Dearomatizative Aminoetherification and Diamination of Indoles Enabled by Photochemical Nitrene Transfer Reactions

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1 General

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware under an argon atmosphere using standard Schlenk techniques. All other solvents and reagents were purified according to standard procedures or were used as received from chemical suppliers. The starting materials were synthesized according to literature procedures. The light employed in this work was bought from GeAo Chemical: model H106062, 40 W blue LEDs, λ = 450 ~ 460 nm. All photo-reactions were performed in borosilicate glass irradiation vessel at a distance of ~3 cm from light source. All reactions involving heating are carried out in an oil bath.

Chromatography: Analytical thin layer chromatography was performed using Qingdao Puke Parting Materials Co. silica gel plates (Silica gel 60 F254). Visualization was by ultraviolet fluorescence (λ = 254 nm) and/or staining with phosphomolybdic acid or potassium permanganate($KMnO_4$). Flash column chromatography was performed using 200-300 mesh silica gel.

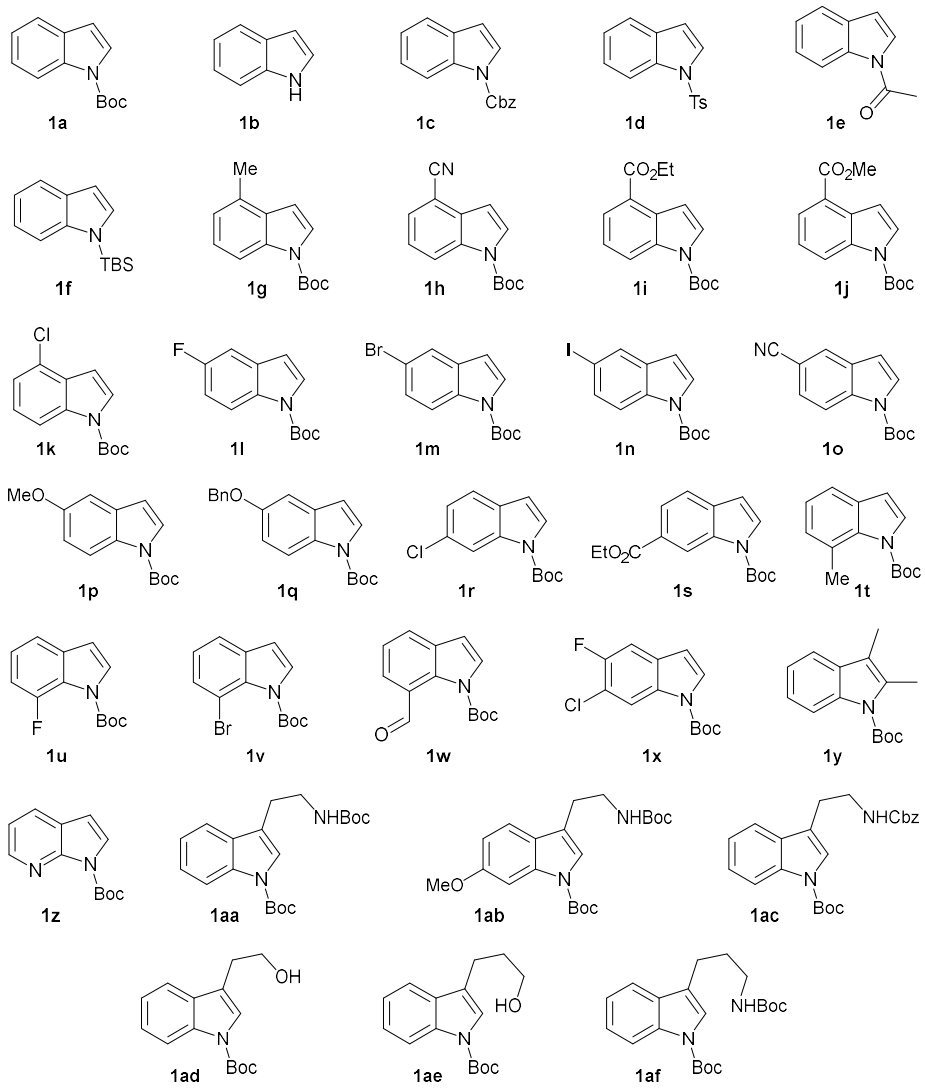
^{1}H-NMR, **^{13}C-NMR**, **and ^{19}F-NMR** spectra were recorded on a JEOL JNM ECZ400R and ECZ600R at 300 K. Spectra were calibrated relative to solvent's residual proton and carbon chemical shift: $CDCl_3$ (δ = 7.26 for ^{1}H-NMR and δ = 77.0 for ^{13}C-NMR), CD_3CN (δ = 1.94 for ^{1}H-NMR and δ = 1.3 and 118.3 for ^{13}C-NMR). Data are reported as follows: chemical shift δ/ppm, integration (^{1}H only), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd= doublet of doublets, m = multiple or combinations thereof; ^{13}C signals are singlets unless otherwise stated), coupling constants *J* in Hz, assignment.

High Resolution Mass Spectrometry (HRMS): All were recorded on Thermo Fisher Scientific LTQ Orbitrap XL using an atmospheric-pressure chemical ionization ($APCI^+$) or positive electrospray ionization (ESI^+). Measured values are reported to 4 decimal places of the calculated value. The calculated values are based on the most abundant isotope.

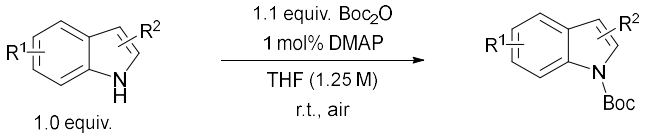
X-ray Crystallography were collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation. The data were collectedand processed using CrysAlisPro.

2 Preparation and Spectral Data of Starting Materials

The **1a-1ab**, [1] **1ac-1af** [2] are prepare by literature reports.

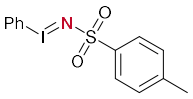


General procedure to synthesize Boc-indole derivatives

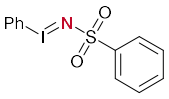


To a solution of indole or its derivatives (5.0 mmol) in THF (4 mL) was added Boc_2O (1.2 g, 5.5 mmol, 1.1 equiv) and DMAP (6.1 mg, 1 mol%). The reaction was stirred at room temperature and monitored by TLC until the reaction was finished, the crude mixture was concentrated under reduced pressure and purified by flash column chromatography (PE :EA = 100:1 to 3:1) to afford product.

The iminoiodinane **2a** - **2l** are prepared by the literature reports.[3]



2a



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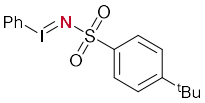
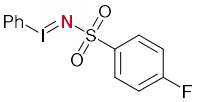
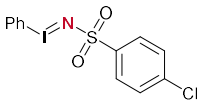


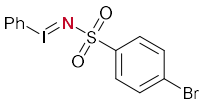
2c



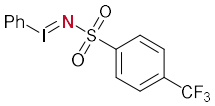
2d



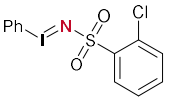
2e



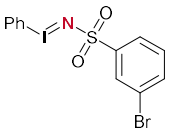
2f



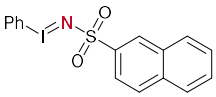
2g



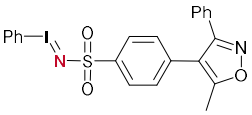
2h



2i

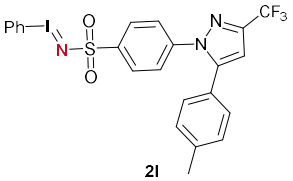


2j



2k

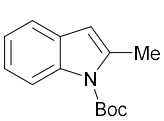
From Valdecoxib



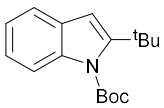
2l

From Celecoxib

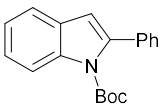
Unsuccessful substrate



N. R.



N. D.



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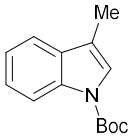

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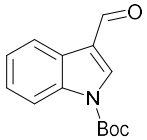

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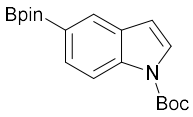

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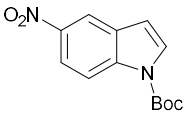
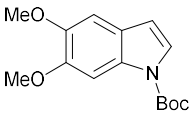


Trace



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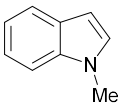

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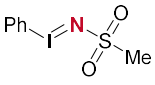

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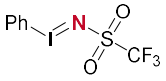

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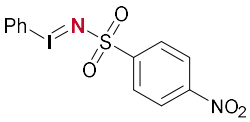

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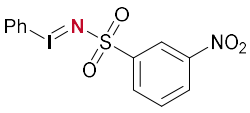
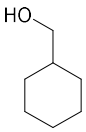


N. R.



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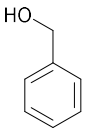


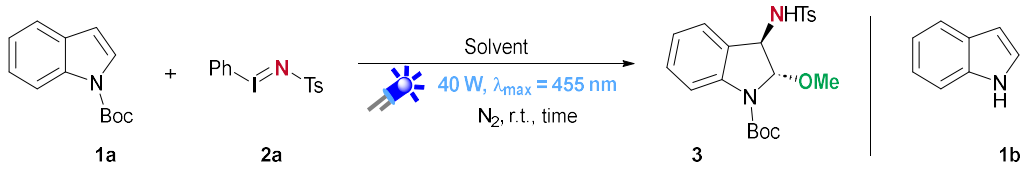
N. D.

N. D. = No target compounds were detected, but the raw materials were consumed.

N. R. = No reaction, Boc-indole derivatives barely reactive, large surplus, iminoiodinane depleted

3 .The Condition Optimization[a,f]

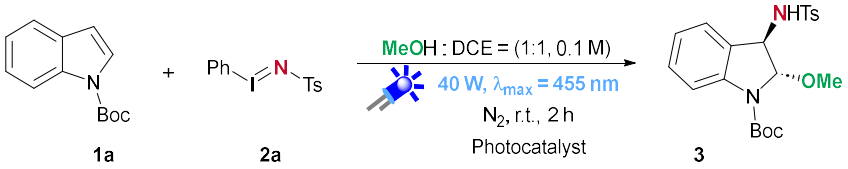
Table 1. The condition optimization of the reaction conditions



1a 2a 3 1b

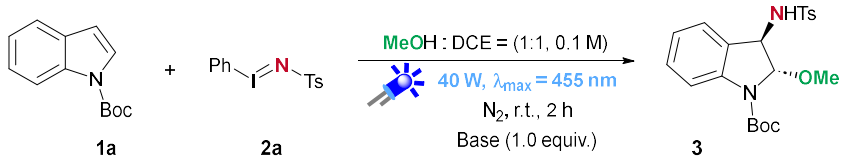
Entry	Solvent (2 mL)	Molar of 1a	Molar of 2a	Time(h)	Yield[b,f]
1[a]	MeOH	0.2 mmol	0.6 mmol	4	59
2	MeOH	0.2 mmol	0.6 mmol	2	58
3[c]	MeOH	0.2 mmol	0.6 mmol	2	N. R.
4[d]	MeOH	0.2 mmol	0.6 mmol	2	trace
5[e]	MeOH	0.2 mmol	0.6 mmol	2	N. D.
6	DCM	0.2 mmol	0.6 mmol	2	N. D.
7	THF	0.2 mmol	0.6 mmol	2	N. D.
8	MeOH	0.2 mmol	0.8 mmol	2	60
9	MeOH	0.2 mmol	1.0 mmol	2	62
10	CH_3CN : MeOH=(1:1)	0.2 mmol	0.6 mmol	2	57
11	DCE : MeOH=(1:1)	0.2 mmol	0.6 mmol	2	68
12	DMF : MeOH=(1:1)	0.2 mmol	0.6 mmol	2	15
13	THF : MeOH=(1:1)	0.2 mmol	0.6 mmol	2	15
14	EtOAc : MeOH=(1:1)	0.2 mmol	0.6 mmol	2	62
15	1,4-Dioxane : MeOH=(1:1)	0.2 mmol	0.6 mmol	2	52
16	DCE(2 mL): MeOH(5 eq)	0.2 mmol	0.6 mmol	2	33
17	DCE(2 mL): MeOH(10 eq)	0.2 mmol	0.6 mmol	2	49

Standard condition: [a]**1a** (0.2 mmol), **2a** (0.6 mmol), $NaHCO_3$, (0.2 mmol) in DCE : MeOH (1 : 1, 2 mL), with 40 W Blue LEDs irradiation at rt for 2 h under N_2 atmosphere. [b] isolated yield. [c] in dark.[d] under air atmosphere.[e] Indole **1b** as substrate. [f] All products exhibit a d.r. ratio exceeding 20:1.



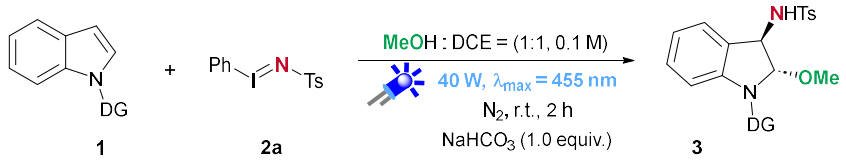
Entry	Photocatalyst (1 mol %)	Molar of 1a	Molar of 2a	Yield[a,b,c]
18	4CzIPN	0.2 mmol	0.6 mmol	55
19	$Ir(ppy)_3$	0.2 mmol	0.6 mmol	29
20	$Ir[(dtbbpy)(ppy_2)PF_6$	0.2 mmol	0.6 mmol	54
21	$Ir[(dF(CF_3)ppy)]_2(dtbbpy)(PF_6)$	0.2 mmol	0.6 mmol	49
22	$Ru(bpy)_3Cl_2$ $6H_2O$	0.2 mmol	0.6 mmol	65
23	$Ru(bpz)_3(PF_6)_2$	0.2 mmol	0.6 mmol	55

Standard condition: [a]**1a** (0.2 mmol), **2a** (0.6 mmol), $NaHCO_3$, (0.2 mmol) in DCE :MeOH (1: 1, 2 mL), with 40 W Blue LEDs irradiation at rt for 2 h under N_2 atmosphere. [b] isolated yield. [c] All products exhibit a d.r. ratio exceeding 20:1.



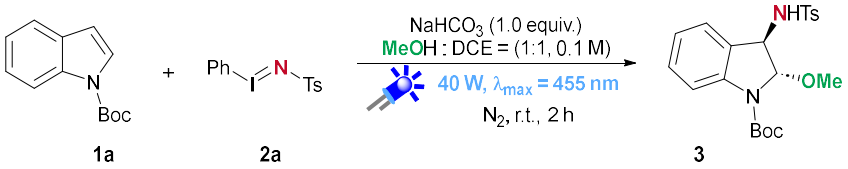
Entry	Molar of 1a	Molar of 2a	Base(1.0 equiv)	Yield[a,b,d]
24	0.2 mmol	0.6 mmol	$NaHCO_3$	72
25	0.2 mmol	0.6 mmol	KH_2PO_4	43
26	0.2 mmol	0.6 mmol	NaH_2PO_4	66
27	0.2 mmol	0.6 mmol	Na_2CO_3	66
28	0.2 mmol	0.6 mmol	DIPEA	Trace
29	0.2 mmol	0.6 mmol	DABCO	38
30	0.2 mmol	0.6 mmol	DMAP	37
31[c]	0.2 mmol	0.6 mmol	$NaHCO_3$	84

Standard condition: [a]**1a** (0.2 mmol), **2a** (0.6 mmol), $NaHCO_3$, (0.2 mmol) in DCE :MeOH (1: 1, 2 mL), with 40 W Blue LEDs irradiation at rt for 2 h under N_2 atmosphere. [b] isolated yield. [c]**1a** (0.2 mmol), **2a** (0.3 mmol), $NaHCO_3$, (0.2 mmol) in DCE :MeOH (1: 1, 2 mL), with 40 W Blue LEDs irradiation at r.t. for 1 h under N_2 atmosphere, add **2a** (0.3 mmol) under N_2 atmosphere again, stirred for 1 h. [d] All products exhibit a d.r. ratio exceeding 20:1.



Entry	Molar of 1	Molar of 2a	Direct group	Yield[a,b,c]
32	0.2 mmol	0.6 mmol	-H	N. D.
33	0.2 mmol	0.6 mmol	-Cbz	74
34	0.2 mmol	0.6 mmol	-Ts	33[d]
35	0.2 mmol	0.6 mmol	-Me	N. D.
36	0.2 mmol	0.6 mmol	-TBS	N. D.

Standard condition: [a]**1a** (0.2 mmol), **2a** (0.6 mmol), $NaHCO_3$, (0.2 mmol) in DCE :MeOH (1: 1, 2 mL), with 40 W Blue LEDs irradiation at rt for 2 h under N_2 atmosphere. [b] isolated yield. [c]**1a** (0.2 mmol), **2a** (0.3 mmol), $NaHCO_3$, (0.2 mmol) in DCE : MeOH (1 : 1, 2 mL), with 40 W Blue LEDs irradiation at r.t. for 1 h under N_2 atmosphere, add **2a** (0.3 mmol) under N_2 atmosphere again, stirred for 1 h. [d] d.r = 5 :1.



General procedure (1): To a 10 mL Schlenk flask equipped with a magnetic stir bar was added **1a** (43.4 mg, 0.2 mmol, 1.0 equiv.), **2a** (111.6 mg, 0.3 mmol, 1.5 equiv.), DCE : MeOH (1 : 1, 2 mL), under an N_2 atmosphere. After the solution was stirred at a distance of ~3 cm from a 40 W blue LED at room temperature for 1 h. Then **2a** (111.6 mg, 0.3 mmol, 1.5 equiv.) was added again under an N_2 atmosphere and stirred at same condition for 1 h. (***Note: for some substrate, 2a (0.9 mmol, 4.5 equiv.) was added 3 times in 3 h under an N_2 atmosphere***.) After the reaction finished, the solvent was removed by vacuum and the crude product was purified by flash chromatography on silica gel silica: 200~300; eluant: petroleum ether/EtOAc (10:1 to 3:1) to provide pure product **3** and as a white solid in 84% yield (67 mg).

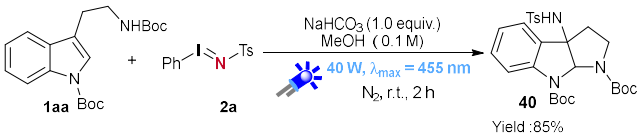
For $CDCl_3$: ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.82 (d, *J* = 8.3 Hz, 2H), 7.71 (s, 1H--NH), 7.38 (d, *J* = 8.0 Hz, 2H), 7.29 - 7.23 (m, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.3 Hz, 1H), 5.33 - 5.26 (m, 1H), 4.73 (d, *J* = 7.4 Hz, 1H), 4.43 (d, *J* = 7.4 Hz, 1H), 3.44 (s, 3H), 2.48 (s, 3H), 1.56 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.0, 143.9, 142.1, 137.4, 130.3, 129.9, 127.2, 125.3, 123.3, 116.1, 95.2, 82.1, 59.0, 56.5, 28.2, 21.6.

For CD_3CN : ^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.79 (d, *J* = 8.3 Hz, 2H), 7.64 (s, 1H--NH), 7.45 (d, *J* = 7.9 Hz, 2H), 7.32 - 7.27 (m, 1H), 7.00 - 6.94 (m, 2H), 6.05 (d, *J* = 8.4 Hz, 1H), 4.98 (s, 1H), 4.39 (d, *J* = 8.4 Hz, 1H), 3.25 (s, 3H), 2.46 (s, 3H), 1.50 (s, 9H).

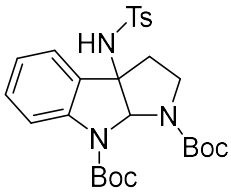
^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 153.0, 145.1, 143.3, 139.2, 131.02, 130.8, 129.1, 128.0, 126.9, 124.2, 116.7, 95.3, 82.6, 60.1, 56.7, 28.4, 21.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{26}N_2NaO_5S^+$: 441.1455; Found: 441.1461.



General procedure (2): To a 10-mL Schlenk tube equipped with a magnetic stir bar was added **1aa** (0.2 mmol, 1.0 equiv.), **2a** (0.6 mmol, 3.0 equiv., ***Note : 2a was added 2 times in 2 h***), $NaHCO_3$ (1.0 equiv.), MeOH (2 mL), (***Note: other similar substrates use DCE : MeOH = 1:1, 0.1 M as solvent***) under an N_2 atmosphere. After the solution was stirred at ~3 cm from a 40 W blue LED at room temperature for 2 h. The solvent was removed by vacuum and the crude product was purified by flash chromatography on silica gel silica: 200~300; eluant: petroleum ether/EtOAc (10:1 to 3:1) to provide pure product **40** and as a white solid in 85% yield (90 mg).

Di-tert-butyl 3a-((4-methylphenyl)sulfonamido)-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (40)



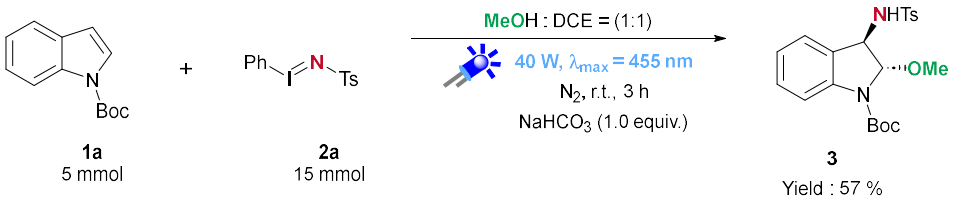
H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.57 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.78 (d, *J* = 7.5 Hz, 1H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.44 (s, 1H), 5.66 (d, *J* = 2.8 Hz, 1H), 3.73 (dd, *J* = 11.6, 7.6 Hz, 1H), 2.68 - 2.62 (m, 1H), 2.35 (s, 3H), 2.34 - 2.29 (m, 1H), 2.21 - 2.16 (m, 1H), 1.58 (s, 9H), 1.46 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 153.6, 152.2, 143.8, 142.9, 138.6, 129.8, 129.3, 128.5, 126.9, 123.9, 123.0, 116.9, 81.5, 80.2, 70.7, 60.4, 44.3, 28.3, 28.3, 21.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{36}N_3O_6S^+$: 530.2319; Found: 530.2317.

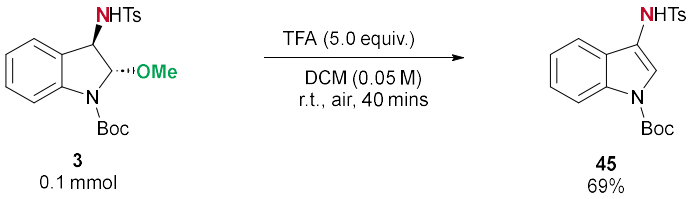
4. Synthetic applications

a) Scale up reaction



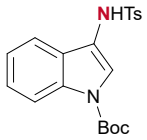
To a 25 mL two-necked round-bottomed flask equipped with a magnetic stir bar was added **1a** (5.0 mmol, 1.0 equiv.), **2a** (15 mmol, 3.0 equiv., added 3 times in 3 h), $NaHCO_3$ (1.0 equiv.), DCE : MeOH (1 : 1, 20 mL), under an N_2 atmosphere. After the solution was stirred at ~3 cm from a 40 W blue LED at room temperature for 3 h. After the reaction finished, the solvent was removed by vacuum and the crude product was purified by flash chromatography on silica gel silica: 200~300; eluant: petroleum ether/EtOAc (10:1 to 5:1) to provide pure product **3** and as a white solid in 57% yield (1.19 g).

b) Aromatization



In a 10-mL Schlenk tube fitted with a magnetic stir bar, compound **3** (0.1 mmol,) and DCM (2 mL) were introduced under an air atmosphere. Trifluoroacetic acid (TFA, 0.5 mmol) was then slowly added to the reaction mixture. Upon reaction termination, saturated $NaHCO_3$ solution was added to quench the reaction, followed by extraction with EtOAc in three portions. The solvent was subsequently removed under vacuum, and the residue was dried over Na_2SO_4. The crude product was purified via flash chromatography on silica gel (particle size 200-300 mesh) using a gradient elution with petroleum ether/EA (from 10:1 to 3:1) to yield the pure product **45** with a 69% yield (27 mg).

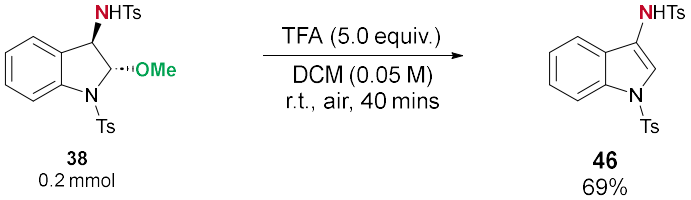
Tert-butyl 3-((4-methylphenyl)sulfonamido)-1H-indole-1-carboxylate (45)



H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.07 (d, *J* = 9.3 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.51 (s, 1H), 7.27 (dd, *J* = 17.3, 8.6 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 2H), 2.35 (s, 3H), 1.64 (s, 9H).

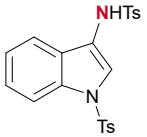
^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 149.4, 143.9, 136.2, 133.8, 129.6, 127.3, 125.9, 125.1, 122.8, 119.5, 117.6, 117.1, 115.2, 84.1, 28.1, 21.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{26}N_2NaO_5S^+$: 441.1455; Found: 441.1461.



In a 10-mL Schlenk tube fitted with a magnetic stir bar, compound **38** (0.2 mmol,) and DCM (2 mL) were introduced under an air atmosphere. Trifluoroacetic acid (TFA, 0.5 mmol) was then slowly added to the reaction mixture. Upon reaction termination, saturated $NaHCO_3$ solution was added to quench the reaction, followed by extraction with EtOAc in three portions. The solvent was subsequently removed under vacuum, and the residue was dried over Na_2SO_4. The crude product was purified via flash chromatography on silica gel (particle size 200-300 mesh) using a gradient elution with petroleum ether/EA (from 10:1 to 3:1) to yield the pure product **46** with a 69% yield (61 mg).

4-methyl-N-(1-tosyl-1H-indol-3-yl)benzenesulfonamide (46)

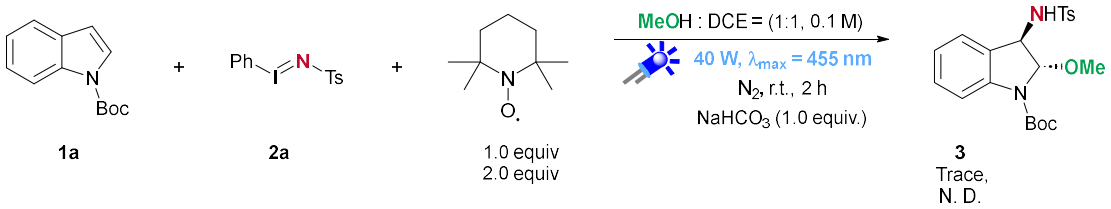


H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.92 (d, *J* = 8.4 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 4H), 7.47 (s, 1H), 7.40 - 7.34 (m, 2H), 7.29 - 7.23 (m, 1H), 7.19 - 7.09 (m, 5H), 2.33 (d, *J* = 5.0 Hz, 6H).

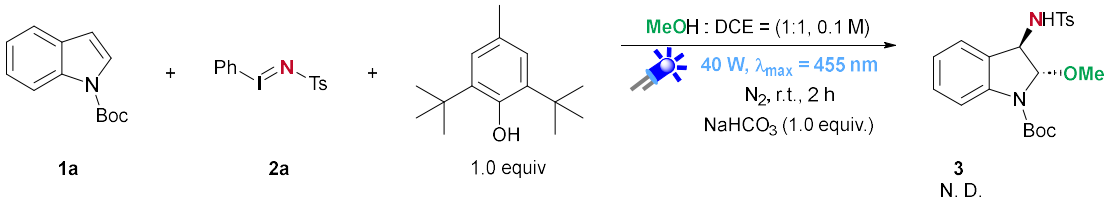
^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 145.0, 144.1, 135.5, 134.7, 133.7, 129.8, 129.6, 127.3, 126.8, 126.1, 125.5, 123.6, 119.4, 118.4, 118.2, 113.8, 21.5, 21.5.

5. Mechanism studies

5.1 Studies on the participation of unpaired electrons [2b, 3]

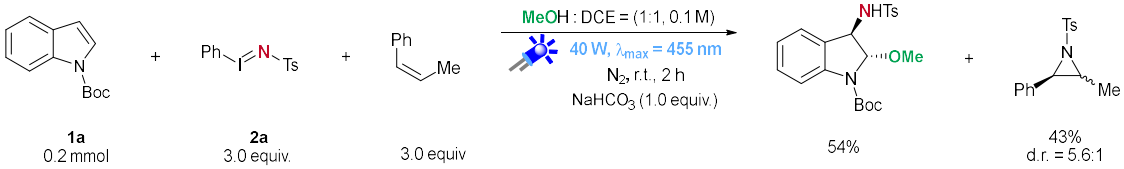


To a 10 mL Schlenk flask equipped with a magnetic stir bar was added **1a** (43.4 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), TEMPO (0.2 mmol or 0.4 mmol) DCE : MeOH (1 : 1, 2 mL), under an N_2 atmosphere. After the solution was stirred at a distance of ~3 cm from a 40 W blue LED at room temperature for 2 h. Product **3** was not detected by TLC.



To a 10 mL Schlenk flask equipped with a magnetic stir bar was added **1a** (43.4 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), BHT (0.2 mmol, 1.0 equiv.) DCE : MeOH (1 : 1, 2 mL), under an N_2 atmosphere. After the solution was stirred at a distance of ~3 cm from a 40 W blue LED at room temperature for 2 h. Product **3** was not detected by TLC.

5.2 Photochemical reaction with the addition of Z-β-methyl styrene



To a 10 mL Schlenk flask equipped with a magnetic stir bar was added **1a** (43.4 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), ***Z*-*β*-methyl styrene** (0.6 mmol, 3.0 equiv.) DCE : MeOH (1 : 1, 2 mL), under an N_2 atmosphere. After the solution was stirred at a distance of ~3 cm from a 40 W blue LED at room temperature for 2 h. The desired aziridination product was isolated

and d.r. = 5.6:1 was detected by crude ^{1}H NMR. Aromatic regions cannot be accurately identified due to multiple components.

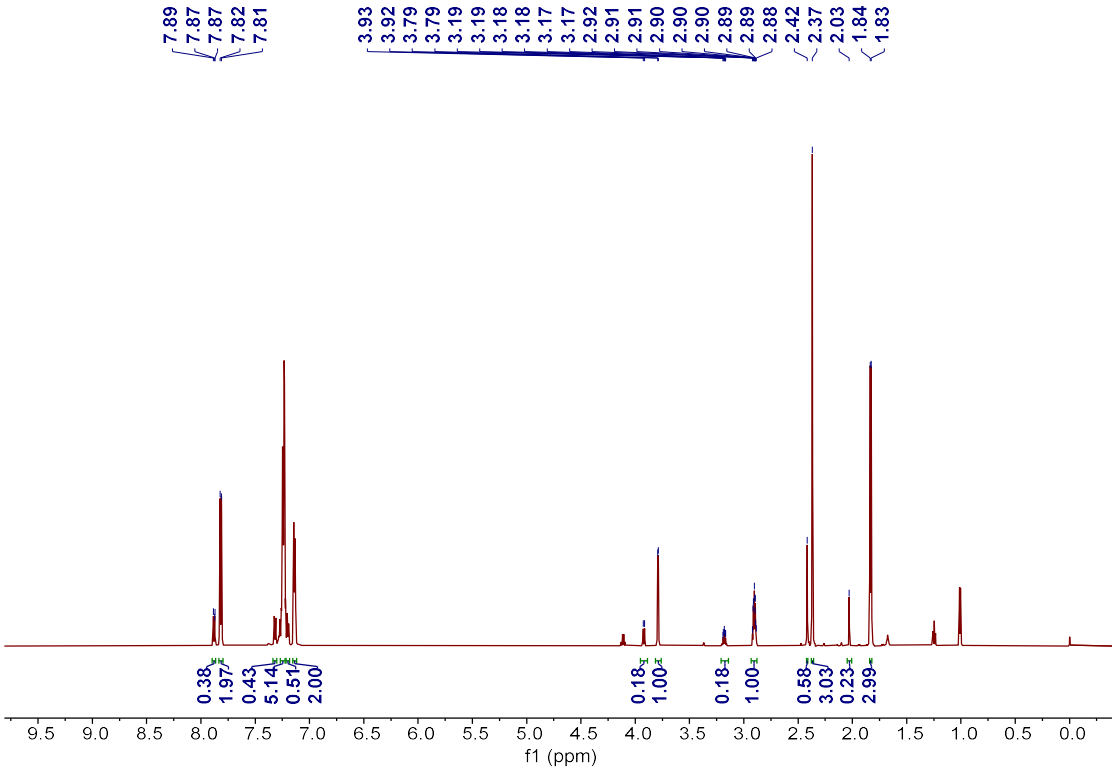
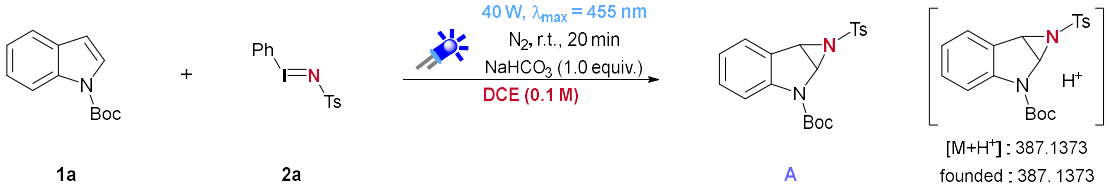


Figure S1. Crude ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Aziridination Product

5.3 Intermediate Detection Experiment

In a 10 mL Schlenk flask, complete with a magnetic stir bar, **1a** (43.4 mg, 0.2 mmol, 1.0 equiv.) and **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.) were introduced. The reaction was carried out solely in a DCE: (2 mL) or in MeOH (2 mL), under a nitrogen atmosphere. After the solution was stirred at a distance of approximately 3 cm from a 40 W blue LED at room temperature for 20 minutes, reaction mixture was immediately subjected to HRMS analysis.



1a 2a A

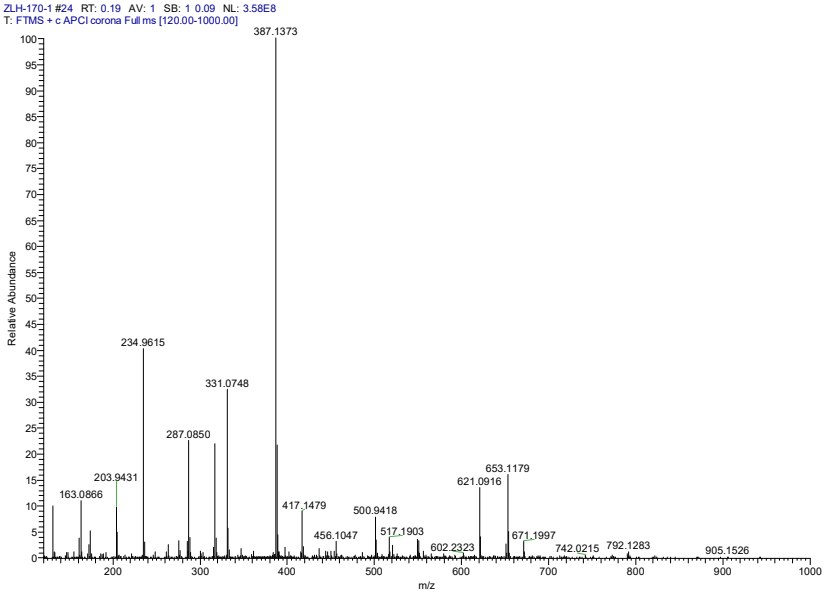
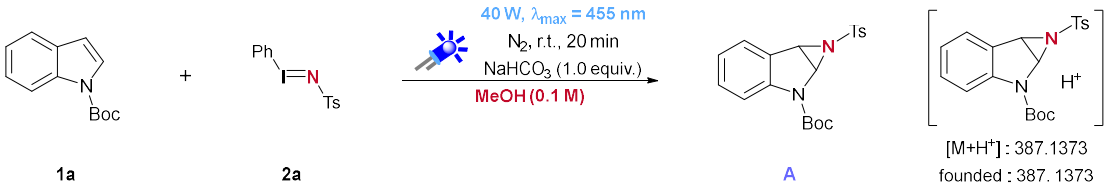


Figure S2. HRMS in DCE (0.1 M)



1a 2a A

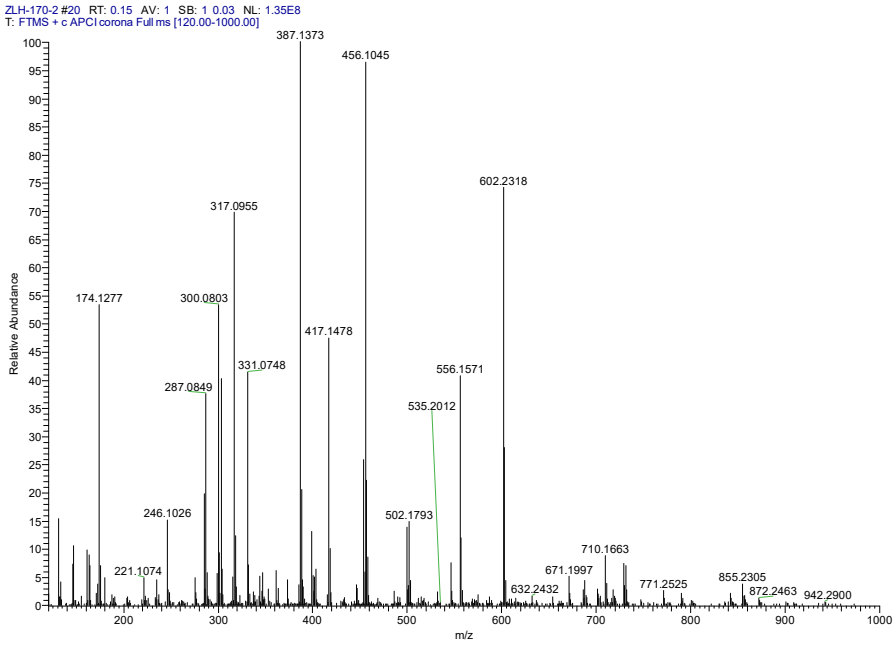
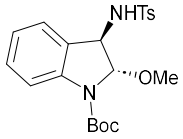


Figure S3. HRMS in MeOH (0.1 M)

6. Spectral Data of Boronated Products

Tert-butyl-2-methoxy-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (3)



According to ***GP-1*** with **1a** (43.4 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **3** and as a white solid in 84% yield (70 mg).

For $CDCl_3$: ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.82 (d, *J* = 8.3 Hz, 2H), 7.71 (s, 1H--NH), 7.38 (d, *J* = 8.0 Hz, 2H), 7.29 - 7.23 (m, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.3 Hz, 1H), 5.33 - 5.26 (m, 1H), 4.73 (d, *J* = 7.4 Hz, 1H), 4.43 (d, *J* = 7.4 Hz, 1H), 3.44 (s, 3H), 2.48 (s, 3H), 1.56 (s, 9H).

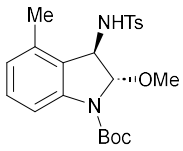
^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.0, 143.9, 142.1, 137.4, 130.3, 129.9, 127.2, 125.3, 123.3, 116.1, 95.2, 82.1, 59.0, 56.5, 28.2, 21.6.

For CD_3CN : ^{1}H NMR (600 MHz, CD_3CN, 300 K): δ (ppm) = 7.79 (d, *J* = 8.3 Hz, 2H), 7.64 (s, 1H--NH), 7.45 (d, *J* = 7.9 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.00 - 6.94 (m, 2H), 6.05 (d, *J* = 8.4 Hz, 1H), 4.98 (s, 1H), 4.39 (d, *J* = 8.4 Hz, 1H), 3.25 (s, 3H), 2.46 (s, 3H), 1.50 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 153.0, 145.1, 143.3, 139.2, 131.02, 130.8, 129.1, 128.0, 126.9, 124.2, 116.7, 95.3, 82.6, 60.1, 56.7, 28.4, 21.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{26}N_2NaO_5S^+$: 441.1455; Found: 441.1461.

Tert-butyl-2-methoxy-4-methyl-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (4)



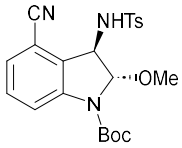
According to ***GP-1*** with **1g** (46.2 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **4** and as a white solid 81% yield (70 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.78 (d, *J* = 7.9 Hz, 2H), 7.56 (s, 1H--NH), 7.35 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.8 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 5.20 (s, 1H), 4.63 (d, *J* = 7.3 Hz, 1H), 4.42 (d, *J* = 7.4 Hz, 1H), 3.40 (s, 3H), 2.45 (s, 3H), 1.91 (s, 3H) 1.53 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) =152.1, 143.8, 142.0, 137.2, 135.7, 130.3, 129.8, 127.3, 125.5, 124.7, 113.6, 94.7, 81.8, 57.9, 56.6, 28.1, 21.5, 17.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{28}N_2NaO_5S^+$: 455.1611; Found: 455.1611.

Tert-butyl-2-methoxy-4-methyl-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (5)



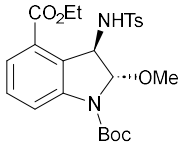
According to ***GP-1*** with **1h** (48.4 mg, 0.2 mmol, 1.0 equiv.), **2a** (334.8 mg, 0.9 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 3 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **5** and as a white solid in 34% yield (30 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.02 (s, 1H--NH), 7.75 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 1H), 5.66 (s, 1H), 4.90 (d, *J* = 6.9 Hz, 1H), 4.51 (d, *J* = 6.5 Hz, 1H), 3.55 (s, 3H), 2.43 (s, 3H), 1.59 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 151.8, 144.2, 136.1, 131.1, 129.8, 127.7, 126.6, 120.77, 115.7, 109.8, 95.5, 83.1, 58.9, 57.1, 28.3, 21.7.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{25}N_3NaO_5S^+$: 466.1407; Found: 466.1403.

1-(tert-butyl) 4-ethyl-2-methoxy-3-((4-methylphenyl)sulfonamido)indoline-1,4-dicarboxylate (6)



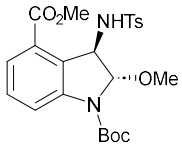
According to ***GP-1*** with **1i** (57.8 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **6** and as a white solid in 57% yield (56 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.98 (s, 1H--NH), 7.49 (d, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 7.8, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 2H), 5.78 (s, 1H), 5.43 (d, *J* = 4.5 Hz, 1H), 4.77 (d, *J* = 4.3 Hz, 1H), 4.26 - 4.14 (m, 2H), 3.49 (s, 3H), 2.37 (s, 3H), 1.58 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.5, 152.22, 144.0, 143.0, 137.2, 130.0, 129.2, 128.0, 127.3, 127.1, 124.5, 120.9, 93.9, 82.2, 61.2, 60.2, 56.5, 28.2, 21.4, 14.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{30}N_2NaO_7S^+$: 513.1666; Found: 513.1666.

Tert-butyl-2-methoxy-4-methyl-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (7)



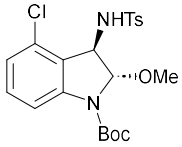
According to ***GP-1*** with **1j** (45 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **7** and as a white solid in 67% yield (64 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.98 (s, 1H--NH), 7.51 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 8.2 Hz, 1H), 7.15 (d, *J* = 8.2 Hz, 2H), 5.69 (s, 1H), 5.36 (s, 1H), 4.80 (d, *J* = 4.6 Hz, 1H), 3.70 (s, 3H), 3.46 (s, 3H), 2.37 (s, 3H), 1.56 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.9, 152.1, 143.8, 143.2, 137.3, 130.1, 129.3, 128.0, 127.1, 124.6, 120.9, 93.9, 82.2, 60.0, 56.4, 52.0, 28.2, 21.4.

