Supporting Information

Switch Strategy for the Synthesis of C4-Ethylamine Indole and C7-Aminoindoline via Controllable Carbon Elimination

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1. General Methods

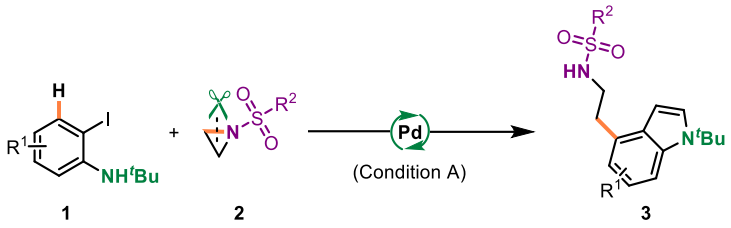
General Procedures. Unless otherwise noted, reactions were performed under an argon atmosphere. Plastic syringes were used to transfer air- and moisture-sensitive reagents. Solvent was freshly distilled/degassed prior to use unless otherwise noted. Analytical TLC was performed with silica gel GF254 plates. For column chromatography, a 200-300 mesh silica gel was employed. Organic solutions were concentrated under reduced pressure using a rotary evaporator. Room temperature (rat) is 23-25 °C.

Materials. Commercial reagents were purchased from Acros, Accela, Adamas, Alfa, Ark, Aladdin, or TCI, and used as received. Other commercially available reagents and solvents were used without further purification.

Instrumentation. Deuterated solvents were purchased from Cambridge Isotope Laboratories.^{1}H NMR spectra were recorded on Varian Mercury plus-400 and plus-600 and Bruker AVANCE III 400 instrument with 400 and 600 MHz frequencies, and ^{13}C NMR spectra were recorded on Varian Mercury plus-400 and plus-600 and Bruker AVANCE III 400 instrument with 151 and 101 MHz frequencies. ^{19}F NMR spectra were recorded on a Varian Mercury plus-400 and Bruker AVANCE III 400 spectrometer with a ^{19}F operating frequency of 376 MHz. Chemical shifts (δ) were reported in ppm relative to the residual solvent signal ($CDCl_3$ δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as s(singlet), d (doublet), t (triplet), dd (doublet of doublets), td (triplet of doublets) or m (multiplet). High-resolution mass spectra (HRMS) (ESI) were obtained with a Bruker Daltonics APEX II 47e and Orbitrap Elite mass spectrometer.

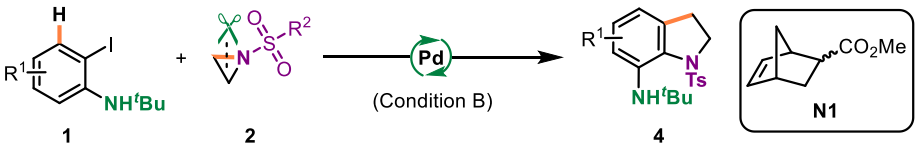
2. General Procedure

a) Synthesis of C4-Ethylamine Indole 3



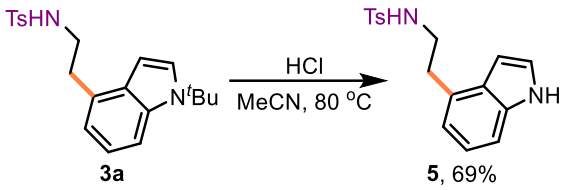
In a 20 mL tube (sealed tube), *o*-iodoaniline **1** (0.2 mmol), aziridines **2** (0.5 mmol, 2.5 equiv), $Pd(OAc)_2$ (10 mol%), PPh_3 (25 mol%), Cs_2CO_3 (0.2 mmol, 1.0 equiv) and CsBr (0.2 mmol, 1.0 equiv) were added and charged with argon more than three times (The tube was sealed with tipping plug). NBD (0.6 mmol, 3.0 equiv) were dissolved in toluene/1,4-dioxane (2 mL, v/v 1:1), and the mixture was injected into the tube via plastic syringes. Then the white medical adhesive tape was used to reinforce the tipping plug. The resulting suspension being placed in a pre-heated oil bath at 90 °C stirring at 900~1200 rpm for 12 h, then rises to 150 °C for 24 h. After the reaction was completed, the residue was purified with chromatography column on silica gel or preparative TLC (PTLC) (petroleum ether/EtOAc = 4:1-8:1).

b) Synthesis of C7-Aminoindoline 4



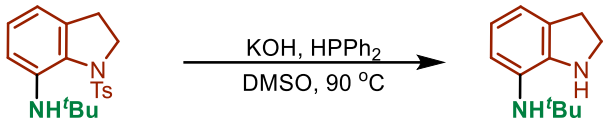
In a 20 mL tube (sealed tube), *o*-iodoaniline **1** (0.2 mmol), aziridines **2** (0.5 mmol, 2.5 equiv), $Pd(OAc)_2$ (10 mol%), P(*p*-Cl-C_6H_4)$_3$ (20 mol%), K_2CO_3 (0.6 mmol, 3.0 equiv) and KI (0.1 mmol, 0.5 equiv) were added and charged with argon more than three times (The tube was sealed with tipping plug). Methyl bicyclo[2.2.1]hept-5-ene-2-carboxylate **N1** (0.2 mmol, 1.0 equiv) were dissolved in toluene (2 mL), and the mixture was injected into the tube via plastic syringes. Then the white medical adhesive tape was used to reinforce the tipping plug. The resulting suspension being placed in a pre-heated oil bath at 100 °C stirring at 900~1200 rpm for 24 h. After the reaction was completed, the residue was purified with chromatography column on silica gel or preparative TLC (PTLC) (petroleum ether/EtOAc = 5:1-10:1).

3. Deprotection of Products



3a **5**, 69%

In a 20 mL tube, concentrated HCl (1 mL) was added dropwise to a solution of **3a** (0.2 mmol, 55.4 mg) in CH_3CN (2 mL) at room temperature, and the reaction mixture was stirred at 80 °C for 24 h. After the reaction was complete, it was diluted with water (5.0 mL), neutralized with saturated $NaHCO_3$ solution, and then extracted with EtOAc (3×15 mL). The combined organic extract was dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel (Petroleum ether/EtOAc = 2:1). The product **5** was obtained with a yield of 69%, 43.6 mg.

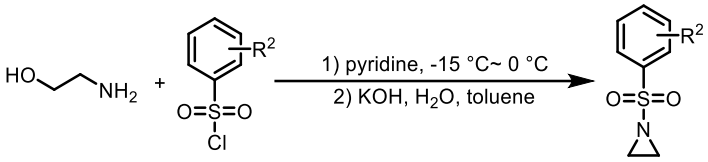


4a **6**, 66%

In a 20 mL tube, the solution of **4a** (0.2 mmol, 1.0 equiv) in DMSO (3.0 mL), KOH (0.5 mmol, 2.5 equiv) was added and the mixture was sealed under an argon atmosphere. Subsequently, $HPPh_2$ (0.22 mmol, 1.1 equiv) was injected into the tube, and the mixture was stirred at 90 °C for 1h. After the reaction was complete, it was diluted with water (5.0 mL), and then extracted with EtOAc (3×15 mL). The combined organic extract was dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum.[1] The residue was purified by column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). The product **6** was obtained with a yield of 66%, 25.2 mg.

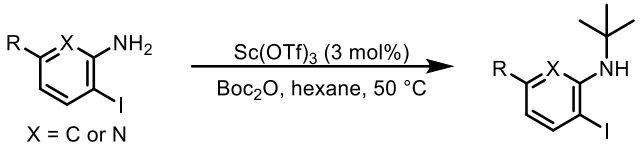
4. Preparation of Substrates

a) Preparation of aziridines



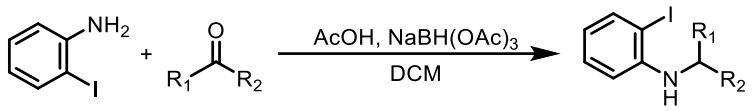
A solution of aryl sulfonyl chloride (52 mmol) in pyridine (32 mL) was cooled to -15°C. A precooled (0°C) solution of aminoethanol (25 mmol) in pyridine (18 mL) was added dropwise over a period of 0.5 h. Then mixture was stirred for 7 h at 0°C and placed in the fridge overnight. Ice/water was added to the reaction mixture, which was then extracted with dichloromethane (DCM) (3×20 mL) and washed with water several times. The organic layer was then dried with anhydrous $MgSO_4$, filtered, the solvent was removed under vacuum. Then the residue was dissolved in toluene (100 mL) and KOH (85 mmol) in water (25 mL) was added to it. The mixture was stirred for 2 h at room temperature. The toluene phase was separated and intensively washed with water until the aqueous phase showed a neutral pH. The organic layer was dried with anhydrous $MgSO_4$ and filtered. The solvent was removed under vacuum, and the residue was purified by column chromatography.[2]

b) Preparation of N-(tert-butyl)-2-iodoaniline



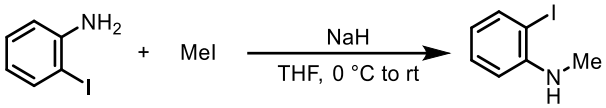
2-Iodoaniline (10.0 mmol) and $Sc(OTf)_3$ (0.147 g, 0.3 mmol) were added to an 100 mL round flask and round flask was charged with argon more than three times. *n*-Hexane (10 mL) and Boc_2O (40 mL) was added into this round flask. The mixture was stirred at 50 ℃ for 24 h. Due to the production of a large amount of gas, the reaction flask needs to be deflated with a balloon. After the reaction was completed, the residue was purified with chromatography column on silica gel (using petroleum ether as eluant).[3]

c) Preparation of N-alkyl-2-iodoaniline



Ketone (15.0 mmol, 1.5 equiv) and AcOH (1.0 equiv, 10.0 mmol, 0.57 mL) were added sequentially to a solution of *o*-iodoaniline (10 mmol) in CH_2Cl_2 (50 mL), and the mixture was stirred at room temperature for 2 hours. Then, $NaBH(OAc)_3$ (30.0 mmol, 3.0 equiv) was added, and stirring at room temperature was continued for an additional 24 hours. The reaction mixture was quenched with 1.0 M NaOH aqueous solution and extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated in vacuum. The crude product was purified by flash column chromatography using petroleum ether as eluant.[3]

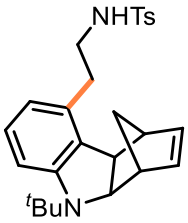
d) Preparation of 2-iodo-N-methylaniline



NaH (1.3 g, 32.0 mmol, 1.0 equiv, 60% dispersion in mineral oil) was added to THF (60 mL) in an oven-dried flask, and then *o*-iodoaniline (7.0 g, 32 mmol, 1.0 equiv) was added slowly to the mixture at 0 °C. The mixture was stirred for 30 minutes. Subsequently, MeI (2.0 mL, 32.0 mmol, 1.0 equiv) was added to the mixture. The mixture was heated to room temperature and stirred overnight. After the reaction was complete, 50 mL water was added slowly and extracted with EtOAc (3 × 40 mL). Then, the combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by silica gel column chromatography (Petroleum ether).[4]

5. Intermediate (VII-1) and Byproduct (II') Detection

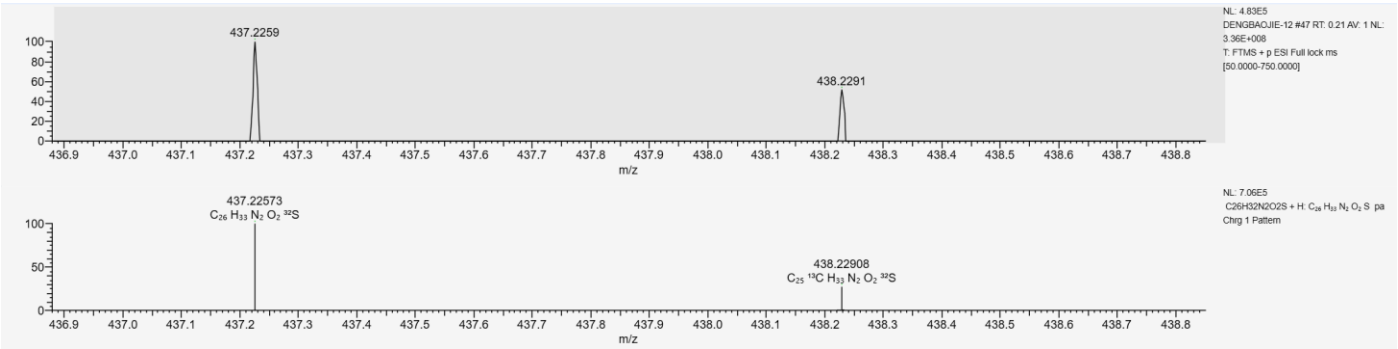
N-(2-((1R,4S,4aR,9aR)-9-(tert-butyl)-4,4a,9,9a-tetrahydro-1H-1,4-methanocarbazol-5-yl)ethyl)-4-methylbenzenesulfonamide (VII-1)



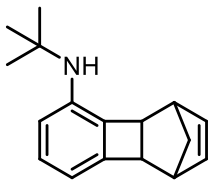
VII-1, <5%

High resolution mass spectrometry (HRMS) spectrum:

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{33}N_2O_2S$ 437.2257; Found 437.2259.



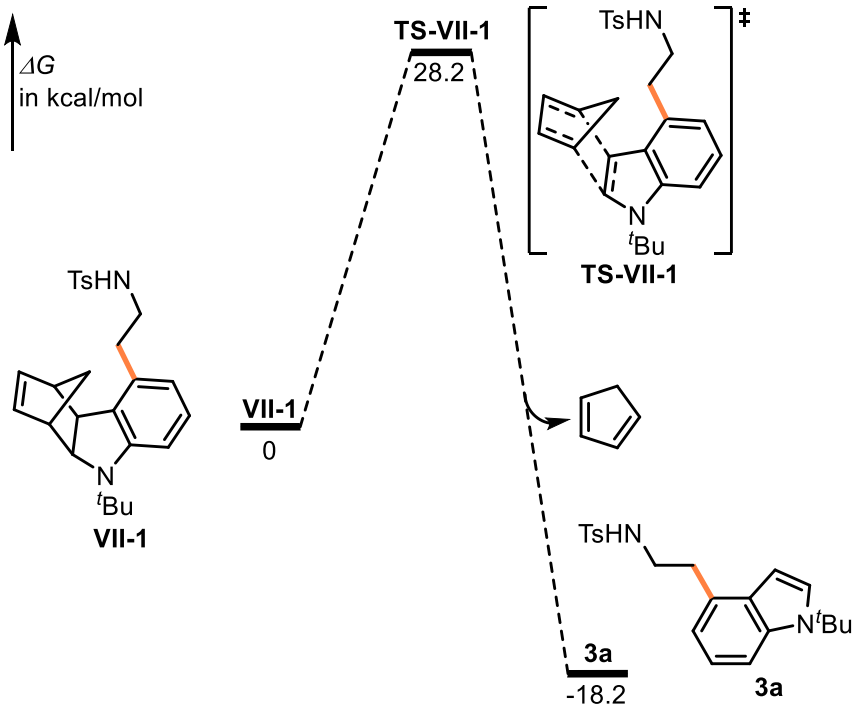
N-(tert-butyl)-1,4,4a,8b-tetrahydro-1,4-methanobiphenylen-5-amine (II')



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 – 7.00 (m, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 6.53 (d, *J* = 7.0 Hz, 1H), 6.24 – 6.14 (m, 2H), 3.01 (s, 2H), 2.77 (d, *J* = 28.6 Hz, 3H), 1.35 (s, 9H), 1.29 (d, *J* = 7.9 Hz, 1H), 0.96 (d, *J* = 9.0 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 146.7, 141.4, 136.6, 136.2, 132.2, 128.3, 114.8, 112.2, 51.6, 46.3, 45.6, 41.4, 41.1, 40.5, 30.3.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{22}N$ 240.1747; Found 240.1747.

6. Density Functional Theory (DFT) Calculation of Retro Diels-Alder Reaction

All calculations were carried out with Gaussian 16.[5] Intermediates and transition states were optimized at the M06-2X level of theory,[6] with 6-311G+(d,p) basis set[7] in 1,4-dioxane at 423.15 K. The solvent was taken into consideration by employing the SMD continuum solvation model.[8] Grimme's DFT-D3 dispersion correction was used to describe the van der waals interaction.[9] Vibrational frequencies were calculated at the same level of theory to confirm stationary point either as a local minimum or a transition state. Transition states were further confirmed by running intrinsic reaction coordinate (IRC) calculations.



VII-1

M06-2X SCF energy in solution: -1667.905182 a.u.

M06-2X free energy in solution: -1667.473737 a.u.

C	8.73804200	-5.35869800	-4.99655700
C	9.60537200	-4.58412000	-6.05460100
C	9.82515200	-6.71993100	-6.71878400
C	8.90057300	-6.84876300	-5.45284300
H	9.10810300	-5.17661100	-3.98603200
C	9.30895400	-5.40364700	-7.32209100
H	9.90236800	-5.07670700	-8.17668600
H	8.25053100	-5.42956100	-7.58964000
C	11.03937500	-5.00296700	-5.78268300
C	11.17065200	-6.27188100	-6.17868000

H	9.40657300	-3.51567700	-6.09604500
H	9.82548700	-7.59597000	-7.36345400
C	6.63326700	-6.27065900	-5.63783000
C	7.25866400	-5.11322900	-5.12821300
C	5.27655500	-6.22115400	-5.97328800
C	6.54735900	-3.95575200	-4.86228700
C	4.56906200	-5.04274000	-5.72364100
H	4.76412200	-7.05491900	-6.42901600
C	5.17558100	-3.92978000	-5.16175500
H	3.51614300	-5.00450600	-5.98081700
H	4.60143900	-3.02987500	-4.96835400
H	9.37166900	-7.47464400	-4.69519000
H	12.03116100	-6.91448500	-6.03878100
H	11.77139800	-4.40214500	-5.25696100
N	7.54017800	-7.31248200	-5.73609200
C	7.20677400	-8.71666500	-6.04192000
C	8.40355800	-9.62125000	-5.72208400
H	8.14262800	-10.64587500	-5.99455200
H	9.30118000	-9.35056300	-6.27879000
H	8.63611100	-9.60918200	-4.65465000
C	6.85848600	-8.86219900	-7.53006800
H	6.55651000	-9.88863300	-7.75712700
H	6.04247500	-8.19599600	-7.81640300
H	7.72562400	-8.61337400	-8.14754700
C	6.04893500	-9.20702800	-5.15684500
H	6.27460700	-9.01307300	-4.10527000
H	5.09480900	-8.73915800	-5.38916900
H	5.92606100	-10.28494300	-5.28858300
C	7.19705400	-2.77211900	-4.18859200
H	8.27388300	-2.74949800	-4.36402000
H	6.78336000	-1.84267400	-4.58512900
C	6.95583400	-2.85181800	-2.67969400
H	5.88498800	-2.77188100	-2.46339200
H	7.30324900	-3.81846000	-2.30895100
N	7.73364700	-1.84053000	-1.93091700
H	7.69553600	-2.03210000	-0.93103500
S	7.24032400	-0.24879400	-2.15743400
O	5.79982300	-0.12165800	-1.97008300
O	7.81827500	0.21606500	-3.40702000
C	8.06758800	0.53017400	-0.79332500
C	7.33810100	0.88285000	0.33334400
C	9.43805300	0.75660700	-0.87924700
C	8.00342600	1.47726400	1.40002700
H	6.26972900	0.70464600	0.36547200
C	10.08320100	1.34616700	0.19658900
H	9.98007400	0.47907400	-1.77580100
C	9.37706900	1.71565500	1.34715100

H	7.44471800	1.76288400	2.28439300
H	11.15102200	1.53009200	0.14468600
C	10.09099600	2.38313700	2.48983400
H	11.04414000	1.89259300	2.69686700
H	10.30442300	3.42770900	2.24584000
H	9.48831100	2.36681400	3.39845600

TS-VII-1

M06-2X SCF energy in solution: -1667.858535 a.u.

M06-2X free energy in solution: -1667.428814 a.u.

Imaginary frequency: -586.57 cm^{-1}

C	8.18854300	-5.13971500	-3.63012000
C	9.42407600	-3.52201600	-4.17817500
C	10.39377200	-5.23419100	-5.35926800
C	8.72640100	-6.22758400	-4.39187800
H	8.37755900	-5.03915900	-2.57321500
C	9.53955600	-4.01764800	-5.59376300
H	10.12240900	-3.28451100	-6.17025700
H	8.59691600	-4.18685900	-6.11455200
C	10.61636600	-3.89945800	-3.52674800
C	11.19506900	-4.94642100	-4.24077100
H	8.83761300	-2.64918400	-3.90960500
H	10.70484900	-5.89147400	-6.16206900
C	6.72125000	-5.70988200	-5.33517500
C	6.88822400	-4.85453200	-4.22024600
C	5.62002500	-5.54440000	-6.18526300
C	5.94774100	-3.86838900	-3.91685400
C	4.68536800	-4.56721300	-5.86242800
H	5.47841300	-6.13872500	-7.07590000
C	4.83399900	-3.74280700	-4.74444400
H	3.82398900	-4.43621900	-6.50759800
H	4.09252100	-2.97832500	-4.53667800
H	9.33388400	-7.00823800	-3.96588100
H	12.04280600	-5.53523800	-3.91254000
H	10.92461000	-3.55715800	-2.54647500
N	7.78849900	-6.59507800	-5.37639700
C	7.97869100	-7.68134800	-6.36106000
C	9.17121400	-8.54932200	-5.95060000
H	9.29398200	-9.33971600	-6.69358400
H	10.10275800	-7.98412200	-5.90693800
H	9.00041300	-9.02445900	-4.98146200
C	8.24299800	-7.08654700	-7.75005200
H	8.34071800	-7.88570100	-8.48963400
H	7.43323800	-6.42739600	-8.06775700
H	9.16884600	-6.50658600	-7.74797000

C	6.74210100	-8.59020900	-6.37296200
H	6.53661900	-8.95495900	-5.36381400
H	5.84721100	-8.09293100	-6.74140600
H	6.93266700	-9.45082700	-7.01862700
C	6.16301500	-2.96128700	-2.73432400
H	7.17020400	-3.10610800	-2.33851000
H	6.08459700	-1.91960800	-3.05832400
C	5.15735500	-3.22007200	-1.61003200
H	4.16625700	-2.85421100	-1.89543700
H	5.08790200	-4.29373500	-1.42505600
N	5.60304200	-2.62751100	-0.33603100
H	5.04961900	-2.91764100	0.46596000
S	5.82708800	-0.98094300	-0.23800700
O	5.79438600	-0.68121400	1.18513500
O	4.94001800	-0.26982000	-1.14727300
C	7.48677500	-0.79016000	-0.85419200
C	8.51137100	-1.51754800	-0.26247000
C	7.72093700	0.04205400	-1.94080300
C	9.79278400	-1.42137300	-0.78867800
H	8.30409700	-2.16485300	0.58197300
C	9.00927800	0.12785000	-2.45230500
H	6.90132300	0.59328400	-2.38610100
C	10.05819200	-0.60807600	-1.89419300
H	10.59856900	-1.98929200	-0.33628900
H	9.20309800	0.76722400	-3.30718500
C	11.43433800	-0.53745500	-2.49560800
H	11.44117100	-1.00726800	-3.48346200
H	11.75255700	0.50037100	-2.61868400
H	12.16847800	-1.05070300	-1.87324600

3a

M06-2X SCF energy in solution: -1473.829869 a.u.

