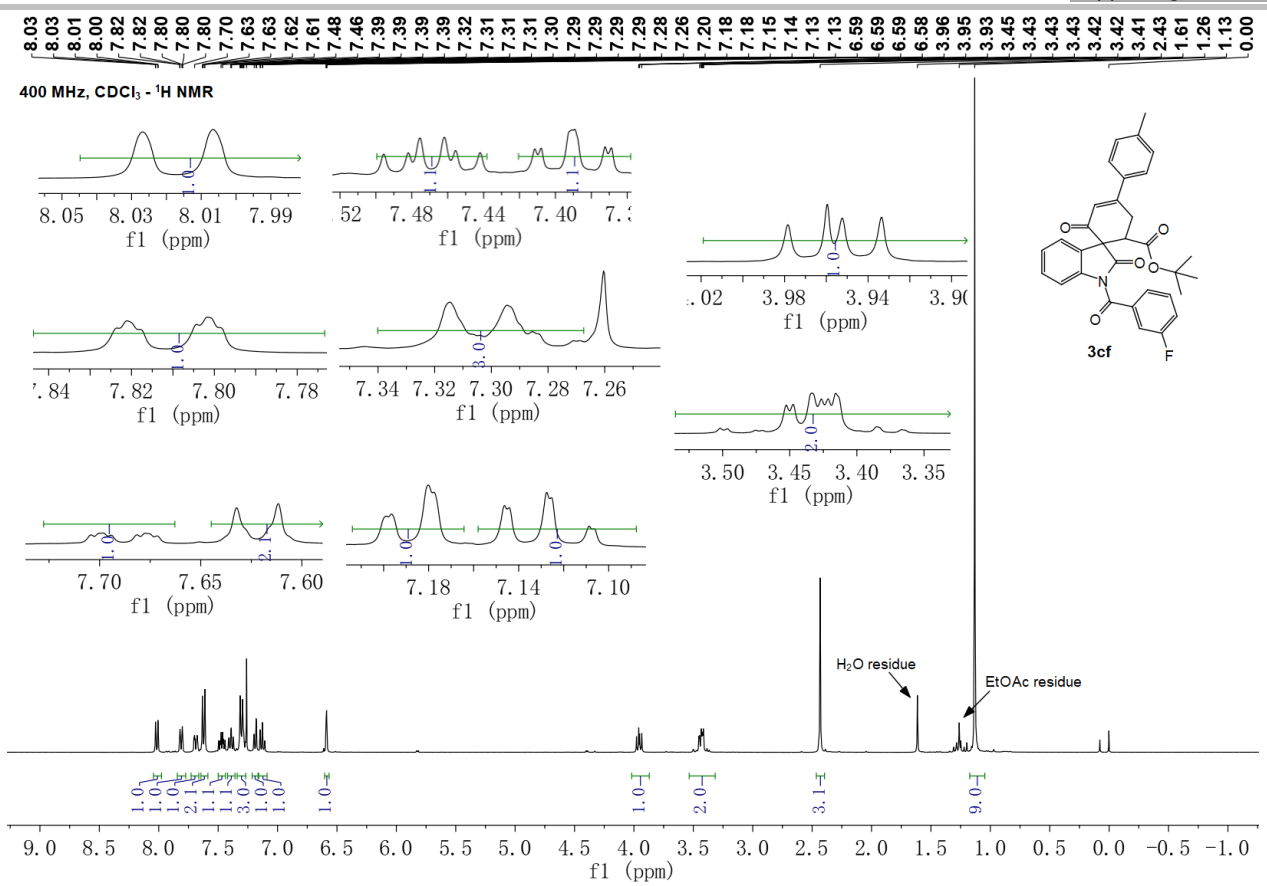
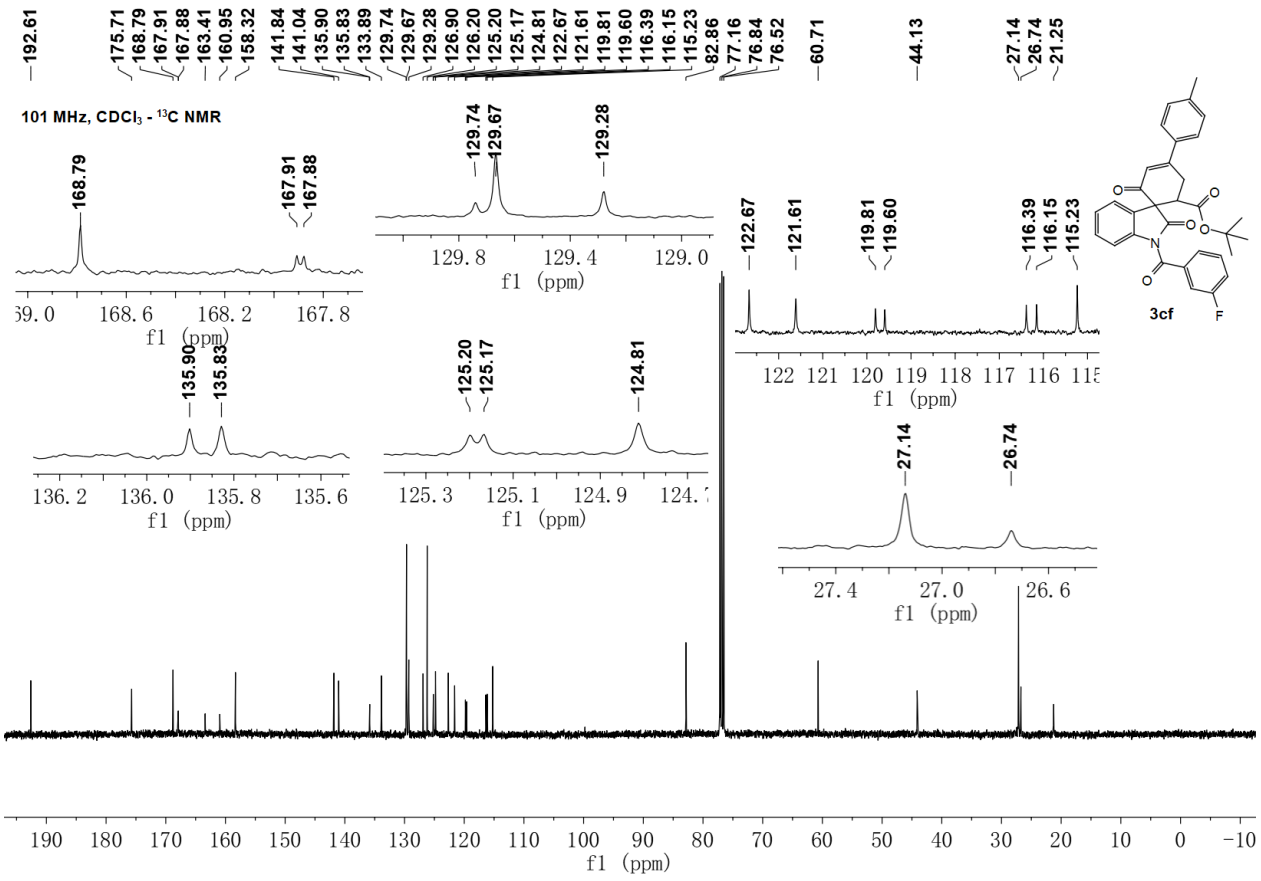
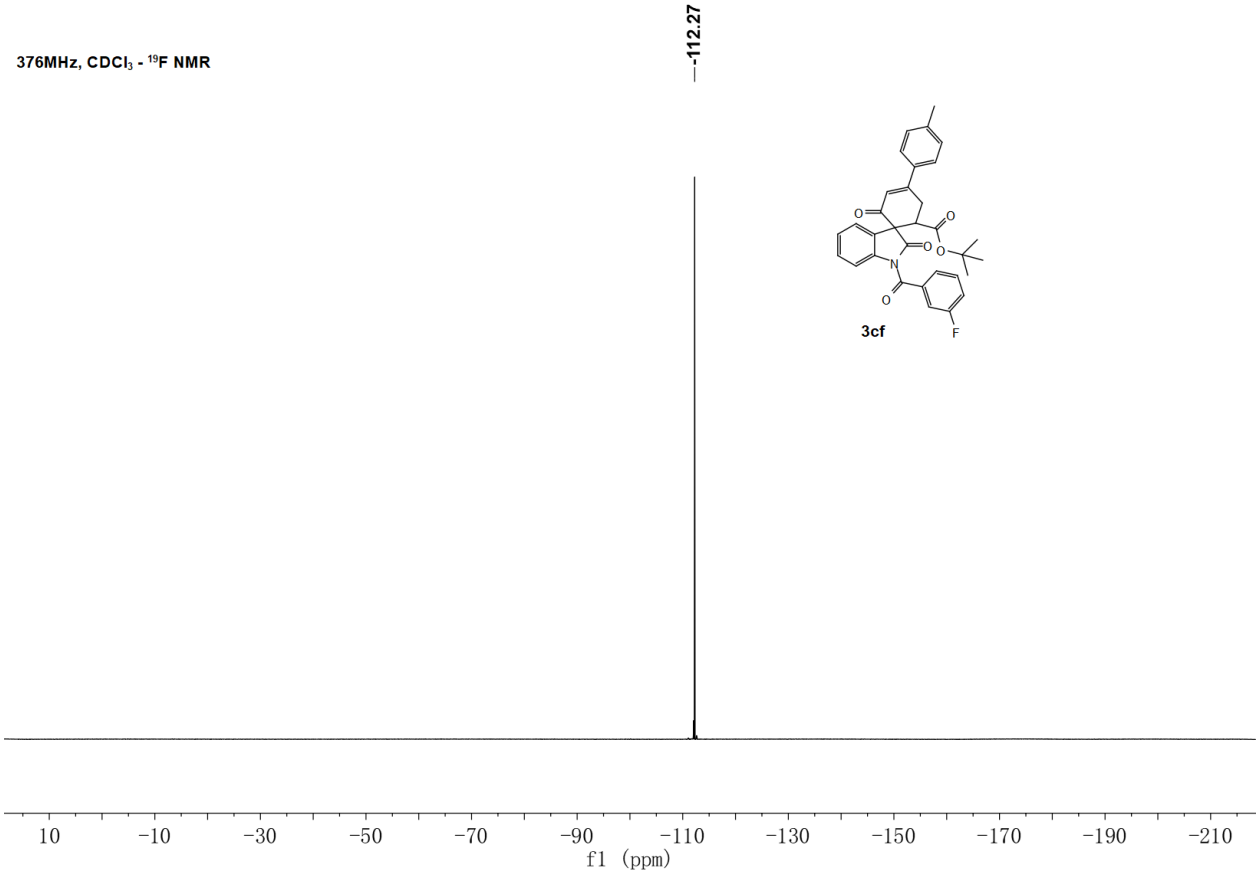
27.13
26.92
f1 (ppm)
3ce
F


112.24
376MHz, CDCl3 - 19F NMR
f1 (ppm)
3ce
F

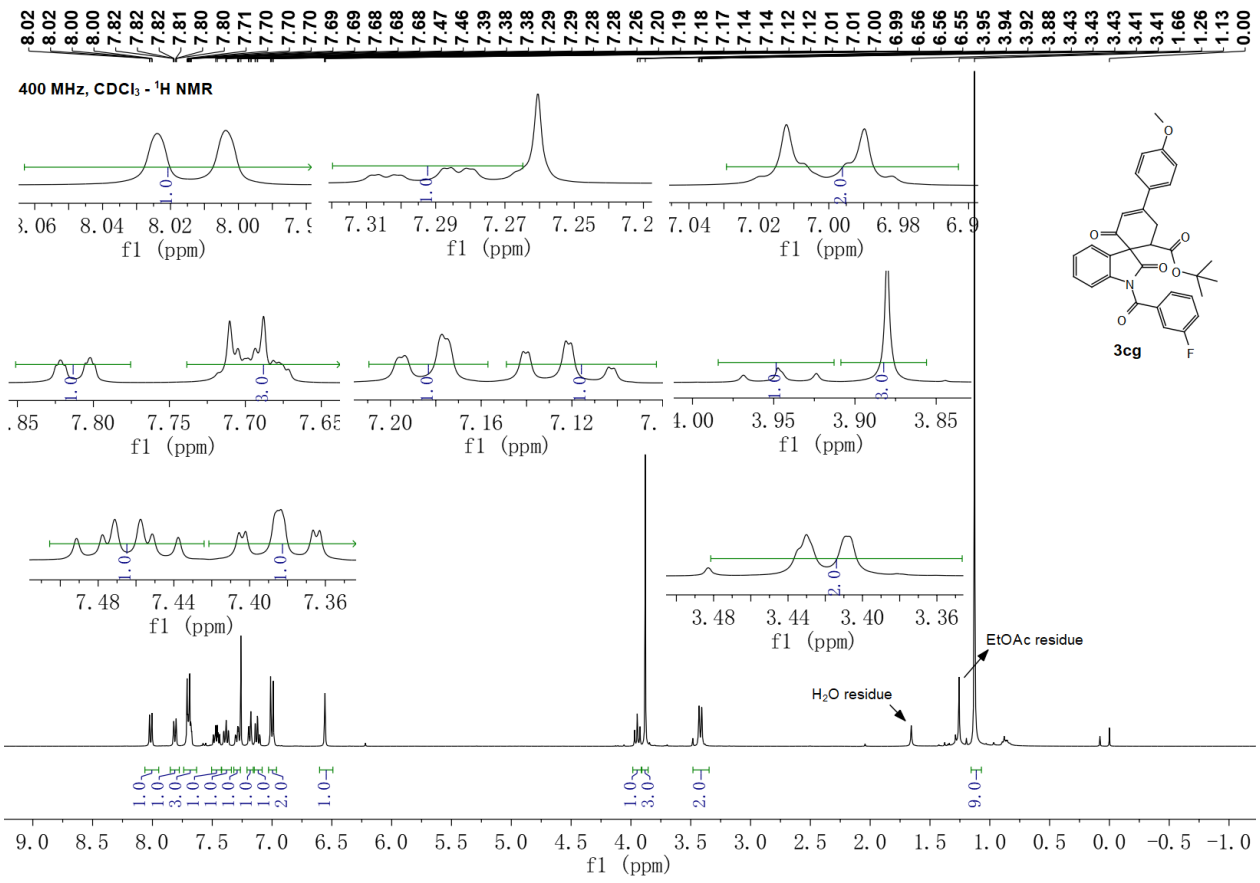

400 MHz, CDCl3 - 1H NMR
H2O residue
EtOAc residue
3cf
f1 (ppm)

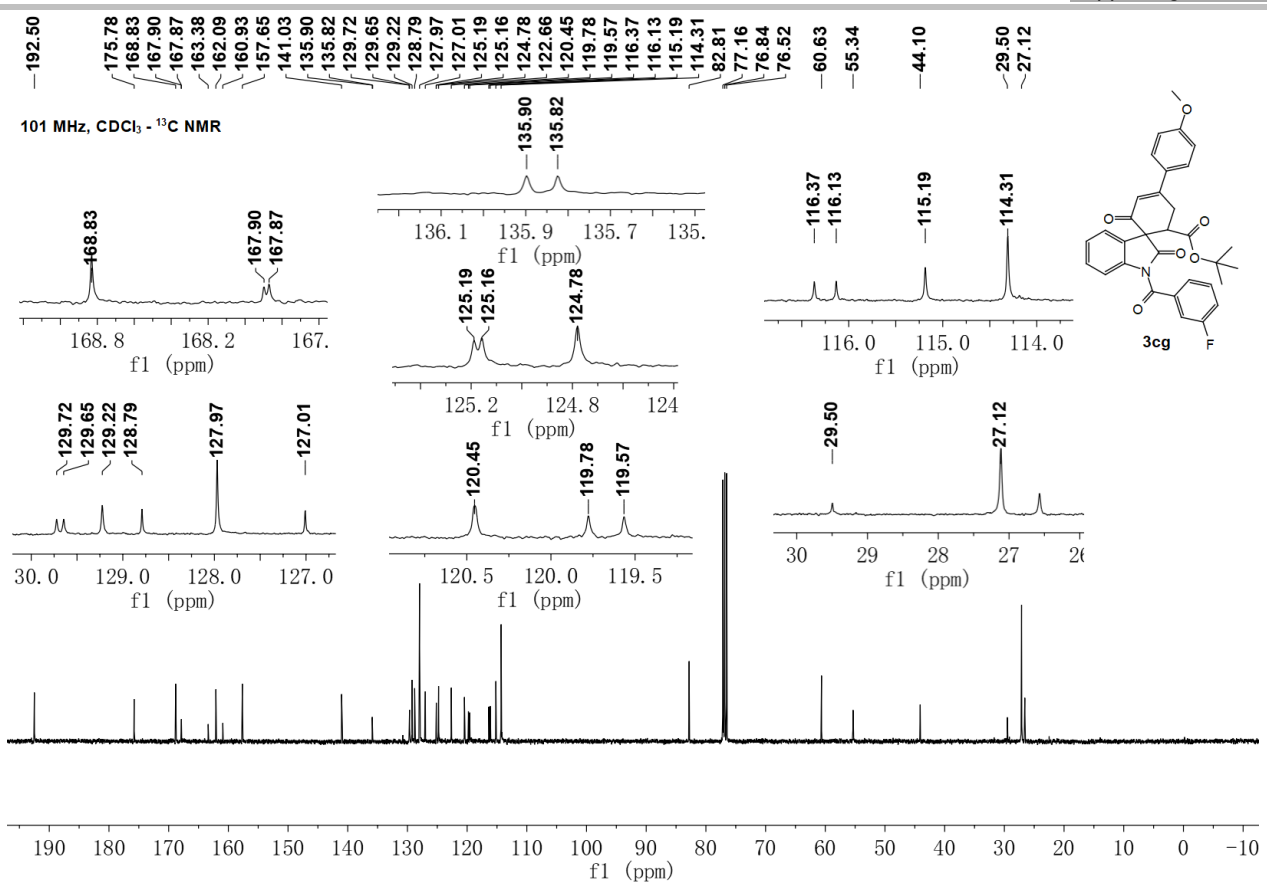

101 MHz, CDCl3 - 13C NMR
3cf
f1 (ppm)

376MHz, $CDCl_3$ - ^{19}F NMR



400 MHz, $CDCl_3$ - ^{1}H NMR

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116.13
115.19
114.31
82.81
77.16
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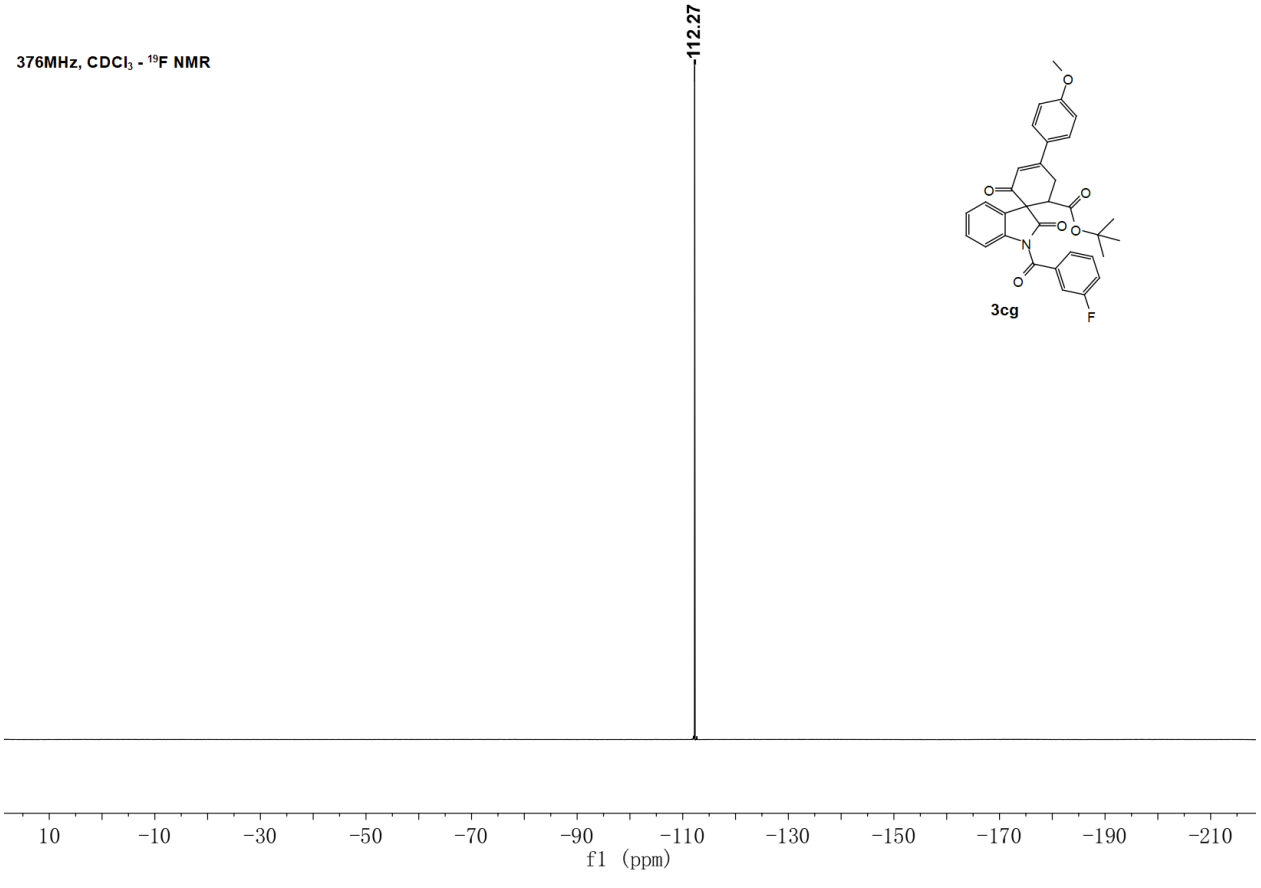
60.63
55.34
44.10
29.50
27.12
101 MHz, CDCl3 - 13C NMR
3cg
f1 (ppm)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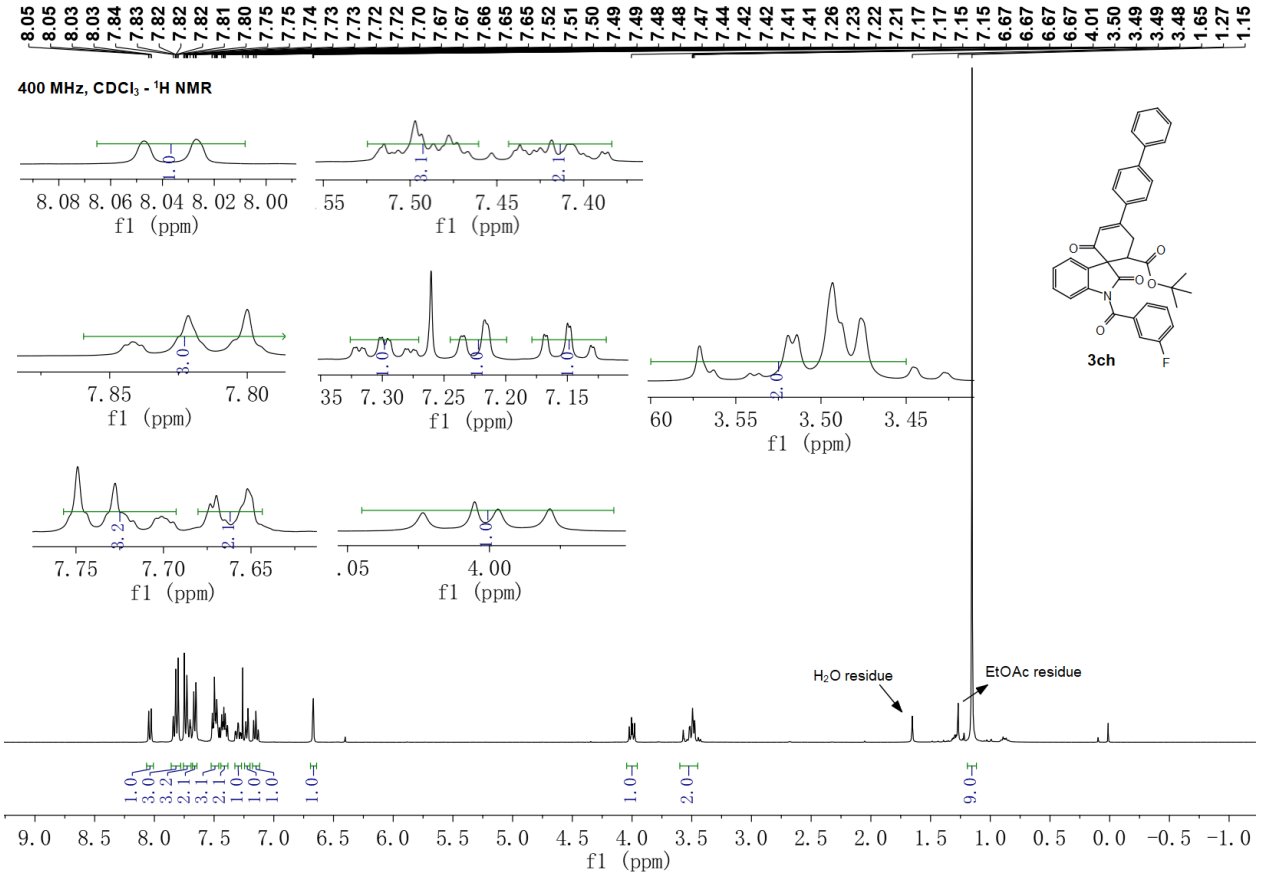
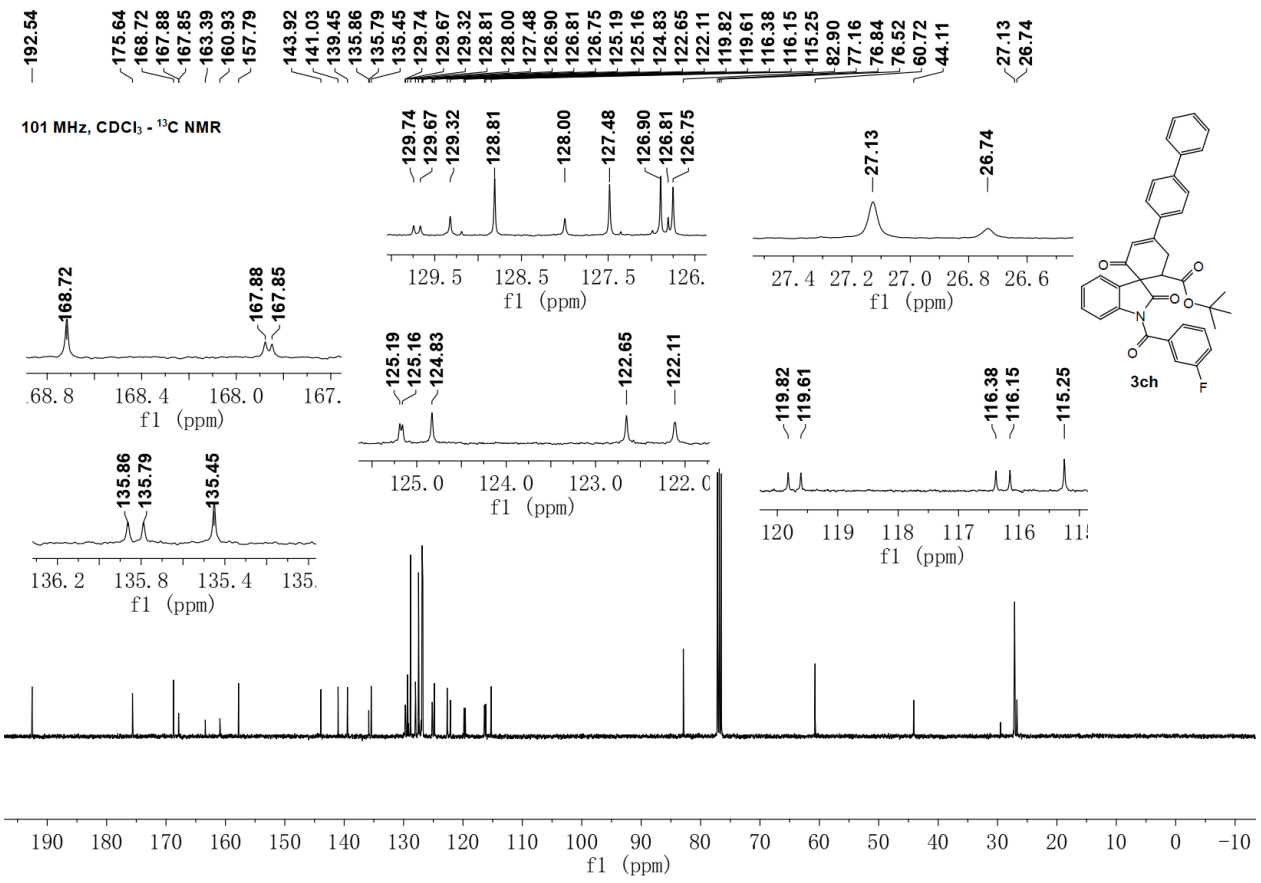
f1 (ppm)