HRMS (APCI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{28}N_2NaO_7S^+$: 499.1509; Found: 499.1507.

Tert-butyl-4-chloro-2-methoxy-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (8)



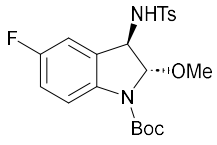
According to ***GP-1*** with **1k** (50.2 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **8** and as a white solid in 55% yield (50 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.78 (d, *J* = 8.0 Hz, 2H), 7.69 (s, 1H--NH), 7.32 (d, *J* = 7.9 Hz, 2H), 7.19 (t, *J* = 8.1 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 5.51 (s, 1H), 4.71 (d, *J* = 5.2 Hz, 1H), 4.38 (d, *J* = 5.2 Hz, 1H), 3.53 (s, 3H), 2.43 (s, 3H), 1.57 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.0, 144.0, 136.3, 131.9, 131.2, 129.8, 127.8, 124.8, 123.3, 114.6, 95.6, 82.6, 58.6, 57.0, 28.3, 28.2, 21.7.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{25}ClN_2NaO_5S^+$: 475.1065; Found: 475.1065.

Tert-butyl-5-fluoro-2-methoxy-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (9)



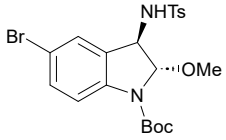
According to ***GP-1*** with **1l** (47 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **9** and as a white solid in 59% yield (51 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.73 (d, *J* = 7.6 Hz, 2H), 7.64 (s, 1H--NH), 7.35 (d, *J* = 7.8 Hz, 2H), 6.93 (t, *J* = 8.9 Hz, 1H), 6.45 (s, 1H), 5.24 (s, 1H), 5.08 (d, *J* = 7.8 Hz, 1H), 4.37 (d, *J* = 8.0 Hz, 1H), 3.38 (s, 3H), 2.46 (s, 3H), 1.52 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 158.8 (d, *J* = 242.6 Hz, C-F), 152.0, 144.1, 138.2, 137.3, 129.9, 129.0, 127.2, 117.0 (d, *J* = 7.96 Hz, C-F), 116.7 (d, *J* = 23.1 Hz, C-F), 112.5 (d, *J* = 24.3 Hz, C-F), 95.5, 82.2, 58.9, 56.4, 28.2, 21.5.

HRMS (APCI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{25}FN_2NaO_5S^+$: 459.1360; Found: 459.1360.

Ttert-butyl-5-bromo-2-methoxy-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (10)



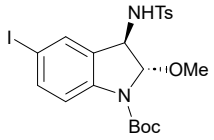
According to ***GP-1*** with **1m** (59 mg, 0.2 mmol, 1.0 equiv.), **2a** (334.8 mg, 0.9 mmol, 4.5 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 3 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **10** and as a white solid in 59% yield (59 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.75 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.34 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.64 (s, 1H), 5.29 (s, 1H), 4.83 (d, *J* = 8.1 Hz, 1H), 4.38 (d, *J* = 8.1 Hz, 1H), 3.42 (s, 3H), 2.49 (s, 3H), 1.54 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 151.8, 144.3, 141.2, 137.3, 133.0, 130.1, 129.6, 128.4, 127.2, 117.6, 115.5, 95.6, 82.5, 58.7, 56.5, 28.2, 21.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{25}BrN_2NaO_5^+$: 519.0560; Found: 519.0560.

Tert-butyl-2-methoxy-4-methyl-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (11)



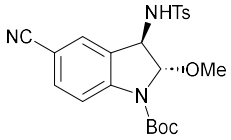
According to ***GP-1*** with **1n** (68.6 mg, 0.2 mmol, 1.0 equiv.), **2a** (334.8 mg, 0.9 mmol, 4.5 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 3 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **11** and as a yellow solid in 52% yield (57 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.71 (d, *J* = 6.7 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 2H), 6.75 (s, 1H), 5.26 (s, 1H), 4.98 (d, *J* = 8.3 Hz, 1H), 4.37 (d, *J* = 8.2 Hz, 1H), 3.40 (s, 3H), 2.50 (s, 3H), 1.53 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) =151.9, 144.3, 142.1, 139.0, 137.4, 134.3, 130.2, 127.3, 118.2, 95.5, 85.7, 82.6, 58.7, 56.6, 28.3, 28.2, 21.8.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{25}IN_2NaO_5S^+$: 567.0421; Found: 567.0421.

Tert-butyl-2-methoxy-4-methyl-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (12)



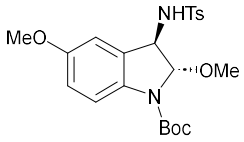
According to ***GP-1*** with **1o** (48.4 mg, 0.2 mmol, 1.0 equiv.), **2a** (334.8 mg, 0.9 mmol, 4.5 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 3 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **12** and as a colorless oil in 68% yield (60 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.76 (d, *J* = 7.9 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 2H), 6.83 (s, 1H), 5.37 (s, 1H), 5.07 (d, *J* = 7.9 Hz, 1H), 4.41 (d, *J* = 7.8 Hz, 1H), 3.45 (s, 3H), 2.50 (s, 3H), 1.55 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 151.4, 145.9, 144.6, 137.1, 134.7, 130.1, 129.4, 128.5, 127.2, 118.5, 116.3, 106.1, 95.9, 83.3, 58.4, 56.8, 28.1, 21.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{25}N_3NaO_5S^+$: 466.1407; Found: 466.1407.

Tert-butyl-2,5-dimethoxy-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (13)



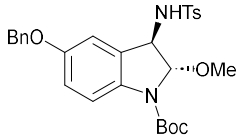
According to ***GP-1*** with **1p** (49.4 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **13** and as a yellow solid in 57% yield (51 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.80 (d, *J* = 8.0 Hz, 2H), 7.63 (s, 1H--NH), 7.37 (d, *J* = 7.9 Hz, 2H), 6.79 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.30 (s, 1H), 5.25 (s, 1H), 4.75 (d, *J* = 7.9 Hz, 1H), 4.41 (d, *J* = 7.8 Hz, 1H), 3.64 (s, 3H), 3.40 (s, 3H), 2.46 (s, 3H), 1.53 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 156.0, 152.2, 143.9, 137.6, 135.7, 129.9, 127.3, 116.9, 115.9, 110.5, 95.4, 81.8, 59.3, 56.4, 55.6, 28.3, 21.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{28}N_2NaO_6S^+$: 471.1560; Found: 471.1561.

Tert-butyl-5-(benzyloxy)-2-methoxy-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (14)



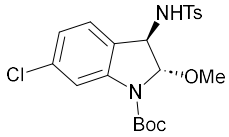
According to ***GP-1*** with **1q** (104.8 mg, 0.2 mmol, 1.0 equiv.), **2a** (334.8 mg, 0.9 mmol, 4.5 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 3 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **14** and as a white solid in 40% yield (42 mg).

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.81 (d, *J* = 8.3 Hz, 2H), 7.41 - 7.31 (m, 7H), 6.88 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.38 (s, 1H), 5.28 (s, 1H), 4.87 (s, 2H), 4.69 (d, *J* = 7.7 Hz, 1H), 4.40 (d, *J* = 7.7 Hz, 1H), 3.42 (s, 3H), 2.44 (s, 3H), 1.54 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) =155.2, 144.0, 137.5, 136.7, 130.0, 128.6, 128.1, 127.5, 127.3, 116.9, 116.8, 111.8, 95.5, 81.9, 70.5, 59.3, 56.5, 28.3, 21.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{32}N_2NaO_6S^+$: 547.1873; Found: 547.1873.

Tert-butyl-6-chloro-2-methoxy-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (15)



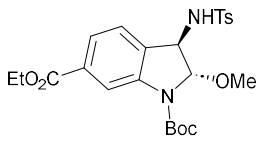
According to ***GP-1*** with **1r** (50.2 mg, 0.2 mmol, 1.0 equiv.), **2a** (334.8 mg, 0.9 mmol, 4.5 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 3 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **15** and as a white solid in 52% yield (47 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.79 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 6.88 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.70 (s, 1H), 5.29 (s, 1H), 4.77 - 4.71 (m, 1H), 4.39 (d, *J* = 7.5 Hz, 1H), 3.42 (s, 3H), 2.47 (s, 3H), 1.55 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 151.7, 144.1, 143.2, 137.3, 136.2, 130.0, 127.2, 126.1, 123.4, 116.5, 95.8, 82.7, 58.7, 56.7, 28.3, 21.7.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{25}ClN_2NaO_5S^+$: 475.1065; Found: 475.1062.

1-(tert-butyl) 6-ethyl-2-methoxy-3-((4-methylphenyl)sulfonamido)indoline-1,6-dicarboxylate (16)



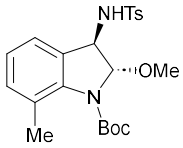
According to ***GP-1*** with **1s** (57.8 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **16** and as a white solid in 64% yield (63 mg).

^{1}H NMR (600 MHz, CD_3CN, 300 K): δ (ppm) = 7.94 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.71 (s, 1H--NH), 7.48 (d, *J* = 1.8 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 6.14 (d, *J* = 8.4 Hz, 1H), 5.11 (s, 1H), 4.46 (d, *J* = 8.3 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.29 (s, 3H), 2.45 (s, 3H), 1.52 (s, 9H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, CD_3CN, 300 K): δ (ppm) = 166.5, 152.7, 147.2, 145.2, 139.2, 132.7, 131.0, 129.3, 128.2, 127.9, 126.4, 116.2, 96.2, 83.4, 61.7, 59.6, 56.9, 28.3, 21.6, 14.7, 1.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{30}N_2NaO_7S^+$: 513.1666; Found: 513.1664.

Tert-butyl-2-methoxy-7-methyl-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (17)



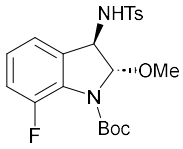
According to ***GP-1*** with **1t** (46.2 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **17** and as a white solid in 70% yield (61 mg).

^{1}H NMR (600 MHz, CD_3CN, 300 K): δ (ppm) = 7.78 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.20 (d, *J* = 8.0 Hz, 1H), 5.04 (s, 1H), 4.22 (d, *J* = 8.0 Hz, 1H), 3.25 (s, 3H), 2.46 (s, 3H), 2.22 (s, 3H), 1.45 (s, 9H).

^{13}C NMR (151 MHz, CD_3CN, 300 K): δ (ppm) = 153.6, 145.1, 142.2, 139.1, 133.0, 131.4, 131.0, 129.9, 128.0, 126.0, 124.0, 97.3, 82.4, 61.0, 56.0, 28.3, 21.6, 20.0.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{28}N_2NaO_5S^+$: 455.1611; Found: 455.1607.

Tert-butyl-7-fluoro-2-methoxy-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (18)



According to ***GP-1*** with **1u** (47 mg, 0.2 mmol, 1.0 equiv.), **2a** (334.8 mg, 0.9 mmol, 4.5 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 3 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **18** and as a colorless oil in 54% yield (47 mg).

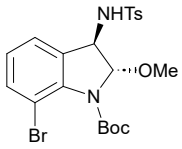
^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.77 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.04 - 6.99 (m, 1H), 6.97 - 6.92 (m, 1H), 6.69 (d, *J* = 7.4 Hz, 1H), 5.27 (s, 1H), 4.94 (d, *J* = 5.2 Hz, 1H), 4.35 (d, *J* = 7.4 Hz, 1H), 3.40 (s, 3H), 2.46 (s, 3H), 1.51 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.4, 151.9 (d, *J* = 254.1 Hz, C-F), 144.0, 137.3, 132.6 (d, *J* = 2.7 Hz, C-F), 129.9, 129.2 (d, *J* = 10.9 Hz, C-F), 127.3, 125.9 (d, *J* = 6.9 Hz, C-F), 121.0 (d, *J* = 3.6 Hz, C-F), 118.2 (d, *J* = 20.5 Hz, C-F), 96.7, 82.5, 59.8, 56.1, 28.0, 21.6.

^{19}F NMR (376 MHz, $CDCl_3$, 300 K): δ (ppm) = δ -116.00 (s).

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{25}FN_2NaO_5S^+$: 459.1360; Found: 459.1359.

Tert-butyl-7-bromo-2-methoxy-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (19)



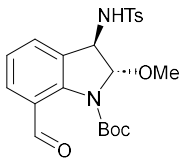
According to ***GP-1*** with **1v** (59 mg, 0.2 mmol, 1.0 equiv.), **2a** (334.8 mg, 0.9 mmol, 4.5 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 3 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **19** and as a colorless oil in 47% yield (47 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.77 (d, *J* = 8.2 Hz, 2H), 7.46 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 6.89 - 6.83 (m, 2H), 5.27 (s, 1H), 4.98 (d, *J* = 7.0 Hz, 1H), 4.31 (d, *J* = 7.0 Hz, 1H), 3.38 (s, 3H), 2.46 (s, 3H), 1.52 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.3, 144.0, 141.7, 137.2, 134.7, 132.8, 129.9, 127.3, 126.3, 124.3, 113.6, 97.5, 82.6, 60.1, 55.8, 28.0, 21.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for$C_{21}H_{25}BrN_2NaO_5S^+$: 519.0560; Found: 519.0566.

Tert-butyl-7-formyl-2-methoxy-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (20)



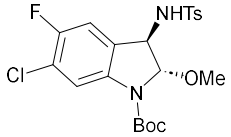
According to ***GP-1*** with **1w** (49 mg, 0.2 mmol, 1.0 equiv.), **2a** (334.8 mg, 0.9 mmol, 4.5 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **20** and as a white solid in 52% yield (46 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 10.00 (s, 1H), 7.74 - 7.70 (m, 3H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.10 - 7.05 (m, 2H), 5.41 (s, 1H), 5.18 (d, *J* = 7.3 Hz, 1H), 4.37 (d, *J* = 7.3 Hz, 1H), 3.41 (s, 3H), 2.45 (s, 3H), 1.48 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 188.6, 153.4, 144.0, 142.5, 137.2, 130.7, 130.3, 129.9, 129.1, 127.2, 125.8, 125.0, 96.7, 83.7, 59.2, 56.1, 27.9, 21.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{26}N_2NaO_6S^+$: 469.1404; Found: 469.1399.

Tert-butyl-6-chloro-5-fluoro-2-methoxy-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (21)



According to ***GP-1*** with **1x** (53.8 mg, 0.2 mmol, 1.0 equiv.), **2a** (334.8 mg, 0.9 mmol, 4.5 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **21** and as a colorless oil in 45% yield (42 mg).

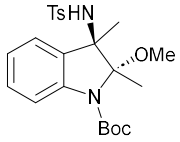
^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.74 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.50 (d, *J* = 7.7 Hz, 1H), 5.27 (s, 1H), 5.04 (d, *J* = 8.0 Hz, 1H), 4.36 (d, *J* = 8.0 Hz, 1H), 3.39 (s, 3H), 2.47 (s, 3H), 1.53 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 155.2 (d, *J* = 246.7 Hz, C-F), 151.7, 144.3, 138.6, 137.2, 130.0, 127.2, 122.6 (d, *J* = 18.9 Hz, C-F), 117.9, 113.3 (d, *J* = 24.1 Hz, C-F), 95.7, 82.7, 58.7, 56.6, 28.1, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$, 300 K) δ (ppm) = -120.86 (s, F).

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{24}ClFN_2NaO_5S^+$ 493.0971: 493.0971; Found: 493.0971.

Tert-butyl-2-methoxy-2,3-dimethyl-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (22)



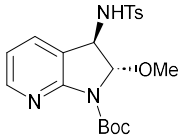
According to ***GP-1*** with **1y** (49 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **22** and as a white solid in 45% yield (40 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.86 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.22 - 7.16 (m, 1H), 7.04 - 7.00 (m, 1H), 5.82 (s, 1H), 3.29 (s, 3H), 2.44 (s, 3H), 1.58 (s, 3H), 1.56 (s, 9H), 1.34 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.7, 143.1, 140.3, 139.3, 136.2, 129.5, 128.5, 127.2, 123.7, 123.6, 116.2, 98.5, 82.0, 68.5, 51.4, 28.3, 21.5, 20.9, 16.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{30}N_2NaO_5S^+$: 469.1768; Found: 469.1767.

Tert-butyl-2-methoxy-3-((4-methylphenyl)sulfonamido)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine-1-carboxylate (23)



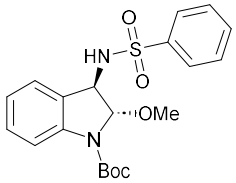
According to ***GP-1*** with **1z** (43.6 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 3 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **23** and as a white solid in 43% yield (36 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.27 (d, *J* = 5.1 Hz, 1H), 7.77 (d, *J* = 6.5 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 7.4 Hz, 1H), 6.81 - 6.77 (m, 1H), 5.51 (d, *J* = 7.9 Hz, 1H), 5.19 (s, 1H), 4.37 (d, *J* = 7.4 Hz, 1H), 3.37 (s, 3H), 2.43 (s, 3H), 1.50 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 155.6, 150.3, 149.7, 143.9, 137.5, 134.4, 129.8, 127.2, 121.4, 118.5, 94.1, 82.4, 57.1, 56.3, 28.1, 21.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{26}N_3O_5S^+$: 420.1588; Found: 420.1588.

Tert-butyl-2-methoxy-3-(phenylsulfonamido)indoline-1-carboxylate (24)



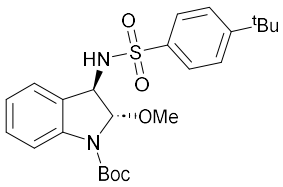
According to ***GP-1*** with **1a** (48.4 mg, 0.2 mmol, 1.0 equiv.), **2b** (214.8 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **24** and as a white solid in 82% yield (66 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.89 (d, *J* = 7.7 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.77 (s, 1H), 5.26 (s, 1H), 4.95 (d, *J* = 7.7 Hz, 1H), 4.43 (d, *J* = 7.6 Hz, 1H), 3.40 (s, 3H), 1.54 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.2, 142.2, 140.6, 133.2, 130.4, 129.5, 127.3, 125.5, 123.5, 116.2, 95.4, 82.2, 59.2, 56.6, 28.4.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{24}N_2NaO_5S^+$: 427.1298; Found: 427.1298.

Tert-butyl-3-((4-(tert-butyl)phenyl)sulfonamido)-2-methoxyindoline-1-carboxylate (25)



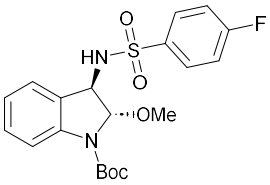
According to ***GP-1*** with **1a** (48.4 mg, 0.2 mmol, 1.0 equiv.), **2c** (249 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1: 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **25** and as a white solid in 79% yield (73 mg).

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.85 (d, *J* = 8.5 Hz, 2H), 7.69 (s, 1H--NH), 7.59 (d, *J* = 8.6 Hz, 2H), 7.28 - 7.22 (m, 1H), 6.91 - 6.86 (m, 1H), 6.76 - 6.69 (m, 1H), 5.33 (s, 1H), 4.68 (t, *J* = 7.0 Hz, 1H), 4.43 (d, *J* = 7.5 Hz, 1H), 3.43 (s, 3H), 1.56 (s, 9H), 1.38 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 157.1, 152.0, 142.1, 137.2, 130.3, 127.1, 126.3, 125.2, 123.3, 116.1, 95.5, 82.1, 77.2, 59.0, 56.5, 35.2, 31.1, 28.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for : $C_{24}H_{32}N_2NaO_5S^+$: 483.1924; Found: 483.1924.

Tert-butyl-3-((4-fluorophenyl)sulfonamido)-2-methoxyindoline-1-carboxylate (26)



According to ***GP-1*** with **1a** (48.4 mg, 0.2 mmol, 1.0 equiv.), **2d** (225.6 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **26** and as a white solid in 75% yield (63 mg).

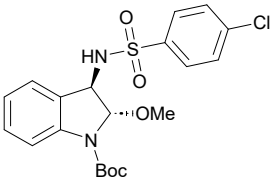
^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 - 7.87 (m, 2H), 7.70 (s, 1H--NH), 7.28 - 7.21 (m, 3H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.83 (s, 1H), 5.28 (s, 1H), 4.91 (d, *J* = 7.7 Hz, 1H), 4.42 (d, *J* = 7.7 Hz, 1H), 3.42 (s, 3H), 1.55 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.2 (d, *J* = 255.9 Hz), 152.1, 142.1, 136.6 (d, *J* = 3.3 Hz), 130.3, 123.0 (d, *J* = 9.3 Hz), 127.21, 125.3, 123.4, 116.5 (d, *J* = 22.6 Hz), 116.2, 95.1, 82.2, 59.1, 56.5, 28.2.

^{19}F NMR (565 MHz, $CDCl_3$, 300 K) δ (ppm) = -104.32 (m).

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{23}FN_2NaO_5S^+$: 445.1204; Found: 445.1204.

Tert-butyl-3-((4-chlorophenyl)sulfonamido)-2-methoxyindoline-1-carboxylate (27)



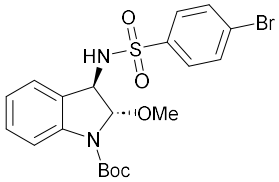
According to ***GP-1*** with **1a** (48.4 mg, 0.2 mmol, 1.0 equiv.), **2e** (235.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **27** and as a yellow oil in 72% yield (63 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.83 (d, *J* = 8.5 Hz, 2H), 7.70 (s, 1H--NH) 7.54 (d, *J* = 8.7 Hz, 2H), 7.29 - 7.24 (m, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 5.28 (s, 1H), 4.88 (d, *J* = 7.6 Hz, 1H), 4.43 (d, *J* = 7.6 Hz, 1H), 3.43 (s, 3H), 1.55 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.1, 139.6, 139.0, 130.4, 129.6, 128.6, 127.1, 125.3, 123.4, 116.2, 95.1, 82.3, 59.2, 56.5, 28.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{23}ClN_2NaO_5S^+$: 461.0908; Found: 461.0903.

Tert-butyl-3-((4-bromophenyl)sulfonamido)-2-methoxyindoline-1-carboxylate (28)



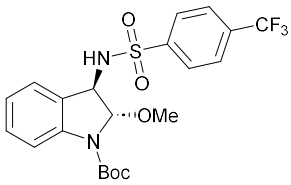
According to ***GP-1*** with **1a** (48.4 mg, 0.2 mmol, 1.0 equiv.), **2f** (261.6 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **28** and as a white solid in 78% yield (75 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.73 - 7.68 (m, 4H), 7.55 (s, 1H--NH), 7.37 (d, *J* = 8.6 Hz, 1H), 6.84 (s, 1H), 5.28 (s, 1H), 5.01 (d, *J* = 8.1 Hz, 1H), 4.39 (d, *J* = 8.0 Hz, 1H), 3.42 (s, 3H), 1.55 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.0, 141.4, 139.5, 133.3, 132.8, 128.8, 128.5, 126.1, 125.9, 117.9, 115.8, 95.4, 82.8, 59.0, 56.7, 28.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{23}BrN_2NaO_5S^+$: 505.0403; Found: 505.0401.

Tert-butyl-2-methoxy-3-((4-(trifluoromethyl)phenyl)sulfonamido)indoline-1-carboxylate (29)



According to ***GP-1*** with **1a** (48.4 mg, 0.2 mmol, 1.0 equiv.), **2g** (255.6 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **29** and as a colorless oil in 75% yield (71mg).

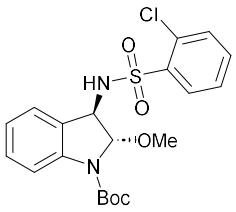
^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.00 (d, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.66 (s, 1H--NH), 7.25 - 7.22 (m, 1H), 6.92 - 6.87 (m, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 5.26 (s, 1H), 4.91 (d, *J* = 7.7 Hz, 1H), 4.44 (d, *J* = 7.7 Hz, 1H), 3.40 (s, 3H), 1.52 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.1, 144.2, 142.1, 134.8 (d, *J* = 34.7 Hz, C-F), 130.5, 127.7, 126.48, 126.5 (d, *J* = 4.5 Hz, C-F), 125.3, 123.5, 122.9 (d, *J* = 273.3 Hz, C-F), 116.3, 95.1, 82.3, 59.3, 56.5, 28.2.

^{19}F NMR (565 MHz, $CDCl_3$, 300 K): δ (ppm) = -63.00 (s, F).

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{23}F_3N_2NaO_5S^+$: 495.1172; Found: 495.1172.

Tert-butyl-3-((2-chlorophenyl)sulfonamido)-2-methoxyindoline-1-carboxylate (30)



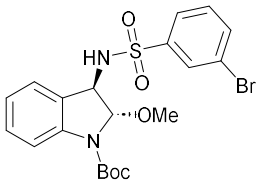
According to ***GP-1*** with **1a** (48.4 mg, 0.2 mmol, 1.0 equiv.), **2h** (235.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **30** and as a yellow oil in 81% yield (71 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.21 - 8.17 (m, 1H), 7.61 - 7.58 (m, 2H), 7.51 - 7.47 (m, 1H), 7.28 (t, *J* = 8.5 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.89 (s, 1H), 5.35 (s, 1H), 5.20 (d, *J* = 7.0 Hz, 1H), 4.37 (d, *J* = 7.0 Hz, 1H), 3.39 (s, 3H), 1.57 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.0, 142.3, 137.4, 134.2, 131.8, 131.5, 131.4, 130.4, 127.5, 125.3, 123.4, 116.2, 95.1, 82.1, 59.3, 56.5, 28.3, 28.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{23}ClN_2NaO_5S^+$: 461.0908; Found: 461.0906.

Tert-butyl-3-((3-bromophenyl)sulfonamido)-2-methoxyindoline-1-carboxylate (31)



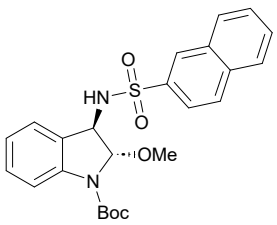
According to ***GP-1*** with **1a** (48.4 mg, 0.2 mmol, 1.0 equiv.), **2i** (214.8 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **31** and as a white solid in 82% yield (67 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.07 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 6.94 (m, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 5.28 (s, 1H), 4.79 (d, *J* = 7.7 Hz, 1H), 4.48 (d, *J* = 7.9 Hz, 1H), 3.45 (s, 3H), 1.56 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.1, 142.4, 136.1, 130.9, 130.5, 130.1, 127.0, 125.6, 125.3, 123.5, 123.3, 116.3, 95.1, 82.3, 59.2, 56.6, 28.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{23}BrN_2NaO_5S^+$: 505.0403; Found: 505.0404.

Tert-butyl-2-methoxy-3-(naphthalene-2-sulfonamido)indoline-1-carboxylate (32)



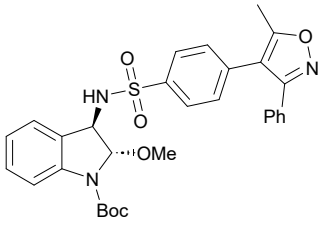
According to ***GP-1*** with **1a** (48.4 mg, 0.2 mmol, 1.0 equiv.), **2i** (408.6 mg, 0.6 mmol, 4.5 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 3 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **32** and as a white solid in 56% yield (51 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) =8.52 (d, *J* = 1.9 Hz, 1H), 8.01 (dd, *J* = 12.5, 8.4 Hz, 2H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.84 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 6.8 Hz, 1H), 7.25 - 7.20 (m, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 5.25 (s, 1H), 4.89 (d, *J* = 7.6 Hz, 1H), 4.50 (d, *J* = 7.6 Hz, 1H), 3.37 (s, 3H), 1.48 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.0, 142.1, 134.9, 132.1, 130.3, 129.8, 129.3, 129.1, 128.7, 128.0, 127.8, 127.3, 125.4, 123.3, 122.1, 116.1, 95.1, 82.1, 59.2, 56.5, 28.2.

HRMS (APCI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{26}N_2NaO_5S^+$: 477.1455; Found: 477.1457.

Tert-butyl -2-methoxy-3-((4-(5-methyl-3-phenylisoxazol-4-yl)phenyl)sulfonamido)indoline-1-carboxylate (33)



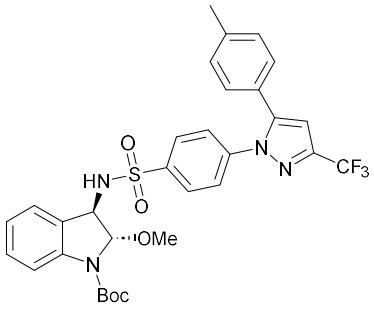
According to ***GP-1*** with **1a** (48.4 mg, 0.2 mmol, 1.0 equiv.), **2k** (309.6 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **33** and as a white solid in 87% yield (98 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.91 -- 7.87 (m, 2H), 7.71 (s, 1H--NH), 7.42 - 7.37 (m, 3H), 7.37 - 7.34 (m, 4H), 7.27 - 7.23 (m, 1H), 6.87 (s, 1H), 6.72 (s, 1H), 5.39 (s, 1H), 5.02 (d, *J* = 33.2 Hz, 1H), 4.45 (d, *J* = 7.6 Hz, 1H), 3.46 (s, 3H), 2.51 (s, 3H), 1.57 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.3, 161.0, 152.1, 142.2, 139.5, 135.6, 130.4, 130.3, 129.7, 128.7, 128.4, 128.4, 127.6, 125.1, 123.2, 116.2, 114.4, 95.6, 82.2, 59.1, 56.5, 28.3, 11.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{32}N_3O_6S^+$: 562.2006; Found: 562.2005.

Tert-butyl-2-methoxy-3-((4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)phenyl)sulfonamido)indoline-1-carboxylate (34)



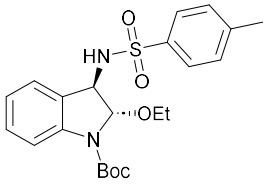
According to ***GP-1*** with **1a** (48.4 mg, 0.2 mmol, 1.0 equiv.), **2i** (349.8 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **34** and as a white solid in 78% yield (98 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) =7.86 (d, *J* = 8.8 Hz, 2H), 7.70 (s, 1H--NH), 7.52 (d, *J* = 8.8 Hz, 2H), 7.28 -- 7.24 (m, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.81 (s, 1H), 6.76 (s, 1H), 5.32 (s, 1H), 4.98 (t, *J* = 7.2 Hz, 1H), 4.41 (d, *J* = 7.7 Hz, 1H), 3.43 (s, 3H), 2.39 (s, 3H), 1.55 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) =152.1, 145.3, 1441 (q, *J* = 339.3 Hz, C-F), 142.2, 139.8, 139.8, 130.4, 129.8, 128.7, 128.1, 127.1, 125.7, 125.6, 125.2, 123.4, 121.0 (q, *J* = 268.8 Hz, C-F), 116.2, 106.4, 95.3, 82.3, 59.1, 56.5, 28.2, 21.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for : $C_{31}H_{31}F_3N_4NaO_5S^+$: 651.1859; Found: 651.1859.

Tert-butyl-2-ethoxy-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (35)



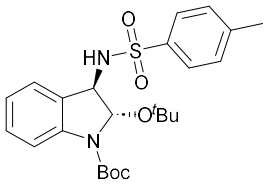
According to ***GP-1*** with **1a** (43.4 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : EtOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **35** and as a white solid in 26% yield (22 mg).

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.79 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.25 - 7.21 (m, 1H), 6.89 (t, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 5.35 (s, 1H), 4.77 (d, *J* = 7.5 Hz, 1H), 4.42 (d, *J* = 7.5 Hz, 1H), 3.71 - 3.63 (m 2H), 2.47 (s, 3H), 1.54 (s, 9H), 1.16 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.2, 144.0, 142.4, 137.6, 130.3, 130.0, 127.4, 125.5, 123.4, 116.1, 94.2, 82.0, 64.7, 59.5, 28.4, 21.7, 15.4

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{28}N_2NaO_5S^+$: 455.1611; Found: 455.1612.

Tert-butyl-2-(tert-butoxy)-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (36)



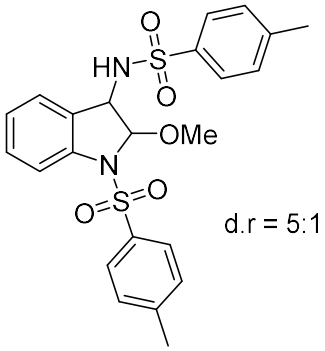
According to ***GP-1*** with **1a** (43.4 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : ^{t}BuOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **36** and as a white solid in 22% yield (20 mg).

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.86 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 8.4 Hz, 1H), 7.12 (s, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 5.65 (d, *J* = 5.5 Hz, 1H), 5.32 (d, *J* = 10.2 Hz, 1H), 4.96 (dd, *J* = 10.2, 5.5 Hz, 1H), 2.44 (s, 3H), 1.56 (s, 9H), 1.16 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 143.77, 138.08, 129.91, 128.72, 127.09, 124.09, 123.6, 117.0, 83.2, 82.2, 76.1, 57.1, 28.3, 28.2, 21.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{32}N_2NaO_5S^+$: 483.1924; Found: 483.1927.

N-(2-methoxy-1-tosylindolin-3-yl)-4-methylbenzenesulfonamide (37)



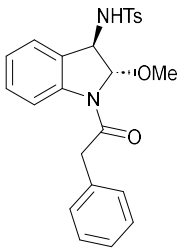
According to ***GP-1*** with **1d** (54.2 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **40** and as a white solid in 33% yield (31 mg, d.r = 5:1).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.73 - 7.70 (m, 2.2 H), 7.67 (d, *J* = 6.0 Hz, 1H), 7.51 (d, *J* = 12 Hz, 0.2 H), 7.47 (d, *J* = 6.0 Hz, 0.2 H), 7.41 - 7.36 (m, 2.8 H), 7.35 - 7.33 (m, 1 H), 7.27 (d, *J* = 6.0 Hz, 0.2 H), 7.23 (d, *J* = 12 Hz, 2 H), 7.20 (d, *J* = 6.0 Hz, 0.4 H), 7.16 (d, *J* = 6.0 Hz, 0.2 H), 7.11 - 7.04 (m, 1.2 H), 6.90 (d, *J* = 6.0 Hz, 1 H), 5.26 (d, *J* = 12 Hz, 0.2 H), 5.02 (s, 1 H), 4.58 (d, *J* = 6.0 Hz, 0.2 H), 4.29 - 4.24 (m, 1.2 H), 3.47 (s, 3 H), 3.23 (s, 0.6 H), 2.51 (s, 0.6 H), 2.48 (s, 3 H), 4.40 - 4.38 (m, 3.6 H).

^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 145.09, 144.69, 144.25, 144.22, 141.10, 138.63, 137.05, 136.71, 135.44, 134.63, 131.55, 130.60, 129.91, 129.89, 129.86, 129.83, 129.79, 129.62, 127.22, 127.18, 127.08, 126.48, 125.82, 125.75, 124.75, 118.35, 118.14, 97.66, 91.13, 59.71, 57.35, 56.09, 56.07, 21.61, 21.58, 21.52.

HRMS (APCI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{24}N_2NaO_5S_2^+$: 495.1019; Found: 495.1021.

Benzyl-2-methoxy-3-((4-methylphenyl)sulfonamido)indoline-1-carboxylate (38)



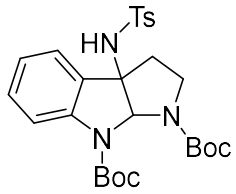
According to ***GP-1*** with **1c** (50.2 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **42** and as a white solid in 74% yield (67 mg).

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.80 (d, *J* = 8.2 Hz, 2H), 7.40 - 7.32 (m, 7H), 7.26 - 7.21 (m, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.82 (s, 1H), 5.44 - 5.25 (m, 2H), 5.17 (s, 1H), 4.84 (s, 1H), 4.45 (d, *J* = 7.4 Hz, 1H), 3.36 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.7, 144.0, 137.3, 135.5, 130.4, 129.9, 128.6, 128.5, 128.4, 128.2, 127.2, 125.3, 123.8, 116.1, 95.4, 67.8, 59.0, 56.4, 21.6.

HRMS (APCI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{24}N_2NaO_5S^+$: 475.1298; Found: 475.1294.

Di-tert-butyl 3a-((4-methylphenyl)sulfonamido)-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (40)



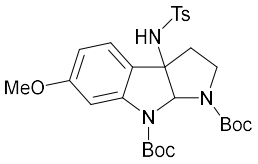
According to ***GP-2*** with **1aa** (72 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in MeOH (2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **42** and as a white solid in 85% yield (90 mg).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.57 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.78 (d, *J* = 7.5 Hz, 1H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.44 (s, 1H), 5.66 (d, *J* = 2.8 Hz, 1H), 3.73 (dd, *J* = 11.6, 7.6 Hz, 1H), 2.68 - 2.62 (m, 1H), 2.35 (s, 3H), 2.34 - 2.29 (m, 1H), 2.21 - 2.16 (m, 1H), 1.58 (s, 9H), 1.46 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 153.6, 152.2, 143.8, 142.9, 138.6, 129.8, 129.3, 128.5, 126.9, 123.9, 123.0, 116.9, 81.5, 80.2, 70.7, 60.4, 44.3, 28.3, 28.3, 21.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{36}N_3O_6S^+$: 530.2319; Found: 530.2317.

Di-tert-butyl 6-methoxy-3a-((4-methylphenyl)sulfonamido)-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (41)



According to ***GP-2*** with **1ab** (78 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **42** and as a white solid in 90% yield (100.6 mg)

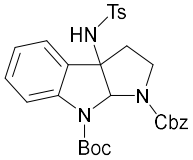
^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.47 (s, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.70 (dd, *J* = 8.9, 1.5 Hz, 1H), 6.45 (s, 1H), 6.15 (s, 1H), 5.76 (s, 1H), 3.75 - 3.71 (m,

1H), 3.50 (s, 3H), 2.69 - 2.64 (m, 1H), 2.35 (s, 3H), 2.29 - 2.23 (m, 1H), 2.19 - 2.15 (m, 1H), 1.58 (s, 9H), 1.47 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 155.8, 153.6, 152.4, 142.8, 138.5, 137.7, 129.2, 127.0, 118.0, 116.0, 108.2, 81.2, 80.7, 80.3, 70.8, 44.1, 28.4, 21.3.

HRMS (APCI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{37}N_3NaO_7S^+$: 582.2244; Found: 582.2243.

1-benzyl 8-(tert-butyl) 3a-((4-methylphenyl)sulfonamido)-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (42)



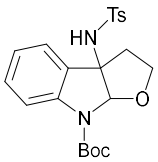
According to ***GP-2*** with **1ac** (78.8 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **42** and as a white solid in 83% yield (93.5 mg)

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.64 (s, 1H), 7.41 - 7.32 (m, 6H), 7.30 - 7.27 (m, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.51 (s, 1H), 5.50 (s, 1H), 5.25 - 5.11 (m, 2H), 3.83 (dd, *J* = 11.6, 7.7 Hz, 1H), 2.77 - 2.70 (m, 1H), 2.41 - 2.37 (m, 1H), 2.36 (s, 3H), 2.23 - 2.19 (m, 1H), 1.54 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.4, 143.8, 143.0, 138.4, 136.7, 130.0, 129.3, 128.4, 127.9, 127.8, 126.9, 123.7, 123.3, 117.2, 81.8, 80.4, 70.8, 67.0, 44.5, 37.1, 28.2, 21.4.

HRMS (APCI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{33}N_3NaO_6S^+$: 586.1982; Found: 586.1989.

Tert-butyl 3a-((4-methylphenyl)sulfonamido)-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indole-8-carboxylate (43)



According to ***GP-2*** with **1ad** (52.2 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **43** and as a white solid in 90% yield (77.4 mg)

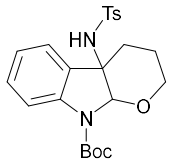
^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.78 (s, 1H), 7.33 (d, *J* = 4.9 Hz, 2H), 7.18 (t, *J* = 7.1 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.67 (d, *J* = 38.9 Hz, 2H), 6.21 (s, 1H), 5.52 (s, 1H), 3.99 -

3.95 (m, 1H), 3.39 - 3.40 (m, 1H), 2.50 - 2.44 (m, 1H), 2.37 (s, 3H), 2.28 - 2.23 (m, 1H), 1.59 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.2, 143.1, 138.3, 129.9, 129.3, 126.9, 124.1, 122.8, 115.0, 97.0, 81.7, 71.0, 66.0, 40.9, 28.3, 21.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{26}N_2NaO_5S^+$: 453.1455; Found: 453.1454.

Tert-butyl 4a-((4-methylphenyl)sulfonamido)-3,4,4a,9a-tetrahydropyrano[2,3-b]indole-9(2H)-carboxylate (44)



According to ***GP-2*** with **1ae** (55 mg, 0.2 mmol, 1.0 equiv.), **2a** (223.2 mg, 0.6 mmol, 3.0 equiv.), in DCE : MeOH (1 : 1, 2 mL) for 2 h under N_2 atmosphere. Purification by silica gel chromatography afforded the desired **44** and as a white solid in 50% yield (44.4 mg)

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.67 (d, *J* = 8.2 Hz, 2H), 7.50 (s, 1H), 7.26 - 7.21 (m, 4H), 7.01 (t, *J* = 7.5 Hz, 1H), 5.57 (d, *J* = 9.2 Hz, 1H), 5.24 (d, *J* = 9.2 Hz, 1H), 3.97 - 3.89 (m, 2H), 2.55 (s, 1H), 2.39 (s, 3H), 2.29 - 2.11 (m, 3H), 1.36 (s, 9H).

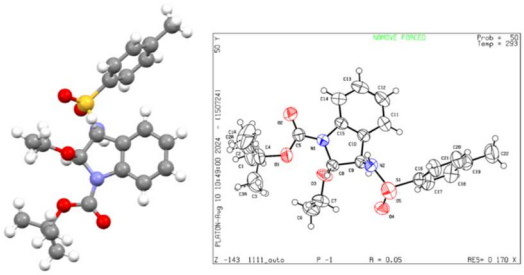
^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 151.2, 143.0, 141.7, 138.9, 131.7, 130.0, 129.2, 126.8, 123.4, 123.3, 116.0, 89.2, 82.1, 76.4, 67.9, 29.5, 28.0, 26.5, 21.4.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{28}N_2NaO_5S^+$: 467.1611; Found: 467.1611.

7. Crystal data

Method for single crystals cultivation: The single crystal for compound **36** (CCDC-: 2407435) were prepared from a mixture solvent of DCM and PE (v/v = 1:1). a pure solid sample (10–20 mg) was dissolved in DCM (2 mL) in a vial at room temperature, and PE (2-3 mL) was added into the above solution slowly while keeping the sample completely dissolved. The vial was properly sealed with parafilm and kept at room temperature to allow the slow evaporation of the solvents until a single crystal was obtained.

(1) Crystal data of 36 (Thermal ellipsoids are shown with 50% probability.)



