

Electronic Supplemental Information

Zn(II)-catalysed Enantioselective Addition of Alcohols and tert-Butyl Hydroperoxide to Isatin-derived N-Boc Ketimines

Jiaqi Hou, Leipeng Xue, Tianxu Yu, Jiahui Li, Shibo Yu, Chao Yao* and Yue-Ming Li*

State Key Laboratory of Medicinal Chemical Biology, College of Pharmacy and Tianjin Key
Laboratory of Molecular Drug Research, Nankai University, Tianjin, 300350, China.

Contents

1. Experimental Section	S1
1.1. General Information	S1
1.2. Optimization of Reaction Conditions.....	S1
1.3 General Procedures for Enantioselective Addition of Alcohols and Peroxides to Isatin-derived N-Boc Ketimines	S2
1.4 Enantioselective Addition of Sulfur-based Nucleophiles to Isatin-derived N-Boc Ketimine	S3
1.5 Enantioselective Addition of Alcohols and Peroxides to Cyclic Ketimine 6	S3
1.6 Computational Studies on the Key Intermediates of the Reactions.	S4
2. Characterization and ee Values of the Products	S14
3. Copies of NMR Spectra of the Products.....	S67
4. References.....	S116

1. Experimental Section

1.1. General Information

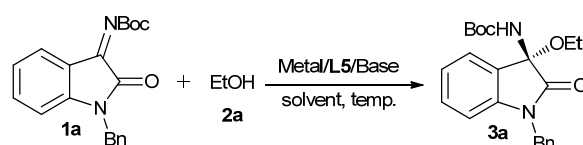
^1H NMR and ^{13}C $\{^1\text{H}\}$ NMR spectra were recorded on 400 MHz nuclear magnetic resonance spectrometer with tetramethylsilane (TMS) as the internal standard. High performance liquid chromatography experiments were performed with Daicel chiral column (AD-H, OD-H, IA, AS-H, etc.). Specific rotations were measured with an automatic polarimeter. High-resolution mass spectra (HRMS) were obtained with Varian 7.0T Fourier transform ion cyclotron resonance mass spectrometer. The solvents (such as petroleum ether, ethyl acetate, dichloromethane, etc.) are analytically pure. The room temperature was 25 °C; the silica gel used for column chromatography was 200-300 mesh. Unless otherwise noted, commercial reagents were used as received. All drying solvents were handled in accordance with standard procedures and aldehydes were treated by vacuum distillation or recrystallization.

Ligands **L1-L8** were prepared as previously reported.¹

1.2. Optimization of Reaction Conditions

The metal salts were first investigated. To our delight, the reaction catalyzed by zinc salts afforded the target products with excellent yield and ee, among which $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was the best salt in terms of both the yield and enantioselectivity (Table S1, entry 6). NiCl_2 could not facilitate the reaction and no product was obtained (Table S1, entry 7). CH_2Cl_2 was still the best medium for the reaction. The addition of base also played a key role in the reaction. In the presence of DIPEA, compound **3a** could be obtained in 89% yield with 96% ee (Table S1, entry 11). The addition of a strong base or no base resulted in sharp decrease in enantioselectivity (Table S1, entry 12-14). In addition, reducing the catalyst loading or lowering the reaction temperature to 0 °C was also detrimental to both the yield and enantioselectivity of the reaction (Table S1, entry 16-17).

Table S1. Optimization of the Reaction Conditions ^a



entry	metal	base	solvent	yield (%) ^b	ee (%) ^c
-------	-------	------	---------	------------------------	---------------------

1	Cu(OTf) ₂	Et ₃ N	CH ₂ Cl ₂	93	72
2	Cu(ClO ₄) ₂ ·6H ₂ O	Et ₃ N	CH ₂ Cl ₂	80	60
3	CuBr ₂	Et ₃ N	CH ₂ Cl ₂	98	47
4	CuOTf	Et ₃ N	CH ₂ Cl ₂	84	64
5	Zn(OTf) ₂	Et ₃ N	CH ₂ Cl ₂	93	75
6	Zn(ClO ₄) ₂ ·6H ₂ O	Et ₃ N	CH ₂ Cl ₂	92	86
7	NiCl ₂	Et ₃ N	CH ₂ Cl ₂	trace	-
8	Zn(ClO ₄) ₂ ·6H ₂ O	Et ₃ N	THF	47	65
9	Zn(ClO ₄) ₂ ·6H ₂ O	Et ₃ N	CHCl ₃	83	76
10	Zn(ClO ₄) ₂ ·6H ₂ O	Et ₃ N	toluene	41	80
11	Zn(ClO ₄) ₂ ·6H ₂ O	DIPEA	CH ₂ Cl ₂	89	96
12	Zn(ClO ₄) ₂ ·6H ₂ O	-	CH ₂ Cl ₂	95	0
13	Zn(ClO ₄) ₂ ·6H ₂ O	NaHCO ₃	CH ₂ Cl ₂	85	12
14	Zn(ClO ₄) ₂ ·6H ₂ O	DBU	CH ₂ Cl ₂	80	89
15	Zn(ClO ₄) ₂ ·6H ₂ O	piperidine	CH ₂ Cl ₂	91	72
16 ^d	Zn(ClO ₄) ₂ ·6H ₂ O	DIPEA	CH ₂ Cl ₂	88	82
17 ^e	Zn(ClO ₄) ₂ ·6H ₂ O	DIPEA	CH ₂ Cl ₂	82	20

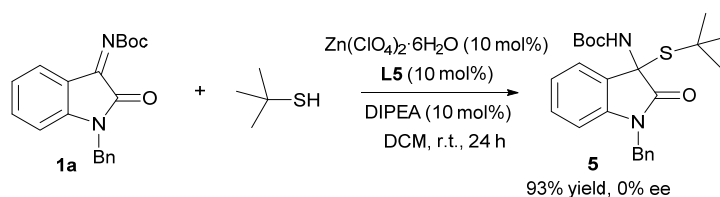
^a Unless otherwise noted, all the reactions were performed with isatin-derived N-Boc ketimine **1a** (0.15 mmol), ethanol **2a** (1.5 mmol), base (0.015mmol), **L5** (10 mol%), and salt (10 mol%) in dry CH₂Cl₂ (2.0 mL) at room temperature for 24 h. ^b Isolated yields. ^c The ee values were determined by HPLC. ^d **L5**:Zn(ClO₄)₂·6H₂O:DIPEA = 1:1:1 (5 mol%). ^e Reaction was carried at 0 °C.

1.3 General Procedures for Enantioselective Addition of Alcohols and Peroxides to Isatin-derived N-Boc Ketimines

Binaphthyl-proline-based chiral ligand **L5** (8.4 mg, 0.015 mmol), Zn(ClO₄)₂·6H₂O (5.6 mg, 0.015 mmol) and DIPEA (2.0 mg, 0.015 mmol) were stirred in a dry reaction tube in DCM (2.0 mL) at room temperature for 1 h, isatin-derived N-Boc ketimine **1** (0.15 mmol) and alcohols (or ^tBuOOH) were then added. The reaction mixture was stirred for 24 h at room

temperature and the reaction was monitored with TLC. After the consumption of ketimine **1**, the reaction mixture was directly purified with flash chromatography (petroleum ether : ethyl acetate = 4:1) on silica gel to give the desired products.

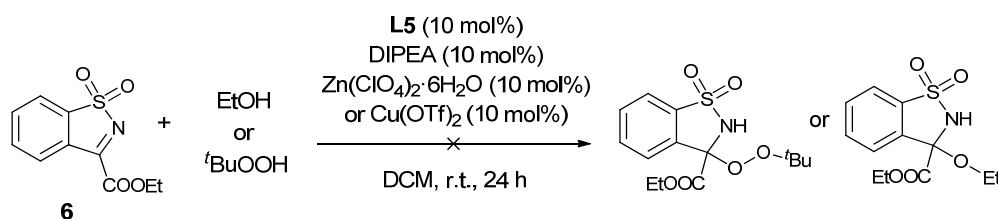
1.4 Enantioselective Addition of Sulfur-based Nucleophiles to Isatin-derived N-Boc Ketimine



Scheme S1. Addition of Sulfur-based Nucleophiles to isatin-derived ketimine **1a**.

Binaphthyl-proline-based chiral ligand **L5** (8.4 mg, 0.015 mmol), $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (5.6 mg, 0.015 mmol) and DIPEA (2.0 mg, 0.015 mmol) were stirred in a dry reaction tube in DCM (2.0 mL) at room temperature for 1 h, isatin-derived N-Boc ketimine **1a** (0.15 mmol) and $t\text{-BuSH}$ were then added. The reaction mixture was stirred for 24 h at room temperature and the reaction was monitored with TLC. After the consumption of ketimine **1a**, the reaction mixture was directly purified with flash chromatography (petroleum ether : ethyl acetate = 4:1) on silica gel to give the desired product **5**.

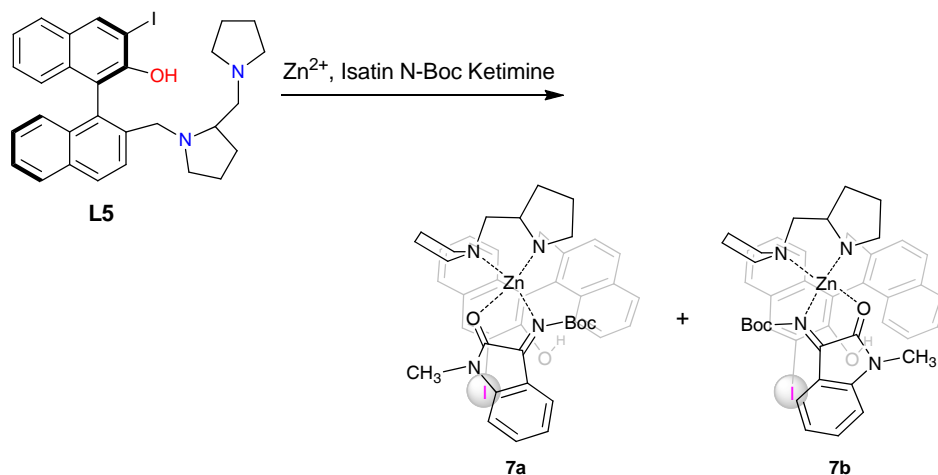
1.5 Enantioselective Addition of Alcohols and Peroxides to Cyclic Ketimine **6**



Scheme S2. Addition of Alcohols and Peroxides to Cyclic Ketimine **6**.

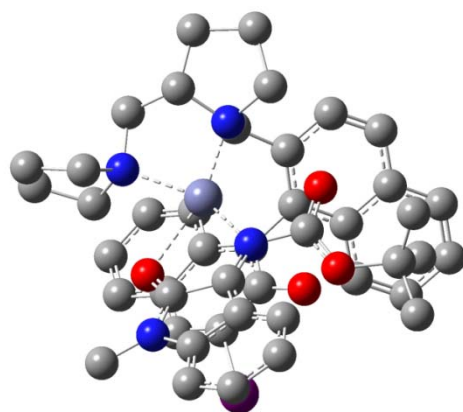
1.6 Computational Studies on the Key Intermediates of the Reactions.

DFT calculations were carried out to get structural insights into the reaction. The following structures **7a** and **7b** were proposed as key intermediates leading to the desired products.



Intermediate **7a** corresponds to Si-attack, and led to products with (S)-configuration. Intermediate **7b** corresponds to Re-attack, and led to products with (R)-configuration. DFT calculations on **7a/7b** were carried out with Gaussian G09 D01 package.² The intermediates were optimized at M06L level of theory³ with 6-31+G(d) basis set for light atoms⁴ and SDD for copper.⁵ Implicit solvation model SMD⁶ was used with dichloromethane as the solvent. Preliminary results showed that **7a** was favored over **7b** ($\Delta E = -2.31$ kcal/mol), suggesting that Si-attack of the nucleophiles on the substrates was the predominant one.

Optimized structure of **7a**:



7a

Coordinates:

Atomic Number	Atomic Type	Coordinates (Angstroms)		
		X	Y	Z
6	0	5.072438	-0.886354	-0.388740
6	0	3.799909	-0.556470	0.022950
6	0	3.337053	-0.892069	1.324251
6	0	4.252672	-1.551494	2.208265
6	0	5.551667	-1.884636	1.752500
6	0	5.955226	-1.568236	0.475894
1	0	5.400195	-0.613680	-1.390474
1	0	3.144278	-0.020088	-0.661165
6	0	2.003129	-0.593868	1.775649
6	0	3.845663	-1.836524	3.531742
1	0	6.227303	-2.390608	2.441887
1	0	6.955661	-1.829646	0.135524
6	0	2.588664	-1.494087	3.958052
6	0	1.642734	-0.893464	3.088669
1	0	4.551534	-2.314009	4.210441
1	0	2.295526	-1.686459	4.990008
6	0	1.054188	0.031289	0.806906
6	0	0.653643	1.401457	0.911194
6	0	0.682506	-0.698331	-0.324808
6	0	1.050378	2.231625	1.990974
6	0	-0.167509	1.975317	-0.112497
6	0	-0.111409	-0.108691	-1.339915
6	0	0.623409	3.539569	2.075597
1	0	1.705359	1.824983	2.761011
6	0	-0.592612	3.321802	0.003913
6	0	-0.536951	1.190005	-1.231079

6	0	-0.213585	4.090390	1.081307
1	0	0.941411	4.156111	2.914813
1	0	-1.225838	3.735680	-0.780877
1	0	-1.145320	1.640640	-2.013386
1	0	-0.544608	5.124190	1.161400
8	0	1.093318	-1.974121	-0.528063
6	0	0.299839	-0.543132	3.664947
1	0	-0.137766	0.308199	3.135139
1	0	0.438111	-0.231418	4.710005
6	0	-0.285294	-2.864153	4.340897
6	0	-1.927763	-1.266793	4.455001
6	0	-0.395360	-2.516025	5.830591
1	0	0.707204	-3.171006	4.010391
1	0	-0.981519	-3.663782	4.067067
6	0	-1.472169	-1.416238	5.901733
1	0	-2.660005	-2.061967	4.237761
1	0	-0.659138	-3.402504	6.415705
1	0	0.561280	-2.149998	6.222183
1	0	-2.317205	-1.684043	6.543410
1	0	-1.065435	-0.472420	6.285290
6	0	-2.524478	0.039874	4.016977
1	0	-3.412515	0.268309	4.620553
1	0	-1.826461	0.873099	4.153924
6	0	-4.341751	-0.397881	2.458931
6	0	-2.808768	1.257884	1.907685
6	0	-5.079892	0.928687	2.683352
1	0	-4.595372	-1.184354	3.177823
1	0	-4.520978	-0.779619	1.451063
6	0	-4.031407	2.022724	2.405386

1	0	-2.851570	1.087832	0.826256
1	0	-1.848186	1.727702	2.148147
1	0	-5.942681	1.000316	2.013543
1	0	-5.463668	1.002298	3.706797
1	0	-4.367902	2.758237	1.667647
1	0	-3.790496	2.572921	3.322983
7	0	-2.884274	-0.074527	2.570636
7	0	-0.728383	-1.641185	3.613290
8	0	-3.036176	-1.048187	-0.191555
6	0	-2.276540	-3.314582	-0.634978
6	0	-3.134241	-2.078567	-0.856674
1	0	1.714900	-2.225749	0.182907
7	0	-1.411862	-3.190778	0.327299
6	0	-0.325680	-4.070201	0.594368
8	0	0.213410	-4.016541	1.684280
8	0	0.009848	-4.802568	-0.443198
6	0	1.200951	-5.735616	-0.371971
6	0	2.459070	-4.932091	-0.106057
1	0	2.440772	-4.446420	0.874618
1	0	3.314330	-5.617439	-0.117458
1	0	2.627221	-4.183987	-0.889374
6	0	1.220374	-6.331596	-1.764565
1	0	2.107476	-6.965206	-1.872267
1	0	0.338579	-6.954318	-1.952440
1	0	1.265906	-5.546655	-2.528140
6	0	0.933147	-6.786388	0.685701
1	0	-0.033491	-7.276784	0.519083
1	0	1.711578	-7.555372	0.621136
1	0	0.952222	-6.369613	1.696459

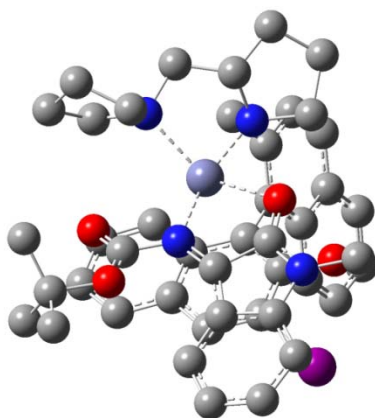
7	0	-3.956972	-2.332349	-1.894125
6	0	-3.732614	-3.637906	-2.358085
6	0	-4.397742	-4.268454	-3.389616
6	0	-2.709059	-4.278851	-1.609397
6	0	-4.046261	-5.596375	-3.663848
1	0	-5.172002	-3.762564	-3.961249
6	0	-2.400853	-5.617905	-1.887277
6	0	-3.073997	-6.267037	-2.916279
1	0	-4.554051	-6.117472	-4.472862
1	0	-1.652217	-6.143364	-1.306116
1	0	-2.837870	-7.303577	-3.143138
6	0	-4.864056	-1.381610	-2.496418
1	0	-4.759979	-0.430331	-1.970983
1	0	-4.609698	-1.240958	-3.552546
1	0	-5.897087	-1.734340	-2.414402
30	0	-1.598456	-1.604984	1.696924
53	0	-0.546651	-1.237530	-3.092223

Energies:

Sum of electronic and zero-point Energies=	-2462.250585
Sum of electronic and thermal Energies=	-2462.202300
Sum of electronic and thermal Enthalpies=	-2462.201356
Sum of electronic and thermal Free Energies=	-2462.330040

Number of imaginary frequency: 0

Optimized structure of **7b**:



7b

Coordinates

Atomic Number	Atomic Type	Coordinates (Angstroms)		
		X	Y	Z
6	0	5.146365	-1.030893	-0.252634
6	0	3.811498	-0.929228	0.069936
6	0	3.376064	-0.963647	1.422230
6	0	4.376731	-1.092853	2.440806
6	0	5.741754	-1.204949	2.075864
6	0	6.123547	-1.178000	0.755188
1	0	5.450199	-0.995487	-1.297228
1	0	3.082040	-0.809171	-0.729061
6	0	1.989214	-0.858025	1.793729
6	0	3.979864	-1.091340	3.796114
1	0	6.482111	-1.306423	2.868956
1	0	7.174612	-1.261032	0.484766
6	0	2.656605	-0.953956	4.130090
6	0	1.644720	-0.834289	3.143974
1	0	4.740112	-1.191815	4.569962
1	0	2.360727	-0.938519	5.178596

6	0	0.999984	-0.780493	0.676348
6	0	0.401201	0.462355	0.293902
6	0	0.847177	-1.894906	-0.151216
6	0	0.552024	1.651231	1.055184
6	0	-0.306888	0.548442	-0.951722
6	0	0.168535	-1.783424	-1.392946
6	0	0.009246	2.843452	0.623623
1	0	1.126037	1.620588	1.980524
6	0	-0.847087	1.790090	-1.367072
6	0	-0.386077	-0.590891	-1.784513
6	0	-0.700523	2.917451	-0.594589
1	0	0.141932	3.742029	1.224278
1	0	-1.376230	1.830052	-2.319785
1	0	-0.876906	-0.500366	-2.753190
1	0	-1.119071	3.867073	-0.922983
8	0	1.398336	-3.097533	0.128775
6	0	0.245251	-0.647691	3.661438
1	0	-0.205654	0.266509	3.249640
1	0	0.310244	-0.500523	4.747555
6	0	-0.103087	-3.109206	3.572658
6	0	-1.805451	-1.819730	4.424207
6	0	0.003899	-3.279642	5.090426
1	0	0.853328	-3.175100	3.049765
1	0	-0.785081	3.840697	325
6	0	-1.144315	-2.426045	5.660888
1	0	-2.532873	-2.542794	4.018569
1	0	-0.070458	-4.334603	5.372373
1	0	0.974726	-2.918372	5.451517
1	0	-1.870569	-3.011641	6.232744

1	0	-0.769673	-1.639966	6.328433
6	0	-2.478061	-0.481924	4.579526
1	0	-3.284051	-0.548267	5.324015
1	0	-1.764039	0.258235	4.952503
6	0	-4.458461	-0.409578	3.141987
6	0	-3.001072	1.491640	3.175018
6	0	-5.228959	0.750978	3.740338
1	0	-4.612185	-1.378680	3.630204
1	0	-4.703774	-0.523382	2.077421
6	0	-4.458958	1.953569	3.206974
1	0	-2.497464	1.799345	2.256451
1	0	-2.430943	1.877030	4.026138
1	0	-6.283920	0.746270	3.446553
1	0	-5.186416	0.711747	4.837359
1	0	-4.793176	2.195941	2.191117
1	0	-4.587664	2.851040	3.820327
7	0	-3.014590	-0.018960	3.263700
7	0	-0.718390	-1.767644	3.373657
8	0	-1.941312	-3.373821	1.134632
6	0	-3.037490	-2.236745	-0.715739
6	0	-2.447585	-3.435501	0.010570
1	0	1.889854	-3.042571	0.970645
7	0	-3.056221	-1.149861	0.000313
6	0	-3.740819	0.052390	-0.328595
8	0	-3.470927	1.071169	0.276090
8	0	-4.680857	-0.132349	-1.231401
6	0	-5.628648	0.991683	-1.592493
6	0	-6.419327	1.366351	-0.356442
1	0	-5.792860	1.843656	0.402252

1	0	-7.201938	2.078676	-0.641249
1	0	-6.909388	0.487673	0.080301
6	0	-6.514390	0.344058	-2.636644
1	0	-7.298437	1.050730	-2.929519
1	0	-5.951473	0.077780	-3.537935
1	0	-6.997684	-0.558238	-2.245453
6	0	-4.834856	2.144570	-2.171988
1	0	-4.197255	1.806318	-2.998017
1	0	-5.535893	2.883929	-2.576441
1	0	-4.214019	2.638119	-1.419136
7	0	-2.639428	-4.518113	-0.761581
6	0	-3.207525	-4.118462	-1.987166
6	0	-3.468803	-4.924398	-3.074422
6	0	-3.444442	-2.718227	-2.004284
6	0	-3.946546	-4.300634	-4.234665
1	0	-3.290509	-5.996629	-3.045897
6	0	-3.882915	-2.116346	-3.192741
6	0	-4.129872	-2.916267	-4.302141
1	0	-4.159780	-4.911144	-5.109769
1	0	-4.008786	-1.041367	-3.254601
1	0	-4.470700	-2.461308	-5.228757
6	0	-2.198774	-5.859926	-0.447576
1	0	-1.731406	-5.843864	0.538645
1	0	-3.052330	-6.544816	-0.438740
1	0	-1.467404	-6.195719	-1.190581
30	0	-1.922769	-1.182159	1.764735
53	0	0.214003	-3.421709	-2.755449

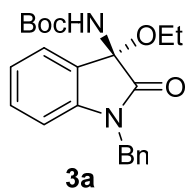
Energies:

Sum of electronic and zero-point Energies=	-2462.248098
Sum of electronic and thermal Energies=	-2462.199851
Sum of electronic and thermal Enthalpies=	-2462.198907
Sum of electronic and thermal Free Energies=	-2462.326363

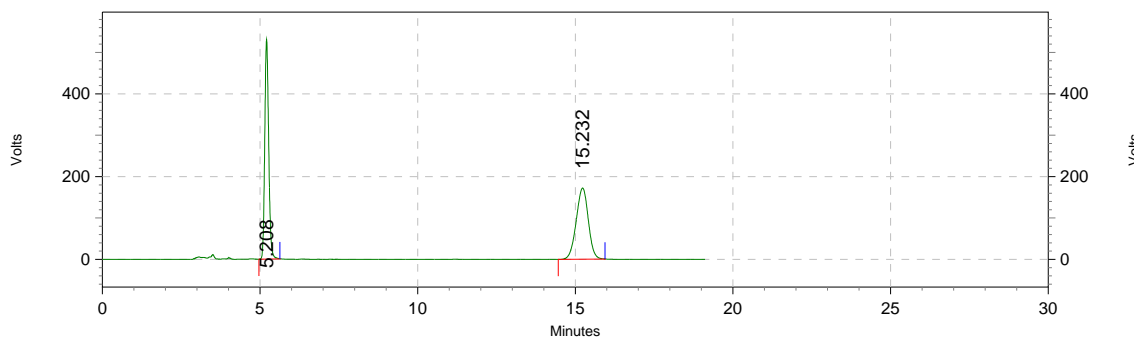
Number of imaginary frequency: 0.

2. Characterization and ee Values of the Products

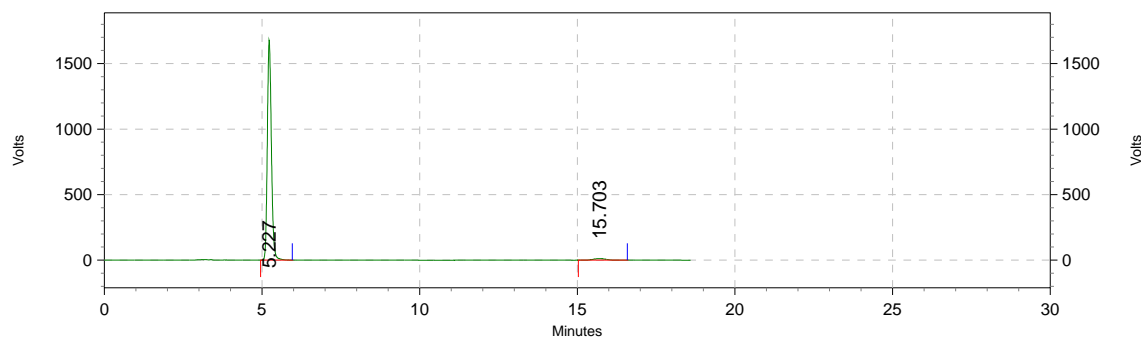
(S)-tert-butyl-(1-benzyl-3-ethoxy-2-oxindolin-3-yl)carbamate (3a)



White solid, 95% yield, 96% ee, mp 121-123 °C. $[\alpha]_D^{20} = -3.00$ (c = 1.00, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, J = 7.0 Hz, 1H), 7.32 (q, J = 8.1 Hz, 4H), 7.27 – 7.18 (m, 2H), 7.06 (t, J = 7.5 Hz, 1H), 6.70 (d, J = 7.8 Hz, 1H), 5.63 (s, 1H), 4.99 (d, J = 15.7 Hz, 1H), 4.84 (d, J = 15.7 Hz, 1H), 3.50 (q, J = 7.0 Hz, 2H), 1.34 (s, 9H), 1.16 (t, J = 7.0 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 172.7, 153.3, 142.9, 135.4, 130.3, 128.8, 127.7, 127.3, 126.3, 125.8, 123.2, 109.5, 84.4, 80.6, 59.7, 44.0, 28.2, 15.3. HRMS-ESI(m/z): [M+Na]⁺ calcd for C₂₂H₂₆N₂NaO₄⁺ 405.1785, found 405.1789. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 5.2 min for (*S*)-isomer and t_R = 15.7 min for (*R*)-isomer.

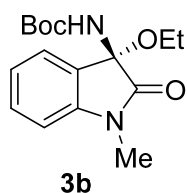


Peaks	Ret. Time	Area	Area%
1	5.208	4569753	50.011
2	15.232	4567736	49.989

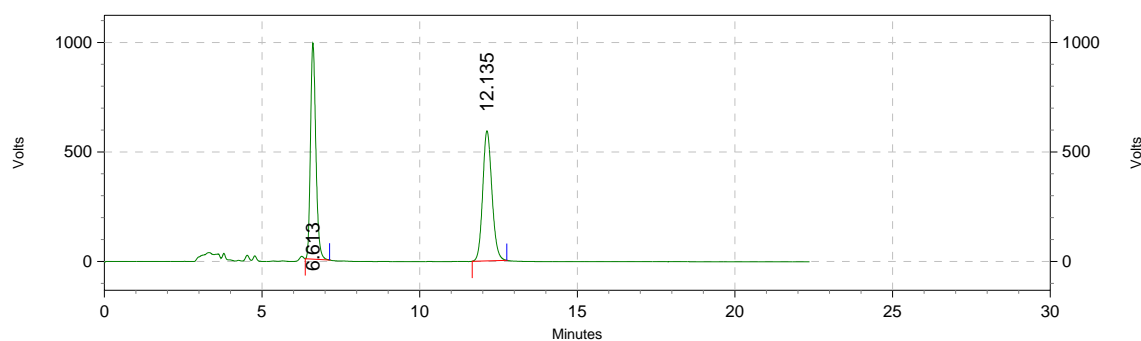


Peaks	Ret. Time	Area	Area%
1	5.227	14940173	97.785
2	15.703	338350	2.215

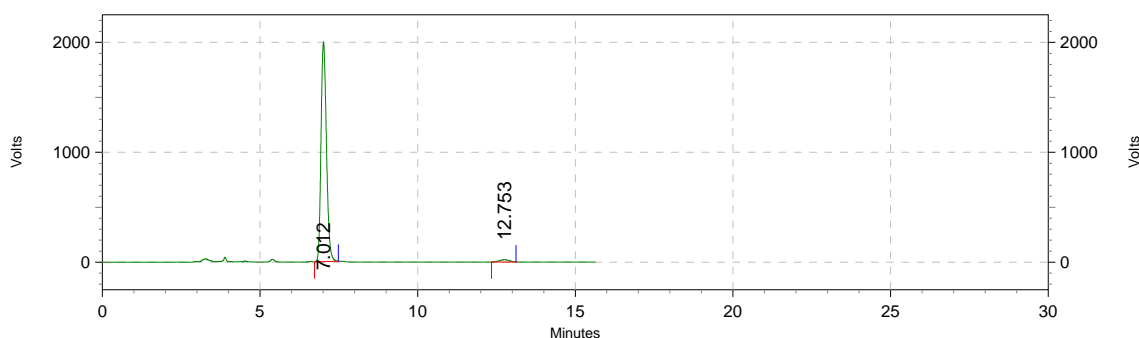
(S)-tert-butyl-(3-ethoxy-1-methyl-2-oxindolin-3-yl)carbamate (3b)⁷



White solid, 93% yield, 96% ee, mp 112-114 °C. $[\alpha]_{\text{D}}^{20} = -8.20$ (c = 1.00, CH₂Cl₂). Reference: $[\alpha]_{\text{D}}^{20} = +21$ (c = 1.0, CH₂Cl₂) for (R)-configuration. ¹H NMR (400 MHz, CDCl₃) δ 7.58 (s, 1H), 7.27 (s, 1H), 7.03 (s, 1H), 6.76 (d, J = 6.1 Hz, 1H), 5.54 (s, 1H), 3.43 – 3.35 (m, 2H), 3.13 (s, 3H), 1.23 (s, 9H), 1.06 (s, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 171.4, 152.2, 142.7, 129.4, 125.3, 124.6, 122.1, 107.4, 83.3, 79.4, 58.6, 27.1, 25.2, 14.2. The ee value was determined by chiral HPLC analysis (Chiralcel IA-H, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 7.0 min for (S)-isomer and t_R = 12.8 min for (R)-isomer.

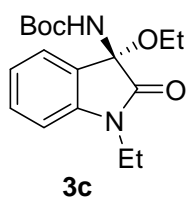


Peaks	Ret. Time	Area	Area%
1	6.613	11702370	49.234
2	12.135	12066623	50.766

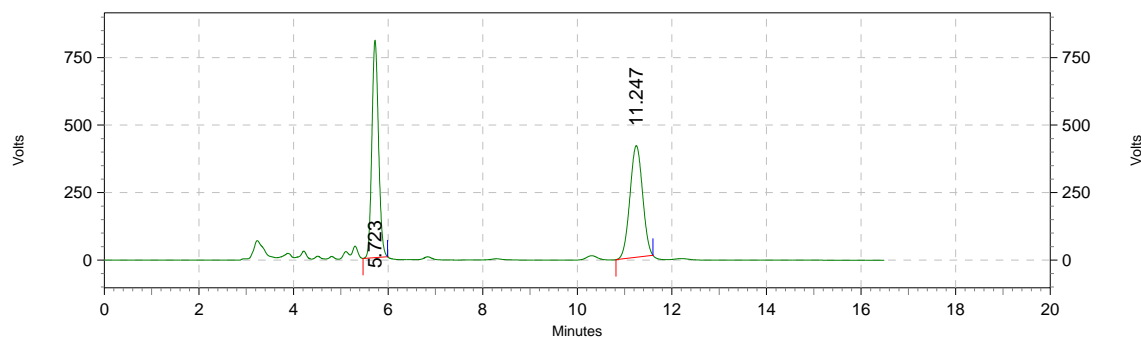


Peaks	Ret. Time	Area	Area%
1	7.012	23870153	98.180
2	12.753	442466	1.820

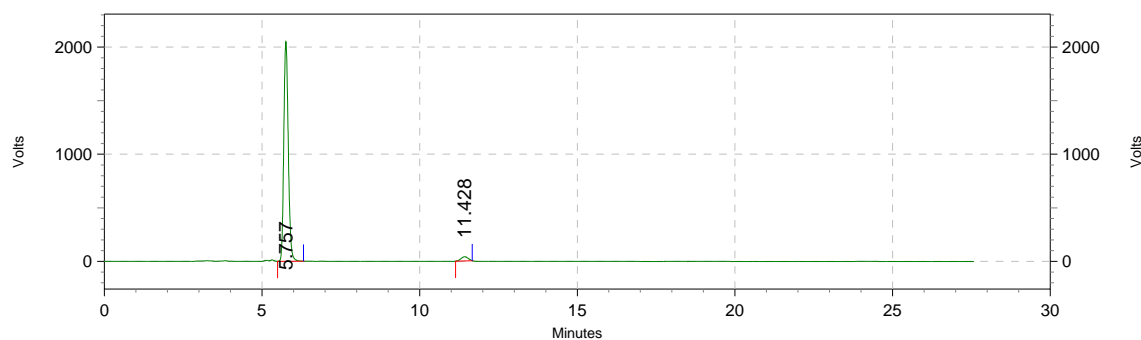
(S)-tert-butyl-(3-ethoxy-1-ethyl-2-oxoindolin-3-yl)carbamate (3c)



White solid, 94% yield, 94% ee, mp 133-135 °C. $[\alpha]_D^{20} = -1.81$ ($c = 1.00$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ 7.72 (s, 1H), 7.34 (s, 1H), 7.10 (s, 1H), 6.86 (s, 1H), 5.51 (s, 1H), 3.76 (d, $J = 43.8$ Hz, 2H), 3.45 (s, 2H), 1.33 (s, 9H), 1.29 (s, 3H), 1.14 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 172.1, 153.2, 142.8, 130.3, 126.4, 126.2, 122.9, 108.5, 84.2, 80.4, 59.5, 34.8, 28.1, 15.2, 12.6. HRMS-ESI(m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{NaO}_4^+$ 343.1628, found 343.1629. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/*i*-PrOH = 70/30 flow rate = 1.0 mL/min, $\lambda = 220$ nm). Retention times: $t_R = 5.7$ min for (*S*)-isomer and $t_R = 11.4$ min for (*R*)-isomer.

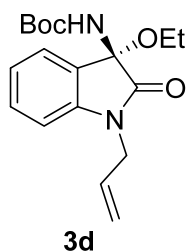


Peaks	Ret. Time	Area	Area%
1	5.723	7845771	50.607
2	11.247	7657623	49.393



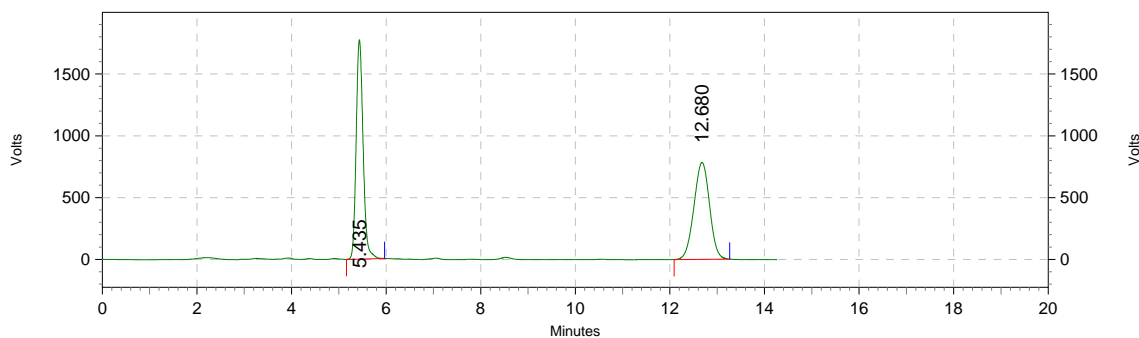
Peaks	Ret. Time	Area	Area%
1	5.757	20289378	97.114
2	11.428	603058	2.886

(S)-tert-butyl-(1-allyl-3-ethoxy-2-oxindolin-3-yl)carbamate (3d)

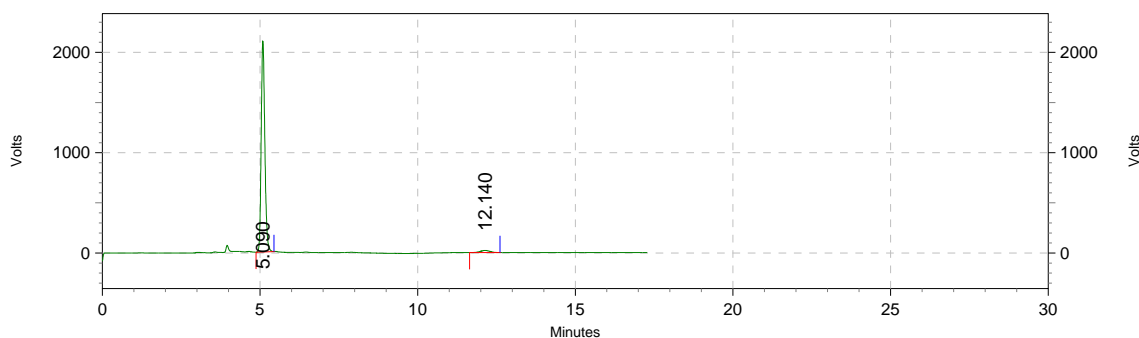


White solid, 92% yield, 94% ee. mp 124-126 °C. $[\alpha]_D^{20} = -11.2$ (c = 1.00, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 7.3 Hz, 1H), 7.31 (td, J = 7.8, 1.2 Hz, 1H), 7.12 – 7.07 (m, 1H), 6.83 (d, J = 7.8 Hz, 1H), 5.84 (ddd, J = 22.4, 10.4, 5.2 Hz, 1H), 5.60 (s, 1H), 5.33 – 5.20 (m, 2H), 4.43 (dd, J = 16.4, 4.9 Hz, 1H), 4.26 (dd, J = 16.3, 4.6 Hz, 1H), 3.48 (q, J = 7.0 Hz,

2H), 1.33 (s, 9H), 1.15 (t, J = 7.0 Hz, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 172.2, 153.2, 142.9, 131.0, 130.3, 126.2, 125.8, 123.1, 117.9, 109.3, 84.3, 80.4, 59.6, 42.4, 28.1, 15.2. HRMS-ESI(m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{NaO}_4^+$ 355.1628, found 355.1631. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, $\lambda = 220$ nm). Retention times: $t_{\text{R}} = 5.4$ min for (*S*)-isomer and $t_{\text{R}} = 12.7$ min for (*R*)-isomer.

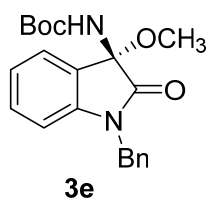


Peaks	Ret. Time	Area	Area%
1	5.435	18080318	50.146
2	12.680	17974877	49.854

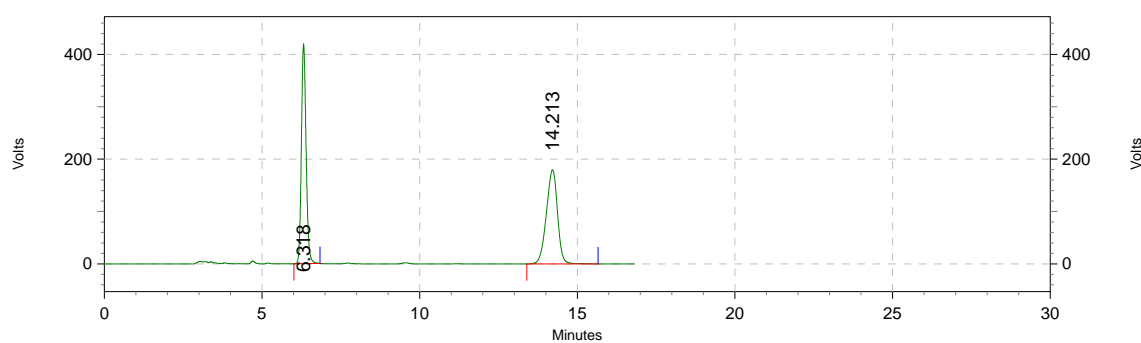


Peaks	Ret. Time	Area	Area%
1	5.090	16879962	97.374
2	12.140	455180	2.626

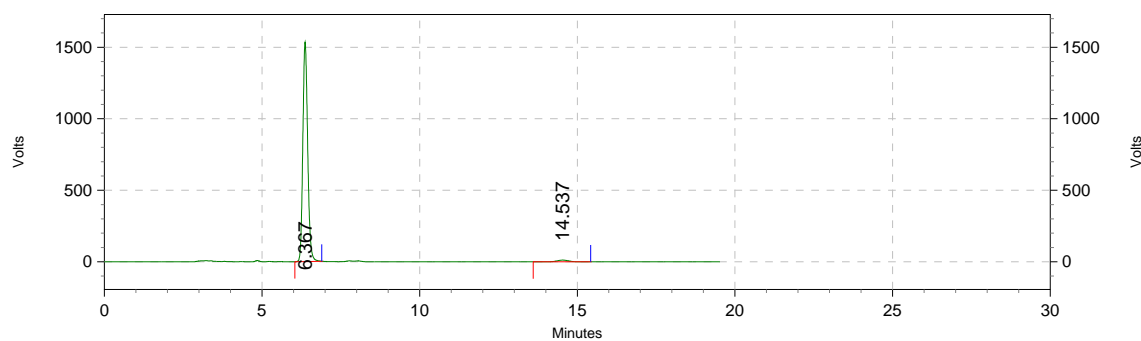
(S)-tert-butyl-(1-benzyl-3-methoxy-2-oxindolin-3-yl)carbamate (3e)⁷



White solid, 95% yield, 96% ee, mp 132-134 °C. $[\alpha]_D^{20} = -4.41$ (c = 1.60, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 6.1 Hz, 1H), 7.33 (s, 4H), 7.27 – 7.20 (m, 2H), 7.08 (t, J = 7.3 Hz, 1H), 6.72 (d, J = 7.7 Hz, 1H), 5.66 (s, 1H), 4.99 (d, J = 15.7 Hz, 1H), 4.84 (d, J = 15.7 Hz, 1H), 3.30 (s, 3H), 1.36 (s, 9H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 172.3, 153.4, 142.9, 135.3, 130.4, 128.9, 127.8, 127.3, 126.4, 125.7, 109.5, 84.6, 80.7, 51.7, 43.9, 28.2. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 6.4 min for (*S*)-isomer and t_R = 14.5 min for (*R*)-isomer.

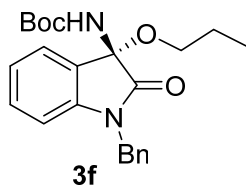


Peaks	Ret. Time	Area	Area%
1	6.318	4351620	49.740
2	14.213	4397084	50.260

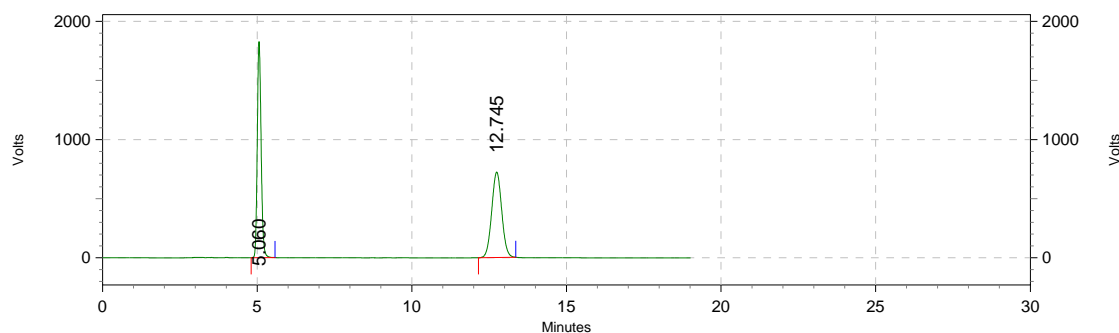


Peaks	Ret. Time	Area	Area%
1	6.367	16395031	98.147
2	14.537	309501	1.853

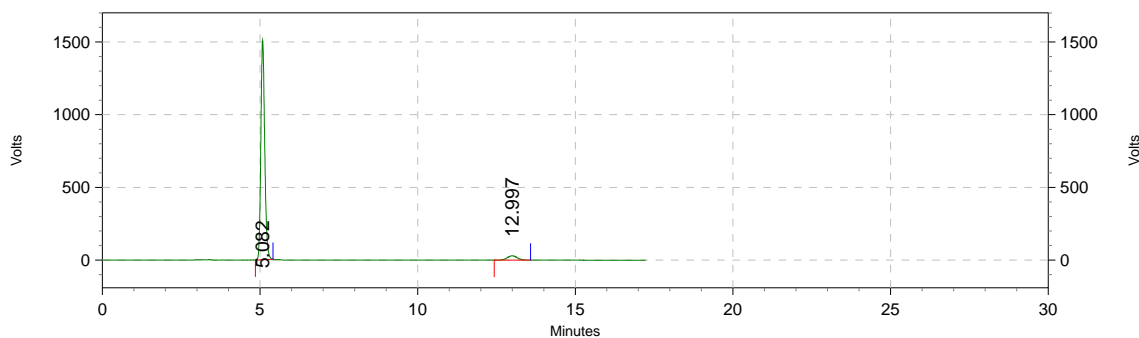
(S)-tert-butyl -(1-benzyl-2-oxo-3-propoxyindolin-3-yl)carbamate (3f)



White solid, 90% yield, 90% ee, mp 120-122 °C. $[\alpha]_D^{20} = -7.181$ (c = 1.30, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 5.6 Hz, 1H), 7.32 (d, J = 8.9 Hz, 4H), 7.27 – 7.18 (m, 2H), 7.07 (t, J = 7.1 Hz, 1H), 6.71 (d, J = 7.5 Hz, 1H), 5.61 (s, 1H), 5.01 (d, J = 15.6 Hz, 1H), 4.82 (d, J = 15.5 Hz, 1H), 3.43 – 3.33 (m, 2H), 1.55 (q, J = 6.6 Hz, 2H), 1.34 (s, 9H), 0.86 (t, J = 6.8 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 172.7, 153.2, 143.0, 135.4, 130.3, 128.8, 127.7, 127.3, 126.3, 125.8, 123.1, 109.5, 84.4, 80.5, 65.6, 43.9, 28.2, 22.9, 10.5. HRMS-ESI(m/z): [M+Na]⁺ calcd for C₂₃H₂₈N₂NaO₄⁺ 419.1941, found 419.1945. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 5.1 min for (*S*)-isomer and t_R = 13.0 min for (*R*)-isomer.

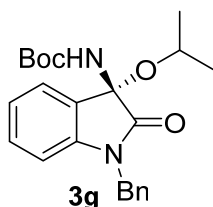


Peaks	Ret. Time	Area	Area%
1	5.060	15705935	49.145
2	12.745	16252137	50.855

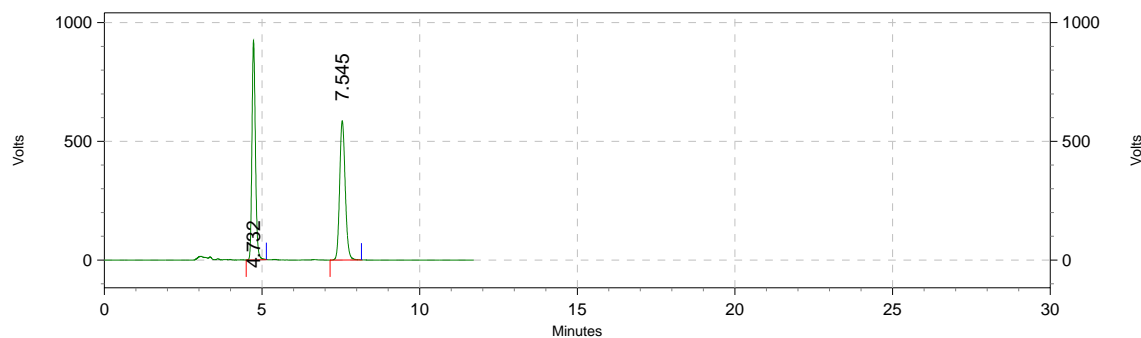


Peaks	Ret. Time	Area	Area%
1	5.082	12873804	95.007
2	12.997	676608	4.993

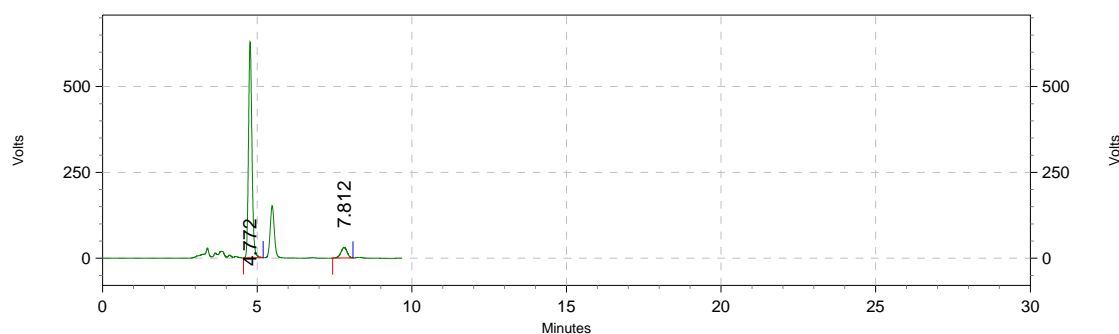
(S)-tert-butyl-(1-benzyl-3-isopropoxy-2-oxoindolin-3-yl)carbamate (3g)



White solid, 70% yield, 83% ee, mp 103-105 °C. $[\alpha]_D^{20} = +1.025$ (c = 1.00, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 6.4 Hz, 1H), 7.32 (d, J = 6.6 Hz, 4H), 7.23 (dd, J = 15.2, 7.4 Hz, 2H), 7.06 (t, J = 7.6 Hz, 1H), 6.71 (d, J = 7.8 Hz, 1H), 5.55 (s, 1H), 5.06 (d, J = 15.7 Hz, 1H), 4.77 (d, J = 15.7 Hz, 1H), 4.08 (p, J = 6.1 Hz, 1H), 1.35 (s, 9H), 1.12 (d, J = 6.2 Hz, 3H), 1.05 (d, J = 6.1 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 173.2, 153.2, 142.7, 135.4, 130.2, 128.8, 127.7, 127.3, 127.0, 126.1, 123.1, 109.4, 83.8, 80.5, 67.1, 43.9, 28.2, 23.8, 23.6. HRMS-ESI(m/z): [M+Na]⁺ calcd for C₂₃H₂₈N₂NaO₄⁺ 419.1941, found 419.1942. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 4.8 min for (S)-isomer and t_R = 7.8 min for (R)-isomer.

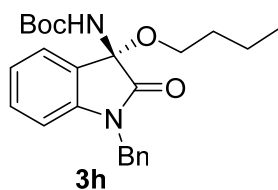


Peaks	Ret. Time	Area	Area%
1	4.732	7076195	49.668
2	7.545	7170911	50.332



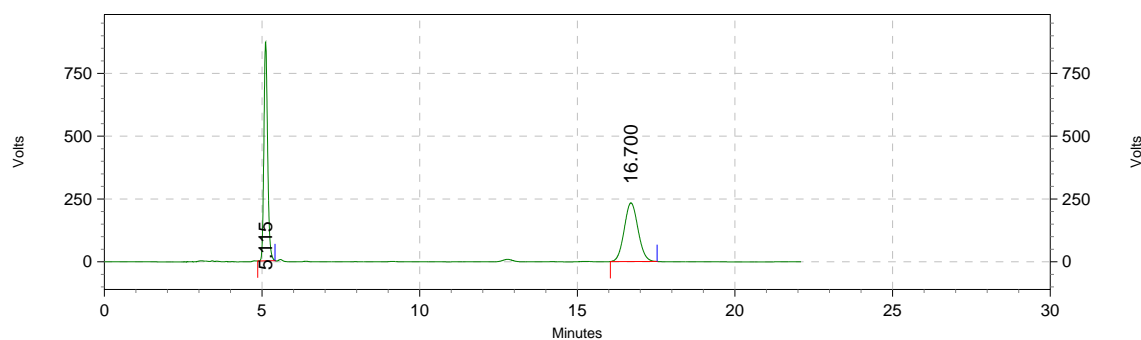
Peaks	Ret. Time	Area	Area%
1	4.772	4880791	91.968
2	7.812	426241	8.032

(S)-tert-butyl-(1-benzyl-3-butoxy-2-oxindolin-3-yl)carbamate (3h)

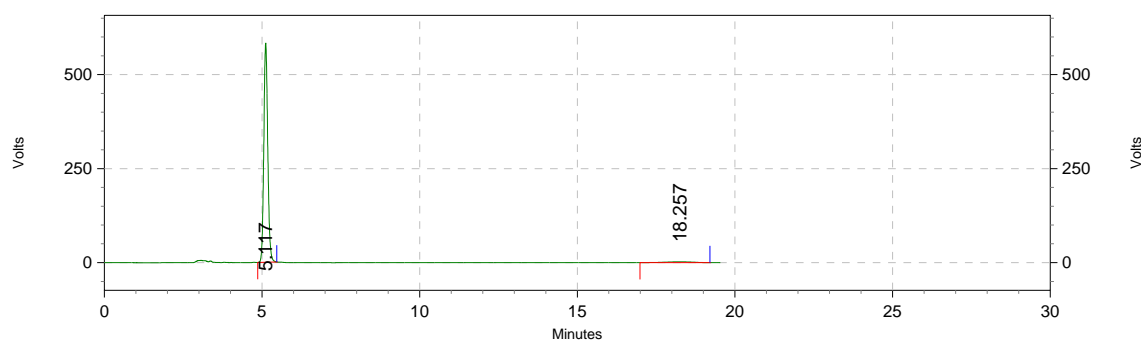


White solid, 92% yield, 95% ee, mp 113-115 °C. $[\alpha]_D^{20} = -11.74$ (c = 1.00, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 6.0 Hz, 1H), 7.32 (d, J = 8.2 Hz, 4H), 7.24 (dt, J = 15.2, 6.6 Hz, 2H), 7.07 (t, J = 7.3 Hz, 1H), 6.71 (d, J = 7.6 Hz, 1H), 5.58 (s, 1H), 5.02 (d, J = 15.7 Hz, 1H), 4.82 (d, J = 15.6 Hz, 1H), 3.41 (q, J = 6.7 Hz, 2H), 1.54 – 1.74 (m, 2H), 1.34 (s, 9H), 0.84 (t, J = 7.2 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 172.7, 153.2, 143.0, 130.3, 128.8, 127.7, 127.3, 126.3, 125.8, 123.1, 109.4, 84.4, 80.5, 63.7, 43.9, 31.6, 28.2, 19.1, 13.8.

HRMS-ESI(m/z): $[M+Na]^+$ calcd for $C_{24}H_{30}N_2NaO_4^+$ 433.2098, found 433.2101. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, $\lambda = 220$ nm). Retention times: $t_R = 5.1$ min for (*S*)-isomer and $t_R = 18.3$ min for (*R*)-isomer.

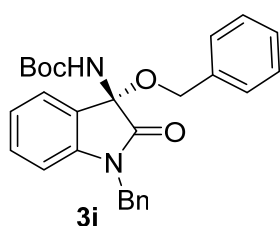


Peaks	Ret. Time	Area	Area%
1	5.115	7208217	50.372
2	16.700	7101871	49.628



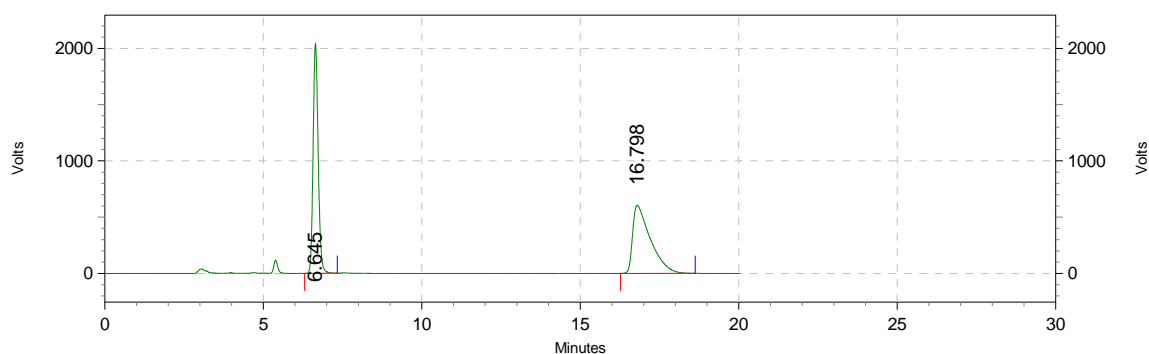
Peaks	Ret. Time	Area	Area%
1	5.117	5086932	97.626
2	18.257	123716	2.374

(*S*)-tert-butyl-(1-benzyl-3-(benzyloxy)-2-oxindolin-3-yl)carbamate (3i**)⁸**

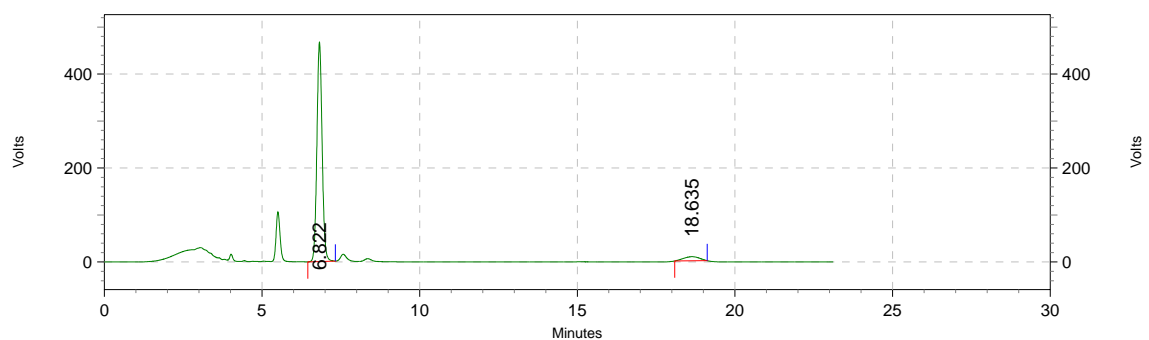


White solid, 90% yield, 89% ee mp 110-112 °C. $[\alpha]_D^{20} = +0.434$ (c = 1.20, CH_2Cl_2). 1H NMR

(400 MHz, CDCl₃) δ 7.81 (d, J = 6.9 Hz, 1H), 7.31 (d, J = 6.5 Hz, 4H), 7.29 – 7.20 (m, 7H), 7.08 (t, J = 7.5 Hz, 1H), 6.71 (d, J = 7.9 Hz, 1H), 5.70 (s, 1H), 4.96 (d, J = 15.7 Hz, 1H), 4.84 (d, J = 15.7 Hz, 1H), 4.60 – 4.51 (m, 2H), 1.36 (s, 9H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 172.4, 153.3, 142.9, 137.2, 135.3, 130.5, 128.9, 128.3, 128.0, 127.8, 127.8, 127.3, 126.4, 126.2, 123.3, 109.6, 84.4, 80.7, 66.1, 44.0, 29.7, 28.2. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 6.8 min for (*S*)-isomer and t_R = 18.6 min for (*R*)-isomer.