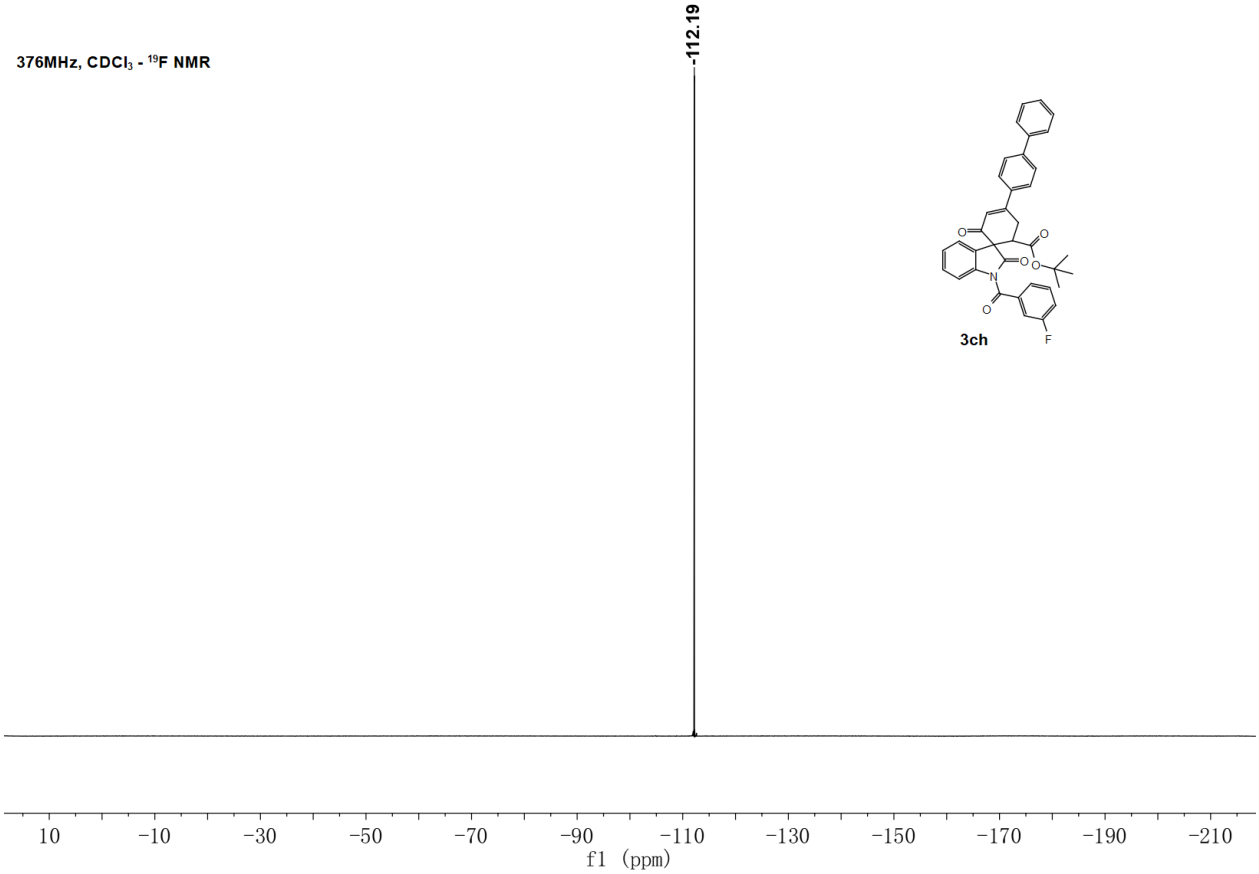

400 MHz, CDCl3 - 1H NMR
H2O residue
EtOAc residue
f1 (ppm)

3ch
F

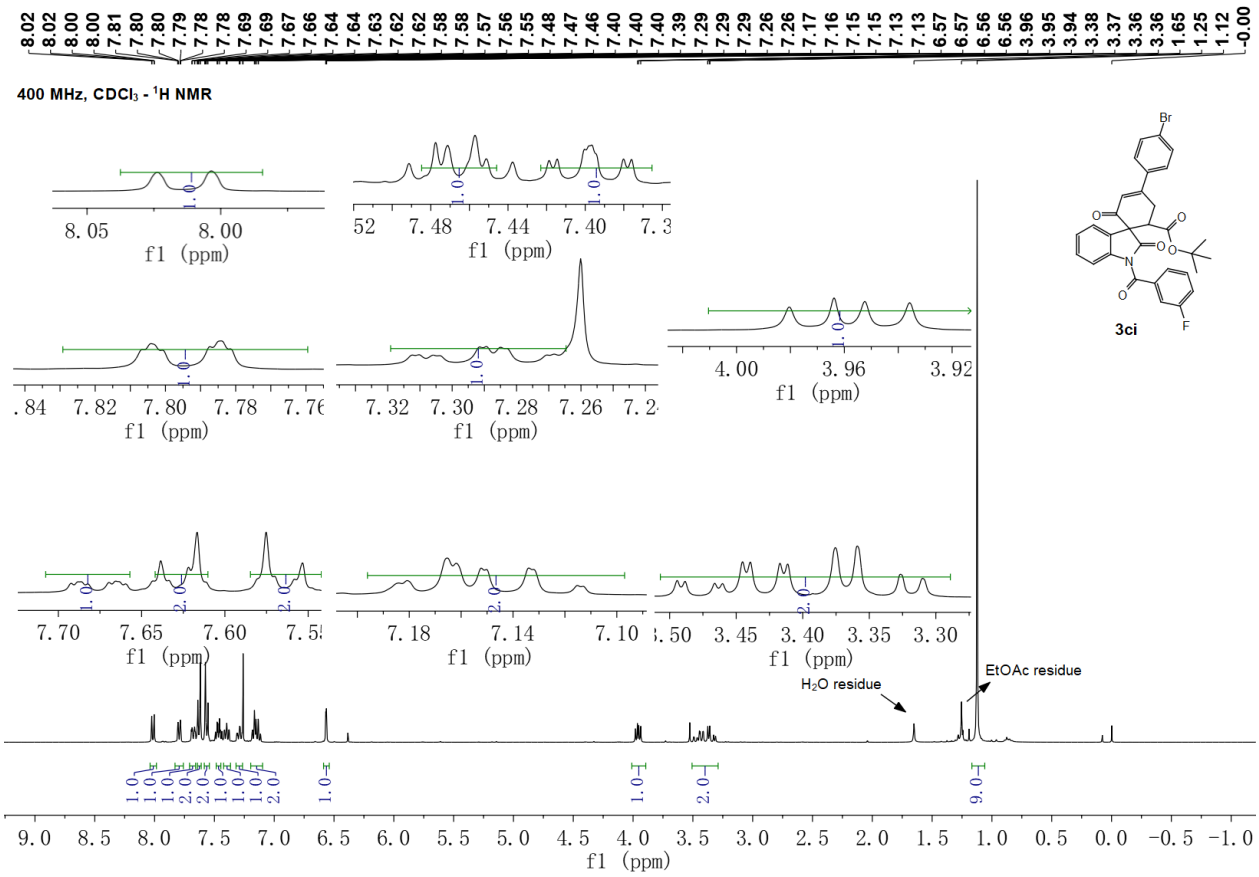

101 MHz, CDCl3 - 13C NMR
f1 (ppm)

3ch
F

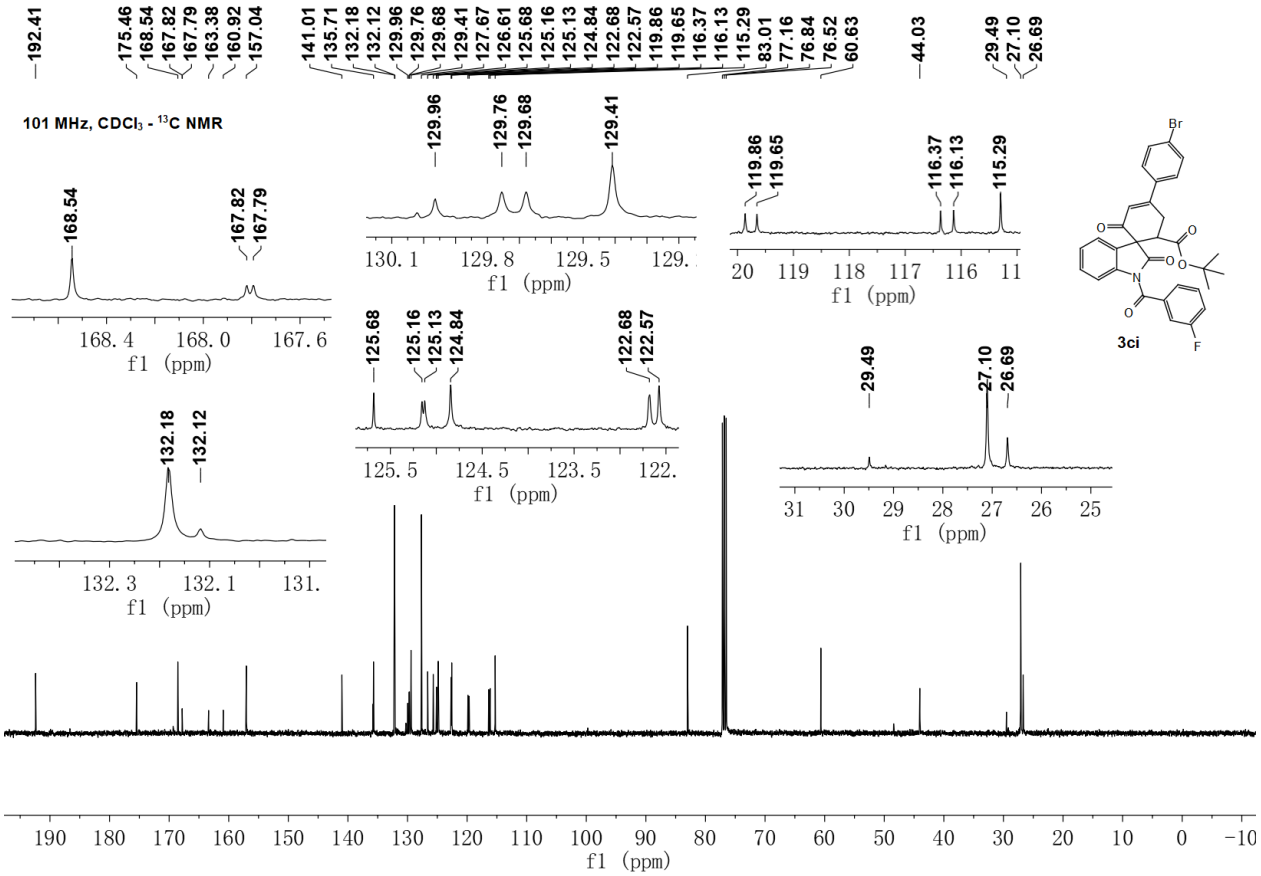
376MHz, $CDCl_3$ - ^{19}F NMR



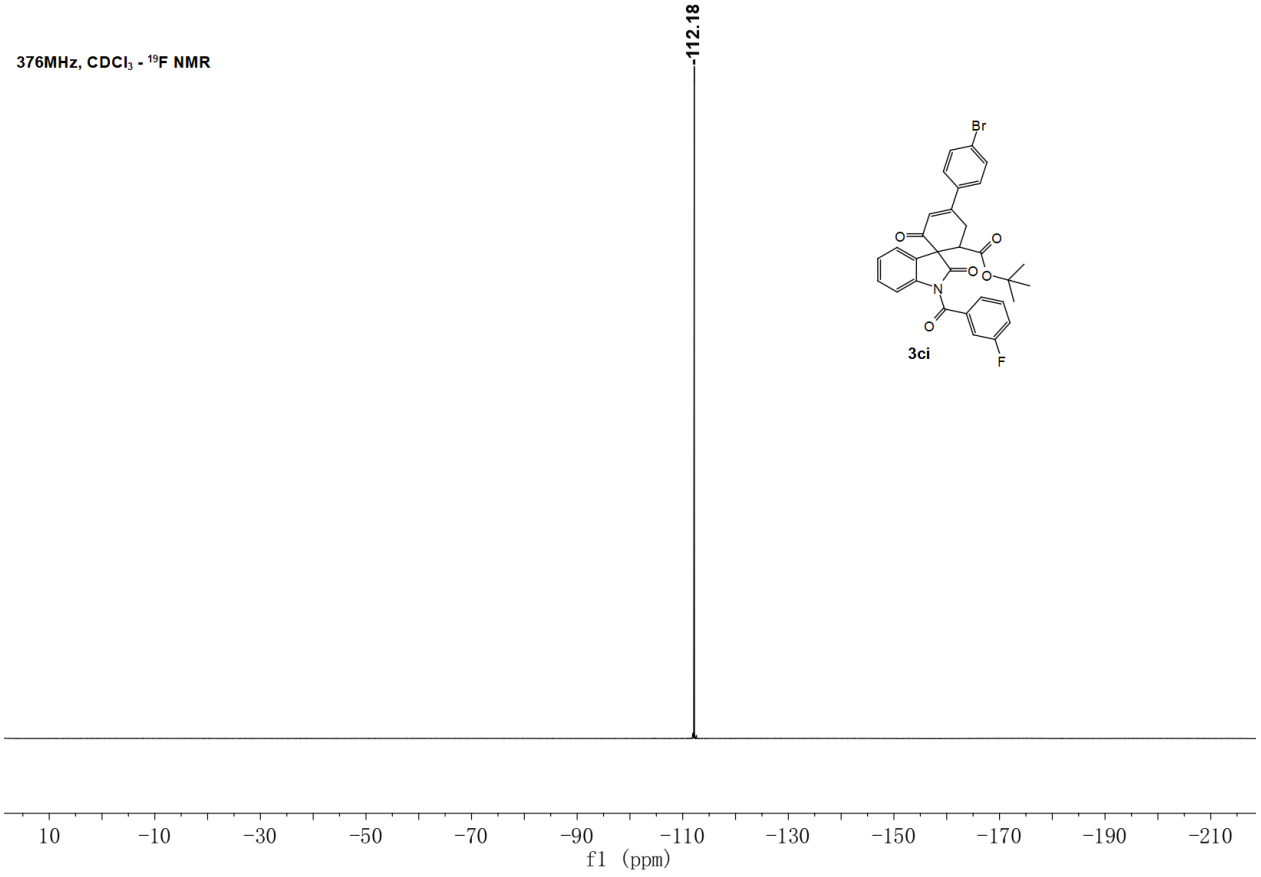
400 MHz, $CDCl_3$ - ^{1}H NMR



101 MHz, $CDCl_3$ - ^{13}C NMR

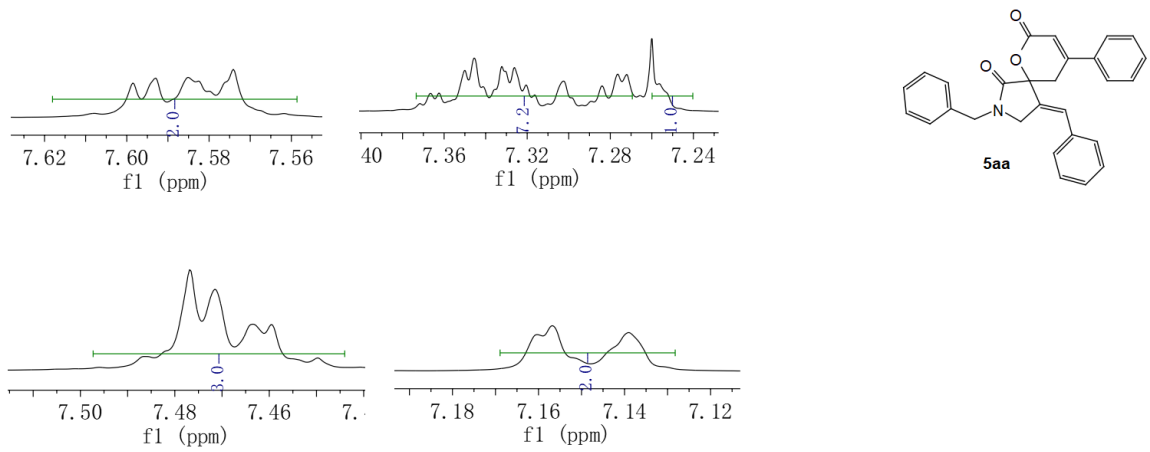


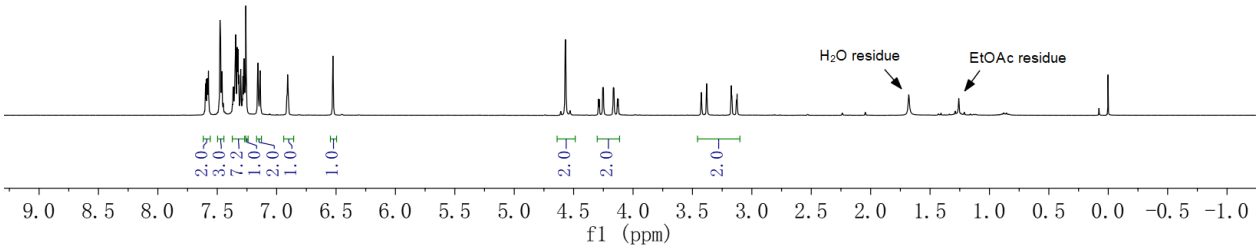
376MHz, $CDCl_3$ - ^{19}F NMR



7.60 7.59 7.59 7.58 7.58 7.58 7.57 7.48 7.47 7.46 7.46 7.37 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.30 7.30 7.30 7.28 7.28 7.27 7.26 7.26 7.25 7.16 7.16 7.14 7.14 7.14 6.91 6.91 6.53 6.53 6.52 4.57 4.57 4.26 4.25 4.17 4.16 3.43 3.42 3.38 3.38 3.17 3.17 3.13 3.12 1.68 0.00

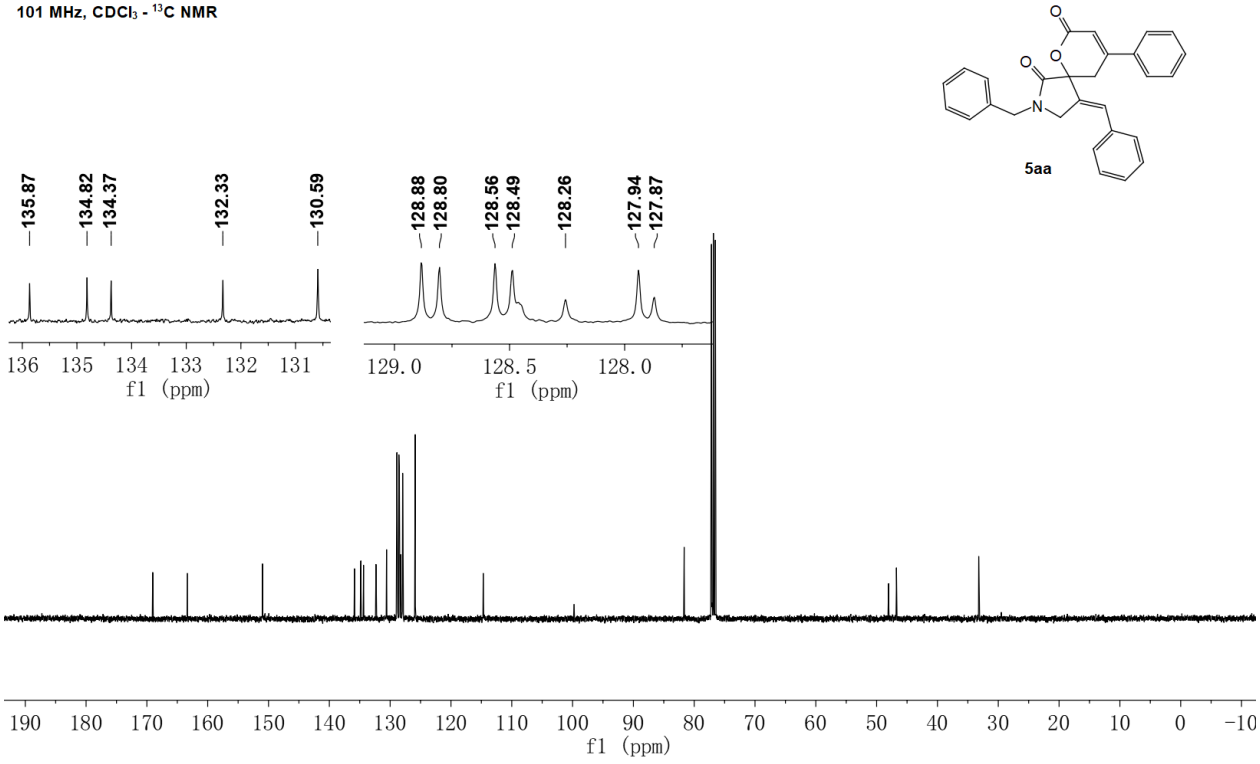
400 MHz, $CDCl_3$ - ^1H NMR



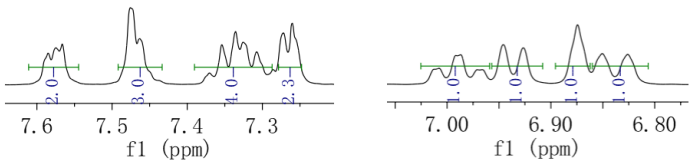


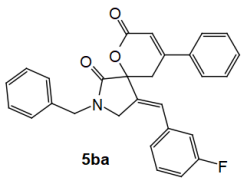
169.04 163.34 150.99 135.87 134.82 134.37 132.33 130.59 128.88 128.80 128.56 128.49 128.26 127.94 127.87 125.88 114.69 99.76 81.65 77.16 76.84 76.52 48.03 46.75 33.21

