Electronic Supplementary Material (ESI) for ChemComm.

Enantioselective and Regioselective Aza-Friedel-Crafts Reaction of Electron-Rich Phenols with Isatin-Derived Ketimines

Liu Cai, Xiangshuai Liu, Jie Wang, Li Chen, Xin Li* and Jin-Pei Cheng

---

State Key Laboratory of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071(P. R. China).

Supporting Information

Contents

1. General information.....3

2. Optimization of reaction conditions.....4

3. General procedure for the the synthesis of **3a** , (rac)-**3a**, and **6**.....6

4. Compared with quinine-derived thiourea.....7

5. Plausible enantio-control model.....7

6. Single crystal X-ray structure of compound **3a**..... 8

7. Analytical data..... 9

8. References.....20

9. NMR and HPLC spectra.....21

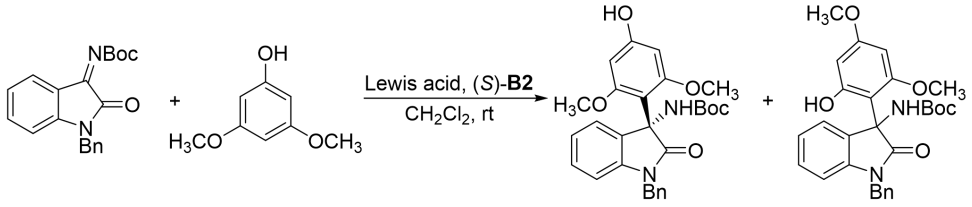
1. General information

Chemicals reagents and solvents were purchased from commercial suppliers and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Brucker-400 (400 MHz for ^{1}H, 100MHz for ^{13}C)spectrometer, ^{19}F NMR were recorded on a Varian NMR 400 spectrometer. The chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift mutiplicities: s = singlet, d = doublet, t =triplet, q = quartet, m = multiplet. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m). HPLC analysis was performed using Chiralcel columns purchased. Mass spectra were obtained using electrospray ionization (ESI) mass spectrometer. ESI-MS studies on catalytic complex were conducted on Thermo LTQ XL. Isatin-derived ketimines (**1a**-**1t**) were prepared according to the reference.[1] Phenols were obtained following the reported procedure.[2]

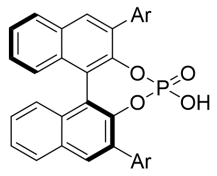
.

2. Optimization of reaction conditions[a-d]

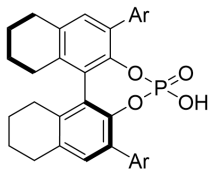
Table S1. Optimization of the catalysts



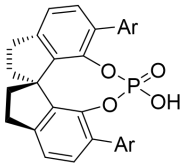
1a **2a** **3a** **4a**



(*S*)-**A1**: Ar= 9-anthyl
(*S*)-**A2**: Ar= 2,4,6-$^{i}Pr_3C_6H_2$
(*S*)-**A3**: Ar= 2,4,6-$Me_3C_6H_2$
(*S*)-**A4**: Ar= 3,5-$Ph_2C_6H_3$
(*S*)-**A5**: Ar= 1-naphthyl
(*S*)-**A6**: Ar= phenanthrenyl
(*S*)-**A7**: Ar= 3,5-$(CF_3)_2C_6H_3$
(*S*)-**A8**: Ar= triphenylsilyl



(*S*)-**B1**: Ar= 2,4,6-$^{i}Pr_3C_6H_2$
(*S*)-**B2**: Ar= 9-anthyl
(*S*)-**B3**: Ar= 2-naphthyl
(*S*)-**B4**: Ar= 4-Ph-C_6H_4

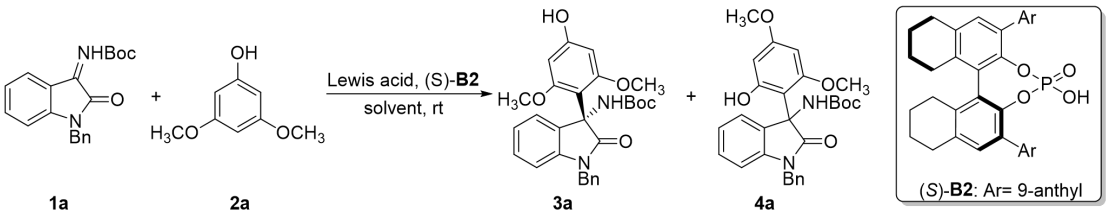


(*S*)-**C1**: Ar= 1-naphthyl
(*S*)-**C2**: Ar= 2,4,6-$^{i}Pr_3C_6H_2$

Entry[a]	CPA	Time (h)	Lewis acid	Yield (%)[b]	*ee* (**3a**)[c]	**3a/4a**[d]
1	**A1**	18	-	77	17	0.7/1
2	**A1**	18	$Bi(OAc)_3$	91	47	1.6/1
3	**A2**	18	$Bi(OAc)_3$	99	61	1.3/1
4	**A3**	18	$Bi(OAc)_3$	83	39	1.8/1
5	**A4**	18	$Bi(OAc)_3$	94	30	1.9/1
6	**A5**	18	$Bi(OAc)_3$	87	44	1.0/1
7	**A6**	18	$Bi(OAc)_3$	76	17	0.2/1
8	**A7**	18	$Bi(OAc)_3$	88	0	0.4/1
9	**A8**	18	$Bi(OAc)_3$	86	-21	0.6/1
10	**B1**	18	$Bi(OAc)_3$	65	66	0.5/1
11	**B2**	18	$Bi(OAc)_3$	99	73	2.3/1
12	**B3**	18	$Bi(OAc)_3$	99	46	0.9/1
13	**B4**	18	$Bi(OAc)_3$	99	30	1.0/1
14	**C1**	18	$Bi(OAc)_3$	87	-41	3.2/1
15	**C2**	18	$Bi(OAc)_3$	98	9	1.0/1

[a]The reaction was carried out with **1a** (0.1 mmol), **2a** (0.1 mmol), CPA (0.03 equiv), lewis acid (0.03 equiv) and solvent (1.0 mL) at rt. [b]Isolated yield. [c]Determined by HPLC analysis. [d]The regioselectivity is determined by HPLC analysis.

Table S2. Optimization of the solvents and lewis acids[a-d]

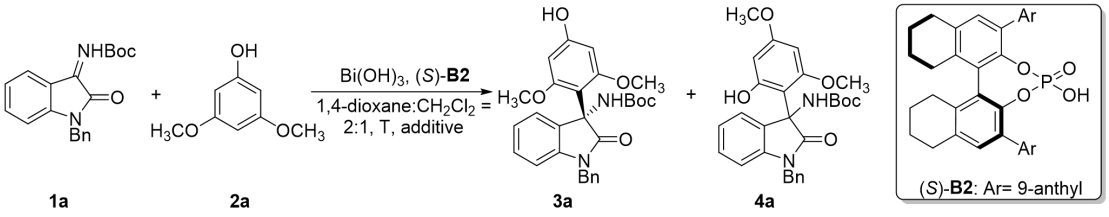


1a **2a** **3a** **4a**

Entry[a]	Lewis acid	Time (h)	Solvent	Yield (%)[b]	*ee* (**3a**)[c]	**3a**/**4a**[d]
1	$Bi(OAc)_3$	18	CH_3CN	82	53	1.5/1
2	$Bi(OAc)_3$	18	*o*-xylene	87	69	0.9/1
3	$Bi(OAc)_3$	18	MTBE	90	82	3.3/1
4	$Bi(OAc)_3$	18	EA	86	86	4.1/1
5	$Bi(OAc)_3$	18	Cyclohexane	59	69	1.2/1
6	$Bi(OAc)_3$	18	$CHCl_3$	73	50	0.8/1
7	$Bi(OAc)_3$	18	1,4-dioxane	66	88	3.2/1
8	$Bi(OAc)_3$	18	THF	62	89	2.9/1
9	$Bi(OAc)_3$	18	1,4-dioxane:CH_2Cl_2 = 1:1	96	84	4.6/1
10	$Bi(OAc)_3$	18	1,4-dioxane:CH_2Cl_2 = 1:2	91	88	4.7/1
11	$Bi(OAc)_3$	18	1,4-dioxane:CH_2Cl_2 = 2:1	98	91	4.8/1
12	$BiCl_3$	18		99	57	2.8/1
13	$BiBr_3$	18		98	67	2.6/1
14	$Bi(OH)_3$	18		91	92	5.3/1
15	$Sc(OAc)_3$	18	1,4-dioxane:CH_2Cl_2 = 2:1	89	71	3.0/1
16	$InBr_3$	18		54	0	1.0/1
17	$Sc(OTf)_3$	18		99	-	0.0/1
18	$Ca(OTf)_2$	18		99	0	0.4/1
19	$Mg(ClO_4)_2$	18		95	0	0.2/1

[a]The reaction was carried out with **1a** (0.1 mmol), **2a** (0.1 mmol), CPA (0.03 equiv), lewis acid (0.03 equiv) and solvent (1.0 mL) at rt. [b]Isolated yield. [c]Determined by HPLC analysis. [d]The regioselectivity is determined by HPLC analysis.

Table S3. Optimization of the ritio of **1a** / **2a**, additive and temperature[a-i]



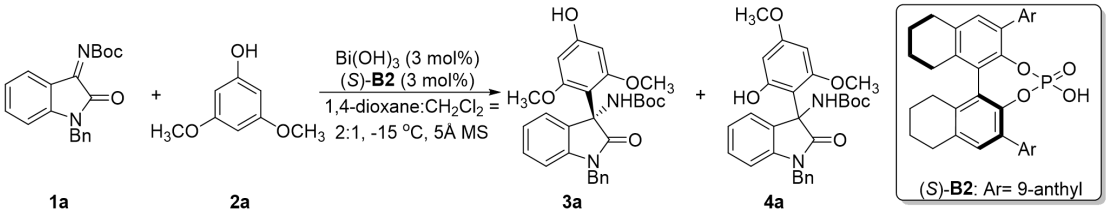
1a **2a** **3a** **4a**

Entry[a]	**1a**:**2a**	Additive (20 mg)	Time (h)	Yield (%)[b]	*ee* (**3a**)[c]	**3a**:**4a**[d]
1	1:1	-	18	91	92	5.3
2	1.2:1	-	18	99	91	6.4
3	1:1.2	-	18	99	89	5.2
4[e]	1.2:1	-	18	99	91	6.4
5[f]	1.2:1	-	18	99	89	5.3
6	1.2:1	3 Å Ms	18	99	92	5.6
7	1.2:1	4 Å Ms	18	99	92	6.1
8	1.2:1	5 Å Ms	18	99	93	6.4
9[g]	1.2:1	5 Å Ms	18	99	97	8.0

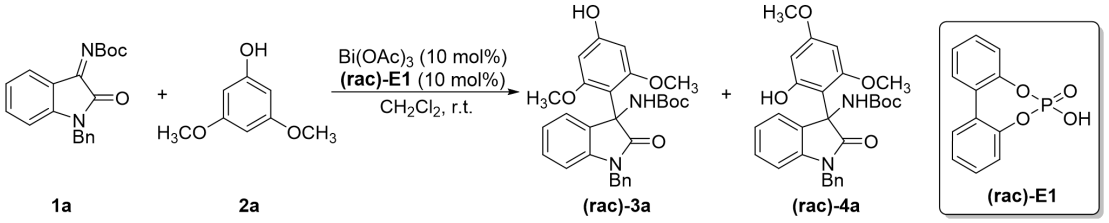
10[h]	1.2:1	5 Å Ms	18	99	97	12.2
11[i]	1.2:1	5 Å Ms	18	99	97	12.2

[a]The reaction was carried out with **1a** (0.1 mmol), **2a** (0.1 mmol), CPA (0.03 equiv), lewis acid (0.03 equiv) and solvent (1.0 mL) at rt. [b]Isolated yield. [c]Determined by HPLC analysis. [d]The regioselectivity is determined by HPLC analysis. [e]CPA/lewis acid = 2:1. [f]CPA/lewis acid = 1:2. [g]T = 0 °C. [h]T = -15 °C. [i]T = -20 °C.

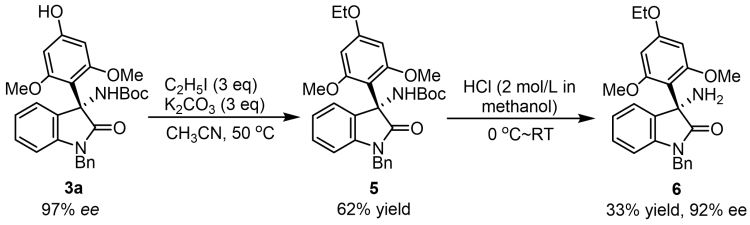
3. General procedure for the the synthesis of 3a , (rac)-3a, and 6



To an oven-dried reaction tube under nitrogen atmosphere, chiral phosphoric acid (*S*)-**B2** (0.003 mmol, 2.1 mg), $Bi(OH)_3$ (0.003 mmol, 0.8 mg) were dissolved in anhydrous solvent (1,4-dioxane:CH_2Cl_2 = 2:1, 1 mL) and stirred for 1 hour at 25 °C. Next, 5 Å MS (20 mg) and the corresponding **1a** (0.12 mmol, 40.4 mg) were added. Then, the reaction was cooled to -15 °C and **2a** (0.1 mmol, 15.4 mg) was added. The mixture was stirred at -15 °C for 36 h. The reaction mixture was purified directly by flash chromatography on silica gel PE/EA (3/1 to 1/1) to give the product **3a** and **4a**.



To an oven-dried reaction tube under nitrogen atmosphere, phosphoric acid (**rac**)-**E1** (0.01 mmol, 2.5 mg), $Bi(OAc)_3$ (0.01 mmol, 3.9 mg) were dissolved in anhydrous CH_2Cl_2 (1 mL), and the corresponding **1a** (0.12 mmol, 40.4 mg) and **2a** (0.1 mmol, 15.4 mg) was added. The mixture was stirred at r.t. for 2h. The reaction mixture was purified directly by flash chromatography on silica gel PE/EA (3/1 to 1/1) to give the product (rac)-**3a** and (rac)-**4a.**

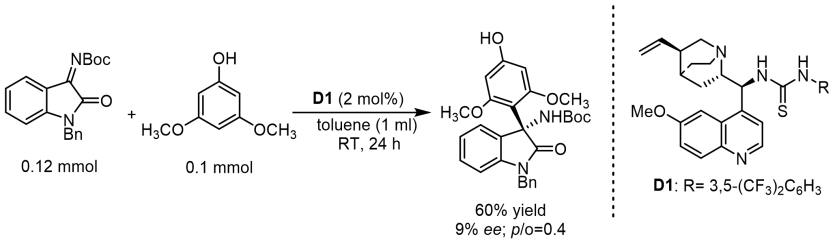


C_2H_5I (0.3 mmol, 24 ul), K_2CO_3 (0.3 mmol, 31.8 mg) and **3a** (0.1 mmol, 49.0 mg) were dissolved in 3mL of CH_3CN and the mixture was stirred at 50 °C until the reaction was completed. Then, the solvent was removed, and the crude mixture was dissolved in DCM and directly poured to the column

chromatograpy, using PE/EA (5:1) as eluent to afford compound **5** (32.1 mg, 62% yield).

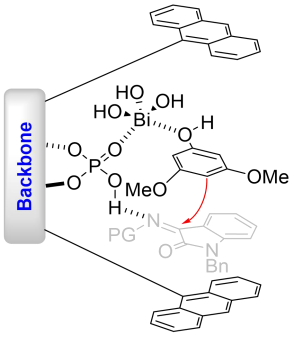
Compound **5** (0.6 mmol, 32.1 mg) was dissolved in 2 M HCl in methanol (5 mL) and stirred at r.t. for 30 min. Reaction was monitored by TLC. After all starting compounds were consumed, reaction content was concentrated in vacuo. Then, reaction mixture diluted with DCM was quenched with 30 mL of 10% (w/w) K_2CO_3(aq) and aqueous phase was washed with DCM (3 × 20 mL). Organic phase, dried over $NaSO_4$ and solvent was evaporated, the crude mixture was dissolved in DCM and directly poured to the column chromatograpy, using PE/EA (1:3) as eluent to afford compound **6** as a colourless oil (8 mg, 33% yield, 92% *ee*).[3]

4. Compared with quinine-derived thiourea



We also carried out a comparative experiment of bifunctional thiourea **D1** catalyzed reaction under Pedro's conditions. As a result, poor enantioselectivity (9% *ee*) and regioselectivity (0.4/1) was obtained.

5. Plausible enantio-control model.



Based on the experimental results, a plausible enantio-control mode of the aza-Friedel-Crafts reaction was proposed. We speculated that the chiral phosphoric acid acted as dual catalyst. When bismuth salt was added, the CPA's acidity was enhanced and the chiral environment was also changed, which makes the enantioselectivity and regioselectivity better controlled. And a lower temperature was beneficial to kinetic control product of **3a**.

6. Single crystal X-ray structure of compound 3a

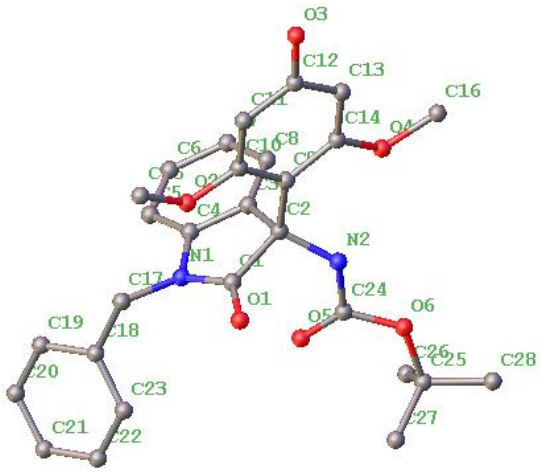


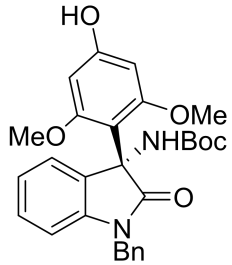
Figure S1 X-ray crystallography data of **3a**

Table S4. Crystal data and structure refinement for CCDC 1936165.

Identification code	CCDC 1936165
Empirical formula	$C_{28}H_{30}N_2O_6$
Formula weight	490.54
Temperature/K	294.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.51250(10)
b/Å	16.33800(10)
c/Å	17.88090(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2486.83(4)
Z	4
ρ_{calc}g/cm^3	1.310
μ/mm^{-1}	0.757
F(000)	1040.0
Crystal size/mm^3	0.36 × 0.22 × 0.08
Radiation	CuKα (λ = 1.54184)

2Θ range for data collection/°	7.33 to 148.99
Index ranges	$-5 \leq h \leq 10$, $-20 \leq k \leq 20$, $-22 \leq l \leq 22$
Reflections collected	16130
Independent reflections	4929 [R_{int} = 0.0214, R_{sigma} = 0.0218]
Data/restraints/parameters	4929/0/336
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0479, wR_2 = 0.1156
Final R indexes [all data]	R_1 = 0.0700, wR_2 = 0.1250
Largest diff. peak/hole / e $Å^{-3}$	0.28/-0.34

7. Analytical data

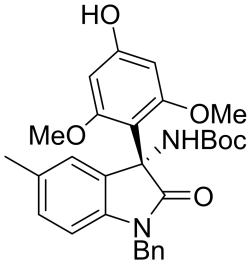


Compound 3a: *tert*-butyl (*R*)-(1-benzyl-3-(4-hydroxy-2,6-dimethoxyphenyl)-2-oxoindolin-3-yl) carbamate, white solid, 49 mg (99% of total yield), *ee* = 97%, regioselectivity ratio (*p*/*o* = 12/1); $[\alpha]_D^{25}$ = -209.0 (c = 1.275, CH_3OH); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 3/1, t_{major} = 7.3 min, t_{minor} = 13.1 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.84 (br, 1H), 7.55 (d, *J* = 7.0 Hz, 2H), 7.39 - 7.20 (m, 4H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 7.4 Hz, 1H), 5.95 (s, 2H), 5.17 - 4.73 (m, 2H), 3.46 (s, 6H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 158.5, 158.0, 143.6, 136.5, 128.6, 128.4, 128.2, 127.4, 123.5, 122.6, 108.6, 106.2, 95.0, 77.2, 63.2, 56.0, 45.0, 28.4.

HRMS (ESI) calcd for $C_{28}H_{31}N_2O_6$ $(M+H)^+$: 491.2177, found: 491.2180.

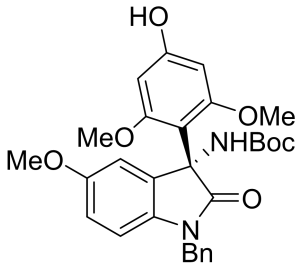


Compound 3b: *tert*-butyl (*R*)-(1-benzyl-3-(4-hydroxy-2,6-dimethoxyphenyl)-5-methyl-2-oxoindolin-3-yl) carbamate, white solid, 50 mg (99% of total yield), *ee* = 98%, regioselectivity ratio (*p*/*o* = 15/1); $[\alpha]_D^{25}$ = -173.3, (c = 0.25, CH_3OH); HPLC condition: chiralpak IA, 210 nm, 1 mL/min, hexane/i-PrOH = 4/1, t_{major} = 10.0 min, t_{minor} = 16.4 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.88 (s, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.39 - 7.14 (m, 3H), 7.05 (s, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 1H), 5.93 (s, 2H), 4.97 (s, 2H), 3.42 (s, 6H), 2.11 (s, 3H), 1.22 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 158.4, 158.0, 141.2, 136.6, 132.0, 128.8, 128.6, 128.2, 127.4, 124.3, 108.4, 106.1, 95.0, 77.3, 63.4, 56.0, 45.1, 28.4, 21.1.

HRMS (ESI) calcd for $C_{29}H_{33}N_2O_6$ $(M+H)^+$: 505.2333, found: 505.2340.

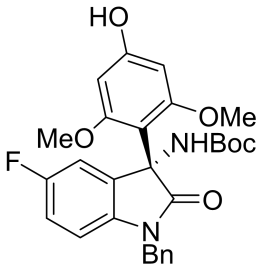


Compound 3c: *tert*-butyl (*R*)-(1-benzyl-3-(4-hydroxy-2,6-dimethoxyphenyl)-5-methoxy-2-oxoindolin-3-yl)carbamate, white solid, 52 mg (99% of total yield), *ee* = 95%, regioselectivity ratio (*p*/*o* = 11/1); $[\alpha]_D^{25}$ = -186.6, (c = 0.89, CH_3OH); HPLC condition: chiralpak IA, 210 nm, 1 mL/min, hexane/i-PrOH = 4/1, t_{major} = 14.4 min, t_{minor} = 23.2 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.76 (br, 1H), 7.53 (d, *J* = 7.3 Hz, 2H), 7.42 - 7.17 (m, 3H), 6.93 (s, 1H), 6.63 (q, *J* = 8.3 Hz, 2H), 5.94 (s, 2H), 5.00 (s, 2H), 3.69 (s, 3H), 3.39 (s, 6H), 1.30 (s, 9H).

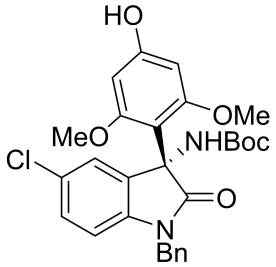
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 158.5, 158.1, 155.8, 137.4, 136.5, 133.1, 128.6, 128.1, 127.4, 112.2, 111.4, 108.9, 106.1 , 95.0, 77.2, 63.4, 56.0, 557, 45.1, 28.4.

HRMS (ESI) calcd for $C_{29}H_{33}N_2O_7$ $(M+H)^+$: 521.2282, found: 521.2284.

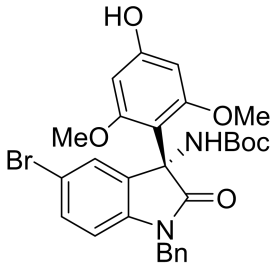


Compound 3d: *tert*-butyl (*R*)-(1-benzyl-5-fluoro-3-(4-hydroxy-2,6-dimethoxyphenyl)-2-oxoindolin-3-yl)carbamate, white solid, 43 mg, (84% of total yield), *ee* = 99%, regioselectivity ratio (*p*/*o* = 22/1); $[\alpha]_D^{25}$ = -207.5, (c = 0.81, CH_3OH); HPLC condition: chiralpak IA, 210 nm, 1 mL/min, hexane/i-PrOH = 4/1, t_{major} = 10.6 min, t_{minor} = 22.2 min.

^{1}H NMR (400 MHz,$CDCl_3$) δ 8.01 (s, 1H), 7.75 (s, 1H), 7.52 (d, *J* = 7.3 Hz, 2H), 7.40 - 7.24 (m, 3H), 7.05 (d, *J* = 6.6 Hz, 1H), 6.81 (t, *J* = 8.3 Hz, 1H), 6.62 (dd, *J* = 8.1, 3.5 Hz, 1H), 5.97 (s, 2H), 5.00 (s, 2H), 3.50 (s, 6H), 1.31 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 159.3 (d, *J* = 239.9 Hz), 158.5, 158.2, 139.6, 136.2, 128.6 , 128.0, 127.5, 114.6 (d, *J* = 23.4 Hz), 111.5 (d, *J* = 25.0 Hz), 109.1 (d, *J* = 8.1 Hz), 105.6, 94.9, 77.2, 63.2, 56.0, 45.1, 28.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ -120.8.
HRMS (ESI) calcd for $C_{28}H_{30}FN_2O_6$ $(M+H)^+$: 509.2082, found: 509.2080.

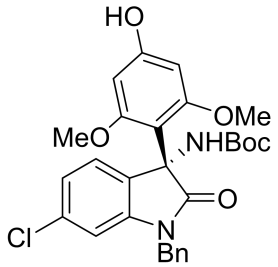


Compound 3e: *tert*-butyl (*R*)-(1-benzyl-5-chloro-3-(4-hydroxy-2,6-dimethoxyphenyl)-2-oxoindolin-3-yl)carbamate, white solid, 52 mg (99% of total yield), *ee* = 99%, regioselectivity ratio (*p*/*o* = 20/1); $[\alpha]_D^{25}$ = -183.9, (c = 0.87, CH_3OH); HPLC condition: chiralpak IA, 210 nm, 1 mL/min, hexane/i-PrOH = 3/1, t_{major} = 6.9 min, t_{minor} = 11.0 min.
^{1}H NMR (400 MHz,$CDCl_3$) δ 7.88 (s, 1H), 7.85 (s, 1H), 7.52 (d, *J* = 7.1 Hz, 2H), 7.39 - 7.22 (m, 4H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 5.96 (s, 2H), 4.99 (s, 2H), 3.50 (s, 6H), 1.34 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) 178.0, 158.5, 158.2, 142.2, 136.0, 133.2, 128.7, 128.4, 128.0, 127.7, 127.6, 123.9, 109.7, 105.5, 94.8, 77.2, 63.1, 56.0), 45.1, 28.4.
HRMS (ESI) calcd for $C_{28}H_{30}ClN_2O_6$ $(M+H)^+$: 525.1787, found: 525.1788.



Compound 3f: *tert*-butyl (*R*)-(1-benzyl-5-bromo-3-(4-hydroxy-2,6-dimethoxyphenyl)-2-oxoindolin-3-yl)carbamate, white solid, 56 mg (99% of total yield), *ee* = 99%, regioselectivity ratio (*p*/*o* = 22/1); $[\alpha]_D^{25}$ = -175.4, (c = 1.29, CH_3OH); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 3/1, t_{major} = 6.9 min, t_{minor} = 10.7 min.
^{1}H NMR (400 MHz,$CDCl_3$) δ 7.85 (s, 1H), 7.71 (s, 1H), 7.52 (d, *J* = 6.1 Hz, 2H), 7.41 - 7.18 (m, 5H), 6.60 (d, *J* = 7.7 Hz, 1H), 5.95 (s, 2H), 4.99 (s, 2H), 3.51 (s, 6H), 1.35 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 158.5, 158.1, 142.7, 136.0, 136.0, 131.2, 128.7, 128.0, 127.6, 126.6, 115.1, 110.2, 105.5, 94.8, 77.2, 63.0, 56.0, 45.1, 28.4.

HRMS (ESI) calcd for $C_{28}H_{30}BrN_2O_6$ $(M+H)^+$: 569.1282, found: 569.1284.

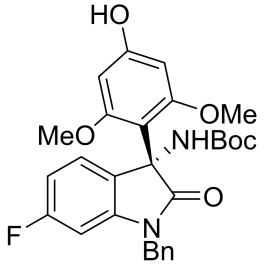


Compound 3g: *tert*-butyl (*R*)-(1-benzyl-6-chloro-3-(4-hydroxy-2,6-dimethoxyphenyl)-2-oxoindolin-3-yl)carbamate, white solid, 52 mg (99% of total yield), *ee* = 97%, regioselectivity ratio (*p*/*o* = 22/1); $[\alpha]_D^{25}$ = -233.7, (c = 0.50, CH_3OH); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 3/1, t_{major} = 5.7 min, t_{minor} = 11.9 min.

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.83 (s, 2H), 7.53 (d, *J* = 7.3 Hz, 2H), 7.38 - 7.28 (m, 3H), 7.19 (d, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.73 (s, 1H), 5.94 (s, 2H), 4.97 (s, 2H), 3.47 (s, 6H), 1.30 (s, 9H).

^{13}C NMR (101 MHz, CDCl3) δ 178.5, 158.4, 158.0, 144.8, 135.9, 134.0, 128.7, 128.1, 127.6, 124.4, 122.5, 109.2, 105.6, 100.0, 94.8, 77.3, 62.7, 56.0, 45.1, 28.4.

HRMS (ESI) calcd for $C_{28}H_{30}ClN_2O_6$ $(M+H)^+$: 525.1787, found: 525.1788.



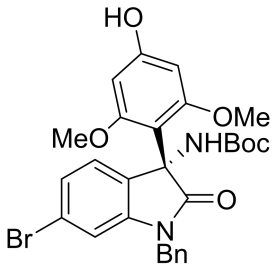
Compound 3h: *tert*-butyl (*R*)-(1-benzyl-6-fluoro-3-(4-hydroxy-2,6-dimethoxyphenyl)-2-oxoindolin-3-yl)carbamate, white solid, 46 mg (99% of total yield), *ee* = 96%, regioselectivity ratio (*p*/*o* = 10/1); $[\alpha]_D^{25}$ = -98.1, (c = 0.50, CH_3OH); HPLC condition: chiralpak IA, 210 nm, 1 mL/min, hexane/i-PrOH = 4/1, t_{major} = 9.3 min, t_{minor} = 20.4 min.

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.82 (s, 2H), 7.53 (d, *J* = 7.1 Hz, 2H), 7.38 - 7.28 (m, 3H), 7.24 - 7.18 (m, 1H), 6.63 - 6.52 (m, 1H), 6.46 (d, *J* = 8.7 Hz, 1H), 5.96 (s, 2H), 4.99 (s, 2H), 3.48 (s, 6H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 163.0 (d, *J* = 244.4 Hz), 158.4, 158.0, 145.2 (d, *J* = 11.9 Hz), 135.9, 128.7, 128.1, 127.6 , 124.5 (d, *J* = 9.7 Hz), 108.6 (d, *J* = 22.3 Hz), 106.1, 97.4 (d, *J* = 27.3 Hz), 94.9, 77.2, 62.7, 56.0 , 45.2, 28.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.7.

HRMS (ESI) calcd for $C_{28}H_{30}FN_2O_6$ $(M+H)^+$: 509.2082, found: 509.2086.

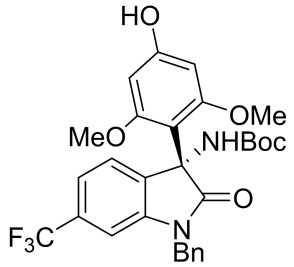


Compound 3i: *tert*-butyl (*R*)-(1-benzyl-6-bromo-3-(4-hydroxy-2,6-dimethoxyphenyl)-2-oxoindolin-3-yl)carbamate, white solid, 56 mg (99% of total yield), *ee* = 99%, regioselectivity ratio (*p*/*o* = 25/1), $[\alpha]_D^{25}$ = -239.3, (c = 0.50, CH_3OH); HPLC condition: chiralpak IA, 210 nm, 1 mL/min, hexane/i-PrOH = 4/1, t_{major} = 8.9 min, t_{minor} = 20.3 min.

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.81 (s, 1H), 7.65 (s, 1H), 7.53 (d, *J* = 7.1 Hz, 2H), 7.40 - 7.21 (m, 3H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.88 (s, 1H), 5.93 (s, 2H), 4.97 (s, 2H), 3.48 (s, 6H), 1.30 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 158.5, 158.0, 145.0, 135.9, 130.6, 128.7, 128.1, 127.6, 125.4, 124.8, 121.9, 111.9, 105.6, 94.8, 77.2, 62.8, 56.0, 45.1, 28.4.

HRMS (ESI) calcd for $C_{28}H_{30}BrN_2O_6$ $(M+H)^+$: 569.1282, found: 569.1285.



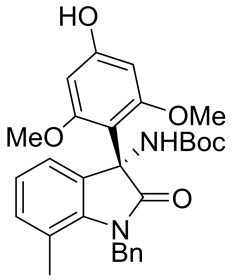
Compound 3j: *tert*-butyl (*R*)-(1-benzyl-3-(4-hydroxy-2,6-dimethoxyphenyl)-2-oxo-6-(trifluoromethyl)indolin-3-yl)carbamate, white solid, 55 mg (99% of total yield), *ee* = 98%, regioselectivity ratio (*p*/*o* = 14/1), $[\alpha]_D^{25}$ = -217.0, (c = 0.47, CH_3OH); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 3/1, t_{major} = 4.6 min, t_{minor} = 10.0 min.

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.82 (s, 1H), 7.67 (d, *J* = 5.6 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.41 - 7.24 (m, 4H), 7.19 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 17.4 Hz, 1H), 5.94 (s, 2H), 5.02 (s, 2H), 3.60 (s, 6H), 1.29 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 158.6, 158.2, 144.2, 135.7, 130.6 (q, *J* = 32.3 Hz), 128.7, 128.1, 127.7, 123.9 (q, *J* = 270.1 Hz), 123.6, 119.8 (d, *J* = 3.7 Hz), 105.2, 94.8, 77.2, 62.8, 56.0, 45.2, 28.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.2.

HRMS (ESI) calcd for $C_{29}H_{30}F_3N_2O_6$ $(M+H)^+$: 559.2050, found: 559.2054.

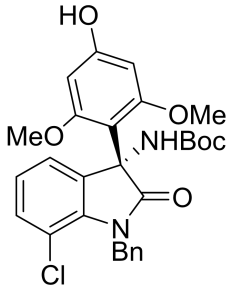


Compound 3k: *tert*-butyl (*R*)-(1-benzyl-3-(4-hydroxy-2,6-dimethoxyphenyl)-7-methyl-2-oxoindolin-3-yl)carbamate, white solid, 42 mg (83% of total yield), *ee* = 97%, regioselectivity ratio (*p*/*o* = 10/1); $[\alpha]_D^{25}$ = -180.2, (c = 0.47, CH_3OH); HPLC condition: chiralpak IA, 210 nm, 1 mL/min, hexane/i-PrOH = 4/1, t_{major} = 28.2 min, t_{minor} = 51.6 min.

^{1}H NMR (400 MHz,$CDCl_3$) δ 8.13 (s, 1H), 7.79 (s, 1H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.32 - 7.15 (m, 2H), 6.93 (d, *J* = 7.3 Hz, 1H), 6.86 (t, *J* = 7.5 Hz, 1H), 6.00 (s, 2H), 5.30 (d, *J* = 16.4 Hz, 1H), 5.18 (d, *J* = 16.2 Hz, 1H), 3.61 (s, 6H), 2.29 (s, 3H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.8, 158.4, 157.9, 141.8, 138.6, 132.6, 128.5, 126.9, 126.7, 122.7, 121.6, 119.1, 106.6, 95.1, 77.3, 62.7, 56.2, 46.7, 28.4, 18.9.

HRMS (ESI) calcd for $C_{29}H_{33}N_2O_6$ $(M+H)^+$: 505.2333, found: 505.2341.

