Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Asymmetric catalytic Friedel–Crafts alkylation with arenes and heteroarenes: construction of 3,3-disubstituted oxindoles

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Content

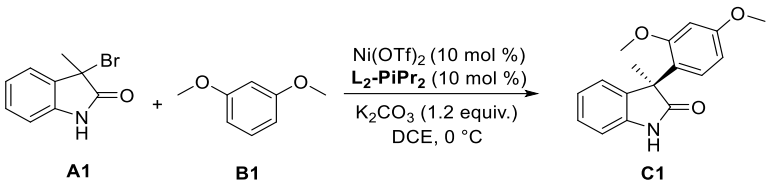
1 General Information

NMR characterization data were collected on bruker ASCEND™ operating at 400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR (with complete proton decoupling), and 376 MHz for ^{19}F NMR (with complete proton decoupling). ^{1}H NMR and ^{13}C NMR: chemical shifts δ were recorded in ppm relative to tetramethylsilane and internally referenced to the residual solvent signal (for ^{1}H NMR, $CDCl_3$: δ = 7.26 ppm, acetone-d_6: δ =2.05 ppm; for ^{13}C NMR: CDCl3: δ = 77.0 ppm, acetone-d6: δ = 29.8 ppm, 206.1 ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz), integration. Ultra Performance Convergence Chromatography (UPC^2) was performed on using Daicel Chiralcel IB-3, AS-3, ID-3, OD-3 at 23 °C with UV detector at 254 nm, and enantiomeric excesses were determined in comparison with the authentic racemates. High resolution mass spectra (HRMS) were performed on Thermo Q-Exactive Focus (FTMS+c ESI) and data were reported as (m/z). Infrared spectra (IR) were recorded on Bruker Tensor II spectrometer with Plantium ATR accessory and the peaks are reported as absorption maxima (ν, cm^{-1}). Optical rotations were measured on Rudolph Research Analytic Automatic Polarimeter, and reported as follows: $[\alpha]_D^T$ (*c*: g/100 mL, in CH_2Cl_2). Melting point ranges were determined on OptiMelt. X-ray crystallographic data were collected by a Bruker D8 Venture Photon II. The experiments requiring substrates 3-Bromo-3-substituted oxindoles[1] and chiral *N*,*N*′-dioxide ligands[2] were synthesized according to known procedures and purified by recrystallization prior to use. All of the starting materials including the metal salts were purchased from TCI, Aladdin, Adamas, Acros, Aldrich and other companies, and used without further purification. The 3/4/5Å MS and inorganic base was purchased from Acros and oven-dried by the muffle furnace for 4 h prior to use. All the solvents were pre-dried over appropriate desiccants, and distilled prior to use. other commercial reagents were used without further purification. Reactions were monitored using thin-layer chromatography (TLC) on GF254 silica gel. Visualization of the developed plates was performed under UV light (254 nm) or using iodine, cobalt thiocyanate or $KMnO_4$. The products were purified by flash column chromatography with silicycle 300-400 mesh silica gel.

2 Typical procedure for preparation of products

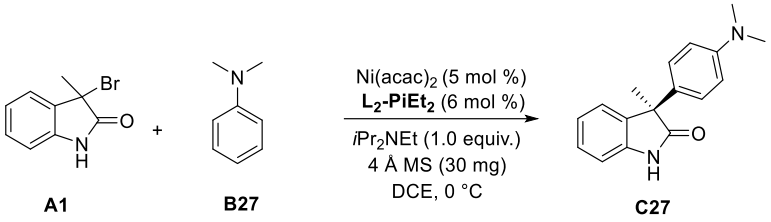
The corresponding racemic products were obtained by using racemic *N*,*N*'-dioxide (±)-**L_2-PiPr$_2$** as the ligand under the respective catalytic reaction conditions.

2.1 Typical procedure for preparation of products (condition A)



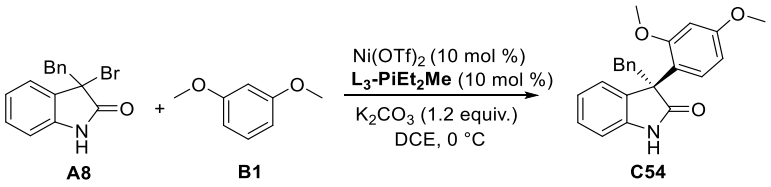
An oven-dried test tube was charged with metal salt $Ni(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol %), **L_2-PiPr$_2$** (6.3 mg, 0.01 mmol, 10 mol %) 3-Bromo-3-substituted oxindoles **A1** (0.10 mmol), K_2CO_3 (16.6 mg, 0.12 mmol, 1.2 equiv.) under N_2 atmosphere. Anhydrous DCE (1.0 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, the arenes **B1** (0.15 mmol 1.5 equiv.) were added and the reaction was performed at 0 °C for 24 hours. The reaction mixture was directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1 to 1:1) to afford the corresponding products **C1**

2.2 Typical procedure for preparation of products (condition B)



An oven-dried test tube was charged with metal salt $Ni(acac)_2$ (1.3 mg, 0.005 mmol, 5 mol %), **L_2-PiEt$_2$** (3.5 mg, 0.006 mmol, 6 mol %) 3-Bromo-3-substituted oxindoles **A1** (22.6 mg, 0.10 mmol, 1 equiv.), 4 Å molecular sieves (30 mg) under N_2 atmosphere. Anhydrous DCE (1.0 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, the arenes **B23** (0.12 mmol 1.2 equiv.), *i*Pr_2NEt (16.5 mg, 0.10 mmol, 1.0 equiv.) was added at 0 °C and the reaction was performed at 0 °C for 12 hours. The reaction mixture was directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1 to 2:1) to afford the corresponding products **C27**.

2.3 Typical procedure for preparation of products (condition C)

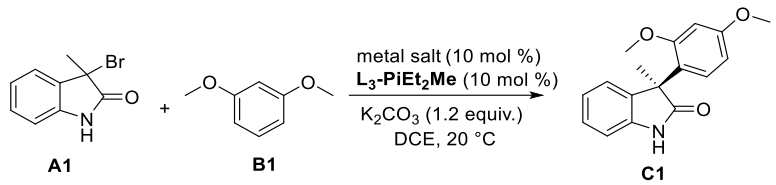


An oven-dried test tube was charged with metal salt $Ni(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol %), **L_3-PiEt$_2$Me** (6.2 mg, 0.01 mmol, 10 mol %) 3-Bromo-3-substituted oxindoles **A8** (0.10 mmol), K_2CO_3 (16.6 mg, 0.12 mmol, 1.2 equiv.) under N_2 atmosphere. Anhydrous DCE (1.0 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, the arenes **B1** (20.7 mg, 0.15 mmol 1.5 equiv.) were added and the reaction was performed at 0 °C for 24 hours. The reaction mixture was directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1 to 1:1) to afford the corresponding products **C54**.

3 Optimization of the reaction conditions

3.1 Optimization of the reaction conditions (condition A)

Table S1. Screening of metal salts

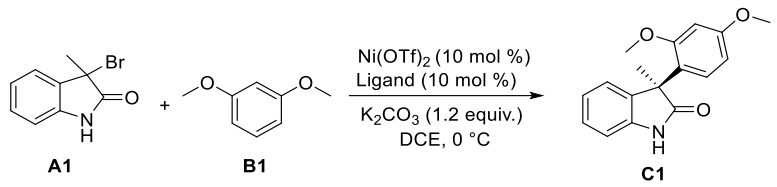


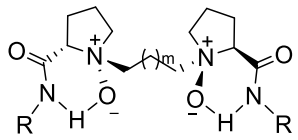
entry[a]	metal salts	yield (%)[b]	ee (%)[c]
1	$Mg(OTf)_2$	34	20
2	$Sc(OTf)_3$	41	11
3	$Fe(OTf)_2$	52	25
4	$Co(OTf)_2$	35	37
5	$Ni(OTf)_2$	60	85
6	$Cu(OTf)_2$	53	38
7	$Zn(OTf)_2$	44	67
8	$Y(OTf)_3$	10	0
9	$La(OTf)_3$	trace	0
10	$Dy(OTf)_3$	trace	0
11	$NiCl_2$	trace	0
12	$Ni(BF_4)_2{\cdot}6H_2O$	21	35
13	$Ni(ClO_4)_2{\cdot}6H_2O$	33	18
14	$Ni(acac)_2$	78	68
15[d]	$Ni(OTf)_2$	62	80
16[e]	$Ni(OTf)_2$	66	88
17[f]	$Ni(OTf)_2$	53	89
18[g]	$Ni(OTf)_2$	60	88
19[h]	$Ni(OTf)_2$	66	88
20[i]	$Ni(OTf)_2$	9	39

[a]The reactions were performed with **A1** (0.10 mmol), **B1** (0.15 mmol), K_2CO_3 (0.12 mmol) and metal salt/**L_3-PiEt$_2$Me** (1:1, 10 mol %)

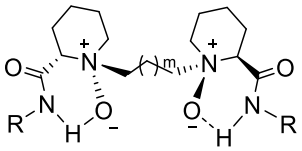
in DCE (1.0 mL) at 20 °C for 24 h. [b]Yield of the isolated product. [c]Determined by UPC[2] analysis on a chiral stationary phase. [d]The reaction was performed at 10 °C. [e]The reaction was performed at 0 °C. [f]The reaction was performed at -10 °C [g]0.12 mmol **B1** was added. [h]0.20 mmol **B1** was added. [i]4 Å molecular sieves (20.0 mg) was added.

Table S2. Screening of ligands

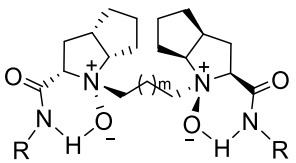




L_3-PrMe$_2$: R = 2,6-$Me_2C_6H_3$ m = 1
L_3-PrEt$_2$Me: R = 2,6-Et_2-MeC_6H_2 m = 1



L_3-PiMe$_2$: R = 2,6-$Me_2C_6H_3$ m = 1
L_3-PiEt$_2$: R = 2,6-$Et_2C_6H_3$ m = 1
L_3-PiEt$_2$Me: R = 2,6-Et_2-4-MeC_6H_2 m = 1
L_3-PiPr$_2$: R = 2,6-*i*$Pr_2C_6H_3$ m = 1
L_4-PiPr$_2$: R = 2,6-*i*$Pr_2C_6H_3$ m = 2
L_2-PiMe$_2$: R = 2,6-$Me_2C_6H_3$ m = 0
L_2-PiEt$_2$: R = 2,6-$Et_2C_6H_3$ m = 0
L_2-PiPr$_2$: R = 2,6-*i*$Pr_2C_6H_3$ m = 0

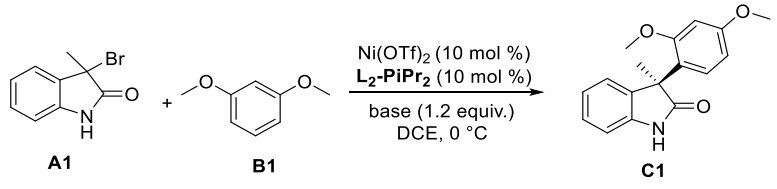


L_3-RaMe$_2$: R = 2,6-$Me_2C_6H_3$ m = 1
L_3-RaEt$_2$Me: R = 2,6-Et_2-MeC_6H_2 m = 1

entry[a]	Ligands	yield (%)[b]	ee (%)[c]
1	**L_3-PrMe$_2$**	41	64
2	**L_3-PrEt$_2$Me**	73	45
3	**L_3-RaMe$_2$**	76	35
4	**L_3-RaEt$_2$Me**	71	40
5	**L_3-PiMe$_2$**	58	74
6	**L_3-PiEt$_2$**	70	90
7	**L_3-PiEt$_2$Me**	66	88
8	**L_3-PiPr$_2$**	86	84
9	**L_4-PiPr$_2$**	77	54
10	**L_2-PiMe$_2$**	78	91
11	**L_2-PiEt$_2$**	61	93
12	**L_2-PiPr$_2$**	80	94

[a]The reactions were performed with **A1** (0.10 mmol), **B1** (0.15 mmol), K_2CO_3 (0.12 mmol) and $Ni(OTf)_2$/Ligand (1:1, 10 mol %) in DCE (1.0 mL) at 0 °C for 24 h. [b]Yield of the isolated product. [c]Determined by UPC[2] analysis on a chiral stationary phase.

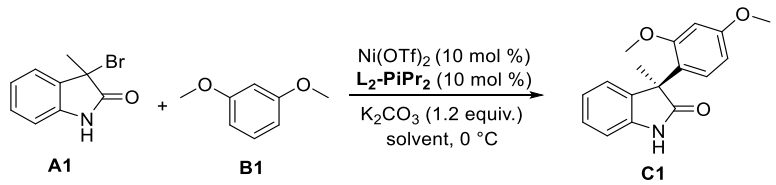
Table S3. Screening of base



entry[a]	base	yield (%)[b]	ee (%)[c]
1	Na_2CO_3	27	77
2	K_2CO_3	80	94
3	Cs_2CO_3	26	34
4	Et_3N	N.D.	-
5	Pr_3N	N.D.	-
6	DMAP	N.D.	-

[a]The reactions were performed with **A1** (0.10 mmol), **B1** (0.15 mmol), base (0.12 mmol) and $Ni(OTf)_2$/**L_2-PiPr$_2$** (1:1, 10 mol %) in DCE (1.0 mL) at 0 °C for 24 h. [b]Yield of the isolated product. [c]Determined by UPC^2 analysis on a chiral stationary phase.

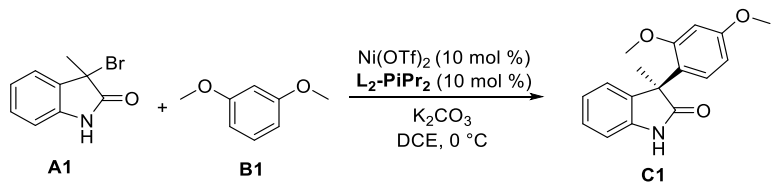
Table S4. Solvent Screening.



entry[a]	solvent	yield (%)[b]	ee (%)[c]
1	CH_2Cl_2	78	94
2	$CHCl_3$	75	86
3	DCE	80	94
4	THF	trace	14
5	Et_2O	N.R.	-
6	toluene	N.R.	-

[a]The reactions were performed with **A1** (0.10 mmol), **B1** (0.15 mmol), K_2CO_3 (0.12 mmol) and $Ni(OTf)_2$/**L_2-PiPr$_2$** (1:1, 10 mol %) in solvent (1.0 mL) at 0 °C for 24 h. [b]Yield of the isolated product. [c]Determined by UPC^2 analysis on a chiral stationary phase.

Table S5. Screening of the amount of base

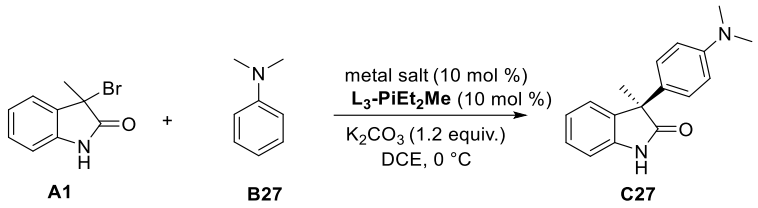


entry[a]	the amount of K_2CO_3 (x mmol)	yield (%)[b]	ee (%)[c]
1	0.10	78	91
2	0.12	81	94
3	0.15	81	91
4	0.20	80	89
5	0.30	79	86

[a]The reactions were performed with **A1** (0.10 mmol), **B1** (0.15 mmol), K_2CO_3 (x mmol) and $Ni(OTf)_2$/**L_2-PiPr$_2$** (1:1, 10 mol %) in DCE (1.0 mL) at 0 °C for 24 h. [b]Yield of the isolated product. [c]Determined by UPC^2 analysis on a chiral stationary phase.

3.2 Optimization of the reaction conditions (condition B)

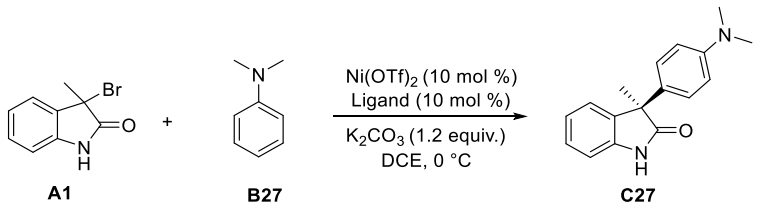
Table S6. Screening of metal salts.

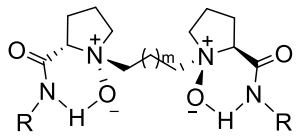


entry[a]	metal salts	yield (%)[b]	ee (%)[c]
1	$Mg(OTf)_2$	92	0
2	$Sc(OTf)_3$	98	0
3	$Fe(OTf)_2$	95	0
4	$Co(OTf)_2$	91	12
5	$Ni(OTf)_2$	96	51
6	$Cu(OTf)_2$	95	23
7	$Zn(OTf)_2$	92	0
8	$Y(OTf)_3$	90	0
9	$La(OTf)_3$	99	0
10	$Tb(OTf)_3$	94	0
11[d]	$Ni(OTf)_2$	96	43
12[e]	$Ni(OTf)_2$	96	51
13[f]	$Ni(OTf)_2$	55	51
14[g]	$Ni(OTf)_2$	25	43

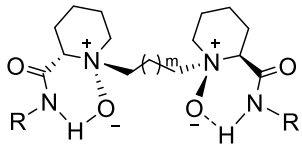
[a]The reactions were performed with **A1** (0.10 mmol), **B12** (0.12 mmol), K_2CO_3 (0.12 mmol) and metal salt/**L_3-PiEt$_2$Me** (1:1, 10 mol %) in DCE (1.0 mL) at 0 °C for 12 h. [b]Yield of the isolated product. [c]Determined by UPC[2] analysis on a chiral stationary phase. [d]The reaction was performed at 10 °C. [e]The reaction was performed at 0 °C. [f]The reaction was performed at -10 °C [g]0.12 mmol **B1** was added. [d]The reaction was performed at 10 °C. [e]The reaction was performed at -10 °C. [f]The reaction was performed at -20 °C [g]The reaction was performed at -30 °C

Table S7. Screening of ligands.

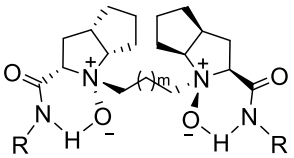




L_3-PrMe$_2$: R = 2,6-$Me_2C_6H_3$ m = 1
L_3-PrEt$_2$Me: R = 2,6-Et_2-MeC_6H_2 m = 1



L_3-PiMe$_2$: R = 2,6-$Me_2C_6H_3$ m = 1
L_3-PiMe$_3$: R = 2,4,6-$Me_2C_6H_2$ m = 1
L_3-PiEt$_2$: R = 2,6-$Et_2C_6H_3$ m = 1
L_3-PiEt$_2$Me: R = 2,6-Et_2-4-MeC_6H_2 m = 1
L_3-PiEt$_2$Br: R = 2,6-Et_2-4-BrC_6H_2 m = 1
L_3-PiPr$_2$: R = 2,6-*i*$Pr_2C_6H_3$ m = 1
L_4-PiPr$_2$: R = 2,6-*i*$Pr_2C_6H_3$ m = 2
L_2-PiMe$_2$: R = 2,6-$Me_2C_6H_3$ m = 0
L_2-PiEt$_2$: R = 2,6-$Et_2C_6H_3$ m = 0
L_2-PiPr$_2$: R = 2,6-*i*$Pr_2C_6H_3$ m = 0

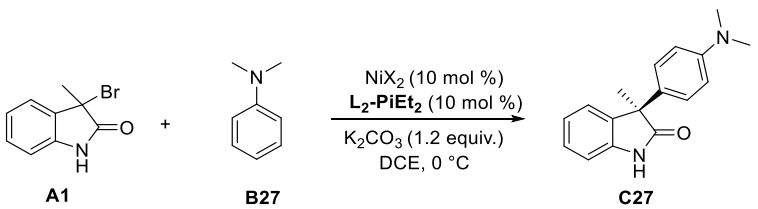


L_3-RaMe$_2$: R = 2,6-$Me_2C_6H_3$ m = 1
L_3-RaEt$_2$Me: R = 2,6-Et_2-MeC_6H_2 m = 1

entry[a]	Ligands	yield (%)[b]	ee (%)[c]
1	**L_3-PrMe$_2$**	91	33
2	**L_3-PrEt$_2$Me**	92	43
3	**L_3-RaMe$_2$**	96	10
4	**L_3-RaEt$_2$Me**	95	47
5	**L_3-PiMe$_2$**	97	53
6	**L_3-PiMe$_3$**	92	58
7	**L_3-PiEt$_2$**	66	54
8	**L_3-PiEt$_2$Me**	83	51
9	**L_3-PiEt$_2$Br**	90	20
10	**L_3-PiPr$_2$**	98	49
11	**L_4-PiPr$_2$**	97	29
12	**L_2-PiPr$_2$**	95	55
13	**L_2-PiMe$_2$**	90	41
14	**L_2-PiEt$_2$**	92	59

[a]The reactions were performed with **A1** (0.10 mmol), **B12** (0.12mmol), K_2CO_3 (0.12 mmol) and $Ni(OTf)_2$/Ligand (1:1, 10 mol %) in DCE (1.0 mL) at 0 °C for 24 h. [b]Yield of the isolated product. [c]Determined by UPC[2] analysis on a chiral stationary phase.

Table S8. Screening of Counterion of Ni(II) salts.

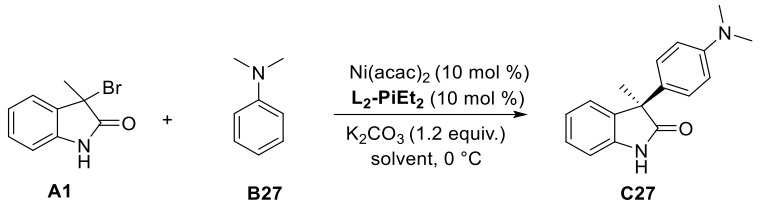


entry[a]	NiX_2	yield (%)[b]	ee (%)[c]
1	$NiCl_2$	95	0
2	$NiBr_2$	95	0
3	$Ni(acac)_2$	91	80

4	$Ni(OTf)_2$	92	59
5	$Ni(BF_4)_2{\cdot}6H_2O$	99	30
6	$Ni(ClO_4)_2{\cdot}6H_2O$	96	28
7	$NiC_2O_4{\cdot}6H_2O$	92	0

[a]The reactions were performed with **A1** (0.10 mmol), **B12** (0.12 mmol), K_2CO_3 (0.12 mmol) and NiX_2/**L_2-PiEt$_2$** (1:1, 10 mol %) in DCE (1.0 mL) at 0 °C for 12 h. [b]Yield of the isolated product. [c]Determined by UPC^2 analysis on a chiral stationary phase.

Table S9. Solvent Screening.

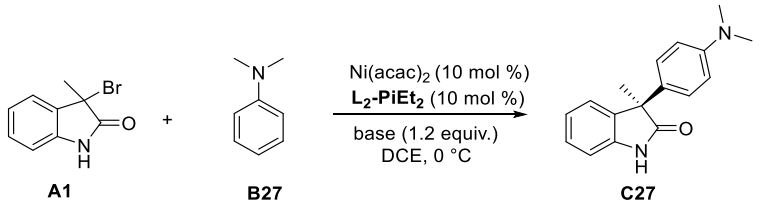


A1 **B27** **C27**

entry[a]	solvent	yield (%)[b]	ee (%)[c]
1	CH_2Cl_2	91	80
2	$CHCl_3$	85	71
3	DCE	91	80
4	THF	42	20
5	Et_2O	11	0
6	toluene	trace	-

[a]The reactions were performed with **A1** (0.10 mmol), **B12** (0.12 mmol), K_2CO_3 (0.12 mmol) and $Ni(acac)_2$/**L_2-PiEt$_2$** (1:1, 10 mol %) in solvent (1.0 mL) at 0 °C for 12 h. [b]Yield of the isolated product. [c]Determined by UPC^2 analysis on a chiral stationary phase.

Table S10. Screening of base

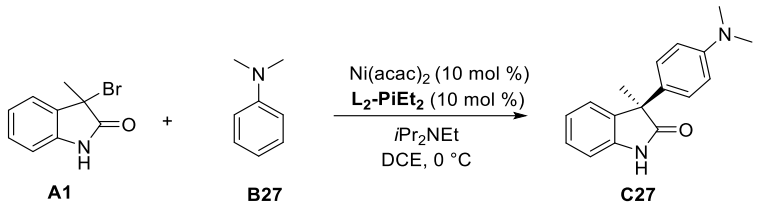


A1 **B27** **C27**

entry[a]	base	yield (%)[b]	ee (%)[c]
1	Na_2CO_3	89	36
2	K_2CO_3	91	80
3	Cs_2CO_3	90	60
4	Et_3N	87	86
5	Pr_3N	85	84
6	*i*Pr_2NEt	86	90
7	DMAP	complex	-

[a]The reactions were performed with **A1** (0.10 mmol), **B1** (0.12mmol), base (0.12 mmol) and $Ni(acac)_2$/**L_2-PiEt$_2$** (1:1, 10 mol %) in DCE (1.0 mL) at 0 °C for 12 h. [b]Yield of the isolated product. [c]Determined by UPC^2 analysis on a chiral stationary phase.

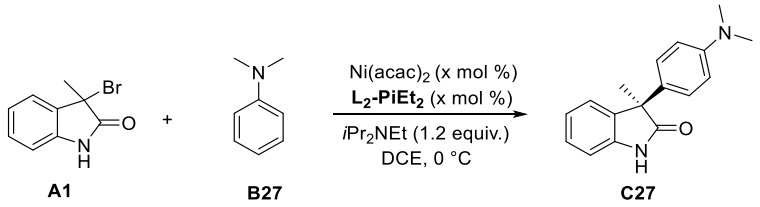
Table S11. Screening of the amount of base



entry[a]	the amount of iPr$_2$NEt (x mmol)	yield (%)[b]	ee (%)[c]
1	0.10	90	90
2	0.12	86	90
3	0.15	82	88
4	0.20	76	82

[a]The reactions were performed with **A1** (0.10 mmol), **B12** (0.12 mmol), iPr$_2$NEt (x mmol) and Ni(acac)$_2$/**L$_2$-PiEt$_2$** (1:1, 10 mol %) in DCE (1.0 mL) at 0 °C for 12 h. [b]Yield of the isolated product. [c]Determined by UPC^2 analysis on a chiral stationary phase.

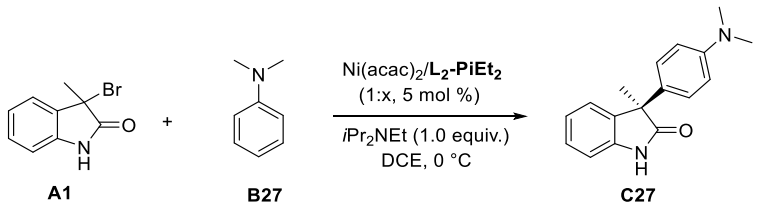
Table S12. Screening of the amount of catalyst



entry[a]	the amount of catalyst (x mmol %)	yield (%)[b]	ee (%)[c]
1	10	90	90
2	5	90	87
3	2	72	88

[a]The reactions were performed with **A1** (0.10 mmol), **B12** (0.12 mmol), iPr$_2$NEt (0.12 mmol) and Ni(acac)$_2$/**L$_2$-PiEt$_2$** (1:1, x mol %) in DCE (1.0 mL) at 0 °C for 12 h. [b]Yield of the isolated product. [c]Determined by UPC^2 analysis on a chiral stationary phase.

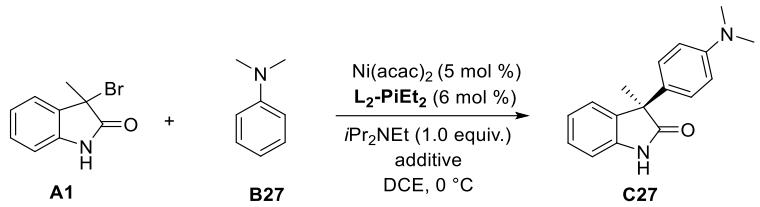
Table S13. Screening of the ratio of Ni(acac)$_2$ and **L$_2$-PiEt$_2$**



entry[a]	x	yield (%)[b]	ee (%)[c]
1	0.8	91	81
2	1.0	90	87
3	1.2	90	91
3	1.6	85	91

[a]The reactions were performed with **A1** (0.10 mmol), **B12** (0.12 mmol), iPr$_2$NEt (0.10 mmol) Ni(acac)$_2$ (0.005 mmol) and **L$_2$-PiEt$_2$** (0.005y mmol) in DCE (1.0 mL) at 0 °C for 12 h. [b]Yield of the isolated product. [c]Determined by UPC^2 analysis on a chiral stationary phase.

Table S14. Screening of the additives

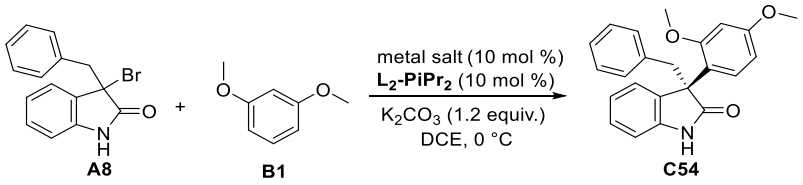


entry[a]	additive	yield (%)[b]	ee (%)[c]
1	$NaBAr^F_4$ (30 mg)	91	88
2	Na_2SO_4 (30 mg)	95	87
3	$MgSO_4$ (30 mg)	94	72
4	3 Å M.S. (30 mg)	90	89
5	4 Å M.S. (30 mg)	94	94
6	5 Å M.S. (30 mg)	89	89

[a]The reactions were performed with **A1** (0.10 mmol), **B12** (0.12 mmol), *i*Pr_2NEt (0.10 mmol), $Ni(acac)_2$ (0.005 mmol), **L_2-PiEt$_2$** (0.006 mmol) and additive in DCE (1.0 mL) at 0 °C for 12 h. [b]Yield of the isolated product. [c]Determined by UPC^2 analysis on a chiral stationary phase.

3.3 Optimization of the reaction conditions (condition C)

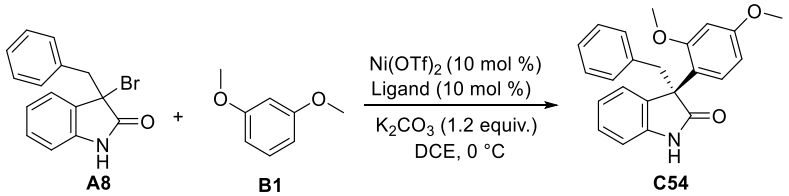
Table S15. Screening of metal salts.

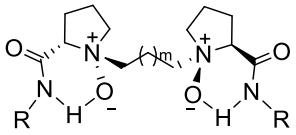


entry[a]	metal salts	yield (%)[b]	ee (%)[c]
1	$Mg(OTf)_2$	68	20
2	$Sc(OTf)_3$	34	0
3	$Fe(OTf)_2$	62	35
4	$Co(OTf)_2$	88	17
5	$Ni(OTf)_2$	89	70
6	$Cu(OTf)_2$	68	28

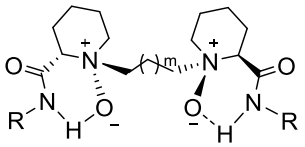
[a]The reactions were performed with **A8**(0.10 mmol), **B1** (0.15 mmol), K_2CO_3 (0.12 mmol) and metal salt/**L_2-PiPr$_2$** (1:1, 10 mol %) in DCE (1.0 mL) at 0 °C for 24 h. [b]Yield of the isolated product. [c]Determined by UPC^2 analysis on a chiral stationary phase.

Table S16. Screening of ligands.

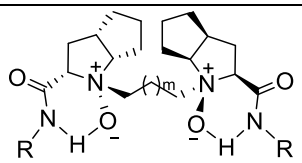




L_3-$PrEt_2Me$: R = 2,6-Et_2-MeC_6H_2 m = 1



L_3-$PiMe_2$: R = 2,6-$Me_2C_6H_3$ m = 1
L_3-$PiEt_2$: R = 2,6-$Et_2C_6H_3$ m = 1
L_3-$PiEt_2Me$: R = 2,6-Et_2-4-MeC_6H_2 m = 1
L_3-$PiPr_2$: R = 2,6-*i*$Pr_2C_6H_3$ m = 1
L_2-$PiMe_2$: R = 2,6-$Me_2C_6H_3$ m = 0
L_2-$PiEt_2$: R = 2,6-$Et_2C_6H_3$ m = 0
L_2-$PiPr_2$: R = 2,6-*i*$Pr_2C_6H_3$ m = 0

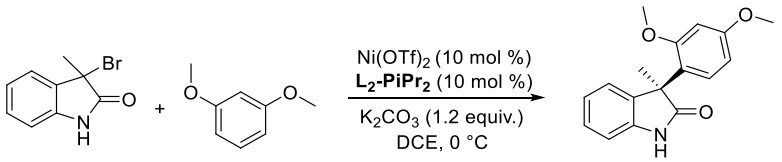


L_3-$RaEt_2Me$: R = 2,6-Et_2-MeC_6H_2 m = 1

entry[a]	Ligands	yield (%)[b]	ee (%)[c]
1	**L_2-$PiMe_2$**	91	50
2	**.L_2-$PiEt_2$**	76	91
3	**L_2-$PiPr_2$**	89	70
4[d]	**L_2-$PiPr_2$**	N.D.	-
5	**L_3-$PiMe_2$**	58	52
6	**L_3-$PiEt_2$**	89	90
7	**L_3-$PiEt_2Me$**	93	93
8	**L_3-$PiPr_2$**	78	83
9	**L_3-$PrEt_2Me$**	91	85
10	**L_3-$RaEt_2Me$**	88	47

[a]The reactions were performed with **A1** (0.10 mmol), **B12** (0.15mmol), K_2CO_3 (0.12 mmol) and $Ni(OTf)_2$/Ligand (1:1, 10 mol %) in DCE (1.0 mL) at 0 °C for 24 h. [b]Yield of the isolated product. [c]Determined by UPC[2] analysis on a chiral stationary phase. [d]*i*Pr_2NEt instead of K_2CO_3

4 Gram-scale synthesis of C1



A1
5 mmol, 1.13 g

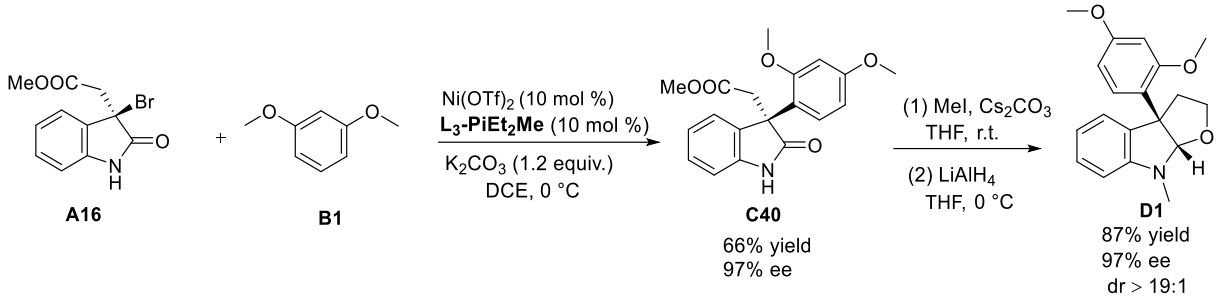
B1
7.5 mmol, 1.04 g

C1
1.06 g, 75% yield, 94% ee

An oven-dried test tube was charged with metal salt $Ni(OTf)_2$ (3.6 mg, 0.5 mmol, 10 mol %), **L_2-$PiPr_2$** (6.3 mg, 0.5 mmol, 10 mol %) 3-Bromo-3-substituted oxindoles **A1** (5.0 mmol), K_2CO_3 (16.6 mg, 6.0 mmol, 1.2 equiv.) under N_2 atmosphere. Anhydrous DCE (15 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, the arenes **B1** (1.0 mL 1.5 equiv.) was added and the reaction was performed at 0 °C for 24 hours. The reaction mixture was filtered (solvent: DCM), and concentrated under reduced pressure, the crude product was subjected to flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (6/1 to 1/1) to afford the corresponding product **C1** (1.06 g, 75% yield, 94% ee).

5 Synthetic transformations

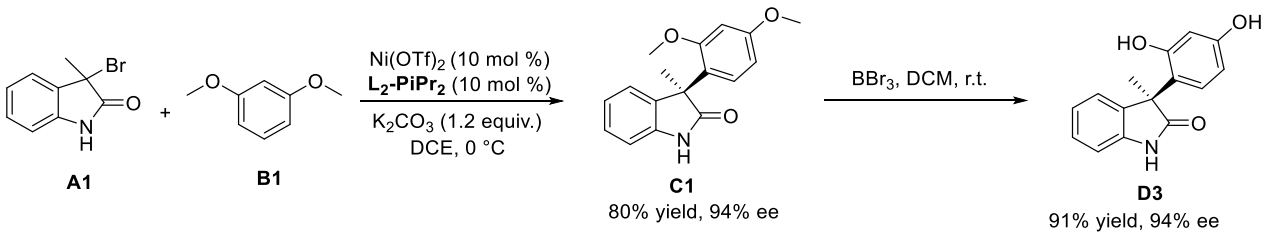
5.1 Procedure for the synthesis of D1



Compound **C40**: An oven-dried test tube was charged with metal salt $Ni(OTf)_2$ (7.2 mg, 0.02 mmol, 10 mol %), **L_3-PiEt$_2$Me** (12.4 mg, 0.02 mmol, 10 mol %) 3-Bromo-3-substituted oxindoles **A16** (56.8 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (33.2 mg, 0.24 mmol, 1.2 equiv.) under N_2 atmosphere. Anhydrous DCE (2.0 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, the arenes **B1** (41.2 μL, 0.30 mmol 1.5 equiv.) was added and the reaction was performed at 0 °C for 24 hours. The reaction mixture was directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4/1 to 2/1, v/v) to afford the corresponding product **C40** (45.1 mg, 66% yield, 97% ee).

Compound **D1**: An oven-dried test tube was charged with **C40** (43.1 mg, 0.13 mmol, 1.0 equiv.) and Cs_2CO_3 (84.7 mg, 0.26 mmol, 2.0 equiv.) and iodomethane (39.9 μL, 0.65 mmol, 5.0 equiv.). Anhydrous THF (1.0 mL) was added and the mixture was stirred at room temperature for 12 hours. Then the mixture was filtered and concentrated under reduced pressure. The residue was dissolved in dry THF under N_2 atmosphere. Anhydrous THF (1.0 mL) was added, the $LiAlH_4$ (1 M in THF, 0.39 mL, 0.39 mmol, 3.0 equiv.) was added in 0 °C and the mixture was stirred at 0 °C for 4 hours and then treated with several drops of $NaSO_4{\cdot}10H_2O$ until the evolution of H_2 ceased. The reaction mixture was directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 19/1 to 9/1, v/v) to afford the corresponding product **D2** (35.9 mg, 87% yield, 97% ee). in 95% yield with 97% ee.

5.2 Procedure for the synthesis of D2

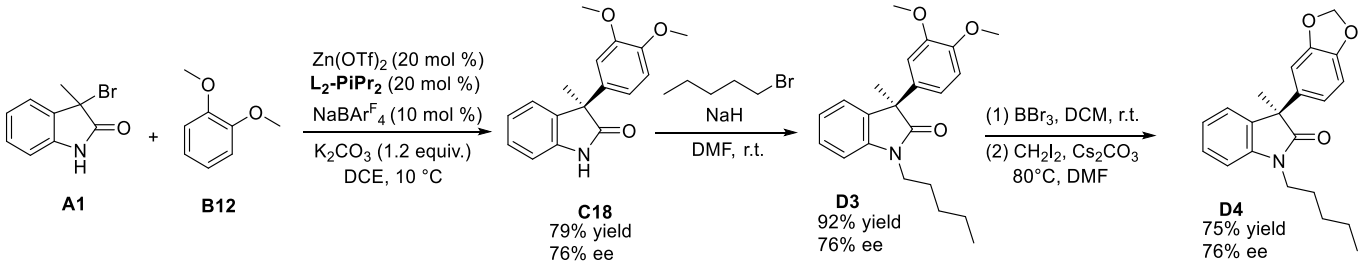


Compound **C1**: An oven-dried test tube was charged with metal salt $Ni(OTf)_2$ (7.2 mg, 0.02 mmol, 10 mol %), **L_2-PiPr$_2$** (12.6 mg, 0.02 mmol, 10 mol %) 3-Bromo-3-substituted oxindoles **A1** (45.2 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (33.2 mg, 0.24 mmol, 1.2 equiv.) under N_2 atmosphere. Anhydrous DCE (2.0 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, the arenes **B1** (39.0 μL, 0.30 mmol 1.5 equiv.) was added and the reaction was performed at 0 °C for 24 hours. The reaction mixture was directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3/1 to 1/1, v/v) to afford the corresponding product **C1** (46.1 mg, 80% yield, 94% ee).

Compound **D2**: An oven-dried test tube was charged with **C1** (28.8 mg, 0.10 mmol, 1.0 equiv.) and BBr_3 (1 M in DCM, 0.30 mL, 0.30 mmol, 3.0 equiv.). Anhydrous DCM (1.0 mL) was added and the mixture was stirred at room temperature for 12 hours. Then 0.2 mL

water was added in 0 °C to quench the reaction. The reaction mixture was directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to 1/2, v/v) to afford the corresponding product **D2** (23.2 mg, 91% yield, 94% ee).

5.3 Procedure for the synthesis of D4

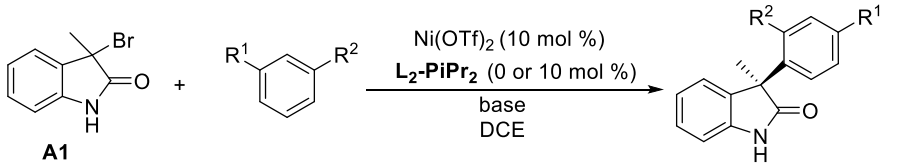


Compound **C40**: An oven-dried test tube was charged with metal salt $Zn(OTf)_2$ (10.8 mg, 0.03 mmol, 20 mol %), **L_3-PiPr$_2$** (18.0 mg, 0.03 mmol, 20 mol %), $NaBAr^F_4$ (13.3 mg, 0.015 mmol,10 mol%) 3-Bromo-3-substituted oxindoles **A1** (33.9 mg, 0.15 mmol, 1.0 equiv.), K_2CO_3 (24.9 mg, 0.18 mmol, 1.2 equiv.) under N_2 atmosphere. Anhydrous DCE (1.5 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, the arenes **B1** (57.3 μL, 0.30 mmol 3.0 equiv.) was added and the reaction was performed at 10 °C for 24 hours. The reaction mixture was directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4/1 to 2/1, v/v) to afford the corresponding product **C18** (34.2 mg, 79% yield, 76% ee).

Compound **D3**: An oven-dried test tube was charged with **C18** (22.8 mg, 0.079 mmol, 1.0 equiv.) and NaH (3.8 mg, 0.158 mmol, 2.0 equiv.) and iodomethane (19.6 μL, 0.158 mmol, 2.0 equiv.). Anhydrous DMF (1.0 mL) was added and the mixture was stirred at room temperature for 12 hours. Then the reaction mixture was directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 9/1 to 4/1, v/v) to afford the corresponding product **D3** (25.6 mg, 92% yield, 76% ee).

Compound **D4**: An oven-dried test tube was charged with **D3** (25.6 mg, 0.073 mmol, 1.0 equiv.) and BBr_3 (1 M in DCM, 0.22 mL, 0.22 mmol, 3.0 equiv.). Anhydrous DCM (1.0 mL) was added and the mixture was stirred at room temperature for 12 hours. Then 0.2 mL water was added in 0 °C to quench the reaction. The resulting mixture was extracted with DCM. The organic layer was washed with brine, dried over anhydrous Na_2SO4, filtered and concentrated under reduced pressure. The crude product is directly used for the next step. An oven-dried test tube was charged with crude product, Cs_2CO_3 (71.7 mg, 0.22 mmol, 3.0 equiv.) and CH_2I_2 (17.7 μL, 0.22 mmol, 3.0 equiv.). Anhydrous DMF (1.0 mL) was added and the mixture was stirred at 80 °C for 12 hours. The reaction mixture was directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 19/1 to 9/1, v/v) to afford the corresponding product **C4** (18.5 mg, 75% yield, 76% ee).

6 Control experiments



B1: R^1 = OMe, R^2 = OMe
B23: R^1 = Me, R^2 = OH

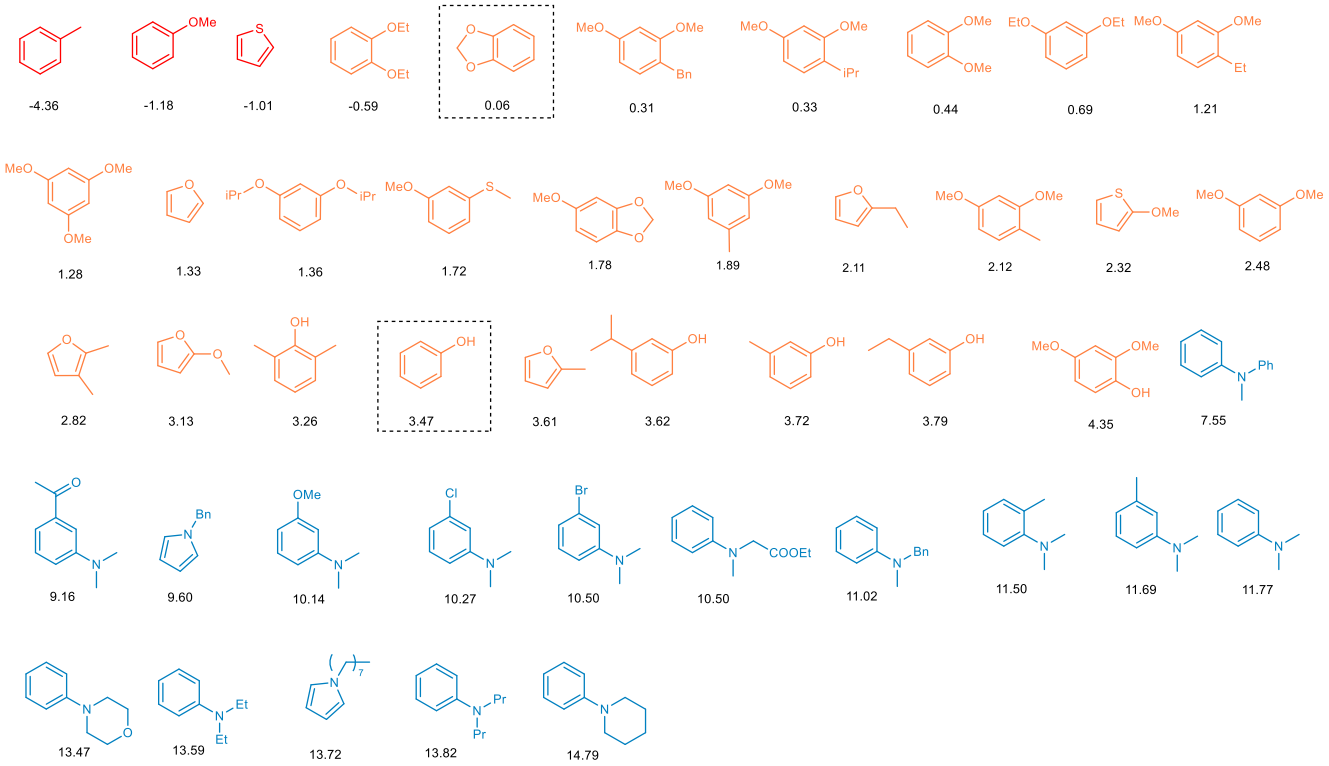
C1: R^1 = OMe, R^2 = OMe
C23: R^1 = Me, R^2 = OH

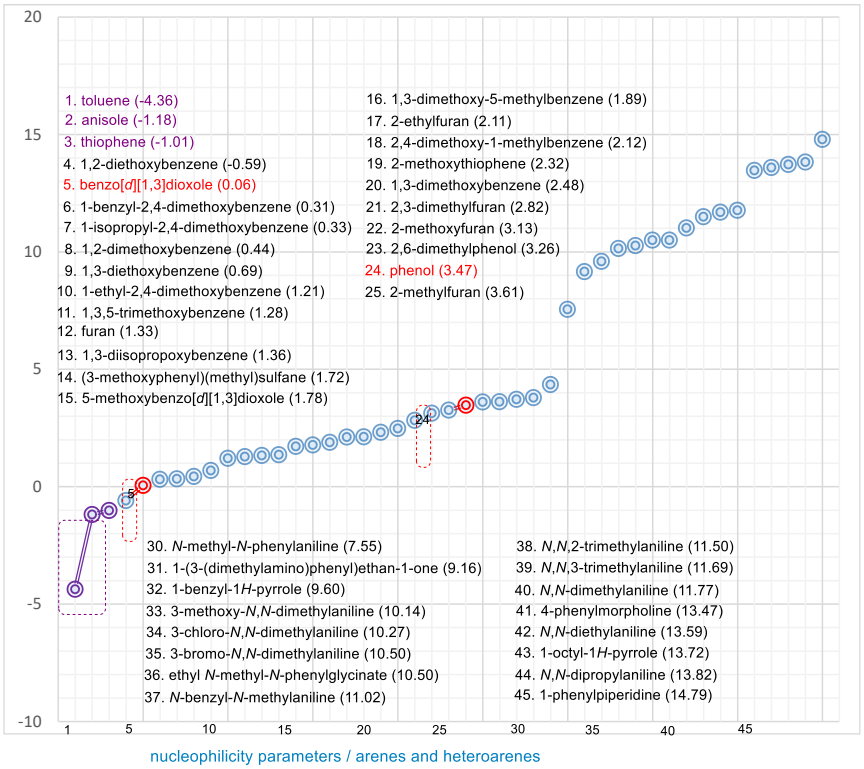
condition: **B1**, K_2CO_3 (1.2 equiv.), 0 °C	**C1**
without **L_2-PiPr$_2$**	78% yield, racemic
with **L_2-PiPr$_2$**	80% yield, 94% ee
condition: **B23**, *i*Pr_2NEt (1.0 equiv.), 20 °C	**C23**
without **L_2-PiPr$_2$**	trace
with **L_2-PiPr$_2$**	53% yield, 89% ee

An oven-dried test tube was charged with corresponding catalyst, K_2CO_3 (0.12 mmol, 1.2 equiv.) 3-Bromo-3-substituted oxindoles **A1** (0.10 mmol, 1 equiv.), under N_2 atmosphere. Anhydrous DCE (1.0 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, the arenes **B1** (0.30 mmol 3.0 equiv.), *i*Pr_2NEt (0.10 mmol, 1.0 equiv.) was added at 0 °C and the reaction was performed at 0 °C for 12 hours. The reaction mixture was directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1 to 1:1) to afford the corresponding products **C1**.

An oven-dried test tube was charged with corresponding catalyst, 3-Bromo-3-substituted oxindoles **A1** (0.10 mmol, 1 equiv.), under N_2 atmosphere. Anhydrous DCE (1.0 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, the arenes **B23** (0.30 mmol 3.0 equiv.), *i*Pr_2NEt (0.10 mmol, 1.0 equiv.) was added at 20 °C and the reaction was performed at 20 °C for 12 hours. The reaction mixture was directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1 to 2:1) to afford the corresponding products **C23**.

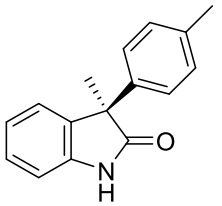
7 Comparison of nucleophilicity parameters for arenes and heteroarenes



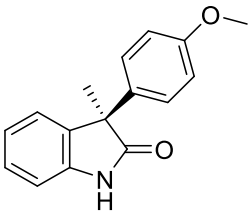


The nucleophilicity of arenes and heteroarenes derived from Mayr's Database.

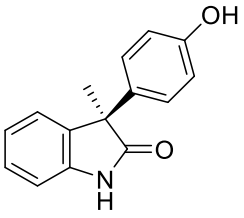
8 Unsuccessful substrate scopes



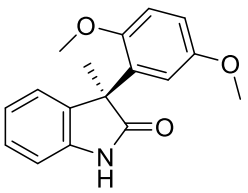
N.R.



N.R.



trace



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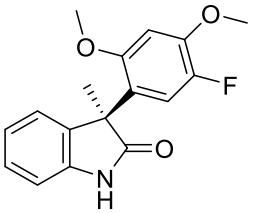

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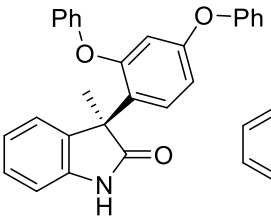

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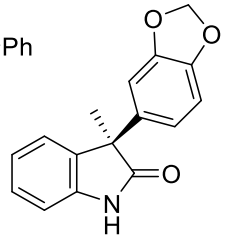

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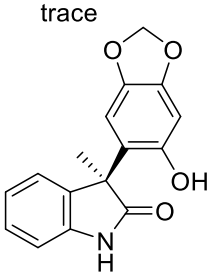
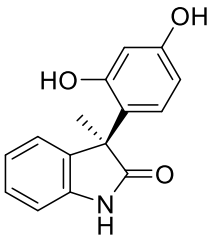
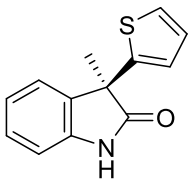


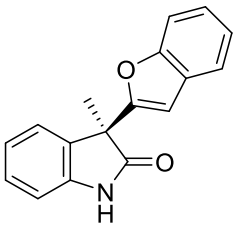
39% yield
24% ee



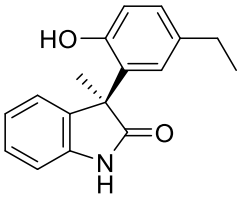
31% yield
40% ee



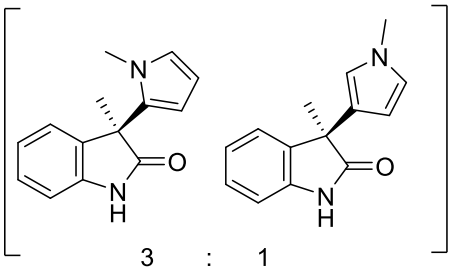
N.R.



16% yield
96% ee



trace



3 : 1
61% yield
42% ee
20% yield
33% ee

9 Bioactivity Study

Cell Culture

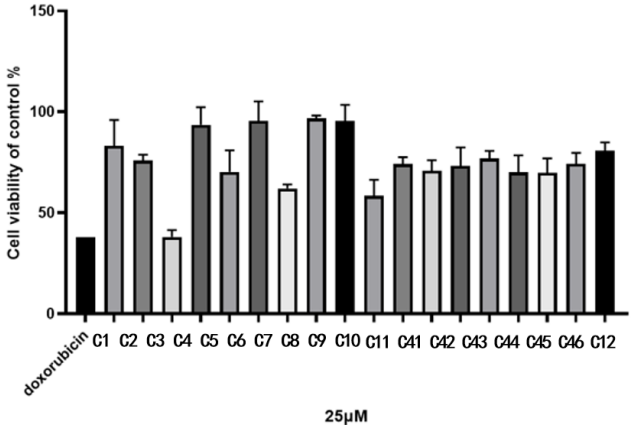
Hepatocellular carcinoma cell line HCCLM3 (obtained from Procell) were cultured with DMEM (Hyclone, Utah) supplemented with 10 % (v/v) FBS (Gibco, New York), 1 % (v/v) penicillin/streptomycin (Beyotime, Shanghai). All cells were cultured in incubator with 5% CO_2 at 37 ℃.

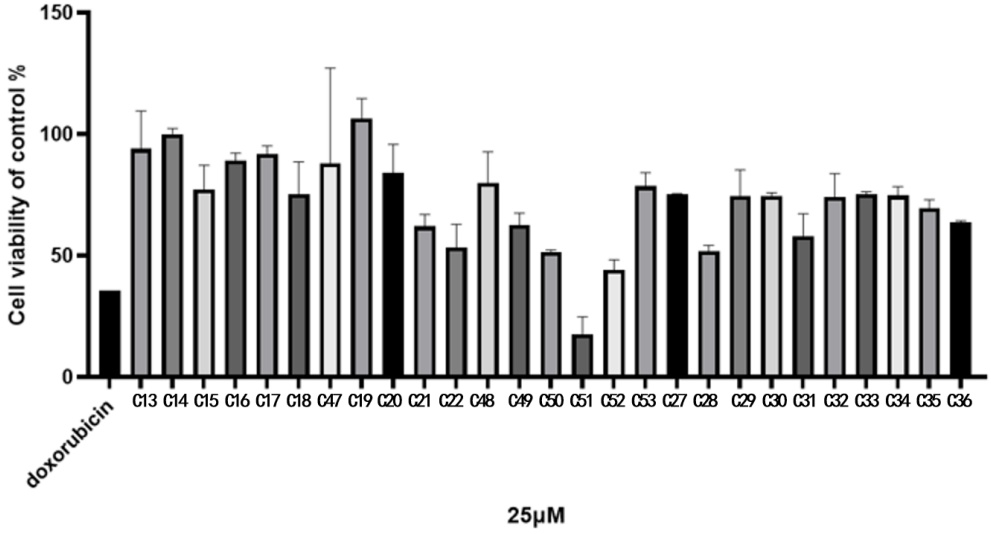
Cell Viability Assay

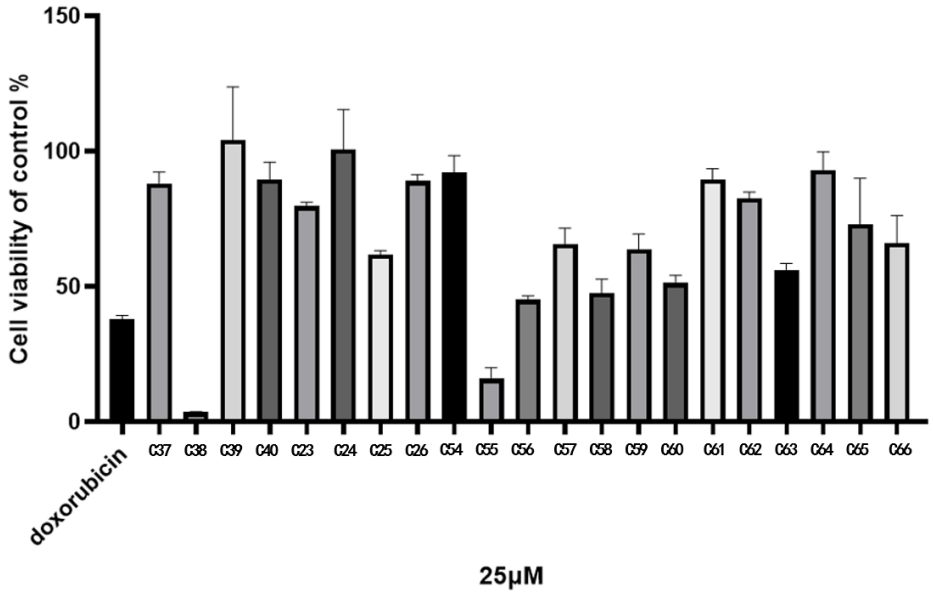
Cells of logarithmic growth stage were inoculated in 96-well plate with density of 1.5*104 per well. Overnight all cells which density at 80 %, were treated with 1 % DMSO (negative control) and other compounds with different concentrations at 37 ℃ for 24h. No FBS DMEM with 10 % (v/v) CCK-8 (Selleck, Houston) was added to each well and incubated for 1h at 37 ℃. The absorbance was determined at 450 nm to calculated cell viability (%). IC_{50} was detected using Graphpad Prism. Each experiment was repeated three times.

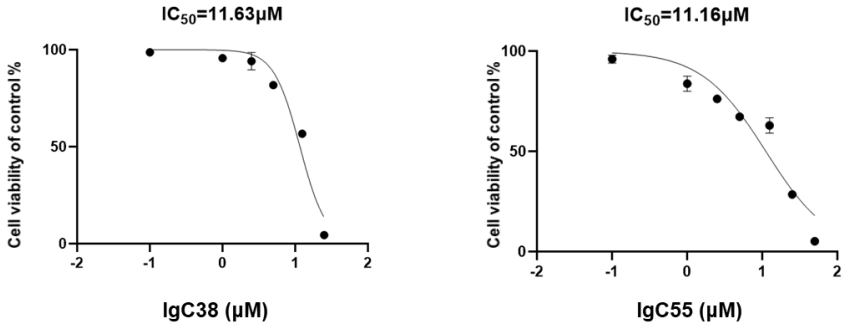
Synthetic compounds inhibit hepatocellular carcinoma viability screening

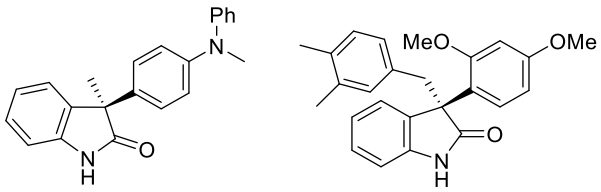
To study the anti-hepatocellular carcinoma (HCCLM3) of synthetic compounds. We measured the HCCLM3 cell viability after exposed to each compound with 25 μM for 24h. The results showed that **C38** and **C55** had strong inhibitory effect on the proliferation and viability of HCCLM3 and the IC_{50} concentrations of **C38** and **C55** treated HCCLM3 cells for 24 h are 11.63 μM and 11.16 μM respectively.


Cell viability of control %
150
100
50
0
doxorubicin
C1 C2 C3 C4 C5 C6 C7 C8 C9 C10 C11 C41 C42 C43 C44 C45 C46 C12
25μM


Cell viability of control %
150
100
50
0
doxorubicin
C13 C14 C15 C16 C17 C18 C47 C19 C20 C21 C22 C48 C49 C50 C51 C52 C53 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36
25μM


Cell viability of control %
150
100
50
0
doxorubicin
C37 C38 C39 C40 C23 C24 C25 C26 C54 C55 C56 C57 C58 C59 C60 C61 C62 C63 C64 C65 C66
25μM





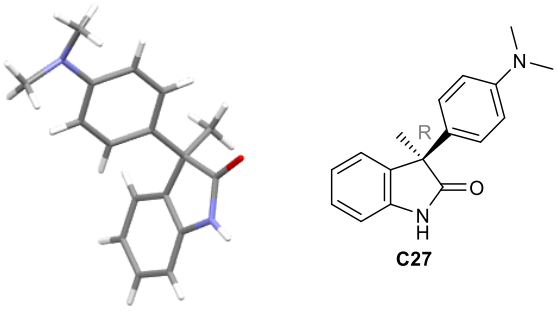
C38 **C55**

IC_{50} 11.63 μM 11.16 μM

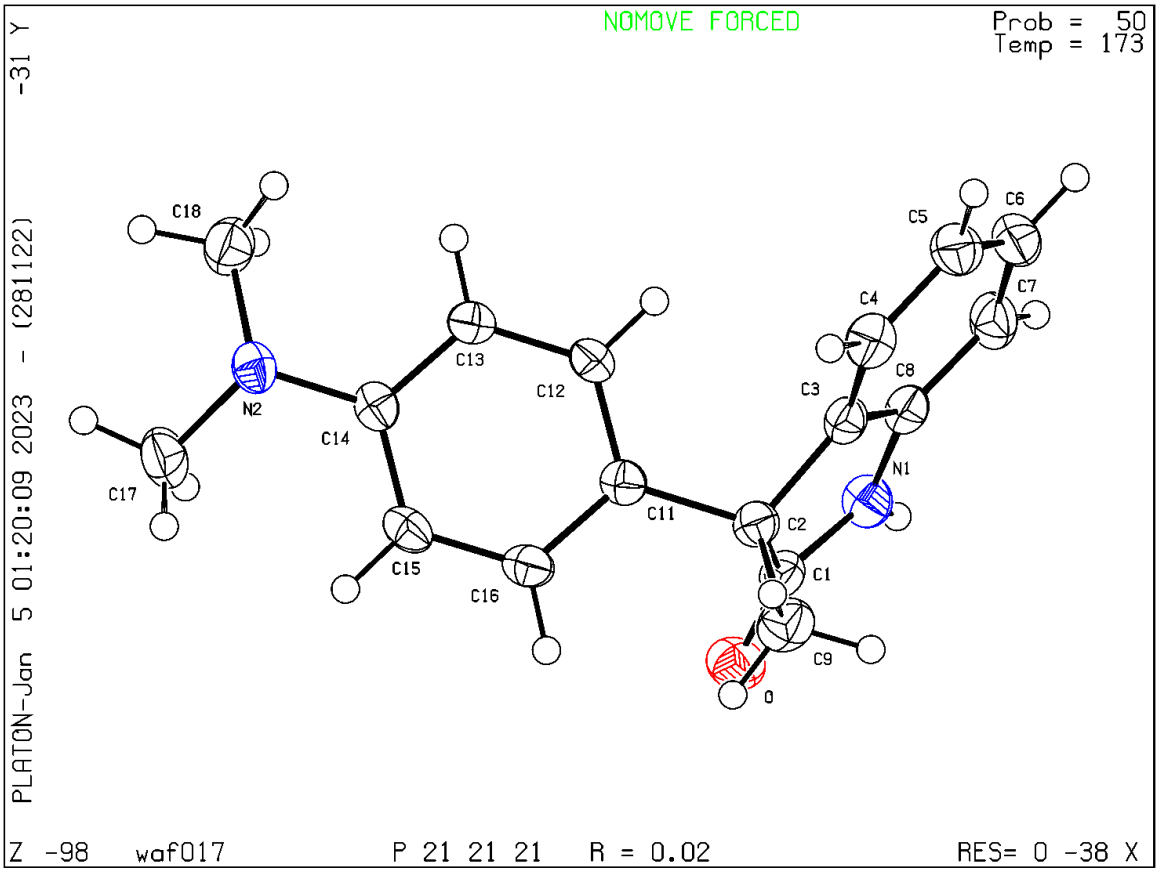
10 Determination of absolute configuration of products

10.1 Determination of absolute configuration of compound C27

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **C27** in ethyl acetate (ca. 0.1 mL) and petroleum ether (0.3 mL) at r.t.. The colourless crystal in block-shape, with approximate dimensions of 0.234 × 0.287 × 0.376 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2) K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package[3]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[4].



C27


NOMOVE FORCED
Prob = 50
Temp = 173
-31 Y
PLATON-Jan 5 01:20:09 2023 - (281122)
C18
N2
C17
C14
C13
C12
C15
C16
C11
C2
C1
C9
O
C3
C4
C5
C6
C7
C8
N1
Z -98 waf017
P 21 21 21 R = 0.02
RES= 0 -38 X

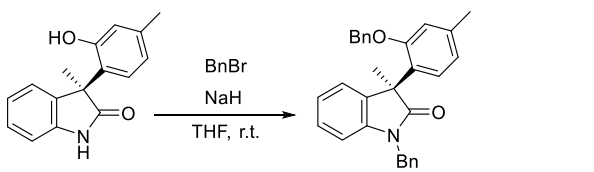
Crystallographic Data for $C_{17}H_{18}N_2O$

Formula	$C_{17}H_{18}N_2O$
Formula mass (amu)	266.33
Space group	P212121
a (Å)	6.4469 (2)
b (Å)	9.2442 (3)
c (Å)	24.0016 (7)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	1430.41 (8)
Z	4
λ (Å)	1.54178
T (K)	173
ρ_{calcd} (g cm^{-3})	1.237
μ (mm^{-1})	0.612
Transmission factors	0.859–0.933
$2\theta_{max}$ (deg)	68.228
No. of unique data, including $F_o^2 < 0$	2611
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	2593
No. of variables	189
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0237
$R_w(F_o^2)$ [b]	0.0640
Goodness of fit	1.106

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

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

10.2 Futher transformation of compound C23'



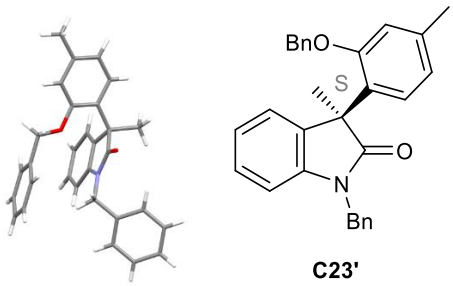
C23
89% ee

C23'
80% yield
95% ee (after recrystallization)

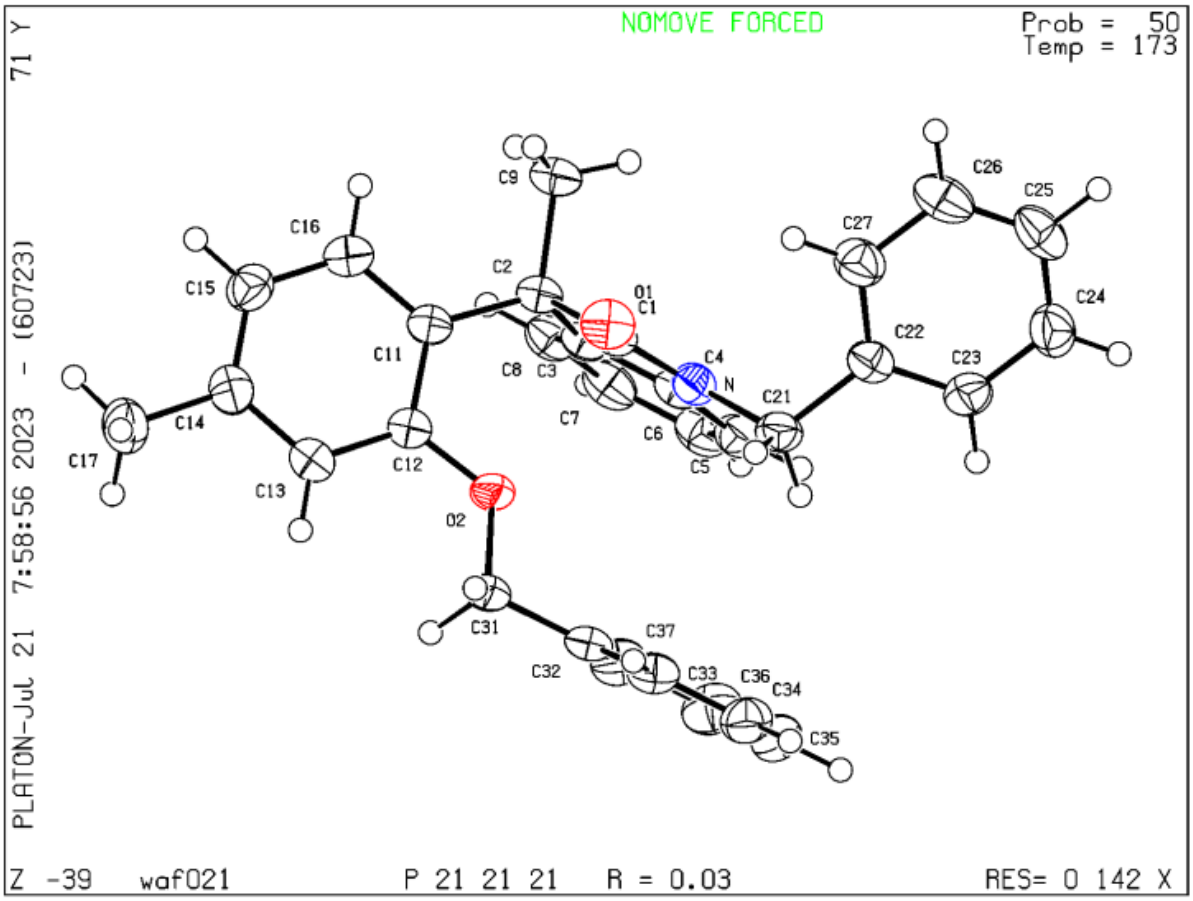
Compound **C23′**: An oven-dried test tube was charged with **C23** (18.0 mg, 0.071 mmol, 1.0 equiv.) and NaH (8.5 mg, 0.335 mmol, 5.0 equiv.) and BnBr (42.2 μL, 0.335 mmol, 5.0 equiv.). Anhydrous THF (1.0 mL) was added and the mixture was stirred at room temperature for 12 hours. Then the reaction mixture was directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 9/1 to 4/1, v/v), the product was recrystallized with dichloromethane and petroleum ether to afford the corresponding product **C23′** (24.6 mg, 80% yield, 95% ee).

10.3 Determination of absolute configuration of compound C23′

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **C23′** in dichloromethane (ca. 0.1 mL) and petroleum ether (0.3 mL) at r.t.. The colourless crystal in block-shape, with approximate dimensions of 0.216 × 0.219 × 0.266 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2) K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package[3]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[4].



C23'


NOMOVE FORCED
Prob = 50
Temp = 173
71 Y
PLATON-Jul 21 7:58:56 2023 - (60723)
C9
C16
C15
C2
O1
C1
C26
C25
C27
C24
C22
C23
C11
C8
C3
C4
N
C21
C7
C6
C5
C14
C17
C13
C12
O2
C31
C37
C32
C33
C36
C34
C35
Z -39 waf021
P 21 21 21
R = 0.03
RES= 0 142 X

Crystallographic Data for $C_{30}H_{27}NO_2$

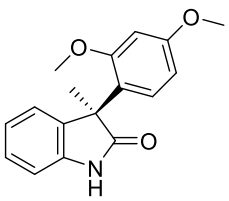
Formula	$C_{30}H_{27}NO_2$
Formula mass (amu)	433.52
Space group	P212121
a (Å)	9.7721(2)
b (Å)	12.5443(2)
c (Å)	19.4584(3)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	2385.41(7)
Z	4
λ (Å)	1.54178
T (K)	173
ρ_{calcd} (g cm^{-3})	1.207
μ (mm^{-1})	0.586
Transmission factors	0.784–0.955
$2\theta_{max}$ (deg)	68.312
No. of unique data, including $F_o^2 < 0$	4326
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	4142
No. of variables	301
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0290
$R_w(F_o^2)$ [b]	0.0705
Goodness of fit	1.038

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

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

11 Characterization of the products

(*S*)-3-(2,4-dimethoxyphenyl)-3-methylindolin-2-one (C1)



C1

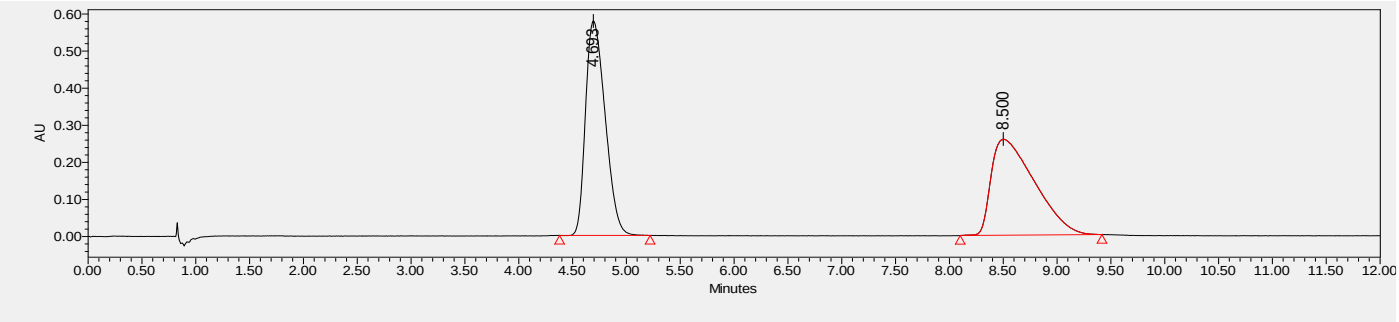
White solid; 22.6 mg, 80% yield, 94% ee; melting point: 85–87 °C; $[\alpha]_D^{16.6}$ = -72.8 (*c* = 0.12 in CH_2Cl_2). **UPCC** DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 4.67 min, t_R (minor) = 8.83 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.56 (s, 1H), 7.55 – 7.43 (d, *J* = 8.5 Hz 1H), 7.17 – 7.05 (m, 1H), 6.94 – 6.78 (m, 2H), 6.62 – 6.52 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.38 – 6.33 (d, *J* = 2.5 Hz, 1H), 3.79 (s, 3H), 3.44 (s, 3H), 1.71 (s, 3H).

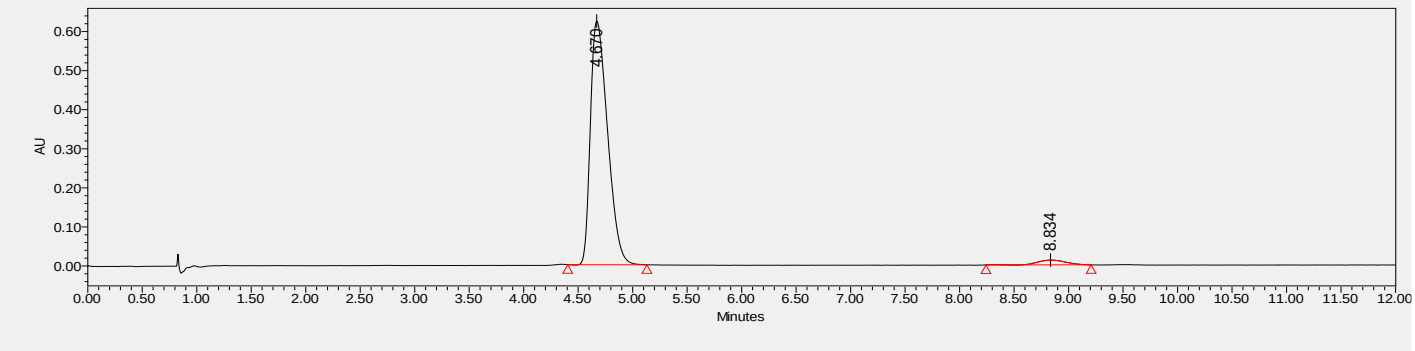
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 183.8, 160.7, 158.2, 140.7, 136.8, 128.3, 127.3, 122.5, 122.2, 122.0, 109.3, 104.6, 100.1, 55.7, 55.5, 50.1, 23.93.

IR: 2932, 1613, 1504, 1470, 1300, 1209, 1142, 1031, 756, 643 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}NO_3Na^+$ 306.1101; found 306.1103.

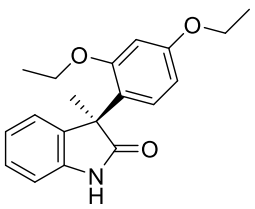


	Retention Time	Area	% Area
1	4.693	7334382	50.41
2	8.500	7215636	49.59



	Retention Time	Area	% Area
1	4.670	6829892	96.85
2	8.834	222370	3.15

(*S*)-3-(2,4-diethoxyphenyl)-3-methylindolin-2-one (C2)



C2

White solid; 26.7 mg, 86% yield, 90% ee; melting point: 131–133 °C; $[\alpha]_D^{15.2}$ = -70.1 (*c* = 0.24 in CH_2Cl_2).

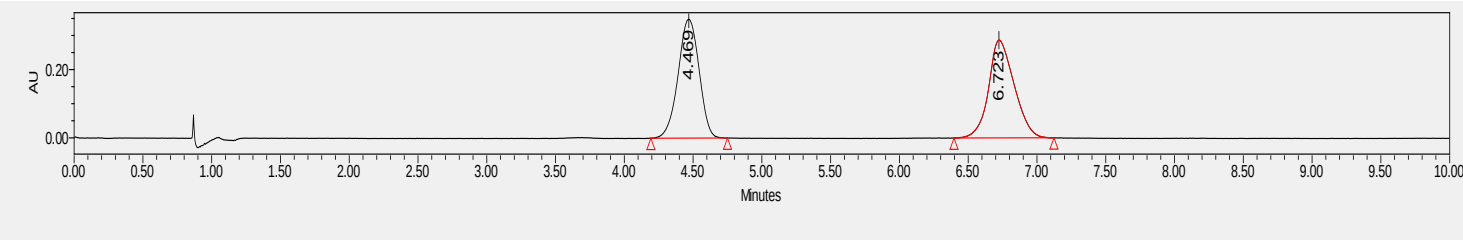
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 4.49 min, t_R (minor) = 6.77 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.93 (s, 1H), 7.53 – 7.40 (d, *J* = 8.6 Hz, 1H), 7.17 – 7.01 (m, 1H), 6.95 – 6.85 (m, 2H), 6.85 – 6.73 (m, 1H), 6.61 – 6.49 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.37 – 6.28 (d, *J* = 2.5 Hz, 1H), 4.01 (q, *J* = 7.0 Hz, 2H), 3.78 (dq, *J* = 8.9, 7.0 Hz, 1H), 3.56 (dq, *J* = 8.9, 7.0 Hz, 1H), 1.71 (s, 3H), 1.39 (t, *J* = 7.0 Hz, 3H), 0.94 (t, *J* = 7.0 Hz, 3H).

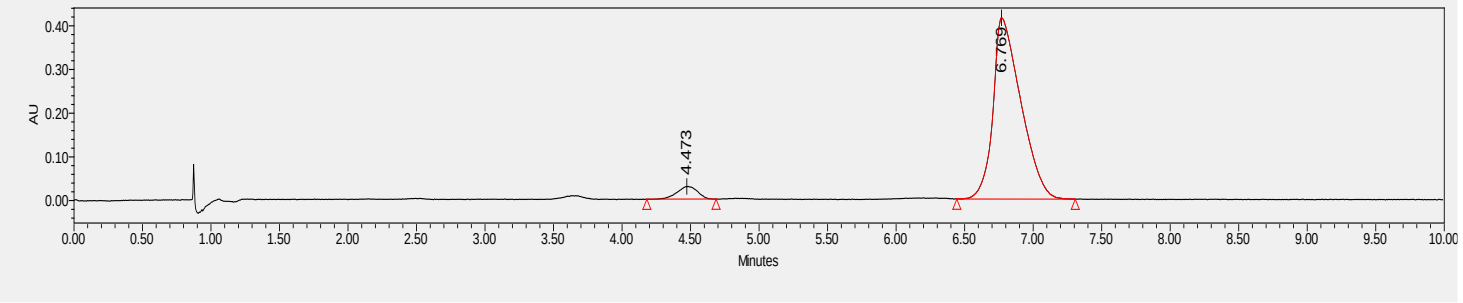
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 184.1, 159.9, 157.3, 141.1, 137.1, 128.2, 127.2, 122.4, 122.1, 121.3, 109.4, 104.6, 100.3, 63.7, 63.6, 50.2, 23.8, 15.0, 13.8.

IR: 2977, 2926, 1613, 1583, 1263, 1188, 1141, 754, 650, 593 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{21}NO_3Na^+$ 334.1414; found 334.1414.

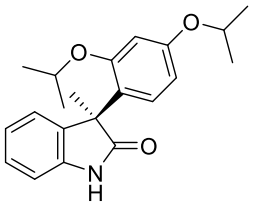


	Retention Time	Area	% Area
1	4.469	3749773	49.75
2	6.723	3787472	50.25



	Retention Time	Area	% Area
1	4.491	509538	5.23
2	6.769	9239624	94.77

(*S*)-3-(2,4-diisopropoxyphenyl)-3-methylindolin-2-one (C3)



C3

White solid; 30.5 mg, 90% yield, 88% ee; melting point: 150–152 °C; $[\alpha]_D^{16.6}$ = -23.6 (*c* = 0.31 in CH_2Cl_2).

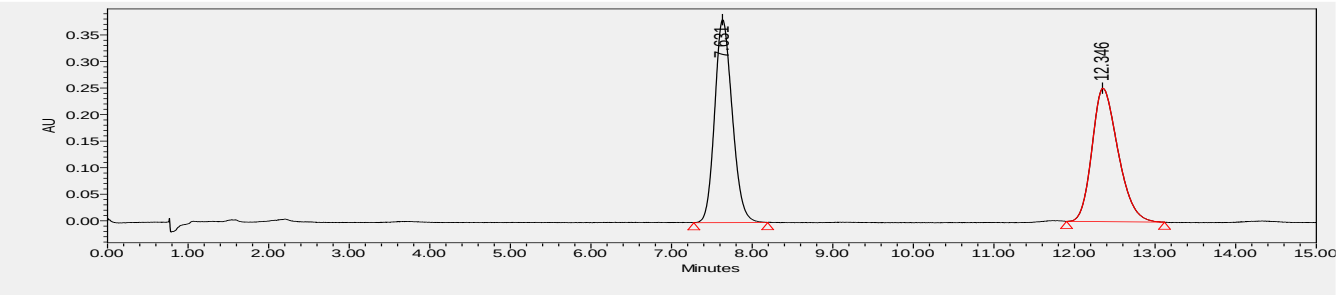
UPCC DAICEL CHIRALCEL OX-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 7.59 min, t_R (minor) = 12.45 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.66 (s, 1H), 7.56 – 7.30 (d, *J* = 8.6 Hz, 1H), 7.17 – 7.06 (m, 1H), 6.98 – 6.83 (m, 2H), 6.84 – 6.73 (m, 1H), 6.57 – 6.42 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.35 – 6.24 (d, *J* = 2.4 Hz, 1H), 4.59 – 4.40 (m, 1H), 4.36 – 4.23 (m, 1H), 1.69 (s, 3H), 1.32 (t, *J* = 6.4 Hz, 6H), 1.10 (d, *J* = 6.0 Hz, 3H), 0.59 (d, *J* = 6.0 Hz, 3H).

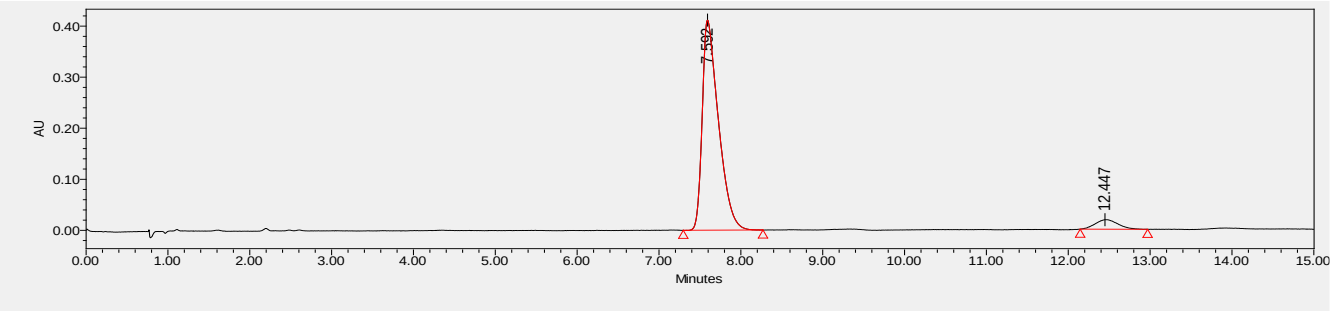
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 183.9, 158.8, 155.8, 141.2, 137.4, 128.4, 127.1, 122.5, 122.0, 121.6, 109.2, 105.4, 101.8, 70.0, 69.2, 50.2, 23.7, 22.4, 22.2, 21.4, 20.6.

IR: 2976, 1613, 1611, 1581, 1191, 1132, 1101, 952, 754, 652 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{25}NO_3Na^+$ 362.1727; found 362.1727.

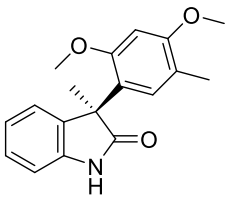


	Retention Time	Area	% Area
1	7.631	5804403	50.74
2	12.346	5634463	49.26



	Retention Time	Area	% Area
1	7.592	5655425	93.96
2	12.447	363808	6.04

(*S*)-3-(2,4-dimethoxy-5-methylphenyl)-3-methylindolin-2-one (C4)



C4

Colorless oil; 26.8 mg, 90% yield, 98% ee; $[\alpha]_D^{14.6}$ = -70.3 (*c* = 0.16 in CH_2Cl_2).

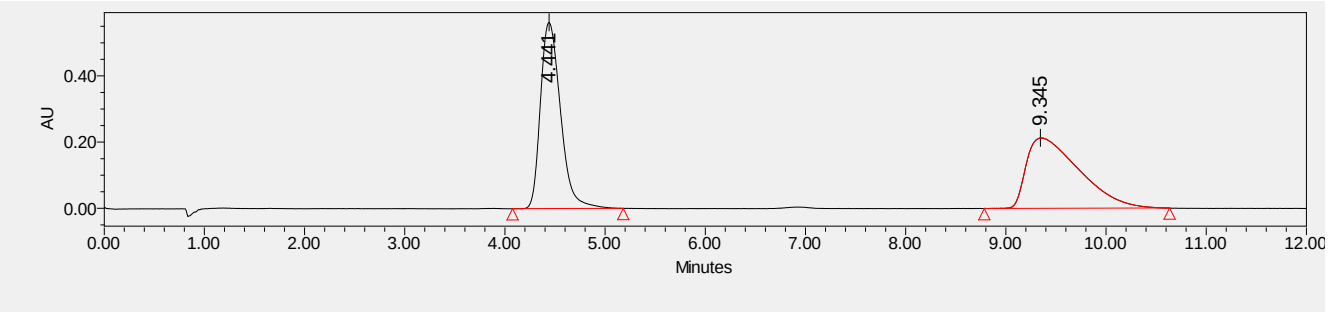
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 4.34 min, t_R (minor) = 9.71 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.30 (s, 1H), 7.17 – 7.07 (m, 1H), 6.93 – 6.81 (m, 3H), 6.35 (s, 1H), 3.78 (s, 3H), 3.43 (s, 3H), 2.22 (s, 3H), 1.71 (s, 3H).

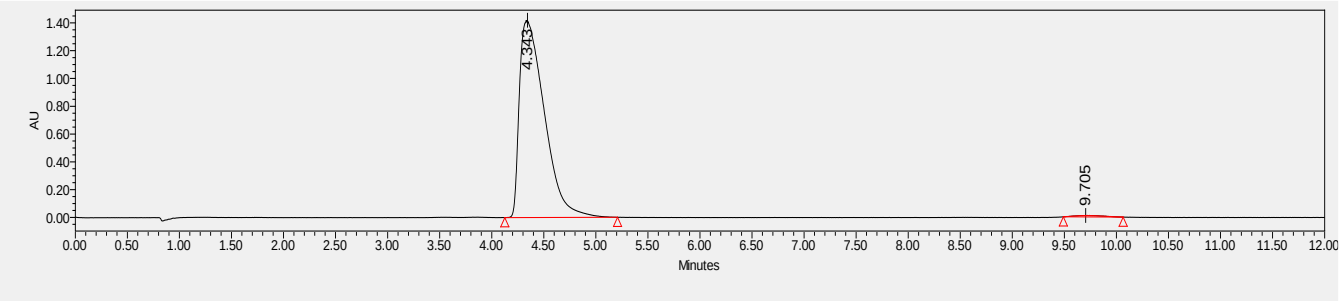
^{13}C NMR (101 MHz, $CDCl_3$) δ 184.2, 158.1, 156.3, 140.8, 137.1, 129.5, 127.2, 122.6, 122.2, 121.1, 118.6, 109.4, 97.0, 56.2, 55.6, 50.0, 23.8, 15.9.

IR: 2931, 1614, 1512, 1581, 1469,1310, 1209, 869, 755, 677 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{19}NO_3Na^+$ 320.1257; found 320.1260.

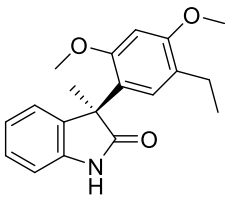


	Retention Time	Area	% Area
1	4.441	7830543	50.19
2	9.345	7772395	49.81



	Retention Time	Area	% Area
1	4.343	23584971	99.16
2	9.705	198825	0.84

(*S*)-3-(5-ethyl-2,4-dimethoxyphenyl)-3-methylindolin-2-one (C5)



C5

White soild; 28.9 mg, 93% yield, 99% ee; melting point: 132–135 °C; $[\alpha]_D^{14.9}$ = -66.2 (*c* = 0.23 in CH_2Cl_2).

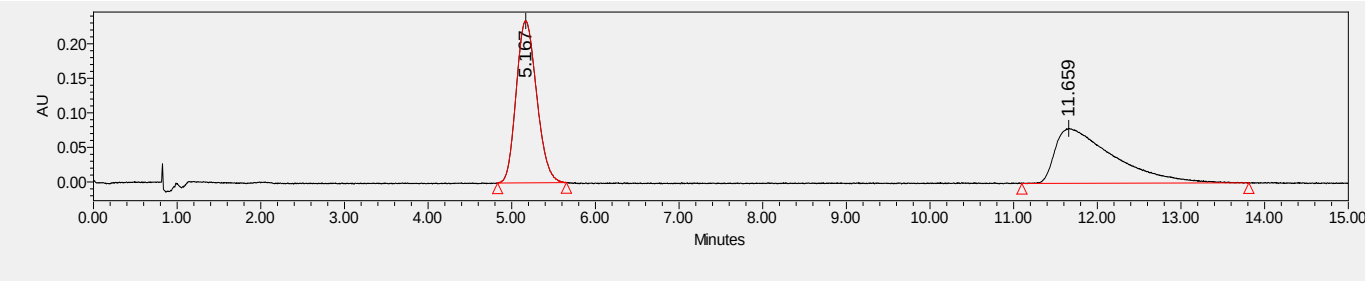
UPCC DAICEL CHIRALCEL AD-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 5.07 min, t_R (minor) = 12.11 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.79 (s, 1H), 7.32 (s, 1H), 7.16 – 7.08 (m, 1H), 6.93 – 6.81 (m, 3H), 6.35 (s, 1H), 3.78 (s, 3H), 3.43 (s, 3H), 2.64 (dq, *J* = 7.5, 2.0 Hz, 2H), 1.72 (s, 3H), 1.23 (t, *J* = 7.5 Hz, 3H).

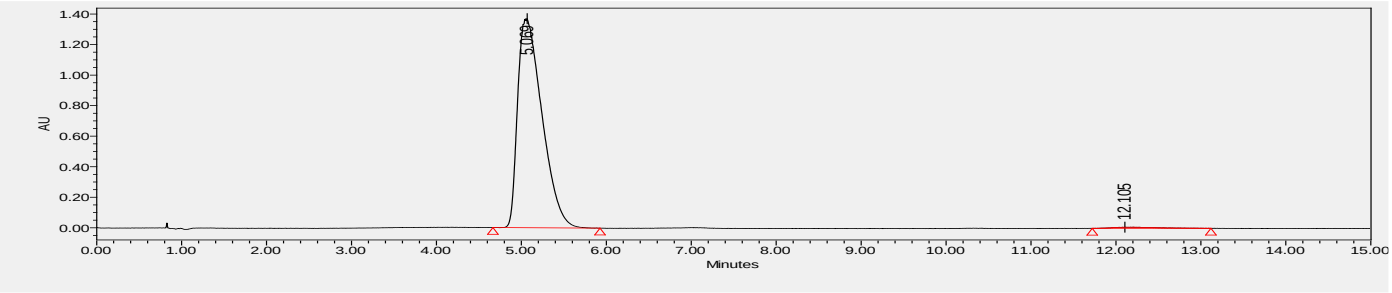
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 184.2, 158.1, 156.3, 140.8, 137.1, 129.5, 127.2, 122.6, 122.2, 121.1, 118.6, 109.4, 97.0, 56.2, 55.6, 50.0, 23.8, 15.9.

IR: 2965, 1615, 1504, 1308, 1207, 1136, 1107, 1034, 754, 676 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{21}NO_3Na^+$ 334.1414; found 334.1415.

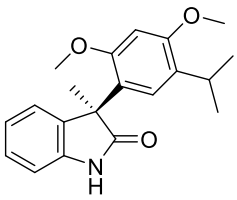


	Retention Time	Area	% Area
1	5.167	3968763	50.79
2	11.659	3845984	49.21



	Retention Time	Area	% Area
1	5.069	27227599	99.05
2	12.105	261493	0.95

(*S*)-3-(5-isopropyl-2,4-dimethoxyphenyl)-3-methylindolin-2-one (C6)



C6

White soild; 29.3 mg, 90% yield, 99% ee; melting point: 167–169 °C; $[\alpha]_D^{14.3}$ = -67.4 (*c* = 0.29 in CH_2Cl_2).

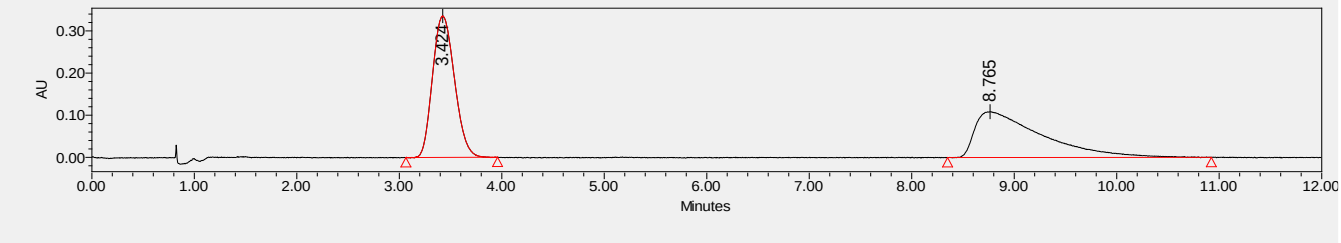
UPCC DAICEL CHIRALCEL AD-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 3.38 min, t_R (minor) = 9.05 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.79 (s, 1H), 7.37 (s, 1H), 7.16 – 7.08 (m, 1H), 6.93 – 6.79 (m, 3H), 6.35 (s, 1H), 3.78 (s, 3H), 3.44 (s, 3H), 3.28 (m, 1H), 1.73 (s, 3H), 1.27 (dd, *J* = 6.9, 5.1 Hz, 6H).

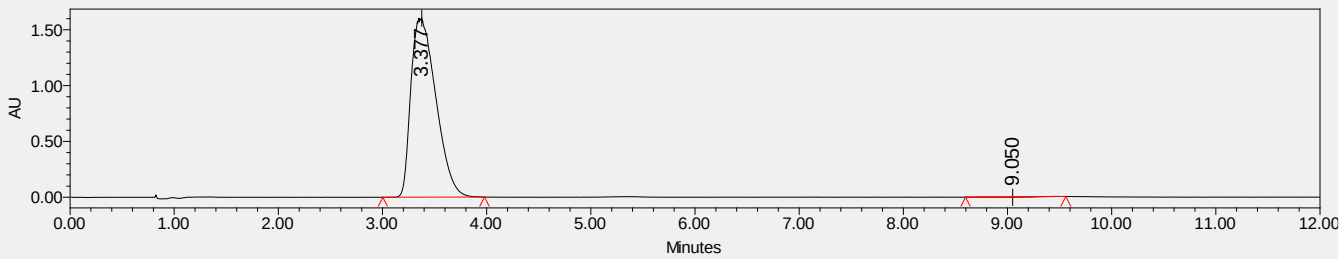
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 184.3, 157.3, 155.9, 140.8, 137.0, 129.0, 127.2, 125.0, 122.6, 122.2, 121.2, 109.4, 97.1, 56.1, 55.7, 50.2, 26.9, 23.8, 23.1, 23.0.

IR: 2960, 1615, 1504, 1469, 1206, 1156, 1123, 1034, 750, 674 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{20}H_{23}NO_3Na^+$ 348.1570; found 348.1573.

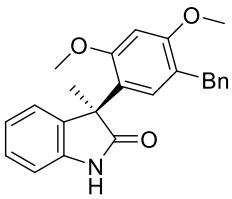


	Retention Time	Area	% Area
1	3.424	4994348	50.37
2	8.765	4920281	49.63



	Retention Time	Area	% Area
1	3.377	26726428	99.72
2	9.050	75418	0.28

(*S*)-3-(5-benzyl-2,4-dimethoxyphenyl)-3-methylindolin-2-one (C7)



C7

Colorless oil; 34.7 mg, 93% yield, 99% ee; $[\alpha]_D^{14.6}$ = -65.4 (*c* = 0.29 in CH_2Cl_2).

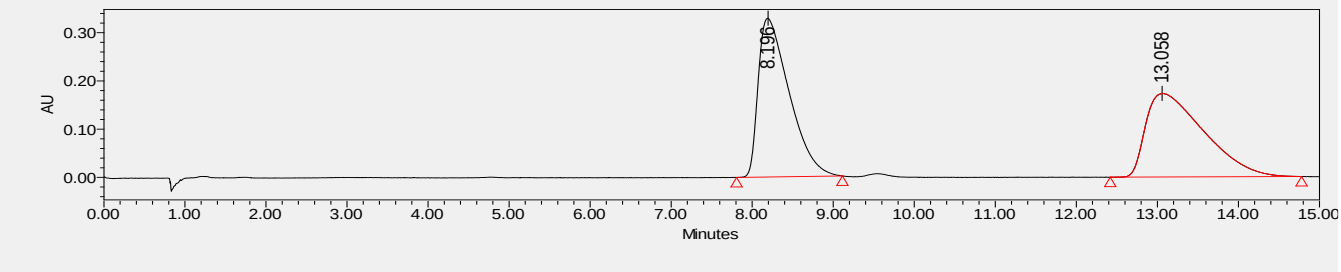
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 8.30 min, t_R (minor) = 13.84 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.90 (s, 1H), 7.34 – 7.15 (m, 5H), 7.13 – 7.07 (m, 1H), 6.92 – 6.83 (m, 1H), 6.82 – 6.76 (m,2H), 6.37 (s, 1H), 3.96 (m, 2H), 3.75 (s, 3H), 3.44 (s, 3H), 1.63 (s, 3H).

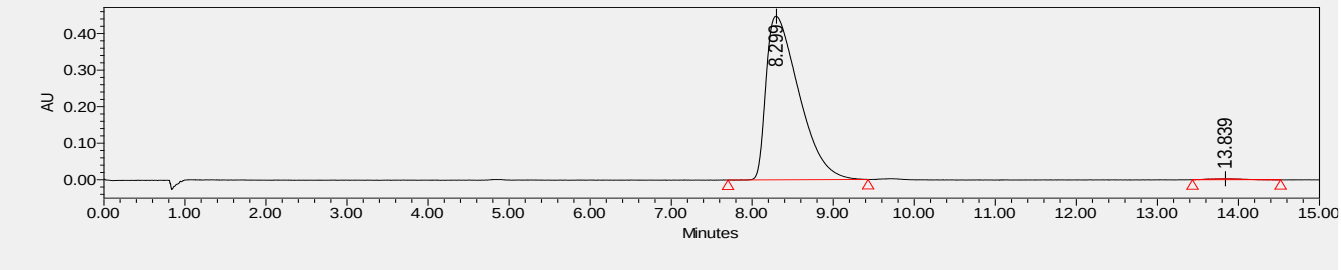
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 184.2, 157.9, 156.7, 141.5, 140.8, 136.9, 129.4, 128.9, 128.4, 127.2, 125.9, 122.5, 122.2, 121.5, 121.3, 109.4, 97.1, 56.1, 55.7, 50.0, 35.7, 23.7.

IR: 2929, 1614, 1505, 1468, 1207, 1132, 1104, 1032, 736, 701, 67 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{24}H_{23}NO_3Na^+$ 396.1570; found 396.1564.

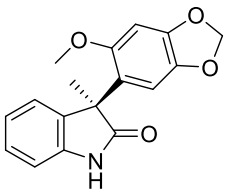


	Retention Time	Area	% Area
1	8.196	8736500	50.29
2	13.058	8636538	49.71



	Retention Time	Area	% Area
1	8.299	12615482	99.44
2	13.839	70835	0.56

(*S*)-3-(6-methoxybenzo[d][1,3]dioxol-5-yl)-3-methylindolin-2-one (C8)



C8

Colorless oil; 33.6 mg, 90% yield, 88% ee; $[\alpha]_D^{14.3}$ = -77.1 (*c* = 0.28 in CH_2Cl_2).

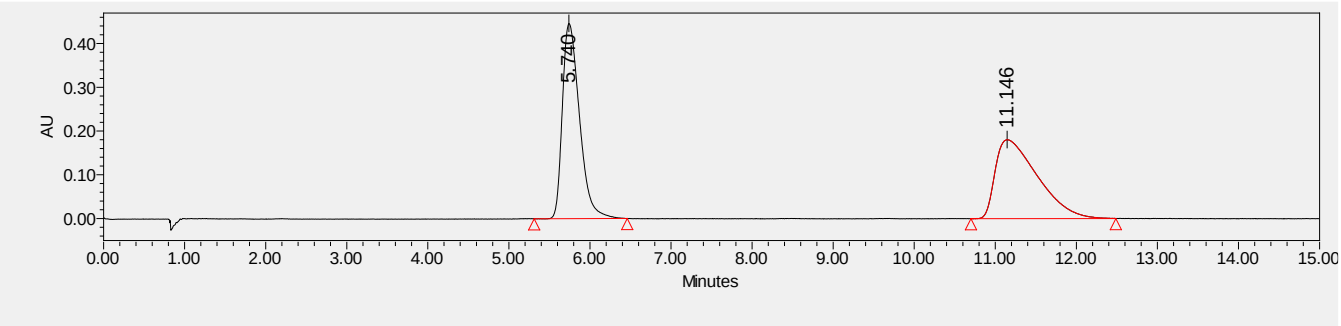
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 5.76 min, t_R (minor) = 11.56 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.97 (s, 1H), 7.18 – 7.08 (m, 2H), 6.95 – 6.87 (m, 2H), 6.88 – 6.79 (m, 1H), 6.44 (s, 1H), 5.94 (m, 2H), 3.35 (s, 3H), 1.68 (s, 3H).