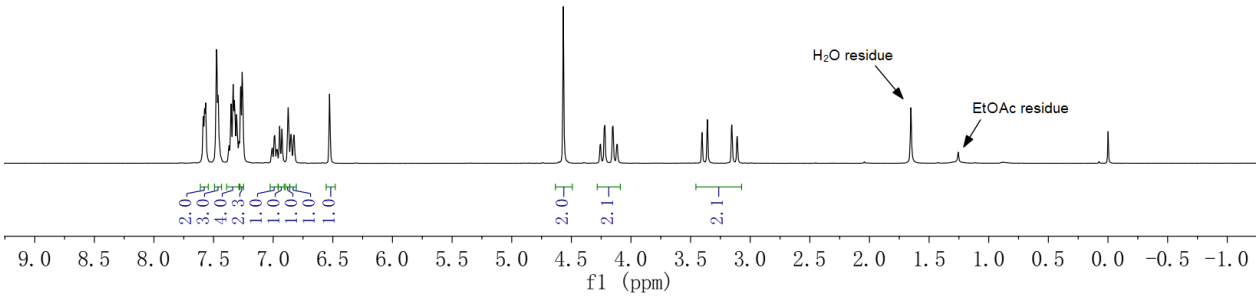
101 MHz, $CDCl_3$ - ^{13}C NMR

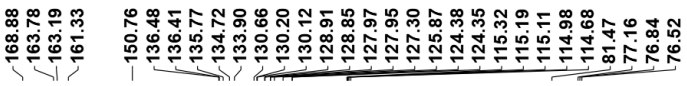


400 MHz, $CDCl_3$ - ^1H NMR

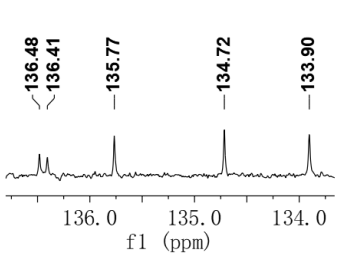


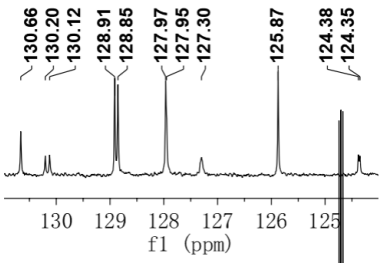


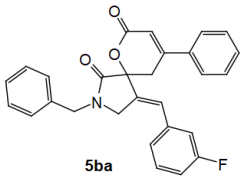


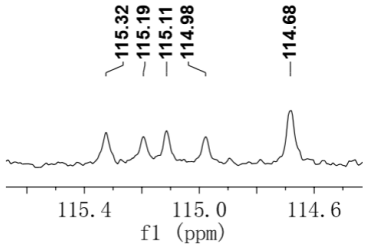


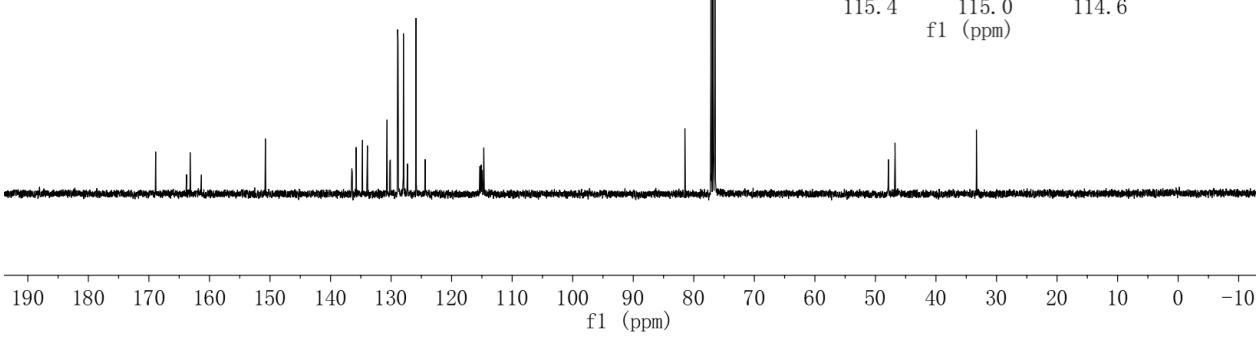
101 MHz, $CDCl_3$ - ^{13}C NMR



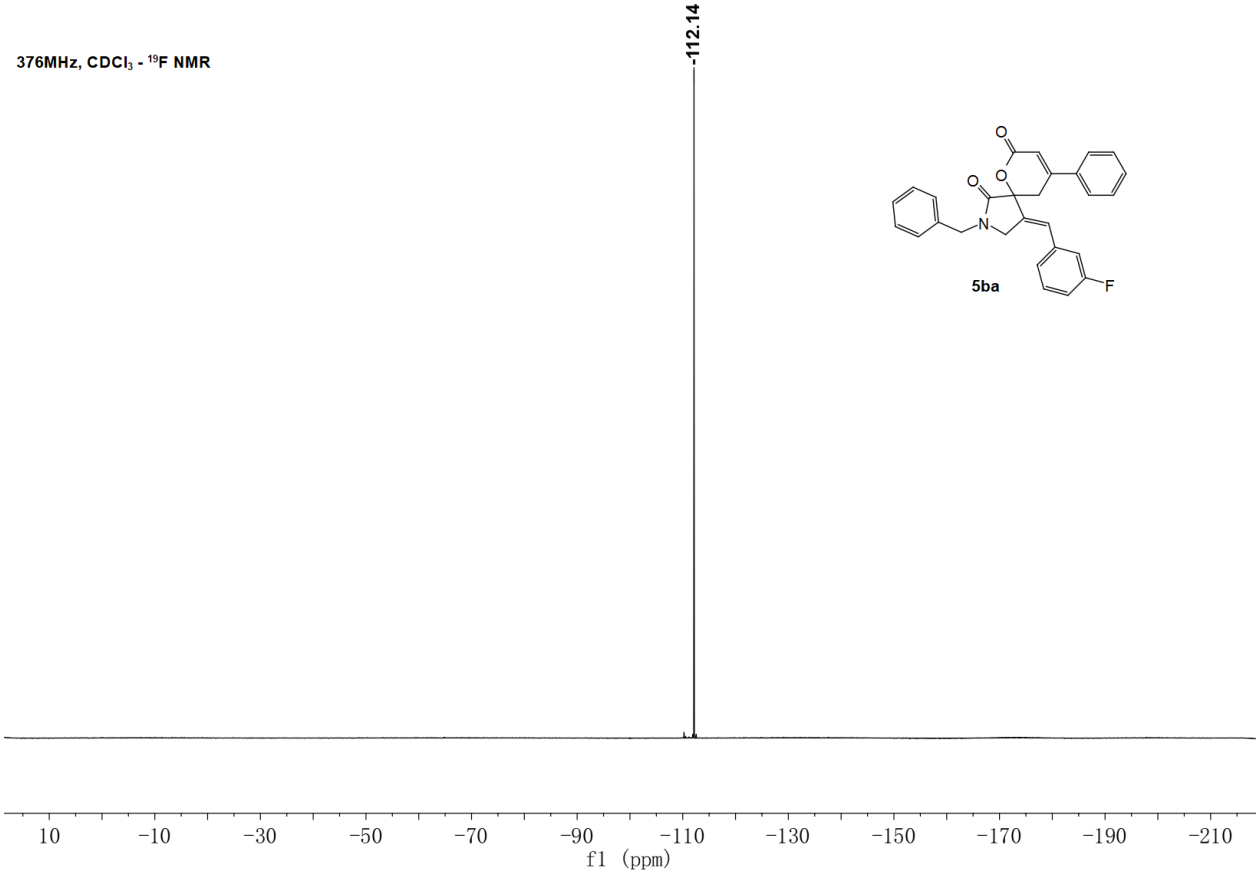


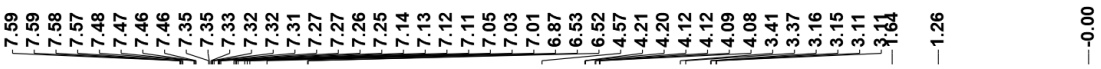




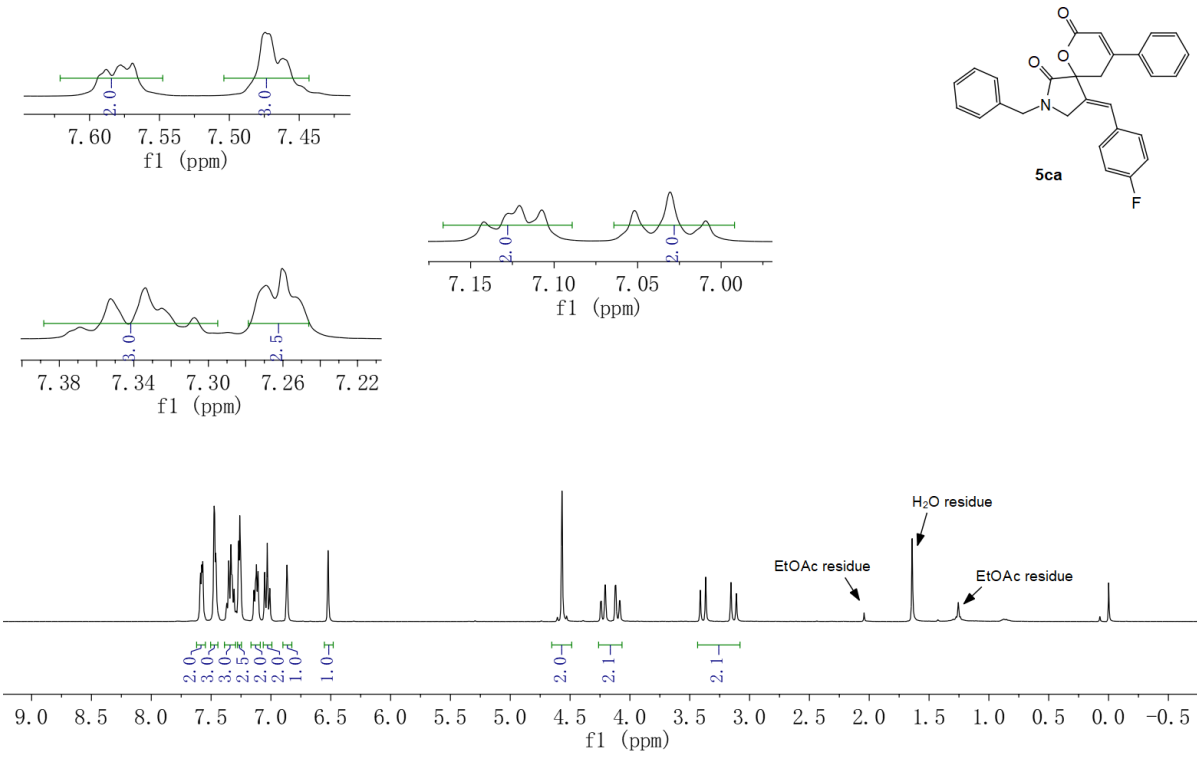


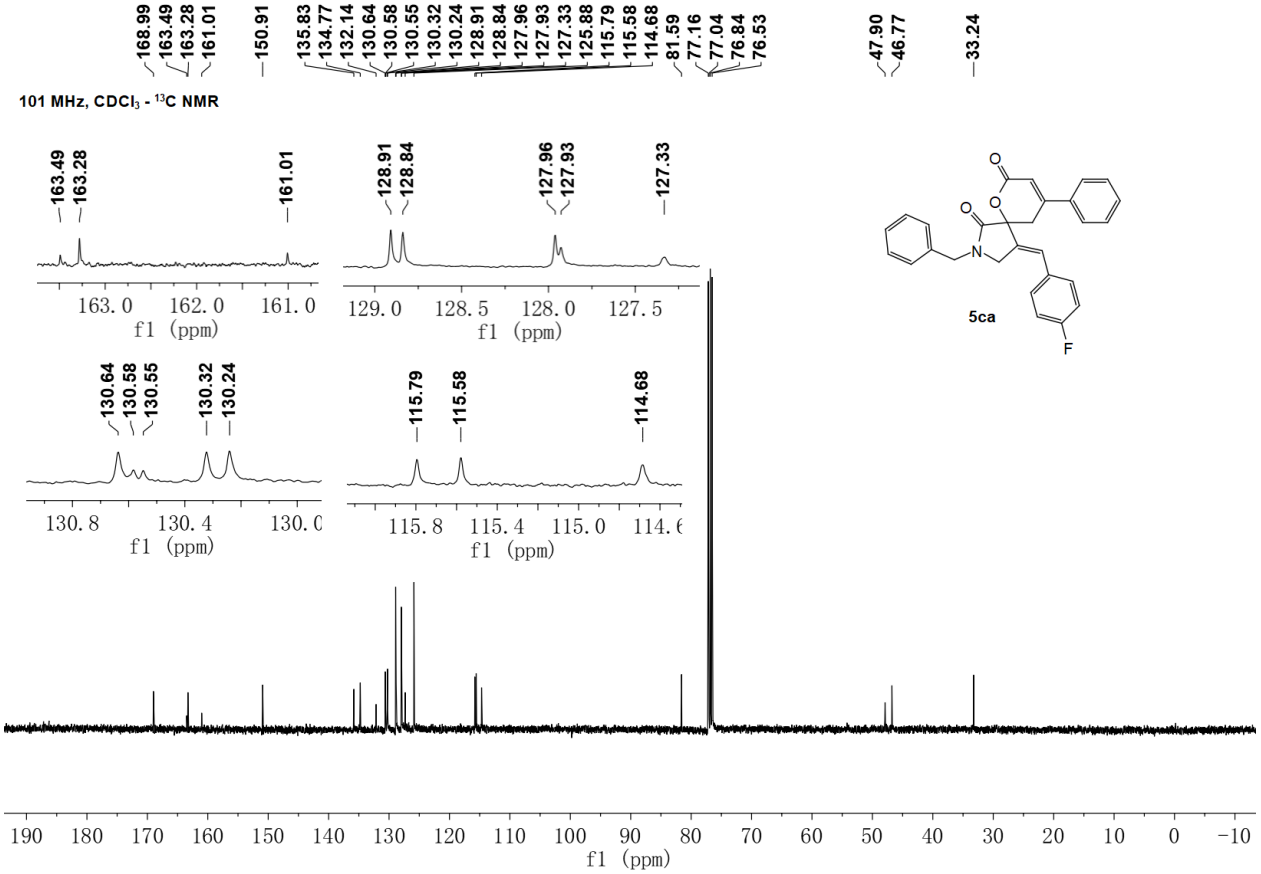
376MHz, $CDCl_3$ - ^{19}F NMR

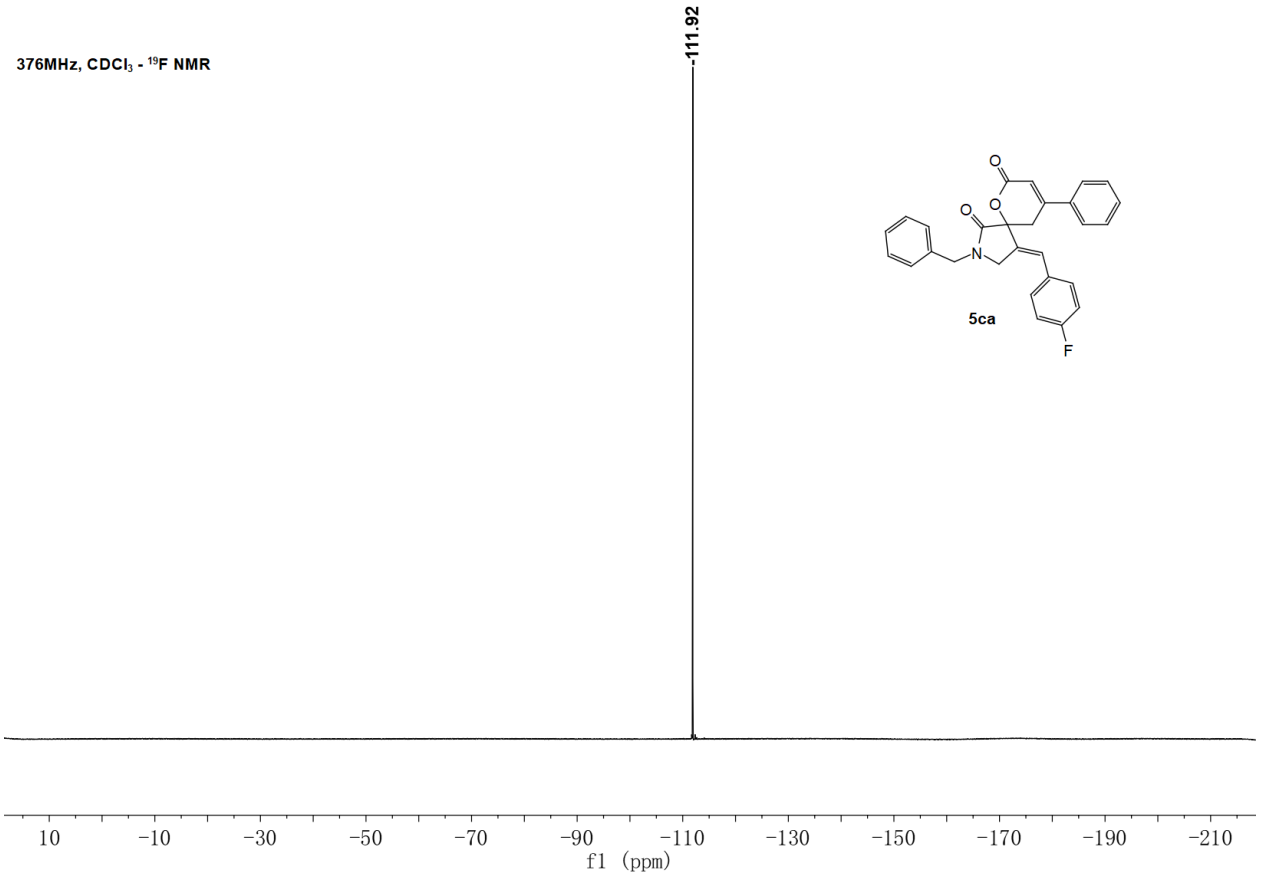


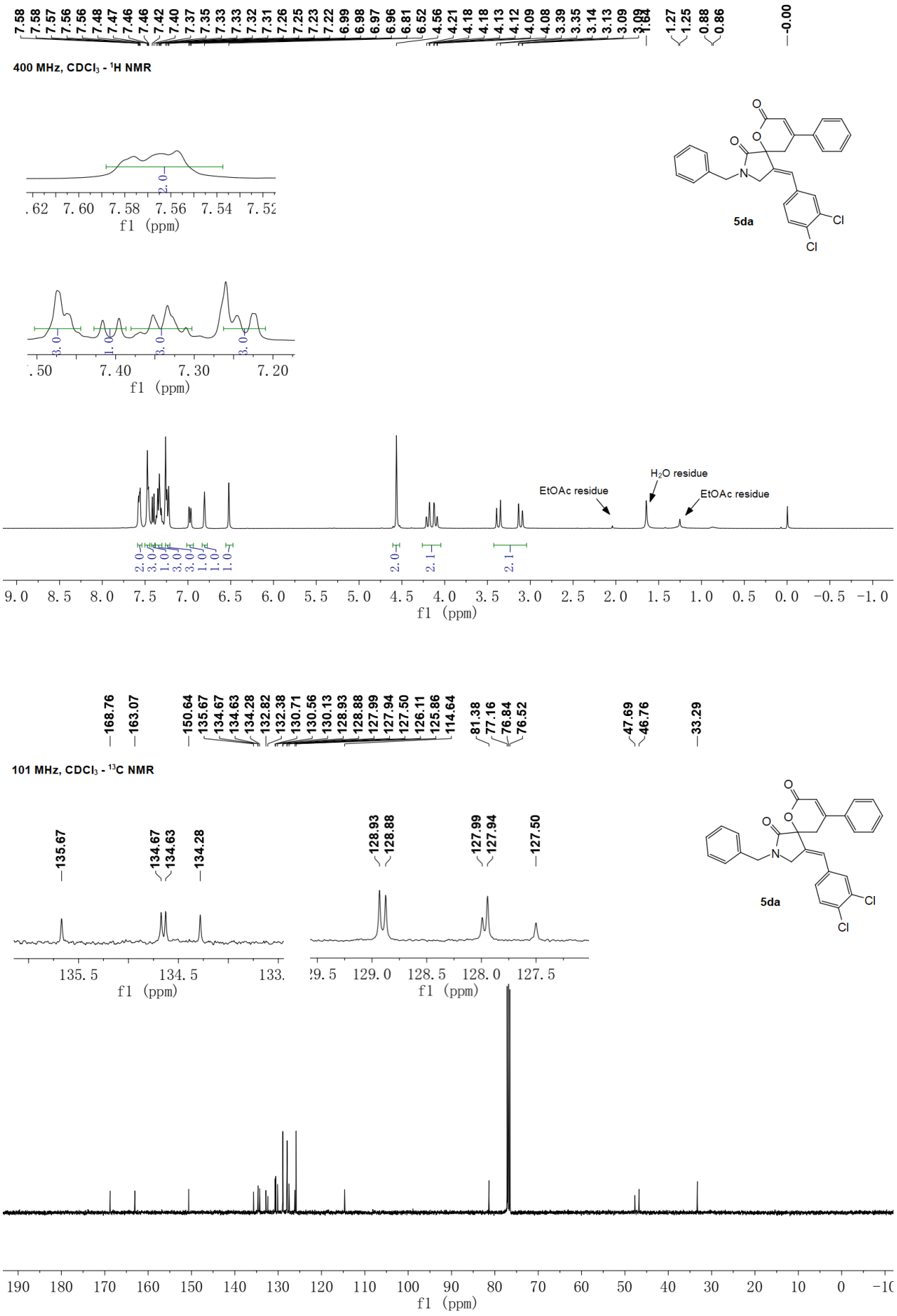


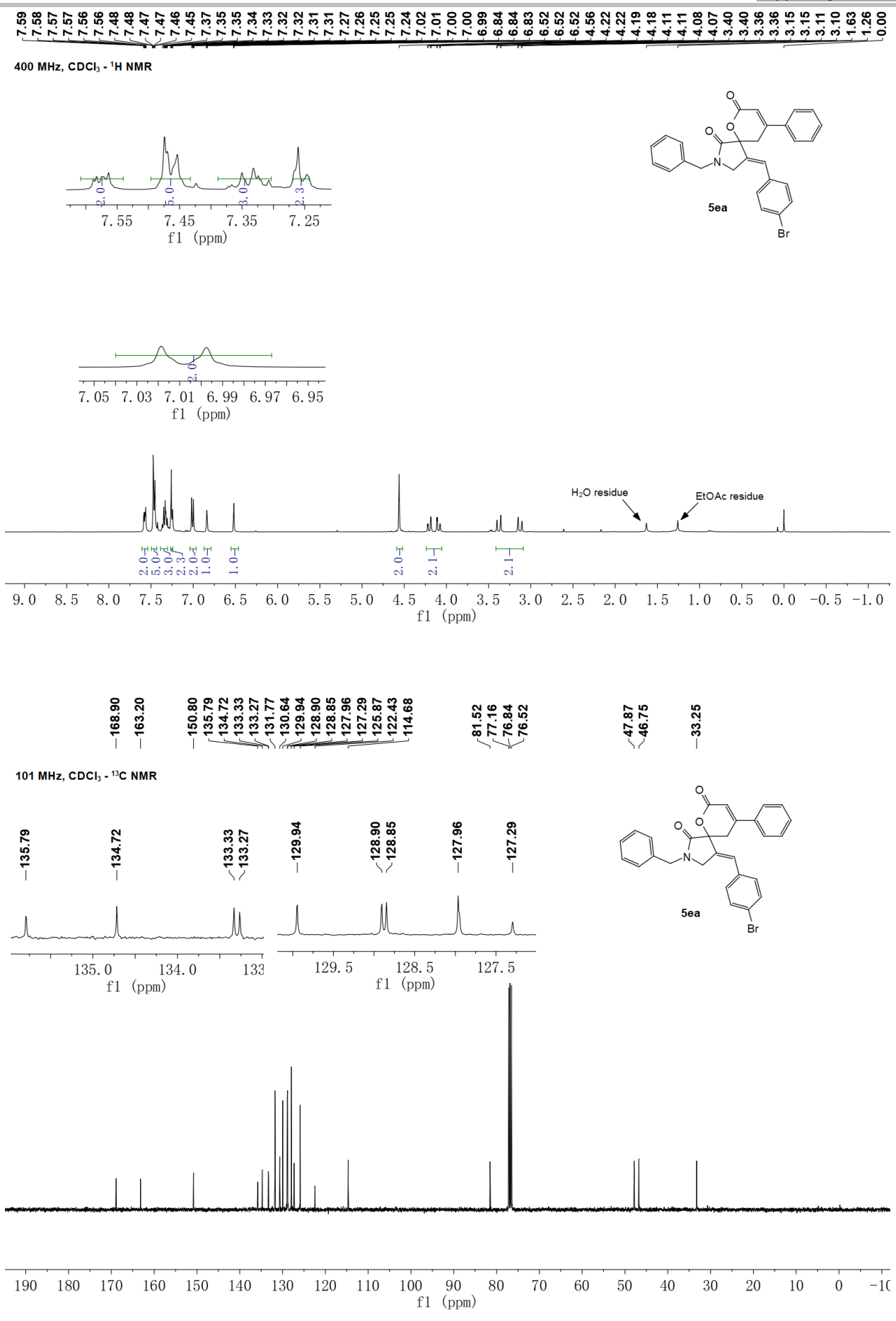
400 MHz, $CDCl_3$ - ^{1}H NMR

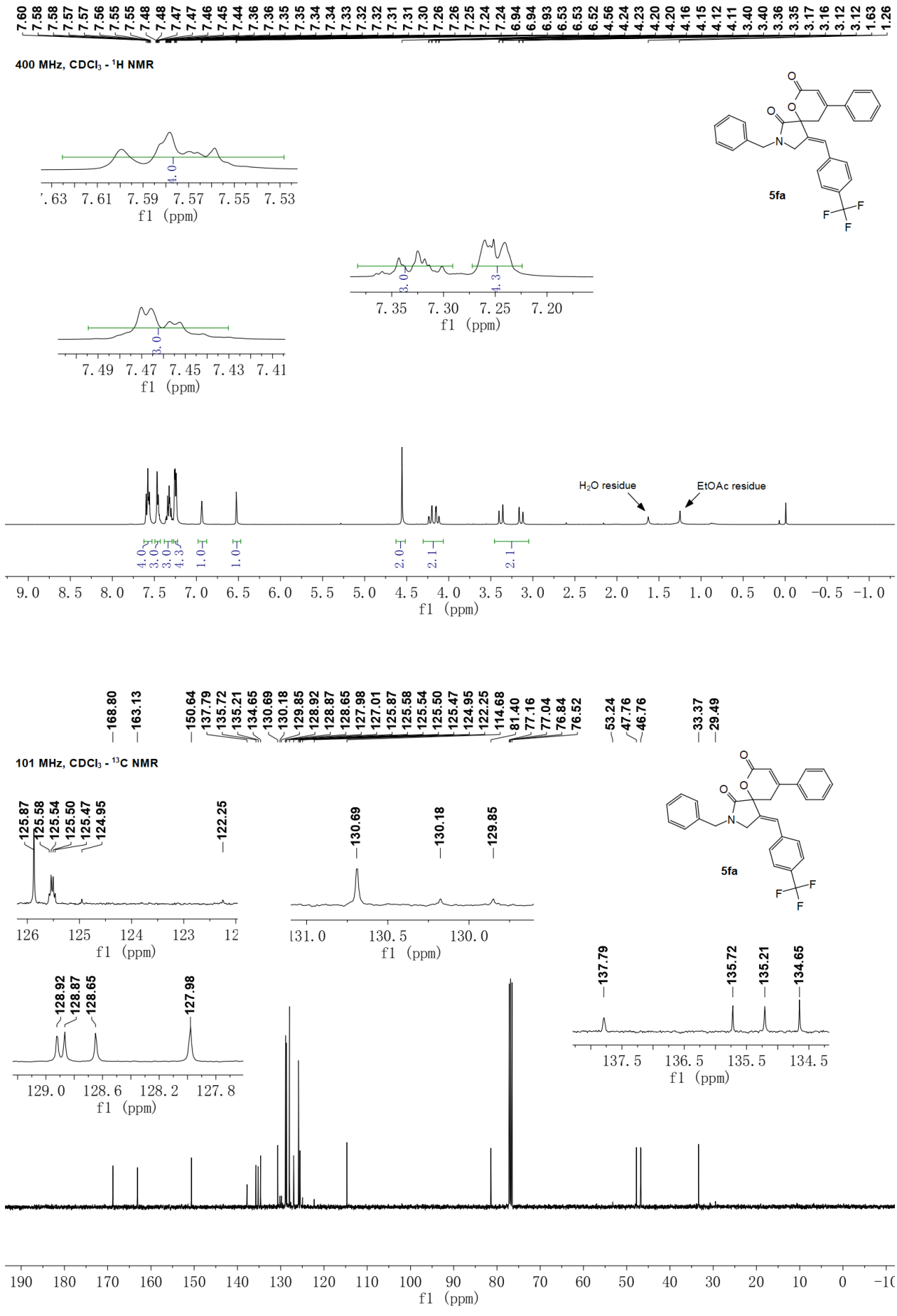



168.99
163.49
163.28
161.01
150.91
135.83
134.77
132.14
130.64
130.58
130.55
130.32
130.24
128.91
128.84
127.96
127.93
127.33
125.88
115.79
115.58
114.68
81.59
77.16
77.04
76.84
76.53
47.90
46.77
33.24
101 MHz, CDCl3 - 13C NMR
5ca
F
f1 (ppm)

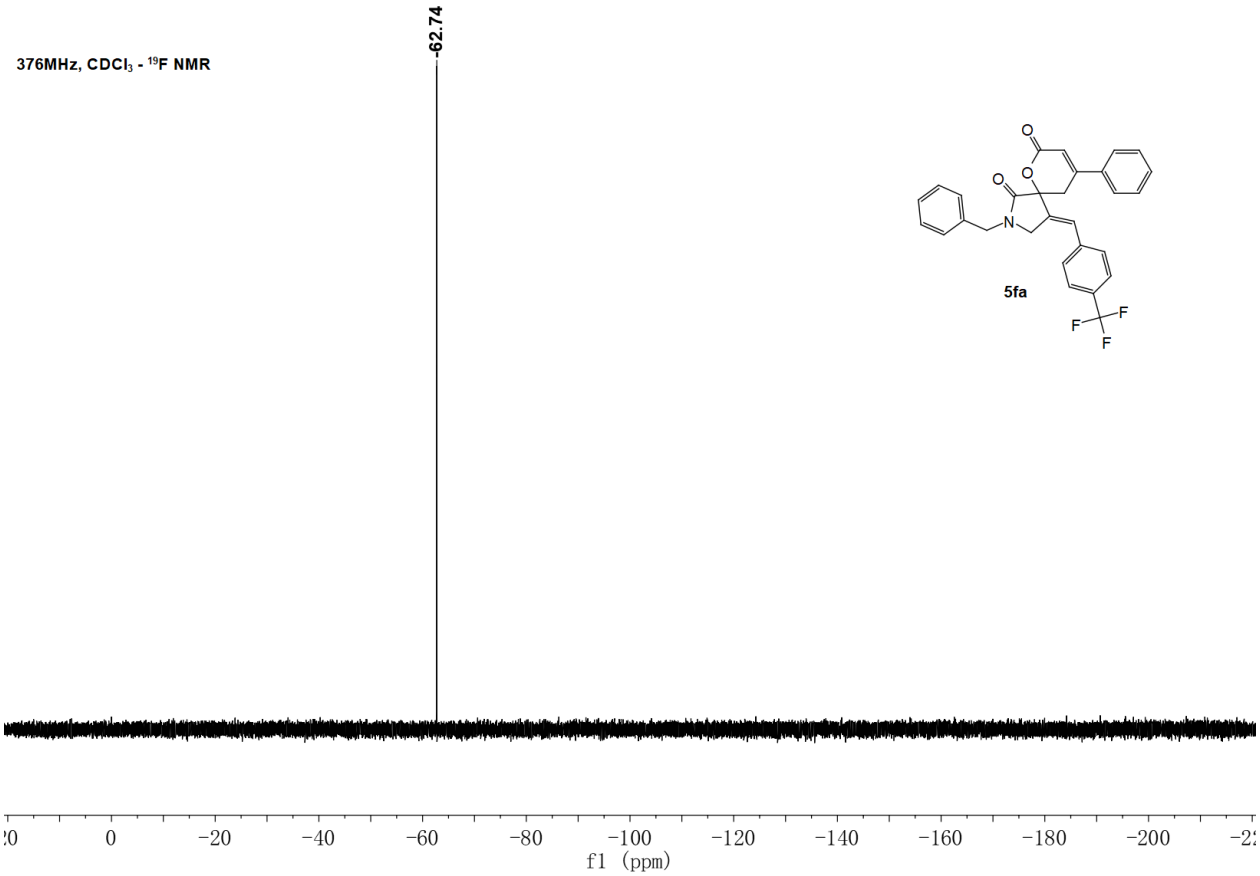

-111.92
376MHz, CDCl3 - 19F NMR
5ca
F
f1 (ppm)