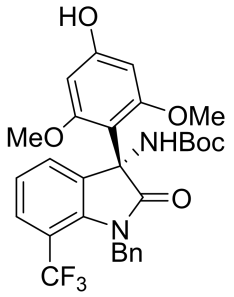


Compound 3l: *tert*-butyl (*R*)-(1-benzyl-7-chloro-3-(4-hydroxy-2,6-dimethoxyphenyl)-2-oxoindolin-3-yl)carbamate, white solid, 50 mg (96% of total yield), *ee* = 96%, regioselectivity ratio (*p*/*o* = 20/1); $[\alpha]_D^{25}$ = -232.8, (c = 0.74, CH_3OH); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 3/1, t_{major} = 4.8 min, t_{minor} = 9.6 min.

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.78 (s, 1H), 7.65 (s, 1H), 7.59 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.1 Hz, 2H), 7.22 (m, 2H), 7.12 (d, *J* = 7.9 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 5.91 (s, 2H), 5.50 (d, *J* = 15.9 Hz, 1H), 5.27 (d, *J* = 16.1 Hz, 1H), 3.48 (s, 6H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.3, 158.5, 158.0, 139.8, 138.2, 131.0, 128.2, 127.8, 126.9, 123.4, 122.2, 114.8, 105.8, 94.9, 77.2, 62.7, 56.1, 46.3, 28.3.

HRMS (ESI) calcd for $C_{28}H_{30}ClN_2O_6$ $(M+H)^+$: 525.1787, found: 525.1790.



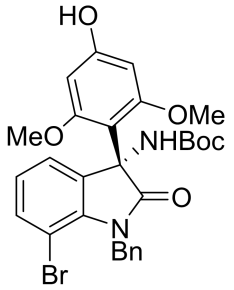
Compound 3m: .*tert*-butyl (*R*)-(1-benzyl-3-(4-hydroxy-2,6-dimethoxyphenyl)-2-oxo-7-(trifluoromethyl)indolin-3-yl)carbamate, white solid, 51 mg (91% of total yield), *ee* = 92%, regioselectivity ratio (*p*/*o* = 5/1); $[\alpha]_D^{25}$ = -180.2, (c = 0.47, CH_3OH); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 3/1, t_{major} = 7.4 min, t_{minor} = 15.3 min.

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.95 (s, 1H), 7.86 (s, 1H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.24 - 7.17 (m, 1H), 7.00 (t, *J* = 7.7 Hz, 1H), 5.91 (d, *J* = 8.4 Hz, 2H), 5.26 (d, *J* = 16.9 Hz, 1H), 5.16 (d, *J* = 16.9 Hz, 1H), 3.57 (s, 6H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 181.2, 158.6, 158.2, 153.6, 142.1, 137.2, 135.1, 128.0, 127.2, 126.6 (d, *J* = 5.8 Hz), 122.2, 112.2 (d, *J* = 29.6 Hz), 105.4, 95.0, 77.2, 61.8, 56.2, 48.2, 28.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -54.2.

HRMS (ESI) calcd for $C_{29}H_{30}F_3N_2O_6$ $(M+H)^+$: 559.2050, found: 559.2054.

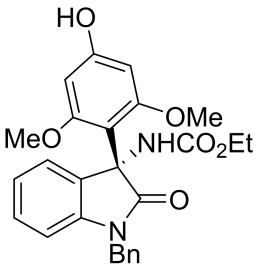


Compound 3n: *tert*-butyl (*R*)-(1-benzyl-7-bromo-3-(4-hydroxy-2,6-dimethoxyphenyl)-2-oxoindolin-3-yl)carbamate, white solid, 55 mg (96% of total yield), *ee* = 94%, regioselectivity ratio (*p*/*o* = 5/1); $[\alpha]_D^{25}$ = -176.0, (c = 0.68, CH_3OH); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 3/1, t_{major} = 6.7 min, t_{minor} = 16.3 min.

^{1}H NMR (400 MHz, DMSO) δ 9.75 (s, 1H), 7.94 (s, 1H), 7.48 (t, *J* = 20.1 Hz, 2H), 7.37 (d, *J* = 7.1 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 3H), 7.23 (t, *J* = 7.1 Hz, 1H), 6.80 (t, *J* = 7.7 Hz, 1H), 6.10 (s, 2H), δ 5.31 (d, *J* = 16.9 Hz, 1H), 5.25 (d, *J* = 16.9 Hz, 1H), 3.63 (s, 6H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, DMSO) δ 176.6, 159.1, 159.0, 153.7, 145.6, 137.0, 128.8, 128.2, 127.7, 125.1, 124.6, 121.1, 111.5, 106.1, 94.4, 79.0, 62.1, 56.6, 44.2, 28.6.

HRMS (ESI) calcd for $C_{28}H_{30}BrN_2O_6$ $(M+H)^+$: 569.1282, found: 569.1281.

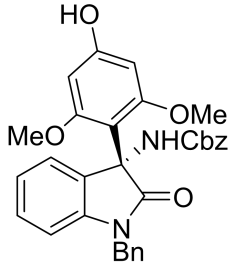


Compound 3o: ethyl (*R*)-(1-benzyl-3-(4-hydroxy-2,6-dimethoxyphenyl)-2-oxoindolin-3-yl) carbamatewhite solid, 31 mg (68% of total yield), *ee* = 97%, regioselectivity ratio (*p*/*o* = 22/1); $[\alpha]_D^{25}$ = -115.4 (c = 0.2, CH_3OH); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 3/1, t_{major} = 11.8 min, t_{minor} = 24.2 min.

^{1}H NMR (400 MHz,$CDCl_3$) δ 8.24 (s, 1H), 8.09 (s, 1H), 7.55 (d, *J* = 7.4 Hz, 2H), 7.39 - 7.22 (m, 4H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 5.94 (s, 2H), 5.06 (d, *J* = 15.7 Hz, 1H), 4.97 (d, *J* = 15.6 Hz, 1H), 4.03 (d, *J* = 7.0 Hz, 1H), 3.93 (s, 1H), 3.48 (s, 6H), 1.16 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 158.5, 158.0, 143.6, 136.5, 128.6, 128.4, 128.2, 127.4, 123.5, 122.6, 108.6, 106.2, 95.0, 77.2, 63.2, 56.0, 45.0, 28.4.

HRMS (ESI) calcd for $C_{26}H_{27}N_2O_6$ $(M+H)^+$: 463.1864, found: 463.1870.

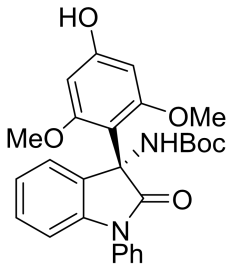


Compound 3p: benzyl (*R*)-(1-benzyl-3-(4-hydroxy-2,6-dimethoxyphenyl)-2-oxoindolin-3-yl) carbamate, white solid, 48 mg (91% of total yield), *ee* = 91%, regioselectivity ratio (*p*/*o* = 4/1); $[\alpha]_D^{25}$ = -205.0, (c = 0.27, CH_3OH); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 3/1, t_{major} = 8.4 min, t_{minor} = 16.0 min.

^{1}H NMR (400 MHz,$CDCl_3$) δ 8.32 (s, 1H), 7.82 (s, 1H), 7.57 (s, 2H), 7.41 - 7.23 (m, 9H), 7.18 (t, *J* = 7.7 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.78 (s, 1H), 5.95 (s, 2H), 5.21 - 4.71 (m 4H), 3.46 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 158.4, 158.0, 143.6, 136.4, 128.8, 128.7, 128.4, 128.1, 128.0, 127.5, 123.6, 122.8, 108.9, 105.6, 95.0, 77.2, 66.7, 63.4, 56.0.

HRMS (ESI) calcd for $C_{31}H_{29}N_2O_6$ $(M+H)^+$: 525.2020, found: 525.2025.

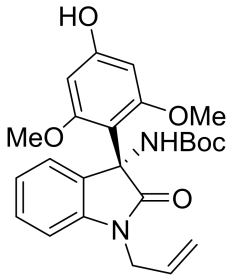


Compound 3q: *tert*-butyl (*R*)-(3-(4-hydroxy-2,6-dimethoxyphenyl)-2-oxo-1-phenylindolin-3-yl)carbamate, white solid, 44 mg (93% of total yield), *ee* = 92%, regioselectivity ratio (*p*/*o* = 6/1); $[\alpha]_D^{25}$ = -161.9, (c = 0.2, CH_3OH); HPLC condition: chiralpak IA, 210 nm, 1 mL/min, hexane/i-PrOH = 4/1, t_{major} = 9.6 min, t_{minor} = 16.0 min.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.75 (s, 1H), 8.03 (s, 1H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 7.1 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.31 (s, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.68 (s, 1H), 6.14 (s, 2H), 3.67 (s, 6H), 1.27 (s, 9H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 175.4, 159.0, 158.9, 153.7, 135.9, 129.8, 128.7, 127.7, 126.8, 123.8, 122.7, 108.6, 106.7, 94.4, 56.8, 28.5.

HRMS (ESI) calcd for $C_{27}H_{29}N_2O_6$ $(M+H)^+$: 476.1947, found: 476.1947.

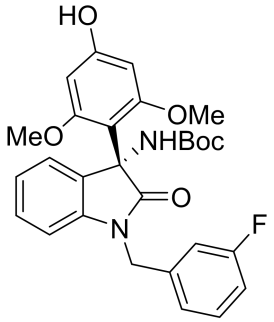


Compound 3r: *tert*-butyl (*R*)-(1-allyl-3-(4-hydroxy-2,6-dimethoxyphenyl)-2-oxoindolin-3-yl) carbamate, white solid, 34 mg (78% of total yield), *ee* = 96%, regioselectivity ratio (*p*/*o* = 17/1); $[\alpha]_D^{25}$ = -205.0, (c = 0.27, CH_3OH); HPLC condition: chiralpak IA, 210 nm, 1 mL/min, hexane/i-PrOH = 4/1, t_{major} = 17.9 min, t_{minor} = 23.8 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.77 (s, 1H), 7.29 (d, *J* = 6.7 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 5.98 (m, 3H), 5.48 (d, *J* = 17.2 Hz, 1H), 5.28 (d, *J* = 10.2 Hz, 1H), 4.69 - 4.22 (m, 2H), 3.64 (s, 6H), 1.28 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 158.5, 158.0, 143.3, 132.2, 128.4, 123.4, 122.5, 118.0, 108.6, 106.2, 94.9, 77.2, 63.1, 56.0, 43.4, 28.3.

HRMS (ESI) calcd for $C_{24}H_{29}N_2O_6$ $(M+H)^+$: 440.1947, found: 440.1947.



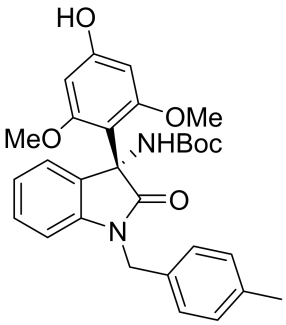
Compound 3s: *tert*-butyl (*R*)-(1-(3-fluorobenzyl)-3-(4-hydroxy-2,6-dimethoxyphenyl)-2-oxoindolin-3-yl)carbamate, white solid, 50 mg (99% of total yield), *ee* = 97%, regioselectivity ratio (*p*/*o* = 12/1), $[\alpha]_D^{25}$ = -229.8, (c = 0.95, CH_3OH); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 3/1, t_{major} = 7.2 min, t_{minor} = 14.8 min.

^{1}H NMR (400 MHz,$CDCl_3$) δ 8.08 - 7.95 (m, 1H), 7.87 (s, 1H), 7.39 - 7.18 (m, 4H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.03 - 6.85 (m, 2H), 6.66 (d, *J* = 7.7 Hz, 1H), 5.96 (s, 2H), 5.18 - 4.75 (m, 2H), 3.53 (s, 6H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 163.1 (d, *J* = 245.7 Hz), 143.3, 139.0 (d, *J* = 7.1 Hz), 131.7, 130.0 (d, *J* = 8.2 Hz), 128.5, 123.5, 123.4, 122.8, 115.0 (d, *J* = 22.2 Hz), 114.33 (d, *J* = 21.3 Hz), 108.5, 106.2, 95.0, 77.2, 63.2, 56.0, 44.5, 28.4.

^{19}F NMR (376 MHz, CDCl3) δ -112.7

HRMS (ESI) calcd for $C_{28}H_{30}FN_2O_6$ $(M+H)^+$:509.2082, found: 509.2087.

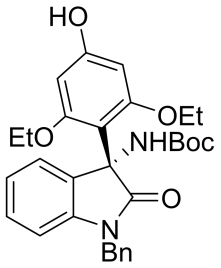


Compound 3t: *tert*-butyl (*R*)-(3-(4-hydroxy-2,6-dimethoxyphenyl)-1-(4-methylbenzyl)-2-oxoindolin-3-yl)carbamate, white solid, 49 mg (97% of total yield), *ee* = 98%, regioselectivity ratio (*p*/*o* = 15/1); $[\alpha]_D^{25}$ = -256.4, (c = 0.95, CH_3OH); HPLC condition: chiralpak IA, 210 nm, 1 mL/min, hexane/i-PrOH = 4/1, t_{major} = 9.3 min, t_{minor} = 16.0 min.

^{1}H NMR (400 MHz,$CDCl_3$) δ 8.11 (s, 1H), 7.81 (s, 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.12 (t, *J* = 8.1 Hz, 3H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 7.7 Hz, 1H), 5.96 (s, 2H), 4.99 (s, 2H), 3.49 (s, 6H), 2.33 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 158.5, 158.0, 143.7, 137.0, 133.4, 129.2, 128.4, 128.1, 123.4, 122.6, 108.7, 106.1, 95.0, 77.3, 63.2, 56.0, 44.8, 28.4, 21.1.

HRMS (ESI) calcd for $C_{29}H_{33}N_2O_6$ $(M+H)^+$: 505.2333, found: 505.2333.

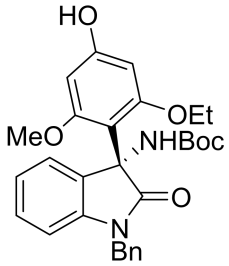


Compound 3u: *tert*-butyl (*R*)-(1-benzyl-3-(2,6-diethoxy-4-hydroxyphenyl)-2-oxoindolin-3-yl) carbamate, white solid, 51 mg (96% of total yield), *ee* = 99%, regioselectivity ratio (*p*/*o* =20/1); $[\alpha]_D^{25}$ = -60.2, (c = 0.4, CH_3OH); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 3/1, t_{major} = 6.6 min, t_{minor} = 13.7 min.

^{1}H NMR (400 MHz,$CDCl_3$) δ 8.43 (s, 1H), 8.21 (s, 1H), 7.61 (d, *J* = 7.3 Hz, 2H), 7.39 - 7.23 (m, 4H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 5.96 (s, 2H), 5.28 (d, *J* = 15.2 Hz, 1H), 4.74 (d, *J* = 15.7 Hz, 1H), 4.34 - 3.23 (m, 4H), 1.35 (m, 15H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 157.9, 143.7, 136.0, 132.1, 128.5, 128.3, 128.2, 127.4, 123.3, 122.7, 108.6, 105.5, 95.3, 79.1, 64.6, 63.5, 45.2, 28.4, 14.5.

HRMS (ESI) calcd for $C_{30}H_{35}N_2O_6$ $(M+H)^+$: 519.2490, found:519.2496.

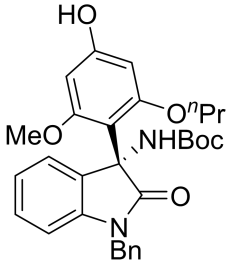


Compound 3v: *tert*-butyl (*R*)-(1-benzyl-3-(2-ethoxy-4-hydroxy-6-methoxyphenyl)-2-oxoindolin-3-yl)carbamate, white solid, 35 mg (70% of total yield), *ee* = 93%, regioselectivity ratio (*p*/*o* =11/1); $[\alpha]_D^{25}$ = -60.2, (c = 0.75, CH_3OH); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 3/1, t_{major} = 6.7 min, t_{minor} = 14.5 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (br, 1H), 8.00 (s, 1H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.38 - 7.19 (m, 4H), 7.12 (t, *J* = 7.3 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.05 (s, 1H), 5.81 (s, 1H), 5.15 - 4.81 (m, 2H), 4.01 (s, 2H), 3.21 (s, 3H), 1.32 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 157.9, 143.7, 136.47, 128.6, 128.4, 128.2, 127.4, 123.3, 122.6, 108.7, 105.8, 95.5, 95.0, 77.3, 64.8, 63.3, 55.9, 45.0, 28.4, 14.7.

HRMS (ESI) calcd for $C_{29}H_{33}N_2O_6$ $(M+H)^+$: 505.2333, found: 505.2338.

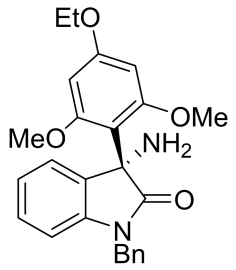


Compound 3w: *tert*-butyl (*R*)-(1-benzyl-3-(4-hydroxy-2-methoxy-6-propoxyphenyl)-2-oxoindolin-3-yl) carbamate, white solid, 46 mg (89% of total yield), *ee* = 88%, regioselectivity ratio (*p*/*o* =8/1); $[\alpha]_D^{2.5}$ = -107.520, (c = 0.62, CH_3OH); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 3/1, t_{major} = 5.7 min, t_{minor} = 14.0 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (br, 1H), 7.98 (s, 1H), 7.56 (d, *J* = 7.1 Hz, 2H), 7.36 - 7.21 (m, 4H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.07 (s, 1H), 5.79 (s, 1H), 5.15 - 4.86 (m, 2H), 3.91 (s, 2H), 3.13 (s, 3H), 1.89 (s, 2H), 1.32 (s, 9H), 1.14 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 157.9, 143.7, 136.5, 128.6, 128.4, 128.2, 127.4, 123.2, 122.6, 108.7, 105.8, 95.3, 94.9, 77.2, 70.8, 63.3, 55.9, 45.0, 28.4, 22.6, 11.1.

HRMS (ESI) calcd for $C_{30}H_{35}N_2O_6$ $(M+H)^+$: 519.2490, found: 519.2484.



Compound 6: (*R*)-3-amino-1-benzyl-3-(4-ethoxy-2,6-dimethoxyphenyl)indolin-2-one white oil, *ee* = 92%, $[\alpha]_D^{2.5}$ = -76.5, (c = 0.25, $CHCl_3$); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 3/2, t_{major} = 10.3 min, t_{minor} = 22.9 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.3 Hz, 2H), 7.39 - 7.25 (m, 4H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 6.76 (d, J = 7.7 Hz, 1H), 6.17 (s, 2H), 5.08 (d, *J* = 15.7 Hz, 1H), 4.96 (d, *J* = 16.0 Hz, 1H), 4.01 (q, *J* = 6.9 Hz, 2H), 3.67 (s, 6H), 3.04 (s, 2H), 1.42 (t, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 142.5, 136.6, 128.6, 128.3, 127.5, 127.3, 126.2, 123.4, 122.4, 109.1, 93.1, 63.6, 61.9, 56.0, 43.9.

HRMS (ESI) calcd for $C_{25}H_{27}N_2O_4$ $(M+H)^+$: 419.5005, found: 419.5005

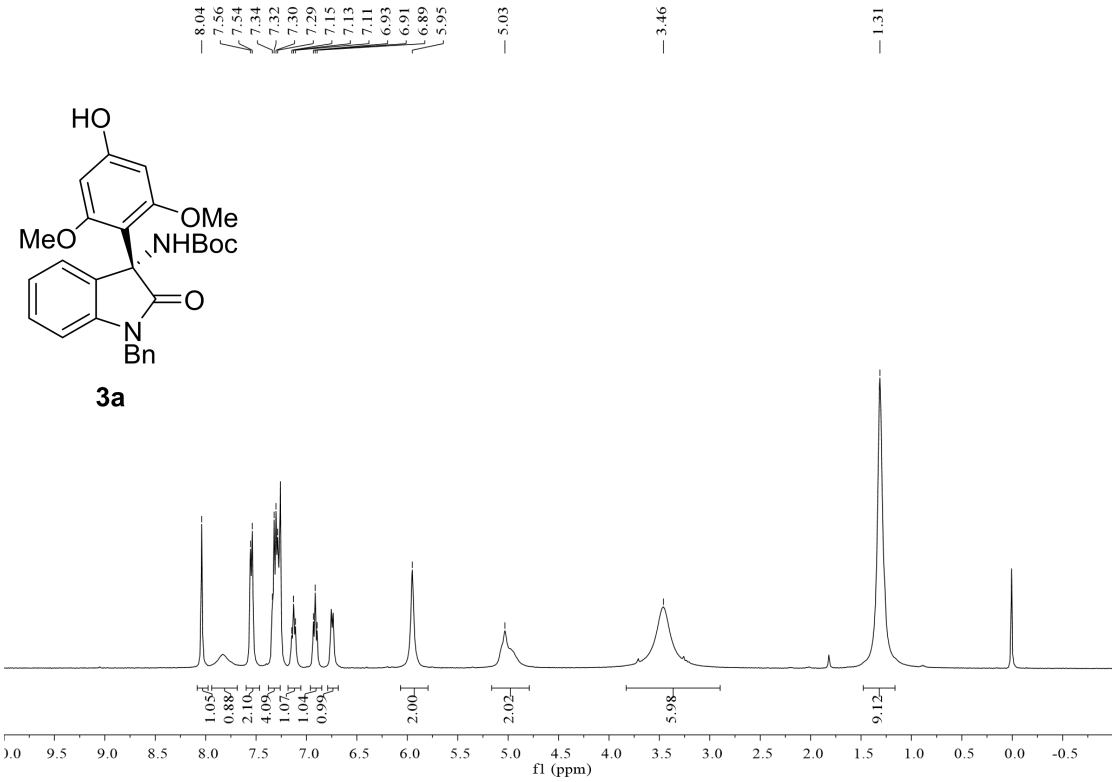
8. References

1 M. Holmquist, G. Blay, M. C. Muñoz, J. R. Pedro, *Adv. Synth. Catal*., 2015, **357**, 3857.

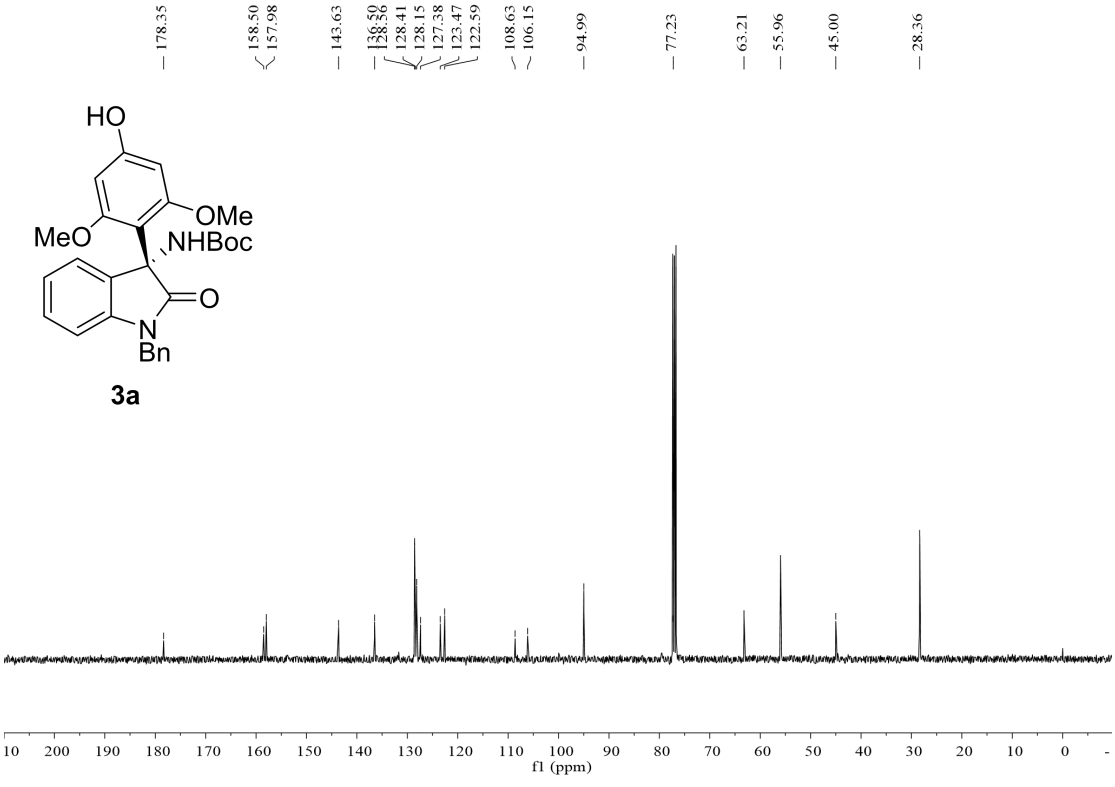
2 D. S. Wang, F. Schellenberger, J. T. Pham, H. -J. Butt, S. Wu, *Chem. Commun.,* 2018, **54** , 3403.

3 M. Montesinos-Magraner, C. Vila, A. Rendón-Patiño, G. Blay, I. Fernández, M. C. Muñoz, J. R. Pedro, *ACS Catal.,* 2016, **6**, 2689.

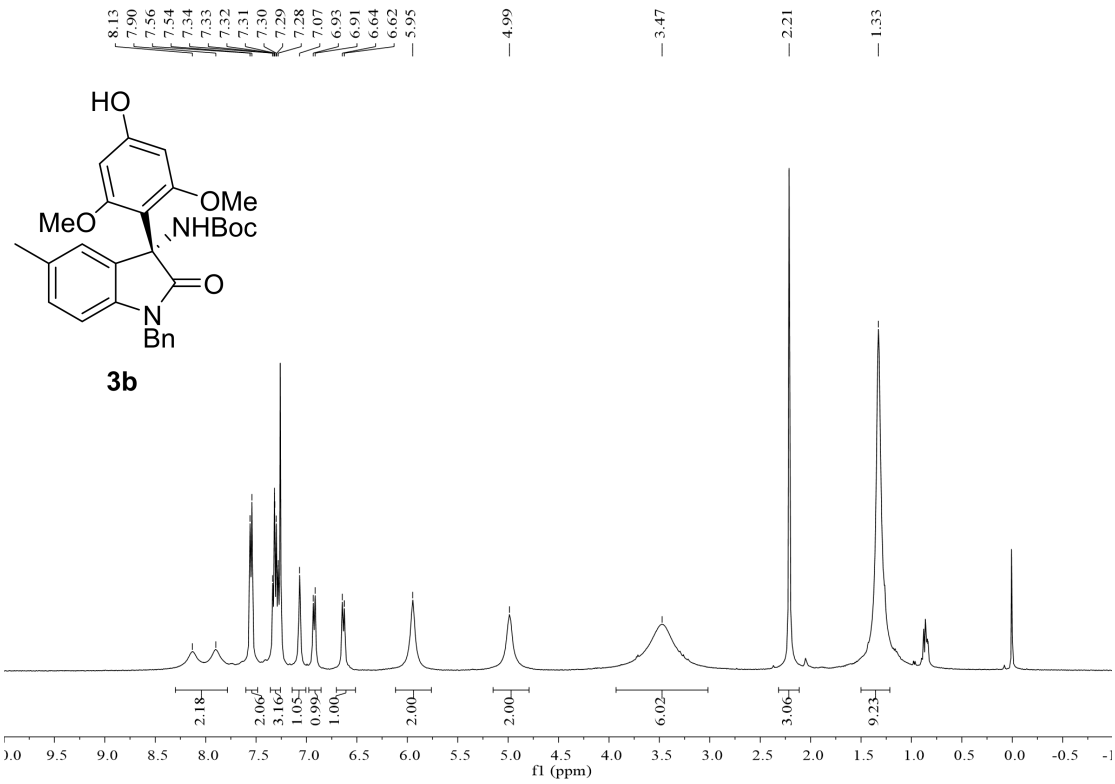
9. NMR and HPLC spectra

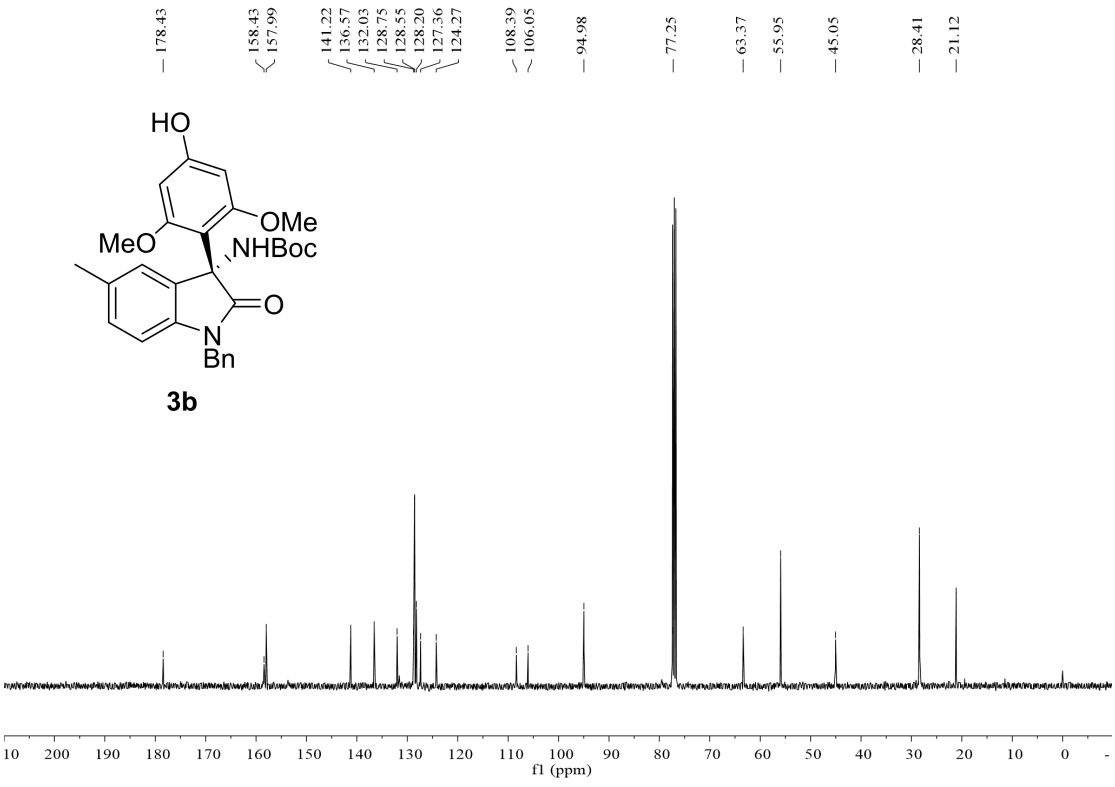


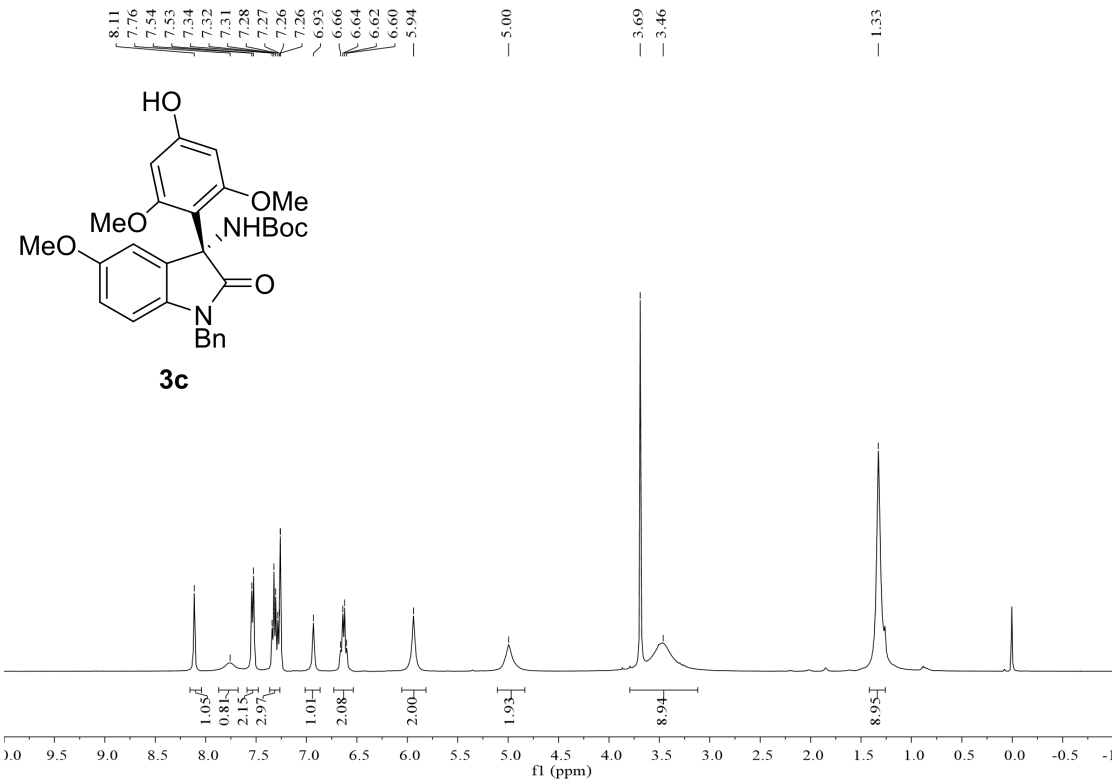
3a



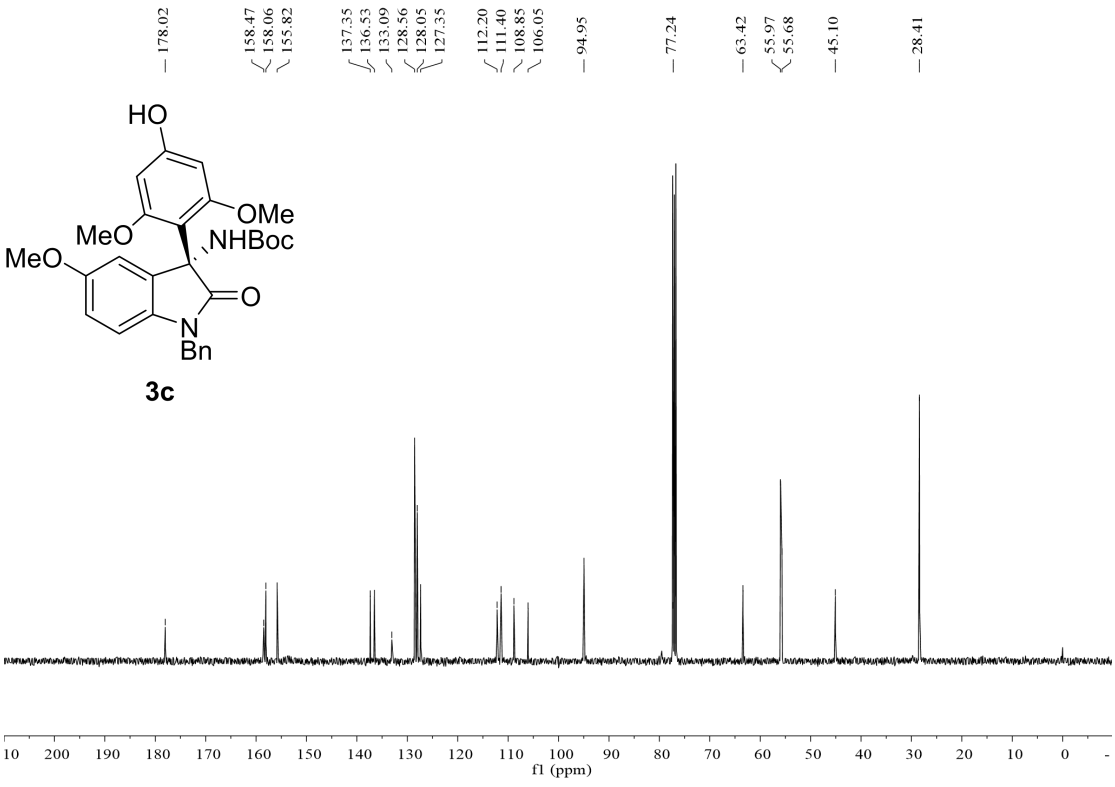
3a


8.13
7.90
7.56
7.54
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.07
6.93
6.91
6.64
6.62
5.95
4.99
3.47
2.21
1.33
HO
OMe
MeO
NHBoc
O
N
Bn
3b
2.18
2.06
3.16
1.05
0.99
1.00
2.00
2.00
6.02
3.06
9.23
f1 (ppm)

