Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Photoredox Asymmetric Catalytic Enantioconvergent Substitution of 3-Chlorooxindoles

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1. General information

General procedures and methods

Experiments involving moisture and/or air sensitive components were performed under a positive pressure of argon in oven-dried glassware equipped with a rubber septum inlet. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccator. Moisture in non-volatile reagents/compounds was removed in high *vacuo* by means of an oil pump and subsequent purging with nitrogen. Solvents were removed *in vacuo* under ~30 mmHg and heated with a water bath at 30–35 ºC using rotary evaporator with aspirator. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated plates, 60 F_{254}. After elution, plate was visualized under UV illumination at 254 nm for UV active material. Further visualization was achieved by staining $Ce(SO_4)_2$ and phosphomolybdic acid solution. For those using the aqueous stains, the TLC plates were heated on a hot plate.

Columns for flash chromatography (FC) contained *silica gel* 200–300 mesh. Columns were packed as slurry of *silica gel* in petroleum ether and equilibrated solution using the appropriate solvent system. The elution was assisted by applying pressure of about 2 atm with an air pump.

Instrumentations

Proton nuclear magnetic resonance (^{1}H NMR) and carbon NMR (^{13}C NMR) were recorded in $CDCl_3$ otherwise stated. Chemical shifts are reported in parts per million (ppm), using the residual solvent signal as an internal standard: $CDCl_3$ (^{1}H NMR: δ 7.26, singlet; ^{13}C NMR: δ 77.0, triplet). Multiplicities were given as: *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *quintet*, *m* (multiplets), *dd* (doublet of doublets), *dt* (doublet of triplets), and *br* (broad). Coupling constants (*J*) were recorded in hertz (Hz). The number of proton atoms (*n*) for a given resonance was indicated by *n*H. The number of carbon atoms (*n*) for a given resonance was indicated by *n*C. HRMS (Analyzer: TOF) was reported in units of mass of charge ratio (m/z). Mass samples were dissolved in CH_3CN (HPLC Grade) unless otherwise stated. Optical rotations were recorded on a polarimeter with a sodium lamp of wavelength 589 nm and reported as follows; $[\alpha]_{\lambda}^{T^{\circ}C}$ (*c* = g/100 mL, solvent). Melting points were determined

on a melting point apparatus.

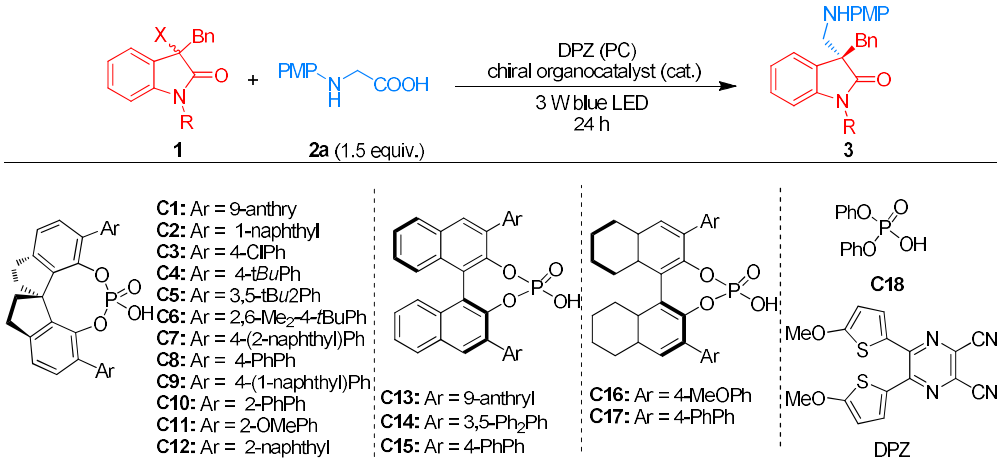
Enantiomeric excesses were determined by chiral High Performance Liquid Chromatography (HPLC) analysis. UV detection was monitored at 254 nm and 210 nm at the same time. HPLC samples were dissolved in HPLC grade isopropanol (IPA) unless otherwise stated.

Materials

All commercial reagents were purchased with the highest purity grade. They were used without further purification unless specified. All solvents used, mainly petroleum ether (PE) and ethyl acetate (EtOAc) were distilled. Anhydrous dichloromethane (DCM), CH_3CN were freshly distilled from CaH_2 and stored under N_2 atmosphere. THF, Et_2O, MTBE, 1,2-dimethoxyethane, *t*BuPh, mesitylene, CPME, and toluene were freshly distilled from sodium/benzophenone before use. All compounds synthesized were stored in a −20 °C freezer and light-sensitive compounds were protected with aluminium foil.

2. Optimization of reaction conditions

Table S1. Optimization of the Reaction Conditions of 1a with 2a.[a]



entry	PC (mol%)	cat. (mol%)	X	R	base (equiv)	solvent (mL)	*T* (°C)	conv. (%)[b]	ee (%)[c]
1[d]	DPZ (0.5)	**C18** (10)	Br	Me	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	--
2[e]	DPZ (0.5)	**C18** (10)	Br	Bn	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	--
3[f]	DPZ (0.5)	**C18** (10)	Br	Boc	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	--
4[g]	DPZ (0.5)	**C18** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	--
5[h]	DPZ (0.5)	--	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	20	--
6	DPZ (0.5)	**C1** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	68

7	DPZ (0.5)	**C2** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	47
8	DPZ (0.5)	**C3** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	9
9	DPZ (0.5)	**C4** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	44
10	DPZ (0.5)	**C5** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	11
11	DPZ (0.5)	**C6** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	11
12	DPZ (0.5)	**C7** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	51
13	DPZ (0.5)	**C8** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	54
14	DPZ (0.5)	**C9** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	36
15	DPZ (0.5)	**C10** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	9
16	DPZ (0.5)	**C11** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	21
17	DPZ (0.5)	**C12** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	17
18	DPZ (0.5)	**C13** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	42
19	DPZ (0.5)	**C14** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	15
20	DPZ (0.5)	**C15** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	19
21	DPZ (0.5)	**C16** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	11
22	DPZ (0.5)	**C17** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	23
23	DPZ (0.5)	**C1** (10)	Br	Ts	$NaHCO_3$ (3.0)	THF (1.0)	25	>95	45

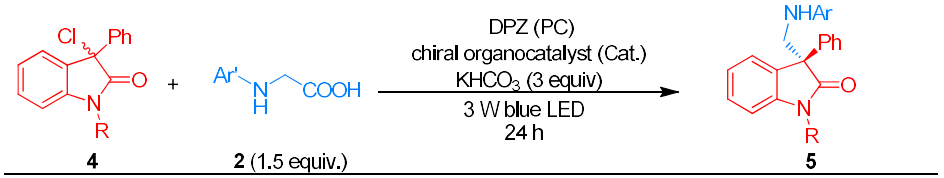
24	DPZ (0.5)	**C1** (10)	Br	Ts	$NaHCO_3$ (3.0)	Et_2O (1.0)	25	0	--
25	DPZ (0.5)	**C1** (10)	Br	Ts	$NaHCO_3$ (3.0)	CH_3CN (1.0)	25	>95	5
26	DPZ (0.5)	**C1** (10)	Br	Ts	$NaHCO_3$ (3.0)	Tol (1.0)	25	>95	38
27	DPZ (0.5)	**C1** (10)	Br	Ts	$NaHCO_3$ (3.0)	DCM (1.0)	25	>95	37
28	DPZ (0.5)	**C1** (10)	Br	Ts	$NaHCO_3$ (3.0)	CPME (1.0)	25	>95	27
29	DPZ (0.5)	**C1** (10)	Br	Ts	$NaHCO_3$ (3.0)	mesitylene (1.0)	25	>95	33
30	DPZ (0.5)	**C1** (10)	Br	Ts	$NaHCO_3$ (3.0)	PhCl (1.0)	25	>95	35
31	DPZ (0.5)	**C1** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	10	>95	78
32	DPZ (0.5)	**C1** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	-25	20	82
33	DPZ (0.5)	**C1** (10)	Br	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	-35	15	84
34[i]	DPZ (0.5)	**C1** (10)	Cl	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	25	>95	--
35	DPZ (0.5)	**C1** (10)	Cl	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	10	>95	76
36	DPZ (0.5)	**C1** (10)	Cl	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	0	80	77
37	DPZ (0.5)	**C1** (10)	Cl	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	-15	60	82
38	DPZ (0.5)	**C1** (10)	Cl	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	-25	50	83
39	DPZ (0.5)	**C1** (10)	Cl	Ts	$NaHCO_3$ (3.0)	MTBE (1.0)	-30	40	85
40	DPZ (0.5)	**C1** (10)	Cl	Boc	$NaHCO_3$ (3.0)	MTBE (1.0)	−30	40	72

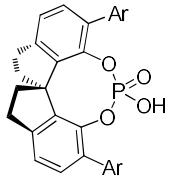
41	DPZ (0.5)	**C1** (10)	Cl	Ms	$NaHCO_3$ (3.0)	MTBE (1.0)	-30	40	82
42	DPZ (0.5)	**C1** (10)	Cl	4-$ClPhSO_2$	$NaHCO_3$ (3.0)	MTBE (1.0)	−30	40	88
43	DPZ (0.5)	**C1** (10)	Cl	4-$BrPhSO_2$	$NaHCO_3$ (3.0)	MTBE (1.0)	-30	40	81
44	DPZ (0.5)	**C1** (10)	Cl	4-*i*$PrPhSO_2$	$NaHCO_3$ (3.0)	MTBE (1.0)	−30	40	75
45	DPZ (0.5)	**C1** (10)	Cl	4-CF_3PhSO_2	$NaHCO_3$ (3.0)	MTBE (1.0)	-30	40	83
46	DPZ (0.5)	**C1** (10)	Cl	4-$FPhSO_2$	$NaHCO_3$ (3.0)	MTBE (1.0)	−30	40	89
47	DPZ (0.5)	**C1** (10)	Cl	2-$MePhSO_2$	$NaHCO_3$ (3.0)	MTBE (1.0)	-30	40	56
48	DPZ (0.5)	**C1** (10)	Cl	4-$FPhSO_2$	Na_2CO_3 (3.0)	MTBE (1.0)	−30	<10	88
49	DPZ (0.5)	**C1** (10)	Cl	4-$FPhSO_2$	K_2CO_3 (3.0)	MTBE (1.0)	-30	0	--
50	DPZ (0.5)	**C1** (10)	Cl	4-$FPhSO_2$	K_3PO_4 (3.0)	MTBE (1.0)	−30	0	--
51	DPZ (0.5)	**C1** (10)	Cl	4-$FPhSO_2$	K_2HPO_4 (3.0)	MTBE (1.0)	-30	30	88
52	DPZ (0.5)	**C1** (10)	Cl	4-$FPhSO_2$	NaOAc (3.0)	MTBE (1.0)	−30	60	25
53	DPZ (0.5)	**C1** (10)	Cl	4-$FPhSO_2$	KH_2PO_4 (3.0)	MTBE (1.0)	-30	20	83
54	DPZ (0.5)	**C1** (10)	Cl	4-$FPhSO_2$	NaF (3.0)	MTBE (1.0)	−30	0	--
55	DPZ (0.5)	**C1** (10)	Cl	4-$FPhSO_2$	KF (3.0)	MTBE (1.0)	-30	30	75
56	DPZ (0.5)	**C1** (10)	Cl	4-$FPhSO_2$	NaH_2PO_4(3.0)	MTBE (1.0)	−30	20	80
57	DPZ (0.5)	**C1** (10)	Cl	4-$FPhSO_2$	Na_2HPO_4(3.0)	MTBE (1.0)	-30	20	86

58	DPZ (0.5)	**C1** (10)	Cl	4-FPhSO$_2$	LiOAc (3.0)	MTBE (1.0)	−30	30	40
59	DPZ (0.2)	**C1** (10)	Cl	4-FPhSO$_2$	NaHCO$_3$ (3.0)	MTBE (1.0)	-30	20	88
60	DPZ (1.0)	**C1** (10)	Cl	4-FPhSO$_2$	NaHCO$_3$ (3.0)	MTBE (1.0)	−30	40	88
61	DPZ (1.0)	**C1** (10)	Cl	4-FPhSO$_2$	NaHCO$_3$ (3.0)	MTBE (1.5)	−30	30	89
62	DPZ (1.0)	**C1** (10)	Cl	4-FPhSO$_2$	NaHCO$_3$ (3.0)	MTBE (2.0)	−30	30	88
63	DPZ (1.0)	**C1** (10)	Cl	4-FPhSO$_2$	NaHCO$_3$ (3.0)	MTBE (3.0)	−30	30	88
64	DPZ (1.0)	**C1** (10)	Cl	4-FPhSO$_2$	NaHCO$_3$ (3.0)	MTBE/THF = 1:1 (1.5)	−40	80	81
65	DPZ (1.0)	**C1** (10)	Cl	4-FPhSO$_2$	NaHCO$_3$ (3.0)	MTBE/THF = 2:1 (1.5)	−40	80	81
66	DPZ (1.0)	**C1** (10)	Cl	4-FPhSO$_2$	NaHCO$_3$ (3.0)	MTBE/THF = 3:1 (1.5)	−40	60	87
67	DPZ (1.0)	**C1** (10)	Cl	4-FPhSO$_2$	NaHCO$_3$ (3.0)	MTBE/THF = 5:1 (1.5)	−30	80	88
68	DPZ (1.0)	**C1** (10)	Cl	4-FPhSO$_2$	NaHCO$_3$ (3.0)	MTBE/THF = 5:1 (1.5)	−42	40	90
69[j]	DPZ (1.0)	**C1** (20)	Cl	4-FPhSO$_2$	KHCO$_3$ (3.0)	MTBE/THF = 5:1 (1.5)	−42	60	90

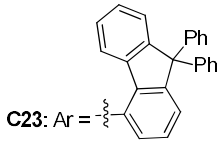
[a] Reaction conditions: **1** (0.05 mmol) and **2a** (0.1 mmol) in 1.5 mL solvent. [b] Determined by TLC analysis. [c] Determined by HPLC analysis on a chiral stationary phase. [d] t = 48 h, yield = 51%. [e] t = 48 h, yield = 57%. [f] t = 48 h, yield = 65%. [g] t = 48 h, yield = 77%. [h] t = 48 h, yield = 17%. [i] t = 48 h, yield = 85%. [j] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), t = 65 h, yield = 91%.

Table S2. Optimization of the Reaction Conditions of 4 with 2.[a]





C1: Ar = 9-anthryl
C4: Ar = 4-*t*BuPh
C7: Ar = 4-(2-naphthyl)Ph
C8: Ar = 4-PhPh
C10: Ar = 2-PhPh
C11: Ar = 2-OMePh
C12: Ar = 2-naphthyl
C19: Ar = 2-OMe5-ClPh
C20: Ar = 3,5-tBu$_2$-4-MeOPh
C21: Ar = 2,4,6-Me$_3$Ph
C22: Ar = 4-TMSPh



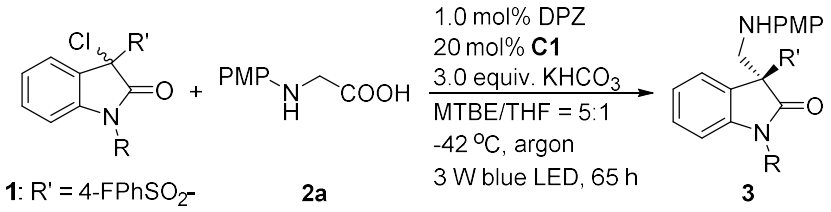
entry	PC (mol%)	cat. (mol%)	Ar′	solvent (mL)	*T* (°C)	conv. (%)[b]	ee (%)[c]
1[d]	DPZ (1.0)	**C1** (20)	PMP	MTBE/THF = 1:1	−42	70	8
2	DPZ (0.5)	**C1** (10)	PMP	MTBE/THF = 1:1	−30	20	62
3	DPZ (0.5)	**C4** (10)	PMP	MTBE/THF = 1:1	−30	40	57
4	DPZ (0.5)	**C7** (10)	PMP	MTBE/THF = 1:1	−30	60	23
5	DPZ (0.5)	**C8** (10)	PMP	MTBE/THF = 1:1	−30	40	36
6	DPZ (0.5)	**C10** (10)	PMP	MTBE/THF = 1:1	−30	50	35
7	DPZ (0.5)	**C11** (10)	PMP	MTBE/THF = 1:1	−30	50	20

8	DPZ (0.5)	**C12** (10)	PMP	MTBE/THF = 1:1	−30	50	31
9	DPZ (0.5)	**C19** (10)	PMP	MTBE/THF = 1:1	−30	40	17
10	DPZ (0.5)	**C20** (10)	PMP	MTBE/THF = 1:1	−30	50	53
11	DPZ (0.5)	**C21** (10)	PMP	MTBE/THF = 1:1	−30	50	65
12	DPZ (0.5)	**C22** (10)	PMP	MTBE/THF = 1:1	−30	20	50
13	DPZ (0.5)	**C23** (10)	PMP	MTBE/THF = 1:1	−30	30	77
14	DPZ (0.5)	**C23** (10)	PMP	THF	−40	60	81
15	DPZ (0.5)	**C23** (10)	PMP	MTBE	−40	30	88
16	DPZ (0.5)	**C23** (10)	PMP	MTBE/THF = 1:1	−40	80	91
17[e]	DPZ (0.5)	**C23** (10)	PMP	MTBE/THF = 2:1	−40	60	93
18	DPZ (0.5)	**C23** (10)	PMP	MTBE/THF = 3:1	−40	50	88
19	DPZ (0.5)	**C23** (10)	2-Br-4-OMePh	MTBE/THF = 2:1	−40	40	51
20	DPZ (0.5)	**C23** (10)	3-CF_3-4-OMePh	MTBE/THF = 2:1	−40	60	89
21	DPZ (0.5)	**C23** (10)	4-OEtPh	MTBE/THF = 2:1	−40	20	56
22	DPZ (1.0)	**C23** (10)	3-CF_3-4-OMePh	MTBE/THF = 2:1	−40	80	89
23	DPZ (1.0)	**C23** (20)	3-CF_3-4-OMePh	MTBE/THF = 2:1	−50	70	90
24[f]	DPZ (1.0)	**C23** (20)	3-CF_3-4-OMePh	MTBE/THF = 2:1	−55	60	90

[a] Reaction conditions: **4** (0.05 mmol) and **2b** (0.075 mmol) in 1.5 mL solvent (R = Me). [b] Determined by TLC analysis. [c] Determined by HPLC analysis on a chiral stationary phase. [d] R = 4-fluorobenzenesulfonyl, 60 h. yield of product = 75%, ee of product = 8%. [e] ee values of other 3-aryl-3-chlorooxindoles were not satisfactory after screening substrate scope. [f] *t* = 60 h, yield = 96% (0.1 mmol scale).

3. General experimental procedures

(1) General procedure for enantioselective substitution of 1 with 2a.



70.0 μL (0.001 mmol, 0.01 equiv.) of DPZ solution (1.0 mg of DPZ in 200 μL of toluene) was added into a 10 mL Schlenk tube, and then solvent was removed in *vacuo*.

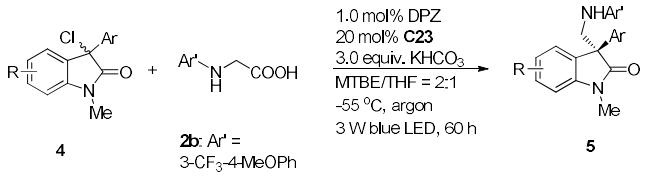
For **3a**–**3p, 3s**–**3t**: **1** (0.10 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), **C1** (0.02 mmol, 0.2 equiv.), $KHCO_3$ (0.30 mmol, 3.0 equiv.) and MTBE/THF = 5:1 (3.0 mL) were sequentially added, degassed three times by freeze-pump-thaw method. The reaction mixture was stirred under an argon atmosphere at −42 °C.

For **3q**: **1** (0.10 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), **C3** (0.02 mmol, 0.2 equiv.), $KHCO_3$ (0.30 mmol, 3.0 equiv.) and MTBE/THF = 5:1 (3.0 mL) were sequentially added, degassed three times by freeze-pump-thaw method. The reaction mixture was stirred under an argon atmosphere at −42 °C.

For **3r**: **1** (0.10 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), **C1** (0.02 mmol, 0.2 equiv.), $KHCO_3$ (0.30 mmol, 3.0 equiv.) and 4 Å MS (30 mg) and MTBE/THF = 5:1 (5.0 mL) were sequentially added, degassed three times by freeze-pump-thaw method. The reaction mixture was stirred under an argon atmosphere at −42 °C.

Then irradiated by a 3 W blue LED (λ = 450−455 nm) for another 65 h. The reaction was monitored by TLC. After completion, the reaction mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with petroleum ether/ethyl acetate (50/1–5/1 ratio). Removing the solvent in *vacuo*, afforded products **3a**−**3t**.

(2) General procedure for enantioselective of 4 with 2b



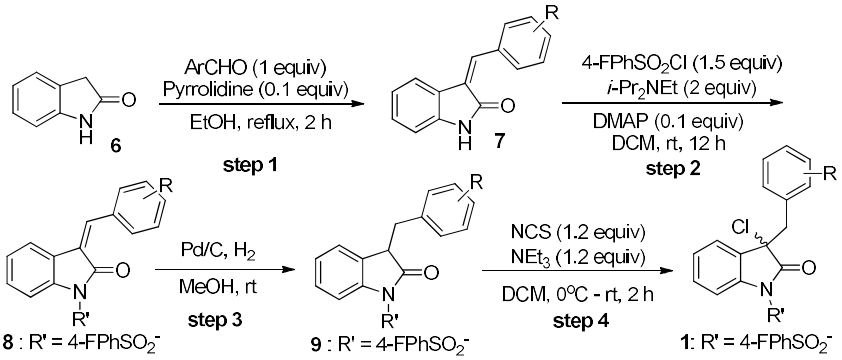
For **5a-5d, 5f-5h, 5j-5s, 5u**: **4** (0.10 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.), **C23** (0.02

mmol, 0.2 equiv.), $KHCO_3$ (0.30 mmol, 3.0 equiv.) and MTBE/THF = 2:1 (3.0 mL) were sequentially added, degassed three times by freeze-pump-thaw method. The reaction mixture was stirred under an argon atmosphere at −55 °C.

For **5e, 5i, 5t**: **4** (0.10 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.), **C23** (0.02 mmol, 0.2 equiv.), $KHCO_3$ (0.30 mmol, 3.0 equiv.) and MTBE/THF = 2:1 (3.0 mL) were sequentially added, degassed three times by freeze-pump-thaw method. The reaction mixture was stirred under an argon atmosphere at −60 °C.

Then irradiated by a 3 W blue LED (λ = 450−455 nm) for another 60 h. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with petroleum ether/ethyl acetate (50/1–5/1 ratio). Removing the solvent in *vacuo*, afforded products **5a**−**5u**.

(3) General Procedure for the Preparation of 1



Step 1: A mixture of **6** (10 mmol), ArCHO (10 mmol) and pyrrolidine (1.0 mmol, 0.1 equiv) in ethanol (30 mL) was heated to reflux for 2 hours and then quenched by water. A large amount of solids are precipitated, suction filtered, dried, afforded product **7** (e.g. **7a,** yellow solid, yield 94%).

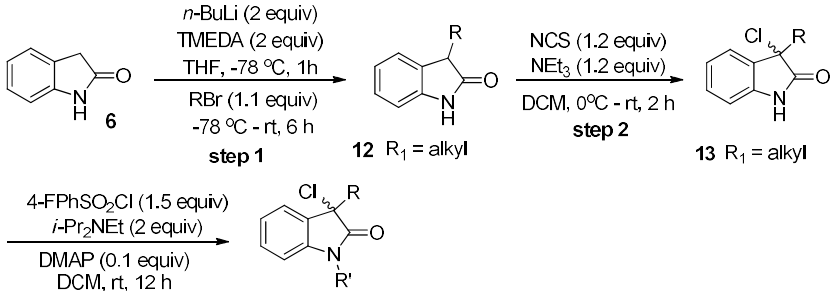
Step 2: **7** (5.0 mmol), 4-$FPhSO_2Cl$ (7.5 mmol, 1.5 equiv), *i*-Pr_2NEt (10 mmol, 2.0 equiv) and DMAP (0.5 mmol, 0.1 equiv) were added in dry DCM (15 mL). The mixture was stirred at room temperature for 6~12 h. TLC monitored until full conversion of **8**. After concentrated in *vacuo*, the residue was subjected to flash chromatograph (petroleum ether / ethyl acetate 4:1) on *silica gel* then removed the solvent in *vacuo*, afforded product **8** (e.g. **8a,** yellow solid, yield 89%).

Step 3: **8** (3.0 mmol), Pd/C (300 mg), H_2 were added in MeOH (10 mL). The mixture was stirred at room temperature for 3~12 h. TLC monitored until full conversion of **9**. After

concentrated in *vacuo*, the residue was subjected to flash chromatograph (petroleum ether/ethyl acetate 10:1) on *silica gel* then removed the solvent in *vacuo*, afforded product **9** (e.g. **9a,** white solid, yield 89%).

Step 4: The product **9** (2.0 mmol) was dissolved in dichloromethane (10 mL), followed by NEt_3 (2.4 mmol, 1.2 equiv) was added under N_2 at 0 °C. After 30 minutes, the NCS (2.4 mmol, 1.2 equiv) was added by all. The reaction was then warmed to room temperature and stirred for 2 hours. After concentrated in *vacuo*, the residue was subjected to flash chromatograph (petroleum ether / ethyl acetate 10:1) on *silica gel* then removed the solvent in *vacuo*, afforded product **1** (e.g. **1a,** white solid, yield 83%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 2H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 8.5 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 2H), 6.72 (d, *J* = 7.5 Hz, 2H), 3.56 (q, *J* = 13.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 167.9, 164.5, 138.2, 133.5, 132.3, 131.0, 130.8, 130.1, 128.1, 127.6, 127.4, 125.4, 125.3, 116.7, 116.4, 113.7, 64.5, 45.5.).

(4) General Procedure for the Preparation of 1r-1v



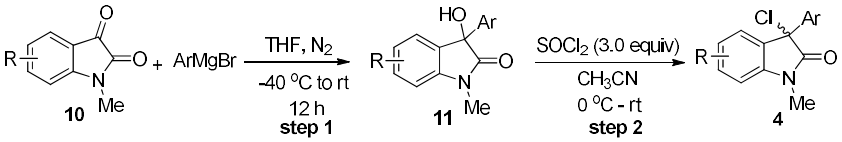
Step 1: *n*-BuLi (10 mmol, 2.0 equiv) was added to a solution of **6** (5 mmol) and TMEDA (10 mmol, 2.0 equiv) in THF (20 mL) at −78 °C and the mixture was stirred for 1 hour. Alkyl bromide (RBr, 5.5 mmol, 1.1 equiv) was then added dropwise and the solution was slowly warmed up to room temperature and stirred for 6-12 h. The reaction was then quenched with aq. NH4Cl and extracted with ethyl ether for 3 times. The combined organic layers were washed with brine, dried over Na_2SO_4. After concentrated in *vacuo*, the residue was subjected to flash chromatograph (petroleum ether / ethyl acetate 5:1) on *silica gel* then removed the solvent in *vacuo*, afforded product **12** (e.g. **12a,** white solid, yield 74%).

Step 2: The product **12** (3.0 mmol) was dissolved in dichloromethane (20 mL), followed by NEt_3 (3.6 mmol, 1.2 equiv) was added under N_2 at 0 °C. After 30 minutes, the NCS (3.6 mmol,

1.2 equiv) was added by all. The reaction was then warmed to room temperature and stirred for 2 hours. After concentrated in *vacuo*, the residue was subjected to flash chromatograph (petroleum ether / ethyl acetate 5:1) on *silica gel* then removed the solvent in *vacuo*, afforded product **13** (e.g. **1a,** white solid, yield 71%).

Step 3: The product **13** (2.0 mmol), 4-FPhSO$_2$Cl (3.0 mmol, 1.5 equiv), *i*-Pr$_2$NEt (4.0 mmol, 2.0 equiv) and DMAP (0.2 mmol, 0.1 equiv) in dry DCM (10 mL). The mixture was stirred at room temperature for 6~12 h. TLC monitored until full conversion of **1r-1v**. After concentrated in *vacuo*, the residue was subjected to flash chromatograph (petroleum ether / ethyl acetate 20:1) on *silica gel* then removed the solvent in *vacuo*, afforded products **1r-1v** (e.g. **1r,** yellow solid, yield 89%: ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.08 (dd, *J* = 8.8, 5.0 Hz, 2H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.20 (dd, *J* = 16.1, 7.8 Hz, 3H), 5.23 – 5.09 (m, 1H), 4.84 (dd, *J* = 22.5, 13.5 Hz, 2H), 2.91 (d, *J* = 6.9 Hz, 2H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 171.6, 168.1, 164.6, 138.1, 133.6, 131.2, 131.1, 131.0, 130.8, 128.9, 127.9, 125.7, 124.9, 121.7, 119.5, 116.7, 116.4, 114.0, 63.5, 43.6.).

(5) General Procedure for the Preparation of 4

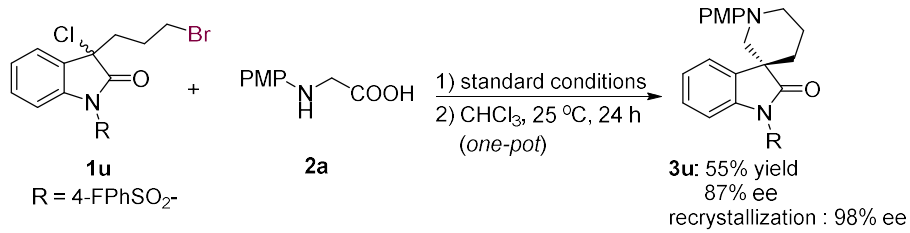


Step 1: A solution of ArMgBr (10 mmol, 2.0 equiv) was added to a stirred cold (−40 °C) suspension of **10** (5 mmol) in THF (30 mL) under an atmosphere of argon. The mixture was allowed to warm to room temperature for 6-12 h. The reaction mixture was diluted with ether, cooled in an ice-bath, and then quenched with 1*N* HCl. The aqueous layer was extracted with ether, and the combined organic layers were washed with water and brine and then dried over Na2SO4. After concentrated in *vacuo*, the residue was subjected to flash chromatograph (petroleum ether/ethyl acetate 3:1) on *silica gel* then removed the solvent in *vacuo*, afforded product **11**(e.g. **11a,** white solid, yield 89%).

Step 2: A solution of **11** (3.0 mmol) in dry CH$_3$CN (8.0 mL) was added SOCl$_2$ (9.0 mmol, 3.0 equiv.) at 0 °C. Subsequently, the mixture was warmed up to room temperature, and stirred for 2~6 h. TLC monitored until full conversion of **4**. Then cooled to 0 °C again, saturated NaHCO$_3$ solutions were added until no gas produced. Then extracted with DCM (3 x 10 mL),

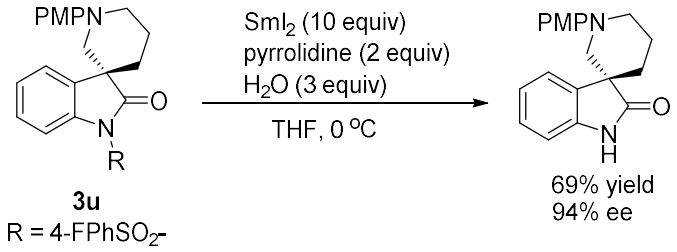
removed the solvent in *vacuo*. The residue was subjected to flash chromatograph (petroleum ether / ethyl acetate 10:1) on *silica gel* then removed the solvent in *vacuo*, afforded product **4** (e.g. **4a,** white solid, yield 93%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.44 – 7.34 (m, 5H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 3.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3, 142.8, 136.6, 130.4, 130.3, 128.9, 128.5, 127.5, 126.0, 123.6, 108.9, 66.1, 26.8).

4. Procedures for the synthesis of 3u-v and the modification

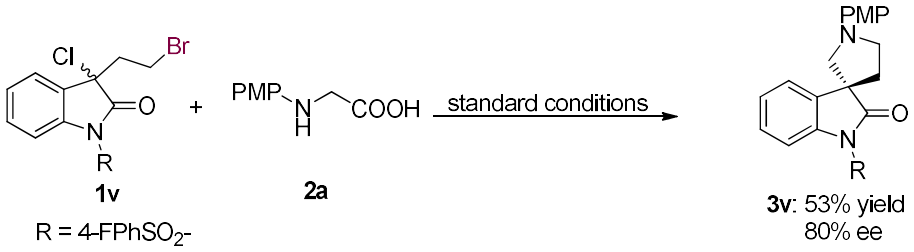


(1) **1u** (0.10 mmol, 1.0 equiv.), **2a** (0.15 mmol, 2.0 equiv.), **C1** (0.02 mmol, 0.2 equiv.), $KHCO_3$ (0.30 mmol, 3.0 equiv.) and MTBE/THF = 5:1 (3.0 mL) were sequentially added, degassed three times by freeze-pump-thaw method. The reaction mixture was stirred under an argon atmosphere at −42 °C. Then irradiated by a 3 W blue LED (λ = 450−455 nm) for another 65 h. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was directly removed the solvent in *vacuo*.

(2) Then the $CHCl_3$ was added and stirred the reaction mixture at 25 °C for 24 h. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with petroleum ether/ethyl acetate (50/1–10/1 ratio). Removing the solvent in *vacuo*, afforded product **3u**.



To a solution of SmI2 (5.2 mL, 0.1 mol/L, 0.52 mmol) in THF was added **3u** (0.052 mmol) followed by pyrrolidine (90 μL, 1.04 mmol) and water (28 μL, 1.56 mmol) under a nitrogen atmosphere. The resulting mixture was diluted with dichloromethane (4 mL) and treated with dilute hydrochloric acid (5 mL, 0.5 M) after 2 hours. The aqueous phase was extracted with three portions of dichloromethane. The organic extract was combined, dried and loaded onto a short silica gel column, followed by gradient elution with petroleum ether/ethyl acetate (20/1–4/1 ratio). Removing the solvent in vacuo, afforded product



1v (0.10 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.), **C1** (0.02 mmol, 0.2 equiv.), $KHCO_3$ (0.30 mmol, 3.0 equiv.) and MTBE/THF = 5:1 (3.0 mL) were sequentially added, degassed three times by freeze-pump-thaw method. The reaction mixture was stirred under an argon atmosphere at −42 °C. Then irradiated by a 3 W blue LED (λ = 450−455 nm) for another 65 h. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with petroleum ether/ethyl acetate (50/1–10/1 ratio). Removing the solvent in *vacuo*, afforded product **3v**.

5. Mechanism studies

The Luminescence Quenching Experiments of DPZ

Emission intensities were recorded on a spectrofluorometer. DPZ solution was excited at 448 nm and the emission intensity at 544 nm was observed. A solution of DPZ (5.0×10^{-5} M) was added to the appropriate amount of quencher in 3.0 mL volumetric flask under N_2. The solution was transferred to a 3.0 mL quartz cell and the emission spectrum of the sample was collected.

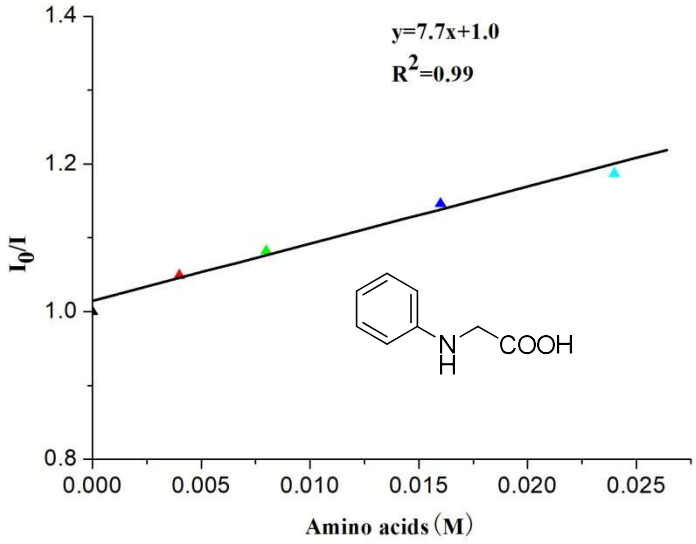


Figure S1. Stern–Volmer quenching experiment of DPZ and $PhNHCH_2COOH$.

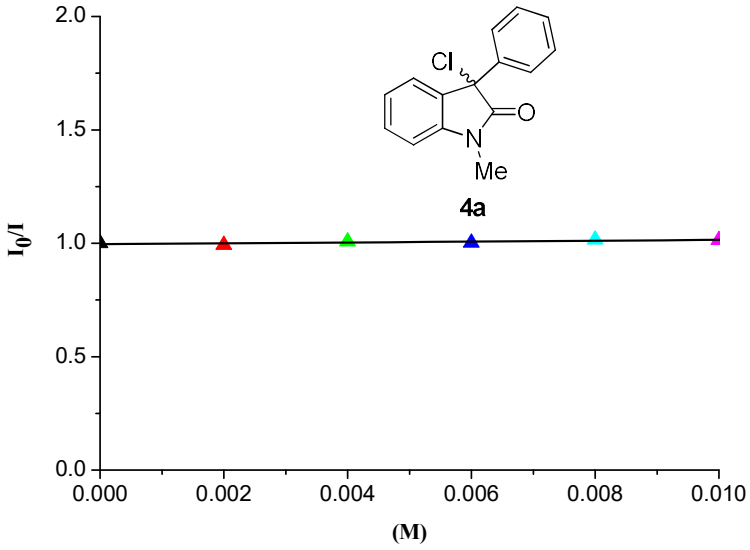


Figure S2. Stern–Volmer quenching experiment of DPZ and **4a**. No quenching observed.

Cyclic voltammetry measurement

Electrochemical potentials were obtained with a standard set of conditions to main internal consistency. Cyclic voltammograms were collected with a potentiostat. Samples were prepared with 0.02 mmol of **1a**, **4a** and 0.02 mmol **2v** in 10 mL of 0.1 M tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile. Measurements employed a radium glassy carbon working electrode, platinum wire counter electrode, saturated KCl silver-silver chloride reference electrode. The obtained value was referenced to Ag/AgCl.

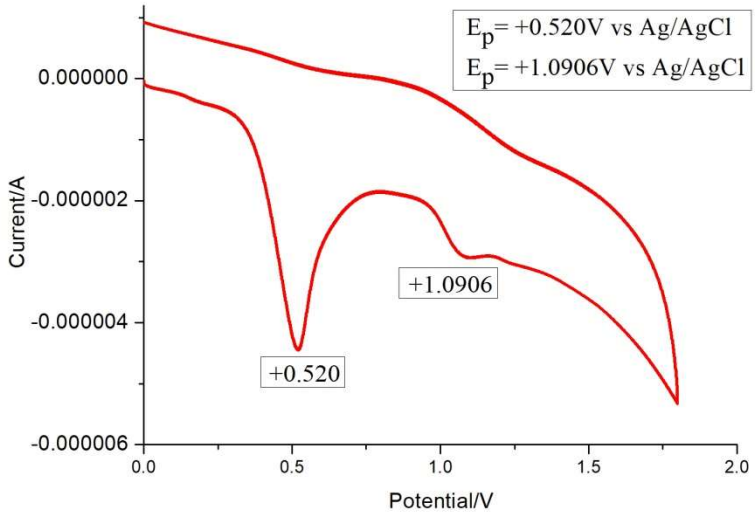


Figure S3. Cyclic voltammogram of $PhNHCH_2CO_2Na$ in MeCN.

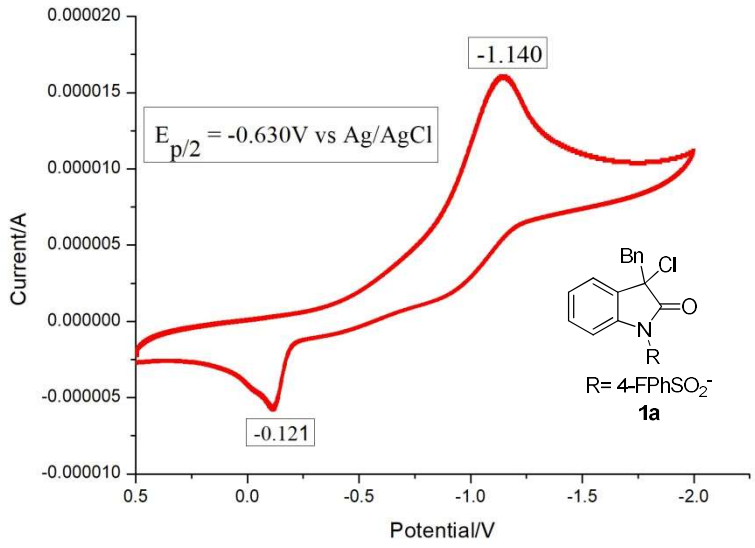


Figure S4. Cyclic voltammogram of **1a** in MeCN.

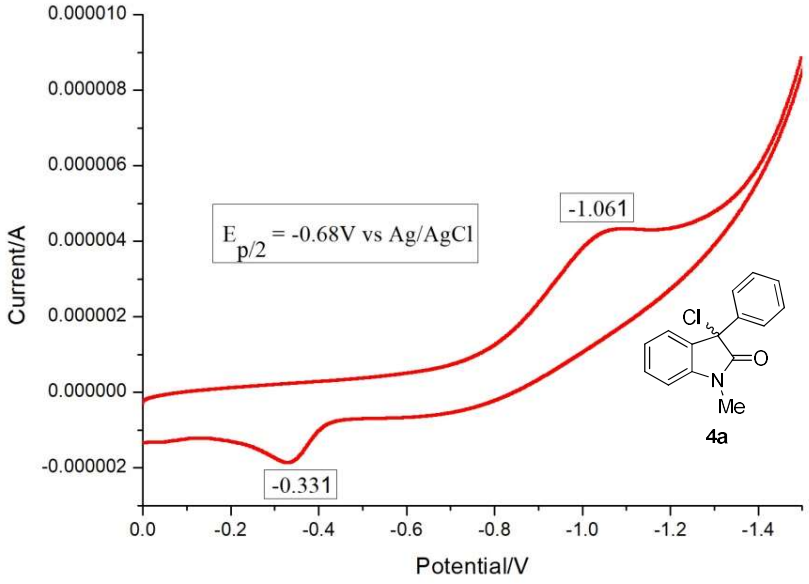


Figure S5. Cyclic voltammogram of **4a** in MeCN.

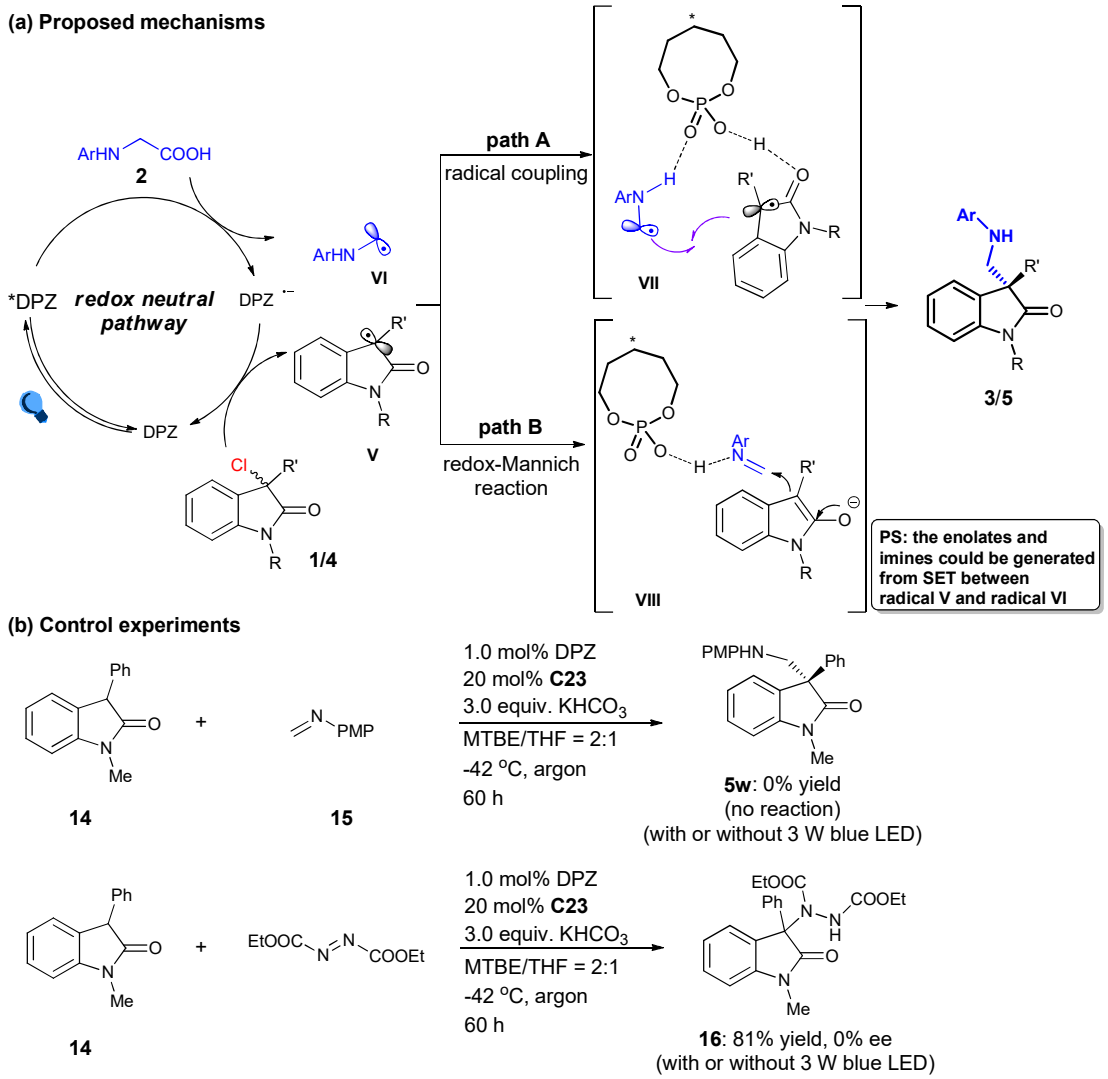


Figure S6. Proposed mechanisms and control experiments.

Descriptions:

In regard to the mechanism of this substitution reaction, the structure of the product indicates that 3-chlorooxindoles **1/4** and *N*-aryl glycines **2** may undergo a SET dehalogenative reduction and SET oxidation−decarboxylation to generate α-amide radicals (**V**) and α-aminomethylene radicals (**VI**), respectively (Figure S6A). Our Stern-Volmer experiments further confirmed that the photoredox catalytic cycle is triggered by the reductive quenching of *DPZ by *N*-aryl glycine **2**. Another crucial issue that must be clarified is the pathway for the formation of the new C−C bonds between two distinct radical species. According to the persistent radical effect, the coupling of nucleophilic and transient radical **VI** with electrophilic radical **V** is possible (see path A, Figure S6A). The improvement in the chemoselectivity achieved

when using a chiral BA catalyst supports this mechanism since the H-bonding interaction between the OH of the CPA and the carbonyl of the oxindole (see **VII**) will stabilise and increase the electrophilicity of radical **V** (Note: CPA is stable in the presence of $KHCO_3$ which was determined by the analyses of ^1H NMR). A Mannich-type reaction (see **VIII**) between the enolates and imines generated from radicals **V** and **VI** through a secondary photoredox catalytic cycle or SET redox reaction between the radicals is also possible (see path B, Figure S6A). Accordingly, 3-phenyl 2-oxindole **14** and imine **15** were subjected to the standard reaction conditions (see Scheme 3 in the manuscript), and no reaction was observed with or without irradiation by a 3 W blue LED (Figure S6B). Subsequently, diethyl azodicarboxylate (DEAD) was tested as the reaction partner instead of imine **15**, and amination product **16** was obtained in 81% yield with 0% ee. These results suggest the robust ability of **6** to generate the corresponding enolate in this reaction system. Accordingly, an ionic addition (path B) could be excluded, and a radical coupling (path A) to form the new C−C bond seems highly plausible.

Furthermore, **1a** could be readily reduced by Et_3N to generate 3-benzyl 2-oxindole through photoredox dehalogenative protonation (*Chem. Sci.* 2019, **10**, 6629) when under the standard reaction conditions (see Table 1). However, no carboxylation product was observed when in the presence of benzoic acid as the nucleophile (see *J. Org. Chem.* 2015, **80**, 12686). Accordingly, a transient quinone methide-type intermediate could be tentatively excluded.

6. Determination of the absolute configurations

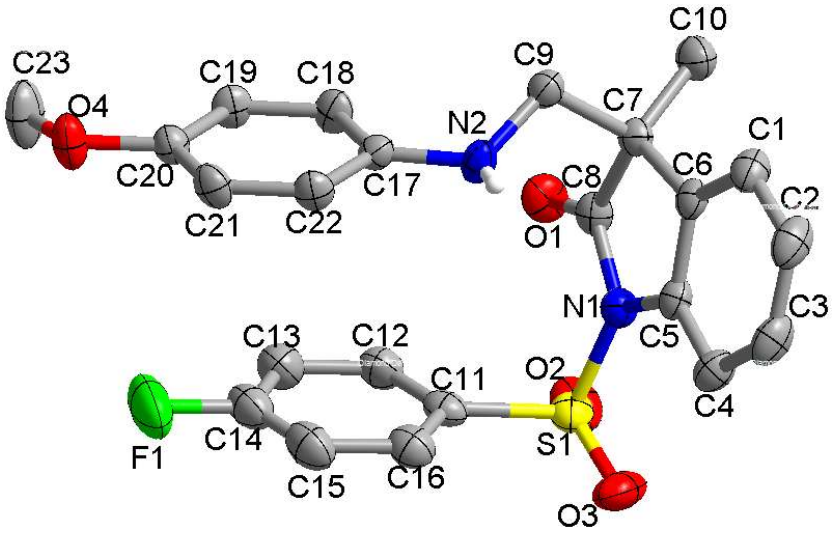


Figure S7. Absolute configuration of **3q** (CCDC 1915398)

Displacement ellipsoids are drawn at the 30% probability level.
(sovlent: ethyl acetate:*n*hexane = 1:6)

Table S3 Crystal data and structure refinement for 201805262.

Identification code	201805262
Empirical formula	$C_{23}H_{21}FN_2O_4S$
Formula weight	440.48
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.17133(16)
b/Å	14.8909(5)
c/Å	22.8926(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2103.76(11)
Z	4
ρ_{calc}g/cm^3	1.391
μ/mm^{-1}	1.732
F(000)	920.0
Crystal size/mm^3	0.15 × 0.1 × 0.03
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.082 to 141.916
Index ranges	-4 ≤ h ≤ 7, -18 ≤ k ≤ 17, -27 ≤ l ≤ 25
Reflections collected	7878

Independent reflections	3984 [R_{int} = 0.0326, R_{sigma} = 0.0560]
Data/restraints/parameters	3984/34/296
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0480, wR_2 = 0.1044
Final R indexes [all data]	R_1 = 0.0657, wR_2 = 0.1137
Largest diff. peak/hole / e $Å^{-3}$	0.22/-0.20
Flack parameter	0.009(15)

Table S4 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for 201805262. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ}tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	-603(8)	4713(3)	2132(2)	59.1(12)
C2	-1989(8)	5381(4)	1935(2)	68.7(15)
C3	-1889(8)	6228(4)	2168(2)	65.6(14)
C4	-369(8)	6455(3)	2585(2)	56.4(12)
C5	1047(6)	5793(3)	2766.0(18)	43.8(10)
C6	908(6)	4920(3)	2549.6(17)	45.2(10)
C7	2508(7)	4322(3)	2849.6(18)	44.1(9)
C8	3801(7)	4983(3)	3216.6(18)	47.9(10)
C9	1353(8)	3694(3)	3285.1(19)	52.3(11)
C10	3948(8)	3768(3)	2443(2)	63.5(13)
C11	2540(50)	6430(30)	4280(11)	53.9(14)
C12	4000(40)	6010(30)	4648(14)	71(3)
C13	3390(30)	5799(19)	5217(10)	81(4)
C14	1380(30)	6039(11)	5383(6)	76(3)
C14A	550(40)	6186(17)	5314(9)	76(3)
C13A	2620(50)	5840(30)	5221(16)	81(4)
C12A	3650(60)	5980(50)	4690(20)	71(3)
C11A	2620(80)	6470(40)	4251(16)	53.9(14)
C16A	550(70)	6810(30)	4344(10)	65(3)
C15A	-480(40)	6669(17)	4875(11)	79(4)
C15	-90(30)	6441(12)	5040(8)	79(4)
C16	490(40)	6643(16)	4466(7)	65(3)
C17	273(7)	3933(3)	4320.8(18)	43.3(9)
C18	2097(7)	3555(3)	4570.6(19)	52.8(11)
C19	2130(7)	3337(3)	5161.1(19)	51.8(11)
C20	376(7)	3513(3)	5510.8(18)	49.4(10)
C21	-1436(7)	3894(3)	5264(2)	55.0(12)
C22	-1492(7)	4107(3)	4679.6(19)	49.4(10)
C23	2133(9)	3049(5)	6378(2)	92(2)

F1	730(30)	5841(13)	5951(6)	127(5)
F1A	-360(50)	6030(20)	5813(10)	127(5)
N1	2864(6)	5839(2)	3155.9(16)	48.0(9)
N2	197(7)	4189(3)	3729.1(17)	53.4(10)
O1	5322(5)	4812(2)	3530.6(15)	66.0(9)
O2	5845(5)	6738(3)	3604.2(17)	82.6(12)
O3	2393(7)	7468(2)	3356.2(18)	85.4(13)
O4	242(6)	3305(3)	6096.4(13)	70.3(10)
S1	3570(2)	6718.5(8)	3576.7(6)	57.8(3)

Table S5 Anisotropic Displacement Parameters ($Å^2×10^3$) for 201805262. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	65(3)	59(3)	54(3)	7(2)	-11(2)	-16(2)
C2	62(3)	79(4)	64(3)	20(3)	-22(3)	-18(3)
C3	50(3)	75(4)	71(3)	27(3)	-16(3)	1(2)
C4	51(3)	55(3)	64(3)	11(2)	-2(2)	3(2)
C5	39(2)	51(2)	41(2)	9.5(19)	-1.1(18)	-4.2(19)
C6	45(2)	50(2)	40(2)	8.5(18)	2.7(19)	-7.3(18)
C7	42(2)	47(2)	43(2)	1.2(19)	4(2)	-1.3(18)
C8	35(2)	61(3)	47(2)	4(2)	3(2)	4(2)
C9	59(3)	48(2)	50(2)	8(2)	4(2)	5(2)
C10	68(3)	65(3)	57(3)	-1(2)	12(3)	-1(3)
C11	52(3)	48(4)	62(3)	-13(3)	2(3)	-7(3)
C12	81(7)	67(4)	64(5)	-8(4)	4(5)	13(7)
C13	101(13)	74(5)	69(4)	-5(3)	3(9)	8(10)
C14	83(8)	76(5)	68(5)	-17(4)	18(6)	-10(6)
C14A	83(8)	76(5)	68(5)	-17(4)	18(6)	-10(6)
C13A	101(13)	74(5)	69(4)	-5(3)	3(9)	8(10)
C12A	81(7)	67(4)	64(5)	-8(4)	4(5)	13(7)
C11A	52(3)	48(4)	62(3)	-13(3)	2(3)	-7(3)
C16A	58(3)	66(9)	70(7)	-9(5)	0(6)	-7(5)
C15A	74(6)	87(8)	75(9)	-19(6)	17(6)	-6(5)
C15	74(6)	87(8)	75(9)	-19(6)	17(6)	-6(5)
C16	58(3)	66(9)	70(7)	-9(5)	0(6)	-7(5)
C17	42(2)	40(2)	48(2)	5.4(18)	3(2)	1.9(17)
C18	39(2)	65(3)	54(3)	7(2)	13(2)	9(2)
C19	37(2)	65(3)	53(2)	3(2)	-5(2)	12(2)
C20	50(2)	57(3)	41(2)	-2.0(19)	0(2)	3(2)
C21	44(2)	72(3)	49(2)	-8(2)	9(2)	9(2)

C22	38(2)	58(3)	52(2)	0(2)	0(2)	13(2)
C23	74(4)	152(6)	50(3)	18(4)	-13(3)	18(4)
F1	175(13)	142(8)	64(6)	-15(5)	37(7)	-33(10)
F1A	175(13)	142(8)	64(6)	-15(5)	37(7)	-33(10)
N1	46(2)	51(2)	47.3(19)	0.2(17)	-2.8(17)	-0.5(16)
N2	50(2)	61(2)	49(2)	14.7(17)	6.7(19)	15(2)
O1	47.9(18)	82(2)	68(2)	-2.5(19)	-15.2(19)	13.4(17)
O2	60(2)	107(3)	81(2)	-20(2)	2(2)	-31(2)
O3	114(3)	45.1(19)	97(3)	5(2)	-25(3)	-4(2)
O4	60(2)	110(3)	40.8(16)	6.6(19)	0.6(16)	14(2)
S1	57.3(7)	54.2(6)	61.7(7)	-2.7(6)	-3.3(6)	-13.0(6)

Table S6 Bond Lengths for 201805262.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.387(7)	C14A	C13A	1.3900
C1	C6	1.369(6)	C14A	C15A	1.3900
C2	C3	1.371(7)	C14A	F1A	1.29(3)
C3	C4	1.380(7)	C13A	C12A	1.3900
C4	C5	1.381(6)	C12A	C11A	1.3900
C5	C6	1.394(6)	C11A	C16A	1.3900
C5	N1	1.434(5)	C11A	S1	1.69(2)
C6	C7	1.496(6)	C16A	C15A	1.3900
C7	C8	1.520(6)	C15	C16	1.396(14)
C7	C9	1.542(6)	C17	C18	1.382(6)
C7	C10	1.528(6)	C17	C22	1.389(6)
C8	N1	1.406(5)	C17	N2	1.408(5)
C8	O1	1.209(5)	C18	C19	1.390(6)
C9	N2	1.444(6)	C19	C20	1.372(6)
C11	C12	1.382(12)	C20	C21	1.375(6)
C11	C16	1.371(12)	C20	O4	1.378(5)
C11	S1	1.785(14)	C21	C22	1.375(6)
C12	C13	1.393(15)	C23	O4	1.387(6)
C13	C14	1.344(17)	N1	S1	1.684(4)
C14	C15	1.342(15)	O2	S1	1.405(3)
C14	F1	1.393(18)	O3	S1	1.424(4)

Table S7 Bond Angles for 201805262.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	C1	C2	119.1(5)	C11A	C12A	C13A	120.0
C3	C2	C1	120.3(5)	C12A	C11A	S1	128(3)

C2	C3	C4	121.6(5)	C16A	C11A	C12A	120.0
C3	C4	C5	117.6(5)	C16A	C11A	S1	112(3)
C4	C5	C6	121.3(4)	C15A	C16A	C11A	120.0
C4	C5	N1	130.4(4)	C16A	C15A	C14A	120.0
C6	C5	N1	108.3(4)	C14	C15	C16	118.3(10)
C1	C6	C5	119.9(4)	C11	C16	C15	118.5(10)
C1	C6	C7	129.5(4)	C18	C17	C22	118.0(4)
C5	C6	C7	110.5(4)	C18	C17	N2	122.4(4)
C6	C7	C8	102.4(3)	C22	C17	N2	119.5(4)
C6	C7	C9	110.6(3)	C17	C18	C19	120.6(4)
C6	C7	C10	115.2(4)	C20	C19	C18	120.7(4)
C8	C7	C9	106.1(3)	C19	C20	C21	118.7(4)
C8	C7	C10	112.4(4)	C19	C20	O4	124.9(4)
C10	C7	C9	109.5(4)	C21	C20	O4	116.3(4)
N1	C8	C7	108.4(3)	C20	C21	C22	121.0(4)
O1	C8	C7	126.8(4)	C21	C22	C17	120.8(4)
O1	C8	N1	124.7(4)	C5	N1	S1	126.6(3)
N2	C9	C7	111.9(3)	C8	N1	C5	109.9(3)
C12	C11	S1	115.2(17)	C8	N1	S1	122.8(3)
C16	C11	C12	121.2(8)	C17	N2	C9	121.5(4)
C16	C11	S1	123.5(17)	C20	O4	C23	117.6(4)
C11	C12	C13	119.7(10)	N1	S1	C11	103.7(15)
C14	C13	C12	116.9(11)	N1	S1	C11A	105(2)
C13	C14	F1	118.3(13)	O2	S1	C11	108.7(11)
C15	C14	C13	125.3(11)	O2	S1	C11A	108.0(18)
C15	C14	F1	116.4(12)	O2	S1	N1	107.5(2)
C13A	C14A	C15A	120.0	O2	S1	O3	120.7(3)
F1A	C14A	C13A	118(2)	O3	S1	C11	109.1(10)
F1A	C14A	C15A	122(2)	O3	S1	C11A	108.7(17)
C14A	C13A	C12A	120.0	O3	S1	N1	105.9(2)

Table S8 Hydrogen Bonds for 201805262.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C4	H4	O3	0.93	2.28	2.881(6)	122.1
N2	H2A	O1[1]	0.84(2)	2.35(3)	3.181(5)	168(4)

[1]-1+X,+Y,+Z

Table S9 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 201805262.

Atom	*x*	*y*	*z*	U(eq)
H1	-698	4134	1984	71
H2	-2991	5253	1643	82
H3	-2869	6661	2041	79
H4	-301	7032	2738	68
H9A	342	3315	3074	63
H9B	2417	3308	3470	63
H10A	4629	4157	2164	95
H10B	3079	3332	2242	95
H10C	5039	3466	2669	95
H12	5384	5870	4515	85
H13	4328	5504	5471	97
H13A	3310	5521	5515	97
H12A	5036	5755	4628	85
H16A	-137	7132	4050	78
H15A	-1863	6898	4937	94
H15	-1462	6581	5182	94
H16	-493	6916	4214	78
H18	3313	3446	4342	63
H19	3355	3068	5321	62
H21	-2642	4009	5496	66
H22	-2728	4371	4523	59
H23A	1836	2948	6784	138
H23B	3196	3516	6340	138
H23C	2676	2507	6205	138
H2A	-1020(50)	4380(30)	3628(19)	46(13)

Table S10 Atomic Occupancy for 201805262.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
C11	0.61(2)	C12	0.61(2)	H12	0.61(2)
C13	0.61(2)	H13	0.61(2)	C14	0.61(2)
C14A	0.39(2)	C13A	0.39(2)	H13A	0.39(2)
C12A	0.39(2)	H12A	0.39(2)	C11A	0.39(2)
C16A	0.39(2)	H16A	0.39(2)	C15A	0.39(2)
H15A	0.39(2)	C15	0.61(2)	H15	0.61(2)
C16	0.61(2)	H16	0.61(2)	F1	0.61(2)
F1A	0.39(2)				

Experimental

The crystal was kept at 293(2) K during data collection. Using Olex2,[1] the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.
2. Sheldrick, G. M. *Acta Cryst. A* **2008**, *64*, 112-122.
3. Sheldrick, G.M. *Acta Cryst. C* **2015**, *71*, 3-8.

Crystal structure determination

Crystal Data for $C_{23}H_{21}FN_2O_4S$ (M =440.48 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 6.17133(16) Å, b = 14.8909(5) Å, c = 22.8926(7) Å, V = 2103.76(11) Å^3, Z = 4, T = 293(2) K, μ(CuKα) = 1.732 mm^{-1}, *Dcalc* = 1.391 g/cm^3, 7878 reflections measured (7.082° ≤ 2Θ ≤ 141.916°), 3984 unique (R_{int} = 0.0326, R_{sigma} = 0.0560) which were used in all calculations. The final R_1 was 0.0480 (I > 2σ(I)) and wR_2 was 0.1137 (all data).

Refinement model description

Number of restraints - 34, number of constraints - unknown.
Details:
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2. Restrained distances
 C12A-C11A
 1.38 with sigma of 0.02
 C13A-C12A
 1.38 with sigma of 0.02
 C11-S1
 1.6 with sigma of 0.02
 N2-H2A
 0.87 with sigma of 0.02
3. Uiso/Uaniso restraints and constraints
Uanis(F1) ≈ Ueq, Uanis(C15) ≈ Ueq, Uanis(C16) ≈ Ueq: with sigma of 0.01 and sigma for terminal atoms of 0.02
Uanis(C14) ≈ Ueq, Uanis(C14A) ≈ Ueq: with sigma of 0.01 and sigma for terminal atoms of 0.02
Uanis(C12) = Uanis(C12A)
Uanis(C13) = Uanis(C13A)
Uanis(C14) = Uanis(C14A)
Uanis(C15) = Uanis(C15A)
Uanis(C16) = Uanis(C16A)
Uanis(F1) = Uanis(F1A)

Uanis(C11) = Uanis(C11A)

4. Others

Sof(C14A)=Sof(C13A)=Sof(H13A)=Sof(C12A)=Sof(H12A)=Sof(C11A)=Sof(C16A)=Sof(H16A)=Sof(C15A)=Sof(H15A)=Sof(F1A)=1-FVAR(1)

Sof(C11)=Sof(C12)=Sof(H12)=Sof(C13)=Sof(H13)=Sof(C14)=Sof(C15)=Sof(H15)=Sof(C16)=Sof(H16)=Sof(F1)=FVAR(1)

5.a Secondary CH2 refined with riding coordinates:

C9(H9A,H9B)

5.b Aromatic/amide H refined with riding coordinates:

C1(H1), C2(H2), C3(H3), C4(H4), C12(H12), C13(H13), C13A(H13A), C12A(H12A), C16A(H16A), C15A(H15A), C15(H15), C16(H16), C18(H18), C19(H19), C21(H21), C22(H22)

5.c Fitted hexagon refined as free rotating group:

C14A(C13A,C12A,C11A,C16A,C15A)

5.d Idealised Me refined as rotating group:

C10(H10A,H10B,H10C), C23(H23A,H23B,H23C)

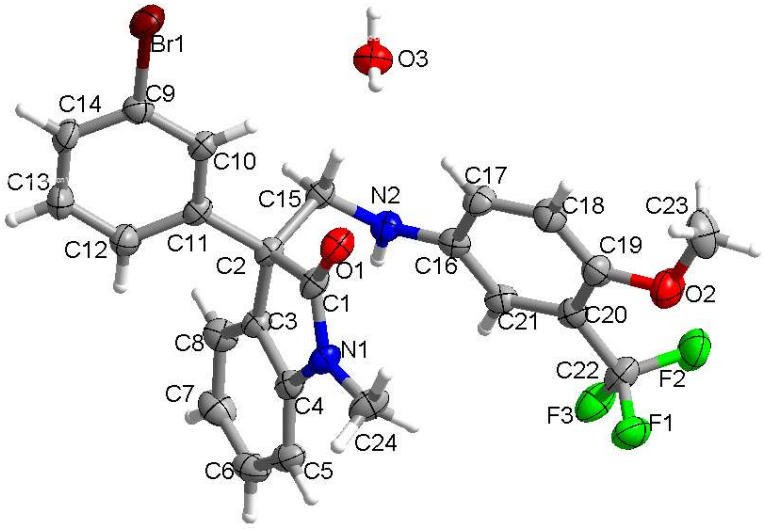


Figure S8. Absolute configuration of **5h** (CCDC 1915399)

Displacement ellipsoids are drawn at the 30% probability level.

(sovlent: ethyl acetate:*n*hexane = 1:3)

Table S11 Crystal data and structure refinement for zgk22075a.

Identification code	zgk22075a
Empirical formula	$C_{48}H_{42}Br_2F_6N_4O_5$
Formula weight	1028.67
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2
a/Å	26.455(2)
b/Å	6.3246(2)

c/Å	14.0068(9)
α/°	90
β/°	109.467(9)
γ/°	90
Volume/Å^3	2209.6(3)
Z	2
ρ_{calc}g/cm^3	1.546
μ/mm^{-1}	3.000
F(000)	1044.0
Crystal size/mm^3	0.14 × 0.05 × 0.04
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.694 to 141.528
Index ranges	-31 ≤ h ≤ 32, -4 ≤ k ≤ 7, -16 ≤ l ≤ 17
Reflections collected	5109
Independent reflections	3058 [R_{int} = 0.0252, R_{sigma} = 0.0412]
Data/restraints/parameters	3058/2/303
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0422, wR_2 = 0.1070
Final R indexes [all data]	R_1 = 0.0481, wR_2 = 0.1114
Largest diff. peak/hole / e Å^{-3}	0.33/-0.33
Flack parameter	-0.001(19)

Table S12 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for zgk22075a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ}tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	3650.4(3)	3846.3(10)	5554.8(5)	62.3(2)
C1	3990(2)	8100(9)	2256(4)	40.8(12)
C2	3761(2)	9663(8)	2857(4)	37.4(11)
C3	3467(2)	11208(9)	2037(4)	40.0(11)
C4	3532(2)	10605(10)	1130(4)	41.9(12)
C5	3311(3)	11741(11)	251(5)	53.2(15)
C6	3021(3)	13526(12)	300(5)	62.1(18)
C7	2954(2)	14175(12)	1196(5)	63.4(18)
C8	3184(2)	13017(9)	2076(5)	49.5(13)
C9	3328(2)	5950(10)	4568(4)	47.6(13)
C10	3646(2)	7014(9)	4113(4)	40.8(12)
C11	3417(2)	8471(9)	3363(4)	39.4(13)
C12	2864(2)	8793(16)	3064(4)	55.9(14)
C13	2558(2)	7737(14)	3554(6)	69(2)
C14	2790(2)	6304(12)	4307(5)	58.1(17)

C15	4239(2)	10771(9)	3689(4)	41.6(12)
C16	4973(2)	11435(9)	2972(4)	41.7(12)
C17	5271(2)	9591(10)	3350(5)	49.4(14)
C18	5698(2)	9050(14)	3040(5)	55.6(14)
C19	5844(2)	10257(12)	2360(5)	53.7(15)
C20	5550(2)	12084(10)	1977(4)	46.7(13)
C21	5114(2)	12642(9)	2280(4)	41.7(12)
C22	5691(3)	13433(12)	1221(5)	61.0(19)
C23	6652(3)	8376(14)	2587(7)	83(3)
C24	4020(3)	7733(13)	521(5)	68(2)
F1	5601.1(18)	12466(8)	333(3)	75.5(12)
F2	6216.7(15)	13948(11)	1536(3)	83.8(12)
F3	5425(2)	15247(7)	1038(4)	79.1(13)
N1	3845.5(17)	8779(10)	1278(3)	45.1(9)
N2	4565.4(19)	12151(8)	3318(4)	44.2(11)
O1	4257.9(18)	6524(7)	2597(3)	51.8(10)
O2	6260(2)	9800(10)	2017(4)	77.5(16)
O3	5000	5642(12)	5000	62.0(17)

Table S13 Anisotropic Displacement Parameters ($Å^2×10^3$) for zgk22075a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	73.6(4)	59.6(4)	62.6(3)	16.9(4)	35.0(3)	5.2(4)
C1	47(3)	31(3)	50(3)	1(2)	25(2)	-2(2)
C2	45(3)	30(2)	41(2)	2(2)	19(2)	4(2)
C3	44(3)	31(3)	45(3)	3(2)	16(2)	-1(2)
C4	46(3)	35(3)	45(3)	1(2)	17(2)	-5(2)
C5	60(4)	54(4)	43(3)	3(3)	14(3)	-10(3)
C6	61(3)	53(5)	58(3)	18(3)	1(3)	-5(3)
C7	58(3)	44(4)	77(4)	8(4)	8(3)	9(3)
C8	54(3)	34(3)	57(3)	-2(3)	16(3)	6(3)
C9	52(3)	49(4)	44(3)	-3(3)	18(2)	-4(3)
C10	43(3)	39(3)	45(3)	-1(2)	21(2)	-1(3)
C11	46(2)	35(3)	41(2)	-5(2)	20(2)	-1(2)
C12	47(3)	68(4)	54(3)	5(4)	19(2)	2(4)
C13	38(3)	95(6)	81(5)	15(4)	30(3)	6(4)
C14	49(3)	67(4)	69(4)	12(4)	33(3)	-7(3)
C15	48(3)	37(3)	44(3)	-2(2)	21(2)	-2(3)
C16	41(3)	36(3)	44(3)	-2(2)	9(2)	0(2)
C17	52(3)	43(3)	55(3)	11(3)	19(3)	3(3)

C18	52(3)	49(4)	65(3)	10(4)	18(2)	10(4)
C19	46(3)	59(4)	54(3)	-6(3)	14(3)	5(3)
C20	48(3)	45(3)	46(3)	-2(3)	15(2)	-6(3)
C21	44(3)	32(3)	46(3)	1(2)	11(2)	2(2)
C22	74(4)	59(5)	60(3)	1(3)	36(3)	-3(4)
C23	54(4)	74(7)	122(7)	-10(5)	31(4)	13(4)
C24	104(6)	59(4)	59(4)	-6(3)	48(4)	6(4)
F1	90(3)	91(3)	52(2)	-2(2)	31(2)	2(3)
F2	74(2)	97(3)	90(3)	-4(4)	40(2)	-28(3)
F3	114(4)	56(3)	87(3)	17(2)	60(3)	7(3)
N1	59(2)	38(2)	46(2)	-5(3)	27.1(18)	2(3)
N2	47(3)	31(2)	56(3)	7(2)	18(2)	3(2)
O1	65(3)	33(2)	68(3)	4.5(19)	36(2)	12(2)
O2	69(3)	88(4)	88(4)	8(3)	43(3)	17(3)
O3	69(4)	55(4)	58(4)	0	14(3)	0

Table S14 Bond Lengths for zgk22075a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C9	1.903(6)	C12	C13	1.394(9)
C1	C2	1.547(7)	C13	C14	1.371(10)
C1	N1	1.362(7)	C15	N2	1.441(7)
C1	O1	1.224(7)	C16	C17	1.408(8)
C2	C3	1.511(7)	C16	C21	1.379(8)
C2	C11	1.528(7)	C16	N2	1.398(7)
C2	C15	1.569(7)	C17	C18	1.382(8)
C3	C4	1.391(8)	C18	C19	1.372(9)
C3	C8	1.379(8)	C19	C20	1.396(9)
C4	C5	1.376(8)	C19	O2	1.371(7)
C4	N1	1.397(8)	C20	C21	1.400(8)
C5	C6	1.380(11)	C20	C22	1.499(9)
C6	C7	1.386(10)	C22	F1	1.335(8)
C7	C8	1.388(9)	C22	F2	1.352(8)
C9	C10	1.387(8)	C22	F3	1.325(9)
C9	C14	1.366(8)	C23	O2	1.404(9)
C10	C11	1.377(8)	C24	N1	1.450(7)
C11	C12	1.394(7)			

Table S15 Bond Angles for zgk22075a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	C1	C2	108.4(5)	C14	C13	C12	120.7(6)

O1	C1	C2	126.0(5)	C9	C14	C13	118.3(6)
O1	C1	N1	125.6(5)	N2	C15	C2	115.7(4)
C1	C2	C15	109.0(4)	C21	C16	C17	118.4(5)
C3	C2	C1	101.3(4)	C21	C16	N2	119.0(5)
C3	C2	C11	115.9(4)	N2	C16	C17	122.5(5)
C3	C2	C15	111.0(4)	C18	C17	C16	120.0(6)
C11	C2	C1	109.9(4)	C19	C18	C17	121.9(7)
C11	C2	C15	109.4(4)	C18	C19	C20	118.6(6)
C4	C3	C2	109.2(5)	O2	C19	C18	124.7(7)
C8	C3	C2	131.0(5)	O2	C19	C20	116.7(6)
C8	C3	C4	119.8(5)	C19	C20	C21	120.1(6)
C3	C4	N1	109.8(5)	C19	C20	C22	120.4(6)
C5	C4	C3	122.0(6)	C21	C20	C22	119.5(6)
C5	C4	N1	128.2(5)	C16	C21	C20	121.1(5)
C4	C5	C6	117.3(6)	F1	C22	C20	112.8(6)
C5	C6	C7	121.9(6)	F1	C22	F2	104.9(5)
C6	C7	C8	119.8(7)	F2	C22	C20	112.2(6)
C3	C8	C7	119.1(6)	F3	C22	C20	112.9(5)
C10	C9	Br1	118.7(4)	F3	C22	F1	107.3(6)
C14	C9	Br1	118.9(5)	F3	C22	F2	106.1(6)
C14	C9	C10	122.3(6)	C1	N1	C4	111.4(5)
C11	C10	C9	119.7(5)	C1	N1	C24	122.7(6)
C10	C11	C2	120.3(4)	C4	N1	C24	125.9(5)
C10	C11	C12	118.6(5)	C16	N2	C15	123.6(5)
C12	C11	C2	121.1(5)	C19	O2	C23	117.6(6)
C13	C12	C11	120.3(7)				

Table S16 Hydrogen Bonds for zgk22075a.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N2	H2	O1[1]	0.86(2)	2.17(3)	2.964(7)	155(4)
O3	H3	N2[2]	0.85	2.33	3.153(8)	164.5

[1]+X,1+Y,+Z; [2]1-X,-1+Y,1-Z

Table S17 Torsion Angles for zgk22075a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C9	C10	C11	177.0(4)	C14	C9	C10	C11	-0.6(9)
Br1	C9	C14	C13	-176.3(6)	C15	C2	C3	C4	114.9(5)
C1	C2	C3	C4	-0.7(6)	C15	C2	C3	C8	-62.9(7)
C1	C2	C3	C8	-178.5(6)	C15	C2	C11	C10	-54.2(6)

C1	C2	C11	C10	65.5(6)	C15	C2	C11	C12	127.3(6)
C1	C2	C11	C12	-113.0(6)	C16	C17	C18	C19	-0.5(10)
C1	C2	C15	N2	66.4(6)	C17	C16	C21	C20	-1.5(8)
C2	C1	N1	C4	-1.5(6)	C17	C16	N2	C15	-30.1(8)
C2	C1	N1	C24	176.5(6)	C17	C18	C19	C20	0.2(10)
C2	C3	C4	C5	-179.2(5)	C17	C18	C19	O2	-179.5(6)
C2	C3	C4	N1	-0.1(6)	C18	C19	C20	C21	-0.5(9)
C2	C3	C8	C7	179.3(6)	C18	C19	C20	C22	-179.2(6)
C2	C11	C12	C13	-178.1(7)	C18	C19	O2	C23	-18.5(10)
C2	C15	N2	C16	-80.8(7)	C19	C20	C21	C16	1.2(9)
C3	C2	C11	C10	179.4(5)	C19	C20	C22	F1	66.8(8)
C3	C2	C11	C12	1.0(8)	C19	C20	C22	F2	-51.5(8)
C3	C2	C15	N2	-44.3(6)	C19	C20	C22	F3	-171.3(6)
C3	C4	C5	C6	0.0(9)	C20	C19	O2	C23	161.9(6)
C3	C4	N1	C1	1.0(6)	C21	C16	C17	C18	1.2(9)
C3	C4	N1	C24	-176.9(6)	C21	C16	N2	C15	154.0(5)
C4	C3	C8	C7	1.8(9)	C21	C20	C22	F1	-111.9(7)
C4	C5	C6	C7	0.5(10)	C21	C20	C22	F2	129.8(6)
C5	C4	N1	C1	-179.9(6)	C21	C20	C22	F3	10.0(9)
C5	C4	N1	C24	2.2(10)	C22	C20	C21	C16	179.9(5)
C5	C6	C7	C8	0.1(10)	N1	C1	C2	C3	1.3(6)
C6	C7	C8	C3	-1.2(10)	N1	C1	C2	C11	124.3(5)
C8	C3	C4	C5	-1.2(9)	N1	C1	C2	C15	-115.8(5)
C8	C3	C4	N1	178.0(5)	N1	C4	C5	C6	-179.0(6)
C9	C10	C11	C2	179.8(5)	N2	C16	C17	C18	-174.7(6)
C9	C10	C11	C12	-1.7(8)	N2	C16	C21	C20	174.5(5)
C10	C9	C14	C13	1.3(11)	O1	C1	C2	C3	-178.9(5)
C10	C11	C12	C13	3.3(10)	O1	C1	C2	C11	-55.9(7)
C11	C2	C3	C4	-119.6(5)	O1	C1	C2	C15	64.0(7)
C11	C2	C3	C8	62.7(8)	O1	C1	N1	C4	178.8(5)
C11	C2	C15	N2	-173.4(5)	O1	C1	N1	C24	-3.2(9)
C11	C12	C13	C14	-2.8(13)	O2	C19	C20	C21	179.2(6)
C12	C13	C14	C9	0.4(12)	O2	C19	C20	C22	0.5(9)

Table S18 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for zgk22075a.

Atom	*x*	*y*	*z*	U(eq)
H5	3356	11323	-352	64
H6	2865	14316	-284	75
H7	2756	15384	1207	76

H8	3147	13455	2683	59
H10	4012	6745	4313	49
H12	2699	9715	2535	67
H13	2193	8009	3368	83
H14	2586	5592	4632	70
H15A	4093	11587	4124	50
H15B	4467	9685	4103	50
H17	5180	8736	3808	59
H18	5893	7833	3300	67
H21	4917	13847	2010	50
H23A	6945	8347	2328	125
H23B	6498	6989	2541	125
H23C	6780	8820	3282	125
H24A	4215	8716	254	103
H24B	3713	7227	-17	103
H24C	4248	6563	825	103
H2	4396(16)	13200(50)	2970(30)	21(12)
H3	5080	4830	5512	93

Experimental

The crystal was kept at 293(2) K during data collection. Using Olex2,[1] the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.
2. Sheldrick, G. M. *Acta Cryst. A* **2008**, *64*, 112-122.
3. Sheldrick, G.M. *Acta Cryst. C* **2015**, *71*, 3-8.

Crystal structure determination

Crystal Data for $C_{48}H_{42}Br_2F_6N_4O_5$ (M =1028.67 g/mol): monoclinic, space group C2 (no. 5), a = 26.455(2) Å, b = 6.3246(2) Å, c = 14.0068(9) Å, β = 109.467(9)°, V = 2209.6(3) Å^3, Z = 2, T = 293(2) K, μ(CuKα) = 3.000 mm^{-1}, *Dcalc* = 1.546 g/cm^3, 5109 reflections measured (6.694° ≤ 2Θ ≤ 141.528°), 3058 unique (R_{int} = 0.0252, R_{sigma} = 0.0412) which were used in all calculations. The final R_1 was 0.0422 (I > 2σ(I)) and wR_2 was 0.1114 (all data).

Refinement model description

Number of restraints - 2, number of constraints - unknown.