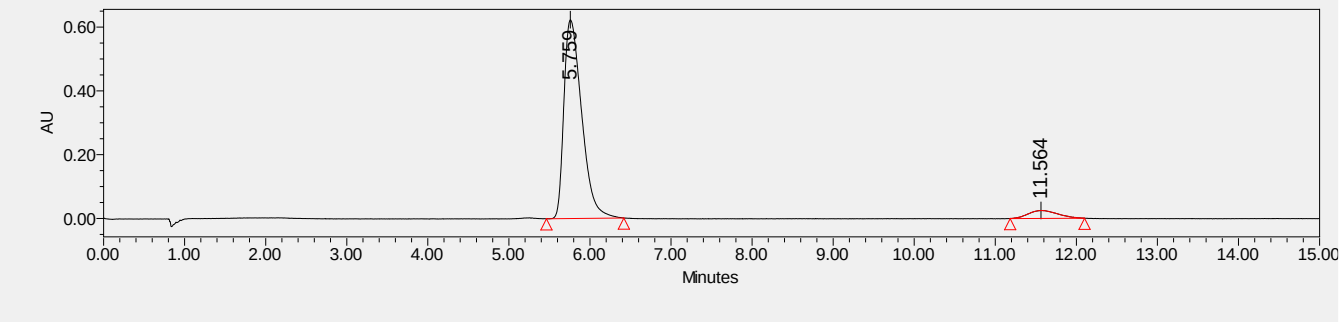
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 183.95, 152.5, 147.7, 141.8, 140.8, 136.7, 127.4, 122.4, 122.3, 109.5, 107.9, 101.5, 96.7, 56.8, 50.3, 24.1.

IR: 3209, 1618, 1504, 1278, 1195, 1165, 1117, 870, 756, 662 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{15}NO_4Na^+$ 320.0893; found 320.0895.

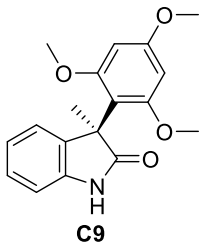


	Retention Time	Area	% Area
1	5.740	6547126	50.11
2	11.146	6519579	49.89



	Retention Time	Area	% Area
1	5.759	9498867	93.83
2	11.564	624503	6.17

(*S*)-3-methyl-3-(2,4,6-trimethoxyphenyl)indolin-2-one (C9)



C9

White soild; 29.4 mg, 94% yield, 96% ee; melting point: 148–151 °C; $[\alpha]_D^{13.1}$ = -184.7 (*c* = 0.18 in CH_2Cl_2).

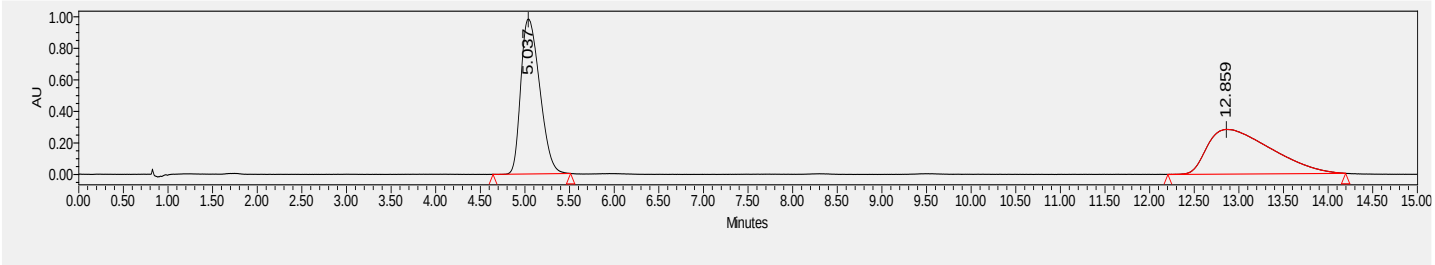
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 5.16 min, t_R (minor) = 13.68 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.28 (s, 1H), 7.16 – 7.06 (m, 2H), 6.94 – 6.83 (m, 2H), 6.14 (s, 2H), 3.77 (s, 3H), 3.69 (s, 6H), 1.88 (s, 3H).

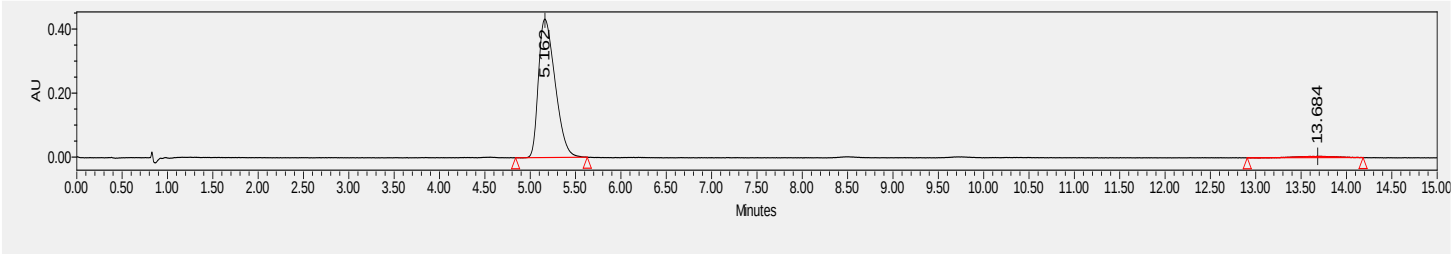
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 185.0, 160.4, 140.1, 137.6, 127.1, 123.2, 122.2, 110.0, 109.1, 92.7, 56.0, 55.4, 50.9, 25.9.

IR: 2934, 1703, 1607, 1585, 1469, 1413, 1326, 1227, 1053, 814, 755 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{19}NO_4Na^+$ 336.1206; found 336.1206.

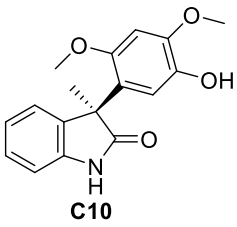


	Retention Time	Area	% Area
1	5.037	14506559	50.72
2	12.859	14093880	49.28



	Retention Time	Area	% Area
1	5.162	5508266	97.91
2	13.684	117820	2.09

(*S*)-3-(5-hydroxy-2,4-dimethoxyphenyl)-3-methylindolin-2-one (C10)



C10

Colorless oil; 17.9 mg, 60% yield, 83% ee; $[\alpha]_D^{12.7}$ = -50.3 (*c* = 0.12 in CH_2Cl_2).

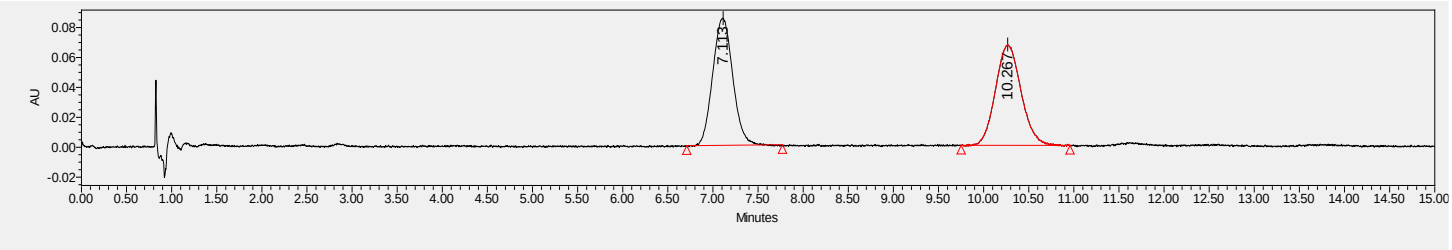
UPCC DAICEL CHIRALCEL AD-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 7.34 min, t_R (minor) = 10.51 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.50 (s, 1H), 7.25 – 7.14 (m, 1H), 7.09 – 6.89 (m, 3H), 6.64 – 6.59 (d, *J* = 2.7 Hz, 1H), 6.49 – 6.43 (d, *J* = 2.8 Hz, 1H), 6.22 – 6.17 (m, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 1.79 (s, 3H).

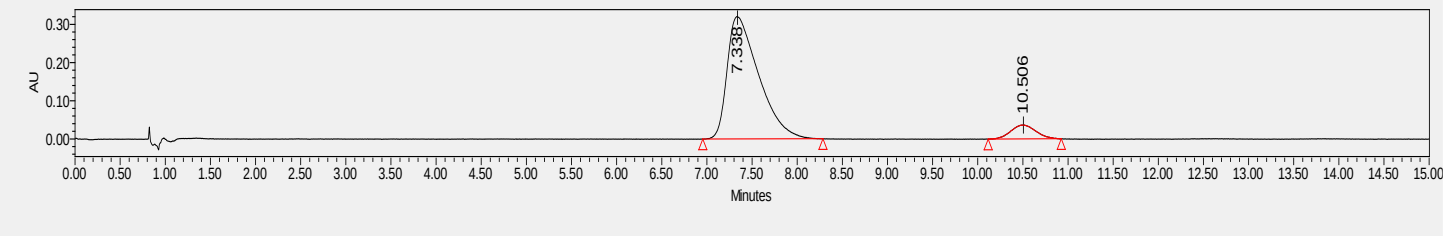
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 183.3, 153.1, 148.0, 140.6, 138.2, 135.4, 127.8, 126.1, 123.6, 122.6, 109.9, 104.5, 98.7, 56.2, 56.0, 51.3, 23.5.

IR: 2924, 2358, 1712, 1618, 1471, 1261, 1231, 1202, 1155, 1047 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M - H]^-$ calcd for $C_{17}H_{17}NO_4Na^+$ 299.1085; found 299.1088.



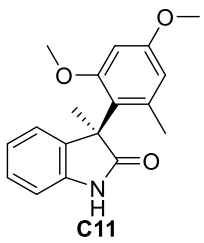
	Retention Time	Area	% Area
1	7.097	368168	49.40
2	10.256	377134	50.60



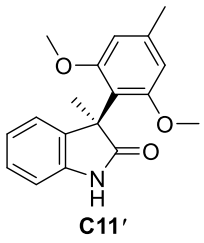
	Retention Time	Area	% Area
1	7.338	7775904	91.78
2	10.506	696338	8.22

(*S*)-3-(2,4-dimethoxy-6-methylphenyl)-3-methylindolin-2-one (C11)

(*S*)-3-(2,6-dimethoxy-4-methylphenyl)-3-methylindolin-2-one (C11')



C11



C11′

C11 : C11′ = 4 : 1

White soild; 25.9 mg, 87% yield, 93% ee_1, 99% ee_2; melting point: 135–137 °C; $[\alpha]_D^{12.7}$ = -121.0 (*c* = 0.19 in CH_2Cl_2).

UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major-major) = 5.16 min, t_R (major-minor) = 15.37 min, t_R (minor-major) = 4.41 min, t_R (minor-minor) = 12.12 min.

^{1}H NMR (400 MHz, $CDCl_3$) **(C11)** *δ* 8.85 (s, 1H), 7.17 – 7.10 (m, 1H), 7.06 – 6.98 (m, 1H), 6.95 – 6.88 (m, 2H), 6.36 – 6.27 (m, 2H), 3.76 (s, 6H), 3.54 (s, 3H), 1.89 (s, 3H).

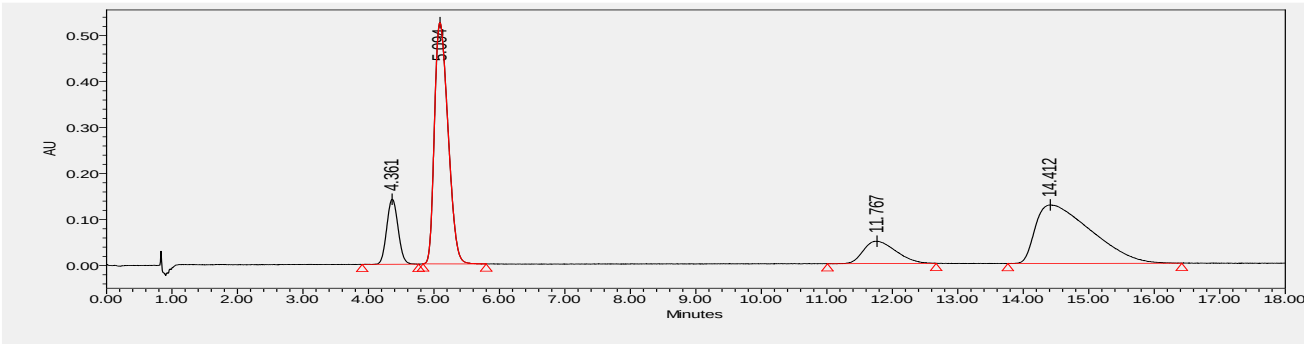
^{13}C NMR (101 MHz, $CDCl_3$) **(C11)** *δ* 185.5, 159.2, 140.1, 139.8, 137.4, 127.3, 123.2, 122.8, 122.3, 109.6, 107.1, 98.3, 55.8, 55.3, 55.3, 53.0, 27.3.

^{1}H NMR (400 MHz, $CDCl_3$) **(C11')** *δ* 8.77 (s, 1H), 7.09 – 7.06 (m, 2H), 6.87 – 6.83 (m, 2H), 6.39 (s, 2H), 3.69 (s, 6H), 2.29 (s, 3H), 1.90 (s, 3H).

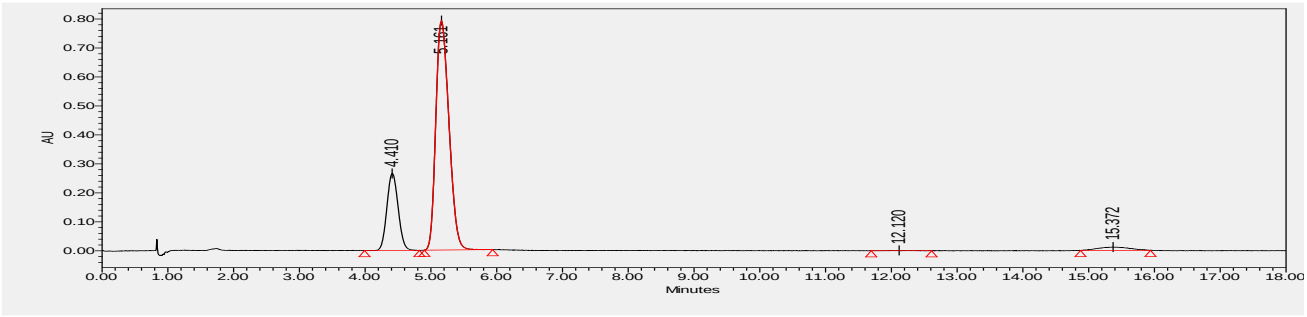
^{13}C NMR (101 MHz, $CDCl_3$) **(C11')** *δ* 185.4, 140.3, 138.9, 137.3, 127.1, 123.2, 122.8, 122.3, 114.5, 110.6, 109.3, 56.0, 51.1, 25.9, 21.8.

IR: 3197, 2925, 1712, 1606, 1579, 1468, 1320, 1234, 1154, 755 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{19}NO_3Na^+$ 320.1257; found 320.1259.

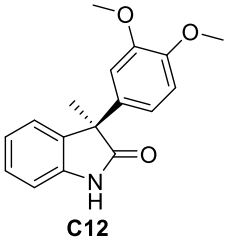


	Retention Time	Area	% Area
1	4.361	1708662	9.26
2	5.094	7551145	40.94
3	11.767	1682350	9.12
4	14.412	7502567	40.68



	Retention Time	Area	% Area
1	4.410	3162620	21.70
2	5.161	11008270	75.54
3	12.120	15685	0.11
4	15.372	386837	2.65

(*R*)-3-(3,4-dimethoxyphenyl)-3-methylindolin-2-one (C12)



C12

Colorless oil; 22.4 mg, 79% yield, 77% ee; $[\alpha]_D^{18.6}$ = 118.6 (*c* = 0.11 in CH_2Cl_2).

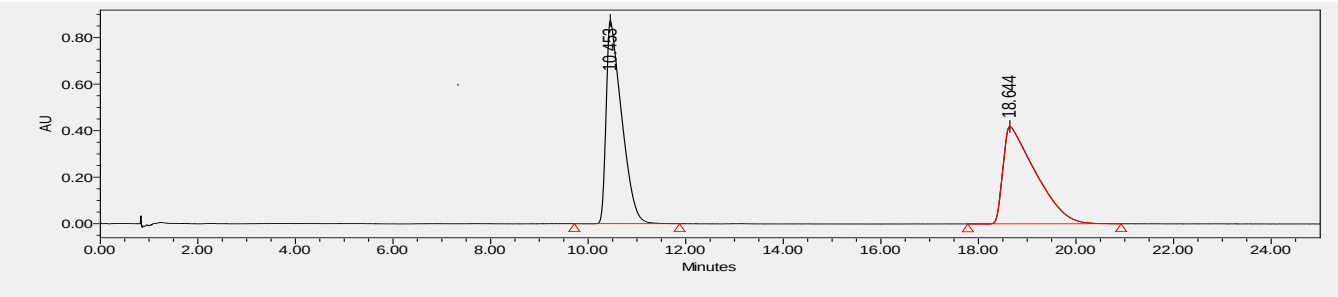
UPCC DAICEL CHIRALCEL OX-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 17.96 min, t_R (minor) = 10.47 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.51 (s, 1H), 7.29 – 7.20 (m, 1H), 7.19 – 7.12 (m, 1H), 7.12 – 7.02 (m, 1H), 7.00 – 6.94 (m, 1H), 6.89 – 6.76 (m, 3H), 3.84 (s, 3H), 3.81 (s, 3H), 1.80 (s, 3H).

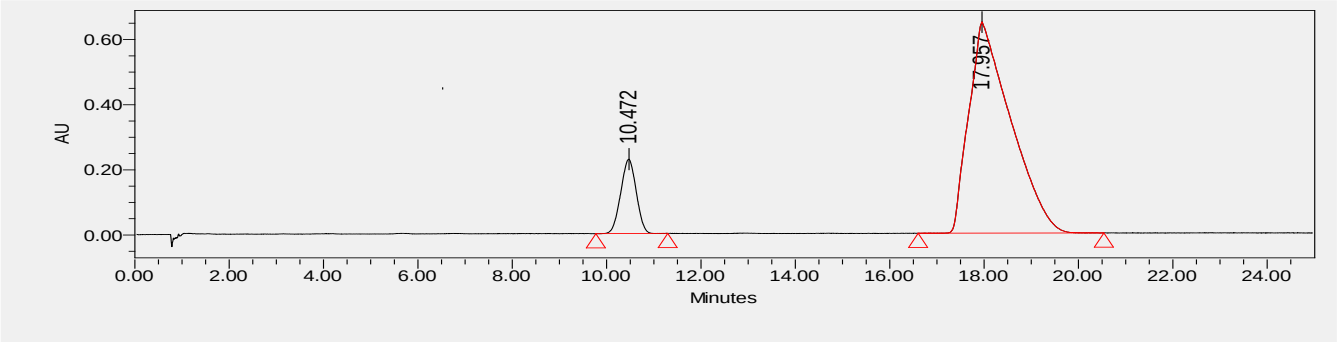
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 181.8, 148.7, 148.2, 140.1, 135.3, 132.8, 127.9, 124.3, 122.6, 118.8, 110.8, 110.0, 109.9, 55.7, 55.7, 52.0, 23.6.

IR: 3291, 2931, 2561, 1710, 1618, 1515, 1470, 1260, 1026, 751 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}NO_3Na^+$ 306.1101; found 306.1099.

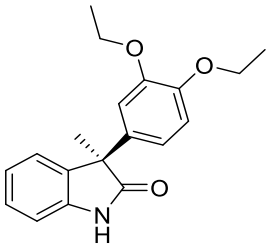


	Retention Time	Area	% Area
1	10.453	19230932	49.96
2	18.644	19265111	50.04



	Retention Time	Area	% Area
1	10.472	5196158	11.52
2	17.957	39926279	88.48

(*R*)-3-(3,4-diethoxyphenyl)-3-methylindolin-2-one (C13)



C13

White solid; 22.1 mg, 71% yield, 78% ee; melting point: 69–75 °C; $[\alpha]_D^{12.4}$ = 65.6 (*c* = 0.43 in CH_2Cl_2).

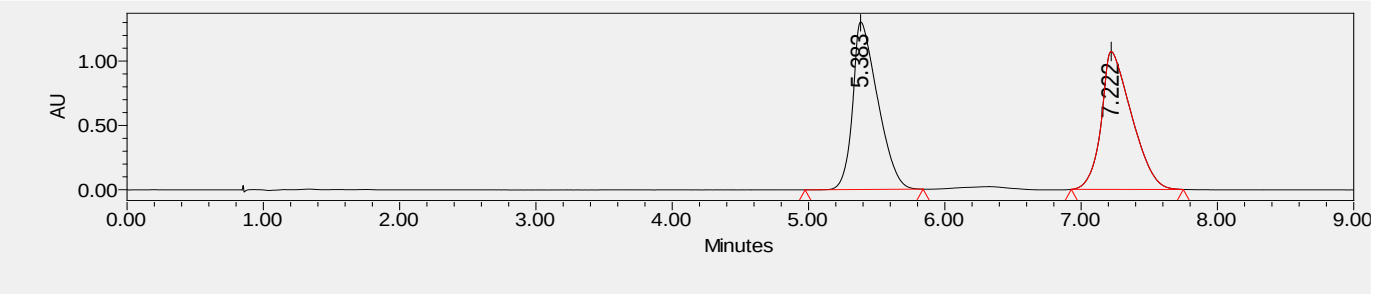
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 7.21 min, t_R (minor) = 5.50 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.66 (s, 1H), 7.26 – 7.20 (m, 1H), 7.16 – 7.13 (m, 1H), 7.08 – 7.03 (m, 1H), 6.98 – 6.94 (m, 1H), 6.87 – 6.77 (m, 3H), 4.08 – 3.98 (m, 5H), 1.78 (s, 3H), 1.44 – 1.35 (m, 7H).

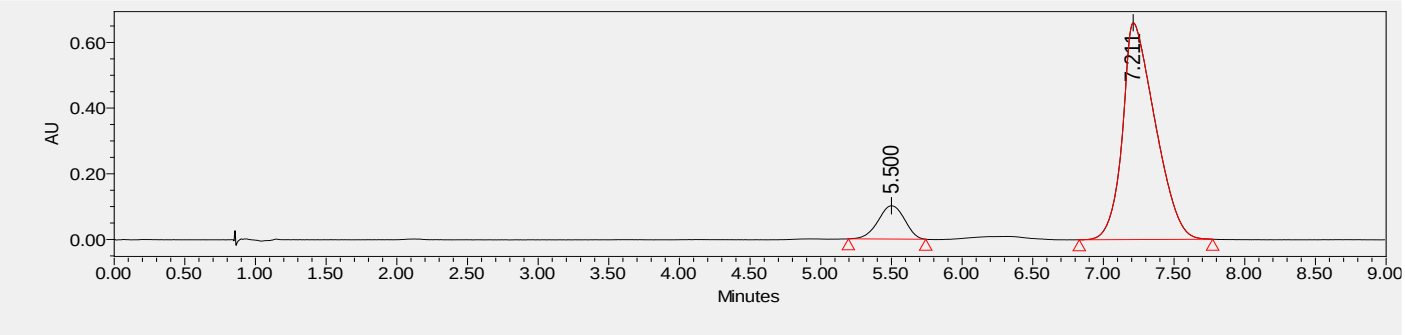
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 182.0, 148.4, 148.0, 140.1, 135.4, 127.8, 124.2, 122.5, 119.0, 113.0, 112.6, 109.9, 64.5, 64.3, 52.0, 23.6, 14.6, 14.6.

IR: 3182, 2979, 1361, 1710, 1619, 1513, 1473, 1144, 1042, 751 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{21}N_2ONa^+$ 312.1594; found 312.1595.

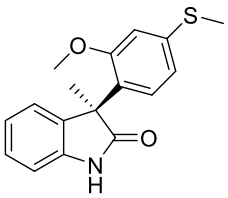


	Retention Time	Area	% Area
1	5.383	16605069	50.07
2	7.222	16559768	49.93



	Retention Time	Area	% Area
1	5.500	1322804	11.10
2	7.211	10593774	88.90

(*S*)-3-(2-methoxy-4-(methylthio)phenyl)-3-methylindolin-2-one (C14)



C14

White solid; 20.3 mg, 68% yield, 50% ee; melting point: 115–120 °C; $[\alpha]_D^{19.1}$ = -23.0 (*c* = 0.28 in CH_2Cl_2).

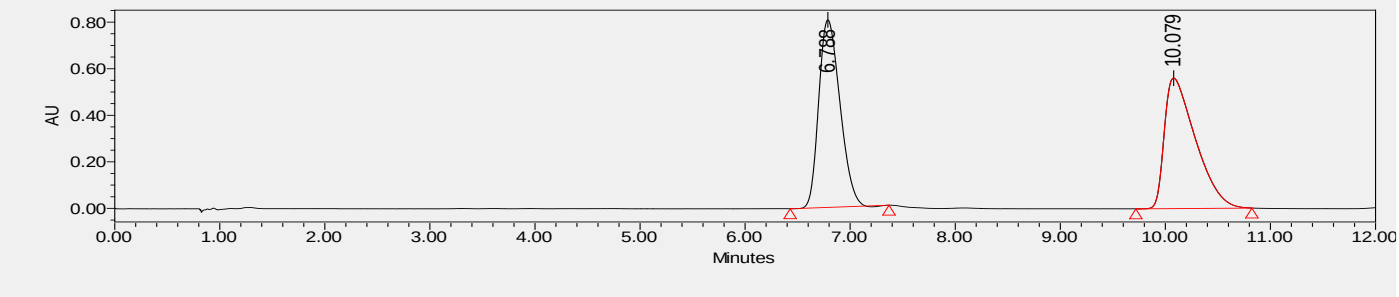
UPCC DAICEL CHIRALCEL OD-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 9.95 min, t_R (minor) = 6.79 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.59 (s, 1H), 7.55 – 7.46 ((d, *J* = 8.1 Hz, 1H), 7.17 – 7.11 (m, 1H), 6.97 – 6.87 (m, 3H), 6.83 – 6.80 (m, 1H), 6.71 – 6.69 (m, 1H), 3.45 (s, 3H), 2.47 (s, 3H), 1.72 (s, 3H).

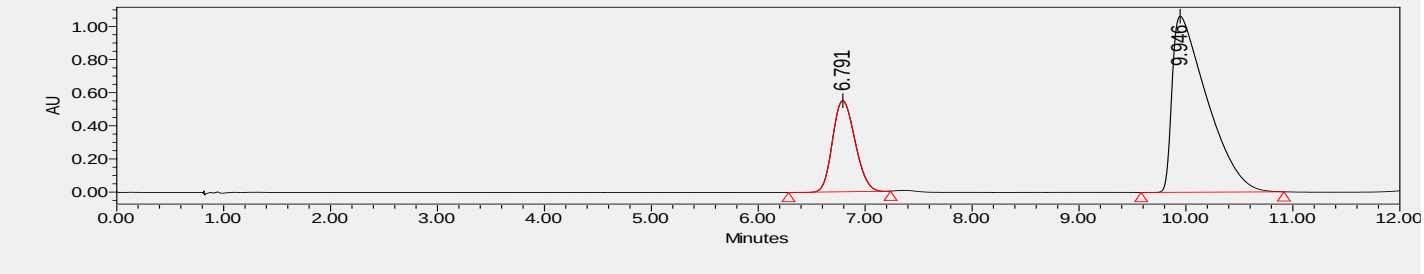
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 183.1, 157.0, 140.4, 139.1, 136.0, 127.8, 127.1, 126.4, 122.2, 122.0, 118.5, 110.6, 109.1, 55.4, 49.9, 23.4, 15.8.

IR: 3214, 2360, 1709 1618, 1598, 1470, 1392, 1111, 1029, 769 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}N_2OSNa^+$ 322.0872; found 322.0872.

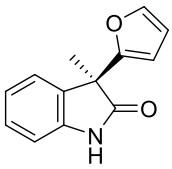


	Retention Time	Area	% Area
1	6.791	8028886	24.92
2	9.946	24194081	75.08



	Retention Time	Area	% Area
1	6.791	8028886	24.92
2	9.946	24194081	75.08

(*S*)-3-(furan-2-yl)-3-methylindolin-2-one (C15)



C15

Colorless oil; 10.0 mg, 47% yield, 95% ee; $[\alpha]_D^{18.4}$ = 12.5 (*c* = 0.11 in CH_2Cl_2).

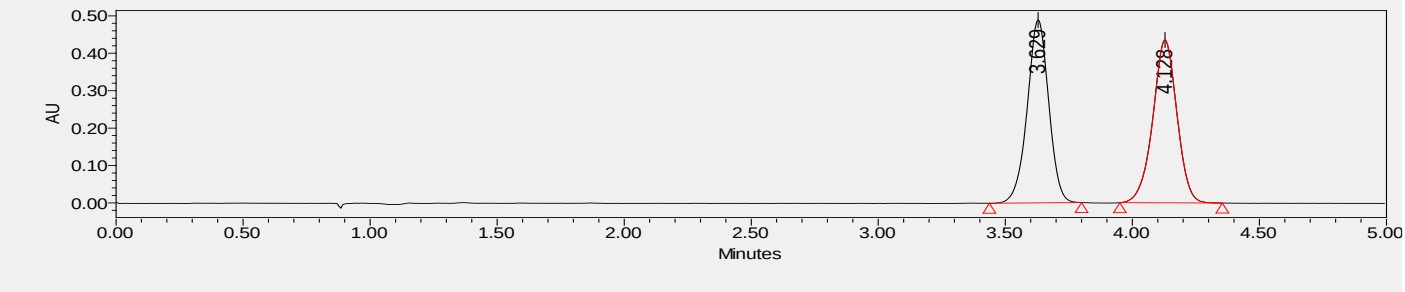
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 95/5, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 3.59 min, t_R (minor) = 4.09 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.82 (s, 1H), 7.37 – 7.32 (m, 1H), 7.29 – 7.20 (m, 2H), 7.09 – 7.01 (m, 1H), 7.00 – 6.93 (m, 1H), 6.34 – 6.27 (m, 1H), 6.25 – 6.19 (m, 1H), 1.79 (s, 3H).

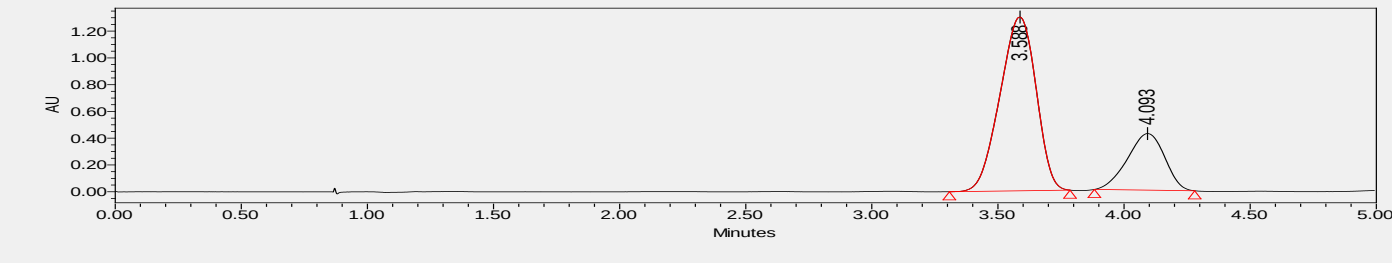
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 179.6, 153.1, 142.7, 140.2, 133.0, 128.5, 124.0, 122.8, 110.2, 106.7, 49.5, 22.3.

IR: 3250, 2561, 1713, 1620, 1472, 1261, 1224, 1013, 751 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{13}H_{11}NO_2Na^+$ 236.0682; found 236.0680.

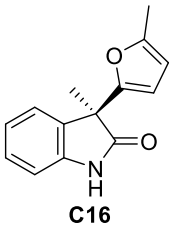


	Retention Time	Area	% Area
1	3.629	2872568	50.02
2	4.128	2870055	49.98



	Retention Time	Area	% Area
1	3.588	12916335	74.84
2	4.093	4341181	25.16

(*S*)-3-methyl-3-(5-methylfuran-2-yl)indolin-2-one (C16)



C16

White solid; 15.9 mg, 70% yield, 95% ee; melting point: 108–110 °C; $[\alpha]_D^{12.4}$ = 52.4 (*c* = 0.21 in CH_2Cl_2).

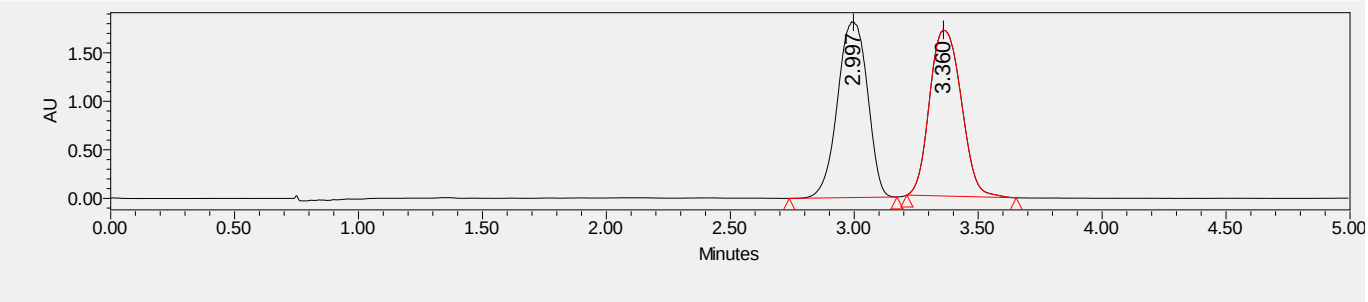
UPCC DAICEL CHIRALCEL OD-3, CO_2/MeOH = 90/10 flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 3.39 min, t_R (minor) = 3.02 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.60 (s, 1H), 7.26 – 7.19 (m, 2H), 7.09 – 7.00 (m, 1H), 6.99 – 6.92 (d, *J* = 7.7 Hz, 1H), 6.12 – 6.06 (d, *J* = 3.1 Hz, 1H), 5.90 – 5.85 (m, 1H), 2.24 – 2.19 (m, 3H), 1.77 – 1.73 (m, 3H).

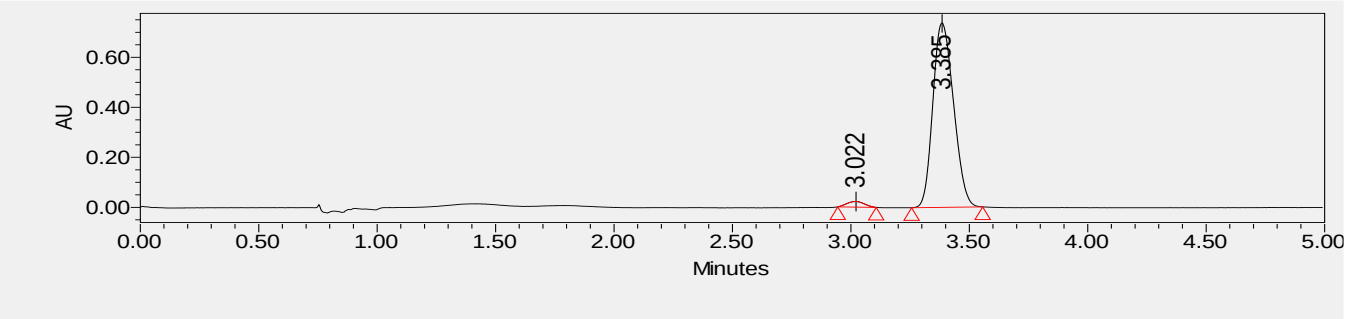
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 179.9, 152.6, 151.3, 140.2, 133.5, 128.4, 124.2, 122.8, 110.2, 107.6, 106.3, 49.5, 22.4, 13.8.

IR: 3219, 2360, 1619, 1471, 1326, 1222, 1145, 1021, 752, 684 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{14}H_{13}NO_2Na^+$ 250.0838; found 250.0836.

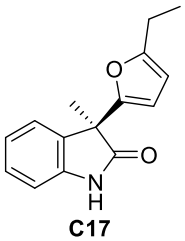


	Retention Time	Area	% Area
1	2.997	15224388	50.08
2	3.360	15177064	49.92



	Retention Time	Area	% Area
1	3.022	113504	2.47
2	3.385	4477880	97.53

(*S*)-3-(5-ethylfuran-2-yl)-3-methylindolin-2-one (C17)



C17

Colorless oil; 17.4 mg, 72% yield, 95% ee; $[\alpha]_D^{18.0}$ = 42.4 (*c* = 0.24 in CH_2Cl_2).

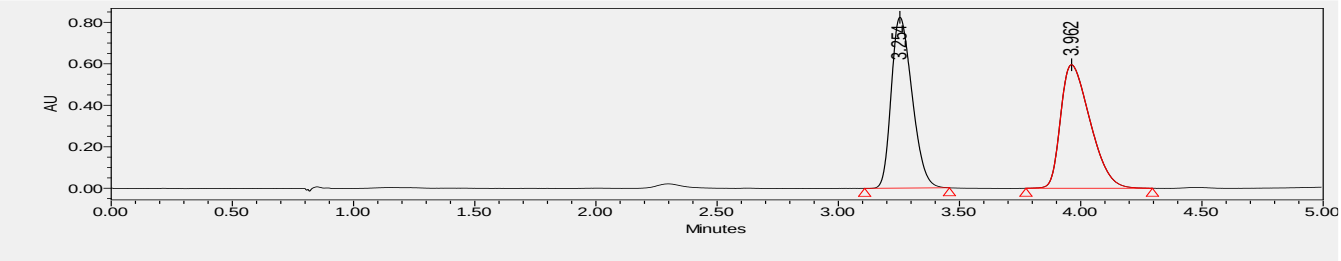
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10 flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 3.29 min, t_R (minor) = 4.08 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.30 (s, 1H), 7.25 – 7.20 (m, 2H), 7.08 – 7.00 (m, 1H), 6.96 – 6.91 (m, 1H), 6.10 – 6.04 (d, *J* = 3.1 Hz, 1H), 5.91 – 5.85 (m, 1H), 2.57 (q, *J* = 7.5 Hz, 1H), 1.75 (s, 3H), 1.16 (t, *J* = 7.5 Hz, 3H).

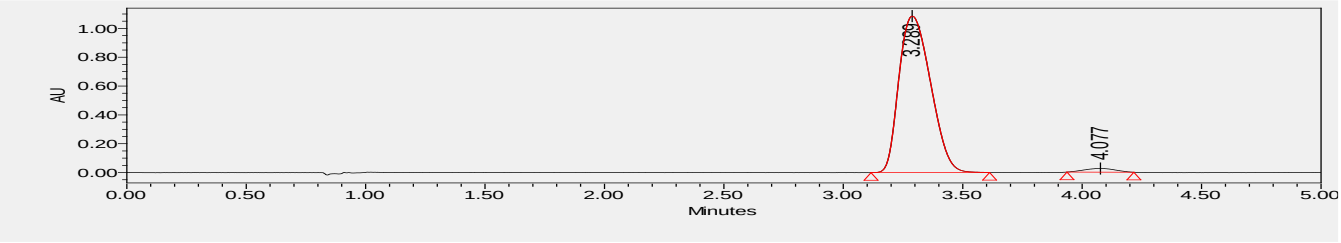
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 179.6, 158.3, 151.1, 140.1, 133.5, 128.4, 124.2, 122.9, 110.1, 107.3, 104.6, 49.5, 22.5, 21.5, 12.0.

IR: 3217, 2361, 1715, 1472, 1261, 1191, 1015, 751 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{15}NO_2Na^+$ 264.0995; found 264.0993.

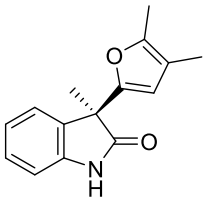


	Retention Time	Area	% Area
1	3.254	4925509	49.45
2	3.962	5034816	50.55



	Retention Time	Area	% Area
1	3.289	10012601	97.75
2	4.077	230082	2.25

(*S*)-3-(4,5-dimethylfuran-2-yl)-3-methylindolin-2-one (C18)



C18

Colorless oil; 20.0 mg, 83% yield, 86% ee; $[\alpha]_D^{19.0}$ = -36.8 (*c* = 0.38 in CH_2Cl_2).

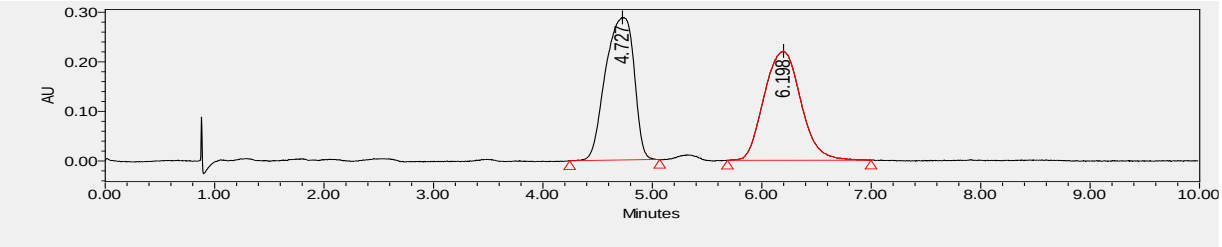
UPCC DAICEL CHIRALCEL ID-3, CO_2/MeOH = 95/5 flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 4.80 min, t_R (minor) = 6.34 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.87 (s, 1H), 7.25 – 7.17 (m, 2H), 7.03 (m, 1H), 6.98 – 6.92 (m, 1H), 5.98 (s, 1H), 2.12 (s, 3H), 1.87 (s, 3H), 1.73 (s, 3H).

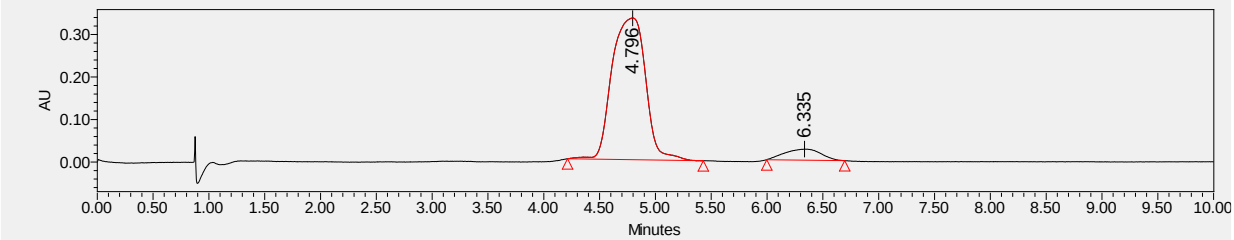
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 180.2, 150.0, 147.8, 140.3, 133.6, 128.4, 124.1, 122.8, 114.6, 110.3, 110.1, 49.5, 22.3, 11.6, 10.0.

IR: 2923, 2361, 1712, 1619, 1472, 1261, 1221, 751, 750 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{15}NO_2Na^+$ 264.0995; found 264.0992.

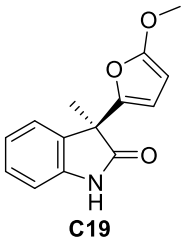


	Retention Time	Area	% Area
1	4.727	5218457	50.47
2	6.198	5121033	49.53



	Retention Time	Area	% Area
1	4.796	7180151	92.92
2	6.335	547454	7.08

(*S*)-3-(5-methoxyfuran-2-yl)-3-methylindolin-2-one (C19)



C19

White solid; 14.4 mg, 59% yield, 77% ee; melting point: 119–121 °C; $[\alpha]_D^{18.2}$ = 32.5 (*c* = 0.20 in CH_2Cl_2).

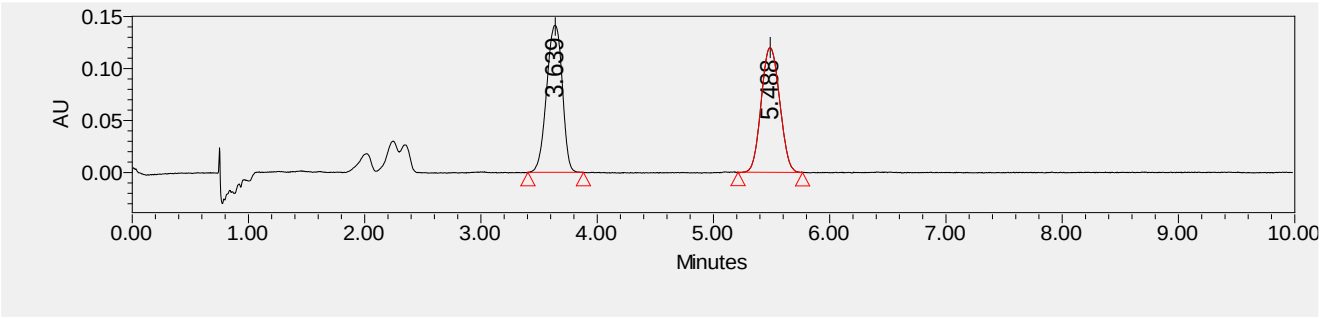
UPCC DAICEL CHIRALCEL OD-3, CO_2/MeOH = 90/10 flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 5.46 min, t_R (minor) = 3.67 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.51 (s, 1H), 7.24 – 7.18 (m, 2H), 7.08 – 7.01 (m, 1H), 6.97 – 6.89 (m, 1H), 6.12 – 6.07 (m, 1H), 5.08 – 5.01 (d, *J* = 3.3 Hz, 1H), 3.77 (s, 3H), 1.71 (s, 3H).

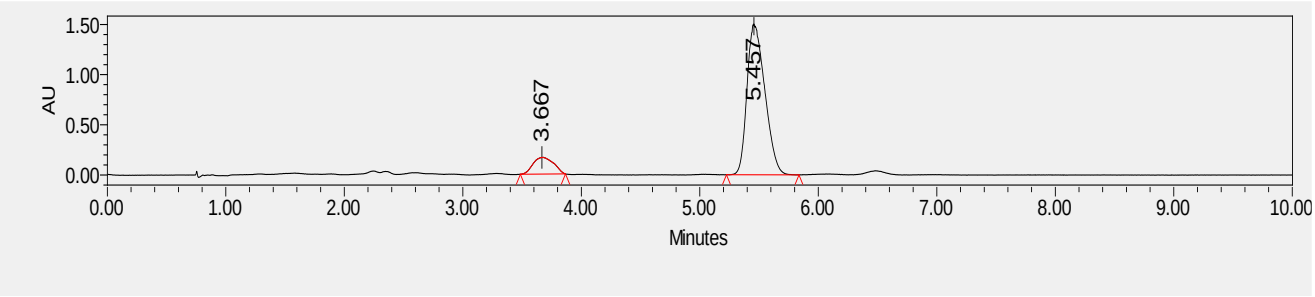
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 179.5, 161.6, 142.9, 140.2, 133.1, 128.5, 124.1, 122.9, 110.2, 108.1, 80.0, 57.7, 49.3, 22.0.

IR: 3250, 2361, 1713, 1616, 1582, 1472, 1261, 1047, 942, 751 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{14}H_{13}NO_3Na^+$ 266.0788; found 266.0787.

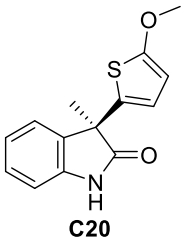


	Retention Time	Area	% Area
1	3.639	1323787	50.07
2	5.488	1320042	49.93



	Retention Time	Area	% Area
1	3.667	2012735	11.32
2	5.457	15764838	88.68

(*R*)-3-(5-methoxythiophen-2-yl)-3-methylindolin-2-one (C20)



C20

Colorless oil; 23.3 mg, 90% yield, 96% ee; $[\alpha]_D^{19.2}$ = 171.4 (*c* = 0.41 in CH_2Cl_2).

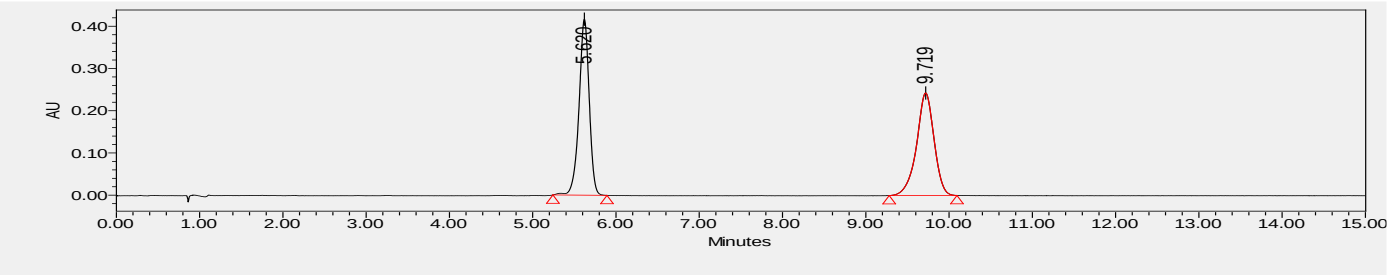
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10 flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 9.56 min, t_R (minor) = 5.62 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.72 (s, 1H), 7.31 – 7.17 (m, 2H), 7.11 – 7.05 (m, 1H), 6.99 – 6.95 (m, 1H), 6.50 – 6.49 (d, *J* = 3.9 Hz, 1H), 6.02 – 5.98 (d, *J* = 3.9 Hz, 1H), 3.82 (s, 3H), 1.77 (s, 3H).

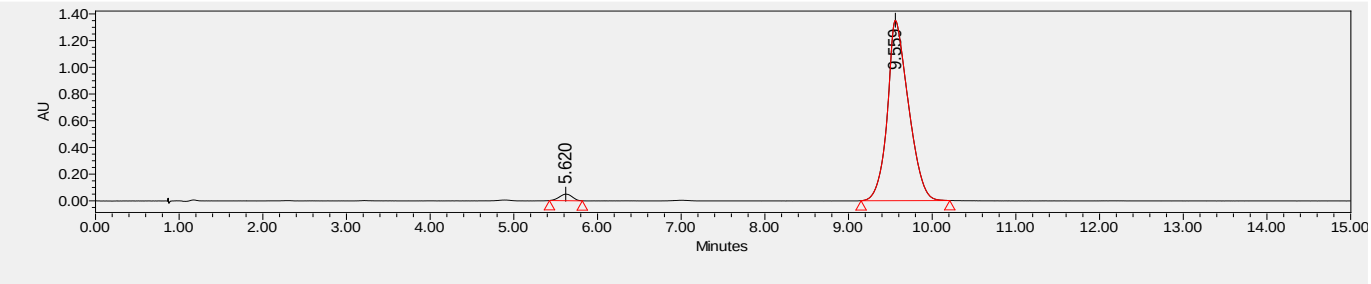
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 180.7, 166.1, 140.3, 134.2, 130.2, 128.7, 124.5, 122.9, 122.5, 110.4, 103.5, 60.4, 50.6, 25.1.

IR: 3214, 2361, 1618, 1556, 1501, 1471, 1325, 1203, 1061, 752 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{14}H_{13}NO_2SNa^+$ 282.0559; found 282.0558.

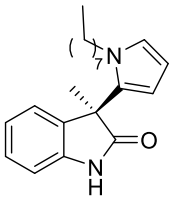


	Retention Time	Area	% Area
1	5.620	3558046	50.17
2	9.719	3534438	49.83



	Retention Time	Area	% Area
1	5.620	522179	2.16
2	9.559	23623439	97.84

(*S*)-3-methyl-3-(1-octyl-1H-pyrrol-2-yl)indolin-2-one (C21)



C21

White solid; 27.9 mg, 86% yield, 91% ee; melting point: 110–115 °C; $[\alpha]_D^{18.4}$ = 21.4 (*c* = 0.31 in CH_2Cl_2).

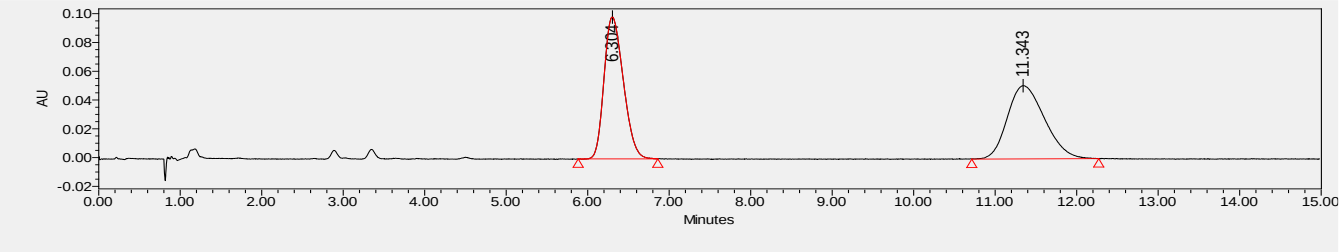
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10 flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 9.56 min, t_R (minor) = 5.62 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.81 (s, 1H), 7.25 – 7.19 (m, 1H), 7.05 – 6.92 (m, 3H), 6.63 – 6.58 (m, 1H), 6.38 – 6.34 (m, 1H), 6.19 – 6.12 (m, 1H), 3.32 (m, 1H), 3.13 (m, 1H), 1.78 (s, 3H), 1.50 – 1.31 (m, 1H), 1.31 – 1.16 (m, 3H), 1.18 – 0.94 (m, 7H), 0.92 – 0.79 (m, 4H).

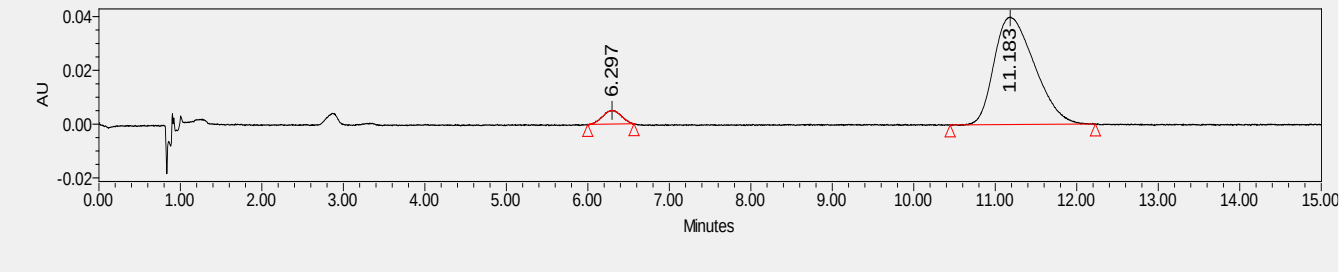
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 181.7, 139.6, 135.1, 129.9, 128.3, 124.0, 123.2, 122.4, 110.3, 109.0, 107.2, 49.0, 46.8, 31.8, 31.1, 29.2, 29.1, 26.9, 25.8, 22.7, 14.2.

IR: 3213, 2926, 2855, 2361, 1619, 1469, 1262, 1222, 751, 720 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{28}N_2ONa^+$ 347.2094; found 347.2098.

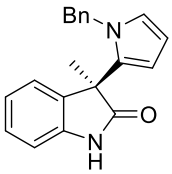


	Retention Time	Area	% Area
1	6.304	1622452	50.13
2	11.343	1613883	49.87



	Retention Time	Area	% Area
1	6.297	68487	4.74
2	11.183	1377000	95.26

(*R*)-3-(4-(dimethylamino)phenyl)-3-methylindolin-2-one (C22)



C22

Colorless oil; 22.4 mg, 70% yield, 87% ee; $[\alpha]_D^{20.1}$ = 31.4 (*c* = 0.32 in CH_2Cl_2).

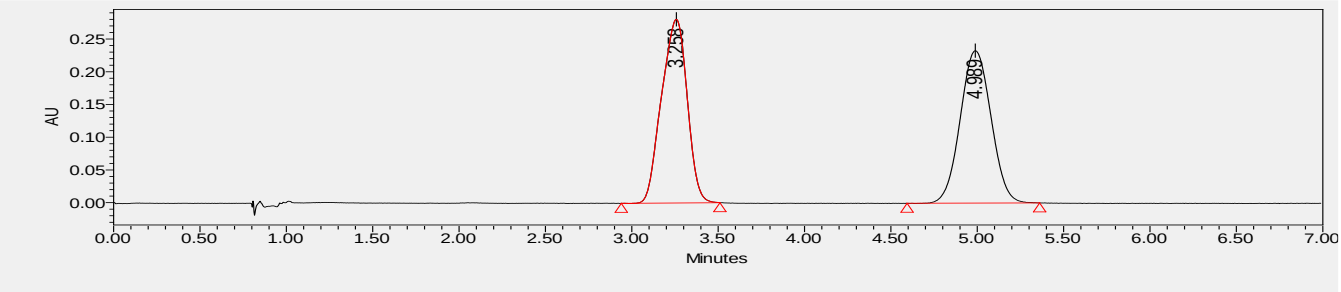
UPCC DAICEL CHIRALCEL OJ-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 3.27 min, t_R (minor) = 5.03 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.73 (s, 1H), 7.21 – 7.04 (m, 4H), 7.02 – 6.85 (m, 3H), 6.74 – 6.67 (m, 2H), 6.53 – 6.40 (m, 2H), 6.20 – 6.16 (m, 1H), 4.52 – 4.34 (m, 2H), 1.78 (s, 3H).

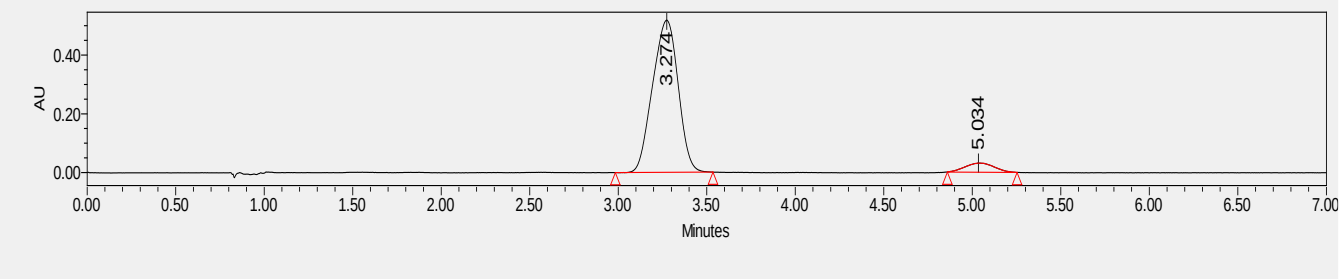
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 181.2, 139.6, 137.6, 134.5, 130.4, 128.4, 127.4, 127.0, 124.0, 123.9, 123.1, 110.4, 109.9, 107.5, 50.4, 49.0, 25.8.

IR: 3206, 1701, 1618, 1470, 1292, 1214, 1187, 1108, 755, 715 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{20}H_{18}N_2ONa^+$ 325.1311; found 325.1308.

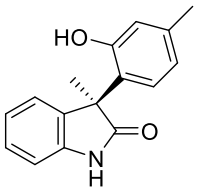


	Retention Time	Area	% Area
1	3.258	2894130	50.08
2	4.989	2885028	49.92



	Retention Time	Area	% Area
1	3.274	5197889	93.67
2	5.034	351243	6.33

(*R*)-3-(4-hydroxy-2-methylphenyl)-3-methylindolin-2-one (C23)



C23

Colorless oil; 13.4 mg, 53% yield, 89% ee; $[\alpha]_D^{19.0}$ = 340.0 (*c* = 0.12 in CH_2Cl_2).

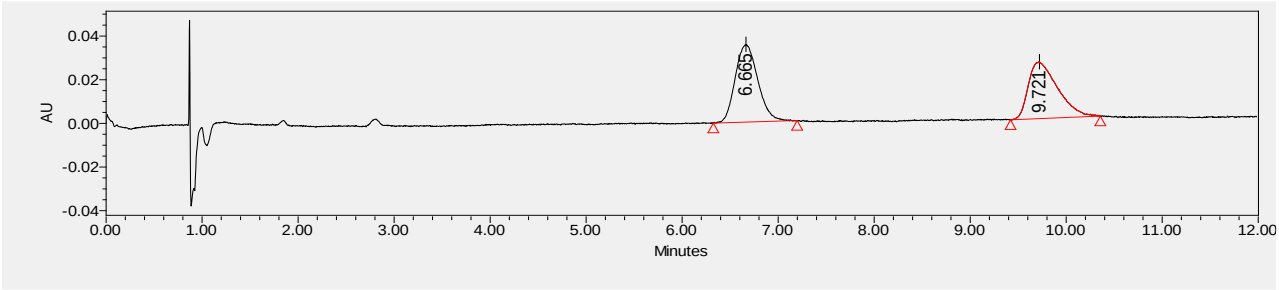
UPCC DAICEL CHIRALCEL ID-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 6.49 min, t_R (minor) = 9.68 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 9.45 (s, 1H), 8.32 (s, 1H), 7.32 – 7.27 (m, 2H), 7.20 – 7.15 (m, 1H), 7.00 – 6.91 (m, 2H), 6.83 – 6.78 (m, 1H), 6.63 – 6.56 (m, 1H), 2.26 (s, 3H), 1.87 (s, 3H).

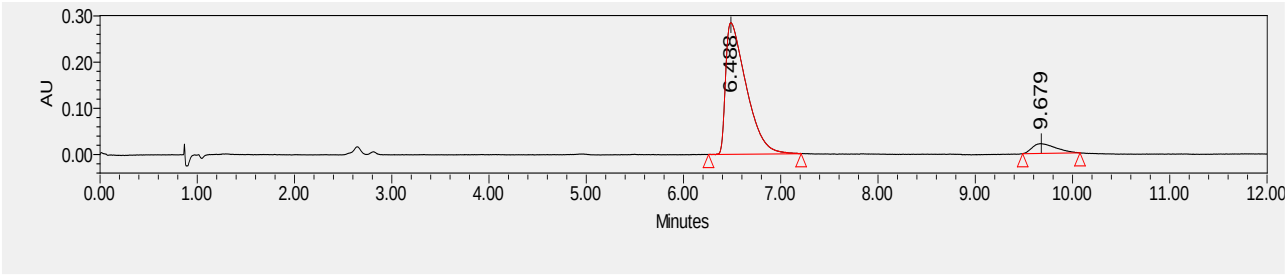
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 184.6, 156.1, 139.7, 139.5, 133.5, 128.4, 127.8, 125.8, 123.1, 122.2, 121.0, 120.2, 110.6, 52.9, 22.6, 20.8.

IR: 3251, 2360, 1691, 1618, 1472, 1276, 1208, 750 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{20}H_{22}N_2O_3Na^+$ 361.1523; found 361.1524.

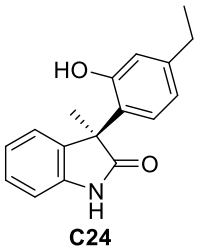


	Retention Time	Area	% Area
1	6.665	533323	50.24
2	9.721	528161	49.76



	Retention Time	Area	% Area
1	6.488	4187461	94.31
2	9.679	252469	5.69

(*R*)-3-(2-ethyl-4-hydroxyphenyl)-3-methylindolin-2-one (C24)



C24

Colorless oil; 8.3 mg, 31% yield, 79% ee; $[\alpha]_D^{17.9}$ = 401.2 (*c* = 0.10 in CH_2Cl_2).

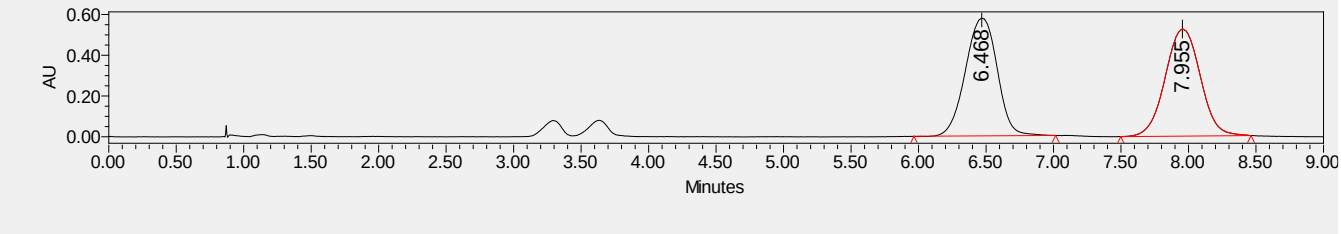
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 8.02 min, t_R (minor) = 6.52 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 9.49 (s, 1H), 8.28 (s, 1H), 7.34 – 7.27 (m, 2H), 7.22 – 7.14 (m, 1H), 7.02 – 6.90 (m, 2H), 6.87 – 6.81 (m, 1H), 6.66 – 6.58 (m, 1H), 2.62 – 2.51 (m, 2H), 1.88 (s, 3H), 1.24 – 1.13 (m, 3H).

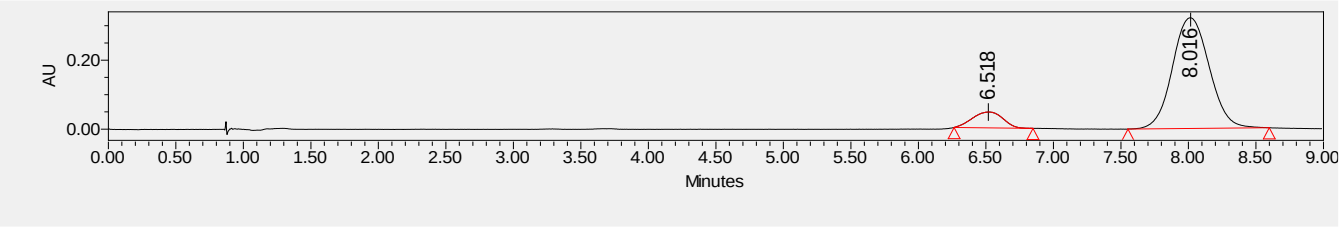
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 184.5, 156.3, 150.7, 139.5, 133.4, 128.4, 127.8, 126.0, 123.1, 122.3, 118.3, 117.7, 110.6, 53.0, 33.5, 23.8, 22.5.

IR: 3251, 2966, 2360, 1691, 1618, 1472, 1332, 1209, 1131, 751 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}NO_2Na^+$ 290.1151; found 290.1151.

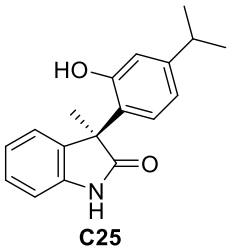


	Retention Time	Area	% Area
1	6.468	9469701	49.94
2	7.955	9492911	50.06



	Retention Time	Area	% Area
1	6.518	716350	10.53
2	8.016	6086319	89.47

(*R*)-3-(4-hydroxy-2-isopropylphenyl)-3-methylindolin-2-one (C25)



C25

Colorless oil; 6.7 mg, 24% yield, 76% ee; $[\alpha]_D^{18.2}$ = 272.1 (*c* = 0.21 in CH_2Cl_2).

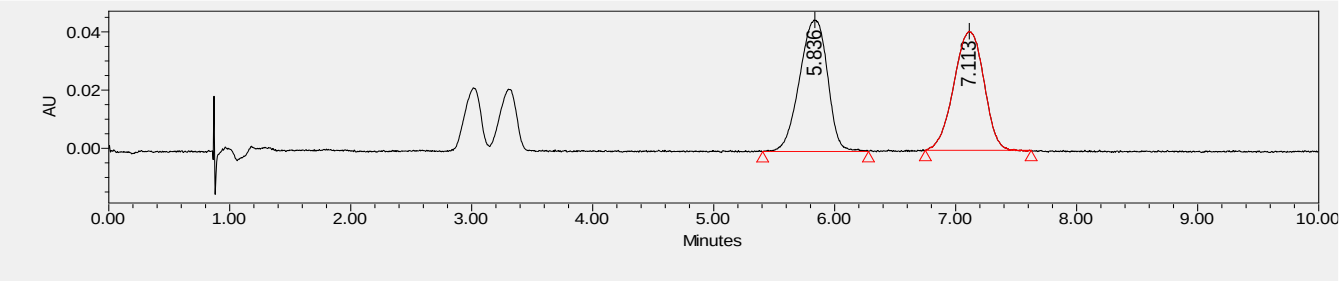
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 7.14 min, t_R (minor) = 5.86 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 9.55 (s, 1H), 8.22 (s, 1H), 7.33 – 7.27 (m, 2H), 7.21 – 7.16 (m, 1H), 7.01 – 6.93 (m, 2H), 6.89 – 6.86 (m, 1H), 6.67 – 6.62 (m, 1H), 2.87 – 2.77 (m, 1H), 1.89 (s, 3H), 1.22 – 1.18 (m, 6H).

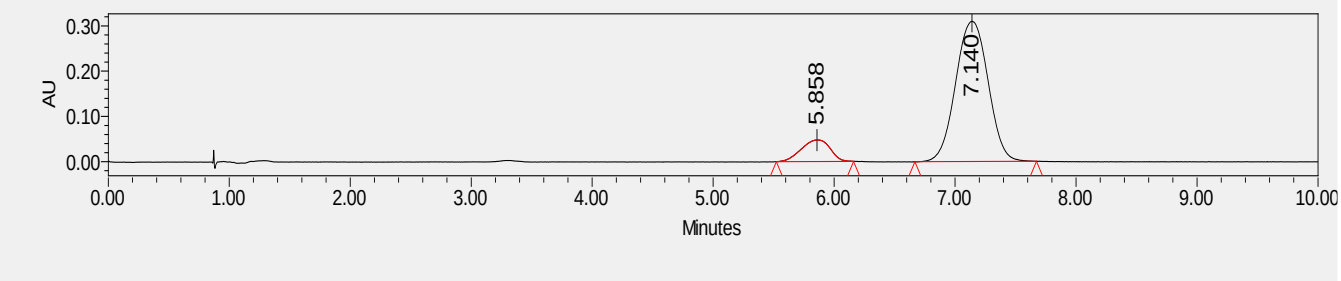
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 184.6, 156.4, 150.8, 139.6, 133.5, 128.5, 127.9, 126.1, 123.3, 118.5, 117.9, 110.7, 53.1, 33.6, 24.0, 23.8, 22.6.

IR: 3249, 2961, 2360, 1693, 1617, 1472, 1276, 751 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{19}NO_2Na^+$ 304.1308; found 304.1309.

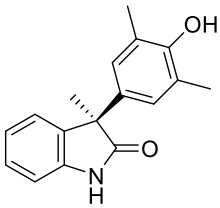


	Retention Time	Area	% Area
1	5.836	724956	50.69
2	7.113	705113	49.31



	Retention Time	Area	% Area
1	5.858	786376	11.98
2	7.140	5778501	88.02

(*R*)-3-(4-hydroxy-3,5-dimethylphenyl)-3-methylindolin-2-one (C26)



C26

Colorless oil; 19.0 mg, 71% yield, 70% ee; $[\alpha]_D^{19.3}$ = 55.8 (*c* = 0.33 in CH_2Cl_2).

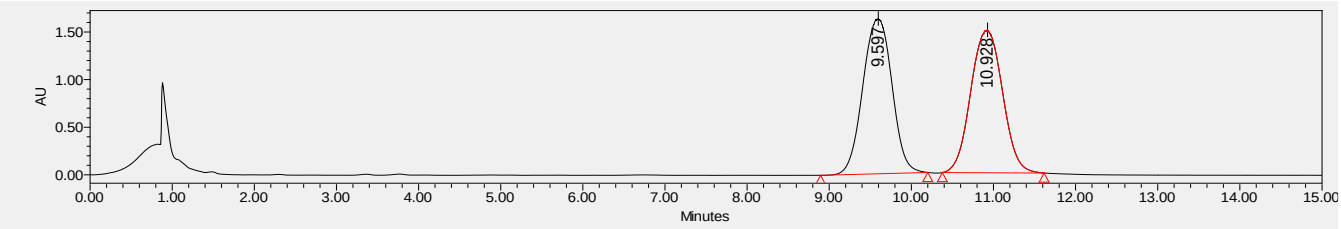
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 11.18 min, t_R (minor) = 9.72 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.91 (s, 1H), 7.24 – 7.18 (m, 1H), 7.11 – 7.07 (m, 1H), 7.06 – 7.00 (m, 1H), 6.98 – 6.93 (m, 1H), 6.86 (s, 2H), 2.15 (s, 6H), 1.76 (s, 3H).

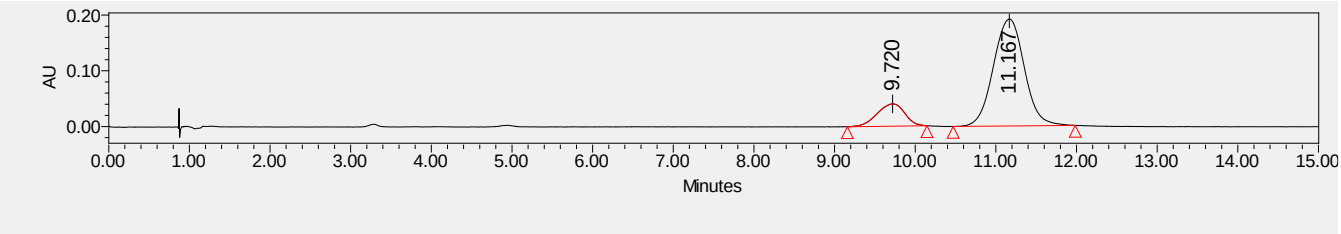
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 182.9, 151.6, 140.3, 136.3, 131.8, 127.9, 126.8, 124.2, 123.3, 122.8, 110.2, 52.1, 23.3, 16.1.

IR: 3260, 2360, 1702, 1619, 1472, 1261, 1184, 750 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}NO_2Na^+$ 304.1308; found 304.1309.

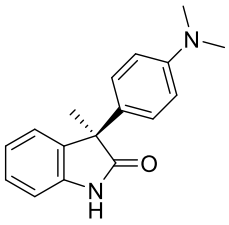


	Retention Time	Area	% Area
1	9.597	40137748	50.00
2	10.928	40142334	50.00



	Retention Time	Area	% Area
1	9.720	894950	14.88
2	11.167	5119528	85.12

(*R*)-3-(4-(dimethylamino)phenyl)-3-methylindolin-2-one (C27)



C27

White solid; 25.3 mg, 95% yield, 95% ee; melting point: 129–133 °C; $[\alpha]_D^{12.4}$ = 148.4 (*c* = 0.63 in CH_2Cl_2).

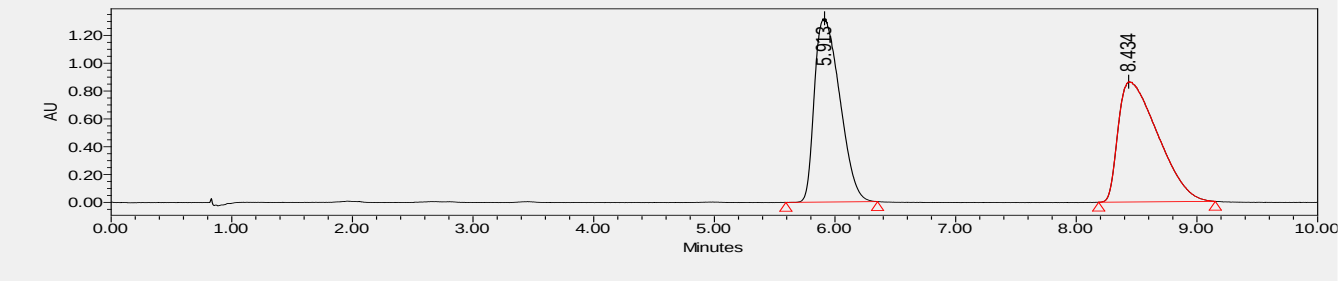
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 5.62 min, t_R (minor) = 8.25 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.42 (s, 1H), 7.26 – 7.10 (m, 4H), 7.08 – 7.00 (m, 1H), 6.97 – 6.91 (d, *J* = 7.8 Hz, 1H), 6.71 – 6.62 (m, 2H), 2.90 (s, 6H), 1.77 (s, 3H).

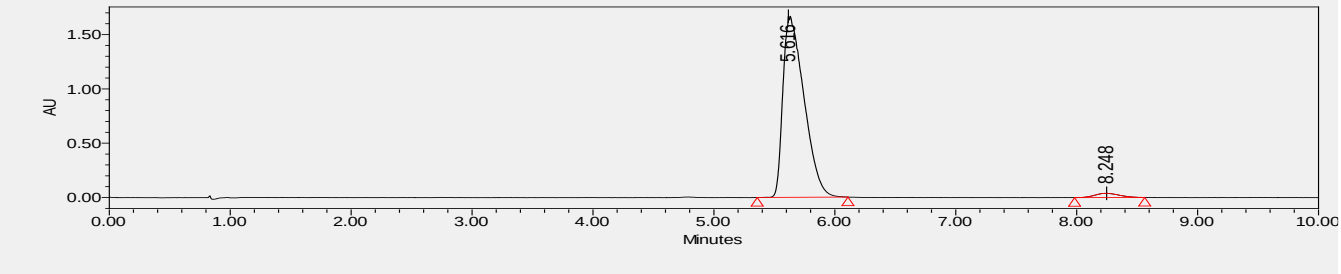
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 182.5, 149.9, 140.5, 136.2, 128.3, 127.9, 127.5, 124.6, 122.7, 112.8, 110.0, 52.0, 40.7, 23.6.

IR: 3207, 1613, 1520, 1471, 1353, 1201, 948, 809, 751, 629 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{18}N_2ONa^+$ 289.1311; found 289.1311. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H).

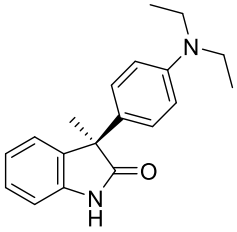


	Retention Time	Area	% Area
1	5.913	19243212	49.40
2	8.434	19709772	50.60



	Retention Time	Area	% Area
1	5.616	20220628	97.41
2	8.248	538014	2.59

(*R*)-3-(4-(diethylamino)phenyl)-3-methylindolin-2-one (C28)



C28

White solid; 28.0 mg, 90% yield, 86% ee; melting point: 163–167 °C; $[\alpha]_D^{13.6}$ = 106.3 (*c* = 0.27 in CH_2Cl_2).

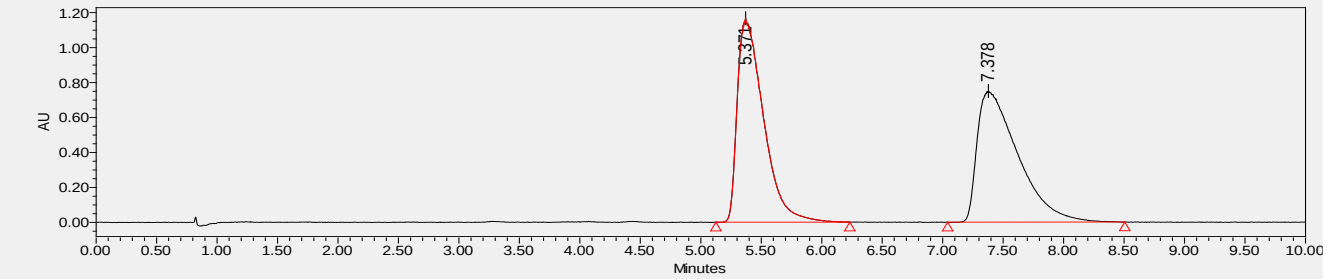
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 5.42 min, t_R (minor) = 7.76 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.97 (s, 1H), 7.24 – 7.16 (m, 1H), 7.18 – 7.09 (m, 3H), 7.09 – 6.96 (m, 1H), 6.98 – 6.91 (d, *J* = 7.7 Hz, 1H), 6.59 (d, *J* = 8.6 Hz, 2H), 3.30 (q, *J* = 7.1 Hz, 4H), 1.77 (s, 3H), 1.11 (t, *J* = 7.0 Hz, 6H).

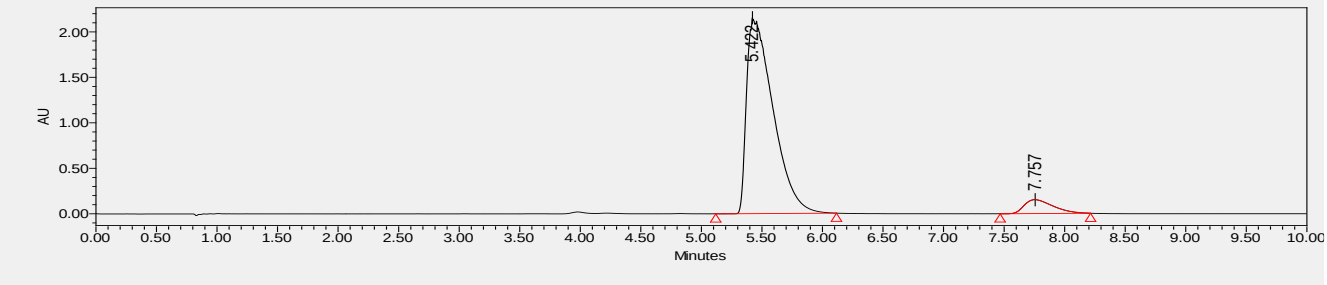
^{13}C NMR (101 MHz, $CDCl_3$) δ 183.1, 147.0, 140.7, 136.3, 127.8, 127.7, 126.9, 124.5, 122.6, 111.7, 110.2, 52.0, 44.4, 23.6, 12.7. ^{1}H NMR (400 MHz, $CDCl_3$)

IR: 3205, 2969, 1614, 1518, 1470, 1201, 1154, 809, 750, 676 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{22}N_2ONa^+$ 317.1624; found 317.1624.

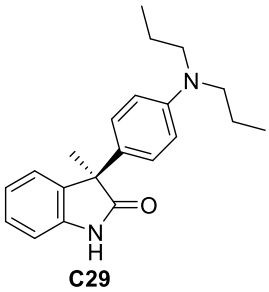


	Retention Time	Area	% Area
1	5.371	17465684	49.93
2	7.378	17515441	50.07



	Retention Time	Area	% Area
1	5.422	32678876	92.85
2	7.757	2514753	7.15

(*R*)-3-(4-(dipropylamino)phenyl)-3-methylindolin-2-one (C29)



C29

Colorless oil; 28.5 mg, 95% yield, 64% ee; $[\alpha]_D^{12.2}$ = 82.8 (*c* = 0.24 in CH_2Cl_2).

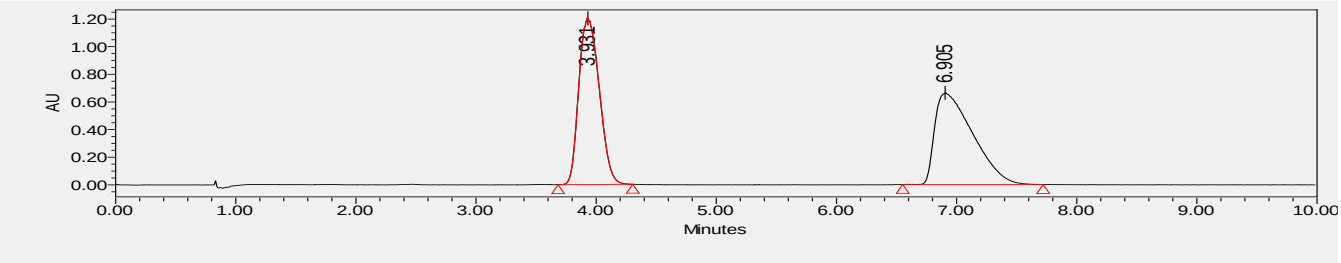
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 3.91 min, t_R (minor) = 7.00 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 9.09 (s, 1H), 7.23 – 7.07 (m, 4H), 7.06 – 6.98 (m, 1H), 6.97 – 6.91 (d, *J* = 7.7 Hz, 1H), 6.59 – 6.50 (m, 2H), 3.18 (t, *J* = 7.4 Hz 4H), 1.76 (s, 3H), 1.56 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 6H).

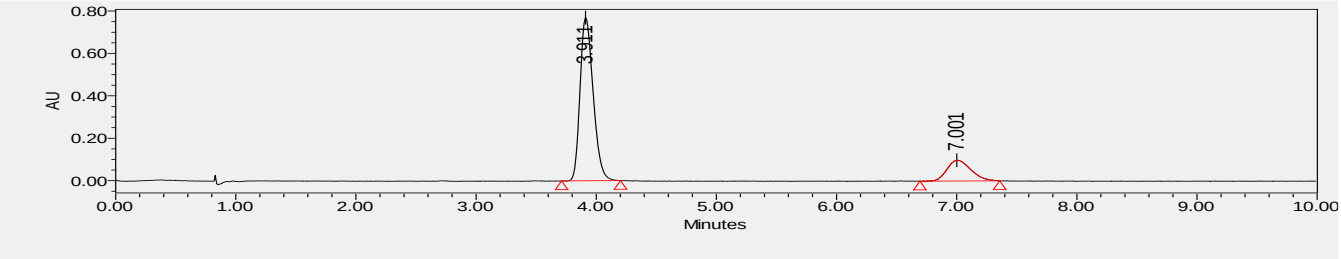
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 183.1, 147.3, 140.6, 136.2, 127.7, 127.5, 126.6, 124.4, 122.5, 111.6, 110.1, 52.9, 51.9, 23.4, 20.4, 11.5.

IR: 3205, 2960, 2872, 1615, 1516, 1200, 1154, 806, 745, 640 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{26}N_2ONa^+$ 345.1937; found 345.1940.

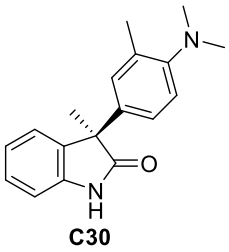


	Retention Time	Area	% Area
1	3.931	14246060	49.43
2	6.905	14576468	50.57



	Retention Time	Area	% Area
1	3.911	5833522	81.18
2	7.001	1352285	18.82

(*R*)-3-(4-(dimethylamino)-3-methylphenyl)-3-methylindolin-2-one (C30)



C30

Colorless oil; 25.8 mg, 92% yield, 98% ee; $[\alpha]_D^{11.2}$ = 100.9 (*c* = 0.25 in CH_2Cl_2).

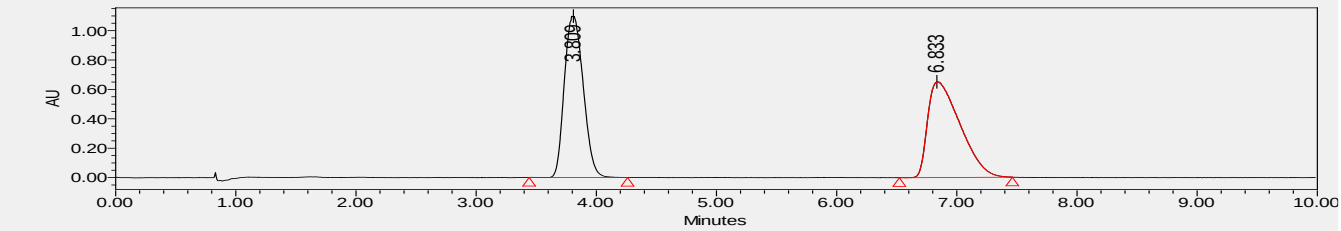
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 3.78 min, t_R (minor) = 6.97 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.95 (s, 1H), 7.24 – 7.18 (m, 1H), 7.16 – 7.11 (m, 1H), 7.09 – 6.99 (m, 3H), 6.99 – 6.91 (m, 2H), 2.65 (s, 6H), 2.26 (s, 3H), 1.79 (s, 3H).

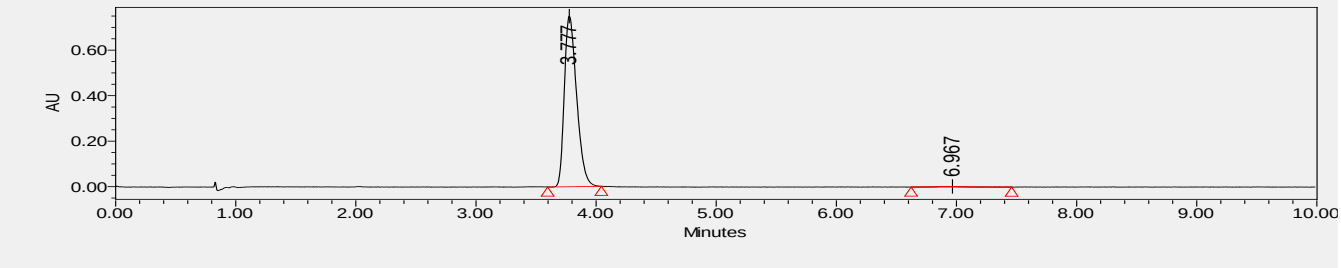
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 182.8, 152.0, 140.6, 136.1, 134.3, 132.2, 129.5, 128.0, 124.7, 124.5, 122.8, 118.5, 110.3, 52.3, 44.2, 23.5, 18.8.

IR: 3207, 2934, 2872, 1618, 1503, 1471, 1322, 817, 750, 640 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{20}N_2ONa^+$ 303.1468; found 303.1468.

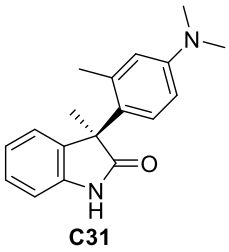


	Retention Time	Area	% Area
1	3.809	12007379	49.64
2	6.833	12183808	50.36



	Retention Time	Area	% Area
1	3.777	5338215	99.13
2	6.967	46755	0.87

(*R*)-3-(4-(dimethylamino)-2-methylphenyl)-3-methylindolin-2-one (C31)



C31

Colorless oil; 26.6 mg, 95% yield, 89% ee; $[\alpha]_D^{14.3}$ = -30.2 (*c* = 0.36 in CH_2Cl_2).

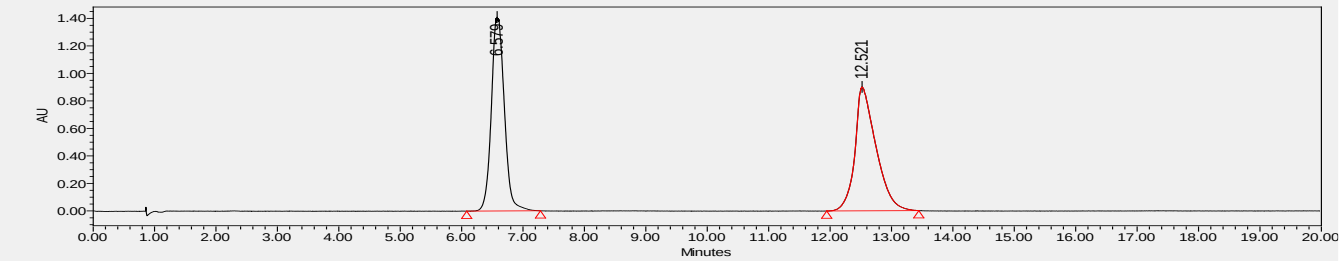
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 12.39 min, t_R (minor) = 6.60 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 9.43 (s, 1H), 7.54 – 7.48 (d, *J* = 8.7 Hz, 1H), 7.19 – 7.11 (m, 1H), 6.97 – 6.83 (m, 3H), 6.69 – 6.62 (m, 1H), 6.49 – 6.43 (m, 1H), 2.92 (s, 6H), 1.77 (s, 3H), 1.70 (s, 3H).

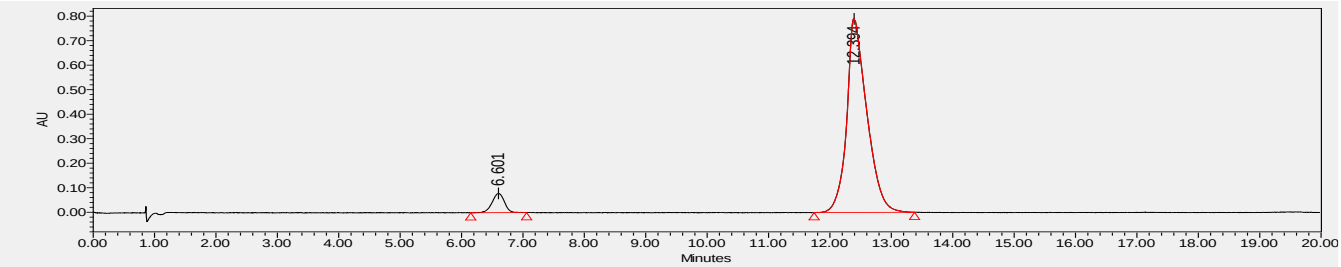
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 183.9, 150.2, 140.3, 137.8, 136.7, 128.4, 127.6, 125.6, 123.2, 122.8, 116.1, 110.2, 110.0, 52.4, 40.6, 26.2, 20.00.

IR: 3209, 1610, 1509, 1470, 1409, 1371, 1219, 1182, 756, 613 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{20}N_2ONa^+$ 303.1468; found 303.1469.

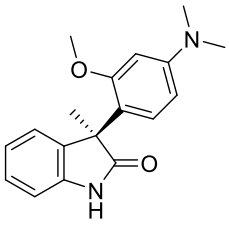


	Retention Time	Area	% Area
1	6.579	20757850	49.13
2	12.521	21493117	50.87



	Retention Time	Area	% Area
1	6.601	1094884	5.74
2	12.394	17974983	94.26

(*S*)-3-(4-(dimethylamino)-2-methoxyphenyl)-3-methylindolin-2-one (C32)



C32

White soild; 29.3 mg, 99% yield, 56% ee; melting point: 179–182 °C; $[\alpha]_D^{13.0}$ = -10.1 (*c* = 0.42 in CH_2Cl_2).

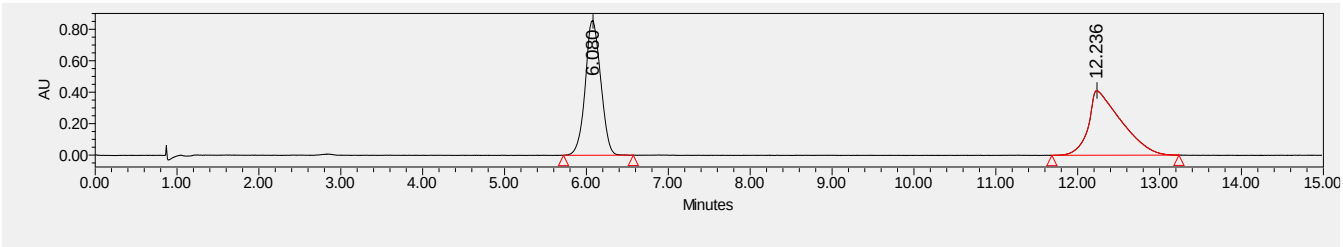
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 6.14 min, t_R (minor) = 13.11 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.93 (s, 1H), 7.45 – 7.38 (d, *J* = 8.6 Hz, 1H), 7.15 – 7.04 (m, 1H), 6.91 – 6.81 (m, 3H), 6.43 – 6.36 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.19 – 6.14 (d, *J* = 2.4 Hz, 1H), 3.43 (s, 3H), 2.92 (s, 6H), 1.69 (s, 3H).

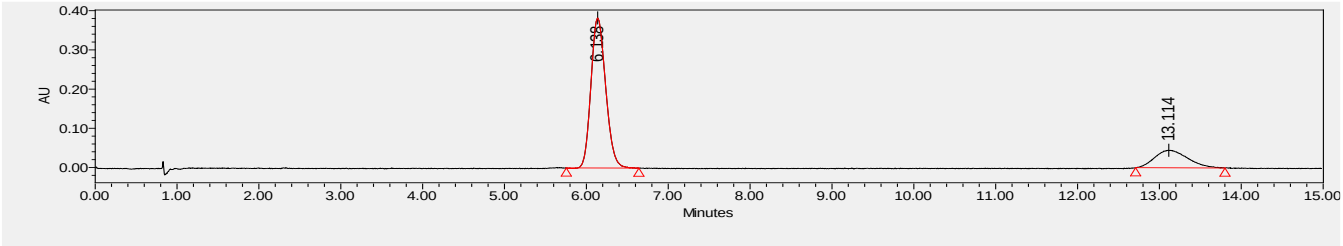
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 184.5, 157.9, 151.6, 140.7, 137.3, 128.0, 126.6, 122.4, 122.0, 117.8, 109.2, 105.0, 97.8, 55.5, 49.8, 40.7, 23.6.

IR: 2930, 1615, 1566, 1515, 1509, 1470, 1243, 1980, 815, 756 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{20}N_2O_2Na^+$ 319.1417; found 319.1420.

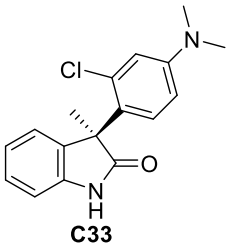


	Retention Time	Area	% Area
1	6.080	11225623	49.61
2	12.236	11403821	50.39



	Retention Time	Area	% Area
1	6.138	4803837	78.14
2	13.114	1343974	21.86

(*S*)-3-(2-chloro-4-(dimethylamino)phenyl)-3-methylindolin-2-one (C33)



C33

Colorless oil; 24.9 mg, 83% yield, 88% ee; $[\alpha]_D^{13.8}$ = -41.4 (*c* = 0.28 in CH_2Cl_2).

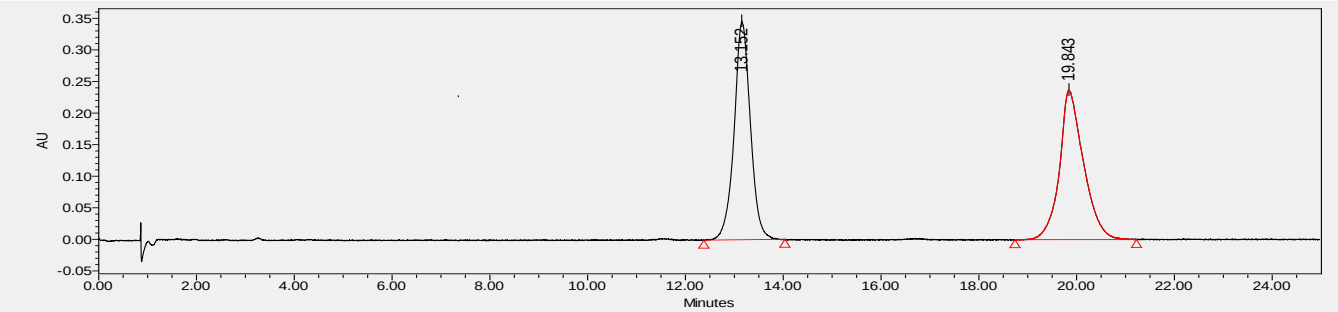
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 19.73 min, t_R (minor) = 13.18 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 9.00 (s, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.20 – 7.11 (m, 1H), 6.97 – 6.87 (m, 3H), 6.85 – 6.79 (m, 1H), 6.70 – 6.65 (m, 1H), 6.64 – 6.59 (m, 1H), 2.92 (s, 6H), 1.76 (s, 3H).

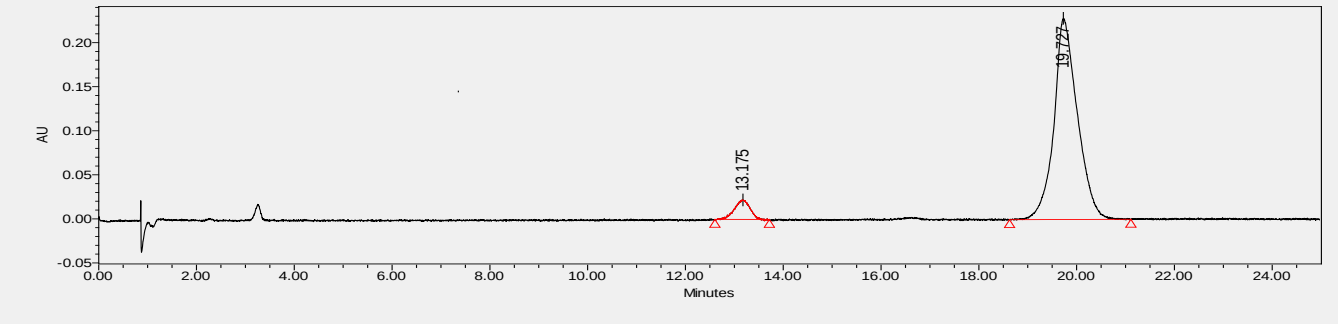
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 183.1, 150.9, 140.9, 136.2, 134.8, 129.6, 127.6, 124.4, 122.6, 122.5, 114.4, 110.6, 110.1, 52.3, 40.4, 25.7.

IR: 3208, 2928, 1613, 1562, 1470, 1356, 1014, 797, 743, 683 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}^{34.9689}ClN_2ONa^+$ 323.0922; found 323.0923, $C_{17}H_{17}^{36.9659}ClN_2ONa^+$ 328.0892; found 328.0889.

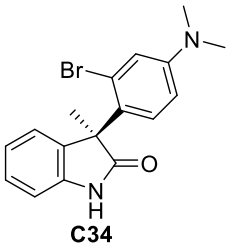


	Retention Time	Area	% Area
1	13.152	7987638	49.71
2	19.843	8081636	50.29



	Retention Time	Area	% Area
1	13.175	490960	6.05
2	19.727	7627211	93.95

(*S*)-3-(2-bromo-4-(dimethylamino)phenyl)-3-methylindolin-2-one (C34)



C34

Colorless oil; 34.5 mg, 94% yield, 88% ee; $[\alpha]_D^{14.1}$ = -31.6 (*c* = 0.28 in CH_2Cl_2).

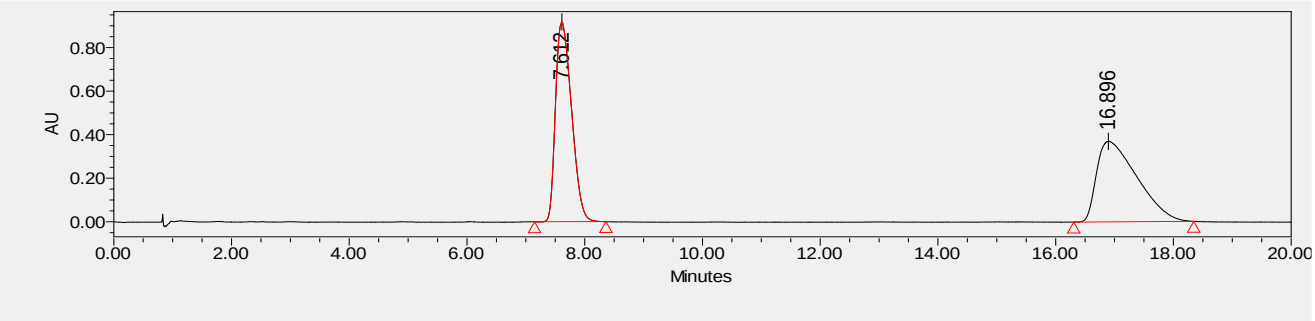
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 7.53 min, t_R (minor) = 17.10 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.75 (s, 1H), 7.56 – 7.49 (d, *J* = 8.8 Hz, 1H), 7.22 – 7.14 (m, 1H), 6.98 – 6.88 (m, 2H), 6.87 – 6.78 (m, 2H), 6.76 – 6.68 (dd, *J* = 8.8, 2.8 Hz, 1H), 2.93 (s, 6H), 1.77 (s, 3H).

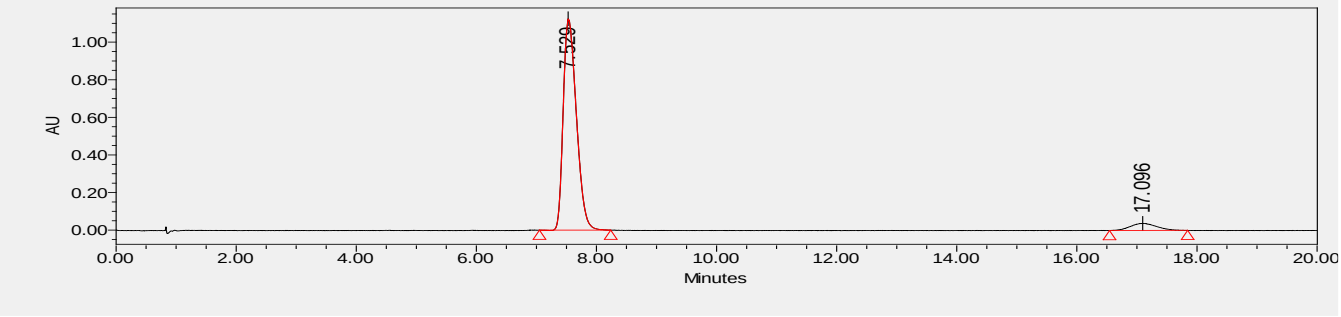
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 182.8, 150.9, 141.0, 136.3, 130.0, 127.7, 125.7, 124.9, 122.8, 122.6, 117.9, 111.1, 110.1, 53.7, 40.4, 26.4.

IR: 3214, 2926, 1606, 1505, 1471, 1218, 1104, 959, 794, 755 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}^{78.9183}BrN_2ONa^+$ 367.0416; found 367.0419, $C_{17}H_{17}^{80.9163}BrN_2ONa^+$ 369.0369; found 369.0369.

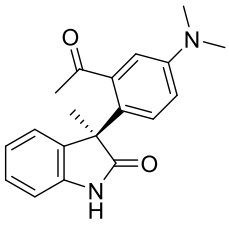


	Retention Time	Area	% Area
1	7.612	17330459	49.63
2	16.896	17590464	50.37



	Retention Time	Area	% Area
1	7.529	17109431	93.80
2	17.096	1131196	6.20

(*R*)-3-(2-acetyl-4-(dimethylamino)phenyl)-3-methylindolin-2-one (C35)



C35

Colorless oil; 22.2 mg, 72% yield, 94% ee; $[\alpha]_D^{11.3}$ = -32.1 (*c* = 0.17 in CH_2Cl_2).

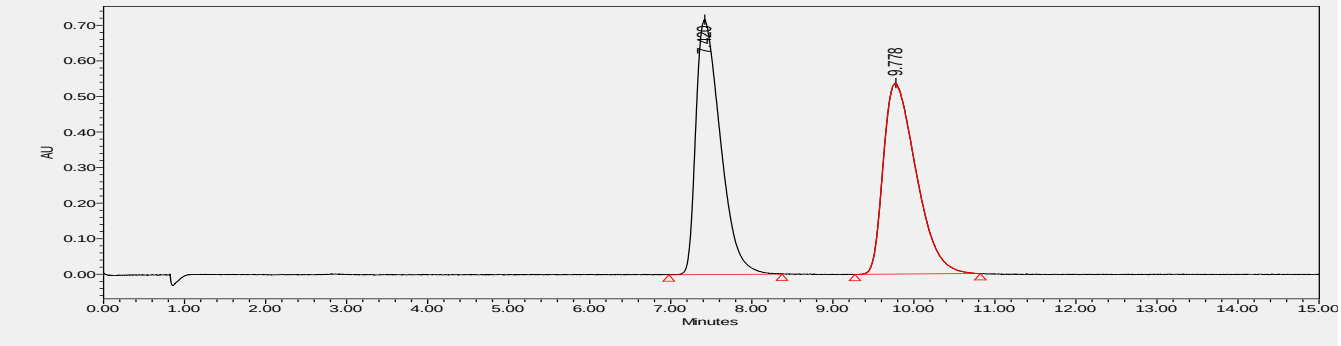
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 9.43 min, t_R (minor) = 7.52 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.85 (s, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.17 (m, 1H), 6.96 – 6.79 (m, 4H), 6.64 (d, *J* = 2.8 Hz, 1H), 2.97 (s, 6H), 1.99 (d, *J* = 4.3 Hz, 3H), 1.74 (s, 3H).

