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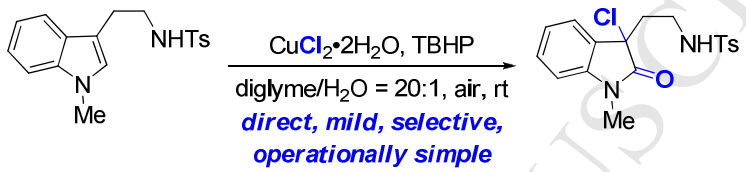

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ABSTRACT

$CuCl_2$/TBHP-mediated direct chlorooxidation of indole derivatives under simple aerobic conditions was reported, leading to facile preparations of a range of 3,3-disubstituted 3-chlorooxindoles in good yields and selectivities.

1. Introduction

Since its early report by Hinman and Bauman in 1964, the 3-halooxindoles and their related reactions have garnered attentions as important structural motifs.[1] They were recognized as versatile electrophiles in a series of substitution reactions to construct complex molecules, and various heteroatoms (O, N, S)[1,2] as well as carbon-based nucleophiles were selectively introduced at the C-3 position of oxindoles through either intermolecular or intramolecular fashion during the past decades.[2a,3] A number of elegant protocols for asymmetric reactions of 3-halooxindoles have also been developed by the groups of Stoltz and Krische *et al.*,[3h-l] thereby generating all-carbon quaternary stereogenic centers or vicinal quaternary carbons in highly stereo-controlled manners. 3-halooxindoles are also used as key intermediates for syntheses of architecturally fascinating natural products, which was exemplified by recent disclosures reported from the groups of Funk, Wang and Dalko and their respective co-workers.[3d-3g] Within this context 3,3-disubstituted 3-halooxindoles represent facile entry to densely functionalized indoles and thus are arguably more interesting and useful. As to preparation of 3,3-disubstituted 3-cholooxindoles, most of the approaches chose oxindole skeletons as starting materials.[3h-i,3k,4] The known methods to those motifs usually leverage on nucleophilic additions of isatin derivatives followed by chlorination using highly reactive reagents such as $SOCl_2$ and CF_3SO_2Cl. However, few reports are available that could allow direct chlorooxidations on their corresponding 3-substituted indoles,[5] and the existing ones may proceed with lower efficiency and/or selectivities, leading to undesirable mixtures of bi- or tri-chloride-substituted products on indole aromatic backbones (see Supporting Information).[5a] The chlorination reagent ^{t}BuOCl is less user-friendly due to its harmful properties.[5e] Thus, the development of a mild, safe, and regioselective chlorooxidation method that is directly implementable on 3-substituted indoles would be of significant synthetic values towards general preparations of 3-chlorooxindoles. Herein, we reported a novel $CuCl_2$/TBHP-mediated[6] chlorooxidation of indoles, which we believe provides a likely simplest approach to 3,3-disubstituted-3-chlorooxindoles under aerobic conditions.

2. Results and discussion

Envisioning that readily available metal chlorides may function as economic chlorination agents, we initially investigated the reaction of *N*-methyl tosyltryptamine (**1a**) with 2 equiv of CuCl using 10 equiv of *tert*-butyl hydroperoxide (TBHP, 70% in water) as the oxidant in DME under ambient conditions (room temperature and in air, entry 1, Table 1). To our delight, the reaction proceeded smoothly to provide 3-chlorooxindole (**2a**) as the desired product in the isolated yield of 46%, which was accompanied by the formation of 3-peroxyoxindole (**3**) byproduct in 15% yield.[7] When $RuCl_3$ was employed in replacement of CuCl, the reaction also furnished product **2a** but the yield was lower (entry 2, 35% yield). Other oxidants, such as di-*tert*-butyl peroxide (DTBP) and 30% H_2O_2 were also screened

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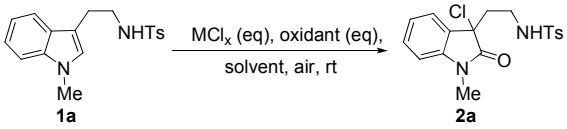
and the reactivities were found to be completely inhibited (entries 3-4). The addition of a base (NaOH) into the reaction system was shown to be detrimental (entry 5). By contrast, addition of an acid (AcOH) seemed to be well-tolerated (entry 6 vs. entry 1). Remarkably, the yield of the product was increased to 68% when a stronger acid (*2M* HCl) was employed, while the amount of byproduct was further reduced (less than 5% in entry 7). Replacing CuCl with $CuCl_2$ and using diglyme as the solvent enhanced further the product yield to 71% (entry 8). Surprisingly, when using the hydrated metal salt $CuCl_2 \cdot 2H_2O$ in the mixed solvent of diglyme/H_2O, the product was obtained in 74% yield in the absence of an acid,[8] while the yield was decreased to 56% under acidic condition (entry 9 vs. entry 10). The reaction seemed to be insensitive to either oxygen or argon atmosphere since only minor difference in product yields were observed (entries 11-12). Finally, control experiments carried out in the absence of either $CuCl_2 \cdot 2H_2O$ or TBHP delivered no product, confirming that the beneficial interactions of both metal chloride and oxidant are essential for bringing about the desired transformation. Collectively these screenings pointed to a set of optimal reagents and conditions that called for the utilizations of 1.4 equivalents of $CuCl_2 \cdot 2H_2O$ and 7 equivalents of TBHP in the mixed aqueous solvents of diglyme/H_2O (20/1) at room temperature and under air.

Table 1. Optimization of the Reaction Conditions.

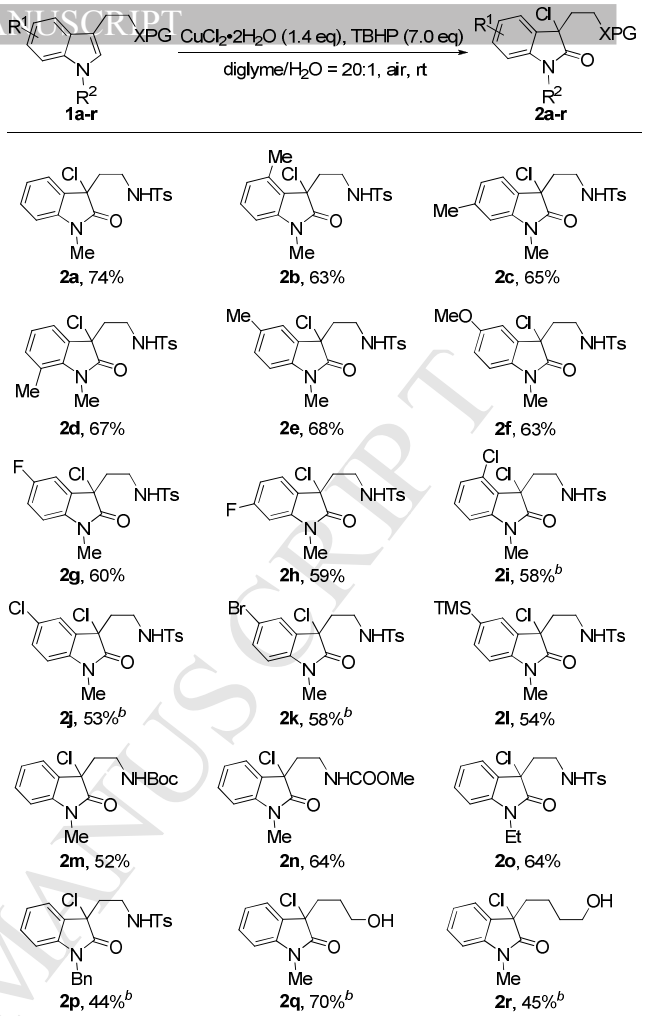


1a **2a**

entry[a]	oxidant (eq)[b]	MCl_x (eq)	additive (eq)	solvent	yield (%)
1	TBHP (10)	CuCl (2.0)	/	DME	46
2	TBHP (10)	$RuCl_3$ (1.0)	/	DME	35
3	DTBP (10)	CuCl (2.0)	/	DME	NR
4	H_2O_2 (10)	CuCl (2.0)	/	DME	NR
5	TBHP (10)	CuCl (2.0)	NaOH (0.1)	DME	NR
6	TBHP (10)	CuCl (2.0)	AcOH (6.0)	DME	45
7[c]	TBHP (7.0)	CuCl (2.0)	HCl (1.5)	DME	68
8[c]	TBHP (7.0)	$CuCl_2$ (2.0)	HCl (1.5)	diglyme	71
9[d]	**TBHP (7.0)**	**$CuCl_2 \cdot 2H_2O$ (1.4)**	**/**	**diglyme/H_2O**	**74**
10[c,d]	TBHP (7.0)	$CuCl_2 \cdot 2H_2O$ (1.4)	HCl (1.5)	diglyme/H_2O	56
11[d,e]	TBHP (7.0)	$CuCl_2 \cdot 2H_2O$ (1.4)	/	diglyme/H_2O	62
12[d,f]	TBHP (7.0)	$CuCl_2 \cdot 2H_2O$ (1.4)	/	diglyme/H_2O	70
13[d]	/	$CuCl_2 \cdot 2H_2O$ (1.4)	/	diglyme/H_2O	0
14[d]	TBHP (7.0)	/	/	diglyme/H_2O	0

[a] Unless otherwise noted, reactions were performed with 1a at 0.10 mmol scale in solvent (0.8 mL) at rt in air for 12-20 h. Isolated yields were reported.
[b] TBHP 70% in water, H_2O_2 30% in water.
[c] *2M* HCl.
[d] Solvent ratio = 20:1.
[e] Under O_2 atmosphere.
[f] Under Ar atmosphere.

The scope of this newly uncovered halooxidation protocol was next explored on a range of indole derivatives (Scheme 1). These reactions all uneventfully afforded the expected products in moderate to good isolated yields (44-74%). The substituents on the indole ring were first examined, and an alkyl group on the indole C-4, C-5, C-6 or C-7 position was founded to be tolerated (**2b**-**2e**). The reactivities evidently also well accommodate either electron-releasing or -withdrawing aryl ring substituents (**2f**, **2l**, **2g**-**2k**). The influence of side-chain nitrogen protecting groups were next investigated, and both Boc and methoxycarbonyl derivatives were capable (**2m**-**2n**). Simple aliphatic groups on the indole nitrogens are readily tolerated, but a benzyl seemed to be less efficient and resulted in lower yield (**2p**). Furthermore, the reaction of indole derivatives bearing a hydroxyalkyl side-chain under heating conditions can also give the expected products (**2q**-**2r**) in the yield of 70% and 45%, respectively. It is notable, however, that indoles bearing no coordinative atoms in their side-chains are not competent substrates, implying the importance of



Scheme 1. Substrate Scope. [a] Unless otherwise noted, the reactions were performed with **1a-r** (0.10 mmol), $CuCl_2$•H_2O (0.14 mmol), and TBHP (70% in H_2O, 0.70 mmol) in diglyme/H_2O (20:1, 0.8 mL) at rt. Isolated yields were reported. [b] Reaction performed at 45 °C.

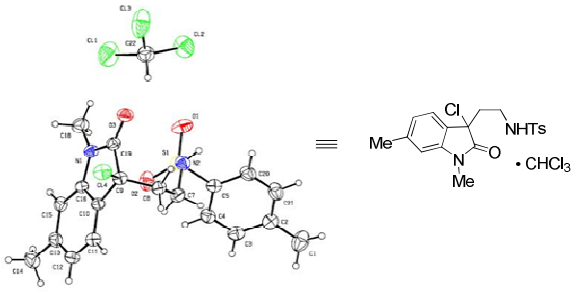
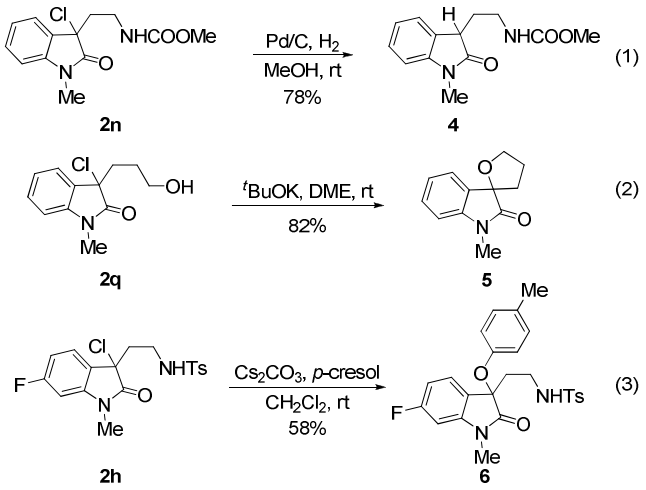


Figure 1. *X*-ray crystallography for **2c**·$CHCl_3$.

directing group effect in the reactions.[9] We were able to grow single crystals of a representative product **2c**, thus unambiguously establishing its structural identity (Figure 1).[10] It merits attention that in all cases examined with this new protocol no chlorination on the indole aromatic backbone was found.

Thus obtained 3-chlorooxindoles could readily engage on many synthetically useful transformations, and some of which were showcased in Scheme 2. Dehalogenation on **2n** under Pd/C-mediated hydrogenation furnished smoothly 2-indolinone (**4**).[11] Base-induced intramolecular nucleophilic displacement in **2q** produced spirocyclic indolin-2-one (**5**), while an intermolecular displacement with **2h** using Funk's standard condition[2a] delivered the oxygenated product (**6**).

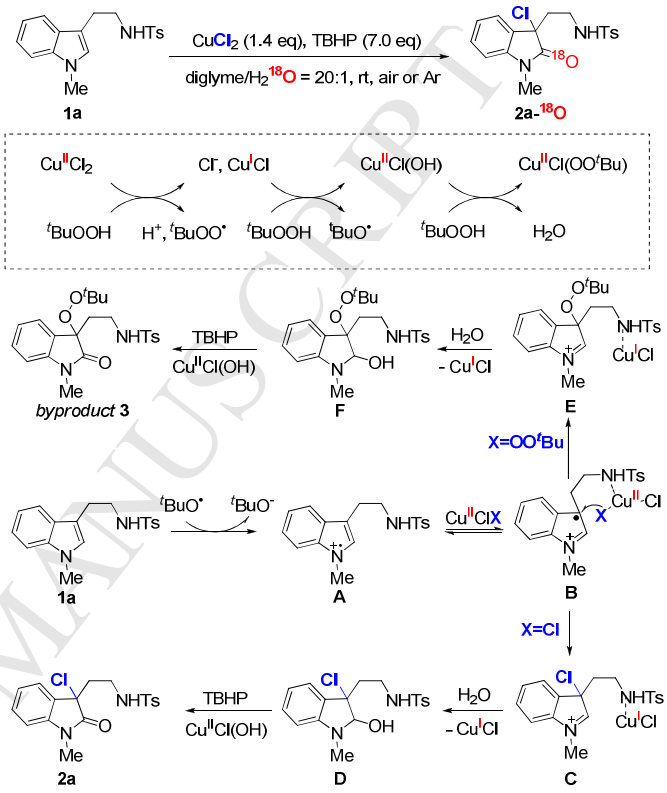


Scheme 2. Derivatizations of 3-Chlorooxindole.

A plausible mechanism could be formulated to accommodate these observed reactivities. As shown in Scheme 3, $CuCl_2$ may react with TBHP to generate the *tert*-butylperoxy radical, CuCl and HCl which was suggested earlier by Kochi and co-workers.[12] CuCl would undergo further reaction with TBHP forming *tert*-butoxyl radical and CuCl(OH). Interaction of CuCl(OH) and TBHP would then produce CuCl(OO^{t}Bu) and H_2O. Thus *in-situ* formed H_2O evidently should constitute an oxygen source when reactions were performed under anhydrous conditions. On the other hand, the ammoniumyl radical cation **A** would be generated by the reaction of substrate **1a** with *tert*-butoxyl radical via a single-electron transfer (SET) pathway, which should readily undergo tautomerization and the side chain coordination with $CuCl_2$ to give the radical cation intermediate **B**.[6h] A chlorine atom transfer of the radical species **B** could then deliver to the iminium ion **C**,[13] which subsequently would react with H_2O to give **2a** through facile oxidation of intermediate **D**.[12b,14] Alternative capture of **B** by *tert*-butoxyl radical would lead to formation of byproduct **3** through a similar sequence. Control experiments were next conduct by treating **1a** with anhydrous $CuCl_2$ and TBHP (5.5 *M* in nonane) in diglyme/$H_2{}^{18}O$ (20/1) at room temperature under either air exposure or Ar atmosphere. Both of them gave the product **2a**-^{18}**O**, confirming that H_2O could function as a viable oxygen source during the oxidation.

3. Conclusion

In summary, guided by a notion that simple metal chloride salt may function as viable chlorination agent, we have designed and uncovered a simple method to prepare 3,3-disubstituted 3-chlorooxindoles directly from their corresponding indole precursors under the synergistic actions of $CuCl_2$•$2H_2O$/TBHP reagents. The protocol is mild, selective, safe, and easy to operate, these merits should enhance its synthetic utilities for practitioners who are interested in accessing to such biologically significant motifs. Our goal is to further pursue and realize catalytic chlorooxidation and the results would be disclosed in due course.



Scheme 3. Proposed Mechanism.

4. Experimental

4.1 General experimental

All reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. All the chemicals were purchased commercially, and used without further purification. $CuCl_2 \cdot 2H_2O$ was purchased from Alfa. Anhydrous tetrahydrofuran (THF) and Et_2O were distilled from sodium-benzophenone, dichloromethane (DCM) were distilled from calcium hydride. All other solvents were purchased as ACS reagents and used without further purification. Thin-Layer chromatography (TLC) was conducted with 0.25 mm Tsingdao silica gel plates (60F-254) and visualized by exposure to UV light (254 nm) or stained with potassium permanganate. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). NMR spectra were recorded on Bruker Advance 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) or Bruker Advance 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. For all the HRMS measurements, the ionization method is ESI and the mass analyzer type is TOF. For full experimental

details, including procedures for all reactions and characterizations of all new compounds (^{1}H NMR, ^{13}C NMR, mass spectrometry), see the Supplementary Information.

4.2 General procedure for $CuCl_2$/TBHP-mediated direct chlorooxidation of indoles

To a 10 mL round-bottomed flask placed with a solution of substrate (0.10 mmol) in diglyme/H_2O (0.8 mL, 20:1 v/v) at room temperature, added $CuCl_2 \cdot 2H_2O$ (0.14 mmol), TBHP (70% in water, 0.70 mmol) via micro-syringe. Then the solution was stirred at room temperature (or warmed to 45 °C). After stirred for 10-16 hours, the reaction was quenched with saturated aqueous Na_2SO_3 and diluted with EtOAc (5 mL) and water (5 mL), the organic layer was separated. The aqueous layer was added 10% H_2SO_4 (0.3 mL) and extracted with EtOAc (2×5 mL). The combined organic layers were washed with water (4×5 mL) and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (Hex/EtOAc = 3:1) to give the desired products as off-white solid.

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Supplementary material

Experimental details and procedures, compound characterization data, copies of ^{1}H, ^{13}C spectra for new compounds, and X-ray crystallographic data.

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7. The crystal structure of the byproduct 3-peroxyoxindole **3n** was deposited at the Cambridge Crystallographic Data Centre (tracking number: 1055715). For more details, see the Supporting Information.
8. The yield of byproduct **3** is lower than 5%.
9. When using a 3-substituted indole, such as 1,3-dimethylindole as the starting material, the yield of chlorooxidation product was lower than 10%.
10. The crystal structure of **2c**•$CHCl_3$ was deposited at the Cambridge Crystallographic Data Centre (tracking number: 1055643).
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Supporting Information

$CuCl_2$/TBHP-Mediated Direct Chlorooxidation of Indoles

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Table of Contents

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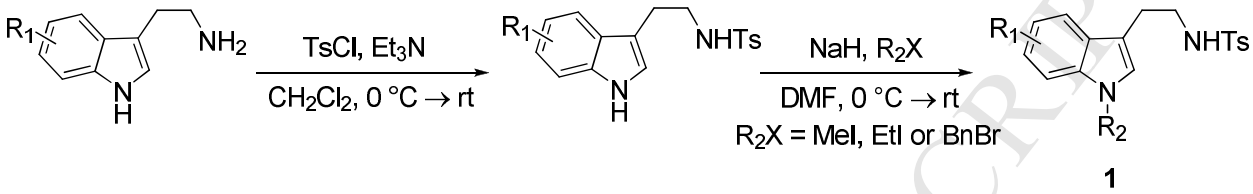
Synthesis of N-tosyl tryptamine derivatives:

N-tosyl tryptamine derivatives prepared according to known literature procedures.[1,2]

General procedure A: (Substrate **1a, 1e-f, 1j-1k, 1o-1p**) [1]



1

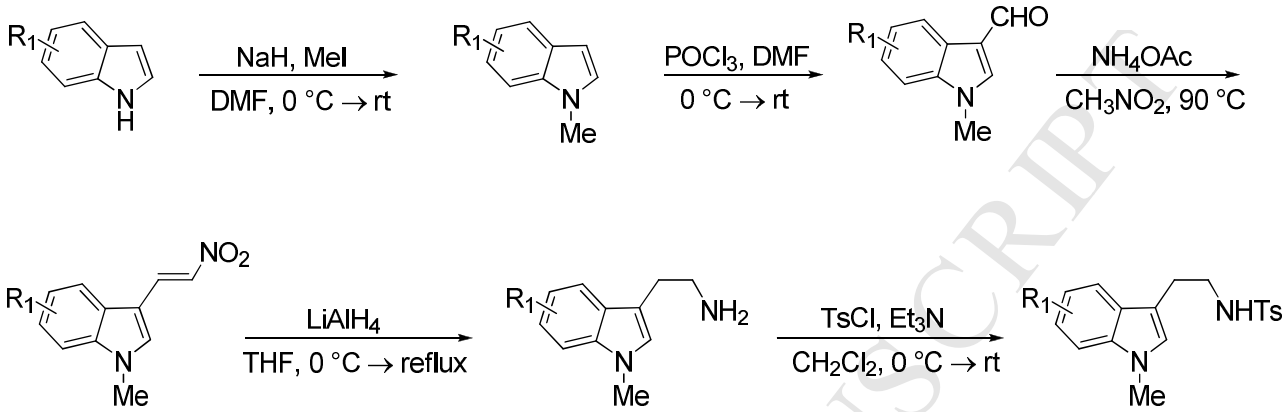
To a solution of tryptamine (5.0 mmol) in CH_2Cl_2 (40 mL) at 0 °C was added Et_3N (15 mmol), then added p-toluenesulfonyl chloride (6.0 mmol) in one portion. The mixture was stirred for 0.5 h, the ice bath removed and allowed to warm up to room temperature. After stirred for an additional 4-8 hours, the reaction was quenched with saturated aqueous NH_4Cl (15 mL). The mixture diluted with water (30 mL), the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 ×20 mL). The combined organic layers were washed with water (2×40 mL) and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (Hex/EtOAc = 5:1) to give the desired products in the yield of 76-88%.

To a solution of tosyltryptamine (2.0 mmol) in DMF (7 mL) at room temperature was added NaH (60% dispersion in mineral oil, 7.0 mmol) slowly, with vigorous stirring, and stirring continued at this temperature for 30 minutes. Then the solution was cooled to 0 °C in an ice bath, and appropriate alkyl halide (2.0 mmol) was added drop-wise by syringe. Stirring was continued at 0 °C for two hours, and the reaction allowed to warm up to room temperature and stirred overnight. The reaction was quenched with saturated aqueous NH_4Cl (3 mL) and diluted with EtOAc (10 mL) and water (10 mL), the organic layer was separated and the aqueous layer was extracted with EtOAc (2×10 mL). The combined organic layers were washed with water (4×20 mL) and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was pre-absorbed onto silica and purified by flash chromatography on silica gel (Hex/EtOAc = 4:1) to give the desired products in the yield of 62-75%.

1. Kieffer, M. E.; Chuang, K. V.; Reisman, S. E. *Chem. Sci.* **2012**, *3*, 3170.

2. Muratore, M. E.; Holloway, C. A.; Pilling, A. W.; Storer, R. I.; Trevitt, G.; Dixon, D. J. *J. Am. Chem. Soc.* **2009**, *131*, 10796.

General procedure B: (Substrate **1b-d, 1g-1i**) [2]



To a solution of indole (12.0 mmol) in DMF (60 mL) at 0 ºC was added NaH (60% dispersion in mineral oil, 14.4 mmol) slowly. The mixture was stirred at this temperature for 30minutes, then methyl iodide (13.2 mmol) was added drop-wise via syringe. Then the reaction was gradually warmed up to room temperature and stirred for 3 hours. The reaction was quenched with saturated aqueous NH_4Cl and diluted with EtOAc (60 mL) and water (60 mL), the organic layer was separated and the aqueous layer was extracted with EtOAc (2×60 mL). The combined organic layers were washed with water (4×60 mL) and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to furnish the desired N-methyl indole as colorless oil that required no further purification.

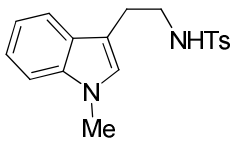
To a cooled solution of DMF (5 mL, 3 mL per 1 mL of $POCl_3$) at 0 ºC was added phosphorus oxychloride (1.6 mL, 18 mmol) drop-wise, and then the mixture was stirred at the same temperature for 1 h. Then N-methyl indole (ca. 12 mmol) was added as a DMF solution (10 mL), forming a heavy suspension that required vigorous stirring. The mixture was then allowed to warm to room temperature and stirred for 5 hours. Then *2M* NaOH (27 mL) was added slowly with vigorous stirring. The mixture was heated to reflux for 20 minutes. Then the reaction was cooled to room temperature and diluted with EtOAc (15 mL) and water (15 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (2×15 mL). The combined organic layers were washed with water (4×15 mL) and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*

to furnish the desired aldehyde as yellowish solid that required no further purification.

Aldehyde (4 mmol) and ammonium acetate (12 mmol) were refluxed in nitromethane (12 mL) for 1 hour. The solvent was removed *in vacuo* and the residue washed with water and filtered, furnishing the desired nitro olefin as yellowish solid that required no further purification.

To an oven-dried 100 mL round-bottomed flask placed with a solution of nitro olefin (3 mmol) in freshly distilled THF (24 mL) with ice-bath cooling, added lithium aluminium hydride powder (24 mmol) cautiously in three portions. Stirring was continued at 0 °C for 30 minutes, and the reaction allowed to heat to reflux and stirring overnight. The reaction was cooled to 0 °C and carefully quenched by the dropwise addition of water (1 mL per 1 g $LiAlH_4$), 10% NaOH (1 mL per 1 g $LiAlH_4$), and water (2 mL per 1 g $LiAlH_4$) under stirring. Filtered and the filtrate was concentrated *in vacuo* to furnish the crude amine. A solution of crude residue in CH_2Cl_2 (15 mL) at 0 °C was added Et_3N (6 mmol), then added p-toluenesulfonyl chloride (2 mmol) in one portion. The mixture was stirred for 0.5 h, the ice bath removed and allowed to warm up to room temperature. After stirred for an additional 4-8 hours, the reaction was quenched with saturated aqueous NH_4Cl (5 mL). The mixture diluted with water (10 mL), the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2×10 mL). The combined organic layers were washed with water (2×20 mL) and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (Hex/EtOAc = 5:1) to give the off-white solid as desired products.

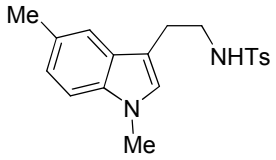
^{1}H NMR and ^{13}C NMR spectra data of N-tosyl tryptamine derivatives



1a

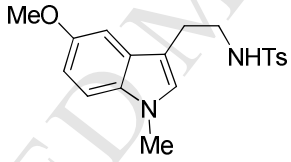
N-tosyl-N'-methyltryptamine (1a): Prepared according to General Procedure A. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 7.9 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 7.25-7.19 (m, 3H), 7.06 (dd, J = 8, 8Hz, 1H), 6.82 (s, 1H), 4.58 (t, J = 5.8 Hz, 1H), 3.72 (s, 3H), 3.26 (q, J = 6.5

Hz, 2H), 2.92 (t, J = 6.6 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 137.1, 136.8, 129.6, 127.4, 127.3, 127.0, 121.8, 119.0, 118.6, 110.0, 109.3,43.2, 32.6, 25.4, 21.5; HRMS calc'd for $C_{18}H_{21}N_2O_2S$ $[M+H]^+$: 329.1318, found 329.1324.



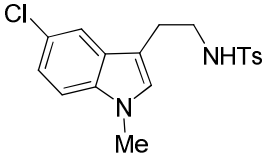
1e

5-methyl-N-tosyl-N'-methyltryptamine (1e): Prepared according to General Procedure A. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 8.3 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.18 (s, 1H), 7.16 (s, 1H), 7.05 (d, J = 8.3 Hz, 1H), 6.77 (s, 1H), 4.57 (t, J = 6.0 Hz, 1H), 3.69 (s, 3H), 3.25 (q, J = 6.5 Hz, 2H), 2.89 (t, J = 6.6 Hz, 2H), 2.42 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 136.8, 135.6, 129.5, 128.2, 127.5, 127.4, 127.0, 123.4, 118.2, 109.2, 109.1,43.1, 32.6, 25.3, 21.5, 21.4; HRMS calc'd for $C_{19}H_{23}N_2O_2S$ $[M+H]^+$: 343.1475, found 343.1474.



1f

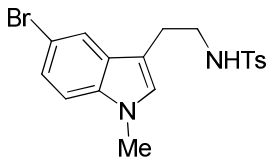
5-methoxy-N-tosyl-N'-methyltryptamine (1f): Prepared according to General Procedure A. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.8 Hz, 1H), 6.88 (dd, J = 8.8, 2.4 Hz, 1H), 6.82 (d, J = 2.3 Hz, 1H), 6.78 (s, 1H), 4.45 (br s, 1H), 3.80 (s, 3H), 3.70 (s, 3H), 3.23 (q, J = 6.5 Hz, 2H), 2.89 (t, J = 6.6 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 143.2, 136.6, 132.5, 129.5, 127.9, 127.5, 127.0, 112.0, 110.1, 109.2, 100.3, 55.8, 42.9, 32.8, 25.3, 21.4; HRMS calc'd for $C_{19}H_{23}N_2O_3S$ $[M+H]^+$: 359.1424, found 359.1423.



1j

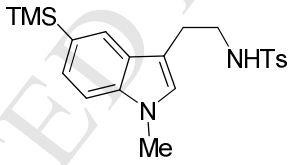
5-chloro-N-tosyl-N'-methyltryptamine (1j): Prepared according to General Procedure A. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 1.7 Hz, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.18

– 7.14 (m, 2H), 6.85 (s, 1H), 6.85 (br s, 1H), 4.45 (s, 1H), 3.71 (s, 3H), 3.22 (q, J = 6.5 Hz, 2H), 2.85 (t, J = 6.6 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 136.5, 135.5, 129.6, 128.7, 128.2, 126.9, 124.8, 122.0, 118.0, 110.3, 109.5, 42.8, 32.8, 25.1, 21.5; HRMS calc'd for $C_{18}H_{20}ClN_2O_2S$ $[M+H]^+$: 363.0929, found 363.0930.



1k

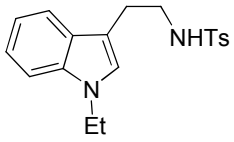
5-bromo-N-tosyl-N'-methyltryptamine (1k): Prepared according to General Procedure A. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 1.7 Hz, 1H), 7.29 (d, J = 1.8 Hz, 1H), 7.27 (s, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.7 Hz, 1H), 6.84 (s, 1H), 4.37 (t, J = 5.7 Hz, 1H), 3.71 (s, 3H), 3.22 (q, J = 6.4 Hz, 2H), 2.85 (t, J = 6.6 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 136.5, 135.8, 129.6, 128.9, 128.6, 127.0, 124.5, 121.1, 112.4, 110.8, 109.6, 42.9, 32.8, 25.1, 21.5; HRMS calc'd for $C_{18}H_{20}BrN_2O_2S$ $[M+H]^+$: 407.0423, found 407.0424, 409.0412.



1l

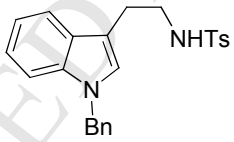
5-TMS-N-tosyl-N'-methyltryptamine (1l): To an oven-dried 10 mL round bottom flask placed with a solution of 5-bromo-N-tosyl-N'-methyltryptamine **1k** (0.204 g, 0.5 mmol) in freshly distilled THF (5 mL) at -78 ºC, added n-BuLi (2.5 M in hexane, 0.44 mL, 1.1 mmol) dropwise via syringe. The reaction was stirred at -78 ºC for 0.5 h, then TMSCl was added (0.086 mL, 1.0 mmol) dropwise via syringe. Then the mixture was gradually warmed up to room temperature and stirred overnight. The reaction was quenched with saturated aqueous NH_4Cl (1 mL) and diluted with EtOAc (5 mL) and water (5 mL), the organic layer was separated and the aqueous layer was extracted with EtOAc (2×5 mL). The combined organic layers were washed with water (2×5 mL) and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (Hex/EtOAc = 4:1) to afford the desired product (0.078 g, 39% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.3 Hz, 2H), 7.60 (s, 1H), 7.40 – 7.28 (m, 2H), 7.22 (t, J = 7.3 Hz, 2H), 6.81 (s,

1H), 4.47 (t, J = 6.2 Hz, 1H), 3.73 (s, 3H), 3.27 (q, J = 6.5 Hz, 2H), 2.95 (t, J = 6.6 Hz, 2H), 2.40 (s, 3H), 0.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 137.6, 136.8, 129.6, 129.1, 127.2, 127.1, 127.0, 126.5, 123.9, 110.0, 109.0, 43.2, 32.6, 25.4, 21.5, -0.6; HRMS calc'd for $C_{21}H_{29}N_2O_2SSi$ $[M+H]^+$: 401.1714, found 401.1715.



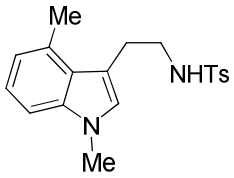
1o

N-tosyl-N'-ethyltryptamine (1o): Prepared according to General Procedure A. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 7.9 Hz, 1H), 7.31 (d, J = 8.3 Hz, 1H), 7.22 (d, J = 8.2 Hz, 3H), 7.07 – 7.02 (m, 1H), 6.89 (s, 1H), 4.63 (s, 1H), 4.11 (q, J = 7.3 Hz, 2H), 3.27 (q, J = 6.6 Hz, 2H), 2.93 (t, J = 6.7 Hz, 2H), 2.40 (s, 3H), 1.43 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 136.8, 136.1, 129.6, 127.4, 126.9, 125.4, 121.6, 118.9, 118.7, 110.0, 109.4, 43.2, 40.7, 25.4, 21.4, 15.4; HRMS calc'd for $C_{19}H_{23}N_2O_2S$ $[M+H]^+$: 343.1475, found 343.1475.



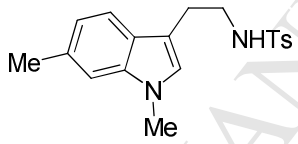
1p

N-tosyl-N'-benzyltryptamine (1p): Prepared according to General Procedure A. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 7.9 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.26 (t, J = 4.1 Hz, 2H), 7.22 – 7.14 (m, 3H), 7.12 – 7.08 (m, 2H), 7.08 – 7.02 (m, 1H), 6.86 (s, 1H), 5.25 (s, 2H), 4.40 (t, J = 6.0 Hz, 1H), 3.28 (q, J = 6.5 Hz, 2H), 2.92 (t, J = 6.7 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 137.3, 136.7, 129.5, 128.7, 127.6, 127.5, 126.9, 126.7, 126.5, 122.0, 119.2, 118.7, 110.6, 109.8，49.9, 43.0, 25.4, 21.4; HRMS calc'd for $C_{24}H_{24}N_2NaO_2S$ $[M+Na]^+$: 427.1456, found 427.1443.



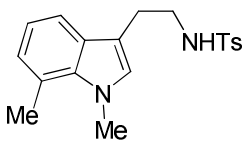
1b

4-methyl-N-tosyl-N'-methyltryptamine (1b): Prepared according to General Procedure B. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.11 (s,1H), 7.11 (d, J = 8.0 Hz, 1H), 6.83 – 6.79 (m, 1H), 6.78 (s, 1H), 4.73 (t, J = 6.1 Hz, 1H), 3.69 (s, 3H), 3.24 (q, J = 6.6 Hz, 1H), 3.07 (t, J = 6.7 Hz, 1H), 2.54 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 137.6, 136.8, 130.6, 129.6, 127.5, 127.0, 125.8, 121.8, 120.8, 110.7, 107.2, 44.3, 32.7, 27.0, 21.5, 20.2; HRMS calc'd for $C_{19}H_{23}N_2O_2S$ $[M+H]^+$: 343.1475, found 343.1473.



1c

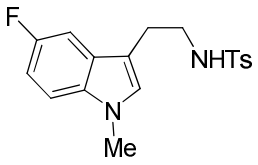
6-methyl-N-tosyl-N'-methyltryptamine (1c): Prepared according to General Procedure B. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 2H), 7.28 (s, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.08 (s, 1H), 6.89 (dd, J = 8.1, 0.8 Hz, 1H), 6.74 (s, 1H), 4.43 (t, J = 6.1 Hz, 1H), 3.69 (s, 3H), 3.24 (q, J = 6.5 Hz, 2H), 2.89 (t, J = 6.6 Hz, 2H), 2.49 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 137.6, 136.8, 131.7, 129.5, 127.0, 126.7, 125.1, 120.7, 118.3, 109.7, 109.3, 77.3, 77.0, 76.7, 43.1, 32.5, 25.4, 21.8, 21.4; HRMS calc'd for $C_{19}H_{23}N_2O_2S$ $[M+H]^+$: 343.1475, found 343.1474.



1d

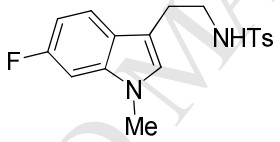
7-methyl-N-tosyl-N'-methyltryptamine (1d): Prepared according to General Procedure B. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.3 Hz, 2H), 7.24 (s, 1H), 7.24 – 7.21 (m, 2H), 6.92-6.88 (m, 2H), 6.70 (s, 1H), 4.61(t,J = 6.1 Hz,1H), 3.98 (s, 3H), 3.24 (q, J = 6.5 Hz, 2H), 2.92 – 2.82 (m, 2H), 2.74 (d, J = 6.6 Hz, 3H), 2.42 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 136.8, 135.8, 129.6, 128.9, 128.4, 127.0, 124.4, 121.4, 119.3, 116.6, 109.6, 43.0, 36.5, 25.3, 21.5, 19.6; HRMS

calc'd for $C_{19}H_{23}N_2O_2S$ $[M+H]^+$: 343.1475, found 343.1473.



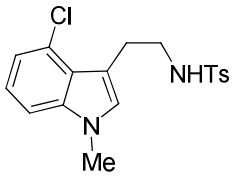
1g

5-fluoro-N-tosyl-N'-methyltryptamine (1g): Prepared according to General Procedure B. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.17 (dd, J = 9.7, 4.3 Hz, 1H), 6.95 (d, J = 9.5 Hz, 2H), 6.86 (s, 1H), 4.52 (t, J = 6.0 Hz, 1H), 3.71 (s, 3H), 3.22 (q, J = 6.5 Hz, 2H), 2.85 (t, J = 6.6 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5 (d, J = 234.6 Hz), 143.4, 136.6, 133.7, 129.6, 129.0, 127.4 (d, J = 9.6 Hz), 126.9, 110.1 (d, J = 20.4 Hz), 109.9 (d, J = 3.8 Hz), 109.8 (d, J = 4.8 Hz), 103.4 (d, J = 23.4 Hz), 42.9, 32.9, 25.2, 21.5; ^{19}F NMR (376 MHz, CDCl3) δ -125.2.; HRMS calc'd for $C_{18}H_{20}FN_2O_2S$ $[M+H]^+$: 347.1224, found 347.1224.



1h

5-fluoro-N-tosyl-N'-methyltryptamine (1h): Prepared according to General Procedure B. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 2H), 7.29 (s, 3H), 7.20 (s, 1H), 6.96 – 6.89 (m, 1H), 6.84 – 6.74 (m, 2H), 4.69 (t, J = 5.7 Hz, 1H), 3.65 (s, 3H), 3.23 (q, J = 6.4 Hz, 2H), 2.87 (t, J = 6.6 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9 (d, J = 235.0 Hz), 143.3, 137.2, 136.6, 129.5, 127.6, 126.9, 123.8, 119.3 (d, J = 10.3 Hz), 110.3, 107.6 (d, J = 24.7 Hz), 95.7 (d, J = 26.3 Hz), 43.1, 32.7, 25.3, 21.5; ^{19}F NMR (376 MHz, CDCl3) δ -120.7; HRMS calc'd for $C_{18}H_{20}FN_2O_2S$ $[M+H]^+$: 347.1224, found 347.1223.

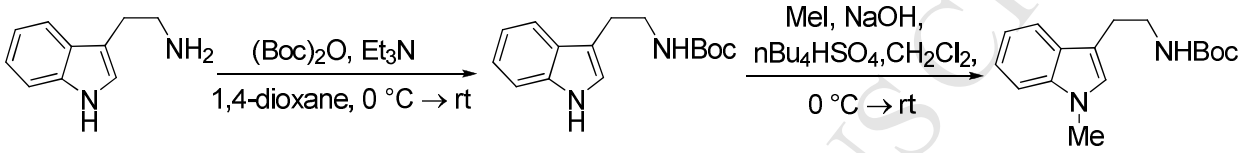


1i

4-chloro-N-tosyl-N'-methyltryptamine (1i): Prepared according to General Procedure B. ^{1}H NMR

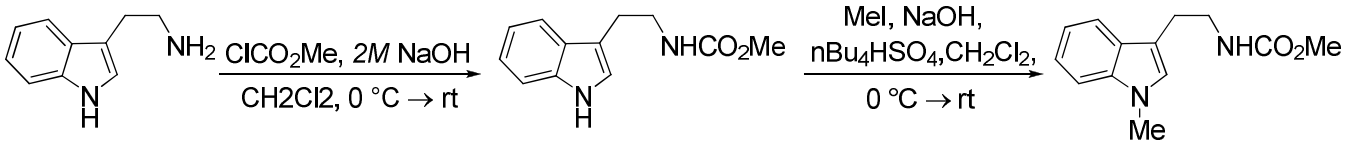
(400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.16 – 7.12 (m, 1H), 7.07 (t, J = 7.8 Hz, 1H), 6.99 (dd, J = 7.4, 0.7 Hz, 1H), 6.84 (s, 1H), 4.67 (t, J = 5.9 Hz, 1H), 3.68 (s, 3H), 3.30 (q, J = 6.4 Hz, 2H), 3.10 (t, J = 6.6 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143, 138.6, 136.8, 129.5, 129.2, 126.9, 126.0, 124.0, 122.1, 119.9, 110.4, 108.1, 44.4, 32.9, 26.3, 21.5; HRMS calc'd for $C_{18}H_{20}ClN_2O_2S$ $[M+H]^+$: 363.0929, found 363.0931.

Procedure for synthesis of substrate 1m-n, 1q-1r



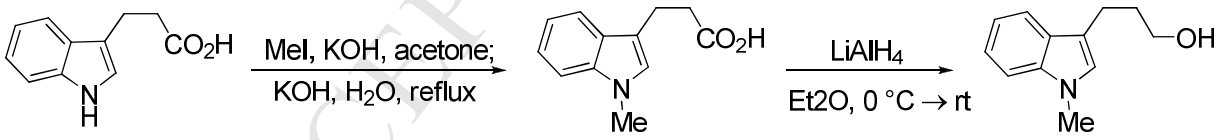
To a yellow suspension of tryptamine (2.0 g, 12.5 mmol) in 1,4-dioxane (10 mL) was added Et_3N (3.6 mL, 26.0 mmol) at 0 °C. Then a solution of $(Boc)_2O$ (3.0 g, 13.8 mmol) in 1,4-dioxane (10 mL) was added via cannula. Then the reaction was allowed to warm up to room temperature and stirred for 2 hours. The reaction solution was concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (Hex/EtOAc = 4:1) to give the desired N-Boc-tryptamine as a white solid (3.102 g, 95%)

A mixture of N-Boc-tryptamine (1.041 g, 4 mmol), NaOH (0.640 g, 16 mmol), nBu_4HSO_4 (0.271 g, 0.8 mmol) was stirred in wet CH_2Cl_2 (20 mL) at 0 °C for 30 minutes, MeI (0.28 mL, 4.4 mmol) was added into the solution. The reaction was allowed to warm up to room temperature and stirred for 24 hours. The reaction was quenched with saturated aqueous NH_4Cl. The mixture diluted with water, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (Hex/EtOAc = 5:1) to give the desired products (0.602 g, 55%) as a white solid.



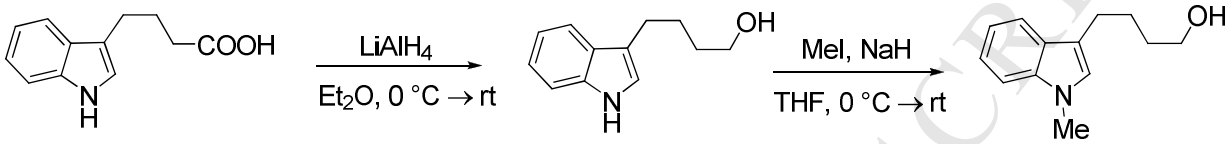
Tryptamine (10 g, 62.4 mmol) was suspended in a vigorously stirred 1:1 v/v mixture of aqueous sodium hydroxide solution (2 M in water, 94 mL, 188 mmol) and CH_2Cl_2 (94 mL). After cooling to 0 °C, methyl chloroformate (9.6 mL, 125 mmol) was added drop-wise. Once the addition was complete, the mixture was allowed to warm to room temperature. After 4 hours, the phases were separated and the aqueous phase extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by crystallisation from a mixture of iso-propanol and hexane to give the desired carbamate (11.246 g, 83%) as a pale beige powder.