Details:

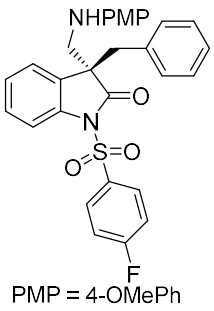
1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups

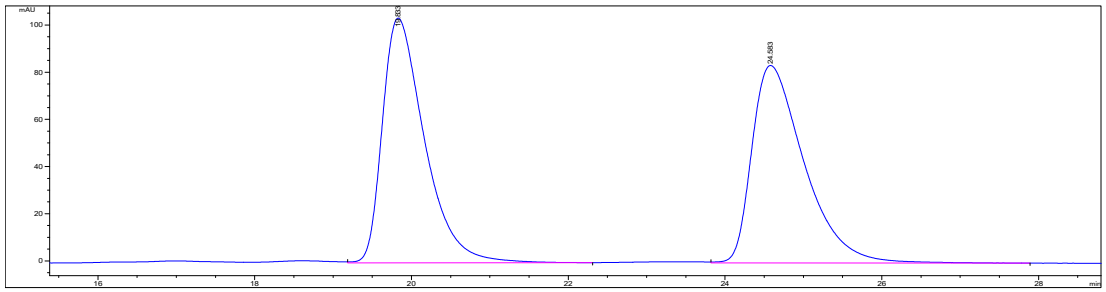
At 1.5 times of:
All C(H,H,H) groups, All O(H) groups
2. Restrained distances
N2-H2
0.87 with sigma of 0.02
3.a Free rotating group:
O3(H3)
3.b Secondary CH2 refined with riding coordinates:
C15(H15A,H15B)
3.c Aromatic/amide H refined with riding coordinates:
C5(H5), C6(H6), C7(H7), C8(H8), C10(H10), C12(H12), C13(H13), C14(H14), C17(H17), C18(H18), C21(H21)
3.d Idealised Me refined as rotating group:
C23(H23A,H23B,H23C), C24(H24A,H24B,H24C)

7. Characterization of adducts

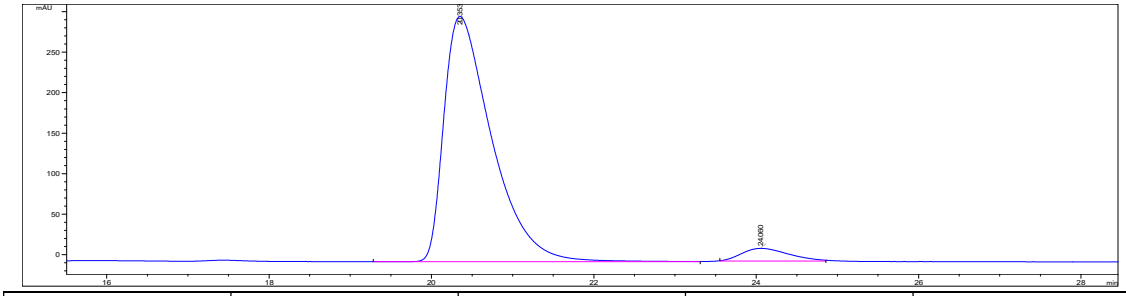


(*R*)-3-benzyl-1-((4-fluorophenyl)sulfonyl)-3-(((4-methoxyphenyl)amino)methyl)indolin-2-one (3a): yellow soild; Mp 44.0 – 45.7 °C; 46.8 mg, 91% yield; 90% ee; $[\alpha]_D^{22}$ + 2.4 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.6, 5.0 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.28 (m, 1H), 7.24 (d, *J* = 3.2 Hz, 2H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.95 (t, *J* = 7.8 Hz, 4H), 6.79 – 6.60 (m, 4H), 6.38 (d, *J* = 8.8 Hz, 2H), 3.70 (d, *J* = 16.1 Hz, 4H), 3.42 (d, *J* = 12.6 Hz, 1H), 3.22 (d, *J* = 13.3 Hz, 1H), 3.07 (d, *J* = 13.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 167.5, 164.1, 152.7, 141.3, 139.5, 134.2, 133.7, 133.7, 130.6, 130.4, 129.6, 129.2, 128.7, 127.9, 126.8, 124.8, 123.9, 116.3, 115.9, 115.1, 114.5, 113.5, 55.8, 55.6, 52.8, 40.8. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 102.2. HRMS (ESI) m/z 517.1597 ($M+H^+$), calc. for $C_{29}H_{26}FN_2O_4S$ 517.1592.

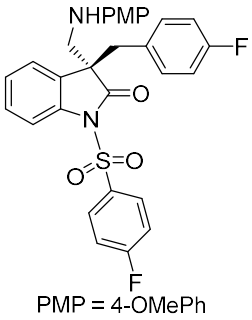
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 20.3 min (major) and 24.1 min (minor).



Entry	Retention	Area	Height	%Area
1	19.833	3873.8	103.7	49.935
2	24.583	3883.8	83.7	50.065

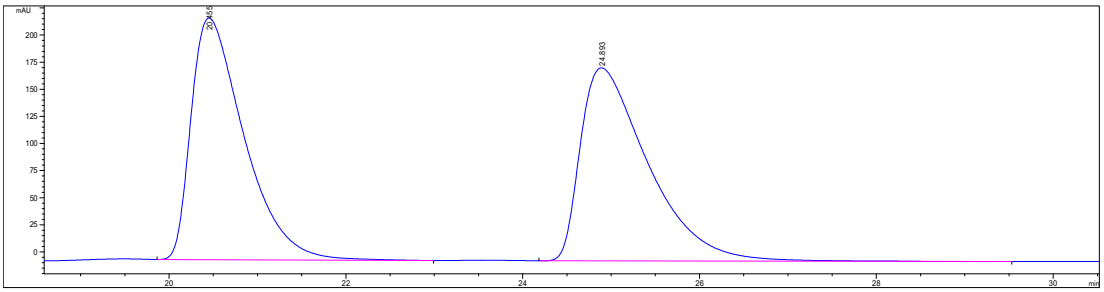


Entry	Retention	Area	Height	%Area
1	20.353	12393.3	302.7	95.162
2	24.06	630.1	15.7	4.838

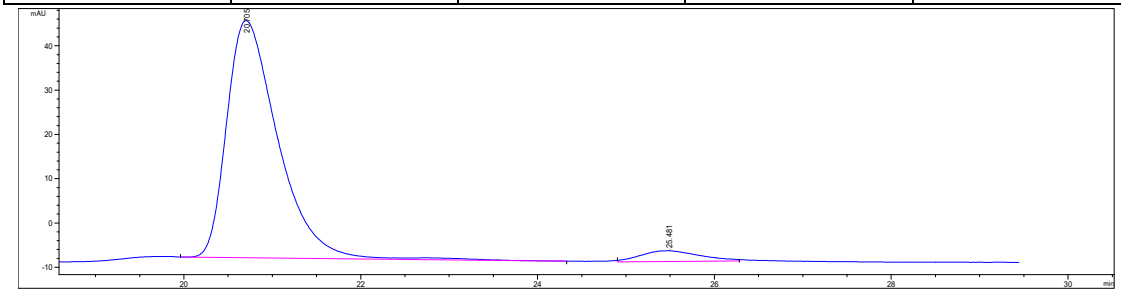


(*R*)-3-(4-fluorobenzyl)-1-((4-fluorophenyl)sulfonyl)-3-(((4-methoxyphenyl)amino)methyl)indolin-2-one (3b): yellow soild; Mp 43.4 – 44.9 °C; 43.4 mg, 81% yield; 90% ee; $[\alpha]_D^{22}$ – 5.7 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.8, 5.0 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.23 (d, *J* = 4.2 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.95 (dd, *J* = 11.7, 5.5 Hz, 4H), 6.73 – 6.66 (m, 4H), 6.38 (d, *J* = 8.9 Hz, 2H), 3.72 (d, *J* = 4.2 Hz, 3H), 3.69 (d, *J* = 12.8 Hz, 1H), 3.42 (d, *J* = 12.7 Hz, 1H), 3.22 (d, *J* = 13.3 Hz, 1H), 3.07 (d, *J* = 13.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 167.6, 164.2, 152.8, 141.3, 139.6, 134.3, 133.9, 133.8, 130.6, 130.5 129.7 129.2 128.7, 127.9, 126.8, 124.8, 123.9, 116.3, 116.0, 115.2, 114.6, 113.6, 55.9, 55.7, 52.9, 40.9. ^{19}F NMR (565 MHz, CDCl3) δ – 101.9, – 115.3. HRMS (ESI) m/z 535.1503 ($M+H^+$), calc. for $C_{29}H_{25}F_2N_2O_4S$ 535.1498.

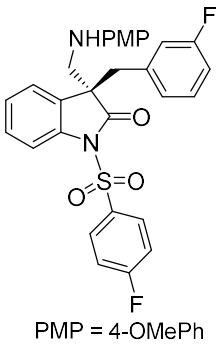
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 20.7 min (major) and 25.5 min (minor).



Entry	Retention	Area	Height	%Area
1	20.455	9306.1	222.9	49.596
2	24.893	9457.8	178	50.404

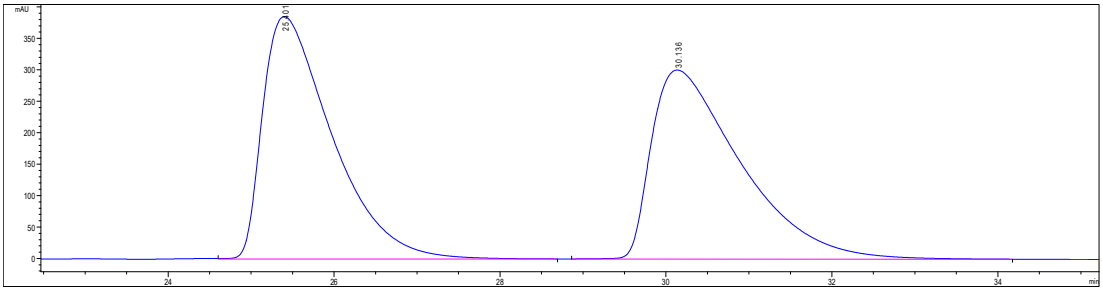


Entry	Retention	Area	Height	%Area
1	20.705	2154.3	53.5	95.056
2	25.481	112.1	2.4	4.944

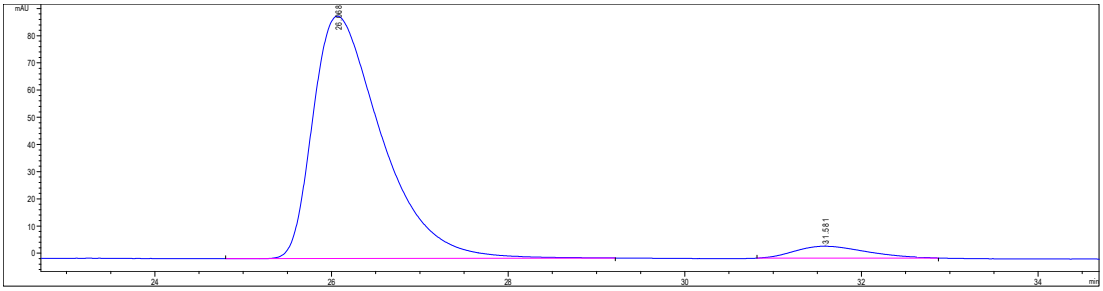


(*R*)-3-(3-fluorobenzyl)-1-((4-fluorophenyl)sulfonyl)-3-(((4-methoxyphenyl)amino)methyl)indolin-2-one (3c): yellow oil; 42.6 mg, 80% yield; 90% ee; $[\alpha]_D^{22}$ + 4.2 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.6, 5.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.26 (m, 3H), 6.97 (t, *J* = 8.5 Hz, 2H), 6.88 (dd, *J* = 14.2, 7.5 Hz, 1H), 6.70 (t, *J* = 8.0 Hz, 3H), 6.47 – 6.34 (m, 4H), 3.73 (m, 4H), 3.44 (d, *J* = 12.5 Hz, 1H), 3.22 (d, *J* = 13.3 Hz, 1H), 3.05 (d, *J* = 13.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 167.7, 164.2, 163.5, 160.3, 153.1, 140.5, 139.5, 136.7, 136.6, 133.64, 133.6, 130.5, 130.4, 129.5, 129.4, 129.3, 128.2, 125.3, 125.3, 125.0, 123.9, 116.7, 116.4, 116.4, 116.1, 115.7, 115.6, 115.5, 114.6, 113.9, 113.7, 113.6, 55.7, 53.0, 40.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 102.0, – 112.7. HRMS (ESI) m/z 535.1503 ($M+H^+$), calc. for $C_{29}H_{25}F_2N_2O_4S$ 535.1498.

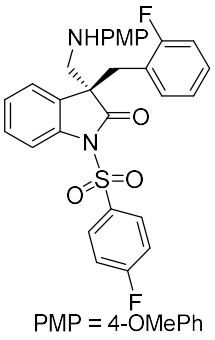
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 26.1 min (major) and 31.6 min (minor).



Entry	Retention	Area	Height	%Area
1	25.401	22391.3	385.8	49.957
2	30.136	22429.9	300.5	50.043

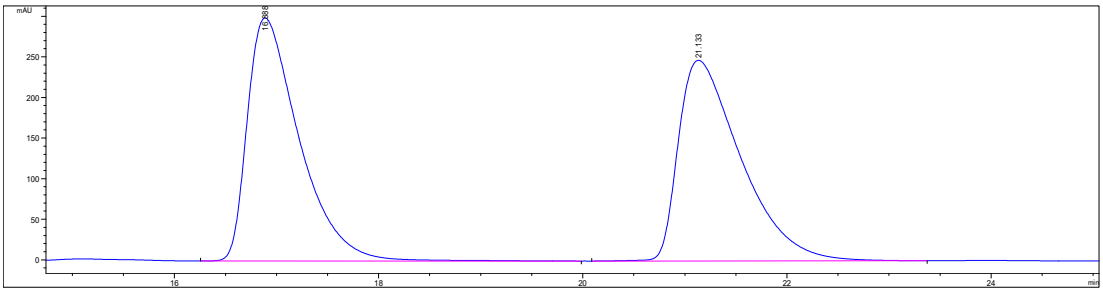


Entry	Retention	Area	Height	%Area
1	26.068	4821.5	89.2	95.025
2	31.581	252.4	4.4	4.975

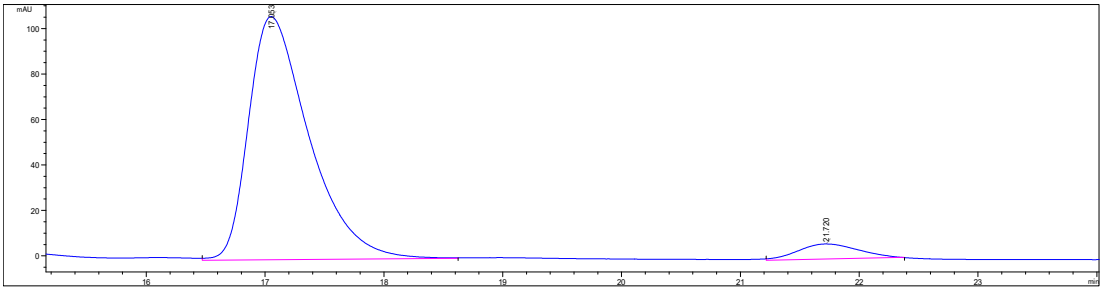


(*R*)-3-(2-fluorobenzyl)-1-((4-fluorophenyl)sulfonyl)-3-(((4-methoxyphenyl)amino)methyl)indolin-2-one (3d): yellow soild; Mp 62.9 – 64.0 °C; 48.6 mg, 91% yield; 88% ee; $[\alpha]_D^{22}$ + 4.6 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.86 (m, 2H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.34 – 7.27 (m, 1H), 7.26 – 7.14 (m, 2H), 7.06 – 6.92 (m, 1H), 6.95 (t, *J* = 8.6 Hz, 2H), 6.86 – 6.71 (m, 3H), 6.66 (d, *J* = 8.9 Hz, 2H), 6.35 (d, *J* = 8.8 Hz, 2H), 3.71 (d, *J* = 10.1 Hz, 4H), 3.44 (d, *J* = 12.8 Hz, 1H), 3.24 (d, *J* = 10.1 Hz, 1H), 3.16 (d, *J* = 13.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.4, 167.6, 164.2, 162.2, 158.9, 153.1, 140.6, 139.4, 133.8, 133.8, 131.4, 131.4, 130.7, 130.6, 129.3, 128.9, 128.8, 128.2, 124.8, 124.3, 123.8, 123.8, 121.9, 121.7, 116.3, 116.0, 115.6, 115.3, 115.0, 114.6, 114.1, 113.3, 55.7, 55.3, 53.1, 33.0. ^{19}F NMR (565 MHz, CDCl3) δ – 102.0, – 115.3. HRMS (ESI) m/z 535.1497 ($M+H^+$), calc. for $C_{29}H_{25}F_2N_2O_4S$ 535.1498.

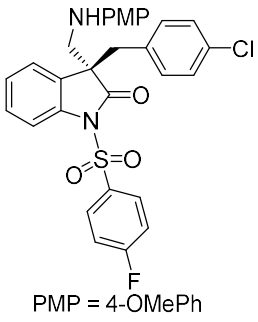
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 17.0 min (major) and 21.7 min (minor).



Entry	Retention	Area	Height	%Area
1	16.888	10582.2	299.3	50.194
2	21.133	10500.6	247.1	49.806

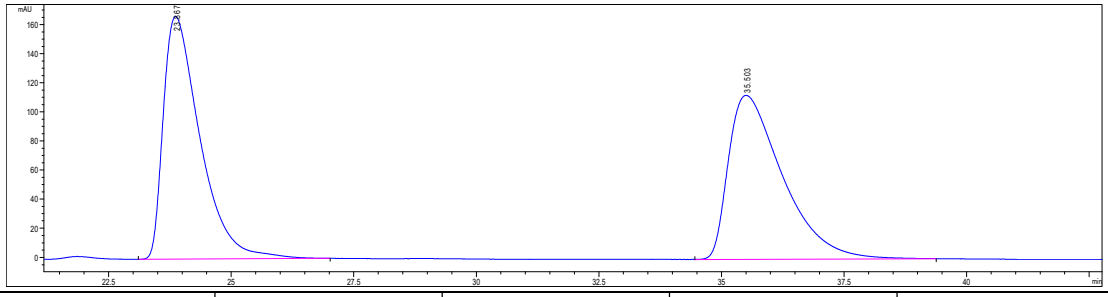


Entry	Retention	Area	Height	%Area
1	17.053	3793.7	107	94.163
2	21.72	235.2	6.7	5.837

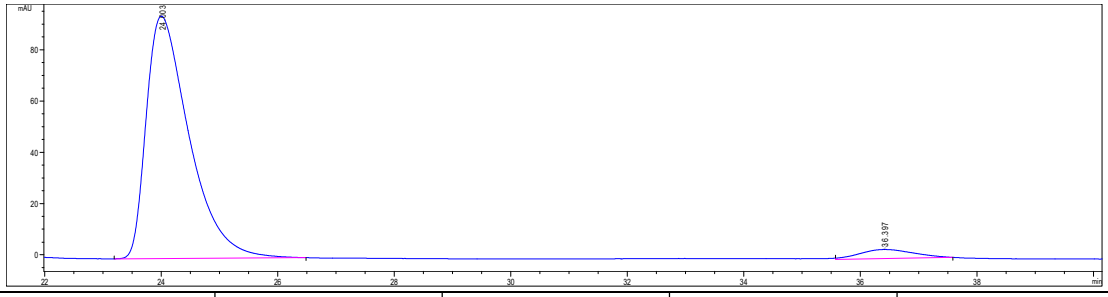


(*R*)-3-(4-chlorobenzyl)-1-((4-fluorophenyl)sulfonyl)-3-(((4-methoxyphenyl)amino)methyl)indolin-2-one (3e): yellow soild; Mp 50.3 – 52.1 °C; 38.1 mg, 69% yield; 90% ee; $[\alpha]_D^{22}$ - 2.2 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ7.85 – 7.77 (m, 3H), 7.34 – 7.26 (m, 3H), 7.01 (t, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.2 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 8.2 Hz, 2H), 6.42 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H), 3.69 (d, *J* = 13.1 Hz, 1H), 3.43 (d, *J* = 12.7 Hz, 1H), 3.20 (d, *J* = 13.3 Hz, 1H), 3.02 (d, *J* = 13.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 167.7, 164.2, 153.0, 140.8, 139.6, 133.7, 133.6, 132.7, 132.7, 130.9, 130.6, 130.5, 129.6, 129.5, 128.3, 128.0, 126.8, 125.0, 123.8, 116.3, 116.0, 115.4, 114.6, 113.7, 55.7, 52.8, 40.1. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 101.5. HRMS (ESI) m/z 551.1208 ($M+H^+$), calc. for $C_{29}H_{25}ClFN_2O_4S$ 551.1202.

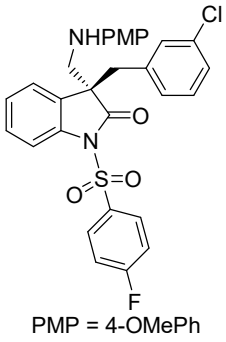
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 24.0 min (major) and 36.4 min (minor).



Entry	Retention	Area	Height	%Area
1	23.867	8695	166.8	50.117
2	35.503	8654.4	112.7	49.883



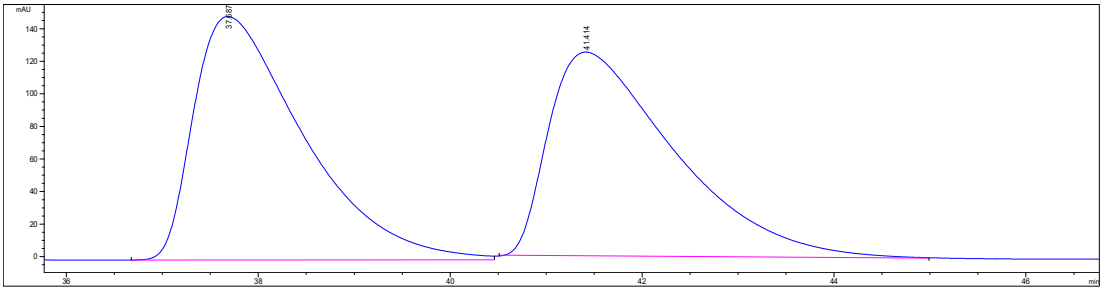
Entry	Retention	Area	Height	%Area
1	24.003	4831.1	94.6	95.494
2	36.397	228	3.6	4.506



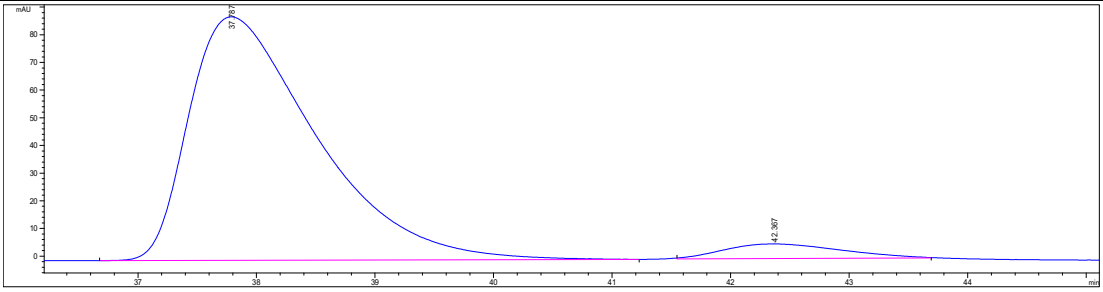
PMP = 4-OMePh

(*R*)-3-(3-chlorobenzyl)-1-((4-fluorophenyl)sulfonyl)-3-(((4-methoxyphenyl)amino)methyl)indolin-2-one (3f): yellow soild; Mp 45.4 – 46.7 °C; 47.4 mg, 86% yield; 90% ee; $[\alpha]_D^{22}$ – 4.0 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.87 – 7.78 (m, 1H), 7.38 – 7.33 (m, 1H), 7.28 (s, 1H), 6.79 – 6.88 (m, 3H), 6.85 (t, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 3H), 6.57 (d, *J* = 7.7 Hz, 2H), 6.41 (d, *J* = 7.9 Hz, 2H), 3.73 (s, 3H), 3.69 (d, *J* = 20.5 Hz, 2H), 3.42 (d, *J* = 12.6 Hz, 2H), 3.19 (d, *J* = 13.4 Hz, 2H), 3.04 (d, *J* = 13.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 167.6, 164.2, 152.9, 140.9, 139.5= 136.3, 133.7, 133.6, 133.6, 130.6, 130.5, 130.3, 129.8, 129.65, 129.5, 129.2, 128.3, 127.9, 127.7, 127.1, 125.0, 123.8, 116.4, 116.1, 115.3, 114.6, 113.7, 55.7, 55.5, 52.8, 40.3. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 101.8. HRMS (ESI) m/z 551.1208 ($M+H^+$), calc. for $C_{29}H_{25}ClFN_2O_4S$ 551.1202.

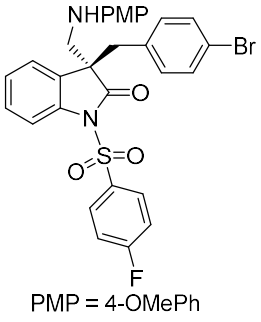
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 37.8 min (major) and 42.3 min (minor).



Entry	Retention	Area	Height	%Area
1	37.687	11902.6	149.5	51.048
2	41.414	11413.8	125	48.952

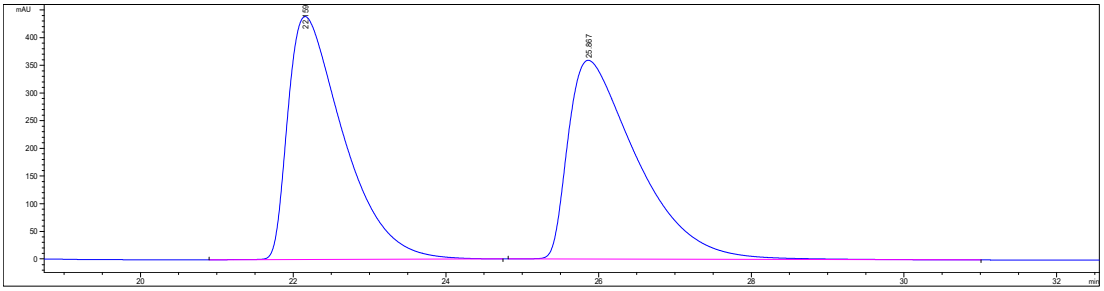


Entry	Retention	Area	Height	%Area
1	37.787	6557.4	88	94.764
2	42.367	365.2	5.3	5.236

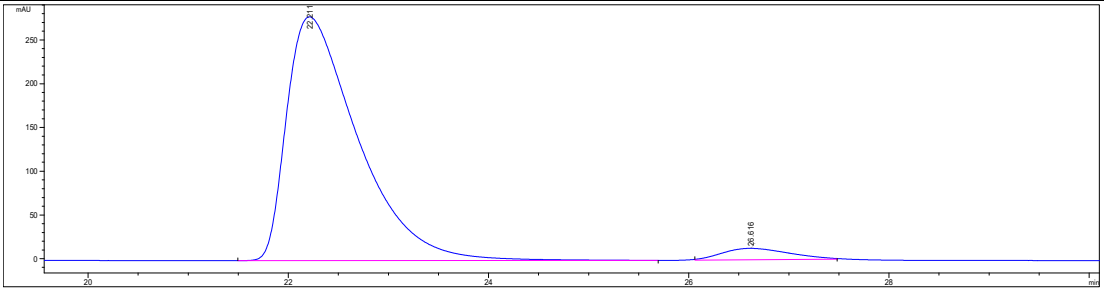


(*R*)-3-(4-bromobenzyl)-1-((4-fluorophenyl)sulfonyl)-3-(((4-methoxyphenyl)amino)methyl)indolin-2-one (3g): yellow soild; Mp 63.1 – 64.5 °C; 48.1 mg, 81% yield; 92% ee; $[\alpha]_D^{22}$ – 3.3 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ7.87 – 7.83 (m, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.24 – 7.23 (m, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.98 – 6.92 (m, 4H), 6.69 (t, *J* = 8.4 Hz, 4H), 6.39 (d, *J* = 8.8 Hz, 2H), 3.70 (d, *J* = 15.2 Hz, 4H), 3.42 (d, *J* = 12.7 Hz, 1H), 3.22 (d, *J* = 13.3 Hz, 1H), 3.07 (d, *J* = 13.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 167.6, 164.2, 152.9, 141.1, 139.6, 134.2, 133.9, 133.8, 130.6, 130.5, 129.7, 129.2, 128.7, 127.9, 126.8, 124.8, 124.0, 116.3, 116.0, 115.3, 114.6, 113.6, 55.8, 55.7, 52.9, 40.9. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 102.2. HRMS (ESI) m/z 597.0692 ($M+H^+$), calc. for. $C_{29}H_{25}BrFN_2O_4S$ 595.0697.

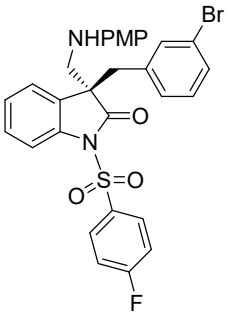
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 22.2 min (major) and 26.6 min (minor).



Entry	Retention	Area	Height	%Area
1	22.159	22185.7	438.9	49.624
2	25.867	22521.9	359	50.376



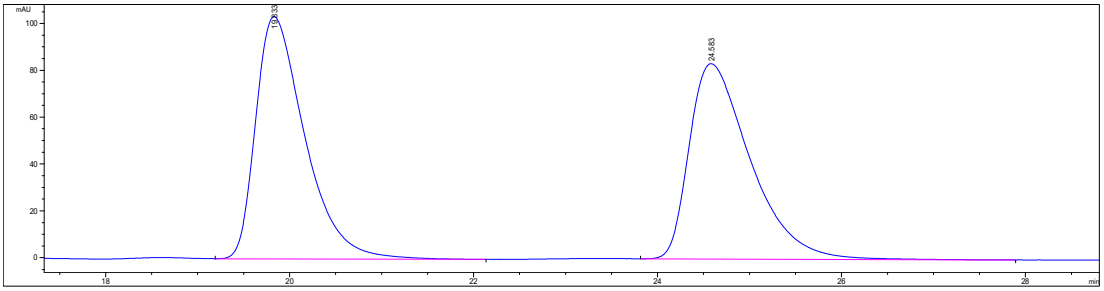
Entry	Retention	Area	Height	%Area
1	22.211	13766.8	278.4	95.909
2	26.614	587.2	13	4.091



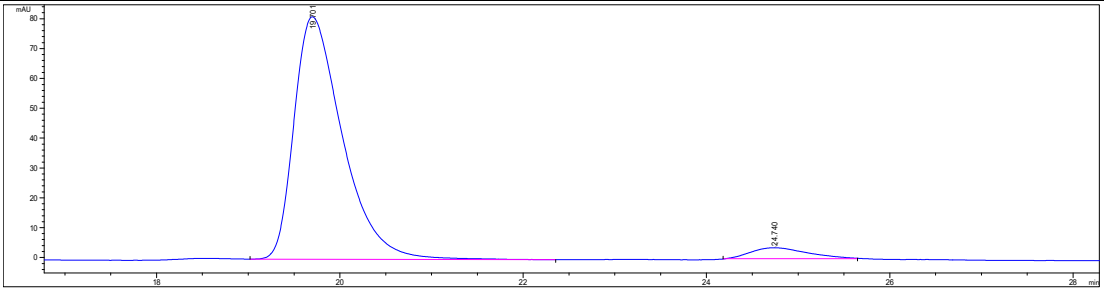
PMP = 4-OMePh

(*R*)-3-(3-bromobenzyl)-1-((4-fluorophenyl)sulfonyl)-3-(((4-methoxyphenyl)amino)methyl)indolin-2-one (3h): yellow oil; 54.6 mg, 91% yield; 90% ee; $[\alpha]_D^{22}$ – 6.7 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ7.88 – 7.83 (m, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.24 (d, *J* = 3.2 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.95 (dd, *J* = 11.5, 5.7 Hz, 4H), 6.73 – 6.66 (m, 4H), 6.39 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H), 3.70 (d, *J* = 16.1 Hz, 3H), 3.42 (d, *J* = 12.7 Hz, 1H), 3.22 (d, *J* = 13.3 Hz, 1H), 3.07 (d, *J* = 13.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 167.6 164.1, 152.8, 141.2, 139.6 134.2, 133.8, 133.8, 130.6, 130.5, 129.7, 129.2, 128.7, 127.9, 126.8, 124.8, 123.9, 116.3, 116.0, 115.2, 114.6, 113.5, 55.8, 55.7, 52.9, 40.9. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 102.2. HRMS (ESI) m/z 595.0692 ($M+H^+$), calc. for $C_{29}H_{25}BrFN_2O_4S$ 595.0697.

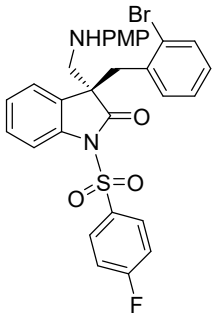
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 19.7 min (major) and 24.7 min (minor).



Entry	Retention	Area	Height	%Area
1	19.833	3840.3	103.4	49.988
2	24.583	3842.2	83.4	50.012



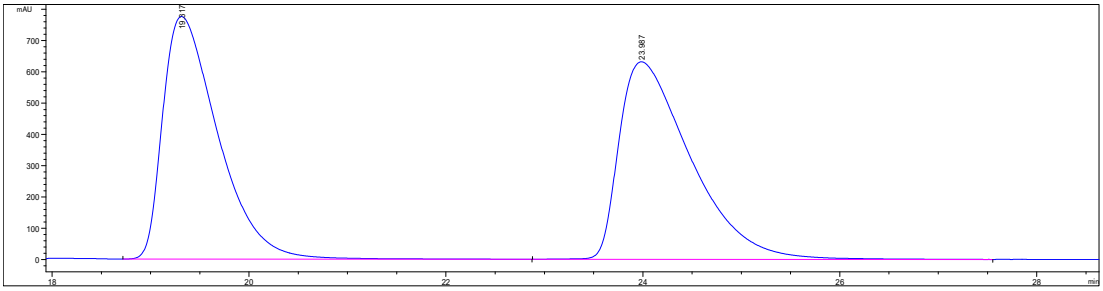
Entry	Retention	Area	Height	%Area
1	19.701	2984.1	81.2	95.040
2	24.74	155.7	3.6	4.960



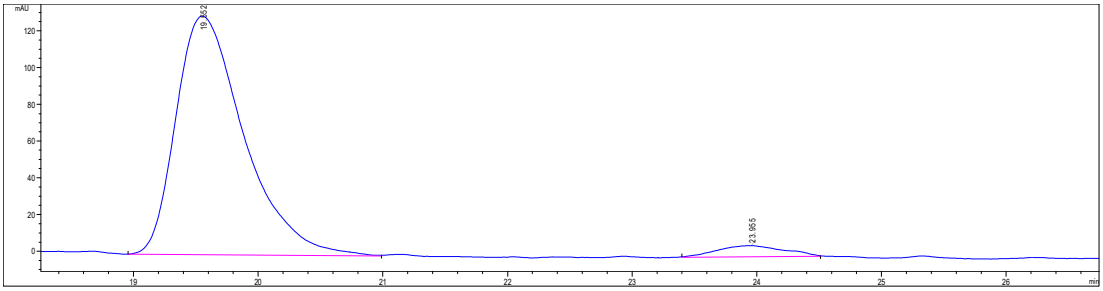
PMP = 4-OMePh

(*R*)-3-(2-bromobenzyl)-1-((4-fluorophenyl)sulfonyl)-3-(((4-methoxyphenyl)amino)methyl)indolin-2-one (3i): yellow oil; 37.8 mg, 63% yield; 89% ee; $[\alpha]_D^{22}$ – 3.2 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.9, 5.0 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.27 (m, 1H), 7.24 (d, *J* = 3.6 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.98 – 6.90 (m, 4H), 6.70 (dd, *J* = 10.4, 8.2 Hz, 4H), 6.38 (d, *J* = 8.9 Hz, 2H), 3.73 (s, 3H), 3.70 (d, *J* = 16.2 Hz, 1H), 3.42 (d, *J* = 12.7 Hz, 1H), 3.22 (d, *J* = 13.3 Hz, 1H), 3.07 (d, *J* = 13.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 167.6, 164.1, 152.8, 141.3, 139.6, 134.3, 133.8, 133.8, 130.6, 130.5, 129.7, 129.2, 128.7, 127.9, 126.8, 124.8, 123.9, 116.3, 116.0, 115.2, 114.6, 113.6, 55.9, 55.7, 52.9, 40.9. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 102.2. HRMS (ESI) m/z 595.0692 ($M+H^+$), calc. for $C_{29}H_{25}BrFN_2O_4S$ 595.0697.

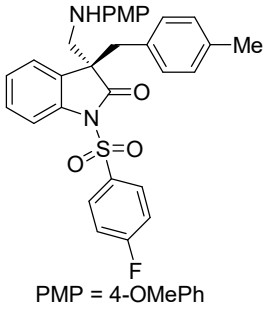
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 19.7 min (major) and 24.7 min (minor).



Entry	Retention	Area	Height	%Area
1	19.317	30173	774.4	48.666
2	23.987	31827	630.8	51.334



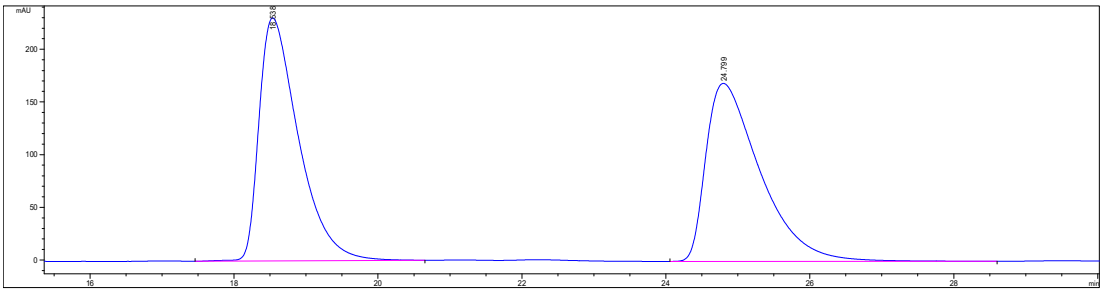
Entry	Retention	Area	Height	%Area
1	19.442	4491.3	123.5	94.470
2	23.733	313.8	7.4	5.530



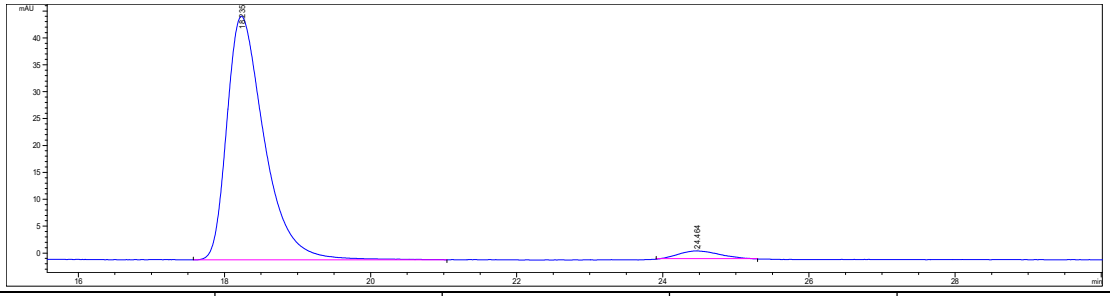
PMP = 4-OMePh

(*R*)-1-((4-fluorophenyl)sulfonyl)-3-(((4-methoxyphenyl)amino)methyl)-3-(4-methylbenzyl)indolin-2-one (3j): yellow soild; Mp 50.0 – 41.7 ºC; 40.6 mg, 77% yield; 93% ee; $[\alpha]_D^{22}$ – 3.7 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.8, 5.0 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.28 (m, 1H), 7.27 – 7.19 (m, 2H), 6.96 (t, *J* = 8.6 Hz, 2H), 6.75 – 6.63 (m, 4H), 6.56 (d, *J* = 7.9 Hz, 2H), 6.40 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H), 3.71 (d, *J* = 14.3 Hz, 1H), 3.43 (d, *J* = 12.7 Hz, 1H), 3.16 (d, *J* = 13.3 Hz, 1H), 3.02 (d, *J* = 13.4 Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 167.6, 164.2, 152.9, 141.0, 139.6, 136.2, 133.9, 133.9, 131.1, 130.6, 130.5, 129.6, 129.2, 128.8, 128.6, 124.8, 124.0, 116.2, 115.9, 115.4, 114.6, 113.6, 55.8, 55.7, 52.9, 40.5, 20.9. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 102.2. RMS (ESI) m/z 5310.1754 ($M+H^+$), calc. for $C_{30}H_{28}FN_2O_4S$ 531.1748.

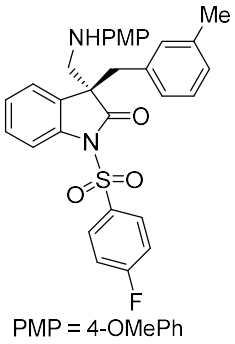
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25 ºC; 254 nm; retention time: 18.2 min (major) and 24.4 min (minor).



Entry	Retention	Area	Height	%Area
1	18.538	8771.2	230.4	49.763
2	24.799	8854.6	168.9	50.237

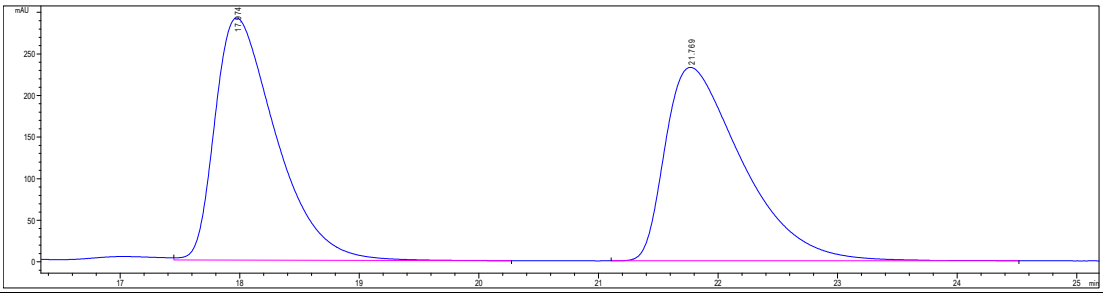


Entry	Retention	Area	Height	%Area
1	18.235	1609.7	45.3	96.701
2	24.464	54.9	1.4	3.299

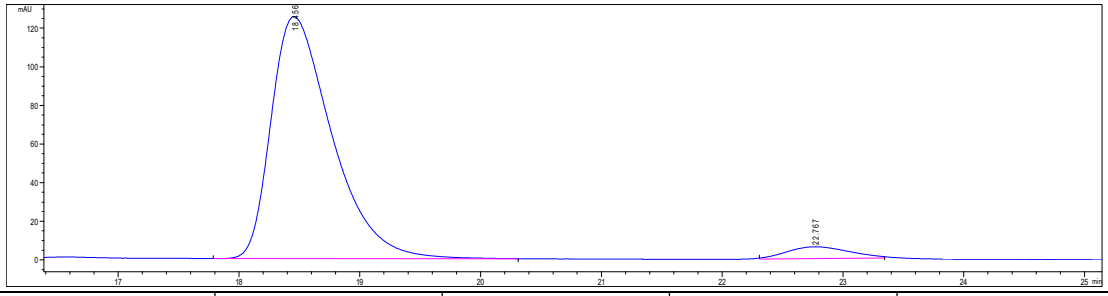


(*R*)-1-((4-fluorophenyl)sulfonyl)-3-(((4-methoxyphenyl)amino)methyl)-3-(3-methylbenzyl)indolin-2-one (3k): yellow soild; Mp 98.2 – 99.7 °C; 50.4 mg, 95% yield; 90% ee; $[\alpha]_D^{22}$ – 4.2 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.9, 5.0 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.27 (m, 1H), 7.24 – 7.21 (m, 2H), 6.93 (t, *J* = 8.6 Hz, 2H), 6.89 – 6.80 (m, 2H), 6.67 (d, *J* = 8.9 Hz, 2H), 6.58 (s, 1H), 6.49 (d, *J* = 6.5 Hz, 1H), 6.37 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H), 3.69 (d, *J* = 12.7 Hz, 1H), 3.40 (d, *J* = 12.7 Hz, 1H), 3.16 (d, *J* = 13.3 Hz, 1H), 3.04 (d, *J* = 13.3 Hz, 1H), 2.12 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.4, 167.5, 164.1, 152.7, 141.3, 139.6, 137.5, 134.1, 133.9, 133.8, 130.6, 130.5, 130.4, 129.1, 128.9, 127.8, 127.6, 126.6, 124.7, 124.0, 116.3, 115.9, 115.1, 114.6, 113.5, 55.8, 55.69, 52.8, 40.9, 21.1. ^{19}F NMR (565 MHz, $CDCl_3$) δ –102.2. HRMS (ESI) m/z 531.1754 ($M+H^+$), calc. for $C_{30}H_{28}FN_2O_4S$ 531.1748.

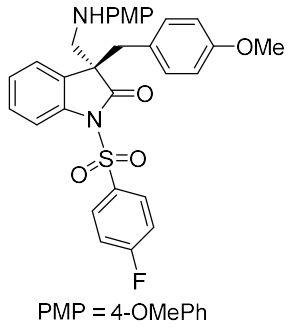
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 18.4 min (major) and 22.8 min (minor).



Entry	Retention	Area	Height	%Area
1	17.974	10327	291	49.794
2	21.769	10412.4	232.5	50.206



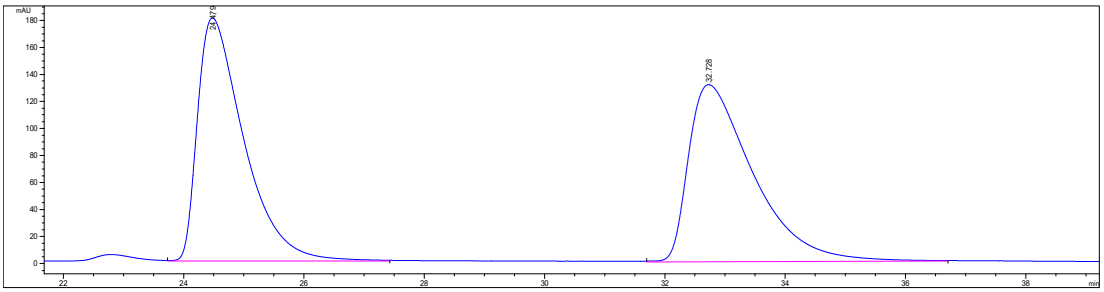
Entry	Retention	Area	Height	%Area
1	18.456	4390	125.4	95.293
2	22.767	216.9	6.1	4.707



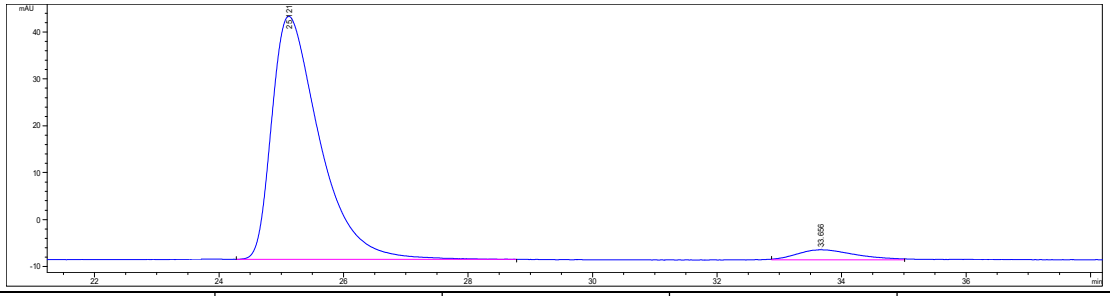
PMP = 4-OMePh

(*R*)-1-((4-fluorophenyl)sulfonyl)-3-(4-methoxybenzyl)-3-(((4-methoxyphenyl)amino)methyl)indolin-2-one (3l): yellow soild; Mp 48.2 – 49.6 ºC; 51.6 mg, 94% yield; 90% ee; $[\alpha]_D^{22}$ – 5.8 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.81 (m, 2H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.27 (m, 1H), 7.24 (d, *J* = 4.3 Hz, 2H), 6.96 (t, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 8.9 Hz, 2H), 6.61 (d, *J* = 8.6 Hz, 2H), 6.46 (d, *J* = 8.6 Hz, 2H), 6.39 (d, *J* = 8.9 Hz, 2H), 3.73 (s, 3H), 3.69 (s, 3H), 3.67 (d, *J* = 10.9 Hz, 1H), 3.39 (d, *J* = 12.6 Hz, 1H), 3.15 (d, *J* = 13.5 Hz, 1H), 3.02 (d, *J* = 13.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 167.5, 164.1, 158.3, 152.7, 141.3, 139.6, 133.9, 133.8, 130.7, 130.6, 130.5, 129.2, 128.9, 126.2, 124.8, 123.9, 116.2, 115.9, 115.1, 114.8, 114.6, 113.6, 113.3, 56.0, 55.7, 54.9, 52.7, 40.1. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 102.1. HRMS (ESI) m/z 547.1703 ($M+H^+$), calc. for $C_{30}H_{28}FN_2O_5S$ 547.1697.

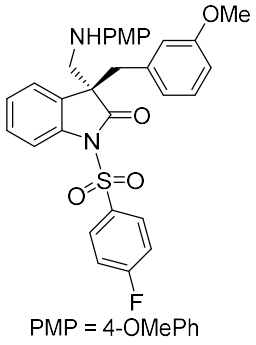
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25 ºC; 254 nm; retention time: 25.1 min (major) and 33.6 min (minor).



Entry	Retention	Area	Height	%Area
1	24.482	9686.4	180	49.714
2	32.73	9798	130.8	50.286

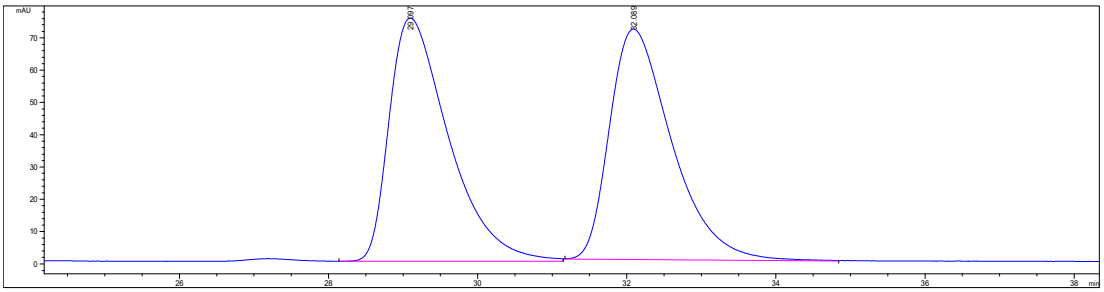


Entry	Retention	Area	Height	%Area
1	25.121	2753.7	51.8	95.278
2	33.656	136.5	2.1	4.722

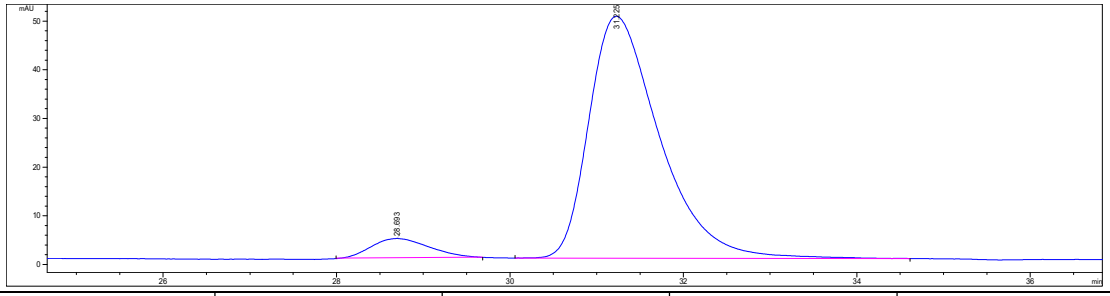


(*R*)-1-((4-fluorophenyl)sulfonyl)-3-(3-methoxybenzyl)-3-(((4-methoxyphenyl)amino)methyl)indolin-2-one (3m): yellow soild; Mp 48.2 – 49.6 °C; 42.6 mg, 78% yield; 89% ee; $[\alpha]_D^{22}$ + 6.7 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.86 – 7.73 (m, 3H), 7.37 – 7.28 (m, 1H), 7.28 – 7.22 (m, 2H), 6.94 (t, *J* = 8.6 Hz, 2H), 6.84 (t, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 8.9 Hz, 2H), 6.58 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.39 (d, *J* = 8.8 Hz, 2H), 6.32 – 6.22 (m, 2H), 3.73 (s, 3H), 3.70 (d, *J* = 17.8 Hz, 1H), 3.57 (s, 3H), 3.42 (d, *J* = 12.9 Hz, 1H), 3.20 (d, *J* = 13.3 Hz, 1H), 3.05 (d, *J* = 13.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 167.6, 164.2, 158.9, 152.8, 141.3, 139.7, 135.8, 133.8, 133.8, 130.5, 130.4, 129.2, 128.9, 124.8, 123.9, 122.0, 116.3, 116.0, 115.2, 114.6, 114.6, 113.6, 113.1, 55.8, 55.7, 54.9, 52.9, 40.9. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 102.2. HRMS (ESI) m/z 547.1703 ($M+H^+$), calc. for $C_{30}H_{28}FN_2O_5S$ 547.1697.

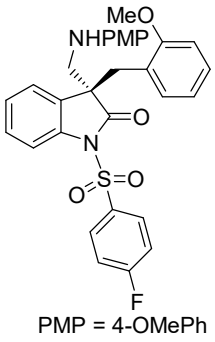
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 28.7 min (minor) and 31.2 min (major).



Entry	Retention	Area	Height	%Area
1	29.097	4179.7	75.3	49.702
2	32.09	4229.9	71.9	50.298

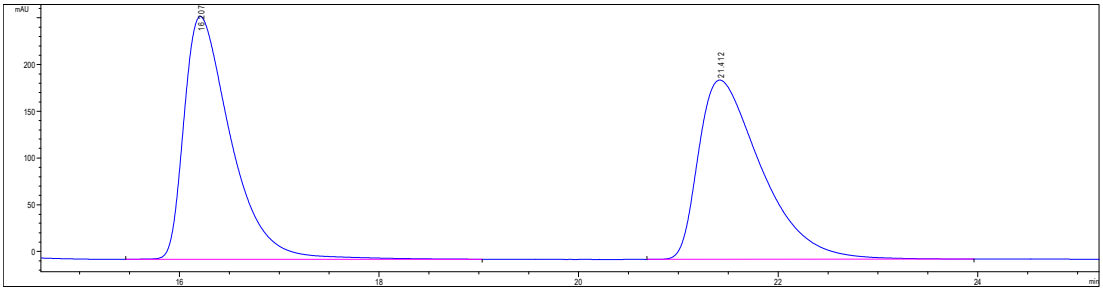


Entry	Retention	Area	Height	%Area
1	28.693	175.3	2.7	5.330
2	31.225	3112.6	40.3	94.670

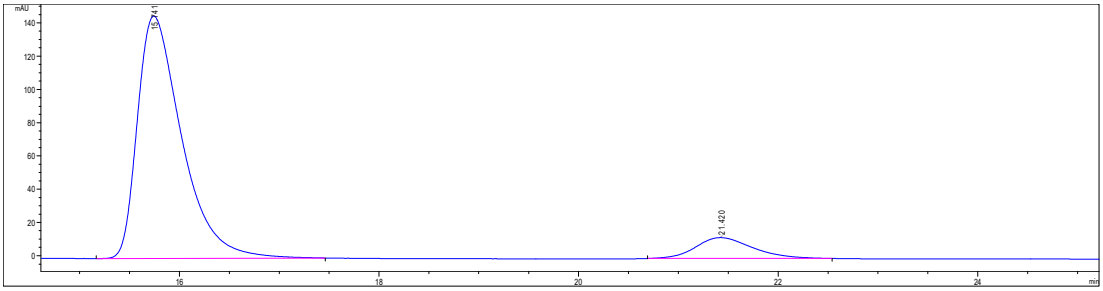


(*R*)-1-((4-fluorophenyl)sulfonyl)-3-(2-methoxybenzyl)-3-(((4-methoxyphenyl)amino)methyl)indolin-2-one (3n): yellow oil; 44.6 mg, 82% yield; 80% ee; $[\alpha]_D^{22}$ + 6.4 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ7.94 – 7.90 (m, 2H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.13 – 7.06 (m, 3H),6.93 – 6.84 (m, 3H), 6.68 – 6.61 (m, 4H), 6.28 (d, *J* = 8.8 Hz, 2H), 3.70 (d, *J* = 15.4 Hz, 4H), 3.59 (s, 3H), 3.39 (d, *J* = 12.7 Hz, 1H), 3.23 (d, *J* = 13.6 Hz, 1H), 3.16 (d, *J* = 13.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 167.5, 164.1, 157.3, 152.8, 141.2, 139.4, 134.0, 133.9, 131.3, 130.6, 130.6, 129.1, 128.7, 128.3, 124.5, 124.2, 123.3, 120.0, 116.2, 115.9, 115.2, 114.5, 113.1, 110.0, 55.7, 55.2, 54.6, 53.3, 34.4. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 102.3. HRMS (ESI) m/z 547.1712 ($M+H^+$), calc. for $C_{30}H_{28}FN_2O_5S$ 547.1697.

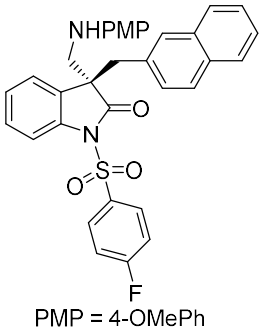
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 15.7 min (major) and 21.4 min (minor).



Entry	Retention	Area	Height	%Area
1	16.207	8469.4	259.8	50.222
2	21.412	8394.5	191.9	49.778

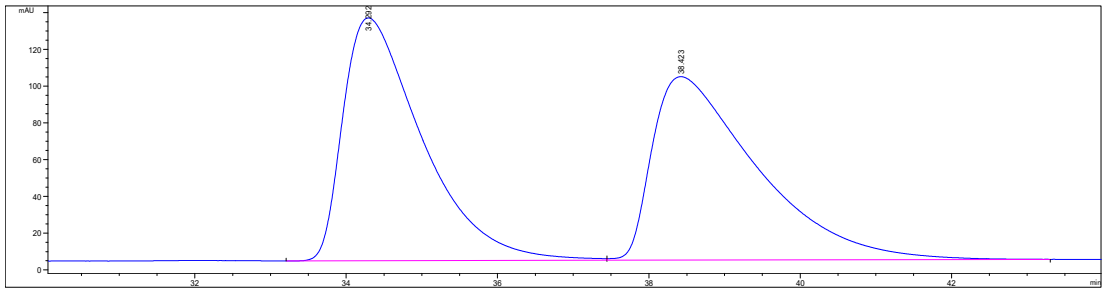


Entry	Retention	Area	Height	%Area
1	15.741	4488.5	145.7	90.081
2	21.42	494.2	12.5	9.919

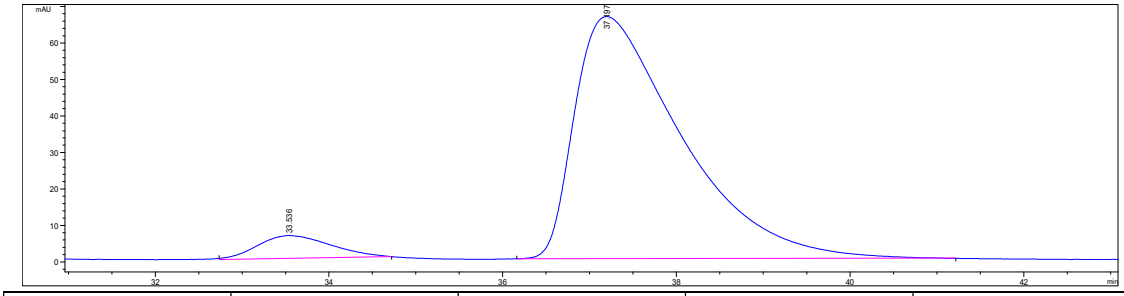


(*R*)-1-((4-fluorophenyl)sulfonyl)-3-(((4-methoxyphenyl)amino)methyl)-3-(naphthalen-2-ylmethyl)indolin-2-one (3o): light yellow soild; Mp 49.0 – 50.4 °C; 50.2 mg, 89% yield; 88% ee; $[\alpha]_D^{22}$ + 285.7 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 1H), 7.67 – 7.62 (m, 3H), 7.51 – 7.48 (m, 1H), 7.44 – 7.27 (m, 6H), 7.18 (s, 1H), 6.72 (d, *J* = 8.7 Hz, 3H), 6.64 (t, *J* = 8.5 Hz, 2H), 6.46 (d, *J* = 8.8 Hz, 2H), 3.76 (d, *J* = 13.7 Hz, 4H), 3.48 (d, *J* = 12.6 Hz, 1H), 3.39 (d, *J* = 13.3 Hz, 1H), 3.26 (d, *J* = 13.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.0, 167.3, 163.9, 152.8, 141.3, 139.6, 133.5, 133.5, 132.8, 132.1, 131.9, 130.2, 130.1, 129.3, 128.8, 128.7, 127.6, 127.5, 127.3, 127.3, 125.9, 125.7, 124.9, 124.0, 116.0, 115.7, 115.2, 114.6, 113.6, 55.8, 55.7, 52.8, 40.9. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 101.4. HRMS (ESI) m/z 567.1754 ($M+H^+$), calc. for $C_{33}H_{28}FN_2O_4S$ 567.1748.

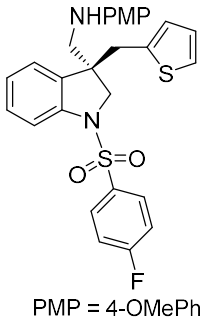
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 33.5 min (minor) and 37.2 min (major).



Entry	Retention	Area	Height	%Area
1	34.292	9604.2	132.1	49.945
2	38.423	9625.2	99.8	50.055

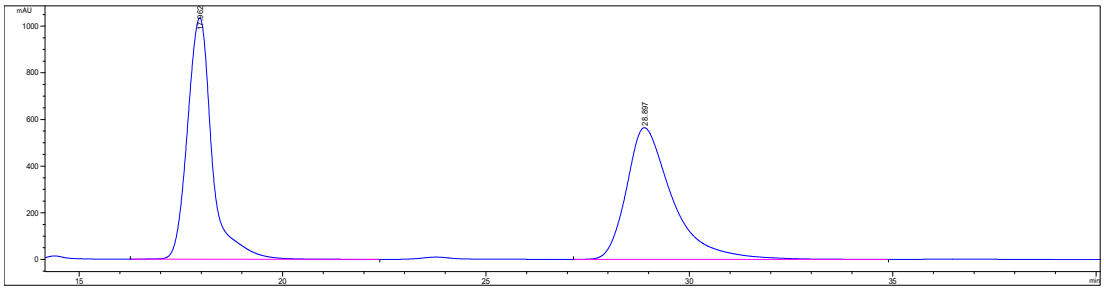


Entry	Retention	Area	Height	%Area
1	33.536	366.5	6.3	6.075
2	37.197	5665.7	66.4	93.925

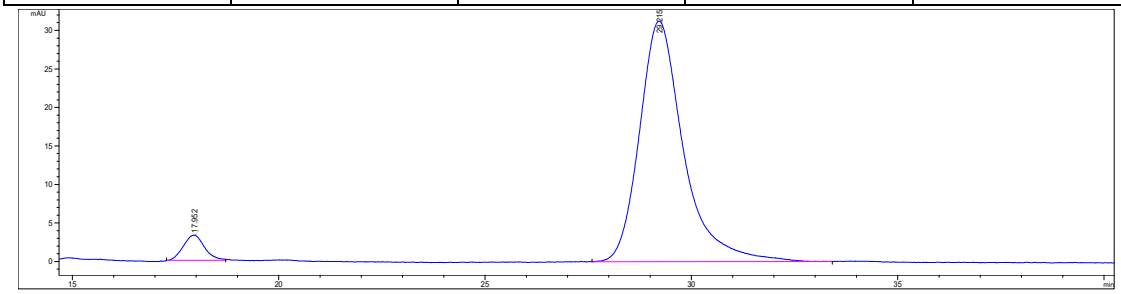


(*R*)-1-((4-fluorophenyl)sulfonyl)-3-(((4-methoxyphenyl)amino)methyl)-3-(thiophen-2-ylmethyl)indolin-2-one (3p): yellow soild; Mp 72.2 – 73.8 °C; 48.6 mg, 93% yield; 90% ee; $[\alpha]_D^{22}$ + 4.1 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ7.89 – 7.82 (m, 3H), 7.40 – 7.35 (m, 1H), 7.31 – 7.24 (m, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 4.8 Hz, 1H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.59 – 6.56 (m, 1H), 6.40 (dd, *J* = 15.8, 5.7 Hz, 3H), 3.73 (s, 3H), 3.67 (d, *J* = 12.7 Hz, 1H), 3.51 (d, *J* = 14.5 Hz, 1H), 3.42 (d, *J* = 12.7 Hz, 1H), 3.25 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 167.6, 164.2, 152.9, 141.0, 139.9, 135.9, 133.8, 133.7, 130.7, 130.6, 129.5, 128.6, 127.1, 126.4, 125.1, 124.6, 123.8, 116.3, 116.0, 115.3, 114.7, 113.7, 55.7, 55.6, 52.7, 35.0. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 102.2. HRMS (ESI) m/z 523.1162 ($M+H^+$), calc. for $C_{27}H_{24}FN_2O_4S_2$ 523.1156.

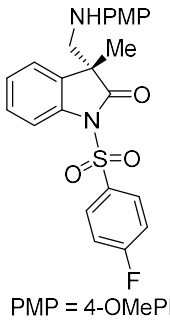
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 17.9 min (minor) and 29.2 min (major).



Entry	Retention	Area	Height	%Area
1	17.962	43417.2	1035.1	49.569
2	28.897	44172.1	564.6	50.431

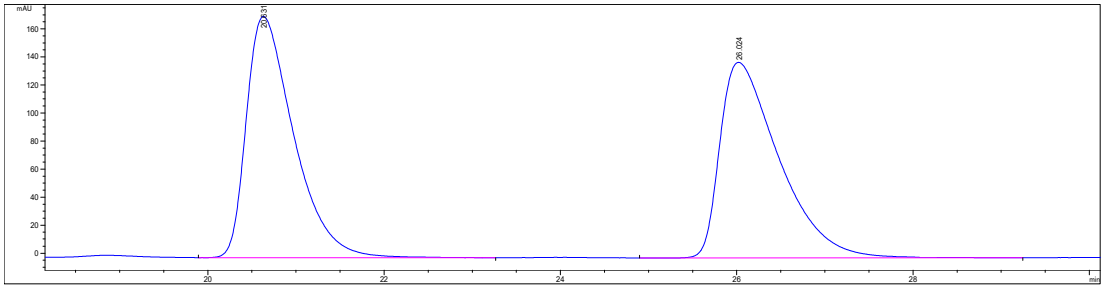


Entry	Retention	Area	Height	%Area
1	17.952	114.8	3.2	4.721
2	29.215	2316.1	31.2	95.279

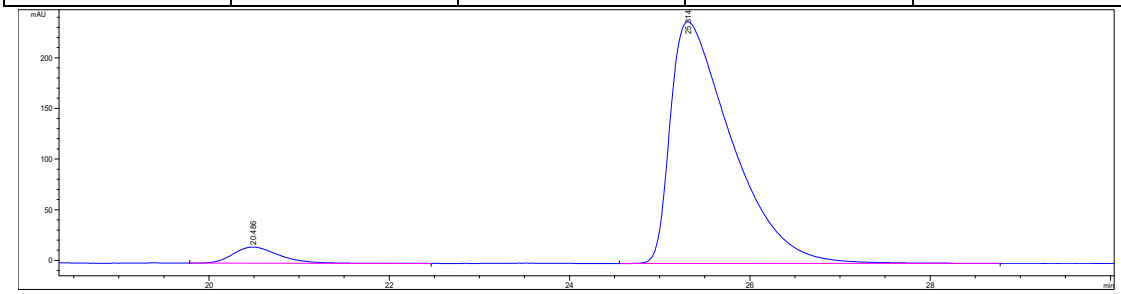


(*R*)-1-((4-fluorophenyl)sulfonyl)-3-(((4-methoxyphenyl)amino)methyl)-3-methylindolin-2-one (3q): white soild; Mp 124.9 – 125.4 ºC; 39.2 mg, 89% yield; 90% ee; $[\alpha]_D^{22}$ + 5.9 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ7.99 – 7.93 (m, 3H), 7.41 – 7.35 (m, 1H), 7.24 (d, *J* = 4.4 Hz, 2H), 6.92 (t, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 8.9 Hz, 2H), 6.27 (d, *J* = 8.8 Hz, 2H), 3.72 (s, 3H), 3.55 (d, *J* = 12.8 Hz, 1H), 3.29 (d, *J* = 12.8 Hz, 1H), 1.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.5, 167.7, 164.2, 153.0, 140.8, 139.1, 133.8, 133.8, 131.2, 130.7, 130.5, 129.1, 125.3, 123.0, 116.3, 116.0, 115.3, 114.5, 113.9, 55.7, 54.1, 50.1, 20.9. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 101.8. HRMS (ESI) m/z 441.1284 ($M+H^+$), calc. for $C_{23}H_{22}FN_2O_4S$ 441.1279.

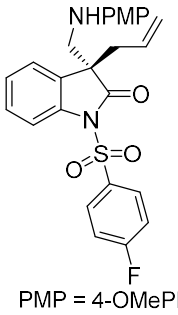
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 ºC; 254 nm; retention time: 20.5 min (minor) and 25.3 min (major).



Entry	Retention	Area	Height	%Area
1	20.631	6431	172	49.803
2	26.024	6481.9	139.4	50.197

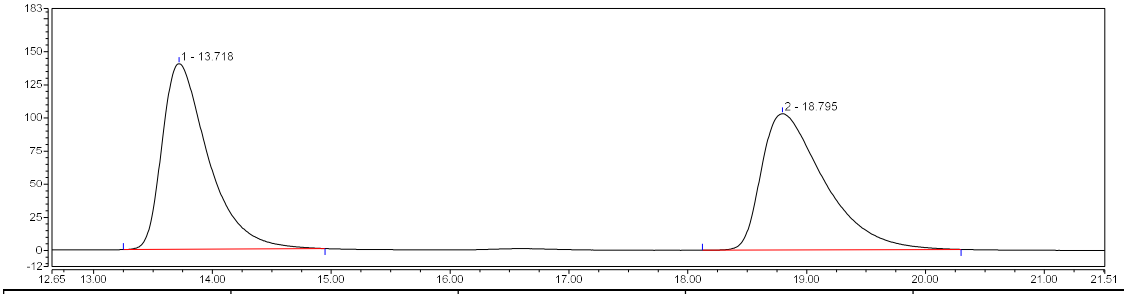


Entry	Retention	Area	Height	%Area
1	20.486	567.3	16	4.794
2	25.314	11267.4	238.6	95.206

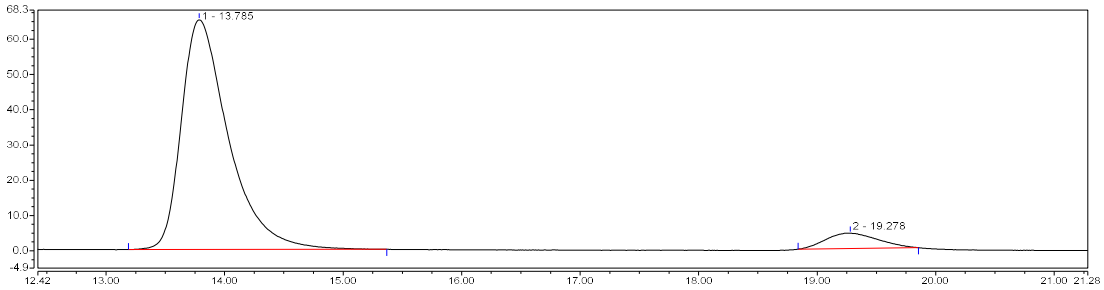


(*R*)-3-allyl-1-((4-fluorophenyl)sulfonyl)-3-(((4-methoxyphenyl)amino)methyl)indolin-2-one (3r): yellow oil; 32.2 mg, 69% yield; 86% ee; $[\alpha]_D^{22}$ – 2.4 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 – 7.71 (m, 3H), 7.38 (td, *J* = 8.7, 4.0 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.06 – 6.80 (m, 2H), 6.63 (t, *J* = 11.6 Hz, 2H), 6.32 (d, *J* = 8.7 Hz, 2H), 5.37 – 5.03 (m, 1H), 4.87 (d, *J* = 16.9 Hz, 1H), 4.76 (d, *J* = 10.1 Hz, 1H), 3.72 (s, 3H), 3.58 (d, *J* = 12.7 Hz, 1H), 3.33 (d, *J* = 12.7 Hz, 1H), 2.65 – 2.47 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.5, 167.7, 164.3, 152.9, 141.1, 139.6, 133.9, 133.9, 130.8, 130.6, 130.4, 129.2, 129.1, 125.2, 123.4, 119.8, 116.2, 115.9, 115.3, 114.5, 113.8, 55.7, 54.5, 52.7, 39.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 102.0. HRMS (ESI) m/z 467.1441 ($M+H^+$), calc. for $C_{25}H_{24}FN_2O_4S$ 467.1435.

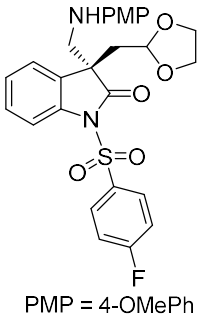
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25 ºC; 254 nm; retention time: 13.8 min (major) and 19.3 min (minor).



Entry	Retention	Area	Height	%Area
1	13.718	63.1919	140.06	50.03
2	18.795	63.1226	102.83	49.97

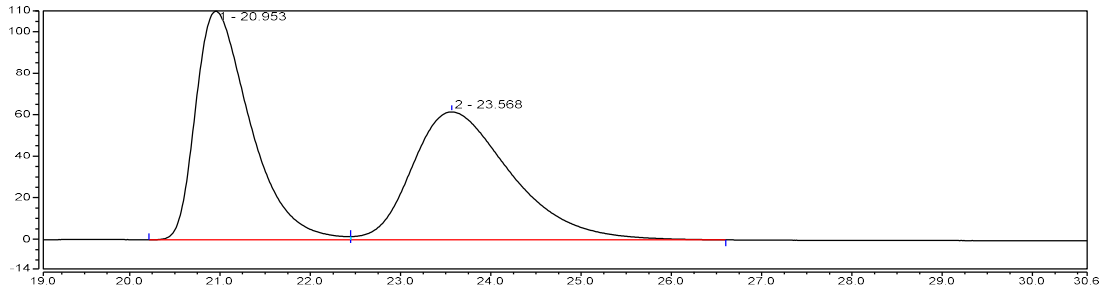


Entry	Retention	Area	Height	%Area
1	13.785	30.0334	65.14	93.11
2	19.278	2.2233	4.39	6.89

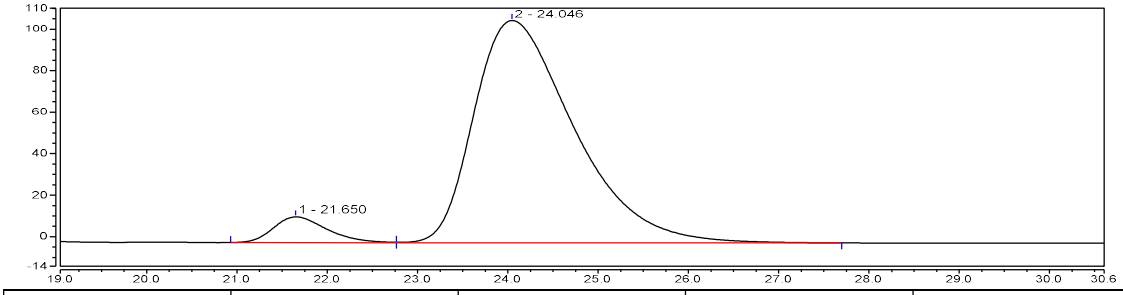


(*R*)-3-((1,3-dioxolan-2-yl)methyl)-1-((4-fluorophenyl)sulfonyl)-3-(((4-methoxyphenyl)amino)methyl)indolin-2-one (3s): yellow oil; 44.2 mg, 86% yield; 88% ee; $[\alpha]_D^{22}$ + 28.9 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.8, 5.0 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.01 (t, *J* = 8.6 Hz, 2H), 6.64 (d, *J* = 8.9 Hz, 2H), 6.32 (d, *J* = 8.9 Hz, 2H), 4.60 (dd, *J* = 7.0, 2.6 Hz, 1H), 3.72 (s, 3H), 3.62 – 3.46 (m, 3H), 3.36 – 3.20 (m, 3H), 2.39 – 2.21 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.4, 167.6, 164.2, 152.7, 141.2, 139.6, 134.1, 134.0, 131.0, 130.8, 129.1, 128.7, 124.7, 123.9, 116.1, 115.8, 115.1, 114.5, 113.5, 101.0, 64.9, 64.1, 55.7, 54.1, 51.4, 37.9. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 102.4. HRMS (ESI) m/z 535.1311 ($M+Na^+$), calc. for $C_{26}H_{26}FN_2O_6SNa$ 535.1310.

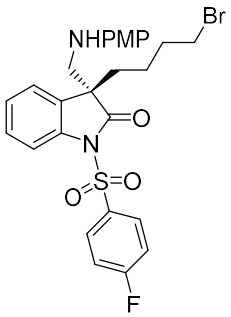
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 21.7 min (minor) and 24.0 min (major).



Entry	Retention	Area	Height	%Area
1	20.953	77.2665	110.12	49.67
2	23.568	78.2994	61.67	50.33



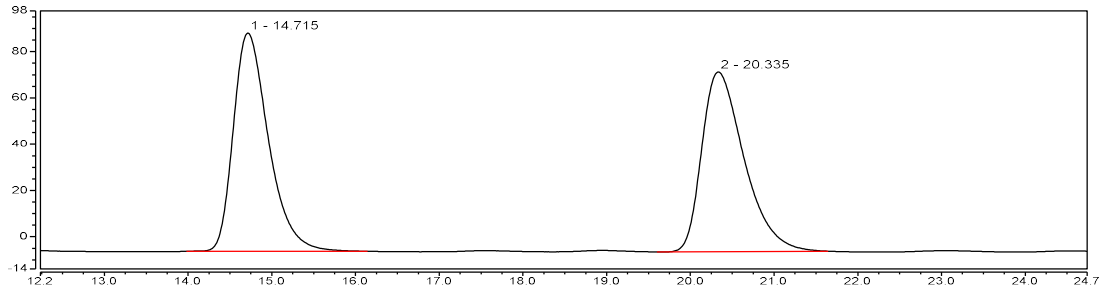
Entry	Retention	Area	Height	%Area
1	21.650	8.5071	12.38	5.83
2	24.046	137.4850	107.09	94.17



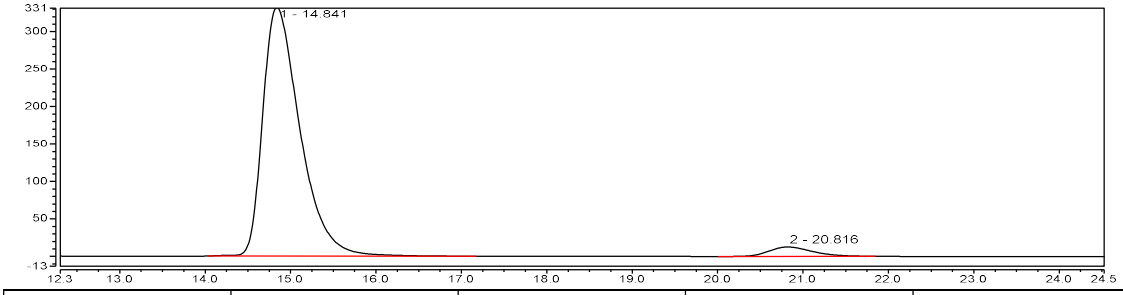
PMP = 4-OMePh

(*R*)-3-(4-bromobutyl)-1-((4-fluorophenyl)sulfonyl)-3-(((4-methoxyphenyl)amino)methyl)indolin-2-one (3t): yellow oil; 48.8 mg, 87% yield; 91% ee; $[\alpha]_D^{22}$ + 39.2 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ8.00 – 7.96 (m, 3H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 6.6 Hz, 1H), 6.95 (t, *J* = 8.5 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 6.27 (d, *J* = 8.8 Hz, 2H), 3.72 (s, 3H), 3.53 (d, *J* = 12.7 Hz, 1H), 3.28 (d, *J* = 12.7 Hz, 1H), 3.23 – 3.13 (m, 2H), 2.85 (s, 1H), 2.01 – 1.91 (m, 1H), 1.79 – 1.58 (m, 3H), 1.00 – 0.88 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 167.7, 164.3, 152.8, 141.2, 139.7, 133.7, 133.7, 130.7, 130.5, 129.3, 125.4, 123.1, 116.3, 116.0, 115.1, 114.5, 113.9, 55.7, 54.7, 53.7, 34.1, 32.6, 32.3, 22.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 101.8. HRMS (ESI) m/z 561.0854 ($M+H^+$), calc. for $C_{26}H_{27}BrFN_2O_4S$ 561.0853.

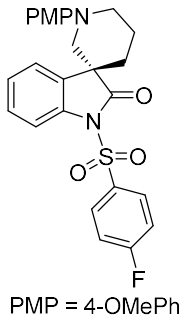
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 21.7 min (major) and 24.0 min (minor).



Entry	Retention	Area	Height	%Area
1	14.715	45.9045	94.36	50.23
2	20.335	45.4843	77.65	49.77

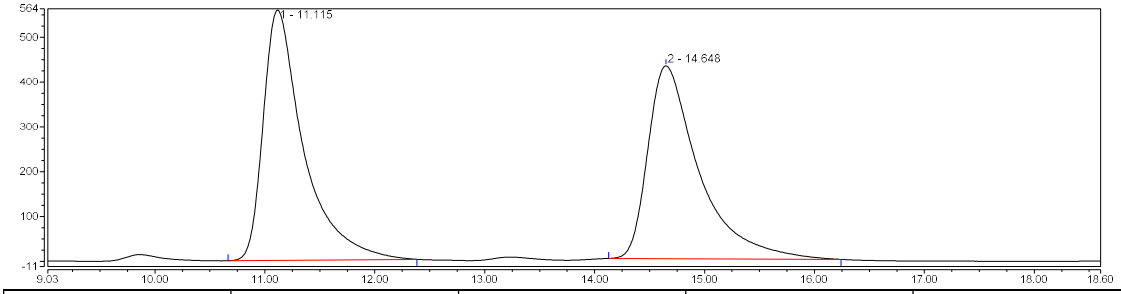


Entry	Retention	Area	Height	%Area
1	14.841	167.8986	332.09	95.79
2	20.816	7.3705	12.60	4.21

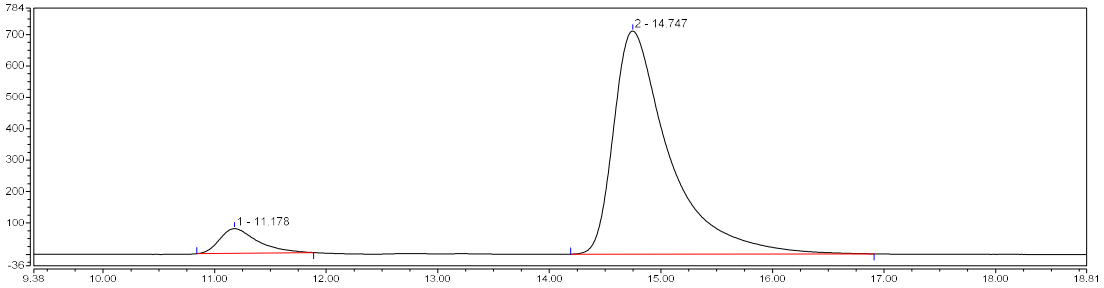


(*R*)-1-((4-fluorophenyl)sulfonyl)-1'-(4-methoxyphenyl)spiro[indoline-3,3'-piperidin]-2-one (3u): light yellow soild; Mp 45.1 – 45.7 °C; 25.6 mg, 55% yield; 87% ee; $[\alpha]_D^{22}$ – 24.0 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 8.9, 5.0 Hz, 2H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.23 – 7.15 (m, 3H), 6.77 (s, 4H), 3.74 (s, 3H), 3.48 (d, *J* = 11.3 Hz, 1H), 3.12 – 3.03 (m, 2H), 2.96 – 2.84 (m, 1H), 2.09 – 1.98 (m, 1H), 1.94 – 1.84 (m, 2H), 1.63 – 1.58 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 167.8, 164.4, 154.4, 145.9, 137.6, 134.1, 134.0, 132.3, 130.9, 130.8, 128.4, 126.0, 124.7, 119.9, 116.6, 116.3, 114.3, 113.3, 58.1, 55.5, 51.2, 48.0, 32.2, 21.1. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 101.7. HRMS (ESI) m/z 467.1428 ($M+H^+$), calc. for $C_{25}H_{23}FN_2O_4S$ 467.1435.

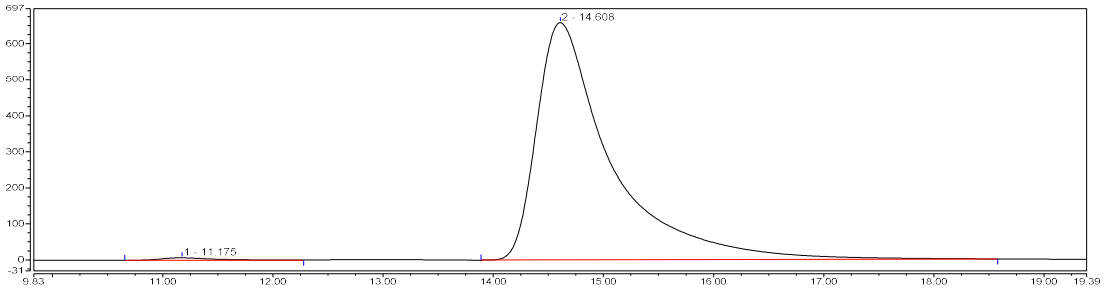
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 11.2 min (minor) and 14.7 min (major).