Identification code	2407435
Empirical formula	$C_{16}H_{18}N_2O_4$
Empirical formula	$C_{22}H_{28}N_2O_5S$
Formula weight	423.45
Temperature/K	293
Crystal system	triclinic
Space group	P-1
a/Å	10.0397(3)
b/Å	10.2947(2)
c/Å	11.3136(4)
α/°	84.709(2)
β/°	76.197(3)
γ/°	89.722(2)
Volume/Å3	1130.54(6)
Z	2

ρ_{calc} g/cm^3	1.244
μ/mm^{-1}	1.561
F(000)	442.0
Crystal size/mm^3	0.08 × 0.06 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/	8.082 to 135.798
Index ranges	-11 ≤ h ≤ 11, -10 ≤ k ≤ 12, -13 ≤ l ≤ 13
Reflections collected	9666
Independent reflections	3941 [R_{int} = 0.0270, R_{sigma} = 0.0342]
Data/restraints/parameters	3941/0/306
Goodness-of-fit on F^2	1.085
Final R indexes [I>=2σ (I)]	R_1 = 0.0500, wR_2 = 0.1419
Final R indexes [all data]	R_1 = 0.0539, wR_2 = 0.1460
Largest diff. peak/hole / e Å-3	0.44/-0.42
Formula weight	302.32
Temperature/K	273.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.0370(5)
b/Å	11.0704(6)
c/Å	18.3838(11)
α/°	90
β/°	101.822(2)
γ/°	90
Volume/Å^3	1600.96(16)
Z	4
ρ_{calc}g/cm^3	1.254

μ/mm^{-1}	0.753
F(000)	640.0
Crystal size/mm^3	0.22 × 0.2 × 0.18
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.83 to 144.1
Index ranges	$-9 \leq h \leq 9$, $-13 \leq k \leq 13$, $-22 \leq l \leq 22$
Reflections collected	18292
Independent reflections	3102 [R_{int} = 0.0684, R_{sigma} = 0.0579]
Data/restraints/parameters	3102/0/201
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0970, wR_2 = 0.2624
Final R indexes [all data]	R_1 = 0.1026, wR_2 = 0.2694
Largest diff. peak/hole / e $Å^{-3}$	0.44/-0.42

8. References:

1. J. C. Reisenbauer, O. Green, A. Franchino, P. Finkelstein, B. Morandi, *Science*, **2022**, *377*, 1104-1109.

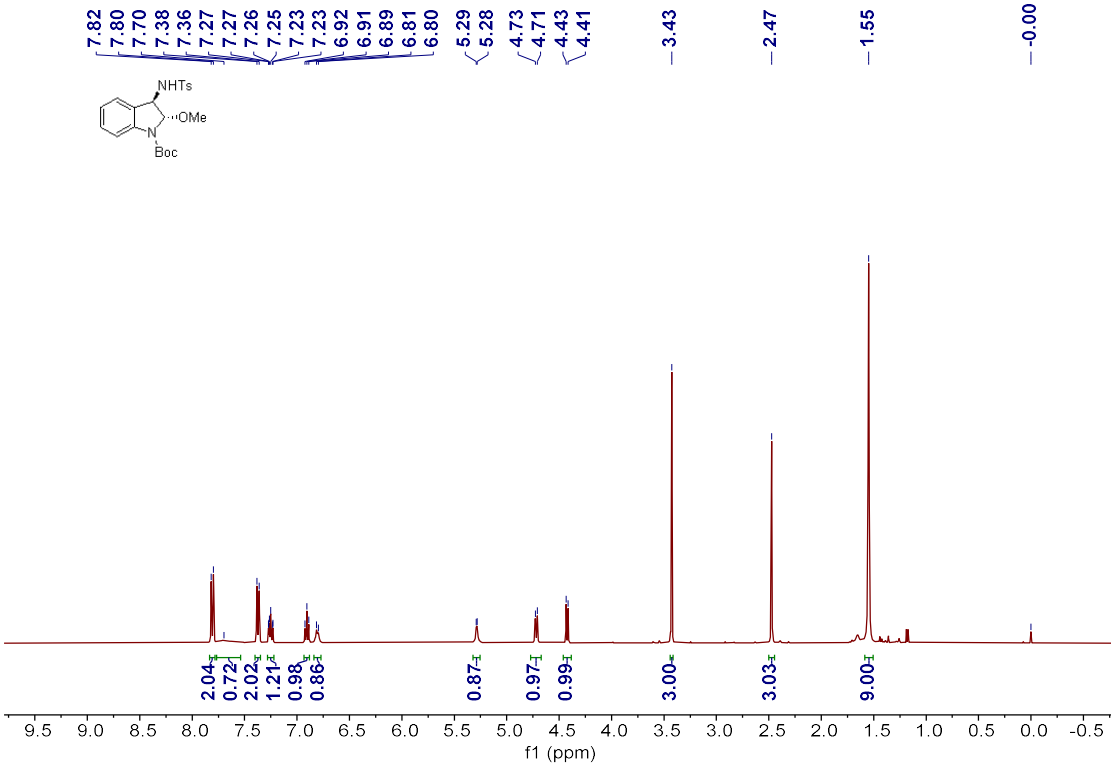
2. X. Xiao, B. Chen, J.-W. Li, J.-B. Zheng, X. Wang, H. Zhao, F.-E. Chen, *Chin. Chem. Lett.*, **2024**, *35*, 109280.

3. (a) Y. Guo, C. Pei, S. Jana, R. M. Koenigs, *ACS Catal*. **2021**, *11*, 337-342; (b) F. Li, W. F. Zhu, C. Empel, O. Datsenko, A. Kumar, Y. Xu, J. H. M. Ehrler, I. Atodiresei1, S. Knapp, P. K. Mykhailiuk, E. Proschak, R. M. Koenigs, *Science*, **2024**, *383*, 498–503; (c) Y. Guo, C. Pei, R. M. Koenigs, *Nat Commun*, **2022**, *13*.

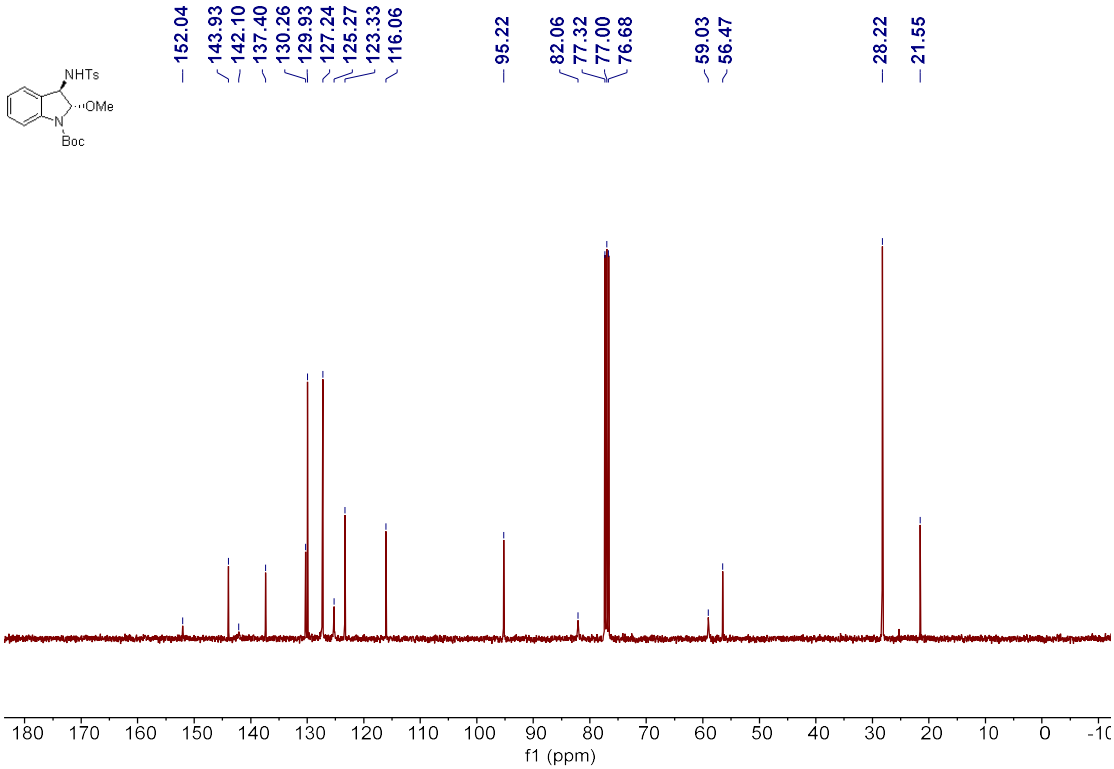
4. Y. Guo, C. Empel, C. Pei, H. Fang, S. Jana, R. M. Koenigs, *Chem Catalysis*, **2022**, *2*, 2012-2023.

Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR Spectra

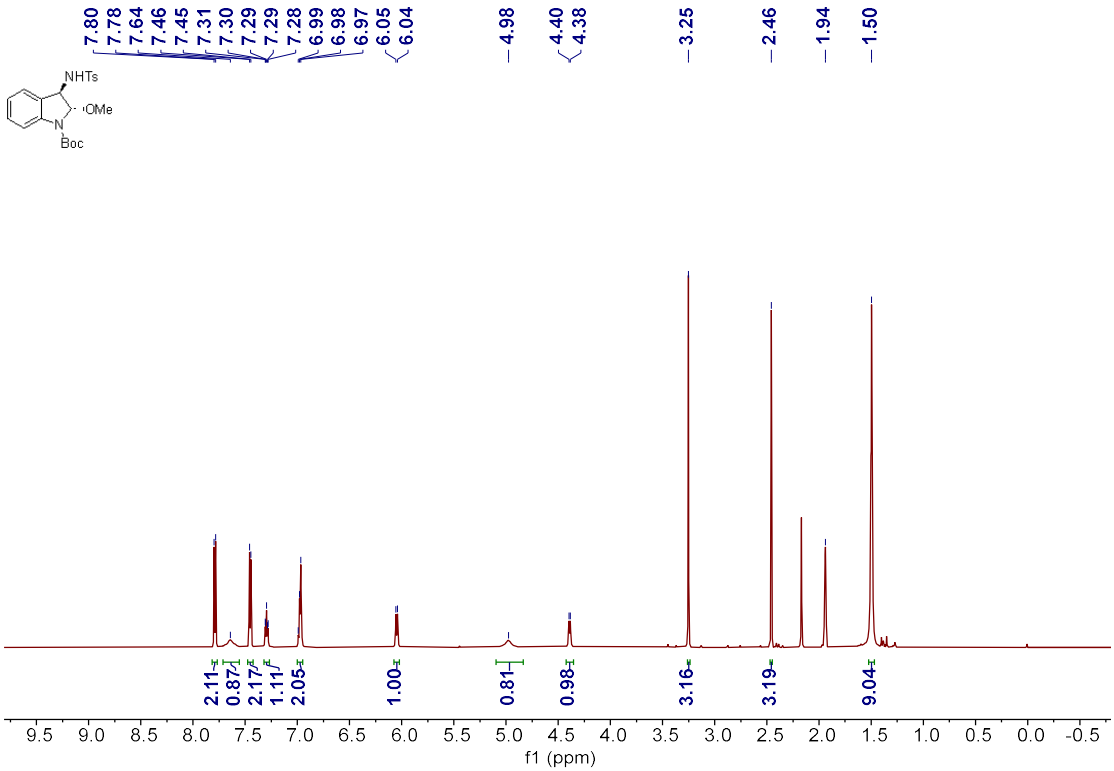
^{1}H NMR (400 MHz) Spectrum of 3 in $CDCl_3$



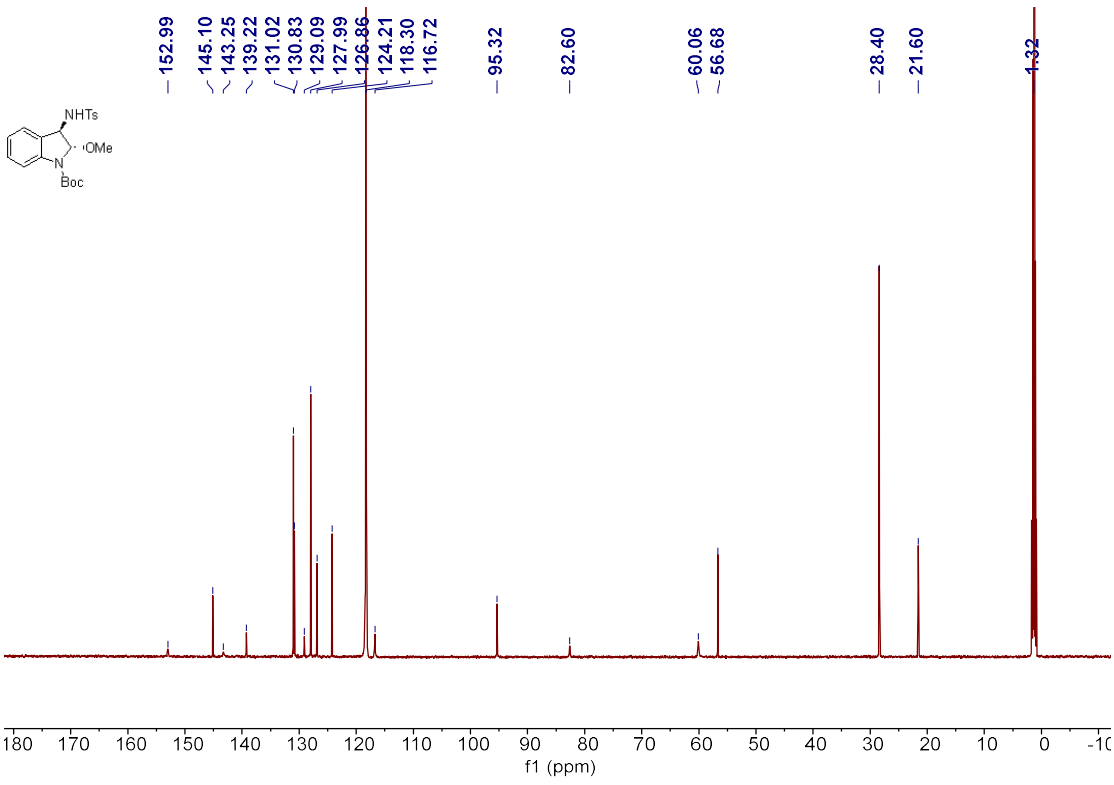
^{13}C NMR (101 MHz) Spectrum of 3 in $CDCl_3$



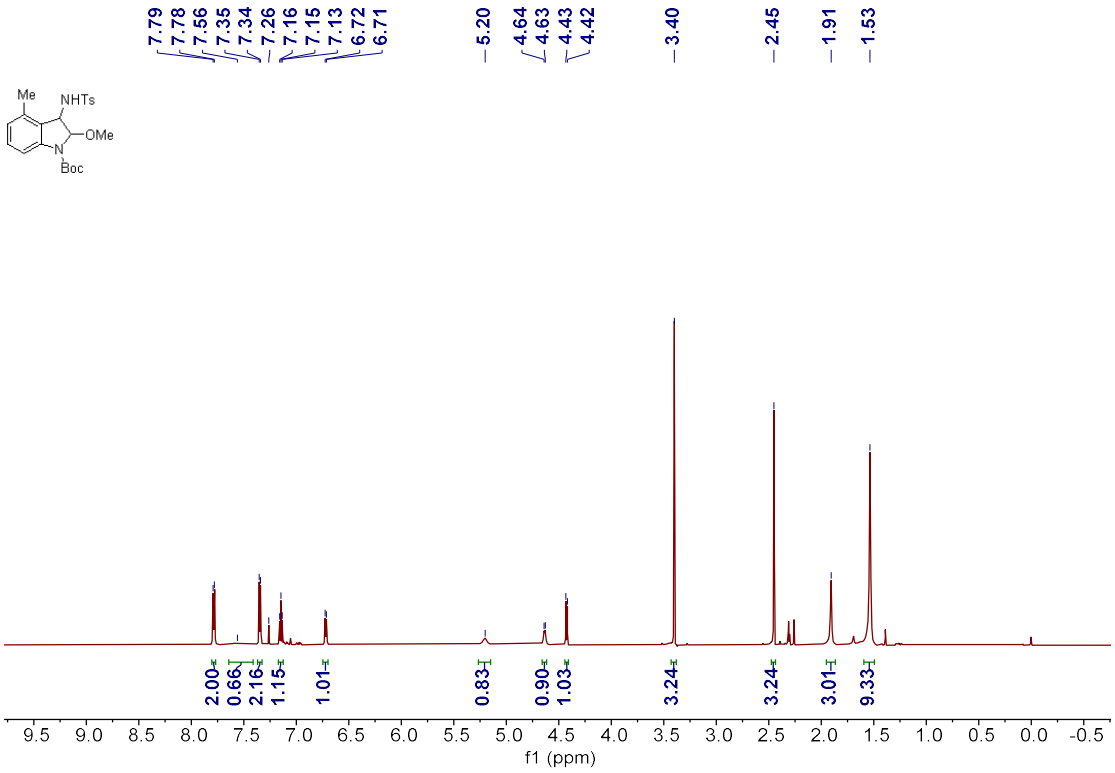
^{1}H NMR (600 MHz) Spectrum of 3 in CD_3CN



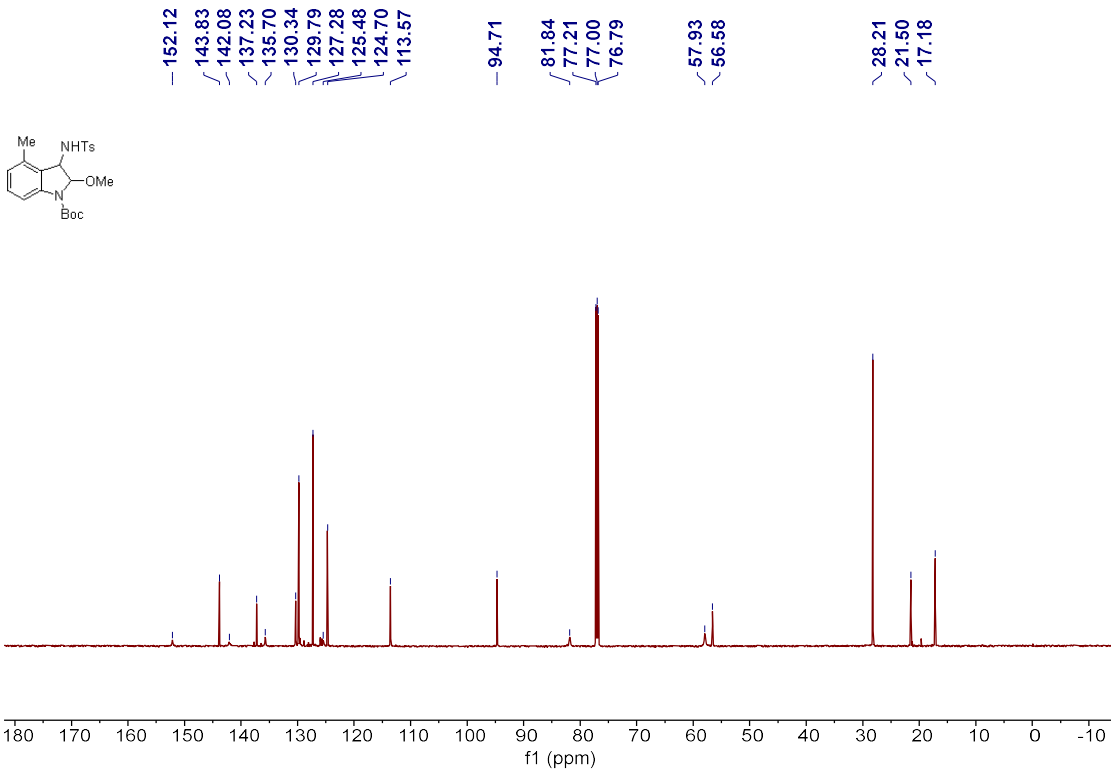
^{13}C NMR (151 MHz) Spectrum of 3 in CD_3CN



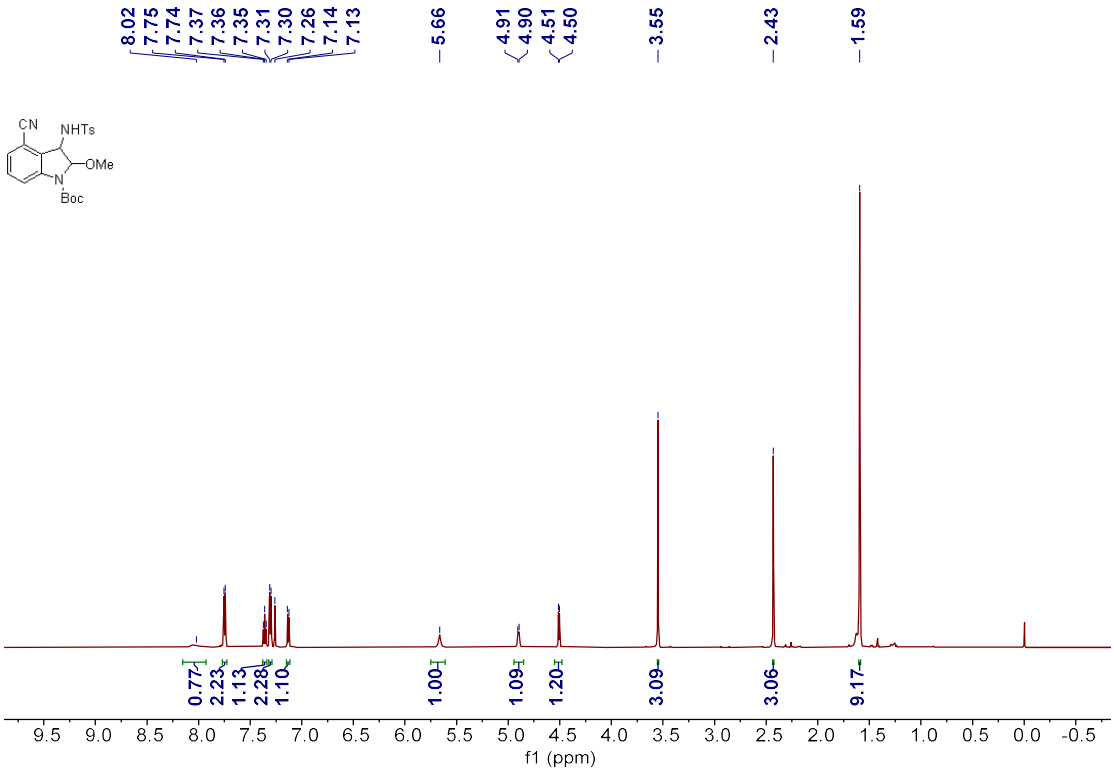
^{1}H NMR (600 MHz) Spectrum of 4 in $CDCl_3$



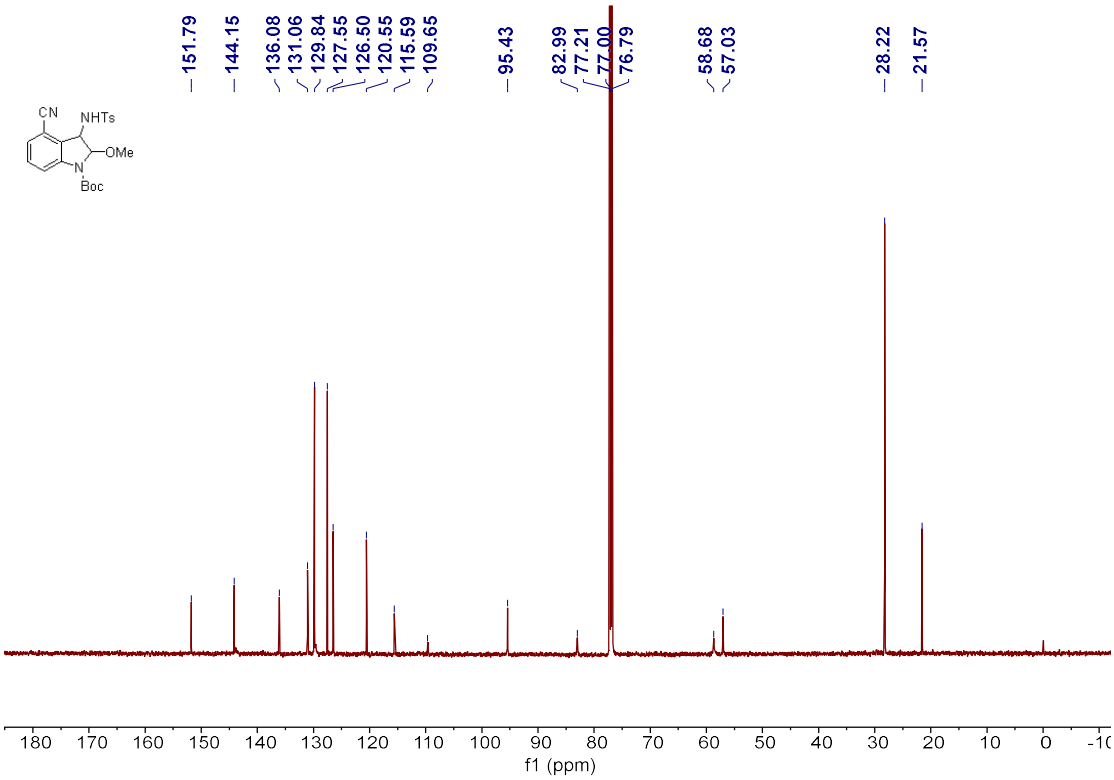
^{13}C NMR (151 MHz) Spectrum of 4 in $CDCl_3$



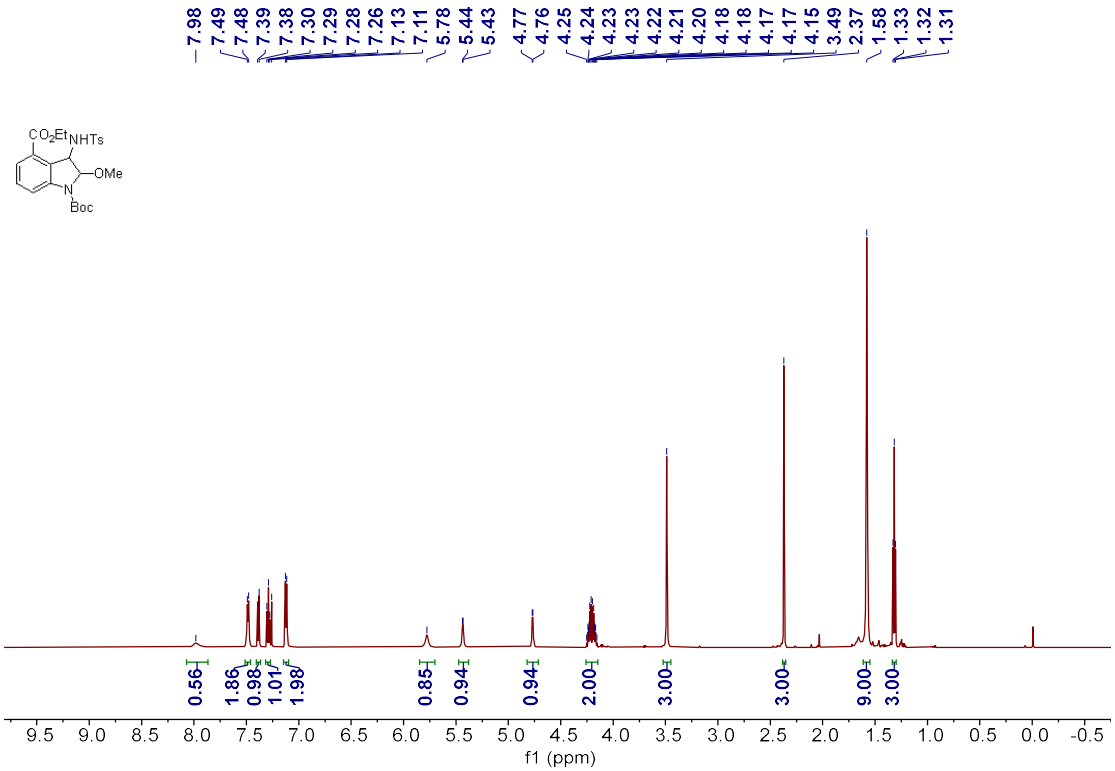
^{1}H NMR (600 MHz) Spectrum of 5 in $CDCl_3$



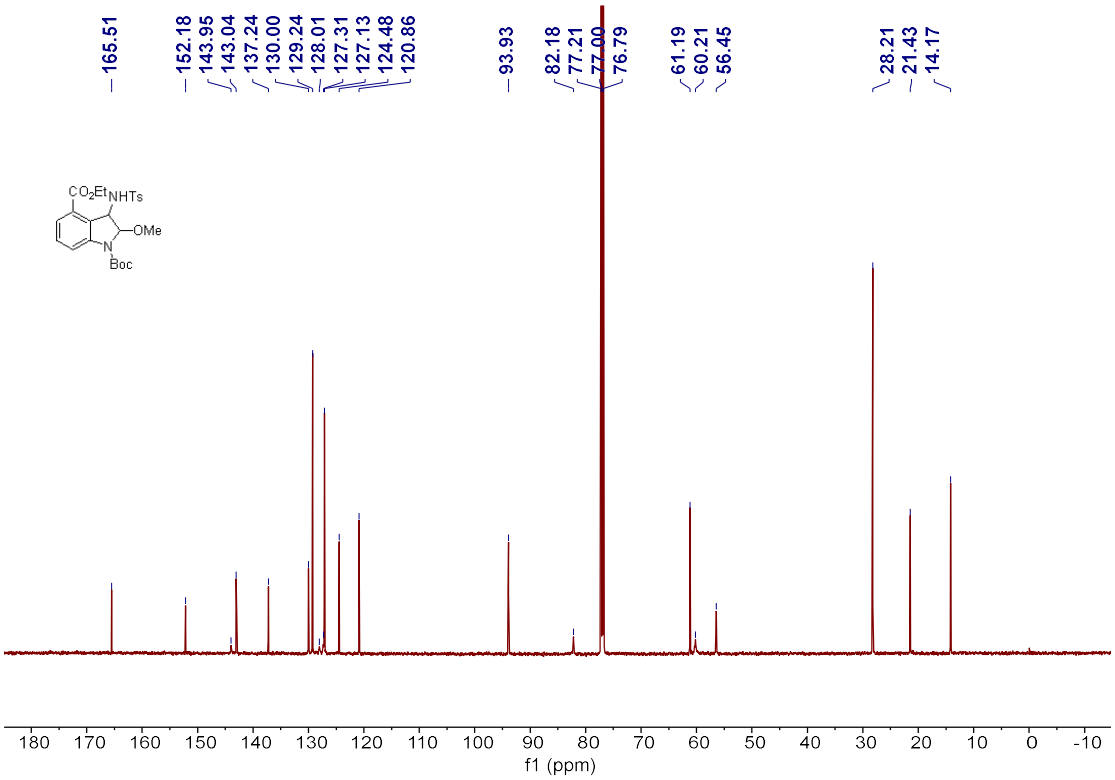
^{13}C NMR (151 MHz) Spectrum of 5 in $CDCl_3$



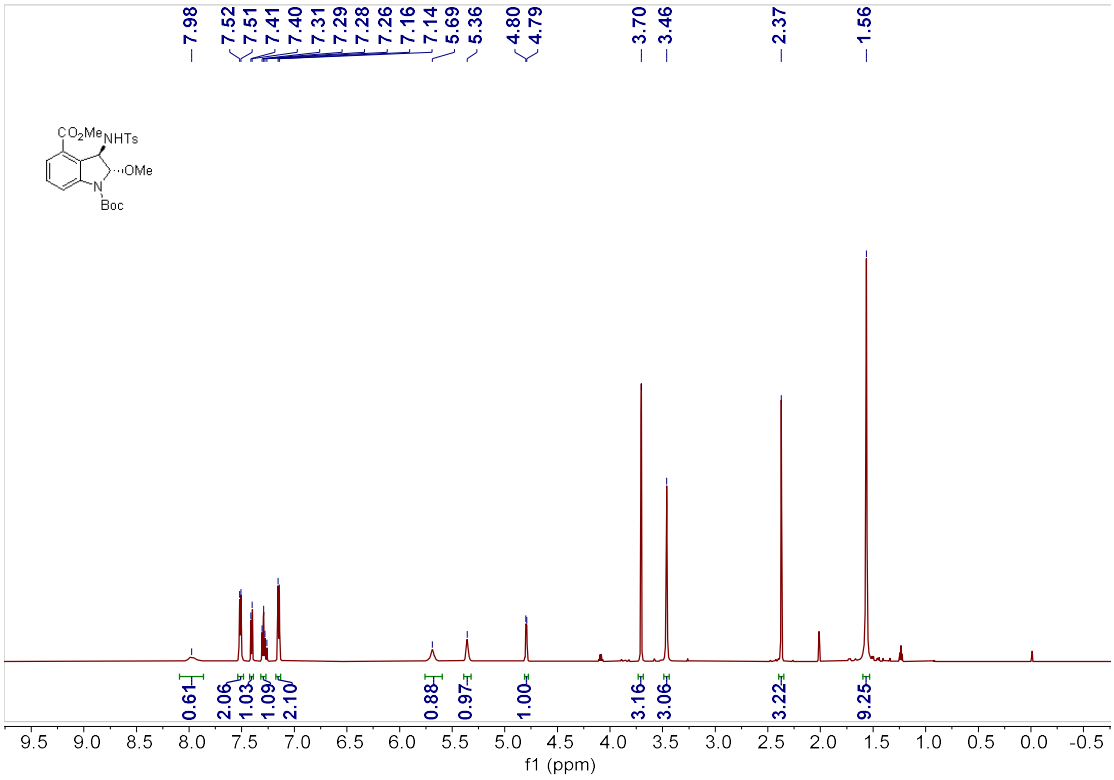
^{1}H NMR (600 MHz) Spectrum of 6 in $CDCl_3$



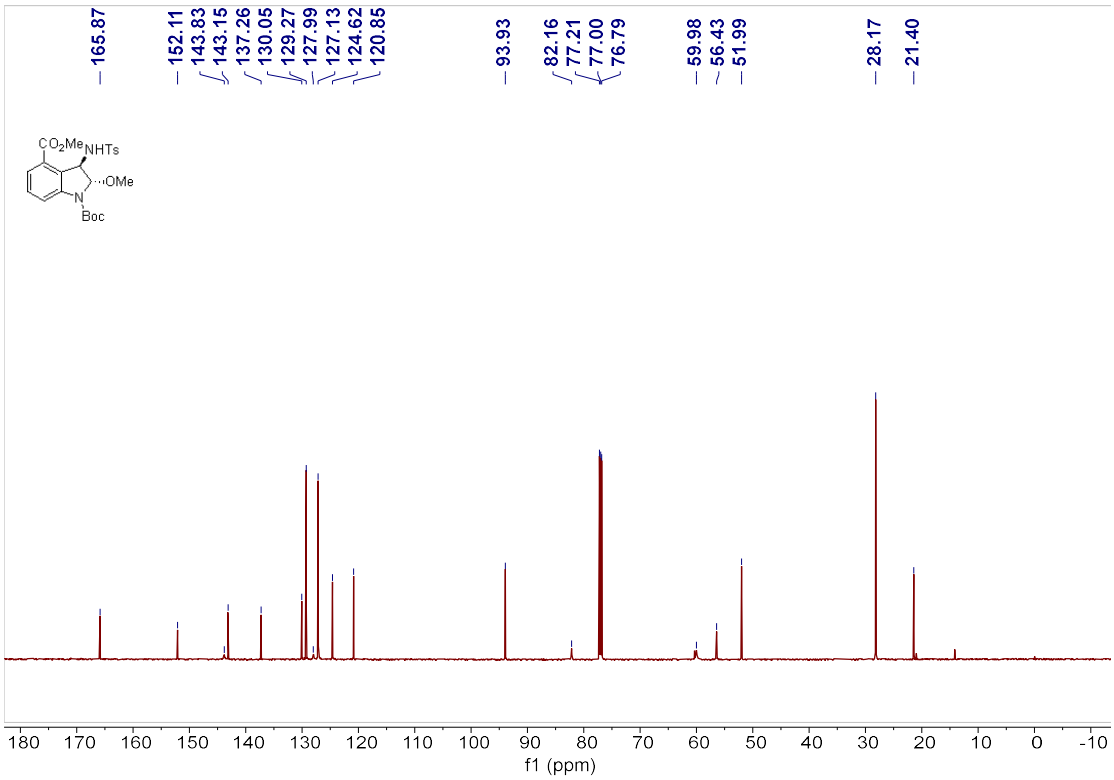
^{13}C NMR (151 MHz) Spectrum of 6 in $CDCl_3$



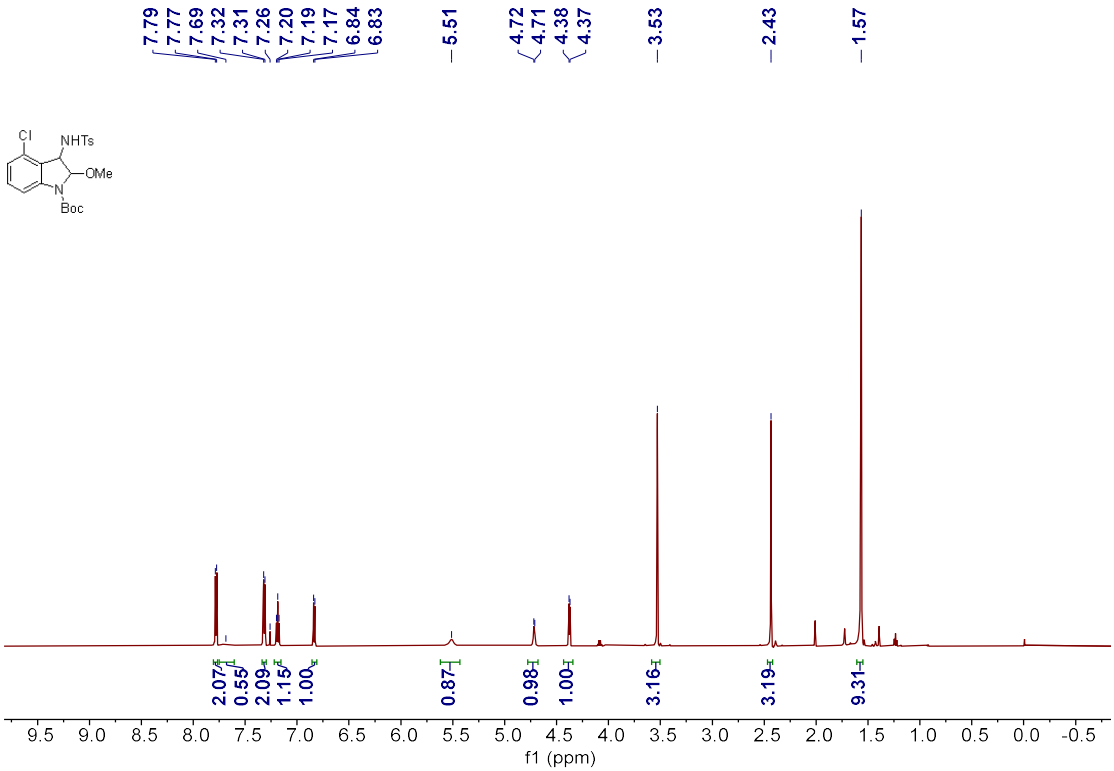
^{1}H NMR (600 MHz) Spectrum of 7 in $CDCl_3$



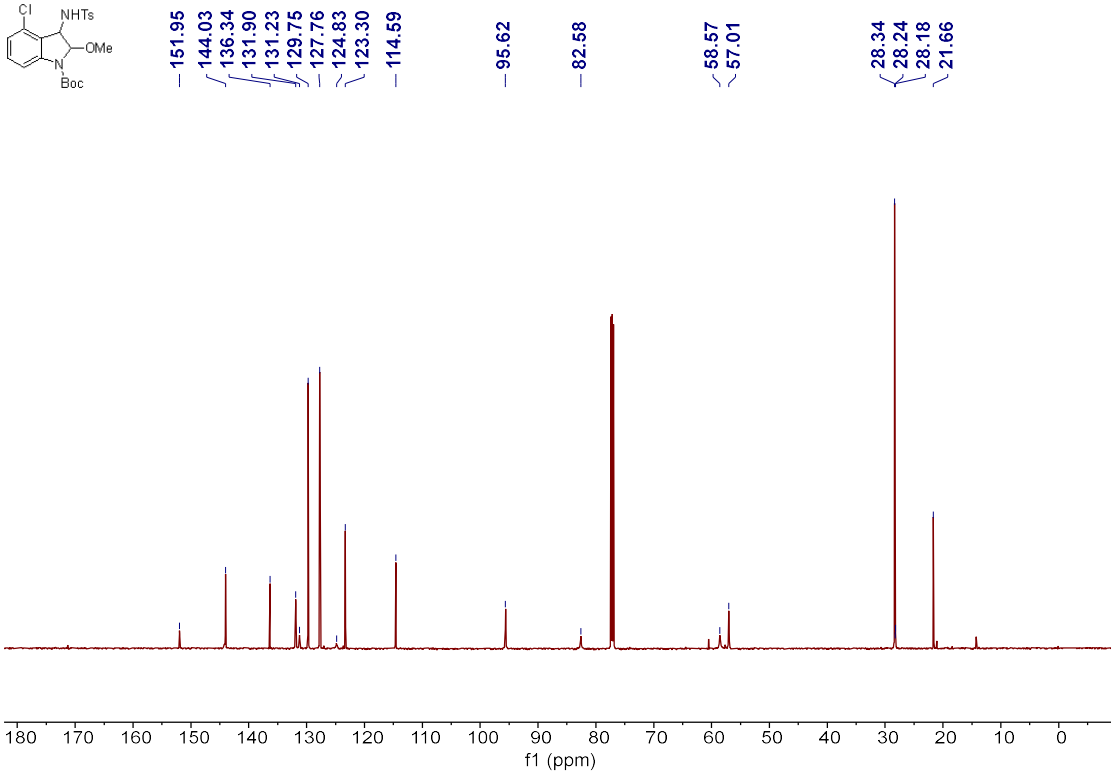
^{13}C NMR (151 MHz) Spectrum of 7 in $CDCl_3$



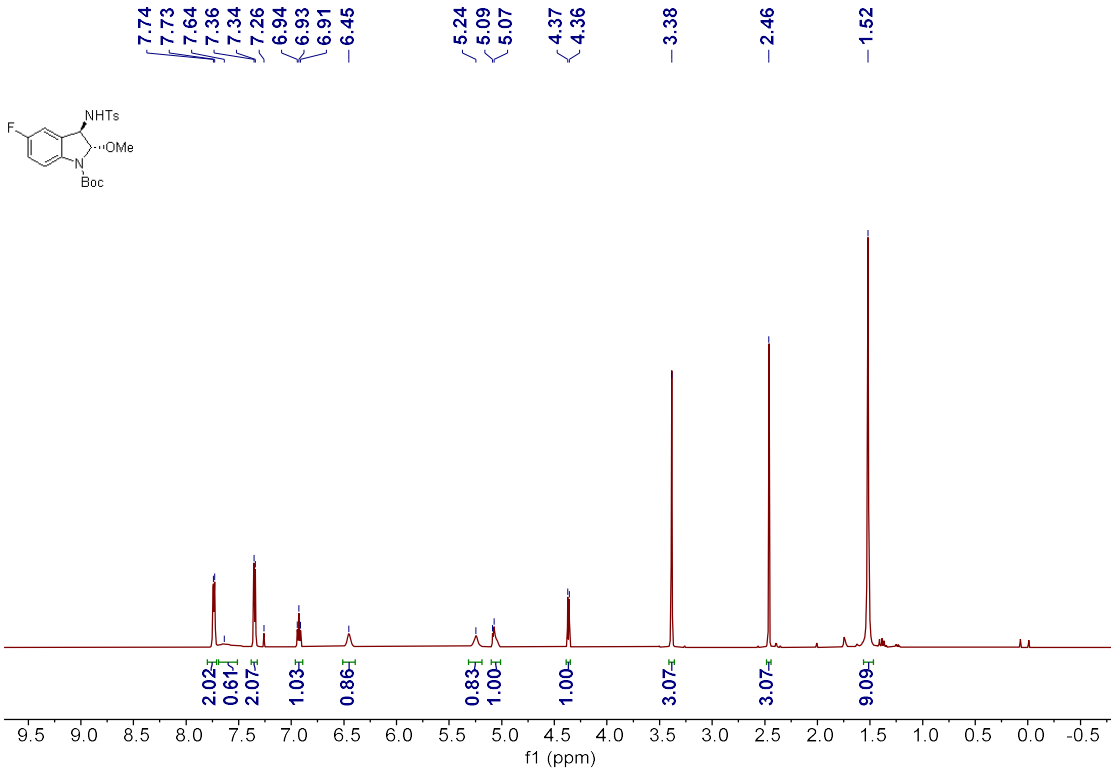
^{1}H NMR (600 MHz) Spectrum of 8 in $CDCl_3$