A mixture of carbamate (1.092 g, 5 mmol), NaOH (0.800 g, 20 mmol), nBu_4HSO_4 (0.153 g, 0.45 mmol) was stirred in wet CH_2Cl_2 (45 mL) at 0 °C for 30 minutes, MeI (0.38 mL, 6 mmol) was added into the solution. The reaction was allowed to warm up to room temperature and stirred for 24 hours. The reaction was quenched with saturated aqueous NH_4Cl. The mixture diluted with water, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (Hex/EtOAc = 5:1) to give the desired products (1.059 g, 91%) as off-white solid.



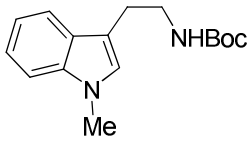
To a solution of indole-3-propionic acid (0.605 g, 3.2 mmol) in acetone (30 mL), was added MeI (1.0 mL, 16 mmol) and KOH (1.068 g, 19.1 mmol) at 0 °C. After 4 hours at rt, the solvent was removed under reduced pressure. The residue was suspended in H_2O (65 mL) and KOH (0.900 g, 16 mmol) was added, and the solution stirred at reflux for 2 h. After cooling to 0 °C, the solution was acidified to pH 1 with aqueous *6M* HCl and filtered and the residue was washed by heptane for three times. The residue was purified by flash chromatography on silica gel (Hex/EtOAc = 2:1) to give the desired product as a white solid. A solution of acid (0.427 g, 2.1 mmol) in freshly distilled Et_2O (15 mL) with ice-bath cooling, added lithium aluminium hydride powder (0.639 g, 6.3 mmol) cautiously.

Stirring was continued at 0 °C for 30 minutes, and the reaction allowed to warm to room temperature and stirring overnight. The reaction was cooled to 0 °C and carefully quenched by the dropwise addition of water (1 mL per 1 g $LiAlH_4$), 10% NaOH (1 mL per 1 g $LiAlH_4$), and water (2 mL per 1 g $LiAlH_4$) under stirring. Filtered and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (Hex/EtOAc = 5:1) to give the desired product (0.303 g, 50% for 2 steps) as colorless oil.



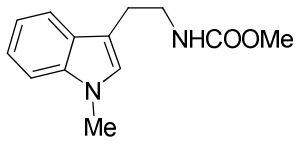
A solution of crude acid (2.032 g, 10 mmol) in freshly distilled Et_2O (100 mL) with ice-bath cooling, added lithium aluminium hydride powder (0.950 g, 2.5 mmol) cautiously. Stirring was continued at 0 °C for 30 minutes, and the reaction allowed to warm to room temperature and stirring for15 hours. The reaction was cooled to 0 °C and carefully quenched by the dropwise addition of water (1 mL per 1 g $LiAlH_4$), 10% NaOH (1 mL per 1 g $LiAlH_4$), and water (2 mL per 1 g $LiAlH_4$) under stirring. Filtered and the filtrate was concentrated *in vacuo* to give the crude alcohol. To a solution of crude alcohol (ca. 8.4 mmol) in THF (40 mL) at 0 ºC was added NaH (60% dispersion in mineral oil, 0.370 g, 9.24 mmol) slowly. The mixture was stirred at this temperature for 0.5 h, then methyl iodide (0.58 mL, 9.24 mmol) was added dropwise via syringe. Then the reaction was gradually warmed up to room temperature and stirred for 12 hours. The reaction was quenched with saturated aqueous NH_4Cl and diluted with EtOAc and water, the organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (Hex/EtOAc = 5:1) to give the desired product (0.730 g, 36% for 2 steps) as colorless oil.

^{1}H NMR and ^{13}C NMR spectra data of 1m-n, 1q-1r



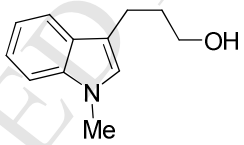
1m

N-Boc-N'-methyltryptamine (1m): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.9 Hz, 1H), 7.31 (d, J = 8.2 Hz, 1H), 7.24 (dd, J = 8.2, 1.1 Hz, 1H), 7.12 (ddd, J = 7.9, 7.0, 1.1 Hz, 1H), 6.89 (s, 1H), 4.64 (s, 1H), 3.76 (s, 3H), 3.48 (q, J = 6.1 Hz, 2H), 2.95 (t, J = 6.7 Hz, 2H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 137.1, 127.8, 126.8, 121.7, 118.9, 118.8, 111.6, 109.2, 79.0, 41.0, 32.6, 28.4, 25.7; HRMS calc'd for $C_{16}H_{22}N_2NaO_2$ $[M+Na]^+$: 297.1579, found 297.1573.



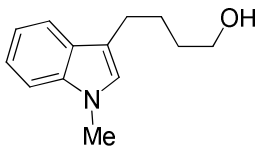
1n

N-methoxycarbonyl-N'-methyltryptamine (1n): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.13 (ddd, *J* = 7.9, 7.0, 1.1 Hz, 1H), 6.89 (s, 1H), 4.78 (s, 1H), 3.76 (s, 3H), 3.67 (s, 3H), 3.51 (dd, *J* = 12.6, 6.3 Hz, 2H), 2.96 (t, *J* = 6.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 137.1, 127.7, 126.8, 121.7, 118.9, 118.8, 111.3, 109.3, 52.0, 41.4, 32.6, 25.7; HRMS calc'd for $C_{13}H_{17}N_2O_2$ $[M+H]^+$: 233.1285, found 233.1282.



1q

N-methyl-Indole-3-propanol (1q): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J = 7.5, 0.6 Hz, 1H), 7.34 (td, J = 7.8, 1.2 Hz, 1H), 7.12 (td, J = 7.6, 0.9 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 3.58 – 3.50 (m, 2H), 3.23 (s, 3H), 2.39 – 2.29 (m, 2H), 1.75 (br s, 1H), 1.50 – 1.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 142.6, 130.2, 129.3, 124.2, 123.5, 108.7, 64.7, 61.9, 35.6, 27.5, 26.6; HRMS calc'd for $C_{12}H_{16}NO$ $[M+H]^+$: 190.1226, found 190.1224.

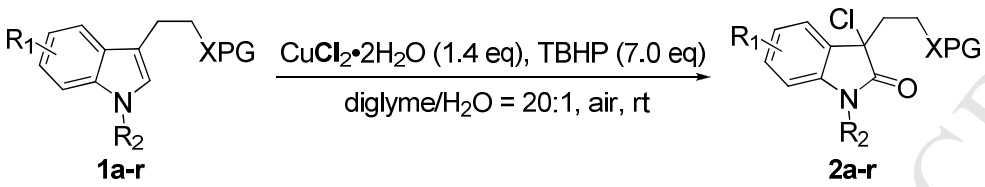


1r

N-methyl-Indole-3-butanol (1r): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 7.9 Hz, 1H), 7.30 (d, J = 8.2 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.11 (ddd, J = 7.0, 5.5, 1.0 Hz, 1H), 6.85 (s, 1H), 3.75 (s, 3H),

3.68 (t, J = 6.6 Hz, 2H), 2.80 (t, J = 7.5 Hz, 2H), 1.85 – 1.72 (m, 2H), 1.73 – 1.62 (m, 3H), 1.40 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.1, 127.9, 126.1, 121.4, 119.0, 118.5, 115.1, 109.1, 62.9, 32.7, 32.5, 26.5, 24.8; HRMS calc'd for $C_{13}H_{18}NO$ $[M+H]^+$: 204.1383, found 204.1382.

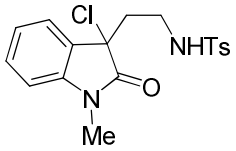
General procedure C for product synthesis



1a-r **2a-r**

To a 10 mL round-bottomed flask placed with a solution of substrate (0.10 mmol) in diglyme/H_2O (0.8 mL, 20:1 v/v) at room temperature, added $CuCl_2 \cdot 2H_2O$ (0.14 mmol), TBHP (70% in water, 0.7 mmol) via micro-syringe. Then the solution was stirred at room temperature (or warmed to 45 °C). After stirred for 10-16 hours, the reaction was quenched with saturated aqueous Na_2SO_3 and diluted with EtOAc (5 mL) and water (5 mL), the organic layer was separated. The aqueous layer was added 10% H_2SO_4 (0.3 mL) and extracted with EtOAc (2×5 mL). The combined organic layers were washed with water (4×5 mL) and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (Hex/EtOAc = 3:1) to give the desired products as off-white solid.

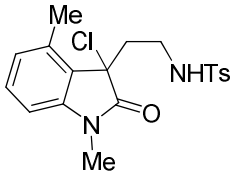
^{1}H NMR and ^{13}C NMR spectra data of products



2a

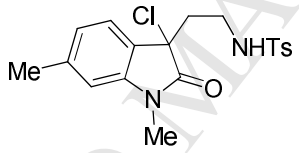
chlorooxindole (2a): Prepared according to General Procedure C. ^{1}H NMR (400 MHz, CD_3CN) δ 7.64 – 7.57 (m, 2H), 7.44 – 7.37 (m, 2H), 7.35 (dd, J = 5.5, 4.8 Hz, 3H), 7.13 (td, J = 7.6, 0.9 Hz, 1H), 6.96 (d, J = 7.9 Hz, 1H), 5.56 (t, J = 6.1 Hz, 1H), 3.15 (s, 3H), 2.85 – 2.77 (m, 2H), 2.45 – 2.29 (m, 5H); ^{13}C NMR (100 MHz, CD_3CN) δ 173.0, 143.6, 142.9 136.9, 130.7, 129.7, 128.4, 126.8, 123.9, 123.2, 109.4, 63.7, 38.8, 37.8, 26.2, 20.5; HRMS calc'd for $C_{18}H_{20}ClN_2O_3S$ $[M+H]^+$:

379.0878, found 379.0828.



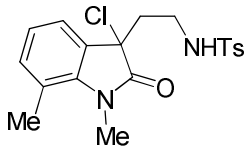
2b

chlorooxindole (2b): Prepared according to General Procedure C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.3 Hz, 2H), 7.33 – 7.21 (m, 3H), 6.90 (d, J = 7.8 Hz, 1H), 6.70 (d, J = 7.8 Hz, 1H), 4.91 (s, 1H), 3.21 (s, 3H), 2.94 – 2.83 (m, 2H), 2.73 - 2.63 (m, 1H), 2.56 – 2.47 (m, 1H), 2.42 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 143.4, 142.9 136.6, 136.0, 130.4, 129.7, 126.9, 126.1, 125.0, 106.8, 64.3, 39.3, 36.9, 26.8, 21.5, 17.7; HRMS calc'd for $C_{19}H_{21}ClN_2NaO_3S$ $[M+Na]^+$: 415.0859, found 415.0854.



2c

chlorooxindole (2c): Prepared according to General Procedure C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 7.6 Hz, 1H), 6.94 (d, J = 7.6 Hz, 1H), 6.68 (s, 1H), 5.28 – 5.12 (m, 1H), 3.20 (s, 3H), 3.17 – 3.02 (m, 2H), 2.54 – 2.43 (m, 1H), 2.41 (s, 3H), 2.40 (s, 3H), 2.34 – 2.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 143.3, 142.4, 141.3, 136.7, 129.6, 127.0, 125.9, 124.2, 123.6, 110.0, 63.8, 39.3, 38.3, 26.7, 21.9, 21.5; HRMS calc'd for $C_{19}H_{21}ClN_2NaO_3S$ $[M+Na]^+$: 415.0859, found . 415.0851

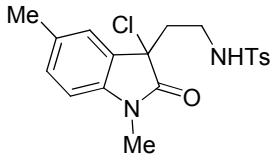


2d

chlorooxindole (2d): Prepared according to General Procedure C.

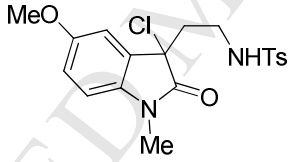
^{1}H NMR (400 MHz, CD_3CN) δ 7.60 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 7.4 Hz, 1H), 7.16 – 7.11 (m, 1H), 7.01 (t, J = 7.6 Hz, 1H), 5.58 (t, J = 6.1 Hz, 1H), 3.42 (s, 3H), 2.81 – 2.73

(m, 2H), 2.54 (s, 3H), 2.45 – 2.35 (m, 4H), 2.34 – 2.25 (m, 1H); ^{13}C NMR (100 MHz, CD_3CN) δ 173.7, 143.6, 140.6, 136.9, 134.1, 129.6, 128.9, 126.8, 123.2, 121.9, 121.3, 63.3, 38.8, 38.1, 29.4, 20.5, 18.0; HRMS calc'd for $C_{19}H_{21}ClN_2NaO_3S$ $[M+Na]^+$: 415.0859, found 415.0851.



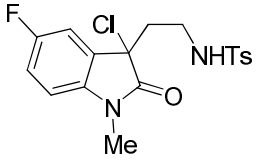
2e

chlorooxindole (2e): Prepared according to General Procedure C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 7.3 Hz, 2H), 7.16 (d, J = 8.0 Hz, 1H), 7.12 (s, 1H), 6.75 (d, J = 7.9 Hz, 1H), 5.30 – 5.22 (m, 1H), 3.20 (s, 3H), 3.17 – 3.03 (m, 2H), 2.54 – 2.43 (m, 1H), 2.41 (s, 3H), 2.35 (s, 3H), 2.34 – 2.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 143.3, 139.9, 136.8, 133.5, 130.9, 129.7, 128.9, 126.9, 124.6, 108.8, 63.9, 39.2, 38.3, 26.8, 21.5, 21.1; HRMS calc'd for $C_{19}H_{22}ClN_2O_3S$ $[M+H]^+$: 393.1034, found 393.1064.



2f

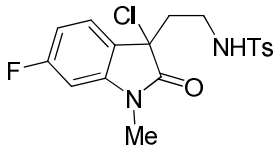
chlorooxindole (2f): Prepared according to General Procedure C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 9.4 Hz, 2H), 6.89 (dd, J = 10.9, 2.5 Hz, 2H), 6.77 (d, J = 8.3 Hz, 1H), 5.29 (t, J = 6.3 Hz, 1H), 3.81 (s, 3H), 3.20 (s, 3H), 3.14 – 3.06 (m, 2H), 2.53 – 2.43 (m, 1H), 2.41 (s, 3H), 2.34 – 2.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 156.6, 143.3, 136.6, 135.6, 129.9, 129.6, 126.9, 115.1, 110.9, 109.6, 63.9, 55.8, 39.1, 38.3, 26.78, 21.4; HRMS calc'd for $C_{19}H_{22}ClN_2O_4S$ $[M+H]^+$: 431.0808, found 431.0802.



2g

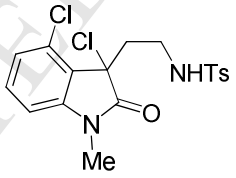
chlorooxindole (2g): Prepared according to General Procedure C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.3 Hz, 2H), 7.31 – 7.23 (m, 2H), 7.13 – 7.01 (m, 2H), 6.81 (dd, J = 8.5, 4.0 Hz, 1H),

5.30 – 5.22 (m, 1H), 3.23 (s, 3H), 3.10 – 3.01 (m, 2H), 2.58 – 2.46 (m, 1H), 2.41 (s, 3H), 2.35 – 2.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 159.5 (d, J= 241 Hz), 143.5, 138.4, 136.5, 129.7, 126.9, 117.1 (d, J = 23.7 Hz), 112.0 (d, J = 25.5 Hz), 109.9 (d, J = 8.0 Hz), 63.3, 39.1, 38.2, 26.9, 21.5; HRMS calc'd for $C_{18}H_{18}ClFN_2NaO_3S$ $[M+Na]^+$: 419.0608, found 419.0605.



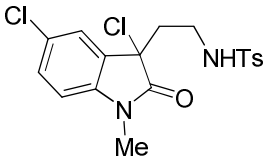
2h

chlorooxindole (2h): Prepared according to General Procedure C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.64 (m, 1H), 7.32 – 7.23 (m, 4H), 6.86 – 6.76 (m, 1H), 6.60 (dd, J = 8.6, 2.3 Hz, 1H), 5.05 (dd, J = 8.0, 4.9 Hz, 1H), 3.22 (s, 3H), 3.12 – 3.03 (m, 2H), 2.58 – 2.47 (m, 1H), 2.41 (s, 3H), 2.39 – 2.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 164.2 (d, J = 249.3 Hz), 144.3 (d, J = 11.8 Hz), 143.4, 136.5, 129.7, 126.9, 125.3 (d, J = 10.1 Hz), 124.1 (d, J = 3.2 Hz), 109.9 (d, J = 22.9 Hz), 98.1 (d, J = 27.8 Hz), 63.1, 39.2, 38.3, 26.9, 21.5; HRMS calc'd for $C_{18}H_{18}ClFN_2NaO_3S$ $[M+Na]^+$: 419.0608, found 419.0602.



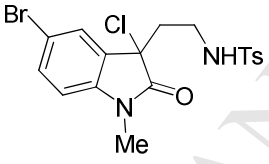
2i

chlorooxindole (2i): Prepared according to General Procedure C. Reaction performed at 45 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.3 Hz, 2H), 7.34 (t, J = 8.1 Hz, 1H), 7.25 (d, J = 9.3 Hz, 2H), 7.08 (d, J = 8.2 Hz, 1H), 6.82 (d, J = 7.4 Hz, 1H), 4.84 – 4.76 (m, 1H), 3.26 (s, 3H), 2.95 – 2.85 (m, 2H), 2.80 – 2.71 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 144.9, 143.4, 136.5, 131.7, 131.7, 129.7, 126.8, 124.5, 124.1, 107.8, 63.5, 39.6, 35.5, 27.1, 21.5; HRMS calc'd for $C_{18}H_{19}Cl_2N_2O_3S$ $[M+H]^+$: 413.0488, found 413.0486.



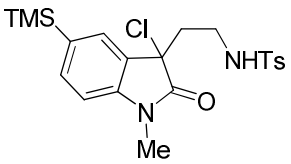
2j

chlorooxindole (2j): Prepared according to General Procedure C. Reaction performed at 45 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.3 Hz, 2H), 7.39 – 7.31 (m, 1H), 7.30 – 7.26 (m, 3H), 6.81 (d, J = 8.3 Hz, 1H), 5.14 – 5.06 (m, 1H), 3.23 (s, 3H), 3.11 – 3.02 (m, 2H), 2.51 (dt, J = 13.8, 6.9 Hz, 1H), 2.41 (s, 3H), 2.36 – 2.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 143.5, 141.1, 136.6, 130.6, 130.3, 129.7, 129.0, 126.9, 124.3, 110.2, 63.0, 39.1, 38.2, 26.9, 21.5; HRMS calc'd for $C_{18}H_{18}Cl_2N_2NaO_3S$ $[M+Na]^+$: 435.0307, found 435.0308.



2k

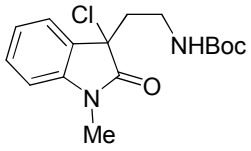
chlorooxindole (2k): Prepared according to General Procedure C. Reaction performed at 45 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.3 Hz, 2H), 7.50 (dd, J = 8.3, 1.9 Hz, 1H), 7.41 (d, J = 1.9 Hz, 1H), 7.28 (d, J = 8.1 Hz, 2H), 6.76 (d, J = 8.3 Hz, 1H), 5.18 (s, 1H), 3.22 (s, 3H), 3.10 – 2.99 (m, 2H), 2.51 (dt, J = 14.1, 6.9 Hz, 1H), 2.41 (s, 3H), 2.31 (dt, J = 14.6, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 143.5, 141.6, 136.5, 133.5, 130.6, 129.7, 127.1, 127.0, 126.9, 116.1, 110.7, 63.0, 39.1, 38.2, 26.9, 21.5; HRMS calc'd for $C_{18}H_{18}BrClN_2NaO_3S$ $[M+Na]^+$: 478.9808, found 478.9803.



2l

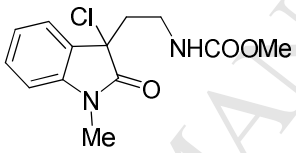
chlorooxindole (2l): Prepared according to General Procedure C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.3 Hz, 2H), 7.51 (dd, J = 7.7, 1.1 Hz, 1H), 7.41 (s, 1H), 7.28 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 7.7 Hz, 1H), 5.26 (dd, J = 8.0, 4.6 Hz, 1H), 3.21 (d, J = 4.0 Hz, 3H), 3.19 – 3.09 (m, 2H), 2.56 – 2.44 (m, 1H), 2.41 (s, 3H), 2.32 (dt, J = 14.7, 6.5 Hz, 1H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 143.3, 142.9, 136.7, 135.8, 135.7, 129.6, 128.6, 128.2, 126.9, 108.6, 63.8, 39.2, 38.4, 26.7,

21.5, -1.0; HRMS calc'd for $C_{21}H_{27}ClN_2NaO_3SSi$ $[M+Na]^+$: 473.1098, found 473.1090.



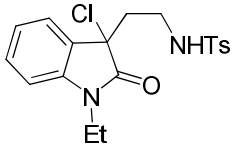
2m

chlorooxindole (2m): Prepared according to General Procedure C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.4 Hz, 1H), 7.35 (t, J = 7.7 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 4.66 (s, 1H), 3.23 (s, 3H), 3.21 – 3.10 (m, 2H), 2.57 – 2.34 (m, 2H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 155.5, 142.4, 130.4, 129.0, 124.3, 123.6, 108.8, 79.3, 63.5, 38.7, 36.4, 28.3, 26.7; HRMS calc'd for $C_{16}H_{21}ClN_2NaO_3$ $[M+Na]^+$: 347.1138, found 347.1134.



2n

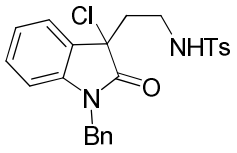
chlorooxindole (2n): Prepared according to General Procedure C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.7 Hz, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.12 (t, J = 7.3 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 5.03 (s, 1H), 3.57 (s, 3H), 3.30 – 3.15 (m, 5H), 2.51 (dt, J = 13.8, 6.8 Hz, 1H), 2.39 (dt, J = 13.9, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 156.7, 142.4, 130.5, 129.0, 124.2, 123.6, 108.9, 63.6, 52.0, 38.8, 36.8, 26.6; HRMS calc'd for $C_{13}H_{15}ClN_2NaO_3$ $[M+Na]^+$: 305.0669, found 305.0664.



2o

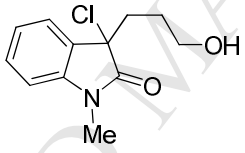
chlorooxindole (2o): Prepared according to General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 2H), 7.37 (td, J = 7.8, 1.1 Hz, 1H), 7.32 (d, J = 4.8 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.13 (t, J = 7.3 Hz, 1H), 6.89 (d, J = 7.9 Hz, 1H), 5.25 – 5.11 (m, 1H), 3.85 – 3.68 (m, 2H), 3.19 – 3.05 (m, 2H), 2.56 – 2.44 (m, 1H), 2.42 (s, 3H), 2.32 (dt, J = 14.6, 6.5 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 143.4, 141.5, 136.9, 130.6, 129.7, 129.3, 127.1, 124.2, 123.6, 109.2, 63.7, 39.3, 38.4, 35.4, 21.5, 12.3; HRMS calc'd for $C_{19}H_{21}ClN_2NaO_3S$ $[M+Na]^+$:

415.0859, found 415.0851.



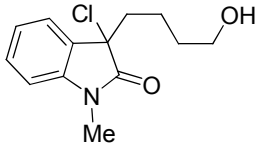
2p

chlorooxindole (2p): Prepared according to General Procedure C. Reaction performed at 45 ºC. ^{1}H NMR (400 MHz, CD_3CN) δ 7.62 – 7.58 (m, 2H), 7.40 (dd, J = 7.5, 0.7 Hz, 1H), 7.37 – 7.32 (m, 3H), 7.32 – 7.26 (m, 5H), 7.11 (td, J = 7.6, 0.9 Hz, 1H), 6.85 (d, J = 7.9 Hz, 1H), 5.60 (t, J = 5.9 Hz, 1H), 4.88 (dd, J = 52.9, 15.9 Hz, 2H), 2.89 – 2.74 (m, 2H), 2.54 – 2.42 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ 173.3, 143.6, 141.8, 136.7, 135.8, 130.6, 129.7, 128.8, 128.3, 127.7, 127.1, 126.8, 124.3, 123.5, 110.0, 63.6, 43.5, 38.7, 37.8, 20.4; HRMS calc'd for $C_{24}H_{23}ClN_2NaO_3S$ $[M+Na]^+$: 477.1016, found 477.1012.



2q

chlorooxindole (2q): Prepared according to General Procedure C. Reaction performed at 45 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J = 7.5, 0.6 Hz, 1H), 7.34 (td, J = 7.8, 1.2 Hz, 1H), 7.12 (td, J = 7.6, 0.9 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 3.56 (td, J = 6.4, 1.6 Hz, 2H), 3.23 (s, 3H), 2.39 – 2.30 (m, 2H), 1.75 (s, 2H), 1.48 – 1.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 142.6, 130.2, 129.3, 124.2, 123.5, 108.7, 64.7, 61.9, 35.6, 27.5, 26.6; HRMS calc'd for $C_{12}H_{14}ClNNaO_2$ $[M+Na]^+$: 262.0611, found 262.0610.

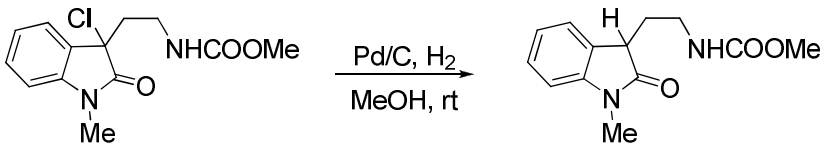


2r

chlorooxindole (2r): Prepared according to General Procedure C. Reaction performed at 45 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.4 Hz, 1H), 7.35 (td, J = 7.8, 1.2 Hz, 1H), 7.12 (td, J = 7.6, 0.9 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 3.60 – 3.50 (m, 2H), 3.24 (s, 3H), 2.37 – 2.20 (m, 2H), 1.68 (s,

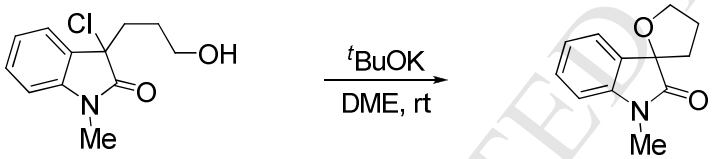
1H), 1.57 1.48 (m, 2H), 1.30 – 1.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 142.7, 130.1, 129.3, 124.1, 123.4, 108.6, 64.8, 62.2, 38.9, 32.2, 26.6, 20.8; HRMS calc'd for $C_{13}H_{16}ClNNaO_2$ $[M+Na]^+$: 276.0767, found 276.0761.

Application and transformation of 3-chlorooxindoles



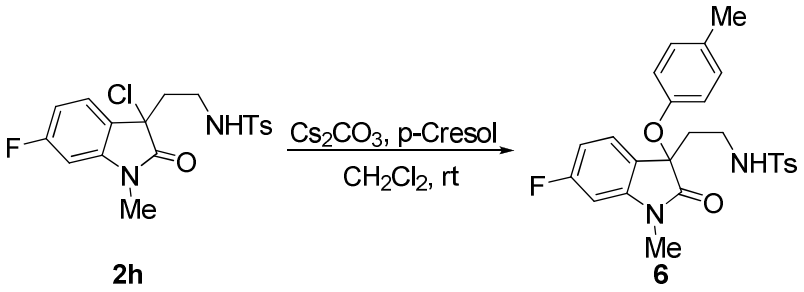
2n **4**

To an oven-dried 10 mL round-bottomed flask placed with a solution of **2n** (0.036 g, 0.127 mmol) in MeOH (5 mL) at room temperature, added 10% Pd/C (10 mmol%) after degassed with H_2 for three times. The reaction was stirred under a balloon hydrogen atmosphere at this temperature for 3 hours. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (Hex/EtOAc = 2:1) to afford the desired product **4** (0.025 g, 78%).



2q **5**

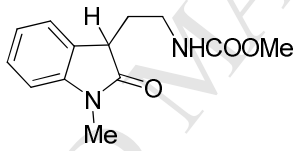
To an oven-dried 10 mL round-bottomed flask placed with a solution of **2q** (0.046 g, 0.192 mmol) in DME (2 mL) at room temperature, added t-BuOK (0.043 g, 0.384 mmol) and stirred at this temperature for 3 hours. Then the reaction was quenched with saturated aqueous NH_4Cl and diluted with EtOAc and water, the organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (Hex/EtOAc = 5:1) to give the desired products (0.031 g, 82%) as colorless oil.



2h **6**

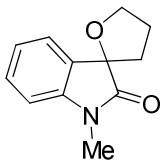
To an oven-dried 10 mL round-bottomed flask placed with a solution of **2h** (0.020 g, 0.050 mmol) and p-cresol (0.008g, 0.075 mmol) in CH_2Cl_2 (0.5 mL) at room temperature, added Cs_2CO_3 (0.033 g, 0.100 mmol) and stirred at this temperature for 13 hours. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (Hex/EtOAc = 3:1) to afford the desired product **6** (0.014 g, 58%).

1H NMR and 13C NMR spectra data of corresponding products



4

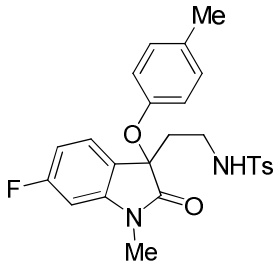
carbamate (4): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.19 (m, 2H), 7.04 (t, J = 7.4 Hz, 1H), 6.80 (d, J = 7.8 Hz, 1H), 5.44 (s, 1H), 3.60 (d, J = 10.4 Hz, 3H), 3.48 – 3.41 (m, 1H), 3.41 – 3.27 (m, 2H), 3.17 (s, 3H), 2.25 – 2.06 (m, 1H), 2.06 - 2.01 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.8, 157.1, 144.0, 128.6, 128.1, 123.8, 122.6, 108.1, 52.0, 43.5, 38.5, 30.7, 26.2; HRMS calc'd for $C_{13}H_{17}N_2O_3$ $[M+H]^+$: 249.1234, found 249.1234.



5

spirocyclic indolin-2-one(5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.20 (m, 2H), 7.05 (t, J = 7.4 Hz, 1H), 6.78 (d, J = 7.6 Hz, 1H), 4.36 – 4.16 (m, 2H), 3.15 (s, 3H), 2.54 – 2.39 (m, 1H), 2.39 – 2.30 (m, 1H), 2.30 – 2.17 (m, 1H), 2.16 – 2.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 143.6, 130.6,

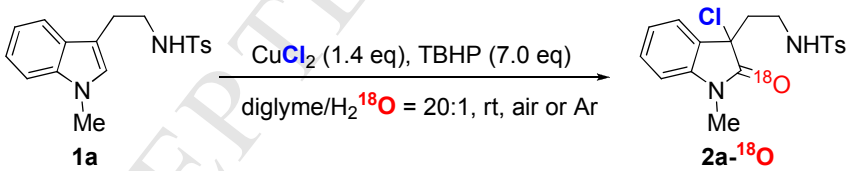
129.6, 123.4, 123.0, 108.2, 82.7, 70.3, 35.9, 26.4, 26.1; HRMS calc'd for $C_{12}H_{14}NO_2$ $[M+H]^+$: 204.1019, found 204.1021.



6

indolin-2-one (6): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.17 (dd, J = 8.2, 5.3 Hz, 1H), 6.84 (d, J = 8.2 Hz, 2H), 6.79 – 6.68 (m, 1H), 6.51 – 6.40 (m, 3H), 5.37 (t, J = 6.1 Hz, 1H), 3.39 – 3.25 (m, 2H), 3.09 (s, 3H), 2.43 (s, 3H), 2.37 – 2.29 (m, 1H), 2.17 (s, 3H), 2.15 – 2.06 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 162.9, 152.4, 144.6 (d, J = 11.6 Hz), 143.3, 136.9, 133.4, 129.6 (d, J = 5.3 Hz), 127.0, 125.8 (d, J = 10.0 Hz), 122.5, 120.2, 109.4 (d, J = 22.5 Hz), 97.8 (d, J = 27.6 Hz), 82.2, 38.2, 37.5, 26.4, 21.5, 20.6; HRMS calc'd for $C_{25}H_{25}FN_2NaO_4S$ $[M+Na]^+$: 491.1417, found 491.1413.

Mechanistic study:



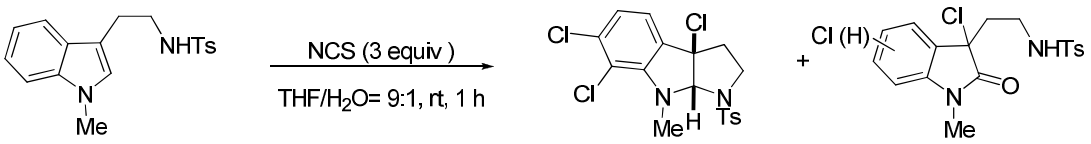
1a **2a-^{18}O**

To a 10 mL round-bottomed flask placed with a solution of substrate **1a** (0.033g, 0.10 mmol) in diglyme/$H_2{}^{18}O$ (0.8 mL, 20:1 v/v) at room temperature, added $CuCl_2$ (0.019g, 0.14 mmol), TBHP (5.5 *M* in nonane, 0.127 mL, 0.7 mmol) via micro-syringe. Then the solution was stirred at room temperature under air or Ar. TLC monitored the reaction was completed, The crude product was analyzed by HRMS. HRMS calc'd for $C_{18}H_{20}ClN_2O_2{}^{18}OS$ $[M+H]^+$: 381.0920, found 381.0922. The result showed that the oxygen source in the product was from the water.

Chlorooxidation of tryptamine derivatives using NCS and DCU

The procedures were according to the known literature.[3,4]

Using NCS as chlorination reagent:[3]

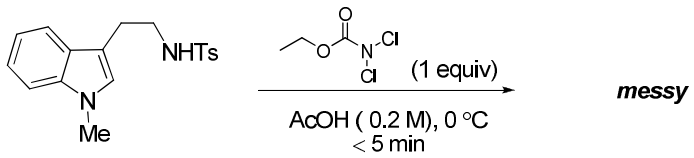


a, 37%

b, *ca.* 55%

two inseperable isomers,
ratio = 1:1

Using DCU as chlorination reagent:[4]



messy

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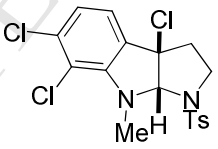
3. Breazzano, S. P.; Boger, D. L. *J. Am. Chem. Soc.* **2011**, *133*, 18495.

4. Leong, S.Y.; Smith, P. W.; Zou, B. *Chin. J. Chem*. **2014**, *32*, 1217.

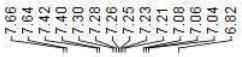
^{1}H NMR and ^{13}C NMR spectra data of compound a

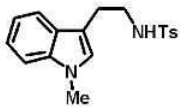


a

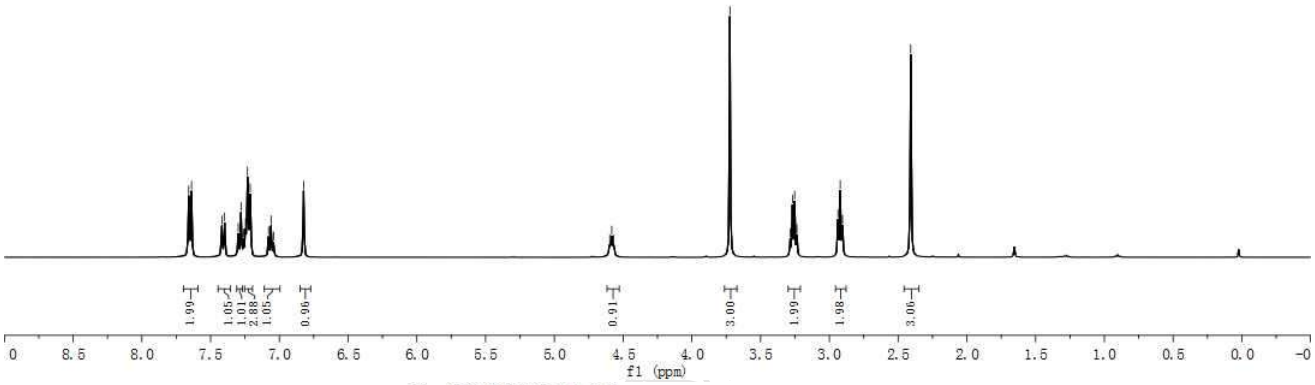
Compound a: ^{1}H NMR (400 MHz, CDCl3) δ 7.78 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 2.0 Hz, 1H), 7.05 (d, J = 2.0 Hz, 1H), 5.49 (s, 1H), 3.68 – 3.57 (m, 1H), 3.38 (s, 3H), 2.96 (td, J = 10.9, 5.5 Hz, 1H), 2.52 – 2.45 (m, 1H), 2.43 (s, 3H), 2.40 – 2.28 (m, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 145.0, 144.0, 135.8, 133.5, 131.9, 129.8, 127.5, 125.0, 122.7, 117.0, 94.0, 73.5, 47.4, 41.6, 36.9, 21.6. HRMS calc'd for $C_{18}H_{18}Cl_3N_2O_2S$ $[M+H]^+$: 431.0149, found 431.0150.

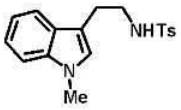
Copies of ^{1}H NMR and ^{13}C NMR spectra:



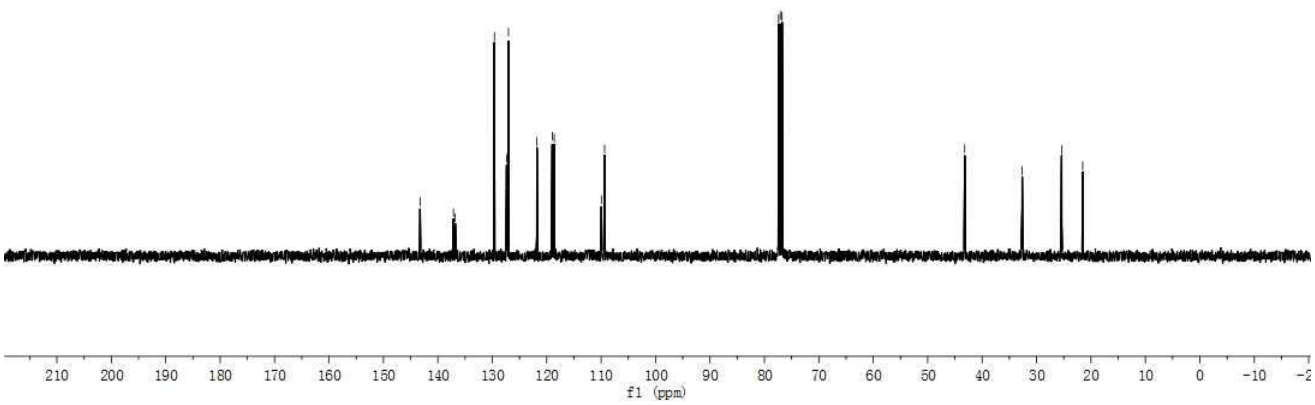


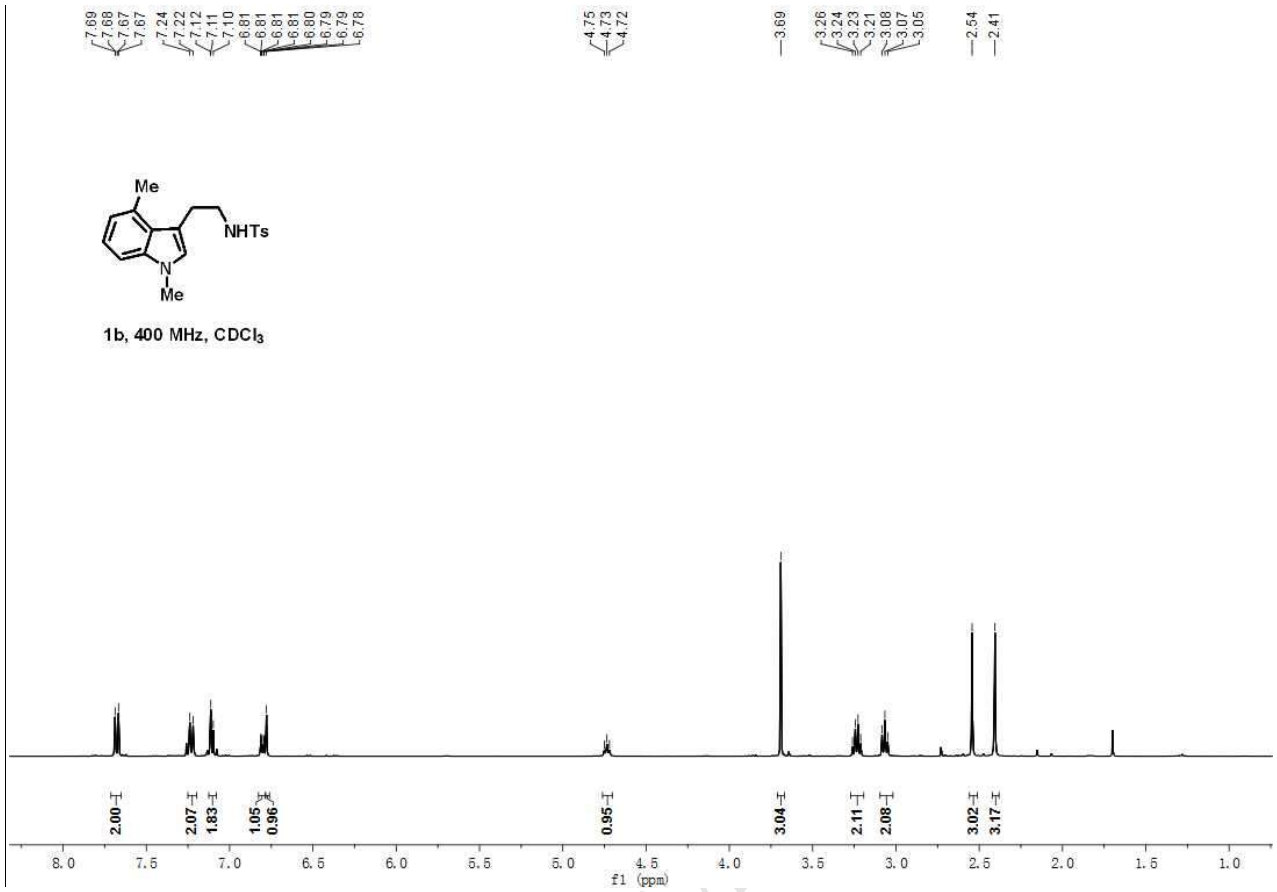
1a, 400 MHz, $CDCl_3$



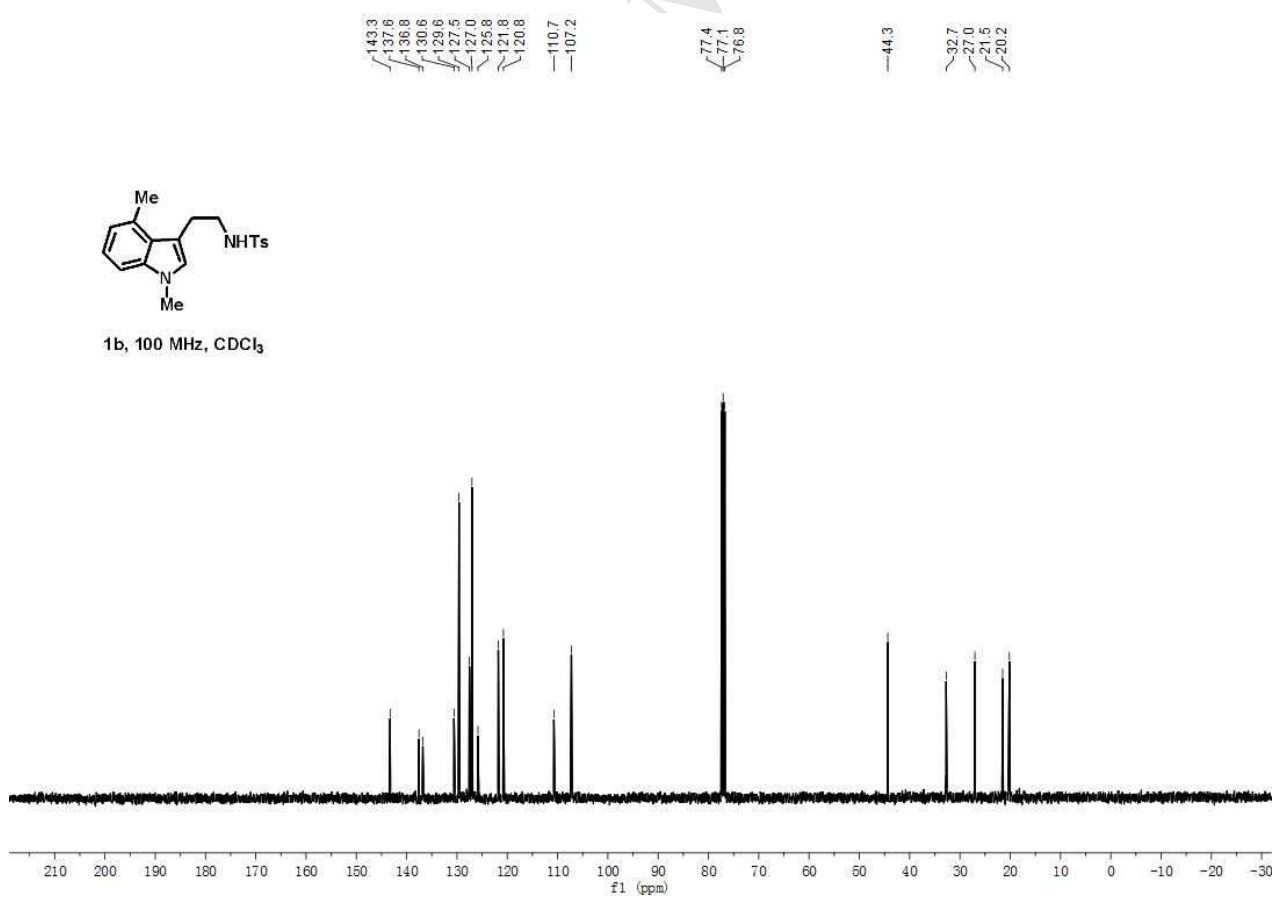


1a, 100 MHz, $CDCl_3$

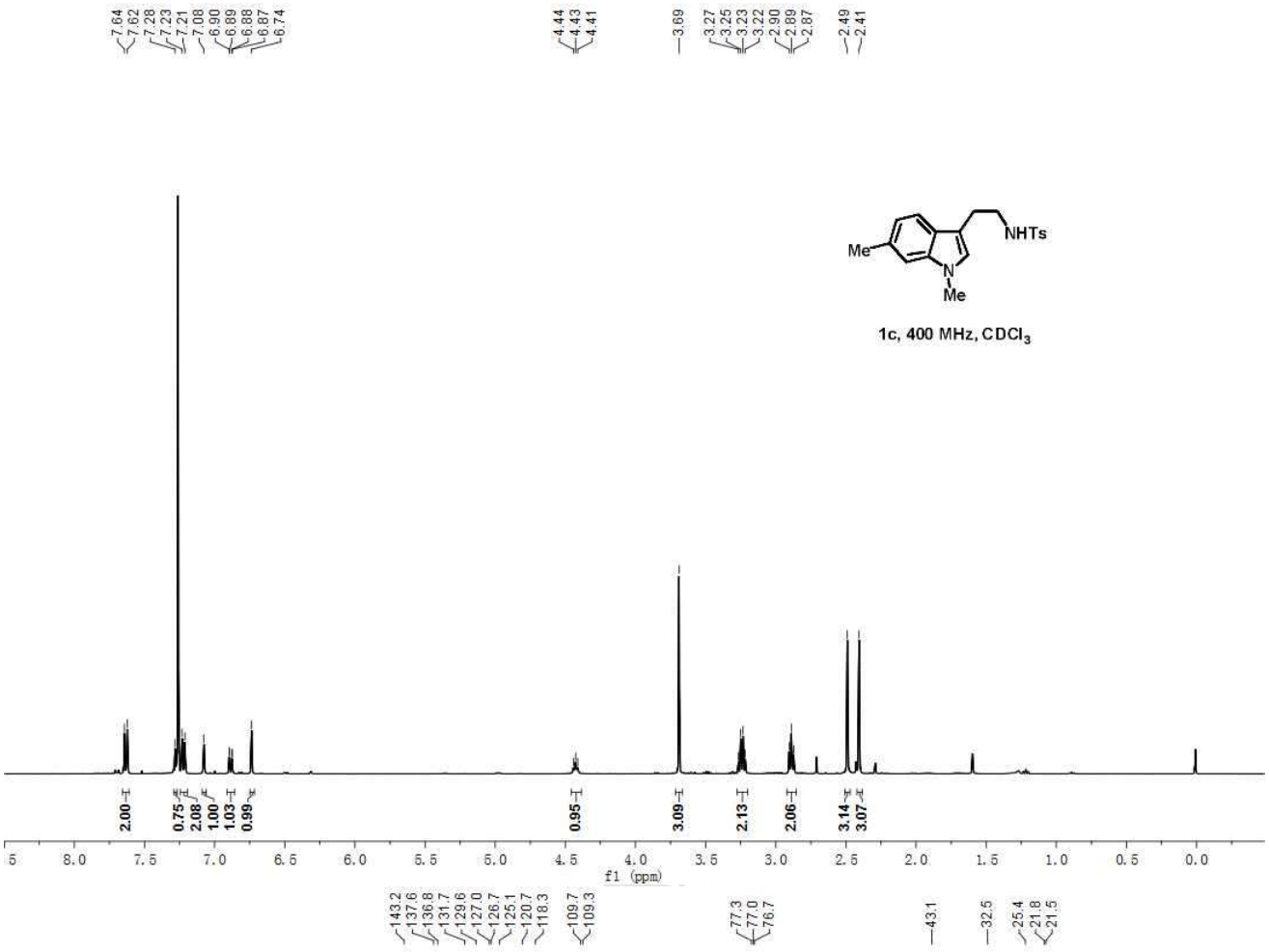




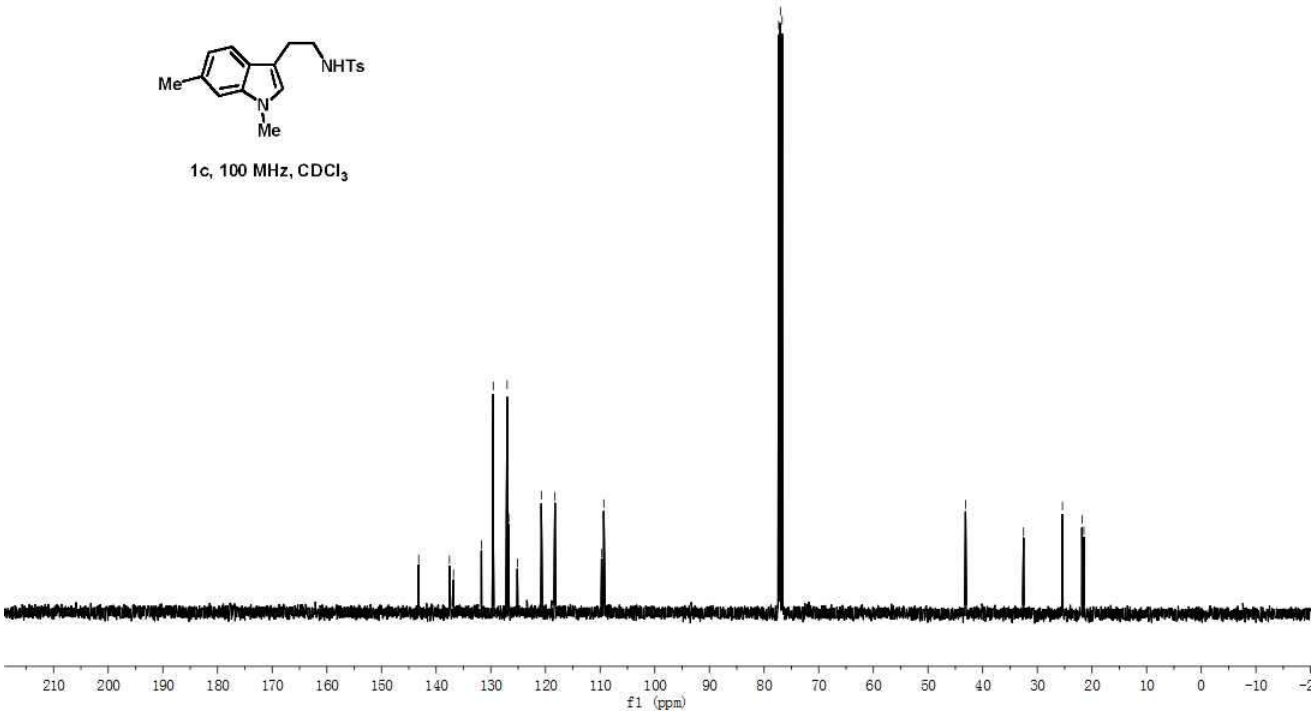
1b, 400 MHz, $CDCl_3$



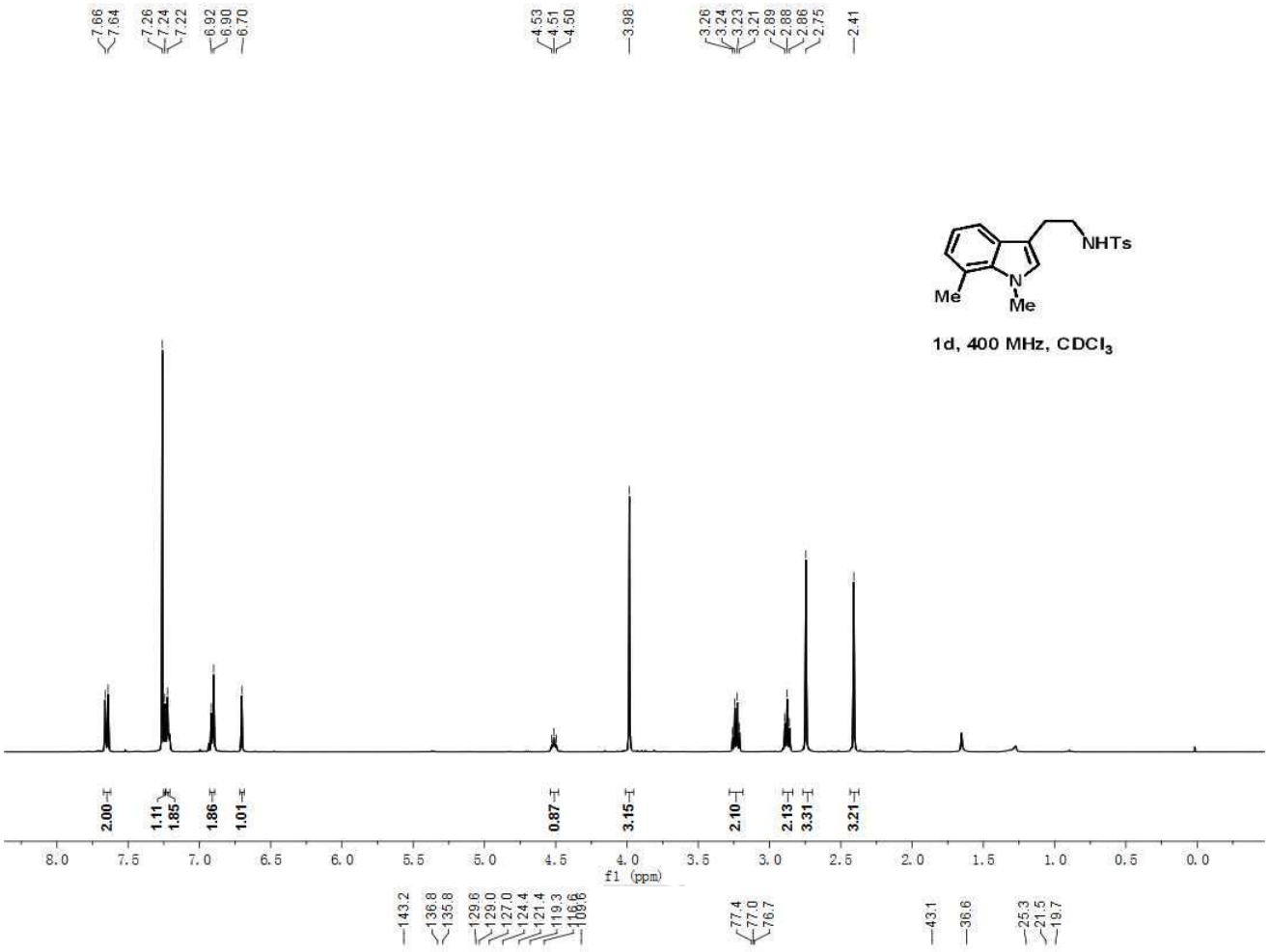
1b, 100 MHz, $CDCl_3$

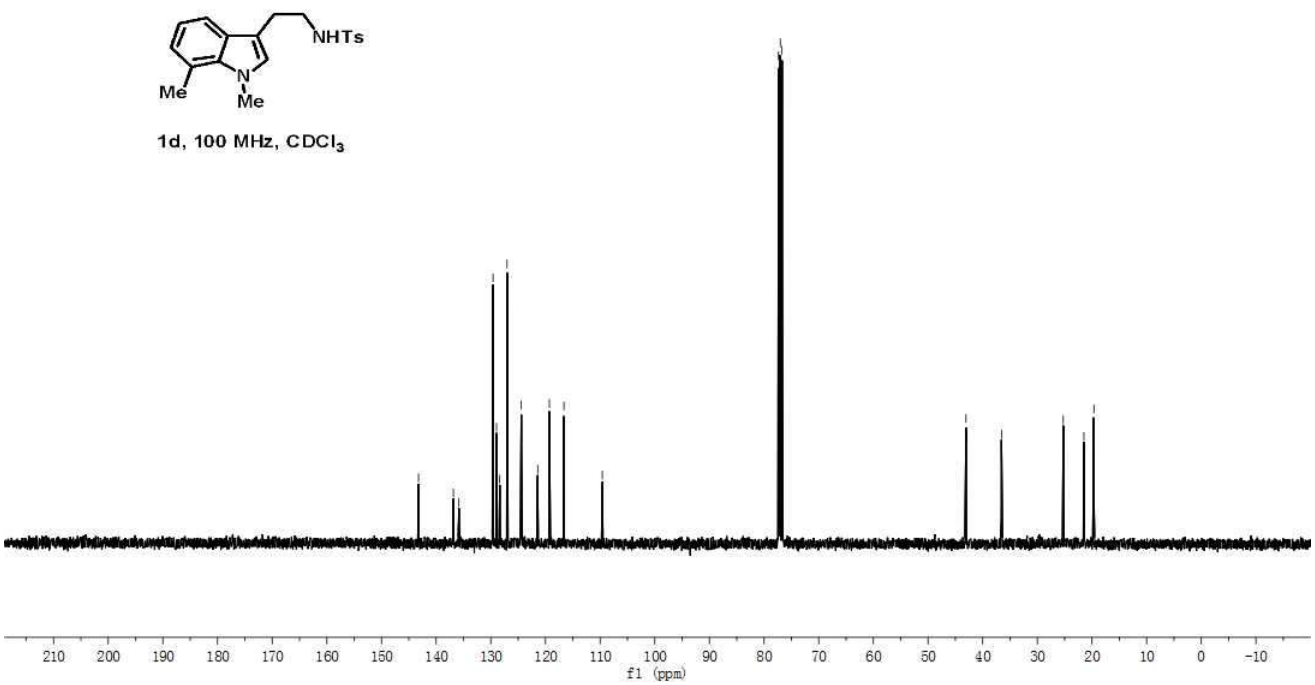


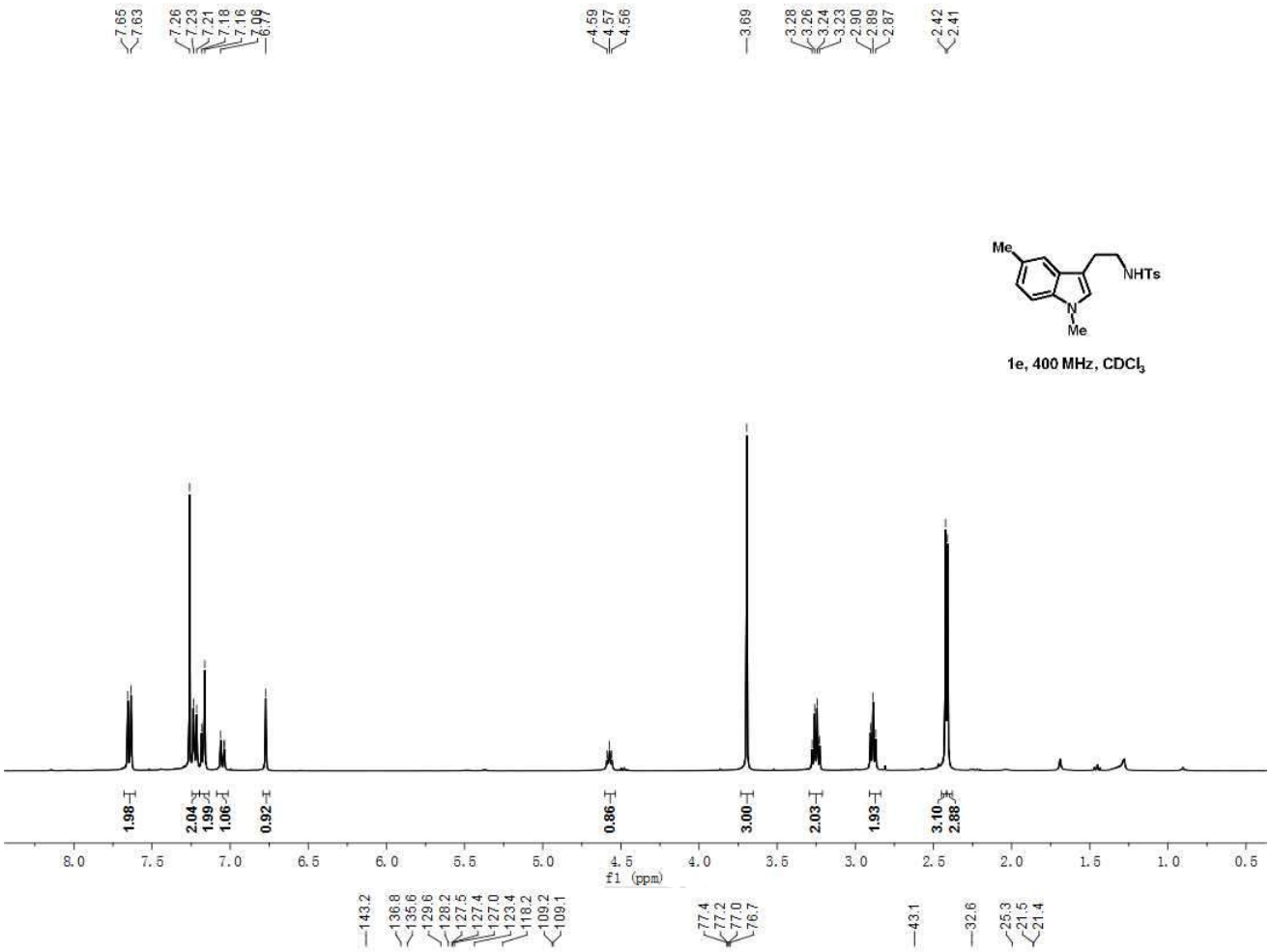
1c, 400 MHz, $CDCl_3$

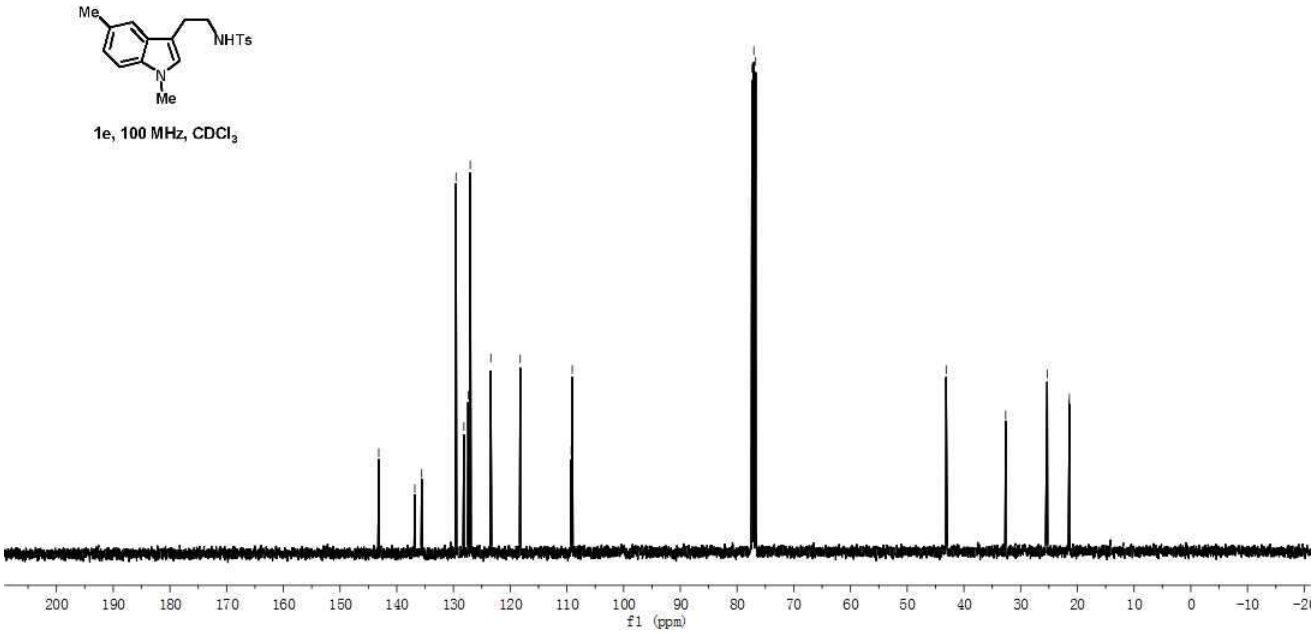


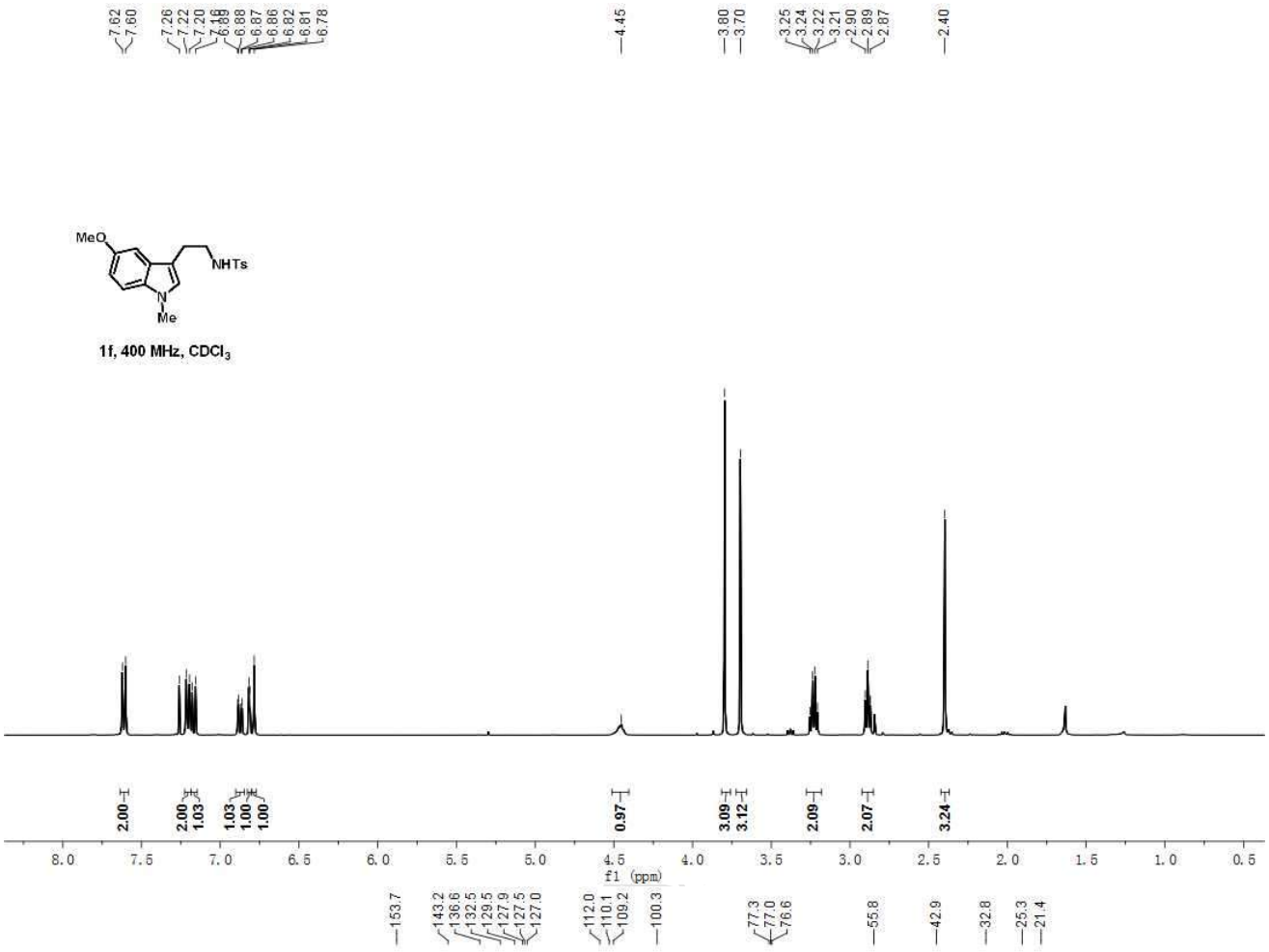
1c, 100 MHz, $CDCl_3$

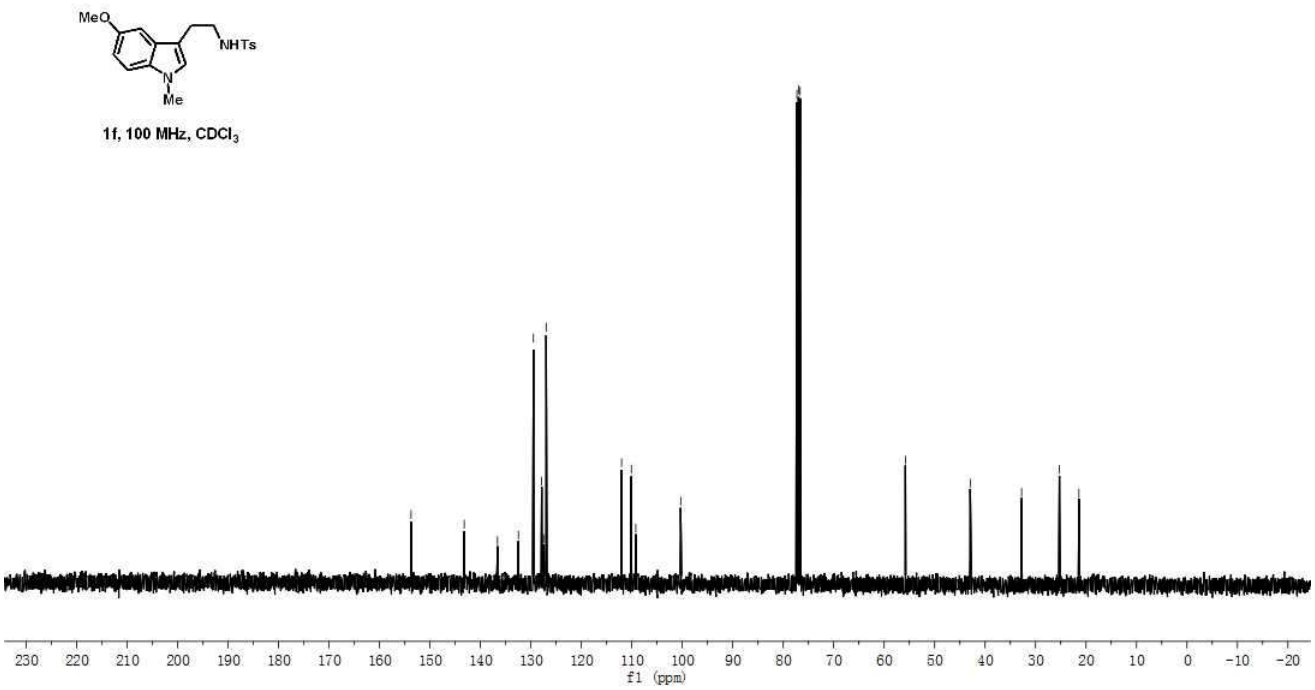

7.66
7.64
7.26
7.24
7.22
6.92
6.90
6.70
4.53
4.51
4.50
3.98
3.26
3.24
3.23
3.21
2.89
2.88
2.86
2.75
2.41
NHTs
Me
N
Me
1d, 400 MHz, CDCl3
2.00
1.11
1.85
1.86
1.01
0.87
3.15
2.10
2.13
3.31
3.21
f1 (ppm)

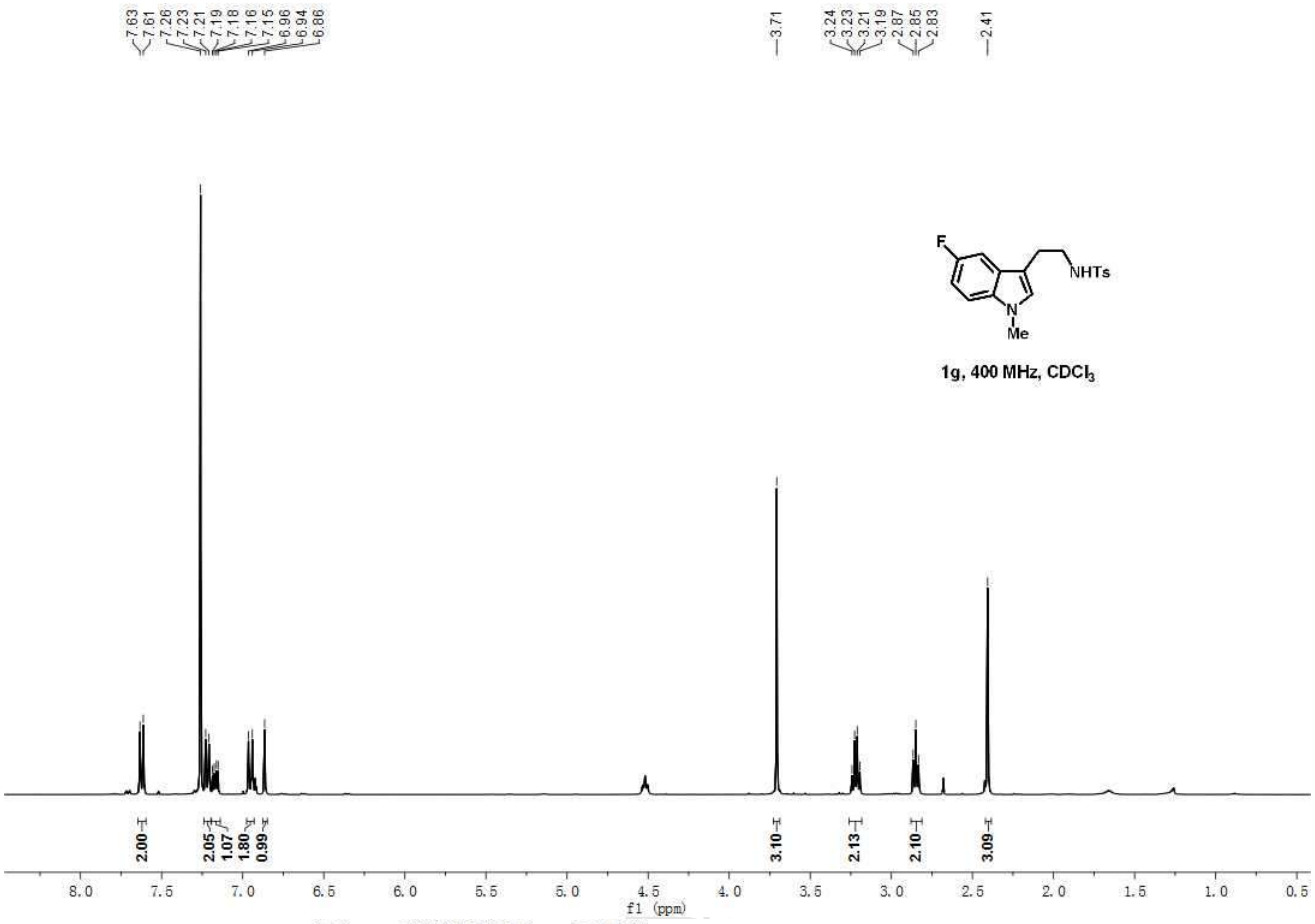

143.2
136.8
135.8
129.6
129.0
127.0
124.4
121.4
119.3
110.6
77.4
77.0
76.7
43.1
36.6
25.3
21.5
19.7
NHTs
Me
N
Me
1d, 100 MHz, CDCl3
f1 (ppm)

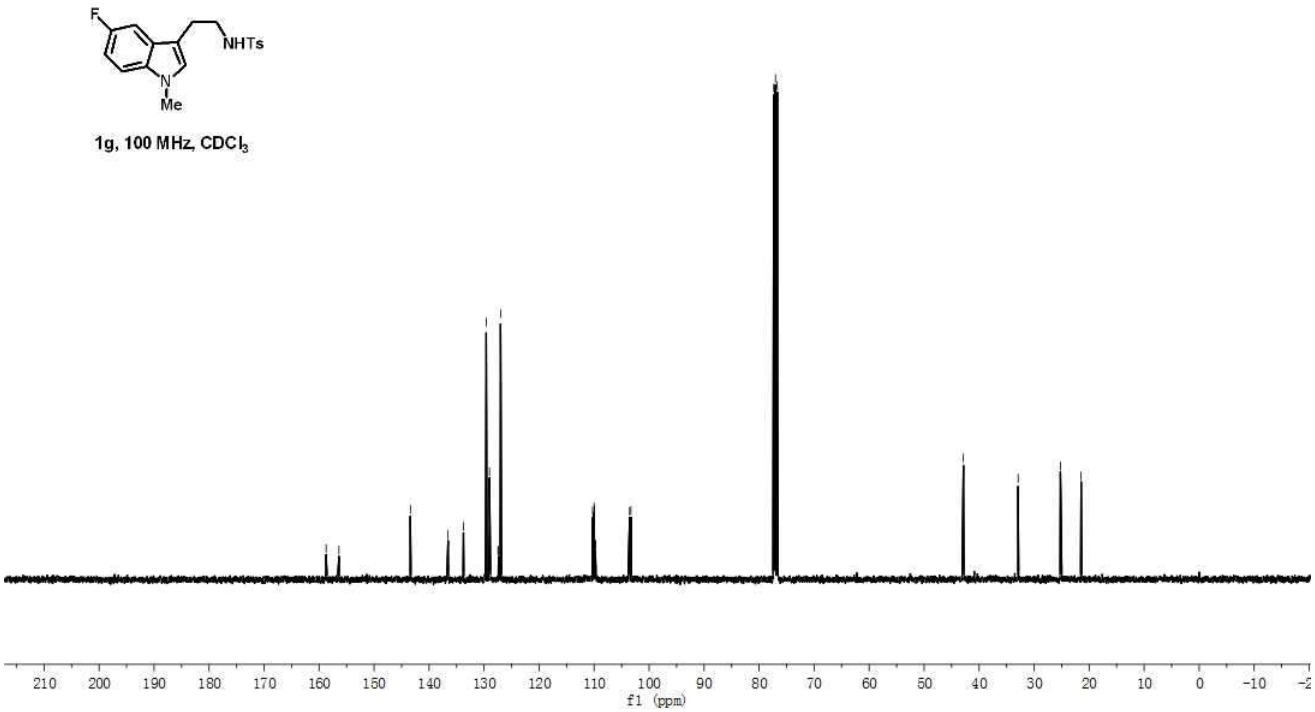

7.65
7.63
7.26
7.23
7.21
7.18
7.16
6.99
6.97
4.59
4.57
4.56
3.69
3.28
3.26
3.24
3.23
2.90
2.89
2.87
2.42
2.41
Me
NHTs
N
Me
1e, 400 MHz, CDCl3
1.98
2.04
1.99
1.06
0.92
0.86
3.00
2.03
1.93
3.10
2.88
f1 (ppm)
143.2
136.8
135.6
129.6
128.2
127.5
127.4
127.0
123.4
118.2
109.2
109.1
77.4
77.2
77.0
76.7
43.1
32.6
25.3
21.5
21.4

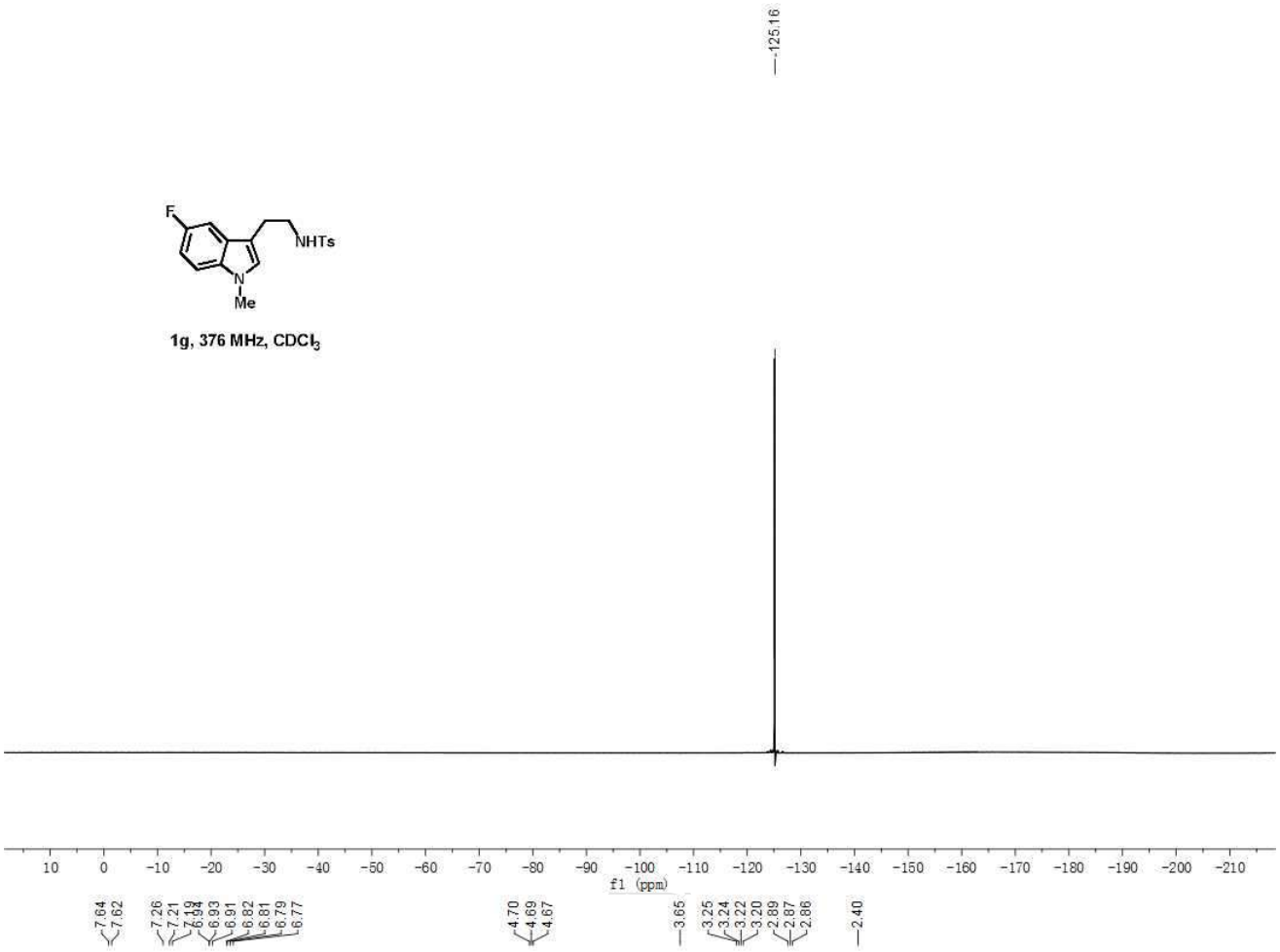

Me
NHTs
N
Me
1e, 100 MHz, CDCl3
f1 (ppm)

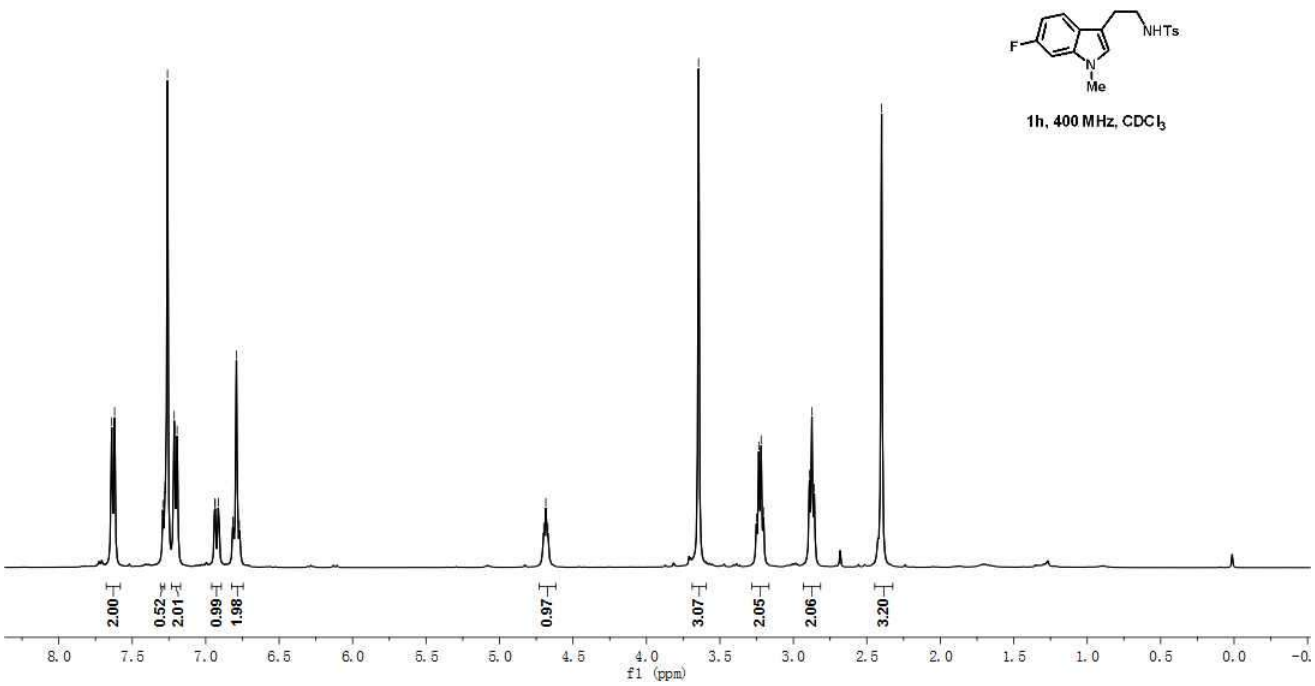

7.62
7.60
7.26
7.22
7.20
6.88
6.87
6.86
6.82
6.81
6.78
4.45
3.80
3.70
3.25
3.24
3.22
3.21
2.90
2.89
2.87
2.40
MeO
NHTs
N
Me
1f, 400 MHz, CDCl3
2.00
2.00
1.03
1.03
1.00
1.00
0.97
3.09
3.12
2.09
2.07
3.24
f1 (ppm)

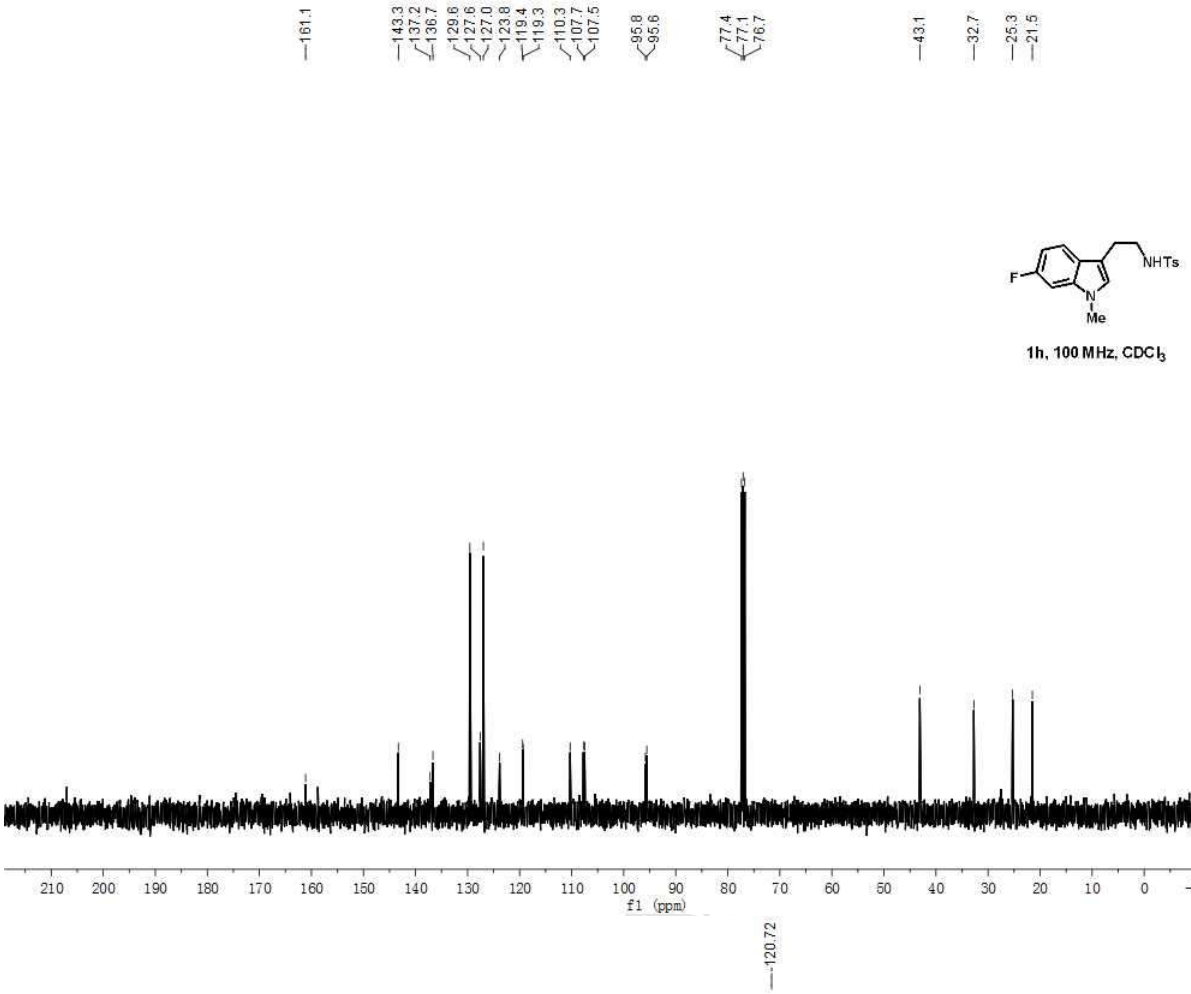

153.7
143.2
136.6
132.5
129.5
127.9
127.5
127.0
112.0
110.1
109.2
100.3
77.3
77.0
76.6
55.8
42.9
32.8
25.3
21.4
MeO
NHTs
N
Me
1f, 100 MHz, CDCl3
f1 (ppm)

