Supporting Information for:

Efficient Construction of Biologically Important Functionalized Polycyclic Spiro-fused Carbocyclicoxindoles via an Asymmetric Organocatalytic Quadruple-Cascade Reaction

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d. Contribute equally

Contents:

(A) General Information.

NMR spectra were recorded on the commercial 400 MHz spectrometer. The chemical shifts were recorded in ppm relative to tetramethylsilane (TMS) and with the solvent resonance as the internal standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, dq = doublet of quartet), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. Enantiomeric excesses (ee) were determined by chiral HPLC analysis on DAICEL CORPORATION AS-H and AD-H columns in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 mL, in solvent). ESI-HRMS spectra were recorded on a commercial apparatus and methanol was used to dissolve the sample. Substituted (*E*)-3-(2-hydroxybenzylidene)oxindole **1** were prepared by Knoevenagel condensation of corresponding Salicylaldehyde derivatives and Oxindole derivatives.[1] α, β-unsaturated aldehydes **2**, diphenylprolinol silyl ether catalysts **3**, additives **4** and solvents were commercially available and used directly without further purification. Several substituted oxindoles were prepared according to the literatures and references therein.[2]

(B) Representative Procedure for the Asymmetric Catalysis

1. Procedure for the optimization of reaction conditions

Crotonaldehyde **2a** (0.244 mmol, 20 μL) was added to a dry tube containing a suspension of (*E*)-3-(2-hydroxybenzylidene)oxindole **1a** (0.1 mmol), chiral diphenylprolinol silyl ether catalyst **3** (20 mol %), addtive **4** and dry solvent 1 mL. The mixture was stirred at 40 ^{o}C or 60 ^{o}C. The reaction progress was detected by TLC. After the time indicated in Tables, reaction mixture was subjected to silica gel column chromatography to yield the corresponding product (petroleum ether/ ethyl acetate, 2/1, *V/V*).

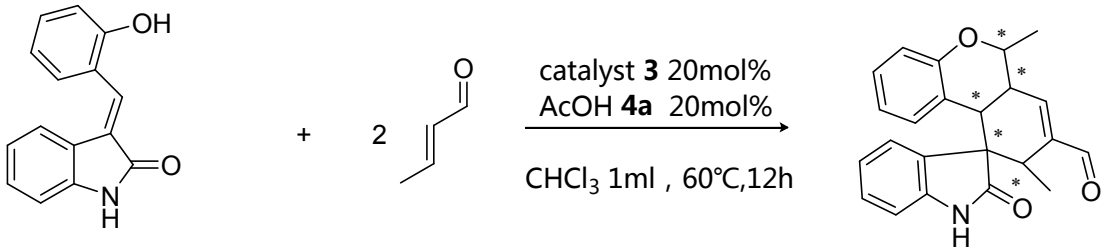
2. Procedure for the investigation of substrate scope

α, β-unsaturated aldehydes **2** (0.244 mmol) was added to a dry tube containing a suspension of substituted (*E*)-3-(2-hydroxybenzylidene)oxindole **1** (0.1 mmol), α,α-L-diphenylprolinol trimethylsilyl ether **3a** (20 mol%), 2-(trifluoromethyl)benzoic acid **4h** (60 mol%) and $CHCl_3$ 1 mL. The mixture was stirred at 40 ^{o}C for 24 h and then heated up to 60 ^{o}C for 12 h. The reaction mixture was subjected to silica gel column

chromatography to yield the corresponding product (generally petroleum ether/ ethyl acetate, 2/1, *V/V*; for **5ia**: dichloromethane/ethyl acetate, 30/1, *V/V*; for **5ma**: petroleum ether/ethyl acetate, 3/1, *V/V*; for **5na**: dichloromethane/methanol, 100/1, *V/V*; for **5ta**: petroleum ether/ethyl acetate, 7/1, *V/V*).

(C) Tables for the Optimization of the Reaction Conditions

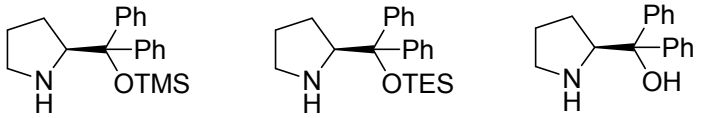
1. Investigation of structures of chiral diphenylprolinol silyl ether catalysts on results



1a
0.1mmol

2a
2.44 equiv

5aa



3a **3b** **3c**

Table S1. Investigation of catalysts[a]

Entry	Catalyst	Yield (%)[b]	Dr[c]	Ee(%)[d]
1	**3a**	60	1:1	98; 90
2	**3b**	55	1:1	92; 90
3	**3c**	Traces	n.d.	n.d.

[a] Reactions were performed with 0.1 mmol **1a** and 0.244 mmol (20 μL) **2a** in the presence of catalyst **3** (20 mol %) and the additive AcOH **4a** (20 mol %) in $CHCl_3$ at 60 ^oC for 12 h.

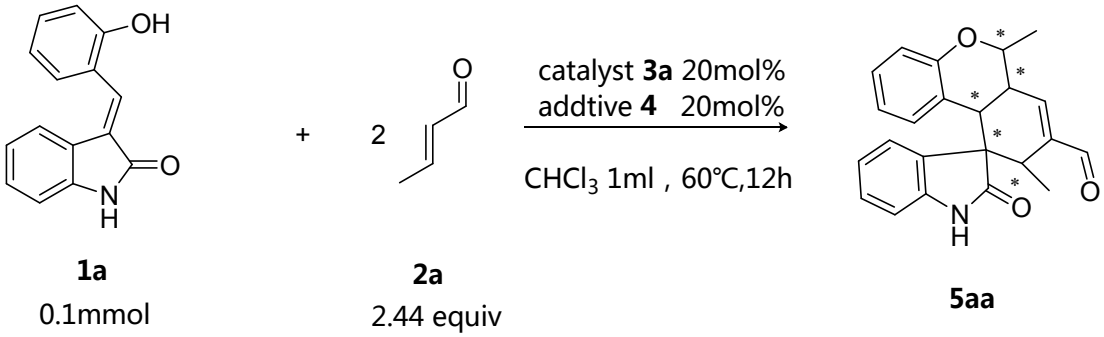
[b] The values are yields of isolated product after silica gel column chromatography.

[c] Determined by ^1H NMR on the crude reaction mixture.

[d] Determined by chiral HPLC.

Trace: little products were detected. n.d.: not determined.

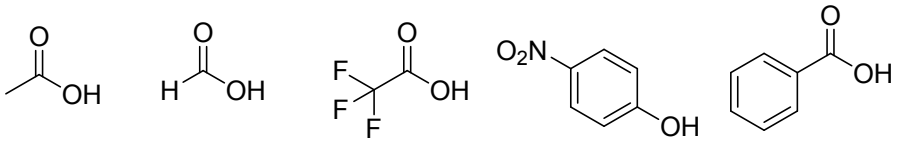
2. The influence of additives on the result[a]



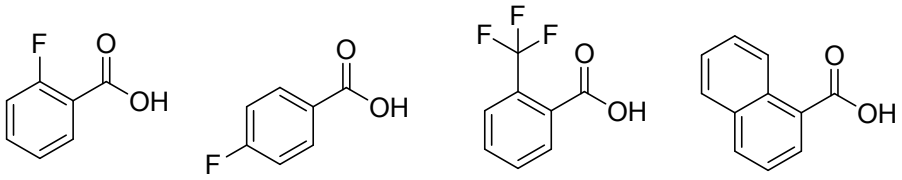
1a
0.1mmol

2a
2.44 equiv

5aa



4a **4b** **4c** **4d** **4e**



4f **4g** **4h** **4i**

Table S2. The influence of additives[a]

Entry	Addtive	Yield (%)[b]	Dr[c]	Ee(%)[d]
1	**4a**	60	1:1	98; 90
2	**4b**	Traces	n.d.	n.d.
3	**4c**	Traces	n.d.	n.d.
4	**4d**	Traces	n.d.	n.d.
5	**4e**	63	1:1	98; 93
6	**4f**	65	1:1	98; 94
7	**4g**	61	1:1	98; 91
8	**4h**	68	2:1	>99; 94
9	**4i**	58	1:1	97; 93

[a] Reactions were performed with 0.1 mmol **1a** and 0.244 mmol (20 μL) **2a** in the presence of the catalyst **3a** (20 mol%) and additive **4** (20 mol%) in $CHCl_3$ at 60 °C for 12h.

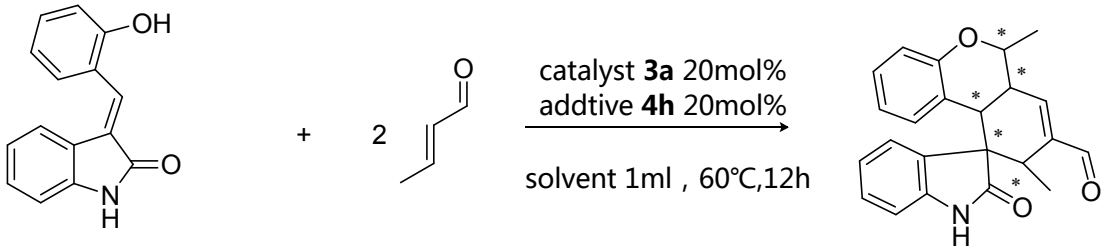
[b] The values are yields of isolated product after silica gel column chromatography.

[c] Determined by ^1H NMR on the crude reaction mixture.

[d] Determined by chiral HPLC.

N.D.: not detected. Trace: little products were detected.

3. Solvent effect[a]



1a
0.1mmol

2a
2.44 equiv

5aa

Table S3. The influence of solvent[a]

Entry	Solvent	Yield (%)[b]	Dr[c]	Ee(%)[d]
1	MeOH	n.r.	n.d.	n.d.
2	EtOH	n.r.	n.d.	n.d.
3	THF	n.r.	n.d.	n.d.
4	dioxane	n.r.	n.d.	n.d.
5	anisole	44	1:2	>99; 92
6	MTBE	n.r.	n.d.	n.d.
7	toluene	55	1:1	>99; 92
8	MeCN	n.r.	n.d.	n.d.
9	EA	n.r.	n.d.	n.d.
10	DMF	n.r.	n.d.	n.d.

11	$CHCl_3$	68	2:1	>99; 94

[a] Reactions were performed with 0.1 mmol **1a** and 0.244 mmol (20 μL) **2a** in the presence of the catalyst **3a** (20 mol %) and the additive **4h** (20 mol %) in solvent at 60 °C for 12 h.

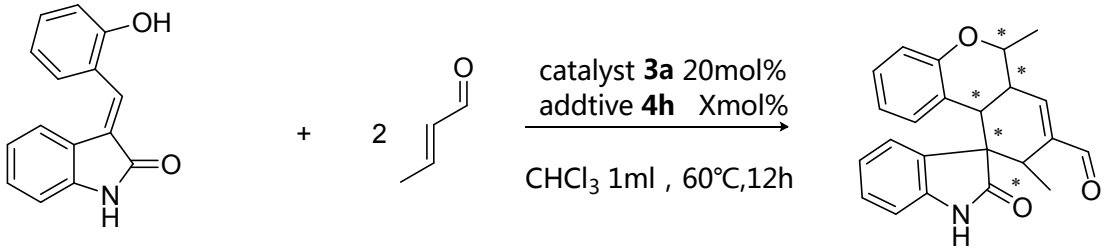
[b] The values are yields of isolated product after silica gel column chromatography.

[c] Determined by ^{1}H NMR on the crude reaction mixture.

[d] Determined by chiral HPLC.

n.r. : no reaction. n.d.: not detected.

4. Investigation of the dosage of additive[a]



1a
0.1mmol

2a
2.44 equiv

5aa

Table S4. Investigation of the dosage of additive[a]

Entry	Additive dosage	Yield (%)[b]	Dr[c]	Ee (%)[d]
1	20 mol %	68	2:1	>99; 94
2	40 mol %	71	2:1	>99; 87
3	60 mol %	83	3:1	99; 85
4	80 mol %	81	2.4:1	97; 80
5	100 mol %	83	2.3:1	95; 75
6	200 mol %	67	1.5:1	96; 78

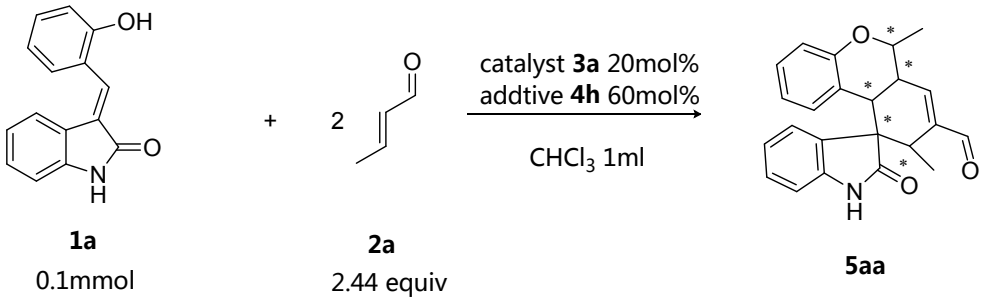
[a] Reactions were performed with 0.1 mmol **1a** and 0.244 mmol (20 μL) **2a** in the presence of the catalyst **3a** (20 mol %) and the additive **4h** (X mol %) in $CHCl_3$ at 60 °C for 12 h.

[b] The values are yields of isolated product after silica gel column chromatography.

[c] Determined by ^{1}H NMR on the crude reaction mixture.

[d] Determined by chiral HPLC.

5. Reaction time and temperature optimization[a]



1a
0.1mmol

2a
2.44 equiv

5aa

Table S5. Reaction time and temperature optimization[a]

Entry	Temperature (°C)	Time (h)	Yield (%)[b]	Dr[c]	Ee(%)[d]
1	60	12	83	3:1	99; 85
2	40	60	72	6:1	97; n.d.
3	25	168	67	5:1	>99; n.d.
4[e]	40→60	36	80	8:1	>99; n.d.

[a] Reactions were performed with 0.1 mmol **1a** and 0.244 mmol (20 μL) **2a** in the presence of the catalyst **3a** (20 mol %) and the additive **4h** (60 mol %) in $CHCl_3$.

[b] The values are yields of isolated product after silica gel column chromatography.

[c] Determined by ^1H NMR on the crude reaction mixture.

[d] Determined by chiral HPLC.

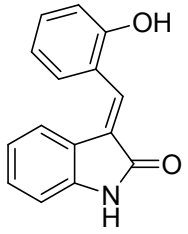
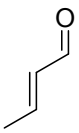
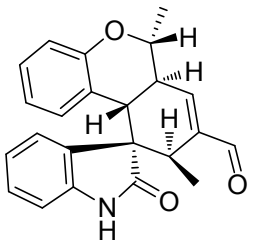
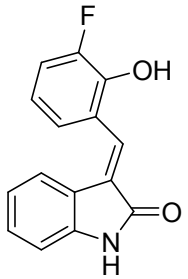
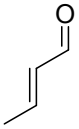
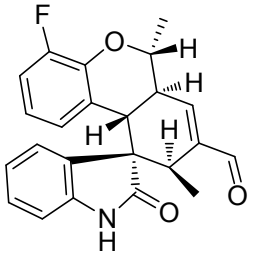
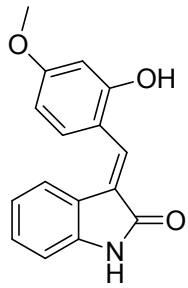
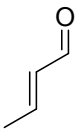
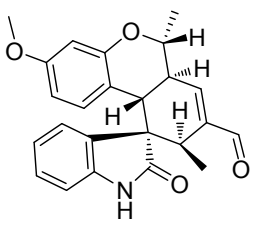
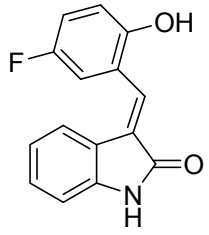
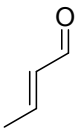
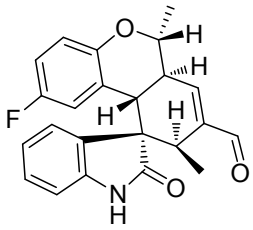
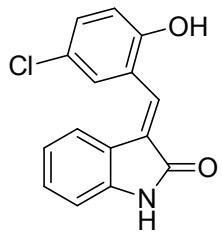
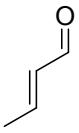
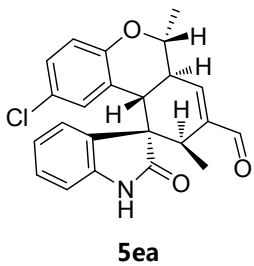
[e] The reaction was conducted at 40 °C for 24 h，then heated up to 60 °C for 12 h.

The optimal conditions: in the presence of the catalyst **3a** (20 mol %) and the additive **4h** (60 mol%), 0.1 mmol **1a** and 0.244 mmol **2a** was stirred in $CHCl_3$ 1mL at 40 °C for 24h and then heated up to 60 °C for 12 h.

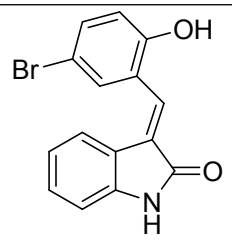
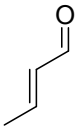
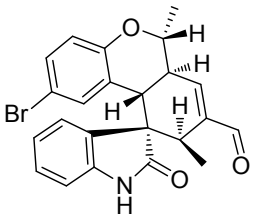
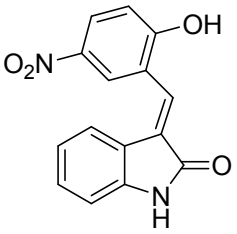
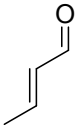
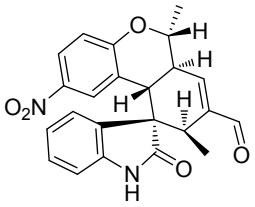
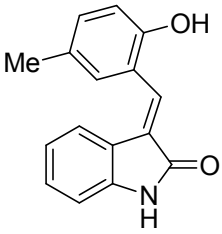
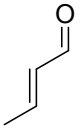
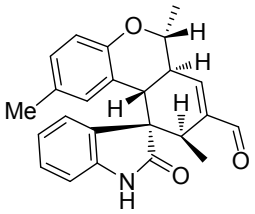
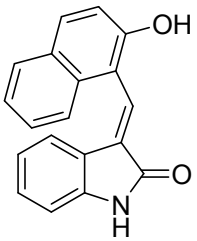
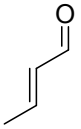
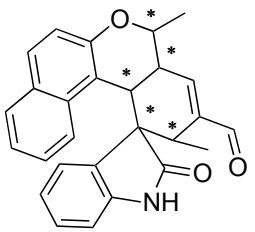
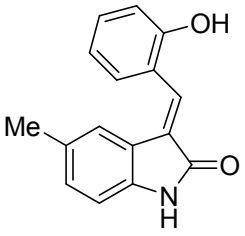
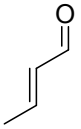
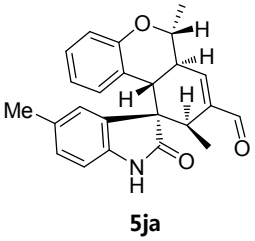
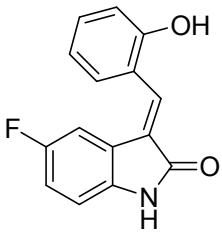
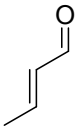
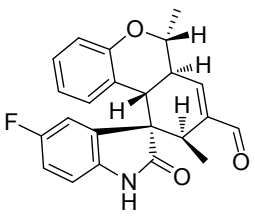
(D) Tables for the Investigation of Substrate Scope[a]

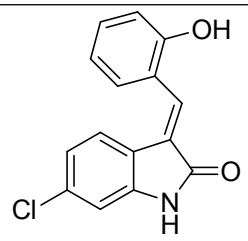
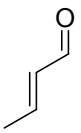
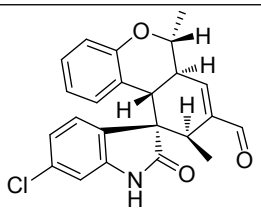
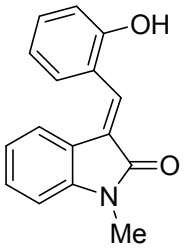
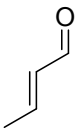
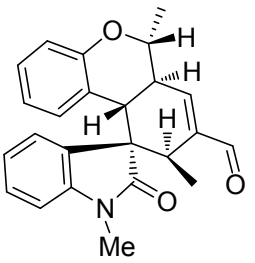
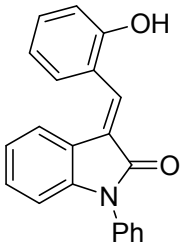
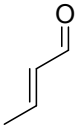
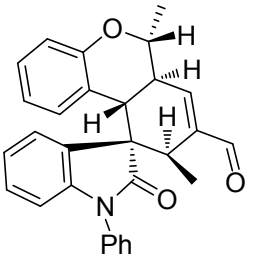
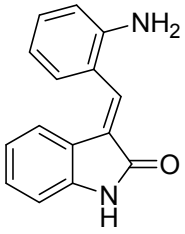
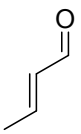
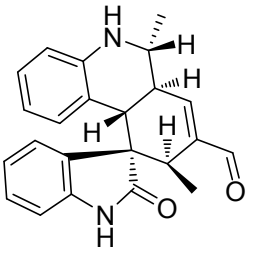
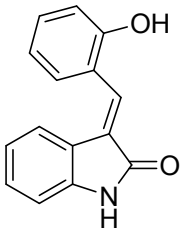
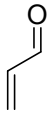
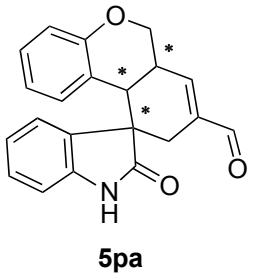
Table S6. The investigation of substrate scope

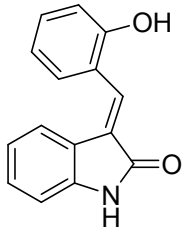
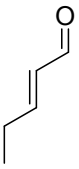
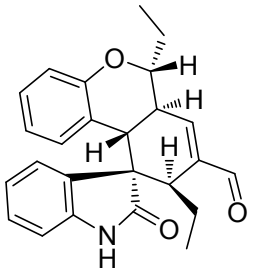
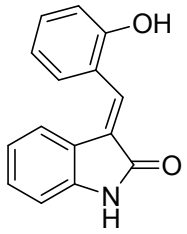
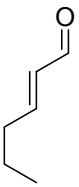
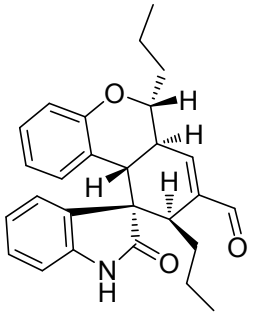
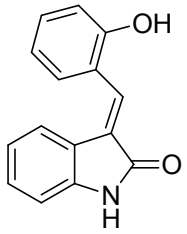
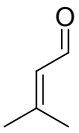
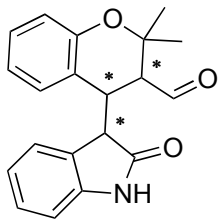
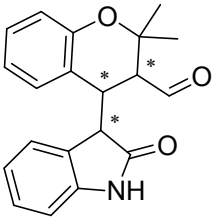
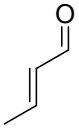
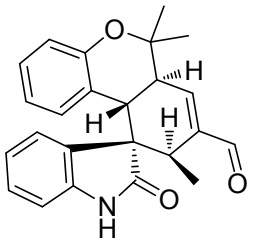
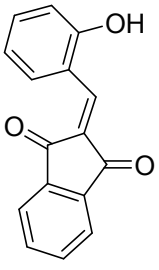
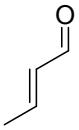
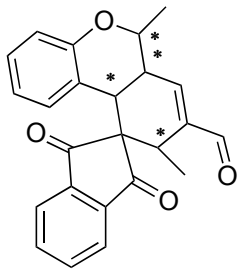
Entry	1	2	5	Yield (%)[b]	Dr[c]	Ee (%)[d]

1	 **1a**	 **2a**	 **5aa**	80	8:1	>99
2	 **1b**	 **2a**	 **5ba**	75	6:1	>99
3	 **1c**	 **2a**	 **5ca**	65	5:1	>99
4	 **1d**	 **2a**	 **5da**	72	7:1	98
5	 **1e**	 **2a**	 **5ea**	65	6:1	98

8

6	 **1f**	 **2a**	 **5fa**	70	7:1	98
7	 **1g**	 **2a**	 **5ga**	35	4:1	98
8	 **1h**	 **2a**	 **5ha**	75	5:1	>99
9	 **1i**	 **2a**	 **5ib**	65	1:4	>99
10	 **1j**	 **2a**	 **5ja**	67	6:1	98
11	 **1k**	 **2a**	 **5ka**	80	6:1	96

12	 **1l**	 **2a**	 **5la**	90	7:1	>99
13	 **1m**	 **2a**	 **5ma**	31	10:1	94
14	 **1n**	 **2a**	 **5na**	45	12:1	92
15	 **1o**	 **2a**	 **5oa**	83	2.5:1	>99
16	 **1a**	 **2b**	 **5pa**	55	1:2.5	64

17	 **1a**	 **2c**	 **5qa**	60	3:1	>99
18	 **1a**	 **2d**	 **5ra**	78	4:1	>99
19[e]	 **1a**	 **2e**	 **5s**	55	>20:1	87
20[f]	 **5sa**	 **2a**	 **5sa**	50	5:1	97
21	 **1t**	 **2a**	 **5ta**	70	2:1	>99

[a] Reactions were performed with 0.1 mmol **1** and 0.244 mmol **2** in the presence of the catalyst **3a** (20 mol %) and the additive **4h** (60 mol %) in $CHCl_3$ 1 mL at 40 °C for 24 h and then heated up to 60 °C for 12 h.

[b] The values are yields of isolated product after silica gel column chromatography.

[c] Determined by ^{1}H NMR on the crude reaction mixture.

[d] Determined by chiral HPLC.

[e] only one molecule of **2e** was involved in the reaction at 40 ^{o}C for 24h to generate **5sa**.

[f] only one molecule of **2a** was employed in the reaction at 60 ^{o}C for 12h to generate **5s**.

(E) Synthesis of several Substituted Oxindole.

Substituted Isatin (10 mmol) was dissolved in hydrazine hydrate (98%, 10 mL, 32.5 mmol) and refluxed for 15-30 min (130 ^{o}C). The reaction mixture was then poured in cold water, extracted with EtOAc and the organic layer was dried over Na_2SO_4. Evaporation of the solvent and recrystallization from hexane/ethyl acetate afforded substituted oxindole.

(F) Synthesis of Substituted (*E*)-3-(2-hydroxybenzylidene)Oxindole.

A reaction mixture of substituted oxindole (1 equiv), substituted salicylaldehyde (1.2 equiv) and piperidine (0.1 equiv) in ethanol (1-2 mL/1 mmol) was stirred at 90 ^{o}C for 3-5 h. After cooled down, the precipitate was filtered and washed with cold ethanol and diethyl ether, successively. Allowed to dry, it was used in subsequent reaction without further purification.

(G) Biological Activity study

Anti-tumor assay

Briefly, targeted cancer cells lines (3×10^3/well) were seeded in 96-well plates and cultured for 24 h, followed by compounds treatment for 24 h. A volume of 20 μL of 5 mg/mL MTT was added per well and incubated for another 4 h at 37 °C, then the supernatant fluid was removed and DMSO was added 150 μL /well for 15-20 min. The absorptions (OD) were measured at 570 nm with Spectra MAX M5 microplate spectrophotometer (Molecular Devices). The effect of compounds on tumor cells viability was expressed by cell growth inhibitory rate at 30 μM or IC_{50} of each cell line. Each assay was carried out at least three times. The results are summarized in **Table S7** and **Table S8**.

Table S7. Cellular evaluation of the polycyclic spiro-fused carbocyclicoxindoles 5 against cancer cell-line MCF-7 (cell growth inhibitory rate at 30 μM)[a]

Entry	Compound	Inhibition rate of anticancer cells proliferation (%)
1	5aa	35.78
2	5ba	29.19

3	5ca	36.31
4	5da	48.72
5	5ea	39.11
6	5fa	68.25
7	5ga	44.55
8	5ha	45.64
9	**5ia**	**99.95**
10	5ja	41.57
11	5ka	13.45
12	5la	83.29
13	5ma	41.78
14	5na	89.02
15	5oa	19.68
16	5pa	64.98
17	5qa	34.20
18	5ra	81.72
19	5sa	31.97

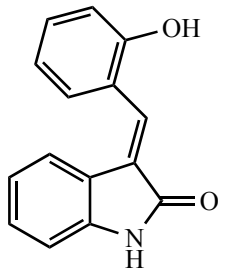
[a] Inhibition rate values were measured by an MTT assay upon 24 h drug treatment. Values were obtained through independent measurement of cell viabilities.

Table S8. Cellular evaluation of the the polycyclic spiro-fused carbocyclicoxindole 5ia against diverse cancer cell-lines (IC_{50} in μM)[a]

Entry	Cell lines	IC_{50} (μM)
1	MCF-7	9.2
2	MDA-MB-231	11.5
3	H1975	14.1
4	FaDu	13.7

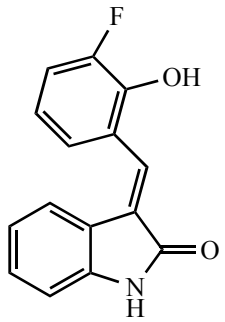
a Values were average of three determinations and deviation from the average is <5% of the average value

(H) Analytical and Spectral Characterization Data



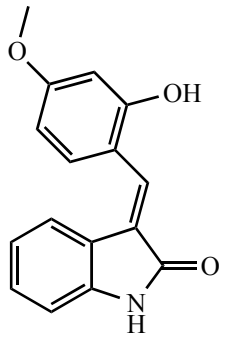
1a

^{1}H NMR (400 MHz, DMSO) δ = 10.57 (s, 1H), 10.19 (s, 1H), 7.69 (s, 1H), 7.64-7.63 (m, 1H), 7.51-7.49 (m, 1H), 7.34-7.30 (m, 1H), 7.23-7.19 (m, 1H), 6.99-6.95(m, 1H), 6.93-6.91 (m, 1H), 6.88-6.83 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ = 168.8, 156.5, 142.6, 132.4, 131.6, 129.6, 129.5, 126.4, 122.3, 121.3, 121.2, 121.0, 118.8, 115.9, 109.9.



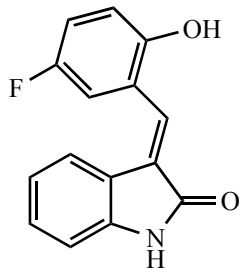
1b

^{1}H NMR (400 MHz, DMSO) δ = 10.61 (s, 1H), 10.28 (s, 1H), 7.65 (s, 1H), 7.45-7.42 (m, 2H), 7.32-7.21 (m, 2H), 6.97-6.83 (m, 3H). ^{13}C NMR (100 MHz, DMSO) δ = 168.5, 151.7(d, *J* = 238 Hz), 143.7 (d, *J* = 15 Hz), 142.8, 130.8(d, *J* = 3 Hz), 130.0, 127.7, 124.9 (d, *J* = 3 Hz), 124.7 (d, *J* = 3 Hz), 122.5, 121.0, 120.9, 119.1(d, *J* = 7 Hz), 117.2 (d, *J* = 19 Hz), 110.0.

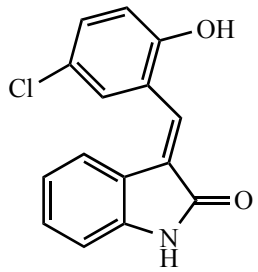


1c

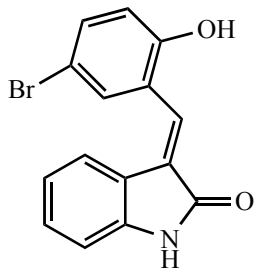
^{1}H NMR (400 MHz, DMSO) δ = 10.50 (s, 1H), 10.35 (s, 1H), 7.68 (s, 1H), 7.65-7.58 (m, 2H), 7.19-7.17 (m, 1H), 6.88-6.85 (m, 2H), 6.58-6.52 (m, 2H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ = 169.1, 162.3, 158.4, 142.2, 132.4, 130.6, 129.1, 124.2, 121.9, 121.5, 120.9, 114.1, 109.8, 105.2, 101.1, 55.2.



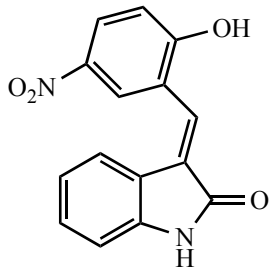
1d ^{1}H NMR (400 MHz, DMSO) δ = 10.61 (s, 1H), 10.21 (s, 1H), 7.59 (s, 1H), 7.45-7.28 (m, 2H), 7.25-7.14 (m, 2H), 6.99-6.96 (m, 1H), 6.90-6.87 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ = 168.6, 154.7(d, *J* = 238 Hz), 152.7 (d, *J* = 1.2 Hz), 142.8, 130.9, 130.0, 127.6, 122.5, 122.1 (d, *J* = 8 Hz), 121.1, 120.9, 117.8 (d, *J* = 23 Hz), 117.0 (d, *J* = 8 Hz), 115.2 (d, *J* = 23 Hz), 110.0.



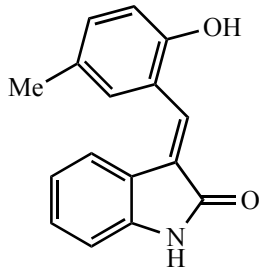
1e ^{1}H NMR (400 MHz, DMSO) δ = 10.61 (s, 1H), 10.49 (s, 1H), 7.60-7.56 (m, 2H), 7.39-7.34 (m, 2H), 7.25-7.21 (m, 1H), 7.00-6.98 (m, 1H), 6.90-6.87 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ = 168.5, 155.2, 142.9, 130.8, 130.6, 130.1, 128.6, 127.7, 123.1, 122.3, 122.2, 121.1, 120.9, 117.6, 110.1.



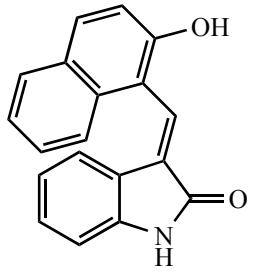
1f ^{1}H NMR (400 MHz, DMSO) δ = 10.61 (s, 1H), 10.53 (s, 1H), 7.73-7.72 (m, 1H), 7.56 (s, 1H), 7.49-7.46 (m, 1H), 7.39-7.37 (m, 1H), 7.25-7.21 (m, 1H), 6.96-6.87 (m, 3H). ^{13}C NMR (100 MHz, DMSO) δ = 168.4, 155.6, 142.9, 133.6, 131.4, 130.5, 130.1, 127.7, 123.7, 122.2, 122.5, 121.1, 120.9, 118.1, 110.1, 109.6.



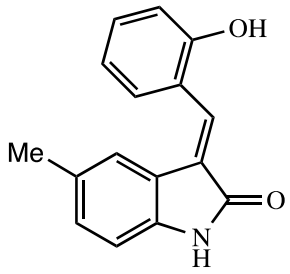
1g ^{1}H NMR (400 MHz, DMSO) δ = 10.67 (s, 1H), 8.51-8.50 (m, 1H), 8.24-8.21 (m, 1H), 7.58 (s, 1H), 7.44-7.42 (m, 1H), 7.27-7.23 (m, 1H), 7.16-7.14 (m, 1H), 6.91-6.84 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ = 168.3, 162.4, 143.1, 139.2, 130.4, 129.4, 128.6, 127.0, 125.5, 122.5, 121.8, 121.3, 120.6, 116.3, 110.2



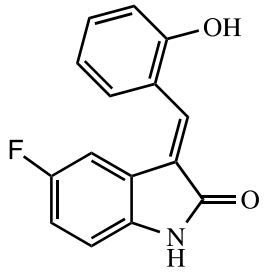
1h ^{1}H NMR (400 MHz, DMSO) δ = 10.55 (s, 1H), 9.94 (s, 1H), 7.67 (s, 1H), 7.52-7.51 (m, 1H), 7.43 (s, 1H), 7.23-7.19 (m, 1H), 7.14-7.11 (m, 1H), 6.89-6.84 (m, 3H). ^{13}C NMR (100 MHz, DMSO) δ = 168.8, 154.2, 142.5, 132.6, 132.1, 129.6, 129.5, 127.3, 126.3, 122.2, 121.3, 121.0, 115.8, 109.9, 20.0.



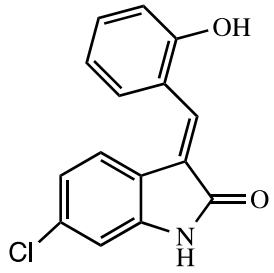
1i ^{1}H NMR (400 MHz, DMSO) δ = 10.61 (s, 1H), 10.34 (s, 1H), 7.93-7.89 (m, 2H), 7.85 (s, 1H), 7.59-7.57 (m, 1H), 7.43-7.37 (m, 1H), 7.35-7.30 (m, 2H), 7.15-7.11 (m, 1H), 6.86-6.84 (m, 1H), 6.66-6.62 (m, 1H), 6.39-6.37 (m, 1H). ^{13}C NMR (100 MHz, DMSO) δ = 168.4, 153.7, 142.5, 131.4, 131.0, 129.6, 129.5, 129.3, 128.6, 127.6, 127.1, 124.1, 123.7, 123.2, 121.7, 120.8, 118.1, 113.7, 109.5.



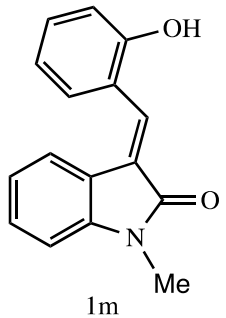
1j ^{1}H NMR (400 MHz, DMSO) δ = 10.46 (s, 1H), 10.17 (s, 1H), 7.66 (s, 1H), 7.64-7.62 (m, 1H), 7.34-7.30 (m, 2H), 7.04-6.92 (m, 3H), 6.77-6.75(m, 1H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ = 168.8, 156.5, 140.3, 132.2, 131.6, 130.1, 129.5, 126.6, 122.8, 121.4, 121.3, 118.7, 115.9, 109.6, 20.8.



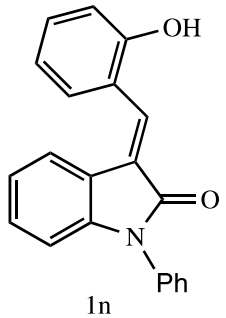
1k ^{1}H NMR (400 MHz, DMSO) δ = 10.60 (s, 1H), 10.29 (s, 1H), 7.76 (s, 1H), 7.61-7.59 (m, 1H), 7.37-7.33 (m, 1H), 7.19-7.17 (m, 1H), 7.09-7.04 (m, 1H), 7.02-6.94 (m, 2H), 6.88-6.84 (m, 1H). ^{13}C NMR (100 MHz, DMSO) δ = 168.7, 157.1 (d, *J* = 235 Hz), 156.5, 138.9, 134.1, 132.0, 129.5, 126.3 (d, *J* = 3 Hz), 122.3 (d, *J* = 9 Hz), 120.9, 118.9, 116.1, 115.8 (d, *J* = 24 Hz), 110.5 (d, *J* = 8 Hz), 109.4 (d, *J* = 26 Hz).