M06-2X free energy in solution: -1473.491811 a.u.

C	8.19531200	-5.88348800	-3.74025300
C	8.28522100	-7.15793200	-4.22204700
H	8.74761000	-5.48810000	-2.90179000
C	6.79919000	-6.13230100	-5.53711400
C	7.24747800	-5.20051800	-4.56694400
C	5.85188800	-5.75766900	-6.50431200
C	6.75460500	-3.88048900	-4.55710600
C	5.38040400	-4.45861700	-6.47730000
H	5.48700900	-6.44300700	-7.25578000
C	5.82306600	-3.53011200	-5.51776400
H	4.64990100	-4.14864500	-7.21549700
H	5.42661600	-2.52002300	-5.52939000

H	8.89772100	-7.96645900	-3.86063800
N	7.45206600	-7.33284900	-5.30657900
C	7.28944700	-8.58592500	-6.08360800
C	8.19342100	-9.67329300	-5.50318700
H	8.05662200	-10.58314100	-6.09021200
H	9.24832900	-9.39511400	-5.55816600
H	7.93671300	-9.90288900	-4.46664900
C	7.70425700	-8.33955600	-7.53795700
H	7.62115900	-9.26943500	-8.10574700
H	7.08423800	-7.58963100	-8.02802600
H	8.74203100	-8.00031100	-7.57941100
C	5.83627700	-9.06048000	-5.98131200
H	5.57054400	-9.23107200	-4.93530700
H	5.13247900	-8.33886200	-6.39505100
H	5.71694100	-9.99991700	-6.52647400
C	7.19506000	-2.91698400	-3.48781600
H	8.26445300	-3.03198100	-3.28588900
H	7.01988400	-1.88911900	-3.81051600
C	6.42758800	-3.16575100	-2.18852700
H	5.35560400	-3.02649000	-2.35296100
H	6.57730800	-4.19536300	-1.85873300
N	6.92882700	-2.30521000	-1.09631100
H	6.99768300	-2.78348600	-0.20285500
S	6.19260500	-0.82702400	-0.87915600
O	5.21699000	-0.88003100	0.19999600
O	5.77009000	-0.39016600	-2.20017900
C	7.54664500	0.18093600	-0.32169400
C	7.47847800	0.78877200	0.92137100
C	8.64252100	0.36083600	-1.16208000
C	8.53590600	1.59713600	1.33138200
H	6.61267800	0.63264600	1.55317300
C	9.68372600	1.16792700	-0.73788600
H	8.67503900	-0.12902300	-2.12901300
C	9.64577400	1.79714300	0.51381500
H	8.49216200	2.07814700	2.30218500
H	10.54334600	1.31683000	-1.38290300
C	10.78863000	2.67262800	0.94866800
H	11.72856500	2.11526900	0.94006700
H	10.90422300	3.51999900	0.26797700
H	10.63100900	3.06264000	1.95460200

Cyclopentadiene

M06-2X SCF energy in solution: -194.063413 a.u.

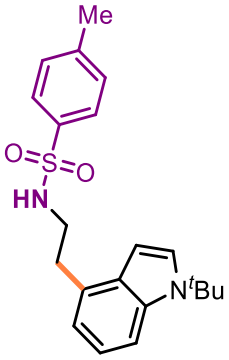
M06-2X free energy in solution: -194.010976 a.u.

C	9.93157500	-4.39954100	-6.36875800
C	10.16104800	-6.63325000	-7.06348500

C	9.32332700	-5.41067700	-7.29485300
H	9.36139400	-5.08141200	-8.34052200
H	8.26564700	-5.59054700	-7.06636000
C	10.95960000	-4.96204400	-5.71110400
C	11.10301200	-6.35833500	-6.14533600
H	9.57753700	-3.38264400	-6.26669000
H	10.00854600	-7.57623300	-7.57081500
H	11.85424300	-7.04327900	-5.77387100
H	11.59109500	-4.47912900	-4.97661300

7. Characterization Data

N-(2-(1-(tert-butyl)-1H-indol-4-yl)ethyl)-4-methylbenzenesulfonamide (3a)



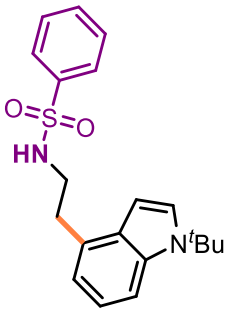
42.9 mg, yield: 58%. Yellow oil. Chromatography column, Petroleum ether/EtOAc = 5:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.27 – 7.23 (m, 3H), 7.10 – 7.02 (m, 1H), 6.78 (d, *J* = 7.1 Hz, 1H), 6.36 (d, *J* = 3.4 Hz, 1H), 4.46 (t, *J* = 6.3 Hz, 1H), 3.32 (q, 2H), 3.03 (t, *J* = 6.9 Hz, 2H), 2.40 (s, 3H), 1.72 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 137.0, 134.9, 129.7, 129.57, 129.56, 127.1, 125.2, 120.8, 118.9, 112.2, 97.9, 55.9, 43.5, 33.4, 29.7, 21.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{27}N_2O_2S$ 371.1788; Found 371.1789.

N-(2-(1-(tert-butyl)-1H-indol-4-yl)ethyl)benzenesulfonamide (3b)



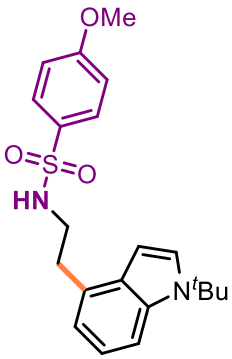
36.4 mg, yield: 51%. Yellow oil. Chromatography column, Petroleum ether/EtOAc = 4:1

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 2H), 7.54 – 7.51 (m, 2H), 7.47 – 7.42 (m, 2H), 7.26 (d, *J* = 3.4 Hz, 1H), 7.08 – 7.04 (m, 1H), 6.77 (d, *J* = 7.1 Hz, 1H), 6.35 (dd, *J* = 3.4, 1.0 Hz, 1H), 4.47 (t, *J* = 6.1 Hz, 1H), 3.35 (q, *J* = 6.7 Hz, 2H), 3.03 (t, *J* = 6.8 Hz, 2H), 1.72 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.0, 134.9, 132.4, 129.6, 129.6, 129.0, 127.0, 125.3, 120.8, 118.9, 112.3, 97.9, 55.9, 43.5, 33.4, 29.8.

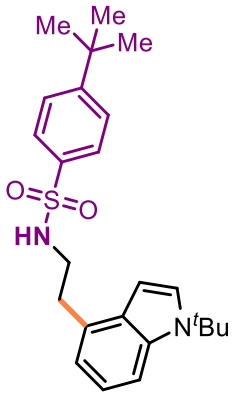
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{25}N_2O_2S$ 357.1631; Found 357.1630.

N-(2-(1-(tert-butyl)-1H-indol-4-yl)ethyl)-4-methoxybenzenesulfonamide (3c)



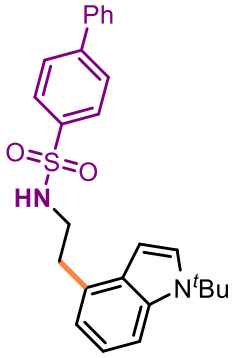
37.2 mg, yield: 48%. Yellow oil. Chromatography column, Petroleum ether/EtOAc = 4:1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 – 7.68 (m, 2H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.25 (d, *J* = 3.4 Hz, 1H), 7.07 – 7.04 (m, 1H), 6.92 – 6.89 (m, 2H), 6.78 (d, *J* = 7.1 Hz, 1H), 6.36 (dd, *J* = 3.4, 0.9 Hz, 1H), 4.46 (t, *J* = 6.2 Hz, 1H), 3.84 (s, 3H), 3.32 (q, *J* = 6.8 Hz, 2H), 3.03 (t, *J* = 6.9 Hz, 2H), 1.72 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 162.7, 134.9, 131.6, 129.7, 129.5, 129.1, 125.2, 120.8, 118.9, 114.1, 112.2, 97.9, 55.8, 55.5, 43.4, 33.3, 29.7.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{27}N_2O_3S$ 387.1737; Found 387.1737.

4-(tert-butyl)-N-(2-(1-(tert-butyl)-1H-indol-4-yl)ethyl)benzenesulfonamide (3d)



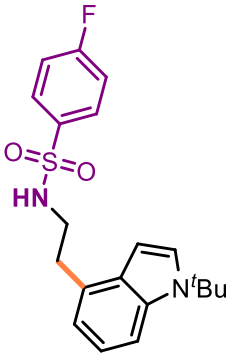
31.9 mg, yield: 39%. Yellow oil. Chromatography column, Petroleum ether/EtOAc = 4:1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.67 (m, 2H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.26 (d, *J* = 3.4 Hz, 1H), 7.08 – 7.03 (m, 1H), 6.77 (d, *J* = 7.1 Hz, 1H), 6.37 (dd, *J* = 3.3, 1.0 Hz, 1H), 4.52 (t, *J* = 5.9 Hz, 1H), 3.34 (q, *J* = 6.7 Hz, 2H), 3.04 (t, *J* = 7.0 Hz, 2H), 1.72 (s, 9H), 1.33 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 156.2, 137.0, 134.9, 129.8, 129.6, 126.9, 126.0, 125.2, 120.8, 118.9, 112.2, 97.9, 55.8, 43.5, 35.1, 33.5, 31.1, 29.7.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{33}N_2O_2S$ 413.2257; Found 413.2256.

N-(2-(1-(tert-butyl)-1H-indol-4-yl)ethyl)-[1,1'-biphenyl]-4-sulfonamide (3e)



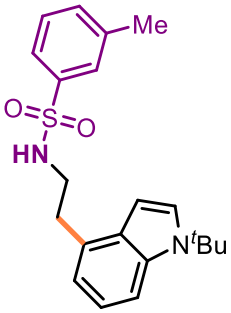
21.2 mg, yield: 25%. Yellow oil. Chromatography column, Petroleum ether/EtOAc = 5:1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 2H), 7.65 – 7.62 (m, 2H), 7.60 – 7.57 (m, 2H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.43 – 7.39 (m, 1H), 7.24 (d, *J* = 3.4 Hz, 1H), 7.08 – 7.05 (m, 1H), 6.80 (d, *J* = 7.1 Hz, 1H), 6.36 (dd, *J* = 3.4, 1.0 Hz, 1H), 4.45 (t, *J* = 6.1 Hz, 1H), 3.39 (q, *J* = 6.6 Hz, 2H), 3.07 (t, *J* = 6.8 Hz, 2H), 1.70 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.4, 139.4, 138.5, 134.9, 129.60, 129.58, 129.0, 128.4, 127.60, 127.55, 127.3, 125.3, 120.8, 119.0, 112.3, 97.9, 55.9, 43.5, 33.4, 29.7.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{29}N_2O_2S$ 433.1944; Found 433.1944.

N-(2-(1-(tert-butyl)-1H-indol-4-yl)ethyl)-4-fluorobenzenesulfonamide (3f)



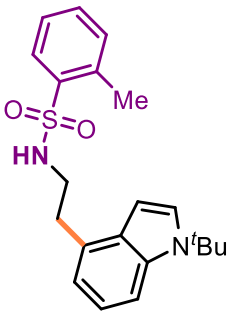
22.6 mg, yield: 30%. Yellow oil. Chromatography column, Petroleum ether/EtOAc = 4:1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 2H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.26 (d, *J* = 3.4 Hz, 1H), 7.10 – 7.05 (m, 3H), 6.77 (dd, *J* = 7.1, 0.8 Hz, 1H), 6.33 (dd, *J* = 3.4, 1.0 Hz, 1H), 4.48 (t, *J* = 6.0 Hz, 1H), 3.34 (q, *J* = 6.7 Hz, 2H), 3.04 (t, *J* = 6.8 Hz, 2H), 1.73 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 164.9 (d, *J* = 254.3 Hz), 135.9 (d, *J* = 3.4 Hz), 134.9, 129.7 (d, *J* = 9.3 Hz), 129.5, 129.5, 125.3, 120.8, 119.0, 116.1 (d, *J* = 22.5 Hz), 112.4, 97.8, 55.9, 43.4, 33.3, 29.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ -105.77 – -105.87 (m).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{24}FN_2O_2S$ 375.1537; Found 375.1536.

N-(2-(1-(tert-butyl)-1H-indol-4-yl)ethyl)-3-methylbenzenesulfonamide (3g)



24.1 mg, yield: 33%. Yellow oil. Chromatography column, Petroleum ether/EtOAc = 4:1.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.27 (d, *J* = 3.4 Hz, 1H), 7.09 – 7.04 (m, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 6.36 (dd, *J* = 3.4, 0.9 Hz, 1H), 4.39 (t, *J* = 4.9 Hz, 1H), 3.36 (q, *J* = 6.6 Hz, 2H), 3.04 (t, *J* = 6.8 Hz, 2H), 2.39 (s, 3H), 1.73 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 139.8, 139.2, 134.9, 133.3, 129.7, 129.6, 128.9, 127.4, 125.3, 124.1, 120.8, 118.9, 112.3, 97.9, 55.9, 43.5, 33.4, 29.8, 21.3.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{27}N_2O_2S$ 371.1788; Found 371.1790.

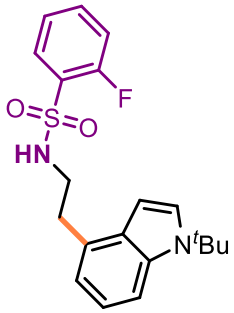
N-(2-(1-(tert-butyl)-1H-indol-4-yl)ethyl)-2-methylbenzenesulfonamide (3h)



39.0 mg, yield: 53%. Yellow oil. Chromatography column, Petroleum ether/EtOAc = 4:1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.89 (m, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.39 (td, *J* = 7.5, 1.4 Hz, 1H), 7.26 – 7.22

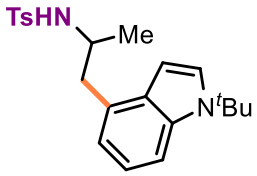
(m, 2H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.06 (t, 1H), 6.78 (d, *J* = 7.1 Hz, 1H), 6.33 (d, *J* = 3.4 Hz, 1H), 4.49 (t, *J* = 5.9 Hz, 1H), 3.30 (q, *J* = 6.5 Hz, 2H), 3.04 (t, *J* = 6.8 Hz, 2H), 2.32 (s, 3H), 1.72 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 137.5, 137.0, 134.9, 132.5, 132.4, 129.6, 129.5, 125.9, 125.3, 120.8, 118.9, 112.3, 97.8, 55.8, 43.3, 33.2, 29.7, 19.8.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{27}N_2O_2S$ 371.1788; Found 371.1787.

N-(2-(1-(tert-butyl)-1H-indol-4-yl)ethyl)-2-fluorobenzenesulfonamide (3i)



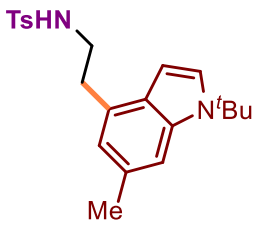
21.6 mg, yield: 29%. Yellow oil. Chromatography column, Petroleum ether/EtOAc = 4:1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (td, *J* = 7.5, 1.8 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.26 (d, *J* = 3.4 Hz, 1H), 7.23 (td, *J* = 7.6, 1.1 Hz, 1H), 7.13 – 7.09 (m, 1H), 7.09 – 7.05 (m, 1H), 6.81 (d, *J* = 7.1 Hz, 1H), 6.36 (dd, *J* = 3.4, 0.9 Hz, 1H), 4.72 (t, *J* = 6.0 Hz, 1H), 3.39 (q, *J* = 6.7 Hz, 2H), 3.07 (t, *J* = 7.0 Hz, 2H), 1.73 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 158.7 (d, *J* = 254.5 Hz), 134.9, 134.7 (d, *J* = 8.6 Hz), 130.3, 129.5 (d, *J* = 3.0 Hz), 128.0 (d, *J* = 13.9 Hz), 125.3, 124.3 (d, *J* = 4.0 Hz), 120.9, 118.9, 116.8 (d, *J* = 21.3 Hz), 112.3, 97.8, 55.9, 43.7, 33.5, 29.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ -121.39 (t, *J* = 10.5 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{24}FN_2O_2S$ 375.1537; Found 375.1537.

N-(1-(1-(tert-butyl)-1H-indol-4-yl)propan-2-yl)-4-methylbenzenesulfonamide (3k)



18.3 mg, yield: 24%. Yellow oil. Chromatography column, Petroleum ether/EtOAc = 5:1.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 3H), 7.24 (d, *J* = 3.3 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.05 – 6.97 (m, 1H), 6.72 (d, *J* = 7.1 Hz, 1H), 6.34 (dd, *J* = 3.3, 0.9 Hz, 1H), 4.58 (d, *J* = 6.4 Hz, 1H), 3.63 (p, *J* = 6.6 Hz, 1H), 3.04 (dd, *J* = 13.5, 6.4 Hz, 1H), 2.86 (dd, *J* = 13.5, 7.3 Hz, 1H), 2.37 (s, 3H), 1.73 (s, 10H), 1.14 (d, *J* = 6.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 142.8, 137.5, 134.9, 130.0, 129.4, 126.9, 125.2, 120.7, 119.7, 112.1, 98.2, 55.8, 50.5, 41.2, 29.8, 21.7, 21.5.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{29}N_2O_2S$ 385.1944; Found 385.1943.

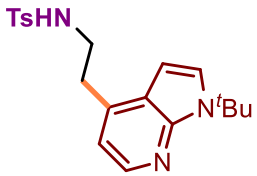
N-(2-(1-(tert-butyl)-6-methyl-1H-indol-4-yl)ethyl)-4-methylbenzenesulfonamide (3j)



29.6 mg, yield: 39%. Yellow oil. Chromatography column, Petroleum ether/EtOAc = 4:1.

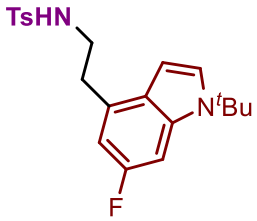
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 – 7.63 (m, 2H), 7.31 (s, 1H), 7.26 – 7.21 (m, 2H), 7.18 (d, *J* = 3.3 Hz, 1H), 6.59 (s, 1H), 6.29 (d, *J* = 3.3 Hz, 1H), 4.44 (t, *J* = 6.0 Hz, 1H), 3.32 (q, *J* = 6.7 Hz, 2H), 2.98 (t, *J* = 6.9 Hz, 2H), 2.43 (s, 3H), 2.40 (s, 3H), 1.71 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 143.1, 137.1, 135.3, 130.4, 129.6, 129.3, 127.4, 127.1, 124.7, 120.8, 112.2, 97.7, 55.7, 43.5, 33.3, 29.7, 22.0, 21.5.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{29}N_2O_2S$ 385.1944; Found 385.1944.

N-(2-(1-(tert-butyl)-1H-pyrrolo[2,3-b]pyridin-4-yl)ethyl)-4-methylbenzenesulfonamide (3n)



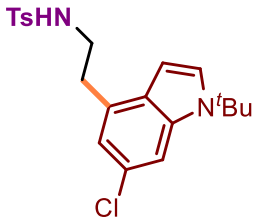
19.1 mg, yield: 26%. Colorless oil. Chromatography column, Petroleum ether/EtOAc = 4:1.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 4.8 Hz, 1H), 7.69 – 7.65 (m, 2H), 7.33 (d, *J* = 3.7 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 4.8 Hz, 1H), 6.34 (d, *J* = 3.6 Hz, 1H), 4.59 (t, *J* = 6.2 Hz, 1H), 3.34 (q, *J* = 6.7 Hz, 2H), 3.03 (t, *J* = 6.9 Hz, 2H), 2.41 (s, 3H), 1.80 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 147.9, 143.4, 141.9, 138.4, 136.9, 129.7, 127.0, 125.5, 121.6, 115.1, 96.1, 56.5, 43.0, 33.1, 29.3, 21.5.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{26}N_3O_2S$ 372.1740; Found 372.1741.

N-(2-(1-(tert-butyl)-6-fluoro-1H-indol-4-yl)ethyl)-4-methylbenzenesulfonamide (3l)



33.4 mg, yield: 43%. Yellow oil. Chromatography column, Petroleum ether/EtOAc = 5:1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 3.5 Hz, 1H), 7.19 (dd, *J* = 11.4, 1.7 Hz, 1H), 6.55 (dd, *J* = 9.9, 2.2 Hz, 1H), 6.35 (dd, *J* = 3.5, 0.9 Hz, 1H), 4.51 (t, *J* = 6.2 Hz, 1H), 3.31 (q, *J* = 6.8 Hz, 2H), 3.00 (t, *J* = 6.9 Hz, 2H), 2.41 (s, 3H), 1.69 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6 (d, *J* = 235.9 Hz), 143.3, 136.9, 134.5 (d, *J* = 12.2 Hz), 130.9 (d, *J* = 9.4 Hz), 129.6, 127.0, 126.0, 125.5 (d, *J* = 3.4 Hz), 107.6 (d, *J* = 24.6 Hz), 98.4 (d, *J* = 27.0 Hz), 98.2, 56.0, 43.4, 33.3 (d, *J* = 2.0 Hz), 29.5, 21.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ -110.46 – -110.62 (m).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{26}FN_2O_2S$ 389.1694; Found 389.1692.