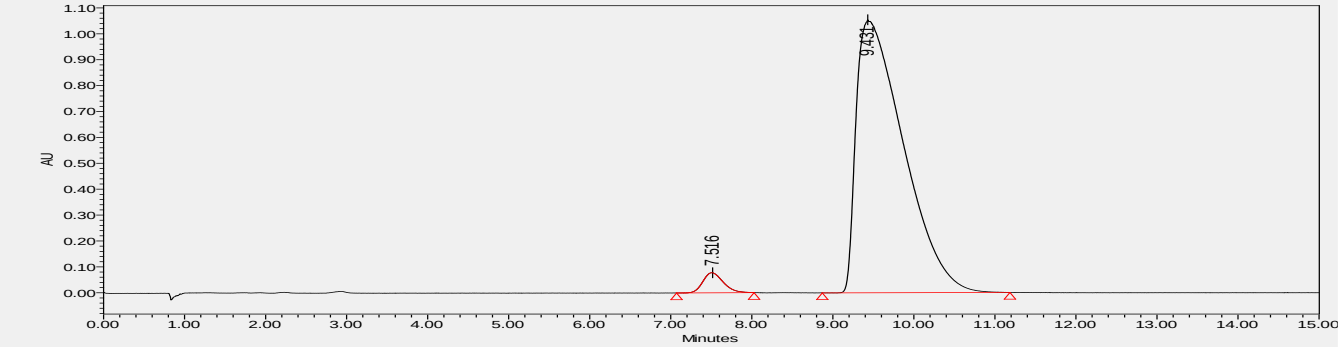
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 204.0, 183.1, 149.3, 141.7, 141.1, 137.4, 129.9, 127.9, 124.2, 123.0, 122.1, 113.8, 111.3, 109.8, 51.2, 40.6, 29.1, 26.5.

IR: 2926, 1711, 1609, 1556, 1472, 1359, 1228, 1164, 806, 757 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{20}N_2O_2Na^+$ 331.1417; found 331.1417.

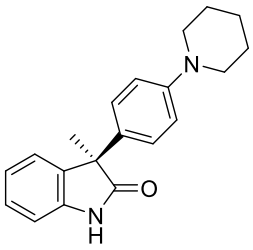


	Retention Time	Area	% Area
1	7.420	15070474	50.03
2	9.778	15054182	49.97



	Retention Time	Area	% Area
1	7.516	1348950	3.06
2	9.431	42753767	96.94

(*R*)-3-methyl-3-(4-(piperidin-1-yl)phenyl)indolin-2-one (C36)



C36

Colorless oil; 30.0 mg, 98% yield, 94% ee; $[\alpha]_D^{10.8}$ = 87.5 (*c* = 0.47 in CH_2Cl_2).

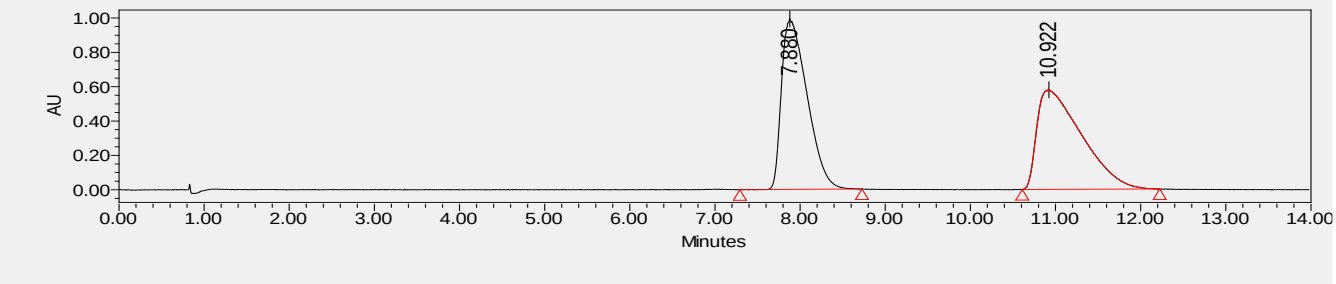
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 7.67 min, t_R (minor) = 10.98 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 9.05 (s, 1H), 7.24 – 7.09 (m, 4H), 7.06 – 6.98 (d, *J* = 7.4, 1H), 6.96 – 6.89 (d, *J* = 7.8 Hz, 1H), 6.89 – 6.80 (m, 2H), 3.10 (t, *J* = 5.4 Hz, 4H), 1.77 (s, 3H), 1.71 – 1.61 (m, 4H), 1.59 – 1.49 (m, 2H).

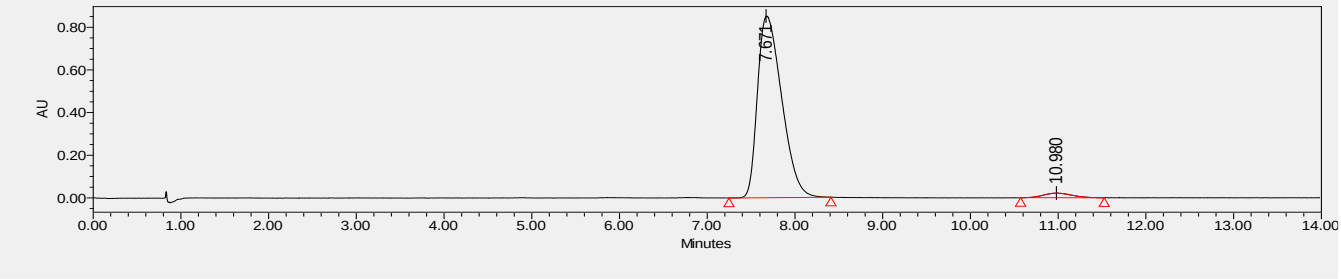
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 182.9, 151.3, 140.6, 136.1, 130.8, 127.9, 127.4, 124.4, 122.7, 116.4, 110.3, 52.2, 50.5, 25.9, 24.4, 23.6.

IR: 3206, 2932, 1616, 1514, 1471, 1384, 1219, 1120, 812, 744 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{20}H_{22}N_2ONa^+$ 329.1624; found 329.1626. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (td, *J* = 7.6, 1.1 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 3.10 (q, 4H).

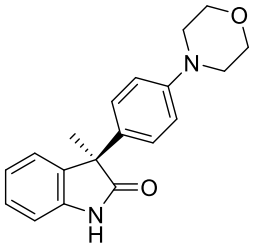


	Retention Time	Area	% Area
1	7.880	20713985	49.56
2	10.922	21084477	50.44



	Retention Time	Area	% Area
1	7.671	16342218	97.15
2	10.980	479299	2.85

(*R*)-3-methyl-3-(4-morpholinophenyl)indolin-2-one (C37)



C37

Colorless oil; 29.6 mg, 96% yield, 80% ee; $[\alpha]_D^{10.2}$ = 81.3 (*c* = 0.67 in CH_2Cl_2).

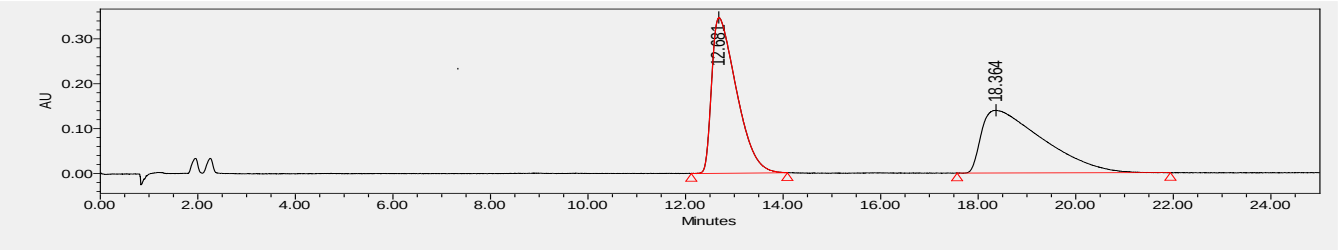
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 12.58 min, t_R (minor) = 19.24 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.85 (s, 1H), 7.25 – 7.17 (m, 3H), 7.15 – 7.10 (m, 1H), 7.08 – 7.00 (m, 1H), 6.98 – 6.92 (m, 1H), 6.87 – 6.79 (m, 2H), 3.83 (t, *J* = 4.9 Hz, 4H), 3.11 (t, *J* = 4.9 Hz, 4H), 1.78 (s, 3H).

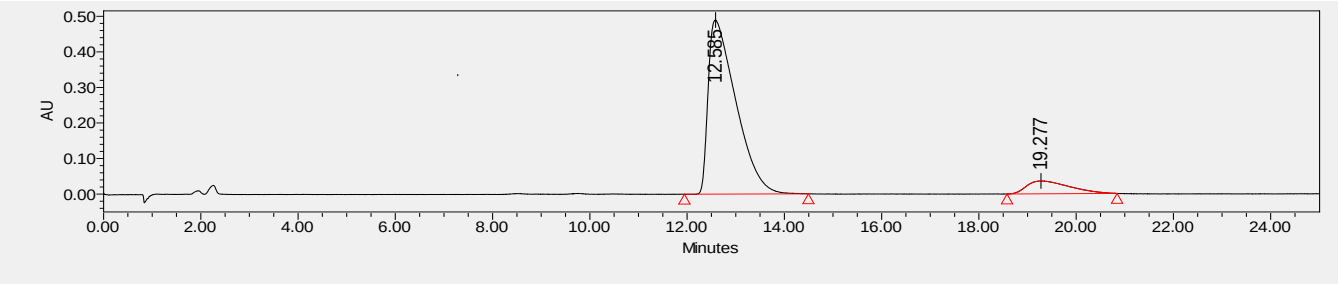
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 182.6, 150.5, 140.6, 135.9, 131.8, 128.1, 127.6, 124.5, 122.8, 115.7, 110.2, 70.0, 52.1, 49.2, 23.6.

IR: 3202, 2924, 2853, 1708, 1616, 1514, 1326, 1119, 930, 814 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{20}N_2O_2Na^+$ 331.1417; found 331.1418.

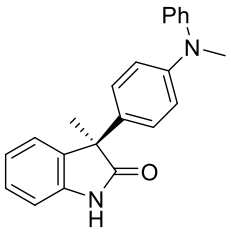


	Retention Time	Area	% Area
1	12.681	12216772	50.00
2	18.364	12214340	50.00



	Retention Time	Area	% Area
1	12.581	9903336	89.86
2	19.244	1118053	10.14

(*R*)-3-methyl-3-(4-(methyl(phenyl)amino)phenyl)indolin-2-one (C38)



C38

Colorless oil; 29.9 mg, 91% yield, 97% ee; $[\alpha]_D^{11.2}$ = 43.4 (*c* = 0.32 in CH_2Cl_2).

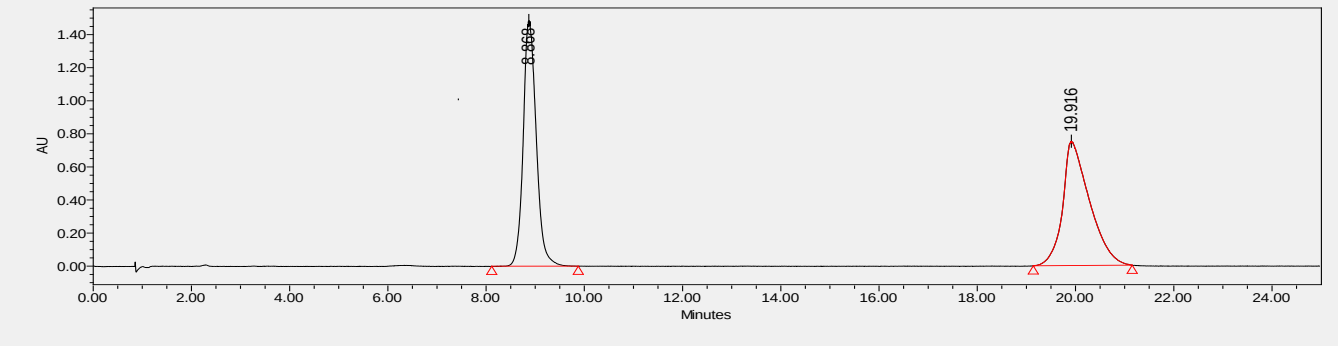
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 19.64 min, t_R (minor) = 8.92 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.76 (s, 1H), 7.32 – 7.14 (m, 6H), 7.10 – 6.99 (m, 3H), 6.98 – 6.87 (m, 4H), 3.27 (s, 3H), 1.79 (3, 1H).

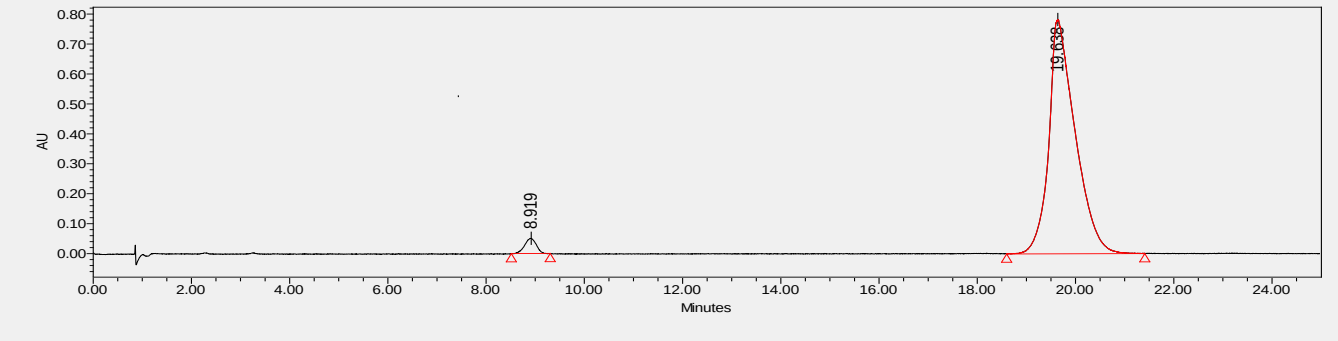
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 182.5, 148.8, 148.2, 140.5, 135.9, 132.7, 129.3, 128.1, 127.5, 124.5, 122.8, 121.9, 121.3, 119.7, 110.3, 52.3, 40.3, 23.6.

IR: 3209, 1615, 1511, 1471, 1344, 1218, 1211, 699 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{22}H_{20}N_2ONa^+$ 351.1468; found 351.1470.

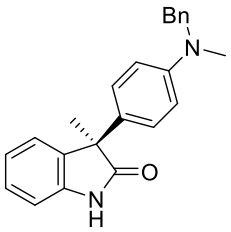


	Retention Time	Area	% Area
1	8.868	27373779	49.03
2	19.916	28459481	50.97



	Retention Time	Area	% Area
1	8.919	832949	2.77
2	19.638	29224671	97.23

(*R*)-3-(4-(benzyl(methyl)amino)phenyl)-3-methylindolin-2-one (C39)



C39

Colorless oil; 33.9 mg, 99% yield, 94% ee; $[\alpha]_D^{10.2}$ = 90.2 (*c* = 0.12 in CH_2Cl_2).

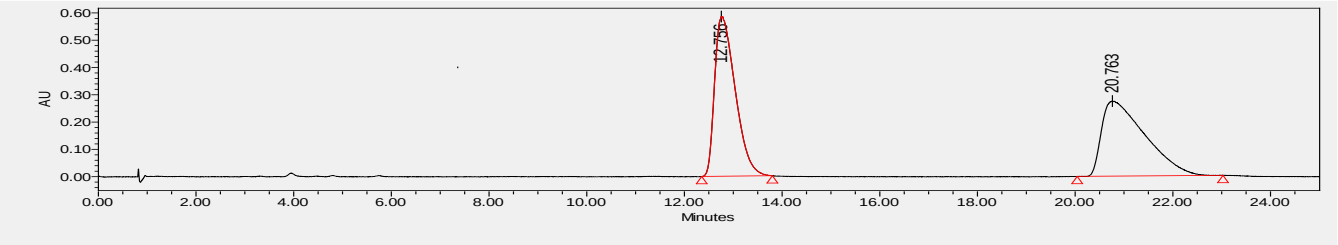
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 12.80 min, t_R (minor) = 21.84 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.83 (s, 1H), 7.32 – 7.17 (m, 6H), 7.15 – 7.11 (m, 3H), 7.06 – 6.97 (m, 1H), 6.96 – 6.90 (m, 1H), 6.70 – 6.62 (m, 2H), 4.47 (s, 2H), 2.98 (s, 3H), 1.76 (s, 3H).

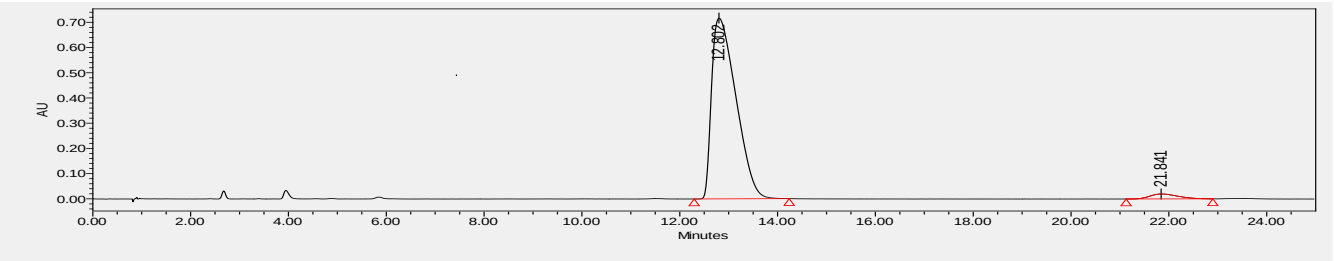
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 182.9, 149.0, 140.6, 139.1, 136.2, 128.7, 128.2, 127.9, 127.6, 127.0, 126.8, 124.5, 122.7, 112.4, 110.2, 56.7, 52.0, 38.7, 23.6.

IR: 2926, 1707, 1615, 1519, 1471, 1373, 1201, 1113, 808, 731 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{23}H_{22}N_2ONa^+$ 365.1624; found 365.1627.

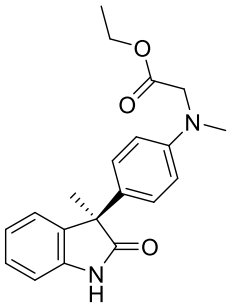


	Retention Time	Area	% Area
1	12.756	17097976	50.18
2	20.763	16977992	49.82



	Retention Time	Area	% Area
1	12.802	24786153	96.97
2	21.841	774766	3.03

ethyl (*R*)-N-methyl-N-(4-(3-methyl-2-oxoindolin-3-yl)phenyl)glycinate (C40)



C40

Colorless oil; 33.5 mg, 99% yield, 93% ee; $[\alpha]_D^{12.8}$ = 88.1 (*c* = 0.22 in CH_2Cl_2).

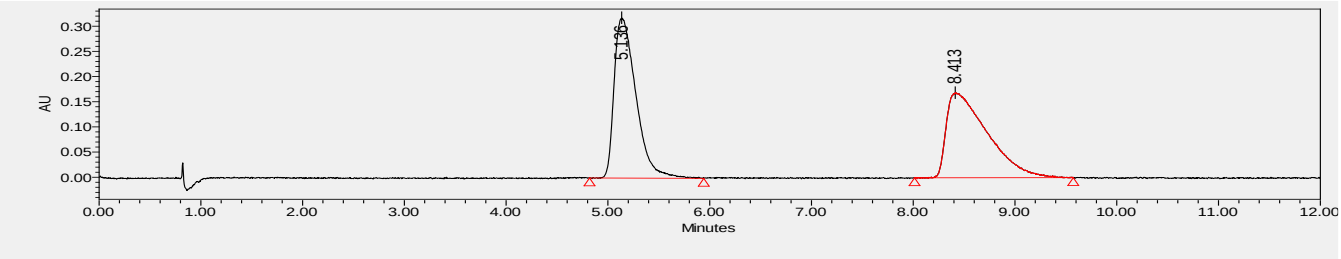
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 5.25 min, t_R (minor) = 8.95 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.92 (s, 1H), 7.24 – 7.08 (m, 4H), 7.06 – 6.98 (m, 1H), 6.97 – 6.90 (d, *J* = 7.7 Hz, 1H), 6.64 – 6.56 (m, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 2H), 3.03 (s, 3H), 1.76 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 2H).

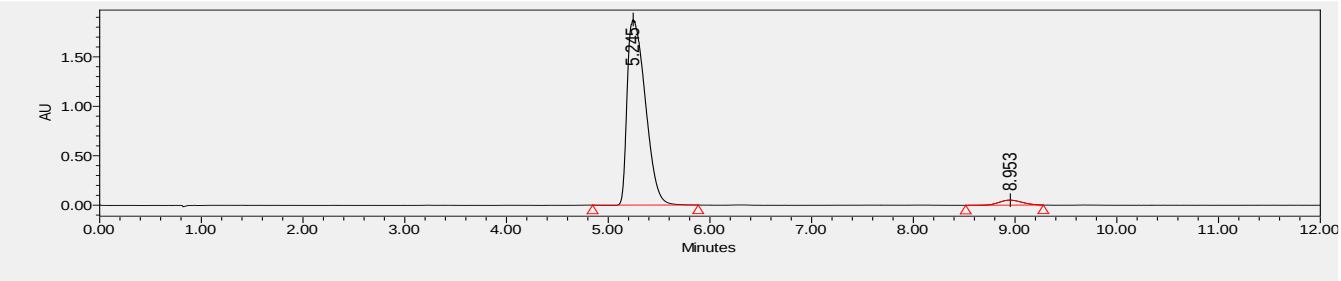
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 182.9, 171.1, 148.1, 140.6, 136.1, 129.0, 127.9, 127.6, 124.5, 122.7, 112.4, 110.2, 61.0, 54.5, 52.0, 39.6, 23.6, 14.3.

IR: 2977, 1615, 1520, 1471, 1370, 1325, 1118, 948, 808, 640 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{20}H_{22}N_2O_3Na^+$ 361.1523; found 361.1524.

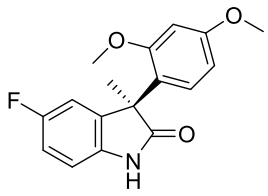


	Retention Time	Area	% Area
1	5.136	4741279	50.16
2	8.413	4710154	49.84



	Retention Time	Area	% Area
1	5.245	23275349	96.68
2	8.953	800447	3.32

(*S*)-3-(2,4-dimethoxyphenyl)-5-fluoro-3-methylindolin-2-one (C41)



C41

Colorless oil; 26.2 mg, 87% yield, 94% ee; $[\alpha]_D^{11.4}$ = -137.5 (*c* = 0.21 in CH_2Cl_2).

UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 6.33 min, t_R (minor) = 4.21 min.

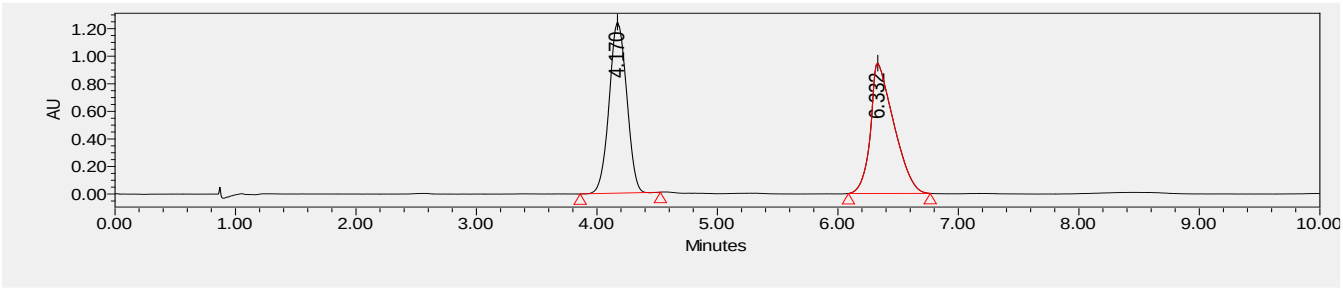
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.96 (s, 1H), 7.51 – 7.41 (d, *J* = 8.6 Hz, 1H), 6.87 – 6.76 (m, 2H), 6.61 – 6.53 (m, 2H), 6.40 – 6.35 (d, *J* = 2.5 Hz, 1H), 3.80 (s, 3H), 3.45 (s, 3H), 1.71 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 184.0, 160.9(J_{C-F}= 282.5 Hz), 160.4, 158.0, 138.6(J_{C-F}= 7.8 Hz), 136.7, 128.3, 121.3, 113.6(J_{C-F}= 23.5 Hz), 110.6(J_{C-F}= 24.6 Hz), 109.9(J_{C-F}= 7.9 Hz), 104.7, 100.0, 55.5, 55.5, 50.7, 23.7.

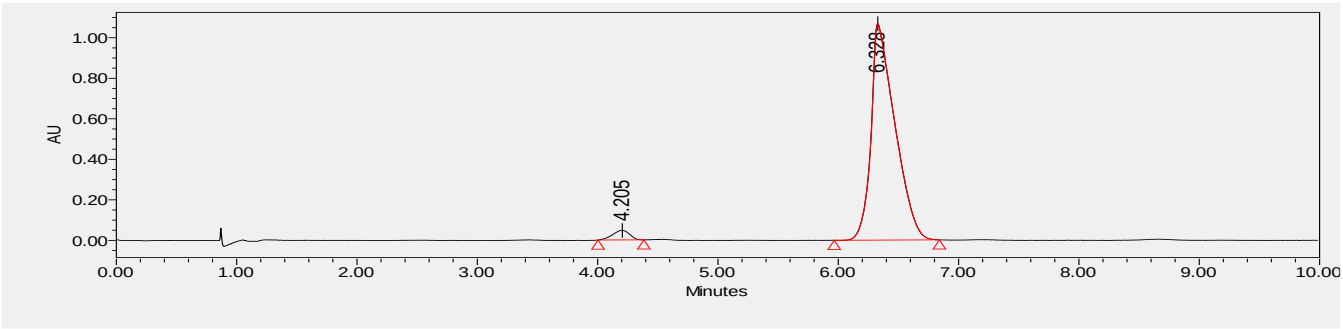
^{19}F NMR (376 MHz, $CDCl_3$) *δ* -121.4.

IR: 3218, 2931, 1611, 1505, 1486, 1306, 1263, 1031, 816, 778 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{16}FNO_3Na^+$ 324.1006; found 324.1008.

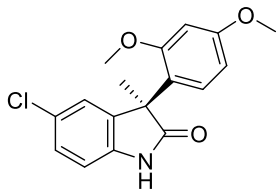


	Retention Time	Area	% Area
1	4.170	12568193	49.73
2	6.332	12703771	50.27



	Retention Time	Area	% Area
1	4.205	461392	3.04
2	6.328	14738106	96.96

(*S*)-5-chloro-3-(2,4-dimethoxyphenyl)-3-methylindolin-2-one (C42)



C42

Colorless oil; 30.2 mg, 95% yield, 89% ee; $[\alpha]_D^{11.4}$ = 155.0 (*c* = 0.51 in CH_2Cl_2).

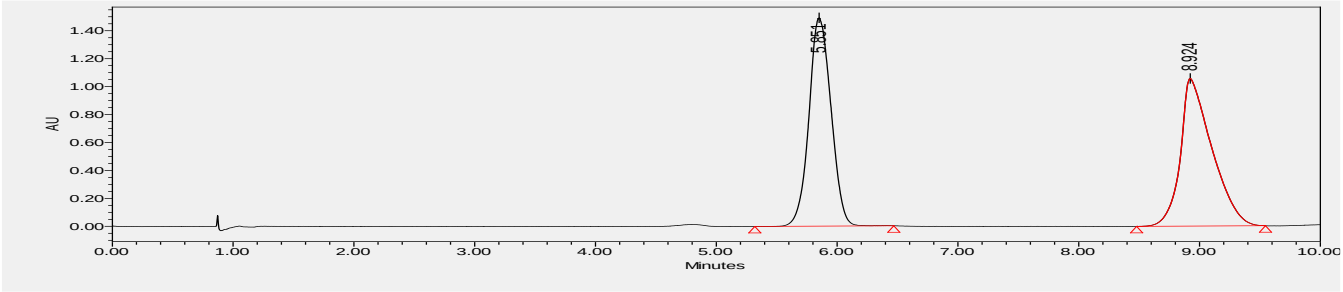
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 8.79 min, t_R (minor) = 5.87 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.99 (s, 1H), 7.49 – 7.41 (d, *J* = 8.5 Hz, 1H), 7.13 – 7.05 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.84 – 6.77 (m, 2H), 6.61 – 6.54 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.40 – 6.35 (d, *J* = 2.5 Hz, 1H), 3.80 (s, 3H), 3.45 (s, 3H), 1.70 (s, 3H).

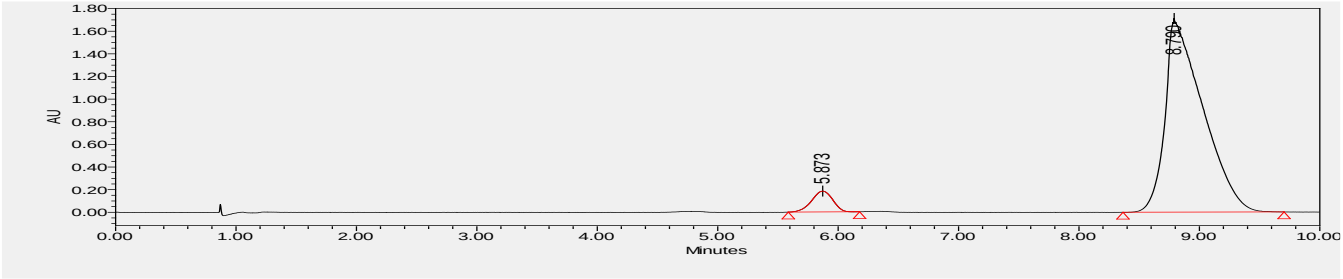
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 183.7, 160.9, 158.0, 139.4, 138.5, 128.3, 127.5, 127.3, 123.0, 121.1, 110.4, 104.7, 100.0, 55.5, 50.4, 23.7. ^{1}H NMR (400 MHz, $CDCl_3$)

IR: 3218, 2931, 1613, 1505, 1479, 1305, 1210, 1182, 818, 753 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{16}^{34.9689}ClNO_3Na^+$ 340.0711; found 340.0714, $C_{17}H_{16}^{36.9659}ClNO_3Na^+$ 342.0681; found 342.0681

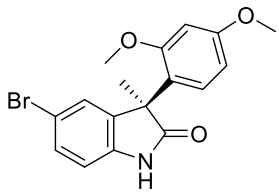


	Retention Time	Area	% Area
1	5.851	18974606	49.89
2	8.924	19054497	50.11



	Retention Time	Area	% Area
1	5.873	2235688	5.67
2	8.790	37207144	94.33

(*S*)-5-bromo-3-(2,4-dimethoxyphenyl)-3-methylindolin-2-one (C43)



C43

Colorless oil; 30.1 mg, 83% yield, 88% ee; $[\alpha]_D^{11.3}$ = 86.3 (*c* = 0.18 in CH_2Cl_2).

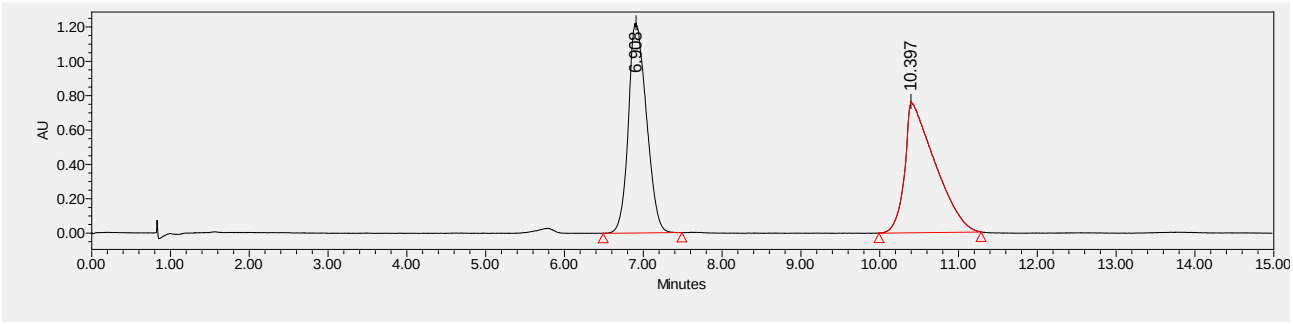
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 10.64 min, t_R (minor) = 7.06 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.85 (s, 1H), 7.50 – 7.42 (d, *J* = 8.6 Hz, 1H), 7.28 – 7.22 (m, 1H), 6.95 – 6.90 (m, 1H), 6.81 – 6.74 (d, *J* = 2.0 Hz, 1H), 6.61 – 6.54 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.40 – 6.35 (d, *J* = 2.5 Hz, 1H), 3.81 (s, 3H), 3.46 (s, 3H), 1.70 (s, 3H).

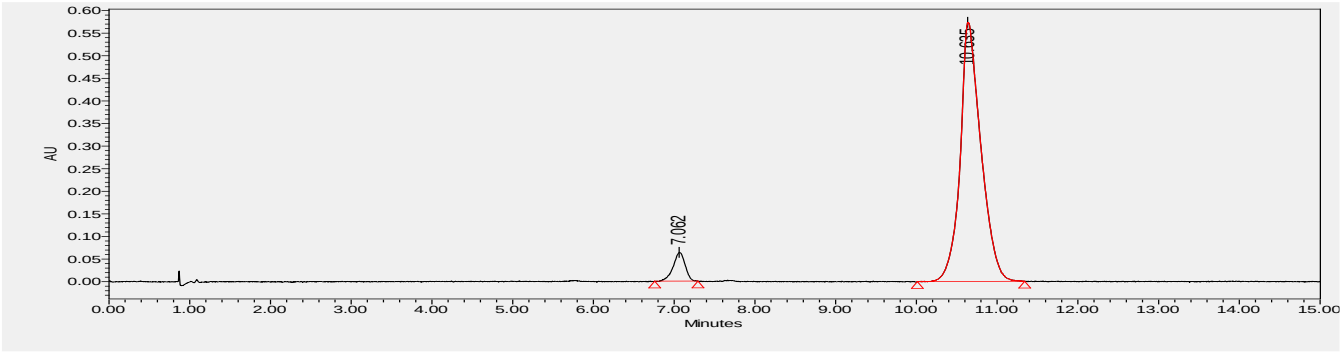
^{13}C NMR (101 MHz, $CDCl_3$) δ 183.4, 160.9, 158.0, 139.8, 138.9, 130.1, 128.28, 125.8, 121.0, 114.8, 110.9, 104.6, 99.9, 55.5, 50.3, 23.7.

IR: 3206, 1613, 1586, 1505, 1475, 1306, 1210, 1143, 1031, 817 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{16}^{78.9183}BrNO_3Na^+$ 384.0206; found 384.0206, $C_{17}H_{16}^{80.9163}BrNO_3Na^+$ 386.0185; found 386.0184

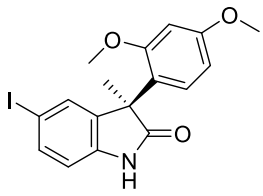


	Retention Time	Area	% Area
1	6.908	19492357	49.04
2	10.397	20251708	50.96



	Retention Time	Area	% Area
1	7.062	650711	5.97
2	10.635	10244410	94.03

(*S*)-3-(2,4-dimethoxyphenyl)-5-iodo-3-methylindolin-2-one (C44)



C44

Colorless oil; 34.4 mg, 84% yield, 86% ee; $[\alpha]_D^{13.3}$ = 137.0 (*c* = 0.11 in CH_2Cl_2).

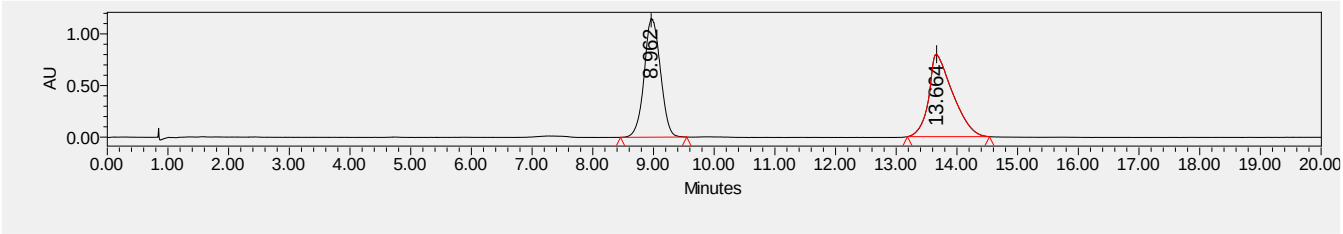
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 13.47min, t_R (minor) = 9.03 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.86 (s, 1H), 7.48 – 7.41 (m, 2H), 7.11 – 7.06 (m, 1H), 6.72 – 6.65 (d, *J* = 8.5 Hz, 1H), 6.61 – 6.54 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.40 – 6.35 (d, *J* = 2.5 Hz, 1H), 3.81 (s, 3H), 3.46 (s, 3H), 1.71 – 1.67 (s, 3H).

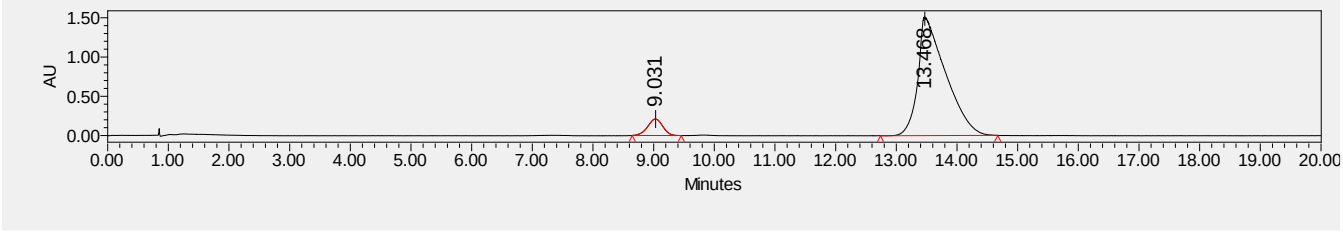
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 183.3, 160.9, 158.0, 140.5, 139.2, 136.1, 131.3, 128.3, 121.0, 111.5, 104.6, 99.9, 84.8, 55.6, 50.1, 23.7.

IR: 3236, 1611, 1586, 1472, 1305, 1210, 1143, 1131, 815, 643, 531 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{16}NIO_3Na^+$ 432.0067; found 432.0072.

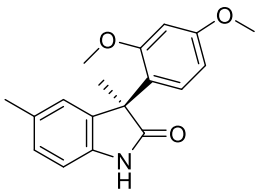


	Retention Time	Area	% Area
1	8.962	21435232	49.52
2	13.664	21849329	50.48



	Retention Time	Area	% Area
1	9.031	3619821	7.02
2	13.468	47928385	92.98

(*S*)-3-(2,4-dimethoxyphenyl)-3,5-dimethylindolin-2-one (C45)



C45

Colorless oil; 23.8 mg, 80% yield, 86% ee; $[\alpha]_D^{13.3}$ = -22.3 (*c* = 0.17 in CH_2Cl_2).

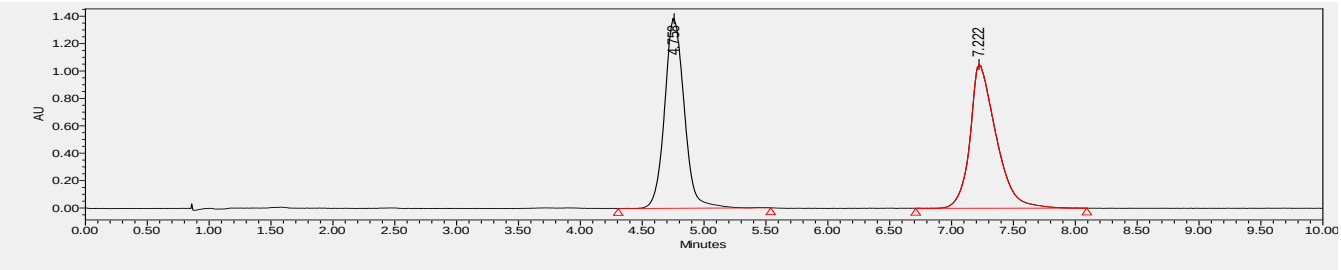
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 7.04 min, t_R (minor) = 4.77 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.50 (s, 1H), 7.51 – 7.44 (d, *J* = 8.6 Hz, 1H), 6.96 – 6.89 (m, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.66 – 6.60 (m, 1H), 6.61 – 6.51 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.40 – 6.35 (d, *J* = 2.5 Hz, 1H), 3.80 (s, 3H), 3.46 (s, 3H), 2.20 (s, 3H), 1.69 (s, 3H).

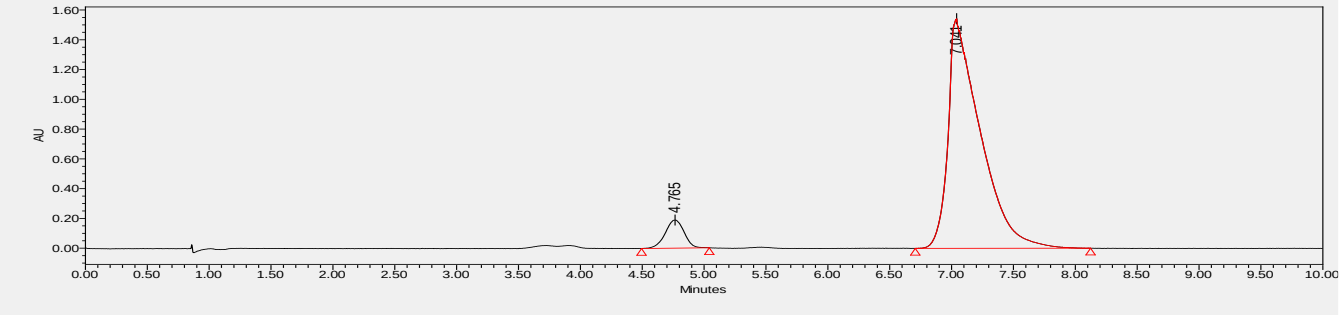
^{13}C NMR (101 MHz, $CDCl_3$) δ 183.8, 160.6, 158.2, 138.3, 136.8, 131.6, 128.2, 127.6, 123.3, 122.2, 109.0, 104.6, 100.1, 55.7, 55.5, 50.1, 24.0, 21.2.

IR: 3236, 2930, 1611, 1586, 1504, 1210, 1143, 1031, 815, 643, 531 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{19}NO_3Na^+$ 320.1257, found 320.1257.

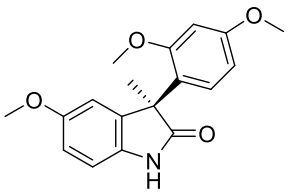


	Retention Time	Area	% Area
1	4.758	15286842	49.96
2	7.222	15309021	50.04



	Retention Time	Area	% Area
1	4.765	1999238	6.66
2	7.041	28004409	93.34

(*S*)-3-(2,4-dimethoxyphenyl)-5-methoxy-3-methylindolin-2-one (C46)



C46

Colorless oil; 20.1 mg, 64% yield, 95% ee; $[\alpha]_D^{12.0}$ = 36.7(*c* = 0.41 in CH_2Cl_2).

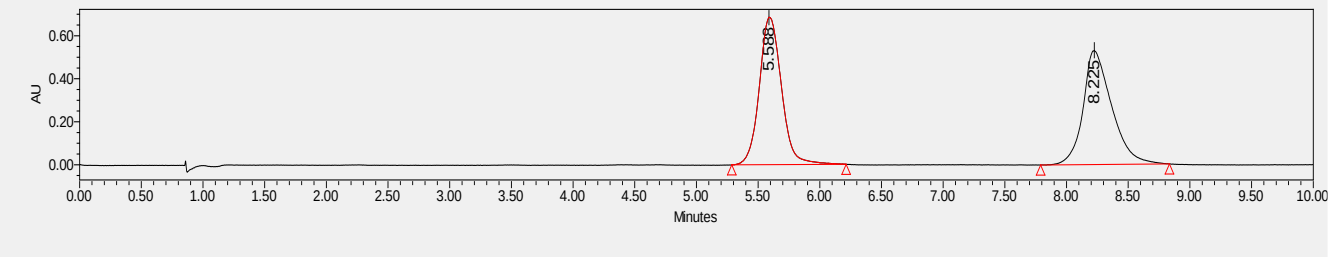
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 8.28 min, t_R (minor) = 5.64 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.44 (s, 1H), 7.50 – 7.42 (d, *J* = 8.6 Hz, 1H), 6.83 – 6.77 (m, 1H), 6.70 – 6.63 (m, 1H), 6.60 – 6.53 (m, 1H), 6.50 – 6.41 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.40 – 6.34 (d, *J* = 2.5 Hz, 1H), 3.80 (s, 3H), 3.68 (s, 3H), 3.46 (s, 3H), 1.70 (s, 3H).

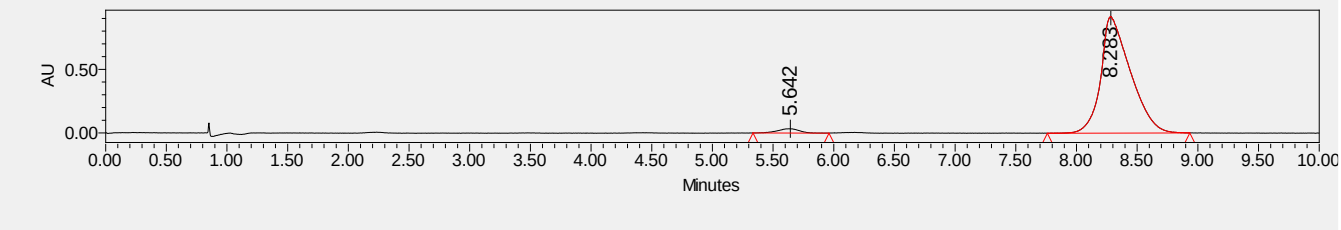
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 183.7, 160.7, 158.2, 155.7, 138.2, 134.2, 128.3, 121.9, 111.7, 109.8, 109.5, 104.6, 100.0, 55.8, 55.7, 55.5, 50.6, 24.0.

IR: 2932, 1609, 1489, 1306, 1265, 1207, 1143, 1030, 808, 736, 643 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{19}NO_4Na^+$ 336.1206, found 336.1206.

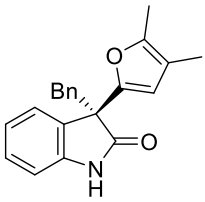


	Retention Time	Area	% Area
1	5.588	8543121	49.99
2	8.225	8546288	50.01



	Retention Time	Area	% Area
1	5.642	416410	2.61
2	8.283	15528559	97.39

(*S*)-3-benzyl-3-(4,5-dimethylfuran-2-yl)indolin-2-one (C47)



C47

White solid; 19.0 mg, 60% yield, 71% ee; melting point: 123–126 °C; $[\alpha]_D^{18.9}$ = 28.8 (*c* = 0.31 in CH_2Cl_2).

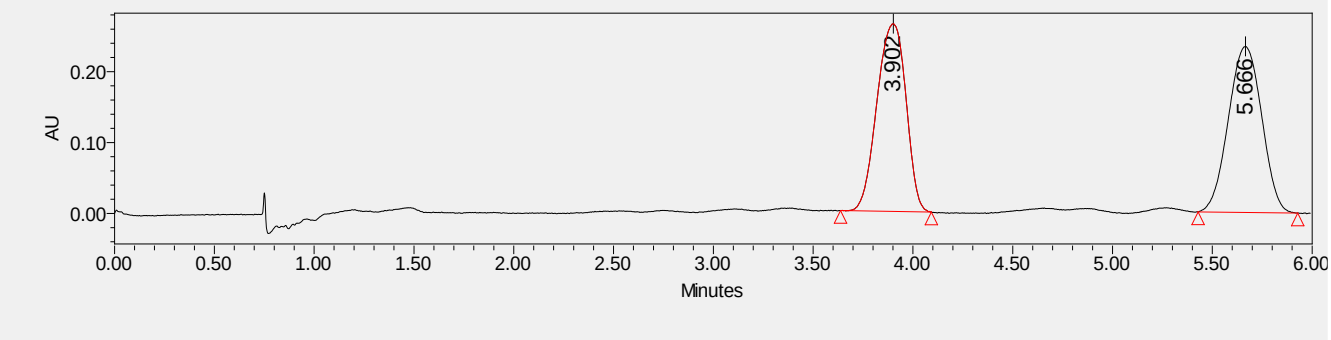
UPCC DAICEL CHIRALCEL OD-3, CO_2/MeOH = 90/10 flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 5.56 min, t_R (minor) = 3.90 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.90 (s, 1H), 7.24 – 7.13 (m, 2H), 7.11 – 6.99 (m, 4H), 6.92 – 6.84 (m, 2H), 6.73 – 6.66 (d, *J* = 7.7 Hz, 1H), 5.94 (s, 1H), 3.50 (m, 2H), 2.20 (s, 3H), 1.88 (s, 3H).

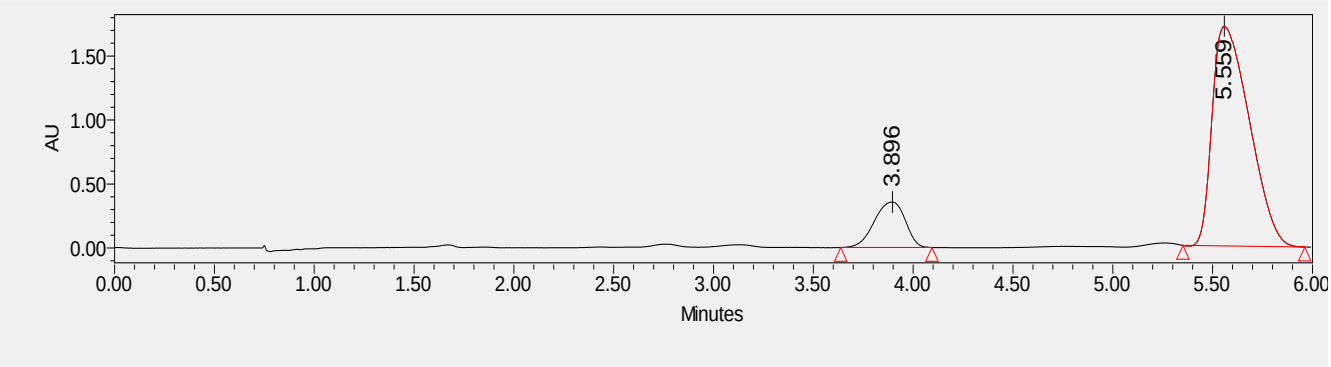
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 177.9, 148.9, 148.0, 140.7, 135.3, 130.3, 128.5, 127.8, 126.8, 125.5, 122.4, 114.8, 110.8, 109.8, 55.3, 42.0, 11.7, 10.0.

IR: 3249, 2361, 1714, 1619, 1472, 1261, 1198, 1009, 751 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{19}NO_2Na^+$ 340.1308; found 340.1306.

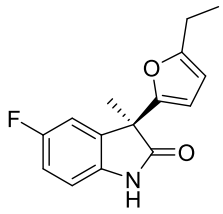


	Retention Time	Area	% Area
1	3.902	2675620	49.60
2	5.666	2718407	50.40



	Retention Time	Area	% Area
1	3.896	3820873	14.66
2	5.559	22237187	85.34

(*S*)-3-(5-ethylfuran-2-yl)-5-fluoro-3-methylindolin-2-one (C48)



C48

Colorless oil; 24.4 mg, 94% yield, 92% ee; $[\alpha]_D^{12.4}$ = 17.4 (*c* = 0.42 in CH_2Cl_2).

UPCC DAICEL CHIRALCEL OXH, CO_2/MeOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 11.63 min, t_R (minor) = 10.96 min.

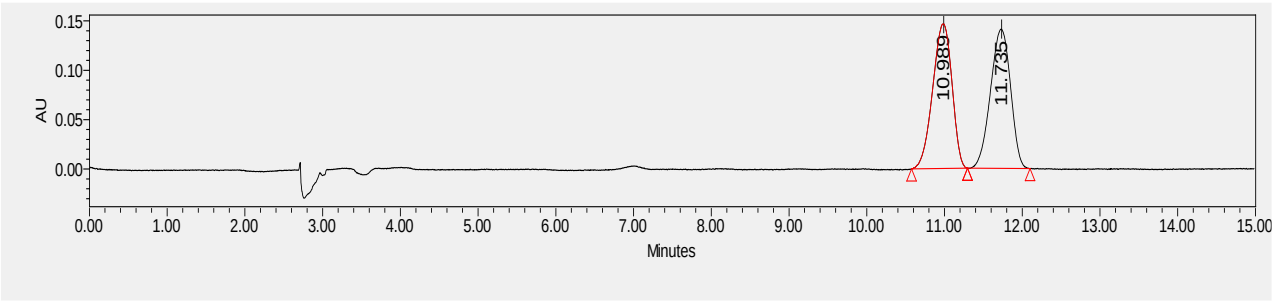
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 9.04 (s, 1H), 7.01 – 6.85 (m, 3H), 6.16 – 6.10 (d, *J* = 3.2 Hz, 1H), 5.93 – 5.87 (m, 1H), 2.57 (q, *J* = 7.6 Hz, 2H), 1.75 (s, 3H), 1.16 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 180.1, 160.6, 158.5, 158.2, 150.4, 136.2, 135.1(d, *J* = 8.3 Hz), 135.1(d, *J* = 8.3 Hz), 114.9(d, *J* = 23.6 Hz), 114.7(d, *J* = 23.6 Hz), 112.2(d, *J* = 21.8 Hz), 112.0(d, *J* = 21.8 Hz), 110.9(d, *J* = 8.1 Hz), 110.9(d, *J* = 8.1 Hz), 107.5(d, *J* = 228.0 Hz), 104.7(d, *J* = 228.0 Hz), 50.1, 22.7, 21.5, 12.0.

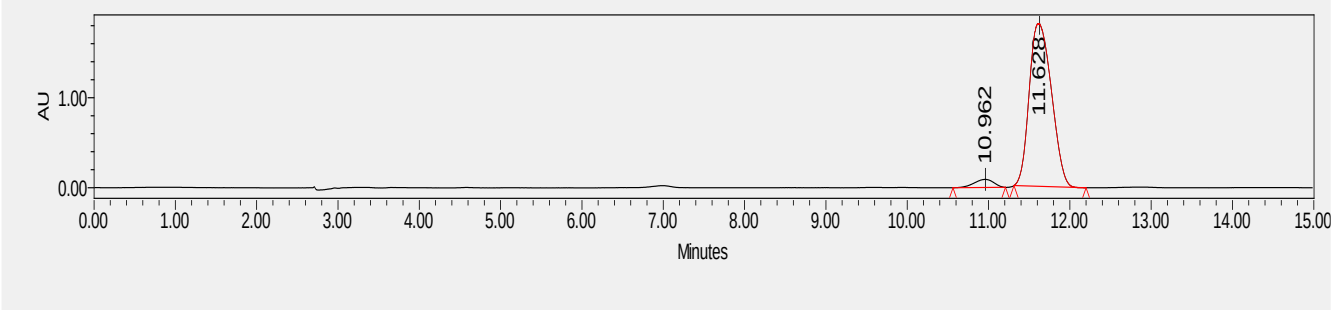
^{19}F NMR (376 MHz, $CDCl_3$) *δ* -120.28.

IR: 3231, 1613, 1520, 1471, 1353, 1201, 948, 809, 751, 629 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{14}FNO_2Na^+$ 282.0901 found 282.0901.

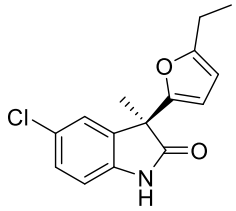


	Retention Time	Area	% Area	Height
1	10.989	2523980	49.92	146467
2	11.735	2532103	50.08	140971



	Retention Time	% Area	Height
1	10.962	4.21	90331
2	11.628	95.79	1810000

(*S*)-3-(5-ethylfuran-2-yl)-5-fluoro-3-methylindolin-2-one (C49)



C49

Colorless oil; 26.2 mg, 95% yield, 95% ee; $[\alpha]_D^{19.0}$ = 104.4 (*c* = 0.52 in CH_2Cl_2).

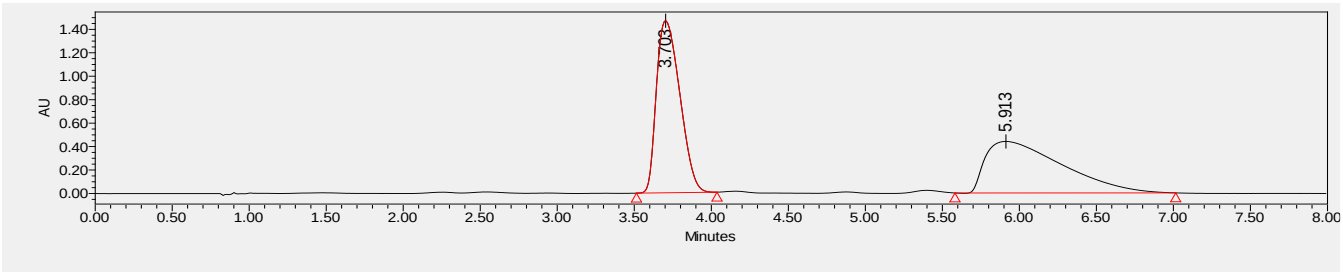
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 3.69 min, t_R (minor) = 6.27 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 9.20 (s, 1H), 7.22 – 7.16 (m, 2H), 6.94 – 6.87 (m, 1H), 6.19 – 6.10 (d, *J* = 3.2 Hz, 1H), 5.96 – 5.89 (m, 1H), 2.57 (q, *J* = 7.6 Hz, 1H), 1.74 (s, 3H), 1.16 (t, *J* = 7.6 Hz, 3H).

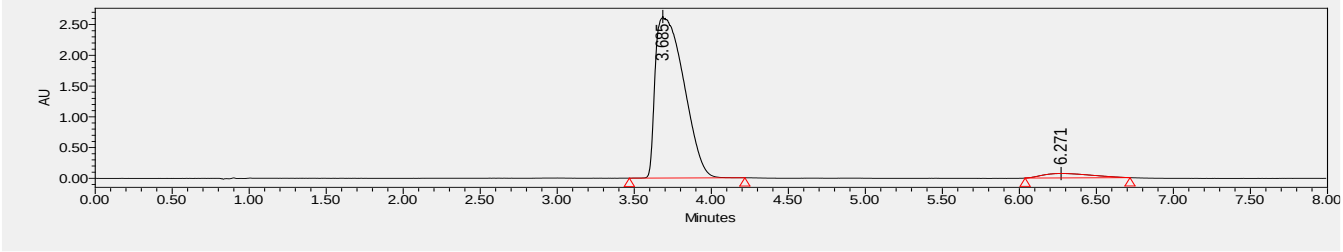
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 179.9, 158.5, 150.3, 138.9, 135.2, 128.4, 128.2, 124.6, 111.4, 107.6, 104.7, 49.9, 22.3, 21.5, 11.9.

IR: 3228, 2975, 1619, 1479, 1187, 1015, 753, 557 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{14}^{34.9689}ClNO_2Na^+$ 298.0606; found 298.0604, $C_{15}H_{14}^{36.9659}ClNO_2Na^+$ 300.0576; found 300.0570

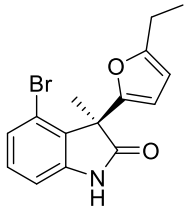


	Retention Time	Area	% Area
1	3.703	15522952	50.41
2	5.913	15269266	49.59



	Retention Time	Area	% Area
1	3.685	33750228	97.61
2	6.271	826780	2.39

(*S*)-4-bromo-3-(5-ethylfuran-2-yl)-3-methylindolin-2-one (C50)



C50

Colorless oil; 22.1 mg, 49% yield, 93% ee; $[\alpha]_D^{18.3}$ = 178.5 (*c* = 0.19 in CH_2Cl_2).

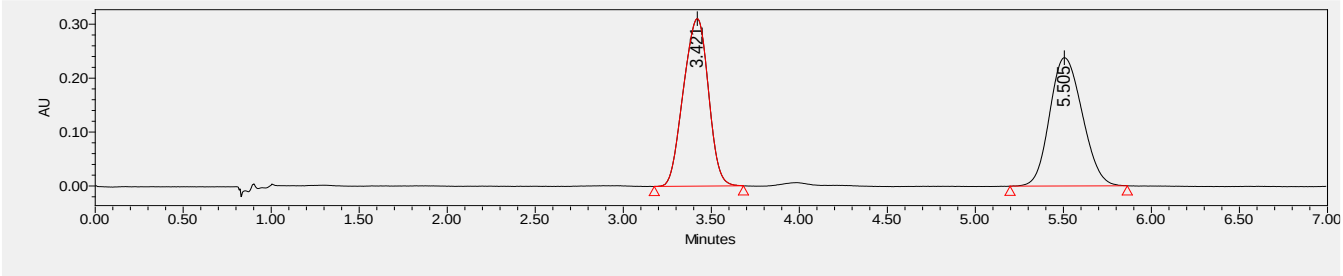
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 3.40 min, t_R (minor) = 5.55 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.74 (s, 1H), 7.18 – 7.06 (m, 2H), 6.94 – 6.87 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.28 – 6.22 (d, *J* = 3.2 Hz, 1H), 5.97 – 5.91 (m, 1H), 2.53 (q, *J* = 7.6 Hz, 2H), 1.88 (s, 3H), 1.13 (t, *J* = 7.6 Hz, 3H).

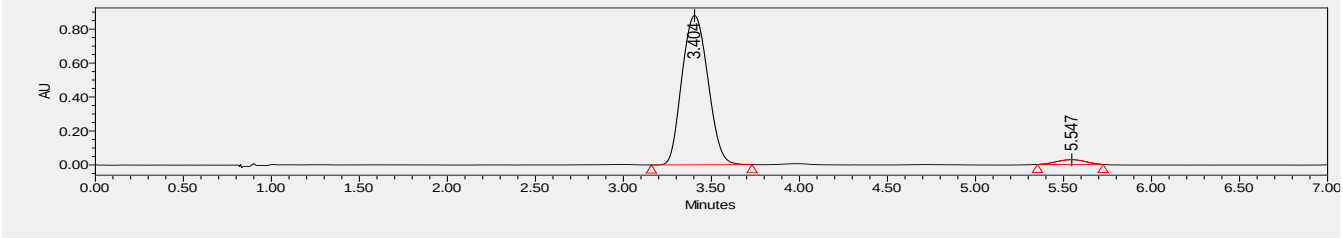
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 179.2, 158.1, 148.9, 142.3, 131.5, 129.9, 127.1, 119.7, 109.3, 109.1, 104.7, 51.3, 21.4, 18.9, 12.0.

IR: 3236, 2361, 1722, 1613, 1583, 1448, 1261, 1172, 751 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{14}^{78.9183}BrNO_2Na^+$ 342.0100; found 342.0100, $C_{15}H_{14}^{80.9163}BrNO_2Na^+$ 344.0008; found 344.0077

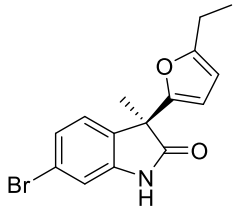


	Retention Time	Area	% Area
1	3.421	3064245	49.97
2	5.505	3068391	50.03



	Retention Time	Area	% Area
1	3.404	9033509	96.56
2	5.547	321982	3.44

(*S*)-6-bromo-3-(5-ethylfuran-2-yl)-3-methylindolin-2-one (C51)



C51

Colorless oil; 29.1 mg, 91% yield, 83% ee; $[\alpha]_D^{18.2}$ = 22.3 (*c* = 0.38 in CH_2Cl_2).

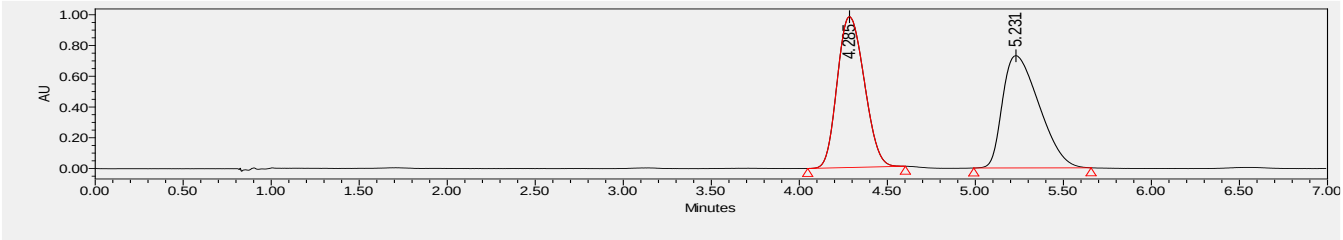
UPCC DAICEL CHIRALCEL AS-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 4.20 min, t_R (minor) = 5.27 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 9.19 (s, 1H), 7.19 – 7.12 (m, 2H), 7.10 – 7.05 (m, 1H), 6.13 – 6.09 (d, *J* = 3.1 Hz, 1H), 5.93 – 5.87 (m, 1H), 2.56 (q, *J* = 7.6 Hz, 2H), 1.73 (s, 3H), 1.16 (t, *J* = 7.6 Hz, 3H).

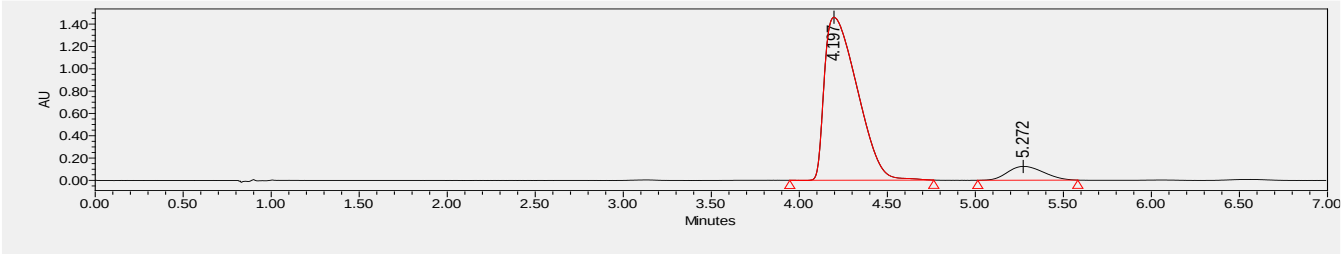
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 180.1, 158.5, 150.3, 141.7, 132.4, 125.8, 125.4, 121.8, 113.8, 107.6, 104.7, 49.4, 22.2, 21.5, 12.0.

IR: 3235, 2975, 2361, 1720, 1610, 1480, 1451, 1276, 1015, 749 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{14}{}^{78.9183}BrNO_2Na^+$ 342.0100; found 342.0100, $C_{15}H_{14}{}^{80.9163}BrNO_2Na^+$ 344.0008; found 344.0079

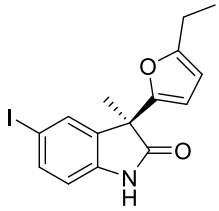


	Retention Time	Area	% Area
1	4.285	10467243	49.84
2	5.231	10533750	50.16



	Retention Time	Area	% Area
1	4.197	18849949	91.49
2	5.272	1752571	8.51

(*S*)-3-(5-ethylfuran-2-yl)-5-iodo-3-methylindolin-2-one (C52)



C52

Colorless oil; 32.5 mg, 92% yield, 91% ee; $[\alpha]_D^{19.9}$ = 56.8 (*c* = 0.24 in CH_2Cl_2).

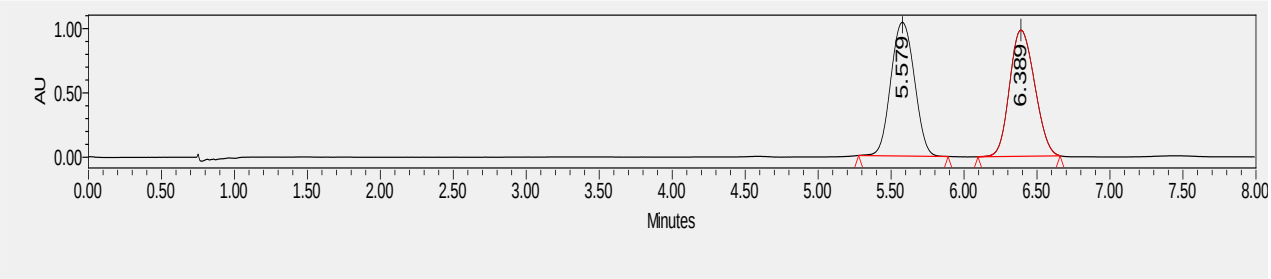
UPCC DAICEL CHIRALCEL OXH, CO_2/MeOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 6.36 min, t_R (minor) = 5.58 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.66 (s, 1H), 7.57 – 7.47 (m, 2H), 6.78 – 6.70 (d, *J* = 8.1 Hz, 1H), 6.15 – 6.10 (d, *J* = 3.2 Hz, 1H), 5.93 – 5.87 (m, 1H), 2.57 (q, *J* = 7.6 Hz, 2H), 1.73 (s, 3H), 1.17 (t, *J* = 7.6 Hz, 3H).

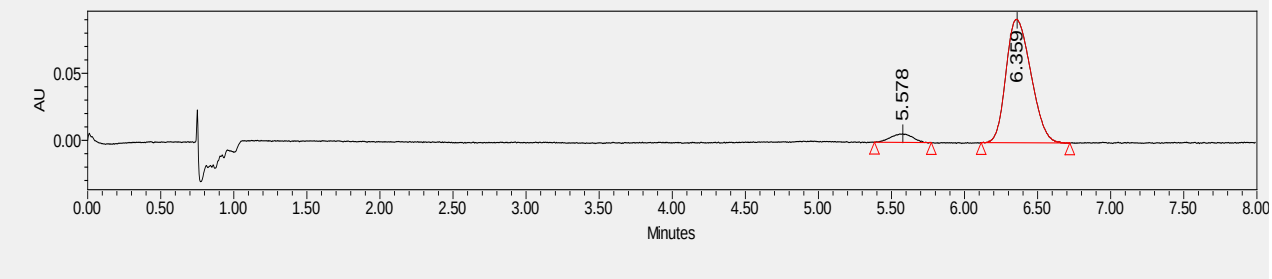
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 179.1, 158.6, 150.3, 139.9, 137.3, 135.9, 133.0, 107.7, 104.7, 85.4, 49.6, 22.3, 21.5, 11.9.

IR: 3357, 2361, 1724, 1611, 1353, 1271, 948, 751 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{14}INO_2Na^+$ 389.9961; found 389.9962.

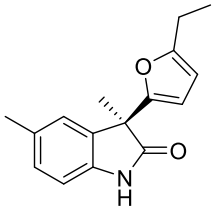


	Retention Time	Area	% Area
1	5.579	11683020	49.99
2	6.389	11687199	50.01



	Retention Time	Area	% Area
1	5.578	55613	4.59
2	6.359	1155068	95.41

(*S*)-3-(5-ethylfuran-2-yl)-3,5-dimethylindolin-2-one (C53)



C53

Colorless oil; 21.4 mg, 84% yield, 95% ee; $[\alpha]_D^{21.7}$ = 73.3 (*c* = 0.29 in CH_2Cl_2).

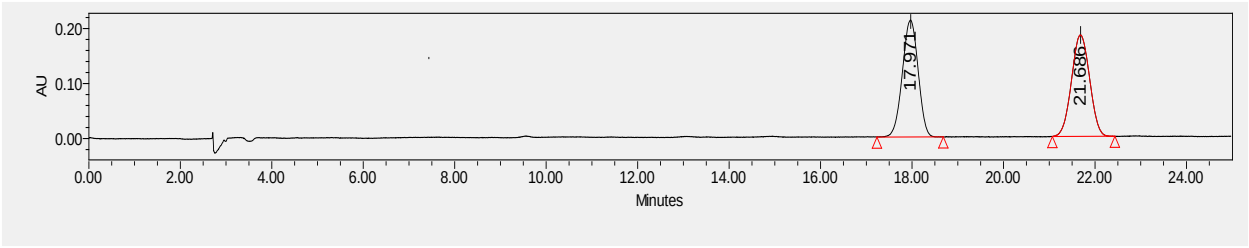
UPCC DAICEL CHIRALCEL OXH, CO_2/MeOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 21.44 min, t_R (minor) = 17.96 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.69 (s, 1H), 7.05 – 6.97 (m, 2H), 6.87 – 6.78 (m, 1H), 6.10 – 6.03 (d, *J* = 3.2 Hz, 1H), 5.94 – 5.88 (m, 1H), 2.58 (q, *J* = 7.6 Hz, 2H), 2.31 (s, 3H), 1.74 (s, 3H), 1.16 (t, *J* = 7.6 Hz, 3H).

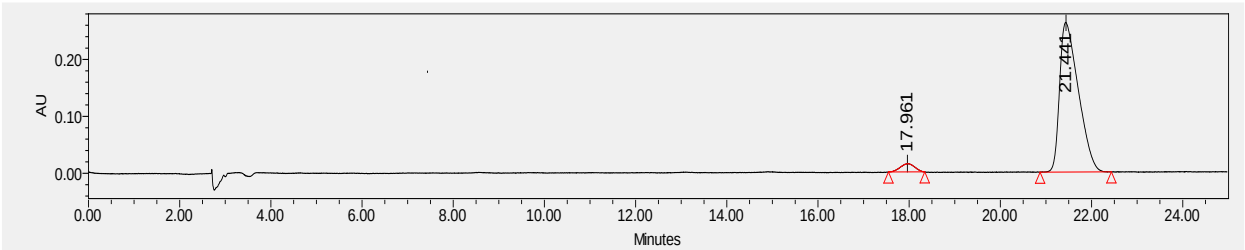
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 180.0, 158.2, 151.3, 137.8, 133.6, 132.3, 128.7, 124.8, 109.9, 107.2, 104.6, 49.7, 22.4, 21.5, 21.3, 12.0.

IR: 3216, 2973, 1624, 1492, 1309, 1207, 956, 812, 812, 690 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{17}NO_2Na^+$ 278.1151; found 278.1152.

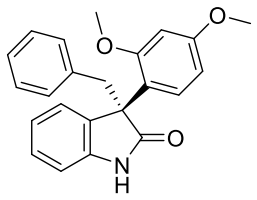


	Retention Time	Area	% Area
1	17.971	5098922	50.14
2	21.686	5069806	49.86



	Retention Time	Area	% Area
1	17.961	1172705	2.59
2	21.441	44192170	97.41

(*S*)-3-benzyl-3-(2,4-dimethoxyphenyl)indolin-2-one (C54)



C54

Yellow solid; 32.7 mg, 91% yield, 93% ee; melting point: 147–151 °C; $[\alpha]_D^{11.8}$ = -33.7 (*c* = 0.12 in CH_2Cl_2).

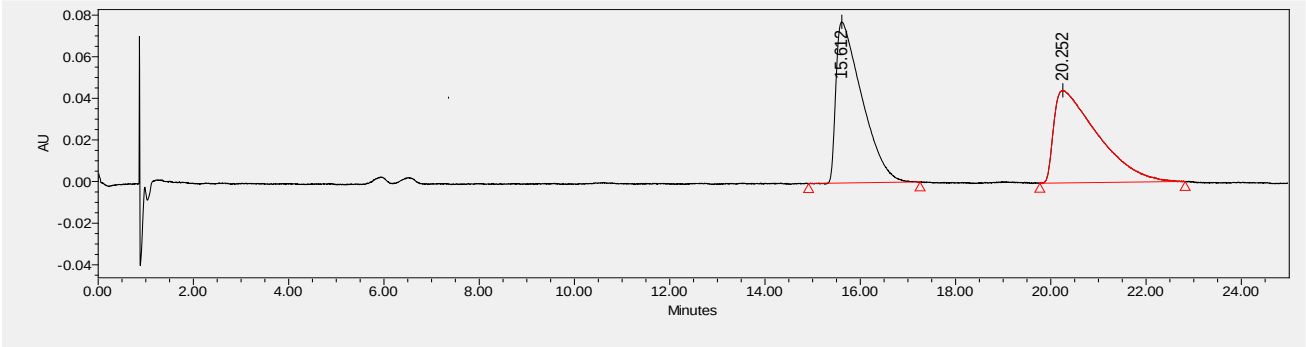
UPCC DAICEL CHIRALCEL OD-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 15.15 min, t_R (minor) = 20.78 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.69 (s, 1H), 7.62 – 7.54 (d, *J* = 8.7 Hz, 1H), 7.18 – 6.88 (m, 6H), 6.84 – 6.72 (m, 2H), 6.66 – 6.56 (m, 1H), 6.53 – 6.44 (m, 1H), 6.43 – 6.31 (d, *J* = 2.5 Hz, 1H), 3.80 (s, 3H), 3.52 (s, 2H), 3.41 (s, 3H).

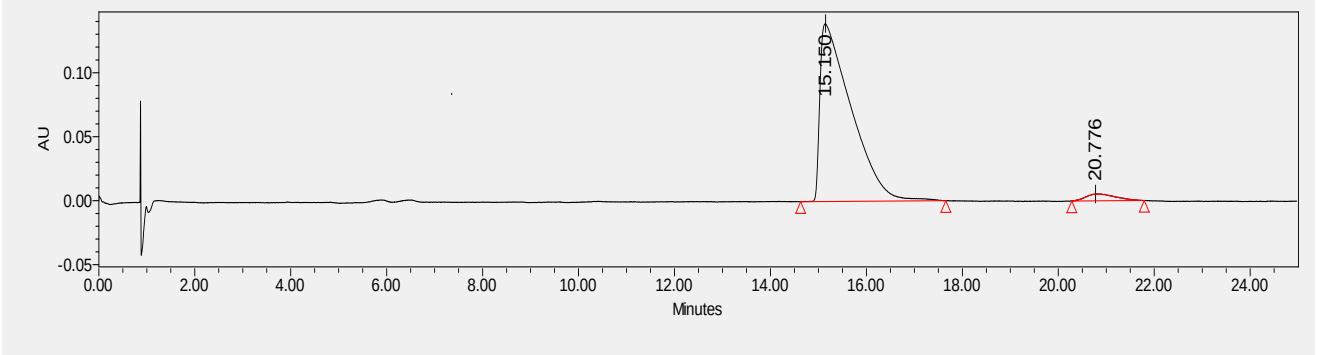
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 181.2, 160.5, 158.3, 141.6, 135.0, 133.8, 130.4, 128.0, 127.5, 126.6, 123.2, 122.4, 121.9, 108.7, 104.8, 100.3, 55.7, 55.5, 55.4, 42.6.

IR: 2926, 1710, 1612, 1503, 1469, 1210, 1139, 1032, 780, 700 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{23}H_{21}NO_3Na^+$ 382.1414; found 382.1416.

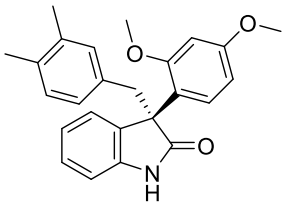


	Retention Time	Area	% Area
1	15.612	2927184	50.84
2	20.252	2830218	49.16



	Retention Time	Area	% Area
1	15.150	6272785	96.48
2	20.776	228838	3.52

(*S*)-3-(2,4-dimethoxyphenyl)-3-(3,4-dimethylbenzyl)indolin-2-one (C55)



C55

White solid; 36.0 mg, 93% yield, 93% ee; melting point: 162–165 °C; $[\alpha]_D^{12.6}$ = -103.7 (*c* = 0.62 in CH_2Cl_2).

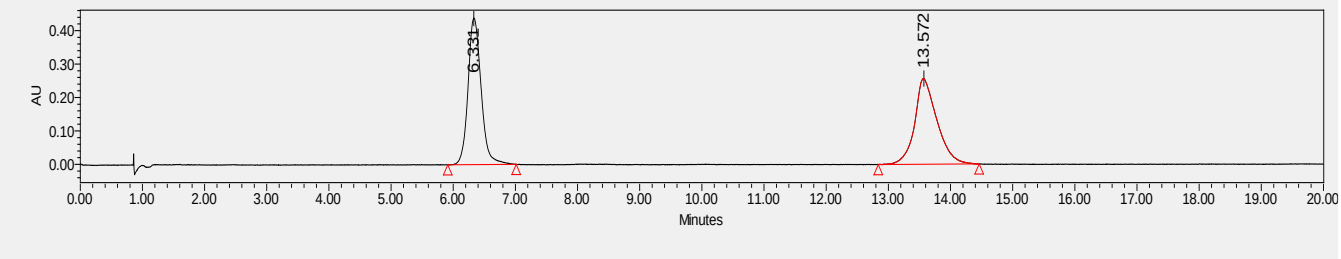
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 13.89 min, t_R (minor) = 6.46 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.63 – 7.55 (d, *J* = 8.6 Hz, 1H), 7.35 (s, 1H), 7.10 – 6.89 (m, 3H), 6.80 – 6.69 (m, 1H), 6.63 – 6.55 (m, 1H), 6.53 – 6.46 (m, 3H), 6.41 – 6.34 (d, *J* = 2.5 Hz, 1H), 3.80 (s, 3H), 3.45 (s, 2H), 3.42 (s, 3H), 2.11 (s, 3H), 2.01 (s, 3H).

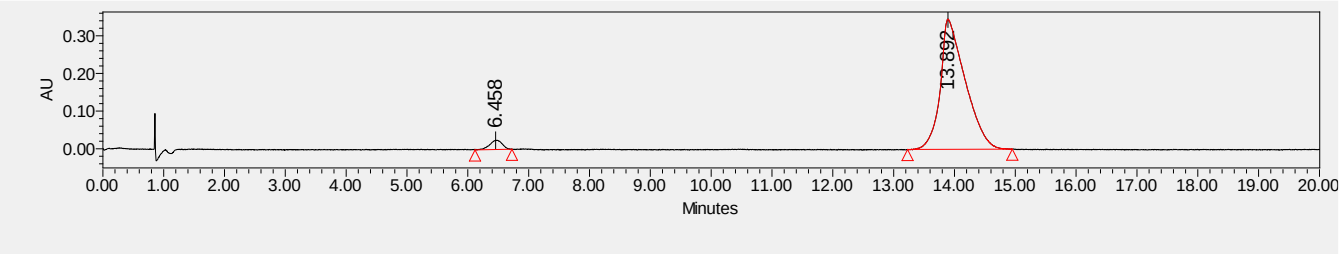
^{13}C NMR (101 MHz, $CDCl_3$) δ 180.9, 160.5, 158.2, 141.6, 135.4, 134.6, 134.2, 132.2, 131.6, 128.7, 128.1, 127.7, 127.3, 123.2, 122.5, 121.8, 108.6, 104.7, 100.3, 55.7, 55.5, 55.2, 42.2, 19.6, 19.5.

IR: 2925, 1612, 1585, 1489, 1209, 1162, 1083, 824, 751, 643 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{25}H_{25}NO_3Na^+$ 410.1727; found 410.1729.

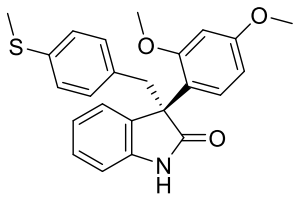


	Retention Time	Area	% Area
1	6.331	6408670	50.20
2	13.572	6358721	49.80



	Retention Time	Area	% Area	Height
1	6.458	356538	3.49	24956
2	13.892	9845416	96.51	345723

(*S*)-3-(2,4-dimethoxyphenyl)-3-(4-(methylthio)benzyl)indolin-2-one (C56)



C56

White solid; 38.1 mg, 94% yield, 92% ee; melting point: 137–139 °C; $[\alpha]_D^{12.5}$ = -142.2 (*c* = 0.64 in CH_2Cl_2).

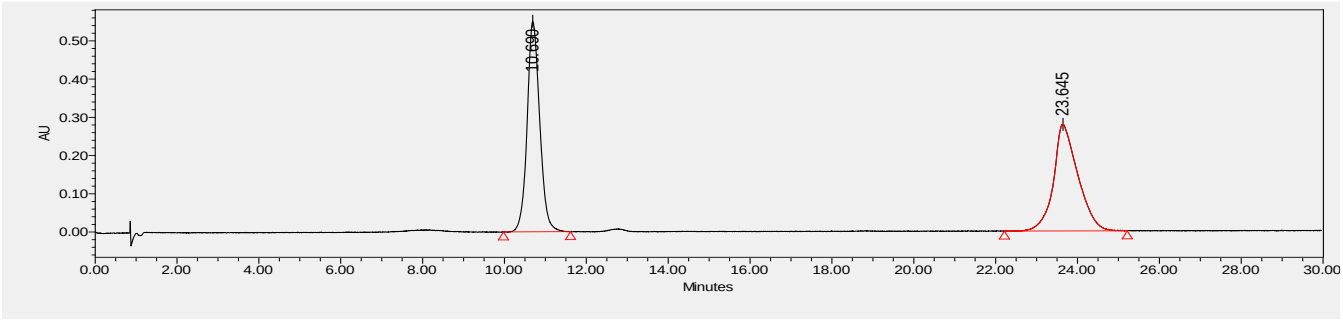
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 23.20 min, t_R (minor) = 10.76 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.65 (s, 1H), 7.60 – 7.48 (d, *J* = 8.6 Hz, 1H), 7.10 – 7.00 (m, 1H), 7.00 – 6.84 (m, 4H), 6.71 – 6.64 (m, 2H), 6.62 – 6.56 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.52 – 6.45 (d, *J* = 7.7 Hz, 1H), 6.41 – 6.36 (d, *J* = 2.6 Hz, 1H), 3.80 (s, 3H), 3.46 (s, 2H), 3.41 (s, 3H), 2.37 (s, 3H).

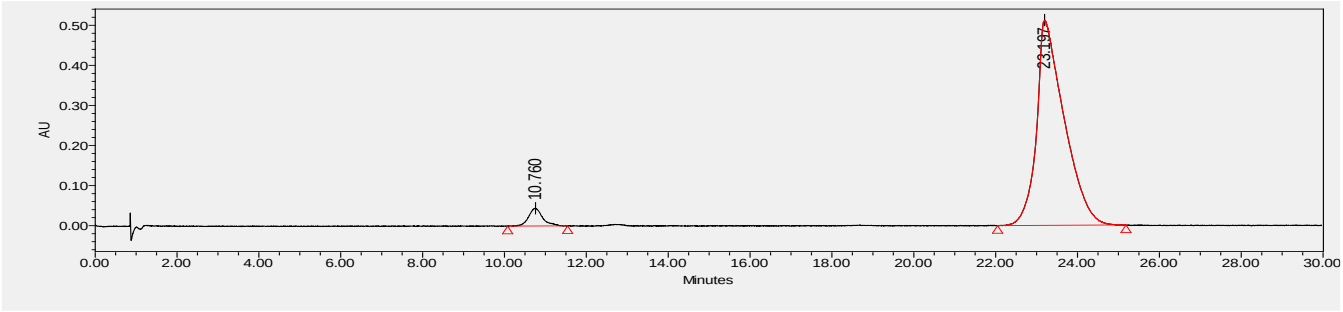
^{13}C NMR (101 MHz, $CDCl_3$) δ 181.0, 160.5, 158.2, 141.6, 136.3, 133.7, 131.8, 130.8, 128.0, 127.5, 125.6, 123.1, 122.3, 121.9, 108.9, 104.7, 100.2, 55.6, 55.5, 55.3, 42.0, 15.8.

IR: 3192, 2923, 1611, 1585, 1209, 1164, 1035, 830, 752, 642 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{24}H_{23}NO_3SNa^+$ 404.1326; found 404.1329.

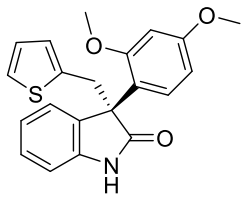


	Retention Time	Area	% Area
1	10.690	11752935	50.49
2	23.645	11523134	49.51



	Retention Time	Area	% Area
1	10.760	1046293	4.18
2	23.197	23971876	95.82

(*S*)-3-(2,4-dimethoxyphenyl)-3-(thiophen-2-ylmethyl)indolin-2-one (C57)



C57

Yellow solid; 34.7 mg, 95% yield, 96% ee; melting point: 190–193 °C; $[\alpha]_D^{14.0}$ = -58.6 (*c* = 0.42 in CH_2Cl_2).

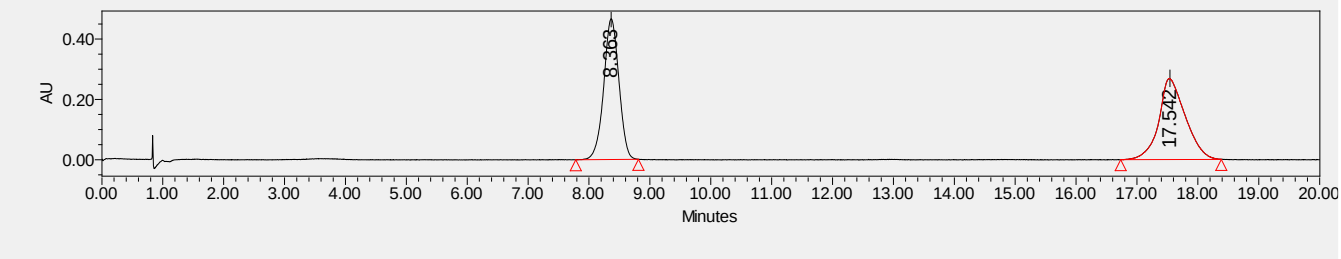
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 17.14 min, t_R (minor) = 8.48 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.88 (s, 1H), 7.58 – 7.44 (d, *J* = 8.6 Hz, 1H), 7.17 – 7.08 (m, 1H), 7.01 – 6.88 (m, 3H), 6.80 – 6.71 (m, 1H), 6.68 – 6.61 (m, 1H), 6.61 – 6.55 (m, 2H), 6.43 – 6.36 (d, *J* = 2.5 Hz, 1H), 3.90 – 3.70 (m, 5H), 3.46 (s, 3H).

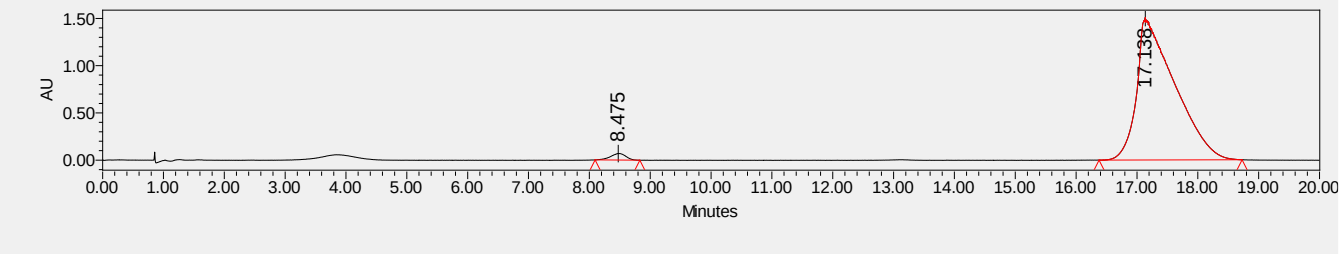
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 180.9, 160.5, 158.2, 142.0, 136.4, 133.6, 127.7, 127.6, 126.1, 124.6, 123.2, 122.1, 121.7, 108.8, 104.6, 100.2, 55.5, 55.4, 55.1, 36.8.

IR: 3203, 1612, 1585, 1470, 1306, 1210, 1034, 830, 752, 701 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{19}NO_3SNa^+$ 404.1326; found 404.1329.

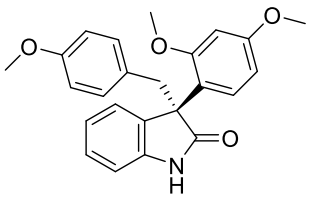


	Retention Time	Area	% Area
1	8.363	8108730	50.04
2	17.542	8096510	49.96



	Retention Time	Area	% Area
1	8.475	1191058	1.80
2	17.138	65112504	98.20

(*S*)-3-(2,4-dimethoxyphenyl)-3-(thiophen-2-ylmethyl)indolin-2-one (C58)



C58

White solid; 38.6 mg, 99% yield, 95% ee; melting point: 130–131 °C; $[\alpha]_D^{16.0}$ = -115.3 (*c* = 0.62 in CH_2Cl_2).

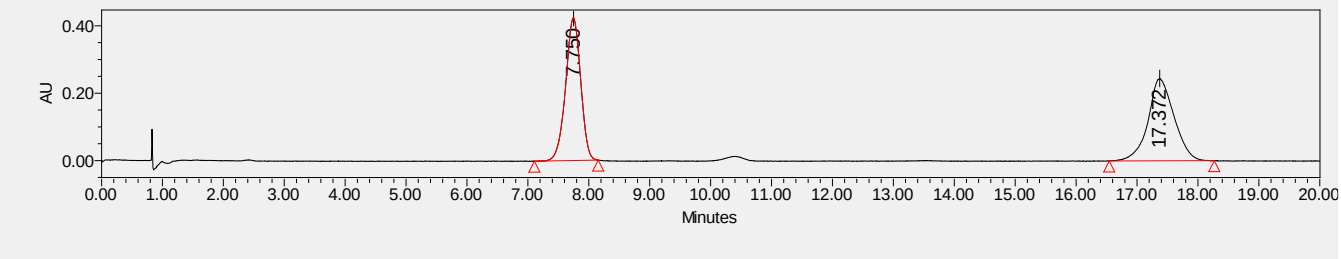
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 16.90 min, t_R (minor) = 7.88 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.63 – 7.55 (d, *J* = 8.7 Hz, 1H), 7.43 (s, 1H), 7.10 – 7.01 (m, 1H), 6.99 – 6.88 (m, 2H), 6.72 – 6.65 (m, 2H), 6.62 – 6.48 (m, 4H), 6.42 – 6.36 (d, *J* = 2.5 Hz, 1H), 3.80 (s, 3H), 3.69 (s, 3H), 3.47 (s, 2H), 3.42 (s, 3H).

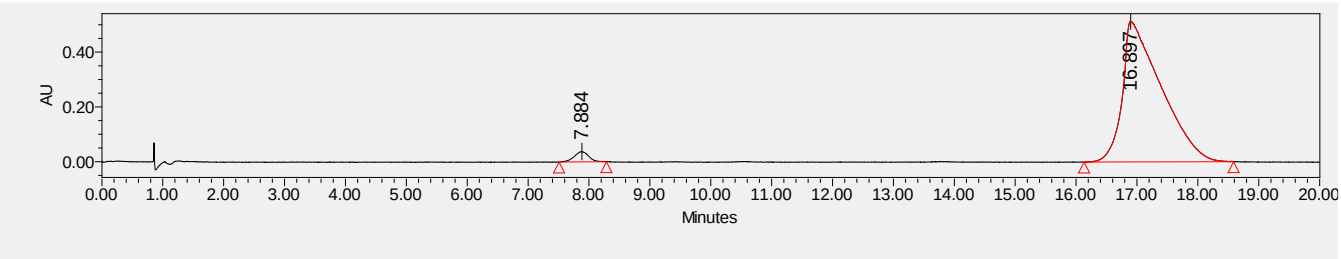
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 181.0, 160.4, 158.2, 158.1, 141.4, 133.9, 131.2, 127.9, 127.3, 126.8, 123.1, 122.3, 121.8, 112.8, 108.6, 104.6, 100.1, 55.6, 55.4, 55.2, 55.0, 41.6.

IR: 3198, 2934, 1611, 1585, 1510, 1248, 1021, 964, 832, 752 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{24}H_{26}NO_4Na^+$ 412.1519; found 412.1522.

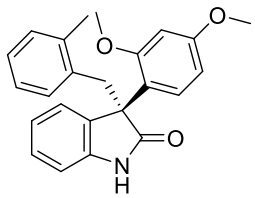


	Retention Time	Area	% Area
1	7.750	7264961	50.14
2	17.372	7224020	49.86



	Retention Time	Area	% Area
1	7.884	613614	2.63
2	16.897	22712296	97.37

(*S*)-3-(2,4-dimethoxyphenyl)-3-(2-methylbenzyl)indolin-2-one (C59)



C59

White solid; 36.6 mg, 98% yield, 98% ee; melting point: 167–170 °C; $[\alpha]_D^{16.0}$ = -68.1 (*c* = 0.33 in CH_2Cl_2).

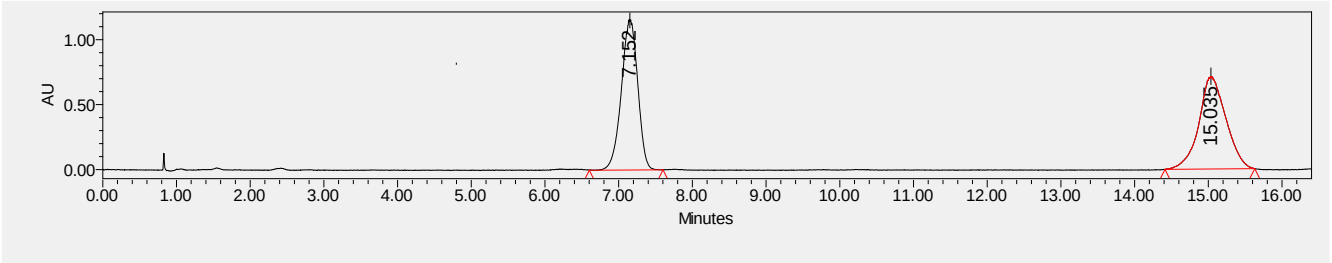
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 14.77 min, t_R (minor) = 7.31 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.76 (s, 1H), 7.69 – 7.60 (d, *J* = 8.6 Hz, 1H), 7.12 – 7.01 (m, 1H), 7.03 – 6.86 (m, 4H), 6.83 – 6.74 (m, 1H), 6.65 – 6.51 (m, 3H), 6.42 – 6.37 (d, *J* = 2.5 Hz, 1H), 3.81 (s, 3H), 3.63 (m, 2H), 3.42 (s, 3H), 2.15 (s, 3H).

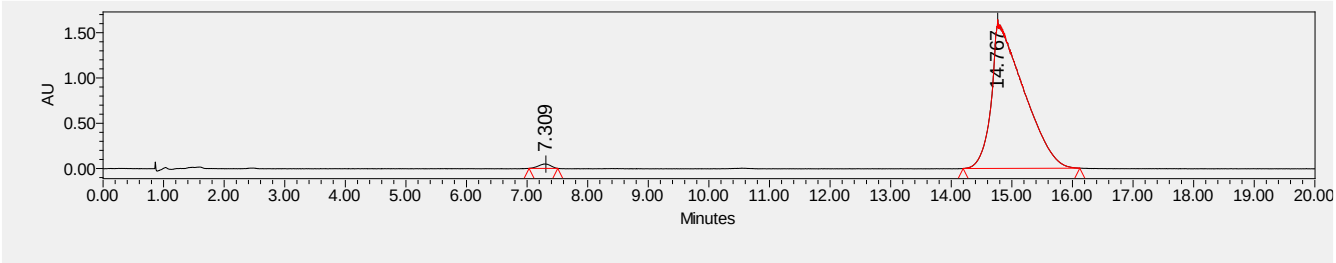
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 181.7, 160.4, 158.1, 141.7, 137.6, 133.9, 133.3, 130.6, 130.1, 127.9, 127.5, 126.6, 124.7, 123.6, 122.7, 121.7, 108.7, 104.7, 100.3, 55.8, 55.4, 55.0, 38.1, 20.0.

IR: 2924, 1613, 1585, 1505, 1469, 1267, 1210, 1139, 1035, 750 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M - H]^-$ calcd for $C_{24}H_{23}NO_3Na^+$ 372.1605; found 372.1608.

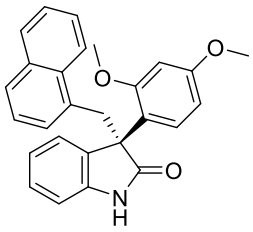


	Retention Time	Area	% Area
1	7.152	17887939	49.78
2	15.035	18046042	50.22



	Retention Time	Area	% Area
1	7.309	688200	1.14
2	14.767	59558811	98.86

(*S*)-3-(2,4-dimethoxyphenyl)-3-(naphthalen-1-ylmethyl)indolin-2-one (C60)



C60

White solid; 34.0 mg, 83% yield, 97% ee; melting point: 197–203 °C; $[\alpha]_D^{16.6}$ = -70.5 (*c* = 0.18 in CH_2Cl_2).

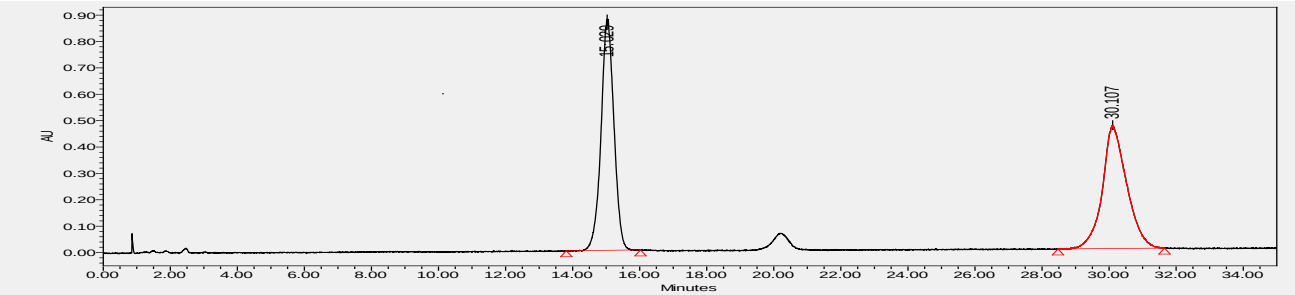
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 30.13 min, t_R (minor) = 15.13 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.11 – 8.02 (m, 1H), 7.78 – 7.66 (m, 2H), 7.65 – 7.55 (d, *J* = 8.2 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.13 – 7.04 (m, 2H), 6.99 – 6.93 (m, 2H), 6.91 – 6.81 (m, 2H), 6.68 – 6.59 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.46 – 6.41 (d, *J* = 2.6 Hz, 1H), 6.37 – 6.30 (m, 1H), 4.16 (d, *J* = 12.8 Hz, 1H), 3.96 (d, *J* = 12.8 Hz, 1H), 3.83 (s, 3H), 3.42 (s, 3H).

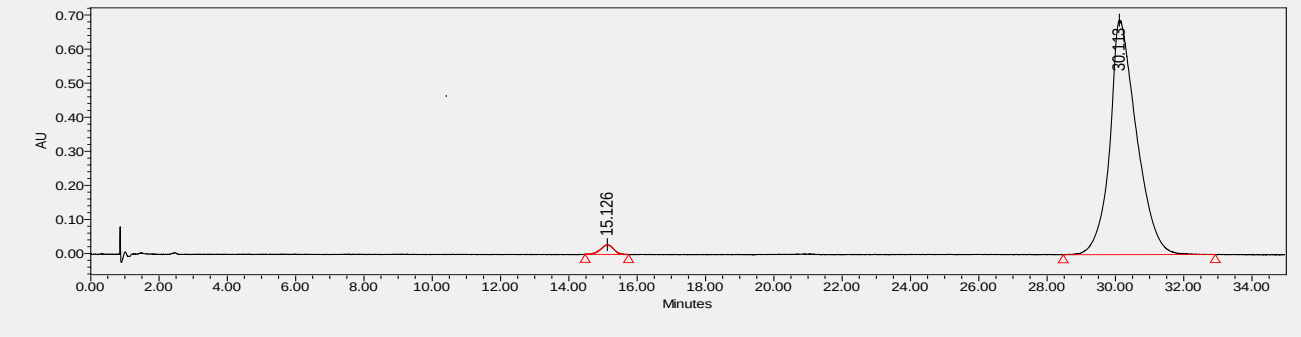
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 181.1, 160.6, 158.3, 141.5, 134.0, 133.5, 132.6, 131.3, 128.5, 128.2, 128.1, 127.5, 125.2, 125.2, 124.8, 124.6, 123.8, 122.7, 121.9, 108.5, 104.8, 100.5, 55.8, 55.6, 55.3, 37.6.

IR: 2927, 1612, 1505, 1470, 1417, 1209, 1139, 1035, 780, 752 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M - H]^-$ calcd for $C_{27}H_{23}NO_3Na^+$ 432.1570; found 432.1573.

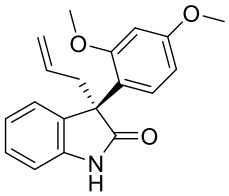


	Retention Time	Area	% Area
1	15.029	23454651	50.03
2	30.107	23428595	49.97



	Retention Time	Area	% Area
1	15.130	643419	1.87
2	30.131	33812932	98.13

(*S*)-3-allyl-3-(2,4-dimethoxyphenyl)indolin-2-one (C61)



C61

Yellow solid; 20.1 mg, 65% yield, 94% ee; melting point: 151–153 °C; $[\alpha]_D^{16.0}$ = -62.3 (*c* = 0.28 in CH_2Cl_2).