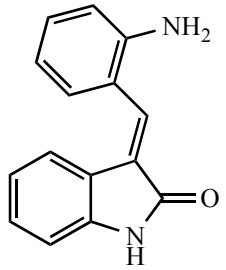
1l ^{1}H NMR (400 MHz, DMSO) δ = 10.73 (s, 1H), 10.27 (s, 1H), 7.74 (s, 1H), 7.61-7.59 (m, 1H), 7.48-7.46 (m, 1H), 7.35-7.31 (m, 1H), 7.00-6.98 (m, 1H), 6.94-6.88 (m, 3H). ^{13}C NMR (100 MHz, DMSO) δ = 168.7, 156.6, 143.9, 133.6, 133.3, 131.9, 129.5, 125.3, 123.5, 121.0, 120.8, 120.2, 118.9, 116.0, 109.9.



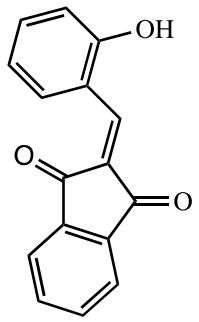
1m ^{1}H NMR (400 MHz, DMSO) δ = 10.23 (s, 1H), 7.78 (s, 1H), 7.64-7.62 (m, 1H), 7.55-7.53 (m, 1H), 7.35-7.29 (m, 2H), 7.04-6.98 (m, 2H), 6.95-6.91 (m, 2H), 3.21 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ = 167.3, 156.5, 143.7, 133.0, 131.7, 129.7, 129.6, 125.5, 122.0, 121.5, 121.2, 120.5, 118.8, 116.0, 108.7, 25.9.



1n ^{1}H NMR (400 MHz, DMSO) δ = 10.30 (s, 1H), 7.88 (s, 1H), 7.71-7.69 (m, 1H), 7.65-7.58 (m, 3H), 7.50-7.47 (m, 3H), 7.38-7.35 (m, 1H), 7.28-7.24 (m, 1H), 7.03-6.95 (m, 3H), 6.79-6.77 (m, 1H). 13C NMR (100 MHz, DMSO) δ = 166.8, 156.6, 143.3, 134.3, 134.1, 131.9, 129.7, 129.6, 128.0, 126.9, 125.1, 122.4, 122.2, 121.1, 120.7, 118.9, 116.1, 109.1.

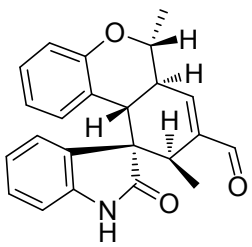


1o ^{1}H NMR (400 MHz, DMSO) δ = 10.51 (s, 1H), 7.57 (s, 1H), 7.48-7.42 (m, 2H), 7.21-7.14 (m, 2H), 6.87-6.77(m, 3H), 6.65-6.61 (m, 1H), 5.52 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ = 168.9, 147.9, 142.3, 133.2, 131.1, 129.3, 129.2, 126.0, 122.3, 121.6, 120.8, 117.9, 115.6, 115.5, 109.7.

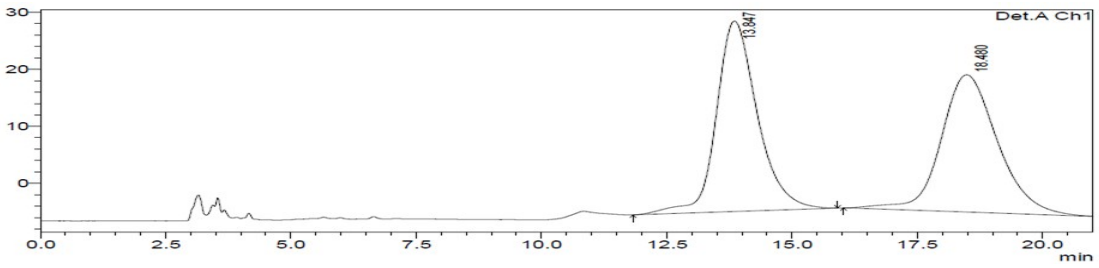


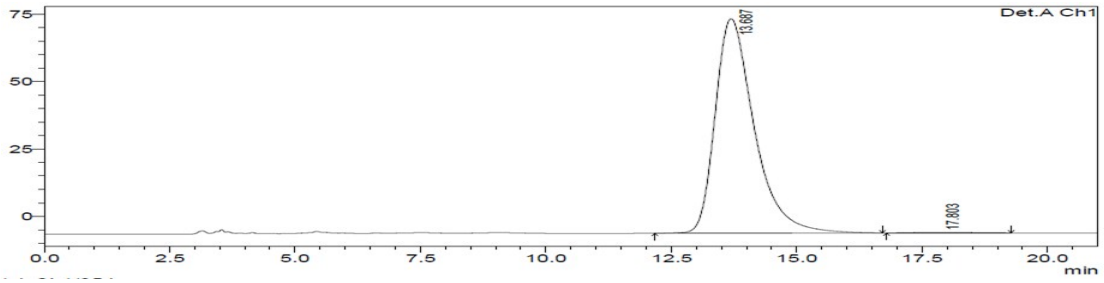
1t ^{1}H NMR (400 MHz, DMSO) δ = 10.89 (s, 1H), 8.91-8.89 (m, 1H), 8.33 (s, 1H), 7.96-7.95 (m, 4H), 7.49-7.45 (m, 1H), 7.02-6.94 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ = 189.9, 188.8, 160.0, 141.8, 139.8, 139.3, 136.0, 135.8, 135.6, 133.1, 127.1, 122.9, 122.8, 119.9, 119.0, 116.0.

6,9-dimethyl-2'-oxo-6,6a,9,10a-tetrahydrospiro[benzo[c]chromene-10,3'-indoline]-8-carbaldehyde (**5aa**)

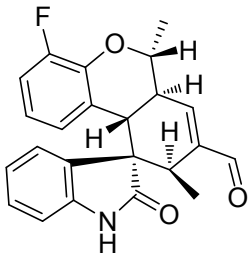


5aa light yellow solid; 80% yield; >99% ee; 8 : 1 dr; m.p. 125 °C - 127 °C; $[\alpha]_D^{22}$ = -49.8 (c = 1.53 in $CHCl_3$); HPLC (DAICEL CORPORATION AS-H), 2-propanol/n-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 13.69 min (major) and 17.80 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.53 (s, 1H), 8.86 (s, 1H), 7.28 (s, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 6.98 (t, *J* = 7.2 Hz, 2H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.86-6.73 (m, 2H), 6.41 (t, *J* = 7.6 Hz, 1H), 5.99 (d, *J* = 7.6 Hz, 1H), 4.40 (dq, *J* = 11.6, 6.0 Hz, 1H), 3.67 (d, *J* = 10.4 Hz, 1H), 3.21 (t, *J* = 10.4 Hz, 1H), 2.81 (q, *J* = 6.4 Hz, 1H), 1.60 (d, *J* = 6.0 Hz, 3H), 1.19 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 193.0, 179.1, 154.6, 147.0, 143.7, 140.0, 131.0, 128.6, 127.9, 126.0, 125.8, 124.2, 122.1, 120.4, 117.2, 110.2, 77.7, 50.6, 44.0, 36.5, 34.8, 20.8, 18.9. HRMS (ESI-TOF) calcd for $C_{23}H_{21}NO_3$ $[M+Na]^+$ = 382.1414, Found 382.1415.



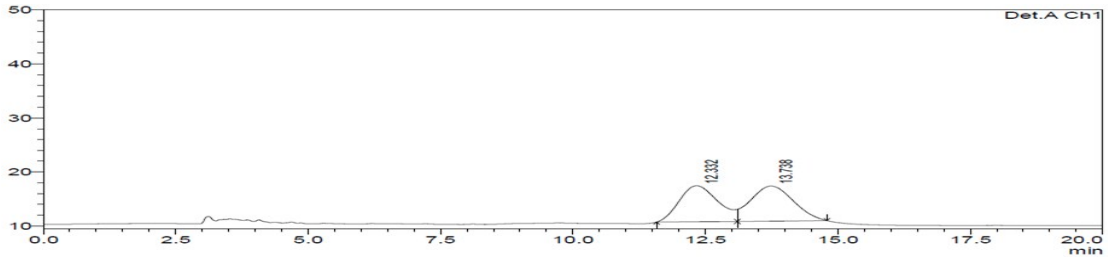


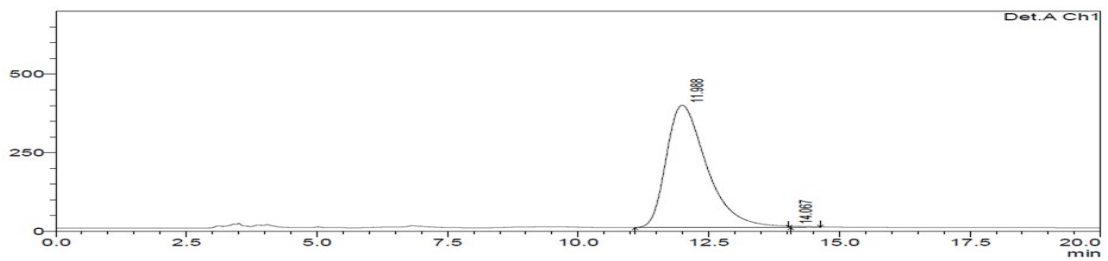
4-fluoro-6,9-dimethyl-2'-oxo-6,6a,9,10a-tetrahydrospiro[benzo[c]chromene-10,3'-indoline]-8-carbaldehyde (5ba)



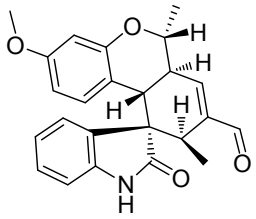
5ba

White solid; 75% yield; >99% ee; 6:1 dr; m.p. 59 °C-61 °C; $[\alpha]_D^{22}$ = -50.0 (c = 0.074 in $CHCl_3$); HPLC (DAICEL CORPORATION AS-H), 2-propanol/*n*-hexane = 15/85, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 11.99 min (major) and 14.07 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.54 (s, 1H), 7.95 (s, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.07-6.94 (m, 2H), 6.88-6.77 (m, 2H), 6.37 (td, *J* = 8.0, 5.2 Hz, 1H), 5.79 (d, *J* = 8.0 Hz, 1H), 4.48 (dq, *J* = 12.0, 6.0 Hz, 1H), 3.69 (d, *J* = 10.4 Hz, 1H), 3.24 (t, *J* = 10.8 Hz, 1H), 2.84 (q, *J* = 6.8 Hz, 1H), 1.68 (d, *J* = 6.0 Hz, 3H), 1.21 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.9, 179.3, 146.3, 143.8, 142.7, 140.0, 130.8, 128.7, 128.3, 125.9, 122.2, 119.9, 119.3, 114.8, 114.6, 110.4, 78.3, 50.7, 43.9, 36.5, 34.8, 20.7, 18.9. HRMS (ESI-TOF) calcd for $C_{23}H_{20}FNO_3$ $[M+Na]^+$ = 400.1319, Found 400.1325.



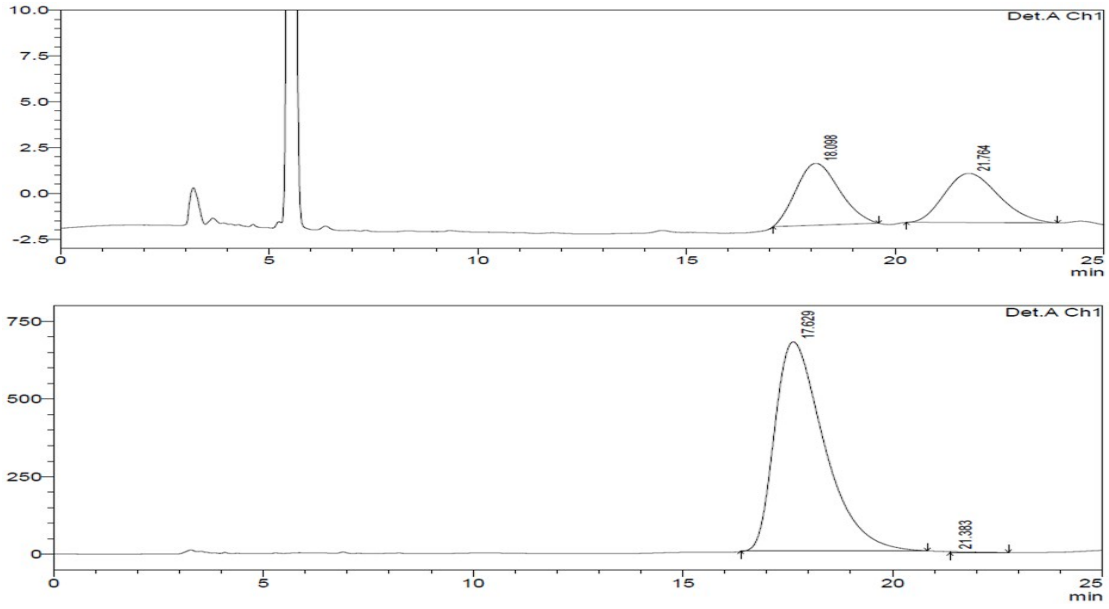


3-methoxy-6,9-dimethyl-2'-oxo-6,6a,9,10a-tetrahydrospiro[benzo[c]chromene-10,3'-indoline]-8-carbaldehyde (**5ca**)

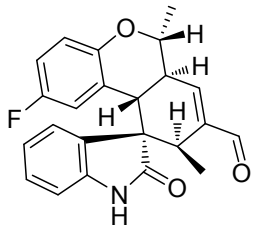


5ca

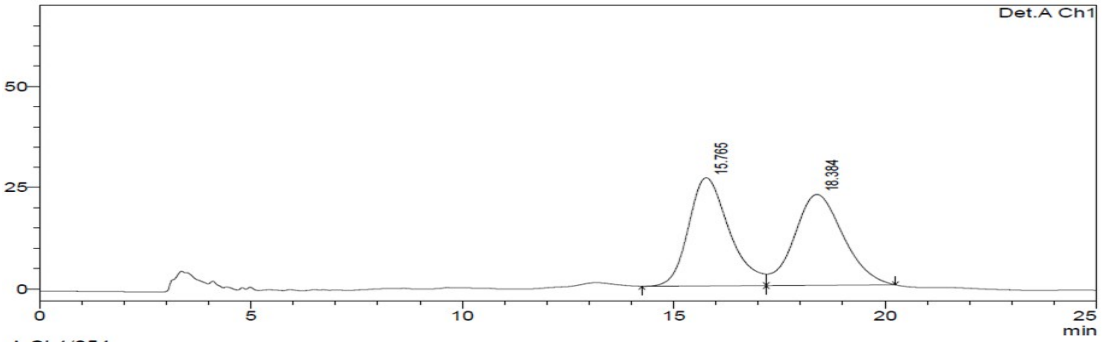
light yellow solid; 65% yield; >99% ee; 5:1 dr; m.p.70 °C-72 °C; $[\alpha]_D^{22}$ = -42.3 (c = 0.40 in $CHCl_3$); HPLC (DAICEL CORPORATION AS-H), 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ= 254 nm, retention time: 17.63 min (major) and 21.38 min (minor); ^1H NMR (400 MHz, $CDCl_3$) δ = 9.53 (s, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 2.4 Hz, 1H), 6.38 (d, *J* = 2.4 Hz, 1H), 6.00 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.88 (d, *J* = 8.8 Hz, 1H), 4.38 (dq, *J* = 12.2, 6.0 Hz, 1H), 3.65 (s, 4H), 3.23 (t, *J* = 10.4 Hz, 1H), 2.81 (q, *J* = 6.8 Hz, 1H), 1.62 (d, *J* = 6.0 Hz, 3H), 1.19 (d, *J* = 4.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 193.0, 179.4, 159.5, 155.7, 146.9, 143.9, 140.1, 131.1, 128.6, 126.0, 124.9, 122.1, 117.5, 110.3, 106.0, 102.8, 77.6, 55.2, 50.9, 44.0, 36.1, 34.7, 20.7, 19.0. HRMS (ESI-TOF) calcd for $C_{24}H_{23}NO_4$ $[M+Na]^+$ = 412.1519, Found 412.1533.

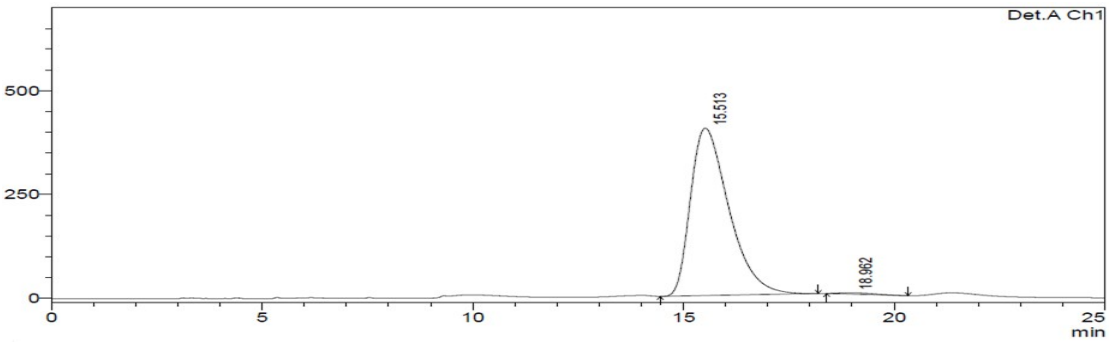


2-fluoro-6,9-dimethyl-2'-oxo-6,6a,9,10a-tetrahydrospiro[benzo[c]chromene-10,3'-indoline]-8-carbaldehyde (**5da**)

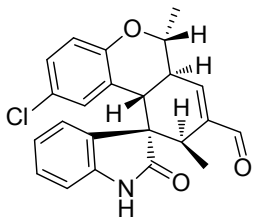


5da White solid; 72% yield; 98% ee; 7:1 dr; m.p. 61 °C-63 °C; $[\alpha]_D^{22}$ = -24.5 (c = 0.33 in $CHCl_3$); HPLC (DAICEL CORPORATION AS-H), 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 15.51 min (major) and 18.96 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.53 (s, 1H), 8.00 (s, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.08-6.97 (m, 2H), 6.81 (d, *J* = 2.4 Hz, 1H), 6.76-6.66 (m, 2H), 5.73 (dd, *J* = 10.0, 2.4 Hz, 1H), 4.37 (dq, *J* = 12.0, 6.0 Hz, 1H), 3.64 (d, *J* = 10.4 Hz, 1H), 3.18 (t, *J* = 10.8 Hz, 1H), 2.83 (q, *J* = 6.8 Hz, 1H), 1.59 (d, *J* = 6.0 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.9, 179.2, 150.6, 146.6, 143.7, 140.1, 130.4, 129.0, 127.1, 127.1, 126.0, 122.3, 117.9, 117.8, 114.3, 114.1, 111.5, 111.3, 110.6, 77.5, 50.6, 43.8, 36.5, 34.8, 20.7, 18.8. HRMS (ESI-TOF) calcd for $C_{23}H_{20}FNO_3$ $[M+Na]^+$ = 400.1319, Found 400.1329.

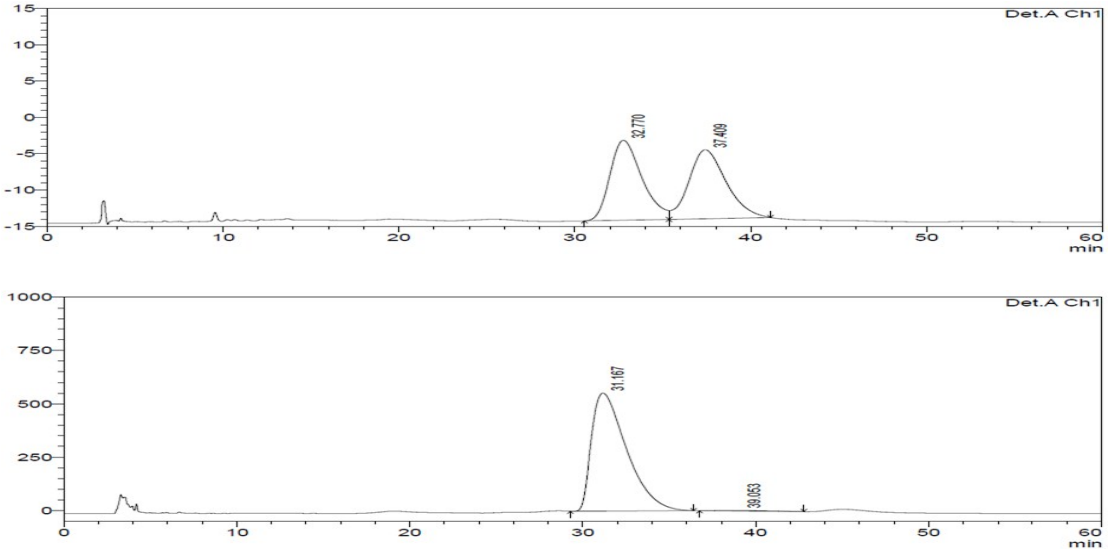




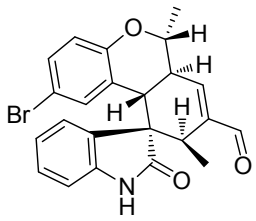
2-chloro-6,9-dimethyl-2'-oxo-6,6a,9,10a-tetrahydrospiro[benzo[c]chromene-10,3'-indoline]-8-carbaldehyde (5ea)



5ea White solid; 65% yield; 98% ee; 6:1 dr; m.p. 54 °C-56 °C; $[\alpha]_D^{22}$ = -61.3 (c = 0.266 in $CHCl_3$); HPLC (DAICEL CORPORATION AS-H), 2-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 31.17 min (major) and 39.05 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.53 (s, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.10-6.99 (m, 2H), 6.95 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.82 (d, *J* = 2.4 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 5.94 (d, *J* = 1.2 Hz, 1H), 4.38 (dq, *J* = 12.0, 6.0 Hz, 1H), 3.63 (d, *J* = 10.4 Hz, 1H), 3.21 (t, *J* = 10.4 Hz, 1H), 2.84 (q, *J* = 6.8 Hz, 1H), 1.60 (d, *J* = 6.0 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 178.8, 153.3, 146.3, 143.8, 140.1, 130.4, 129.0, 127.8, 126.9, 126.0, 125.0, 124.7, 122.3, 118.3, 110.4, 77.7, 50.5, 43.5, 36.5, 34.7, 20.6, 18.9. HRMS (ESI-TOF) calcd for $C_{23}H_{20}ClNO_3$ $[M+Na]^+$ = 416.1024, Found 416.1033.

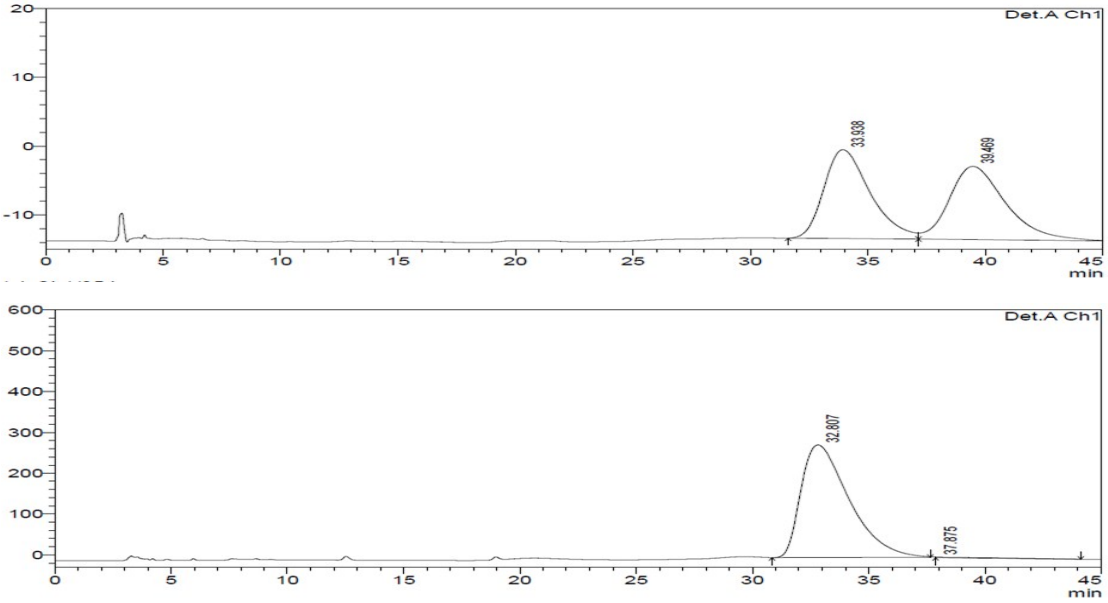


2-bromo-6,9-dimethyl-2'-oxo-6,6a,9,10a-tetrahydrospiro[benzo[c]chromene-10,3'-indoline]-8-carbaldehyde (5fa)

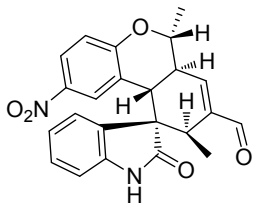


5fa White solid; 70% yield; 98% ee; 7:1 dr; m.p. 94 °C-96 °C; $[\alpha]_D^{22}$ = -72.6 (c = 1.15 in $CHCl_3$); HPLC (DAICEL CORPORATION AS-H), 2-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, λ= 254 nm, retention time: 32.81 min (major) and 37.87 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.54 (s, 1H),

7.70 (s, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.12-7.00 (m, 3H), 6.82 (d, *J* = 2.4 Hz, 1H), 6.67 (d, *J* = 8.8 Hz, 1H), 6.08 (d, *J* = 1.2 Hz, 1H), 4.38 (dq, *J* = 12.0, 6.0 Hz, 1H), 3.64 (d, *J* = 10.4 Hz, 1H), 3.21 (t, *J* = 11.2 Hz, 1H), 2.85 (q, *J* = 6.8 Hz, 1H), 1.61 (d, *J* = 6.0 Hz, 3H), 1.22 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.9, 178.9, 153.8, 146.3, 143.8, 140.0, 130.7, 130.4, 129.0, 127.7, 127.3, 126.0, 122.4, 118.7, 112.4, 110.4, 77.7, 50.6, 43.4, 36.5, 34.6, 20.6, 18.9. HRMS (ESI-TOF) calcd for $C_{23}H_{20}BrNO_3$ $[M+Na]^+$ = 460.0519, Found 460.0525.

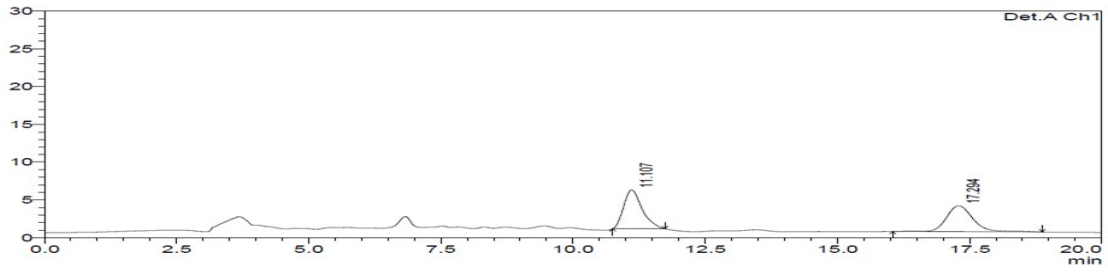


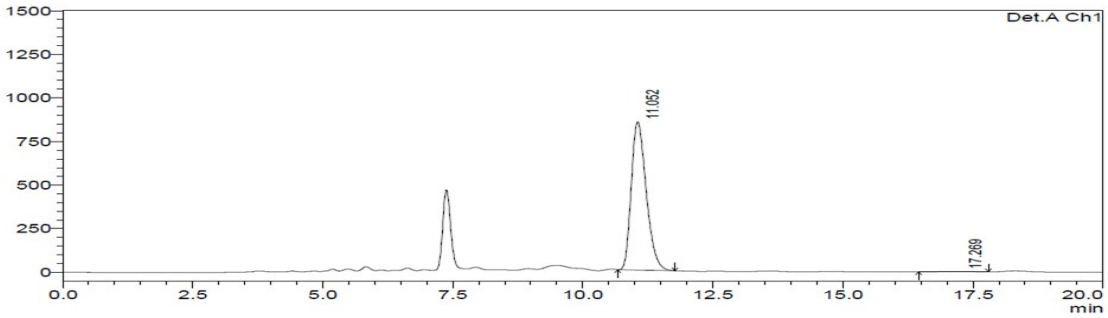
6,9-dimethyl-2-nitro-2'-oxo-6,6a,9,10a-tetrahydrospiro[benzo[c]chromene-10,3'-indoline]-8-carbaldehyde (5ga)



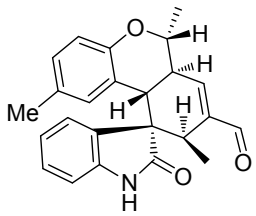
5ga

White solid; 35% yield; 98% ee; 4:1 dr; m.p. 104 °C-106 °C; $[\alpha]_D^{22}$ = -87.1 (c = 0.31 in $CHCl_3$); HPLC (DAICEL CORPORATION AD-H), 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 11.05 min (major) and 17.27 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.58 (s, 1H), 7.93 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.78 (s, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.17-7.07 (m, 2H), 7.04 (d, *J* = 1.6 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.53 (dq, *J* = 12.4, 6.0 Hz, 1H), 3.70 (d, *J* = 10.4 Hz, 1H), 3.31 (t, *J* = 10.8 Hz, 1H), 2.92 (q, *J* = 6.8 Hz, 1H), 1.71 (d, *J* = 6.0 Hz, 3H), 1.26 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.7, 178.7, 160.4, 145.0, 144.3, 140.9, 140.3, 129.9, 129.4, 125.8, 125.0, 124.3, 122.5, 121.7, 117.3, 111.1, 79.0, 50.5, 42.7, 36.6, 34.4, 20.4, 19.1. HRMS (ESI-TOF) calcd for $C_{23}H_{20}N_2O_5$ $[M+Na]^+$ = 427.1264, Found 427.1277.



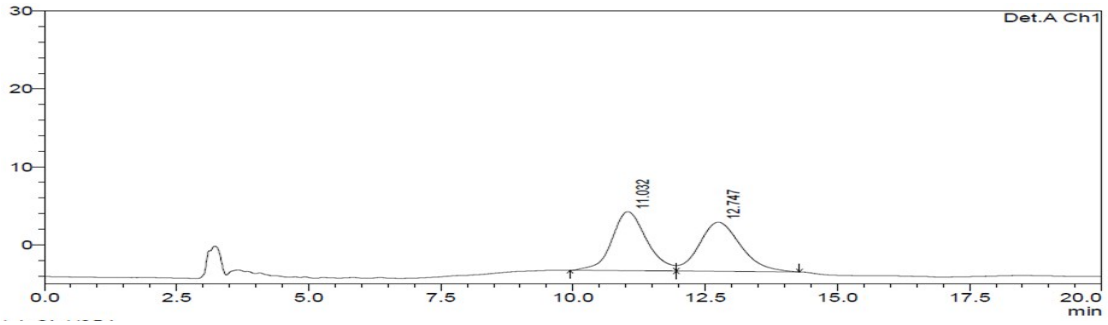


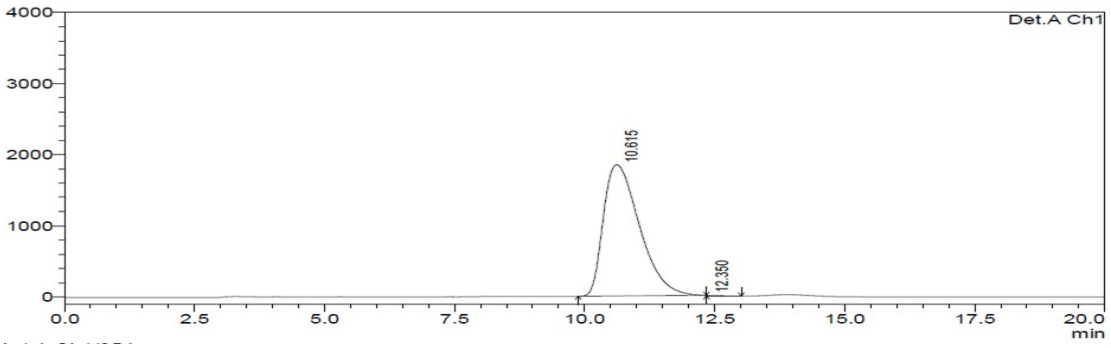
2,6,9-trimethyl-2'-oxo-6,6a,9,10a-tetrahydrospiro[benzo[c]chromene-10,3'-indoline]-8-carbaldehyde (**5ha**)



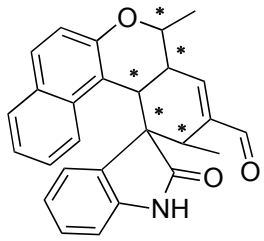
5ha

White solid; 75% yield; >99% ee; 5:1 dr; m.p. 75 ^{o}C-77 ^{o}C; $[\alpha]_D^{22}$ = -44.3 (c = 0.33 in $CHCl_3$); HPLC (DAICEL CORPORATION AS-H), 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ= 254 nm, retention time: 10.61 min (major) and 12.35 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.54 (s, 1H), 7.71 (s, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.07-6.94 (m, 2H), 6.82 (dd, *J* = 14.8, 5.2 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 1H), 5.78 (s, 1H), 4.37 (dq, *J* = 12.0, 6.0 Hz, 1H), 3.66 (d, *J* = 10.4 Hz, 1H), 3.20 (t, *J* = 10.4 Hz, 1H), 2.83 (q, *J* = 7.2 Hz, 1H), 1.84 (s, 3H), 1.60 (d, *J* = 6.0 Hz, 3H), 1.22 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 193.1, 179.3, 152.3, 147.2, 143.7, 140.2, 131.1, 129.3, 128.6, 128.3, 126.2, 125.3, 125.1, 122.1, 116.8, 110.0, 50.7, 44.1, 36.5, 34.7, 20.7, 20.7, 18.9. HRMS (ESI-TOF) calcd for $C_{24}H_{23}NO_3$ $[M+Na]^+$ = 396.1570, Found 396.1575.



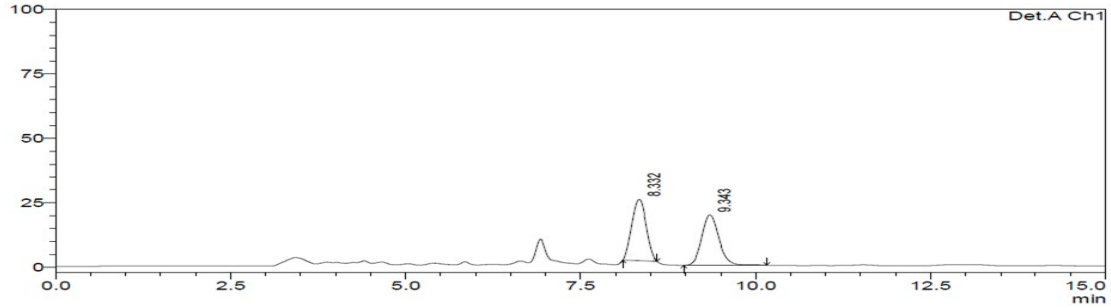


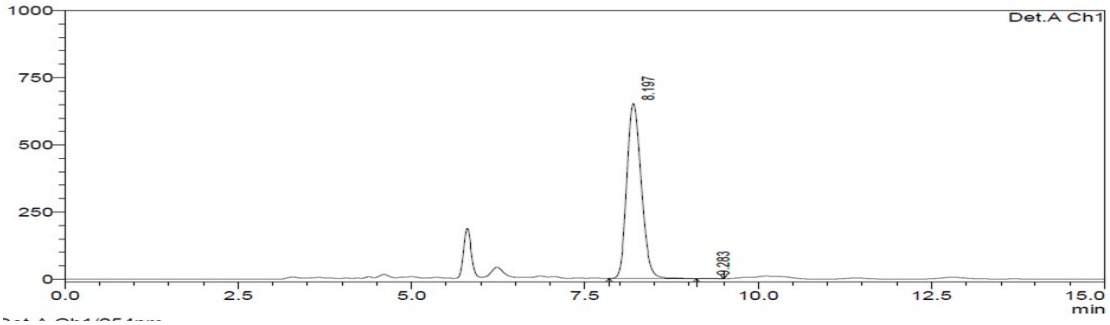
2,5-dimethyl-2'-oxo-2,4a,5,12c-tetrahydrospiro[dibenzo[c,f]chromene-1,3'-indoline]-3-carbaldehyde (**5ib**)



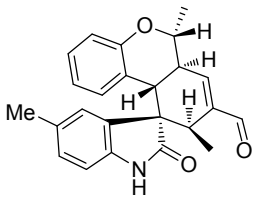
5ib

White solid; 65% yield; >99% ee; 1:4 dr; m.p. 60 °C-62 °C; $[\alpha]_D^{22}$ = 55.6 (c = 0.16 in $CHCl_3$); HPLC (DAICEL CORPORATION AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.20 min (major) and 9.28 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.71 (s, 1H), 7.60-7.50 (m, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.05 (dd, *J* = 16.0, 8.4 Hz, 4H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.62 (q, *J* = 8.4 Hz, 2H), 4.92 (dd, *J* = 6.4, 4.0 Hz, 1H), 3.66 (dt, *J* = 12.0, 4.4 Hz, 1H), 3.50-3.44 (m, 1H), 3.17 (d, *J* = 6.8 Hz, 1H), 1.33 (d, *J* = 6.8 Hz, 4H), 0.98 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 191.1, 178.6, 152.3, 151.9, 142.2, 141.8, 134.8, 133.0, 129.3, 129.2, 128.5, 128.0, 124.3, 123.8, 123.2, 122.8, 122.5, 120.1, 114.5, 109.9, 70.7, 56.4, 43.3, 42.5, 41.4, 22.7, 14.1. HRMS (ESI-TOF) calcd for $C_{27}H_{23}NO_3$ $[M+Na]^+$ = 432.1570, Found 432.1585.