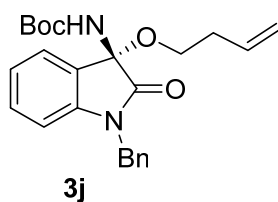


Peaks	Ret. Time	Area	Area%
1	6.645	22754903	49.191
2	16.798	23503093	50.809

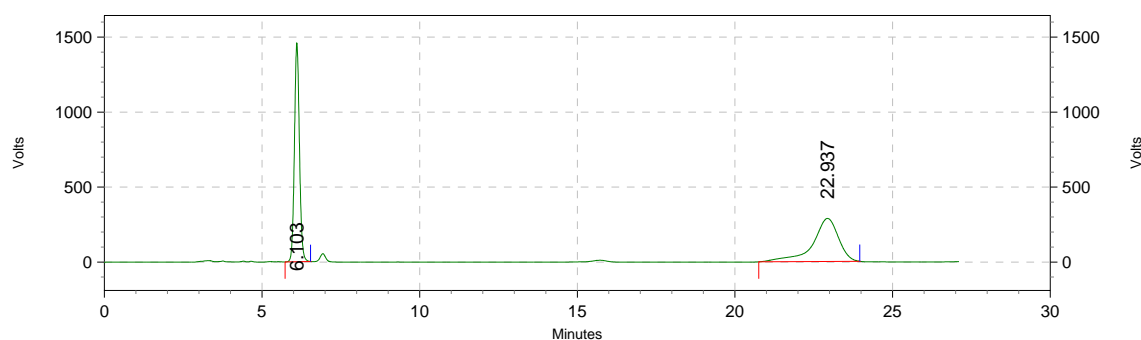


Peaks	Ret. Time	Area	Area%
1	6.822	5379906	94.623
2	18.635	305721	5.377

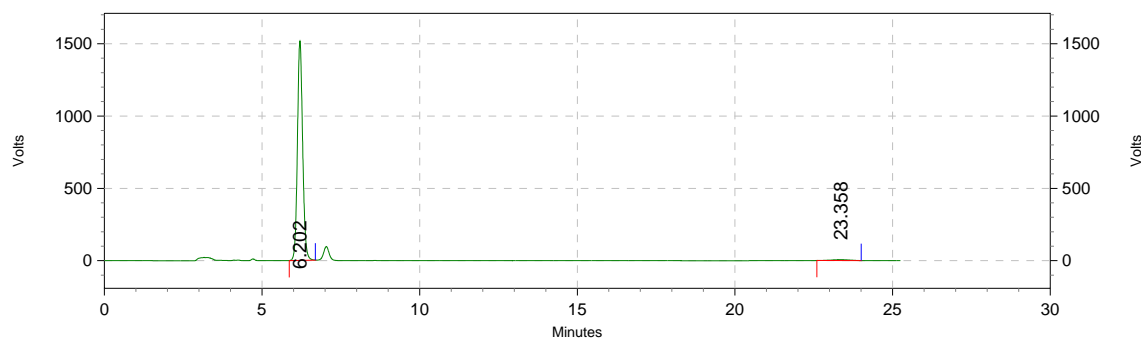
(S)-tert-butyl-(1-benzyl-3-(but-3-en-1-yloxy)-2-oxoindolin-3-yl)carbamate (3j)



White solid, 96% yield, 97% ee, mp 100-102 °C. $[\alpha]_D^{20} = -3.315$ ($c = 1.20$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 7.0$ Hz, 1H), 7.32 (t, $J = 8.3$ Hz, 4H), 7.26 – 7.18 (m, 2H), 7.06 (t, $J = 7.5$ Hz, 1H), 6.70 (d, $J = 7.8$ Hz, 1H), 5.74 (dd, $J = 17.0, 10.2, 6.7$ Hz, 1H), 5.64 (s, 1H), 5.02 (dd, $J = 15.6, 9.9$ Hz, 3H), 4.81 (d, $J = 15.7$ Hz, 1H), 3.49 (t, $J = 6.8$ Hz, 2H), 2.29 (q, $J = 6.8$ Hz, 2H), 1.34 (s, 9H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 172.5, 153.3, 142.9, 135.4, 134.6, 130.4, 128.8, 127.7, 127.3, 126.2, 125.9, 123.2, 116.8, 109.5, 84.4, 80.6, 63.4, 43.9, 34.0, 28.2. HRMS-ESI(m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{28}\text{N}_2\text{NaO}_4^+$ 431.1941, found 431.1946. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/*i*-PrOH = 80/20 flow rate = 1.0 mL/min, $\lambda = 220$ nm). Retention times: $t_R = 6.2$ min for (*S*)-isomer and $t_R = 23.4$ min for (*R*)-isomer.

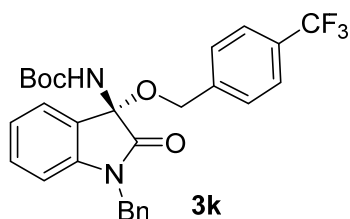


Peaks	Ret. Time	Area	Area%
1	6.103	16102483	49.752
2	22.937	16262858	50.248

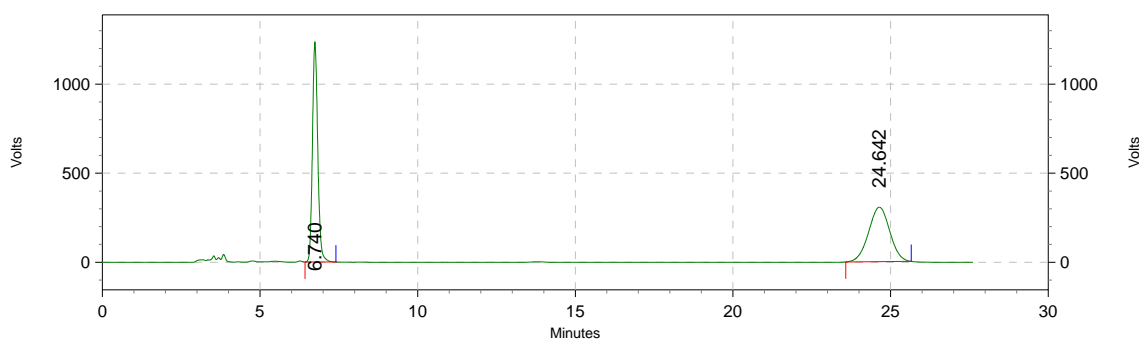


Peaks	Ret. Time	Area	Area%
1	6.202	17509036	98.651
2	23.358	239508	1.349

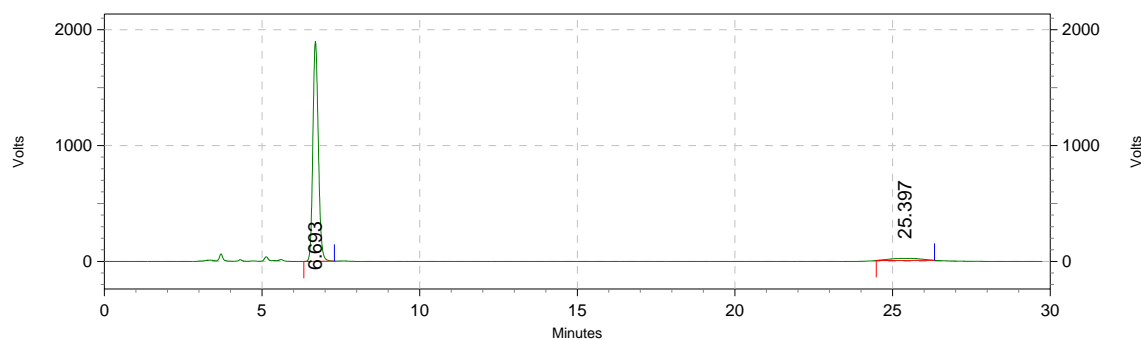
(S)-tert-butyl-(1-benzyl-2-oxo-3-((4-(trifluoromethyl)benzyl)oxy)indolin-3-yl)carbamate
(3k)



White solid, 97% yield, 90% ee, mp 136-138 °C. $[\alpha]_D^{20} = -9.063$ ($c = 1.20$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 6.3$ Hz, 1H), 7.53 (d, $J = 7.9$ Hz, 2H), 7.40 (d, $J = 7.8$ Hz, 2H), 7.36 – 7.20 (m, 6H), 7.08 (t, $J = 7.5$ Hz, 1H), 6.74 (d, $J = 7.8$ Hz, 1H), 5.89 (s, 1H), 4.95 (d, $J = 15.7$ Hz, 1H), 4.83 (d, $J = 15.7$ Hz, 1H), 4.68 (s, 2H), 1.37 (s, 9H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 172.2, 153.4, 142.7, 141.5, 135.2, 130.6, 129.8 (q, $^2J_{\text{C-F}} = 32.5$ Hz), 128.9, 127.9, 127.3, 126.8, 126.7, 126.2, 125.2 (q, $^3J_{\text{C-F}} = 3.7$ Hz), 124.2 (q, $^1J_{\text{C-F}} = 272.0$ Hz), 123.5, 84.3, 80.9, 65.2, 44.0, 28.2. ^{19}F NMR (CDCl_3) δ -62.5. HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{28}\text{H}_{27}\text{F}_3\text{N}_2\text{NaO}_4^+$ 535.1815, found 535.1821. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/*i*-PrOH = 70/30 flow rate = 1.0 mL/min, $\lambda = 220$ nm). Retention times: $t_R = 6.7$ min for (*S*)-isomer and $t_R = 25.4$ min for (*R*)-isomer.

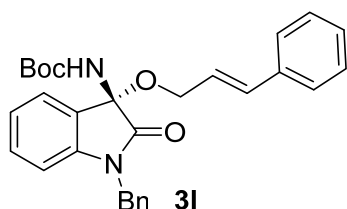


Peaks	Ret. Time	Area	Area%
1	6.740	14520761	50.492
2	24.642	14237872	49.508

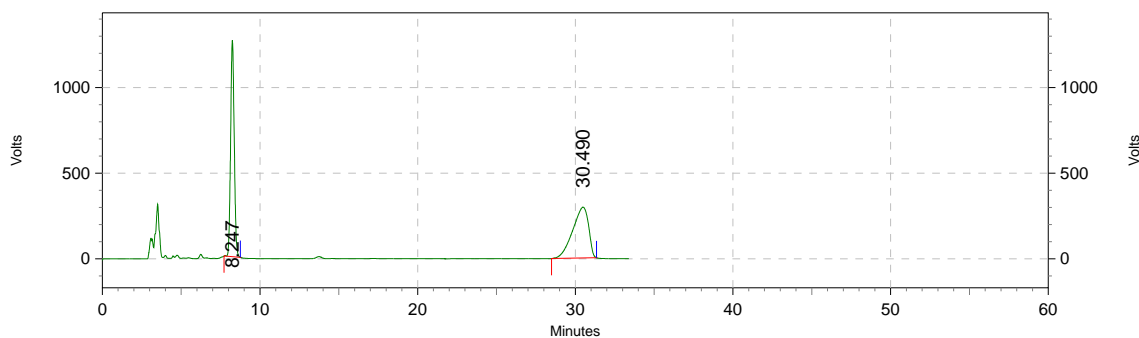


Peaks	Ret. Time	Area	Area%
1	6.693	22861263	95.002
2	25.397	1202779	4.998

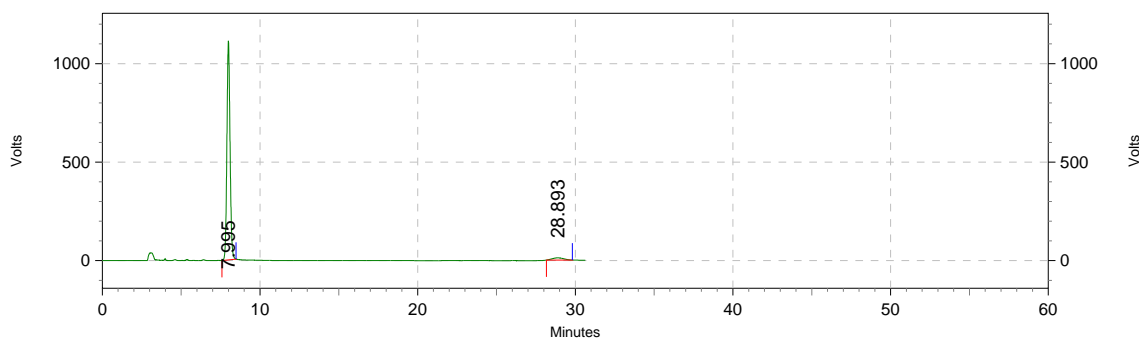
(S)-tert-butyl-(1-benzyl-3-(cinnamyloxy)-2-oxoindolin-3-yl)carbamate (3l)



White solid, 94% yield, 93% ee, mp 106-108 °C. $[\alpha]_D^{20} = -7.66$ ($c = 1.00$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 5.9$ Hz, 1H), 7.30 (d, $J = 11.3$ Hz, 9H), 7.23 (d, $J = 7.0$ Hz, 2H), 7.09 (t, $J = 7.3$ Hz, 1H), 6.71 (d, $J = 7.5$ Hz, 1H), 6.49 (d, $J = 15.9$ Hz, 1H), 6.26 – 6.16 (m, 1H), 5.67 (s, 1H), 4.91 (d, $J = 16.7$ Hz, 2H), 4.22 (d, $J = 5.7$ Hz, 2H), 1.37 (s, 9H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 172.5, 153.3, 142.8, 136.5, 135.3, 132.9, 130.5, 128.9, 128.5, 127.8, 127.3, 126.6, 126.4, 126.1, 125.0, 123.3, 109.6, 84.2, 80.7, 65.1, 44.0, 28.2. HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{29}\text{H}_{30}\text{N}_2\text{NaO}_4^+$ 493.2098, found 493.2101. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/*i*-PrOH = 70/30 flow rate = 1.0 mL/min, $\lambda = 220$ nm). Retention times: $t_R = 8.0$ min for (*S*)-isomer and $t_R = 28.9$ min for (*R*)-isomer.

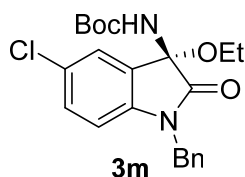


Peaks	Ret. Time	Area	Area%
1	8.247	20259718	49.323
2	30.490	20815772	50.677



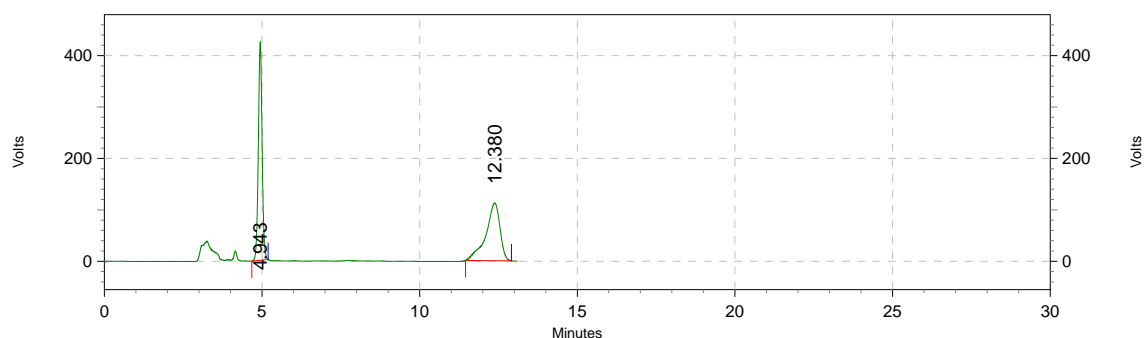
Peaks	Ret. Time	Area	Area%
1	7.995	15504999	96.489
2	28.893	564178	3.511

(S)-tert-butyl-(1-benzyl-5-chloro-3-ethoxy-2-oxoindolin-3-yl)carbamate (3m)

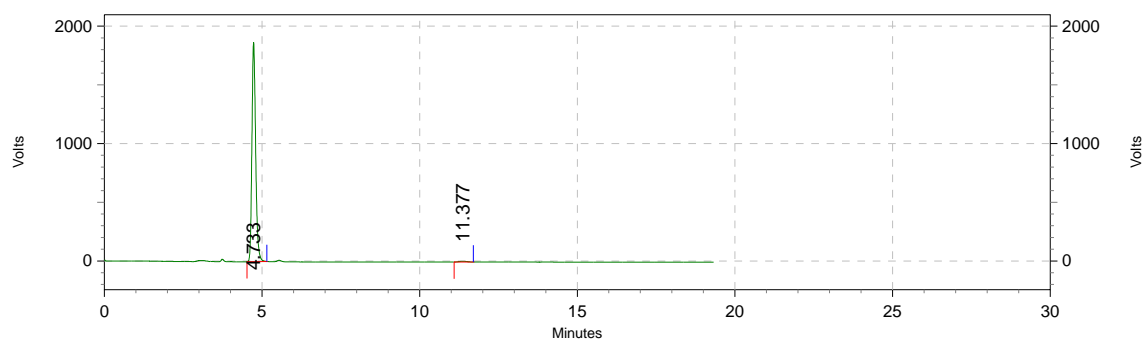


White solid, 98% yield, 99% ee, mp 165-167 °C. $[\alpha]_D^{20} = +9.98$ (c = 1.20, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.65 (m, 1H), 7.35 – 7.27 (m, 5H), 7.19 (dd, J = 8.4, 2.2 Hz, 1H), 6.61 (d, J = 8.3 Hz, 1H), 5.57 (s, 1H), 4.98 – 4.82 (m, 2H), 3.52 (q, J = 7.0 Hz, 2H), 1.38 (s, 9H), 1.17 (t, J = 7.0 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 172.3, 153.2, 141.4, 134.9, 127.9, 127.2, 126.2, 110.5, 84.2, 80.9, 59.8, 44.1, 28.2, 15.2. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₂H₂₅ClN₂NaO₄⁺ 439.1395, found 439.1400. The ee value was determined by

chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, $\lambda = 220$ nm). Retention times: $t_R = 4.7$ min for (*S*)-isomer and $t_R = 11.4$ min for (*R*)-isomer.

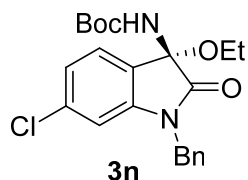


Peaks	Ret. Time	Area	Area%
1	4.943	3524071	50.390
2	12.380	3469545	49.610



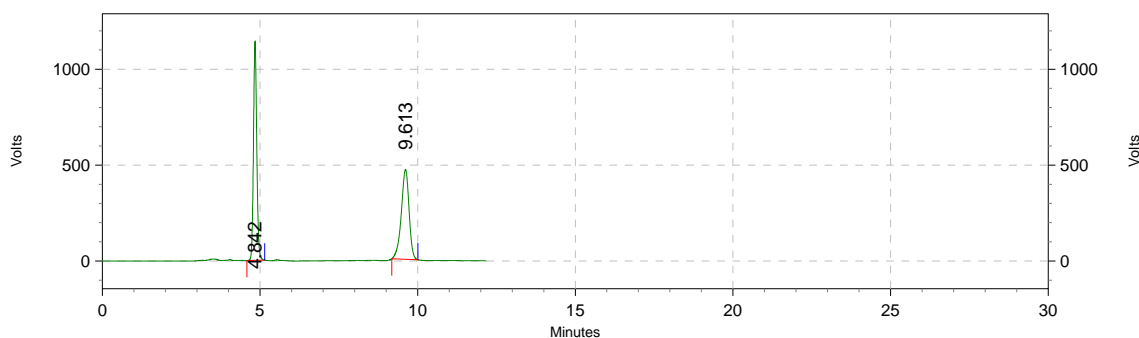
Peaks	Ret. Time	Area	Area%
1	4.733	15443537	99.277
2	11.377	112431	0.723

(*S*)-tert-butyl-(1-benzyl-6-chloro-3-ethoxy-2-oxindolin-3-yl)carbamate (3n)

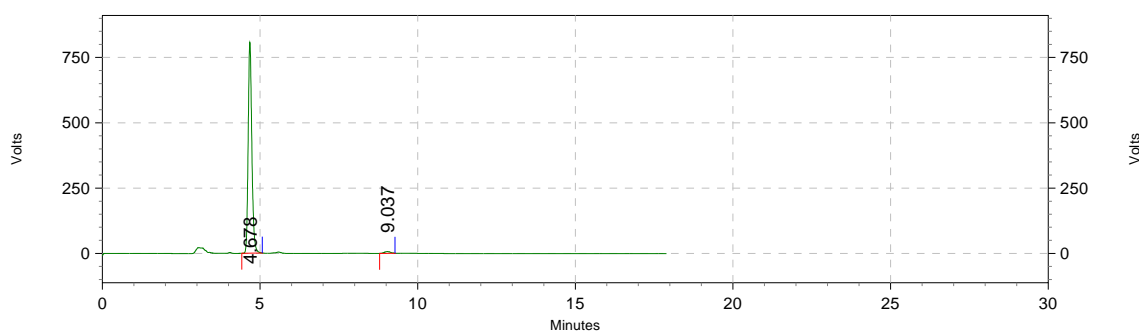


White solid, 97% yield, 97% ee, mp 148-150 °C. $[\alpha]_D^{20} = -7.13$ (c = 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, J = 7.9 Hz, 1H), 7.33 (d, J = 3.0 Hz, 5H), 7.04 (dd, J = 8.0, 1.8

Hz, 1H), 6.70 (d, J = 1.6 Hz, 1H), 5.60 (s, 1H), 4.95 (d, J = 15.8 Hz, 1H), 4.83 (d, J = 15.8 Hz, 1H), 3.49 (q, J = 7.0 Hz, 2H), 1.36 (s, 9H), 1.16 (t, J = 7.0 Hz, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 172.7, 153.3, 144.2, 136.1, 134.8, 129.0, 127.9, 127.2, 126.9, 124.7, 123.1, 110.1, 83.9, 80.8, 59.8, 44.1, 28.2, 15.2. HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{25}\text{ClN}_2\text{NaO}_4^+$ 439.1395, found 439.1397. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_{R} = 4.7 min for (*S*)-isomer and t_{R} = 9.0 min for (*R*)-isomer.

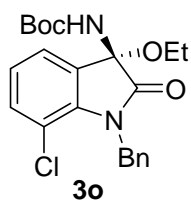


Peaks	Ret. Time	Area	Area%
1	4.842	8308036	50.914
2	9.613	8009738	49.086

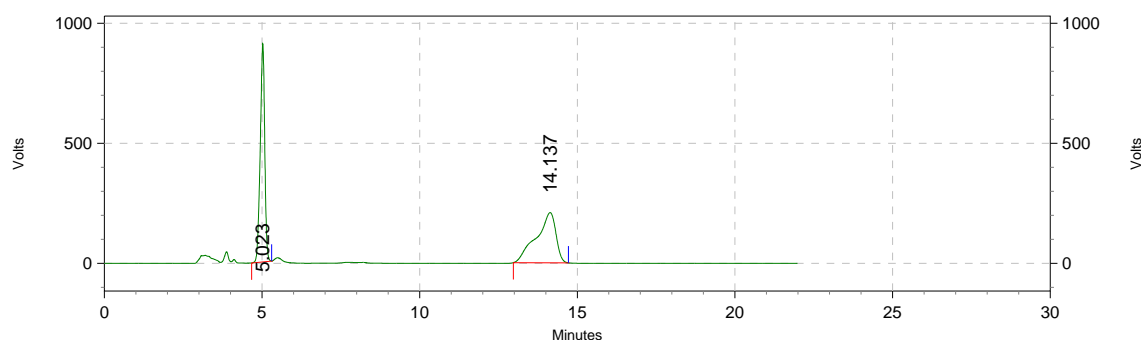


Peaks	Ret. Time	Area	Area%
1	4.678	6541220	98.647
2	9.037	89688	1.353

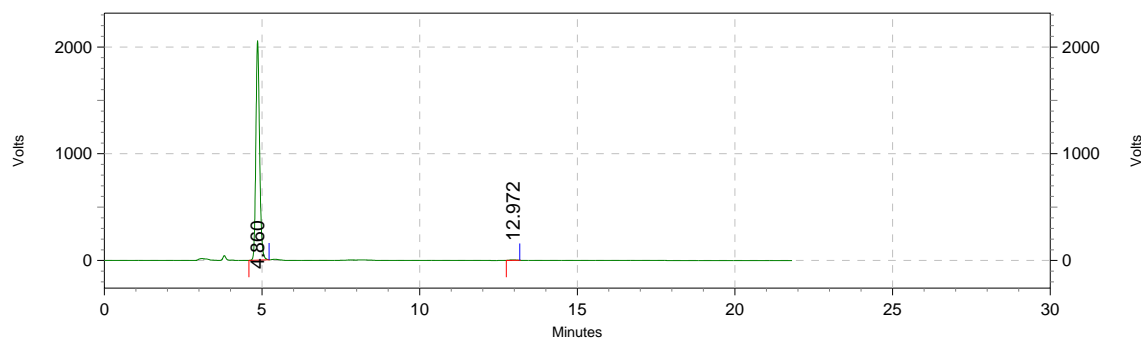
(S)-tert-butyl-(1-benzyl-7-chloro-3-ethoxy-2-oxindolin-3-yl)carbamate (3o)



White solid, 97% yield, 99% ee, mp 143-145 °C. $[\alpha]_D^{20} = -7.13$ (c = 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 7.1 Hz, 1H), 7.30 (d, J = 4.4 Hz, 4H), 7.22 (td, J = 8.3, 2.7 Hz, 2H), 7.05 – 7.00 (m, 1H), 5.54 (s, 1H), 5.35 (d, J = 3.2 Hz, 2H), 3.49 (q, J = 7.0 Hz, 2H), 1.35 (s, 9H), 1.15 (t, J = 7.0 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 173.3, 153.1, 139.1, 137.2, 133.0, 129.6, 128.6, 127.2, 126.5, 124.1, 123.9, 115.8, 83.6, 80.9, 59.8, 45.1, 28.1, 15.2. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₂H₂₅ClN₂NaO₄⁺ 439.1395, found 439.1400. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 4.9 min for (S)-isomer and t_R = 13.0 min for (R)-isomer.

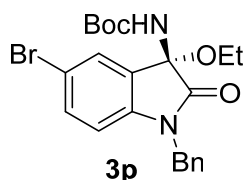


Peaks	Ret. Time	Area	Area%
1	5.023	9056216	50.124
2	14.137	9011238	49.876

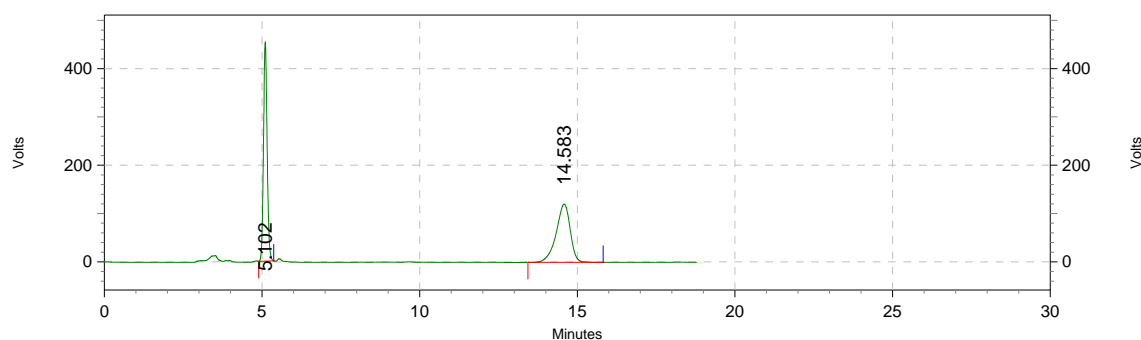


Peaks	Ret. Time	Area	Area%
1	4.860	16841351	99.716
2	12.972	47945	0.284

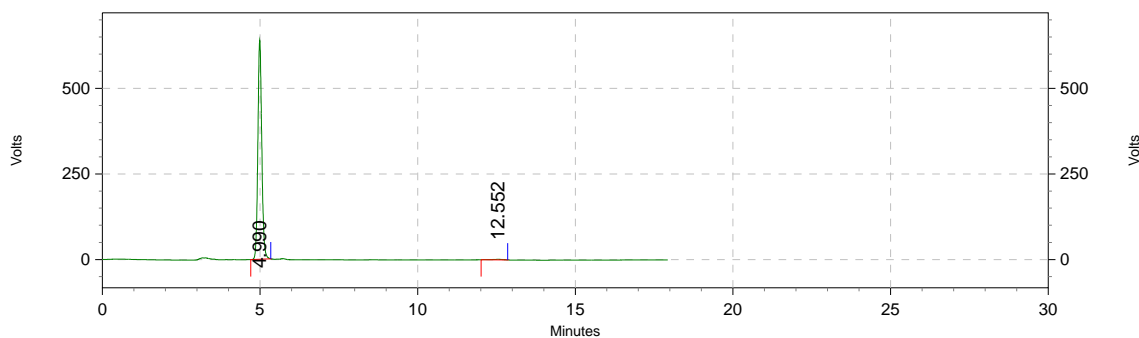
(S)-tert-butyl-(1-benzyl-5-bromo-3-ethoxy-2-oxindolin-3-yl)carbamate (3p)



White solid, 96% yield, 99% ee, mp 170-172 °C. $[\alpha]_D^{20} = +7.86$ (c = 1.40, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.83 – 7.77 (m, 1H), 7.35 – 7.27 (m, 6H), 6.56 (d, J = 8.3 Hz, 1H), 5.55 (s, 1H), 4.95 (d, J = 15.8 Hz, 1H), 4.85 (d, J = 15.8 Hz, 1H), 3.52 (q, J = 7.0 Hz, 2H), 1.38 (s, 9H), 1.17 (t, J = 7.0 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 172.1, 153.2, 141.9, 134.9, 133.1, 128.9, 128.9, 128.4, 127.9, 127.2, 116.1, 111.0, 84.1, 80.9, 59.8, 44.0, 28.2, 15.2. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₂H₂₅BrN₂NaO₄⁺ 483.0890, found 483.0896. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 5.0 min for (*S*)-isomer and t_R = 12.6 min for (*R*)-isomer.

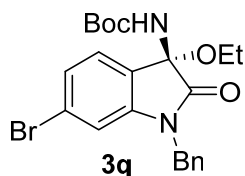


Peaks	Ret. Time	Area	Area%
1	5.102	3651149	49.373
2	14.583	3743865	50.627

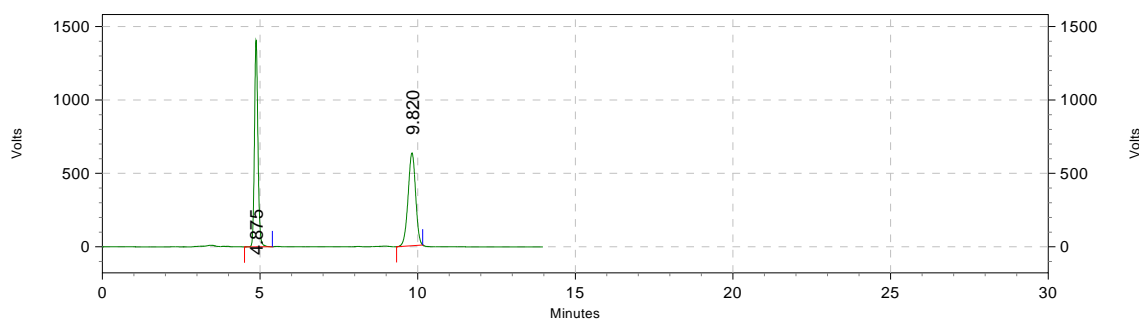


Peaks	Ret. Time	Area	Area%
1	4.990	5515995	99.303
2	12.552	38714	0.697

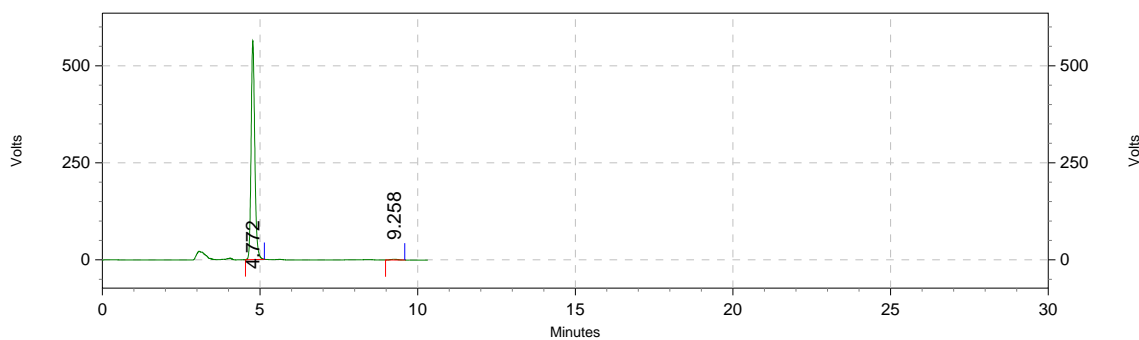
(S)-tert-butyl-(1-benzyl-6-bromo-3-ethoxy-2-oxindolin-3-yl)carbamate (3q)



White solid, 96% yield, 99% ee, mp 141-143 °C. $[\alpha]_D^{20} = -2.81$ ($c = 1.10$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, $J = 7.8$ Hz, 1H), 7.31 (d, $J = 10.0$ Hz, 5H), 7.22 – 7.19 (m, 1H), 6.86 – 6.83 (m, 1H), 5.61 (s, 1H), 4.94 (d, $J = 15.8$ Hz, 1H), 4.83 (d, $J = 15.8$ Hz, 1H), 3.49 (q, $J = 7.0$ Hz, 2H), 1.36 (s, 9H), 1.15 (t, $J = 7.0$ Hz, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 172.6, 153.3, 144.3, 134.8, 129.0, 127.9, 127.2, 126.1, 125.2, 124.1, 112.9, 84.0, 80.8, 59.8, 44.1, 28.2, 15.2. HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{25}\text{BrN}_2\text{NaO}_4^+$ 483.0890, found 483.0894. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/*i*-PrOH = 70/30 flow rate = 1.0 mL/min, $\lambda = 220$ nm). Retention times: $t_R = 4.8$ min for (*S*)-isomer and $t_R = 9.3$ min for (*R*)-isomer.

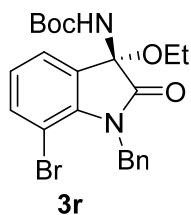


Peaks	Ret. Time	Area	Area%
1	4.875	10776967	50.741
2	9.820	10462081	49.259

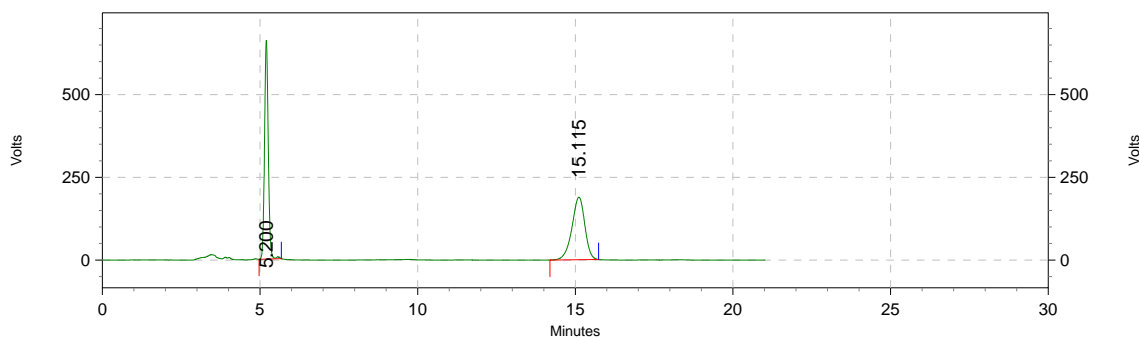


Peaks	Ret. Time	Area	Area%
1	4.772	4567953	99.351
2	9.258	29859	0.649

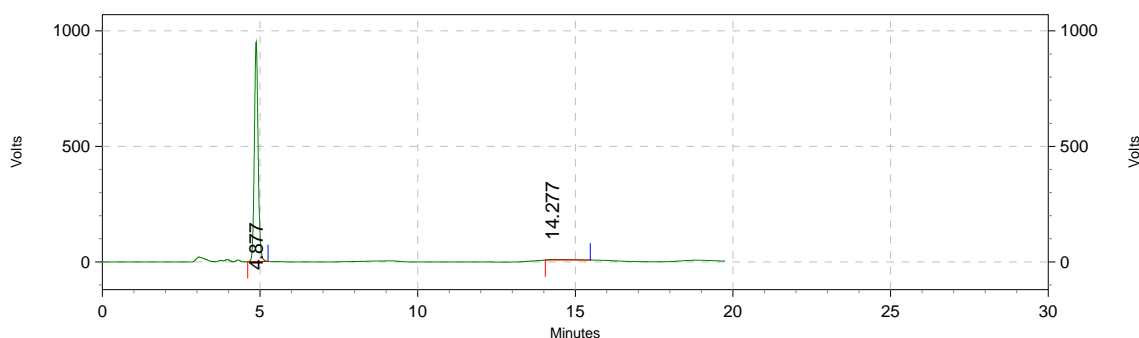
(S)-tert-butyl-(1-benzyl-7-bromo-3-ethoxy-2-oxindolin-3-yl)carbamate (3r)



White solid, 95% yield, 97% ee, mp 143-147 °C. $[\alpha]_D^{20} = -11.00$ (c = 1.20, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, J = 7.1 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.33 – 7.28 (m, 4H), 7.24 (d, J = 6.0 Hz, 1H), 6.96 (t, J = 7.8 Hz, 1H), 5.55 (s, 1H), 5.44 (d, J = 16.5 Hz, 1H), 5.37 (d, J = 16.5 Hz, 1H), 3.50 (q, J = 7.0 Hz, 2H), 1.35 (s, 9H), 1.15 (t, J = 7.0 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 173.5, 153.1, 140.6, 137.1, 136.4, 130.0, 128.6, 127.1, 126.4, 124.5, 102.8, 83.5, 80.9, 59.8, 44.8, 28.1, 15.2. HRMS-ESI(m/z): [M+Na]⁺ calcd for C₂₂H₂₅BrN₂NaO₄⁺ 483.0890, found 483.0892. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 4.9 min for (S)-isomer and t_R = 14.3 min for (R)-isomer.

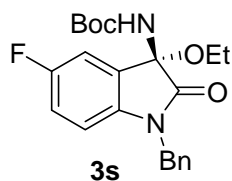


Peaks	Ret. Time	Area	Area%
1	5.200	5413974	50.332
2	15.115	5342497	49.668



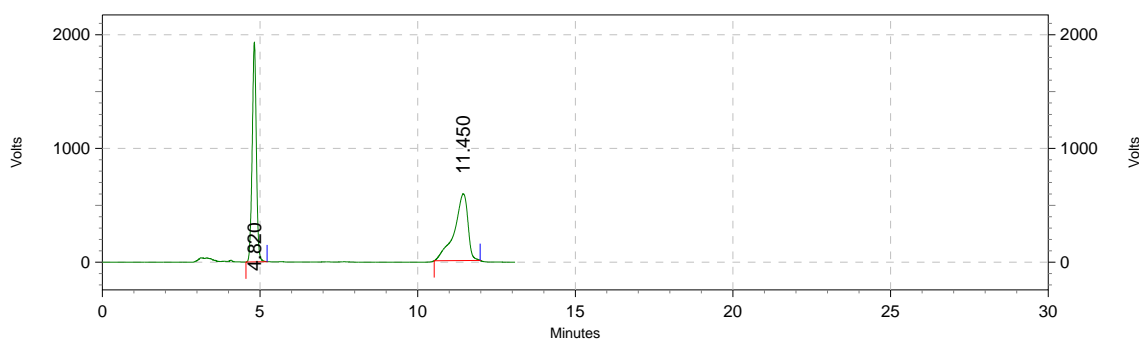
Peaks	Ret. Time	Area	Area%
1	4.877	7881997	98.360
2	14.277	131428	1.640

(S)-tert-butyl-(1-benzyl-3-ethoxy-5-fluoro-2-oxindolin-3-yl)carbamate (3s)

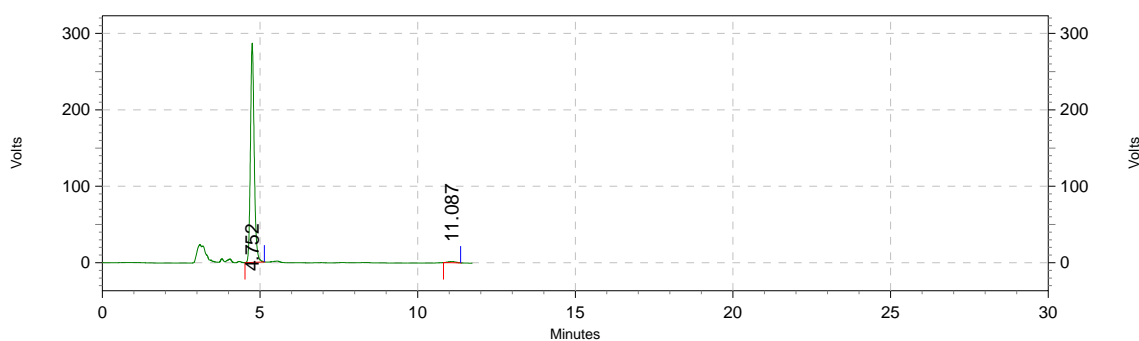


White solid, 93% yield, 98% ee, mp 130-132 °C. $[\alpha]_D^{20} = -11.53$ (c = 1.00, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, J = 6.1 Hz, 1H), 7.23 (d, J = 4.3 Hz, 4H), 7.20 – 7.16 (m, 1H), 6.82 (td, J = 8.8, 2.7 Hz, 1H), 6.52 (dd, J = 8.6, 4.0 Hz, 1H), 5.58 (s, 1H), 4.87 (d, J = 15.8 Hz, 1H), 4.77 (d, J = 15.8 Hz, 1H), 3.45 (q, J = 7.0 Hz, 2H), 1.29 (s, 9H), 1.09 (t, J = 7.0 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 172.4, 159.4 (d, ¹J_{C-F} = 242.0 Hz), 153.3, 138.7, 135.0, 128.9, 128.1 (d, ³J_{C-F} = 8.2 Hz), 127.8, 127.2, 116.6 (d, ²J_{C-F} = 23.7 Hz), 114.2 (d,

$^2J_{C-F} = 25.3$ Hz), 110.1 (d, $^3J_{C-F} = 7.8$ Hz), 84.2, 80.8, 59.8, 44.1, 28.2, 15.2. ^{19}F NMR (CDCl_3) δ -119.4. HRMS-ESI(m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{25}\text{FN}_2\text{NaO}_4^+$ 423.1691, found 423.1690. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/*i*-PrOH = 70/30 flow rate = 1.0 mL/min, $\lambda = 220$ nm). Retention times: $t_{\text{R}} = 4.8$ min for (*S*)-isomer and $t_{\text{R}} = 11.1$ min for (*R*)-isomer.

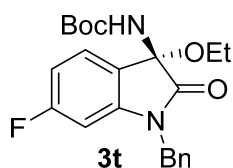


	Ret. Time	Area	Area%
1	4.820	17644938	50.098
2	11.450	17575726	49.902



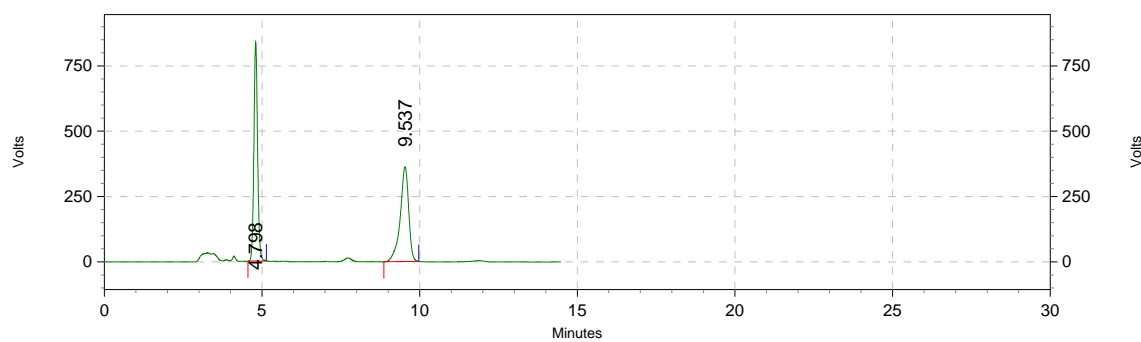
Peaks	Ret. Time	Area	Area%
1	4.752	2370868	98.965
2	11.087	24788	1.035

(*S*)-tert-butyl-(1-benzyl-3-ethoxy-6-fluoro-2-oxindolin-3-yl)carbamate (3t)

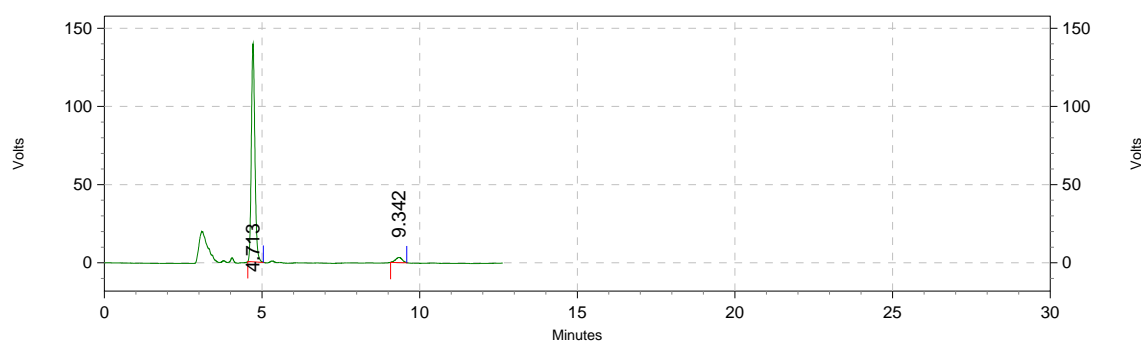


White solid, 94% yield, 92% ee, mp 145-147 °C. $[\alpha]_{\text{D}}^{20} = +13.52$ ($c = 1.00$, CH_2Cl_2). ^1H

NMR (400 MHz, CDCl₃) δ 7.68 – 7.60 (m, 1H), 7.33 (d, J = 5.7 Hz, 5H), 6.77 – 6.70 (m, 1H), 6.46 – 6.40 (m, 1H), 5.55 (s, 1H), 4.95 (d, J = 15.8 Hz, 1H), 4.83 (d, J = 15.8 Hz, 1H), 3.49 (q, J = 7.0 Hz, 2H), 1.37 (s, 9H), 1.17 (t, J = 7.0 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 173.0, 164.1 (d, ¹J_{C-F} = 248.1 Hz), 153.3, 144.7 (d, ³J_{C-F} = 11.5 Hz), 134.8, 129.5, 129.0, 127.9, 127.4 (d, ³J_{C-F} = 14.9 Hz), 121.8, 109.3 (d, ²J_{C-F} = 22.5 Hz), 98.4 (d, ²J_{C-F} = 27.9 Hz), 83.9, 80.7, 59.7, 44.1, 28.2, 15.2. ¹⁹F NMR (CDCl₃) δ -108.6. HRMS-ESI(m/z): [M+Na]⁺ calcd for C₂₂H₂₅FN₂NaO₄⁺ 423.1691, found 423.1694. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 4.7min for (*S*)-isomer and t_R = 9.3 min for (*R*)-isomer.

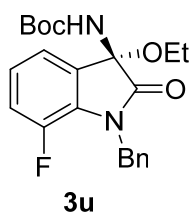


Peaks	Ret. Time	Area	Area%
1	4.798	6812894	50.242
2	9.537	6747213	49.758

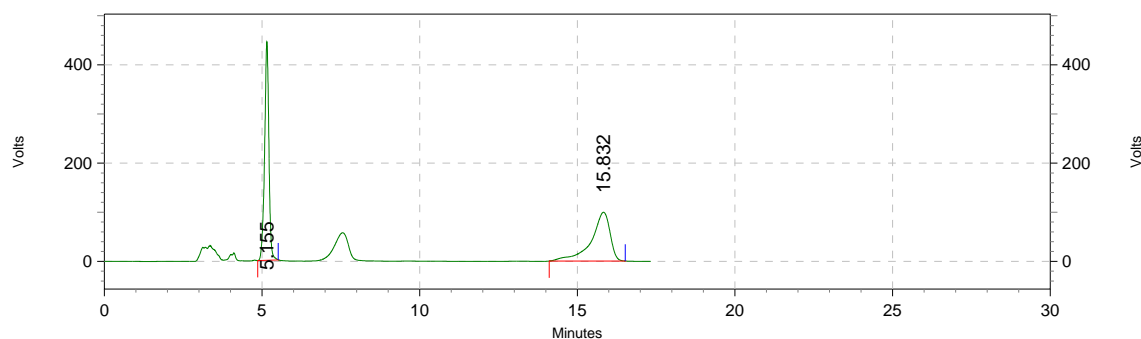


Peaks	Ret. Time	Area	Area%
1	4.713	1094280	95.831
2	9.342	47609	4.169

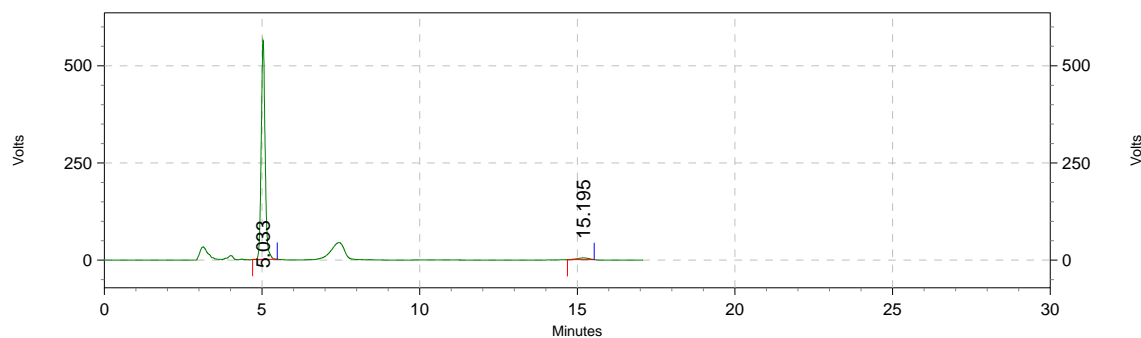
(S)-tert-butyl-(1-benzyl-3-ethoxy-7-fluoro-2-oxoindolin-3-yl)carbamate (3u)



White solid, 89% yield, 96% ee, mp 150-152 °C. $[\alpha]_D^{20} = -3.32$ (c = 1.00, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.44 (s, 1H), 7.38 (d, J = 7.3 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.05 – 6.98 (m, 2H), 5.52 (s, 1H), 5.11 (d, J = 15.3 Hz, 1H), 5.00 (d, J = 15.3 Hz, 1H), 3.45 (q, J = 7.0 Hz, 2H), 1.34 (s, 9H), 1.14 (t, J = 7.0 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 172.5, 153.1, 147.6 (d, ¹J_{C-F} = 244.9 Hz), 136.6, 129.6 (d, ³J_{C-F} = 8.8 Hz), 129.3, 128.6, 127.6 (d, ²J_{C-F} = 10.5 Hz), 123.9 (d, ³J_{C-F} = 6.3 Hz), 121.4, 118.6 (d, ²J_{C-F} = 19.6 Hz), 84.2, 80.8, 59.8, 45.7, 28.1, 15.2. ¹⁹F NMR (CDCl₃) δ -133.5. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₂H₂₅FN₂NaO₄⁺ 423.1691, found 423.1690. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 5.0 min for (*S*)-isomer and t_R = 15.2 min for (*R*)-isomer.

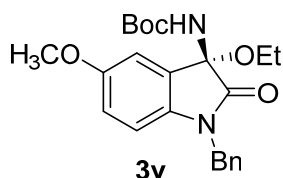


Peaks	Ret. Time	Area	Area%
1	5.155	4211821	50.567
2	15.832	4117344	49.433

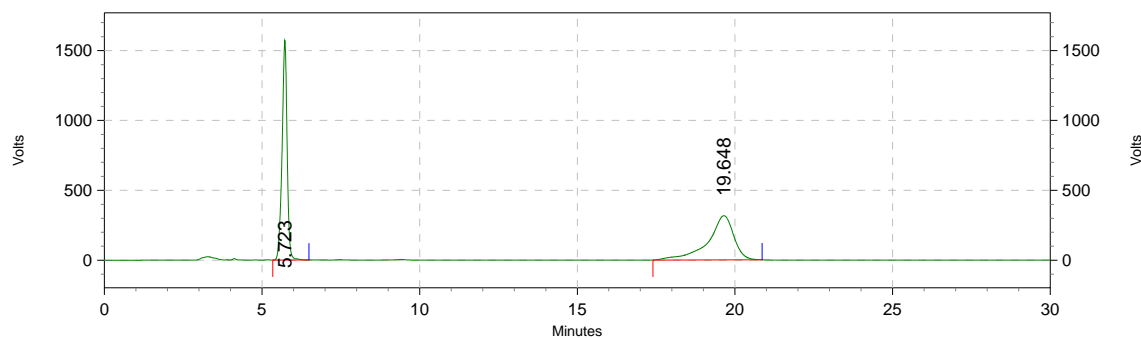


Peaks	Ret. Time	Area	Area%
1	5.033	4820085	97.710
2	15.195	112962	2.290

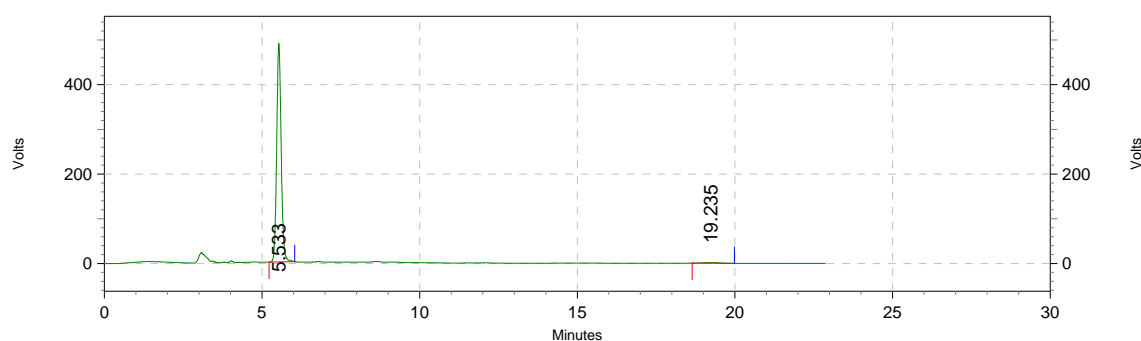
(S)-tert-butyl-(1-benzyl-3-ethoxy-5-methoxy-2-oxindolin-3-yl)carbamate (3v)



White solid, 93% yield, 98% ee, mp 102-104 °C. $[\alpha]_D^{20} = +5.84$ (c = 1.00, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.32 (t, J = 5.6 Hz, 5H), 7.24 (dd, J = 5.7, 1.8 Hz, 1H), 6.74 (dd, J = 8.5, 2.4 Hz, 1H), 6.59 (d, J = 8.5 Hz, 1H), 5.63 (s, 1H), 4.96 (d, J = 15.7 Hz, 1H), 4.83 (d, J = 15.6 Hz, 1H), 3.76 (d, J = 1.5 Hz, 3H), 3.51 (q, J = 7.0 Hz, 2H), 1.36 (s, 9H), 1.17 (t, J = 7.0 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 172.4, 156.3, 153.3, 136.2, 135.4, 128.8, 127.7, 127.5, 127.3, 115.0, 112.7, 110.0, 84.6, 80.6, 59.7, 55.8, 44.0, 29.7, 28.2, 15.3. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₃H₂₈N₂NaO₅⁺ 435.1890, found 435.1894. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 5.5 min for (S)-isomer and t_R = 19.2 min for (R)-isomer.

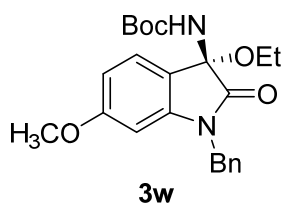


Peaks	Ret. Time	Area	Area%
1	5.723	17661158	49.632
2	19.648	17923352	50.368



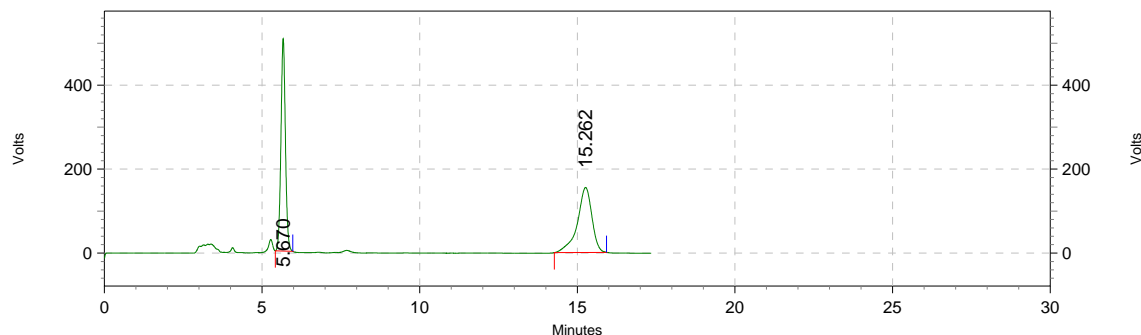
Peaks	Ret. Time	Area	Area%
1	5.533	4809542	98.904
2	19.235	53278	1.096

(S)-tert-butyl-(1-benzyl-3-ethoxy-6-methoxy-2-oxindolin-3-yl)carbamate (3w)

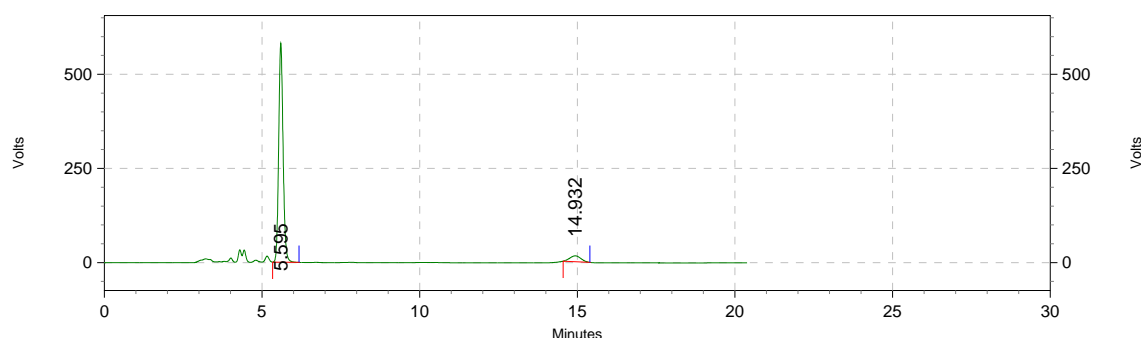


White solid, 89% yield, 87% ee, mp 130-133 °C. $[\alpha]_D^{20} = +3.07$ (c = 1.00, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, J = 8.3 Hz, 1H), 7.25 – 7.13 (m, 5H), 6.45 (dd, J = 8.3, 2.2 Hz, 1H), 6.20 (d, J = 2.2 Hz, 1H), 5.55 (s, 1H), 4.86 (d, J = 15.7 Hz, 1H), 4.73 (d, J = 15.7 Hz, 1H), 3.62 (s, 3H), 3.38 (qd, J = 7.0, 5.2 Hz, 2H), 1.27 (s, 9H), 1.06 (t, J = 7.0 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 173.3, 161.6, 153.4, 144.4, 135.4, 128.8, 127.7, 127.3, 127.0, 118.1, 106.5, 97.7, 84.3, 80.4, 59.6, 55.4, 44.0, 28.2, 15.3. HRMS-ESI (m/z): [M+Na]⁺ calcd

for $C_{23}H_{28}N_2NaO_5^+$ 435.1890, found 435.1892. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, $\lambda = 220$ nm). Retention times: $t_R = 5.6$ min for (*S*)-isomer and $t_R = 14.9$ min for (*R*)-isomer.

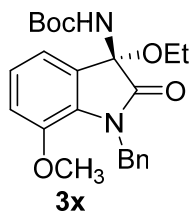


Peaks	Ret. Time	Area	Area%
1	5.670	5005159	50.211
2	15.262	4963074	49.789



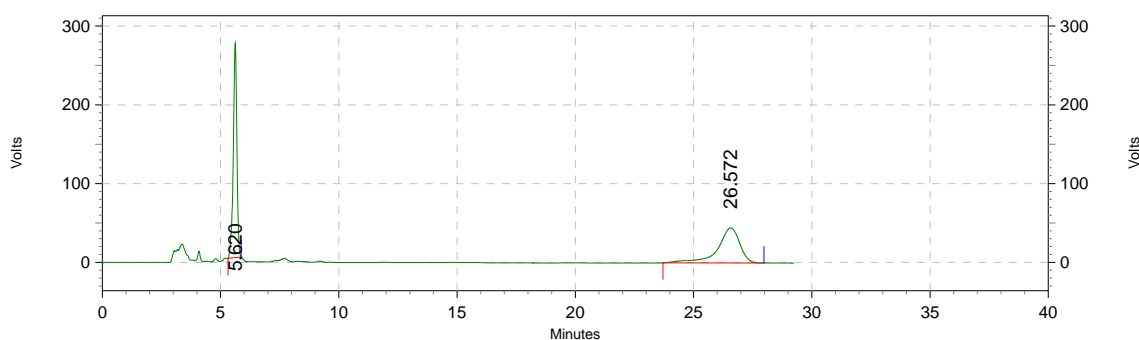
Peaks	Ret. Time	Area	Area%
1	5.595	5644703	93.630
2	14.932	384006	6.370

(*S*)-tert-butyl-(1-benzyl-3-ethoxy-7-methoxy-2-oxindolin-3-yl)carbamate (3x)

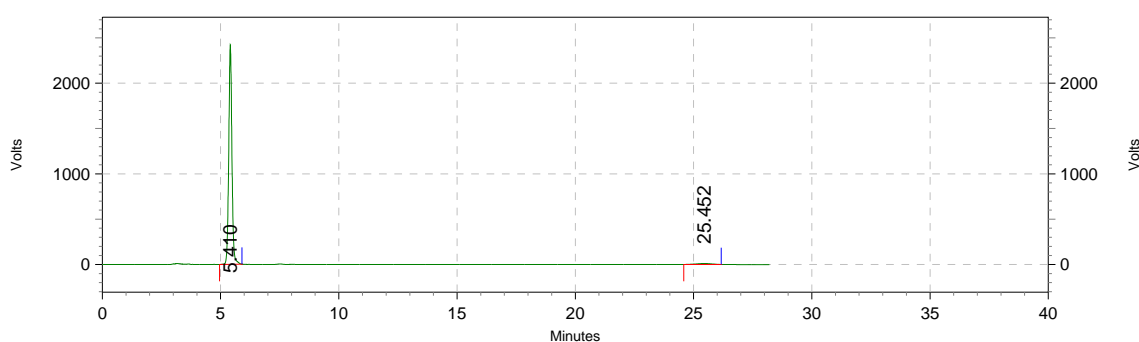


White solid, 92% yield, 96% ee, mp 143-145 °C. $[\alpha]_D^{20} = -6.47$ ($c = 1.20$, CH_2Cl_2). 1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, $J = 7.3$ Hz, 2H), 7.27 (t, $J = 7.3$ Hz, 3H), 7.20 (t, $J = 7.2$ Hz,

1H), 7.03 (t, J = 7.9 Hz, 1H), 6.86 (d, J = 8.3 Hz, 1H), 5.58 (s, 1H), 5.18 (s, 2H), 3.64 (s, 3H), 3.43 (q, J = 7.0 Hz, 2H), 1.33 (s, 9H), 1.12 (t, J = 7.0 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 173.1, 153.2, 145.2, 138.1, 131.0, 128.3, 128.0, 127.3, 127.0, 123.9, 118.1, 114.6, 84.3, 80.5, 59.6, 55.8, 46.0, 28.1, 15.2. HRMS-ESI(m/z): [M+Na]⁺ calcd for C₂₃H₂₈N₂NaO₅⁺ 435.1890, found 435.1893. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 5.4 min for (*S*)-isomer and t_R = 25.5 min for (*R*)-isomer.