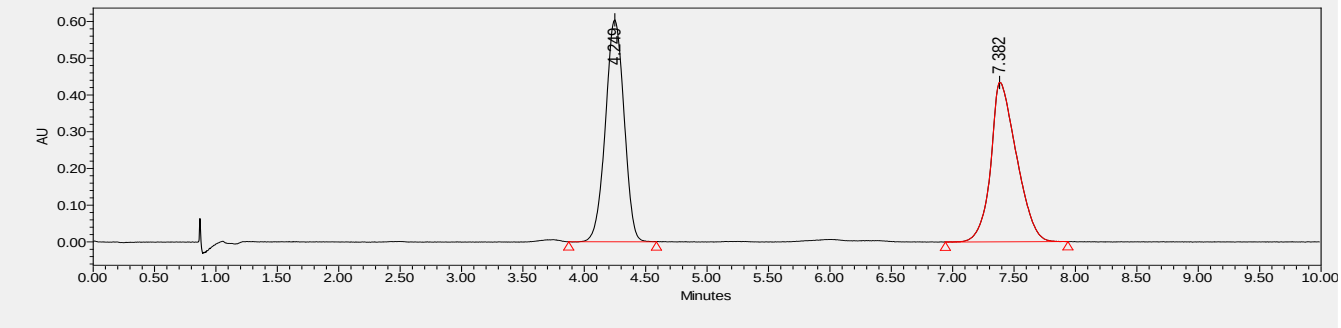
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 7.03 min, t_R (minor) = 4.09 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.54 (s, 1H), 7.54 – 7.44 (d, *J* = 8.6 Hz, 1H), 7.17 – 7.08 (m, 1H), 6.93 – 6.81 (m, 3H), 6.59 – 6.52 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.40 – 6.34 (d, *J* = 2.5 Hz, 1H), 5.54 – 5.40 (m, 1H), 5.08 – 4.99 (m, 1H), 4.95 – 4.89 (m, 1H), 3.79 (s, 3H), 3.44 (s, 3H), 2.98 (d, *J* = 7.2 Hz, 2H).

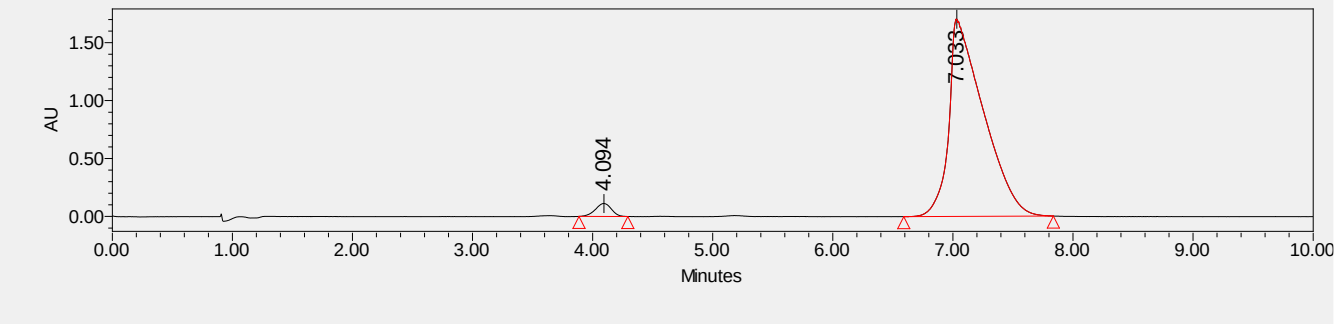
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 181.9, 160.5, 158.4, 141.5, 134.4, 131.9, 128.2, 127.4, 122.9, 122.1, 121.9, 119.3, 1089.0, 104.7, 100.2, 55.7, 55.5, 54.0, 41.0.

IR: 3209, 1614, 1505, 1470, 1268, 1209, 1141, 1034, 925, 752 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M - H]^-$ calcd for $C_{19}H_{19}NO_3Na^+$ 332.1257; found 332.1259.

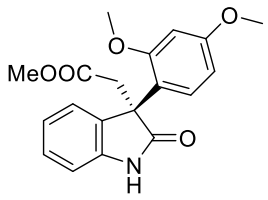


	Retention Time	Area	% Area
1	4.249	6379634	50.20
2	7.382	6329206	49.80



	Retention Time	Area	% Area
1	4.094	1034344	2.94
2	7.033	34153371	97.06

methyl (*S*)-2-(3-(2,4-dimethoxyphenyl)-2-oxoindolin-3-yl)acetate (C62)



C62

White solid; 22.5 mg, 66% yield, 97% ee; melting point: 186–188 °C; $[\alpha]_D^{16.8}$ = -89.0 (*c* = 0.25 in CH_2Cl_2).

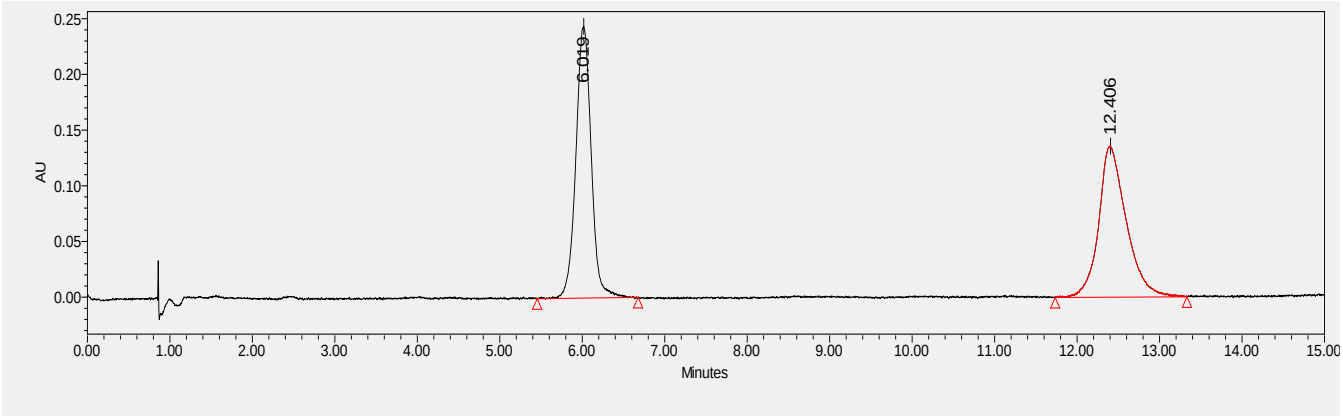
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 12.09 min, t_R (minor) = 6.04 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.38 (s, 1H), 7.32 – 7.28 (d, *J* = 8.7 Hz, 1H), 7.18 – 7.09 (m, 2H), 6.95 – 6.83 (m, 2H), 6.51 – 6.46 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.42 – 6.38 (d, *J* = 2.5 Hz, 1H), 3.77 (s, 3H), 3.59 – 3.55 (m, 4H), 3.48 (s, 3H), 3.28 (d, *J* = 15.1 Hz, 1H).

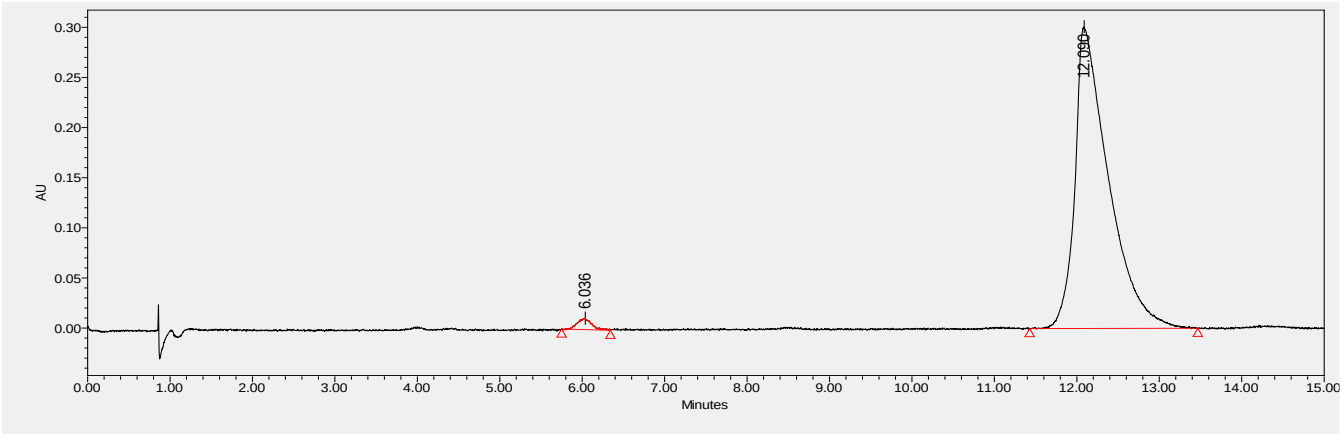
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 181.0, 170.3, 160.5, 158.5, 141.5, 133.1, 128.2, 127.9, 123.8, 122.1, 120.6, 109.2, 104.4, 100.2, 55.4, 52.4, 51.7, 40.2.

IR: 2928, 1716, 1613, 1506, 1470, 1263, 1210, 1031, 921, 753 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M - H]^-$ calcd for $C_{19}H_{19}NO_5Na^+$ 364.1155; found 364.1158.

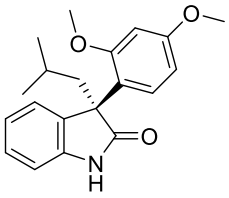


	Retention Time	Area	% Area
1	6.019	3154376	50.07
2	12.406	3145448	49.93



	Retention Time	Area	% Area
1	6.036	135037	1.56
2	12.090	8519999	98.44

(*S*)-3-(2,4-dimethoxyphenyl)-3-isobutylindolin-2-one (C63)



C63

White solid; 30.6 mg, 94% yield, 94% ee; melting point: 157–159 °C; $[\alpha]_D^{16.2}$ = -47.2 (*c* = 0.44 in CH_2Cl_2).

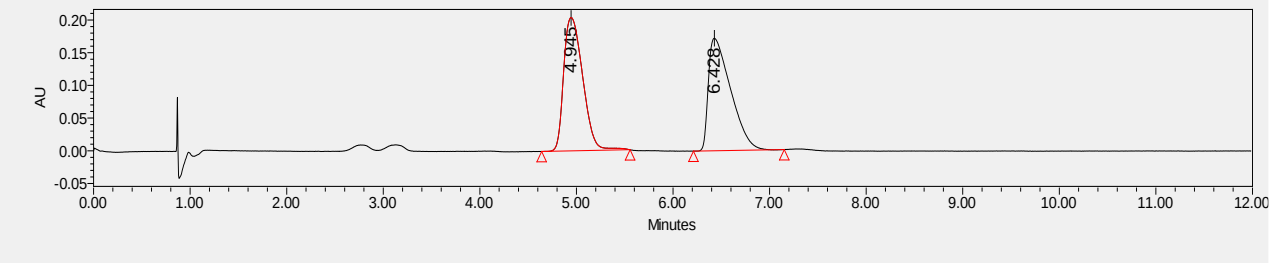
UPCC DAICEL CHIRALCEL ID-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 4.87 min, t_R (minor) = 6.58 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 9.09 (s, 1H), 7.54 – 7.47 (d, *J* = 8.6 Hz, 1H), 7.15 – 7.07 (m, 1H), 6.90 – 6.80 (m, 3H), 6.59 – 6.51 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.40 – 6.34 (d, *J* = 2.6 Hz, 1H), 3.78 (s, 3H), 3.42 (s, 3H), 2.32 – 2.14 (m, 2H), 1.53 – 1.41 (m, 1H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.53 (d, *J* = 6.7 Hz, 3H).

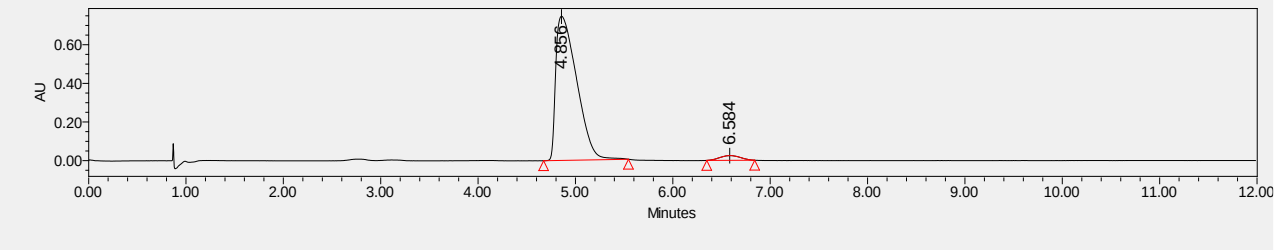
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 183.3, 160.3, 158.2, 142.1, 135.1, 128.1, 127.3, 123.3, 123.1, 122.1, 109.0, 104.6, 100.2, 55.7, 55.5, 53.6, 45.4, 25.1, 24.7, 24.0.

IR: 3207, 2955, 1612, 1585, 1469, 1264, 1209, 1036, 752, 646 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M - H]^-$ calcd for $C_{20}H_{23}NO_3Na^+$ 348.1570; found 348.1572.



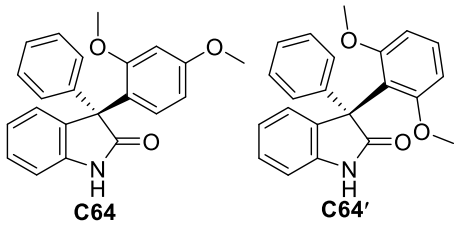
	Retention Time	Area	% Area
1	4.945	2793588	50.42
2	6.428	2747004	49.58



	Retention Time	Area	% Area
1	4.856	11127062	96.89
2	6.584	357077	3.11

(*S*)-3-(2,4-dimethoxyphenyl)-3-phenylindolin-2-one (C64)

(*S*)-3-(2,6-dimethoxyphenyl)-3-phenylindolin-2-one (C64')



C64 : C64′ = 9 : 1

White soild; 30.4 mg, 88% yield, 84% ee_1, 99% ee_2; melting point: 101–105 °C; $[\alpha]_D^{15.3}$ = -221.0 (*c* = 0.22 in CH_2Cl_2).

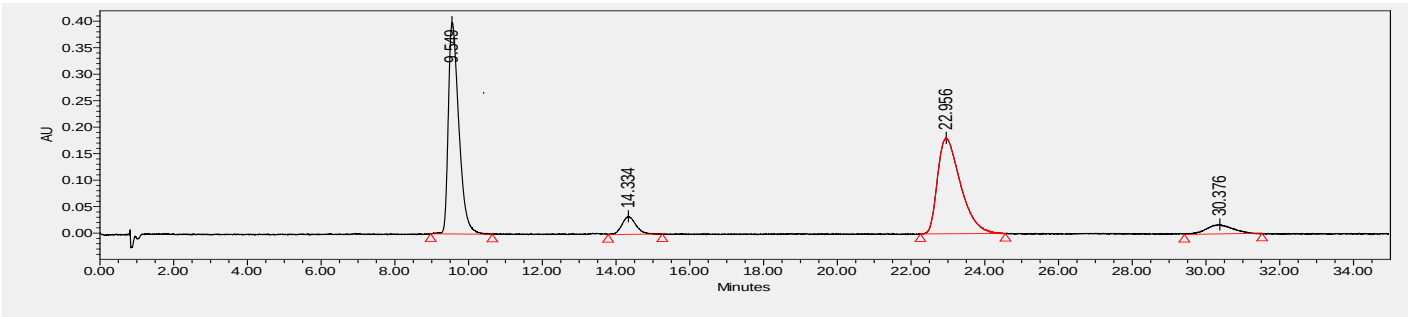
UPCC DAICEL CHIRALCEL OD-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major-major) = 9.61 min, t_R (major-minor) = 23.26 min, t_R (minor-major) = 14.36 min, t_R (minor-minor) = 30.48 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.96 – 8.44 (m, 1H), 7.52 – 7.39 (m, 2H), 7.34 – 7.25 (m, 3H), 7.23 – 7.17 (m, 1H), 7.05 – 6.96 (m, 2H), 6.92 – 6.87 (m, 1H), 6.84 – 6.76 (m, H), 6.45 – 6.34 (m, 2H), 3.76 (m, 3H), 3.51 (m, 3H).

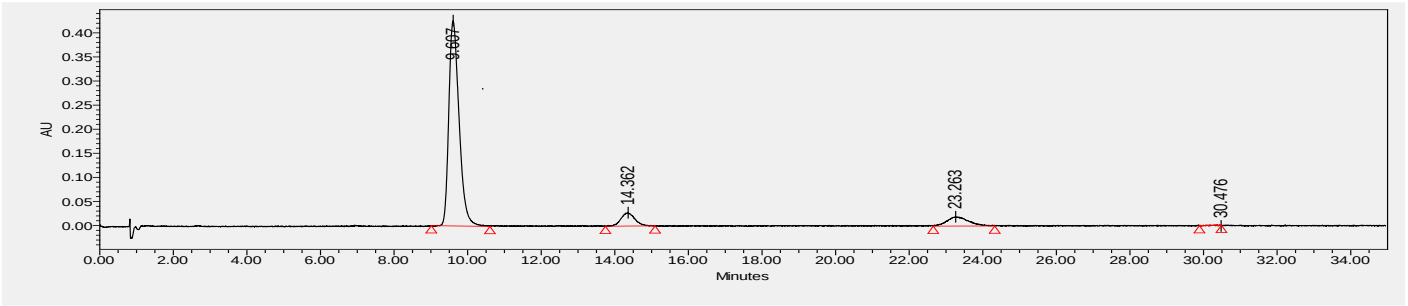
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 181.6, 160.3, 158.3, 141.3, 138.9, 133.1, 131.0, 129.1, 128.12, 127.9, 127.6, 125.8, 124.3, 121.9, 109.6, 104.6, 100.0, 59.7, 55.7, 55.4.

IR: 3211, 1712, 1613, 1503, 1470, 1261, 1209, 1128, 1033, 700 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{22}H_{19}NO_3Na^+$ 368.1257; found 368.1263.

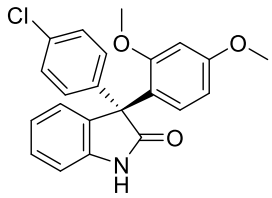


	Retention Time	Area	% Area
1	9.549	7894156	45.24
2	14.334	880264	5.04
3	22.956	7803460	44.72
4	30.376	870927	4.99



	Retention Time	Area	% Area
1	9.607	8256329	84.46
2	14.362	720973	7.38
3	23.263	783595	8.02
4	30.476	14070	0.14

(*S*)-3-(4-chlorophenyl)-3-(2,4-dimethoxyphenyl)indolin-2-one (C65)



C65

White soild; 36.8 mg, 97% yield, 93% ee; melting point: 180–183 °C; $[\alpha]_D^{14.8}$ = 200.0 (*c* = 0.14 in CH_2Cl_2).

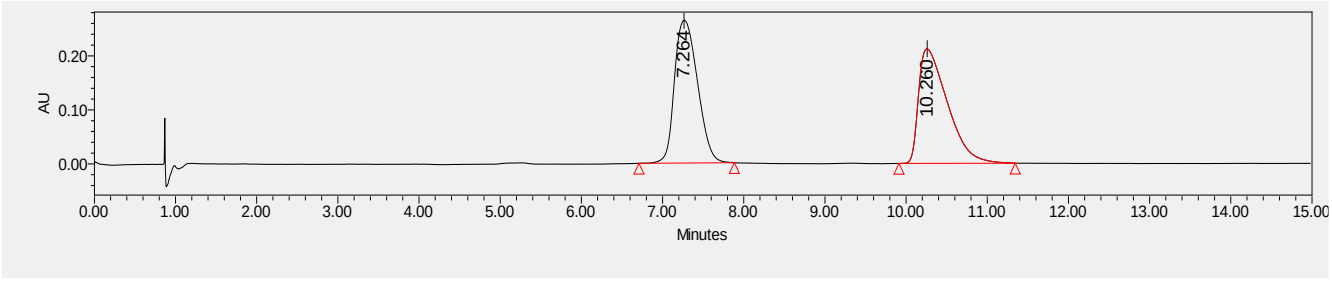
UPCC DAICEL CHIRALCEL ID-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 7.07 min, t_R (minor) = 10.46 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.63 (s, 1H), 7.43 – 7.33 (m, 2H), 7.26 – 7.16 (m, 3H), 7.07 – 6.97 (m, 2H), 6.94 – 6.88 (m, 1H), 6.82 – 6.76 (m, 1H), 6.43 – 6.38 (m, 2H), 3.77 (s, 3H), 3.53 (s, 3H).

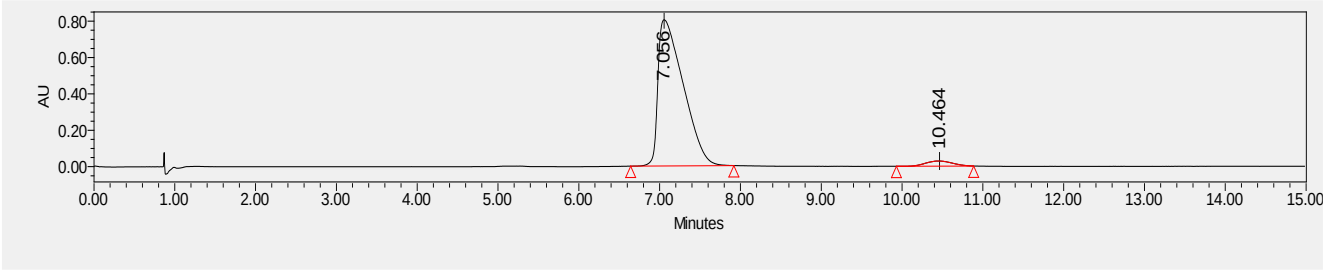
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 181.0, 160.6, 158.3, 141.3, 141.2, 134.2, 132.5, 130.8, 129.4, 129.2, 128.3, 127.9, 127.5, 125.9, 123.8, 122.4, 109.9, 104.7, 100.2, 59.6, 55.8, 55.5.

IR: 2929, 1712, 1613, 1504, 1471, 1263, 1209, 1131, 1035, 696 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{22}H_{18}^{34.9689}ClNO_3Na^+$ 402.0867; found 402.0871, $C_{22}H_{18}^{36.9659}ClNO_3Na^+$ 404.0838; found 404.0839.

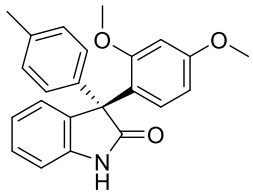


	Retention Time	Area	% Area
1	7.264	5214900	49.98
2	10.260	5219449	50.02



	Retention Time	Area	% Area
1	7.056	17425775	96.43
2	10.464	645252	3.57

(*S*)-3-(2,4-dimethoxyphenyl)-3-(p-tolyl)indolin-2-one (C66)



C66

White soild; 28.0 mg, 78% yield, 81% ee; melting point: 225–231 °C; $[\alpha]_D^{14.6}$ = -113.9 (*c* = 0.11 in CH_2Cl_2).

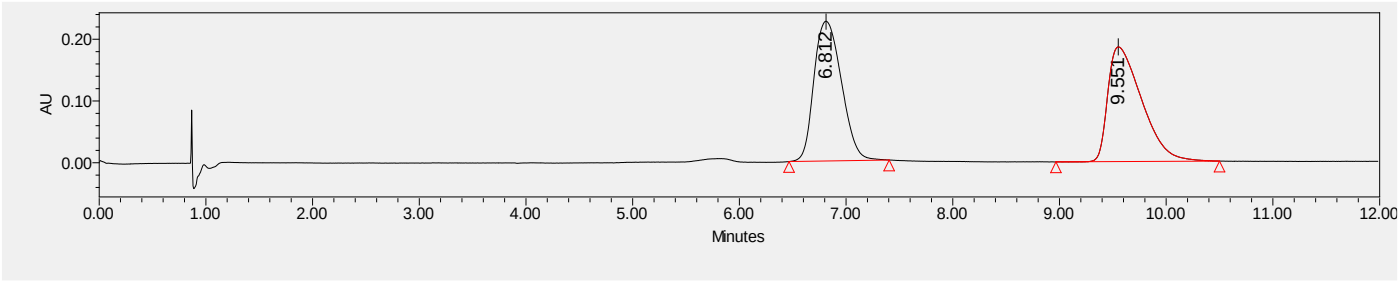
UPCC DAICEL CHIRALCEL ID-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 6.79 min, t_R (minor) = 9.71 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.47 (s, 1H), 7.34 – 7.28 (m, 1H), 7.23 – 7.15 (m, 3H), 7.13 – 7.07 (m, 1H), 7.03 – 6.95 (m, 2H), 6.92 – 6.88 (m, 1H), 6.85 – 6.75 (m, 1H), 6.43 – 6.34 (m, 2H), 3.76 (d, 3H), 3.45 (d, *J* = 46.4 Hz, 3H), 2.29 (s, 3H).

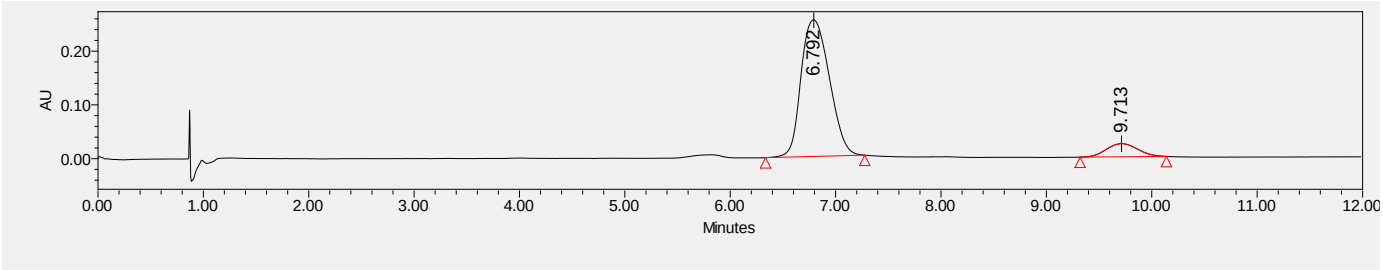
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 181.7, 160.1, 158.4, 141.3, 138.8, 137.9, 133.4, 131.2, 129.9, 128.5, 128.1, 127.9, 126.3, 125.9, 124.4, 122.0, 109.6, 104.7, 100.0, 59.7, 55.8, 55.5, 21.7.

IR: 2924, 1710, 1613, 1504, 1471, 1289, 1209, 1147, 1033, 785 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{23}H_{21}NO_3Na^+$ 382.1414; found 382.1417.

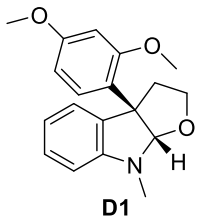


	Retention Time	Area	% Area
1	6.812	4050674	49.75
2	9.551	4091635	50.25



	Retention Time	Area	% Area
1	6.792	4749792	90.41
2	9.713	503758	9.59

(3a*S*,8a*S*)-3a-(2,4-dimethoxyphenyl)-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (D1)



D1

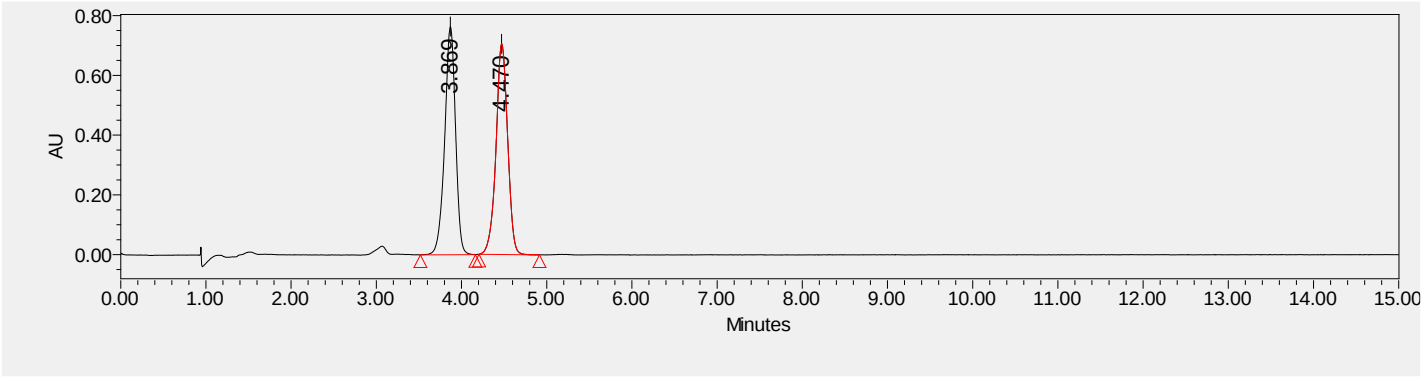
White soild; 34.5 mg, 87% yield, 97% ee; melting point: 97–100 °C; $[\alpha]_D^{18.8}$ = 124.7 (*c* = 0.54 in CH_2Cl_2). **UPCC** DAICEL CHIRALCEL IB-3, CO_2/MeOH = 95/5, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 3.76 min, t_R (minor) = 4.36 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.18 – 7.07 (m, 2H), 7.05 – 6.98 (m, 1H), 6.71 – 6.63 (m, 1H), 6.49 – 6.45 (m, 1H), 6.43 – 6.36 (m, 2H), 5.59 (s, 1H), 4.11 – 4.05 (m, 1H), 3.77 (s, 1H), 3.73 (s, 3H), 3.59 – 3.51 (m, 1H), 2.96 (s, 3H), 2.89 – 2.80 (m, 1H), 2.35 – 2.30 (m, 1H).

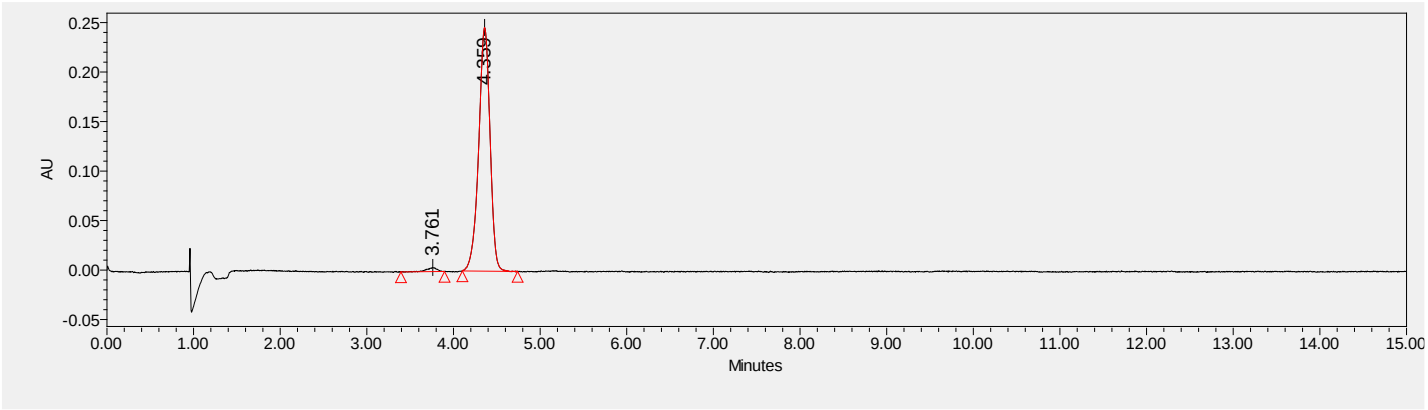
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 160.0, 158.7, 151.4, 133.3, 128.7, 128.3, 124.8, 124.0, 117.3, 105.4, 103.9, 103.8, 99.9, 67.5, 58.8, 55.5, 39.7, 31.5.

IR: 2925, 1607, 1583, 1500, 1465, 1260, 1209, 1158, 953, 834 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{19}NO_3Na^+$ 334.1414; found 334.1416.

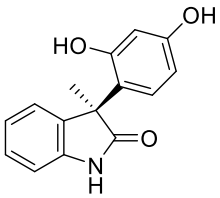


	Retention Time	Area	% Area
1	3.869	6746994	50.12
2	4.470	6714579	49.88



	Retention Time	Area	% Area
1	3.761	33846	1.49
2	4.359	2238599	98.51

(*S*)-3-(2,4-dihydroxyphenyl)-3-methylindolin-2-one (D2)



D2

Yellow soild; 23.2 mg, 91% yield, 94% ee; melting point: 81–86 °C; $[\alpha]_D^{19.0}$ = 989.3 (*c* = 0.23 in CH_2Cl_2).

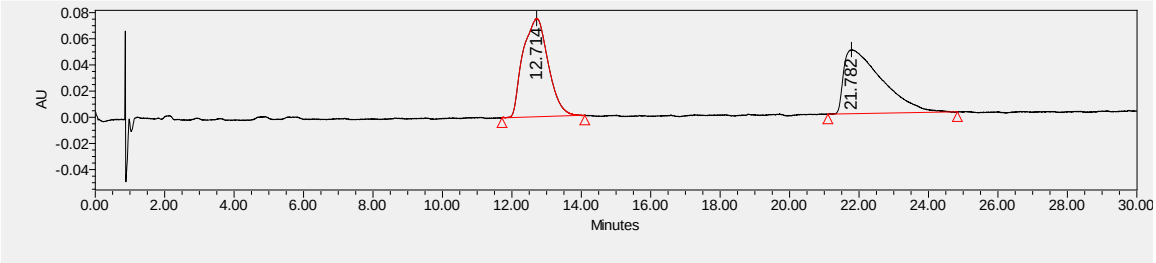
UPCC DAICEL CHIRALCEL ID-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 12.0 min, t_R (minor) = 22.8 min.

^{1}H NMR (400 MHz, acetone-d_6) δ 9.64 (s, 1H), 7.22 – 7.15 (m, 1H), 7.14 – 7.06 (m, 2H), 7.04 – 6.93 (m, 2H), 6.36 – 6.28 (m, 2H), 1.69 (s, 3H).

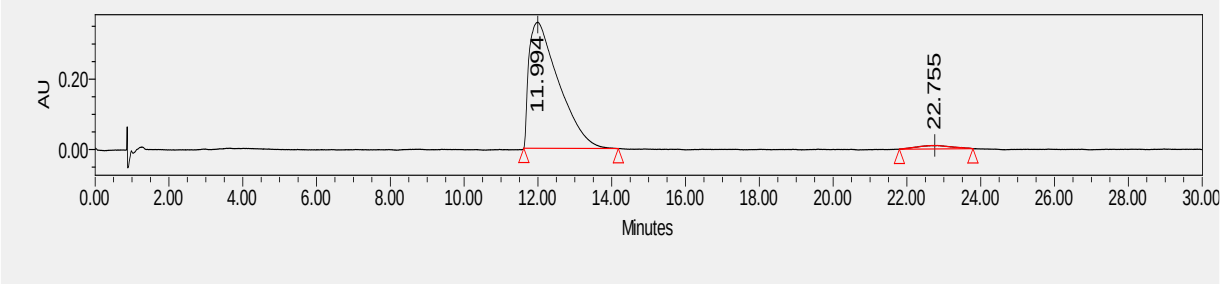
^{13}C NMR (101 MHz, acetone-d_6) δ 184.1, 158.8, 157.7, 142.2, 136.3, 129.2, 128.3, 124.7, 122.6, 118.9, 110.4, 107.1, 105.1, 51.7, 23.6.

IR: 3265 1680, 1617, 1521, 1470, 1377, 1204, 841, 755, 690 cm^{-1}.

HRMS (FTMS+c ESI) m/z: [M - H$^-$] calcd for $C_{15}H_{12}NO_3^-$ 254.0823; found 254.0825.

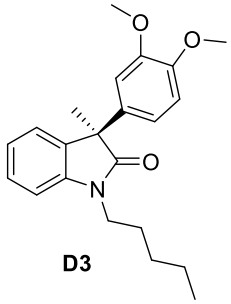


	Retention Time	Area	% Area
1	12.714	3776966	50.27
2	21.782	3735765	49.73



	Retention Time	Area	% Area
1	11.994	20088333	96.97
2	22.755	627655	3.03

(*R*)-3-(3,4-dimethoxyphenyl)-3-methyl-1-pentylindolin-2-one (D3)



D3

Colorless oil; 25.6 mg, 92% yield, 76% ee; $[\alpha]_D^{18.5}$ = 31.0 (*c* = 0.17 in CH_2Cl_2).

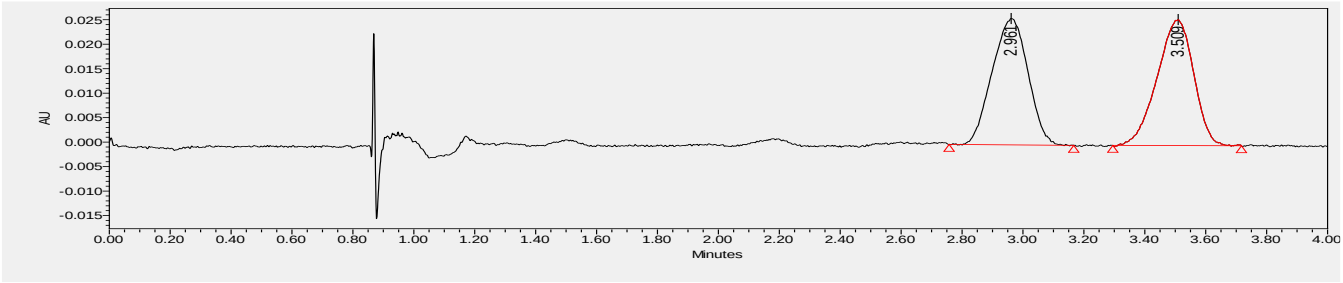
UPCC DAICEL CHIRALCEL IB-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 3.55 min, t_R (minor) = 3.01 min.

^{1}H NMR (400 MHz, $CDCl_3$) 7.33 – 7.28 (m, 1H), 7.22 – 7.16 (m, 1H), 7.10 – 7.05 (m, 1H), 6.95 – 6.90 (m, 1H), 6.88 – 6.84 (m, 1H), 6.83 – 6.74 (m, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 3.79 – 3.62 (m, 2H), 1.75 (s, 3H), 1.73 – 1.65 (m, 2H), 1.43 – 1.27 (m, 4H), 0.90 – 0.82 (m, 3H).

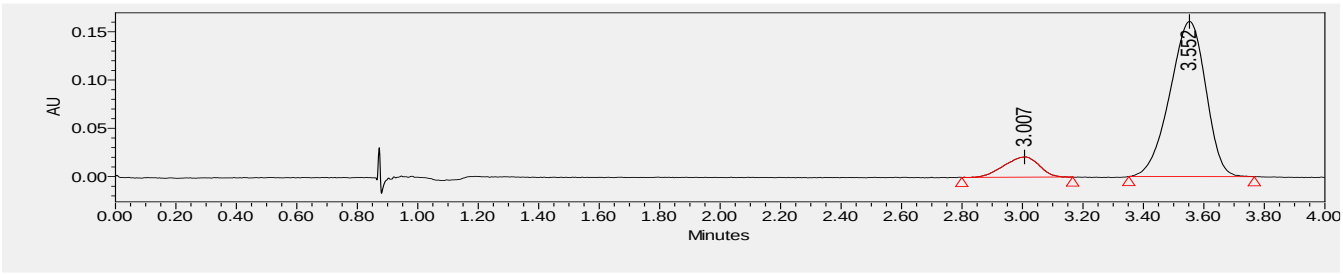
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 179.6, 149.0, 148.4, 142.7, 135.2, 133.6, 128.1, 124.4, 122.6, 119.0, 111.1, 110.4, 108.7, 56.0, 56.0, 51.7, 40.2, 29.1, 27.2, 24.2, 22.5, 14.1.

IR: 2930, 2361, 1712, 1609, 1515, 1488, 1465, 1354, 1260, 1027 cm^{-1}.

HRMS (FTMS+c ESI) m/z: [M + Na^+] calcd for $C_{22}H_{27}NO_3Na^+$ 376.1883; found 376.1883.

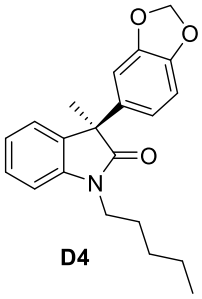


	Retention Time	Area	% Area
1	2.961	211608	49.66
2	3.509	214505	50.34



	Retention Time	Area	% Area
1	3.007	168930	11.31
2	3.552	1324385	88.69

(*S*)-3-(2,4-dihydroxyphenyl)-3-methylindolin-2-one (D4)



D4

Colorless oil; 18.5 mg, 75% yield, 76% ee; $[\alpha]_D^{18.5}$ = 78.3 (*c* = 0.11 in CH_2Cl_2).

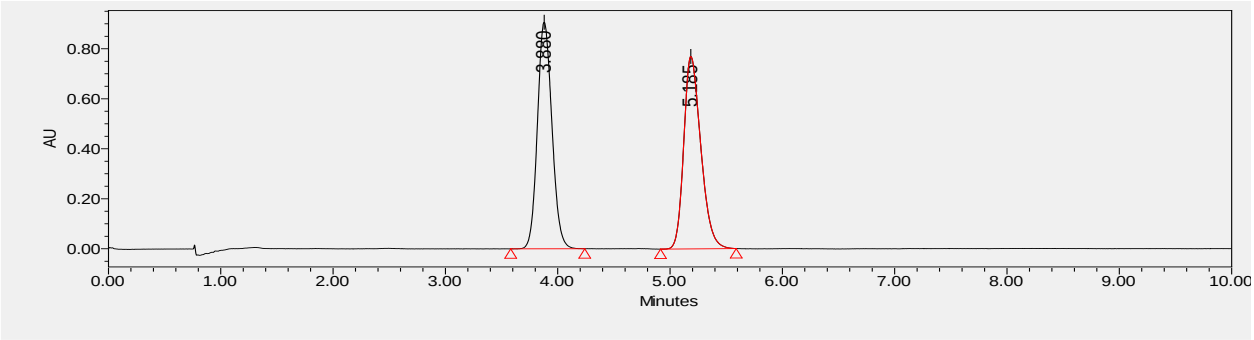
UPCC DAICEL CHIRALCEL OX-3, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_R (major) = 5.10 min, t_R (minor) = 3.76 min.

^{1}H NMR (400 MHz, acetone-d_6) *δ* 7.28 – 7.19 (m, 1H), 7.12 – 7.02 (m, 2H), 6.84 – 6.75 (m, 1H), 6.75 – 6.72 (m, 2H), 5.96 – 5.93 (m, 2H), 3.84 – 3.65 (m, 2H), 1.73 – 1.64 (m, 5H), 1.39 – 1.26 (m, 4H), 0.90 – 0.82 (m, 3H).

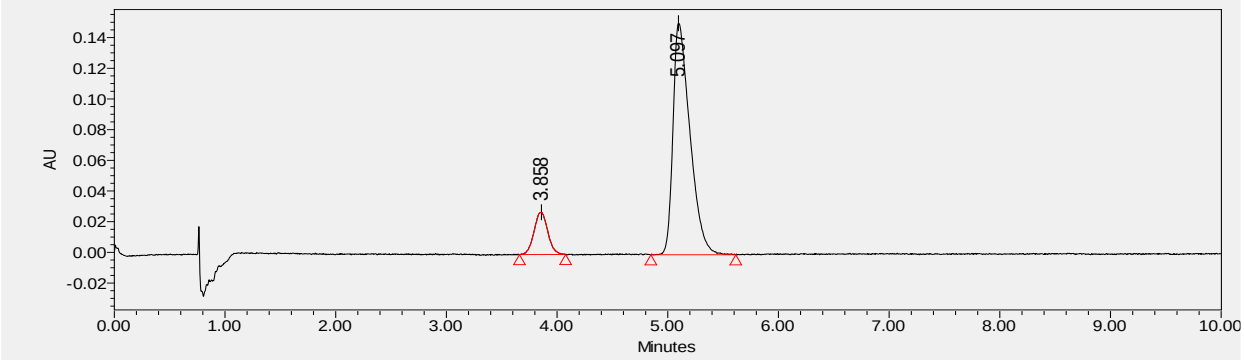
^{13}C NMR (101 MHz, acetone-d_6) *δ* 179.3, 148.7, 147.5, 143.5, 136.3, 136.0, 128.9, 124.9, 123.1, 120.6, 109.6, 108.5, 108.1, 102.0, 52.2, 40.3, 27.8, 24.0, 22.9, 14.2.

IR: 2927, 2361, 1711, 1609, 1488, 1466, 11354, 1354, 1103, 957 cm^{-1}.

HRMS (FTMS+c ESI) m/z: [M + Na^+] calcd for $C_{21}H_{23}NO_3Na^+$ 360.1570; found 360.1568.

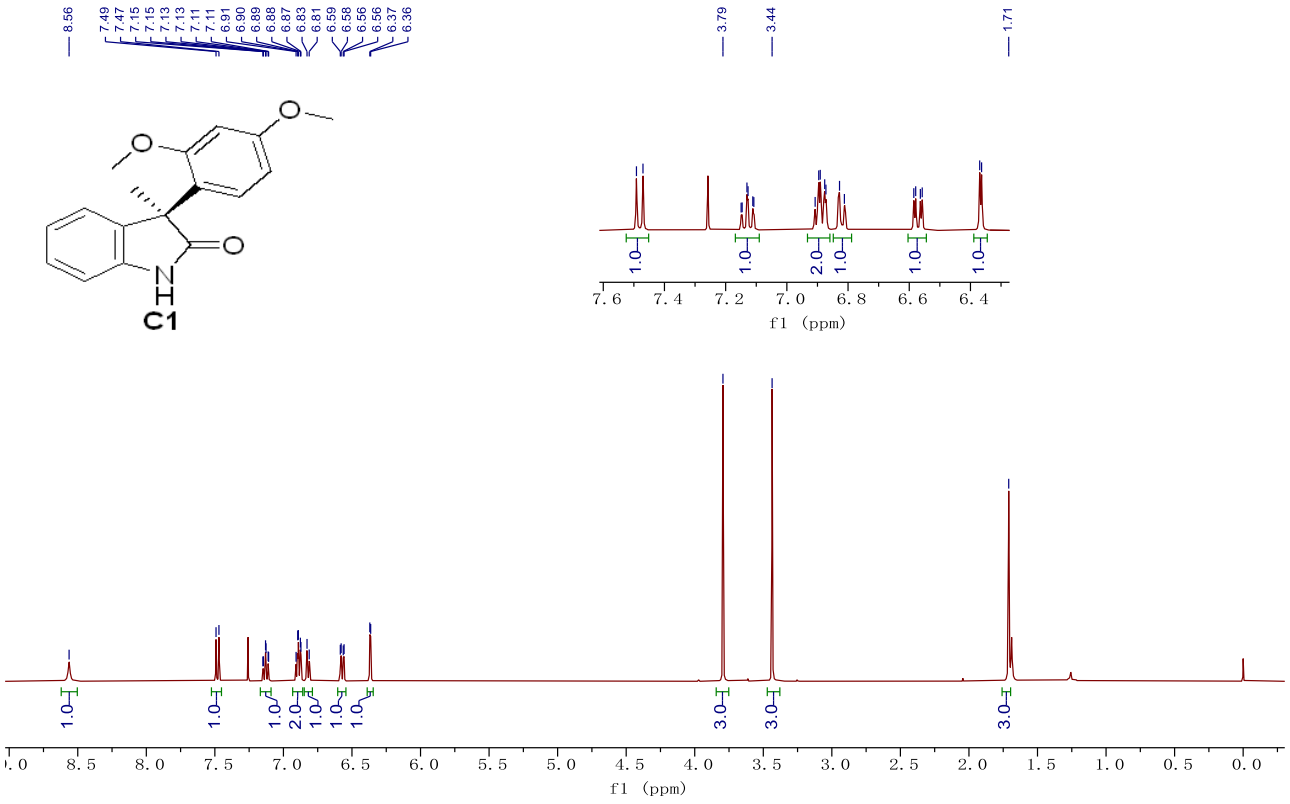


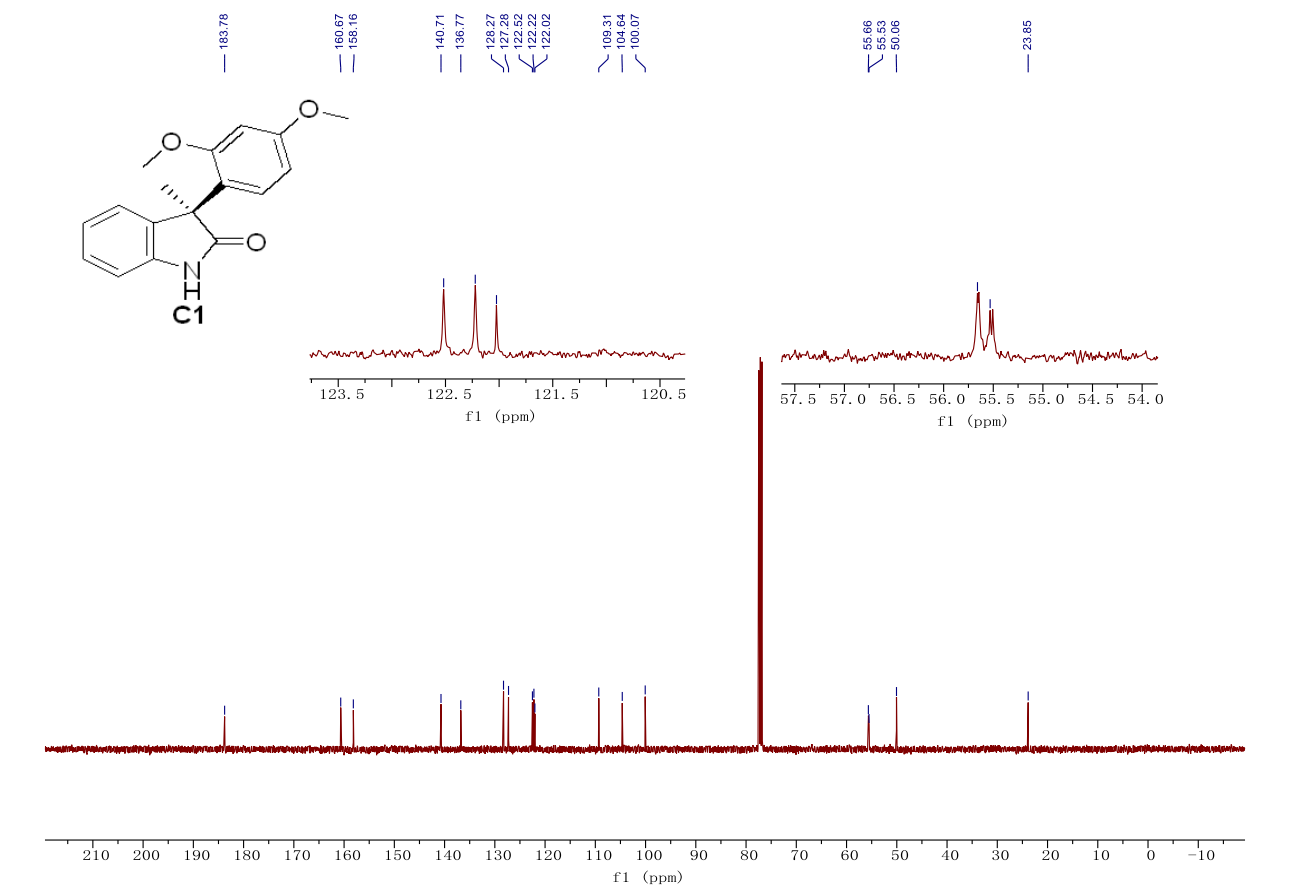
	Retention Time	Area	% Area
1	3.880	8153887	50.10
2	5.185	8121733	49.90

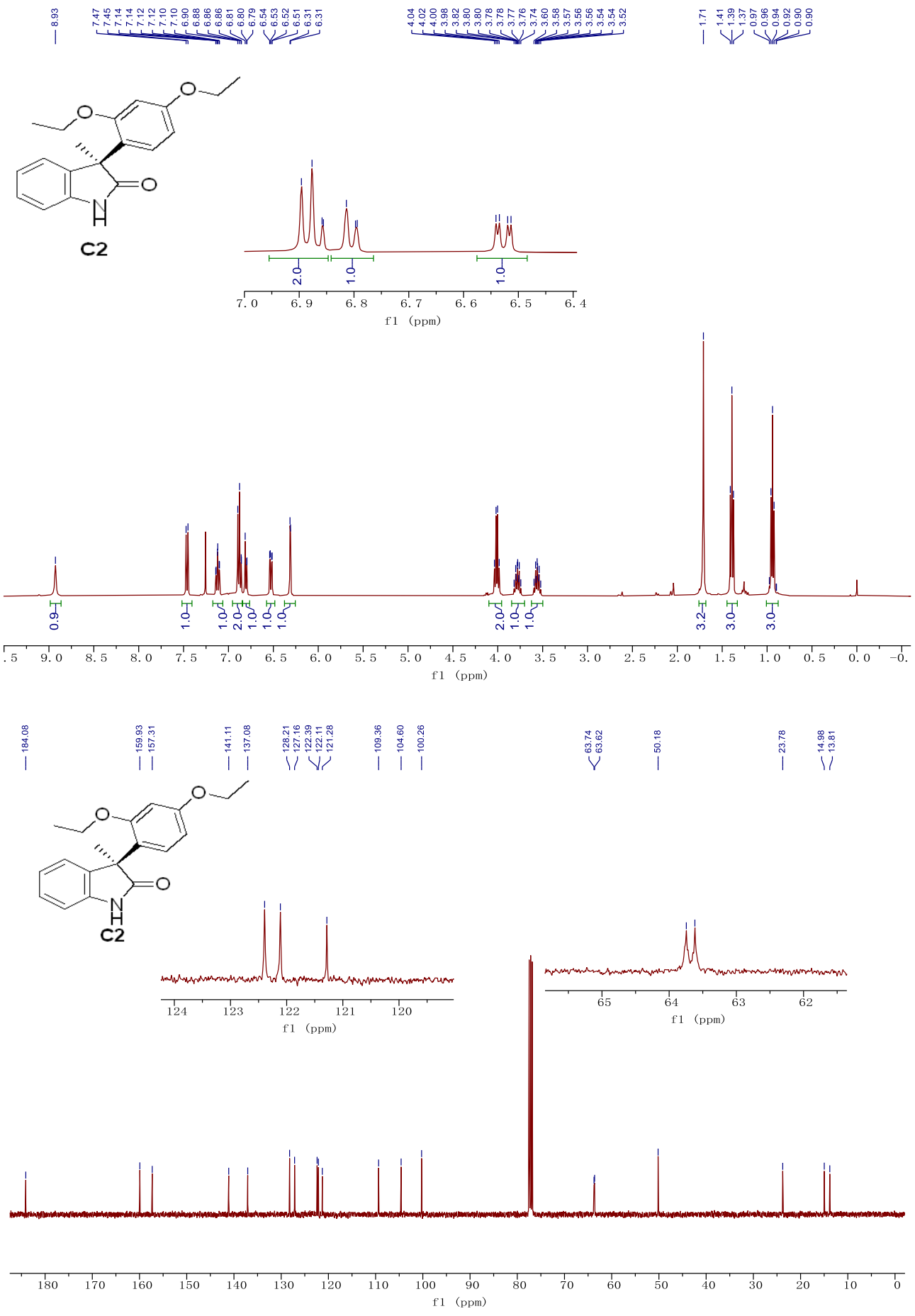


	Retention Time	Area	% Area
1	3.858	221098	12.10
2	5.097	1606579	87.90

12 Copies of NMR spectra for products



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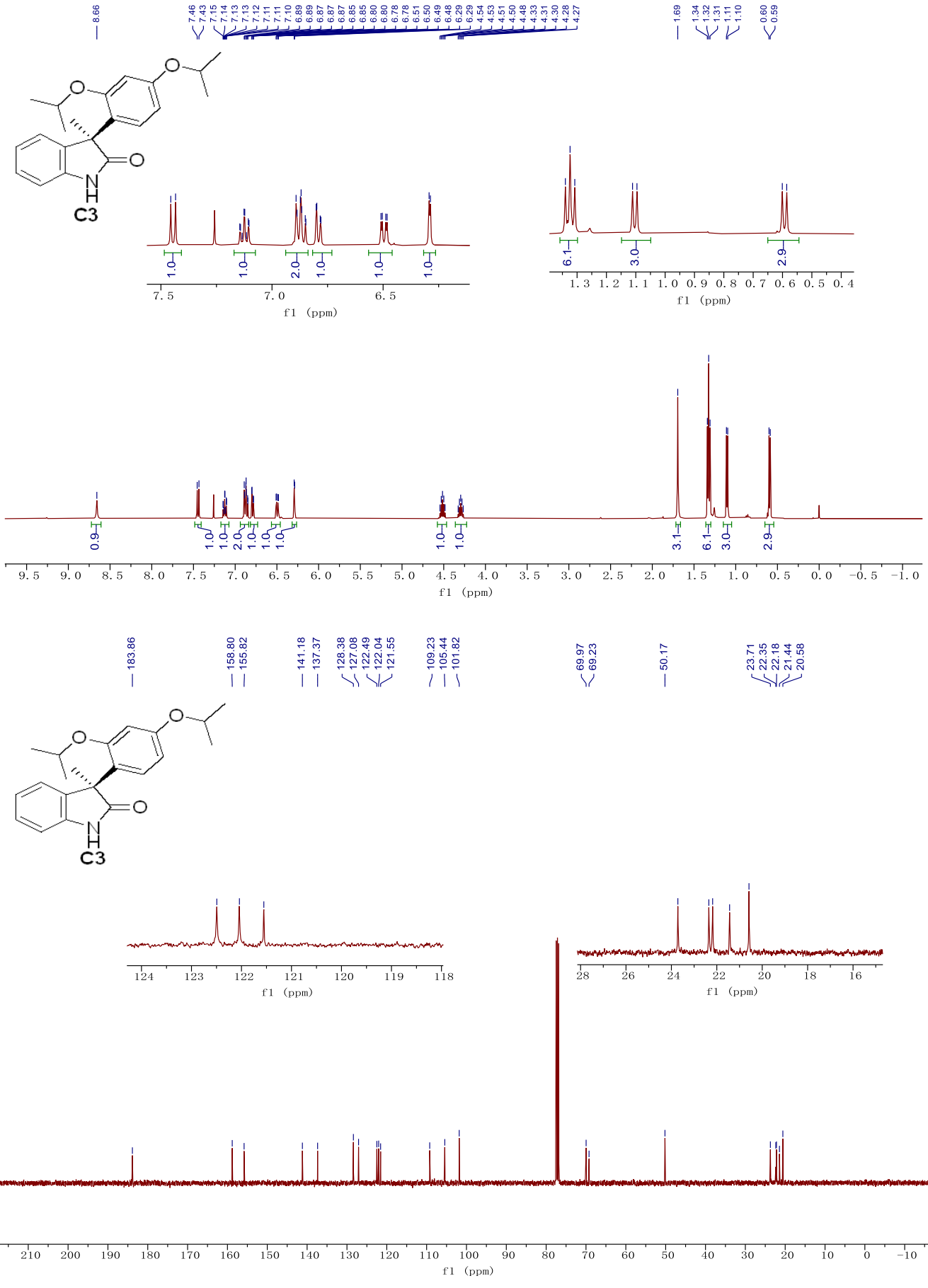
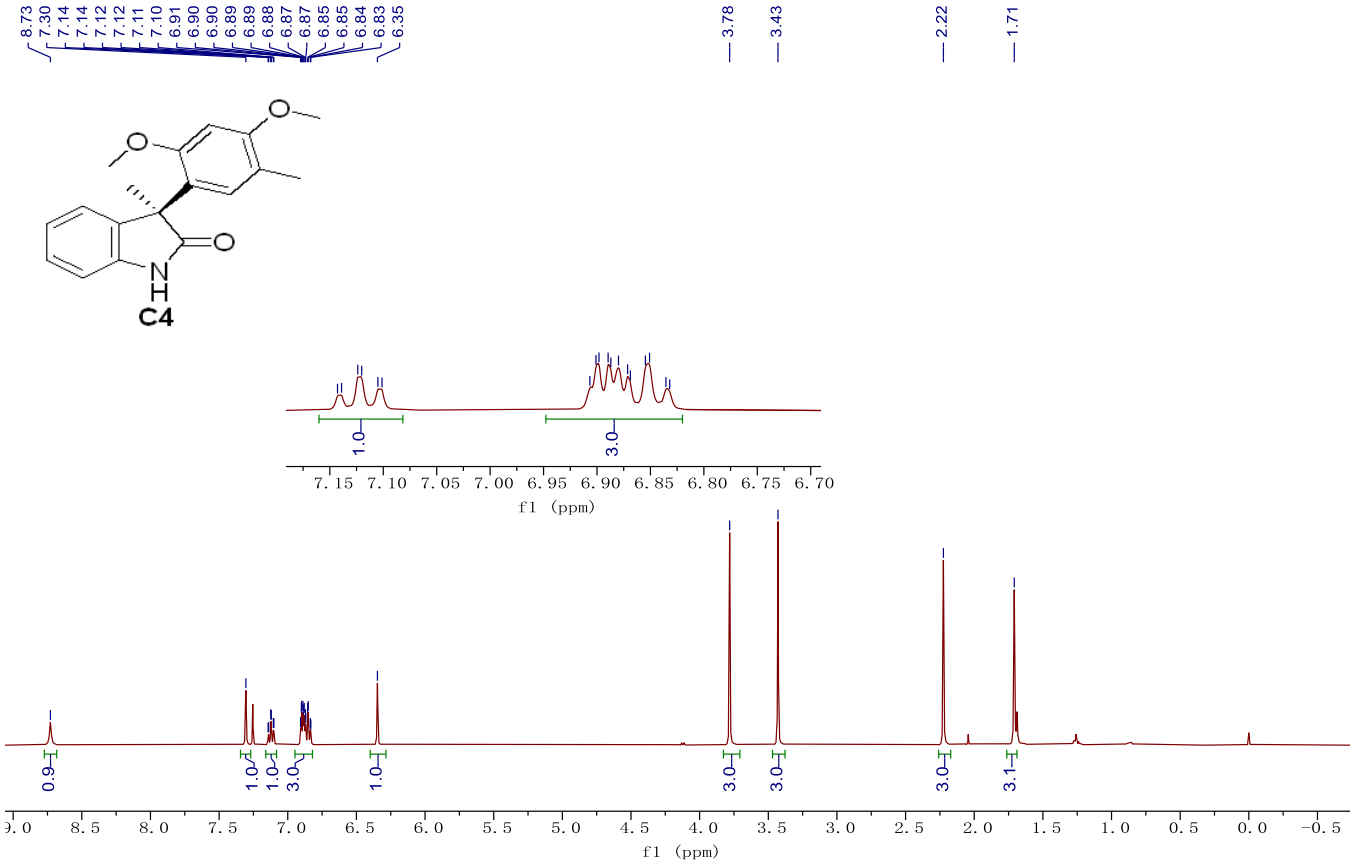
7.10
7.10
6.90
6.88
6.86
6.86
6.81
6.80
6.79
6.54
6.53
6.52
6.51
6.31
6.31
4.04
4.02
4.00
3.98
3.82
3.80
3.80
3.78
3.78
3.77
3.76
3.74
3.60
3.58
3.57
3.56
3.56
3.54
3.54
3.52
1.71
1.41
1.39
1.37
0.97
0.96
0.94
0.92
0.90
0.90
C2
2.0
1.0
1.0
7.0 6.9 6.8 6.7 6.6 6.5 6.4
f1 (ppm)
0.9
1.0
1.0
2.0
1.0
1.0
1.0
2.0
1.0
1.0
3.2
3.0
3.0
f1 (ppm)
184.08
159.93
157.31
141.11
137.08
128.21
127.16
122.39
122.11
121.28
109.36
104.60
100.26
63.74
63.62
50.18
23.78
14.98
13.81
C2
124 123 122 121 120
f1 (ppm)
65 64 63 62
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


C3
f1 (ppm)
C3
f1 (ppm)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7.12
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7.10
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6.90
6.90
6.89
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6.88
6.87
6.87
6.85
6.85
6.84
6.83
6.35
3.78
3.43
2.22
1.71
C4
1.0
3.0
f1 (ppm)
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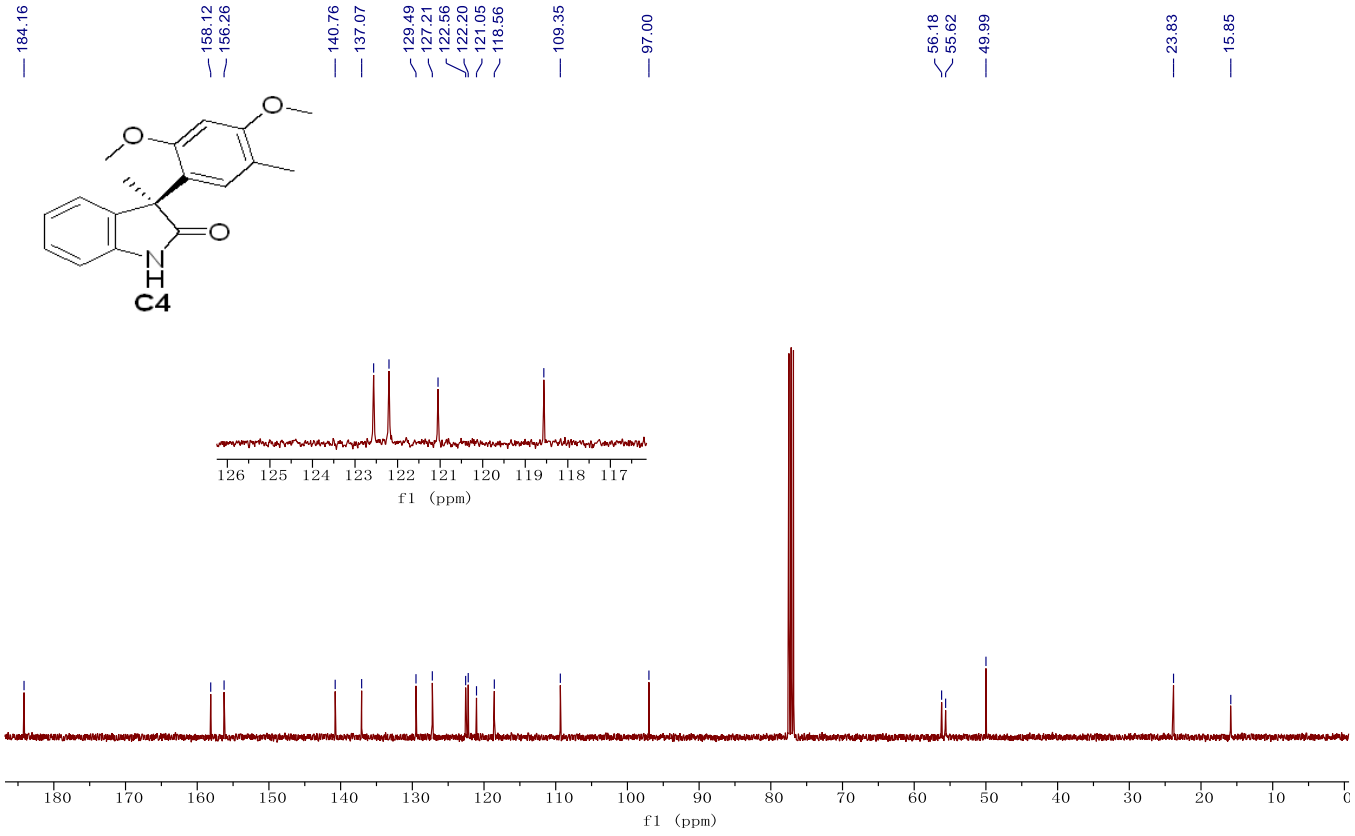
1.0
1.0
3.0
1.0
3.0
3.0
3.0
3.1
f1 (ppm)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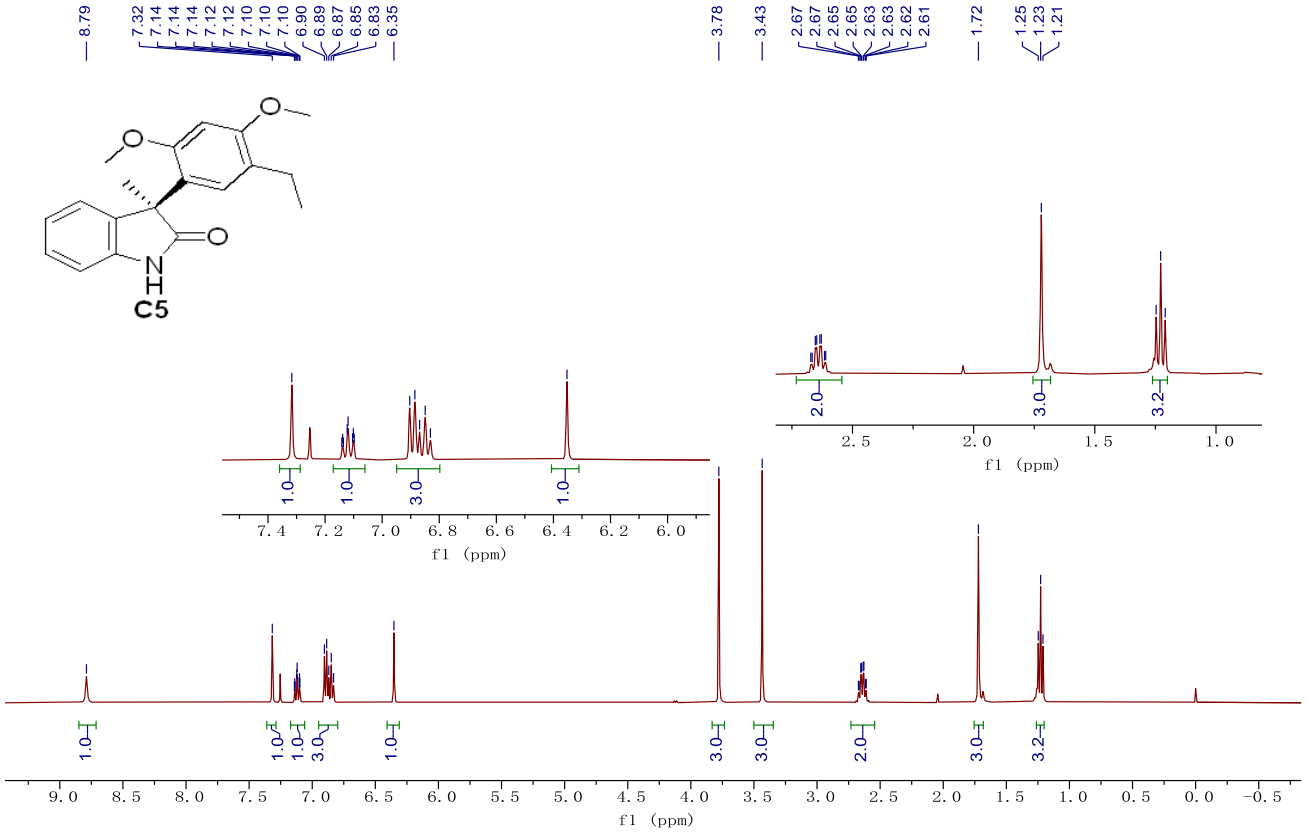
156.26
140.76
137.07
129.49
127.21
122.56
122.20
121.05
118.56
109.35
97.00
56.18
55.62
49.99
23.83
15.85
C4
f1 (ppm)
f1 (ppm)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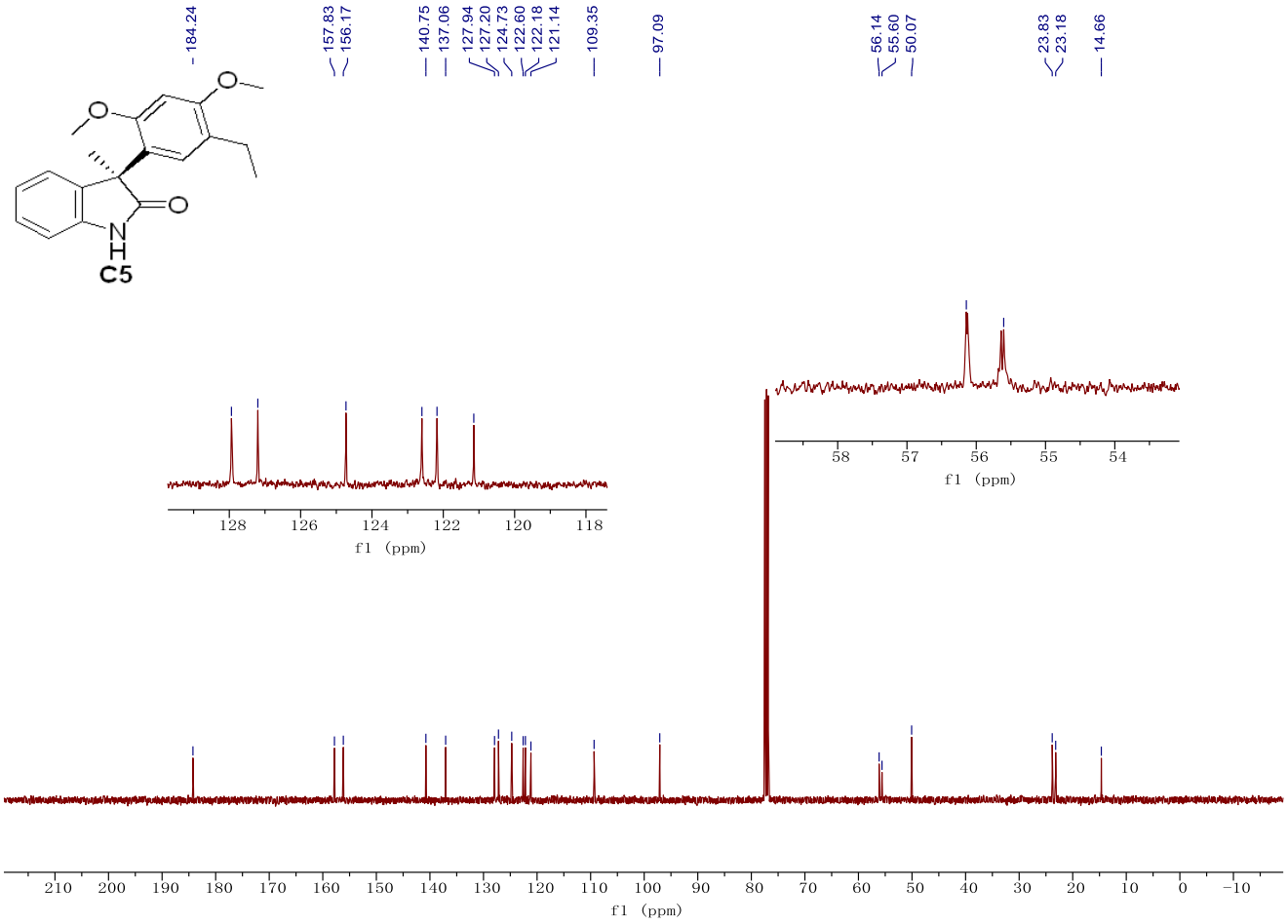
7.32
7.14
7.14
7.14
7.12
7.12
7.10
7.10
7.10
6.90
6.89
6.87
6.85
6.83
6.35
3.78
3.43
2.67
2.67
2.65
2.65
2.63
2.63
2.62
2.61
1.72
1.25
1.23
1.21
C5
f1 (ppm)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127.20
124.73
122.60
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121.14
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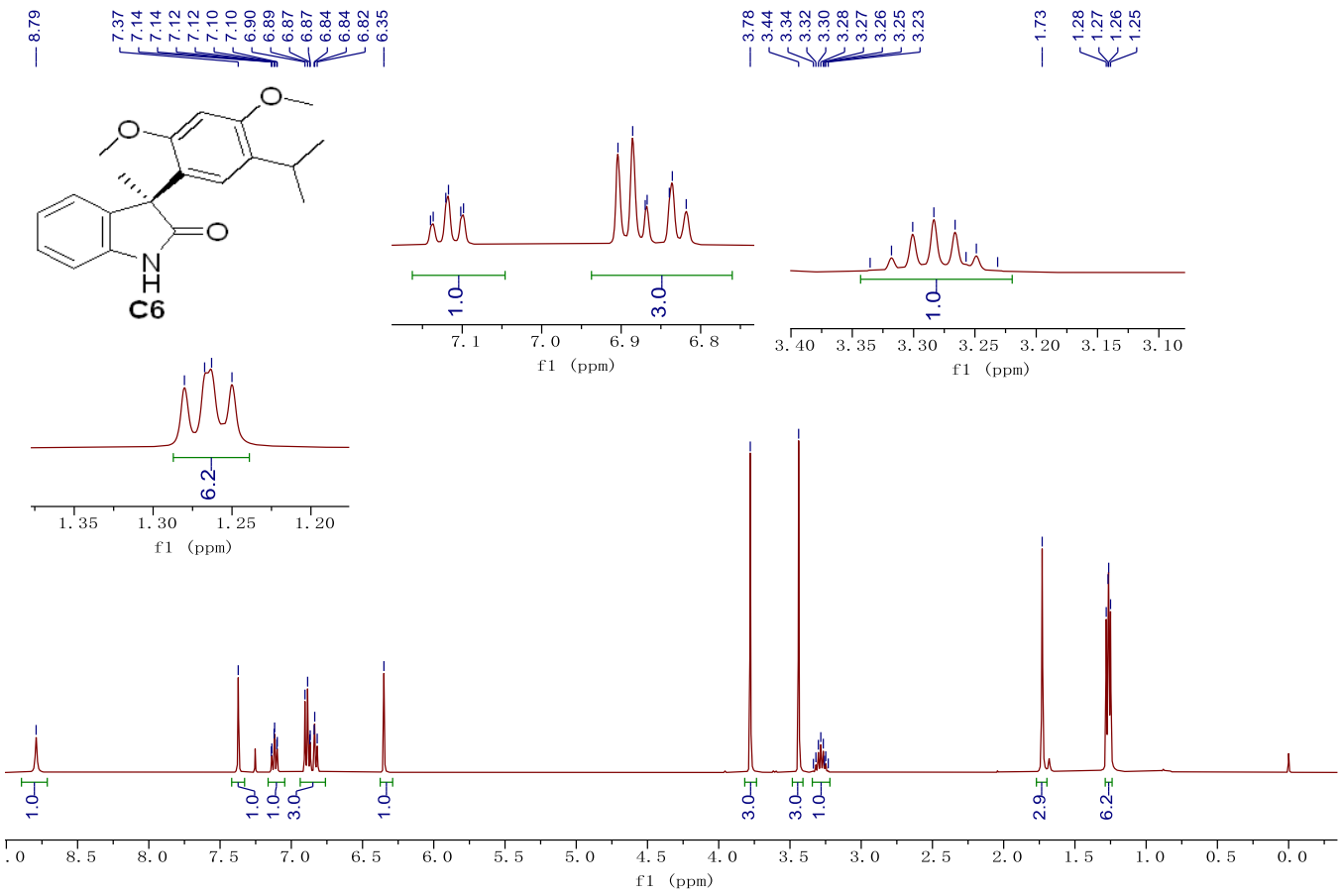
97.09
56.14
55.60
50.07
23.83
23.18
14.66
C5
f1 (ppm)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7.12
7.10
7.10
6.90
6.89
6.87
6.87
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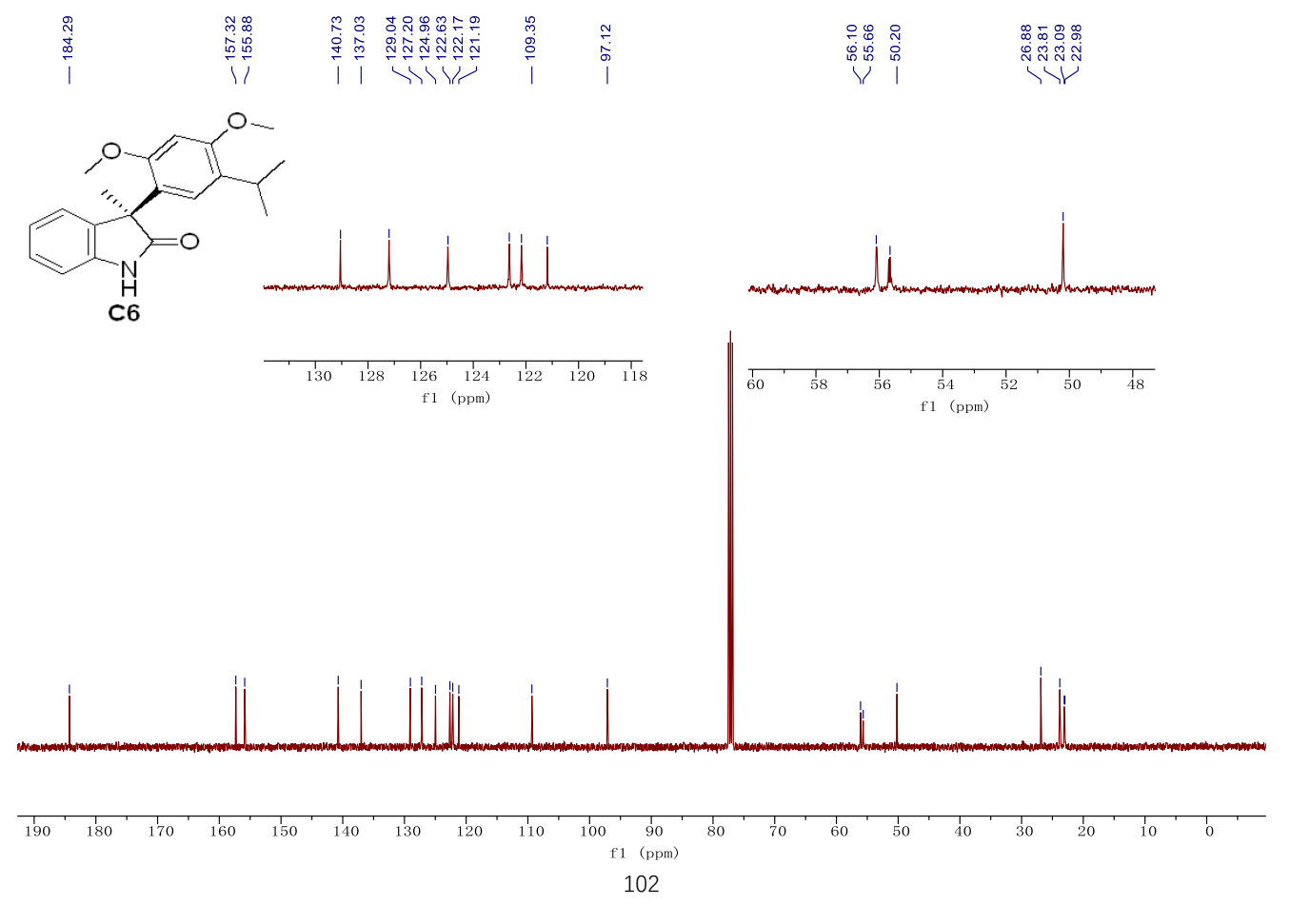
6.84
6.82
6.35
3.78
3.44
3.34
3.32
3.30
3.28
3.27
3.26
3.25
3.23
1.73
1.28
1.27
1.26
1.25
C6
1.0
3.0
1.0
6.2
f1 (ppm)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122.17
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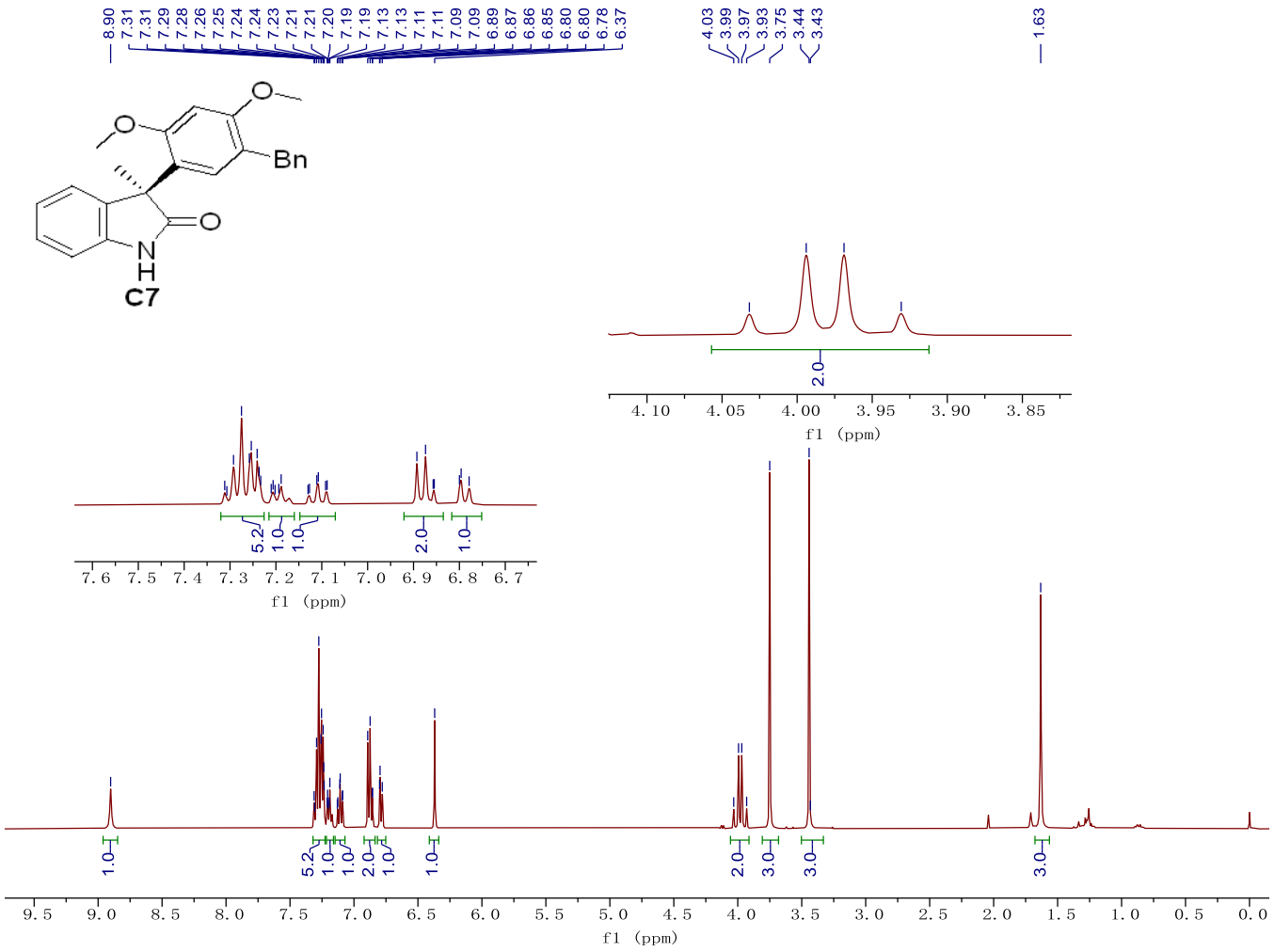
56.10
55.66
50.20
26.88
23.81
23.09
22.98
C6
f1 (ppm)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7.20
7.19
7.19
7.13
7.13
7.11
7.11
7.09
7.09
6.89
6.87
6.86
6.85
6.80
6.80
6.78
6.37
4.03
3.99
3.97
3.93
3.75
3.44
3.43
1.63
Bn
O
O
N
H
C7
2.0
4.10
4.05
4.00
3.95
3.90
3.85
f1 (ppm)
5.2
1.0
1.0
2.0
1.0
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)
1.0
5.2
1.0
1.0
2.0
1.0
1.0
2.0
3.0
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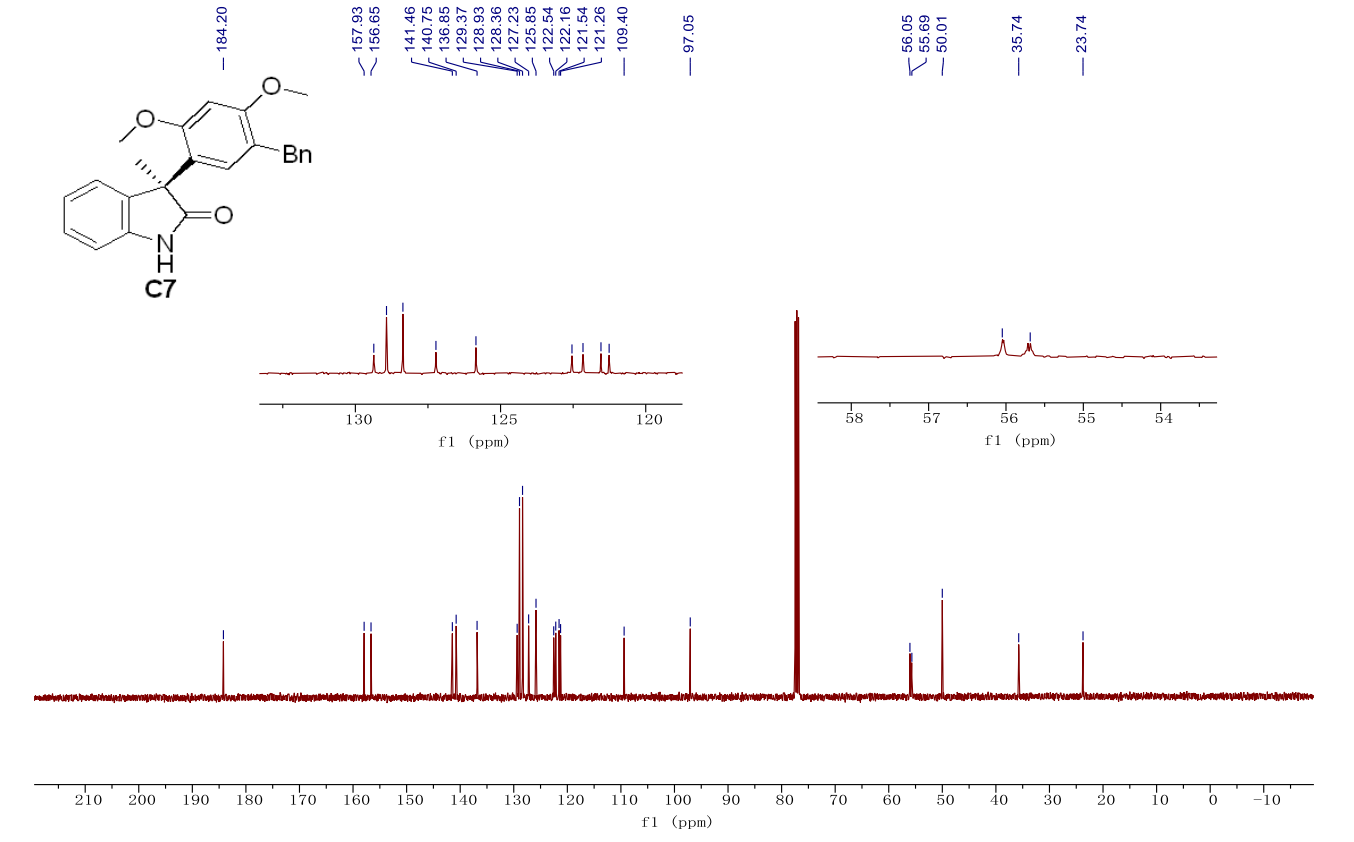
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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128.36
127.23
125.85
122.54
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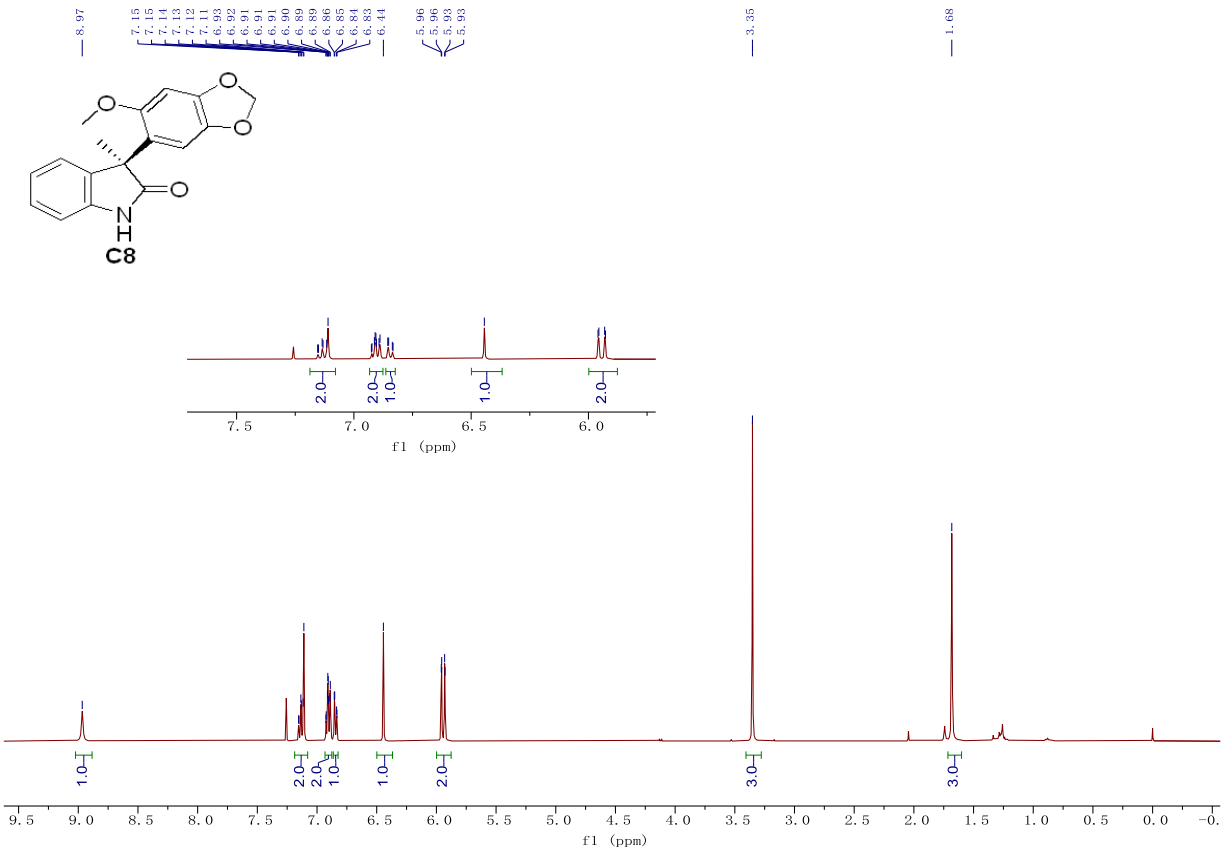
121.54
121.26
109.40
97.05
56.05
55.69
50.01
35.74
23.74
Bn
O
O
N
H
C7
130
125
120
f1 (ppm)
58
57
56
55
54
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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7.14
7.13
7.12
7.11
6.93
6.92
6.91
6.91
6.91
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6.89
6.89
6.86
6.85
6.84
6.83
6.44
5.96
5.96
5.93
5.93
3.35
1.68
C8
2.0
2.0
1.0
1.0
2.0
7.5
7.0
6.5
6.0
f1 (ppm)
1.0
2.0
2.0
1.0
1.0
2.0
3.0
3.0
9.5
9.0
8.5
8.0
7.5
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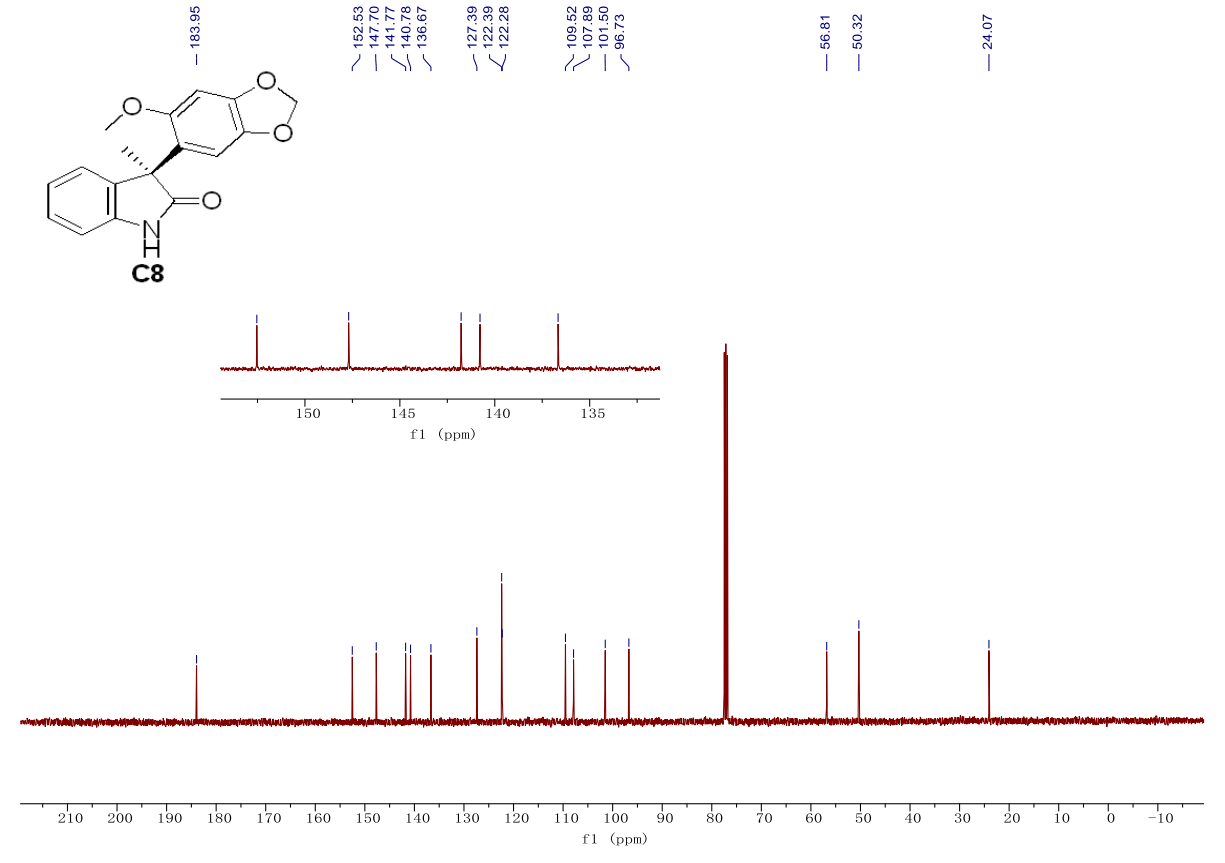
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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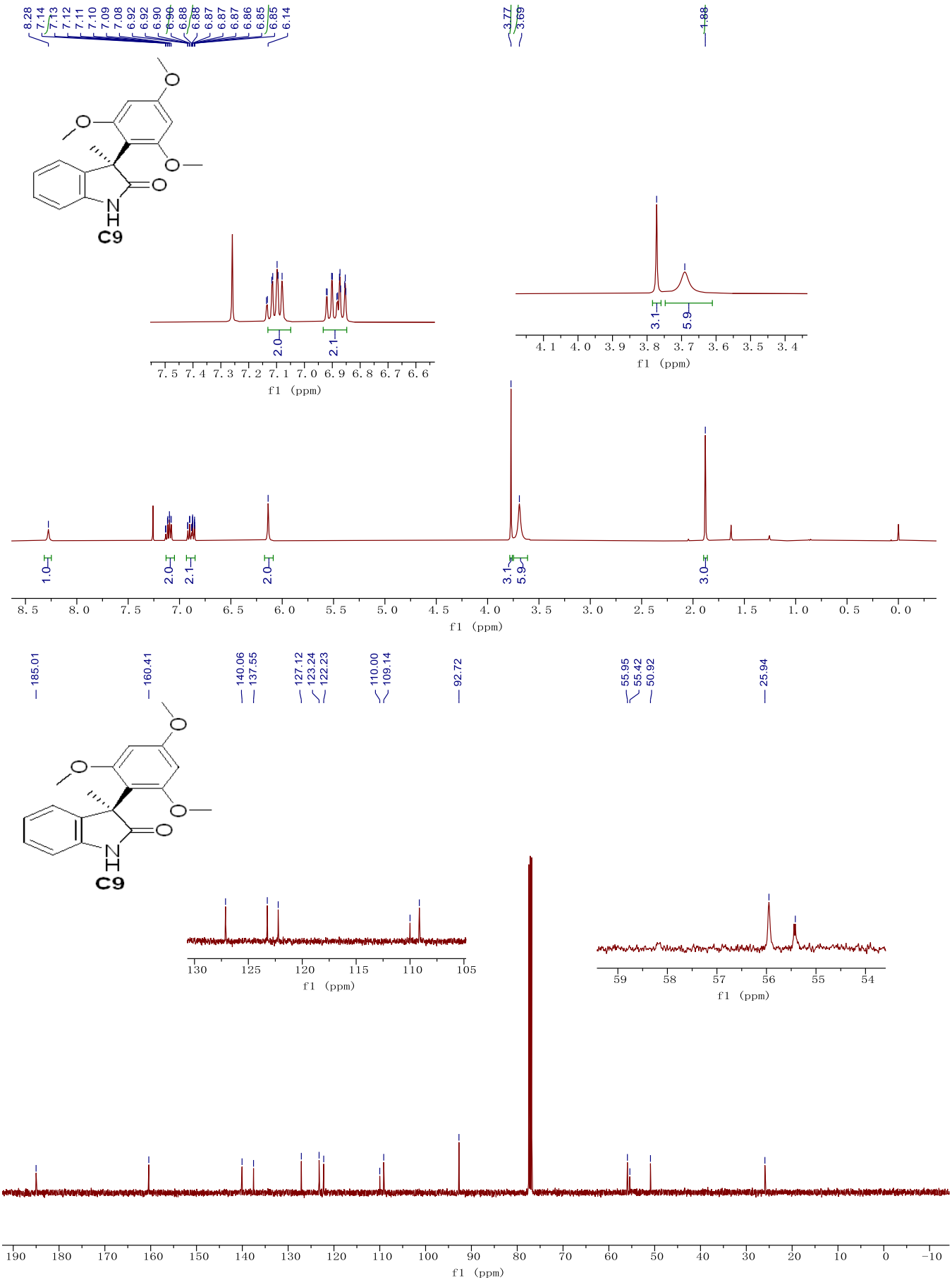
122.39
122.28
109.52
107.89
101.50
96.73
56.81
50.32
24.07
C8
150
145
140
135
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.12
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7.10
7.09
7.08
6.92
6.92
6.90
6.90
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6.88
6.87
6.87
6.87
6.86
6.85
6.85
6.14
3.77
3.69
1.88
C9
2.0
2.1
3.1
5.9
f1 (ppm)
1.0
2.0
2.1
2.0
3.1
5.9
3.0
f1 (ppm)
185.01
160.41
140.06
137.55
127.12
123.24
122.23
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92.72
55.95
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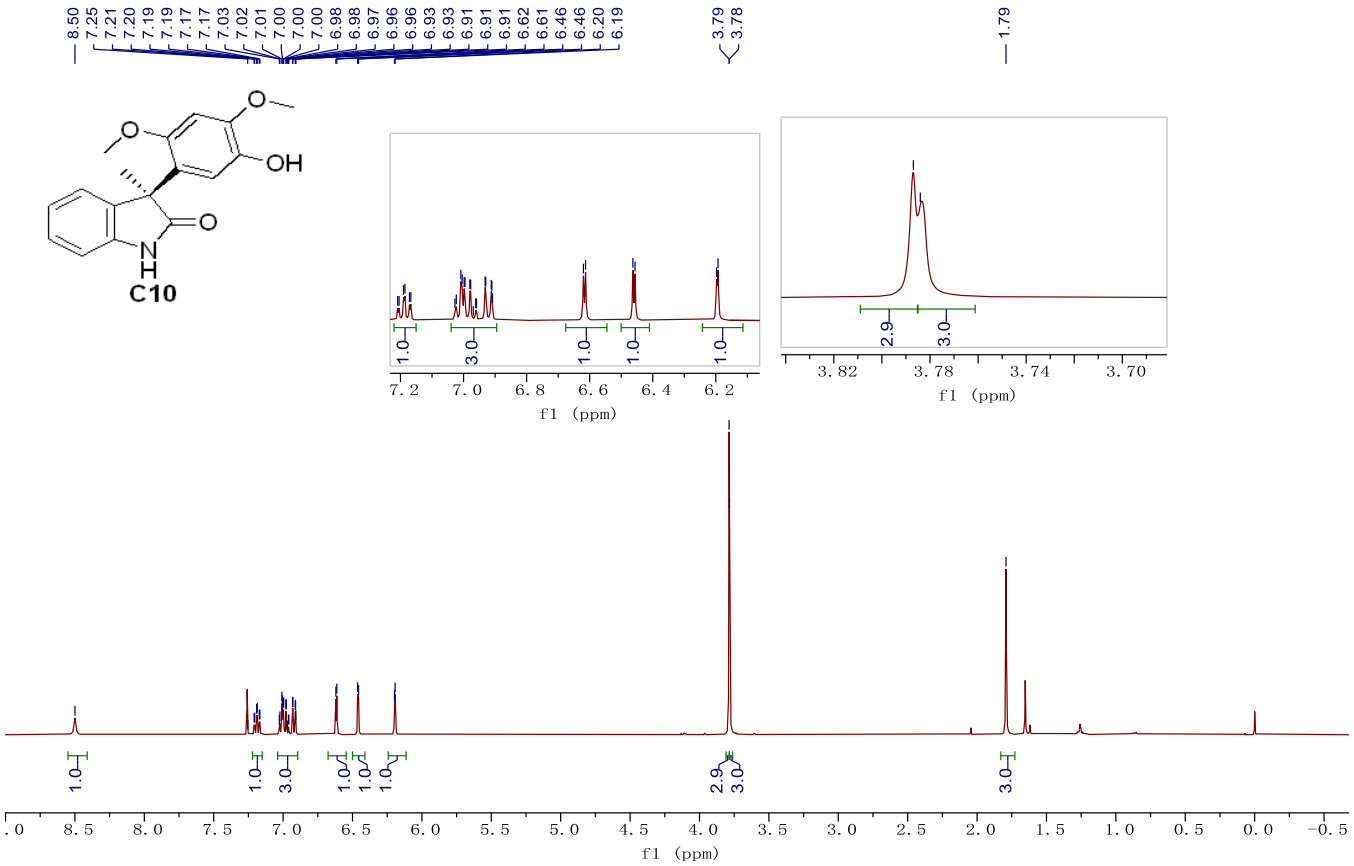
50.92
25.94
C9
f1 (ppm)
f1 (ppm)
f1 (ppm)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7.19
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7.17
7.03
7.02
7.01
7.00
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7.00
6.98
6.98
6.97
6.96
6.96
6.93
6.93
6.91
6.91
6.91
6.62
6.61
6.46
6.20
6.19
3.79
3.78
1.79
OH
O
O
N
H
C10
1.0
3.0
1.0
1.0
1.0
2.9
3.0
f1 (ppm)
f1 (ppm)
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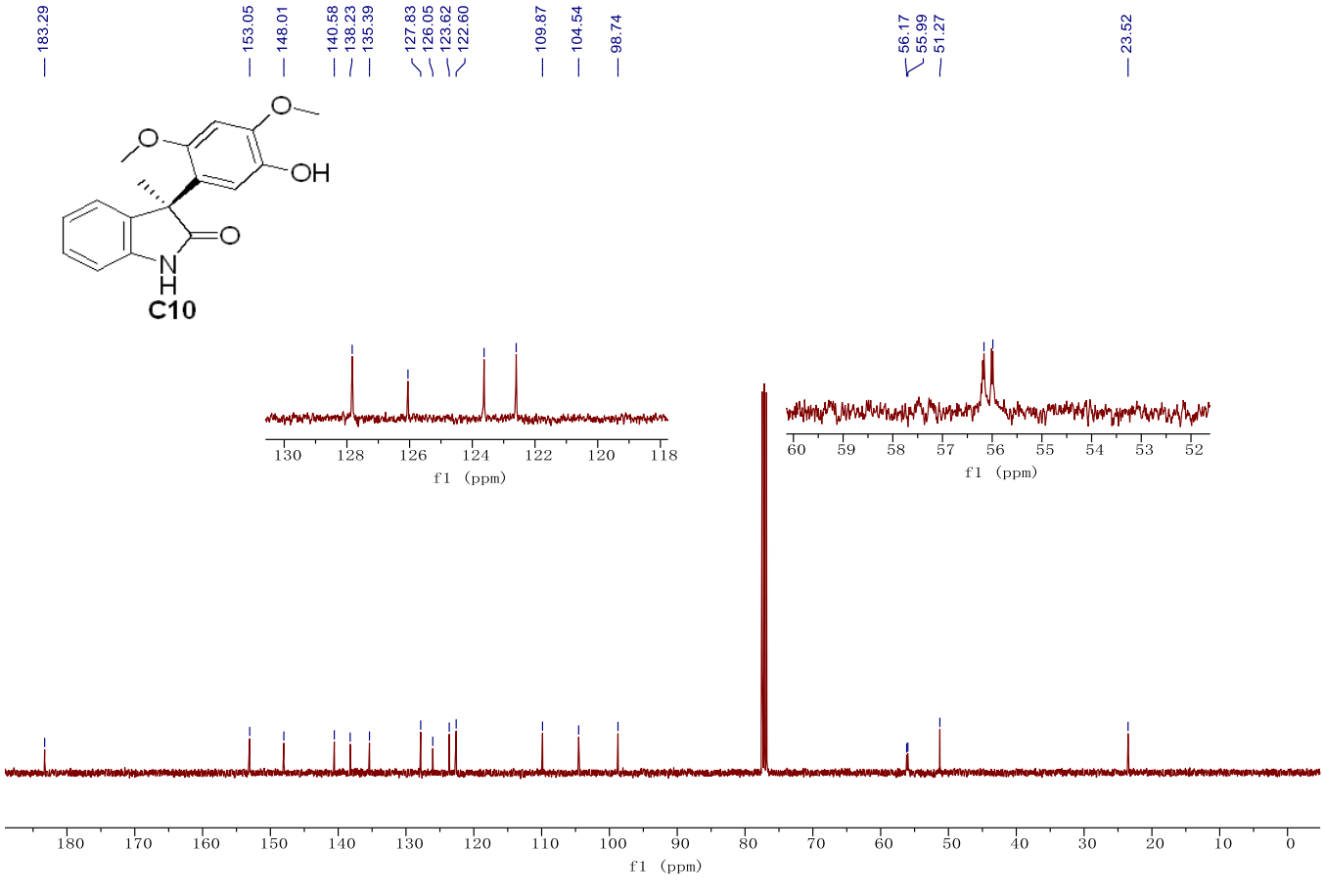
1.0
3.0
1.0
1.0
1.0
2.9
3.0
3.0
f1 (ppm)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126.05
123.62
122.60
109.87
104.54
98.74
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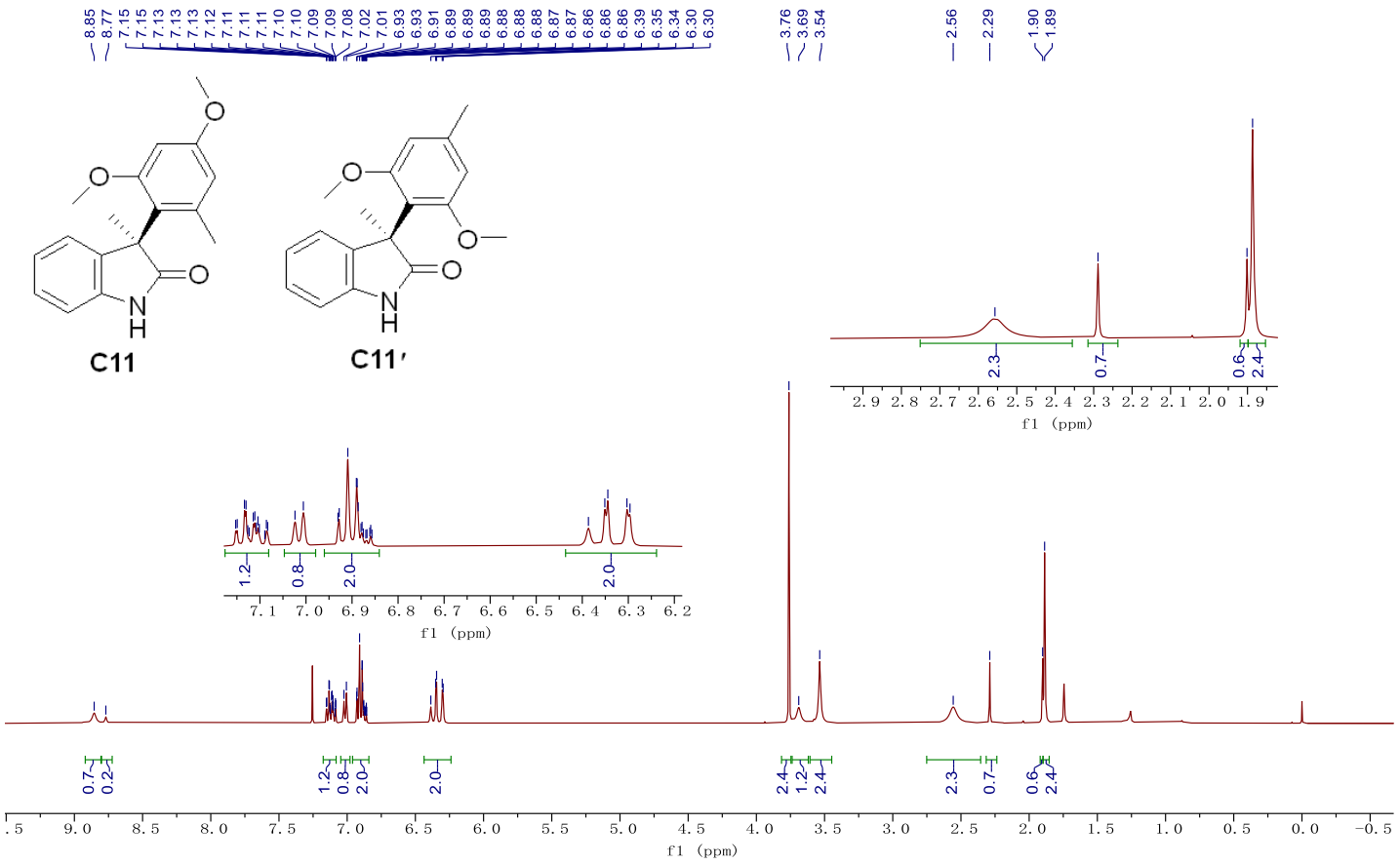
51.27
23.52
OH
O
O
N
H
C10
f1 (ppm)
f1 (ppm)
f1 (ppm)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7.11
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7.10
7.09
7.09
7.08
7.02
7.01
6.93
6.93
6.91
6.89
6.89
6.89
6.88
6.88
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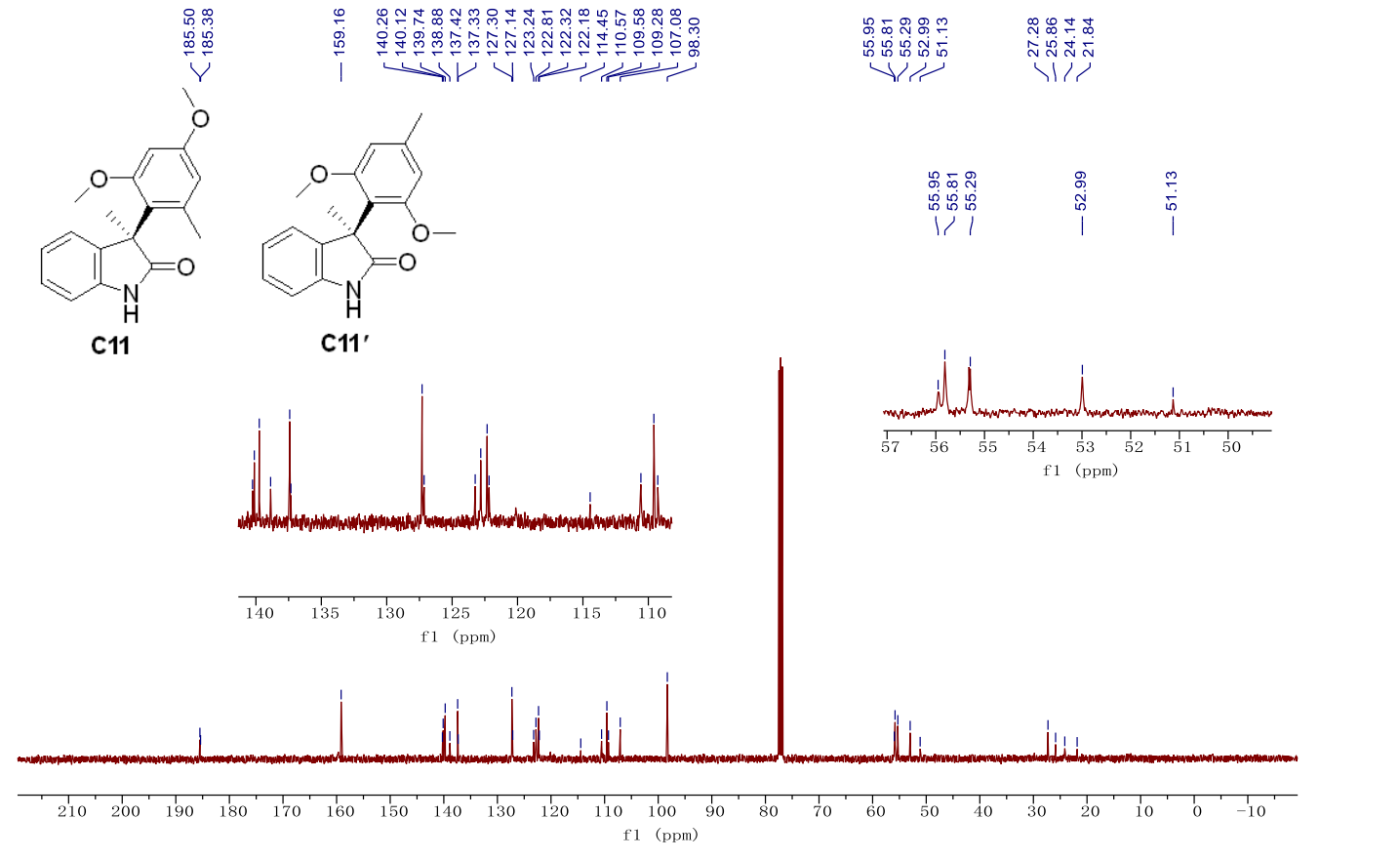
2.29
1.90
1.89
C11
C11′
f1 (ppm)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127.14
123.24
122.81
122.32
122.18
114.45
110.57
109.58
109.28
107.08
98.30
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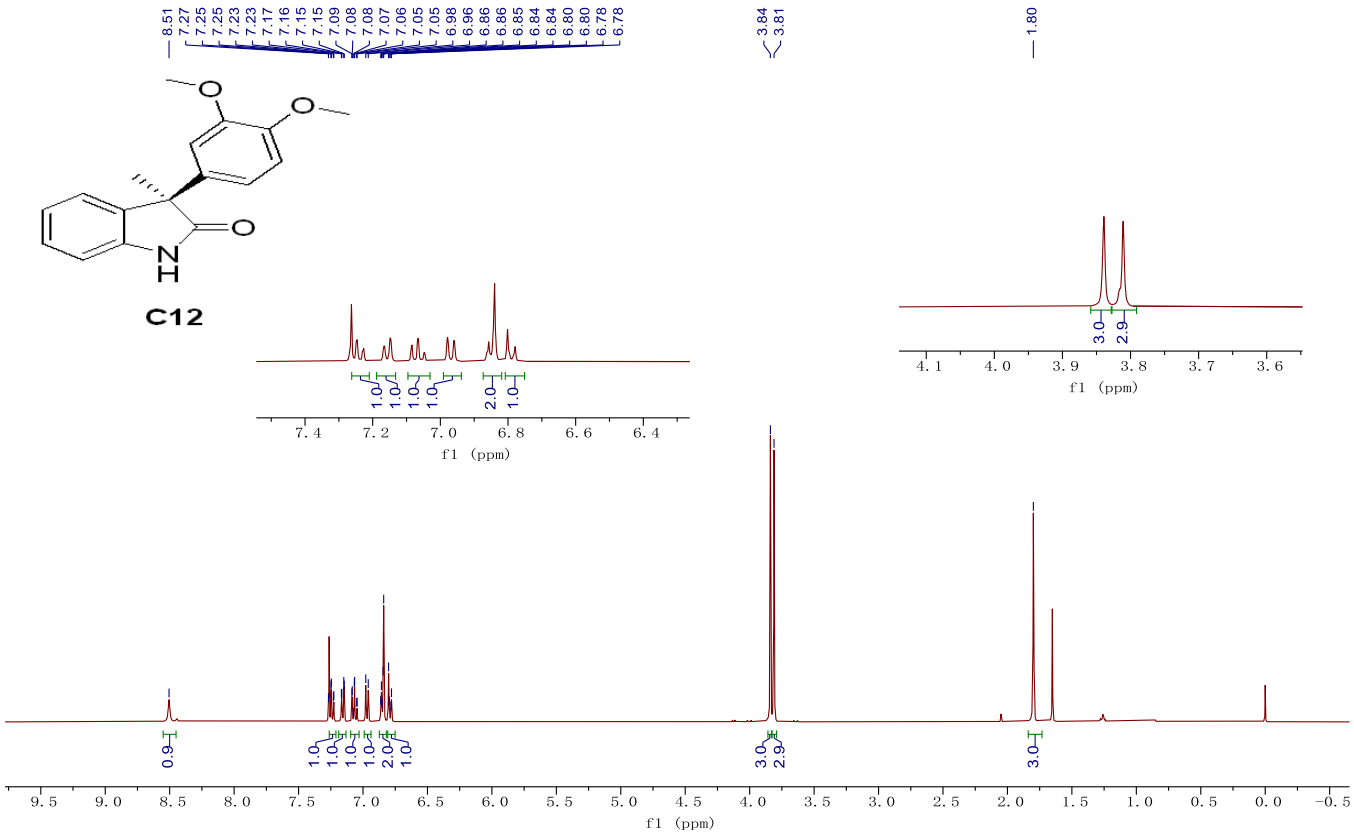
55.81
55.29
52.99
51.13
27.28
25.86
24.14
21.84
C11
C11′
f1 (ppm)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7.15
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7.08
7.08
7.07
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7.05
7.05
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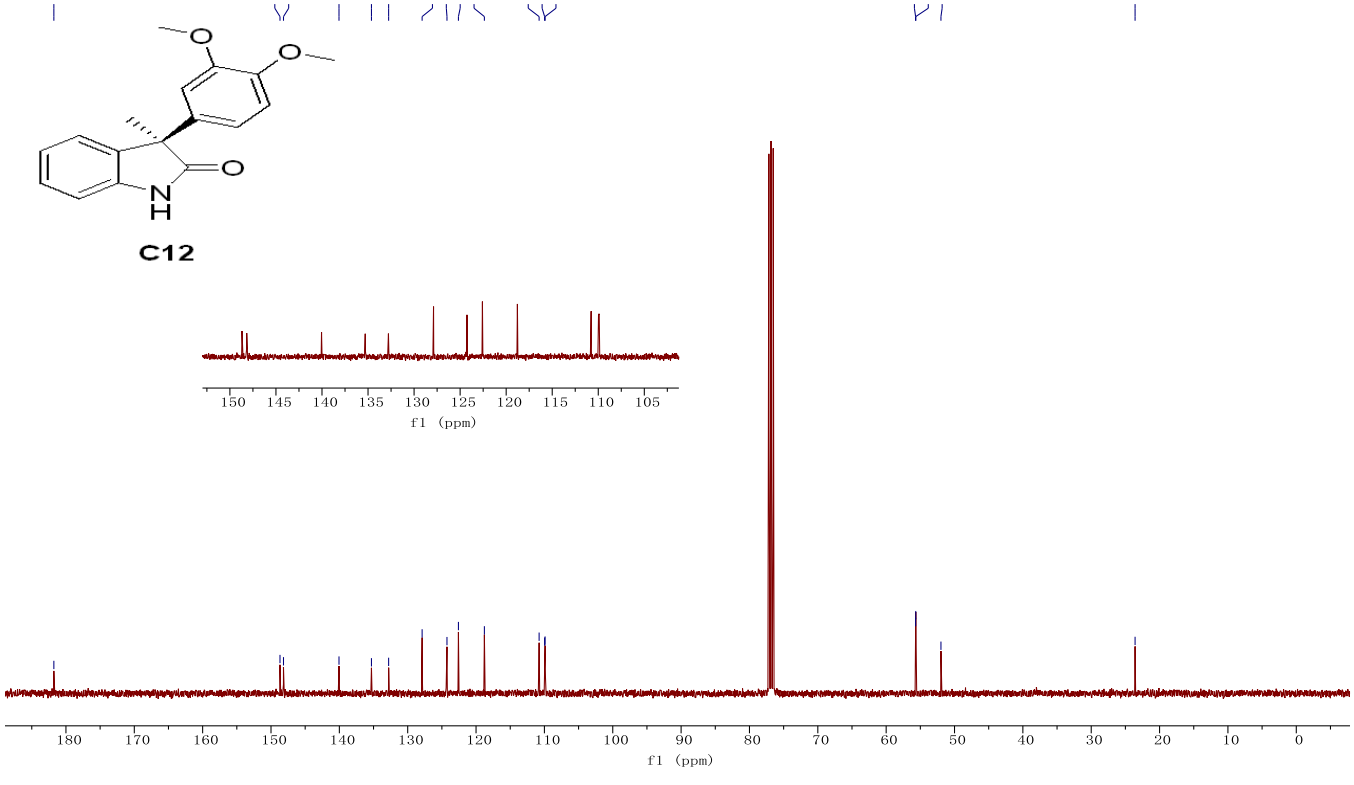
3.84
3.81
1.80
C12
f1 (ppm)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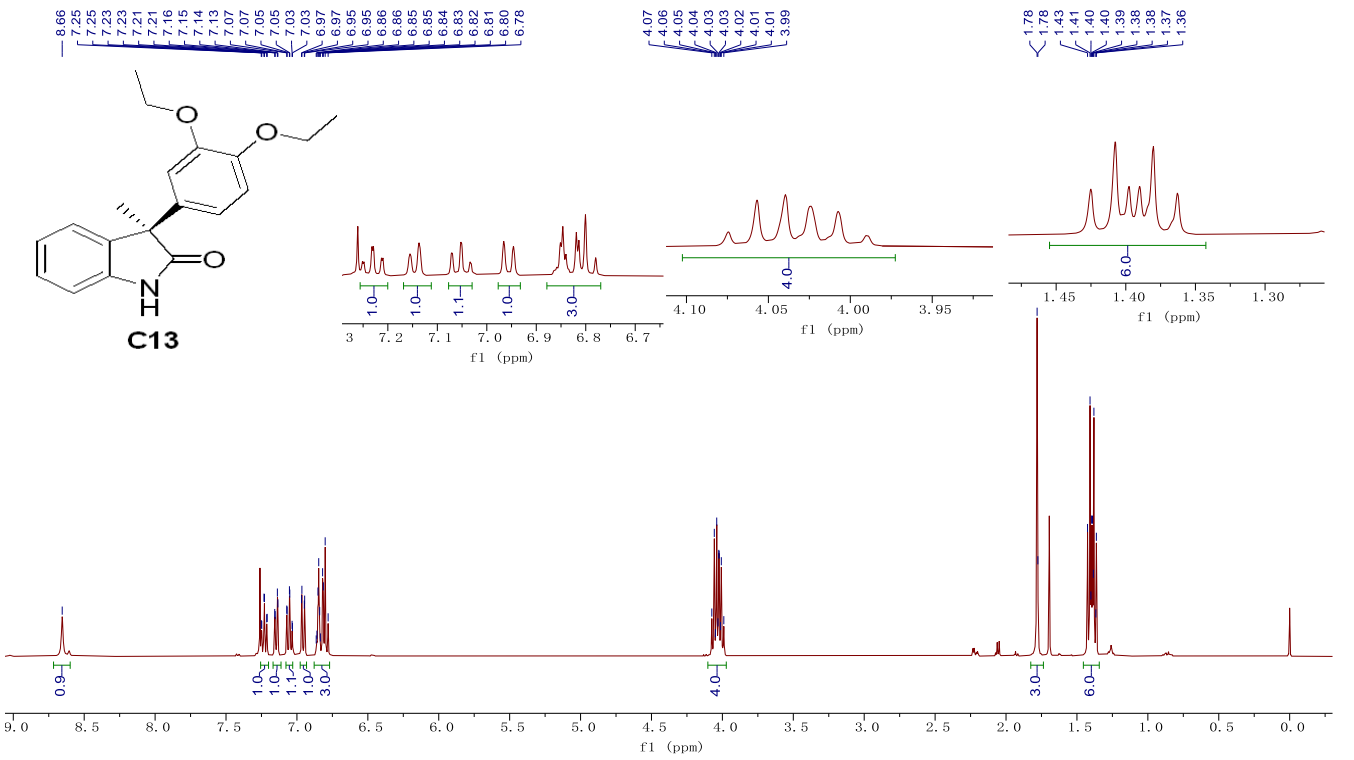
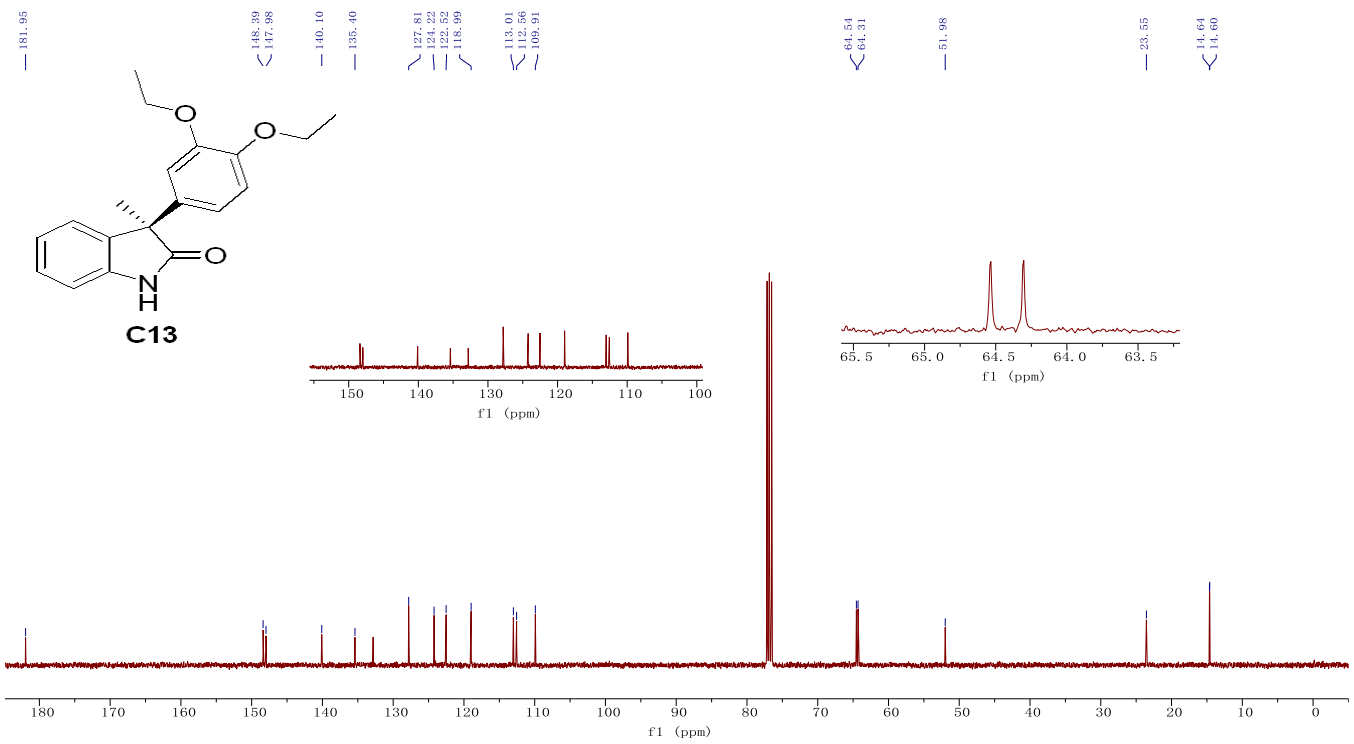
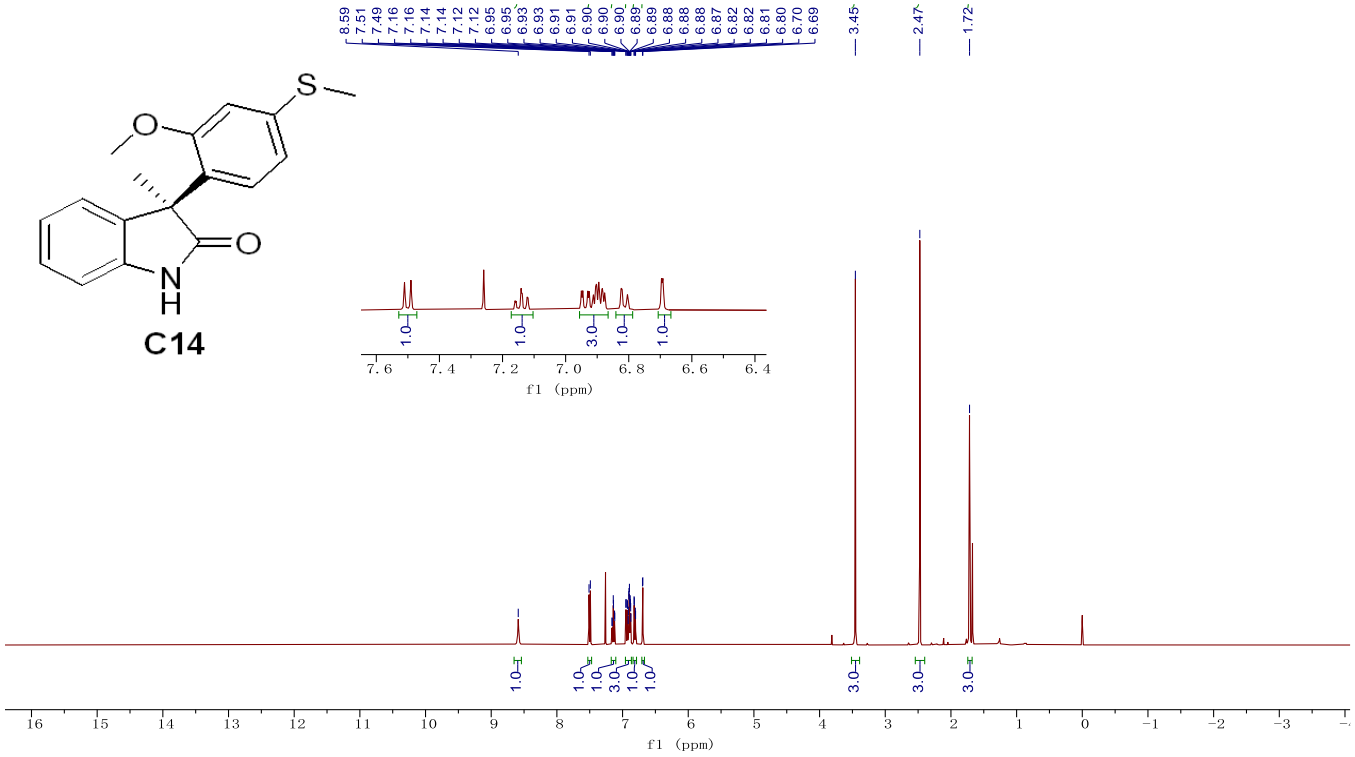
55.67
51.99
23.58
C12
f1 (ppm)