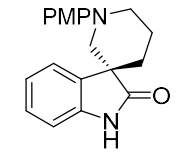
Entry	Retention	Area	Height	%Area
1	11.115	237.3479	558.97	50.59
2	14.648	231.7963	430.36	49.41



Entry	Retention	Area	Height	%Area
1	11.178	30.8886	78.54	6.50
2	14.747	410.4764	710.10	93.50



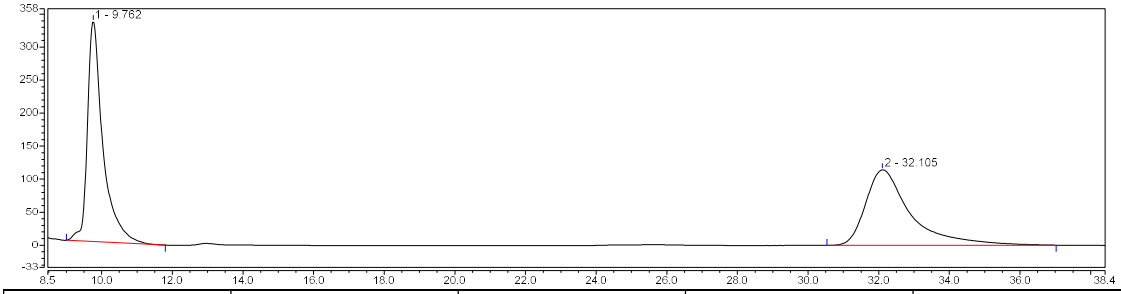
Entry	Retention	Area	Height	%Area
1	11.175	4.0615	6.99	0.78
2	14.608	513.9811	658.67	99.22



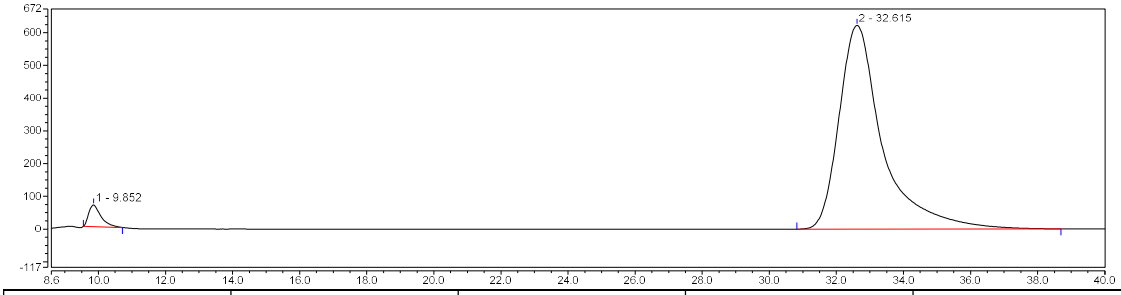
PMP = 4-OMePh

(R)-1'-(4-methoxyphenyl)spiro[indoline-3,3'-piperidin]-2-one: light yellow oil; 11.1 mg, 69% yield; 94% ee; $[\alpha]_D^{22}$ – 19.0 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.85 (d, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 3.75 (s, 3H), 3.61 (d, *J* = 12.0 Hz, 1H), 3.27 (d, *J* = 11.5 Hz, 1H), 3.16 (d, *J* = 11.6 Hz, 1H), 2.92 (t, *J* = 10.5 Hz, 1H), 2.24 – 2.15 (m, 1H), 2.06 – 1.90 (m, 2H), 1.73 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.9, 154.3, 139.8, 134.1, 127.7, 126.1, 122.2, 119.9, 114.4, 109.6, 58.0, 55.6, 51.5, 48.6, 31.4, 21.7. HRMS (ESI) m/z 309.1598 ($M+H^+$), calc. for $C_{19}H_{21}N_2O_2$ 309.1603.

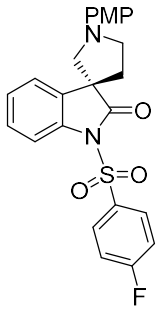
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 9.9 min (minor) and 32.6 min (major).



Entry	Retention	Area	Height	%Area
1	9.762	169.9554	333.15	50.27
2	32.105	168.1119	114.39	49.73



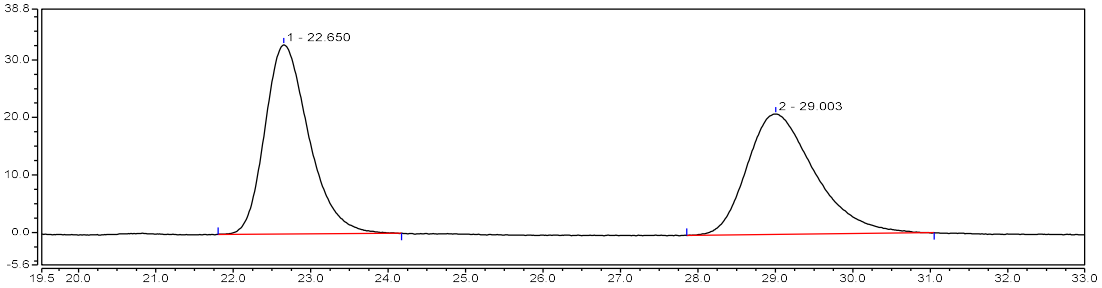
Entry	Retention	Area	Height	%Area
1	9.852	28.1943	66.05	2.93
2	32.615	935.6188	622.36	97.07



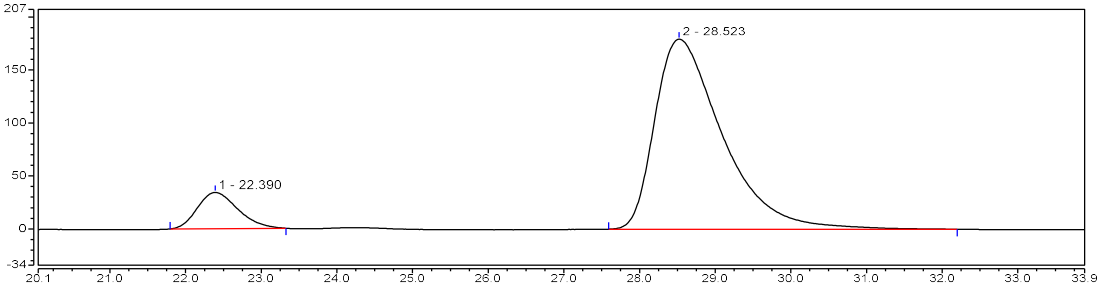
PMP = 4-OMePh

(*R*)-1-((4-fluorophenyl)sulfonyl)-1'-(4-methoxyphenyl)spiro[indoline-3,3'-pyrrolidin]-2-one (3v): yellow soild; Mp 59.7 – 60.1 °C; 24.0 mg, 53% yield; 80% ee; $[\alpha]_D^{22}$ + 15.2 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 8.7, 5.0 Hz, 2H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.34 – 7.28 (m, 4H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 8.7 Hz, 2H), 3.84 (s, 3H), 2.80 – 2.02 (m, 3H), 3.53 (d, *J* = 9.2 Hz, 1H), 2.60 – 2.51 (m, 1H), 2.29 – 2.21 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 167.9, 164.5, 151.7, 141.8, 137.8, 133.9, 133.9, 132.1, 131.0, 130.9, 129.9, 128.9, 125.6, 123.3, 116.8, 116.5, 114.9, 113.5, 113.3, 57.9, 55.8, 53.2, 47.8, 37.4. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 101.5. HRMS (ESI) m/z 453.1262 ($M+H^+$), calc. for $C_{24}H_{21}FN_2O_4S$ 453.1279.

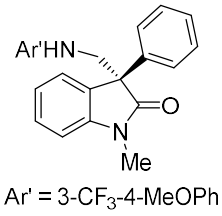
The ee was determined by HPLC analysis: CHIRALPAK IF (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 22.4 min (minor) and 28.5 min (major).



Entry	Retention	Area	Height	%Area
1	22.650	21.5731	32.89	50.48
2	29.003	21.1664	20.93	49.52

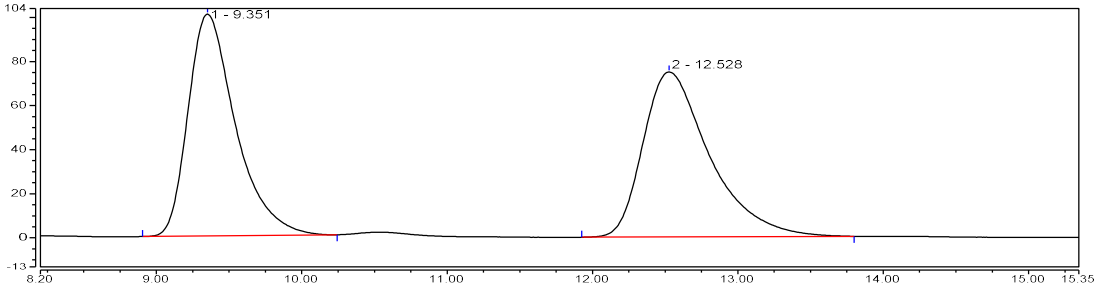


Entry	Retention	Area	Height	%Area
1	22.390	21.1346	34.16	10.23
2	28.523	185.5568	179.30	89.77

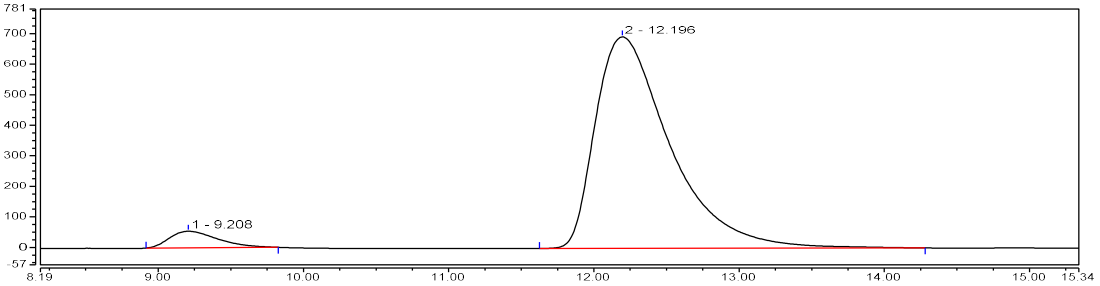


(*R*)-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methyl-3-phenylindolin-2-one (5a): yellow soild; Mp 108.6 – 109.7 °C; 40.8 mg, 96% yield; 90% ee; $[\alpha]_D^{22}$ + 272.8 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 (t, *J* = 6.7 Hz, 2H), 7.38 – 7.29 (m, 4H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 6.73 (d, *J* = 12.5 Hz, 2H), 4.11 (d, *J* = 12.2 Hz, 1H), 3.79 (s, 2H), 3.72 (d, *J* = 12.3 Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.4, 150.1, 144.0, 141.0, 137.5, 130.3, 128.9, 128.8 127.8, 127.1 125.4 124.9, 122.9，121.8, 119.4, 119.0, 118.6, 118.1, 113.9, 113.0, 113.0, 112.9, 112.8, 108.7, 56.8, 56.7, 51.6, 26.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.2. HRMS (ESI) m/z 449.1448 ($M+Na^+$), calc. for $C_{24}H_{21}F_3N_2O_2Na$ 449.1447.

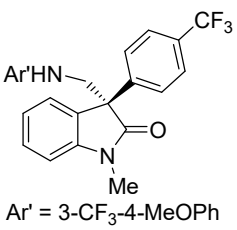
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 9.2 min (minor) and 12.2 min (major).



Entry	Retention	Area	Height	%Area
1	9.351	38.0730	100.66	48.96
2	12.528	39.6948	74.86	51.04

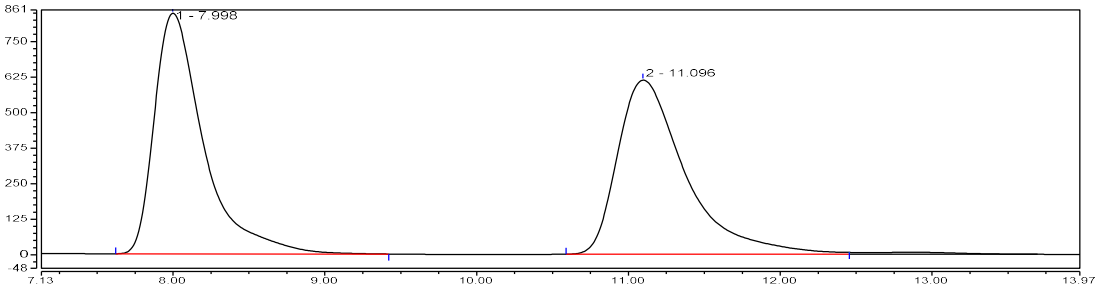


Entry	Retention	Area	Height	%Area
1	9.208	20.8402	54.42	4.80
2	12.196	413.0288	692.54	95.20

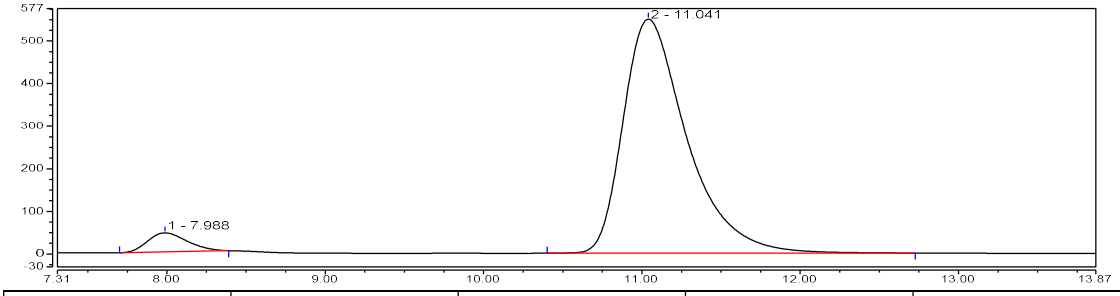


(*R*)-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methyl-3-(4-(trifluoromethyl)phenyl)indolin-2-one (5b): yellow soild; Mp 101.1 – 101.9 °C; 41.4 mg, 84% yield; 90% ee; $[\alpha]_D^{22}$ + 87.6 (*c* 1.0, $CHCl_3$);^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (s, 4H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.3 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 6.76 – 6.70 (m, 2H), 4.12 (d, *J* = 12.4 Hz, 1H), 3.80 (s, 3H), 3.71 (d, *J* = 12.4 Hz, 1H), 3.20 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 150.2, 144.0, 141.6, 140.9, 130.2, 129.8, 129.6, 129.3, 128.8, 127.6, 125.8, 125.7, 125.7, 125.7, 125.6, 125.4, 124.8, 123.1, 122.1, 121.7, 119.4, 119.0, 118.2, 113.9, 113.0, 113.0, 112.9, 112.8, 109.0, 56.8, 56.9, 51.7, 26.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.3, – 62.7. HRMS (ESI) m/z 517.1318 ($M+Na^+$), calc. for $C_{25}H_20F_6N_2O_2Na$ 517.1321.

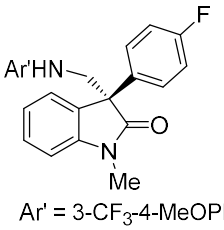
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 8.0 min (minor) and 11.0 min (major).



Entry	Retention	Area	Height	%Area
1	7.998	318.2000	846.19	50.08
2	11.096	317.1368	612.26	49.92



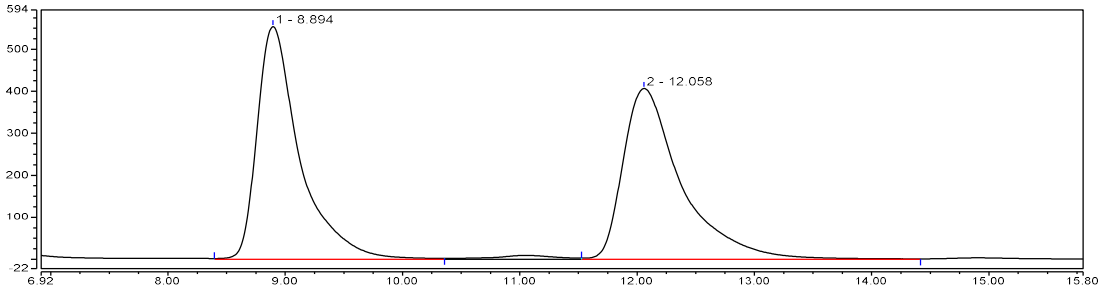
Entry	Retention	Area	Height	%Area
1	7.988	12.9342	44.73	4.81
2	11.041	256.1243	549.14	95.19



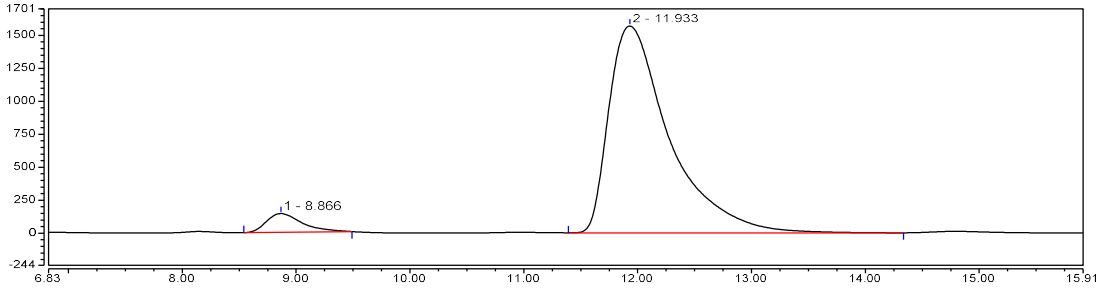
Ar' = 3-CF_3-4-MeOPh

(*R*)-3-(4-fluorophenyl)-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methylindolin-2-one (5c): yellow soild; Mp 128.3 – 129.4 ºC; 39.6 mg, 89% yield; 90% ee; $[\alpha]_D^{22}$ + 25.3 (*c* 1.0, $CHCl_3$);^{1}H NMR (300 MHz, $CDCl_3$) δ7.45 – 7.39 (m, 3H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.02 (t, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 1H), 6.75 – 6.70 (m, 2H), 4.06 (d, *J* = 12.3 Hz, 1H), 3.79 (s, 3H), 3.68 (d, *J* = 12.3 Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 163.9, 160.6, 150.2, 144.0, 140.9, 133.2, 133.2, 130.0, 129.1, 129.0, 128.8, 125.4, 124.9, 123.0, 121.7, 119.8, 119.4, 119.0, 118.6, 118.2, 115.8, 115.5, 113.8, 113.1, 113.0, 112.9, 112.9, 108.8, 56.6, 56.2, 51.8, 26.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.2, – 114.5. HRMS (ESI) m/z 467.1349 ($M+Na^+$), calc. for $C_{24}H_{20}F_4N_2O_2Na$ 467.1353.

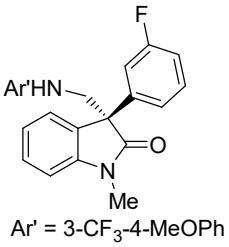
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 ºC; 254 nm; retention time: 8.9 min (minor) and 11.9 min (major).



Entry	Retention	Area	Height	%Area
1	8.894	232.7814	553.74	49.94
2	12.058	233.3846	406.45	50.06

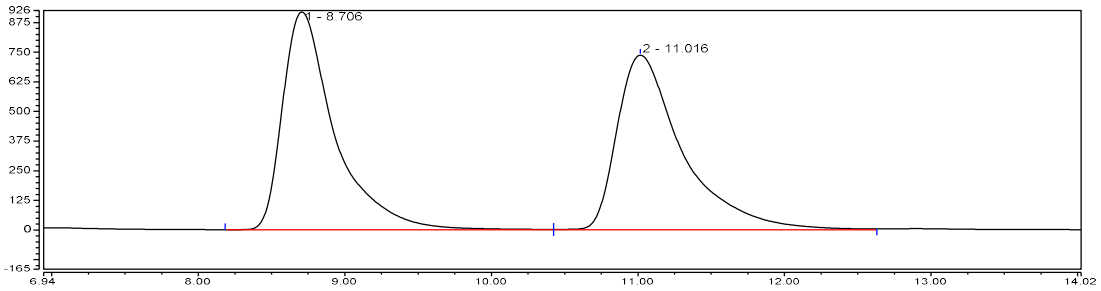


Entry	Retention	Area	Height	%Area
1	8.866	51.7685	142.42	5.09
2	11.933	964.3318	1567.95	94.91

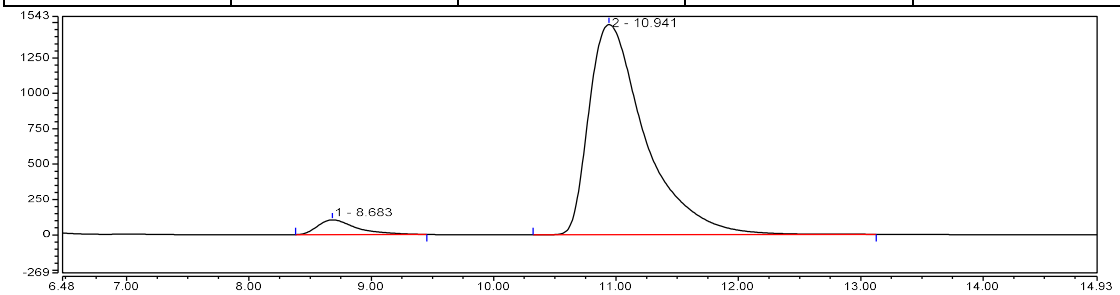


(*R*)-3-(3-fluorophenyl)-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methylindolin-2-one (5d): yellow soild; Mp 97.8 – 99.1 ºC; 41.2 mg, 93% yield; 92% ee; $[\alpha]_D^{22}$ + 39.7 (*c* 1.0, $CHCl_3$);^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.28 (m, 4H), 7.20 – 7.16 (m, 2H), 7.03 – 6.95 (m, 2H), 6.84 (d, *J* = 8.8 Hz, 1H), 6.79 – 6.68 (m, 2H), 4.10 (d, *J* = 12.4 Hz, 1H), 3.82 (s, 3H), 3.72 (d, *J* = 12.3 Hz, 1H), 3.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 164.5, 161.3, 150.2, 144.0, 140.9, 140.0, 140.0, 130.3, 130.2, 129.7, 129.2, 125.4, 124.9, 123.0, 122.8, 122.8, 121.7, 119.8, 119.4, 119.0, 118.6, 118.2, 114.9, 114.6, 114.3, 113.8, 113.1, 113.0, 112.9, 112.9, 108.8, 56.7, 51.7, 26.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.2, – 111.9. HRMS (ESI) m/z 467.1353 ($M+Na^+$), calc. for $C_{24}H_{20}F_4N_2O_2Na$ 467.1352.

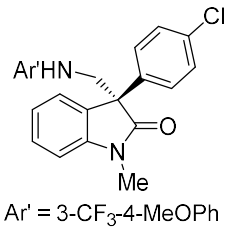
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 ºC; 254 nm; retention time: 8.7 min (minor) and 10.9 min (major).



Entry	Retention	Area	Height	%Area
1	8.706	380.3338	918.55	49.88
2	11.016	382.1397	736.16	50.12

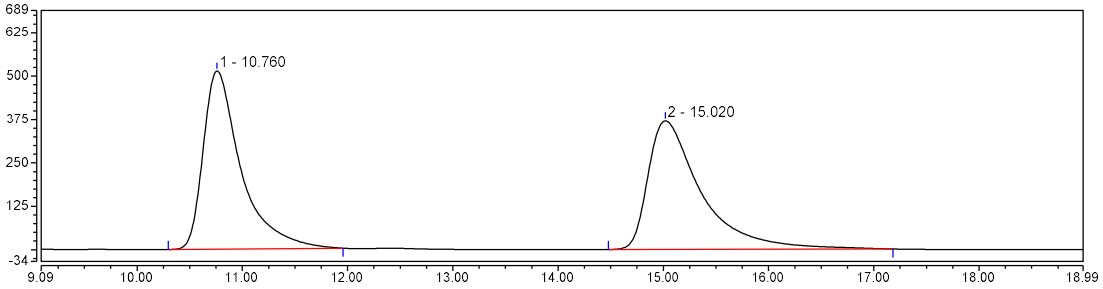


Entry	Retention	Area	Height	%Area
1	8.683	34.9871	102.08	4.25
2	10.941	788.9214	1484.10	95.75

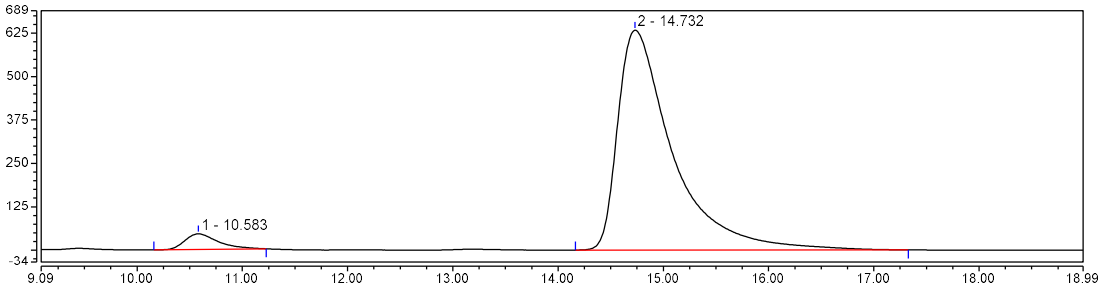


(*R*)-3-(4-chlorophenyl)-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methylindolin-2-one (5e): yellow soild; Mp 103.9 – 105.3 °C; 36.4 mg, 79% yield; 92% ee; $[\alpha]_D^{22}$ + 19.7 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ7.42 – 7.28 (m, 6H), 7.16 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 1H), 6.74 – 6.70 (m, 2H), 4.06 (d, *J* = 12.3 Hz, 1H), 3.80 (s, 3H), 3.67 (d, *J* = 12.3 Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.1, 150.2, 144.0, 140.8, 136.0, 133.8, 129.8, 129.2, 128.9, 128.6, 125.3, 124.8, 123.0, 121.7, 119.4, 119.0, 118.2, 113.8, 113.0, 113.0, 112.9, 112.8, 108.8, 56.6, 56.3, 51.7, 26.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.3. HRMS (ESI) m/z 483.1058 ($M+Na^+$), calc. for $C_{24}H_{20}ClF_3N_2O_2Na$ 483.1057.

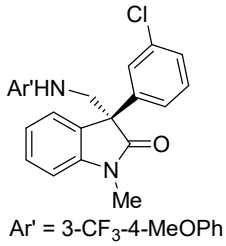
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 10.6 min (minor) and 14.7 min (major).



Entry	Retention	Area	Height	%Area
1	10.760	213.4105	513.35	49.62
2	15.020	216.6798	370.38	50.38



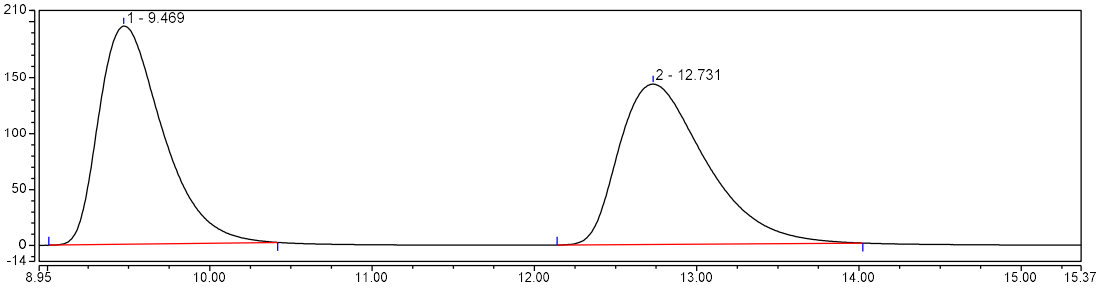
Entry	Retention	Area	Height	%Area
1	10.583	16.5035	44.99	4.13
2	14.732	382.6569	633.03	95.87



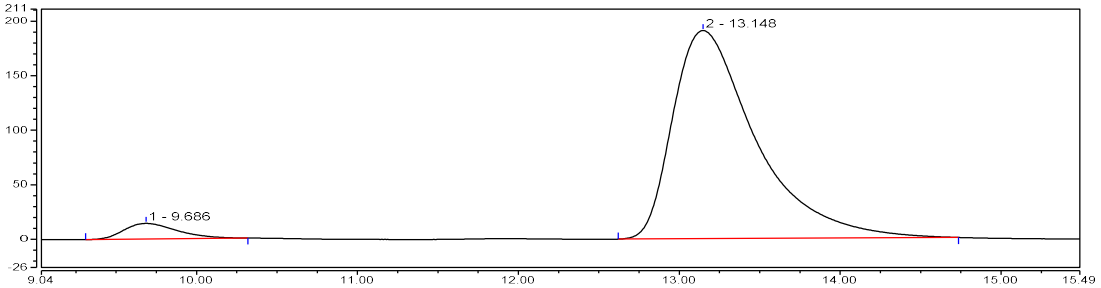
Ar' = 3-CF_3-4-MeOPh

(*R*)-3-(3-chlorophenyl)-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methylindolin-2-one (3f): yellow soild; Mp 116.2 – 127.8 ºC; 44.1 mg, 96% yield; 92% ee; $[\alpha]_D^{22}$ + 167.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 4H), 7.27 (s, 1H), 7.16 (t, *J* = 7.0 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.77 – 6.66 (m, 2H), 4.07 (d, *J* = 12.2 Hz, 1H), 3.79 (s, 3H), 3.68 (d, *J* = 12.1 Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 150.2, 144.0, 140.9, 139.6, 134.7, 130.0, 129.6, 129.2, 128.0, 127.4, 125.4, 124.9, 123.1, 121.7, 119.4, 119.0, 118.6, 118.2, 113.8, 113.1, 113.0, 112.9, 112.9, 108.9, 56.6, 56.6, 51.7, 26.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.2. HRMS (ESI) m/z 483.1058 ($M+Na^+$), calc. for $C_{24}H_{20}ClF_3N_2O_2Na$ 483.1056.

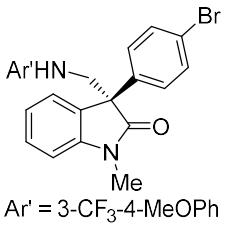
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 ºC; 254 nm; retention time: 9.7 min (minor) and 13.1 min (major).



Entry	Retention	Area	Height	%Area
1	9.469	90.7983	195.71	50.35
2	12.731	89.5468	143.49	49.65

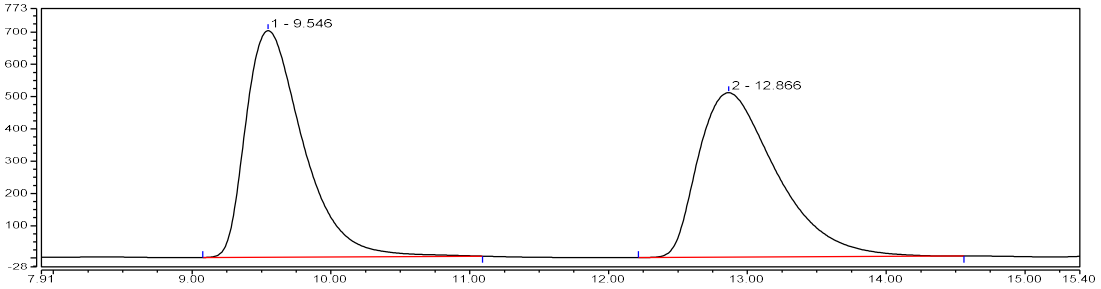


Entry	Retention	Area	Height	%Area
1	9.686	5.4603	14.32	4.57
2	13.148	114.0374	190.73	95.43

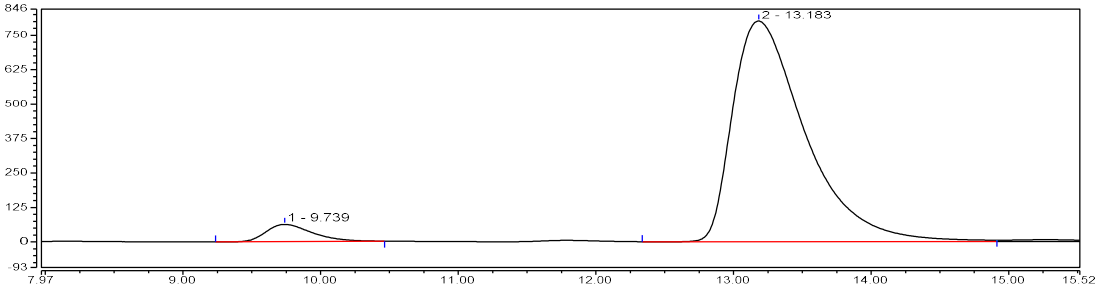


(*R*)-3-(4-bromophenyl)-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methylindolin-2-one (5g): yellow soild; Mp 142.1 – 143.6 ºC; 47.4 mg, 94% yield; 91% ee; $[\alpha]_D^{22}$ + 229.8 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.30 (m, 6H), 7.16 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 6.75 – 6.70 (m, 2H), 4.06 (d, *J* = 12.4 Hz, 1H), 3.80 (s, 3H), 3.67 (d, *J* = 12.3 Hz, 1H), 3.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.0, 150.1, 144.0, 141.0, 136.6, 131.9, 131.8, 130.1, 129.8, 129.2, 128.9, 125.4, 124.8, 123.0, 122.0, 121.7, 119.4, 119.0, 118.6, 118.1, 113.8, 113.0, 112.9, 112.8, 112.7, 108.8, 56.6, 56.4, 51.6, 26.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.3. HRMS (ESI) m/z 527.0552 ($M+Na^+$), calc. for $C_{24}H_{20}BrF_3N_2O_2Na$ 527.0551.

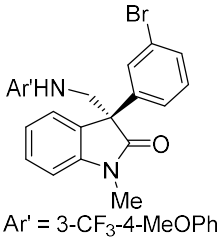
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 ºC; 254 nm; retention time: 9.7 min (minor) and 13.2 min (major).



Entry	Retention	Area	Height	%Area
1	9.546	335.4755	701.73	50.11
2	12.866	334.0106	509.47	49.89

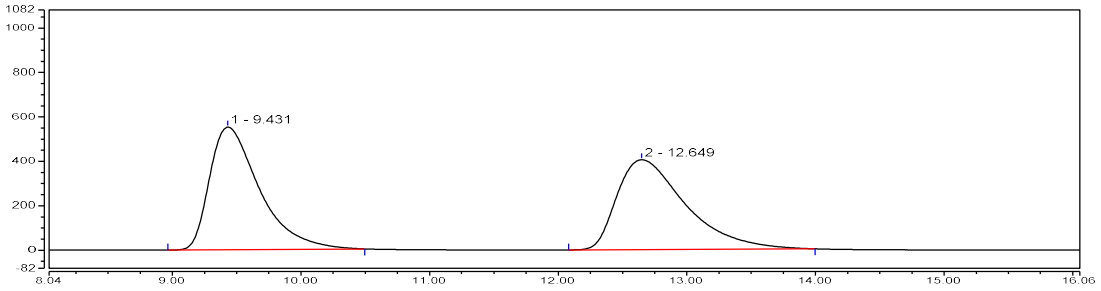


Entry	Retention	Area	Height	%Area
1	9.739	23.9089	62.33	4.66
2	13.183	488.7835	801.25	95.34

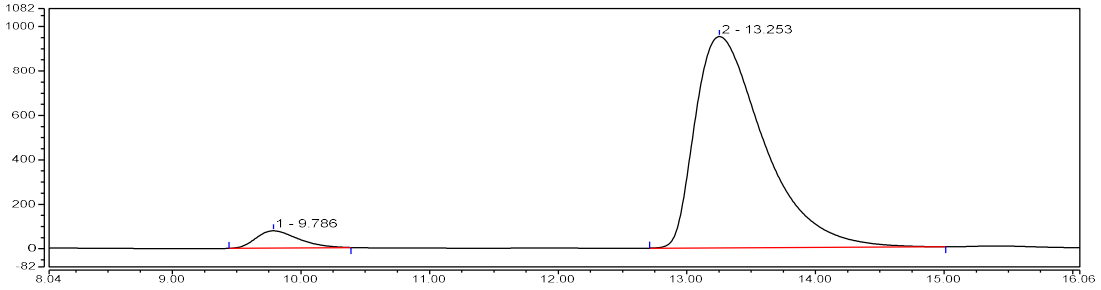


(*R*)-3-(3-bromophenyl)-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methylindolin-2-one (5h): yellow soild; Mp 102.1 – 103.5 °C; 48.8 mg, 97% yield; 90% ee; $[\alpha]_D^{22}$ + 11.7 (*c* 1.0, $CHCl_3$);^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.58 – 7.42 (m, 4H), 7.39 – 7.27 (m, 2H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 6.87 – 6.82 (m, 2H), 4.19 (d, *J* = 12.3 Hz, 1H), 3.91 (s, 3H), 3.80 (d, *J* = 12.4 Hz, 1H), 3.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 150.2, 144.0, 140.9, 139.8, 131.0, 130.3, 130.2, 129.6, 129.2, 128.9, 128.8, 127.8, 127.1, 125.8, 125.4, 124.9, 124.9, 123.1, 122.9, 122.9, 121.7, 119.8, 119.4, 119.0, 118.6, 118.2, 113.9, 113.1, 113.0, 113.0, 112.9, 108.9, 56.6, 56.5, 51.8, 26.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.2. HRMS (ESI) m/z 527.0552 ($M+Na^+$), calc. for $C_{24}H_{20}BrF_3N_2O_2Na$ 527.0551.

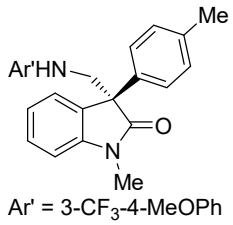
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 9.8 min (minor) and 13.2 min (major).



Entry	Retention	Area	Height	%Area
1	9.431	250.2936	552.58	49.99
2	12.649	250.3803	404.60	50.01

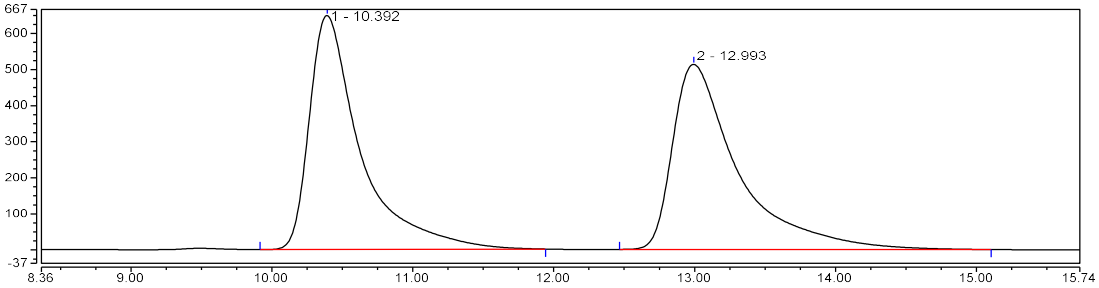


Entry	Retention	Area	Height	%Area
1	9.786	29.2858	77.34	4.73
2	13.253	589.5037	951.35	95.27

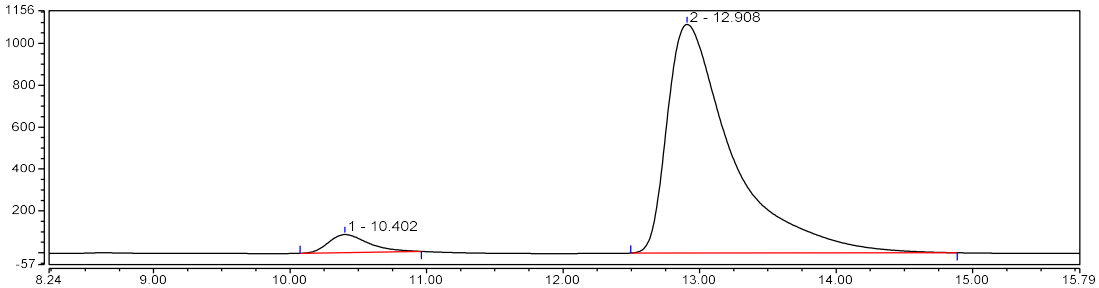


(*R*)-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methyl-3-(p-tolyl)indolin-2-one (5i): yellow soild; Mp 135.2 – 136.7 °C; 38.1 mg, 86% yield; 91% ee; $[\alpha]_D^{22}$ + 15.0 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 3H), 7.19 – 7.10 (m, 3H), 6.92 (d, *J* = 7.7 Hz, 1H), 6.82 (d, *J* = 8.6 Hz, 1H), 6.73 (d, *J* = 11.3 Hz, 2H), 4.10 (t, *J* = 12.7 Hz, 1H), 3.79 (s, 3H), 3.70 (d, *J* = 12.2 Hz, 1H), 3.22 (d, *J* = 18.1 Hz, 3H), 2.41 – 2.26 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.6, 150.0, 144.0, 141.1, 137.6, 134.4, 130.5, 129.5, 129.0, 128.8, 126.9, 125.4, 124.9, 122.8, 121.8, 119.8, 119.4, 119.0, 118.6, 118.2, 118.0, 113.9, 113.0, 112.9, 112.8, 112.7, 108.6, 56.7, 56.4, 51.5, 26.4, 21.0. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.2. HRMS (ESI) m/z 463.1604 ($M+Na^+$), calc. for $C_{25}H_{23}F_3N_2O_2Na$ 463.1602.

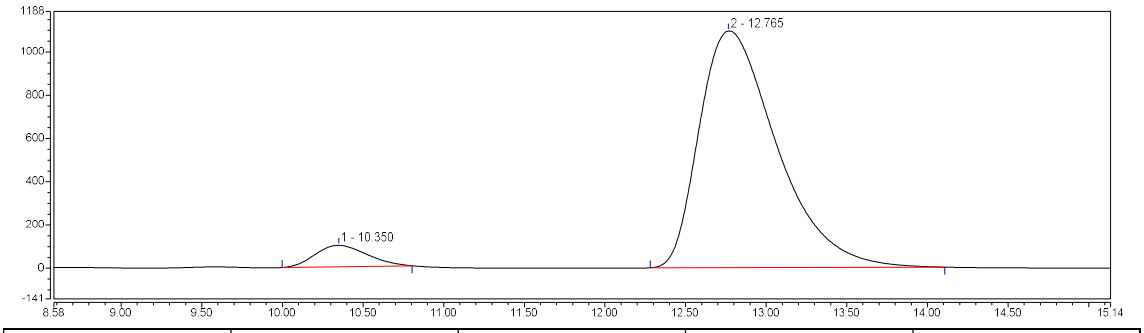
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 10.4 min (minor) and 12.9 min (major).



Entry	Retention	Area	Height	%Area
1	10.392	272.6481	648.53	49.76
2	12.993	275.3302	512.92	50.24

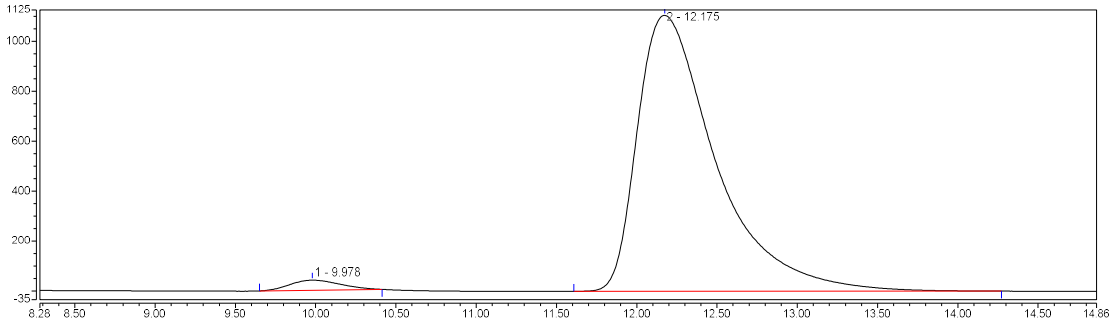


Entry	Retention	Area	Height	%Area
1	10.402	29.3010	86.40	4.65
2	12.908	601.0367	1092.18	95.35



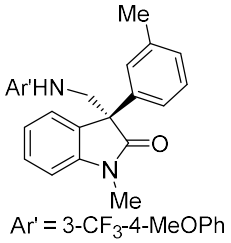
Entry	Retention	Area	Height	%Area
1	10.350	36.9581	99.11	5.71
2	12.765	609.7776	1094.57	94.29

The synthesis of **5i** in a 1.0 mmol scale



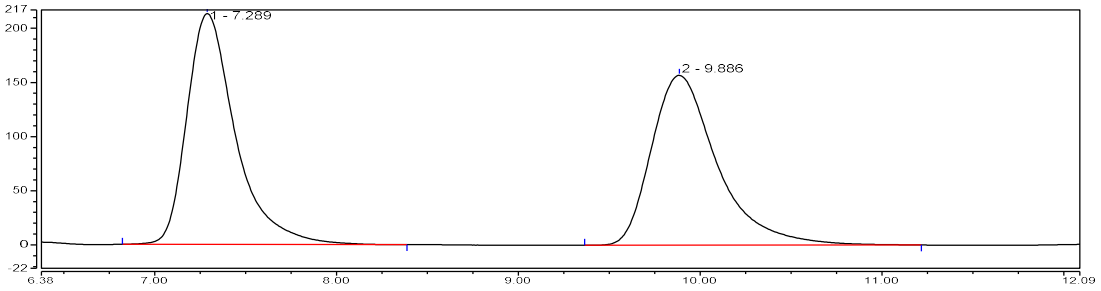
Entry	Retention	Area	Height	%Area
1	9.978	14.6232	40.35	2.29
2	12.175	624.9434	1104.94	97.71

The ee value was obtained after a single recrystallization (PE : EA = 1 : 4).

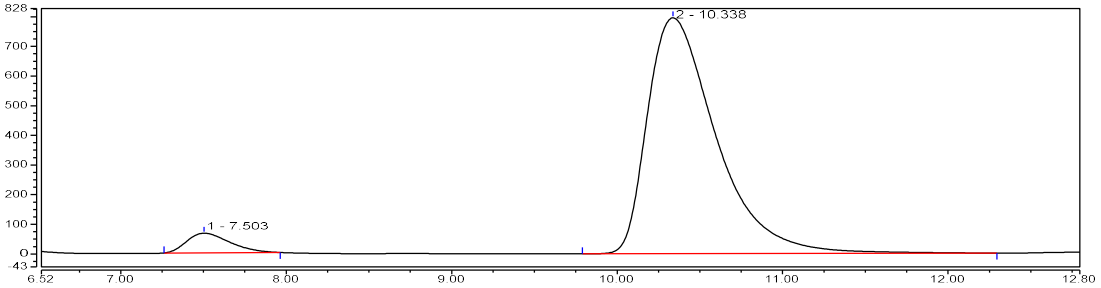


(*R*)-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methyl-3-(m-tolyl)indolin-2-one (5j): yellow soild; Mp 76.8 – 77.8 °C; 41.4 mg, 95% yield; 90% ee; $[\alpha]_D^{22}$ + 10.9 (*c* 1.0, $CHCl_3$);^{1}H NMR (300 MHz, $CDCl_3$) δ7.40 – 7.34 (m, 7.5 Hz, 2H), 7.22 (d, *J* = 5.3 Hz, 3H), 7.19 – 7.06 (m, 2H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 1H), 6.73 (d, *J* = 12.6 Hz, 2H), 4.09 (d, *J* = 12.2 Hz, 1H), 3.80 (s, 3H), 3.71 (d, *J* = 12.2 Hz, 1H), 3.20 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.5, 150.0, 144.0, 141.2, 138.5, 137.4, 130.5, 129.0, 128.8, 128.6, 128.6, 127.7, 125.4, 124.9, 124.1, 122.8, 121.8, 119.8, 119.7, 119.0, 118.6, 118.2, 118.1, 113.9, 113.0, 112.9, 112.8, 112.7, 108.6, 56.7, 56.7, 51.5, 26.5, 21.6. ^{19}F NMR (565 MHz, CDCl3) δ – 62.2. HRMS (ESI) m/z 463.1604 ($M+Na^+$), calc. for $C_{25}H_{23}F_3N_2O_2Na$ 463.1601.

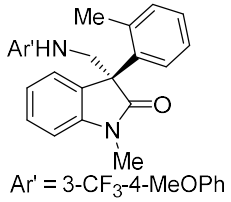
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 7.5 min (minor) and 10.3 min (major).



Entry	Retention	Area	Height	%Area
1	7.289	66.1198	213.15	50.11
2	9.886	65.8339	156.86	49.89

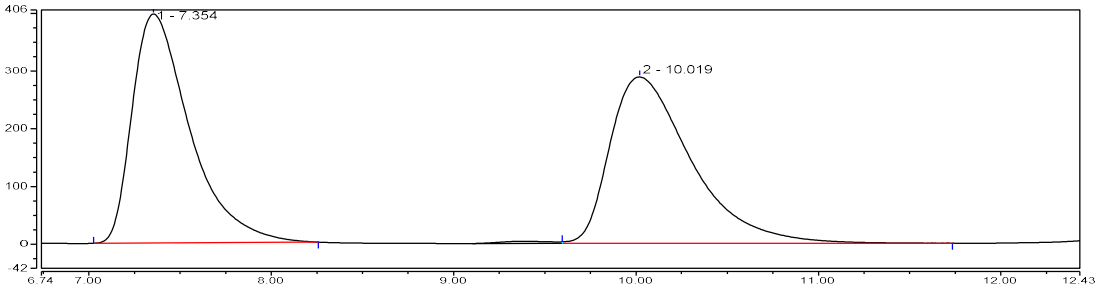


Entry	Retention	Area	Height	%Area
1	7.503	19.8578	66.16	4.94
2	10.338	382.2460	794.95	95.06

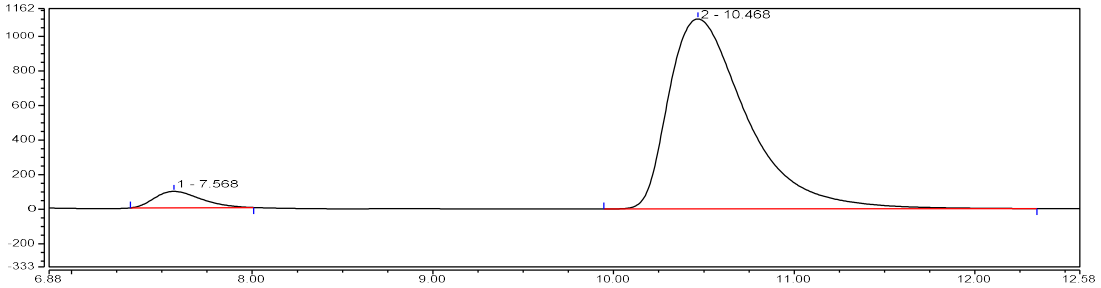


(*R*)-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methyl-3-(o-tolyl)indolin-2-one (5k): yellow soild; Mp 75.9 – 77.3 °C; 36.6 mg, 83% yield; 90% ee; $[\alpha]_D^{22}$ + 14.2 (*c* 1.0, $CHCl_3$);^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 2H), 7.23 – 7.21 (m, 3H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.12 – 7.08 (m, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 1H), 6.76 – 6.71 (m, 2H), 4.09 (d, *J* = 12.2 Hz, 1H), 3.80 (s, 3H), 3.71 (d, *J* = 12.2 Hz, 1H), 3.20 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.5, 150.0, 144.0, 141.2, 138.5, 137.4, 130.5, 128.8, 128.6, 128.6, 127.7, 125.4, 124.9, 124.1, 122.8, 121.8, 119.8, 119.4, 119.0, 118.6, 118.2, 118.1, 113.9, 113.0, 112.9, 112.8, 112.7, 108.6, 56.7, 56.7, 51.5, 26.5, 21.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.2. HRMS (ESI) m/z 463.1604 ($M+Na^+$), calc. for $C_{25}H_{23}F_3N_2O_2Na$ 463.1602.

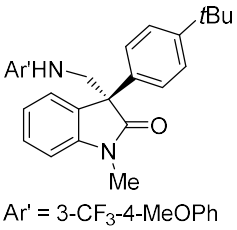
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 7.6 min (minor) and 10.5 min (major).



Entry	Retention	Area	Height	%Area
1	7.354	147.3393	397.75	49.74
2	10.019	148.9029	288.58	50.26

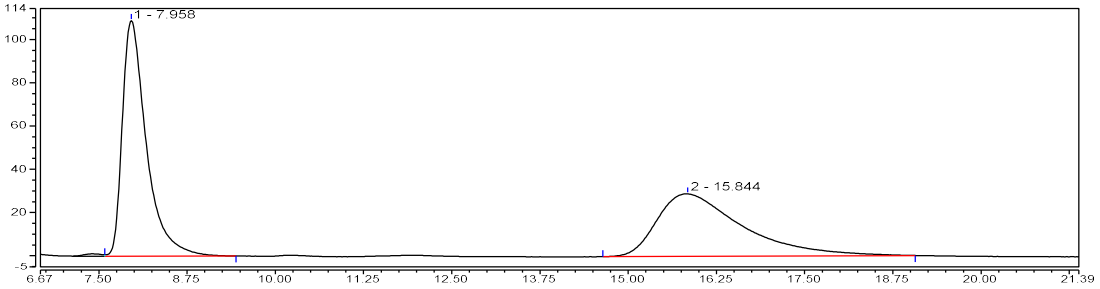


Entry	Retention	Area	Height	%Area
1	7.568	28.1437	94.88	4.87
2	10.468	549.2533	1099.02	95.13

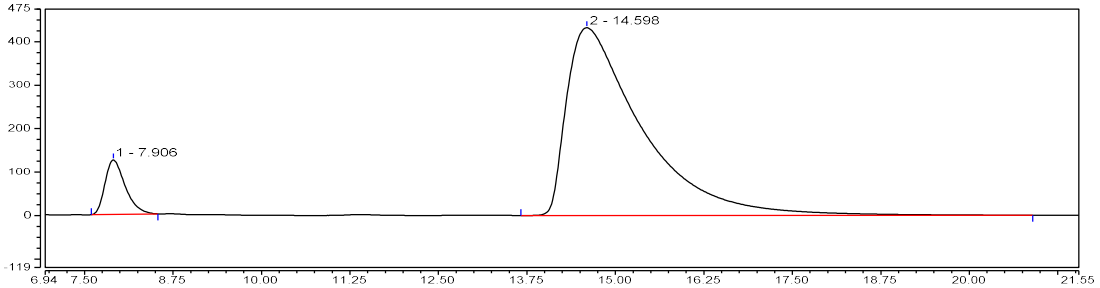


(*R*)-3-(4-(tert-butyl)phenyl)-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methylindolin-2-one (5l): yellow soild; Mp 128.4 – 129.7 ºC; 46.2 mg, 96% yield; 86% ee; $[\alpha]_D^{22}$ + 19.1 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 6H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.6 Hz, 1H), 6.78 – 6.68 (m, 2H), 4.09 (d, *J* = 12.2 Hz, 1H), 3.79 (s, 3H), 3.72 (d, *J* = 12.2 Hz, 1H), 3.19 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.6, 150.7, 150.0, 144.1, 141.1, 134.3, 130.4, 128.8, 126.7, 125.7, 125.4, 125.0, 122.8, 121.8, 119.8, 119.4, 119.0, 118.6, 118.2, 118.0, 113.8, 113.0, 112.9, 112.8, 112.8, 108.6, 56.7, 56.5, 51.6, 34.4, 31.2, 26.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.2. HRMS (ESI) m/z 505.2073 ($M+Na^+$), calc. for $C_{28}H_{29}F_3N_2O_2Na$ 505.2072.

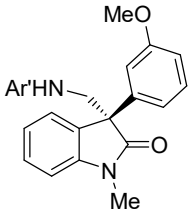
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 ºC; 254 nm; retention time: 7.9 min (minor) and 14.6 min (major).



Entry	Retention	Area	Height	%Area
1	7.958	42.9664	108.90	51.62
2	15.844	40.2747	28.91	48.38



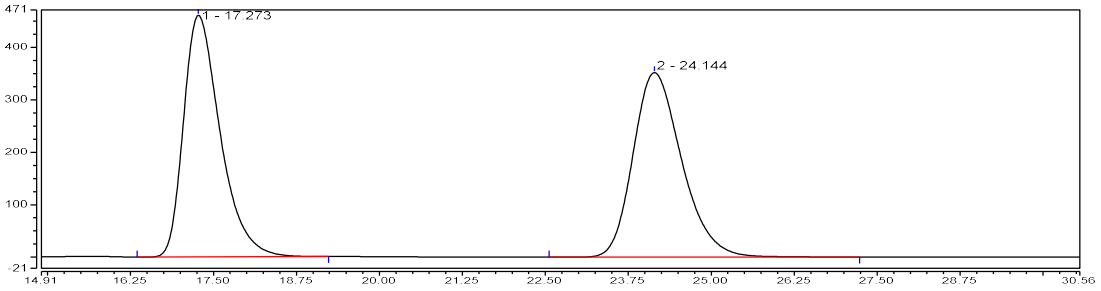
Entry	Retention	Area	Height	%Area
1	7.906	41.4605	125.35	7.22
2	14.598	532.5776	431.75	92.78



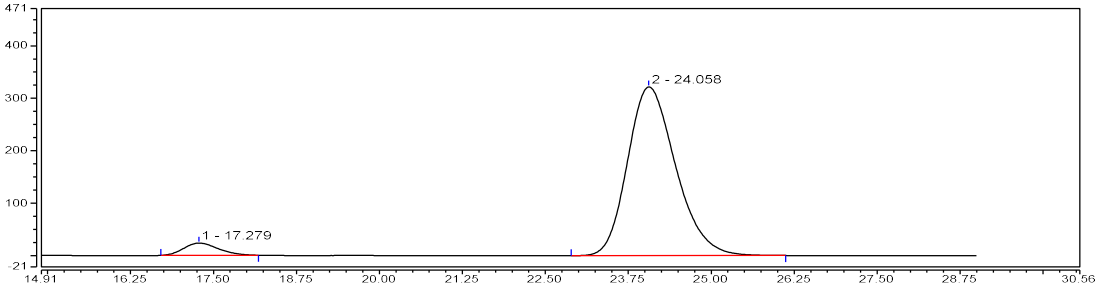
Ar' = 3-CF_3-4-MeOPh

(*R*)-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-3-(3-methoxyphenyl)-1-methylindolin-2-one (5m): yellow soild; Mp 84.2 – 85.9 °C; 44.2 mg, 97% yield; 90% ee; $[\alpha]_D^{22}$ + 114.3 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.3 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.02 – 6.97 (m, 2H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.82 – 6.77 (m, 2H), 6.73 – 6.68 (m, 2H), 4.04 (d, *J* = 12.3 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.69 (d, *J* = 12.3 Hz, 1H), 3.16 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 159.8, 150.1, 144.0, 141.1, 139.0, 130.2, 129.8, 129.0, 128.9, 125.4, 124.9, 122.9, 121.8, 119.4, 119.0, 118.6, 118.1, 113.9, 113.7, 113.0, 112.9, 112.8, 112.7, 112.5, 108.7, 56.7, 56.7, 55.2, 51.6, 26.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.2. HRMS (ESI) m/z 479.1553 ($M+Na^+$), calc. for $C_{24}H_{20}F_4N_2O_2Na$ 479.1552.

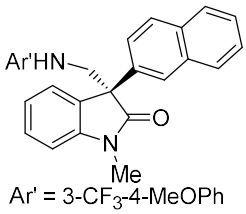
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 17.3 min (minor) and 24.1 min (major).



Entry	Retention	Area	Height	%Area
1	17.273	294.7126	460.62	49.68
2	24.144	298.4564	351.57	50.32

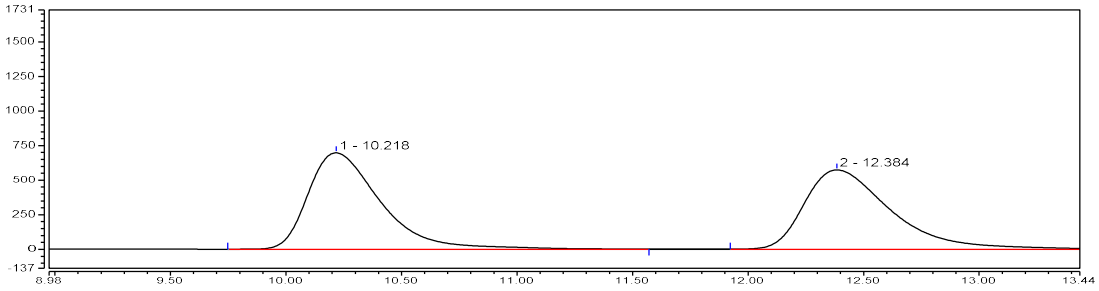


Entry	Retention	Area	Height	%Area
1	17.279	14.0857	23.33	4.95
2	24.058	270.4545	321.50	95.05

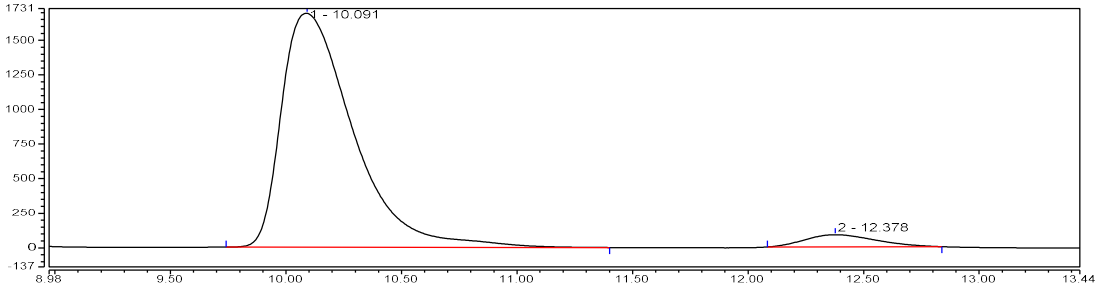


(*R*)-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methyl-3-(naphthalen-2-yl)indolin-2-one (5n): yellow soild; Mp 136.2 – 137.9 °C; 44.4 mg, 93% yield; 90% ee; $[\alpha]_D^{22}$ + 16.2 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 – 7.74 (m, 4H), 7.63 – 7.55 (m, 1H), 7.52 – 7.35 (m, 4H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 2H), 4.21 (d, *J* = 12.2 Hz, 1H), 3.82 (d, *J* = 13.8 Hz, 4H), 3.80 (s, 3H), 3.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.4, 150.0, 144.0, 141.2, 134.8, 133.2, 132.7, 130.5, 129.0, 128.6, 128.1, 127.5, 126.3, 126.3, 126.2, 125.4, 125.0, 124.7, 123.0, 121.8, 119.8, 119.4, 119.0, 118.6, 118.0, 113.9, 112.9, 112.8, 112.7, 112.7, 108.7, 56.9, 56.7, 51.4, 26.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.2. HRMS (ESI) m/z 499.1604 ($M+Na^+$), calc. for $C_{28}H_{23}F_3N_2O_2Na$ 499.1603.

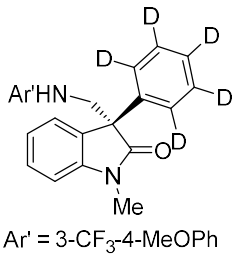
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 10.1 min (major) and 12.4 min (minor).



Entry	Retention	Area	Height	%Area
1	10.218	255.1570	697.59	50.34
2	12.384	251.7067	574.18	49.66



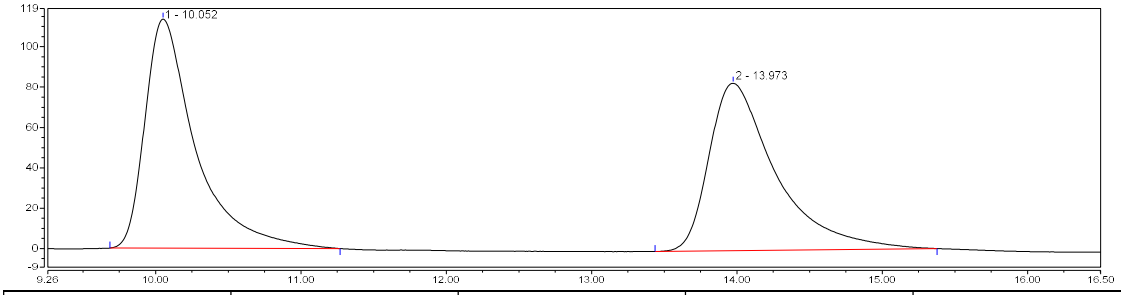
Entry	Retention	Area	Height	%Area
1	10.091	608.0216	1691.15	95.14
2	12.378	31.0421	87.67	4.86



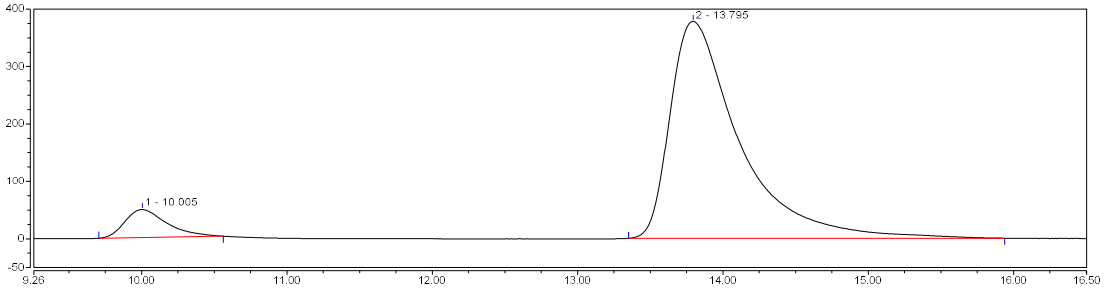
Ar' = 3-CF_3-4-MeOPh

(*R*)-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methyl-3-(phenyl-d5)indolin-2-one (5o): yellow soild; Mp 117.8 – 119.2 °C; 39.4 mg, 92% yield; 86% ee; $[\alpha]_D^{22}$ + 107.4 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 4.1 Hz, 2H), 7.20 – 7.10 (m, 1H), 6.93 (d, *J* = 6.5 Hz, 1H), 6.77 (dd, *J* = 26.4, 9.0 Hz, 3H), 4.10 (d, *J* = 11.5 Hz, 1H), 3.79 (s, 3H), 3.72 (d, *J* = 11.7 Hz, 1H), 3.20 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.4, 150.0, 144.0, 141.1, 137.3, 130.3, 128.9, 128.3, 128.0, 127.0, 126.7, 126.3, 125.4, 124.9, 122.9, 121.8, 119.7, 119.3, 118.9, 118.0, 113.8, 112.9, 112.8, 112.8, 112.7, 108.7, 56.7, 56.7, 51.6, 26.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.2. HRMS (ESI) m/z 454.1765 ($M+Na^+$), calc. for $C_{24}H_{16}D_5F_3N_2O_2Na$ 454.1761.

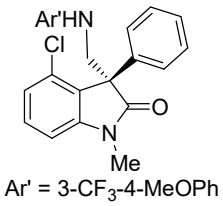
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 10.0 min (minor) and 13.8 min (major).



Entry	Retention	Area	Height	%Area
1	10.052	45.6376	113.45	50.82
2	13.973	44.1625	83.00	49.18

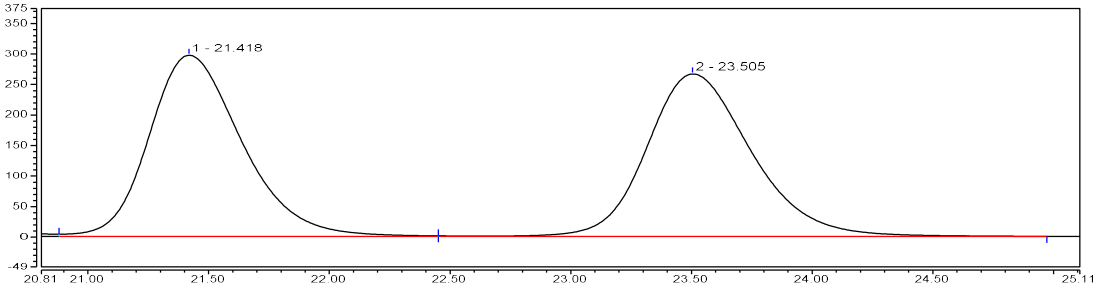


Entry	Retention	Area	Height	%Area
1	10.005	16.2437	48.65	7.23
2	13.795	208.5805	377.84	92.77

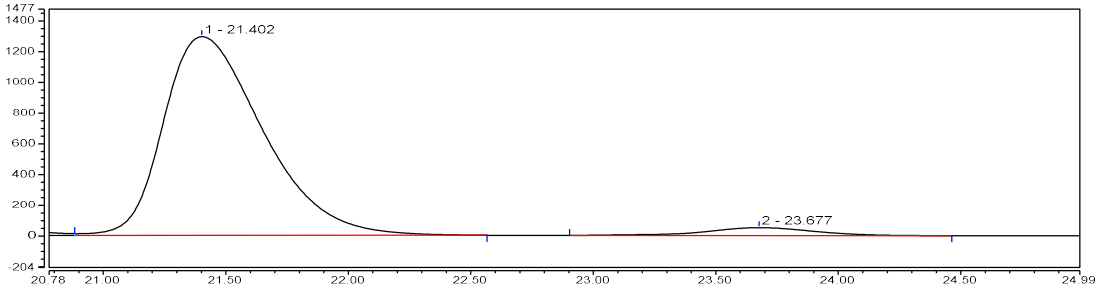


(*R*)-4-chloro-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methyl-3-phenylindolin-2-one (5p): yellow soild; Mp 96.1 – 97.5 °C; 43.6 mg, 95% yield; 92% ee; $[\alpha]_D^{22}$ + 50.3 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.7.26 – 7.16 (m, 2H), 7.00 (d, *J* = 8.2 Hz, 0H), 6.74 – 6.65 (m, 1H), 6.58 (s, 0H), 4.36 (d, *J* = 12.9 Hz, 0H), 4.06 (d, *J* = 12.8 Hz, 0H), 3.69 (s, 1H), 2.98 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.6, 159.8, 150.1, 144.0, 141.1, 139.0, 130.2, 129.8, 129.0, 128.9, 125.4, 124.9, 122.9, 121.8, 119.4, 119.0, 118.6, 118.1, 113.9, 113.7, 113.0, 112.9, 112.8, 112.7, 112.5, 108.7, 56.7, 56.6, 55.2, 51.6, 26.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.2. HRMS (ESI) m/z 483.1058 ($M+Na^+$), calc. for $C_{24}H_{20}ClF_3N_2O_2Na$ 483.1057.

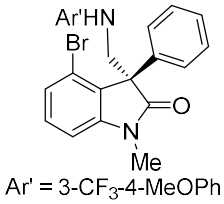
The ee was determined by HPLC analysis: CHIRALPAK IB-INB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 21.4 min (major) and 23.7 min (minor).



Entry	Retention	Area	Height	%Area
1	21.418	132.7841	296.81	49.75
2	23.505	134.0928	266.09	50.25

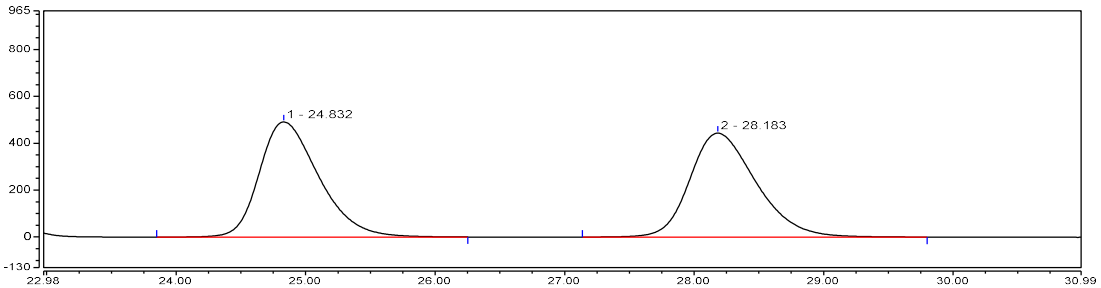


Entry	Retention	Area	Height	%Area
1	21.402	610.0310	1293.32	95.82
2	23.677	26.5944	51.73	4.18

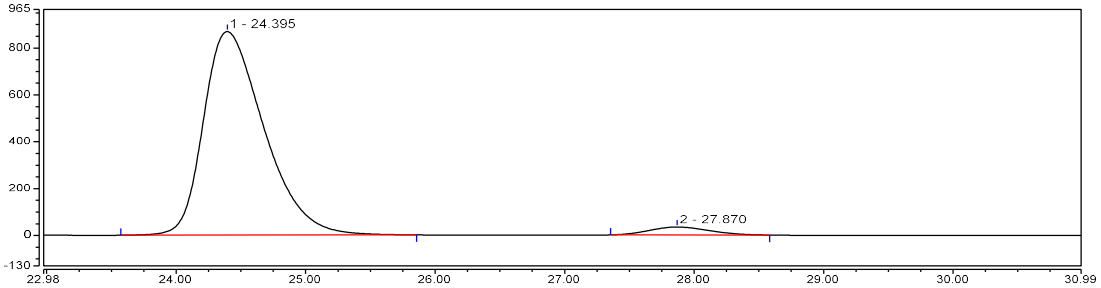


(*R*)-4-bromo-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methyl-3-phenylindolin-2-one (5q): yellow soild; Mp 108.4 – 109.7 ºC; 40.4 mg, 80% yield; 93% ee; $[\alpha]_D^{22}$ + 54.2 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.0 Hz, 3H), 7.28 – 7.22 (m, 4H), 6.88 – 6.79 (m, 3H), 6.70 (d, *J* = 2.2 Hz, 1H), 4.46 (d, *J* = 12.8 Hz, 1H), 4.24 (d, *J* = 12.8 Hz, 1H), 3.80 (s, 3H), 3.06 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.2, 150.2, 146.9, 140.7, 135.9, 130.6, 128.9, 128.8, 128.7, 128.3, 127.9, 126.9, 126.9, 125.3, 121.7, 120.1, 119.6, 119.2, 118.8, 118.4, 118.1, 113.9, 113.8, 113.7, 113.7, 107.5, 59.5, 56.6, 48.8, 26.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.2. HRMS (ESI) m/z 527.0552 ($M+Na^+$), calc. for $C_{24}H_{20}BrF_3N_2O_2Na$ 527.0553.

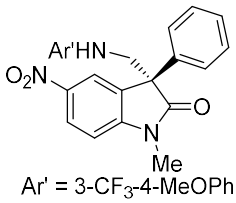
The ee was determined by HPLC analysis: CHIRALPAK IB-INB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 ºC; 254 nm; retention time: 24.4 min (major) and 27.9 min (minor).



Entry	Retention	Area	Height	%Area
1	24.832	262.7038	491.70	49.92
2	28.183	263.5718	443.53	50.08

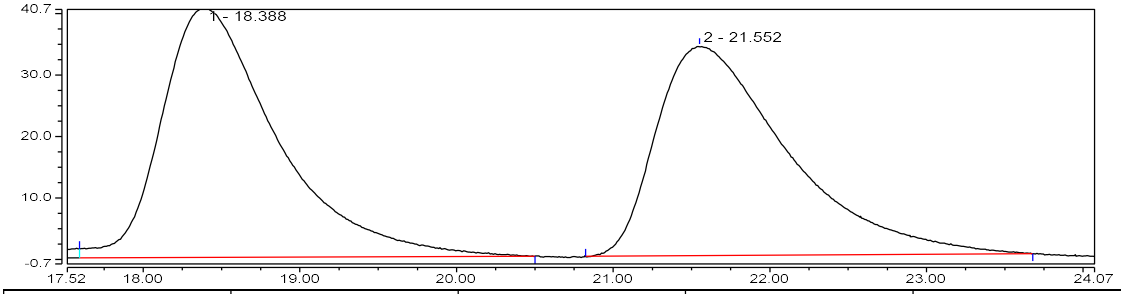


Entry	Retention	Area	Height	%Area
1	24.395	471.4294	869.21	96.30
2	27.870	18.1041	33.90	3.70

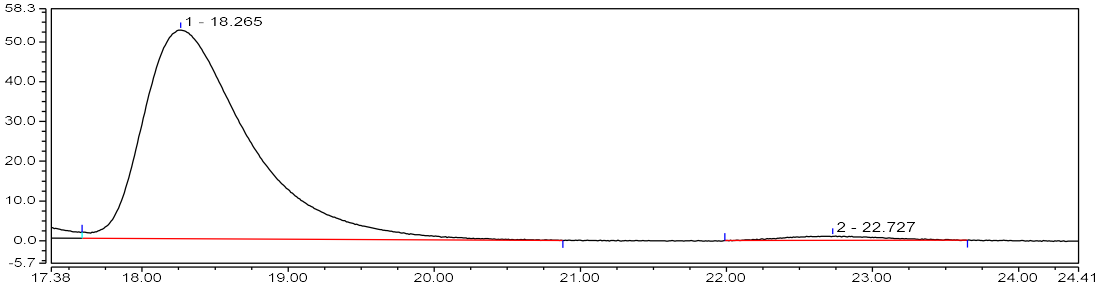


(*R*)-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methyl-5-nitro-3-phenylindolin-2-one (5r): yellow soild; Mp 62.2 – 62.9 °C; 30.0 mg, 64% yield; 88% ee; $[\alpha]_D^{22}$ + 2.1 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, CD_2Cl_2) δ 8.33 (d, *J* = 8.7 Hz, 1H), 8.26 (s, 1H), 7.40 – 7.35 (m, 5H), 6.99 (d, *J* = 8.6 Hz, 1H), 6.78 (dd, *J* = 22.8, 10.1 Hz, 3H), 4.11 (d, *J* = 12.8 Hz, 1H), 3.87 (d, *J* = 12.7 Hz, 1H), 3.79 (s, 3H), 3.27 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 177.6, 150.4, 149.7, 143.5, 140.6, 135.8, 131.5, 129.9, 129.2, 129.1, 128.5, 128.3, 126.9, 126.1, 125.3, 121.6, 120.9, 119.5, 119.1, 118.4, 113.8, 113.3, 113.2, 113.1, 113.1, 108.2, 57.2, 56.6, 52.0, 26.9. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.3. HRMS (ESI) m/z 494.1307 ($M+Na^+$), calc. for $C_{24}H_{20}F_3N_3NaO_4$ 494.1304.

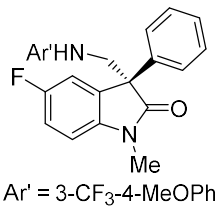
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 18.3 min (major) and 22.7 min (minor).



Entry	Retention	Area	Height	%Area
1	18.388	34.6558	40.64	51.17
2	21.552	33.0661	34.10	48.83

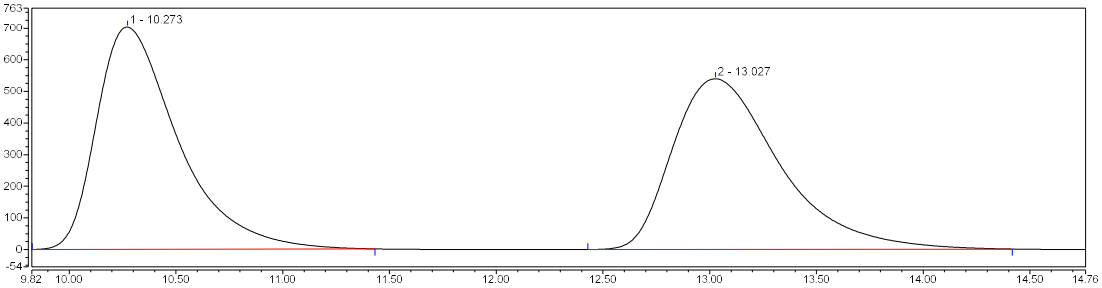


Entry	Retention	Area	Height	%Area
1	18.265	43.2647	52.30	97.61
2	22.727	1.0594	1.21	2.39

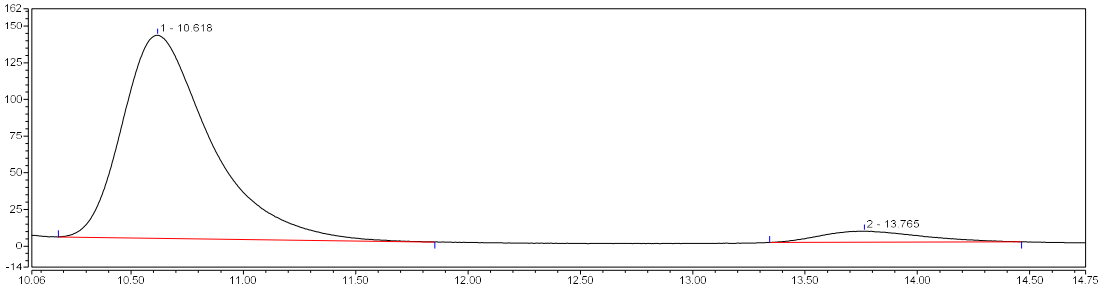


(*R*)-5-fluoro-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methyl-3-phenylindolin-2-one (5s): white soild; Mp 118.7 – 119.4 ºC; 43.0 mg, 97% yield; 95% ee; $[\alpha]_D^{22}$ + 17.0 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 5H), 7.13 – 7.04 (m, 2H), 6.87 – 6.81 (m, 2H), 6.74 (d, *J* = 7.8 Hz, 2H), 4.07 (d, *J* = 12.4 Hz, 1H), 3.80 (s, 3H), 3.74 (d, *J* = 12.4 Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.1, 160.7, 157.7, 150.1, 141.0, 134.0, 136.9, 132.2, 132.1, 128.9, 128.0, 127.0, 125.4, 121.7, 119.9, 119.5, 119.1, 118.1, 115.3, 115.0, 113.9, 113.3, 113.0, 112.9, 112.9, 112.8, 109.2, 109.1, 57.3, 56.7, 51.5, 26.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.3, – 112.0. HRMS (ESI) m/z 467.1350 ($M+Na^+$), calc. for $C_{24}H_{20}F_4N_2NaO_2$ 467.1353.

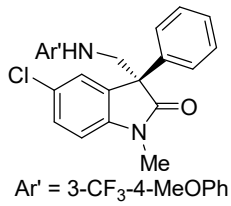
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 ºC; 254 nm; retention time: 10.6 min (major) and 13.8 min (minor).



Entry	Retention	Area	Height	%Area
1	10.273	310.6909	703.23	49.73
2	13.027	314.0770	539.69	50.27

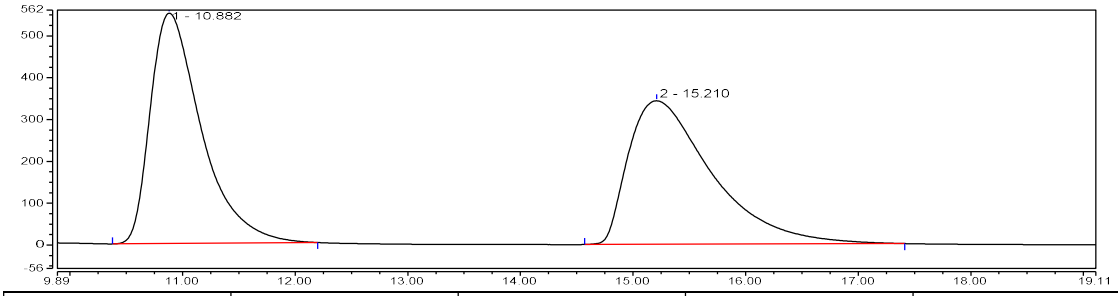


Entry	Retention	Area	Height	%Area
1	10.618	62.9956	138.38	94.03
2	13.765	4.0004	7.63	5.97

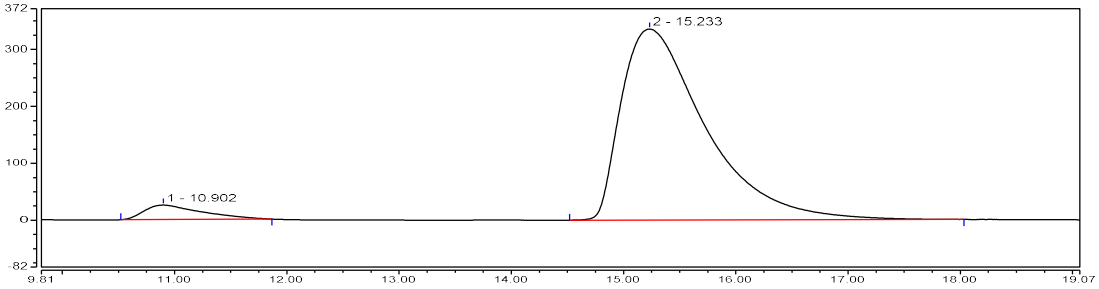


(*R*)-5-chloro-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methyl-3-phenylindolin-2-one (5t): yellow oil; 44.2 mg, 96% yield; 90% ee; $[\alpha]_D^{22}$ + 6.2 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 7H), 6.85 – 6.74 (m, 4H), 4.09 (d, *J* = 12.5 Hz, 1H), 3.80 (s, 3H), 3.74 (d, *J* = 12.5 Hz, 1H), 3.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.0, 150.3, 142.6, 140.6, 136.7, 132.1, 129.0, 128.9, 128.3, 128.1, 126.9, 125.4, 125.3, 121.7, 119.4, 119.0, 118.5, 118.4, 118.4, 113.8, 113.2, 109.6, 57.1, 56.7, 51.6, 26.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.2. HRMS (ESI) m/z 483.1058 ($M+Na^+$), calc. for $C_{24}H_{20}ClF_3N_2O_2Na$ 483.1057.