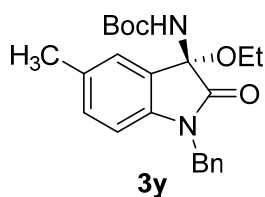


Peaks	Ret. Time	Area	Area%
1	5.620	2840100	49.643
2	26.572	2880907	50.357

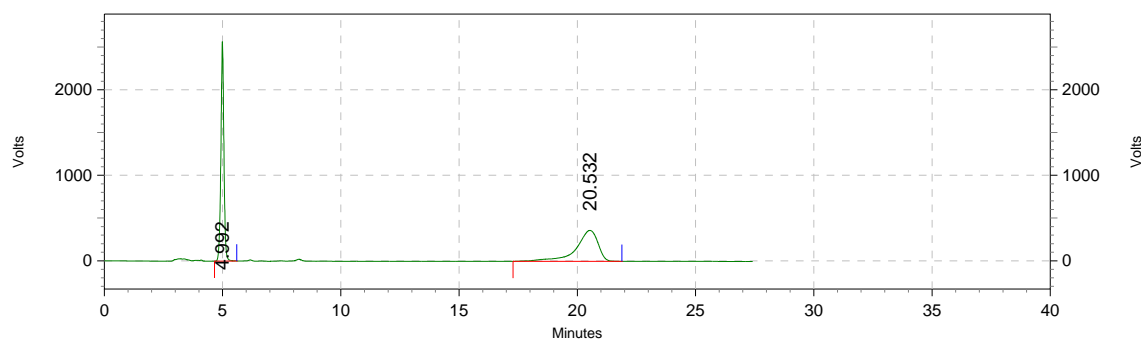


Peaks	Ret. Time	Area	Area%
1	5.410	22702000	98.021
2	25.452	458343	1.979

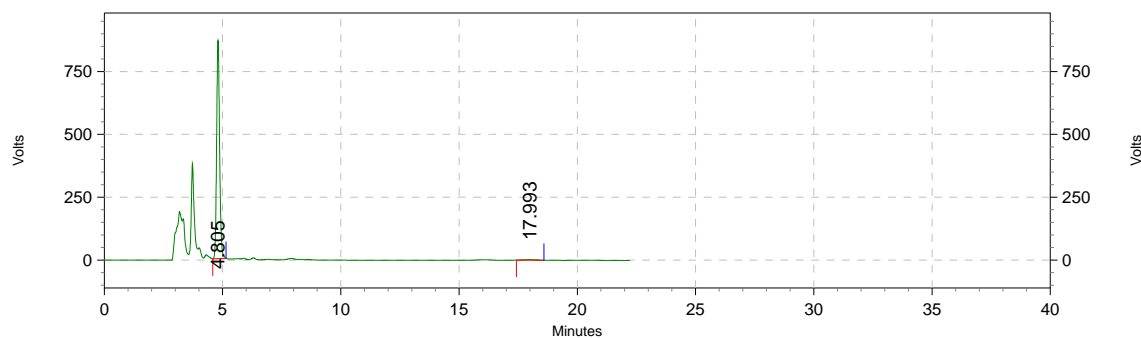
(S)-tert-butyl-(1-benzyl-3-ethoxy-5-methyl-2-oxindolin-3-yl)carbamate (3y)



White solid, 89% yield, 98% ee, mp 132-136 °C. $[\alpha]_D^{20} = +1.31$ (c = 1.00, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.50 (s, 1H), 7.34 – 7.28 (m, 4H), 7.26 – 7.22 (m, 1H), 7.03 – 6.99 (m, 1H), 6.58 (d, J = 8.0 Hz, 1H), 5.57 (s, 1H), 4.96 (d, J = 15.7 Hz, 1H), 4.83 (d, J = 15.7 Hz, 1H), 3.50 (q, J = 7.0 Hz, 2H), 2.31 (s, 3H), 1.36 (s, 9H), 1.16 (t, J = 7.0 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 172.6, 153.3, 140.5, 135.5, 132.8, 130.6, 128.8, 127.6, 127.3, 126.5, 109.2, 84.5, 80.5, 59.6, 43.9, 28.2, 21.1, 15.3. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₃H₂₈N₂NaO₄⁺ 419.1941, found 419.1946. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 4.8 min for (S)-isomer and t_R = 18.0 min for (R)-isomer.

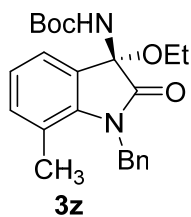


Peaks	Ret. Time	Area	Area%
1	4.992	22872948	49.679
2	20.532	23168365	50.321

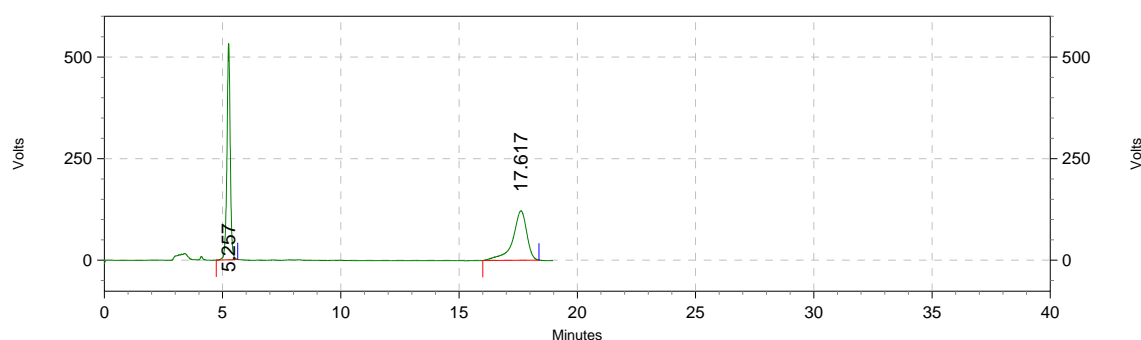


Peaks	Ret. Time	Area	Area%
1	4.805	7550686	98.925
2	17.993	82084	1.075

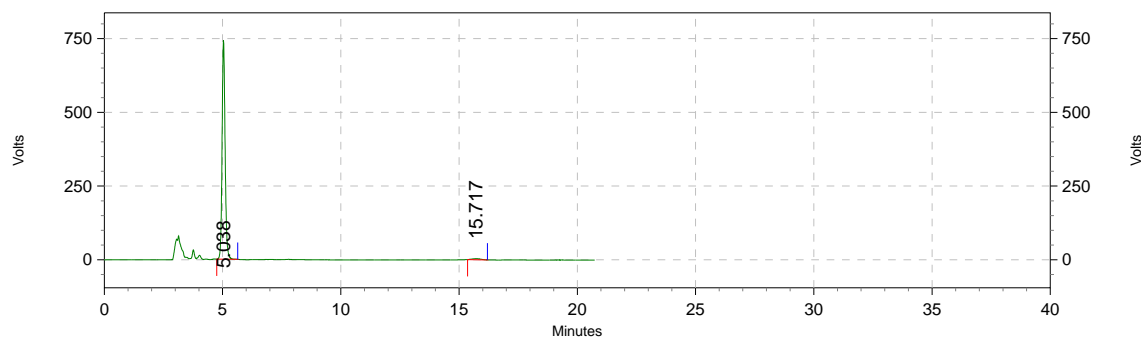
(S)-tert-butyl-(1-benzyl-3-ethoxy-7-methyl-2-oxindolin-3-yl)carbamate (3z)



White solid, 89% yield, 97% ee, mp 144-146 °C. $[\alpha]_D^{20} = -2.93$ (c = 1.00, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.47 (m, 1H), 7.34 – 7.27 (m, 3H), 7.26 – 7.21 (m, 2H), 7.02 – 6.98 (m, 2H), 5.58 (s, 1H), 5.19 (s, 2H), 3.54 (q, J = 7.0 Hz, 2H), 2.23 (s, 3H), 1.36 (s, 9H), 1.17 (t, J = 7.0 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 173.7, 153.3, 141.1, 137.3, 134.5, 128.9, 127.2, 125.8, 123.3, 123.2, 120.1, 83.8, 80.5, 59.6, 45.3, 28.2, 18.8, 15.3. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₃H₂₈N₂NaO₄⁺ 419.1941, found 419.1941. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 5.0 min for (*S*)-isomer and t_R = 15.7 min for (*R*)-isomer.

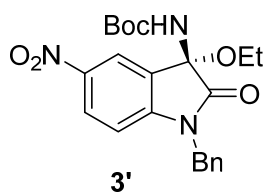


Peaks	Ret. Time	Area	Area%
1	5.257	5136947	50.816
2	17.617	4971907	49.184

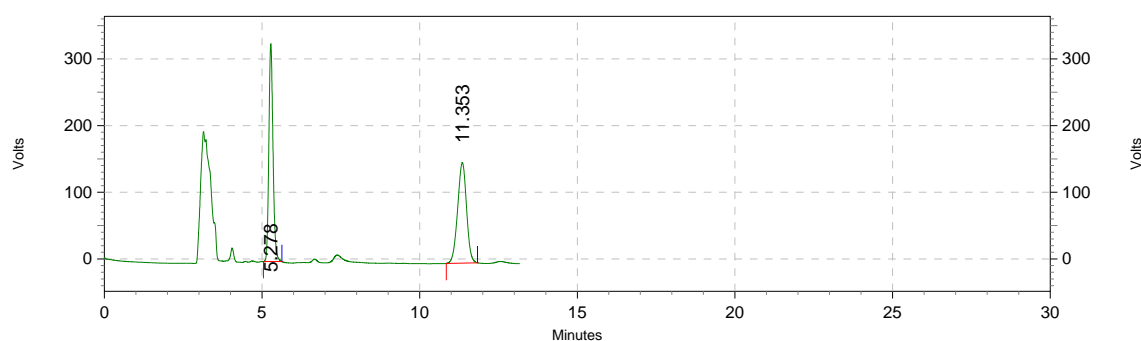


Peaks	Ret. Time	Area	Area%
1	5.038	6578253	98.677
2	15.717	88185	1.323

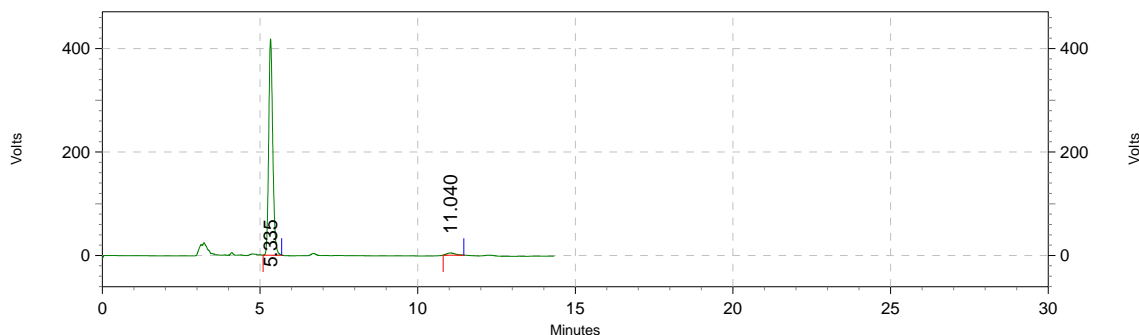
(S)-tert-butyl-(1-benzyl-3-ethoxy-5-nitro-2-oxindolin-3-yl)carbamate (3')



White solid, 92% yield, 96% ee, mp 120-122 °C. $[\alpha]_D^{20} = +6.72$ (c = 1.20, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 8.49 (d, J = 2.3 Hz, 1H), 8.18 (dd, J = 8.7, 2.3 Hz, 1H), 7.34 (d, J = 4.5 Hz, 4H), 7.29 (dd, J = 9.5, 4.5 Hz, 1H), 6.80 (d, J = 8.7 Hz, 1H), 5.75 (s, 1H), 5.04 – 4.93 (m, 2H), 3.59 (q, J = 7.0 Hz, 2H), 1.38 (s, 9H), 1.19 (t, J = 7.0 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 172.8, 153.3, 148.5, 143.8, 134.3, 129.1, 128.1, 127.6, 127.2, 121.1, 109.4, 83.7, 81.3, 60.1, 44.3, 28.2, 15.2. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₂H₂₅N₃NaO₆⁺ 450.1636, found 450.1640. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30 flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 5.3 min for (S)-isomer and t_R = 11.0 min for (R)-isomer.

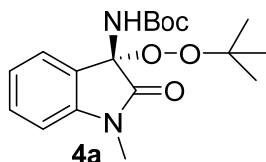


Peaks	Ret. Time	Area	Area%
1	5.278	2976587	50.158
2	11.353	2957798	49.842

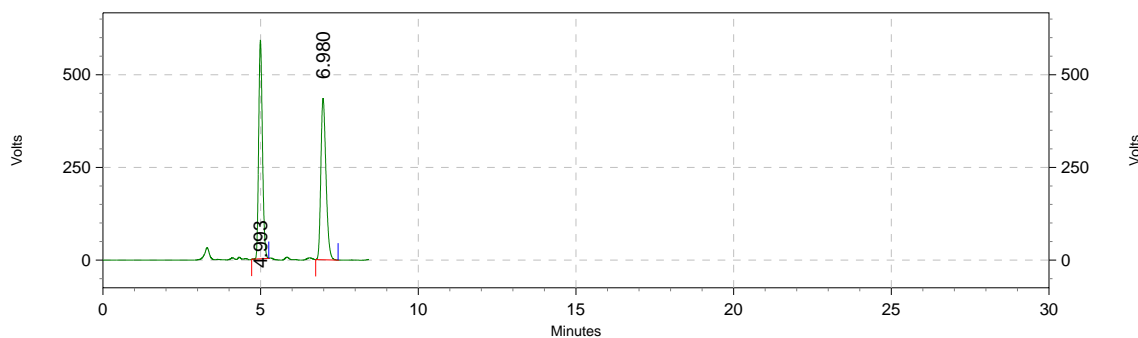


Peaks	Ret. Time	Area	Area%
1	5.335	3738987	97.985
2	11.040	76891	2.015

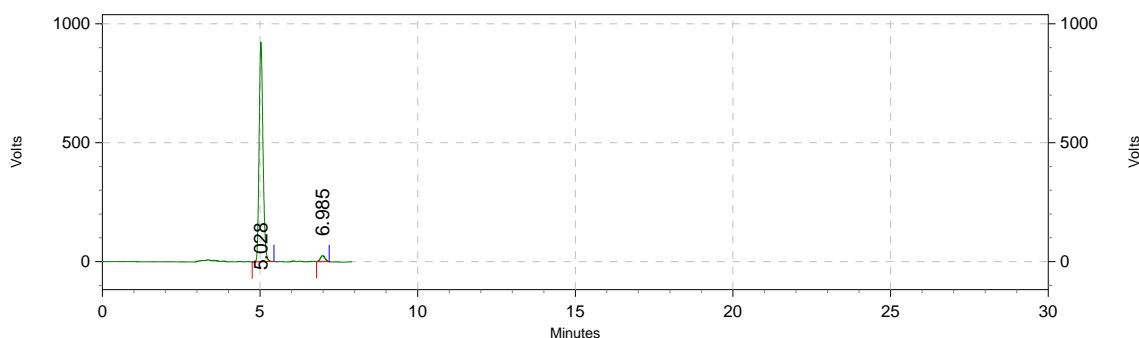
(S)-tert-butyl-(3-(tert-butylperoxy)-1-methyl-2-oxindolin-3-yl)carbamate (4a)⁹



White solid, 83% yield, 94% ee, mp 97-99 °C. $[\alpha]_{\text{D}}^{20} = +8.76$ (c = 2.60, CH₂Cl₂). $[\alpha]_{\text{D}}^{20} = +1.83$ (c = 2.00, CHCl₃). Reported results for (R)-**4a**: $[\alpha]_{\text{D}}^{22} = -3,8$ (c 1.0, CHCl₃, 84% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.66 (s, 1H), 7.25 (t, J = 7.4 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 6.73 (d, J = 7.7 Hz, 1H), 5.83 (s, 1H), 3.09 (s, 3H), 1.23 (s, 9H), 1.07 (s, 9H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 170.1, 153.0, 143.8, 130.6, 127.1, 125.3, 122.5, 108.2, 87.2, 81.3, 80.4, 28.0, 26.2. The ee value was determined by chiral HPLC analysis (Chiralcel AD-H, hexane/i-PrOH = 80/20 flow rate = 1.0 mL/min, λ = 254 nm). Retention times: t_R = 5.0 min for (S)-isomer and t_R = 7.0 min for (R)-isomer.

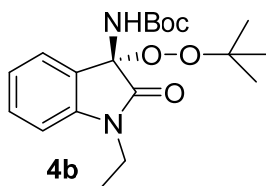


Peaks	Ret. Time	Area	Area%
1	4.993	4898571	49.882
2	6.980	4921736	50.118



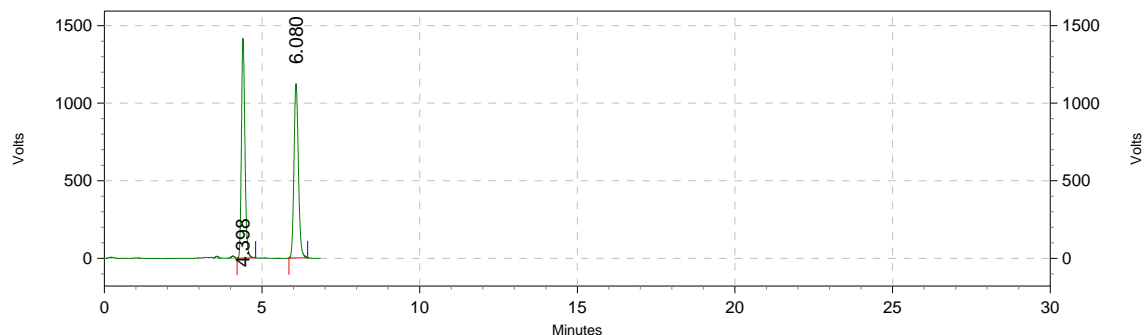
Peaks	Ret. Time	Area	Area%
1	5.028	7867884	96.813
2	6.985	258979	3.187

(S)-tert-butyl-(3-(tert-butyloxy)-1-ethyl-2-oxindolin-3-yl)carbamate (4b)

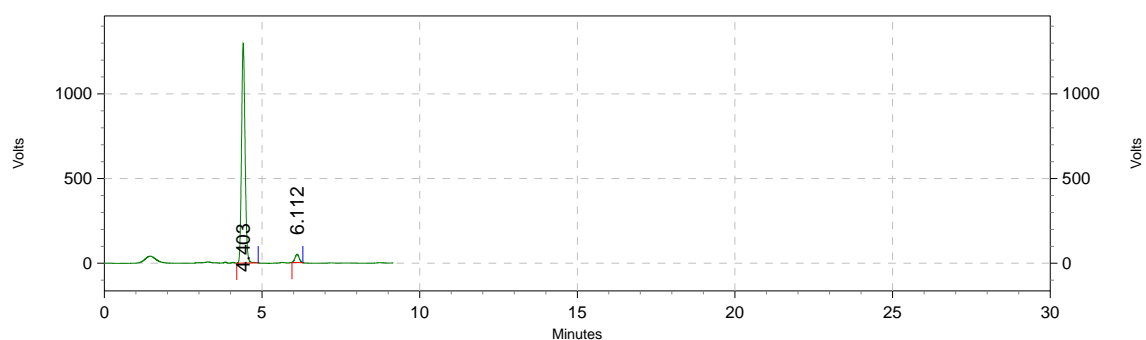


White solid, 84% yield, 92% ee, mp 108-110 °C. $[\alpha]_D^{20} = +7.50$ (c = 4.00, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, J = 6.5 Hz, 1H), 7.34 (td, J = 7.8, 1.2 Hz, 1H), 7.08 – 7.03 (m, 1H), 6.84 (d, J = 7.8 Hz, 1H), 5.86 (s, 1H), 3.83 (dq, J = 14.4, 7.2 Hz, 1H), 3.68 (dt, J = 14.2, 7.1 Hz, 1H), 1.34 (s, 9H), 1.27 (t, J = 7.2 Hz, 3H), 1.15 (s, 9H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 170.0, 153.2, 143.0, 130.6, 127.6, 125.4, 122.4, 108.3, 87.1, 81.3, 80.4, 34.9, 28.1, 26.2, 12.5. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₉H₂₈N₂NaO₅⁺ 387.1890, found 387.1893.

The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/*i*-PrOH = 80/20 flow rate = 1.0 mL/min, $\lambda = 254$ nm). Retention times: $t_R = 4.4$ min for (*S*)-isomer and $t_R = 6.1$ min for (*R*)-isomer.

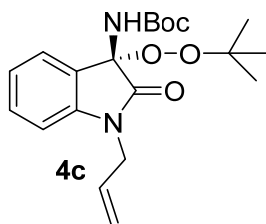


Peaks	Ret. Time	Area	Area%
1	4.398	10898389	49.946
2	6.080	10921879	50.054



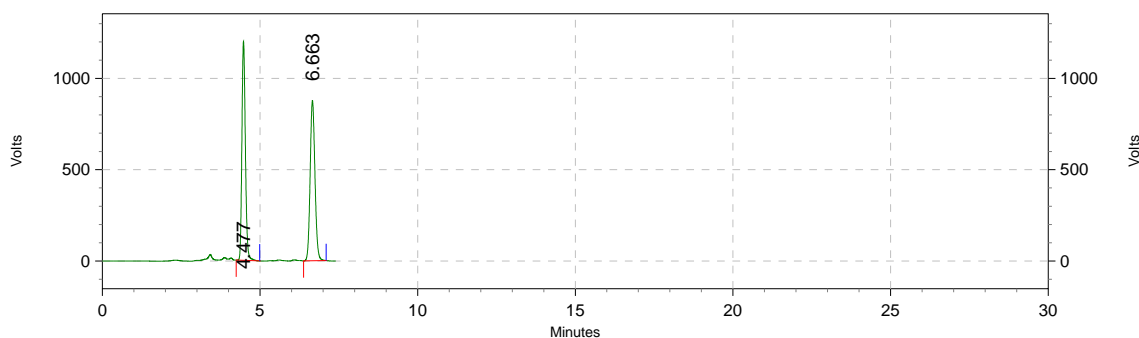
Peaks	Ret. Time	Area	Area%
1	4.403	10084797	95.829
2	6.112	438967	4.171

(*S*)-tert-butyl-(1-allyl-3-(tert-butyloxy)-2-oxindolin-3-yl)carbamate (4c)

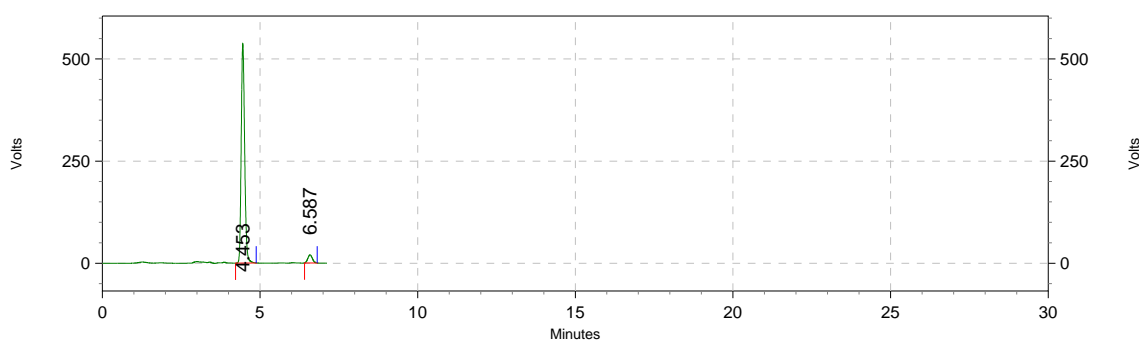


Yellow oil, 85% yield, 91% ee. $[\alpha]_D^{20} = +4.34$ ($c = 1.20$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ 7.75 – 7.66 (m, 1H), 7.23 (t, $J = 7.5$ Hz, 1H), 6.98 (t, $J = 7.4$ Hz, 1H), 6.72 (d, $J =$

7.6 Hz, 1H), 5.79 (s, 2H), 5.16 (dd, $J = 28.3, 13.7$ Hz, 2H), 4.40 (d, $J = 16.3$ Hz, 1H), 4.11 (d, $J = 16.1$ Hz, 1H), 1.27 (s, 9H), 1.07 (s, 9H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.2, 153.1, 143.1, 130.8, 130.5, 127.3, 125.3, 122.5, 117.5, 109.1, 87.2, 81.4, 80.5, 42.3, 28.1, 26.2. HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{28}\text{N}_2\text{NaO}_5^+$ 399.1890, found 399.1893. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/*i*-PrOH = 80/20 flow rate = 1.0 mL/min, $\lambda = 254$ nm). Retention times: $t_{\text{R}} = 4.5$ min for (*S*)-isomer and $t_{\text{R}} = 6.6$ min for (*R*)-isomer.

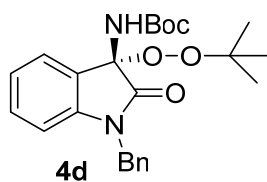


Peaks	Ret. Time	Area	Area%
1	4.477	9192382	49.759
2	6.663	9281383	50.241

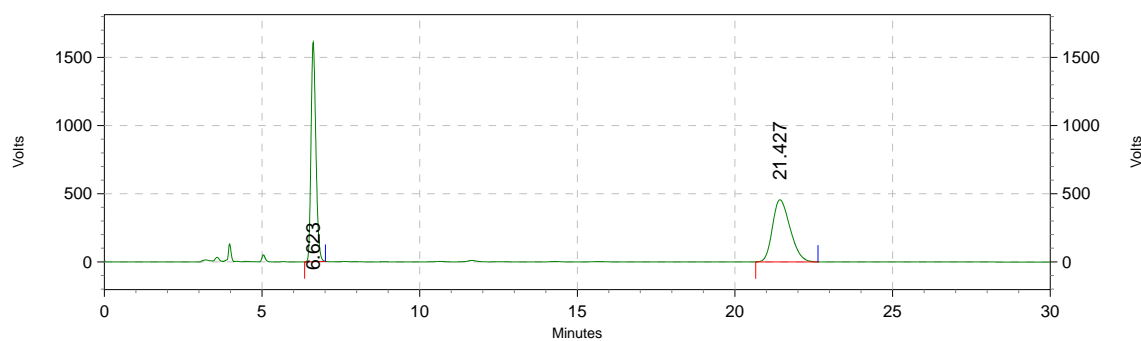


Peaks	Ret. Time	Area	Area%
1	4.453	4084850	95.357
2	6.587	198900	4.643

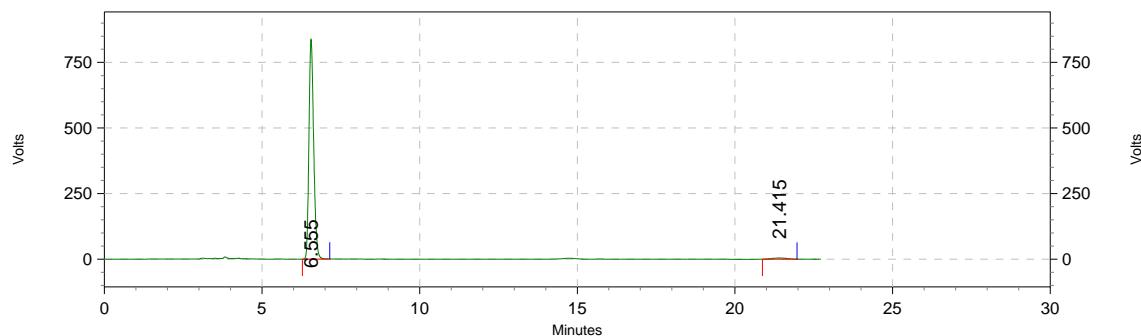
(S)-tert-butyl-(1-benzyl-3-(tert-butylperoxy)-2-oxoindolin-3-yl)carbamate (4d)¹⁰



White solid, 86% yield, 97% ee, mp 107-109 °C. $[\alpha]_D^{20} = -6.87$ (c = 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, J = 6.5 Hz, 1H), 7.30 (d, J = 8.0 Hz, 4H), 7.26 – 7.18 (m, 2H), 7.04 (d, J = 7.3 Hz, 1H), 6.65 (d, J = 7.8 Hz, 1H), 5.89 (s, 1H), 5.09 (d, J = 15.9 Hz, 1H), 4.75 (d, J = 15.9 Hz, 1H), 1.36 (s, 9H), 1.16 (s, 9H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 170.7, 153.2, 143.1, 135.2, 130.5, 128.9, 128.7, 127.6, 127.4, 127.1, 125.3, 122.6, 109.3, 87.3, 81.5, 80.7, 43.9, 28.1, 26.3. The ee value was determined by chiral HPLC analysis (Chiralcel AD-H, hexane/i-PrOH = 80/20 flow rate = 1.0 mL/min, λ = 254 nm). Retention times: t_R = 6.6 min for (*S*)-isomer and t_R = 21.4 min for (*R*)-isomer.

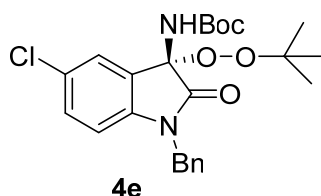


Peaks	Ret. Time	Area	Area%
1	6.623	17266269	49.400
2	21.427	17685943	50.600

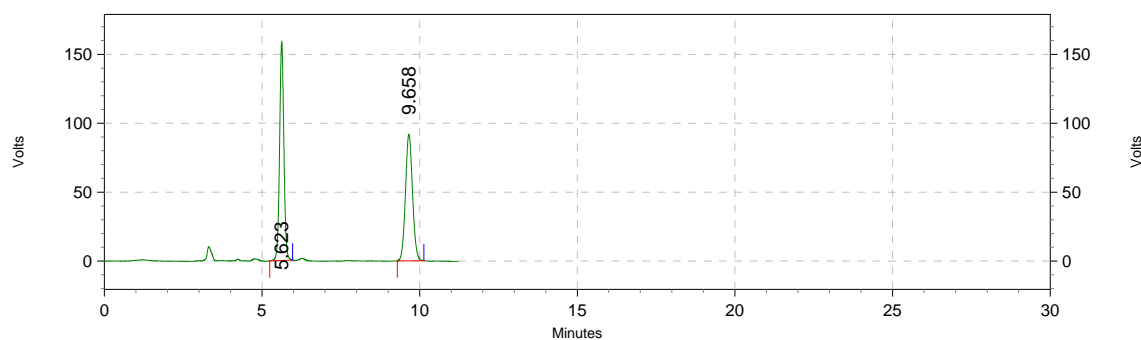


Peaks	Ret. Time	Area	Area%
1	6.555	8693882	98.299
2	21.415	150446	1.701

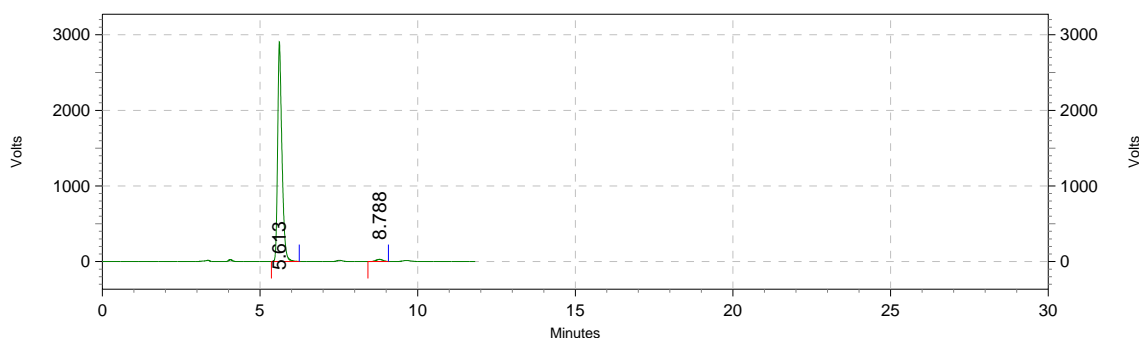
(S)-tert-butyl-(1-benzyl-3-(tert-butylperoxy)-5-chloro-2-oxoindolin-3-yl)carbamate (4e)



White solid, 87% yield, 97% ee, mp 140-142 °C. $[\alpha]_D^{20} = -7.30$ (c = 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 1H), 7.29 (s, 5H), 7.17 (d, J = 8.3 Hz, 1H), 6.56 (d, J = 8.3 Hz, 1H), 5.88 (s, 1H), 5.06 (d, J = 15.9 Hz, 1H), 4.75 (d, J = 15.9 Hz, 1H), 1.39 (s, 9H), 1.17 (s, 9H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 170.3, 153.2, 141.6, 134.8, 130.3, 128.8, 128.1, 127.8, 127.0, 110.3, 87.1, 81.8, 81.0, 53.5, 44.0, 29.7, 28.2, 26.3. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₄H₂₉ClN₂NaO₅⁺ 483.1657, found 483.1661. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 80/20 flow rate = 1.0 mL/min, λ = 254 nm). Retention times: t_R = 5.6 min for (*S*)-isomer and t_R = 8.8 min for (*R*)-isomer.

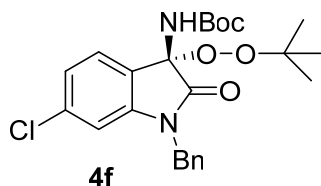


	Ret. Time	Area	Area%
1	5.623	1495209	51.209
2	9.658	1424603	48.791

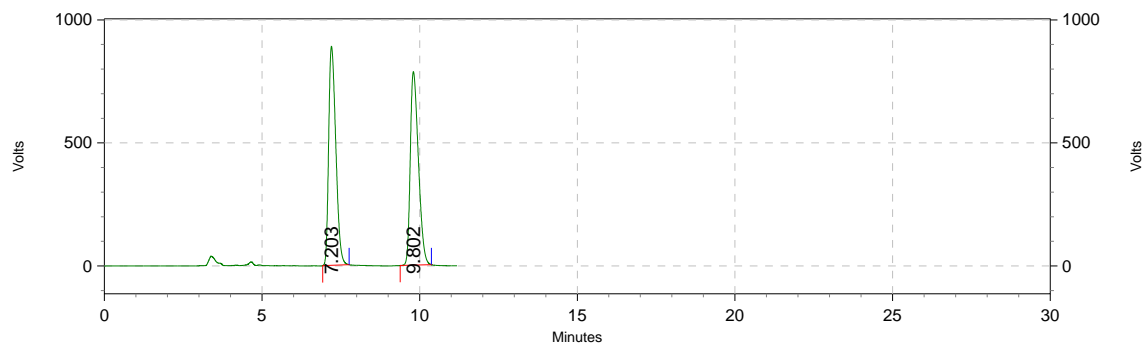


Peaks	Ret. Time	Area	Area%
1	5.613	27414146	98.470
2	8.788	426017	1.530

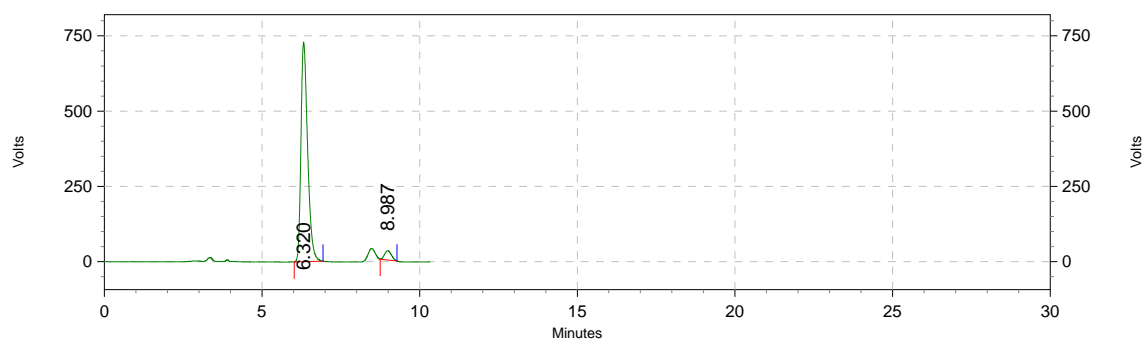
(S)-tert-butyl-(1-benzyl-3-(tert-butylperoxy)-6-chloro-2-oxindolin-3-yl)carbamate (4f)



White solid, 74% yield, 92% ee, mp 114-116 °C. $[\alpha]_D^{20} = -2.59$ ($c = 1.0$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 7.6$ Hz, 1H), 7.30 (d, $J = 4.0$ Hz, 4H), 7.25 (s, 1H), 7.01 (d, $J = 8.0$ Hz, 1H), 6.65 (s, 1H), 5.90 (s, 1H), 5.06 (d, $J = 16.0$ Hz, 1H), 4.73 (d, $J = 16.0$ Hz, 1H), 1.38 (s, 9H), 1.16 (s, 9H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.7, 153.2, 144.3, 136.3, 134.7, 128.9, 127.8, 127.0, 123.7, 122.6, 109.9, 86.8, 81.7, 80.9, 53.5, 44.0, 28.1, 26.3. HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{29}\text{ClN}_2\text{NaO}_5^+$ 483.1657, found 483.1658. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/*i*-PrOH = 80/20 flow rate = 1.0 mL/min, $\lambda = 254$ nm). Retention times: $t_R = 6.3$ min for (*S*)-isomer and $t_R = 9.0$ min for (*R*)-isomer.

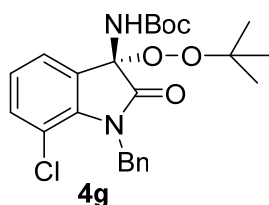


Peaks	Ret. Time	Area	Area%
1	7.203	13971763	49.843
2	9.802	14059761	50.157



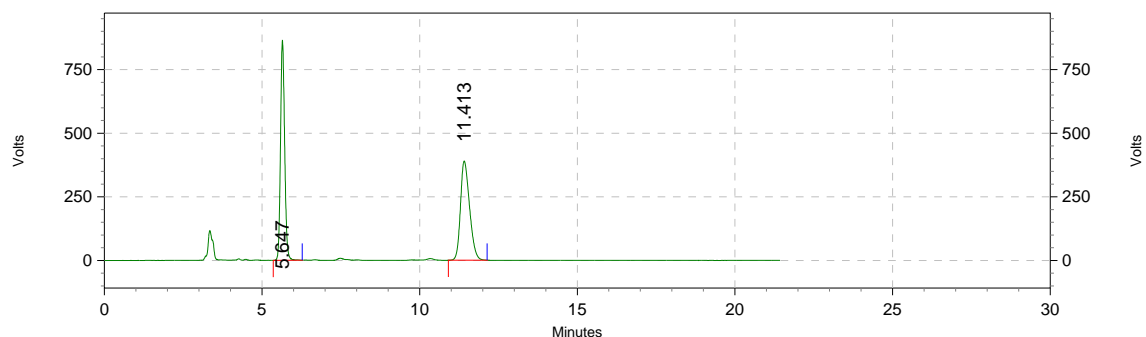
Peaks	Ret. Time	Area	Area%
1	6.320	10680211	95.801
2	8.987	468120	4.199

(S)-tert-butyl-(1-benzyl-3-(tert-butylperoxy)-7-chloro-2-oxoindolin-3-yl)carbamate (4g)

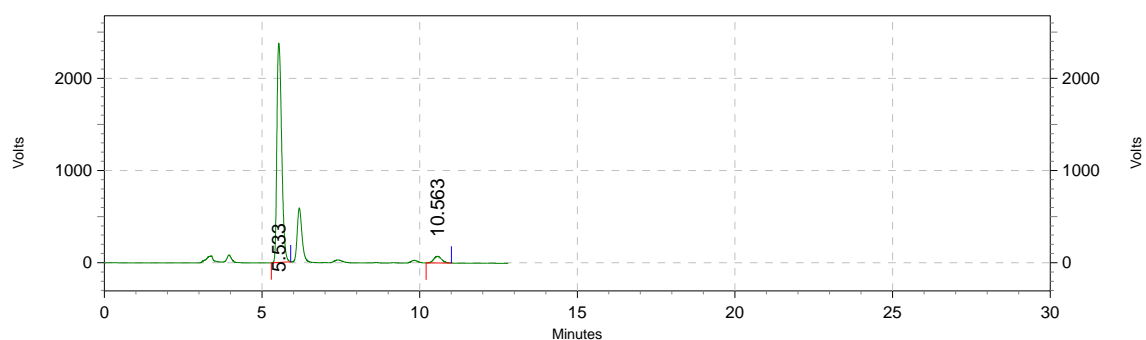


White solid, 84% yield, 90% ee, mp 125-127 °C. $[\alpha]_D^{20} = -3.81$ (c = 1.8, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, J = 5.7 Hz, 1H), 7.20 (s, 4H), 7.10 (d, J = 8.2 Hz, 2H), 6.89 (t, J = 7.6 Hz, 1H), 5.81 (s, 1H), 5.31 (d, J = 16.3 Hz, 1H), 5.23 (d, J = 16.3 Hz, 1H), 1.28 (s, 9H), 1.07 (s, 9H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 171.2, 153.1, 139.2, 137.1, 133.2, 129.5, 128.5, 127.1, 126.4, 125.5, 123.6, 115.5, 86.6, 81.8, 81.0, 45.1, 28.1, 26.3. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₄H₂₉ClN₂NaO₅⁺ 483.1657, found 483.1662. The ee value was

determined by chiral HPLC analysis (Chiralcel IA-H, hexane/*i*-PrOH = 80/20 flow rate = 1.0 mL/min, $\lambda = 254$ nm). Retention times: $t_R = 5.5$ min for (*S*)-isomer and $t_R = 10.6$ min for (*R*)-isomer.

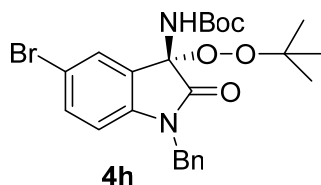


Peaks	Ret. Time	Area	Area%
1	5.647	7901627	50.344
2	11.413	7793574	49.656



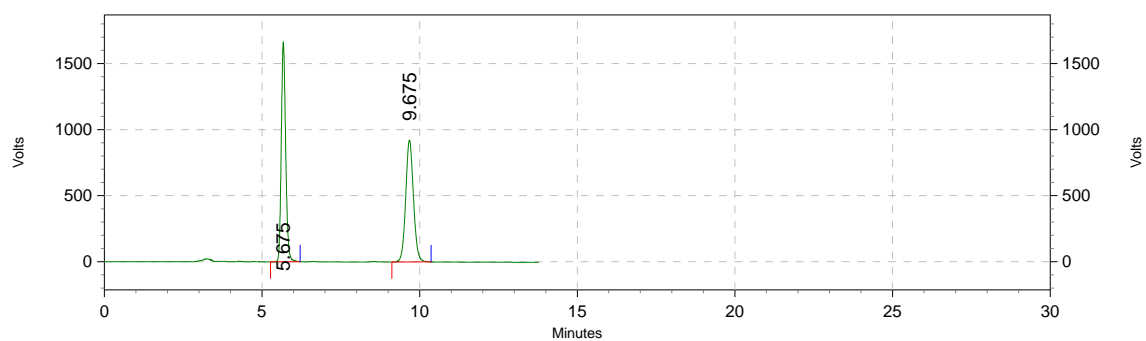
Peaks	Ret. Time	Area	Area%
1	5.533	24988804	95.140
2	10.563	1276597	4.860

(*S*)-tert-butyl-(1-benzyl-5-bromo-3-(tert-butylperoxy)-2-oxoindolin-3-yl)carbamate(4h)

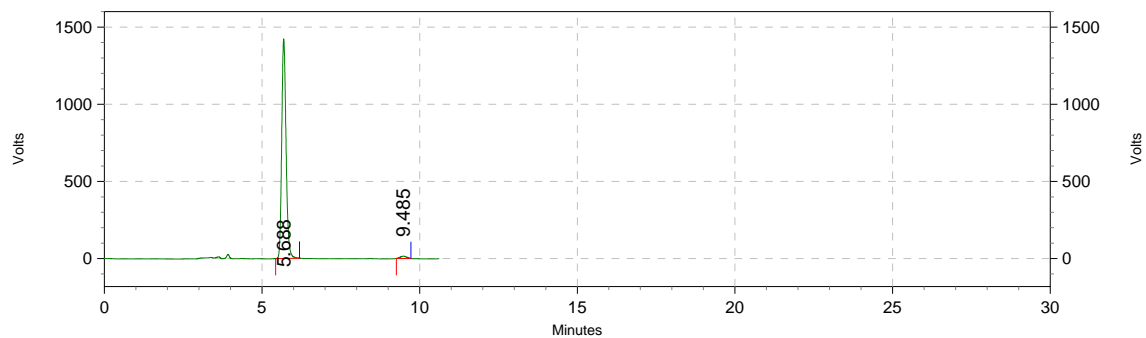


White solid, 89% yield, 96% ee, mp 142-144 °C. $[\alpha]_D^{20} = -10.25$ ($c = 2.4$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ 7.93 (s, 1H), 7.32 (dd, $J = 8.3, 2.1$ Hz, 1H), 7.29 (d, $J = 4.5$ Hz, 4H), 7.25 (dd, $J = 8.9, 4.7$ Hz, 1H), 6.51 (d, $J = 8.3$ Hz, 1H), 5.87 (s, 1H), 5.06 (d, $J = 16.0$ Hz, 1H), 4.75 (d, $J = 16.0$ Hz, 1H), 1.39 (s, 9H), 1.17 (s, 9H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ

170.2, 153.2, 142.1, 134.7, 133.3, 130.5, 128.8, 127.8, 127.0, 115.4, 110.9, 87.0, 81.8, 81.0, 44.0, 28.2, 26.3. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{24}H_{29}BrN_2NaO_5^+$ 527.1152, found 527.1157. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 80/20 flow rate = 1.0 mL/min, $\lambda = 254$ nm). Retention times: $t_R = 5.7$ min for (*S*)-isomer and $t_R = 9.5$ min for (*R*)-isomer.

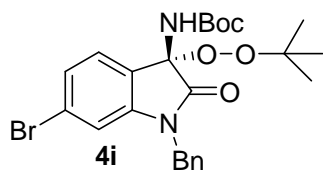


Peaks	Ret. Time	Area	Area%
1	5.675	16130018	50.626
2	9.675	15730928	49.374

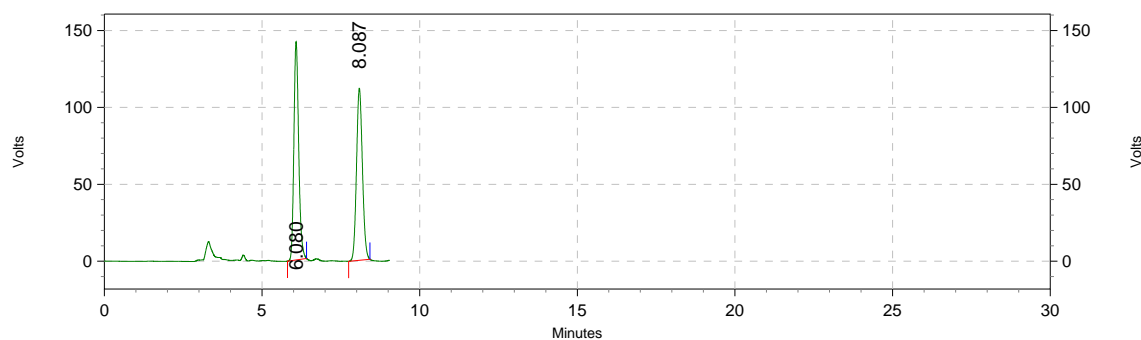


Peaks	Ret. Time	Area	Area%
1	5.688	13622732	98.505
2	9.485	206735	1.495

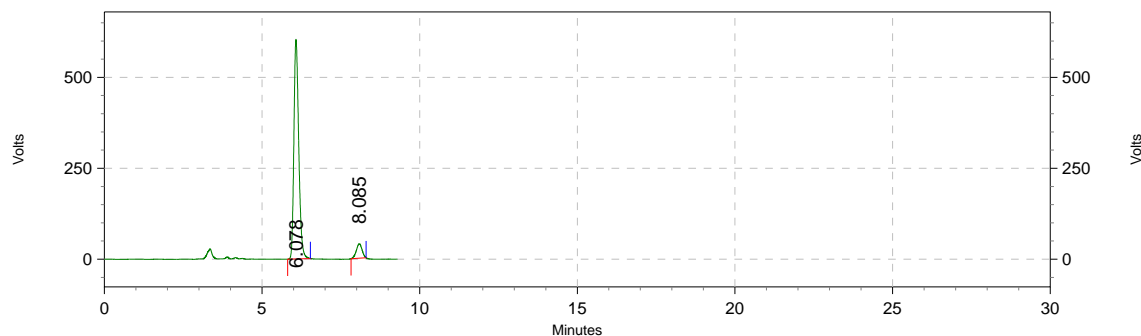
(S)-tert-butyl-(1-benzyl-6-bromo-3-(tert-butylperoxy)-2-oxoindolin-3-yl)carbamate (4i)



White solid, 75% yield, 86% ee, mp 114-116 °C. $[\alpha]_D^{20} = +4.50$ (c = 2.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 7.8 Hz, 1H), 7.30 (d, J = 4.4 Hz, 4H), 7.25 (d, J = 4.6 Hz, 1H), 7.17 (dd, J = 8.0, 1.6 Hz, 1H), 6.80 (d, J = 1.6 Hz, 1H), 5.91 (s, 1H), 5.05 (d, J = 16.0 Hz, 1H), 4.72 (d, J = 16.0 Hz, 1H), 1.38 (s, 9H), 1.16 (s, 9H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 170.6, 153.2, 144.4, 134.6, 128.9, 127.8, 124.4, 112.7, 86.8, 81.7, 80.9, 43.9, 28.2, 26.3. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₄H₂₉BrN₂NaO₅⁺ 527.1152, found 527.1157. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 80/20 flow rate = 1.0 mL/min, λ = 254 nm). Retention times: t_R = 6.1 min for (*S*)-isomer and t_R = 8.1 min for (*R*)-isomer.

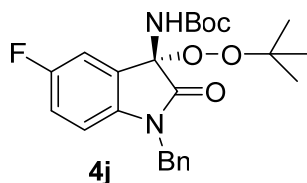


Peaks	Ret. Time	Area	Area%
1	6.080	1496785	50.742
2	8.087	1452989	49.258

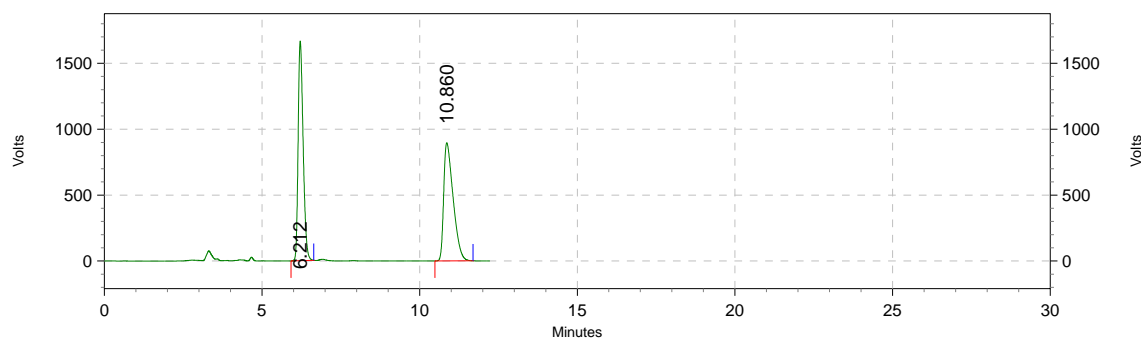


Peaks	Ret. Time	Area	Area%
1	6.078	6405098	92.727
2	8.085	502371	7.273

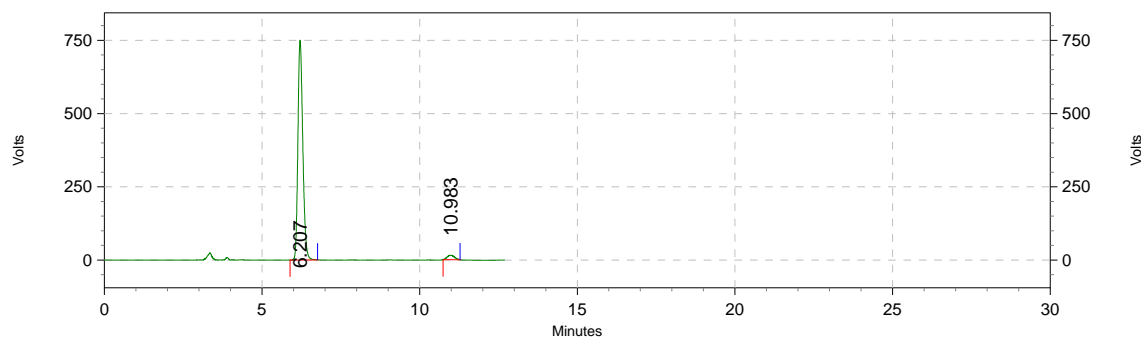
(S)-tert-butyl-(1-benzyl-3-(tert-butoxymethyl)-5-fluoro-2-oxindolin-3-yl)carbamate (4j)



White solid, 89% yield, 94% ee, mp 113-115 °C. $[\alpha]_{\text{D}}^{20} = -15.34$ (c = 2.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, J = 6.7 Hz, 1H), 7.29 (d, J = 4.4 Hz, 5H), 6.90 (td, J = 8.8, 2.7 Hz, 1H), 6.55 (dd, J = 8.6, 4.1 Hz, 1H), 5.89 (s, 1H), 5.07 (d, J = 16.0 Hz, 1H), 4.74 (d, J = 16.0 Hz, 1H), 1.39 (s, 9H), 1.17 (s, 9H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 170.5, 159.0 (d, ¹J_{C-F} = 241.0 Hz), 153.2, 139.0, 134.9, 128.8, 127.7, 127.1, 116.7 (d, ²J_{C-F} = 23.2 Hz), 115.8 (d, ²J_{C-F} = 25.5 Hz), 109.9 (d, ³J_{C-F} = 7.7 Hz), 87.1, 81.7, 80.9, 44.0, 28.2, 26.3. ¹⁹F NMR (CDCl₃) δ -120.0. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₄H₂₉FN₂NaO₅⁺ 467.1953, found 467.1958. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 80/20 flow rate = 1.0 mL/min, λ = 254 nm). Retention times: t_R = 6.2 min for (*S*)-isomer and t_R = 11.0 min for (*R*)-isomer.

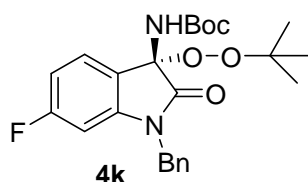


Peaks	Ret. Time	Area	Area%
1	6.212	18344528	49.696
2	10.860	18568833	50.304

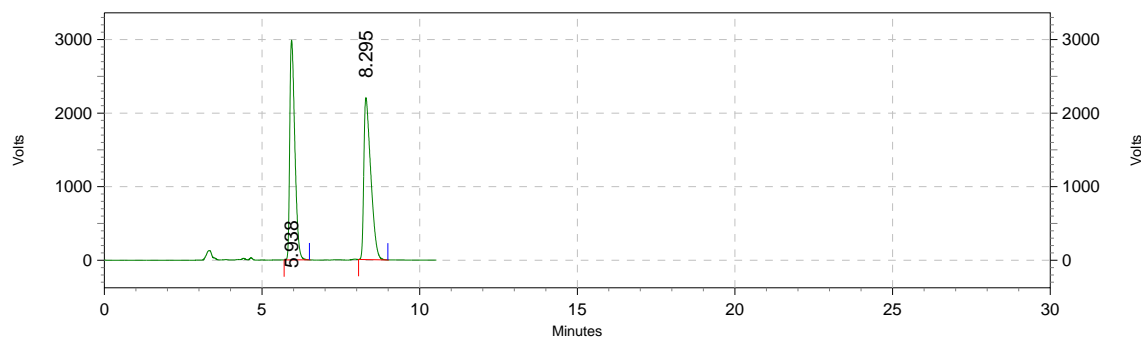


Peaks	Ret. Time	Area	Area%
1	6.207	8066786	97.043
2	10.983	245803	2.957

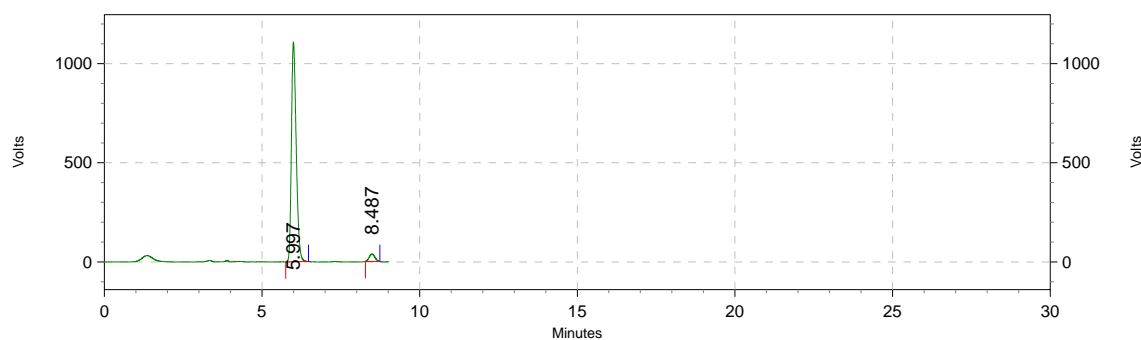
(S)-tert-butyl-(1-benzyl-3-(tert-butylperoxy)-6-fluoro-2-oxindolin-3-yl)carbamate (4k)



White solid, 88% yield, 92% ee, mp 110-112 °C. $[\alpha]_D^{20} = -2.55$ (c = 2.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.65 (m, 1H), 7.25 – 7.13 (m, 5H), 6.65 – 6.55 (m, 1H), 6.29 (dd, J = 8.8, 2.1 Hz, 1H), 5.83 (s, 1H), 4.96 (d, J = 16.0 Hz, 1H), 4.63 (d, J = 15.9 Hz, 1H), 1.28 (s, 9H), 1.07 (s, 9H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 171.0, 164.2 (d, ¹J_{C-F} = 247.8 Hz), 153.2, 144.9 (d, ³J_{C-F} = 11.4 Hz), 134.7, 129.1 (d, ³J_{C-F} = 8.7 Hz), 128.9, 127.8, 127.1, 120.8, 108.8 (d, ²J_{C-F} = 21.9 Hz), 98.2 (d, ²J_{C-F} = 27.5 Hz), 86.8, 81.6, 80.8, 44.0, 28.1, 26.3. ¹⁹F NMR (CDCl₃) δ -108.2. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₄H₂₉FN₂NaO₅⁺ 467.1953, found 467.1958. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 80/20 flow rate = 1.0 mL/min, λ = 254 nm). Retention times: t_R = 6.0 min for (*S*)-isomer and t_R = 8.5 min for (*R*)-isomer.