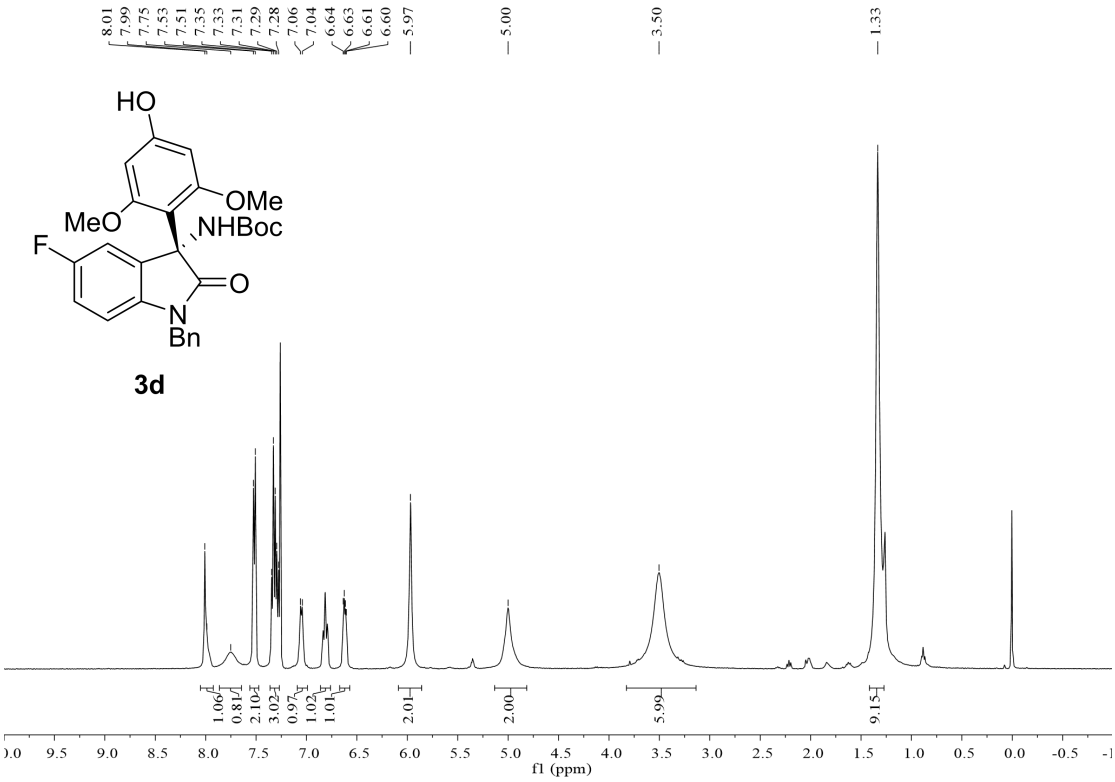

178.43
158.43
157.99
141.22
136.57
132.03
128.75
128.55
128.20
127.36
124.27
108.39
106.05
94.98
77.25
63.37
55.95
45.05
28.41
21.12
HO
OMe
MeO
NHBoc
O
N
Bn
3b
f1 (ppm)

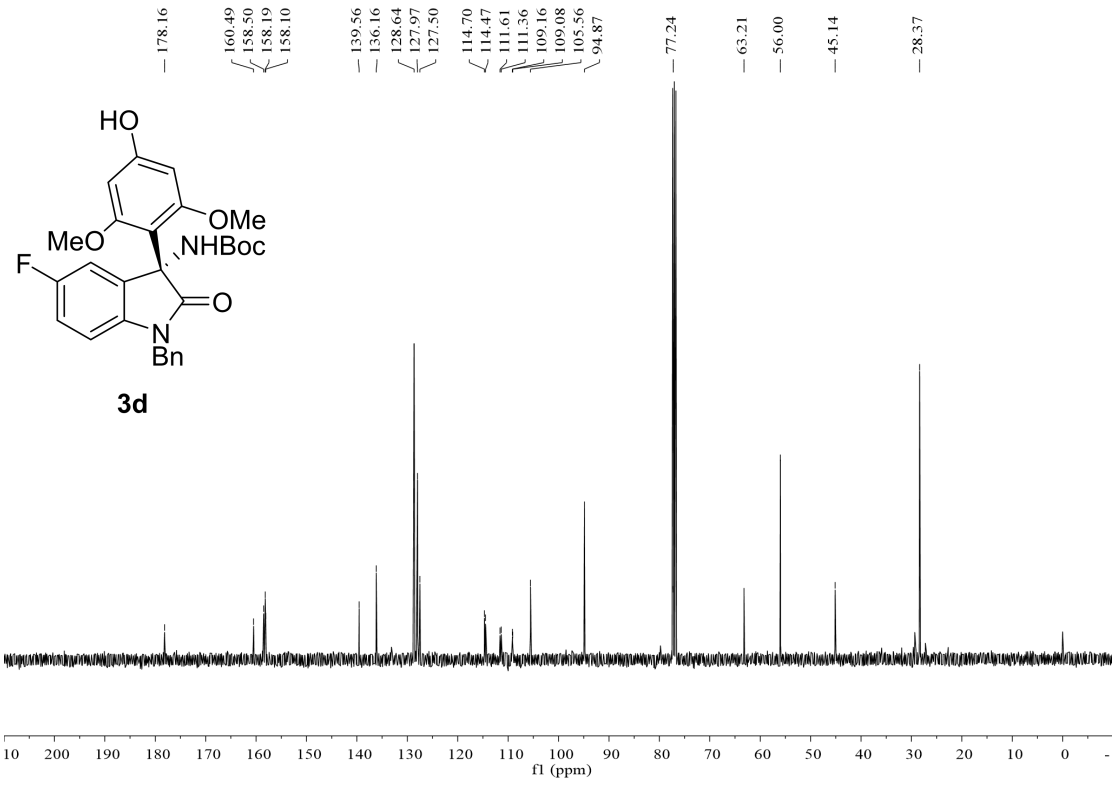

8.11
7.76
7.54
7.53
7.34
7.32
7.31
7.28
7.27
7.26
7.26
6.93
6.66
6.64
6.62
6.60
5.94
5.00
3.69
3.46
1.33
HO
OMe
MeO
NHBoc
MeO
O
N
Bn
1.05
0.81
2.15
2.97
1.01
2.08
2.00
1.93
8.94
8.95
f1 (ppm)

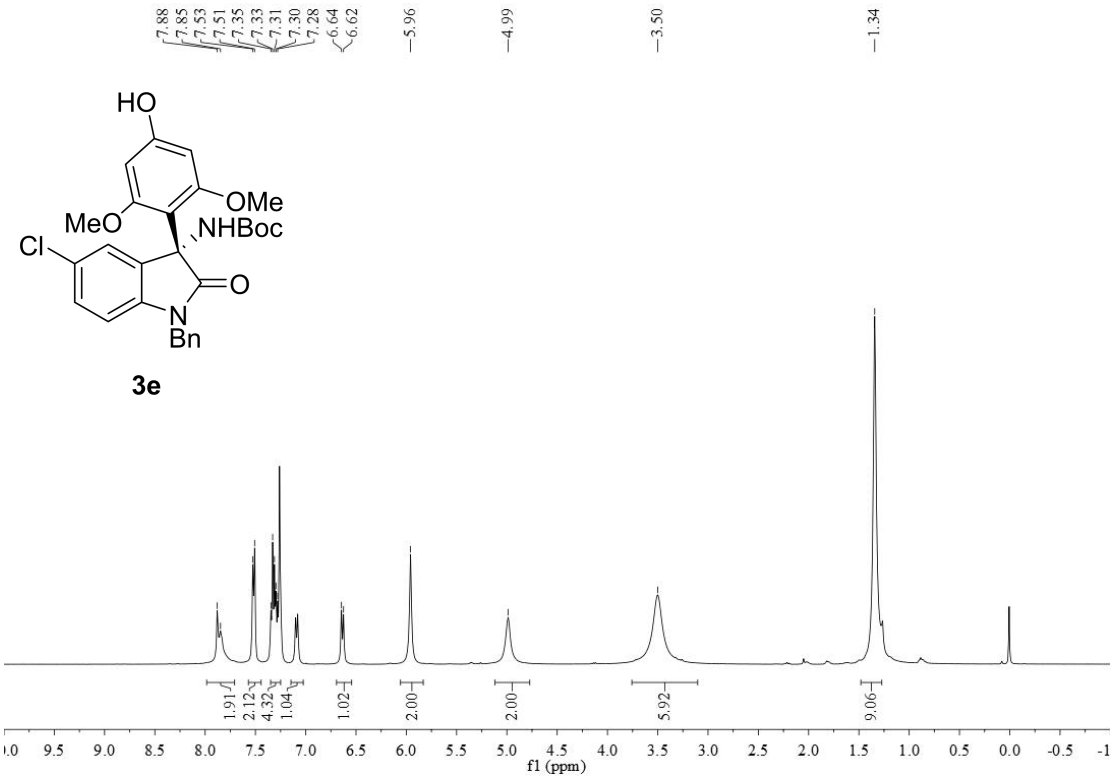
3c


178.02
158.47
158.06
155.82
137.35
136.53
133.09
128.56
128.05
127.35
112.20
111.40
108.85
106.05
94.95
77.24
63.42
55.97
55.68
45.10
28.41
HO
OMe
MeO
NHBoc
MeO
O
N
Bn
f1 (ppm)

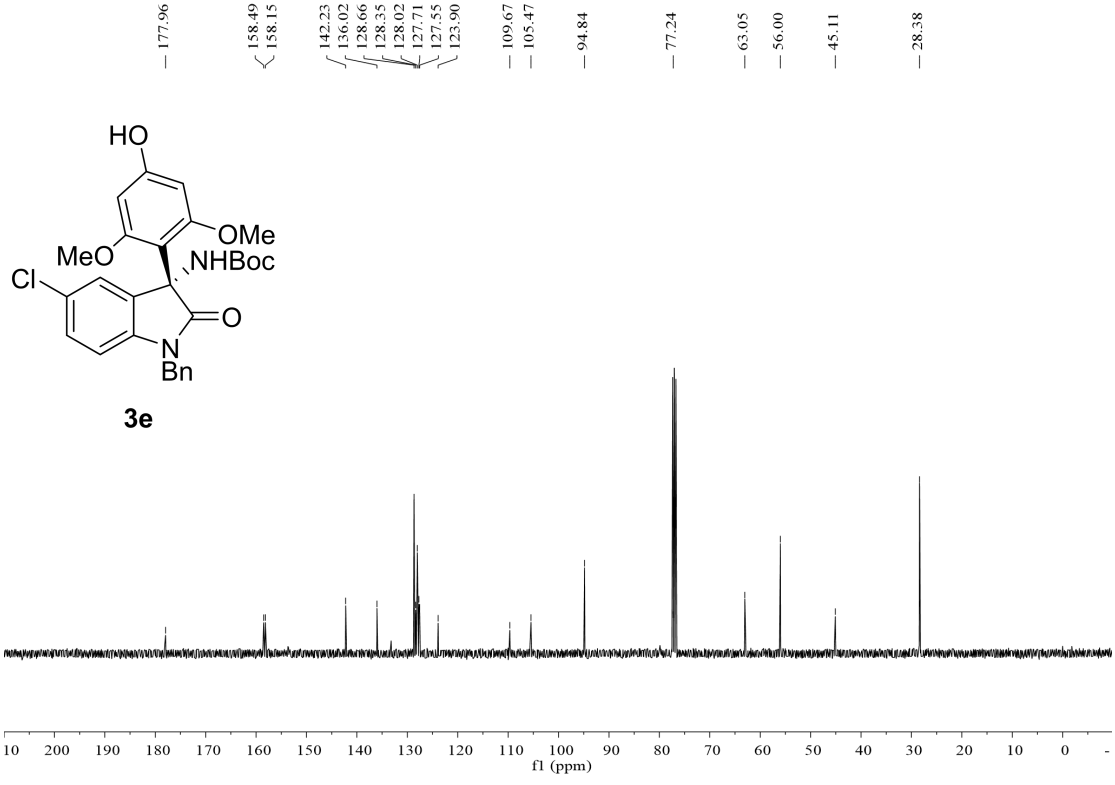
3c


8.01
7.99
7.75
7.53
7.51
7.35
7.33
7.31
7.29
7.28
7.06
7.04
6.64
6.63
6.61
6.60
5.97
5.00
3.50
1.33
HO
OMe
MeO
NHBoc
F
O
N
Bn
3d
1.06
0.81
2.10
3.02
0.97
1.02
1.01
2.01
2.00
5.99
9.15
f1 (ppm)

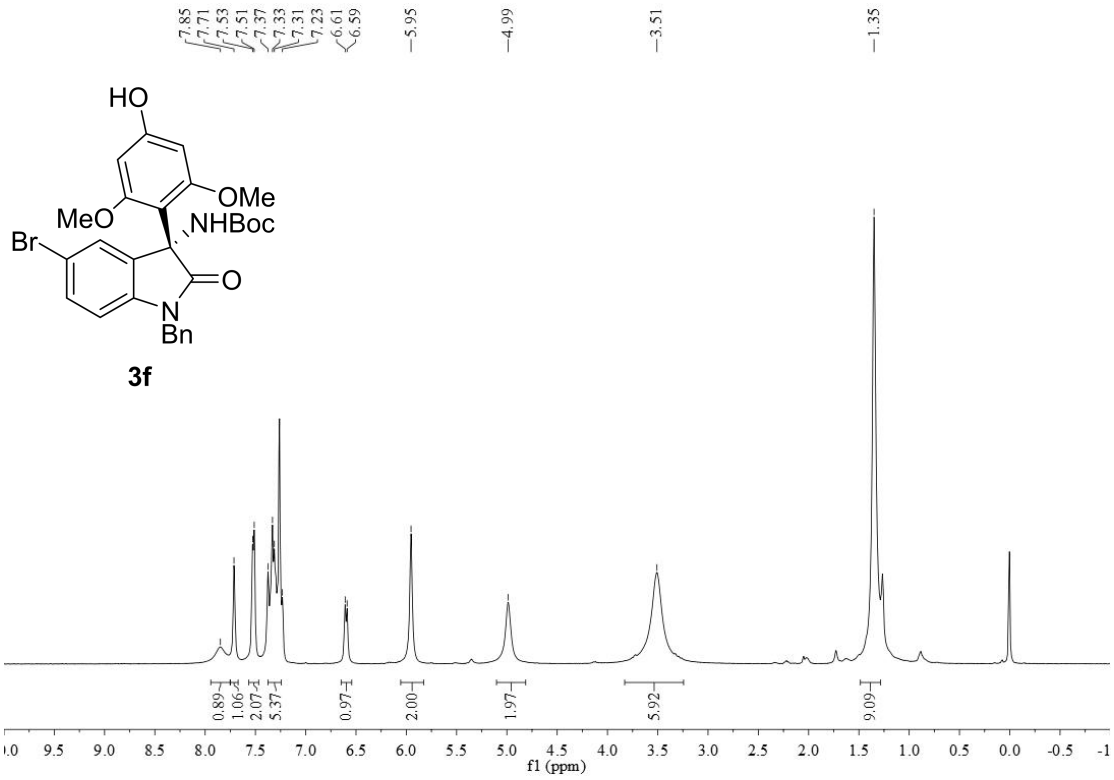

178.16
160.49
158.50
158.19
158.10
139.56
136.16
128.64
127.97
127.50
114.70
114.47
111.61
111.36
109.16
109.08
105.56
94.87
77.24
63.21
56.00
45.14
28.37
HO
OMe
MeO
NHBoc
F
O
N
Bn
3d
f1 (ppm)


7.88
7.85
7.53
7.51
7.35
7.33
7.31
7.30
7.28
6.64
6.62
5.96
4.99
3.50
1.34
HO
OMe
MeO
NHBoc
Cl
O
N
Bn
1.91
2.12
4.32
1.04
1.02
2.00
2.00
5.92
9.06
f1 (ppm)

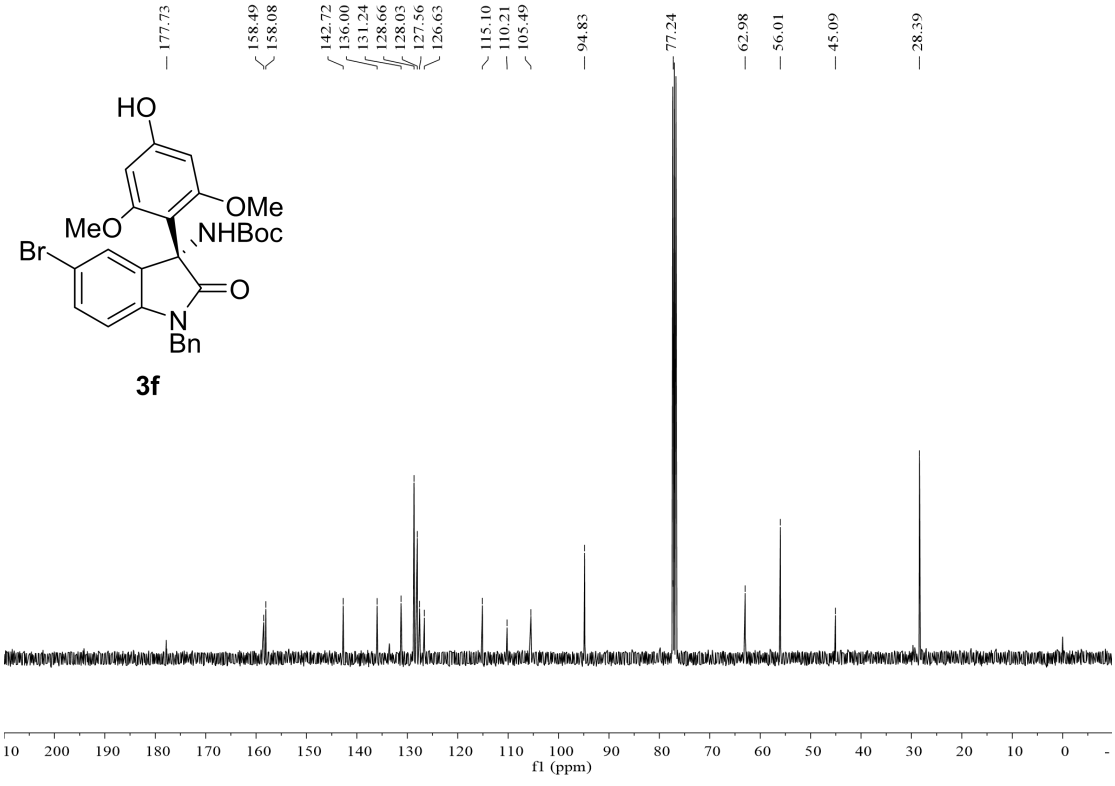
3e


177.96
158.49
158.15
142.23
136.02
128.66
128.35
128.02
127.71
127.55
123.90
109.67
105.47
94.84
77.24
63.05
56.00
45.11
28.38
HO
OMe
MeO
NHBoc
Cl
O
N
Bn
f1 (ppm)

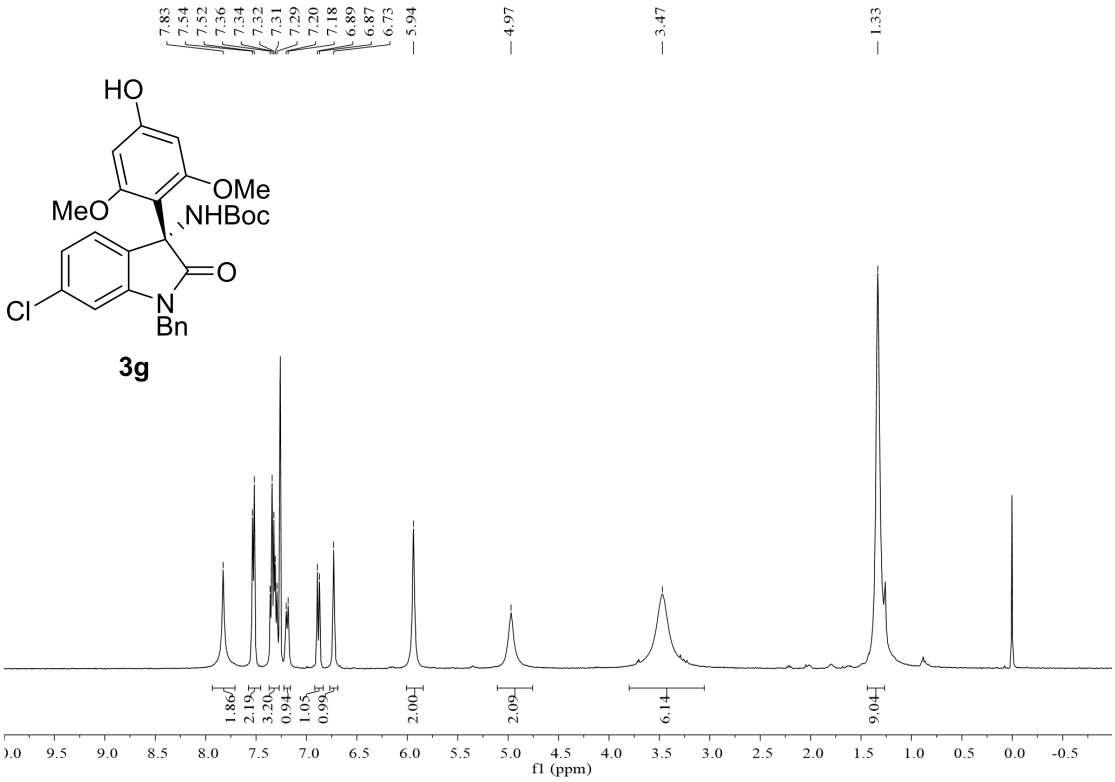
3e

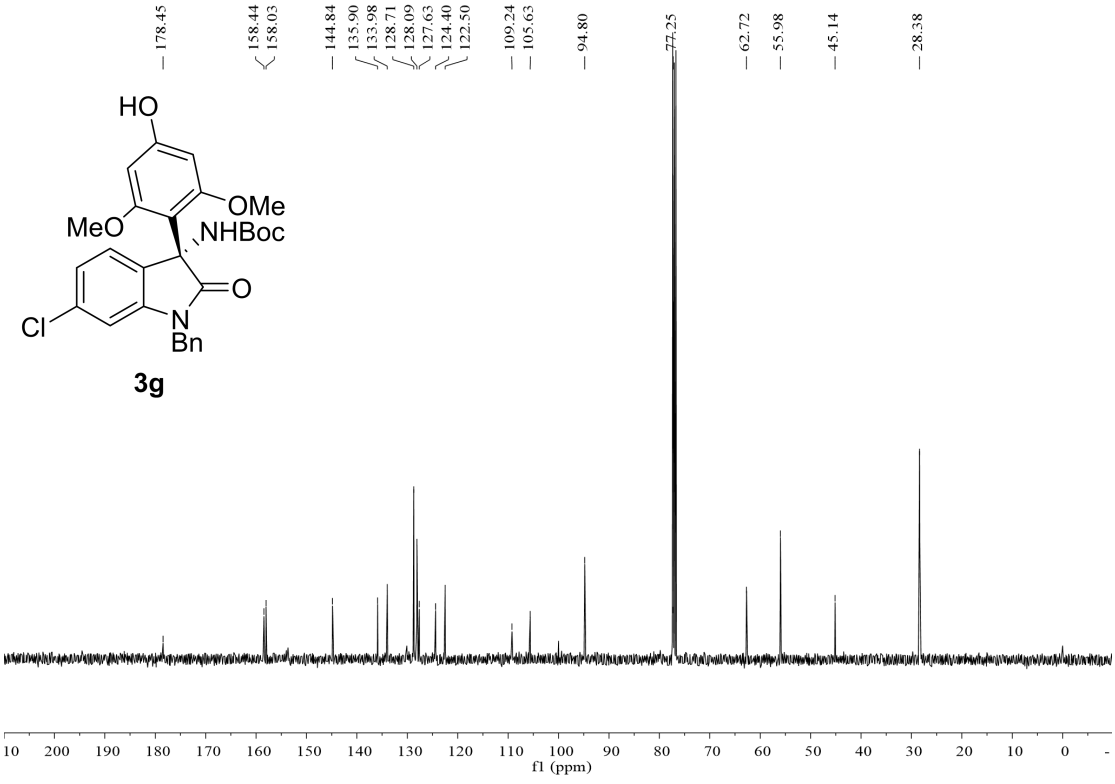

7.85
7.71
7.53
7.51
7.37
7.33
7.31
7.23
6.61
6.59
5.95
4.99
3.51
1.35
HO
OMe
MeO
NHBoc
Br
O
N
Bn
0.89
1.06
2.07
5.37
0.97
2.00
1.97
5.92
9.09
f1 (ppm)

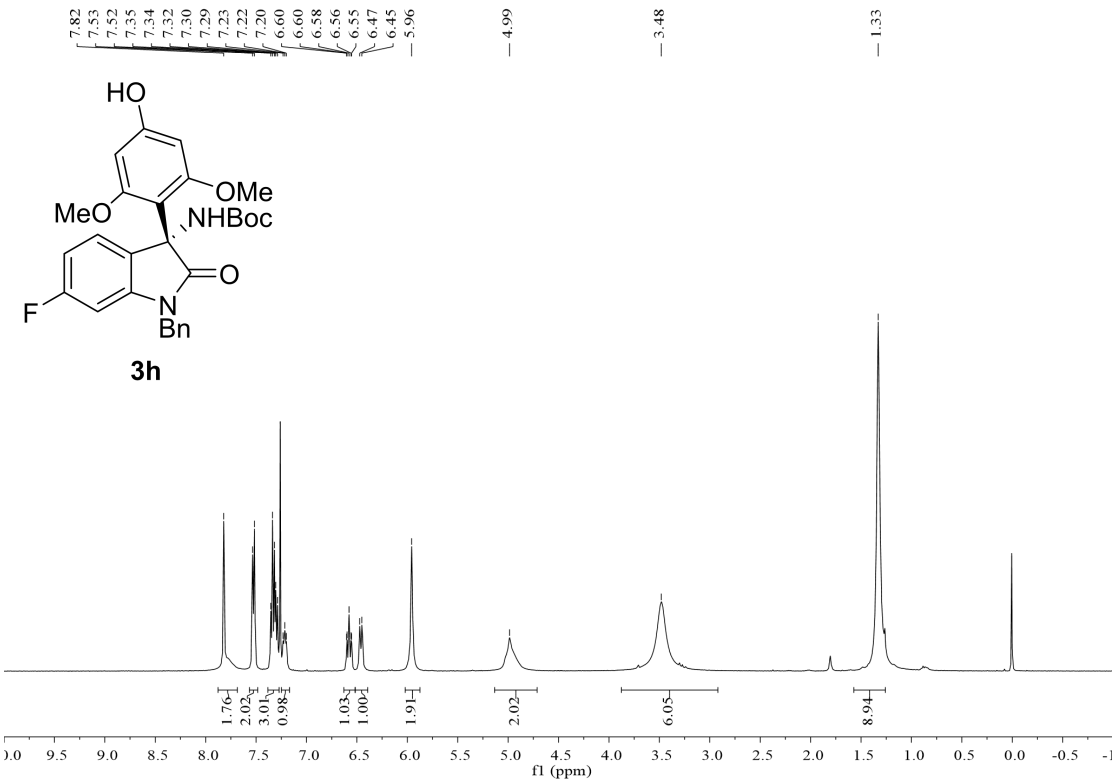
3f


177.73
158.49
158.08
142.72
136.00
131.24
128.66
128.03
127.56
126.63
115.10
110.21
105.49
94.83
77.24
62.98
56.01
45.09
28.39
HO
OMe
MeO
NHBoc
Br
O
N
Bn
f1 (ppm)

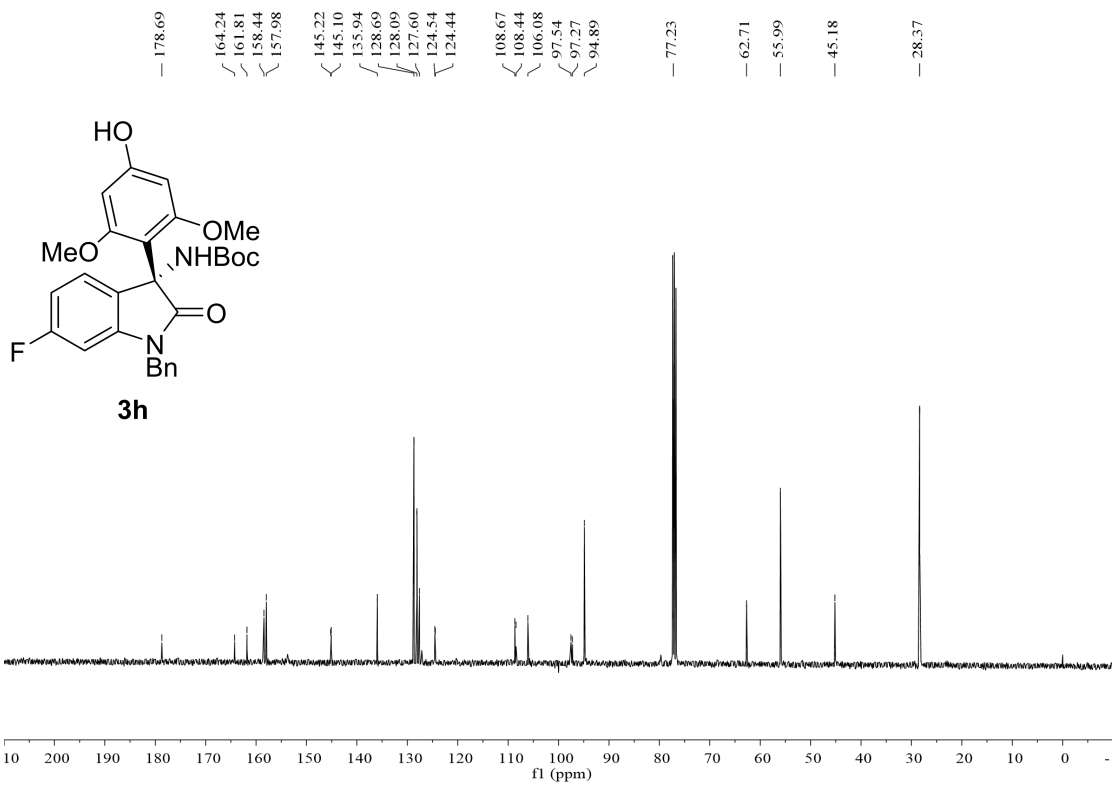
3f


7.83
7.54
7.52
7.36
7.34
7.32
7.31
7.29
7.20
7.18
6.89
6.87
6.73
5.94
4.97
3.47
1.33
HO
OMe
MeO
NHBoc
O
N
Bn
Cl
3g
1.86
2.19
3.20
0.94
1.05
0.99
2.00
2.09
6.14
9.04
f1 (ppm)

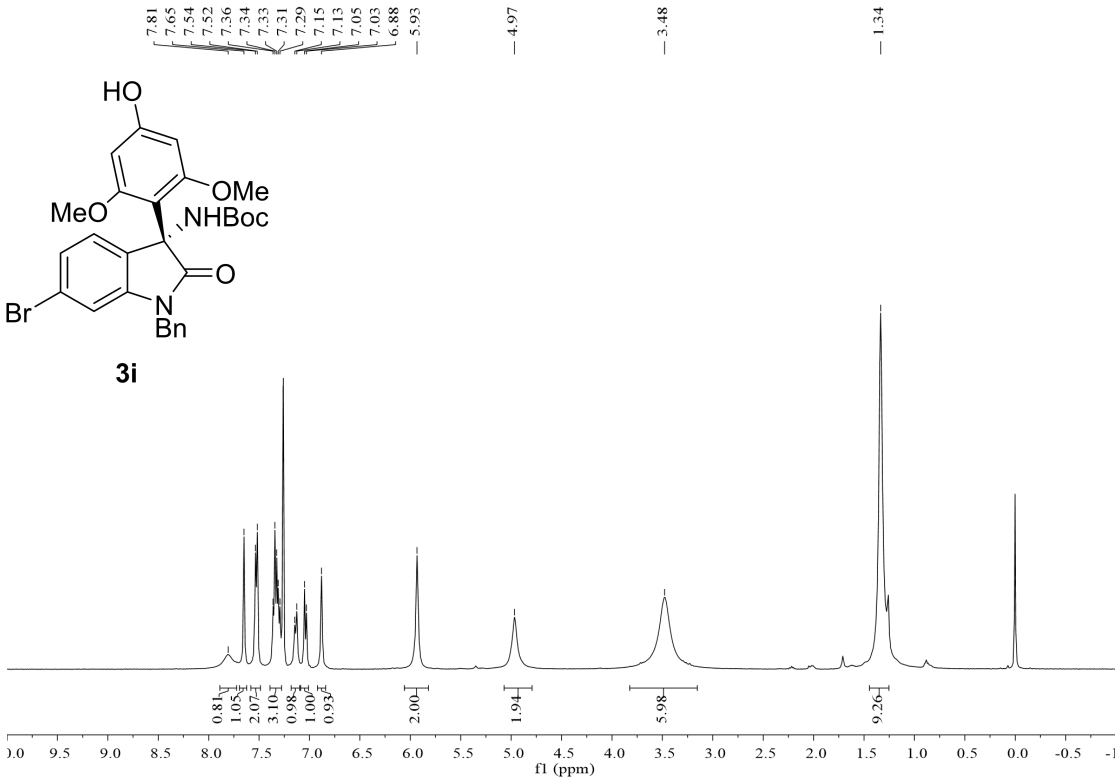

178.45
158.44
158.03
144.84
135.90
133.98
128.71
128.09
127.63
124.40
122.50
109.24
105.63
94.80
77.25
62.72
55.98
45.14
28.38
HO
OMe
MeO
NHBoc
O
N
Bn
Cl
3g
f1 (ppm)

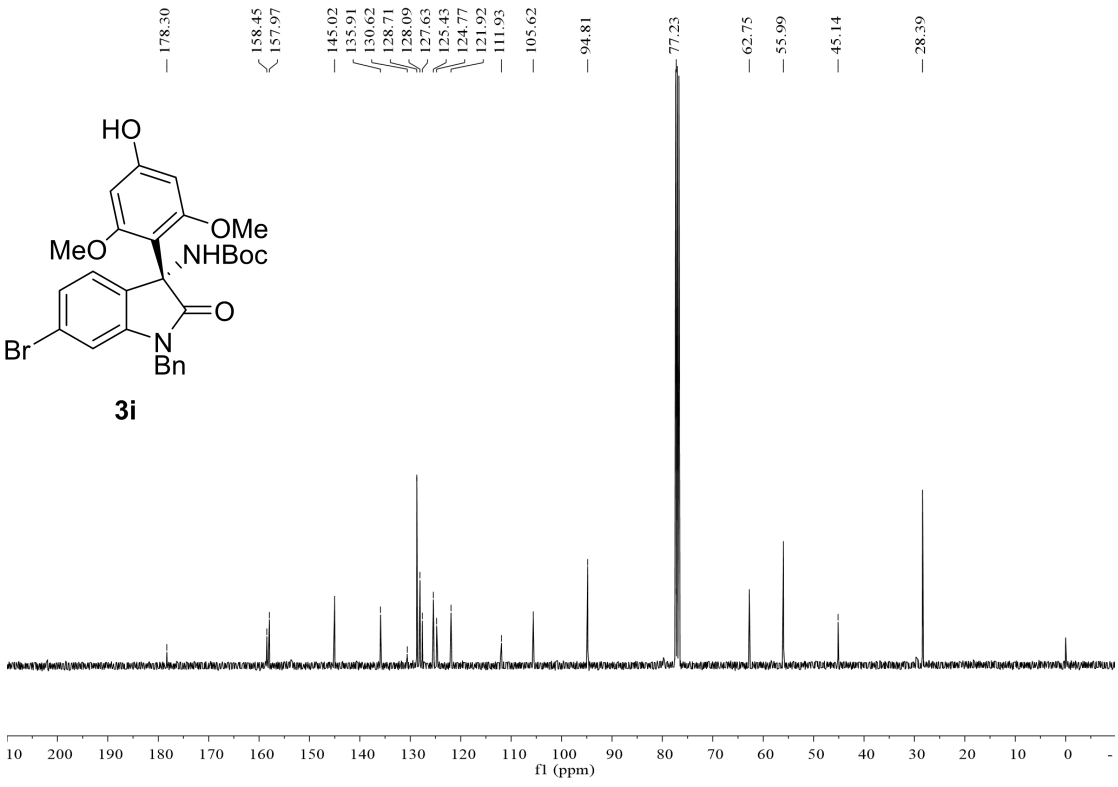

7.82
7.53
7.52
7.35
7.34
7.32
7.30
7.29
7.23
7.22
7.20
6.60
6.60
6.58
6.56
6.55
6.47
6.45
5.96
4.99
3.48
1.33
HO
OMe
MeO
NHBoc
O
N
Bn
F
1.76
2.02
3.01
0.98
1.03
1.00
1.91
2.02
6.05
8.94
f1 (ppm)