N-(2-(1-(tert-butyl)-6-chloro-1H-indol-4-yl)ethyl)-4-methylbenzenesulfonamide (3m)



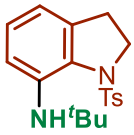
31.1 mg, yield: 38%. Yellow oil. Chromatography column, Petroleum ether/EtOAc = 5:1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 6.4 Hz, 2H), 7.50 (s, 1H), 7.28 – 7.25 (m, 3H), 6.71 (d, *J* = 1.7 Hz, 1H),

6.35 (dd, *J* = 3.4, 1.0 Hz, 1H), 4.41 (t, *J* = 6.2 Hz, 1H), 3.34 – 3.30 (m, 2H), 2.98 (t, *J* = 6.9 Hz, 2H), 2.42 (s, 3H), 1.71 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.4, 137.0, 135.1, 131.0, 129.7, 128.2, 127.0, 126.6, 126.0, 119.4, 111.9, 98.3, 56.1, 43.4, 33.2, 29.7, 21.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{26}ClN_2O_2S$ 405.1398; Found 405.1400.

N-(tert-butyl)-1-tosylindolin-7-amine (4a)



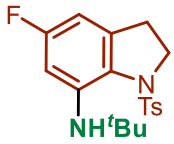
38.7 mg, yield: 56%. Yellow oil. Chromatography column, Petroleum ether/EtOAc = 10:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.98 – 6.92 (m, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.34 (d, *J* = 7.1 Hz, 1H), 5.56 (s, 1H), 3.96 (t, *J* = 7.3 Hz, 2H), 2.37 (s, 3H), 2.08 (t, *J* = 7.4 Hz, 2H), 1.44 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.1, 141.3, 138.5, 133.8, 129.6, 129.3, 127.7, 127.5, 114.6, 112.9, 53.5, 51.3, 29.8, 29.2, 21.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{25}N_2O_2S$ 345.1631; Found 345.1630.

N-(tert-butyl)-5-fluoro-1-tosylindolin-7-amine (4b)



38.0 mg, yield: 52%. Green oil. Chromatography column, Petroleum ether/EtOAc = 10:1.

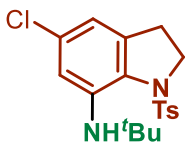
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.50 (dd, *J* = 12.5, 2.5 Hz, 1H), 6.00 (dd, *J* = 7.7, 2.2 Hz, 1H), 5.74 (s, 1H), 3.97 (t, *J* = 7.3 Hz, 2H), 2.39 (s, 3H), 2.05 (t, *J* = 7.4 Hz, 2H), 1.45 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.2 (d, *J* = 242.1 Hz), 144.3, 142.2 (d, *J* = 12.6 Hz), 139.8 (d, *J* = 11.5 Hz), 133.5, 129.4, 127.7, 124.8 (d, *J* = 2.0 Hz), 100.1 (d, *J* = 27.9 Hz), 98.9 (d, *J* = 24.5 Hz), 53.8, 51.2, 29.5, 29.5 (d, *J* = 2.3 Hz), 21.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.51 – -113.66 (m).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{24}FN_2O_2S$ 363.1537; Found 363.1537.

N-(tert-butyl)-5-chloro-1-tosylindolin-7-amine (4c)



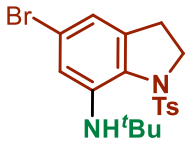
57.4 mg, yield: 76%. Brown oil. Chromatography column, Petroleum ether/EtOAc = 10:1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.20 – 7.17 (m, 2H), 6.78 (d, *J* = 2.1 Hz, 1H), 6.30 – 6.25 (m, 1H), 5.72 (s, 1H), 3.96 (t, *J* = 7.4 Hz, 2H), 2.39 (s, 3H), 2.05 (t, *J* = 7.4 Hz, 2H), 1.45 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.4, 141.8, 139.7, 133.5, 132.7, 129.5, 127.6, 127.5, 113.1, 112.2, 53.7, 51.2, 29.6, 29.2, 21.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{24}ClN_2O_2S$ 379.1242; Found 379.1241.

5-bromo-N-(tert-butyl)-1-tosylindolin-7-amine (4d)



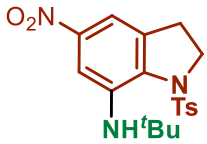
66.1 mg, yield: 78%. Brown oil. Chromatography column, Petroleum ether/EtOAc = 10:1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 1.9 Hz, 1H), 6.44 – 6.41 (m, 1H), 5.72 (s, 1H), 3.95 (t, *J* = 7.4 Hz, 2H), 2.39 (s, 3H), 2.06 (t, *J* = 7.4 Hz, 2H), 1.45 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.4, 142.1, 140.1, 133.5, 129.5, 128.0, 127.6, 120.7, 115.9, 115.1, 53.6, 51.2, 29.6, 29.1, 21.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{24}BrN_2O_2S$ 423.0736; Found 423.0738.

N-(tert-butyl)-5-nitro-1-tosylindolin-7-amine (4e)



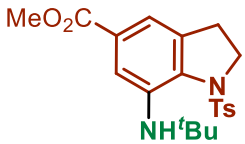
72.5 mg, yield: 93%. Brown oil. Chromatography column, Petroleum ether/EtOAc = 10:1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 2.3 Hz, 1H), 7.50 – 7.47 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.13 (m, 1H), 5.97 (s, 1H), 4.07 (t, *J* = 7.5 Hz, 2H), 2.40 (s, 3H), 2.21 (t, *J* = 7.5 Hz, 2H), 1.51 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.3, 144.9, 141.1, 139.2, 133.6, 133.4, 129.8, 127.4, 107.7, 106.9, 54.0, 51.4, 29.4, 29.0, 21.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{24}N_3O_4S$ 390.1482; Found 390.1482.

methyl 7-(tert-butylamino)-1-tosylindoline-5-carboxylate (4f)



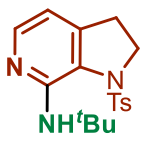
49.2 mg, yield: 61%. Yellow oil. Chromatography column, Petroleum ether/EtOAc = 8:1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.47 – 7.44 (m, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.00 (s, 1H), 5.75 (s, 1H), 4.01 (t, *J* = 7.5 Hz, 2H), 3.88 (s, 3H), 2.38 (s, 3H), 2.14 (t, *J* = 7.4 Hz, 2H), 1.48 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 144.4, 140.9, 138.6, 133.6, 132.9, 129.5, 129.2, 127.5, 115.2, 113.7, 53.8, 52.1, 51.3, 29.7, 29.0, 21.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{27}N_2O_4S$ 403.1686; Found 403.1685.

N-(tert-butyl)-1-tosyl-2,3-dihydro-1H-pyrrolo[2,3-c]pyridin-7-amine (4g)



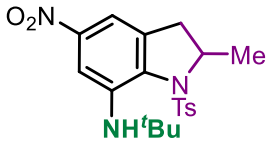
38.3 mg, yield: 56%. Colourless oil. Chromatography column, Petroleum ether/EtOAc = 10:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 4.9 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.20 – 7.17 (m, 2H), 6.25 – 6.20 (m, 2H), 3.97 (t, *J* = 7.6 Hz, 2H), 2.38 (s, 3H), 2.11 (t, *J* = 7.5 Hz, 2H), 1.54 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.9, 145.9, 145.6, 144.4, 133.4, 129.5, 127.6, 123.5, 108.2, 52.9, 51.4, 29.3, 29.1, 21.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{24}N_3O_2S$ 346.1584; Found 346.1583.

N-(tert-butyl)-2-methyl-5-nitro-1-tosylindolin-7-amine (4h)



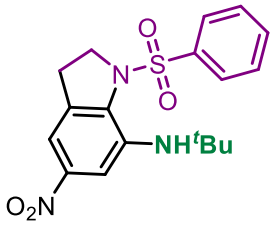
41.4 mg, yield: 51%. Yellow oil. Chromatography column, Petroleum ether/EtOAc = 10:1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 2.3 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.21 – 7.18 (m, 2H), 7.17 – 7.14 (m, 1H), 5.95 (s, 1H), 4.55 (p, *J* = 7.3 Hz, 1H), 2.39 (s, 3H), 2.26 (dd, *J* = 15.7, 7.9 Hz, 1H), 2.04 (d, *J* = 15.7 Hz, 1H), 1.50 (s, 9H), 1.23 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.2, 144.7, 141.8, 138.0, 133.5, 132.3, 129.7, 127.3, 108.3, 107.7, 61.6, 51.6, 35.7, 29.5, 21.6, 21.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{26}N_3O_4S$ 404.1639; Found 404.1640.

N-(tert-butyl)-5-nitro-1-(phenylsulfonyl)indolin-7-amine (4i)



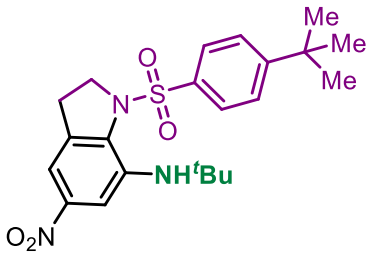
62.1 mg, yield: 83%. Yellow oil. Chromatography column, Petroleum ether/EtOAc = 8:1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 2.3 Hz, 1H), 7.63 – 7.58 (m, 3H), 7.44 – 7.41 (m, 2H), 7.14 – 7.11 (m, 1H), 5.97 (s, 1H), 4.08 (t, *J* = 7.5 Hz, 2H), 2.19 (t, *J* = 7.5 Hz, 2H), 1.51 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.3, 141.0, 139.2, 136.2, 133.8, 133.3, 129.1, 127.4, 107.7, 106.9, 54.0, 51.4, 29.3, 29.0.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{22}N_3O_4S$ 376.1326; Found 376.1326.

N-(tert-butyl)-1-((4-(tert-butyl)phenyl)sulfonyl)-5-nitroindolin-7-amine (4j)



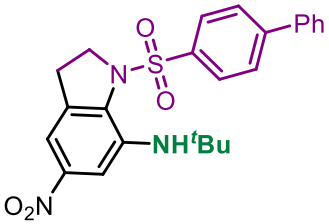
78.8 mg, yield: 91%. Yellow oil. Chromatography column, Petroleum ether/EtOAc =10:1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 2.3 Hz, 1H), 7.54 – 7.52 (m, 2H), 7.44 – 7.41 (m, 2H), 7.16 – 7.14 (m, 1H), 5.98 (s, 1H), 4.06 (t, *J* = 7.5 Hz, 2H), 2.19 (t, *J* = 7.5 Hz, 2H), 1.51 (s, 9H), 1.30 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.0, 147.3, 141.1, 139.2, 133.6, 133.3, 127.3, 126.1, 107.8, 106.9, 54.0, 51.4, 35.2, 31.0, 29.4, 29.0.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{30}N_3O_4S$ 432.1952; Found 432.1953.

1-([1,1'-biphenyl]-4-ylsulfonyl)-N-(tert-butyl)-5-nitroindolin-7-amine (4k)



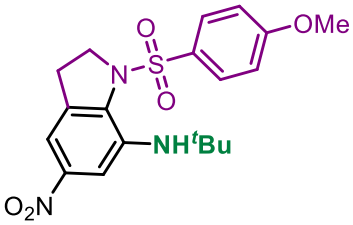
82.6 mg, yield: 92%. Yellow oil. Chromatography column, Petroleum ether/EtOAc =8:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.63 (m, 5H), 7.59 – 7.55 (m, 2H), 7.48 – 7.38 (m, 3H), 7.17 – 7.13 (m, 1H), 6.00 (s, 1H), 4.11 (t, *J* = 7.5 Hz, 2H), 2.26 (t, *J* = 7.5 Hz, 2H), 1.52 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.3, 146.6, 141.0, 139.2, 138.5, 134.8, 133.4, 129.0, 128.8, 127.9, 127.5, 127.2, 107.7, 107.0, 54.1, 51.4, 29.3, 29.1.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{26}N_3O_4S$ 452.1639; Found 452.1640.

N-(tert-butyl)-1-((4-methoxyphenyl)sulfonyl)-5-nitroindolin-7-amine (4l)



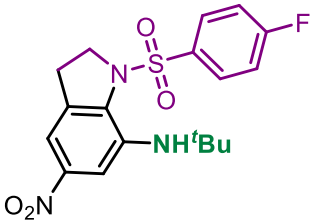
71.3 mg, yield: 88%. Yellow oil. Chromatography column, Petroleum ether/EtOAc =5:1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 2.3 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.16 – 7.13 (m, 1H), 6.89 – 6.85 (m, 2H), 5.96 (s, 1H), 4.06 (t, *J* = 7.5 Hz, 2H), 3.84 (s, 3H), 2.24 (t, *J* = 7.5 Hz, 2H), 1.50 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.8, 147.3, 141.1, 139.3, 133.7, 129.5, 127.8, 114.3, 107.7, 106.9, 55.6, 54.0, 51.4, 29.3, 29.1.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{24}N_3O_5S$ 406.1431; Found 406.1432.

N-(tert-butyl)-1-((4-fluorophenyl)sulfonyl)-5-nitroindolin-7-amine (4m)



62.3 mg, yield: 79%. Yellow oil. Chromatography column, Petroleum ether/EtOAc =8:1.

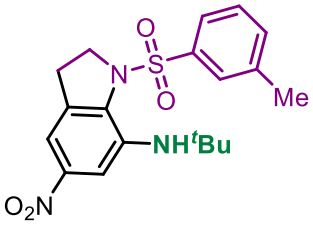
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 2.3 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.17 – 7.15 (m, 1H), 7.14 – 7.08 (m, 2H), 5.91 (s, 1H), 4.08 (t, *J* = 7.5 Hz, 2H), 2.25 (t, *J* = 7.5 Hz, 2H), 1.51 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8 (d, *J* = 257.6 Hz), 147.5, 141.1, 139.1, 133.0, 132.4 (d, *J* = 3.4 Hz), 130.2 (d, *J* = 9.6 Hz), 116.5 (d, *J* = 22.6 Hz), 107.8, 106.9, 54.1, 51.5, 29.4, 29.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -102.46 – -102.57 (m).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}FN_3O_4S$ 394.1231; Found 394.1232.

N-(tert-butyl)-5-nitro-1-(m-tolylsulfonyl)indolin-7-amine (4n)



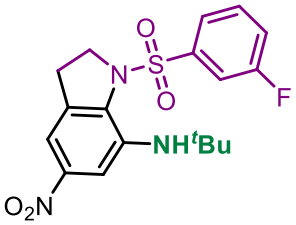
63.8 mg, yield: 82%. Yellow oil. Chromatography column, Petroleum ether/EtOAc =8:1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 2.2 Hz, 1H), 7.44 (s, 1H), 7.41 – 7.36 (m, 2H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.15 – 7.12 (m, 1H), 5.97 (s, 1H), 4.08 (t, *J* = 7.5 Hz, 2H), 2.32 (s, 3H), 2.22 (t, *J* = 7.5 Hz, 2H), 1.51 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.2, 141.0, 139.4, 139.2, 136.1, 134.5, 133.5, 128.9, 127.7, 124.5, 107.7, 106.9, 54.1, 51.4, 29.3, 29.0, 21.2.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{24}N_3O_4S$ 390.1482; Found 390.1482.

N-(tert-butyl)-1-((3-fluorophenyl)sulfonyl)-5-nitroindolin-7-amine (4o)



63.7 mg, yield: 81%. Yellow oil. Chromatography column, Petroleum ether/EtOAc =8:1.

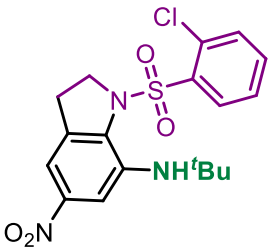
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 2.3 Hz, 1H), 7.43 – 7.36 (m, 3H), 7.34 – 7.28 (m, 1H), 7.19 – 7.14 (m, 1H), 5.91 (s, 1H), 4.11 (t, *J* = 7.5 Hz, 2H), 2.29 (t, *J* = 7.5 Hz, 2H), 1.51 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.1 (d, *J* = 253.1 Hz), 147.5, 140.9, 139.0, 138.3 (d, *J* = 6.6 Hz), 132.8, 131.0 (d, *J* = 7.9 Hz), 123.3 (d, *J* = 3.5 Hz), 121.1 (d, *J* = 20.9 Hz), 114.8 (d, *J* = 24.7 Hz), 107.8, 106.9, 54.2, 51.5, 29.3, 29.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -108.56 – -108.64 (m).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}FN_3O_4S$ 394.1231; Found 394.1232.

N-(tert-butyl)-1-((2-chlorophenyl)sulfonyl)-5-nitroindolin-7-amine (4p)



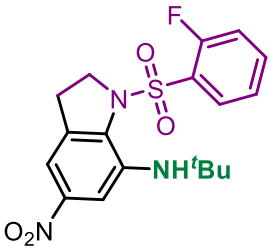
59.7 mg, yield: 73%. Yellow oil. Chromatography column, Petroleum ether/EtOAc =5:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.63 (d, *J* = 2.3 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.41 – 7.36 (m, 1H), 7.25 – 7.21 (m, 1H), 5.93 (s, 1H), 4.10 (t, *J* = 7.4 Hz, 2H), 2.55 (t, *J* = 7.4 Hz, 2H), 1.48 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.4, 140.8, 138.9, 135.2, 134.7, 132.9, 132.7, 132.6, 132.3, 127.3, 107.6, 107.0, 54.2, 51.4, 29.4, 29.3.

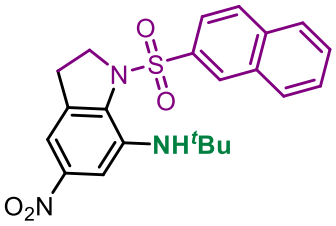
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}ClN_3O_4S$ 410.0936; Found 410.0937.

N-(tert-butyl)-1-((2-fluorophenyl)sulfonyl)-5-nitroindolin-7-amine (4q)



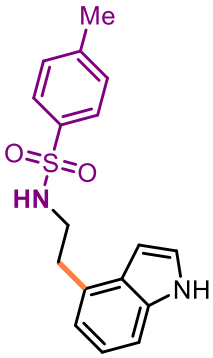
33.6 mg, yield: 43%. Yellow oil. Chromatography column, Petroleum ether/EtOAc =5:1.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 1H), 7.64 (d, *J* = 2.3 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.28 – 7.23 (m, 1H), 7.21 – 7.19 (m, 1H), 7.14 – 7.09 (m, 1H), 5.91 (s, 1H), 4.16 (t, *J* = 7.5 Hz, 2H), 2.53 (t, *J* = 7.5 Hz, 2H), 1.49 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2 (d, *J* = 258.4 Hz), 147.4, 140.9, 138.7, 136.3 (d, *J* = 8.6 Hz), 132.4, 131.2, 124.9 (d, *J* = 14.4 Hz), 124.7 (d, *J* = 3.9 Hz), 117.5 (d, *J* = 22.0 Hz), 107.7, 106.8, 54.2, 51.4, 29.23, 29.20.
^{19}F NMR (376 MHz, $CDCl_3$) δ -106.02 – -106.13 (m).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}FN_3O_4S$ 394.1231; Found 394.1234.

N-(tert-butyl)-1-(naphthalen-2-ylsulfonyl)-5-nitroindolin-7-amine (4r)



73.7 mg, yield: 87%. Yellow oil. Chromatography column, Petroleum ether/EtOAc =8:1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.87 (dd, *J* = 8.3, 3.1 Hz, 2H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.70 (d, *J* = 2.2 Hz, 1H), 7.66 – 7.63 (m, 1H), 7.61 – 7.58 (m, 1H), 7.49 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.06 (s, 1H), 6.04 (s, 1H), 4.14 (t, *J* = 7.5 Hz, 2H), 2.16 (t, *J* = 7.5 Hz, 2H), 1.55 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 147.3, 141.0, 139.1, 135.1, 133.49, 133.46, 131.9, 129.4, 129.21, 129.19, 129.1, 128.0, 127.8, 122.1, 107.7, 106.9, 54.2, 51.4, 29.4, 29.1.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{24}N_3O_4S$ 426.1482; Found 426.1484.

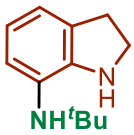
N-(2-(1H-indol-4-yl)ethyl)-4-methylbenzenesulfonamide (5)



43.6 mg, yield: 69%. Colourless oil. Chromatography column, Petroleum ether/EtOAc =2:1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 2.9 Hz, 1H), 7.03 (t, *J* = 7.7 Hz, 1H), 6.76 (d, *J* = 7.1 Hz, 1H), 6.38 (t, *J* = 2.6 Hz, 1H), 4.62 (t, *J* = 6.2 Hz, 1H), 3.28 (q, *J* = 6.7 Hz, 2H), 3.00 (t, *J* = 7.0 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 136.6, 135.7, 129.5, 129.4, 127.1, 126.9, 124.2, 121.9, 119.6, 110.0, 100.1, 43.4, 33.4, 21.4.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{19}N_2O_2S$ 315.1162; Found 315.1160.