C13
f1 (ppm)


C13
f1 (ppm)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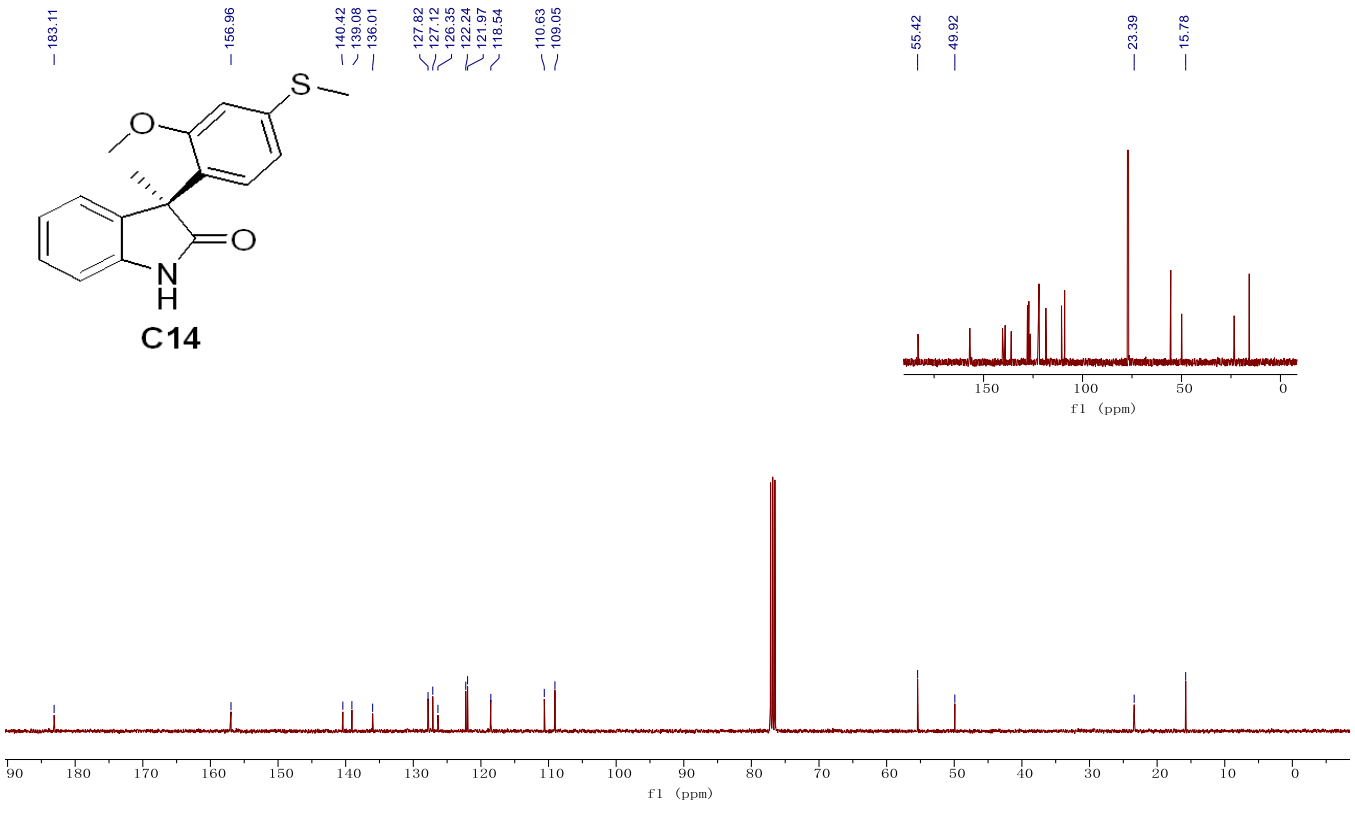
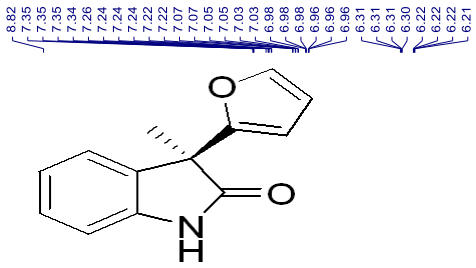
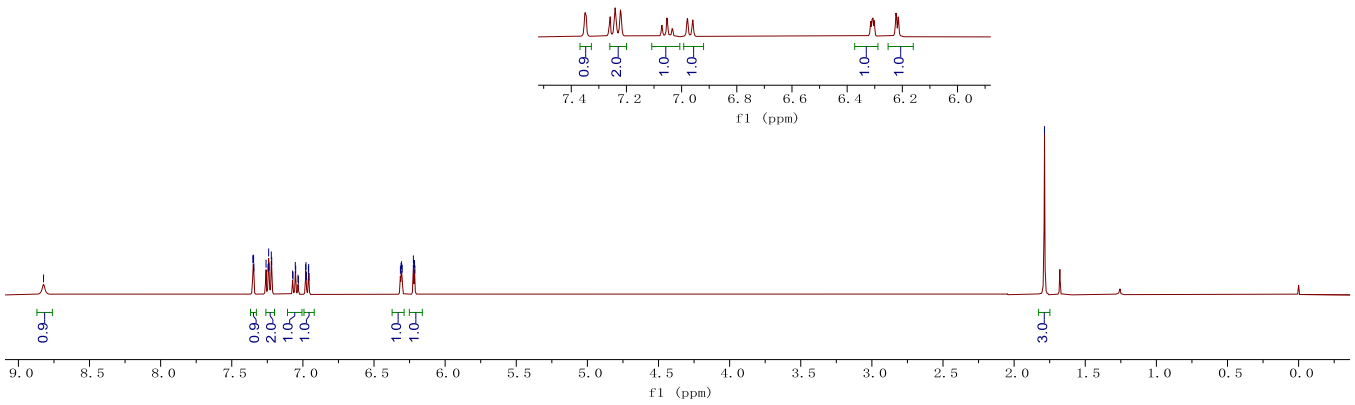
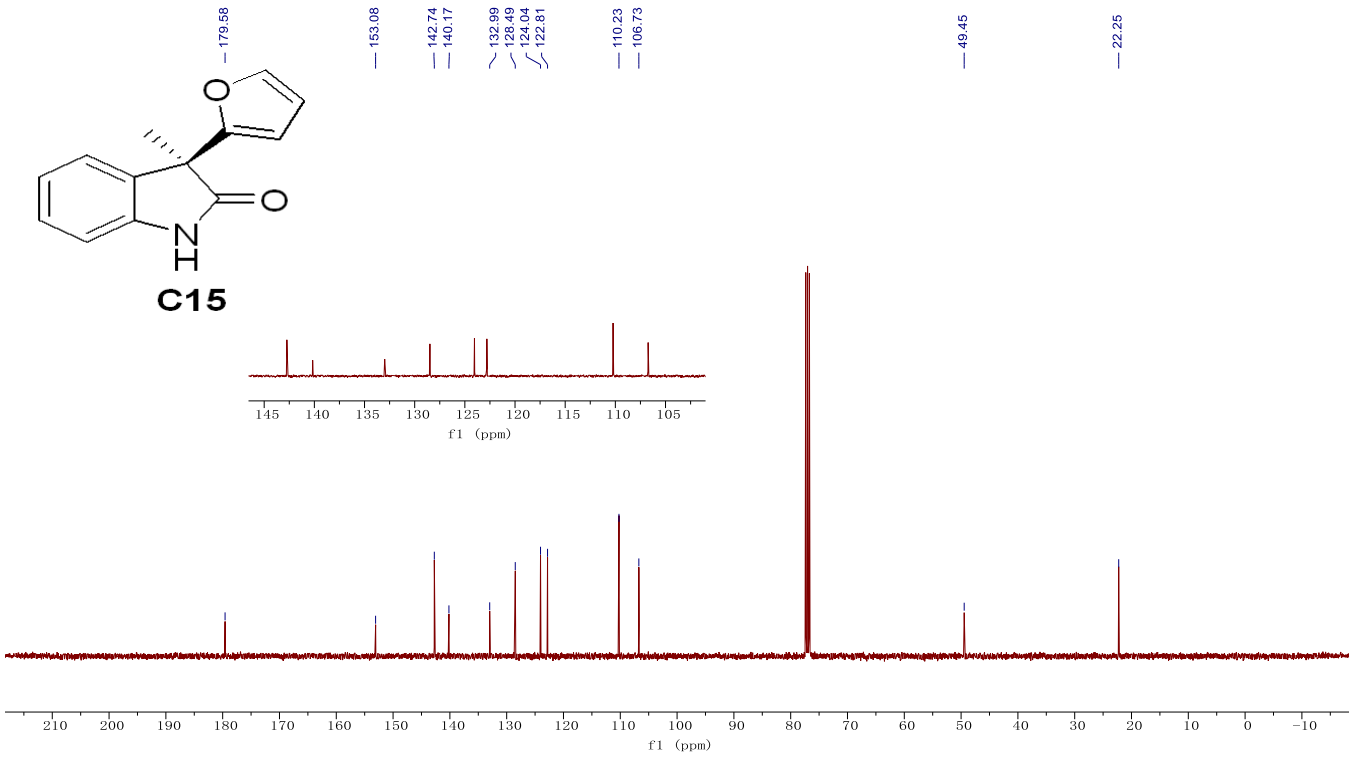
f1 (ppm)


C14
f1 (ppm)
f1 (ppm)

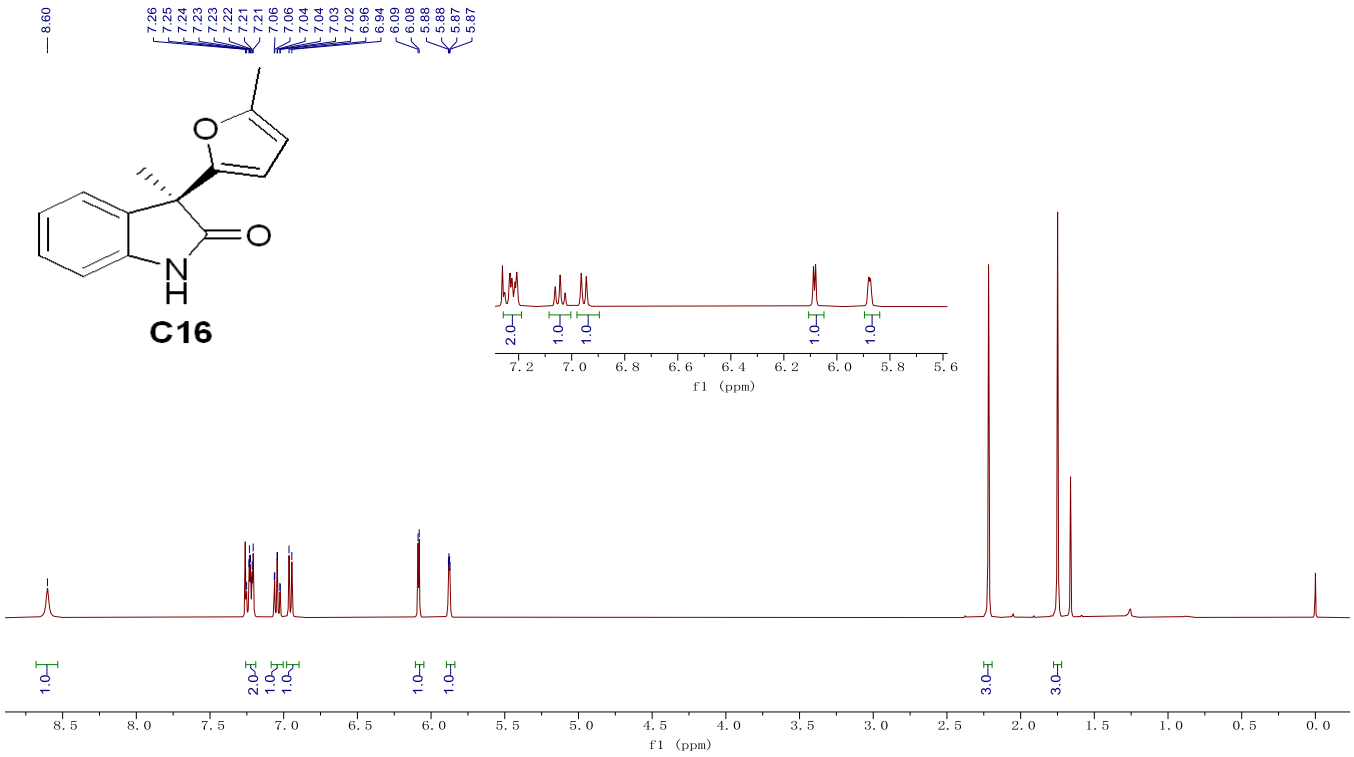


C15





C15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7.24
7.23
7.23
7.22
7.21
7.21
7.06
7.06
7.04
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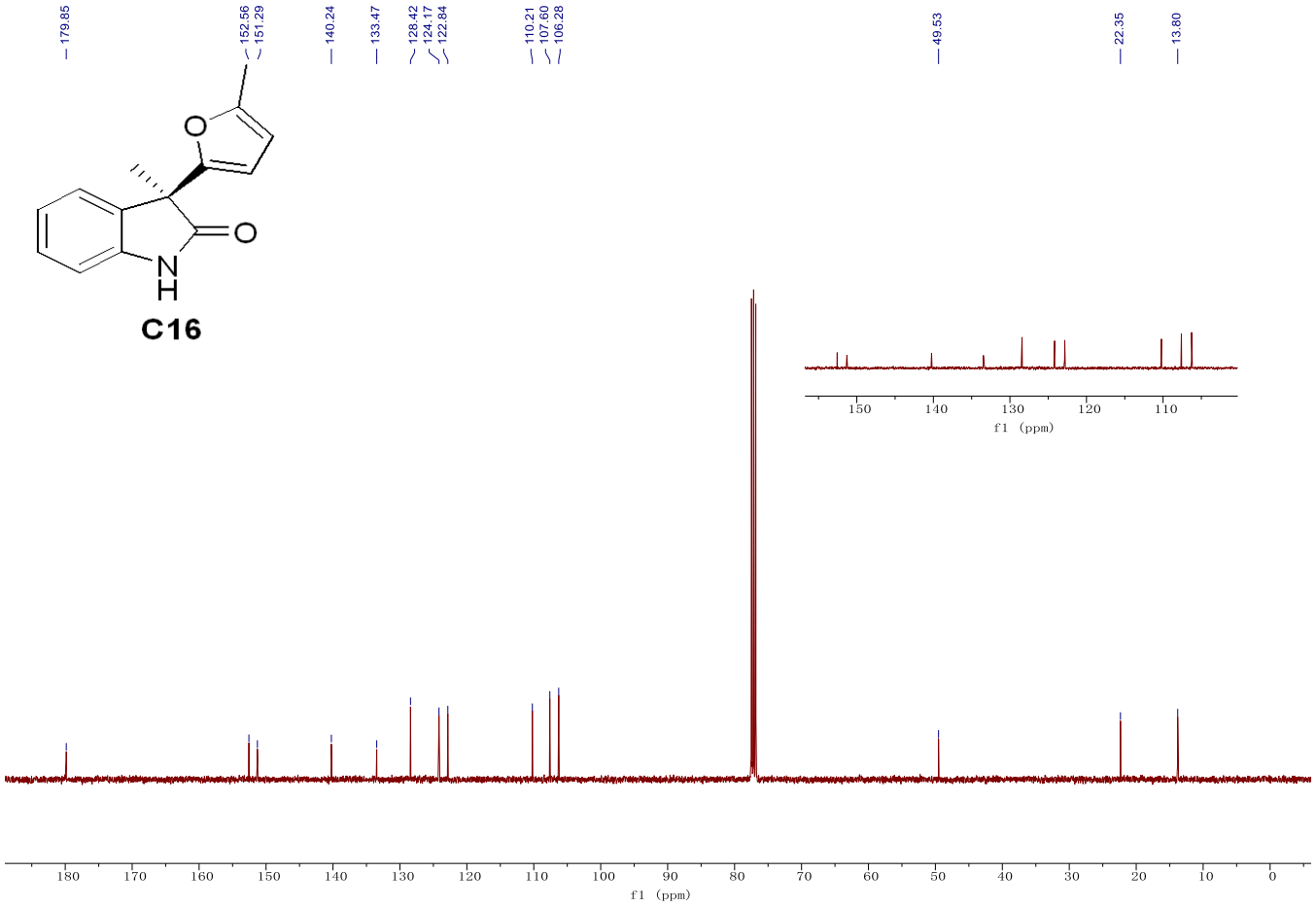
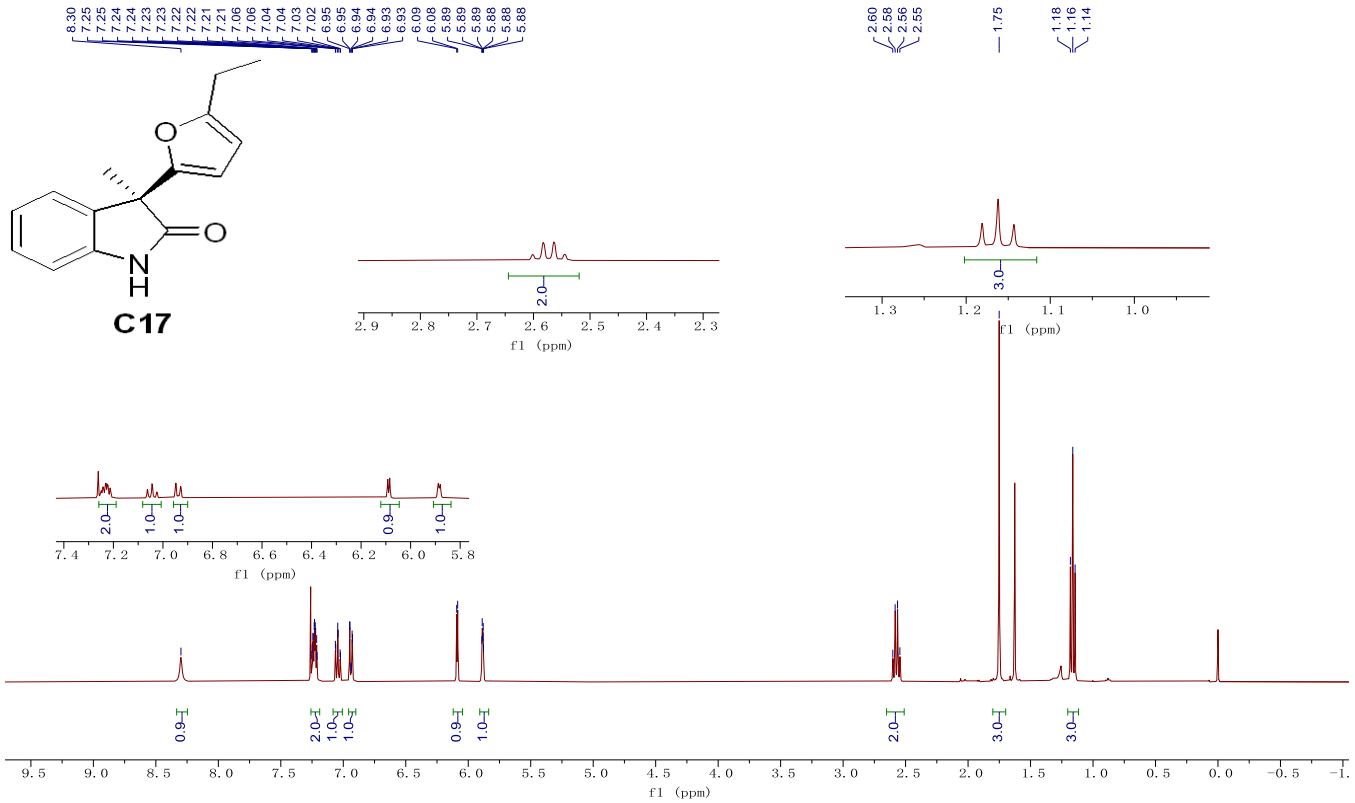
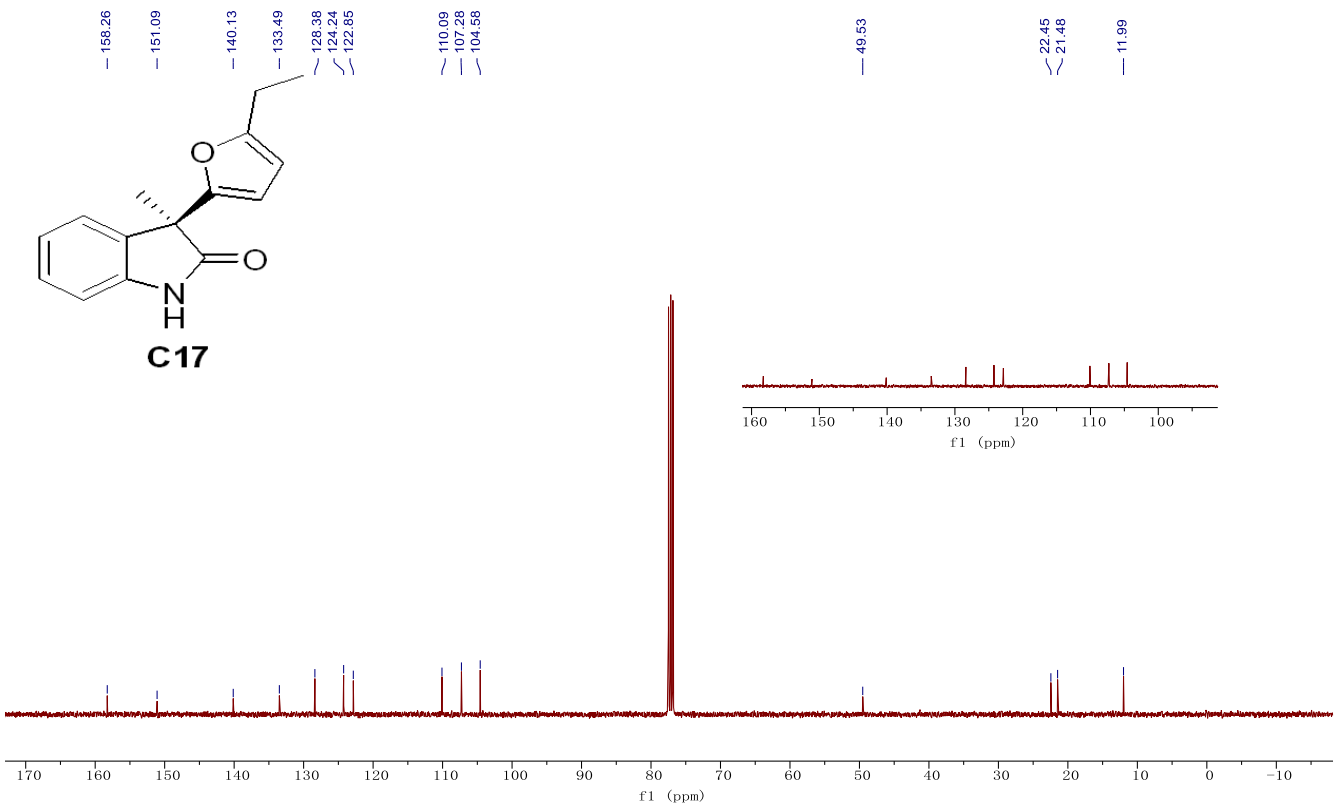
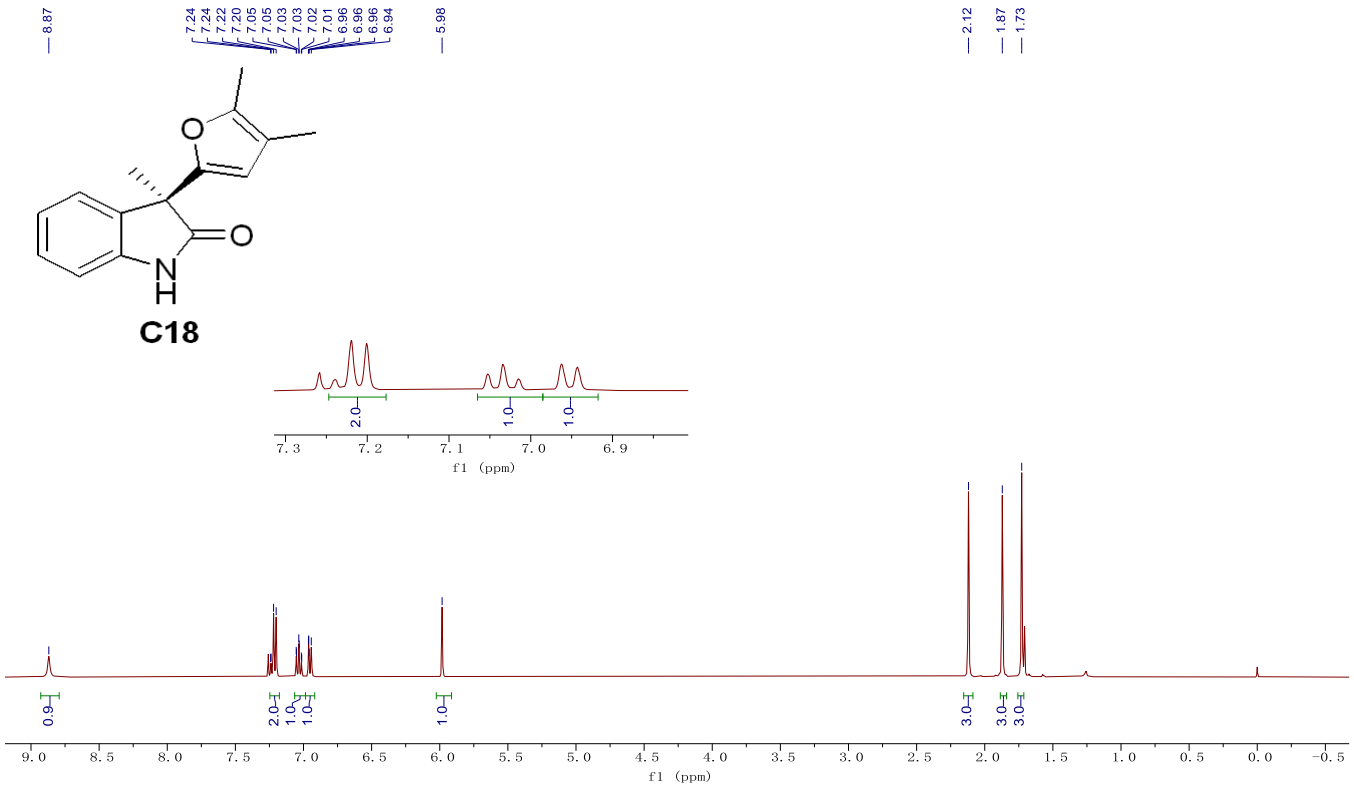
7.03
7.02
6.96
6.94
6.09
6.08
5.88
5.88
5.87
5.87
O
O
N
H
C16
2.0
1.0
1.0
1.0
1.0
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
f1 (ppm)
1.0
2.0
1.0
1.0
1.0
1.0
3.0
3.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

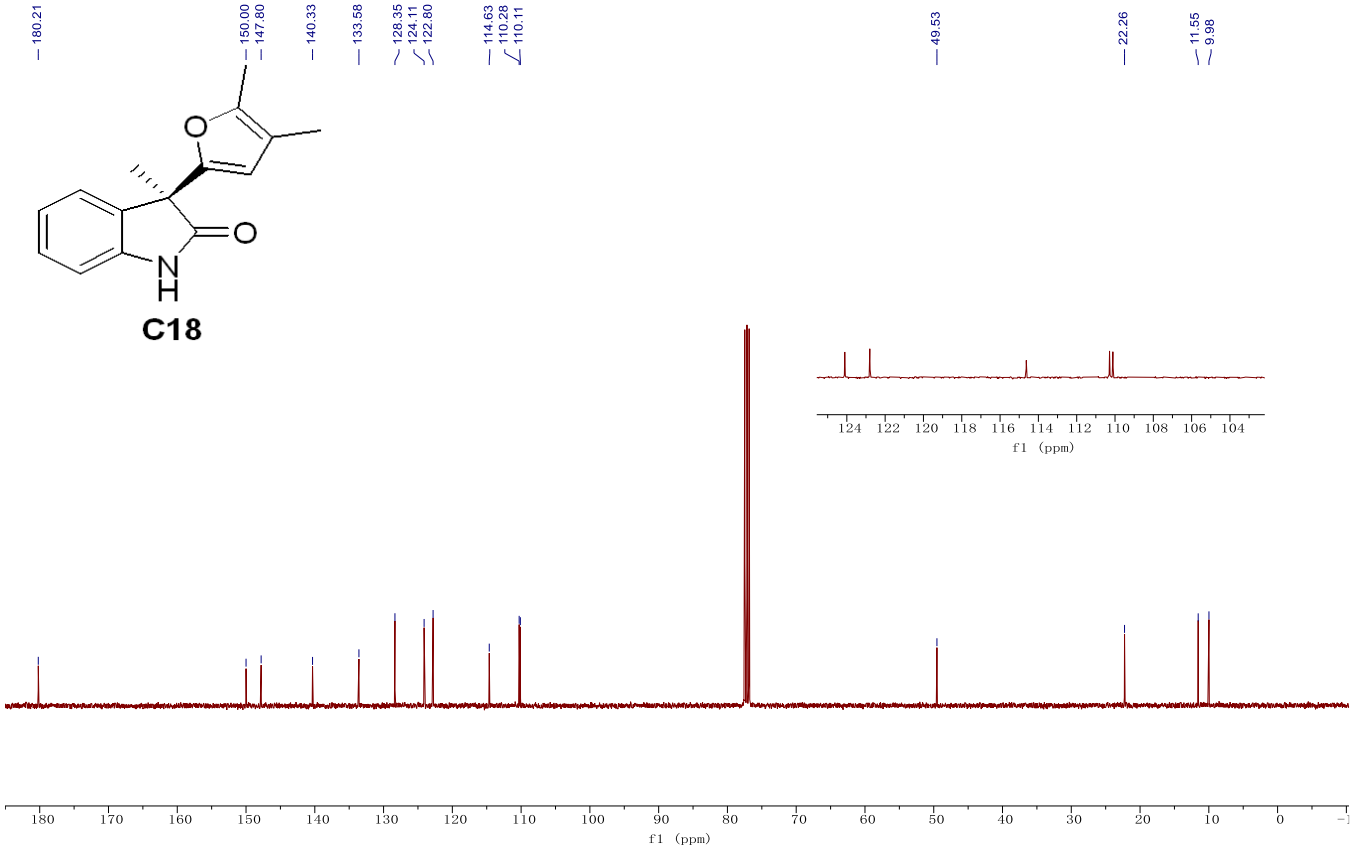

179.85
152.56
151.29
140.24
133.47
128.42
124.17
122.84
110.21
107.60
106.28
49.53
22.35
13.80
O
O
N
H
C16
150
140
130
120
110
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



V




8.87
7.24
7.24
7.22
7.20
7.05
7.05
7.03
7.03
7.02
7.01
6.96
6.96
6.96
6.94
5.98
2.12
1.87
1.73
O
O
N
H
C18
2.0
1.0
1.0
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
0.9
2.0
1.0
1.0
1.0
3.0
3.0
3.0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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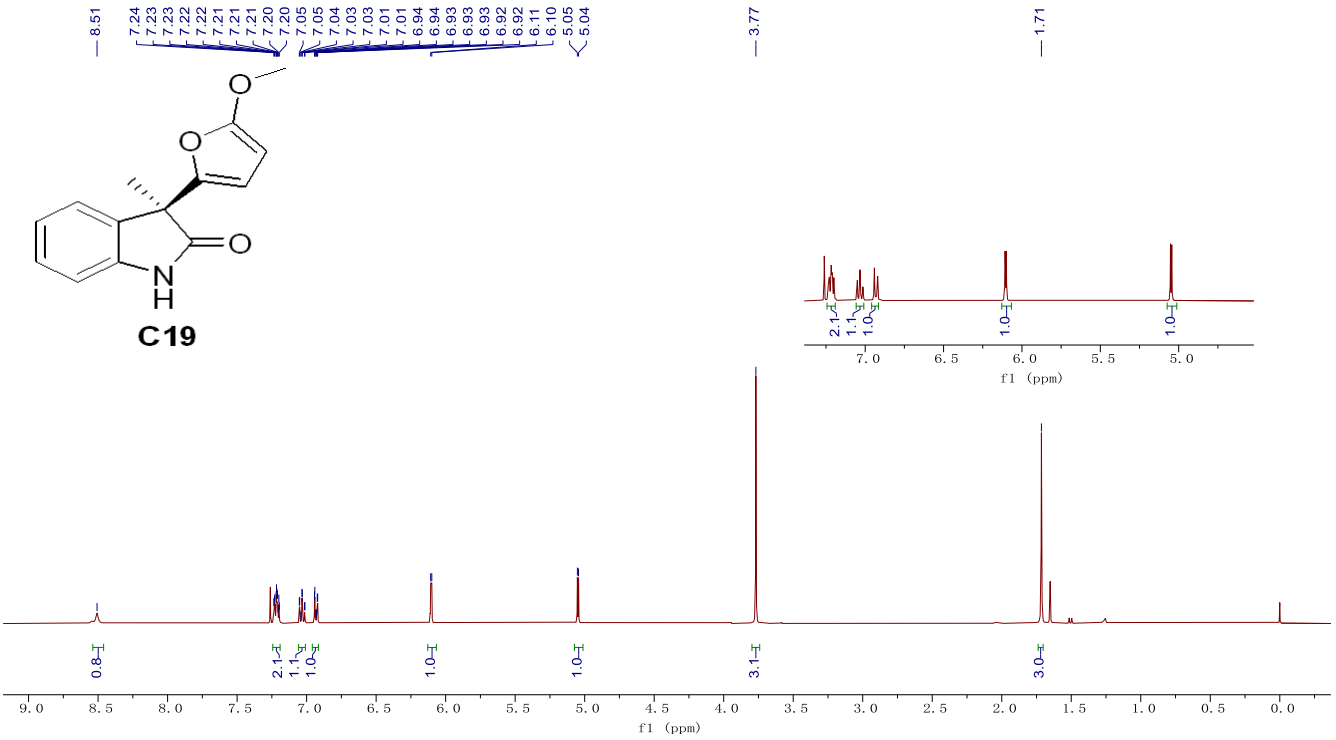
150.00
147.80
140.33
133.58
128.35
124.11
122.80
114.63
110.28
110.11
49.53
22.26
11.55
9.98
O
O
N
H
C18
124
122
120
118
116
114
112
110
108
106
104
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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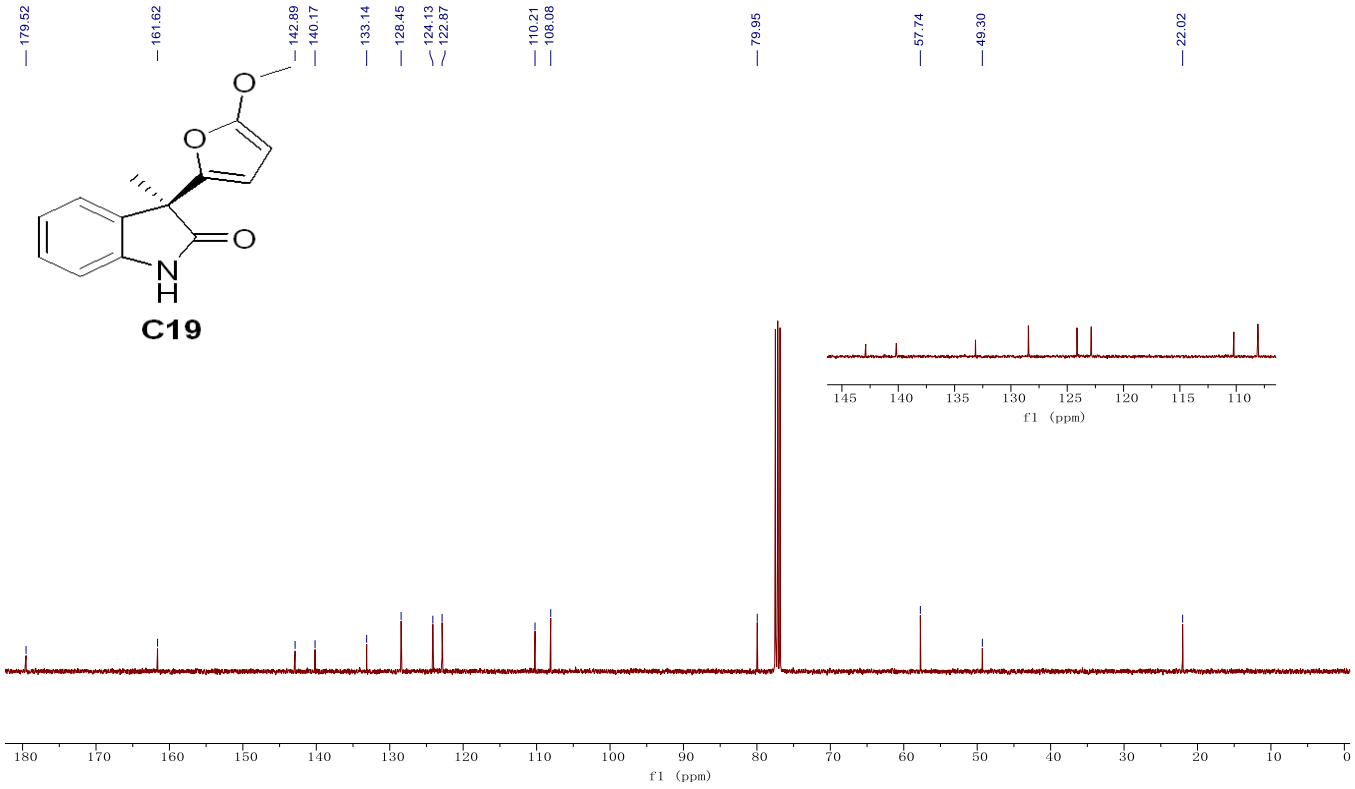
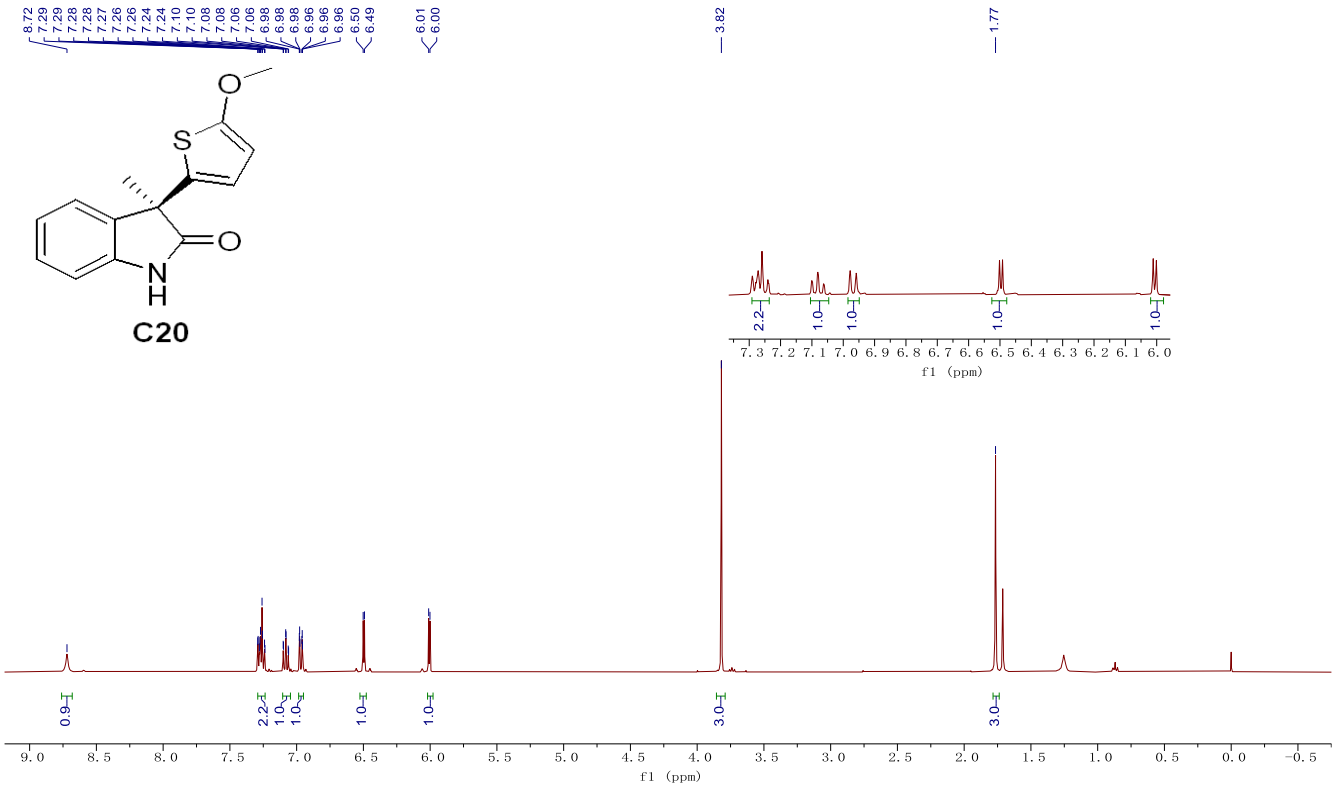
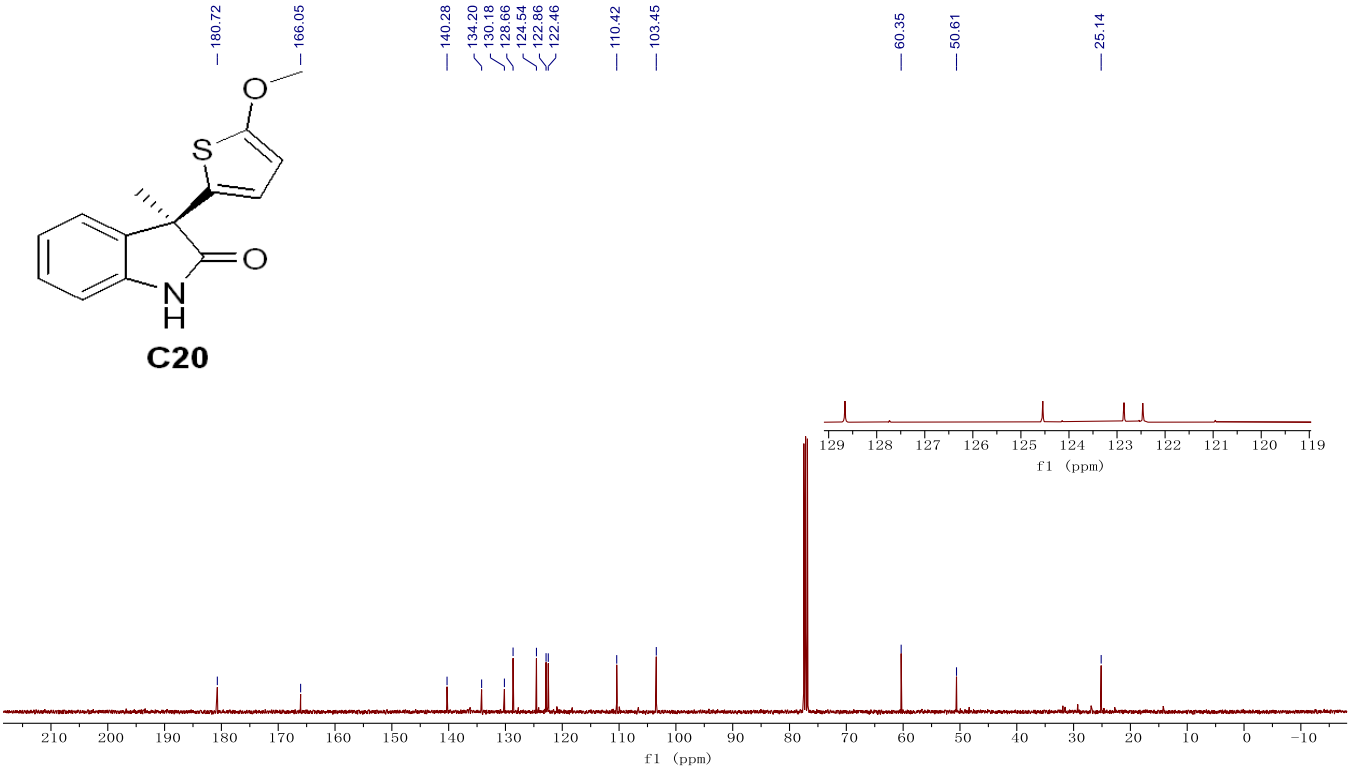
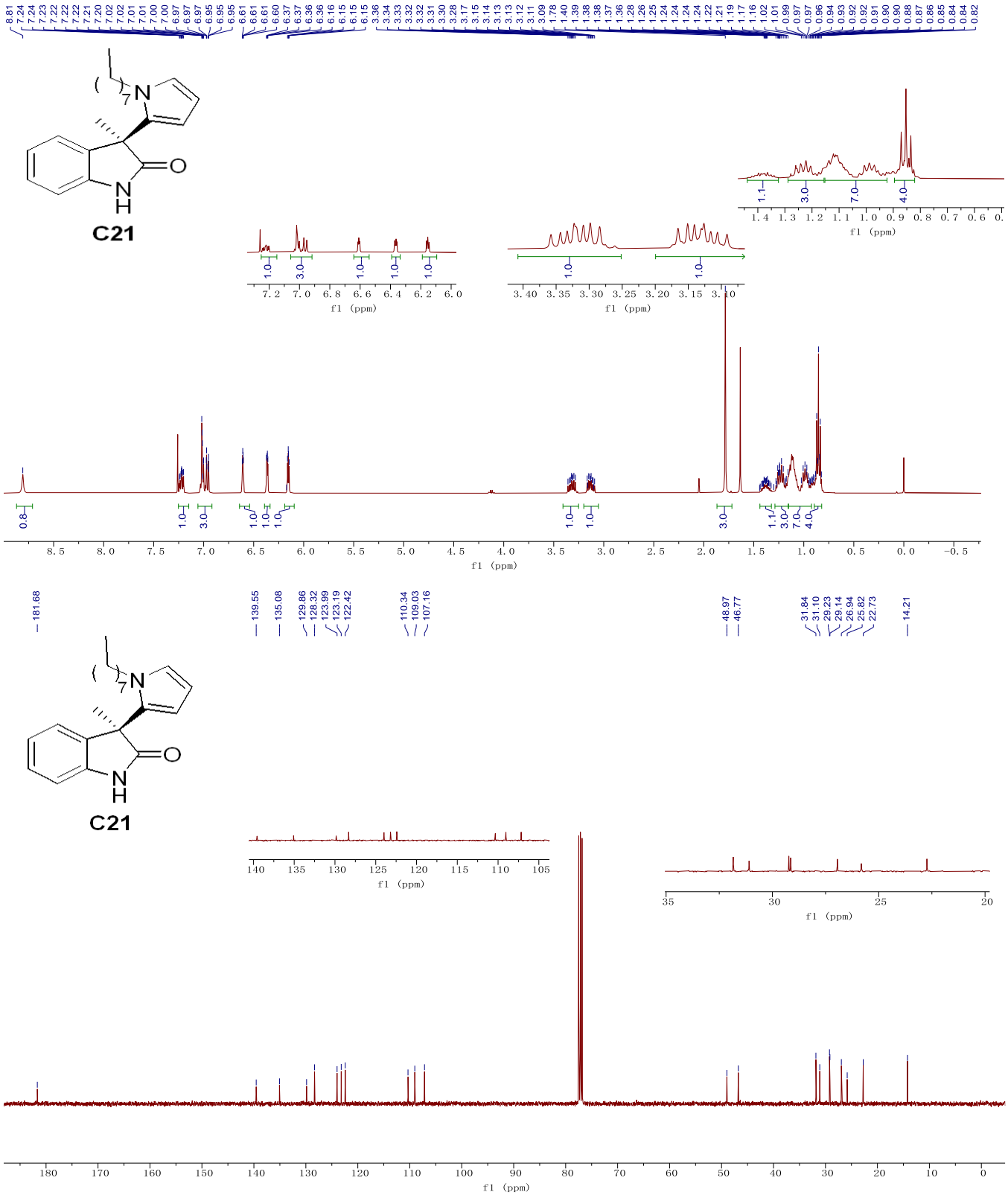
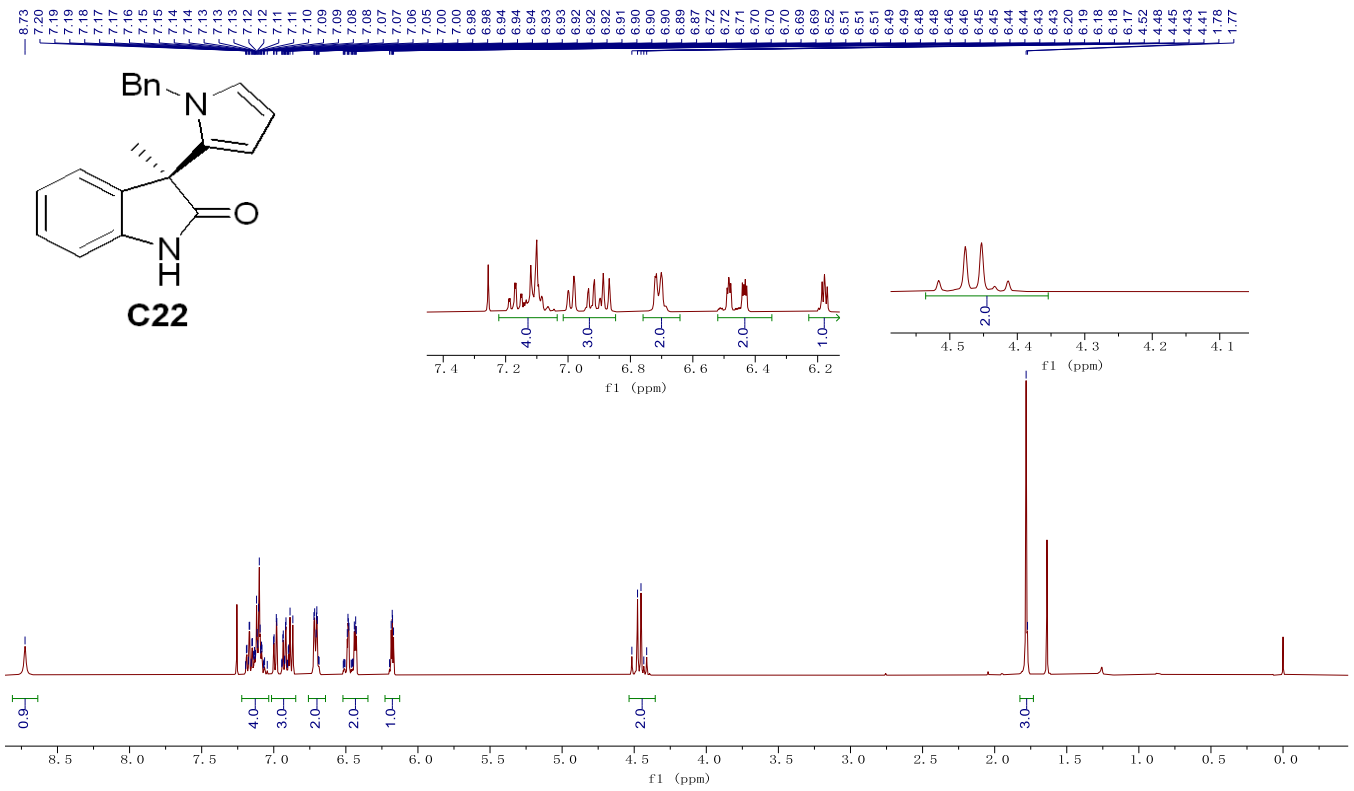
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.21
7.20
7.20
7.05
7.05
7.04
7.03
7.03
7.01
7.01
6.94
6.94
6.93
6.93
6.93
6.92
6.92
6.11
6.10
5.05
5.04
3.77
1.71
C19
0.8
2.1
1.1
1.0
1.0
1.0
3.1
3.0
f1 (ppm)

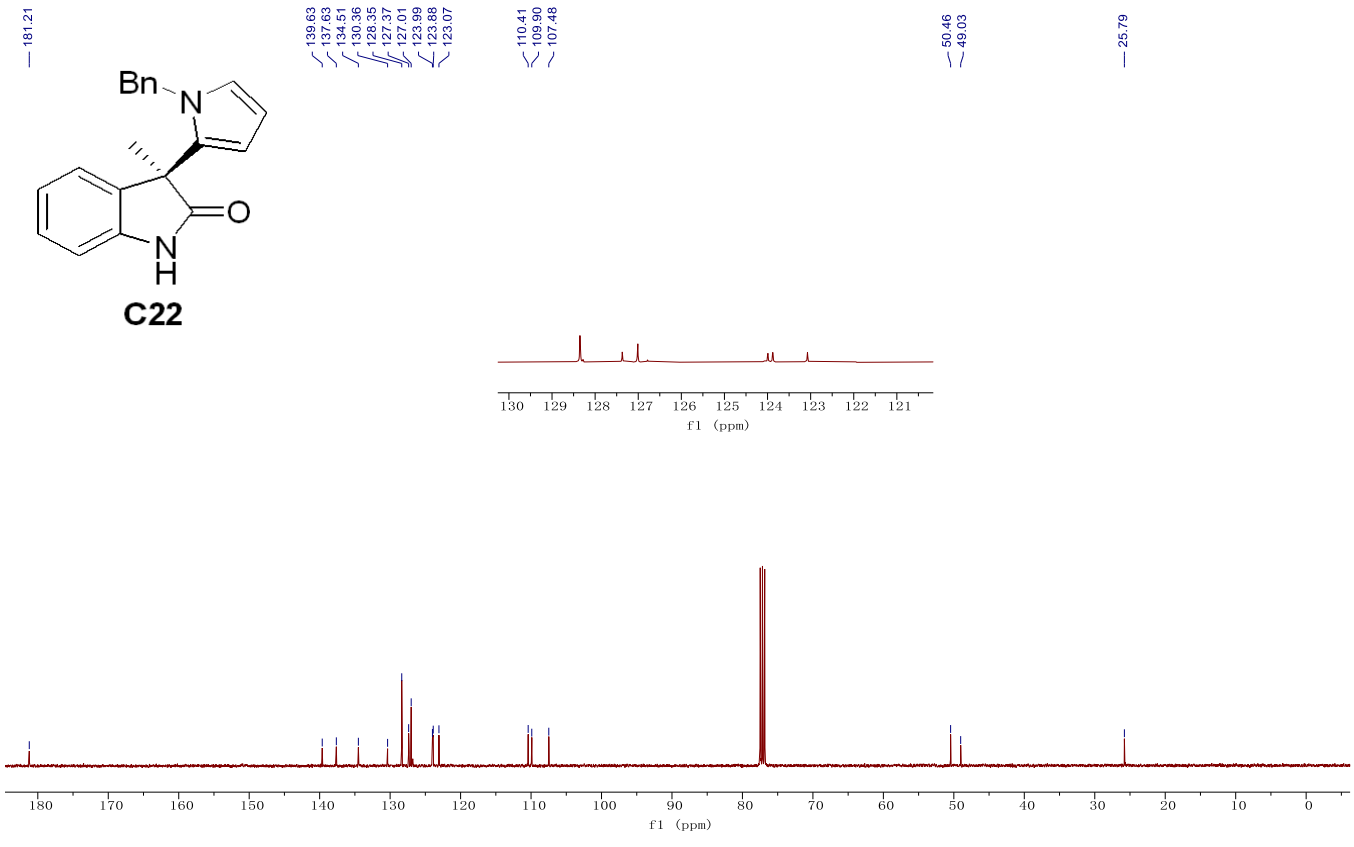

179.52
161.62
142.89
140.17
133.14
128.45
124.13
122.87
110.21
108.08
79.95
57.74
49.30
22.02
C19
f1 (ppm)

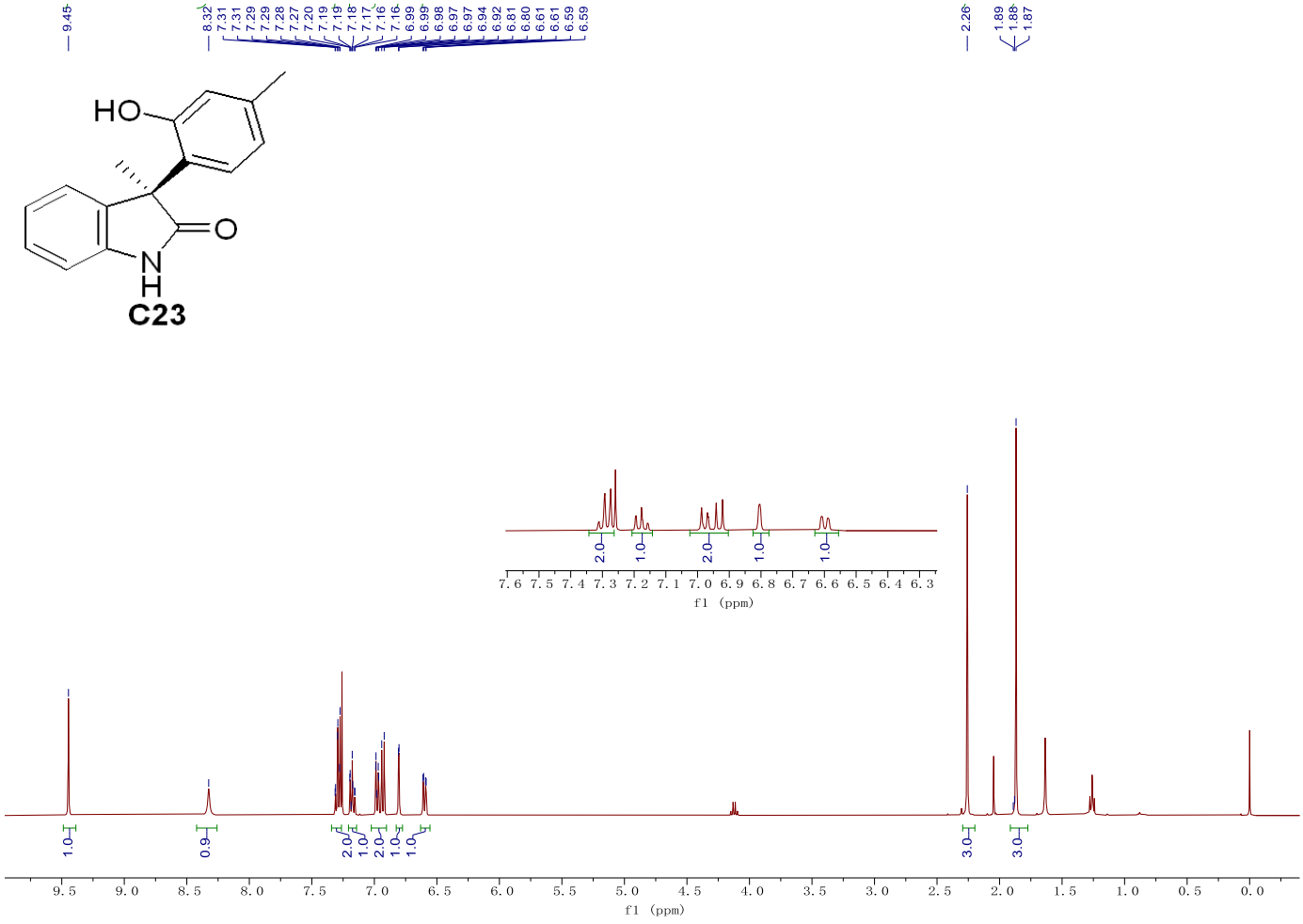

8.72
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.24
7.24
7.10
7.08
7.08
7.06
7.06
6.98
6.98
6.96
6.96
6.96
6.50
6.49
6.01
6.00
3.82
1.77
O
S
O
N
H
C20
2.2
1.0
1.0
1.0
1.0
f1 (ppm)
0.9
2.2
1.0
1.0
1.0
1.0
3.0
3.0
f1 (ppm)

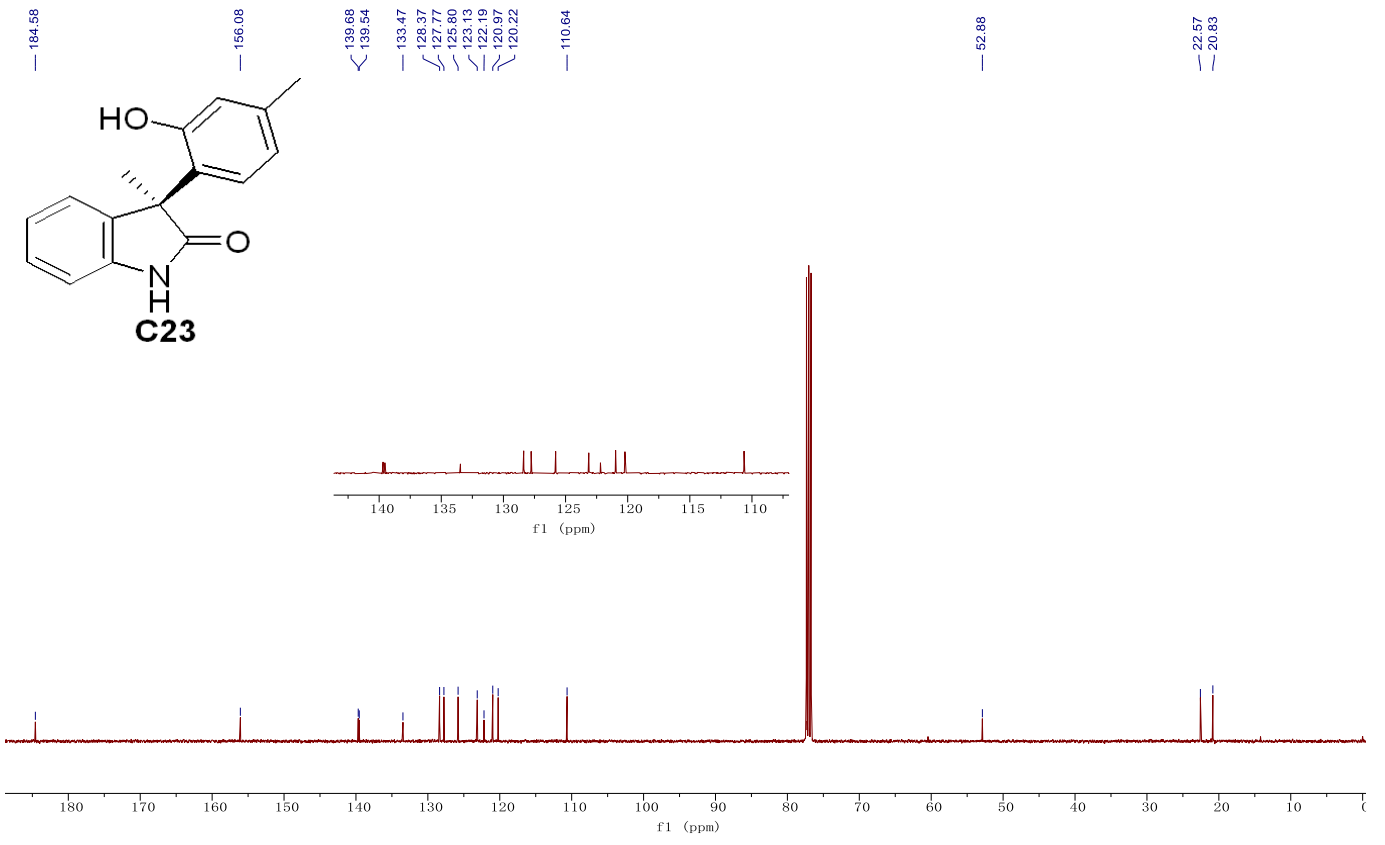

180.72
166.05
140.28
134.20
130.18
128.66
124.54
122.86
122.46
110.42
103.45
60.35
50.61
25.14
O
S
O
N
H
C20
f1 (ppm)
f1 (ppm)

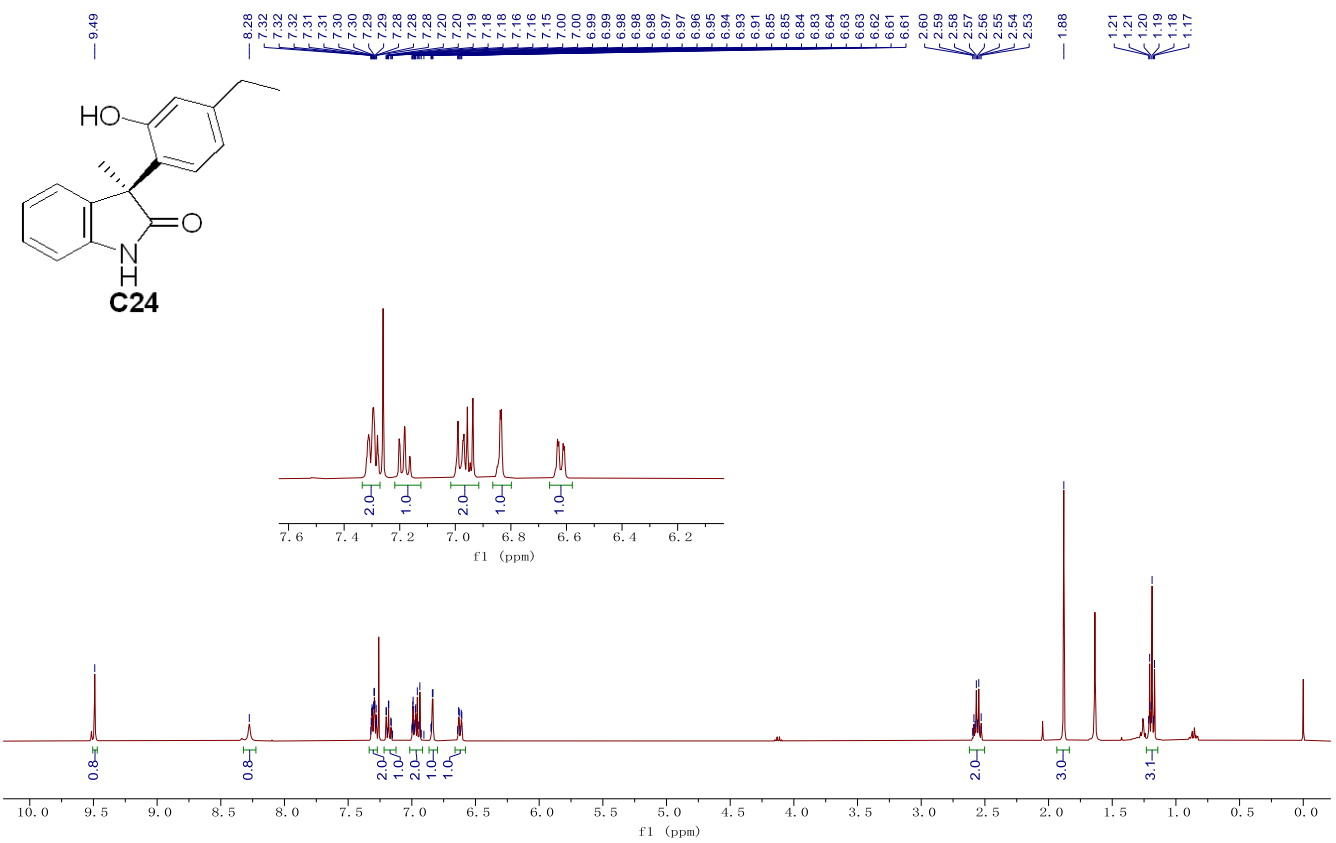

C21
f1 (ppm)
C21
f1 (ppm)

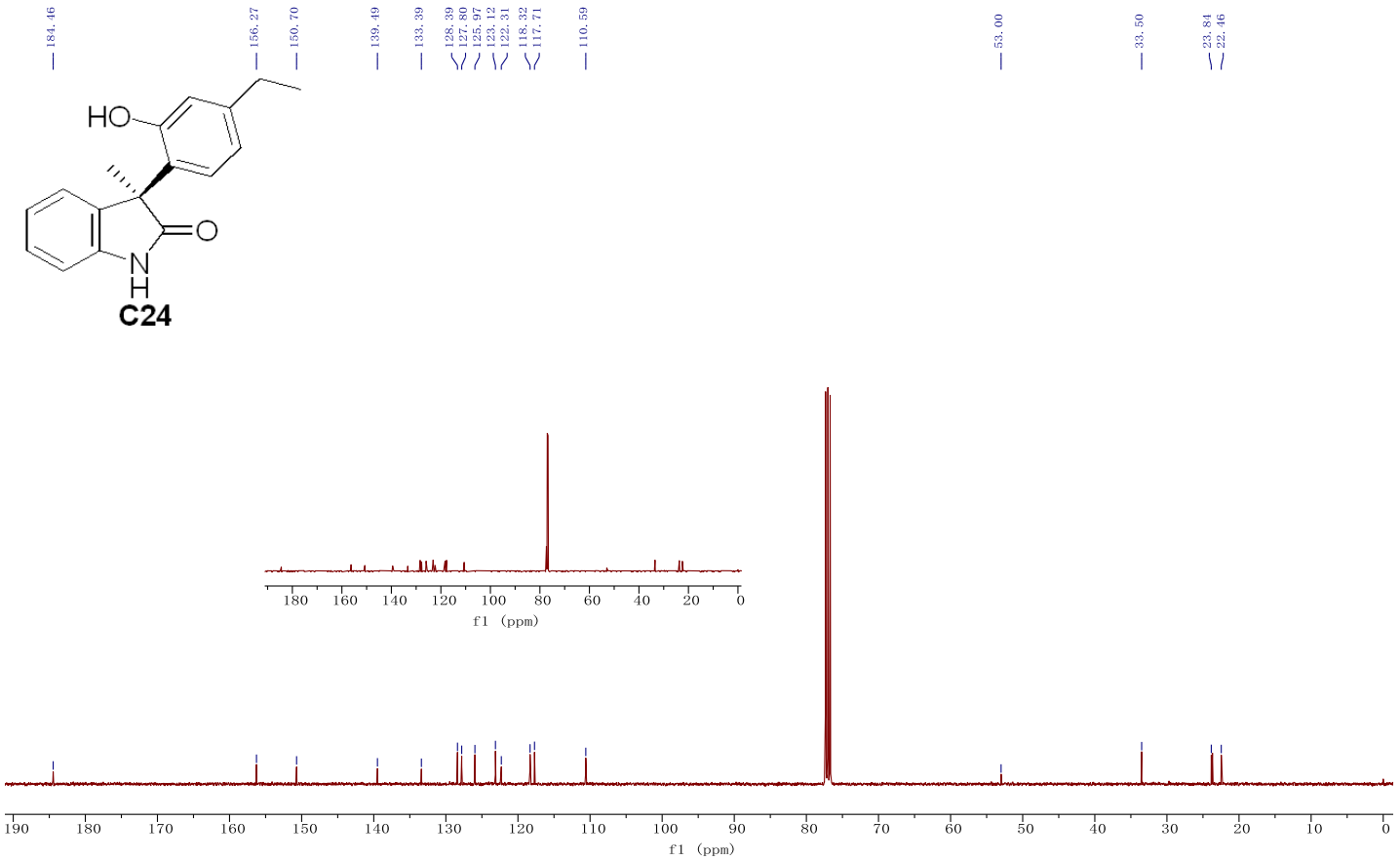

8.73 7.20 7.19 7.19 7.18 7.17 7.17 7.16 7.15 7.15 7.14 7.14 7.13 7.13 7.13 7.12 7.12 7.11 7.11 7.10 7.09 7.09 7.08 7.08 7.07 7.07 7.06 7.05 7.00 7.00 6.98 6.98 6.94 6.94 6.94 6.93 6.93 6.92 6.92 6.92 6.91 6.90 6.90 6.90 6.89 6.87 6.72 6.72 6.71 6.70 6.70 6.70 6.69 6.69 6.52 6.51 6.51 6.49 6.49 6.48 6.48 6.46 6.46 6.45 6.45 6.44 6.44 6.43 6.43 6.20 6.19 6.18 6.18 6.17 4.52 4.48 4.45 4.43 4.41 1.78 1.77
Bn
N
O
N
H
C22
4.0
3.0
2.0
2.0
1.0
7.4 7.2 7.0 6.8 6.6 6.4 6.2
f1 (ppm)
2.0
4.5 4.4 4.3 4.2 4.1
f1 (ppm)
0.9
4.0
3.0
2.0
2.0
1.0
2.0
3.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

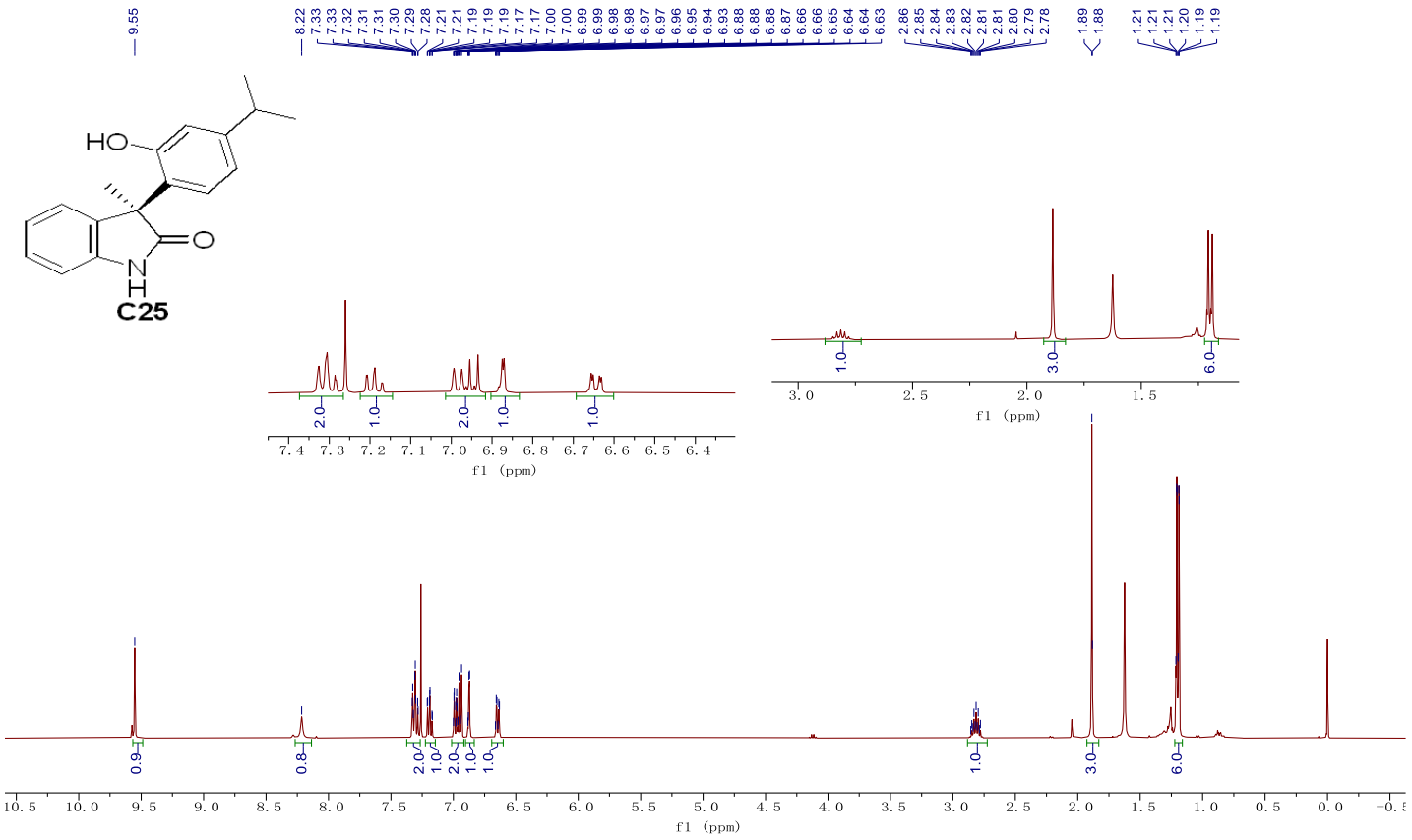

181.21
139.63
137.63
134.51
130.36
128.35
127.37
127.01
123.99
123.88
123.07
110.41
109.90
107.48
50.46
49.03
25.79
Bn
N
O
N
H
C22
130 129 128 127 126 125 124 123 122 121
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.45
8.32
7.31
7.31
7.29
7.29
7.28
7.27
7.20
7.19
7.19
7.18
7.17
7.16
7.16
6.99
6.99
6.98
6.97
6.97
6.94
6.92
6.81
6.80
6.61
6.61
6.59
6.59
2.26
1.89
1.88
1.87
HO
O
N
H
C23
f1 (ppm)
f1 (ppm)