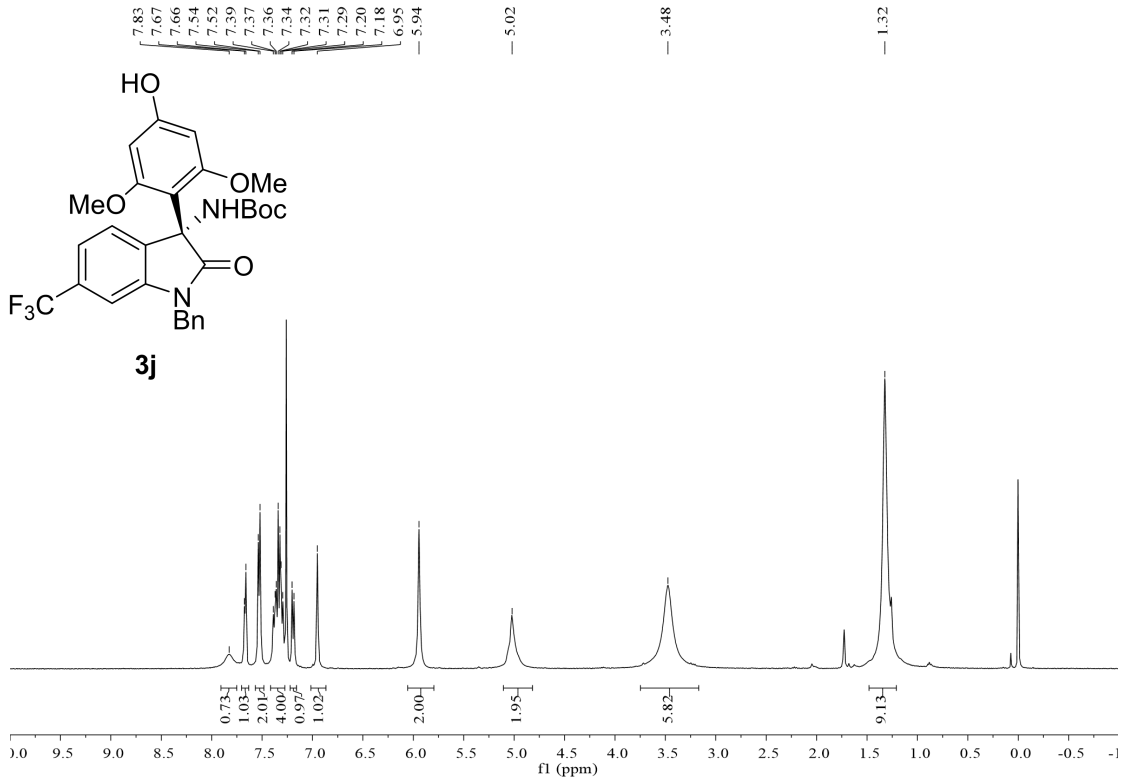
3h


178.69
164.24
161.81
158.44
157.98
145.22
145.10
135.94
128.69
128.09
127.60
124.54
124.44
108.67
108.44
106.08
97.54
97.27
94.89
77.23
62.71
55.99
45.18
28.37
HO
OMe
MeO
NHBoc
O
N
Bn
F
f1 (ppm)

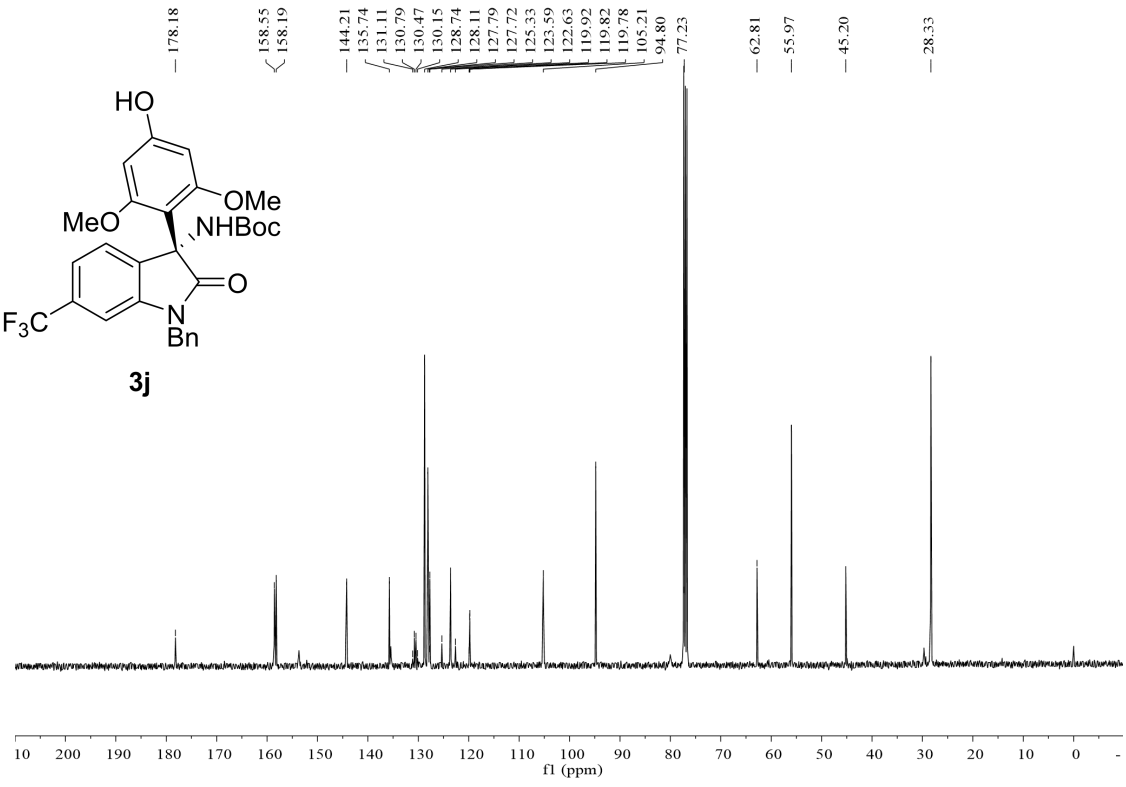
3h


7.81
7.65
7.54
7.52
7.36
7.34
7.33
7.31
7.29
7.15
7.13
7.05
7.03
6.88
5.93
4.97
3.48
1.34
HO
OMe
MeO
NHBoc
O
N
Bn
Br
3i
0.81
1.05
2.07
3.10
0.98
1.00
0.93
2.00
1.94
5.98
9.26
f1 (ppm)

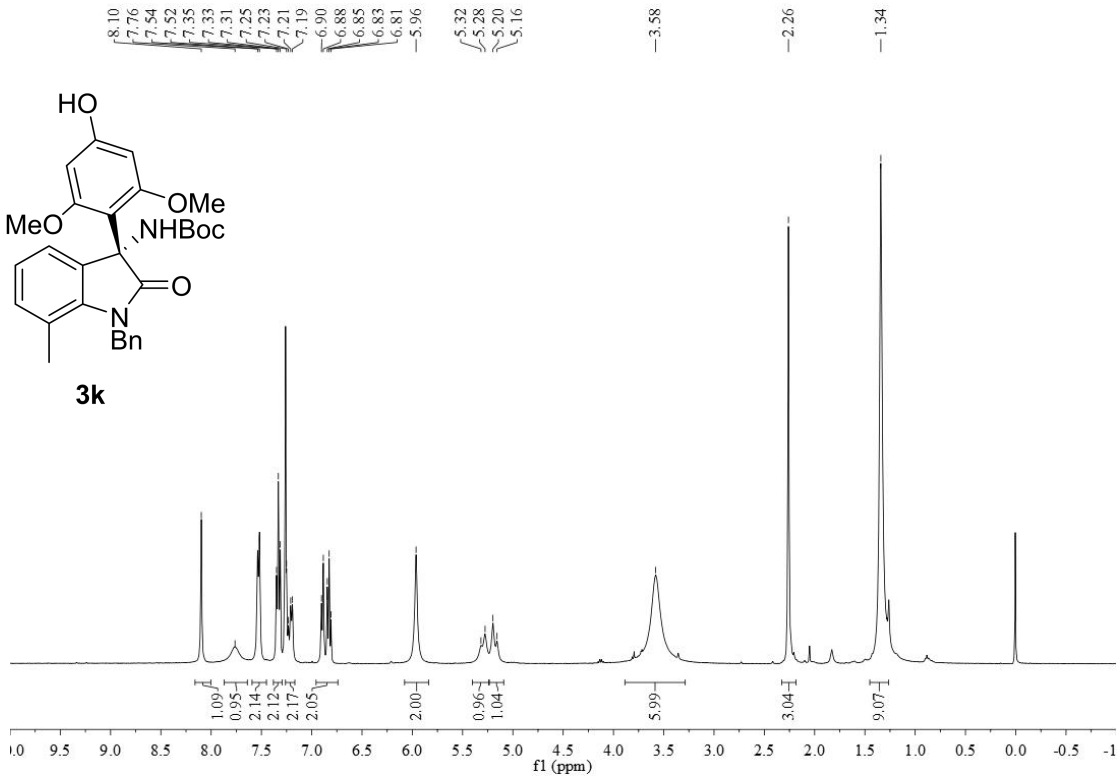

178.30
158.45
157.97
145.02
135.91
130.62
128.71
128.09
127.63
125.43
124.77
121.92
111.93
105.62
94.81
77.23
62.75
55.99
45.14
28.39
HO
OMe
MeO
NHBoc
O
N
Bn
Br
3i
f1 (ppm)

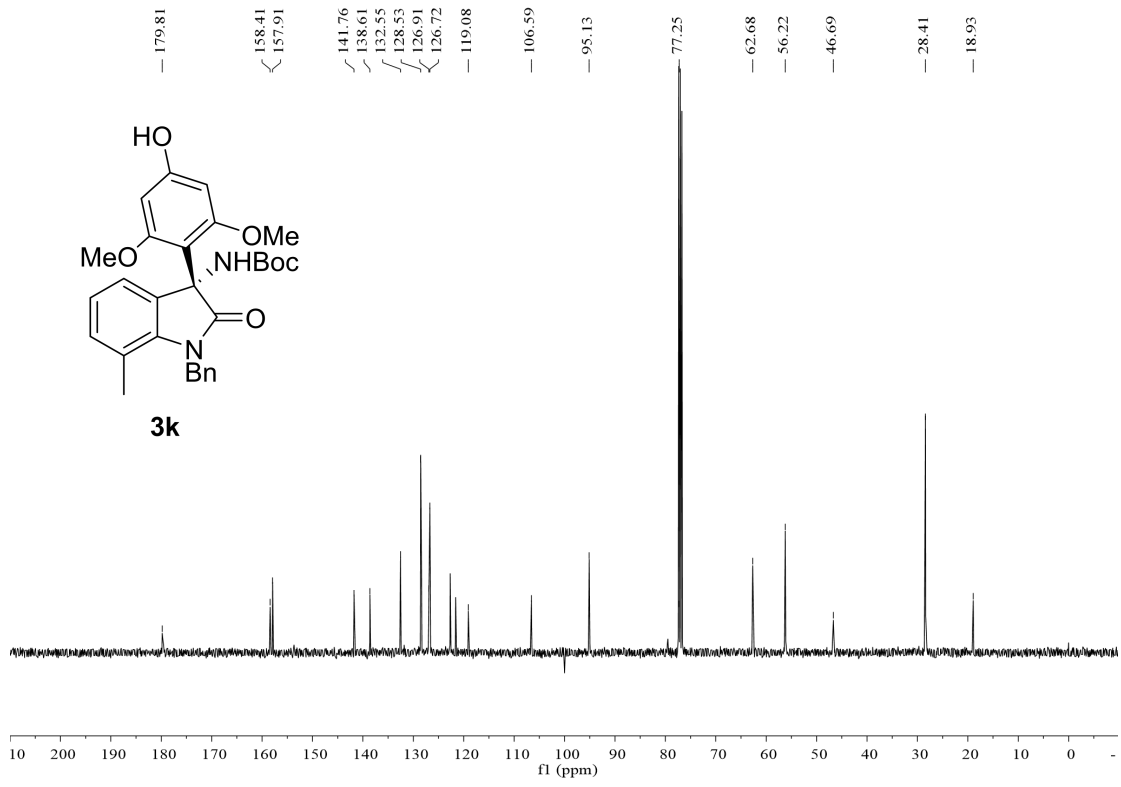

7.83
7.67
7.66
7.54
7.52
7.39
7.37
7.36
7.34
7.32
7.31
7.29
7.20
7.18
6.95
5.94
5.02
3.48
1.32
HO
OMe
MeO
NHBoc
O
N
Bn
F3C
0.73
1.03
2.01
4.00
0.97
1.02
2.00
1.95
5.82
9.13
f1 (ppm)

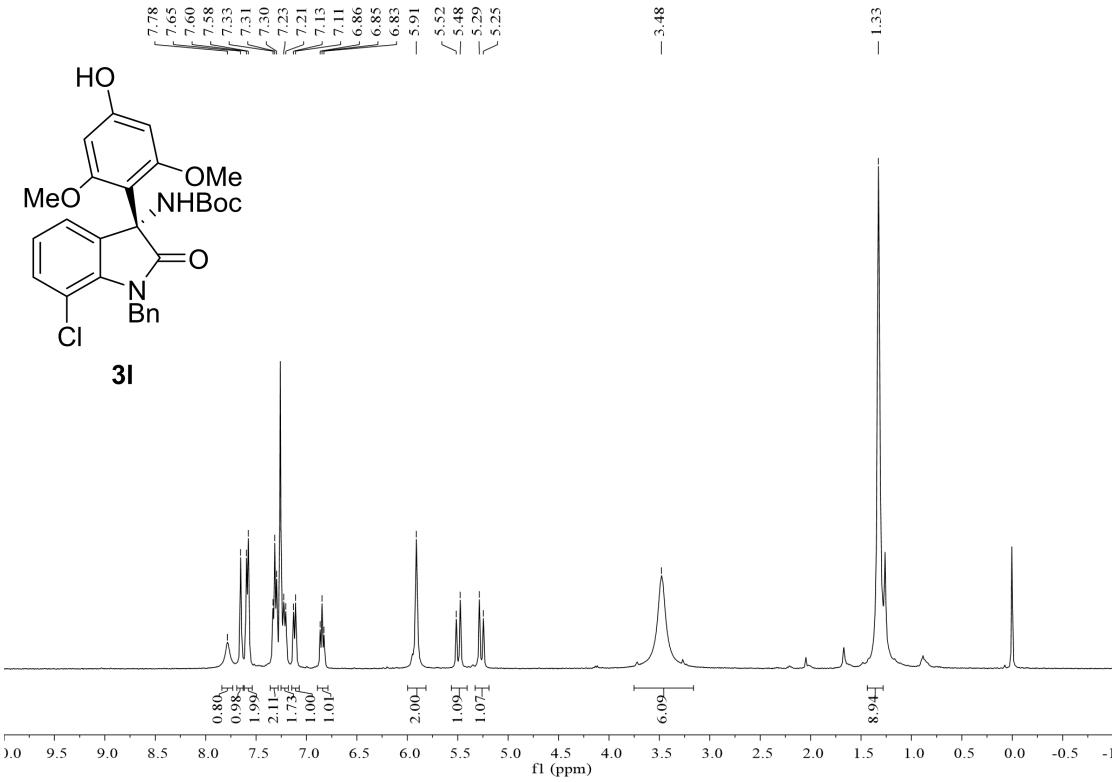
3j

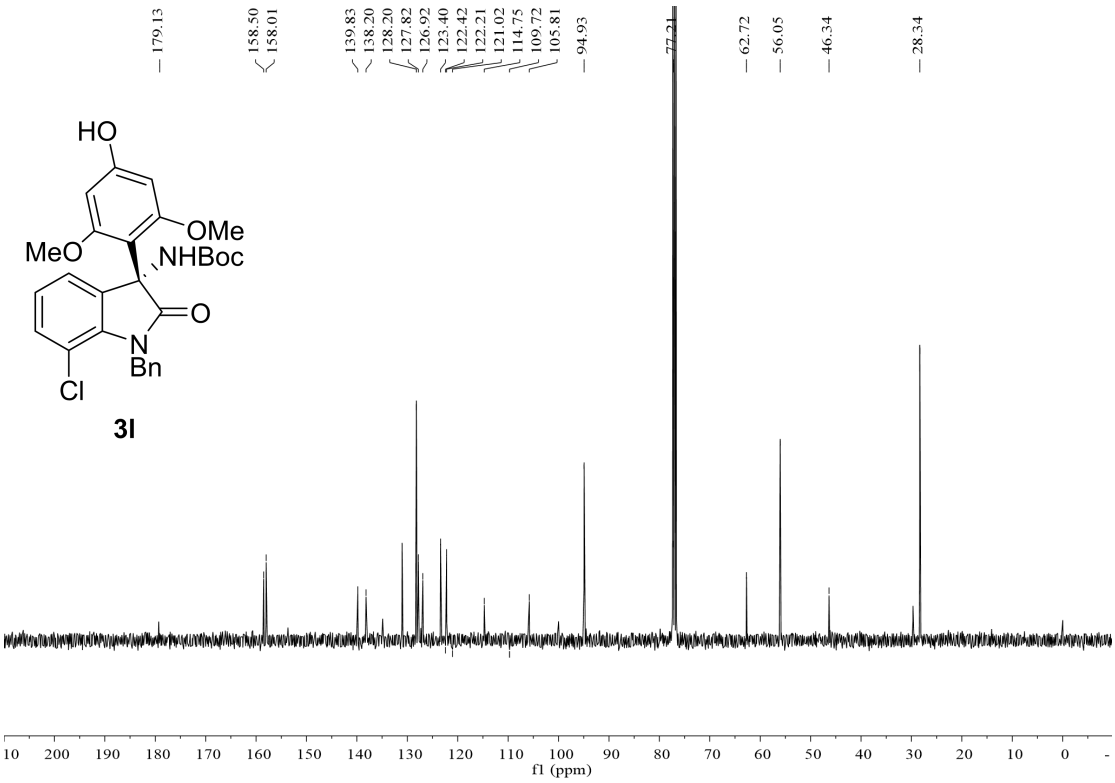

178.18
158.55
158.19
144.21
135.74
131.11
130.79
130.47
130.15
128.74
128.11
127.79
127.72
125.33
123.59
122.63
119.92
119.82
119.78
105.21
94.80
77.23
62.81
55.97
45.20
28.33
HO
OMe
MeO
NHBoc
O
N
Bn
F3C
f1 (ppm)

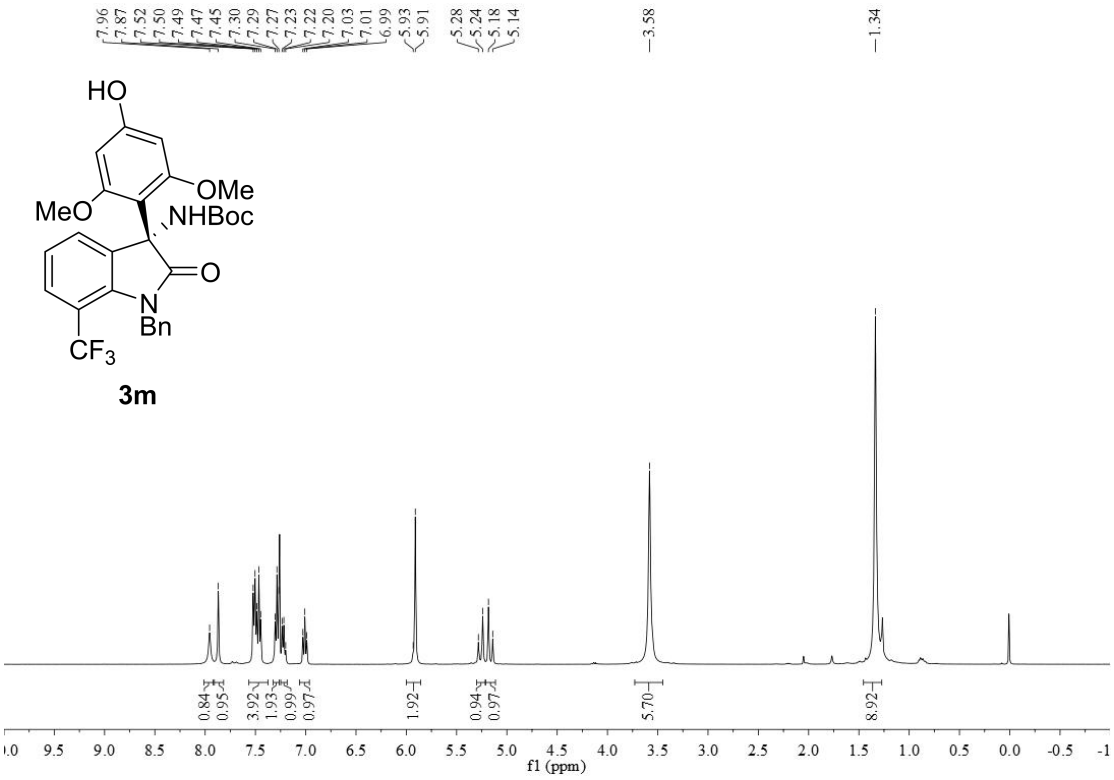
3j

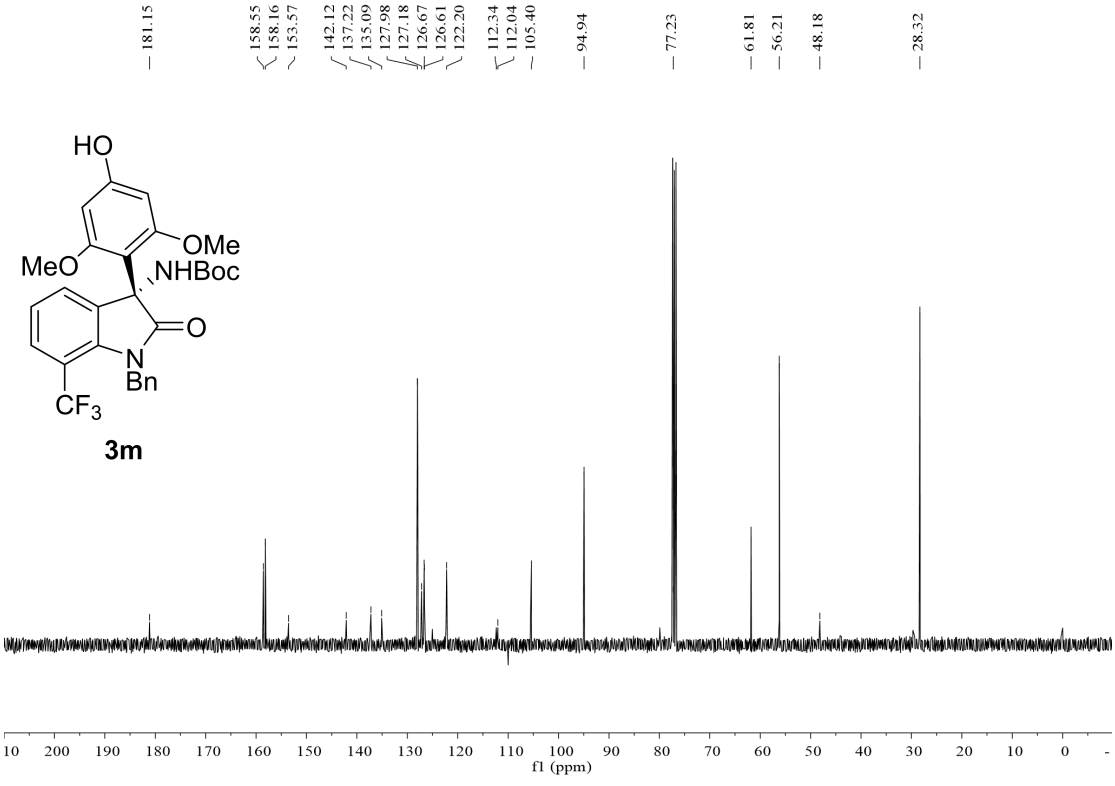

8.10
7.76
7.54
7.52
7.35
7.33
7.31
7.25
7.23
7.21
7.19
6.90
6.88
6.85
6.83
6.81
5.96
5.32
5.28
5.20
5.16
3.58
2.26
1.34
HO
OMe
MeO
NHBoc
O
N
Bn
3k
1.09
0.95
2.14
2.12
2.17
2.05
2.00
0.96
1.04
5.99
3.04
9.07
f1 (ppm)

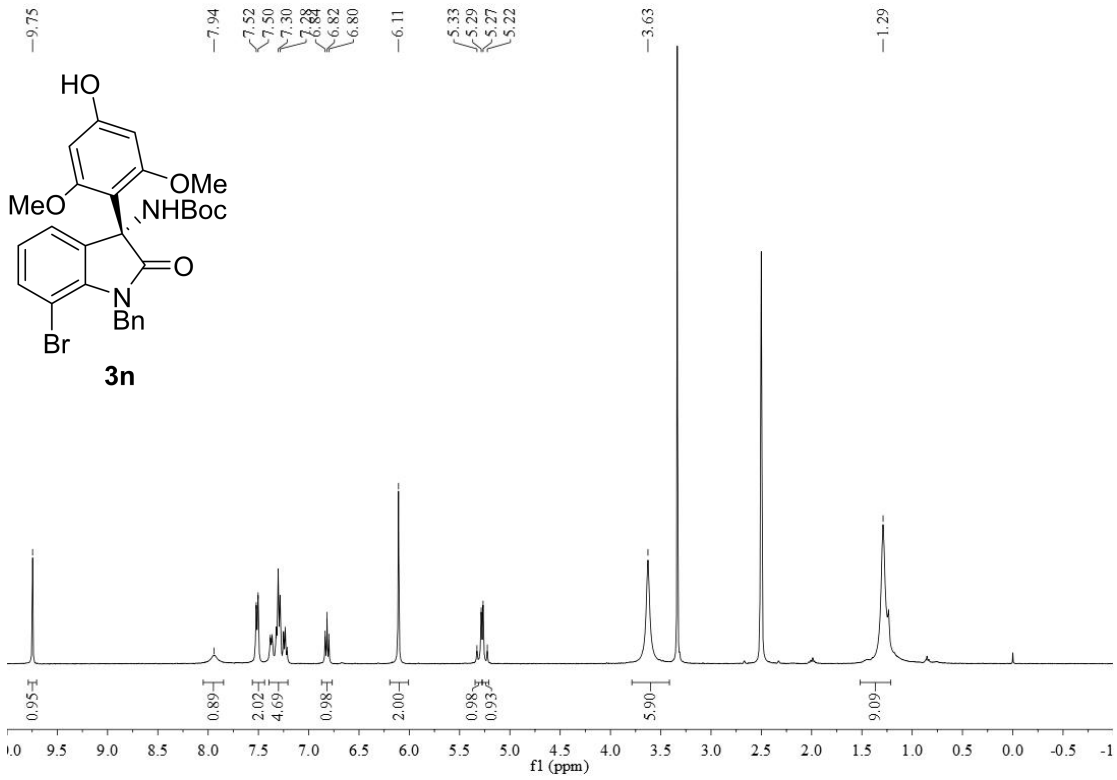

179.81
158.41
157.91
141.76
138.61
132.55
128.53
126.91
126.72
119.08
106.59
95.13
77.25
62.68
56.22
46.69
28.41
18.93
HO
OMe
MeO
NHBoc
O
N
Bn
3k
f1 (ppm)

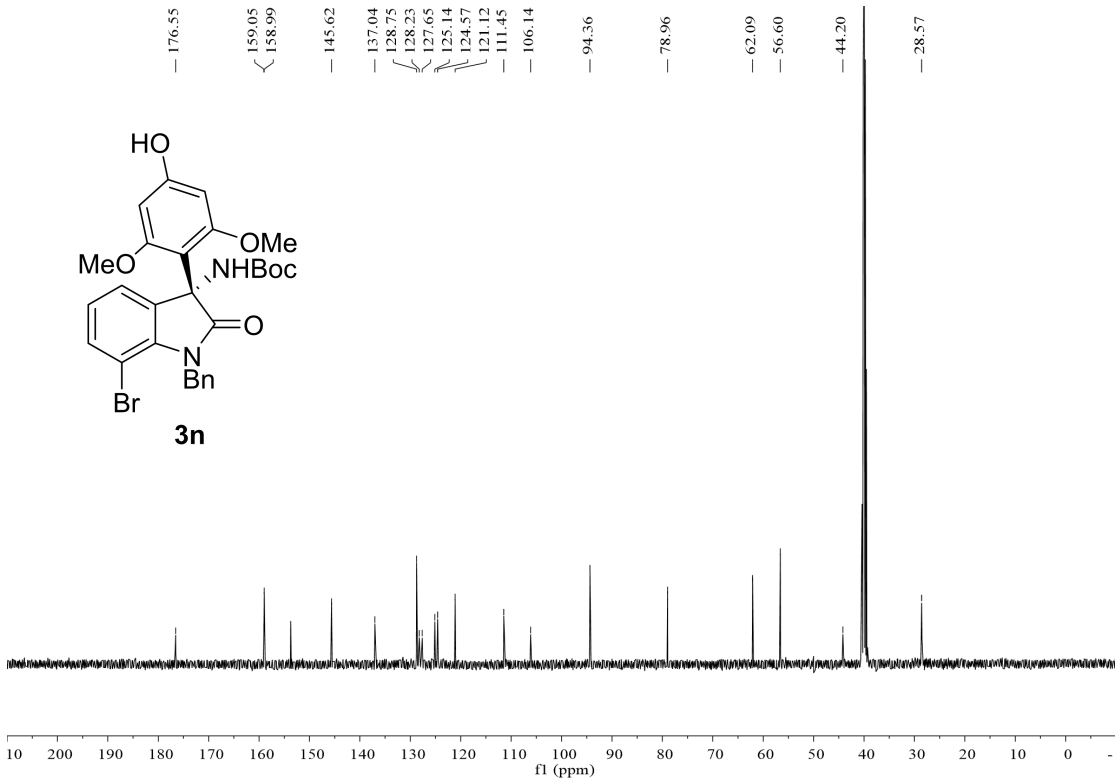

7.78
7.65
7.60
7.58
7.33
7.31
7.30
7.23
7.21
7.13
7.11
6.86
6.85
6.83
5.91
5.52
5.48
5.29
5.25
3.48
1.33
HO
OMe
MeO
NHBoc
O
N
Bn
Cl
3l
0.80
0.98
1.99
2.11
1.73
1.00
1.01
2.00
1.09
1.07
6.09
8.94
f1 (ppm)

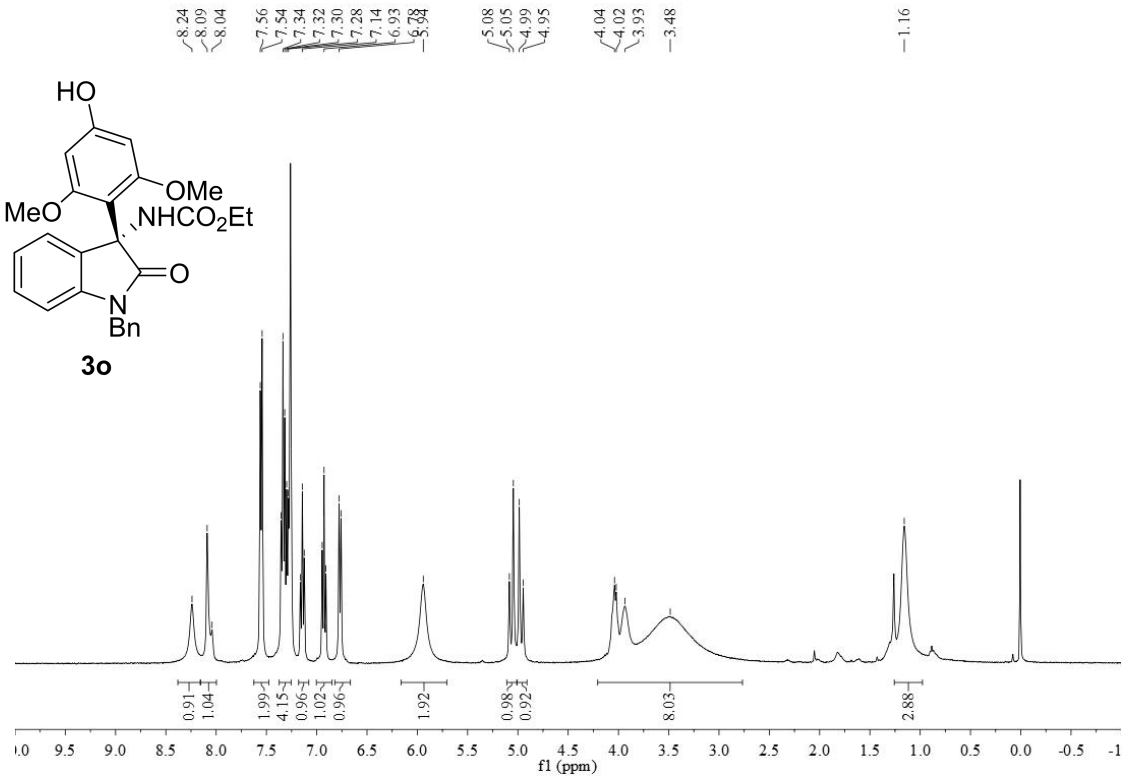

179.13
158.50
158.01
139.83
138.20
128.20
127.82
126.92
123.40
122.42
122.21
121.02
114.75
109.72
105.81
94.93
77.21
62.72
56.05
46.34
28.34
HO
OMe
MeO
NHBoc
O
N
Bn
Cl
3l
f1 (ppm)

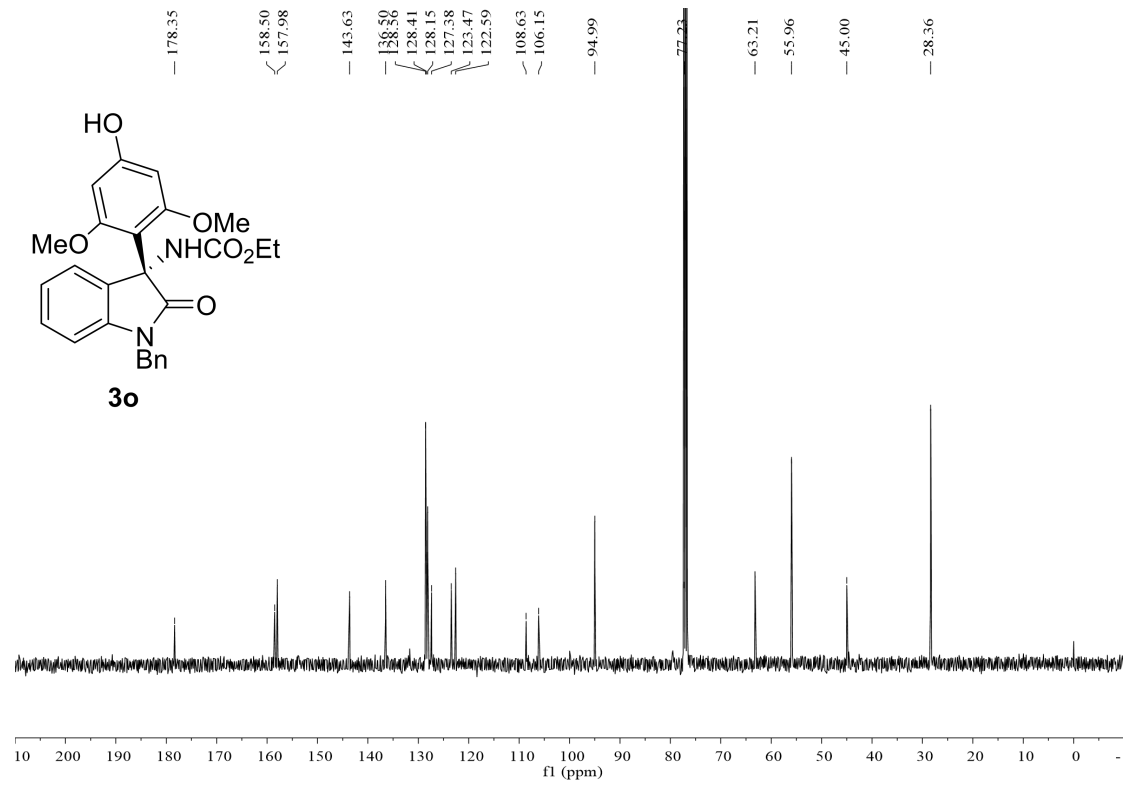

7.96
7.87
7.52
7.50
7.49
7.47
7.45
7.30
7.29
7.27
7.23
7.22
7.20
7.03
7.01
6.99
5.93
5.91
5.28
5.24
5.18
5.14
3.58
1.34
HO
OMe
MeO
NHBoc
O
N
Bn
CF3
3m
0.84
0.95
3.92
1.93
0.99
0.97
1.92
0.94
0.97
5.70
8.92
f1 (ppm)