N-(2-(1H-indol-4-yl)ethyl)-4-methylbenzenesulfonamide (6)

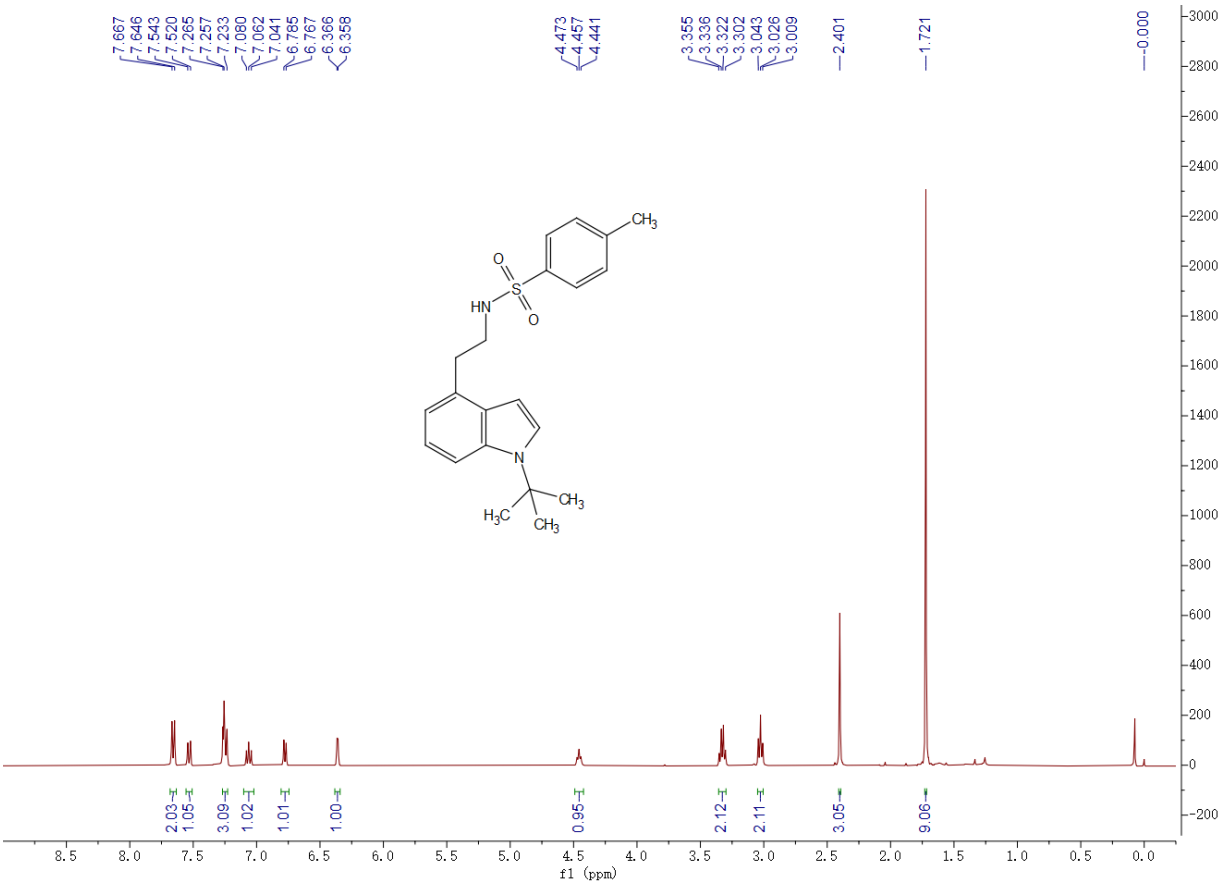


25.2 mg, yield: 66%. Colourless oil. Chromatography column, Petroleum ether/EtOAc =5:1.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 1H), 6.71 – 6.69 (m, 2H), 3.52 (t, *J* = 8.4 Hz, 2H), 3.13 (s, 2H), 3.06 (t, 2H), 1.33 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 144.1, 138.5, 133.8, 129.3, 127.6, 127.4, 53.5, 29.8, 29.2, 21.6.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{19}N_2$ 191.1543; Found 191.1541.

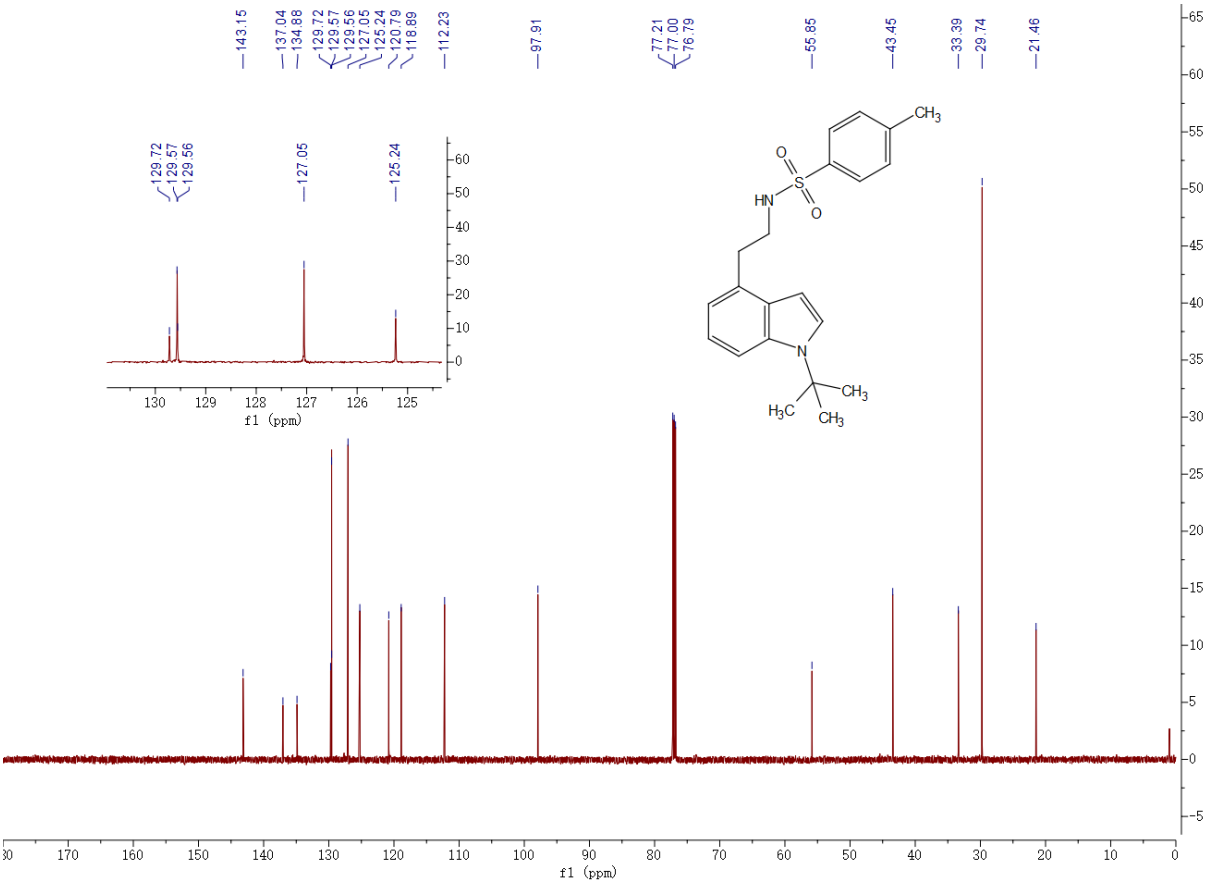
8. NMR Spectroscopic Data

N-(2-(1-(tert-butyl)-1H-indol-4-yl)ethyl)-4-methylbenzenesulfonamide (3a)

^{1}H NMR (400 MHz, $CDCl_3$)

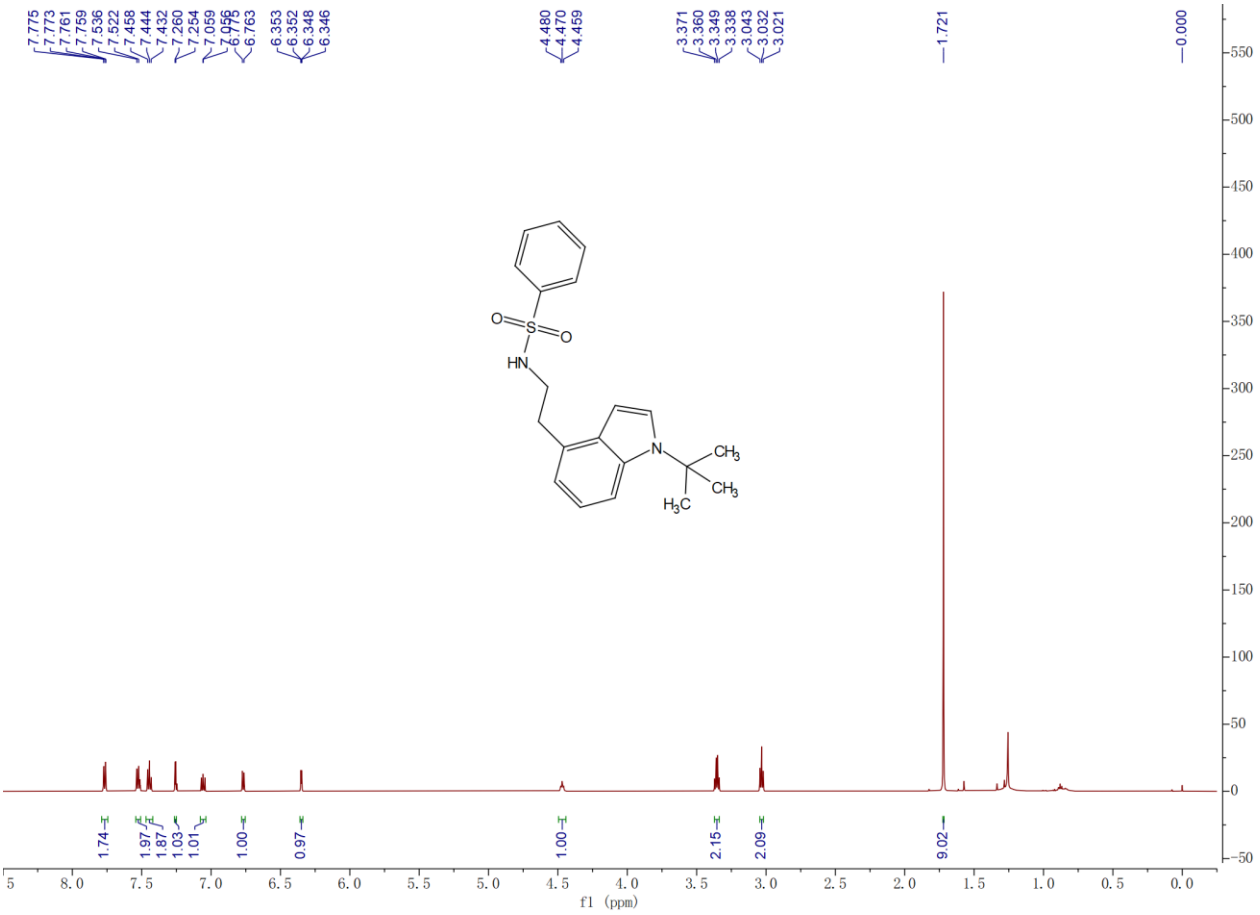


^{13}C NMR (151 MHz, $CDCl_3$)

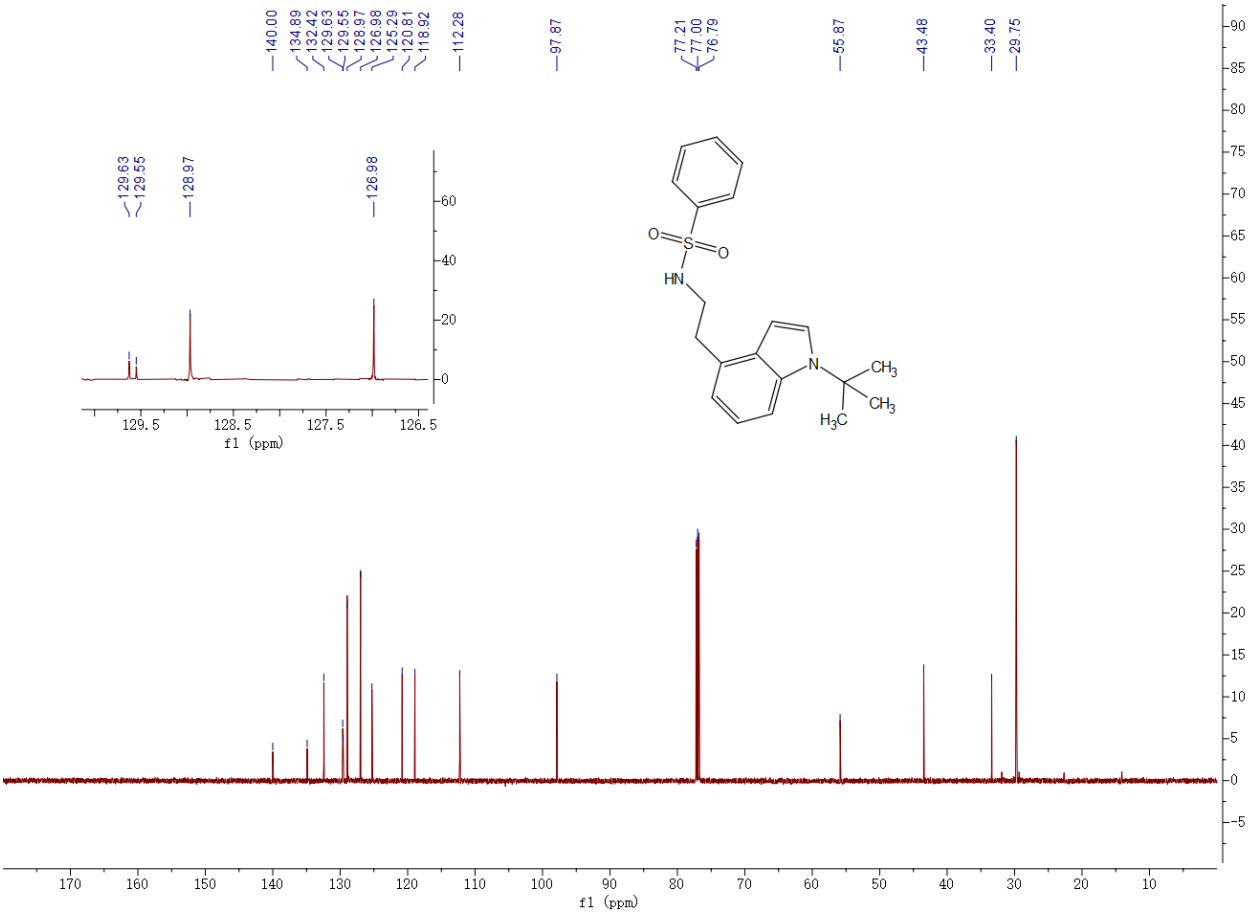


N-(2-(1-(tert-butyl)-1H-indol-4-yl)ethyl)benzenesulfonamide (3b)

^{1}H NMR (600 MHz, $CDCl_3$)

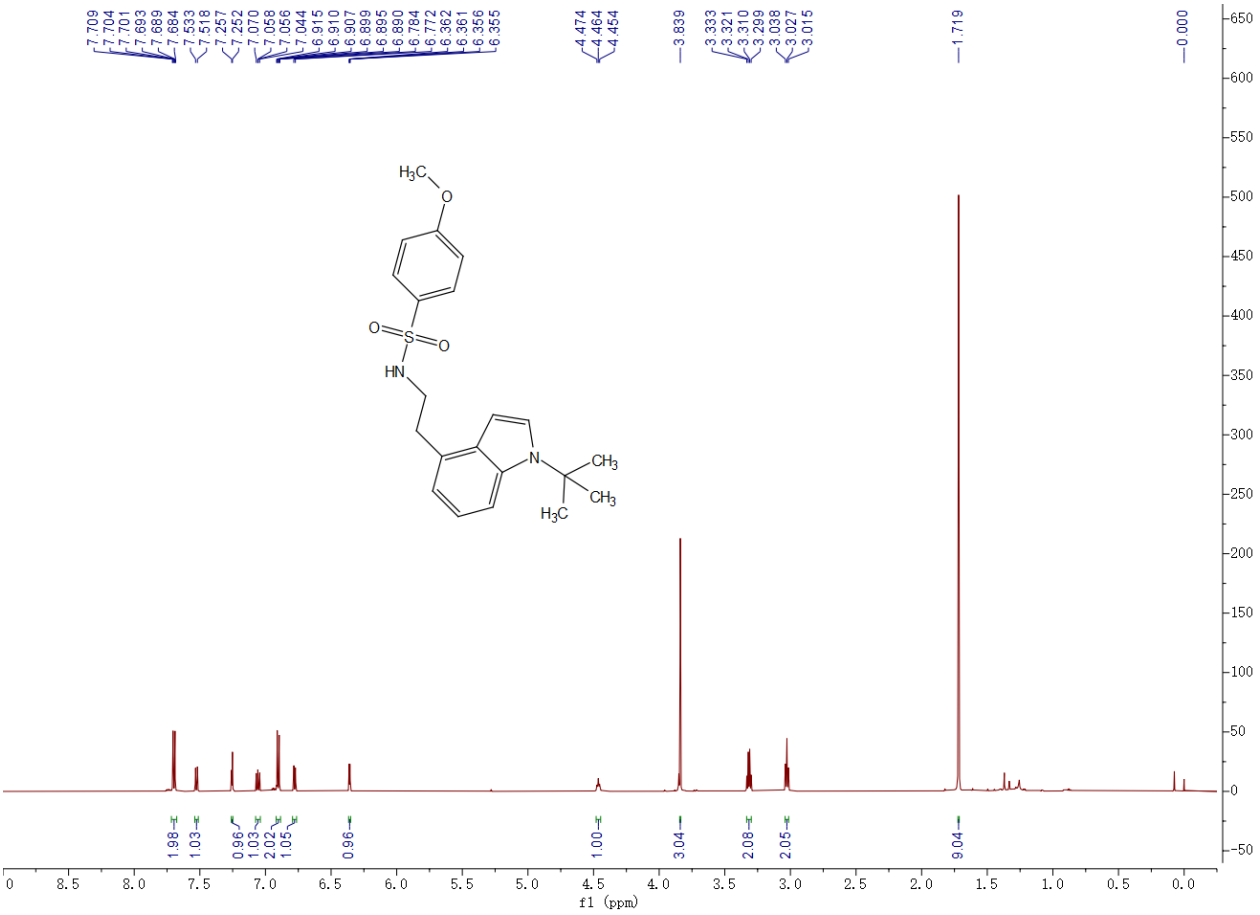


^{13}C NMR (151 MHz, $CDCl_3$)

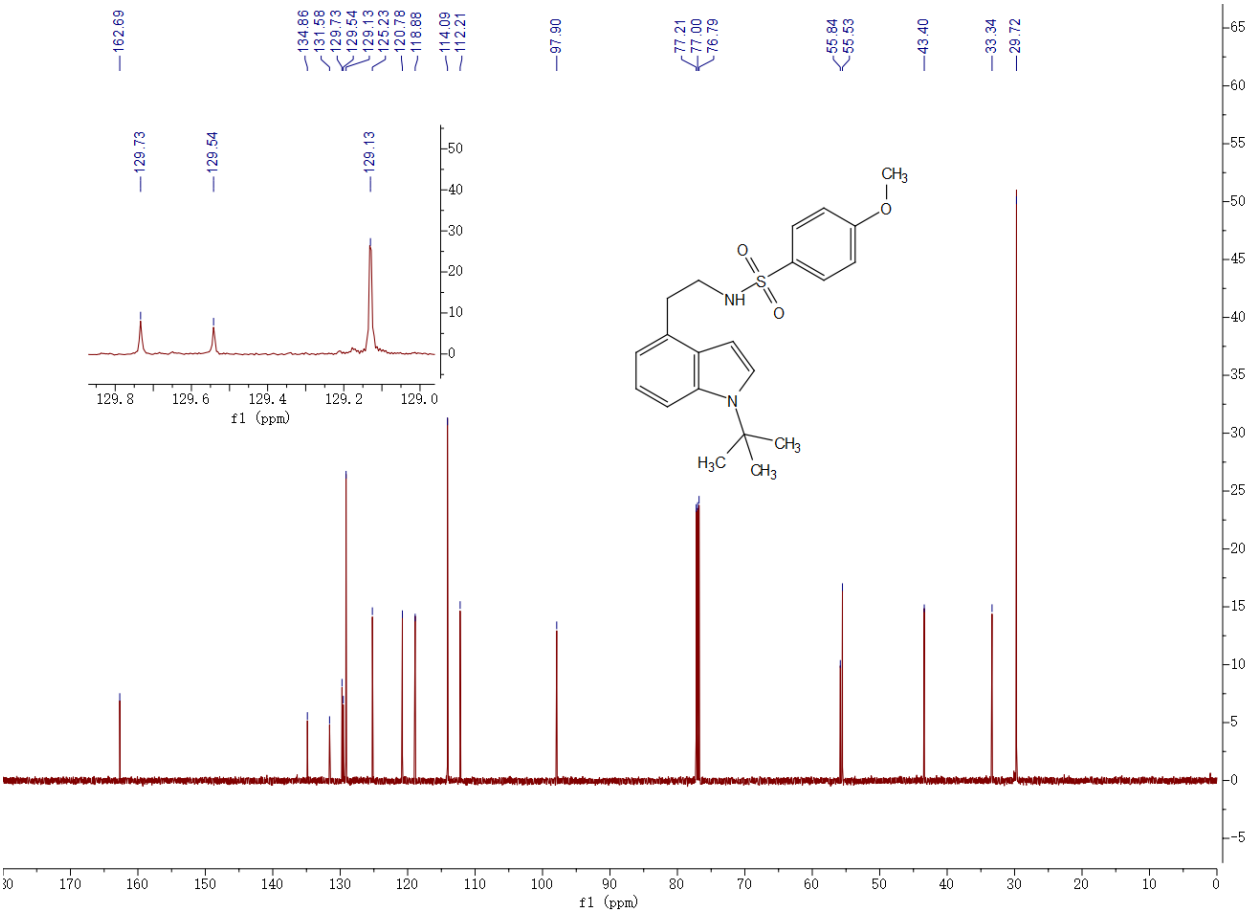


N-(2-(1-(tert-butyl)-1H-indol-4-yl)ethyl)-4-methoxybenzenesulfonamide (3c)

^{1}H NMR (600 MHz, $CDCl_3$)