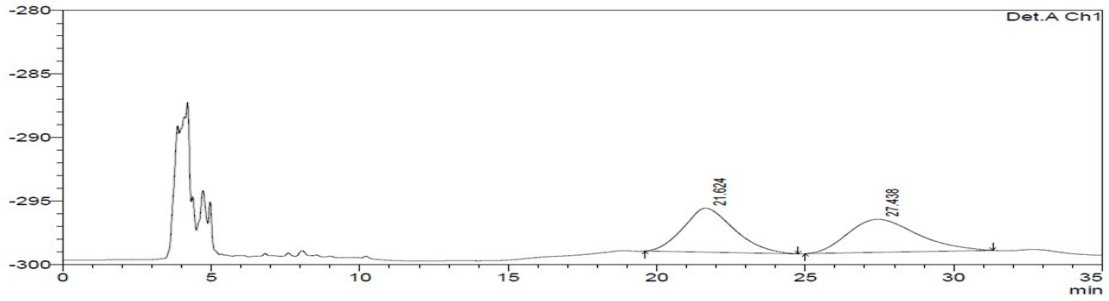


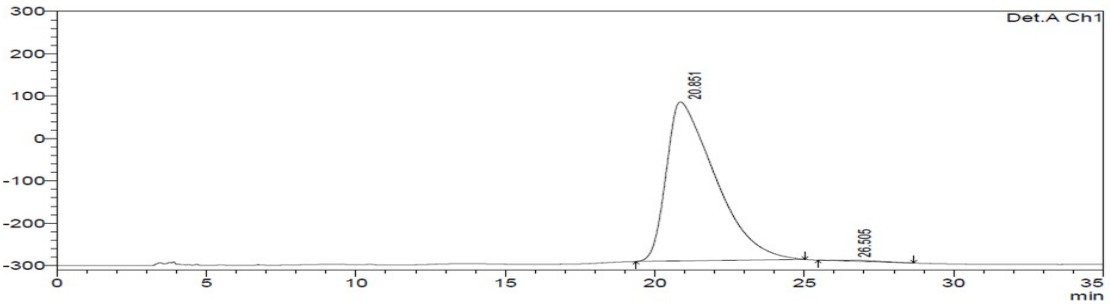


5',6,9-trimethyl-2'-oxo-6,6a,9,10a-tetrahydrospiro[benzo[c]chromene-10,3'-indoline]-8-carbaldehyde (**5ja**)

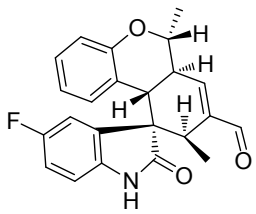


5ja White solid; 67% yield; 98% ee; 6:1 dr; m.p. 122 °C-124 °C; $[\alpha]_D^{22}$ = -56.4 (c = 0.69 in $CHCl_3$); HPLC (DAICEL CORPORATION AS-H), 2-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 20.85 min (major) and 26.50 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.53 (s, 1H), 8.34 (s, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.03-6.95 (m, 2H), 6.82 (t, *J* = 8.0 Hz, 3H), 6.45 (t, *J* = 7.6 Hz, 1H), 6.03 (d, *J* = 7.6 Hz, 1H), 4.40 (dq, *J* = 12.0, 6.0 Hz, 1H), 3.65 (d, *J* = 10.4 Hz, 1H), 3.20 (t, *J* = 10.4 Hz, 1H), 2.80 (q, *J* = 6.8 Hz, 1H), 2.28 (s, 3H), 1.61 (d, *J* = 6.0 Hz, 3H), 1.20 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 193.1, 179.9, 154.6, 147.0, 143.9, 137.8, 131.4, 131.0, 128.9, 127.8, 126.6, 126.0, 124.5, 120.5, 117.1, 110.2, 77.7, 50.8, 44.1, 36.5, 34.8, 21.3, 20.8, 19.0. HRMS (ESI-TOF) calcd for $C_{24}H_{23}NO_3$ $[M+Na]^+$ = 396.1570, Found 396.1581.



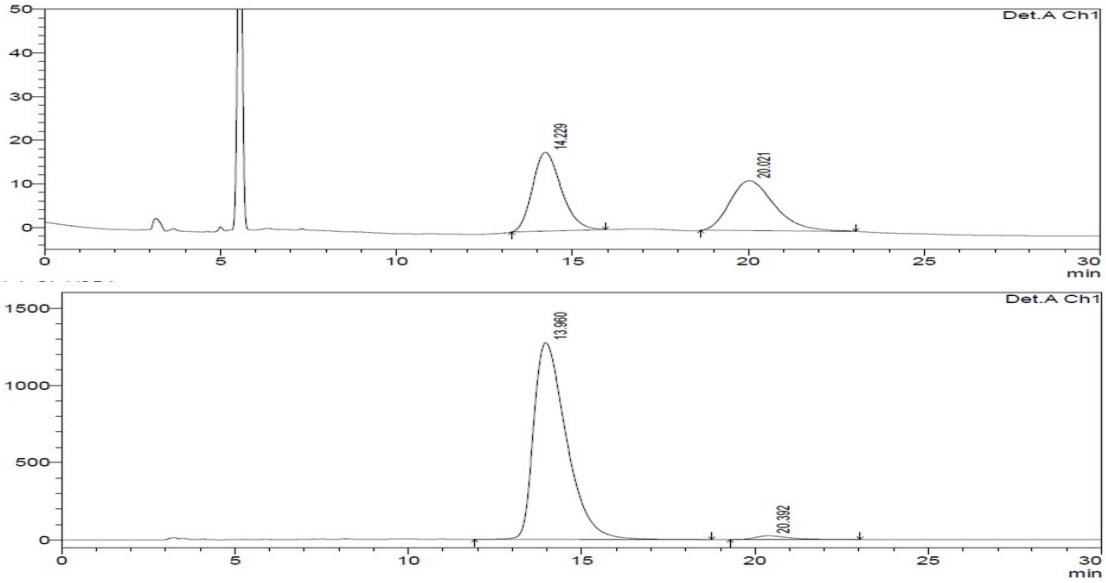


5'-fluoro-6,9-dimethyl-2'-oxo-6,6a,9,10a-tetrahydrospiro[benzo[c]chromene-10,3'-indoline]-8-carbaldehyde (**5ka**)

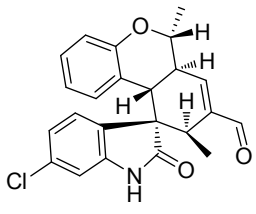


5ka

White solid; 80% yield; 96% ee; 6:1 dr; m.p. 109 °C-111 °C; $[\alpha]_D^{22}$ = -43.7 (c = 0.35 in $CHCl_3$); HPLC (DAICEL CORPORATION AS-H), 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ= 254 nm, retention time: 13.96 min (major) and 20.39 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.54 (s, 1H), 7.96 (s, 1H), 7.02 (dt, *J* = 8.8, 4.4 Hz, 2H), 6.96-6.87 (m, 2H), 6.88-6.76 (m, 2H), 6.48 (t, *J* = 7.6 Hz, 1H), 6.00 (d, *J* = 7.6 Hz, 1H), 4.40 (dq, *J* = 12.0, 6.0 Hz, 1H), 3.63 (d, *J* = 10.4 Hz, 1H), 3.19 (t, *J* = 10.8 Hz, 1H), 2.84 (q, *J* = 6.8 Hz, 1H), 1.61 (d, *J* = 6.0 Hz, 3H), 1.21 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.8, 179.2, 159.8, 154.6, 146.8, 143.4, 136.1, 132.7, 128.0, 125.5, 124.0, 120.5, 117.3, 115.0, 113.8, 110.8, 92.8, 77.6, 51.2, 44.1, 36.6, 34.8, 20.8, 18.8. HRMS (ESI-TOF) calcd for $C_{23}H_{20}FNO_3$ $[M+Na]^+$ = 400.1319, Found 400.1320.



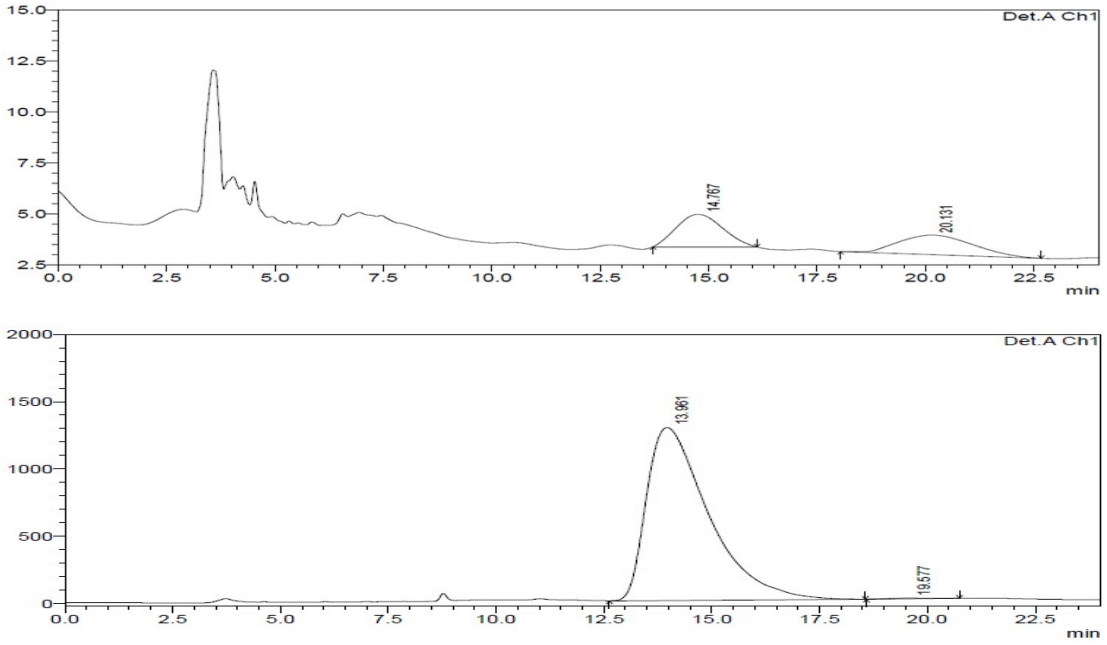
6'-chloro-6,9-dimethyl-2'-oxo-6,6a,9,10a-tetrahydrospiro[benzo[c]chromene-10,3'-indoline]-8-carbaldehyde (5la)



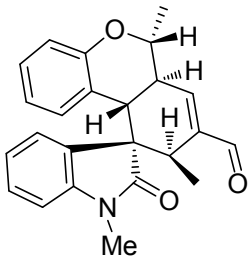
5la

light yellow solid; 90% yield; >99% ee; 7:1 dr; m.p. 139 °C-141 °C; $[\alpha]_D^{22}$ = -29.0 (c = 1.12 in $CHCl_3$); HPLC (DAICEL CORPORATION AS-H), 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 13.96 min (major) and 19.58 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.53 (s, 1H), 8.99 (s, 1H), 7.09-6.92 (m, 4H), 6.84 (dd, *J* = 12.4, 5.2 Hz, 2H), 6.48 (t, *J* = 7.6

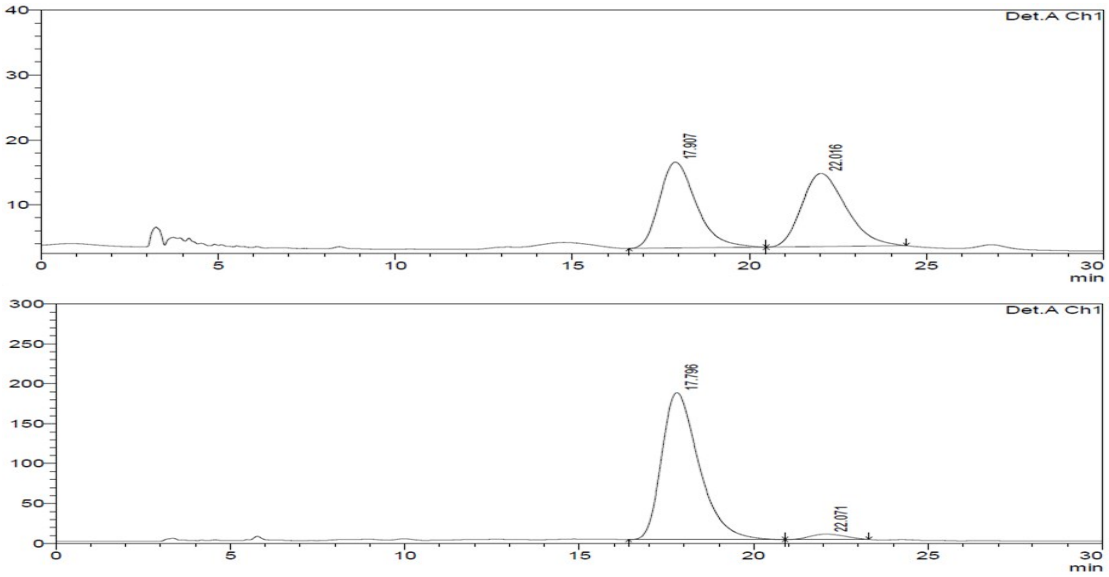
Hz, 1H), 5.99 (d, *J* = 7.6 Hz, 1H), 4.40 (dq, *J* = 12.0, 6.0 Hz, 1H), 3.65 (d, *J* = 10.4 Hz, 1H), 3.18 (t, *J* = 10.4 Hz, 1H), 2.80 (q, *J* = 6.8 Hz, 1H), 1.63 (d, *J* = 6.0 Hz, 3H), 1.17 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 193.0, 180.1, 154.6, 147.0, 143.5, 141.5, 134.3, 129.4, 128.1, 126.6, 125.6, 124.0, 122.1, 120.6, 117.3, 111.3, 77.7, 50.7, 44.1, 36.4, 34.8, 20.8, 18.9. HRMS (ESI-TOF) calcd for $C_{23}H_{20}ClNO_3$ $[M+Na]^+$ = 416.1024, Found 416.1023.



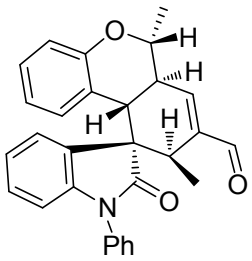
1',6,9-trimethyl-2'-oxo-6,6a,9,10a-tetrahydrospiro[benzo[c]chromene-10,3'-indoline]-8-carbaldehyde (**5ma**)



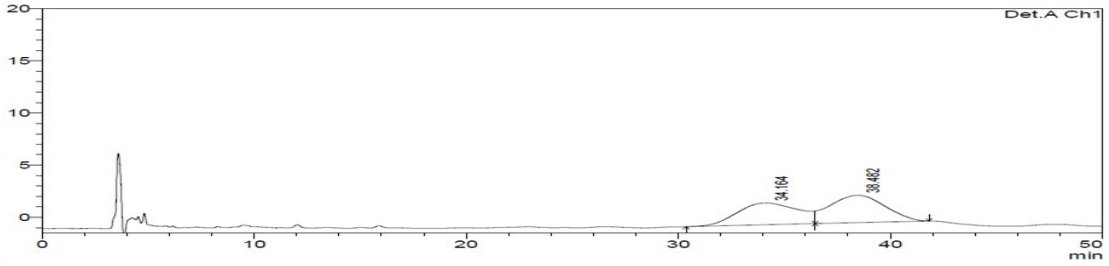
5ma White solid; 31% yield; 94% ee; 10:1 dr; m.p. 62 °C-64 °C; $[\alpha]_D^{22}$ = -52.0 (c = 0.10 in $CHCl_3$); HPLC (DAICEL CORPORATION AS-H), 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ= 254 nm, retention time: 17.80 min (major) and 22.07 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.53 (s, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.28 (s, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.99 (dd, *J* = 7.2, 4.0 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.41 (t, *J* = 7.6 Hz, 1H), 5.86 (d, *J* = 7.6 Hz, 1H), 5.02-4.87 (m, 1H), 3.79-3.69 (m, 2H), 3.19 (s, 3H), 2.69 (dd, *J* = 14.0, 6.8 Hz, 1H), 1.42 (d, *J* = 6.4 Hz, 3H), 1.24 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.8, 177.5, 154.9, 146.9, 143.4, 143.2, 130.7, 128.7, 127.9, 125.6, 125.6, 124.2, 122.1, 120.1, 117.2, 108.8, 77.3, 77.2, 77.0, 76.7, 73.5, 58.5, 50.4, 41.4, 34.7, 19.1, 18.4, 17.8. HRMS (ESI-TOF) calcd for $C_{24}H_{23}NO_3$ $[M+Na]^+$ = 396.1570, Found 396.1573.

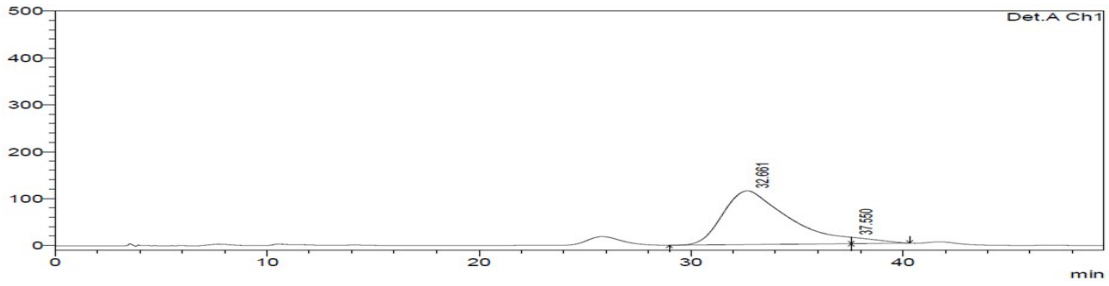


6,9-dimethyl-2'-oxo-1'-phenyl-6,6a,9,10a-tetrahydrospiro[benzo[c]chromene-10,3'-indoline]-8-carbaldehyde (5na)

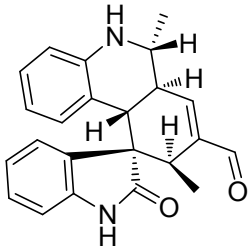


5na White solid; 45% yield; 92% ee; 12:1 dr; m.p. 72 °C-74 °C; $[\alpha]_D^{22}$ = -25.6 (c = 0.50 in $CHCl_3$); HPLC (DAICEL CORPORATION AS-H, 2-propanol/*n*-hexane = 3/97, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 32.66 min (major) and 37.55 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 6.8 Hz, 4H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 2.0 Hz, 1H), 6.49 (t, *J* = 7.2 Hz, 1H), 6.14 (d, *J* = 7.6 Hz, 1H), 5.05-4.87 (m, 1H), 3.86-3.74 (m, 2H), 2.91 (q, *J* = 6.8 Hz, 1H), 1.44 (d, *J* = 6.4 Hz, 3H), 1.31 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.8, 177.0, 155.1, 146.8, 143.3, 134.2, 130.4, 129.6, 128.6, 128.2, 128.0, 126.7, 125.9, 125.8, 124.2, 122.6, 120.1, 117.3, 110.1, 73.6, 50.4, 41.5, 34.9, 31.1, 19.0, 17.8. HRMS (ESI-TOF) calcd for $C_{29}H_{25}NO_3$ $[M+Na]^+$ = 458.1727, Found 458.1728.

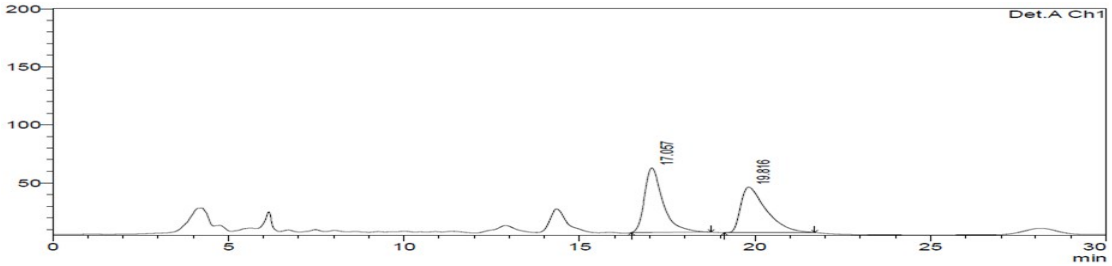


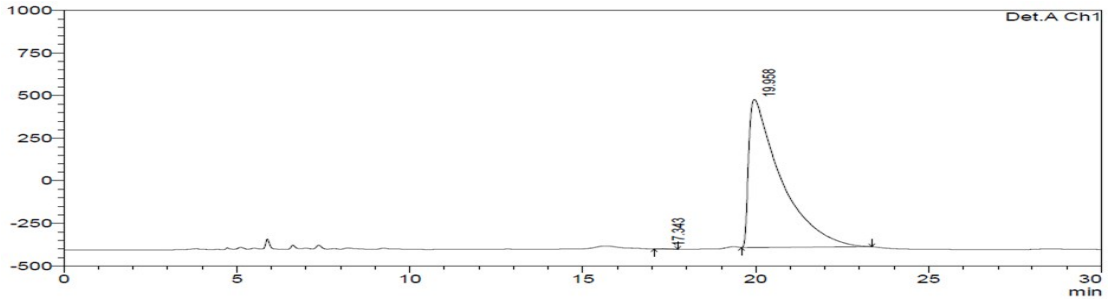


6',9'-dimethyl-2-oxo-6',6a',9',10a'-tetrahydro-5'H-spiro[indoline-3,10'-phenanthridine]-8'-carbaldehyde (5oa)

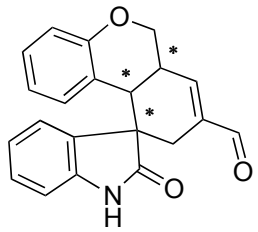


5oa light orange solid; 83% yield; >99% ee; 2.5:1 dr; m.p. 121 °C-123 °C; $[\alpha]_D^{22}$ = -88.8 (c = 0.55 in $CHCl_3$); HPLC (DAICEL CORPORATION AD-H), 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ= 254 nm, retention time: 19.96 min (major) and 17.34 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.54 (s, 1H), 8.37 (s, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 7.00-6.89 (m, 3H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.48 (d, *J* = 7.6 Hz, 1H), 6.21 (t, *J* = 7.6 Hz, 1H), 5.94 (d, *J* = 7.6 Hz, 1H), 3.65-3.46 (m, 2H), 2.92 (t, *J* = 10.0 Hz, 1H), 2.80 (q, *J* = 6.8 Hz, 1H), 1.47 (d, *J* = 6.0 Hz, 3H), 1.18 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 193.4, 180.2, 149.0, 144.5, 143.3, 140.1, 131.5, 128.3, 127.2, 125.8, 124.1, 123.0, 121.9, 117.0, 113.5, 110.3, 53.8, 51.0, 43.3, 37.8, 35.0, 22.4, 18.9. HRMS (ESI-TOF) calcd for $C_{23}H_{22}N_2O_2$ $[M+Na]^+$ = 381.1573, Found 381.1584.



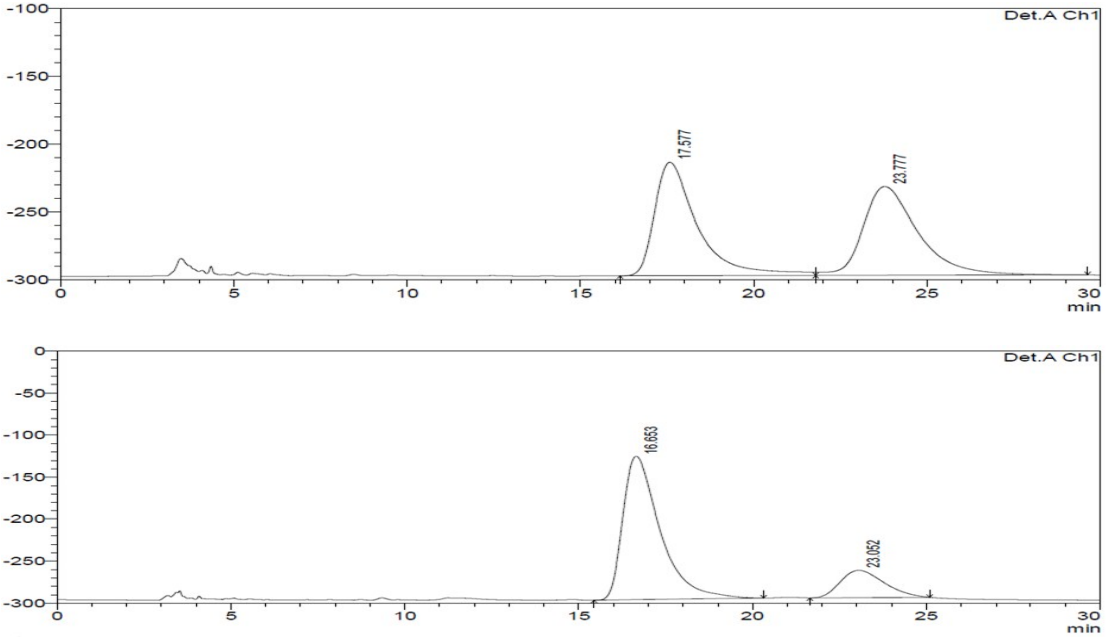


2'-oxo-6,6a,9,10a-tetrahydrospiro[benzo[c]chromene-10,3'-indoline]-8-carbaldehyde (5pa)

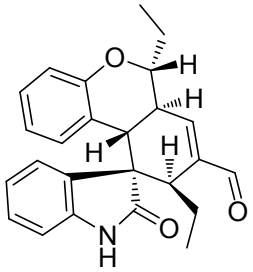


5pa

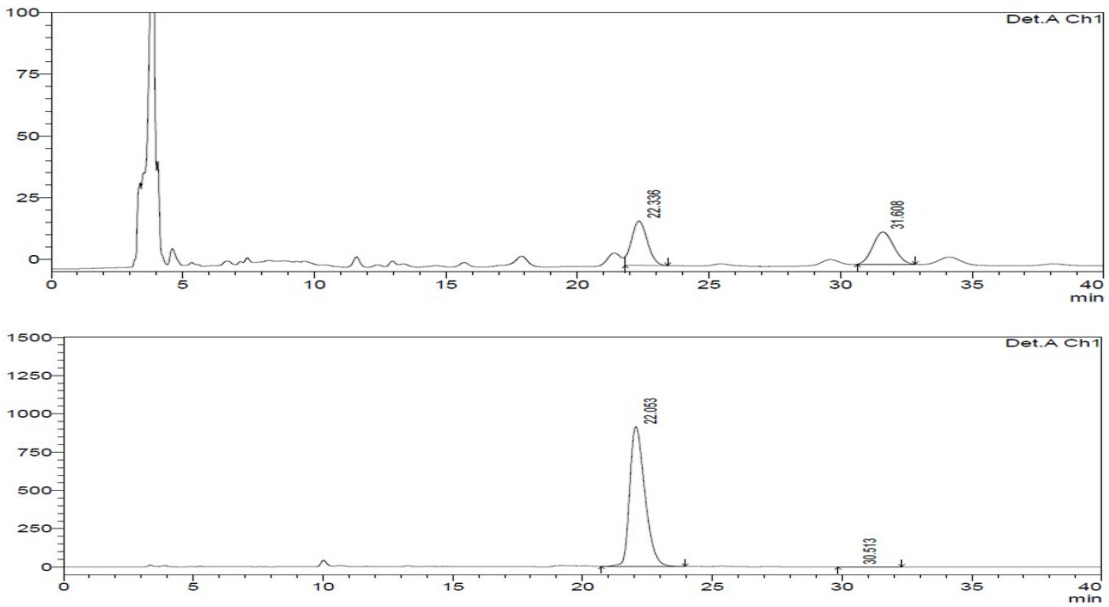
light yellow solid; 55% yield; 64% ee; 1:2.5 dr; m.p. 98 °C-100 °C; $[\alpha]_D^{22}$ = 14.6 (c = 0.35 in $CHCl_3$); HPLC (DAICEL CORPORATION AS-H), 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 16.65 min (major) and 23.05 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.57 (s, 1H), 8.28 (s, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.06-6.93 (m, 2H), 6.82 (s, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.44 (t, *J* = 7.2 Hz, 1H), 6.18 (d, *J* = 8.0 Hz, 1H), 4.68 (dd, *J* = 10.0, 4.0 Hz, 1H), 4.18-4.07 (m, 1H), 3.95 (t, *J* = 11.2 Hz, 1H), 3.51 (d, *J* = 10.4 Hz, 1H), 2.78 (d, *J* = 18.8 Hz, 1H), 2.65 (d, *J* = 18.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.7, 179.7, 154.8, 146.3, 139.9, 138.3, 134.5, 128.7, 128.4, 125.4, 123.6, 122.9, 122.6, 120.4, 117.1, 110.4, 70.2, 47.5, 41.4, 35.6, 34.4. HRMS (ESI-TOF) calcd for $C_{21}H_{17}NO_3$ $[M+Na]^+$ = 354.1101, Found 354.1103.



6,9-diethyl-2'-oxo-6,6a,9,10a-tetrahydrospiro[benzo[c]chromene-10,3'-indoline]-8-carbaldehyde (5qa)



5qa yellow solid; 60% yield; >99% ee; 3:1 dr; m.p. 53 °C-55 °C; $[\alpha]_D^{22}$ = -86.3 (c = 0.23 in $CHCl_3$); HPLC (DAICEL CORPORATION AD-H, 2-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, λ= 220 nm, retention time: 22.05 min (major) and 30.51 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.58 (s, 1H), 8.03 (s, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.00 (dd, *J* = 16.4, 7.6 Hz, 3H), 6.85 (dd, *J* = 13.6, 5.2 Hz, 2H), 6.46 (t, *J* = 7.6 Hz, 1H), 5.99 (d, *J* = 7.6 Hz, 1H), 4.33-4.17 (m, 1H), 3.70 (d, *J* = 10.4 Hz, 1H), 3.19 (t, *J* = 10.0 Hz, 1H), 2.74 (t, *J* = 5.8 Hz, 1H), 2.12-2.03 (m, 1H), 1.93-1.84 (m, 1H), 1.78 (dt, *J* = 14.4, 7.2 Hz, 1H), 1.54-1.45 (m, 1H), 1.17 (t, *J* = 7.2 Hz, 3H), 0.73 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 193.1, 179.5, 154.9, 147.6, 142.6, 140.1, 131.0, 128.6, 127.8, 126.7, 125.7, 123.9, 122.3, 120.5, 117.2, 110.3, 82.1, 51.2, 42.2, 40.8, 37.6, 27.3, 26.4, 13.1, 9.2. HRMS (ESI-TOF) calcd for $C_{25}H_{25}NO_3$ $[M+Na]^+$ = 410.1727, Found 410.1725.



2'-oxo-6,9-dipropyl-6,6a,9,10a-tetrahydrospiro[benzo[c]chromene-10,3'-indoline]-8-carbaldehyde (**5ra**)

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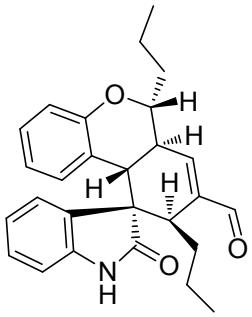
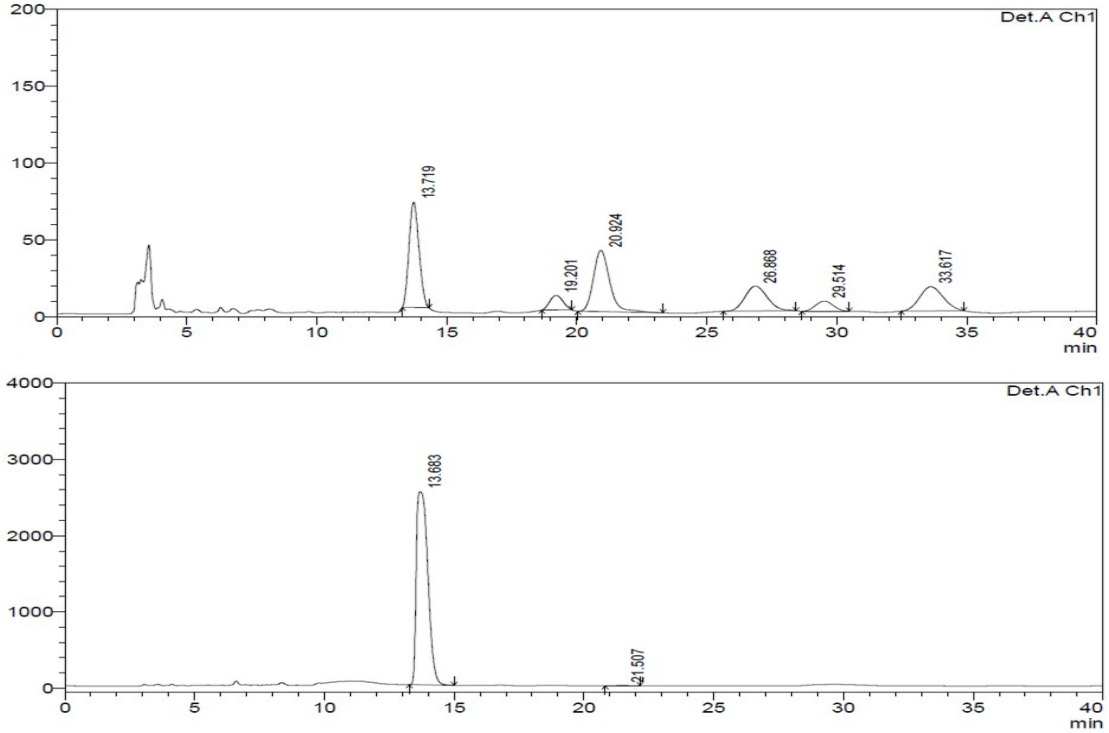
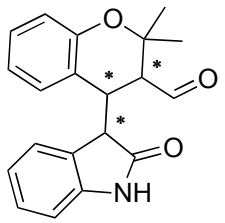


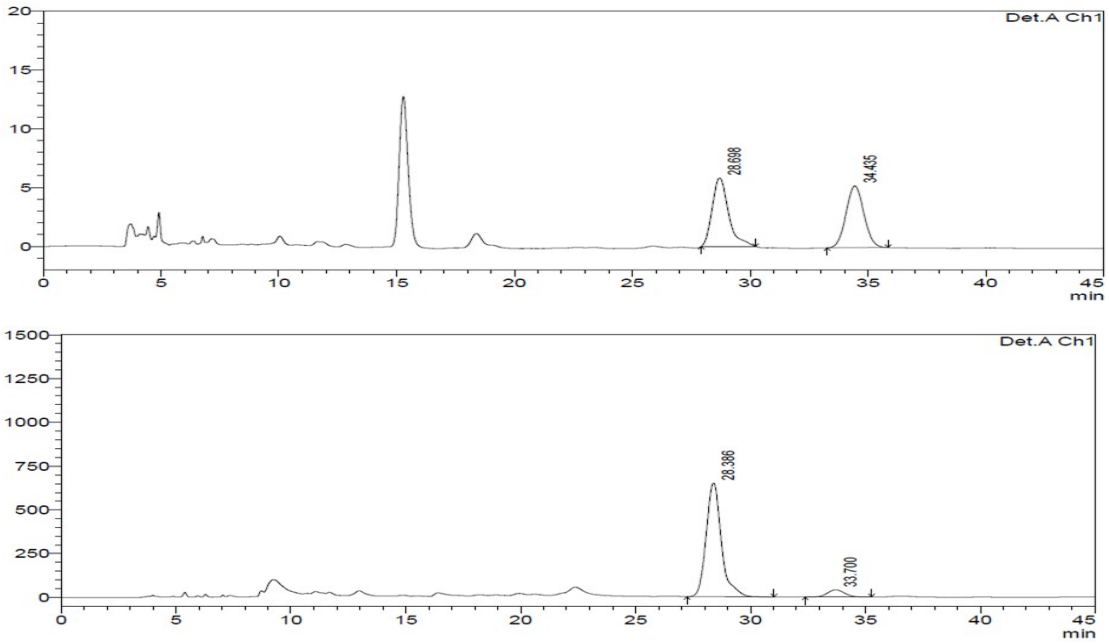
5ra yellow solid; 78% yield; >99% ee; 4:1 dr; m.p. 129 °C-131 °C; $[\alpha]_D^{22}$ = -84.7 (c = 0.66 in $CHCl_3$); HPLC (DAICEL CORPORATION AD-H), 2-propanol/*n*-hexane = 7/93, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 13.68 min (major) and 21.51 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.57 (s, 1H), 8.60 (s, 1H), 7.30 (td, *J* = 7.6, 0.8 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.06-6.93 (m, 3H), 6.83 (t, *J* = 5.6 Hz, 2H), 6.46 (t, *J* = 7.6 Hz, 1H), 5.98 (d, *J* = 7.6 Hz, 1H), 4.39-4.19 (m, 1H), 3.69 (d, *J* = 10.4 Hz, 1H), 3.16 (td, *J* = 10.8, 1.6 Hz, 1H), 2.76 (t, *J* = 5.6 Hz, 1H), 1.99-1.88 (m, 1H), 1.79-1.72 (m, 3H), 1.66-1.55 (m, 1H), 1.46-1.34 (m, 1H), 1.23-1.15 (m, 1H), 1.05 (t, *J* = 7.2 Hz, 4H), 0.96-0.79 (m, 3H), 0.75 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 193.1, 180.3, 154.8, 147.3, 143.1, 140.2, 131.0, 128.6, 127.7, 126.8, 125.4, 124.0, 122.3, 120.6, 117.3, 110.6, 80.9, 51.2, 42.7, 39.9, 37.6, 36.6, 36.0, 22.1, 18.2, 14.2, 14.1. HRMS (ESI-TOF) calcd for $C_{27}H_{29}NO_3$ $[M+Na]^+$ = 438.2040, Found 438.2042.