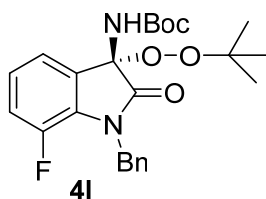


Peaks	Ret. Time	Area	Area%
1	5.938	33480556	49.805
2	8.295	33742819	50.195



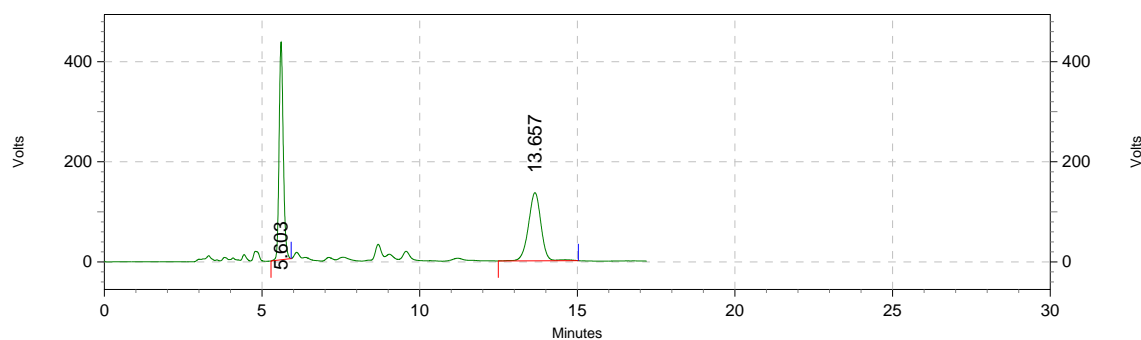
Peaks	Ret. Time	Area	Area%
1	5.997	11689604	96.104
2	8.487	473890	3.896

(S)-tert-butyl-(1-benzyl-3-(tert-butylperoxy)-7-fluoro-2-oxindolin-3-yl)carbamate (4I)

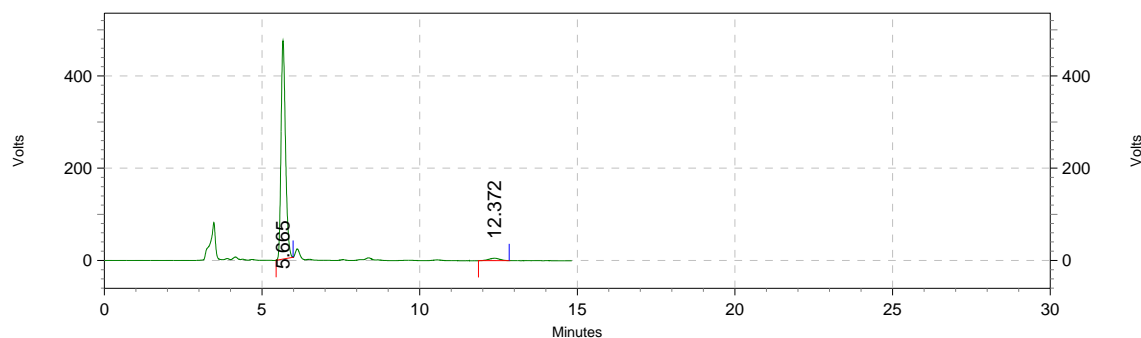


White solid, 88% yield, 95% ee, mp 109-111 °C. $[\alpha]_D^{20} = -4.87$ ($c = 1.0$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ 7.47 (s, 1H), 7.28 (d, $J = 6.6$ Hz, 2H), 7.19 (dt, $J = 11.8, 7.4$ Hz, 3H), 6.91 (d, $J = 7.2$ Hz, 2H), 5.79 (s, 1H), 5.09 (d, $J = 15.5$ Hz, 1H), 4.88 (d, $J = 15.5$ Hz, 1H), 1.27 (s, 9H), 1.06 (s, 9H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.4, 153.1, 147.4 (d, $^1J_{\text{C-F}} = 244.2$ Hz), 136.5, 129.7 (d, $^3J_{\text{C-F}} = 8.9$ Hz), 129.5, 128.5, 127.5, 127.2, 123.3 (d, $^3J_{\text{C-F}} = 6.0$ Hz), 123.0, 118.8 (d, $^2J_{\text{C-F}} = 19.5$ Hz), 87.1, 81.7, 80.9, 45.6, 28.1, 26.2. ^{19}F NMR (CDCl_3) δ

-134.0. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{24}H_{29}FN_2NaO_5^+$ 467.1953, found 467.1956. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 80/20 flow rate = 1.0 mL/min, $\lambda = 254$ nm). Retention times: $t_R = 5.7$ min for (*S*)-isomer and $t_R = 12.4$ min for (*R*)-isomer.



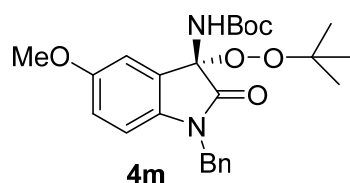
Peaks	Ret. Time	Area	Area%
1	5.603	4005885	51.582
2	13.657	3760162	48.418



Peaks	Ret. Time	Area	Area%
1	5.665	4640253	97.380
2	12.372	124826	2.620

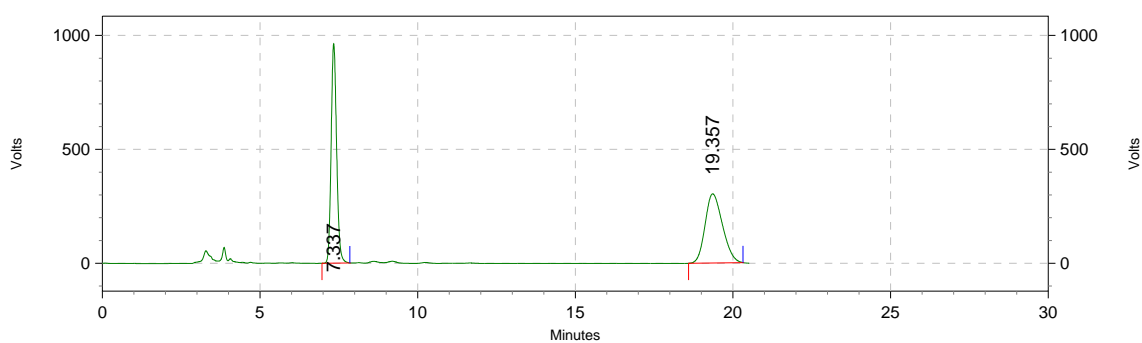
(*S*)-tert-butyl-(1-benzyl-3-(tert-butylperoxy)-5-methoxy-2-oxindolin-3-yl)carbamate

(4m)

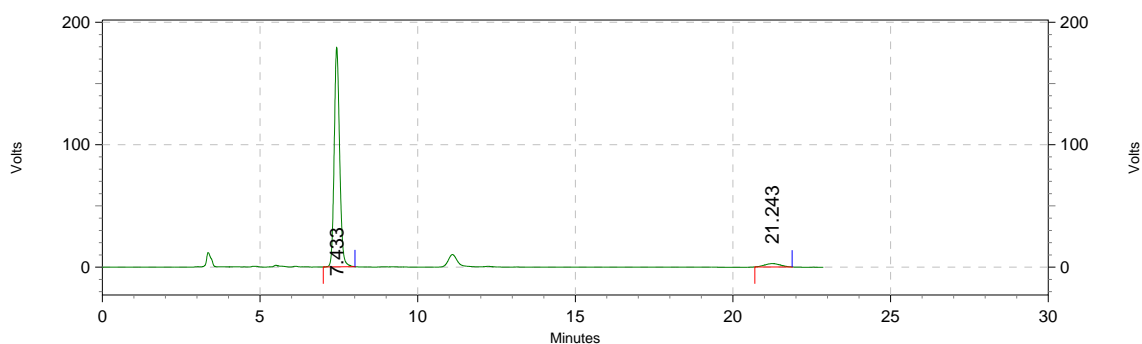


White solid, 86% yield, 91% ee, mp 137-139 °C. $[\alpha]_D^{20} = -7.84$ (c = 1.0, CH_2Cl_2). 1H NMR

(400 MHz, CDCl₃) δ 7.37 (s, 1H), 7.23 – 7.14 (m, 5H), 6.66 (dd, J = 8.5, 2.7 Hz, 1H), 6.45 (d, J = 8.5 Hz, 1H), 5.80 (s, 1H), 4.98 (d, J = 15.9 Hz, 1H), 4.65 (d, J = 15.9 Hz, 1H), 3.67 (s, 3H), 1.29 (s, 9H), 1.09 (s, 9H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 170.5, 155.8, 153.2, 136.4, 135.3, 128.7, 127.6, 127.1, 126.6, 115.2, 114.4, 109.7, 87.6, 81.5, 80.7, 55.8, 43.9, 28.2, 26.3. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₅H₃₂N₂NaO₆⁺ 479.2153, found 479.2156. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 80/20 flow rate = 1.0 mL/min, λ = 254 nm). Retention times: t_R = 7.4 min for (*S*)-isomer and t_R = 21.2 min for (*R*)-isomer.



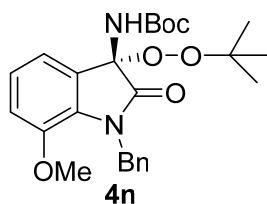
Peaks	Ret. Time	Area	Area%
1	7.337	11652083	50.065
2	19.357	11621983	49.935



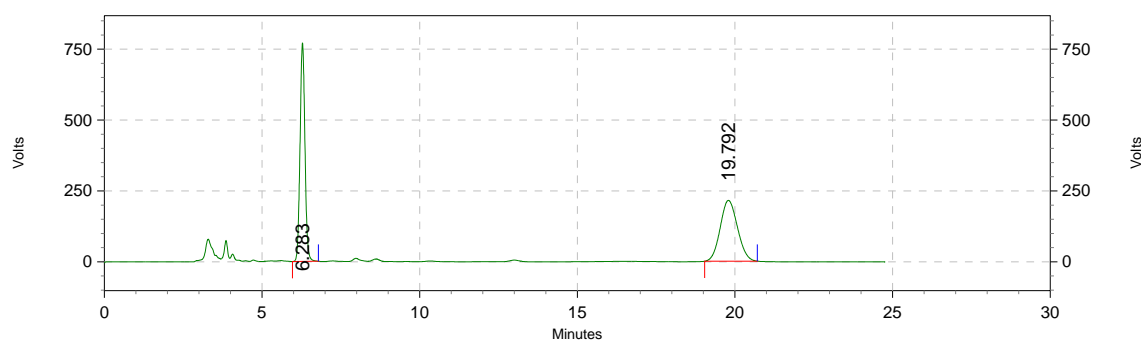
Peaks	Ret. Time	Area	Area%
1	7.433	2146151	95.784
2	21.243	94454	4.216

(S)-tert-butyl-(1-benzyl-3-(tert-butylperoxy)-7-methoxy-2-oxoindolin-3-yl)carbamate

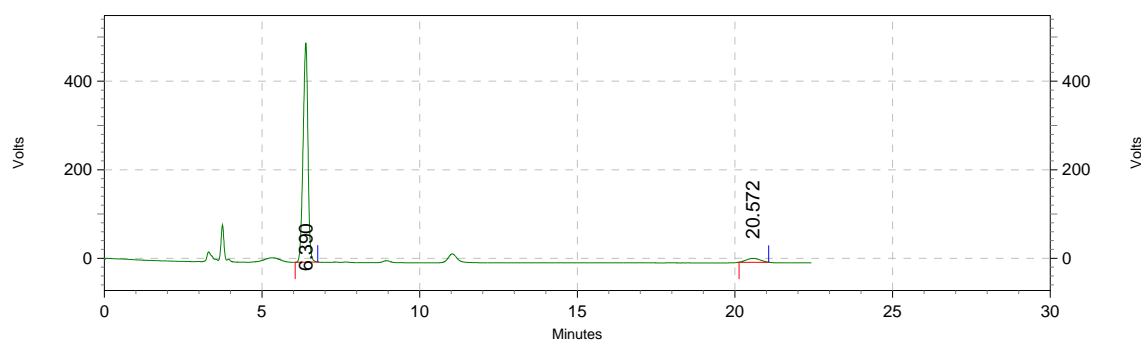
(4n)



Yellow oil, 83% yield, 91% ee. $[\alpha]_D^{20} = -1.26$ ($c = 1.0$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ 7.38 (d, $J = 6.6$ Hz, 1H), 7.31 (d, $J = 7.2$ Hz, 2H), 7.27 – 7.17 (m, 3H), 6.98 (t, $J = 7.9$ Hz, 1H), 6.84 (d, $J = 8.3$ Hz, 1H), 5.88 (s, 1H), 5.25 – 5.10 (m, 2H), 3.58 (s, 3H), 1.34 (s, 9H), 1.14 (s, 9H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.9, 153.2, 145.0, 138.0, 131.2, 128.2, 126.9, 123.2, 119.8, 115.0, 87.3, 81.4, 80.6, 55.8, 45.9, 29.7, 28.1, 26.3. HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{32}\text{N}_2\text{NaO}_6^+$ 479.2153, found 479.2155. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/*i*-PrOH = 80/20 flow rate = 1.0 mL/min, $\lambda = 254$ nm). Retention times: $t_R = 6.3$ min for (*S*)-isomer and $t_R = 20.6$ min for (*R*)-isomer.

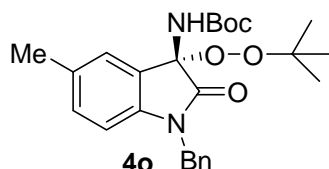


Peaks	Ret. Time	Area	Area%
1	6.283	8325774	50.545
2	19.792	8146350	49.455

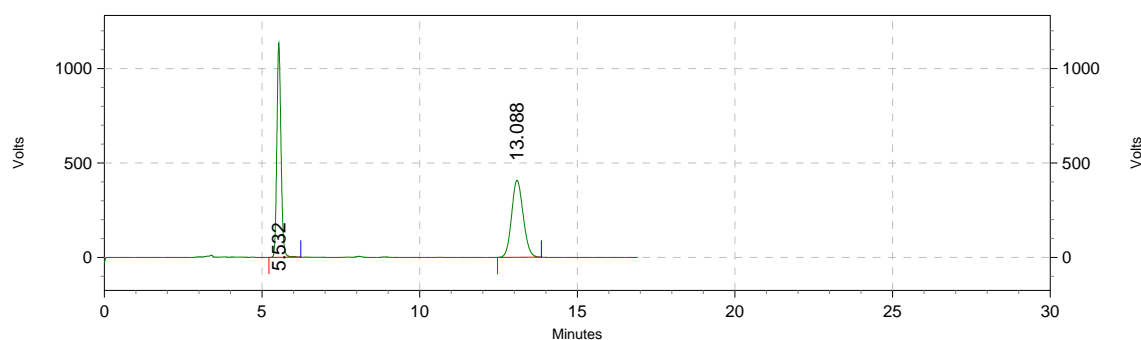


Peaks	Ret. Time	Area	Area%
1	6.390	5290982	95.282
2	20.572	261985	4.718

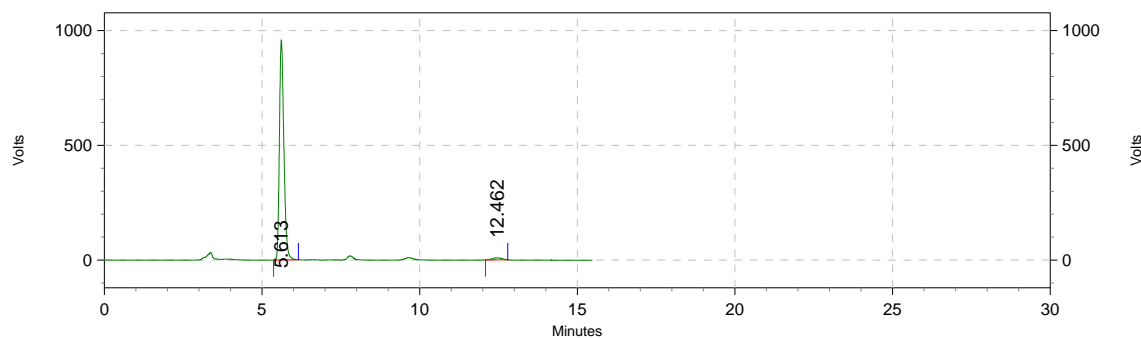
(S)-tert-butyl-(1-benzyl-3-(tert-butylperoxy)-5-methyl-2-oxindolin-3-yl)carbamate (4o)



White solid, 84% yield, 96% ee, mp 122-124 °C. $[\alpha]_D^{20} = -3.54$ (c = 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.62 (s, 1H), 7.26 (dd, J = 16.3, 8.7 Hz, 5H), 6.99 (d, J = 7.5 Hz, 1H), 6.52 (d, J = 7.9 Hz, 1H), 5.92 (s, 1H), 5.03 (d, J = 15.9 Hz, 1H), 4.73 (d, J = 15.8 Hz, 1H), 2.29 (s, 3H), 1.37 (s, 9H), 1.17 (s, 9H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 170.7, 153.3, 140.7, 135.4, 132.1, 130.8, 128.7, 128.1, 127.5, 127.1, 125.2, 109.1, 87.4, 81.4, 80.6, 43.8, 28.2, 26.3, 21.1. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₅H₃₂N₂NaO₅⁺ 463.2203, found 463.2205. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 80/20 flow rate = 1.0 mL/min, λ = 254 nm). Retention times: t_R = 5.6 min for (*S*)-isomer and t_R = 12.5 min for (*R*)-isomer.

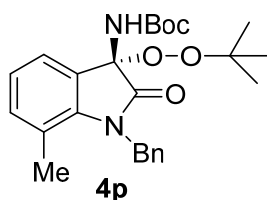


Peaks	Ret. Time	Area	Area%
1	5.532	10432594	50.113
2	13.088	10385436	49.887

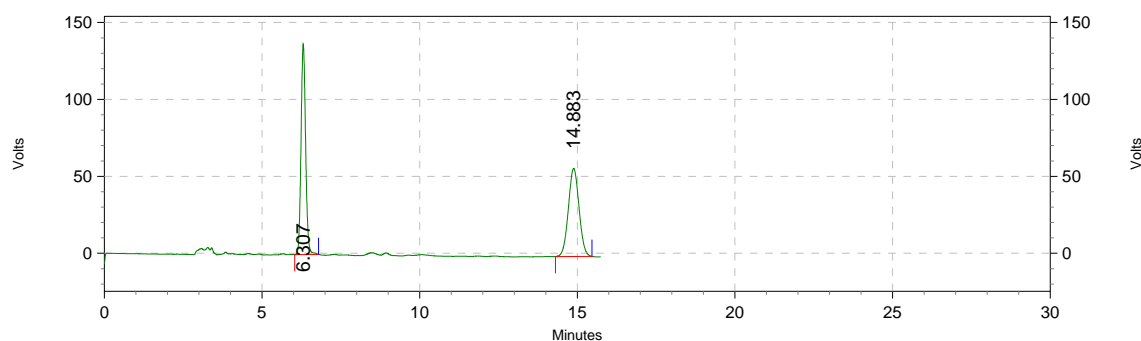


Peaks	Ret. Time	Area	Area%
1	5.613	9429475	98.022
2	12.462	190241	1.978

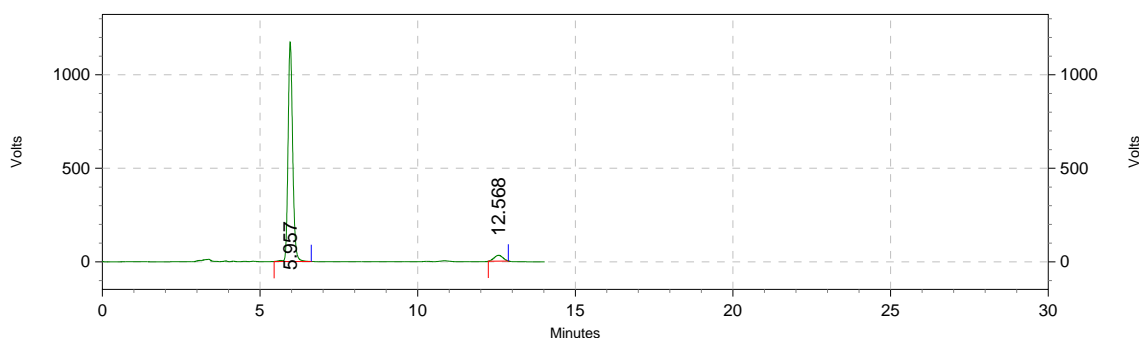
(S)-tert-butyl-(1-benzyl-3-(tert-butylperoxy)-7-methyl-2-oxindolin-3-yl)carbamate (4p)



White solid, 83% yield, 91% ee, mp 126-128 °C. $[\alpha]_D^{20} = +3.35$ (c = 2.2, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, J = 6.6 Hz, 1H), 7.26 (p, J = 8.7, 8.1 Hz, 5H), 7.01 – 6.92 (m, 2H), 5.93 (s, 1H), 5.32 (d, J = 17.0 Hz, 1H), 5.05 (d, J = 17.0 Hz, 1H), 2.21 (s, 3H), 1.37 (s, 9H), 1.18 (s, 9H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 171.6, 153.2, 141.1, 137.2, 134.7, 128.8, 127.2, 126.1, 125.7, 124.9, 122.7, 119.8, 86.9, 81.5, 80.6, 45.2, 28.2, 26.4, 25.9, 18.8. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₅H₃₂N₂NaO₅⁺ 463.2203, found 463.2203. The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 80/20 flow rate = 1.0 mL/min, λ = 254 nm). Retention times: t_R = 6.0 min for (*S*)-isomer and t_R = 12.6 min for (*R*)-isomer.

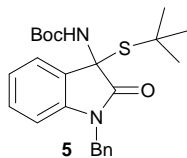


Peaks	Ret. Time	Area	Area%
1	6.307	1379877	50.606
2	14.883	1346824	49.394

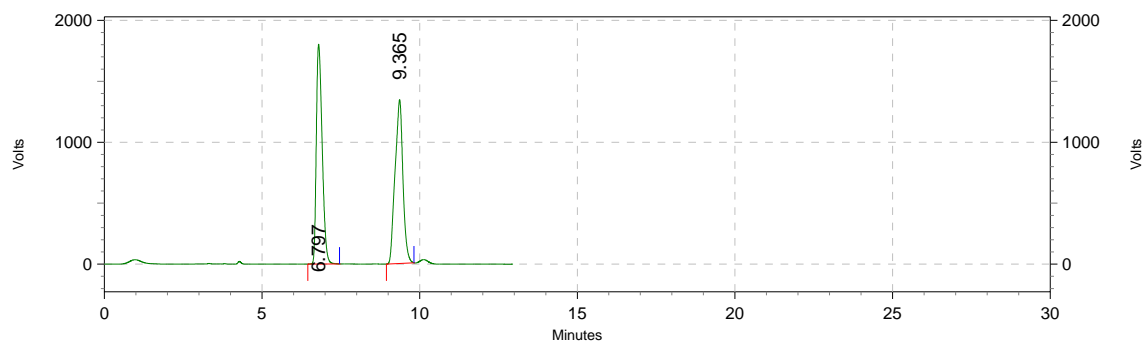


Peaks	Ret. Time	Area	Area%
1	5.957	11967667	95.276
2	12.568	593373	4.724

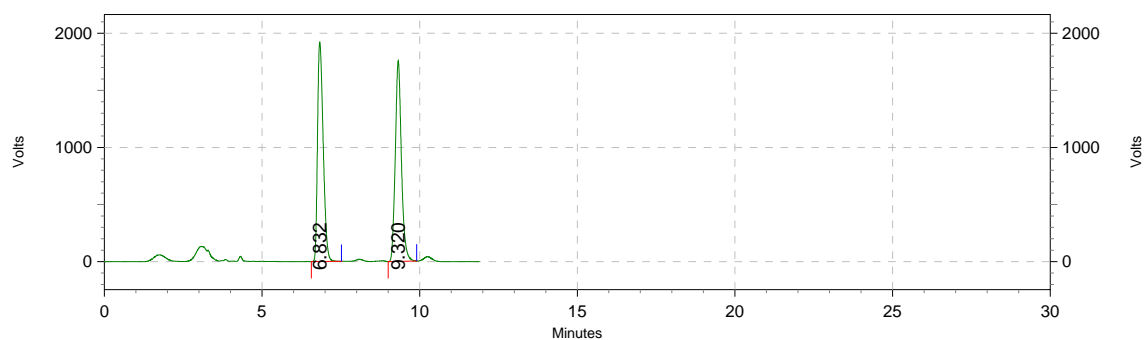
Tert-butyl (1-benzyl-3-(tert-butylthio)-2-oxindolin-3-yl)carbamate (**5**)¹¹



White solid, 93% yield, 0 % ee. m p = 64-66 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.28 (m, 5H), 7.24 (s, 1H), 7.16 (t, J = 7.5 Hz, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.64 (d, J = 7.8 Hz, 1H), 5.62 (s, 1H), 5.26 (s, 1H), 4.69 (s, 1H), 1.50 (s, 9H), 1.26 (s, 9H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 174.0, 153.1, 140.9, 135.8, 129.4, 128.8, 127.5, 127.1, 122.8, 109.0, 80.8, 64.8, 50.3, 44.0, 31.7, 28.1. The ee value was determined by chiral HPLC analysis (Chiralcel IC, hexane/i-PrOH = 90/10 flow rate = 1.0 mL/min, λ = 254 nm). Retention times: t_R = 6.7 min for (S)-isomer and t_R = 9.3 min for (R)-isomer.

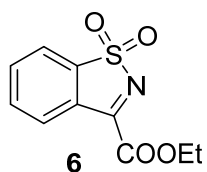


Peaks	Ret. Time	Area	Area%
1	6.797	23240903	50.030
2	9.365	23212827	49.970



Peaks	Ret. Time	Area	Area%
1	6.832	23927844	50.092
2	9.320	23840247	49.908

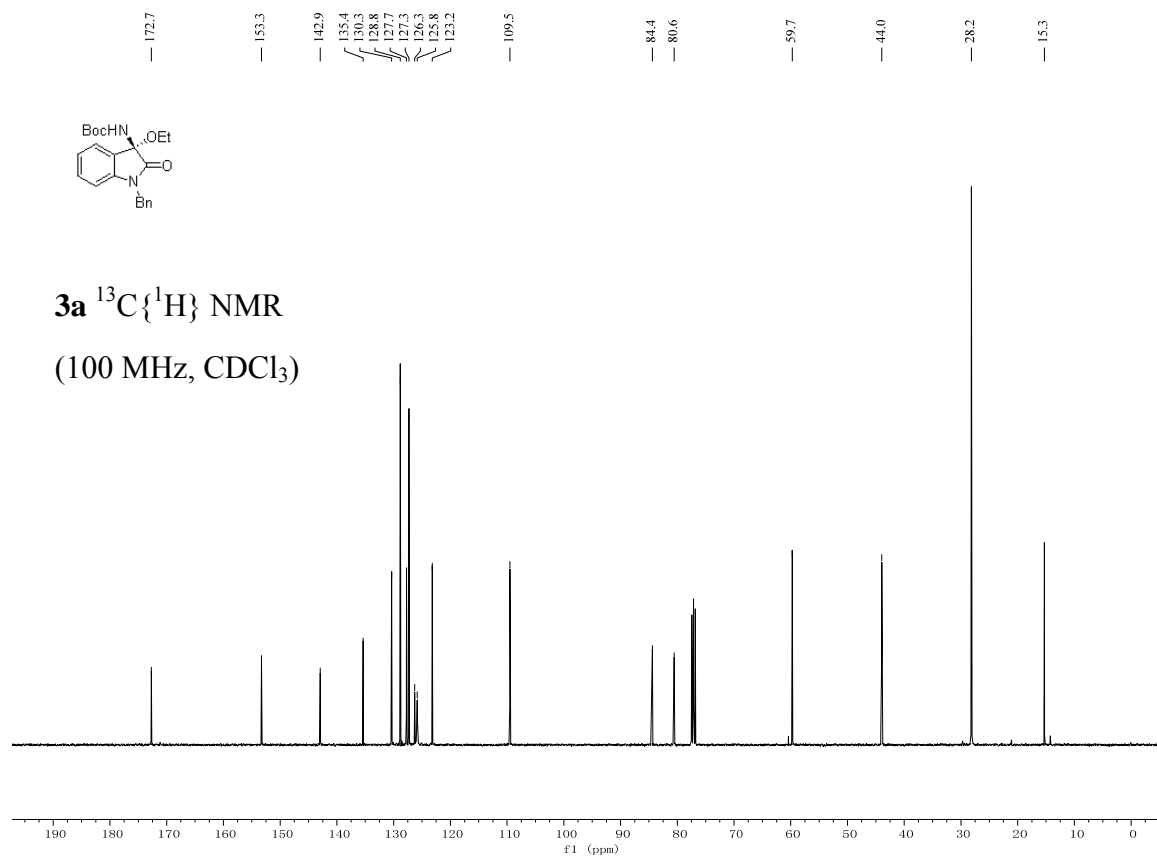
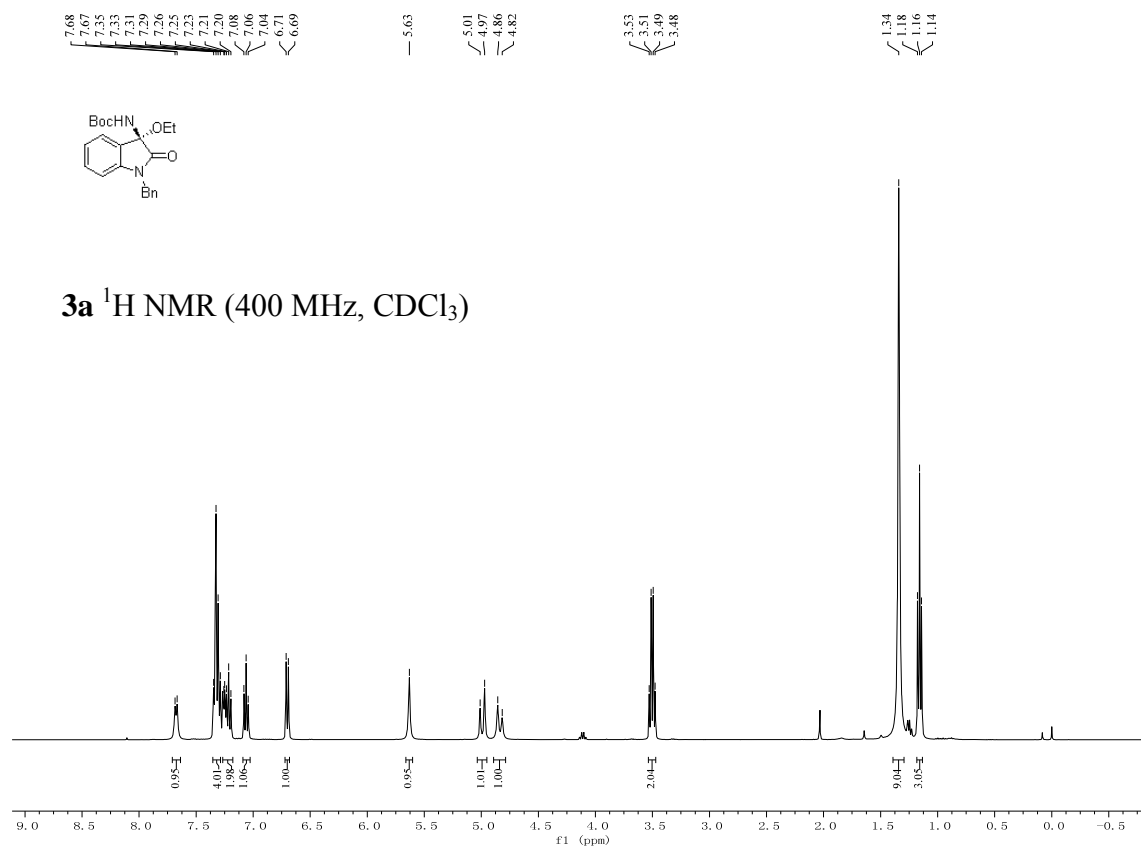
Ethyl benzo[d]isothiazole-3-carboxylate 1,1-dioxide (**6**)

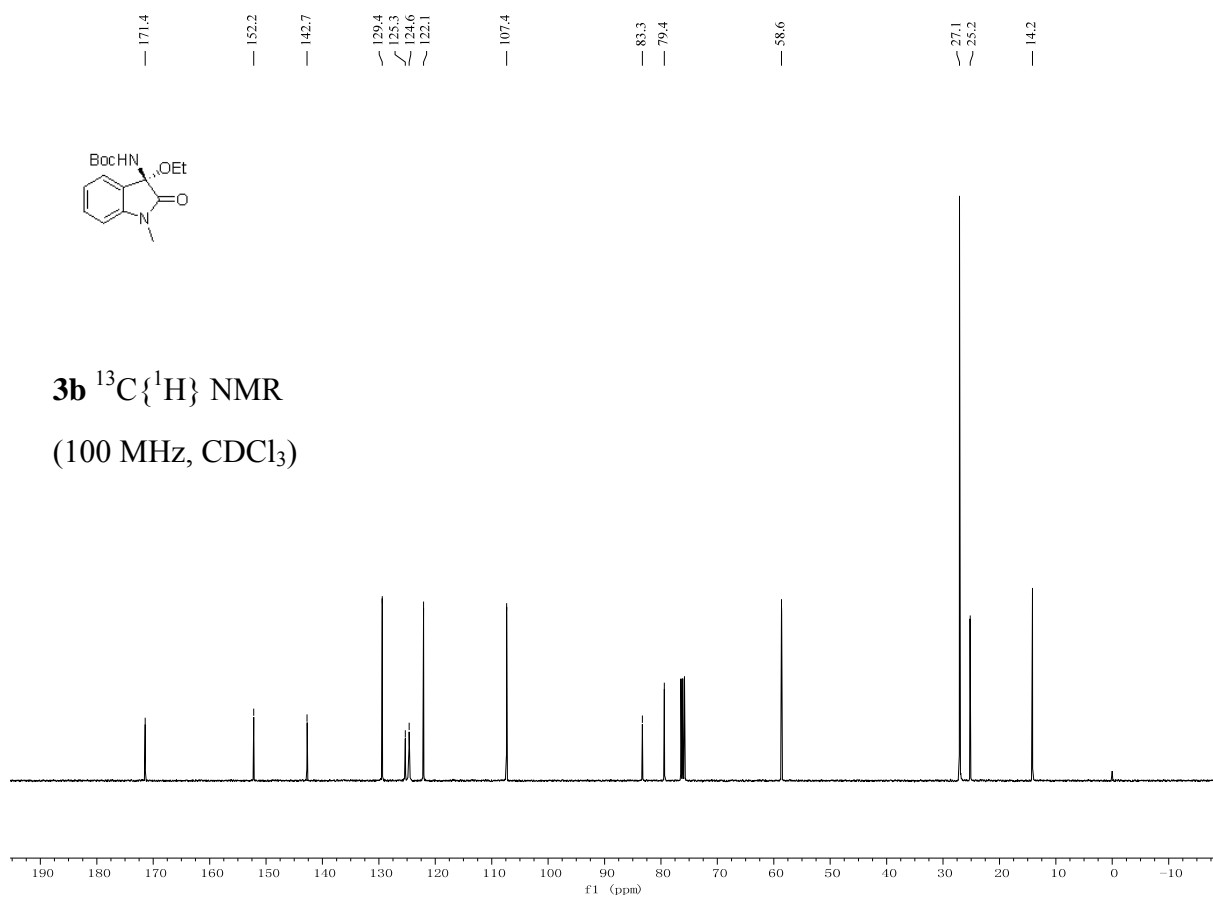
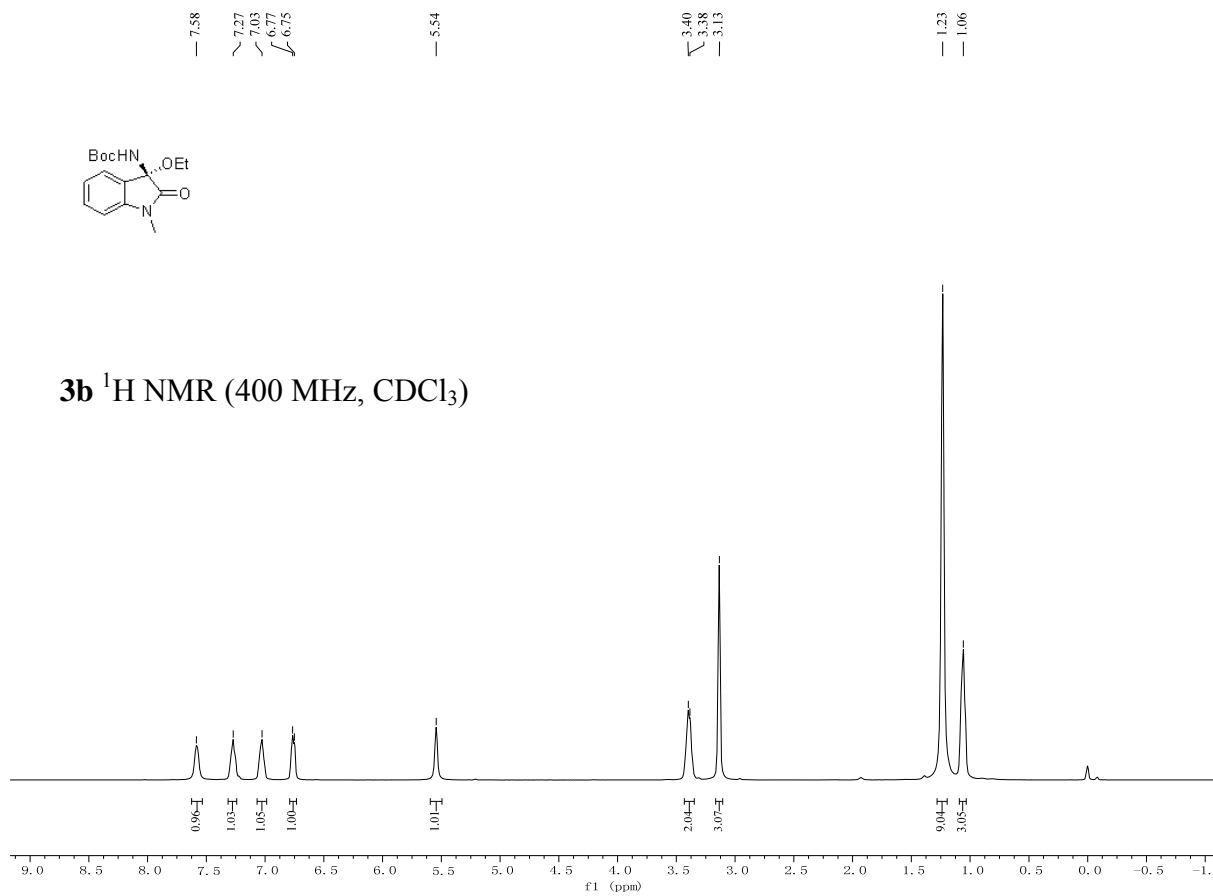


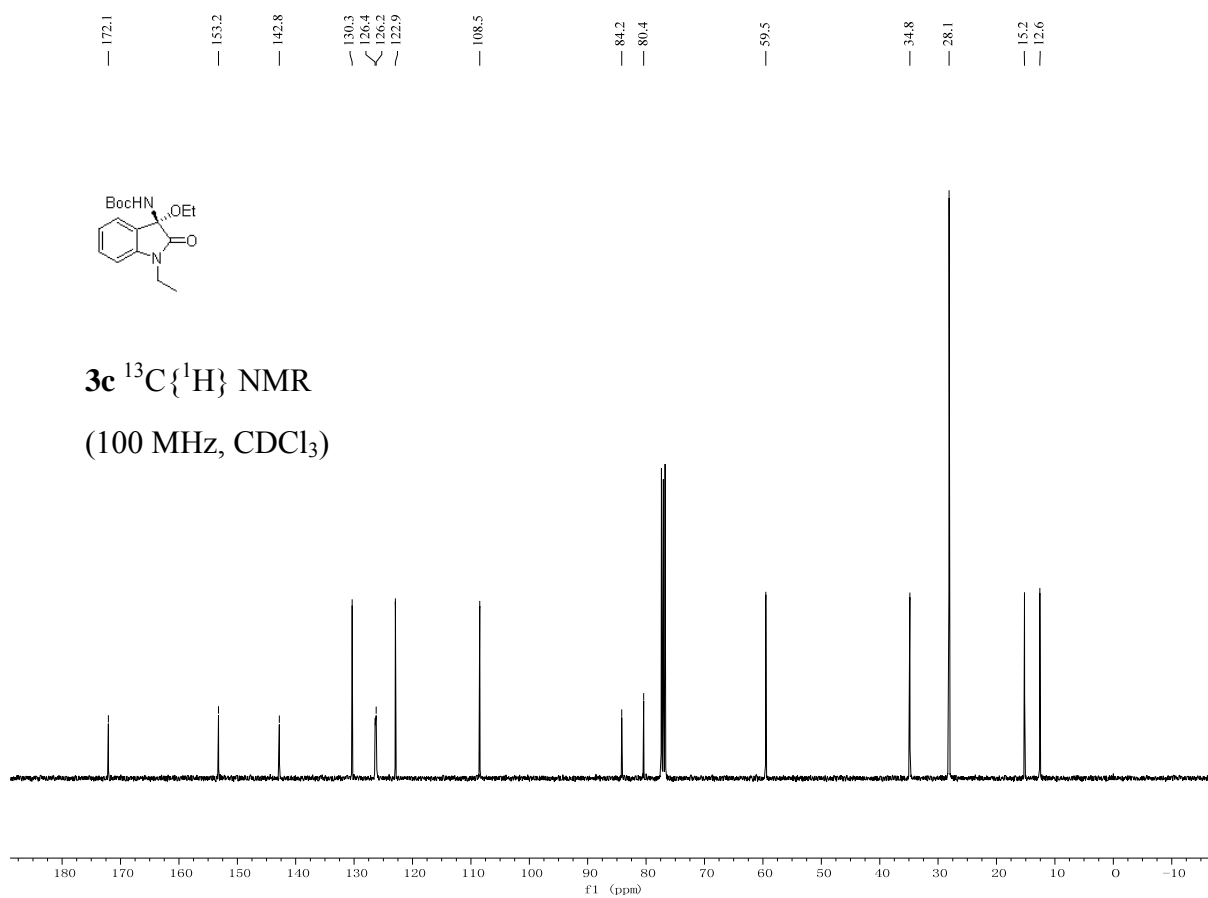
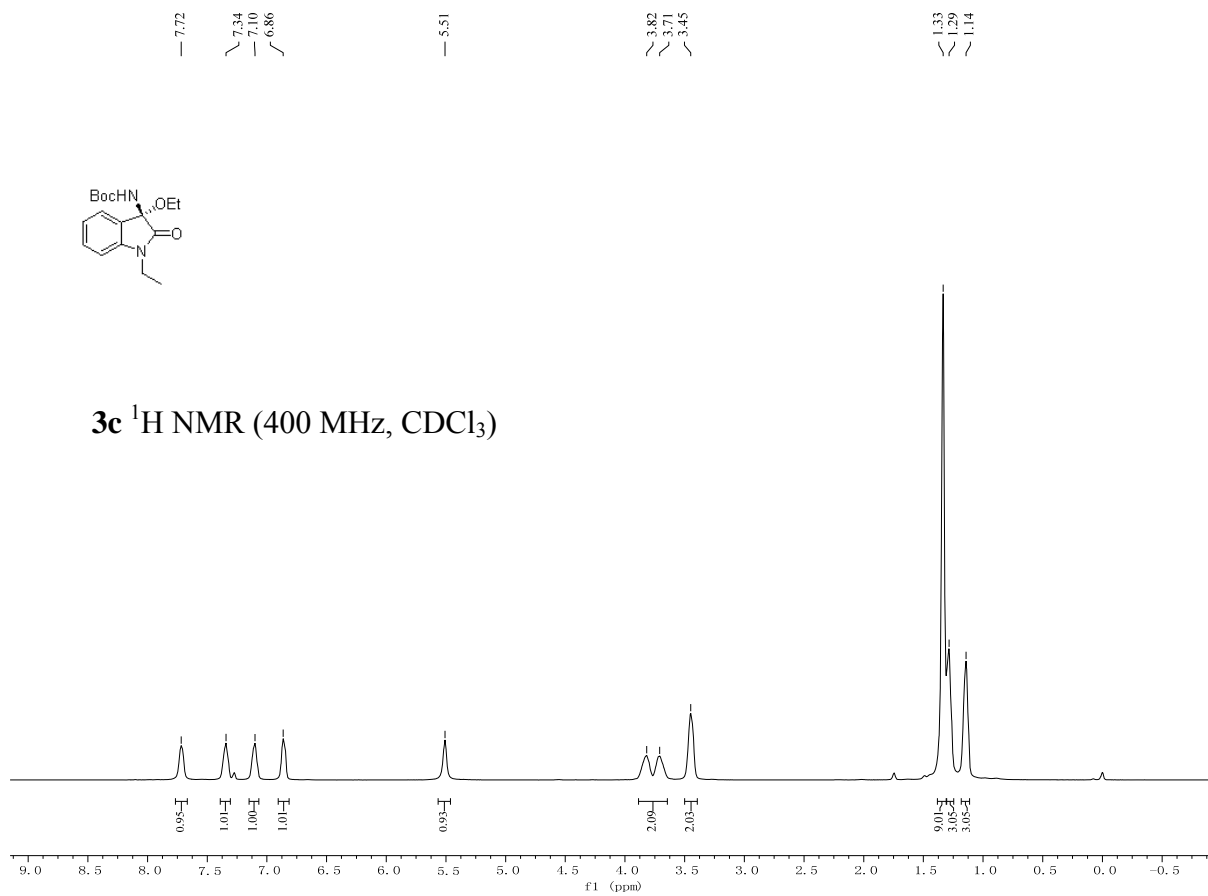
Compound **6** was synthesized according to the known procedures.¹² White solid, 93% yield.

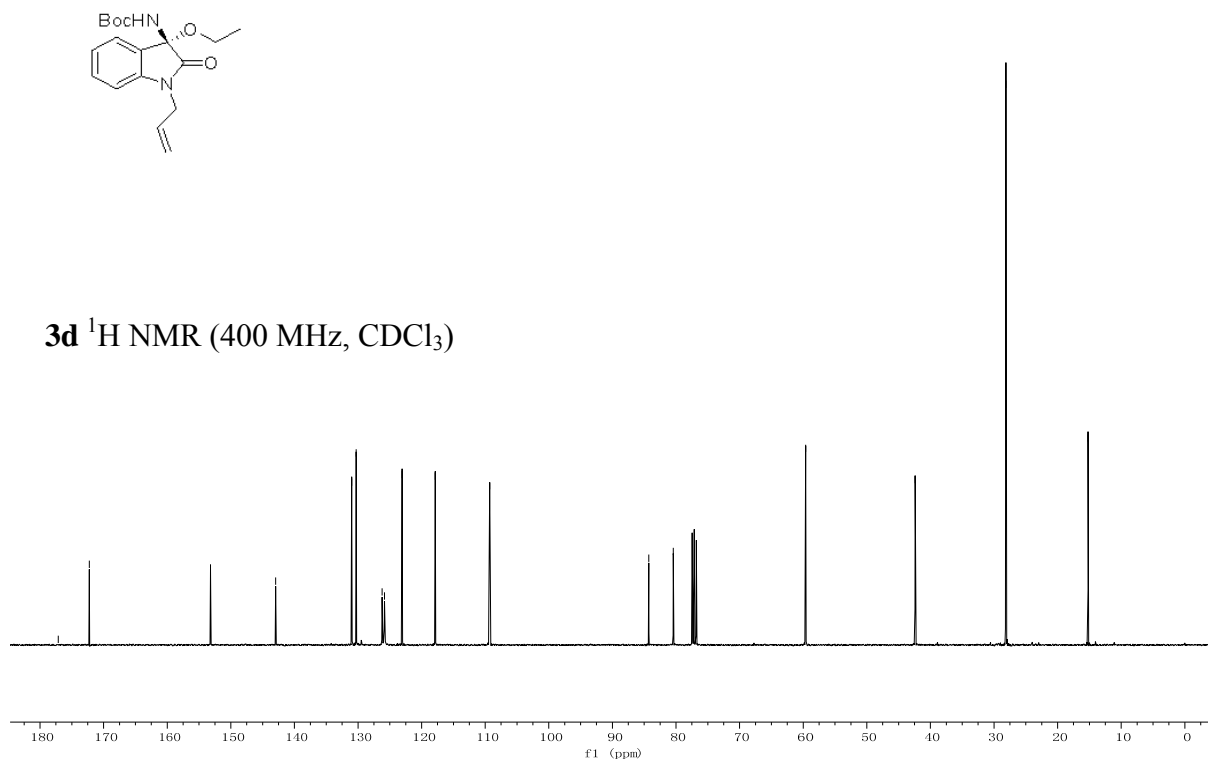
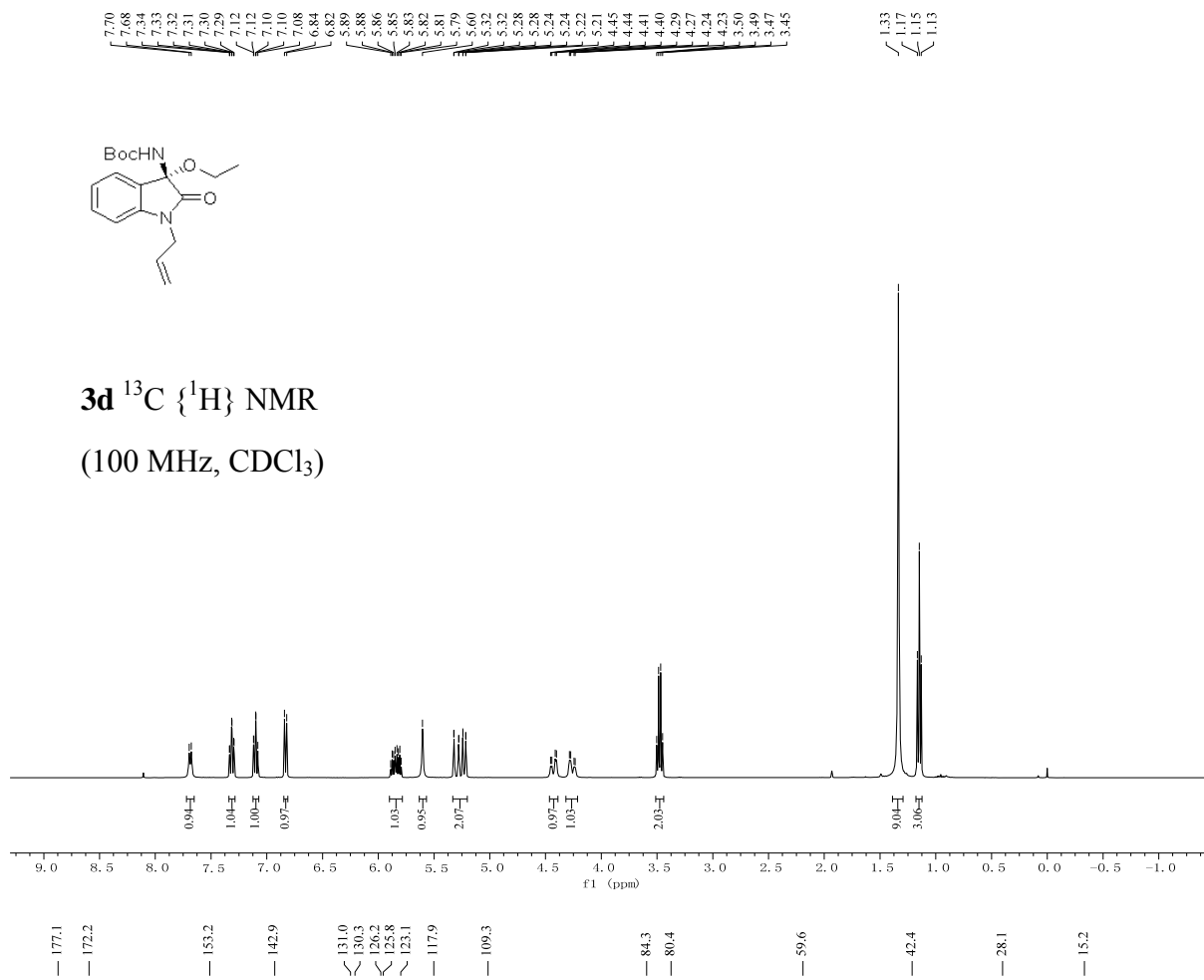
¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 6.4 Hz, 1H), 7.94 (d, *J* = 6.5 Hz, 1H), 7.81 (d, *J* = 12.6 Hz, 2H), 4.55 (q, *J* = 7.0 Hz, 2H), 1.48 (t, *J* = 7.0 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 160.4, 160.3, 140.2, 134.5, 134.3, 128.2, 127.7, 123.0, 63.9, 14.0.

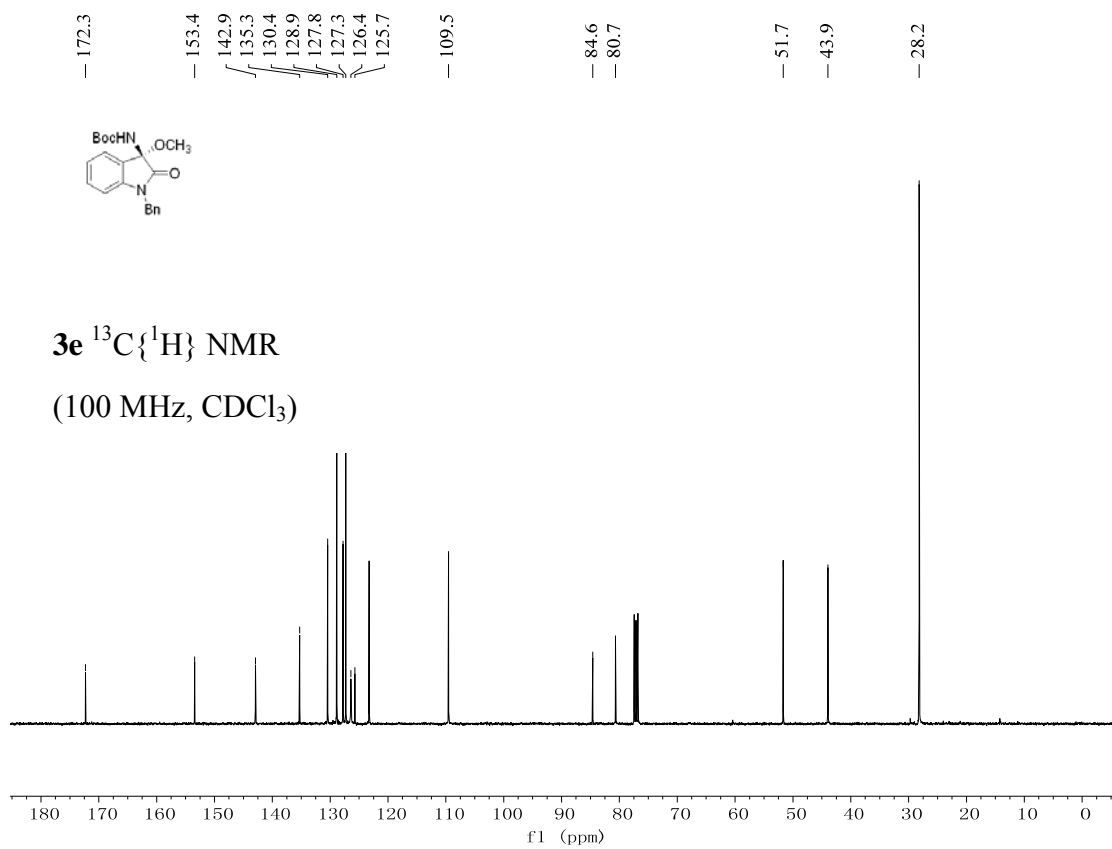
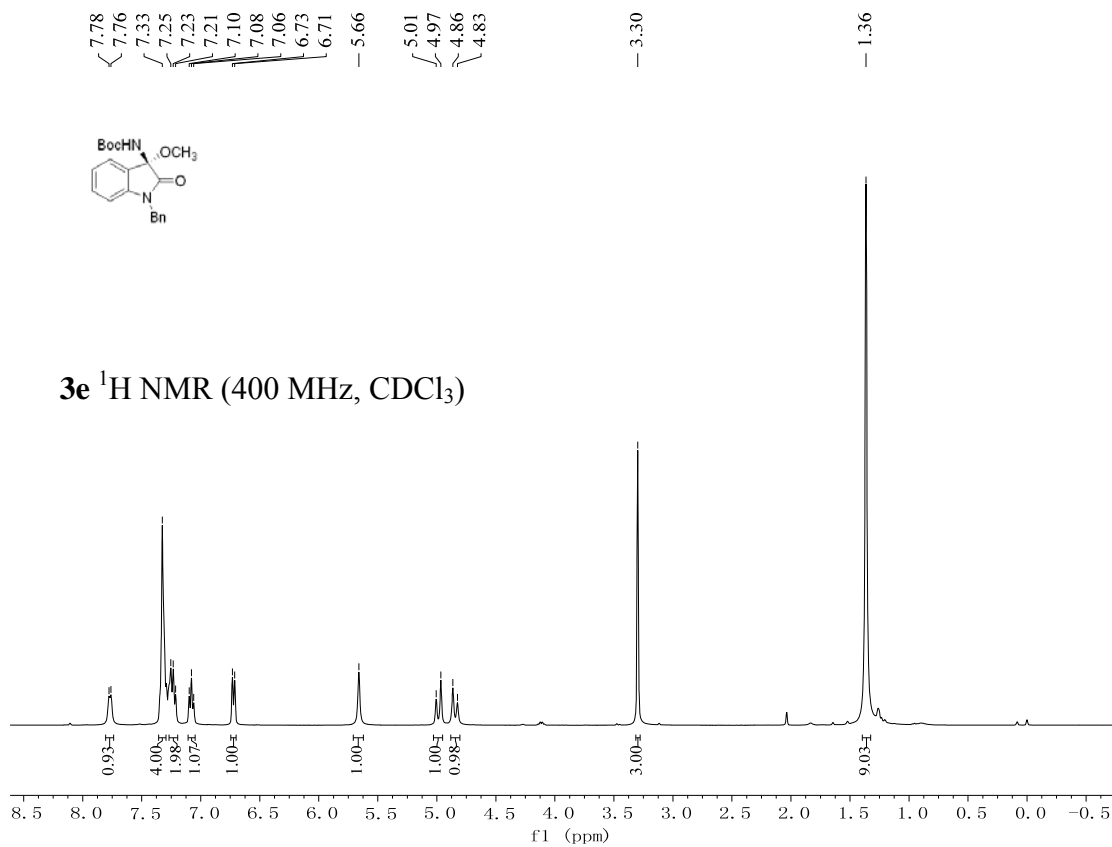
3. Copies of NMR Spectra of the Products

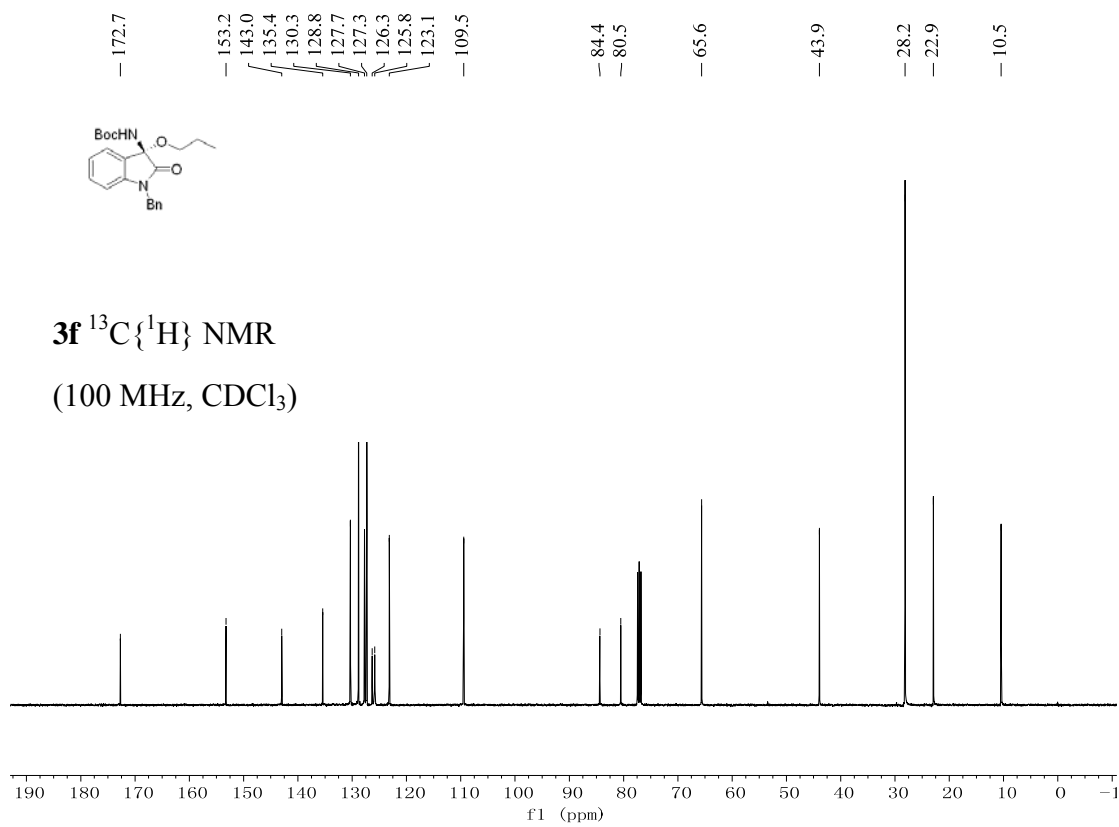
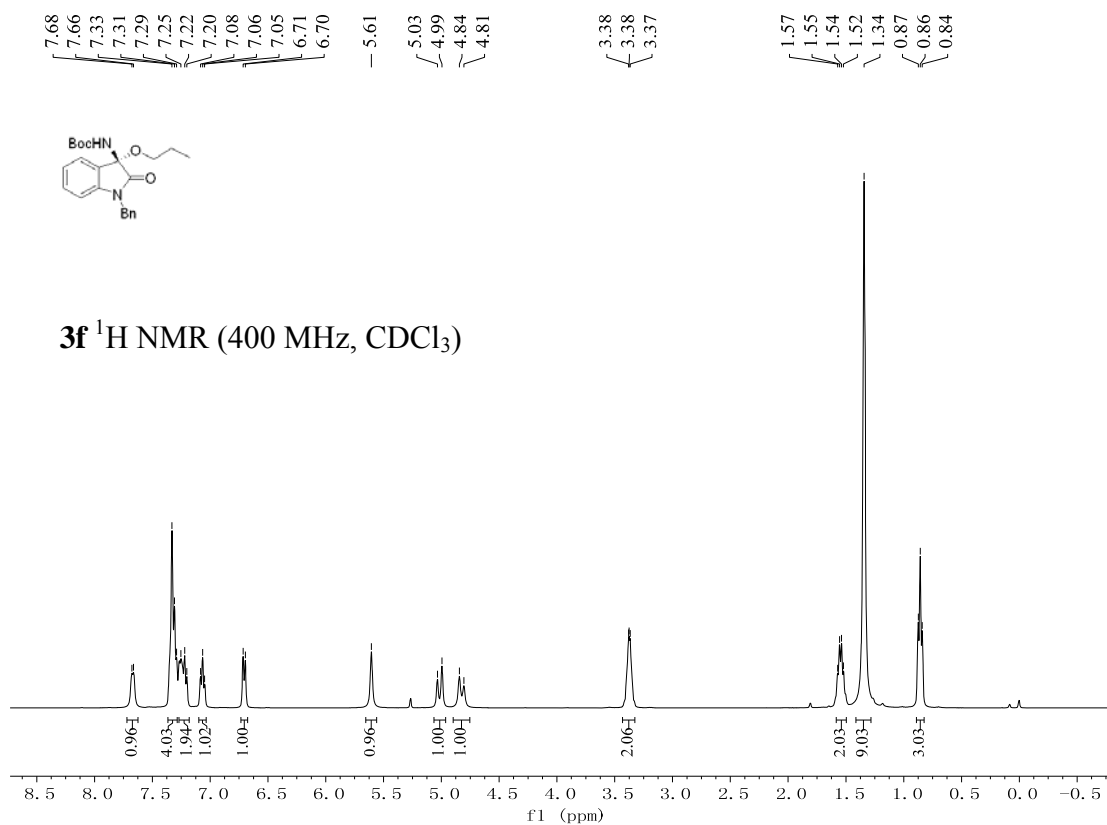