184.58
156.08
139.68
139.54
133.47
128.37
127.77
125.80
123.13
122.19
120.97
120.22
110.64
52.88
22.57
20.83
HO
O
N
H
C23
f1 (ppm)
f1 (ppm)


HO
O
N
H
C24
f1 (ppm)


HO
O
N
H
C24
f1 (ppm)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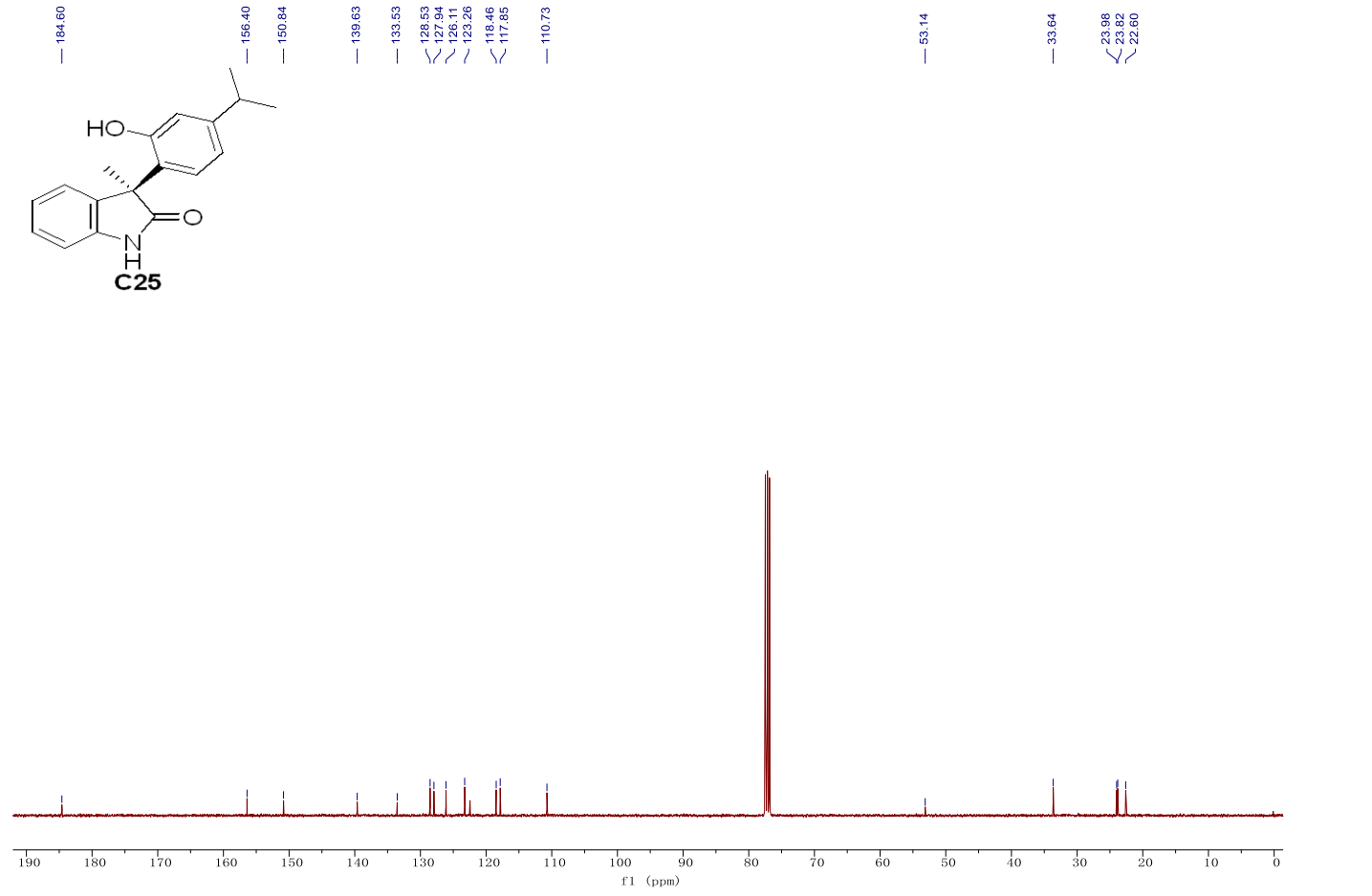
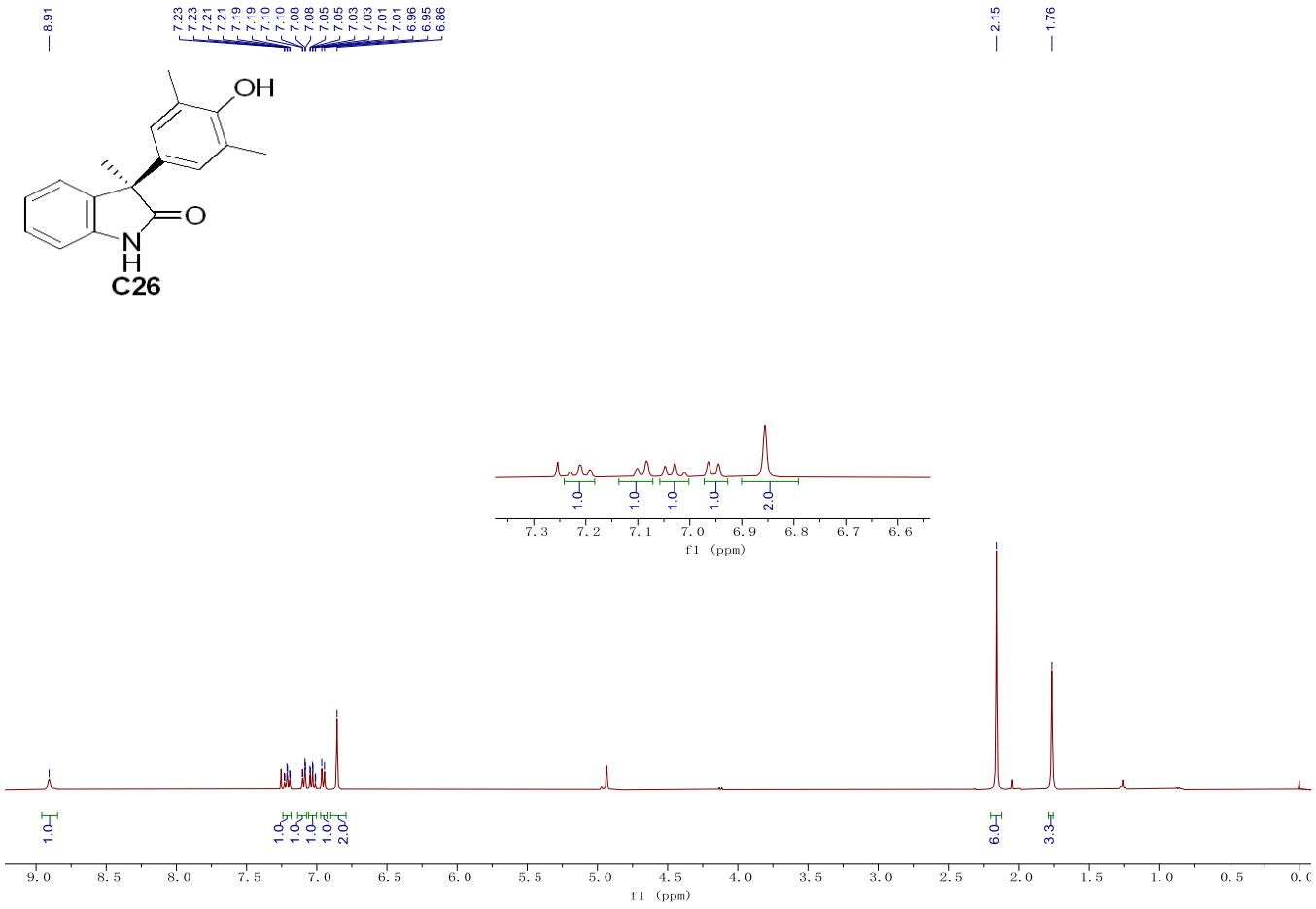
7.33
7.32
7.31
7.30
7.29
7.28
7.21
7.19
7.17
7.00
6.99
6.98
6.97
6.96
6.95
6.94
6.93
6.88
6.87
6.66
6.65
6.64
6.63
2.86
2.85
2.84
2.83
2.82
2.81
2.80
2.79
2.78
1.89
1.88
1.21
1.20
1.19
HO
O
N
H
C25
f1 (ppm)


184.60
156.40
150.84
139.63
133.53
128.53
127.94
126.11
123.26
118.46
117.85
110.73
53.14
33.64
23.98
23.82
22.60
HO
O
N
H
C25
f1 (ppm)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7.23
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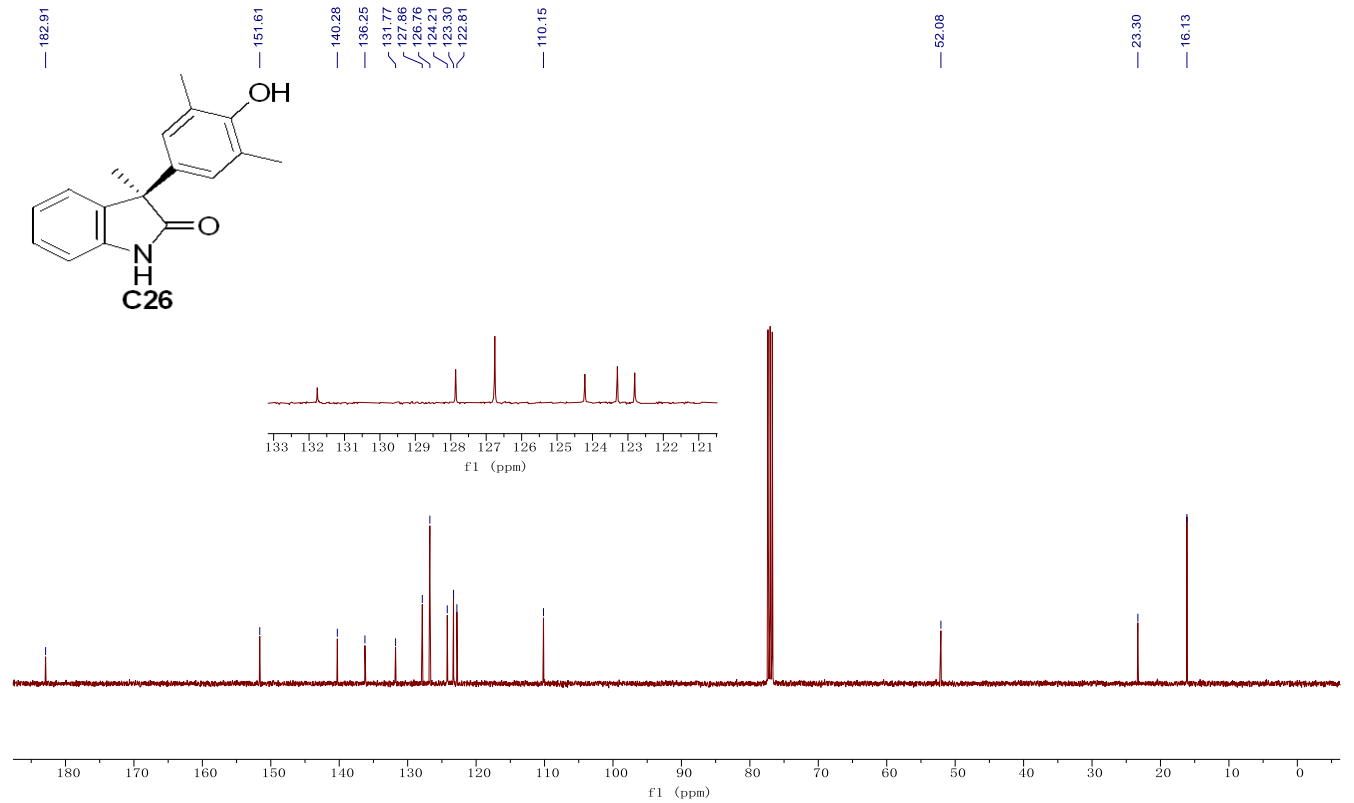
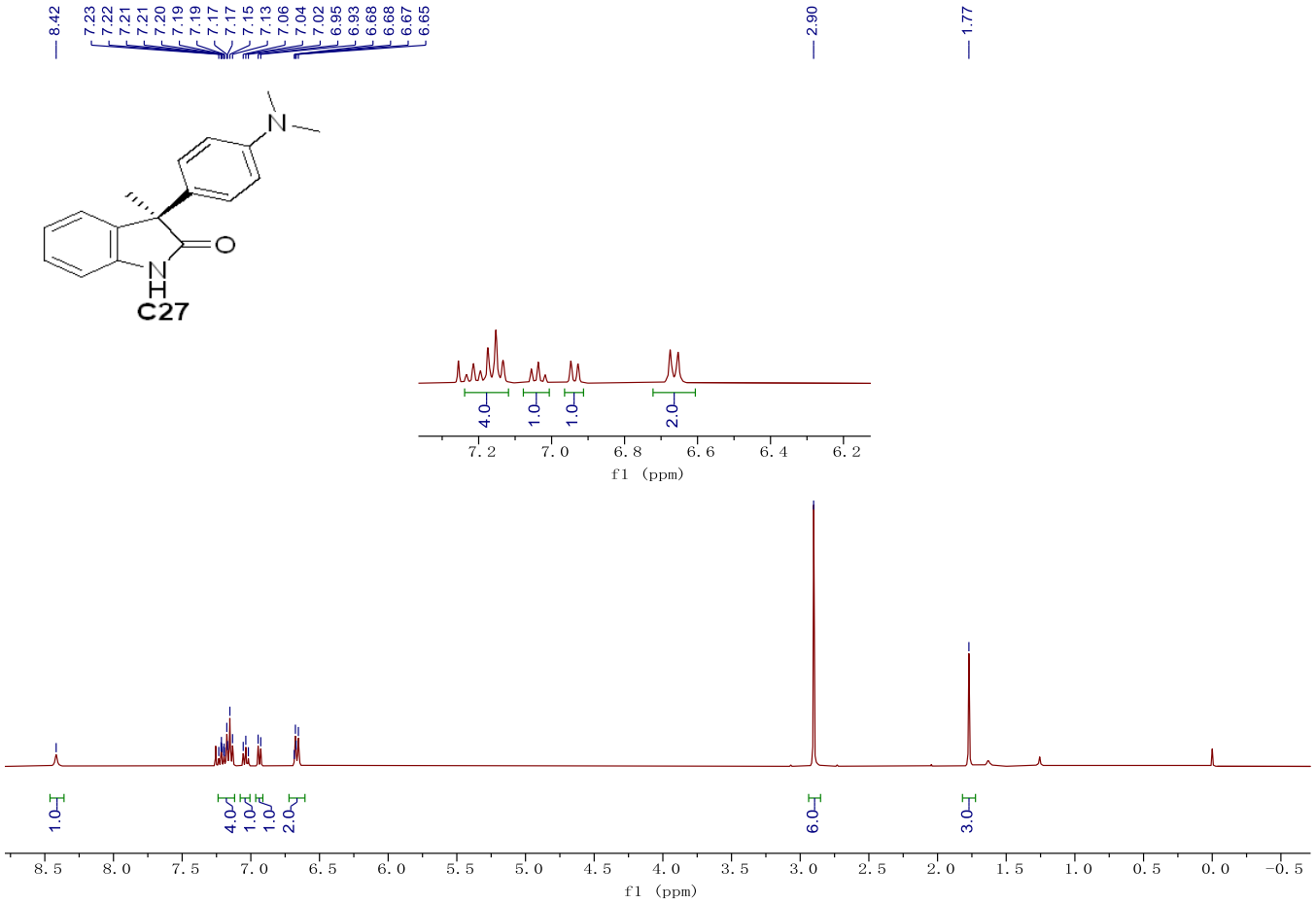
7.21
7.19
7.19
7.10
7.10
7.08
7.08
7.05
7.05
7.03
7.03
7.01
7.01
6.96
6.95
6.86
2.15
1.76
OH
O
N
H
C26
1.0
1.0
1.0
1.0
2.0
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
f1 (ppm)
1.0
1.0
1.0
1.0
1.0
2.0
6.0
3.3
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


182.91
151.61
140.28
136.25
131.77
127.86
126.76
124.21
123.30
122.81
110.15
52.08
23.30
16.13
OH
O
N
H
C26
133
132
131
130
129
128
127
126
125
124
123
122
121
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.23
7.22
7.21
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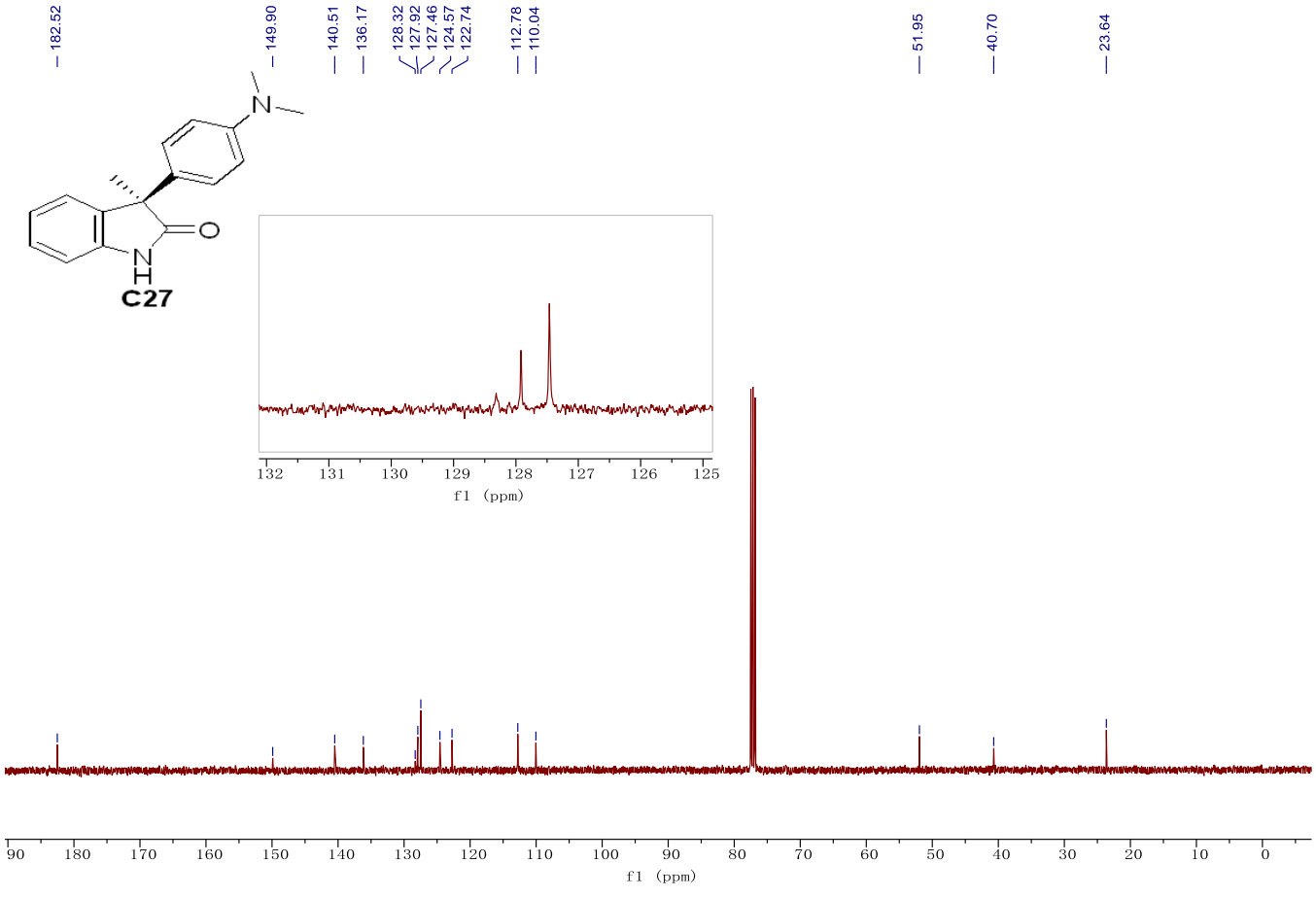
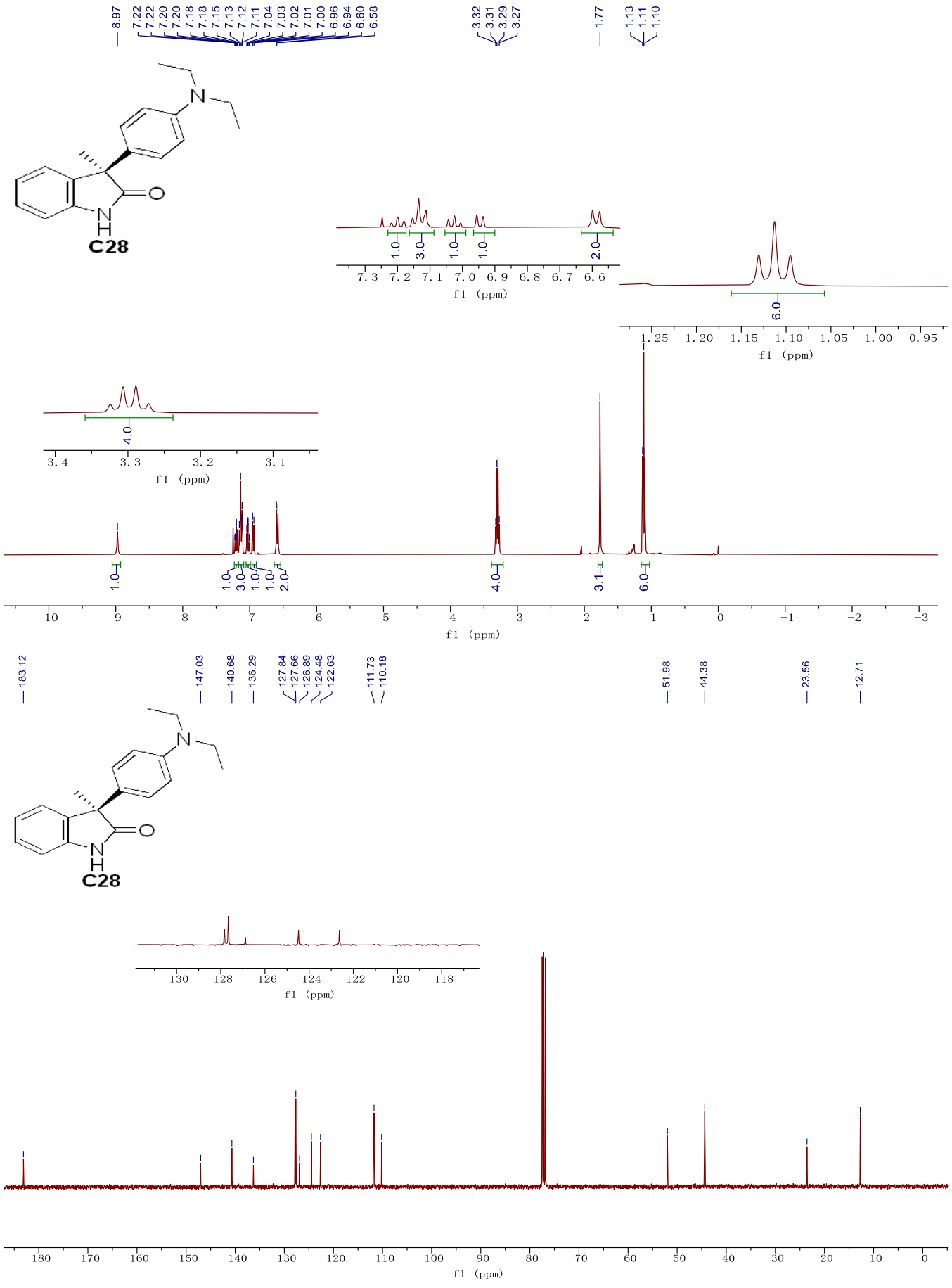
7.20
7.19
7.19
7.17
7.17
7.15
7.13
7.06
7.04
7.02
6.95
6.93
6.68
6.68
6.67
6.65
2.90
1.77
C27
4.0
1.0
1.0
2.0
7.2
7.0
6.8
6.6
6.4
6.2
f1 (ppm)
1.0
4.0
1.0
1.0
2.0
6.0
3.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


182.52
149.90
140.51
136.17
128.32
127.92
127.46
124.57
122.74
112.78
110.04
51.95
40.70
23.64
C27
132
131
130
129
128
127
126
125
f1 (ppm)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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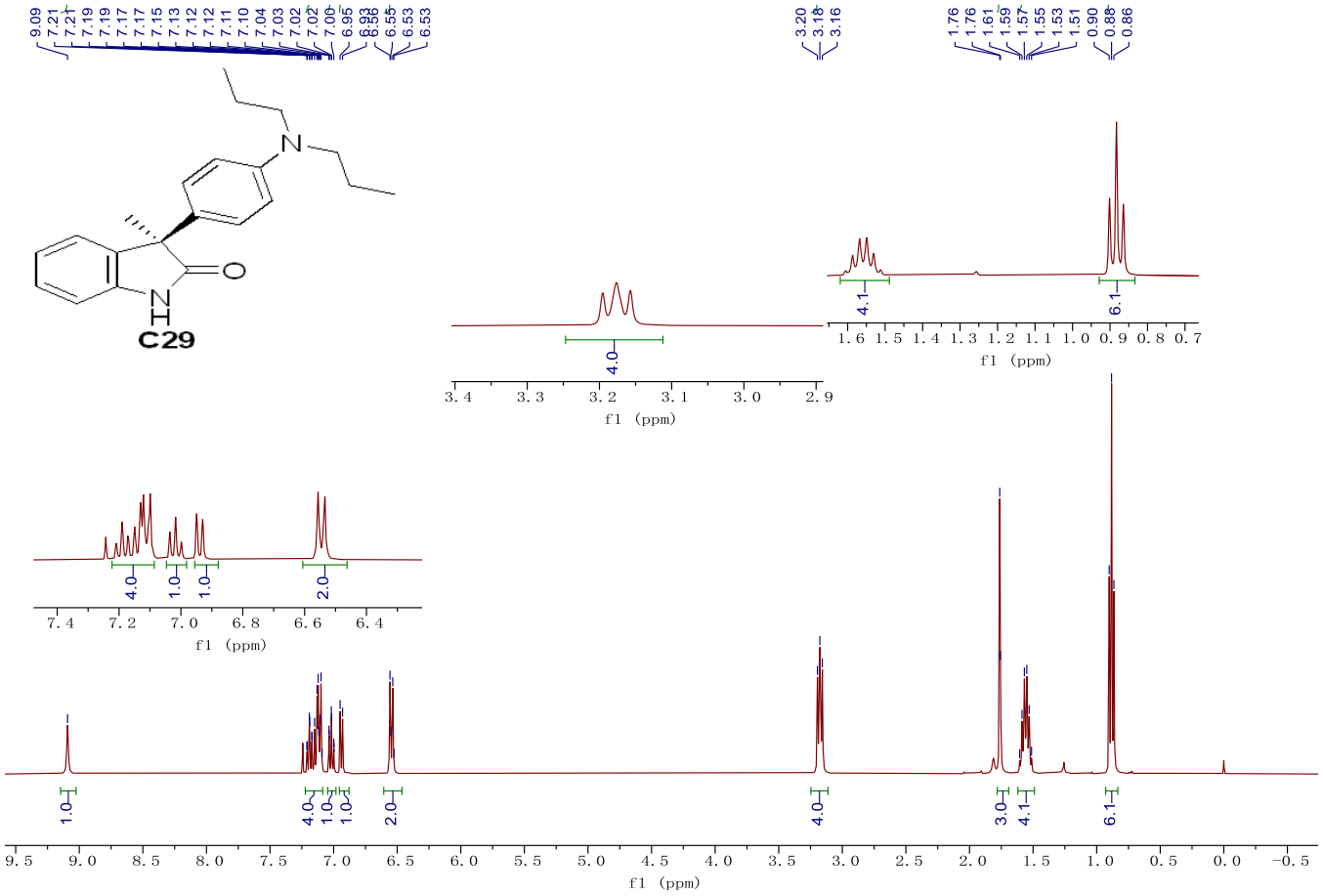
7.20
7.20
7.18
7.18
7.15
7.13
7.12
7.11
7.04
7.03
7.02
7.01
7.00
6.96
6.94
6.60
6.58
3.32
3.31
3.29
3.27
1.77
1.13
1.11
1.10
C28
1.0
3.0
1.0
1.0
2.0
7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
6.0
1.25 1.20 1.15 1.10 1.05 1.00 0.95
f1 (ppm)
4.0
3.4 3.3 3.2 3.1
f1 (ppm)
1.0
1.0
3.0
1.0
1.0
2.0
4.0
3.1
6.0
10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)
183.12
147.03
140.68
136.29
127.84
127.66
126.89
124.48
122.63
111.73
110.18
51.98
44.38
23.56
12.71
C28
130 128 126 124 122 120 118
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.09
7.21
7.21
7.19
7.19
7.17
7.17
7.15
7.13
7.12
7.12
7.11
7.10
7.04
7.03
7.02
7.02
7.00
6.95
6.55
6.53
6.53
3.20
3.18
3.16
1.76
1.76
1.61
1.59
1.57
1.55
1.53
1.51
0.90
0.86
C29
4.0
4.1
6.1
f1 (ppm)
4.0
1.0
1.0
2.0
f1 (ppm)
1.0
4.0
1.0
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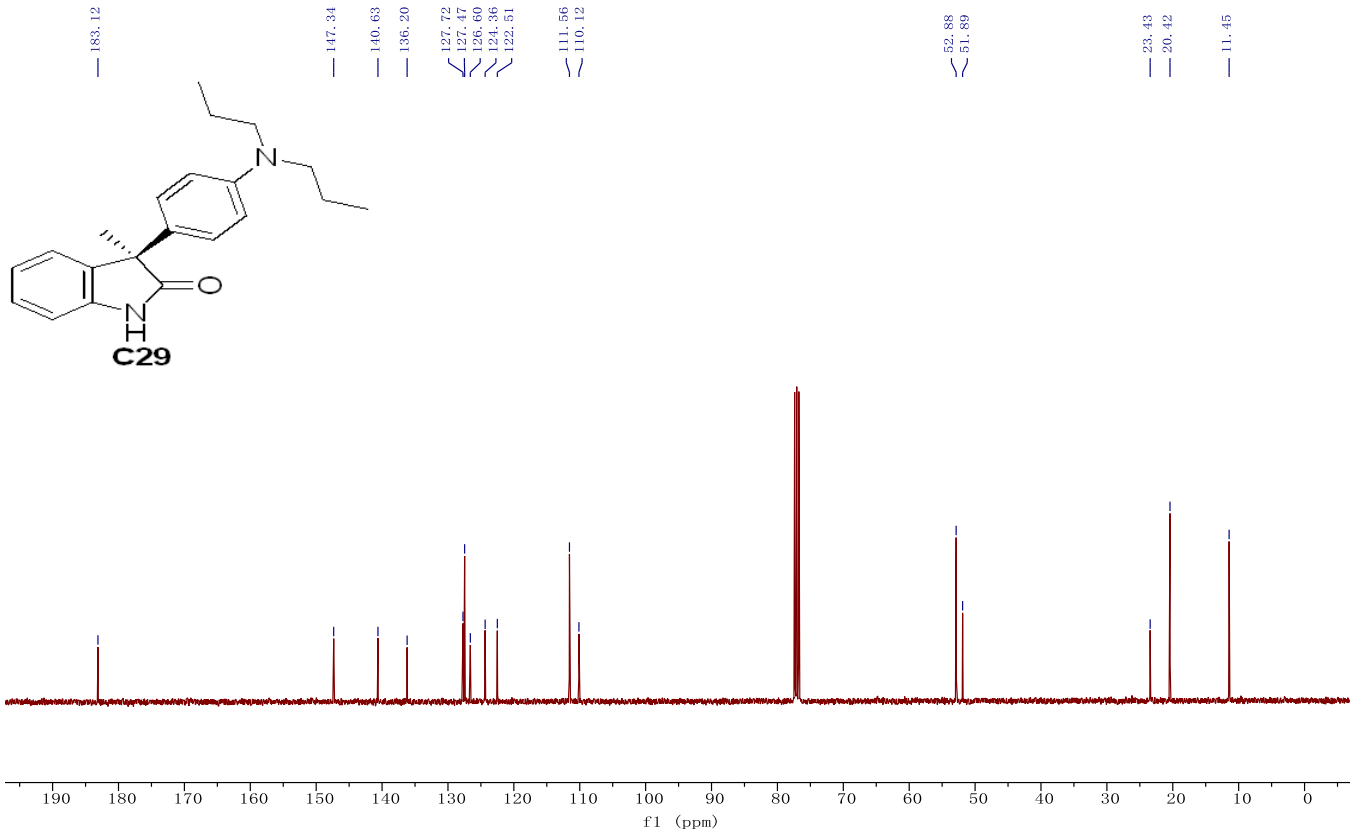
2.0
4.0
3.0
4.1
6.1
f1 (ppm)


183.12
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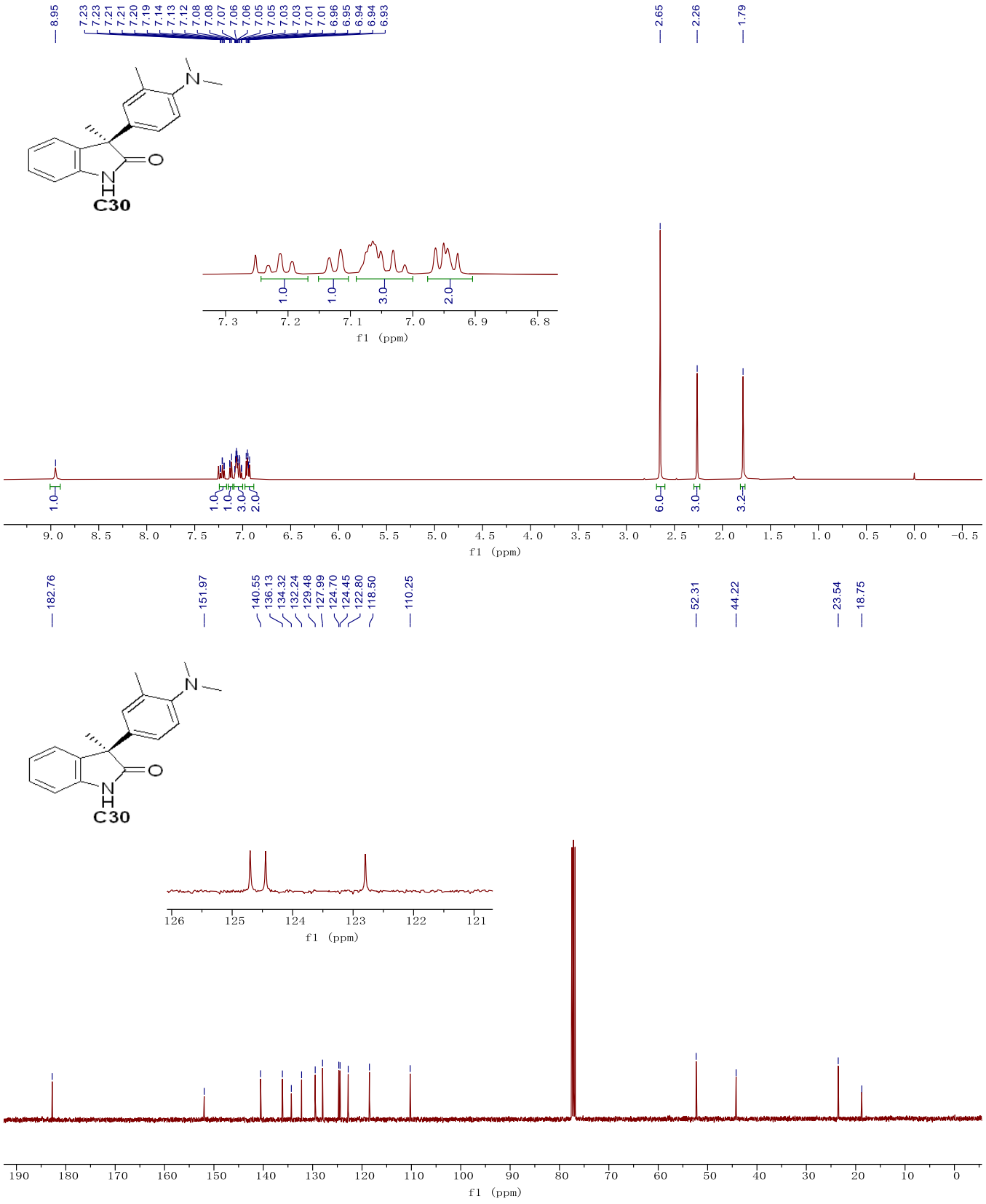
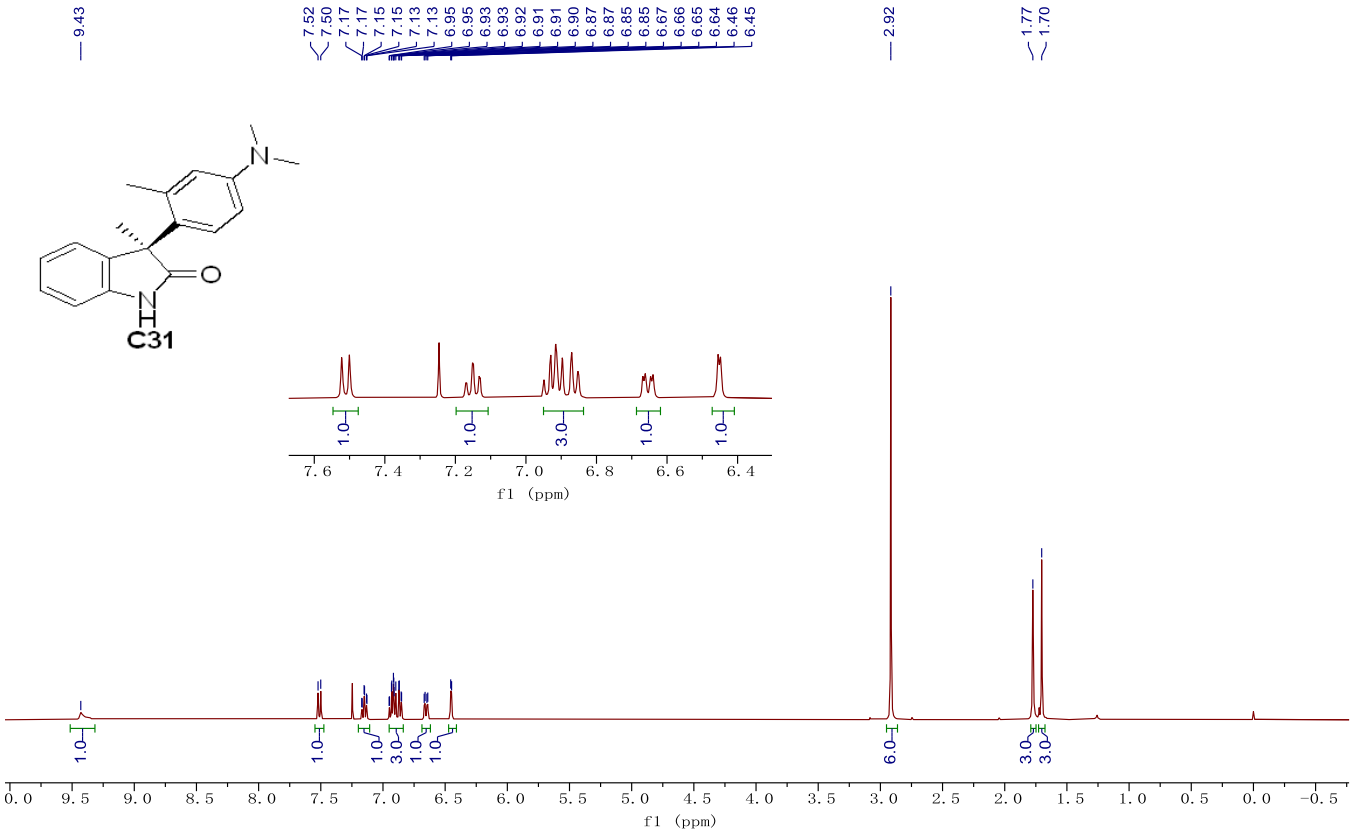
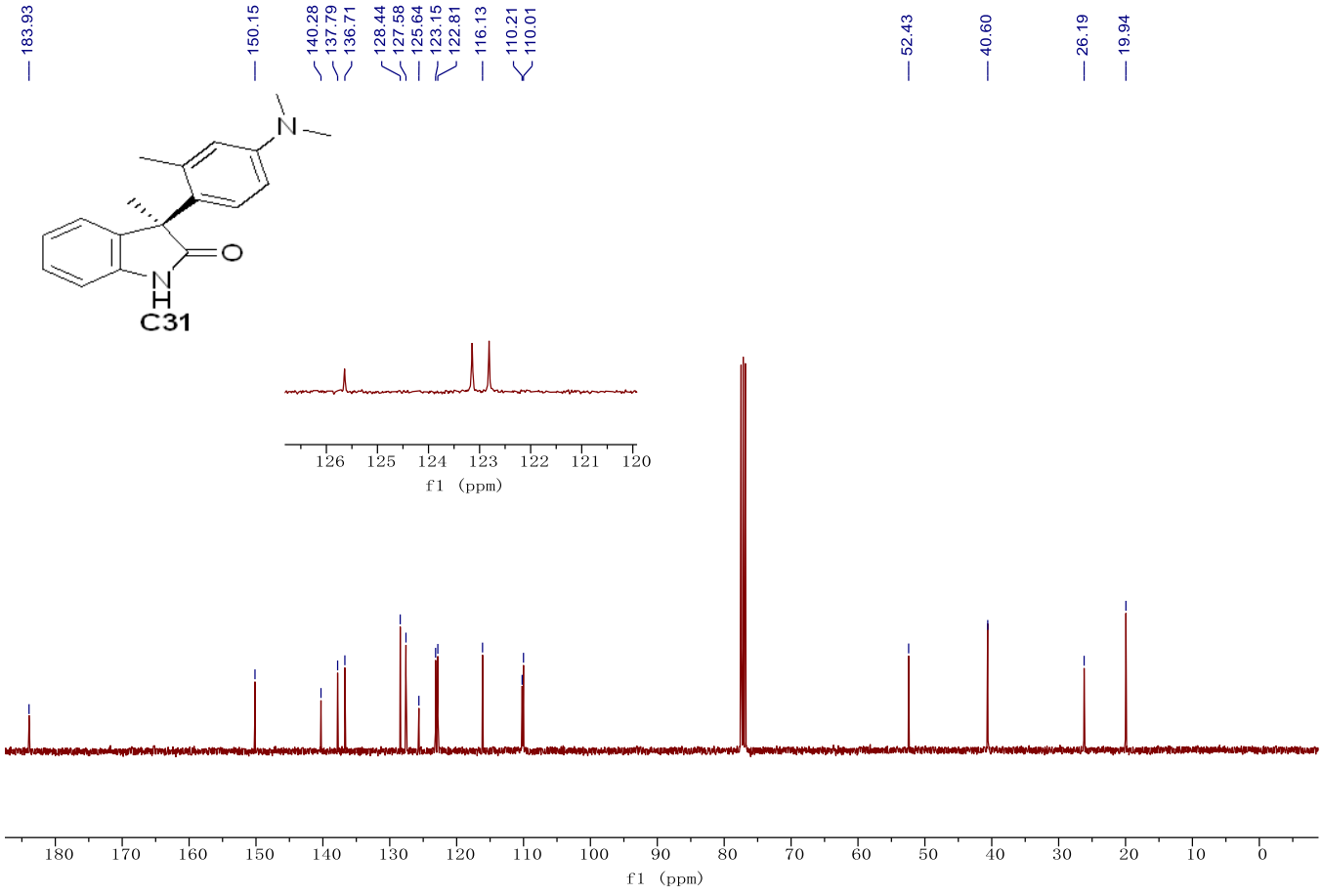
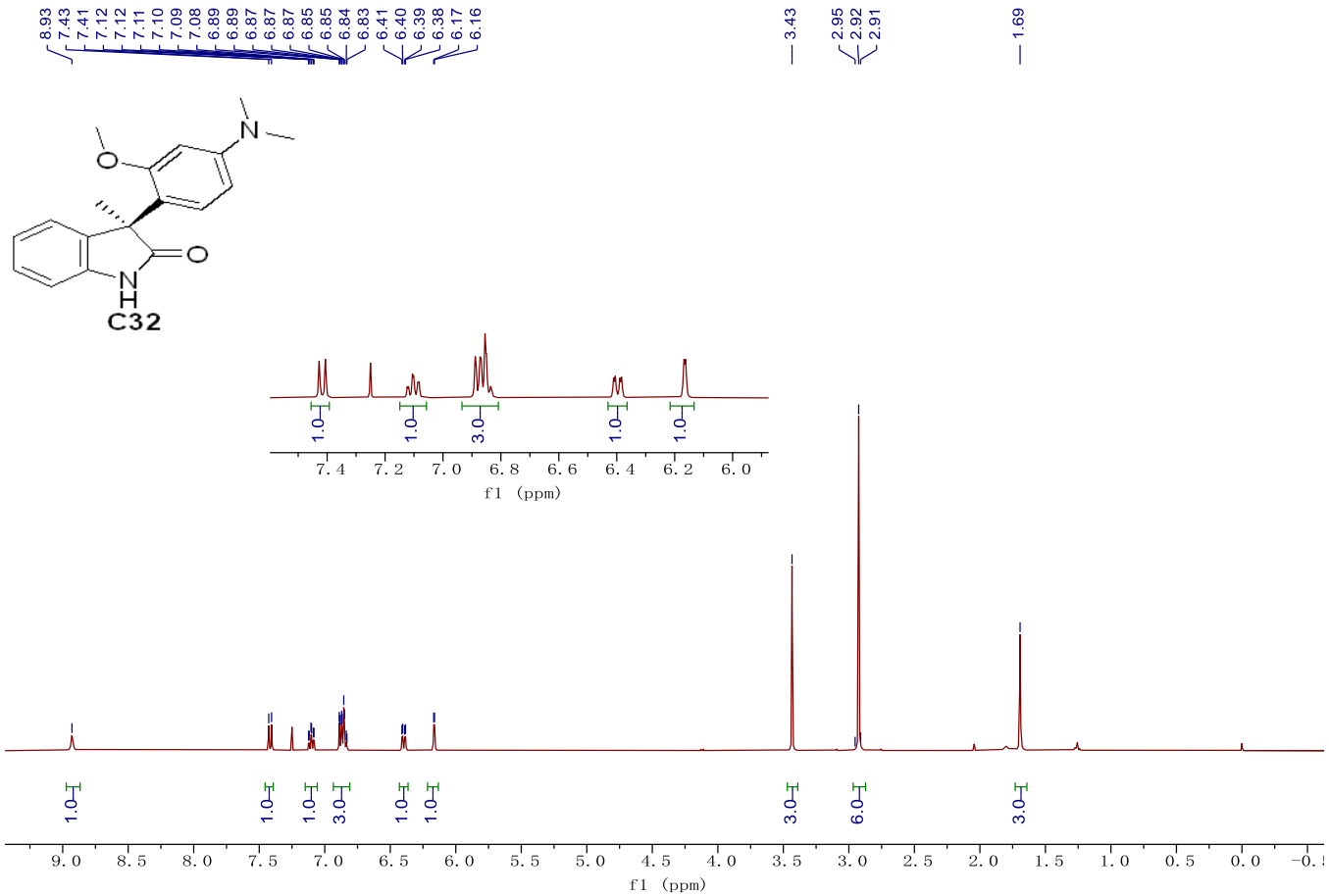
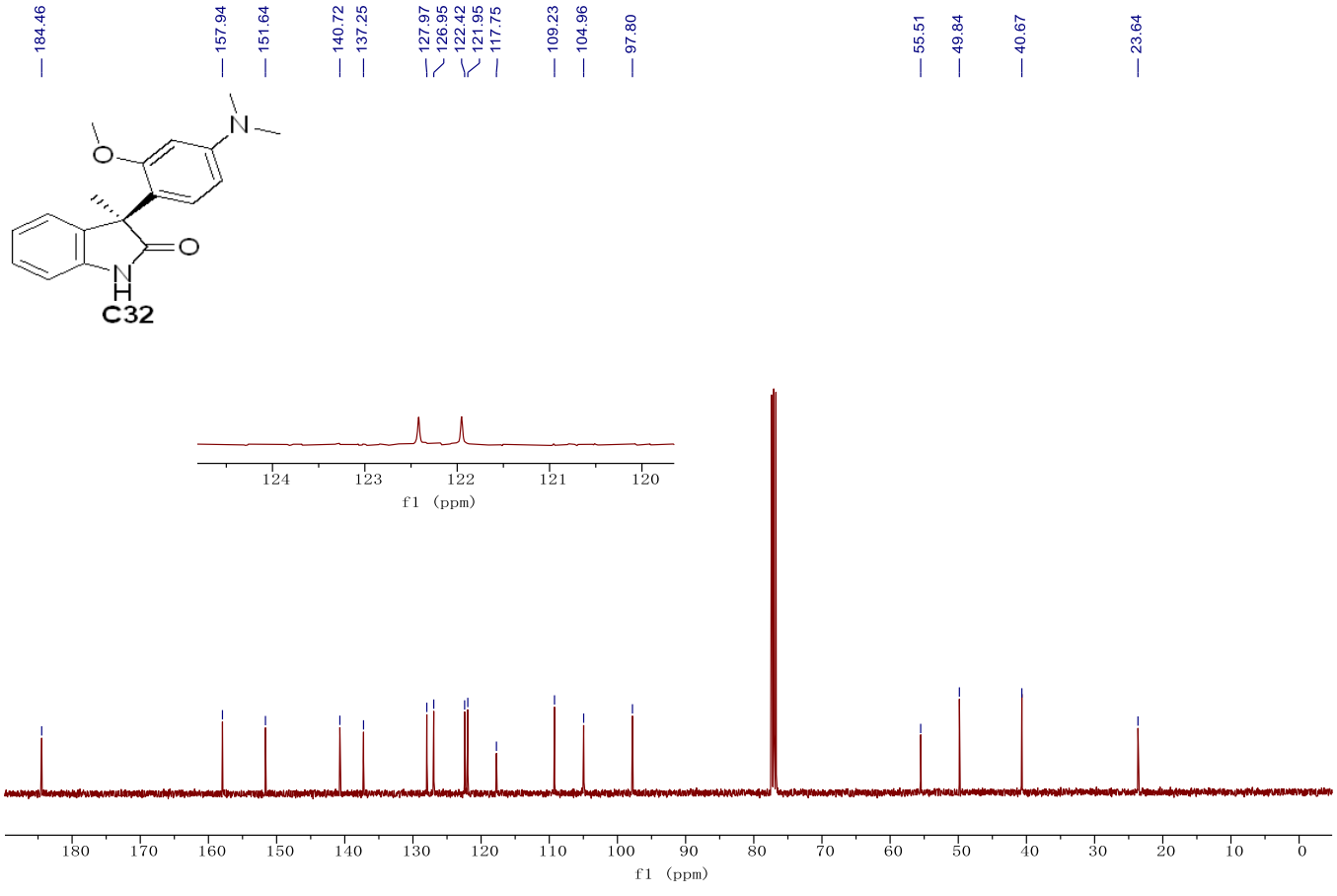
136.20
127.72
127.47
126.60
124.36
122.51
111.56
110.12
52.88
51.89
23.43
20.42
11.45
C29
f1 (ppm)

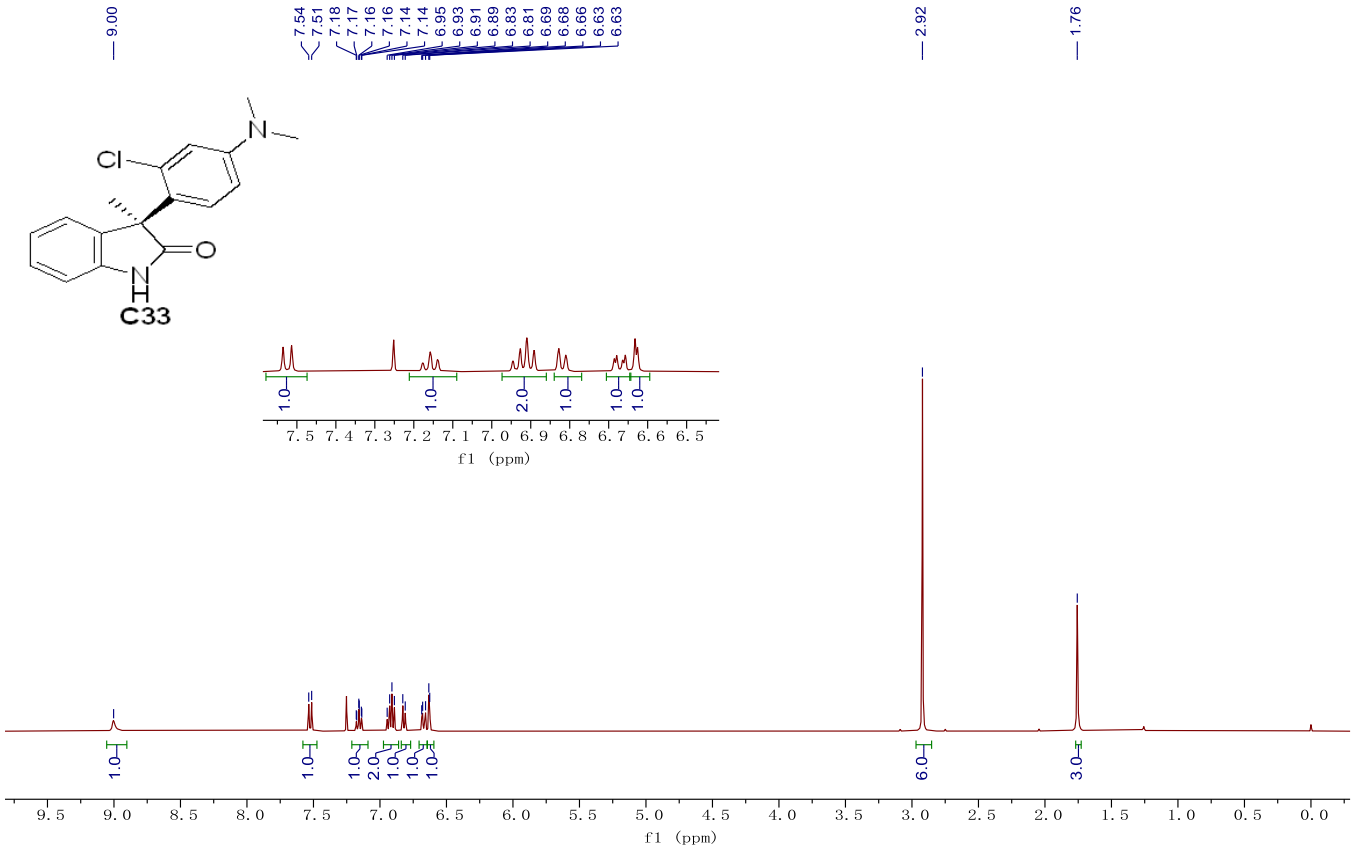

8.95
7.23
7.23
7.21
7.21
7.20
7.19
7.14
7.13
7.12
7.08
7.08
7.07
7.06
7.06
7.05
7.05
7.03
7.03
7.01
7.01
6.96
6.95
6.94
6.94
6.93
2.65
2.26
1.79
C30
1.0
1.0
3.0
2.0
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
1.0
1.0
1.0
3.0
2.0
6.0
3.0
3.2
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
182.76
151.97
140.55
136.13
134.32
132.24
129.48
127.99
124.70
124.45
122.80
118.50
110.25
52.31
44.22
23.54
18.75
C30
126
125
124
123
122
121
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

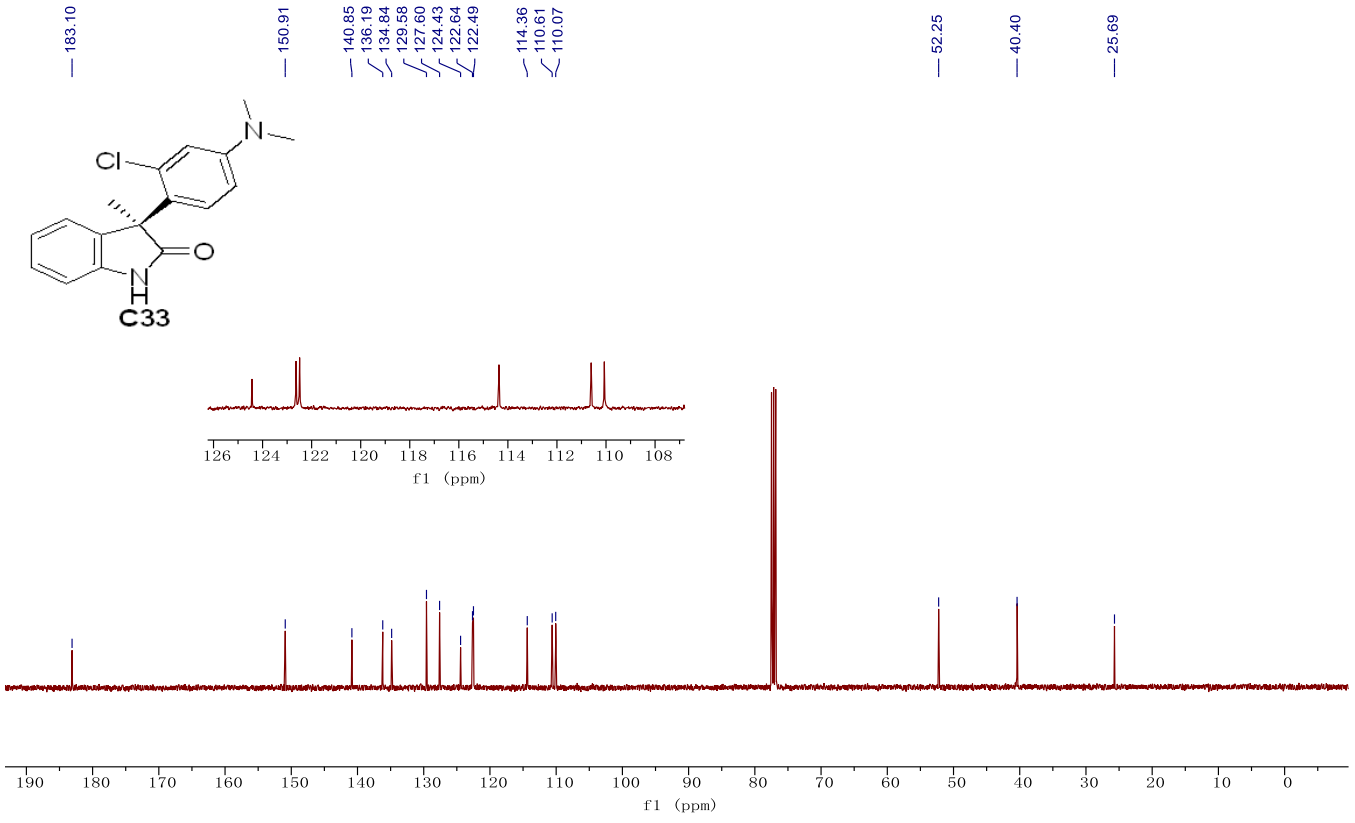

9.43
7.52
7.50
7.17
7.15
7.15
7.13
7.13
6.95
6.95
6.93
6.93
6.92
6.91
6.91
6.90
6.87
6.87
6.85
6.85
6.67
6.66
6.65
6.64
6.46
6.45
2.92
1.77
1.70
C31
1.0
1.0
3.0
1.0
1.0
7.6
7.4
7.2
7.0
6.8
6.6
6.4
f1 (ppm)
1.0
1.0
1.0
3.0
1.0
1.0
6.0
3.0
3.0
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

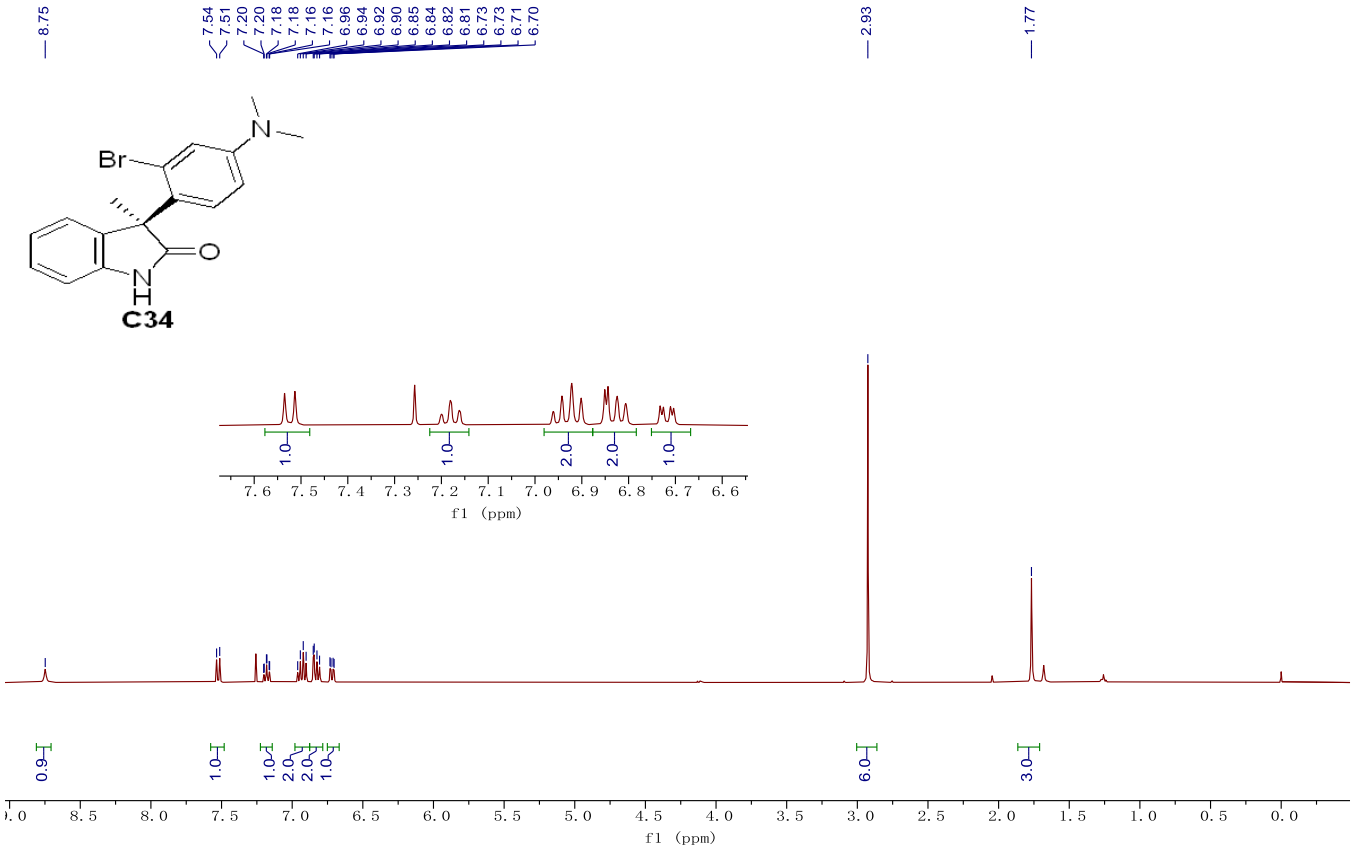

183.93
150.15
140.28
137.79
136.71
128.44
127.58
125.64
123.15
122.81
116.13
110.21
110.01
52.43
40.60
26.19
19.94
C31
126
125
124
123
122
121
120
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

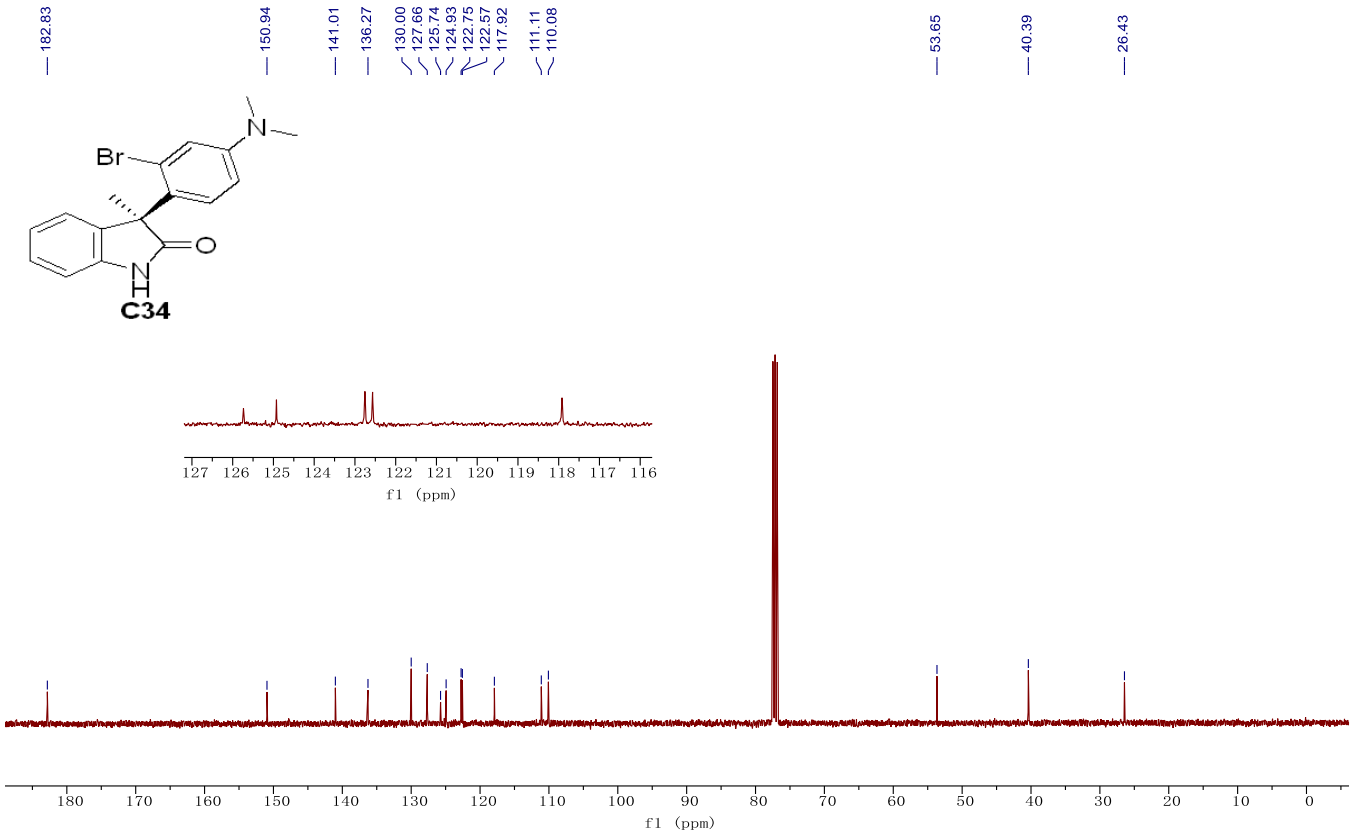

8.93
7.43
7.41
7.12
7.12
7.11
7.10
7.09
7.08
6.89
6.89
6.87
6.87
6.87
6.85
6.85
6.84
6.83
6.41
6.40
6.39
6.38
6.17
6.16
3.43
2.95
2.92
2.91
1.69
C32
1.0
1.0
3.0
1.0
1.0
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
f1 (ppm)
1.0
1.0
1.0
3.0
1.0
1.0
3.0
6.0
3.0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

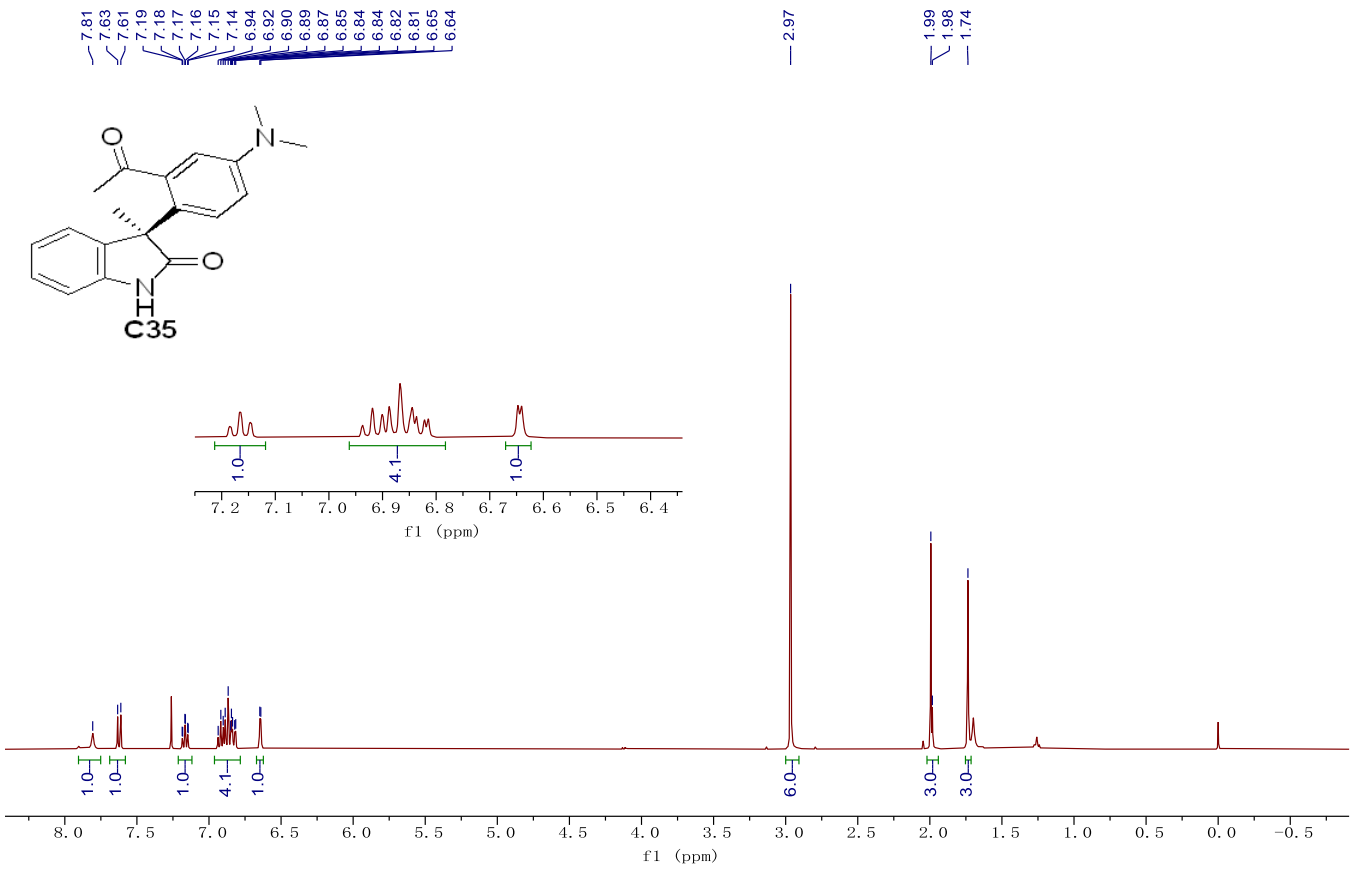

184.46
157.94
151.64
140.72
137.25
127.97
126.95
122.42
121.95
117.75
109.23
104.96
97.80
55.51
49.84
40.67
23.64
C32
124
123
122
121
120
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

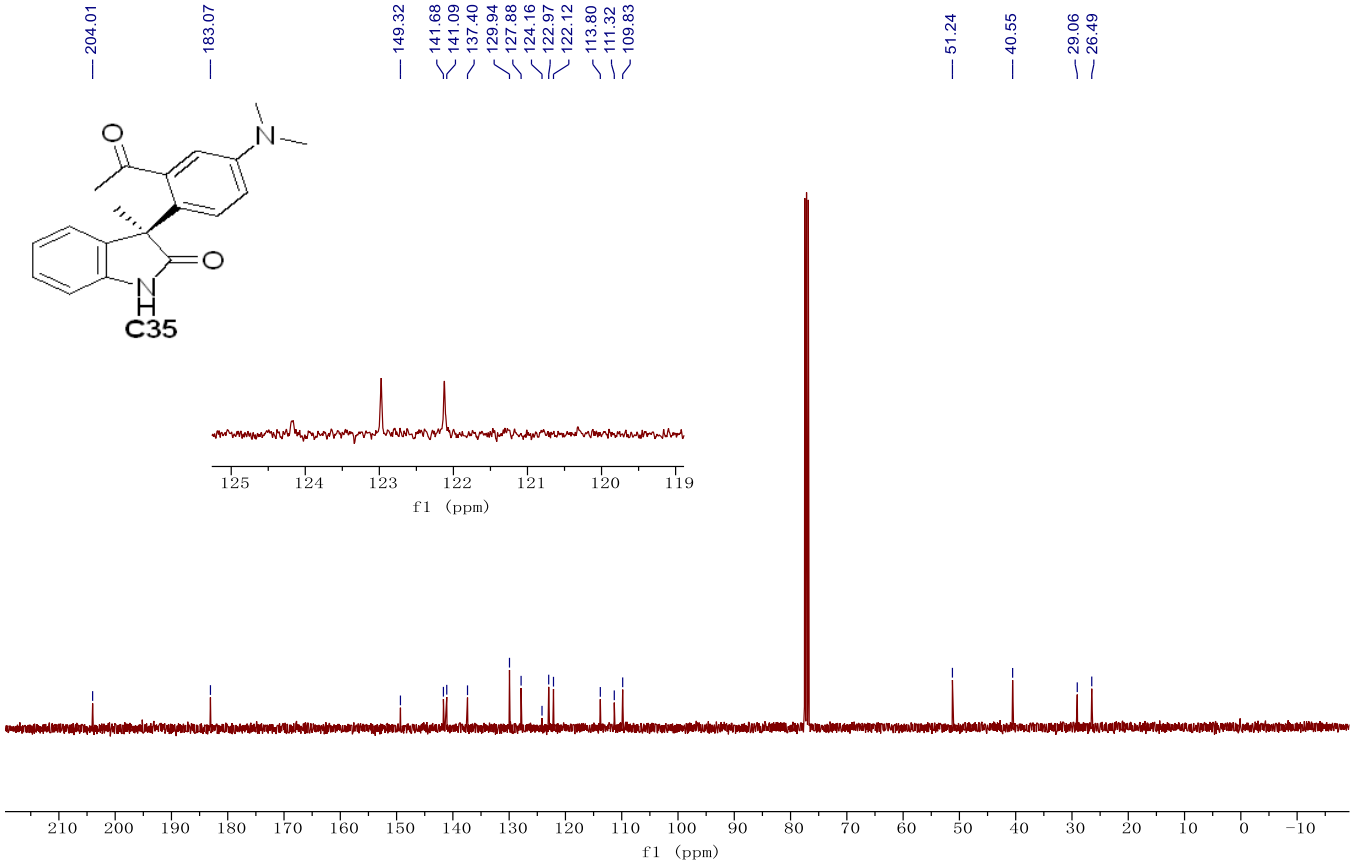

9.00
7.54
7.51
7.18
7.17
7.16
7.16
7.14
7.14
6.95
6.93
6.91
6.89
6.83
6.81
6.69
6.68
6.66
6.63
6.63
2.92
1.76
Cl
N
O
N
H
C33
1.0
1.0
2.0
1.0
1.0
1.0
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5
f1 (ppm)
1.0
1.0
1.0
2.0
1.0
1.0
6.0
3.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

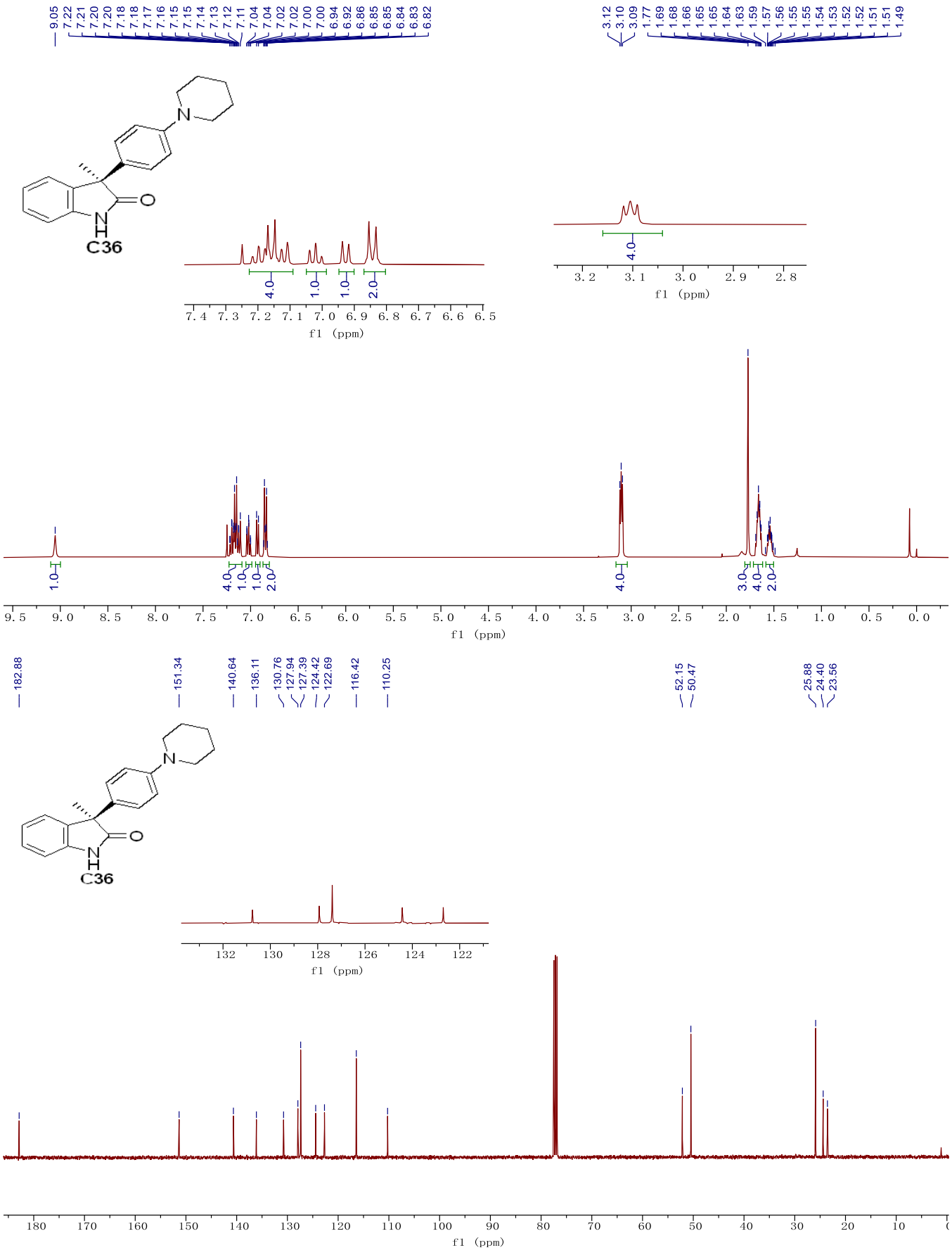

183.10
150.91
140.85
136.19
134.84
129.58
127.60
124.43
122.64
122.49
114.36
110.61
110.07
52.25
40.40
25.69
Cl
N
O
N
H
C33
126 124 122 120 118 116 114 112 110 108
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

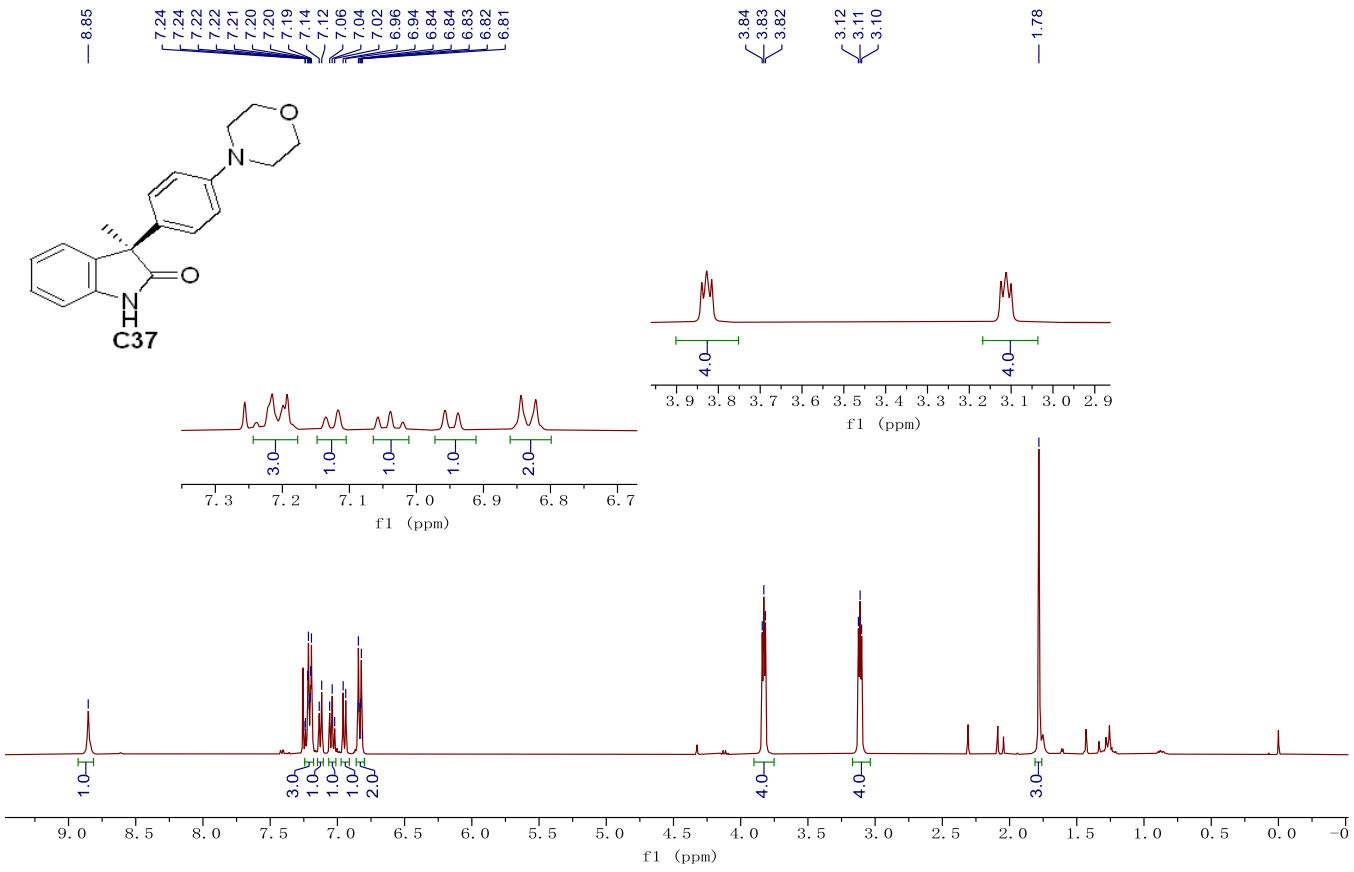

8.75
7.54
7.51
7.20
7.20
7.18
7.18
7.16
7.16
6.96
6.94
6.92
6.90
6.85
6.84
6.82
6.81
6.73
6.73
6.71
6.70
2.93
1.77
Br
N
O
N
H
C34
1.0
1.0
2.0
2.0
1.0
f1 (ppm)
0.9
1.0
1.0
2.0
2.0
1.0
6.0
3.0
f1 (ppm)

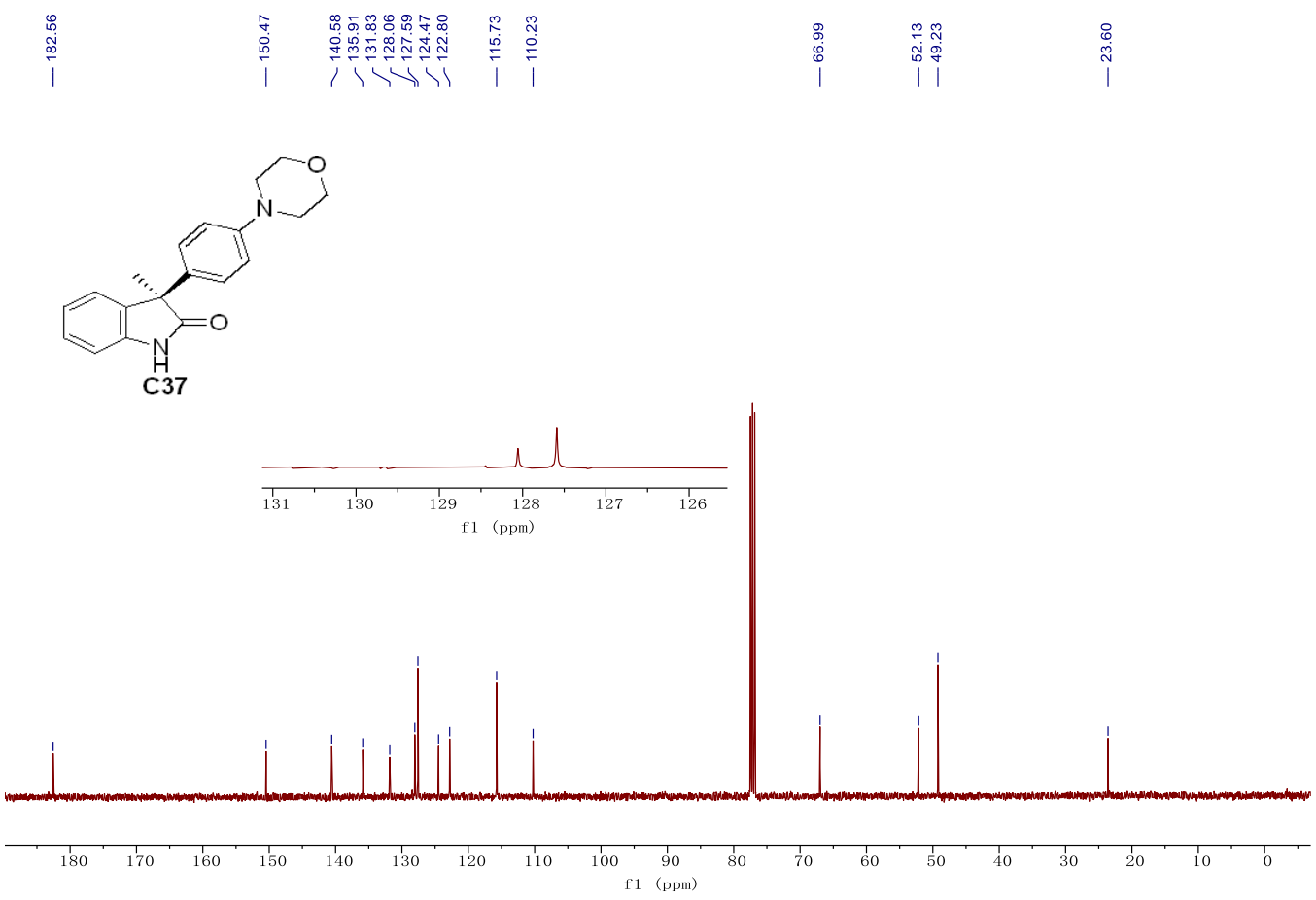

182.83
150.94
141.01
136.27
130.00
127.66
125.74
124.93
122.75
122.57
117.92
111.11
110.08
53.65
40.39
26.43
Br
N
O
N
H
C34
f1 (ppm)
f1 (ppm)

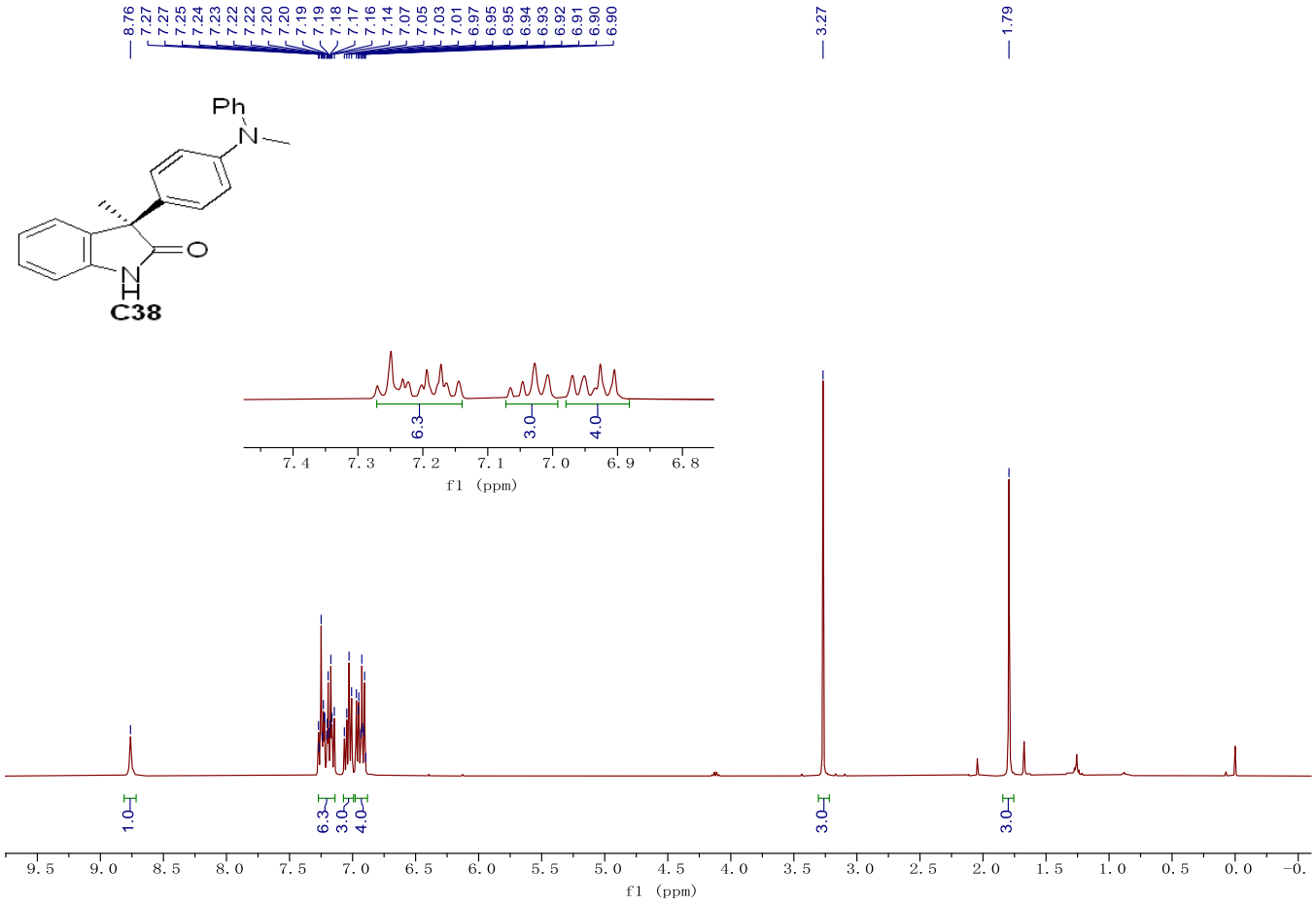

7.81
7.63
7.61
7.19
7.18
7.17
7.16
7.15
7.14
6.94
6.92
6.90
6.89
6.87
6.85
6.84
6.84
6.82
6.81
6.65
6.64
2.97
1.99
1.98
1.74
C35
1.0
4.1
1.0
f1 (ppm)
6.0
3.0
3.0

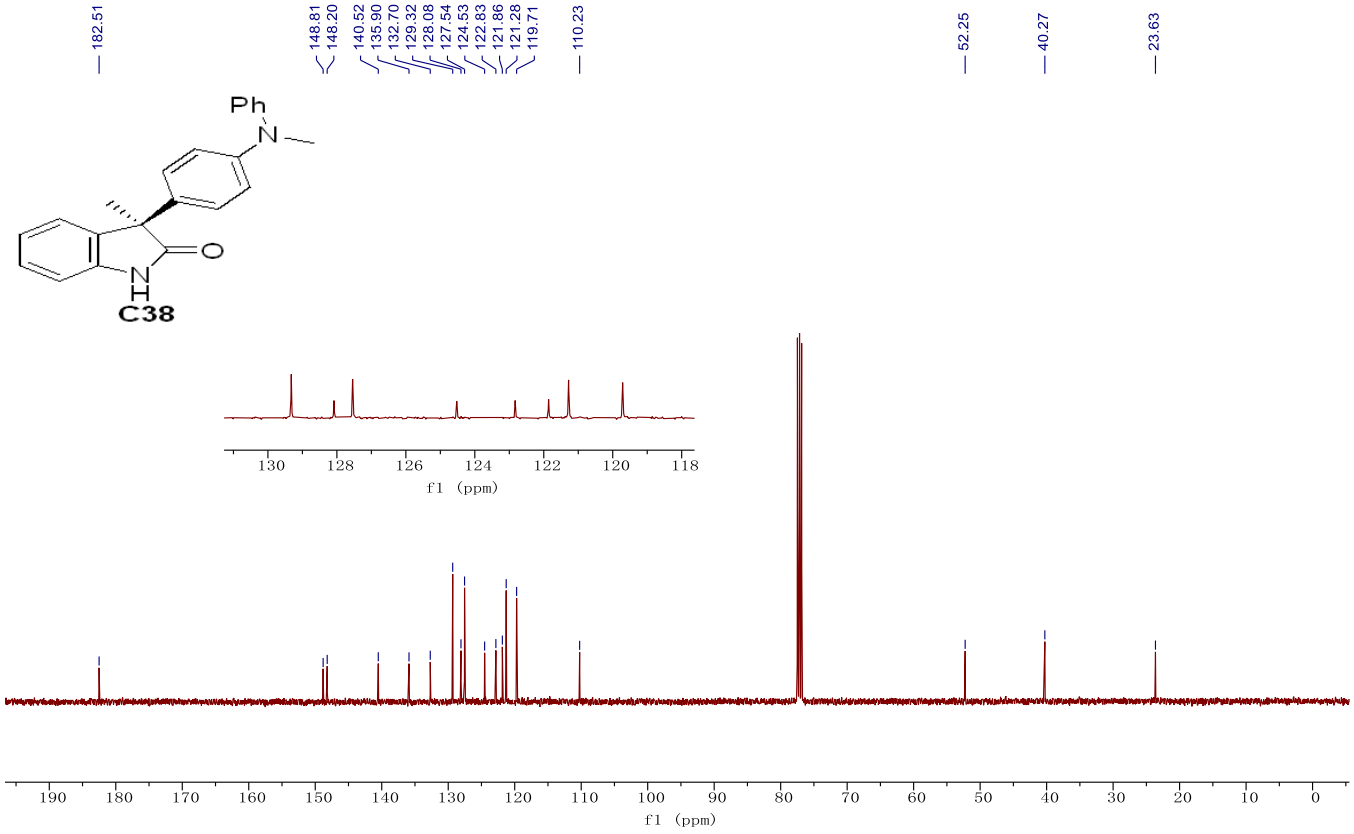

204.01
183.07
149.32
141.68
141.09
137.40
129.94
127.88
124.16
122.97
122.12
113.80
111.32
109.83
51.24
40.55
29.06
26.49
C35
f1 (ppm)
f1 (ppm)

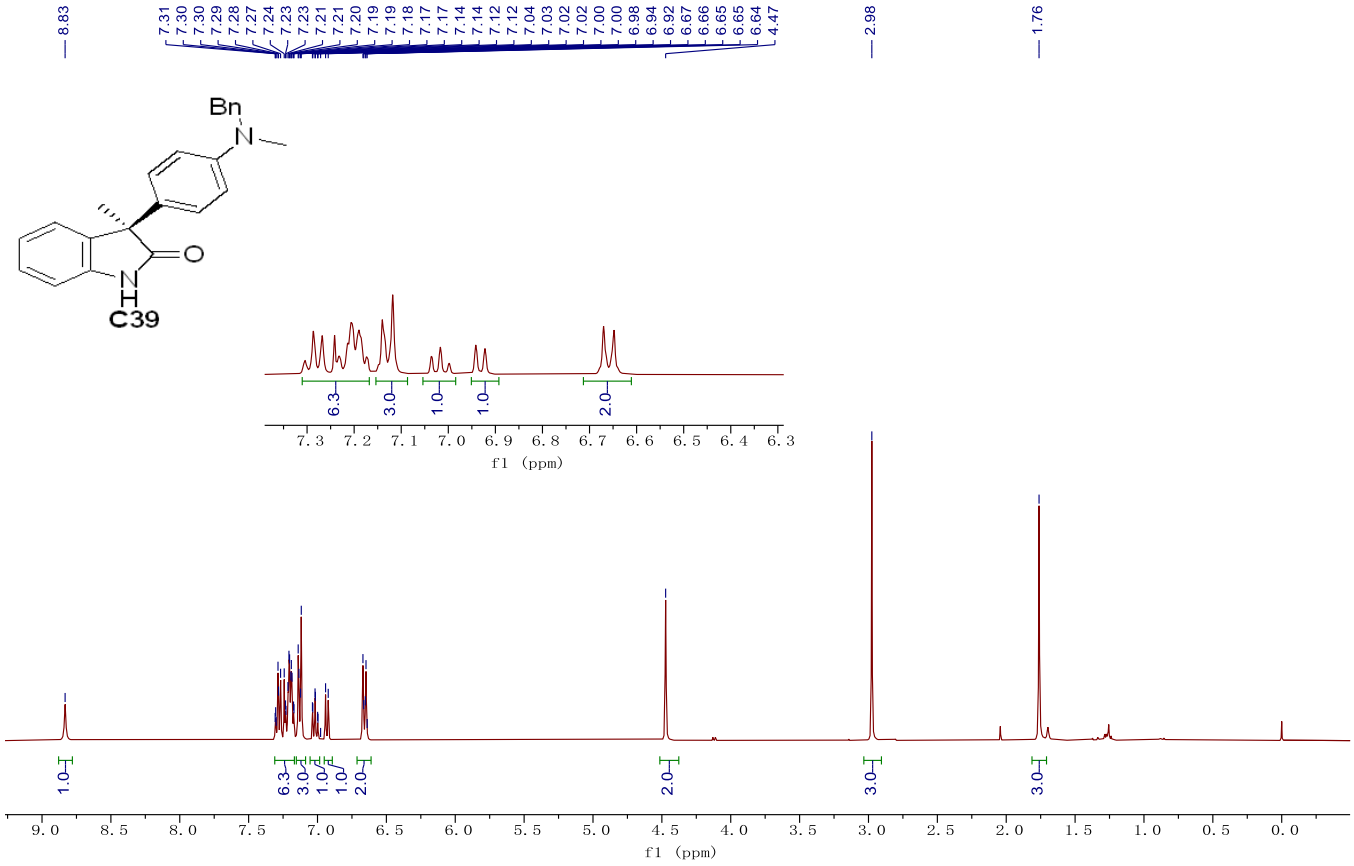

9.05 7.22 7.21 7.20 7.20 7.18 7.18 7.17 7.16 7.15 7.15 7.14 7.13 7.12 7.11 7.04 7.04 7.02 7.02 7.00 7.00 6.94 6.92 6.86 6.85 6.85 6.84 6.83 6.82
3.12 3.10 3.09 1.77 1.69 1.68 1.66 1.65 1.65 1.64 1.63 1.59 1.57 1.56 1.55 1.55 1.54 1.53 1.52 1.52 1.51 1.51 1.49
C36
4.0 1.0 1.0 2.0
7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5
f1 (ppm)
4.0
3.2 3.1 3.0 2.9 2.8
f1 (ppm)
1.0 4.0 1.0 1.0 2.0 4.0 3.0 4.0 2.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
182.88 151.34 140.64 136.11 130.76 127.94 127.39 124.42 122.69 116.42 110.25 52.15 50.47 25.88 24.40 23.56
C36
132 130 128 126 124 122
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

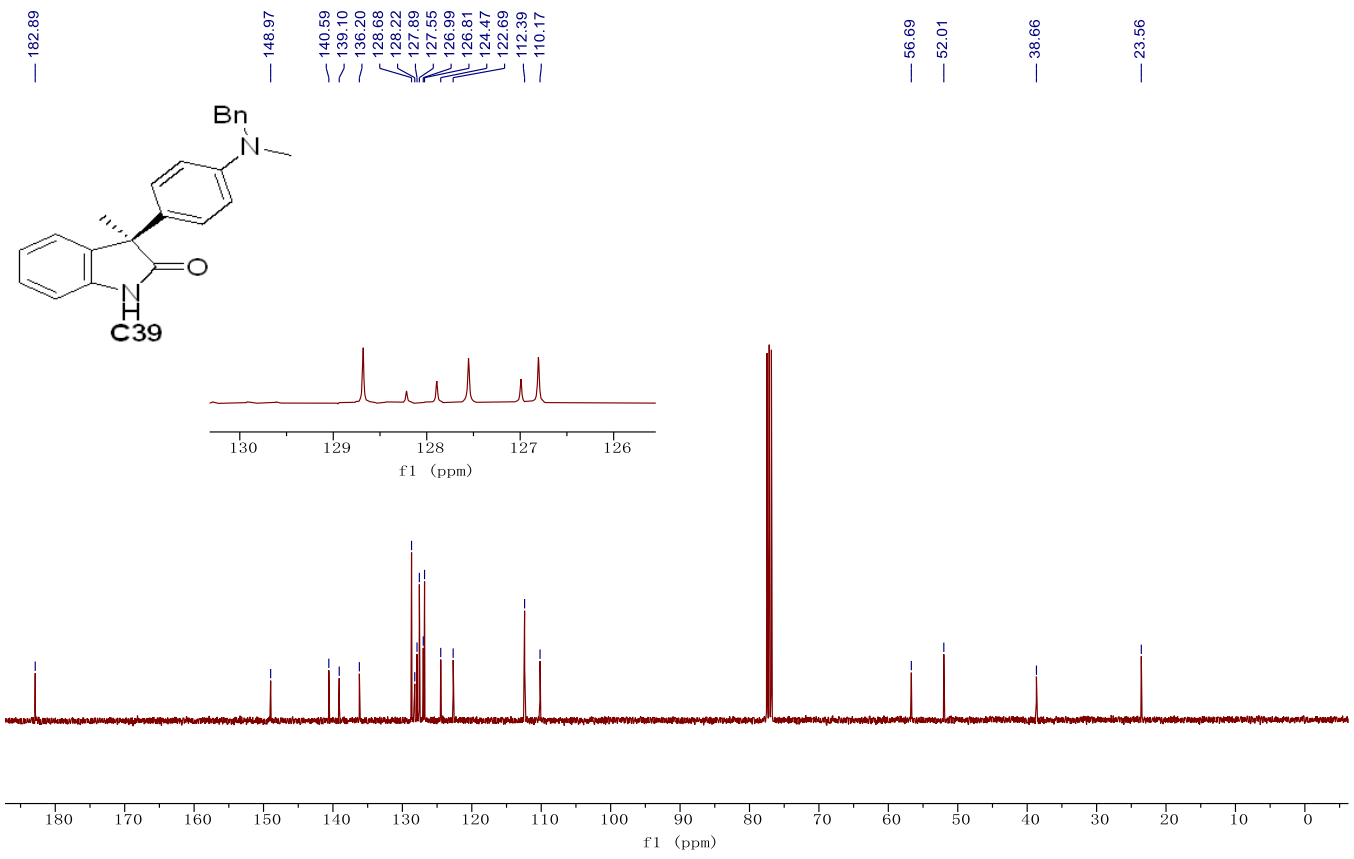

8.85
7.24
7.24
7.22
7.22
7.21
7.20
7.20
7.19
7.14
7.12
7.06
7.04
7.02
6.96
6.94
6.84
6.84
6.83
6.82
6.81
3.84
3.83
3.82
3.12
3.11
3.10
1.78
C37
f1 (ppm)