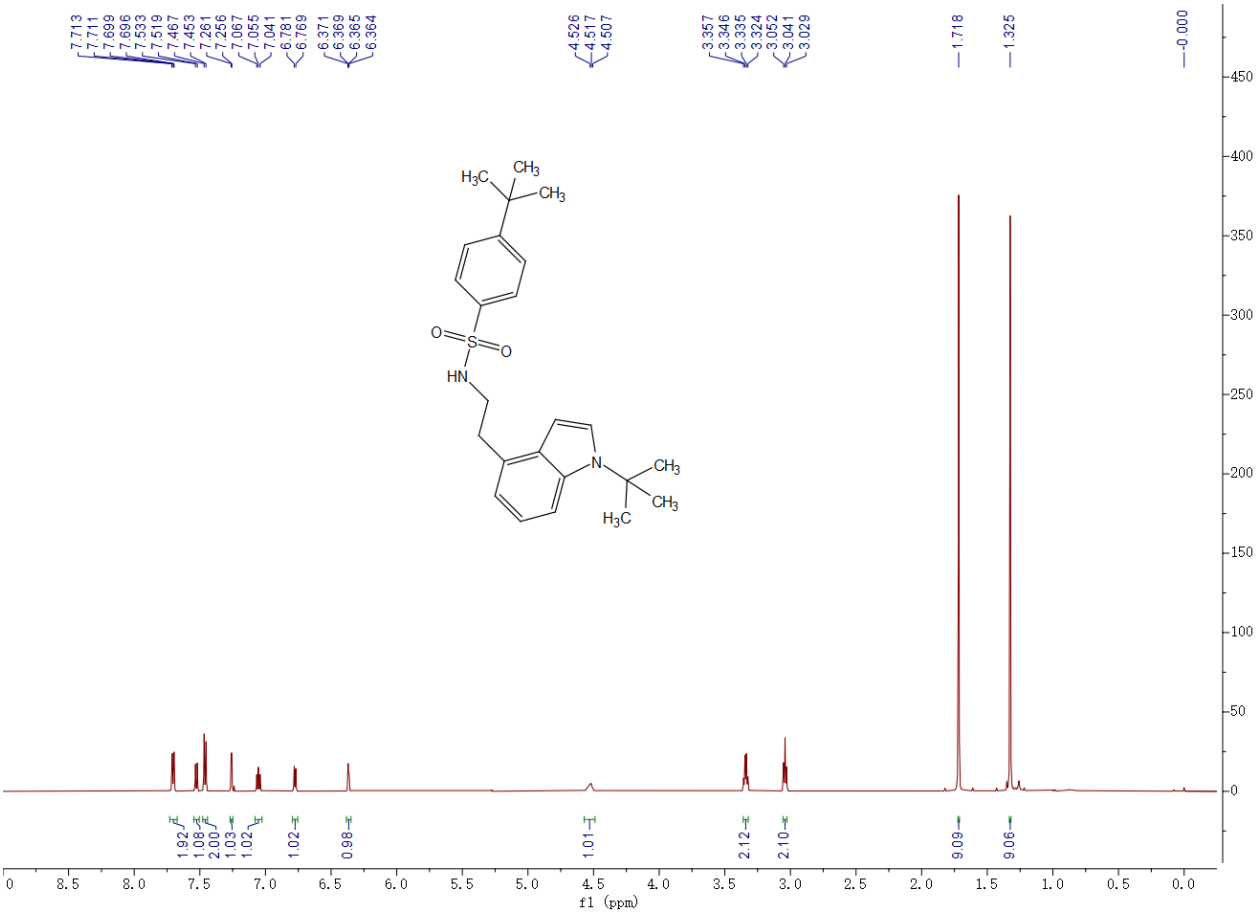


^{13}C NMR (151 MHz, $CDCl_3$)

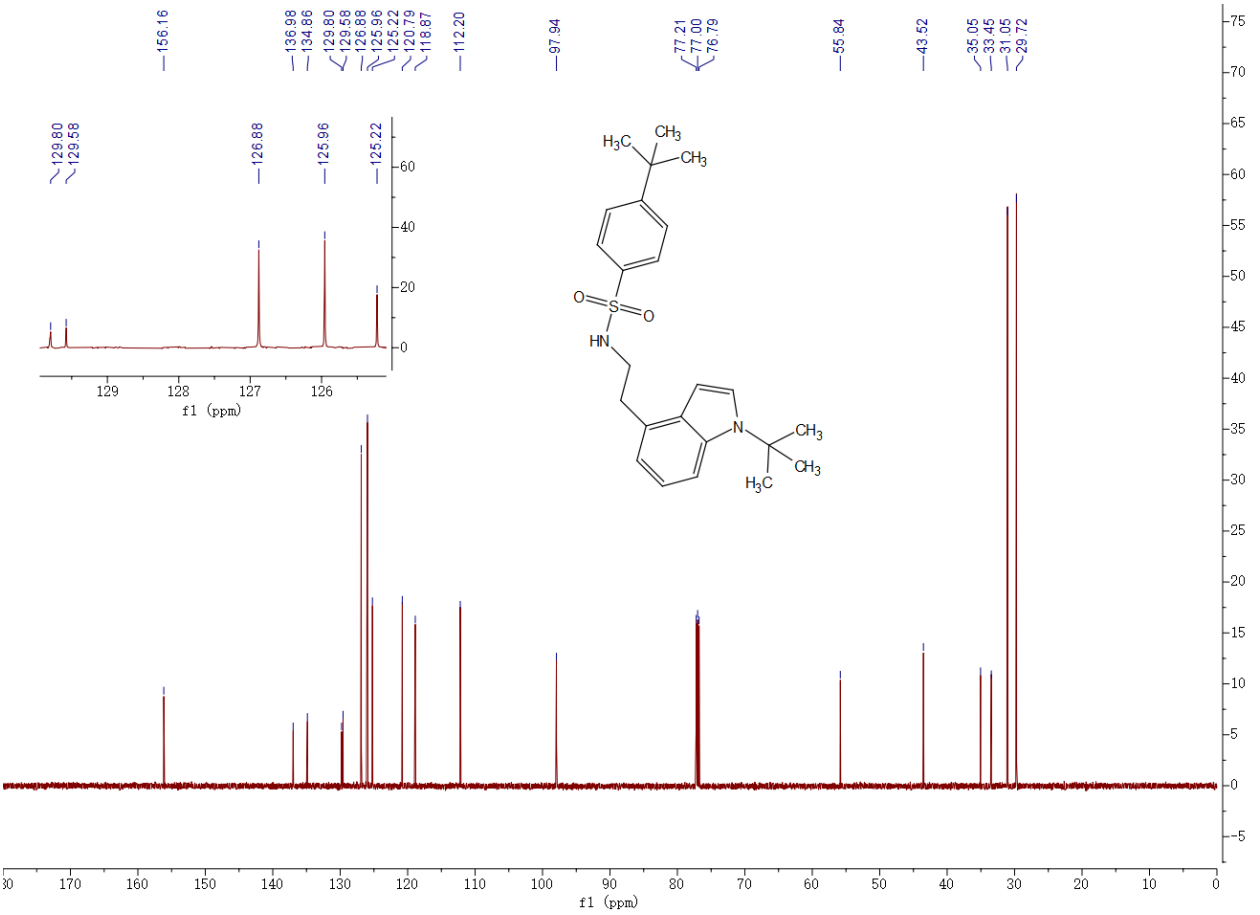


4-(tert-butyl)-N-(2-(1-(tert-butyl)-1H-indol-4-yl)ethyl)benzenesulfonamide (3d)

^{1}H NMR (600 MHz, $CDCl_3$)

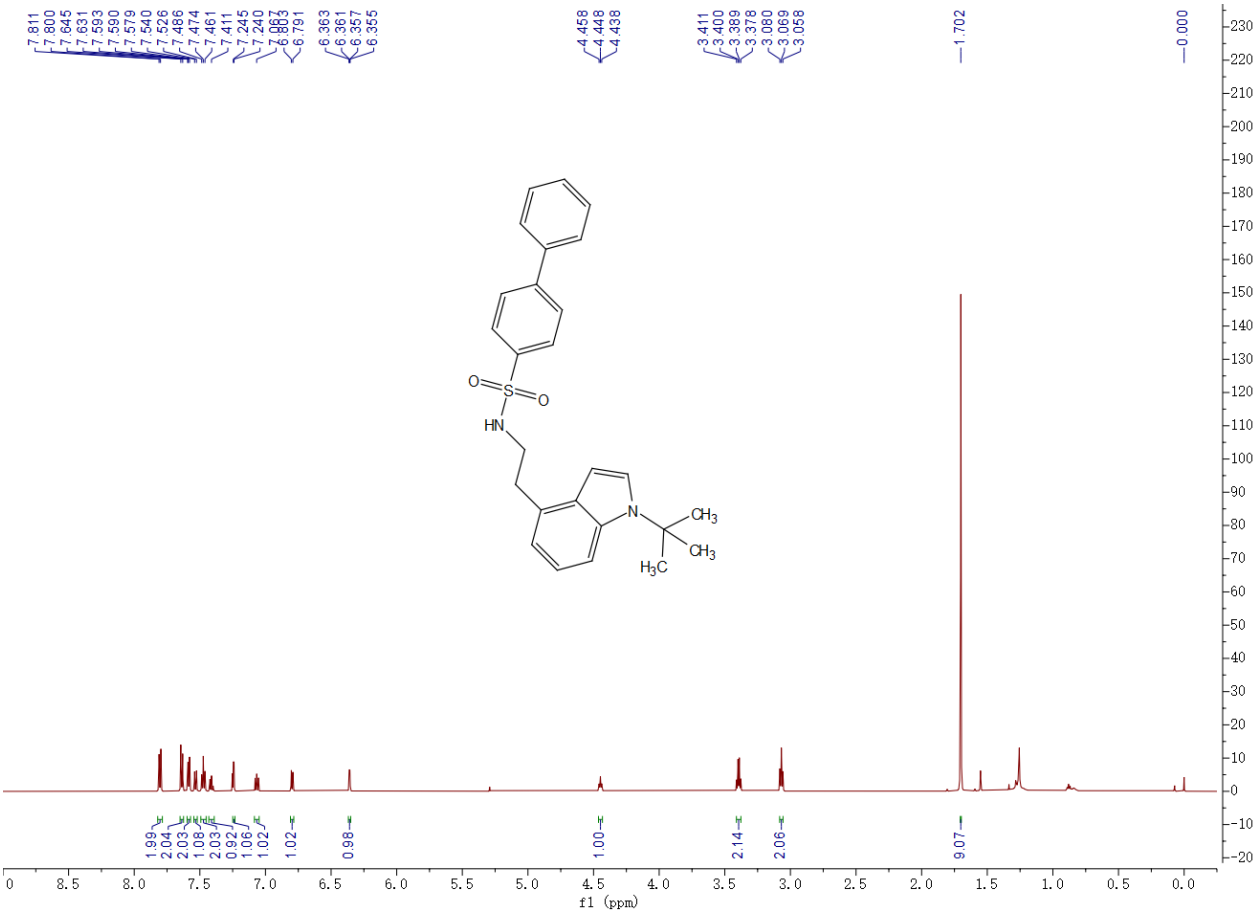


^{13}C NMR (151 MHz, $CDCl_3$)

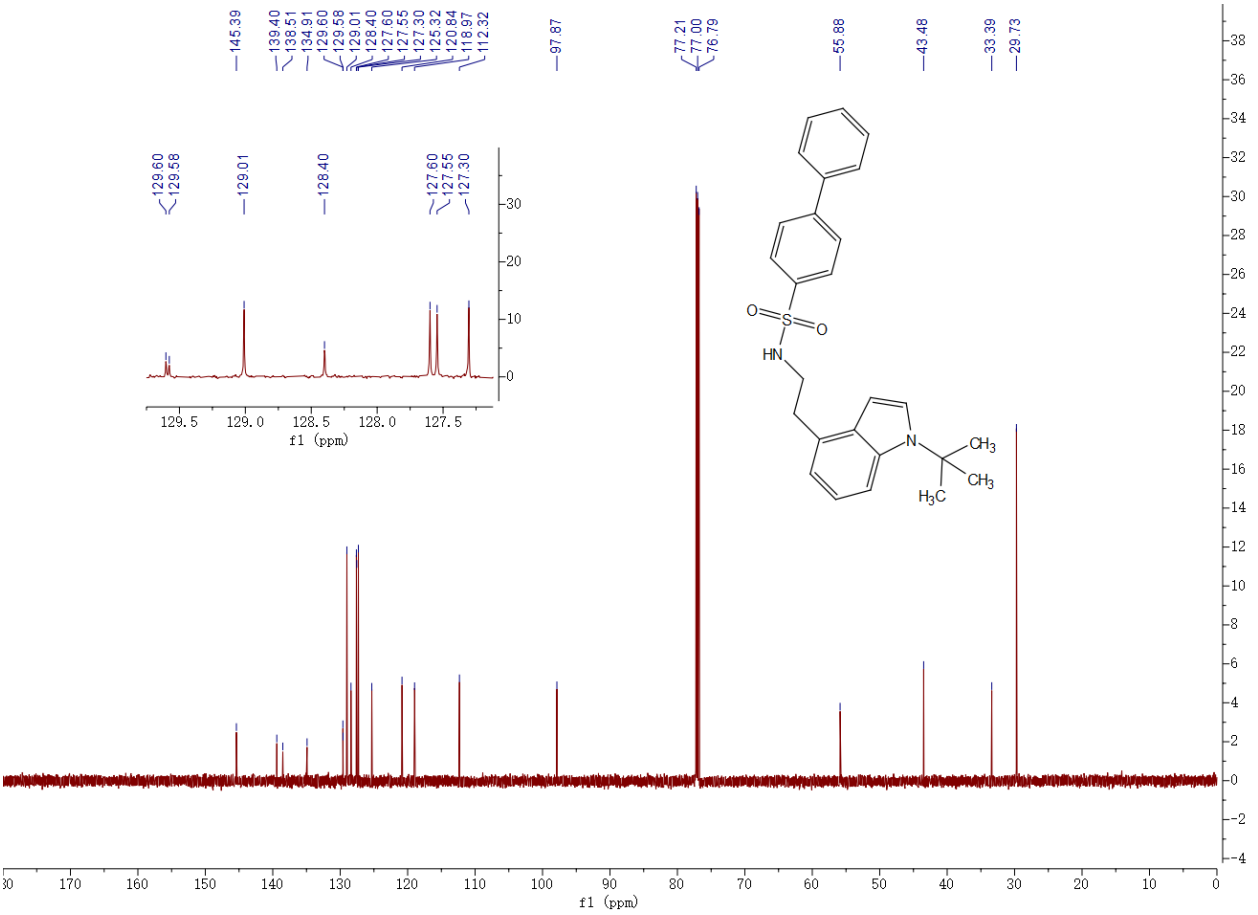


N-(2-(1-(tert-butyl)-1H-indol-4-yl)ethyl)-[1,1'-biphenyl]-4-sulfonamide (3e)

^{1}H NMR (600 MHz, $CDCl_3$)

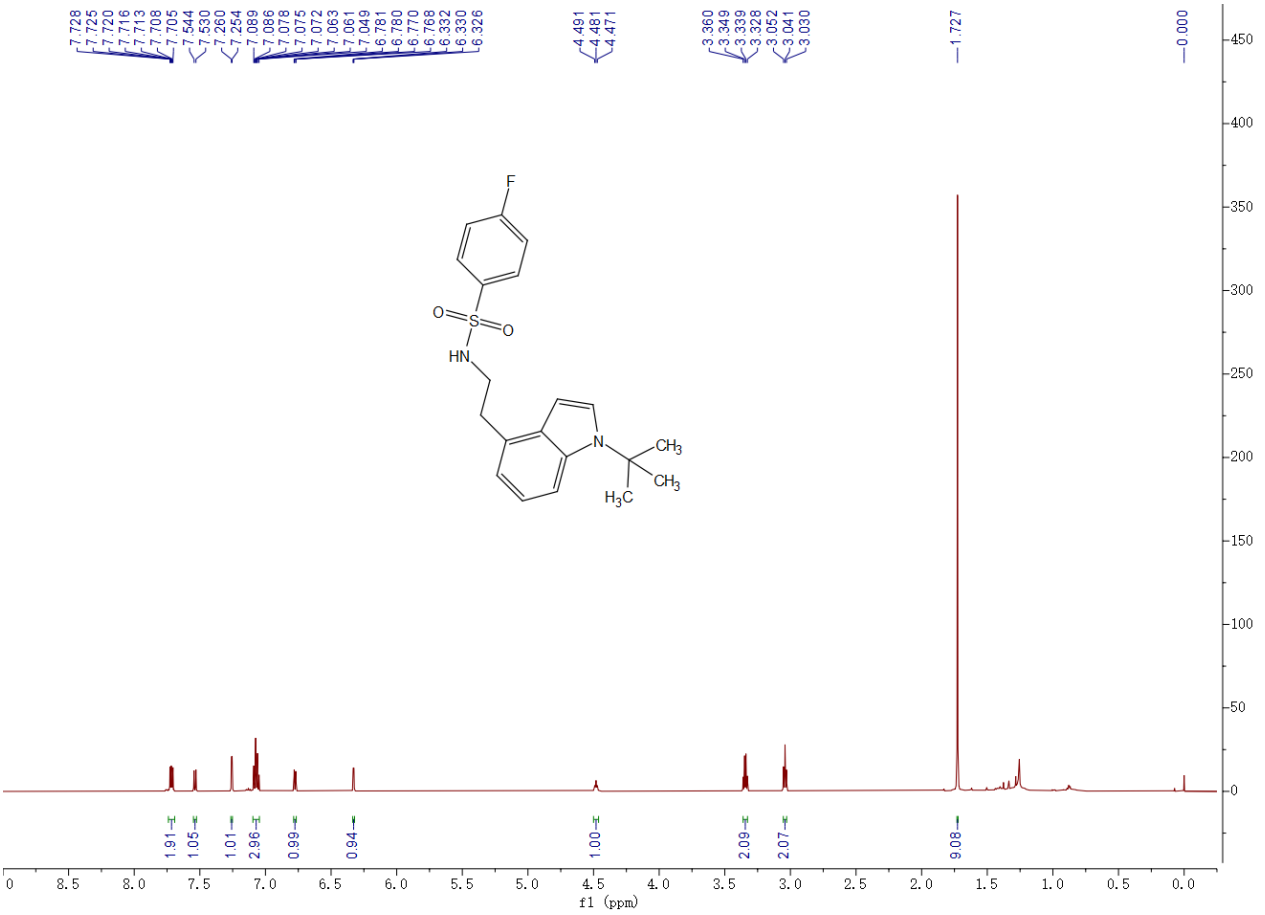


^{13}C NMR (151 MHz, $CDCl_3$)

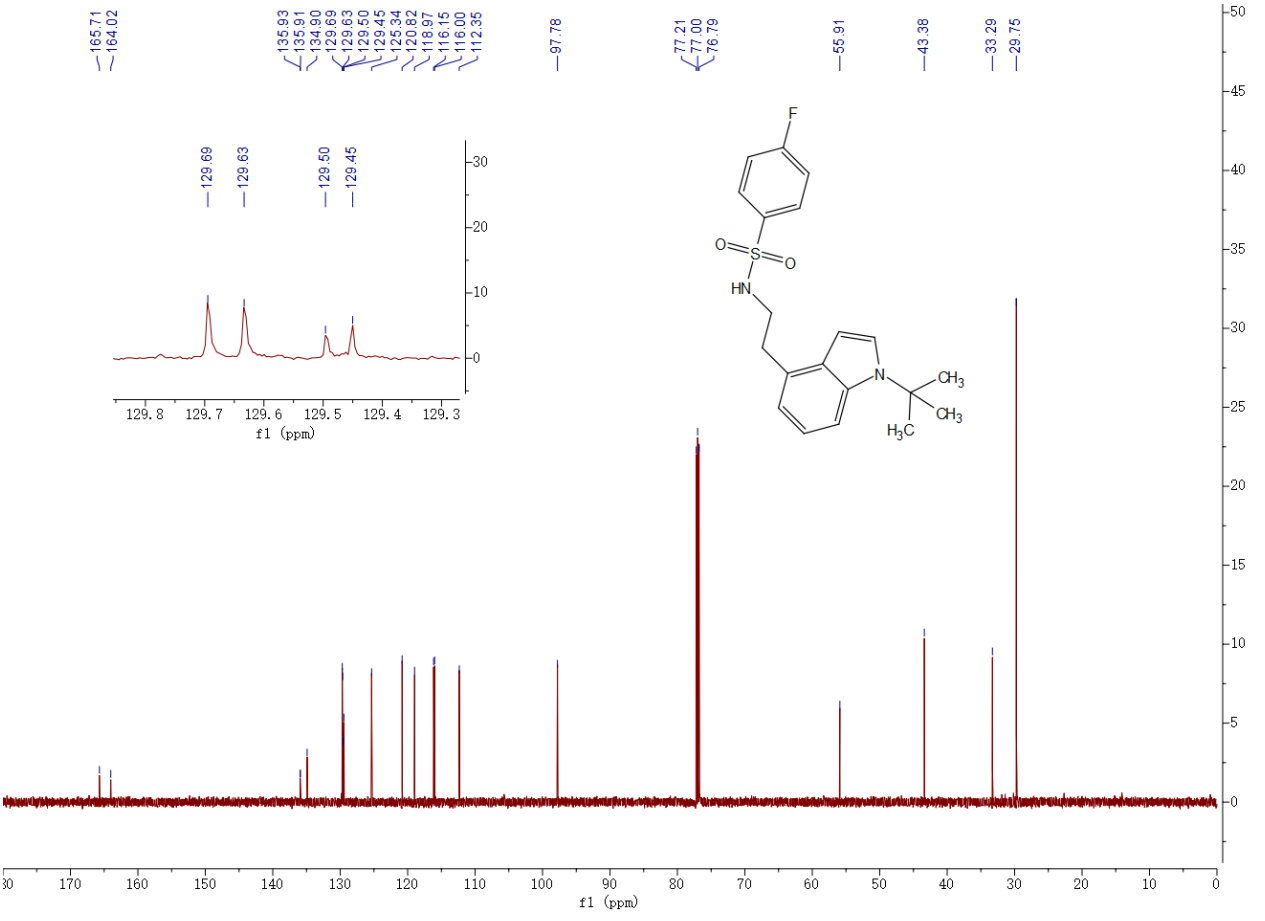


N-(2-(1-(tert-butyl)-1H-indol-4-yl)ethyl)-4-fluorobenzenesulfonamide (3f)