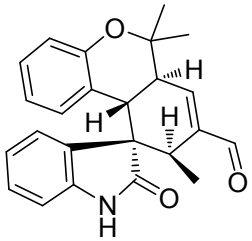
2,2-dimethyl-4-(2-oxoindolin-3-yl)chroman-3-carbaldehyde (**5s**)



5s White solid; 55% yield; 87% ee; >20:1 dr; m.p. 95 °C- 97 °C; $[\alpha]_D^{22}$ = 23.6 (c = 0.6 in $CHCl_3$); HPLC (DAICEL CORPORATION AD-H, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 28.39 min (major) and 33.70 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.70 (d, *J* = 4.0 Hz, 1H), 8.65 (s, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.20 (dd, *J* = 14.4, 7.2 Hz, 2H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.85 (dd, *J* = 14.4, 7.6 Hz, 3H), 6.33 (d, *J* = 7.2 Hz, 1H), 4.28 (dd, *J* = 10.8, 2.4 Hz, 1H), 4.06 (d, *J* = 2.0 Hz, 1H), 1.36 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 202.2, 178.5, 153.6, 141.5, 128.6, 128.5, 127.4, 126.4, 124.4, 122.9, 121.5, 121.1, 118.2, 110.3, 74.2, 57.1, 49.8, 33.4, 28.1, 21.2. HRMS (ESI-TOF) calcd for $C_{20}H_{19}NO_3$ $[M+Na]^+$=344.1257, Found 344.1248

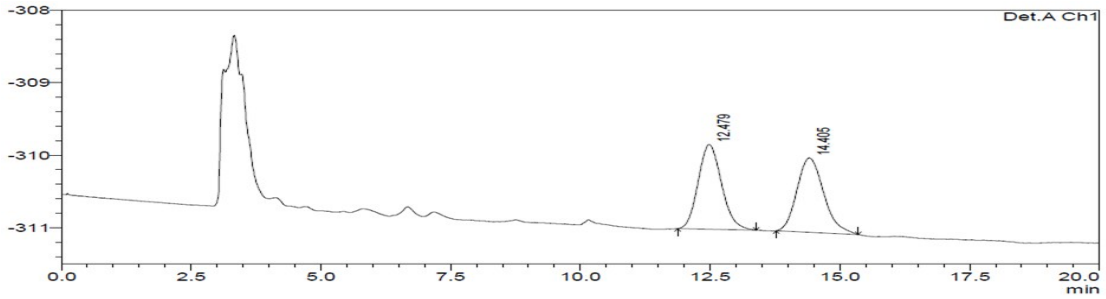


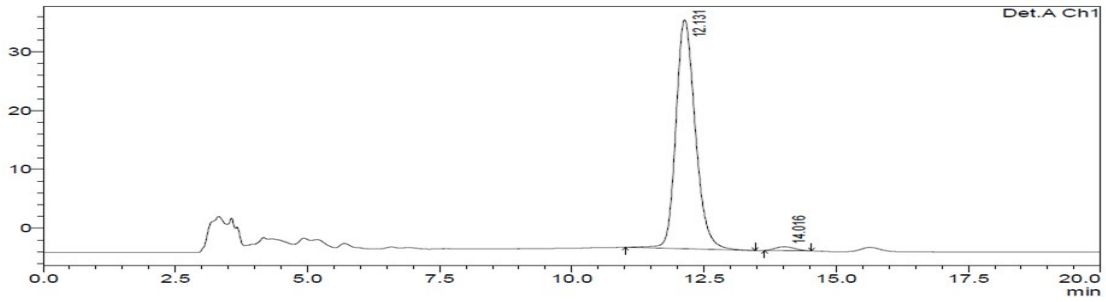
6,6,9-trimethyl-2'-oxo-6,6a,9,10a-tetrahydrospiro[benzo[c]chromene-10,3'-indoline]-8-carbaldehyde (**5sa**)



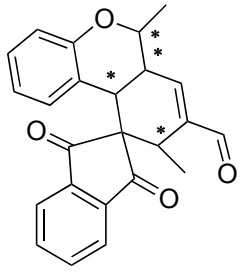
5sa White solid; 50% yield; 97% ee; 5:1 dr; m.p. 65 °C-67 °C; $[\alpha]_D^{22}$ = -59.2 (c = 0.31 in $CHCl_3$); HPLC (DAICEL CORPORATION AS-H, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 12.13 min

(major) and 14.02 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.54 (s, 1H), 8.19 (s, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.06-6.91 (m, 3H), 6.81 (dd, *J* = 14.4, 5.2 Hz, 2H), 6.49 (t, *J* = 7.6 Hz, 1H), 6.06 (d, *J* = 7.6 Hz, 1H), 3.65 (d, *J* = 10.8 Hz, 1H), 3.25 (d, *J* = 10.8 Hz, 1H), 2.81 (q, *J* = 6.8 Hz, 1H), 1.61 (s, 3H), 1.43 (s, 3H), 1.23 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.9, 179.7, 154.5, 147.7, 143.3, 140.1, 131.1, 128.5, 128.0, 127.7, 125.8, 123.8, 122.1, 120.8, 117.7, 110.3, 79.6, 50.7, 48.2, 34.5, 33.0, 28.8, 24.5, 18.8. HRMS (ESI-TOF) calcd for $C_{24}H_{23}NO_3$ $[M+Na]^+$ = 396.1570, Found 396.1576.





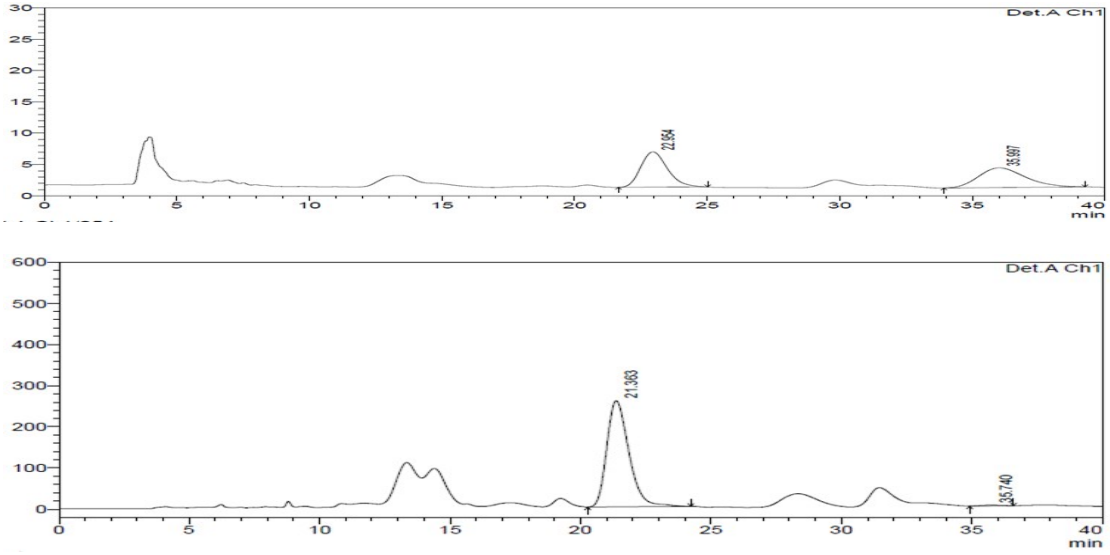
6,9-dimethyl-1',3'-dioxo-1',3',6,6a,9,10a-hexahydrospiro[benzo[c]chromene-10,2'-indene]-8-carbaldehyde (**5ta**)



5ta

White solid; 70% yield; >99% ee; 2：1 dr; m.p. 220 °C-222 °C; $[\alpha]_D^{22}$ = -45.3 (c = 0.21 in $CHCl_3$); HPLC (DAICEL CORPORATION AS-H), 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ= 254 nm, retention time: 21.36 min (major) and 35.74 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.49 (s, 1H), 8.16-8.07 (m, 1H), 7.98-7.86 (m, 3H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.84 (dd, *J* = 15.2, 5.2 Hz, 2H), 6.47 (t, *J* = 7.6 Hz, 1H), 6.23 (d, *J* = 7.6 Hz, 1H), 4.40 (dq, *J* = 12.0, 6.0 Hz, 1H), 3.79 (d, *J* = 10.8 Hz, 1H), 3.25 (t, *J* = 10.8 Hz, 1H), 2.89 (q, *J* = 6.8 Hz, 1H), 1.64 (d, *J* = 6.0 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =

200.4, 199.7, 192.6, 154.5, 147.1, 143.7, 141.1, 141.0, 136.1, 136.0, 128.2, 124.4, 124.1, 124.1, 123.9, 120.1, 117.3, 77.6, 56.3, 43.7, 35.9, 33.9, 20.6, 18.0. HRMS (ESI-TOF) calcd for $C_{24}H_{20}O_4$ $[M+Na]^+$ = 395.1254, Found 395.1259.

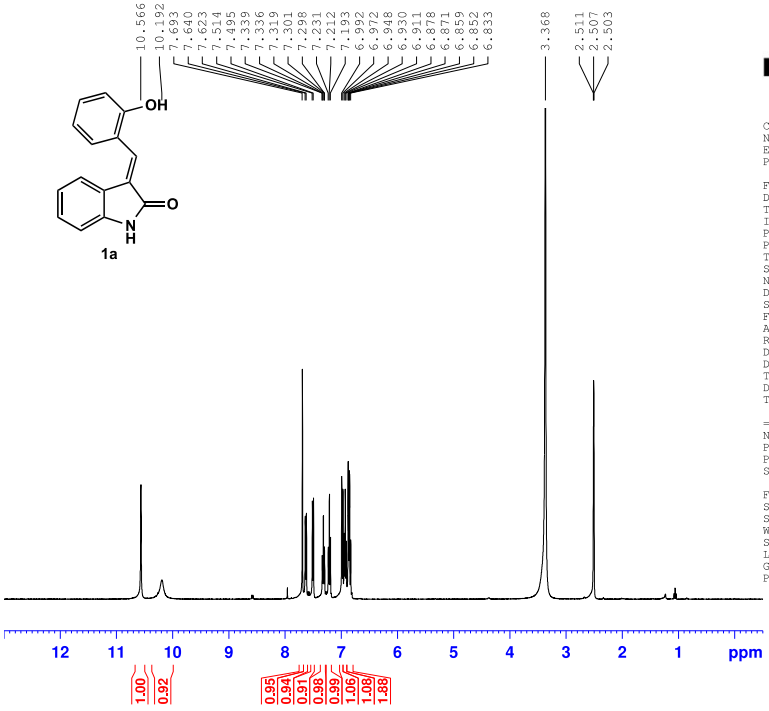


(I) References

(1) Synthesis and anti-tyrosine kinase activity of 3-(substituted-benzylidene)-1, 3-dihydro-indolin derivatives: investigation of their role against p60c-Src receptor tyrosine kinase with the application of receptor docking studies. Sureyya Olgen, Eiichi Akaho, Dogu Nebioglu aS. Olgen et al. / Il Farmaco 60 (2005) 497–506

(2) Synthesis and In Vitro Evaluation of Oxindole Derivatives as Potential Radioligands for 5-HT7 Receptor Imaging with PET Quick ViewFull Text By Herth, Matthias M. et al From ACS Chemical Neuroscience, 3(12), 1002-1007; 2012

(J) Copies of NMR Spectra



BRUKER

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PROCNO                   1

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TE             294.8 K
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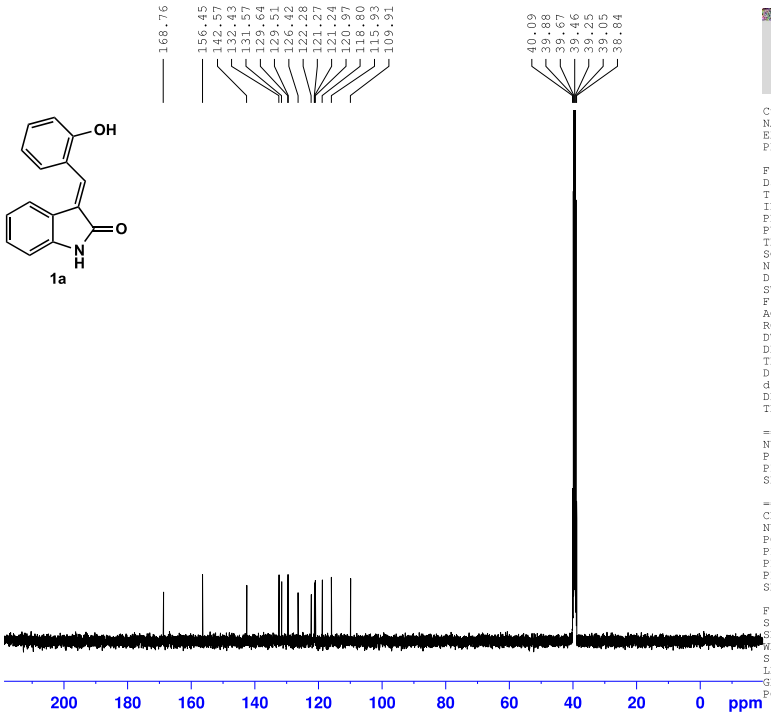
38

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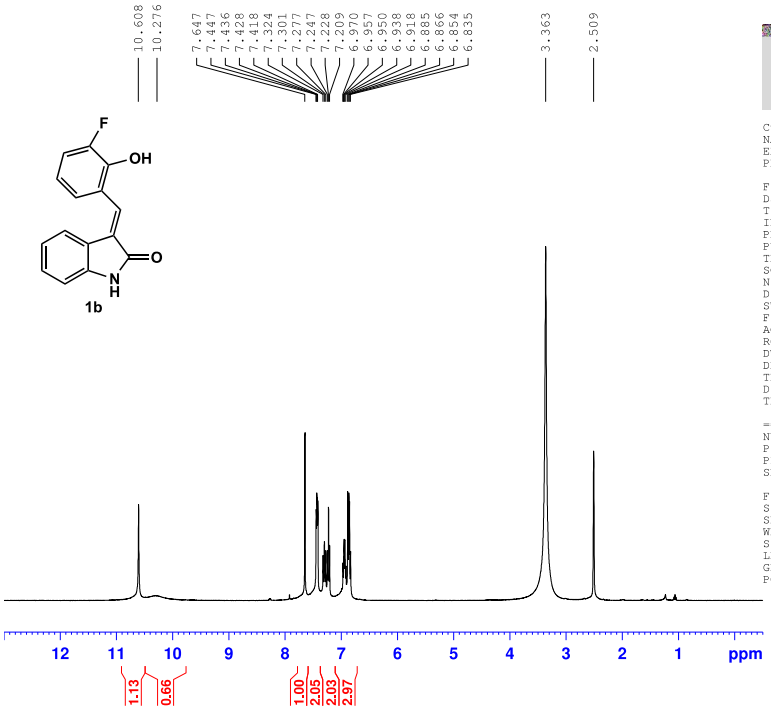
PULPROG          zgpg30
TD                65536
SOLVENT             DMSO
NS                   256
DS                     0
SWH            24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                  2050
DW                20.800 usec
DE                 6.50 usec
TE                300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                20.70 usec
PL1               -1.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             60.00 usec
PL12              10.77 dB
PL13              13.05 dB
PL2               -2.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF           100.6128193 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```




```
Current Data Parameters
NAME      2015-01-22 LJ-1b
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150123
Time               2.43
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                65536
SOLVENT             DMSO
NS                    16
DS                     0
SWH             8223.685 Hz
FIDRES         0.125483 Hz
AQ             3.9846387 sec
RG                   256
DW                60.800 usec
DE                 6.50 usec
TE                296.5 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 1H
P1                13.80 usec
PL1               -2.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF           400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```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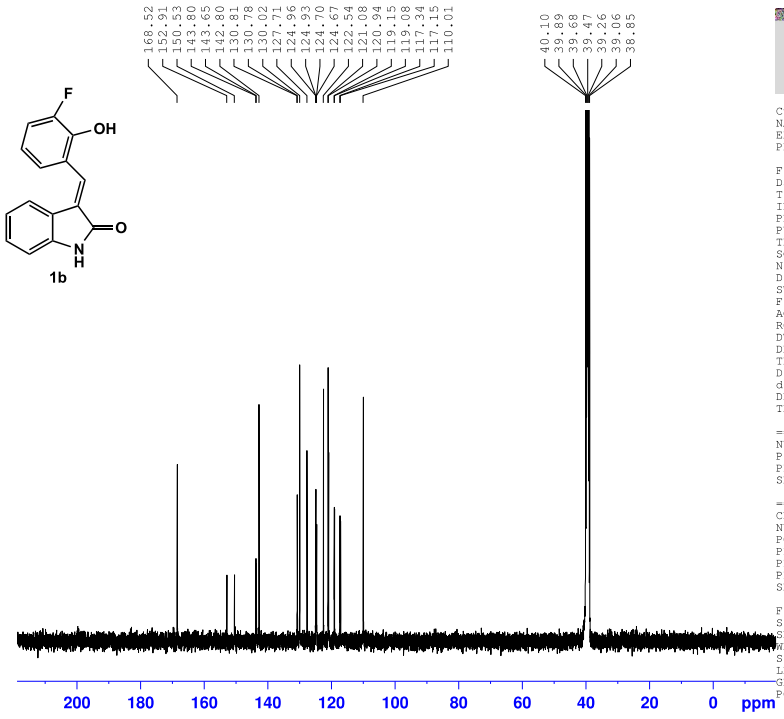


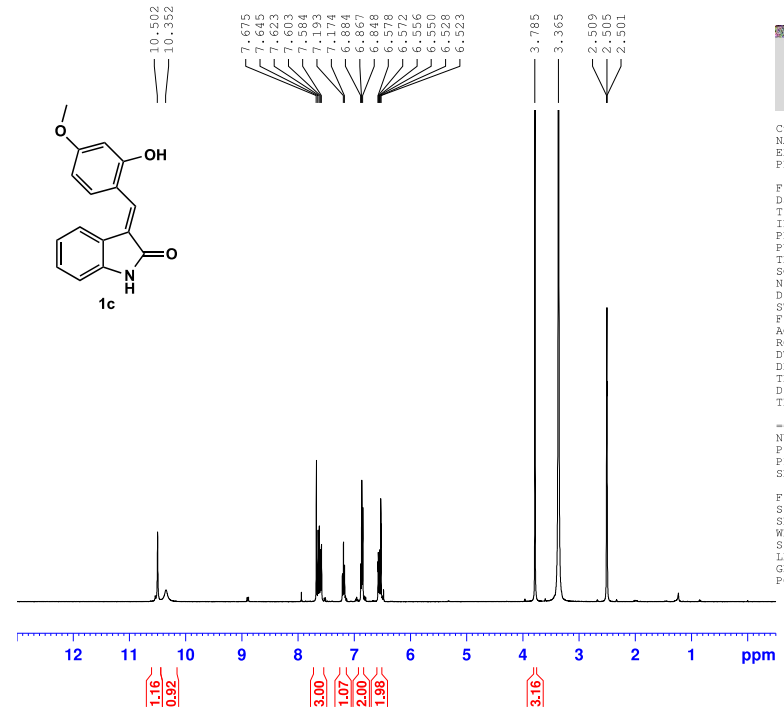
Current Data Parameters
NAME 2015-01-22 LJ-1b
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150123
Time 4.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 2048
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 20.70 usec
PL1 -1.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 60.00 usec
PL12 10.77 dB
PL13 13.05 dB
PL2 -2.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6128193 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

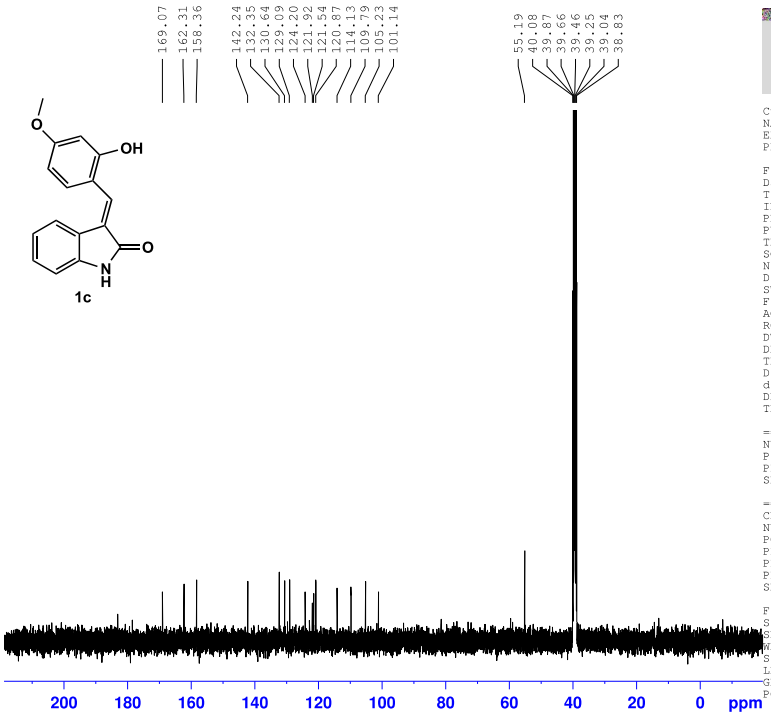


Current Data Parameters
NAME 2015-01-22 LJ-11
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150122
Time 22.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 287
DW 60.800 usec
DE 6.50 usec
TE 294.6 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -2.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300014 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



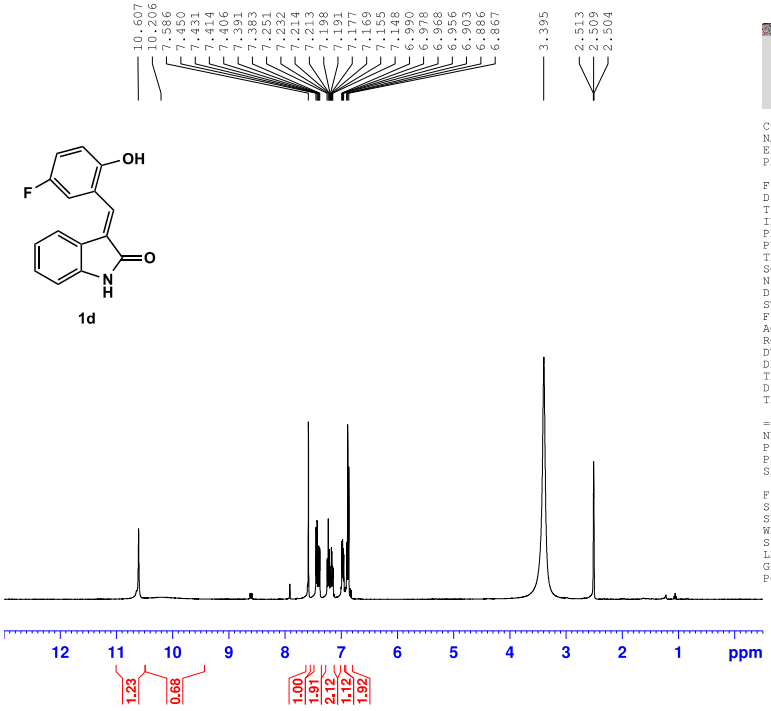

```
Current Data Parameters
NAME      2015-01-22 LJ-1l
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_           20150122
Time               22.26
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT             DMSO
NS                    256
DS                      0
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                   2050
DW                20.800 usec
DE                 6.50 usec
TE                300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  20.70 usec
PL1                 -1.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              60.00 usec
PL12               10.77 dB
PL13               13.05 dB
PL2                -2.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF           100.6128193 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```




```
Current Data Parameters
NAME      2015-01-22 LJ-1d
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20150122
Time               21.28
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                65536
SOLVENT             DMSO
NS                    16
DS                     0
SWH            8223.685 Hz
FIDRES         0.125483 Hz
AQ             3.9846387 sec
RG                   144
DW                60.800 usec
DE                 6.50 usec
TE                294.5 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.80 usec
PL1                -2.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF           400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```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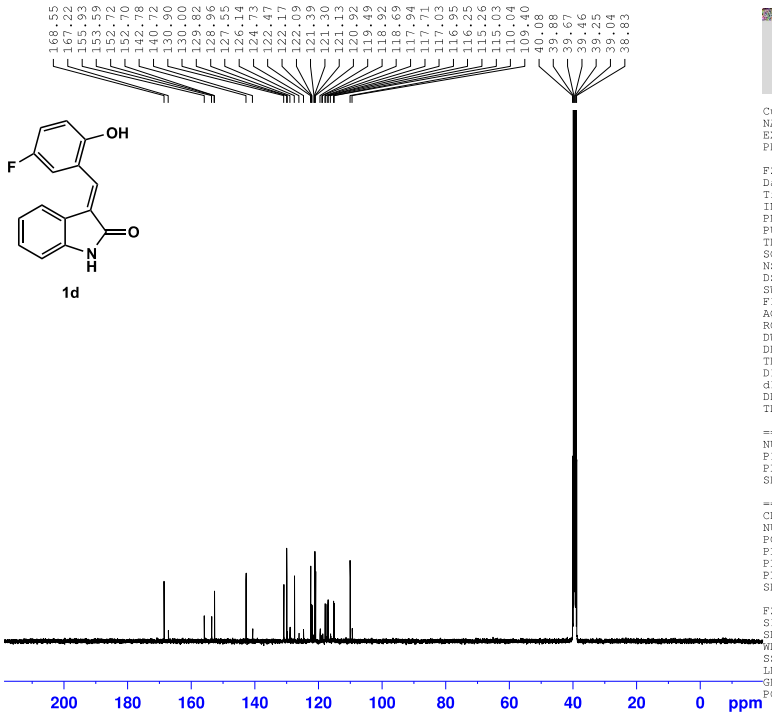


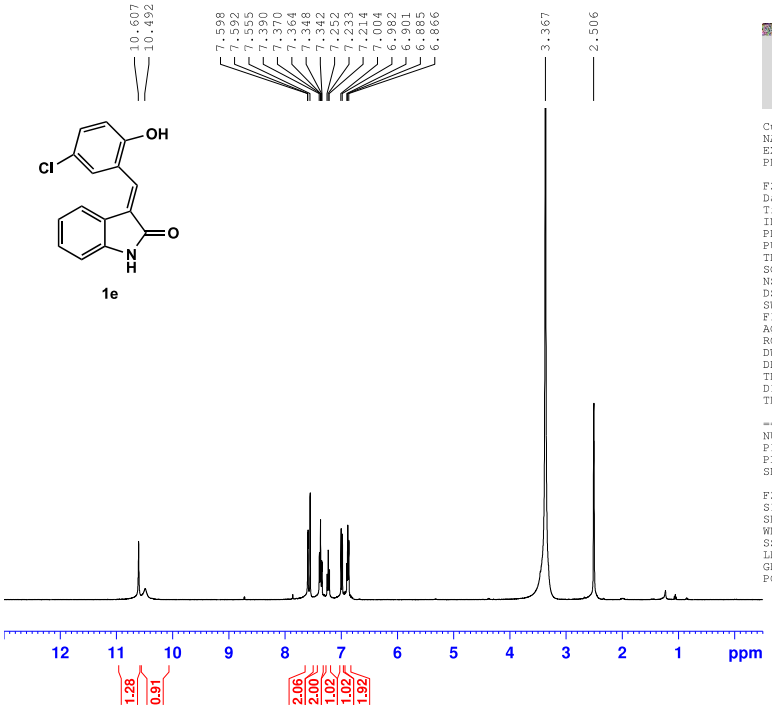
Current Data Parameters
NAME 2015-01-22 LJ-1d
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150123
Time 7.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 2048
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 20.70 usec
PL1 -1.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 60.00 usec
PL12 10.77 dB
PL13 13.05 dB
PL2 -2.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6128193 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



Current Data Parameters
NAME 2015-01-22 LJ-1e
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150122
Time 23.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 287
DW 60.800 usec
DE 6.50 usec
TE 294.8 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -2.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300011 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

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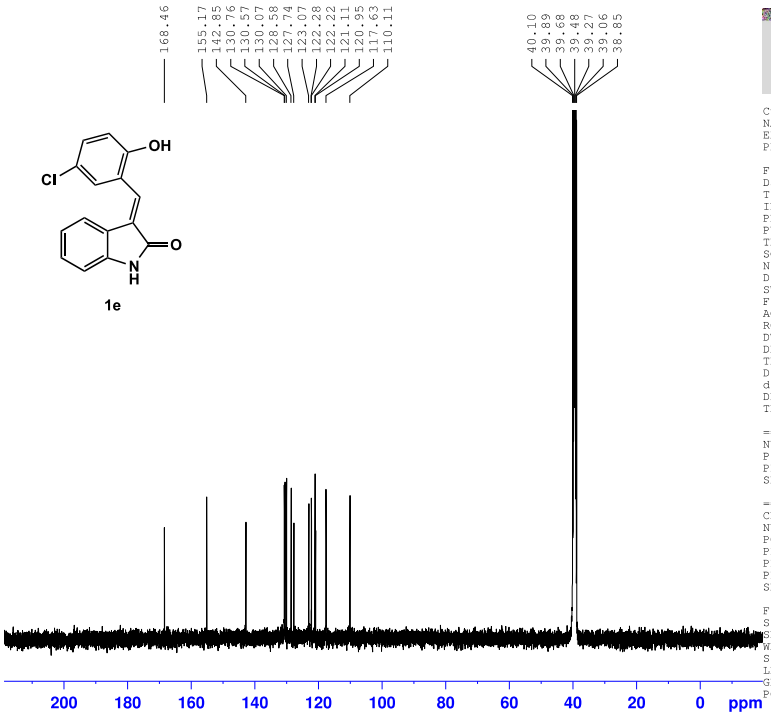


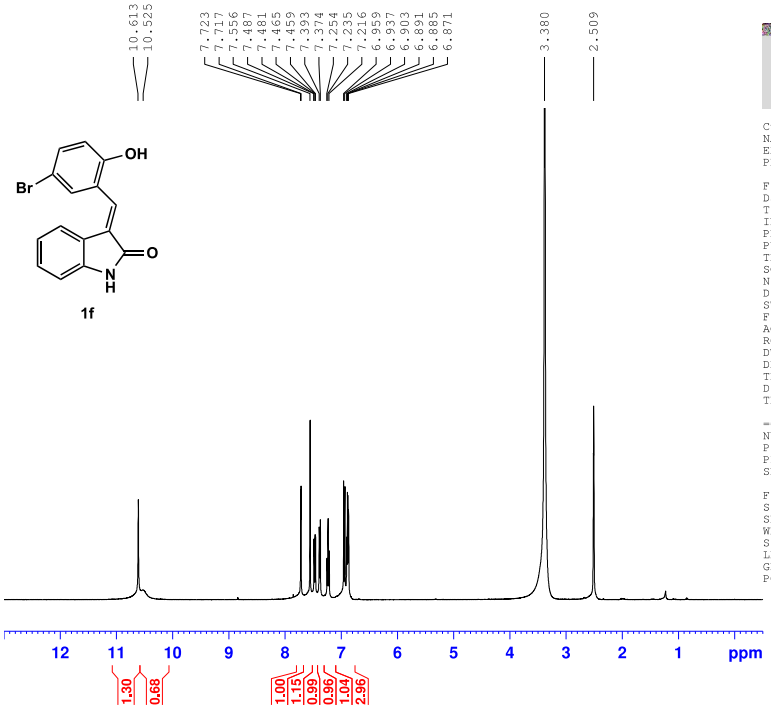

```
Current Data Parameters
NAME      2015-01-23 LJ-1e
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150126
Time                 13.57
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT              DMSO
NS                   1969
DS                      0
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   2050
DW                20.800 usec
DE                 6.50 usec
TE                297.9 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   13C
P1                   20.70 usec
PL1                  -1.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                60.00 usec
PL12                 10.77 dB
PL13                 13.05 dB
PL2                  -2.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF           100.6128193 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```




```
Current Data Parameters
NAME      2015-01-22 LJ-1f
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150122
Time                 22.53
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT              DMSO
NS                     16
DS                      0
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9846387 sec
RG                    256
DW                60.800 usec
DE                 6.50 usec
TE                294.3 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                    1H
P1                   13.80 usec
PL1                  -2.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF           400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```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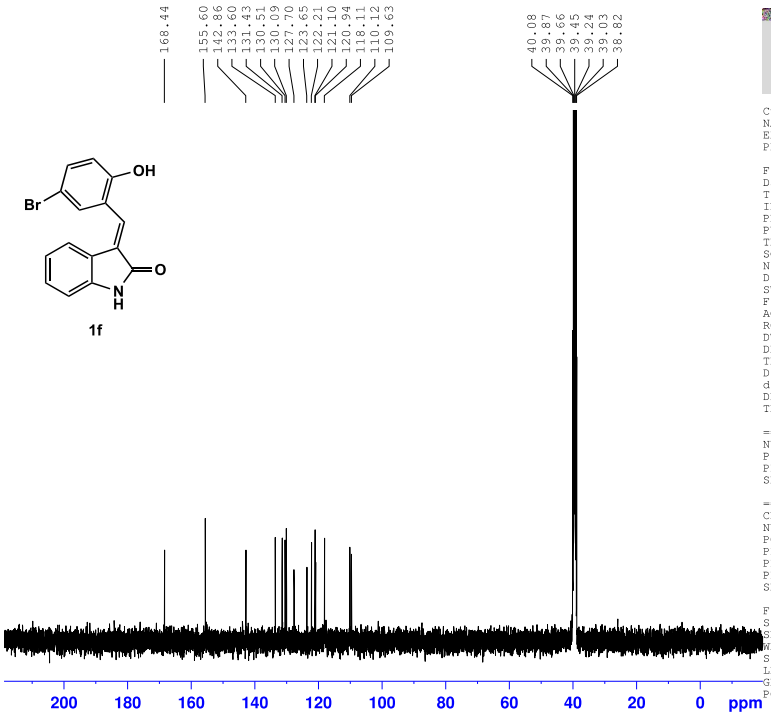


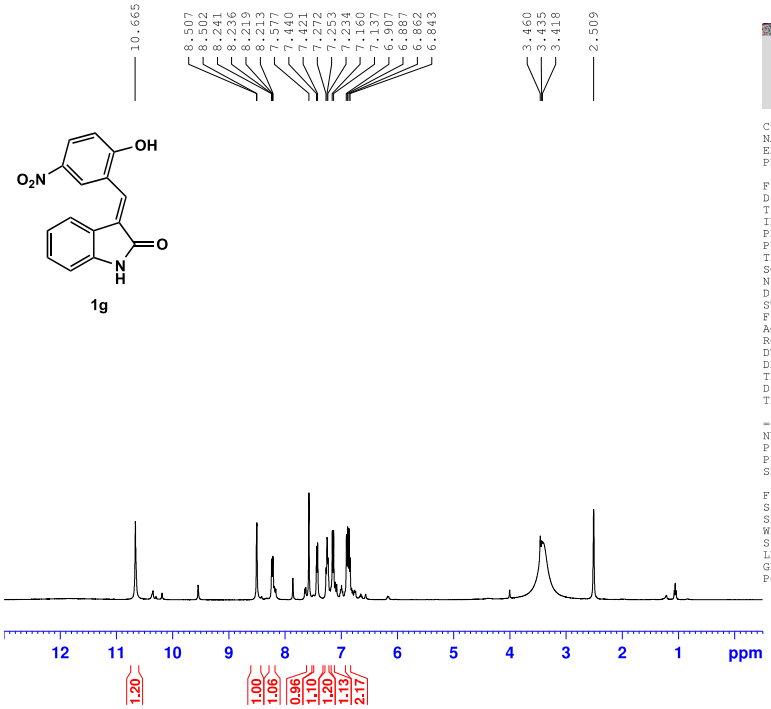

```
Current Data Parameters
NAME      2015-01-22 LJ-1f
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150122
Time              23.09
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT            DMSO
NS                  256
DS                    0
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 2050
DW               20.800 usec
DE                6.50 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 20.70 usec
PL1                -1.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             60.00 usec
PL12              10.77 dB
PL13              13.05 dB
PL2               -2.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6128193 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```




```
Current Data Parameters
NAME      2015-01-22 LJ-1g
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150122
Time              22.31
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               65536
SOLVENT            DMSO
NS                   16
DS                    0
SWH            8223.685 Hz
FIDRES         0.125483 Hz
AQ            3.9846387 sec
RG                  144
DW               60.800 usec
DE                6.50 usec
TE               294.4 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 1H
P1                 13.80 usec
PL1                -2.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```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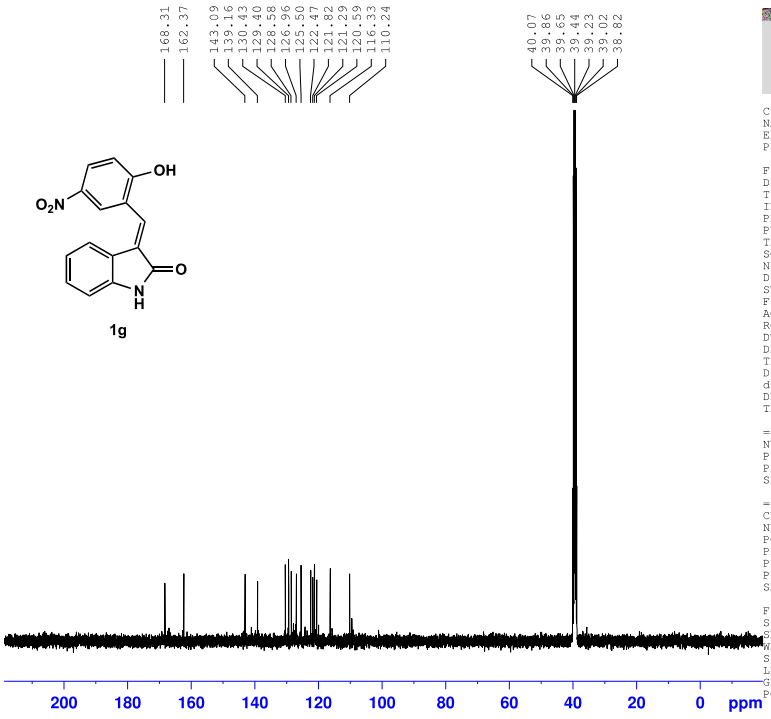


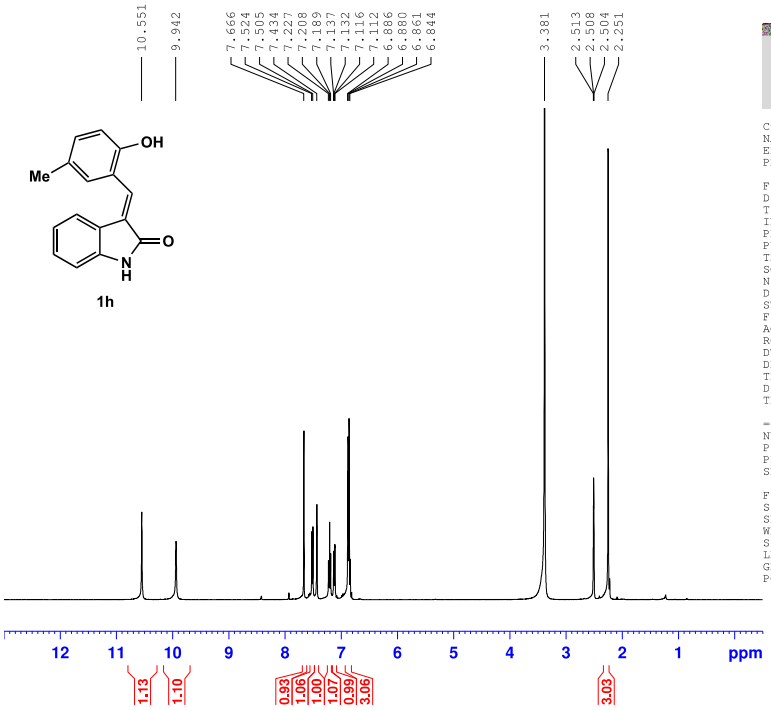