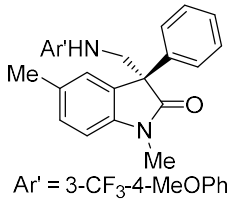
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 10.9 min (minor) and 15.2 min (major).



Entry	Retention	Area	Height	%Area
1	10.882	289.5424	550.79	49.56
2	15.210	294.7370	342.96	50.44

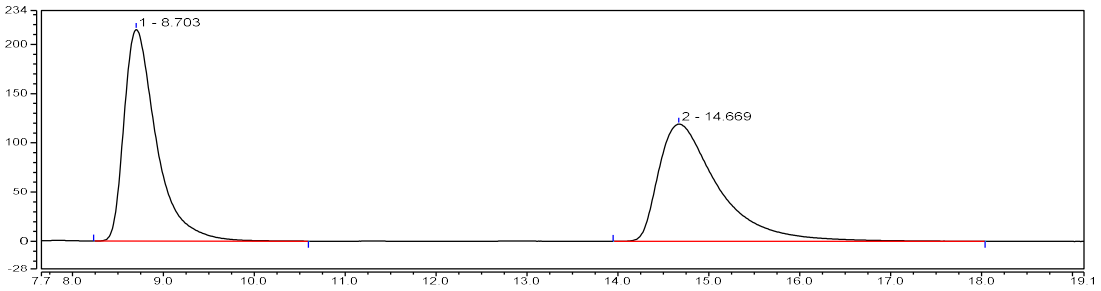


Entry	Retention	Area	Height	%Area
1	10.902	15.0400	25.45	4.91
2	15.233	291.1575	335.51	95.09

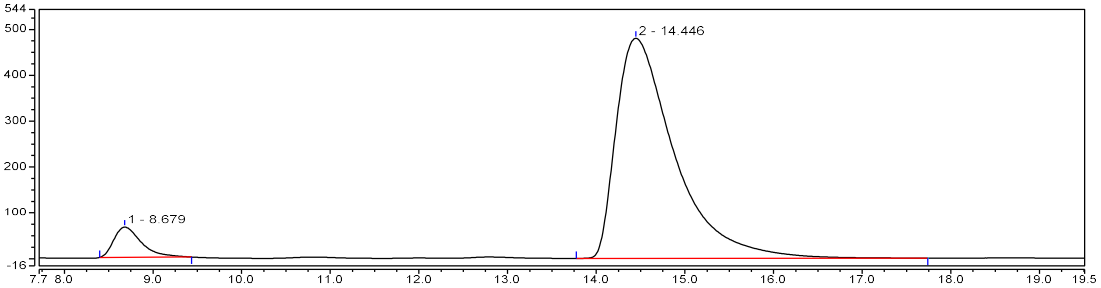


(*R*)-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1,5-dimethyl-3-phenylindolin-2-one (5u): yellow soild; Mp 93.1 – 94.6 °C; 33.0 mg, 75% yield; 87% ee; $[\alpha]_D^{22}$ + 3.7 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.1 Hz, 2H), 7.39 – 7.28 (m, 3H), 7.20 – 7.11 (m, 2H), 6.82 (d, *J* = 7.6 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 4.11 (d, *J* = 12.2 Hz, 1H), 3.80 (s, 3H), 3.69 (d, *J* = 12.2 Hz, 1H), 3.19 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.4, 150.0, 141.6, 141.2, 137.7, 132.5, 130.5, 129.2, 128.8, 127.7, 127.1, 125.6, 125.4, 121.8, 119.7, 119.3, 118.9, 118.5, 118.2, 118.0, 113.9, 112.8, 112.7, 112.6, 112.5, 108.4, 56.8, 56.7, 51.4, 26.5, 21.2. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.2. HRMS (ESI) m/z 463.1604 ($M+Na^+$), calc. for $C_{25}H_{23}F_3N_2O_2Na$ 463.1604.

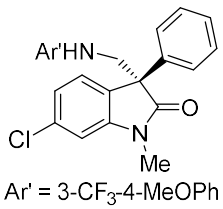
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 8.7 min (minor) and 14.4 min (major).



Entry	Retention	Area	Height	%Area
1	8.703	88.6109	214.72	49.43
2	14.669	90.6490	119.12	50.57

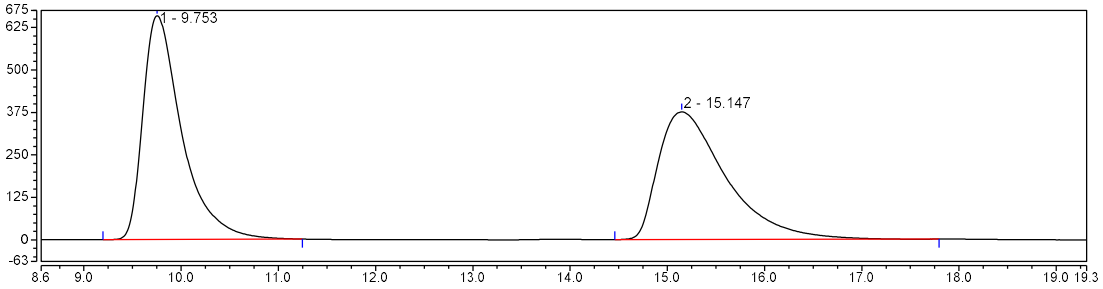


Entry	Retention	Area	Height	%Area
1	8.679	23.7536	65.96	6.10
2	14.446	365.5965	479.99	93.90

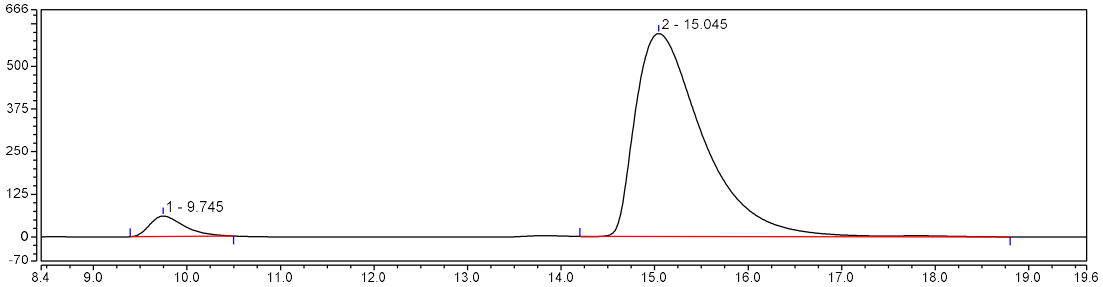


(*R*)-6-chloro-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methyl-3-phenylindolin-2-one (5v): yellow soild; Mp 117.5 – 118.9 ºC; 42.0 mg, 91% yield; 90% ee; $[\alpha]_D^{22}$ + 104.0 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.37 – 7.27 (m, 4H), 7.12 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.92 (d, *J* = 1.5 Hz, 1H), 6.82 (d, *J* = 9.4 Hz, 1H), 6.74 (d, *J* = 7.2 Hz, 2H), 4.07 (d, *J* = 12.4 Hz, 1H), 3.80 (s, 3H), 3.75 (d, *J* = 12.4 Hz, 1H), 3.17 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 150.2, 145.3, 141.0, 136.9, 134.8, 128.9, 128.7, 128.0, 127.0, 125.9, 125.3, 122.6, 121.7, 119.4, 119.0, 118.1, 113.9, 113.0, 113.0, 112.9, 112.8, 109.4, 56.7, 51.6, 26.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.3. HRMS (ESI) m/z 483.1058 ($M+Na^+$), calc. for $C_{24}H_{20}ClF_3N_2O_2Na$ 483.1057.

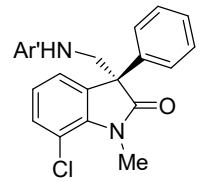
The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 ºC; 254 nm; retention time: 9.7 min (minor) and 15.0 min (major).



Entry	Retention	Area	Height	%Area
1	9.753	304.8869	658.21	50.28
2	15.147	301.5195	375.43	49.72



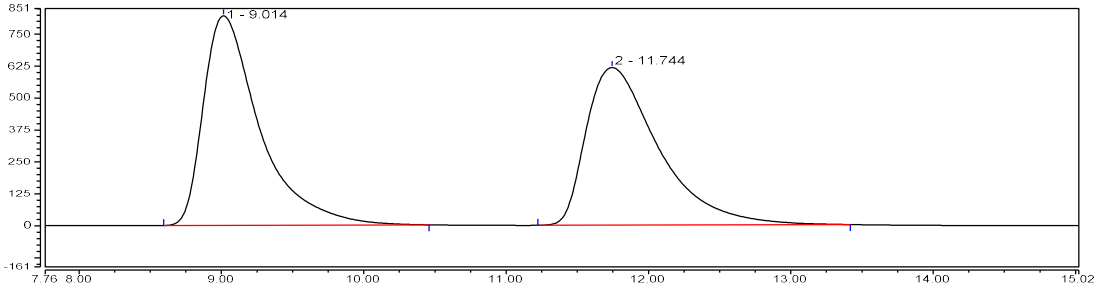
Entry	Retention	Area	Height	%Area
1	9.745	25.8440	60.19	4.98
2	15.045	492.9664	594.96	95.02



Ar' = 3-CF_3-4-MeOPh

(*R*)-7-chloro-3-(((4-methoxy-3-(trifluoromethyl)phenyl)amino)methyl)-1-methyl-3-phenylindolin-2-one (5w): yellow soild; Mp 69.9 – 71.1 °C; 43.8 mg, 95% yield; 88% ee; $[\alpha]_D^{22}$ + 25.8 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ7.39 – 7.28 (m, 6H), 7.22 (d, *J* = 7.3 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 9.4 Hz, 1H), 6.74 (d, *J* = 7.0 Hz, 3H), 4.11 (d, *J* = 12.4 Hz, 1H), 3.80 (s, 3H), 3.72 (d, *J* = 12.4 Hz, 1H), 3.57 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.8, 150.2, 141.0, 140.0, 137.2, 133.3, 131.2, 128.9, 128.0, 127.0, 125.4, 123.6, 123.4, 121.7, 119.8, 119.4, 119.0, 118.6, 118.1, 116.1, 113.8, 113.0, 112.9, 112.8, 112.7, 56.7, 56.6, 51.7, 23.0. ^{19}F NMR (565 MHz, $CDCl_3$) δ – 62.2. HRMS (ESI) m/z 483.1058 ($M+Na^+$), calc. for $C_{24}H_{20}ClF_3N_2O_2Na$ 483.1057.

The ee was determined by HPLC analysis: CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 9.1 min (minor) and 11.8 min (major).



Entry	Retention	Area	Height	%Area
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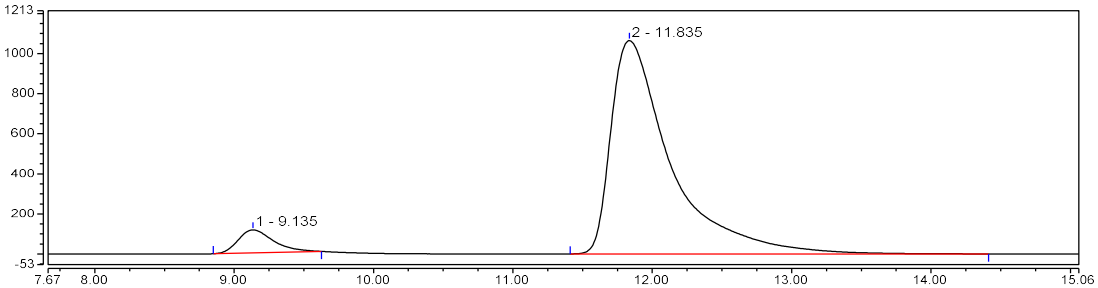
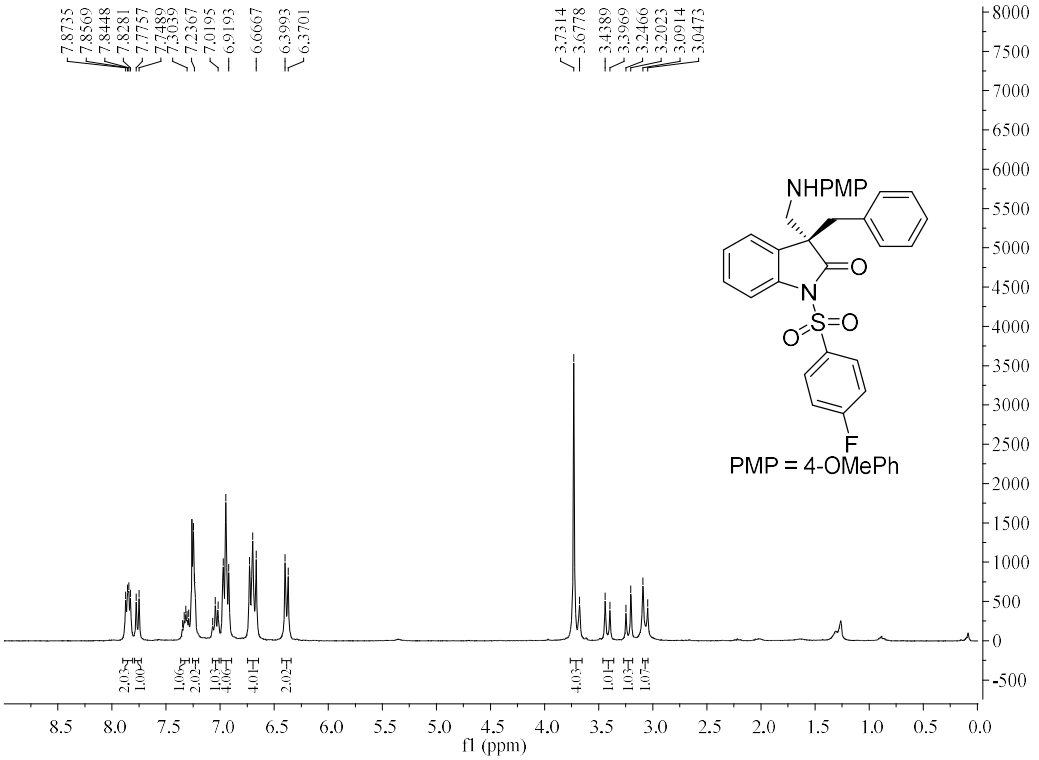
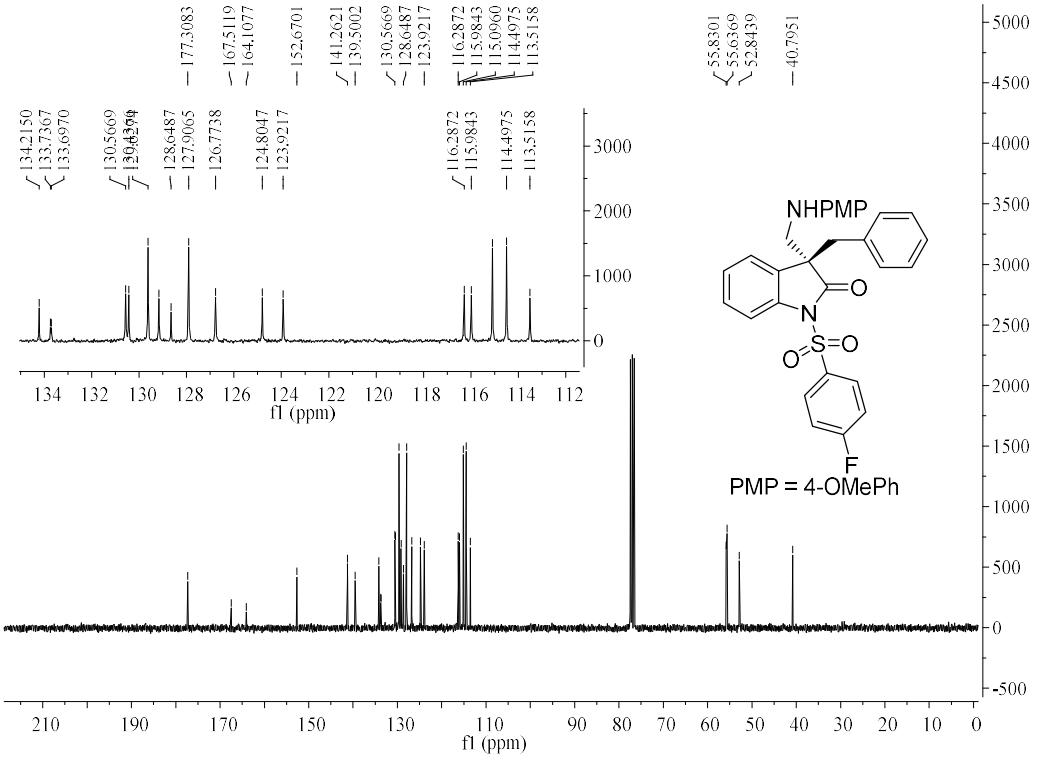
2	11.744	363.9976	617.11	49.13

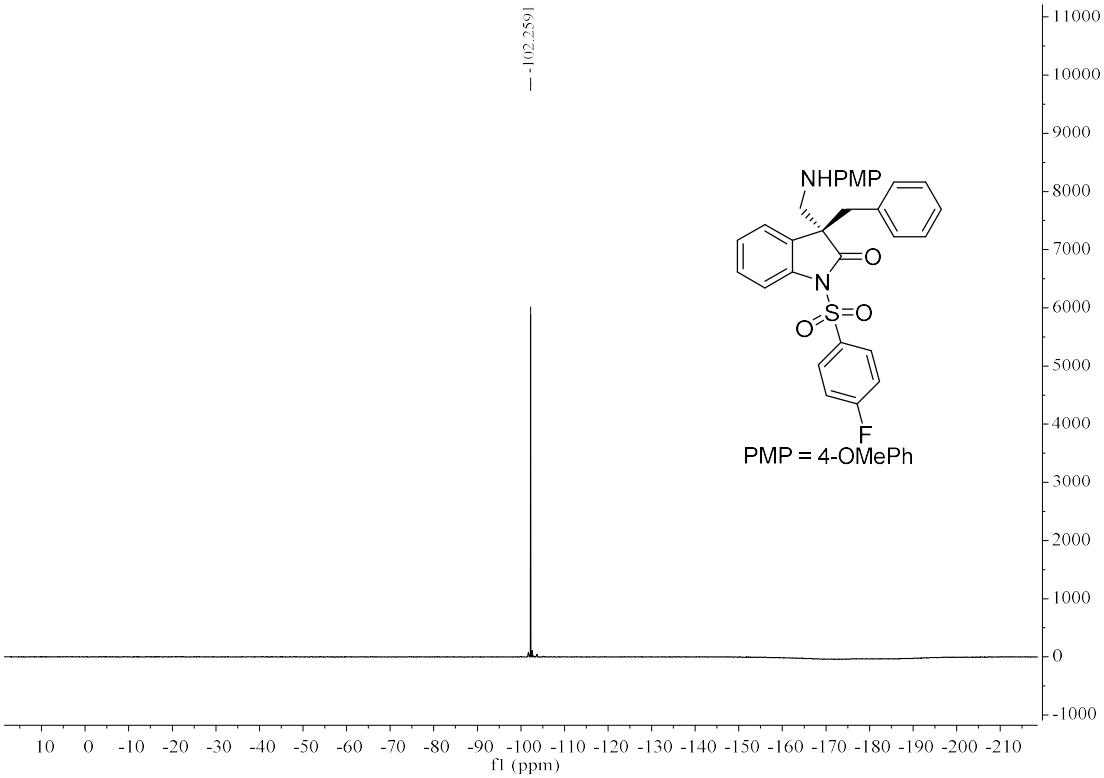


Entry	Retention	Area	Height	%Area
1	9.135	33.8320	115.05	6.02
2	11.835	528.2793	1064.29	93.98

8. Copies of NMR spectra



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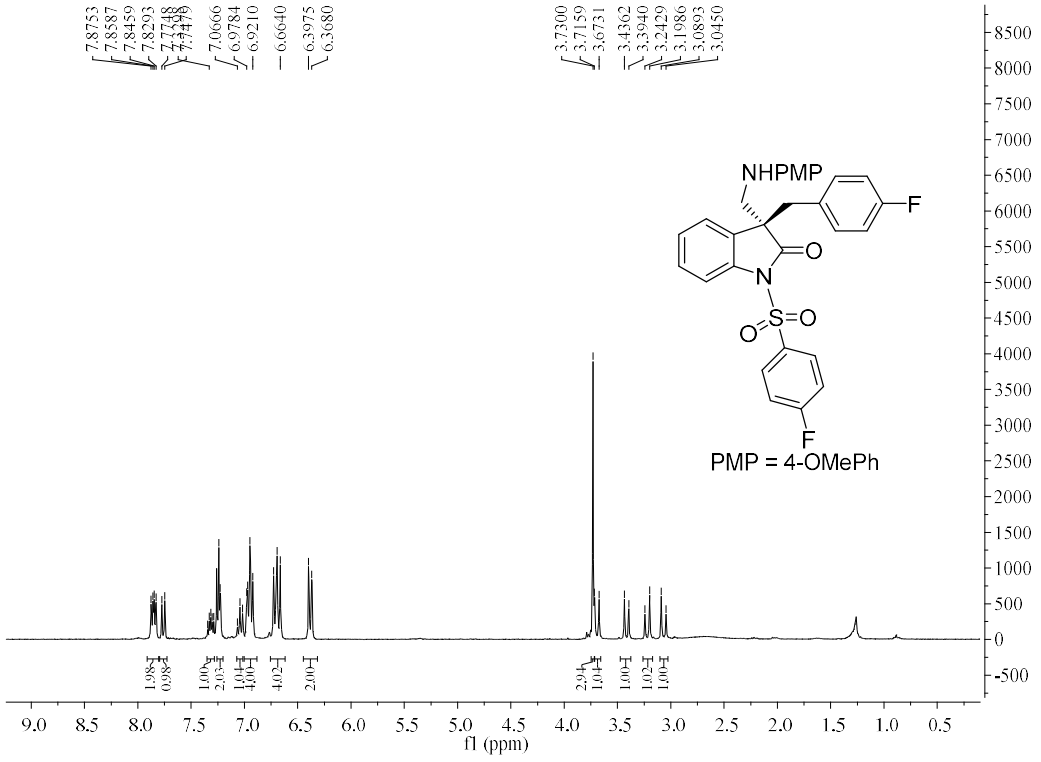
NHPMP
O
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)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7.8459
7.8293
7.7248
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7.4478
7.0666
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6.3680
3.7300
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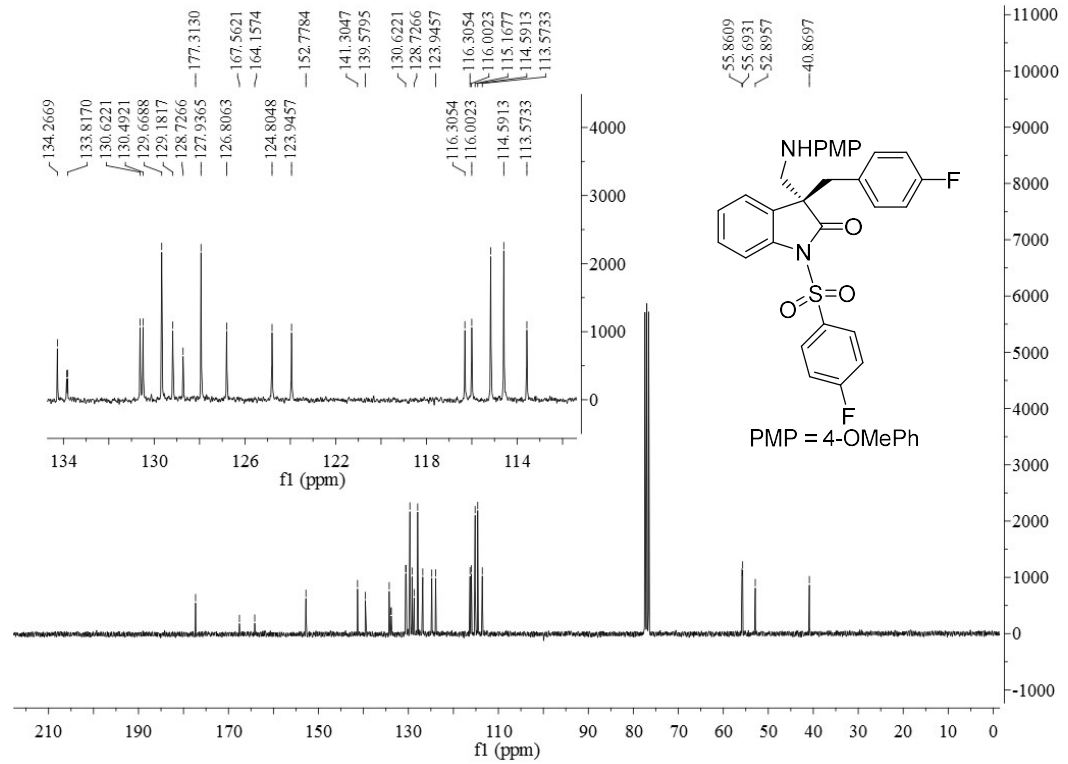
3.1986
3.0893
3.0450
NHPMP
F
O
N
S=O
O
F
PMP = 4-OMePh
1.98
0.98
1.00
2.03
1.04
4.00
4.02
2.00
2.94
1.04
1.00
1.02
1.00
f1 (ppm)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115.1677
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113.5733
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55.6931
52.8957
40.8697
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129.6688
129.1817
128.7266
127.9365
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124.8048
123.9457
116.3054
116.0023
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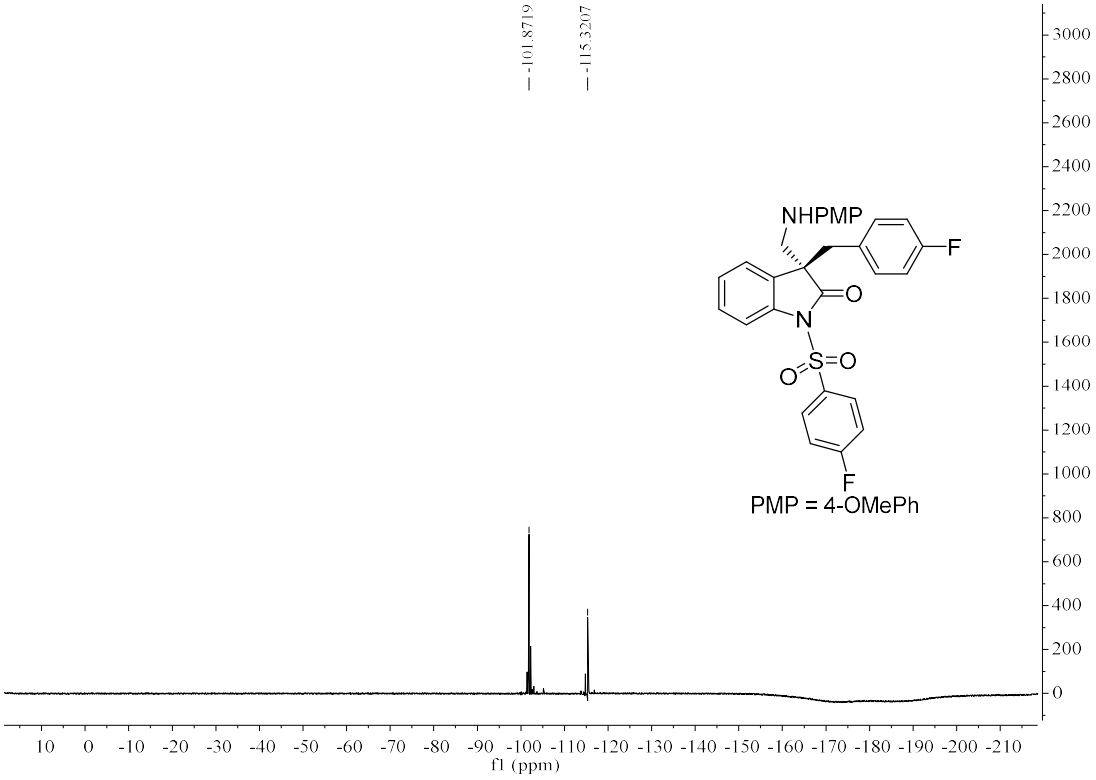
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)
f1 (ppm)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S=O
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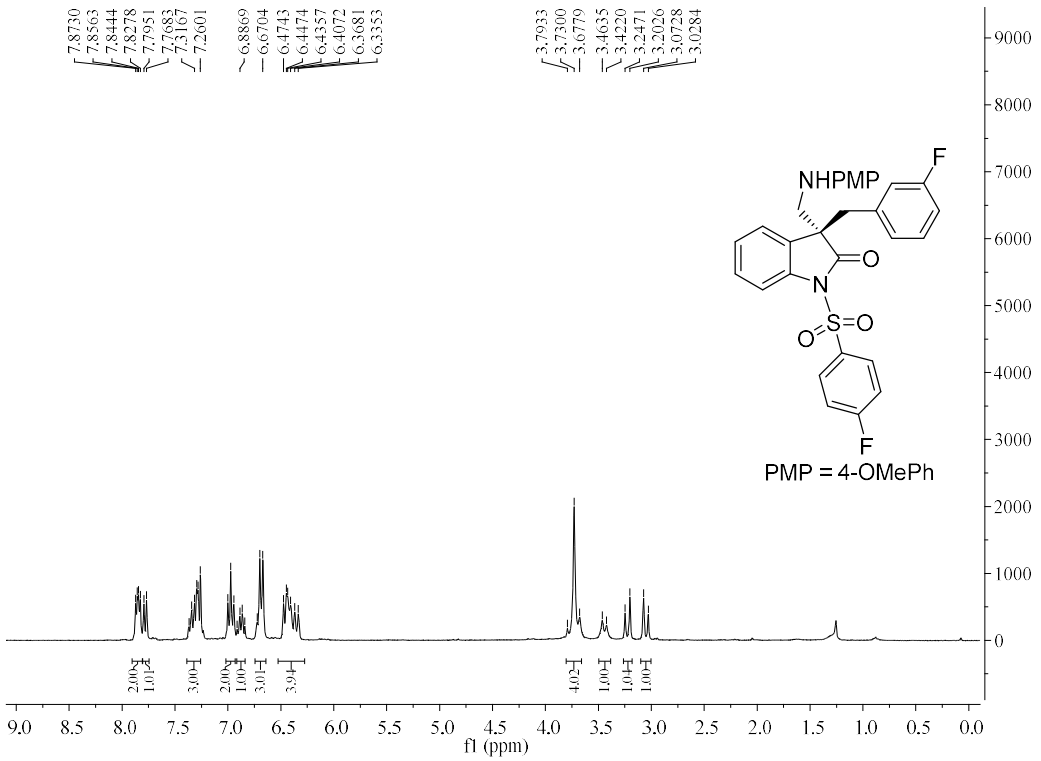
PMP = 4-OMePh
f1 (ppm)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6.4743
6.4474
6.4357
6.4072
6.3681
6.3353
3.7933
3.7300
3.6779
3.4635
3.4220
3.2471
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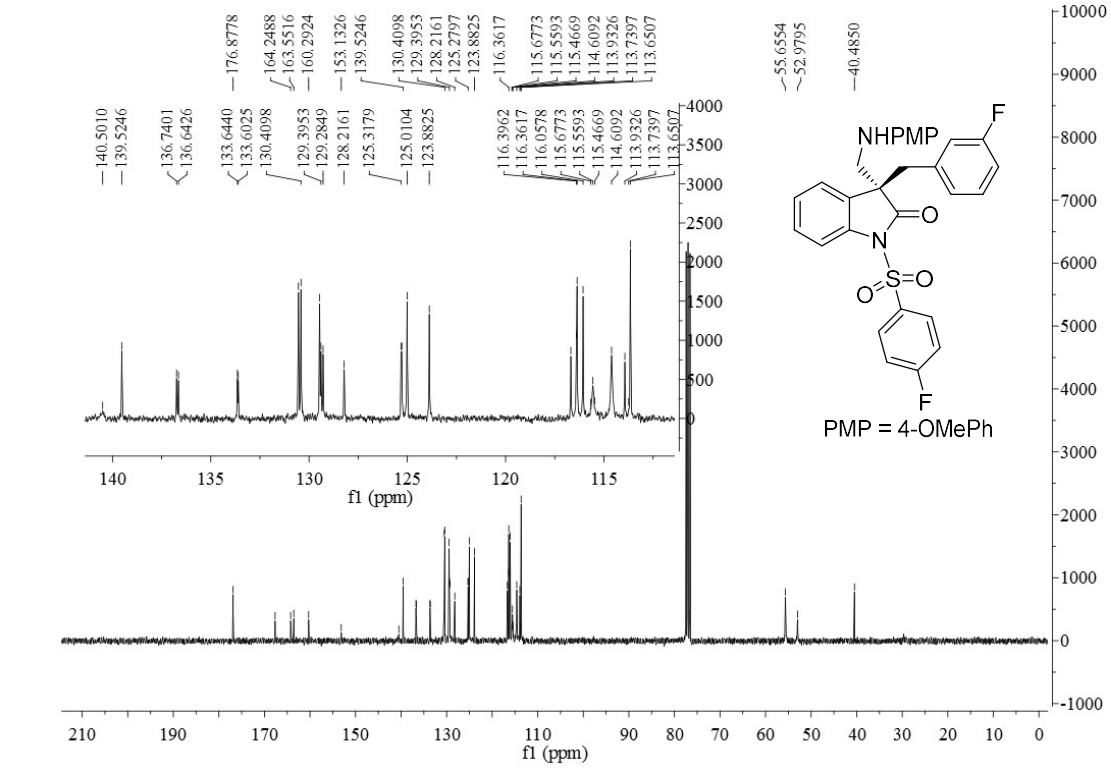
3.0284
NHPMP
F
O
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)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116.3617
115.6773
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115.4669
114.6092
113.9326
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52.9795
40.4850
140.5010
139.5246
136.7401
136.6426
133.6440
133.6025
130.4098
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116.3962
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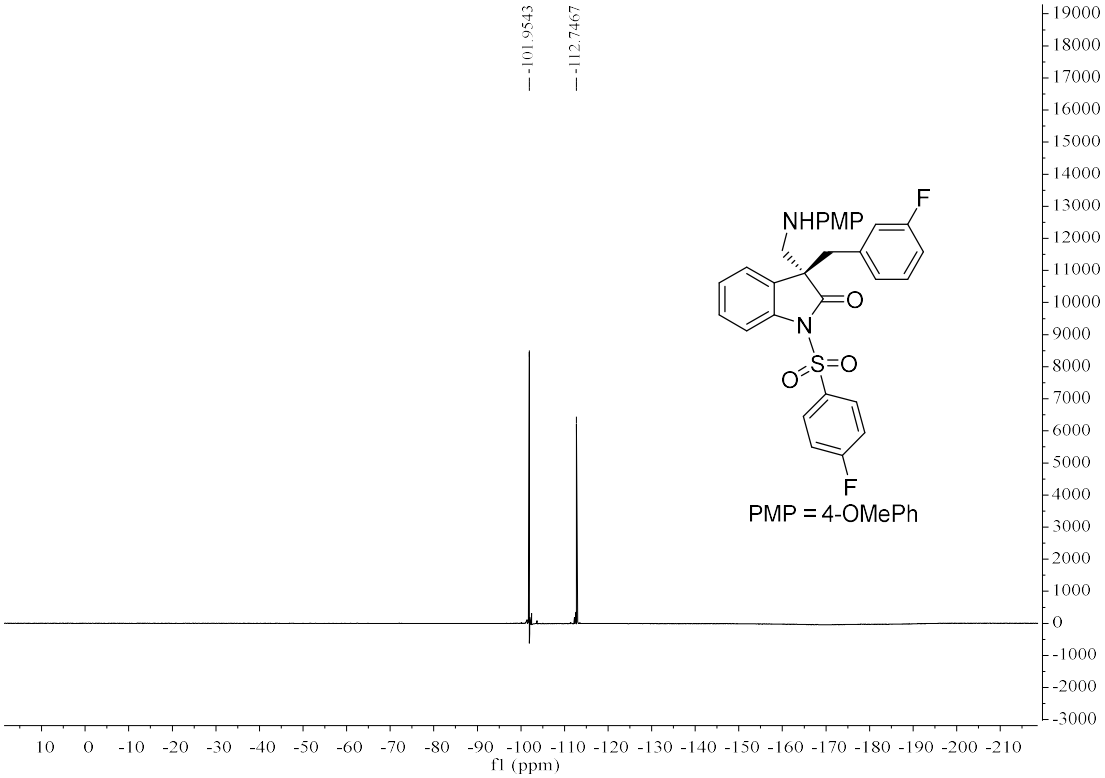
NHPMP
F
O
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)
f1 (ppm)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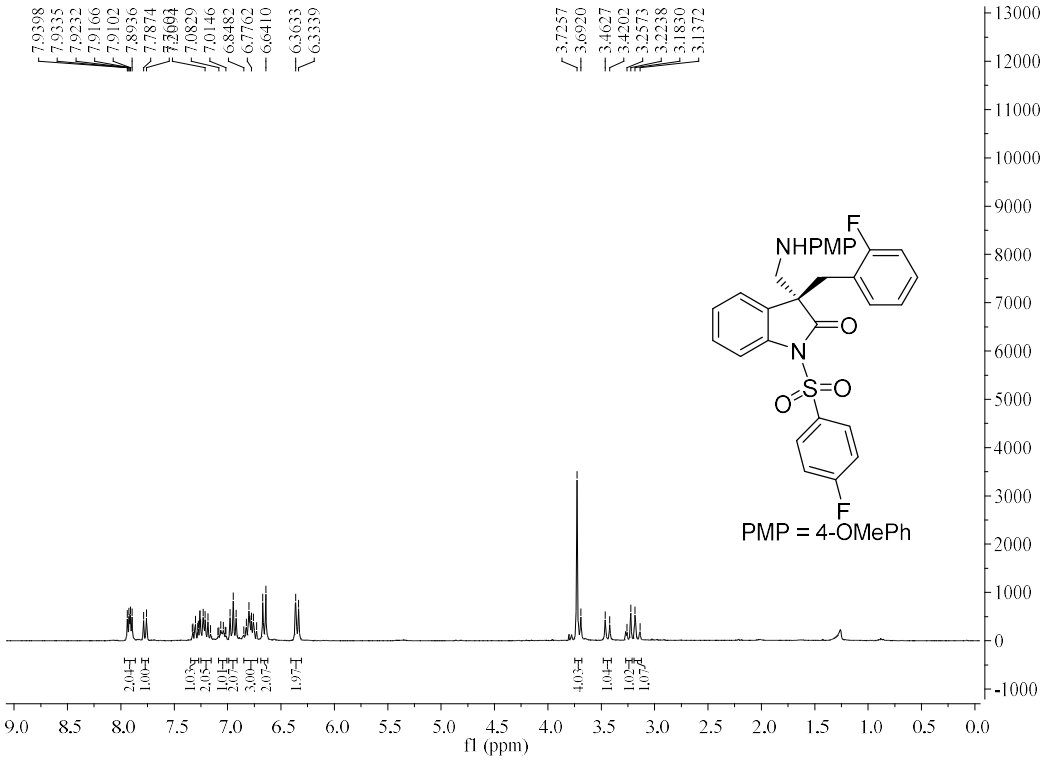
PMP = 4-OMePh
f1 (ppm)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6.6410
6.3633
6.3339
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3.2573
3.2238
3.1830
3.1372
2.04
1.00
1.03
2.05
1.01
2.01
3.00
2.07
1.97
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1.04
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1.07
NHPMP
F
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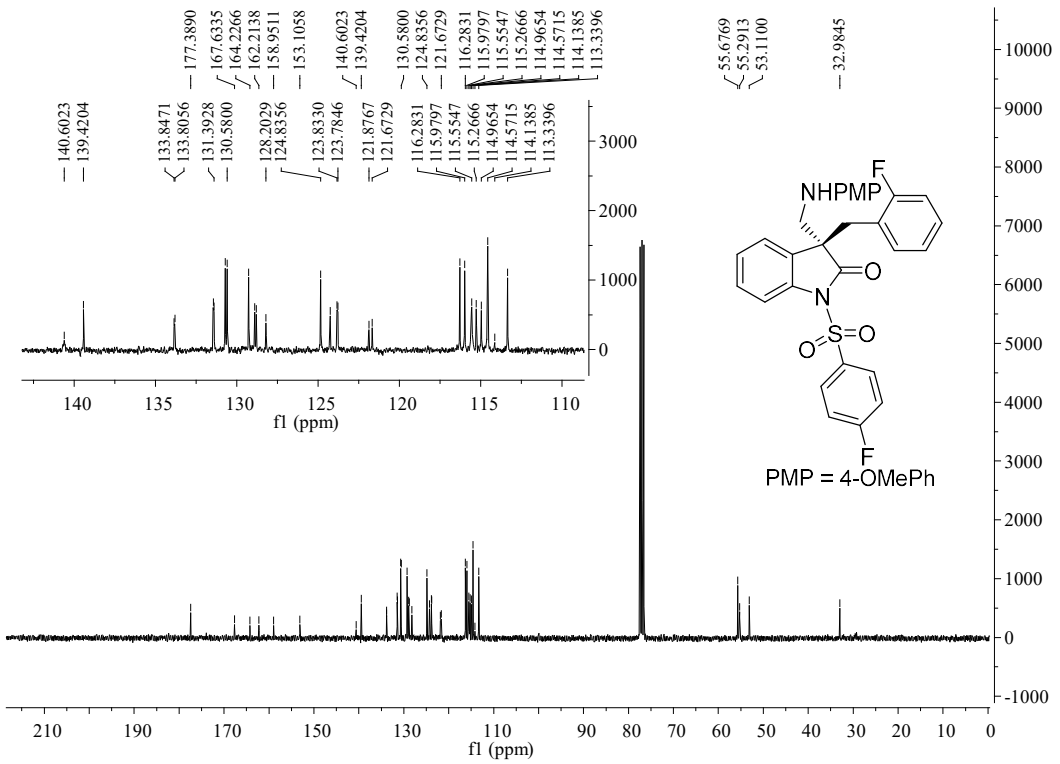
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)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115.9797
115.5547
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55.2913
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fl (ppm)
NHPMP
F
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N
S=O
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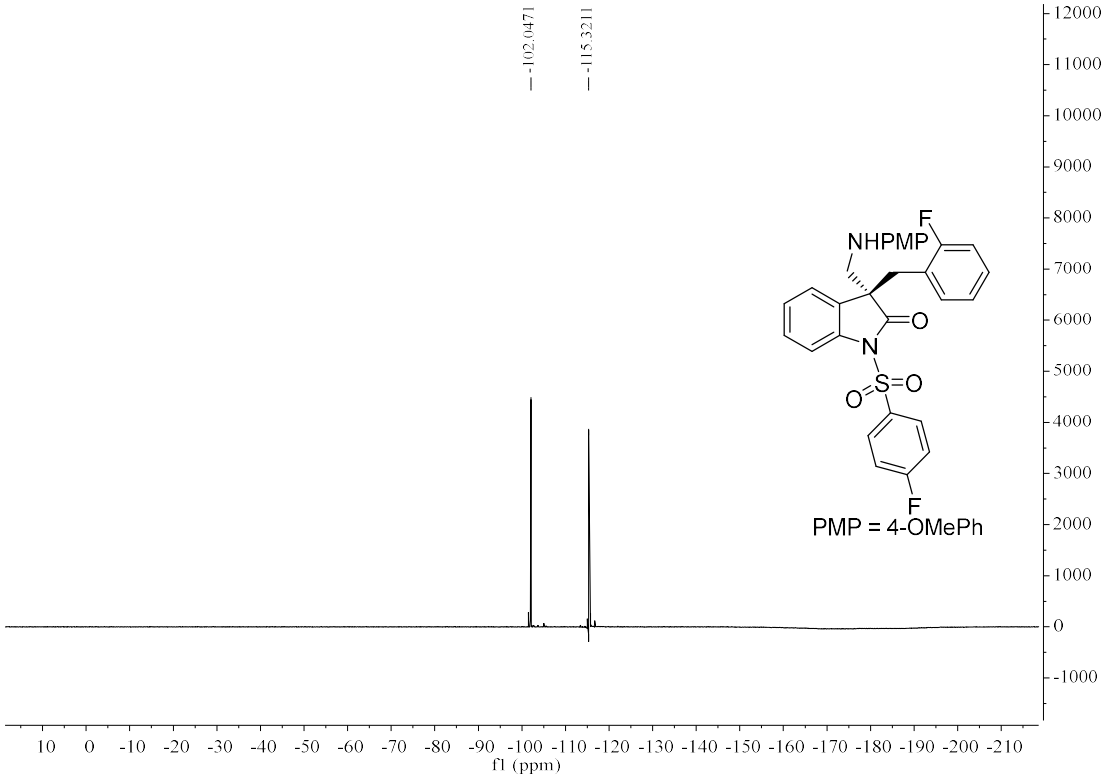
PMP = 4-OMePh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F
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N
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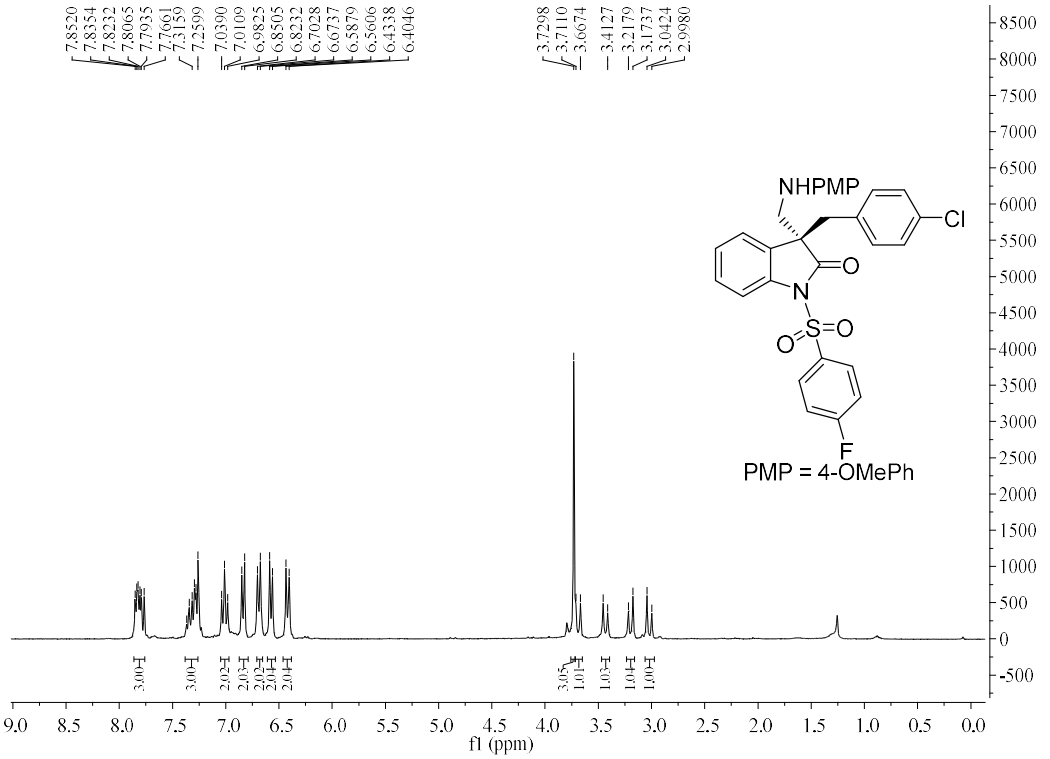
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Cl
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N
S=O
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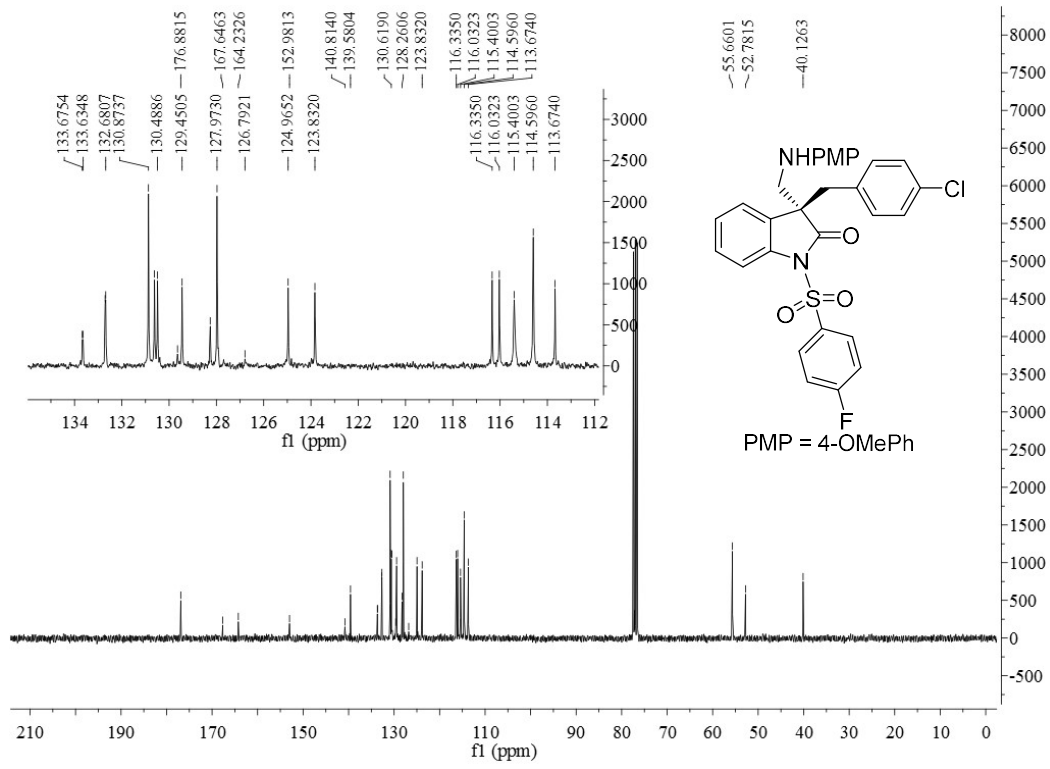
F
PMP = 4-OMePh
f1 (ppm)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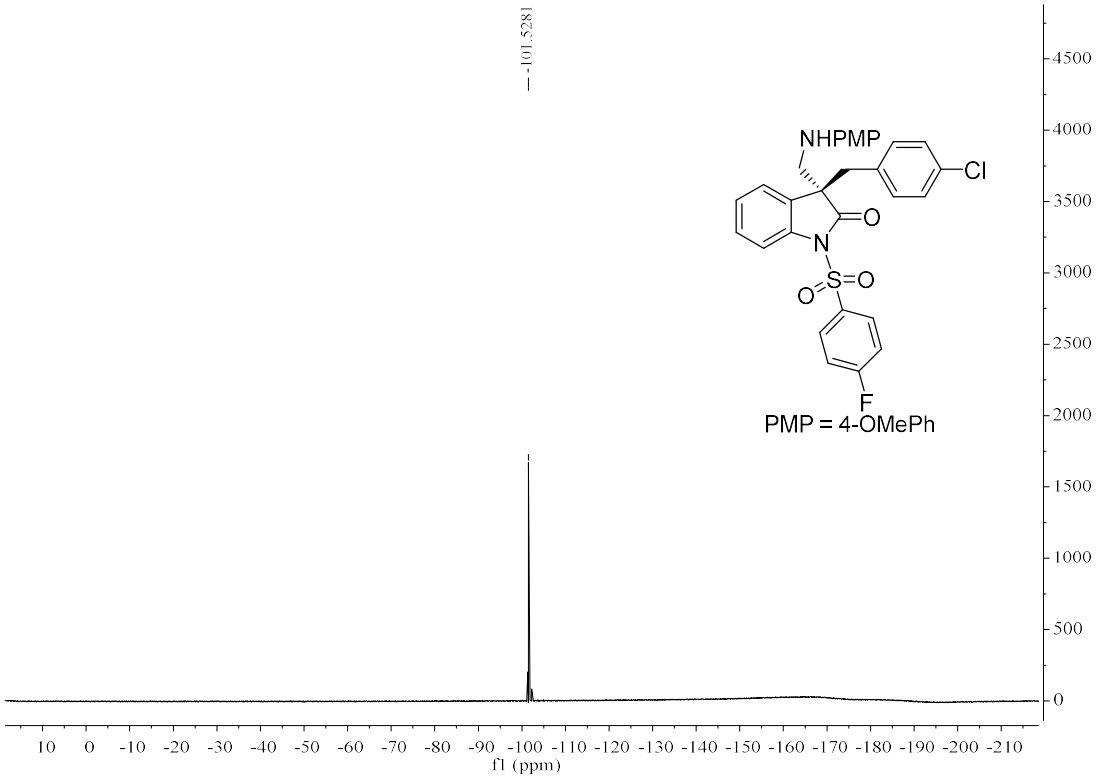
PMP = 4-OMePh
f1 (ppm)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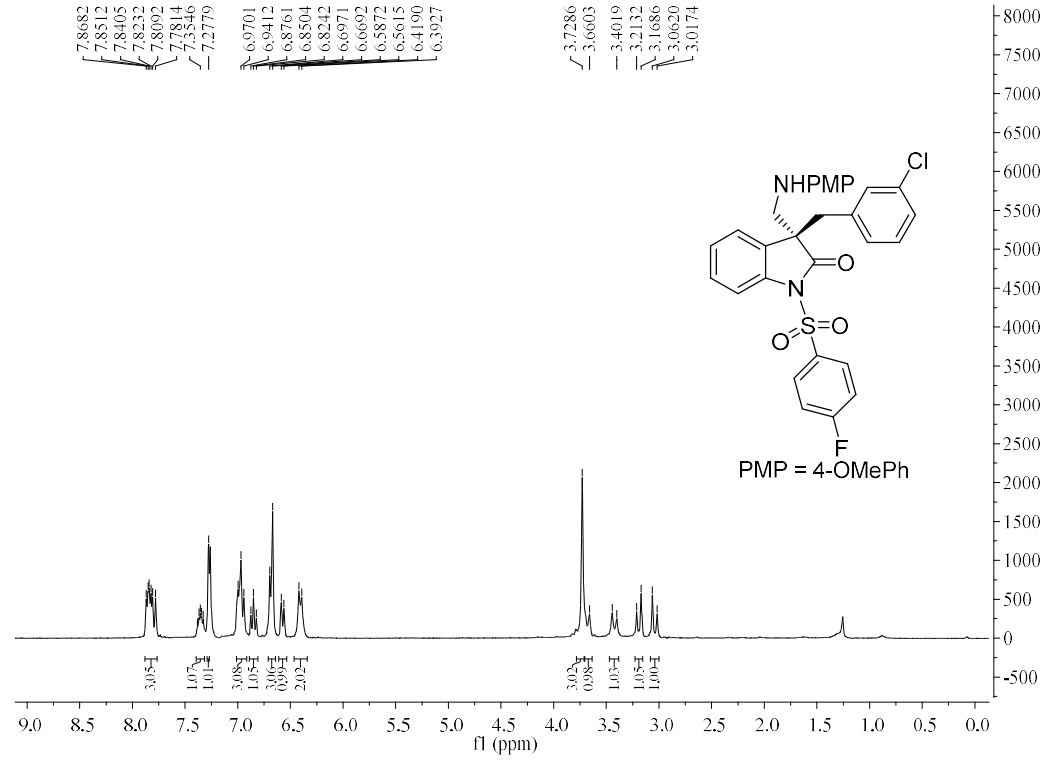
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6.4190
6.3927
3.7286
3.6603
3.4019
3.2132
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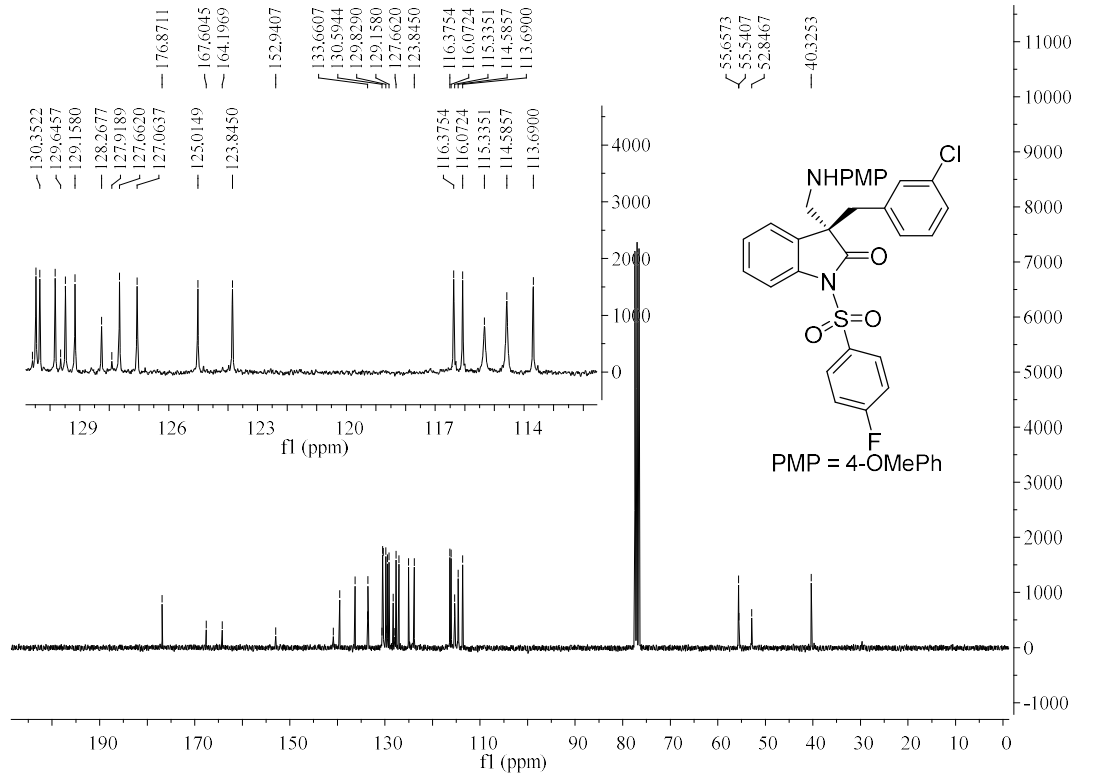
NHPMP
Cl
O
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)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127.0637
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116.3754
116.0724
115.3351
114.5857
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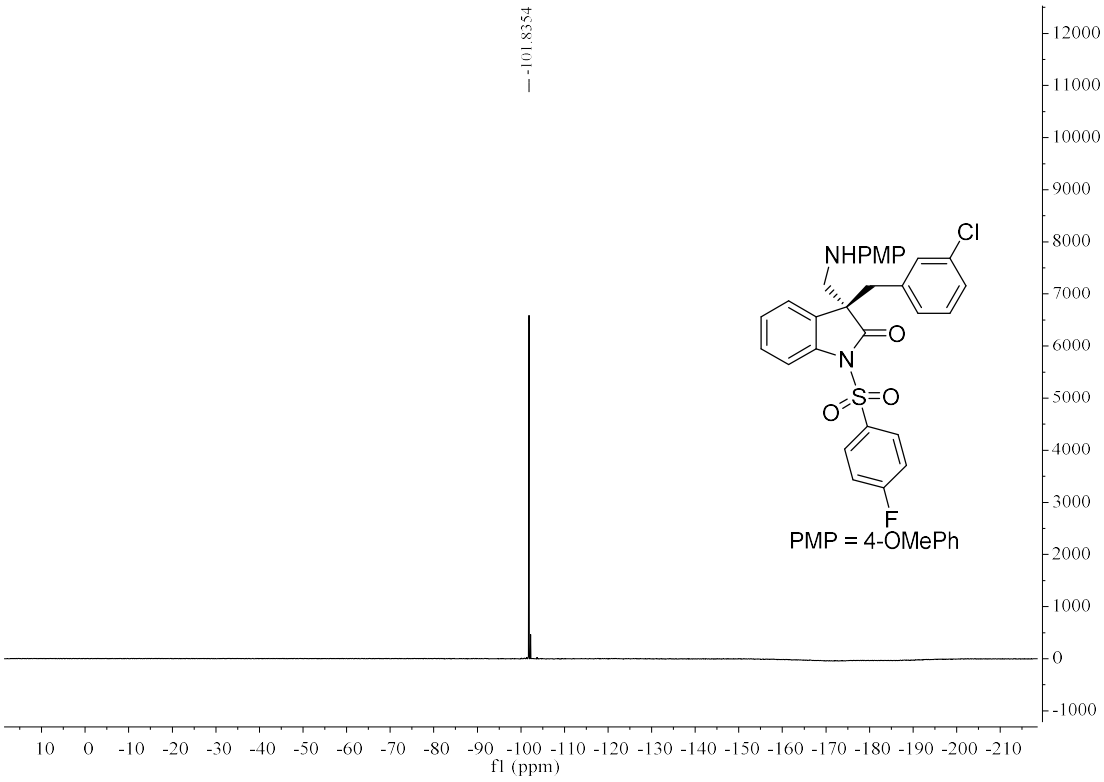
f1 (ppm)
NHPMP
Cl
O
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)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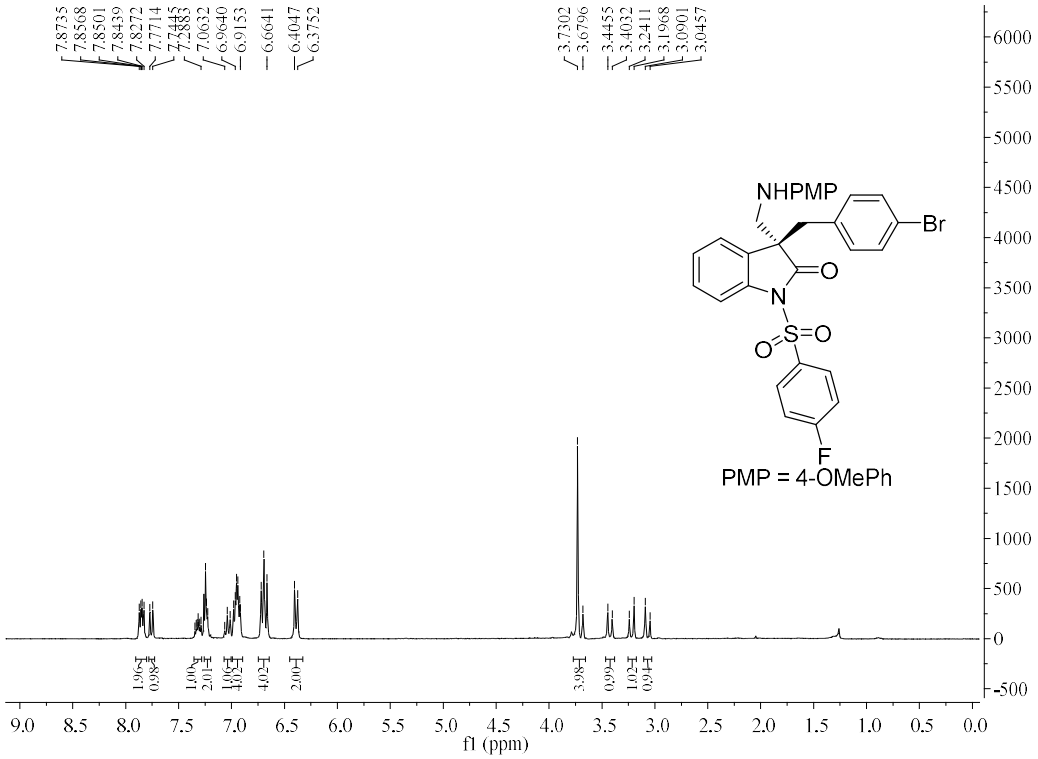
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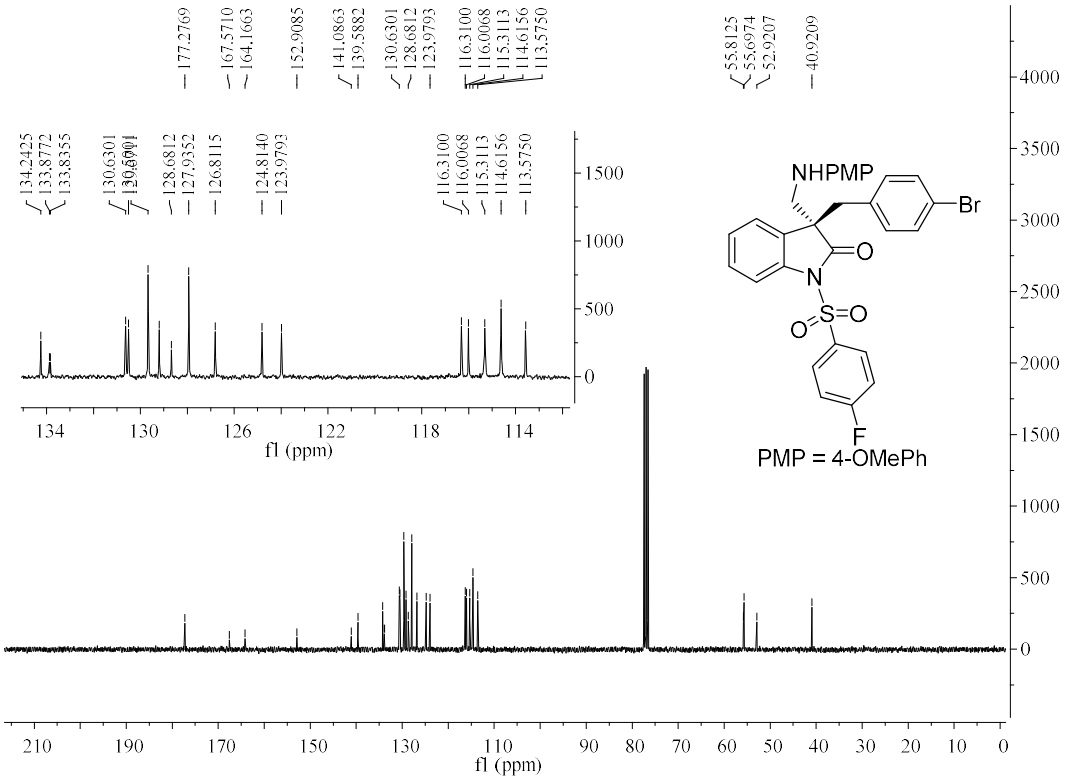
Br
O
N
O=S=O
F
PMP = 4-OMePh
fl (ppm)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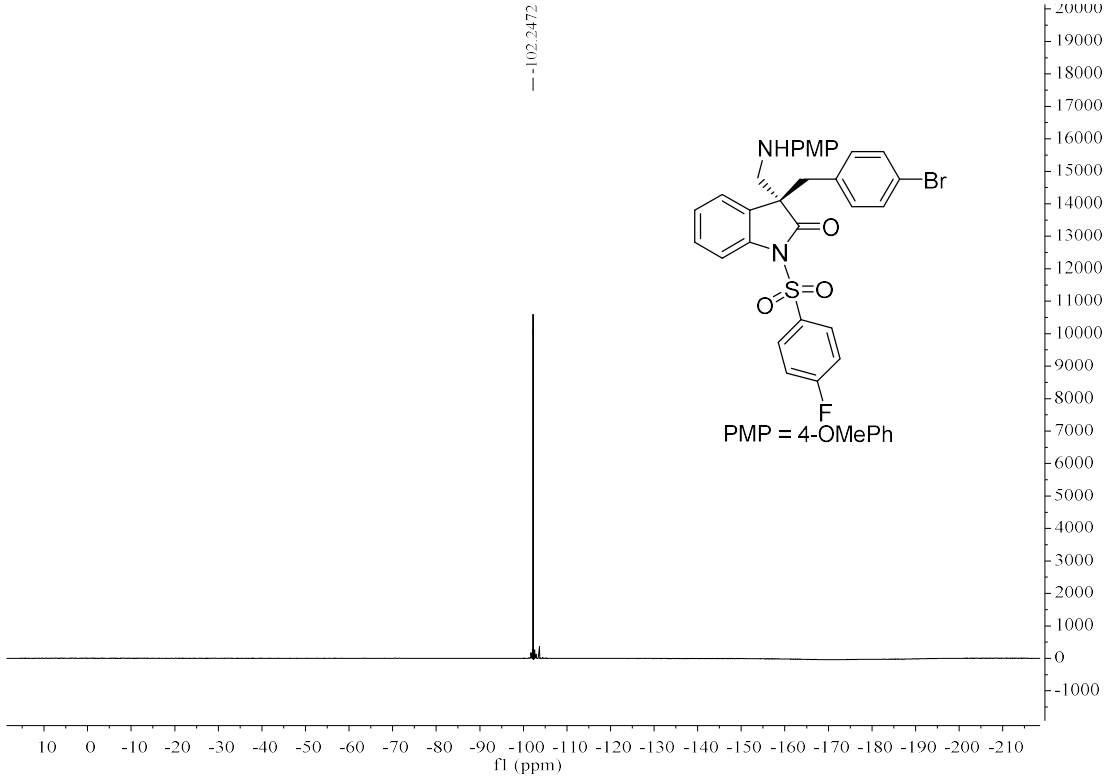
Br
O
N
O=S=O
F
PMP = 4-OMePh
fl (ppm)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O
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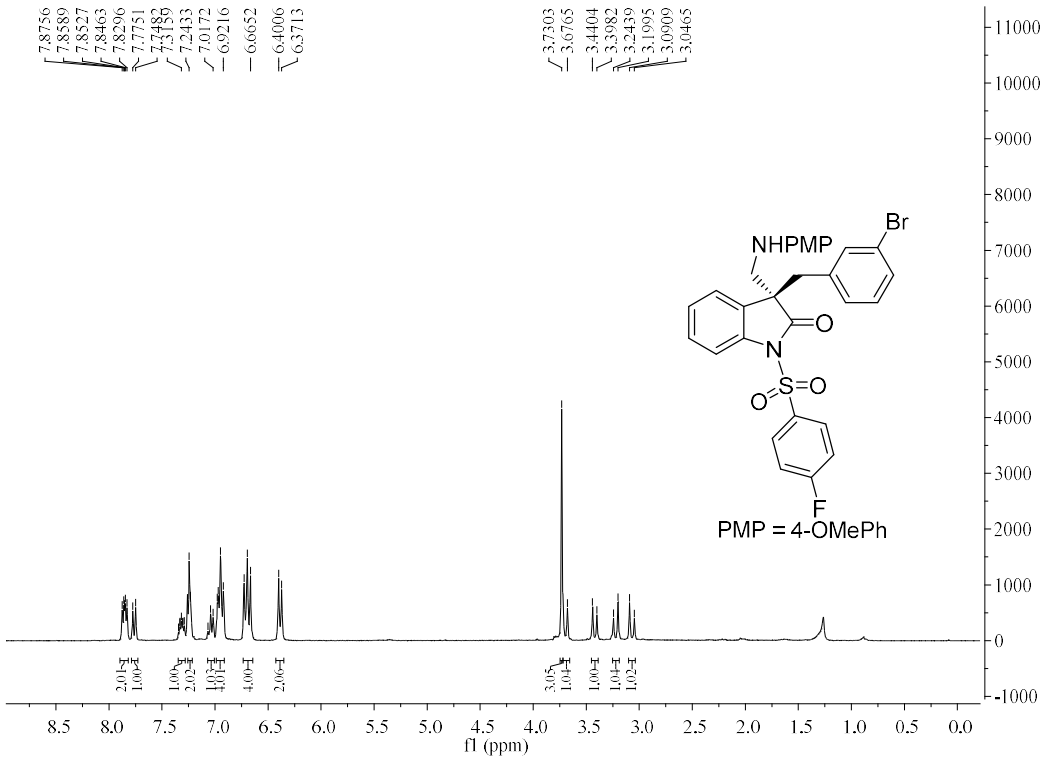
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6.6652
6.4006
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3.7303
3.6765
3.4404
3.3982
3.2439
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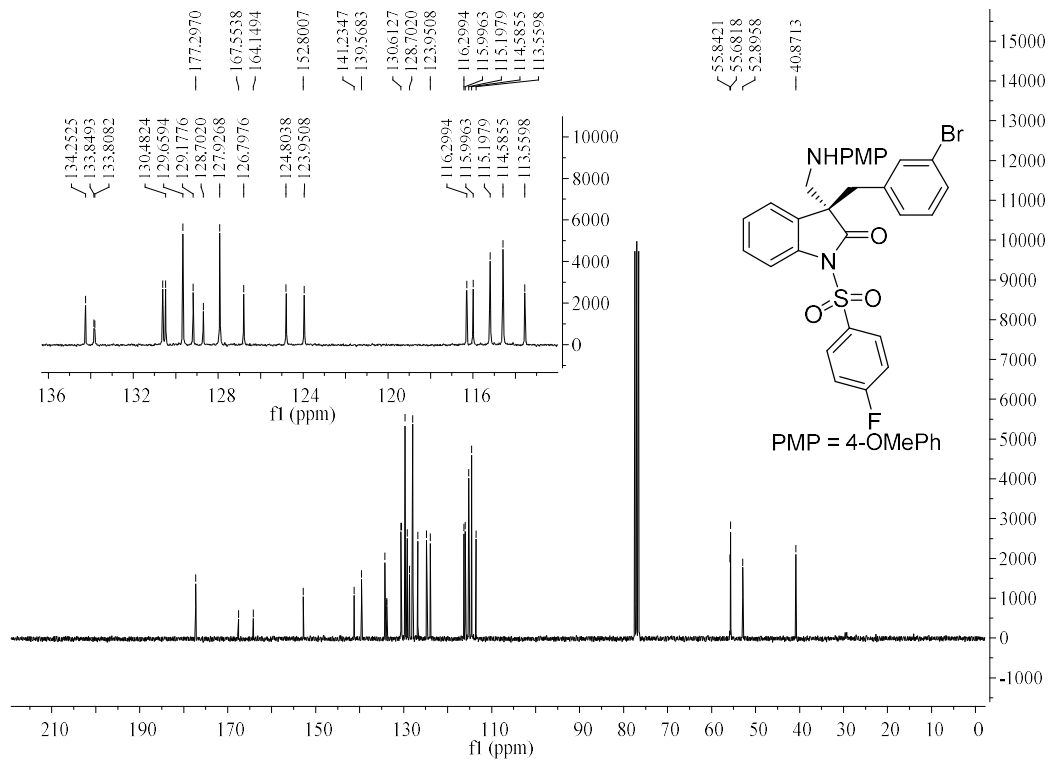
3.0465
NHPMP
Br
O
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)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129.1776
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124.8038
123.9508
116.2994
115.9963
115.1979
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NHPMP
Br
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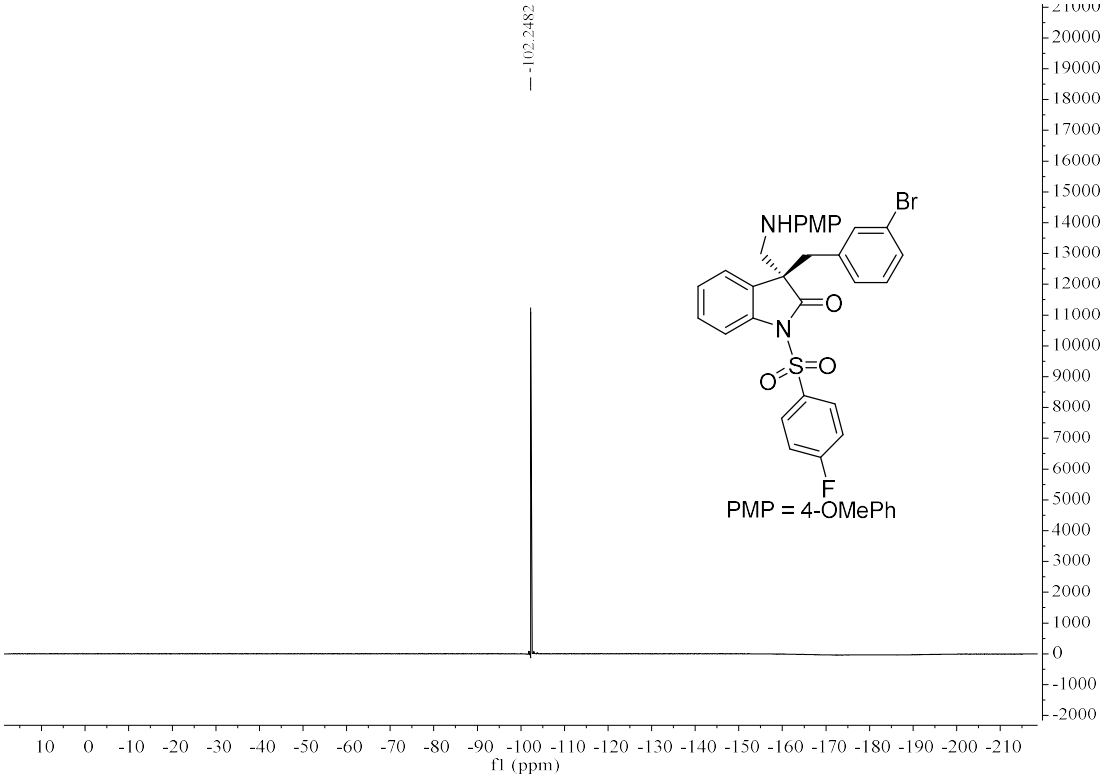
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)
f1 (ppm)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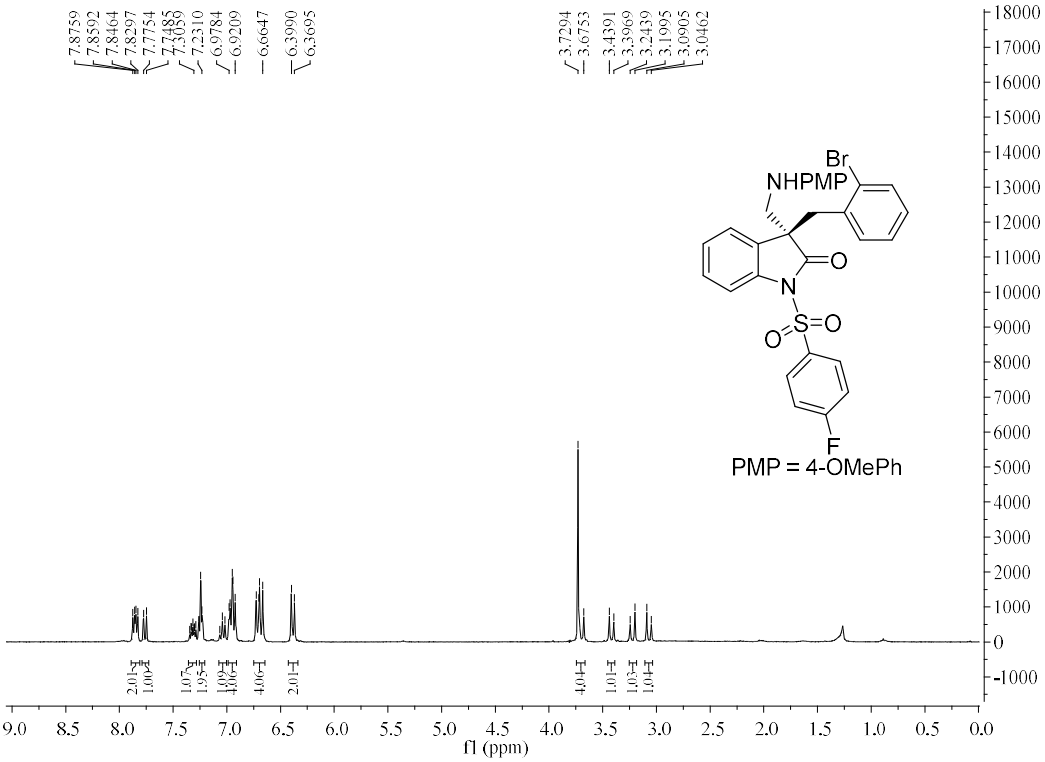
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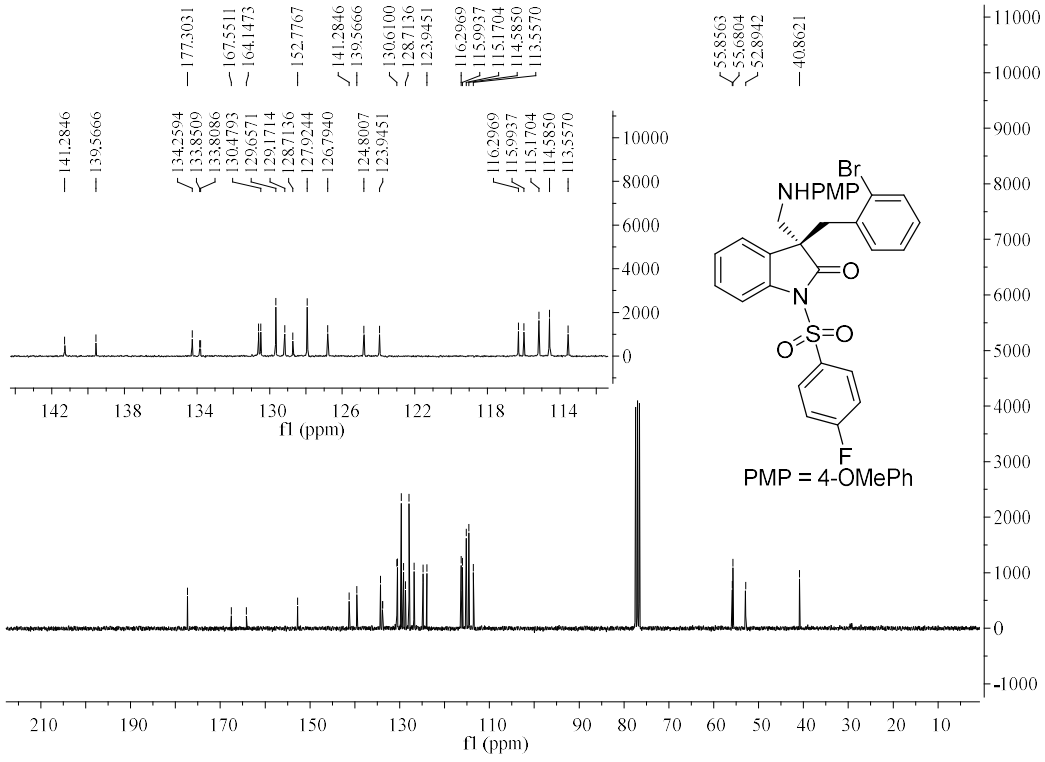
Br
NHPMP
O
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)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Br
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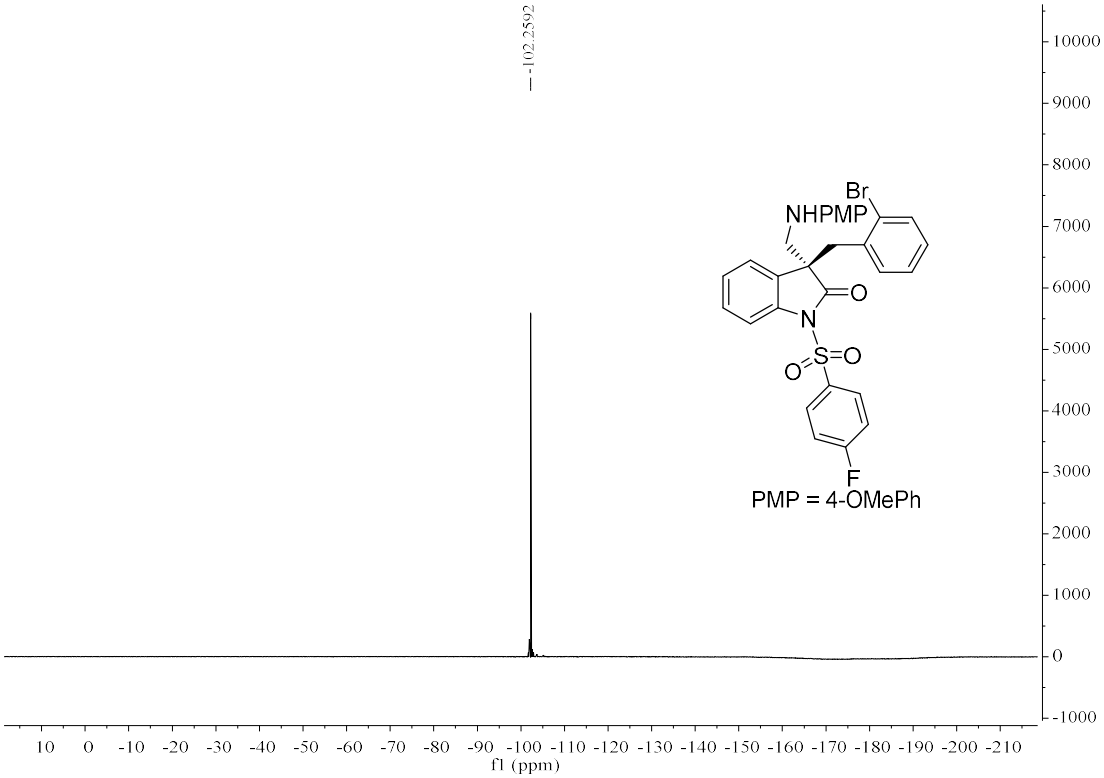
PMP = 4-OMePh
f1 (ppm)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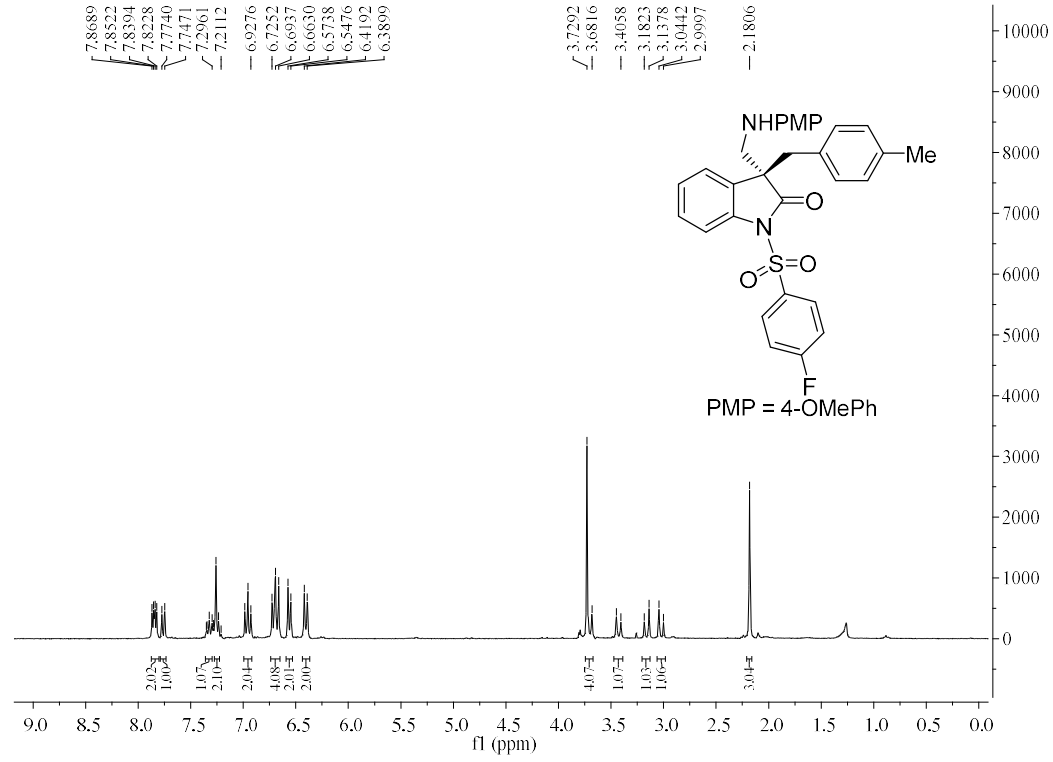
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6.5476
6.4192
6.3899
3.7292
3.6816
3.4058
3.1823
3.1378
3.0442
2.9997
2.1806
NHPMP
Me
O
N
S=O
O
F
PMP = 4-OMePh
2.02
1.00
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4.08
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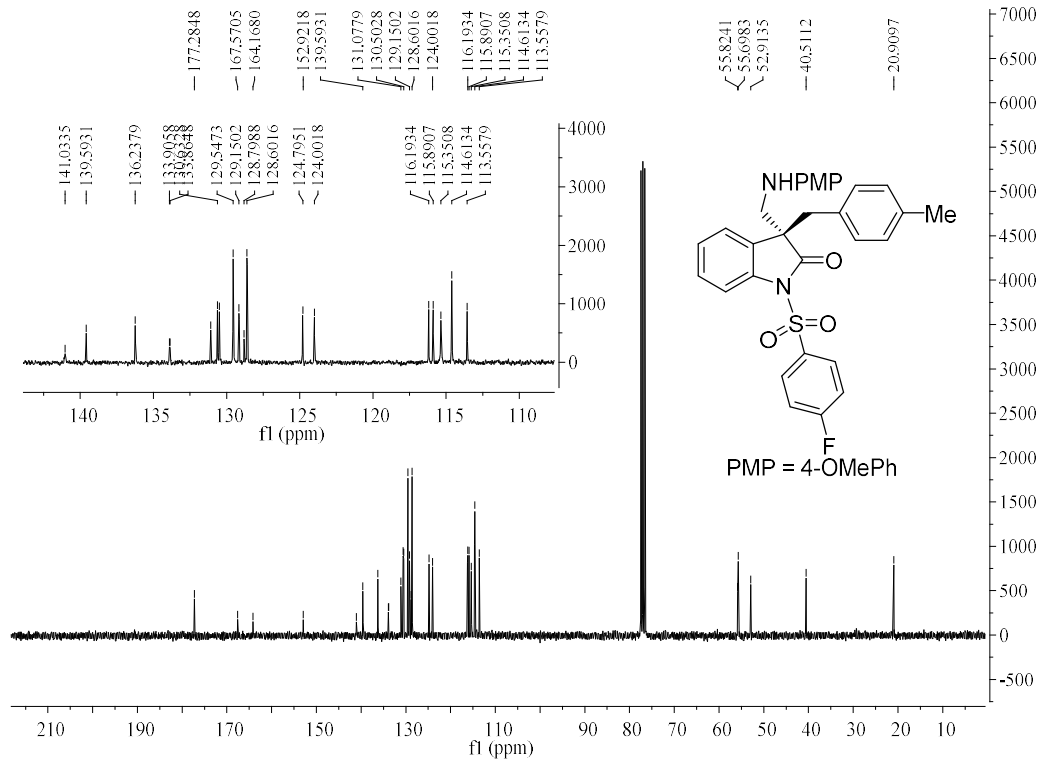
2.00
4.07
1.07
1.03
1.06
3.04
f1 (ppm)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Me
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N
S=O
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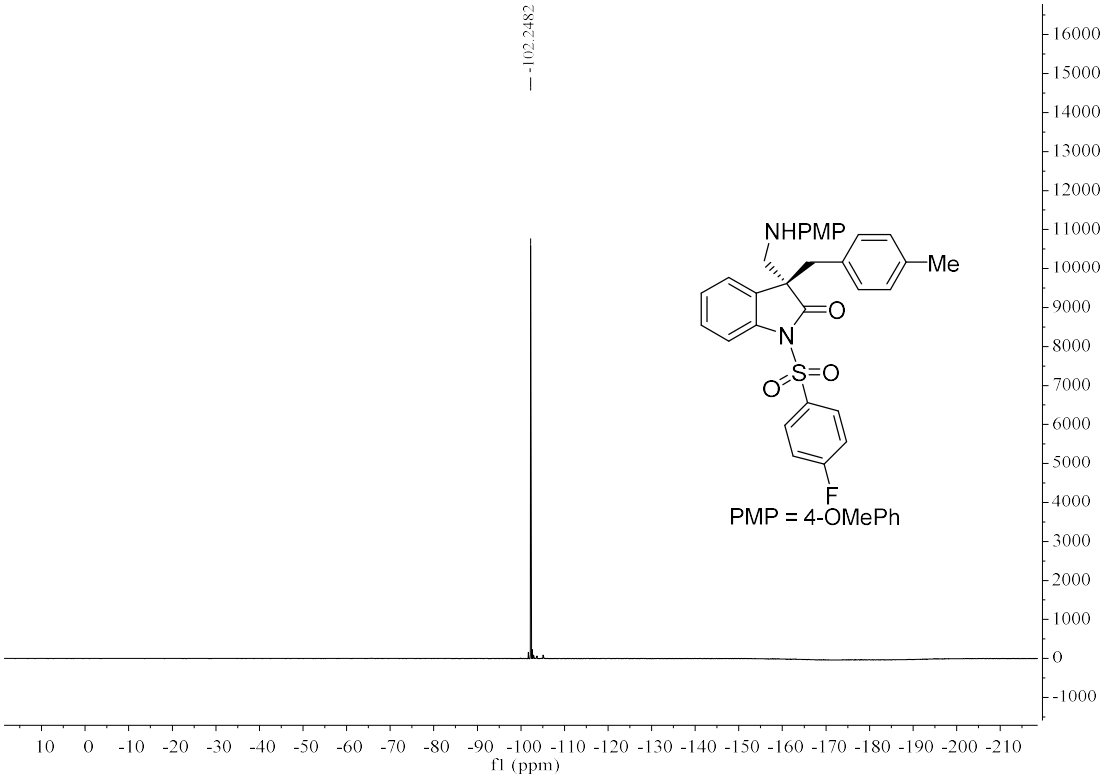
F
PMP = 4-OMePh
f1 (ppm)
f1 (ppm)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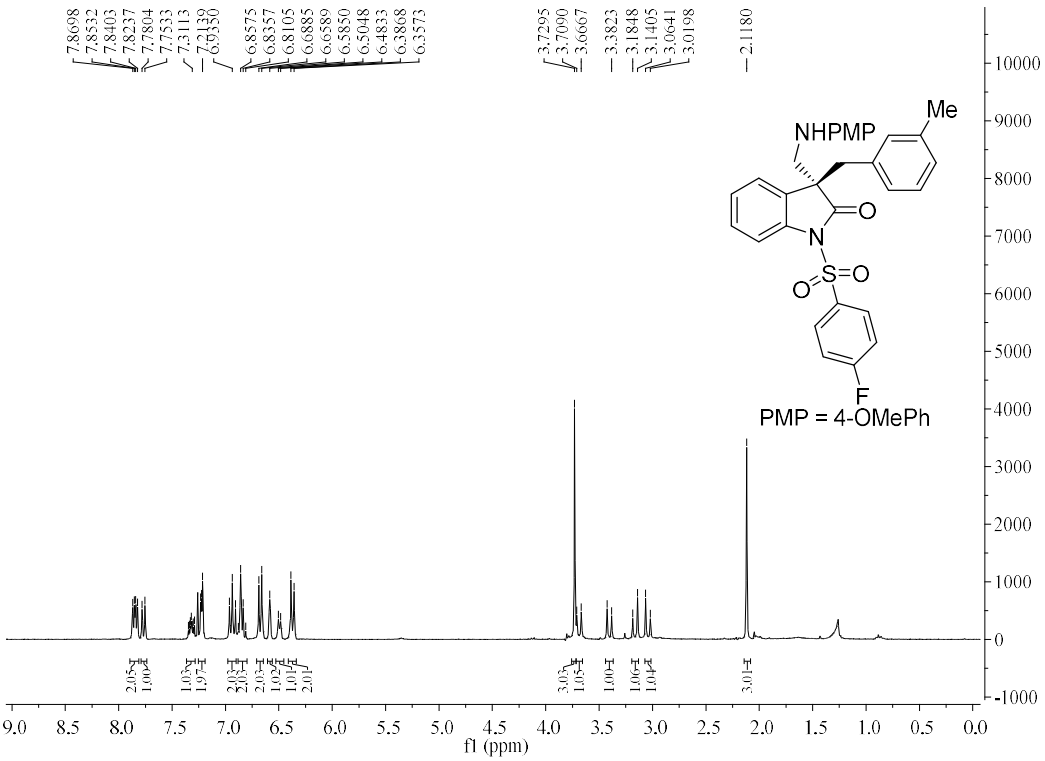
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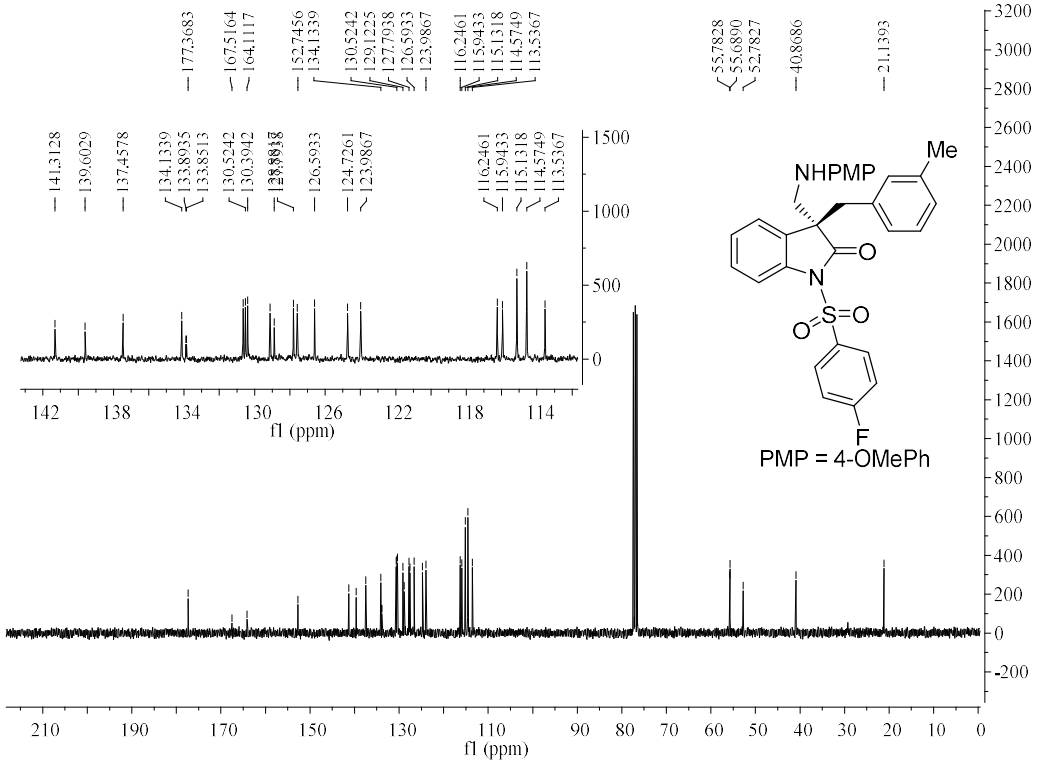
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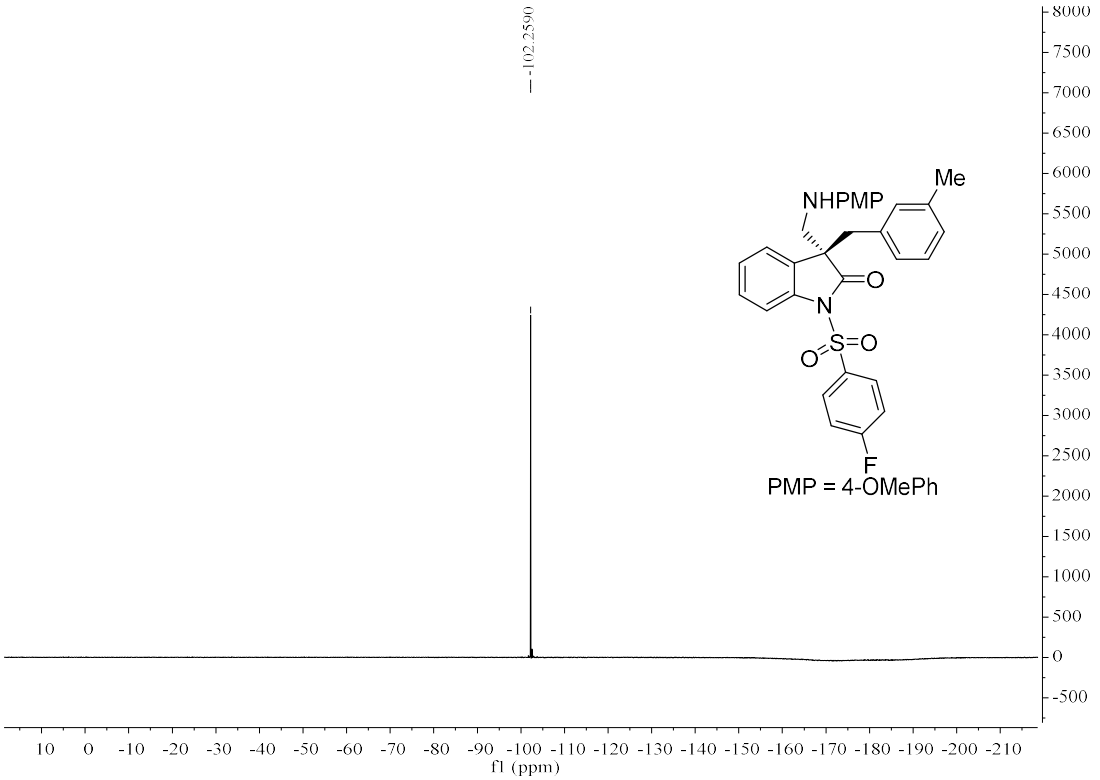
PMP = 4-OMePh
f1 (ppm)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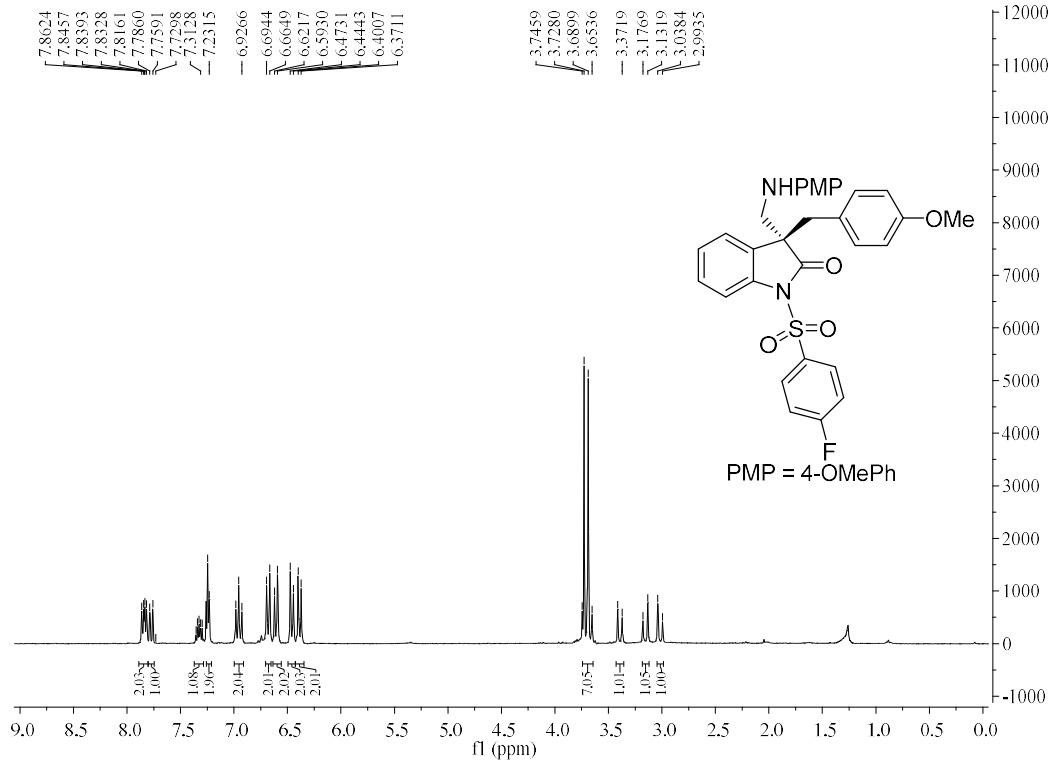
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3.7459
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3.3719
3.1769
3.1319
3.0384
2.9935
NHPMP
OMe
O
N
O=S=O
F
PMP = 4-OMePh
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1.00
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2.03
2.01
7.05
1.01
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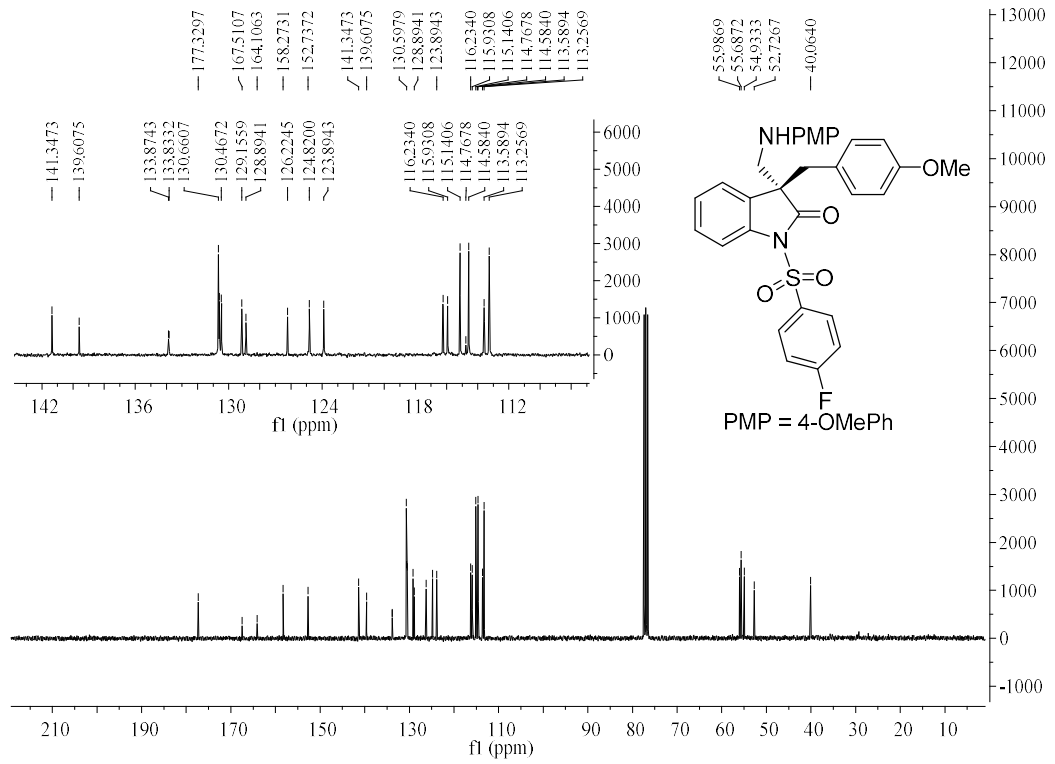
1.00
f1 (ppm)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113.2569
55.9869
55.6872
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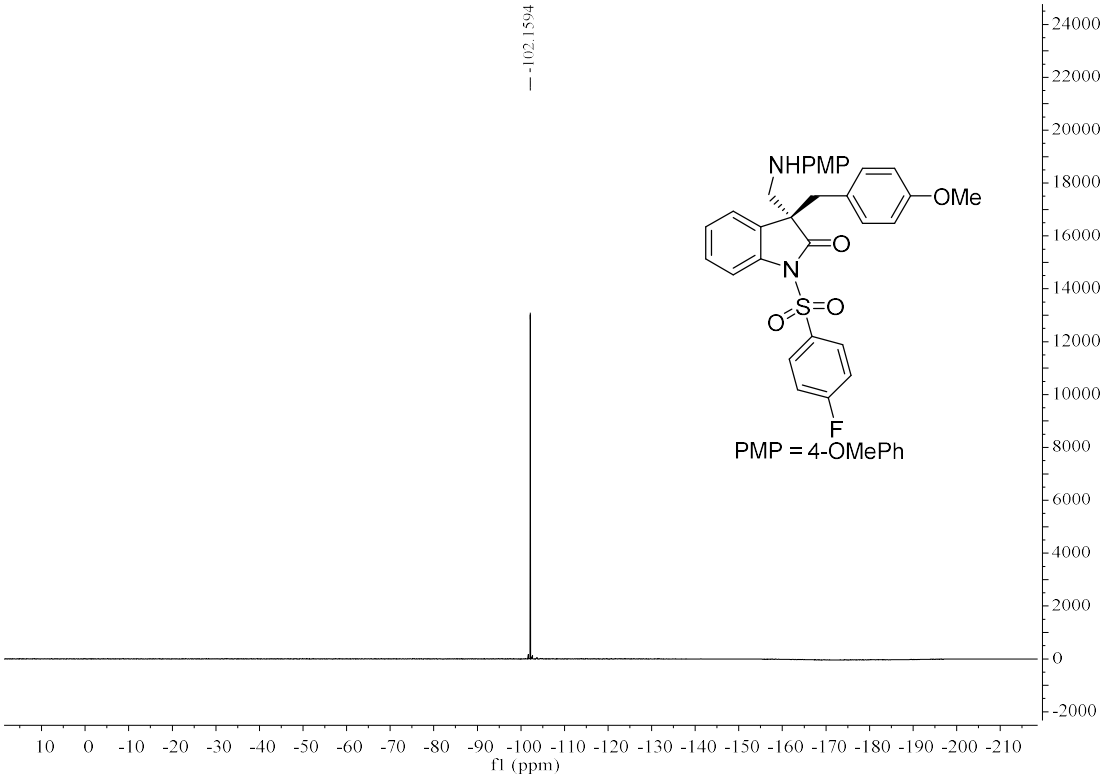
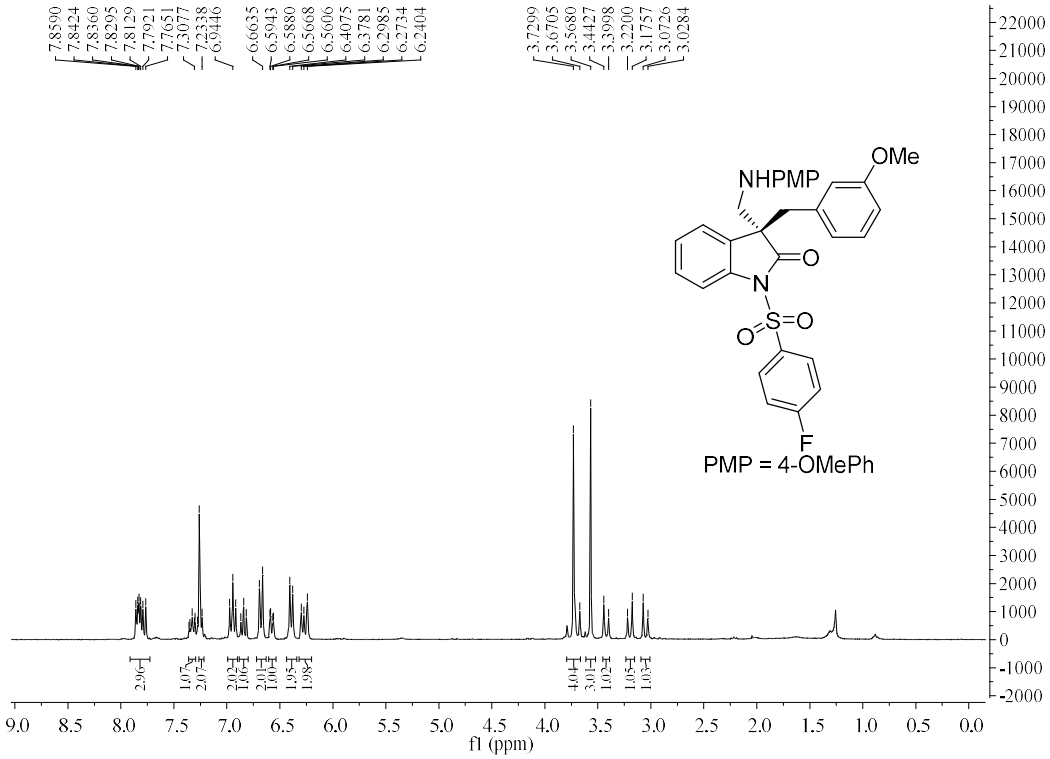
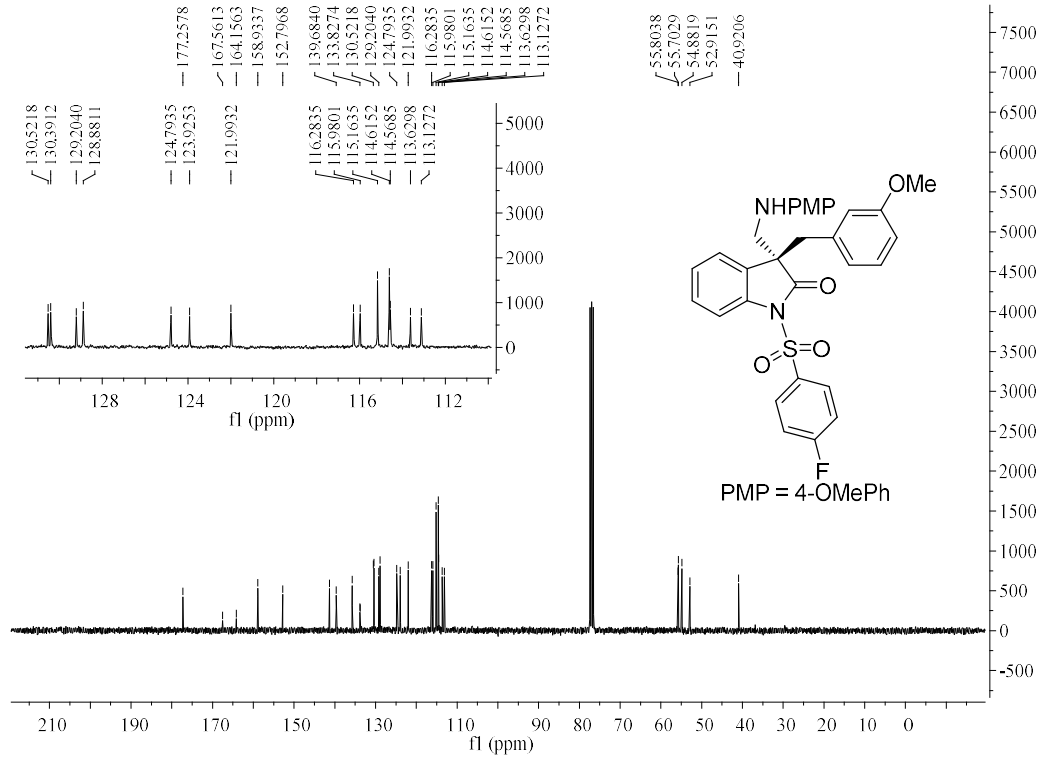
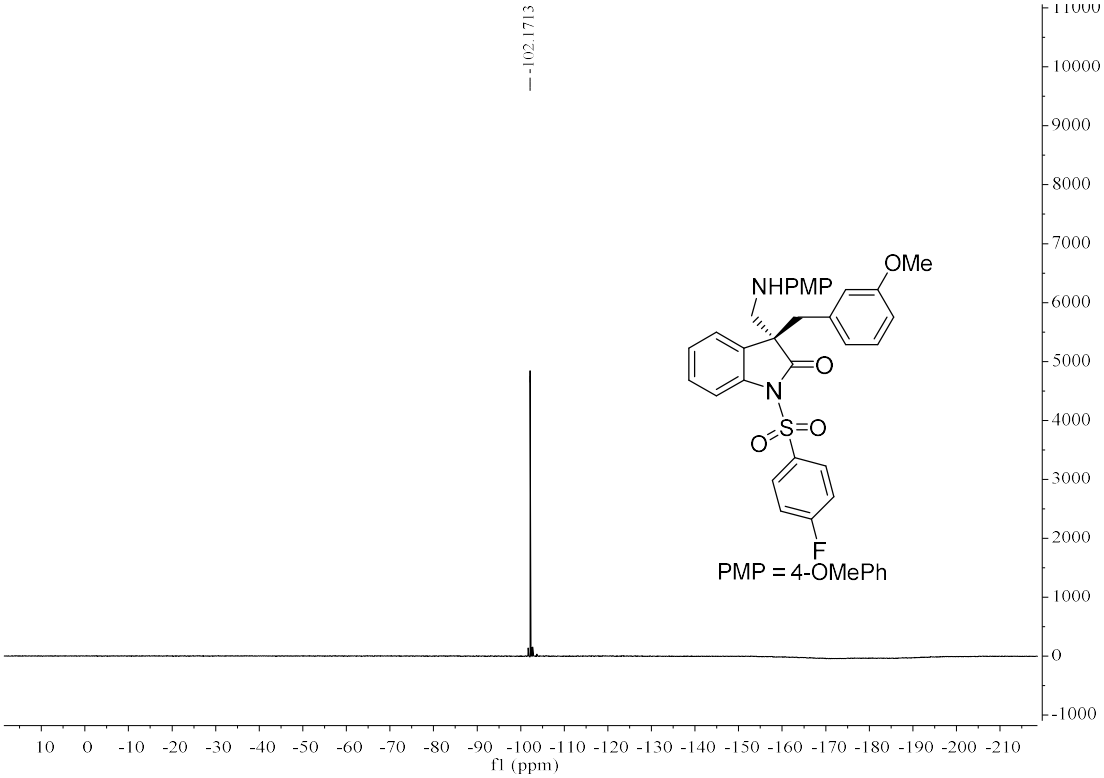
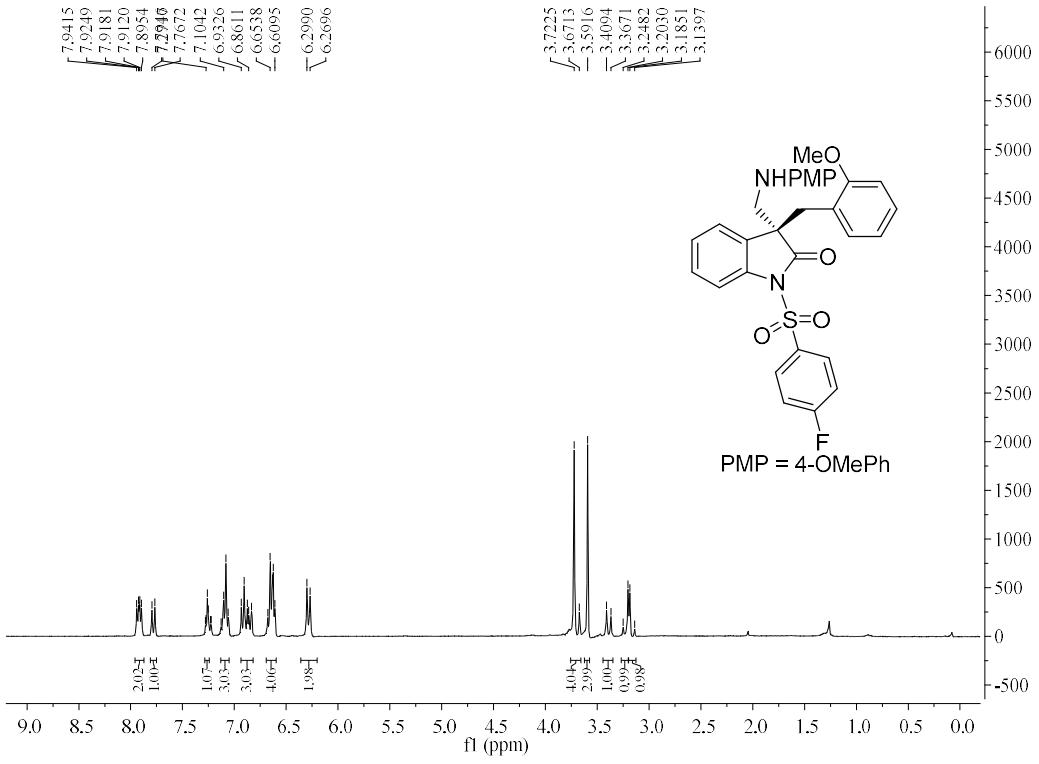
NHPMP
OMe
O
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)