7.58 7.58 7.57 7.56 7.56 7.48 7.47 7.46 7.46 7.42 7.40 7.37 7.35 7.33 7.33 7.32 7.31 7.26 7.25 7.23 7.22 6.99 6.98 6.97 6.96 6.81 6.52 4.56 4.21 4.18 4.13 4.12 4.09 4.08 3.39 3.35 3.14 3.13 3.09 3.09 1.27 1.25 0.88 0.86 0.00
400 MHz, CDCl3 - 1H NMR
5da
Cl
Cl
f1 (ppm)
EtOAc residue
H2O residue
EtOAc residue
f1 (ppm)
168.76 163.07 150.64 135.67 134.67 134.63 134.28 132.82 132.38 130.71 130.56 130.13 128.93 128.88 127.99 127.94 127.50 126.11 125.86 114.64 81.38 77.16 76.84 76.52 47.69 46.76 33.29
101 MHz, CDCl3 - 13C NMR
135.67 134.67 134.63 134.28 128.93 128.88 127.99 127.94 127.50
5da
Cl
Cl
f1 (ppm)
f1 (ppm)
f1 (ppm)

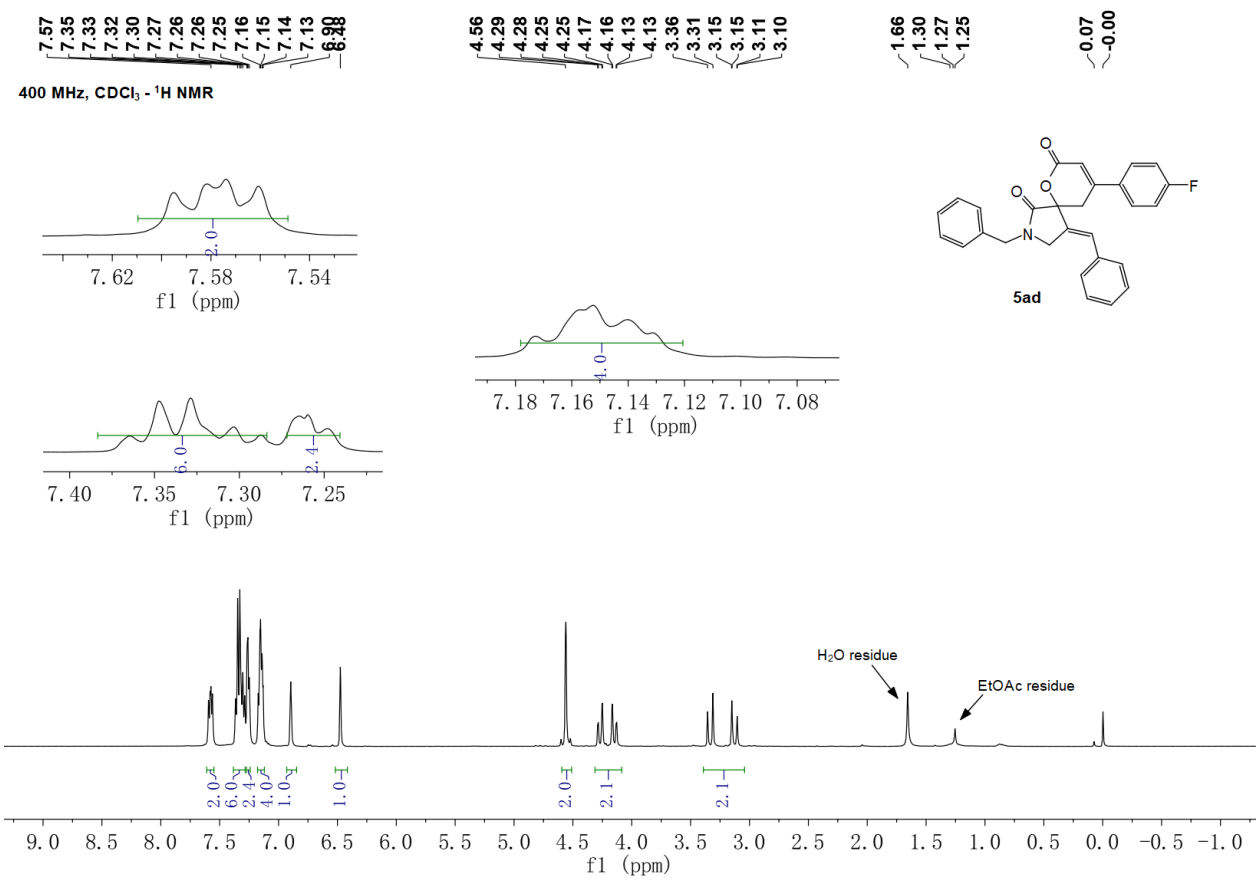

400 MHz, CDCl3 - 1H NMR
5ea
Br
H2O residue
EtOAc residue
f1 (ppm)
101 MHz, CDCl3 - 13C NMR
5ea
Br
f1 (ppm)

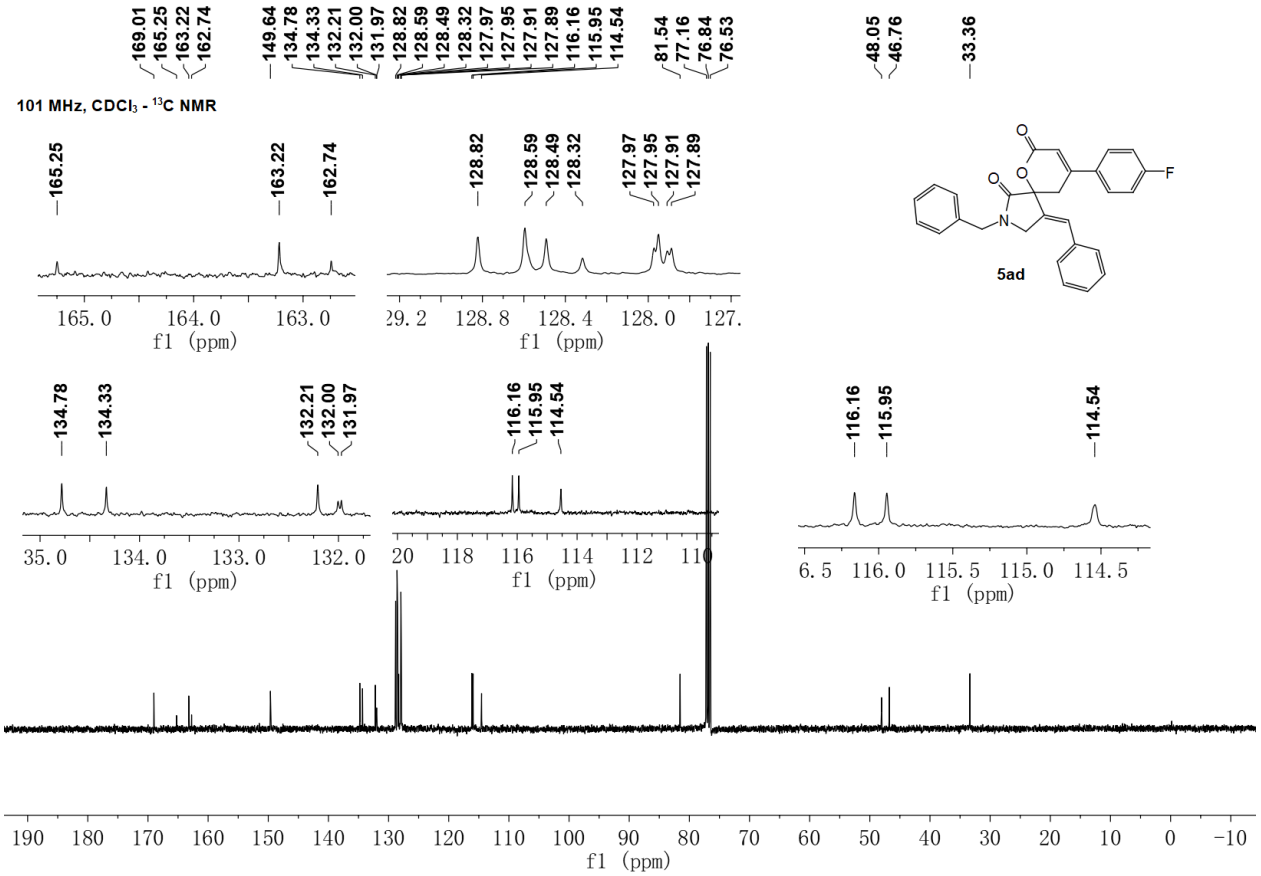

400 MHz, CDCl3 - 1H NMR
5fa
H2O residue
EtOAc residue
f1 (ppm)
101 MHz, CDCl3 - 13C NMR
5fa
f1 (ppm)

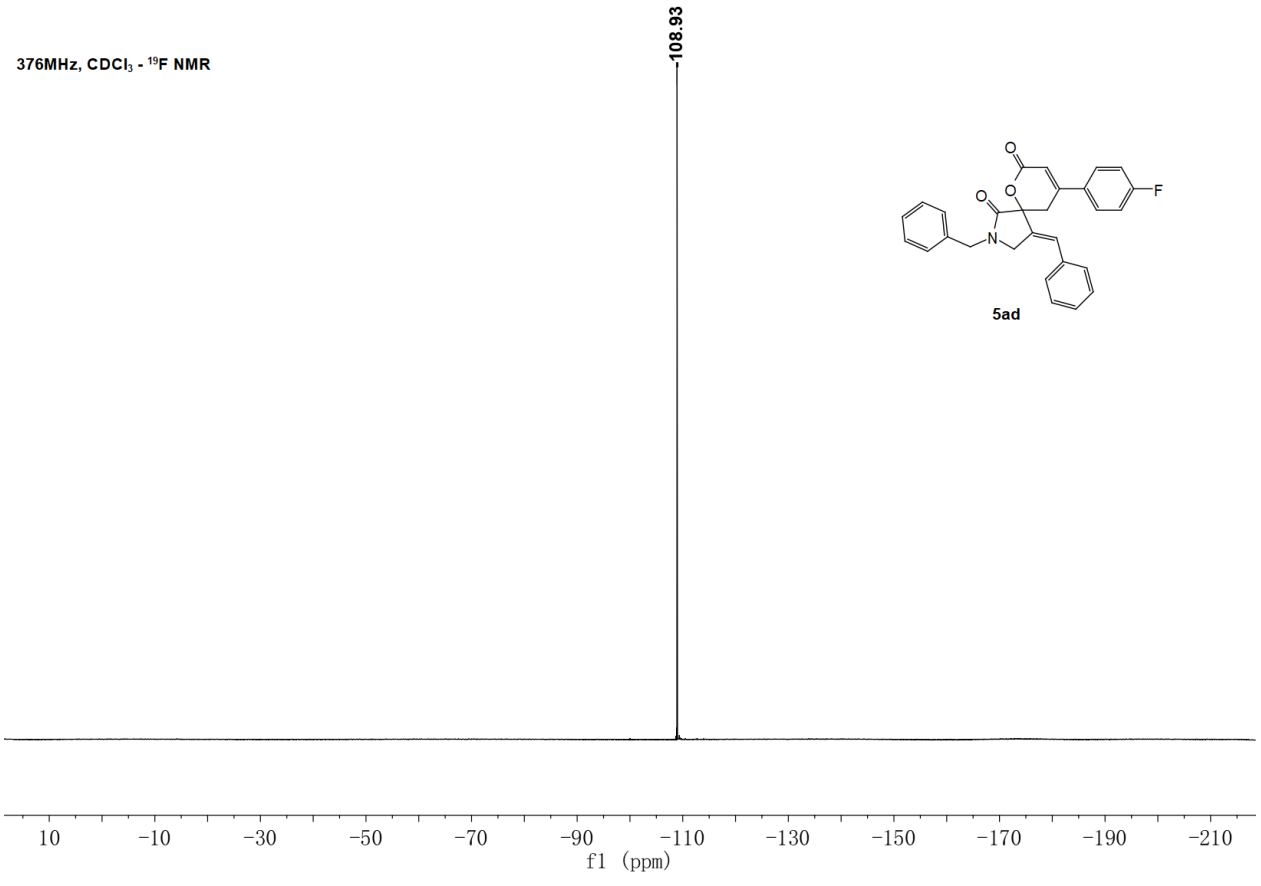
376MHz, $CDCl_3$ - ^{19}F NMR



400 MHz, $CDCl_3$ - ^{1}H NMR

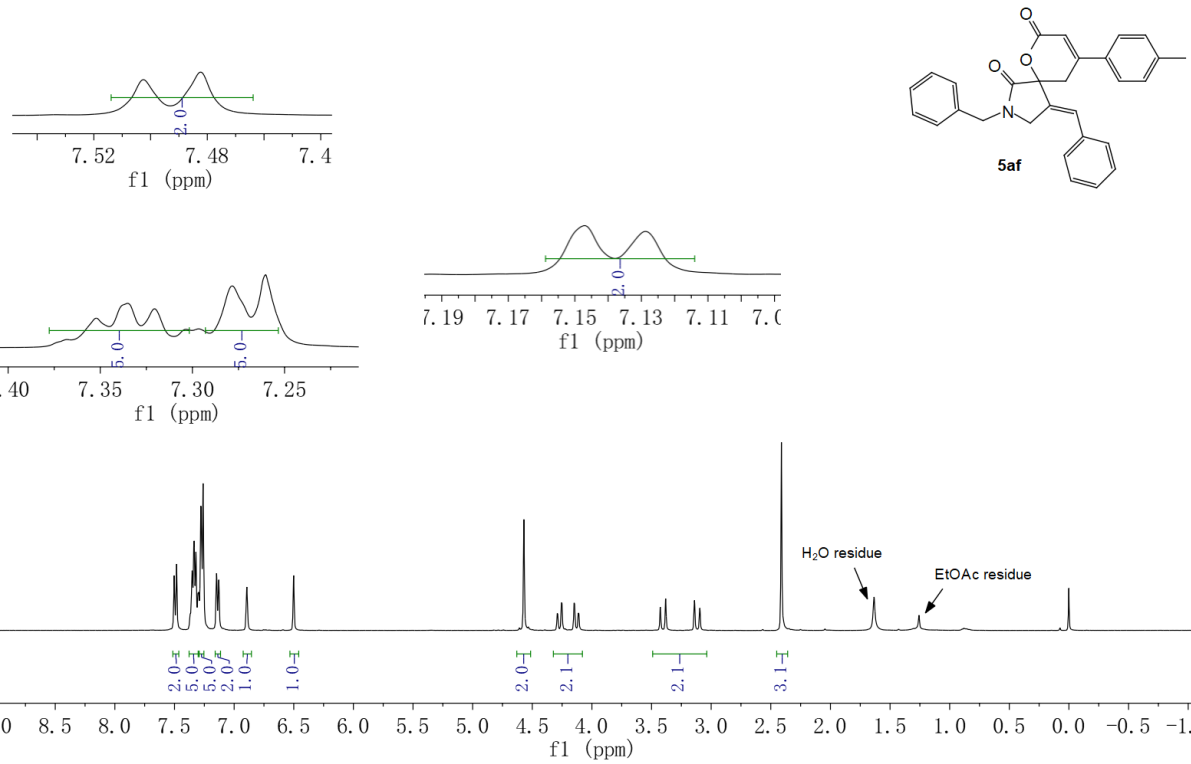



169.01
165.25
163.22
162.74
149.64
134.78
134.33
132.21
132.00
131.97
128.82
128.59
128.49
128.32
127.97
127.95
127.91
127.89
116.16
115.95
114.54
81.54
77.16
76.84
76.53
48.05
46.76
33.36
101 MHz, CDCl3 - 13C NMR
5ad
f1 (ppm)


108.93
376MHz, CDCl3 - 19F NMR
5ad
f1 (ppm)

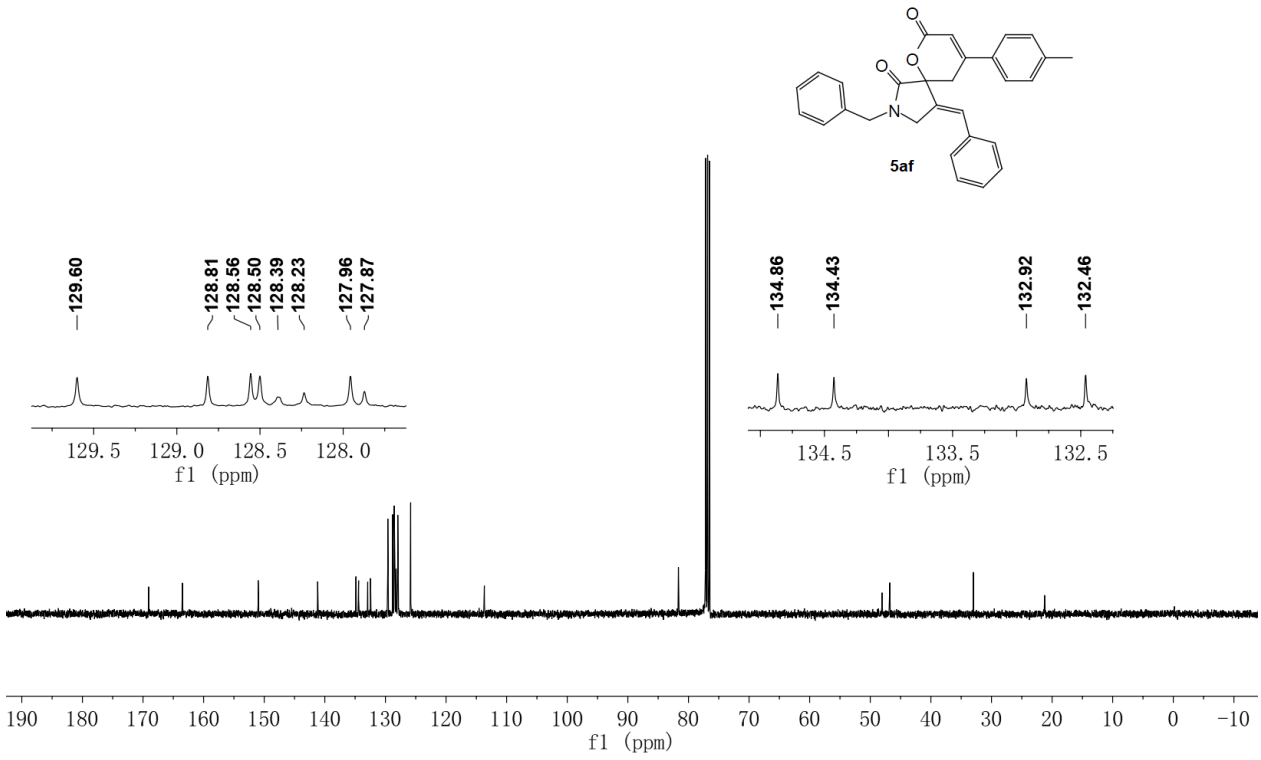
7.50 7.48 7.37 7.37 7.35 7.34 7.33 7.32 7.30 7.28 7.26 7.15 7.13 6.89 6.50 4.57 4.29 4.29 4.26 4.25 4.15 4.14 4.11 4.11 3.43 3.42 3.38 3.38 3.14 3.14 3.10 3.09 2.41 1.63 1.26 0.00

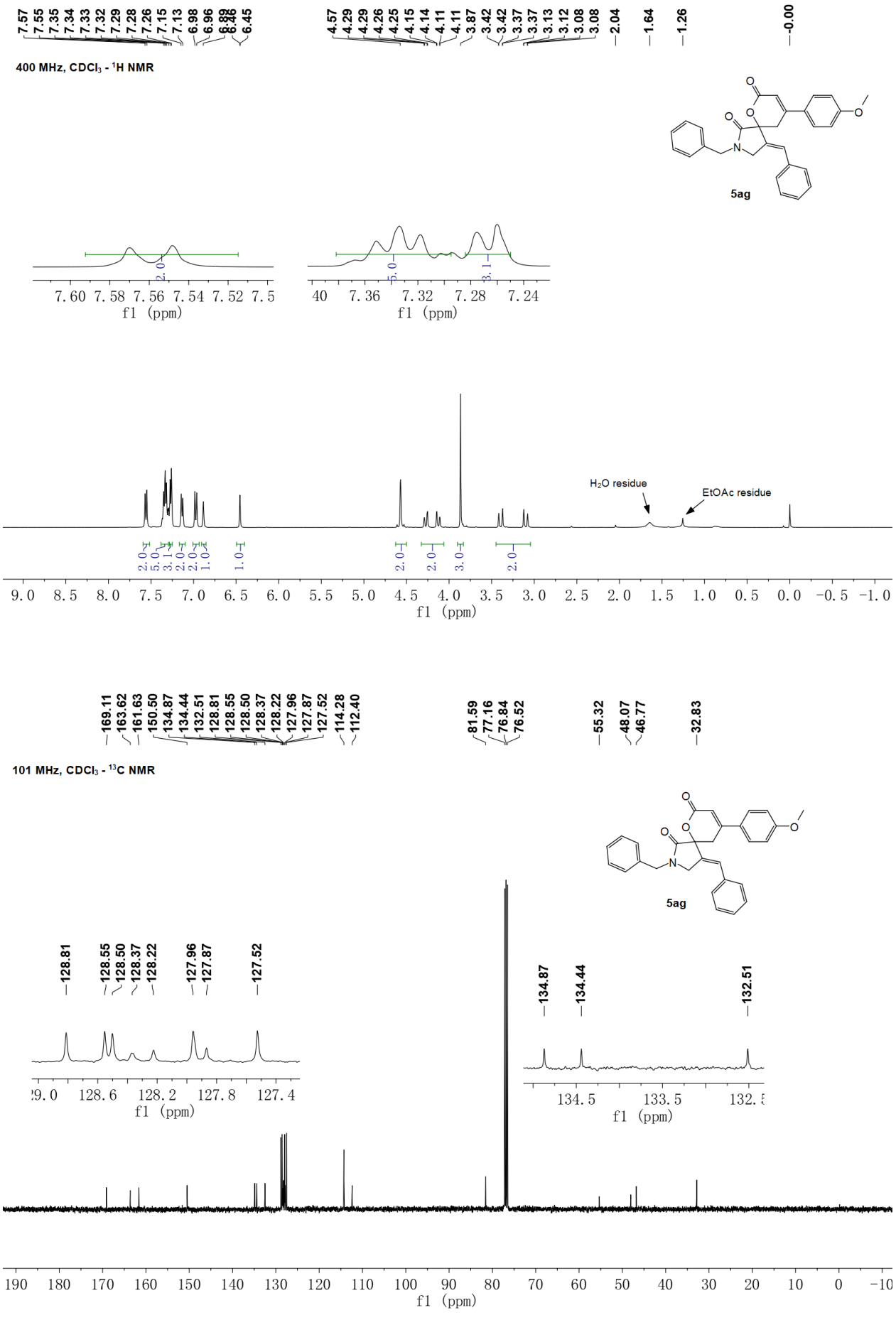
400 MHz, $CDCl_3$ - ^1H NMR



169.08 163.49 150.99 141.18 134.86 134.43 132.92 132.46 129.60 128.81 128.56 128.50 128.39 128.23 127.96 127.87 125.84 113.68 81.66 77.16 76.84 76.52 48.06 46.77 32.98 21.24

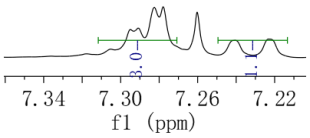
101 MHz, $CDCl_3$ - ^{13}C NMR

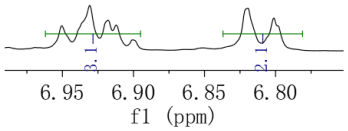


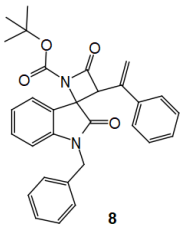

7.57
7.55
7.35
7.34
7.33
7.32
7.29
7.28
7.26
7.15
7.13
6.98
6.96
6.45
4.57
4.29
4.29
4.26
4.25
4.15
4.14
4.11
4.11
3.87
3.42
3.42
3.37
3.37
3.13
3.12
3.08
3.08
2.04
1.64
1.26
0.00
400 MHz, CDCl3 - 1H NMR
5ag
f1 (ppm)
H2O residue
EtOAc residue
169.11
163.62
161.63
150.50
134.87
134.44
132.51
128.81
128.55
128.50
128.37
128.22
127.96
127.87
127.52
114.28
112.40
81.59
77.16
76.84
76.52
55.32
48.07
46.77
32.83
101 MHz, CDCl3 - 13C NMR
5ag
f1 (ppm)

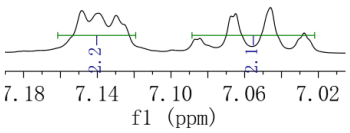
7.31 7.30 7.29 7.28 7.28 7.27 7.26 7.24 7.24 7.22 7.22 7.16 7.16 7.15 7.14 7.13 7.12 7.12 7.09 7.08 7.08 7.07 7.06 7.05 7.03 7.03 7.02 6.95 6.95 6.94 6.94 6.93 6.92 6.91 6.90 6.82 6.82 6.81 6.80 6.80 6.46 6.44 5.81 5.80 5.62 5.62 5.04 5.01 5.00 4.98 4.97 4.97 4.66 4.62 1.60 1.28 0.00

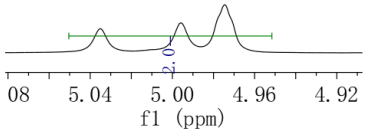
400 MHz, $CDCl_3$ - ^1H NMR

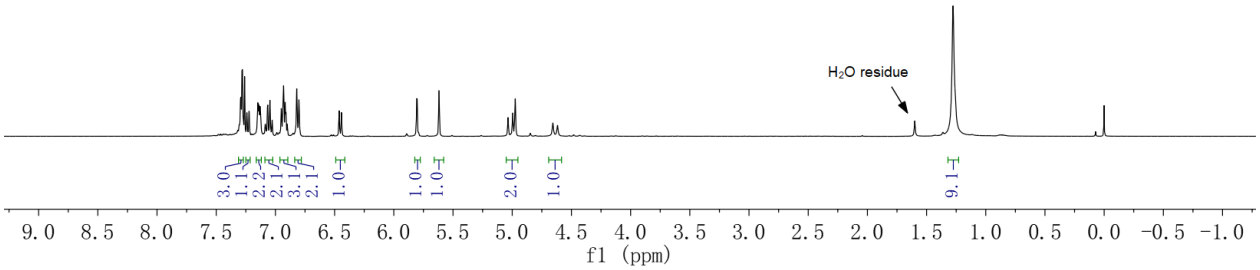












173.14 163.62 143.09 138.29 137.65 134.92 129.93 128.63 128.02 127.63 127.52 127.11 126.86 125.00 124.18 122.34 122.14 116.44 108.86