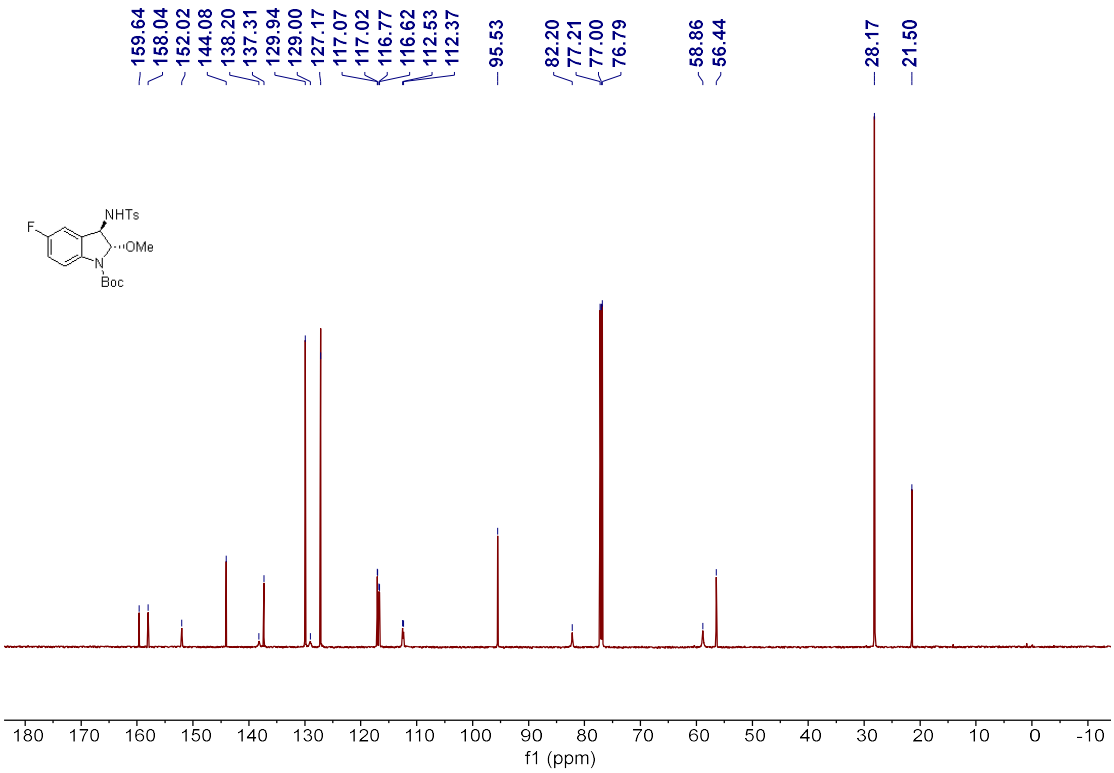
^{13}C NMR (151 MHz) Spectrum of 8 in $CDCl_3$



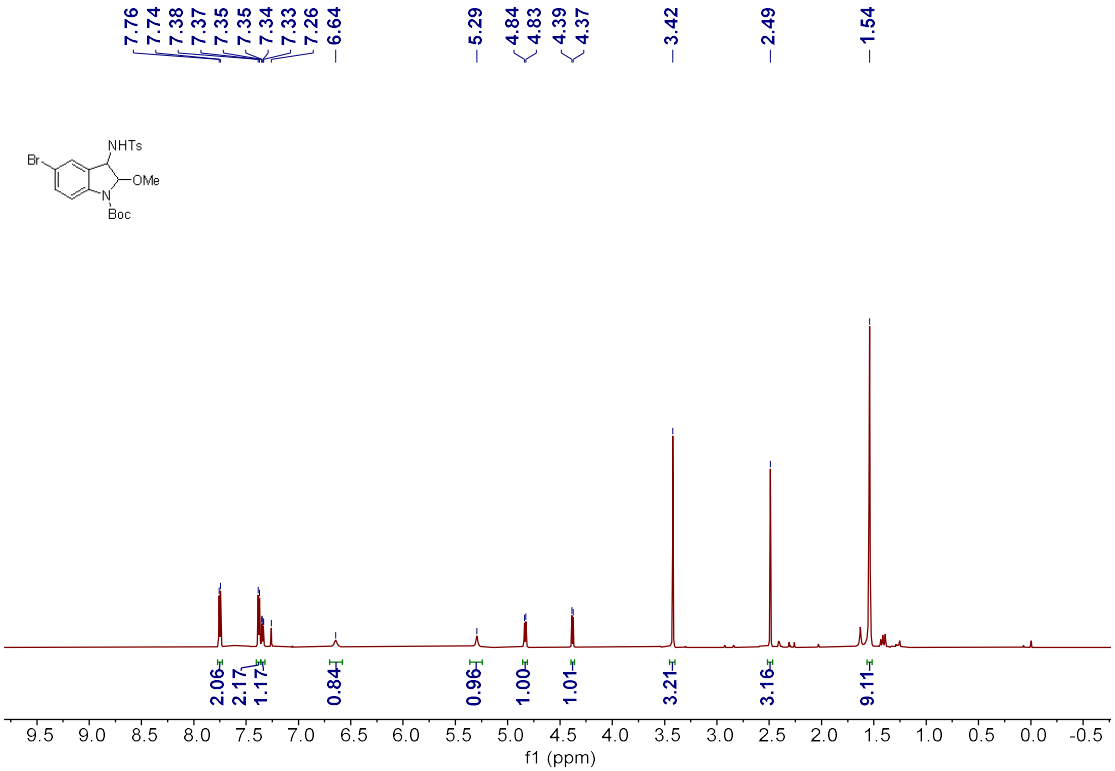
^{1}H NMR (600 MHz) Spectrum of 9 in $CDCl_3$



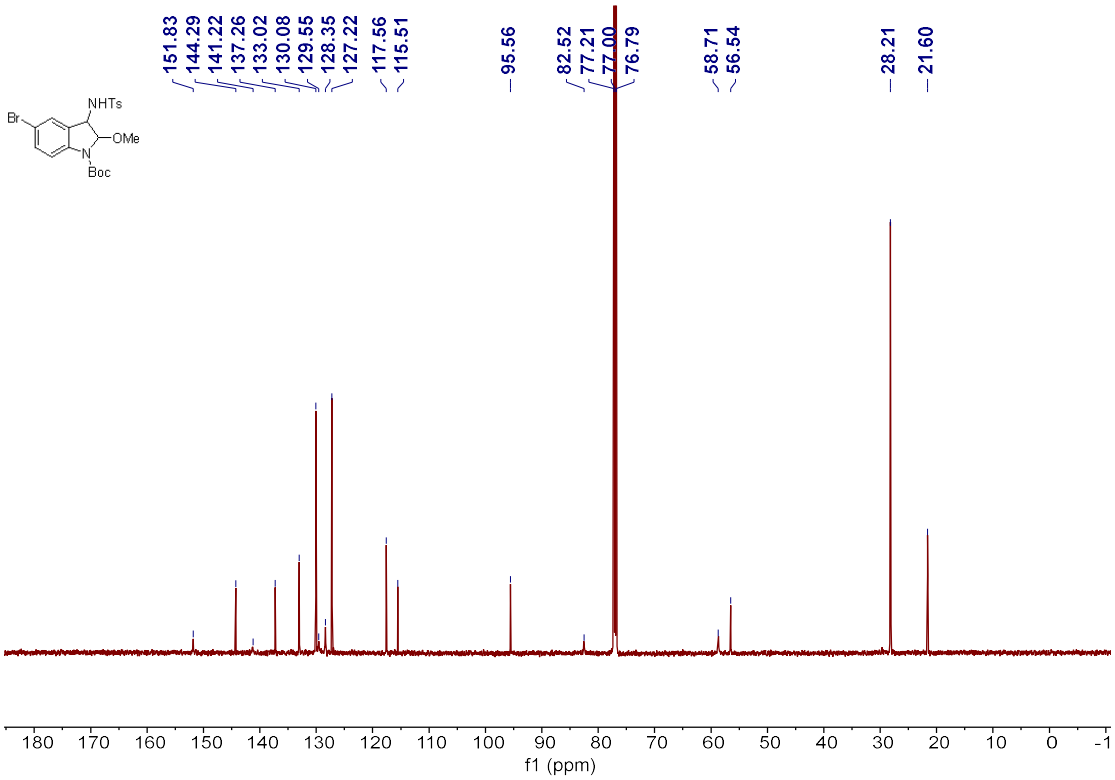
^{13}C NMR (151 MHz) Spectrum of 9 in $CDCl_3$



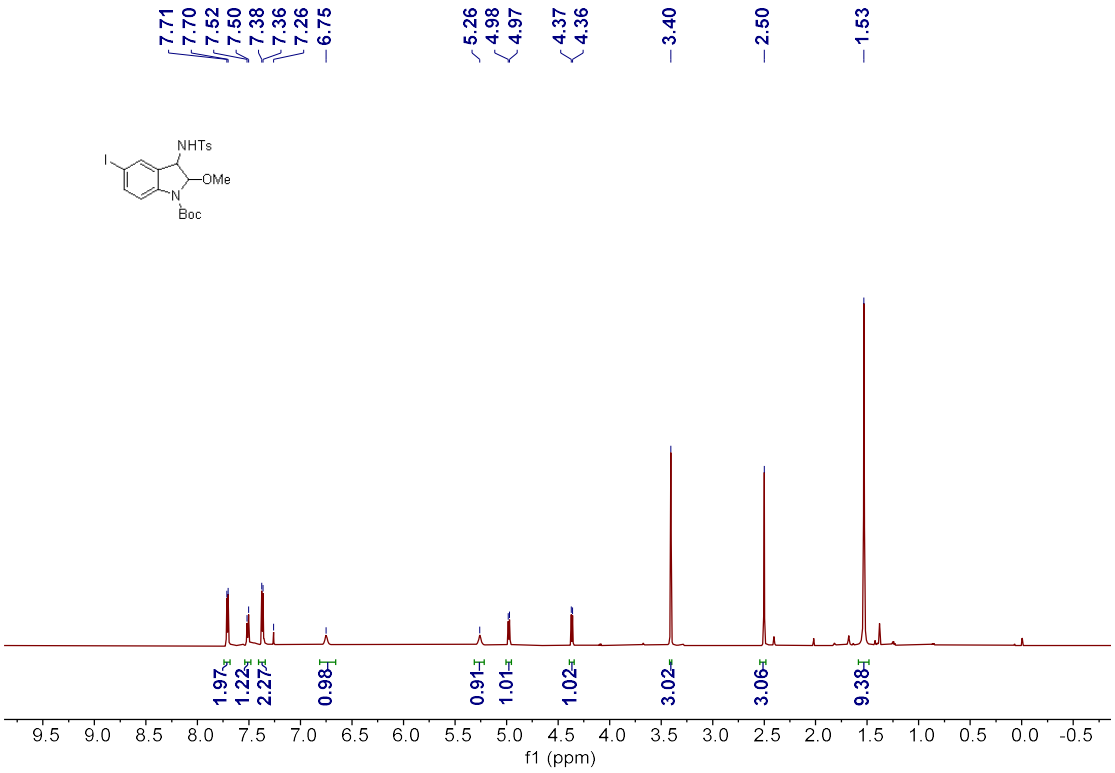
^{1}H NMR (600 MHz) Spectrum of 10 in $CDCl_3$



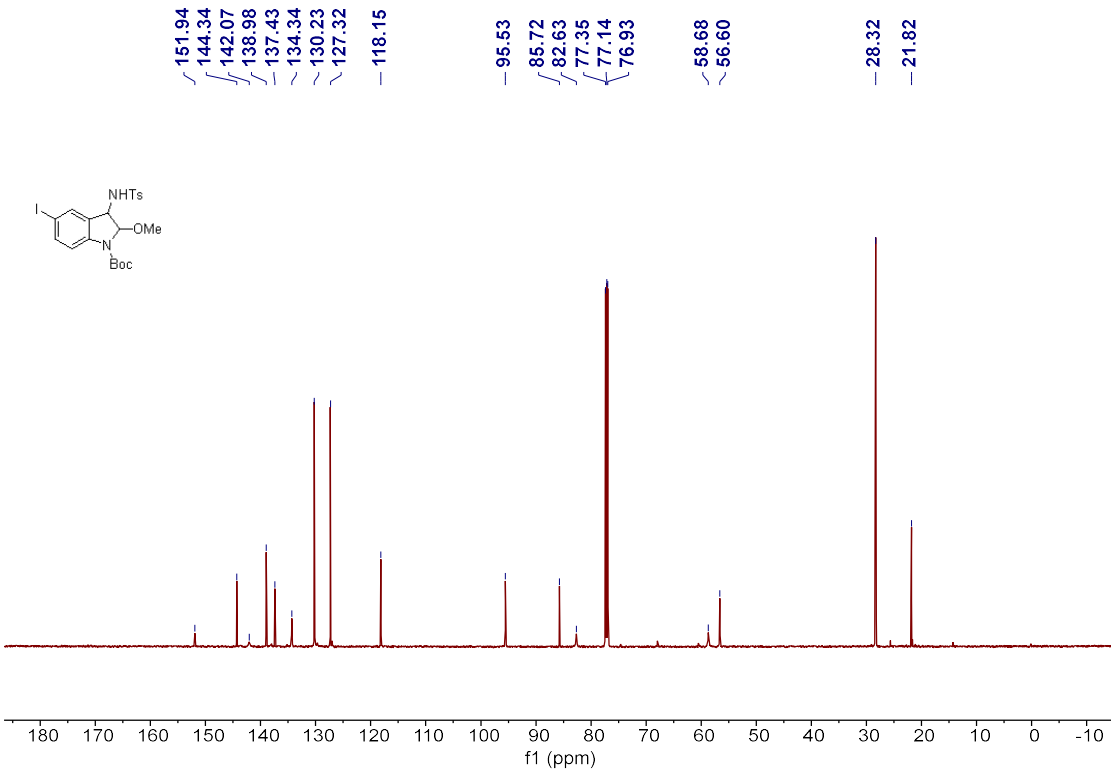
^{13}C NMR (151 MHz) Spectrum of 10 in $CDCl_3$



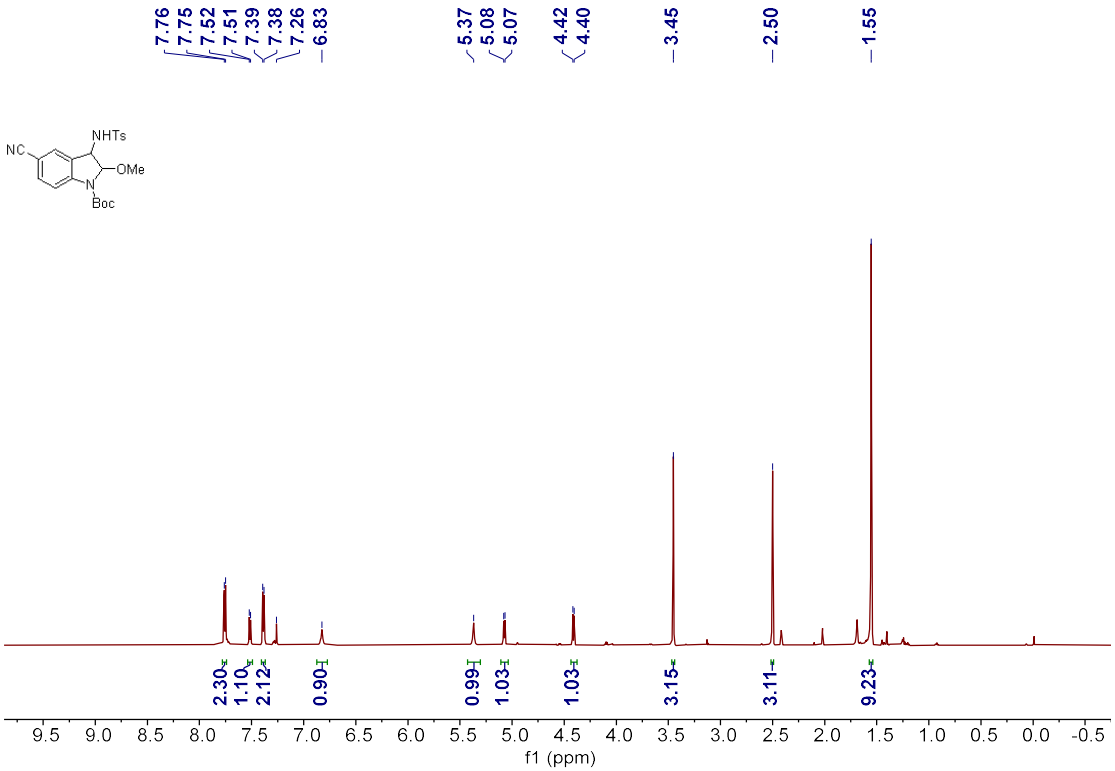
^{1}H NMR (600 MHz) Spectrum of 11 in $CDCl_3$



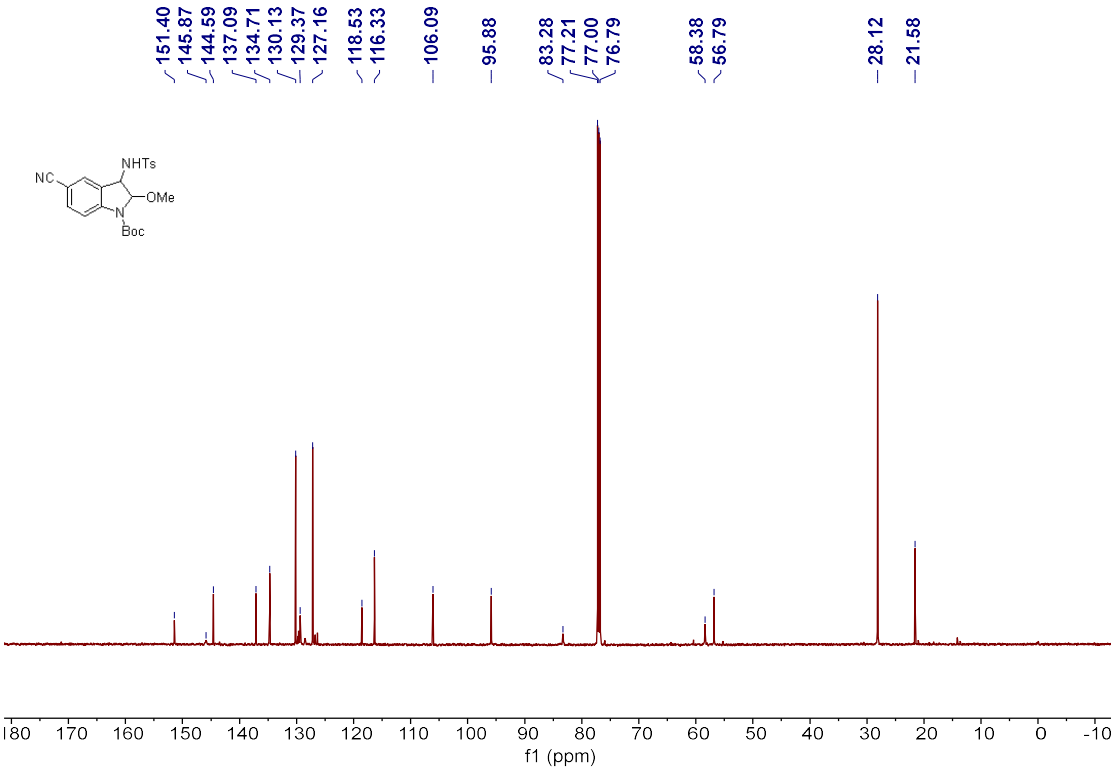
^{13}C NMR (151 MHz) Spectrum of 11 in $CDCl_3$



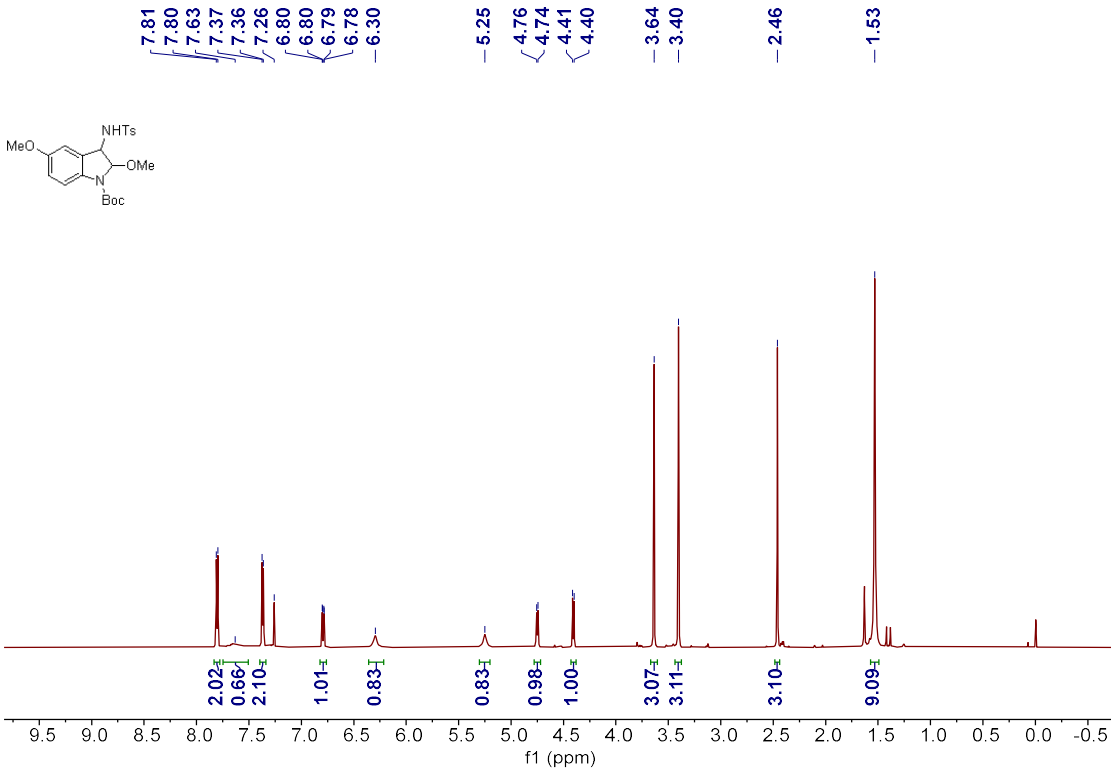
^{1}H NMR (600 MHz) Spectrum of 12 in $CDCl_3$



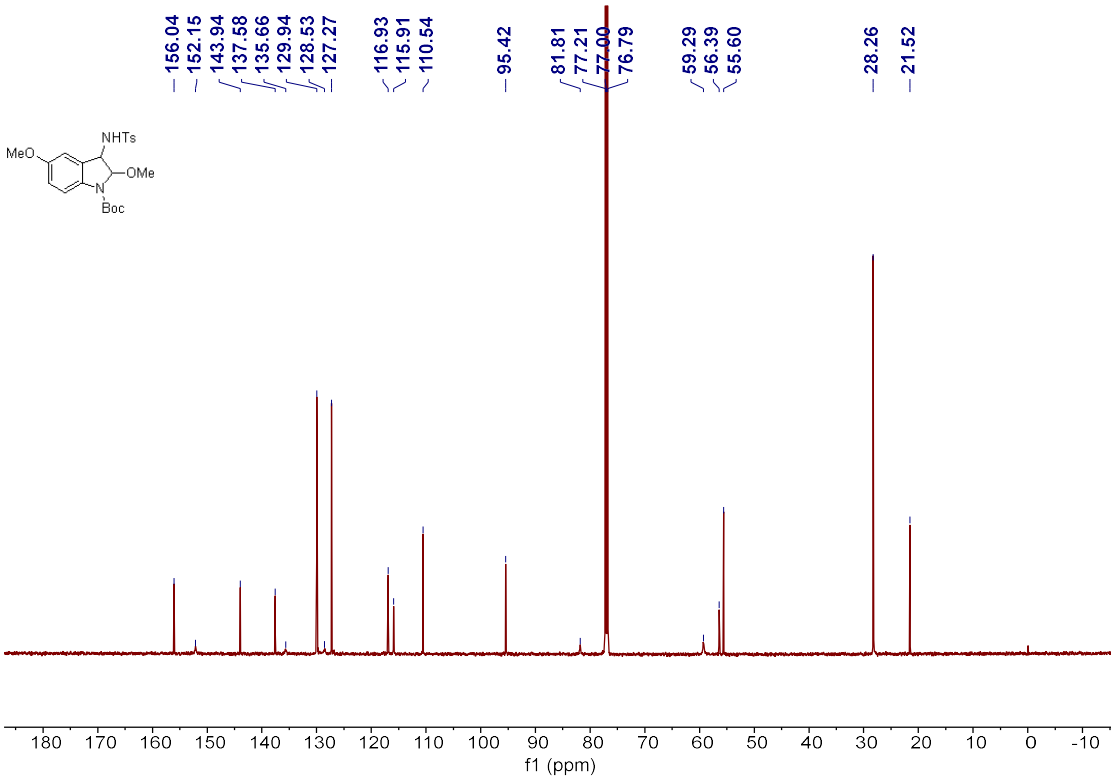
^{13}C NMR (151 MHz) Spectrum of 12 in $CDCl_3$



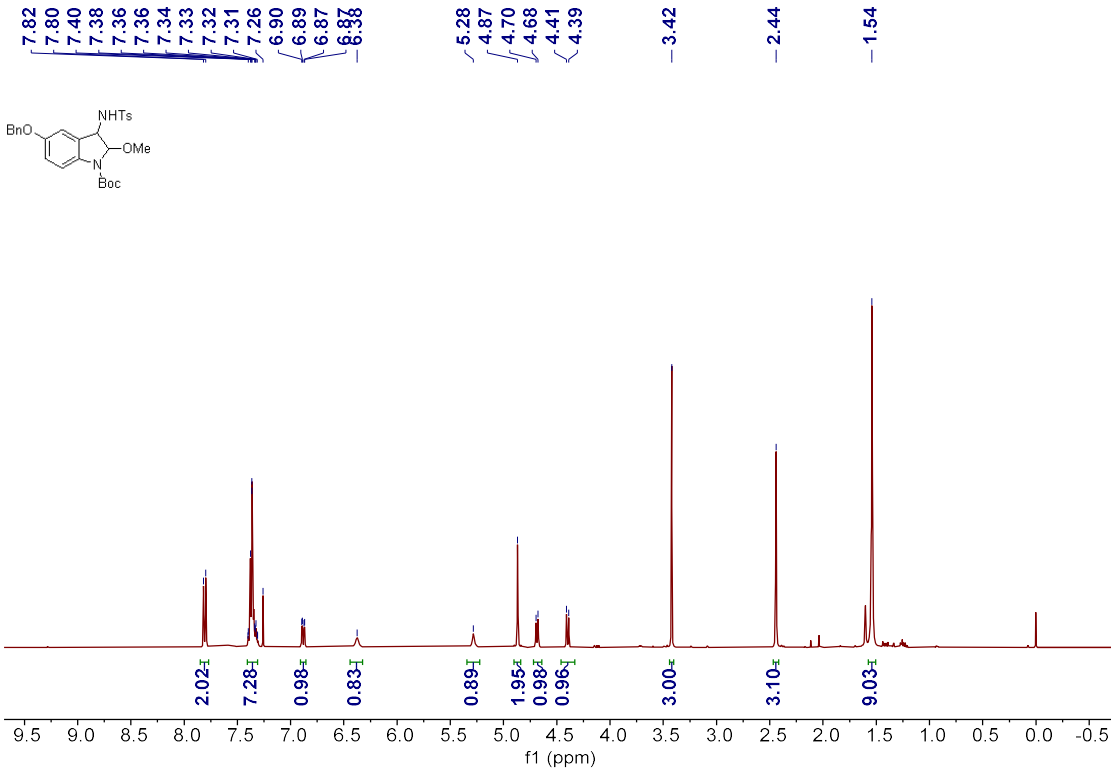
^{1}H NMR (600 MHz) Spectrum of 13 in $CDCl_3$



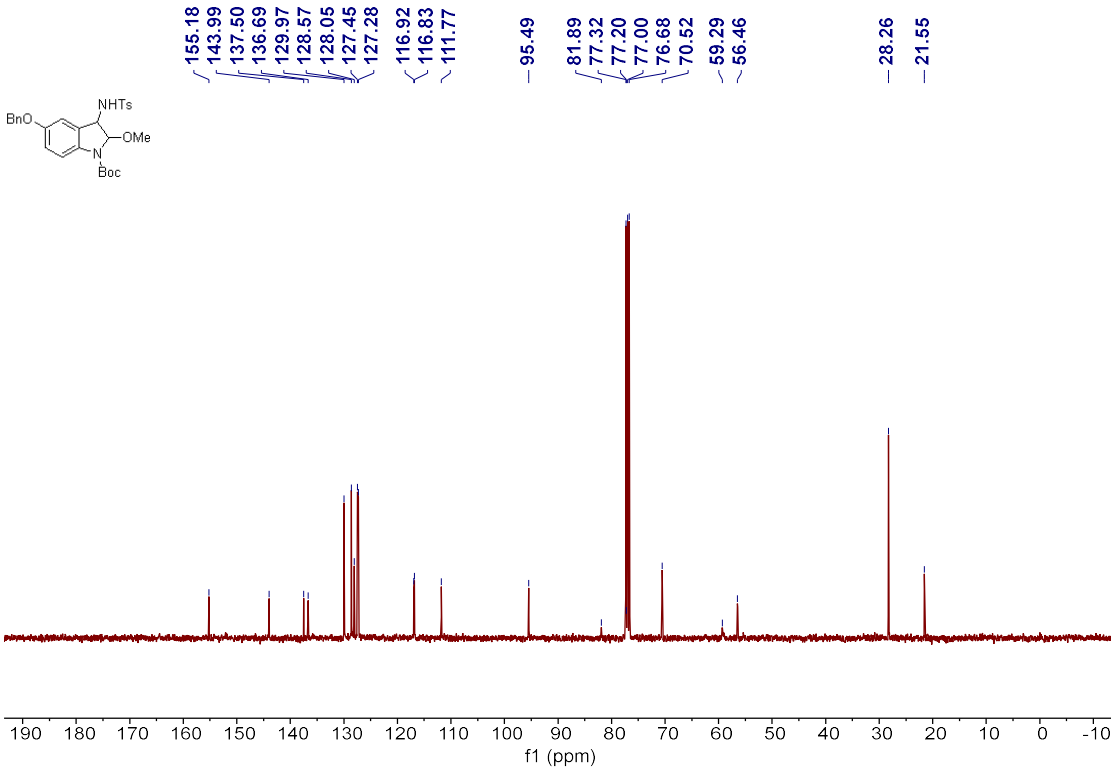
^{13}C NMR (151 MHz) Spectrum of 13 in $CDCl_3$



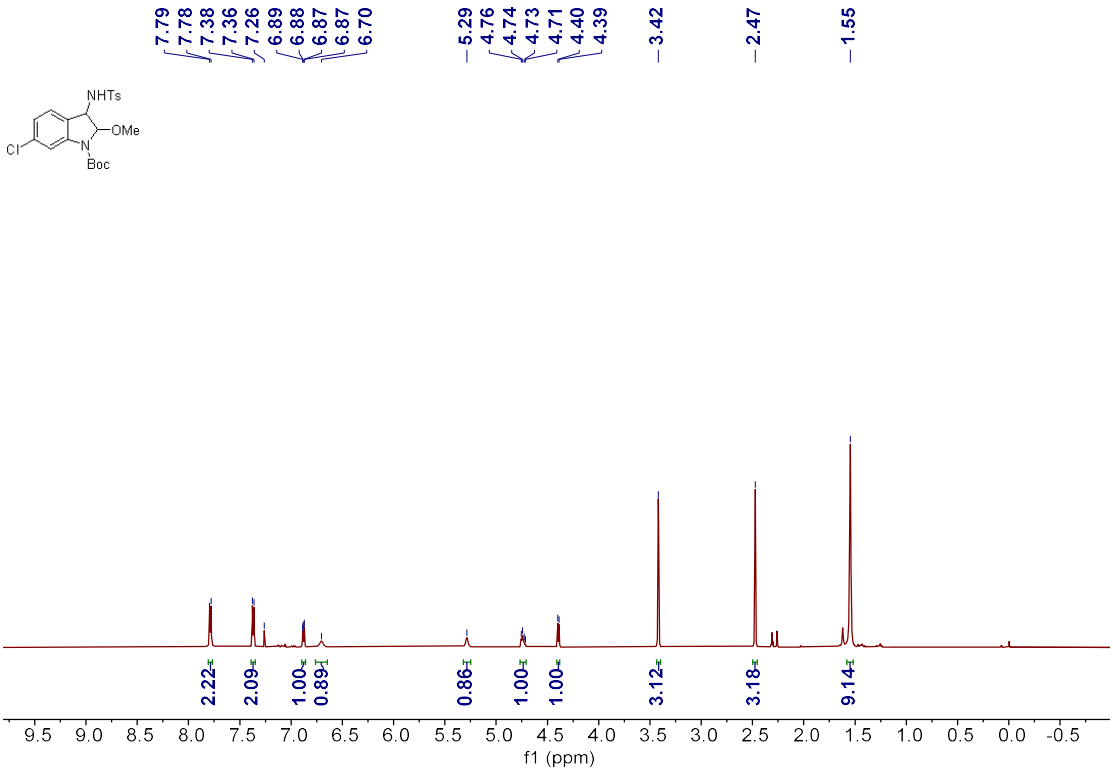
^{1}H NMR (400 MHz) Spectrum of 14 in $CDCl_3$



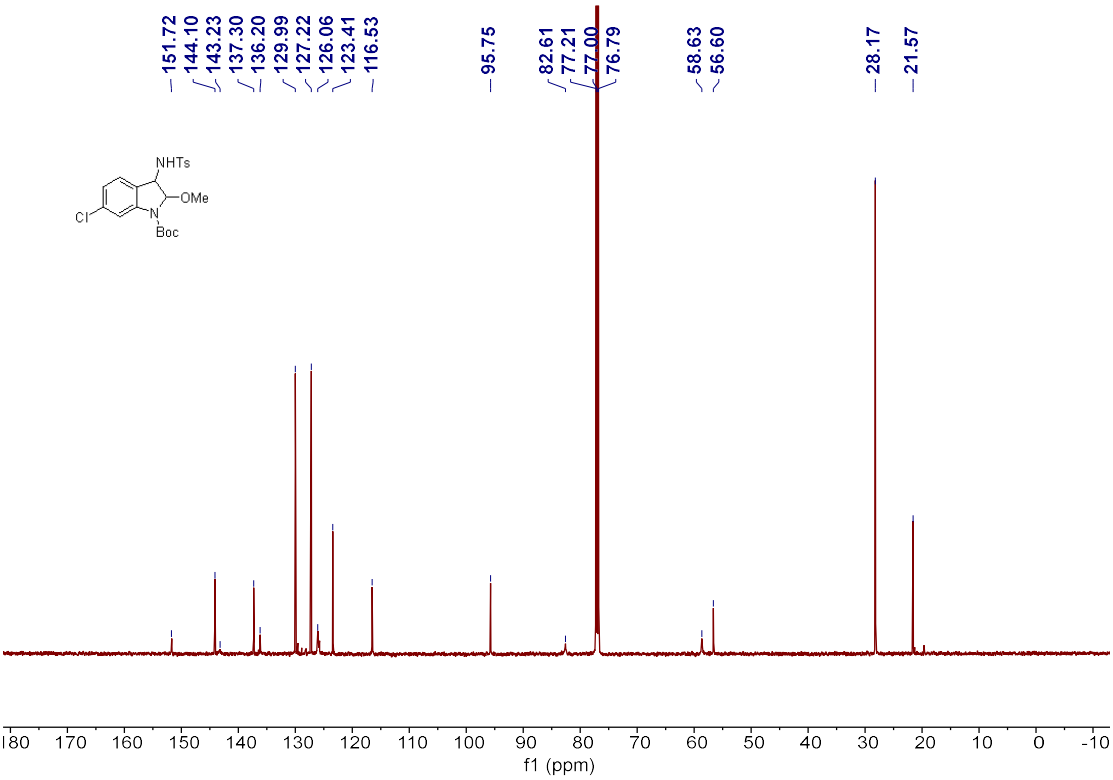
^{13}C NMR (101 MHz) Spectrum of 14 in $CDCl_3$



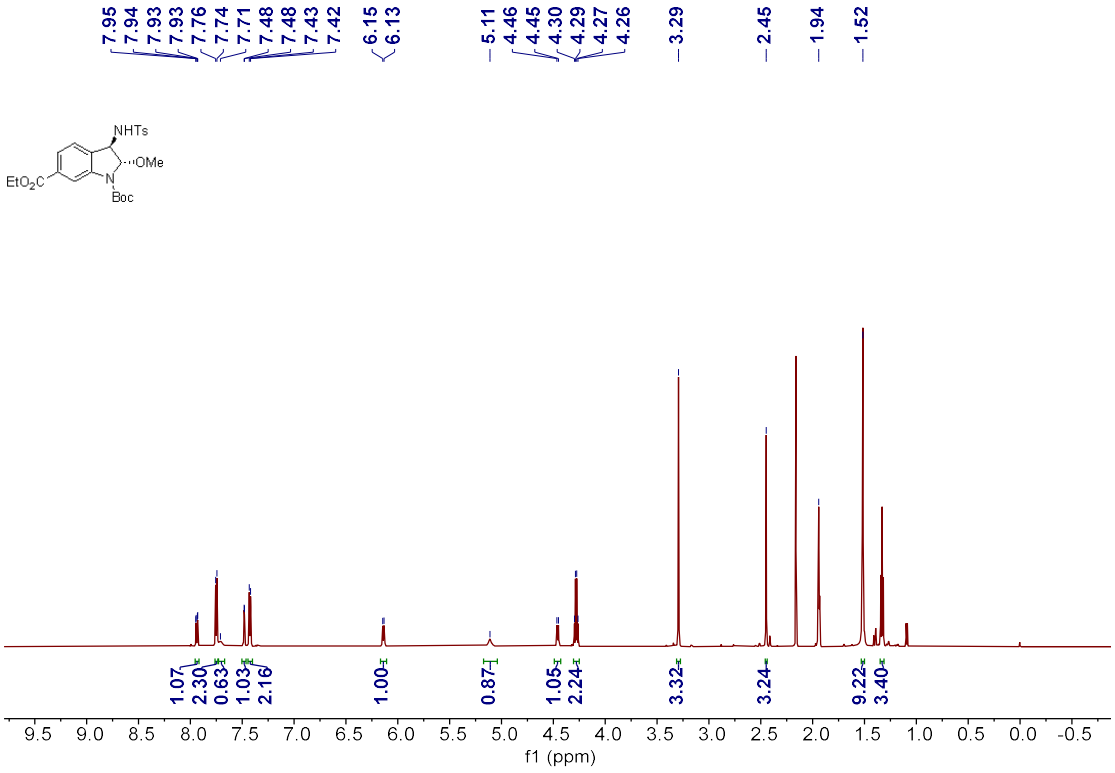
^{1}H NMR (600 MHz) Spectrum of 15 in $CDCl_3$



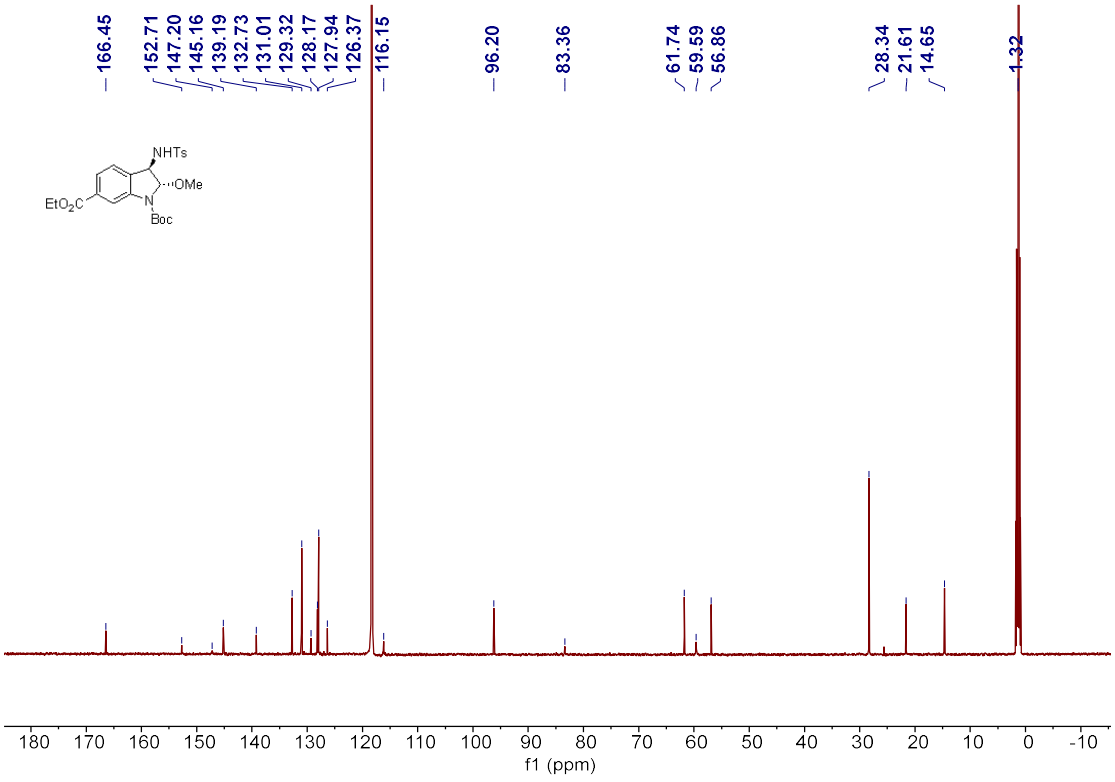
^{13}C NMR (151 MHz) Spectrum of 15 in $CDCl_3$