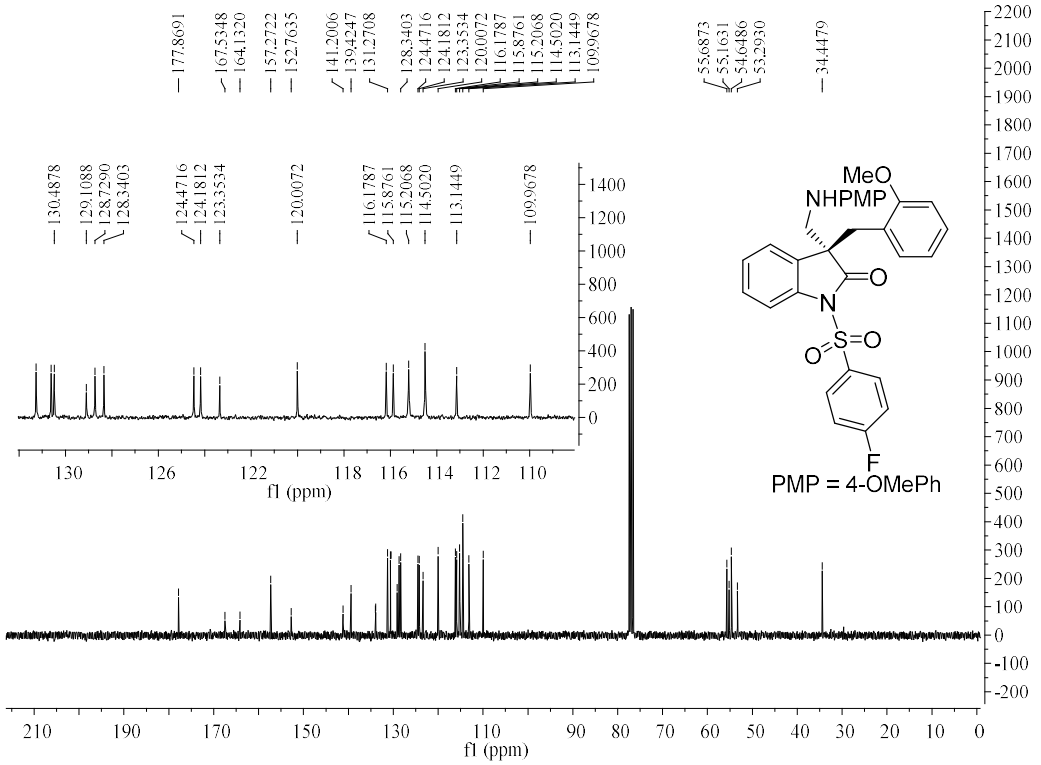

-102.1594
NHPMP
OMe
O
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)

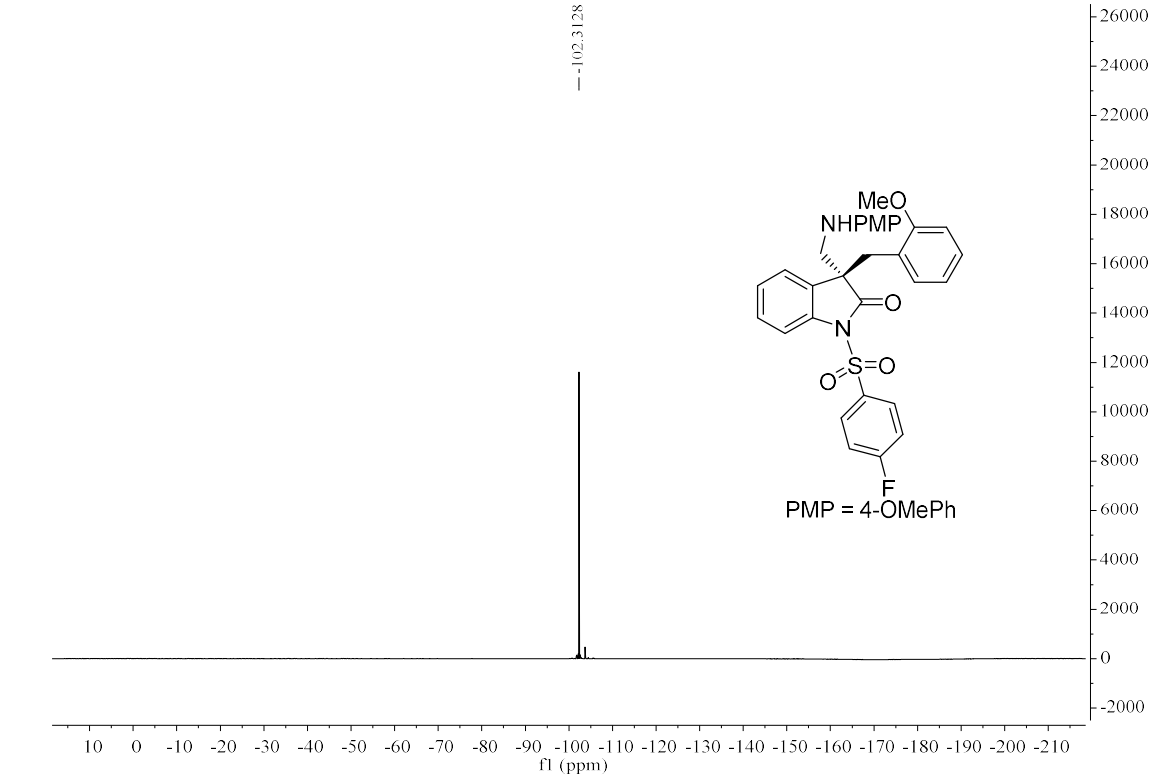

NHPMP
OMe
O
N
S=O
O
F
PMP = 4-OMePh
fl (ppm)

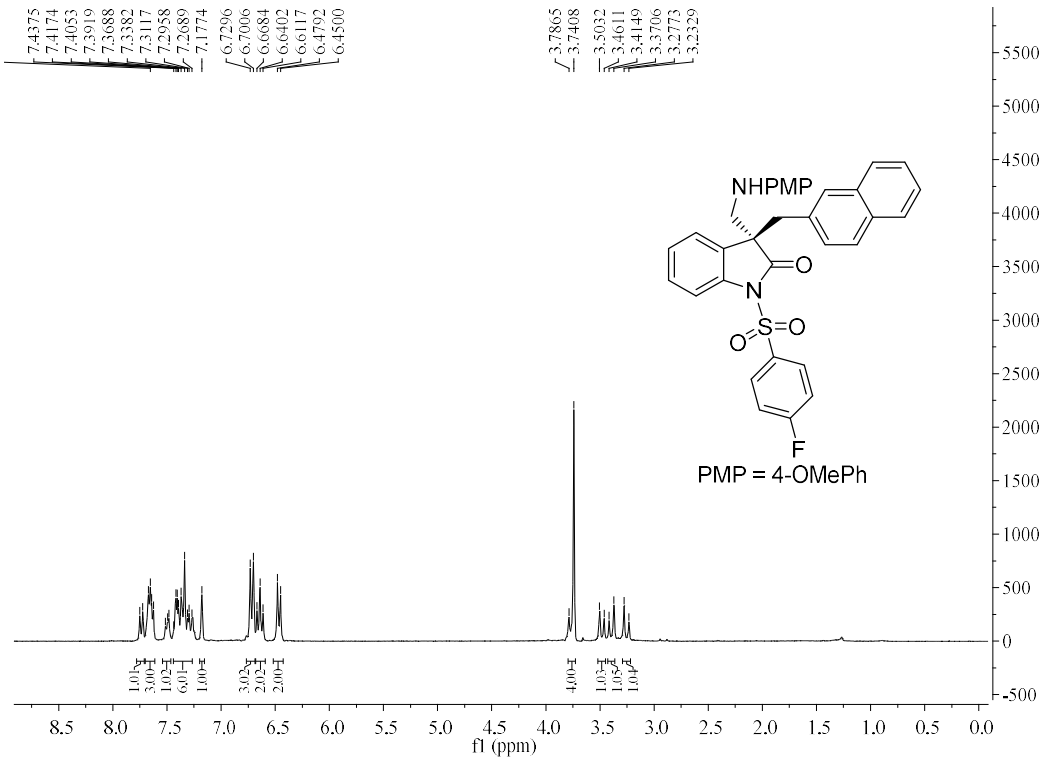

NHPMP
OMe
O
N
S=O
O
F
PMP = 4-OMePh
fl (ppm)


-102.1713
NHPMP
OMe
O
N
S
O
O
F
PMP = 4-OMePh
f1 (ppm)


7.9415
7.9249
7.9181
7.9120
7.8954
7.7672
7.1042
6.9326
6.8611
6.6538
6.6095
6.2990
6.2696
3.7225
3.6713
3.5916
3.4094
3.3671
3.2482
3.2030
3.1851
3.1397
2.02
1.00
1.07
3.05
3.03
4.06
1.98
4.04
2.99
1.00
0.99
0.98
MeO
NHPMP
O
N
S
O
O
F
PMP = 4-OMePh
f1 (ppm)


177.8691
167.5348
164.1320
157.2722
152.7635
141.2006
139.4247
131.2708
128.3403
124.4716
124.1812
123.3534
120.0072
116.1787
115.8761
115.2068
114.5020
113.1449
109.9678
55.6873
55.1631
54.6486
53.2930
34.4479
130.4878
129.1088
128.7290
128.3403
fl (ppm)
MeO
NHPMP
O
N
O=S=O
F
PMP = 4-OMePh


-102.3128
fl (ppm)
MeO
NHPMP
O
N
O=S=O
F
PMP = 4-OMePh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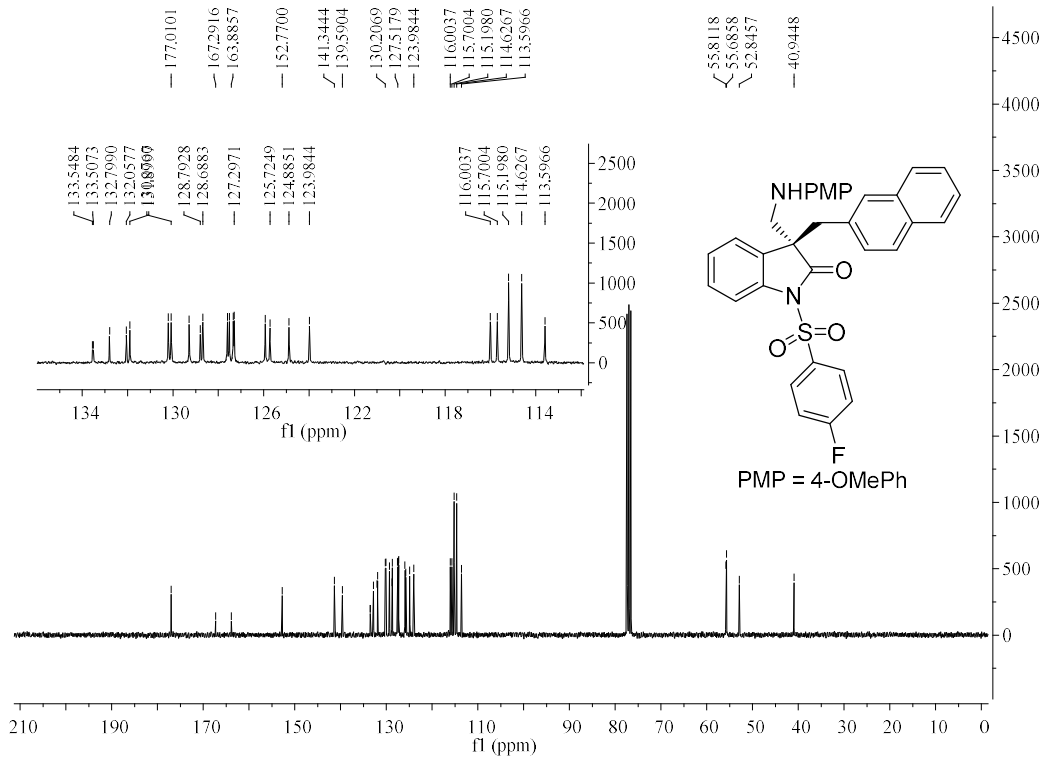
7.4174
7.4053
7.3919
7.3688
7.3382
7.3117
7.2958
7.2689
7.1774
6.7296
6.7006
6.6684
6.6402
6.6117
6.4792
6.4500
3.7865
3.7408
3.5032
3.4611
3.4149
3.3706
3.2773
3.2329
NHPMP
O
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)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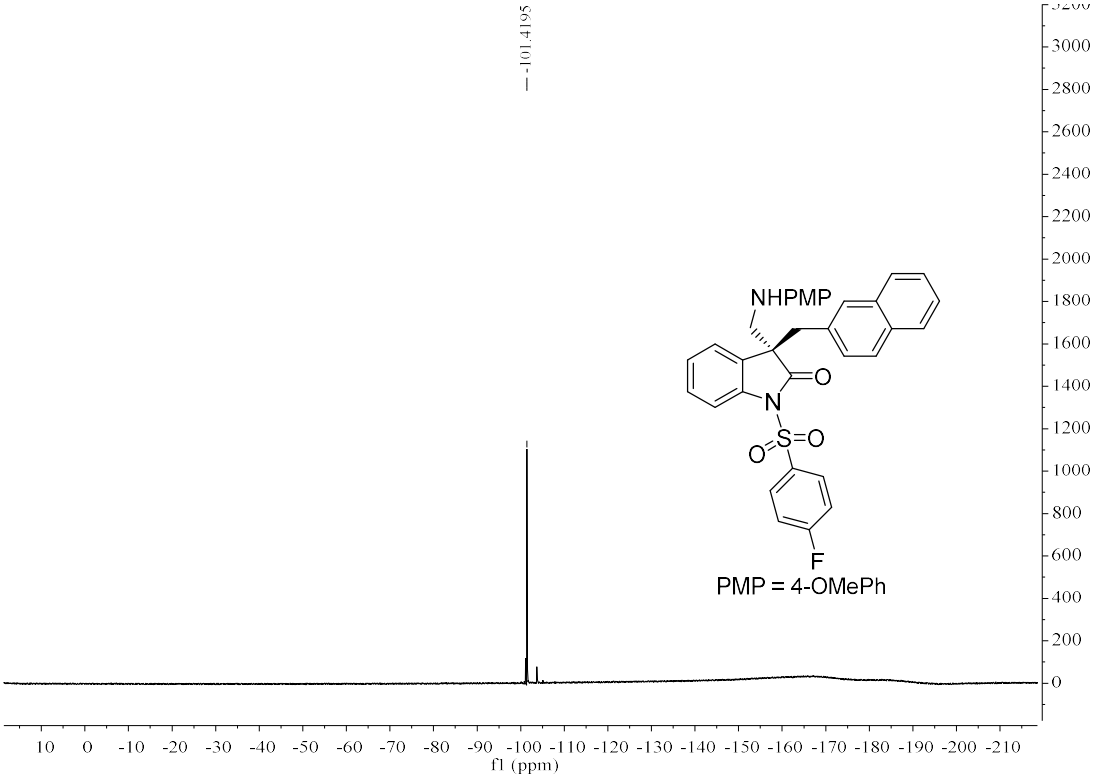
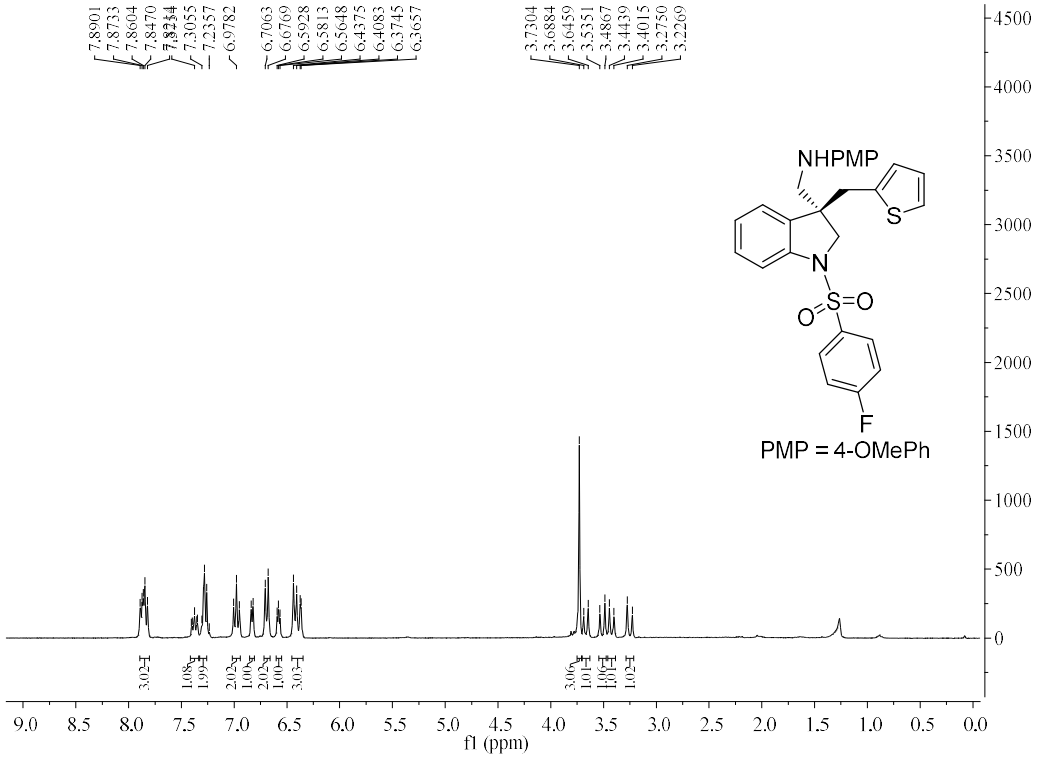
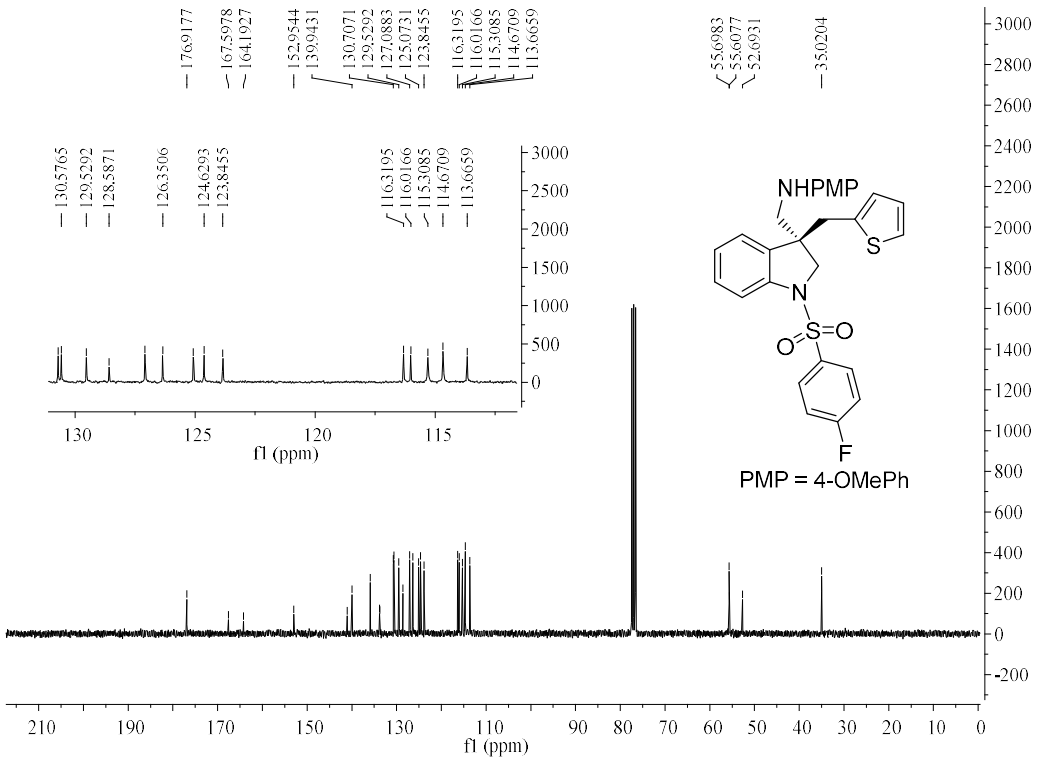
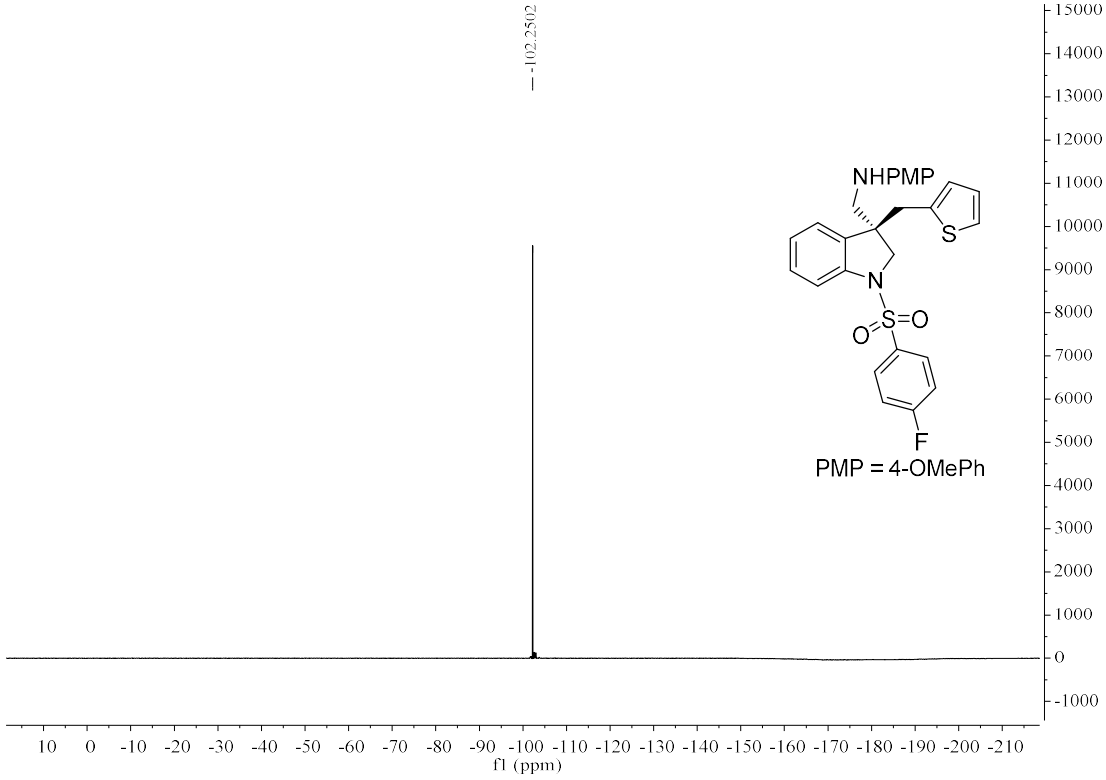
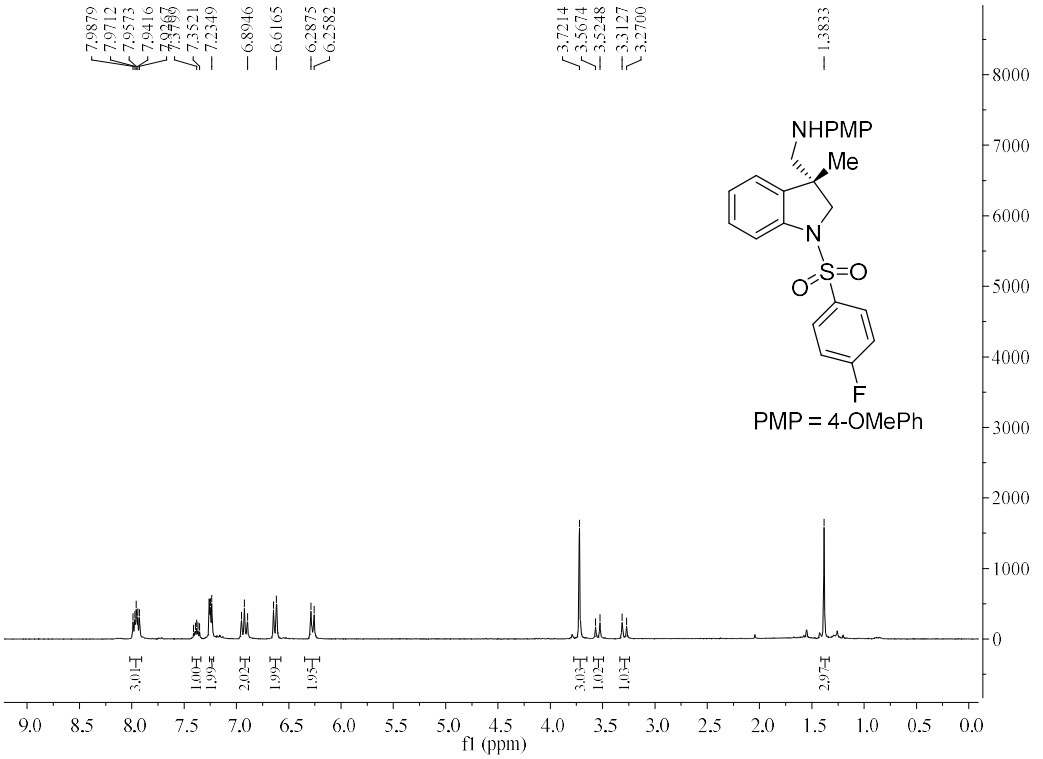
167.2916
163.8857
152.7700
141.3444
139.5904
130.2069
127.5179
123.9844
116.0037
115.7004
115.1980
114.6267
113.5966
55.8118
55.6858
52.8457
40.9448
133.5484
133.5073
132.7990
132.0577
128.7928
128.6883
127.2971
125.7249
124.8851
123.9844
116.0037
115.7004
115.1980
114.6267
113.5966
NHPMP
O
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)

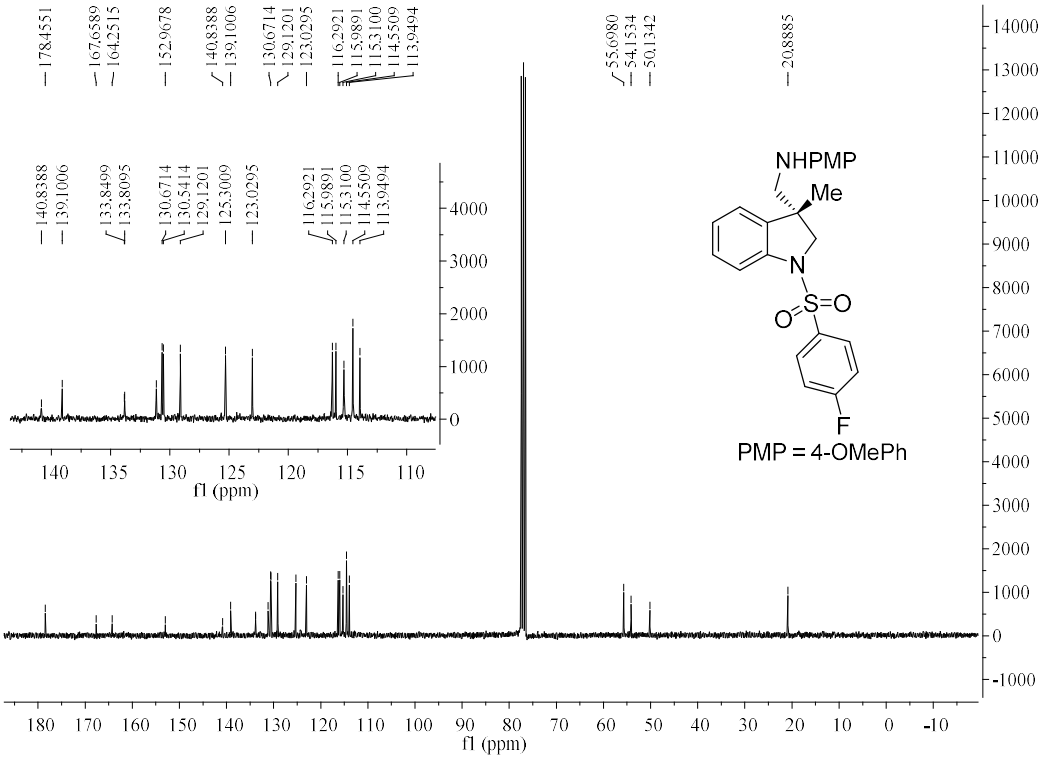

-101.4195
NHPMP
O
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)


7.8901
7.8733
7.8604
7.8470
7.3055
7.2357
6.9782
6.7063
6.6769
6.5928
6.5813
6.5648
6.4375
6.4083
6.3745
6.3657
3.7304
3.6884
3.6459
3.5351
3.4867
3.4439
3.4015
3.2750
3.2269
NHPMP
S
N
S=O
O
F
PMP = 4-OMePh
3.02
1.08
1.99
2.03
1.00
2.02
1.00
3.03
3.06
1.01
1.00
1.02
f1 (ppm)


176.9177
167.5978
164.1927
152.9544
139.9431
130.7071
129.5292
127.0883
125.0731
123.8455
116.3195
116.0166
115.3085
114.6709
113.6659
55.6983
55.6077
52.6931
35.0204
130.5765
129.5292
128.5871
126.3506
124.6293
123.8455
116.3195
116.0166
115.3085
114.6709
113.6659
f1 (ppm)
NHPMP
S
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)


-102.2502
NHPMP
S
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)


7.9879
7.9712
7.9573
7.9416
7.3521
7.2349
6.8946
6.6165
6.2875
6.2582
3.7214
3.5674
3.5248
3.3127
3.2700
1.3833
NHPMP
Me
N
S=O
O
F
PMP = 4-OMePh
3.01
1.00
1.99
2.02
1.99
1.95
3.03
1.02
1.03
2.97
f1 (ppm)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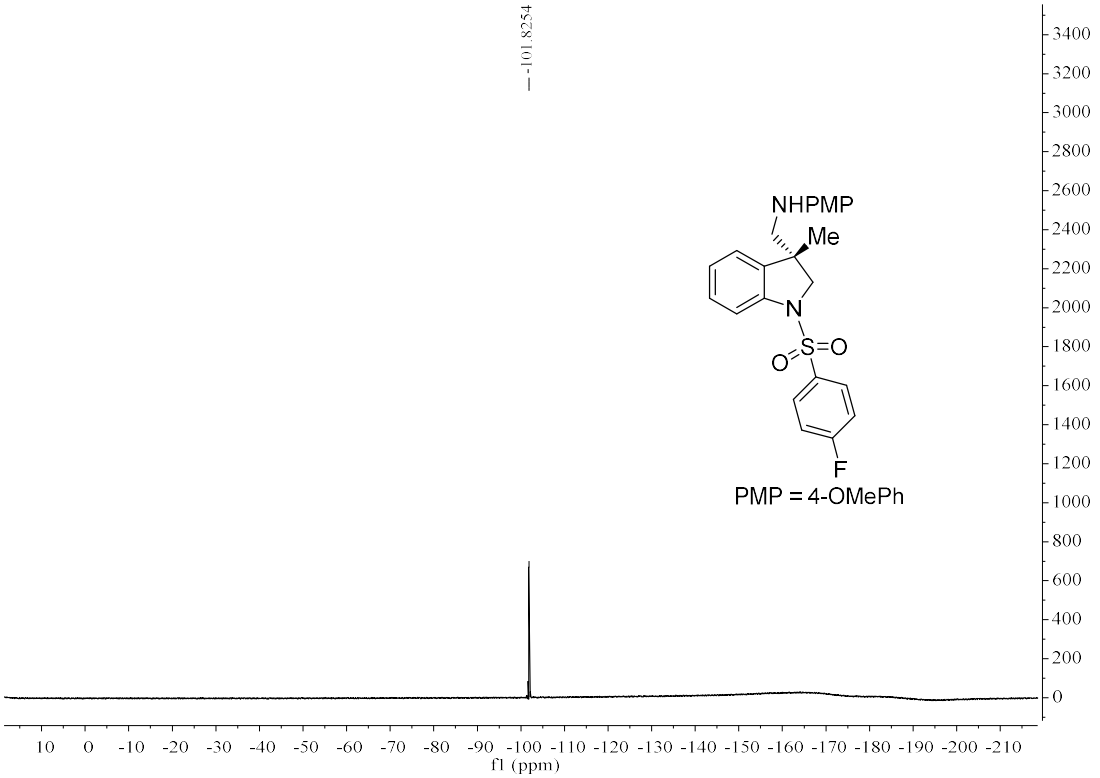
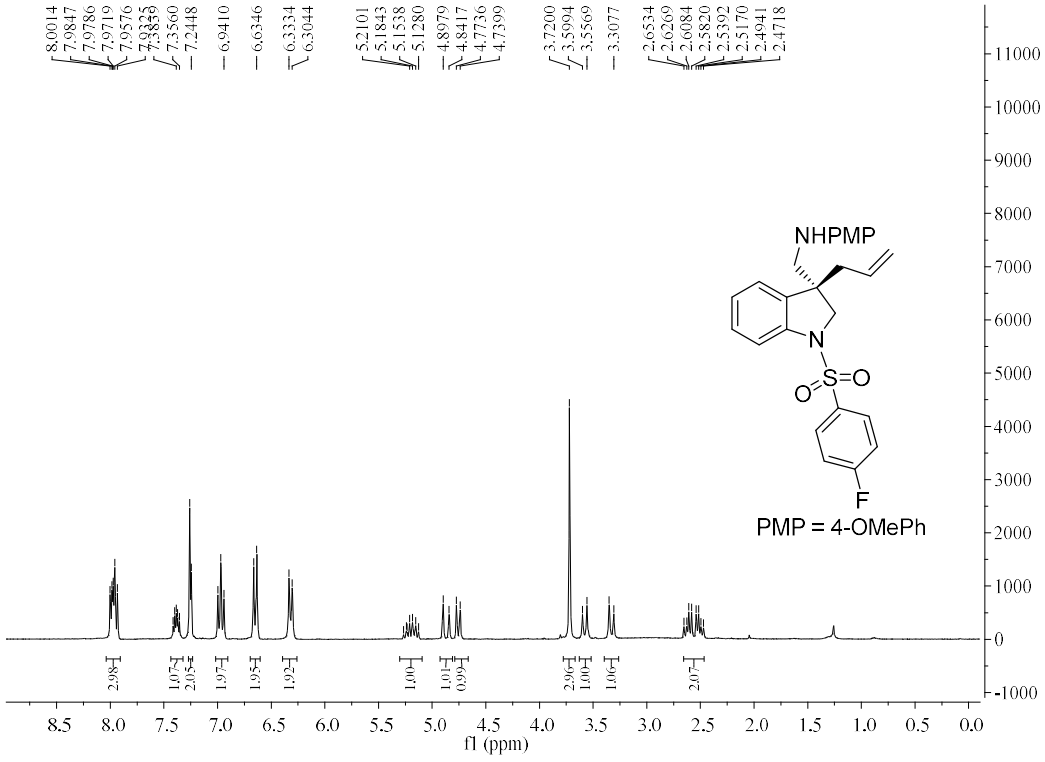
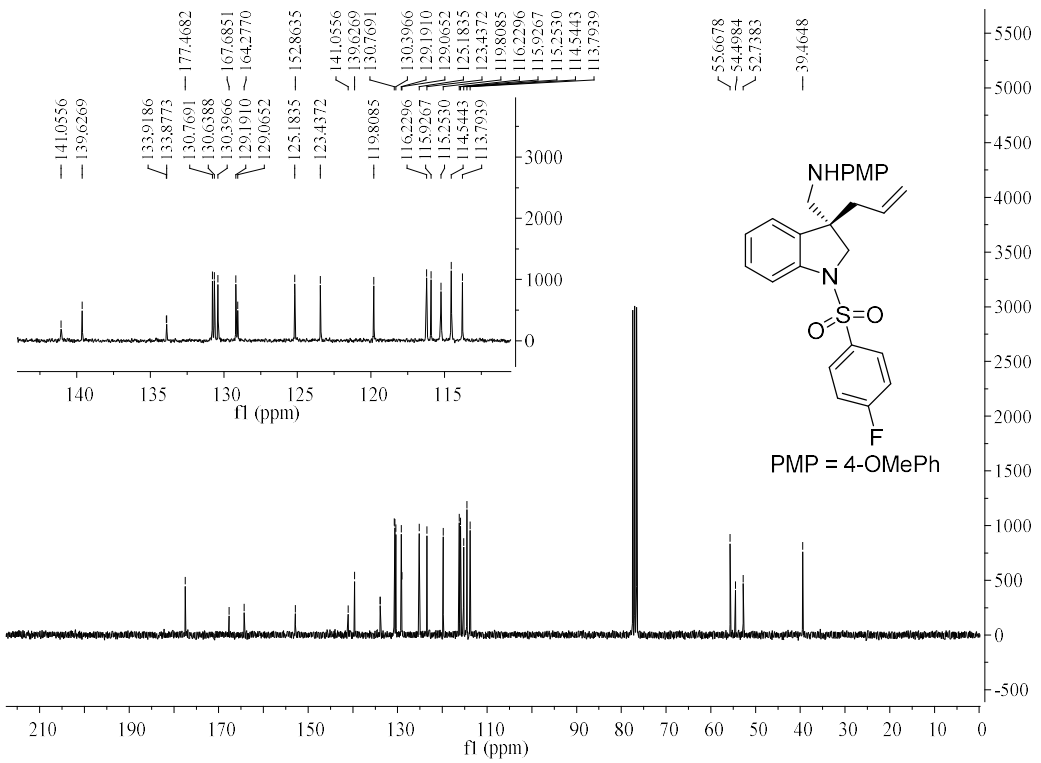
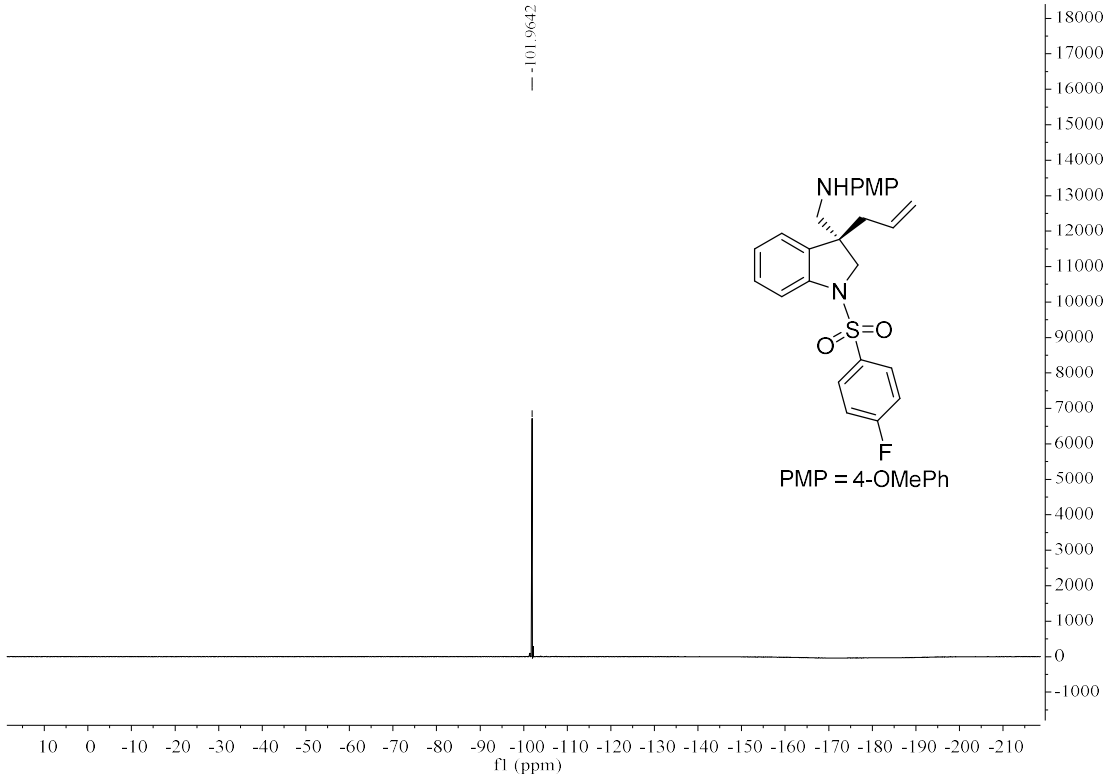
167.6589
164.2515
152.9678
140.8388
139.1006
130.6714
129.1201
123.0295
116.2921
115.9891
115.3100
114.5509
113.9494
55.6980
54.1534
50.1342
20.8885
NHPMP
Me
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)


-101.8254
NHPMP
Me
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)


8.0014
7.9847
7.9786
7.9719
7.9576
7.9325
7.3858
7.3560
7.2448
6.9410
6.6346
6.3334
6.3044
5.2101
5.1843
5.1538
5.1280
4.8979
4.8417
4.7736
4.7399
3.7200
3.5994
3.5569
3.3077
2.6534
2.6269
2.6084
2.5820
2.5392
2.5170
2.4941
2.4718
NHPMP
N
S=O
O
F
PMP = 4-OMePh
2.98
1.07
2.05
1.97
1.95
1.92
1.00
1.01
0.99
2.96
1.00
1.06
2.07
f1 (ppm)