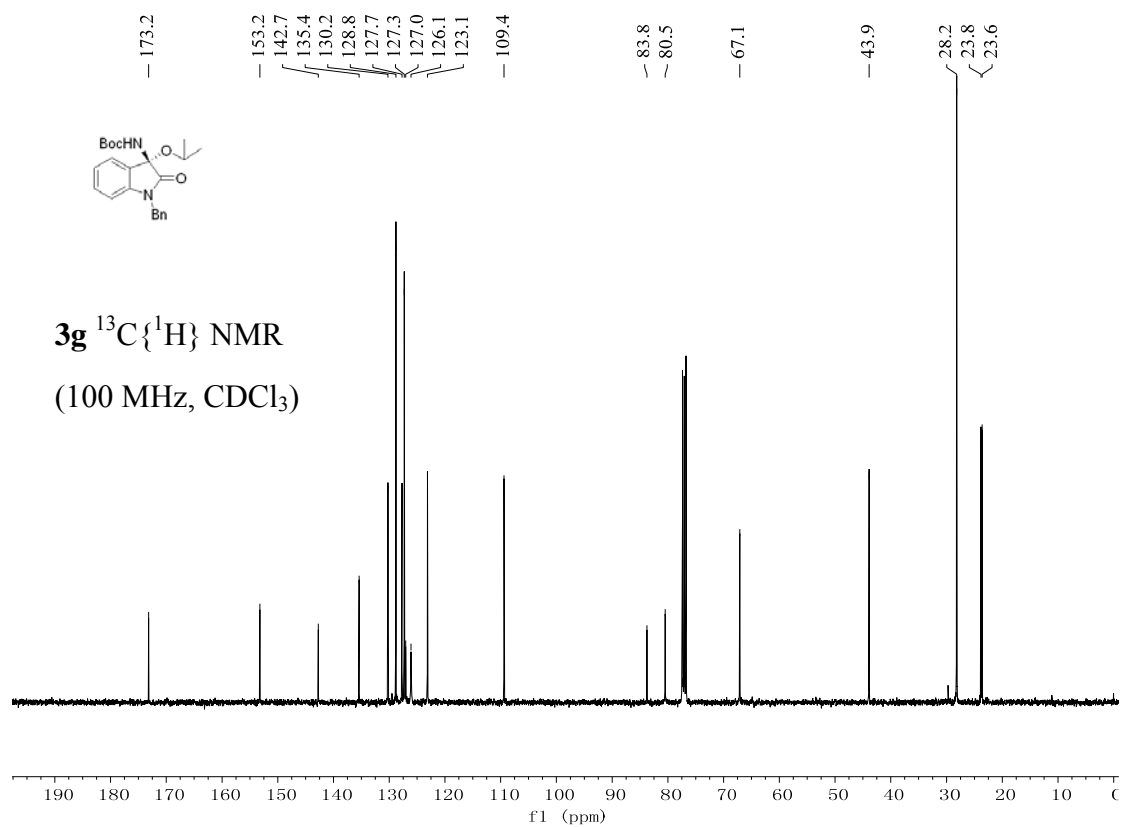
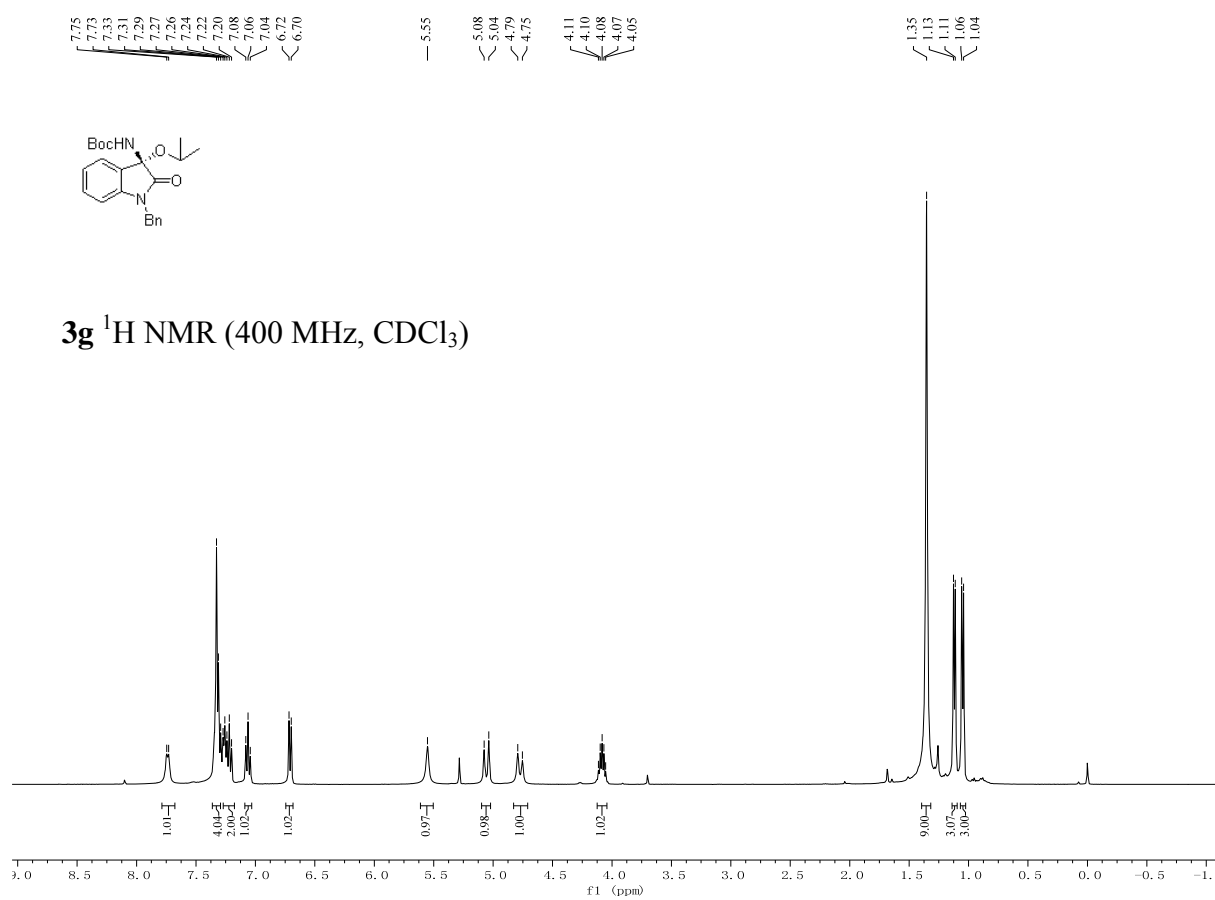


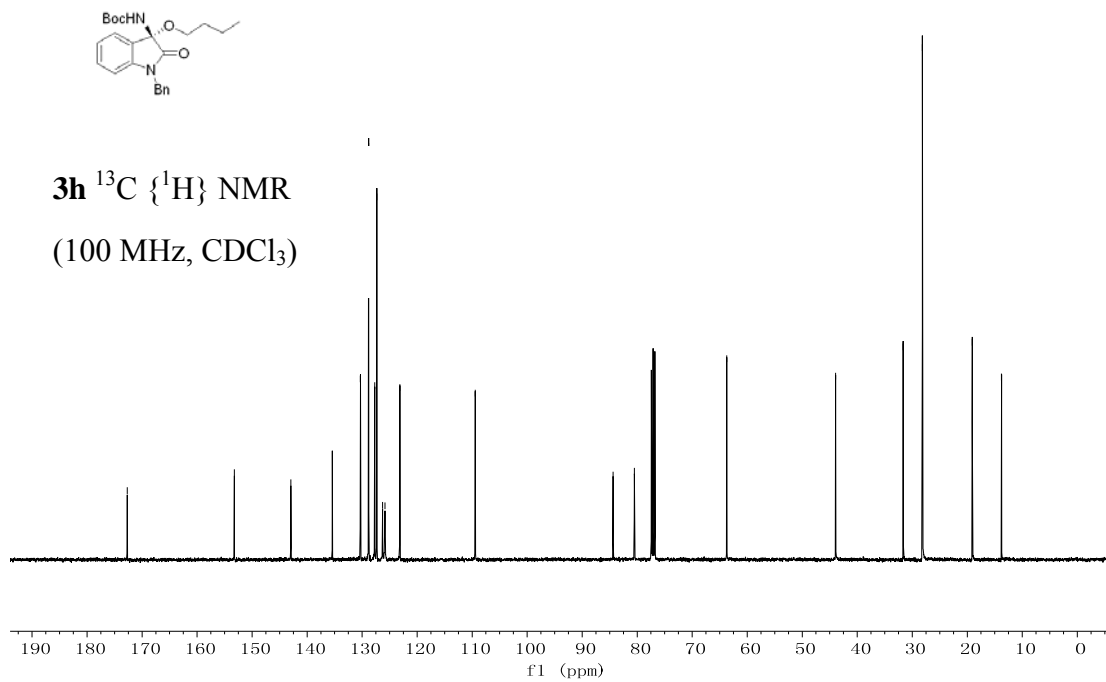
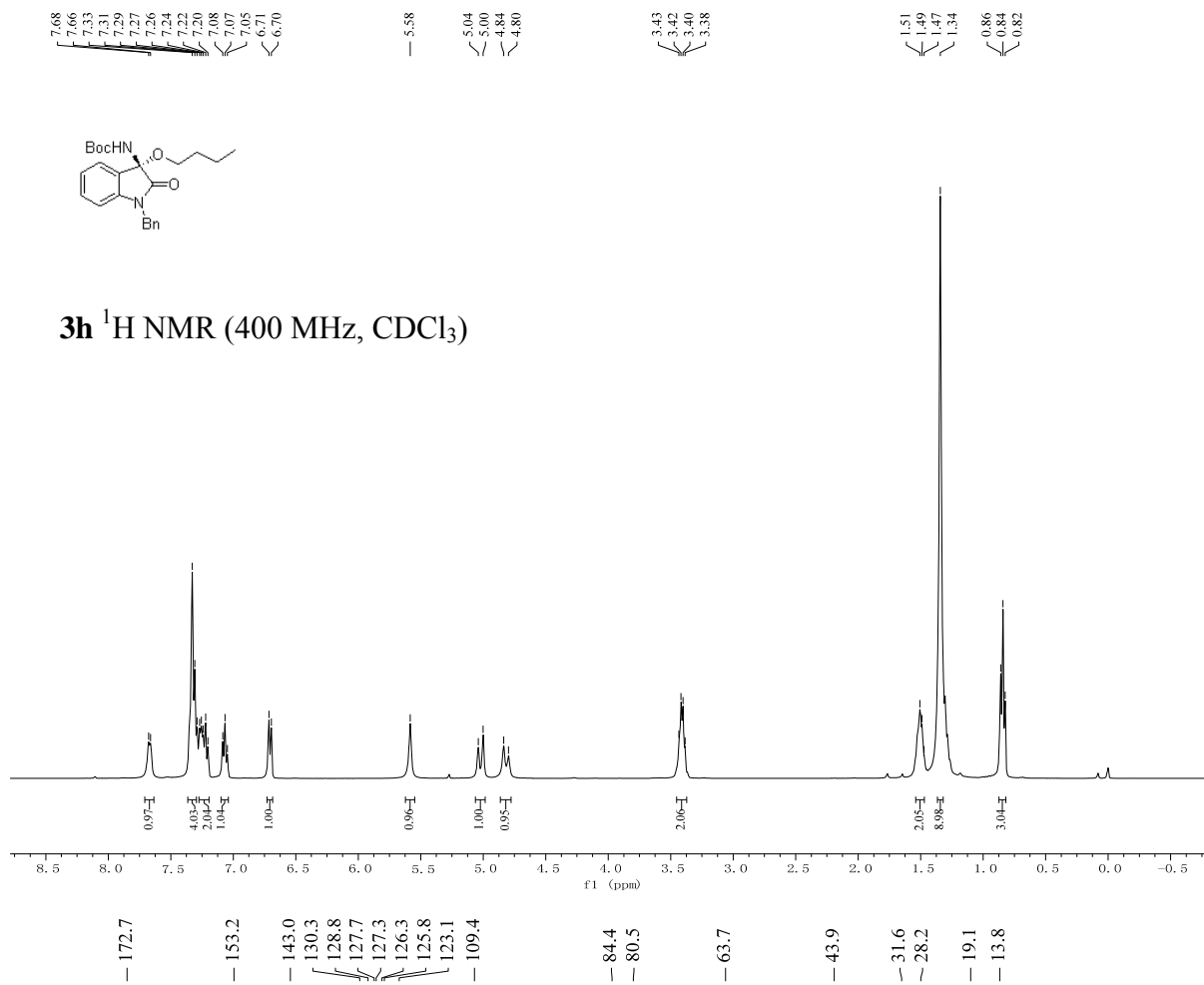


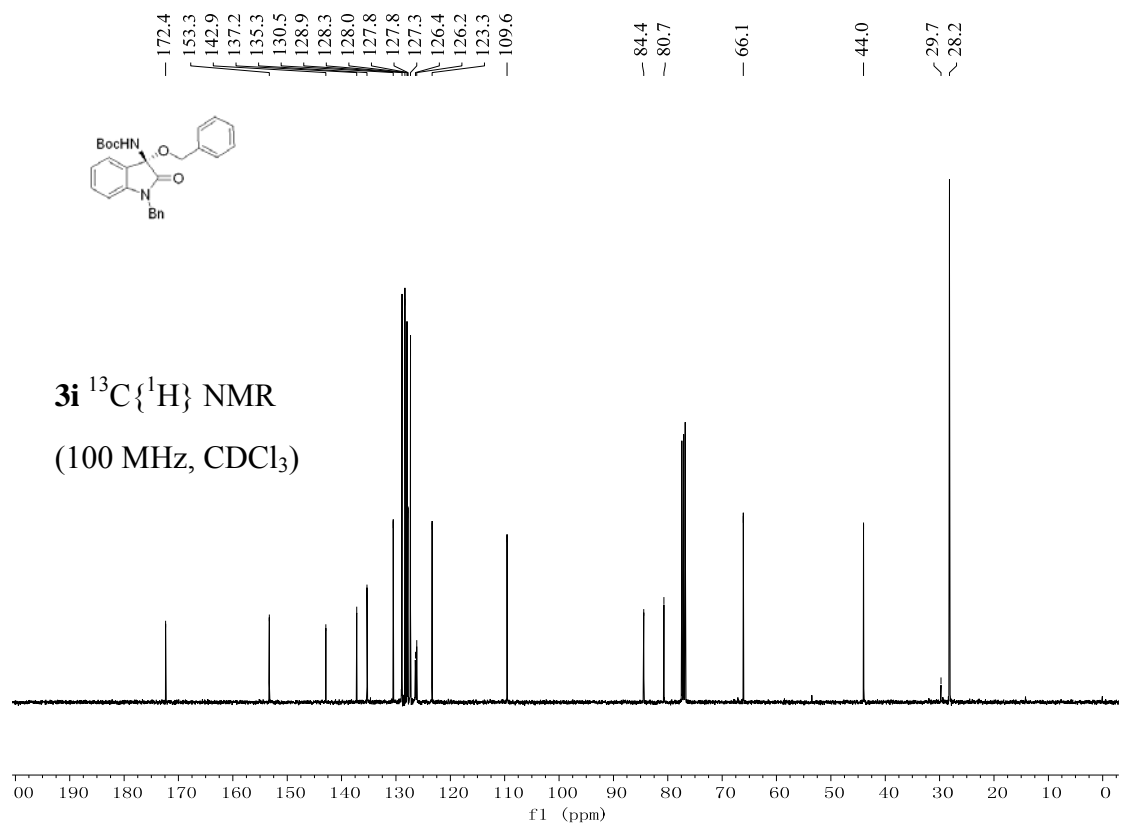
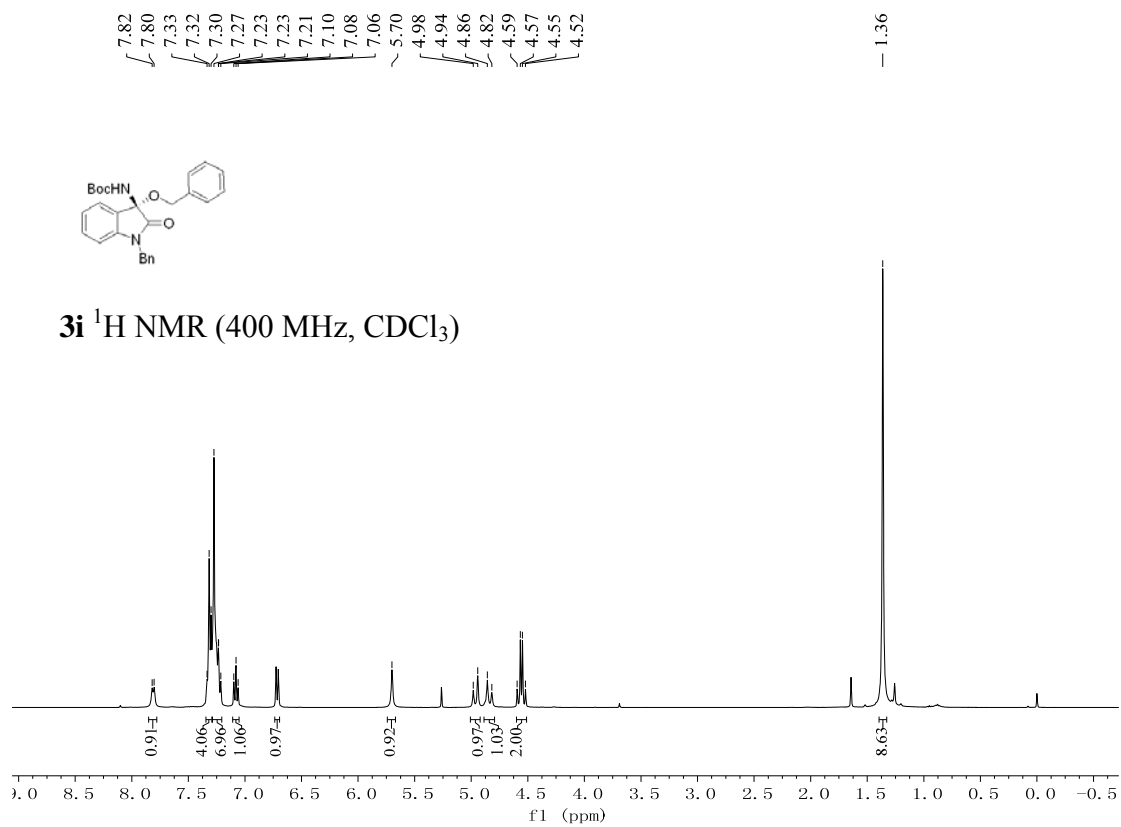






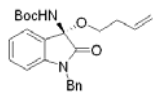




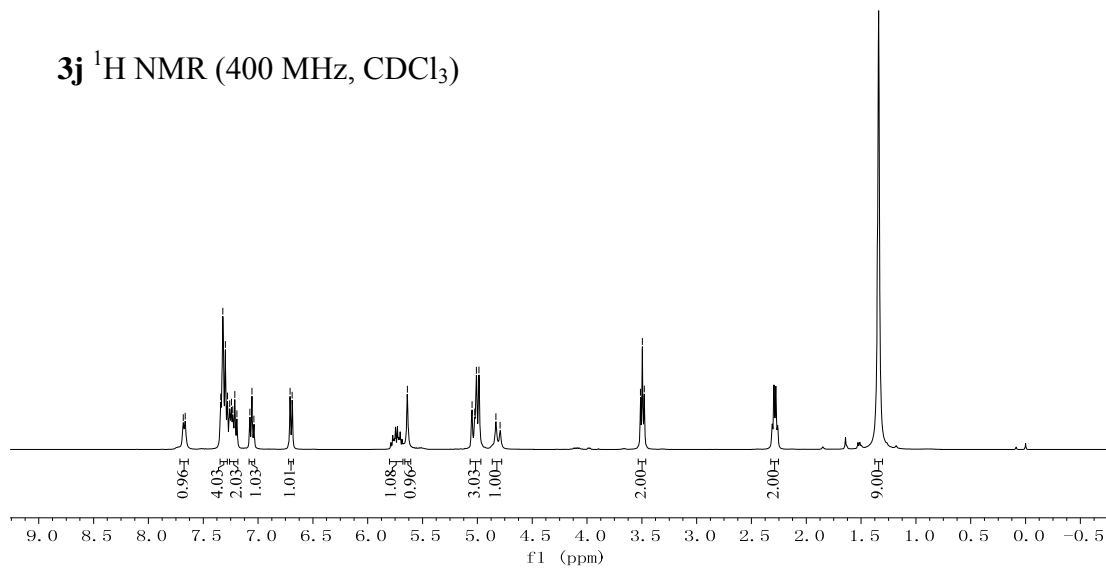


7.68
7.66
7.34
7.32
7.30
7.28
7.26
7.24
7.23
7.21
7.19
7.08
7.06
7.04
6.71
6.69
— 5.64
5.05
5.02
5.01
4.99
4.83
4.79

3.51
3.49
3.48



3j ^1H NMR (400 MHz, CDCl_3)



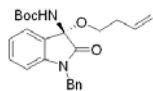
— 172.5
— 153.3
— 142.9
— 135.4
— 134.6
— 130.4
— 128.8
— 127.7
— 127.3
— 126.2
— 125.9
— 123.2
— 116.8
— 109.5

— 84.4
— 80.6

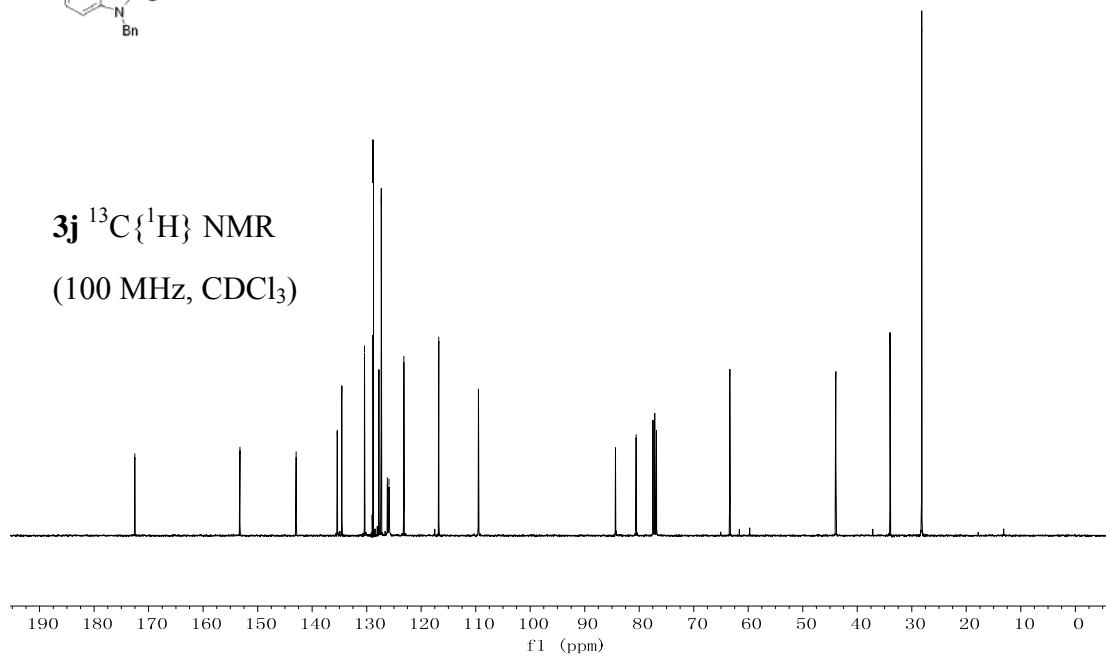
— 63.4

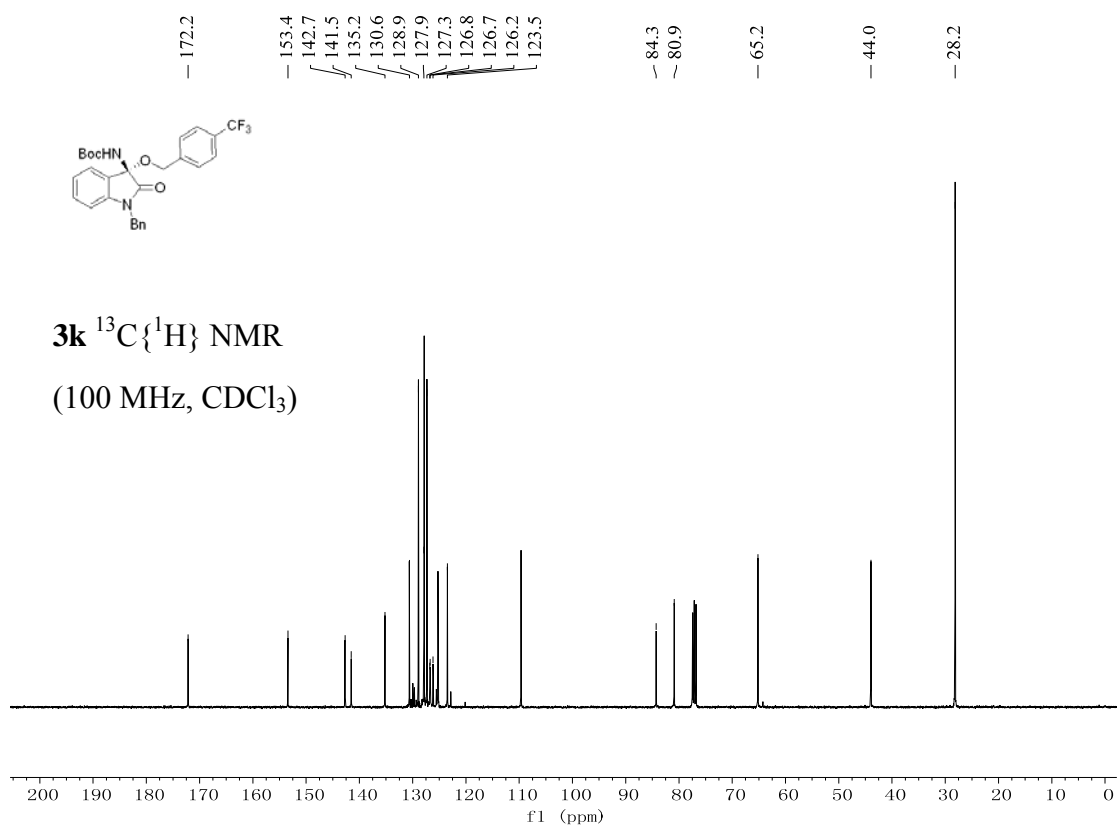
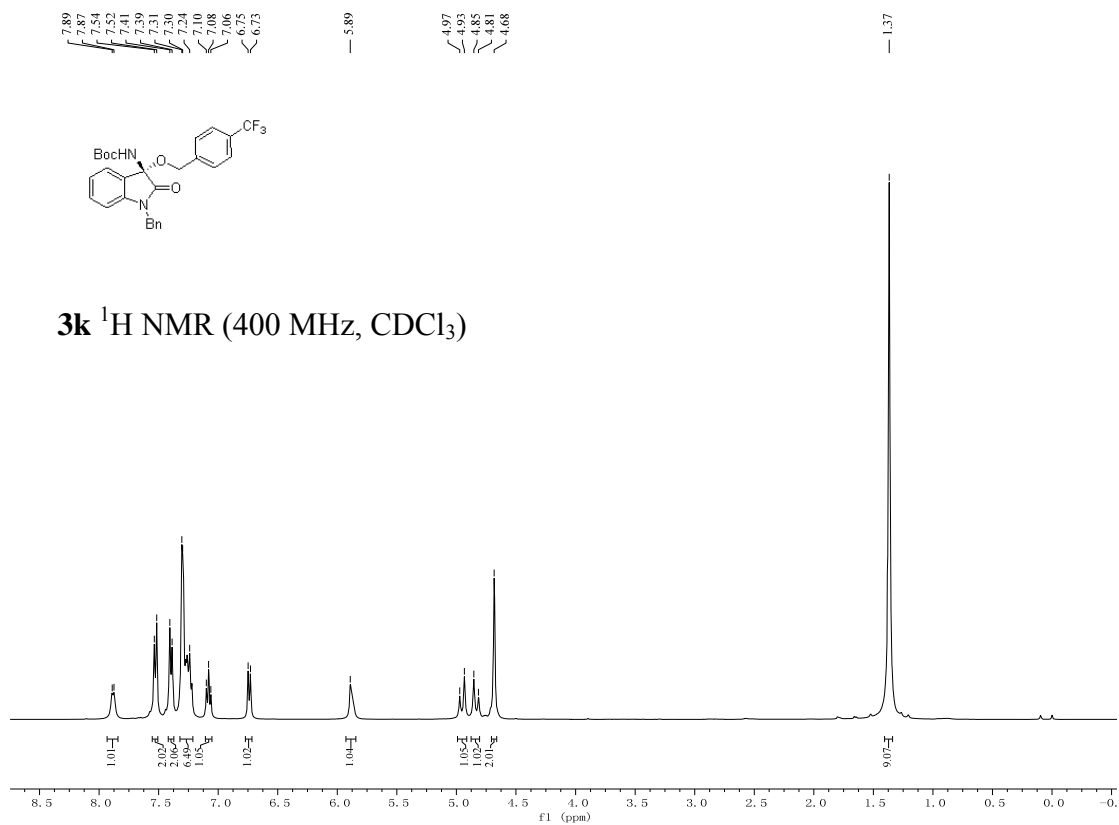
— 43.9

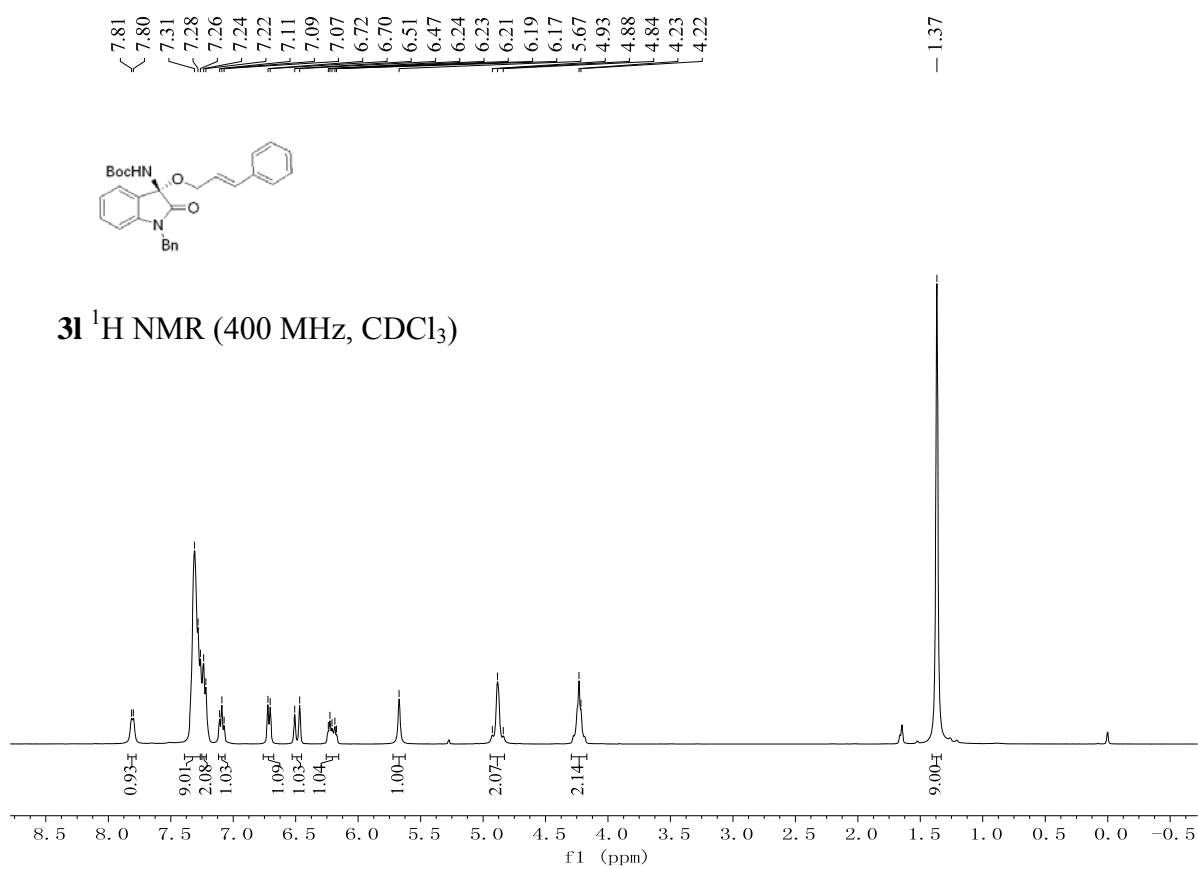
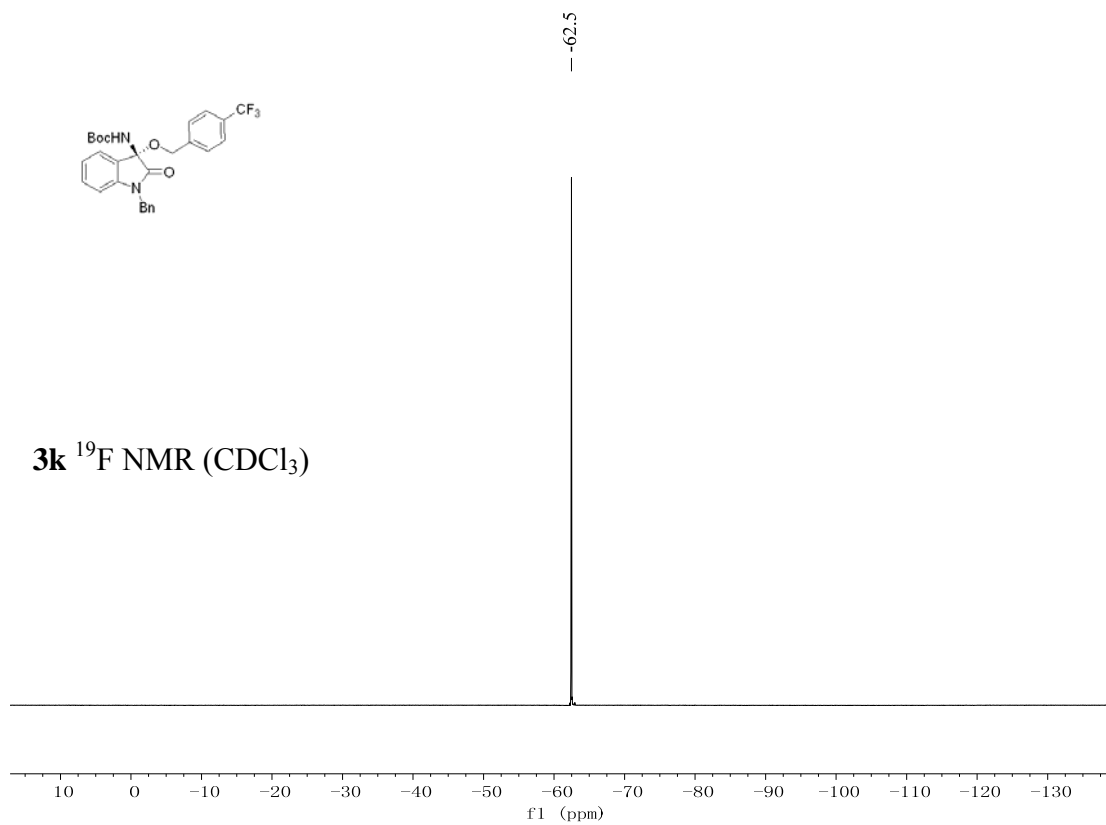
— 34.0
— 28.2

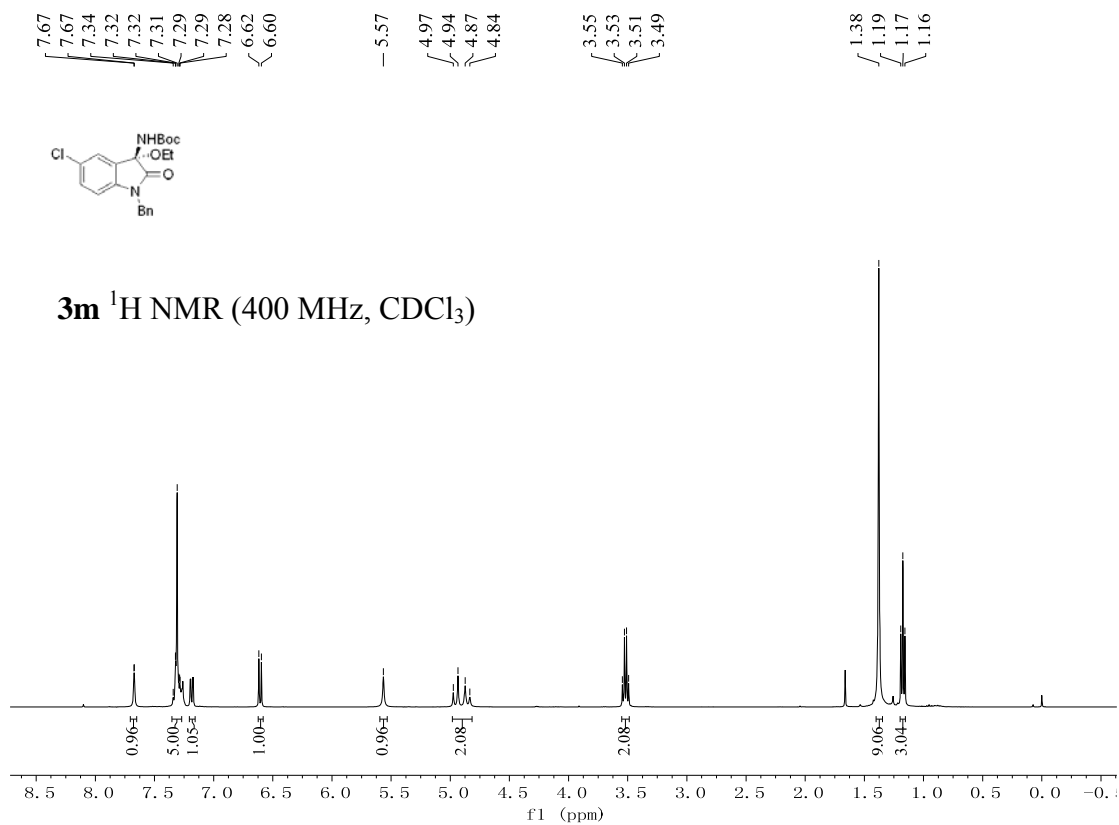
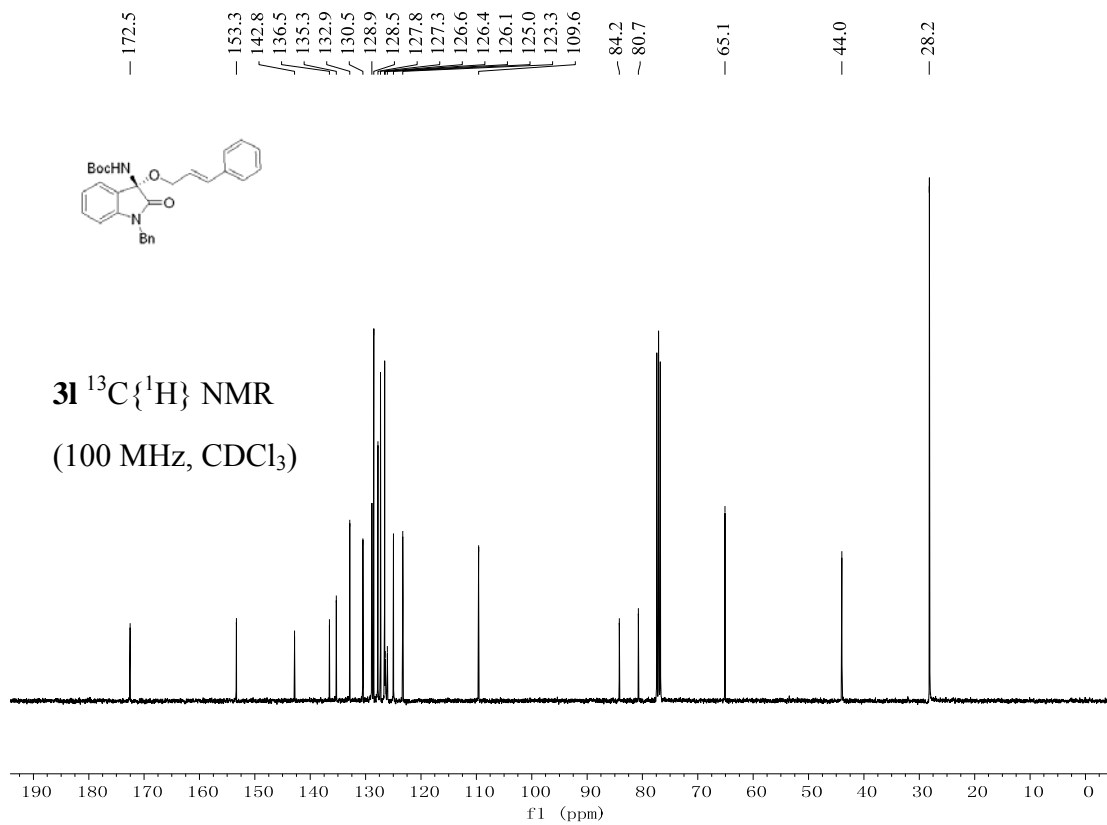


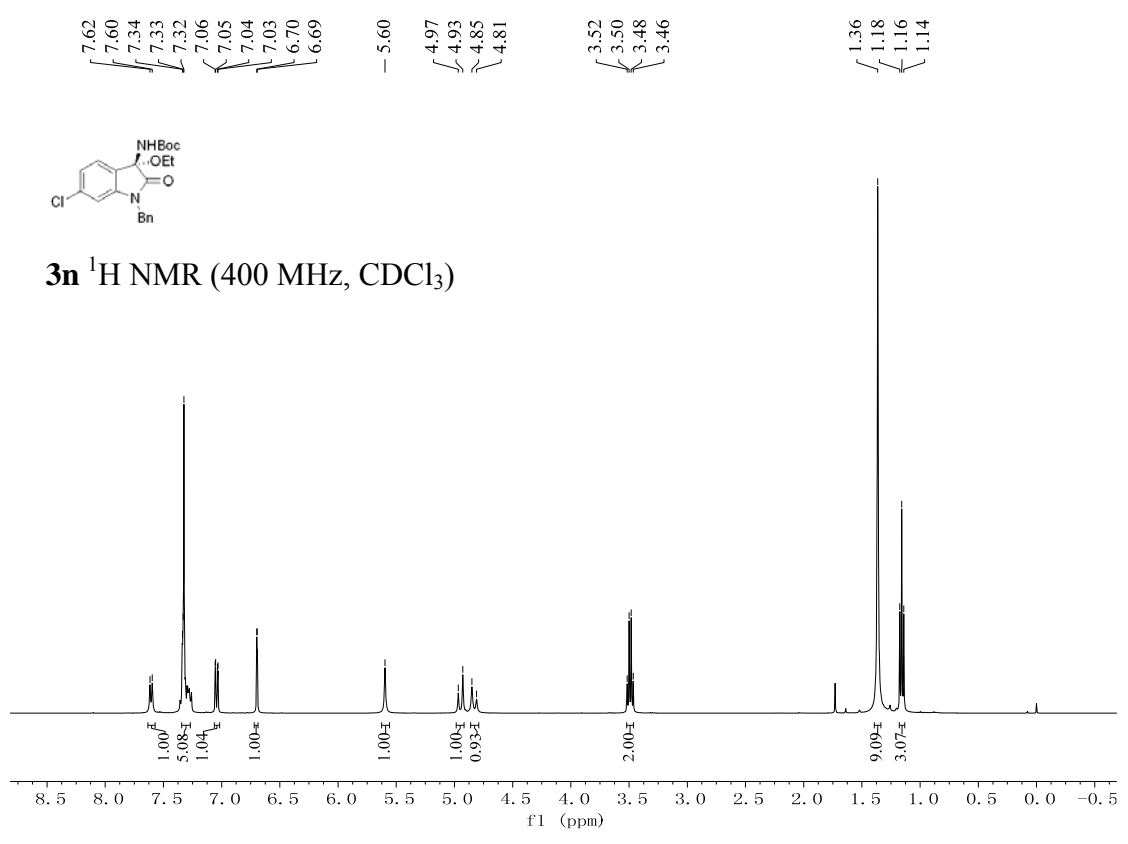
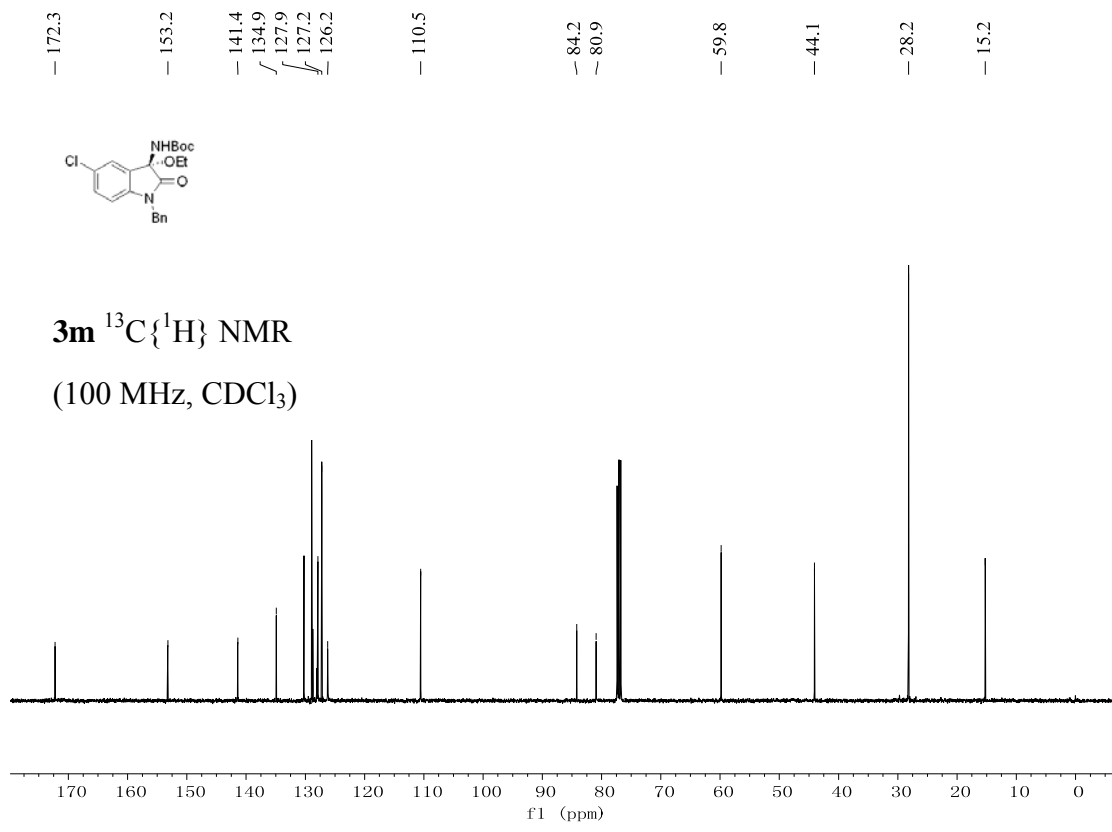
3j $^{13}\text{C}\{^1\text{H}\}$ NMR
(100 MHz, CDCl_3)

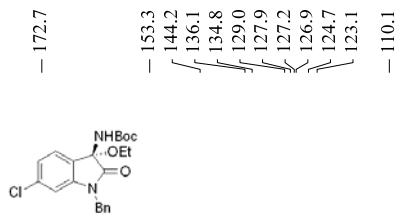






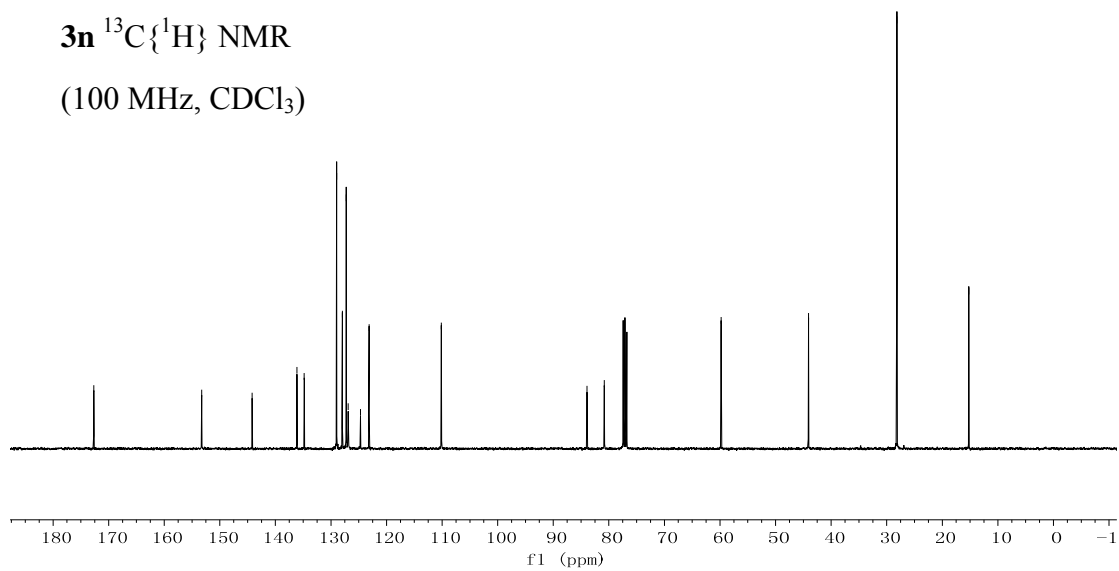




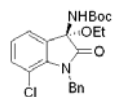


3n $^{13}\text{C}\{^1\text{H}\}$ NMR

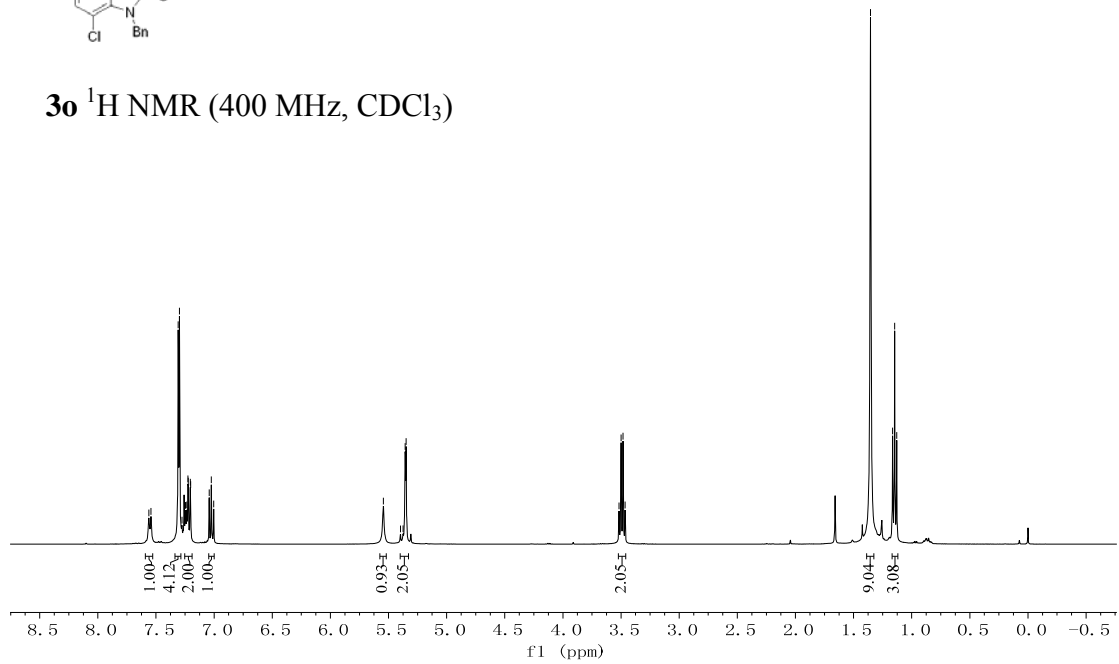
(100 MHz, CDCl_3)

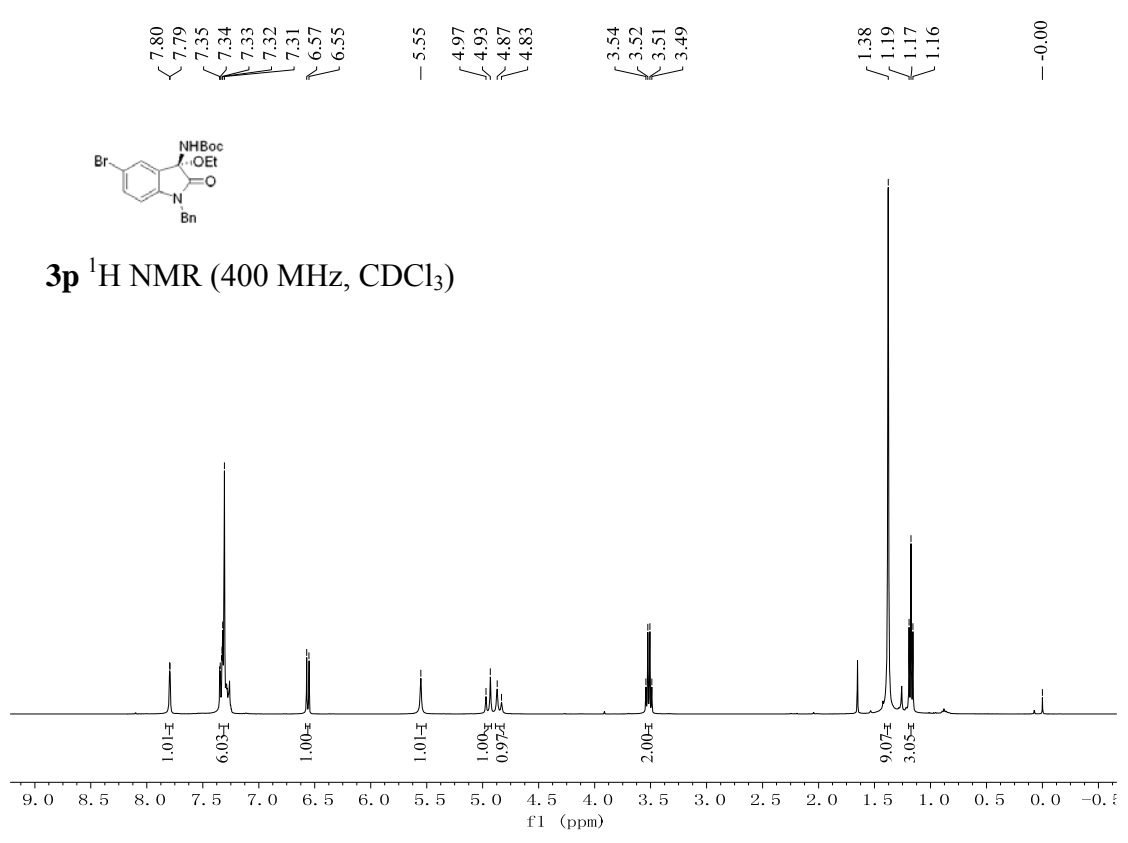
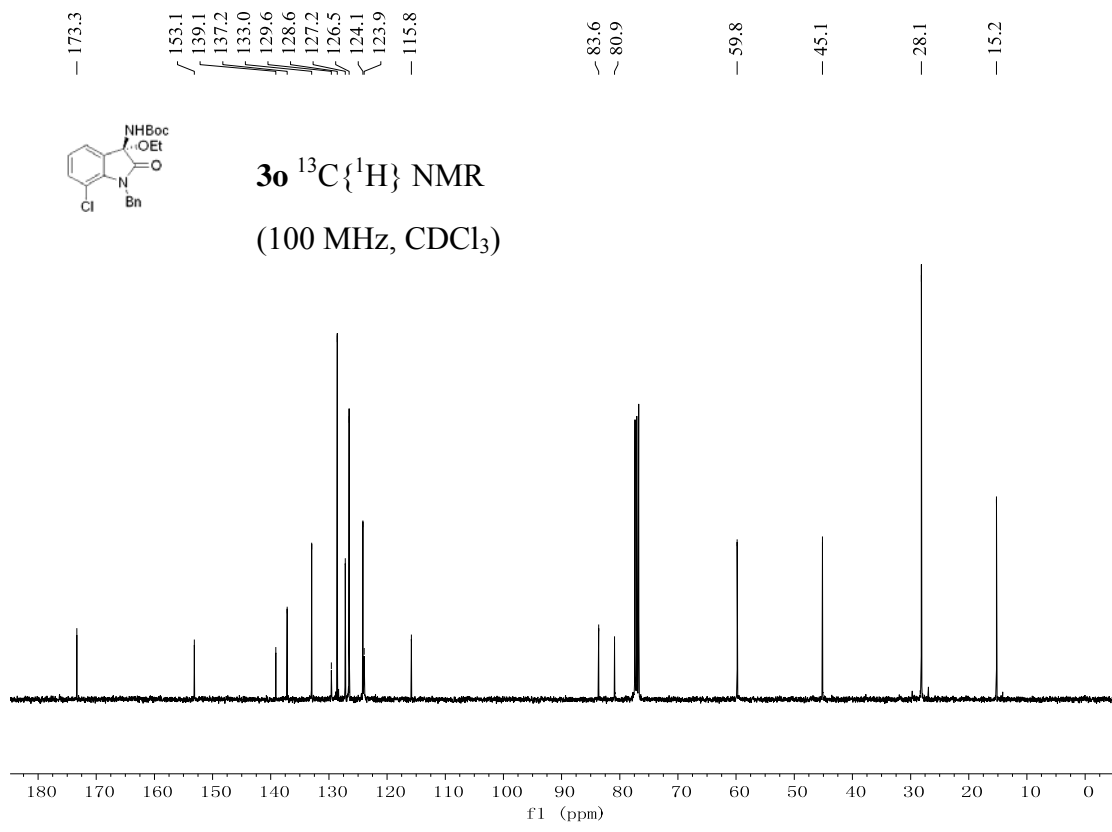