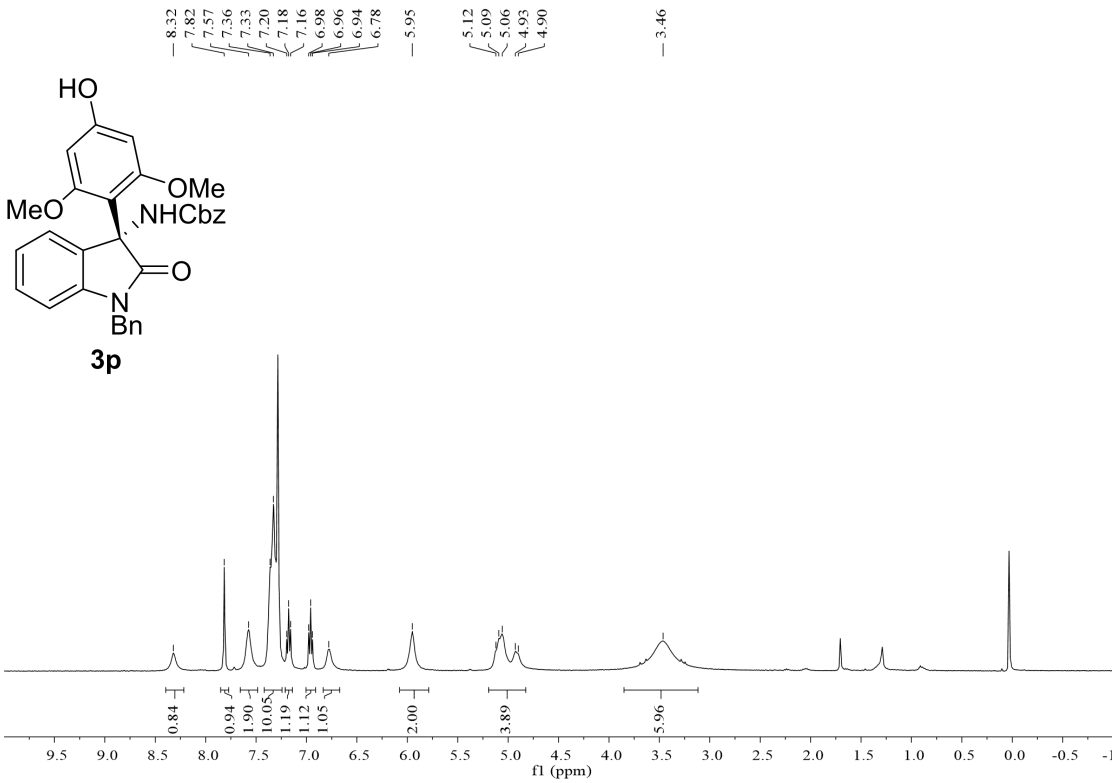

181.15
158.55
158.16
153.57
142.12
137.22
135.09
127.98
127.18
126.67
126.61
122.20
112.34
112.04
105.40
94.94
77.23
61.81
56.21
48.18
28.32
HO
OMe
MeO
NHBoc
O
N
Bn
CF3
3m
f1 (ppm)

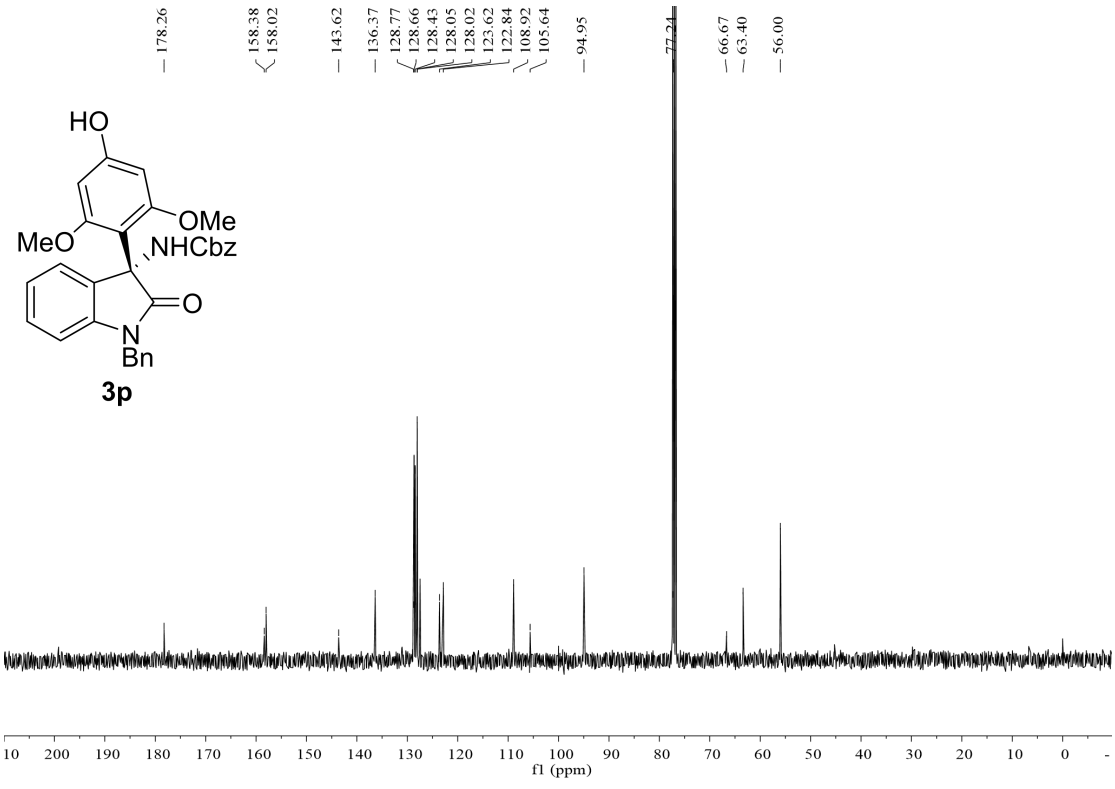

9.75
7.94
7.52
7.50
7.30
7.28
6.84
6.82
6.80
6.11
5.33
5.29
5.27
5.22
3.63
1.29
HO
OMe
MeO
NHBoc
O
N
Bn
Br
3n
0.95
0.89
2.02
4.69
0.98
2.00
0.98
0.93
5.90
9.09
f1 (ppm)

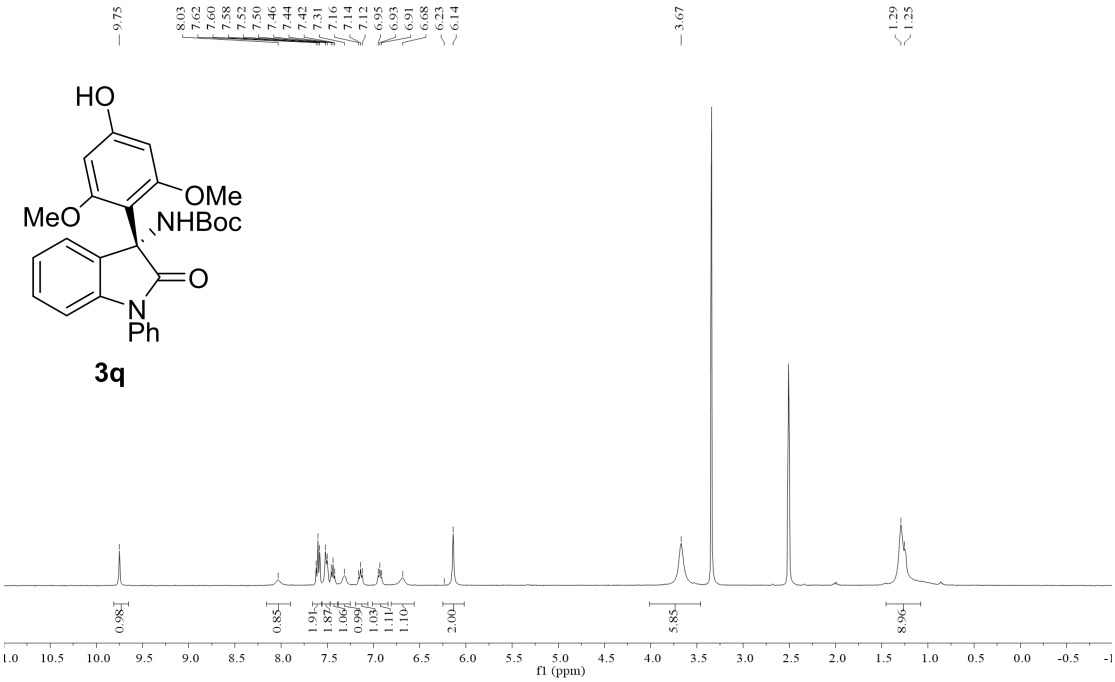

176.55
159.05
158.99
145.62
137.04
128.75
128.23
127.65
125.14
124.57
121.12
111.45
106.14
94.36
78.96
62.09
56.60
44.20
28.57
HO
OMe
MeO
NHBoc
O
N
Bn
Br
3n
f1 (ppm)

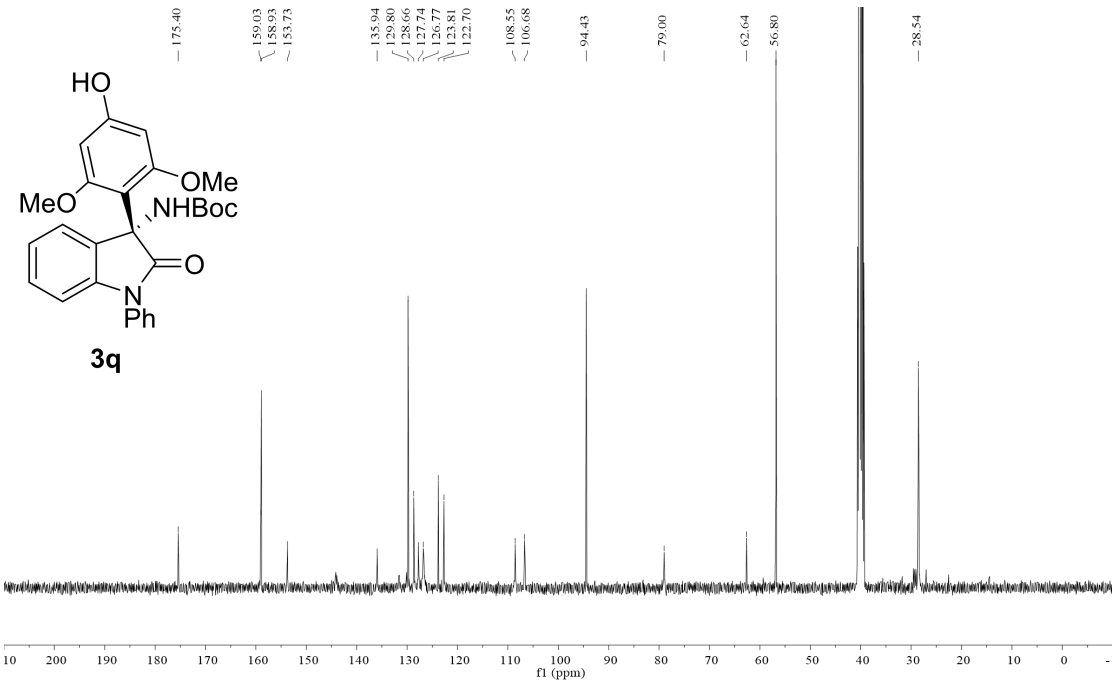

8.24
8.09
8.04
7.56
7.54
7.34
7.32
7.30
7.28
7.14
6.93
6.78
5.94
5.08
5.05
4.99
4.95
4.04
4.02
3.93
3.48
1.16
HO
OMe
MeO
NHCO2Et
O
N
Bn
3o
0.91
1.04
1.99
4.15
0.96
1.02
0.96
1.92
0.98
0.92
8.03
2.88
f1 (ppm)

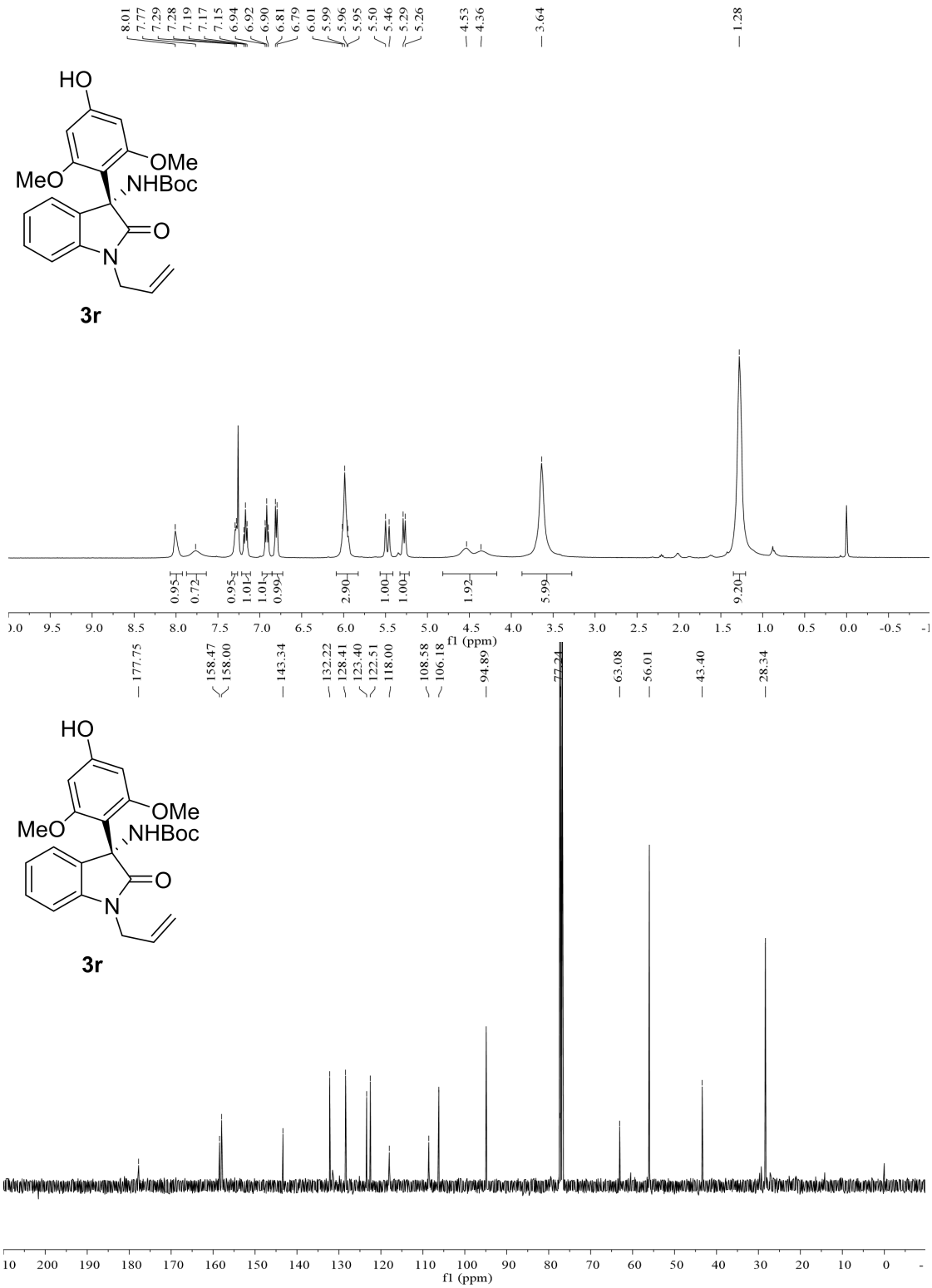

178.35
158.50
157.98
143.63
130.50
128.56
128.41
128.15
127.38
123.47
122.59
108.63
106.15
94.99
77.23
63.21
55.96
45.00
28.36
HO
OMe
MeO
NHCO2Et
O
N
Bn
3o
f1 (ppm)

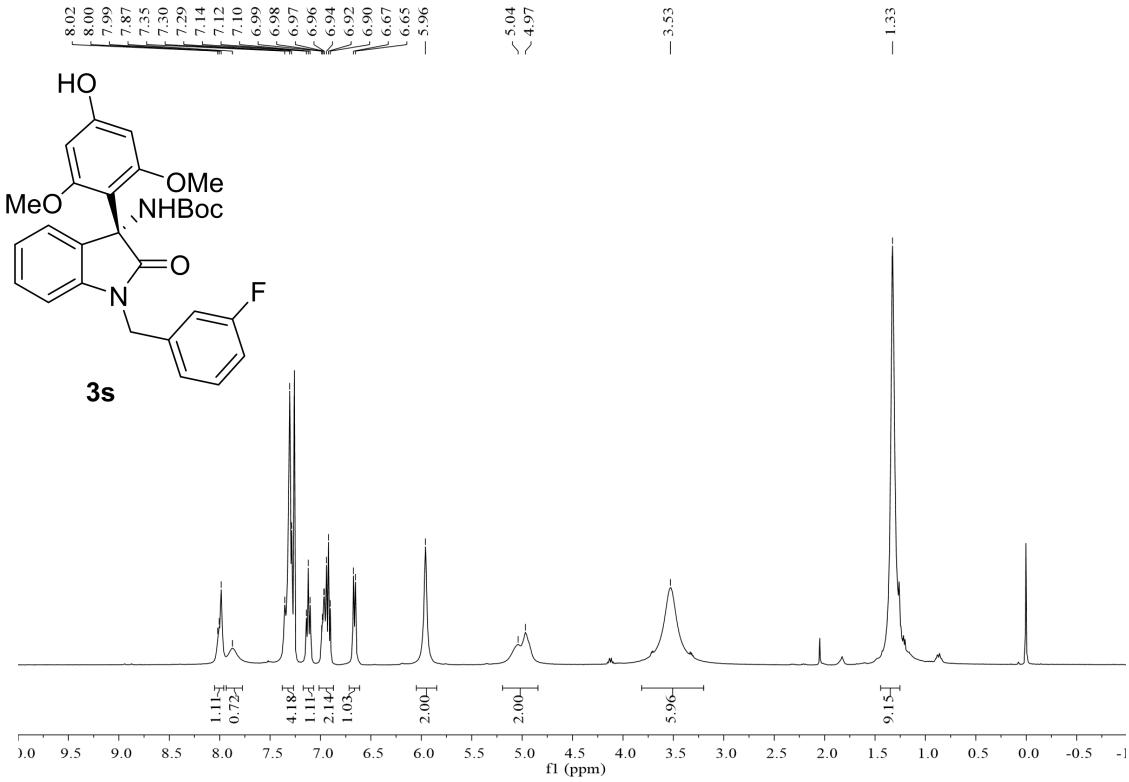

8.32
7.82
7.57
7.36
7.33
7.20
7.18
7.16
6.98
6.96
6.94
6.78
5.95
5.12
5.09
5.06
4.93
4.90
3.46
HO
OMe
MeO
NHCbz
O
N
Bn
3p
0.84
0.94
1.90
10.05
1.19
1.12
1.05
2.00
3.89
5.96
f1 (ppm)

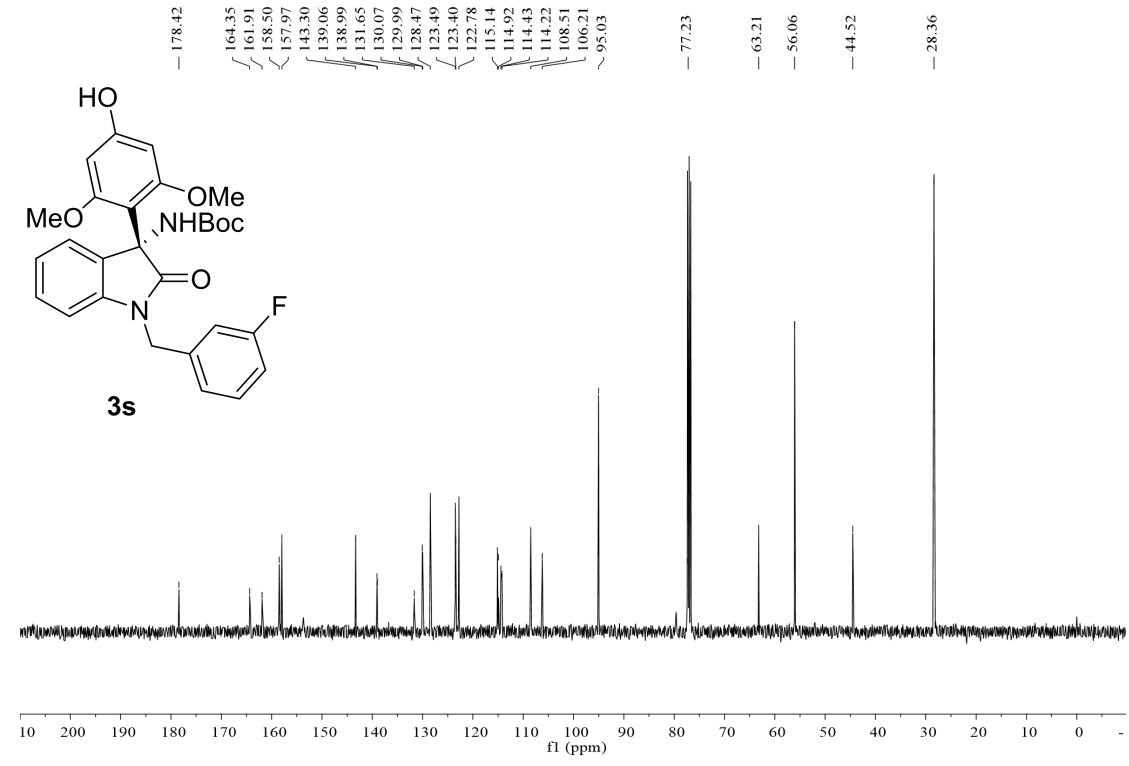

178.26
158.38
158.02
143.62
136.37
128.77
128.66
128.43
128.05
128.02
123.62
122.84
108.92
105.64
94.95
77.24
66.67
63.40
56.00
HO
OMe
MeO
NHCbz
O
N
Bn
3p
f1 (ppm)

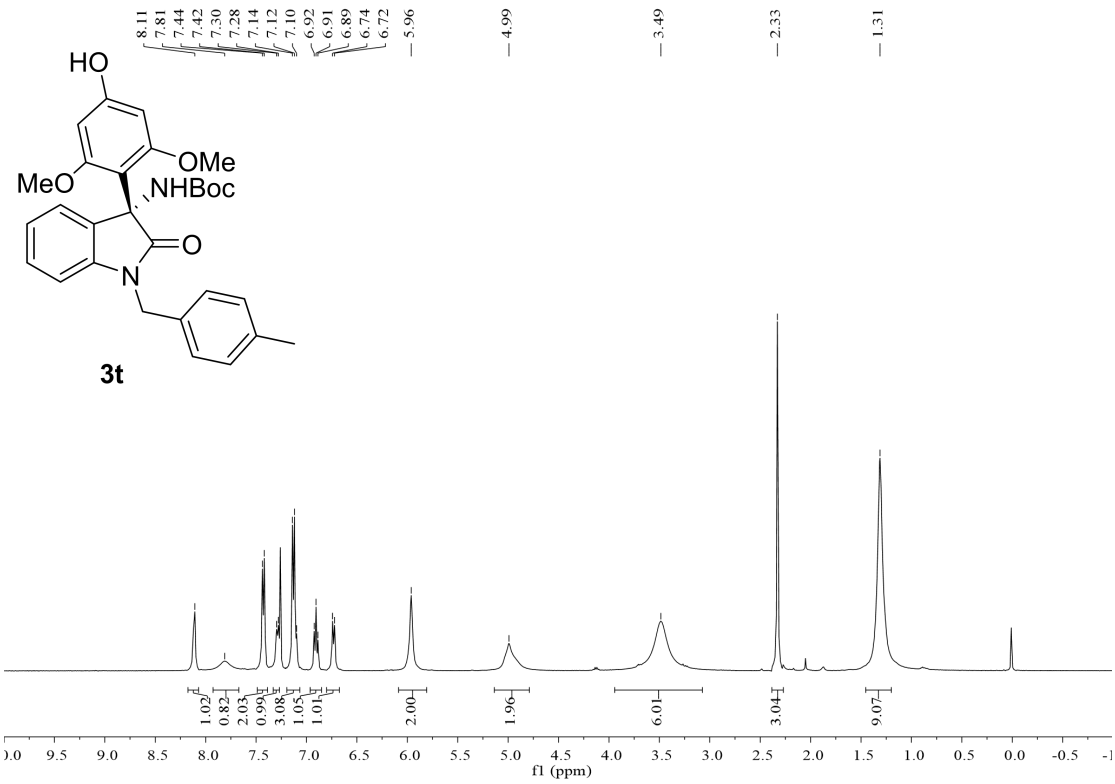

9.75
8.03
7.62
7.60
7.58
7.52
7.50
7.46
7.44
7.42
7.31
7.16
7.14
7.12
6.95
6.93
6.91
6.68
6.23
6.14
3.67
1.29
1.25
HO
OMe
MeO
NHBoc
O
N
Ph
3q
0.98
0.85
1.91
1.87
1.06
0.99
1.03
1.11
1.10
2.00
5.85
8.96
f1 (ppm)


175.40
159.03
158.93
153.73
135.94
129.80
128.66
127.74
126.77
123.81
122.70
108.55
106.68
94.43
79.00
62.64
56.80
28.54
HO
OMe
MeO
NHBoc
O
N
Ph
3q
f1 (ppm)

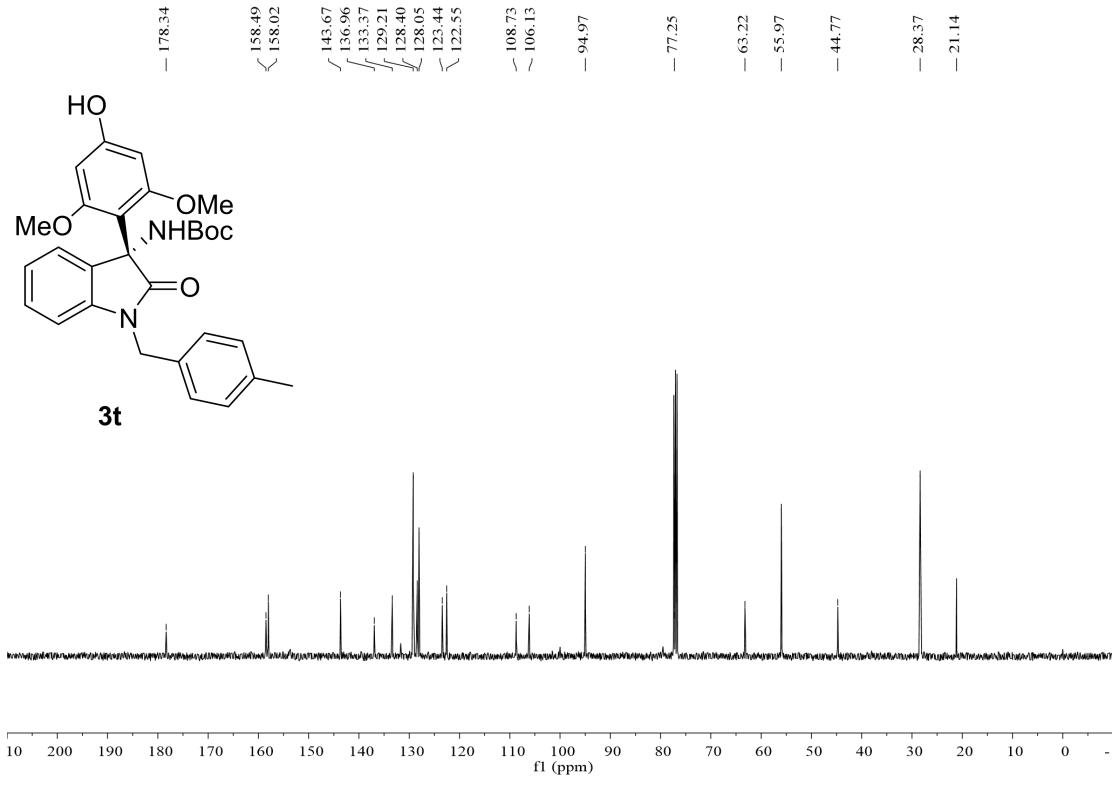

8.01
7.77
7.29
7.28
7.19
7.17
7.15
6.94
6.92
6.90
6.81
6.79
6.01
5.99
5.96
5.95
5.50
5.46
5.29
5.26
4.53
4.36
3.64
1.28
HO
OMe
MeO
NHBoc
O
N
3r
0.95
0.72
0.95
1.01
1.01
0.99
2.90
1.00
1.00
1.92
5.99
9.20
f1 (ppm)
177.75
158.47
158.00
143.34
132.22
128.41
123.40
122.51
118.00
108.58
106.18
94.89
77.24
63.08
56.01
43.40
28.34
HO
OMe
MeO
NHBoc
O
N
3r
f1 (ppm)


8.02
8.00
7.99
7.87
7.35
7.30
7.29
7.14
7.12
7.10
6.99
6.98
6.97
6.96
6.94
6.92
6.90
6.67
6.65
5.96
5.04
4.97
3.53
1.33
HO
OMe
MeO
NHBoc
O
N
F
3s
1.11
0.72
4.18
1.11
2.14
1.03
2.00
2.00
5.96
9.15
f1 (ppm)

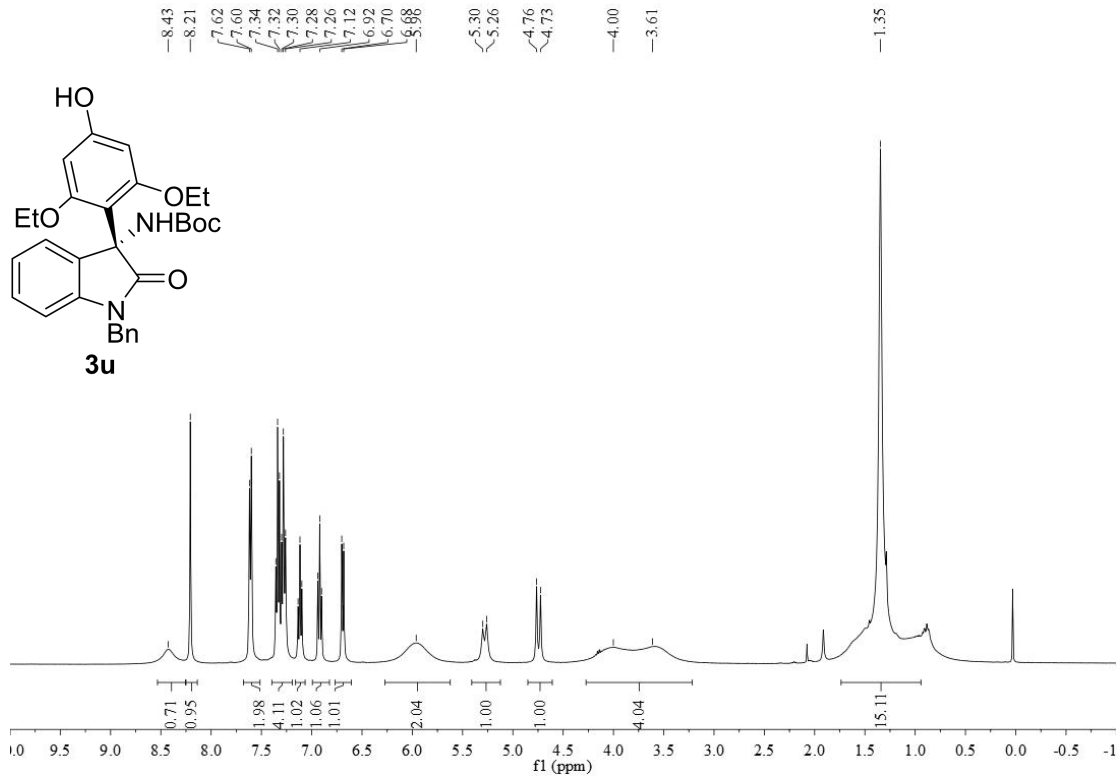

178.42
164.35
161.91
158.50
157.97
143.30
139.06
138.99
131.65
130.07
129.99
128.47
123.49
123.40
122.78
115.14
114.92
114.43
114.22
108.51
106.21
95.03
77.23
63.21
56.06
44.52
28.36
HO
OMe
MeO
NHBoc
O
N
F
3s
f1 (ppm)

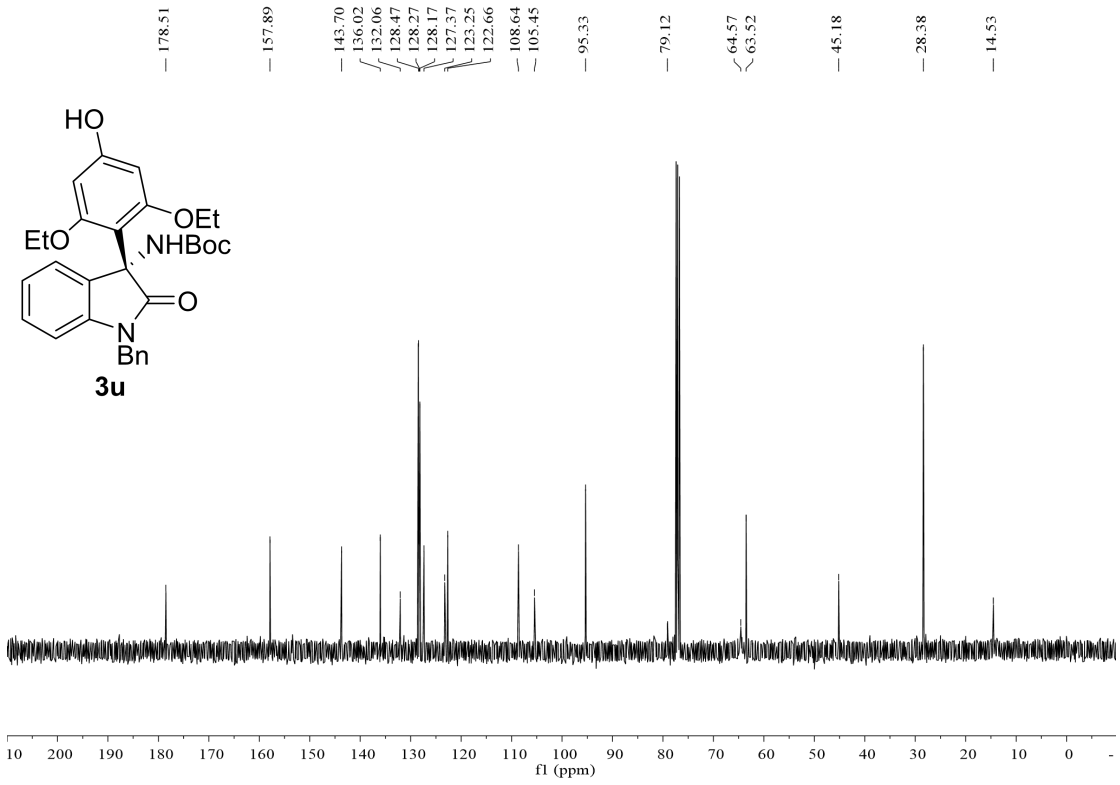

8.11
7.81
7.44
7.42
7.30
7.28
7.14
7.12
7.10
6.92
6.91
6.89
6.74
6.72
5.96
4.99
3.49
2.33
1.31
HO
OMe
MeO
NHBoc
O
N
1.02
0.82
2.03
0.99
3.08
1.05
1.01
2.00
1.96
6.01
3.04
9.07
f1 (ppm)