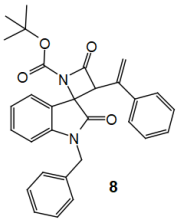
83.97 77.16 77.04 76.84 76.53

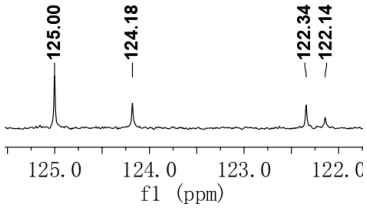
62.55

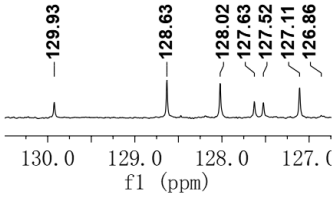
44.04

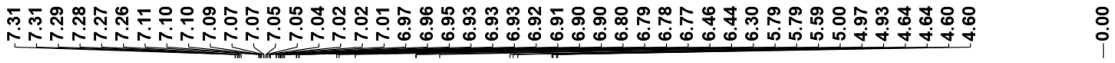
27.52

101 MHz, $CDCl_3$ - ^{13}C NMR

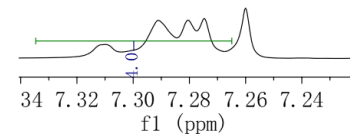


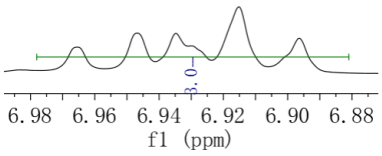


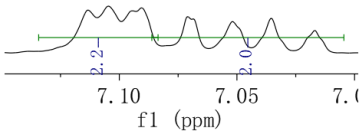


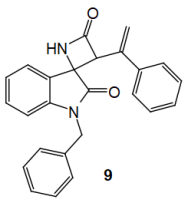


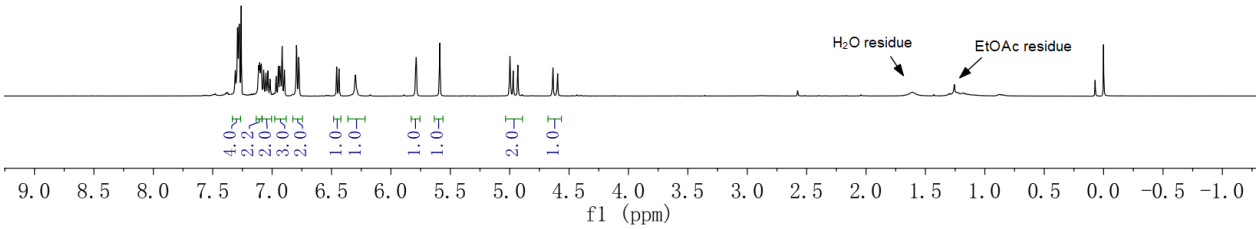
400 MHz, $CDCl_3$ - ^1H NMR

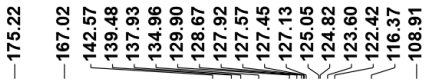




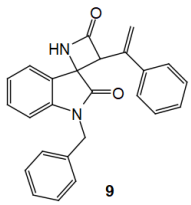


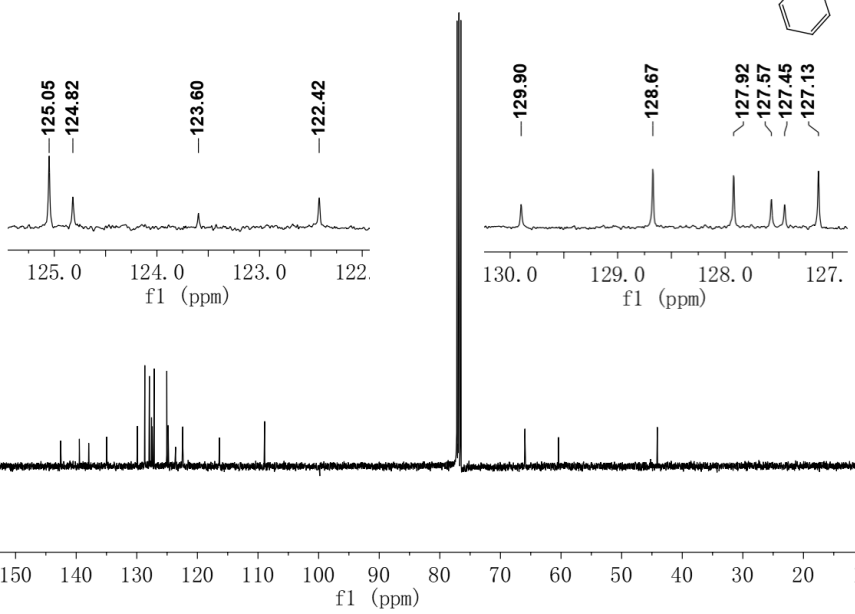


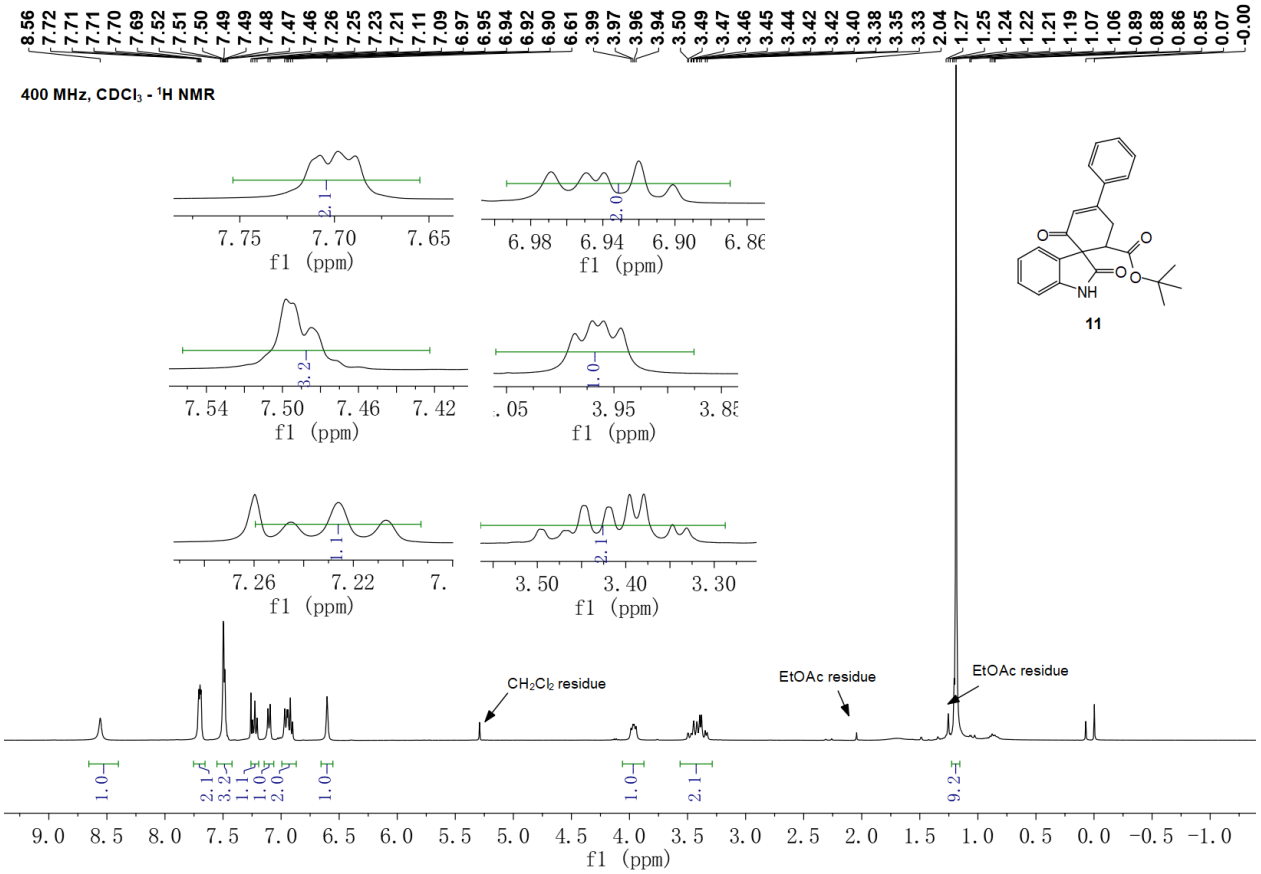


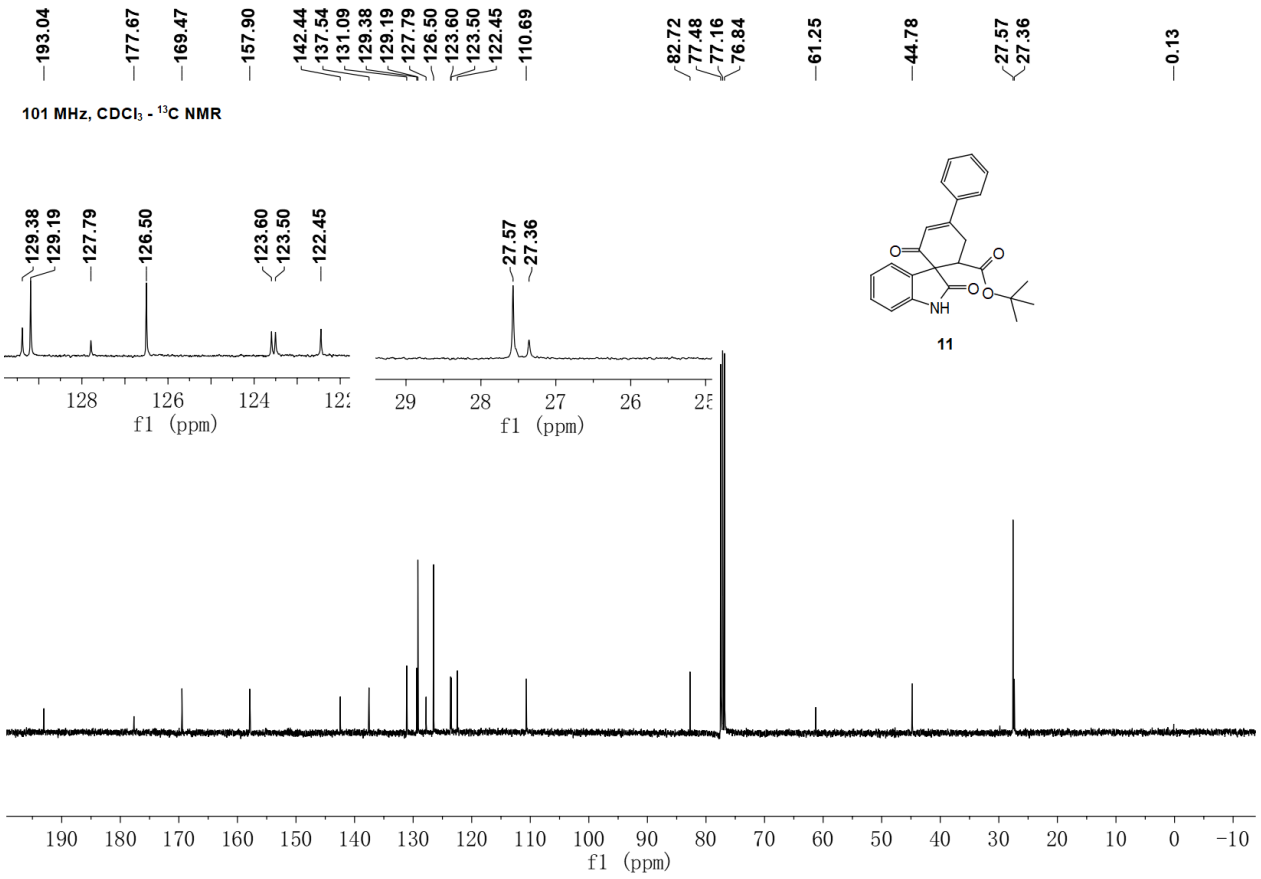


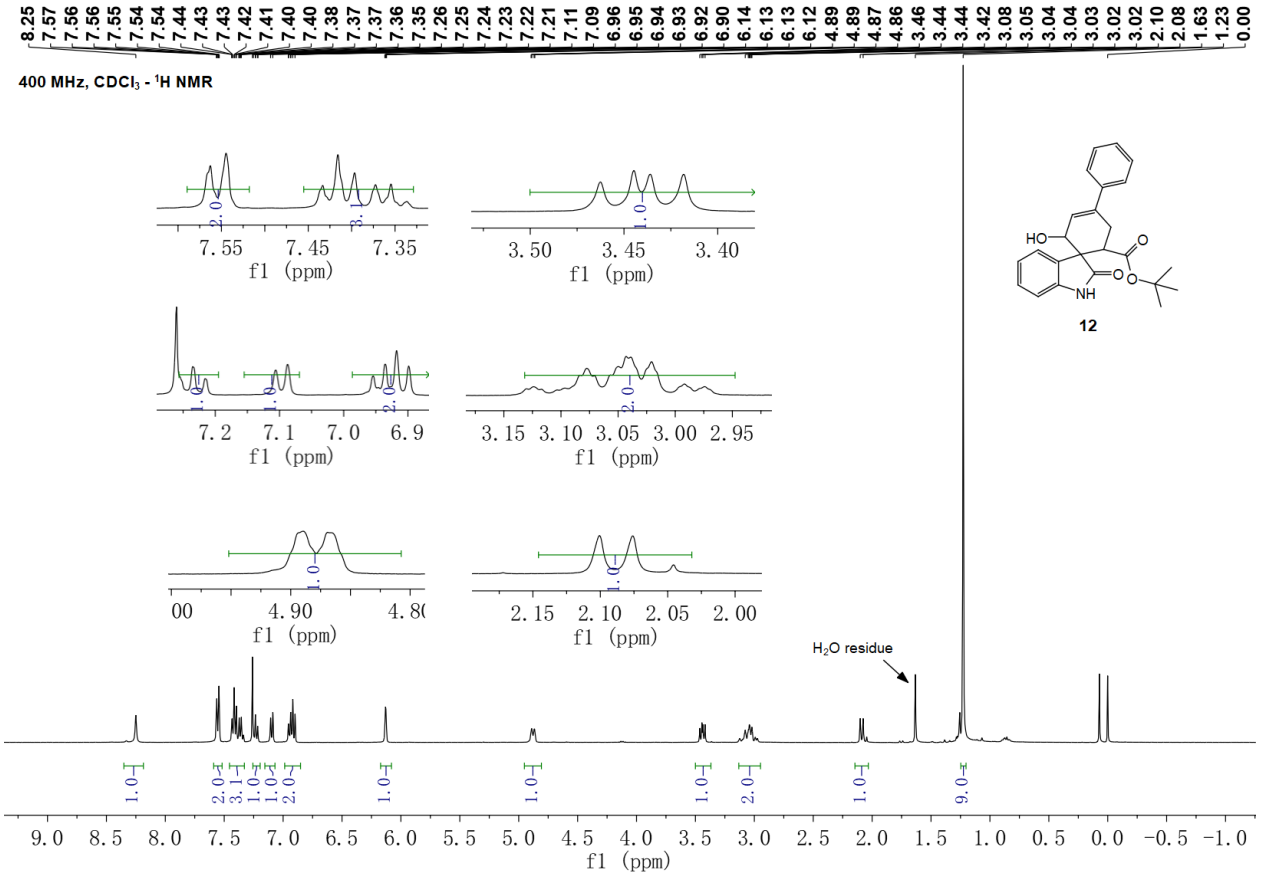
101 MHz, $CDCl_3$ - ^{13}C NMR

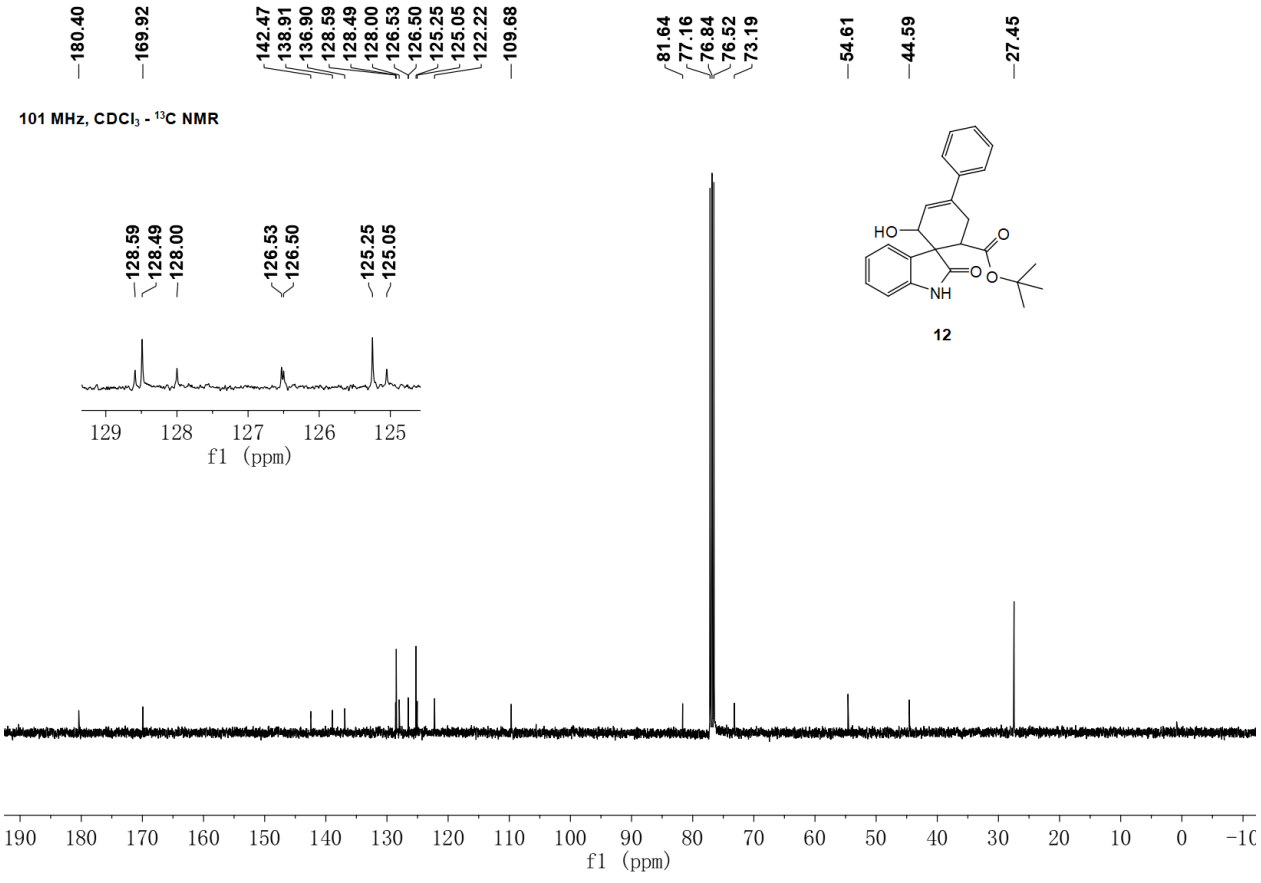




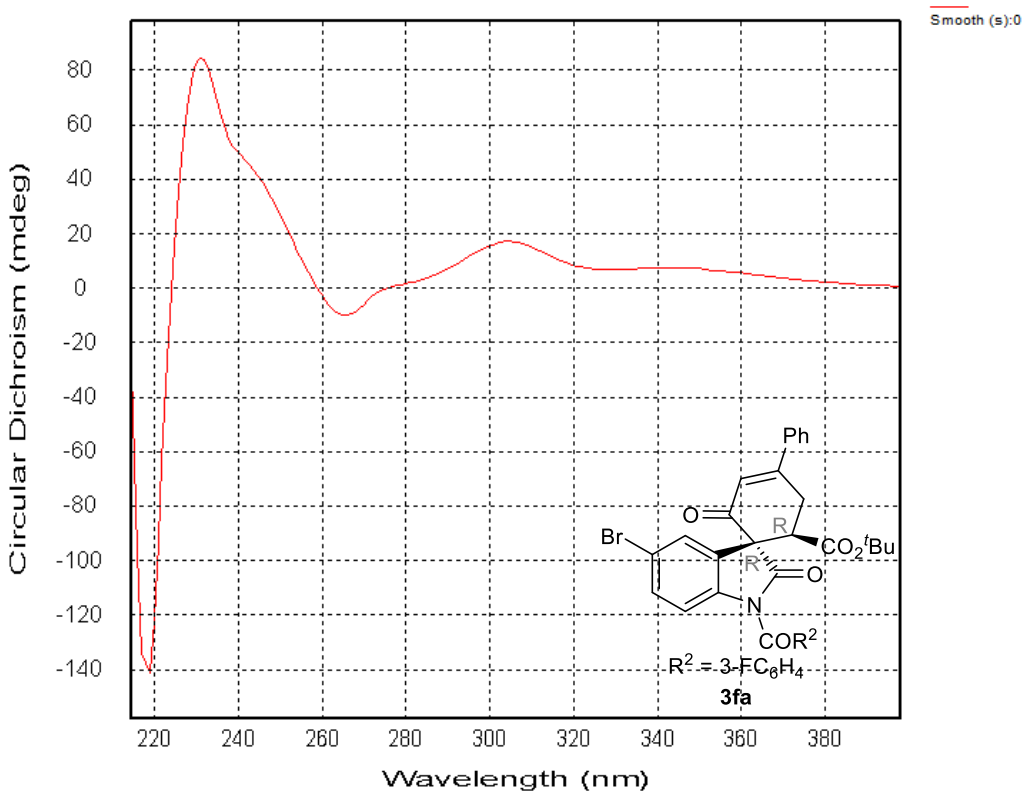

400 MHz, CDCl3 - 1H NMR
11
CH2Cl2 residue
EtOAc residue
EtOAc residue
f1 (ppm)

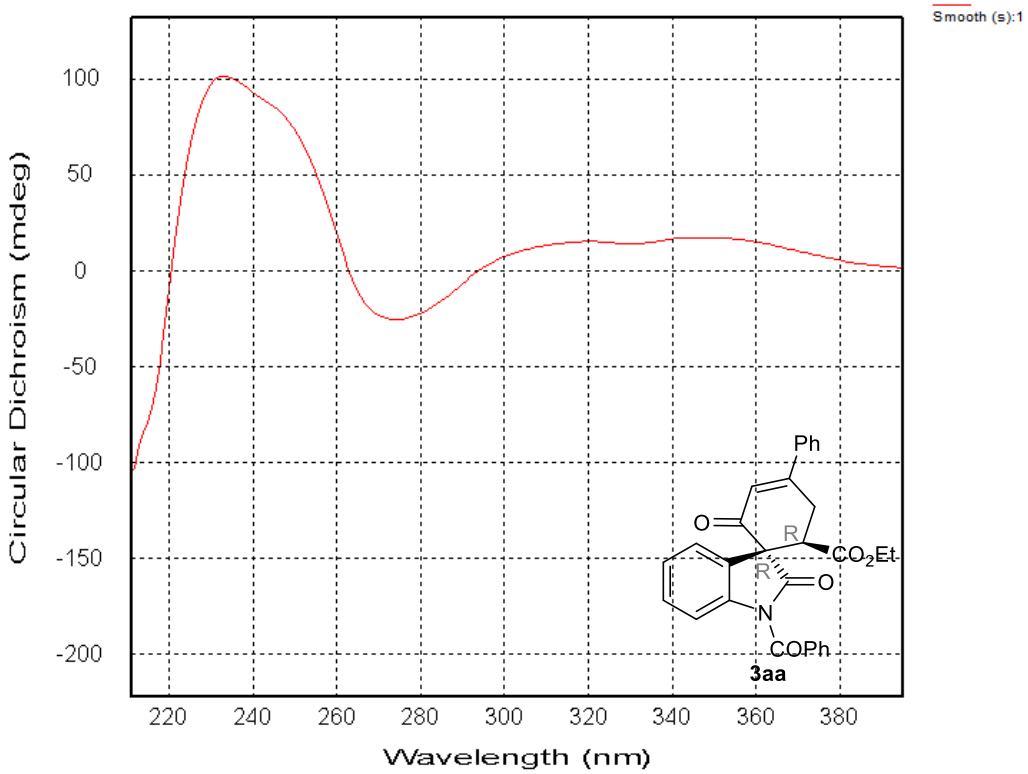

101 MHz, CDCl3 - 13C NMR
11
f1 (ppm)

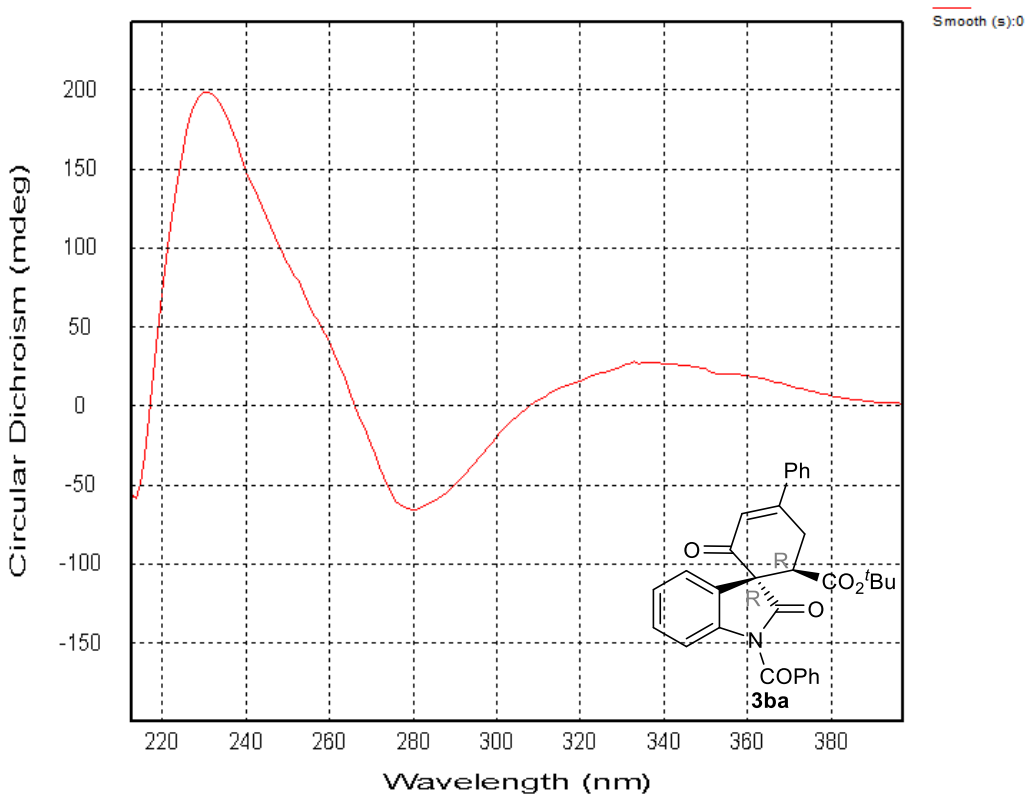

8.25 7.57 7.56 7.56 7.55 7.54 7.54 7.44 7.43 7.43 7.42 7.41 7.40 7.40 7.38 7.37 7.37 7.36 7.35 7.26 7.25 7.24 7.23 7.22 7.21 7.11 7.09 6.96 6.95 6.94 6.93 6.92 6.90 6.14 6.13 6.12 4.89 4.87 4.86 3.46 3.44 3.42 3.08 3.05 3.04 3.04 3.03 3.02 3.02 2.10 2.08 1.63 1.23 0.00
400 MHz, CDCl3 - 1H NMR
f1 (ppm)
H2O residue
HO
O
O
NH
O
12


180.40 169.92 142.47 138.91 136.90 128.59 128.49 128.00 126.53 126.50 125.25 125.05 122.22 109.68 81.64 77.16 76.84 76.52 73.19 54.61 44.59 27.45
101 MHz, CDCl3 - 13C NMR
128.59 128.49 128.00 126.53 126.50 125.25 125.05
f1 (ppm)
HO
O
O
NH
O
12