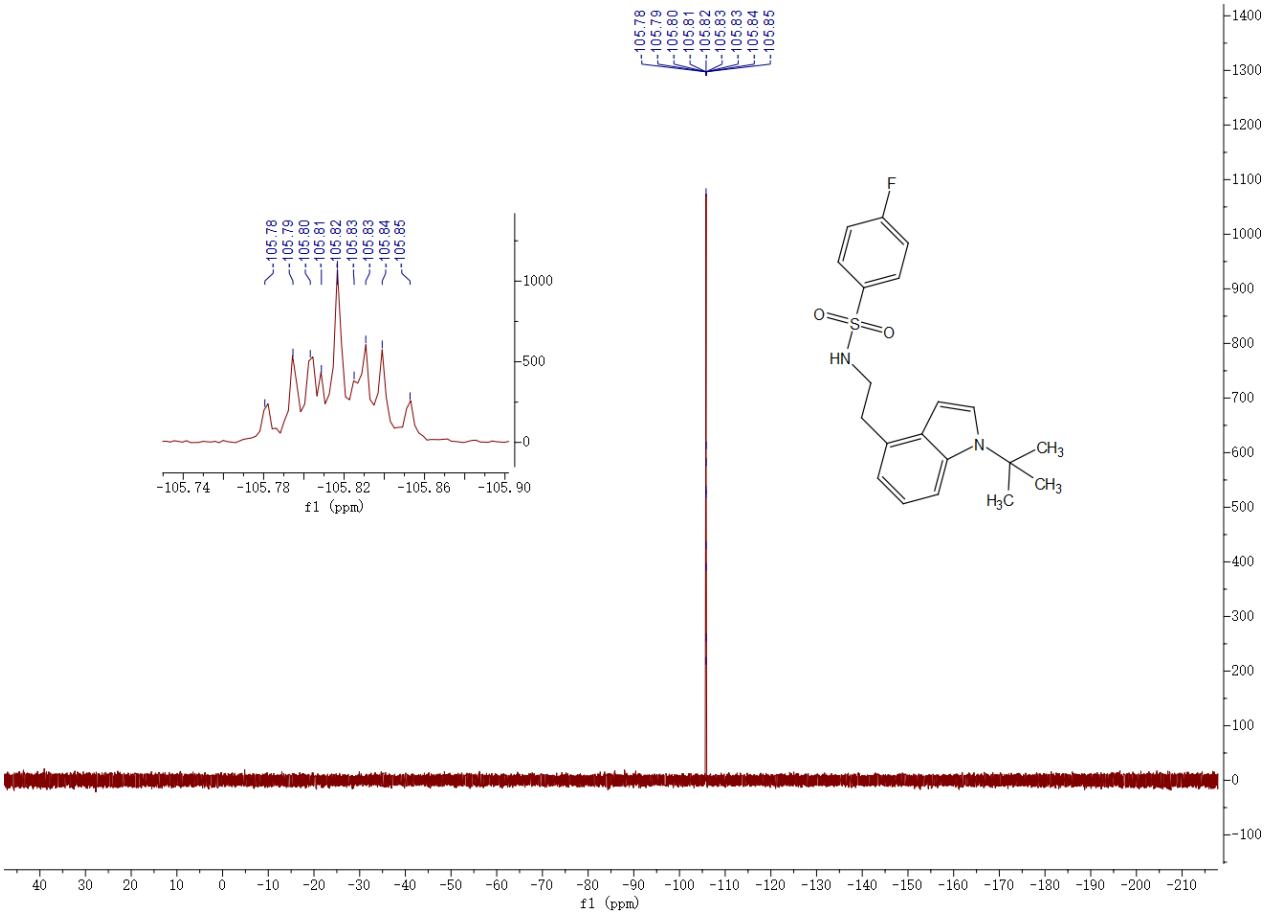
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

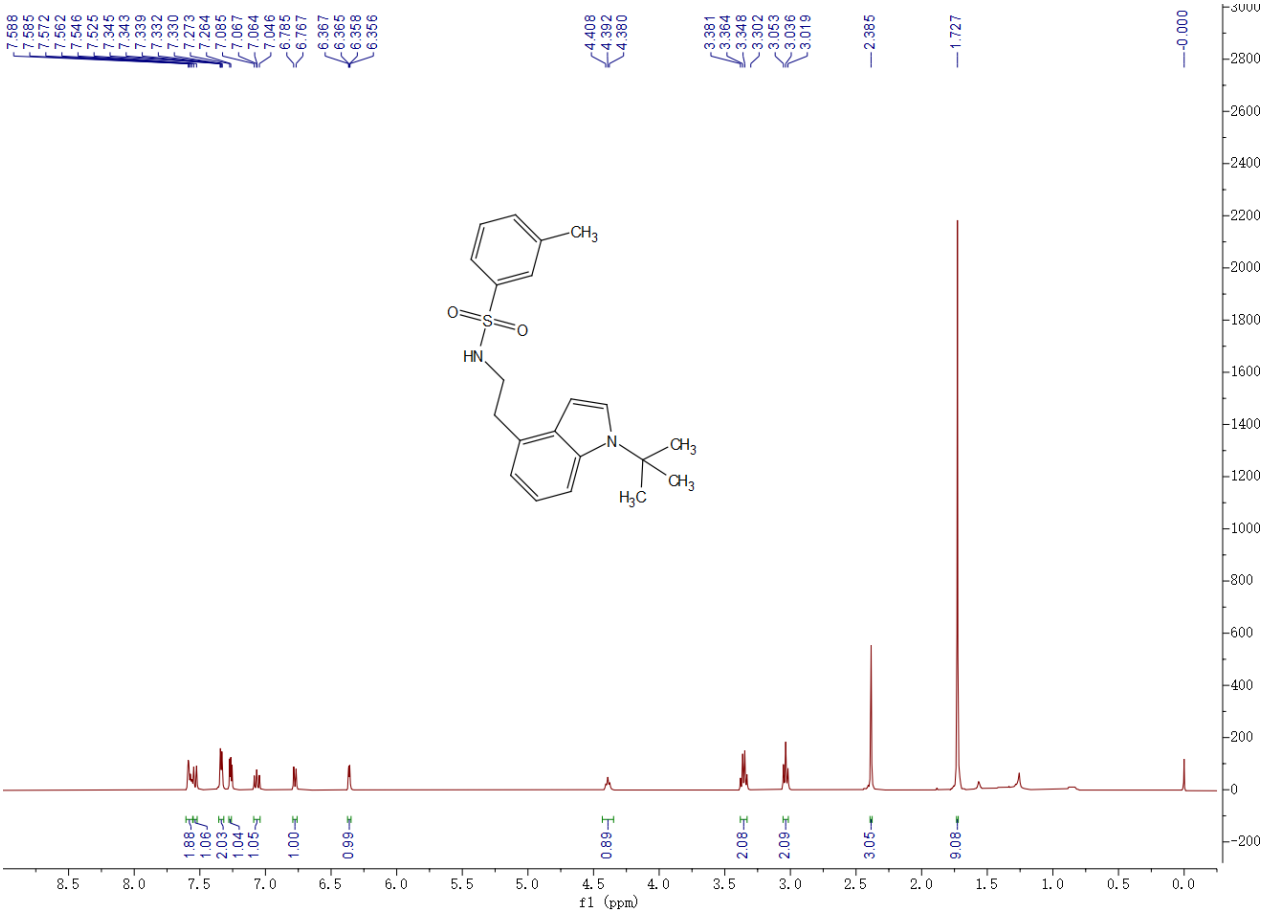


^{19}F NMR (376 MHz, $CDCl_3$)

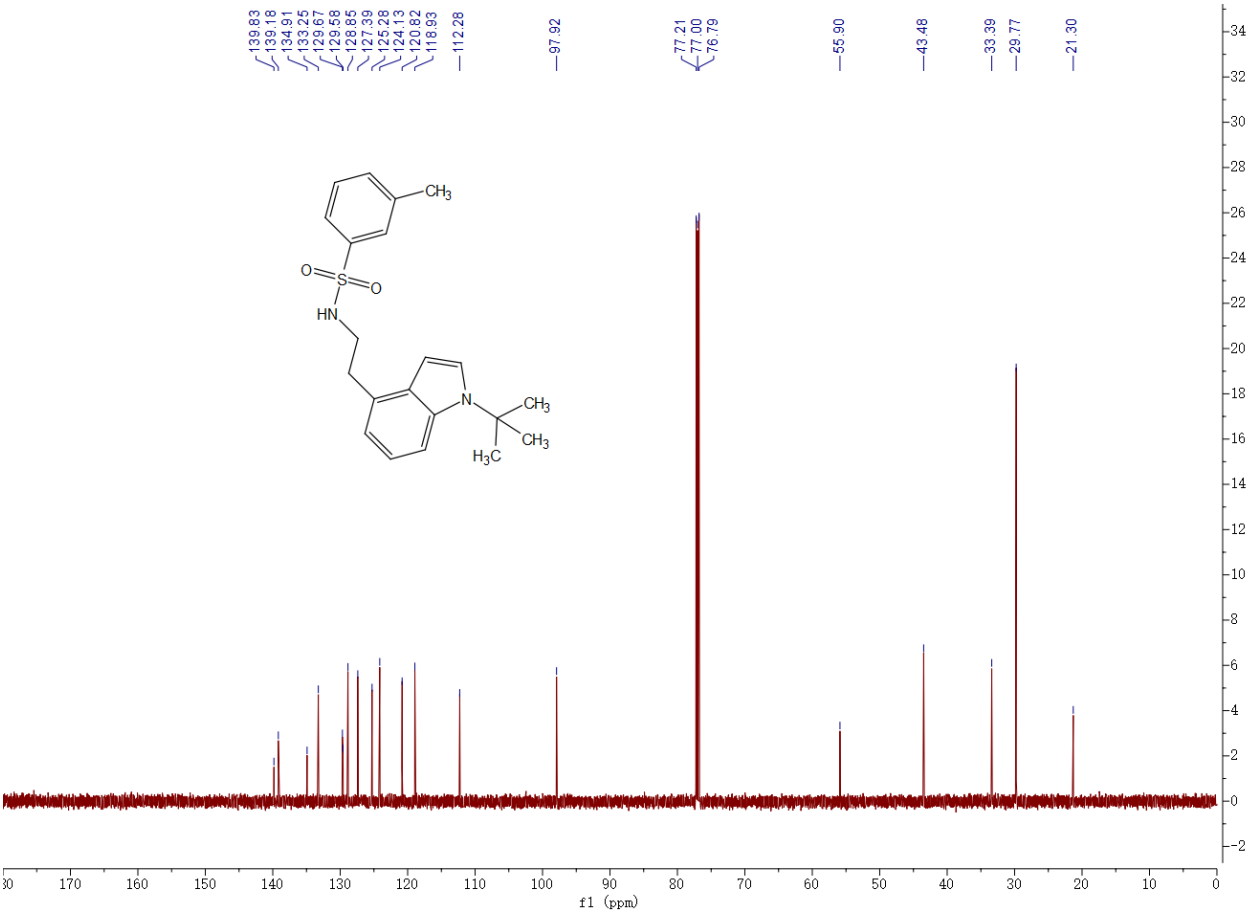


N-(2-(1-(tert-butyl)-1H-indol-4-yl)ethyl)-3-methylbenzenesulfonamide (3g)

^{1}H NMR (400 MHz, $CDCl_3$)

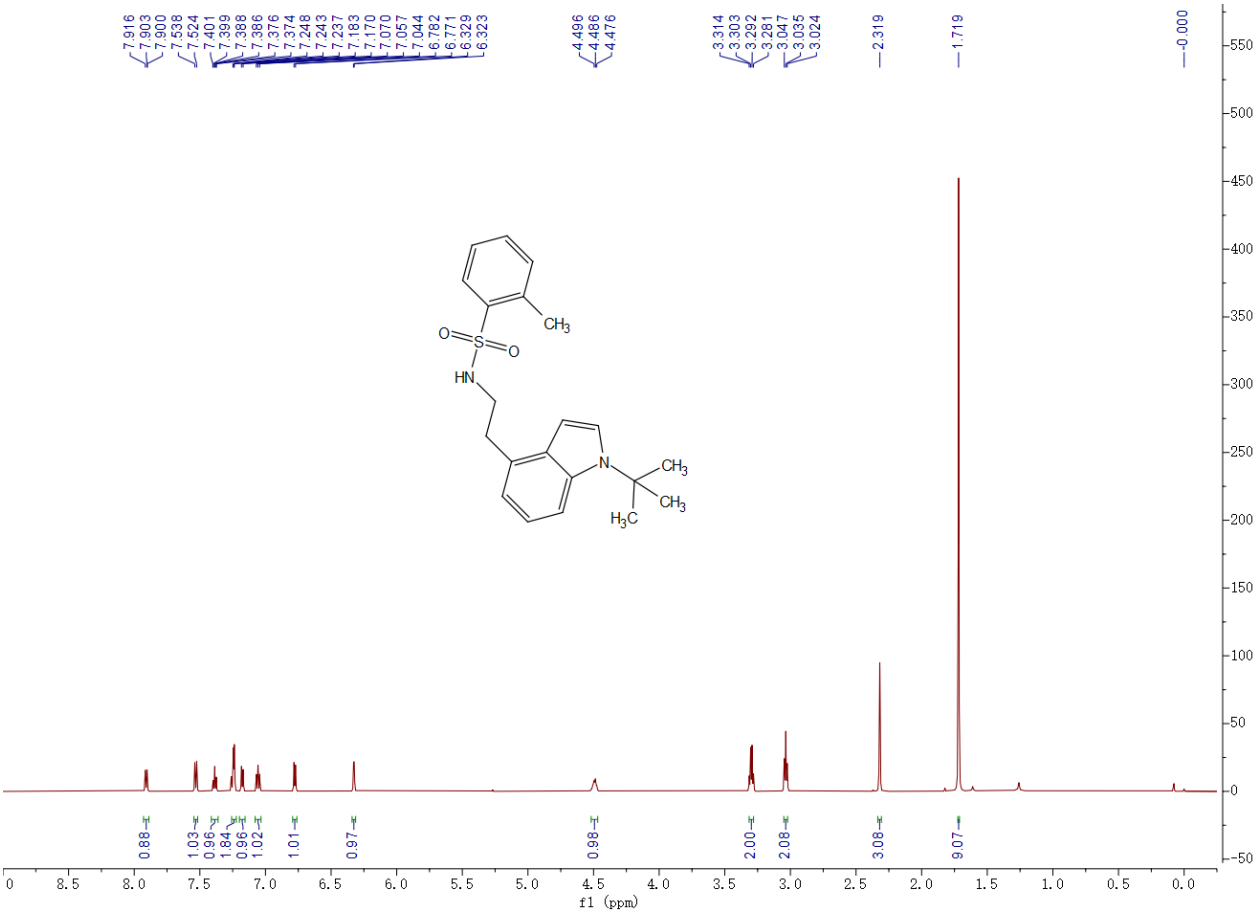


^{13}C NMR (151 MHz, $CDCl_3$)

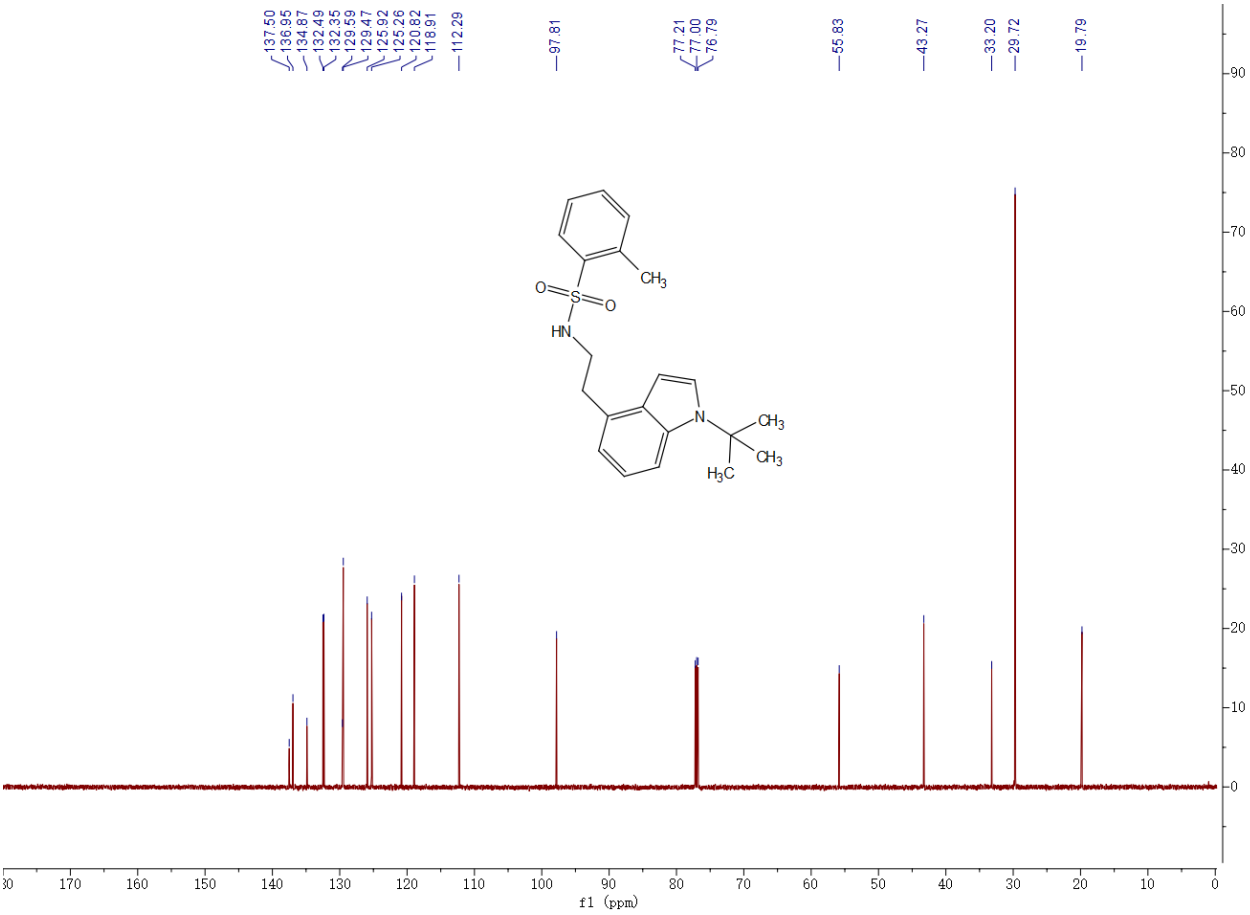


N-(2-(1-(tert-butyl)-1H-indol-4-yl)ethyl)-2-methylbenzenesulfonamide (3h)

^{1}H NMR (600 MHz, $CDCl_3$)

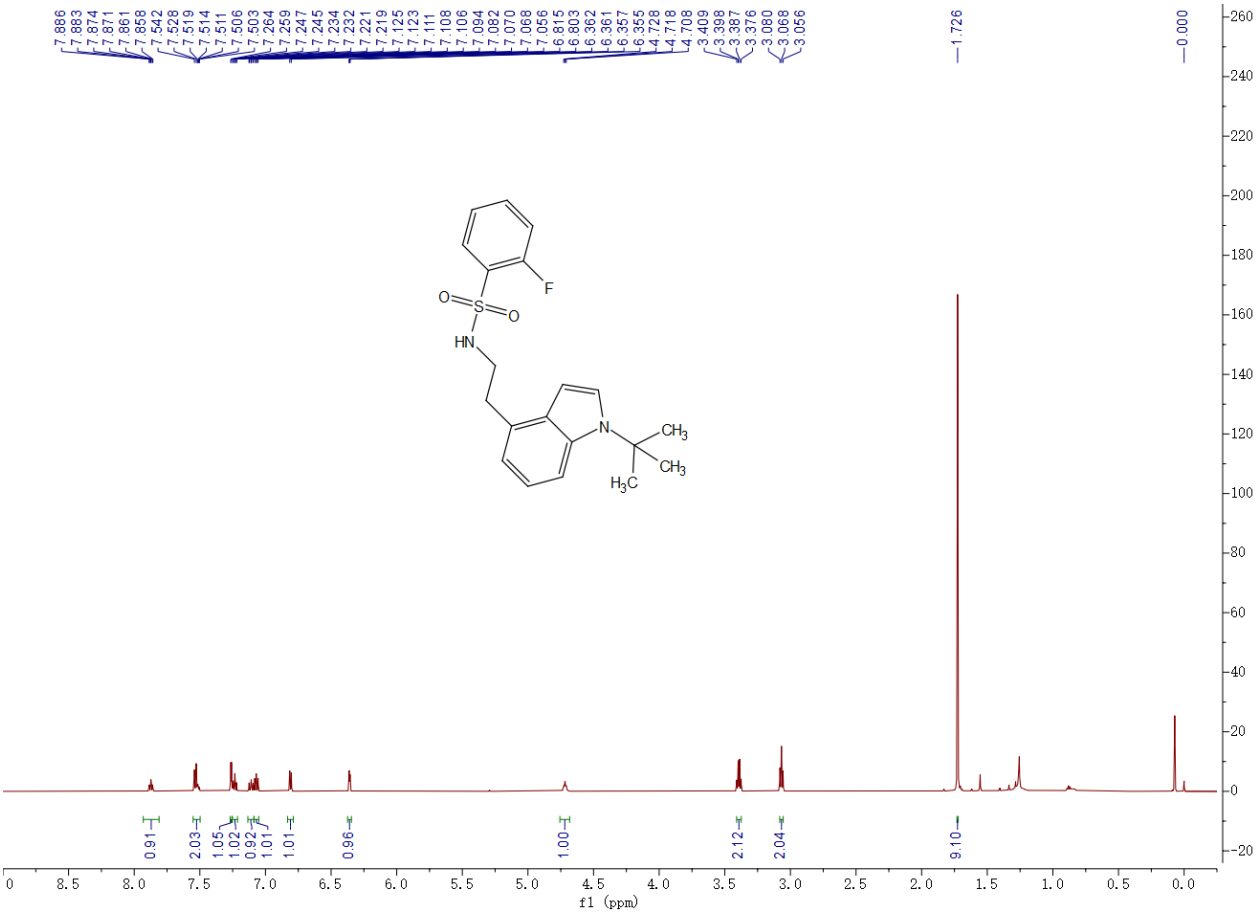


^{13}C NMR (151 MHz, $CDCl_3$)