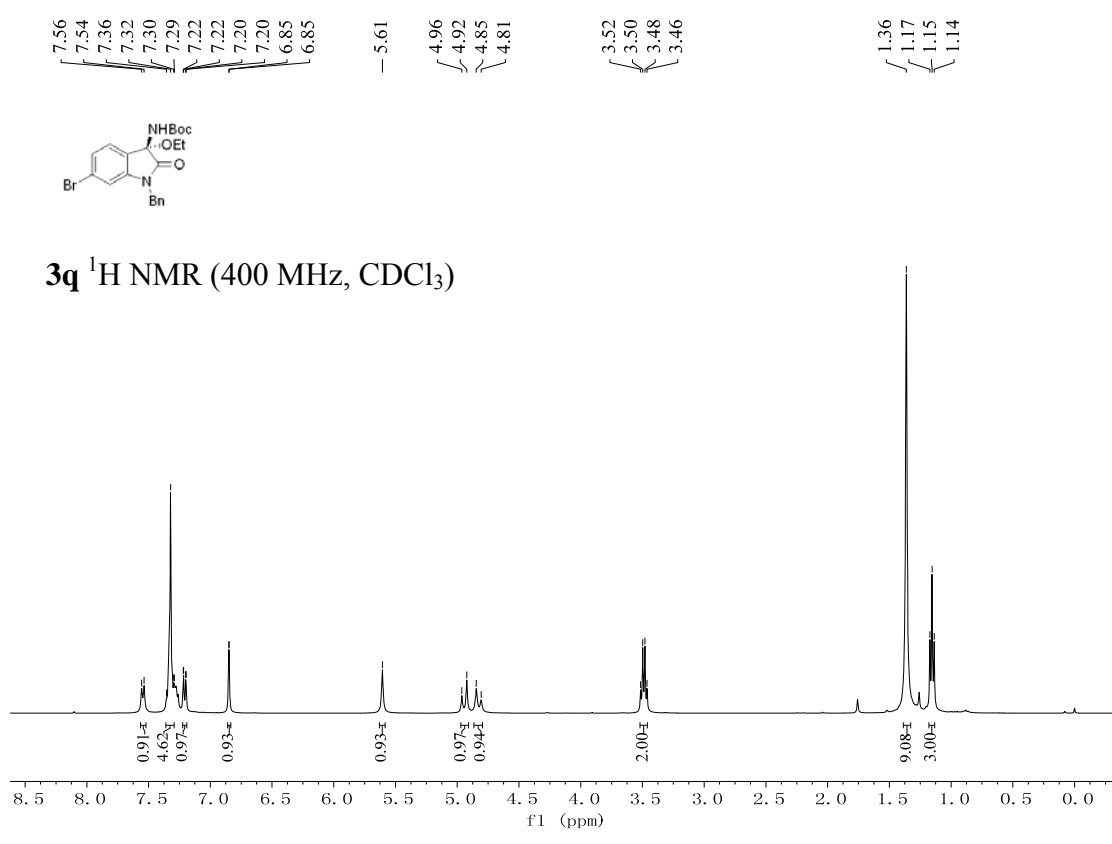
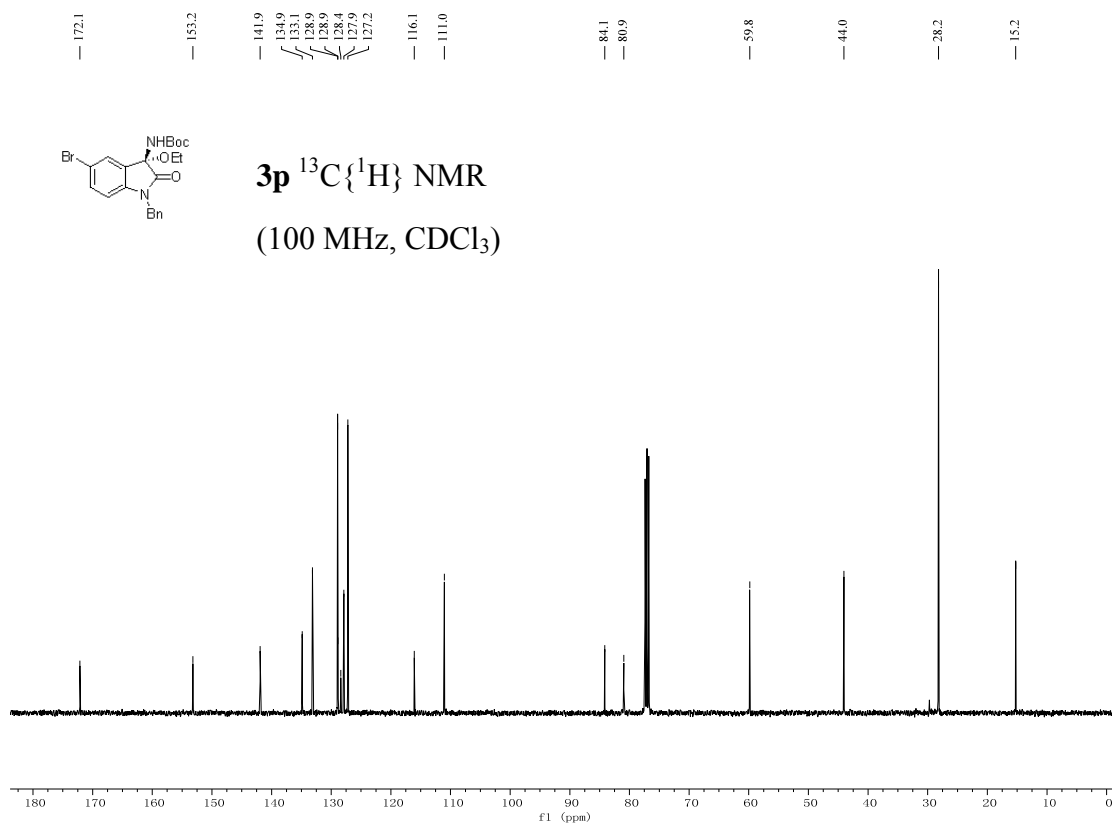
δ 7.56
 δ 7.54
 δ 7.31
 δ 7.30
 δ 7.28
 δ 7.25
 δ 7.24
 δ 7.23
 δ 7.22
 δ 7.20
 δ 7.20
 δ 7.04
 δ 7.02
 δ 7.00
 δ 5.54
 δ 5.40
 δ 5.38
 δ 5.36
 δ 5.35
 δ 3.52
 δ 3.50
 δ 3.48
 δ 3.46
 δ 1.35
 δ 1.16
 δ 1.15
 δ 1.13

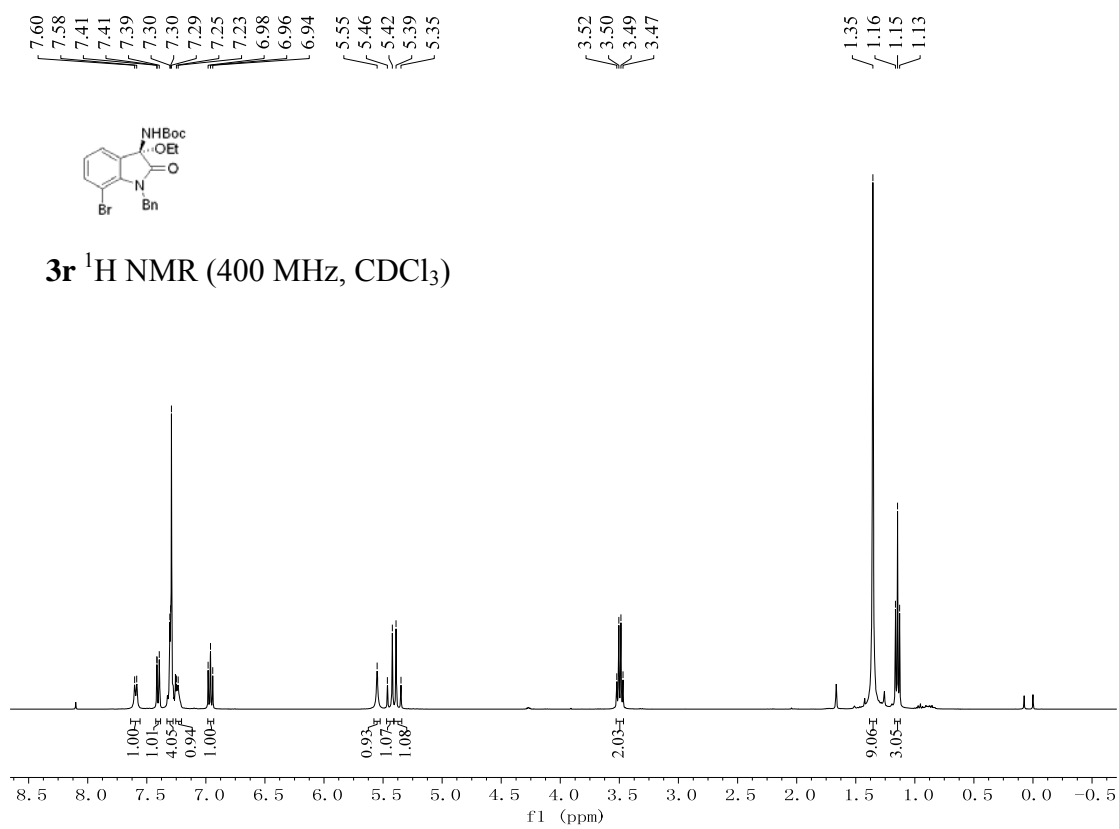
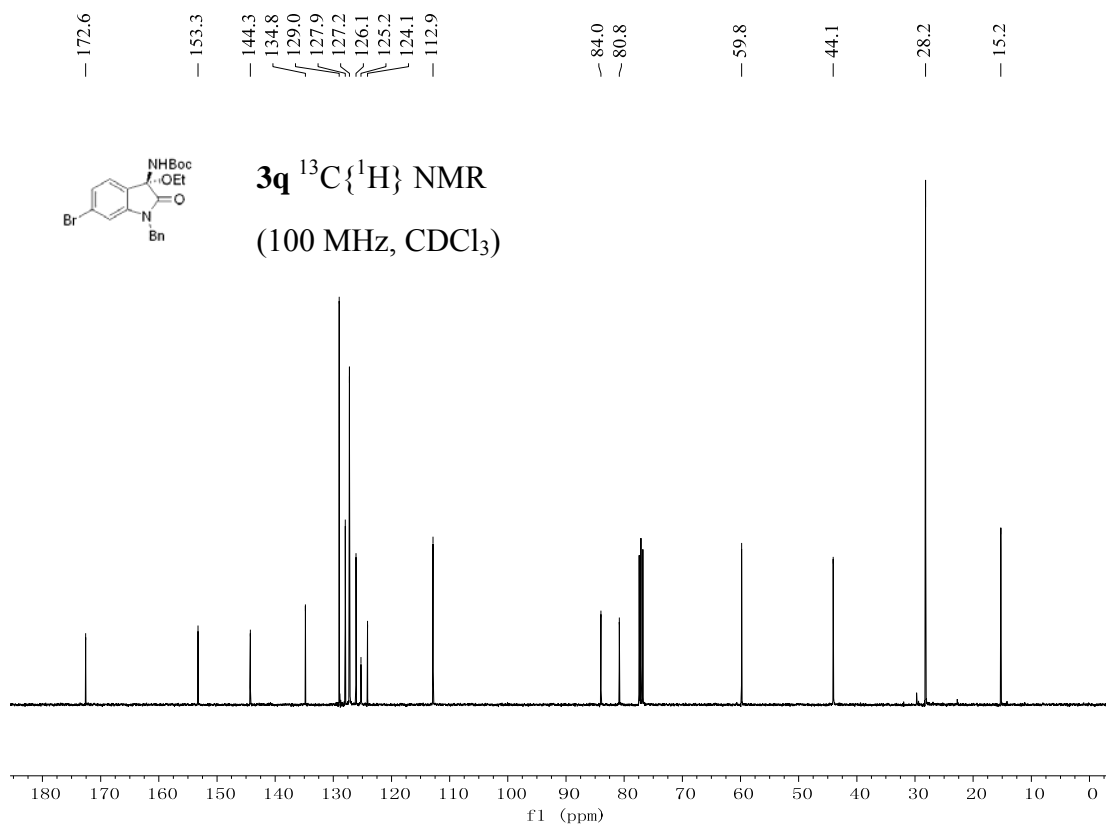


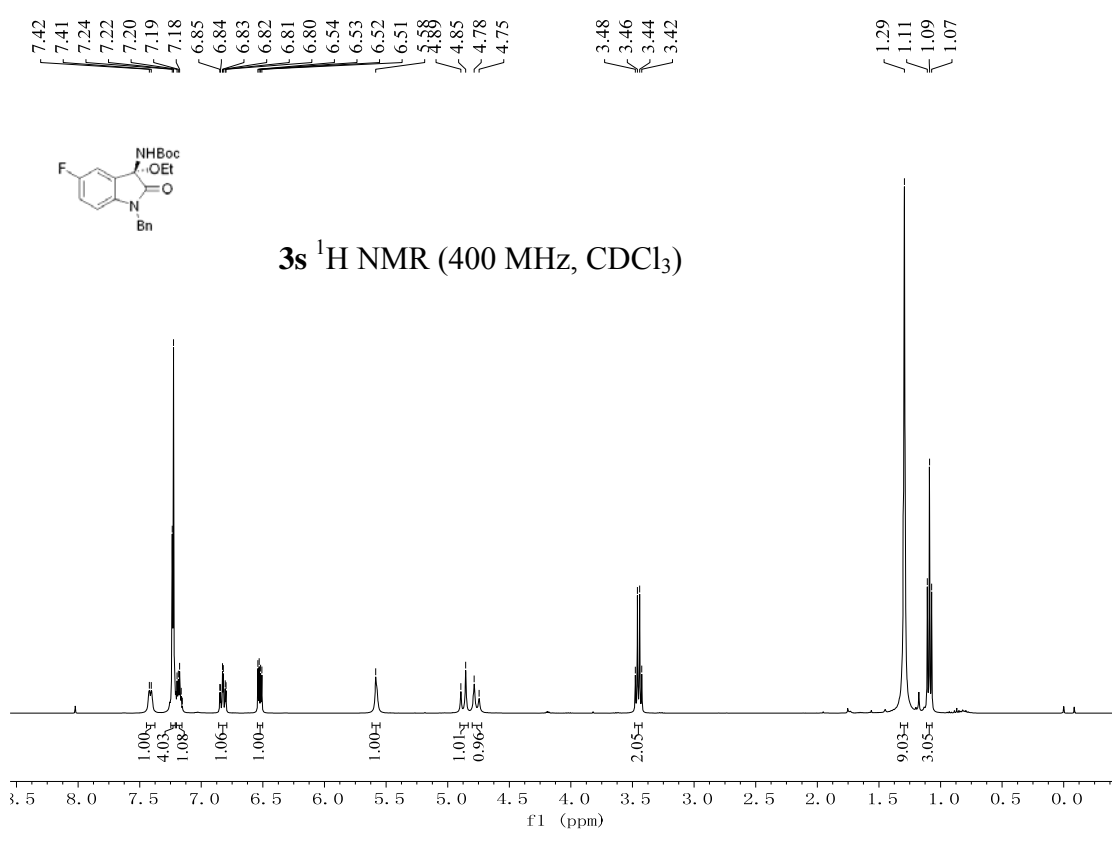
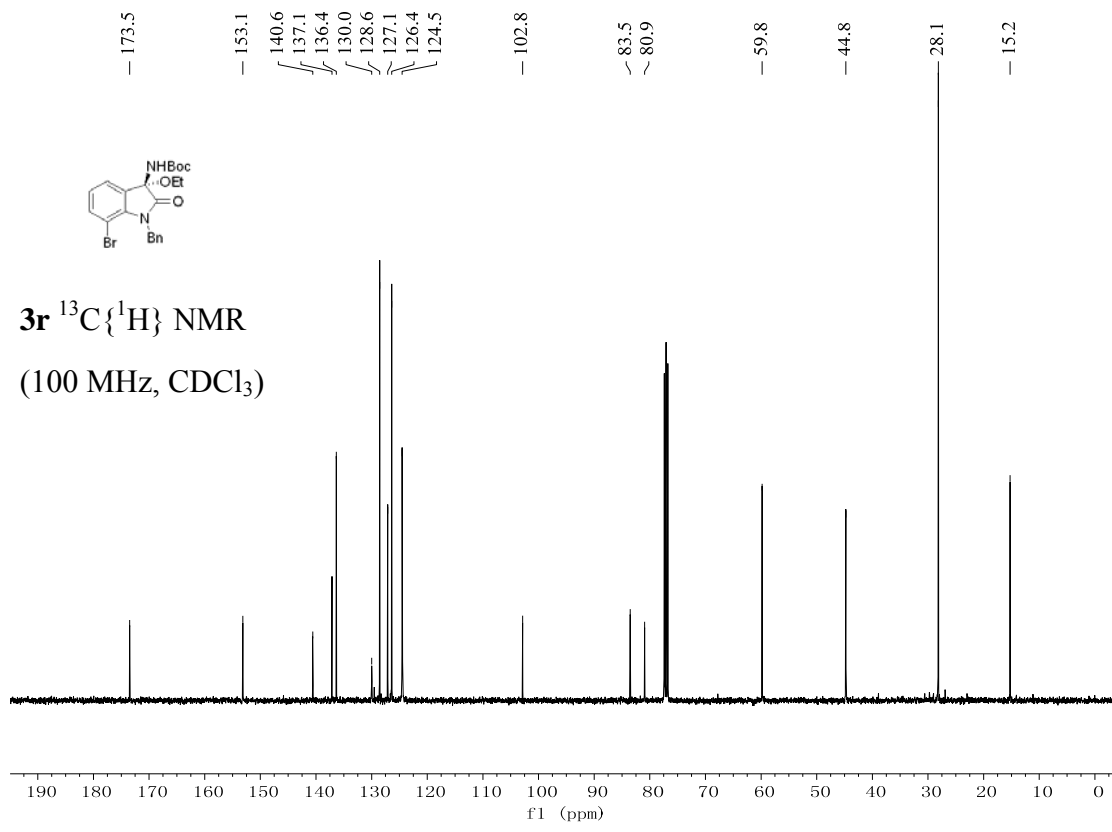
3o ^1H NMR (400 MHz, CDCl_3)

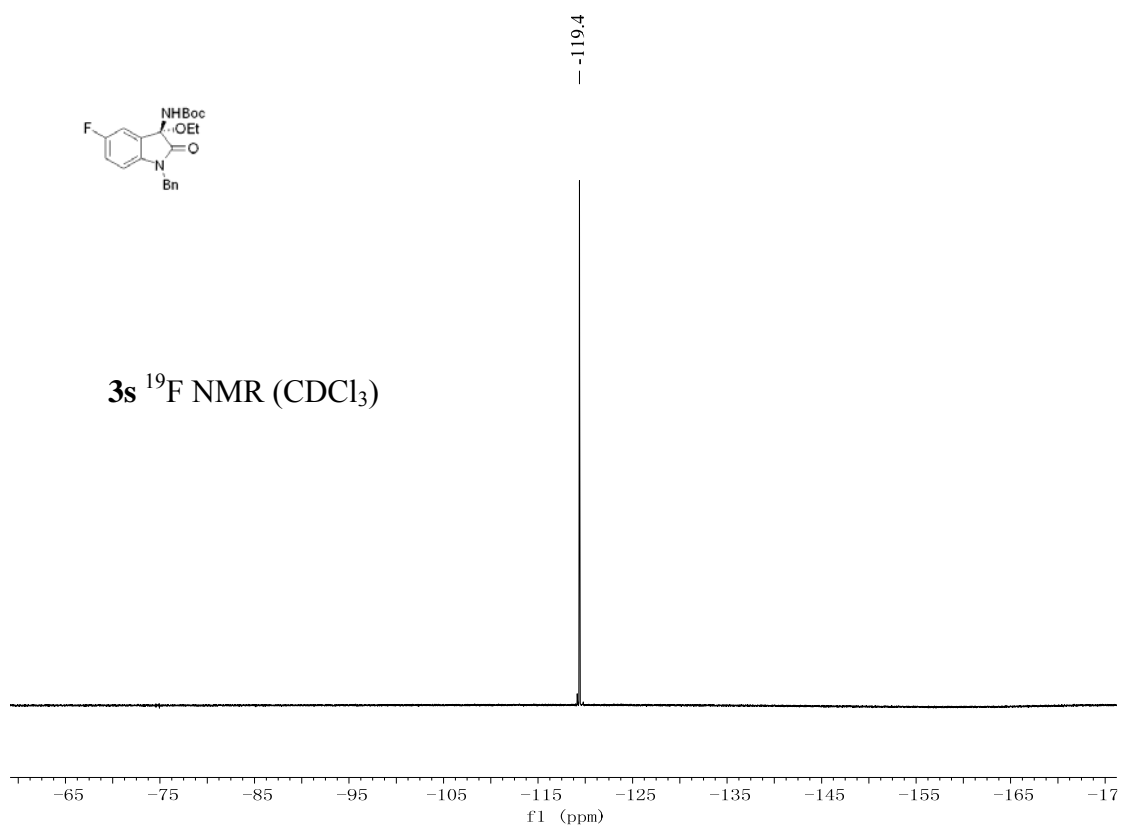
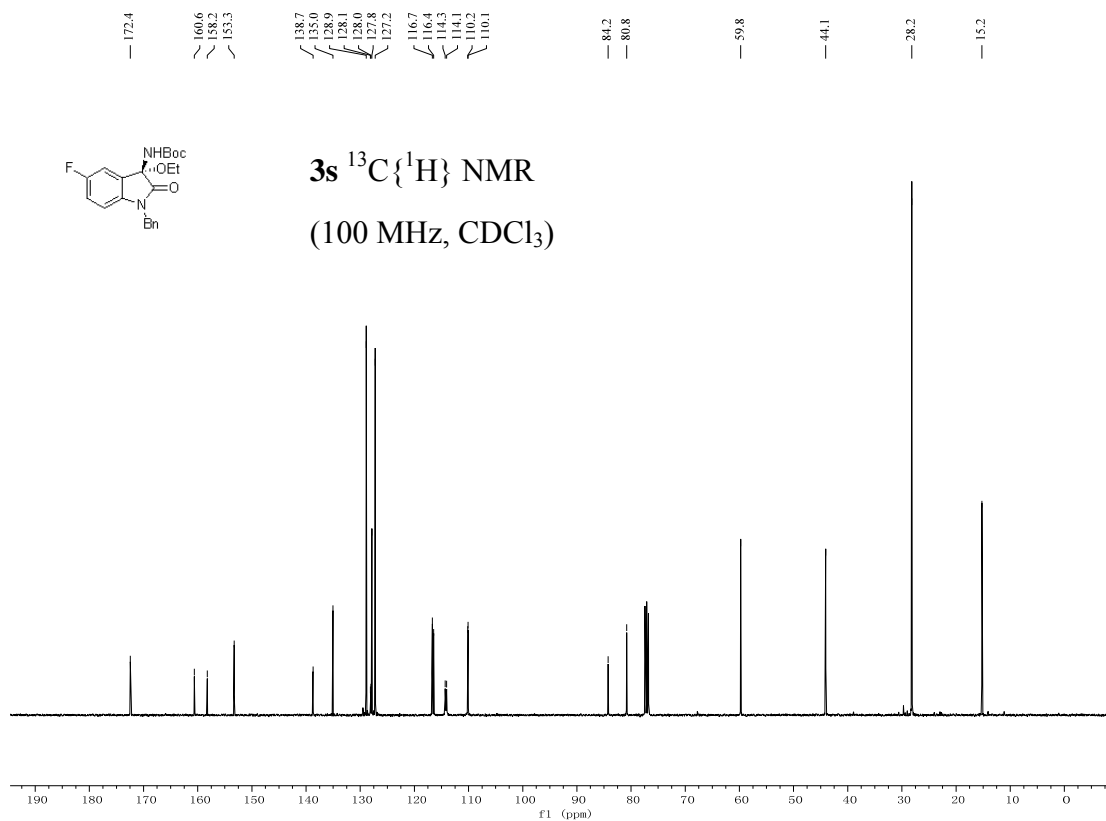


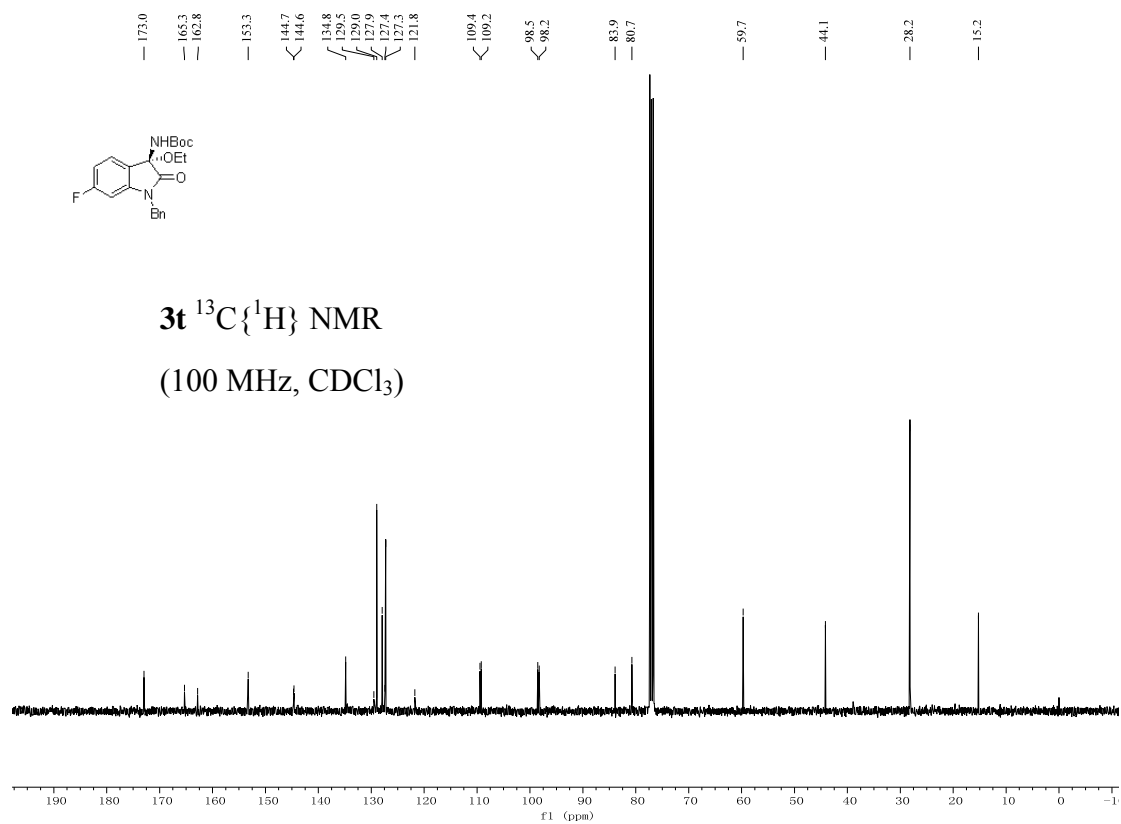
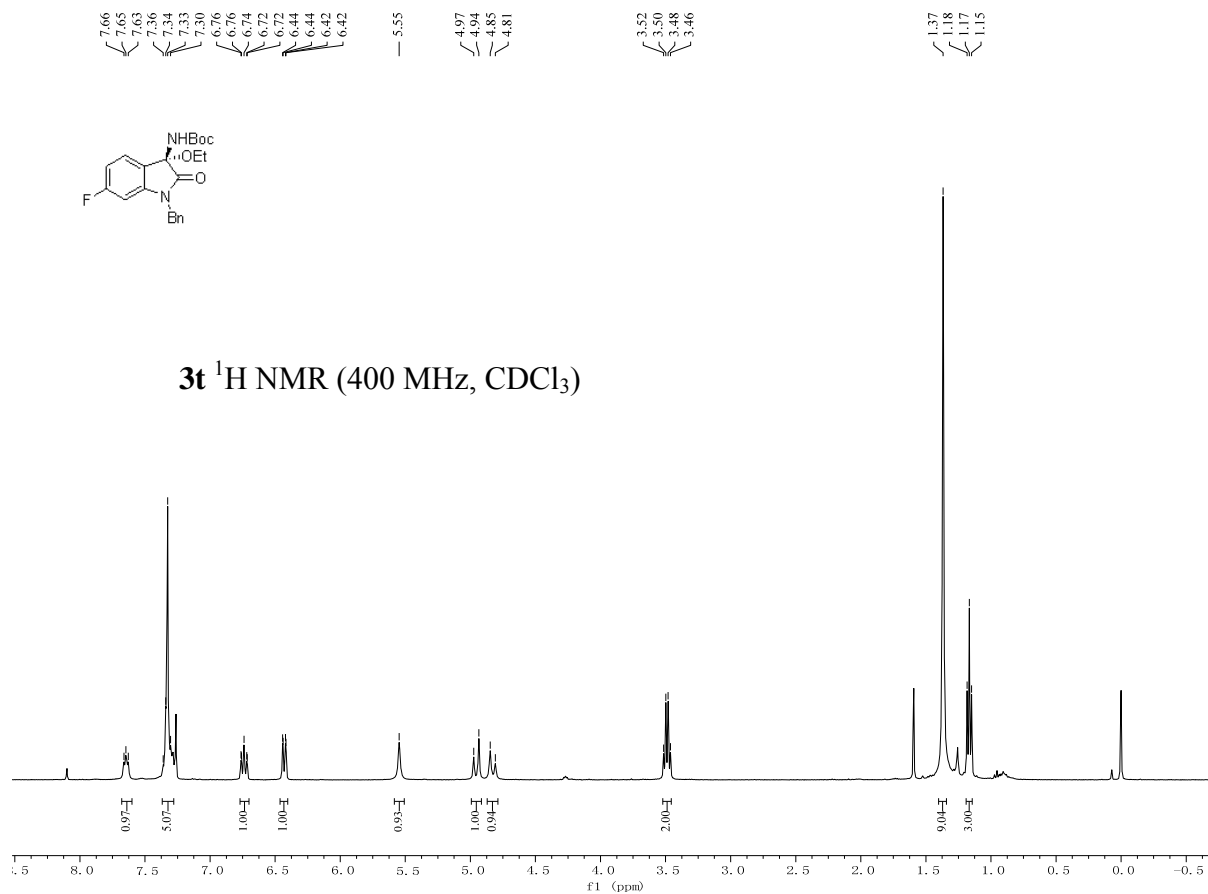


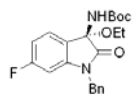




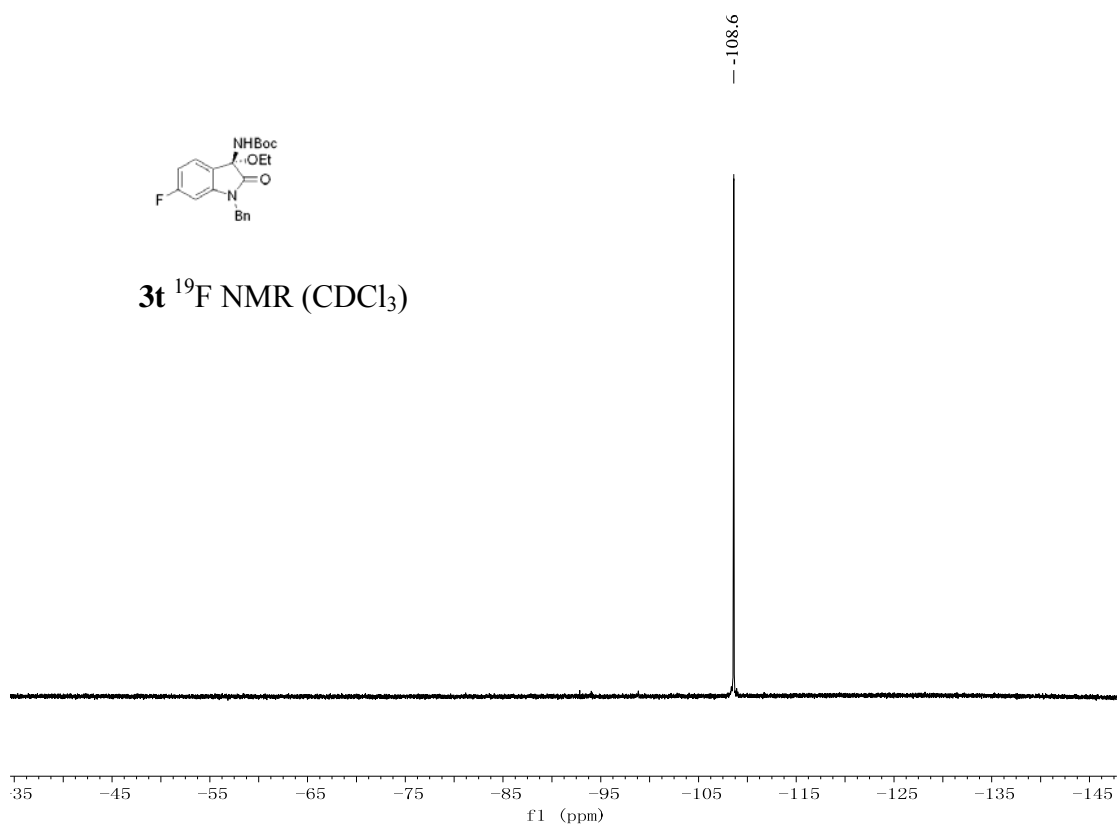








3t ^{19}F NMR (CDCl_3)

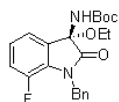


7.44
7.36
7.32
7.32
7.31
7.26
7.27
7.03
7.02
7.01

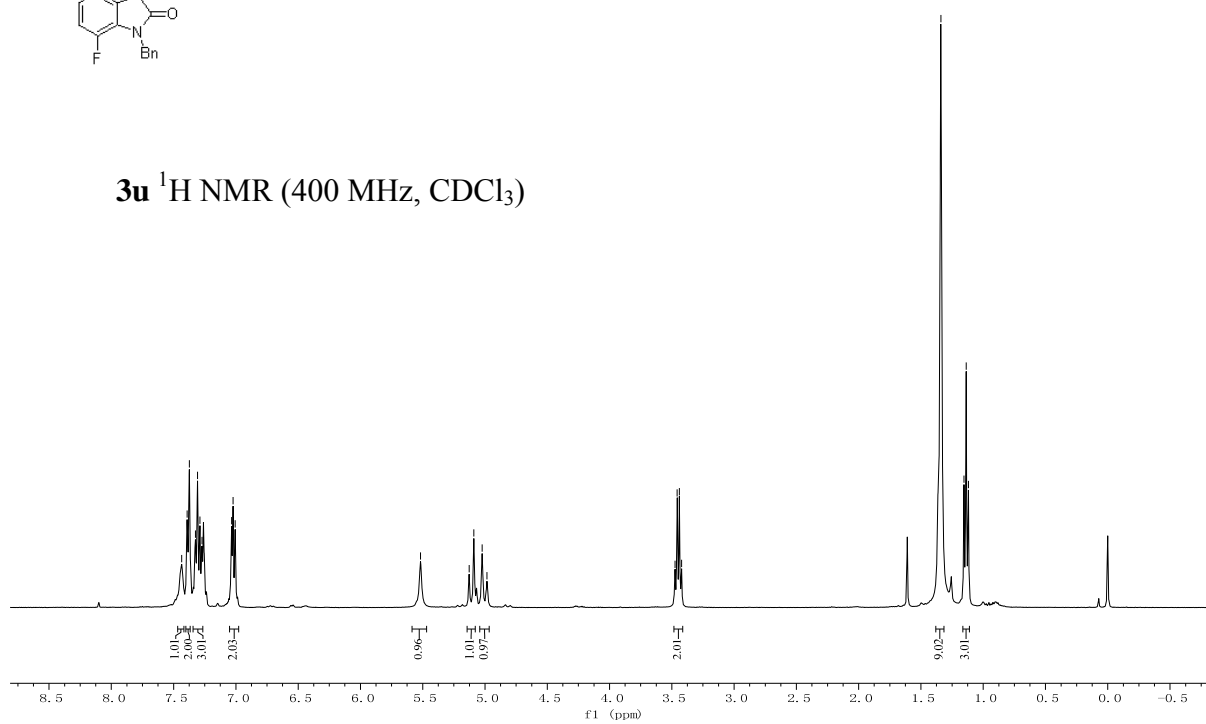
5.52
5.13
5.06
5.02
4.98

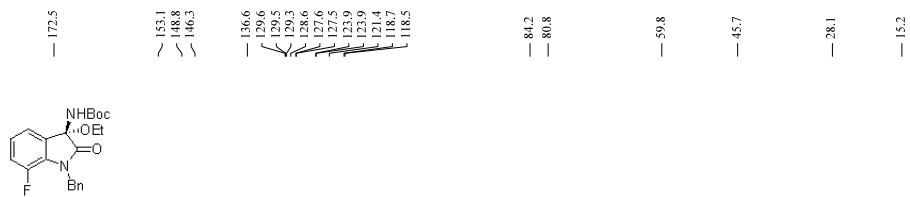
3.47
3.46
3.44
3.42

1.34
1.15
1.14
1.12

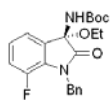
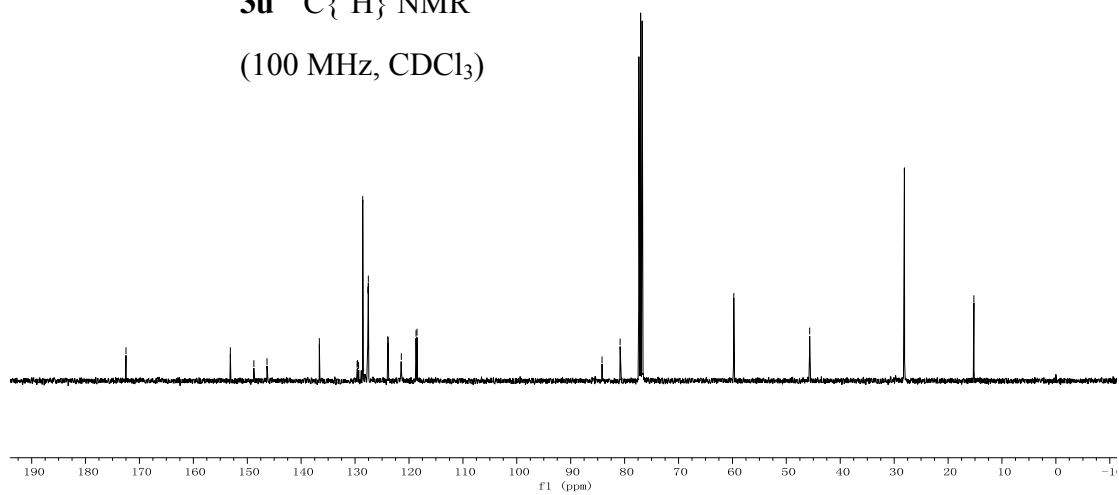


3u ^1H NMR (400 MHz, CDCl_3)

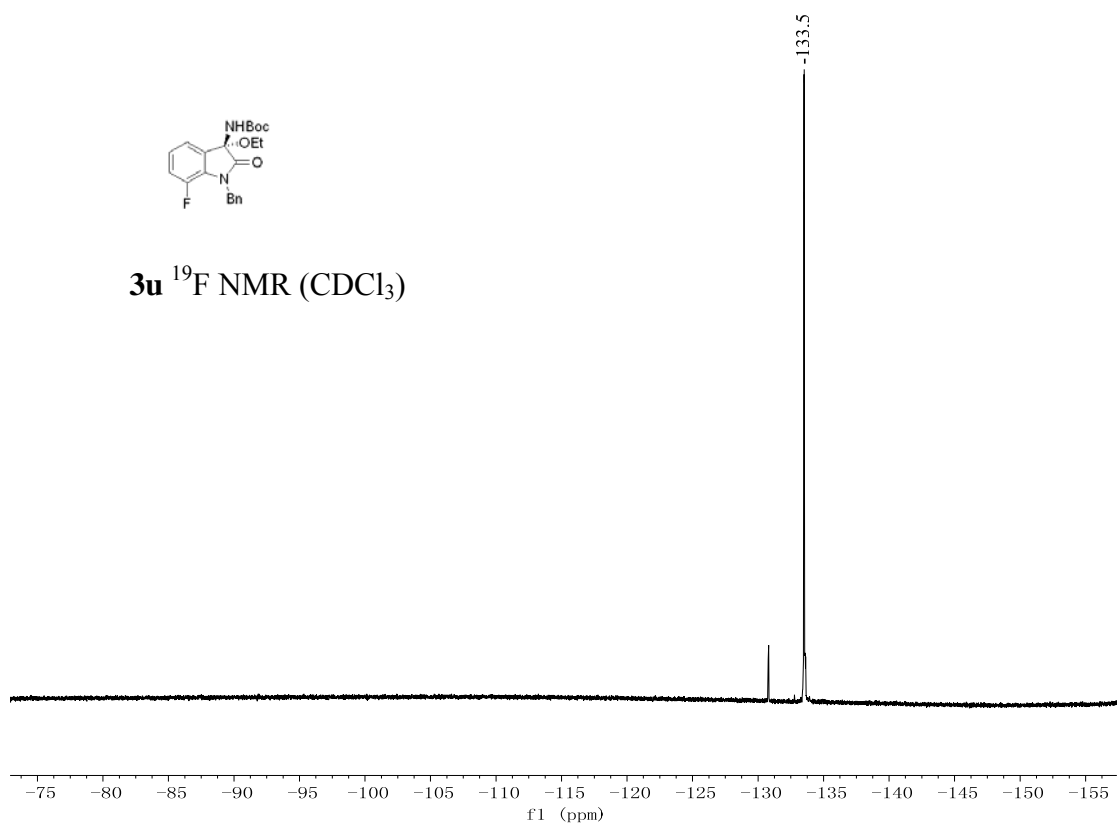


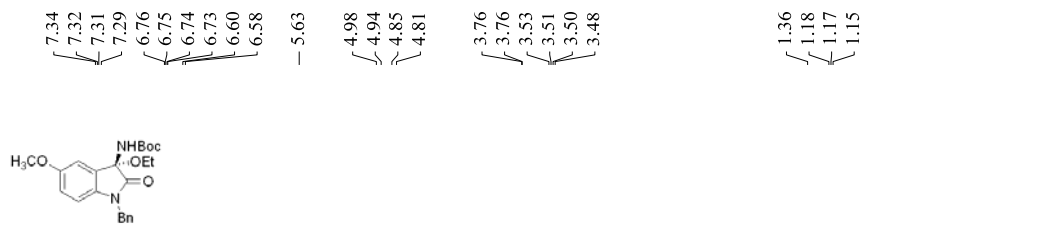


3u $^{13}\text{C}\{^1\text{H}\}$ NMR
(100 MHz, CDCl_3)

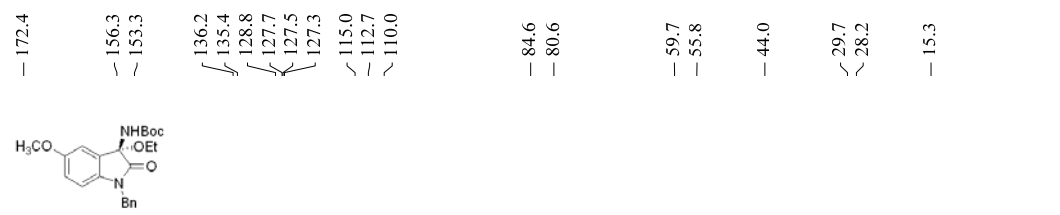
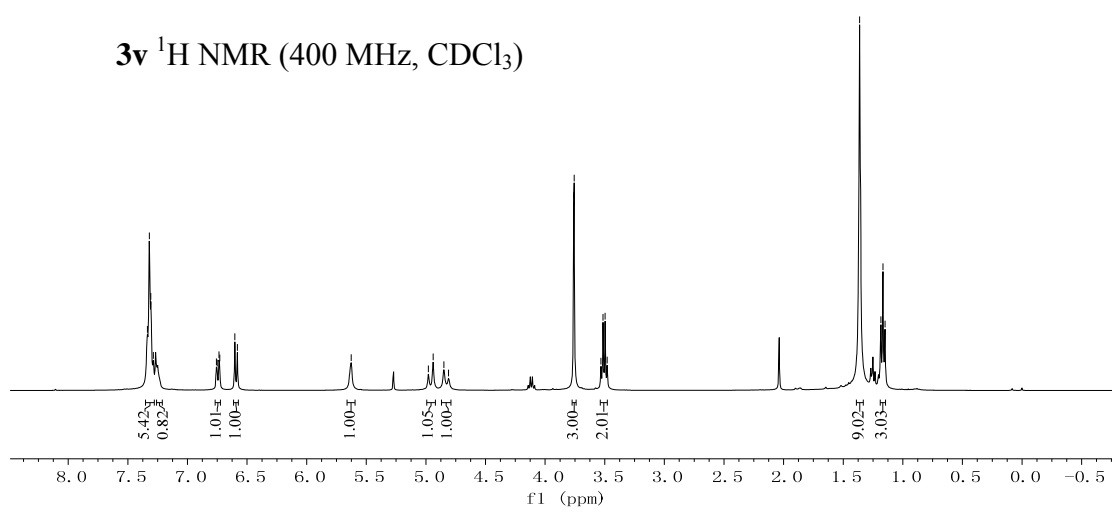


3u ^{19}F NMR (CDCl_3)

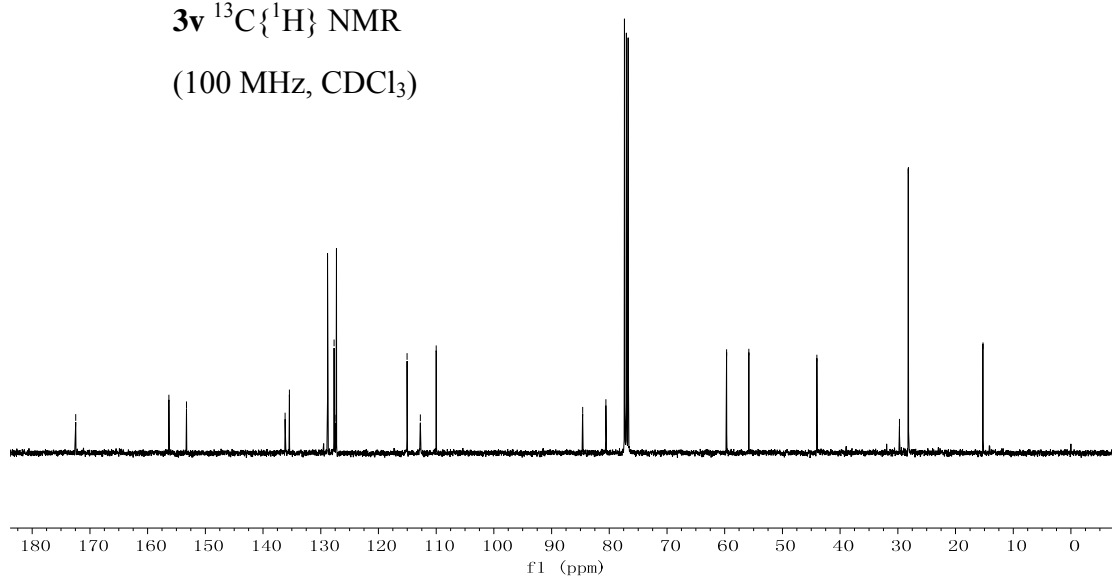


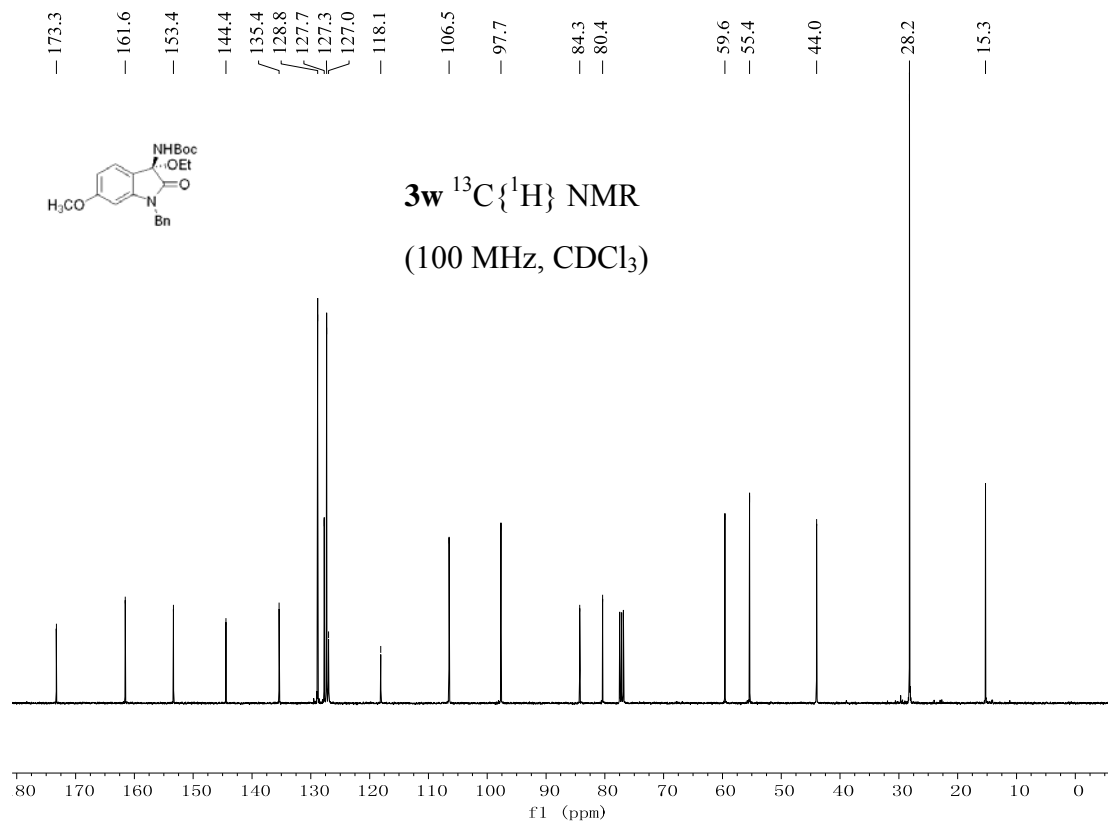
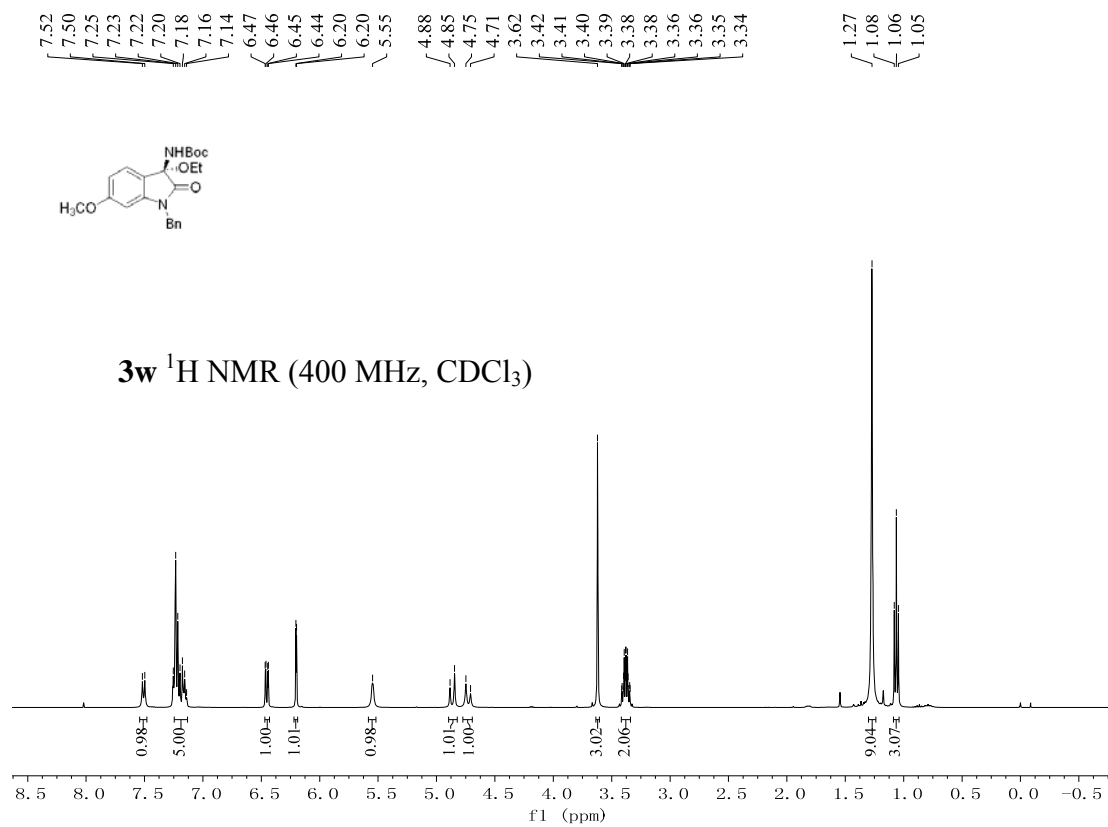


3v ^1H NMR (400 MHz, CDCl_3)



3v $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



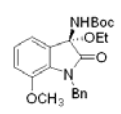


7.35
7.33
7.29
7.27
7.25
7.22
7.20
7.18
7.05
7.03
7.01
6.87
6.85

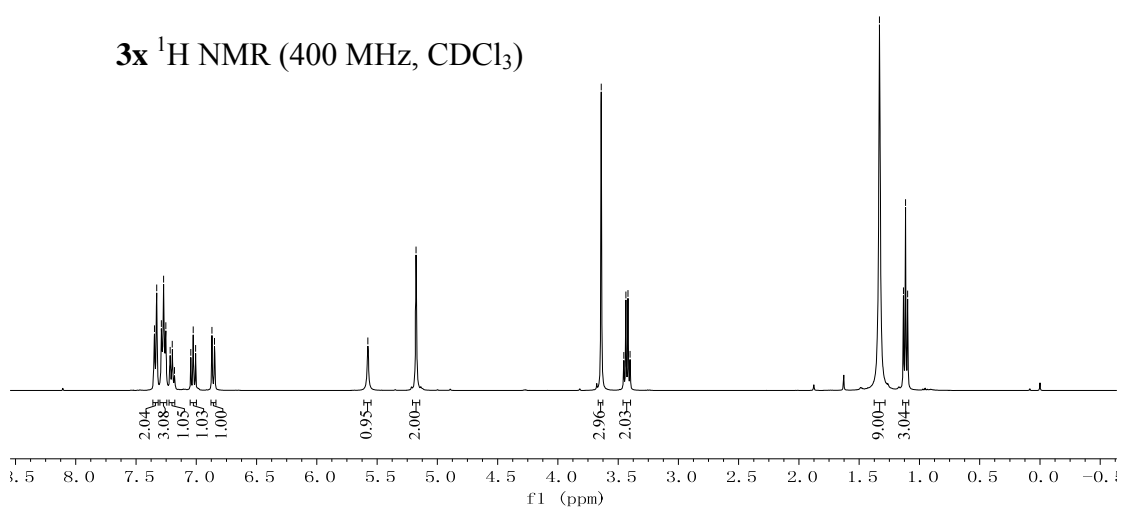
— 5.58 —
— 5.18 —

3.64
3.45
3.44
3.42
3.40

1.33
1.13
1.12
1.10



3x ¹H NMR (400 MHz, CDCl₃)



173.1
153.2
145.2
138.1
131.0
128.3
128.0
127.3
127.0
123.9
118.1
114.6

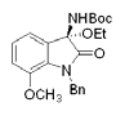
84.3
80.5

59.6
55.8

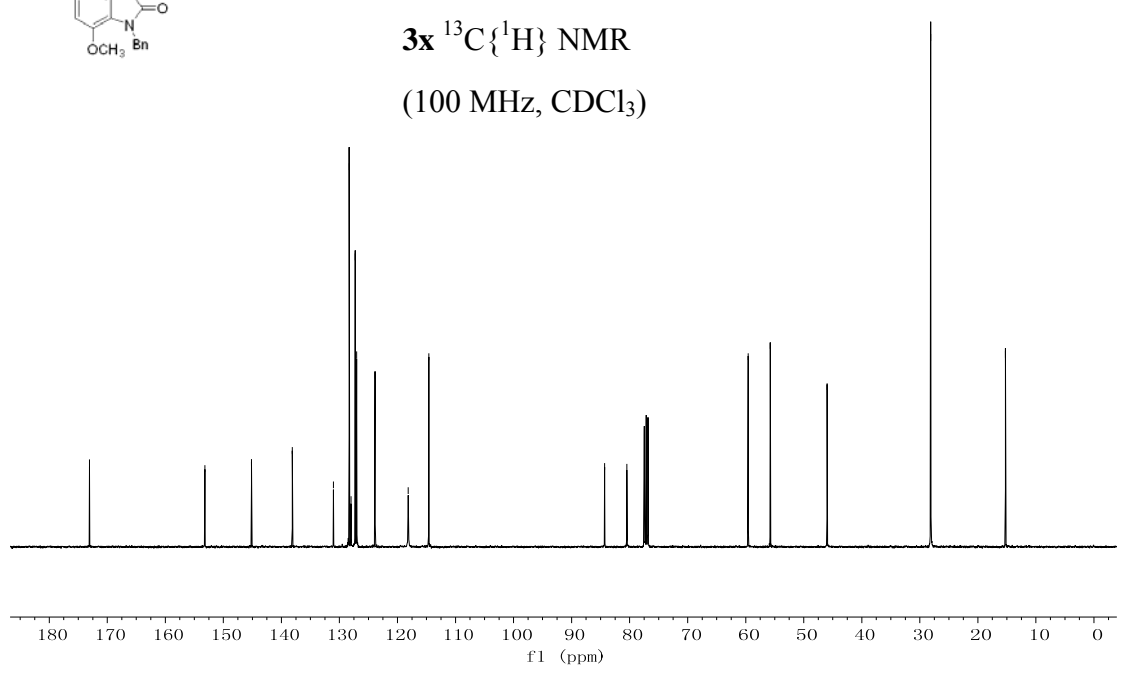
46.0

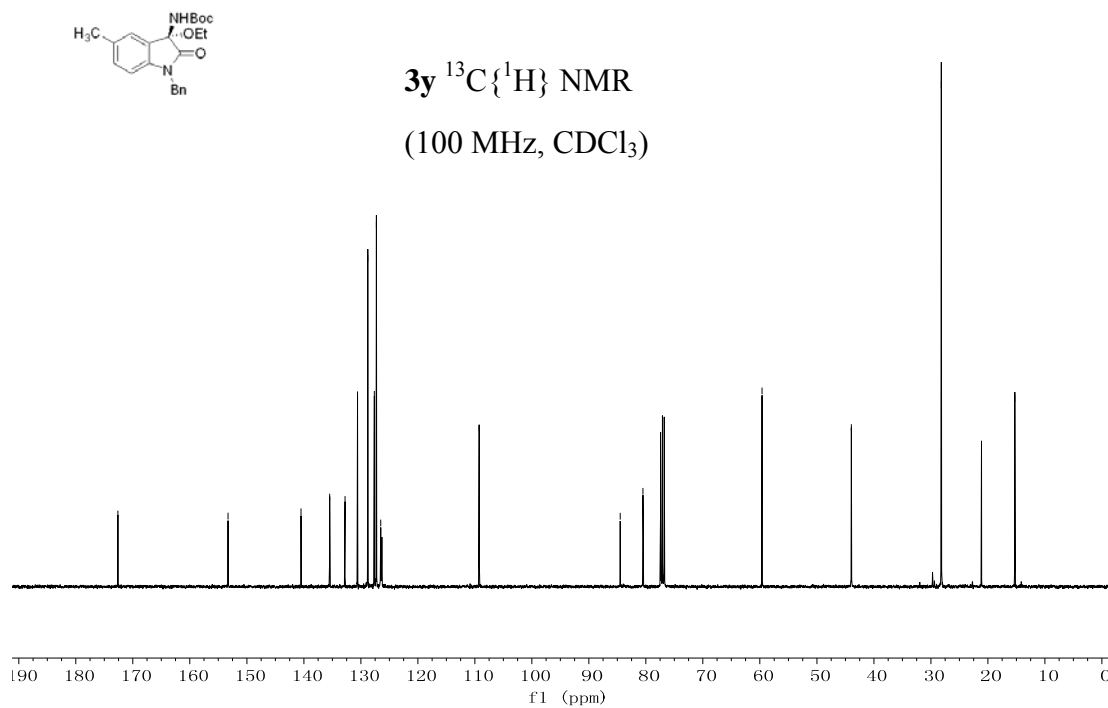
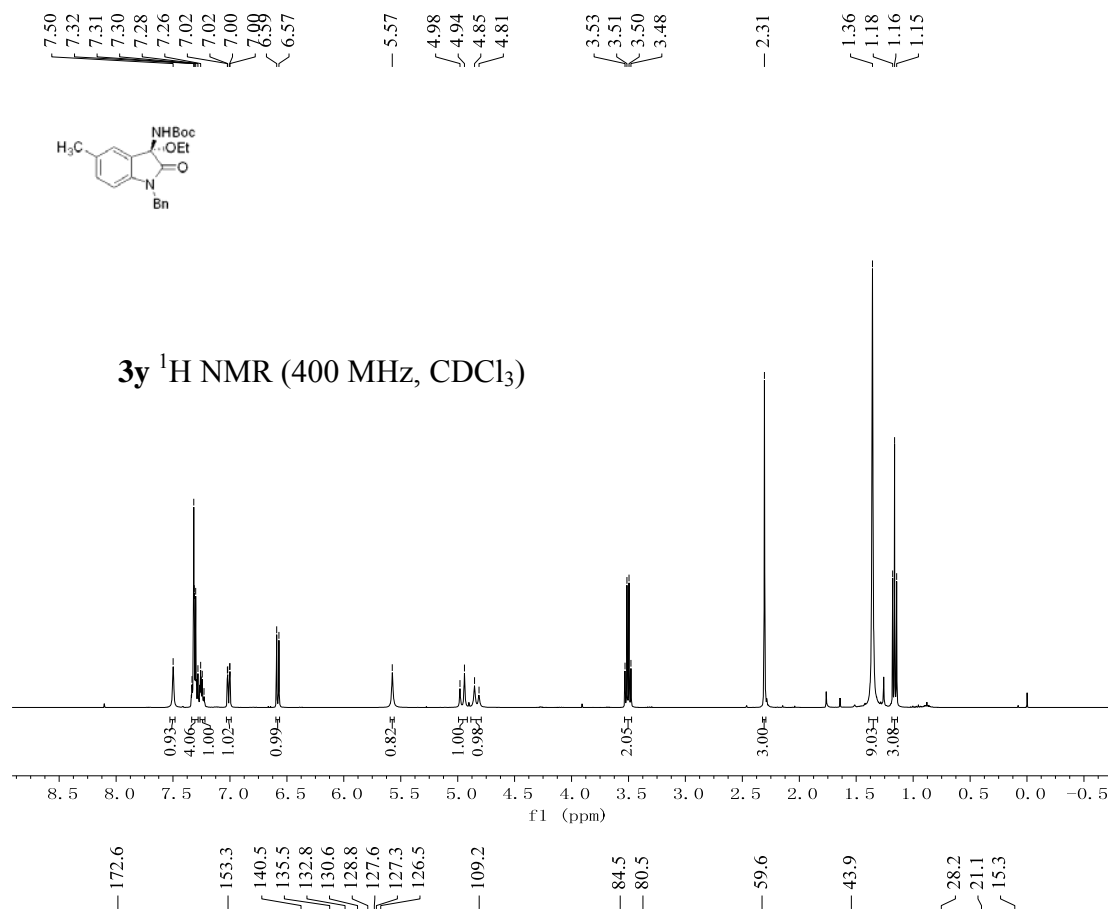
28.1