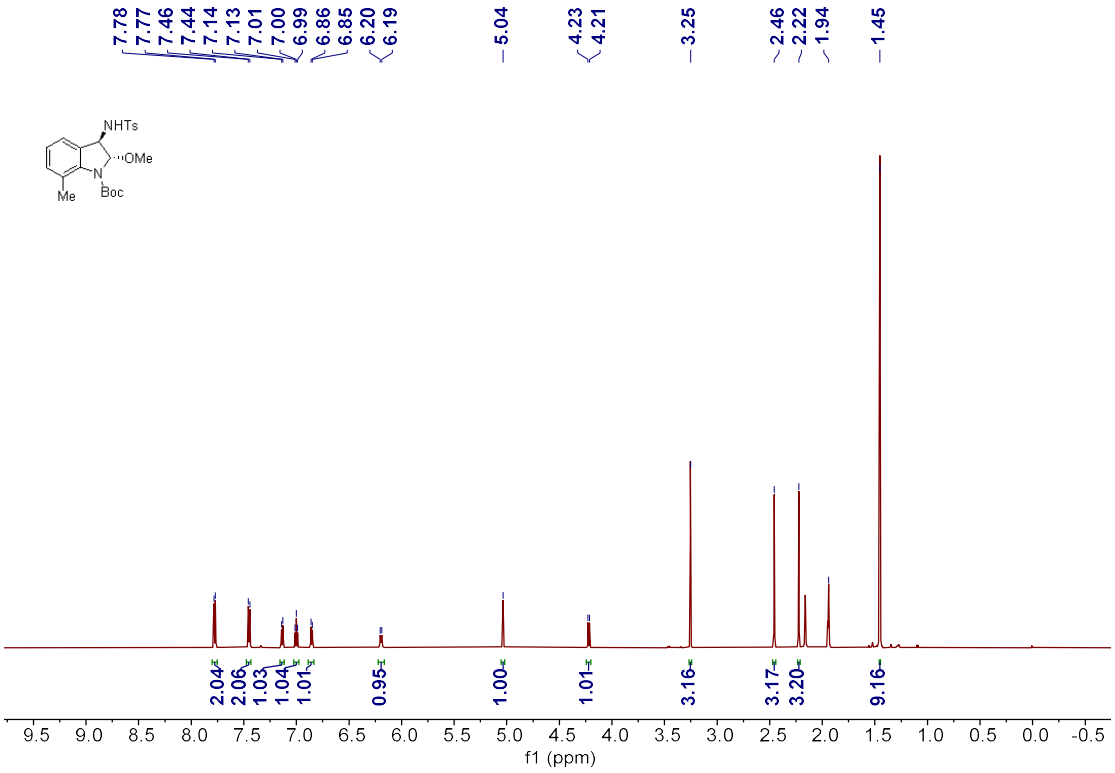
^{1}H NMR (600 MHz) Spectrum of 16 in CD_3CN



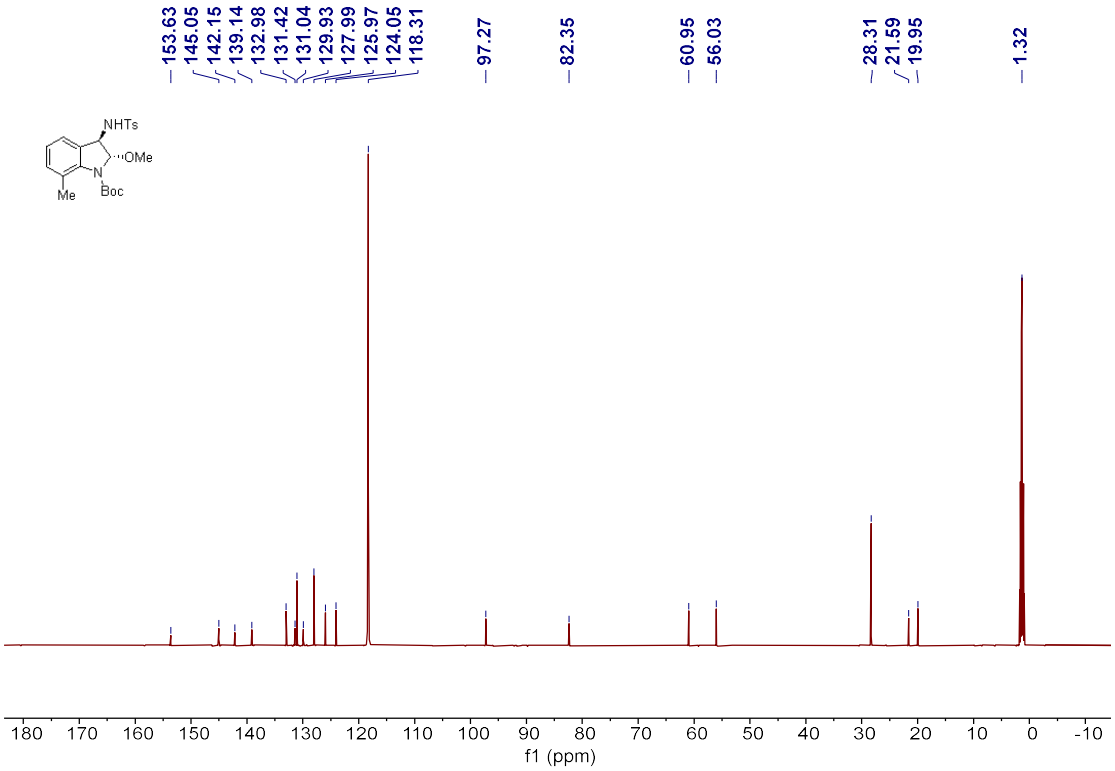
^{13}C NMR (151 MHz) Spectrum of 16 in CD_3CN



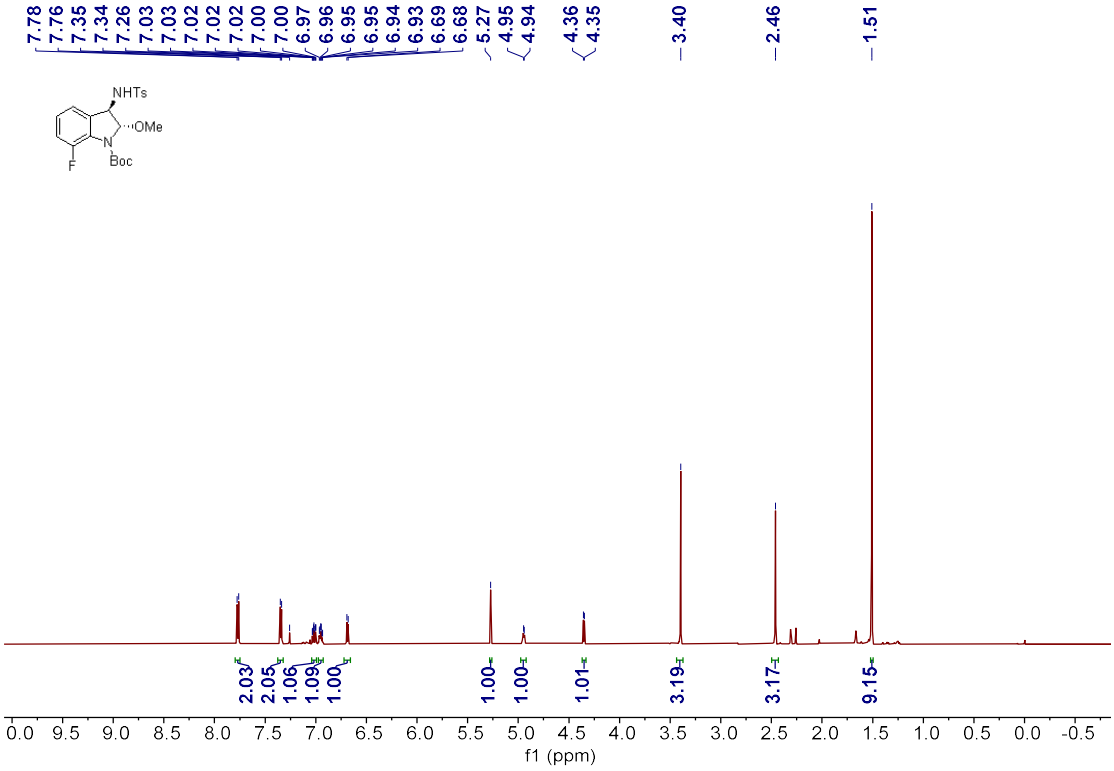
^{1}H NMR (600 MHz) Spectrum of 17 in CD_3CN



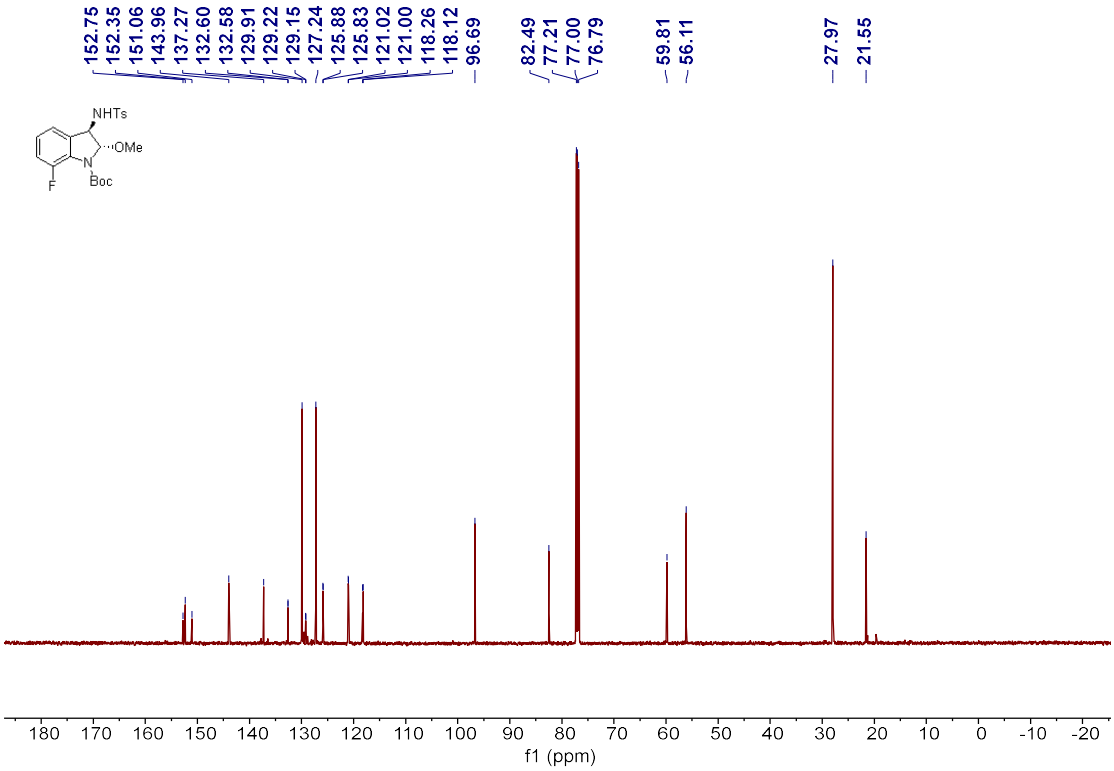
^{13}C NMR (151 MHz) Spectrum of 17 in CD_3CN



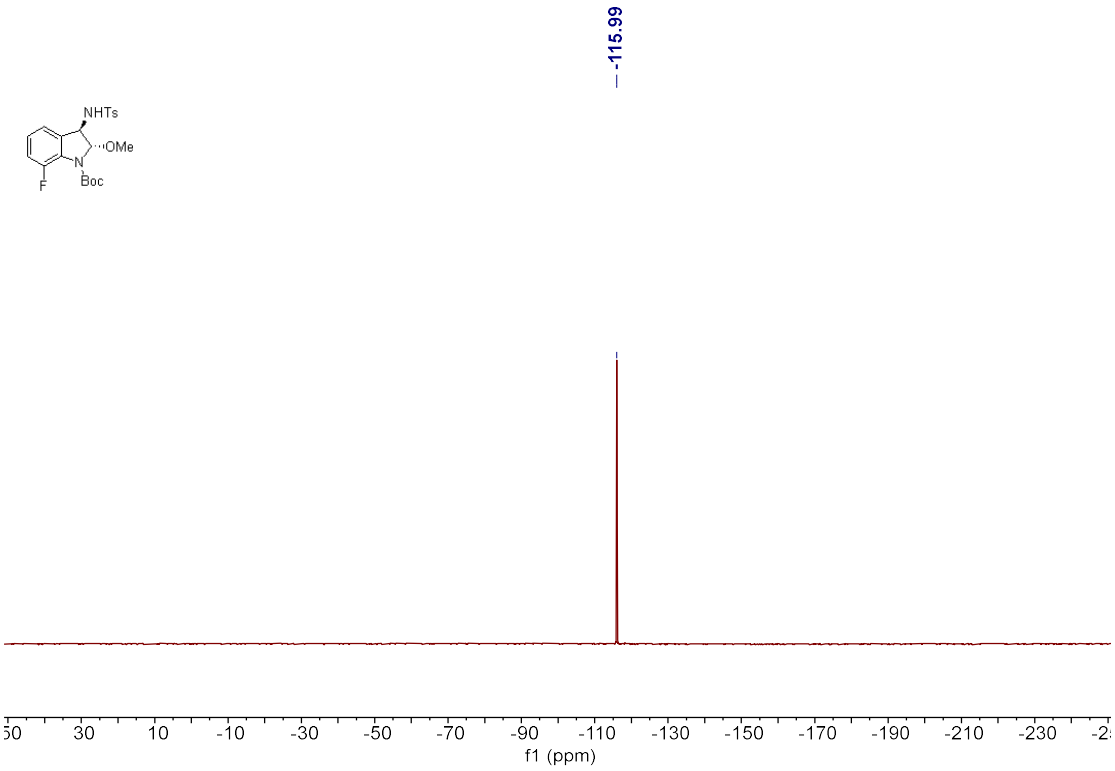
^{1}H NMR (600 MHz) Spectrum of 18 in $CDCl_3$



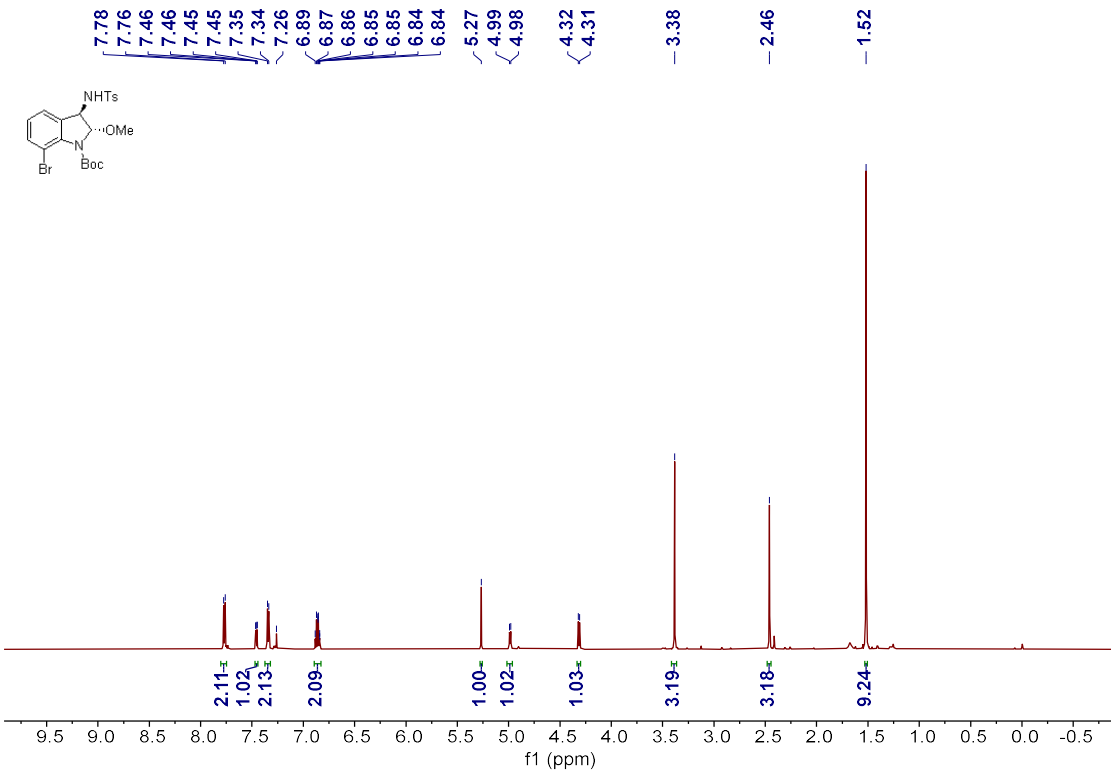
^{13}C NMR (151 MHz) Spectrum of 18 in $CDCl_3$



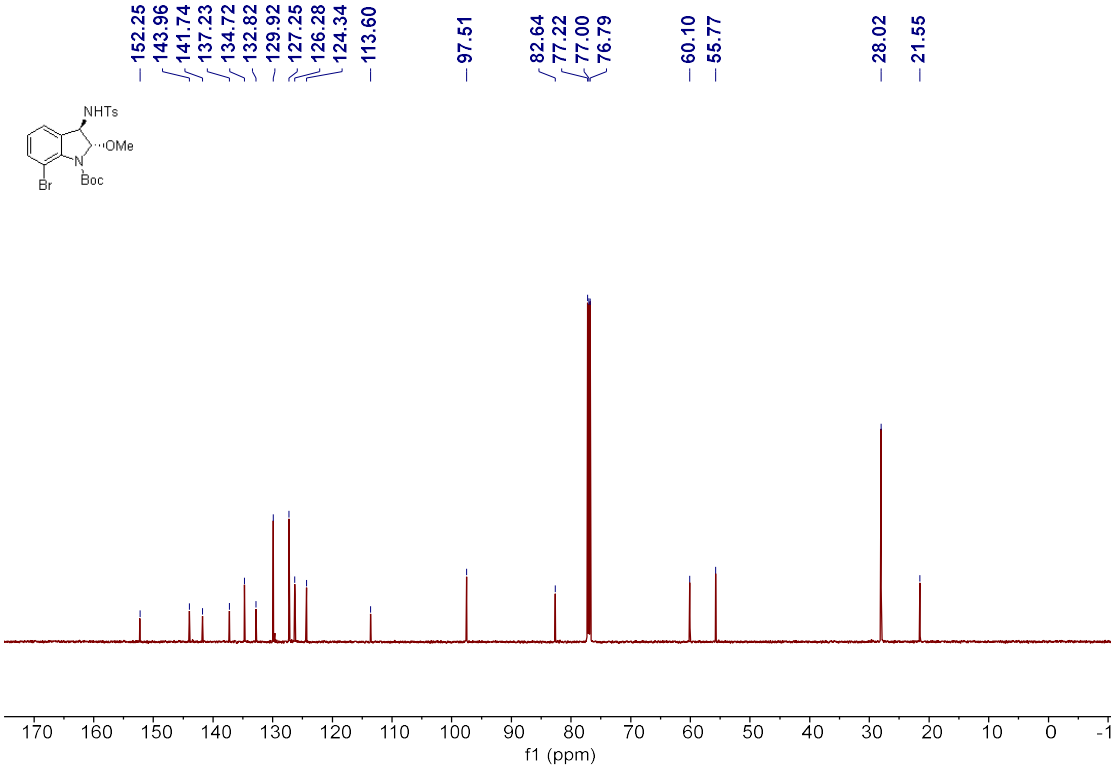
^{19}F NMR (376 MHz) Spectrum of 18 in $CDCl_3$



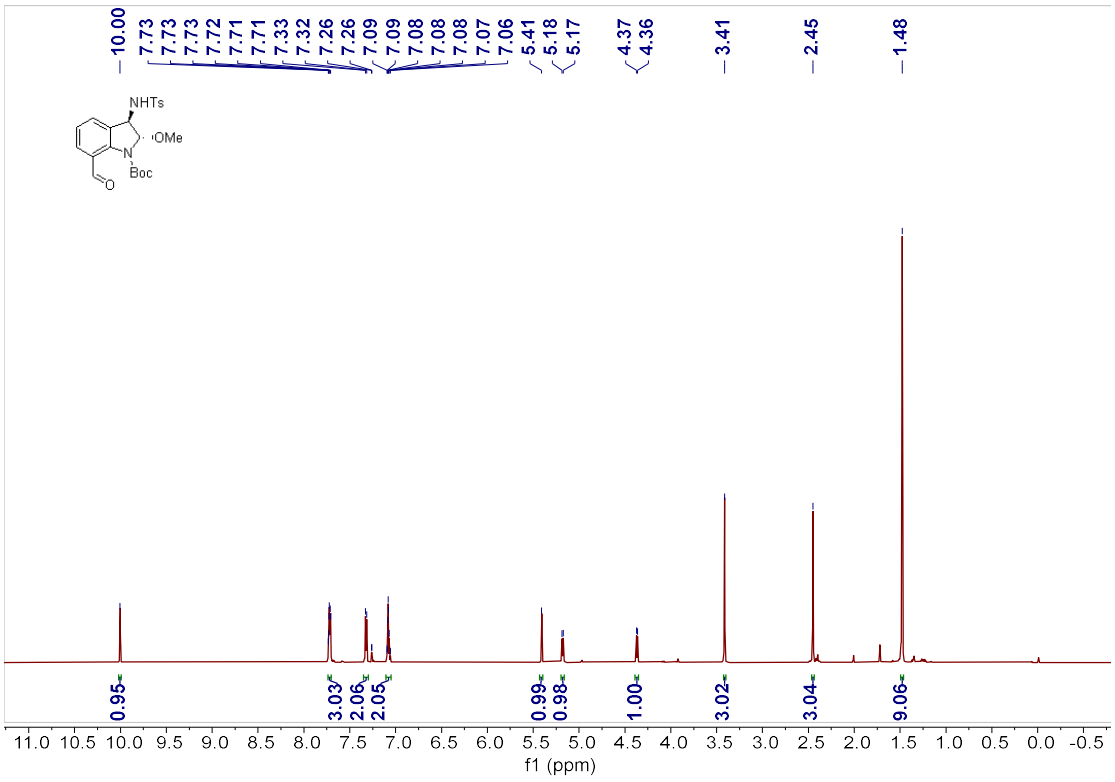
^{1}H NMR (600 MHz) Spectrum of 19 in $CDCl_3$



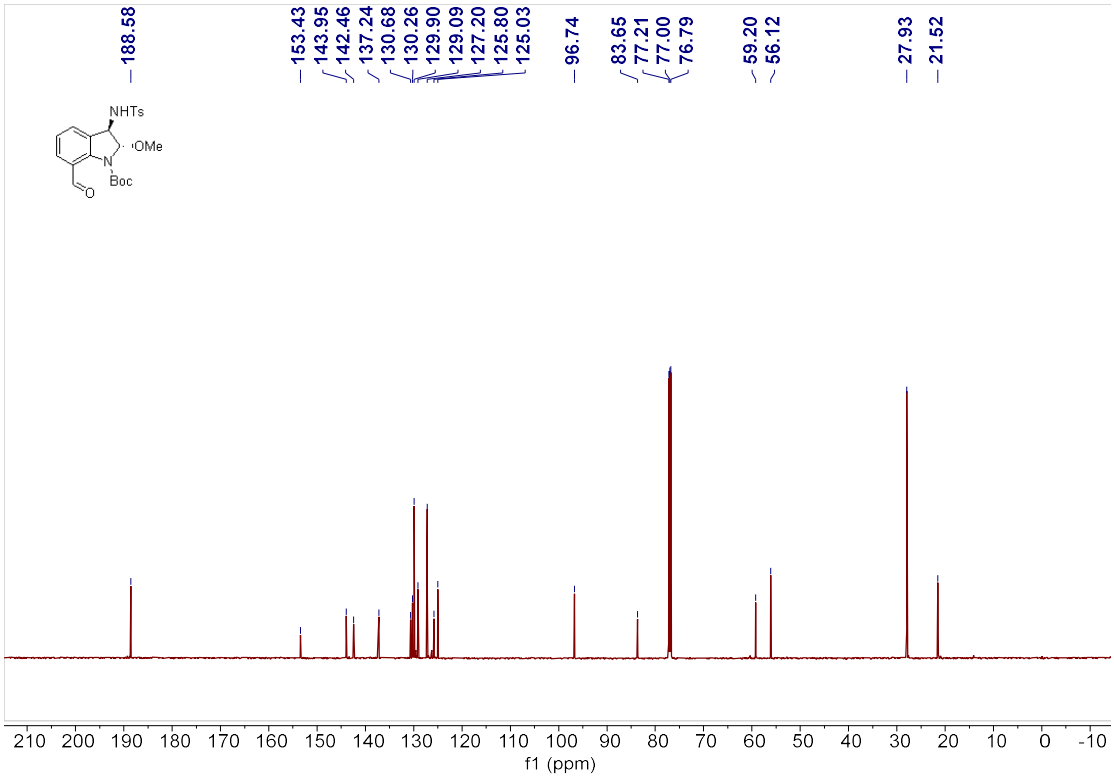
^{13}C NMR (151 MHz) Spectrum of 19 in $CDCl_3$



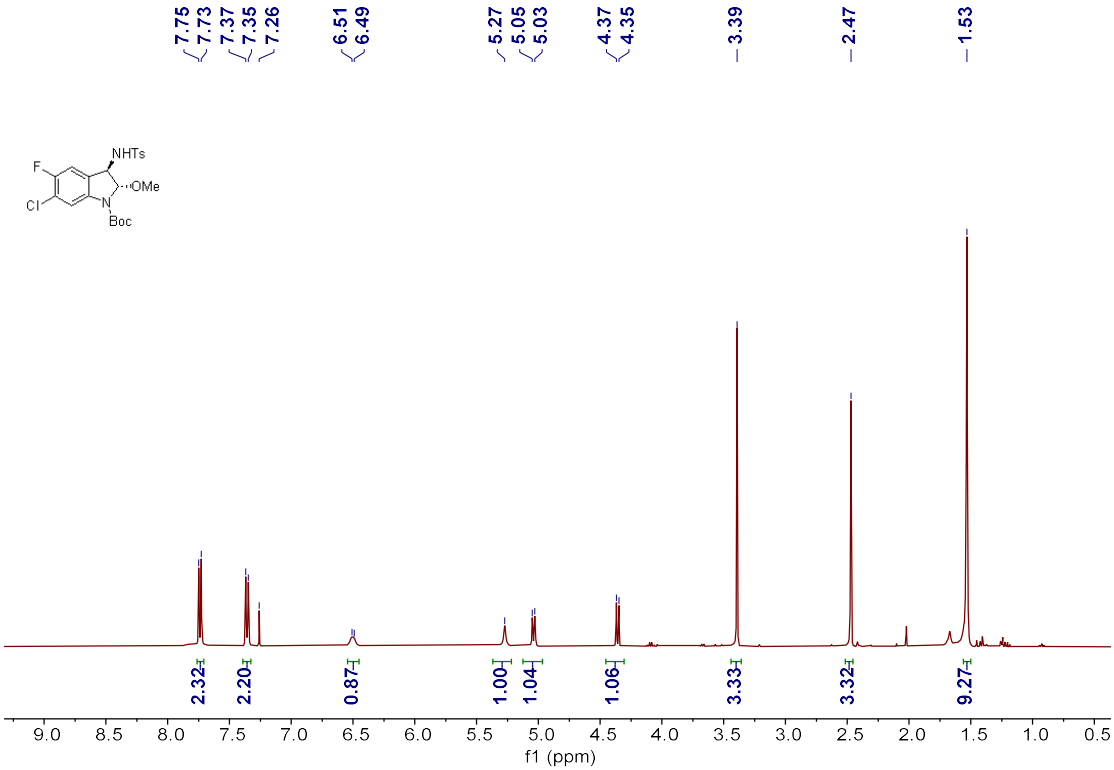
^{1}H NMR (600 MHz) Spectrum of 20 in $CDCl_3$



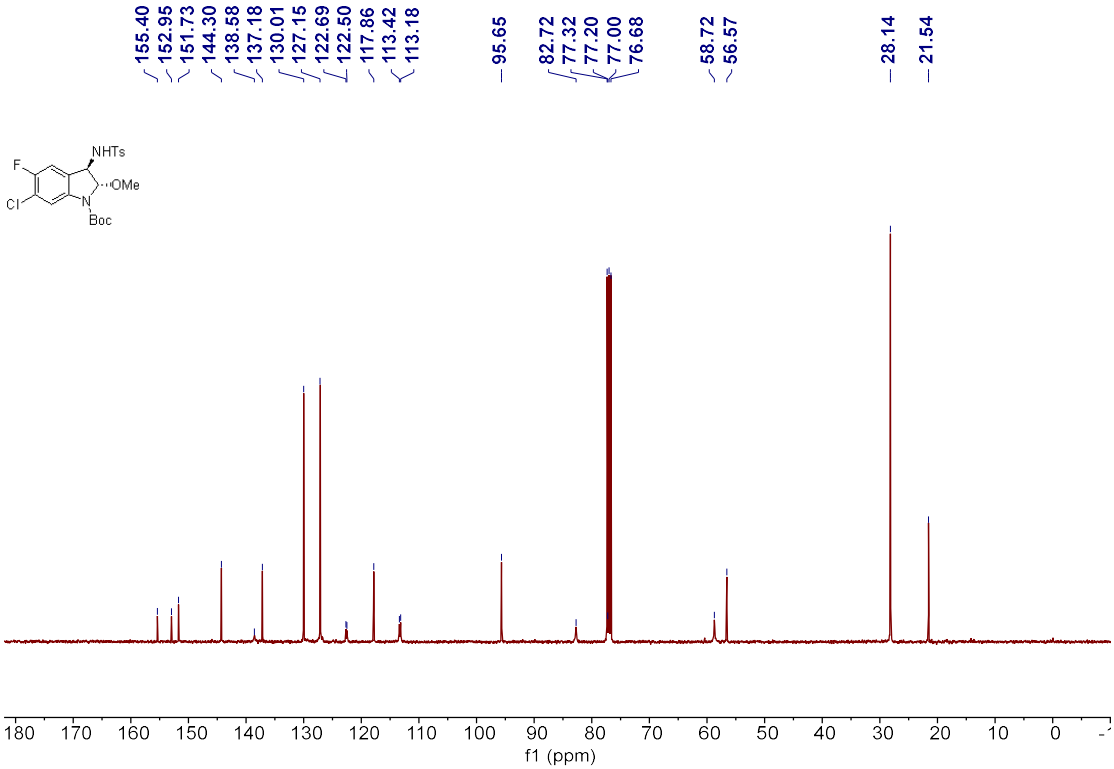
^{13}C NMR (151 MHz) Spectrum of 20 in $CDCl_3$



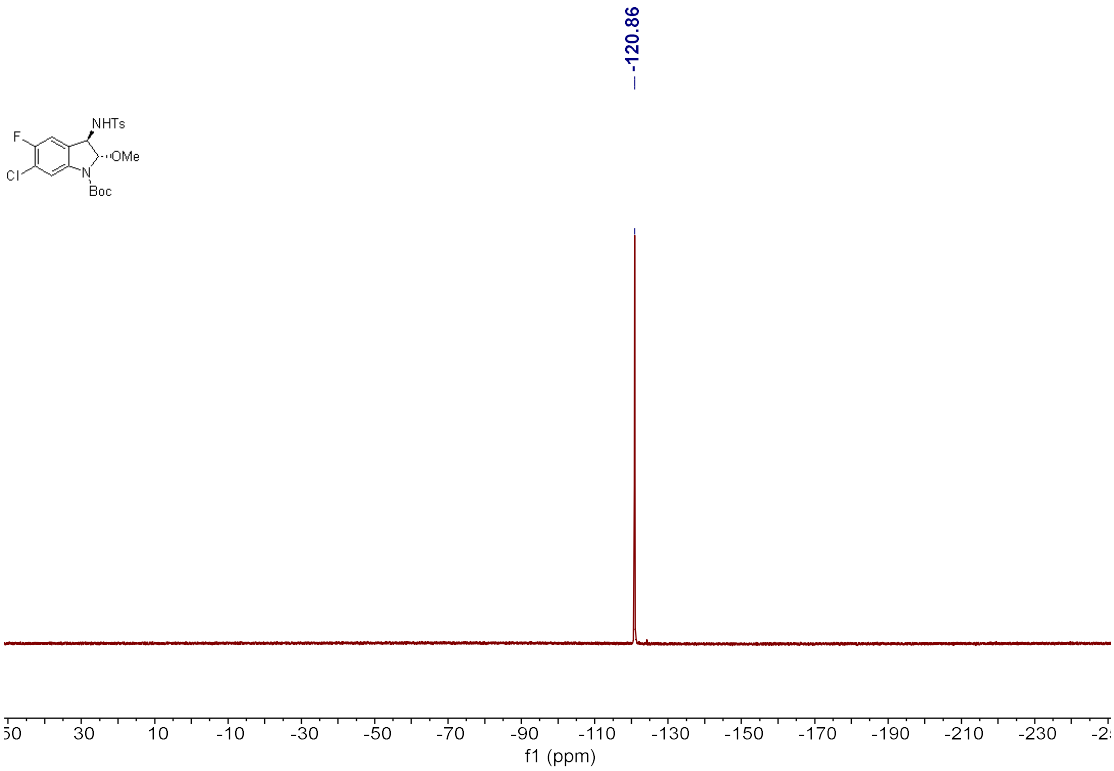
^{1}H NMR (400 MHz) Spectrum of 21 in $CDCl_3$



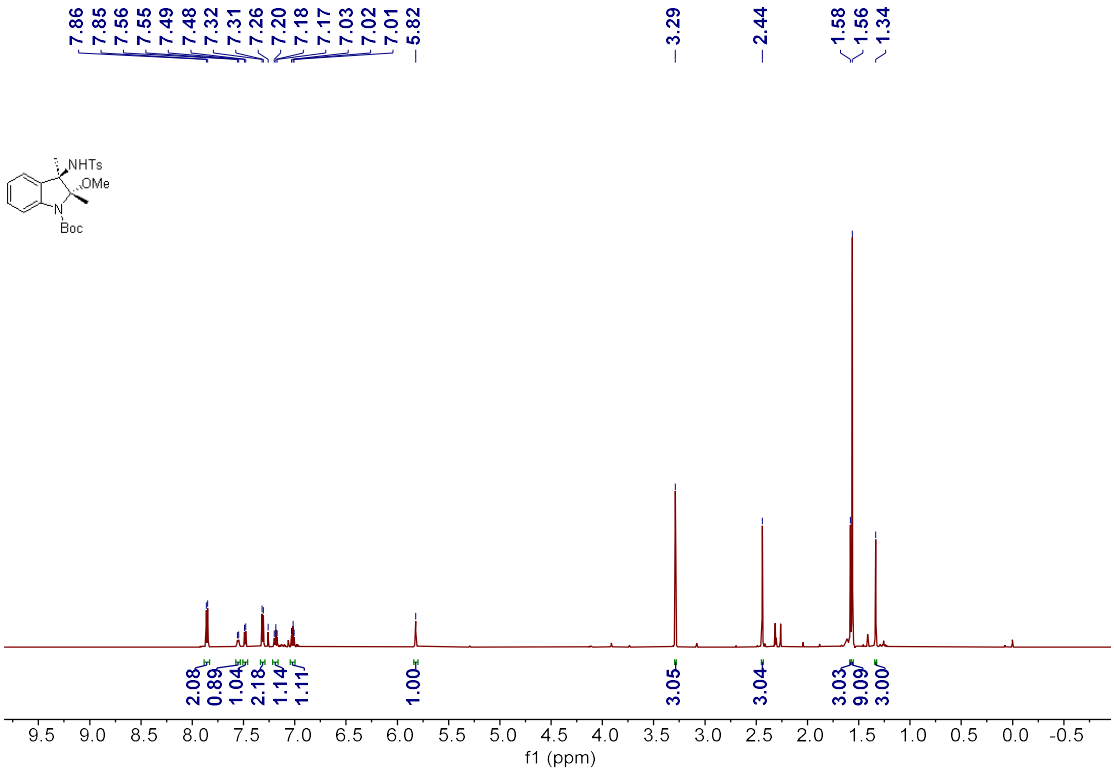
^{13}C NMR (101 MHz) Spectrum of 21 in $CDCl_3$



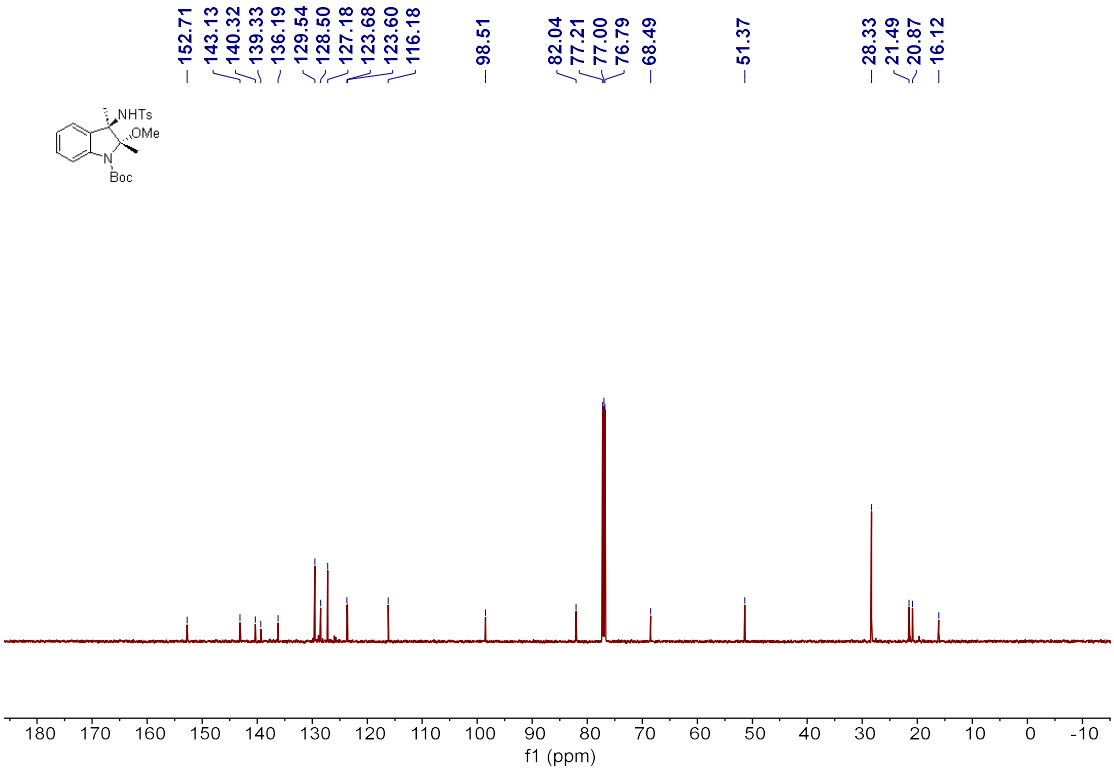
^{19}F NMR (376 MHz) Spectrum of 22 in $CDCl_3$



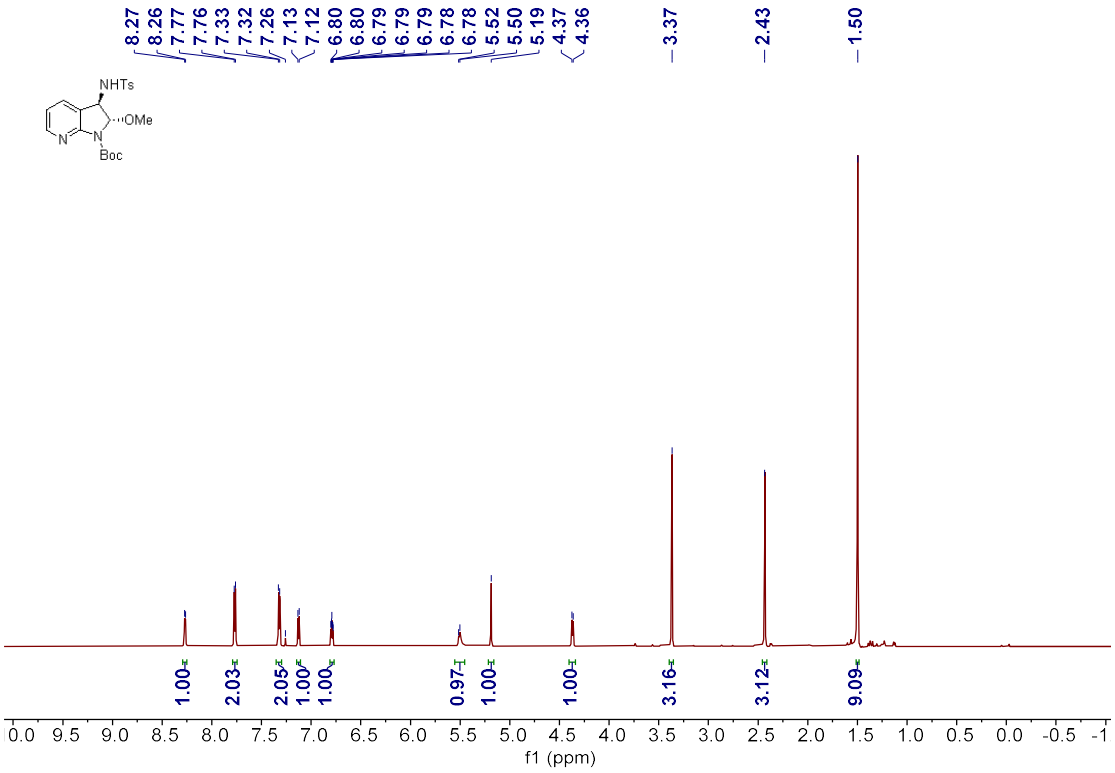
^{1}H NMR (600 MHz) Spectrum of 22 in $CDCl_3$



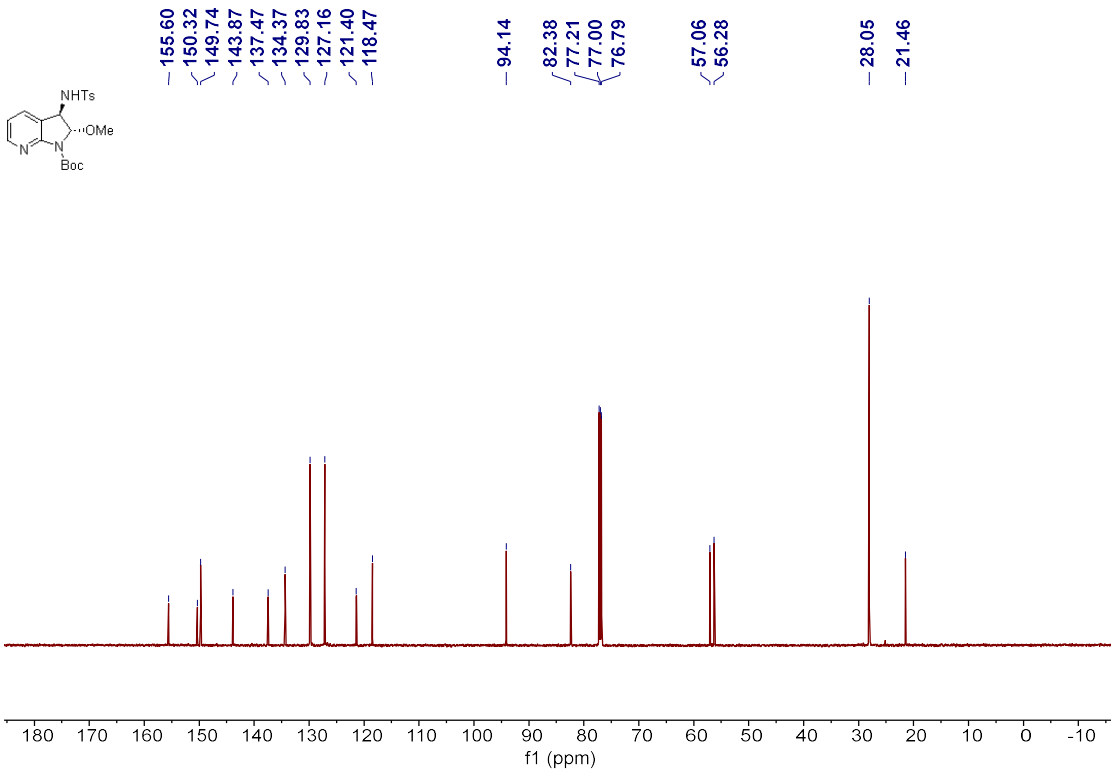
^{13}C NMR (151 MHz) Spectrum of 22 in $CDCl_3$