```
Current Data Parameters
NAME      2015-01-22 LJ-1g
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20150122
Time              22.47
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT           DMSO
NS                 256
DS                   0
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG                2050
DW              20.800 usec
DE               6.50 usec
TE              295.6 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1               20.70 usec
PL1              -1.00 dB
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2            60.00 usec
PL12             10.77 dB
PL13             13.05 dB
PL2              -2.00 dB
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6128193 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```




```
Current Data Parameters
NAME      2015-01-22 LJ-1h
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20150122
Time              23.35
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               65536
SOLVENT           DMSO
NS                  16
DS                   0
SWH           8223.685 Hz
FIDRES        0.125483 Hz
AQ            3.9846387 sec
RG                 144
DW              60.800 usec
DE               6.50 usec
TE              295.1 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               1H
P1               13.80 usec
PL1              -2.00 dB
SFO1       400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300000 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```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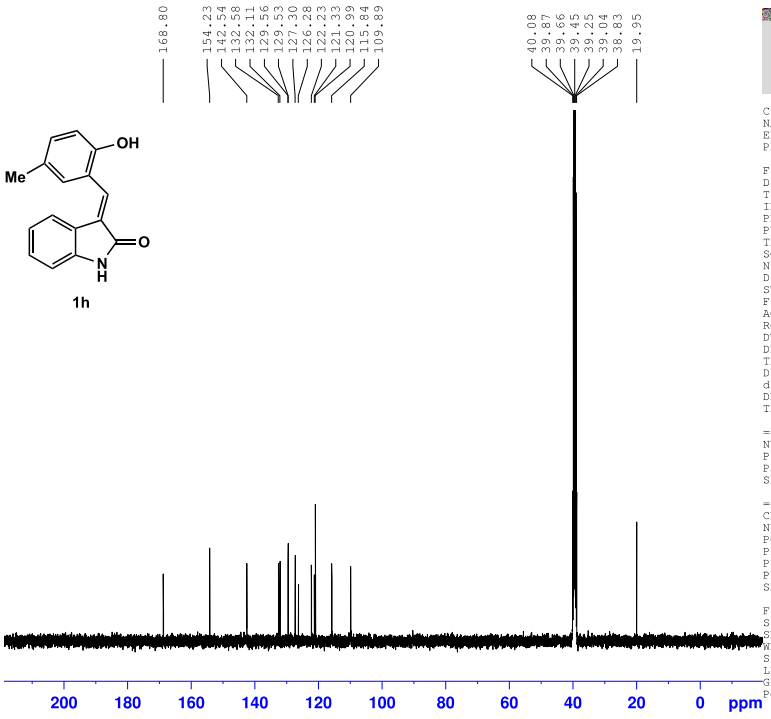


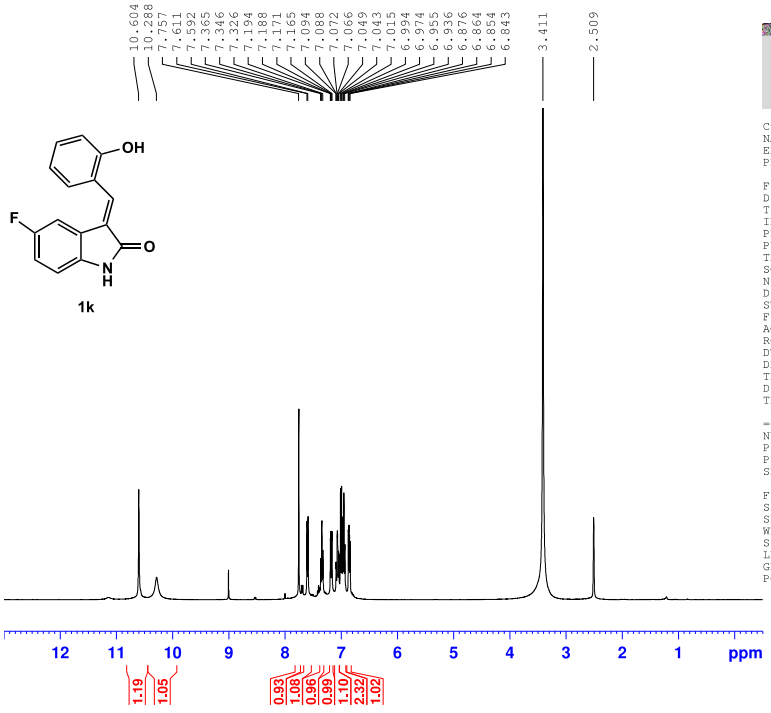

```
Current Data Parameters
NAME      2015-01-22 LJ-1h
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150122
Time               23.51
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT             DMSO
NS                   256
DS                     0
SWH            24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                  2050
DW                20.800 usec
DE                 6.50 usec
TE                300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                  20.70 usec
PL1                 -1.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              60.00 usec
PL12               10.77 dB
PL13               13.05 dB
PL2                -2.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6128193 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```




```
Current Data Parameters
NAME      2015-01-22 LJ-1k
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150123
Time               0.39
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT             DMSO
NS                    16
DS                     0
SWH             8223.685 Hz
FIDRES         0.125483 Hz
AQ             3.9846387 sec
RG                   128
DW                60.800 usec
DE                 6.50 usec
TE                295.5 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.80 usec
PL1                -2.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```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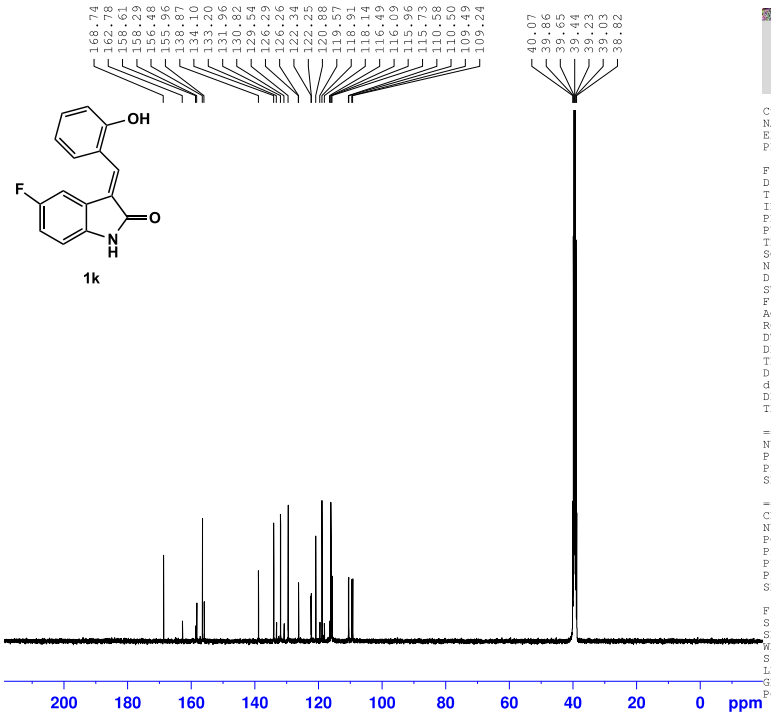


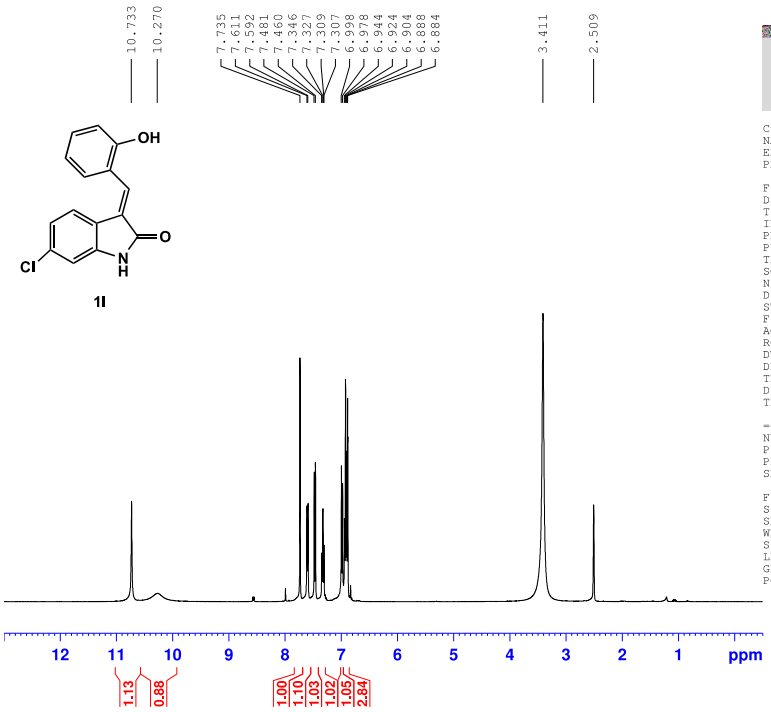

```
Current Data Parameters
NAME      2015-01-22 LJ-1k
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20150123
Time                2.37
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                 2048
DS                    0
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 2050
DW               20.800 usec
DE                6.50 usec
TE               297.8 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 20.70 usec
PL1                -1.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              60.00 usec
PL12               10.77 dB
PL13               13.05 dB
PL2                -2.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6128193 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



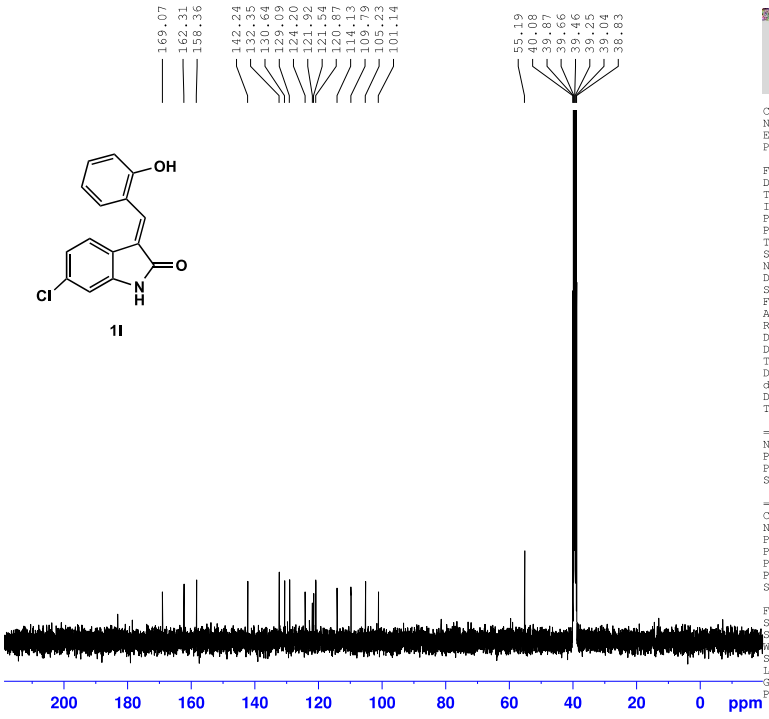

```
Current Data Parameters
NAME      2015-01-22 LJ-1c
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20150122
Time               20.44
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                65536
SOLVENT            DMSO
NS                   16
DS                    0
SWH            8223.685 Hz
FIDRES         0.125483 Hz
AQ             3.9846387 sec
RG                  128
DW               60.800 usec
DE                6.50 usec
TE               294.8 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.80 usec
PL1                -2.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```


47



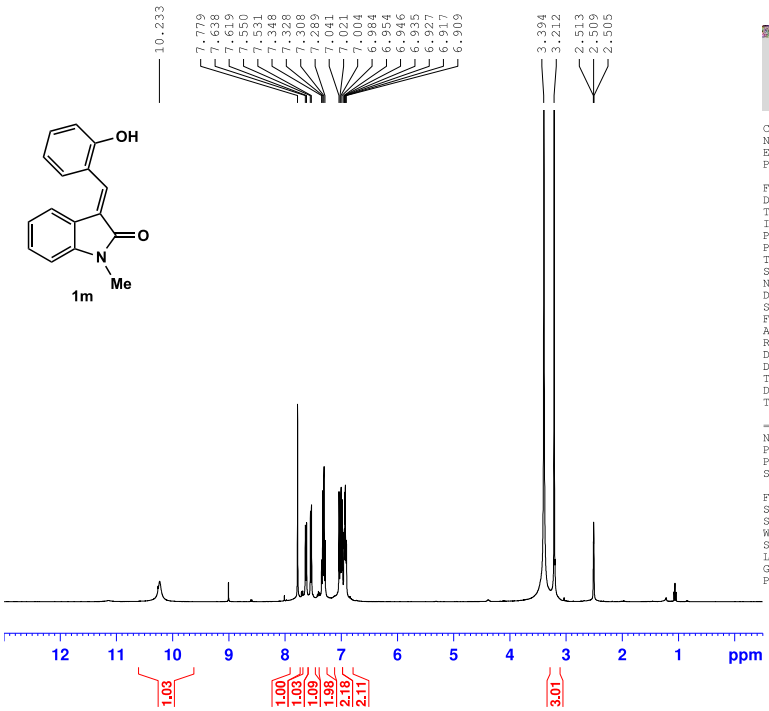

```
Current Data Parameters
NAME      2015-01-22 LJ-1l
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150122
Time               22.26
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD              65536
SOLVENT           DMSO
NS                  256
DS                    0
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 2050
DW               20.800 usec
DE                6.50 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 20.70 usec
PL1                -1.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              60.00 usec
PL12               10.77 dB
PL13               13.05 dB
PL2                -2.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6128193 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



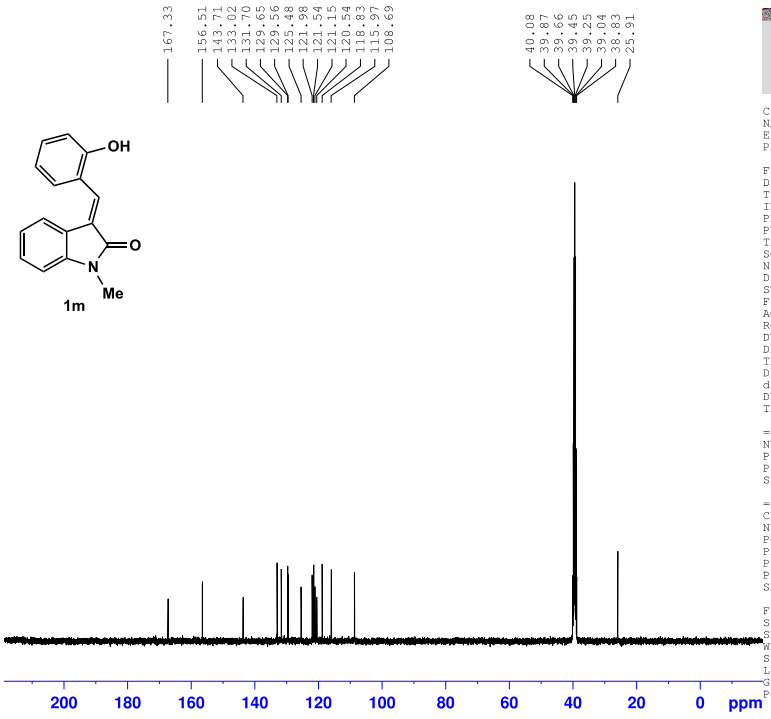

```
Current Data Parameters
NAME      2015-01-22 LJ-1m
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150123
Time               0.16
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD              65536
SOLVENT           DMSO
NS                   16
DS                    0
SWH            8223.685 Hz
FIDRES         0.125483 Hz
AQ             3.9846387 sec
RG                  114
DW               60.800 usec
DE                6.50 usec
TE               295.3 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 1H
P1                 13.80 usec
PL1                -2.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```


48



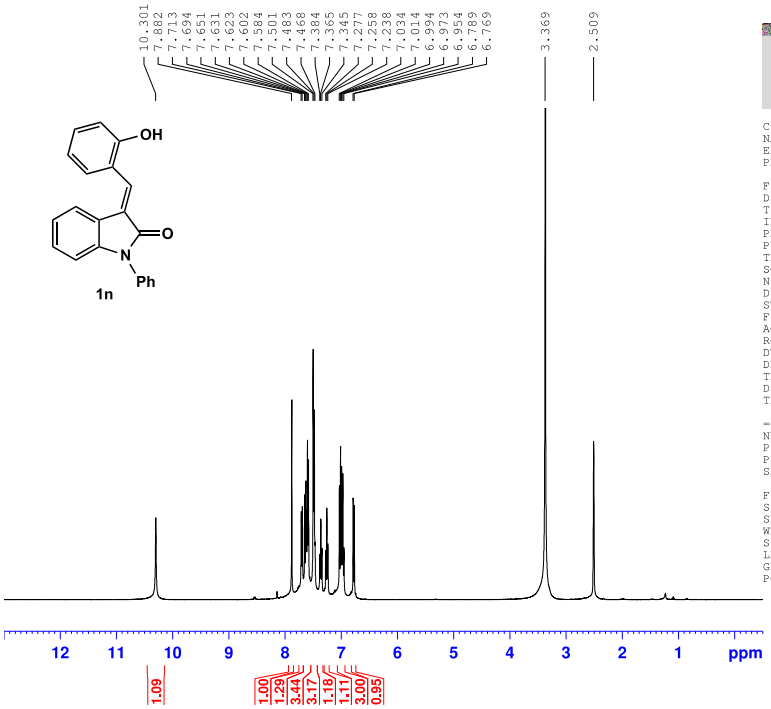

```
Current Data Parameters
NAME      2015-01-22 LJ-1m
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150123
Time                0.33
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                   256
DS                     0
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                  2050
DW                20.800 usec
DE                 6.50 usec
TE                300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 20.70 usec
PL1                -1.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              60.00 usec
PL12               10.77 dB
PL13               13.05 dB
PL2                -2.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF           100.6128193 MHz
WDW                    EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```




```
Current Data Parameters
NAME      2015-01-22 LJ-1n
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150122
Time               20.23
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT            DMSO
NS                   16
DS                    0
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9846387 sec
RG                   256
DW                60.800 usec
DE                 6.50 usec
TE                294.8 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 1H
P1                 13.80 usec
PL1                -2.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF           400.1300000 MHz
WDW                    EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```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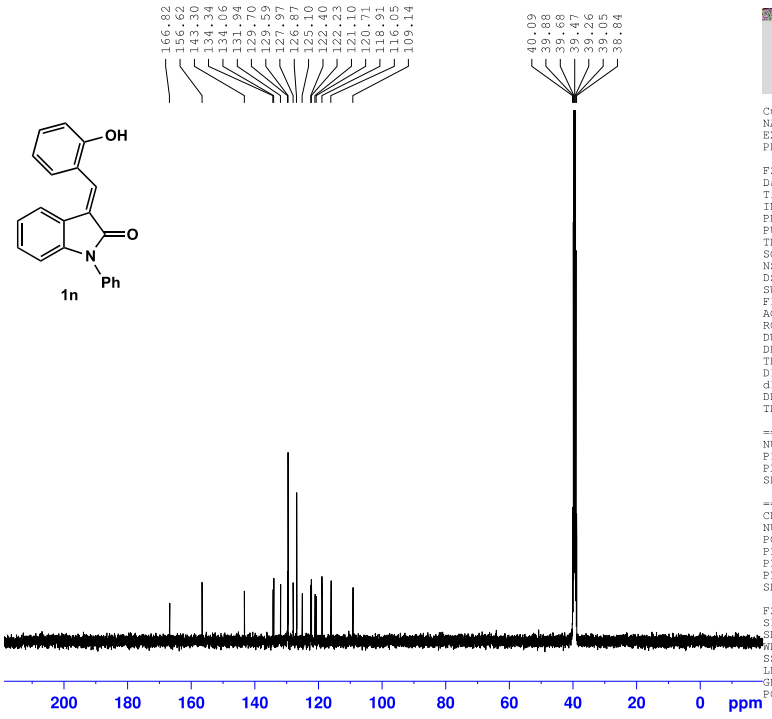


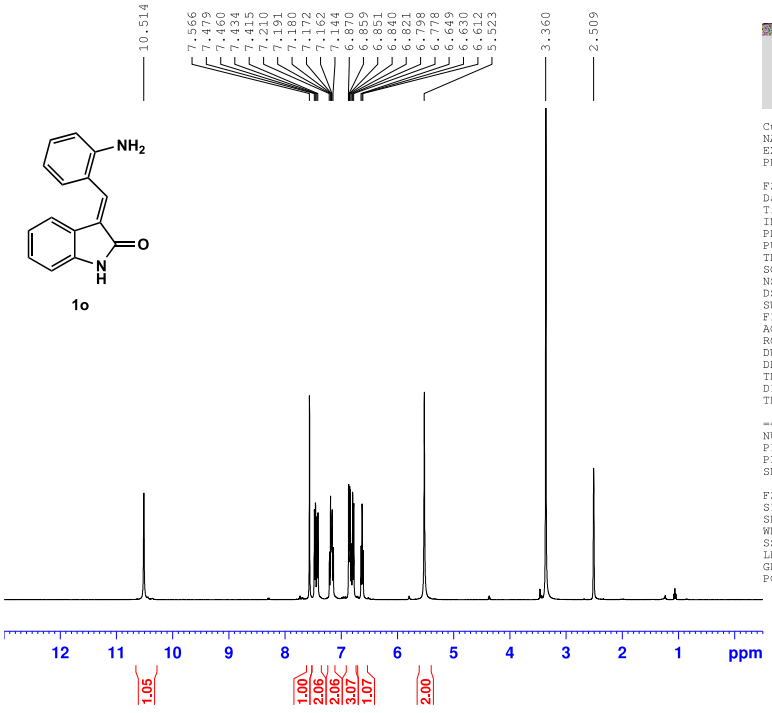

```
Current Data Parameters
NAME      2015-01-22 LJ-1n
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20150122
Time               20.39
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT             DMSO
NS                   256
DS                     0
SWH            24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                  2050
DW                20.800 usec
DE                 6.50 usec
TE                300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 20.70 usec
PL1                -1.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              60.00 usec
PL12               10.77 dB
PL13               13.05 dB
PL2                -2.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6128193 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



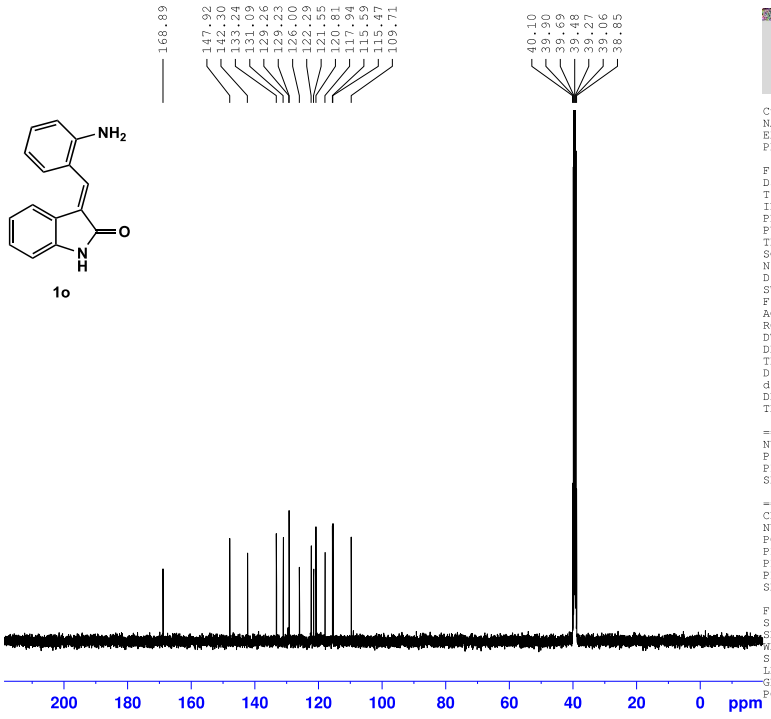

```
Current Data Parameters
NAME      2015-01-22 LJ-1o
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20150123
Time               4.46
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT             DMSO
NS                    16
DS                     0
SWH             8223.685 Hz
FIDRES         0.125483 Hz
AQ             3.9846387 sec
RG                   161
DW                60.800 usec
DE                 6.50 usec
TE                296.8 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.80 usec
PL1                -2.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```


50



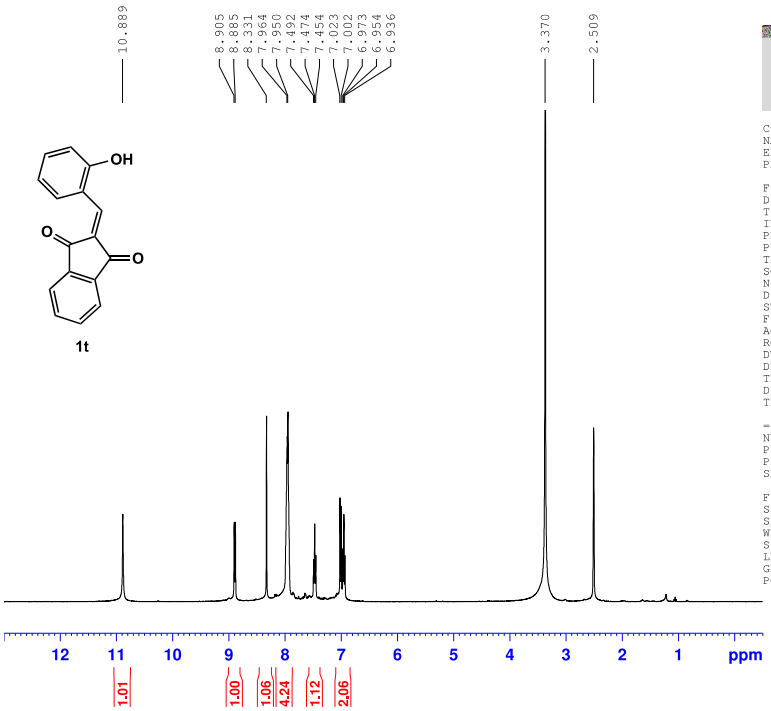