15.2



3x ¹³C {¹H} NMR
(100 MHz, CDCl₃)





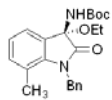
7.51
7.50
7.49
7.33
7.31
7.29
7.26
7.25
7.23
7.22
7.21
7.00
6.99
6.99

— 5.58 — 5.19

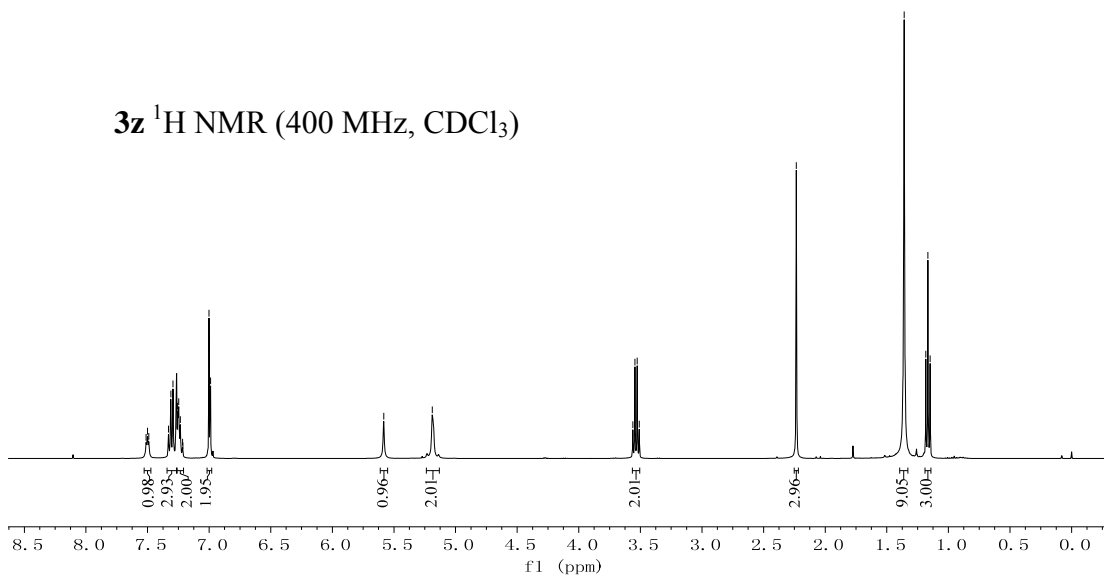
3.56
3.54
3.53
3.51

— 2.23

1.36
1.18
1.17
1.15



3z ^1H NMR (400 MHz, CDCl_3)



173.7

153.3

141.1
137.3
134.5
128.9
127.2
125.8
123.3
123.2
120.1

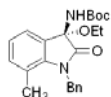
83.8
80.5

59.6

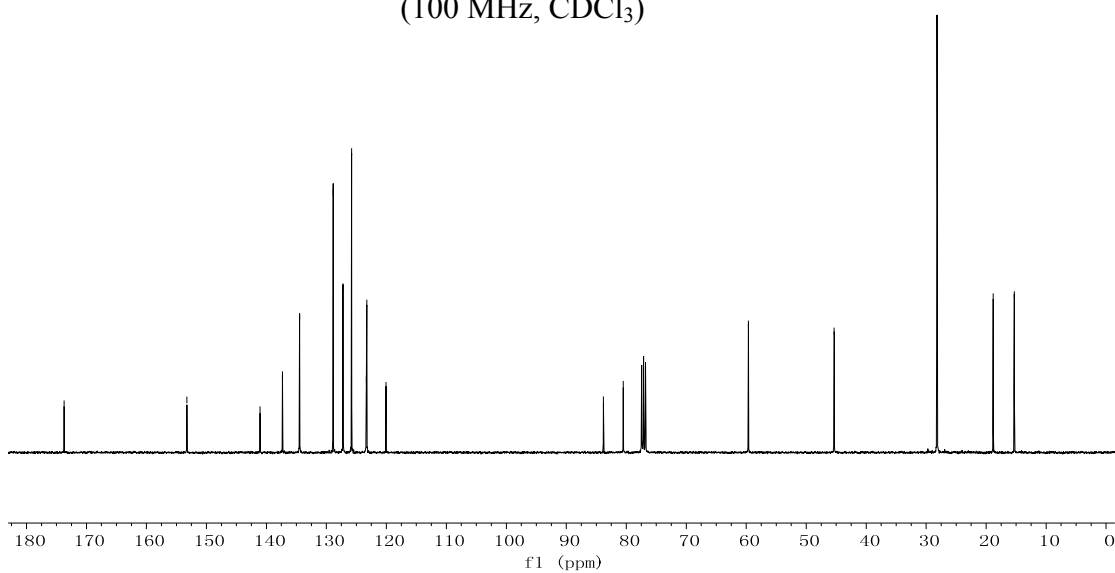
45.3

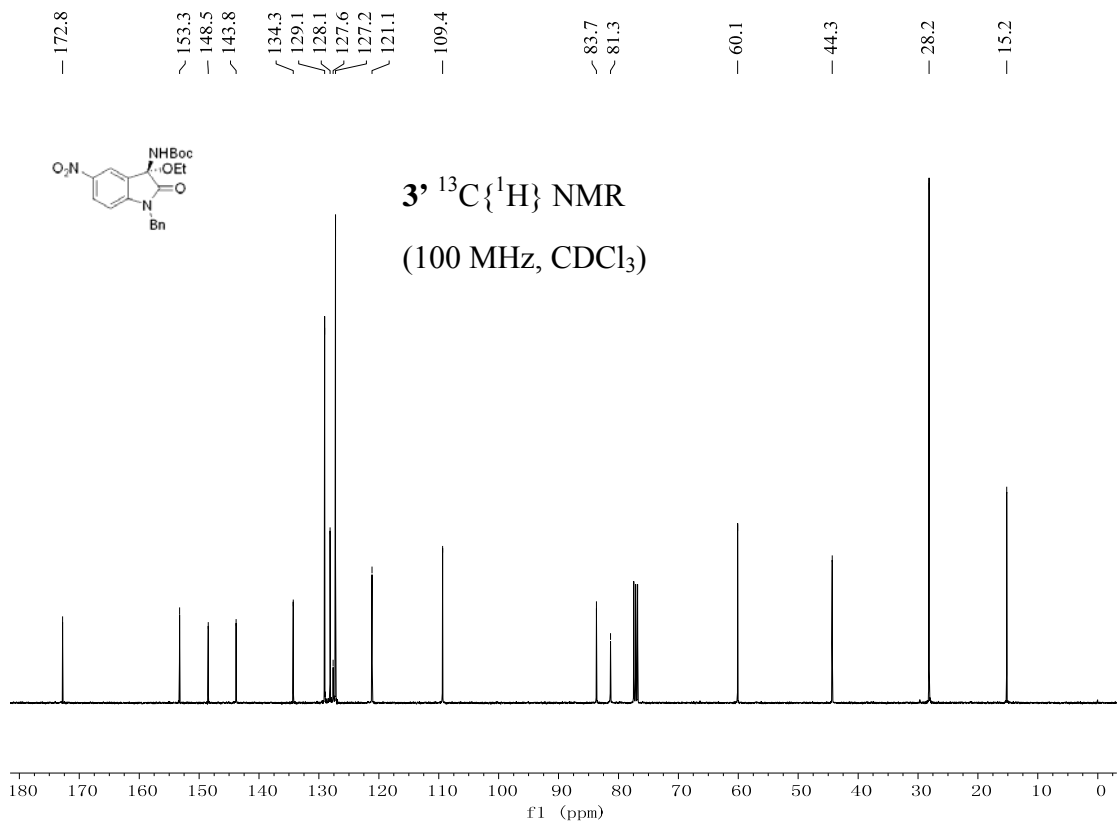
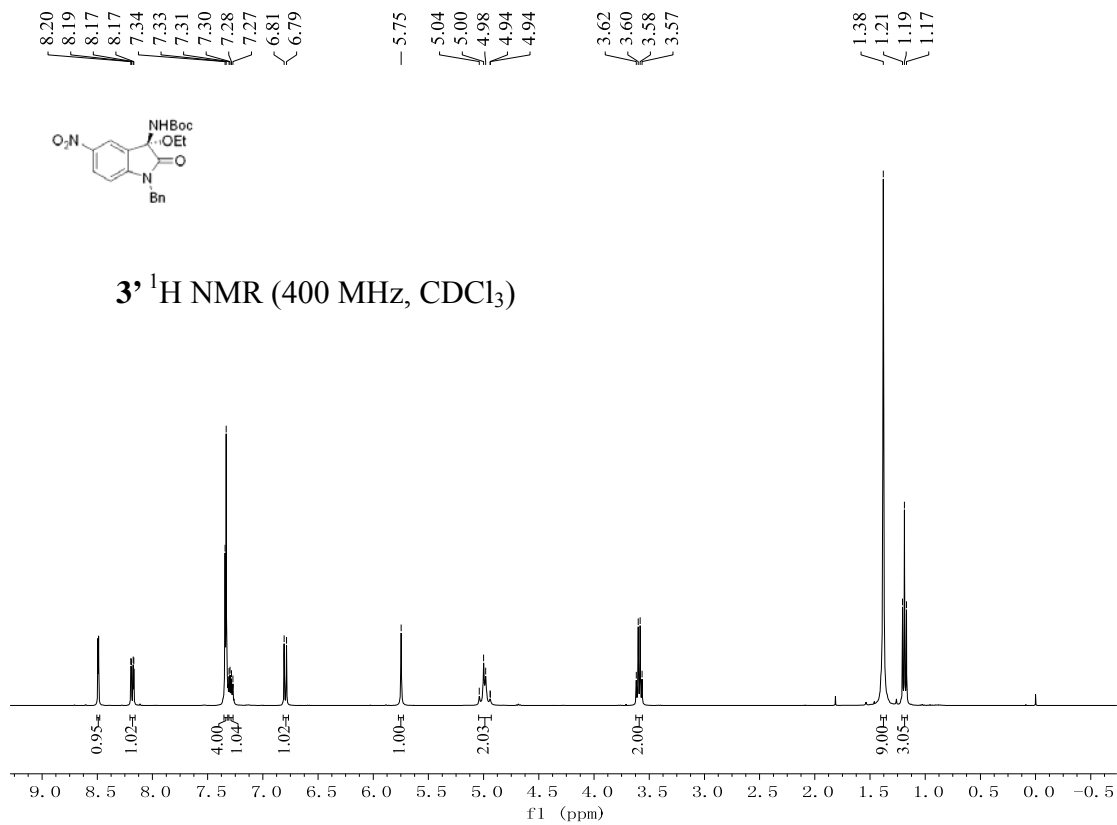
28.2

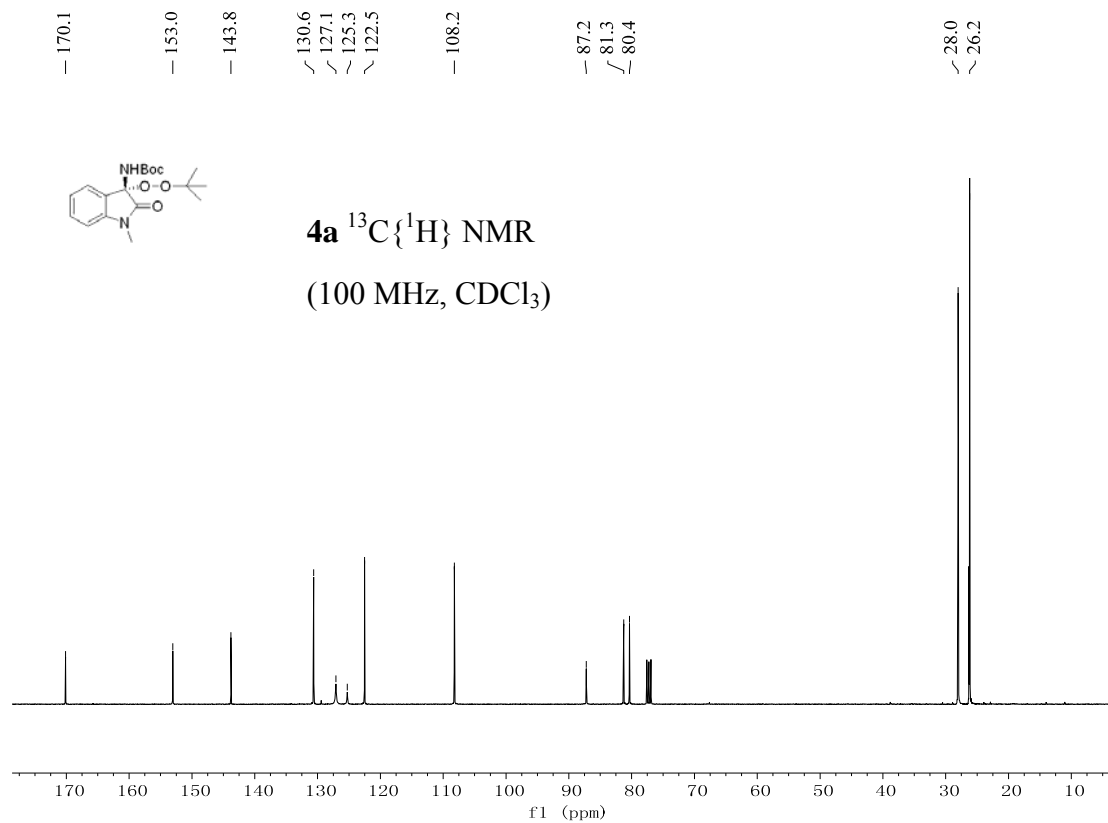
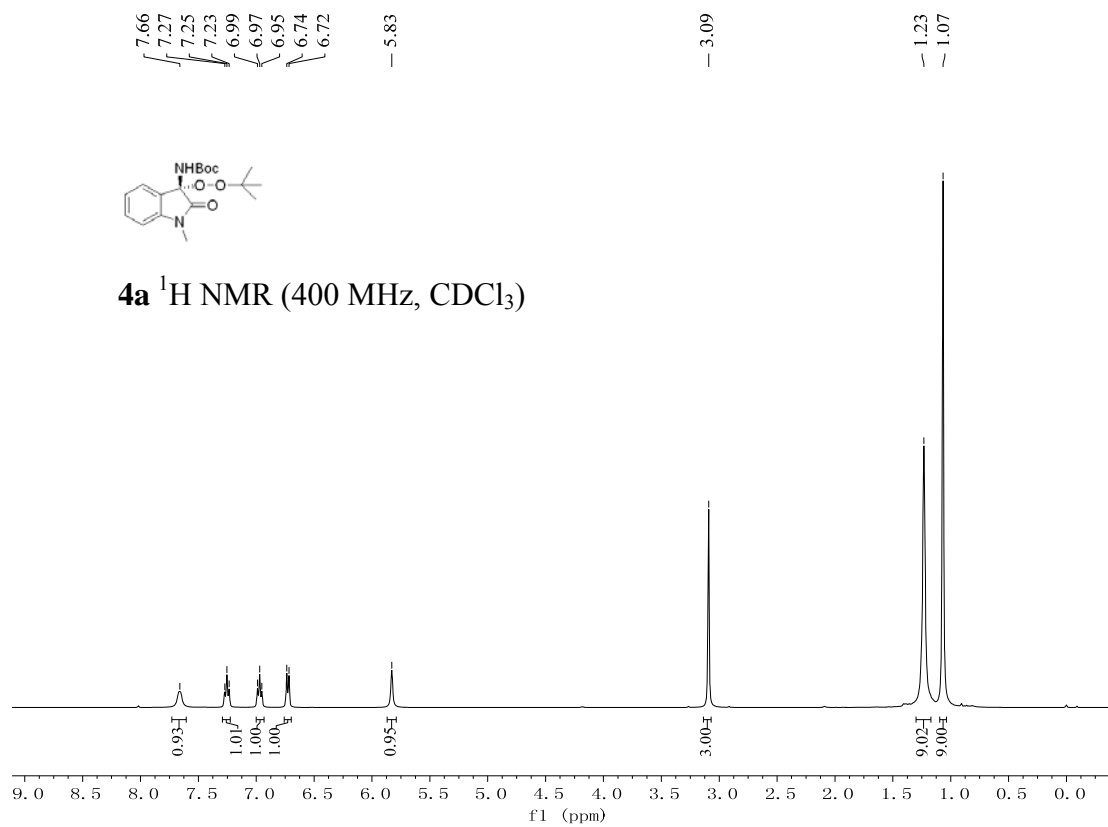
18.8
15.3

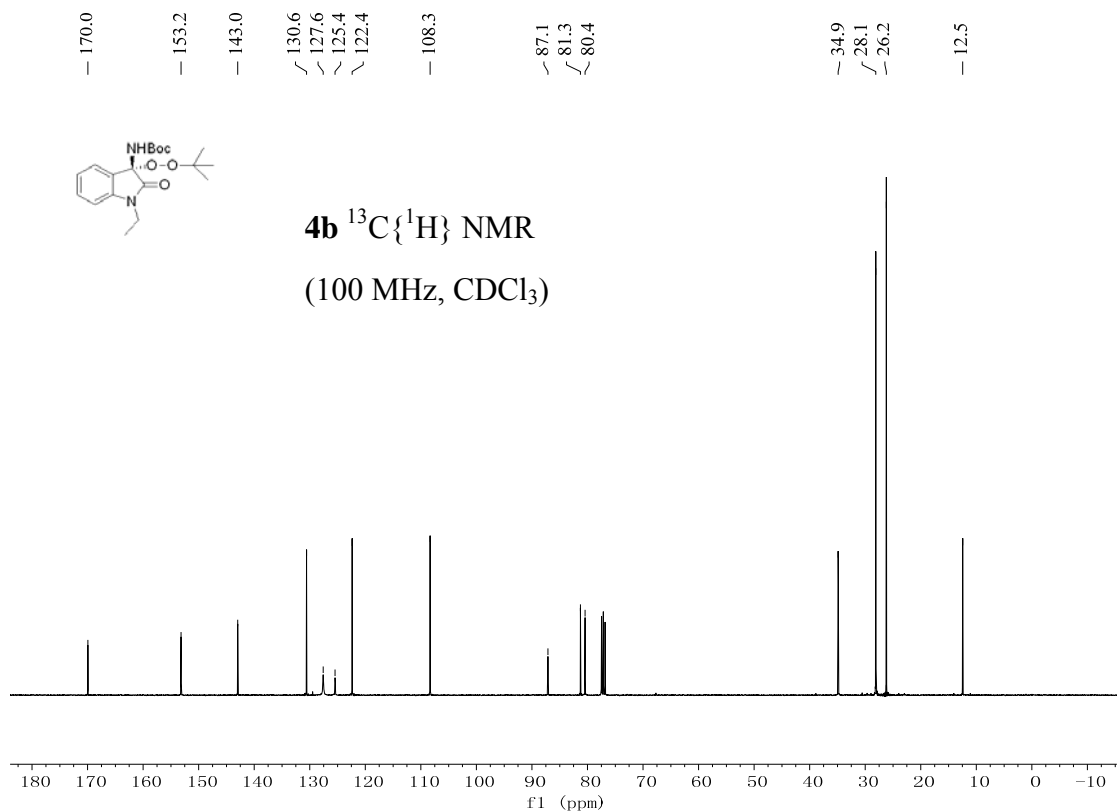
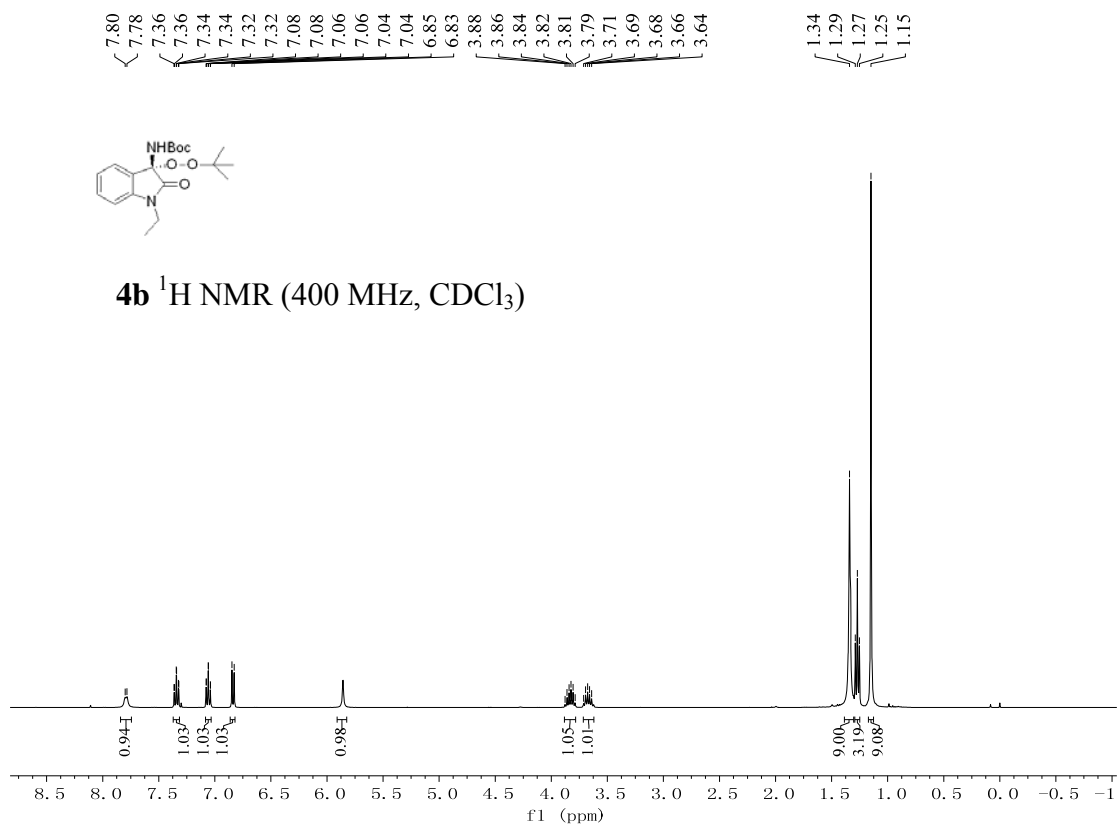


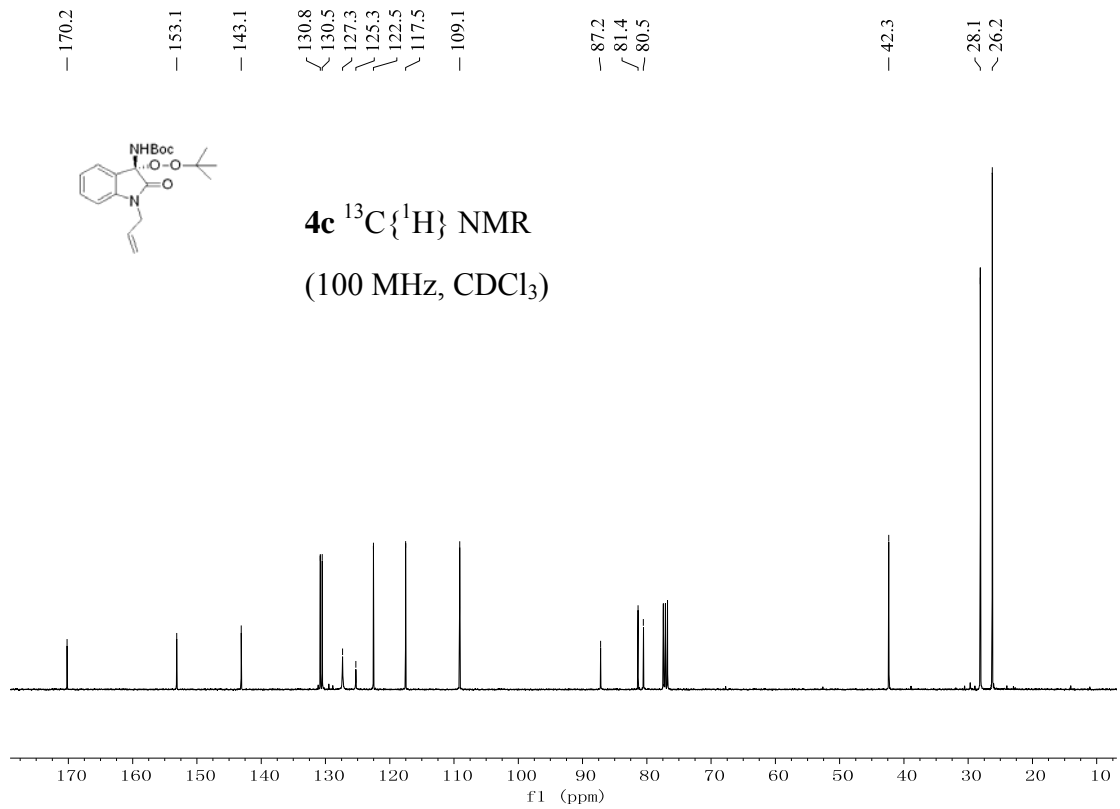
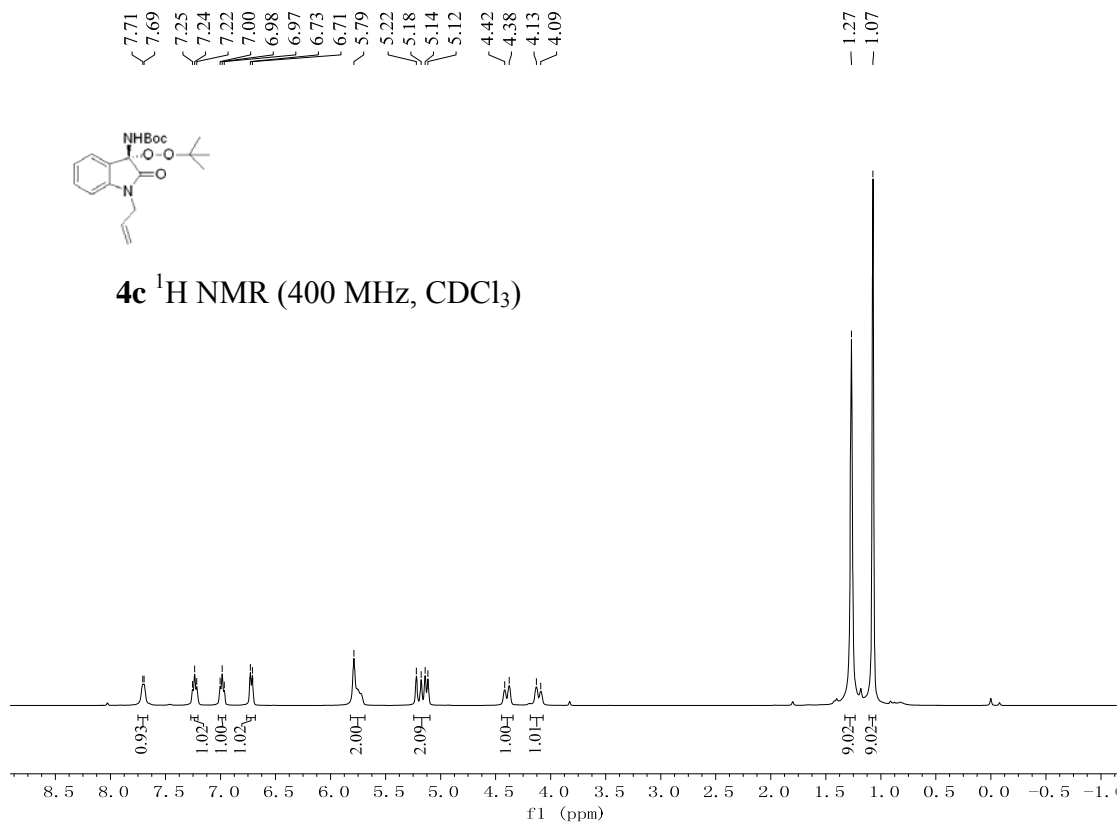
3z ^{13}C { ^1H } NMR
(100 MHz, CDCl_3)

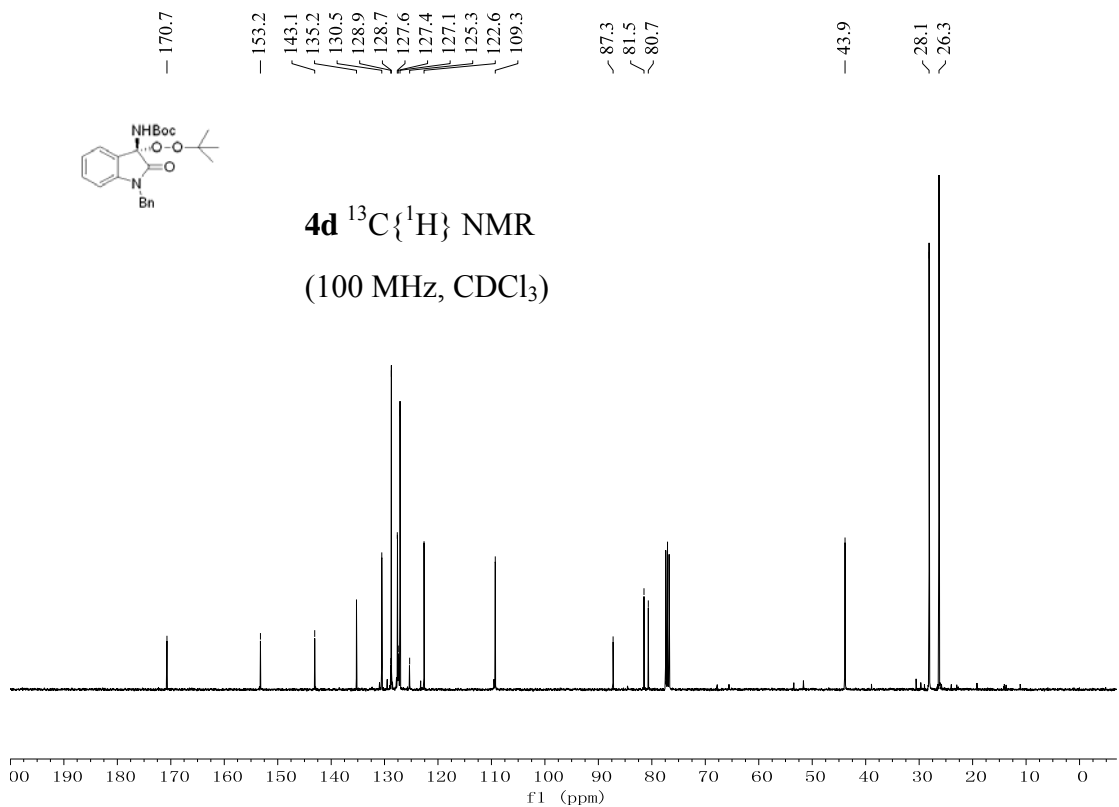
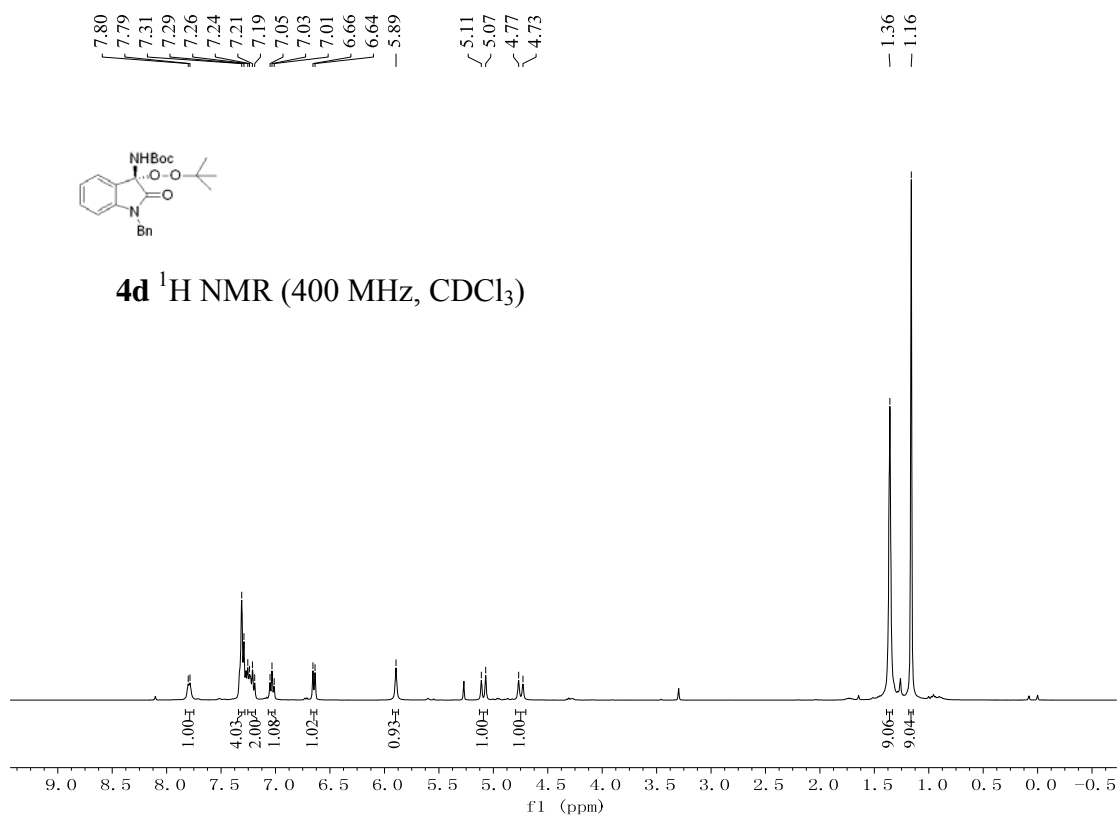


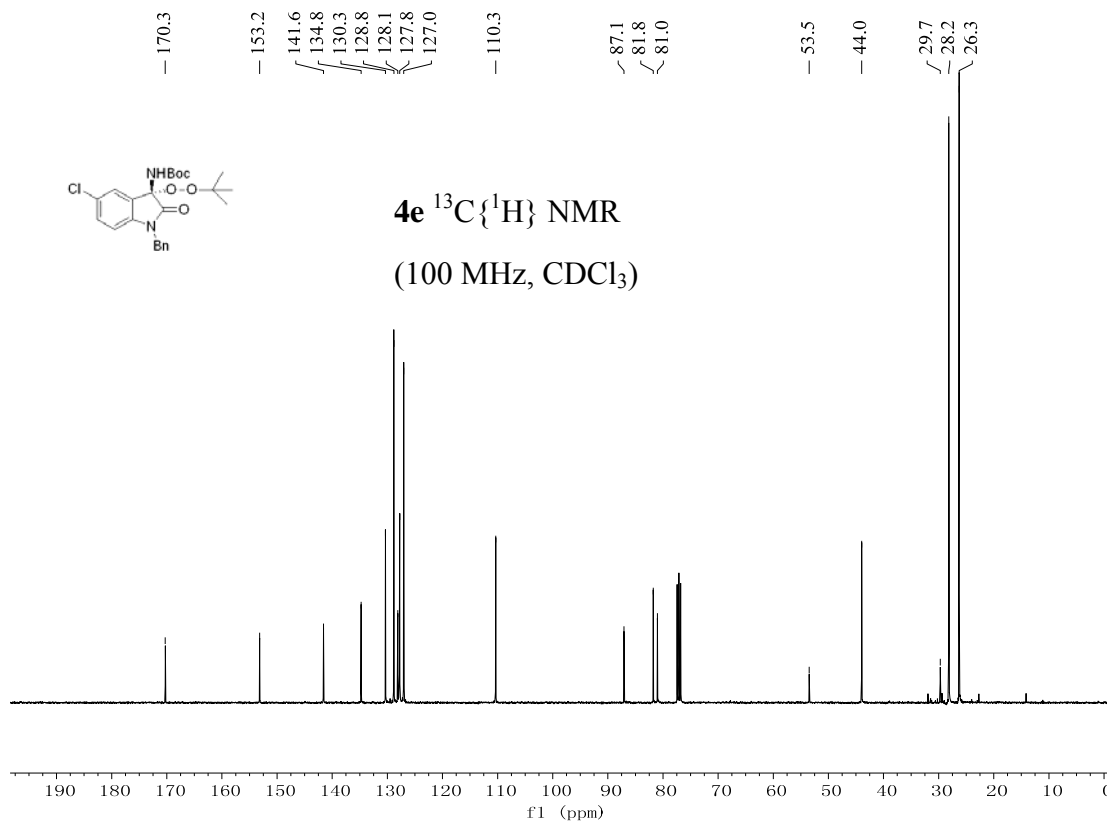
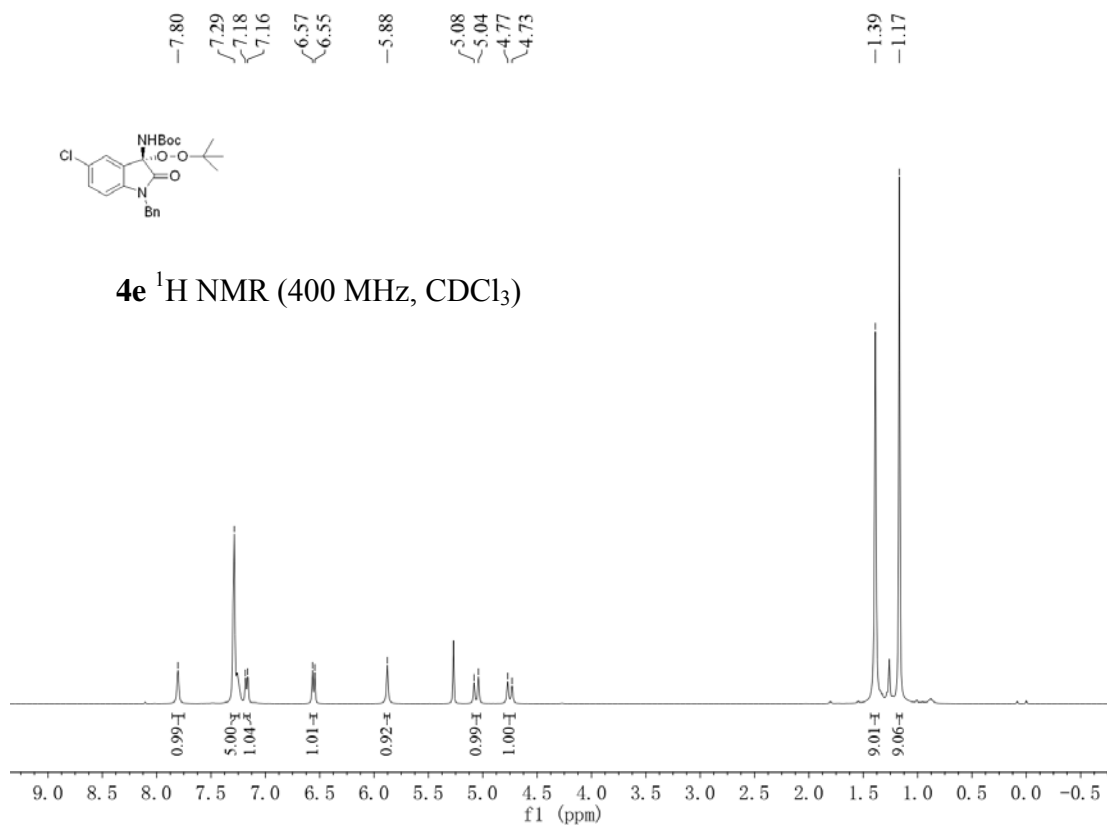


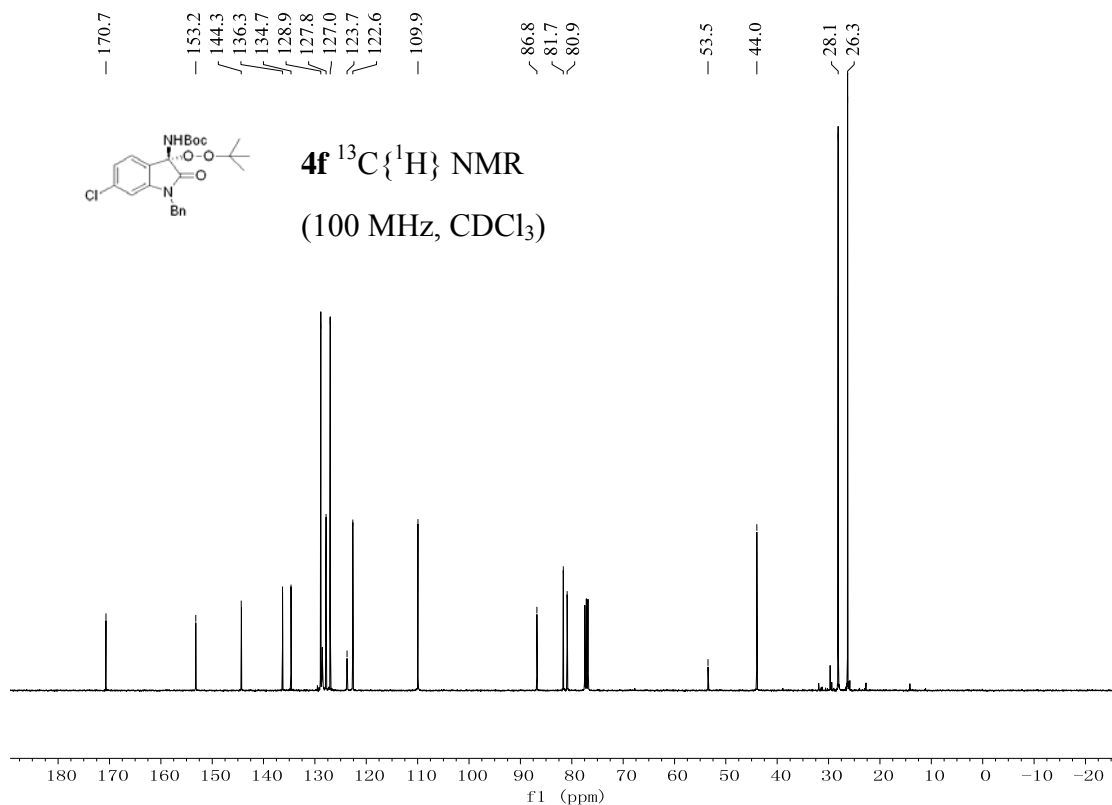
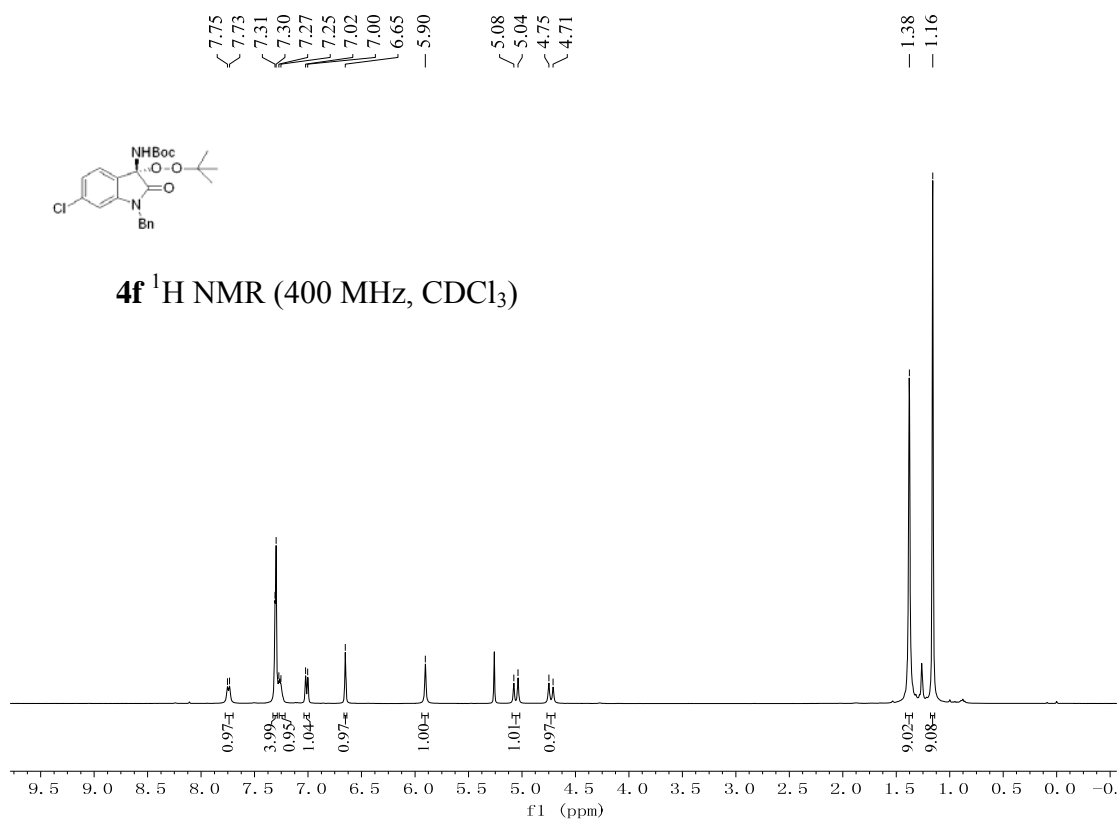


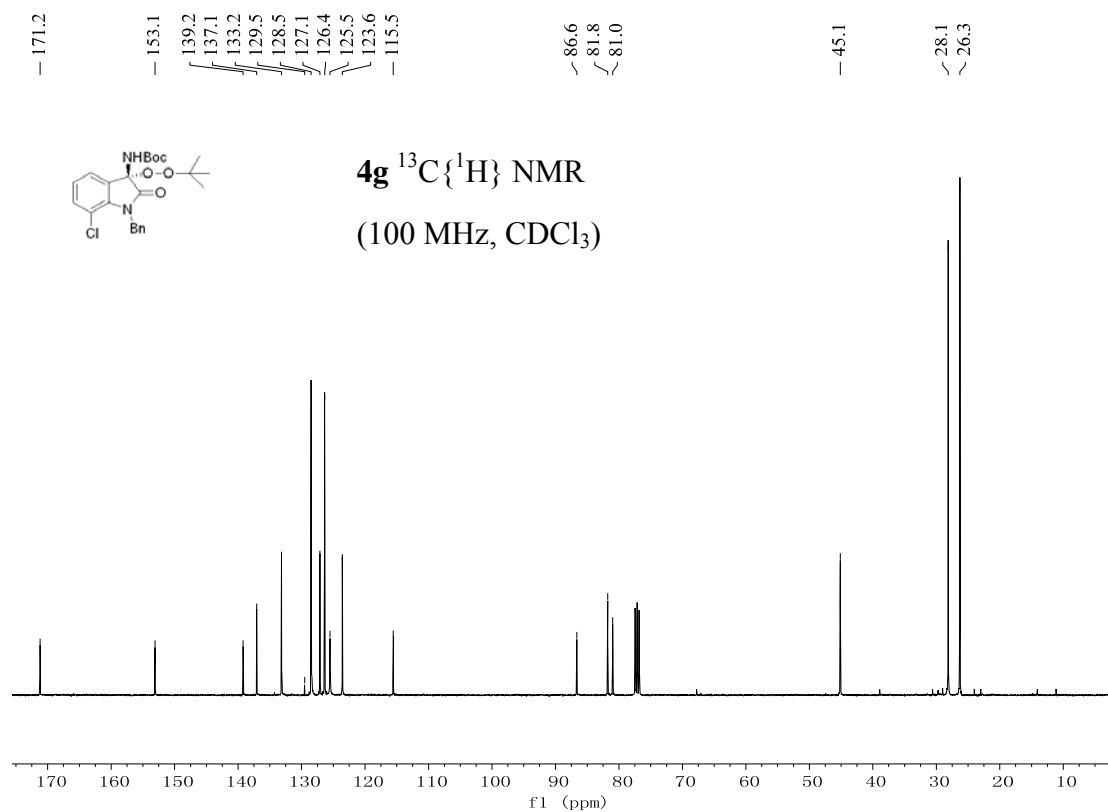
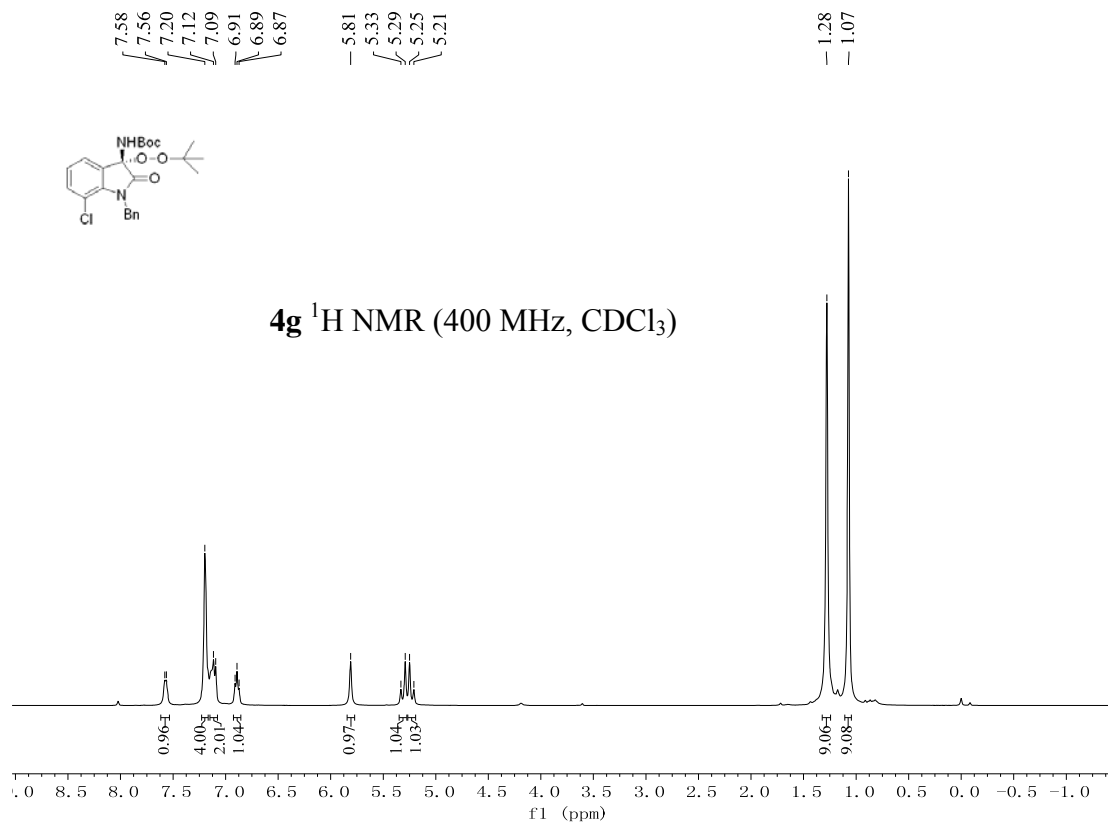


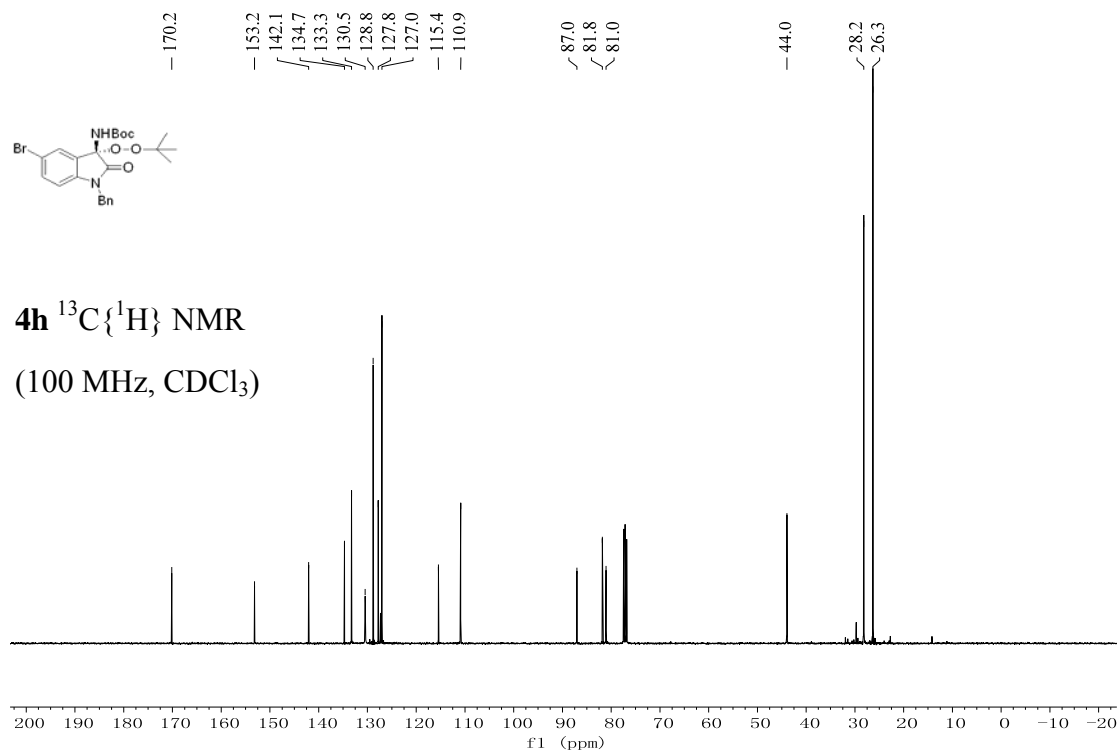
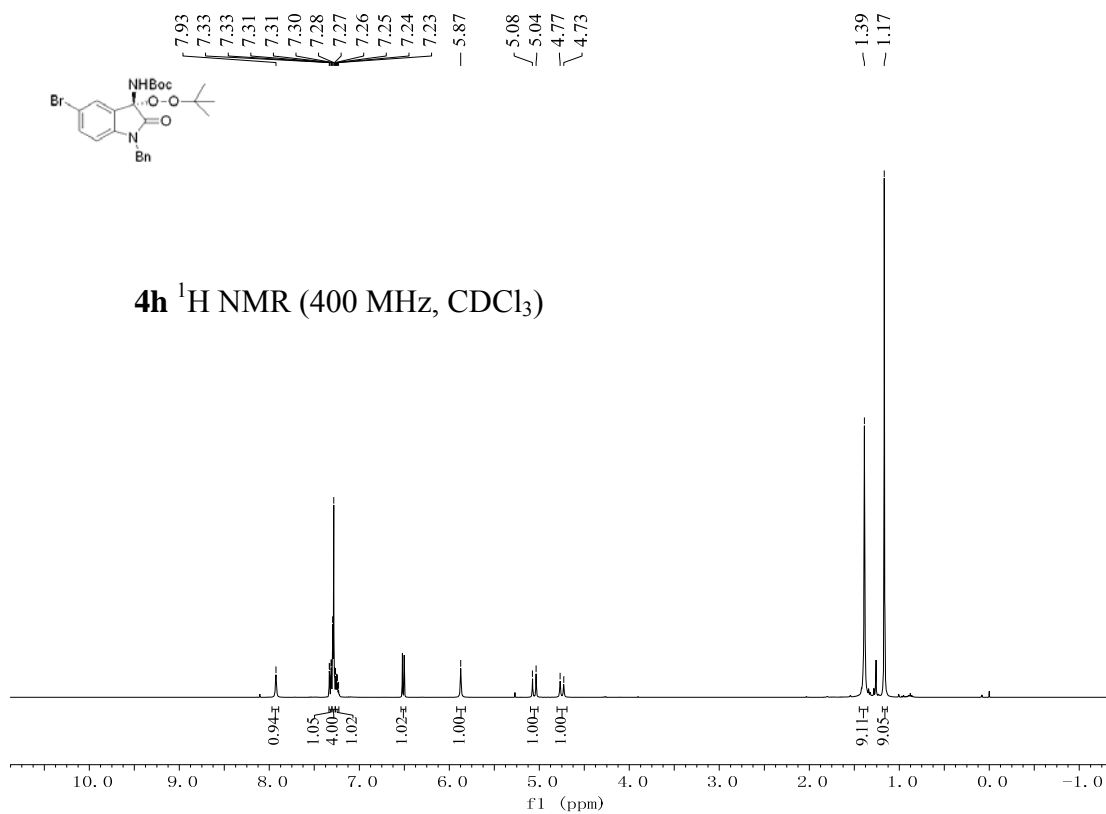


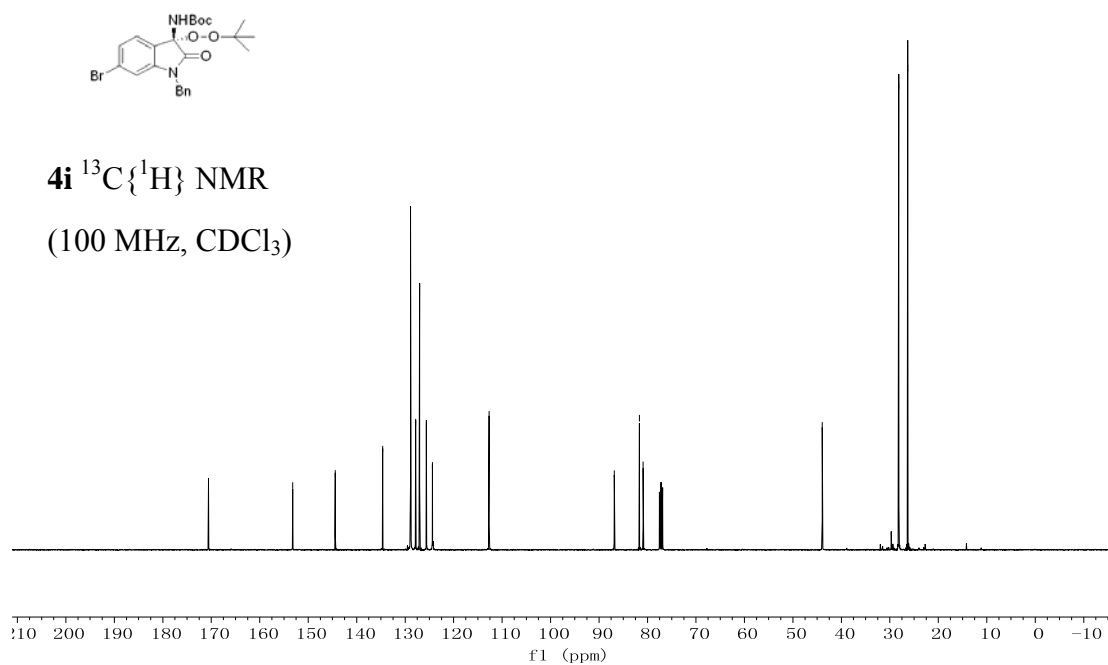
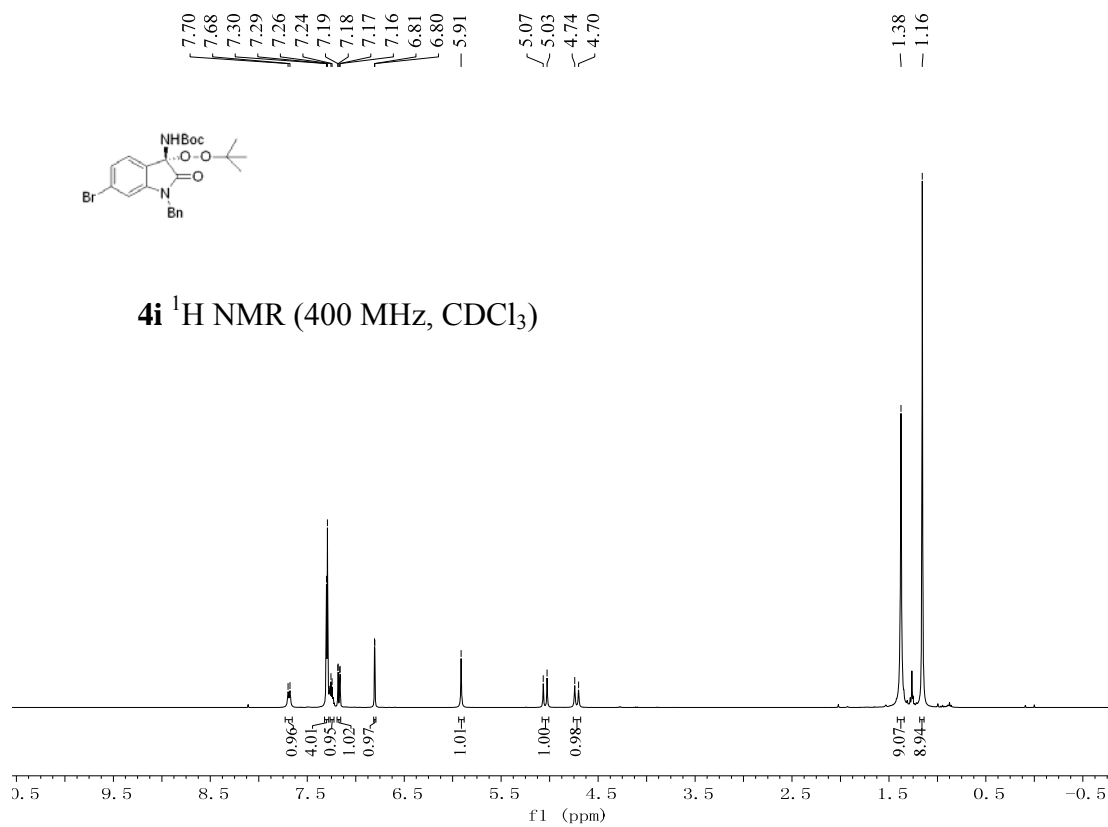