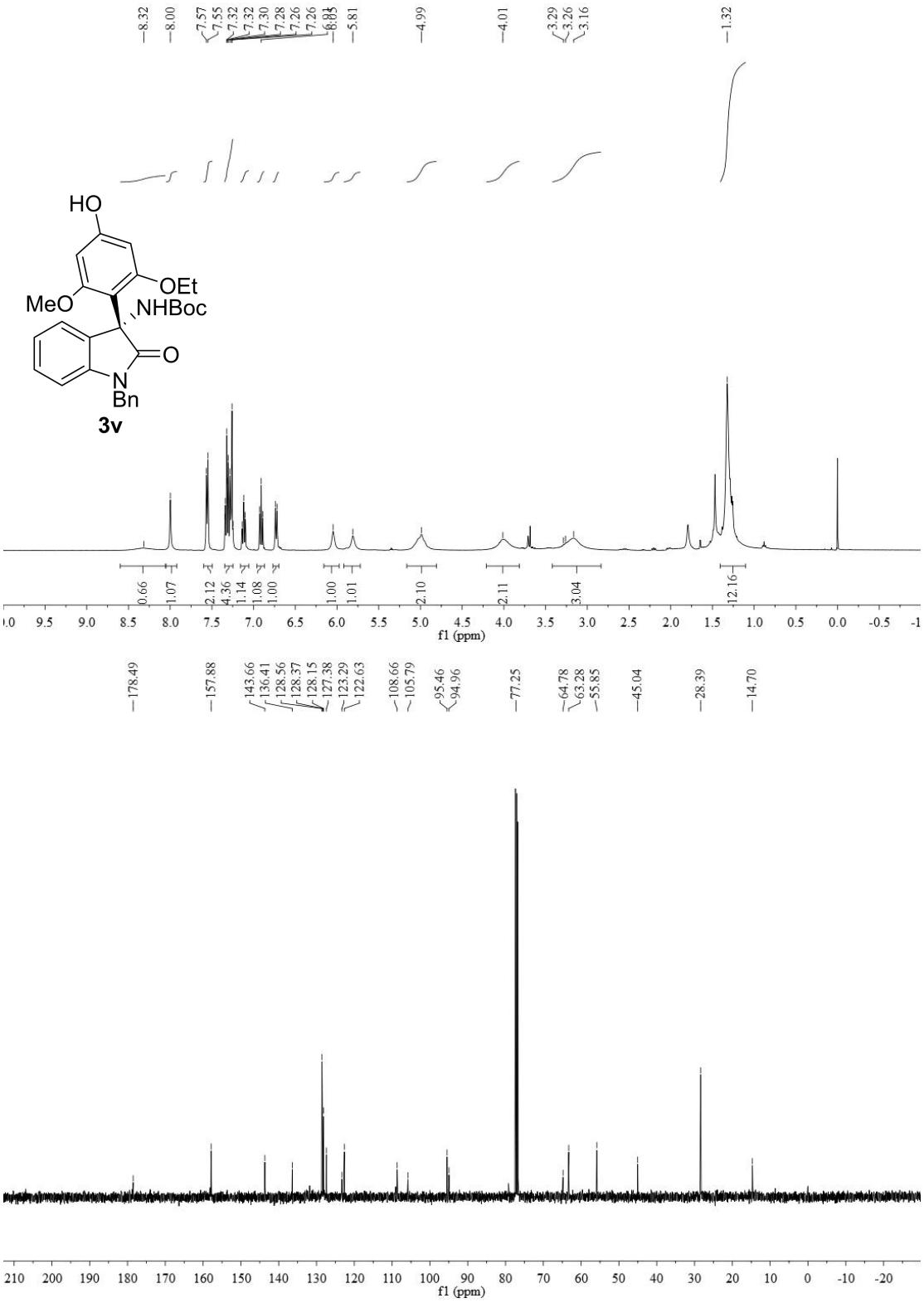
3t

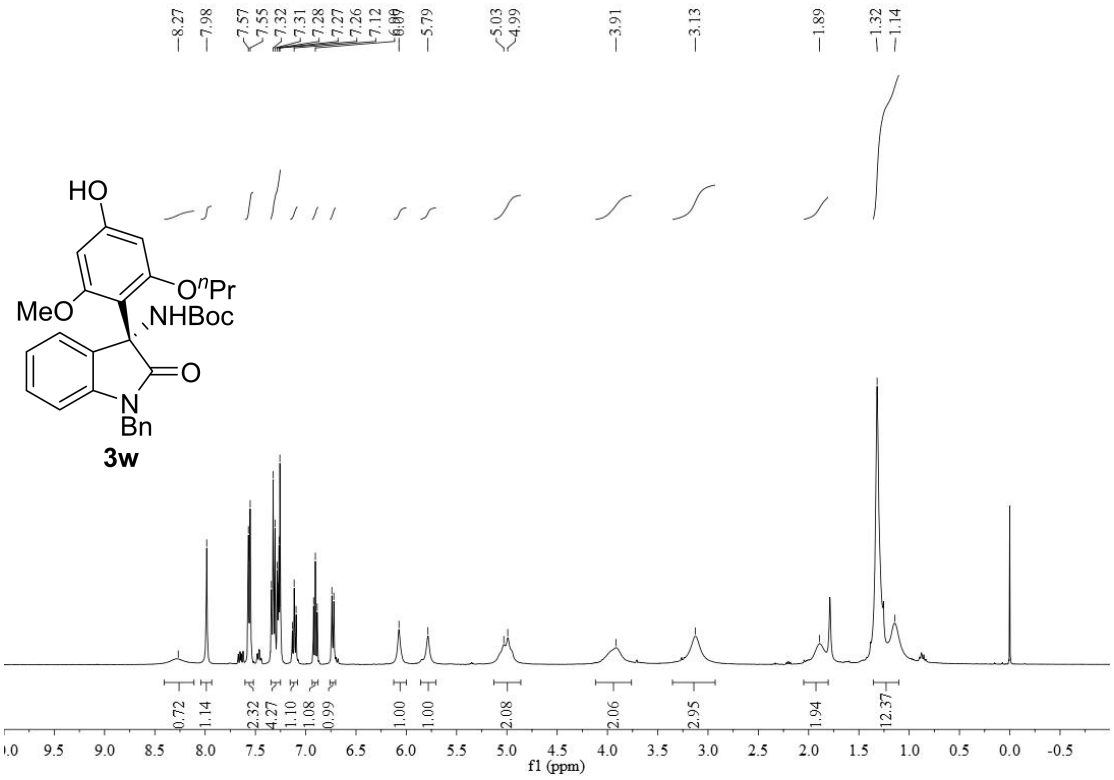

178.34
158.49
158.02
143.67
136.96
133.37
129.21
128.40
128.05
123.44
122.55
108.73
106.13
94.97
77.25
63.22
55.97
44.77
28.37
21.14
HO
OMe
MeO
NHBoc
O
N
f1 (ppm)

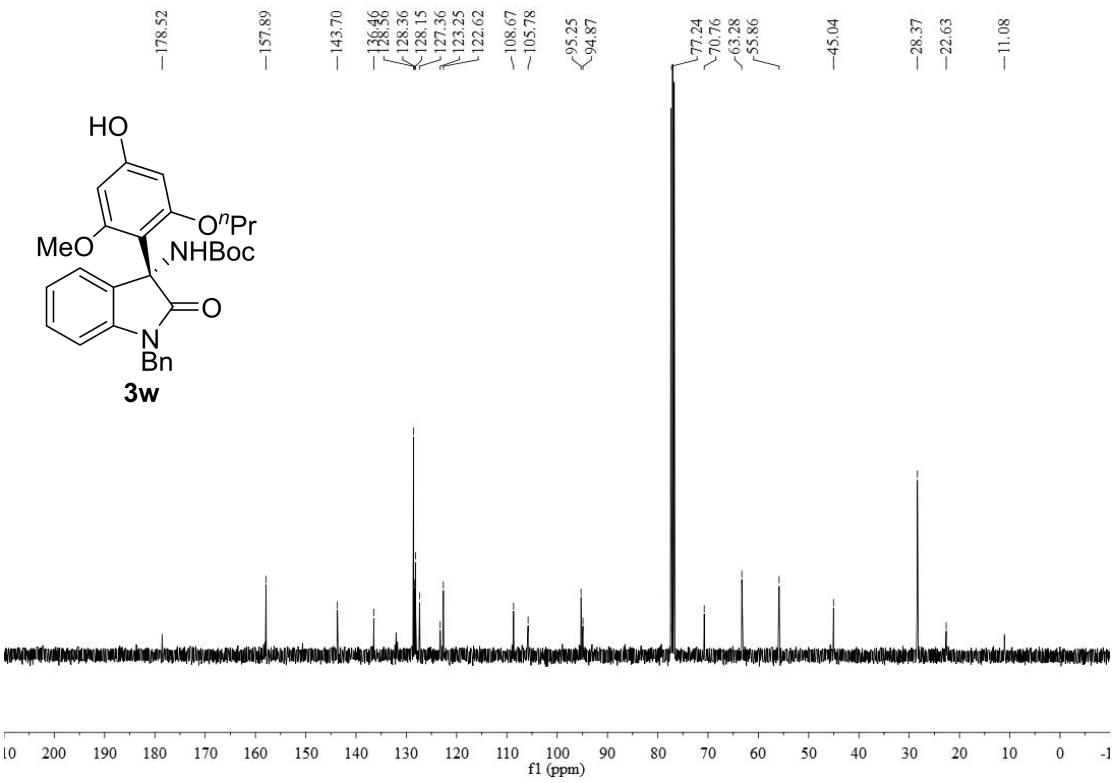
3t

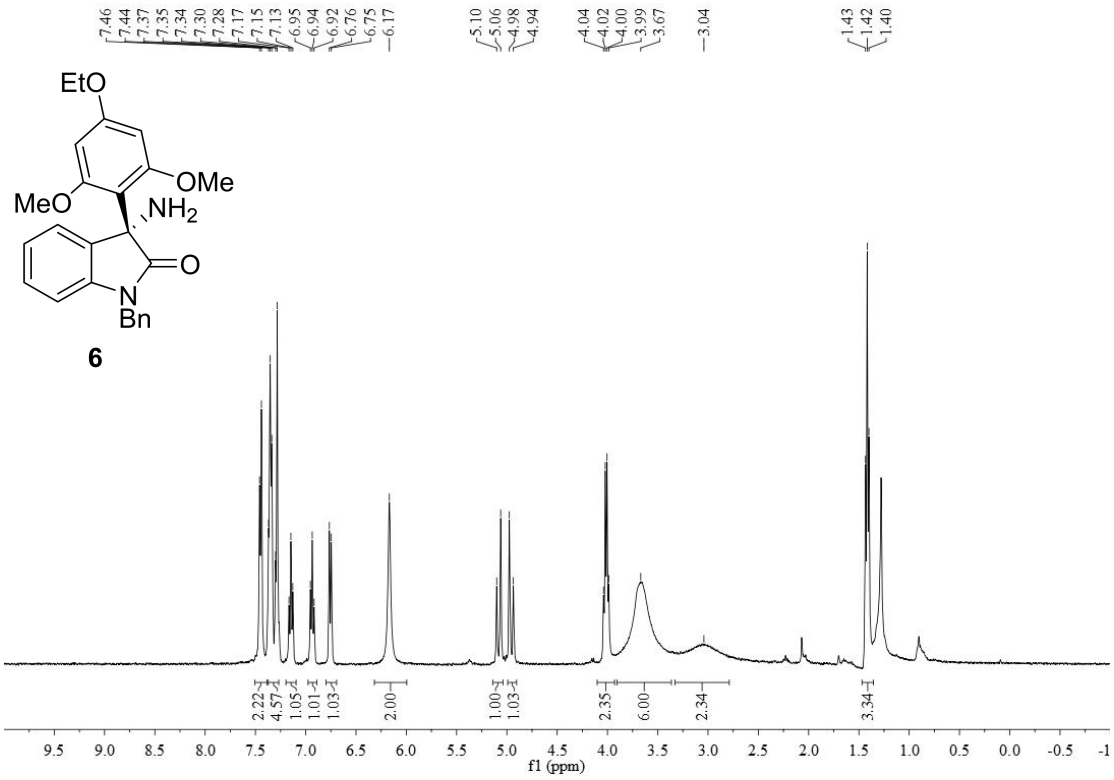

8.43
8.21
7.62
7.60
7.34
7.32
7.30
7.28
7.26
7.12
6.92
6.70
6.68
5.98
5.30
5.26
4.76
4.73
4.00
3.61
1.35
HO
OEt
EtO
NHBoc
O
N
Bn
3u
0.71
0.95
1.98
4.11
1.02
1.06
1.01
2.04
1.00
1.00
4.04
15.11
f1 (ppm)

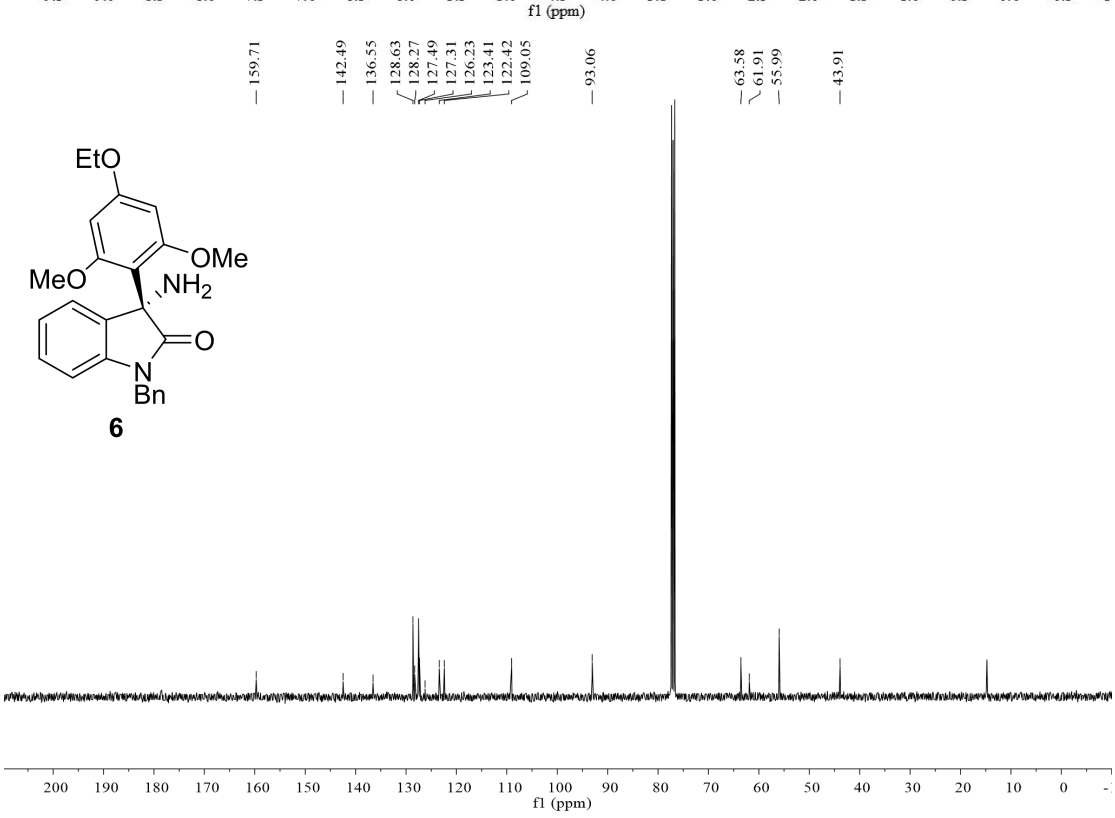

178.51
157.89
143.70
136.02
132.06
128.47
128.27
128.17
127.37
123.25
122.66
108.64
105.45
95.33
79.12
64.57
63.52
45.18
28.38
14.53
HO
OEt
EtO
NHBoc
O
N
Bn
3u
f1 (ppm)

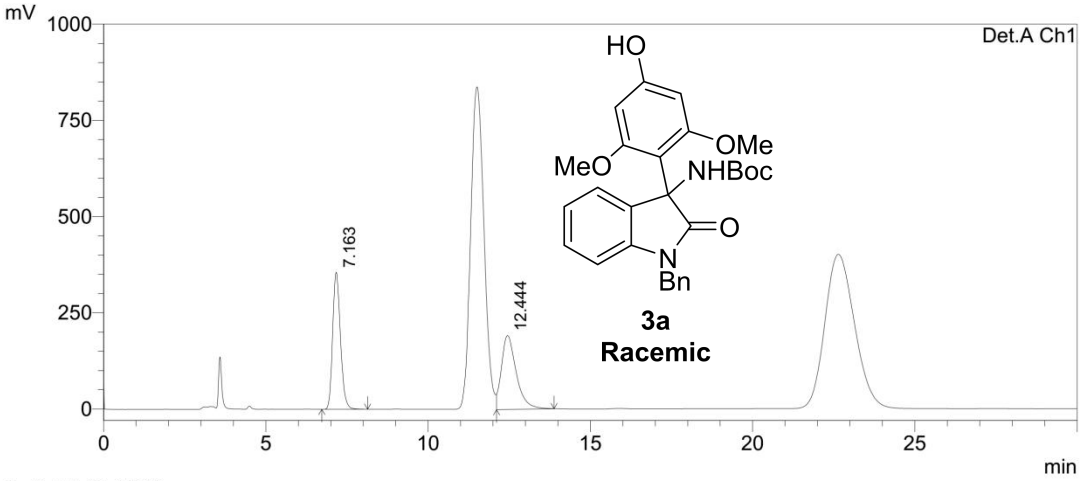

HO
OEt
MeO
NHBoc
O
N
Bn
3v
f1 (ppm)
f1 (ppm)


HO
MeO
O^{n}Pr
NHBoc
O
N
Bn
3w
f1 (ppm)


HO
MeO
O^{n}Pr
NHBoc
O
N
Bn
3w
f1 (ppm)


7.46
7.44
7.37
7.35
7.34
7.30
7.28
7.17
7.15
7.13
6.95
6.94
6.92
6.76
6.75
6.17
5.10
5.06
4.98
4.94
4.04
4.02
4.00
3.99
3.67
3.04
1.43
1.42
1.40
EtO
OMe
MeO
NH2
O
N
Bn
6
2.22
4.57
1.05
1.01
1.03
2.00
1.00
1.03
2.35
6.00
2.34
3.34
f1 (ppm)


159.71
142.49
136.55
128.63
128.27
127.49
127.31
126.23
123.41
122.42
109.05
93.06
63.58
61.91
55.99
43.91
EtO
OMe
MeO
NH2
O
N
Bn
6
f1 (ppm)

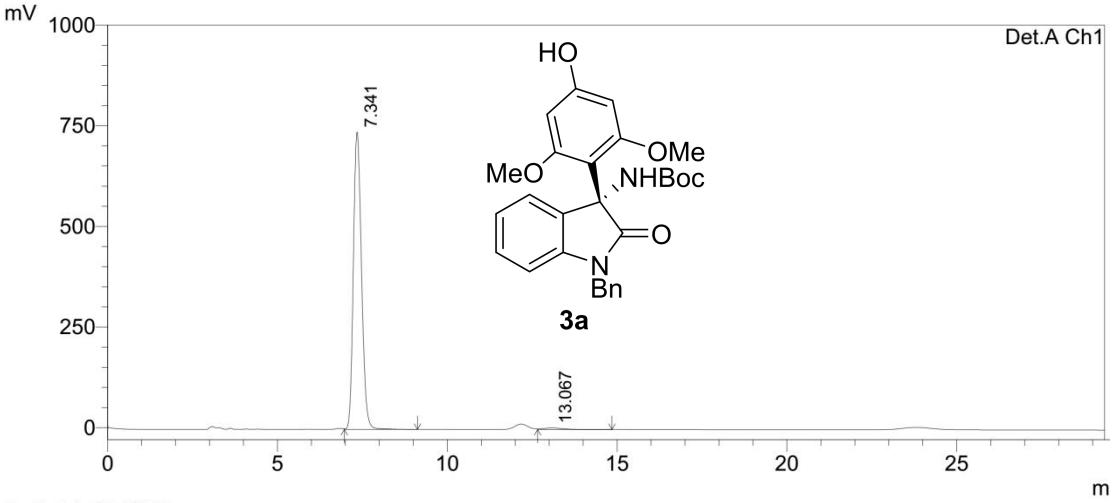


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.163	5948608	356138	49.483	64.969
2	12.444	6072829	192024	50.517	35.031
Total		12021437	548162	100.000	100.000

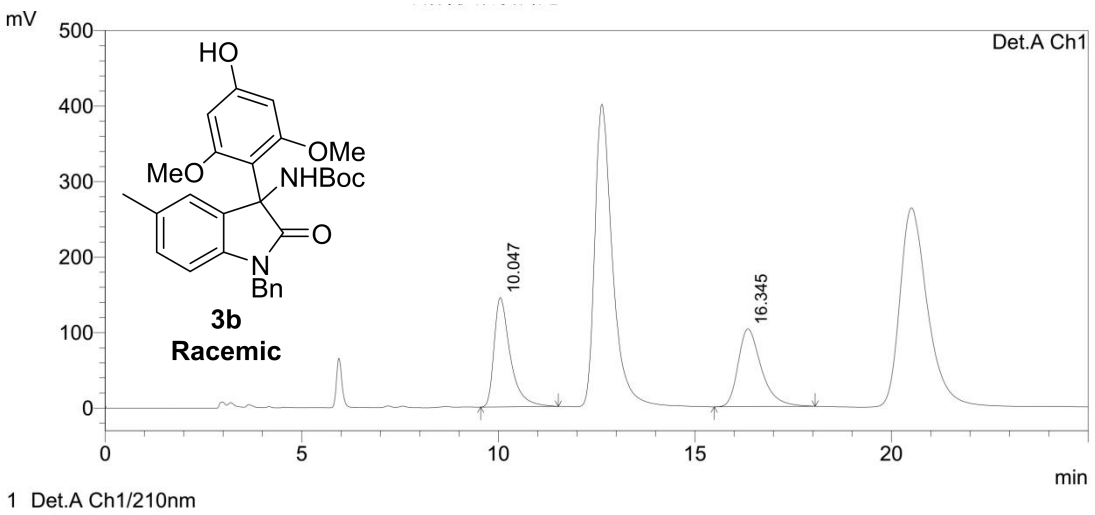


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.341	12311432	738514	98.605	99.432
2	13.067	174118	4219	1.395	0.568
Total		12485550	742732	100.000	100.000

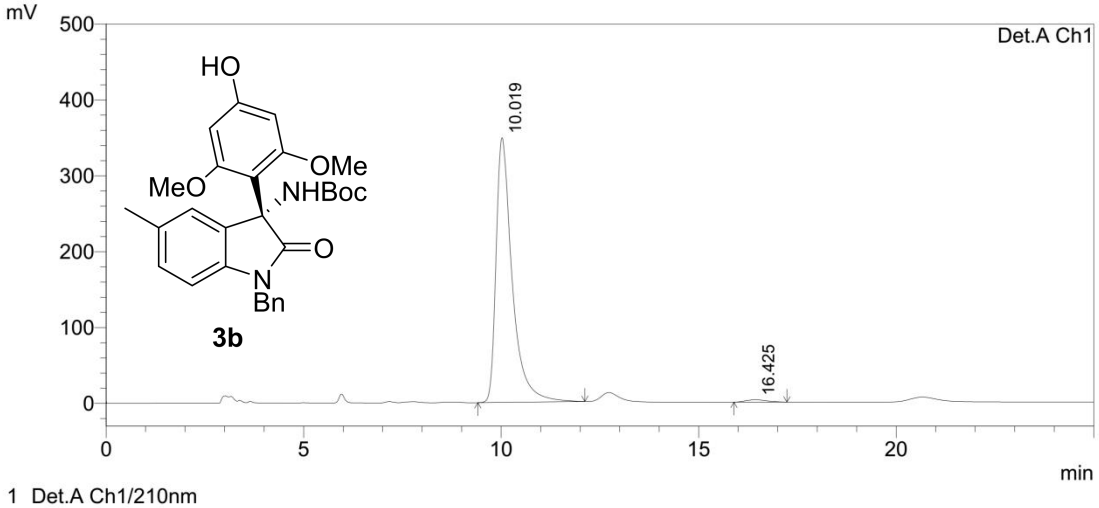


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.047	4138462	144866	49.478	58.466
2	16.345	4225713	102912	50.522	41.534
Total		8364175	247778	100.000	100.000

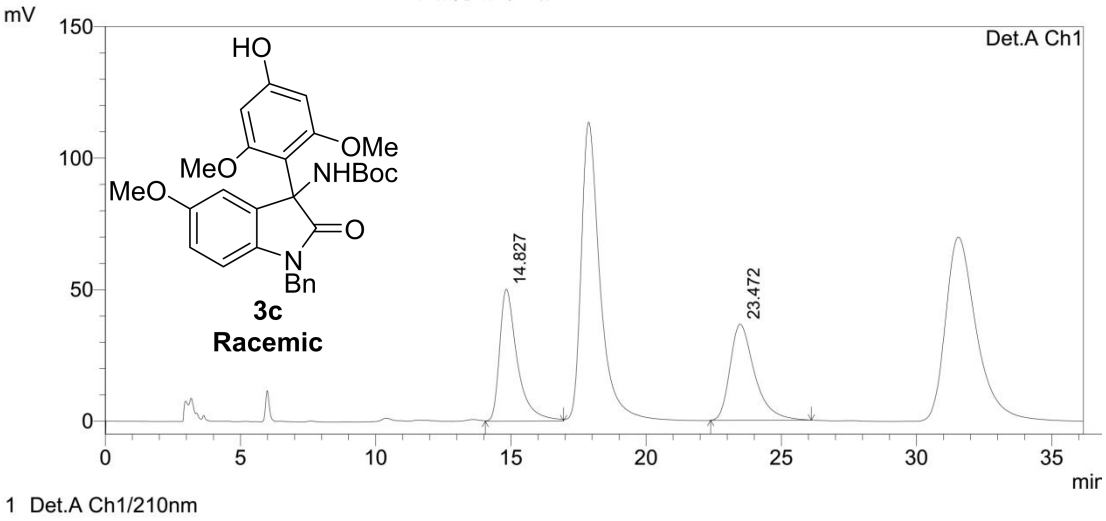


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

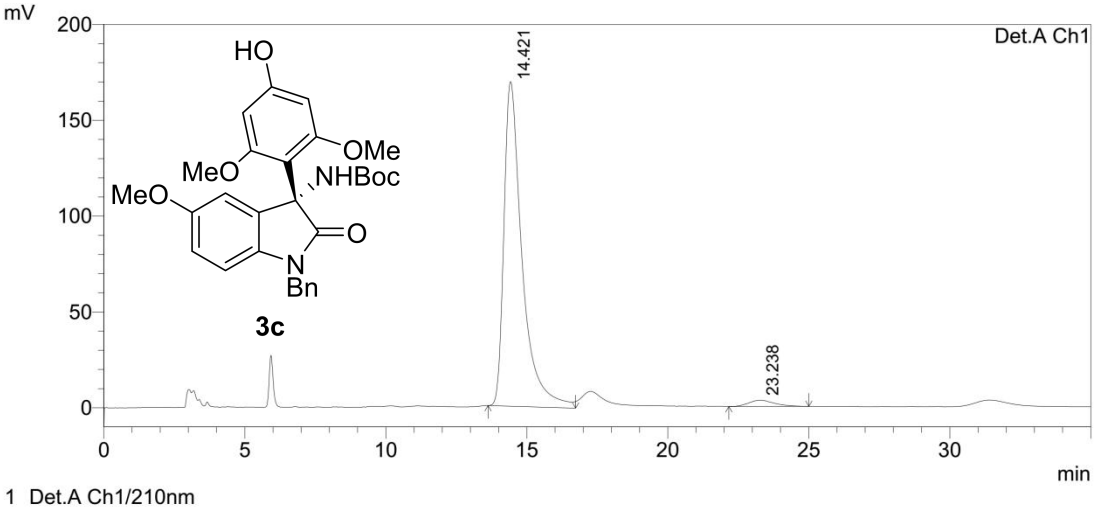
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.019	9890640	348917	98.811	99.102
2	16.425	118977	3160	1.189	0.898
Total		10009616	352077	100.000	100.000



PeakTable

Detector A Ch1 210nm

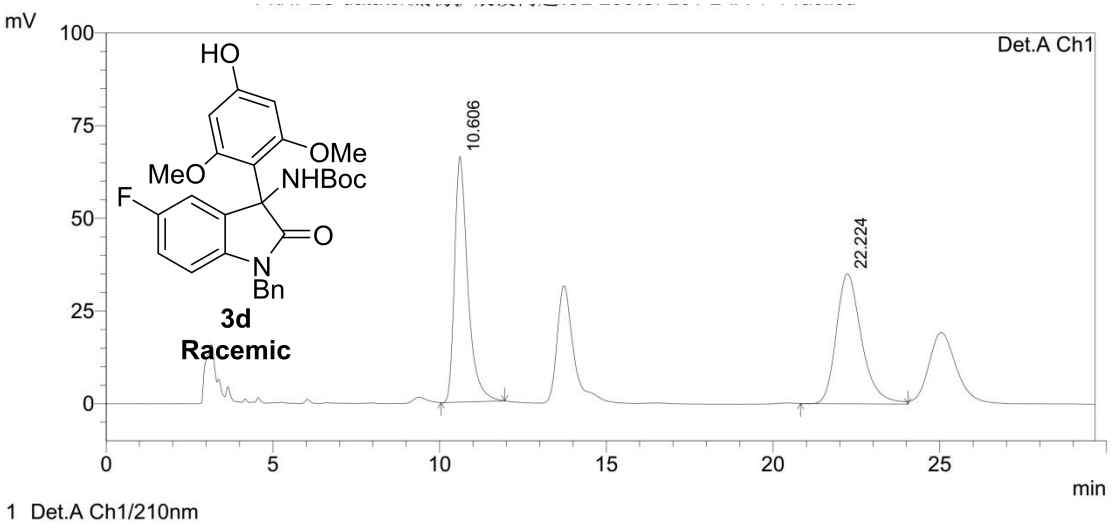
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.827	2275098	50222	49.669	57.886
2	23.472	2305423	36537	50.331	42.114
Total		4580522	86759	100.000	100.000



PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.421	7577280	169370	97.321	98.092
2	23.238	208547	3295	2.679	1.908
Total		7785828	172664	100.000	100.000

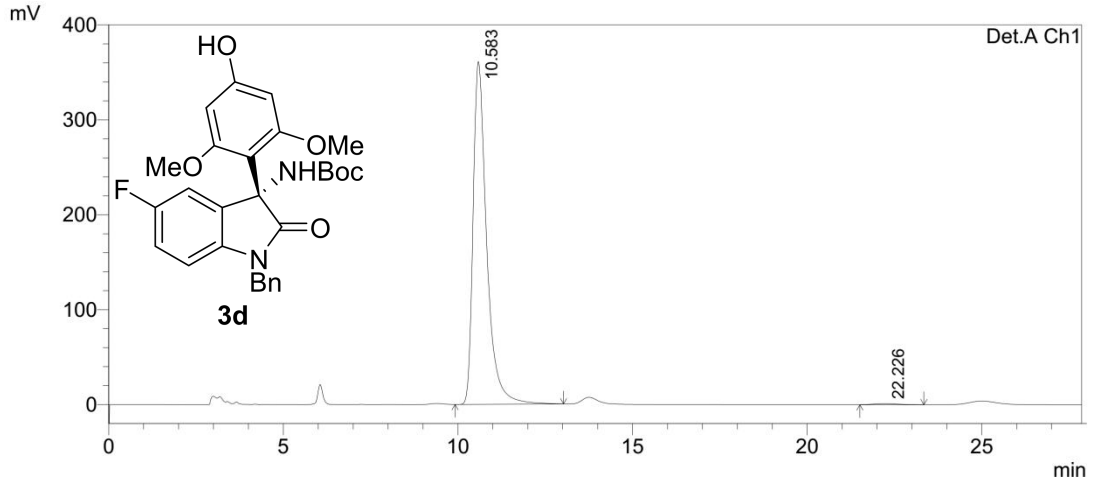


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.606	1829157	66203	49.645	65.354
2	22.224	1855300	35096	50.355	34.646
Total		3684457	101299	100.000	100.000

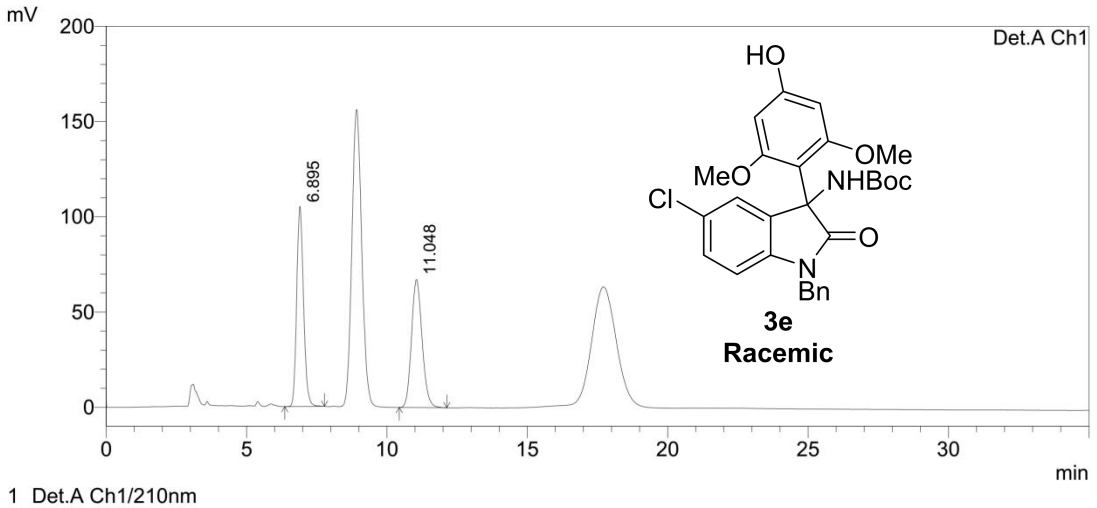


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.583	9744095	361085	99.440	99.687
2	22.226	54878	1135	0.560	0.313
Total		9798973	362220	100.000	100.000

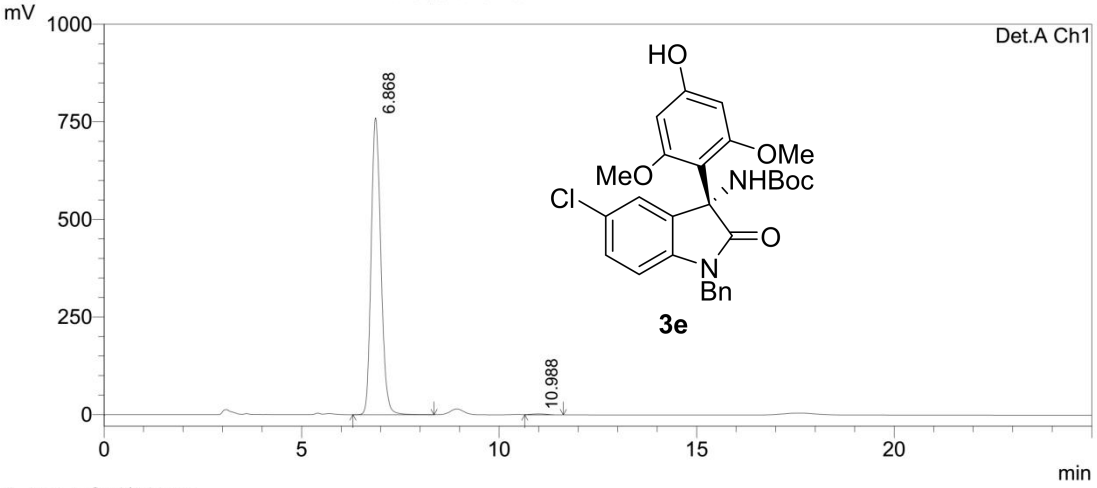


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.895	1778393	105128	50.123	60.994
2	11.048	1769674	67229	49.877	39.006
Total		3548066	172357	100.000	100.000