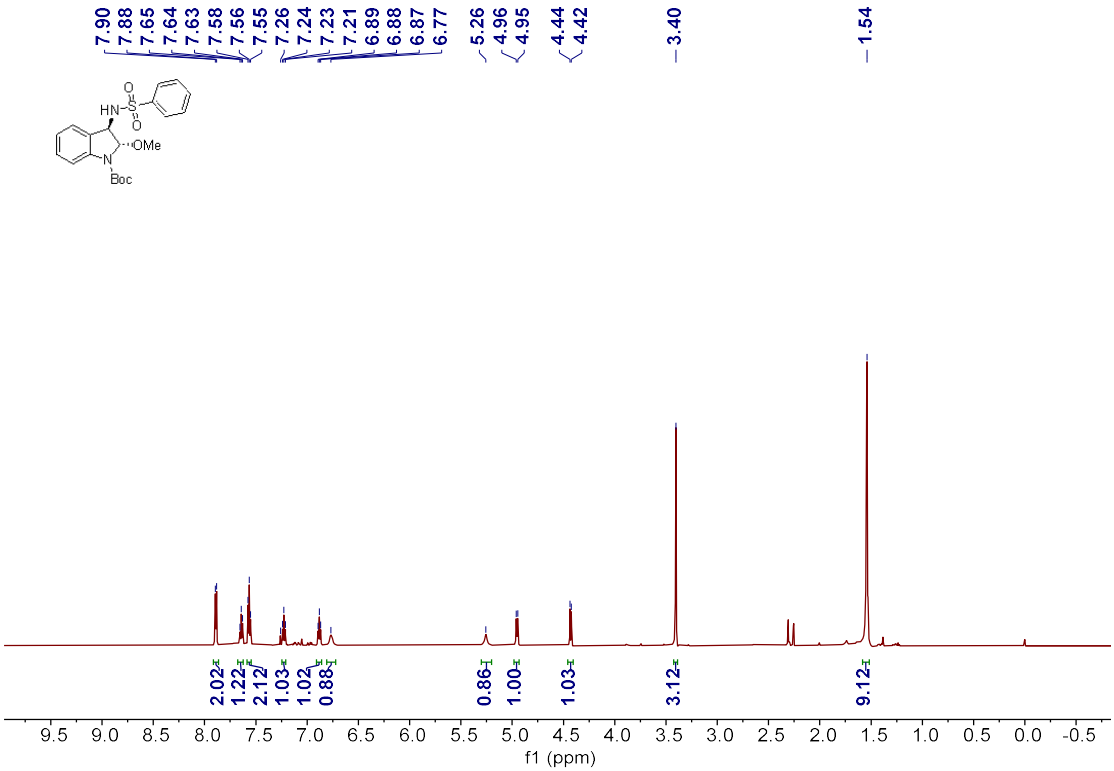
^{1}H NMR (600 MHz) Spectrum of 23 in $CDCl_3$



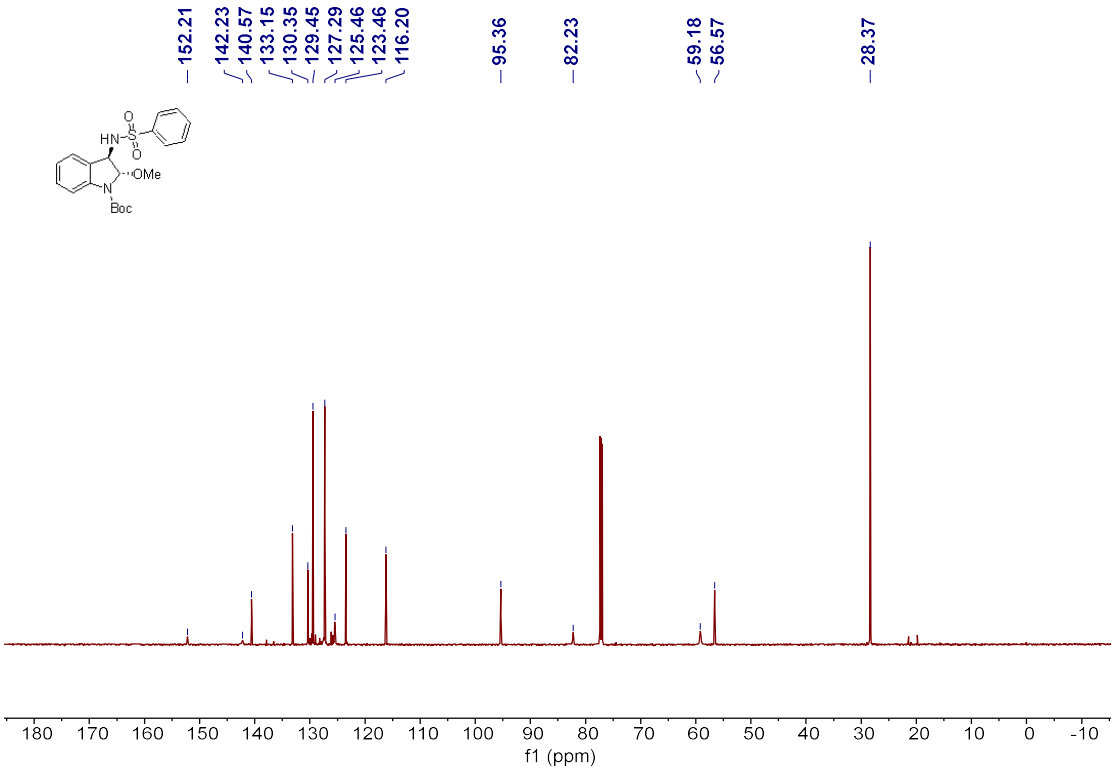
^{13}C NMR (151 MHz) Spectrum of 23 in $CDCl_3$



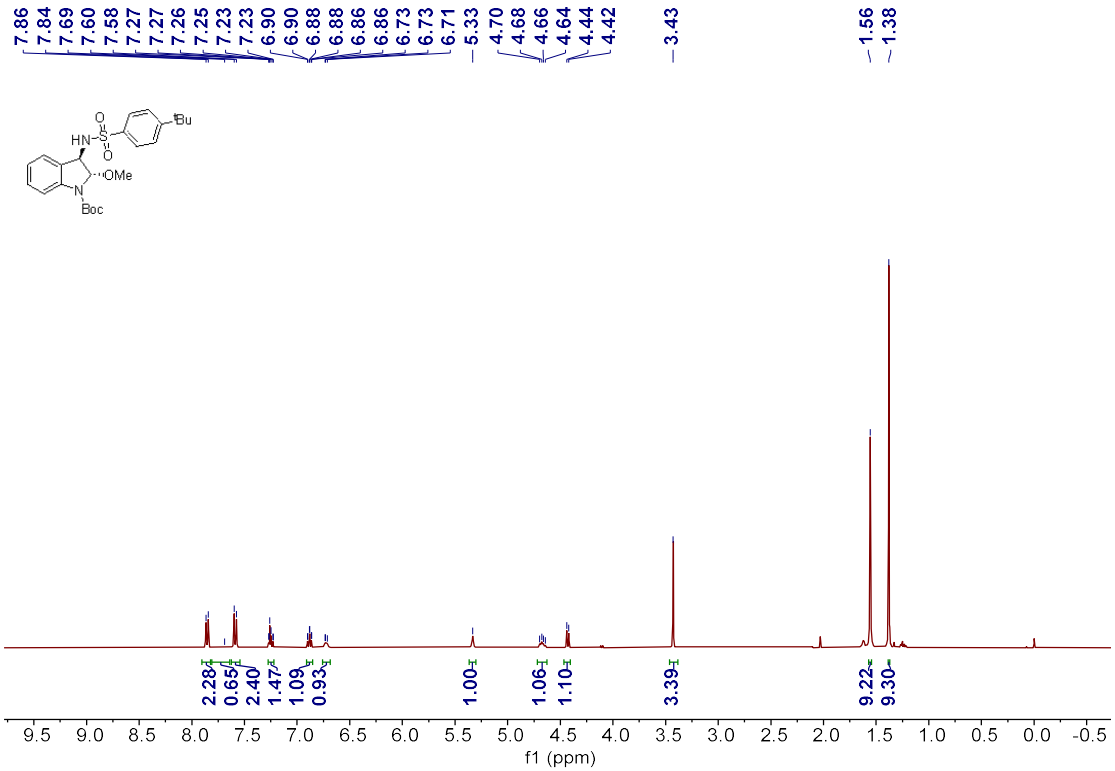
^{1}H NMR (600 MHz) Spectrum of 24 in $CDCl_3$



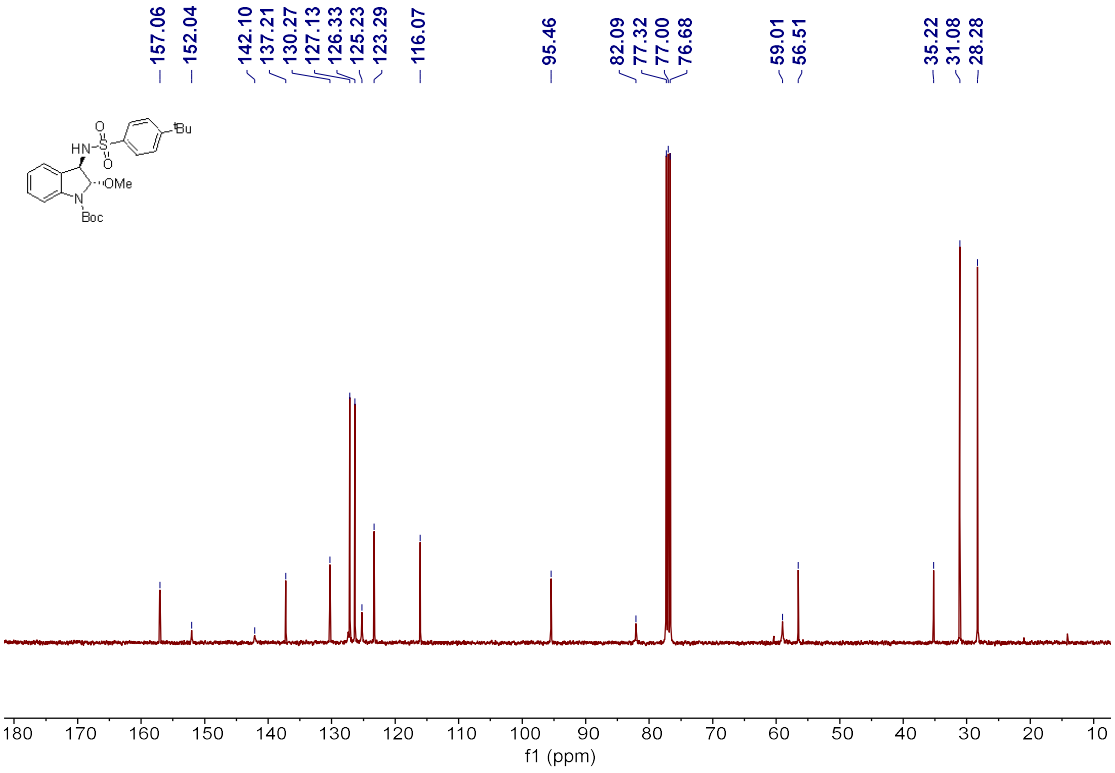
^{13}C NMR (151 MHz) Spectrum of 24 in $CDCl_3$



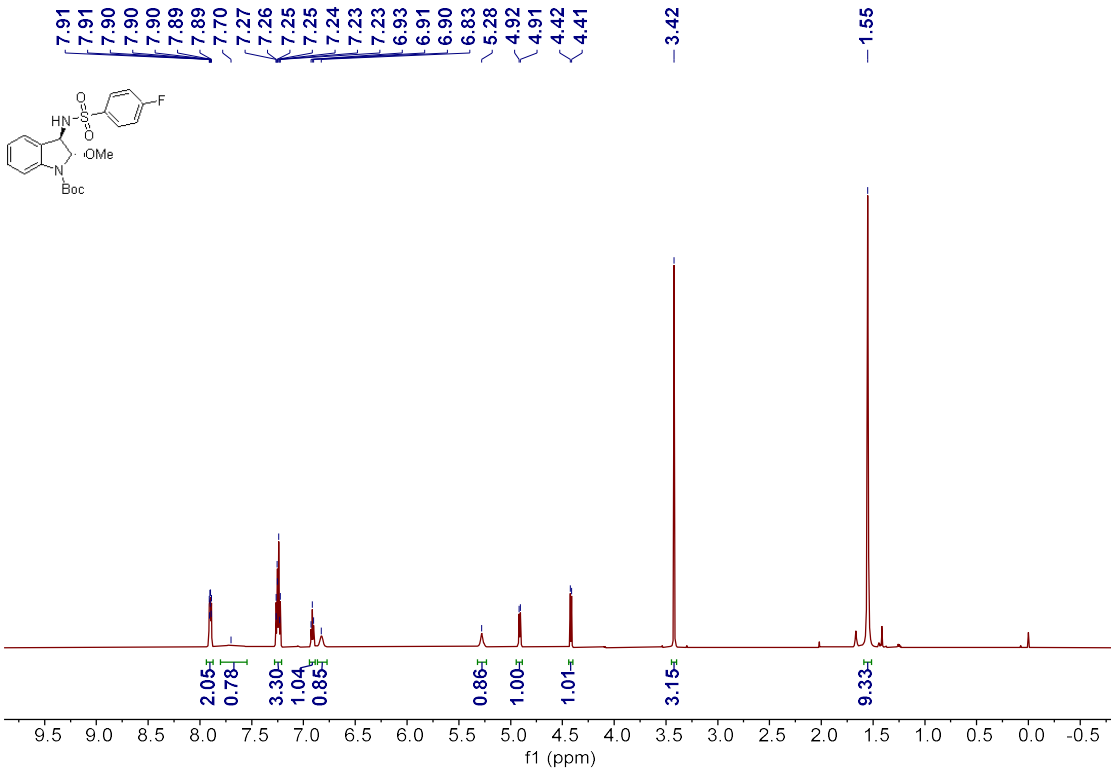
^{1}H NMR (600 MHz) Spectrum of 25 in $CDCl_3$



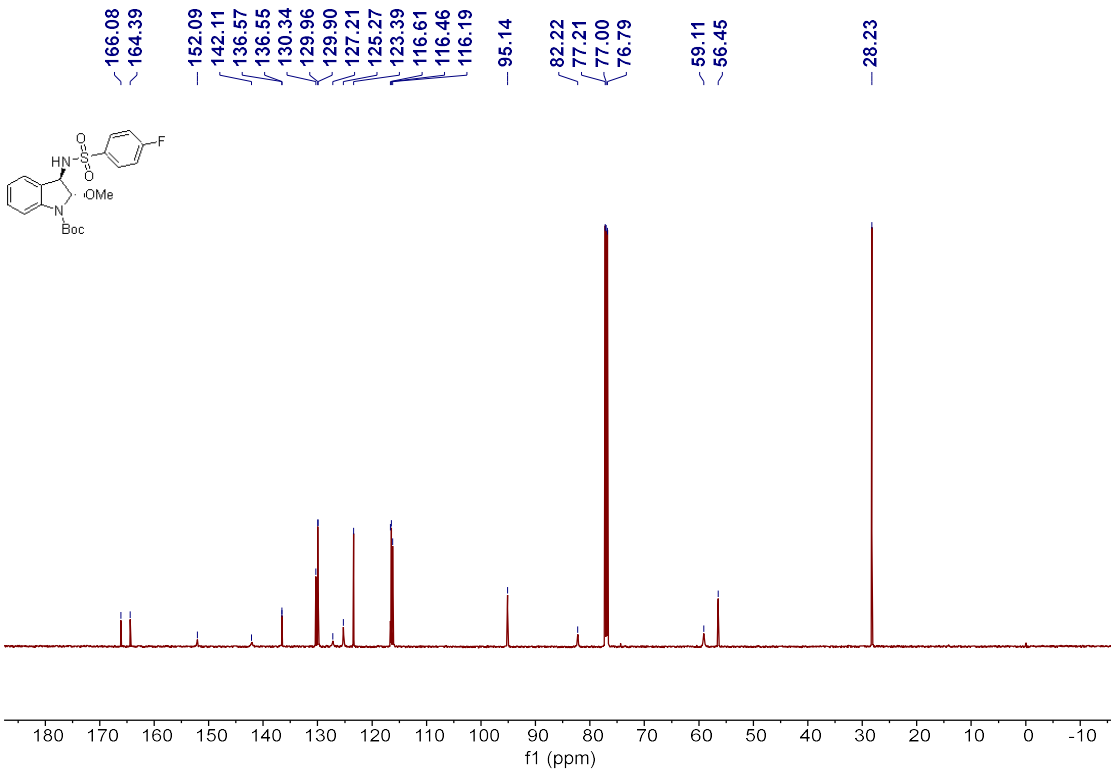
^{13}C NMR (151 MHz) Spectrum of 25 in $CDCl_3$



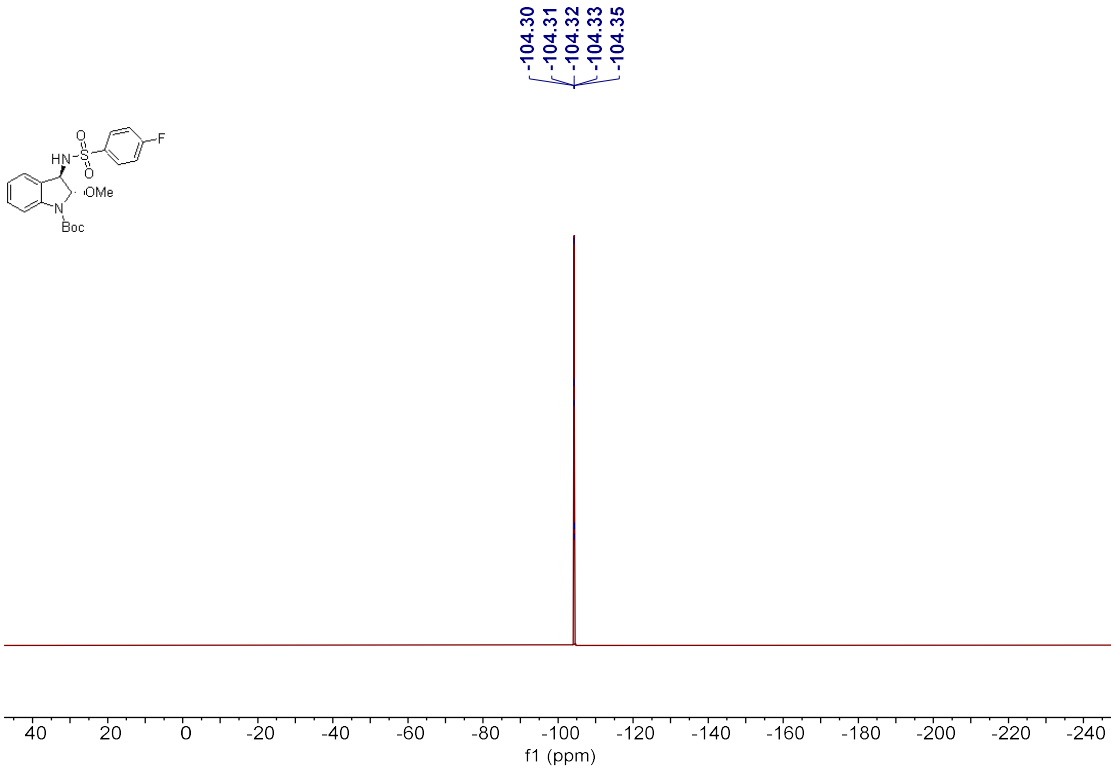
^{1}H NMR (600 MHz) Spectrum of 26 in $CDCl_3$



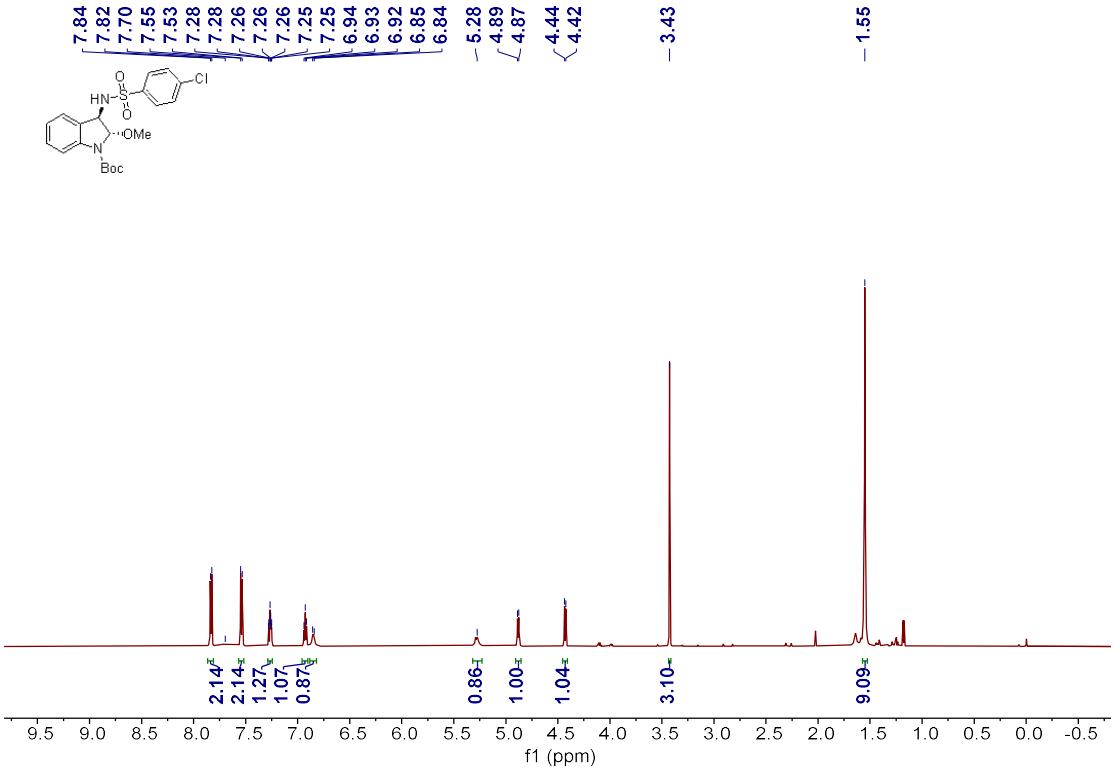
^{13}C NMR (151 MHz) Spectrum of 26 in $CDCl_3$



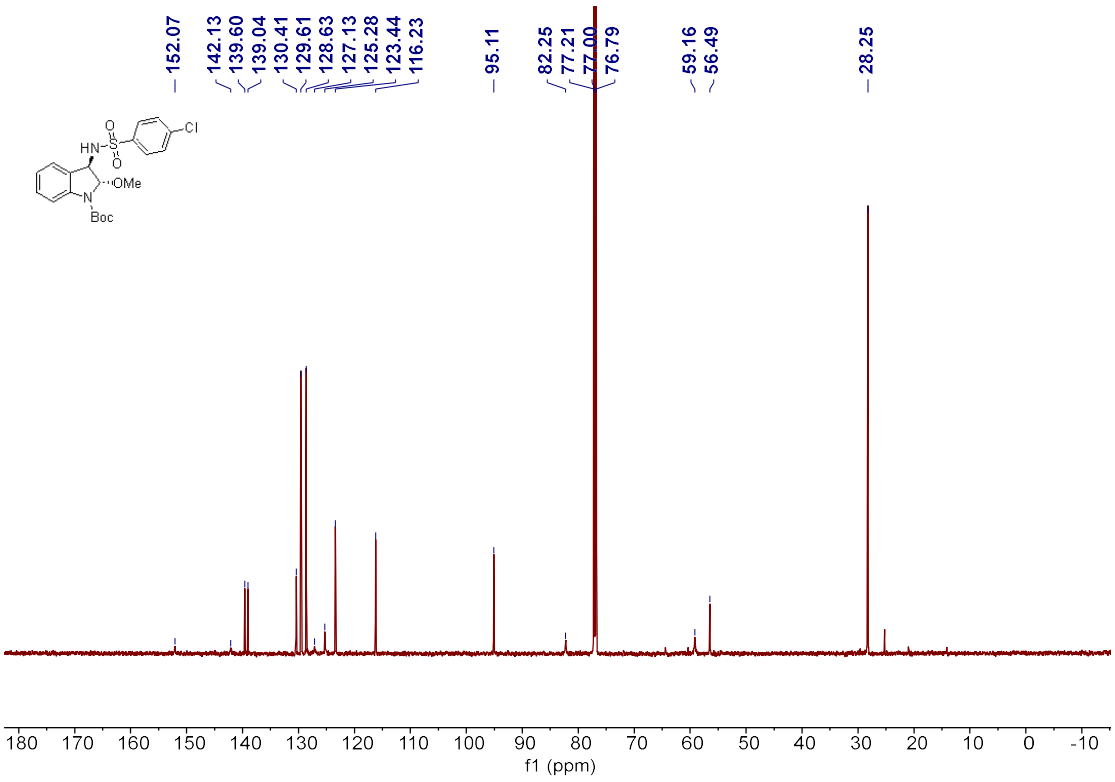
^{19}F NMR (565 MHz) Spectrum of 26 in $CDCl_3$



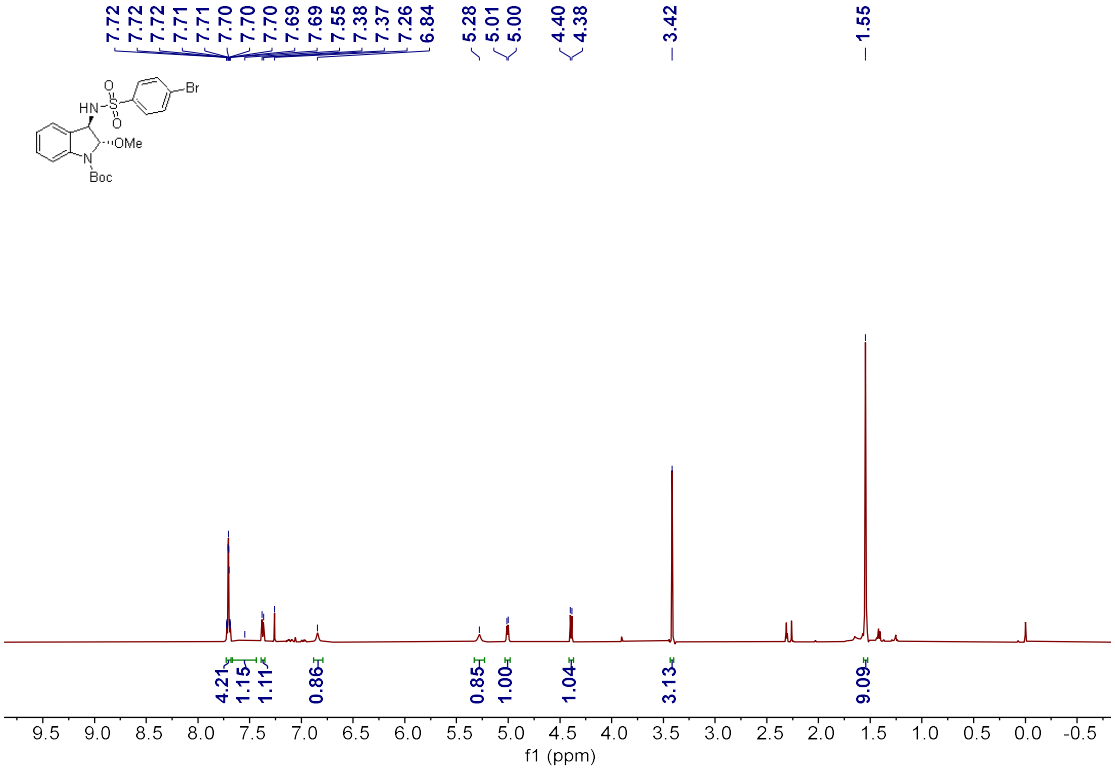
^{1}H NMR (600 MHz) Spectrum of 27 in $CDCl_3$



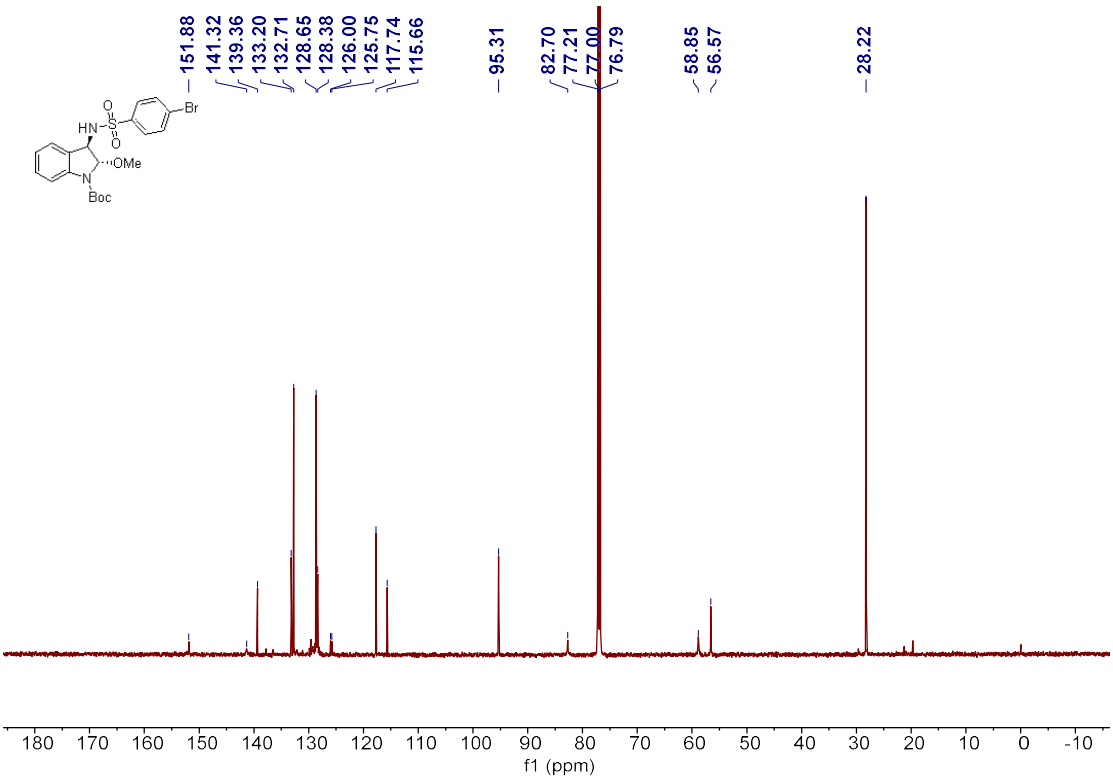
^{13}C NMR (151 MHz) Spectrum of 27 in $CDCl_3$



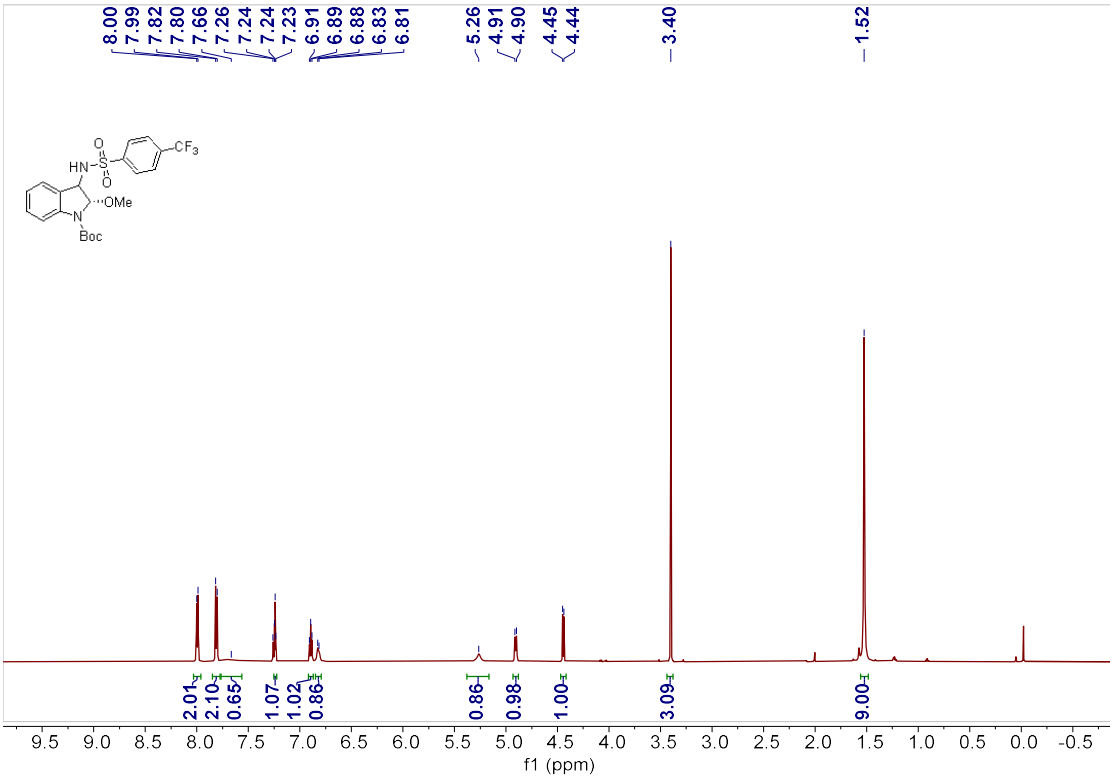
^{1}H NMR (600 MHz) Spectrum of 28 in $CDCl_3$



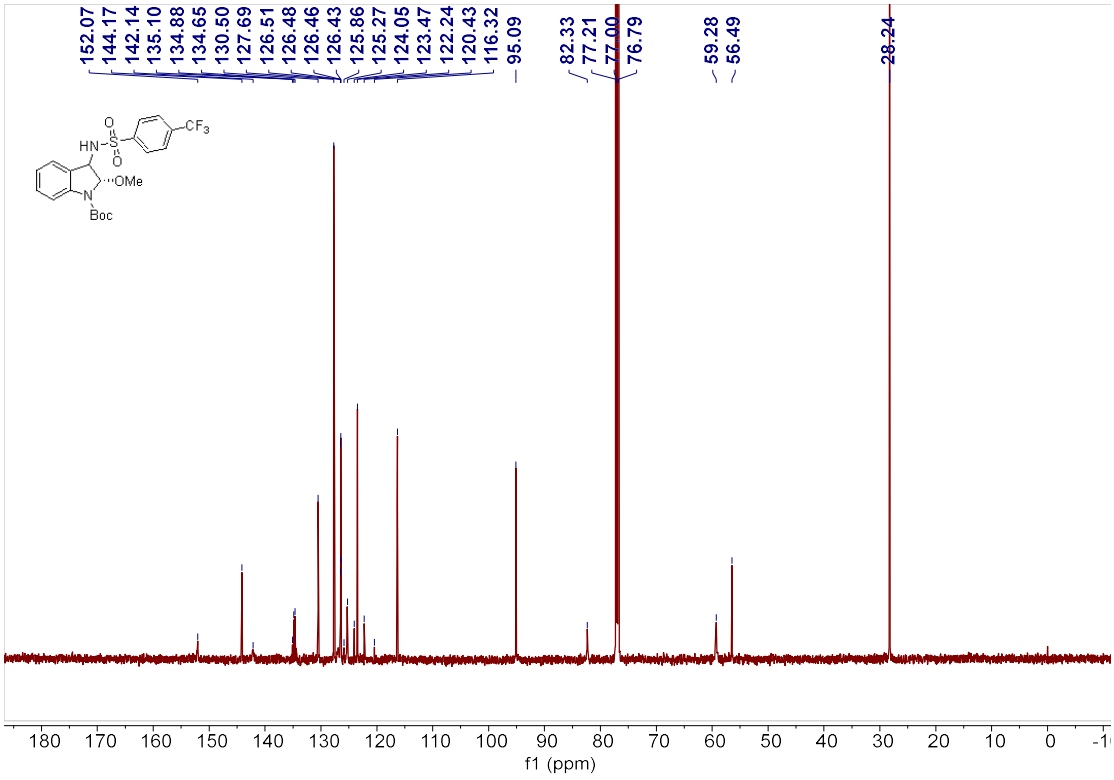
^{13}C NMR (151 MHz) Spectrum of 28 in $CDCl_3$



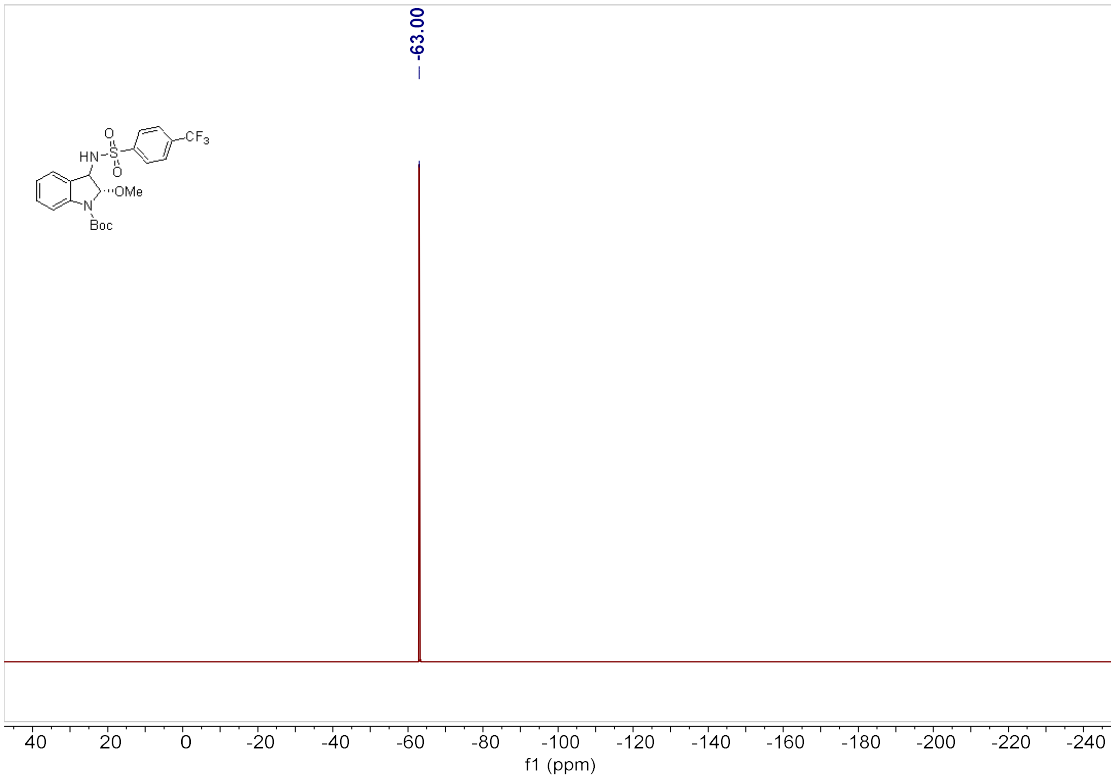
^{1}H NMR (600 MHz) Spectrum of 29 in $CDCl_3$



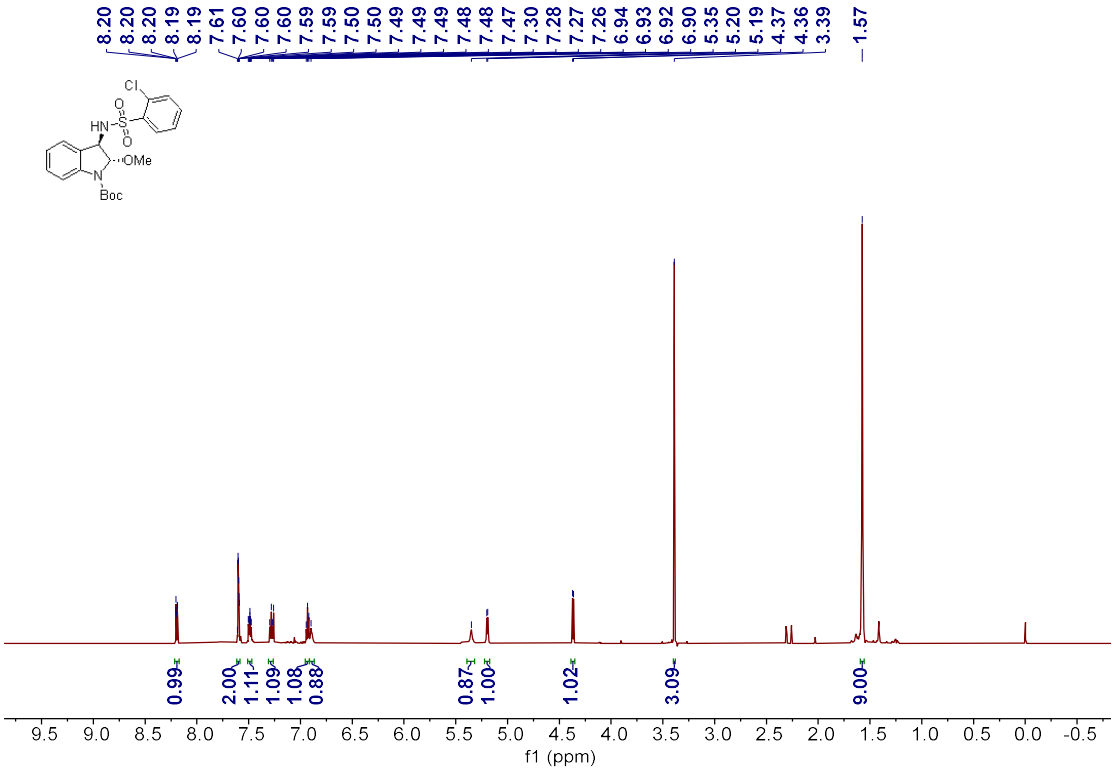
^{13}C NMR (151 MHz) Spectrum of 29 in $CDCl_3$



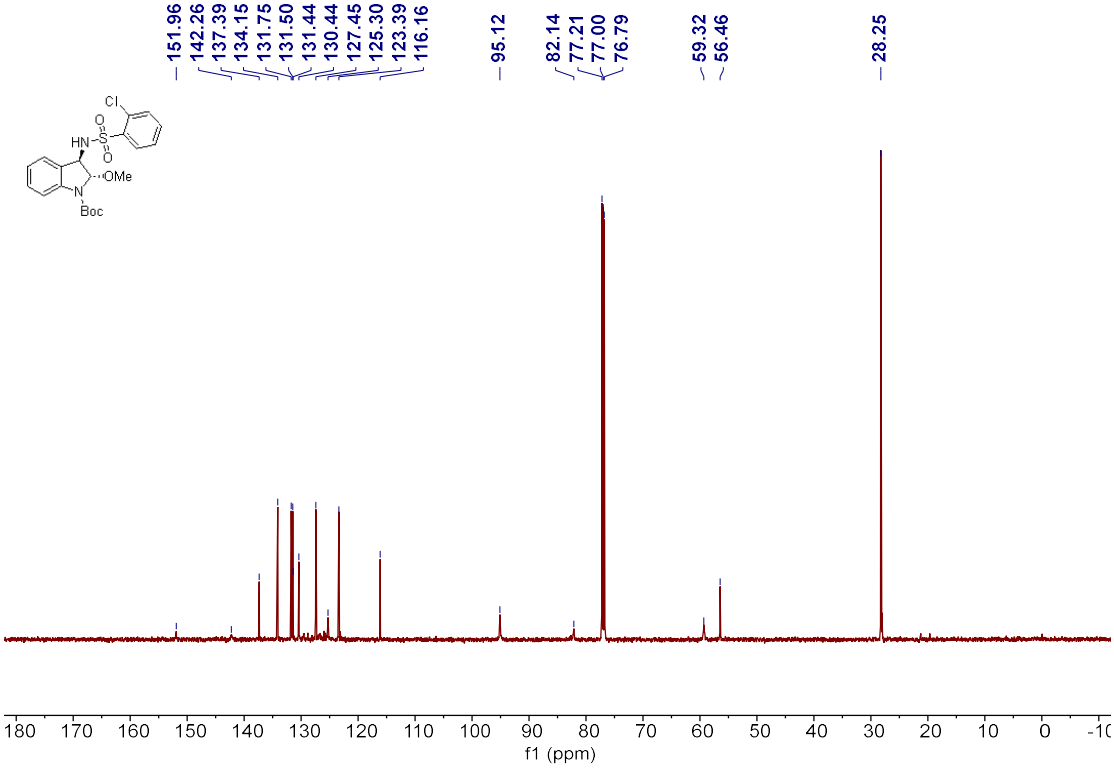
^{19}F NMR (565 MHz) Spectrum of 29 in $CDCl_3$