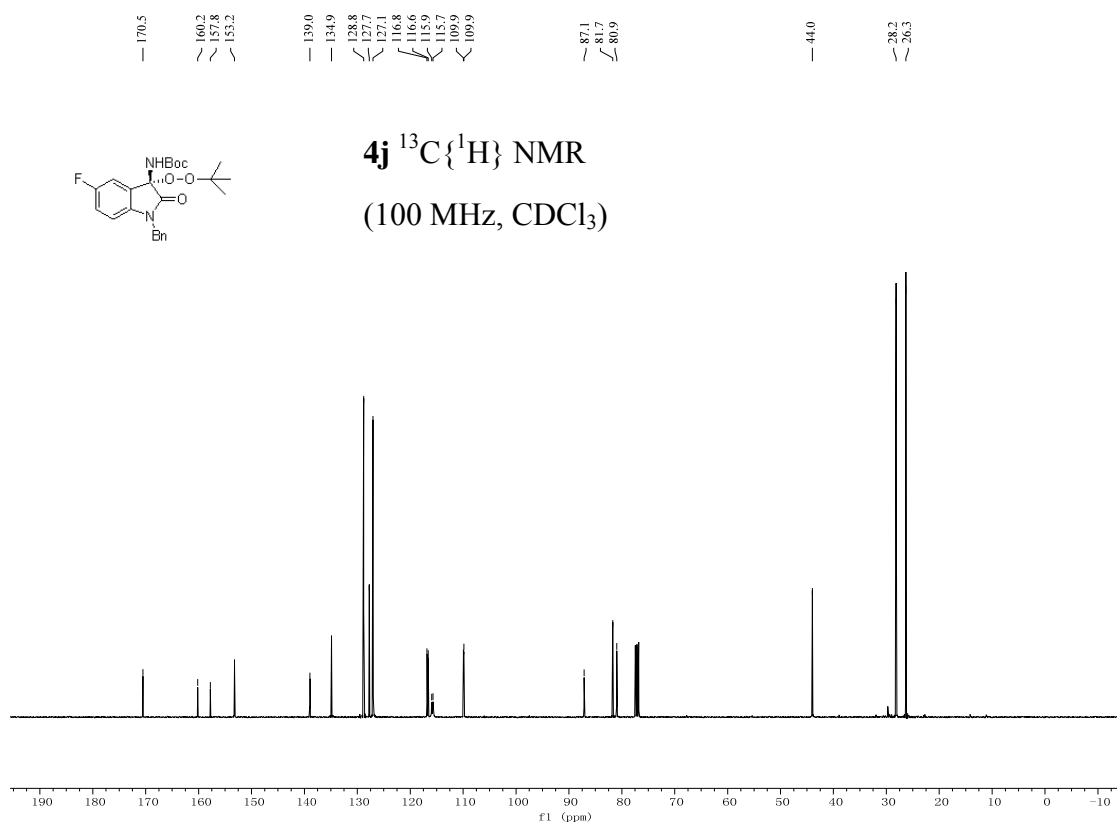
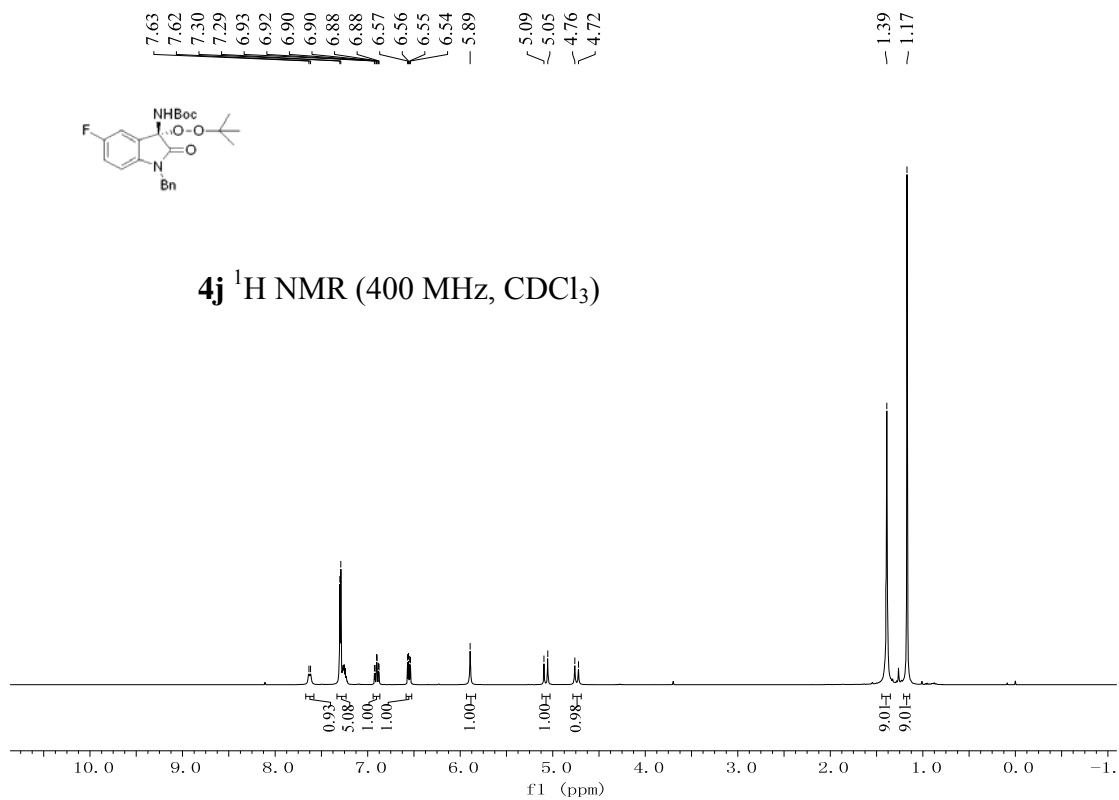


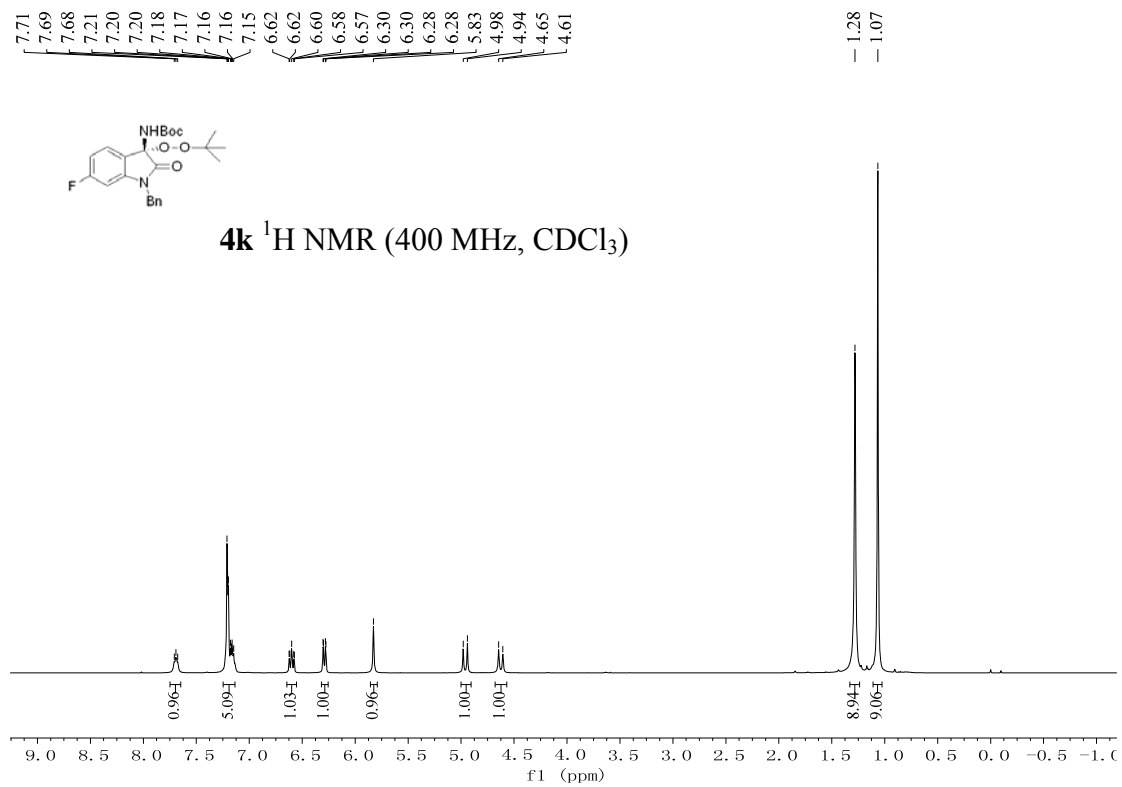
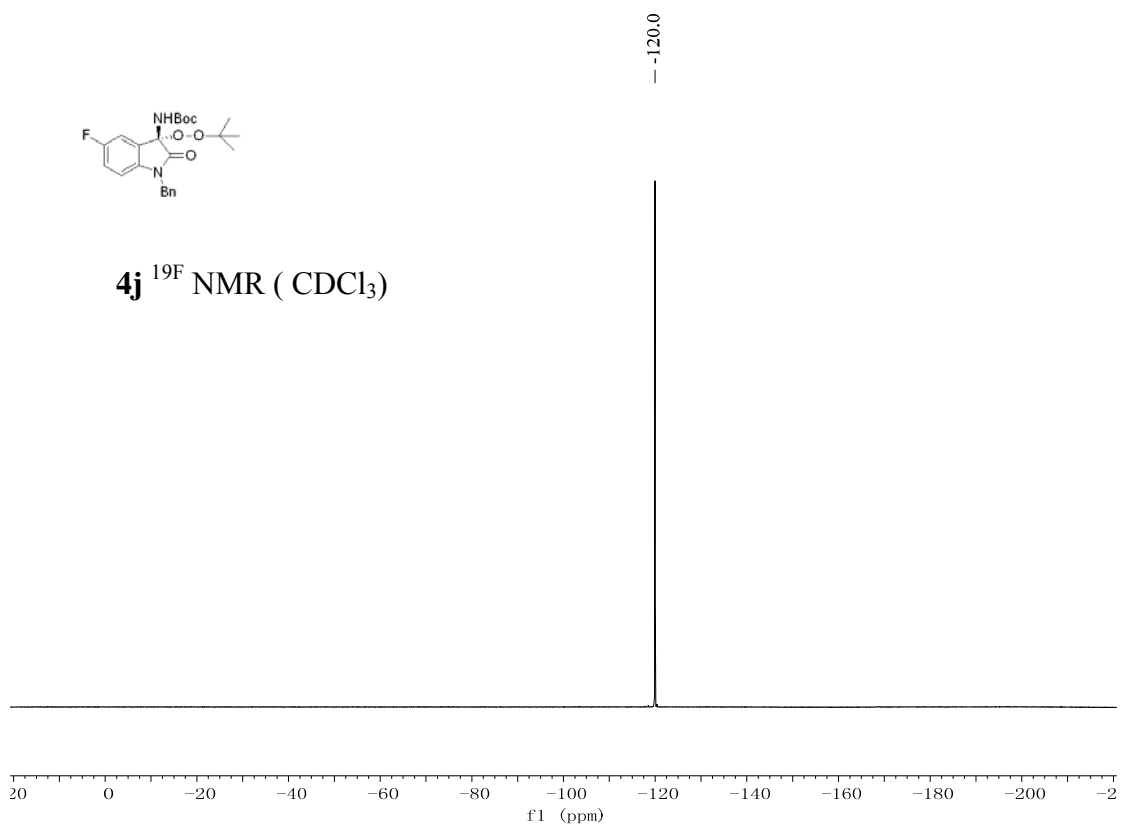


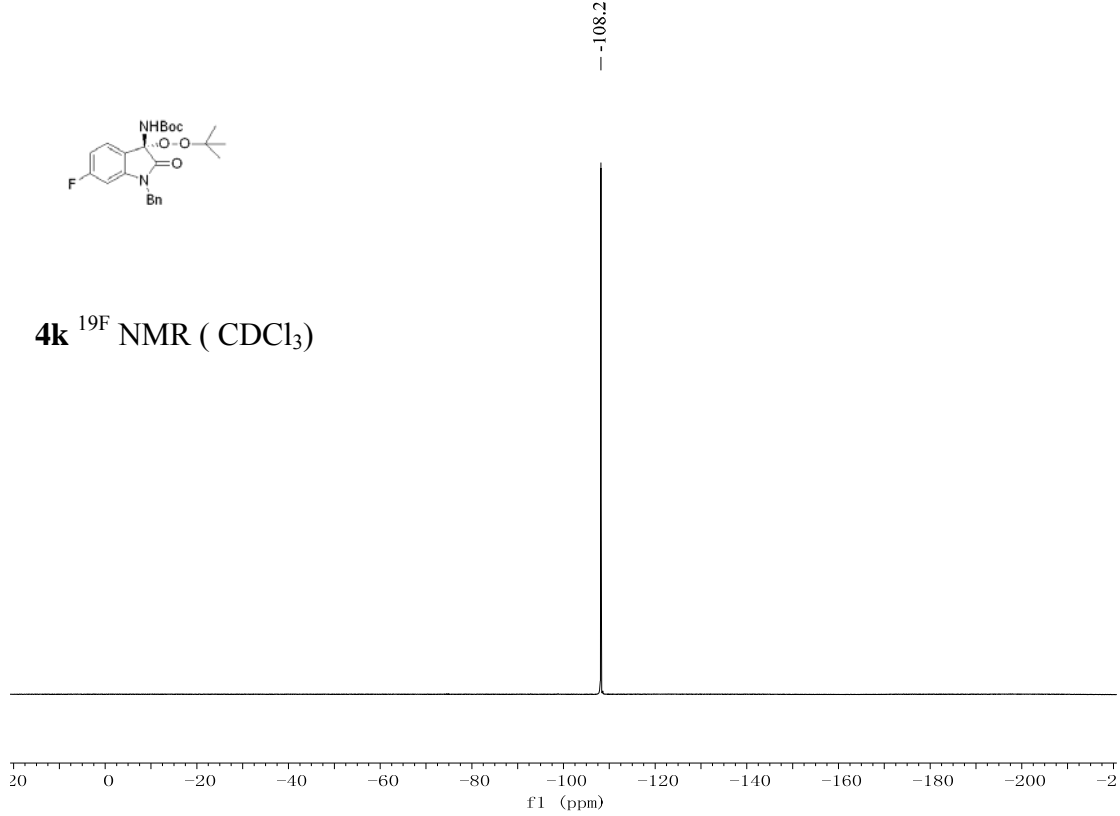
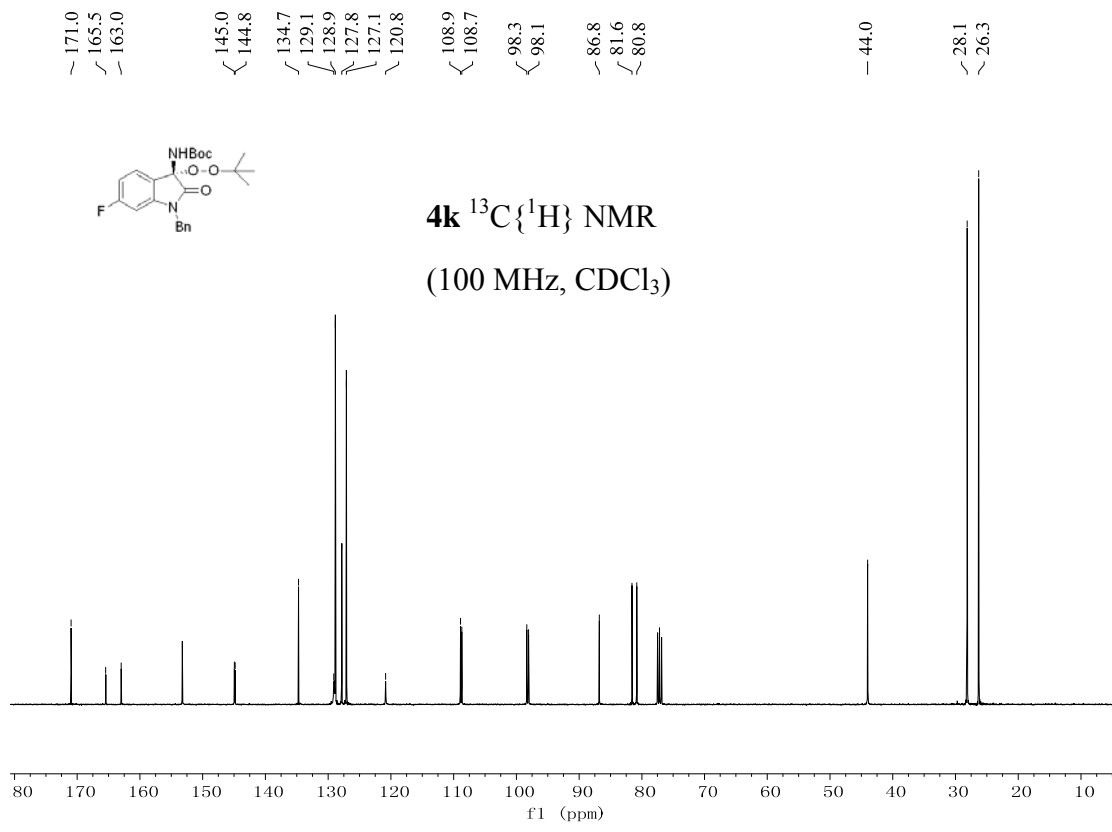


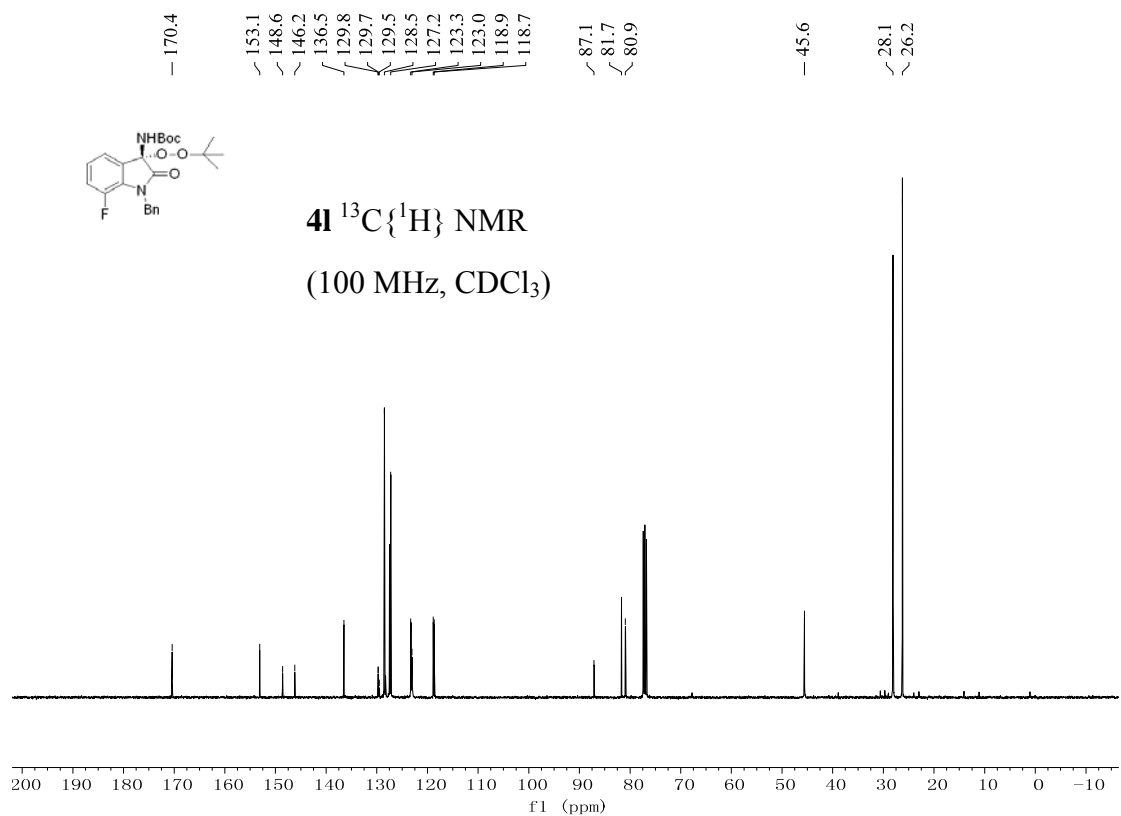
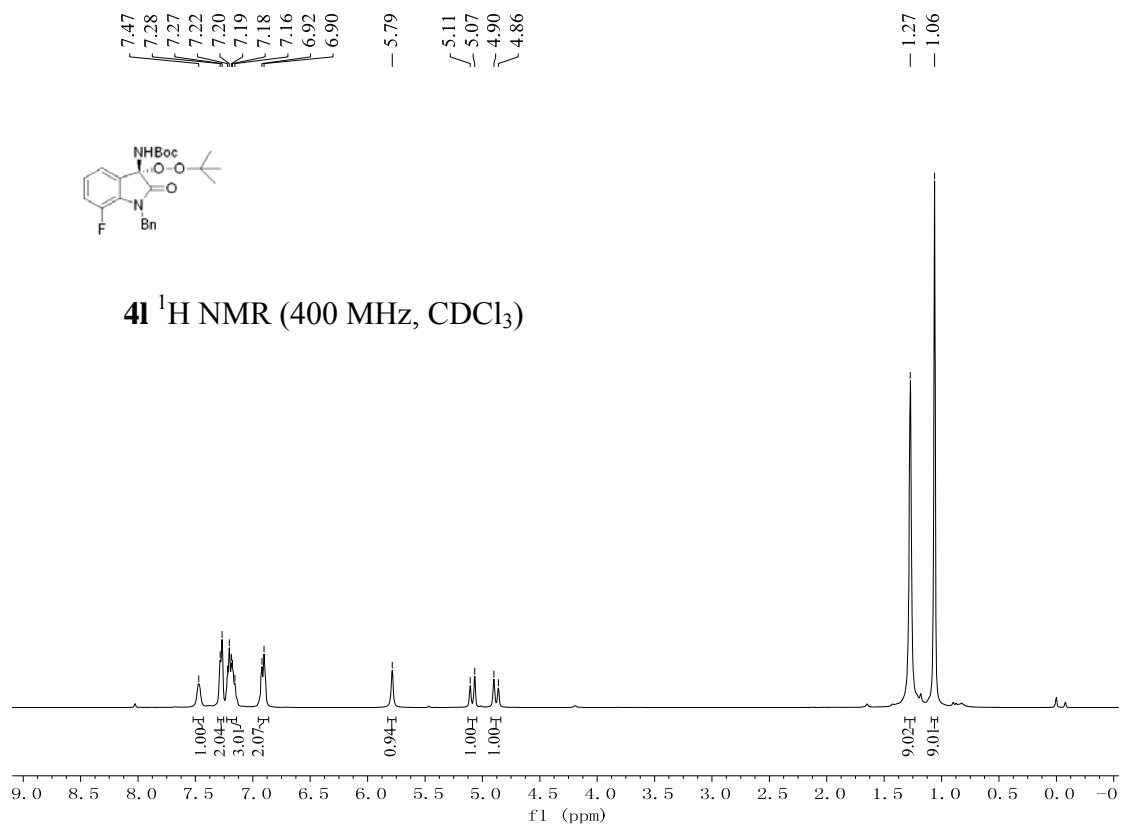


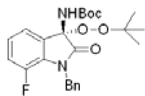




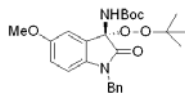
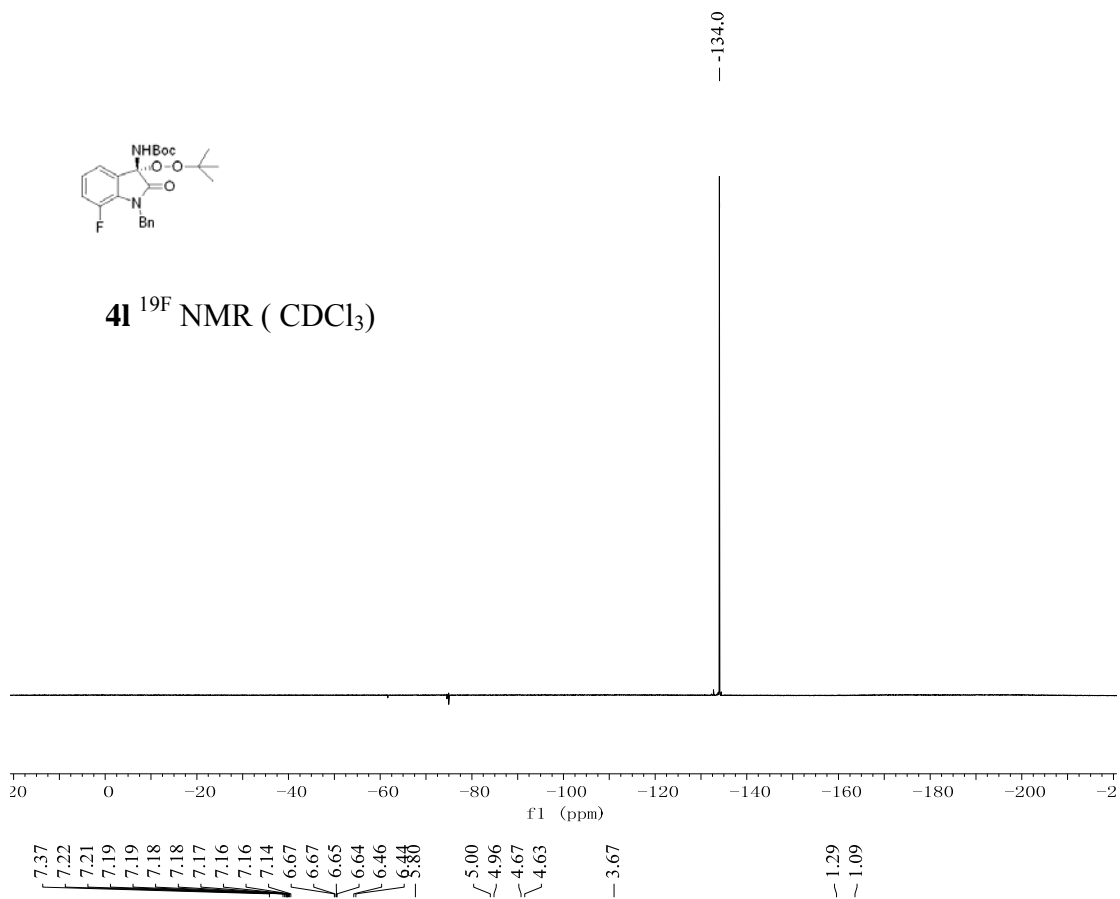




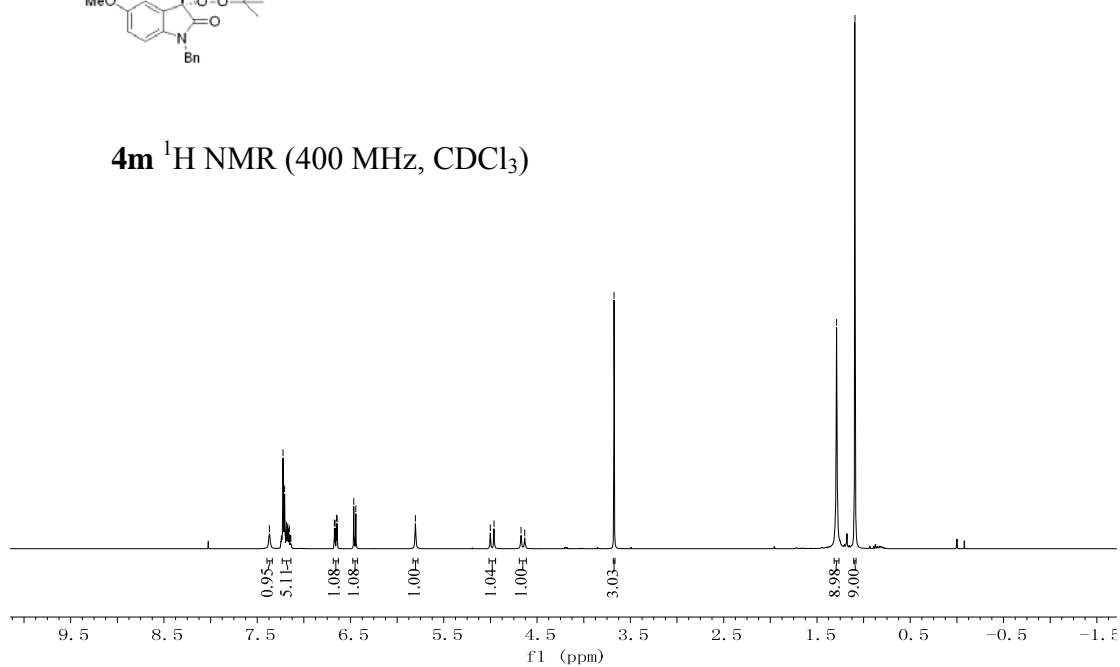


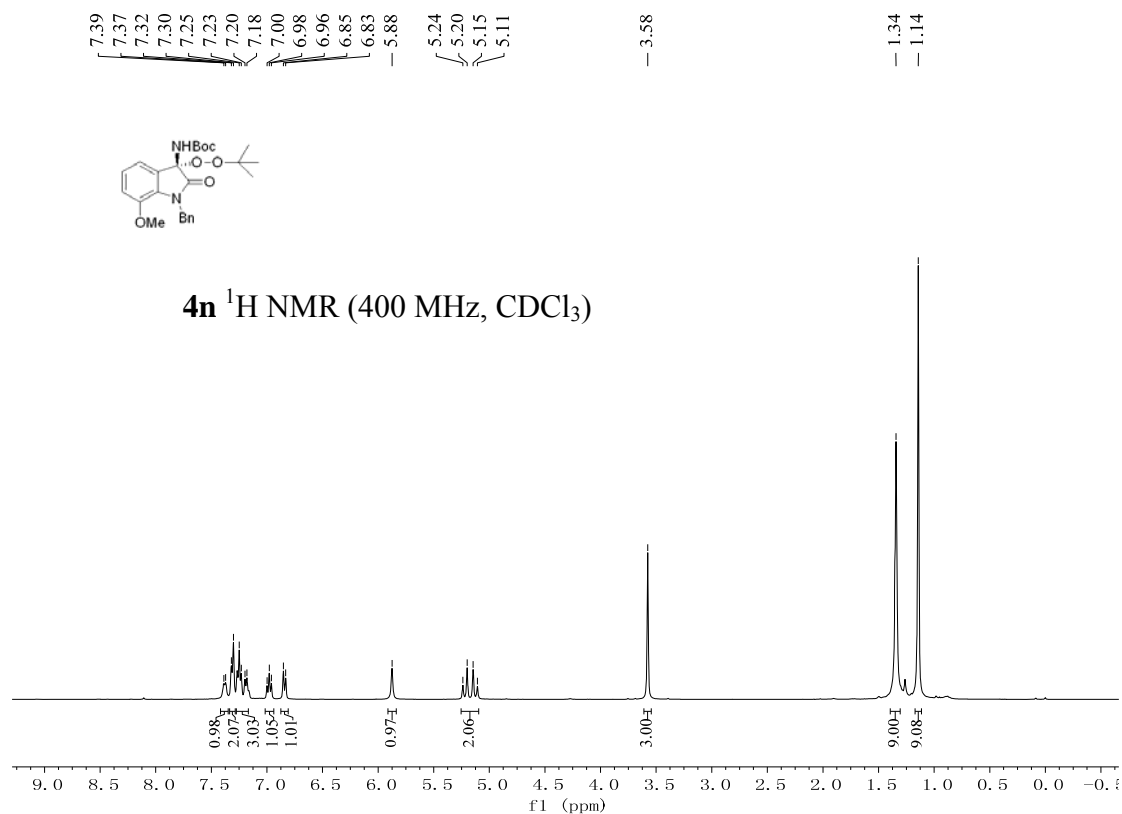
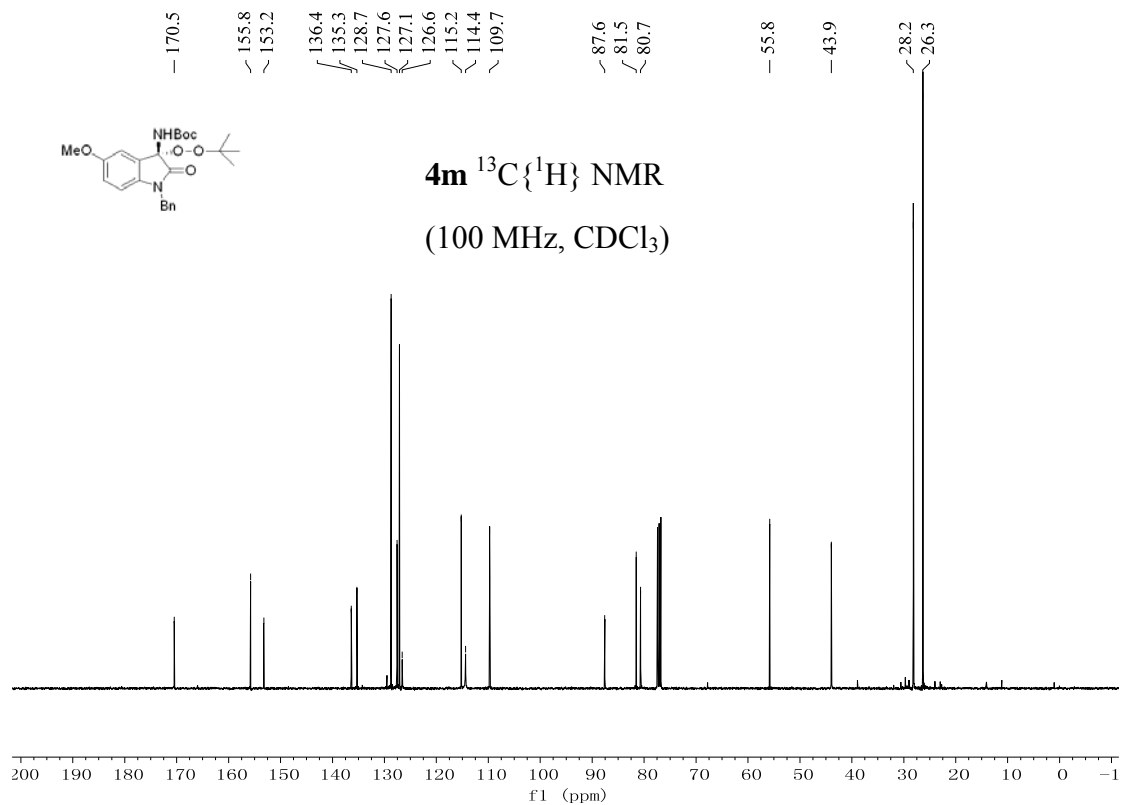


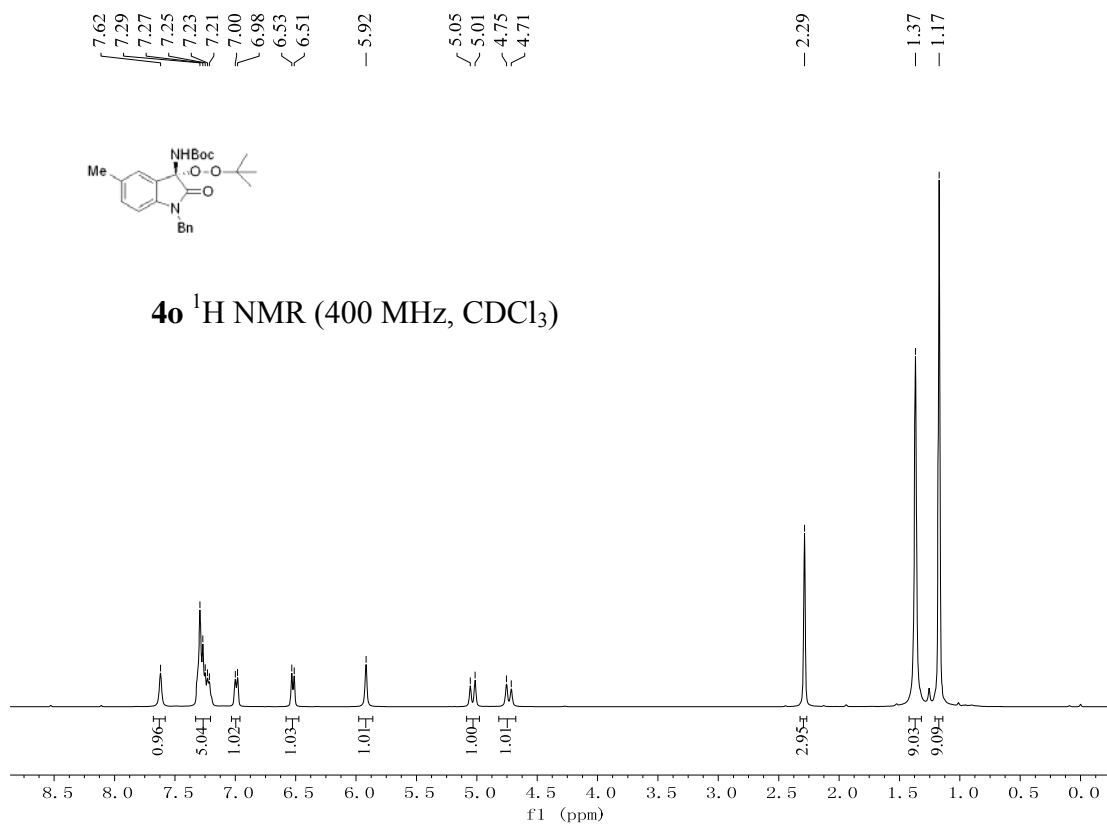
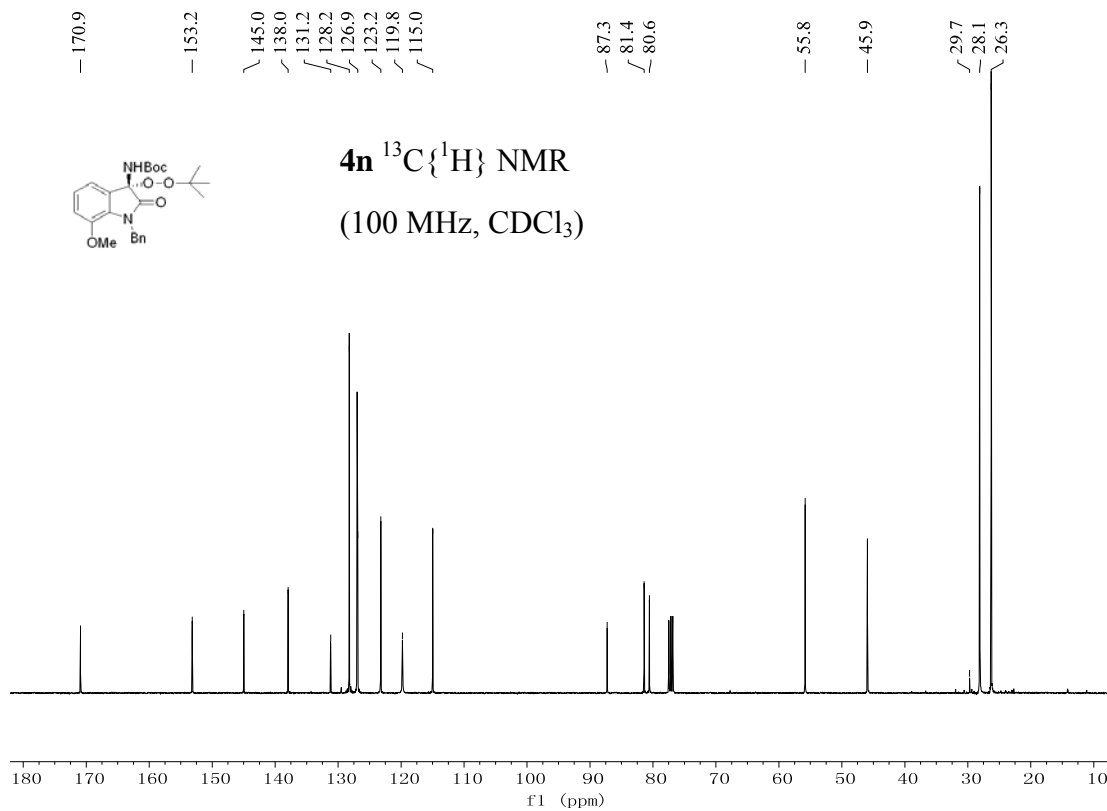
4l ^{19}F NMR (CDCl_3)

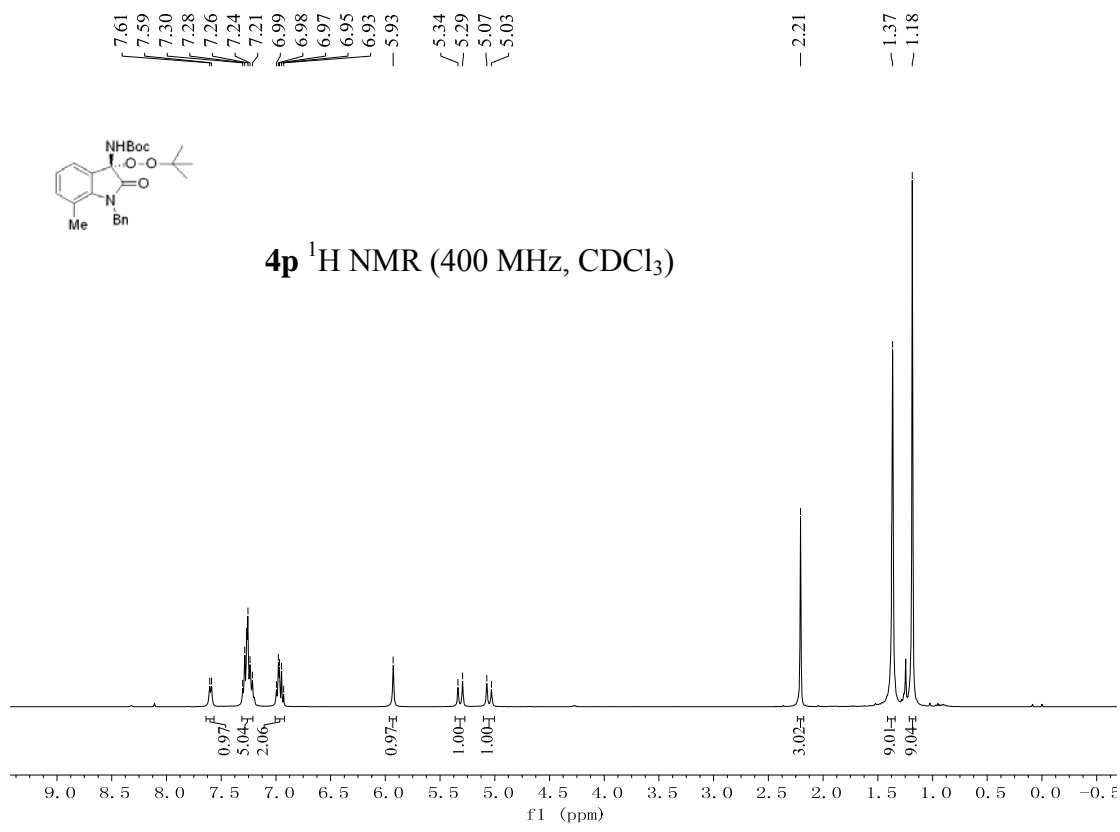
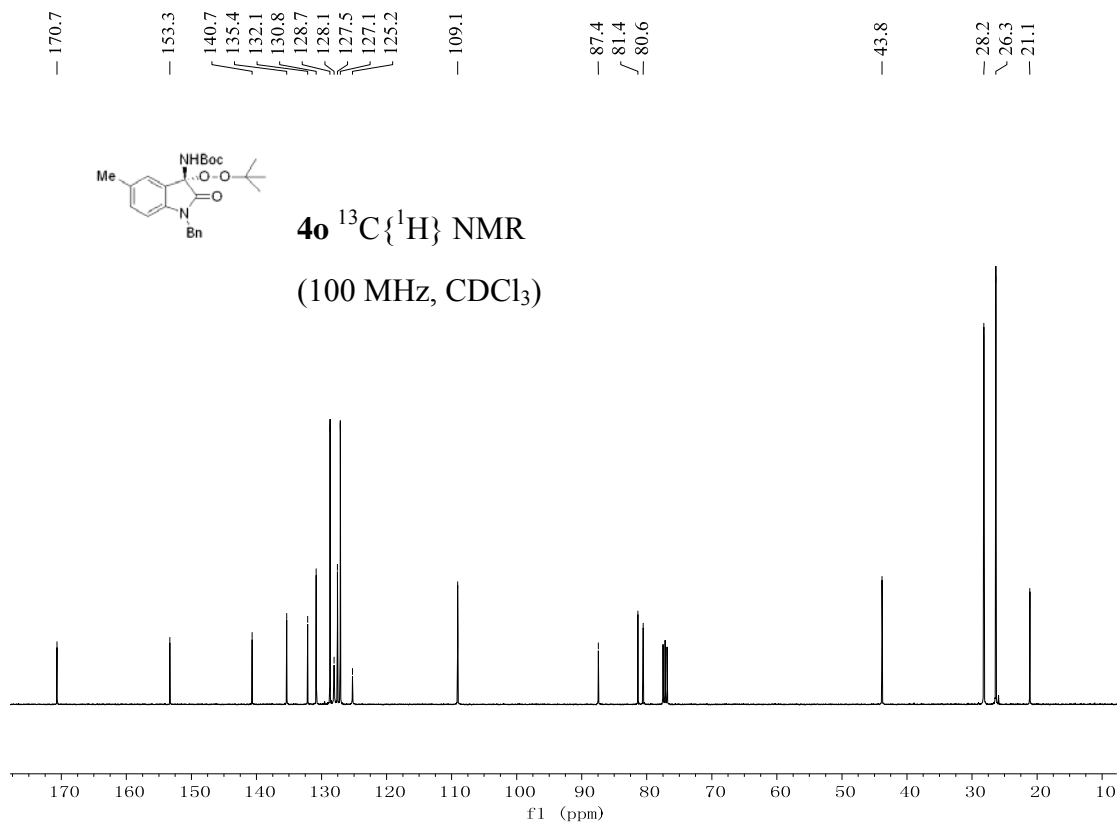


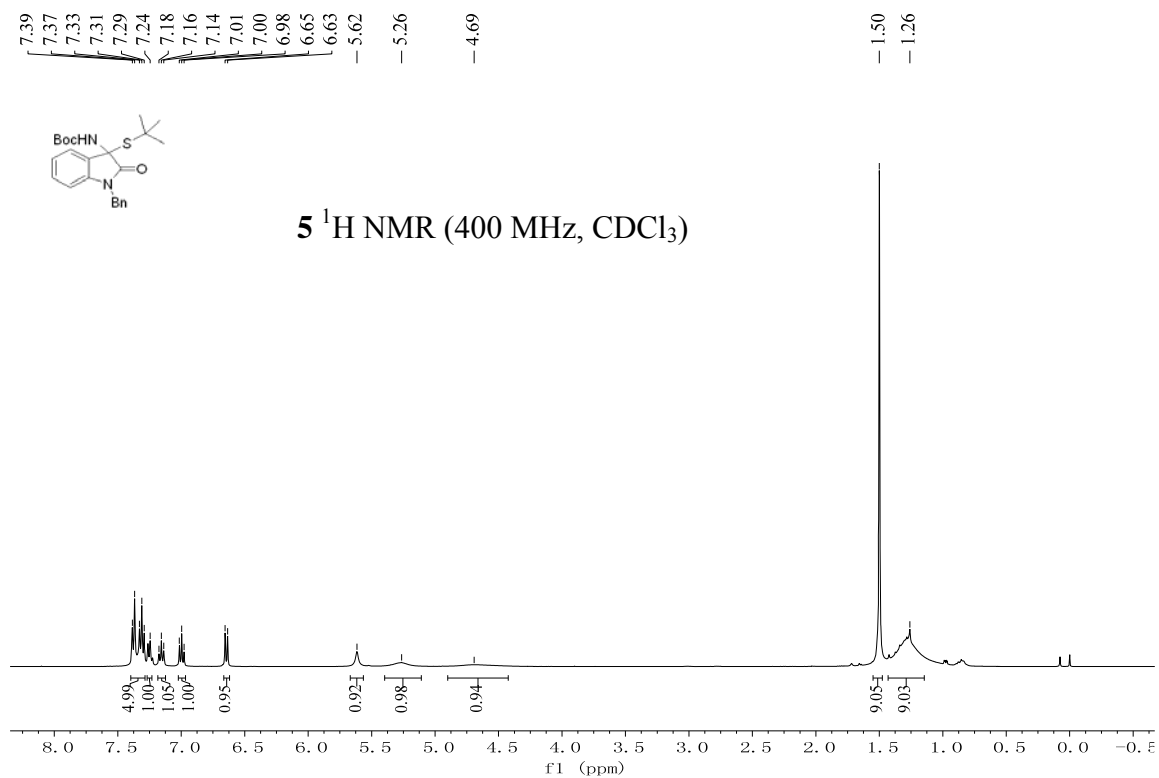
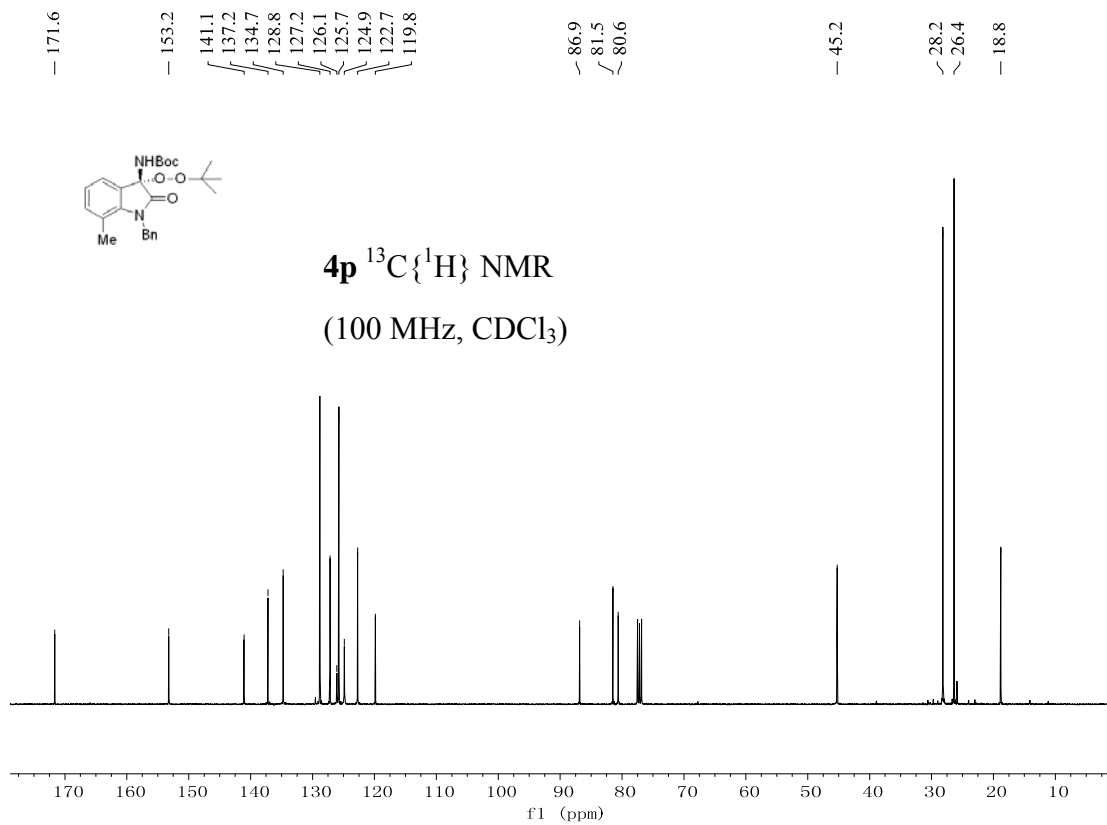
4m ^1H NMR (400 MHz, CDCl_3)

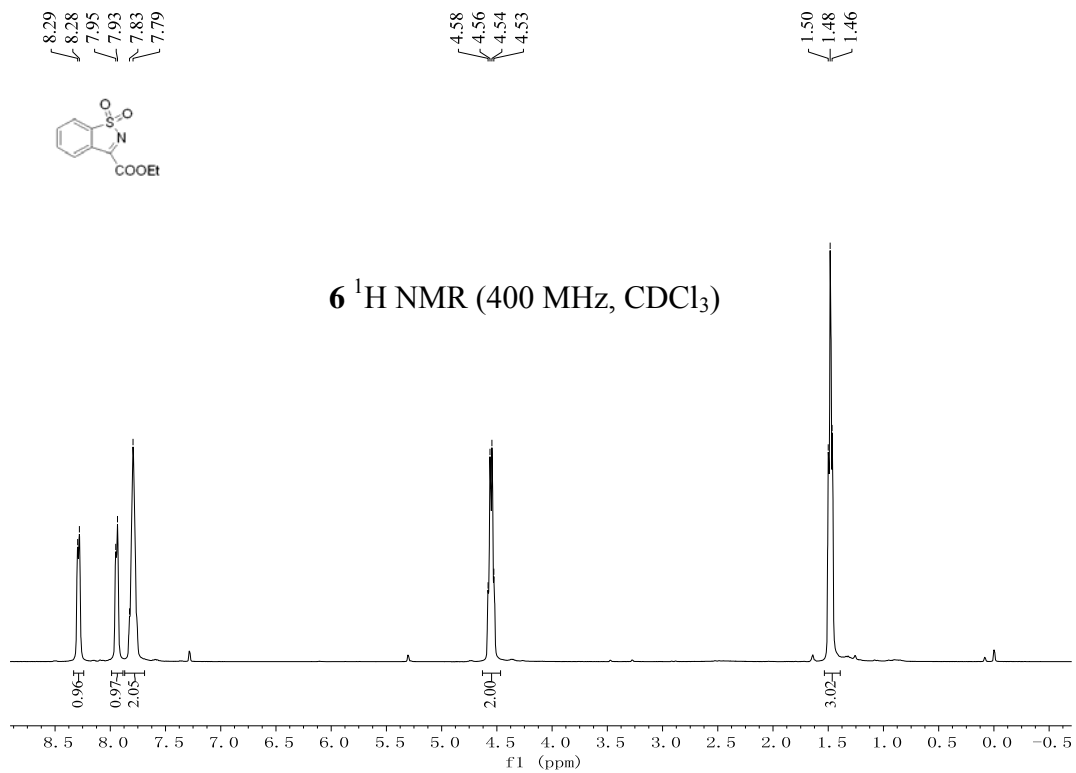
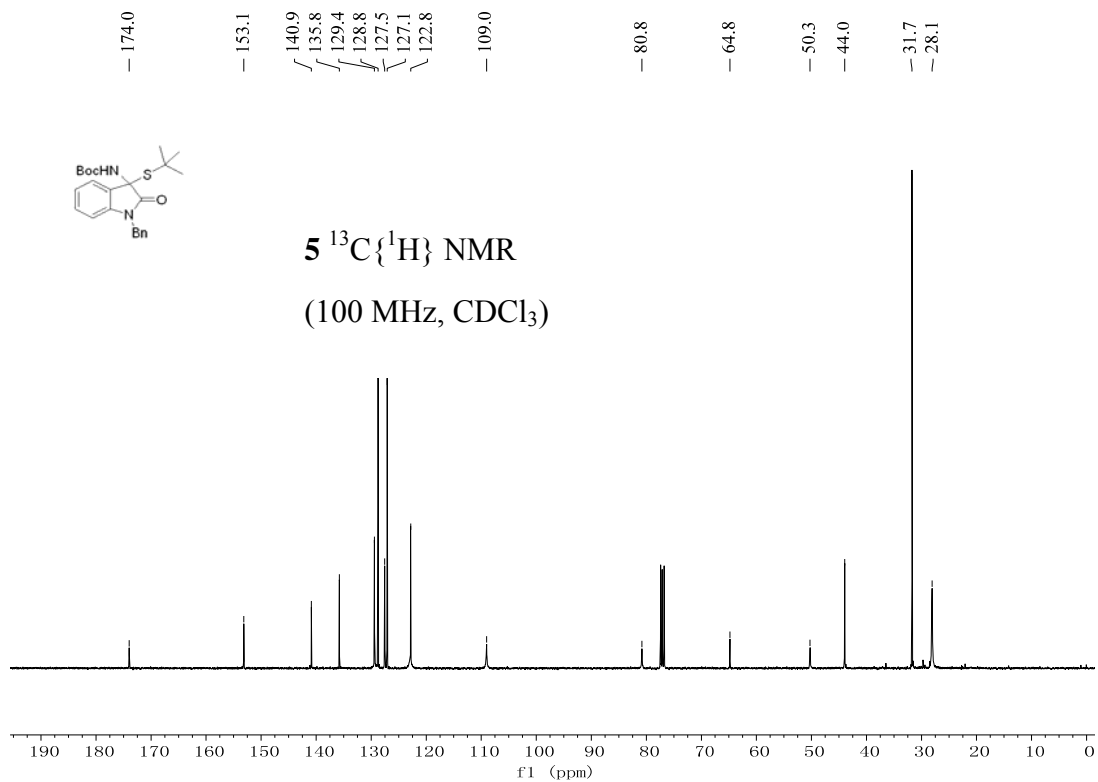


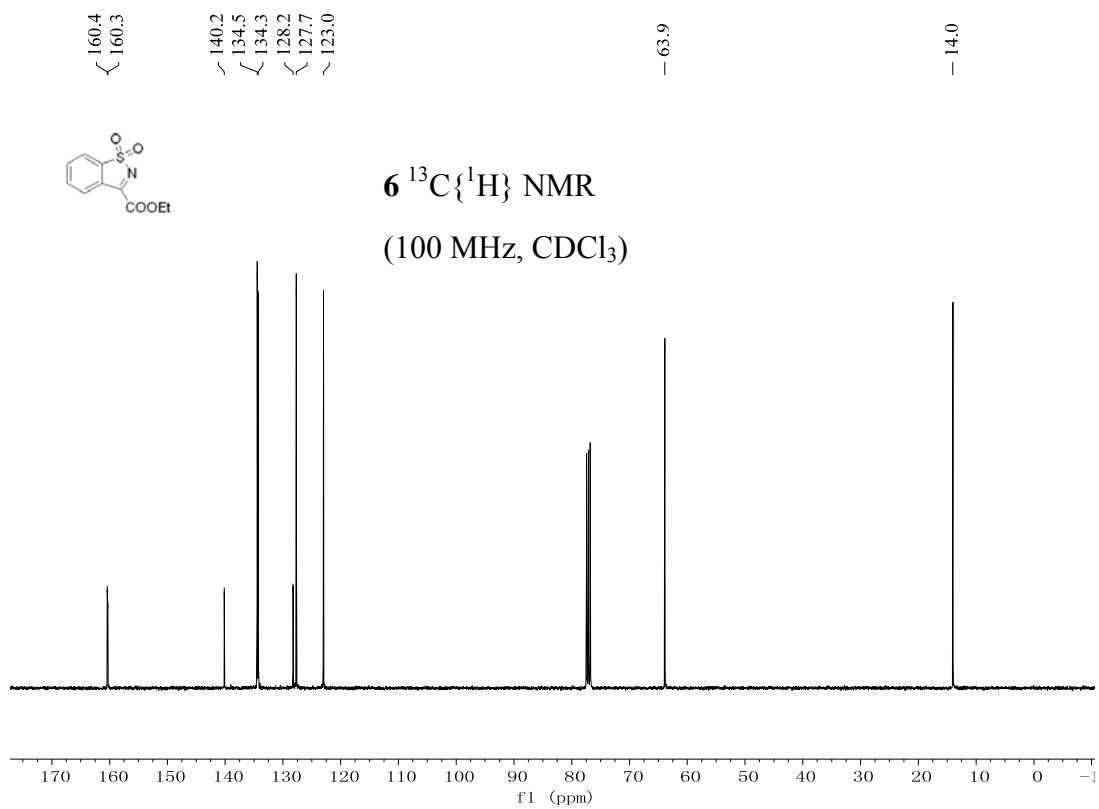












4. References

1. (a) C. Yao, Y. Chen, C. Wang, R. Sun, H. Chang, R. Jiang, L. Li, X. Wang and Y.-M. Li, *The Journal of Organic Chemistry*, 2022; (b) S. Yu, Q. Cai, C. Wang, J. Hou, J. Liang, Z. Jiao, C. Yao and Y.-M. Li, *The Journal of Organic Chemistry*, 2023, **88**, 3046-3053.
2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox. Gaussian 09, Revision D. 01. Gaussian, Inc., 2013.
3. Y. Zhao and D. G. Truhlar, *J. Chem. Phys.*, 2006, **125**, 194101.
4. (a) R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724-728; (b) W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257-2261; (c) P. C. Hariharan and J. A. Pople, *Theoret. Chim. Acta*, 1973, **28**, 213-222; (d) T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. V. R. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294-301.
5. M. Dolg, U. Wedig, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1987, **86**, 866-872.
6. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378-6396.
7. J. Lu, F. Sha and X.-Y. Wu, *Tetrahedron Letters*, 2019, **60**, 1161-1165.
8. J. Liu, F.-M. Zhu, Y.-B. Chu, L.-H. Huang and Y.-F. Zhou, *Tetrahedron: Asymmetry*, 2015, **26**, 1130-1137.
9. T. Arai, K. Tsuchiya and E. Matsumura, *Org. Lett.*, 2015, **17**, 2416-2419.
10. D.-L. Kong, L. Cheng, T. Yue, H.-R. Wu, W.-C. Feng, D. Wang and L. Liu, *The Journal of*

Organic Chemistry, 2016, **81**, 5337-5344.

11. C. Beceño, P. Chauhan, A. Rembiak, A. Wang and D. Enders, *Advanced Synthesis & Catalysis*, 2015, **357**, 672-676.
12. H. Wang, T. Jiang and M.-H. Xu, *Journal of the American Chemical Society*, 2013, **135**, 971-974.