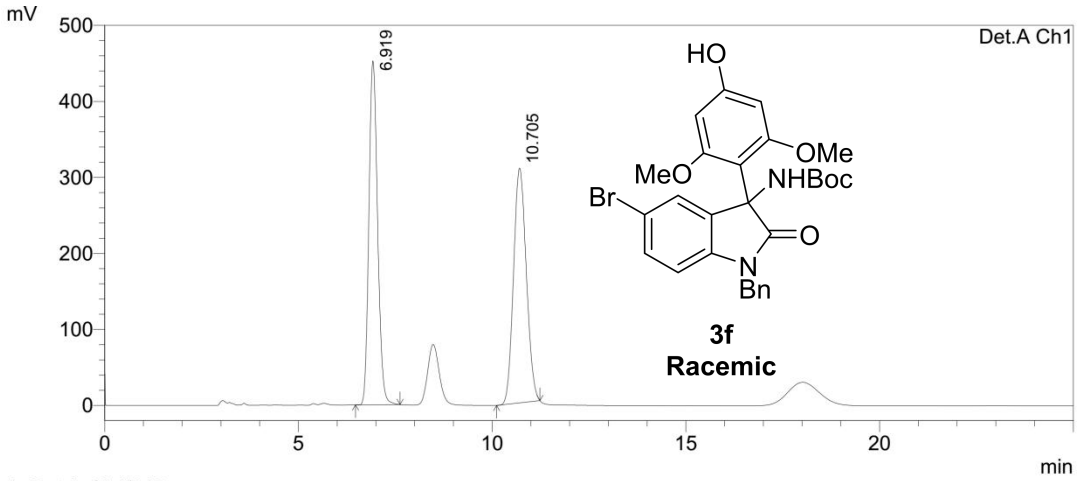


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.868	13014591	760718	99.506	99.666
2	10.988	64650	2549	0.494	0.334
Total		13079241	763267	100.000	100.000

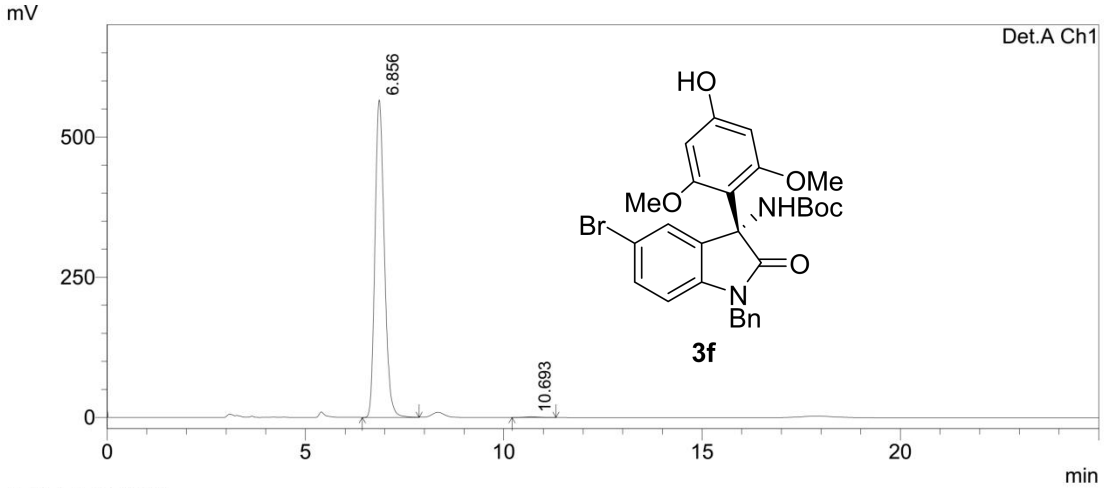


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.919	7050457	452616	49.847	59.439
2	10.705	7093874	308860	50.153	40.561
Total		14144331	761476	100.000	100.000

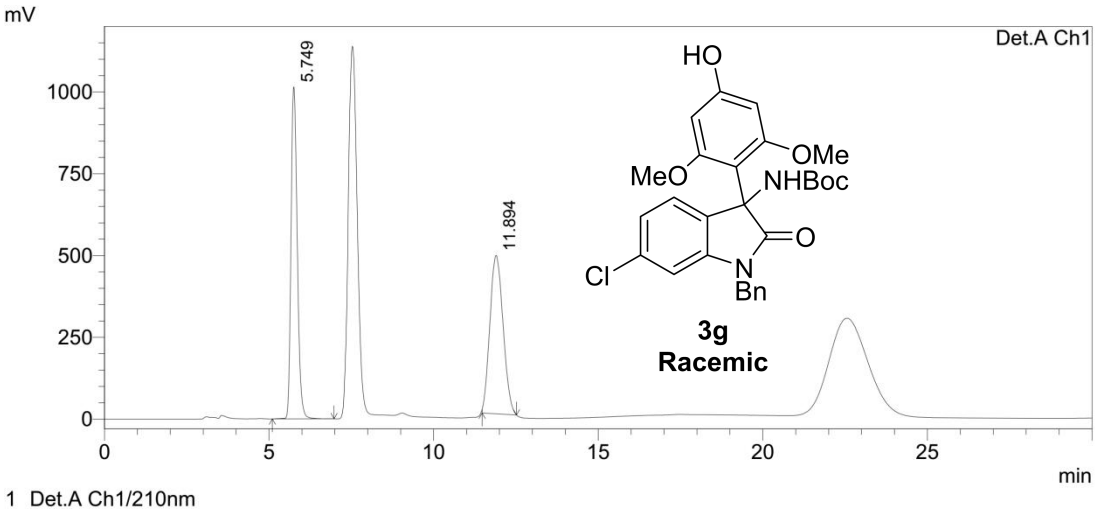


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.856	9312749	566106	99.645	99.747
2	10.693	33204	1434	0.355	0.253
Total		9345952	567540	100.000	100.000

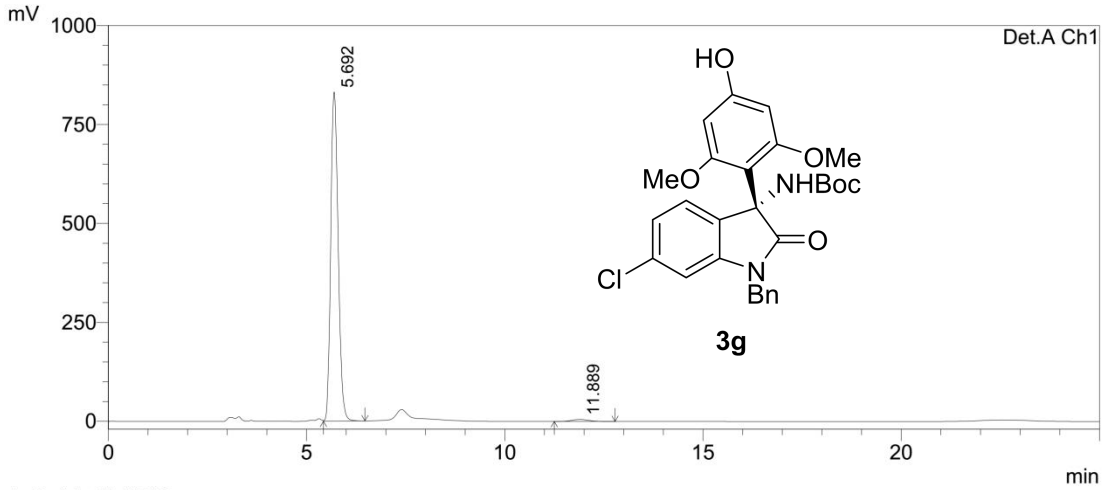


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.749	13378936	1014710	49.772	67.698
2	11.894	13501262	484171	50.228	32.302
Total		26880198	1498881	100.000	100.000

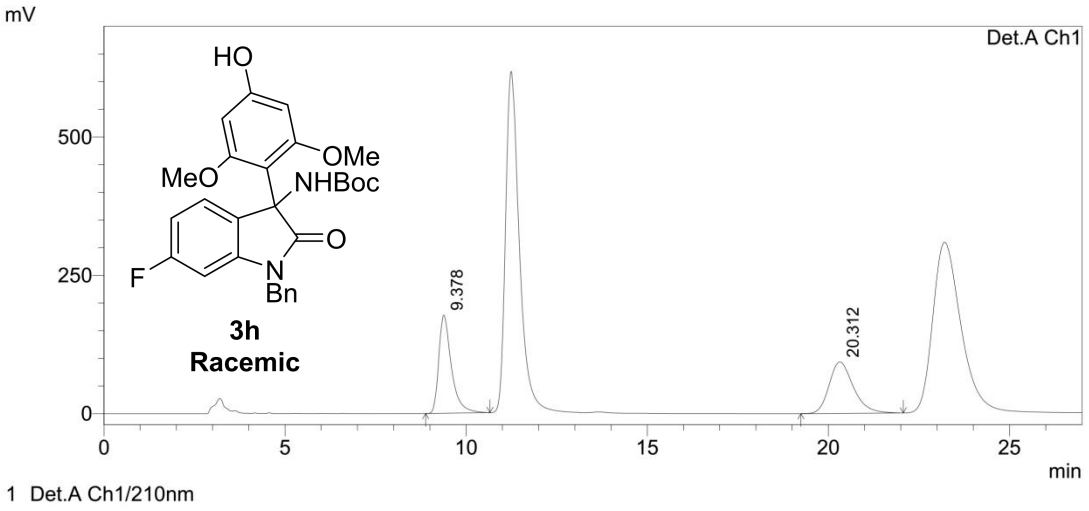


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.692	10845020	831289	98.668	99.404
2	11.889	146359	4988	1.332	0.596
Total		10991379	836277	100.000	100.000

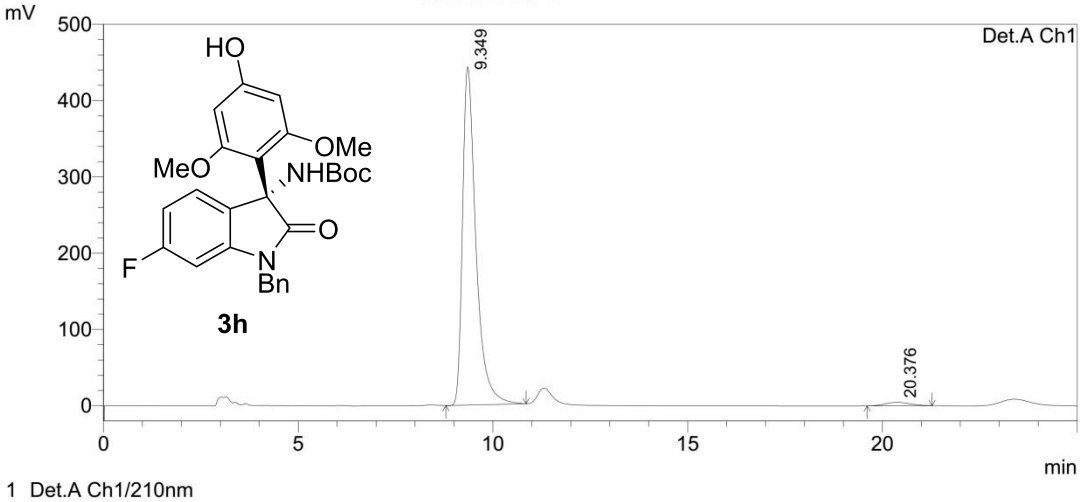


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.378	4300324	177435	49.839	65.605
2	20.312	4328046	93024	50.161	34.395
Total		8628370	270459	100.000	100.000

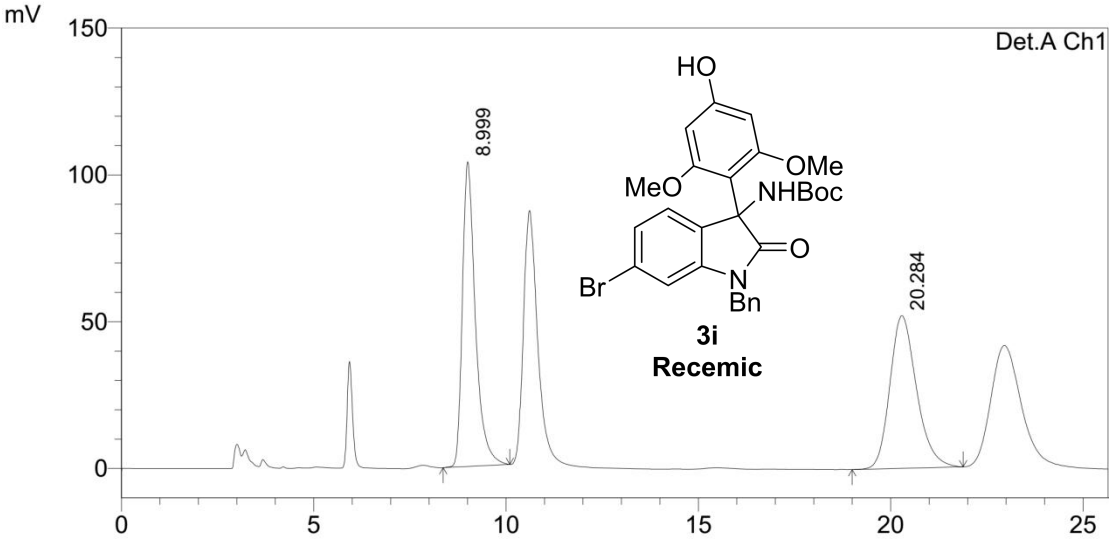


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.349	10596001	443399	98.147	98.986
2	20.376	200050	4544	1.853	1.014
Total		10796051	447943	100.000	100.000

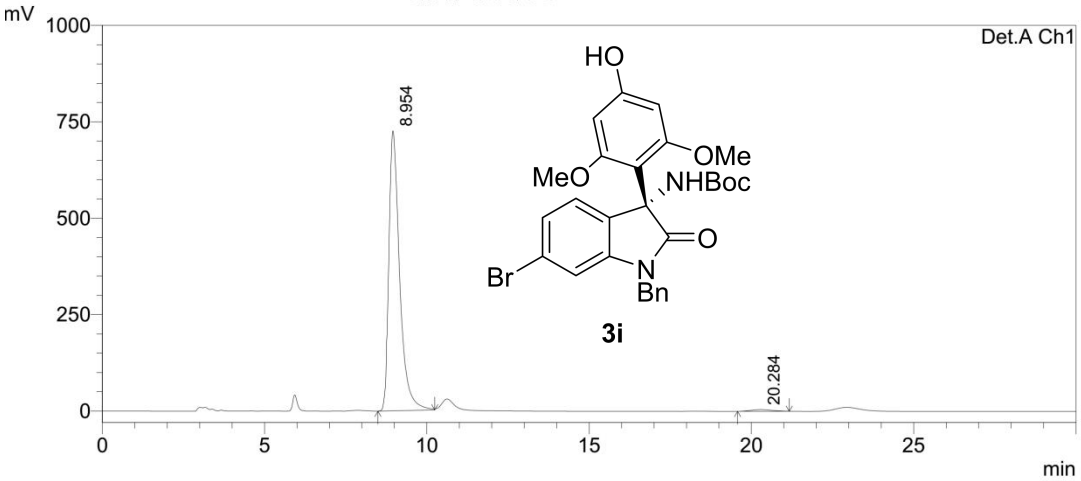


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.999	2440080	103791	49.335	66.615
2	20.284	2505823	52017	50.665	33.385
Total		4945903	155807	100.000	100.000

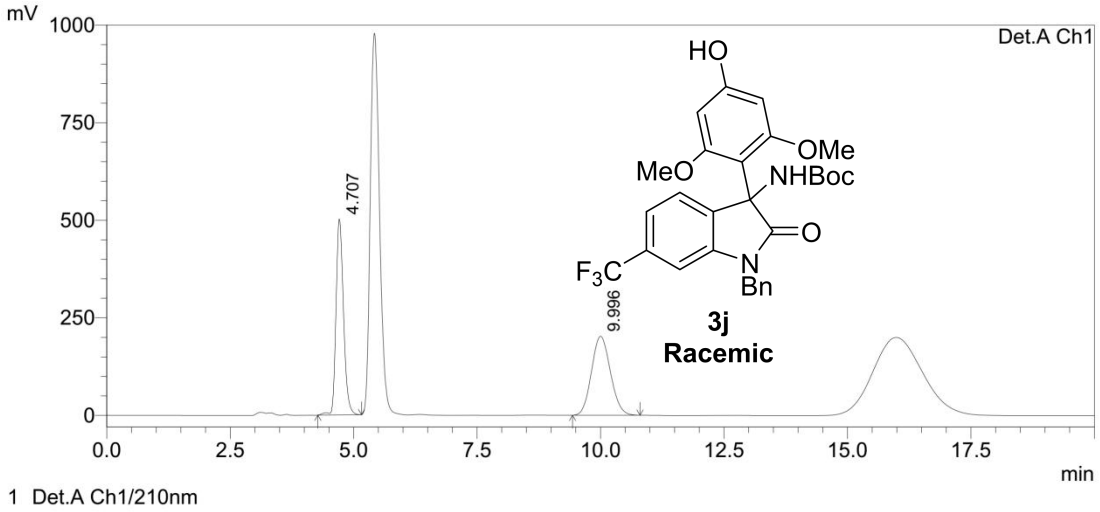


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.954	16810095	726043	98.864	99.401
2	20.284	193134	4376	1.136	0.599
Total		17003229	730418	100.000	100.000

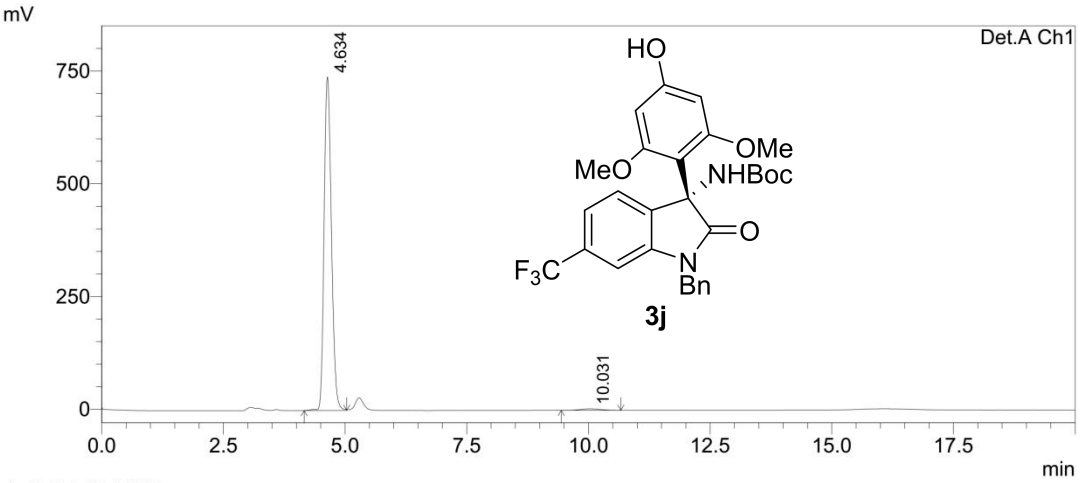


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.707	5293700	501957	49.575	71.268
2	9.996	5384563	202362	50.425	28.732
Total		10678263	704319	100.000	100.000

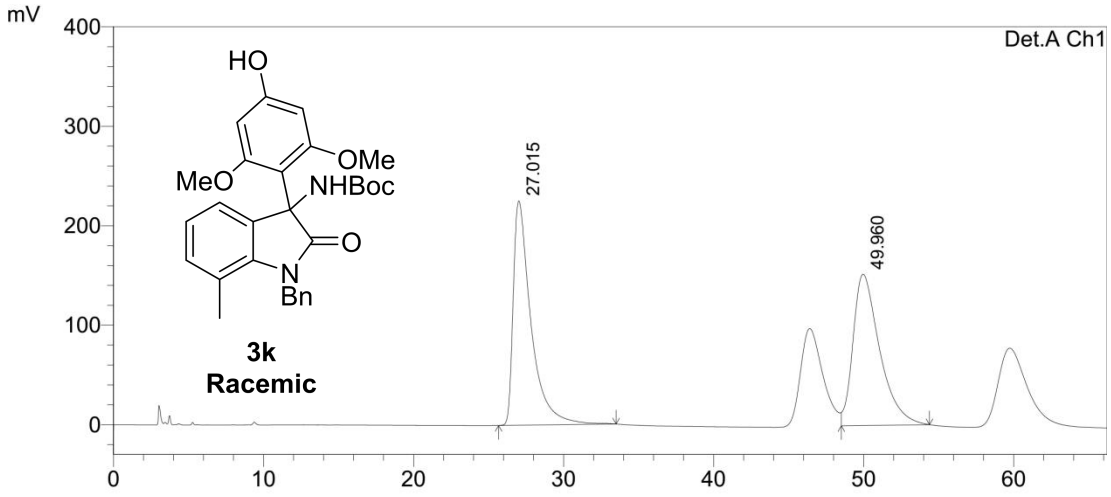


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.634	7748525	739386	98.820	99.553
2	10.031	92513	3319	1.180	0.447
Total		7841038	742705	100.000	100.000

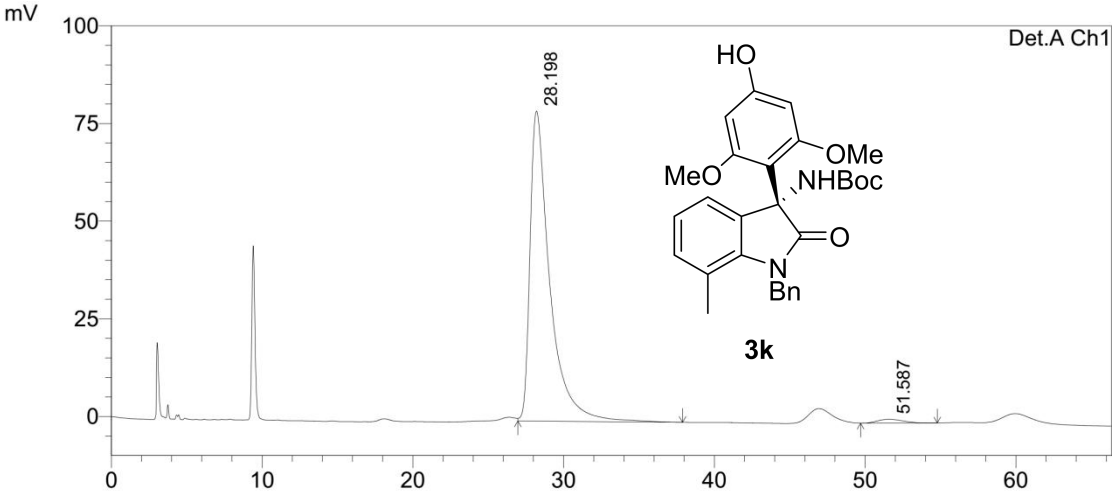


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.015	18562659	225576	49.707	59.718
2	49.960	18781210	152162	50.293	40.282
Total		37343869	377737	100.000	100.000

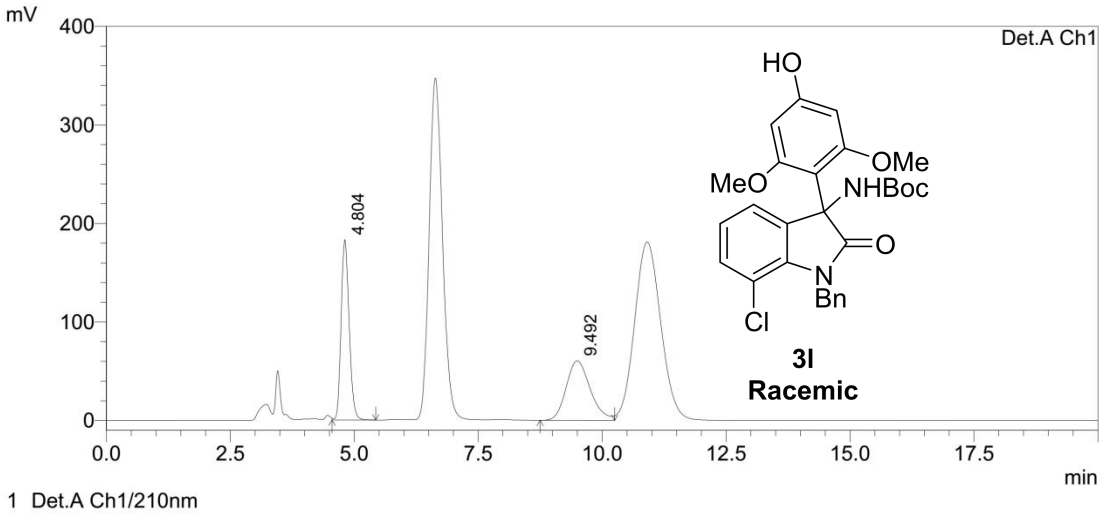


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.198	7223228	79361	98.485	98.780
2	51.587	111142	980	1.515	1.220
Total		7334370	80341	100.000	100.000

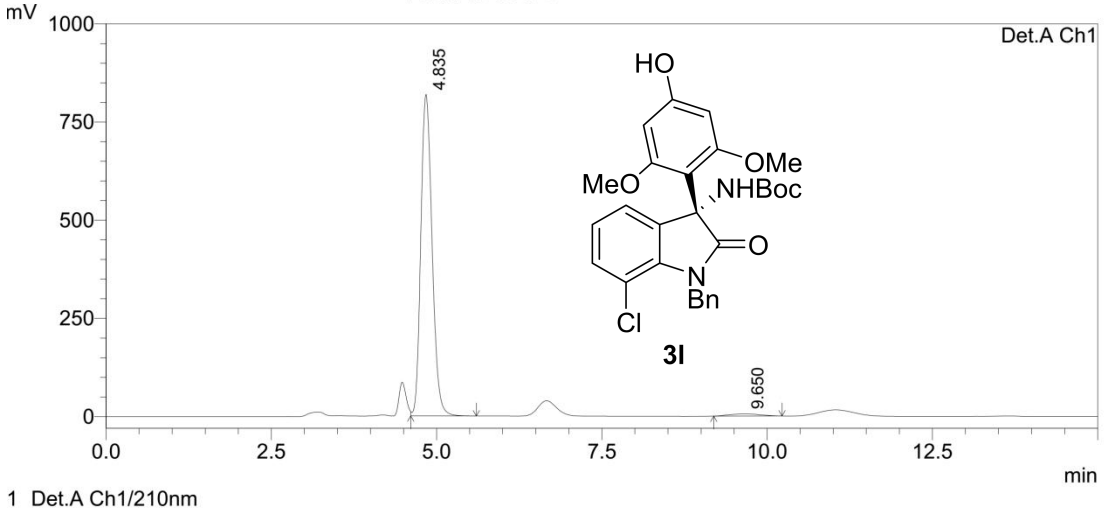


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.804	2061841	183174	50.173	75.161
2	9.492	2047639	60536	49.827	24.839
Total		4109480	243711	100.000	100.000

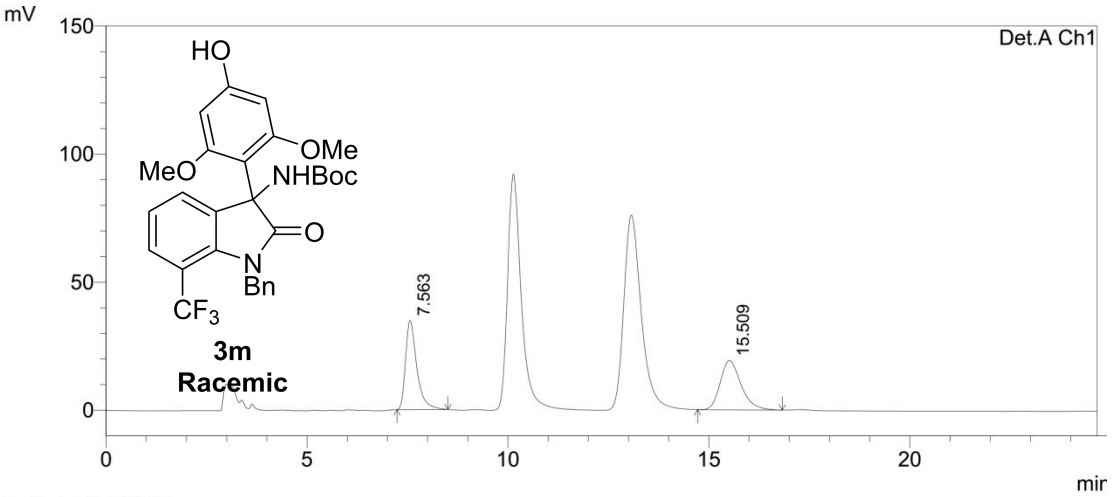


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.835	9700470	818904	98.154	99.295
2	9.650	182397	5811	1.846	0.705
Total		9882868	824715	100.000	100.000

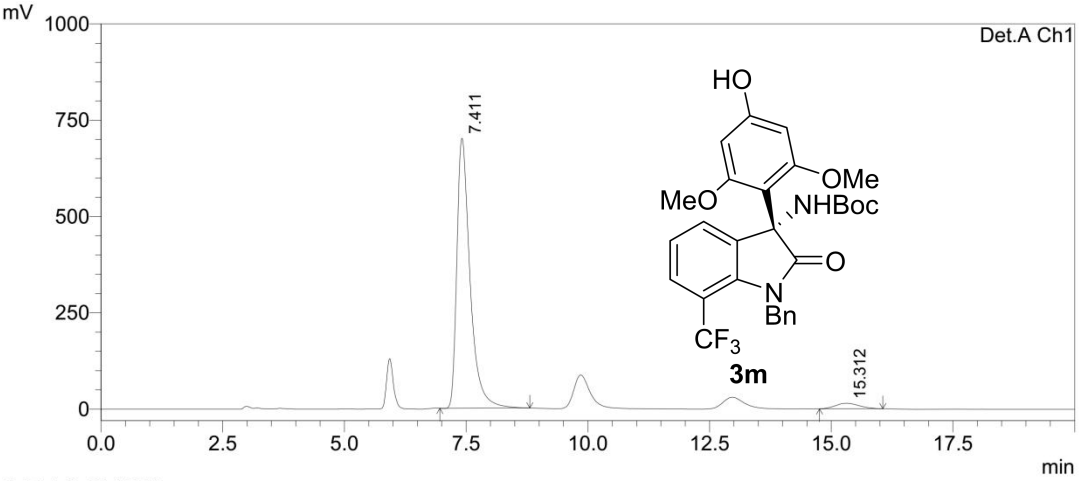


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.563	678759	34851	49.526	64.469
2	15.509	691749	19207	50.474	35.531
Total		1370509	54058	100.000	100.000

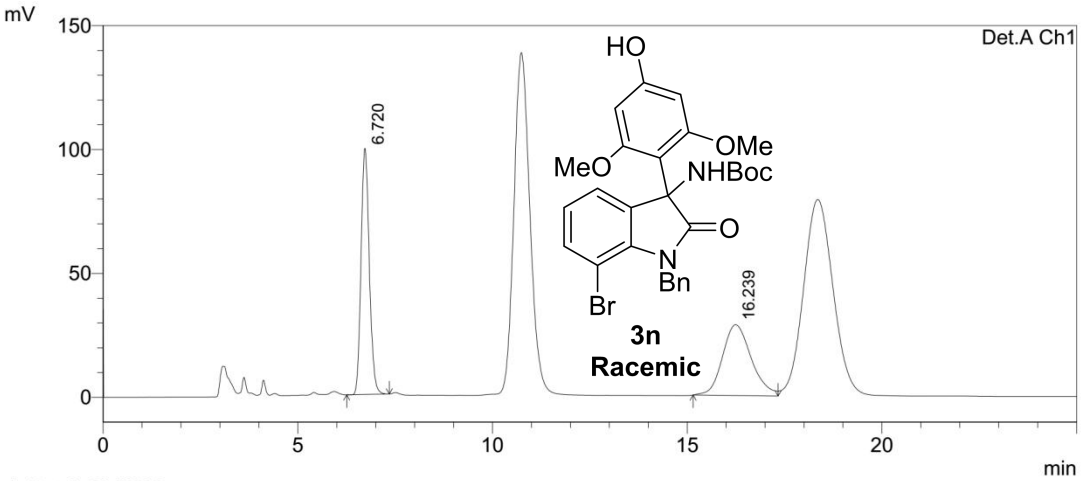


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.411	13190640	701009	96.384	97.973
2	15.312	494840	14506	3.616	2.027
Total		13685481	715515	100.000	100.000

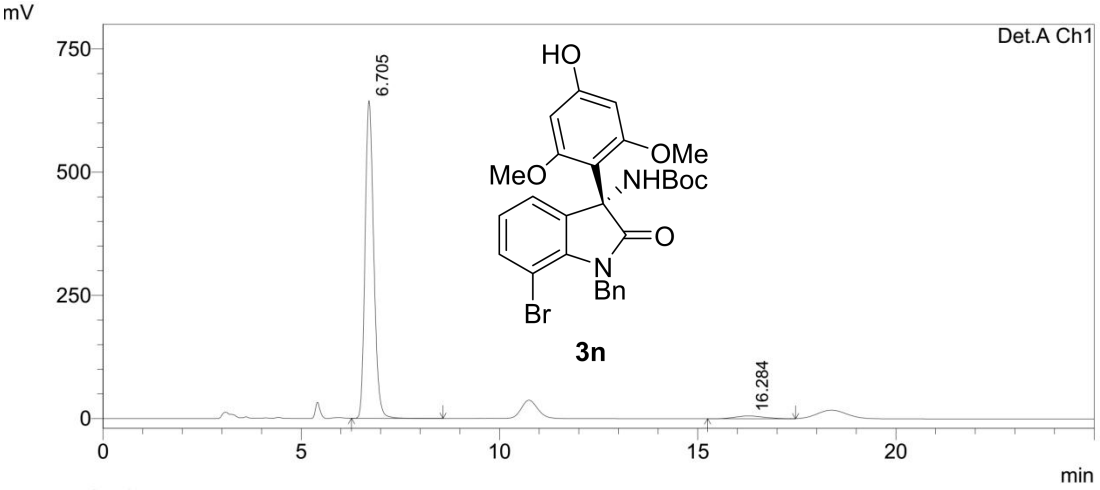


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.720	1462876	99348	49.932	77.668
2	16.239	1466869	28566	50.068	22.332
Total		2929746	127914	100.000	100.000

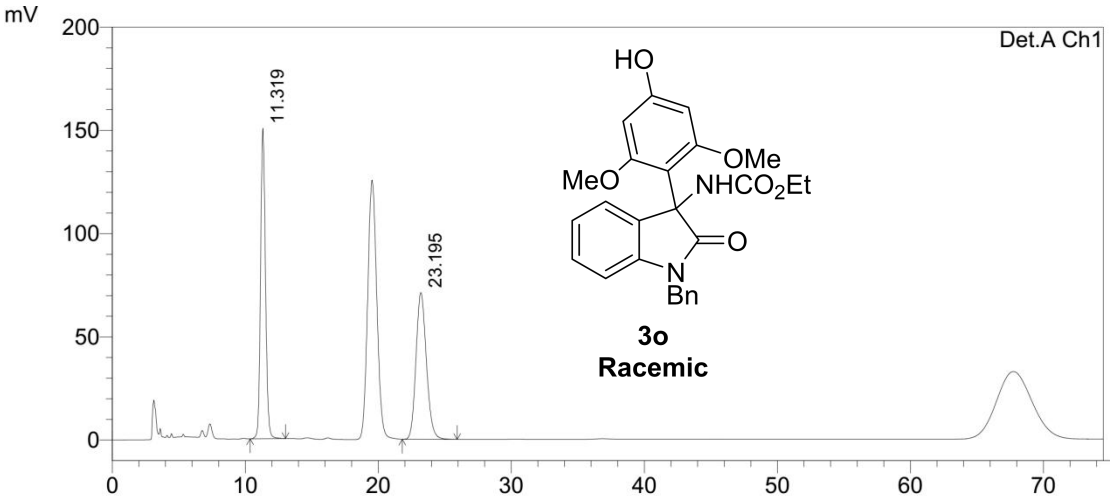


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.705	9787126	644729	96.867	99.098
2	16.284	316517	5869	3.133	0.902
Total		10103643	650597	100.000	100.000