141.0556
139.6269
133.9186
133.8773
177.4682
130.7691
130.6388
167.6851
130.3966
164.2770
129.1910
129.0652
125.1835
152.8635
123.4372
141.0556
139.6269
130.7691
119.8085
130.3966
129.1910
129.0652
125.1835
123.4372
116.2296
115.9267
115.2530
114.5443
113.7939
55.6678
54.4984
52.7383
39.4648
NHPMP
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)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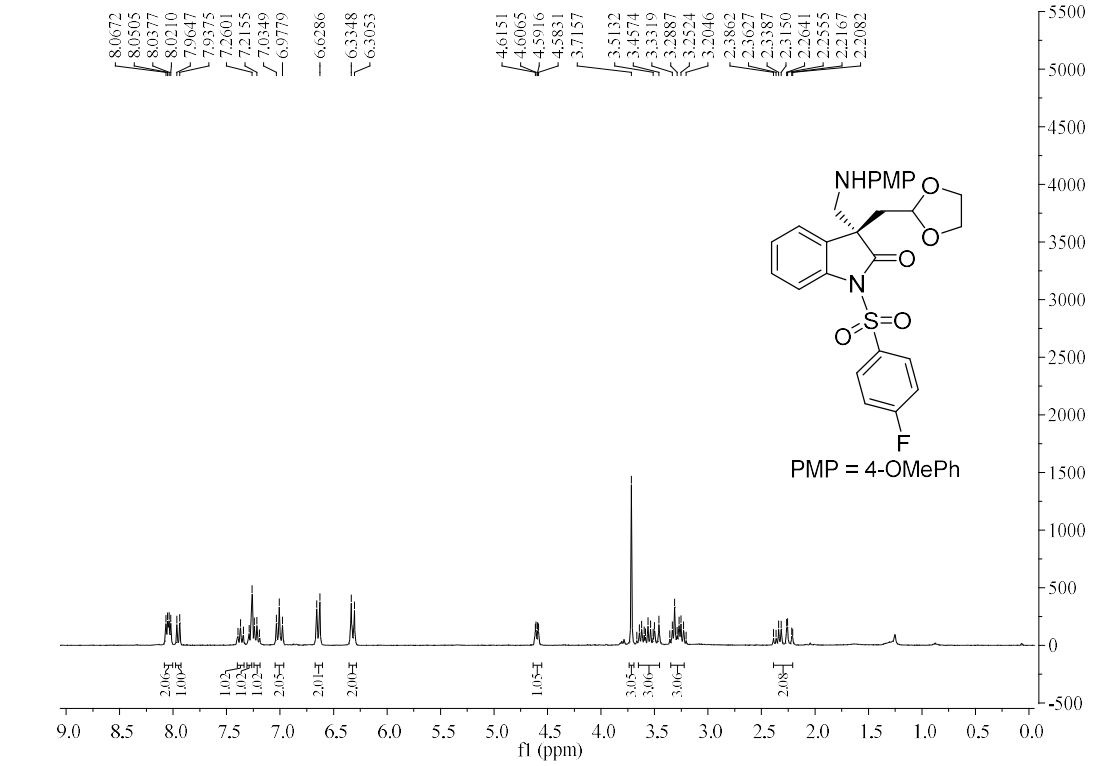
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)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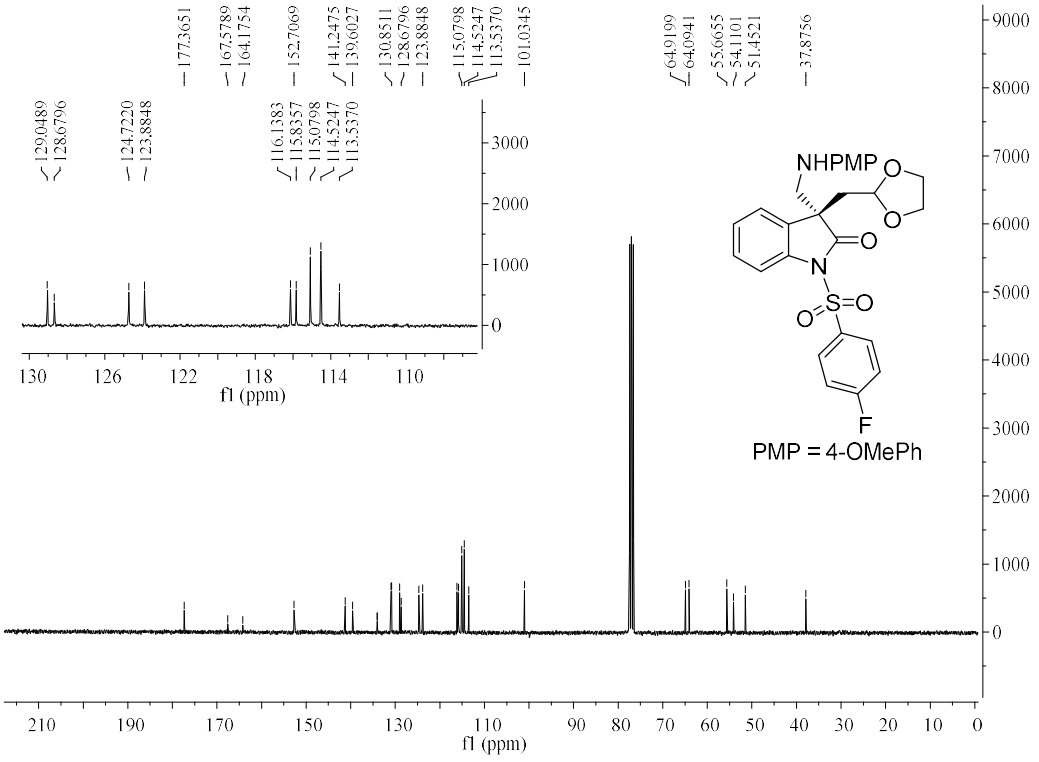
8.0505
8.0377
8.0210
7.9647
7.9375
7.2601
7.2155
7.0349
6.9779
6.6286
6.3348
6.3053
4.6151
4.6065
4.5916
4.5831
3.7157
3.5132
3.4574
3.3319
3.2887
3.2524
3.2046
2.3862
2.3627
2.3387
2.3150
2.2641
2.2555
2.2167
2.2082
NHPMP
O
O
O
N
S=O
O
F
PMP = 4-OMePh
2.06
1.00
1.03
1.03
1.02
2.05
2.01
2.00
1.05
3.05
3.06
3.06
2.08
f1 (ppm)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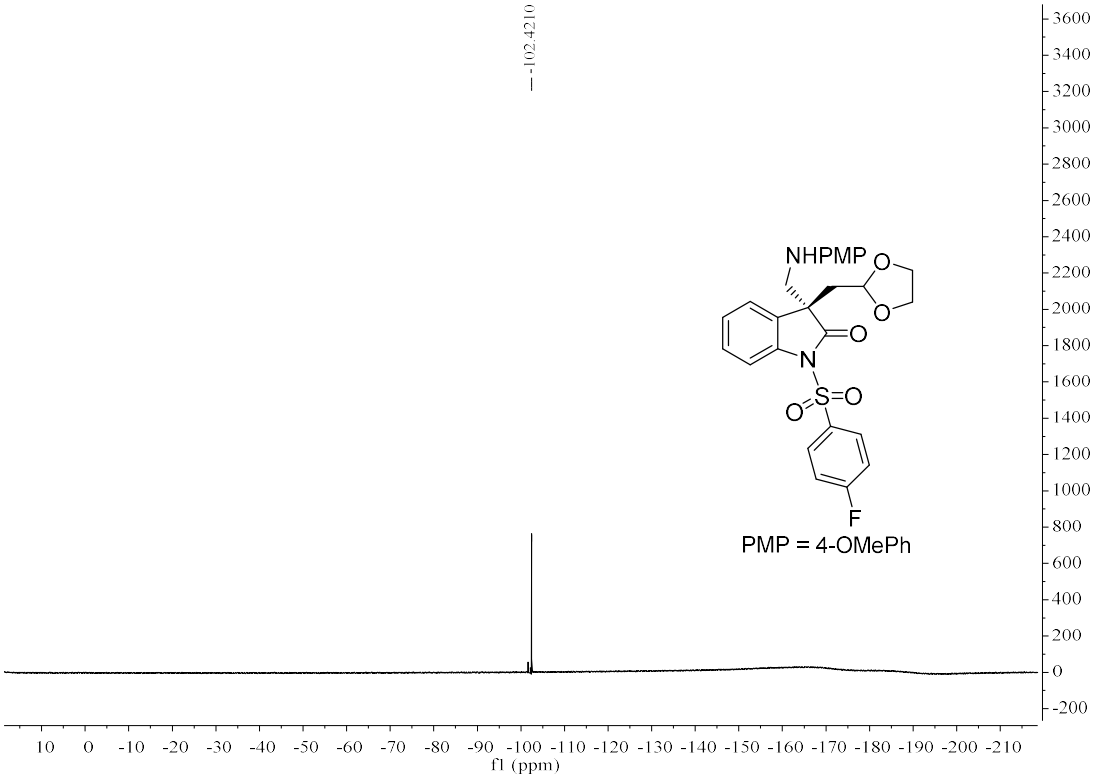
167.5789
164.1754
152.7069
141.2475
139.6027
130.8511
128.6796
123.8848
115.0798
114.5247
113.5370
101.0345
64.9199
64.0941
55.6655
54.1101
51.4521
37.8756
129.0489
128.6796
124.7220
123.8848
116.1383
115.8357
115.0798
114.5247
113.5370
NHPMP
O
O
O
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)
f1 (ppm)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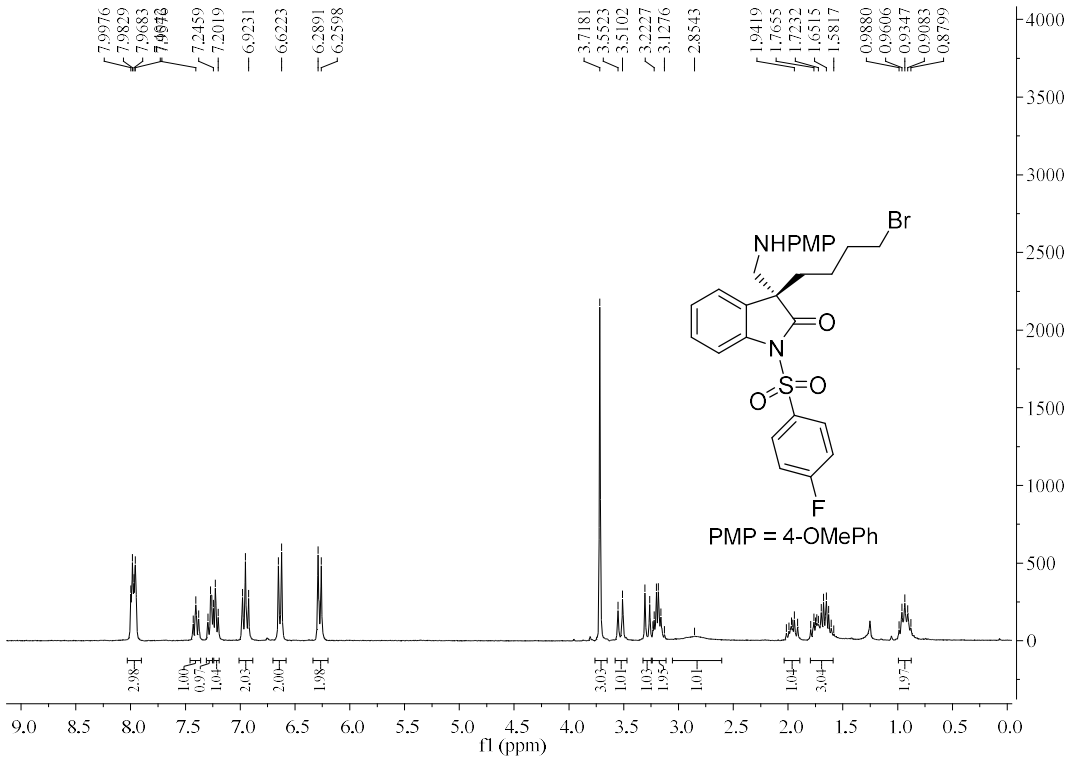
O
O
N
O=S=O
F
PMP = 4-OMePh
f1 (ppm)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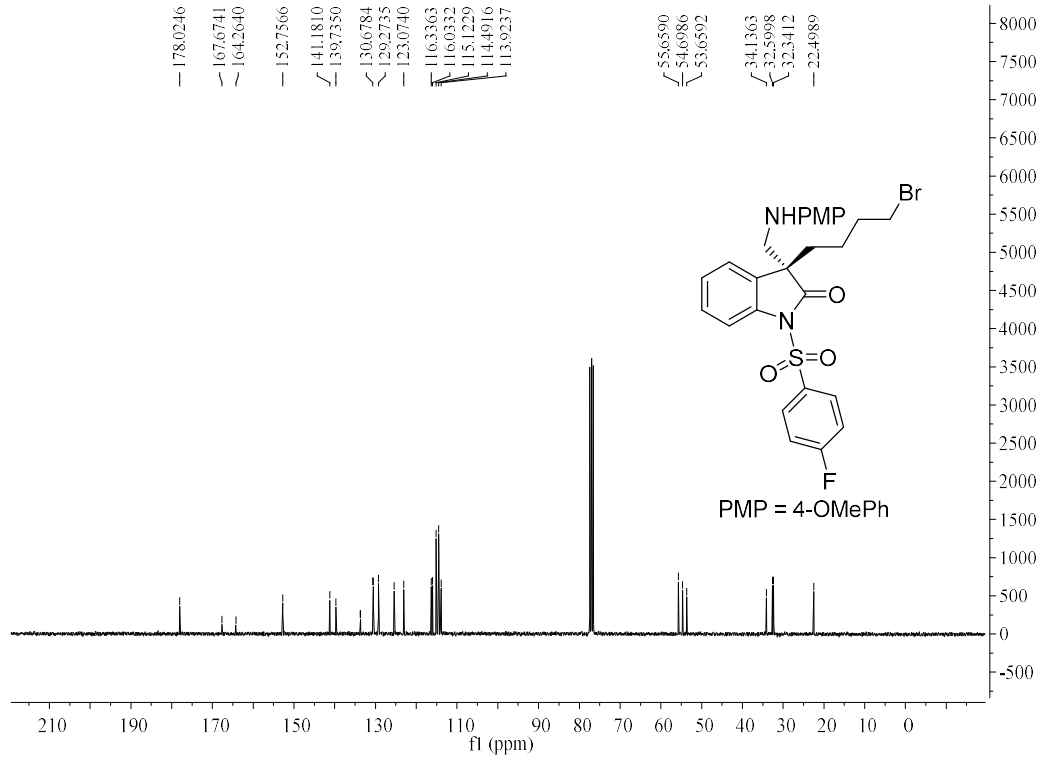
7.9829
7.9683
7.2459
7.2019
6.9231
6.6223
6.2891
6.2598
3.7181
3.5523
3.5102
3.2227
3.1276
2.8543
1.9419
1.7655
1.7232
1.6515
1.5817
0.9880
0.9606
0.9347
0.9083
0.8799
Br
NHPMP
O
N
O=S=O
F
PMP = 4-OMePh
2.98
1.00
0.97
1.04
2.03
2.00
1.98
3.03
1.01
1.03
1.95
1.01
1.04
3.04
1.97
f1 (ppm)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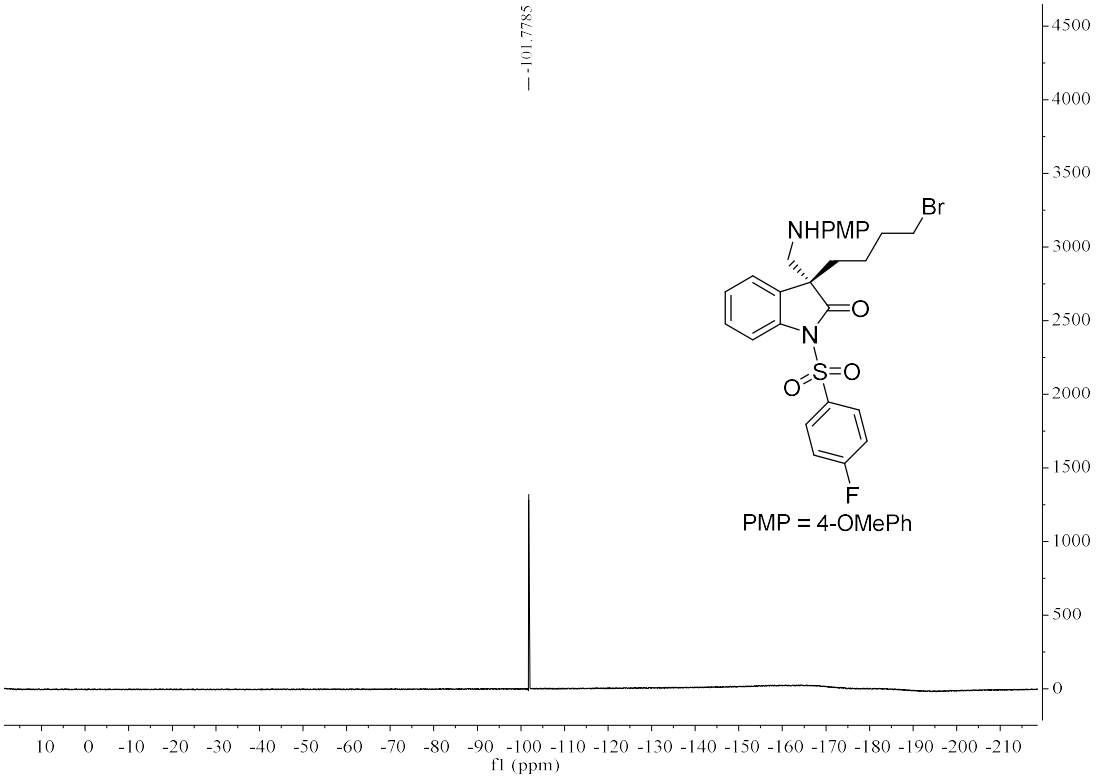
164.2640
152.7566
141.1810
139.7350
130.6784
129.2735
123.0740
116.3363
116.0332
115.1229
114.4916
113.9237
55.6590
54.6986
53.6592
34.1363
32.5998
32.3412
22.4989
Br
NHPMP
O
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)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Br
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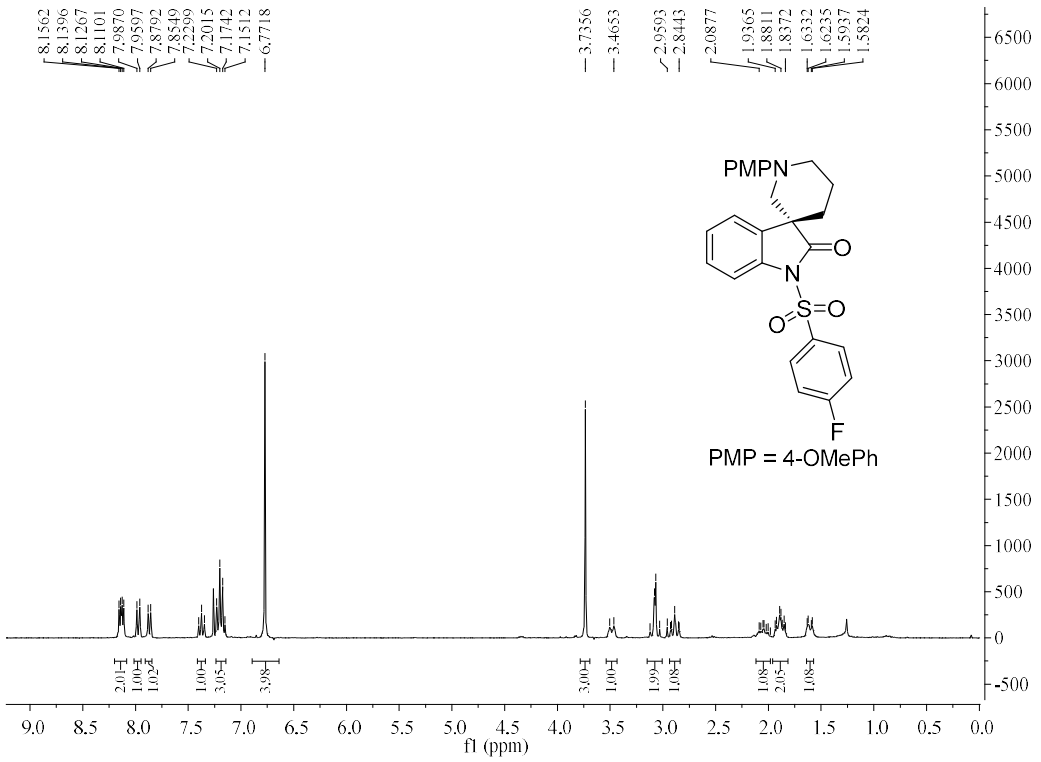
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)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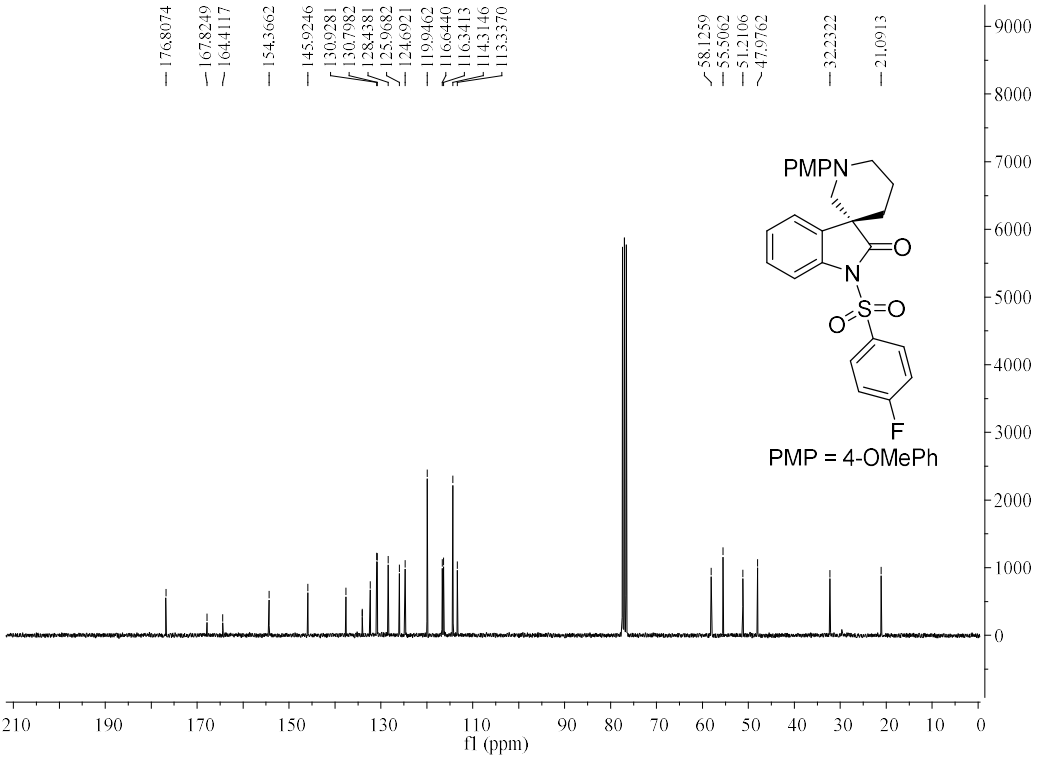
8.1396
8.1267
8.1101
7.9870
7.9597
7.8792
7.8549
7.2299
7.2015
7.1742
7.1512
6.7718
3.7356
3.4653
2.9593
2.8443
2.0877
1.9365
1.8811
1.8372
1.6332
1.6235
1.5937
1.5824
PMPN
O
N
S=O
O
F
PMP = 4-OMePh
2.01
1.00
1.02
1.00
3.05
3.98
3.00
1.00
1.99
1.08
1.08
2.05
1.08
f1 (ppm)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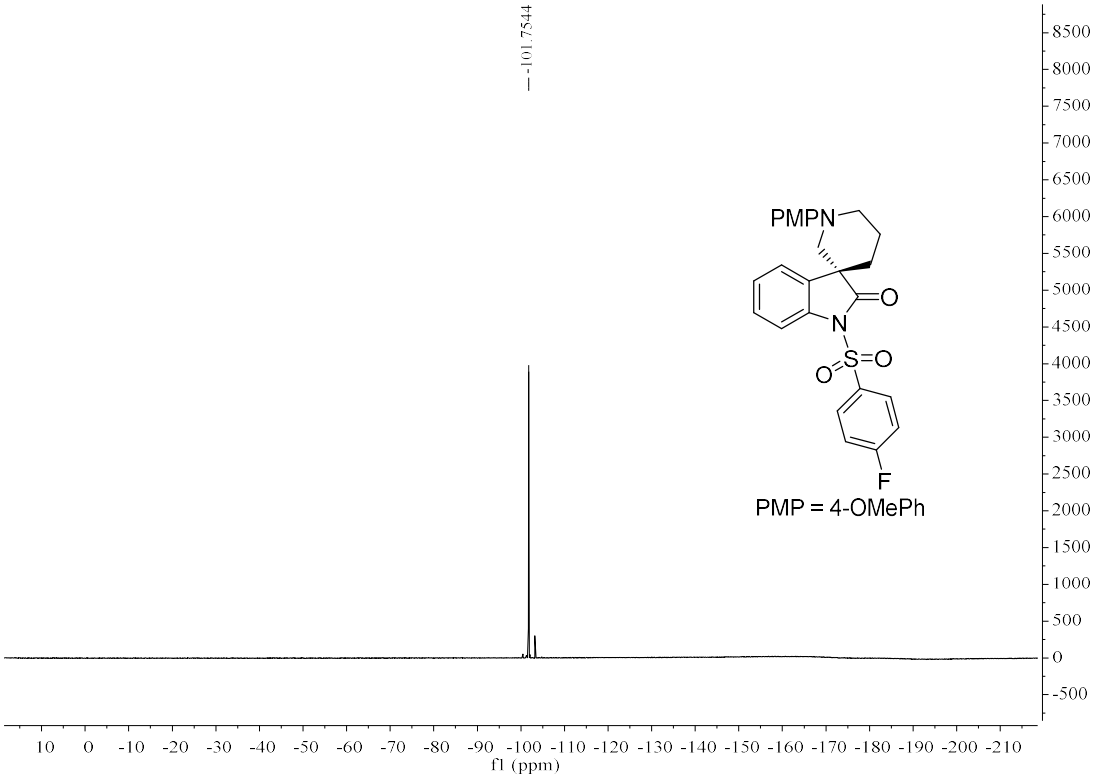
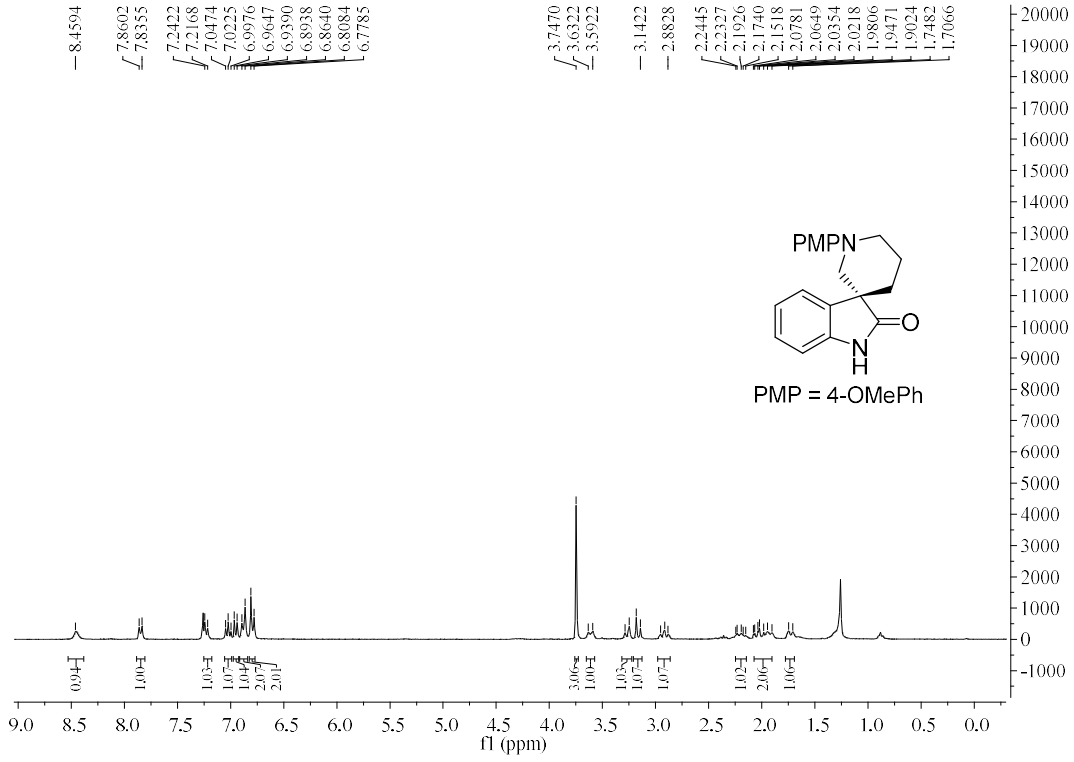
167.8249
164.4117
154.3662
145.9246
130.9281
130.7982
128.4381
125.9682
124.6921
119.9462
116.6440
116.3413
114.3146
113.3370
58.1259
55.5062
51.2106
47.9762
32.2322
21.0913
PMPN
O
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)


-101.7544
PMPN
O
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)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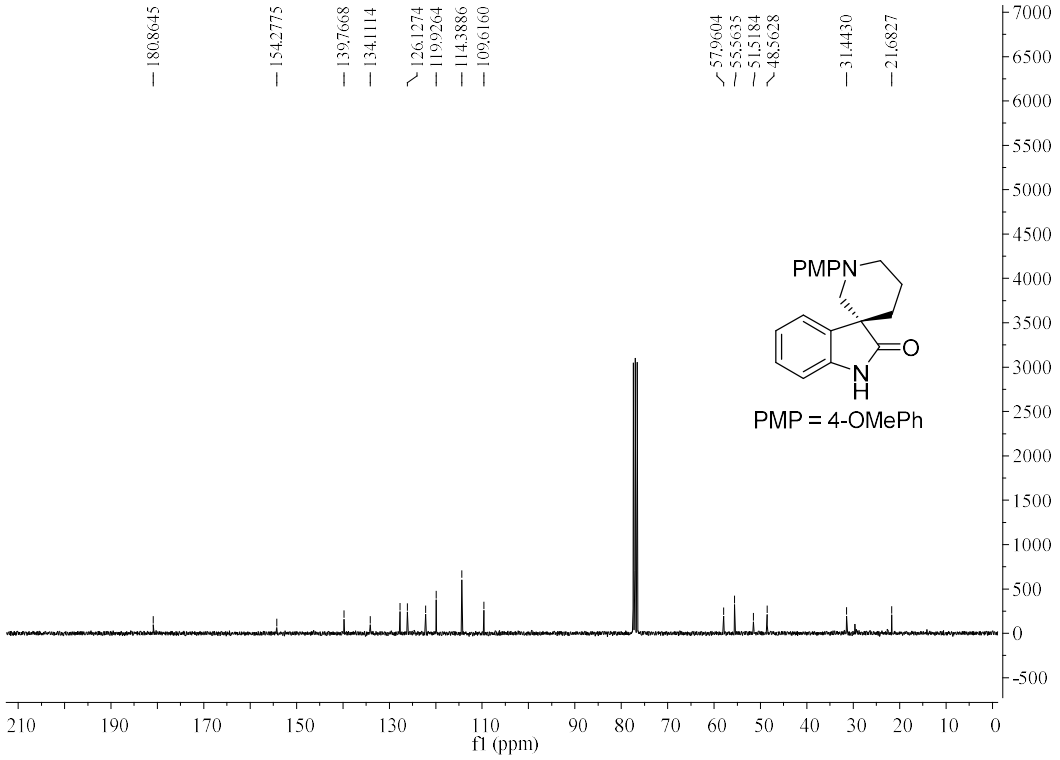
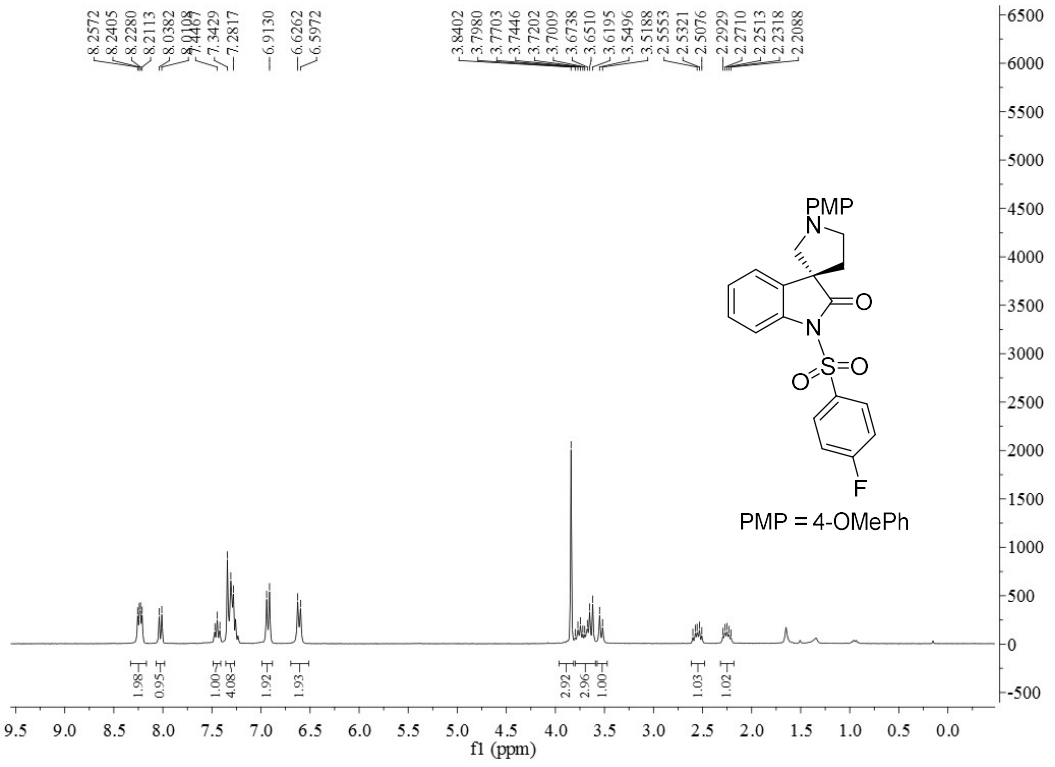
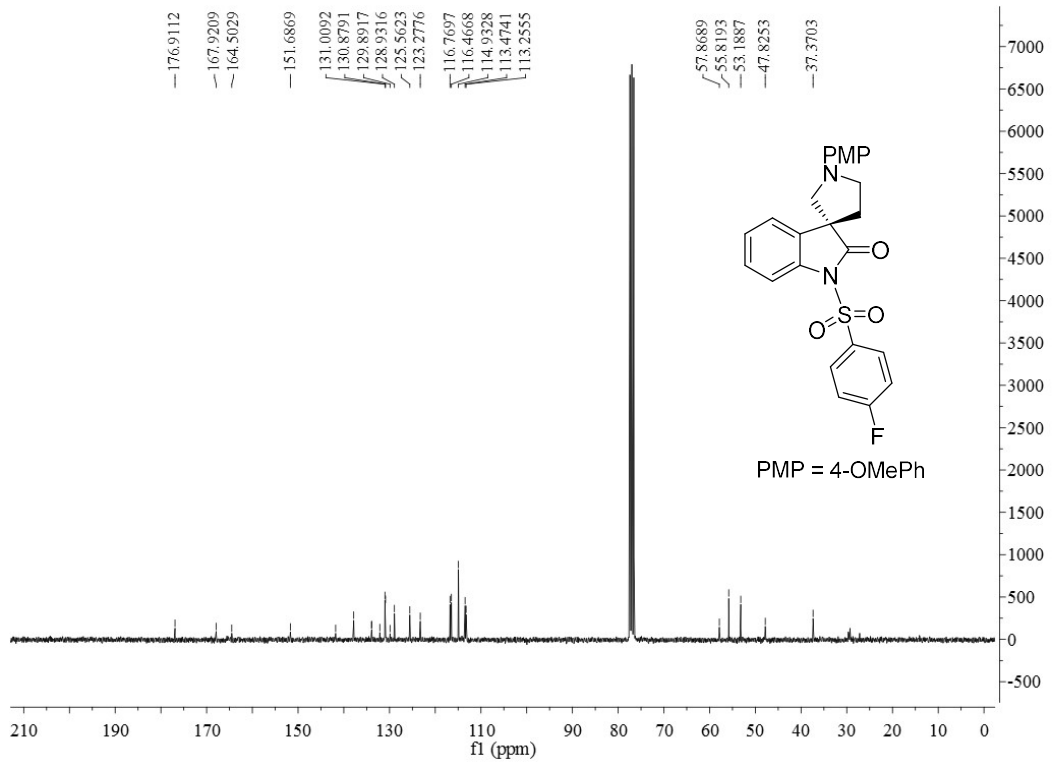
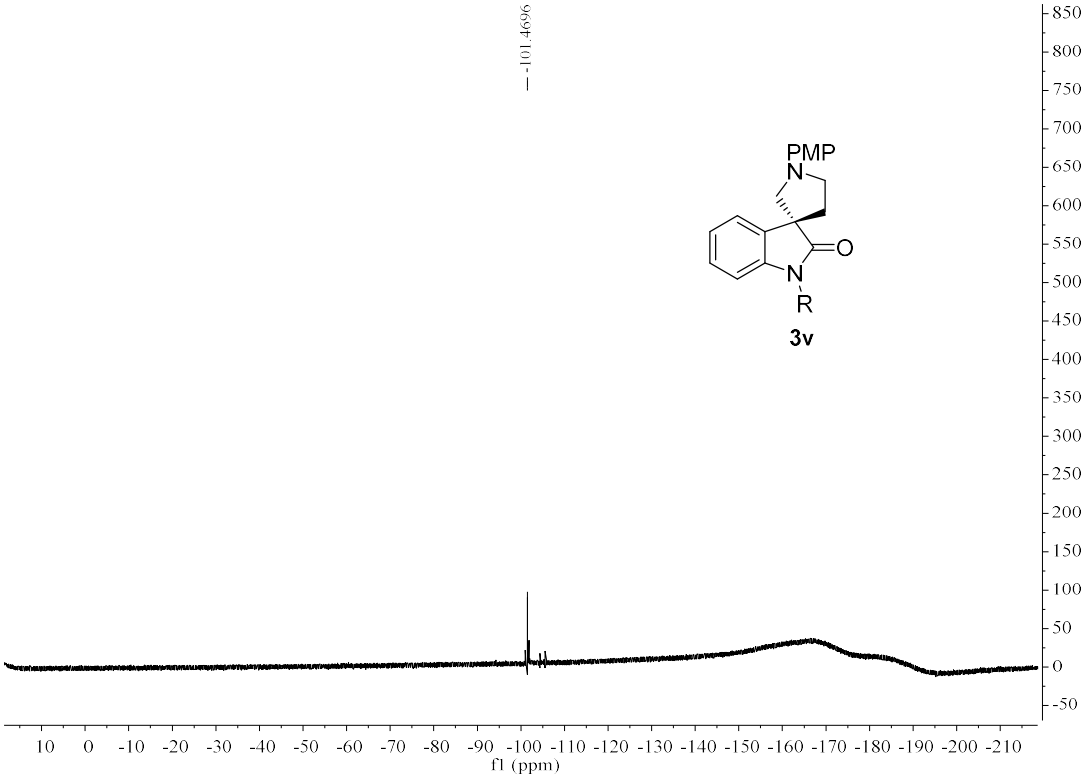
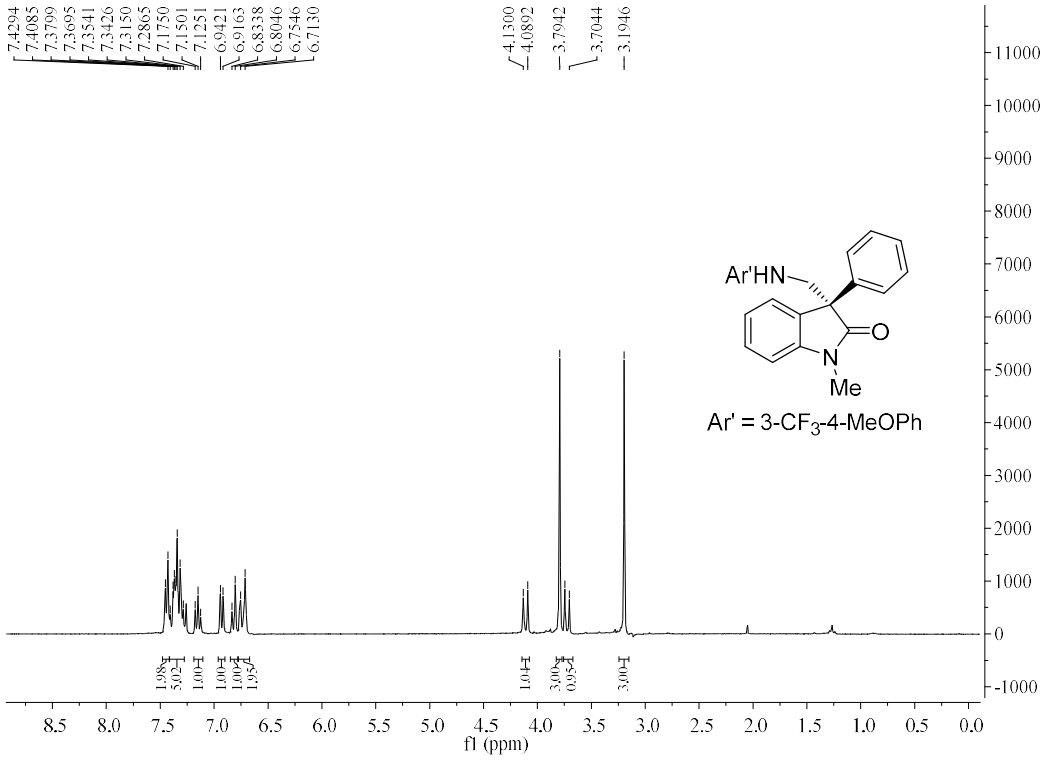
7.8355
7.2422
7.2168
7.0474
7.0225
6.9976
6.9647
6.9390
6.8938
6.8640
6.8084
6.7785
3.7470
3.6322
3.5922
3.1422
2.8828
2.2445
2.2327
2.1926
2.1740
2.1518
2.0781
2.0649
2.0354
2.0218
1.9806
1.9471
1.9024
1.7482
1.7066
PMPN
O
N
H
PMP = 4-OMePh
0.94
1.00
1.03
1.07
1.04
2.07
2.01
3.06
1.00
1.05
1.07
1.07
1.02
2.06
1.06
f1 (ppm)


180.8645
154.2775
139.7668
134.1114
126.1274
119.9264
114.3886
109.6160
57.9604
55.5635
51.5184
48.5628
31.4430
21.6827
PMPN
O
N
H
PMP = 4-OMePh
f1 (ppm)


8.2572
8.2405
8.2280
8.2113
8.0382
7.4487
7.3429
7.2817
6.9130
6.6262
6.5972
3.8402
3.7980
3.7703
3.7446
3.7202
3.7009
3.6738
3.6510
3.6195
3.5496
3.5188
2.5553
2.5321
2.5076
2.2929
2.2710
2.2513
2.2318
2.2088
PMP
N
O
N
S=O
O
F
PMP = 4-OMePh
1.98
0.95
1.00
4.08
1.92
1.93
2.92
2.96
1.00
1.03
1.02
f1 (ppm)


176.9112
167.9209
164.5029
151.6869
131.0092
130.8791
129.8917
128.9316
125.5623
123.2776
116.7697
116.4668
114.9328
113.4741
113.2555
57.8689
55.8193
53.1887
47.8253
37.3703
PMP
N
O
N
S=O
O
F
PMP = 4-OMePh
f1 (ppm)


-101.4696
PMP
N
O
N
R
3v
f1 (ppm)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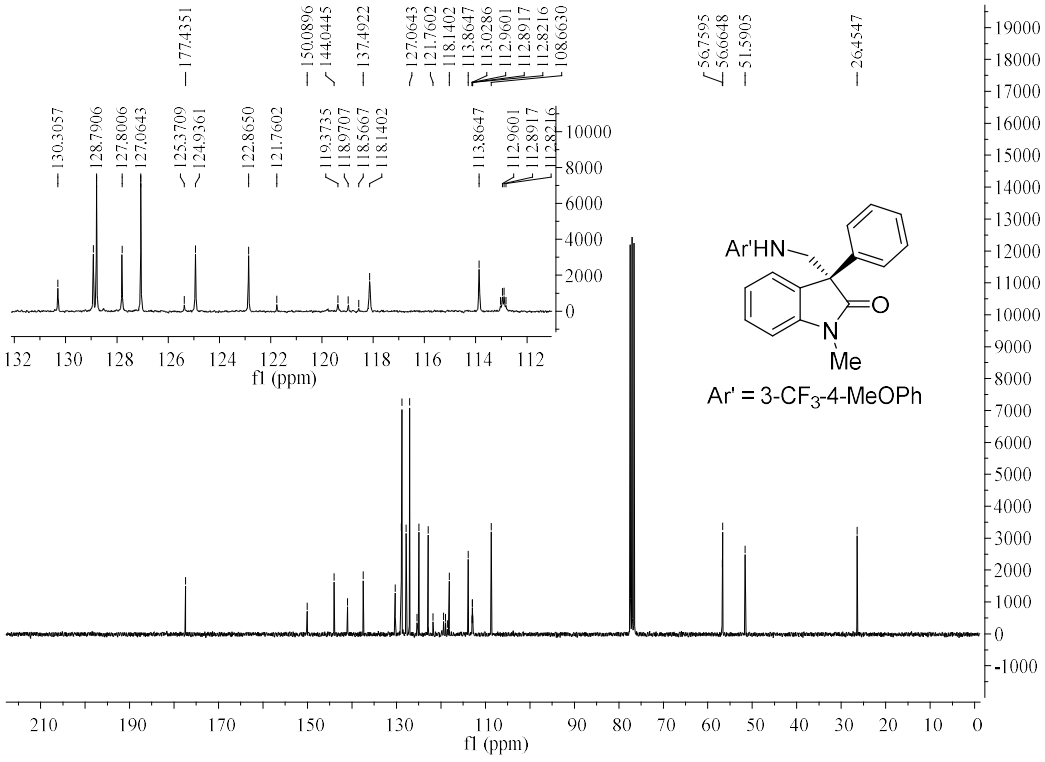
7.4085
7.3799
7.3695
7.3541
7.3426
7.3150
7.2865
7.1750
7.1501
7.1251
6.9421
6.9163
6.8338
6.8046
6.7546
6.7130
4.1300
4.0892
3.7942
3.7044
3.1946
1.98
5.02
1.00
1.00
1.00
1.95
1.04
3.00
0.95
3.00
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
fl (ppm)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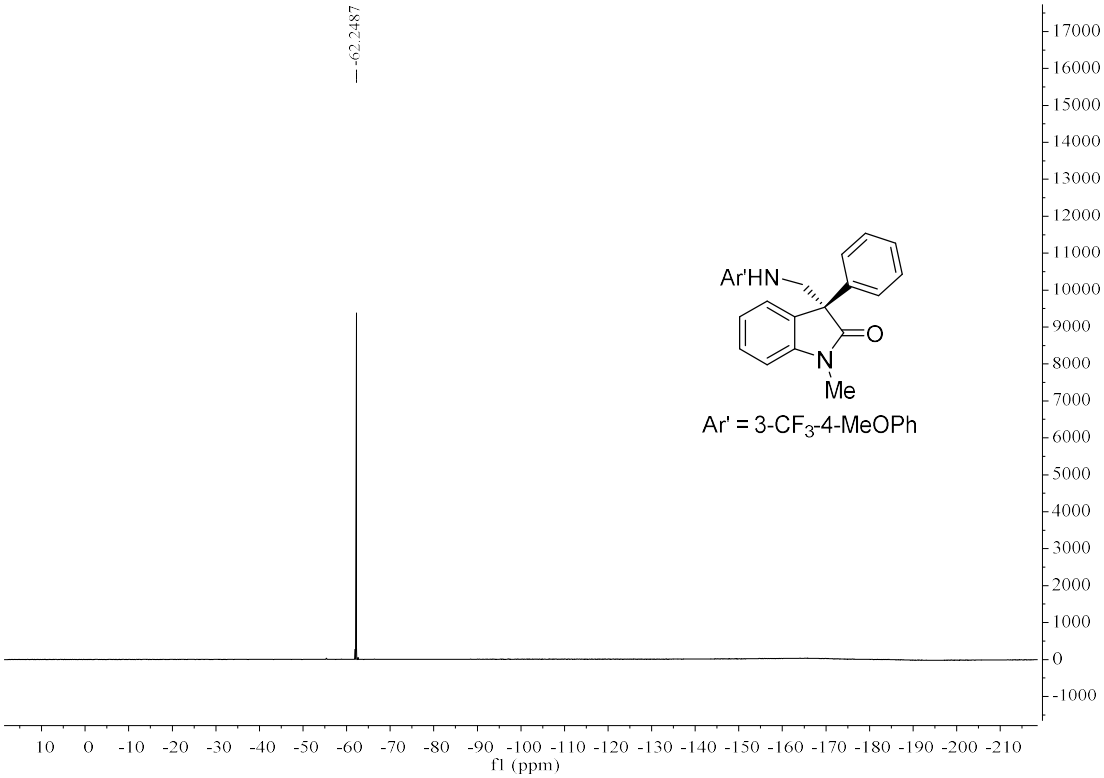
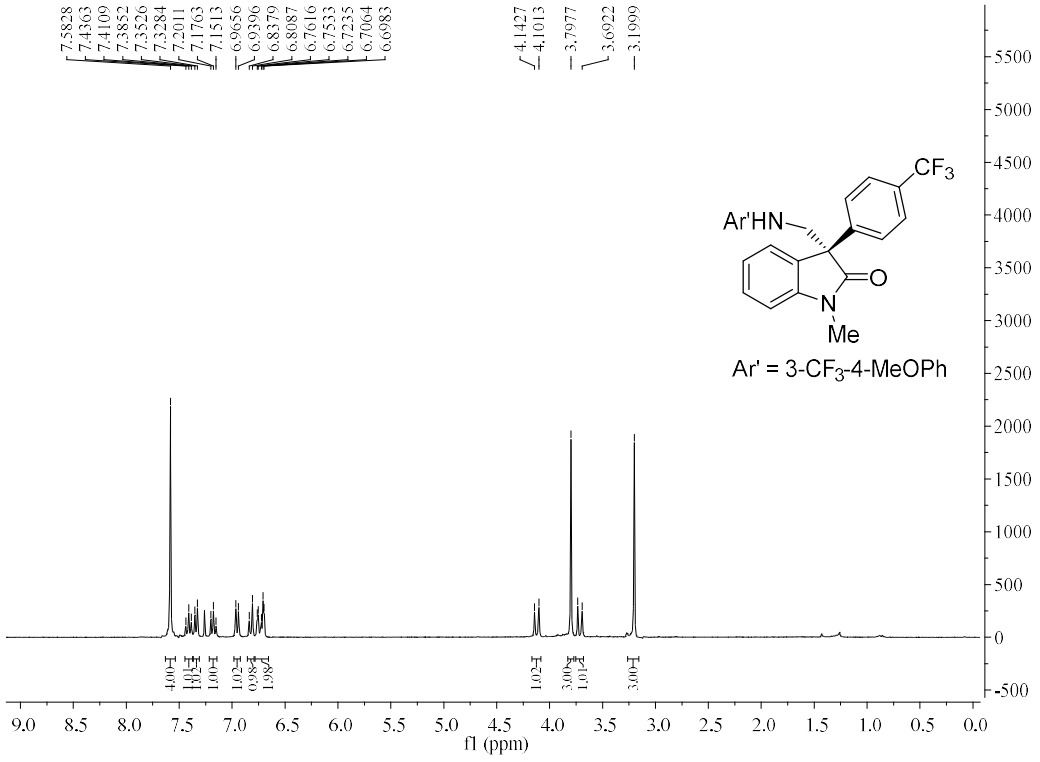
150.0896
144.0445
137.4922
127.0643
121.7602
118.1402
113.8647
113.0286
112.9601
112.8917
112.8216
108.6630
56.7595
56.6648
51.5905
26.4547
130.3057
128.7906
127.8006
127.0643
125.3709
124.9361
122.8650
121.7602
119.3735
118.9707
118.5667
118.1402
113.8647
112.9601
112.8917
112.8216
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
fl (ppm)
fl (ppm)


-62.2487
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)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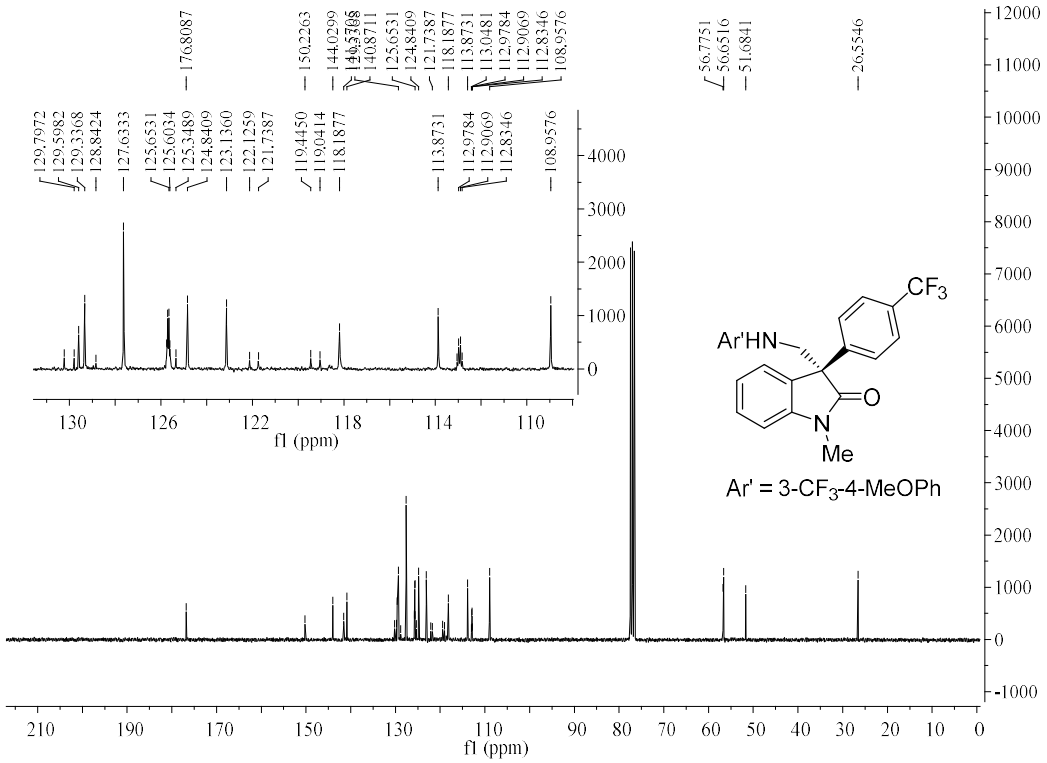
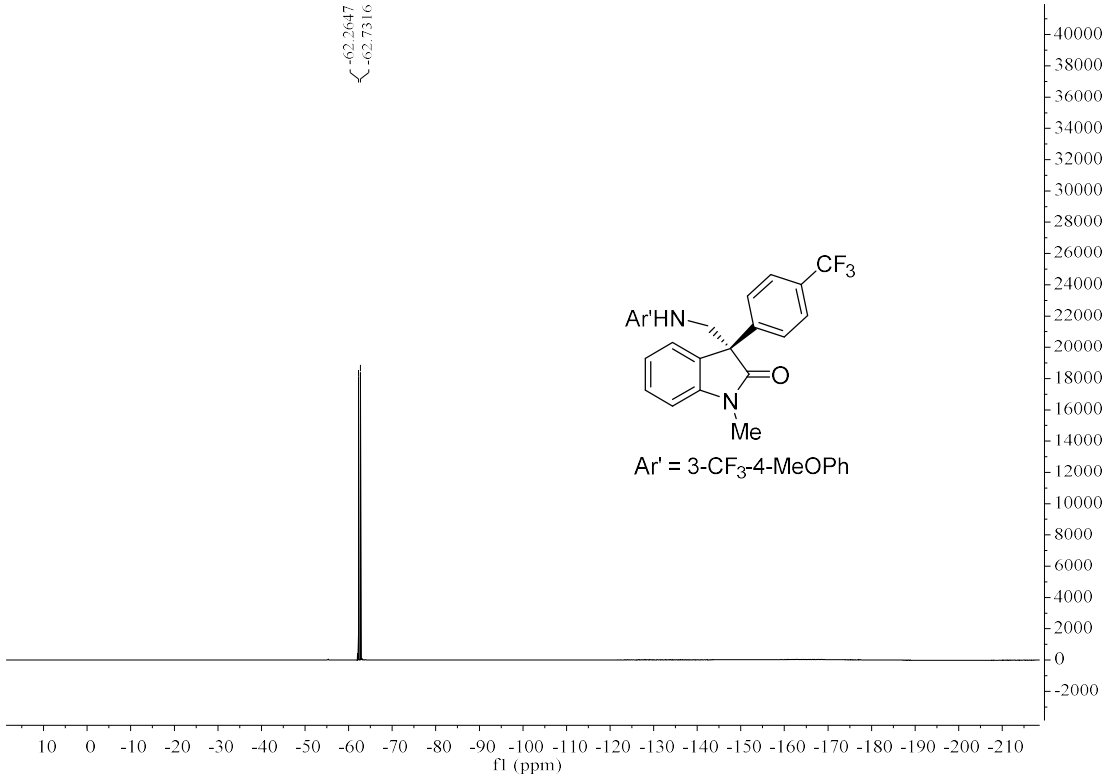
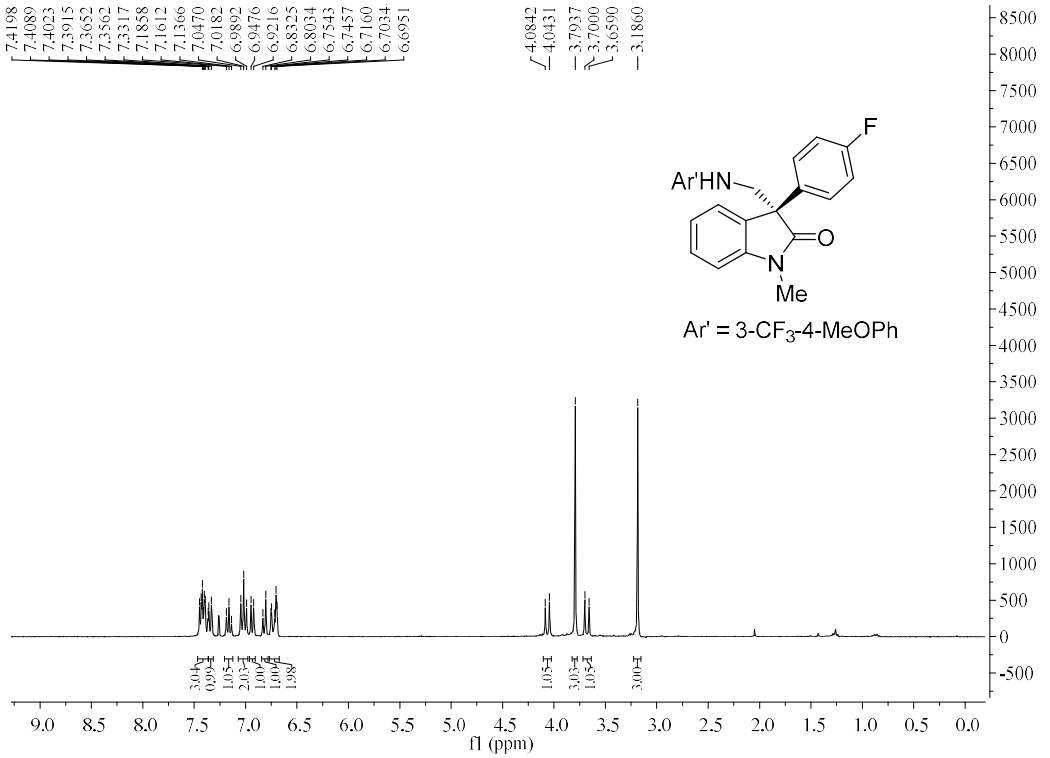
7.4363
7.4109
7.3852
7.3526
7.3284
7.2011
7.1763
7.1513
6.9656
6.9396
6.8379
6.8087
6.7616
6.7533
6.7235
6.7064
6.6983
4.1427
4.1013
3.7977
3.6922
3.1999
CF3
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
4.00H
1.01H
1.00H
1.02H
0.98H
1.98H
1.02H
3.00H
1.01H
3.00H
f1 (ppm)


Ar'HN
CF3
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


Ar'HN
CF3
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)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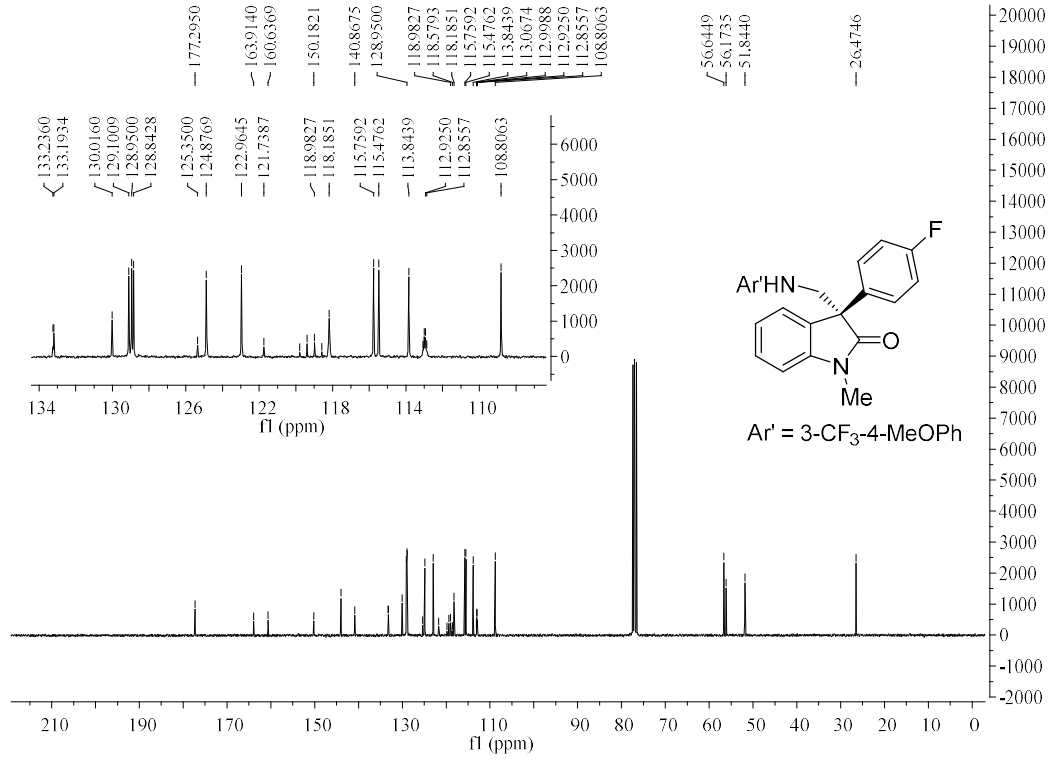
7.4089
7.4023
7.3915
7.3652
7.3562
7.3317
7.1858
7.1612
7.1366
7.0470
7.0182
6.9892
6.9476
6.9216
6.8325
6.8034
6.7543
6.7457
6.7160
6.7034
6.6951
4.0842
4.0431
3.7937
3.7000
3.6590
3.1860
F
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)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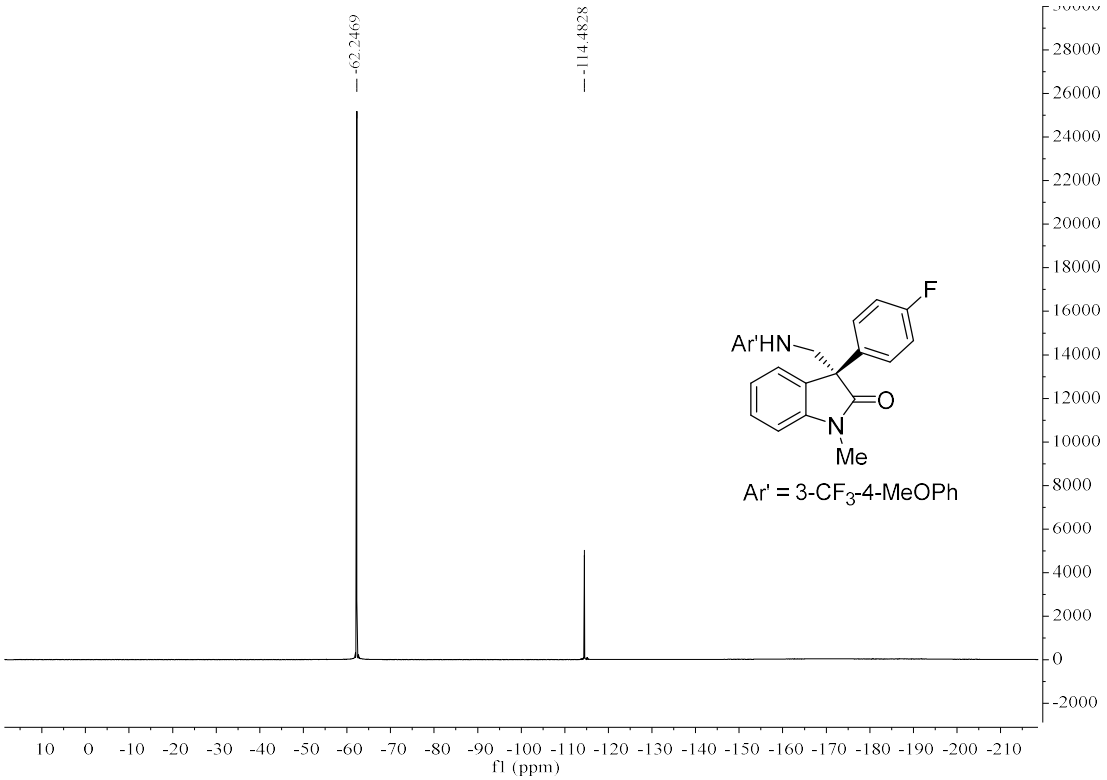
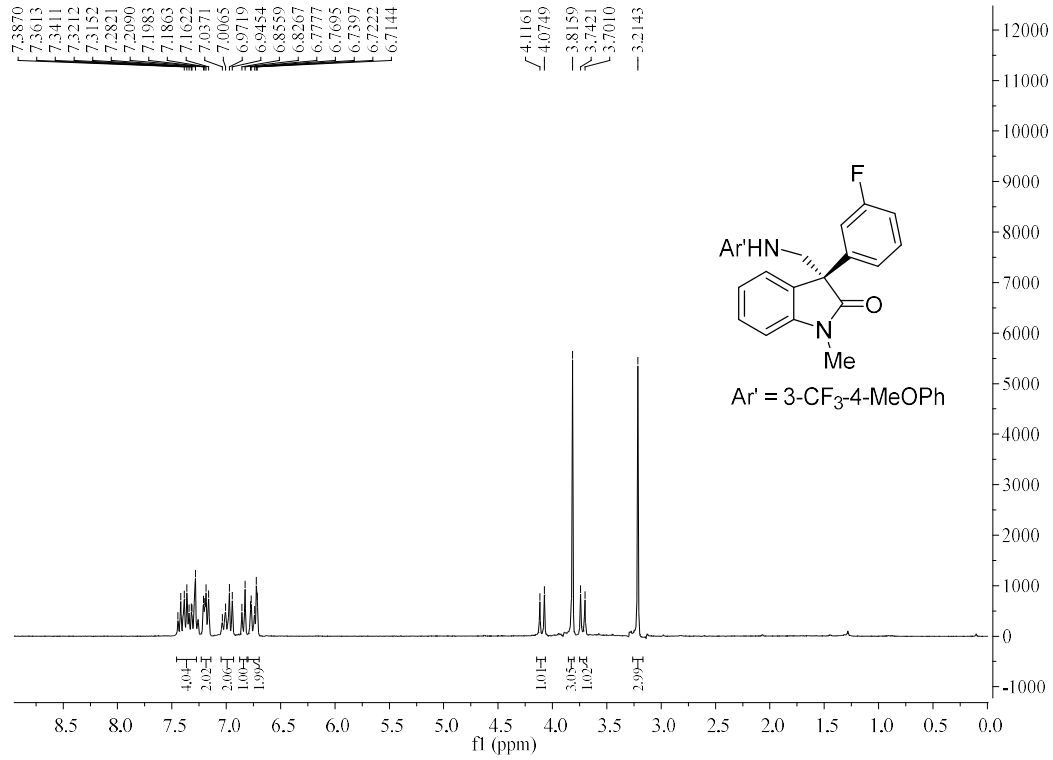
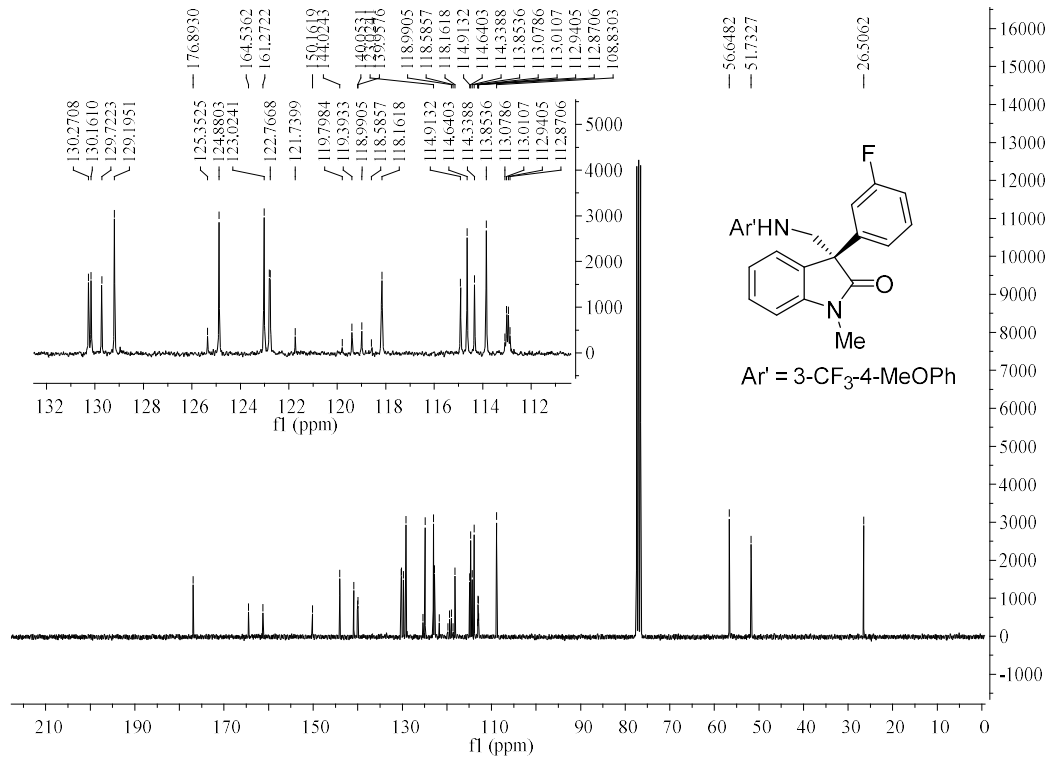
160.6369
150.1821
140.8675
128.9500
118.9827
118.5793
118.1851
115.7592
115.4762
113.8439
113.0674
112.9988
112.9250
112.8557
108.8063
56.6449
56.1735
51.8440
26.4746
133.2360
133.1934
130.0160
129.1009
128.9500
128.8428
125.3500
124.8769
122.9645
121.7387
118.9827
118.1851
115.7592
115.4762
113.8439
112.9250
112.8557
108.8063
F
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


-62.2469
-114.4828
F
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


7.3870
7.3613
7.3411
7.3212
7.3152
7.2821
7.2090
7.1983
7.1863
7.1622
7.0371
7.0065
6.9719
6.9454
6.8559
6.8267
6.7777
6.7695
6.7397
6.7222
6.7144
4.1161
4.0749
3.8159
3.7421
3.7010
3.2143
F
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
4.04
2.02
2.06
1.00
1.99
1.01
3.05
1.02
2.99
f1 (ppm)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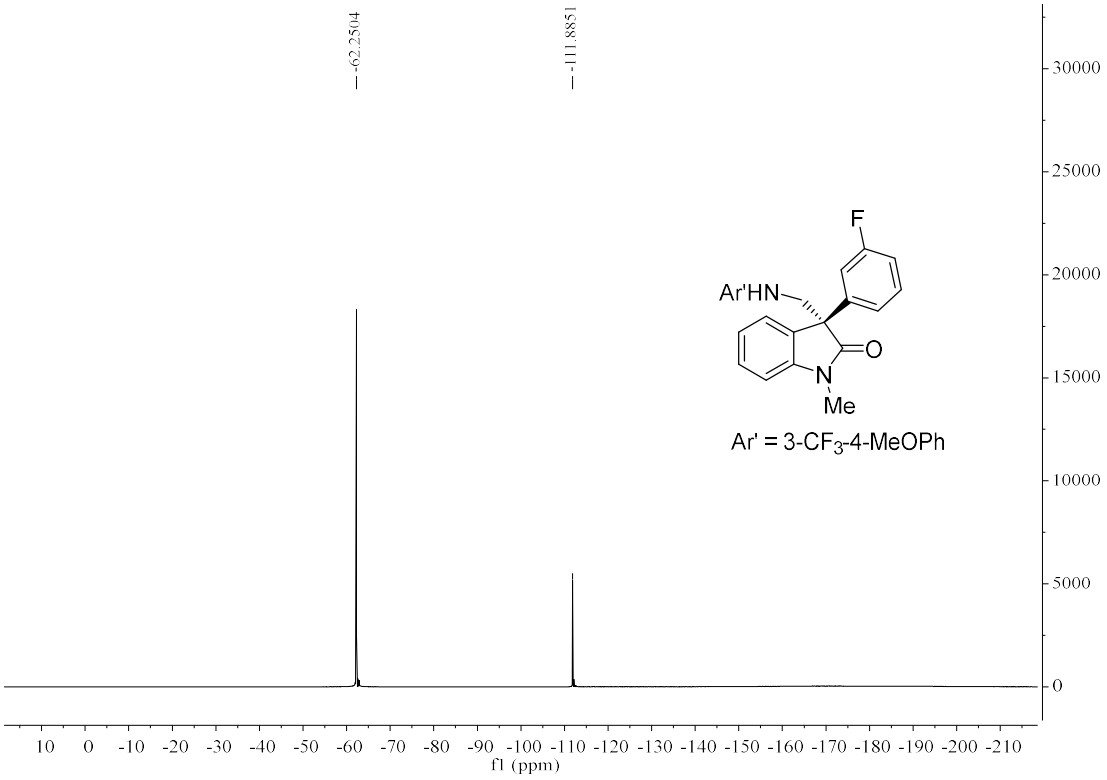
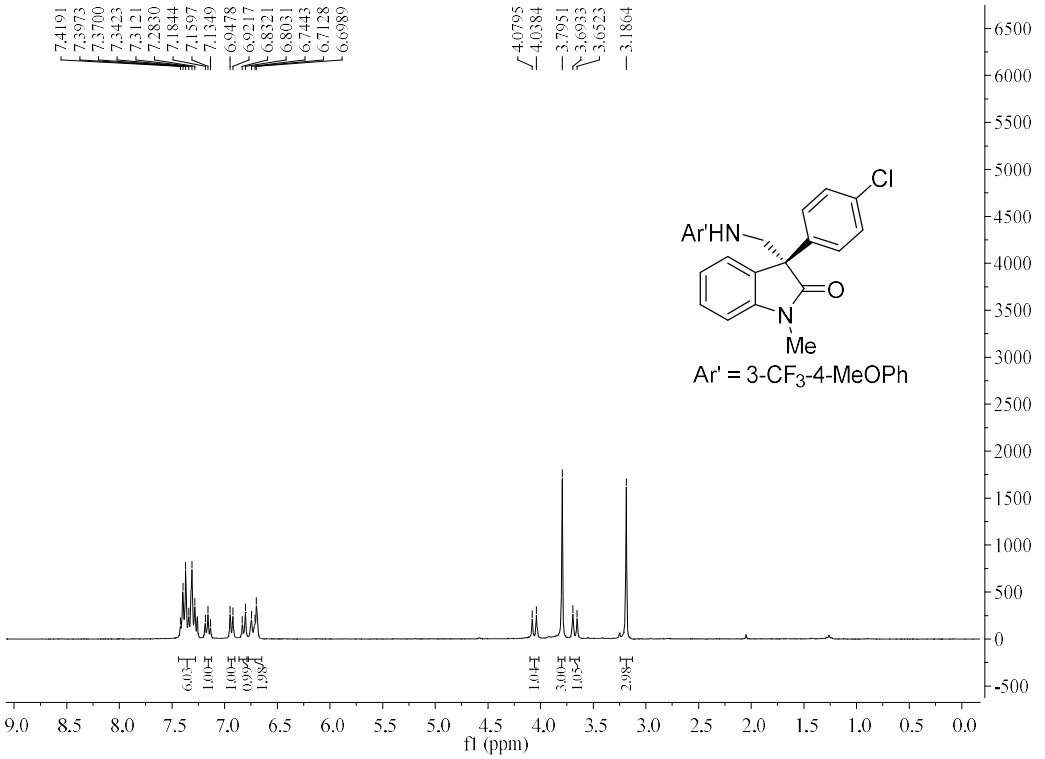
164.5362
161.2722
150.1619
144.0243
140.0531
139.9576
130.2708
130.1610
129.7223
129.1951
125.3525
124.8803
123.0241
122.7668
121.7399
119.7984
119.3933
118.9905
118.5857
118.1618
114.9132
114.6403
114.3388
113.8536
113.0786
113.0107
112.9405
112.8706
108.8303
56.6482
51.7327
26.5062
Ar'HN
F
O
N
Me
Ar' = 3-CF3-4-MeOPh
fl (ppm)


-62.2504
-111.8851
Ar'HN
F
O
N
Me
Ar' = 3-CF3-4-MeOPh
fl (ppm)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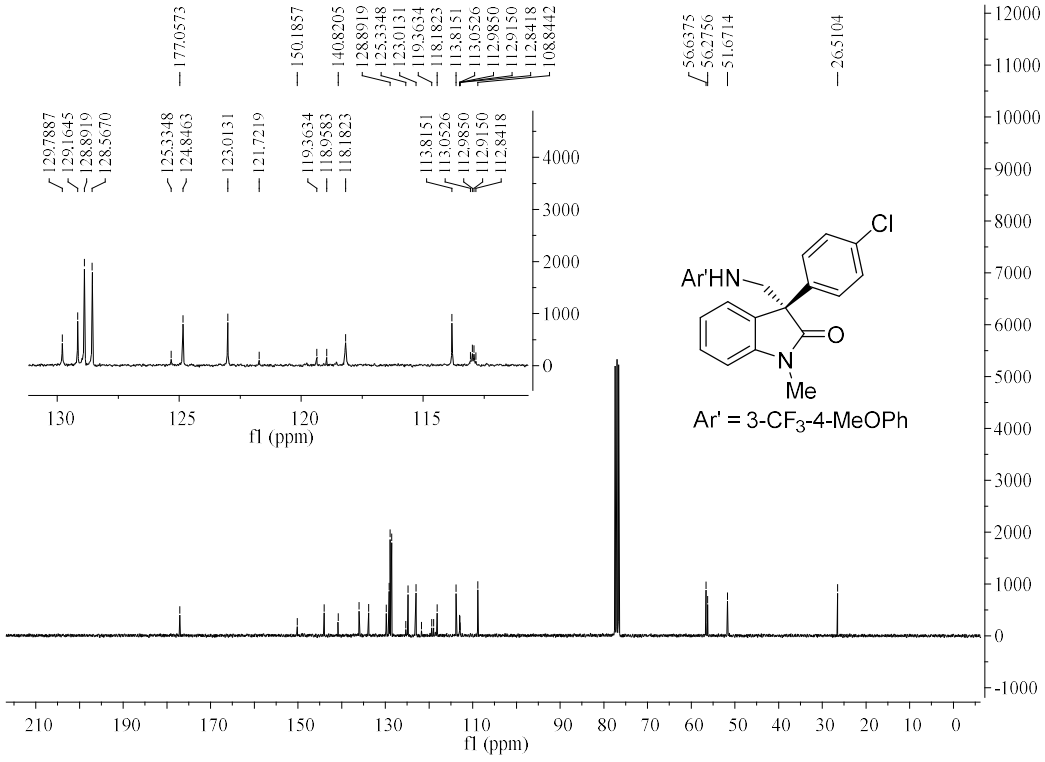
7.3423
7.3121
7.2830
7.1844
7.1597
7.1349
6.9478
6.9217
6.8321
6.8031
6.7443
6.7128
6.6989
4.0795
4.0384
3.7951
3.6933
3.6523
3.1864
6.03
1.00
1.00
0.99
1.98
1.04
3.00
1.05
2.98
Cl
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)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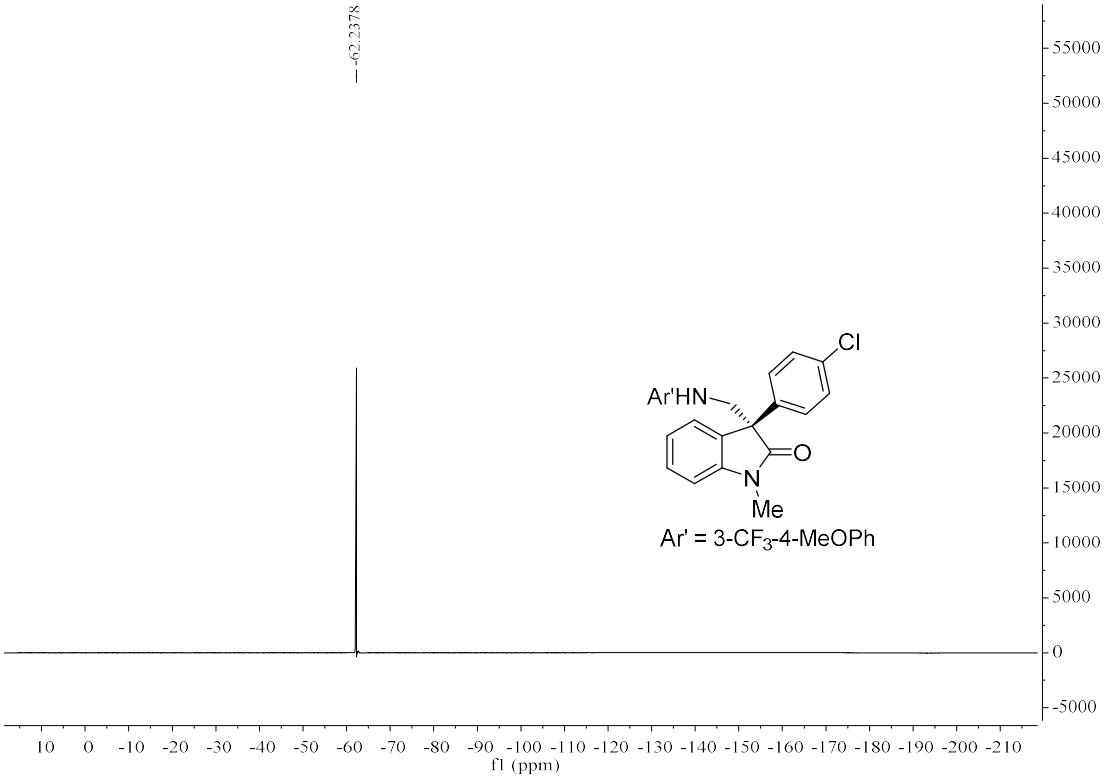
128.8919
125.3348
123.0131
119.3634
118.1823
113.8151
113.0526
112.9850
112.9150
112.8418
108.8442
56.6375
56.2756
51.6714
26.5104
129.7887
129.1645
128.8919
128.5670
125.3348
124.8463
123.0131
121.7219
119.3634
118.9583
118.1823
113.8151
113.0526
112.9850
112.9150
112.8418
Cl
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


-62.2378
Cl
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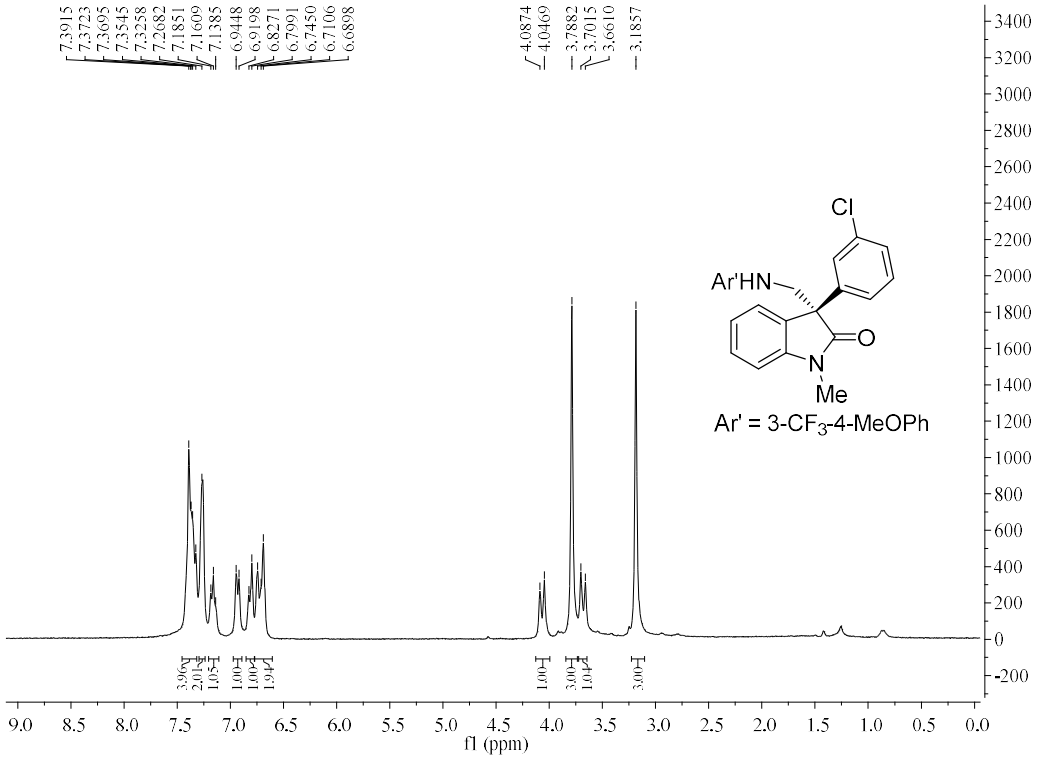
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)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7.3695
7.3545
7.3258
7.2682
7.1851
7.1609
7.1385
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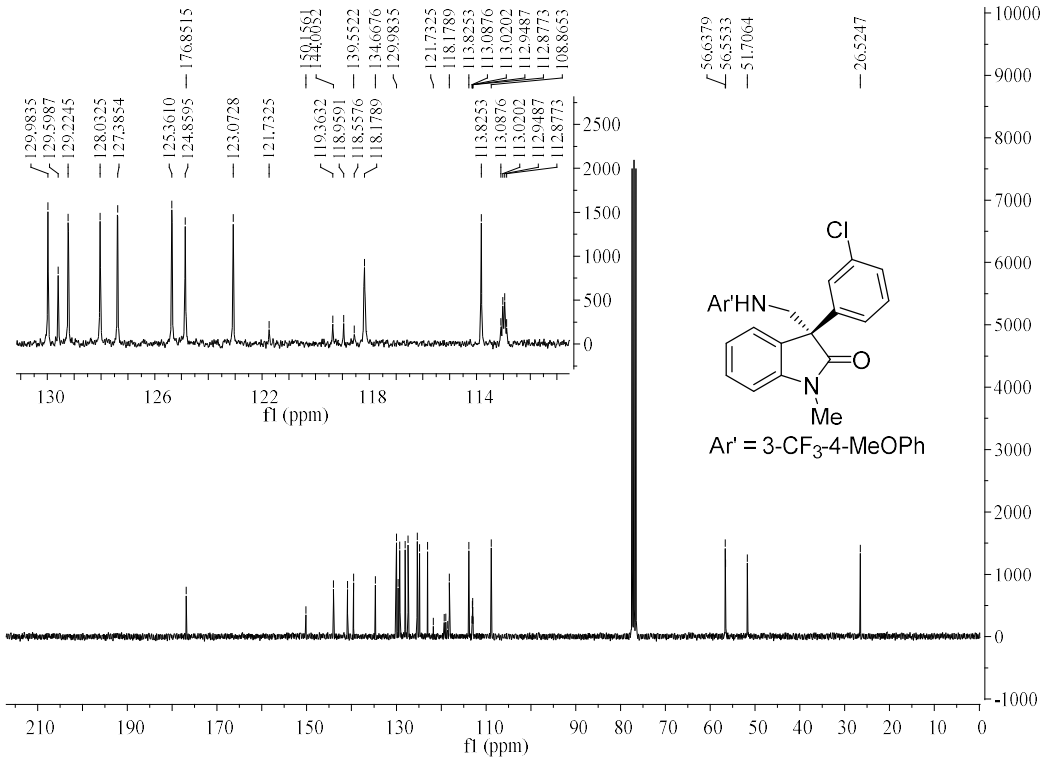
6.9198
6.8271
6.7991
6.7450
6.7106
6.6898
4.0874
4.0469
3.7882
3.7015
3.6610
3.1857
Cl
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)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121.7325
119.3632
118.9591
118.5576
118.1789
113.8253
113.0876
113.0202
112.9487
112.8773
176.8515
150.1561
144.0052
139.5522
134.6676
129.9835
121.7325
118.1789
113.8253
113.0876
113.0202
112.9487
112.8773
108.8653
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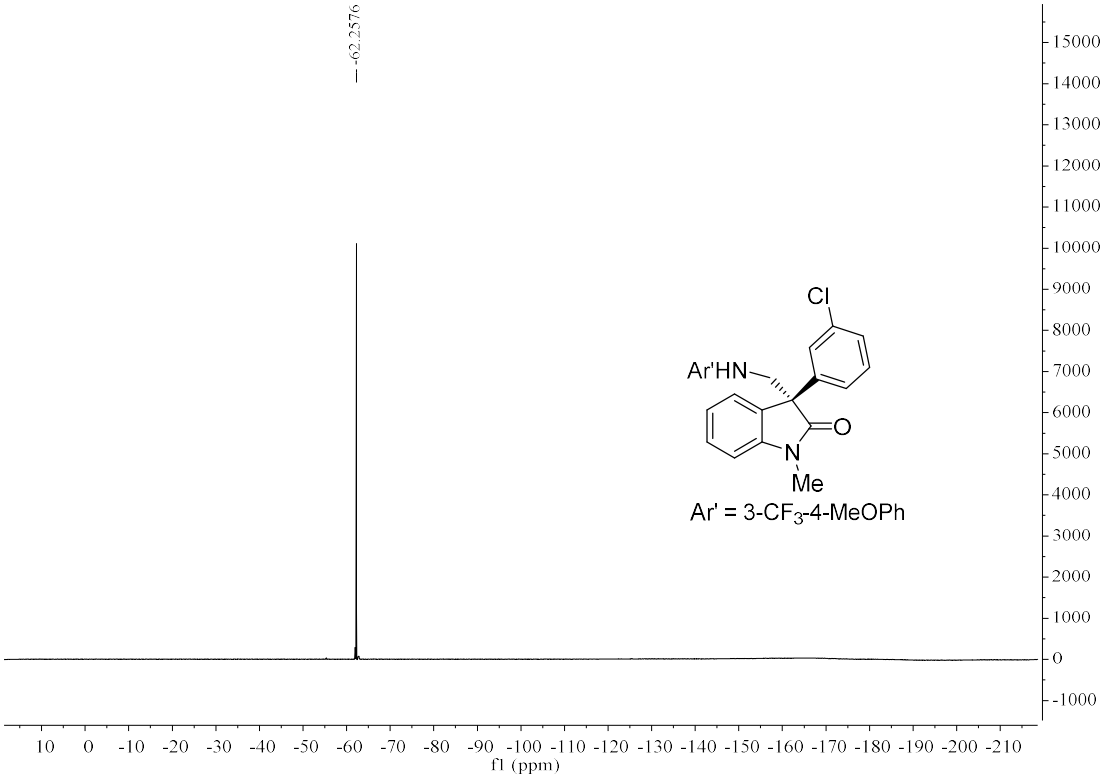
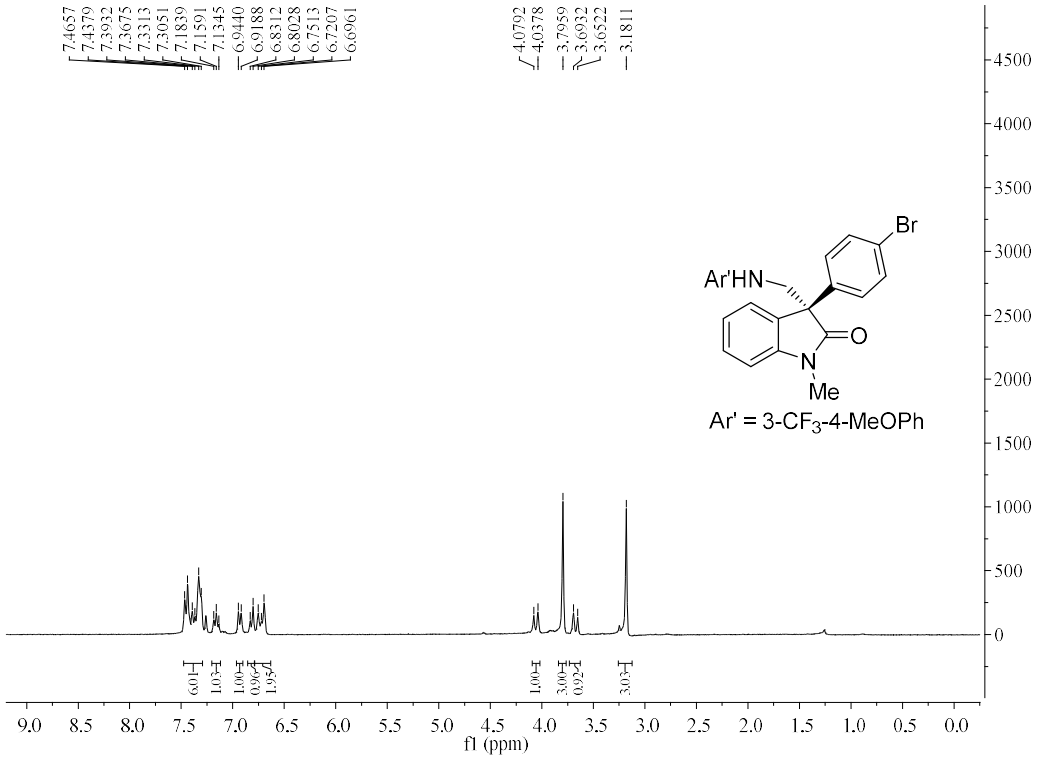
56.5533
51.7064
26.5247
fl (ppm)
Cl
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh