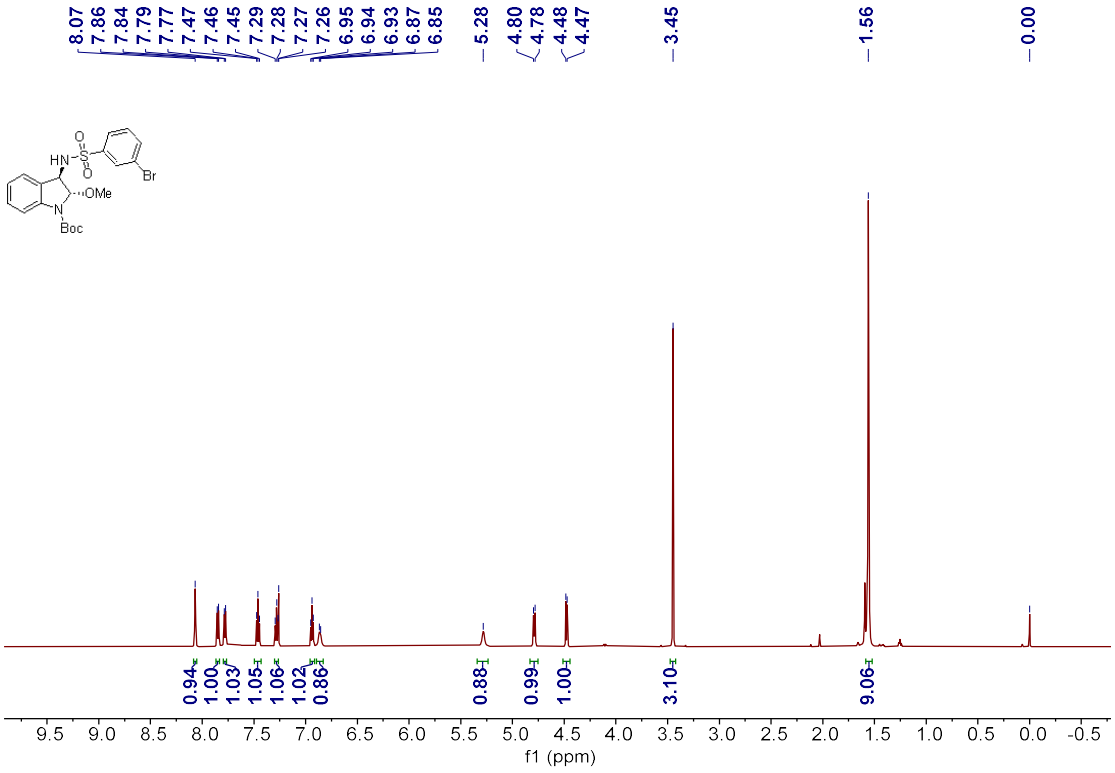
^{1}H NMR (600 MHz) Spectrum of 30 in $CDCl_3$



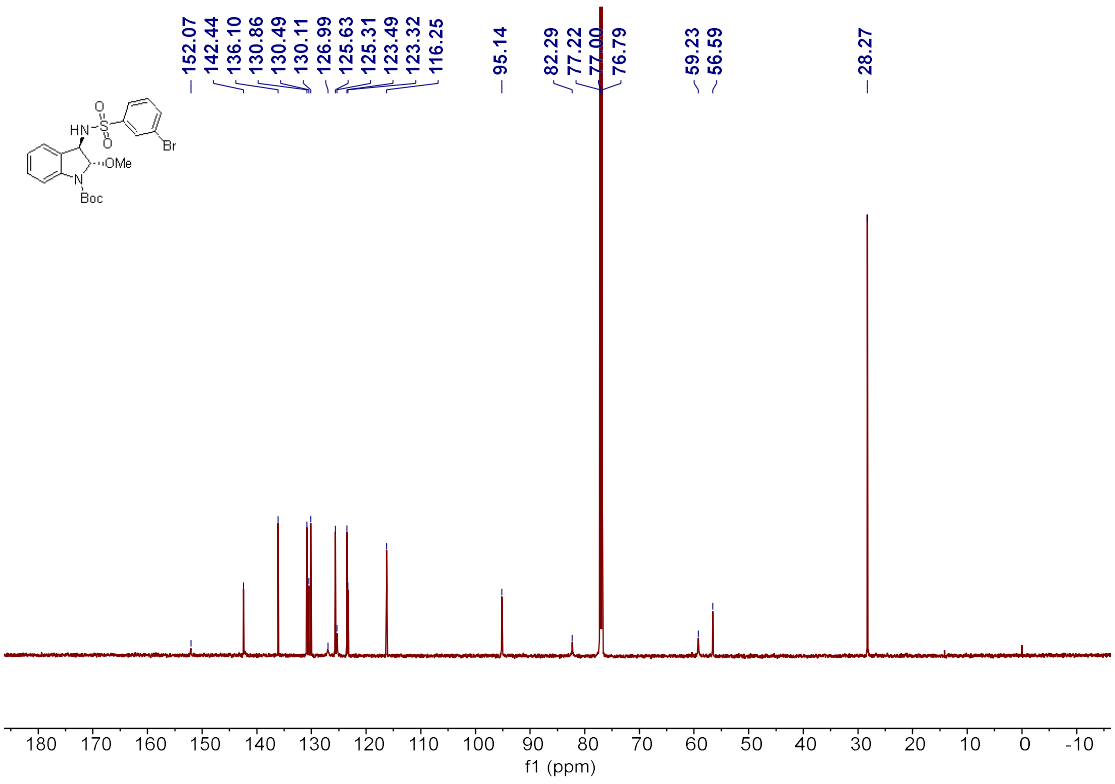
^{13}C NMR (151 MHz) Spectrum of 30 in $CDCl_3$



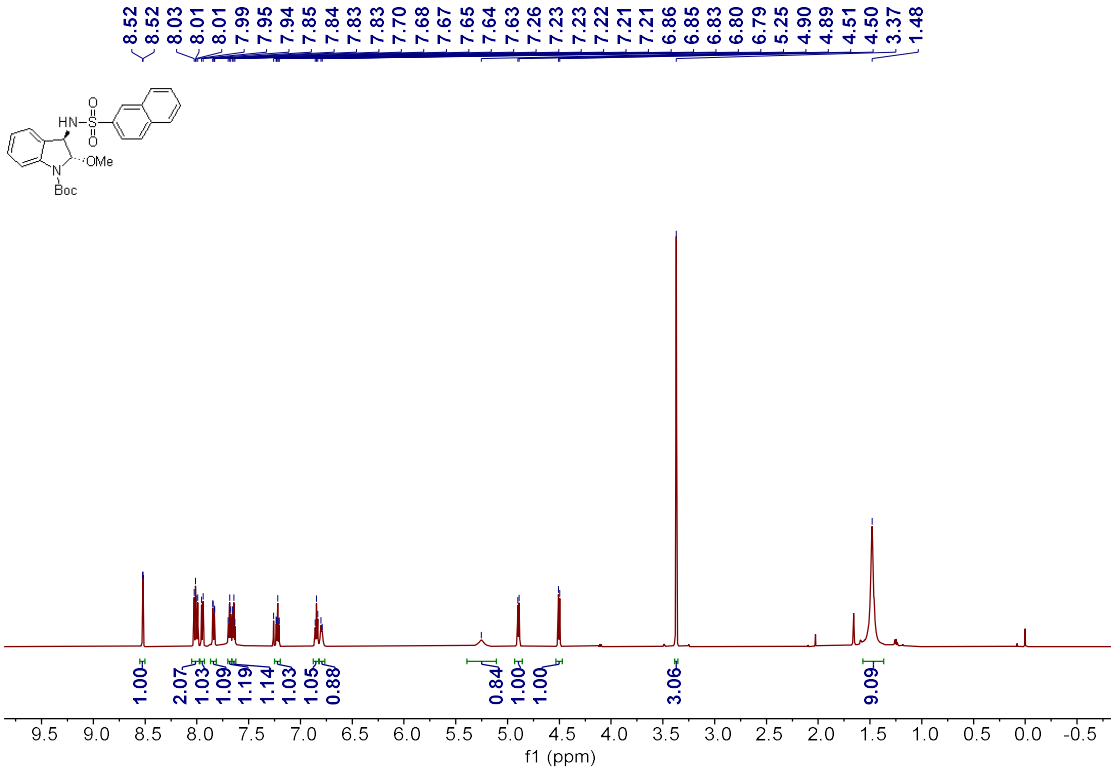
^{1}H NMR (600 MHz) Spectrum of 31 in $CDCl_3$



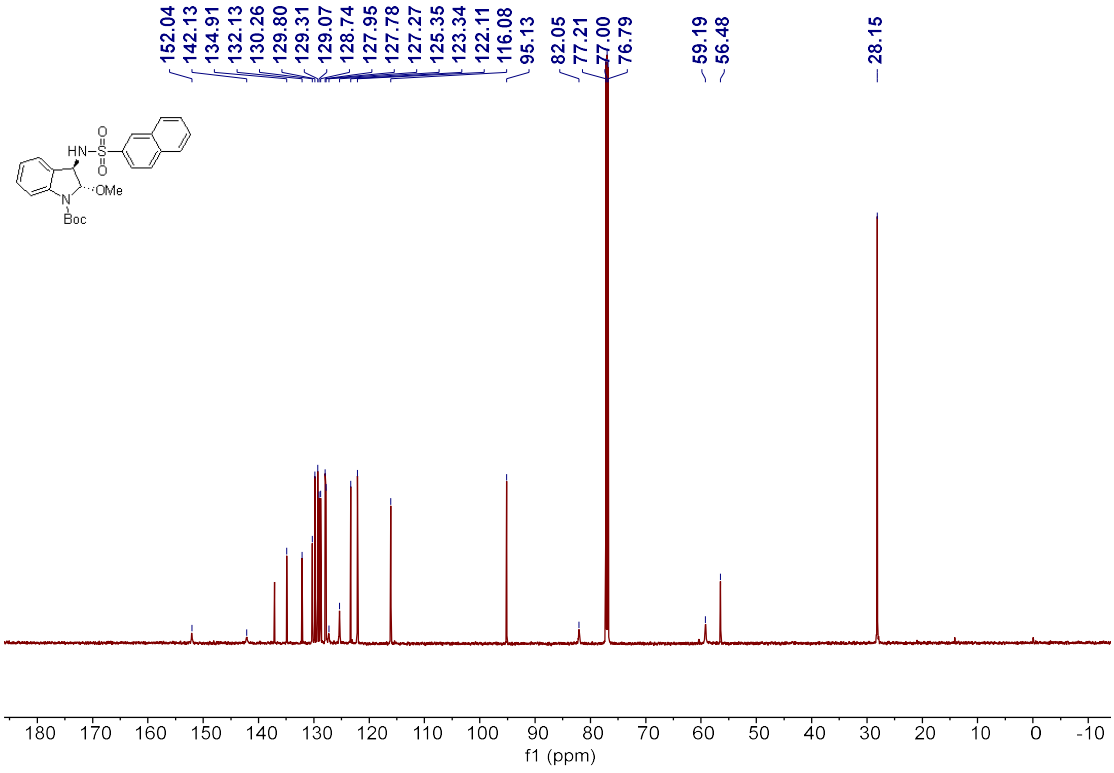
^{13}C NMR (151 MHz) Spectrum of 31 in $CDCl_3$



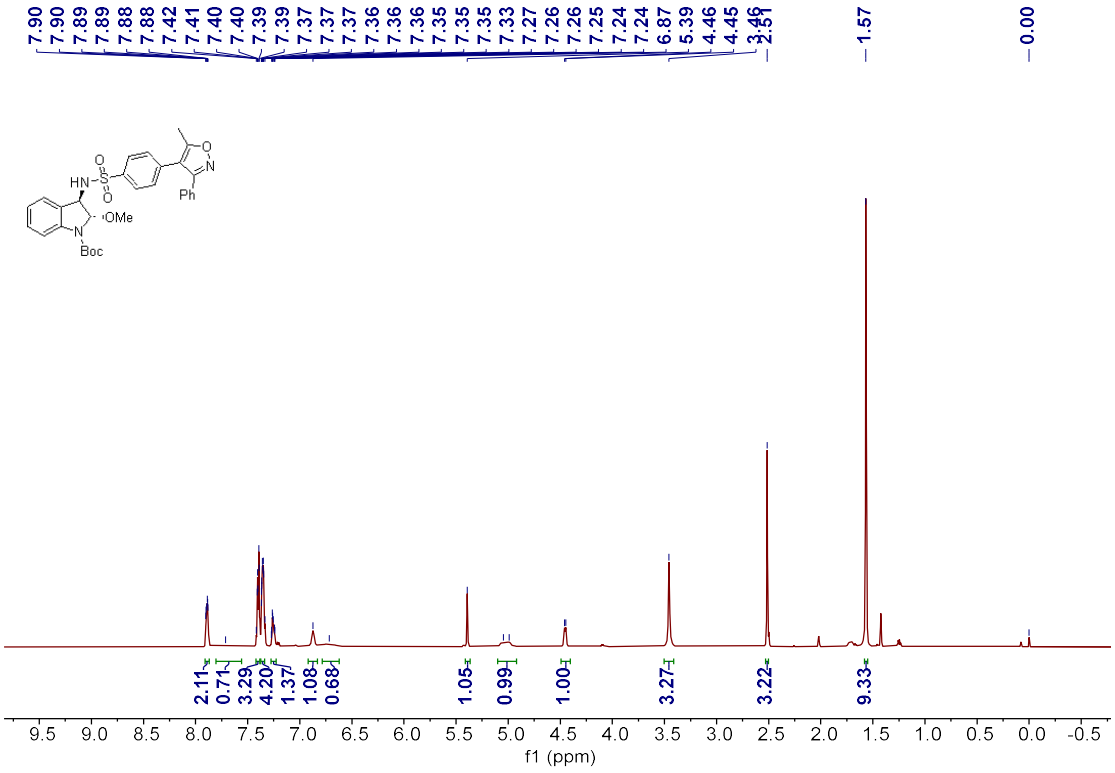
^{1}H NMR (600 MHz) Spectrum of 32 in $CDCl_3$



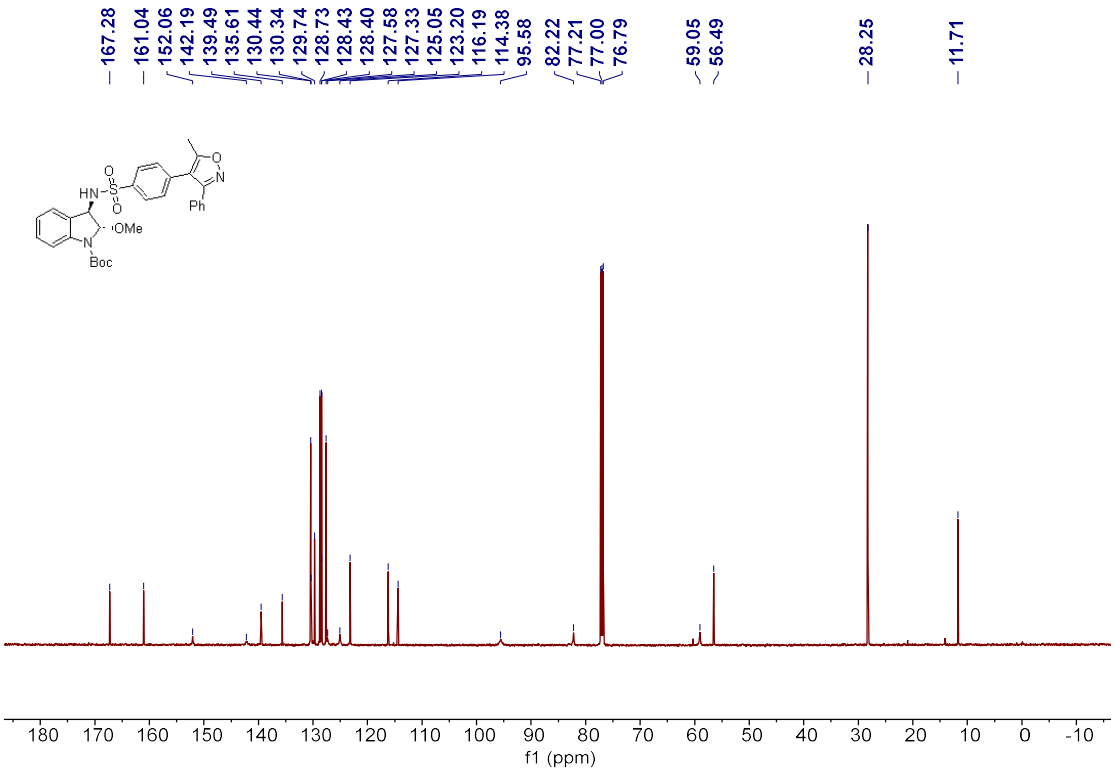
^{13}C NMR (151 MHz) Spectrum of 32 in $CDCl_3$



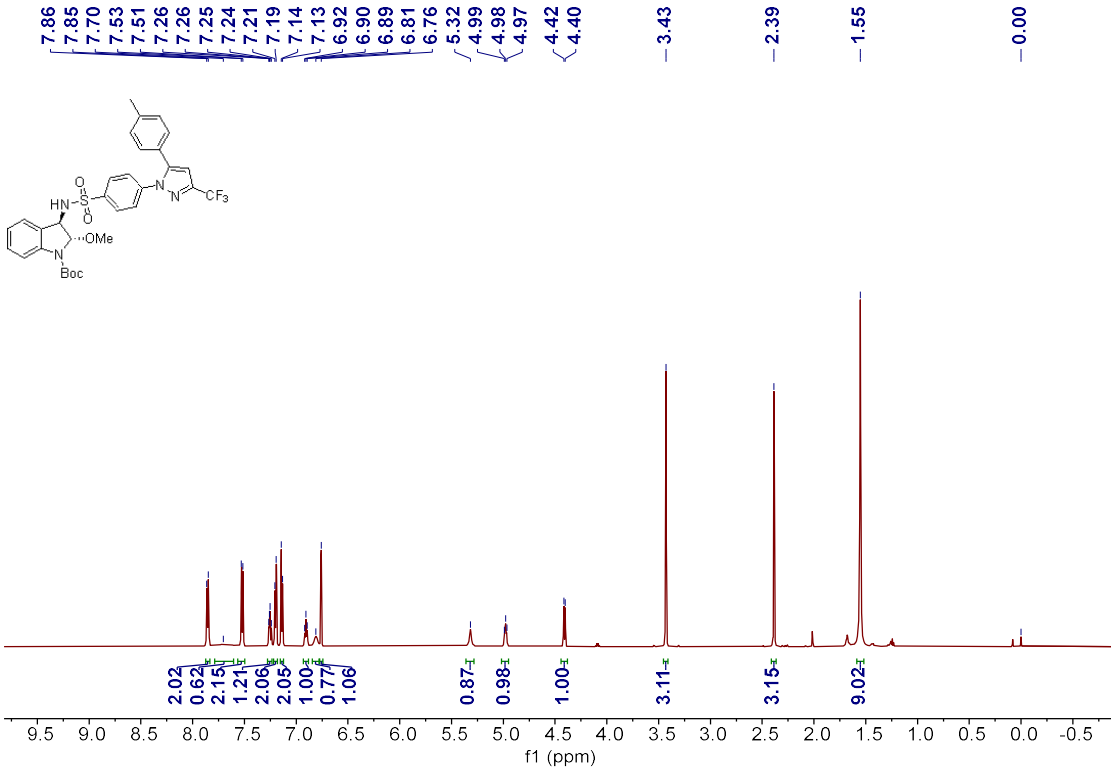
^{1}H NMR (600 MHz) Spectrum of 33 in $CDCl_3$



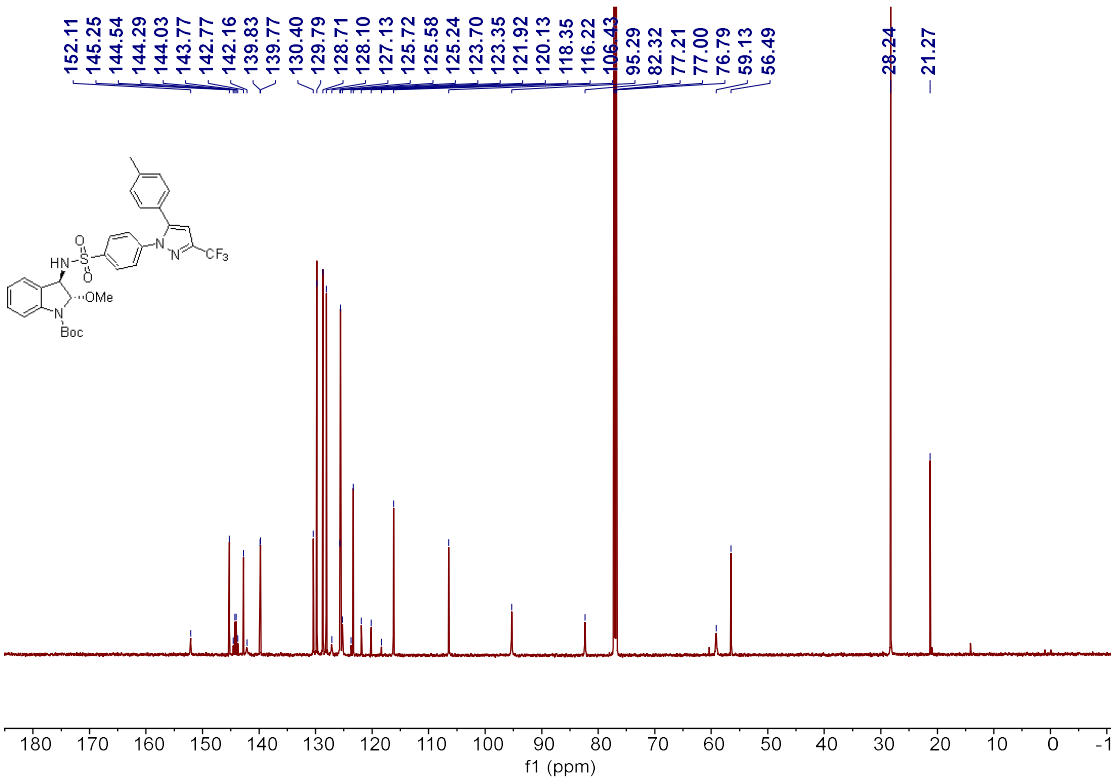
^{13}C NMR (151 MHz) Spectrum of 33 in $CDCl_3$



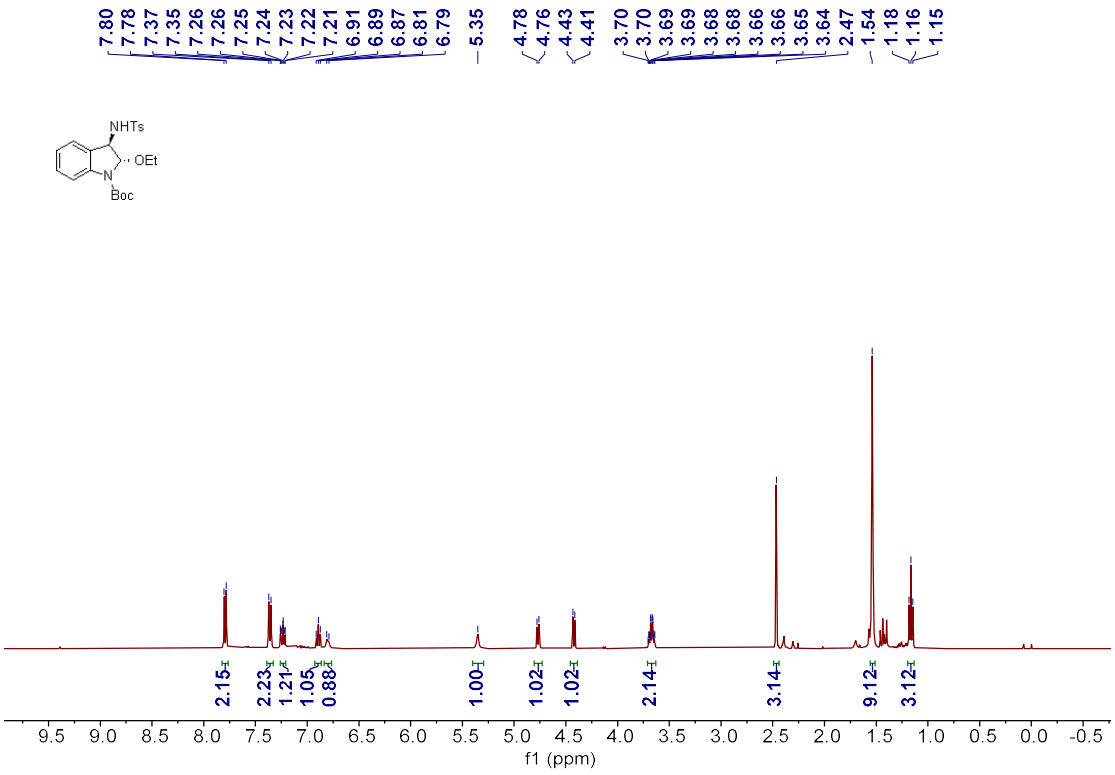
^{1}H NMR (600 MHz) Spectrum of 34 in $CDCl_3$



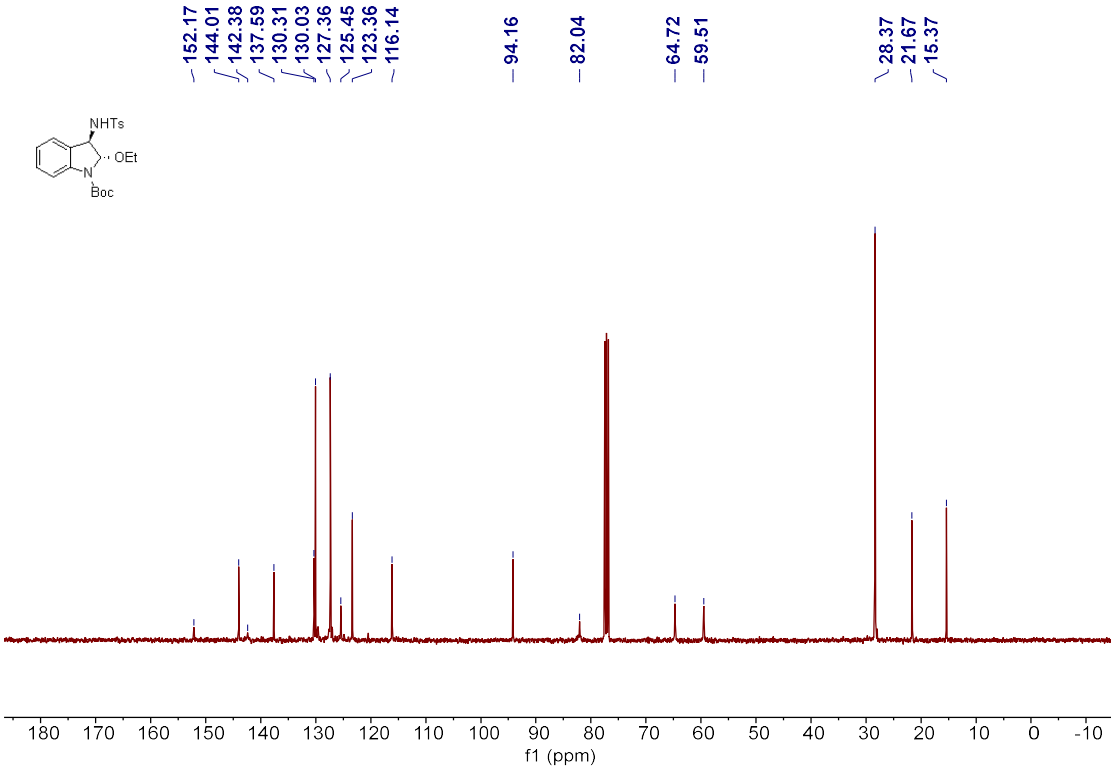
^{13}C NMR (151 MHz) Spectrum of 34 in $CDCl_3$



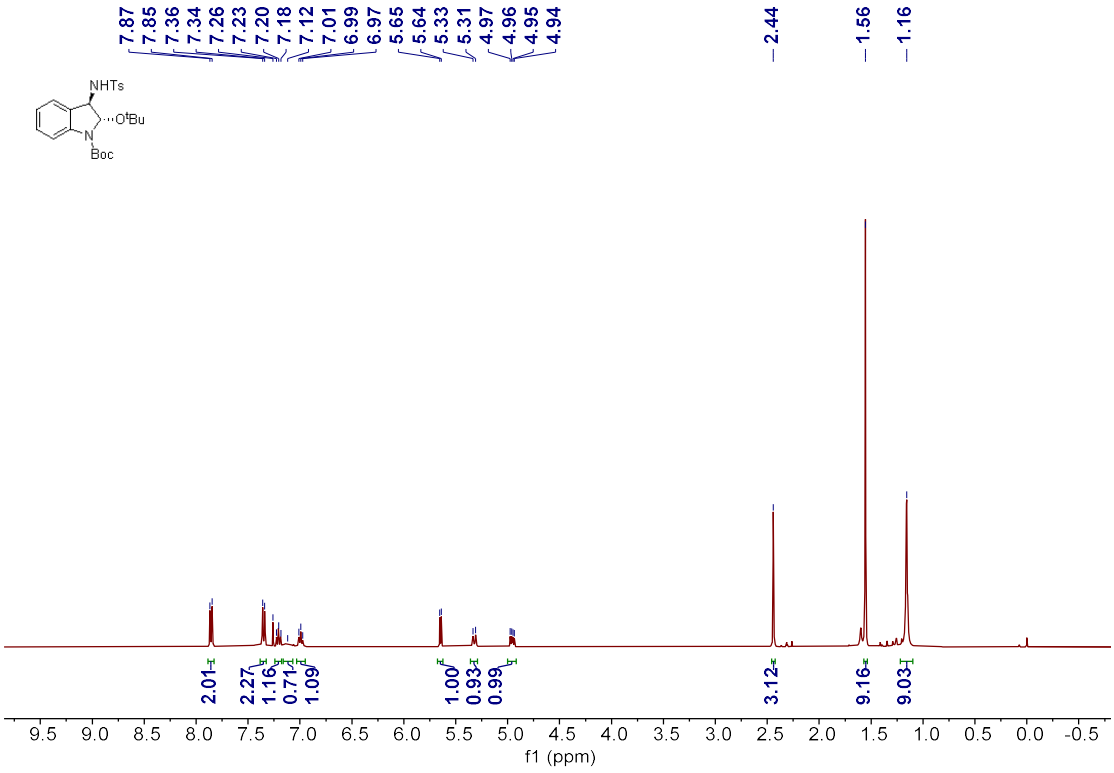
^{1}H NMR (400 MHz) Spectrum of 35 in $CDCl_3$



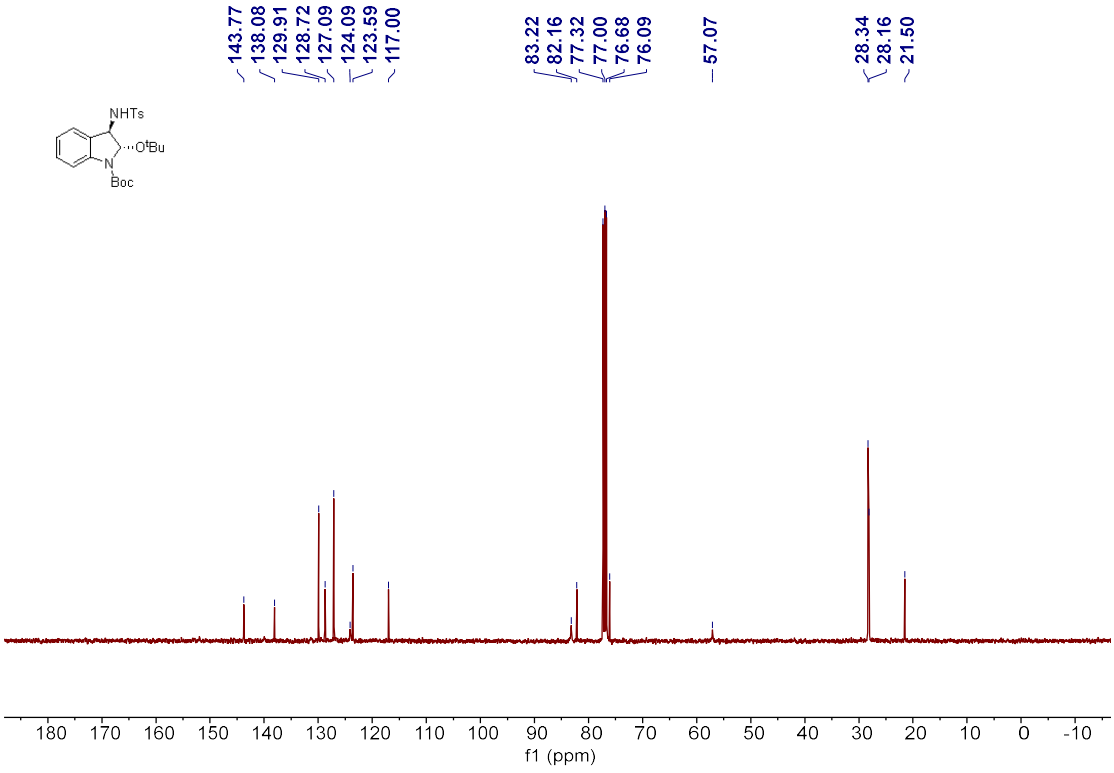
^{13}C NMR (101 MHz) Spectrum of 35 in $CDCl_3$



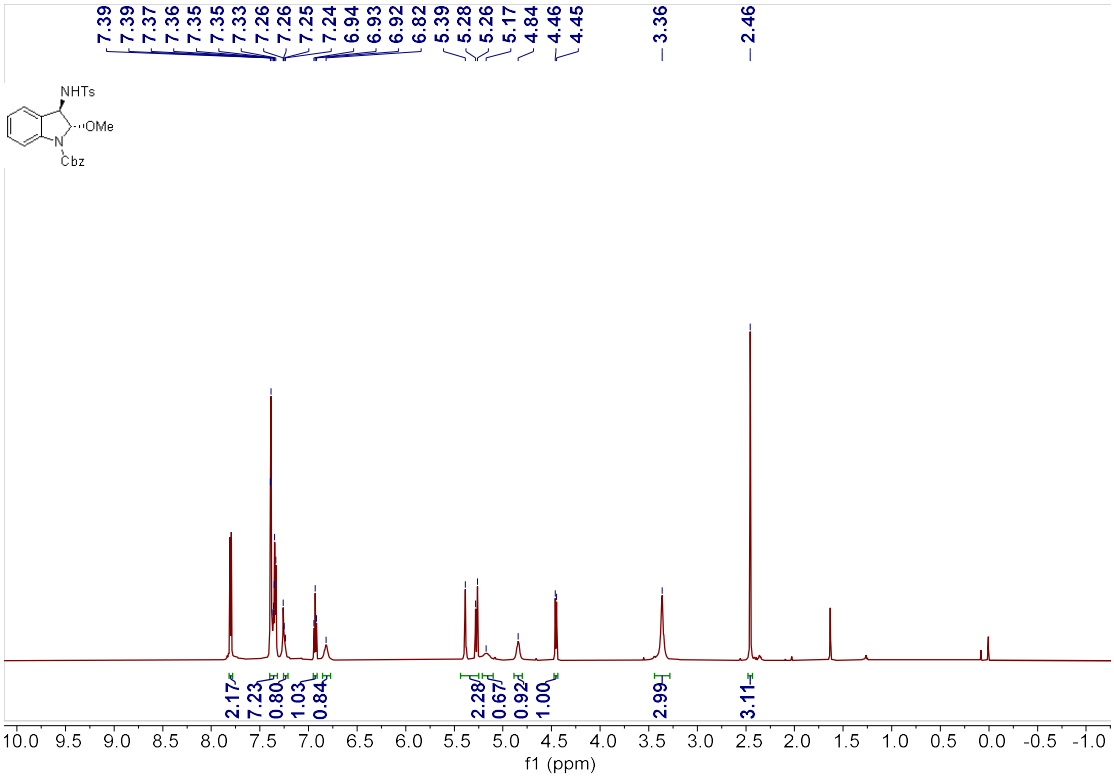
^{1}H NMR (400 MHz) Spectrum of 36 in $CDCl_3$



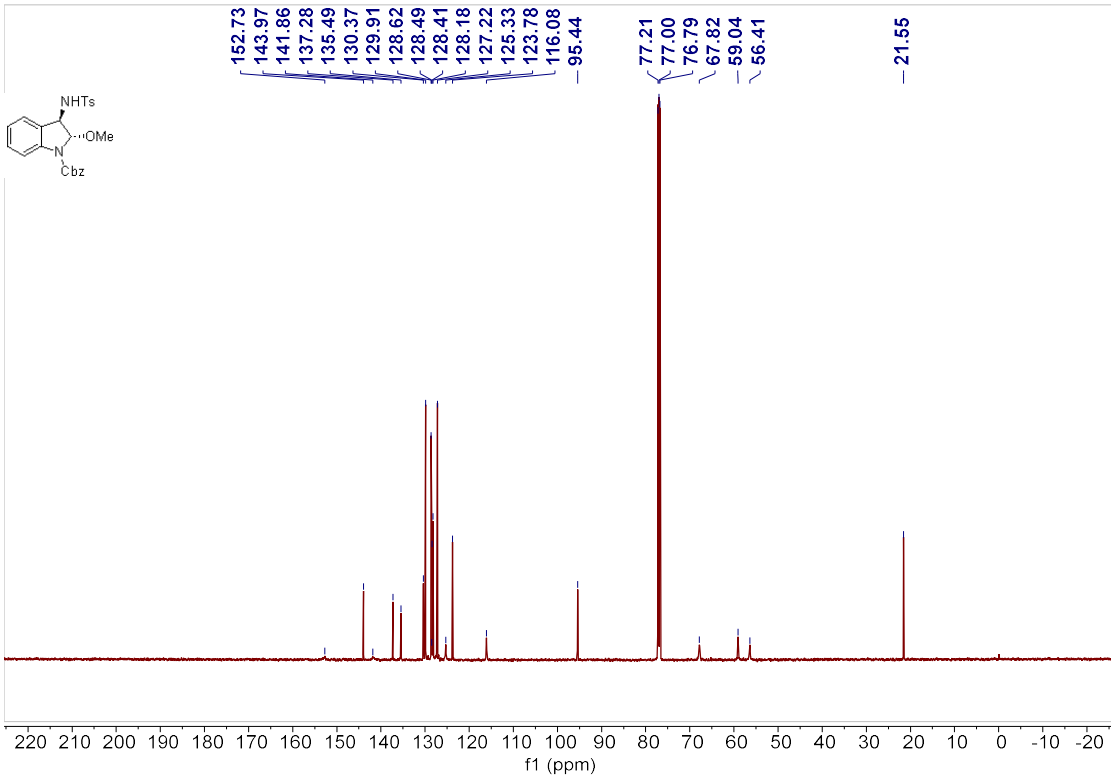
^{13}C NMR (101 MHz) Spectrum of 36 in $CDCl_3$



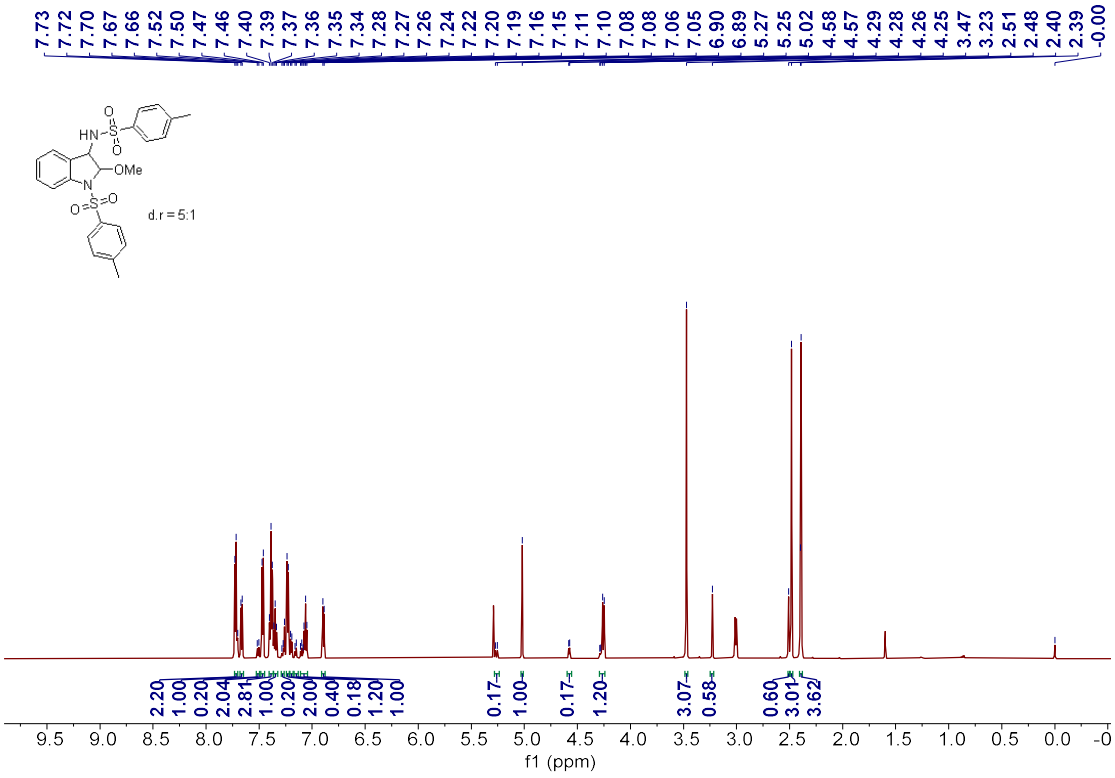
^{1}H NMR (400 MHz) Spectrum of 37 in $CDCl_3$