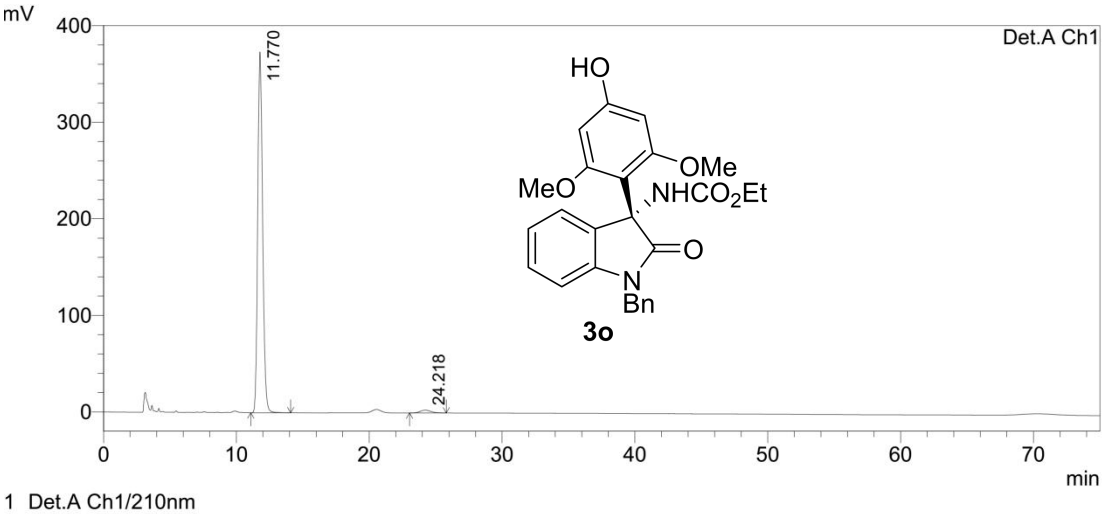


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.319	3861020	150439	49.909	67.896
2	23.195	3875165	71134	50.091	32.104
Total		7736185	221573	100.000	100.000

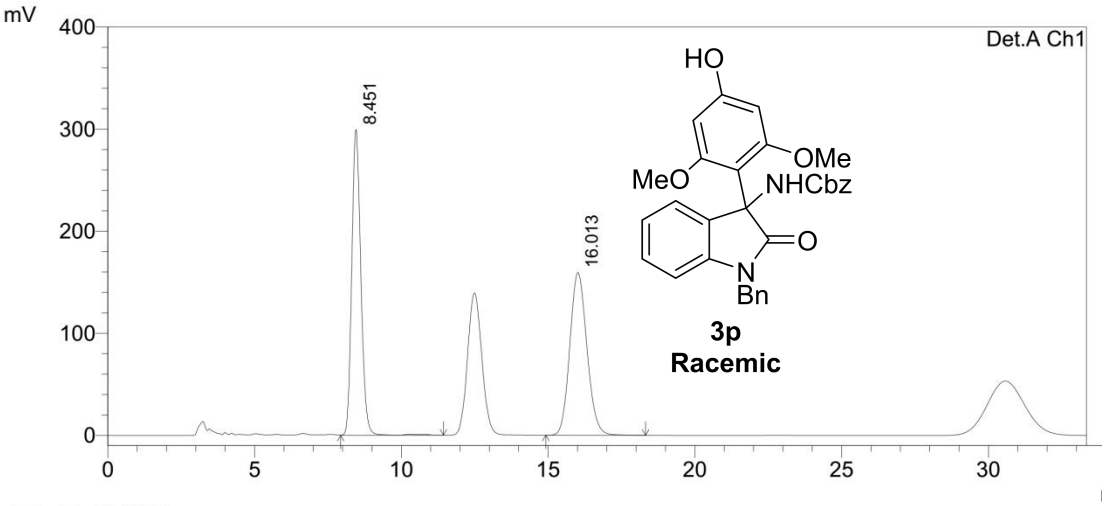


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.770	9604634	373725	98.324	99.218
2	24.218	163756	2944	1.676	0.782
Total		9768390	376669	100.000	100.000

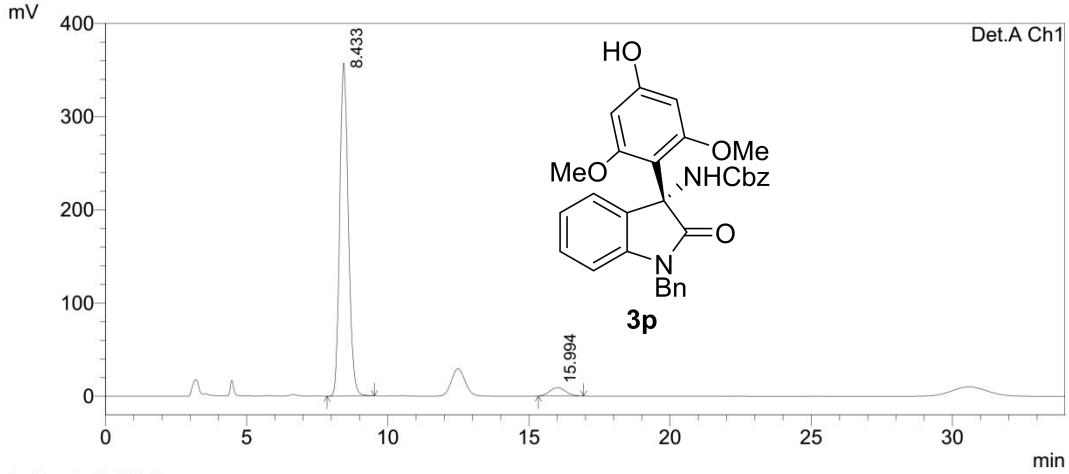


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.451	6402705	299366	49.806	65.262
2	16.013	6452615	159348	50.194	34.738
Total		12855320	458715	100.000	100.000

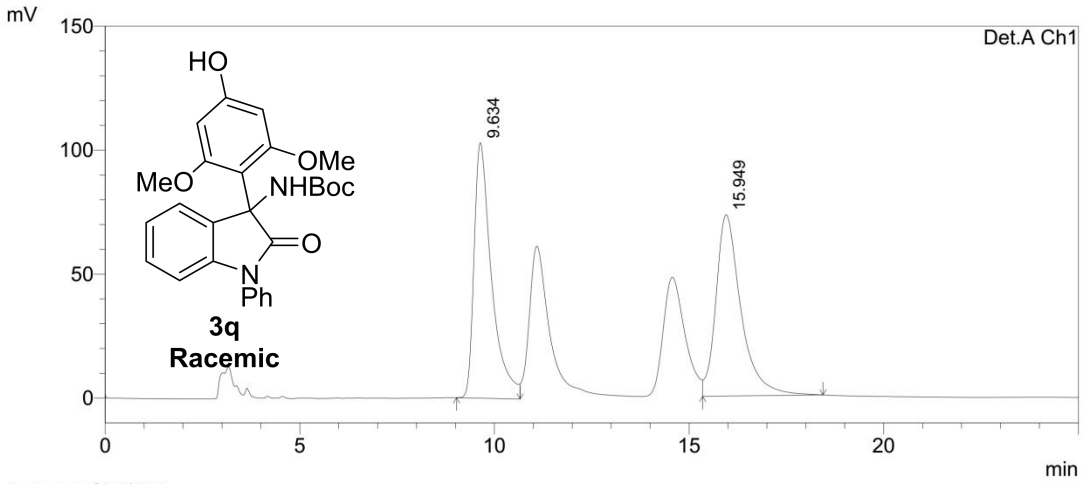


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.433	7571766	357537	95.494	97.516
2	15.994	357323	9106	4.506	2.484
Total		7929089	366644	100.000	100.000

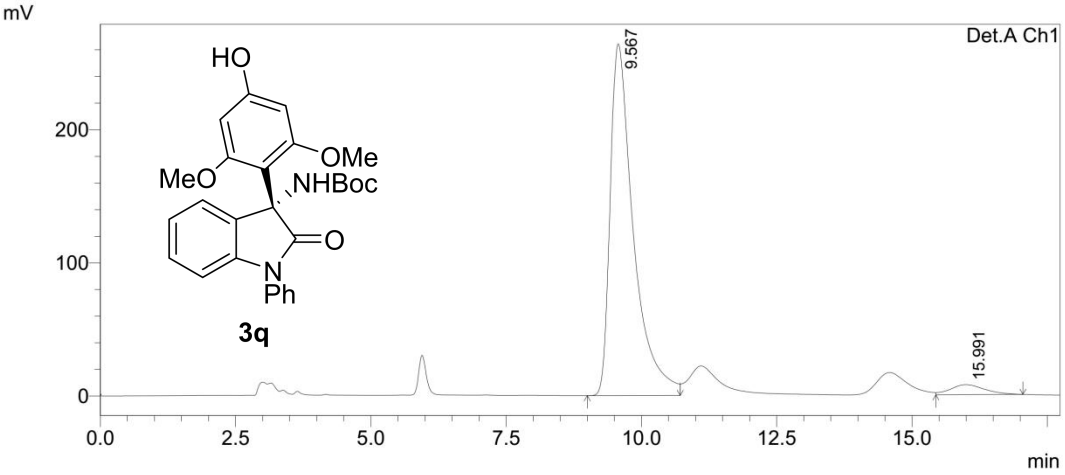


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.634	3224205	102966	49.630	58.469
2	15.949	3272254	73138	50.370	41.531
Total		6496459	176103	100.000	100.000

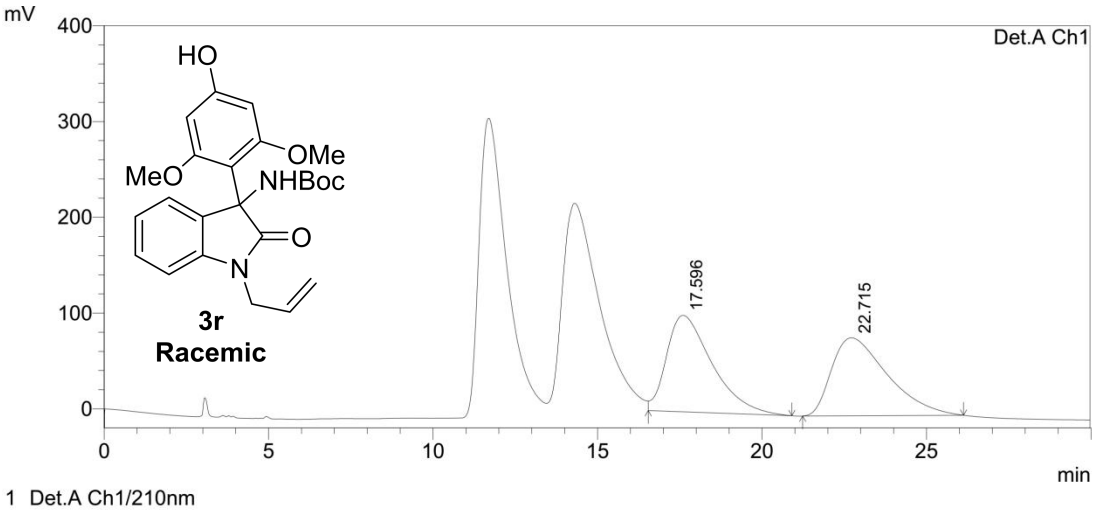


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.567	7891290	264107	95.918	97.199
2	15.991	335850	7611	4.082	2.801
Total		8227141	271718	100.000	100.000

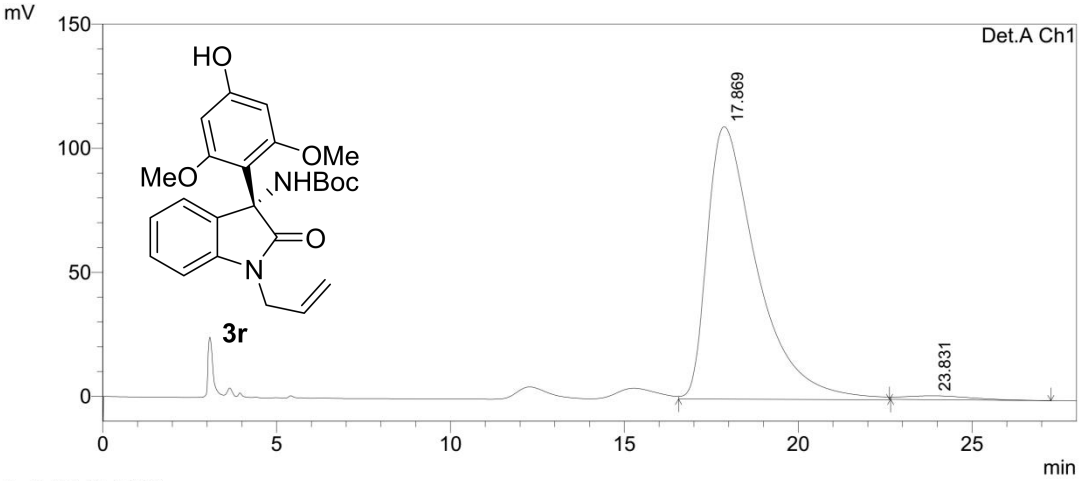


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.596	9694741	100657	50.175	55.276
2	22.715	9627038	81441	49.825	44.724
Total		19321779	182099	100.000	100.000

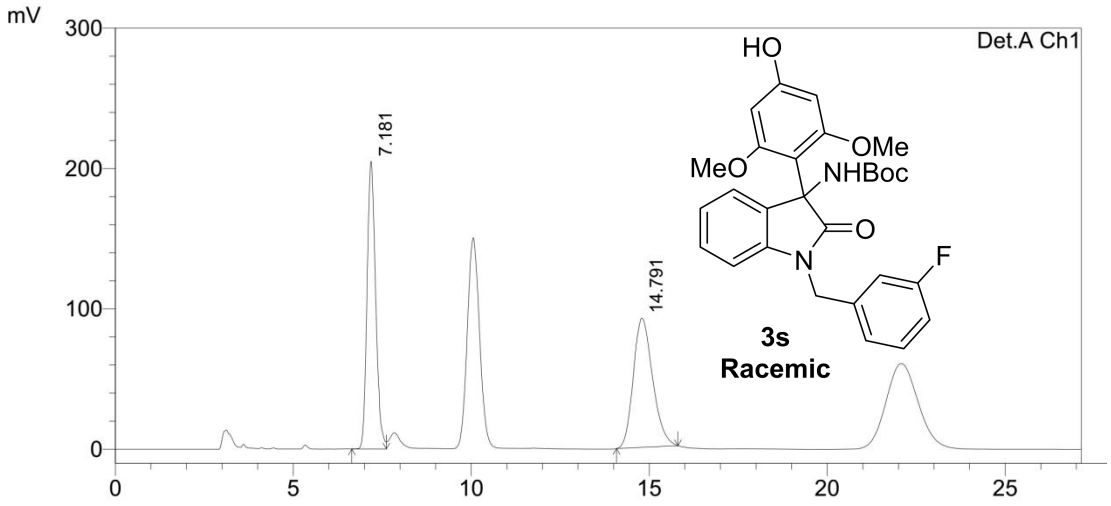


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.869	10986818	109777	98.096	98.596
2	23.831	213292	1564	1.904	1.404
Total		11200109	111341	100.000	100.000

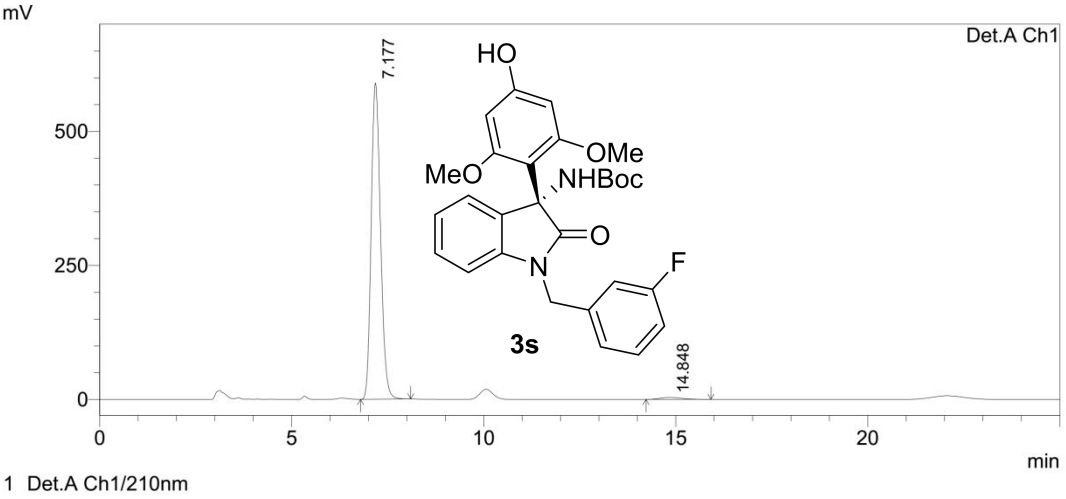


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.181	3429992	204947	49.650	68.990
2	14.791	3478408	92123	50.350	31.010
Total		6908400	297070	100.000	100.000

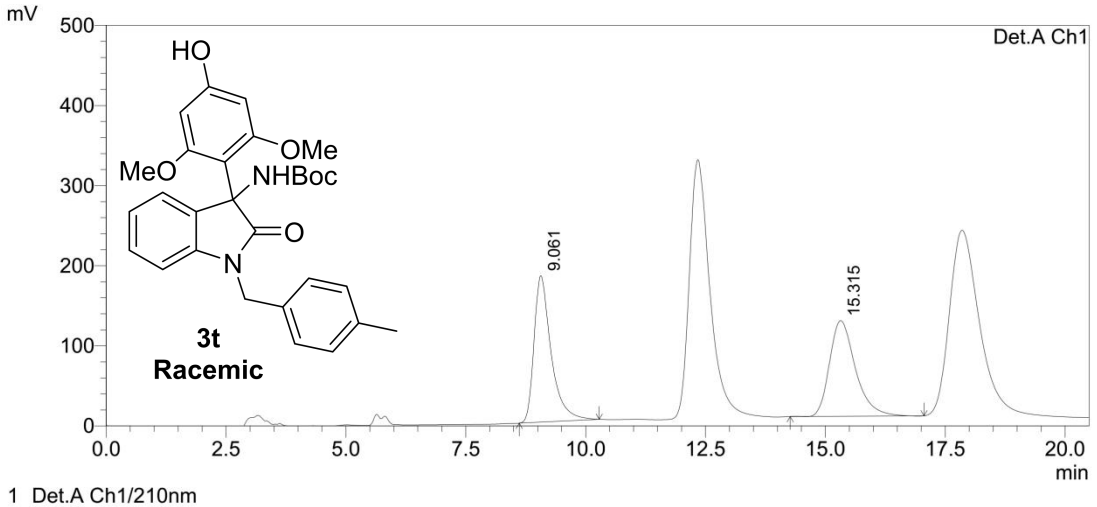


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.177	9923557	589825	98.397	99.329
2	14.848	161663	3985	1.603	0.671
Total		10085219	593810	100.000	100.000

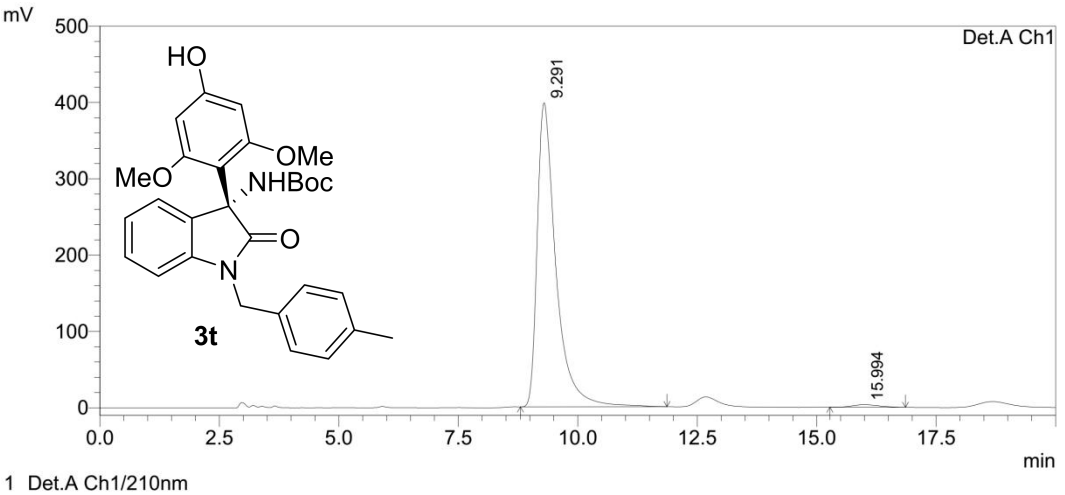


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.061	4537680	182801	50.411	60.513
2	15.315	4463726	119286	49.589	39.487
Total		9001406	302087	100.000	100.000

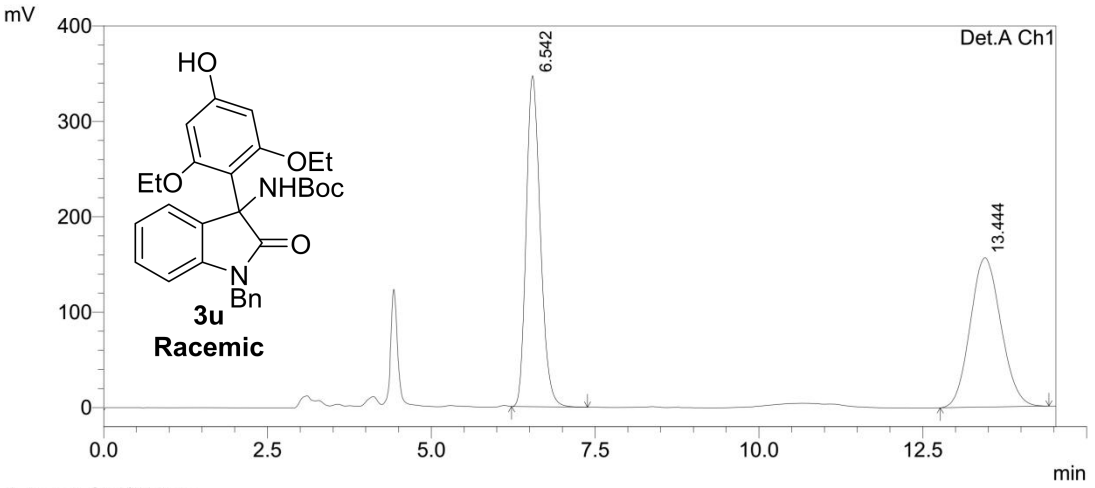


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.291	10844558	398302	98.819	99.148
2	15.994	129597	3423	1.181	0.852
Total		10974156	401725	100.000	100.000

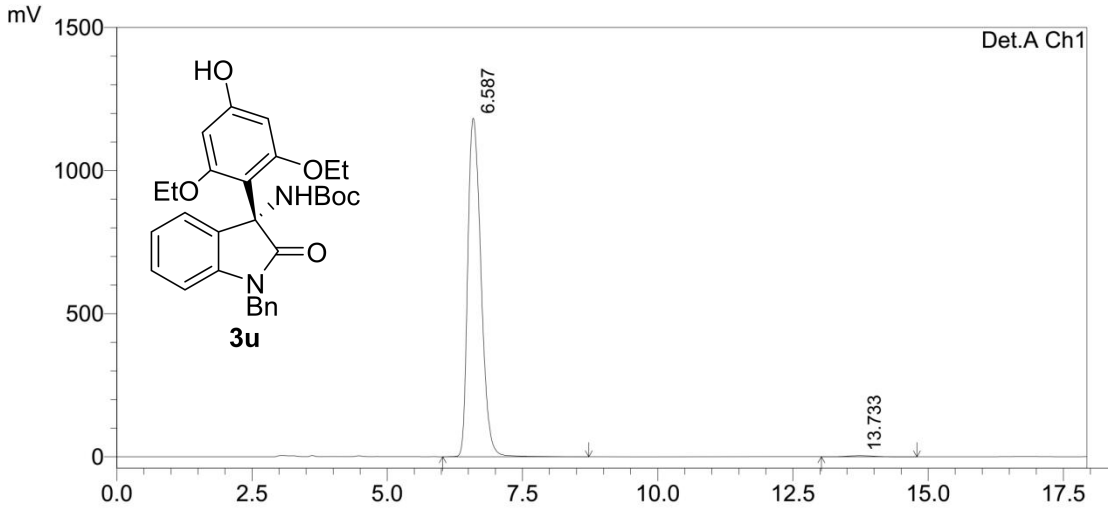


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.542	5219493	346672	50.523	68.892
2	13.444	5111346	156535	49.477	31.108
Total		10330839	503208	100.000	100.000

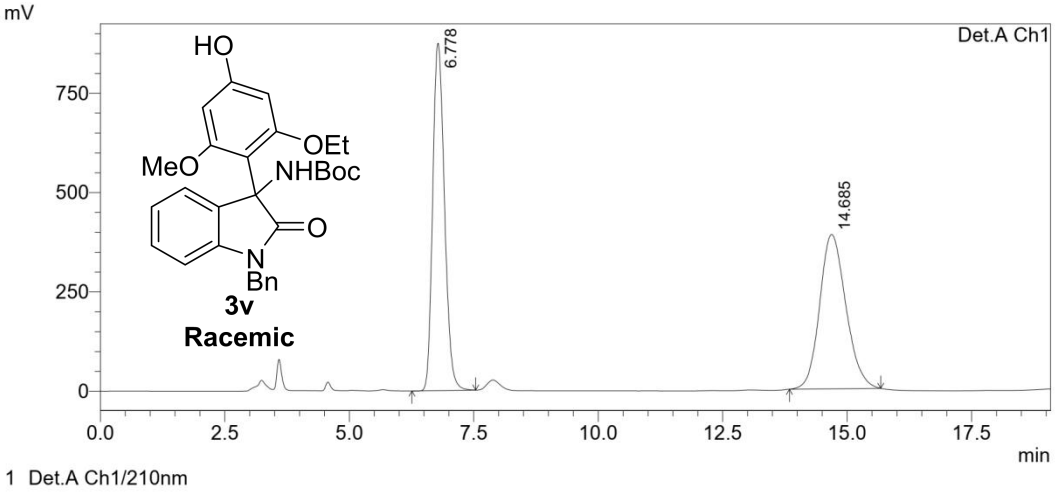


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.587	20118688	1183357	99.364	99.693
2	13.733	128685	3647	0.636	0.307
Total		20247373	1187004	100.000	100.000

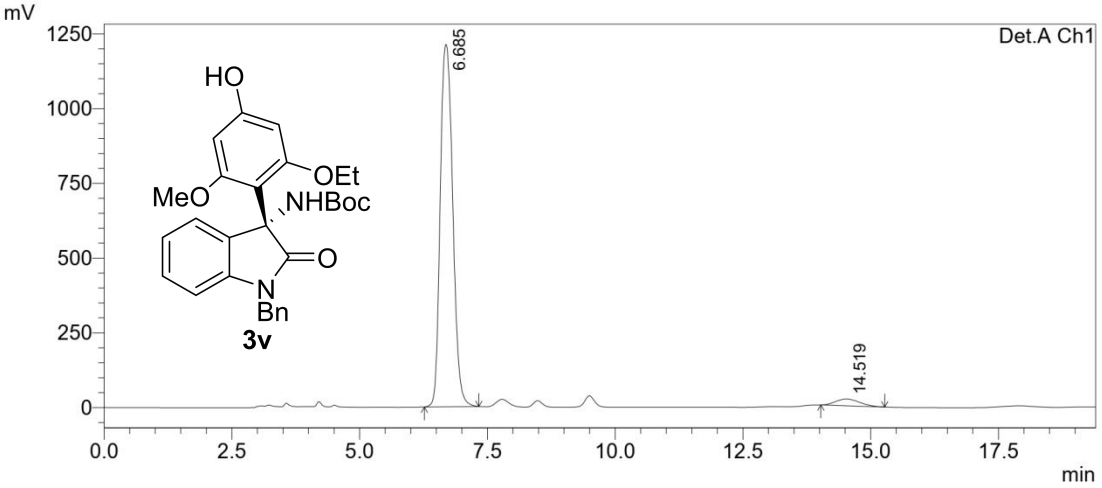


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.778	14409719	873199	50.320	69.213
2	14.685	14226343	388404	49.680	30.787
Total		28636063	1261602	100.000	100.000

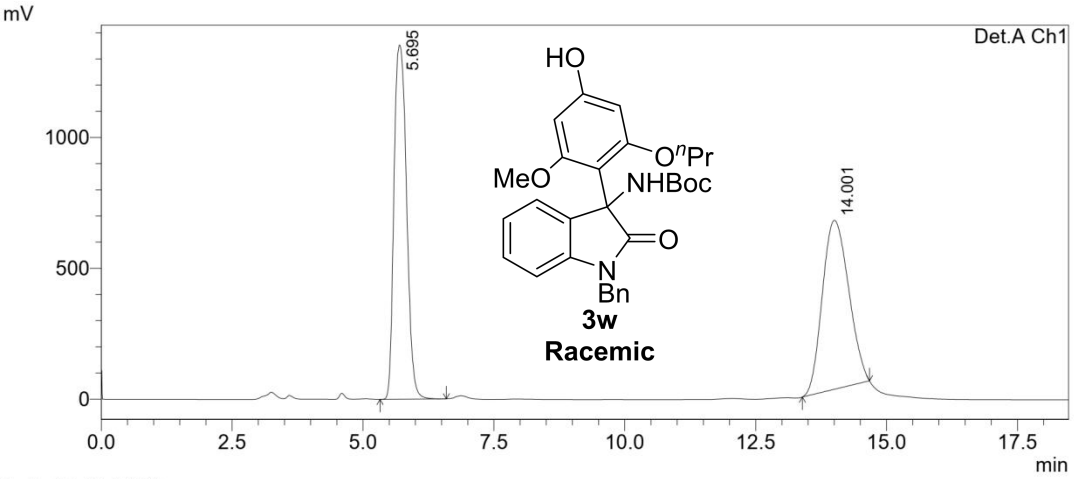


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.685	20610211	1212068	96.523	98.168
2	14.519	742516	22615	3.477	1.832
Total		21352727	1234683	100.000	100.000

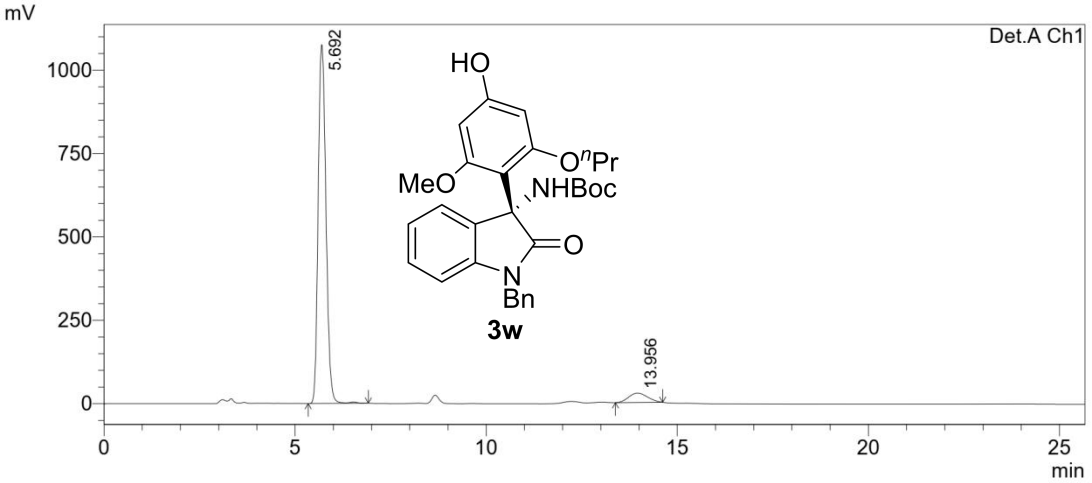


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.695	22608081	1351783	50.087	67.689
2	14.001	22529330	645258	49.913	32.311
Total		45137411	1997041	100.000	100.000

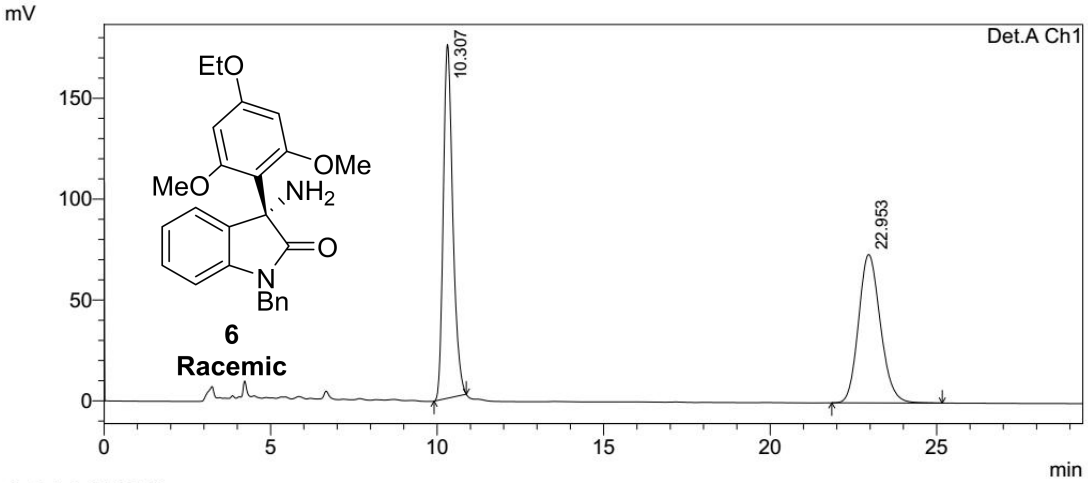


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.692	15244097	1076038	94.000	97.442
2	13.956	973027	28243	6.000	2.558
Total		16217124	1104281	100.000	100.000

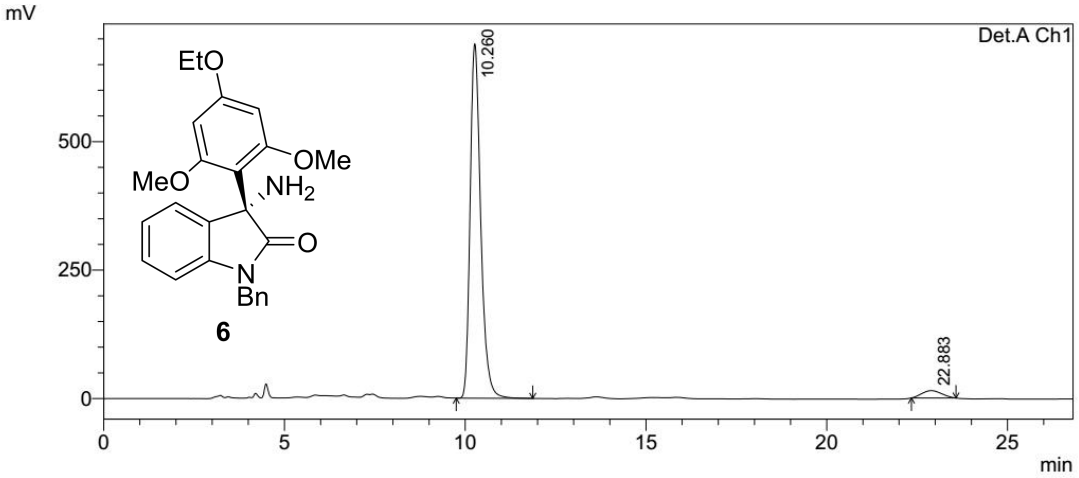


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.307	3482038	175328	50.937	70.445
2	22.953	3353975	73560	49.063	29.555
Total		6836013	248887	100.000	100.000



1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.260	14000467	689763	96.232	97.971
2	22.883	548211	14287	3.768	2.029
Total		14548679	704050	100.000	100.000