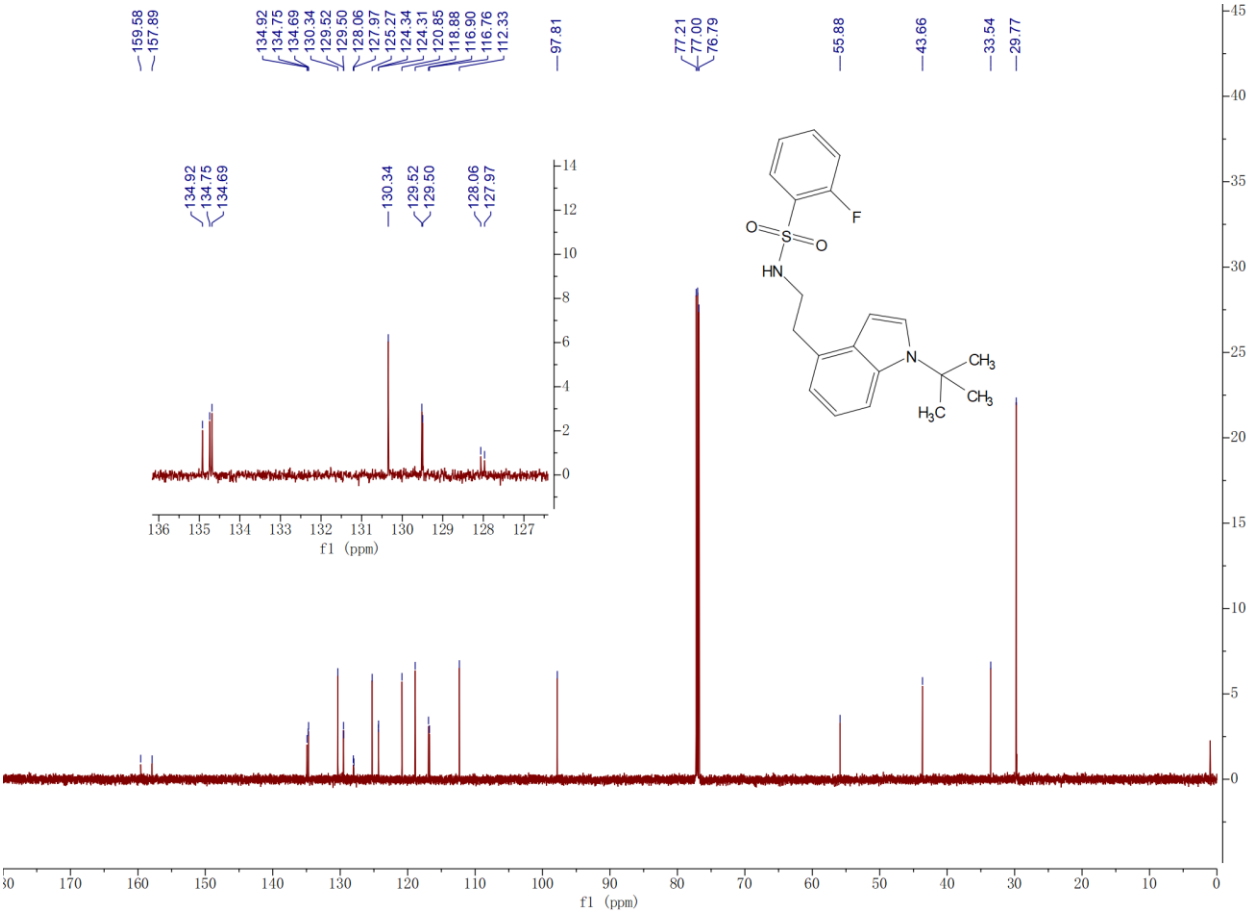


N-(2-(1-(tert-butyl)-1H-indol-4-yl)ethyl)-2-fluorobenzenesulfonamide (3i)

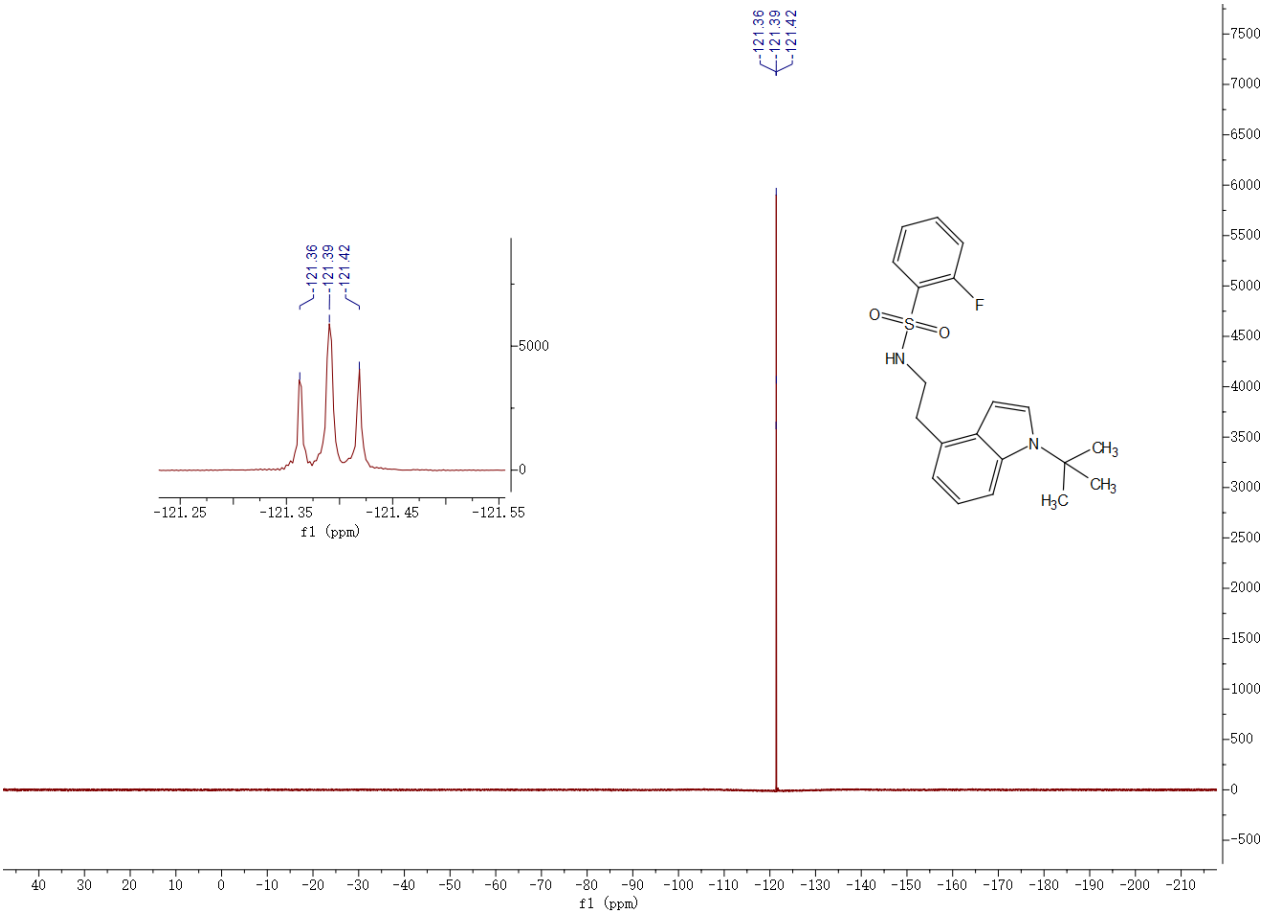
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

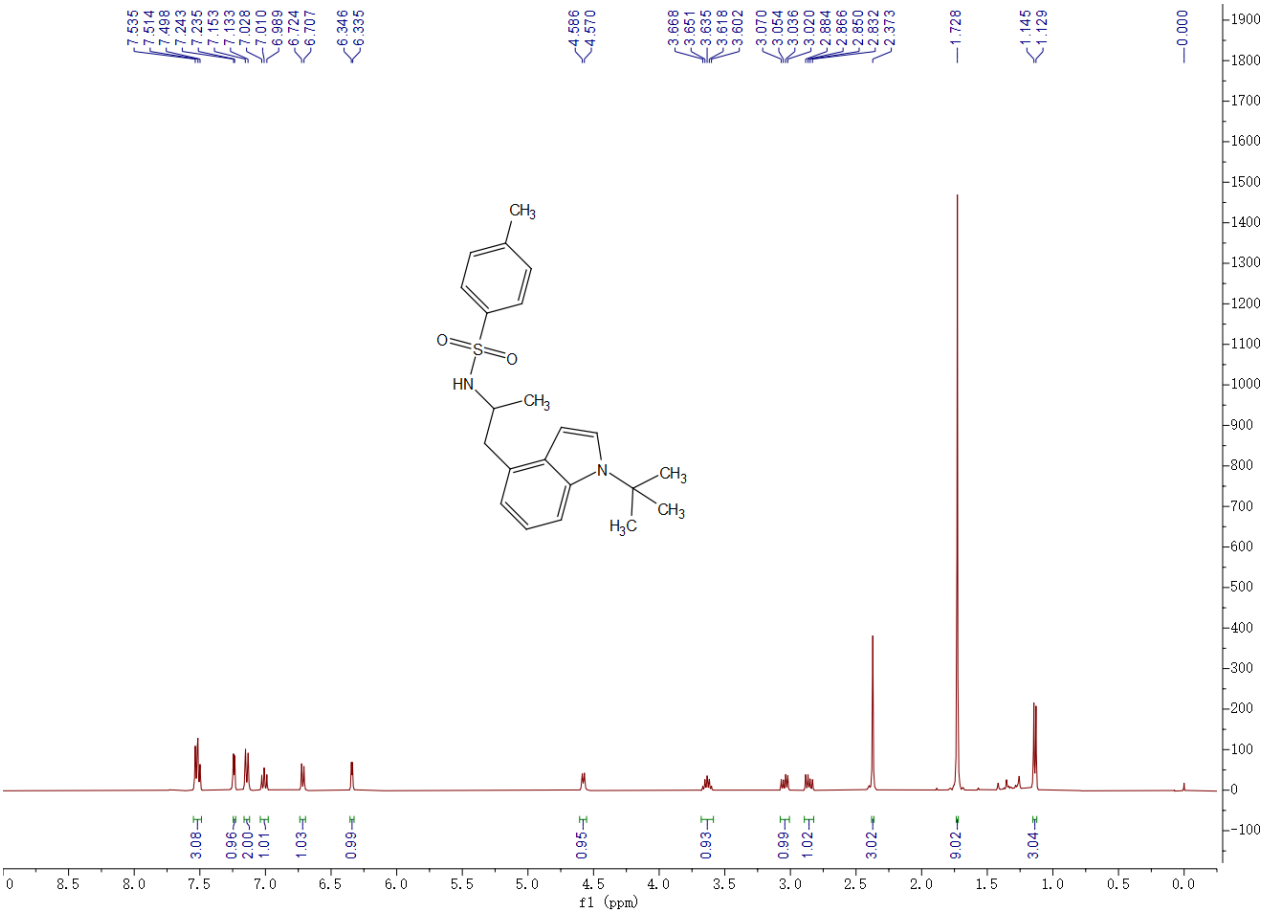


^{19}F NMR (376 MHz, $CDCl_3$)

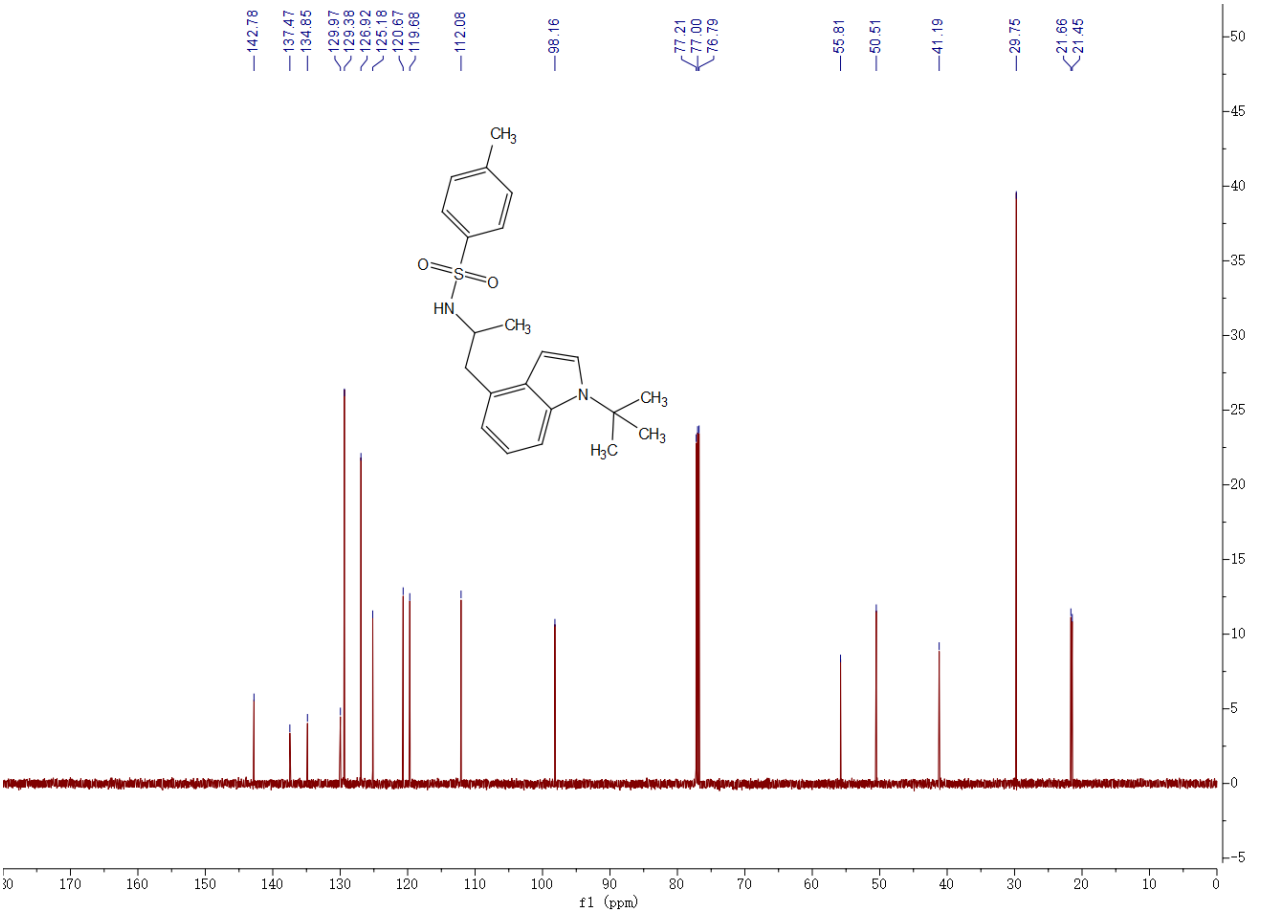


N-(1-(1-(tert-butyl)-1H-indol-4-yl)propan-2-yl)-4-methylbenzenesulfonamide (3k)

^{1}H NMR (400 MHz, $CDCl_3$)

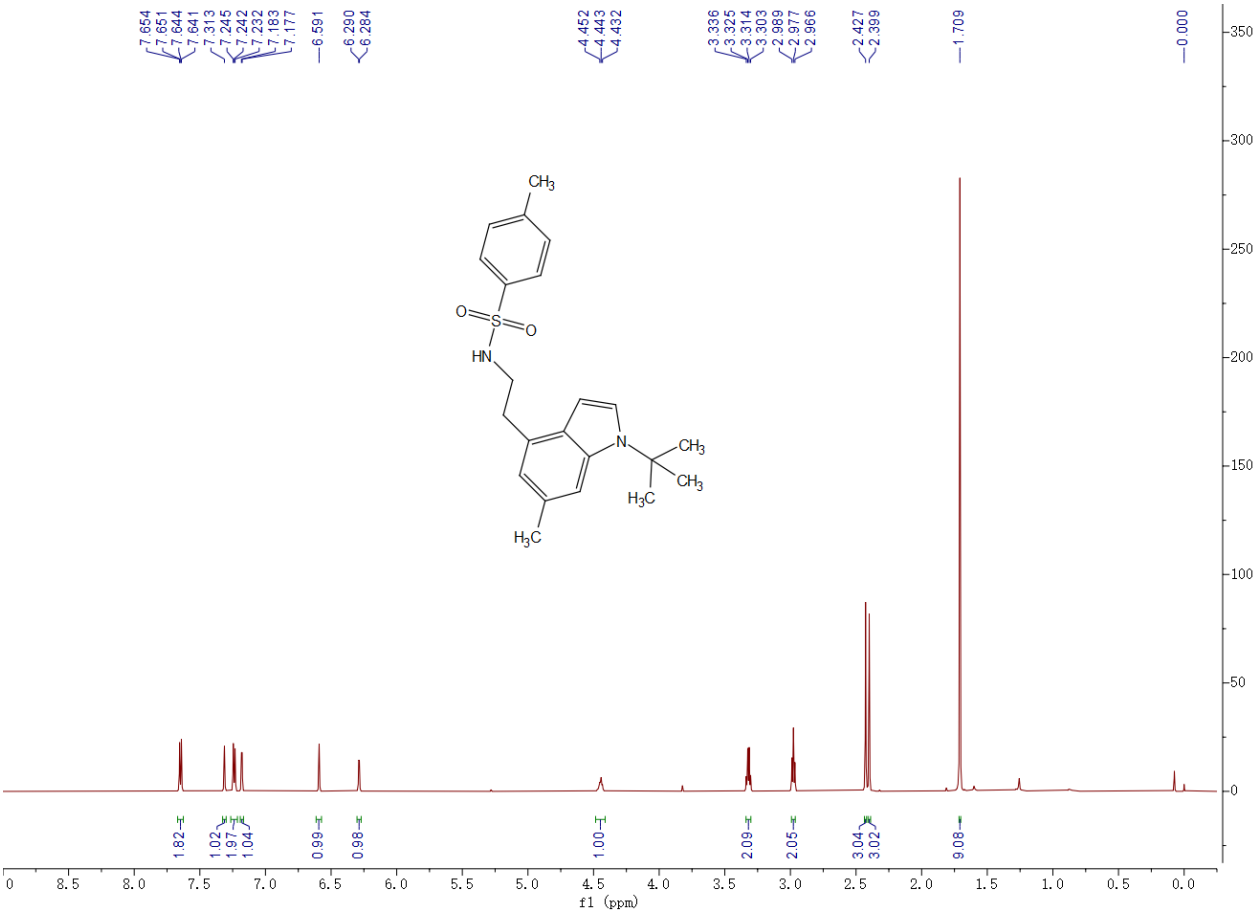


^{13}C NMR (151 MHz, $CDCl_3$)

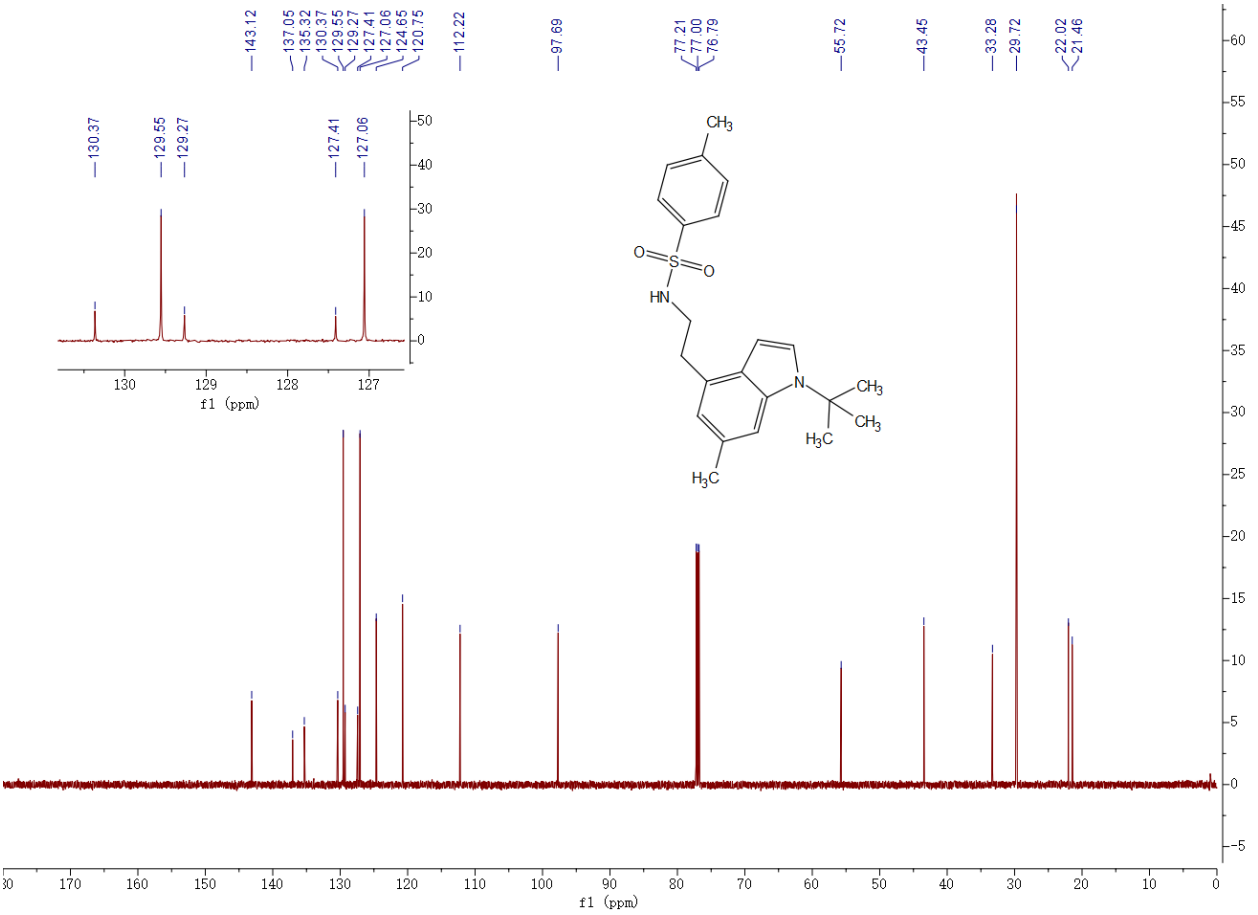


N-(2-(1-(tert-butyl)-6-methyl-1H-indol-4-yl)ethyl)-4-methylbenzenesulfonamide (3j)

^{1}H NMR (600 MHz, $CDCl_3$)