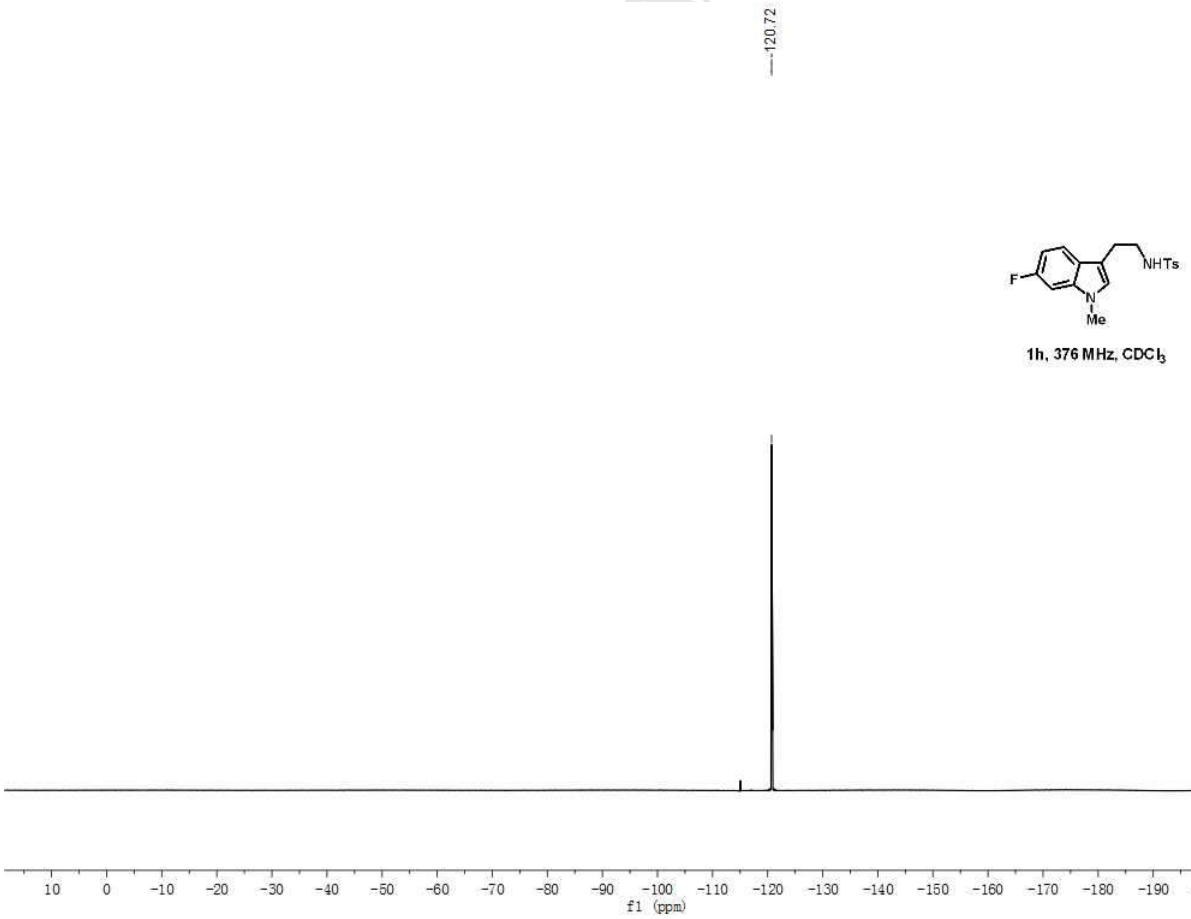

7.63
7.61
7.26
7.23
7.21
7.19
7.18
7.16
7.15
6.96
6.94
6.86
3.71
3.24
3.23
3.21
3.19
2.87
2.85
2.83
2.41
F
NHTs
N
Me
1g, 400 MHz, CDCl3
2.00
2.05
1.07
1.80
0.99
3.10
2.13
2.10
3.09
f1 (ppm)

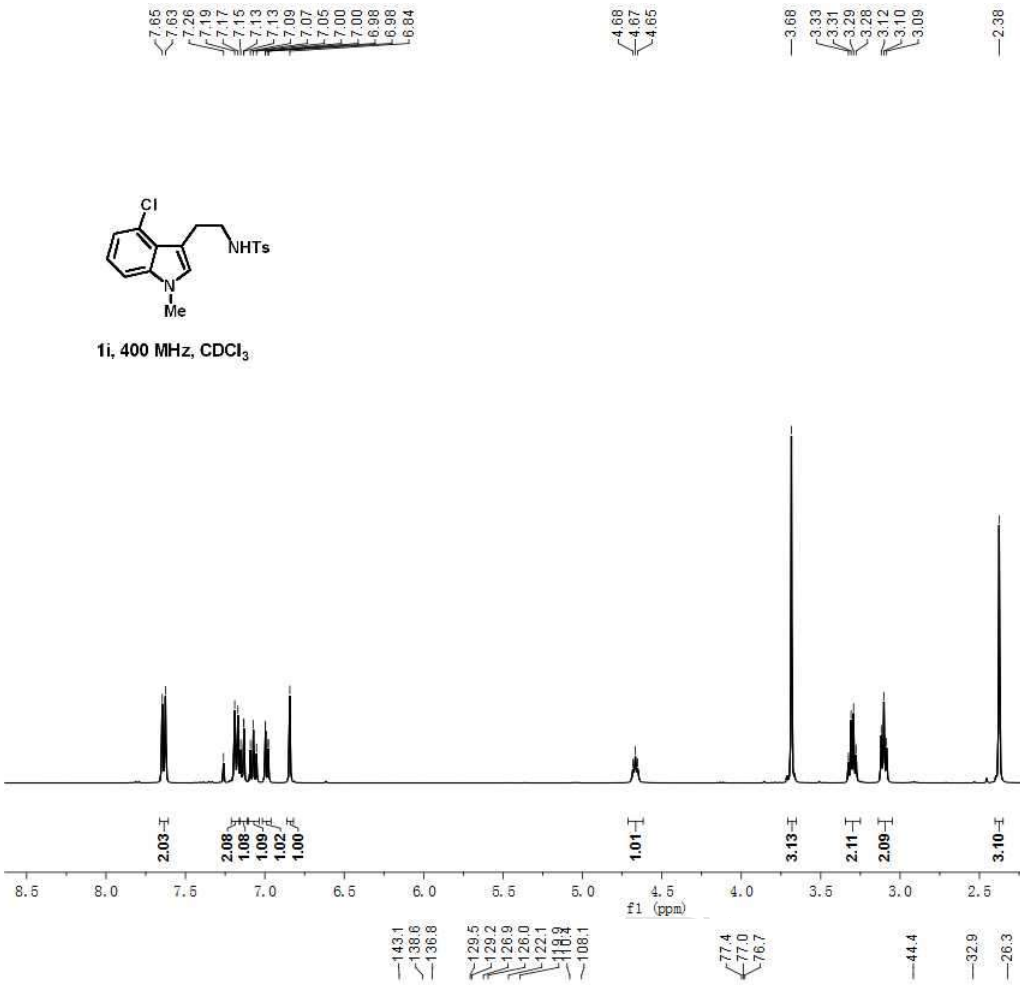

158.7
156.4
143.4
136.6
133.8
129.6
129.0
127.5
127.4
127.0
110.3
110.0
103.3
77.3
77.0
76.7
42.9
32.9
25.2
21.5
F
NHTs
N
Me
1g, 100 MHz, CDCl3
f1 (ppm)

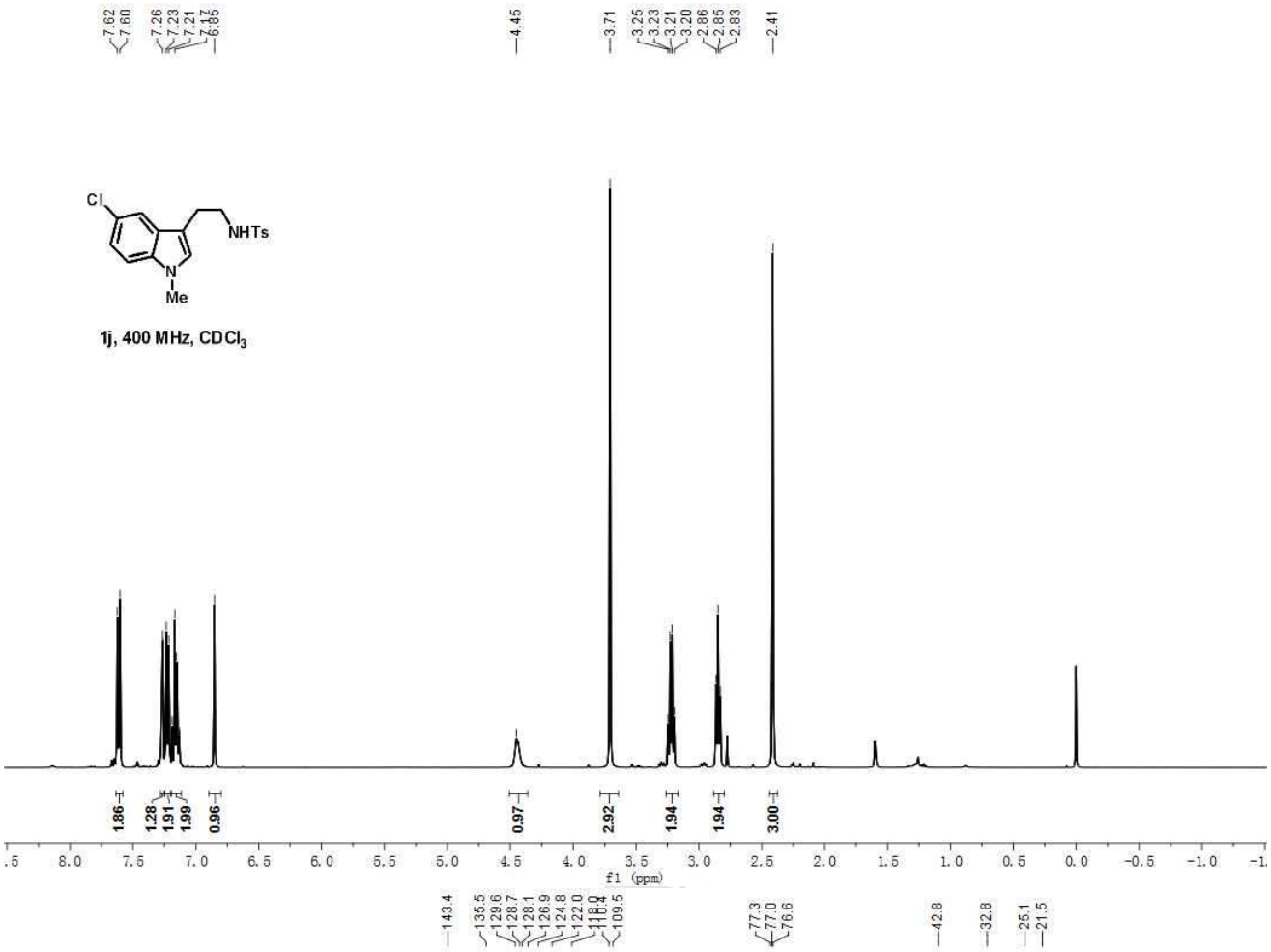

-125.16
F
NHTs
N
Me
1g, 376 MHz, CDCl3
f1 (ppm)
7.64
7.62
7.26
7.21
7.19
6.93
6.91
6.82
6.81
6.79
6.77
4.70
4.69
4.67
3.65
3.25
3.24
3.22
3.20
2.89
2.87
2.86
2.40


F
NHTs
N
Me
1h, 400 MHz, CDCl3
2.00
0.52
2.01
0.99
1.98
0.97
3.07
2.05
2.06
3.20
f1 (ppm)

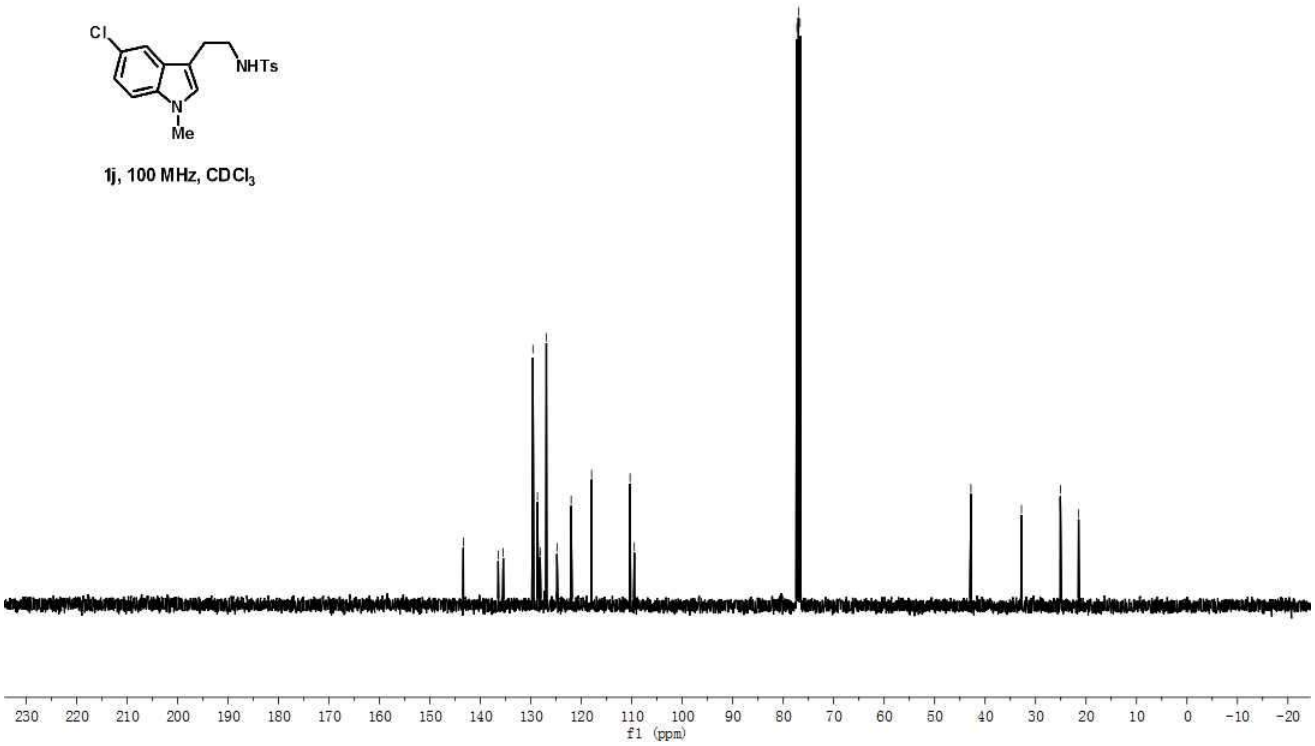

161.1
143.3
137.2
136.7
129.6
127.6
127.0
123.8
119.4
119.3
110.3
107.7
107.5
95.8
95.6
77.4
77.1
76.7
43.1
32.7
25.3
21.5
F
NHTs
N
Me
1h, 100 MHz, CDCl3
f1 (ppm)


-120.72
F
NHTs
N
Me
1h, 376 MHz, CDCl3
f1 (ppm)

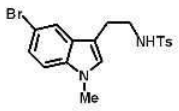

7.65
7.63
7.26
7.19
7.17
7.15
7.13
7.13
7.09
7.07
7.05
7.00
7.00
6.98
6.84
4.68
4.67
4.65
3.68
3.33
3.31
3.29
3.28
3.12
3.10
3.09
2.38
Cl
NHTs
N
Me
1i, 400 MHz, CDCl3
2.03
2.08
1.08
1.09
1.02
1.00
1.01
3.13
2.11
2.09
3.10
f1 (ppm)
143.1
138.6
136.8
129.5
129.2
126.9
126.0
122.1
118.9
118.4
108.1
77.4
77.0
76.7
44.4
32.9
26.3
21.5
Cl
NHTs
N
Me
1i, 100 MHz, CDCl3
f1 (ppm)



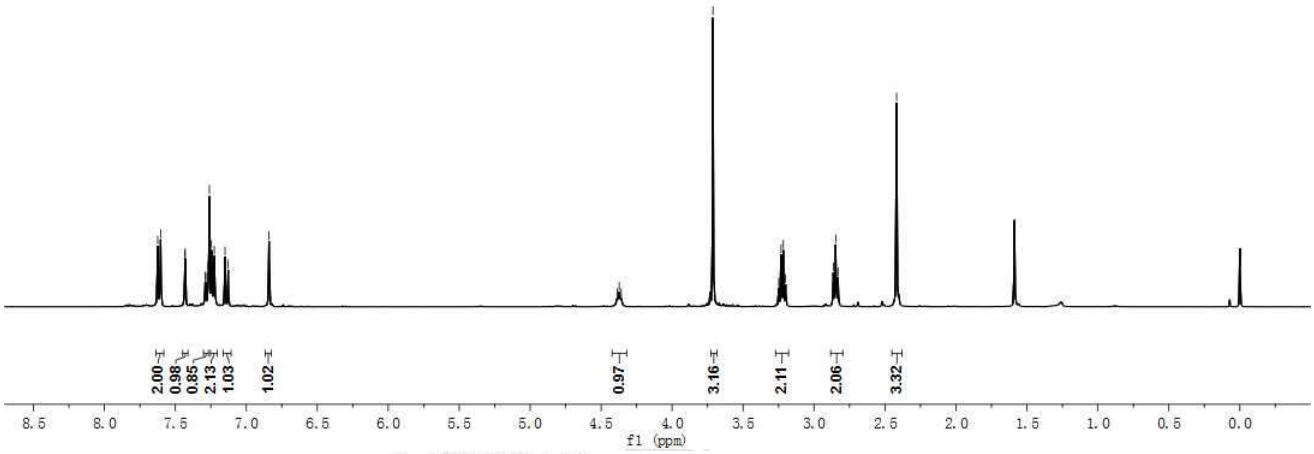
1j, 400 MHz, $CDCl_3$

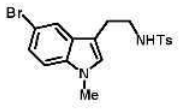


1j, 100 MHz, $CDCl_3$

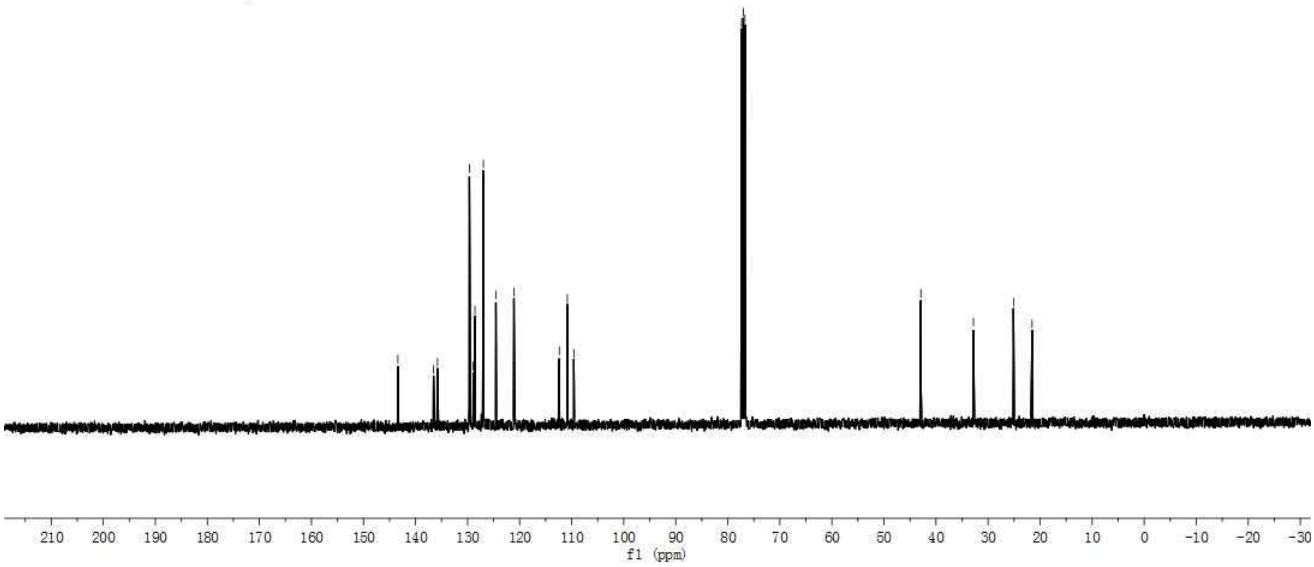


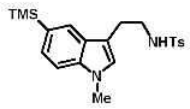
1k, 400 MHz, $CDCl_3$



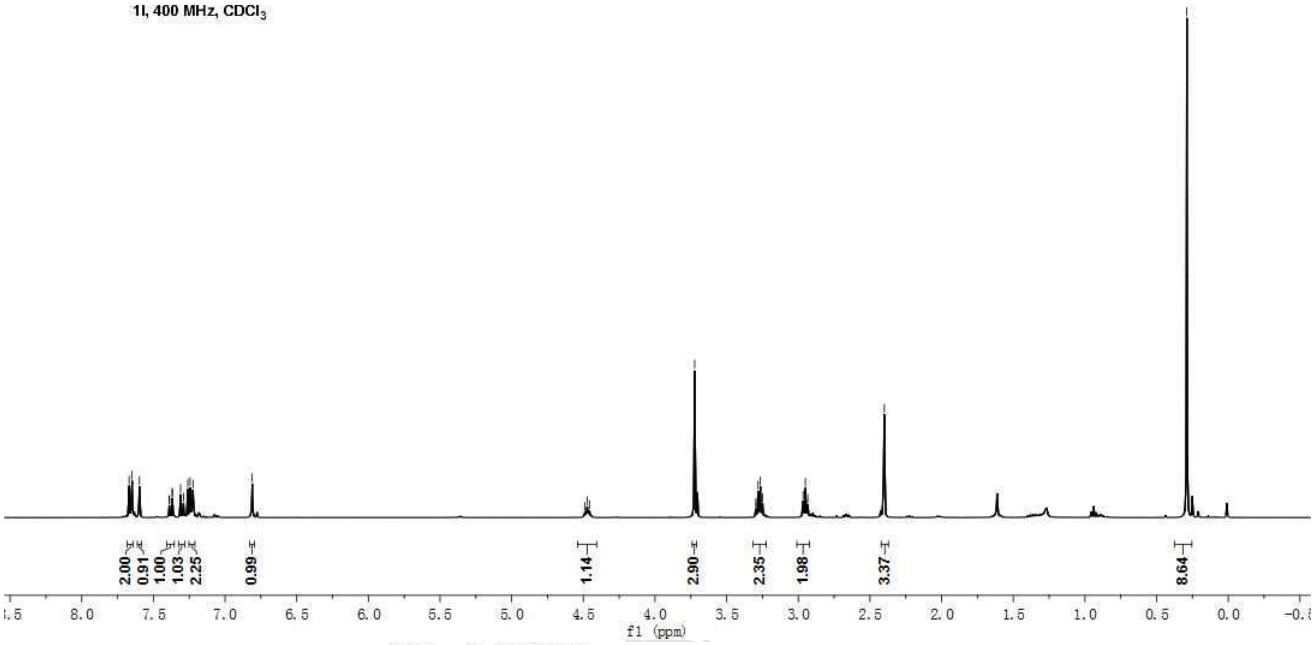


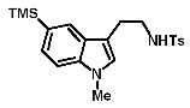
1k, 100 MHz, $CDCl_3$



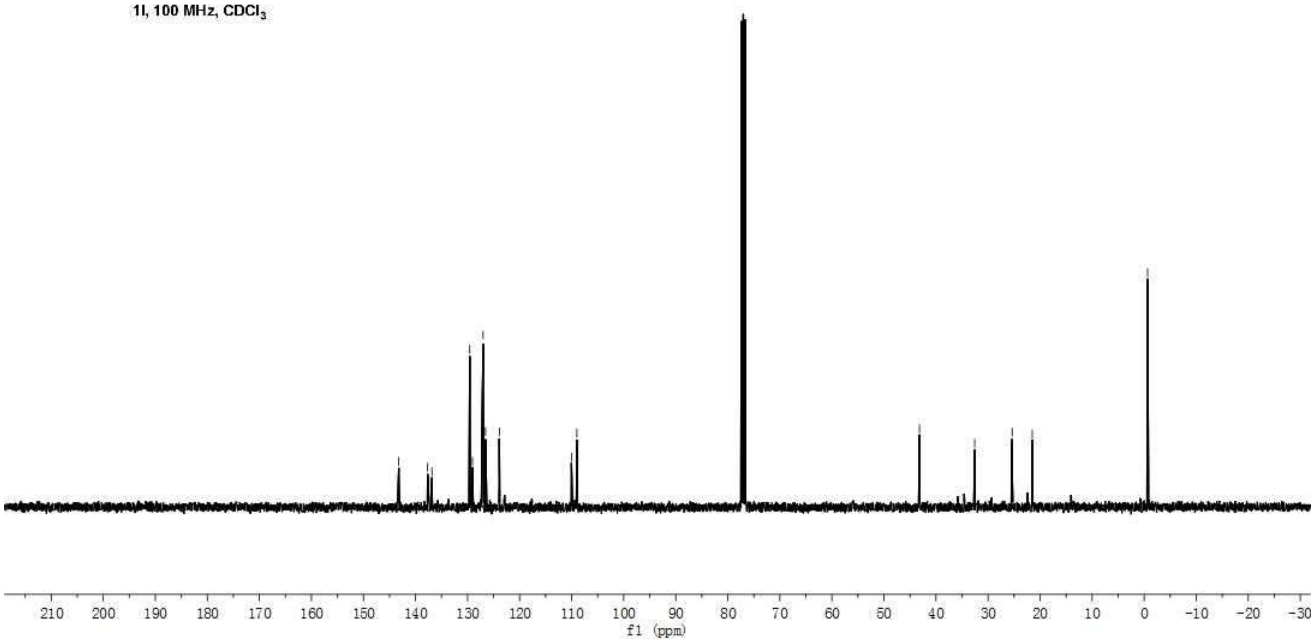


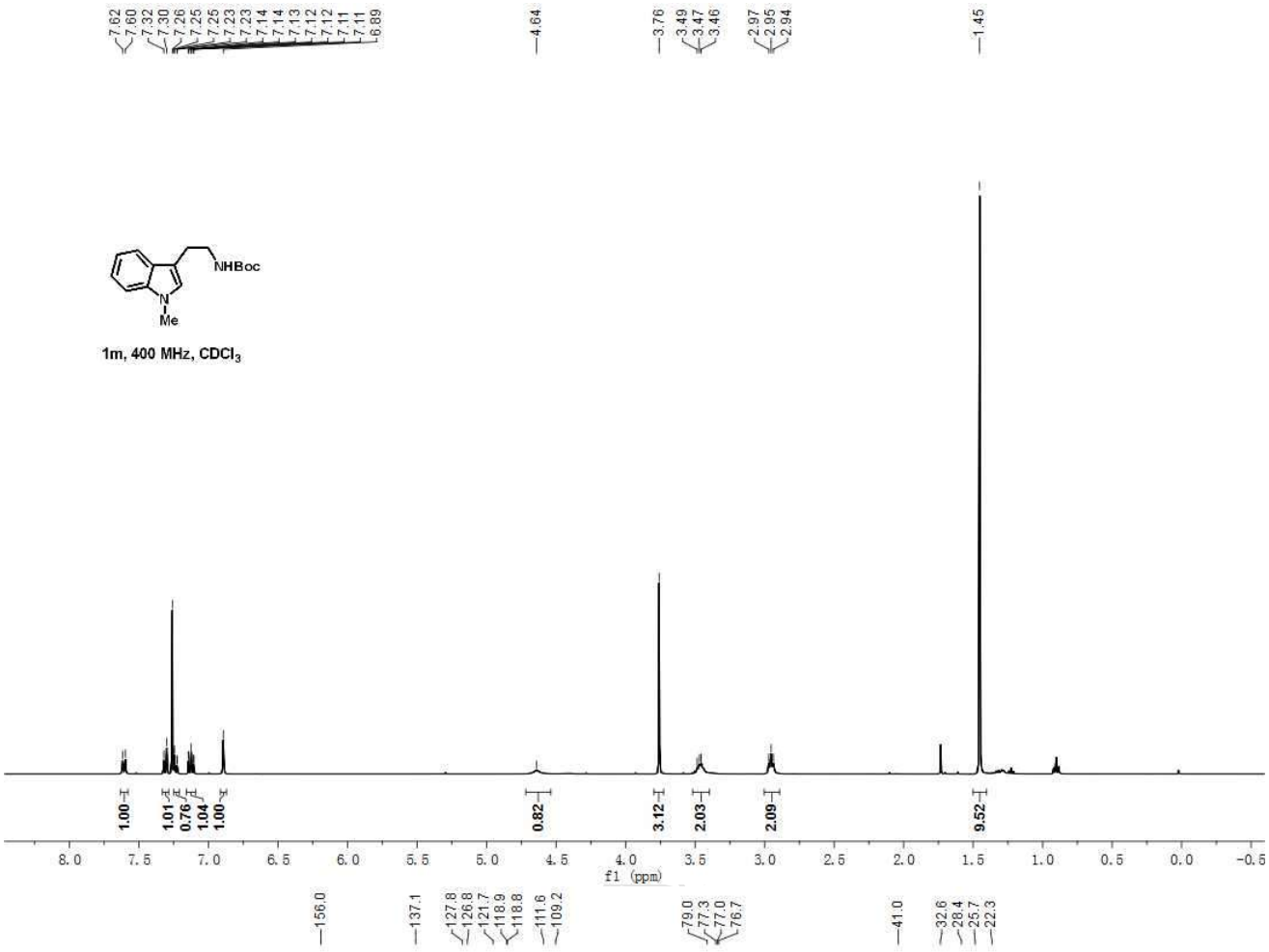
1l, 400 MHz, $CDCl_3$

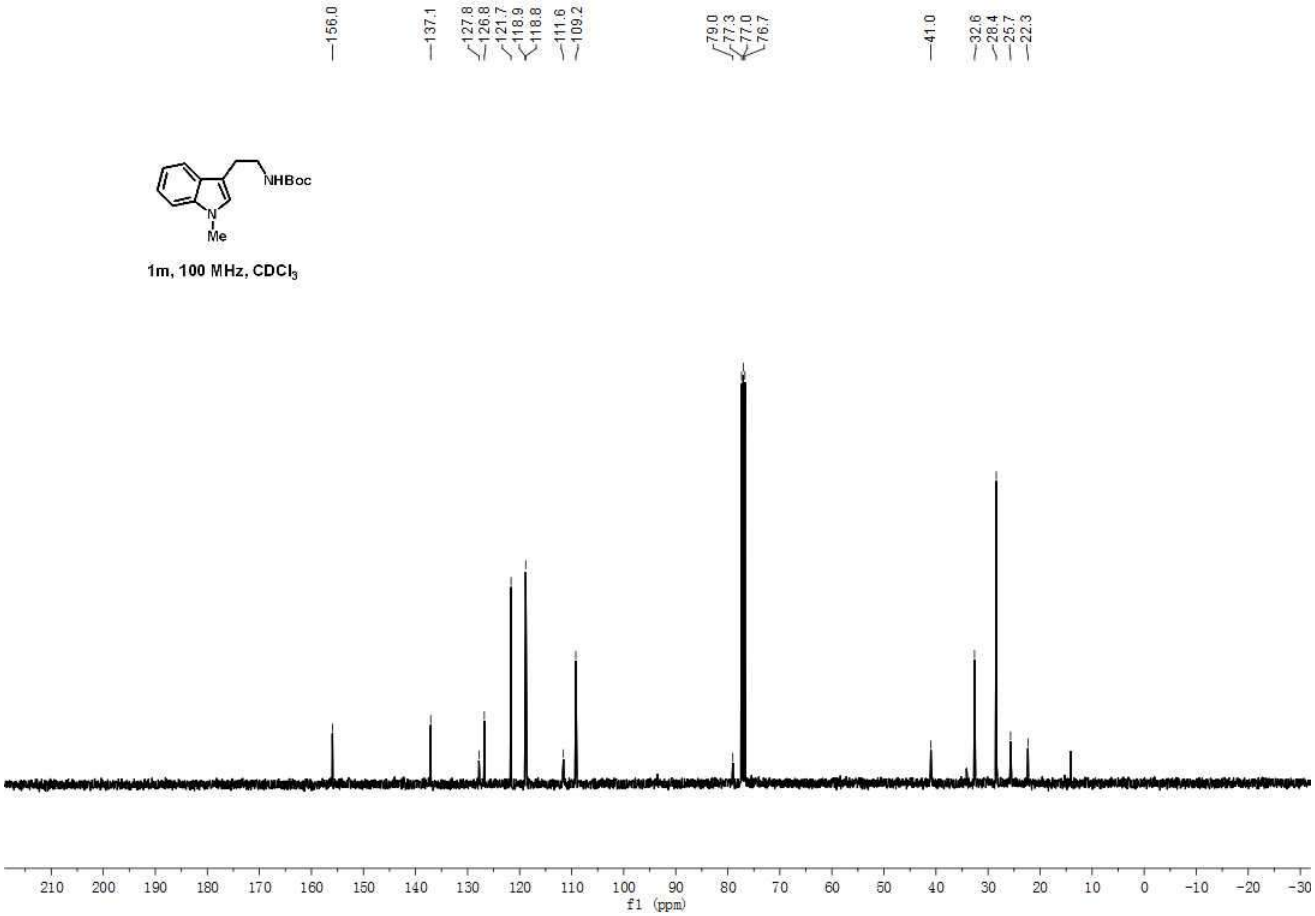


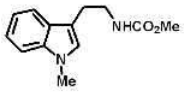


1l, 100 MHz, $CDCl_3$

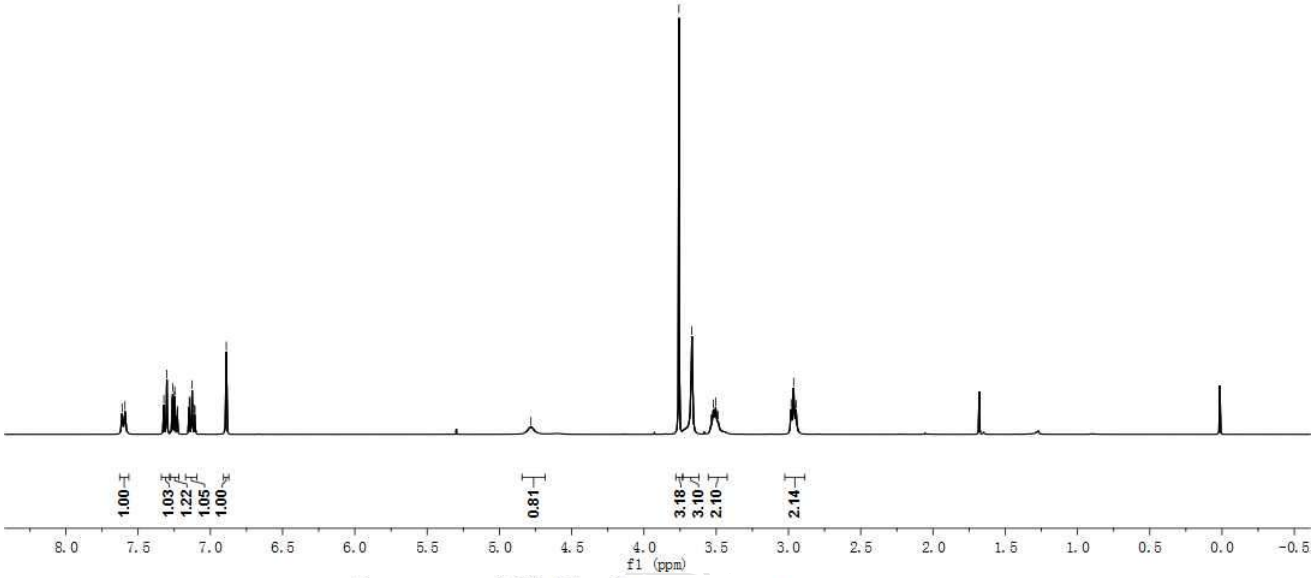


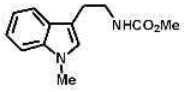

7.62
7.60
7.32
7.30
7.26
7.25
7.25
7.23
7.23
7.14
7.14
7.13
7.12
7.12
7.11
7.11
6.89
4.64
3.76
3.49
3.47
3.46
2.97
2.95
2.94
1.45
NHBoc
N
Me
1m, 400 MHz, CDCl3
1.00
1.01
0.76
1.04
1.00
0.82
3.12
2.03
2.09
9.52
f1 (ppm)


156.0
137.1
127.8
126.8
121.7
118.9
118.8
111.6
109.2
79.0
77.3
77.0
76.7
41.0
32.6
28.4
25.7
22.3
NHBoc
N
Me
1m, 100 MHz, CDCl3
f1 (ppm)