-62.2576
fl (ppm)
Cl
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh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7.1345
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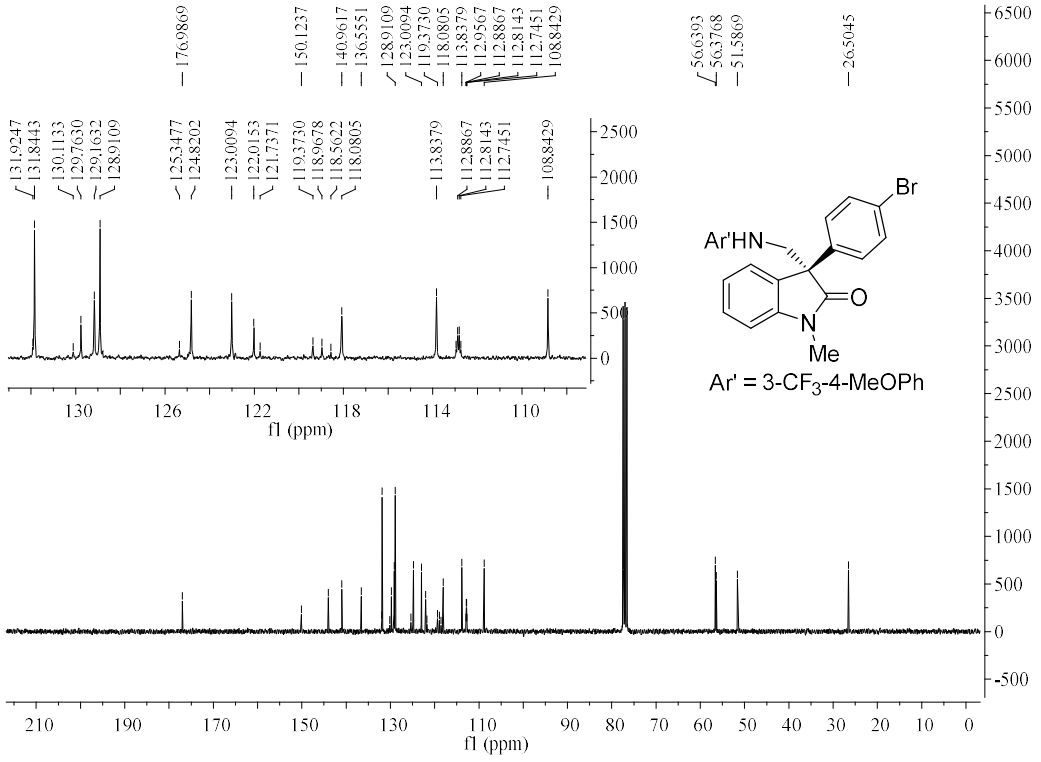
6.9188
6.8312
6.8028
6.7513
6.7207
6.6961
4.0792
4.0378
3.7959
3.6932
3.6522
3.1811
6.01H
1.03H
1.00H
0.96H
1.95H
1.00H
3.00H
0.92H
3.05H
Br
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)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112.8867
112.8143
112.7451
108.8429
56.6393
56.3768
51.5869
26.5045
131.9247
131.8443
130.1133
129.7630
129.1632
128.9109
125.3477
124.8202
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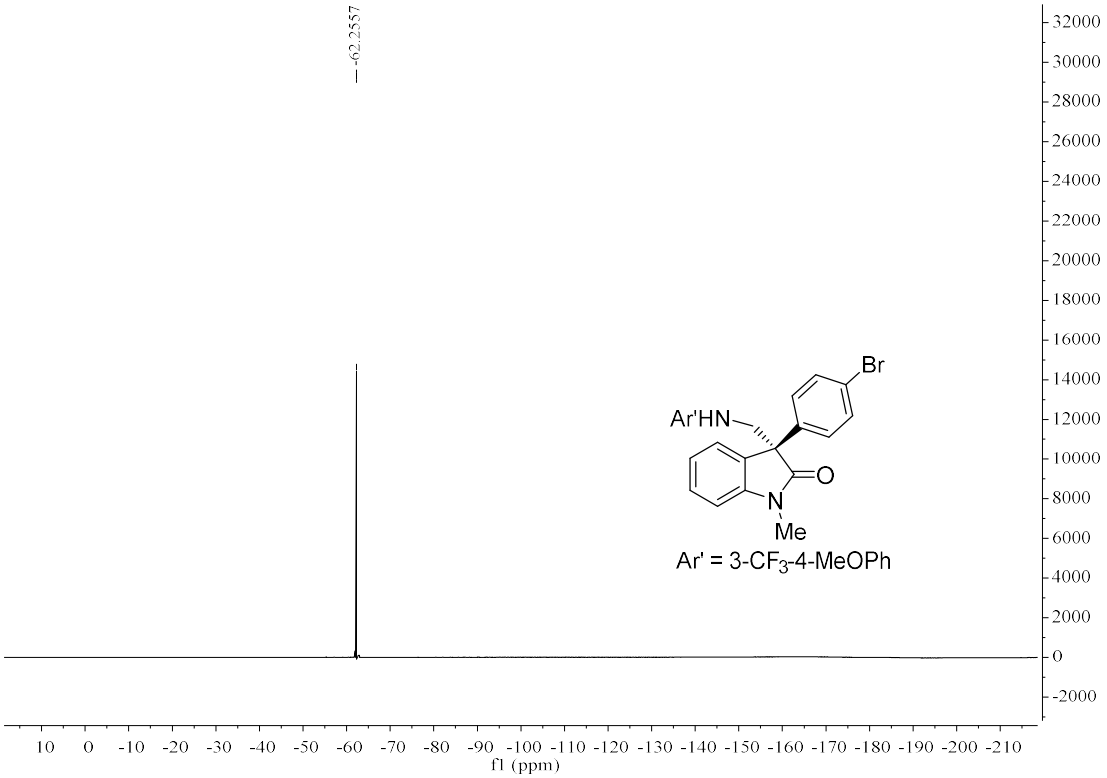
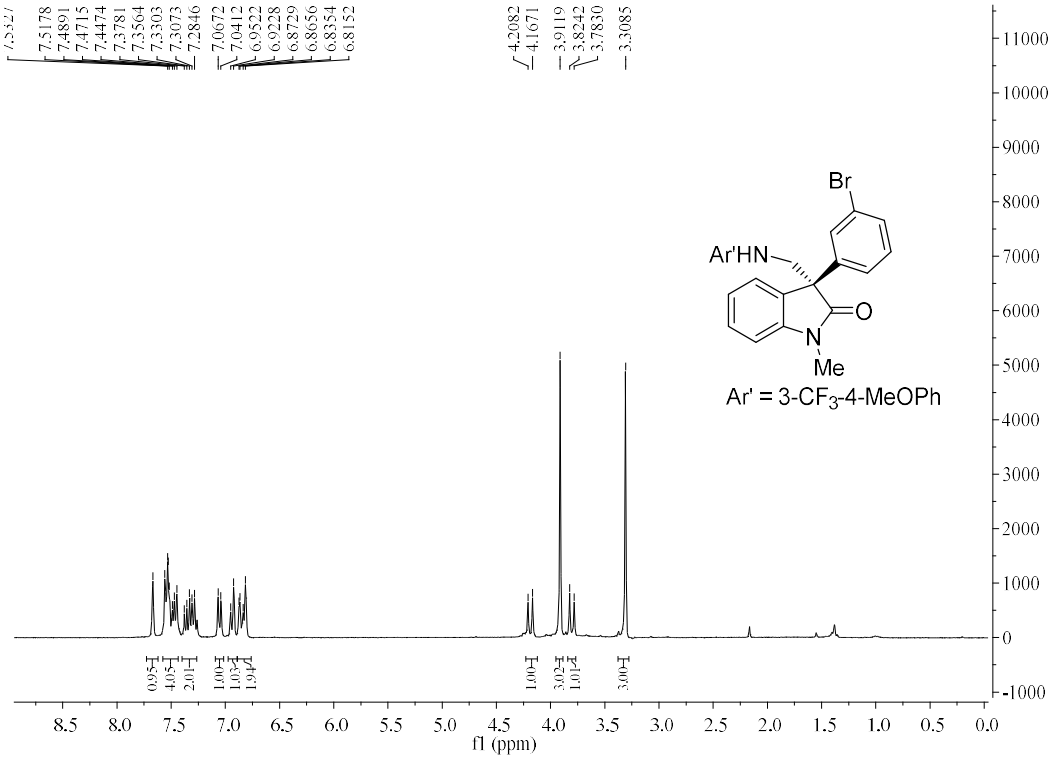
121.7371
119.3730
118.9678
118.5622
118.0805
113.8379
112.8867
112.8143
112.7451
108.8429
Br
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)
f1 (ppm)


-62.2557
Br
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)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7.4474
7.3781
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7.3303
7.3073
7.2846
7.0672
7.0412
6.9522
6.9228
6.8729
6.8656
6.8354
6.8152
4.2082
4.1671
3.9119
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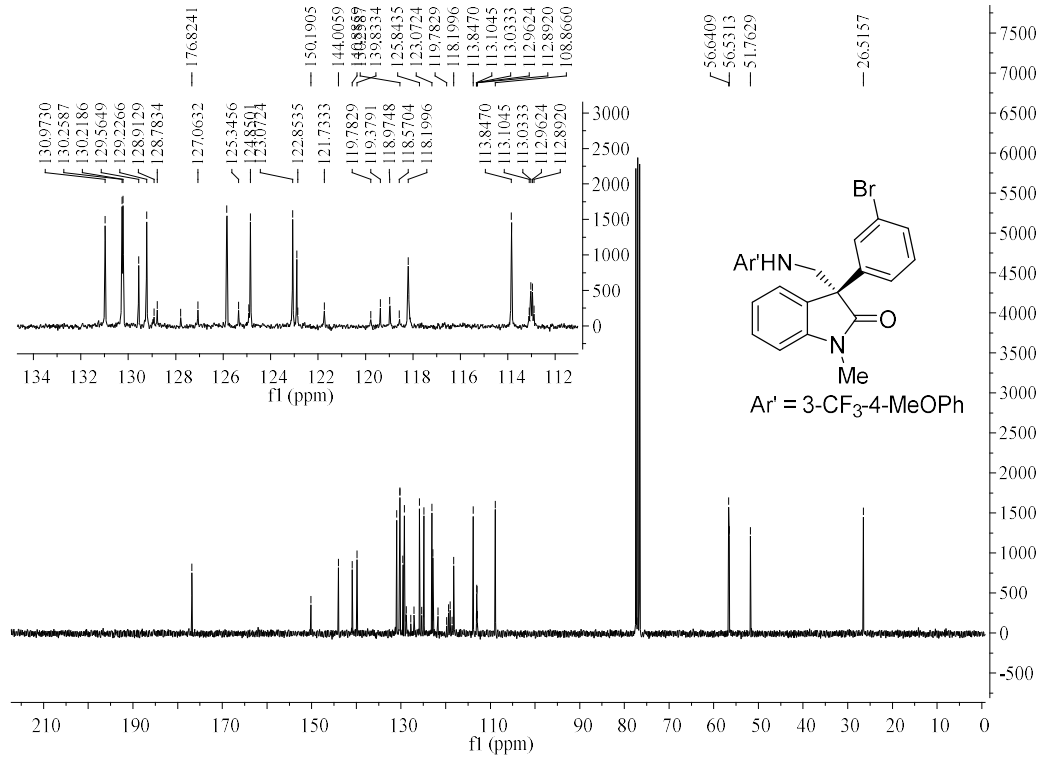
3.3085
Br
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)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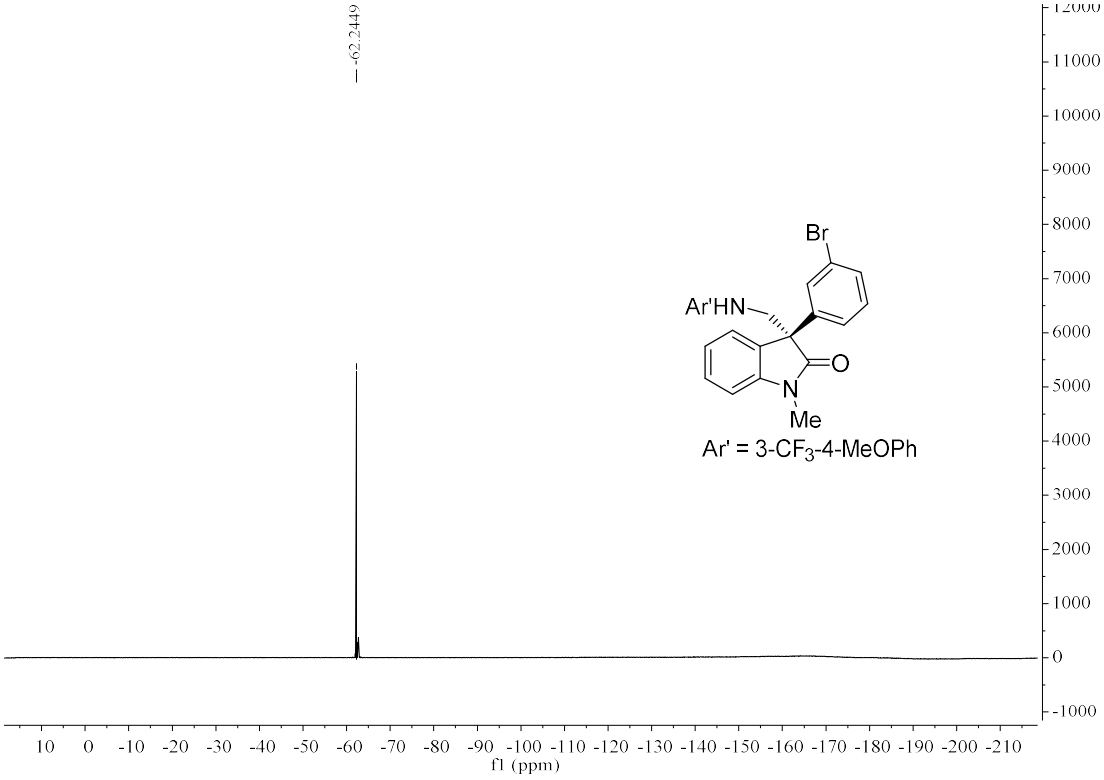
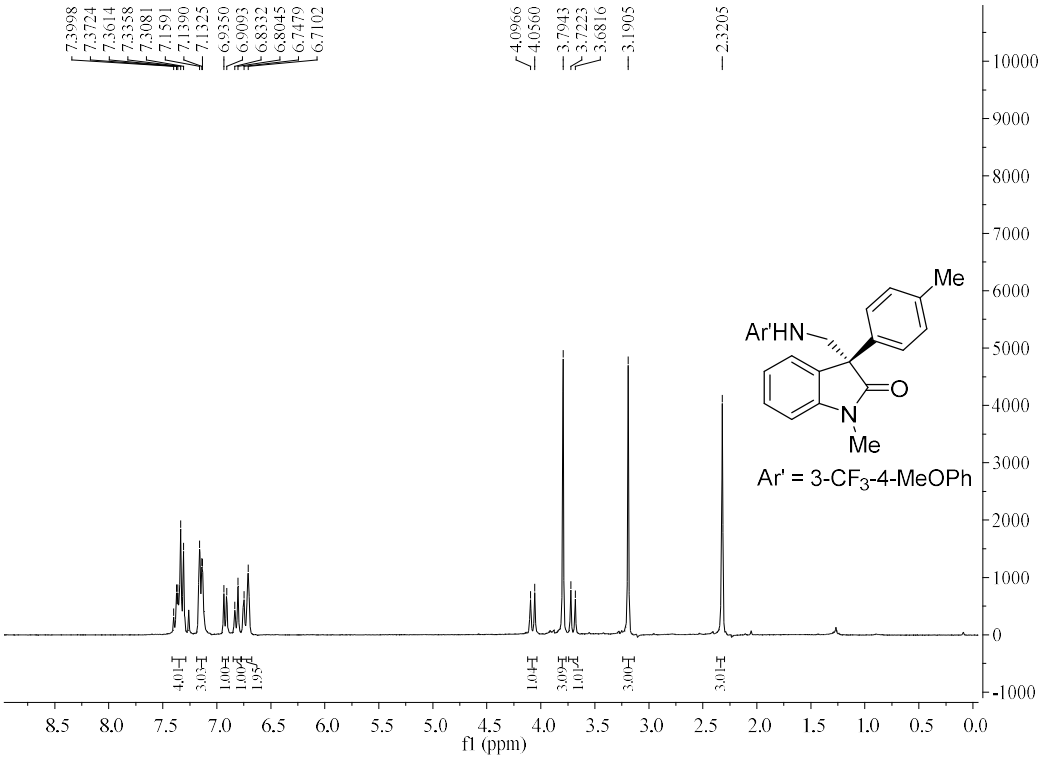
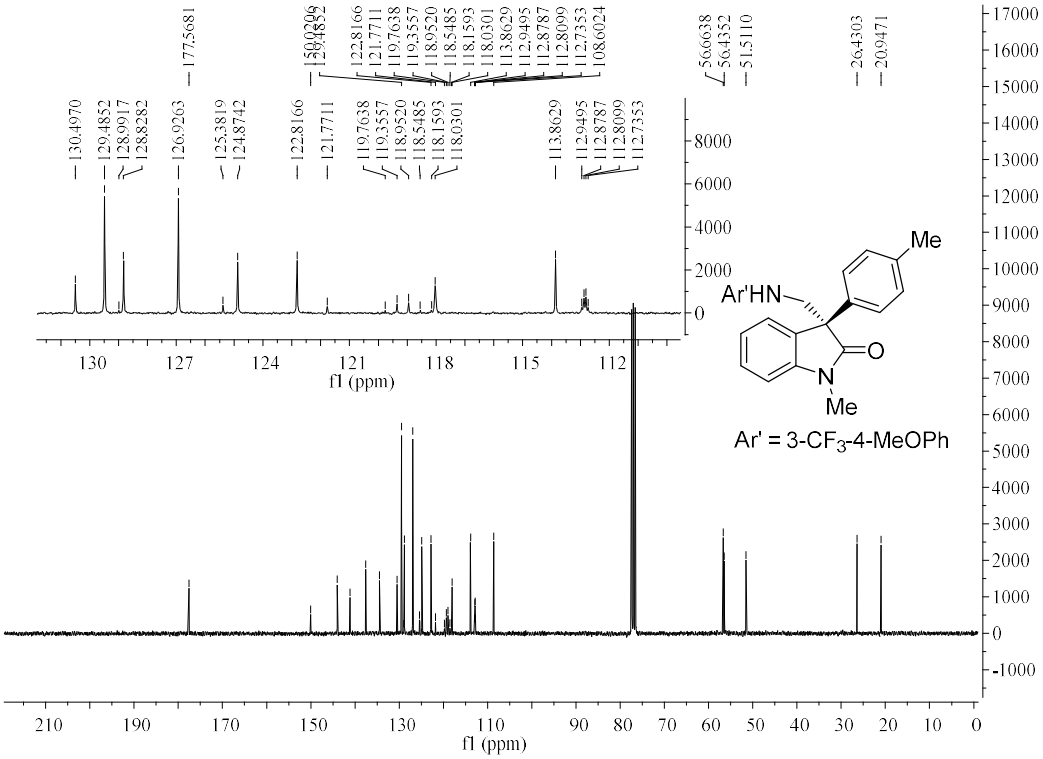
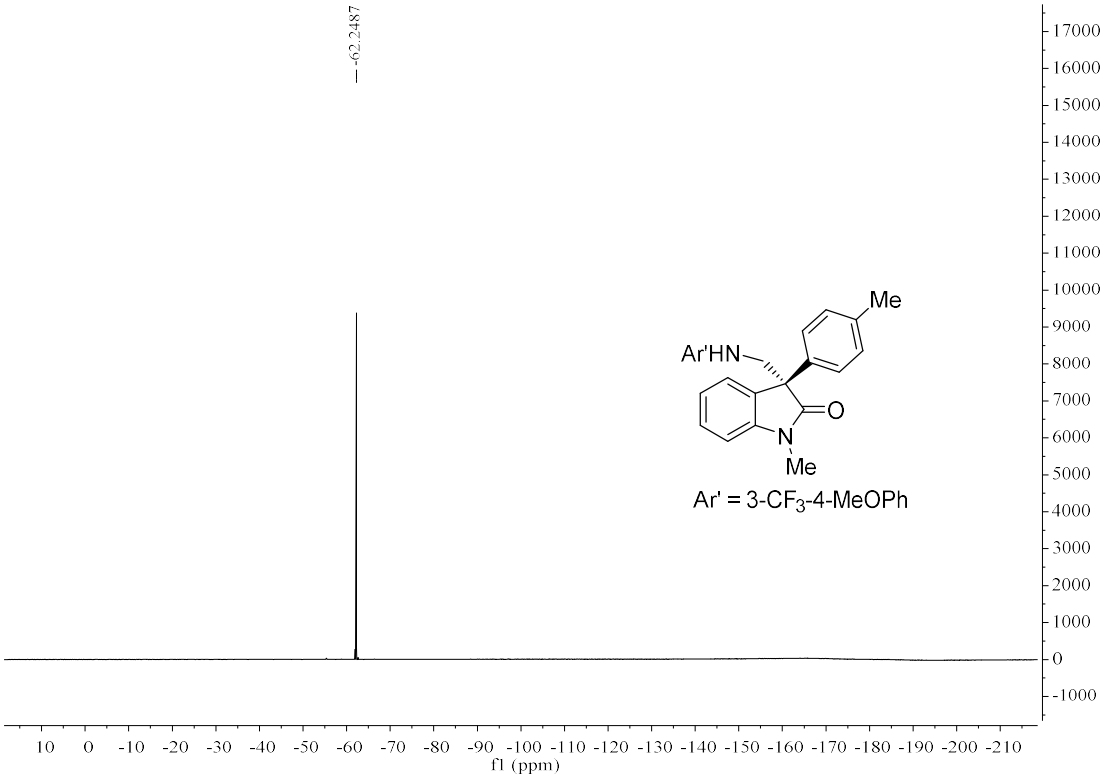
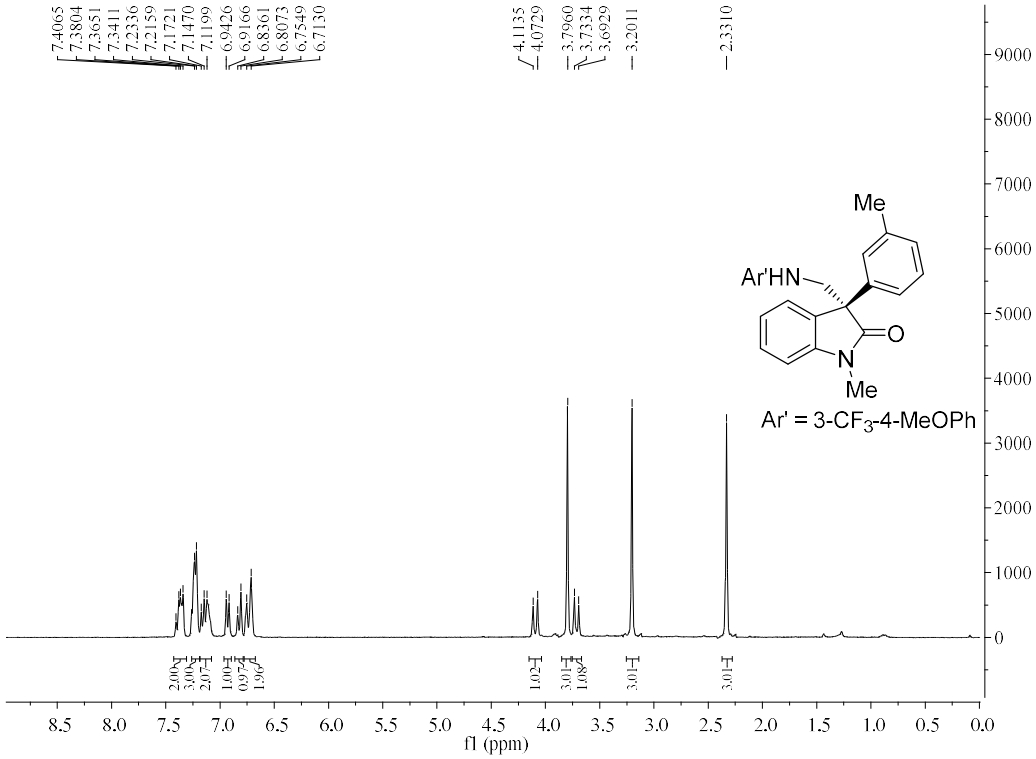
119.7829
119.3791
118.9748
118.5704
118.1996
113.8470
113.1045
113.0333
112.9624
112.8920
fl (ppm)
Br
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
fl (ppm)

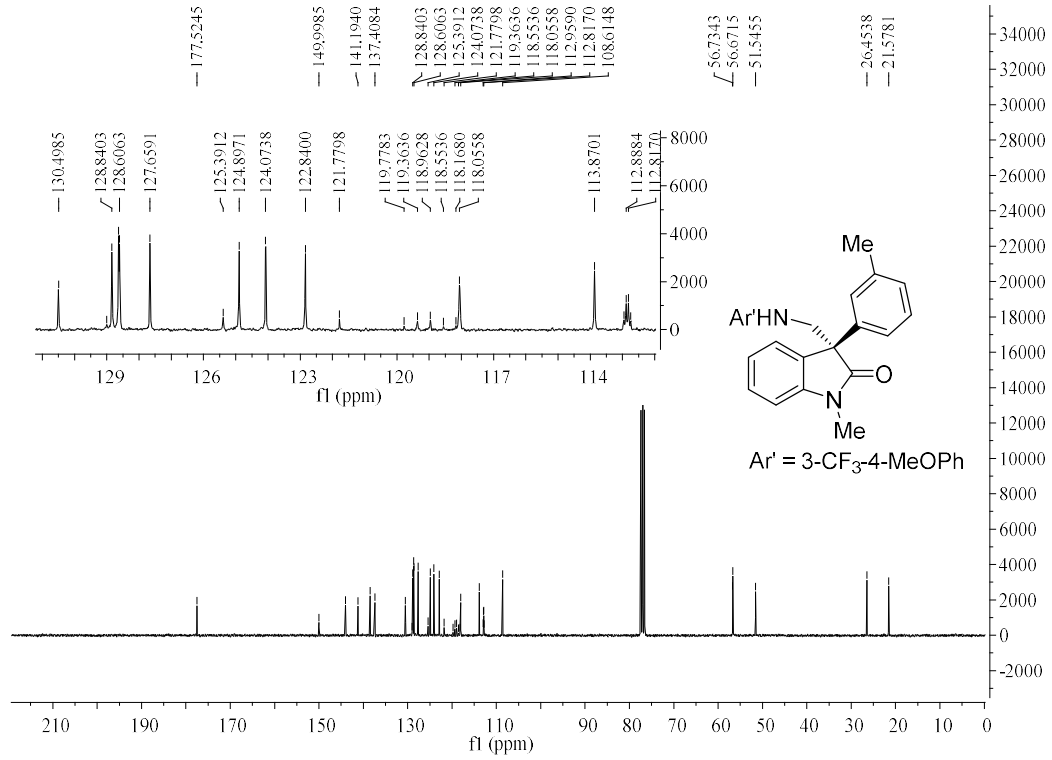

-62.2449
Br
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
fl (ppm)


7.3998
7.3724
7.3614
7.3358
7.3081
7.1591
7.1390
7.1325
6.9350
6.9093
6.8332
6.8045
6.7479
6.7102
4.0966
4.0560
3.7943
3.7223
3.6816
3.1905
2.3205
Me
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


177.5681
150.0296
129.4852
122.8166
121.7711
119.7638
119.3557
118.9520
118.5485
118.1593
118.0301
113.8629
112.9495
112.8787
112.8099
112.7353
108.6024
56.6638
56.4352
51.5110
26.4303
20.9471
130.4970
129.4852
128.9917
128.8282
126.9263
125.3819
124.8742
122.8166
121.7711
119.7638
119.3557
118.9520
118.5485
118.1593
118.0301
113.8629
112.9495
112.8787
112.8099
112.7353
Me
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)
f1 (ppm)


-62.2487
Ar'HN
Me
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


7.4065
7.3804
7.3651
7.3411
7.2336
7.2159
7.1721
7.1470
7.1199
6.9426
6.9166
6.8361
6.8073
6.7549
6.7130
4.1135
4.0729
3.7960
3.7334
3.6929
3.2011
2.3310
Ar'HN
Me
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)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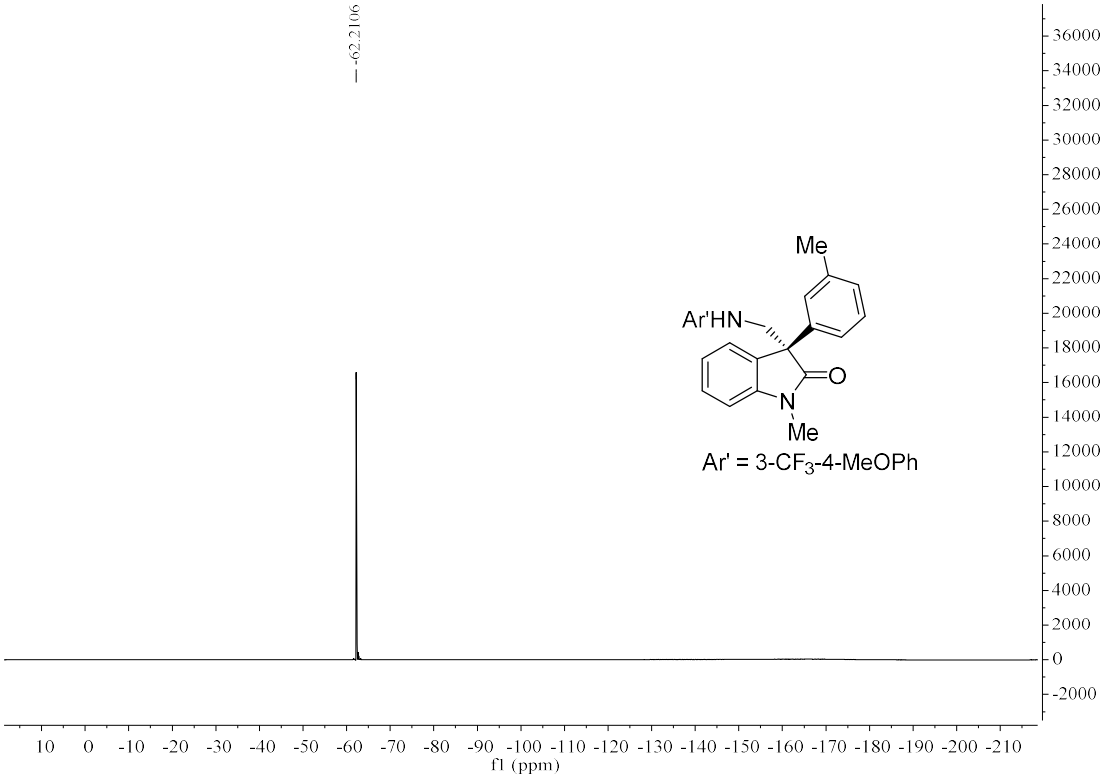
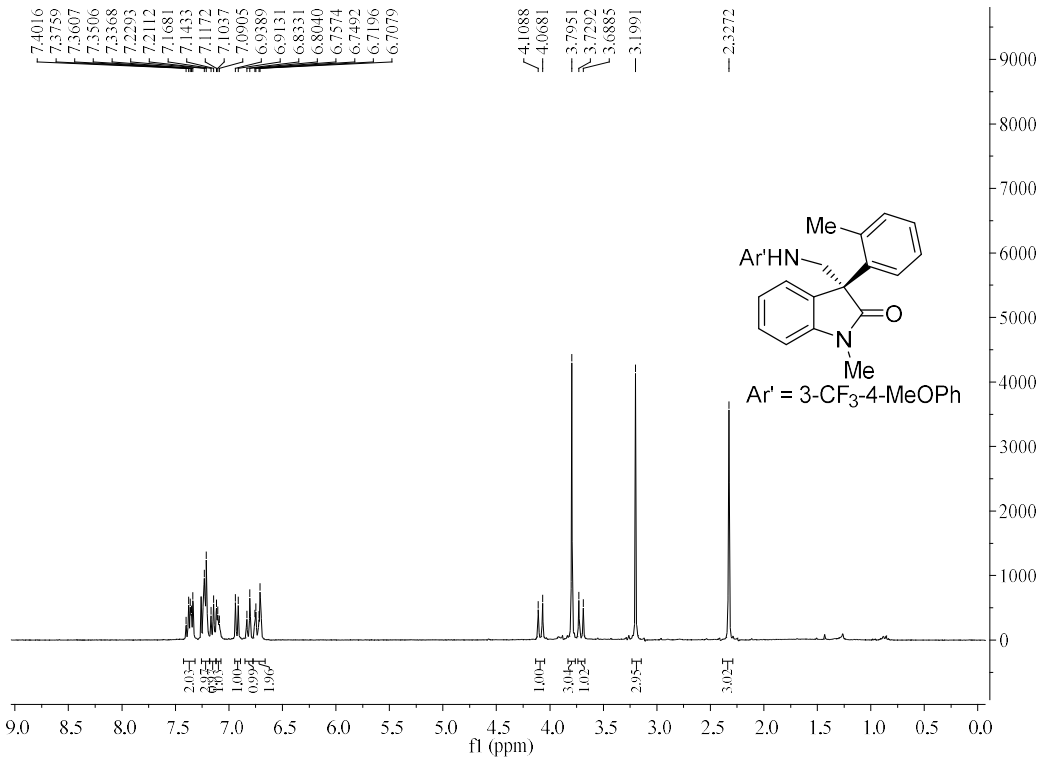
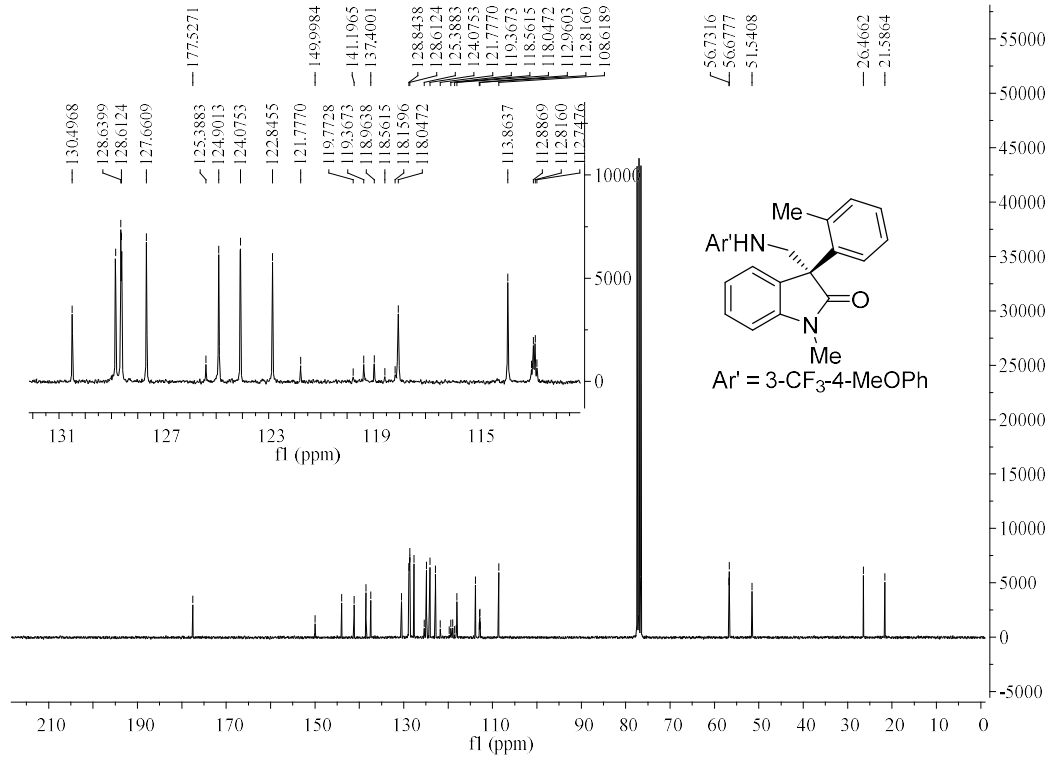
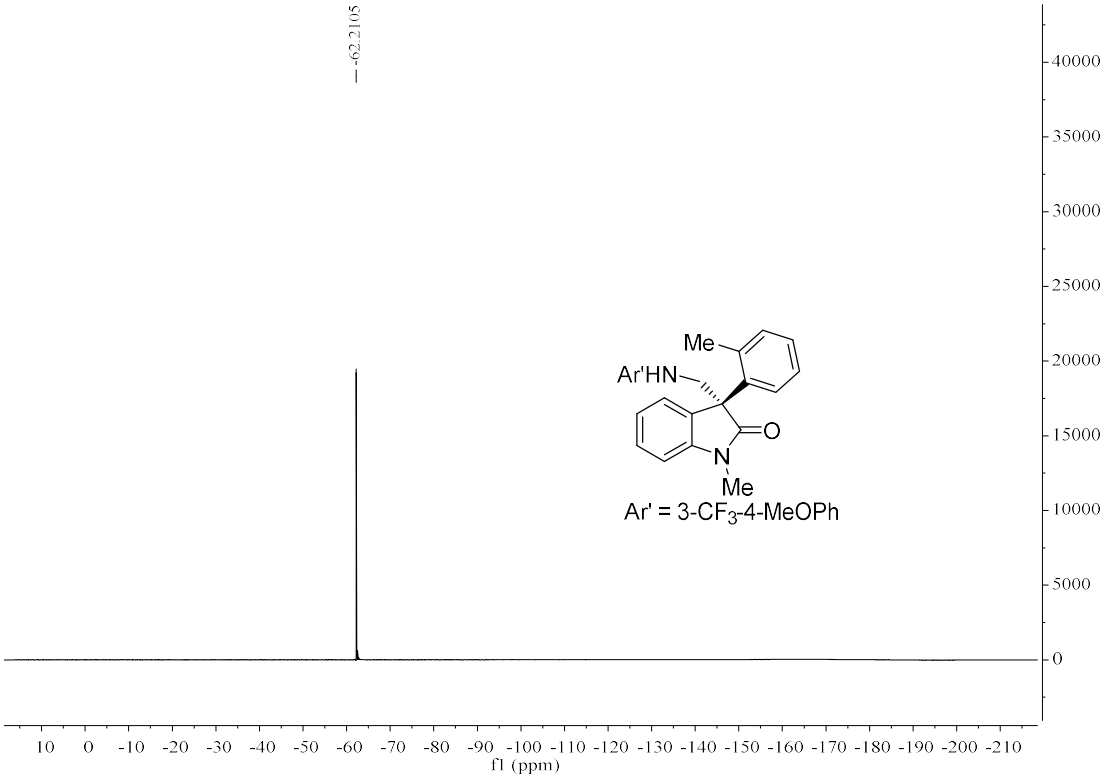
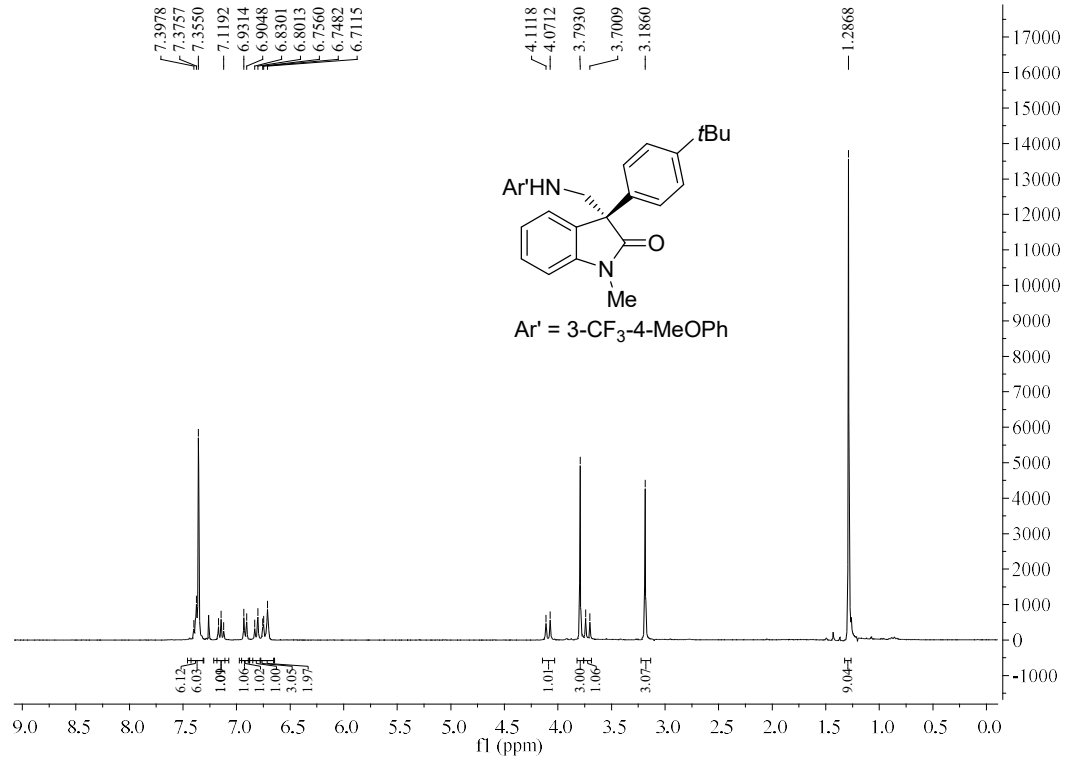
149.9985
141.1940
137.4084
128.8403
128.6063
125.3912
124.0738
121.7798
119.3636
118.5536
118.0558
112.9590
112.8170
108.6148
56.7343
56.6715
51.5455
26.4538
21.5781
130.4985
128.8403
128.6063
127.6591
125.3912
124.8971
124.0738
122.8400
121.7798
119.7783
119.3636
118.9628
118.5536
118.1680
118.0558
113.8701
112.8884
112.8170
f1 (ppm)
Me
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)

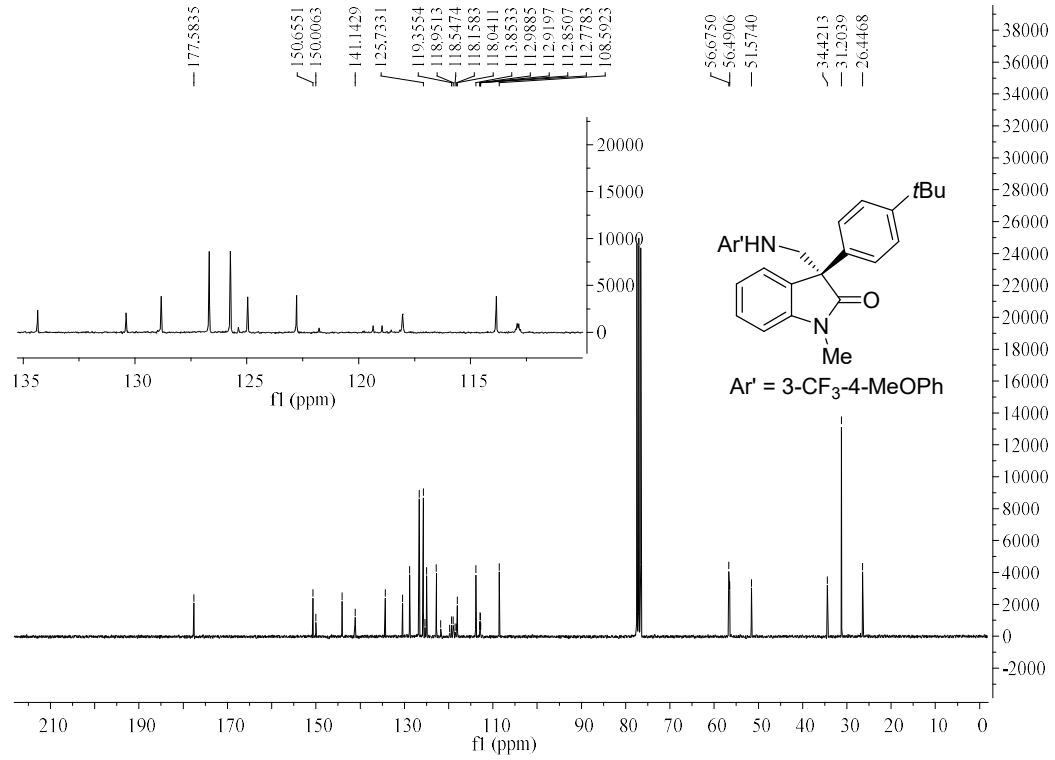

-62.2106
Me
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)

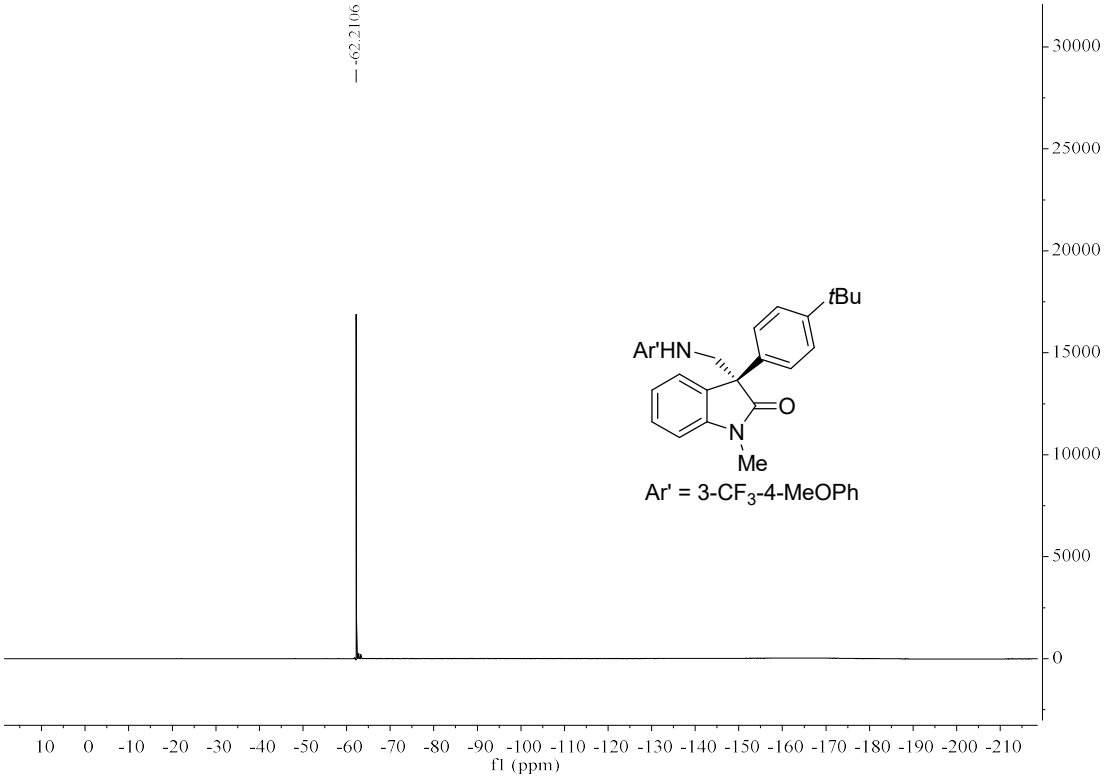

Me
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
fl (ppm)

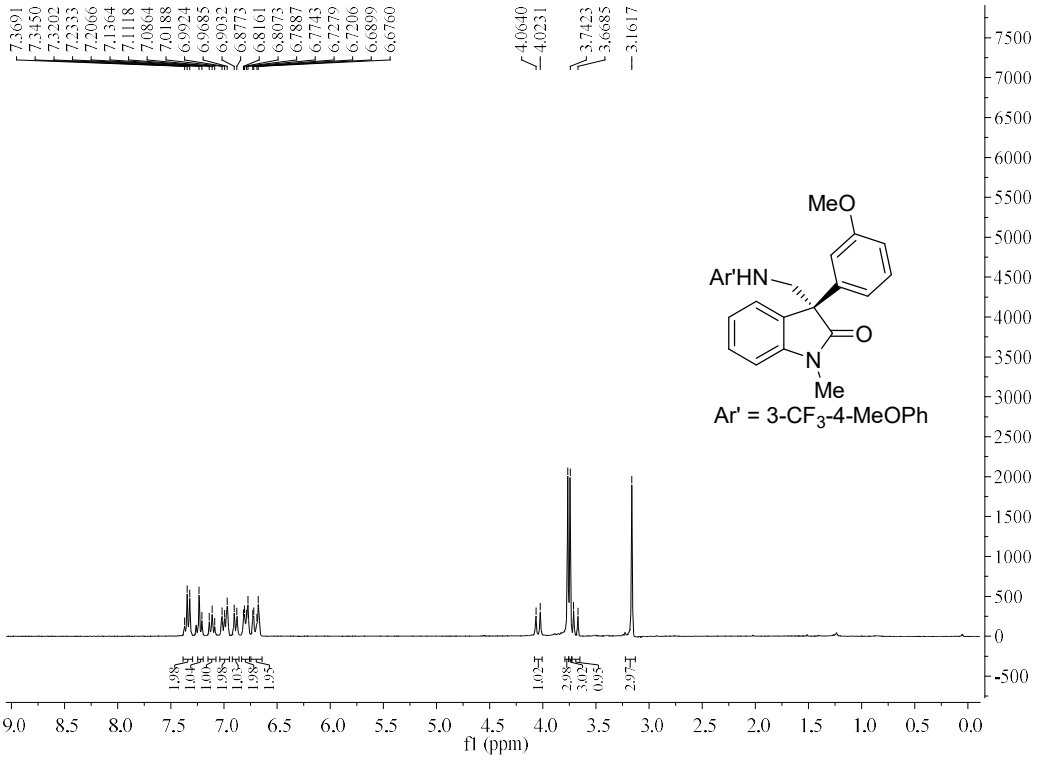

Me
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
fl (ppm)

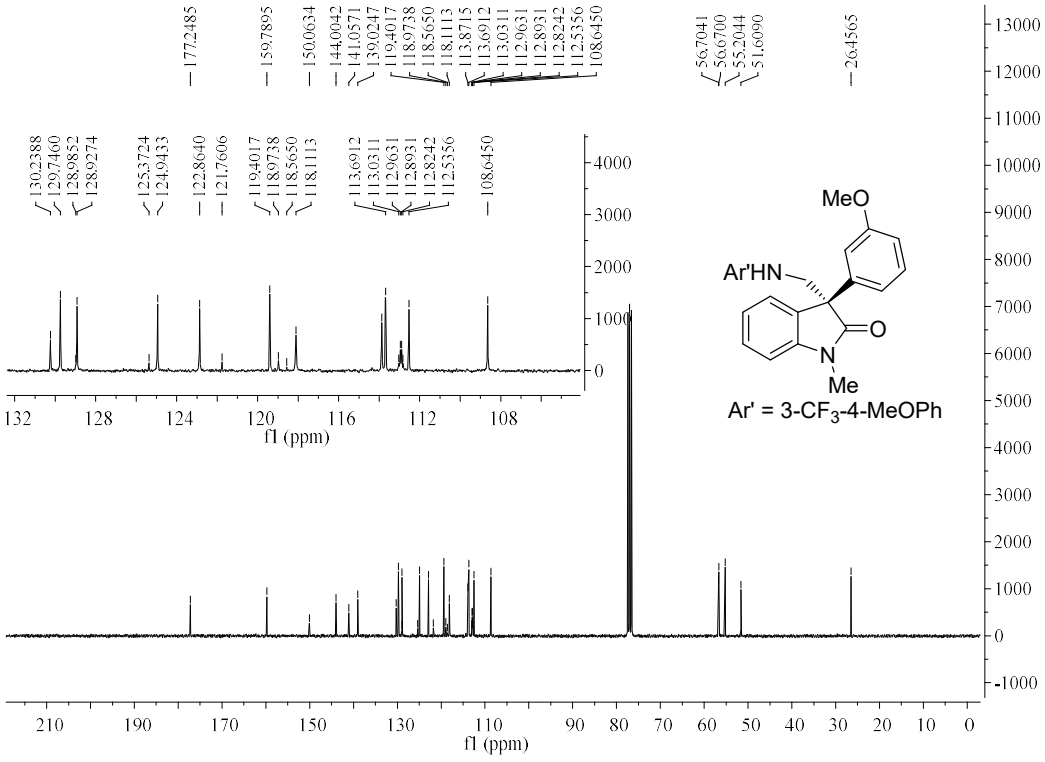

-62.2105
Me
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)

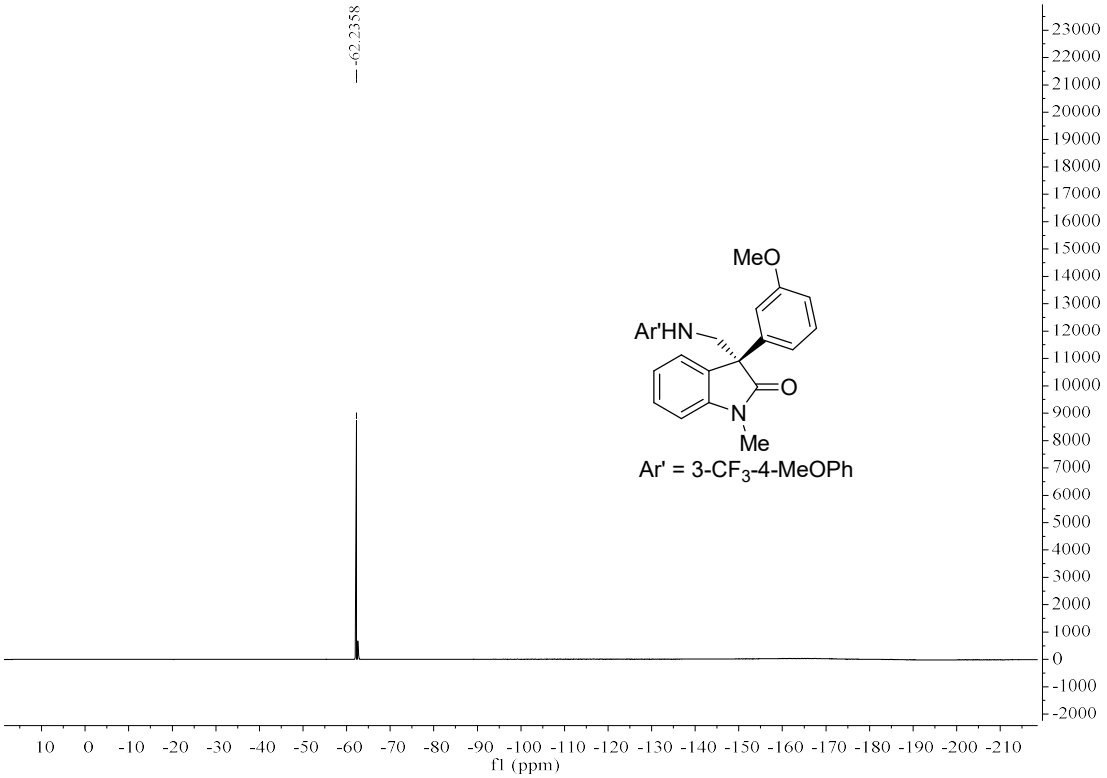

7.3978
7.3757
7.3550
7.1192
6.9314
6.9048
6.8301
6.8013
6.7560
6.7482
6.7115
4.1118
4.0712
3.7930
3.7009
3.1860
1.2868
tBu
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
6.12
6.03
1.04
1.06
1.02
1.00
3.05
1.97
1.01
3.00
1.06
3.07
9.04
f1 (ppm)

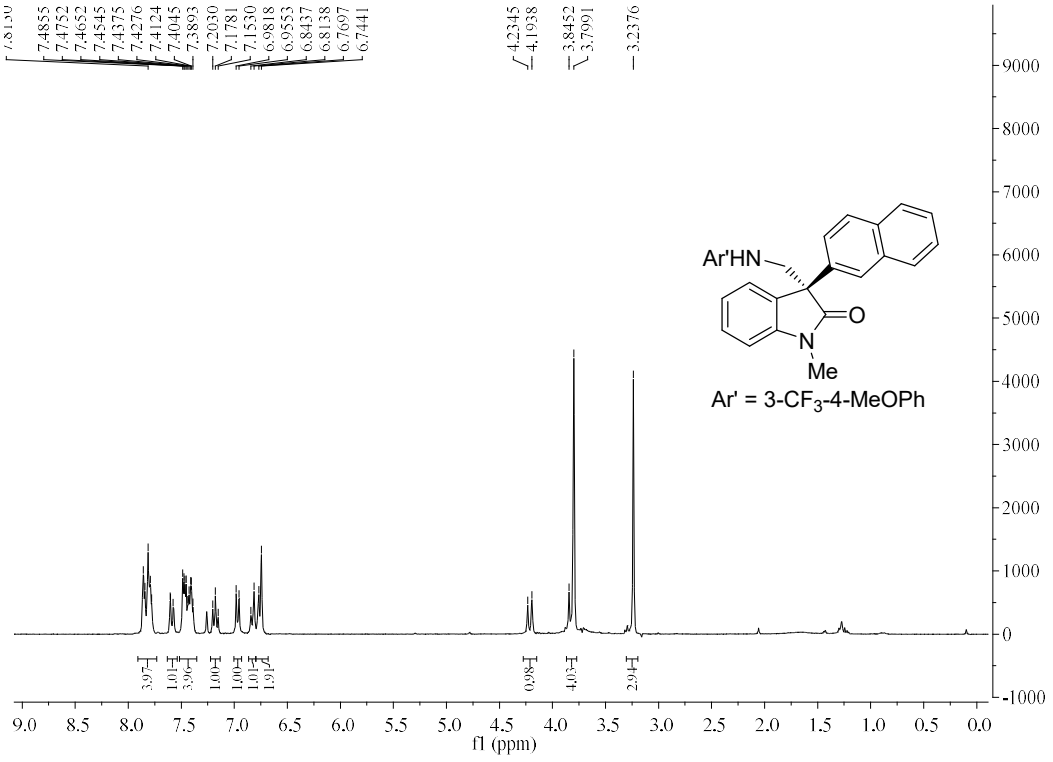

177.5835
150.6551
150.0063
141.1429
125.7331
119.3554
118.9513
118.5474
118.1583
118.0411
113.8533
112.9885
112.9197
112.8507
112.7783
108.5923
56.6750
56.4906
51.5740
34.4213
31.2039
26.4468
fl (ppm)
tBu
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh

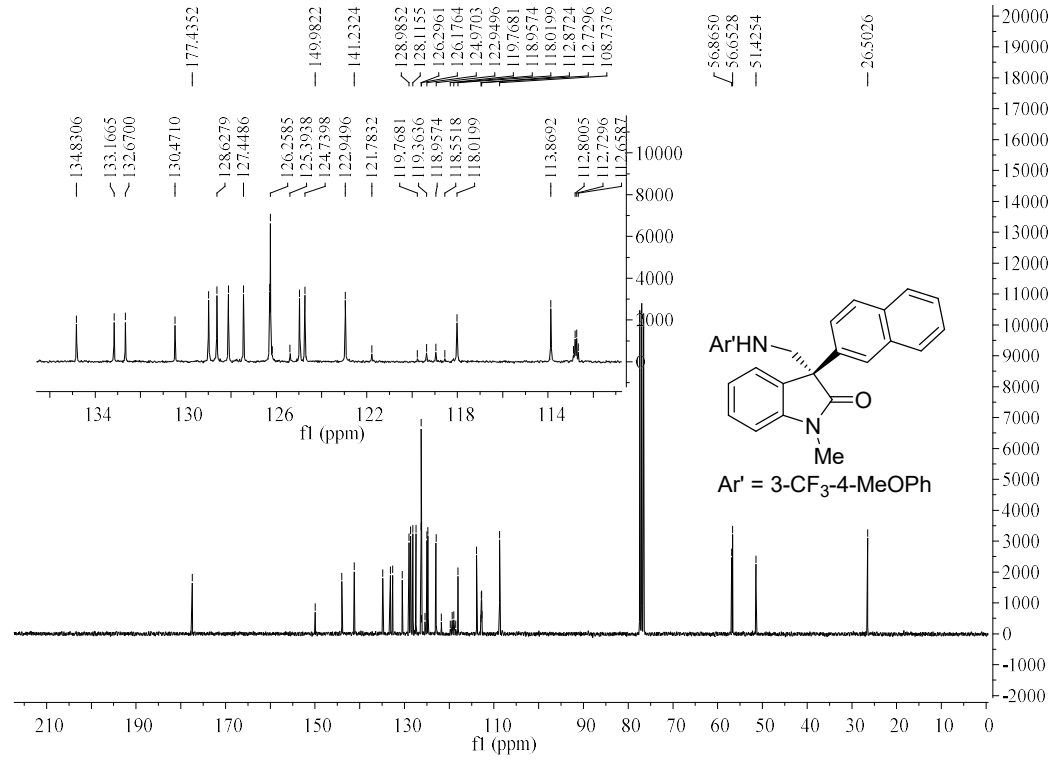

-62.2106
fl (ppm)
tBu
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh


MeO
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


MeO
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


-62.2358
MeO
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


7.8139
7.4855
7.4752
7.4652
7.4545
7.4375
7.4276
7.4124
7.4045
7.3893
7.2030
7.1781
7.1530
6.9818
6.9553
6.8437
6.8138
6.7697
6.7441
4.2345
4.1938
3.8452
3.7991
3.2376
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
3.97
1.01
3.96
1.00
1.00
1.01
1.91
0.98
4.03
2.94
f1 (ppm)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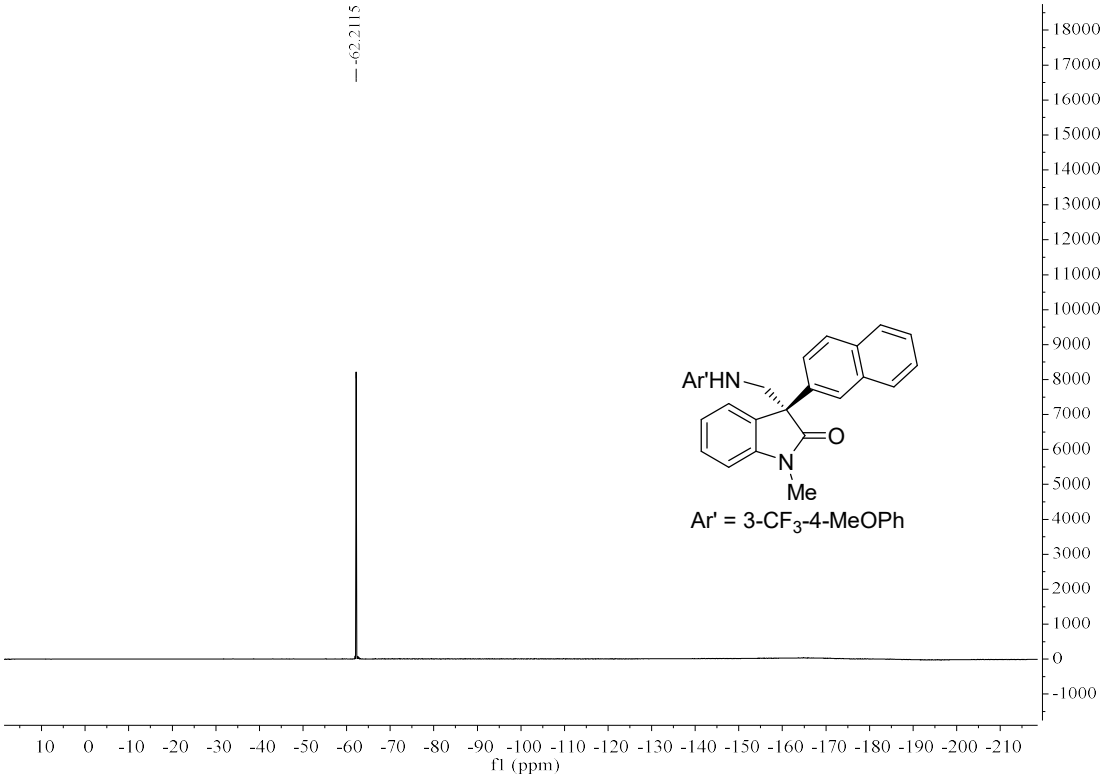
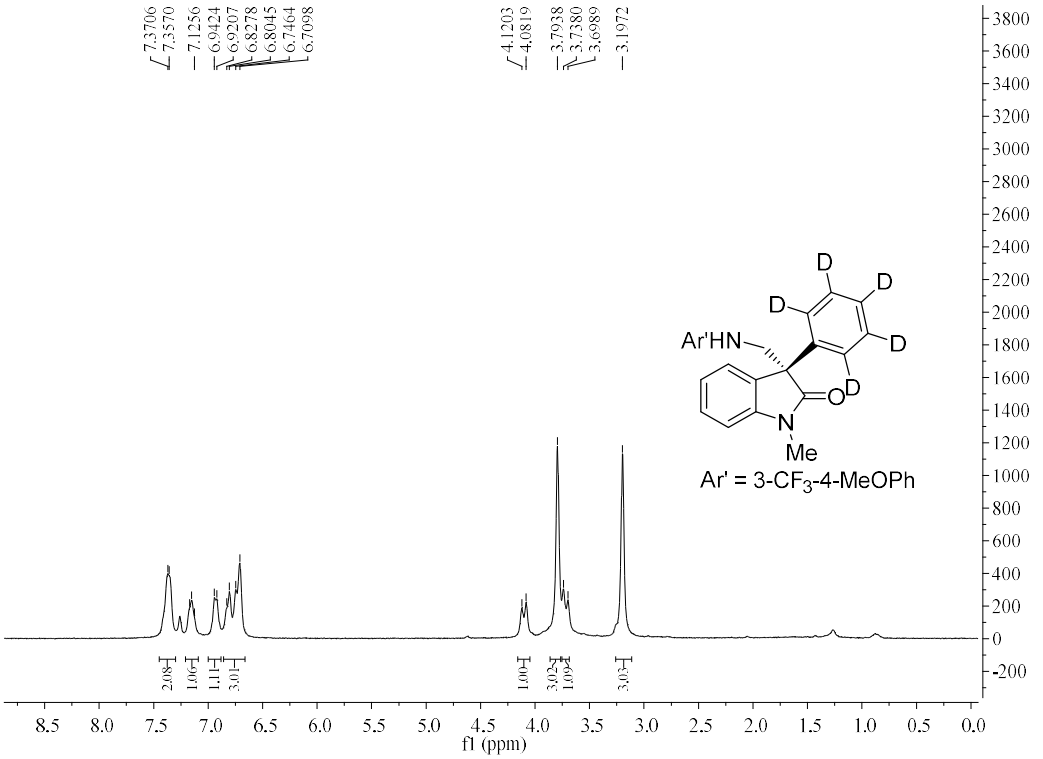
149.9822
141.2324
128.9852
128.1155
126.2961
126.1764
124.9703
122.9496
119.7681
118.9574
118.0199
112.8724
112.7296
108.7376
56.8650
56.6528
51.4254
26.5026
134.8306
133.1665
132.6700
130.4710
128.6279
127.4486
126.2585
125.3938
124.7398
122.9496
121.7832
119.7681
119.3636
118.9574
118.5518
118.0199
113.8692
112.8005
112.7296
112.6587
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


-62.2115
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)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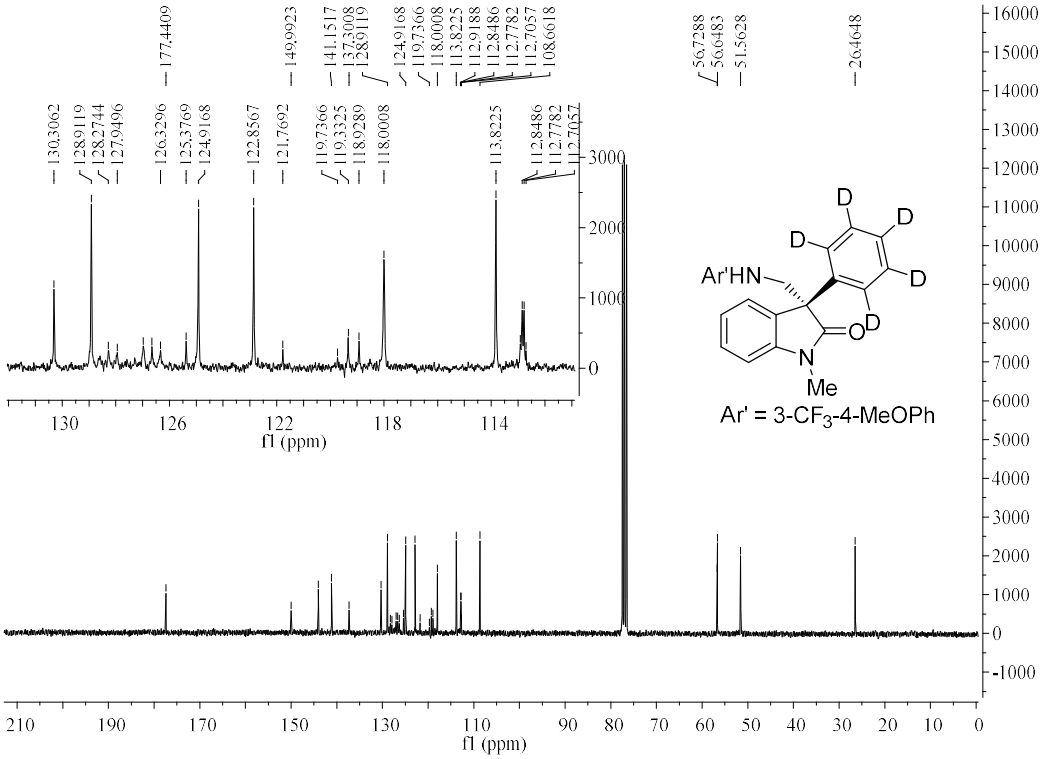
7.3570
7.1256
6.9424
6.9207
6.8278
6.8045
6.7464
6.7098
4.1203
4.0819
3.7938
3.7380
3.6989
3.1972
2.08
1.06
1.11
3.01
1.00
3.02
1.09
3.03
D
D
D
D
D
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
fl (ppm)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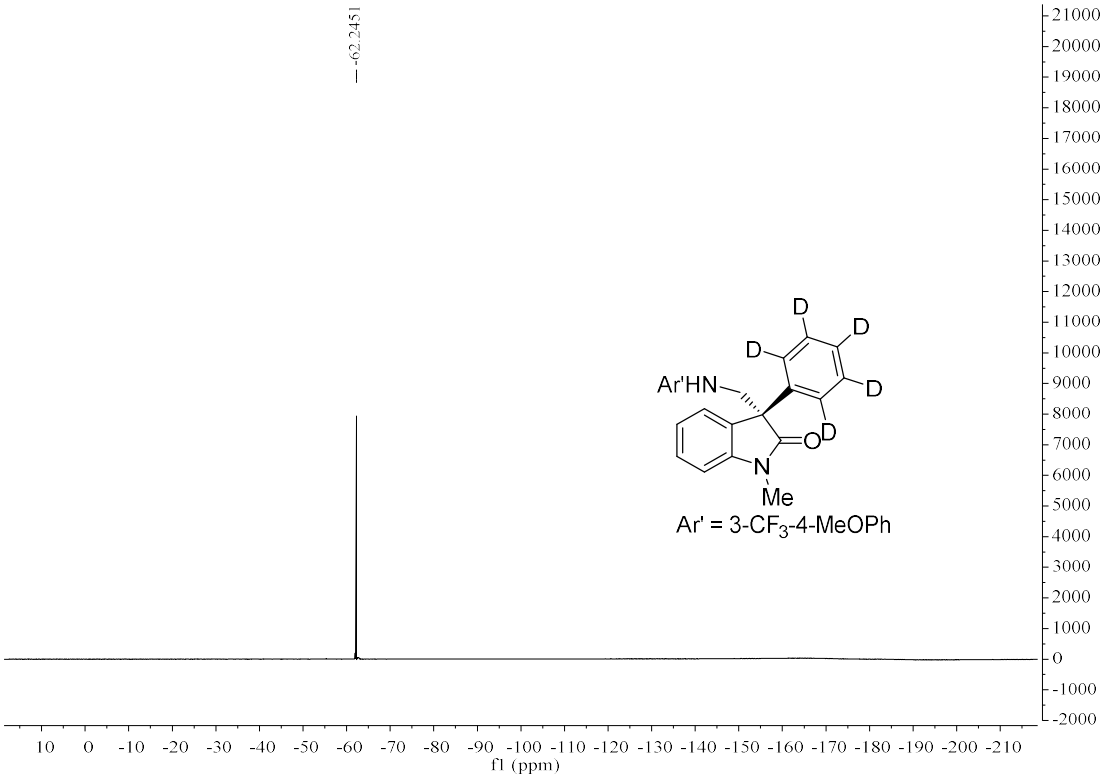
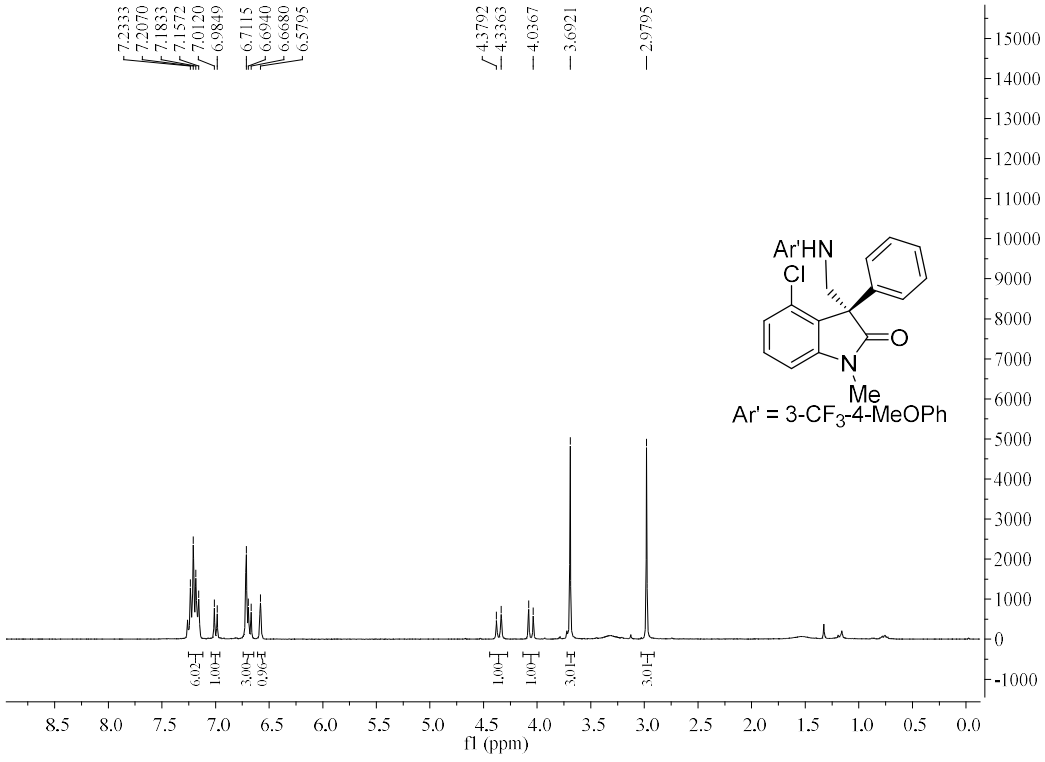
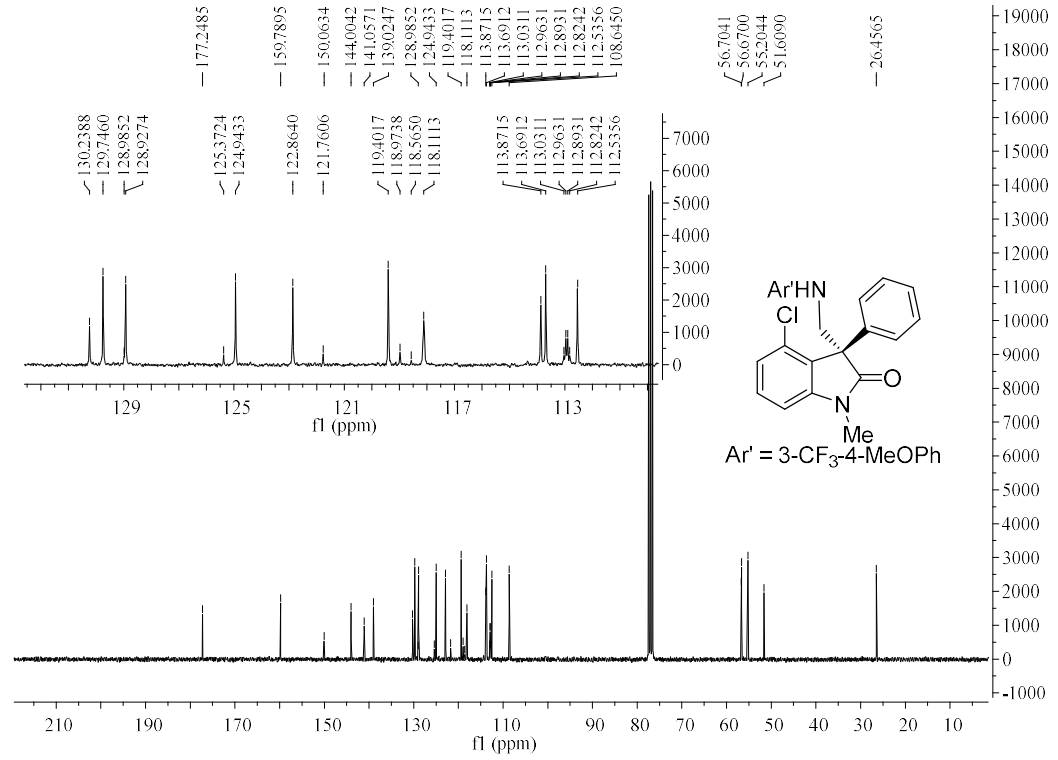
141.1517
137.3008
128.9119
124.9168
119.7366
118.0008
113.8225
112.9188
112.8486
112.7782
112.7057
108.6618
56.7288
56.6483
51.5628
26.4648
130.3062
128.9119
128.2744
127.9496
126.3296
125.3769
124.9168
122.8567
121.7692
119.7366
119.3325
118.9289
118.0008
113.8225
112.8486
112.7782
112.7057
D
D
D
D
D
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
fl (ppm)