15 Copies of CD spectra for products



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150
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-150
220
240
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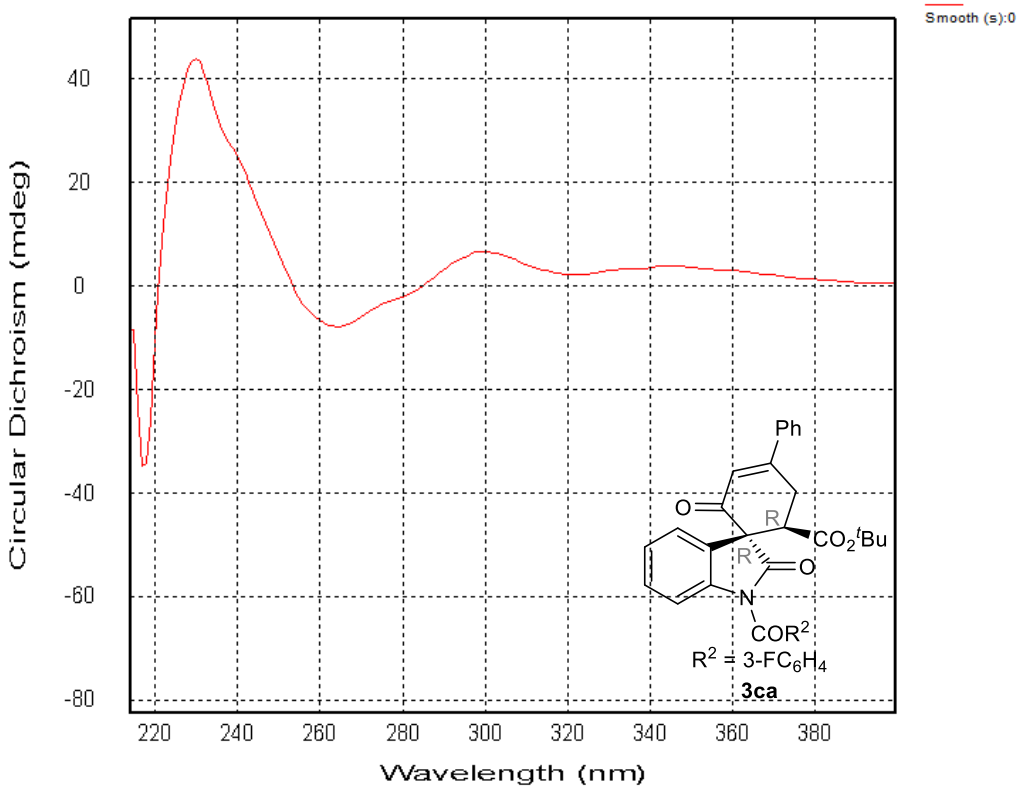
300
320
340
360
380
Wavelength (nm)
Ph
O
R
CO2tBu
R'
O
N
COPh
3ba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20
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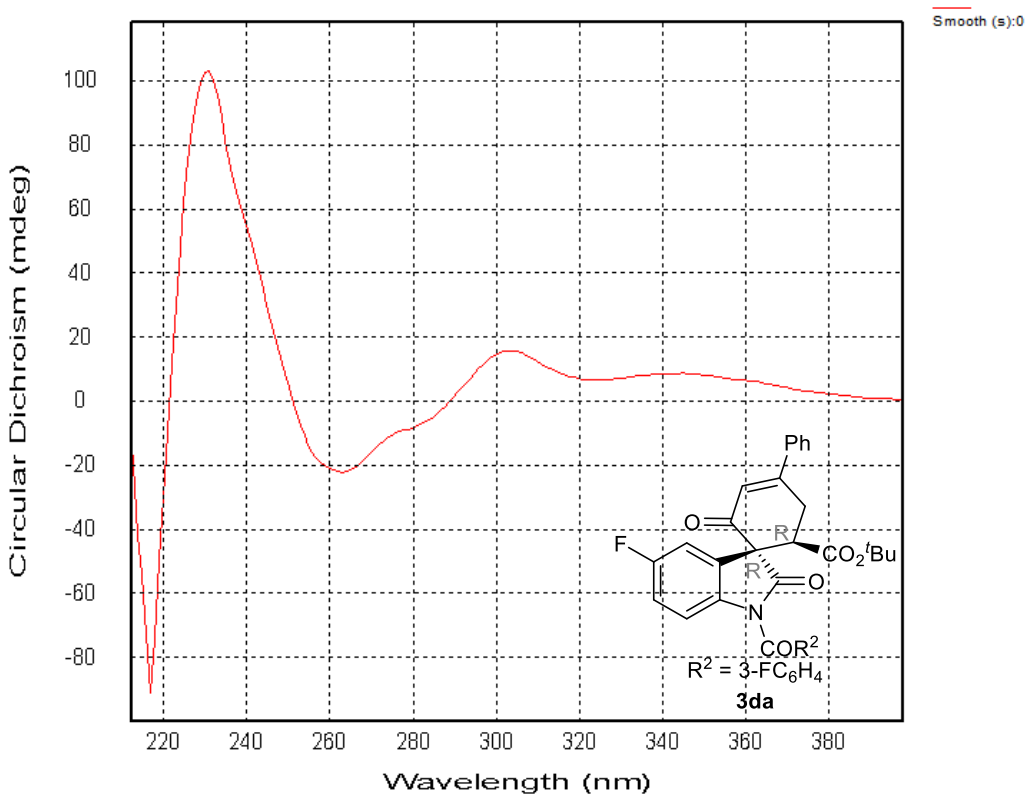
240
260
280
300
320
340
360
380
Wavelength (nm)
Ph
O
R
CO2tBu
R'
O
N
COR2
R2 = 3-FC6H4
3ca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260
280
300
320
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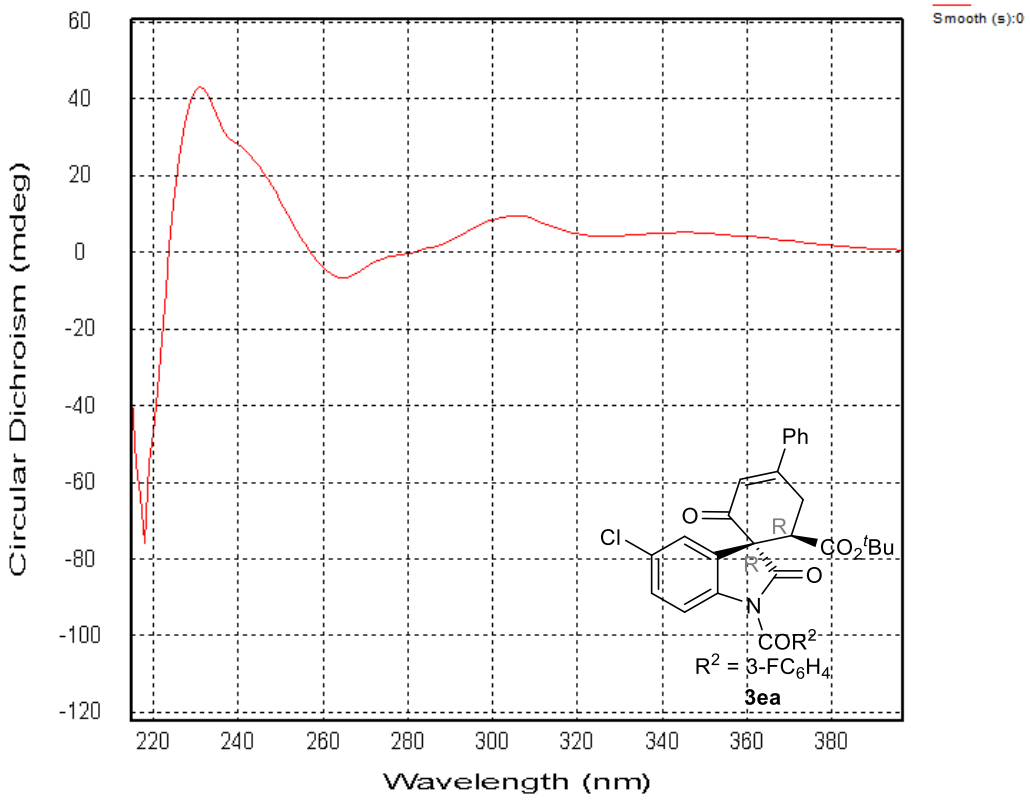
Wavelength (nm)
Ph
O
F
R
R
CO2tBu
O
N
COR2
R2 = 3-FC6H4
3da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240
260
280
300
320
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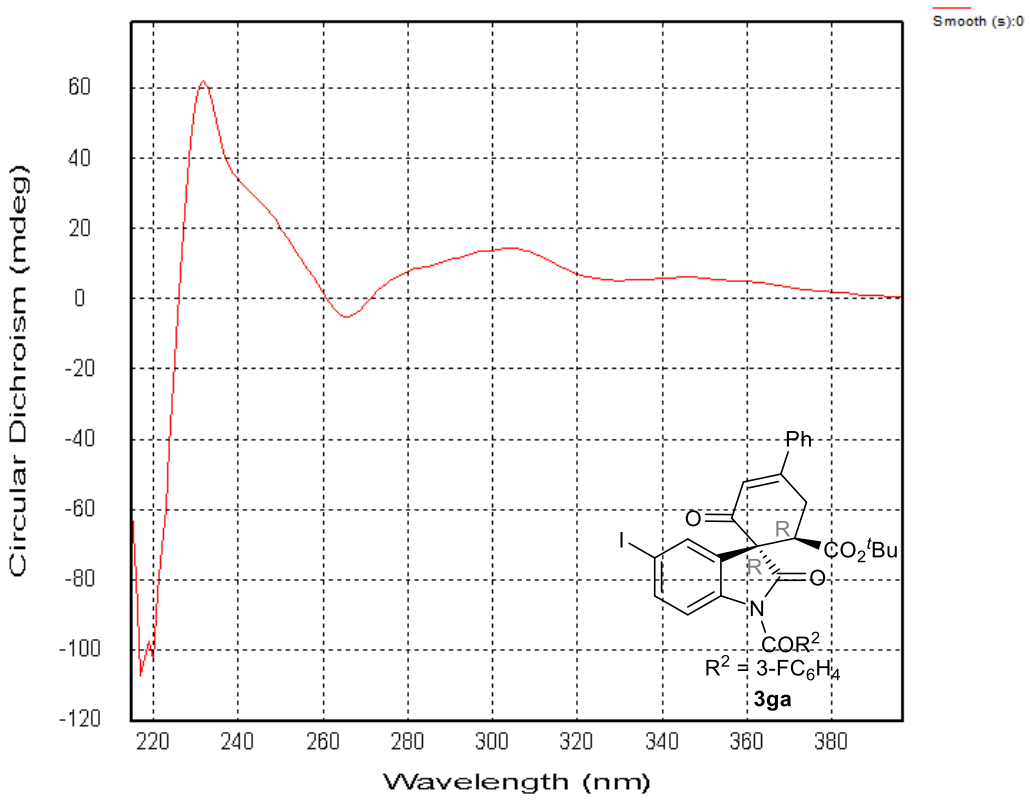
360
380
Wavelength (nm)
Ph
O
Cl
R
R
CO2tBu
O
N
COR2
R2 = 3-FC6H4
3ea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240
260
280
300
320
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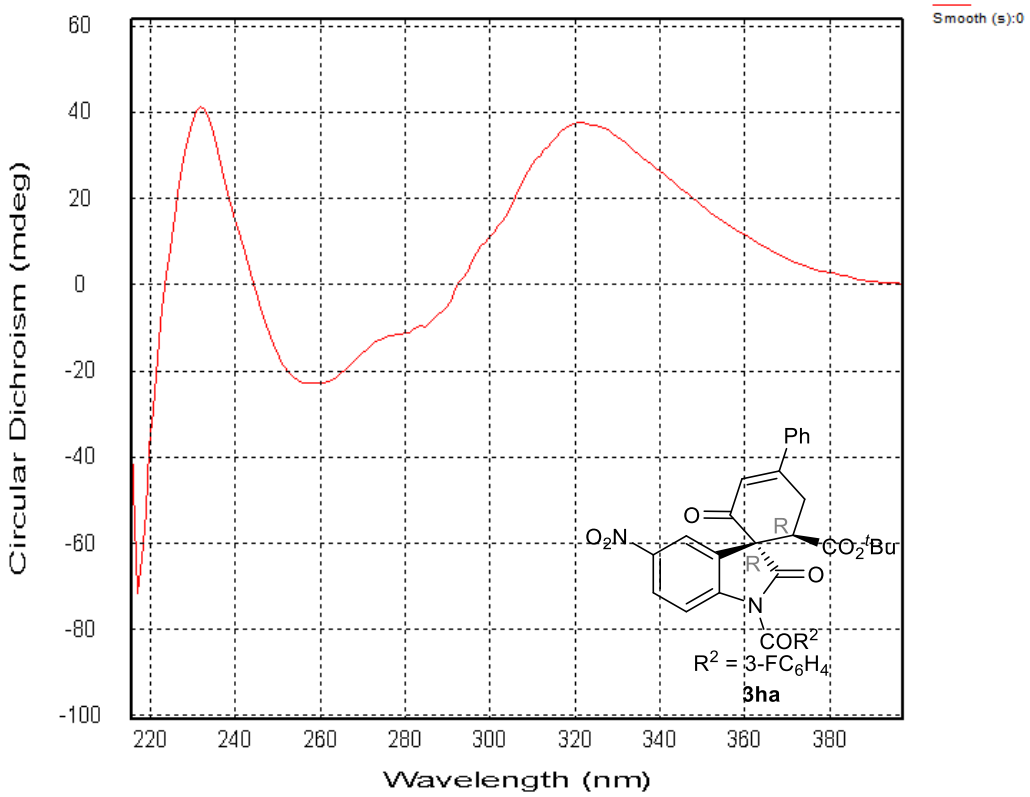
Wavelength (nm)
Ph
O
R
CO2tBu
I
R
O
N
COR2
R2 = 3-FC6H4
3ga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280
300
320
340
360
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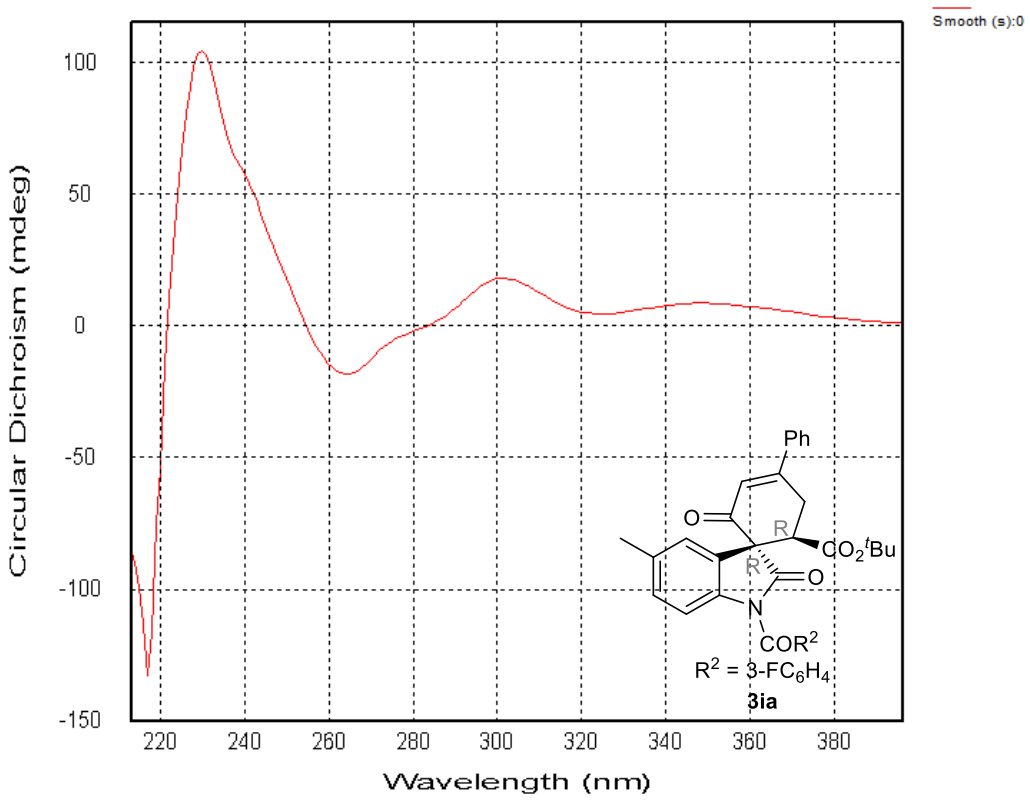
Wavelength (nm)
Ph
O
R
CO2tBu
O2N
R
O
N
COR2
R2 = 3-FC6H4
3ha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300
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360
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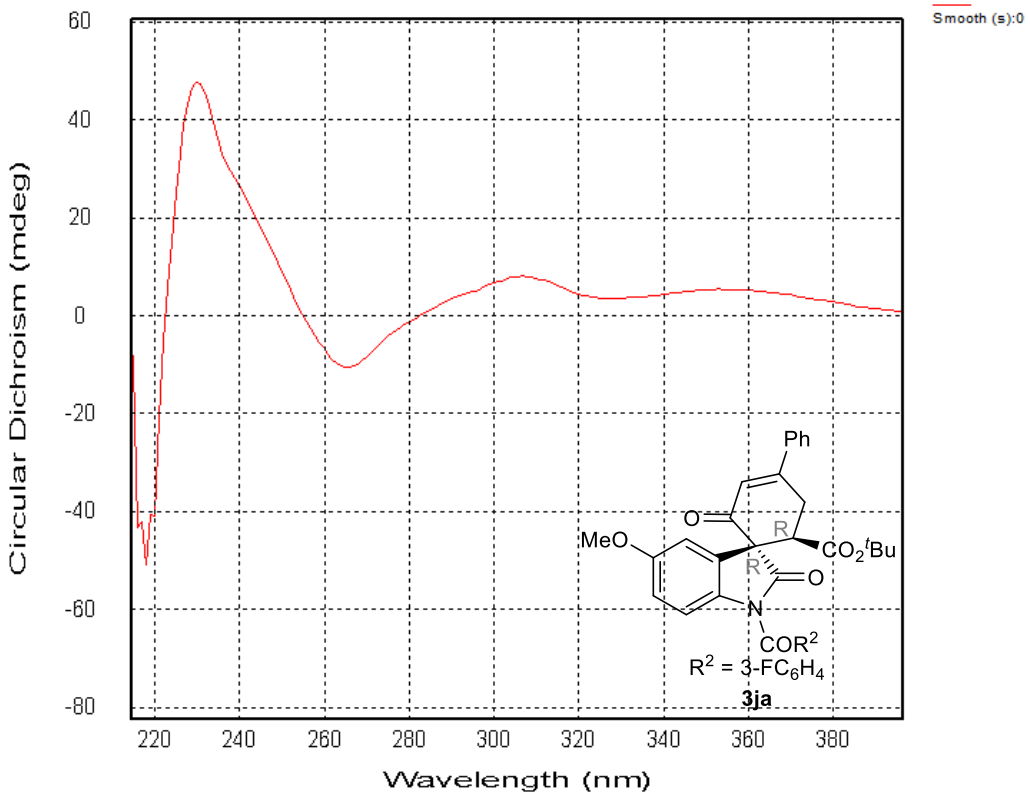
Wavelength (nm)
Ph
O
R
CO2tBu
R
O
N
COR2
R2 = 3-FC6H4
3ia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240
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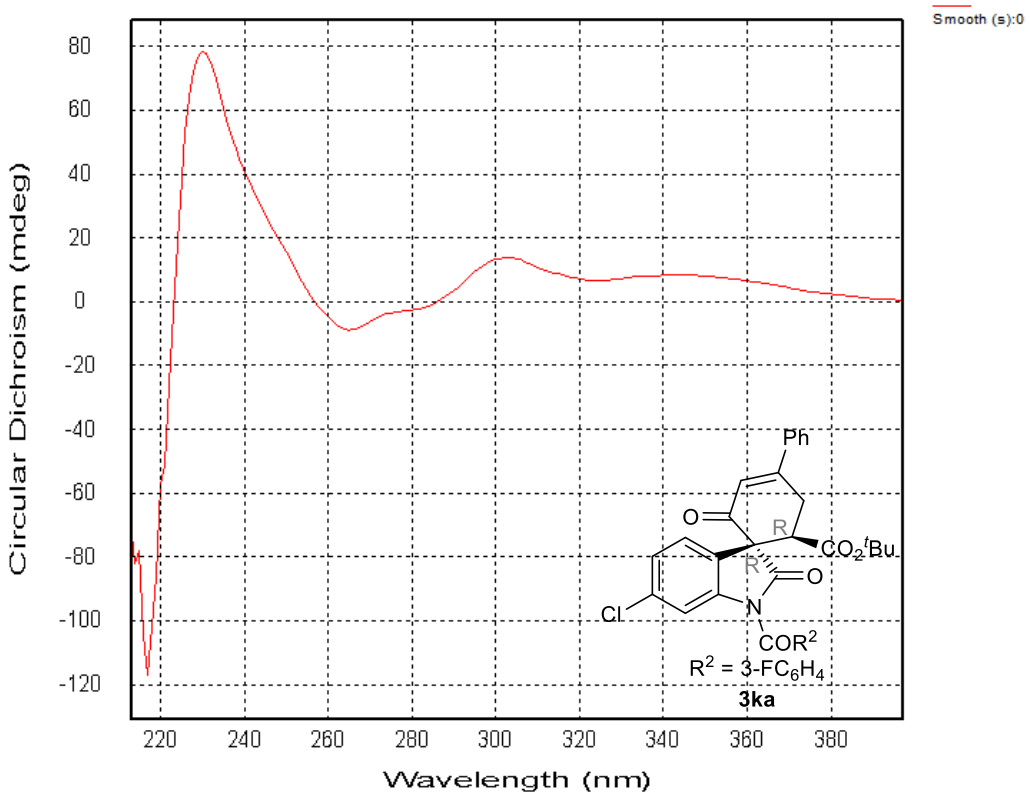
280
300
320
340
360
380
Wavelength (nm)
Ph
O
MeO
R
CO2tBu
R
O
N
COR2
R2 = 3-FC6H4
3ja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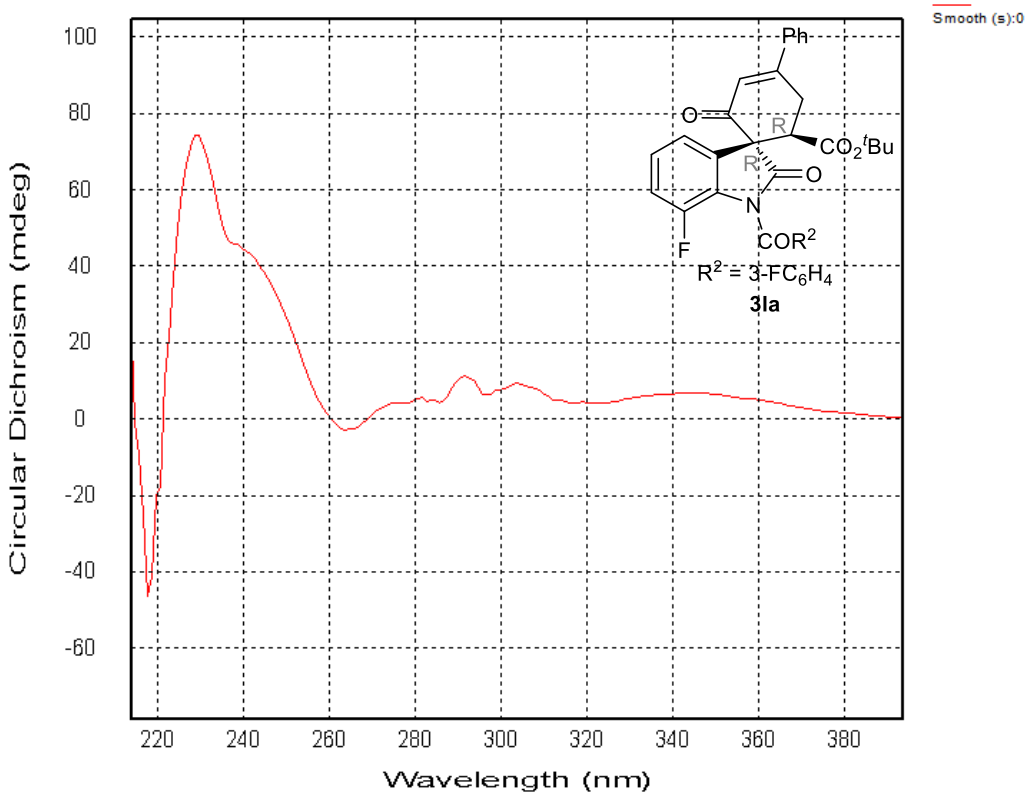
300
320
340
360
380
Wavelength (nm)
Ph
O
R
CO2tBu
R
O
Cl
N
COR2
R2 = 3-FC6H4
3ka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60
40
20
0
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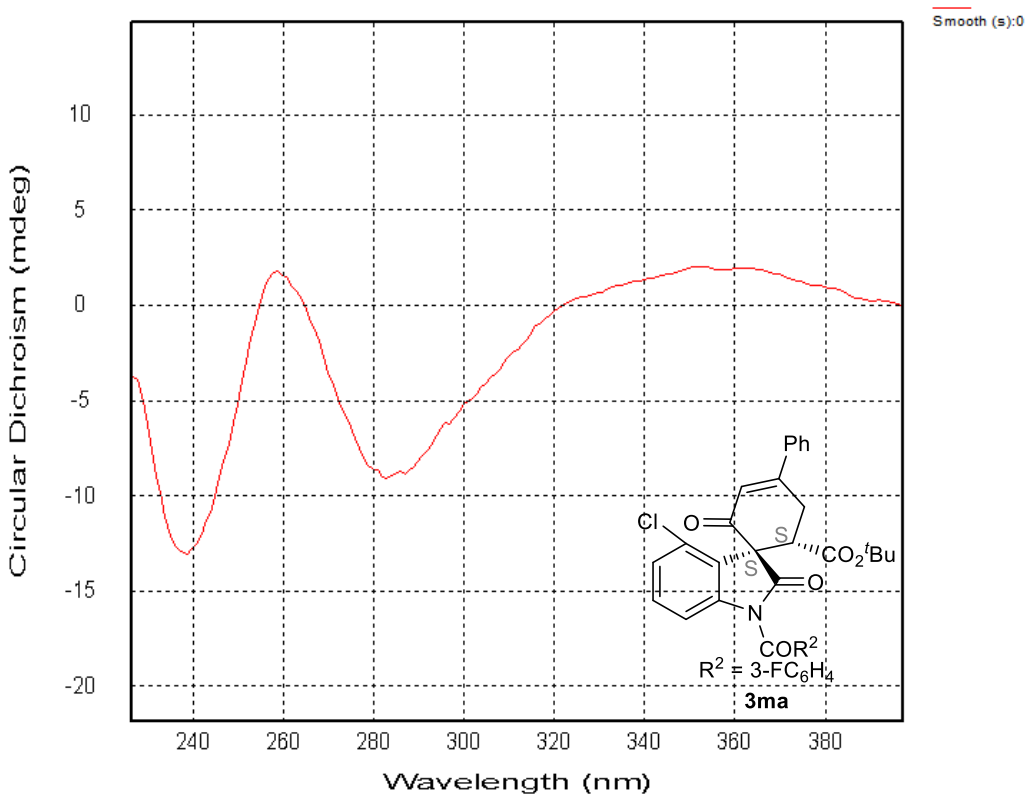
-60
220
240
260
280
300
320
340
360
380
Wavelength (nm)
Ph
O
R
CO2tBu
R
O
N
F
COR2
R2 = 3-FC6H4
3la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-15
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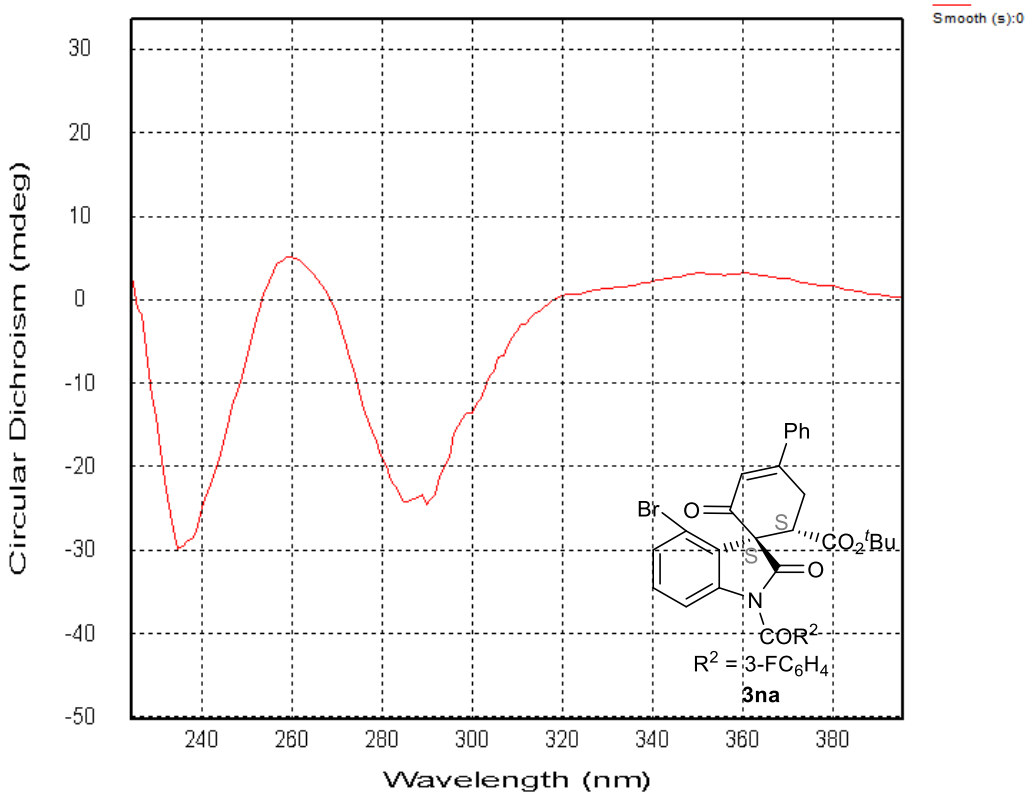
240
260
280
300
320
340
360
380
Wavelength (nm)
Ph
Cl
O
S
S
CO2tBu
O
N
COR2
R2 = 3-FC6H4
3ma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20