```
Current Data Parameters
NAME      2015-01-22 LJ-1o
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150123
Time                5.02
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                   256
DS                     0
SWH            24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                  2050
DW                20.800 usec
DE                 6.50 usec
TE                300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 20.70 usec
PL1                -1.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              60.00 usec
PL12               10.77 dB
PL13               13.05 dB
PL2                -2.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF           100.6128193 MHz
WDW                    EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```




```
Current Data Parameters
NAME      2015-01-22 LJ-1t
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150122
Time               21.49
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT            DMSO
NS                   16
DS                    0
SWH             8223.685 Hz
FIDRES         0.125483 Hz
AQ             3.9846387 sec
RG                   287
DW                60.800 usec
DE                 6.50 usec
TE                294.5 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 1H
P1                 13.80 usec
PL1                -2.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF           400.1300000 MHz
WDW                    EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```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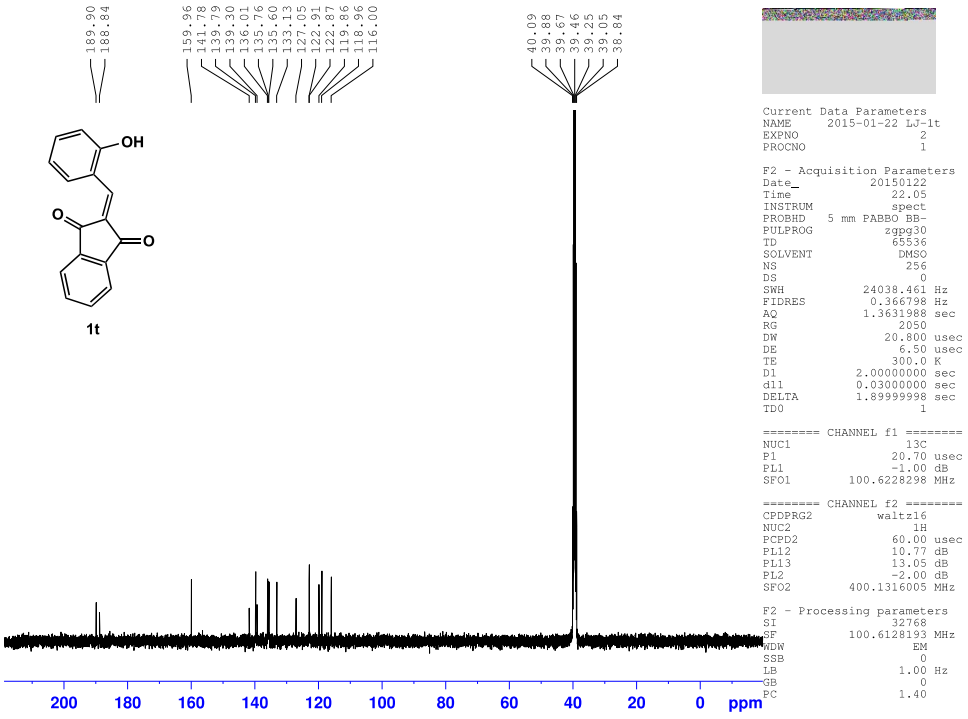
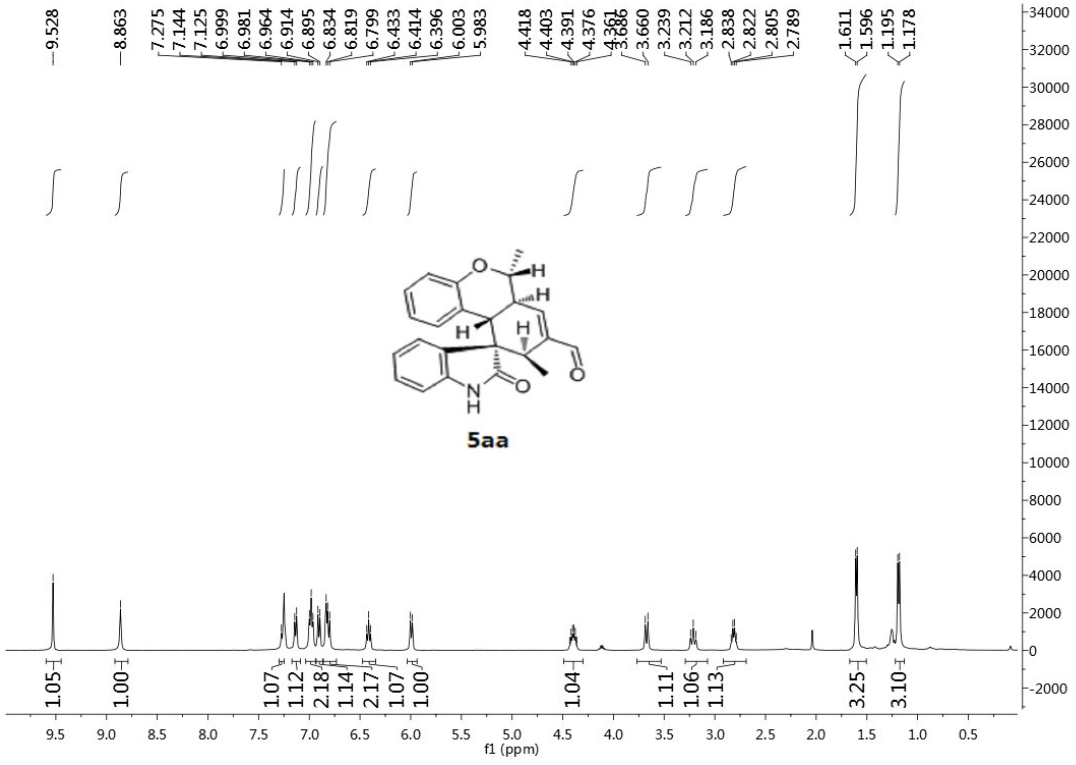
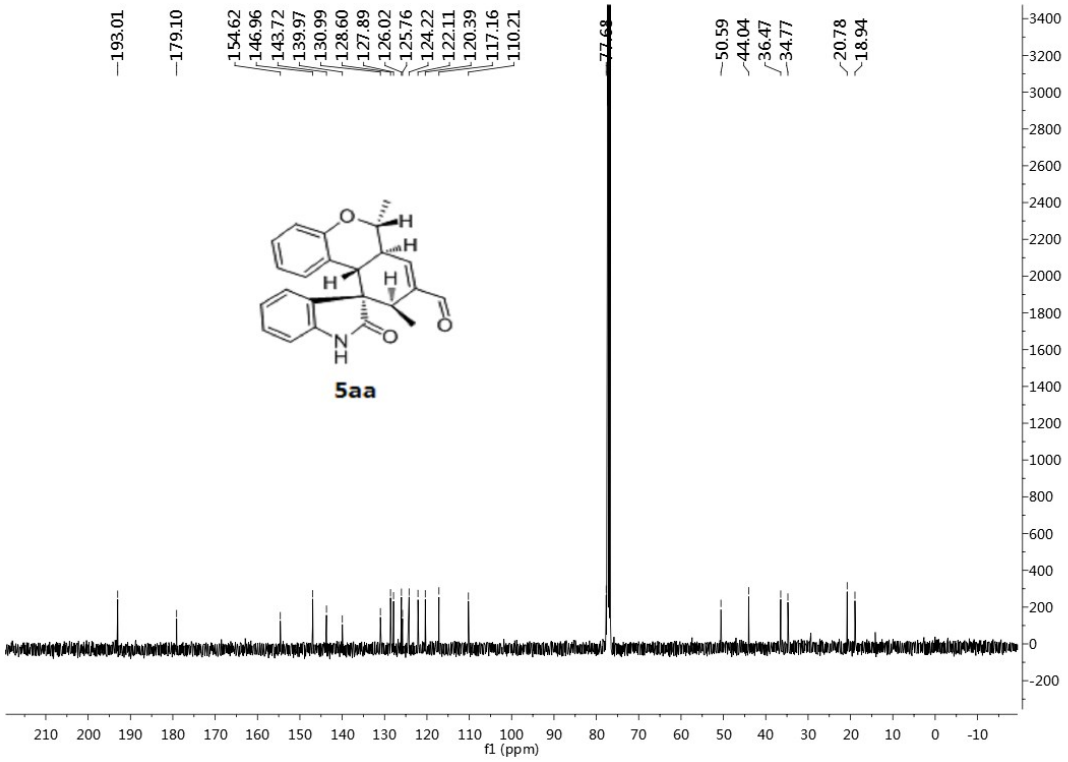
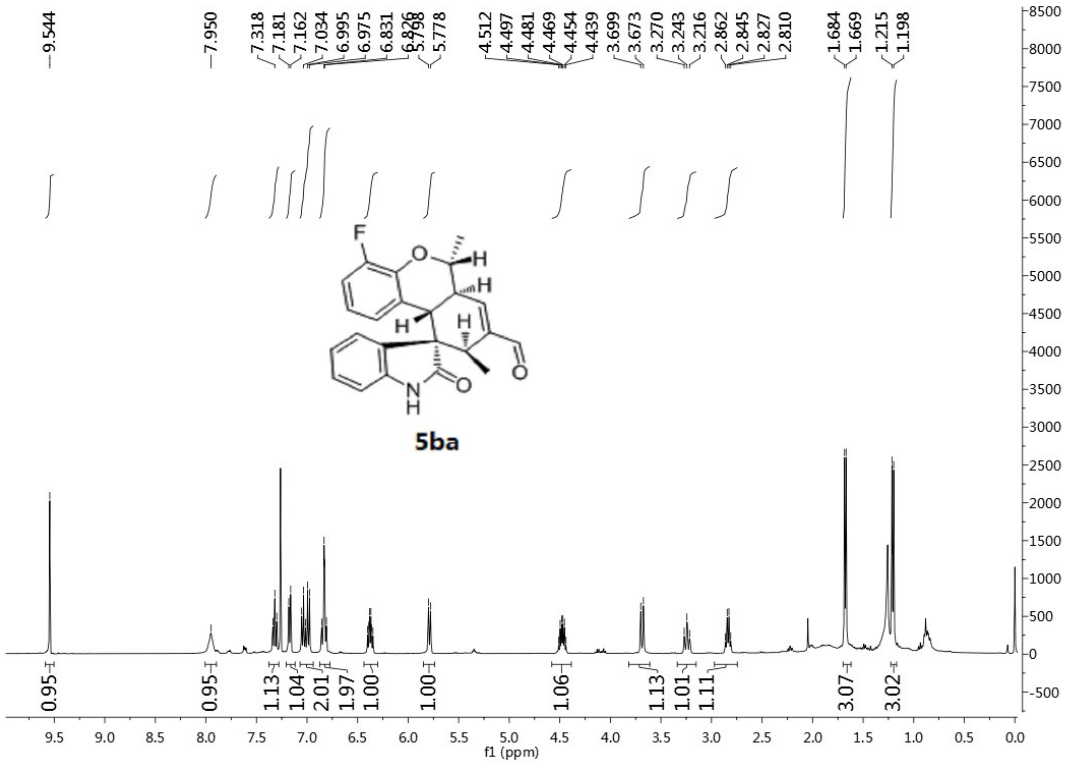

189.90
188.84
159.96
141.78
139.79
139.30
136.01
135.76
135.60
133.13
127.05
122.91
122.87
119.86
118.96
116.00
40.09
39.88
39.67
39.46
39.25
39.05
38.84
OH
O
O
1t
200
180
160
140
120
100
80
60
40
20
0
ppm
Current Data Parameters
NAME 2015-01-22 LJ-1t
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150122
Time 22.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 256
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 20.70 usec
PL1 -1.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 60.00 usec
PL12 10.77 dB
PL13 13.05 dB
PL2 -2.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6128193 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


9.528
8.863
7.275
7.144
7.125
6.999
6.981
6.964
6.914
6.895
6.834
6.819
6.799
6.433
6.414
6.396
6.003
5.983
4.418
4.403
4.391
4.376
4.361
3.660
3.239
3.212
3.186
2.838
2.822
2.805
2.789
1.611
1.596
1.195
1.178
H
H
H
H
O
O
N
H
5aa
1.05
1.00
1.07
1.12
2.18
1.14
2.17
1.07
1.00
1.04
1.11
1.06
1.13
3.25
3.10
f1 (ppm)

52

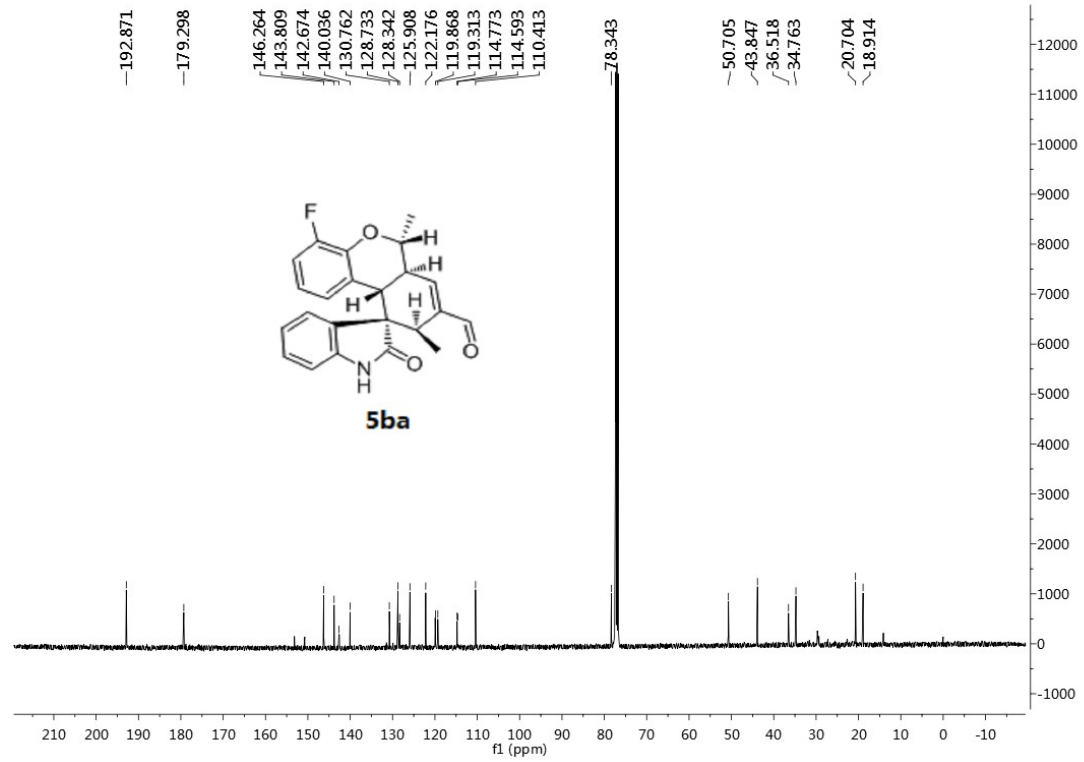

193.01
179.10
154.62
146.96
143.72
139.97
130.99
128.60
127.89
126.02
125.76
124.22
122.11
120.39
117.16
110.21
77.68
50.59
44.04
36.47
34.77
20.78
18.94
f1 (ppm)

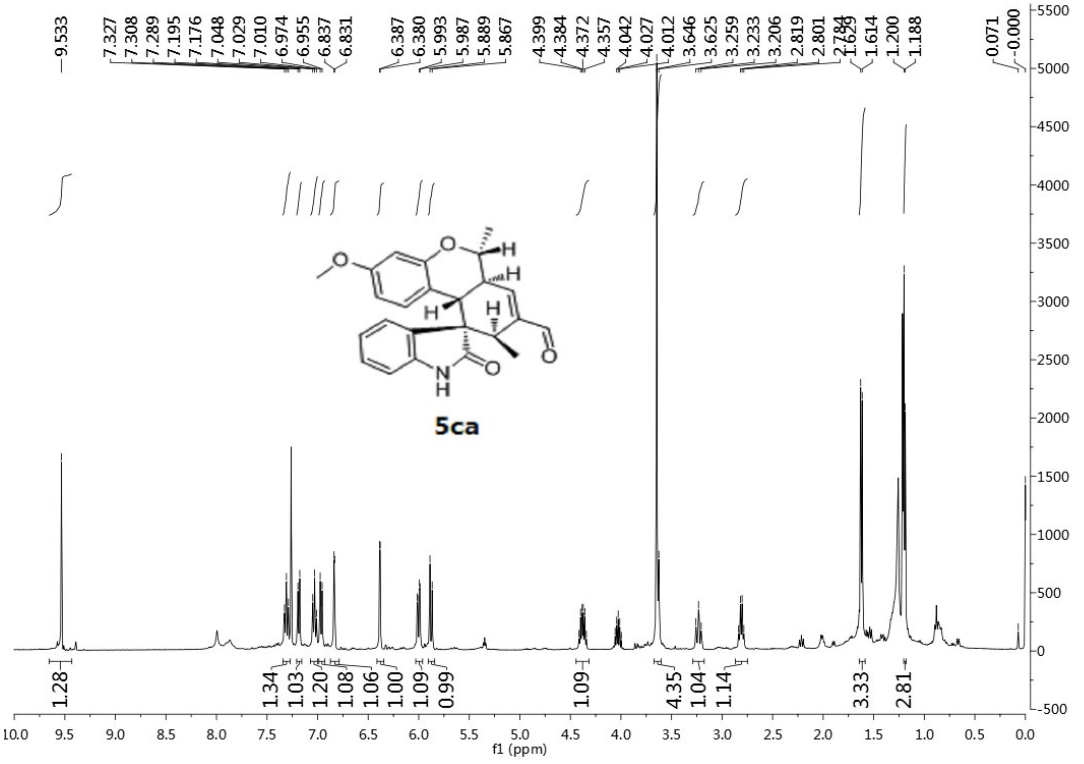
5aa


9.544
7.950
7.318
7.181
7.162
7.034
6.995
6.975
6.831
5.798
5.778
4.512
4.497
4.481
4.469
4.454
4.439
3.699
3.673
3.270
3.243
3.216
2.862
2.845
2.827
2.810
1.684
1.669
1.215
1.198
0.95
0.95
1.13
1.04
2.01
1.97
1.00
1.00
1.06
1.13
1.01
1.11
3.07
3.02
f1 (ppm)

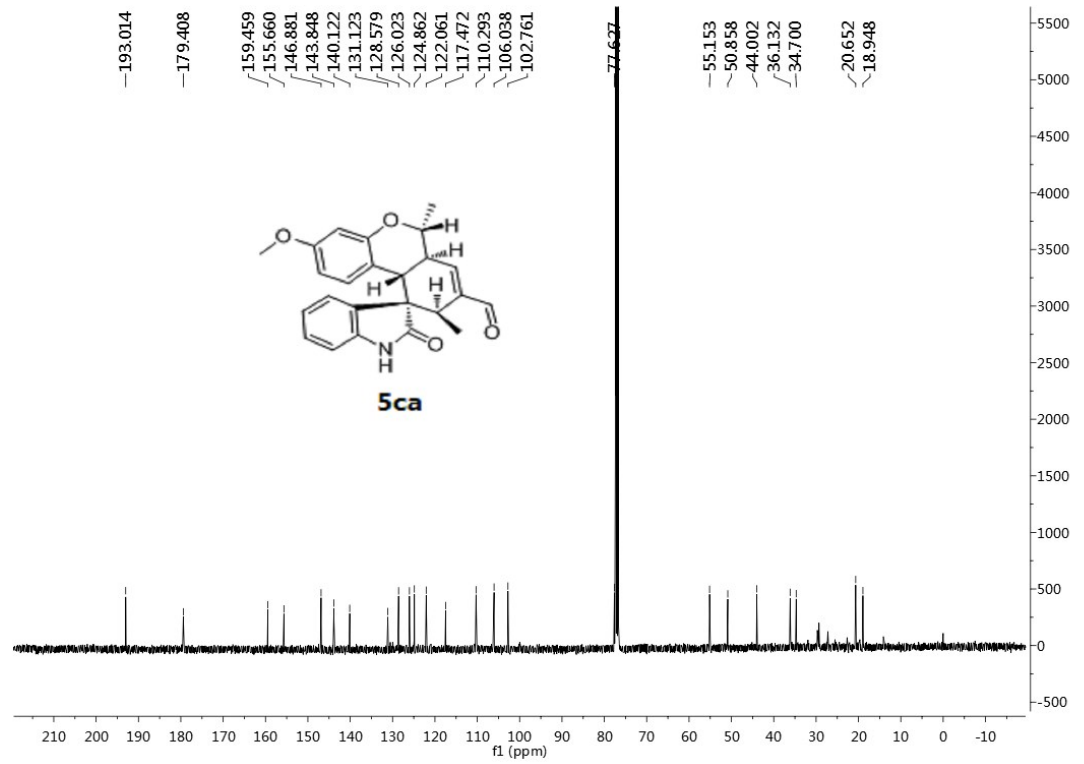
5ba

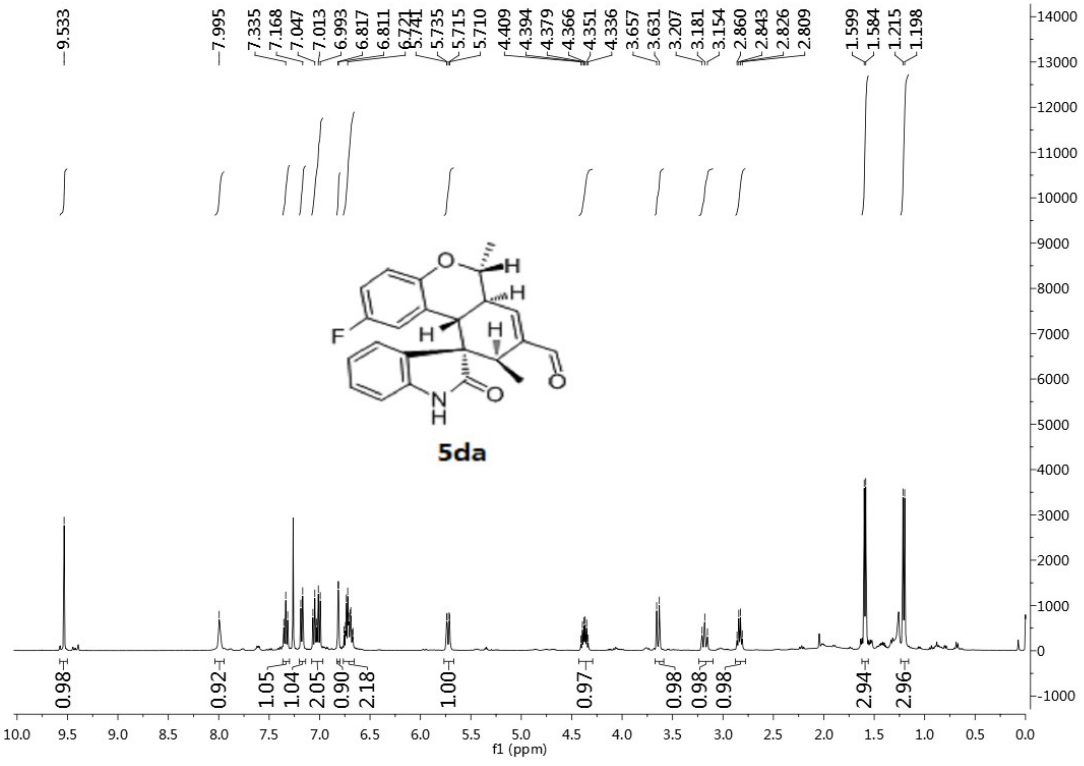
53


192.871
179.298
146.264
143.809
142.674
140.036
130.762
128.733
128.342
125.908
122.176
119.868
119.313
114.773
114.593
110.413
78.343
50.705
43.847
36.518
34.763
20.704
18.914
F
O
H
H
H
H
O
N
H
O
5ba
f1 (ppm)

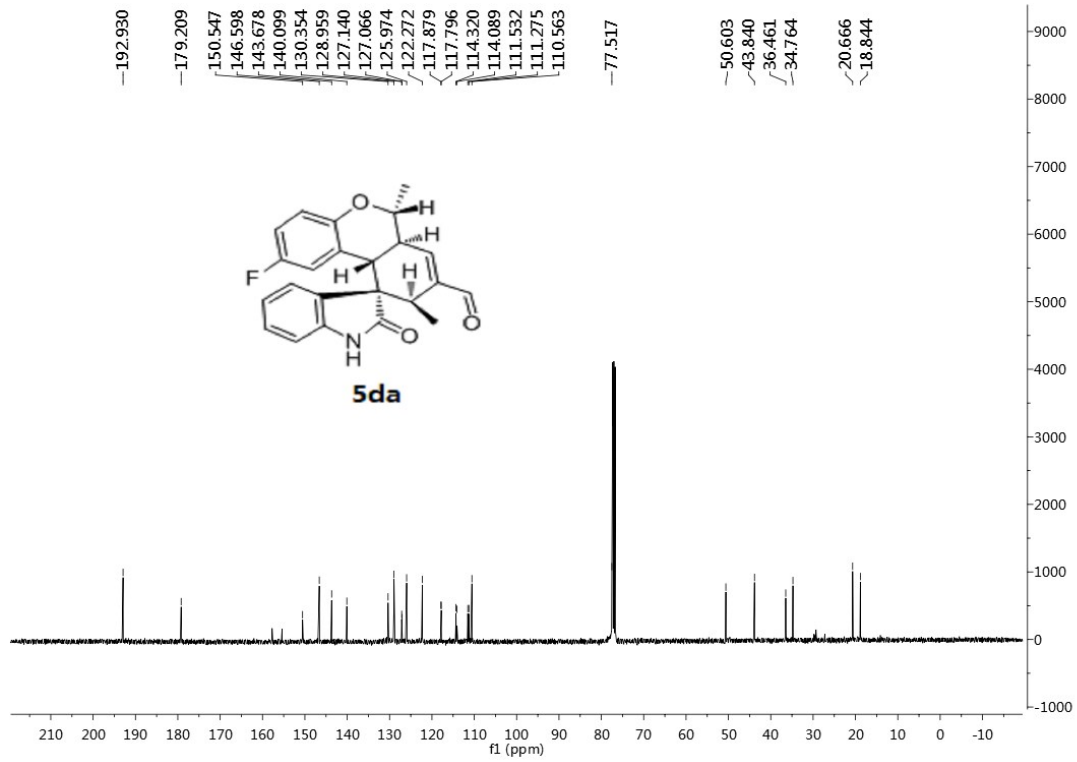

9.533
7.327
7.308
7.289
7.195
7.176
7.048
7.029
7.010
6.974
6.955
6.837
6.831
6.387
6.380
5.993
5.987
5.889
5.867
4.399
4.384
4.372
4.357
4.042
4.027
4.012
3.646
3.625
3.259
3.233
3.206
2.819
2.801
1.614
1.200
1.188
0.071
-0.000
O
H
H
H
H
O
N
H
O
5ca
1.28
1.34
1.03
1.20
1.08
1.06
1.00
1.09
0.99
1.09
4.35
1.04
1.14
3.33
2.81
f1 (ppm)

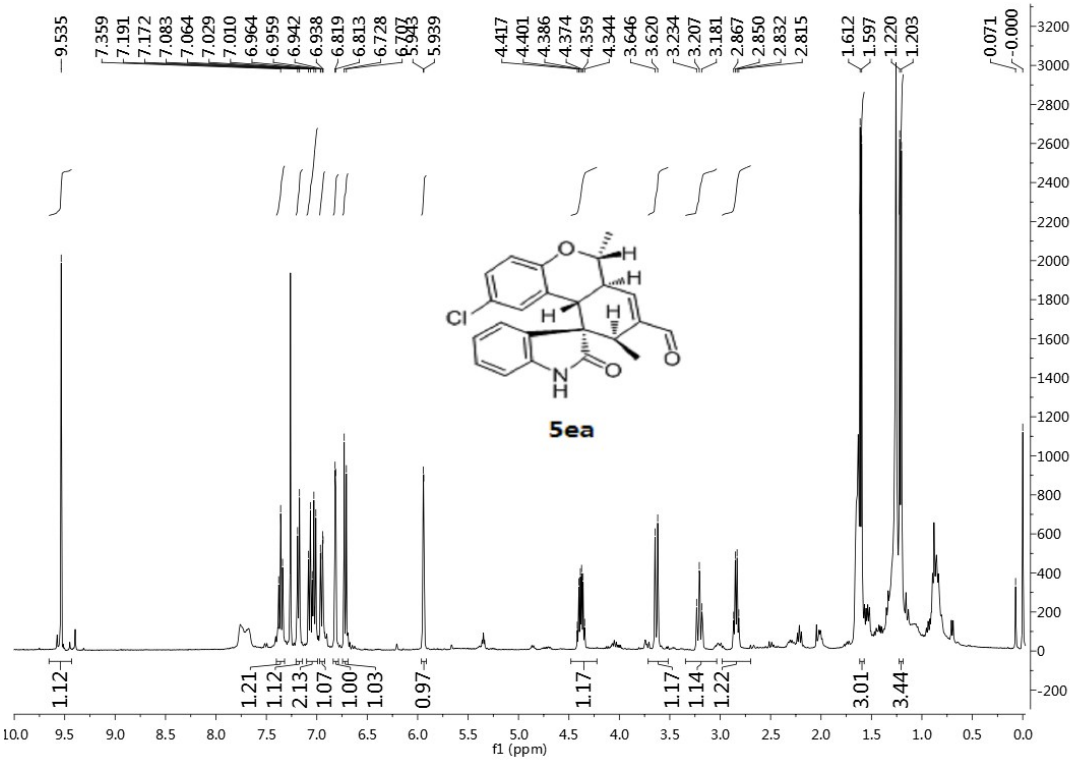
54


193.014
179.408
159.459
155.660
146.881
143.848
140.122
131.123
128.579
126.023
124.862
122.061
117.472
110.293
106.038
102.761
77.637
55.153
50.858
44.002
36.132
34.700
20.652
18.948
5ca
f1 (ppm)

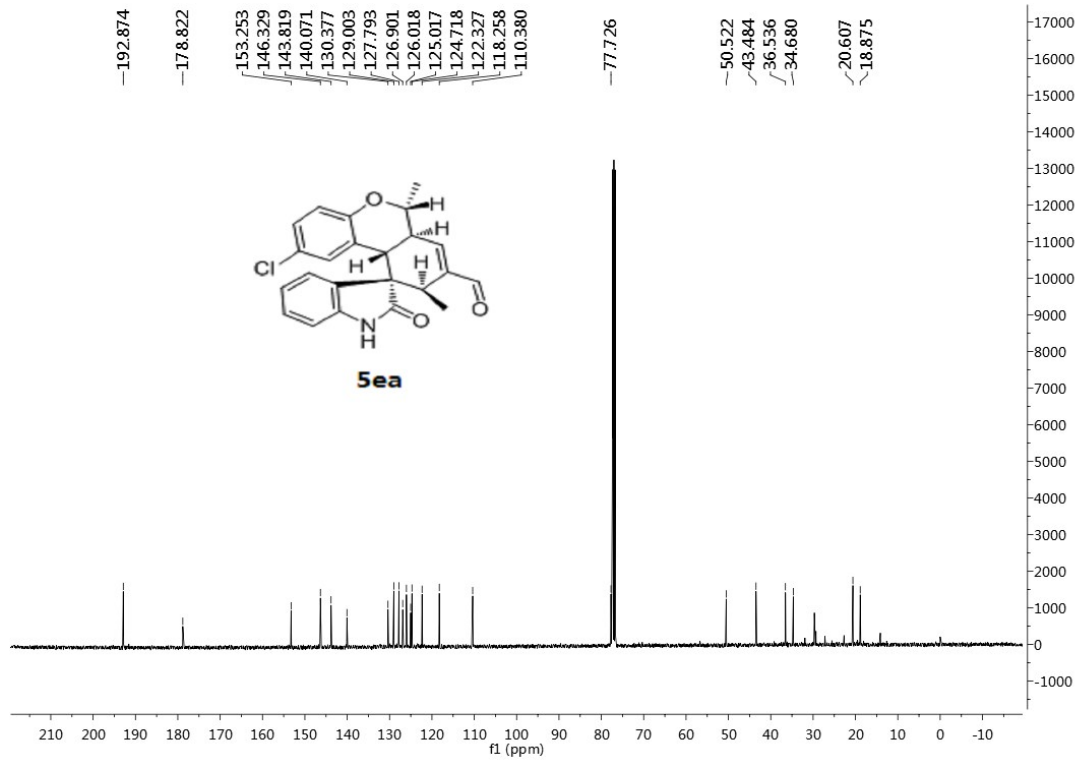

9.533
7.995
7.335
7.168
7.047
7.013
6.993
6.817
6.811
6.721
5.741
5.735
5.715
5.710
4.409
4.394
4.379
4.366
4.351
4.336
3.657
3.631
3.207
3.181
3.154
2.860
2.843
2.826
2.809
1.599
1.584
1.215
1.198
5da
0.98
0.92
1.05
1.04
2.05
0.90
2.18
1.00
0.97
0.98
0.98
0.98
2.94
2.96
f1 (ppm)

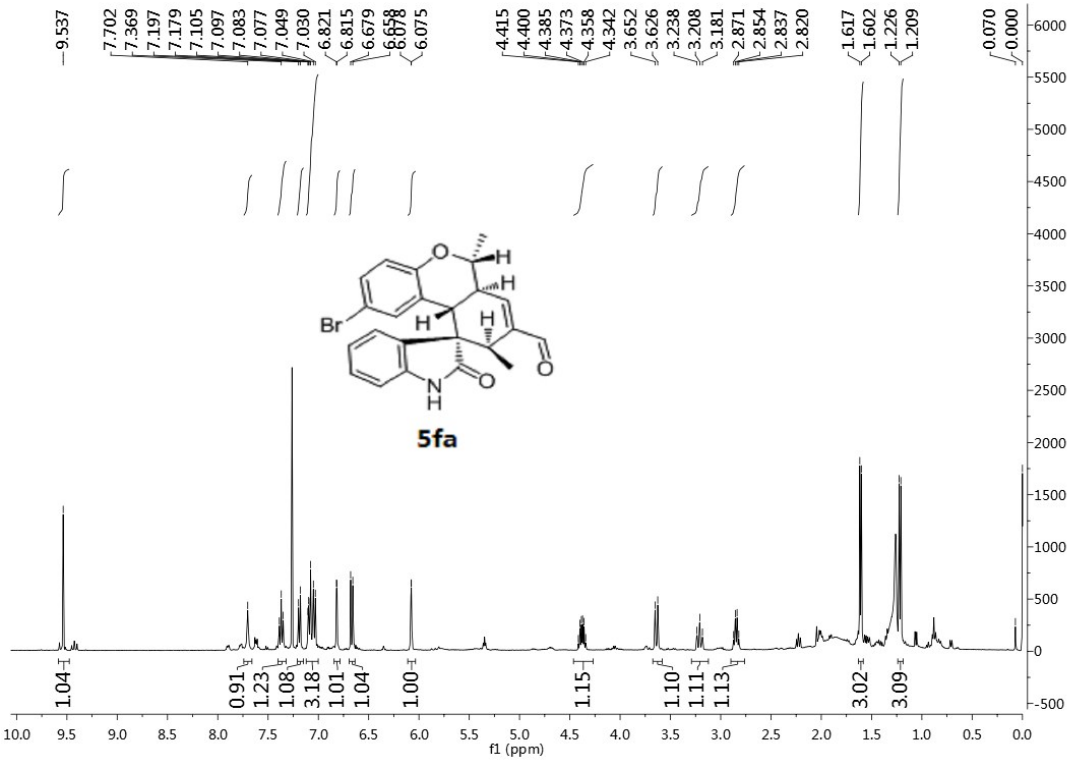
55


192.930
179.209
150.547
146.598
143.678
140.099
130.354
128.959
127.140
127.066
125.974
122.272
117.879
117.796
114.320
114.089
111.532
111.275
110.563
77.517
50.603
43.840
36.461
34.764
20.666
18.844
F
O
H
N
5da
f1 (ppm)

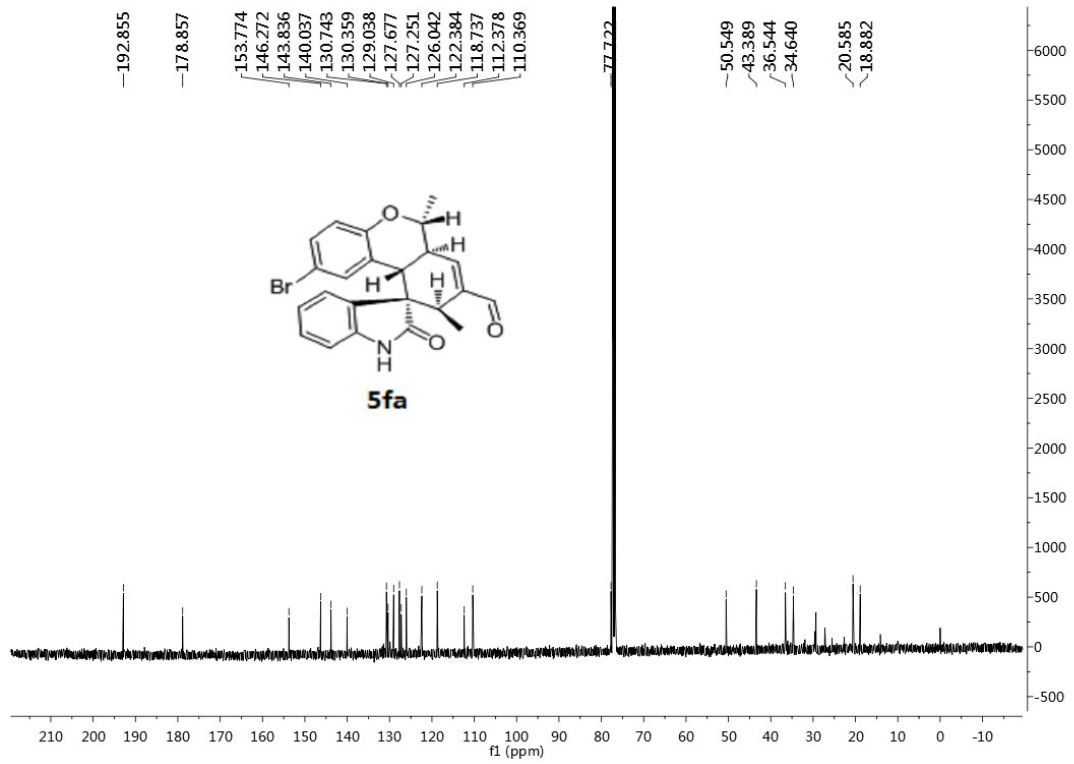

9.535
7.359
7.191
7.172
7.083
7.064
7.029
7.010
6.964
6.959
6.942
6.938
6.819
6.813
6.728
5.939
4.417
4.401
4.386
4.374
4.359
4.344
3.646
3.620
3.234
3.207
3.181
2.867
2.850
2.832
2.815
1.612
1.597
1.220
1.203
0.071
-0.000
Cl
O
H
N
5ea
1.12
1.21
1.12
2.13
1.07
1.00
1.03
0.97
1.17
1.17
1.14
1.22
3.01
3.44
f1 (ppm)

56


192.874
178.822
153.253
146.329
143.819
140.071
130.377
129.003
127.793
126.901
126.018
125.017
124.718
122.327
118.258
110.380
77.726
50.522
43.484
36.536
34.680
20.607
18.875
Cl
O
H
N
O
5ea
f1 (ppm)


9.537
7.702
7.369
7.197
7.179
7.105
7.097
7.083
7.077
7.049
7.030
6.821
6.815
6.679
6.658
6.078
6.075