-62.2451
D
D
D
D
D
D
Ar'HN
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


7.2333
7.2070
7.1833
7.1572
7.0120
6.9849
6.7115
6.6940
6.6680
6.5795
4.3792
4.3363
4.0367
3.6921
2.9795
Ar'HN
Cl
O
N
Me
Ar' = 3-CF3-4-MeOPh
6.02
1.00
3.09
0.96
1.00
1.00
3.01
3.01
f1 (ppm)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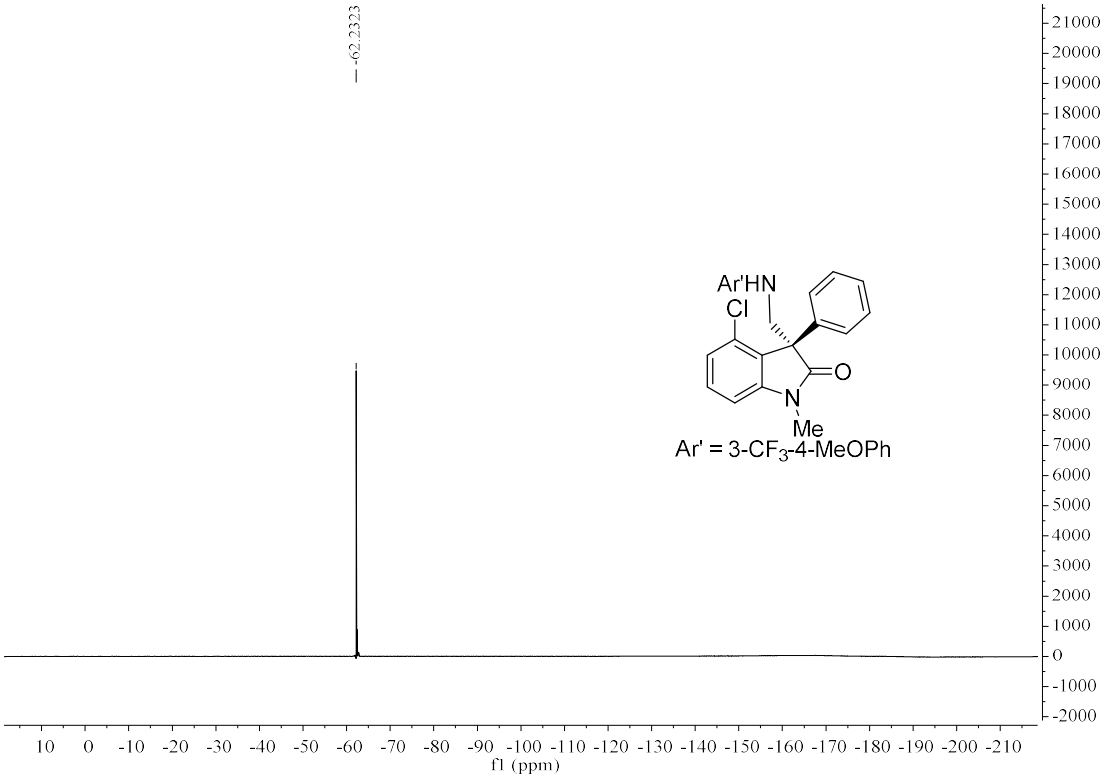
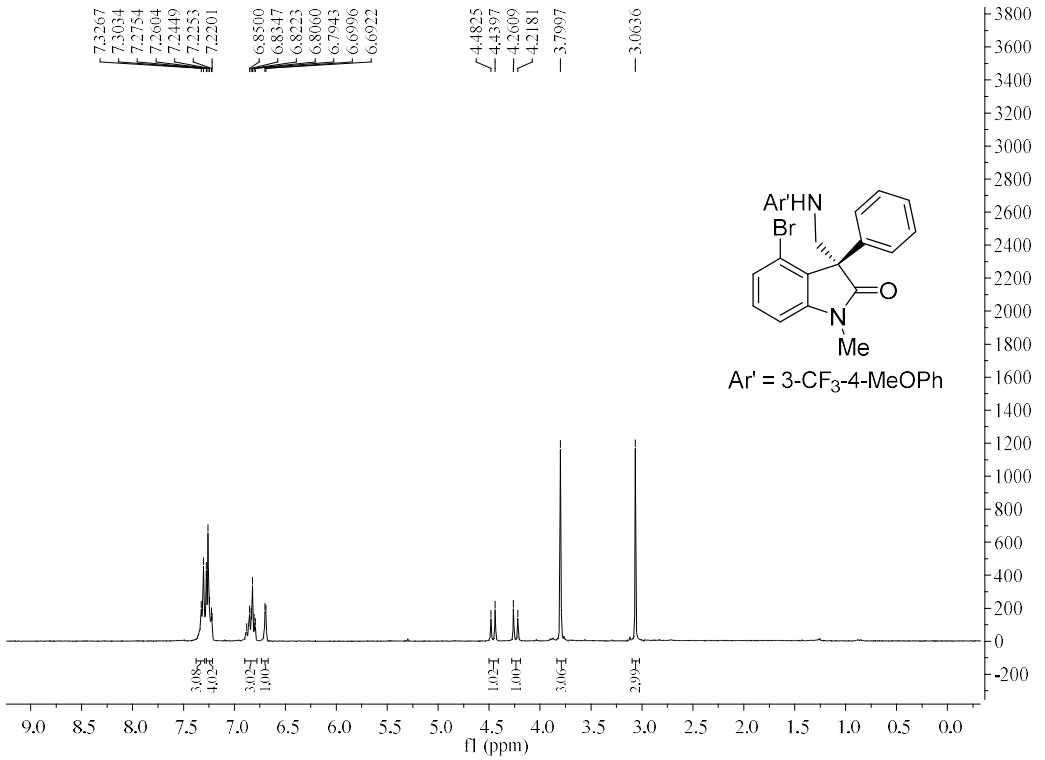
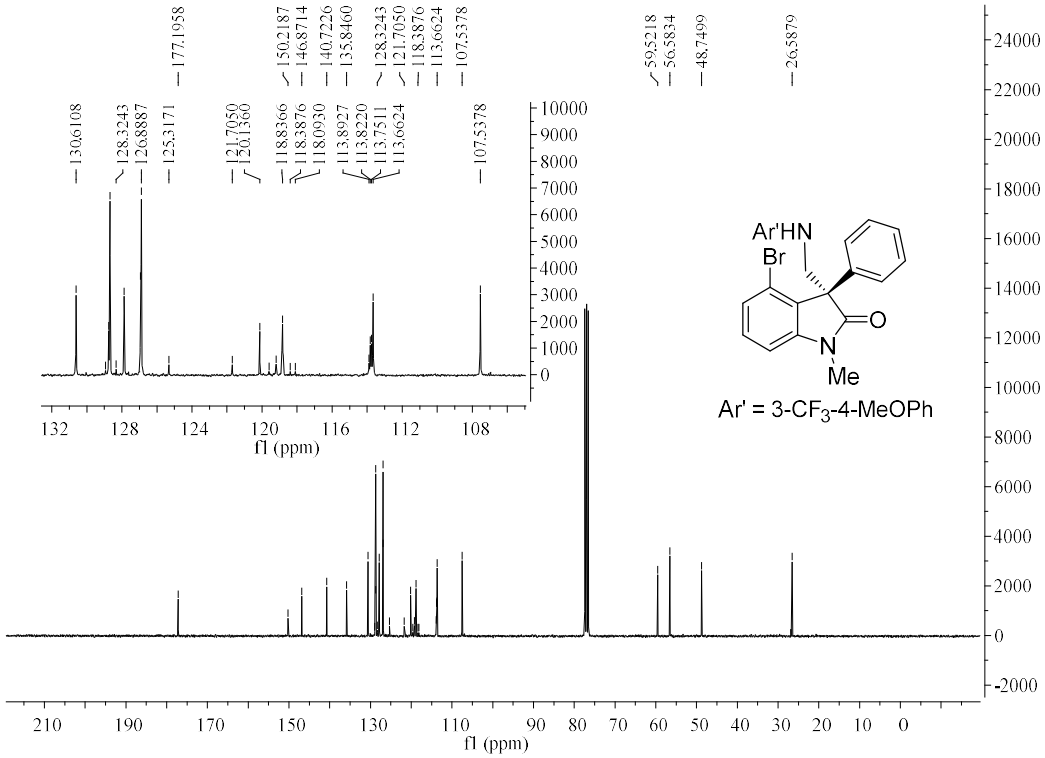
144.0042
141.0571
139.0247
128.9852
124.9433
119.4017
118.1113
113.8715
113.6912
113.0311
112.9631
112.8931
112.8242
112.5356
108.6450
56.7041
56.6700
55.2044
51.6090
26.4565
130.2388
129.7460
128.9852
128.9274
125.3724
124.9433
122.8640
121.7606
119.4017
118.9738
118.5650
118.1113
113.8715
113.6912
113.0311
112.9631
112.8931
112.8242
112.5356
fl (ppm)
Ar'HN
Cl
O
N
Me
Ar' = 3-CF3-4-MeOPh
fl (ppm)


-62.2323
Ar'HN
Cl
O
N
Me
Ar' = 3-CF3-4-MeOPh
fl (ppm)


7.3267
7.3034
7.2754
7.2604
7.2449
7.2253
7.2201
6.8500
6.8347
6.8223
6.8060
6.7943
6.6996
6.6922
4.4825
4.4397
4.2609
4.2181
3.7997
3.0636
3.08
4.02
3.02
1.00
1.02
1.00
3.06
2.99
Ar'HN
Br
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)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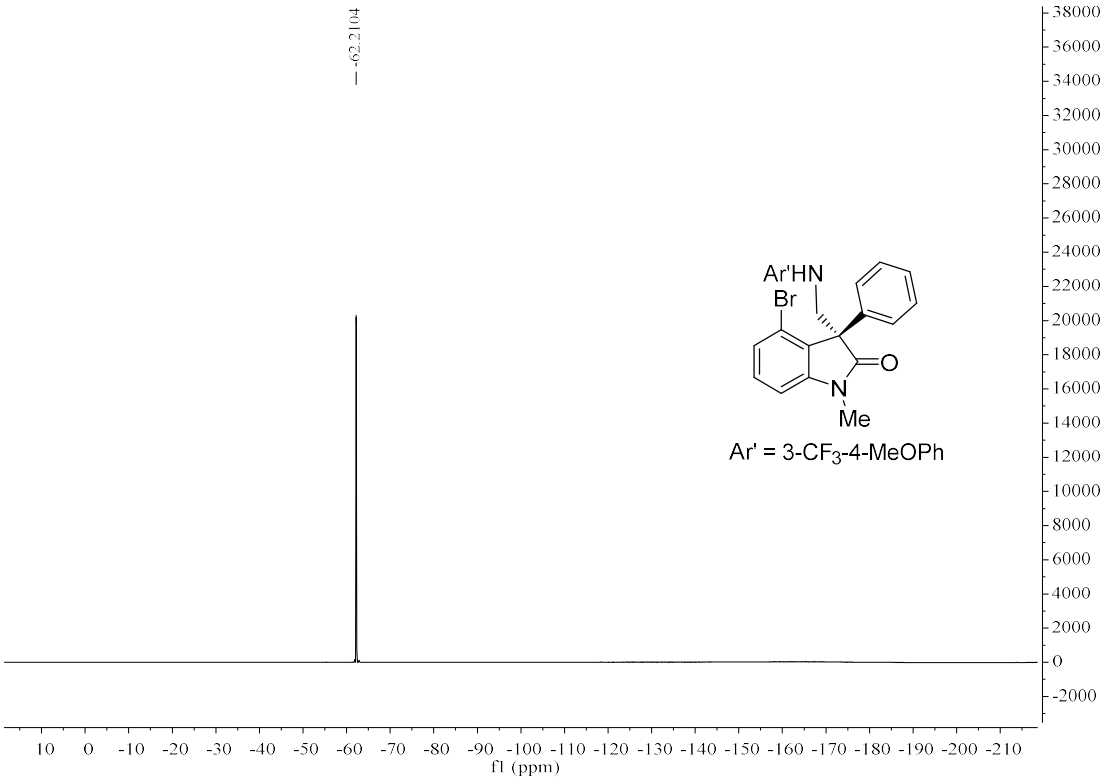
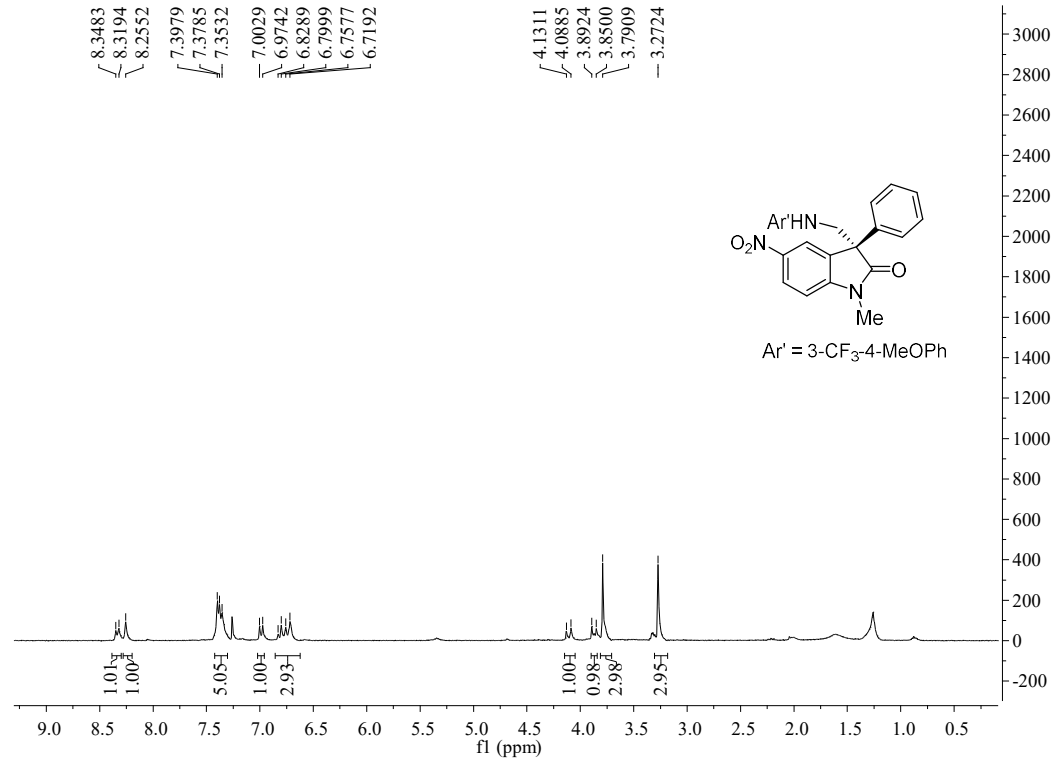
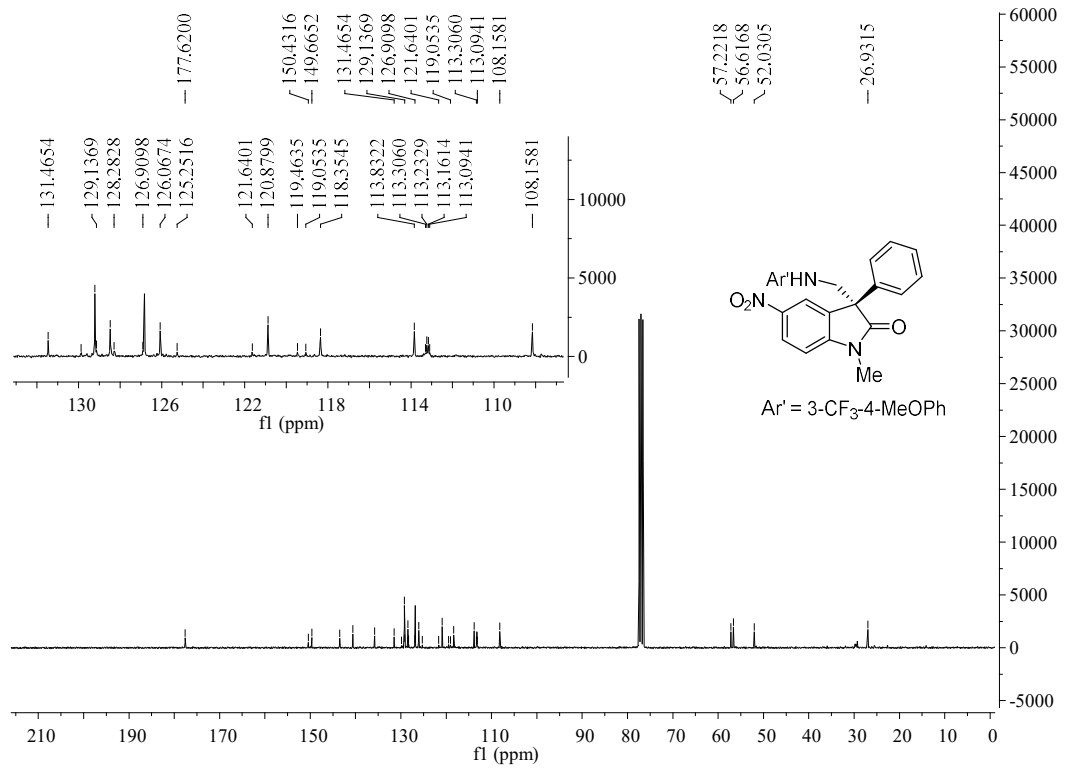
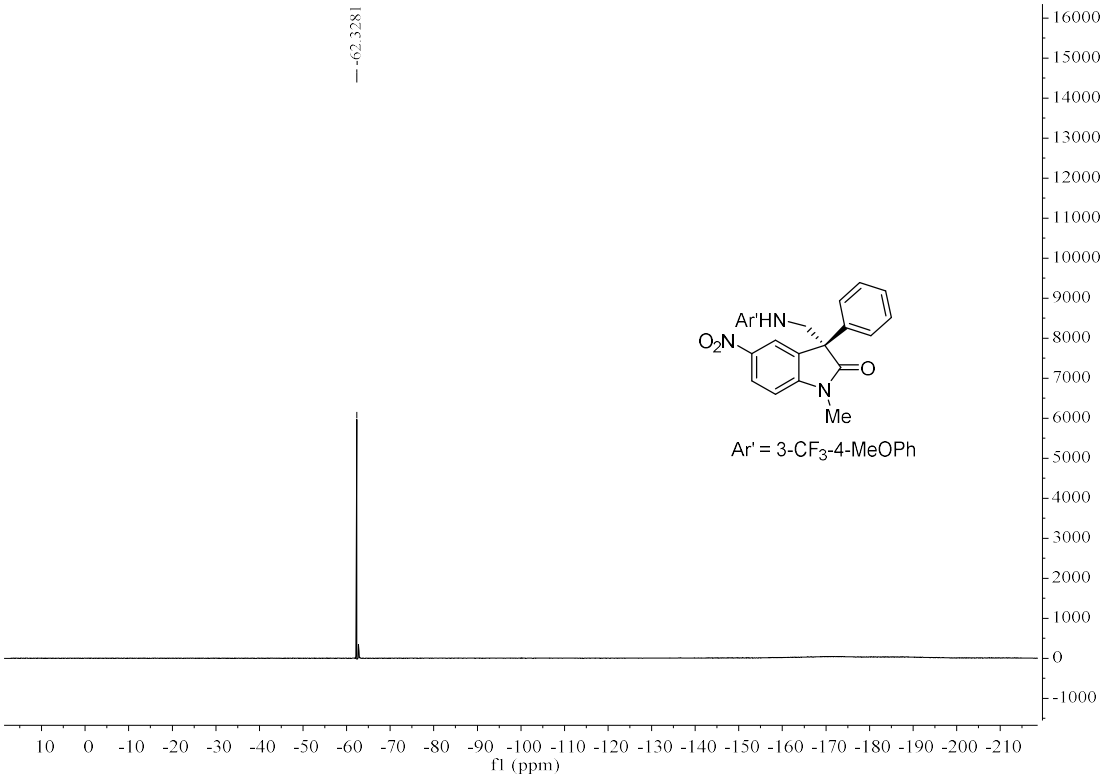
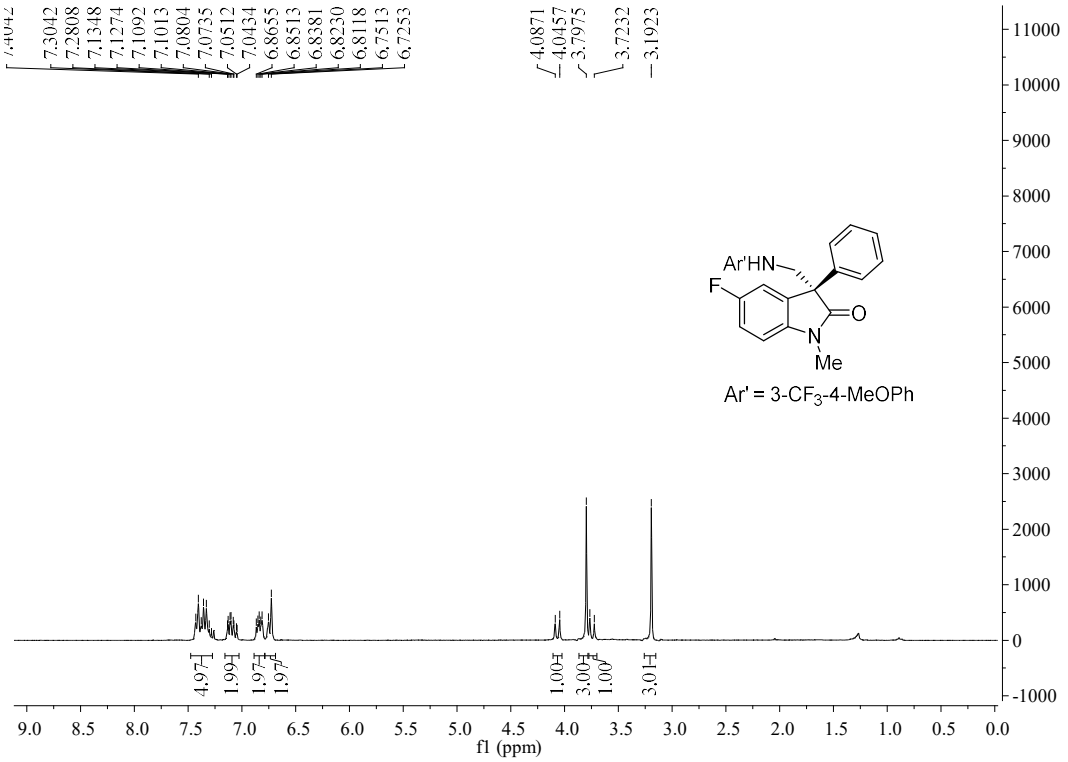
146.8714
140.7226
135.8460
128.3243
121.7050
118.3876
113.6624
107.5378
59.5218
56.5834
48.7499
26.5879
130.6108
128.3243
126.8887
125.3171
121.7050
120.1360
118.8366
118.3876
118.0930
113.8927
113.8220
113.7511
113.6624
107.5378
Ar'HN
Br
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


-62.2104
Ar'HN
Br
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


8.3483
8.3194
8.2552
7.3979
7.3785
7.3532
7.0029
6.9742
6.8289
6.7999
6.7577
6.7192
4.1311
4.0885
3.8924
3.8500
3.7909
3.2724
Ar'HN
O2N
O
N
Me
Ar' = 3-CF3-4-MeOPh
1.01
1.00
5.05
1.00
2.93
1.00
0.98
2.98
2.95
f1 (ppm)


177.6200
150.4316
149.6652
131.4654
129.1369
126.9098
121.6401
119.0535
113.3060
113.0941
108.1581
57.2218
56.6168
52.0305
26.9315
Ar'HN
O2N
O
N
Me
Ar' = 3-CF3-4-MeOPh
fl (ppm)


-62.3281
Ar'HN
O2N
O
N
Me
Ar' = 3-CF3-4-MeOPh
fl (ppm)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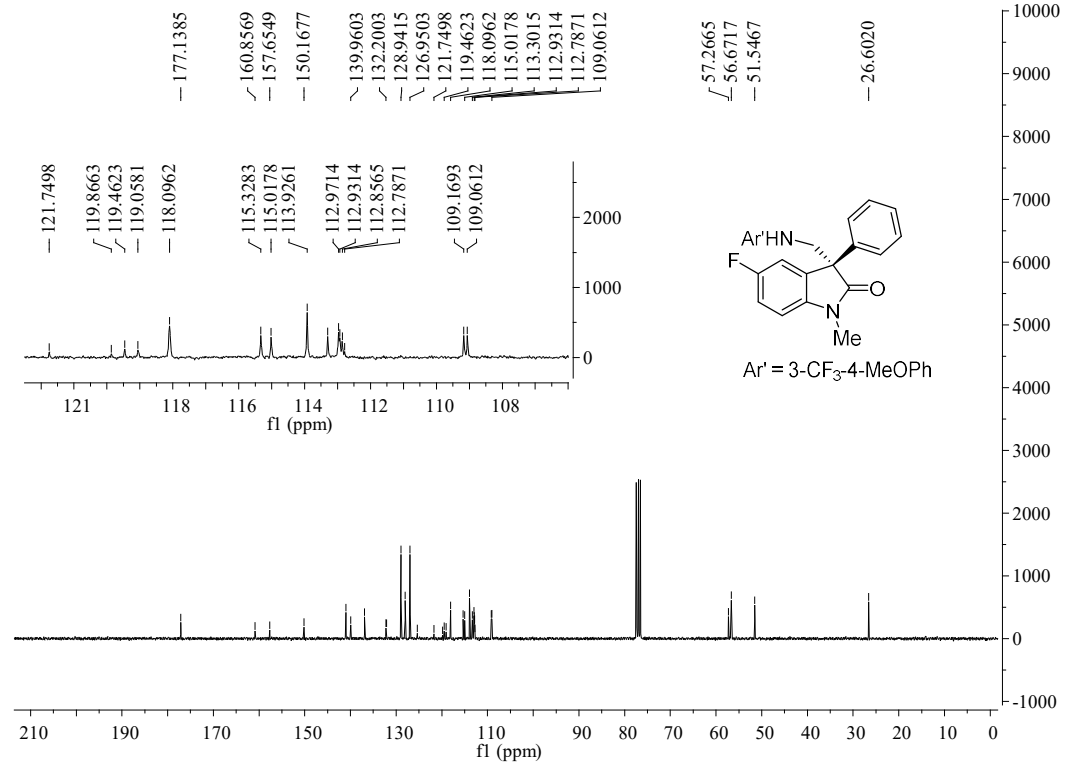
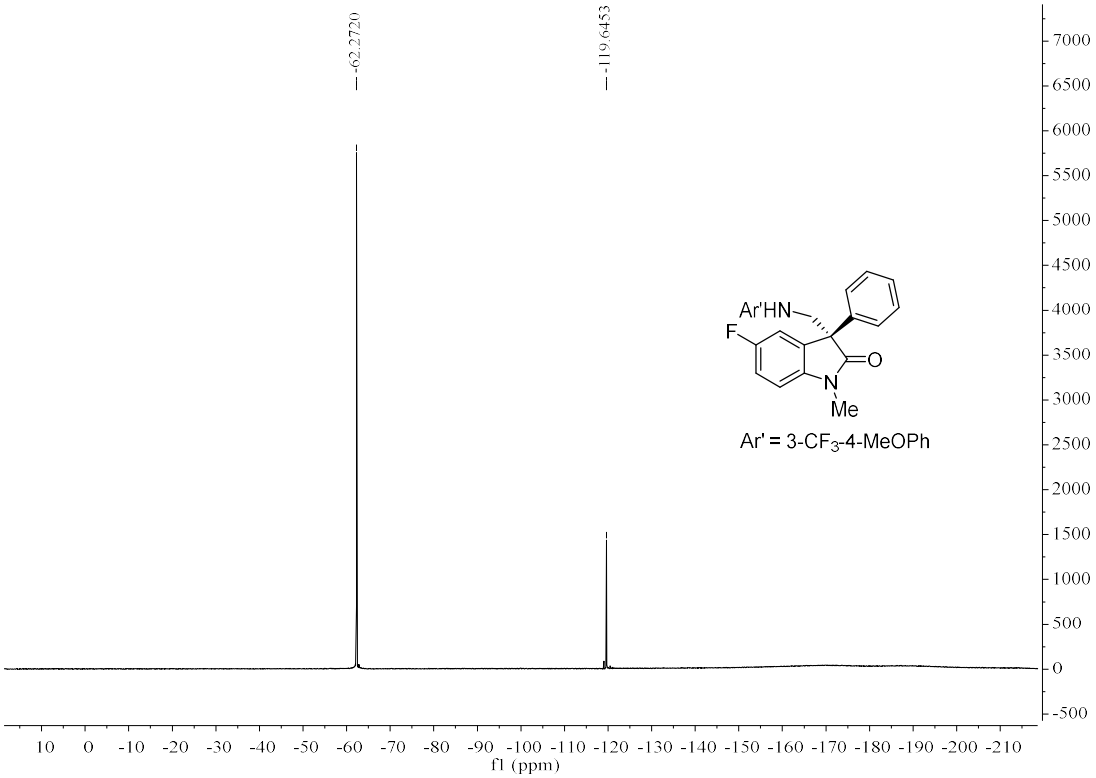
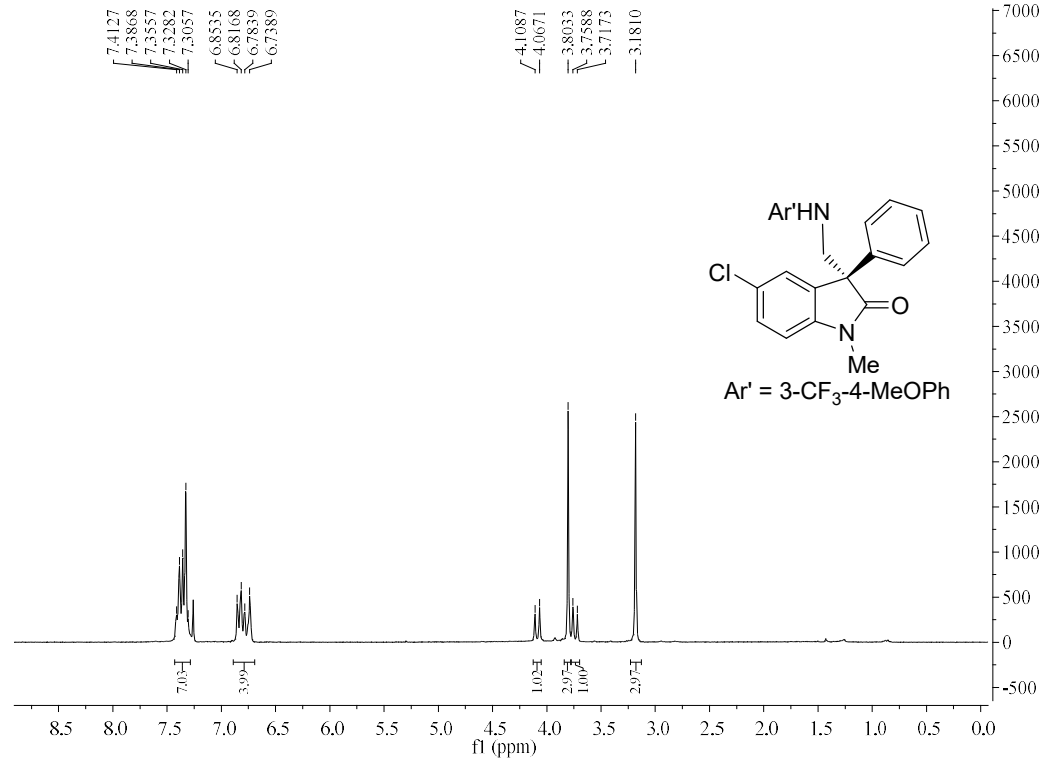
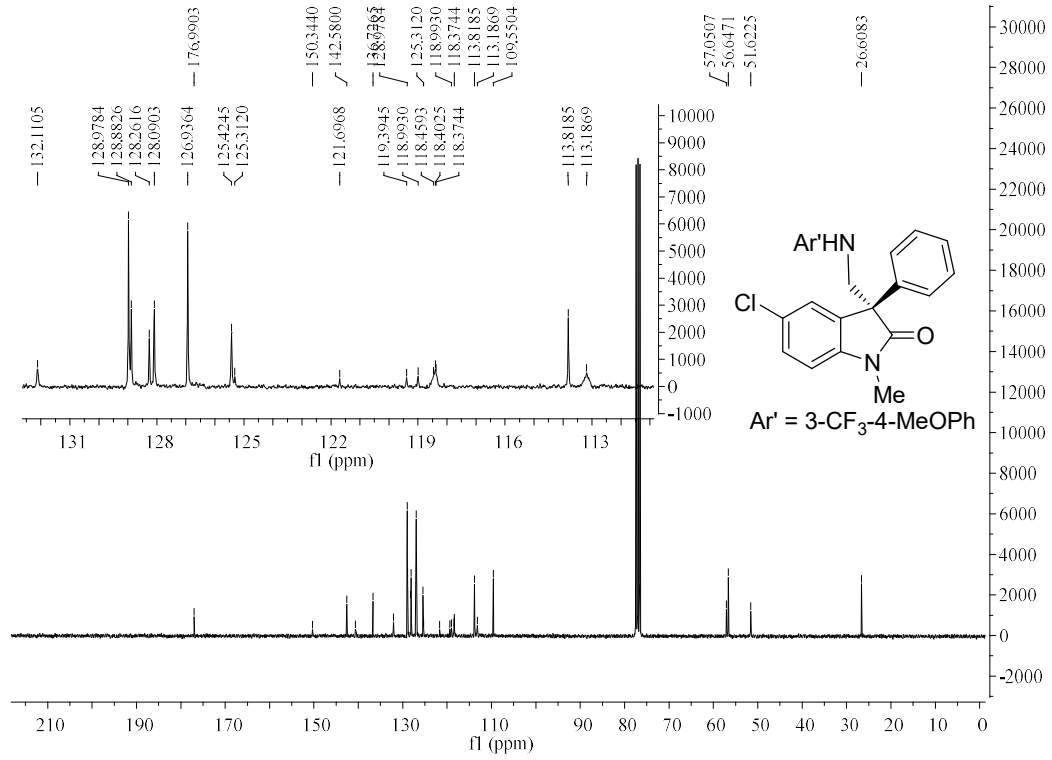
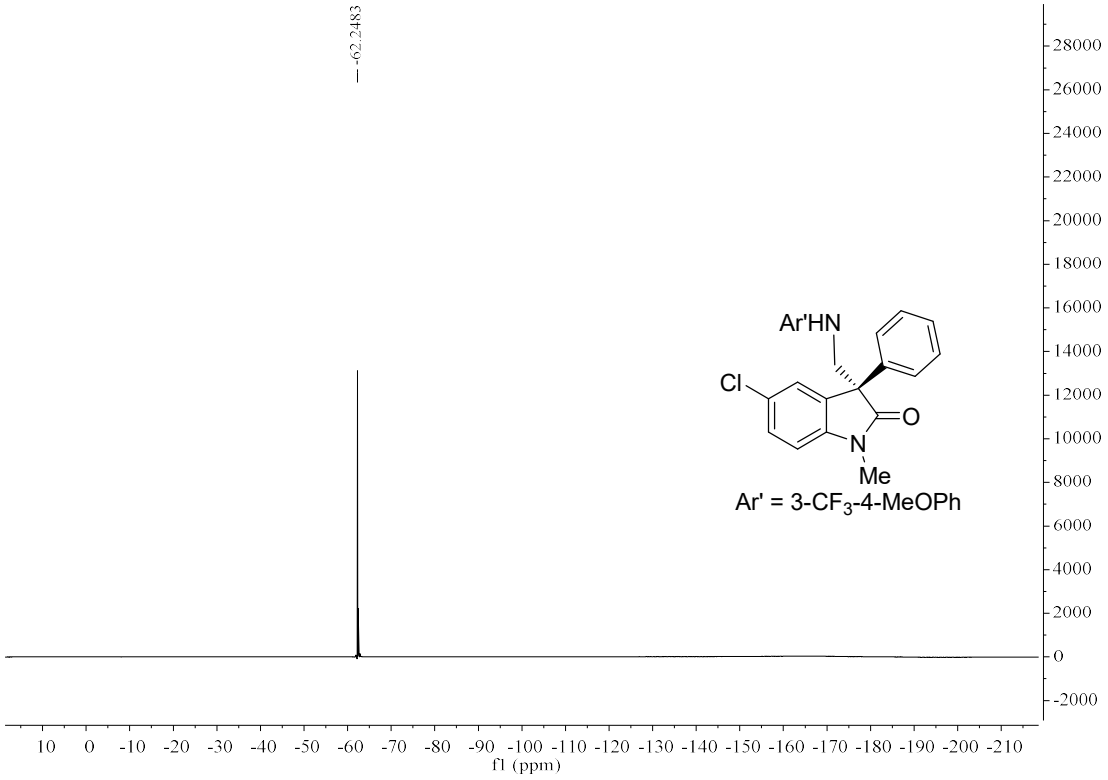
7.3042
7.2808
7.1348
7.1274
7.1092
7.1013
7.0804
7.0735
7.0512
7.0434
6.8655
6.8513
6.8381
6.8230
6.8118
6.7513
6.7253
4.0871
4.0457
3.7975
3.7232
3.1923
Ar'HN
F
O
N
Me
Ar' = 3-CF3-4-MeOPh
4.97H
1.99H
1.97H
1.97H
1.00H
3.00H
1.00H
3.01H
fl (ppm)

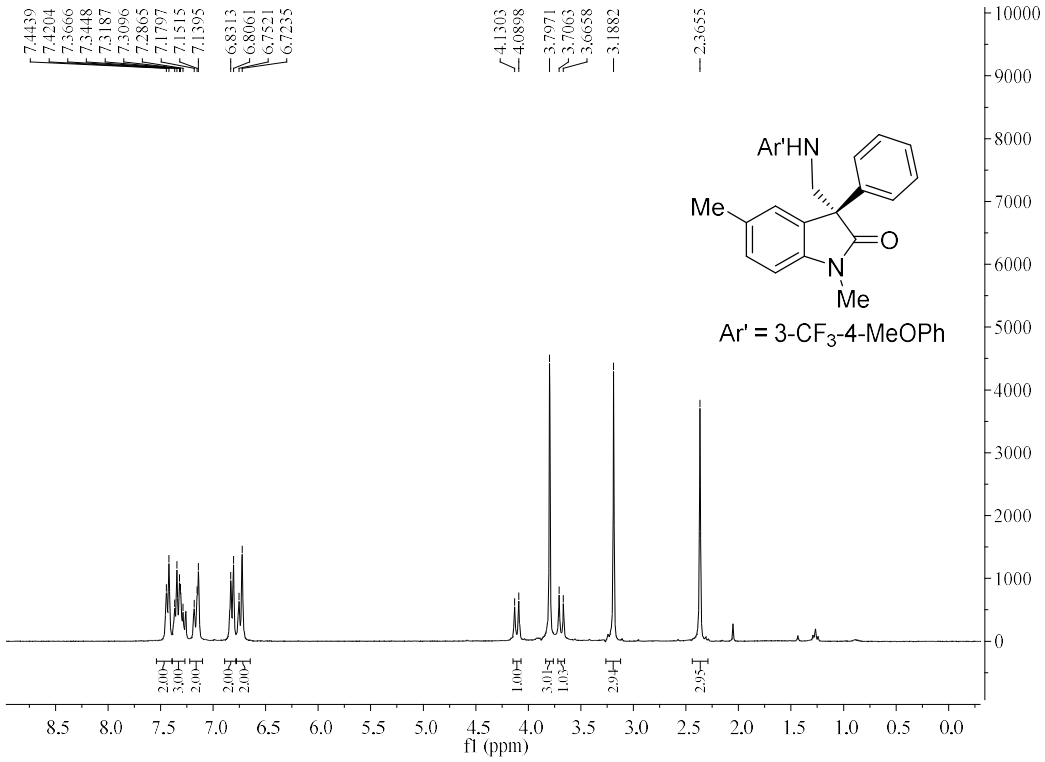

177.1385
160.8569
157.6549
150.1677
139.9603
132.2003
128.9415
126.9503
121.7498
119.4623
118.0962
115.0178
113.3015
112.9314
112.7871
109.0612
57.2665
56.6717
51.5467
26.6020
121.7498
119.8663
119.4623
119.0581
118.0962
115.3283
115.0178
113.9261
112.9714
112.9314
112.8565
112.7871
109.1693
109.0612
Ar'HN
F
O
N
Me
Ar' = 3-CF3-4-MeOPh
fl (ppm)
fl (ppm)

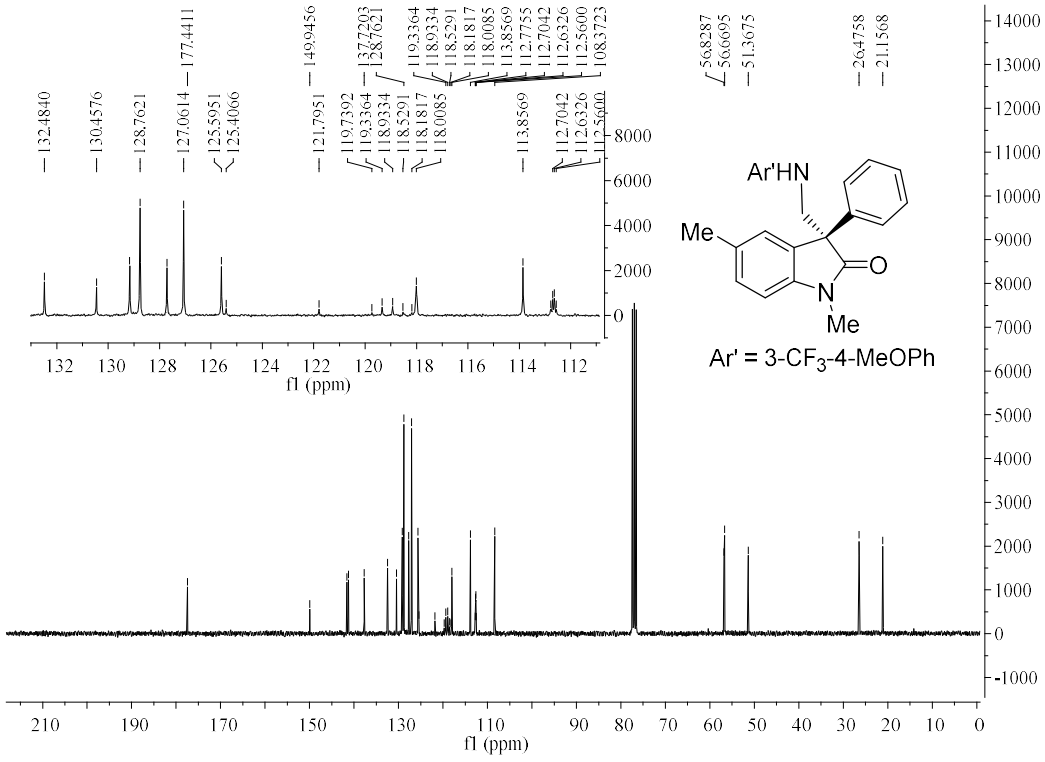

-62.2720
-119.6453
Ar'HN
F
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)

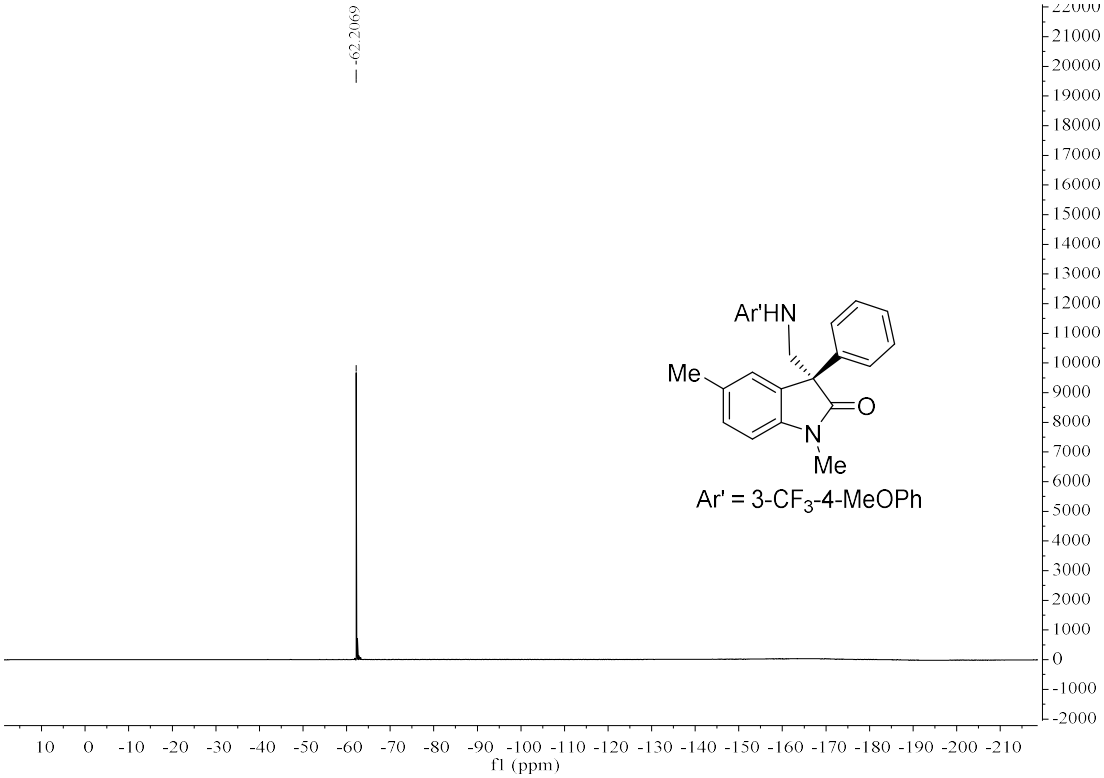

7.4127
7.3868
7.3557
7.3282
7.3057
6.8535
6.8168
6.7839
6.7389
4.1087
4.0671
3.8033
3.7588
3.7173
3.1810
Ar'HN
Cl
O
N
Me
Ar' = 3-CF3-4-MeOPh
7.03
3.99
1.02
2.95
1.00
2.97
f1 (ppm)

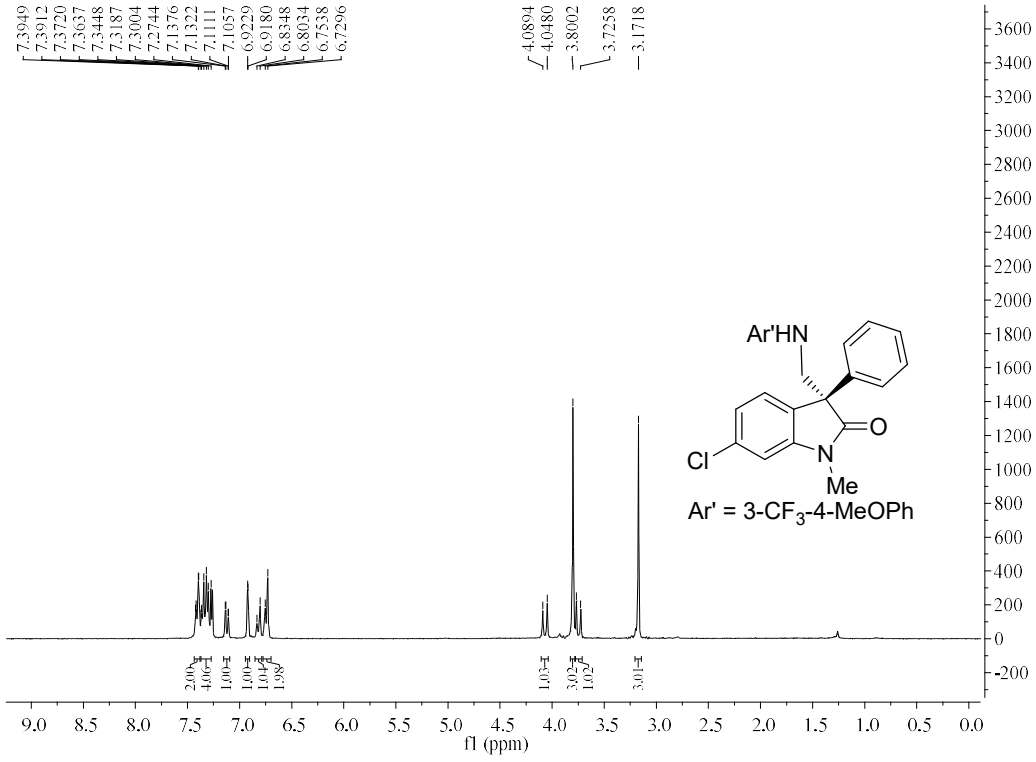

Ar'HN
Cl
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)

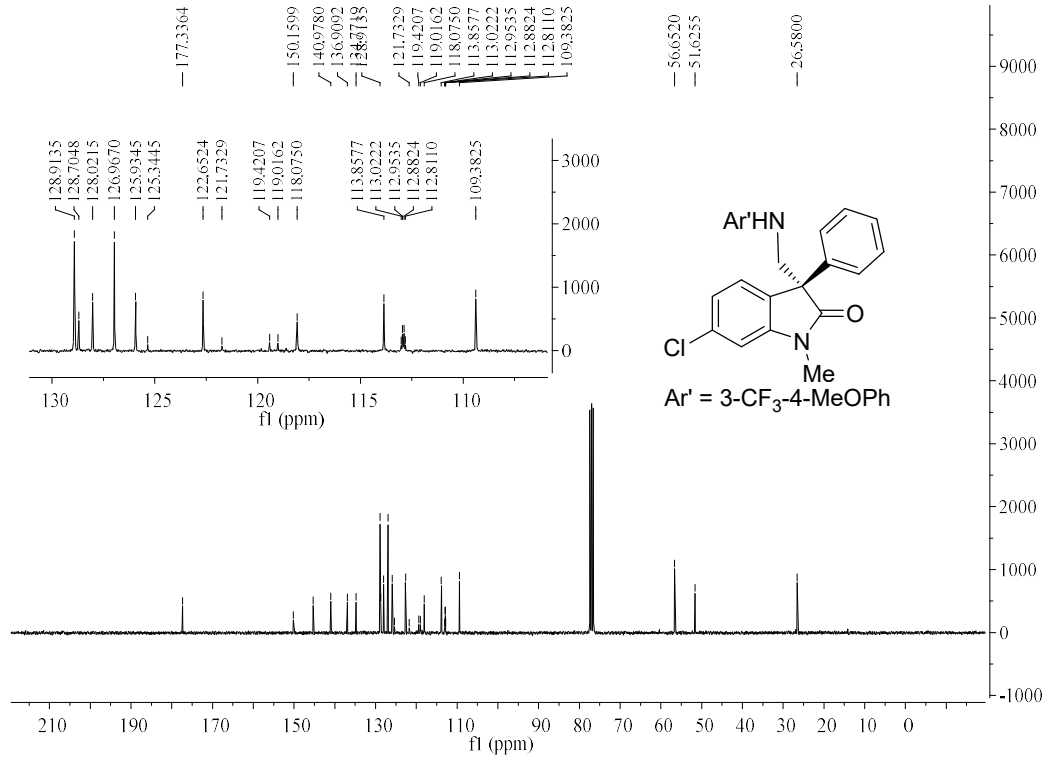

-62.2483
Ar'HN
Cl
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


7.4439
7.4204
7.3666
7.3448
7.3187
7.3096
7.2865
7.1797
7.1515
7.1395
6.8313
6.8061
6.7521
6.7235
4.1303
4.0898
3.7971
3.7063
3.6658
3.1882
2.3655
Ar'HN
Me
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


132.4840
130.4576
128.7621
127.0614
177.4411
125.5951
125.4066
149.9456
121.7951
137.7203
128.7621
119.7392
119.3364
118.9334
118.5291
118.1817
118.0085
119.3364
118.9334
118.5291
118.1817
118.0085
113.8569
112.7755
112.7042
112.6326
112.5600
108.3723
56.8287
56.6695
51.3675
26.4758
21.1568
Ar'HN
Me
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


-62.2069
Ar'HN
Me
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


7.3949
7.3912
7.3720
7.3637
7.3448
7.3187
7.3004
7.2744
7.1376
7.1322
7.1111
7.1057
6.9229
6.9180
6.8348
6.8034
6.7538
6.7296
4.0894
4.0480
3.8002
3.7258
3.1718
Ar'HN
Cl
O
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)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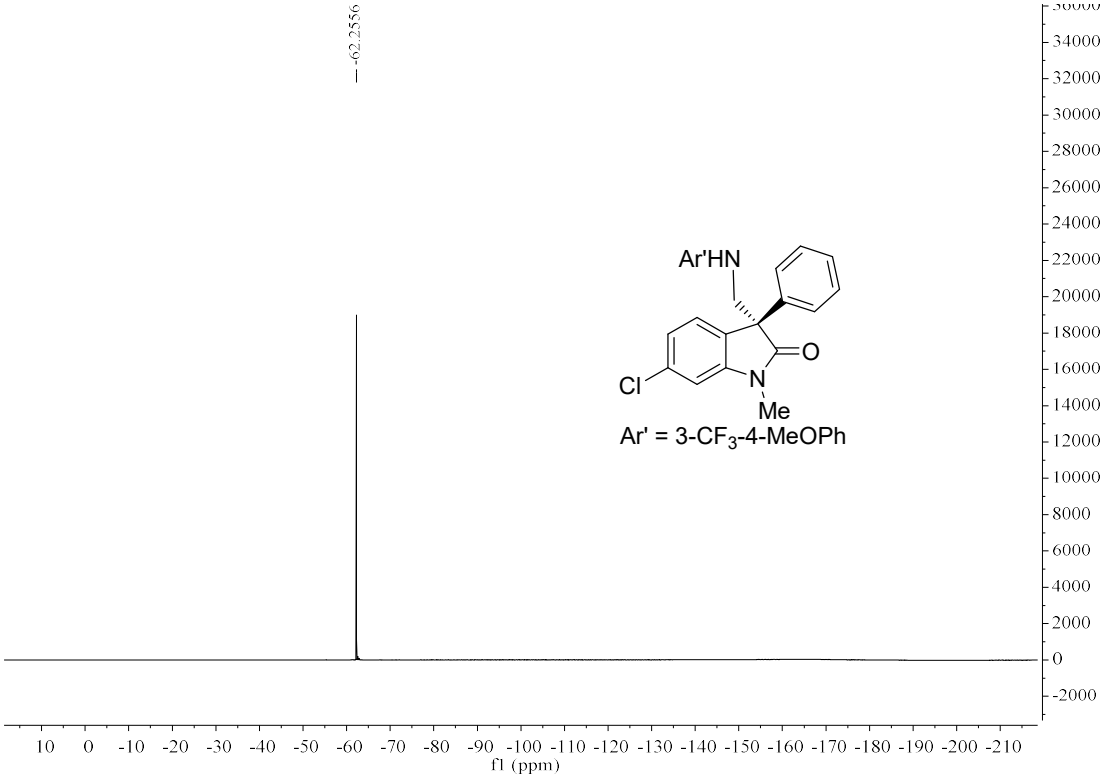
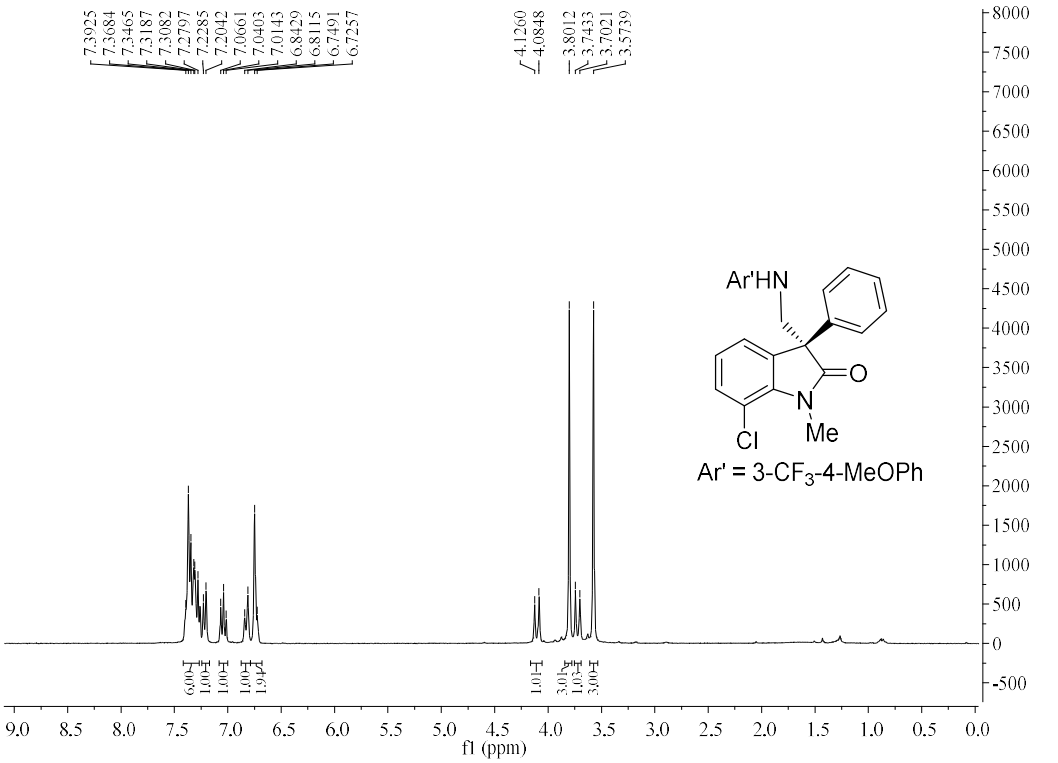
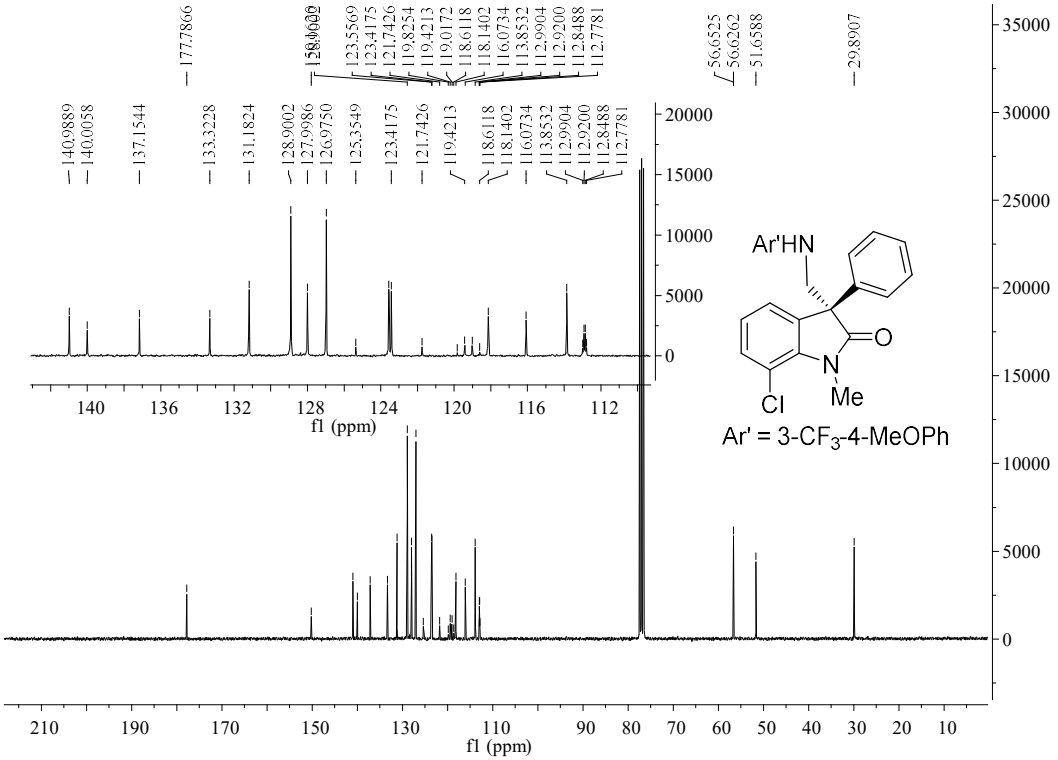
150.1599
140.9780
136.9092
121.7329
119.4207
119.0162
118.0750
113.8577
113.0222
112.9535
112.8824
112.8110
109.3825
56.6520
51.6255
26.5800
128.9135
128.7048
128.0215
126.9670
125.9345
125.3445
122.6524
121.7329
119.4207
119.0162
118.0750
113.8577
113.0222
112.9535
112.8824
112.8110
109.3825
f1 (ppm)
Ar'HN
O
Cl
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


-62.2556
Ar'HN
O
Cl
N
Me
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


7.3925
7.3684
7.3465
7.3187
7.3082
7.2797
7.2285
7.2042
7.0661
7.0403
7.0143
6.8429
6.8115
6.7491
6.7257
4.1260
4.0848
3.8012
3.7433
3.7021
3.5739
6.00
1.00
1.00
1.00
1.94
1.01
3.01
1.03
3.00
Ar'HN
O
N
Me
Cl
Ar' = 3-CF3-4-MeOPh
f1 (ppm)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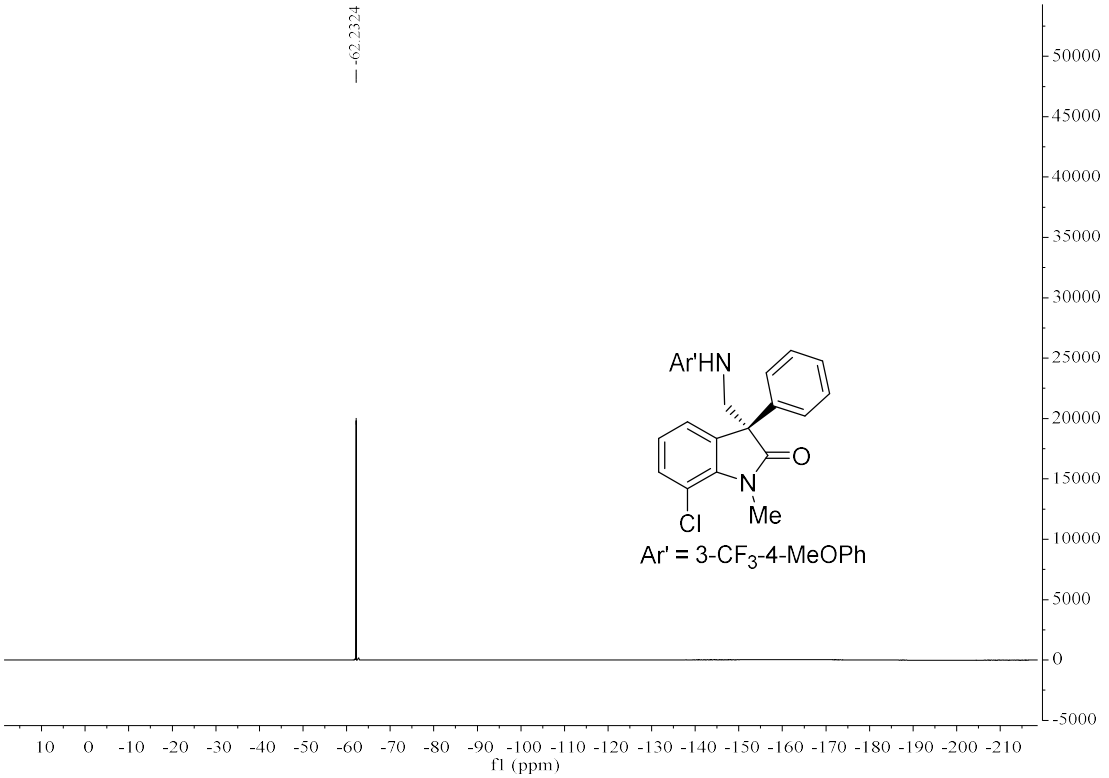
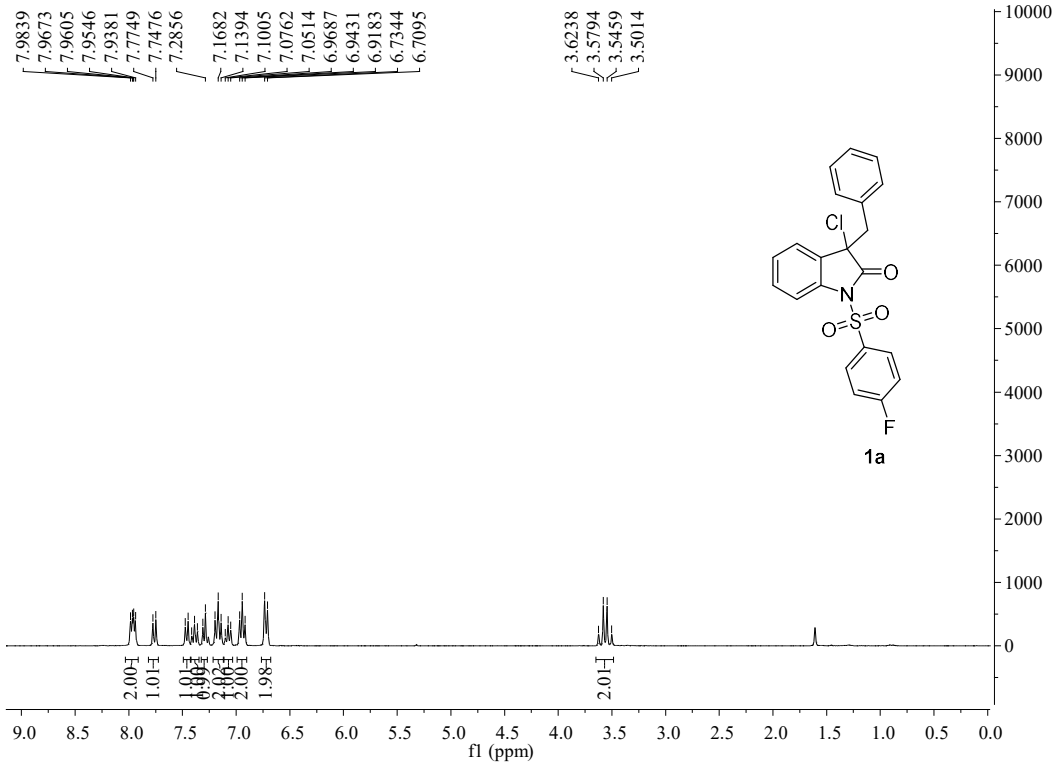
140.0058
137.1544
133.3228
131.1824
128.9002
127.9986
126.9750
125.3549
123.4175
121.7426
119.4213
118.6118
118.1402
116.0734
113.8532
112.9904
112.9200
112.8488
112.7781
56.6525
56.6262
51.6588
29.8907
Ar'HN
O
N
Me
Cl
Ar' = 3-CF3-4-MeOPh
f1 (ppm)


-62.2324
Ar'HN
O
N
Me
Cl
Ar' = 3-CF3-4-MeOPh
f1 (ppm)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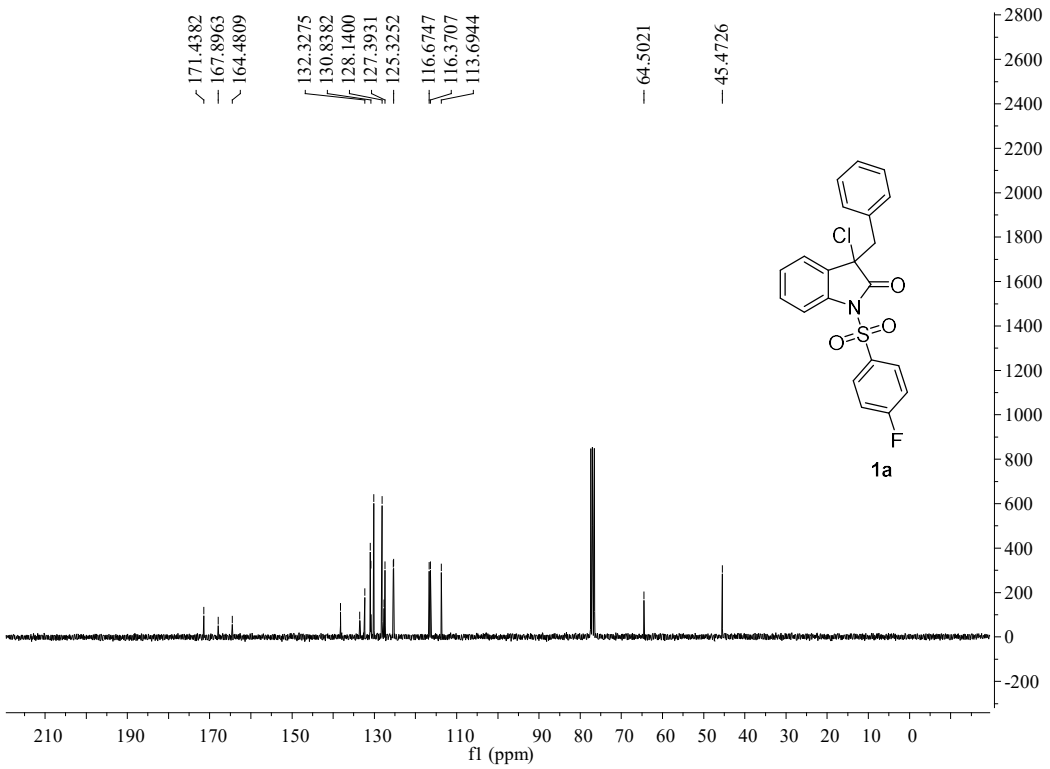
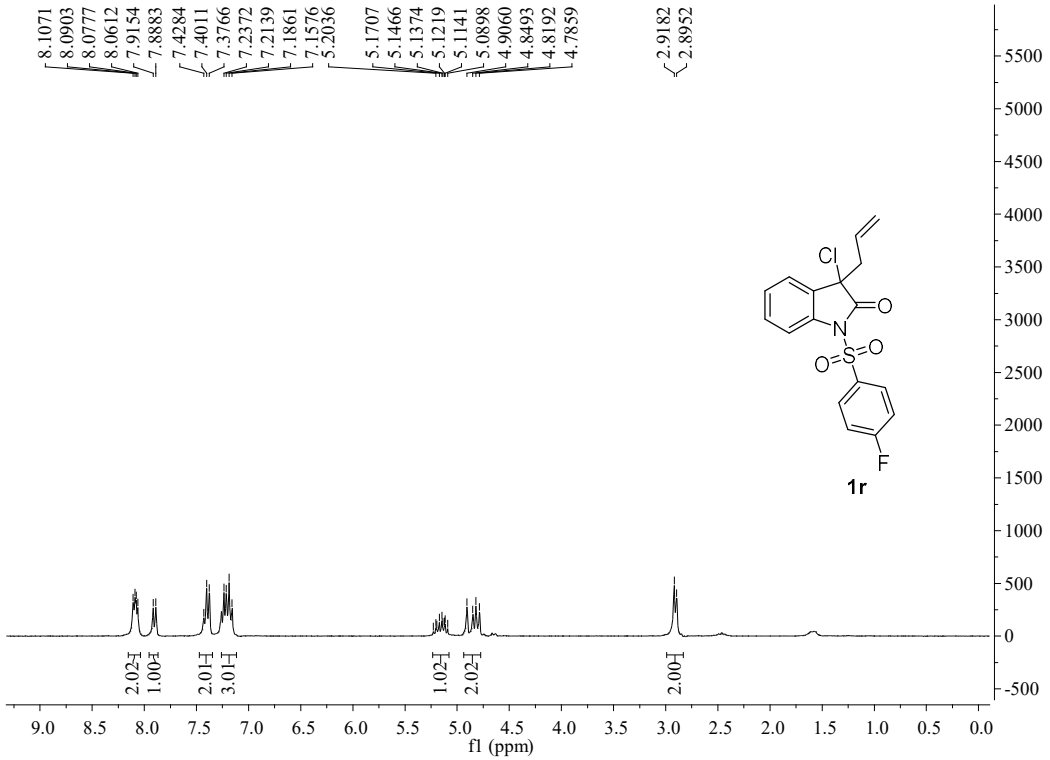
7.9605
7.9546
7.9381
7.7749
7.7476
7.2856
7.1682
7.1394
7.1005
7.0762
7.0514
6.9687
6.9431
6.9183
6.7344
6.7095
3.6238
3.5794
3.5459
3.5014
Cl
O
N
O=S=O
F
1a
2.00
1.01
2.01
1.98
f1 (ppm)


171.4382
167.8963
164.4809
132.3275
130.8382
128.1400
127.3931
125.3252
116.6747
116.3707
113.6944
64.5021
45.4726
Cl
O
N
O=S=O
F
1a
fl (ppm)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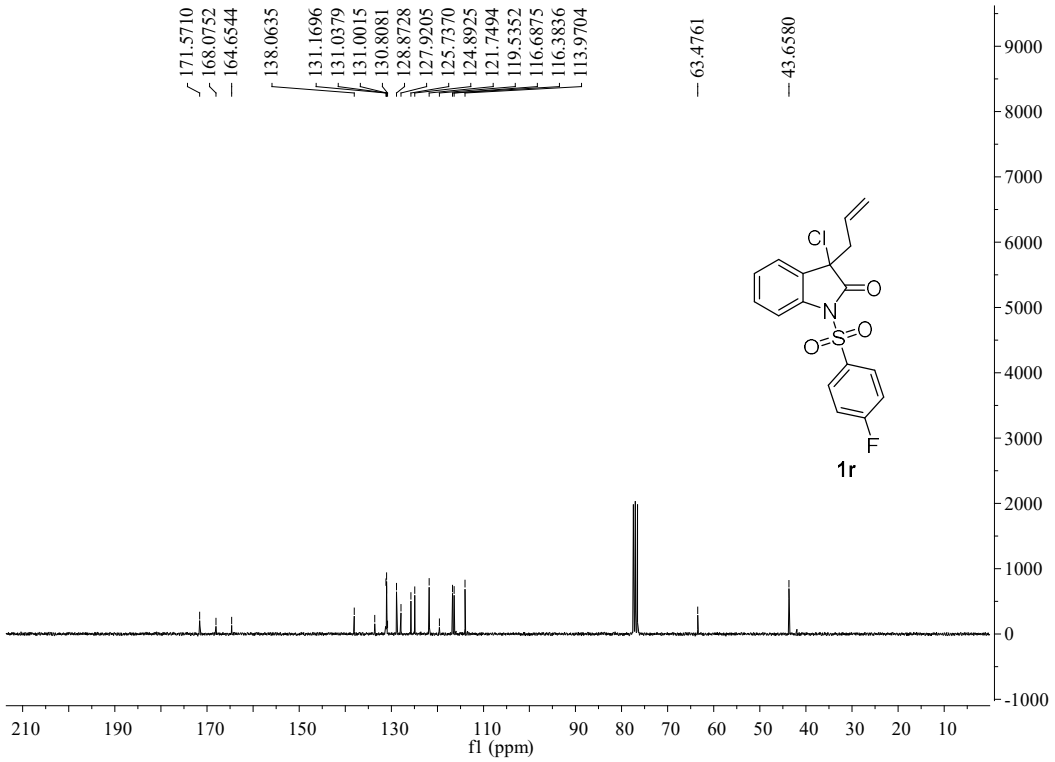
8.0903
8.0777
8.0612
7.9154
7.8883
7.4284
7.4011
7.3766
7.2372
7.2139
7.1861
7.1576
5.2036
5.1707
5.1466
5.1374
5.1219
5.1141
5.0898
4.9060
4.8493
4.8192
4.7859
2.9182
2.8952
Cl
O
N
O=S=O
F
1r
2.02
1.00
2.01
3.01
1.02
2.02
2.00
fl (ppm)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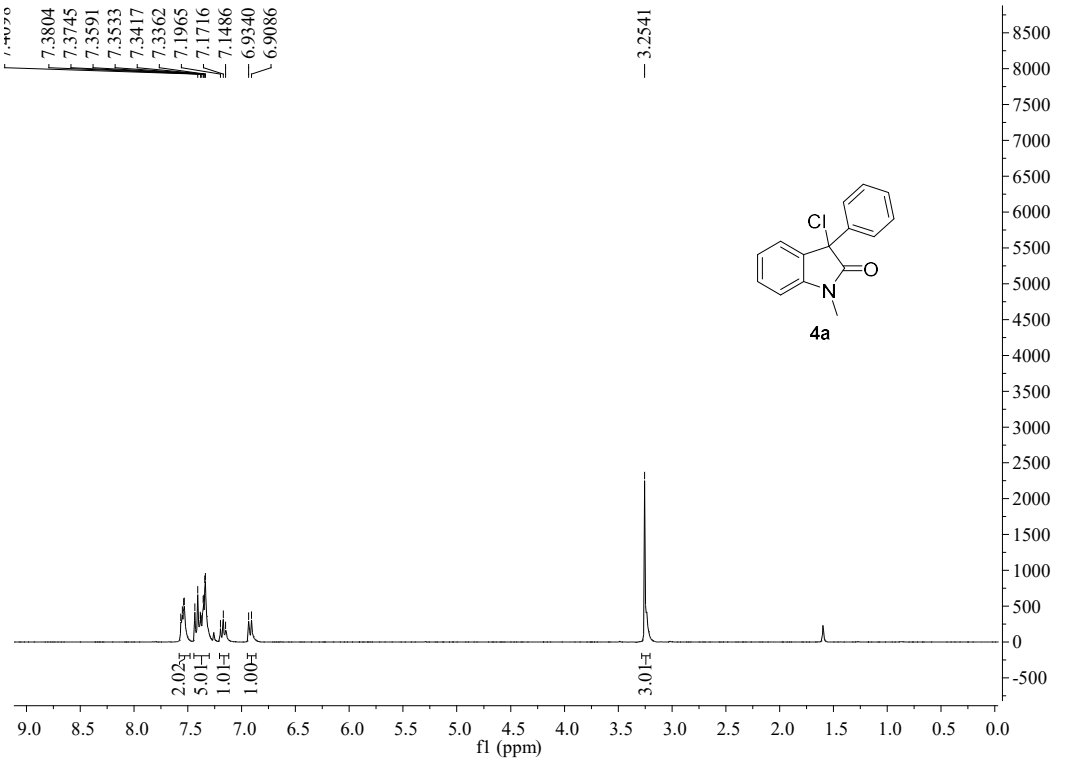
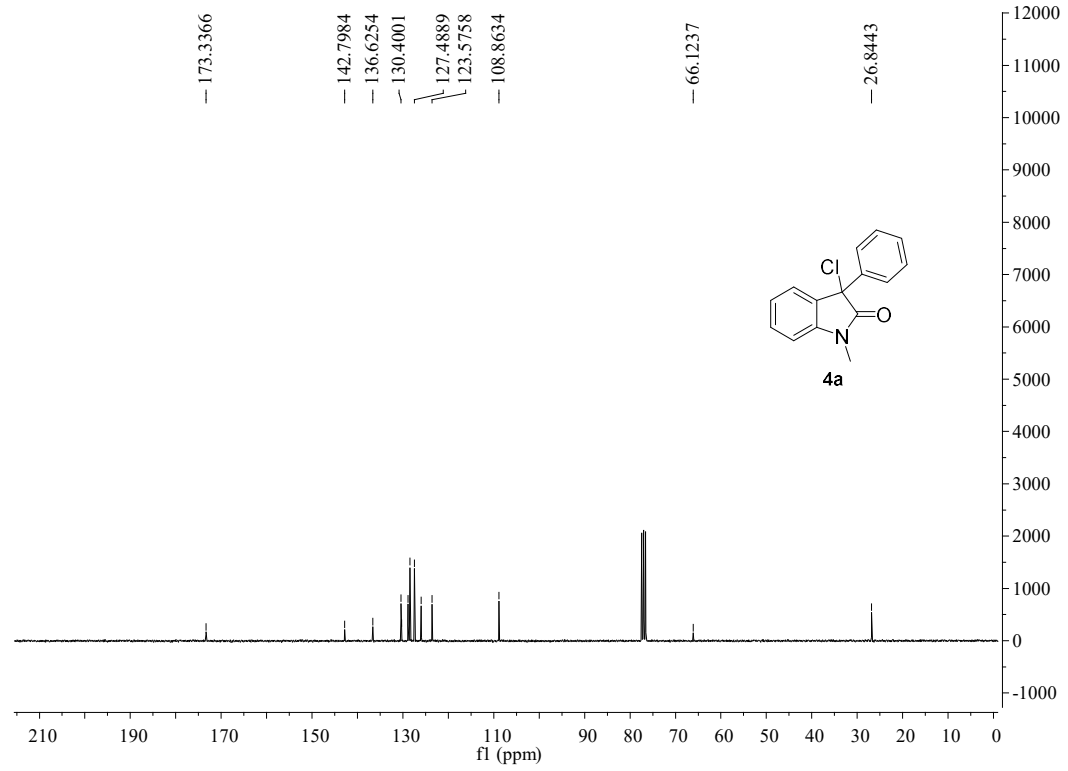
168.0752
164.6544
138.0635
131.1696
131.0379
131.0015
130.8081
128.8728
127.9205
125.7370
124.8925
121.7494
119.5352
116.6875
116.3836
113.9704
63.4761
43.6580
Cl
O
N
O=S=O
F
1r
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.3804
7.3745
7.3591
7.3533
7.3417
7.3362
7.1965
7.1716
7.1486
6.9340
6.9086
3.2541
Cl
O
N
4a
2.02
5.01
1.01
1.00
3.01
fl (ppm)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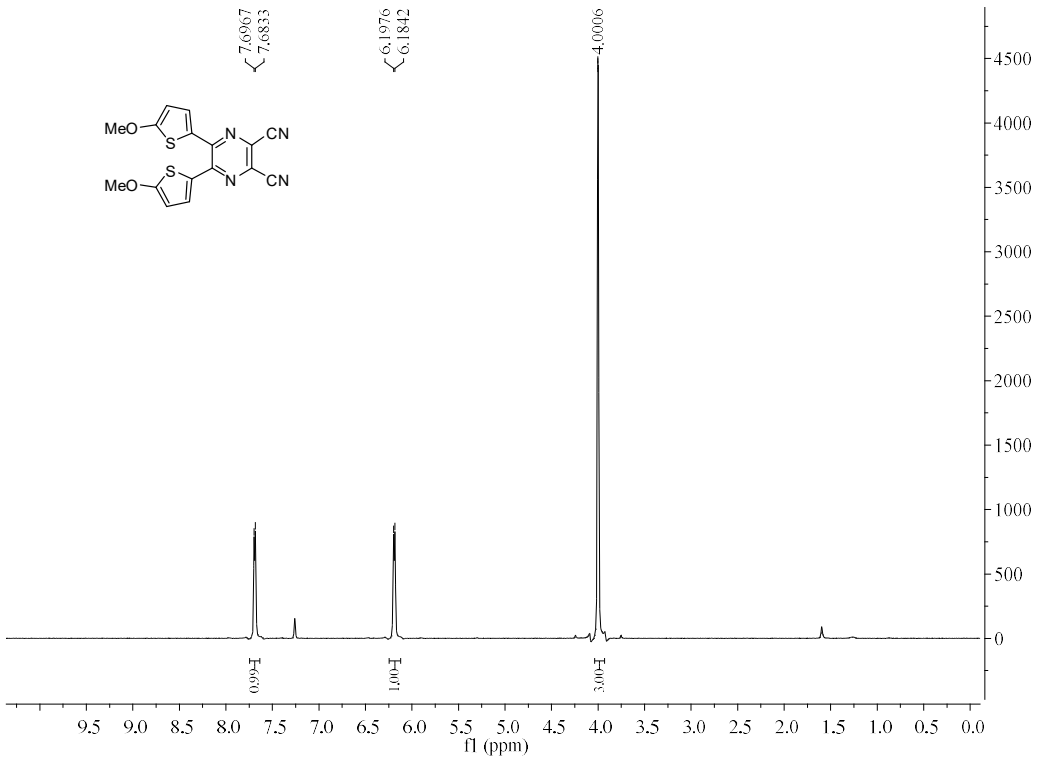
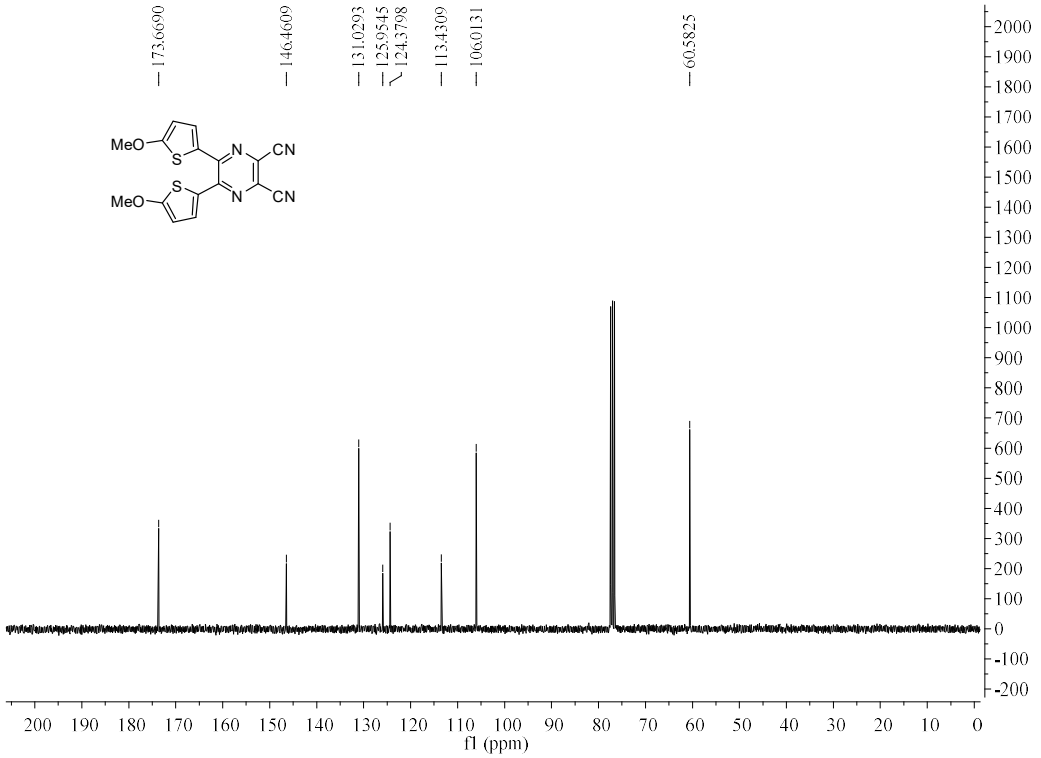
142.7984
136.6254
130.4001
127.4889
123.5758
108.8634
66.1237
26.8443
Cl
O
N
4a
fl (ppm)


7.6967
7.6833
6.1976
6.1842
4.0006
MeO
S
N
CN
MeO
S
N
CN
0.99
1.00
3.00
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)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131.0293
125.9545
124.3798
113.4309
106.0131
60.5825
MeO
S
N
CN
MeO
S
N
CN
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)