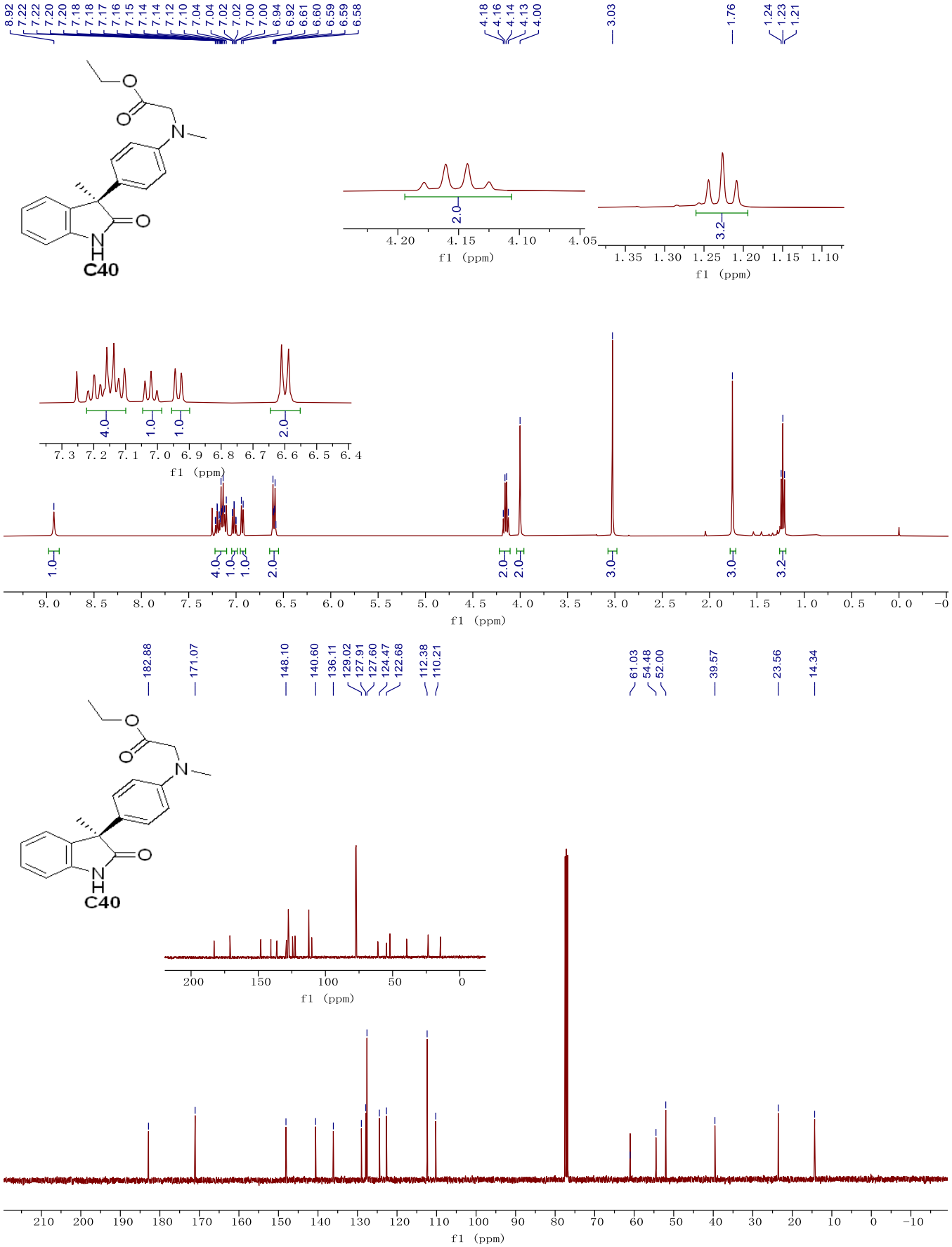

182.56
150.47
140.58
135.91
131.83
128.06
127.59
124.47
122.80
115.73
110.23
66.99
52.13
49.23
23.60
C37
f1 (ppm)

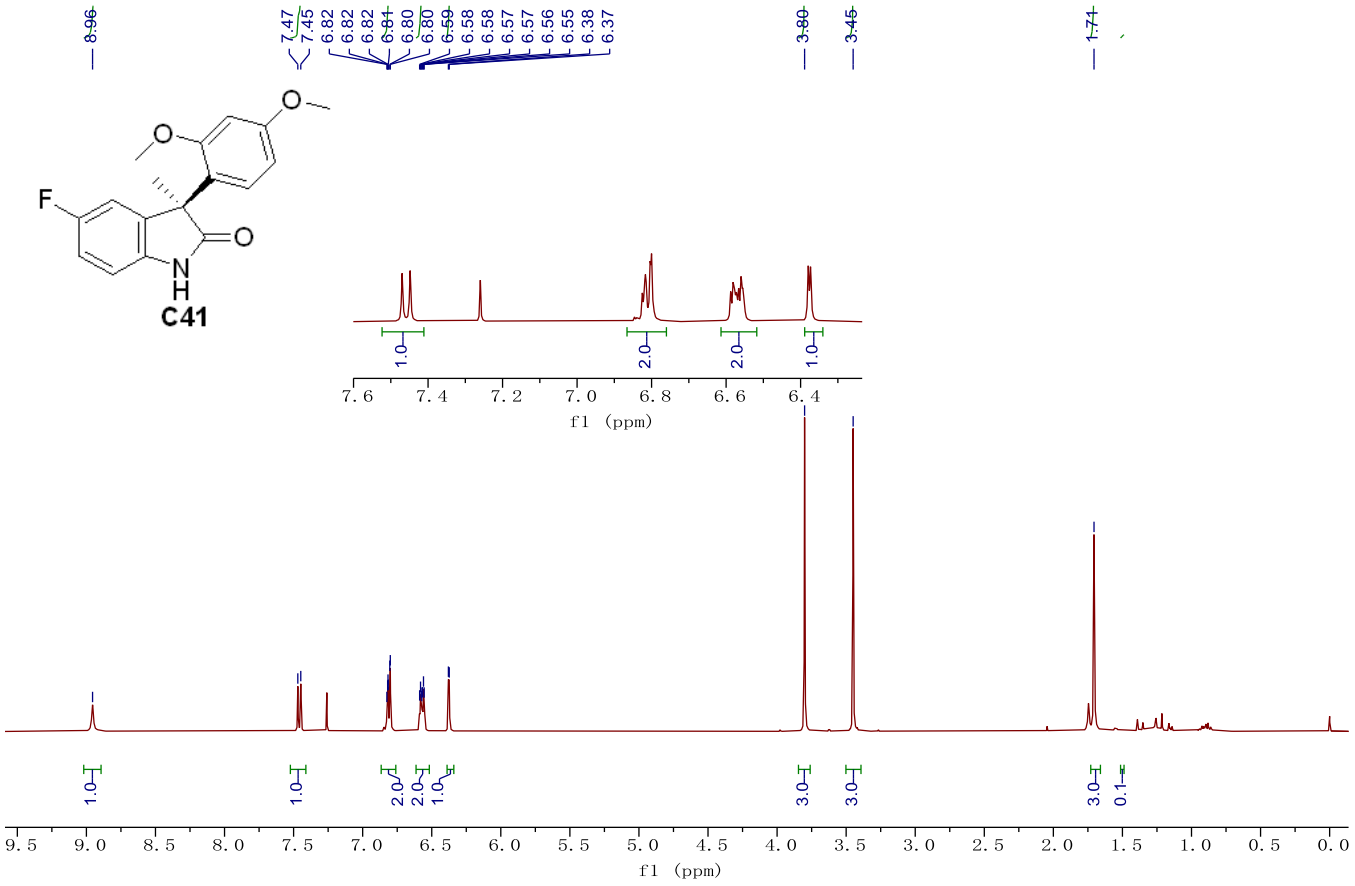

8.76
7.27
7.27
7.25
7.24
7.23
7.22
7.22
7.20
7.20
7.19
7.19
7.18
7.17
7.16
7.14
7.07
7.05
7.03
7.01
6.97
6.95
6.95
6.94
6.93
6.92
6.91
6.90
6.90
3.27
1.79
Ph
N
O
N
H
C38
6.3
3.0
4.0
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
1.0
6.3
3.0
4.0
3.0
3.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

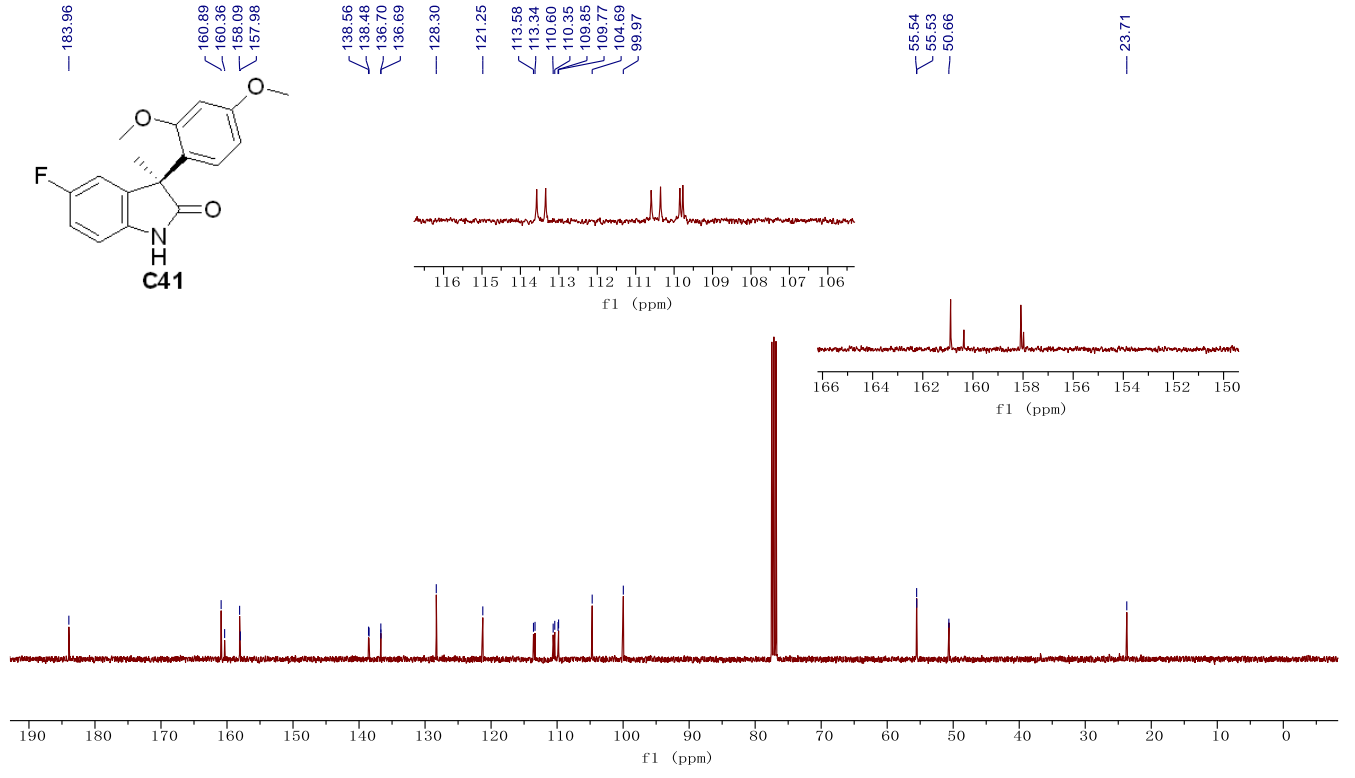

182.51
148.81
148.20
140.52
135.90
132.70
129.32
128.08
127.54
124.53
122.83
121.86
121.28
119.71
110.23
52.25
40.27
23.63
Ph
N
O
N
H
C38
130
128
126
124
122
120
118
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

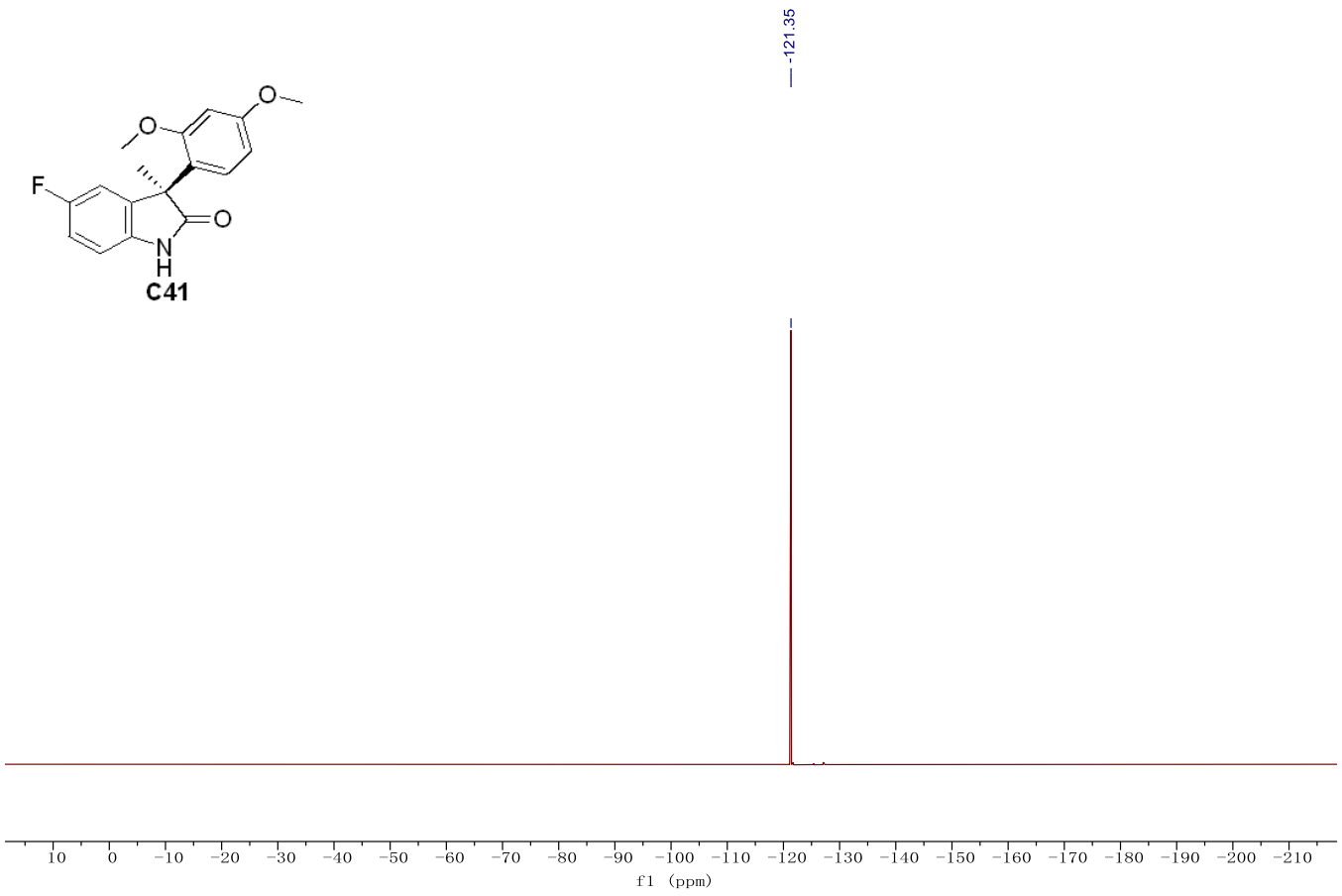

8.83
7.31
7.30
7.30
7.29
7.28
7.27
7.24
7.23
7.23
7.21
7.21
7.20
7.19
7.19
7.18
7.17
7.17
7.14
7.14
7.12
7.12
7.04
7.03
7.02
7.02
7.00
7.00
6.98
6.94
6.92
6.67
6.66
6.65
6.65
6.64
4.47
2.98
1.76
Bn
N
O
N
H
C39
6.3
3.0
1.0
1.0
2.0
f1 (ppm)
1.0
6.3
3.0
1.0
1.0
2.0
2.0
3.0
3.0
f1 (ppm)

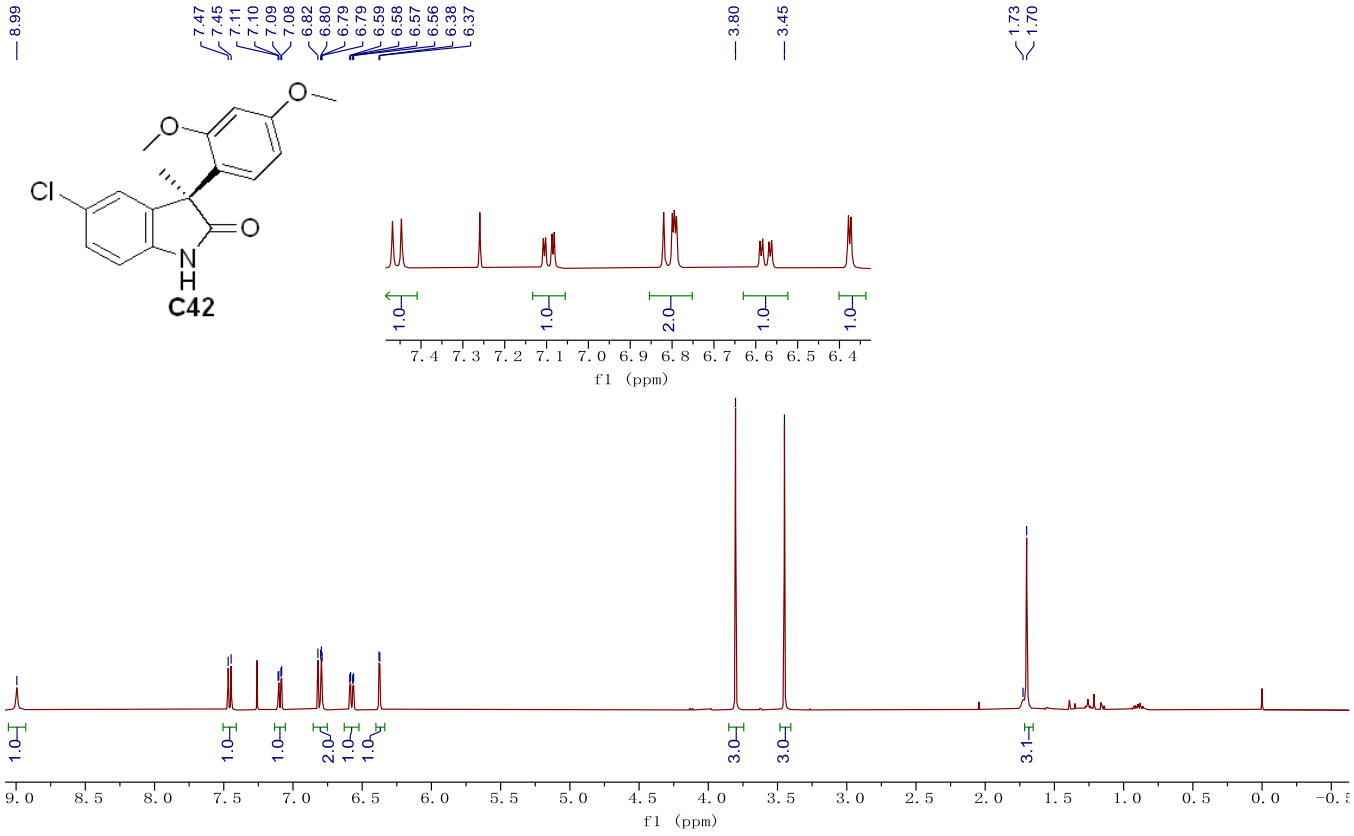

182.89
148.97
140.59
139.10
136.20
128.68
128.22
127.89
127.55
126.99
126.81
124.47
122.69
112.39
110.17
56.69
52.01
38.66
23.56
Bn
N
O
N
H
C39
f1 (ppm)
f1 (ppm)

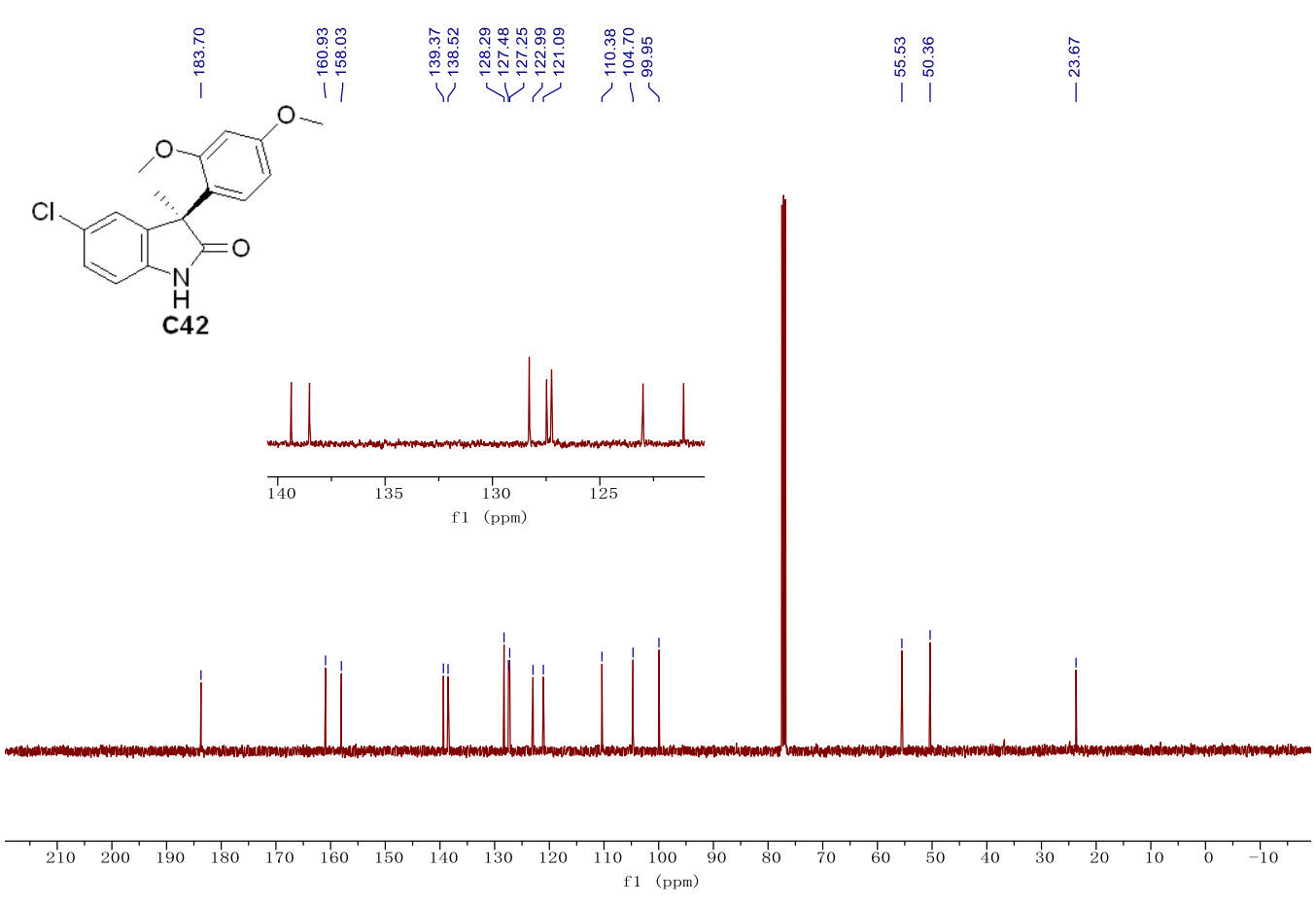

8.92 7.22 7.22 7.20 7.20 7.18 7.18 7.17 7.16 7.15 7.14 7.14 7.12 7.10 7.04 7.04 7.02 7.02 7.00 7.00 6.94 6.92 6.61 6.60 6.59 6.59 6.58
4.18 4.16 4.14 4.13 4.00
3.03
1.76
1.24 1.23 1.21
C40
2.0
3.2
4.0 1.0 1.0 2.0
1.0 4.0 1.0 1.0 2.0 2.0 3.0 3.0 3.2
f1 (ppm)
182.88 171.07 148.10 140.60 136.11 129.02 127.91 127.60 124.47 122.68 112.38 110.21
61.03 54.48 52.00 39.57 23.56 14.34
C40
f1 (ppm)

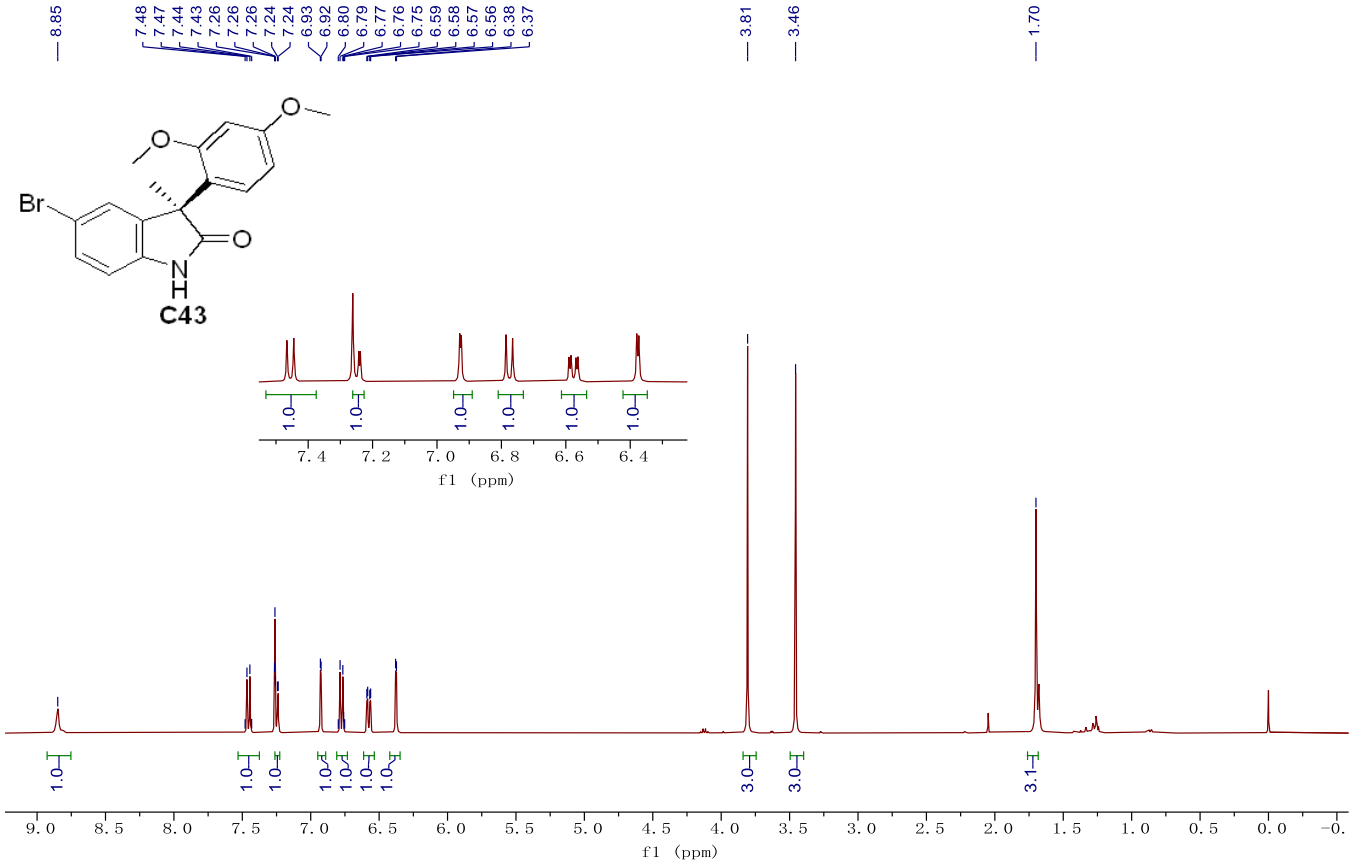

8.96
7.47
7.45
6.82
6.82
6.82
6.81
6.80
6.80
6.59
6.58
6.58
6.57
6.57
6.56
6.55
6.38
6.37
3.80
3.45
1.71
F
O
O
O
N
H
C41
1.0
2.0
2.0
1.0
7.6
7.4
7.2
7.0
6.8
6.6
6.4
f1 (ppm)
1.0
1.0
2.0
2.0
1.0
3.0
3.0
3.0
0.1
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

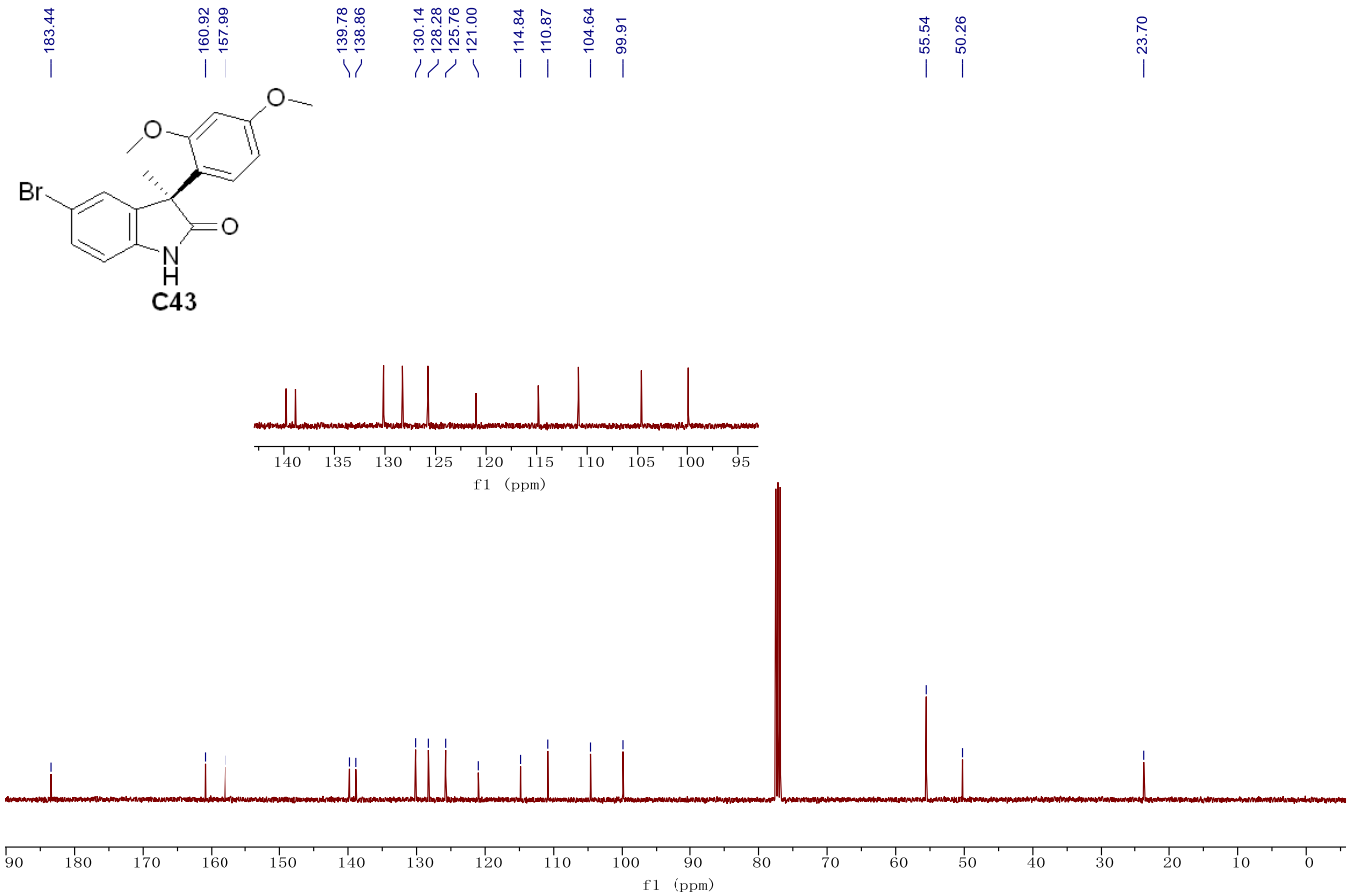

183.96
160.89
160.36
158.09
157.98
138.56
138.48
136.70
136.69
128.30
121.25
113.58
113.34
110.60
110.35
109.85
109.77
104.69
99.97
55.54
55.53
50.66
23.71
F
O
O
O
N
H
C41
116
115
114
113
112
111
110
109
108
107
106
f1 (ppm)
166
164
162
160
158
156
154
152
150
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

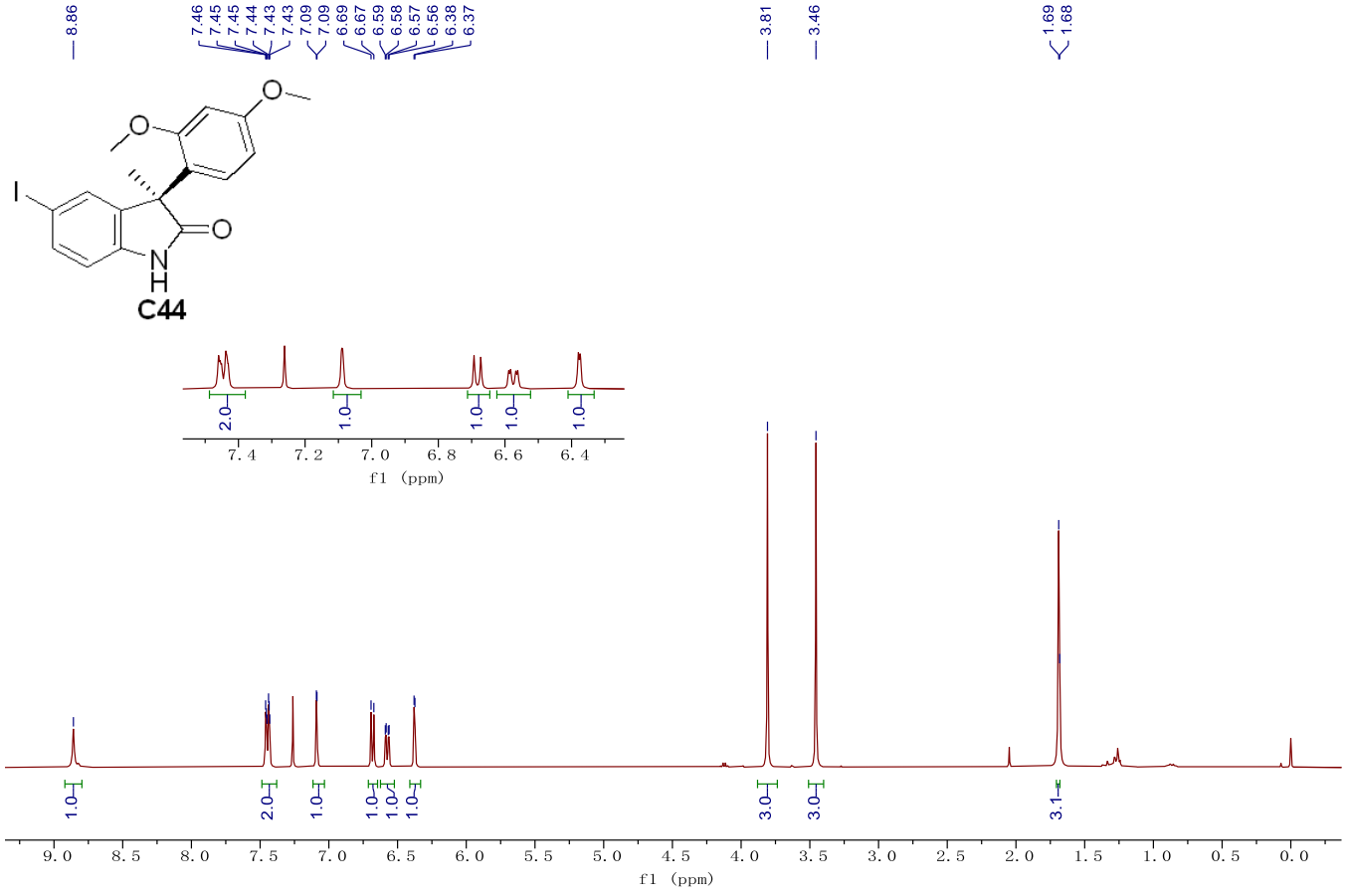

-121.35
F
O
O
O
N
H
C41
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

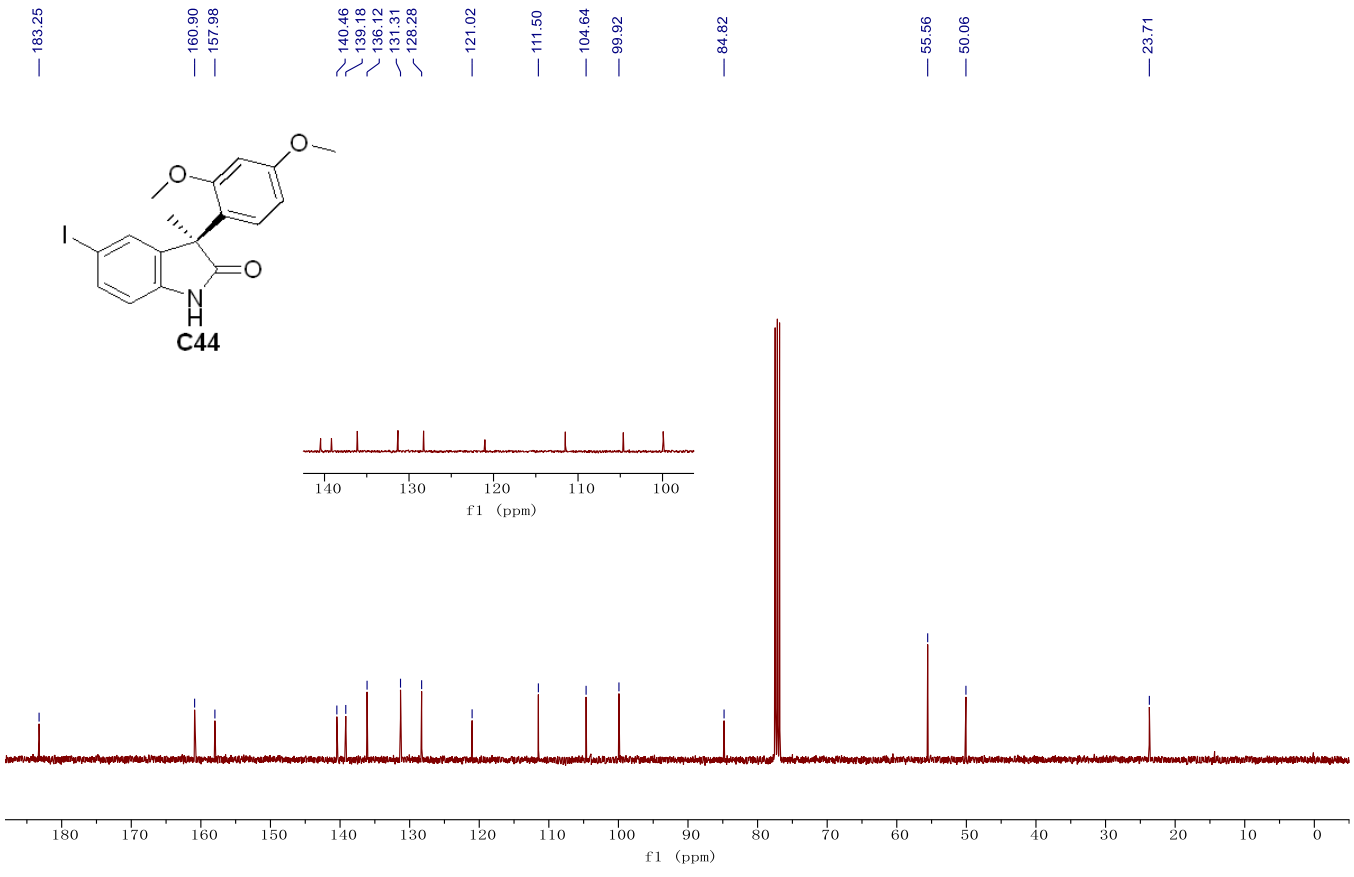

8.99
7.47
7.45
7.11
7.10
7.09
7.08
6.82
6.80
6.79
6.79
6.59
6.58
6.57
6.56
6.38
6.37
3.80
3.45
1.73
1.70
Cl
O
O
O
N
H
C42
f1 (ppm)

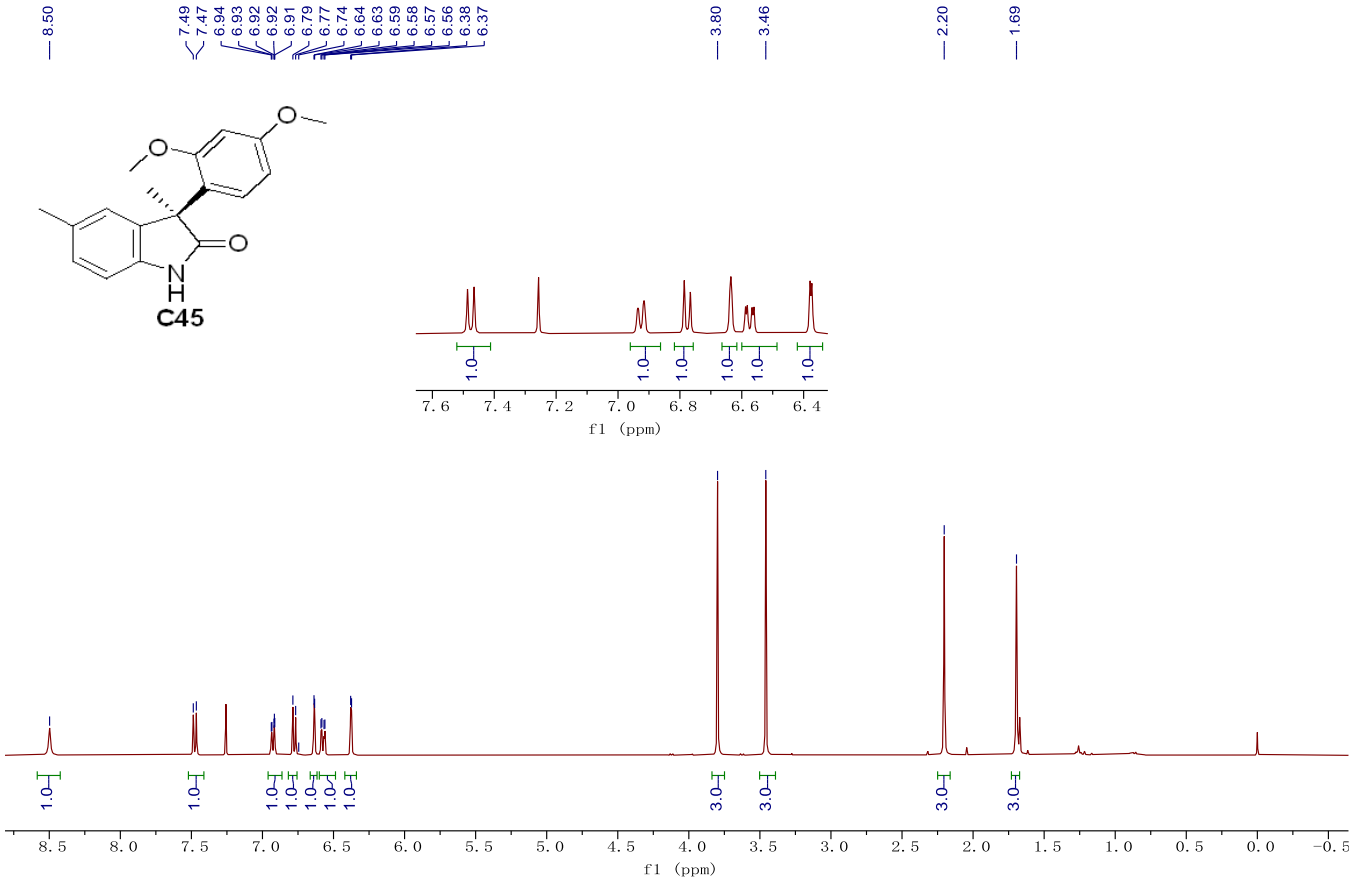

183.70
160.93
158.03
139.37
138.52
128.29
127.48
127.25
122.99
121.09
110.38
104.70
99.95
55.53
50.36
23.67
Cl
O
O
O
N
H
C42
f1 (ppm)

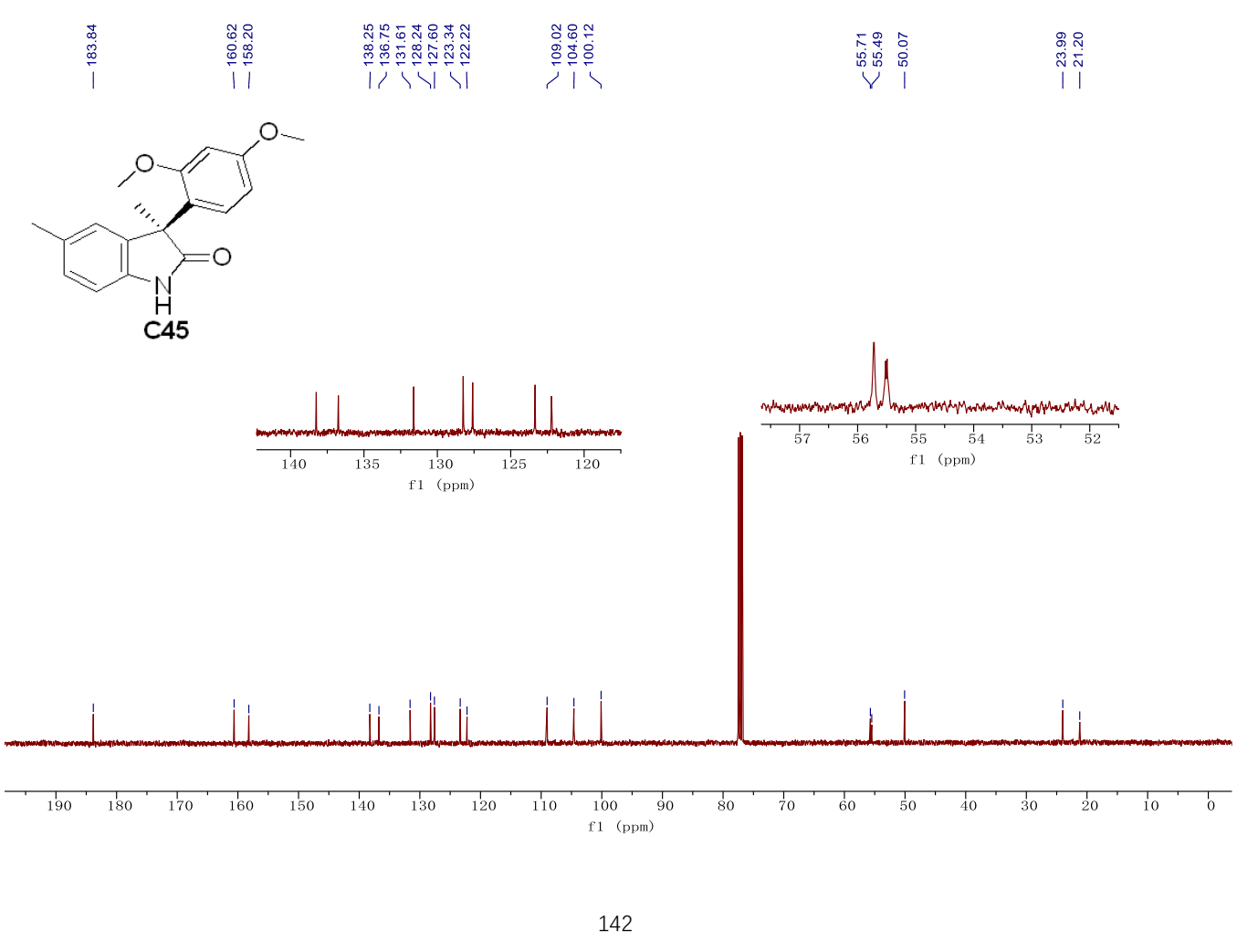

8.85
7.48
7.47
7.44
7.43
7.26
7.26
7.26
7.24
7.24
6.93
6.92
6.80
6.79
6.77
6.76
6.75
6.59
6.58
6.57
6.56
6.38
6.37
3.81
3.46
1.70
Br
O
O
N
H
O
C43
f1 (ppm)
f1 (ppm)


183.44
160.92
157.99
139.78
138.86
130.14
128.28
125.76
121.00
114.84
110.87
104.64
99.91
55.54
50.26
23.70
Br
O
O
N
H
O
C43
f1 (ppm)
f1 (ppm)


8.86
7.46
7.45
7.45
7.44
7.43
7.43
7.09
7.09
6.69
6.67
6.59
6.58
6.57
6.56
6.38
6.37
3.81
3.46
1.69
1.68
C44
2.0
1.0
1.0
1.0
1.0
7.4
7.2
7.0
6.8
6.6
6.4
f1 (ppm)
1.0
2.0
1.0
1.0
1.0
1.0
3.0
3.0
3.1
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


183.25
160.90
157.98
140.46
139.18
136.12
131.31
128.28
121.02
111.50
104.64
99.92
84.82
55.56
50.06
23.71
C44
140
130
120
110
100
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.50
7.49
7.47
6.94
6.93
6.92
6.92
6.91
6.79
6.77
6.74
6.64
6.63
6.59
6.58
6.57
6.56
6.38
6.37
3.80
3.46
2.20
1.69
C45
f1 (ppm)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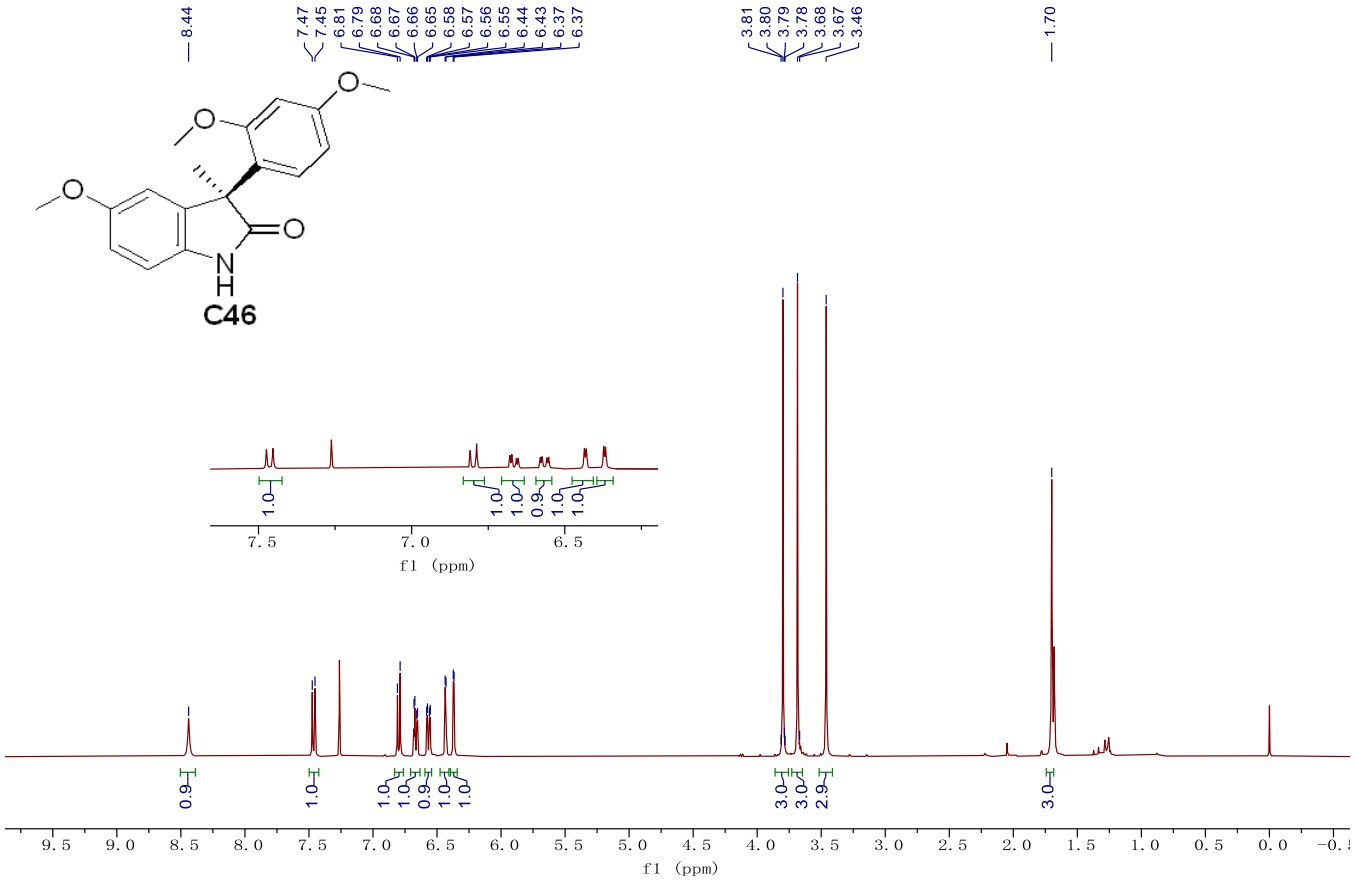
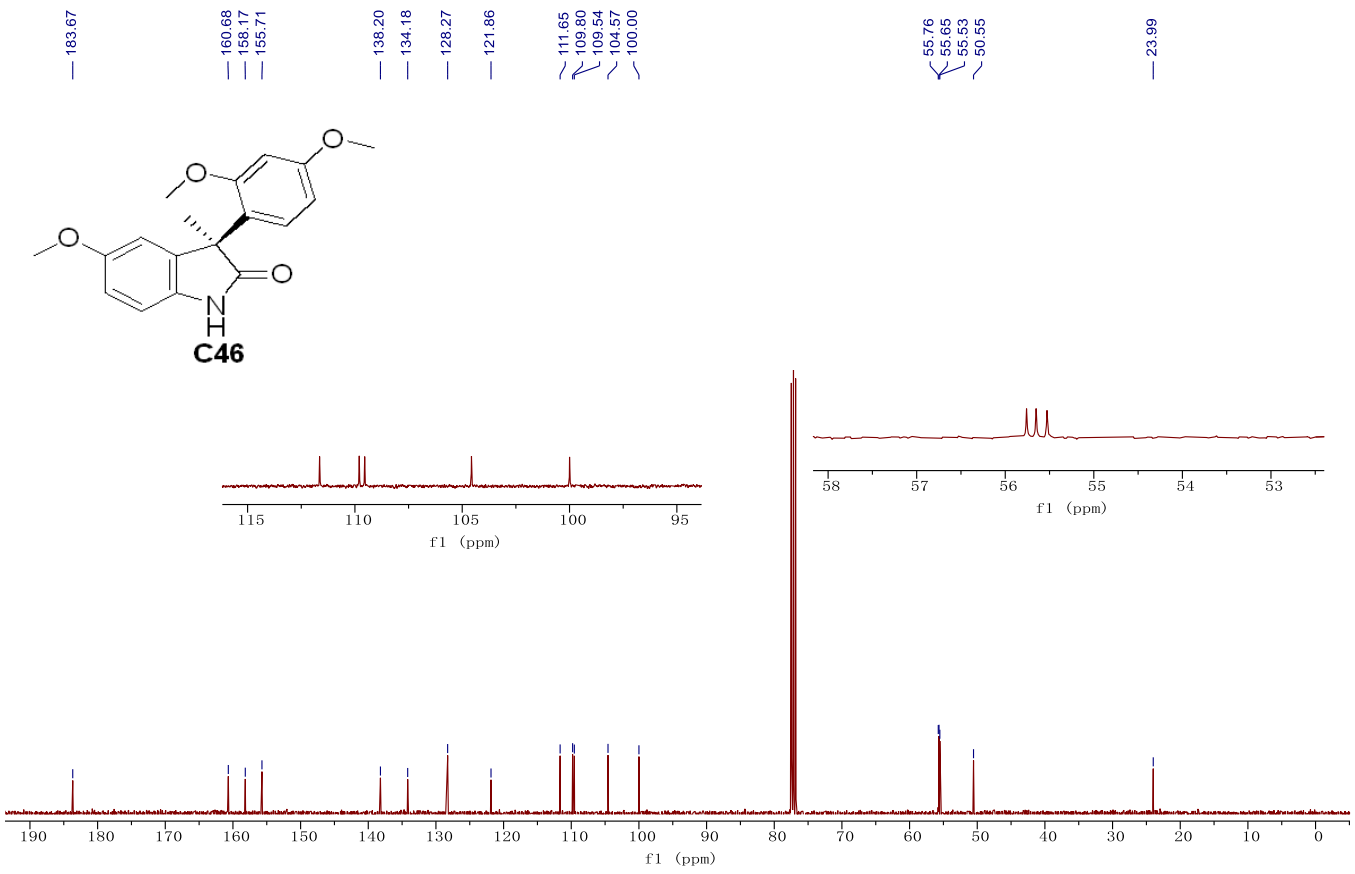
158.20
138.25
136.75
131.61
128.24
127.60
123.34
122.22
109.02
104.60
100.12
55.71
55.49
50.07
23.99
21.20
C45
f1 (ppm)


8.44
7.47
7.45
6.81
6.79
6.68
6.67
6.66
6.65
6.58
6.57
6.56
6.55
6.44
6.43
6.37
6.37
3.81
3.80
3.79
3.78
3.68
3.67
3.46
1.70
C46
f1 (ppm)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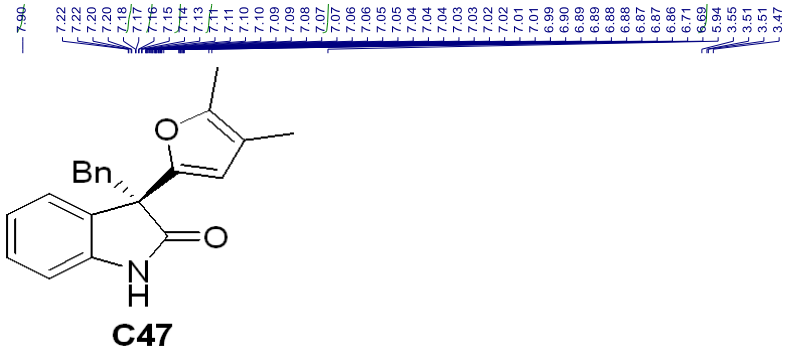
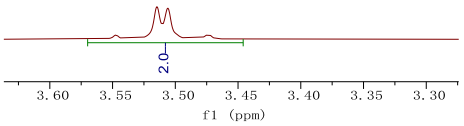
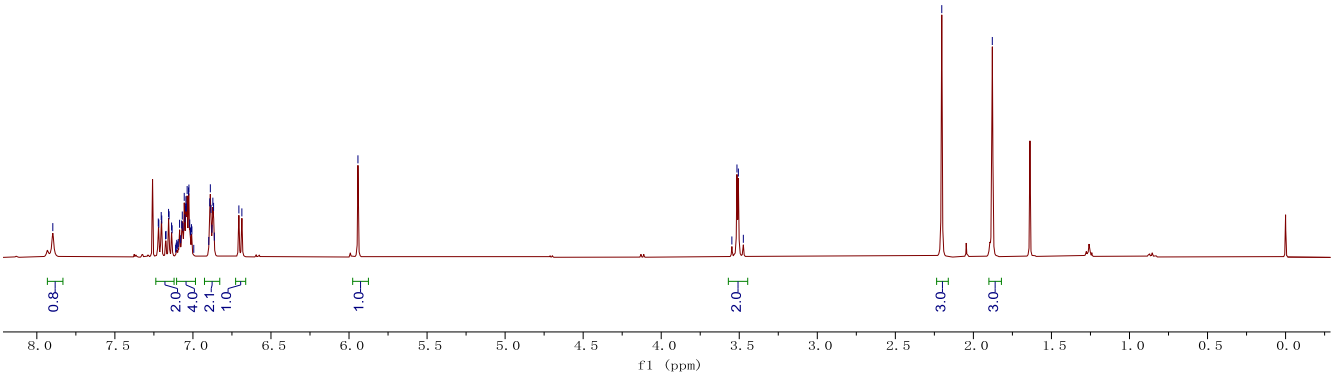
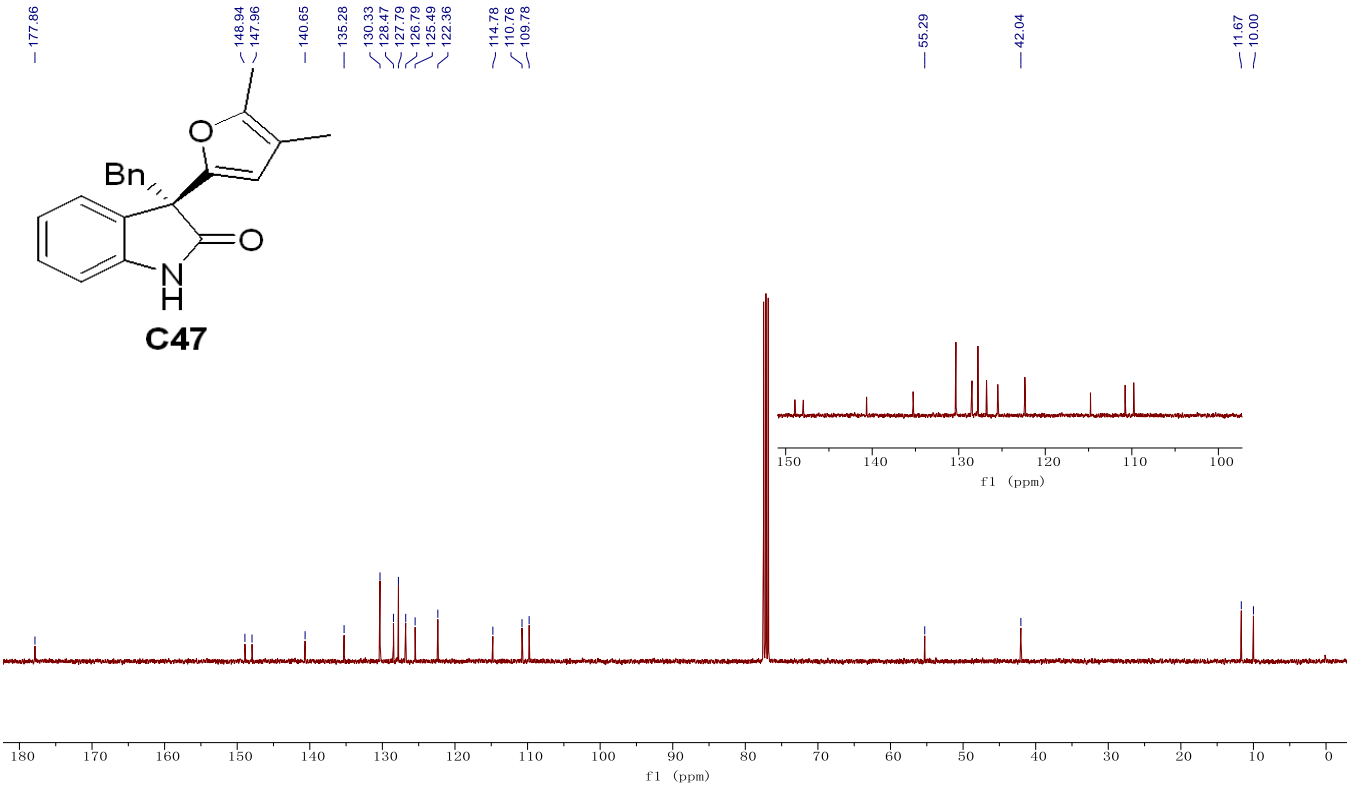
158.17
155.71
138.20
134.18
128.27
121.86
111.65
109.80
109.54
104.57
100.00
55.76
55.65
55.53
50.55
23.99
C46
f1 (ppm)


7.90
7.22
7.22
7.20
7.20
7.18
7.17
7.16
7.15
7.14
7.13
7.11
7.11
7.10
7.10
7.09
7.09
7.08
7.07
7.07
7.06
7.06
7.05
7.05
7.04
7.04
7.03
7.03
7.02
7.02
7.01
7.01
6.99
6.90
6.89
6.89
6.88
6.88
6.87
6.87
6.86
6.71
6.69
5.94
3.55
3.51
3.51
3.47
2.20
1.88
O
Bn
O
N
H

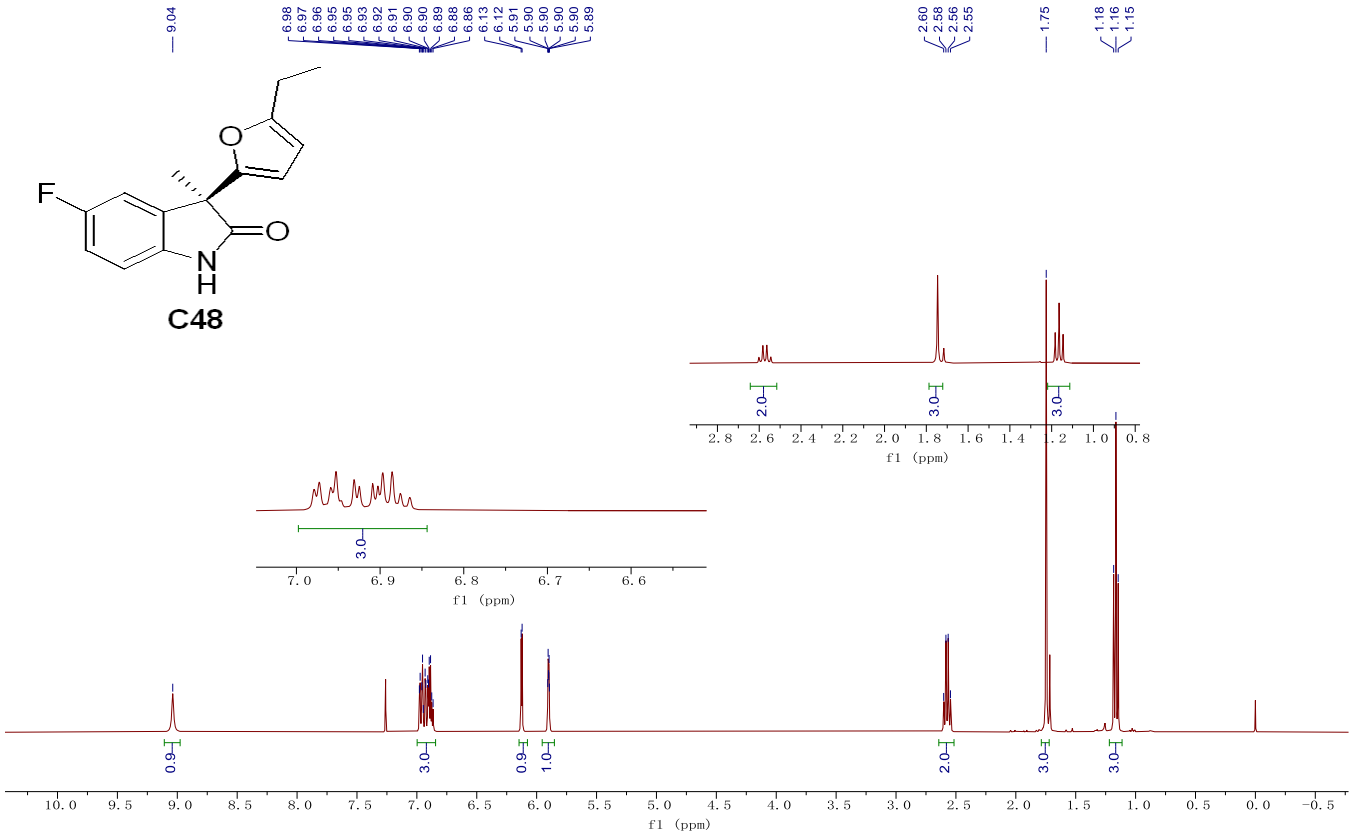
C47

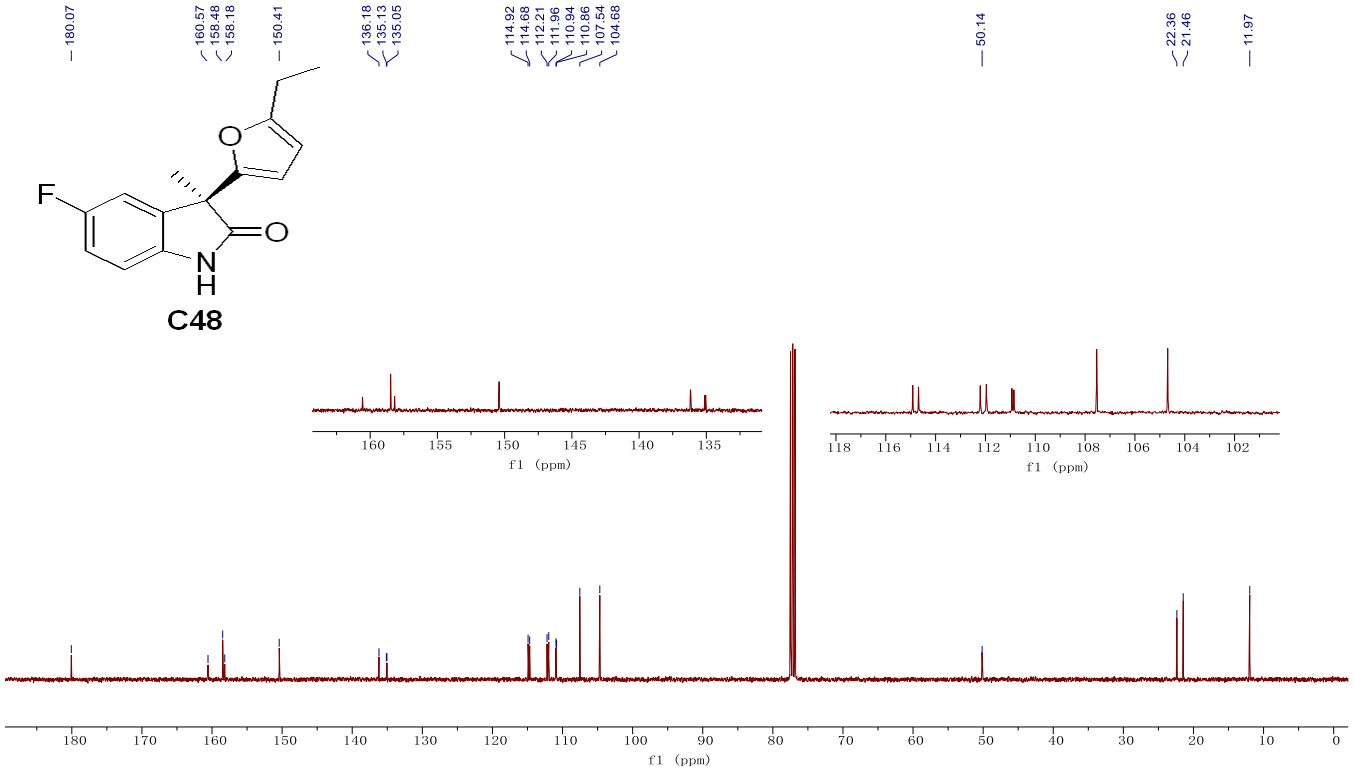

2.0
3.60
3.55
3.50
3.45
3.40
3.35
3.30
f1 (ppm)

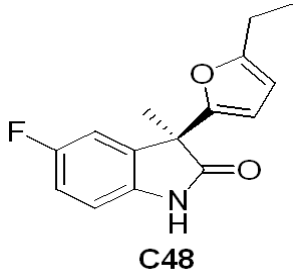

0.8
2.0
4.0
2.1
1.0
1.0
2.0
3.0
3.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


177.86
148.94
147.96
140.65
135.28
130.33
128.47
127.79
126.79
125.49
122.36
114.78
110.76
109.78
55.29
42.04
11.67
10.00
O
Bn
O
N
H
150
140
130
120
110
100
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

C47

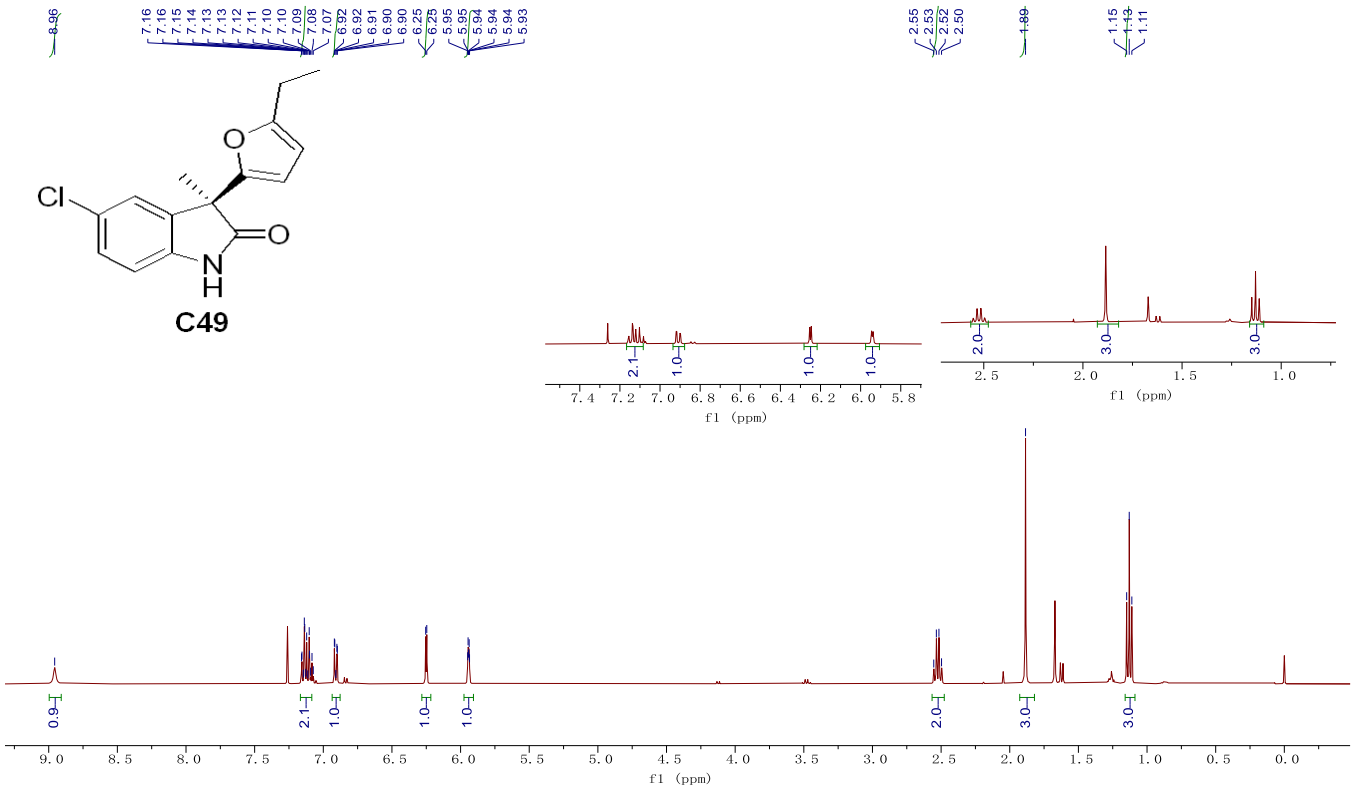

9.04
6.98
6.97
6.96
6.95
6.95
6.93
6.92
6.91
6.90
6.90
6.89
6.88
6.86
6.13
6.12
5.91
5.90
5.90
5.90
5.90
5.89
2.60
2.58
2.56
2.55
1.75
1.18
1.16
1.15
F
O
O
N
H
C48
2.0
3.0
3.0
3.0
f1 (ppm)
0.9
3.0
0.9
1.0
2.0
3.0
3.0
f1 (ppm)

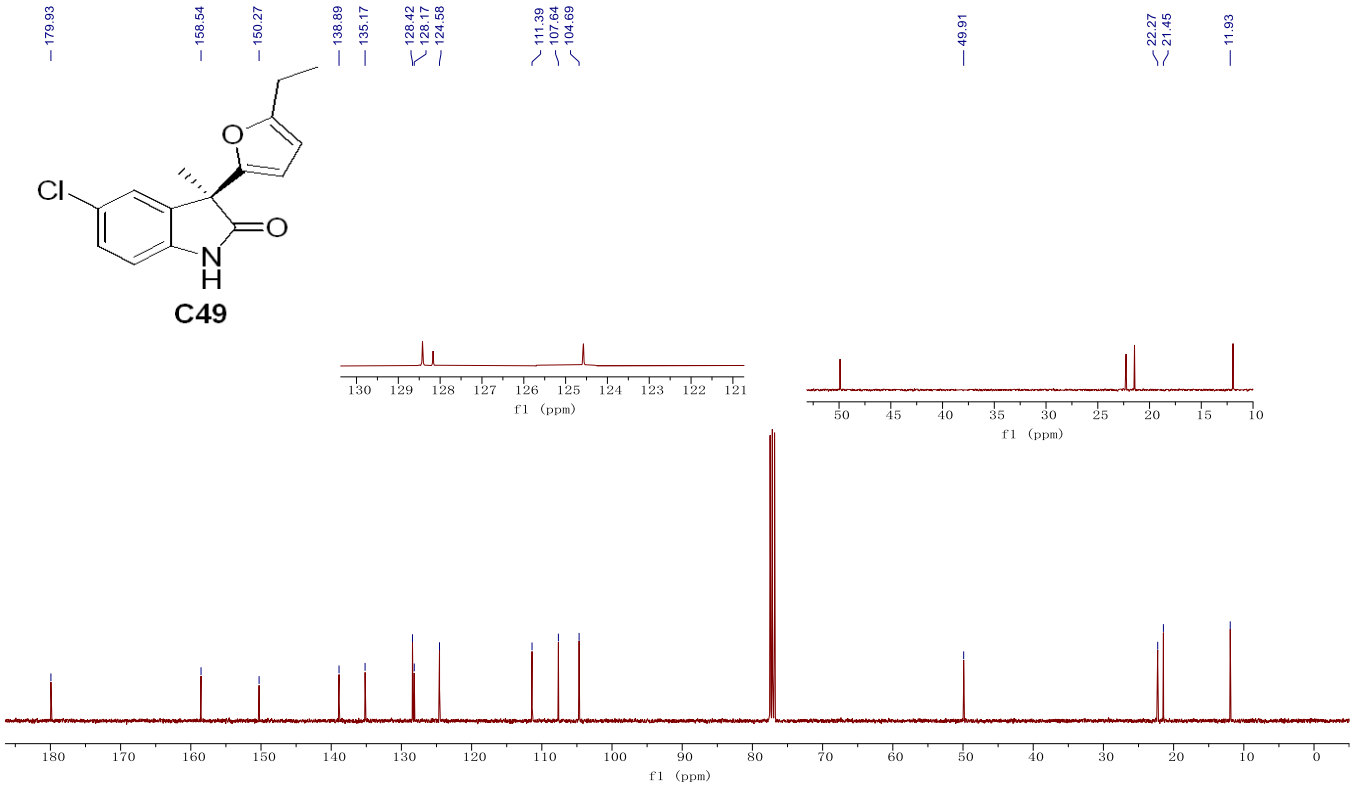

180.07
160.57
158.48
158.18
150.41
136.18
135.13
135.05
114.92
114.68
112.21
111.96
110.94
110.86
107.54
104.68
50.14
22.36
21.46
11.97
F
O
O
N
H
C48
f1 (ppm)
f1 (ppm)
f1 (ppm)

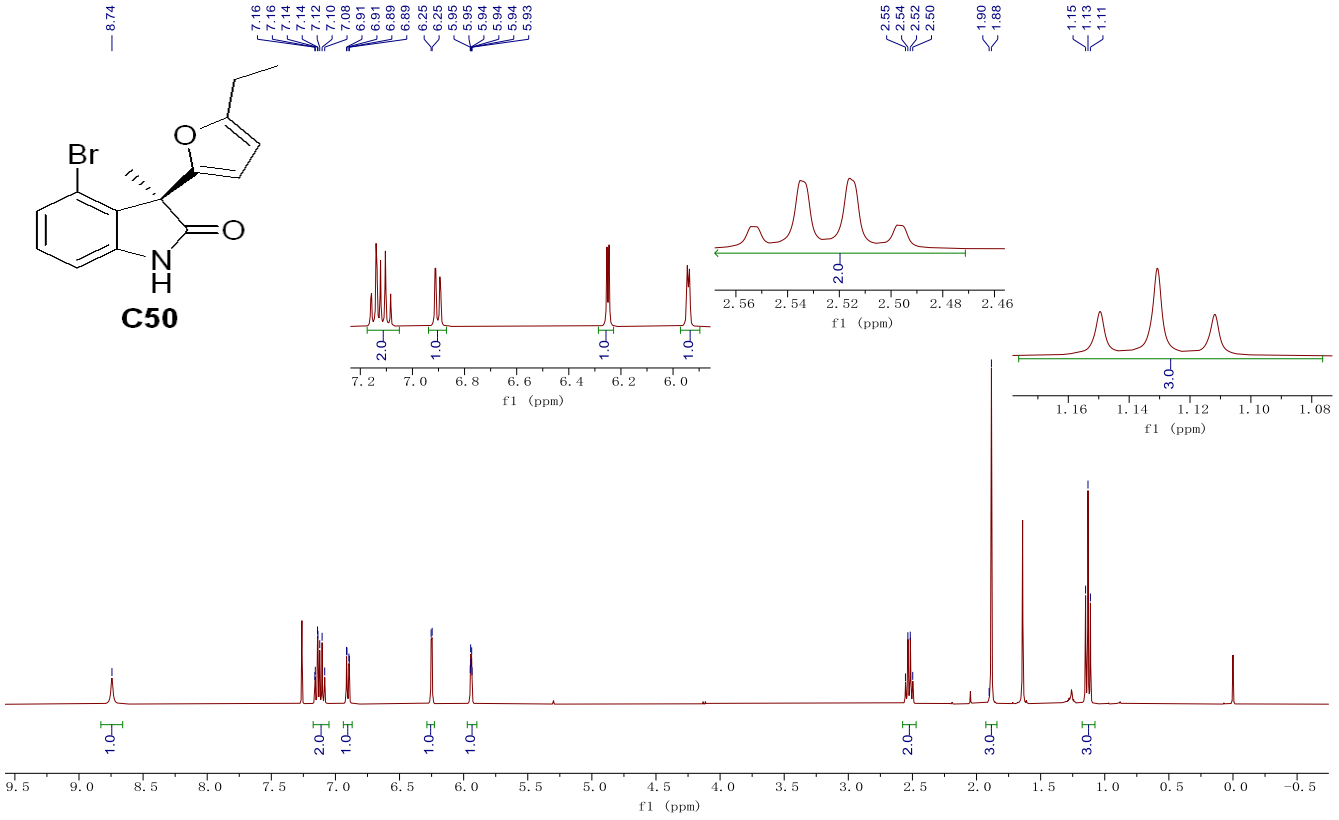

F
O
O
N
H

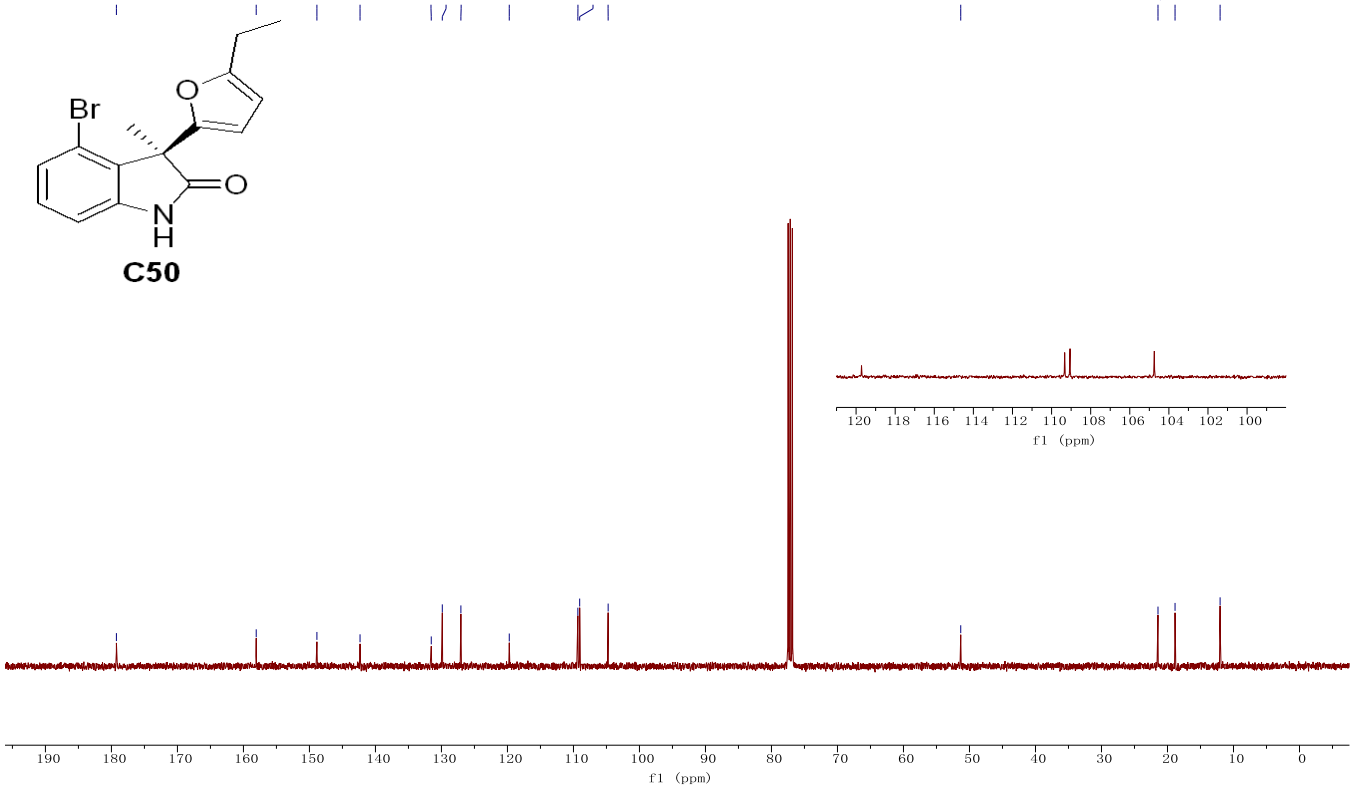
C48

-120.28
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)


C49
f1 (ppm)


C49
f1 (ppm)


8.74
7.16
7.16
7.14
7.14
7.12
7.10
7.08
6.91
6.91
6.89
6.89
6.25
6.25
5.95
5.95
5.94
5.94
5.94
5.93
2.55
2.54
2.52
2.50
1.90
1.88
1.15
1.13
1.11
Br
O
O
N
H
C50
f1 (ppm)


179.24
158.06
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142.33
131.54
129.87
127.05
119.72
109.33
109.06
104.74
51.32
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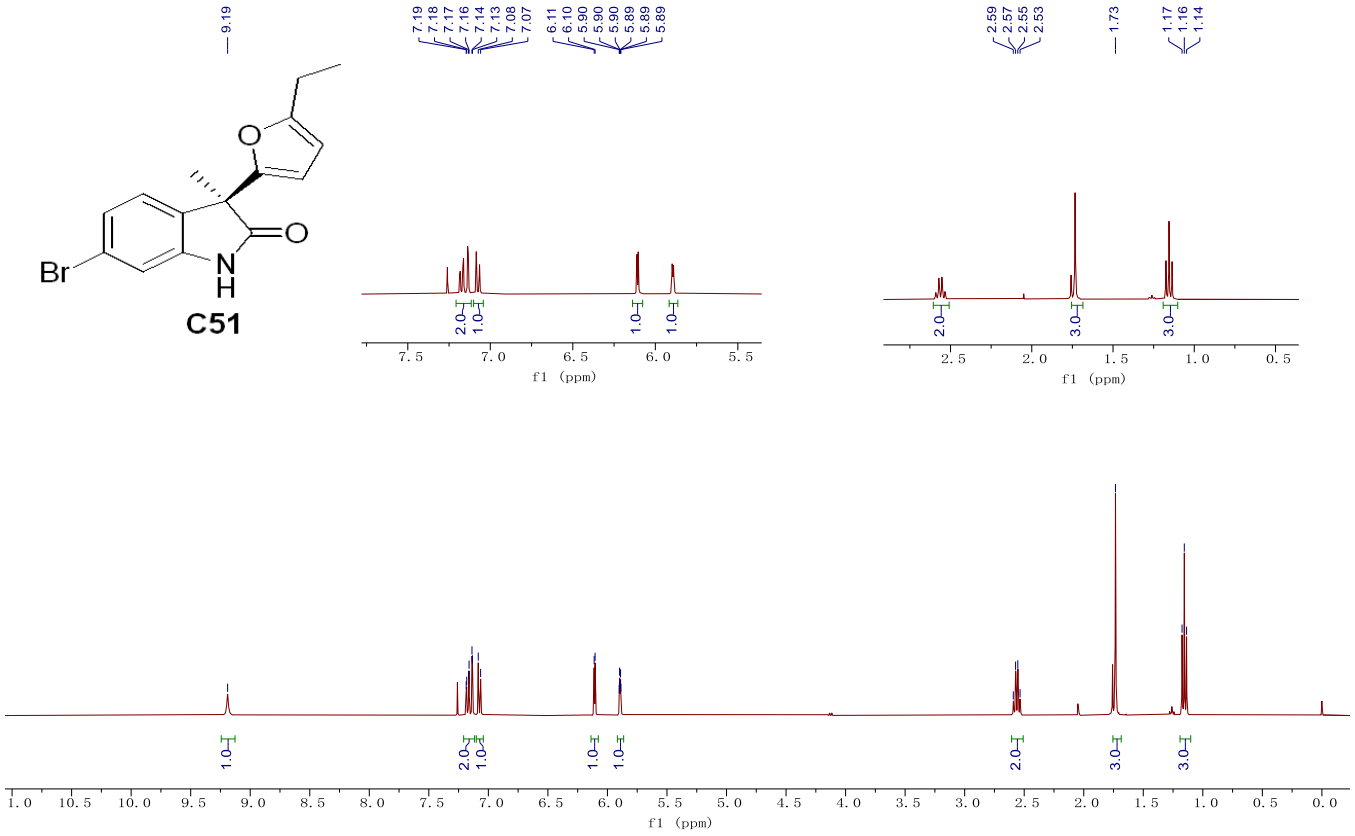
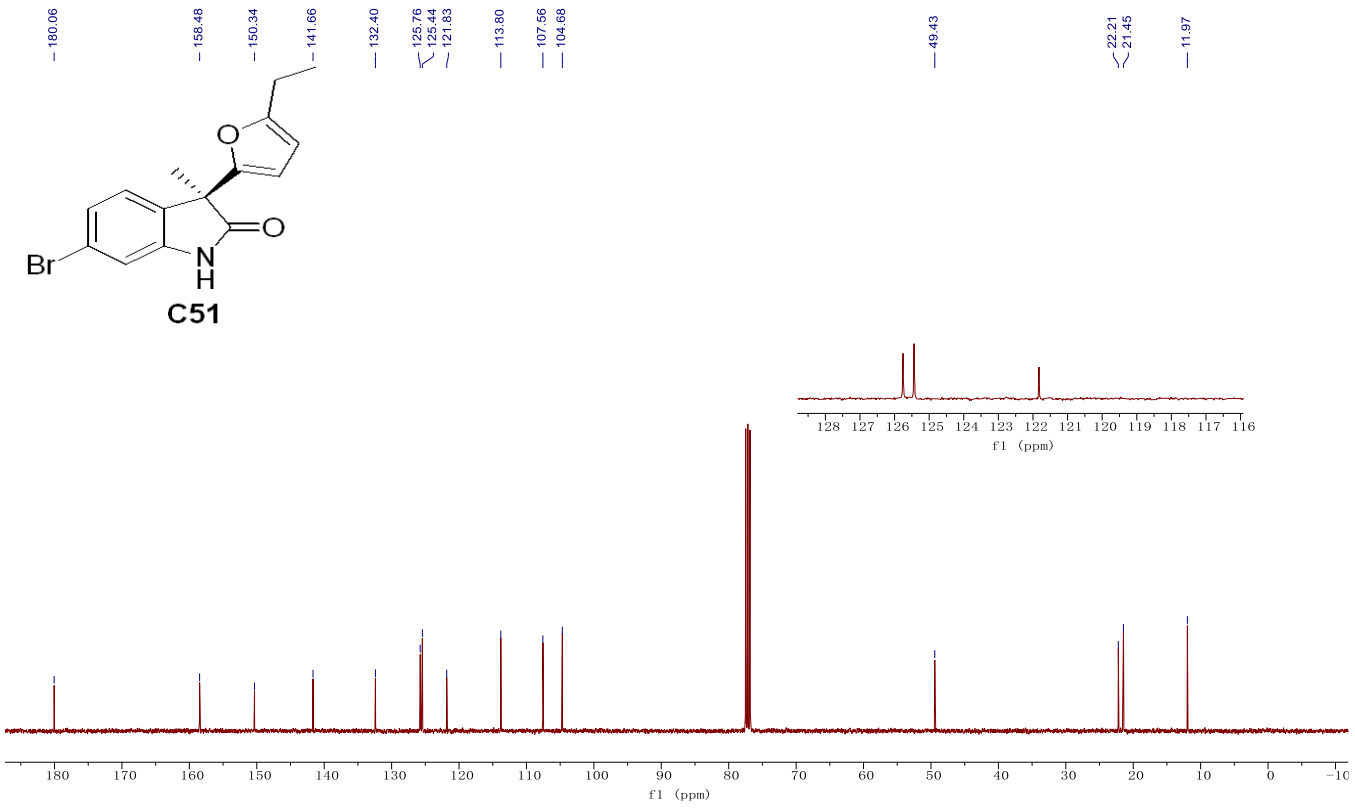
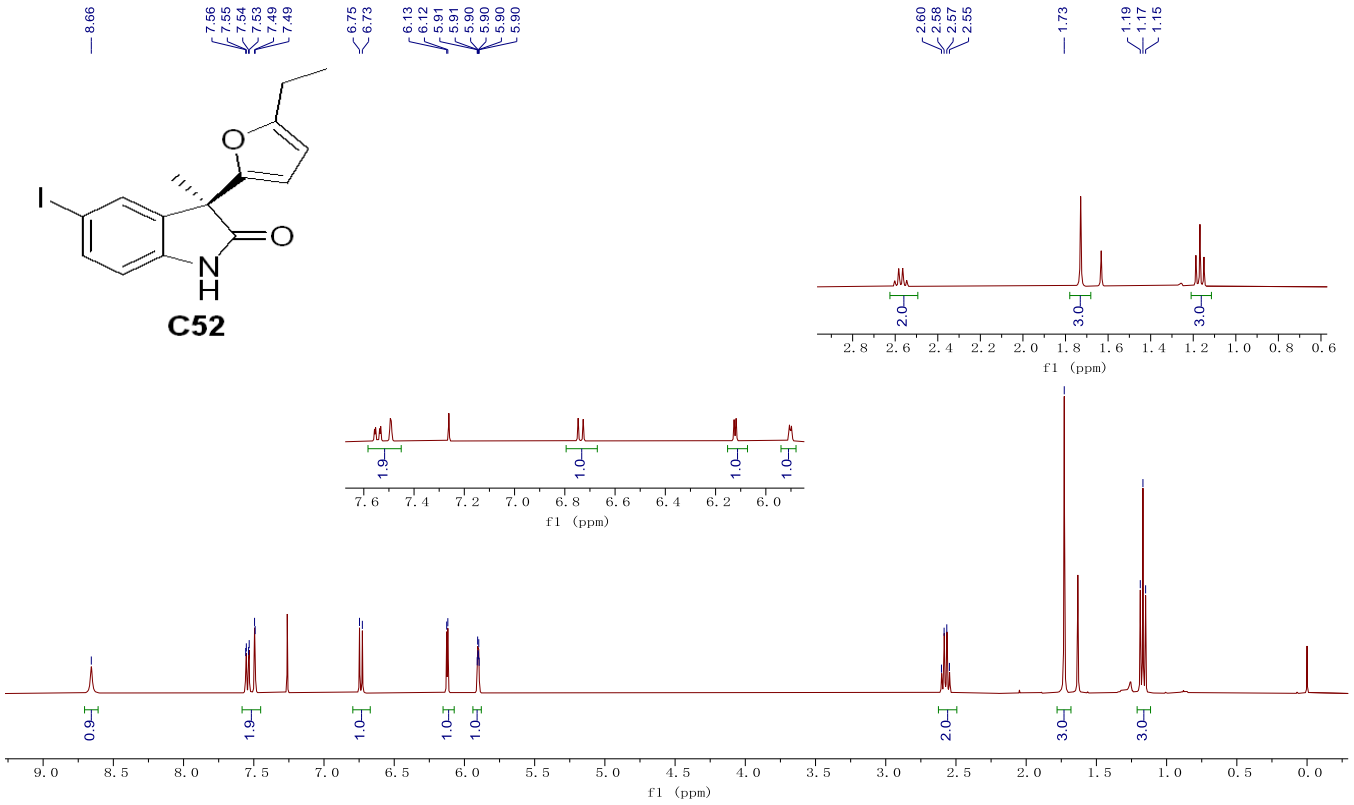
Br
O
O
N
H
C50
f1 (ppm)

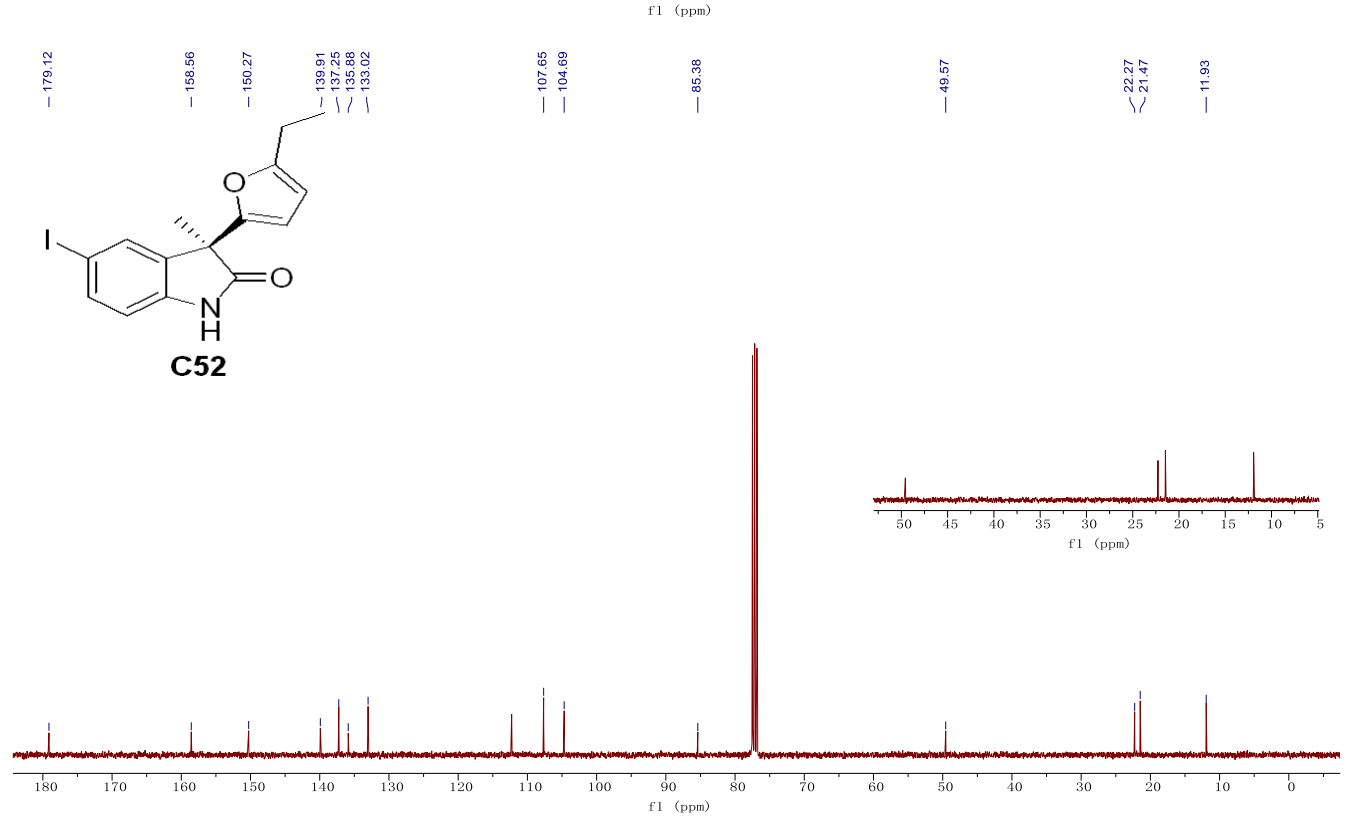

9.19
7.19
7.18
7.17
7.16
7.14
7.13
7.08
7.07
6.11
6.10
5.90
5.90
5.90
5.89
5.89
5.89
2.59
2.57
2.55
2.53
1.73
1.17
1.16
1.14
Br
O
O
N
H
C51
f1 (ppm)

f1 (ppm)


180.06
158.48
150.34
141.66
132.40
125.76
125.44
121.83
113.80
107.56
104.68
49.43
22.21
21.45
11.97
Br
O
O
N
H
C51
f1 (ppm)

f1 (ppm)