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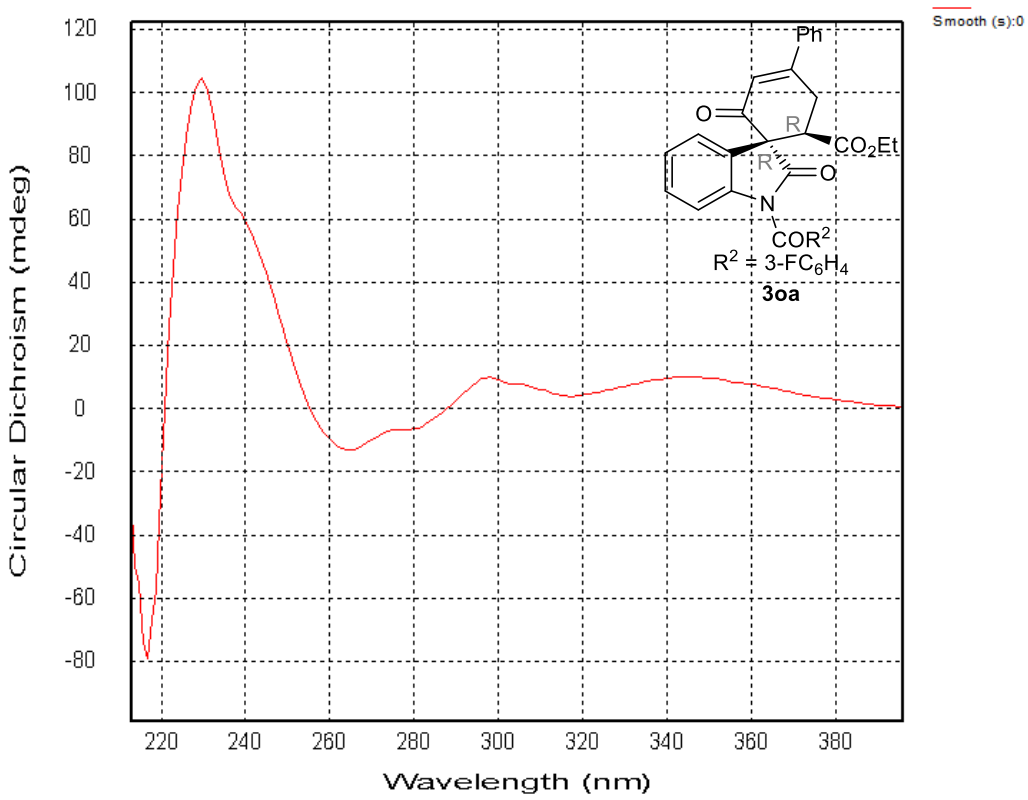
-30
-40
-50
240
260
280
300
320
340
360
380
Wavelength (nm)
Ph
Br
O
S
S
CO2tBu
O
N
COR2
R2 = 3-FC6H4
3na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40
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0
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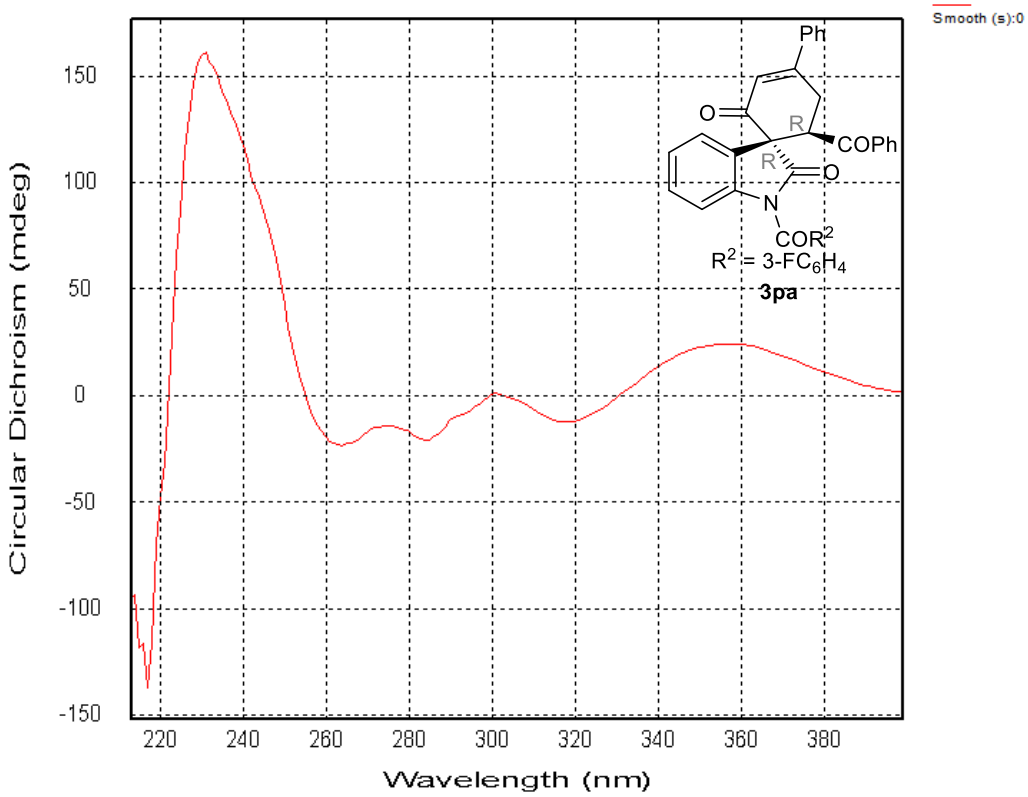
-60
-80
220
240
260
280
300
320
340
360
380
Wavelength (nm)
Ph
O
R
CO2Et
R
O
N
COR2
R2 = 3-FC6H4
3oa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Circular Dichroism (mdeg)
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100
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-50
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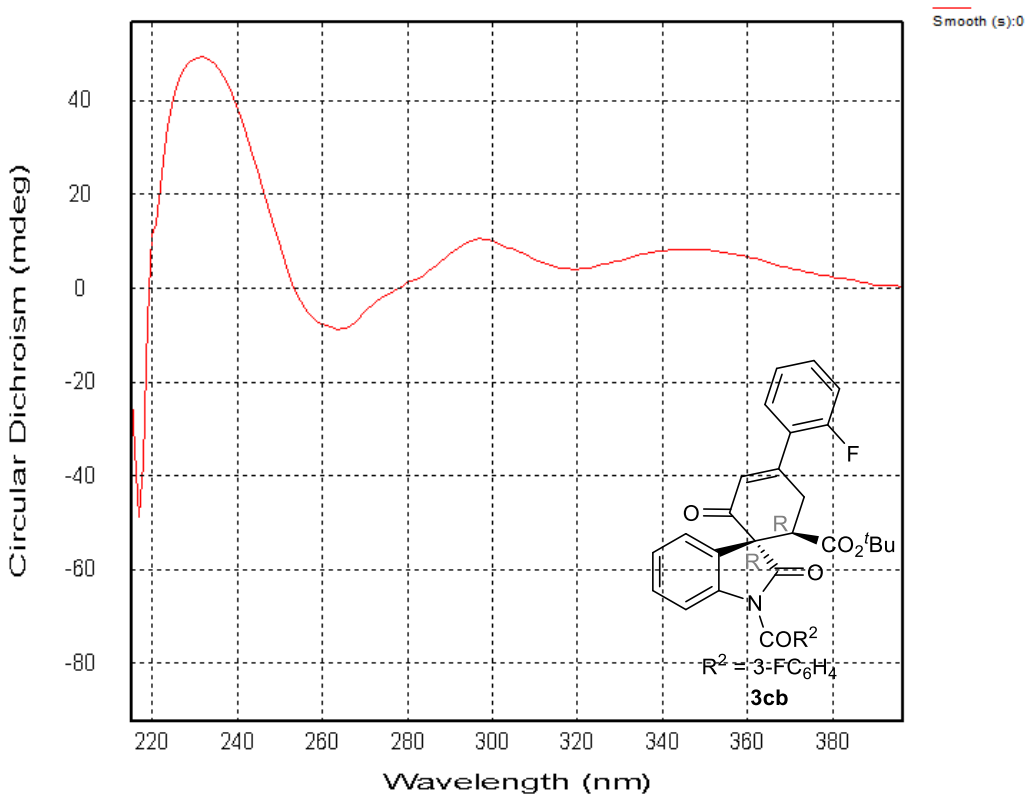
-150
220
240
260
280
300
320
340
360
380
Wavelength (nm)
Ph
O
R
COPh
R
O
N
COR2
R2 = 3-FC6H4
3pa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240
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280
300
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360
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Wavelength (nm)
F
O
R
CO2tBu
R
O
N
COR2
R2 = 3-FC6H4
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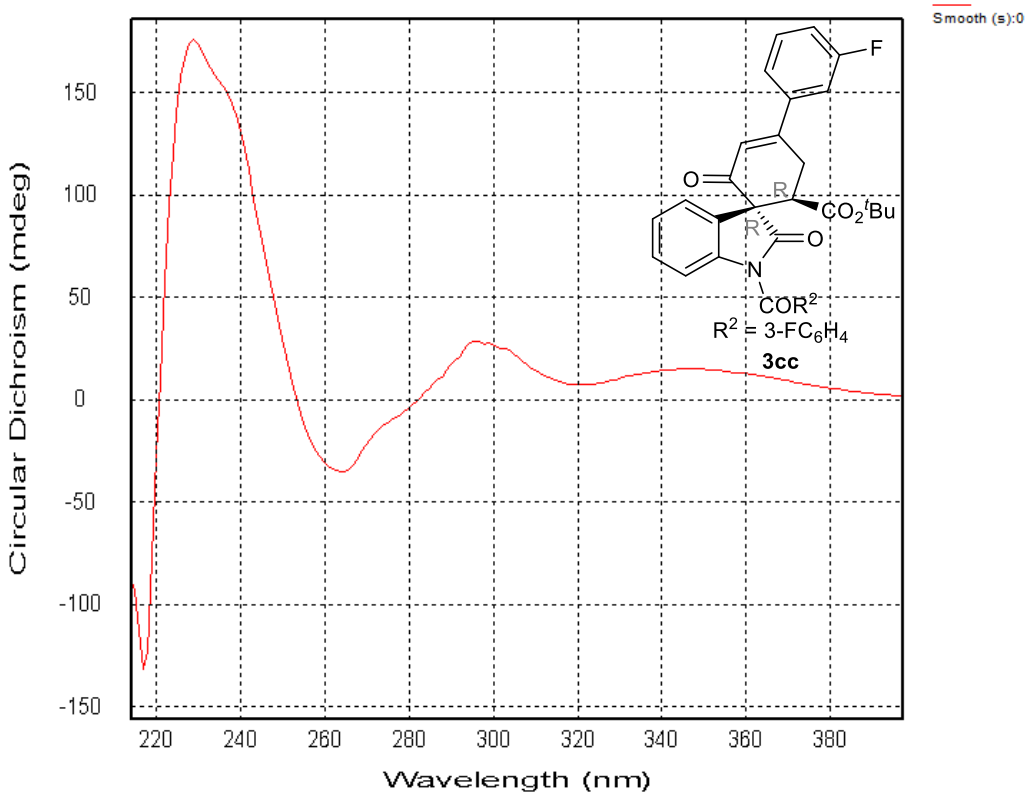
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240
260
280
300
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360
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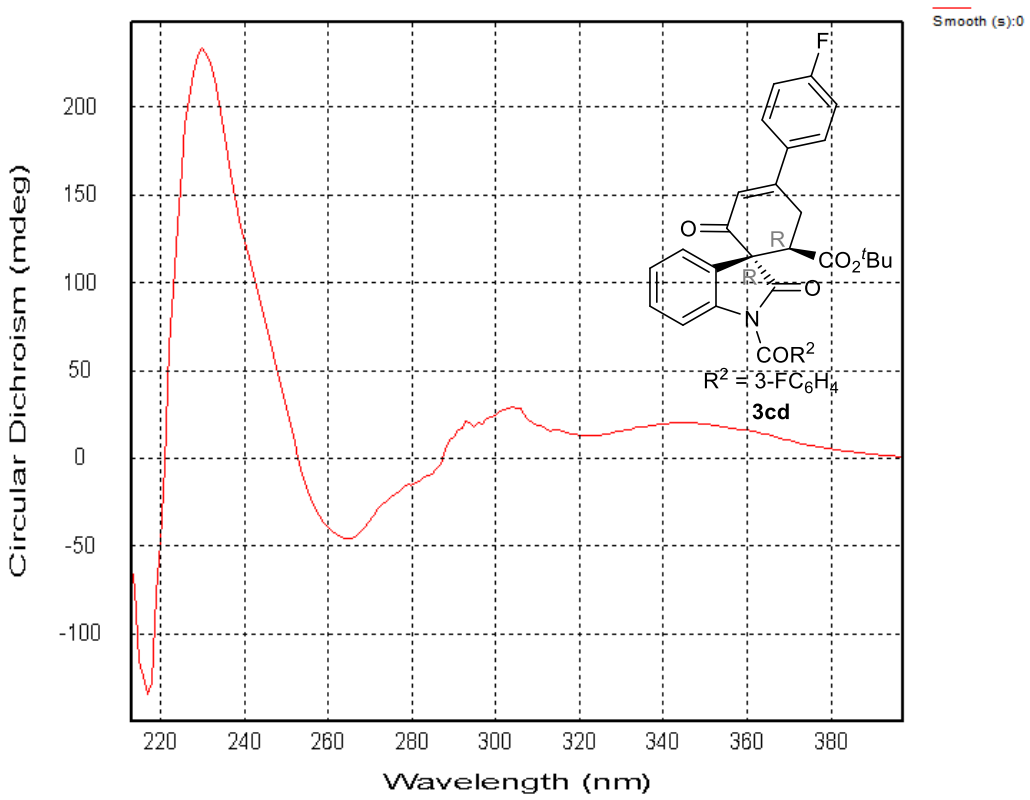
Wavelength (nm)
F
O
R
CO2tBu
R
O
N
COR2
R2 = 3-FC6H4
3cc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300
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Wavelength (nm)
F
O
R
CO2tBu
R
O
N
COR2
R2 = 3-FC6H4
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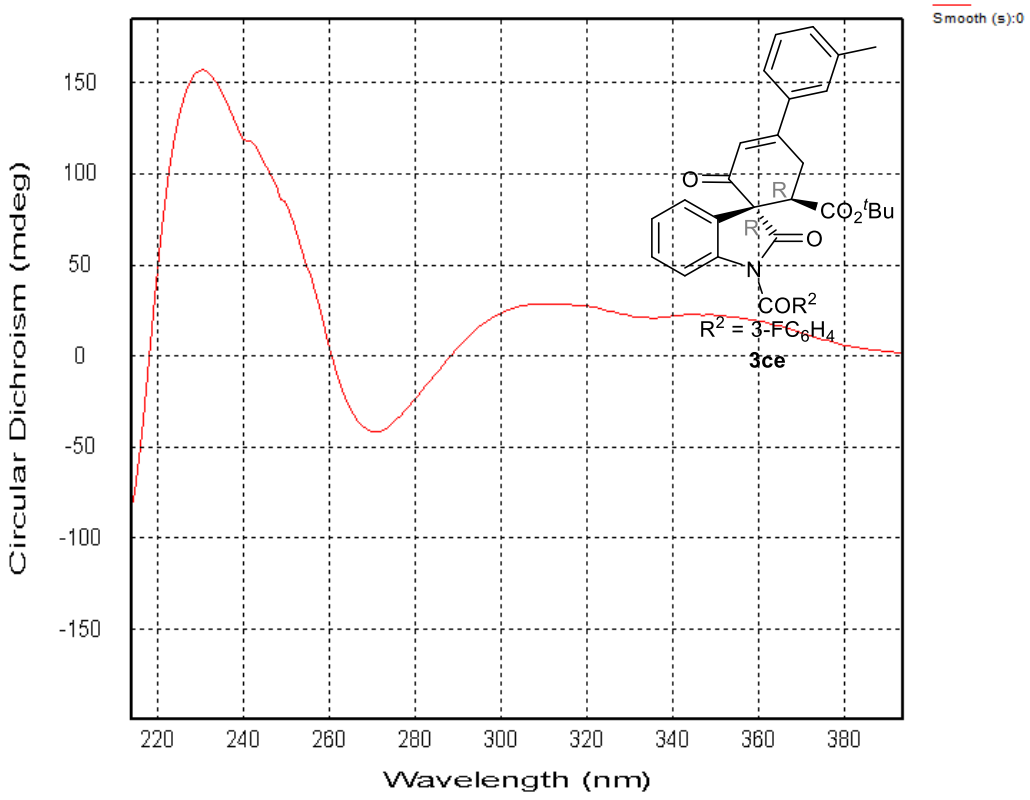
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240
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360
380
Wavelength (nm)
O
R
CO2tBu
R
O
N
COR2
R2 = 3-FC6H4
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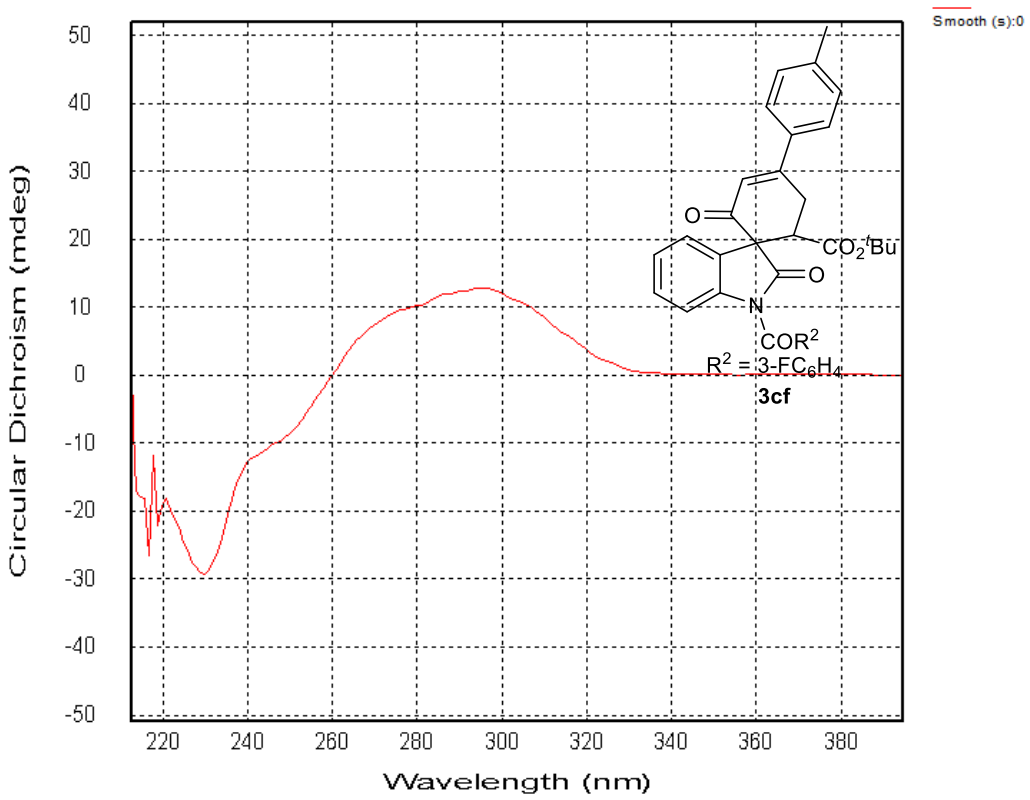
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-20
-30
-40
-50
220
240
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300
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340
360
380
Wavelength (nm)
O
CO2tBu
O
N
COR2
R2 = 3-FC6H4
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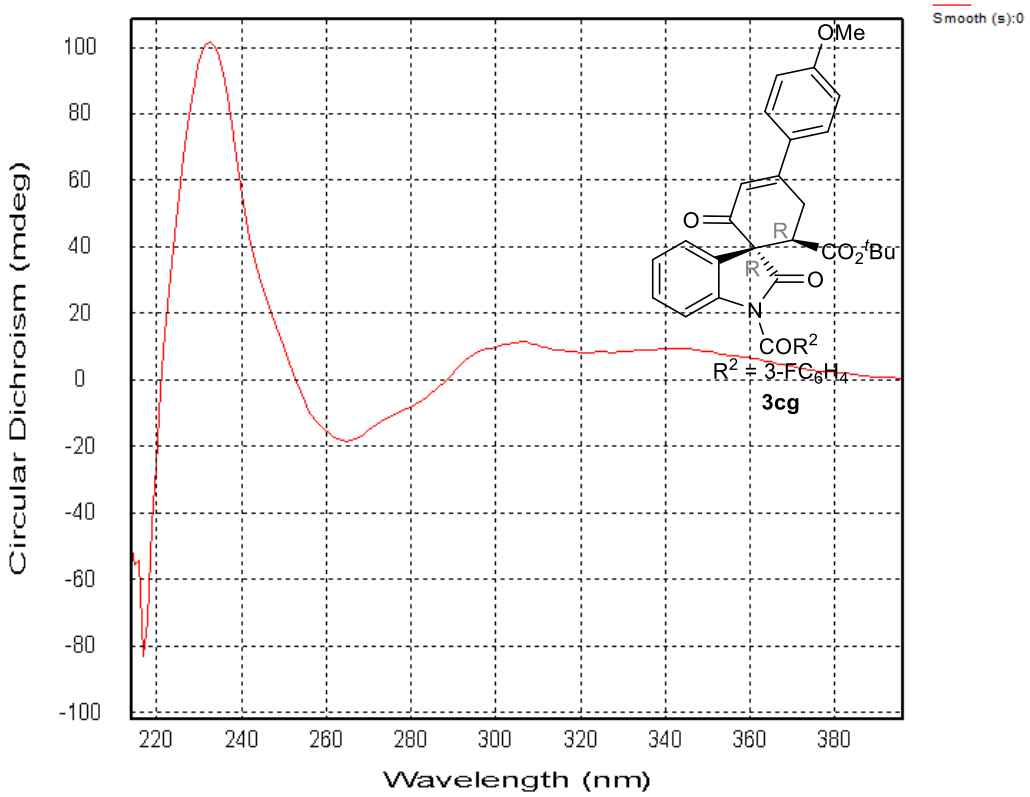
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260
280
300
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360
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Wavelength (nm)
OMe
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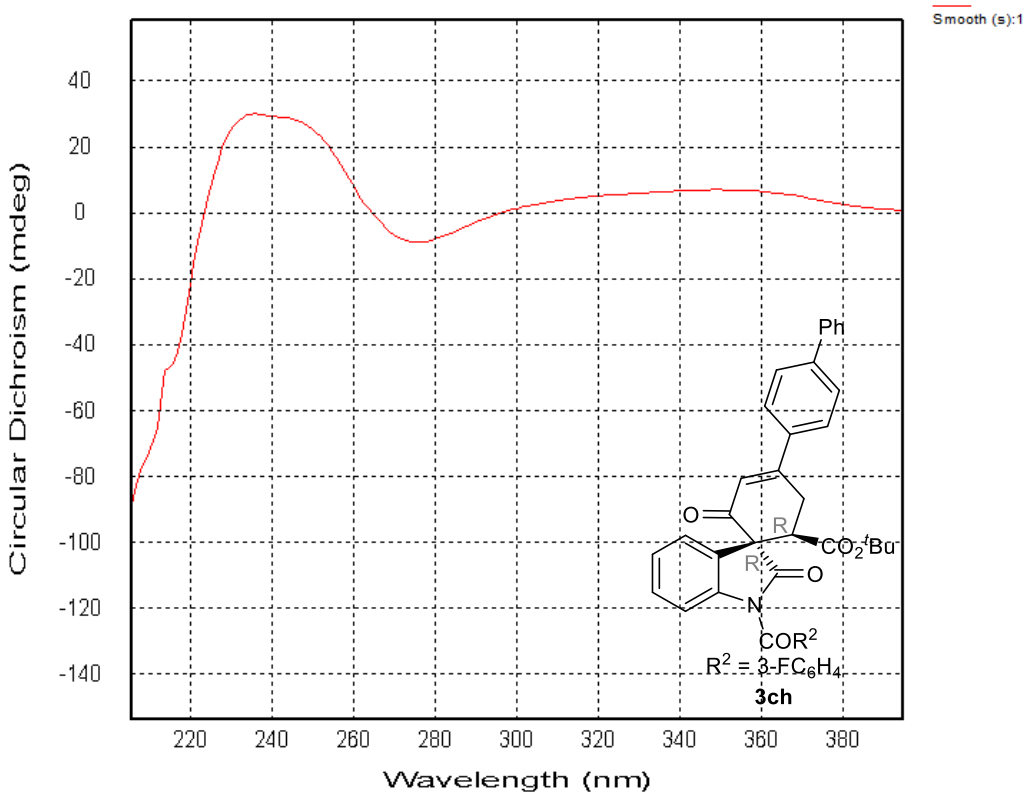
R
CO2tBu
R
O
N
COR2
R2 = 3-FC6H4