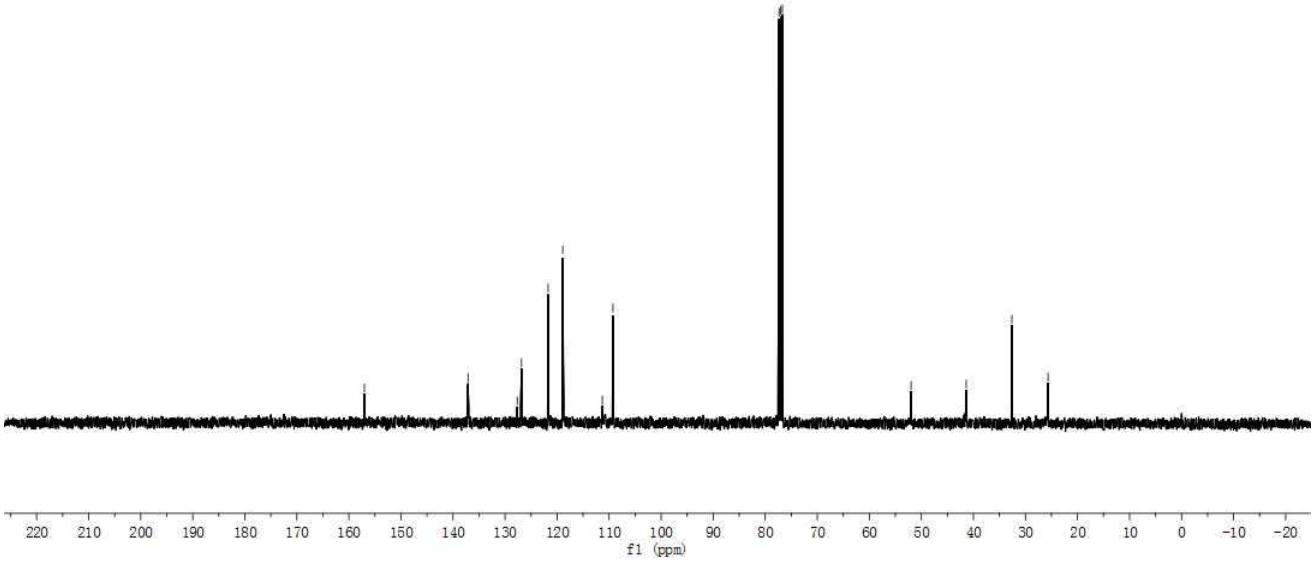


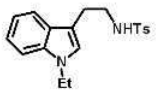
1n, 400M, $CDCl_3$



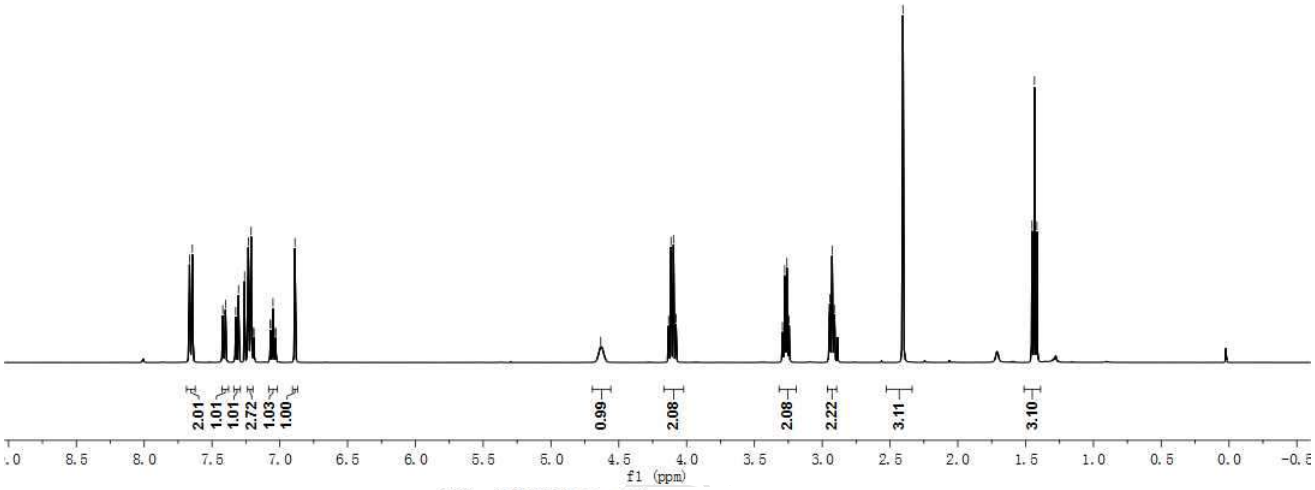


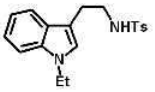
1n, 100M, $CDCl_3$



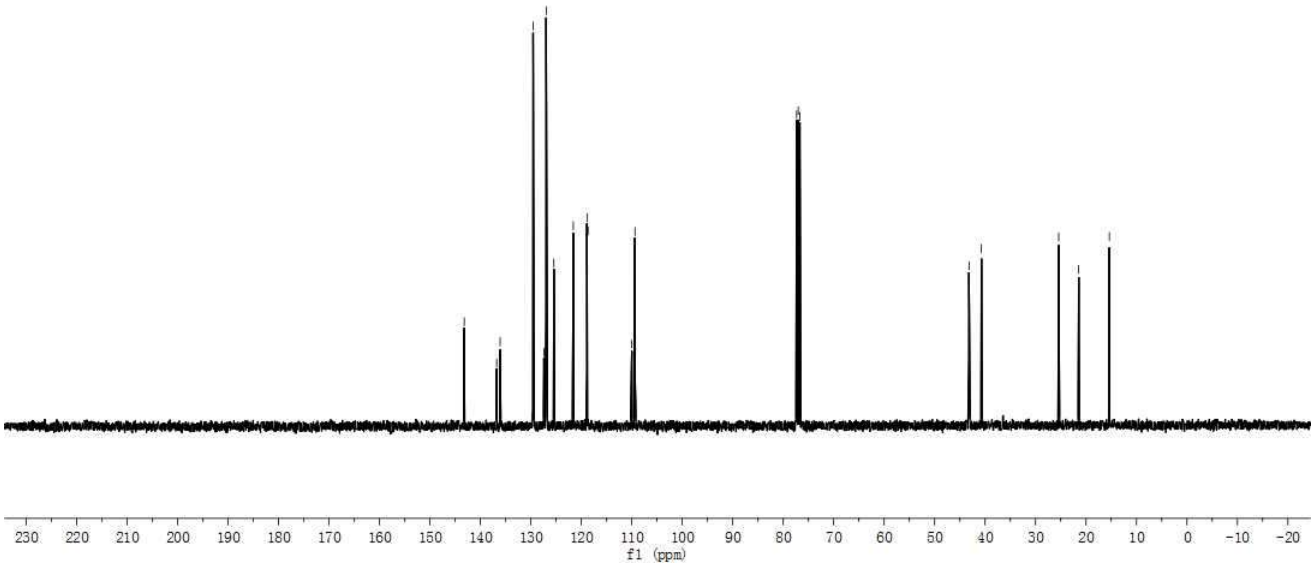


1o, 400M, $CDCl_3$

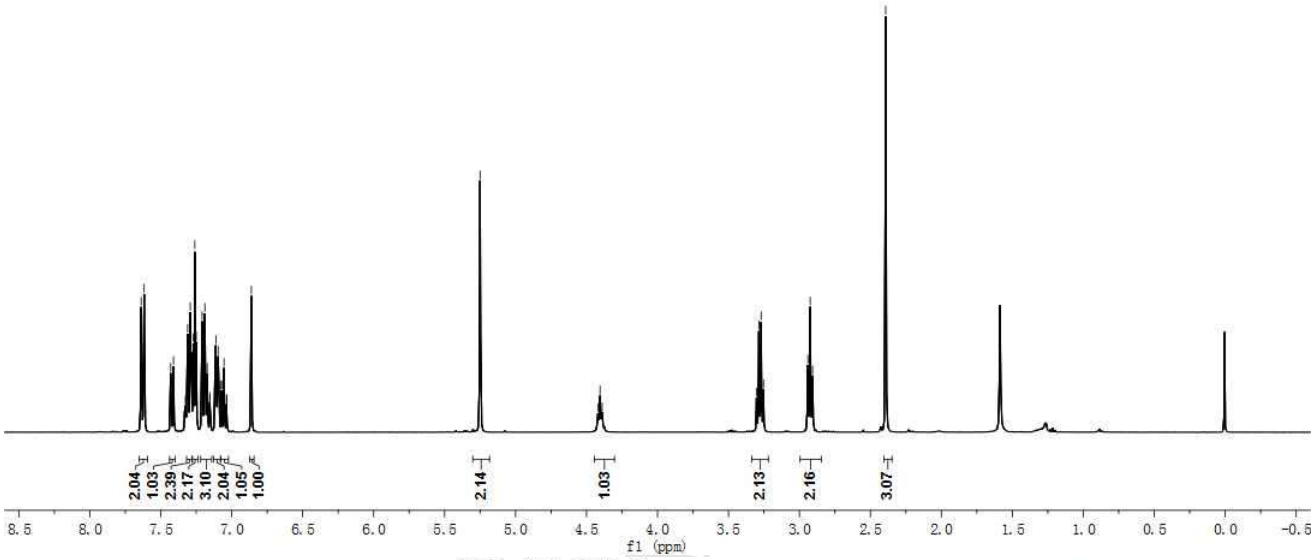


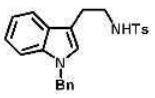


1o, 100M, $CDCl_3$

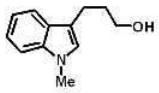


1p, 400M, $CDCl_3$

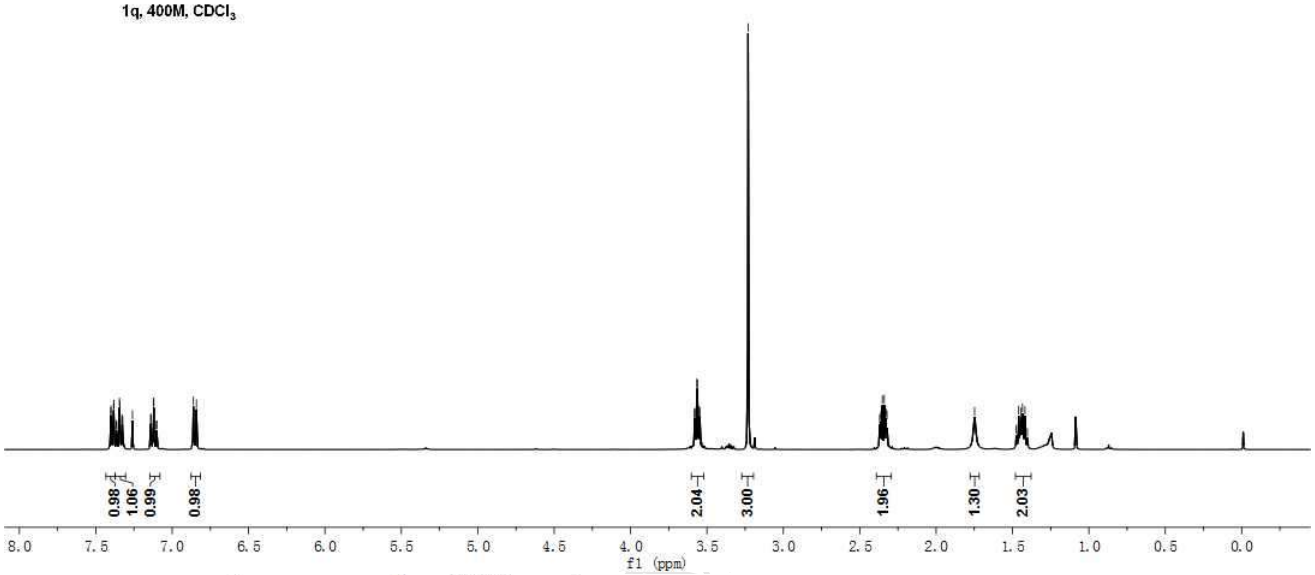


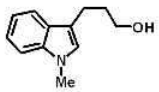


1p, 100M, $CDCl_3$

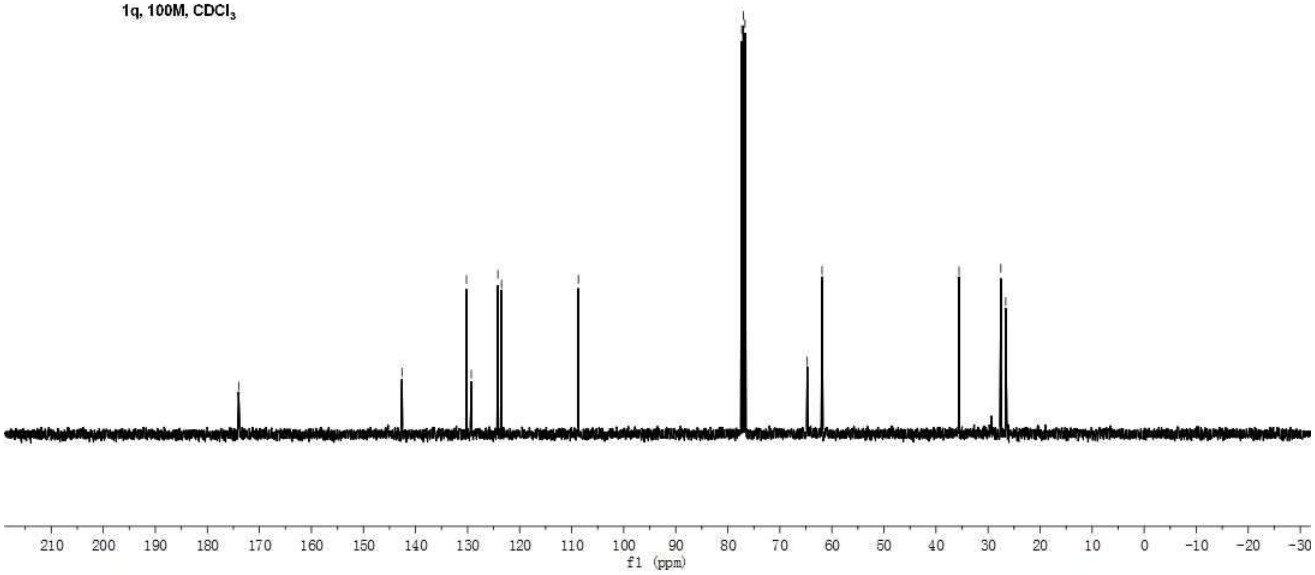


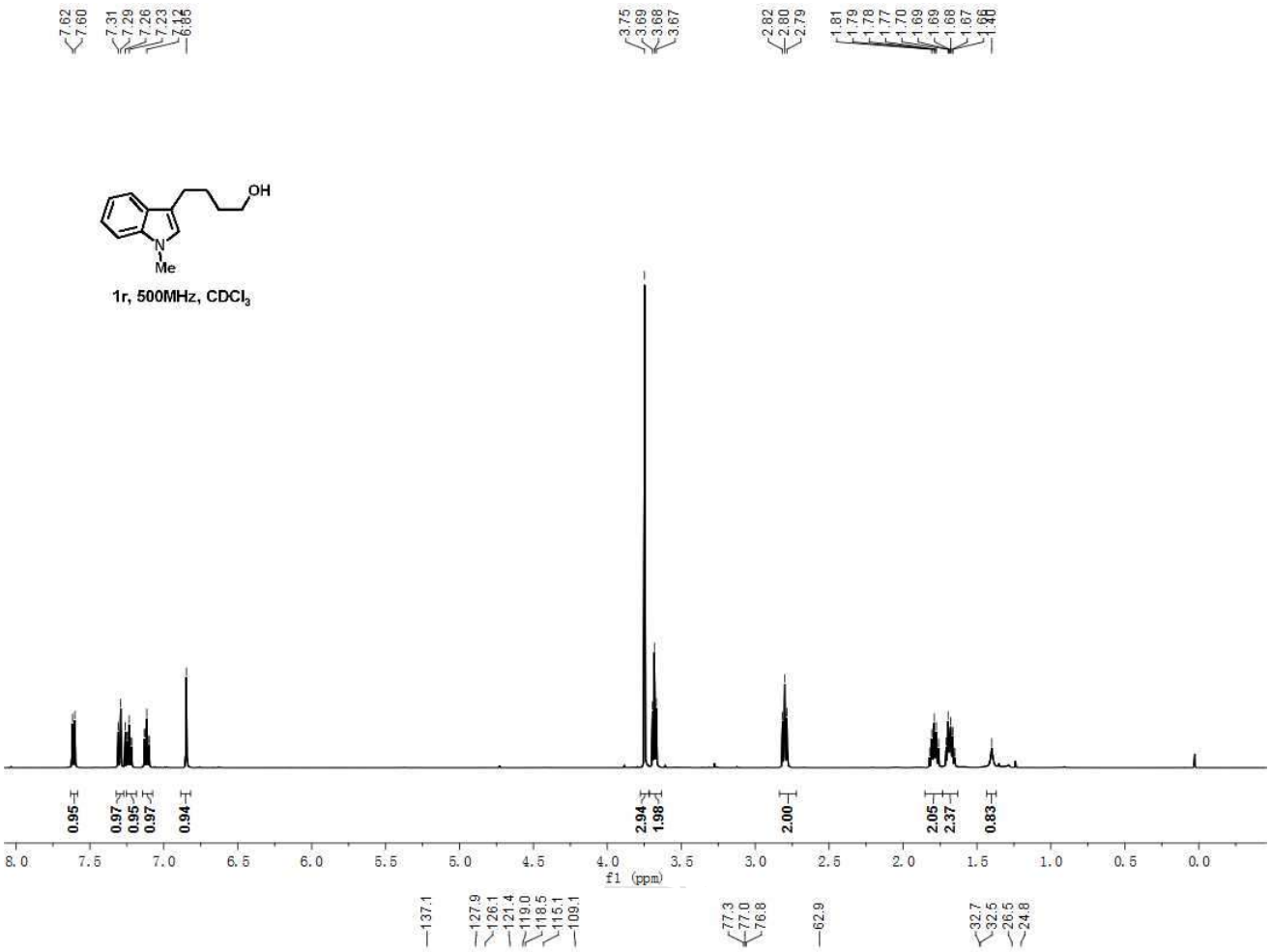
1q, 400M, $CDCl_3$

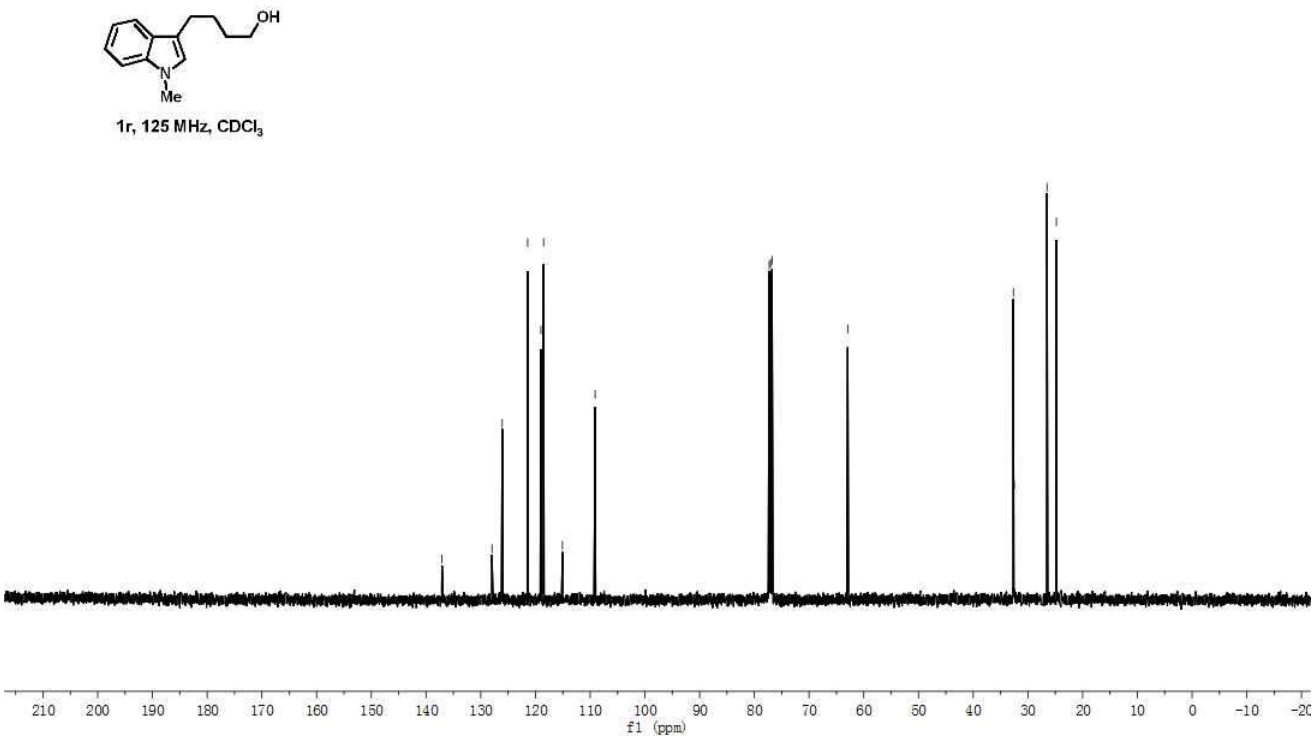


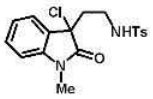


1q, 100M, $CDCl_3$

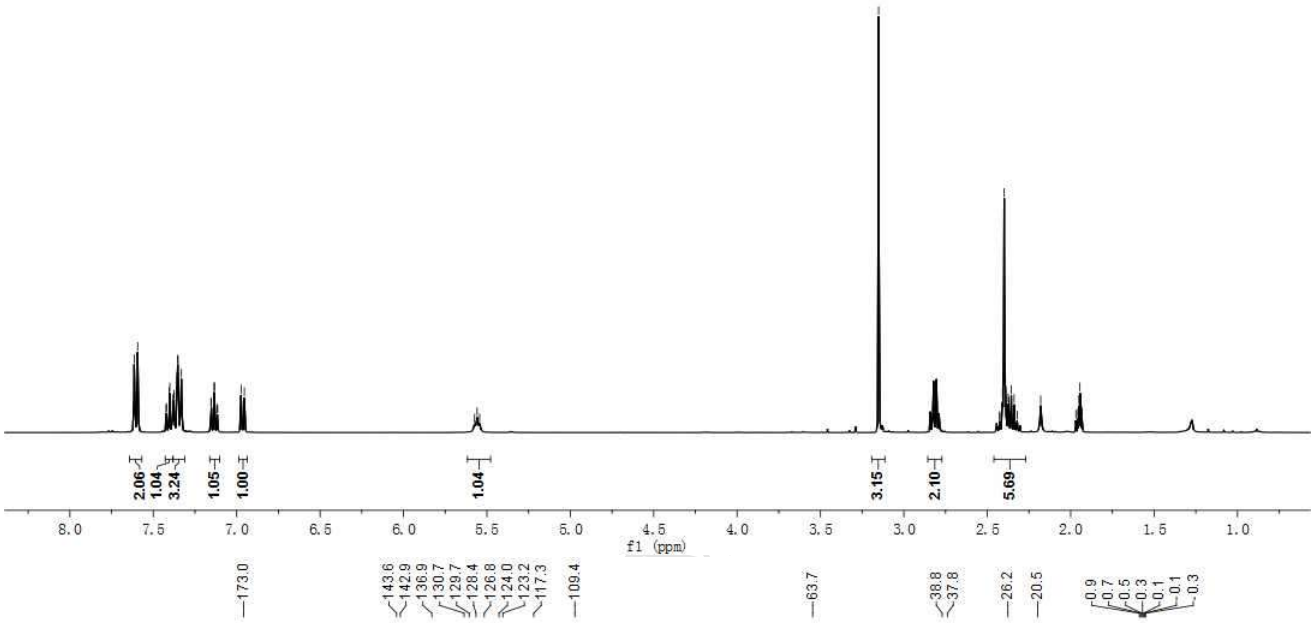


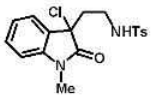

7.62
7.60
7.31
7.29
7.26
7.23
6.85
3.75
3.69
3.68
3.67
2.82
2.80
2.79
1.81
1.79
1.78
1.77
1.70
1.69
1.69
1.68
1.67
OH
N
Me
1r, 500MHz, CDCl3
0.95
0.97
0.95
0.97
0.94
2.94
1.98
2.00
2.05
2.37
0.83
f1 (ppm)


137.1
127.9
126.1
121.4
119.0
118.5
115.1
109.1
77.3
77.0
76.8
62.9
32.7
32.5
26.5
24.8
OH
N
Me
1r, 125 MHz, CDCl3
f1 (ppm)

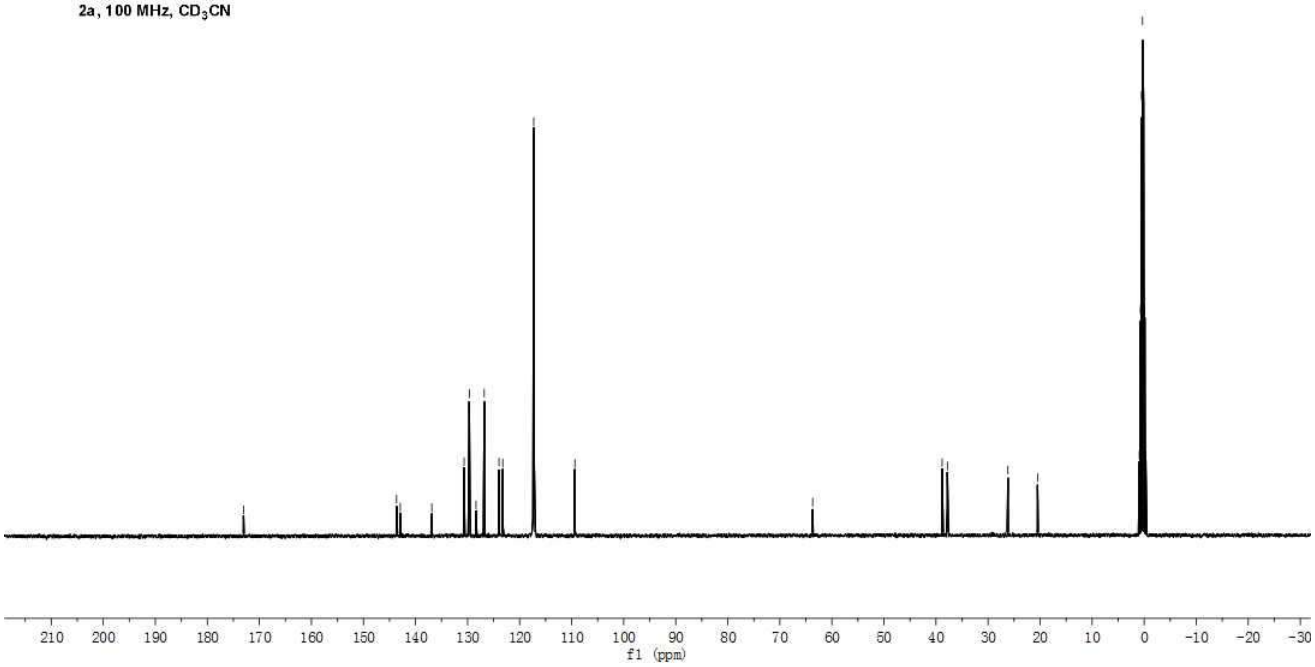


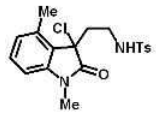
2a, 400 MHz, CD_3CN



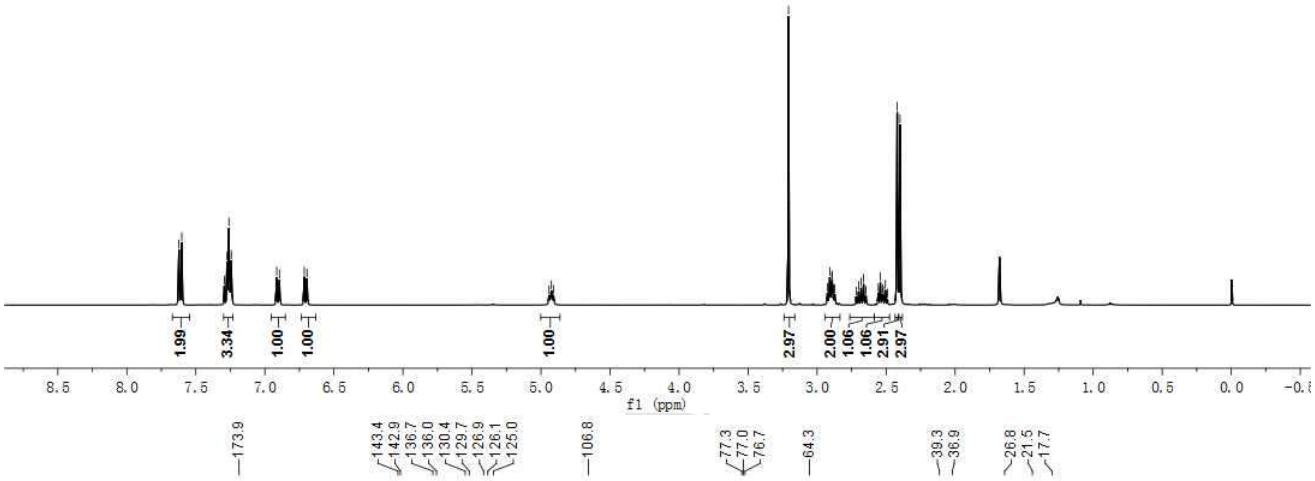


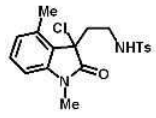
2a, 100 MHz, CD_3CN



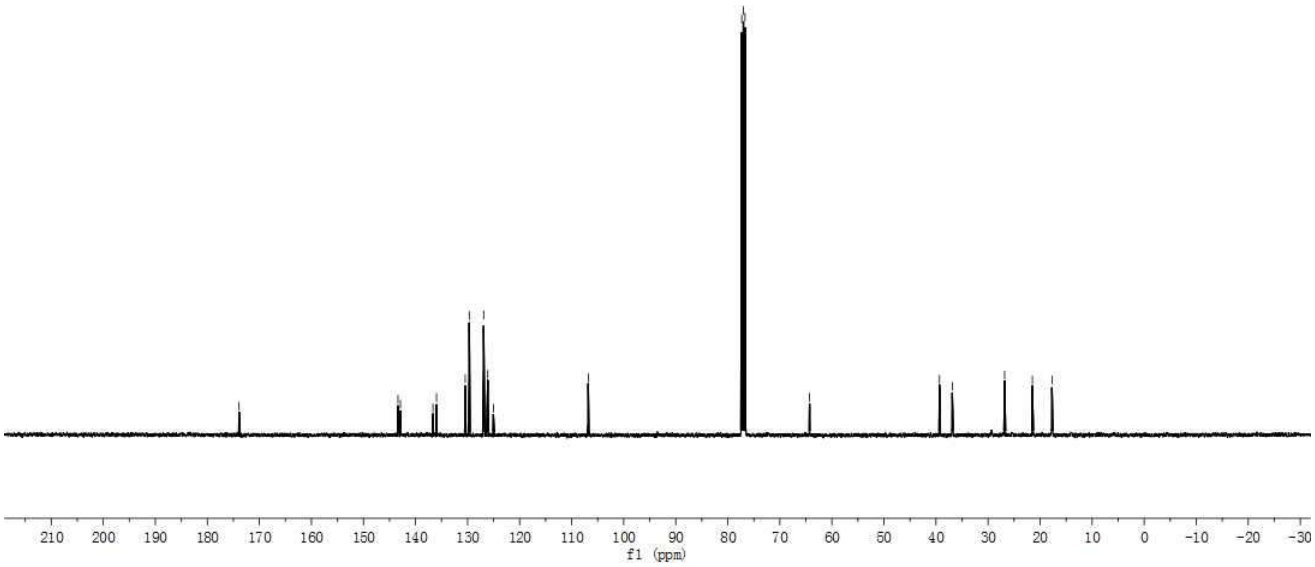


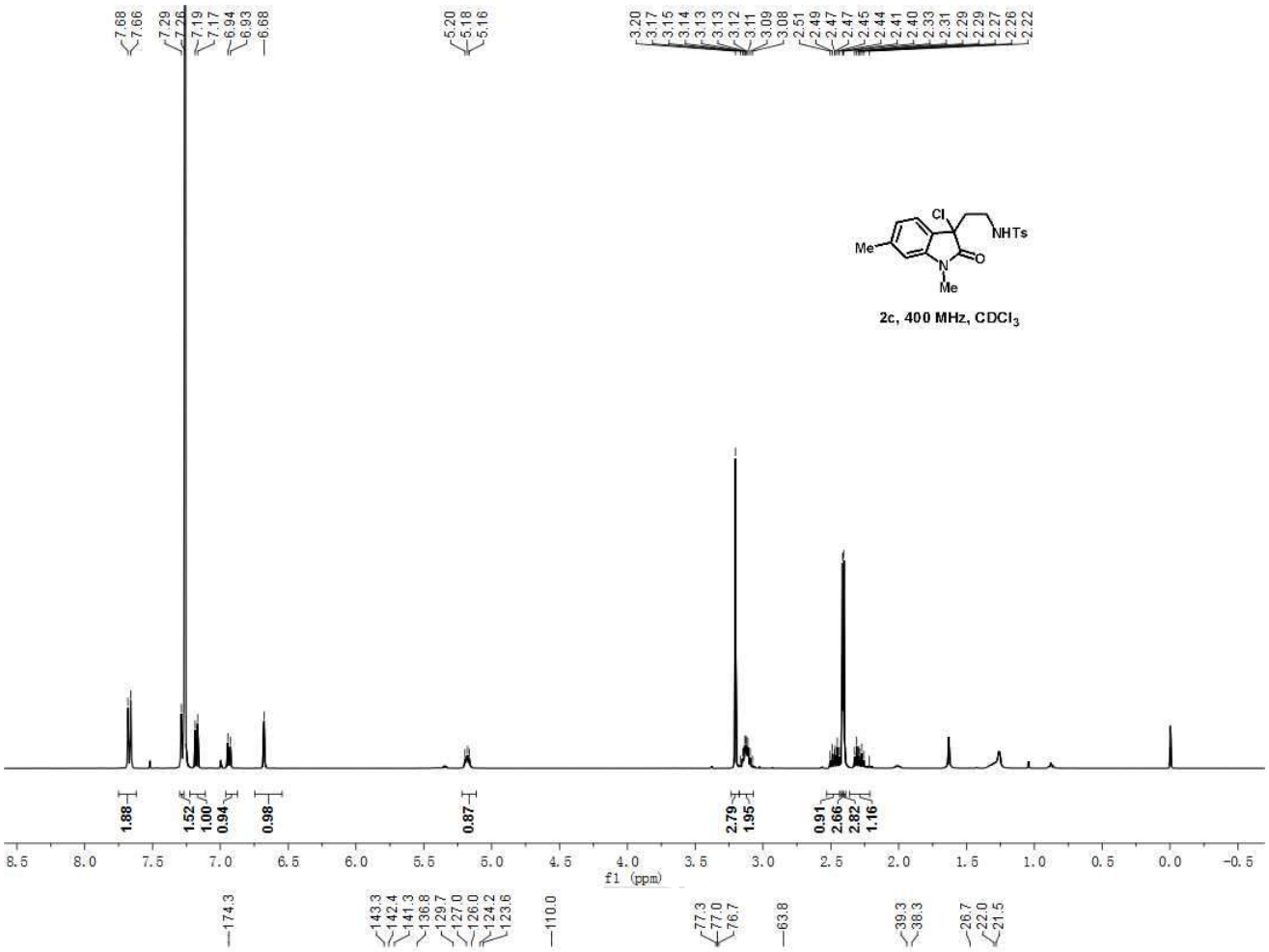
2b, 400 MHz, $CDCl_3$



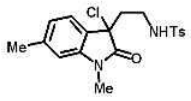


2b, 100 MHz, $CDCl_3$

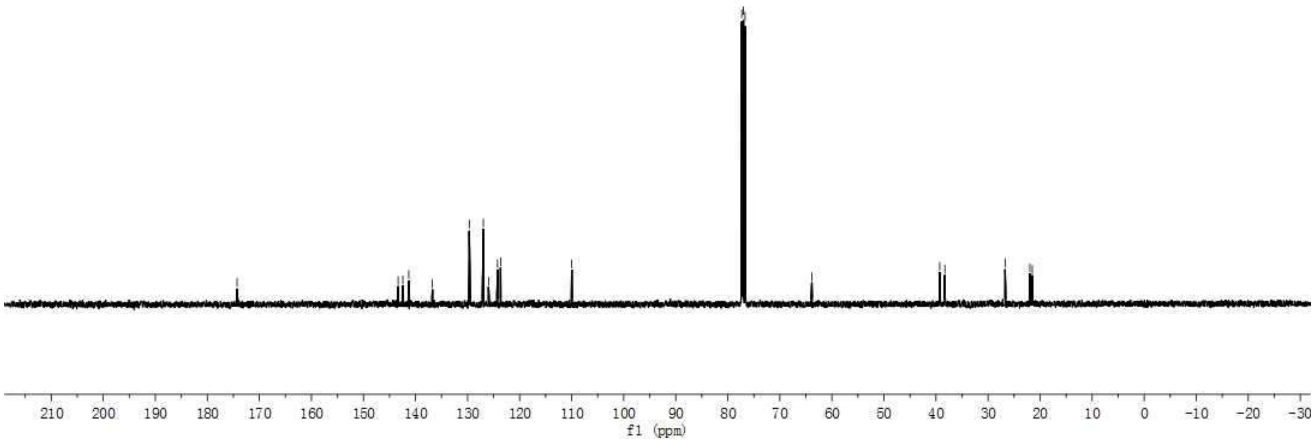


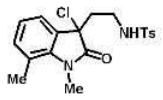


2c, 400 MHz, $CDCl_3$

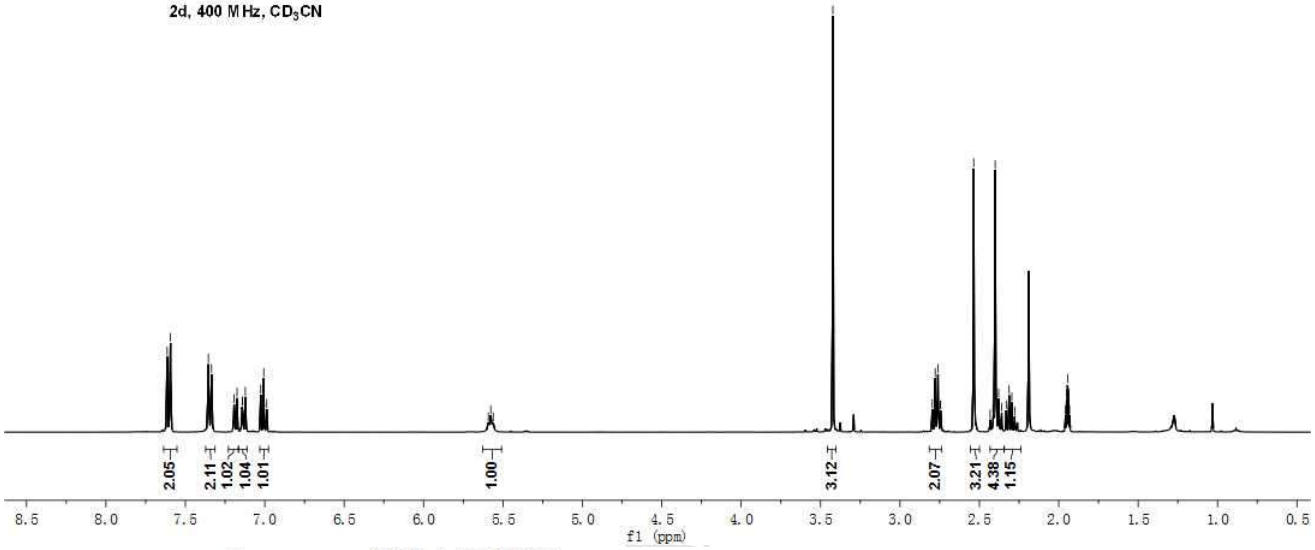


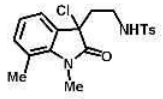
2c, 100 MHz, $CDCl_3$



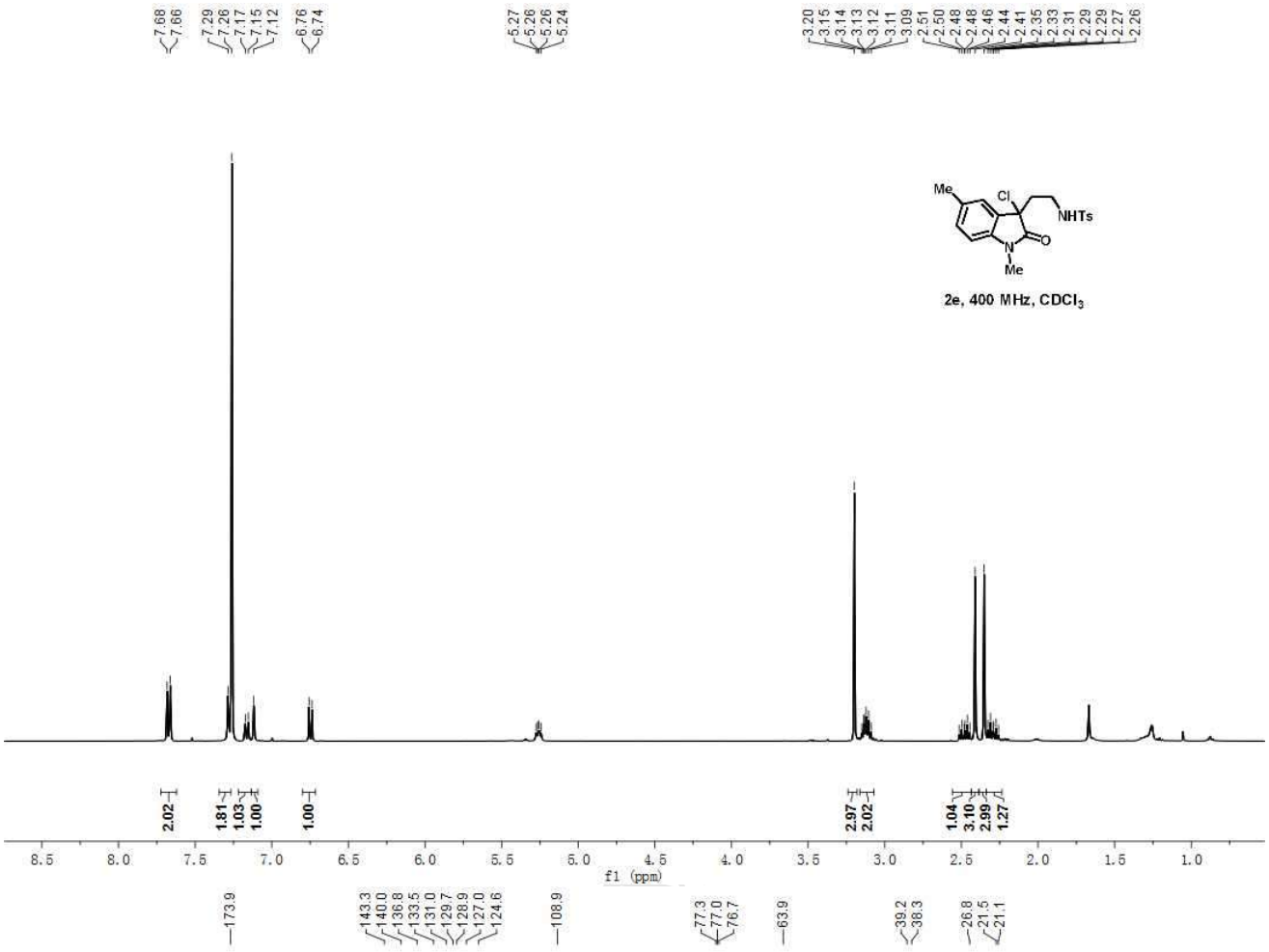


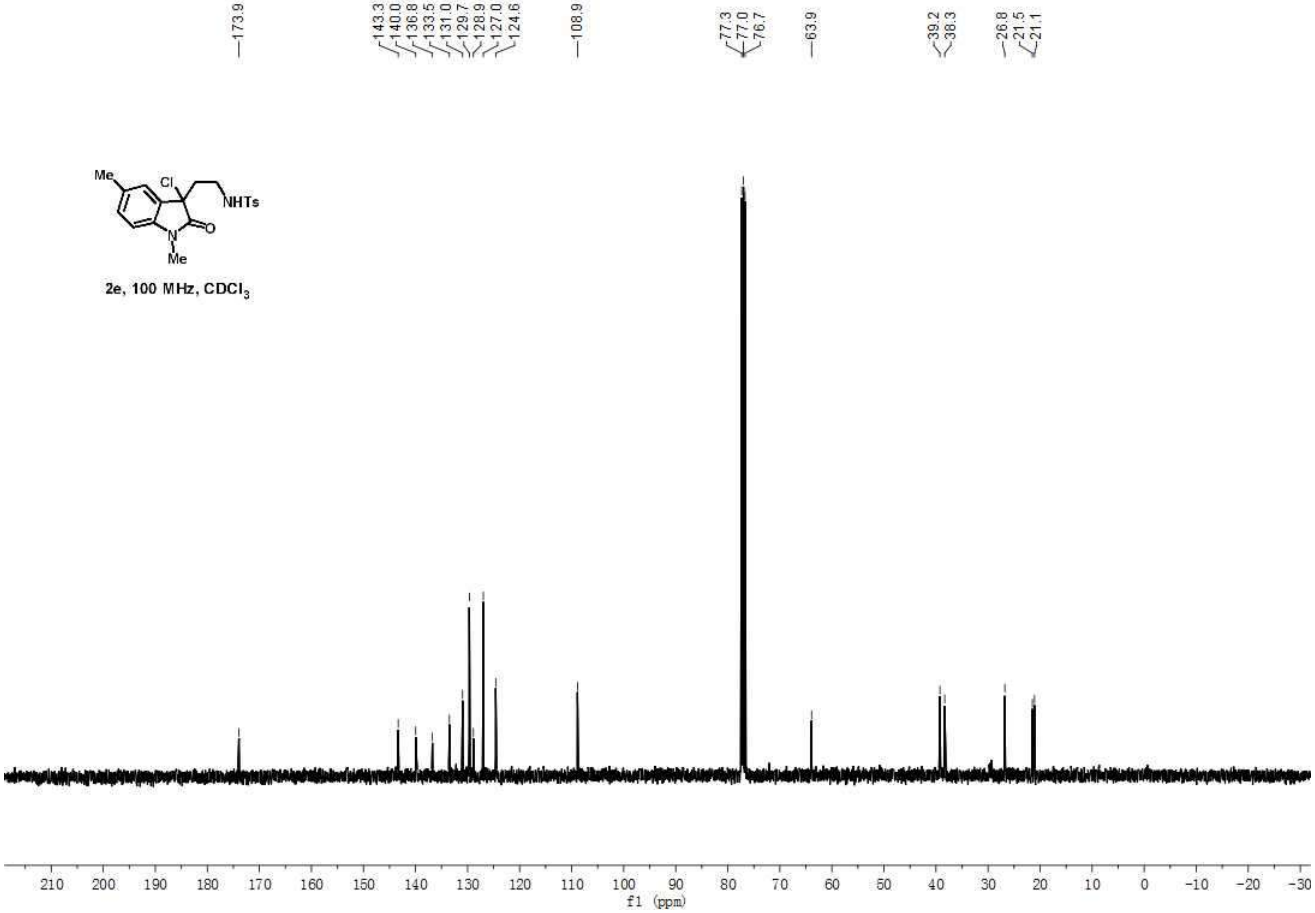
2d, 400 MHz, CD_3CN

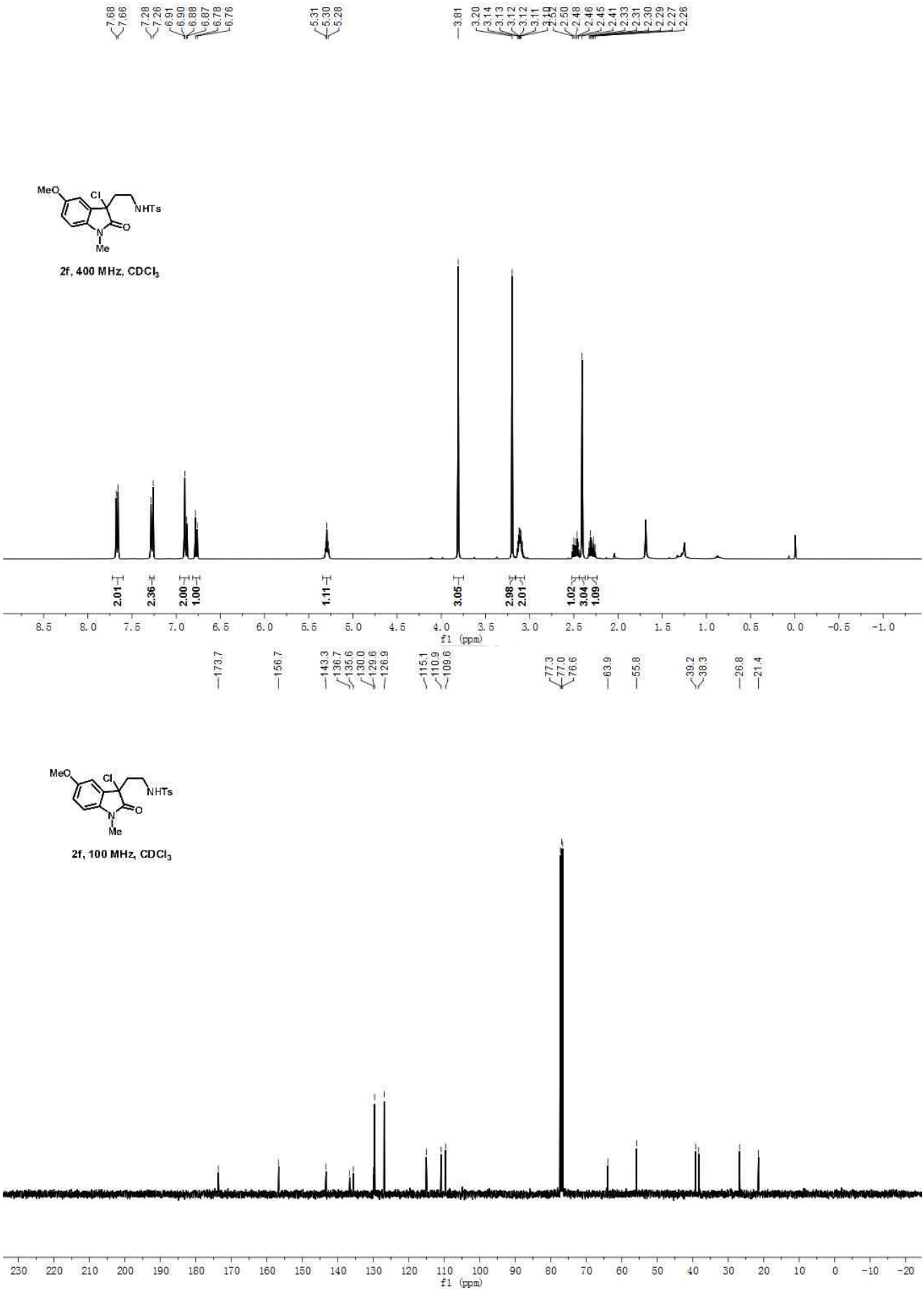


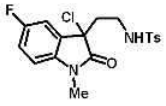


2d, 100 MHz, CD_3CN

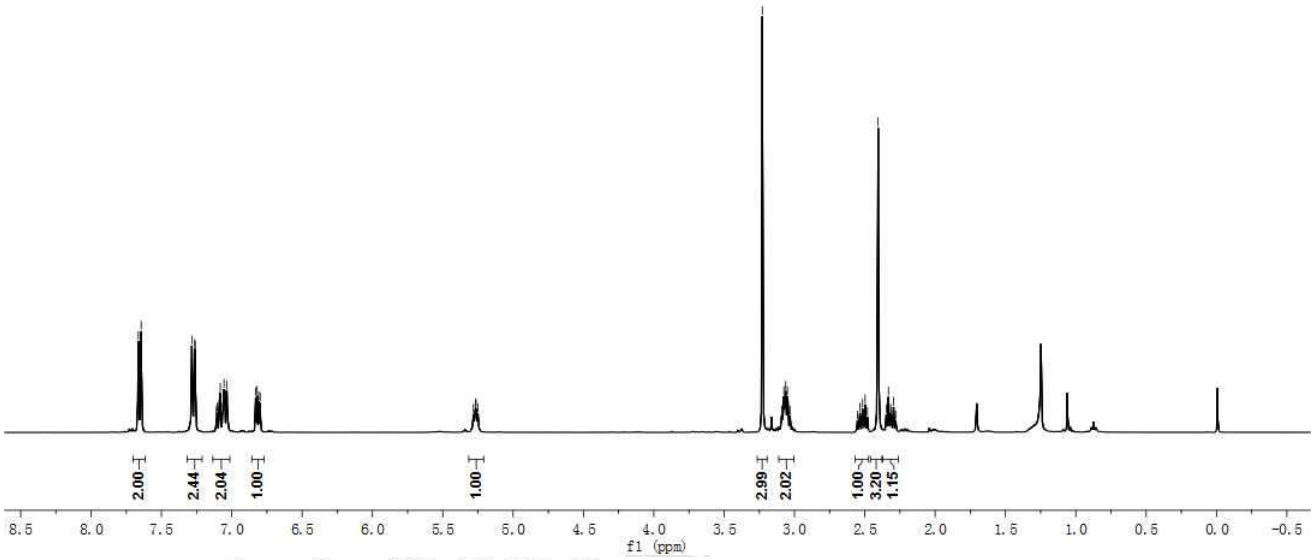

7.68
7.66
7.29
7.26
7.17
7.15
7.12
6.76
6.74
5.27
5.26
5.26
5.24
3.20
3.15
3.14
3.13
3.12
3.11
3.09
2.51
2.50
2.48
2.48
2.46
2.44
2.41
2.35
2.33
2.31
2.29
2.29
2.27
2.26
Me
Cl
NHTs
O
N
Me
2e, 400 MHz, CDCl3
2.02
1.81
1.03
1.00
1.00
2.97
2.02
1.04
3.10
2.99
1.27
f1 (ppm)