4.415
4.400
4.385
4.373
4.358
4.342
3.652
3.626
3.238
3.208
3.181
2.871
2.854
2.837
2.820
1.617
1.602
1.226
1.209
0.070
0.000
Br
O
H
N
O
5fa
1.04
0.91
1.23
1.08
3.18
1.01
1.04
1.00
1.15
1.10
1.11
1.13
3.02
3.09
f1 (ppm)

57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178.857
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140.037
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130.359
129.038
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127.251
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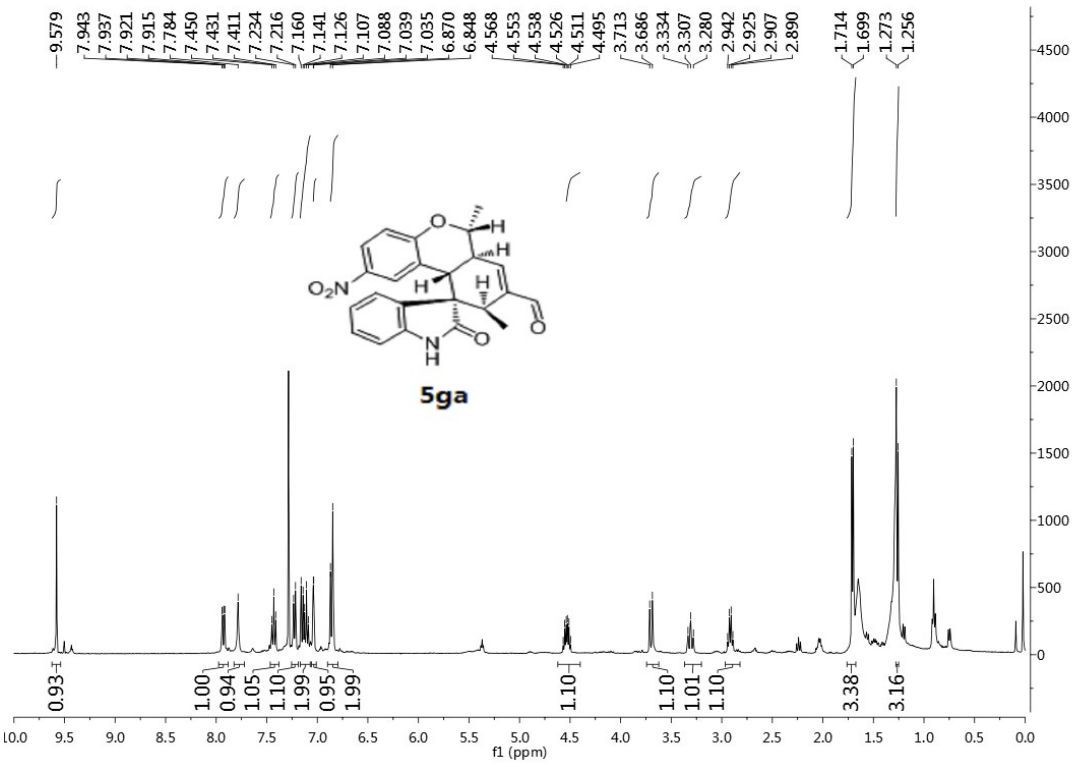
122.384
118.737
112.378
110.369
77.722
50.549
43.389
36.544
34.640
20.585
18.882
Br
O
H
N
O
f1 (ppm)

5fa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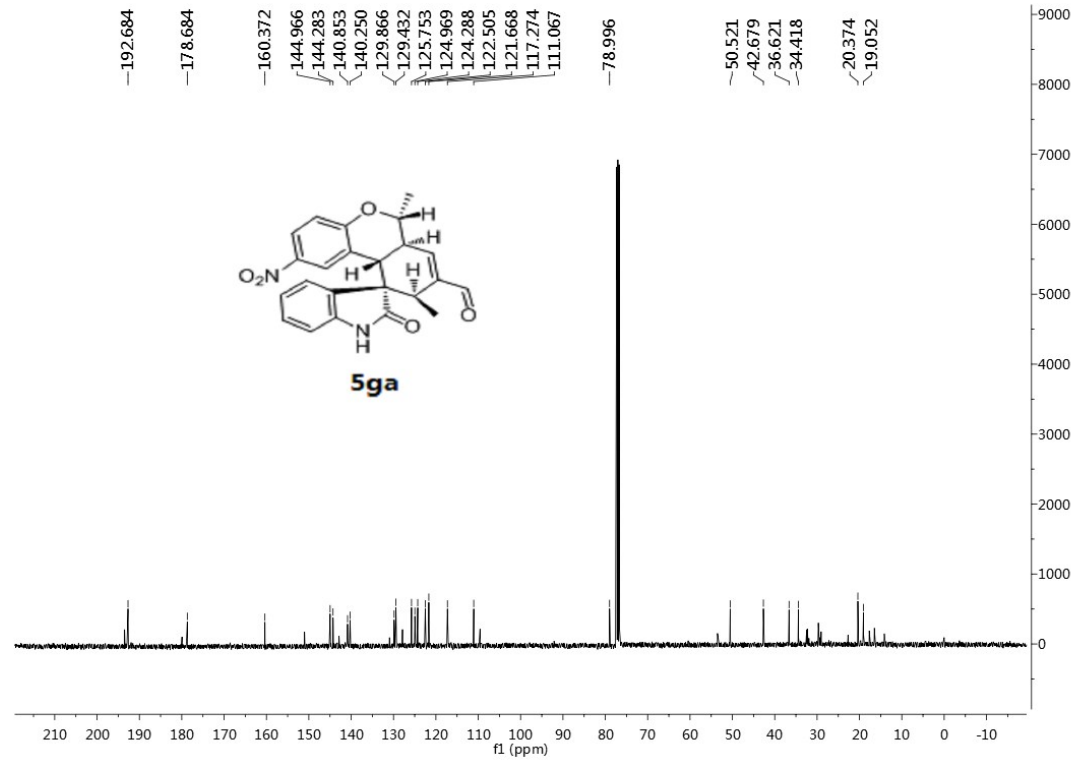
7.234
7.216
7.160
7.141
7.126
7.107
7.088
7.039
7.035
6.870
6.848
4.568
4.553
4.538
4.526
4.511
4.495
3.713
3.686
3.334
3.307
3.280
2.942
2.925
2.907
2.890
1.714
1.699
1.273
1.256
O2N
O
H
N
O
0.93
1.00
0.94
1.05
1.10
1.99
0.95
1.99
1.10
1.10
1.01
1.10
3.38
3.16
f1 (ppm)

5ga

58


192.684
178.684
160.372
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144.283
140.853
140.250
129.866
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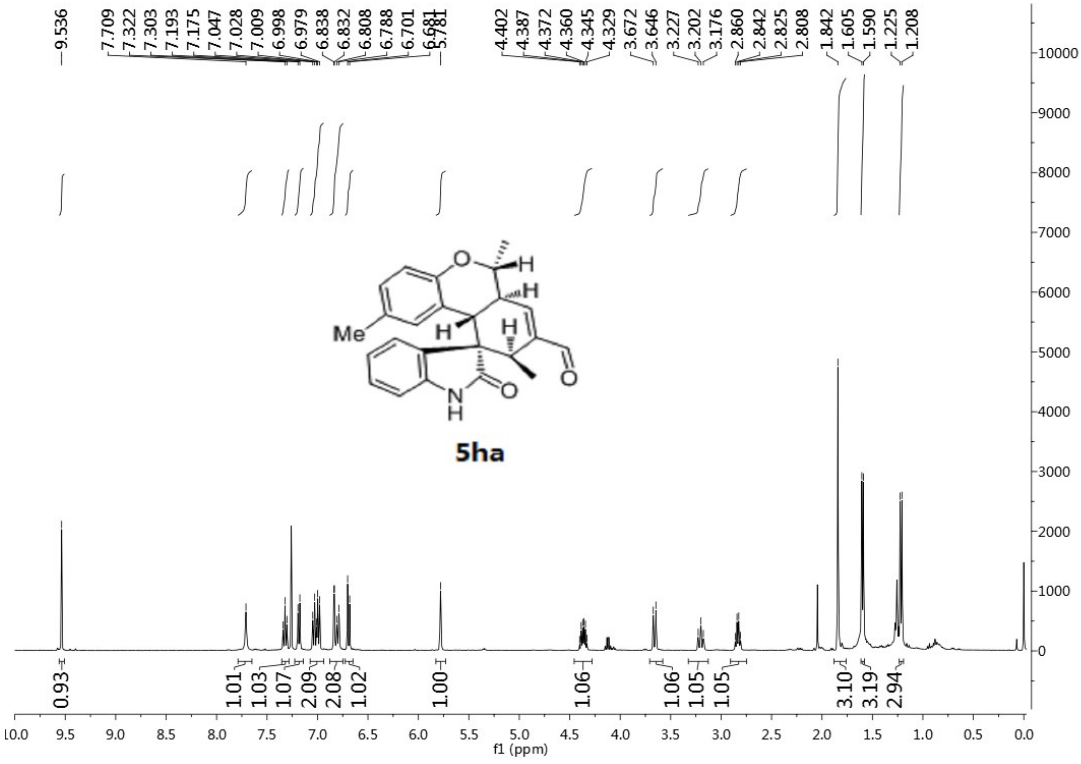
125.753
124.969
124.288
122.505
121.668
117.274
111.067
78.996
50.521
42.679
36.621
34.418
20.374
19.052
O2N
O
H
N
5ga
f1 (ppm)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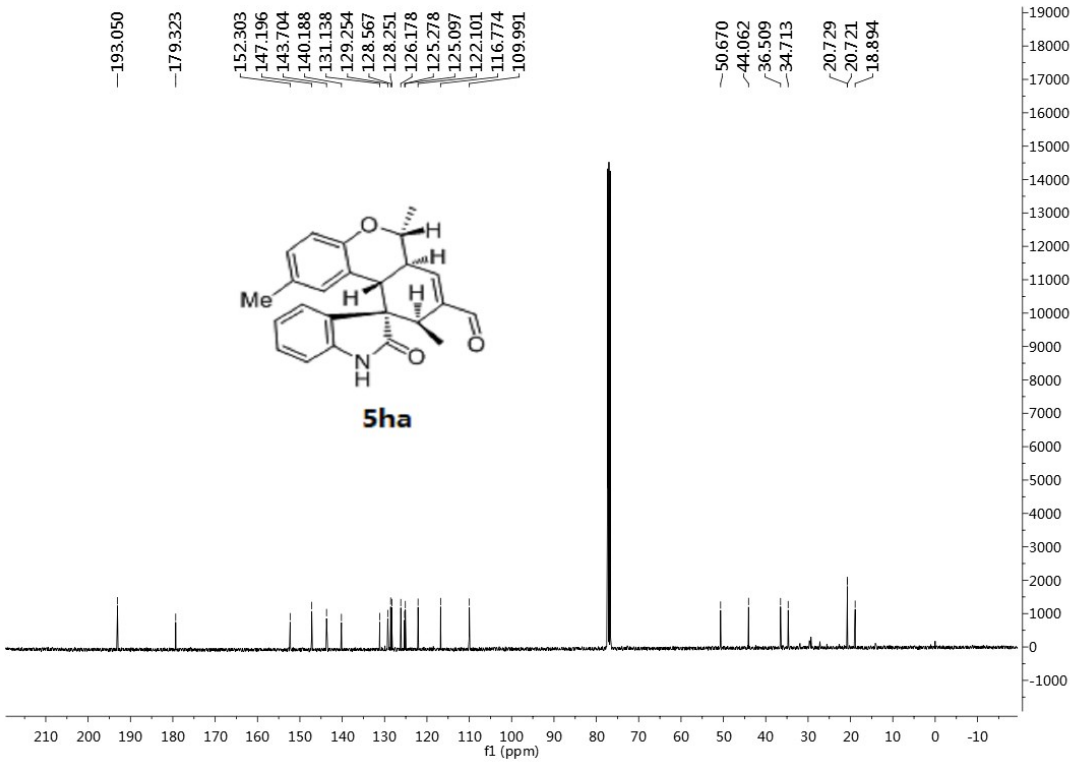
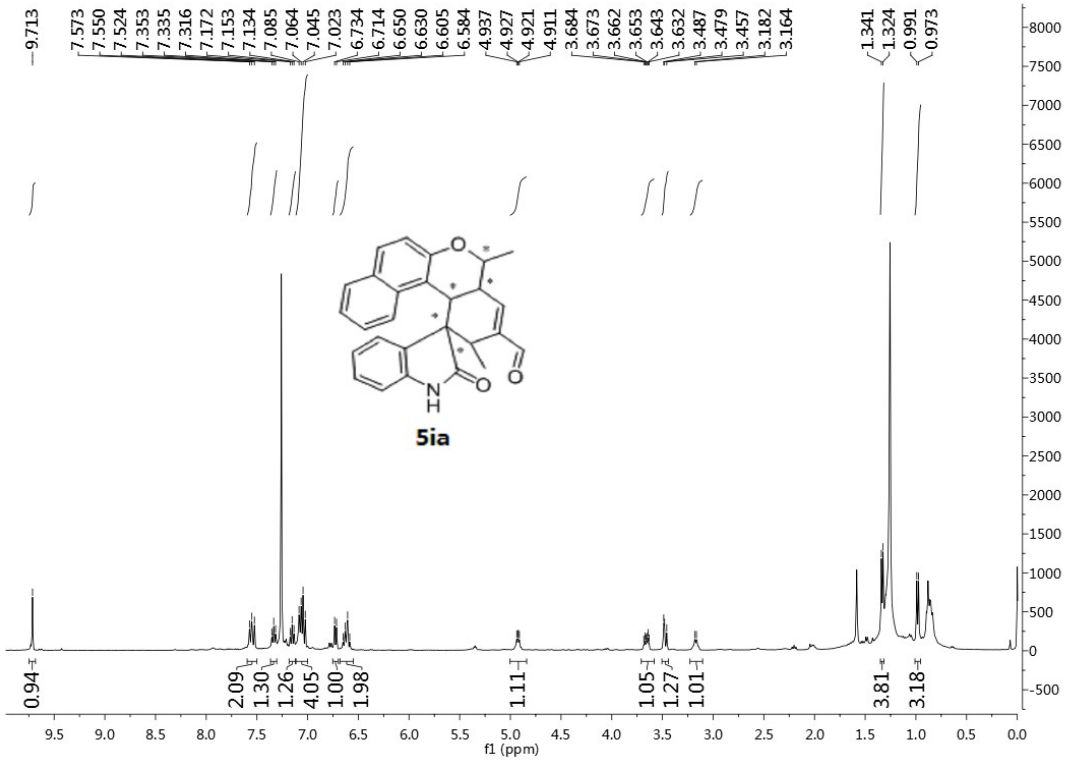
7.175
7.047
7.028
7.009
6.998
6.979
6.838
6.832
6.808
6.788
6.701
5.781
4.402
4.387
4.372
4.360
4.345
4.329
3.672
3.646
3.227
3.202
3.176
2.860
2.842
2.825
2.808
1.842
1.605
1.590
1.225
1.208
Me
O
H
N
5ha
0.93
1.01
1.03
1.07
2.09
2.08
1.02
1.00
1.06
1.06
1.05
1.05
3.10
3.19
2.94
f1 (ppm)

59


193.050
179.323
152.303
147.196
143.704
140.188
131.138
129.254
128.567
128.251
126.178
125.278
125.097
122.101
116.774
109.991
50.670
44.062
36.509
34.713
20.729
20.721
18.894
Me
5ha
f1 (ppm)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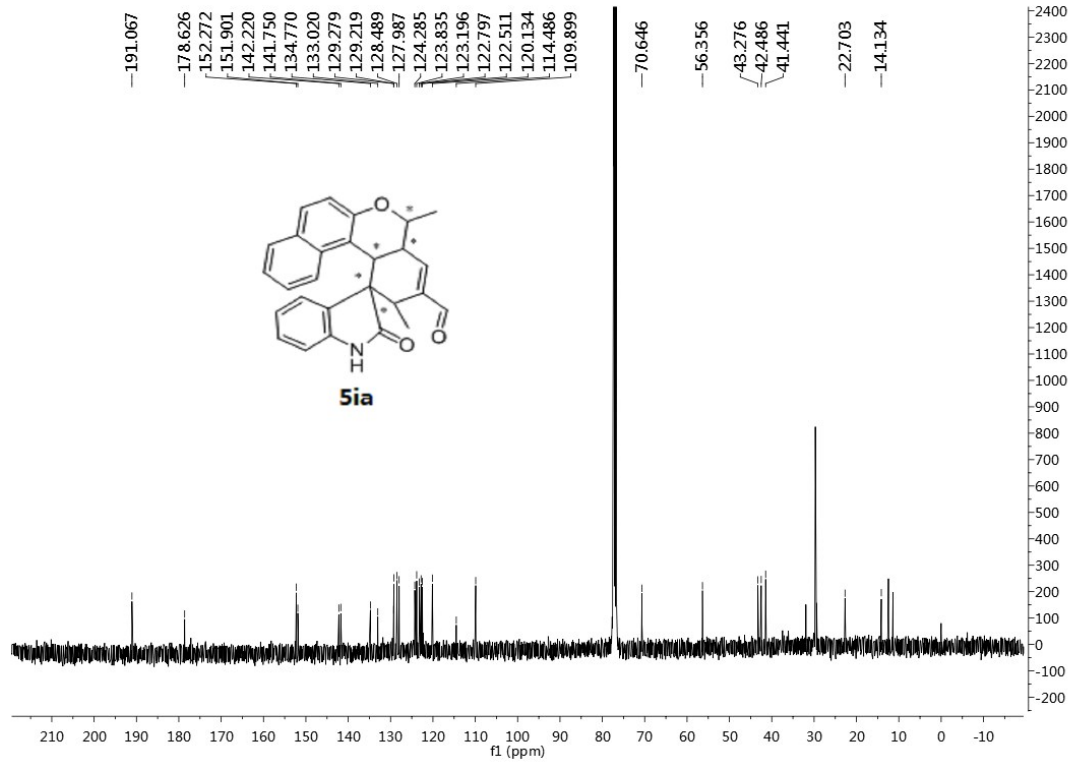
7.550
7.524
7.353
7.335
7.316
7.172
7.153
7.134
7.085
7.064
7.045
7.023
6.734
6.714
6.650
6.630
6.605
6.584
4.937
4.927
4.921
4.911
3.684
3.673
3.662
3.653
3.643
3.632
3.487
3.479
3.457
3.182
3.164
1.341
1.324
0.991
0.973
0.94
2.09
1.30
1.26
4.05
1.00
1.98
1.11
1.05
1.27
1.01
3.81
3.18
5ia
f1 (ppm)

60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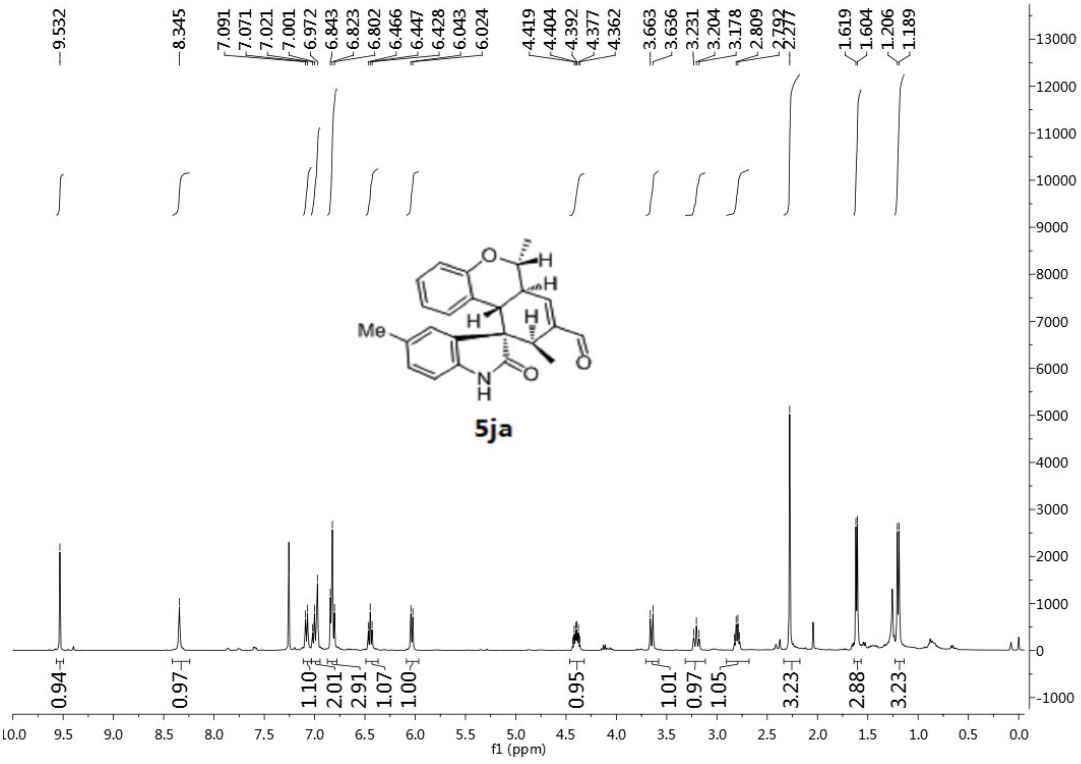
178.626
152.272
151.901
142.220
141.750
134.770
133.020
129.279
129.219
128.489
127.987
124.285
123.835
123.196
122.797
122.511
120.134
114.486
109.899
70.646
56.356
43.276
42.486
41.441
22.703
14.134
f1 (ppm)

5ia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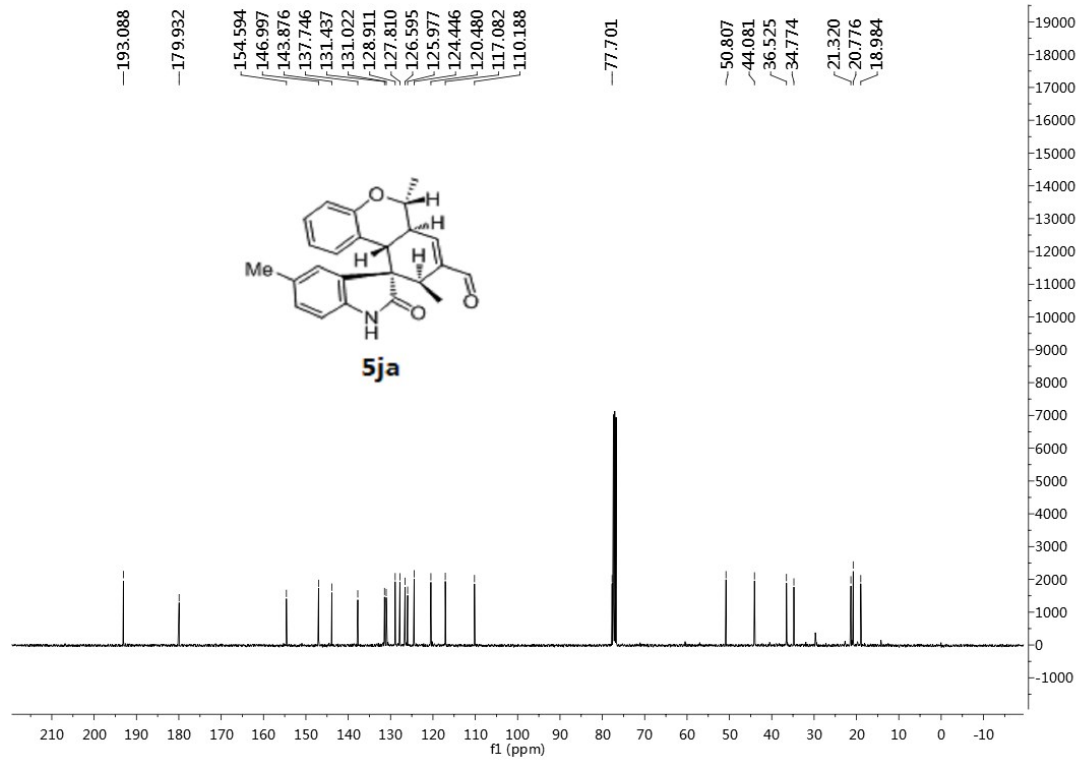
8.345
7.091
7.071
7.021
7.001
6.972
6.843
6.823
6.802
6.466
6.447
6.428
6.043
6.024
4.419
4.404
4.392
4.377
4.362
3.663
3.636
3.231
3.204
3.178
2.809
2.792
2.277
1.619
1.604
1.206
1.189
0.94
0.97
1.10
2.01
2.91
1.07
1.00
0.95
1.01
0.97
1.05
3.23
2.88
3.23
f1 (ppm)

5ja

61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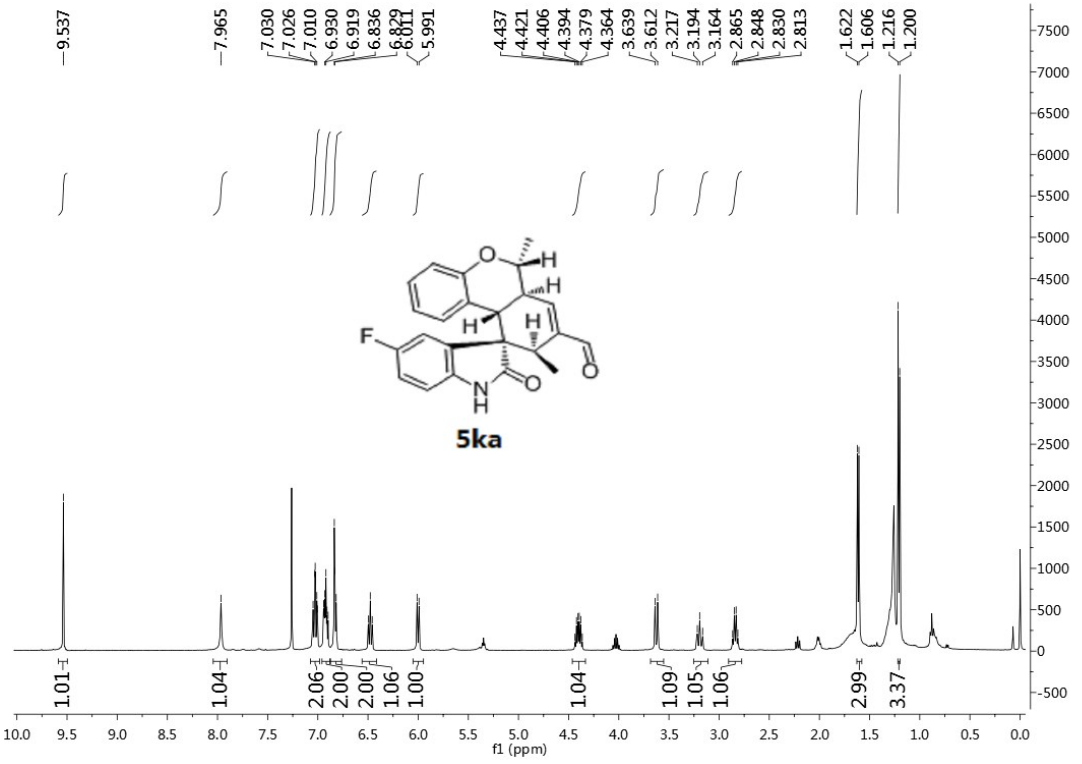
179.932
154.594
146.997
143.876
137.746
131.437
131.022
128.911
127.810
126.595
125.977
124.446
120.480
117.082
110.188
77.701
50.807
44.081
36.525
34.774
21.320
20.776
18.984
Me
O
H
N
O
f1 (ppm)

5ja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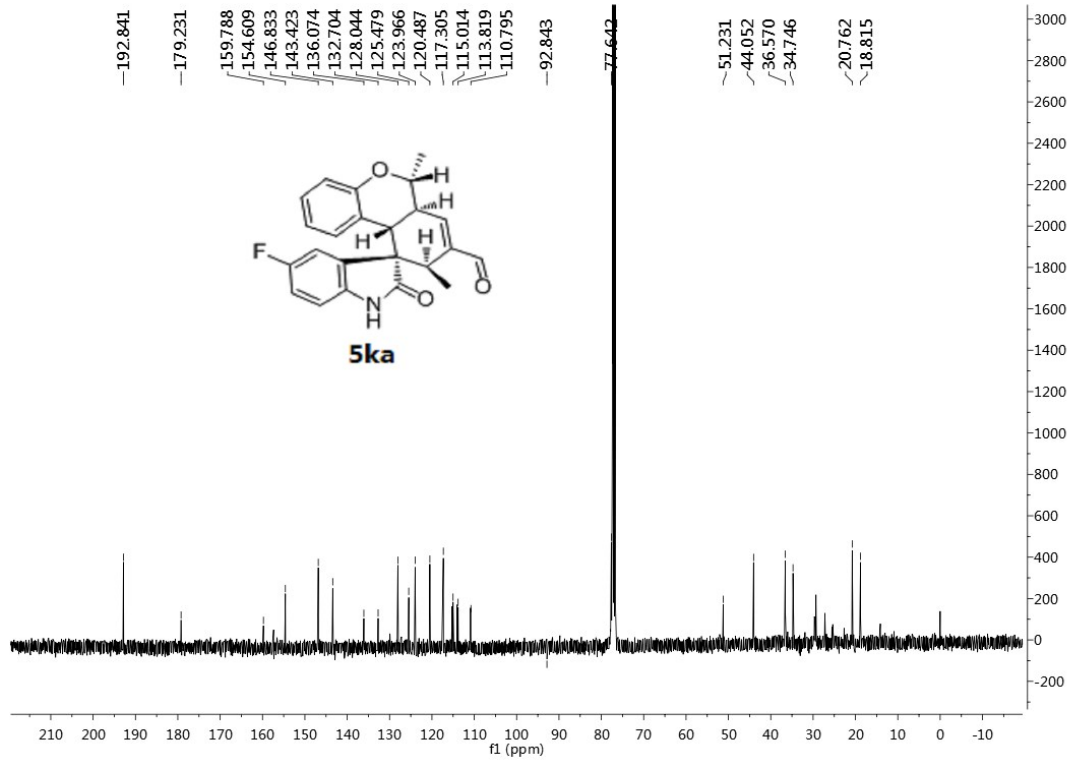
7.965
7.030
7.026
7.010
6.930
6.919
6.836
6.829
6.811
5.991
4.437
4.421
4.406
4.394
4.379
4.364
3.639
3.612
3.217
3.194
3.164
2.865
2.848
2.830
2.813
1.622
1.606
1.216
1.200
F
O
H
N
O
1.01
1.04
2.06
2.00
2.00
1.06
1.00
1.04
1.09
1.05
1.06
2.99
3.37
f1 (ppm)

5ka

62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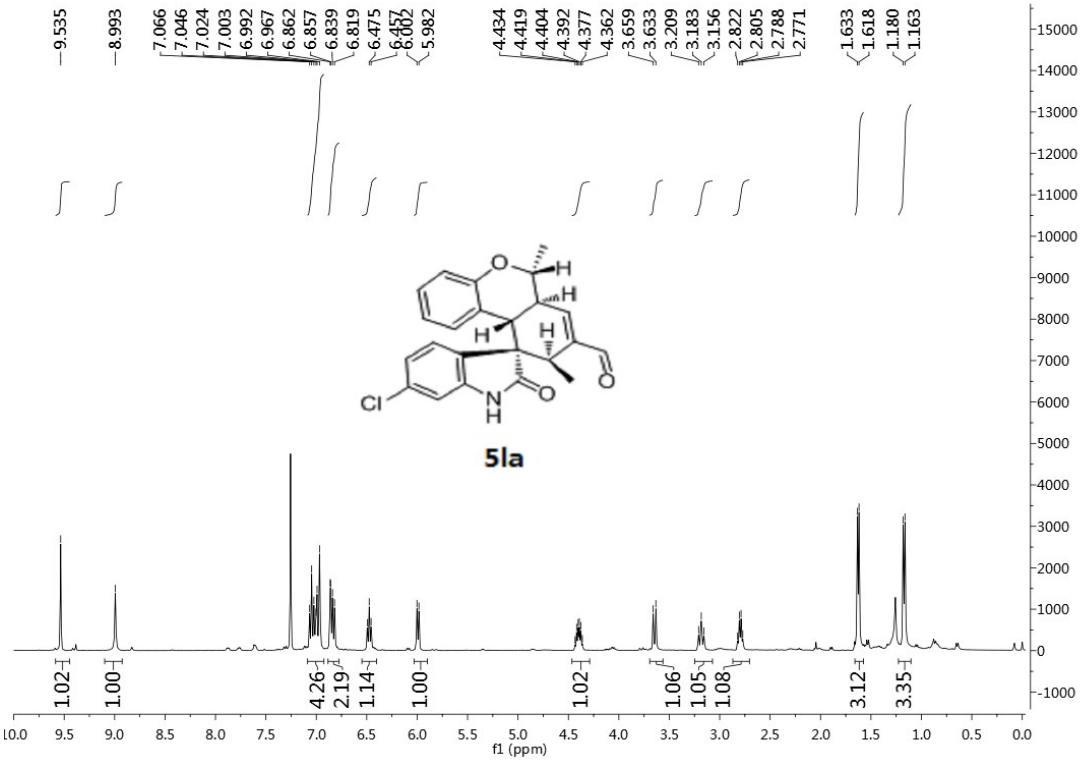
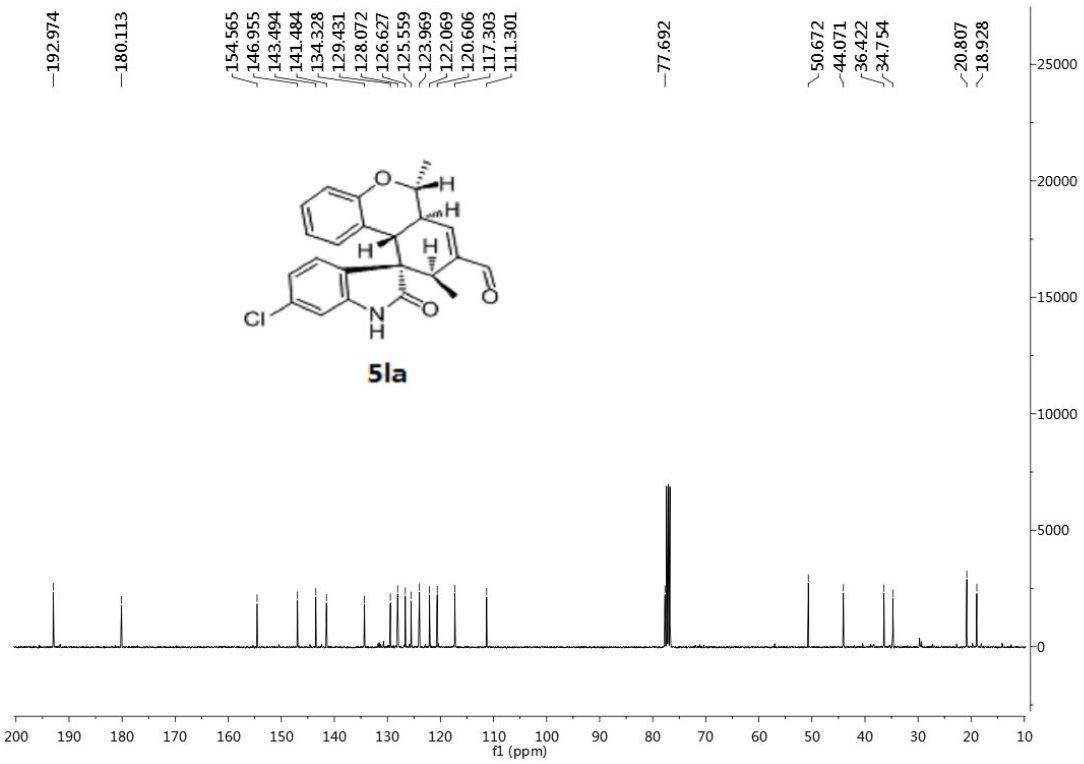
179.231
159.788
154.609
146.833
143.423
136.074
132.704
128.044
125.479
123.966
120.487
117.305
115.014
113.819
110.795
92.843
77.642
51.231
44.052
36.570
34.746
20.762
18.815
5ka
f1 (ppm)


9.535
8.993
7.066
7.046
7.024
7.003
6.992
6.967
6.862
6.857
6.839
6.819
6.475
6.457
6.402
5.982
4.434
4.419
4.404
4.392
4.377
4.362
3.659
3.633
3.209
3.183
3.156
2.822
2.805
2.788
2.771
1.633
1.618
1.180
1.163
5la
1.02
1.00
4.26
2.19
1.14
1.00
1.02
1.06
1.05
1.08
3.12
3.35
f1 (ppm)

63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180.113
154.565
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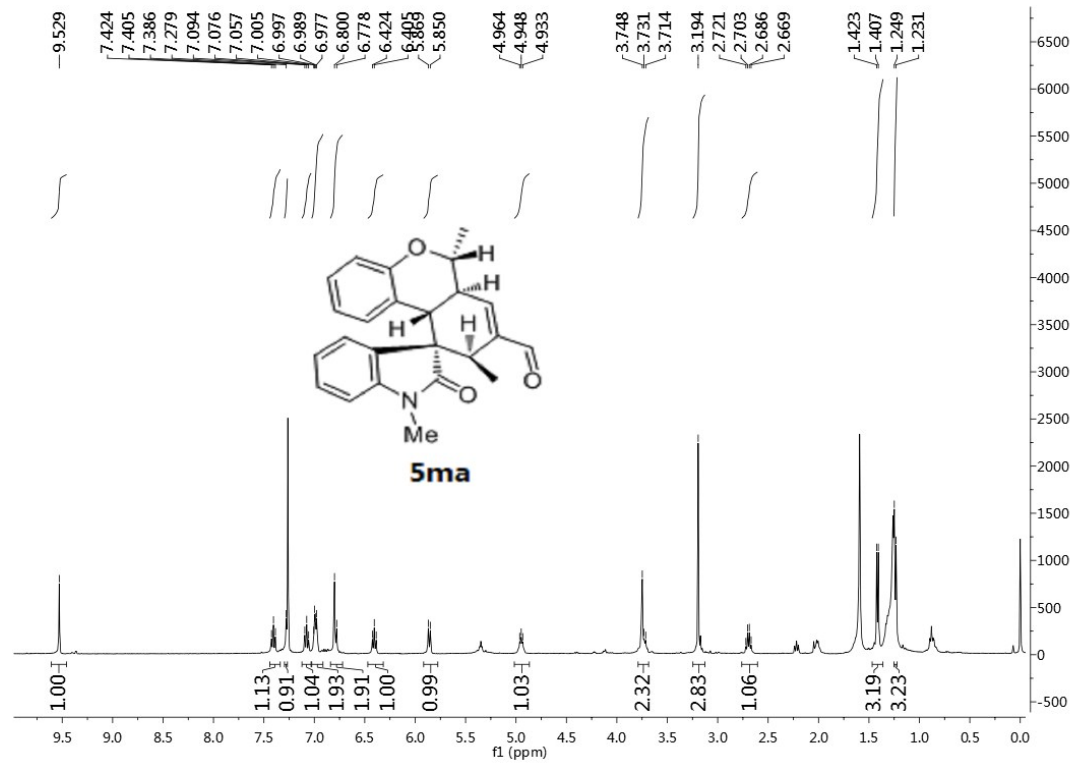
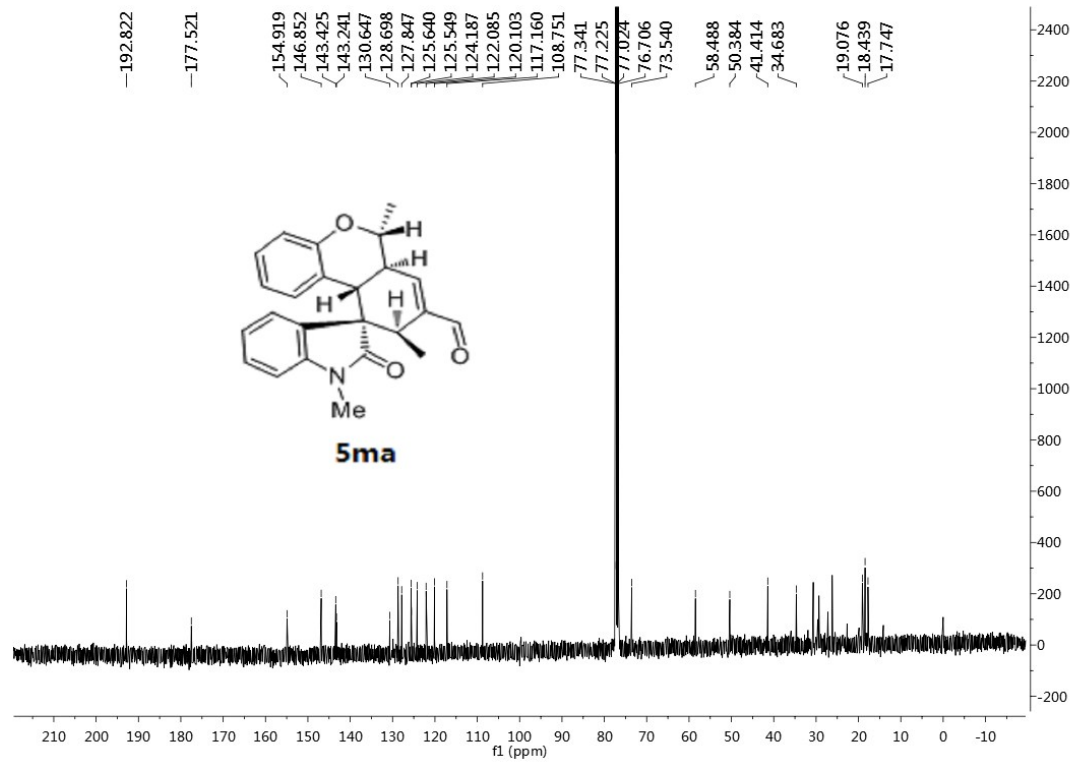
143.494
141.484
134.328
129.431
128.072
126.627
125.559
123.969
122.069
120.606
117.303
111.301
77.692
50.672
44.071
36.422
34.754
20.807
18.928
Cl
5la
f1 (ppm)


9.529
7.424
7.405
7.386
7.279
7.094
7.076
7.057
7.005
6.997
6.989
6.977
6.800
6.778
6.424
5.850
4.964
4.948
4.933
3.748
3.731
3.714
3.194
2.721
2.703
2.686
2.669
1.423
1.407
1.249
1.231
Me
5ma
1.00
1.13
0.91
1.04
1.93
1.91
1.00
0.99
1.03
2.32
2.83
1.06
3.19
3.23
f1 (ppm)

64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177.521
154.919
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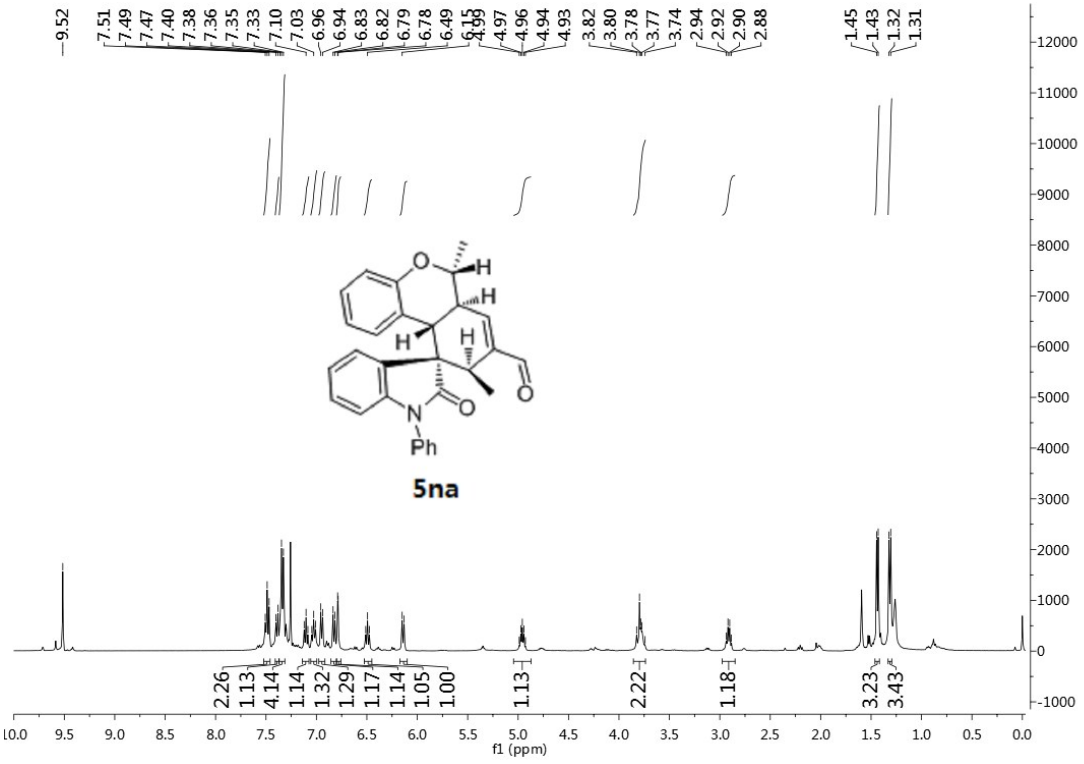
143.425
143.241
130.647
128.698
127.847
125.640
125.549
124.187
122.085
120.103
117.160
108.751
77.341
77.225
77.024
76.706
73.540
58.488
50.384
41.414
34.683
19.076
18.439
17.747
Me
5ma
f1 (ppm)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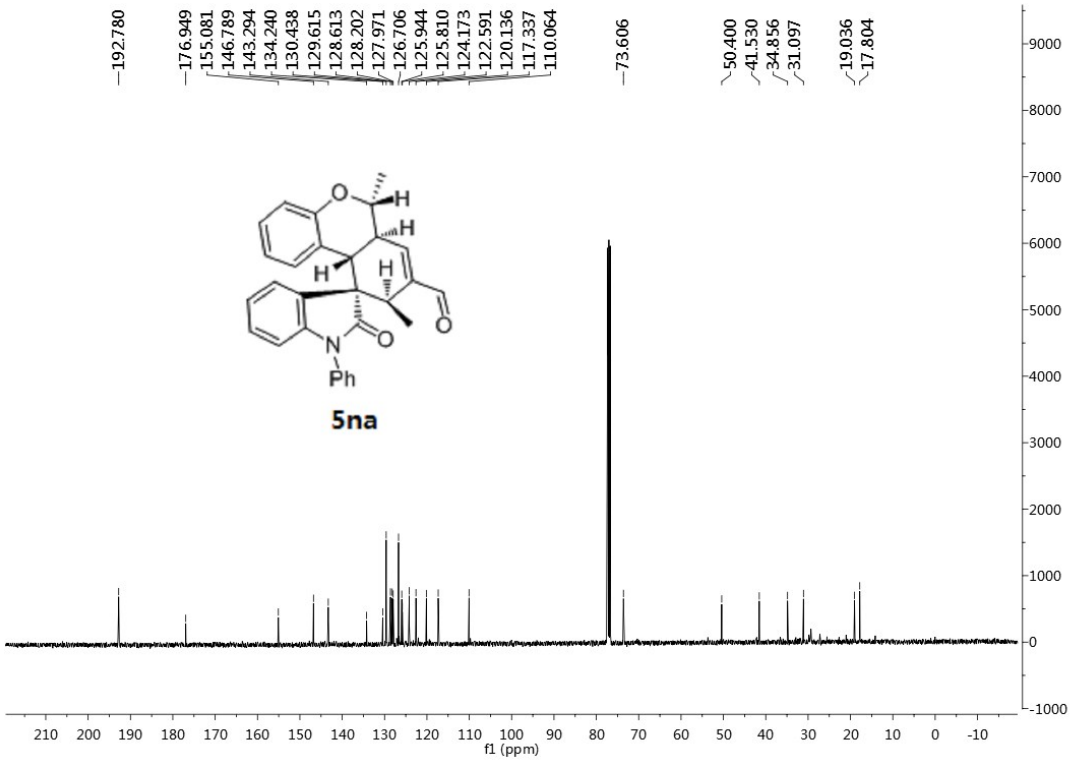
7.33
7.10