3cg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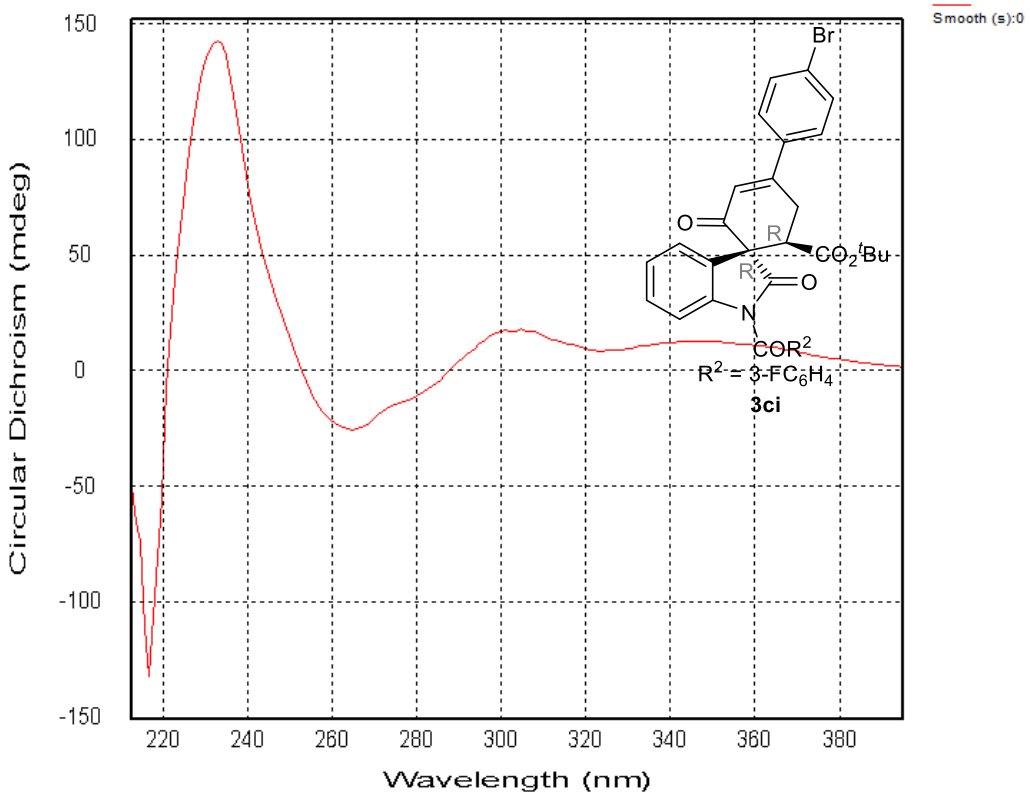
240
260
280
300
320
340
360
380
Wavelength (nm)
Ph
O
R
CO2tBu
R
O
N
COR2
R2 = 3-FC6H4
3ch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220
240
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280
300
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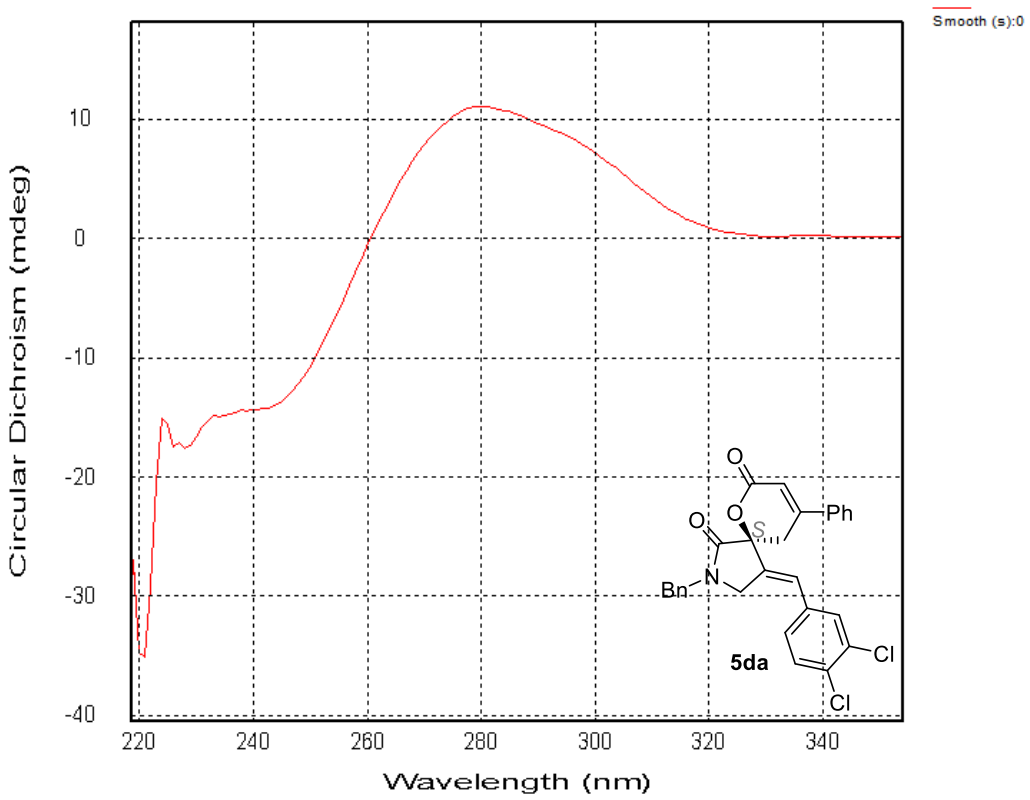
340
360
380
Wavelength (nm)
Br
O
R
CO2tBu
R
O
N
COR2
R2 = 3-FC6H4
3ci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300
320
340
Wavelength (nm)
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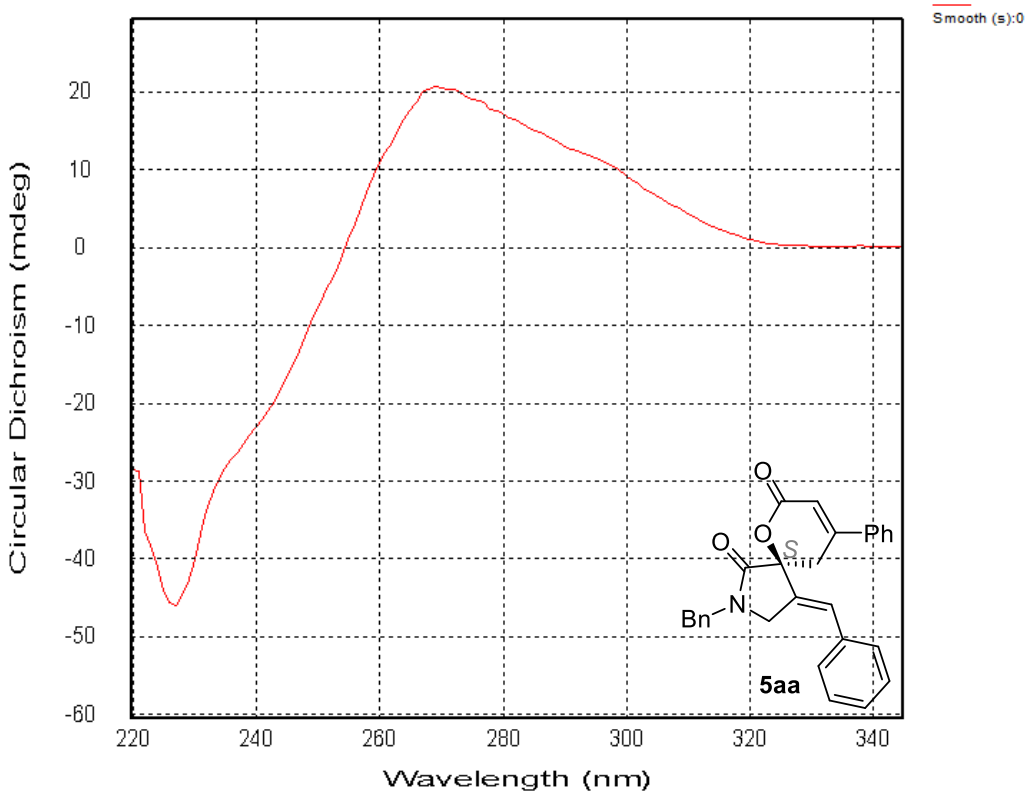
O
O
Ph
S
N
Bn
Cl
Cl
5da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300
320
340
Wavelength (nm)
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O
O
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S
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Bn
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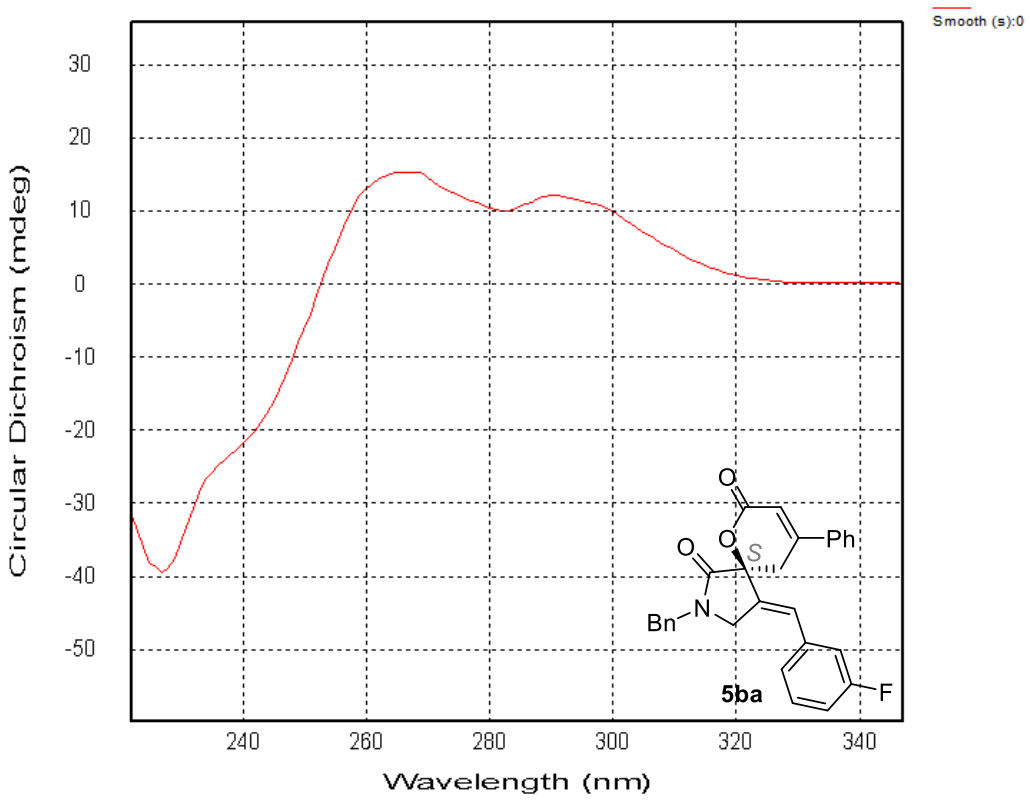
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0
-10
-20
-30
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240
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280
300
320
340
Wavelength (nm)
O
O
O
S
Ph
Bn
N
F
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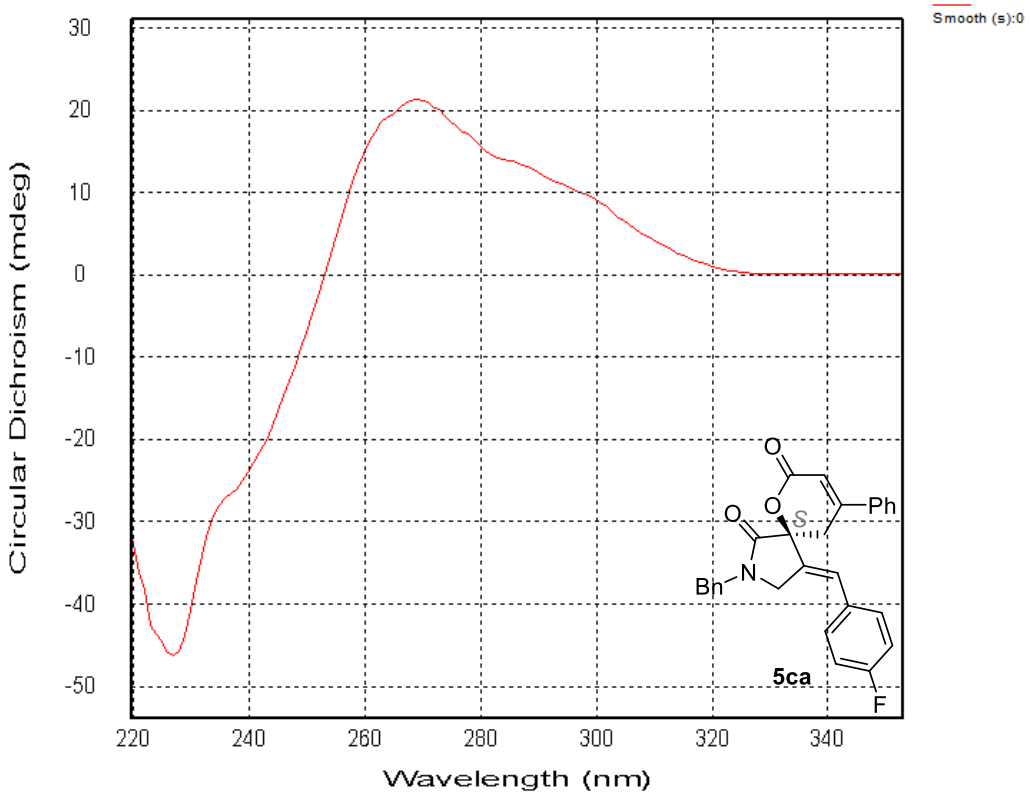
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280
300
320
340
Wavelength (nm)
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O
O
S
Ph
Bn
N
F
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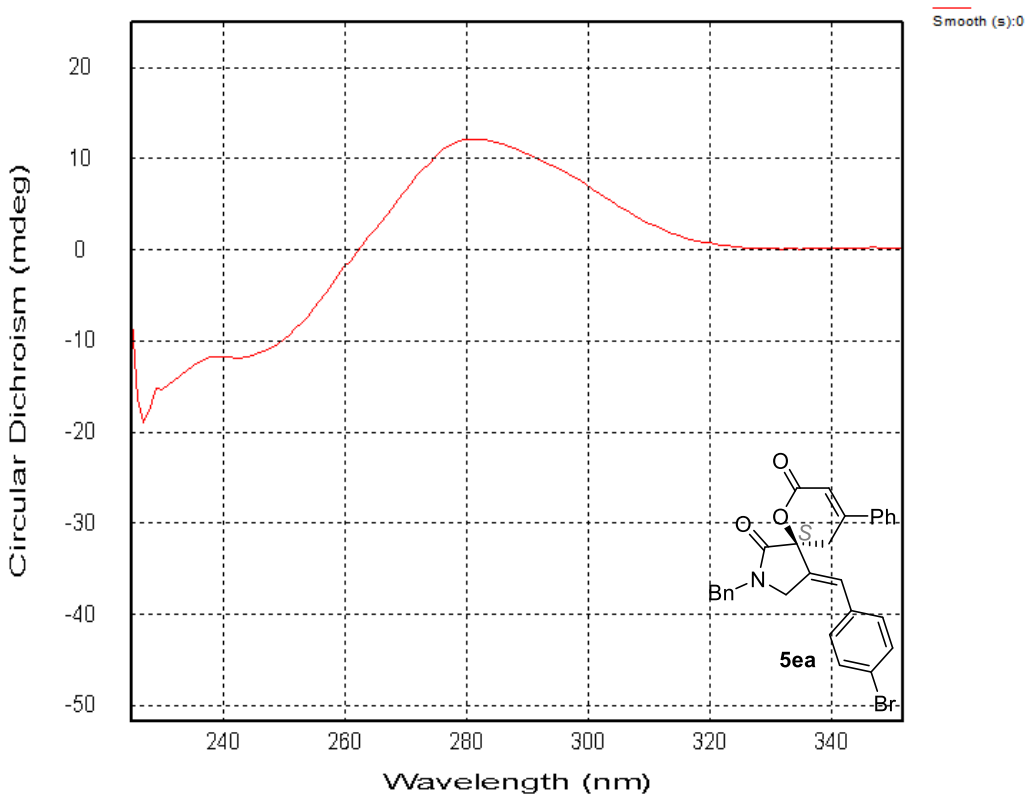
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20
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0
-10
-20
-30
-40
-50
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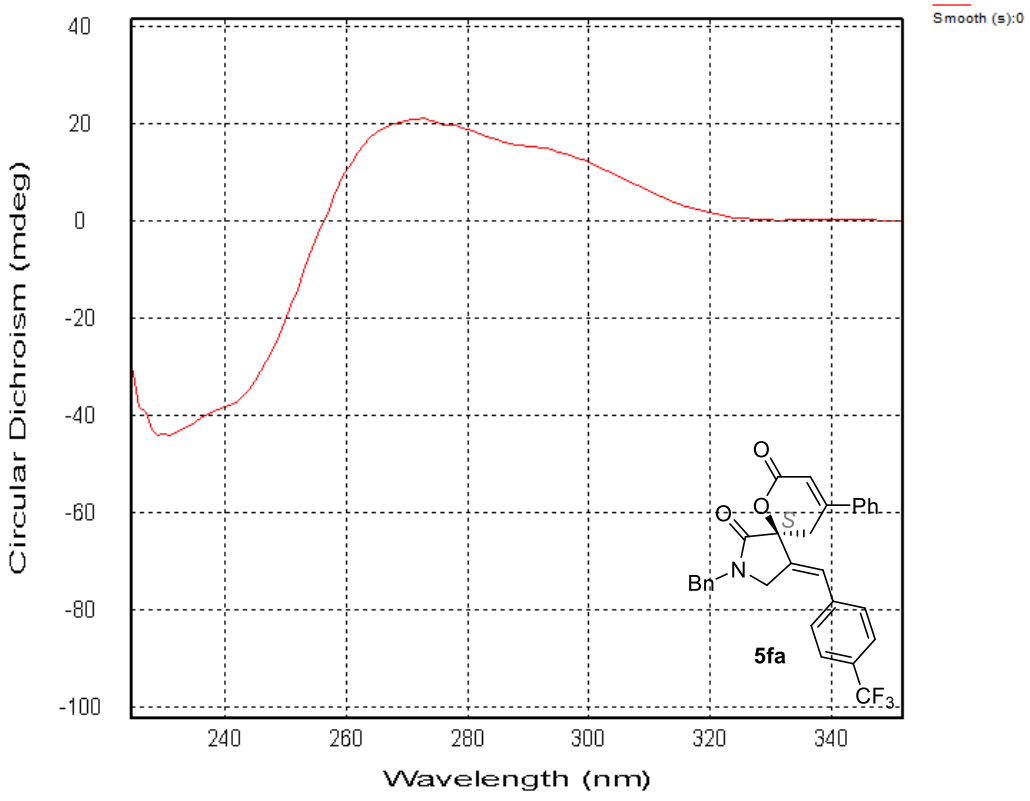
280
300
320
340
Wavelength (nm)
O
O
O
Ph
S
Bn
N
5ea
Br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Circular Dichroism (mdeg)
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-20
-40
-60
-80
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280
300
320
340
Wavelength (nm)
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O
O
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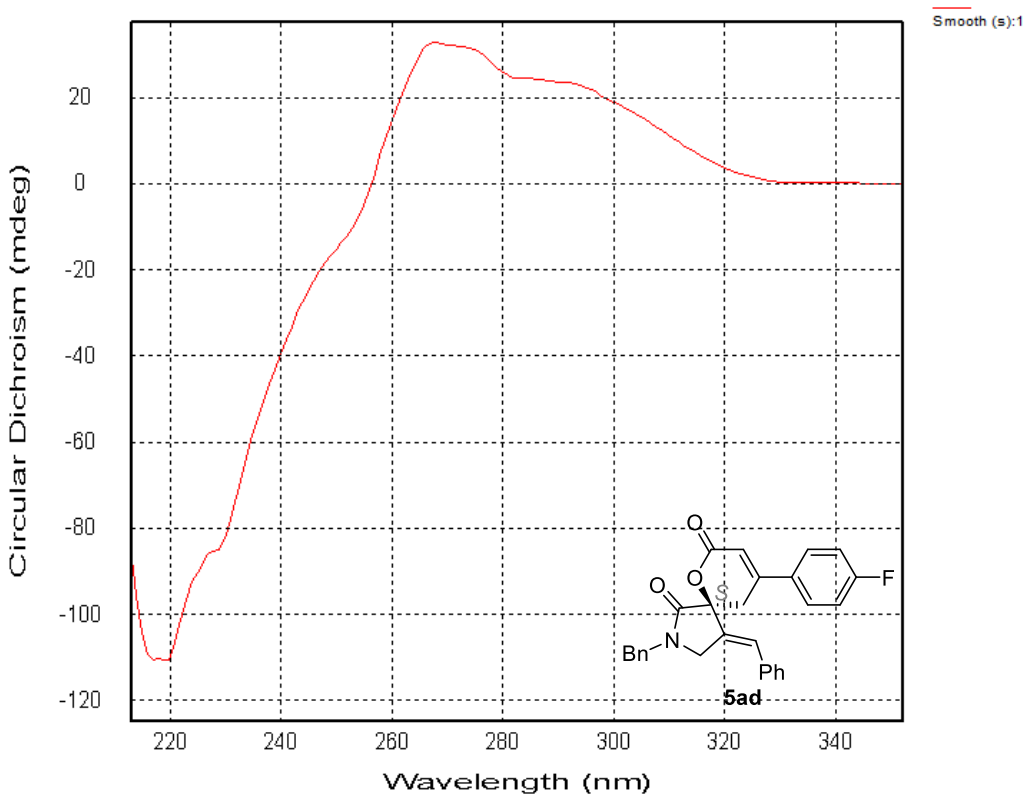
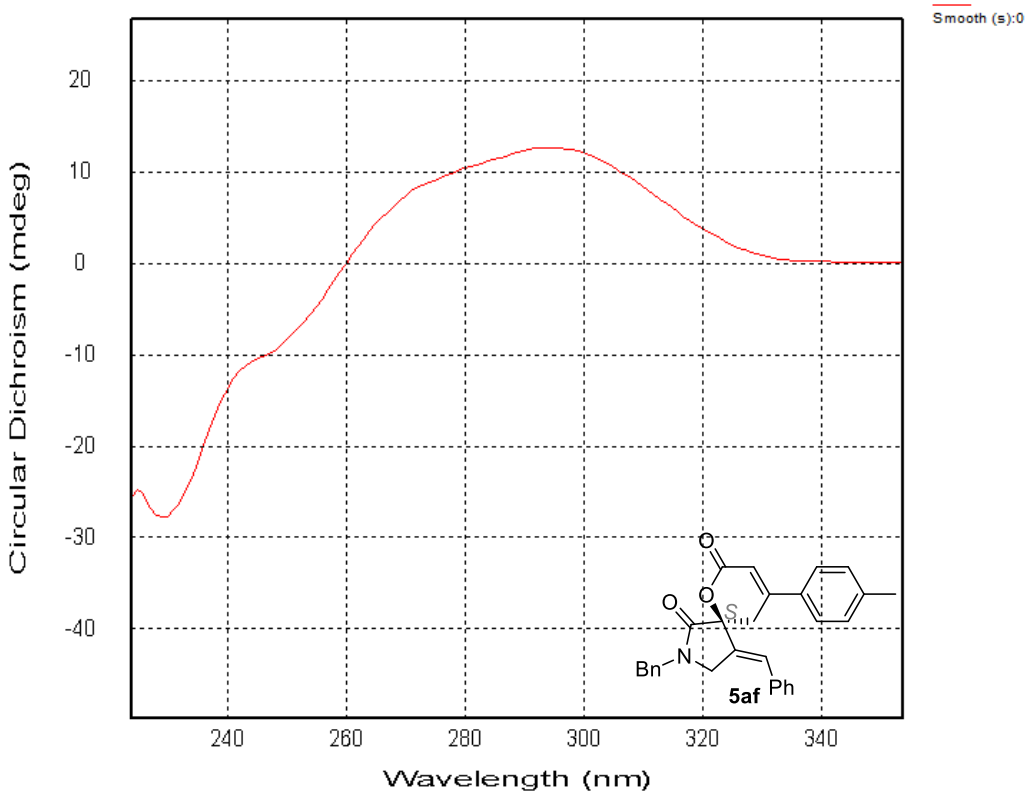
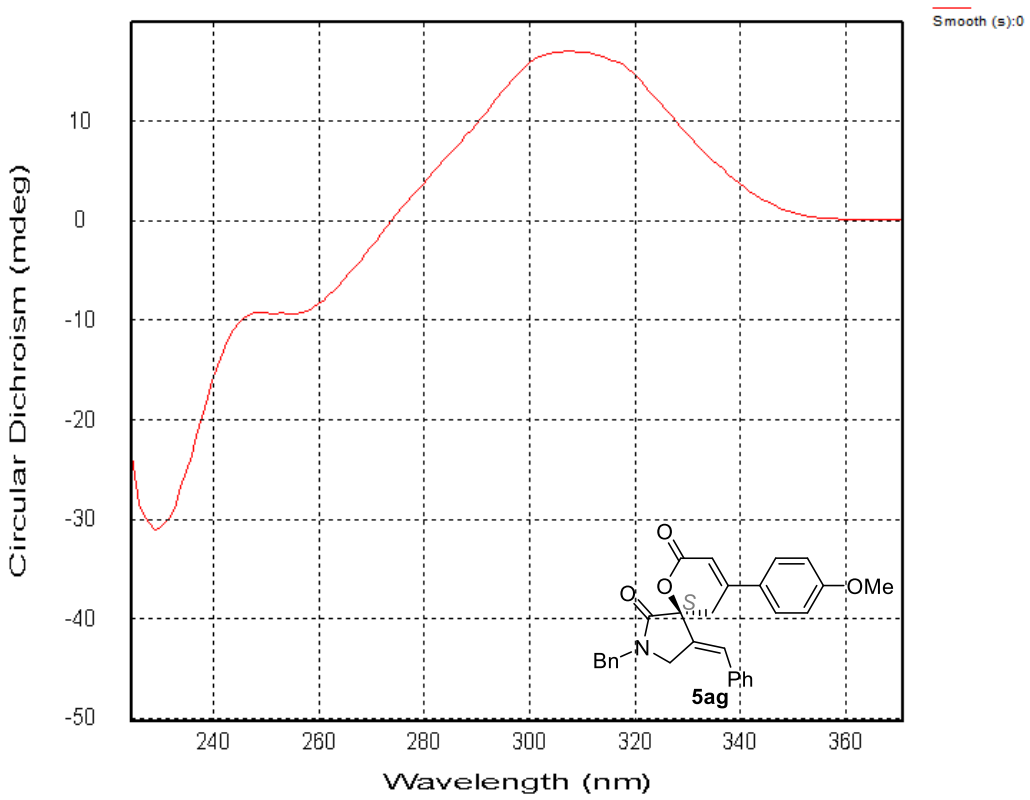
CF3


Smooth (s):1
Circular Dichroism (mdeg)
20
0
-20
-40
-60
-80
-100
-120
220
240
260
280
300
320
340
Wavelength (nm)
O
O
O
S
F
Bn
N
Ph
5ad


Smooth (s):0
Circular Dichroism (mdeg)
20
10
0
-10
-20
-30
-40
240
260
280
300
320
340
Wavelength (nm)
O
O
O
S
Bn
N
5af
Ph


Smooth (s):0
Circular Dichroism (mdeg)
10
0
-10
-20
-30
-40
-50
240
260
280
300
320
340
360
Wavelength (nm)
O
O
O
S
N
Bn
Ph
OMe
5ag