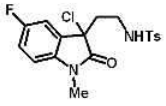

173.9
143.3
140.0
136.8
133.5
131.0
129.7
128.9
127.0
124.6
108.9
77.3
77.0
76.7
63.9
39.2
38.3
26.8
21.5
21.1
Me
Cl
NHTs
O
N
Me
2e, 100 MHz, CDCl3
f1 (ppm)


7.68
7.66
7.28
7.26
6.91
6.90
6.88
6.87
6.78
6.76
5.31
5.30
5.28
3.81
3.20
3.14
3.13
3.12
3.12
3.11
3.10
2.52
2.50
2.48
2.46
2.45
2.41
2.33
2.31
2.30
2.29
2.27
2.26
MeO
Cl
NHTs
O
N
Me
2f, 400 MHz, CDCl3
2.01
2.36
2.00
1.00
1.11
3.05
2.98
2.01
1.02
3.04
1.09
f1 (ppm)
173.7
156.7
143.3
136.7
135.6
130.0
129.6
126.9
115.1
110.9
109.6
77.3
77.0
76.6
63.9
55.8
39.2
38.3
26.8
21.4
MeO
Cl
NHTs
O
N
Me
2f, 100 MHz, CDCl3
f1 (ppm)

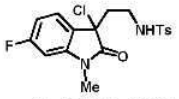


2g, 400 MHz, $CDCl_3$

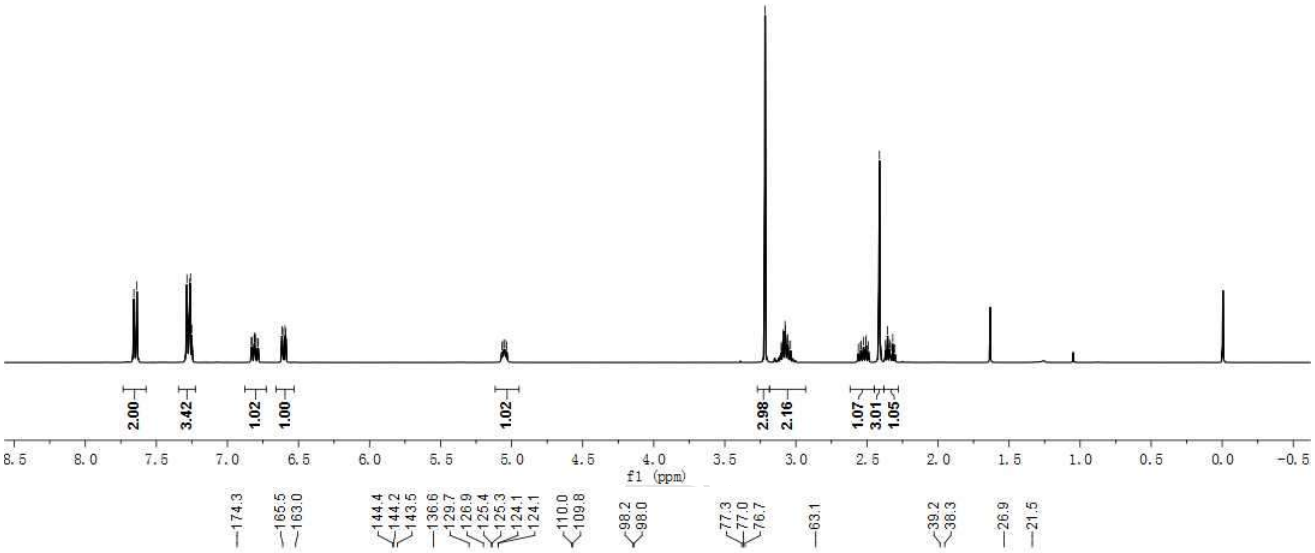


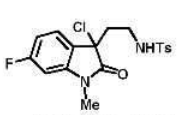


2g, 100 MHz, $CDCl_3$

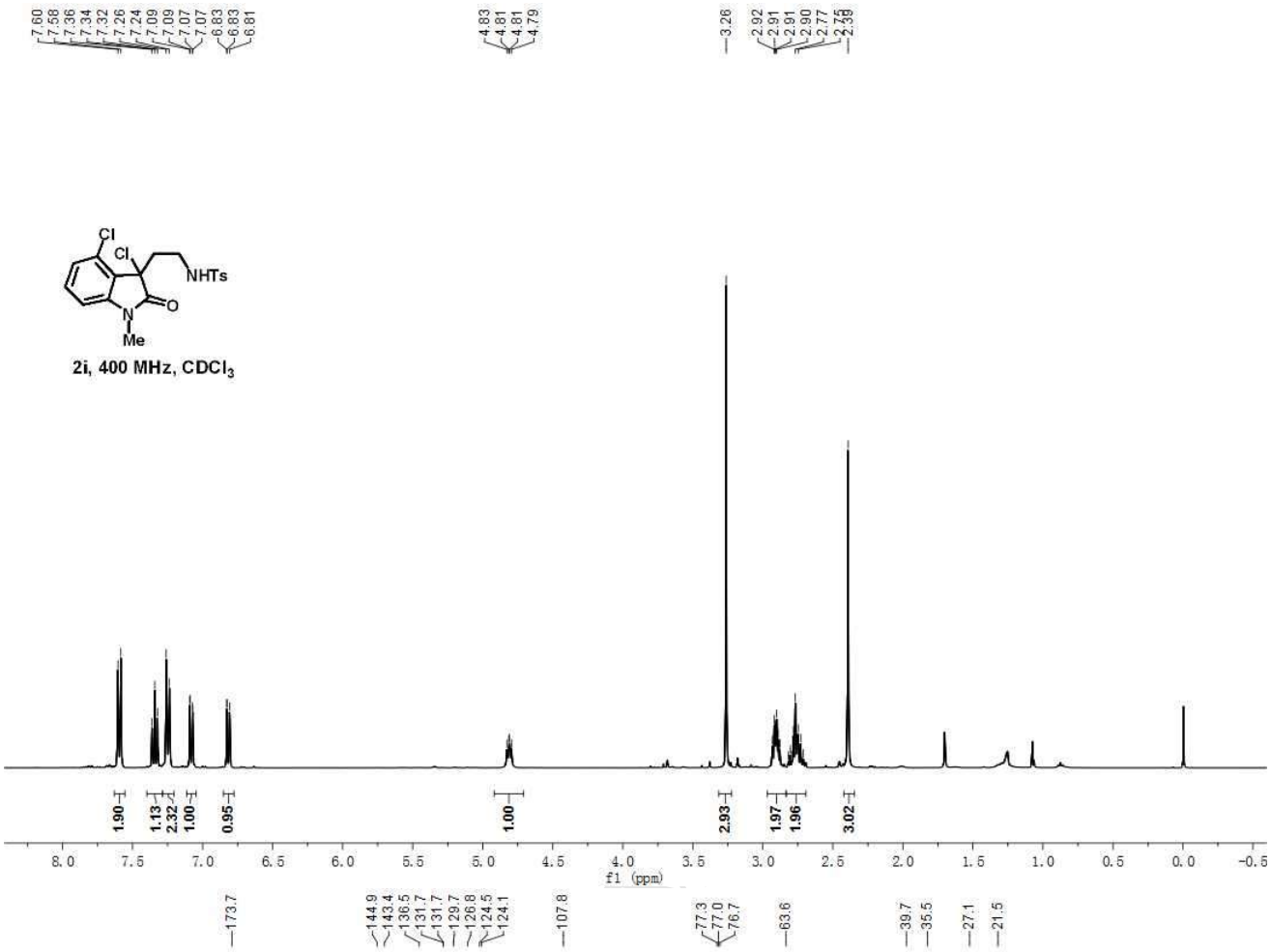


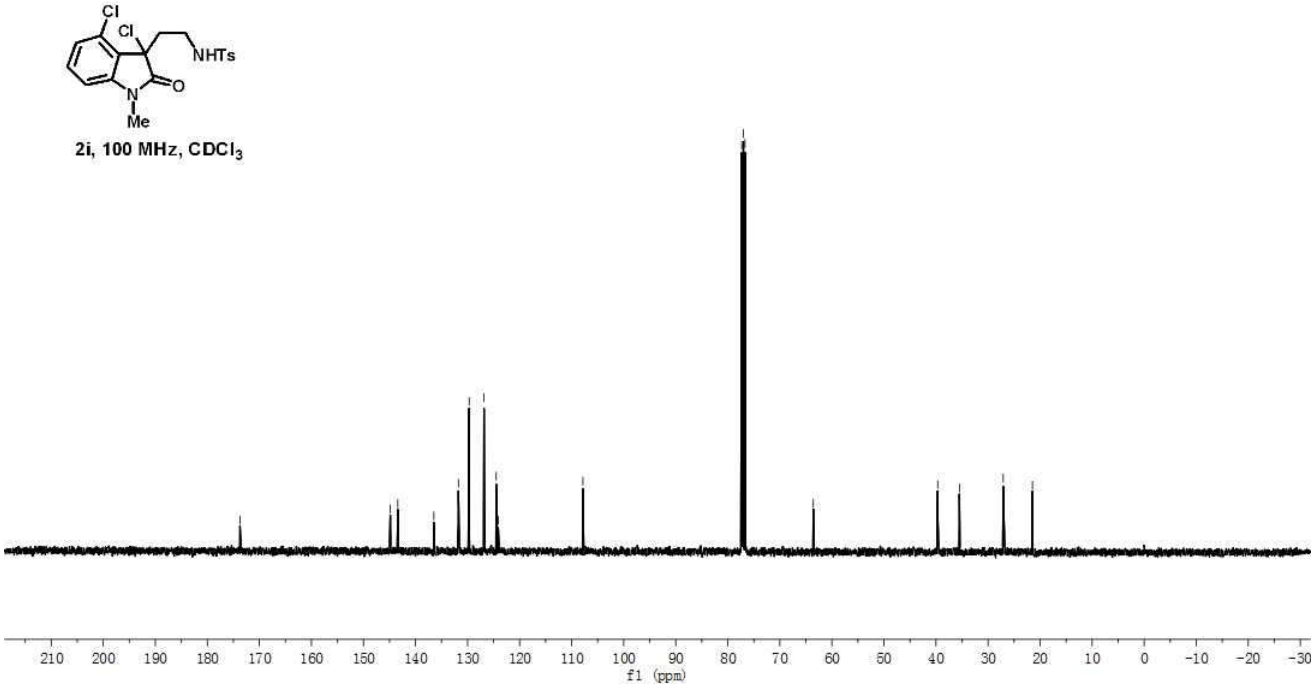
2h, 400 MHz, $CDCl_3$

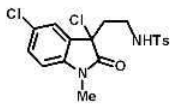




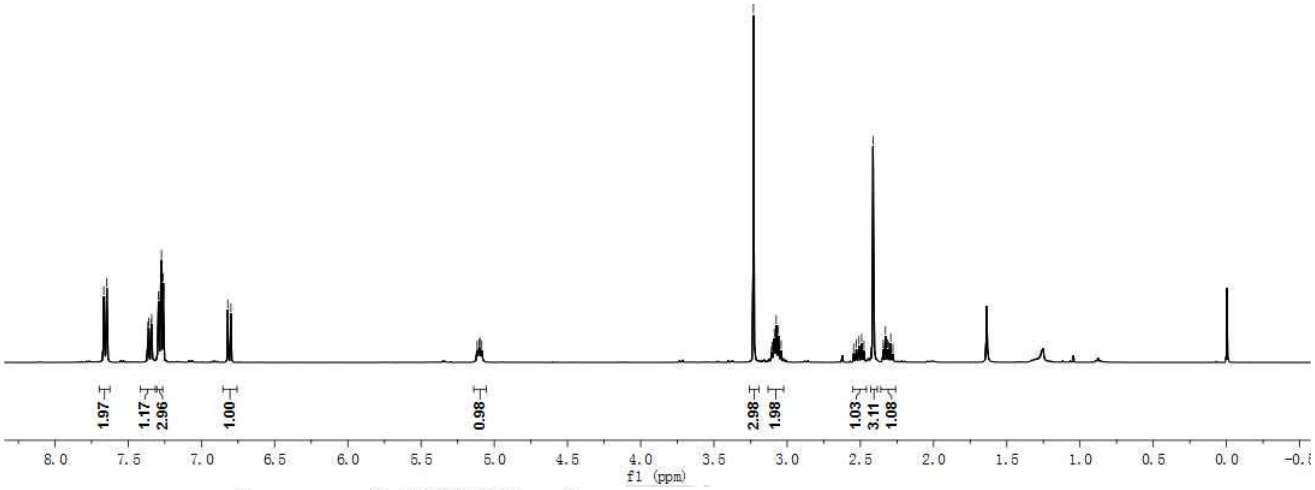
2h, 100 MHz, $CDCl_3$

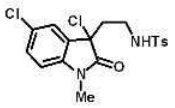

7.60
7.58
7.36
7.34
7.32
7.26
7.24
7.09
7.09
7.07
7.07
6.83
6.83
6.81
4.83
4.81
4.81
4.79
3.26
2.92
2.91
2.91
2.90
2.77
2.39
Cl
Cl
NHTs
O
N
Me
2i, 400 MHz, CDCl3
1.90
1.13
2.32
1.00
0.95
1.00
2.93
1.97
1.96
3.02
f1 (ppm)
173.7
144.9
143.4
136.5
131.7
131.7
129.7
126.8
124.5
124.1
107.8
77.3
77.0
76.7
63.6
39.7
35.5
27.1
21.5


Cl
Cl
NHTs
O
N
Me
2i, 100 MHz, CDCl3
f1 (ppm)

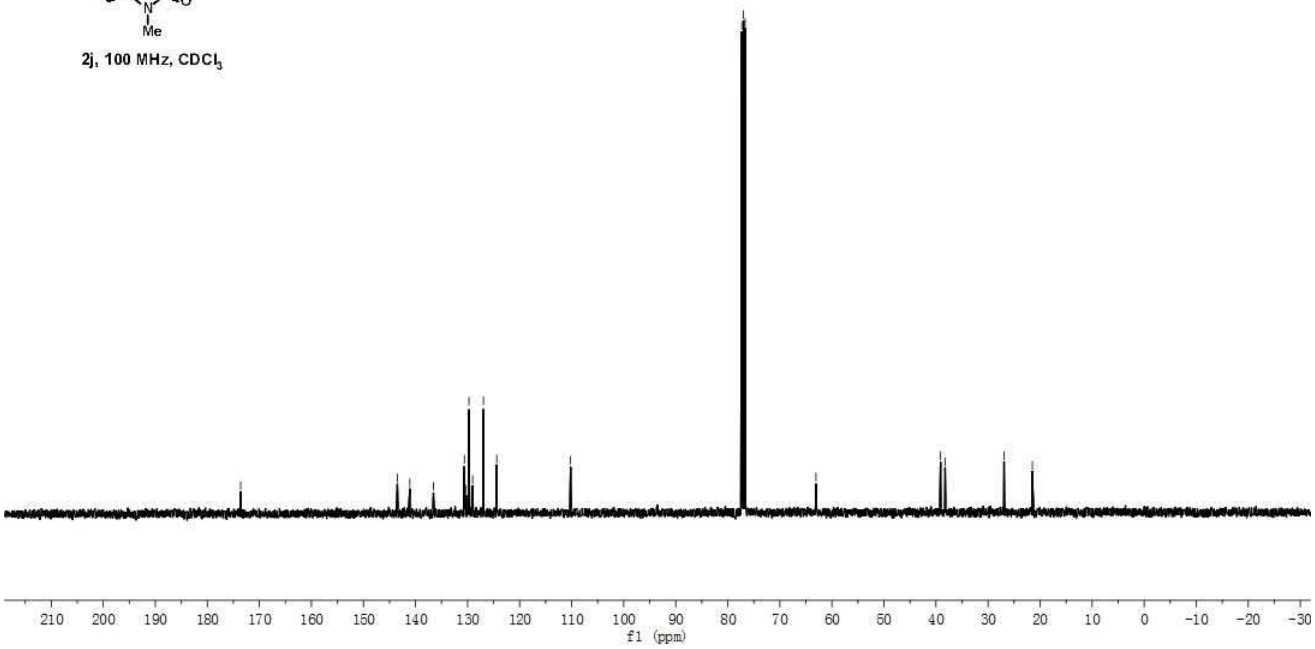


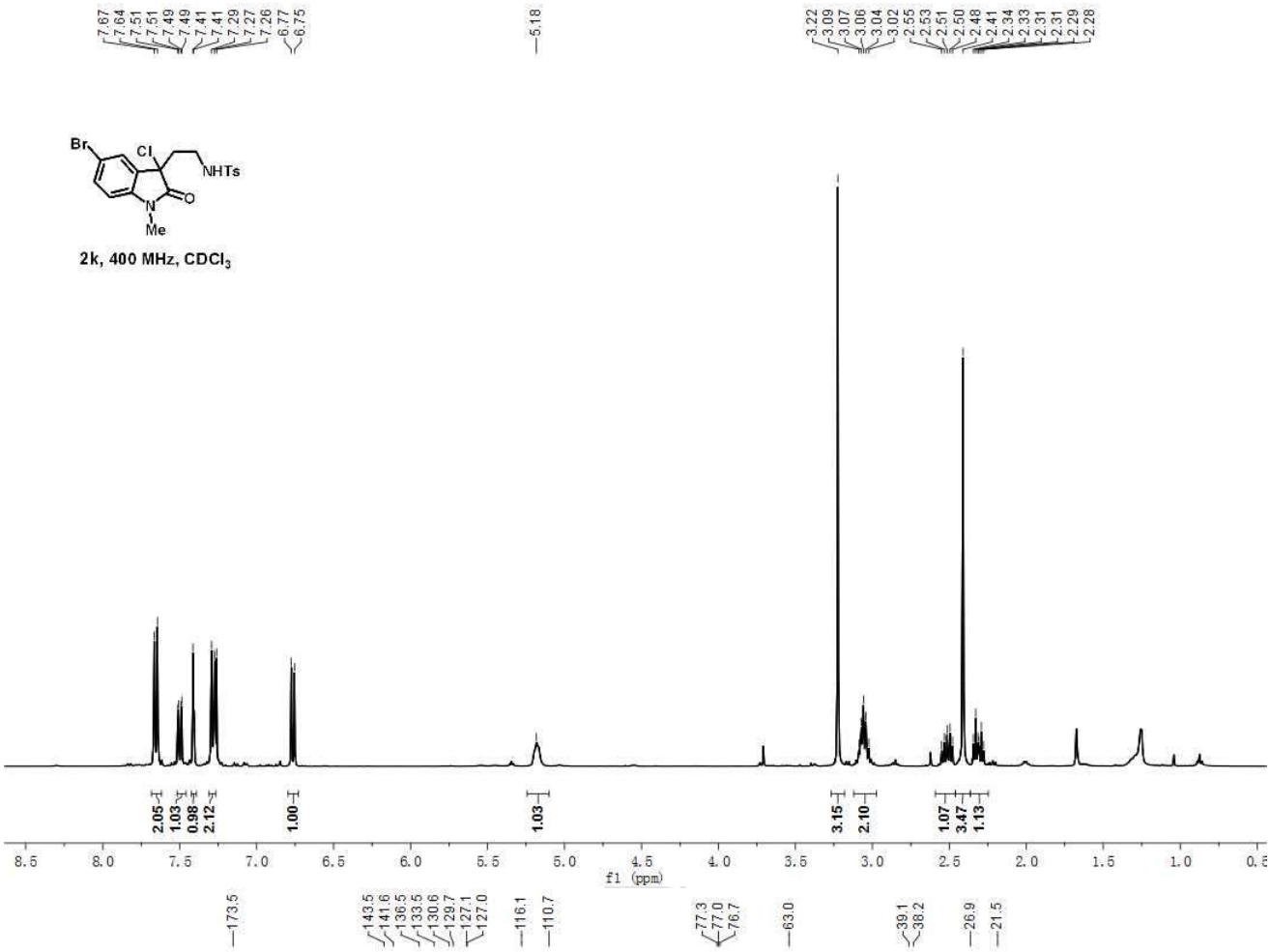
2j, 400 MHz, $CDCl_3$

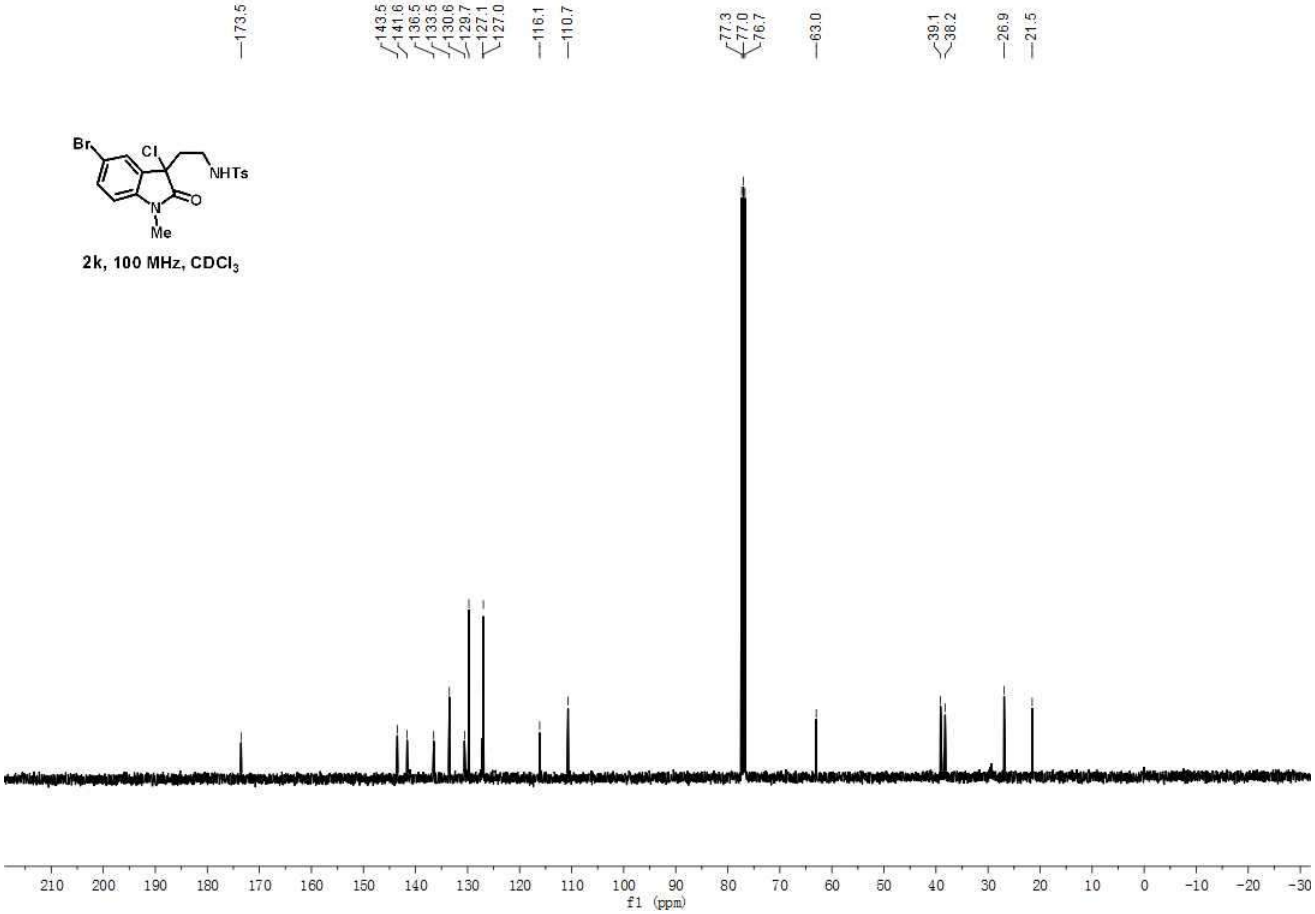


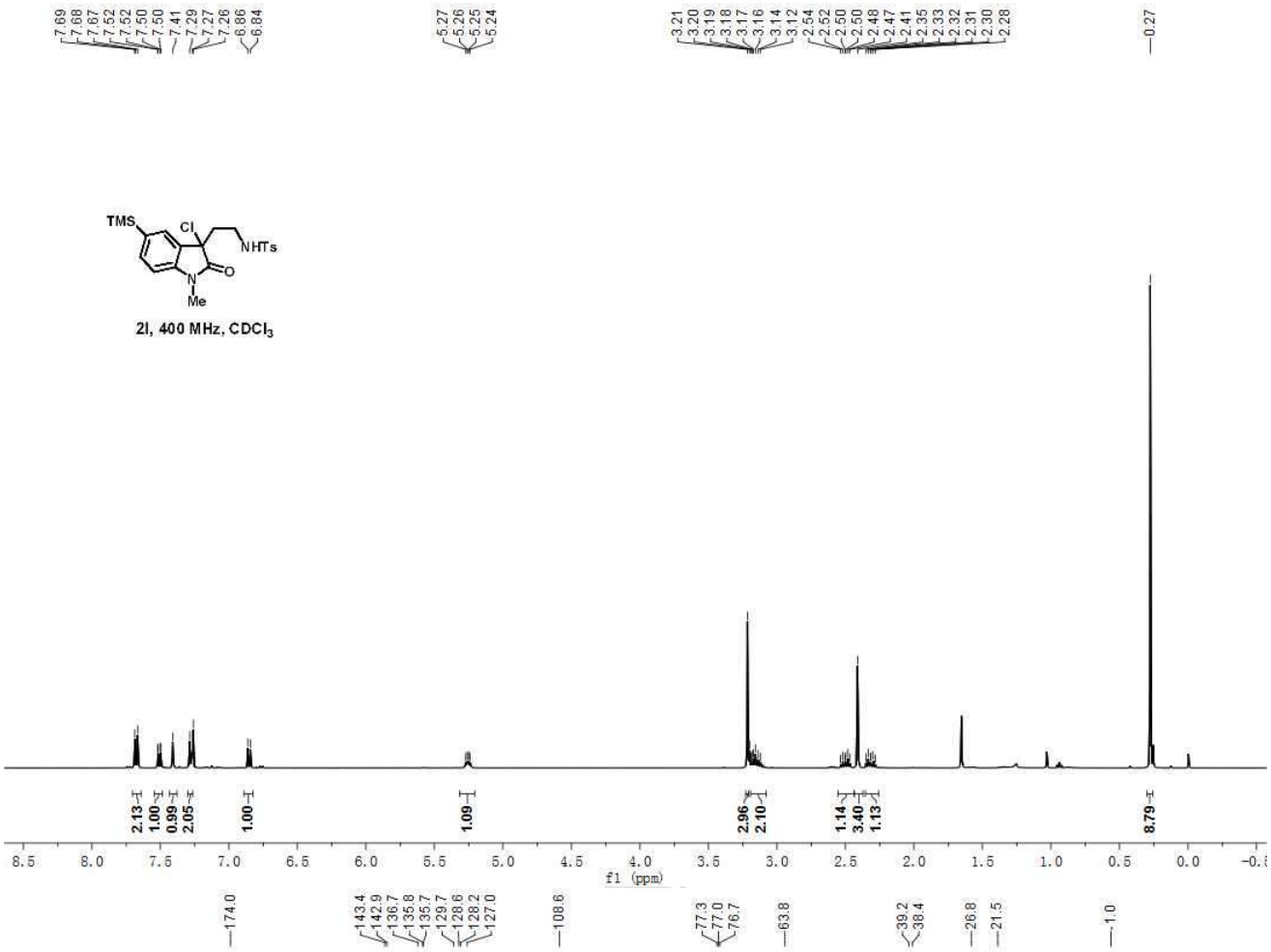


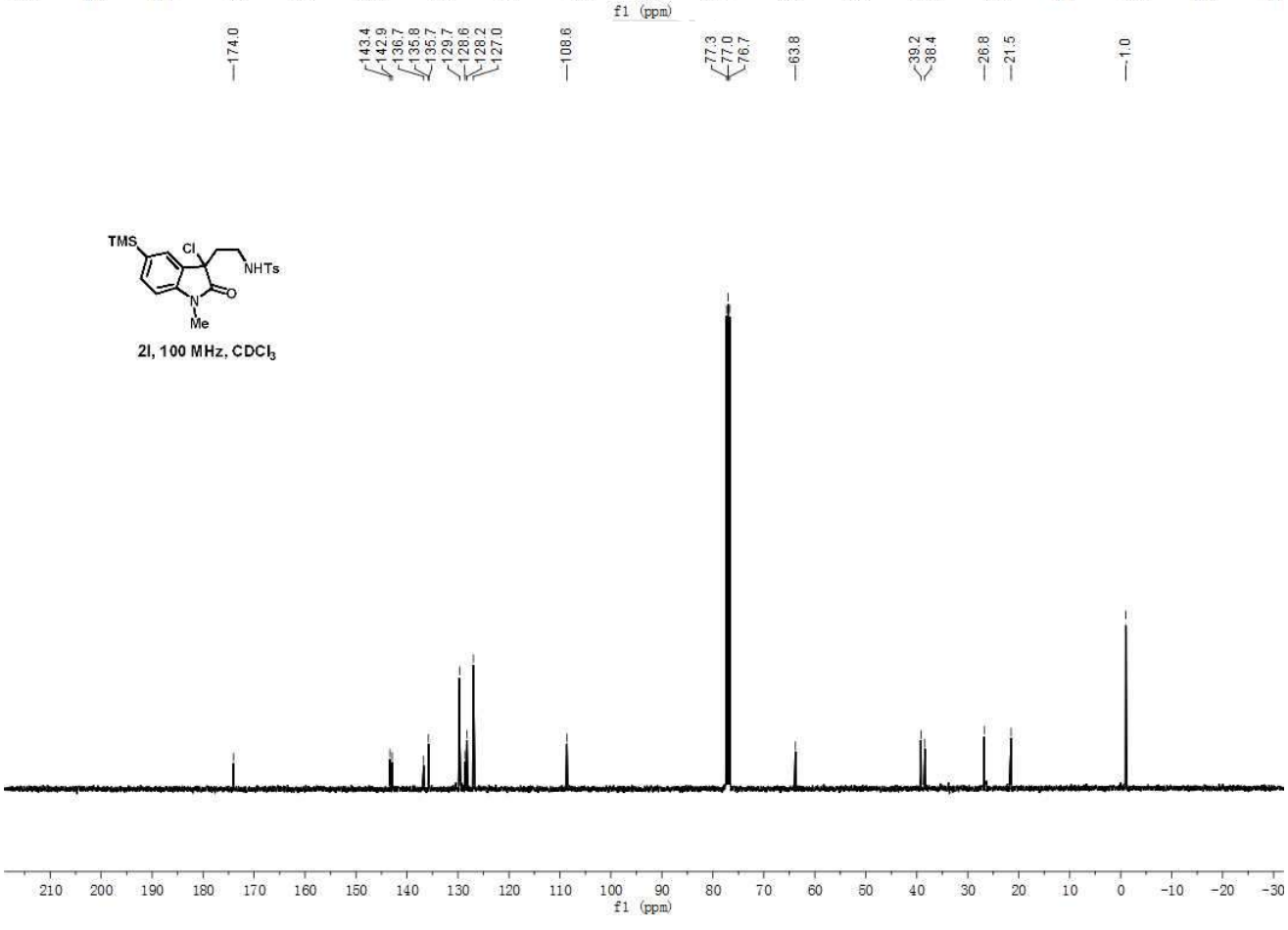
2j, 100 MHz, $CDCl_3$

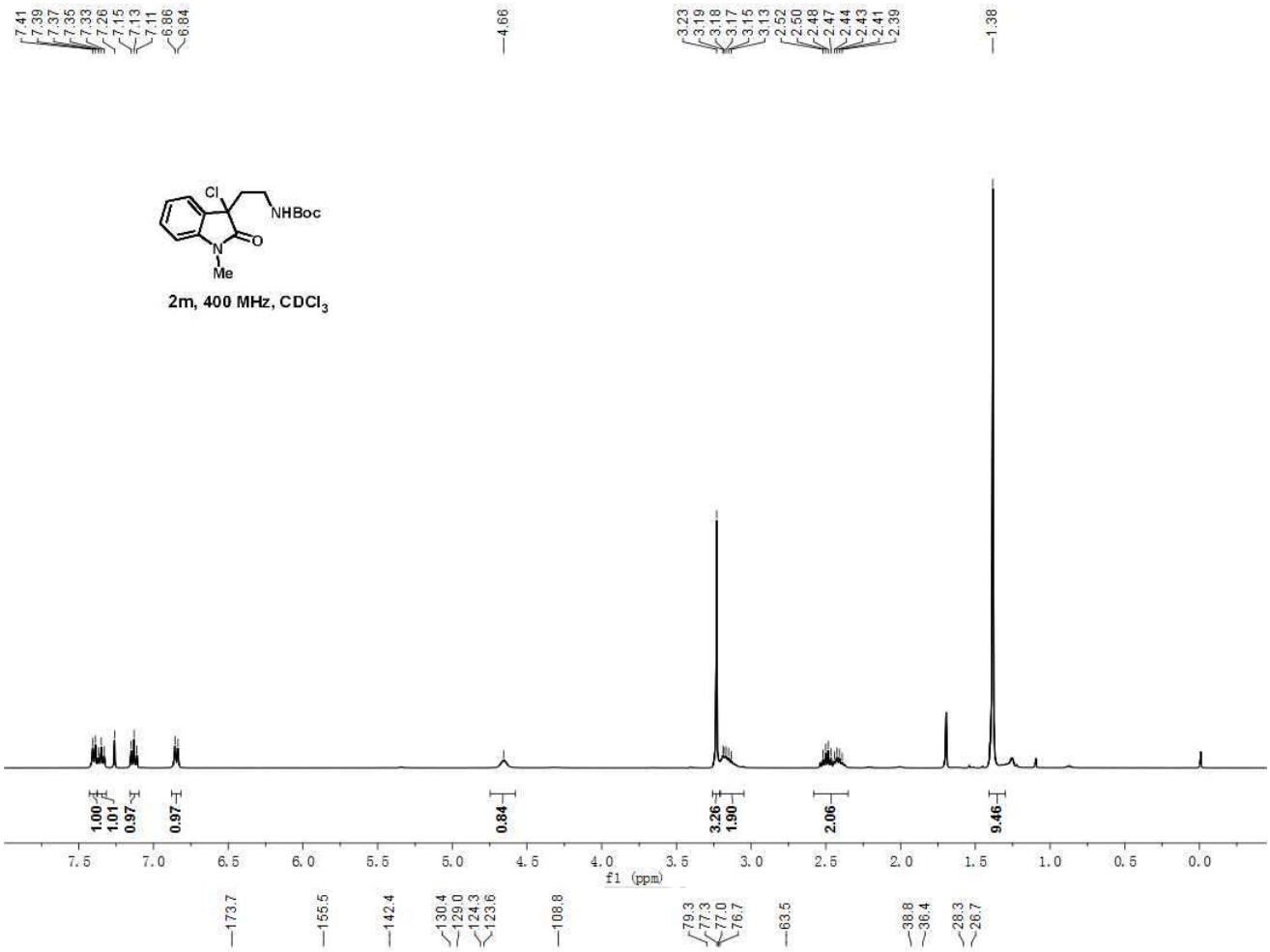



7.67
7.64
7.51
7.51
7.49
7.49
7.41
7.41
7.29
7.27
7.26
6.77
6.75
5.18
3.22
3.09
3.07
3.06
3.04
3.02
2.55
2.53
2.51
2.50
2.48
2.41
2.34
2.33
2.31
2.29
2.28
Br
Cl
NHTs
N
O
Me
2k, 400 MHz, CDCl3
2.05
1.03
0.98
2.12
1.00
1.03
3.15
2.10
1.07
3.47
1.13
f1 (ppm)

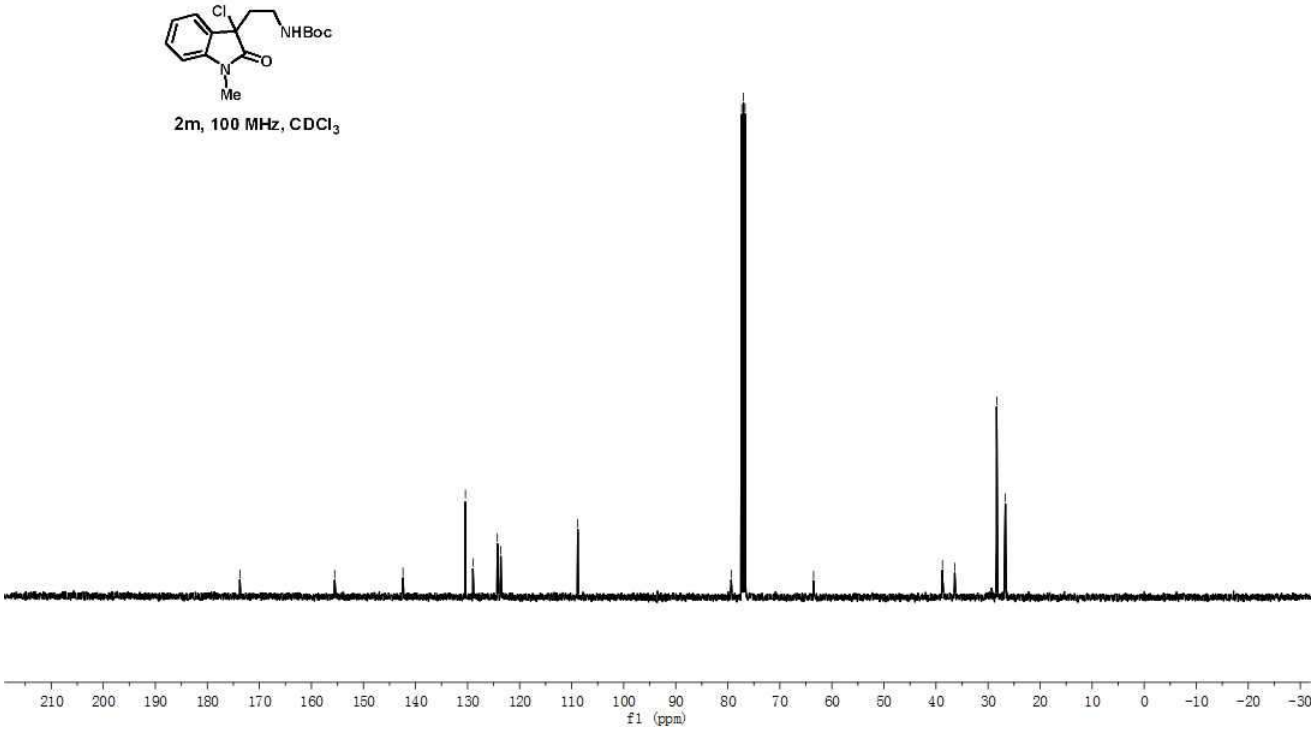

173.5
143.5
141.6
136.5
133.5
130.6
129.7
127.1
127.0
116.1
110.7
77.3
77.0
76.7
63.0
39.1
38.2
26.9
21.5
Br
Cl
NHTs
N
O
Me
2k, 100 MHz, CDCl3
f1 (ppm)


7.69
7.68
7.67
7.52
7.52
7.50
7.50
7.41
7.29
7.27
7.26
6.86
6.84
5.27
5.26
5.25
5.24
3.21
3.20
3.19
3.18
3.17
3.16
3.14
3.12
2.54
2.52
2.50
2.50
2.48
2.47
2.41
2.35
2.33
2.32
2.31
2.30
2.28
0.27
TMS
Cl
NHTs
O
N
Me
2l, 400 MHz, CDCl3
2.13
1.00
0.99
2.05
1.00
1.09
2.96
2.10
1.14
3.40
1.13
8.79
f1 (ppm)

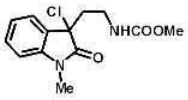

174.0
143.4
142.9
136.7
135.8
135.7
129.7
128.6
128.2
127.0
108.6
77.3
77.0
76.7
63.8
39.2
38.4
26.8
21.5
1.0
TMS
Cl
NHTs
O
N
Me
2l, 100 MHz, CDCl3
f1 (ppm)