7.03
6.96
6.94
6.83
6.82
6.79
6.78
6.49
4.99
4.97
4.96
4.94
4.93
3.82
3.80
3.78
3.77
3.74
2.94
2.92
2.90
2.88
1.45
1.43
1.32
1.31
Ph
5na
2.26
1.13
4.14
1.14
1.32
1.29
1.17
1.14
1.05
1.00
1.13
2.22
1.18
3.23
3.43
f1 (ppm)

65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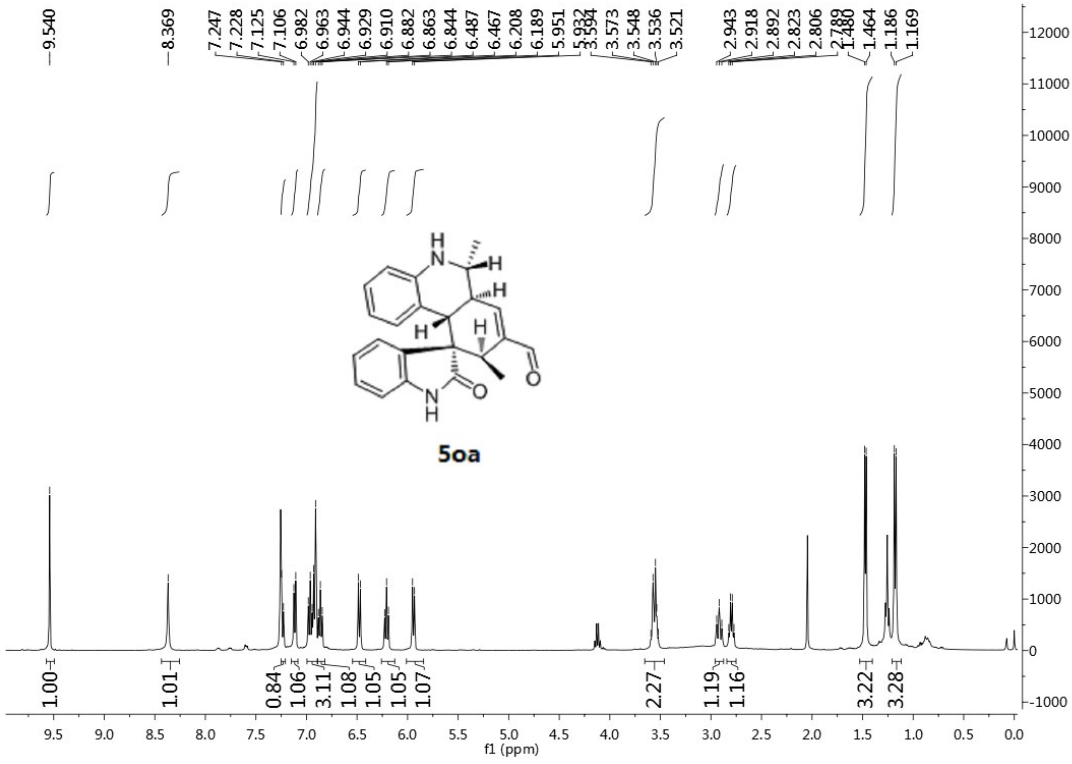
129.615
128.613
128.202
127.971
126.706
125.944
125.810
124.173
122.591
120.136
117.337
110.064
73.606
50.400
41.530
34.856
31.097
19.036
17.804
Ph
f1 (ppm)

5na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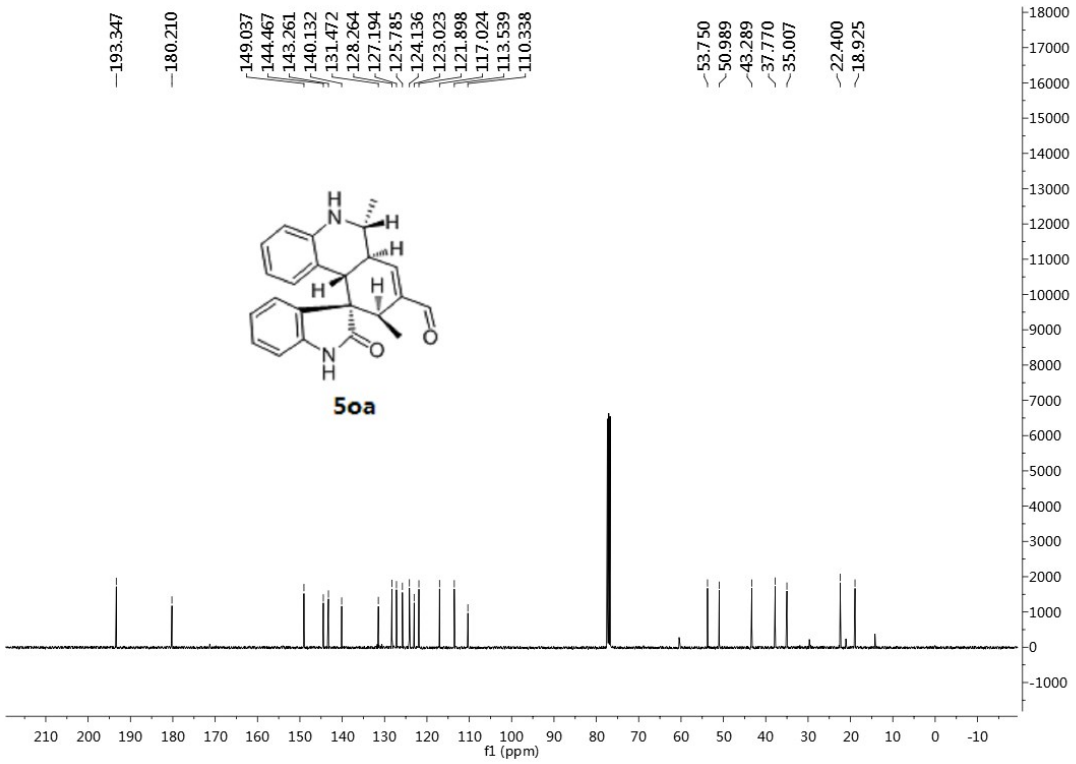
6.963
6.944
6.929
6.910
6.882
6.863
6.844
6.487
6.467
6.208
6.189
5.951
3.573
3.548
3.536
3.521
2.943
2.918
2.892
2.823
2.806
1.464
1.186
1.169
1.00
1.01
0.84
1.06
3.11
1.08
1.05
1.05
1.07
2.27
1.19
1.16
3.22
3.28
f1 (ppm)

5oa

66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140.132
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128.264
127.194
125.785
124.136
123.023
121.898
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35.007
22.400
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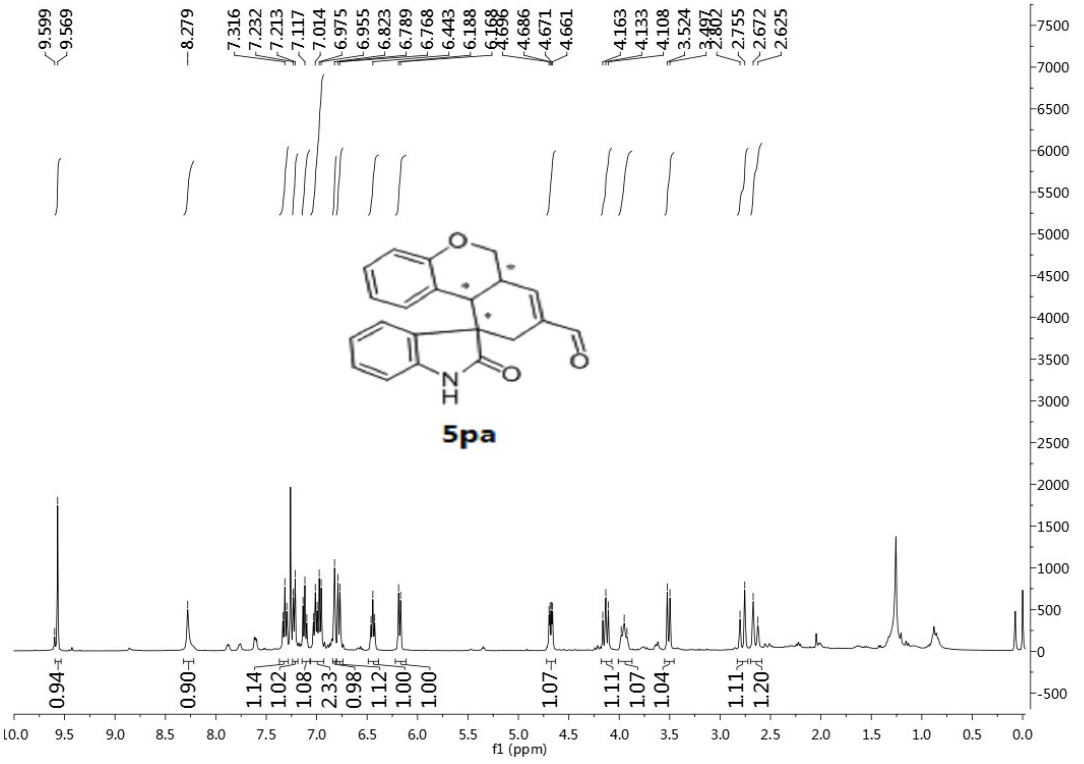
5oa
f1 (ppm)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7.014
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6.955
6.823
6.789
6.768
6.443
6.188
4.686
4.671
4.661
4.163
4.133
4.108
3.524
2.755
2.672
2.625
5pa
0.94
0.90
1.14
1.02
1.08
2.33
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1.00
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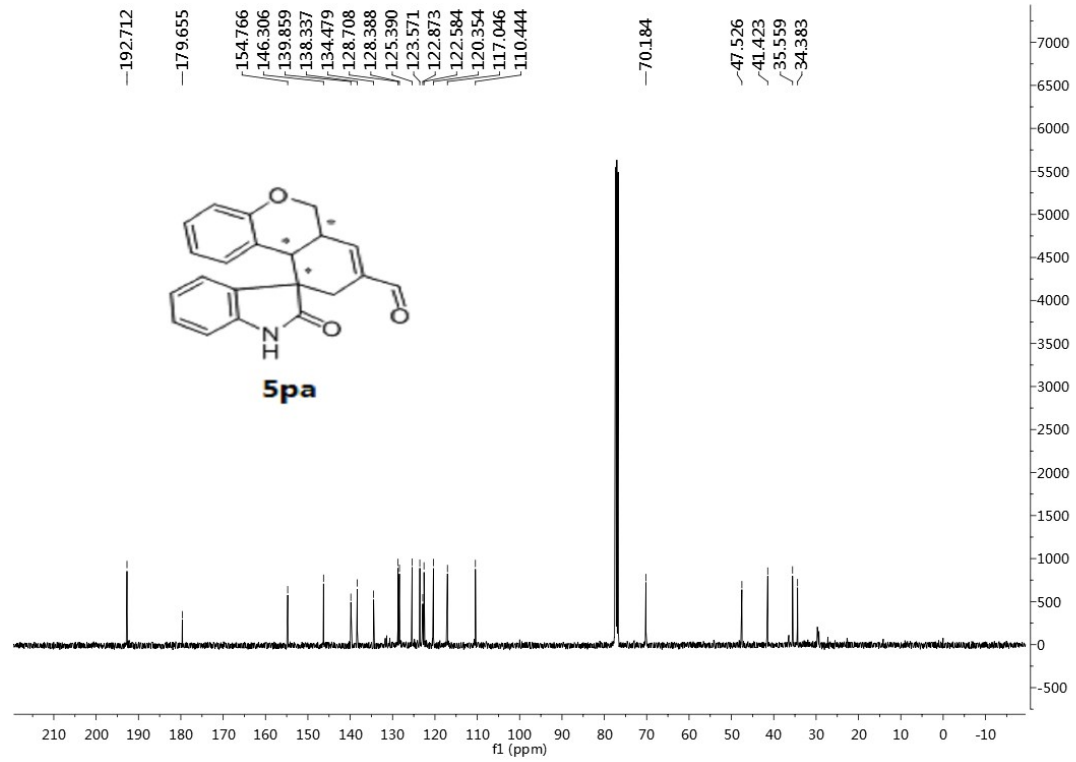
1.07
1.04
1.11
1.20
f1 (ppm)

67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128.708
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125.390
123.571
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117.046
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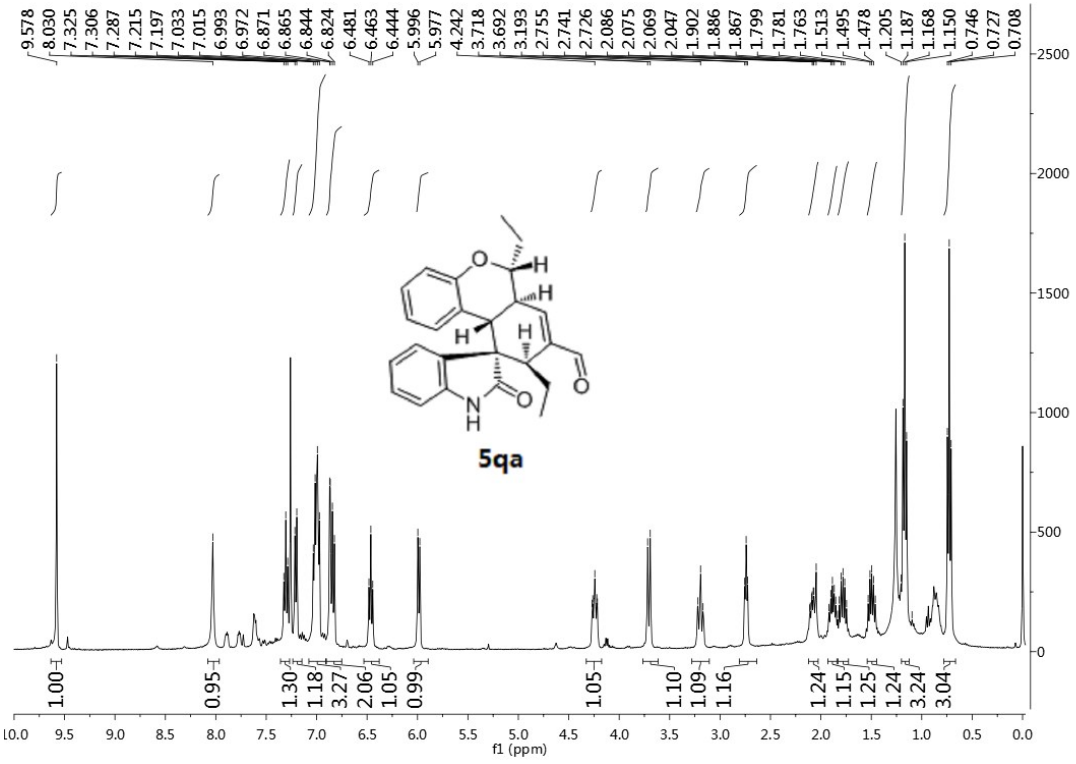
47.526
41.423
35.559
34.383
5pa
f1 (ppm)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6.865
6.844
6.824
6.481
6.463
6.444
5.996
5.977
4.242
3.718
3.692
3.193
2.755
2.741
2.726
2.086
2.075
2.069
2.047
1.902
1.886
1.867
1.799
1.781
1.763
1.513
1.495
1.478
1.205
1.187
1.168
1.150
0.746
0.727
0.708
1.00
0.95
1.30
1.18
3.27
2.06
1.05
0.99
1.05
1.10
1.09
1.16
1.24
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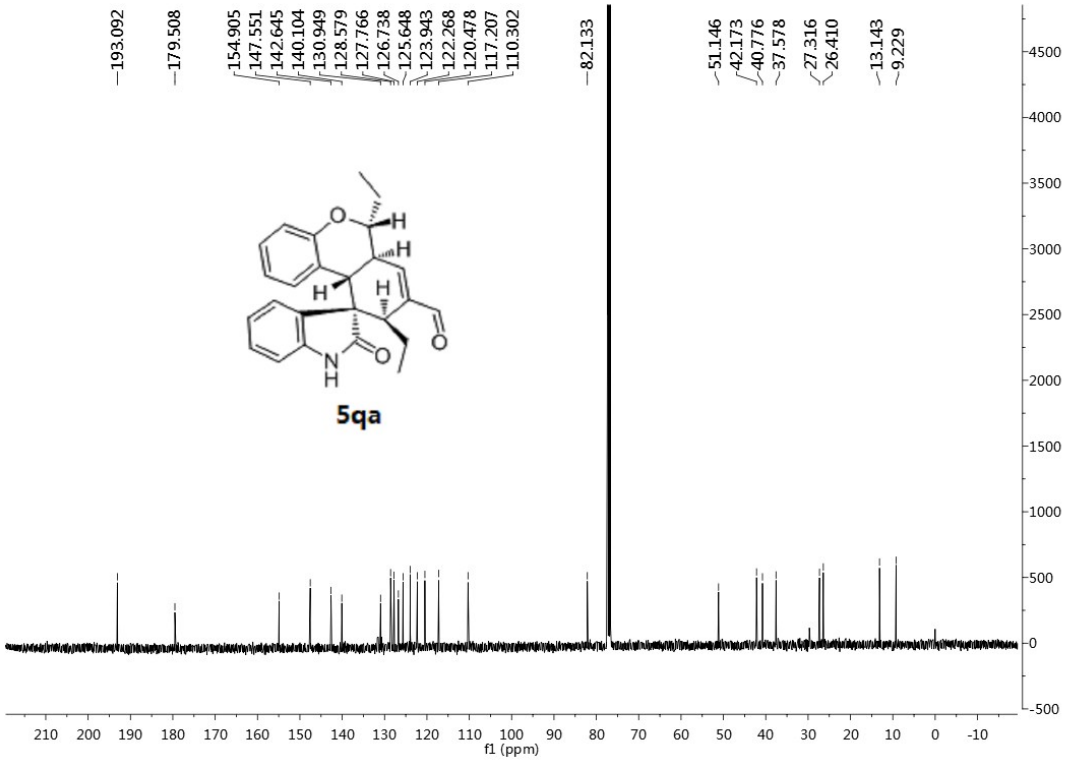
1.25
1.24
3.24
3.04
5qa
f1 (ppm)

68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126.738
125.648
123.943
122.268
120.478
117.207
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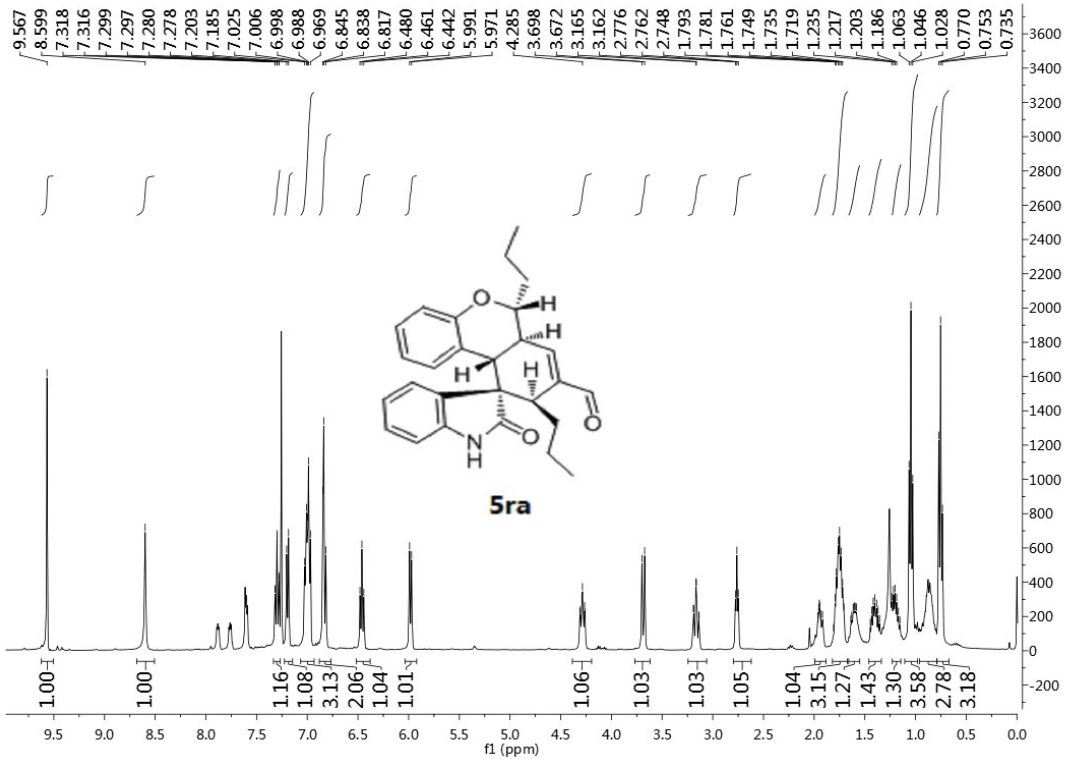
37.578
27.316
26.410
13.143
9.229
5qa
f1 (ppm)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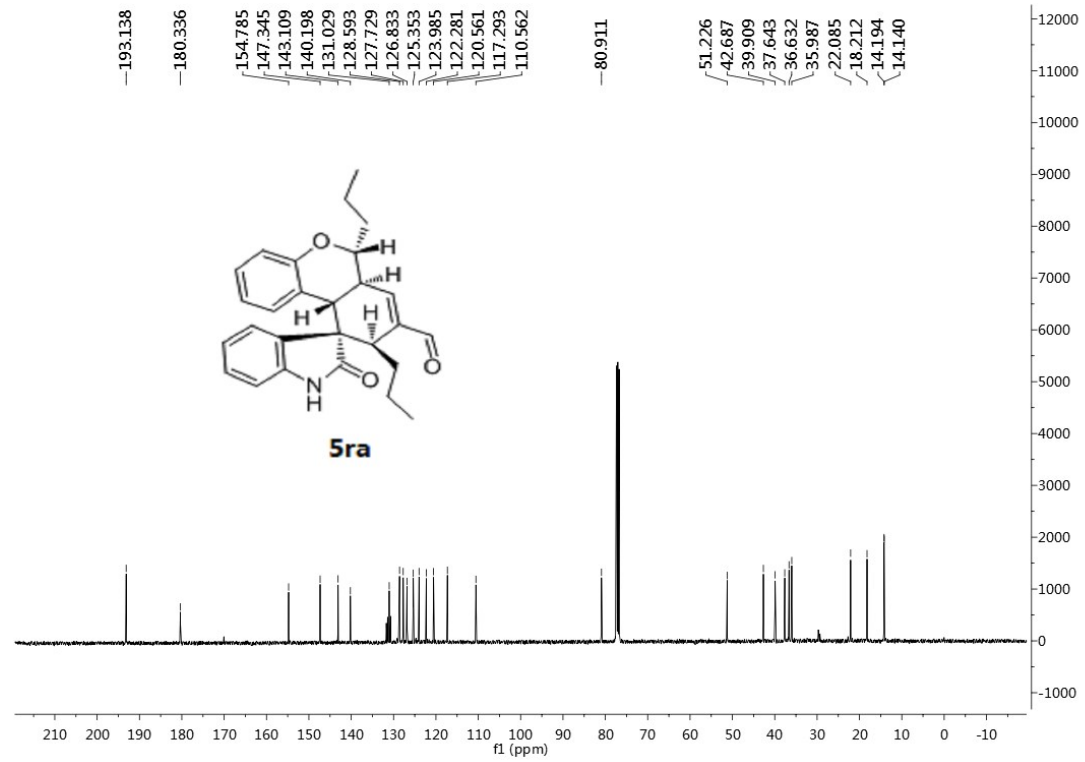
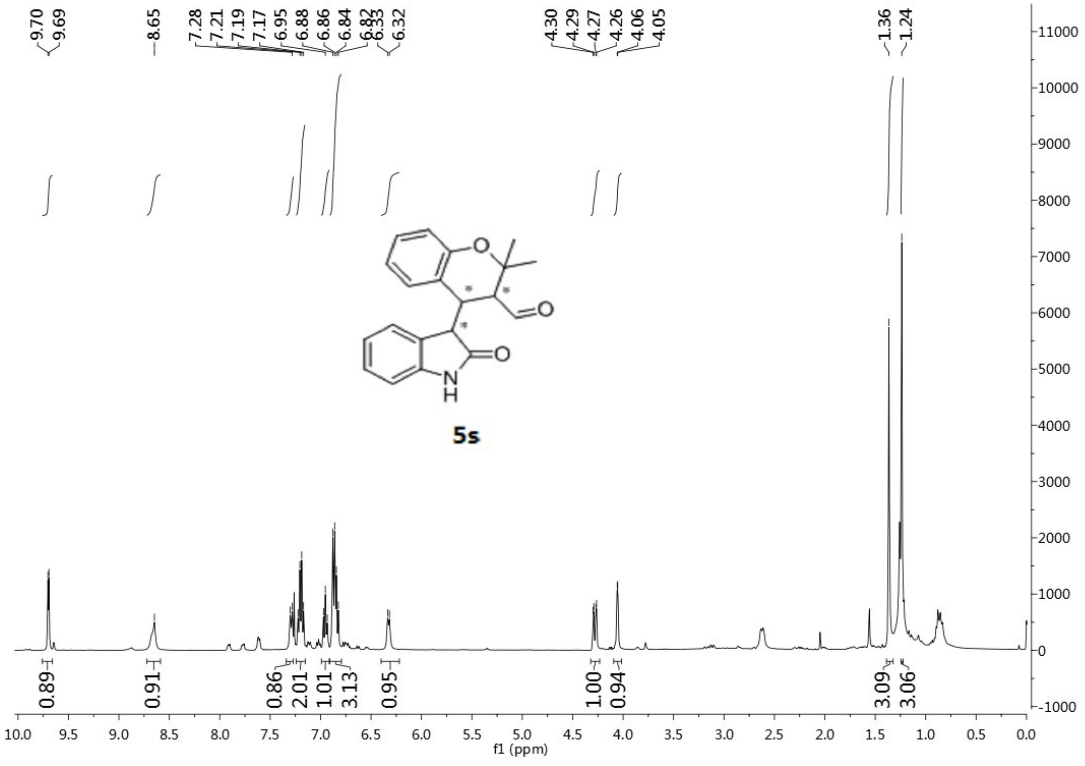
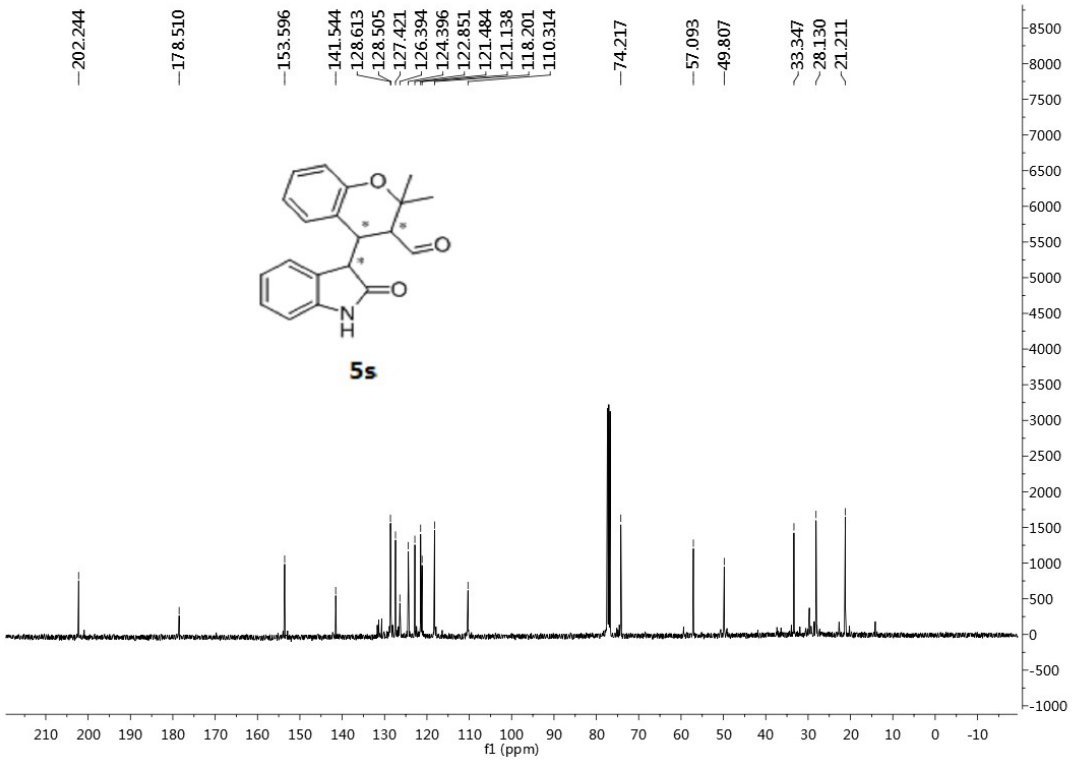
7.025
7.006
6.998
6.988
6.969
6.845
6.838
6.817
6.480
6.461
6.442
5.991
4.285
3.698
3.672
3.165
3.162
2.776
2.762
2.748
1.793
1.781
1.761
1.749
1.735
1.719
1.235
1.217
1.203
1.186
1.063
1.046
1.028
0.770
0.753
0.735
1.00
1.00
1.16
1.08
3.13
2.06
1.04
1.01
1.06
1.03
1.03
1.05
1.04
3.15
1.27
1.43
1.30
3.58
2.78
3.18
5ra
f1 (ppm)

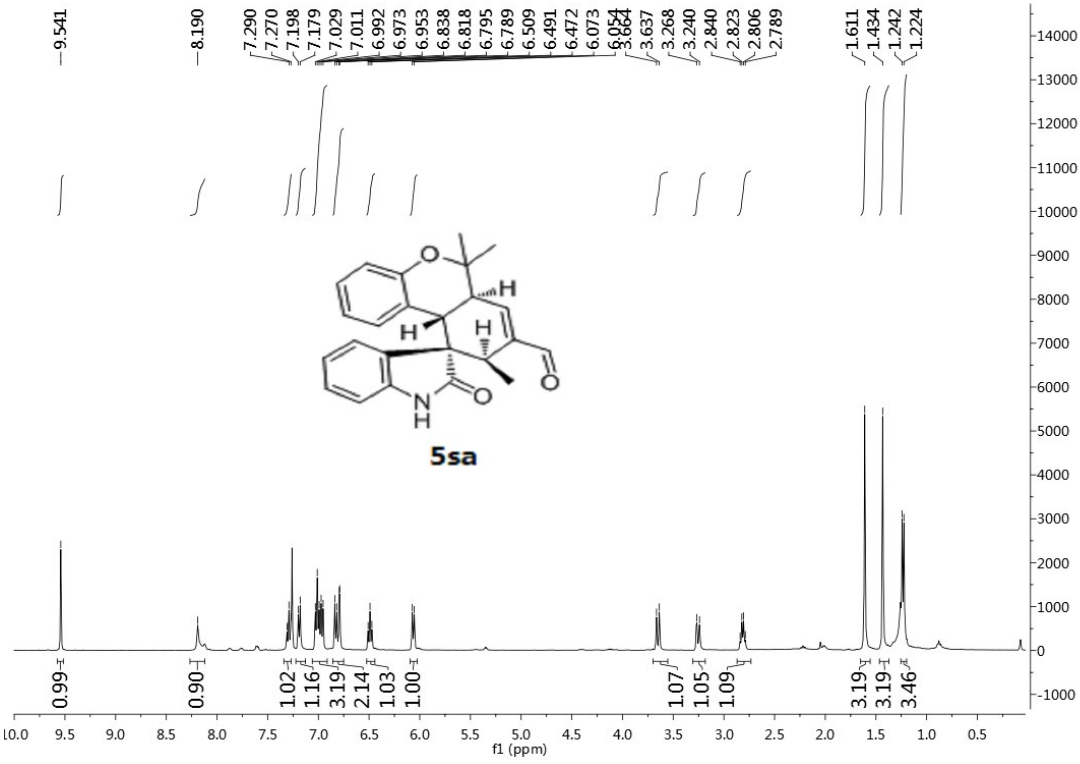
69


193.138
180.336
154.785
147.345
143.109
140.198
131.029
128.593
127.729
126.833
125.353
123.985
122.281
120.561
117.293
110.562
80.911
51.226
42.687
39.909
37.643
36.632
35.987
22.085
18.212
14.194
14.140
5ra
f1 (ppm)

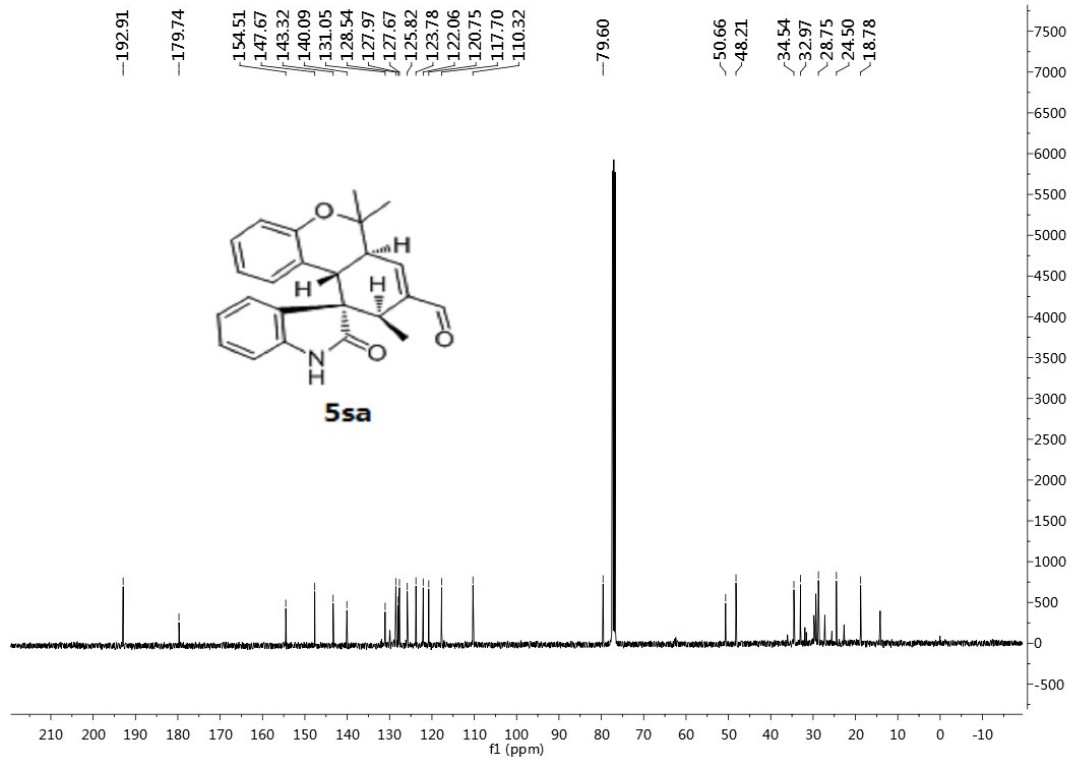

9.70
9.69
8.65
7.28
7.21
7.19
7.17
6.95
6.88
6.86
6.84
6.33
6.32
4.30
4.29
4.27
4.26
4.06
4.05
1.36
1.24
5s
0.89
0.91
0.86
2.01
1.01
3.13
0.95
1.00
0.94
3.09
3.06
f1 (ppm)

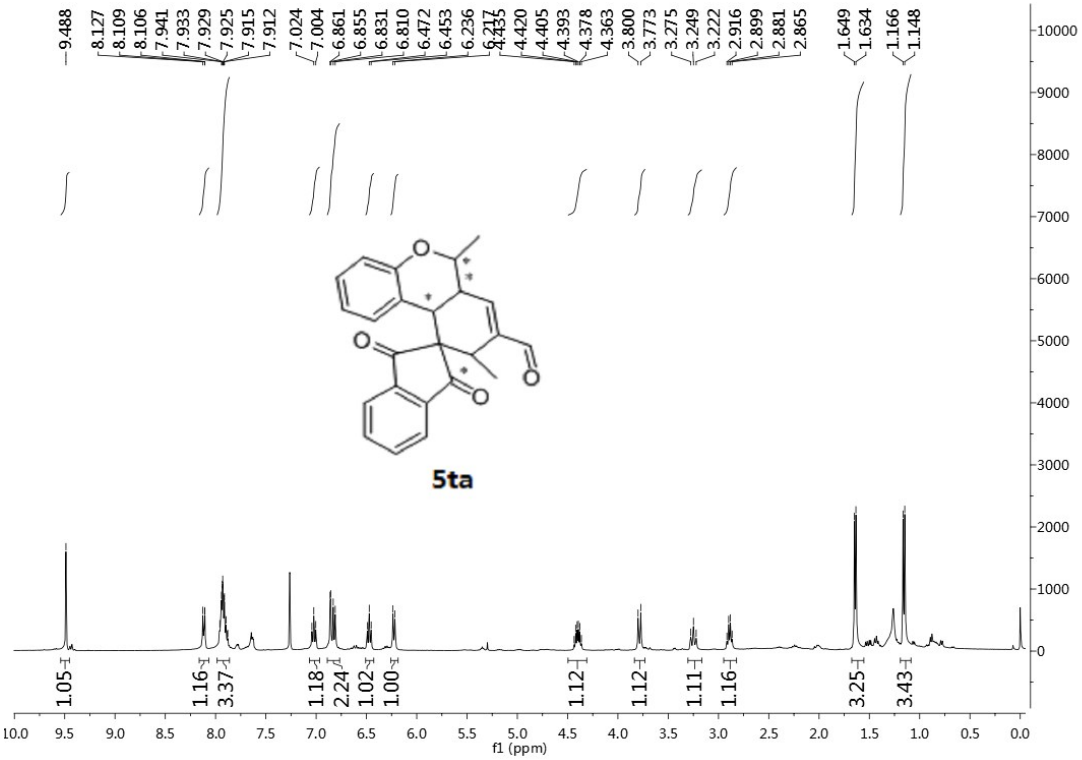
70


202.244
178.510
153.596
141.544
128.613
128.505
127.421
126.394
124.396
122.851
121.484
121.138
118.201
110.314
74.217
57.093
49.807
33.347
28.130
21.211
5s
f1 (ppm)

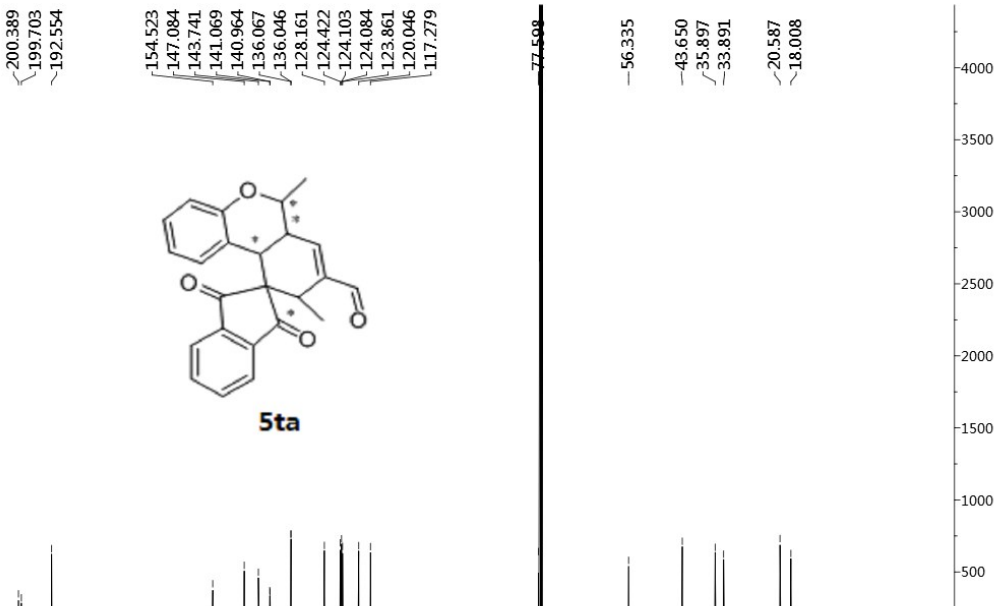

9.541
8.190
7.290
7.270
7.198
7.179
7.029
7.011
6.992
6.973
6.953
6.838
6.818
6.795
6.789
6.509
6.491
6.472
6.073
6.054
3.664
3.637
3.268
3.240
2.840
2.823
2.806
2.789
1.611
1.434
1.242
1.224
0.99
0.90
1.02
1.16
3.19
2.14
1.03
1.00
1.07
1.05
1.09
3.19
3.19
3.46
5sa
f1 (ppm)

71

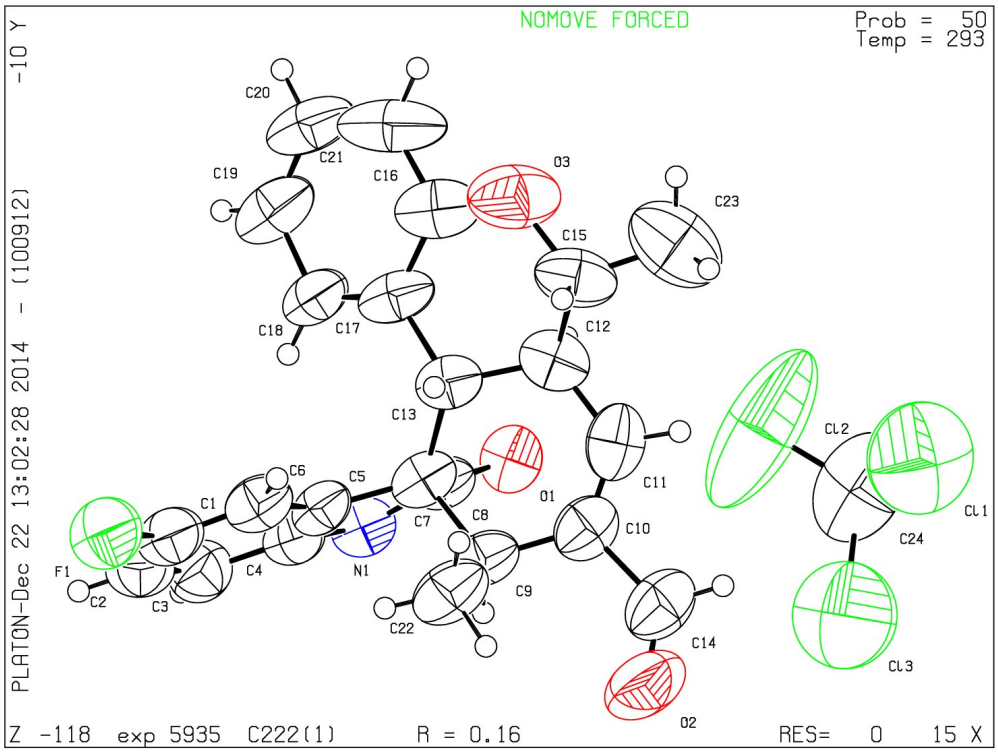

192.91
179.74
154.51
147.67
143.32
140.09
131.05
128.54
127.97
127.67
125.82
123.78
122.06
120.75
117.70
110.32
79.60
50.66
48.21
34.54
32.97
28.75
24.50
18.78
5sa
f1 (ppm)


9.488
8.127
8.109
8.106
7.941
7.933
7.929
7.925
7.915
7.912
7.024
7.004
6.861
6.855
6.831
6.810
6.472
6.453
6.236
4.420
4.405
4.393
4.378
4.363
3.800
3.773
3.275
3.249
3.222
2.916
2.899
2.881
2.865
1.649
1.634
1.166
1.148
5ta
1.05
1.16
3.37
1.18
2.24
1.02
1.00
1.12
1.12
1.11
1.16
3.25
3.43
f1 (ppm)

72



5ta



Bond precision:	C-C = 0.0148 A		Wavelength=1.54184
Cell:	a=12.9969(4)	b=17.0693(8)	c=23.6874(7)
	alpha=90	beta=90	gamma=90
Temperature:	293 K		
	Calculated		Reported
Volume	5255.0(3)		5255.0(3)
Space group	C 2 2 21		C222(1)

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Moiety formula	C23 H19 F N O3, C H Cl3	C23 H19 F N O3, C H Cl3
Sum formula	C24 H20 Cl3 F N O3	C24 H20 Cl3 F N O3
Mr	495.76	495.76
Dx,g cm-3	1.253	1.253
Z	8	8
Mu (mm-1)	3.421	3.421
F000	2040.0	2040.0
F000'	2054.10	
h,k,lmax	15,20,28	15,20,28
Nref	4718[2615]	4044
Tmin,Tmax	0.696,0.686	0.684,0.705
Tmin'	0.632	

Correction method= MULTI-SCAN

Data completeness= 1.55/0.86 Theta(max)= 67.250

R(reflections)= 0.1558(2392) wR2(reflections)= 0.3935(4044)

S = 1.305 Npar= 292

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