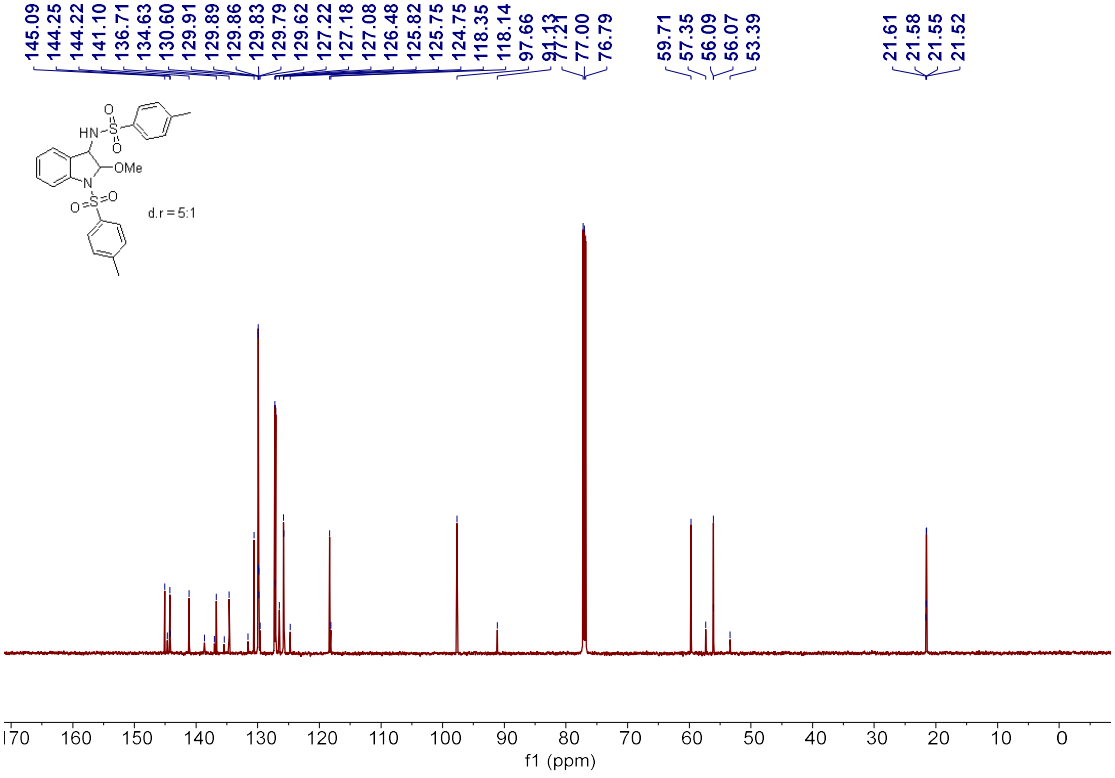
^{13}C NMR (101 MHz) Spectrum of 37 in $CDCl_3$



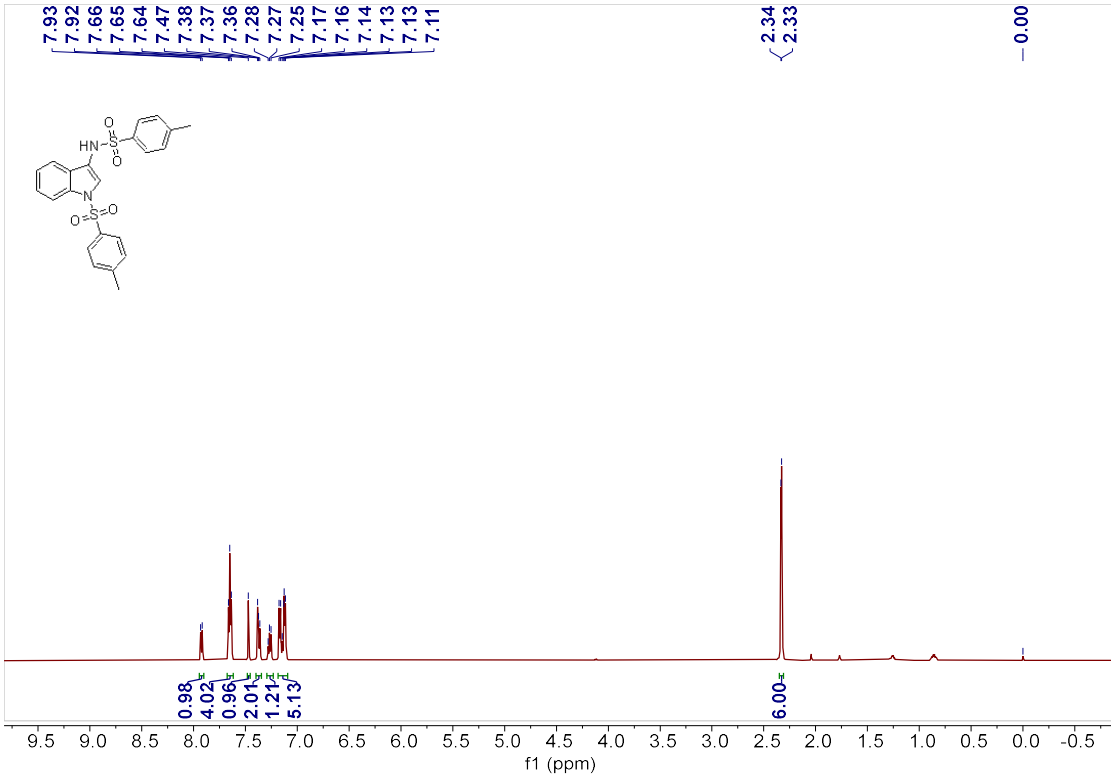
^{1}H NMR (600 MHz) Spectrum of 38 in $CDCl_3$



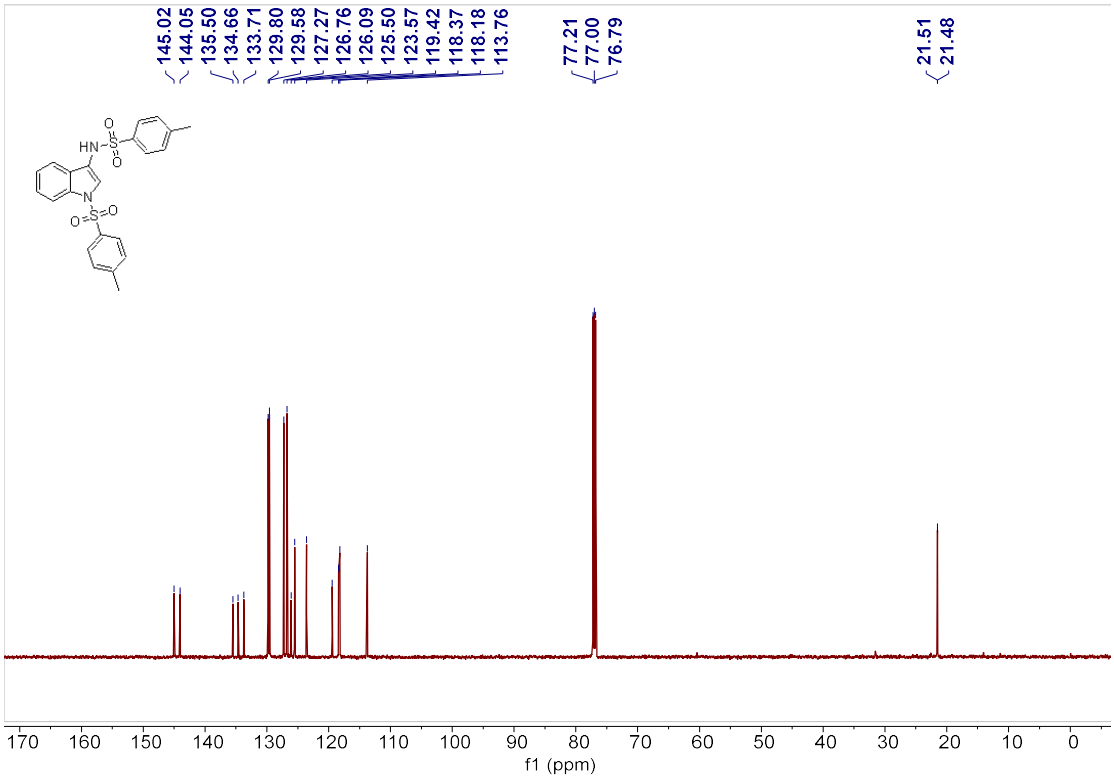
^{13}C NMR (151 MHz) Spectrum of 38 in $CDCl_3$



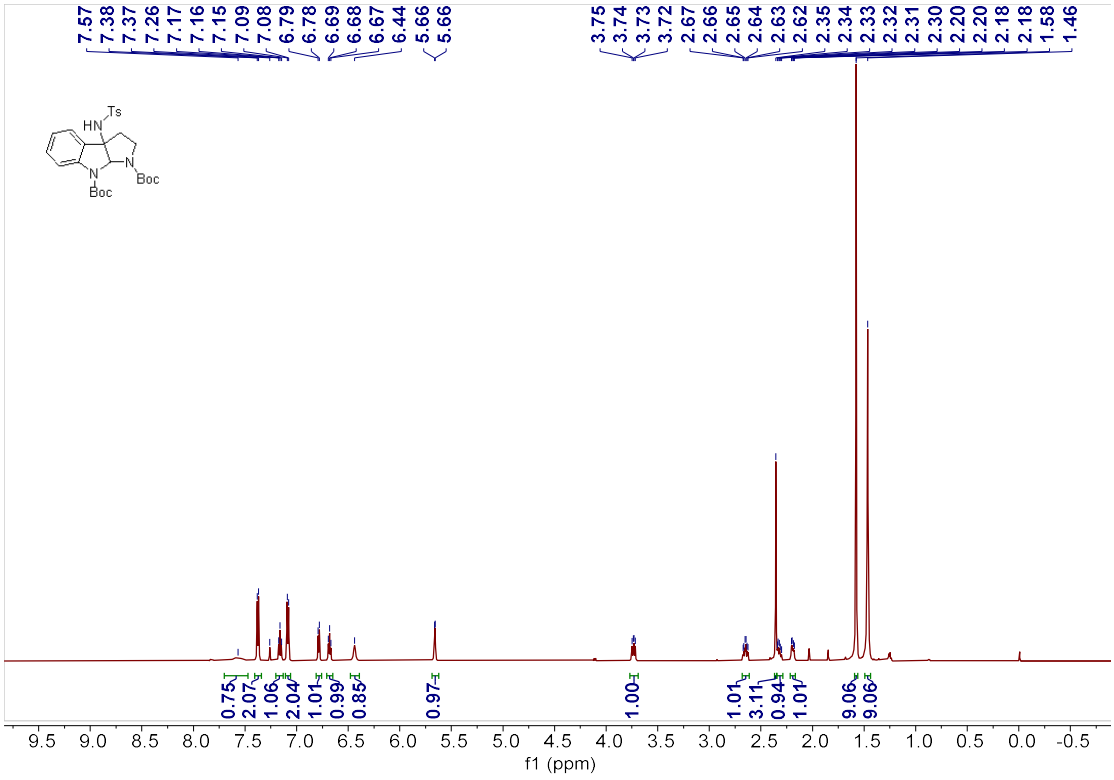
^{1}H NMR (600 MHz) Spectrum of 47 in $CDCl_3$



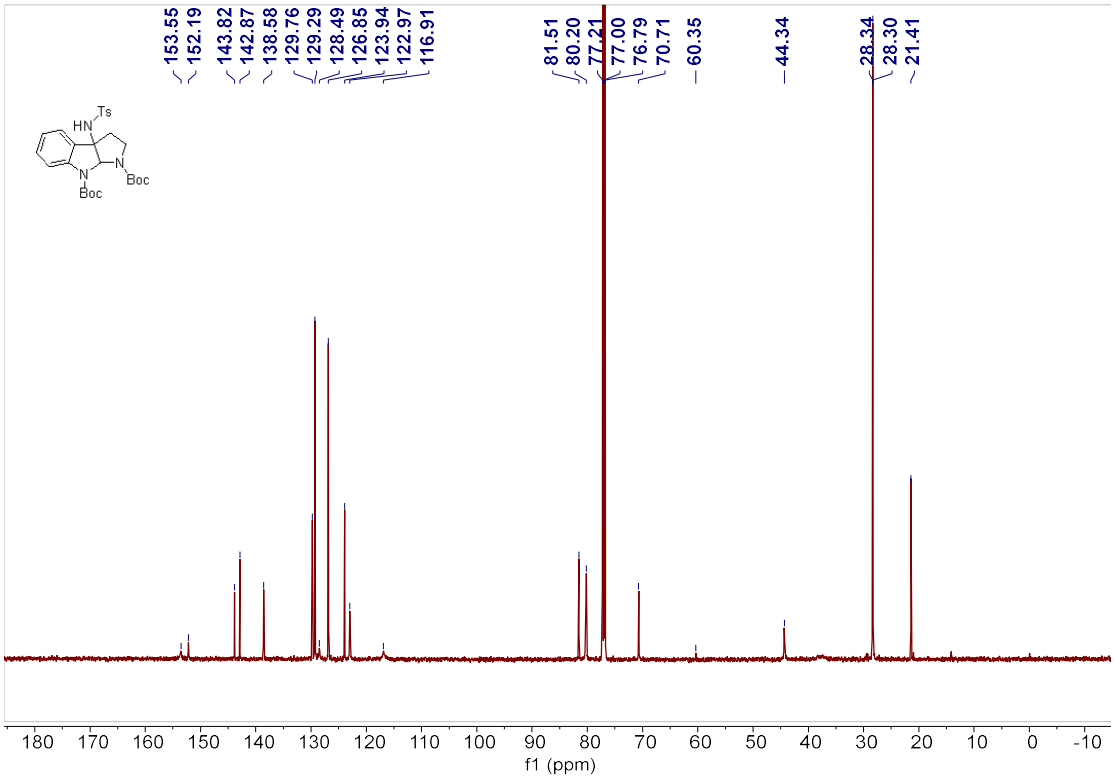
^{13}C NMR (151 MHz) Spectrum of 47 in $CDCl_3$



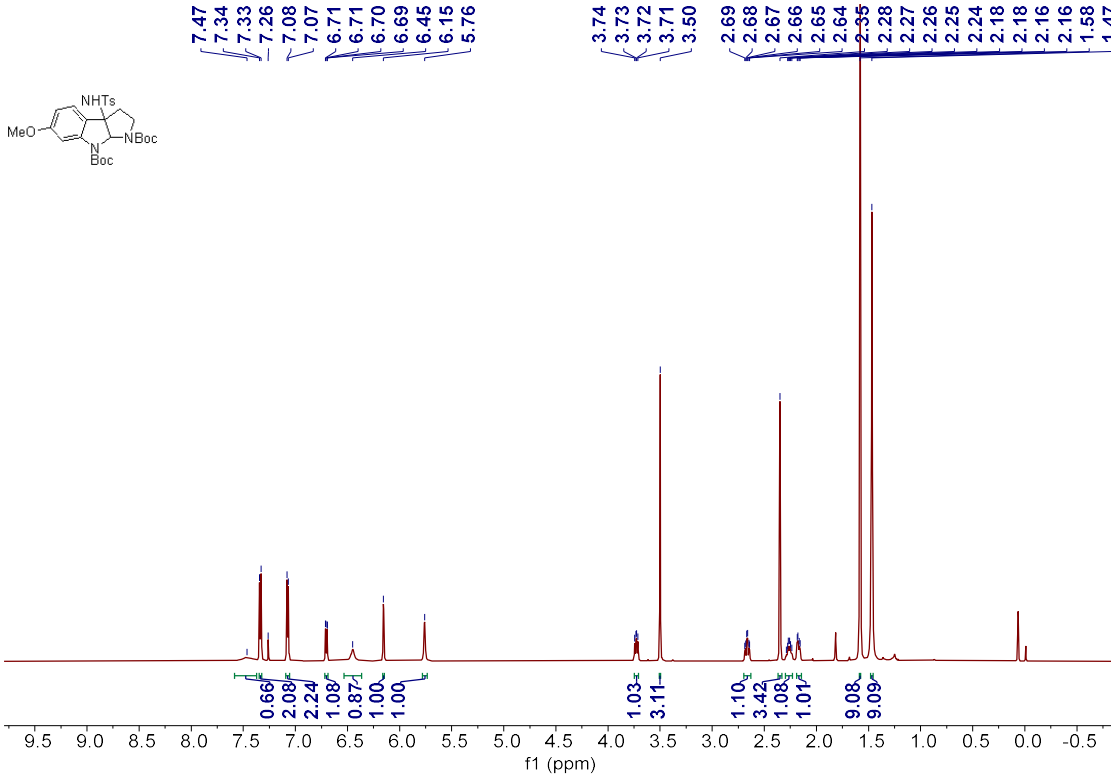
^{1}H NMR (600 MHz) Spectrum of 40 in $CDCl_3$



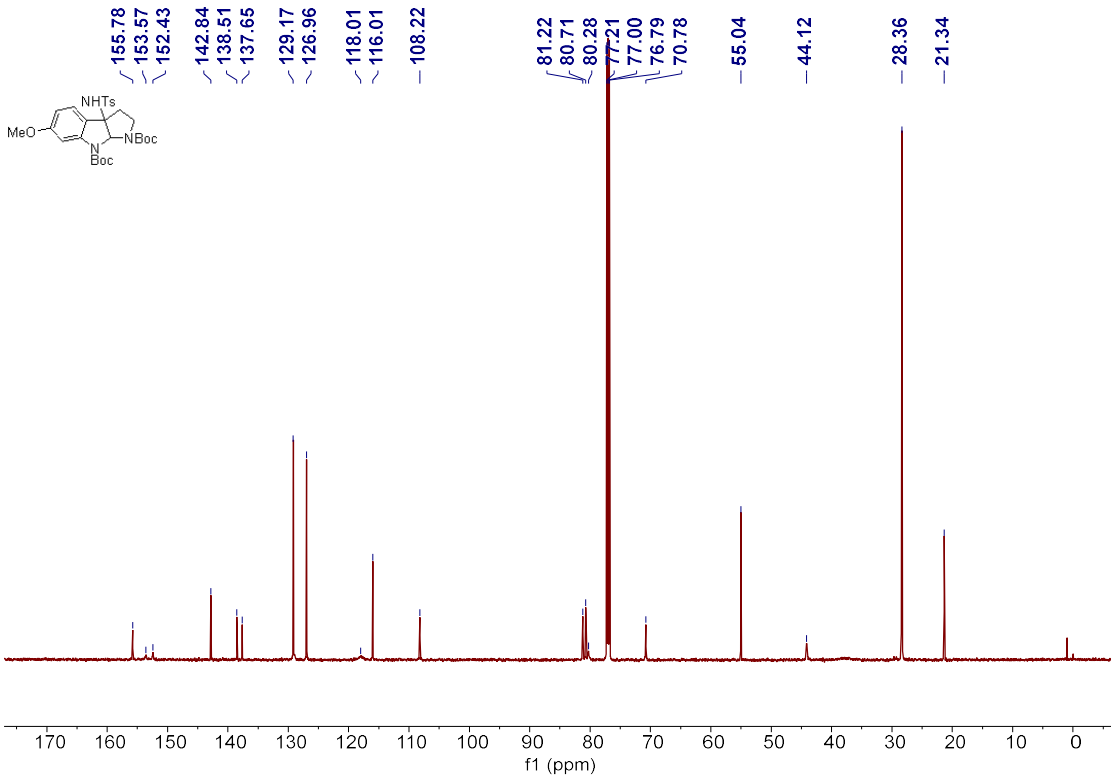
^{13}C NMR (151 MHz) Spectrum of 40 in $CDCl_3$



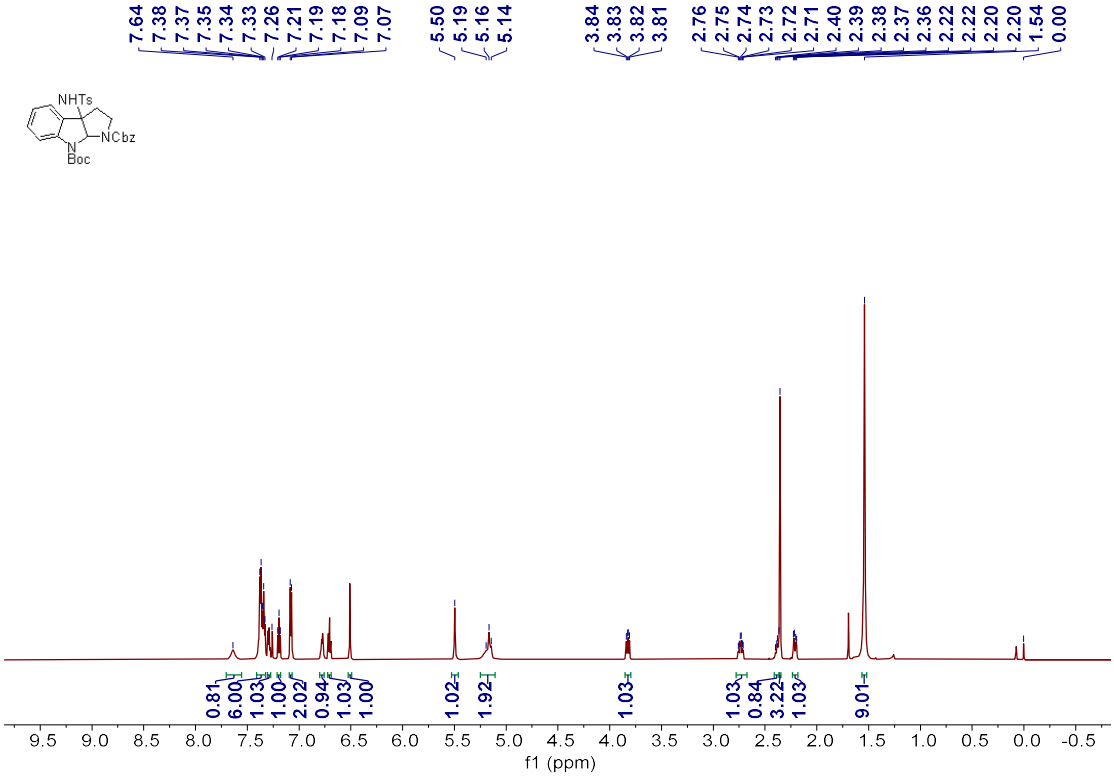
^{1}H NMR (600 MHz) Spectrum of 41 in $CDCl_3$



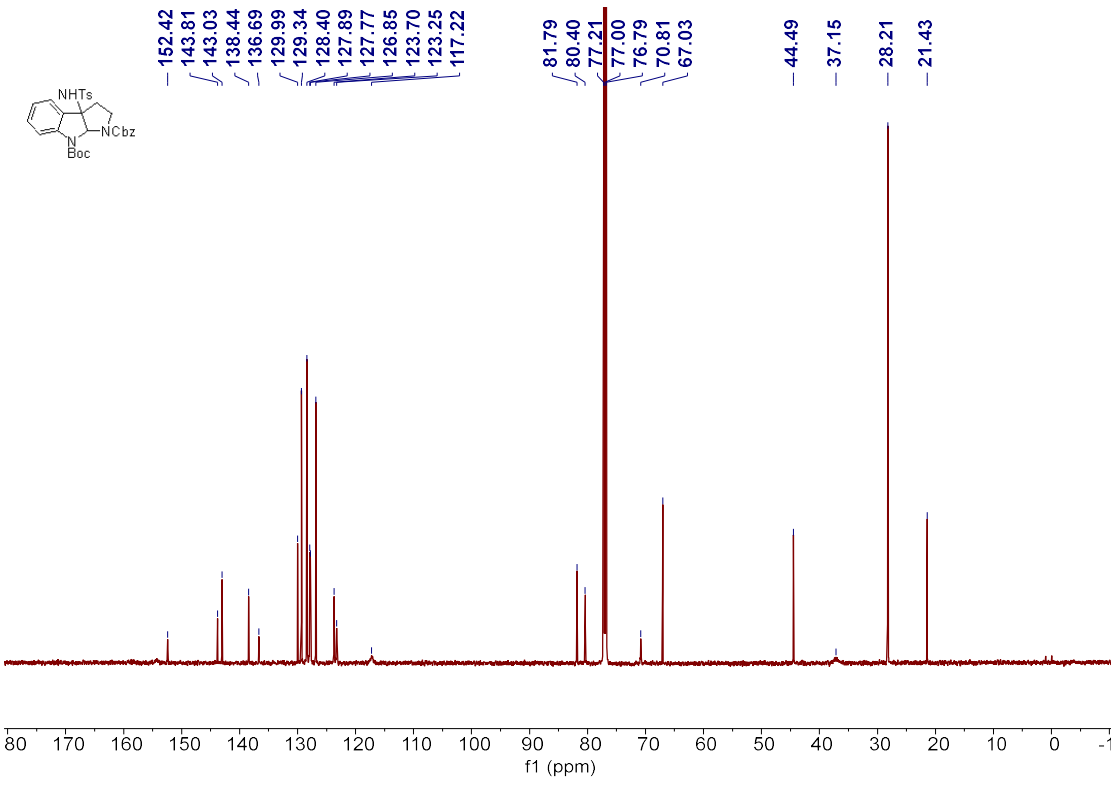
^{13}C NMR (151 MHz) Spectrum of 41 in $CDCl_3$



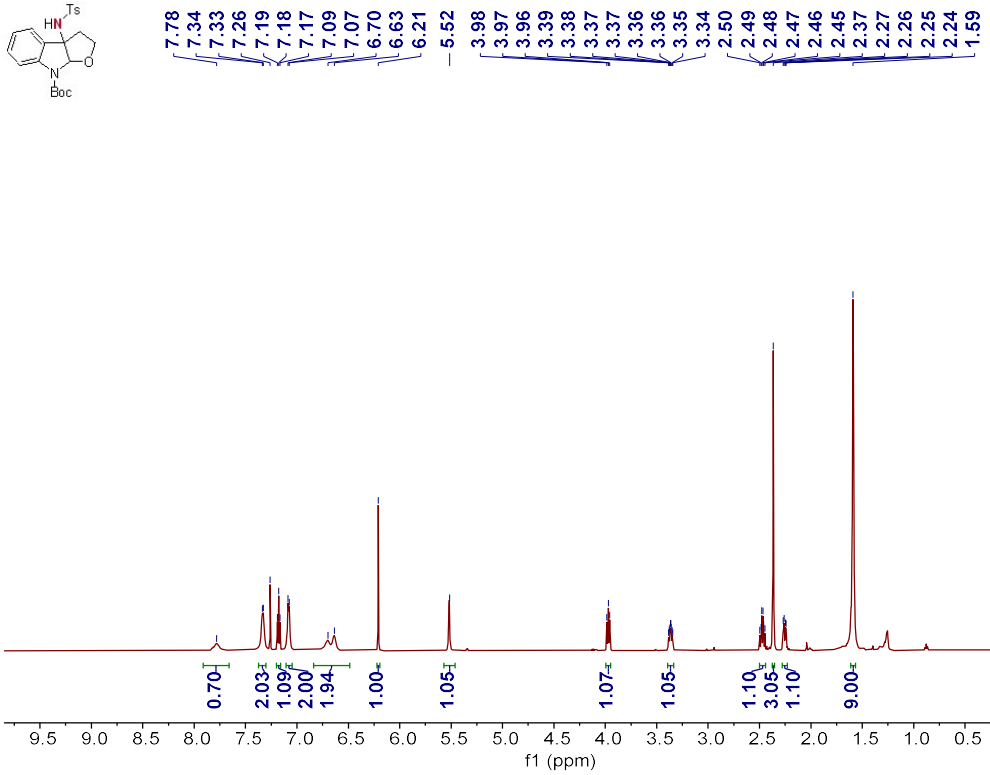
^{1}H NMR (600 MHz) Spectrum of 42 in $CDCl_3$



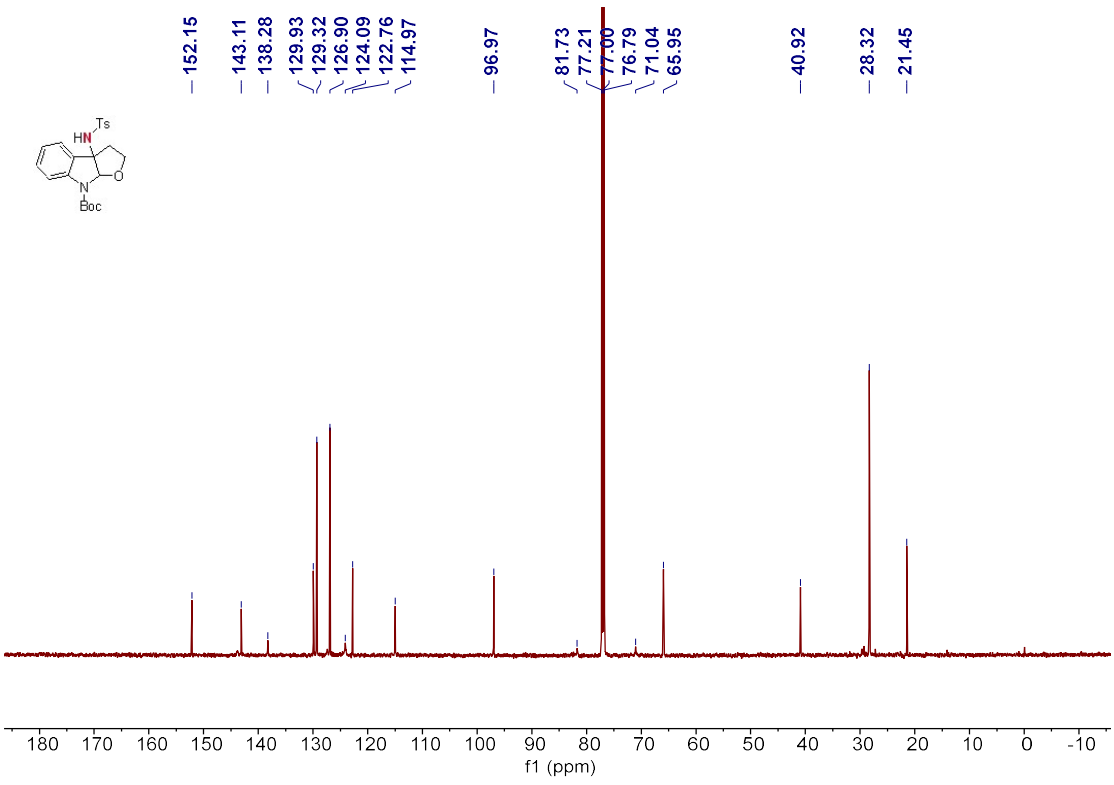
^{13}C NMR (151 MHz) Spectrum of 42 in $CDCl_3$



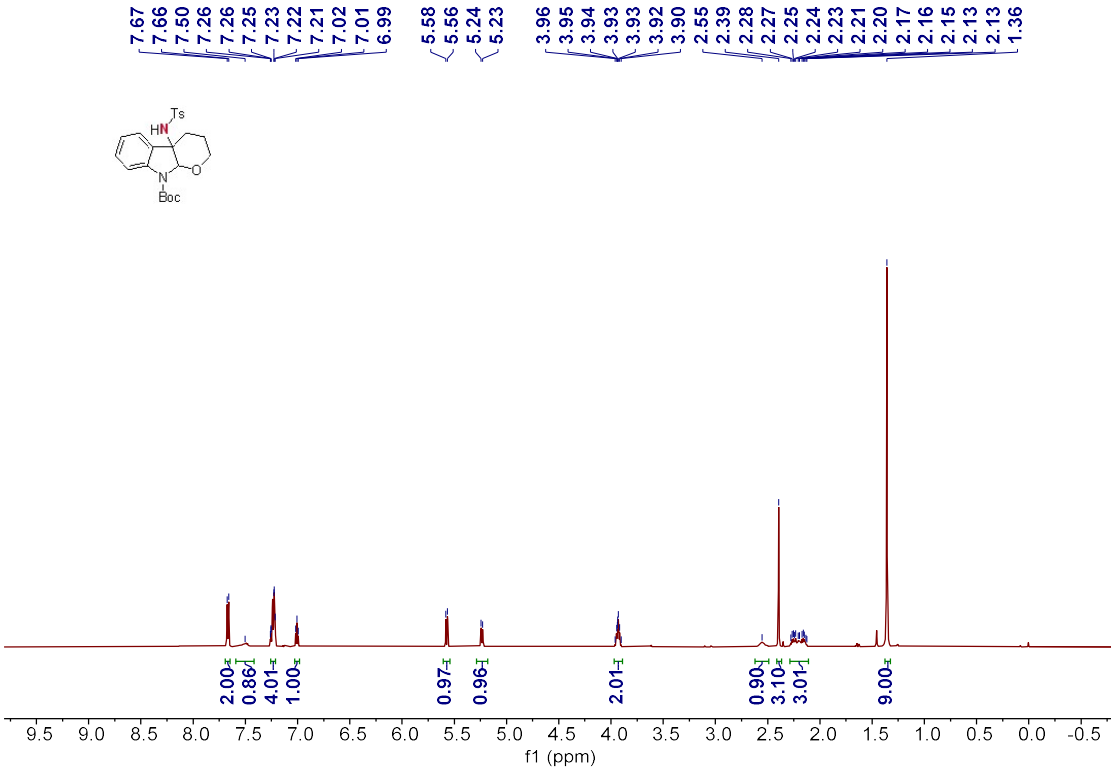
^{1}H NMR (600 MHz) Spectrum of 43 in $CDCl_3$



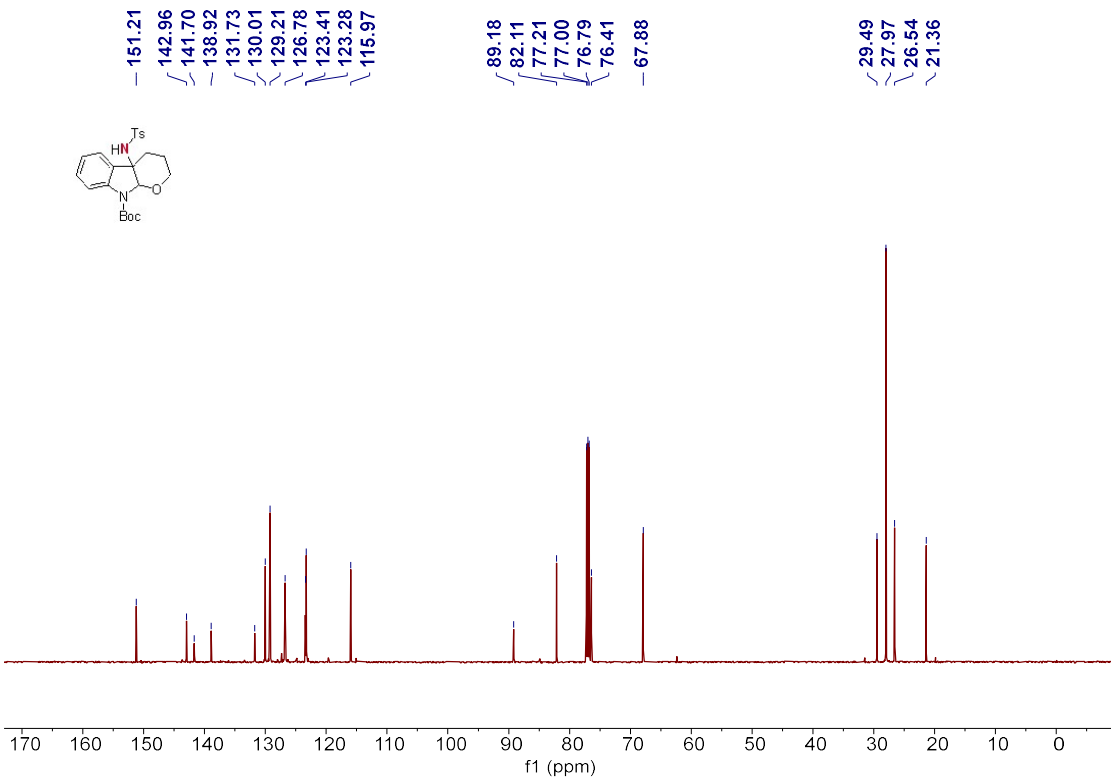
^{13}C NMR (151 MHz) Spectrum of 43 in $CDCl_3$



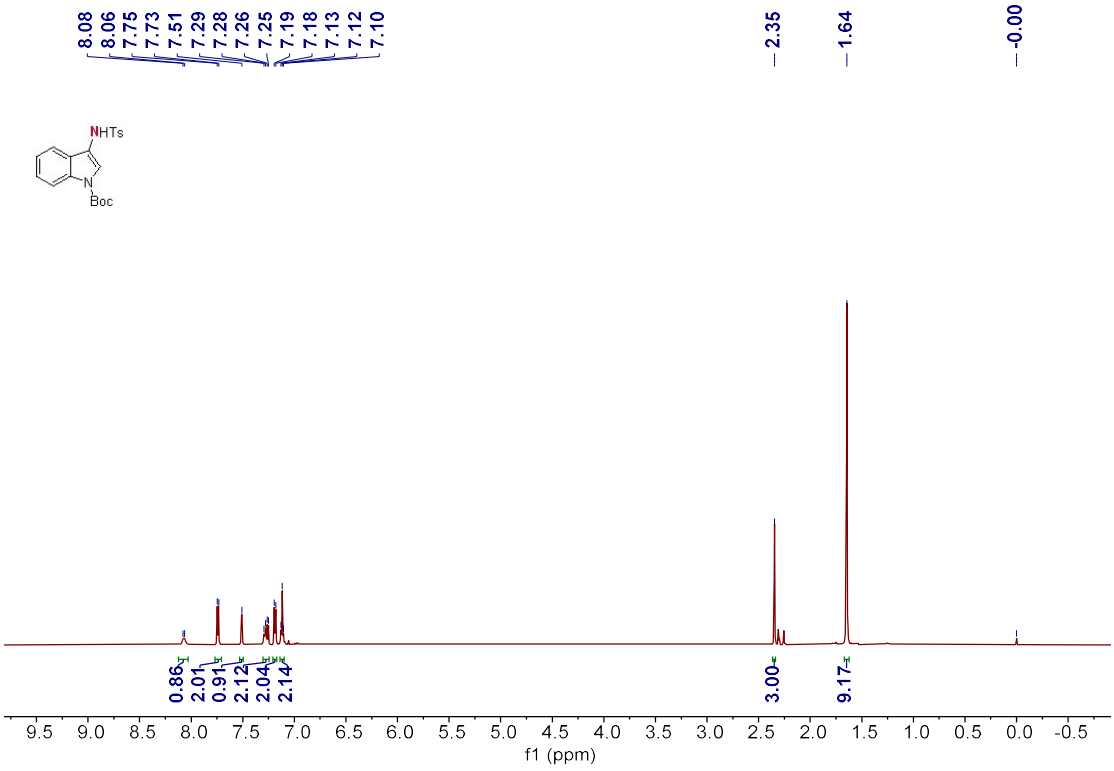
^{1}H NMR (600 MHz) Spectrum of 44 in $CDCl_3$



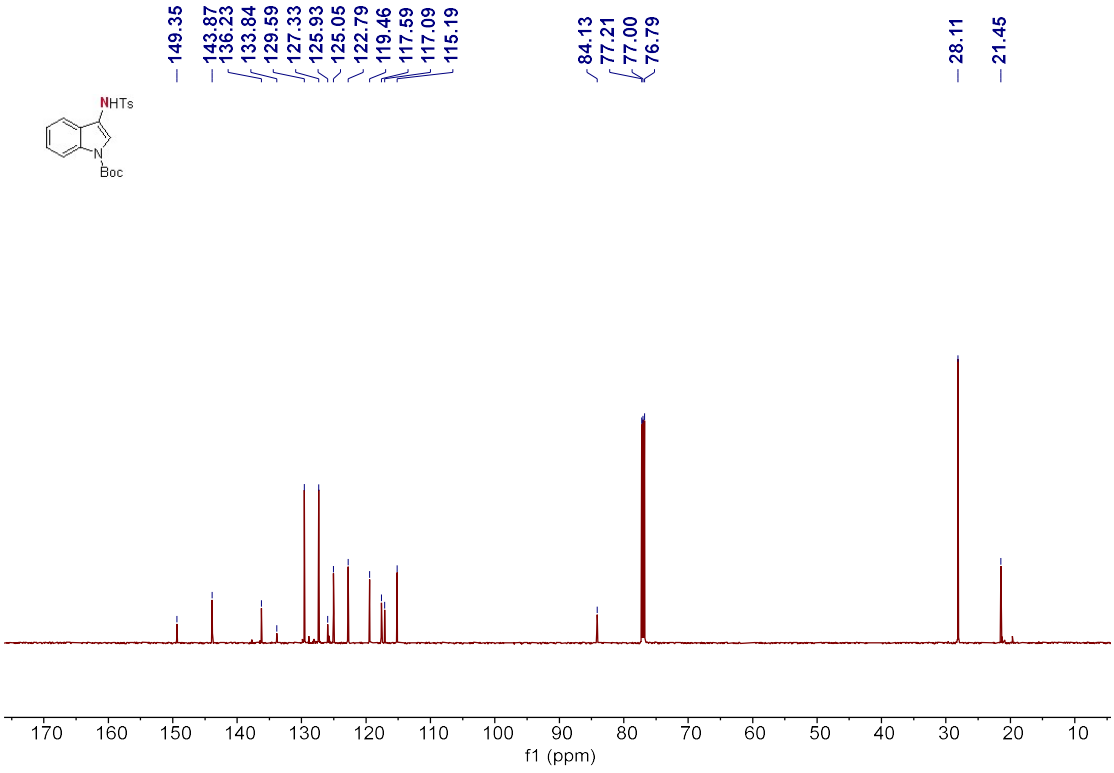
^{13}C NMR (151 MHz) Spectrum of 44 in $CDCl_3$



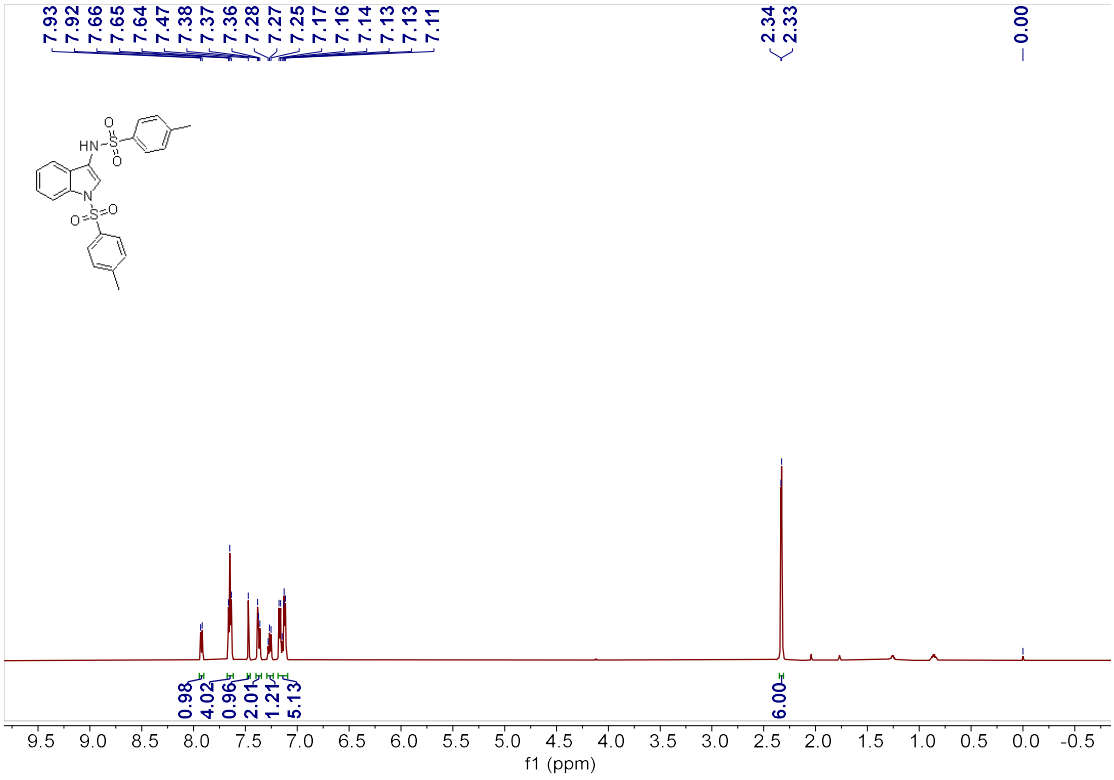
^{1}H NMR (600 MHz) Spectrum of 45 in $CDCl_3$



^{13}C NMR (151 MHz) Spectrum of 45 in $CDCl_3$



^{1}H NMR (600 MHz) Spectrum of 45 in $CDCl_3$



^{13}C NMR (151 MHz) Spectrum of 45 in $CDCl_3$