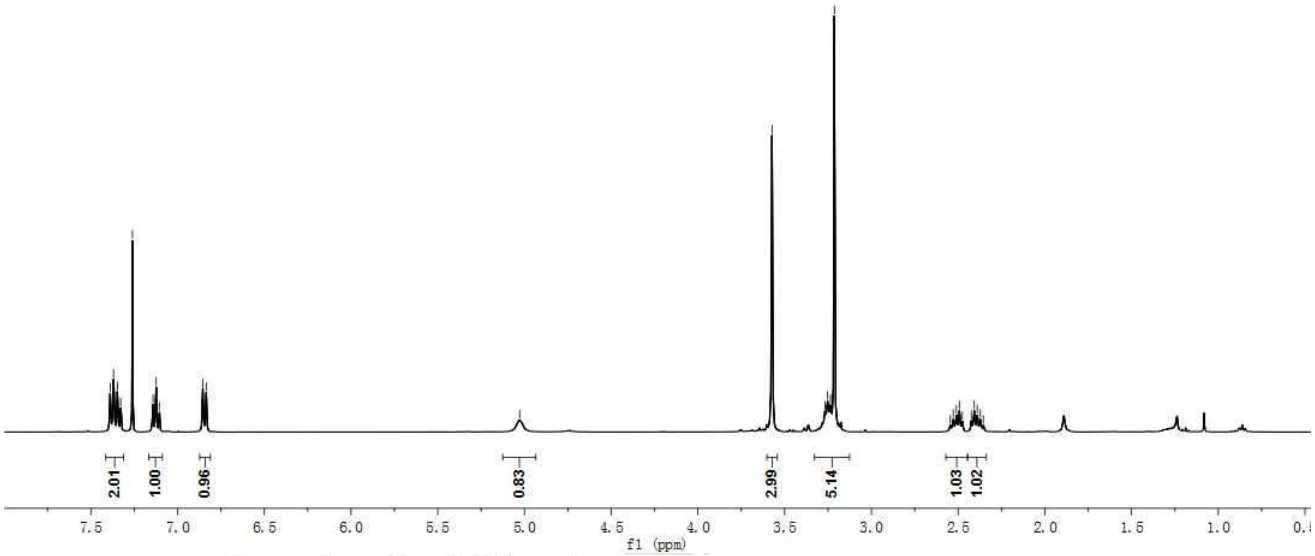
2m, 400 MHz, $CDCl_3$

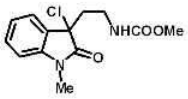


2m, 100 MHz, $CDCl_3$

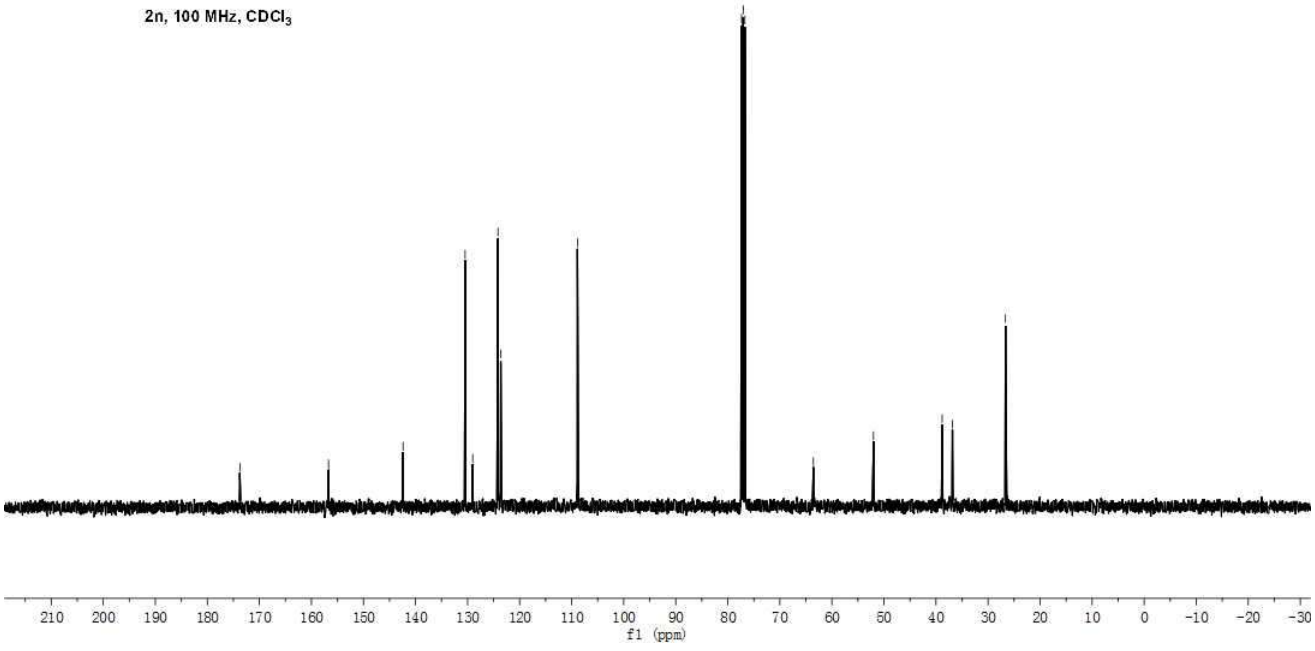


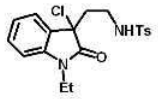
2n, 400 MHz, $CDCl_3$



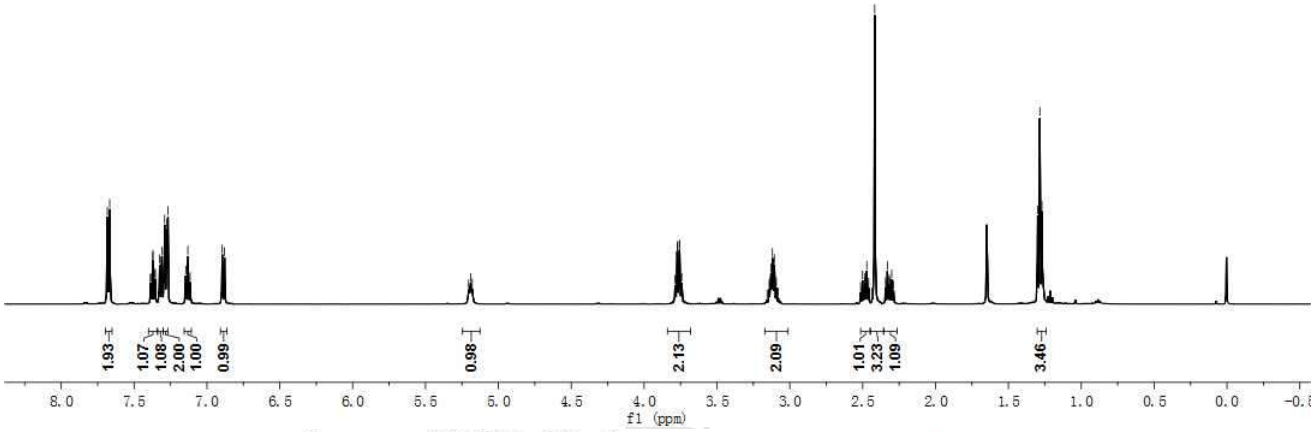


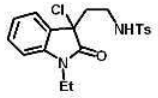
2n, 100 MHz, $CDCl_3$



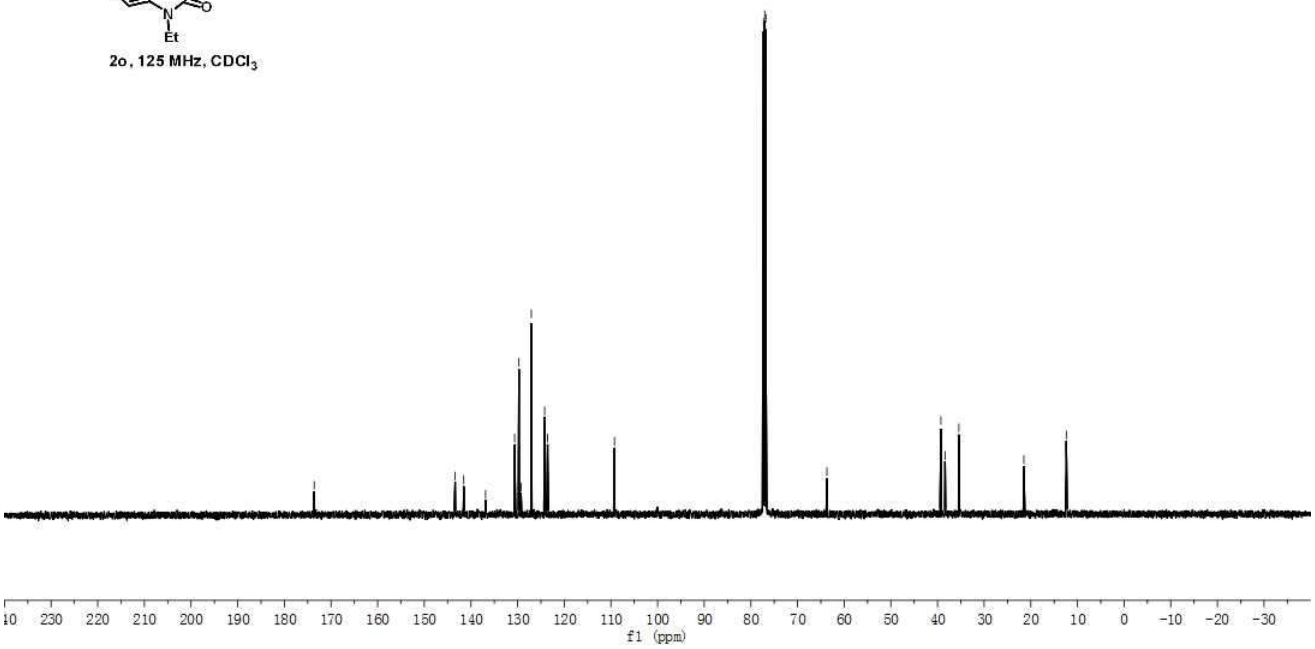


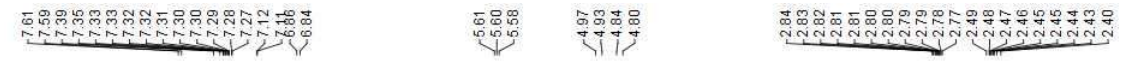
2o, 500 MHz, $CDCl_3$

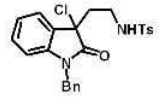




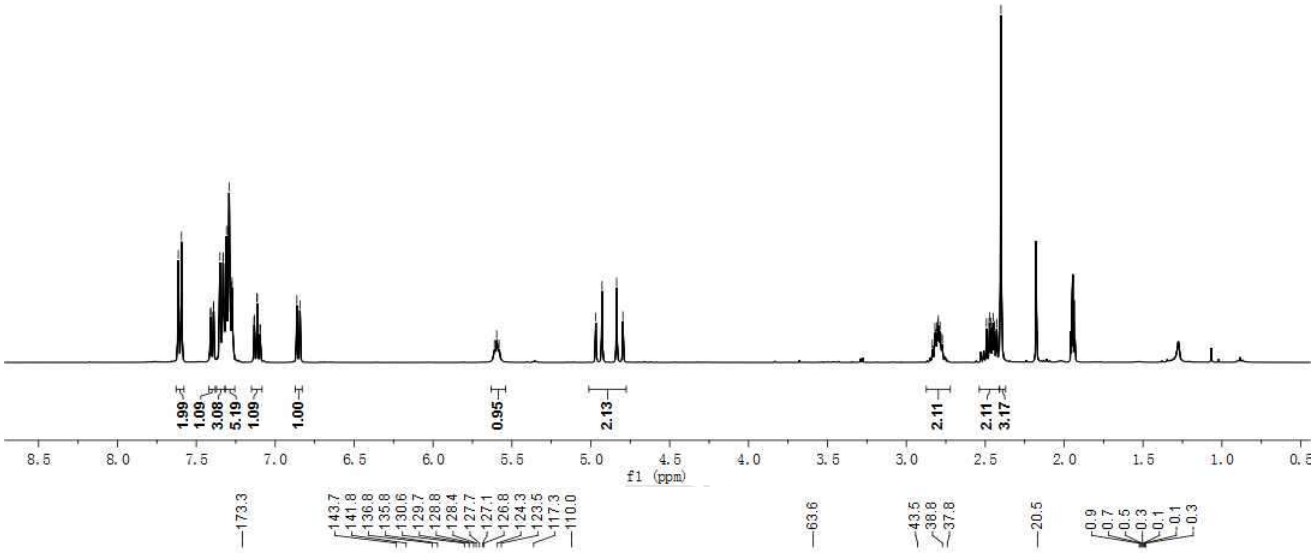
2o, 125 MHz, $CDCl_3$

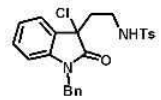




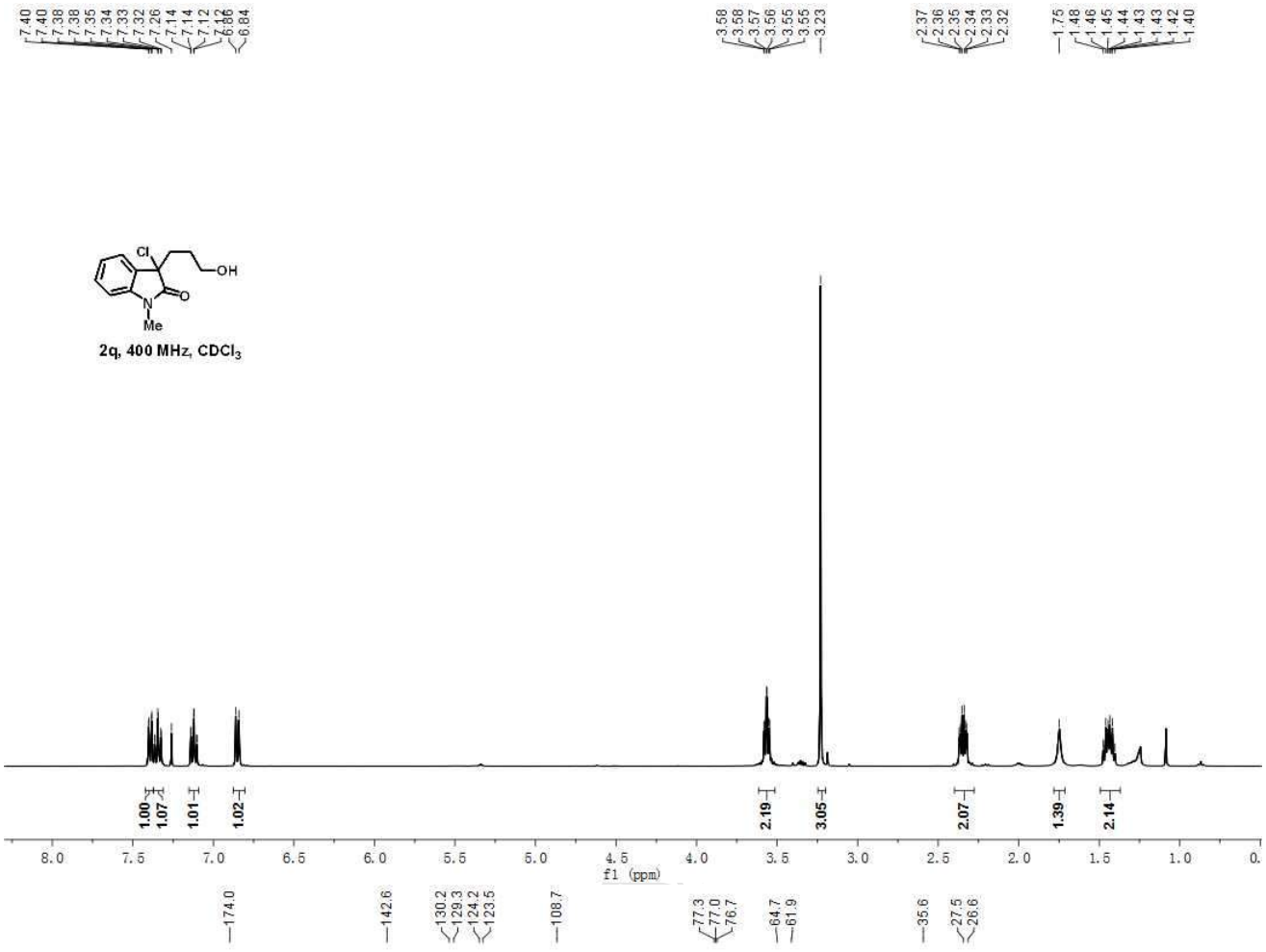


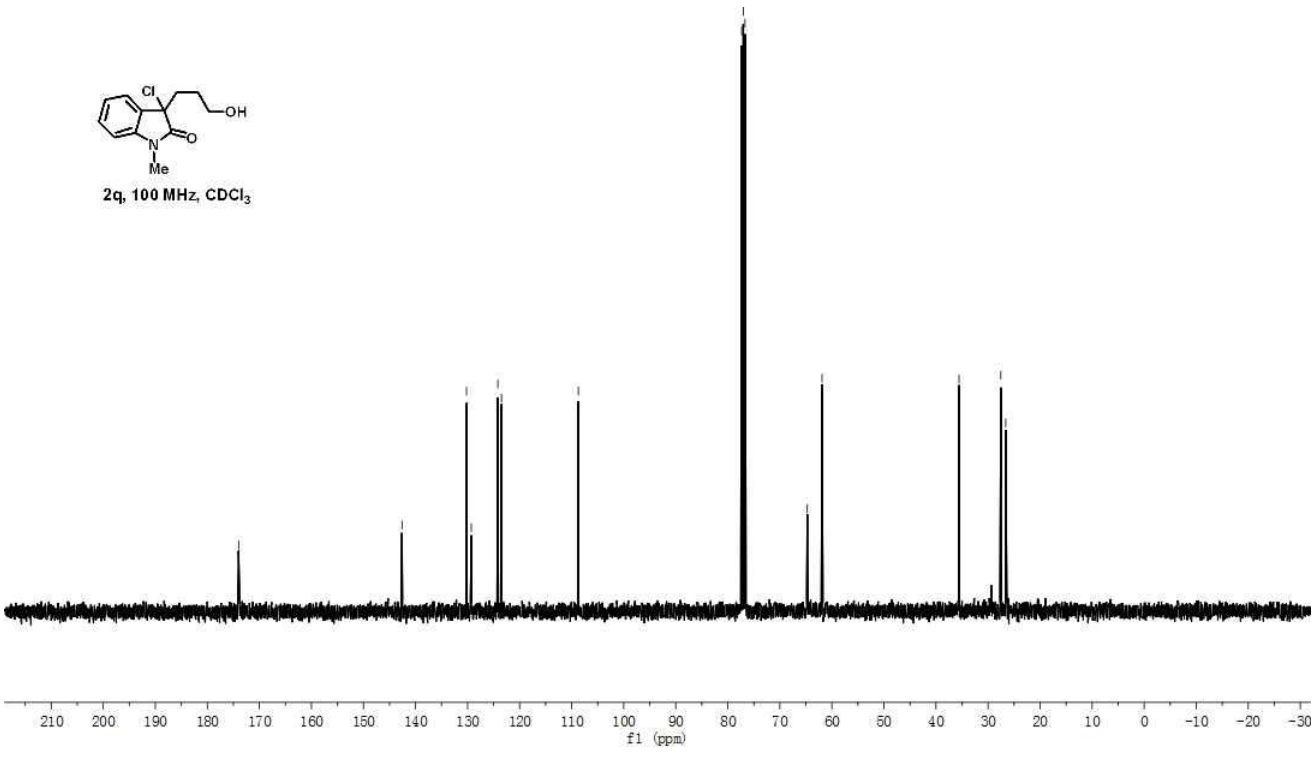
2p, 400 MHz, CD_3CN

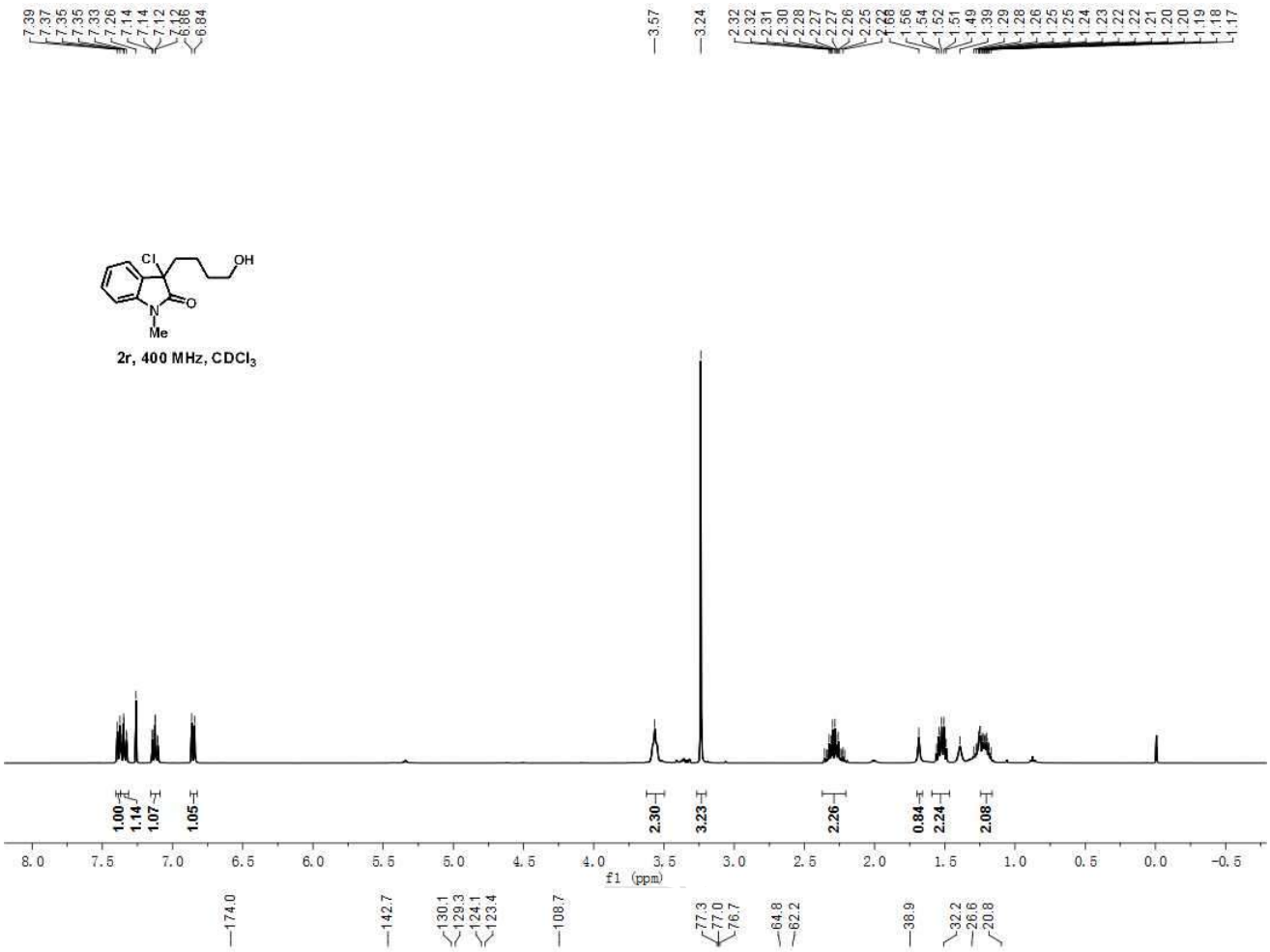


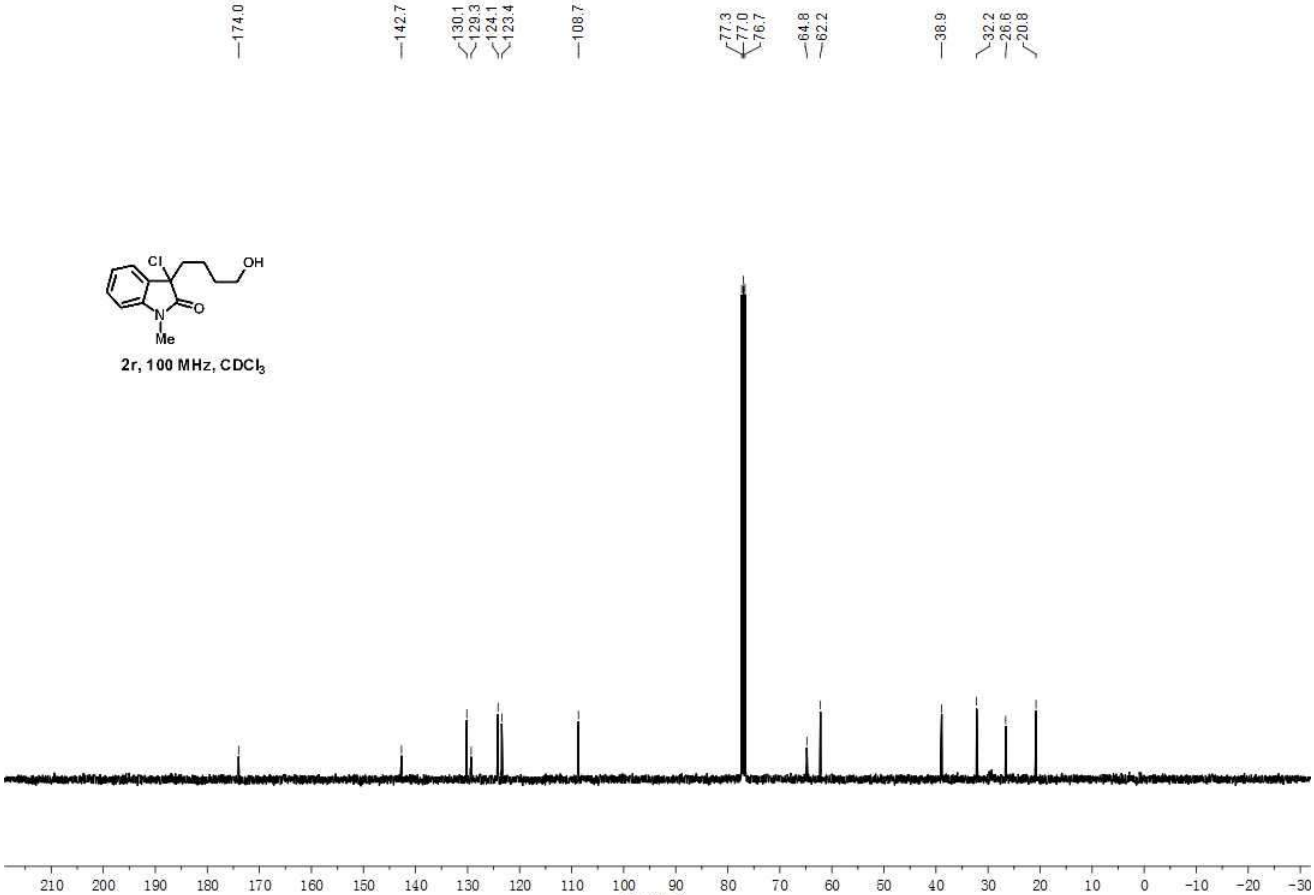


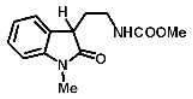
2p, 100 MHz, CD_3CN


7.40
7.40
7.38
7.38
7.35
7.34
7.33
7.32
7.26
7.14
7.12
6.86
6.84
3.58
3.58
3.57
3.56
3.55
3.55
3.23
2.37
2.36
2.35
2.34
2.33
2.32
1.75
1.48
1.46
1.45
1.44
1.43
1.42
1.40
Cl
OH
N
O
Me
2q, 400 MHz, CDCl3
1.00
1.07
1.01
1.02
2.19
3.05
2.07
1.39
2.14
f1 (ppm)

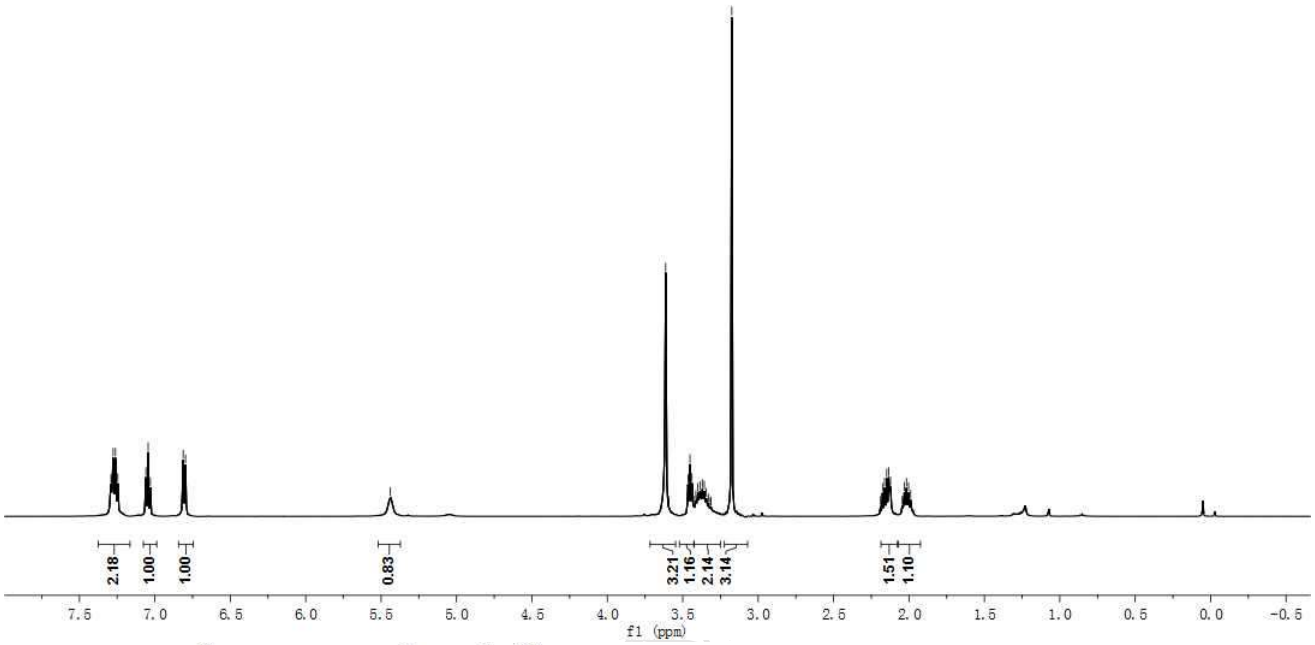

174.0
142.6
130.2
129.3
124.2
123.5
108.7
77.3
77.0
76.7
64.7
61.9
35.6
27.5
26.6
Cl
OH
N
O
Me
2q, 100 MHz, CDCl3
f1 (ppm)

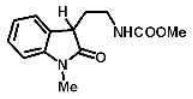

7.39
7.37
7.35
7.35
7.33
7.26
7.14
7.12
6.86
6.84
3.57
3.24
2.32
2.32
2.31
2.30
2.28
2.27
2.27
2.26
2.25
1.68
1.56
1.54
1.52
1.51
1.49
1.39
1.29
1.28
1.26
1.25
1.25
1.24
1.23
1.22
1.22
1.21
1.20
1.20
1.19
1.18
1.17
Cl
OH
O
N
Me
2r, 400 MHz, CDCl3
1.00
1.14
1.07
1.05
2.30
3.23
2.26
0.84
2.24
2.08
f1 (ppm)


174.0
142.7
130.1
129.3
124.1
123.4
108.7
77.3
77.0
76.7
64.8
62.2
38.9
32.2
26.6
20.8
Cl
OH
O
N
Me
2r, 100 MHz, CDCl3
f1 (ppm)

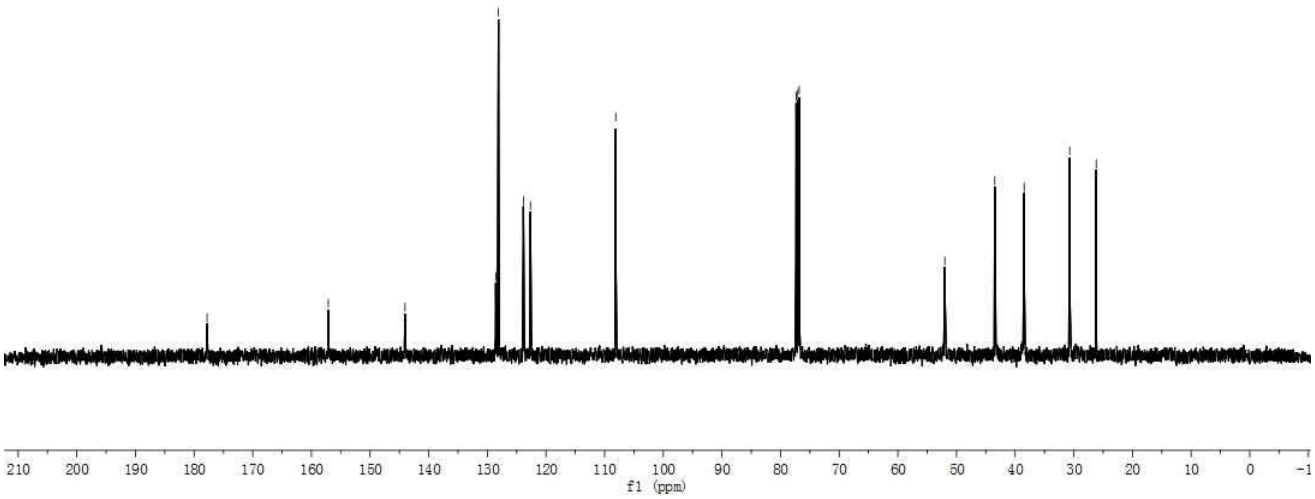


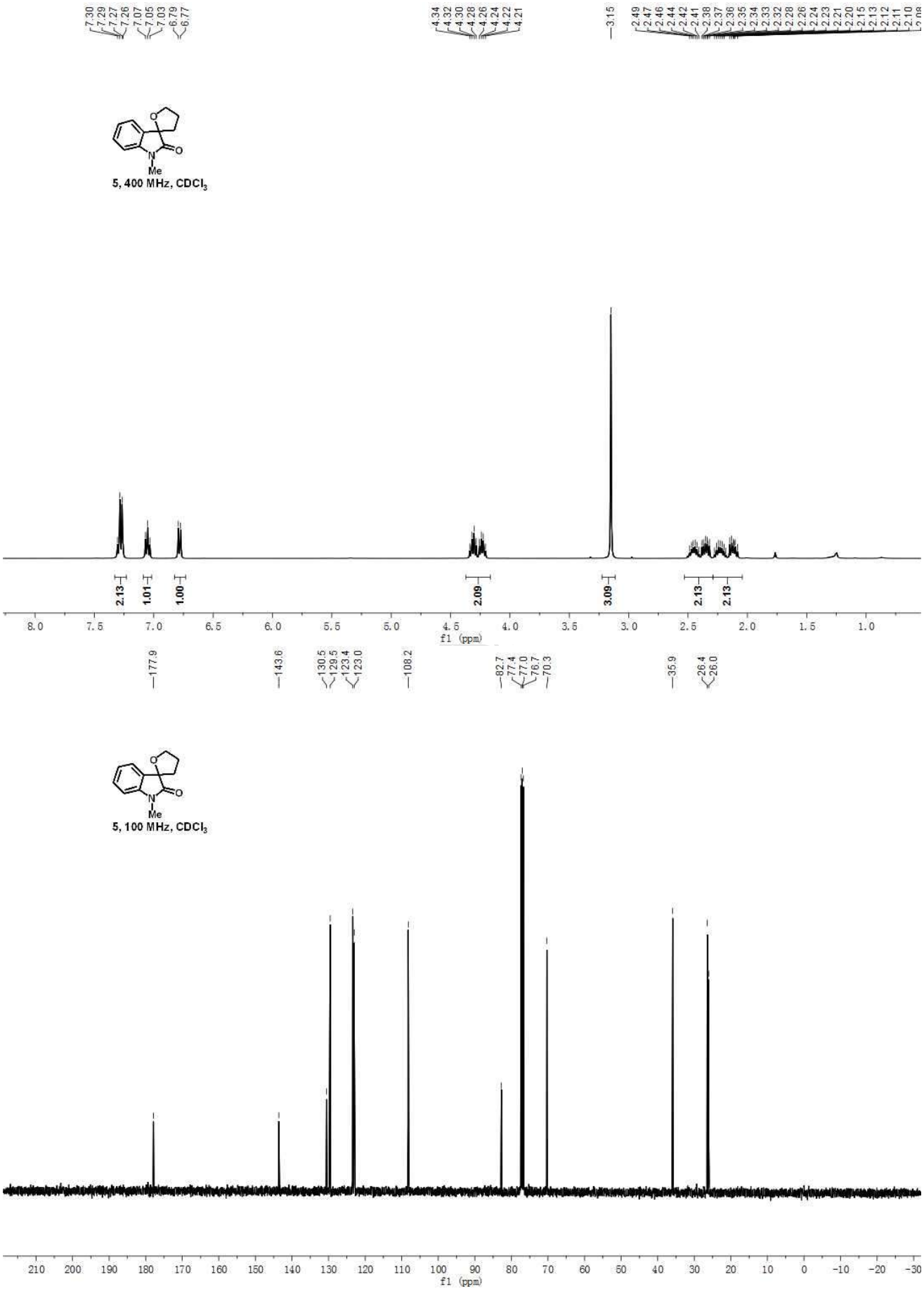
4, 500 MHz, $CDCl_3$

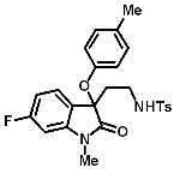




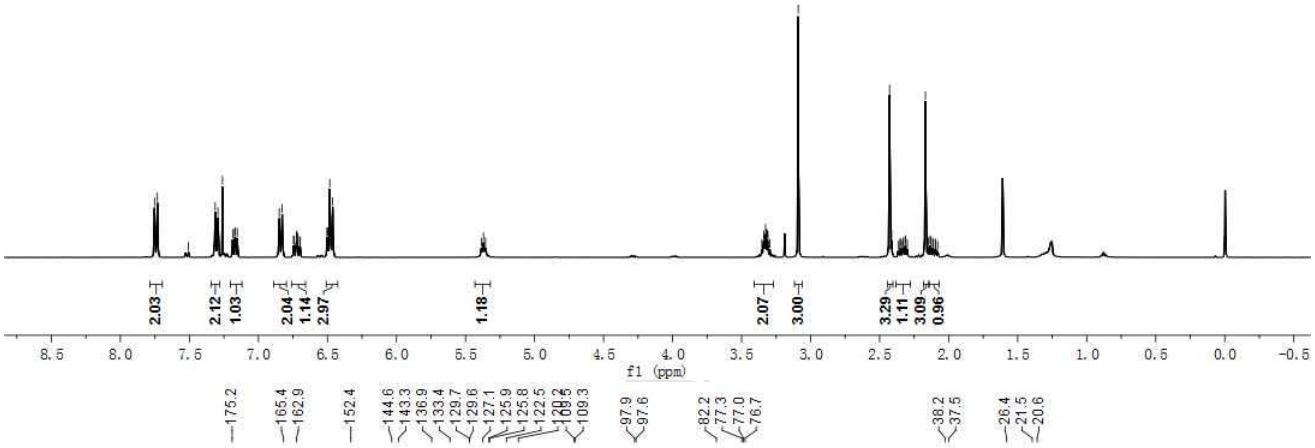
4, 126 MHz, $CDCl_3$



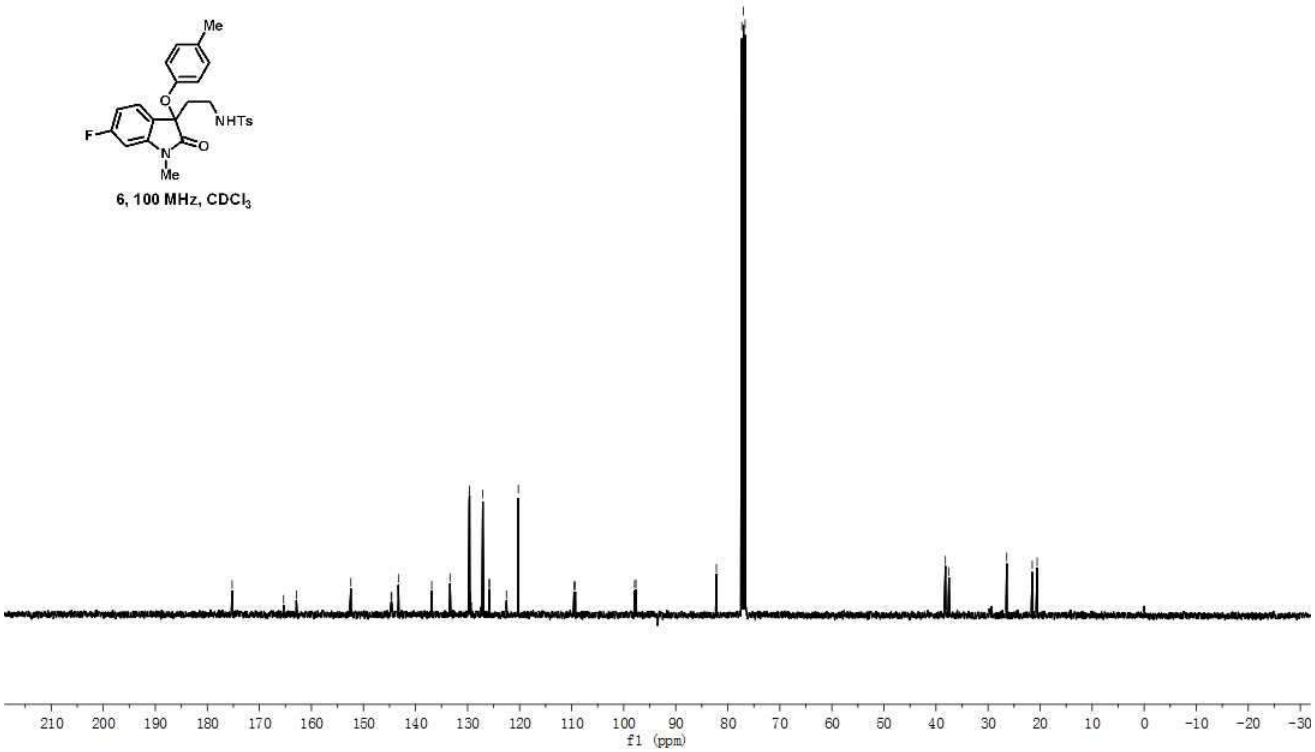

7.30
7.29
7.27
7.26
7.07
7.05
7.03
6.79
6.77
4.34
4.32
4.30
4.28
4.26
4.24
4.22
4.21
3.15
2.49
2.47
2.46
2.44
2.42
2.41
2.38
2.37
2.36
2.35
2.34
2.33
2.32
2.28
2.26
2.24
2.23
2.21
2.20
2.15
2.13
2.12
2.11
2.10
Me
5, 400 MHz, CDCl3
2.13
1.01
1.00
2.09
3.09
2.13
2.13
f1 (ppm)
177.9
143.6
130.5
129.5
123.4
123.0
108.2
82.7
77.4
77.0
76.7
70.3
35.9
26.4
26.0
Me
5, 100 MHz, CDCl3
f1 (ppm)