8.66
7.56
7.55
7.54
7.53
7.49
7.49
6.75
6.73
6.13
6.12
5.91
5.91
5.90
5.90
5.90
5.90
2.60
2.58
2.57
2.55
1.73
1.19
1.17
1.15
C52
f1 (ppm)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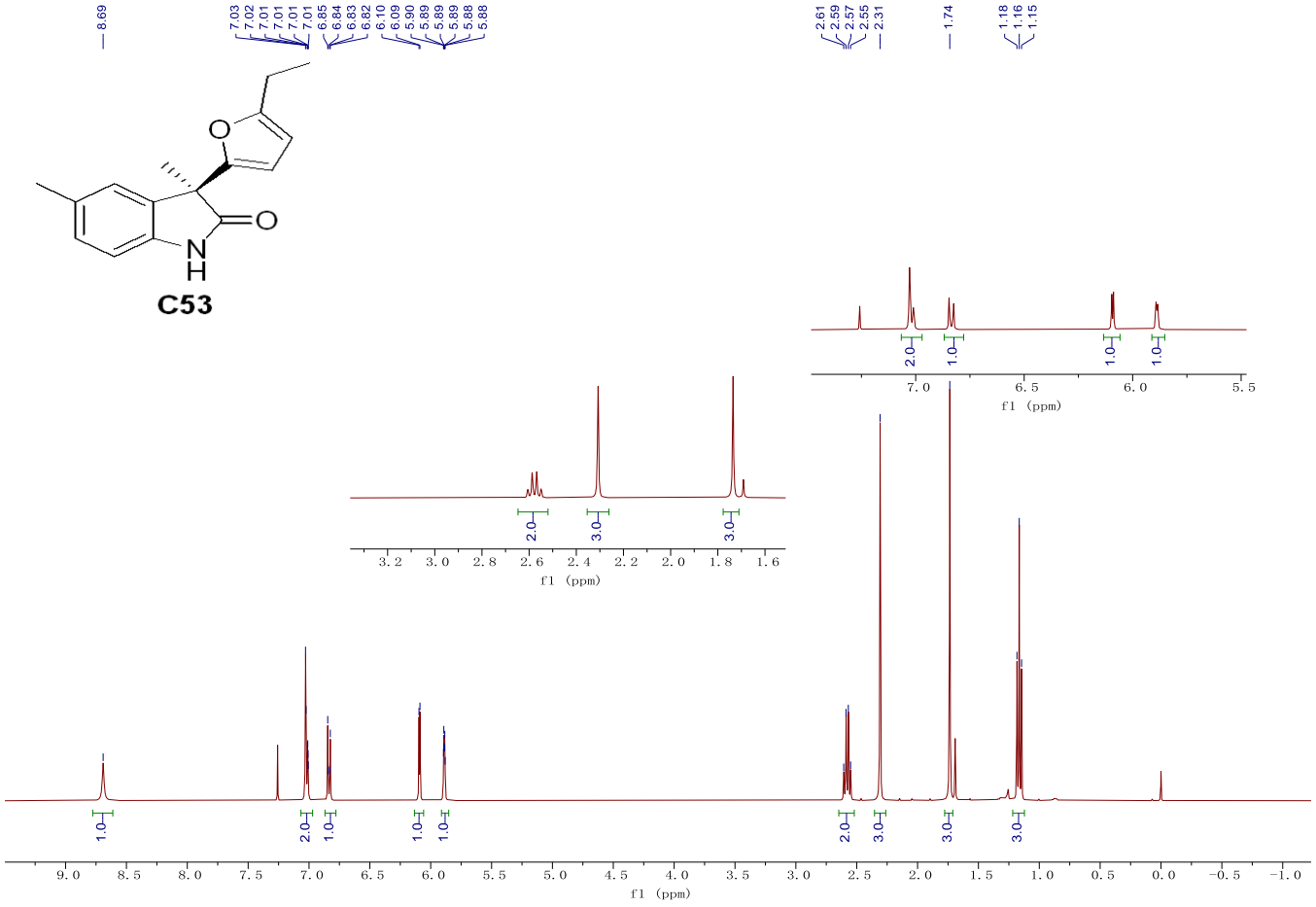
150.27
139.91
137.25
135.88
133.02
107.65
104.69
85.38
49.57
22.27
21.47
11.93
C52
f1 (ppm)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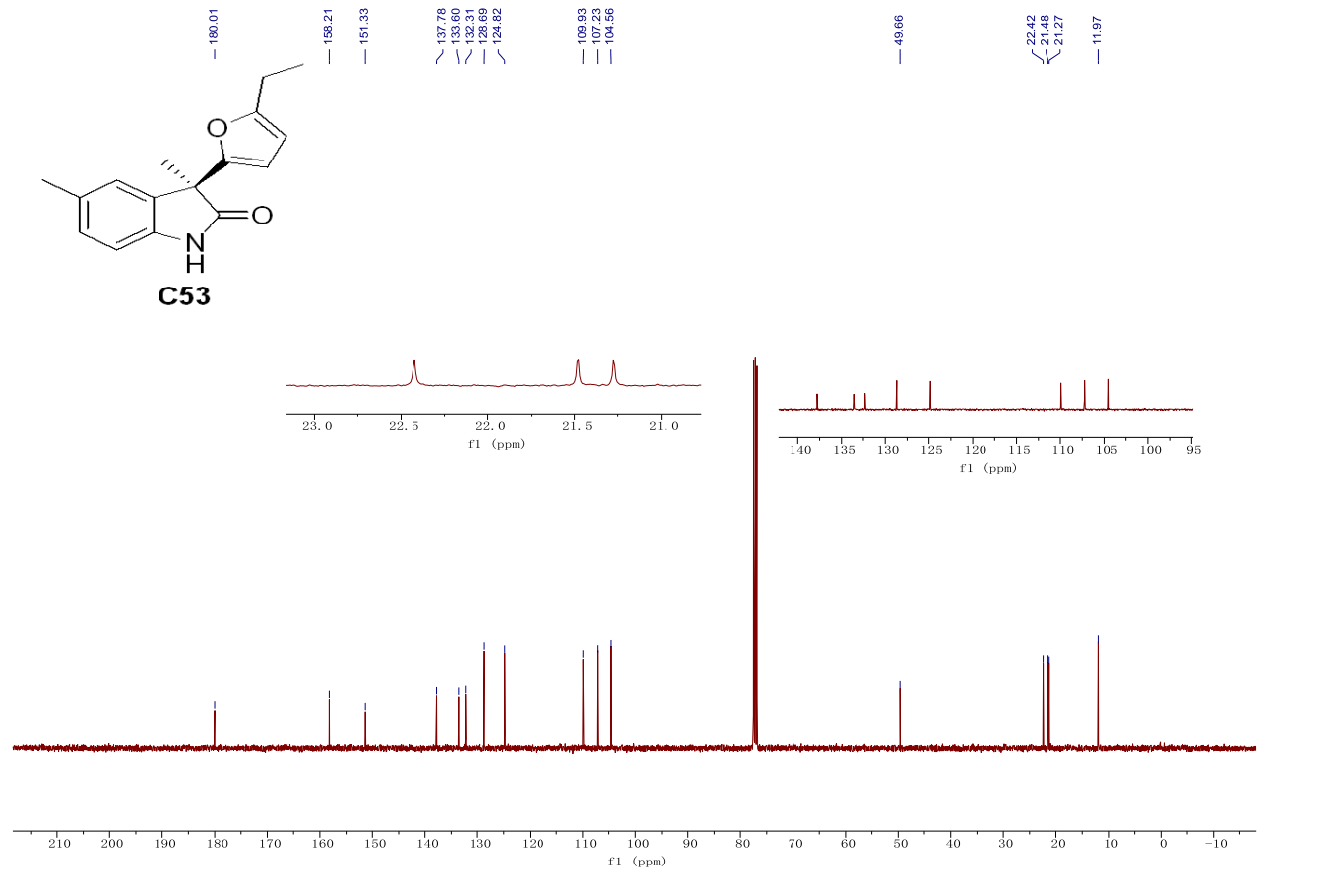
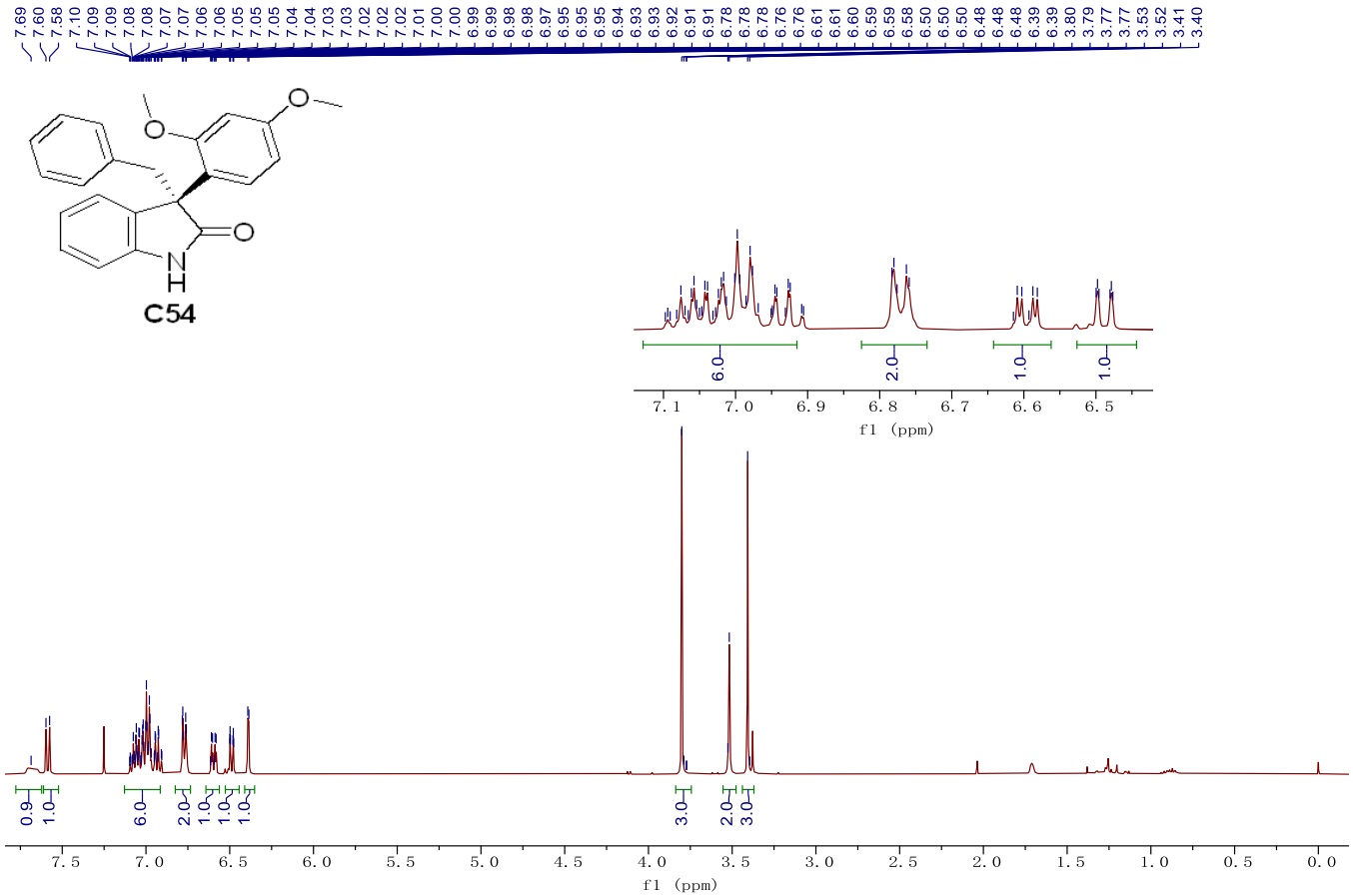
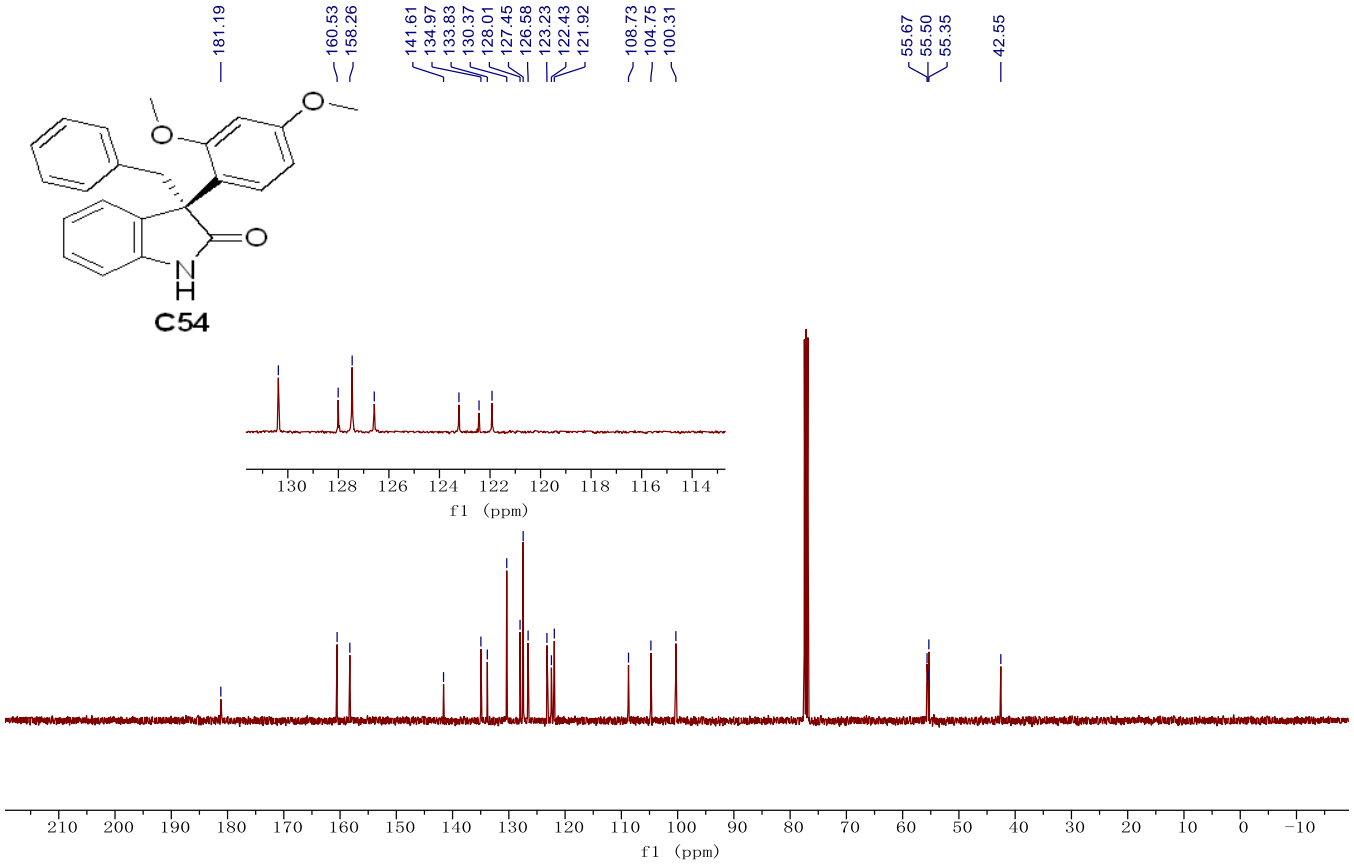
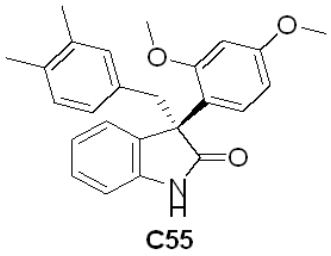
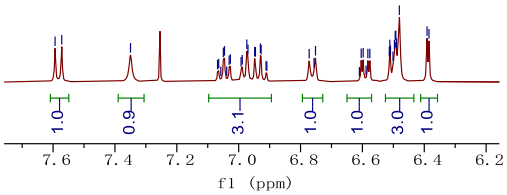
7.03
7.02
7.01
7.01
7.01
7.01
6.85
6.84
6.83
6.82
6.10
6.09
5.90
5.89
5.89
5.89
5.88
5.88
2.61
2.59
2.57
2.55
2.31
1.74
1.18
1.16
1.15
O
O
N
H
C53
f1 (ppm)

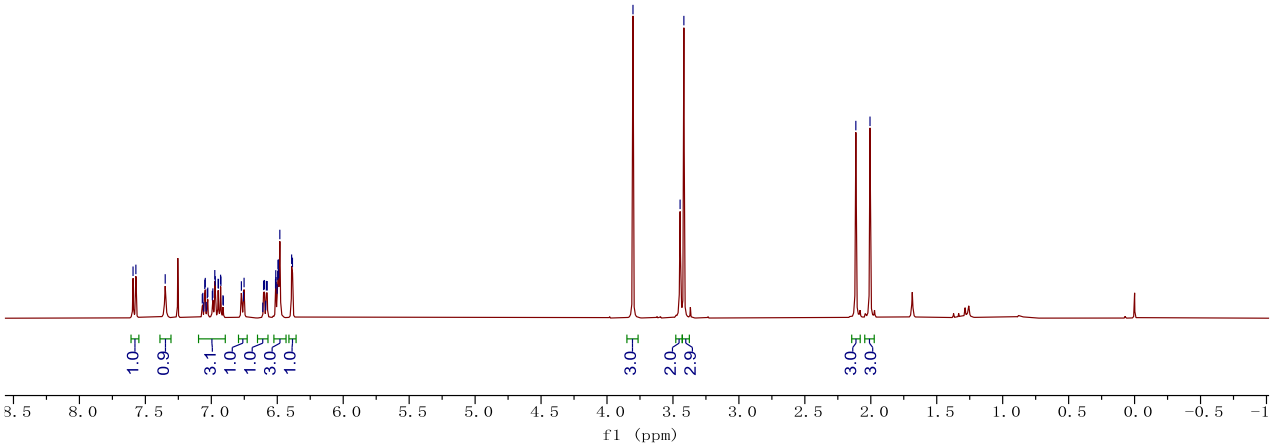

180.01
158.21
151.33
137.78
133.60
132.31
128.69
124.82
109.93
107.23
104.56
49.66
22.42
21.48
21.27
11.97
O
O
N
H
C53
f1 (ppm)

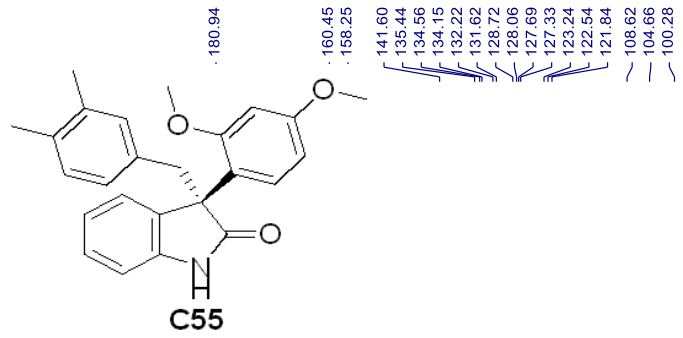

C54
f1 (ppm)


C54
f1 (ppm)

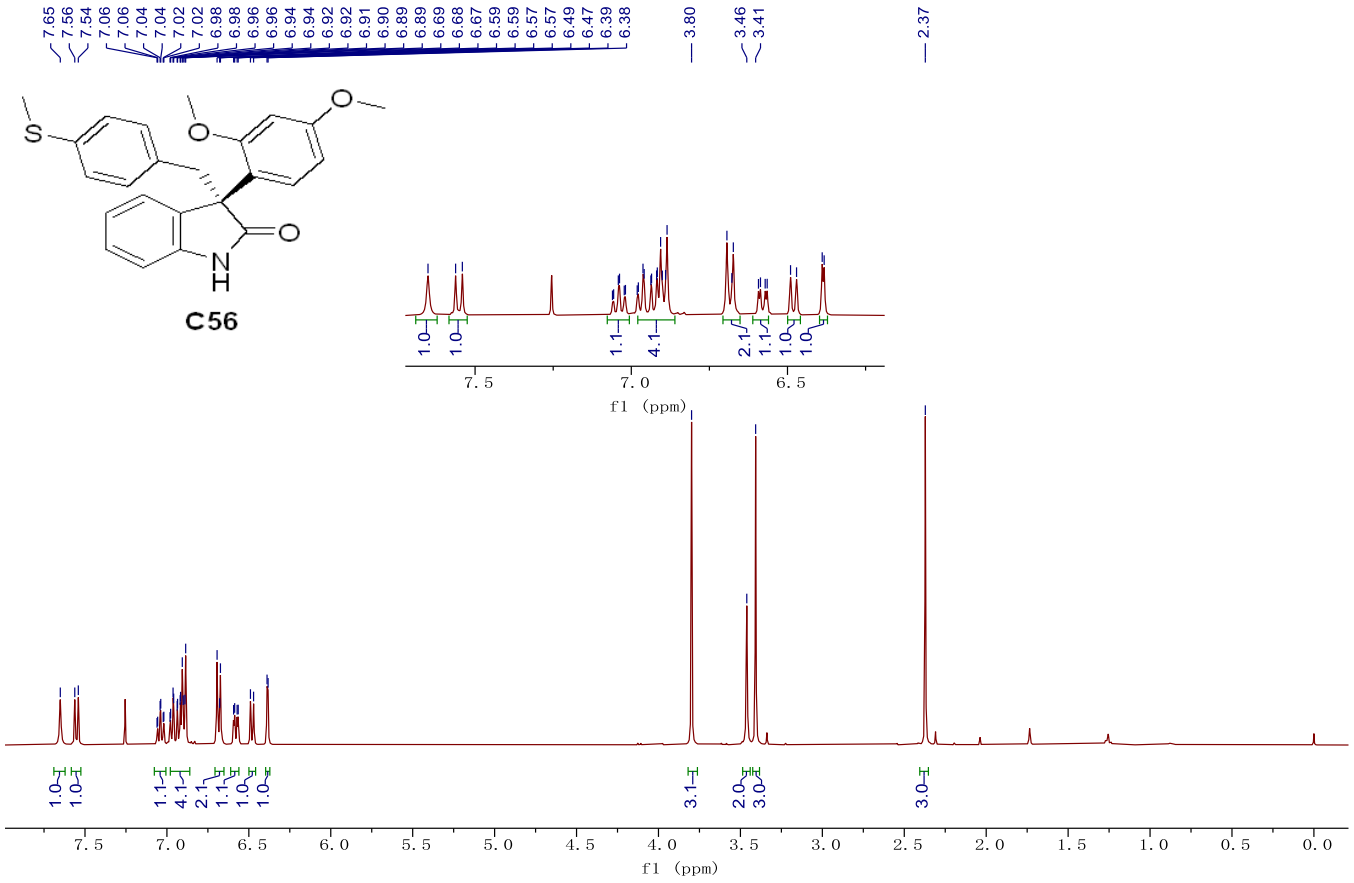

C55

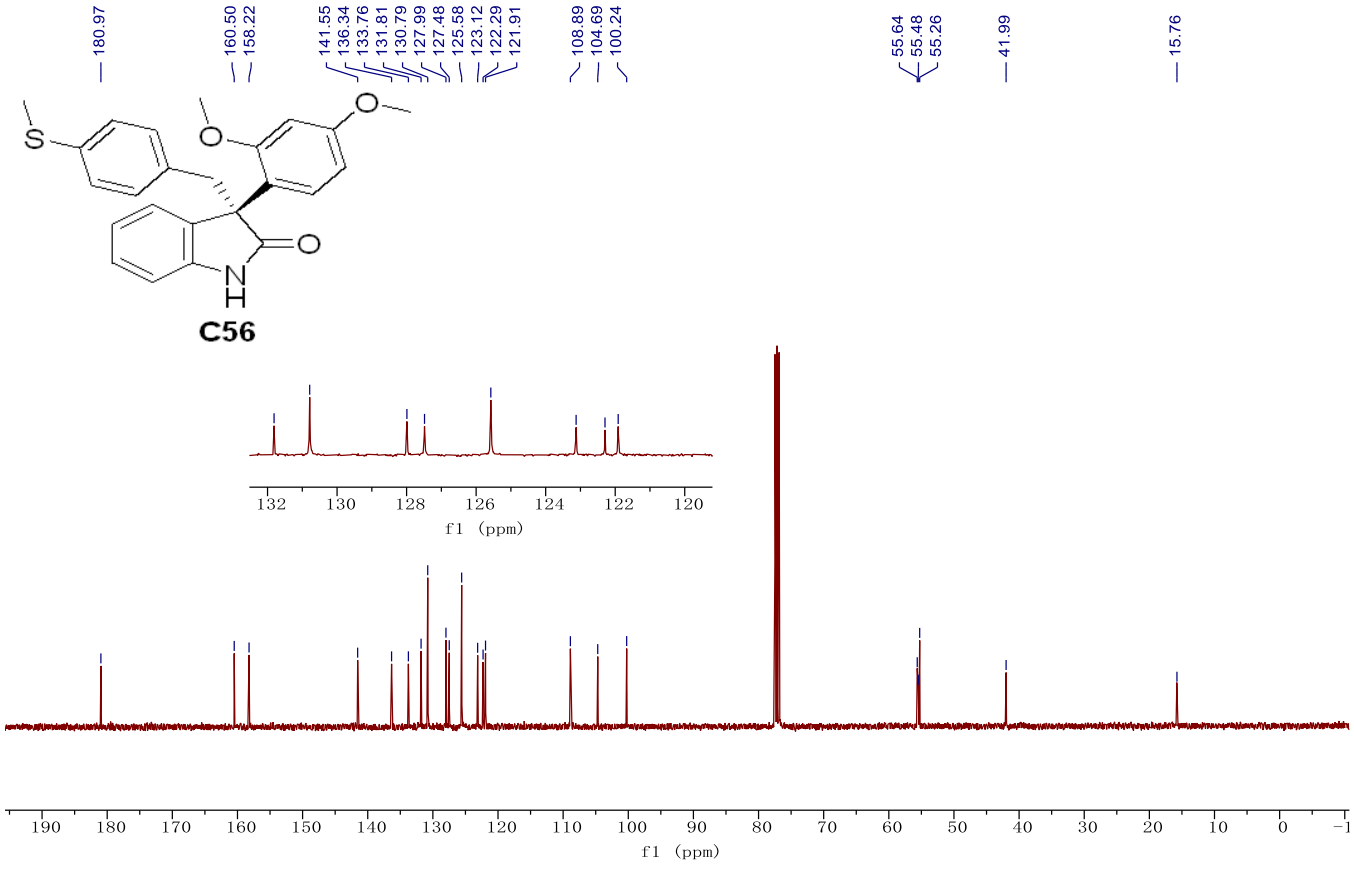

1.0
0.9
3.1
1.0
1.0
3.0
1.0
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
f1 (ppm)

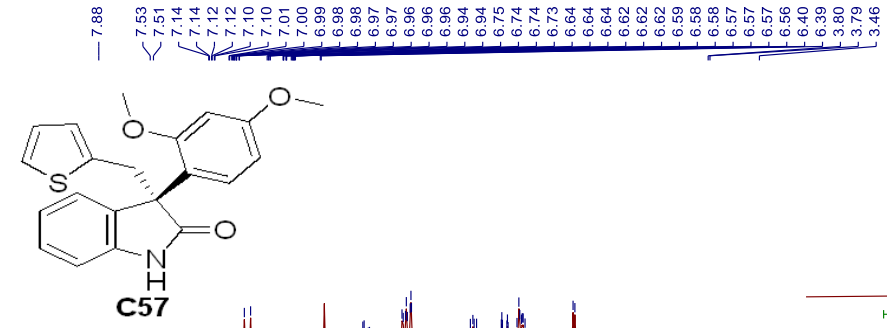

1.0
0.9
3.1
1.0
1.0
3.0
1.0
3.0
2.0
2.9
3.0
3.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

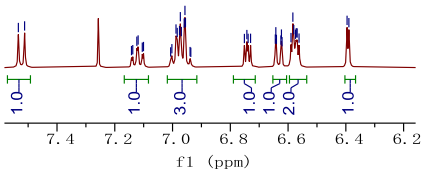

C55

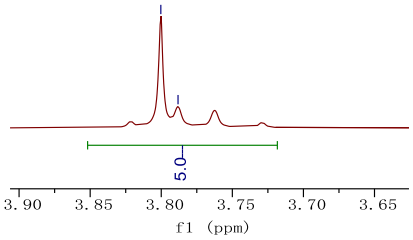
180.94
160.45
158.25
141.60
135.44
134.56
134.15
132.22
131.62
128.72
128.06
127.69
127.33
123.24
122.54
121.84
108.62
104.66
100.28
55.70
55.51
55.24
42.16
19.58
19.48
136
134
132
130
128
126
124
122
120
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

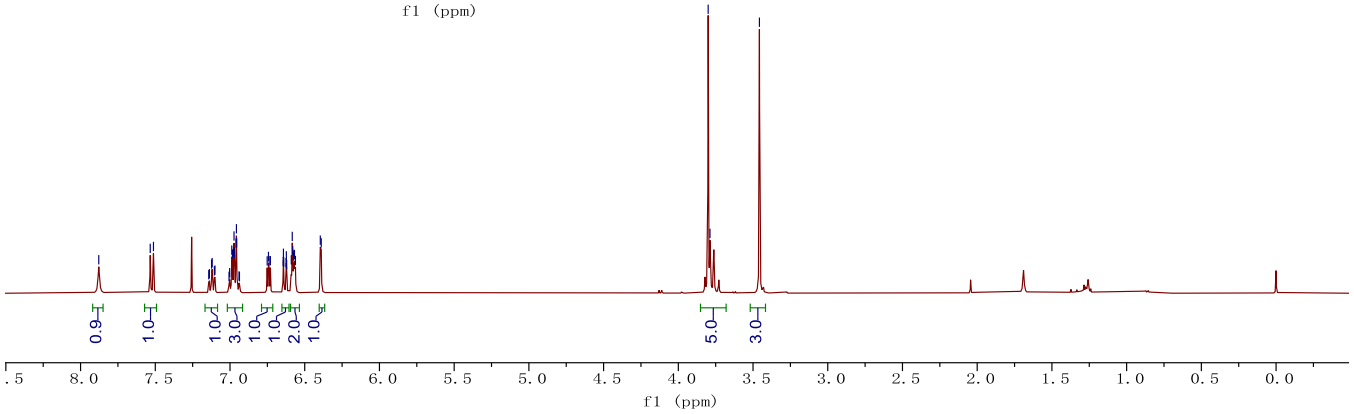

7.65
7.56
7.54
7.06
7.06
7.04
7.04
7.02
7.02
6.98
6.98
6.96
6.96
6.94
6.94
6.92
6.92
6.91
6.90
6.89
6.89
6.69
6.68
6.67
6.59
6.59
6.57
6.57
6.49
6.47
6.39
6.38
3.80
3.46
3.41
2.37
S
O
O
O
N
H
C56
1.0
1.0
1.1
4.1
2.1
1.1
1.0
1.0
3.1
2.0
3.0
3.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

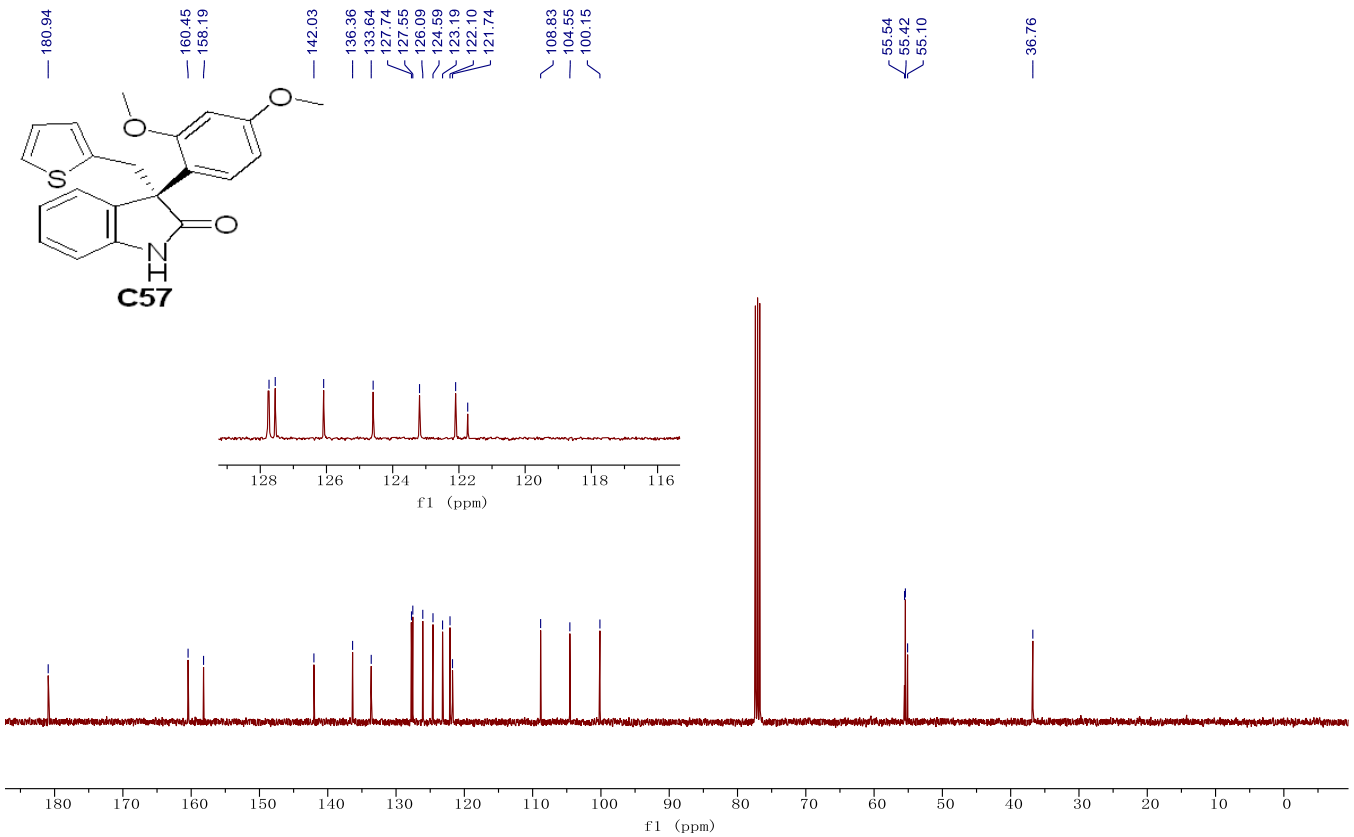

180.97
160.50
158.22
141.55
136.34
133.76
131.81
130.79
127.99
127.48
125.58
123.12
122.29
121.91
108.89
104.69
100.24
55.64
55.48
55.26
41.99
15.76
S
O
O
O
N
H
C56
132
130
128
126
124
122
120
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

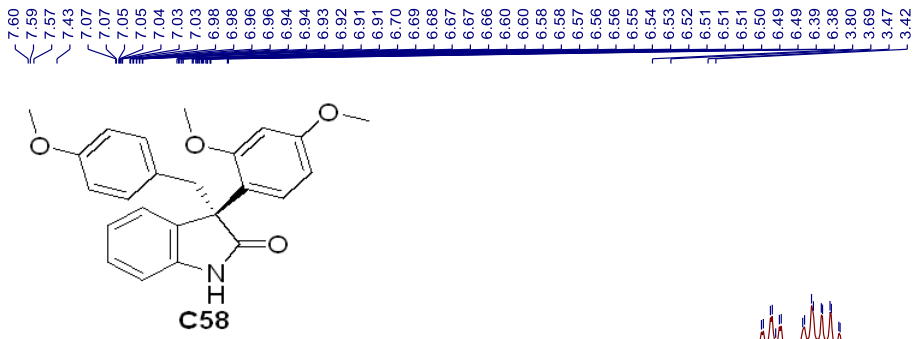

7.88
7.53
7.51
7.14
7.12
7.12
7.10
7.10
7.01
7.00
6.99
6.98
6.98
6.97
6.97
6.96
6.96
6.96
6.96
6.94
6.94
6.75
6.74
6.74
6.73
6.64
6.64
6.64
6.62
6.62
6.62
6.59
6.58
6.58
6.57
6.57
6.57
6.56
6.40
6.39
3.80
3.79
3.46
O
O
S
O
N
H
C57


1.0
1.0
3.0
1.0
1.0
2.0
1.0
7.4
7.2
7.0
6.8
6.6
6.4
6.2
f1 (ppm)


5.0
3.90
3.85
3.80
3.75
3.70
3.65
f1 (ppm)

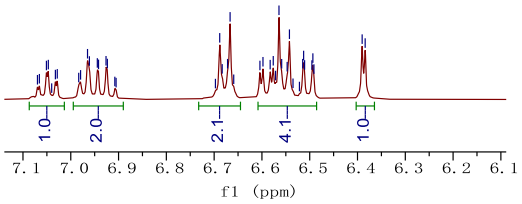

0.9
1.0
1.0
3.0
1.0
1.0
2.0
1.0
5.0
3.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


180.94
160.45
158.19
142.03
136.36
133.64
127.74
127.55
126.09
124.59
123.19
122.10
121.74
108.83
104.55
100.15
55.54
55.42
55.10
36.76
O
O
S
O
N
H
C57
128
126
124
122
120
118
116
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

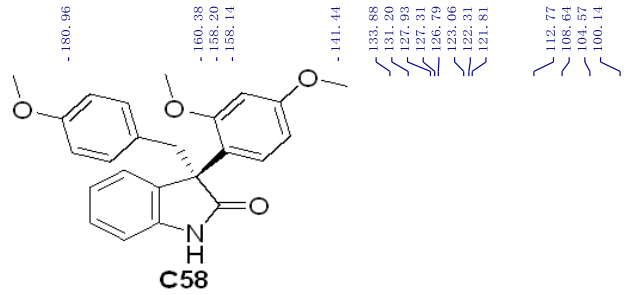

7.60
7.59
7.57
7.43
7.07
7.07
7.05
7.05
7.04
7.03
7.03
6.98
6.98
6.96
6.96
6.94
6.94
6.93
6.92
6.91
6.91
6.70
6.69
6.68
6.67
6.67
6.66
6.60
6.60
6.58
6.58
6.57
6.56
6.56
6.55
6.54
6.53
6.52
6.51
6.51
6.51
6.50
6.49
6.49
6.39
6.38
3.80
3.69
3.47
3.42

O
O
O
N
H

C58

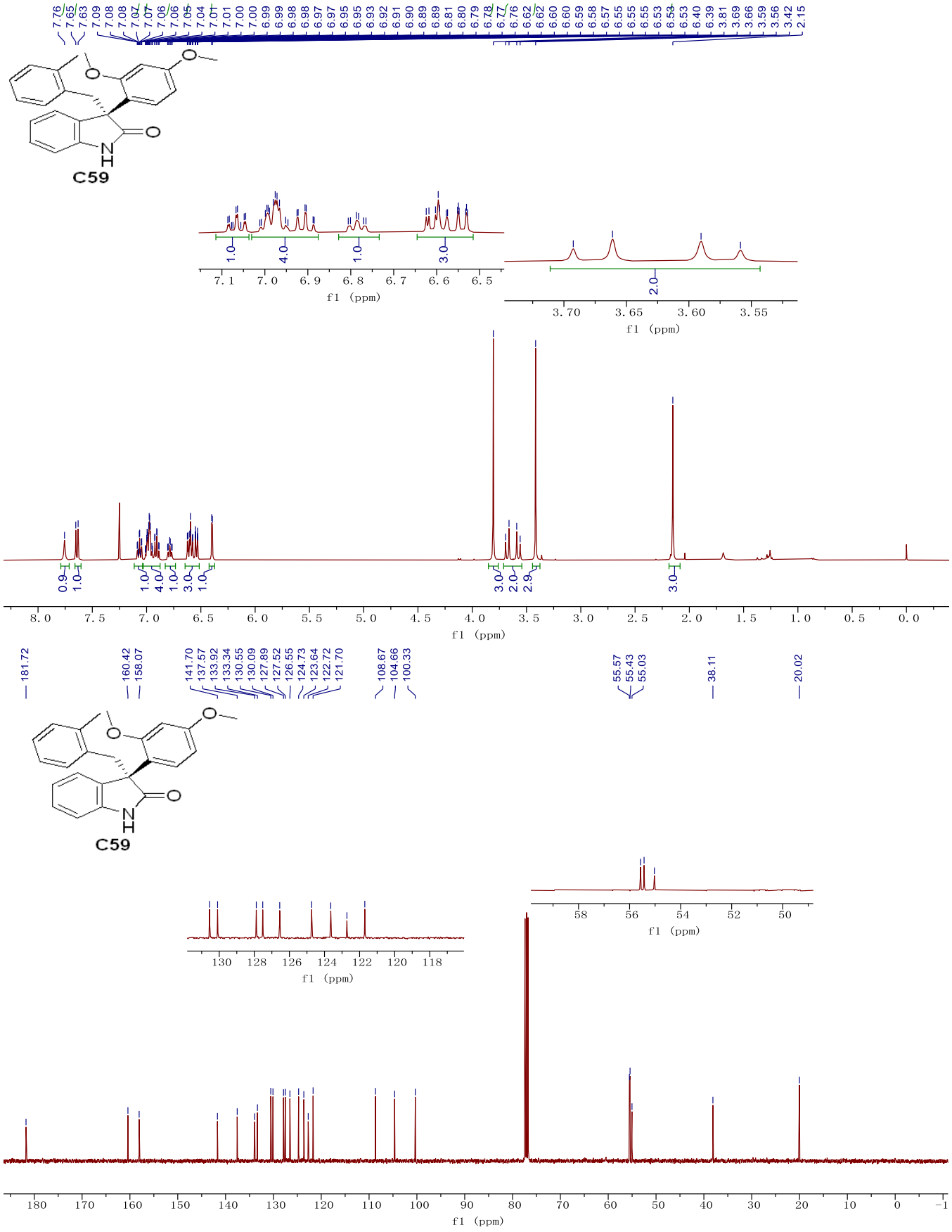

1.0
2.0
2.1
4.1
1.0
7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1
f1 (ppm)

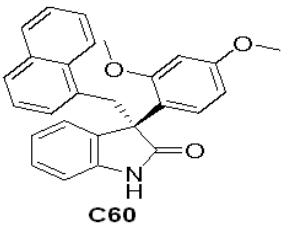
1.0
1.0
1.0
2.0
2.1
4.1
1.0
3.0
3.0
2.0
3.1
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

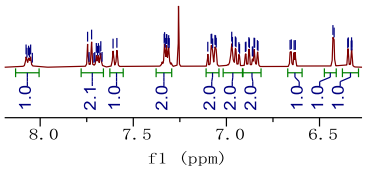

O
O
O
N
H

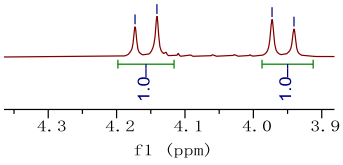
C58

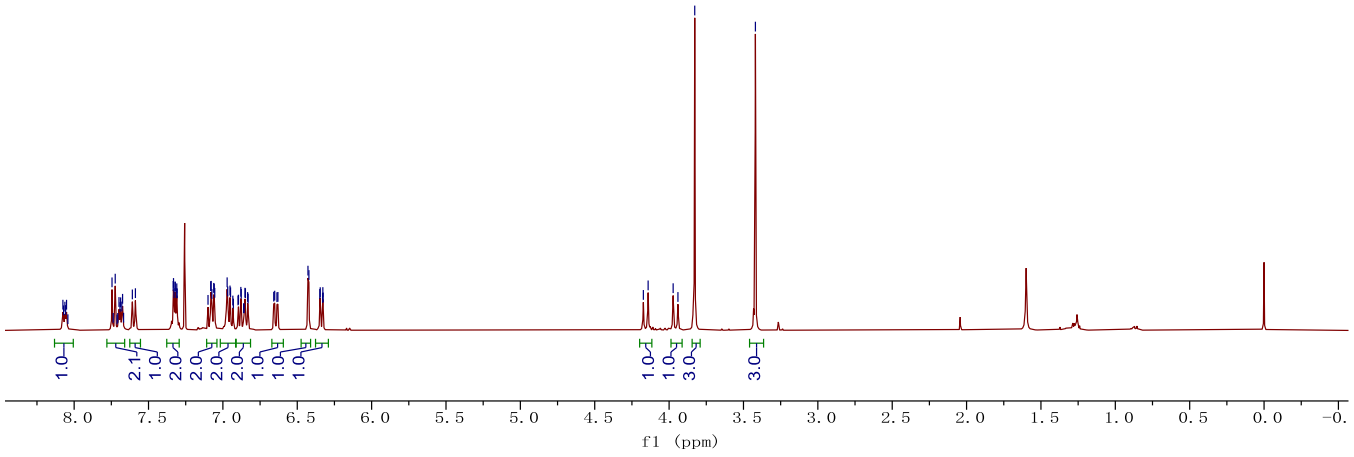
180.96
160.38
158.20
158.14
141.44
133.88
131.20
127.93
127.31
126.79
123.06
122.31
121.81
112.77
108.64
104.57
100.14
55.58
55.41
55.20
55.04
41.64
128 127 126 125 124 123 122 121 120 119 118
f1 (ppm)
57 56 55 54 53 52
f1 (ppm)
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

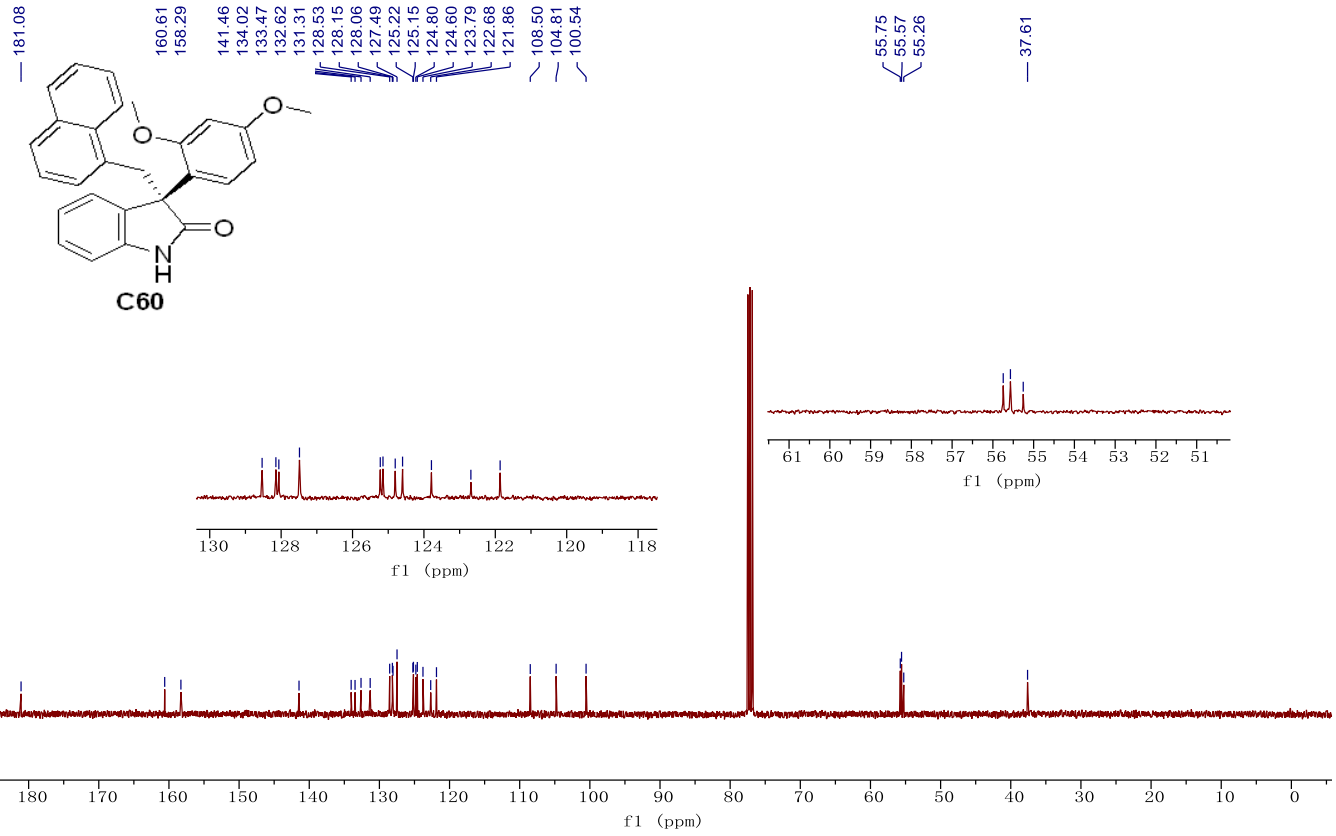

C59
f1 (ppm)
C59
f1 (ppm)

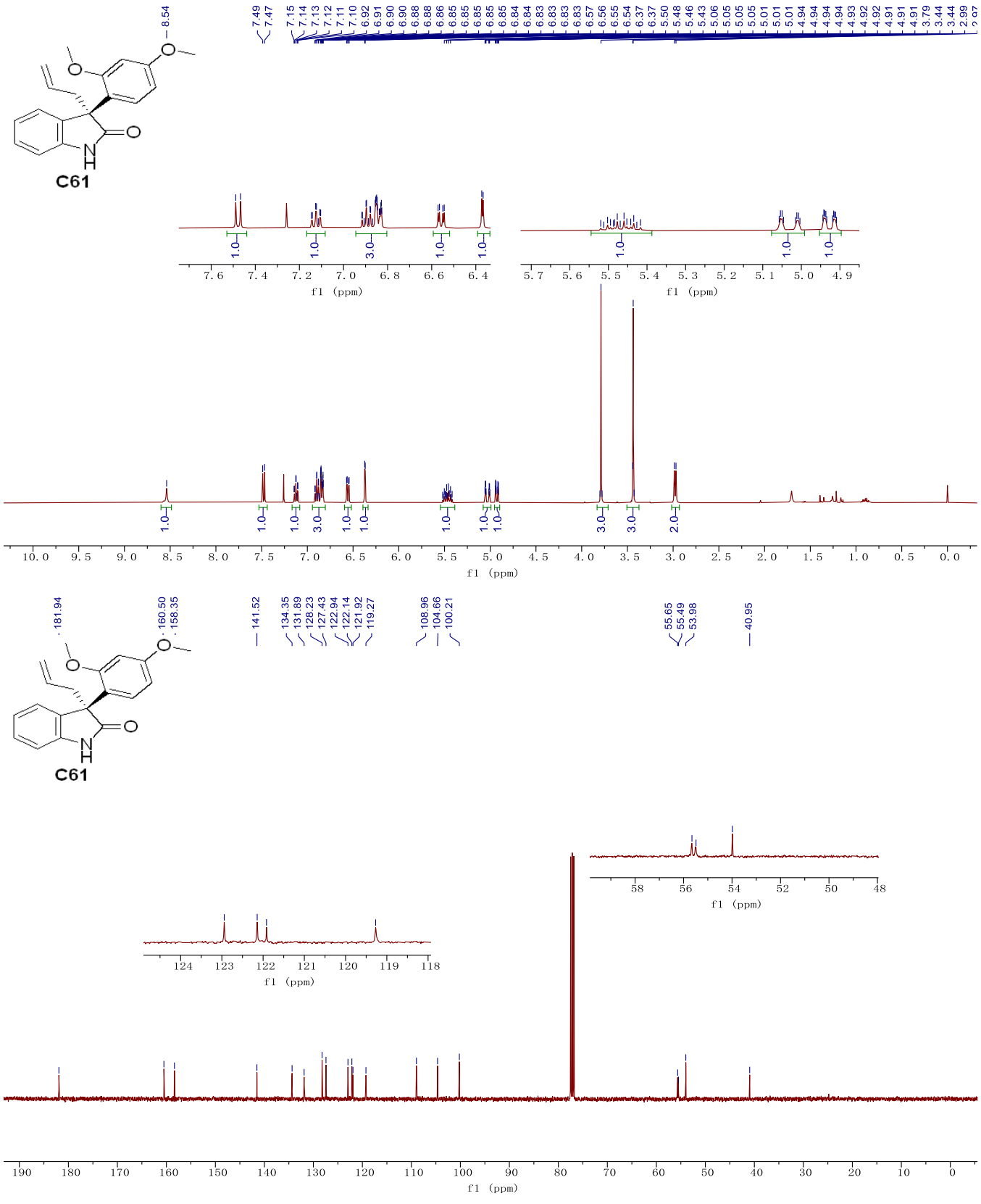

C60

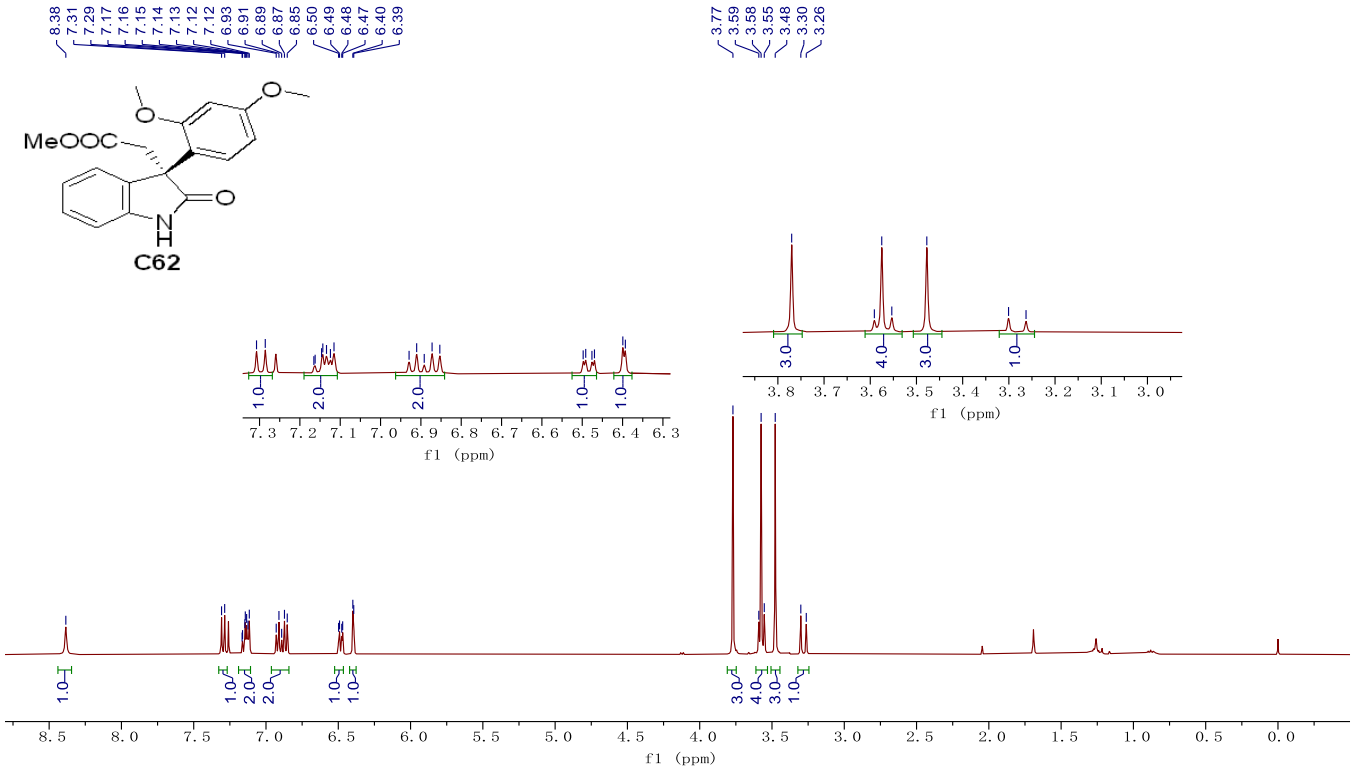

f1 (ppm)

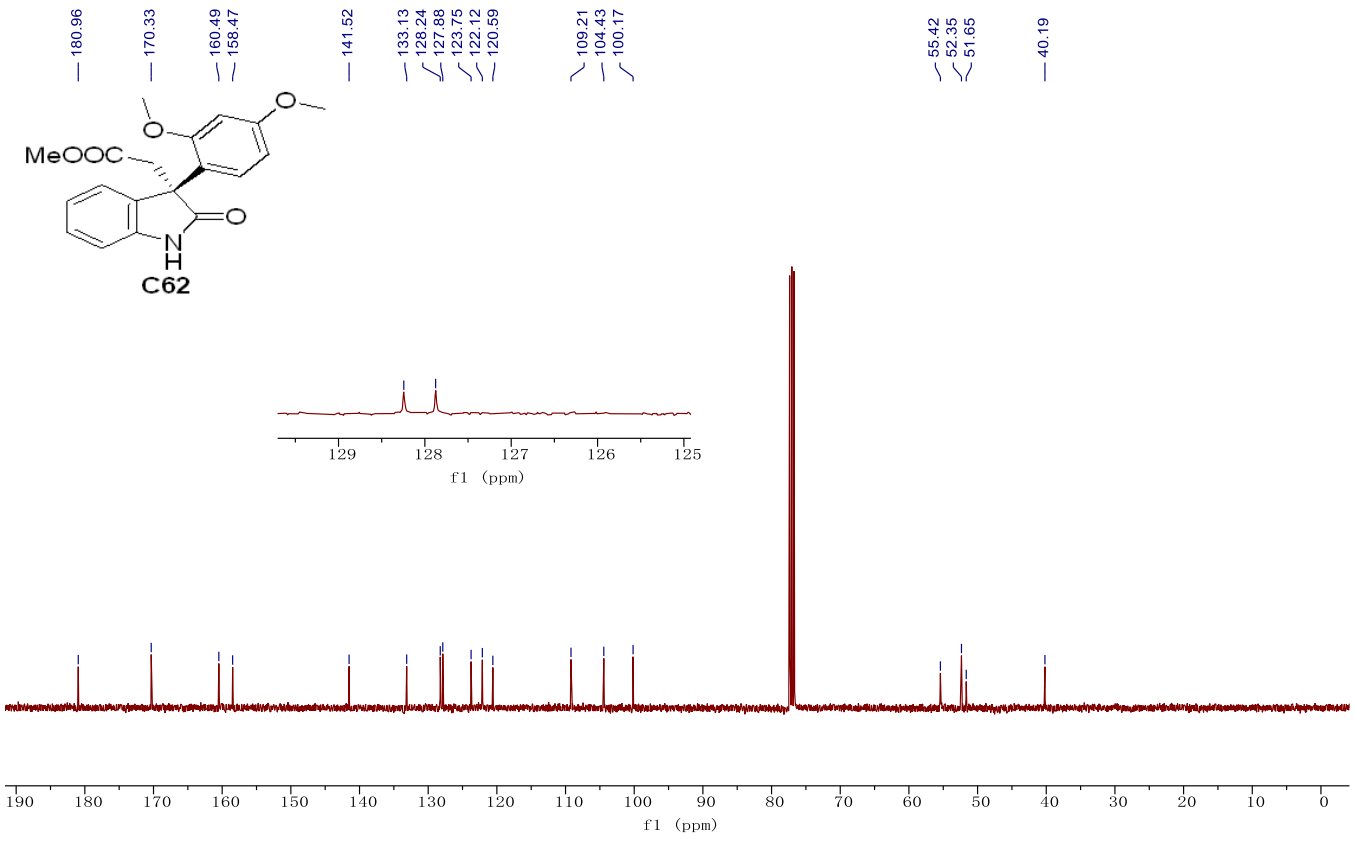

f1 (ppm)

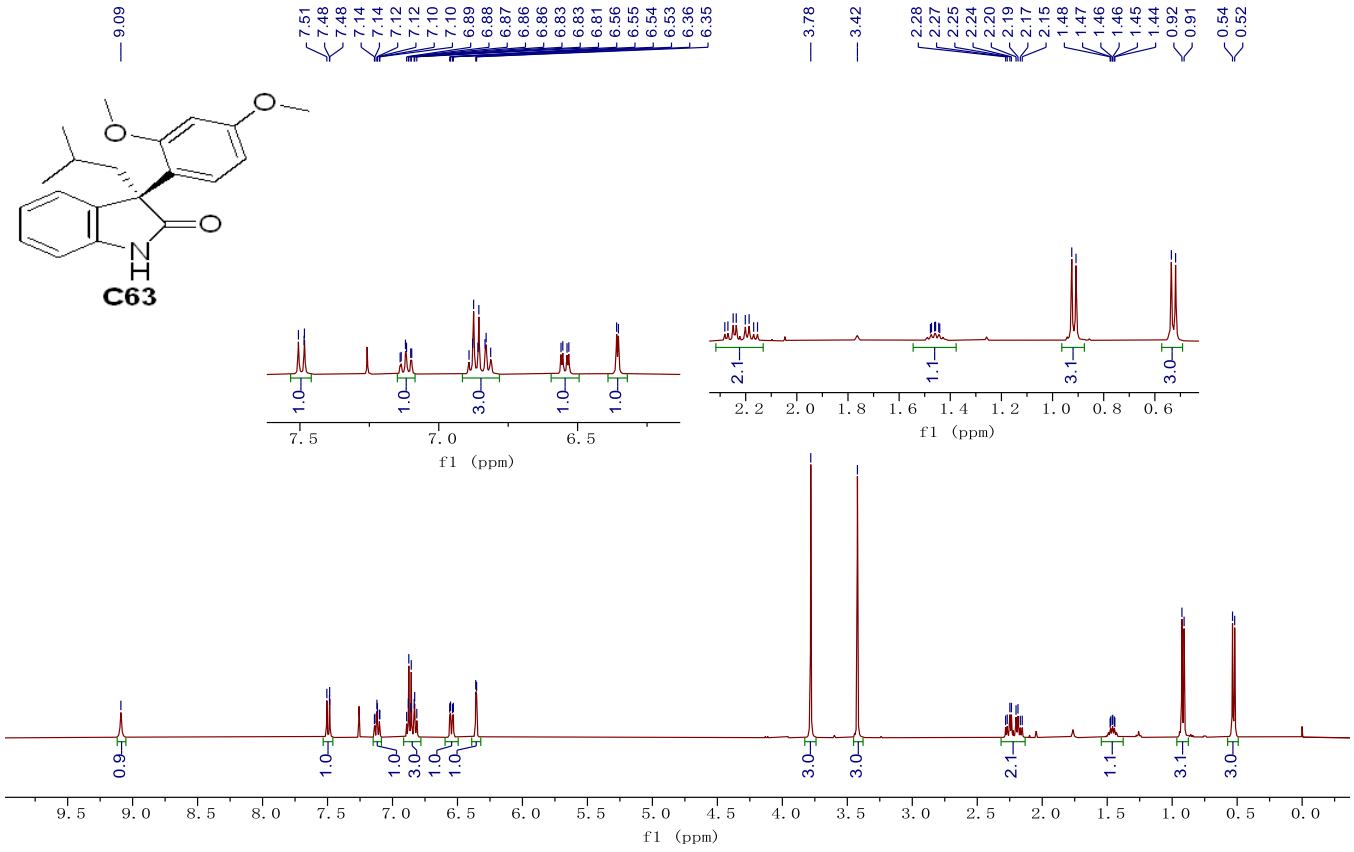

f1 (ppm)

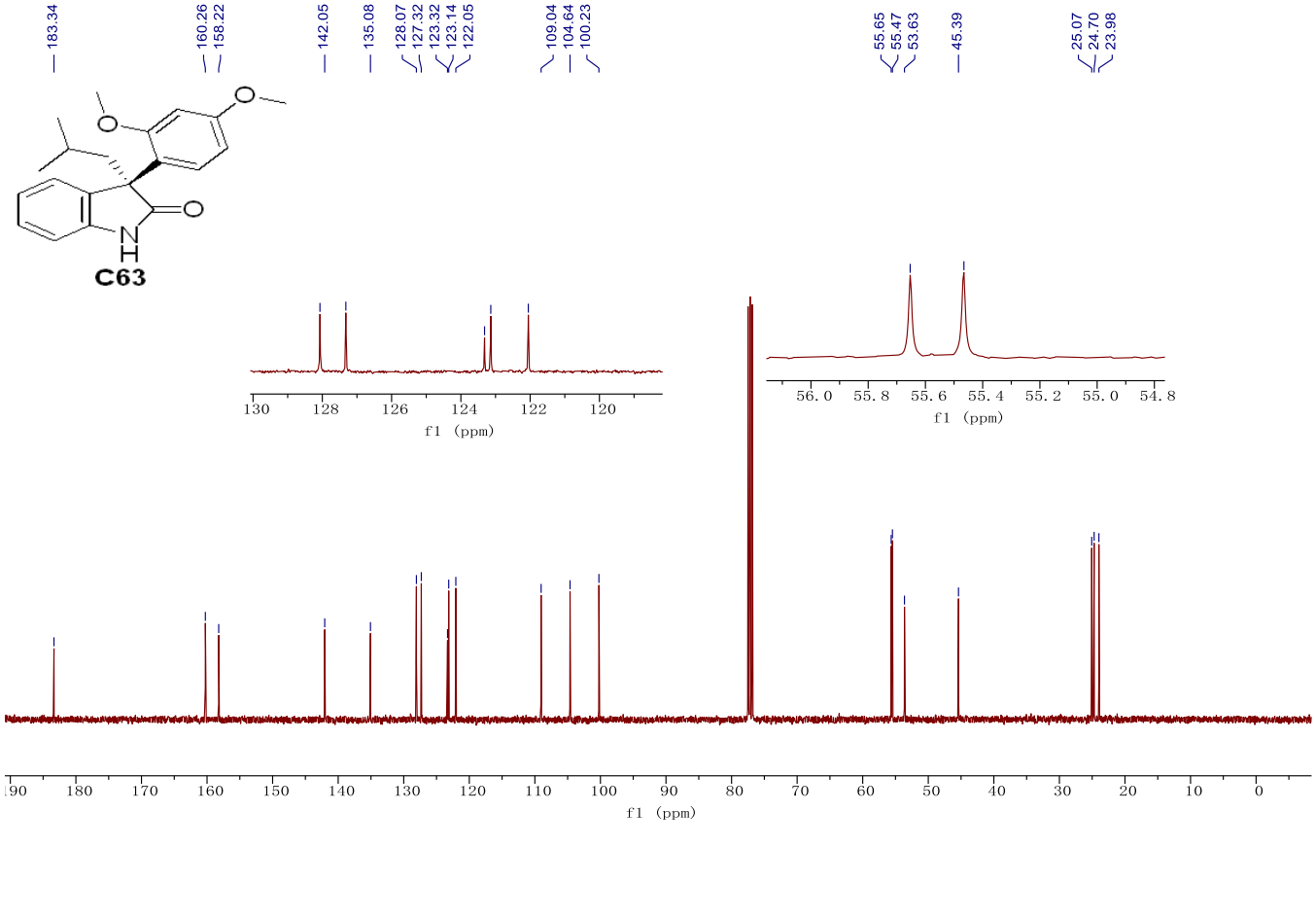

C60
f1 (ppm)
f1 (ppm)
f1 (ppm)

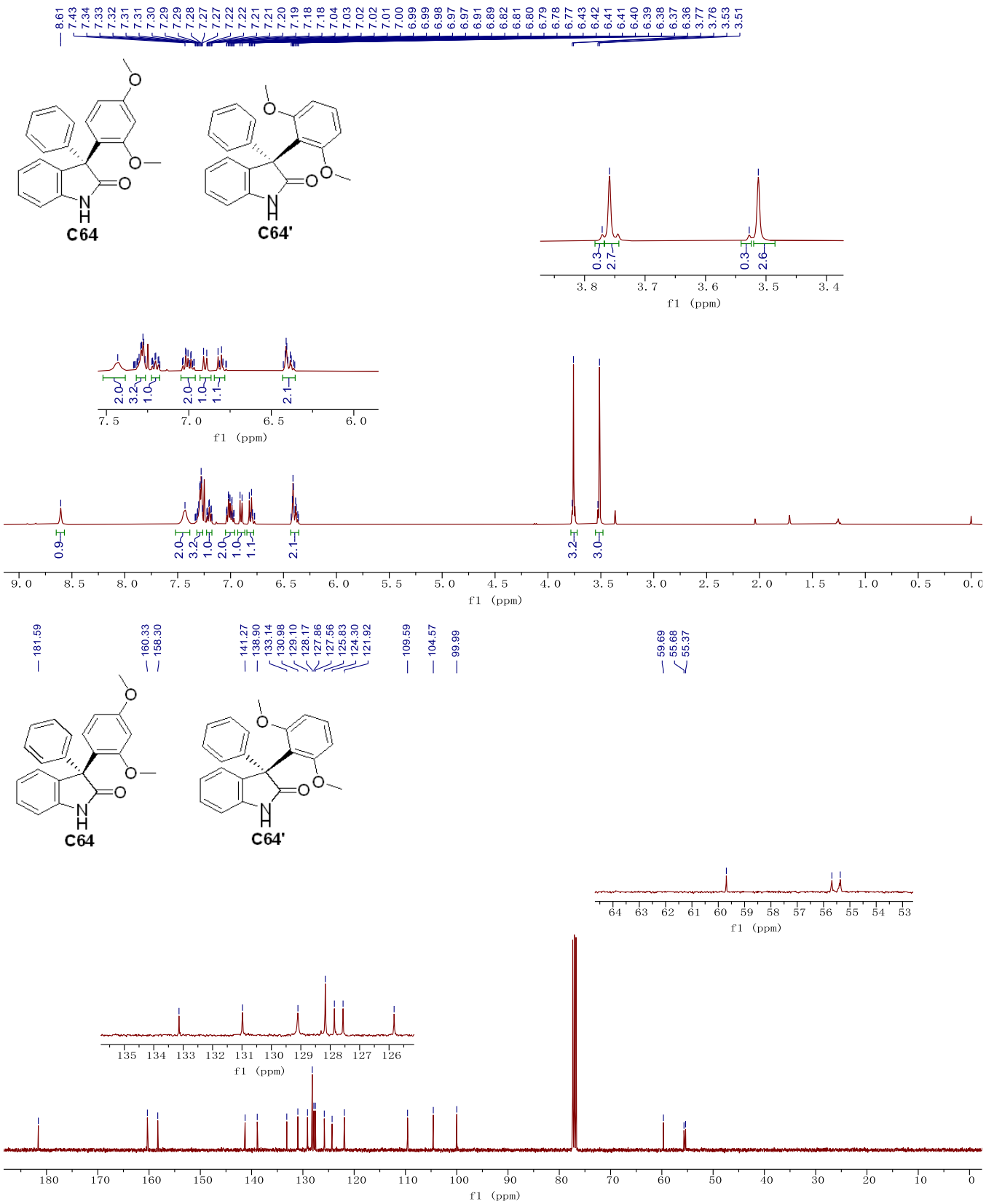

C61
f1 (ppm)
C61
f1 (ppm)

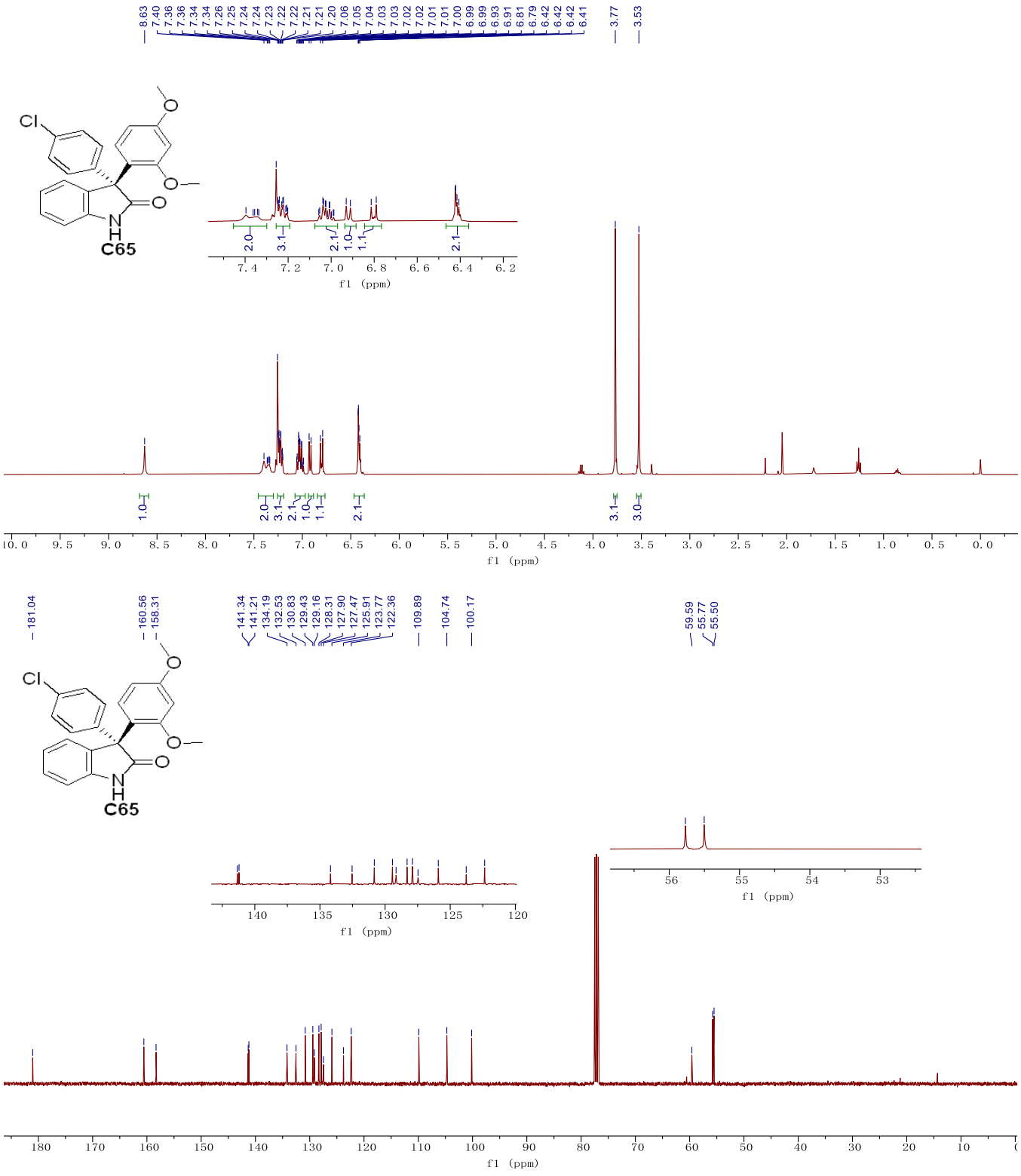

8.38
7.31
7.29
7.17
7.16
7.15
7.14
7.13
7.12
7.12
7.12
6.93
6.91
6.89
6.87
6.85
6.50
6.49
6.48
6.47
6.40
6.39
3.77
3.59
3.58
3.55
3.48
3.30
3.26
MeOOC
O
O
N
H
O
C62
f1 (ppm)

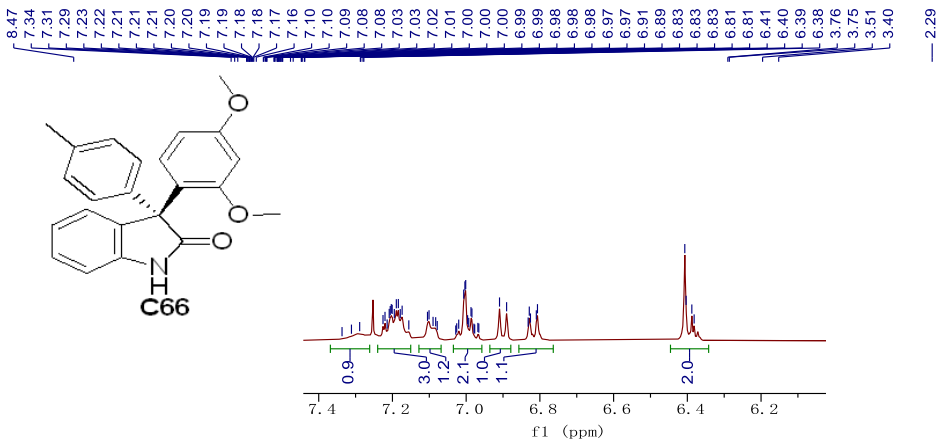

180.96
170.33
160.49
158.47
141.52
133.13
128.24
127.88
123.75
122.12
120.59
109.21
104.43
100.17
55.42
52.35
51.65
40.19
MeOOC
O
O
N
H
O
C62
f1 (ppm)

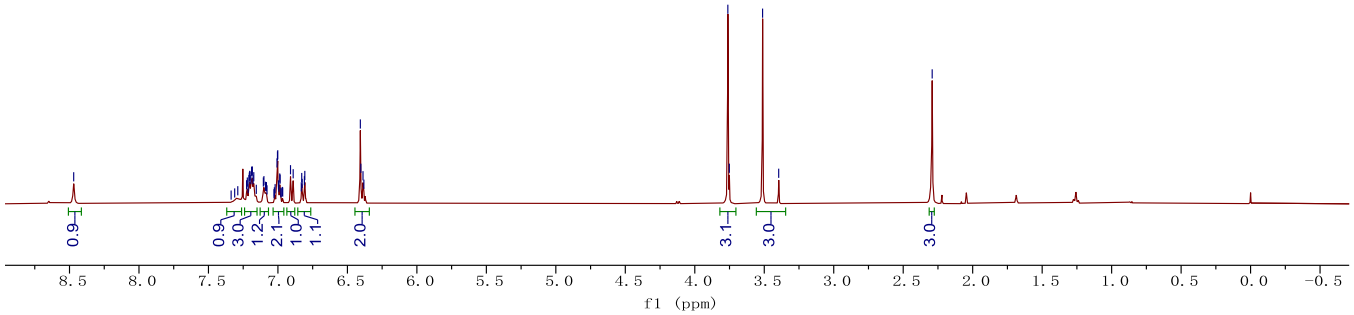

9.09
7.51
7.48
7.48
7.14
7.14
7.12
7.12
7.10
7.10
6.89
6.88
6.87
6.86
6.86
6.83
6.83
6.81
6.56
6.55
6.54
6.53
6.36
6.35
3.78
3.42
2.28
2.27
2.25
2.24
2.20
2.19
2.17
2.15
1.48
1.47
1.46
1.46
1.45
1.44
0.92
0.91
0.54
0.52
C63
f1 (ppm)

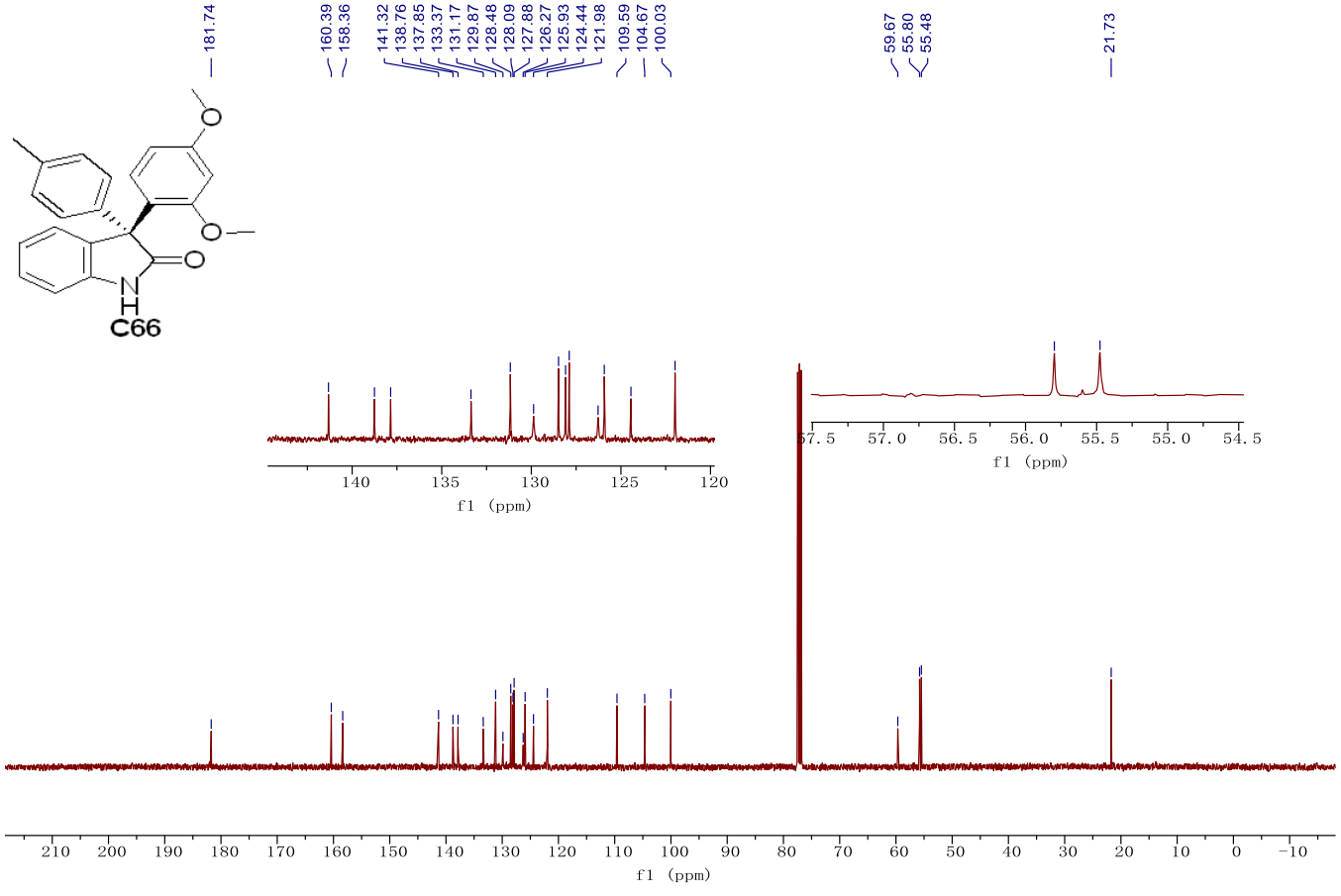

183.34
160.26
158.22
142.05
135.08
128.07
127.32
123.32
123.14
122.05
109.04
104.64
100.23
55.65
55.47
53.63
45.39
25.07
24.70
23.98
C63
f1 (ppm)


8.61 7.43 7.34 7.33 7.32 7.31 7.31 7.30 7.29 7.29 7.28 7.27 7.27 7.22 7.21 7.21 7.20 7.19 7.18 7.18 7.04 7.03 7.02 7.02 7.01 7.00 6.99 6.99 6.98 6.97 6.97 6.91 6.89 6.82 6.81 6.80 6.79 6.78 6.77 6.43 6.42 6.41 6.41 6.40 6.39 6.38 6.37 6.36 3.77 3.76 3.53 3.51
C64
C64'
0.3 2.7 0.3 2.6
3.8 3.7 3.6 3.5 3.4
f1 (ppm)
2.0 3.2 1.0 2.0 1.0 1.1 2.1
7.5 7.0 6.5 6.0
f1 (ppm)
0.9 2.0 3.2 1.0 2.0 1.0 1.1 2.1 3.2 3.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
181.59 160.33 158.30 141.27 138.90 133.14 130.98 129.10 128.17 127.86 127.56 125.83 124.30 121.92 109.59 104.57 99.99 59.69 55.68 55.37
C64
C64'
64 63 62 61 60 59 58 57 56 55 54 53
f1 (ppm)
135 134 133 132 131 130 129 128 127 126
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

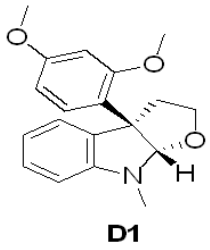

8.63
7.40
7.36
7.36
7.34
7.34
7.26
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.21
7.20
7.06
7.05
7.04
7.03
7.03
7.02
7.02
7.01
7.01
7.00
6.99
6.99
6.93
6.91
6.81
6.79
6.42
6.42
6.42
6.41
3.77
3.53
Cl
O
O
O
N
H
C65
2.0
3.1
2.1
1.0
1.1
2.1
f1 (ppm)
1.0
2.0
3.1
2.1
1.0
1.1
2.1
3.1
3.0
f1 (ppm)
181.04
160.56
158.31
141.34
141.21
134.19
132.53
130.83
129.43
129.16
128.31
127.90
127.47
125.91
123.77
122.36
109.89
104.74
100.17
59.59
55.77
55.50
Cl
O
O
O
N
H
C65
f1 (ppm)
f1 (ppm)
f1 (ppm)


8.47 7.34 7.31 7.29 7.23 7.22 7.21 7.21 7.21 7.20 7.20 7.19 7.19 7.18 7.18 7.17 7.16 7.10 7.10 7.09 7.08 7.08 7.03 7.03 7.02 7.01 7.00 7.00 7.00 6.99 6.99 6.98 6.98 6.98 6.97 6.97 6.91 6.89 6.83 6.83 6.83 6.81 6.81 6.41 6.40 6.39 6.38 3.76 3.75 3.51 3.40 2.29
C66
0.9 3.0 1.2 2.1 1.0 1.1 2.0
7.4 7.2 7.0 6.8 6.6 6.4 6.2
f1 (ppm)

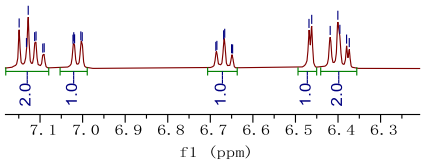

0.9 0.9 3.0 1.2 2.1 1.0 1.1 2.0 3.1 3.0 3.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

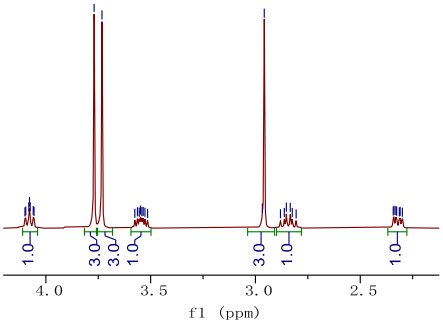

181.74 160.39 158.36 141.32 138.76 137.85 133.37 131.17 129.87 128.48 128.09 127.88 126.27 125.93 124.44 121.98 109.59 104.67 100.03 59.67 55.80 55.48 21.73
C66
140 135 130 125 120
f1 (ppm)
57.5 57.0 56.5 56.0 55.5 55.0 54.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

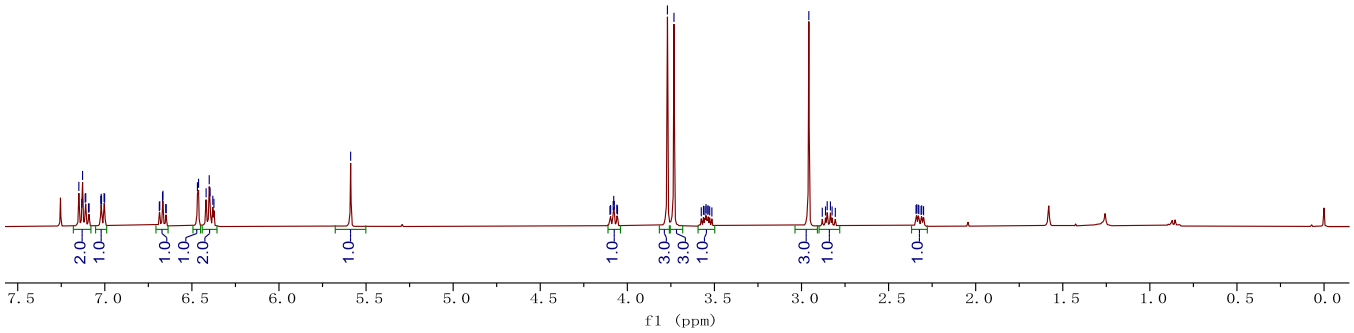

7.15 7.13 7.13 7.11 7.11 7.09 7.09 7.02 7.02 7.02 7.00 7.00 6.69 6.68 6.67 6.67 6.65 6.65 6.47 6.46 6.42 6.40 6.40 6.38 6.37 5.59 4.10 4.10 4.08 4.08 4.07 4.06 4.06 3.77 3.73 3.58 3.56 3.55 3.55 3.54 3.54 3.53 3.51 2.96 2.88 2.86 2.85 2.83 2.82 2.81 2.34 2.34 2.33 2.33 2.31 2.31 2.30



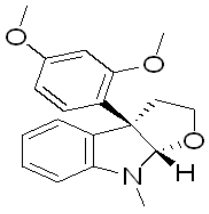
D1


2.0 1.0 1.0 1.0 2.0
7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3
f1 (ppm)

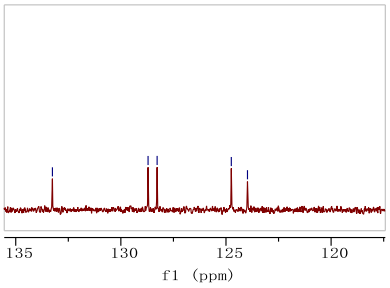

1.0 3.0 3.0 1.0 3.0 1.0 1.0
4.0 3.5 3.0 2.5
f1 (ppm)


2.0 1.0 1.0 1.0 2.0 1.0 1.0 3.0 3.0 1.0 3.0 1.0 1.0
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

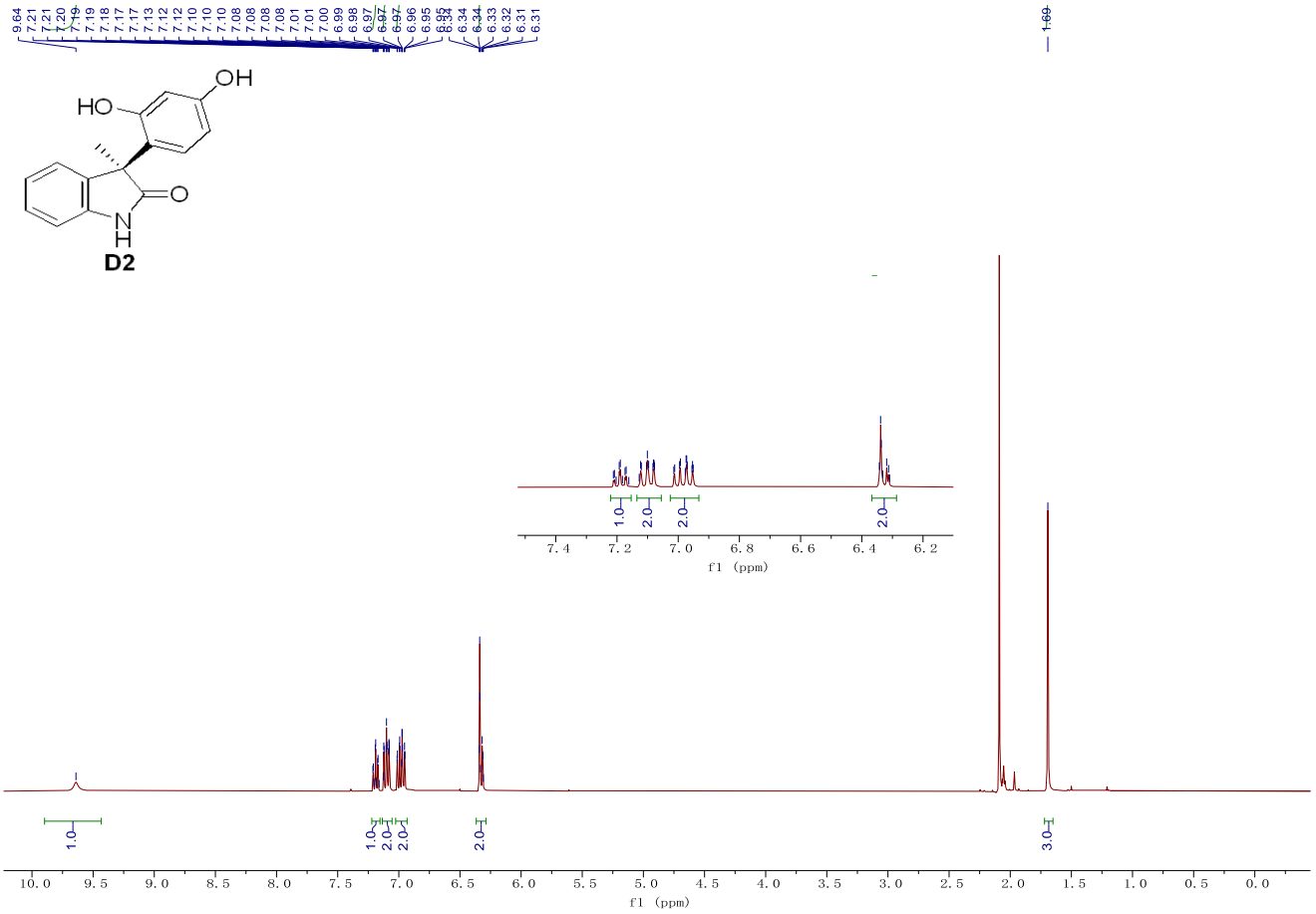

160.01 158.72 151.42 133.26 128.71 128.28 124.75 123.98 117.30 105.39 103.94 103.81 99.89 67.51 58.84 55.49 39.68 31.53

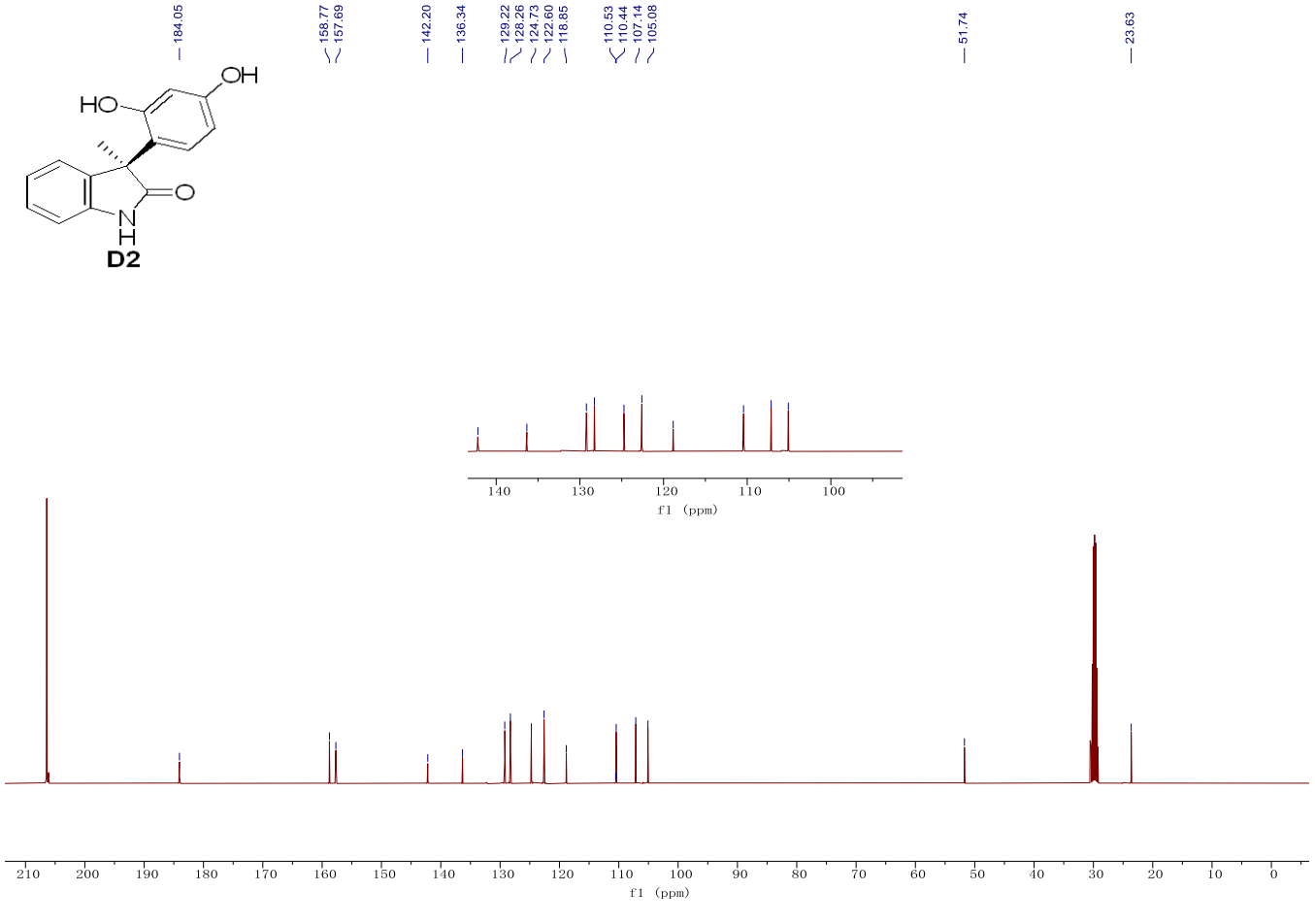


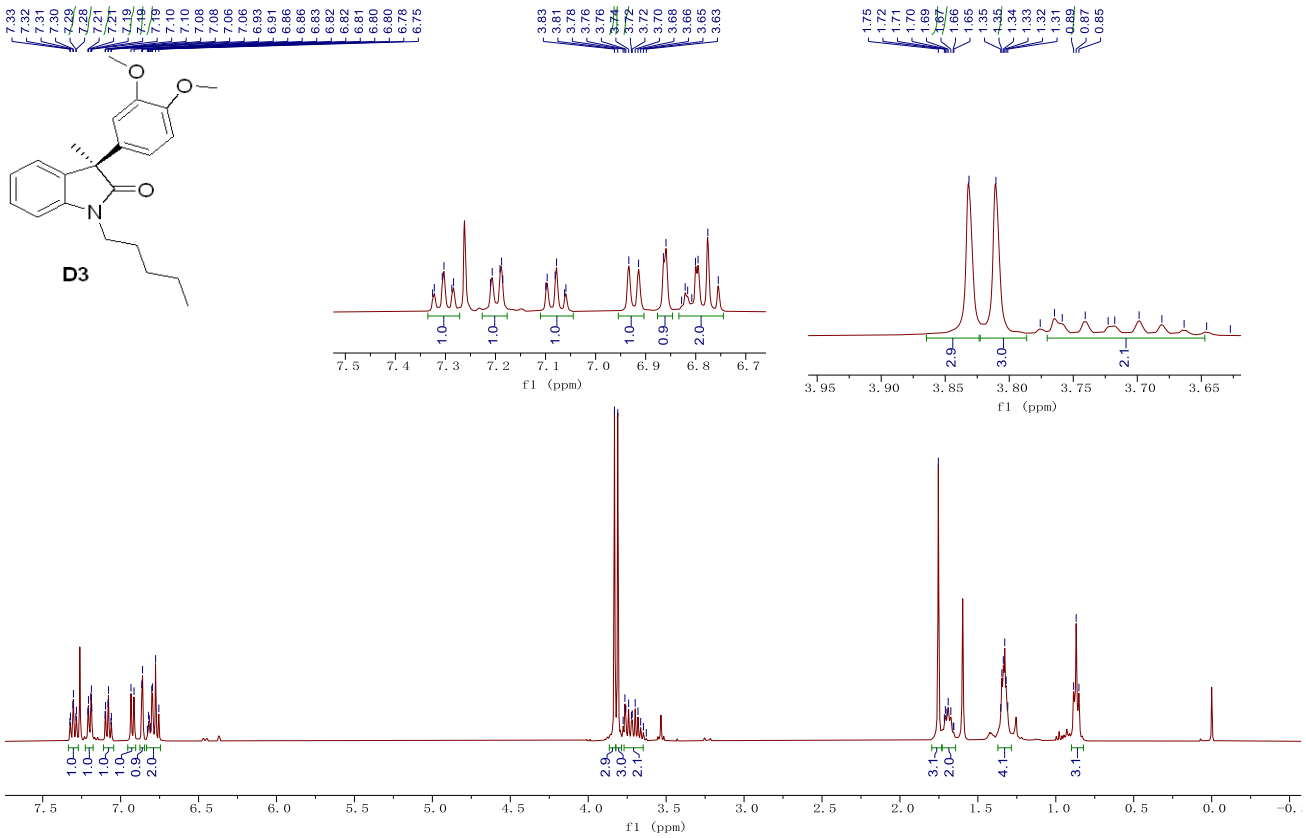
D1

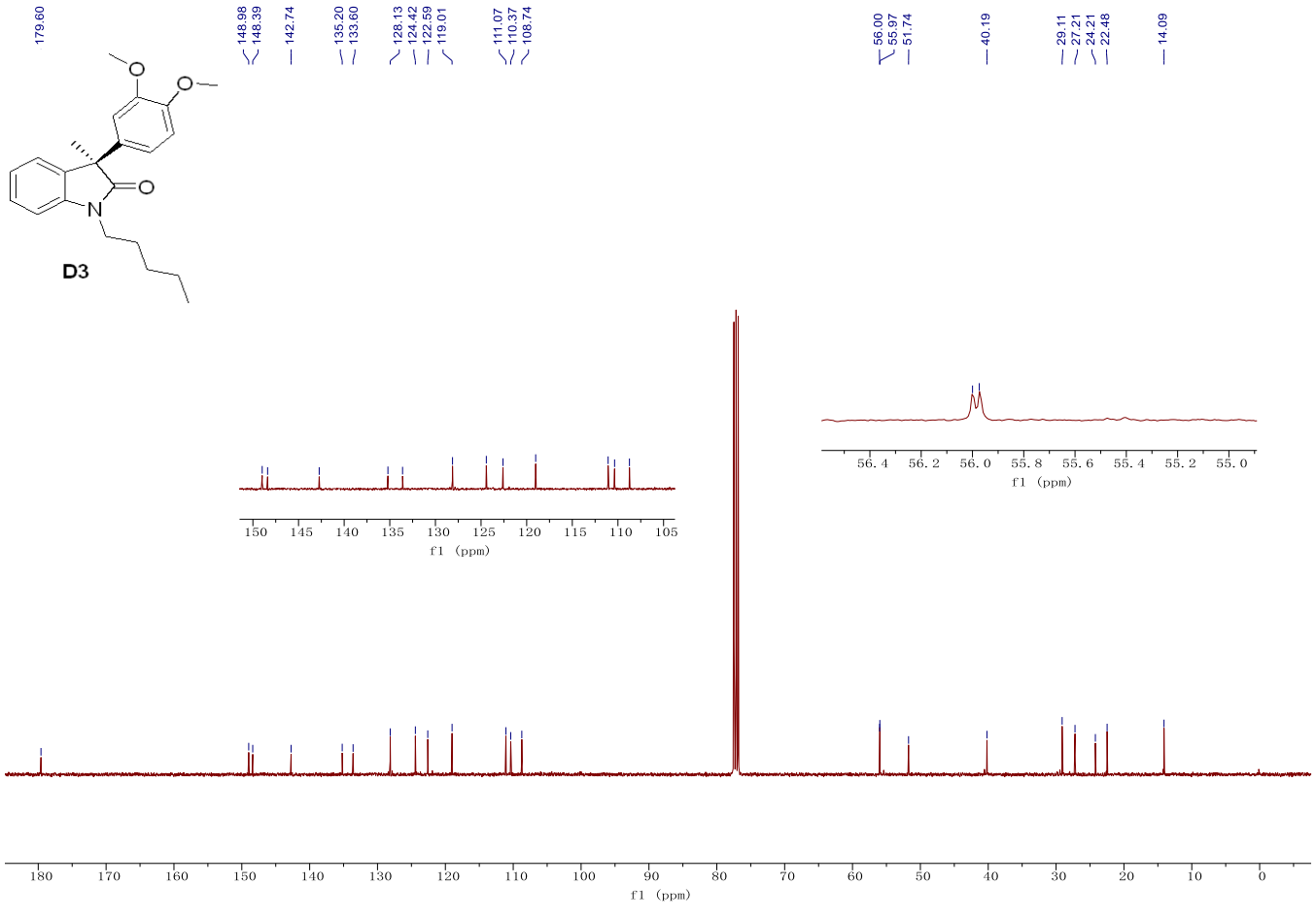

135 130 125 120
f1 (ppm)

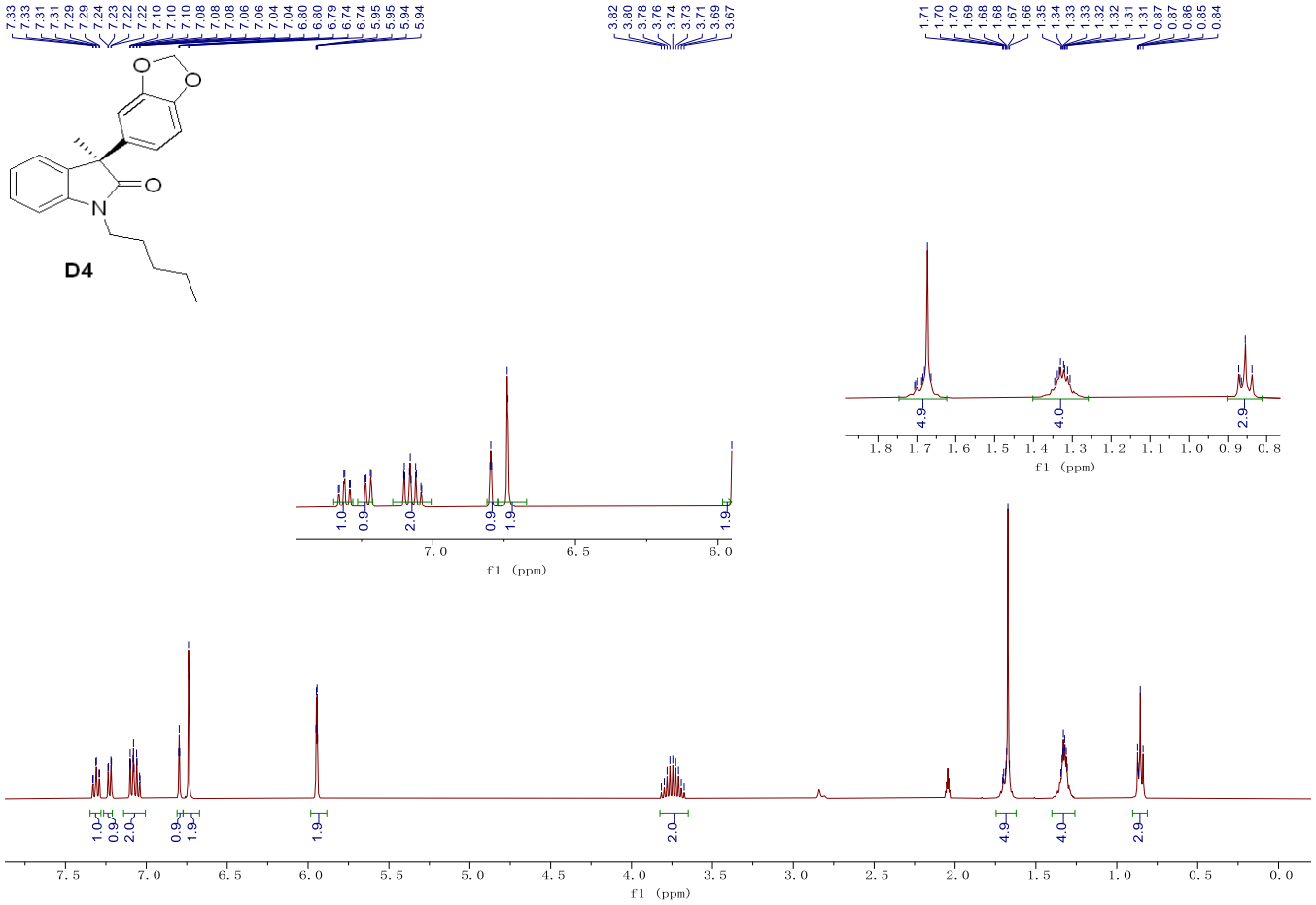
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

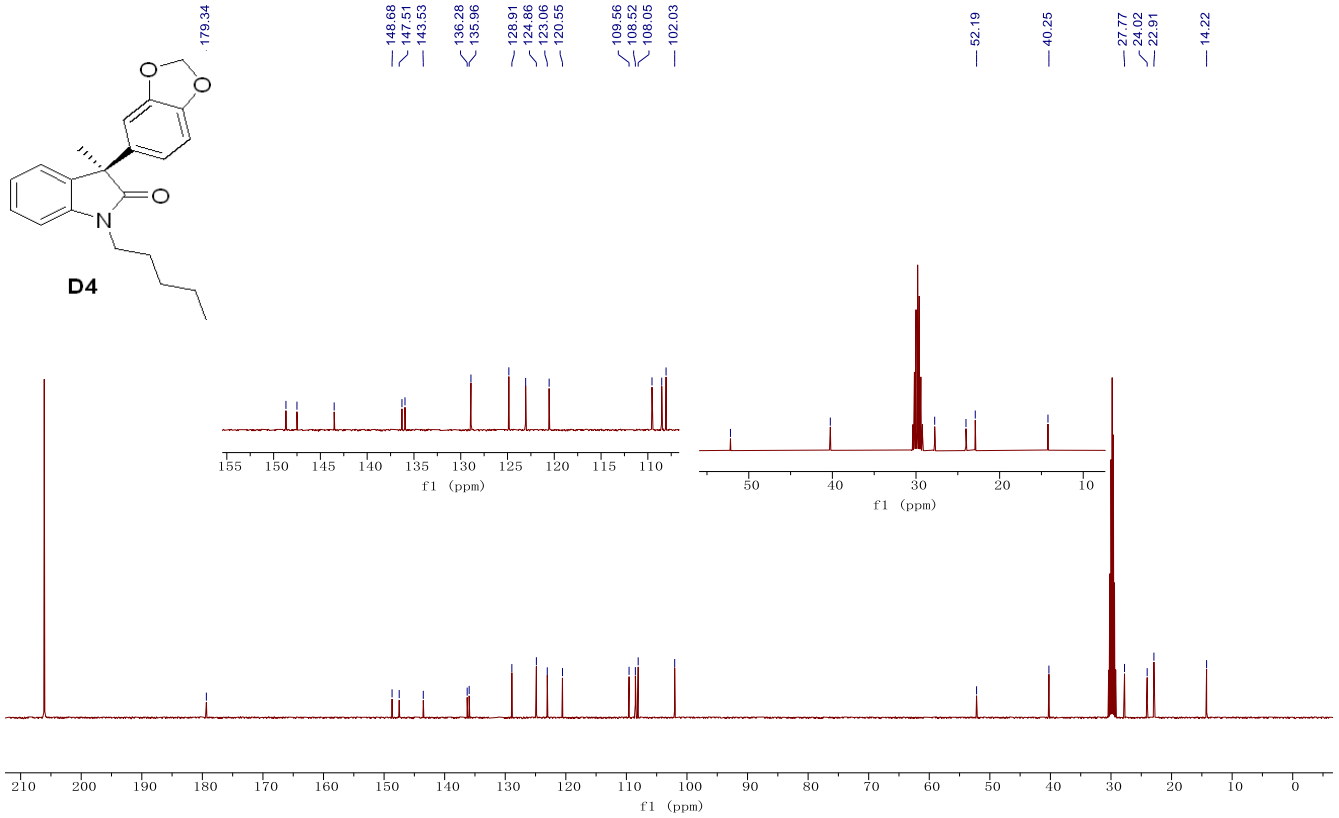

9.64
7.21
7.21
7.20
7.19
7.19
7.18
7.17
7.17
7.13
7.12
7.12
7.10
7.10
7.10
7.08
7.08
7.08
7.08
7.08
7.01
7.01
7.00
6.99
6.98
6.97
6.97
6.97
6.96
6.95
6.95
6.94
6.34
6.34
6.33
6.32
6.31
6.31
1.69
OH
HO
O
N
H
D2
1.0
2.0
2.0
2.0
7.4
7.2
7.0
6.8
6.6
6.4
6.2
f1 (ppm)
1.0
1.0
2.0
2.0
2.0
3.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


184.05
158.77
157.69
142.20
136.34
129.22
128.26
124.73
122.60
118.85
110.53
110.44
107.14
105.08
51.74
23.63
OH
HO
O
N
H
D2
140
130
120
110
100
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


D3
f1 (ppm)


D3
f1 (ppm)


D4
f1 (ppm)


D4
f1 (ppm)

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