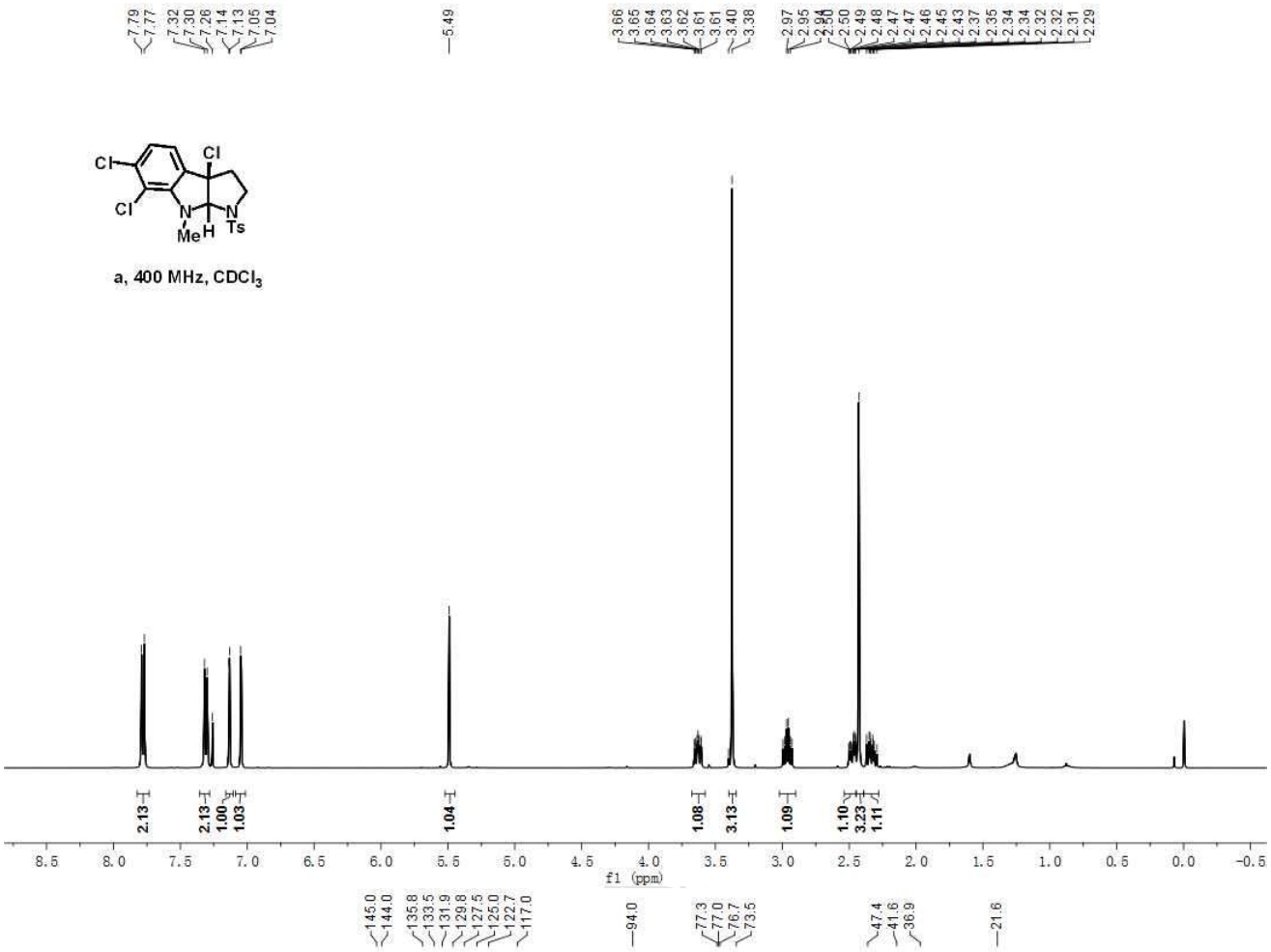


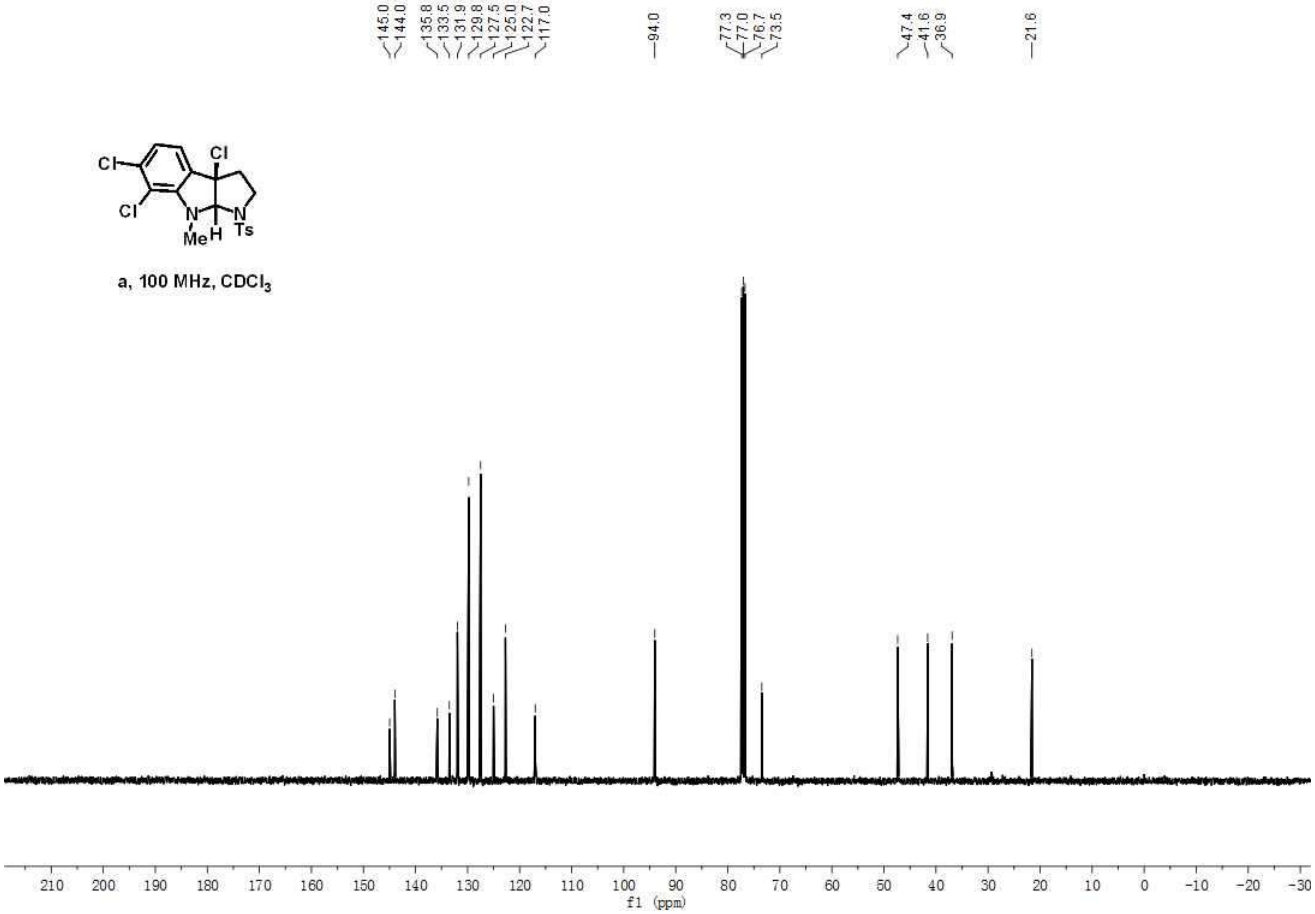
6, 400 MHz, $CDCl_3$

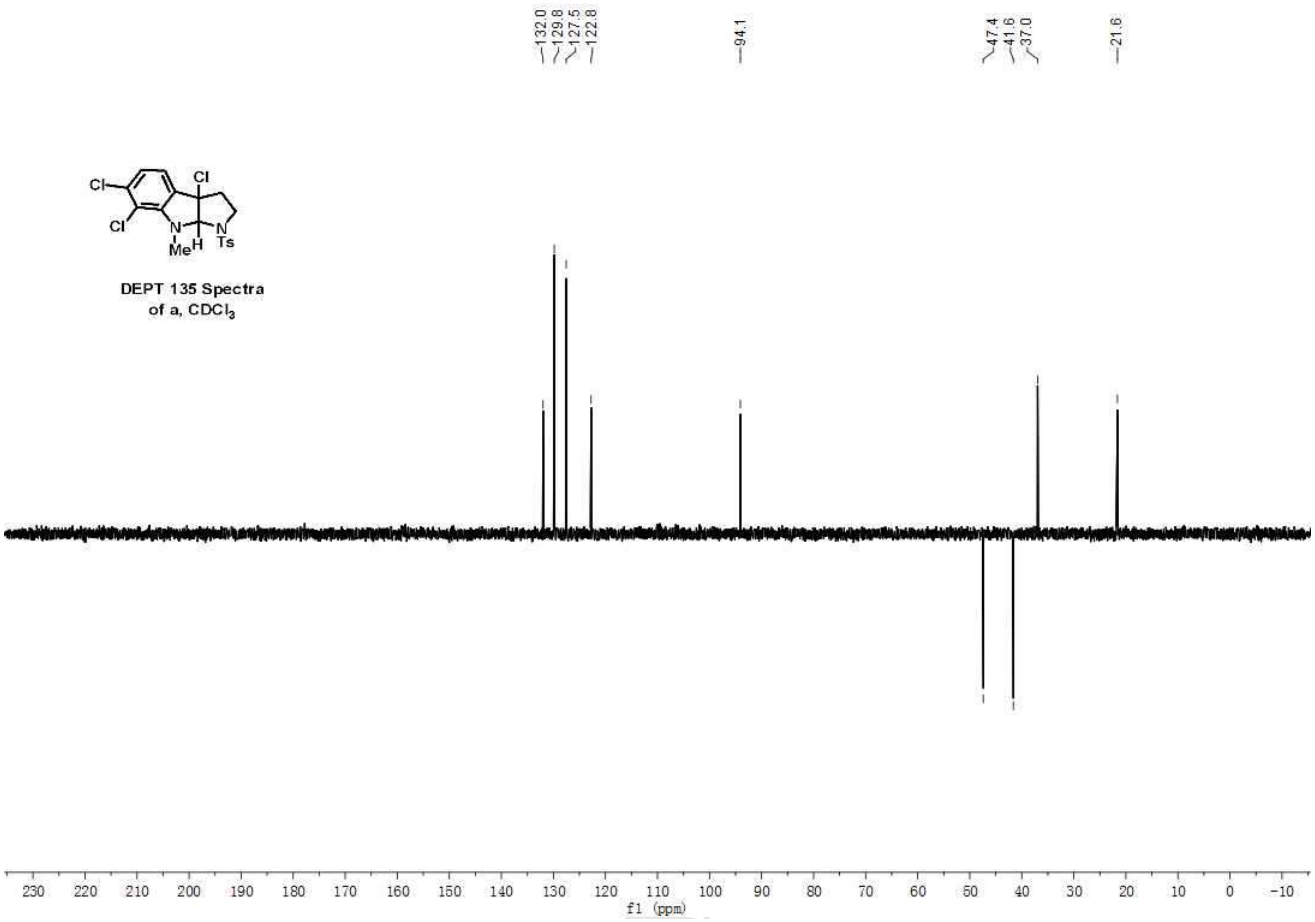


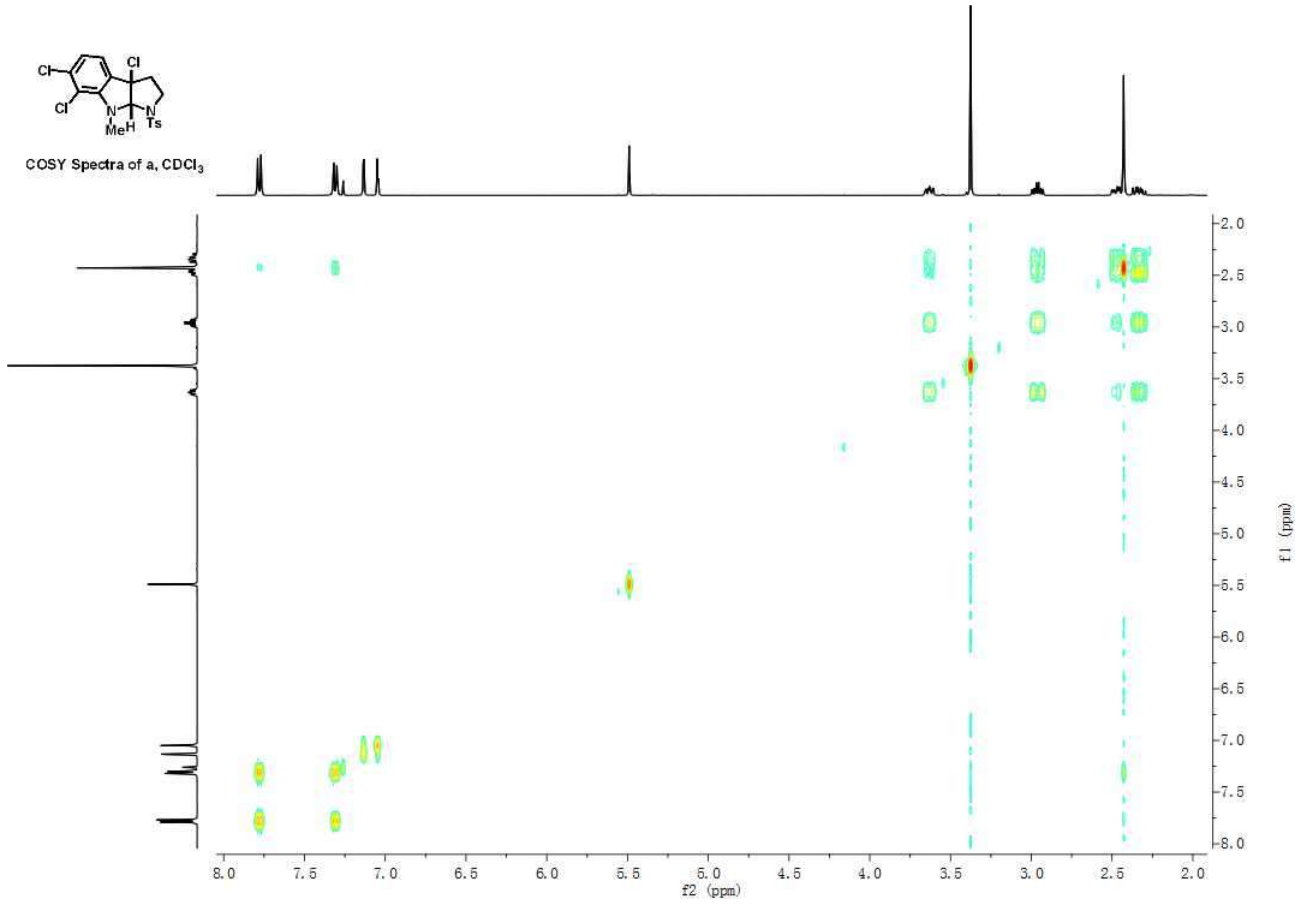
6, 100 MHz, $CDCl_3$

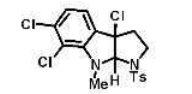



7.79
7.77
7.32
7.30
7.26
7.14
7.13
7.05
7.04
5.49
3.66
3.65
3.64
3.63
3.62
3.61
3.61
3.40
3.38
2.97
2.95
2.94
2.50
2.49
2.48
2.47
2.47
2.46
2.45
2.43
2.37
2.35
2.34
2.34
2.32
2.32
2.31
2.29
Cl
Cl
Cl
N
Me
H
N
Ts
a, 400 MHz, CDCl3
2.13
2.13
1.00
1.03
1.04
1.08
3.13
1.09
1.10
3.23
1.11
f1 (ppm)

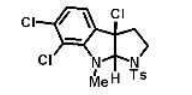

145.0
144.0
135.8
133.5
131.9
129.8
127.5
125.0
122.7
117.0
94.0
77.3
77.0
76.7
73.5
47.4
41.6
36.9
21.6
Cl
Cl
Cl
N
Me
H
N
Ts
a, 100 MHz, CDCl3
f1 (ppm)


132.0
129.8
127.5
122.8
94.1
47.4
41.6
37.0
21.6
Cl
Cl
Cl
N
Me
H
N
Ts
DEPT 135 Spectra
of a, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

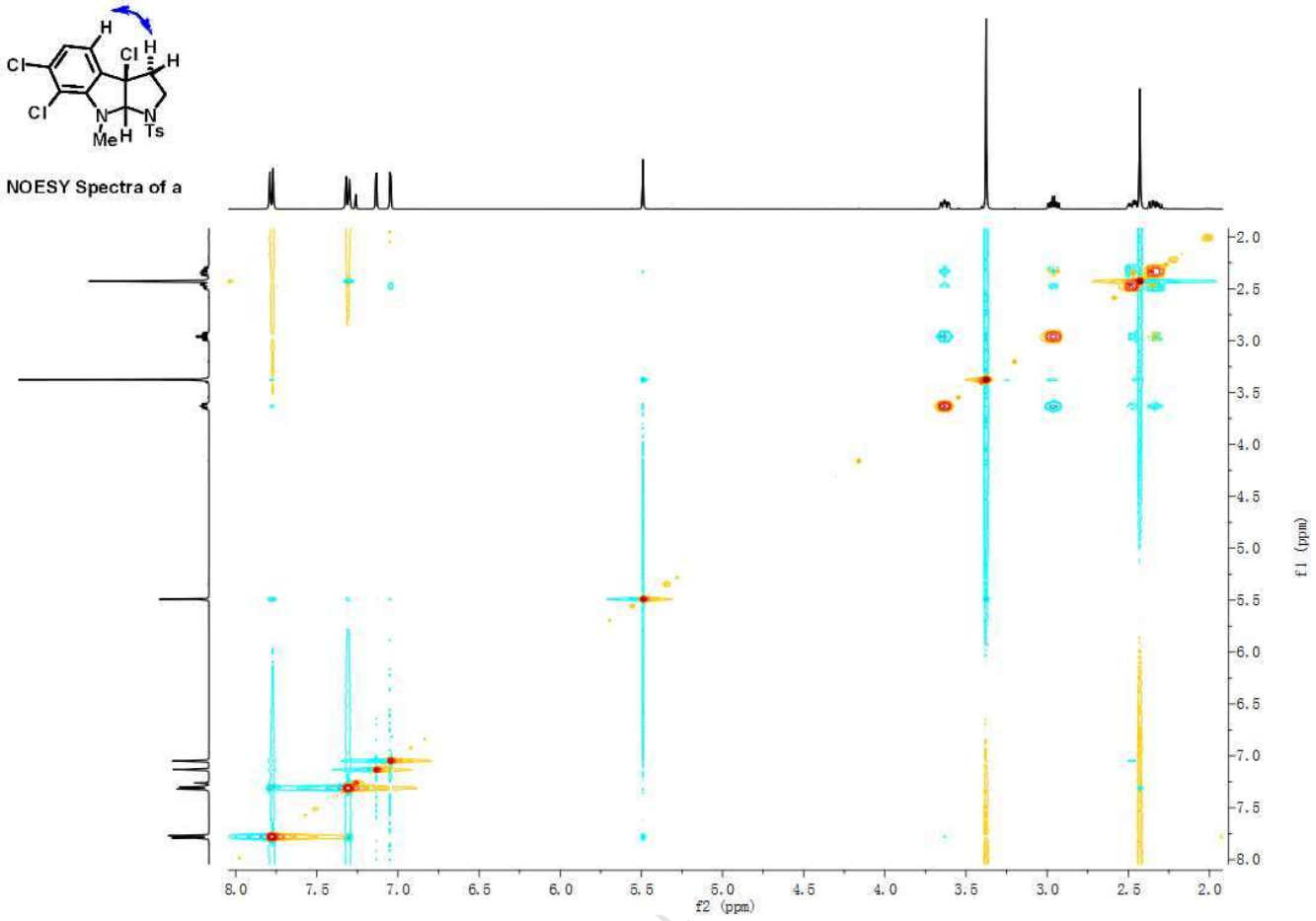

Cl
Cl
Cl
N
Me
H
N
Ts
COSY Spectra of a, CDCl3
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
f2 (ppm)
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0
f1 (ppm)



HSQC Spectra of a, $CDCl_3$

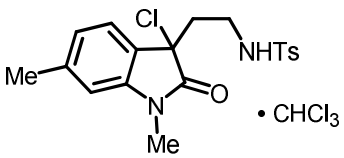


HMBC Spectra of a, $CDCl_3$



Crystal structures of product 2c·$CHCl_3$ and byproduct 3n

Crystal Structure of chlorooxindole 2c·$CHCl_3$



2c • $CHCl_3$

Table 1. Crystal data and structure refinement for c4.

Identification code	shelx
Empirical formula	C20 H22 Cl4 N2 O3 S
Formula weight	512.25
Temperature	293(2) K

Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.4986(3) Å	α= 94.153(7)°.
	b = 11.7221(3) Å	β= 110.479(8)°.
	c = 11.7911(8) Å	γ = 103.567(7)°.
Volume	1178.24(12) $Å^3$	
Z	2	
Density (calculated)	1.444 Mg/m^3	
Absorption coefficient	5.602 mm^{-1}	
F(000)	528	
Crystal size	0.200 x 0.200 x 0.030 mm^3	
Theta range for data collection	6.993 to 68.232°.	
Index ranges	-9<=h<=10, -13<=k<=14, -14<=l<=13	
Reflections collected	14730	
Independent reflections	4179 [R(int) = 0.0454]	
Completeness to theta = 67.679°	97.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.493 and 0.244	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4179 / 1 / 277	
Goodness-of-fit on F^2	1.089	
Final R indices [I>2sigma(I)]	R1 = 0.0658, wR2 = 0.1734	
R indices (all data)	R1 = 0.0725, wR2 = 0.1833	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.728 and -0.851 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for c4. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	3732(2)	343(2)	1086(2)	147(1)
Cl(2)	5388(2)	244(1)	3622(1)	102(1)
Cl(3)	6542(2)	2142(2)	2514(1)	135(1)
Cl(4)	2910(1)	7383(1)	2873(1)	62(1)
S(1)	2036(1)	2578(1)	4318(1)	55(1)
O(1)	3240(4)	2081(3)	4227(3)	80(1)
O(2)	648(3)	2448(3)	3264(2)	75(1)
O(3)	4350(2)	5201(2)	2966(2)	56(1)
N(1)	1797(3)	4280(2)	1693(2)	46(1)
N(2)	2874(3)	3985(2)	4791(3)	52(1)
C(1)	69(6)	475(4)	8245(4)	85(1)
C(2)	559(4)	999(3)	7272(3)	56(1)
C(3)	-546(4)	995(3)	6135(3)	56(1)
C(4)	-119(4)	1482(3)	5232(3)	51(1)
C(5)	1459(3)	1980(3)	5468(3)	47(1)
C(7)	1983(4)	4810(3)	4914(3)	53(1)
C(8)	2560(4)	5980(3)	4521(3)	49(1)
C(9)	2165(3)	5901(2)	3143(3)	45(1)
C(10)	469(3)	5400(2)	2348(3)	42(1)
C(11)	-837(4)	5713(3)	2365(3)	50(1)
C(12)	-2299(4)	5040(3)	1531(3)	55(1)
C(13)	-2455(4)	4080(3)	696(3)	53(1)
C(14)	-4064(4)	3376(4)	-214(4)	71(1)
C(15)	-1138(4)	3764(3)	685(3)	50(1)
C(16)	310(3)	4432(2)	1519(3)	42(1)
C(18)	2073(5)	3324(3)	1024(3)	62(1)
C(19)	2950(3)	5099(3)	2626(3)	44(1)
C(20)	2581(4)	1990(3)	6593(3)	59(1)
C(21)	2128(4)	1505(3)	7486(3)	65(1)
C(22)	4880(5)	1150(4)	2546(4)	75(1)

Table 3. Bond lengths [Å] and angles [°] for c4.

Cl(1)-C(22)	1.736(5)
Cl(2)-C(22)	1.724(4)
Cl(3)-C(22)	1.742(5)
Cl(4)-C(9)	1.811(3)
S(1)-O(2)	1.428(3)
S(1)-O(1)	1.431(3)
S(1)-N(2)	1.615(3)
S(1)-C(5)	1.762(3)
O(3)-C(19)	1.220(4)
N(1)-C(19)	1.357(4)
N(1)-C(16)	1.411(4)
N(1)-C(18)	1.449(4)
N(2)-C(7)	1.456(4)
N(2)-H(6)	0.826(19)
C(1)-C(2)	1.501(5)
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600
C(2)-C(3)	1.382(5)
C(2)-C(21)	1.392(5)
C(3)-C(4)	1.381(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.392(4)
C(4)-H(4)	0.9300
C(5)-C(20)	1.379(5)
C(7)-C(8)	1.521(5)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(9)	1.525(4)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(10)	1.497(4)
C(9)-C(19)	1.542(4)
C(10)-C(11)	1.379(4)
C(10)-C(16)	1.386(4)
C(11)-C(12)	1.392(5)

C(11)-H(11)	0.9300
C(12)-C(13)	1.384(5)
C(12)-H(12)	0.9300
C(13)-C(15)	1.390(5)
C(13)-C(14)	1.517(4)
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-C(16)	1.381(4)
C(15)-H(15)	0.9300
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
C(20)-C(21)	1.380(5)
C(20)-H(20)	0.9300
C(21)-H(21)	0.9300
C(22)-H(22)	0.9800

O(2)-S(1)-O(1)	120.28(19)
O(2)-S(1)-N(2)	107.58(16)
O(1)-S(1)-N(2)	105.12(17)
O(2)-S(1)-C(5)	107.40(16)
O(1)-S(1)-C(5)	107.61(16)
N(2)-S(1)-C(5)	108.39(14)
C(19)-N(1)-C(16)	111.7(2)
C(19)-N(1)-C(18)	123.4(3)
C(16)-N(1)-C(18)	124.8(3)
C(7)-N(2)-S(1)	121.2(2)
C(7)-N(2)-H(6)	114(3)
S(1)-N(2)-H(6)	113(3)
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(3)-C(2)-C(21)	118.2(3)
C(3)-C(2)-C(1)	120.6(3)

C(21)-C(2)-C(1)	121.2(3)
C(4)-C(3)-C(2)	121.4(3)
C(4)-C(3)-H(3)	119.3
C(2)-C(3)-H(3)	119.3
C(3)-C(4)-C(5)	119.3(3)
C(3)-C(4)-H(4)	120.3
C(5)-C(4)-H(4)	120.3
C(20)-C(5)-C(4)	120.3(3)
C(20)-C(5)-S(1)	119.6(2)
C(4)-C(5)-S(1)	120.2(2)
N(2)-C(7)-C(8)	111.0(3)
N(2)-C(7)-H(7A)	109.4
C(8)-C(7)-H(7A)	109.4
N(2)-C(7)-H(7B)	109.4
C(8)-C(7)-H(7B)	109.4
H(7A)-C(7)-H(7B)	108.0
C(7)-C(8)-C(9)	114.5(2)
C(7)-C(8)-H(8A)	108.6
C(9)-C(8)-H(8A)	108.6
C(7)-C(8)-H(8B)	108.6
C(9)-C(8)-H(8B)	108.6
H(8A)-C(8)-H(8B)	107.6
C(10)-C(9)-C(8)	115.4(2)
C(10)-C(9)-C(19)	103.0(2)
C(8)-C(9)-C(19)	114.1(2)
C(10)-C(9)-Cl(4)	110.5(2)
C(8)-C(9)-Cl(4)	107.35(19)
C(19)-C(9)-Cl(4)	106.0(2)
C(11)-C(10)-C(16)	120.2(3)
C(11)-C(10)-C(9)	131.3(3)
C(16)-C(10)-C(9)	108.5(2)
C(10)-C(11)-C(12)	118.4(3)
C(10)-C(11)-H(11)	120.8
C(12)-C(11)-H(11)	120.8
C(13)-C(12)-C(11)	121.4(3)
C(13)-C(12)-H(12)	119.3
C(11)-C(12)-H(12)	119.3
C(12)-C(13)-C(15)	120.1(3)

C(12)-C(13)-C(14)	120.0(3)
C(15)-C(13)-C(14)	119.9(3)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(16)-C(15)-C(13)	118.3(3)
C(16)-C(15)-H(15)	120.9
C(13)-C(15)-H(15)	120.9
C(15)-C(16)-C(10)	121.7(3)
C(15)-C(16)-N(1)	128.7(3)
C(10)-C(16)-N(1)	109.6(2)
N(1)-C(18)-H(18A)	109.5
N(1)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
N(1)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
O(3)-C(19)-N(1)	126.3(3)
O(3)-C(19)-C(9)	126.5(3)
N(1)-C(19)-C(9)	107.2(2)
C(5)-C(20)-C(21)	119.5(3)
C(5)-C(20)-H(20)	120.3
C(21)-C(20)-H(20)	120.3
C(20)-C(21)-C(2)	121.3(3)
C(20)-C(21)-H(21)	119.3
C(2)-C(21)-H(21)	119.3
Cl(2)-C(22)-Cl(1)	112.4(3)
Cl(2)-C(22)-Cl(3)	110.7(3)
Cl(1)-C(22)-Cl(3)	109.9(2)
Cl(2)-C(22)-H(22)	107.9
Cl(1)-C(22)-H(22)	107.9
Cl(3)-C(22)-H(22)	107.9

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for c4. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

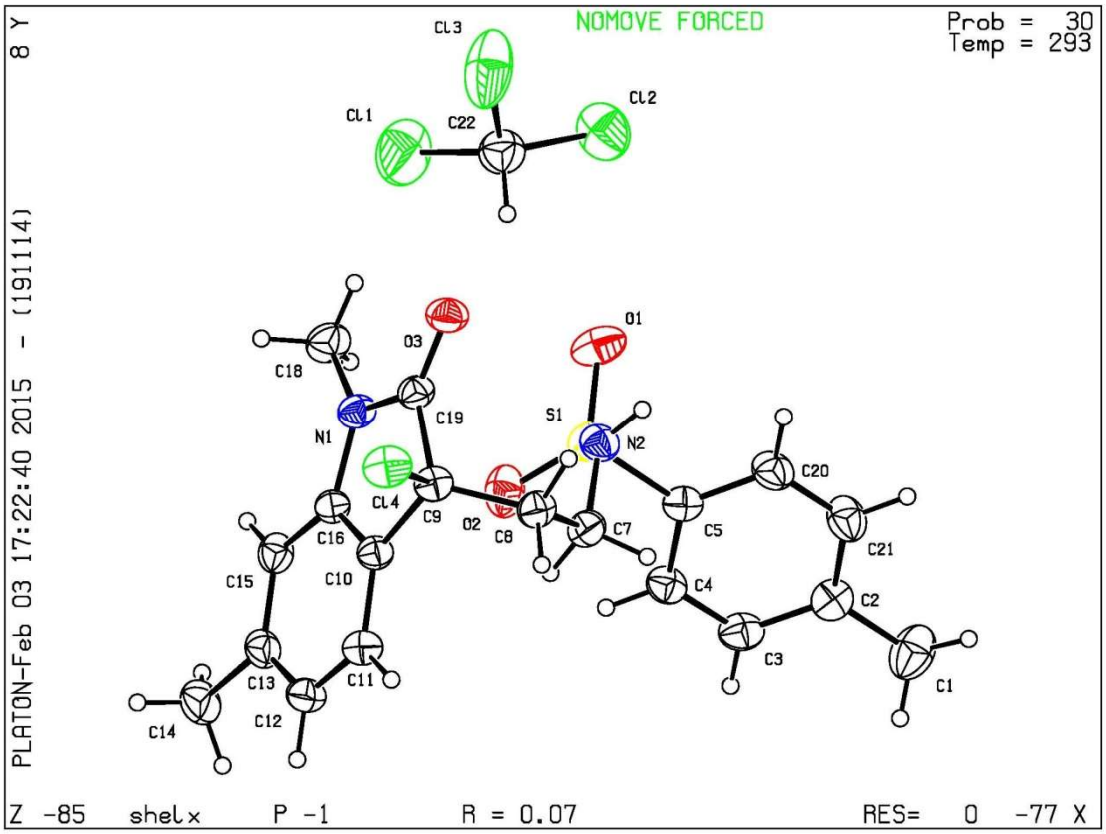
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	92(1)	204(2)	89(1)	-10(1)	16(1)	-24(1)
Cl(2)	101(1)	87(1)	118(1)	45(1)	39(1)	22(1)
Cl(3)	141(1)	127(1)	81(1)	28(1)	26(1)	-44(1)
Cl(4)	62(1)	42(1)	84(1)	10(1)	35(1)	5(1)
S(1)	57(1)	54(1)	56(1)	4(1)	26(1)	10(1)
O(1)	90(2)	76(2)	102(2)	10(2)	63(2)	31(2)
O(2)	75(2)	78(2)	52(1)	6(1)	14(1)	1(1)
O(3)	40(1)	66(1)	62(1)	6(1)	21(1)	12(1)
N(1)	44(1)	45(1)	47(1)	0(1)	20(1)	12(1)
N(2)	42(1)	53(2)	57(2)	11(1)	17(1)	8(1)
C(1)	93(3)	81(3)	71(2)	9(2)	38(2)	-5(2)
C(2)	58(2)	44(2)	60(2)	2(1)	23(2)	5(1)
C(3)	45(2)	50(2)	68(2)	-2(1)	23(2)	1(1)
C(4)	43(2)	47(2)	54(2)	-2(1)	12(1)	8(1)
C(5)	44(2)	40(1)	55(2)	1(1)	20(1)	9(1)
C(7)	50(2)	60(2)	50(2)	8(1)	23(1)	14(1)
C(8)	46(2)	49(2)	47(2)	-4(1)	17(1)	6(1)
C(9)	43(2)	37(1)	52(2)	3(1)	20(1)	5(1)
C(10)	39(1)	41(1)	46(2)	6(1)	17(1)	8(1)
C(11)	48(2)	49(2)	58(2)	9(1)	24(1)	15(1)
C(12)	43(2)	68(2)	60(2)	18(2)	23(1)	20(2)
C(13)	39(2)	64(2)	49(2)	17(1)	13(1)	7(1)
C(14)	44(2)	91(3)	59(2)	13(2)	8(2)	4(2)
C(15)	49(2)	50(2)	43(2)	5(1)	14(1)	4(1)
C(16)	38(1)	45(1)	44(1)	9(1)	17(1)	9(1)
C(18)	68(2)	59(2)	62(2)	-4(2)	29(2)	21(2)
C(19)	41(2)	47(2)	47(2)	7(1)	21(1)	8(1)
C(20)	39(2)	64(2)	65(2)	12(2)	14(2)	7(1)
C(21)	52(2)	67(2)	59(2)	14(2)	9(2)	5(2)
C(22)	78(3)	76(3)	77(3)	16(2)	34(2)	28(2)

Table 5. Hydrogen bonds for c4 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(6)...O(3)#1	0.826(19)	2.11(2)	2.904(3)	162(4)
C(22)-H(22)...O(1)	0.98	2.32	3.191(5)	147.4

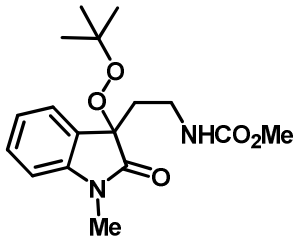
Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1



ORTEP drawing of $C_{20}H_{22}Cl_4N_2O_3S$, showing the atomic numbering scheme.

Crystal Structure of peroxylindole 3n



Empirical Formula	$C_{17}H_{24}N_2O_5$
Formula Weight	336.39
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.20 X 0.20 X 0.20 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 9.6342(2) Å
	b = 9.6998(2) Å
	c = 11.2007(7) Å
	α = 85.494(6) ^{o}
	β = 67.876(5) ^{o}
	γ = 71.103(5) ^{o}
	V = 916.25(8) Å^3
Space Group	P-1 (#2)
Z value	2
D_{calc}	1.219 g/cm^3
F_{000}	360.00
(CuK)	7.462 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku Saturn70 CCD
Radiation	CuKα (λ = 1.54187 Å) graphite monochromated
Voltage, Current	45kV, 1mA
Temperature	20.0°C
Detector Aperture	70 x 70 mm
Data Images	1480 exposures
ω oscillation Range (χ=45.0, ϕ=90.0)	-134.0 - 46.0°
Exposure Rate	2.0 sec./°
Detector Swing Angle	-44.00°
ω oscillation Range (χ=54.0, ϕ=180.0)	-134.0 - 46.0°
Exposure Rate	2.0 sec./°
Detector Swing Angle	-44.00°
ω oscillation Range (χ=54.0, ϕ=270.0)	-134.0 - -14.0°
Exposure Rate	2.0 sec./°
Detector Swing Angle	-44.00°
ω oscillation Range (χ=15.0, ϕ=0.0)	-24.0 - 6.0°
Exposure Rate	2.0 sec./°
Detector Swing Angle	-44.00°
ω oscillation Range (χ=54.0, ϕ=0.0)	-180.0 - 0.0°
Exposure Rate	2.0 sec./°
Detector Swing Angle	-44.00°
ω oscillation Range (χ=15.0, ϕ=0.0)	-180.0 - 0.0°

Exposure Rate	2.0 sec./^{o}
Detector Swing Angle	-44.00^{o}
ω oscillation Range (χ=15.0, ϕ=180.0)	-180.0 - 0.0^{o}
Exposure Rate	2.0 sec./^{o}
Detector Swing Angle	-44.00^{o}
ω oscillation Range (χ=54.0, ϕ=180.0)	-180.0 - -30.0^{o}
Exposure Rate	2.0 sec./^{o}
Detector Swing Angle	-44.00^{o}
ω oscillation Range (χ=54.0, ϕ=90.0)	-180.0 - -56.0^{o}
Exposure Rate	2.0 sec./^{o}
Detector Swing Angle	-44.00^{o}
ω oscillation Range (χ=45.0, ϕ=0.0)	-157.0 - -67.0^{o}
Exposure Rate	2.0 sec./^{o}
Detector Swing Angle	-44.00^{o}
ω oscillation Range (χ=54.0, ϕ=270.0)	-180.0 - -114.0^{o}
Exposure Rate	2.0 sec./^{o}
Detector Swing Angle	-44.00^{o}
ω oscillation Range (χ=45.0, ϕ=90.0)	-134.0 - 46.0^{o}
Exposure Rate	2.0 sec./^{o}
Detector Swing Angle	-44.16^{o}
ω oscillation Range (χ=54.0, ϕ=180.0)	-134.0 - 46.0^{o}
Exposure Rate	2.0 sec./^{o}

Detector Swing Angle	-44.16^{o}
ω oscillation Range (χ=54.0, ϕ=270.0)	-134.0 - -14.0^{o}
Exposure Rate	2.0 sec./^{o}
Detector Swing Angle	-44.16^{o}
ω oscillation Range (χ=15.0, ϕ=0.0)	-24.0 - 6.0^{o}
Exposure Rate	2.0 sec./^{o}
Detector Swing Angle	-44.16^{o}
ω oscillation Range (χ=54.0, ϕ=0.0)	-180.0 - 0.0^{o}
Exposure Rate	5.0 sec./^{o}
Detector Swing Angle	-90.16^{o}
ω oscillation Range (χ=15.0, ϕ=0.0)	-180.0 - 0.0^{o}
Exposure Rate	5.0 sec./^{o}
Detector Swing Angle	-90.16^{o}
ω oscillation Range (χ=15.0, ϕ=180.0)	-180.0 - 0.0^{o}
Exposure Rate	5.0 sec./^{o}
Detector Swing Angle	-90.16^{o}
ω oscillation Range (χ=54.0, ϕ=180.0)	-180.0 - -30.0^{o}
Exposure Rate	5.0 sec./^{o}
Detector Swing Angle	-90.16^{o}
ω oscillation Range (χ=54.0, ϕ=90.0)	-180.0 - -56.0^{o}
Exposure Rate	5.0 sec./^{o}
Detector Swing Angle	-90.16^{o}

ω oscillation Range (χ=45.0, ϕ=0.0)	-157.0 - -67.0°
Exposure Rate	5.0 sec./°
Detector Swing Angle	-90.16°
ω oscillation Range (χ=54.0, ϕ=270.0)	-180.0 - -114.0°
Exposure Rate	5.0 sec./°
Detector Swing Angle	-90.16°
Detector Position	41.17 mm
Pixel Size	0.034 mm
2_{max}	136.5°
No. of Reflections Measured	Total: 10511 Unique: 3253 (R_{int} = 0.048)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.708 - 0.861)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELX97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma w (Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\sigma^2(Fo^2) + (0.2000 \cdot P)^2 + 0.0000 \cdot P]$ where $P=(Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	136.5^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	3253
No. Variables	217
Reflection/Parameter Ratio	14.99
Residuals: R1 (I>2.00 (I))	0.1108
Residuals: R (All reflections)	0.1241
Residuals: wR2 (All reflections)	0.3305
Goodness of Fit Indicator	1.445
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.66 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.99 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
O(1)	0.5132(2)	0.6283(2)	0.81230(16)	3.997
O(2)	0.5235(2)	0.6051(2)	0.68029(17)	4.469
O(4)	0.2510(3)	0.5032(3)	0.8996(3)	5.577
O(5)	0.2651(3)	0.9603(3)	1.2626(2)	5.932
O(7)	0.3832(3)	0.7986(3)	1.3801(2)	5.888
N(3)	0.1155(3)	0.7343(3)	0.8627(2)	4.321
N(9)	0.4657(3)	0.7544(3)	1.1710(2)	5.146
C(6)	0.2878(3)	0.8591(3)	0.8444(2)	3.709
C(8)	0.1426(3)	0.8700(3)	0.8377(2)	3.901
C(10)	0.3516(3)	0.7058(3)	1.0240(2)	3.907
C(12)	0.2376(3)	0.6316(3)	0.8821(3)	3.911

C(13)	0.3408(4)	0.9781(3)	0.8200(3)	4.369
C(14)	0.0482(4)	0.9982(4)	0.8087(3)	4.886
C(15)	0.6867(3)	0.5907(3)	0.5965(3)	4.544
C(16)	0.3619(4)	0.8468(3)	1.2699(3)	4.365
C(17)	0.4634(4)	0.7747(4)	1.0424(3)	4.997
C(18)	0.2463(4)	1.1086(4)	0.7889(3)	5.159
C(19)	0.1035(4)	1.1179(4)	0.7851(3)	5.569
C(20)	0.8004(4)	0.4718(4)	0.6400(3)	5.629
C(21)	0.6900(5)	0.5469(5)	0.4678(3)	6.972
C(22)	-0.0238(4)	0.7054(5)	0.8617(4)	6.314
C(23)	0.7131(5)	0.7356(4)	0.5933(4)	7.005
C(24)	0.2729(7)	0.8845(5)	1.4958(4)	7.964
C(25)	0.3545(3)	0.7087(3)	0.8860(2)	3.459

$B_{eq} = 8/3 \quad ^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos \quad + 2U_{13}(aa^*cc^*)\cos \quad + 2U_{23}(bb^*cc^*)\cos \quad)$

Table 2. Atomic coordinates and B $_{iso}$ involving hydrogens/B_{eq}

atom	x	y	z	B_{eq}
H(10A)	0.2448	0.7564	1.0821	4.69
H(10B)	0.3786	0.6051	1.0483	4.69
H(11)	0.5362	0.6805	1.1839	6.18
H(13)	0.4372	0.9724	0.8240	5.24
H(14)	-0.0485	1.0046	0.8050	5.86
H(17A)	0.5692	0.7309	0.9795	6.00
H(17B)	0.4301	0.8781	1.0281	6.00
H(18)	0.2813	1.1895	0.7708	6.19
H(19)	0.0417	1.2059	0.7664	6.68
H(20A)	0.7793	0.3816	0.6400	6.75
H(20B)	0.7876	0.4967	0.7256	6.75
H(20C)	0.9067	0.4612	0.5822	6.75
H(21A)	0.6178	0.6246	0.4414	8.37
H(21B)	0.6595	0.4606	0.4768	8.37
H(21C)	0.7950	0.5277	0.4041	8.37
H(22A)	-0.0948	0.7937	0.8458	7.58
H(22B)	-0.0760	0.6709	0.9437	7.58
H(22C)	0.0081	0.6327	0.7949	7.58
H(23A)	0.6381	0.8077	0.5652	8.40
H(23B)	0.8184	0.7277	0.5346	8.40
H(23C)	0.6999	0.7638	0.6782	8.40
H(24A)	0.2977	0.8411	1.5684	9.56
H(24B)	0.1676	0.8882	1.5078	9.56
H(24C)	0.2796	0.9816	1.4886	9.56

$B_{eq} = 8/3\ \ ^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\ + 2U_{13}(aa^*cc^*)\cos\ + 2U_{23}(bb^*cc^*)\cos\ )$

Table 3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13} U_{23}
O(1)	0.0366	0.0655	0.0405	-0.0088	-0.0092 -0.0047
O(2)	0.0434	0.0742	0.0429	-0.0144	-0.0068 -0.0115
O(4)	0.0590	0.0568	0.0920	-0.0242	-0.0181 -0.0004
O(5)	0.0769	0.0669	0.0799	-0.0059	-0.0392 -0.0091
O(7)	0.1037	0.0679	0.0536	-0.0179	-0.0379 -0.0027
N(3)	0.0388	0.0650	0.0597	-0.0171	-0.0153 -0.0065
N(9)	0.0679	0.0721	0.0541	-0.0112	-0.0287 -0.0067
C(6)	0.0400	0.0538	0.0416	-0.0118	-0.0116 0.0017
C(8)	0.0385	0.0599	0.0437	-0.0093	-0.0128 -0.0042
C(10)	0.0427	0.0570	0.0415	-0.0133	-0.0092 -0.0014
C(12)	0.0386	0.0539	0.0522	-0.0127	-0.0137 -0.0016
C(13)	0.0477	0.0551	0.0590	-0.0148	-0.0175 0.0068
C(14)	0.0435	0.0710	0.0597	-0.0044	-0.0174 -0.0028
C(15)	0.0443	0.0609	0.0506	-0.0153	-0.0001 -0.0003
C(16)	0.0623	0.0573	0.0530	-0.0225	-0.0253 0.0003
C(17)	0.0668	0.0826	0.0472	-0.0336	-0.0199 0.0015
C(18)	0.0599	0.0539	0.0707	-0.0118	-0.0184 0.0097
C(19)	0.0603	0.0643	0.0674	-0.0070	-0.0139 0.0064
C(20)	0.0453	0.0737	0.0722	-0.0093	-0.0071 0.0116
C(21)	0.0840	0.1008	0.0510	-0.0192	0.0004

	-0.0108				
C(22)	0.0473	0.0975	0.0998	-0.0294	-0.0237
	-0.0130				
C(23)	0.0793	0.0675	0.0940	-0.0314	0.0024
	0.0014				
C(24)	0.1496	0.0886	0.0543	-0.0353	-0.0257
	-0.0150				
C(25)	0.0346	0.0489	0.0419	-0.0094	-0.0108
	0.0008				

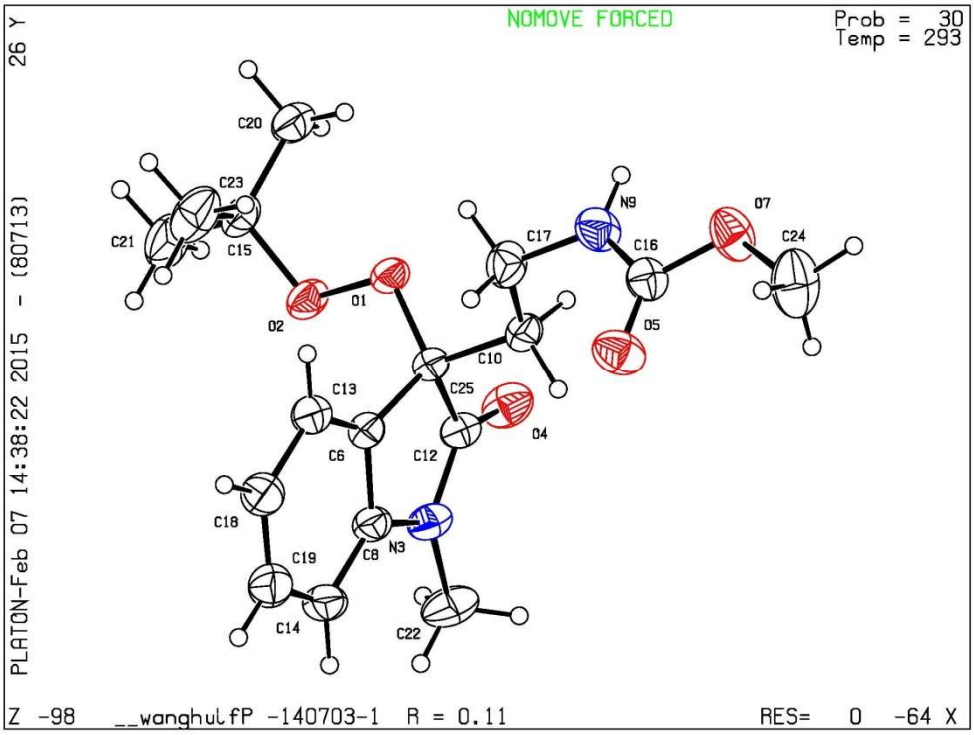
The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
O(1)	O(2)	1.474(4)	O(1)	C(25)	1.416(2)
O(2)	C(15)	1.463(4)	O(4)	C(12)	1.217(4)
O(5)	C(16)	1.211(2)	O(7)	C(16)	1.350(4)
O(7)	C(24)	1.436(4)	N(3)	C(8)	1.410(6)
N(3)	C(12)	1.350(3)	N(3)	C(22)	1.461(7)
N(9)	C(16)	1.331(5)	N(9)	C(17)	1.445(5)
C(6)	C(8)	1.398(7)	C(6)	C(13)	1.377(7)
C(6)	C(25)	1.506(3)	C(8)	C(14)	1.381(2)
C(10)	C(17)	1.518(9)	C(10)	C(25)	1.534(6)
C(12)	C(25)	1.554(9)	C(13)	C(18)	1.406(2)
C(14)	C(19)	1.395(9)	C(15)	C(20)	1.504(3)
C(15)	C(21)	1.520(7)	C(15)	C(23)	1.503(8)
C(18)	C(19)	1.366(9)			

Table 5. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
N(9)	H(11)	0.860	C(10)	H(10A)	0.970
C(10)	H(10B)	0.970	C(13)	H(13)	0.930
C(14)	H(14)	0.930	C(17)	H(17A)	0.970
C(17)	H(17B)	0.970	C(18)	H(18)	0.930
C(19)	H(19)	0.930	C(20)	H(20A)	0.960
C(20)	H(20B)	0.960	C(20)	H(20C)	0.960
C(21)	H(21A)	0.960	C(21)	H(21B)	0.960
C(21)	H(21C)	0.960	C(22)	H(22A)	0.960
C(22)	H(22B)	0.960	C(22)	H(22C)	0.960
C(23)	H(23A)	0.960	C(23)	H(23B)	0.960
C(23)	H(23C)	0.960	C(24)	H(24A)	0.960
C(24)	H(24B)	0.960	C(24)	H(24C)	0.960



ORTEP drawing of $C_{17}H_{24}N_2O_5$, showing the atomic numbering scheme.