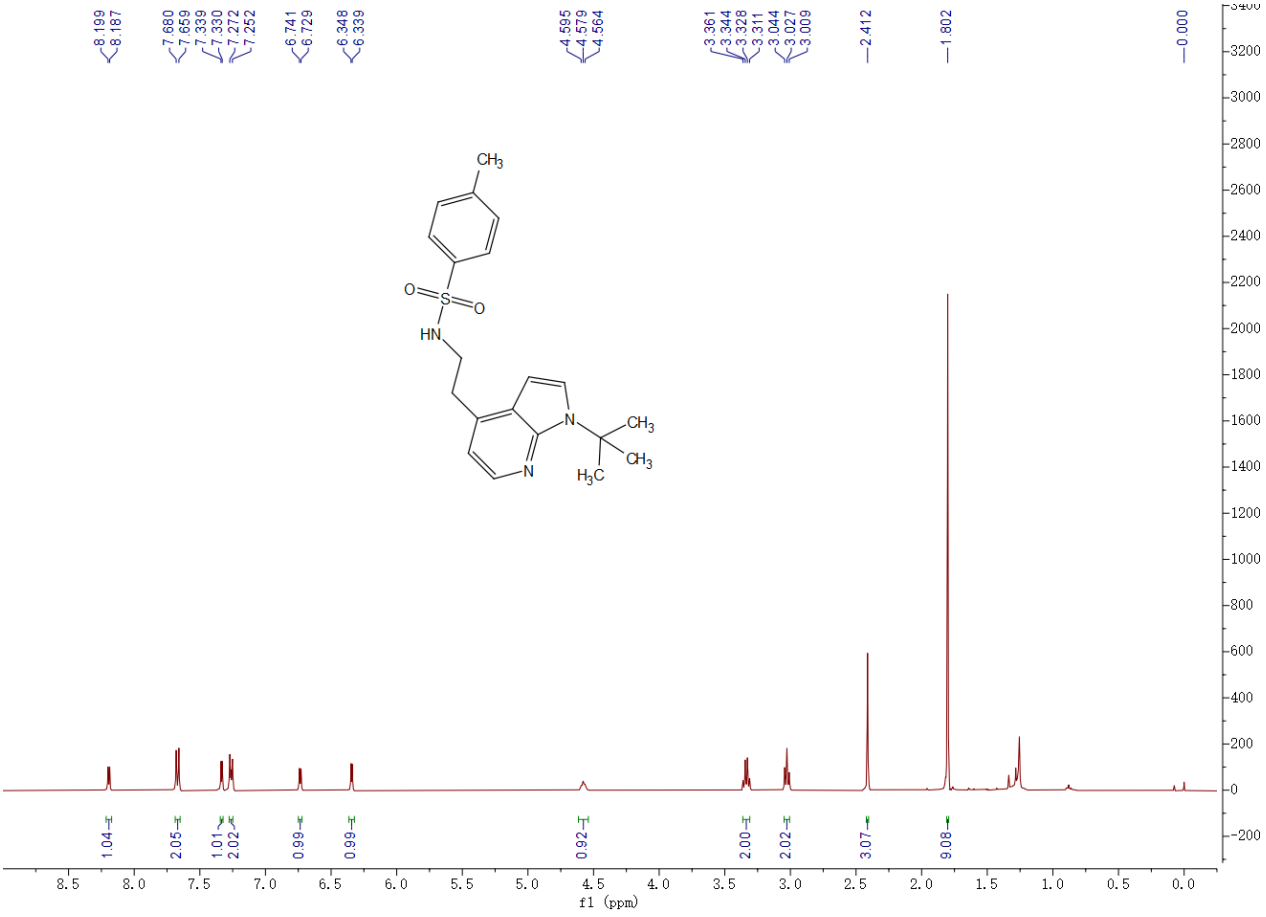


^{13}C NMR (151 MHz, $CDCl_3$)

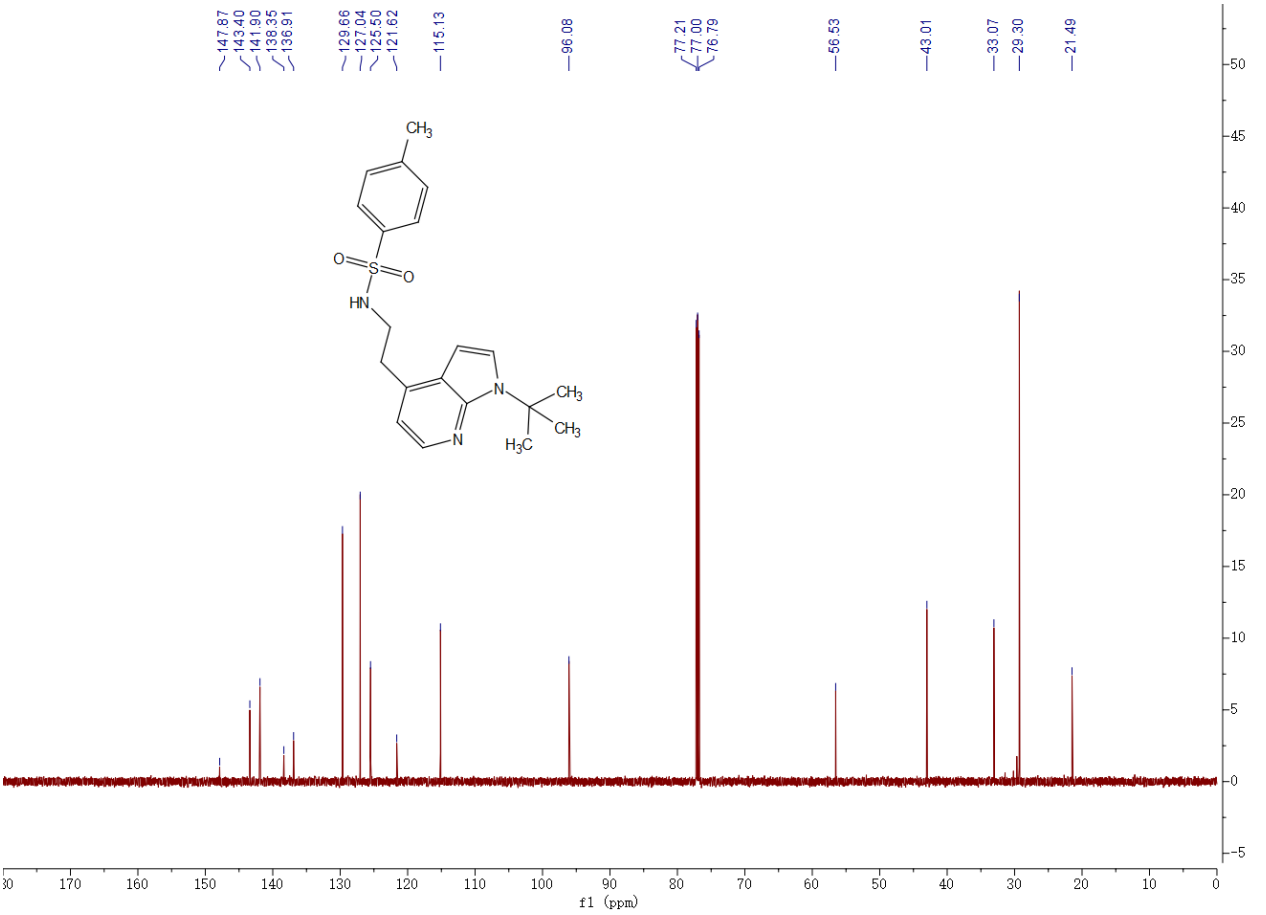


N-(2-(1-(tert-butyl)-1H-pyrrolo[2,3-b]pyridin-4-yl)ethyl)-4-methylbenzenesulfonamide (3n)

^{1}H NMR (400 MHz, $CDCl_3$)

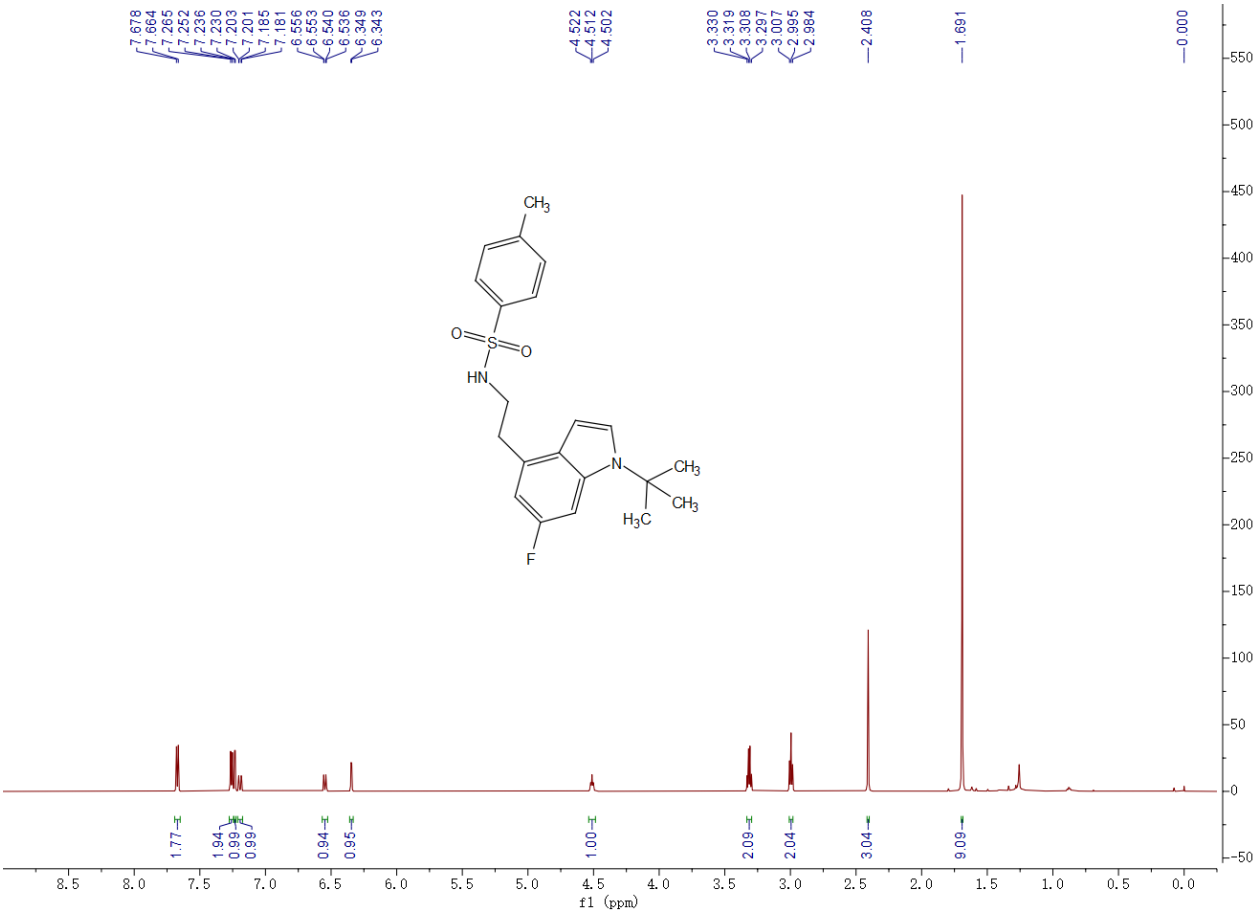


^{13}C NMR (151 MHz, $CDCl_3$)

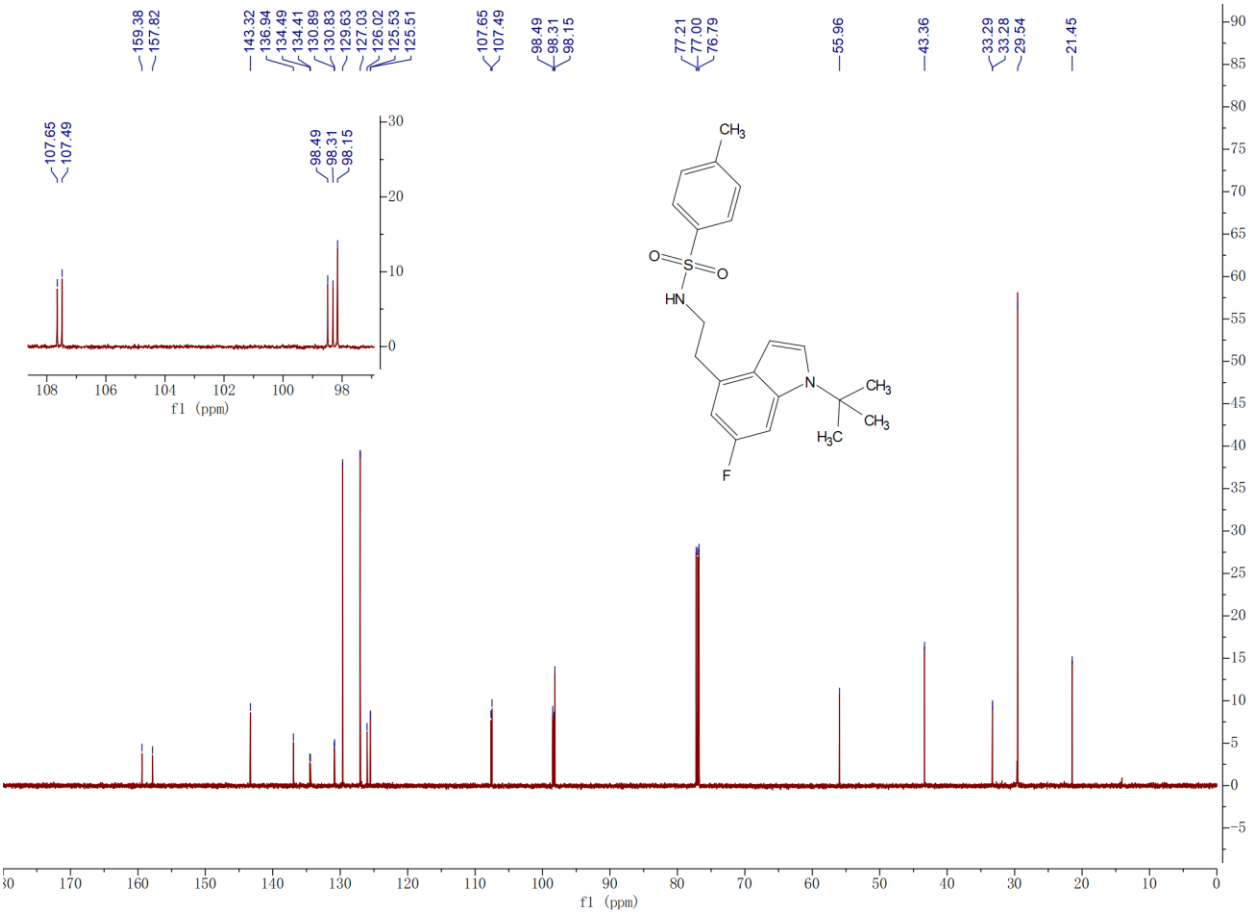


N-(2-(1-(tert-butyl)-6-fluoro-1H-indol-4-yl)ethyl)-4-methylbenzenesulfonamide (3l)

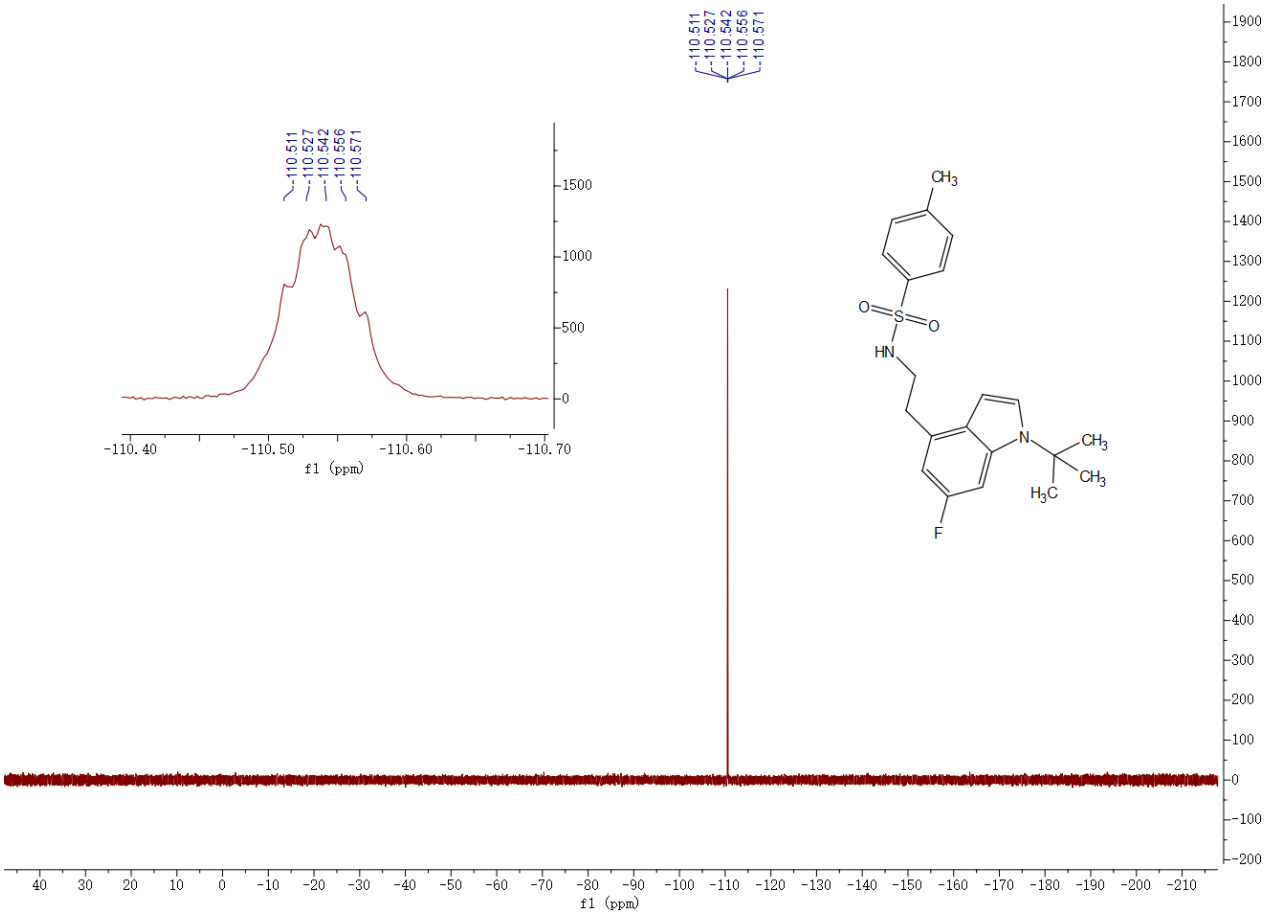
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

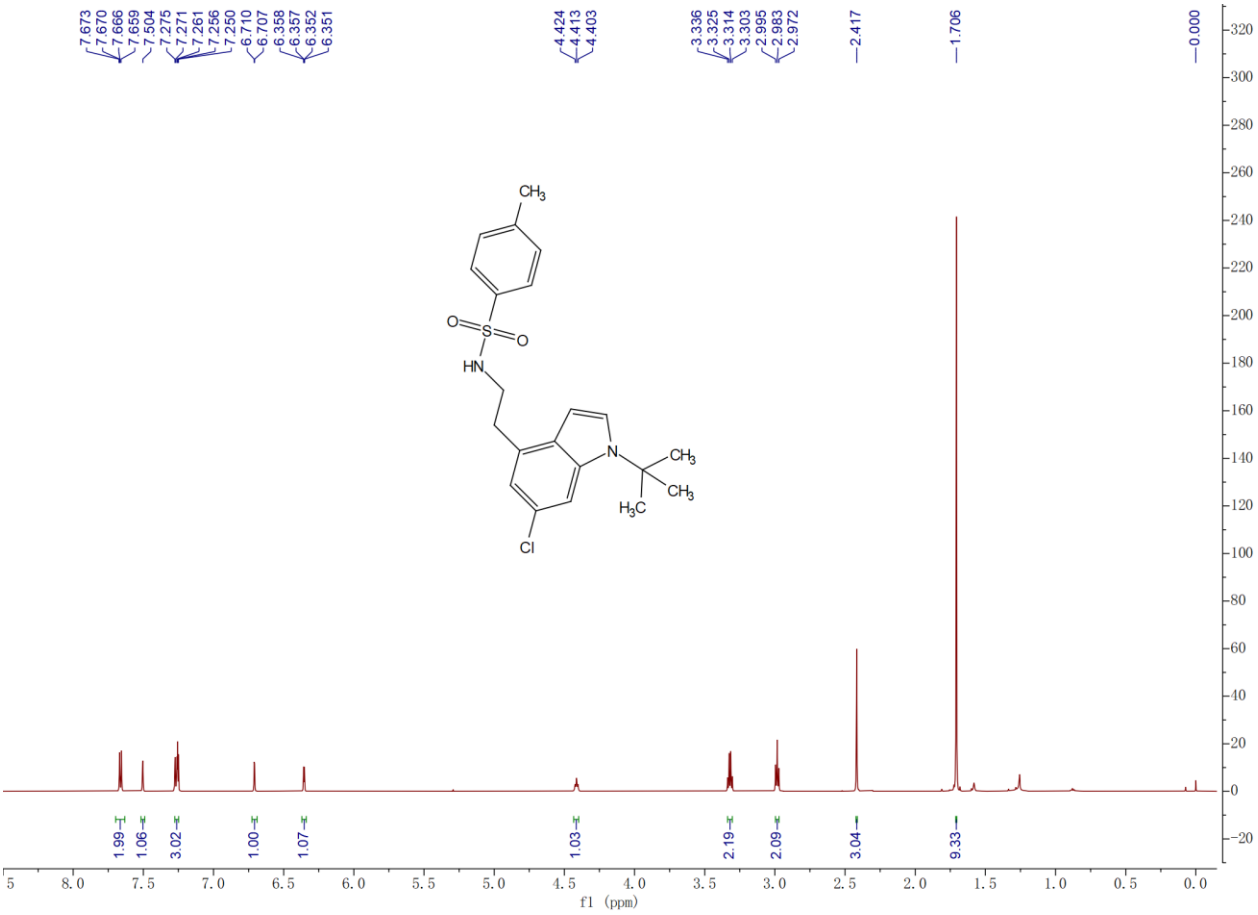


^{19}F NMR (376 MHz, $CDCl_3$)

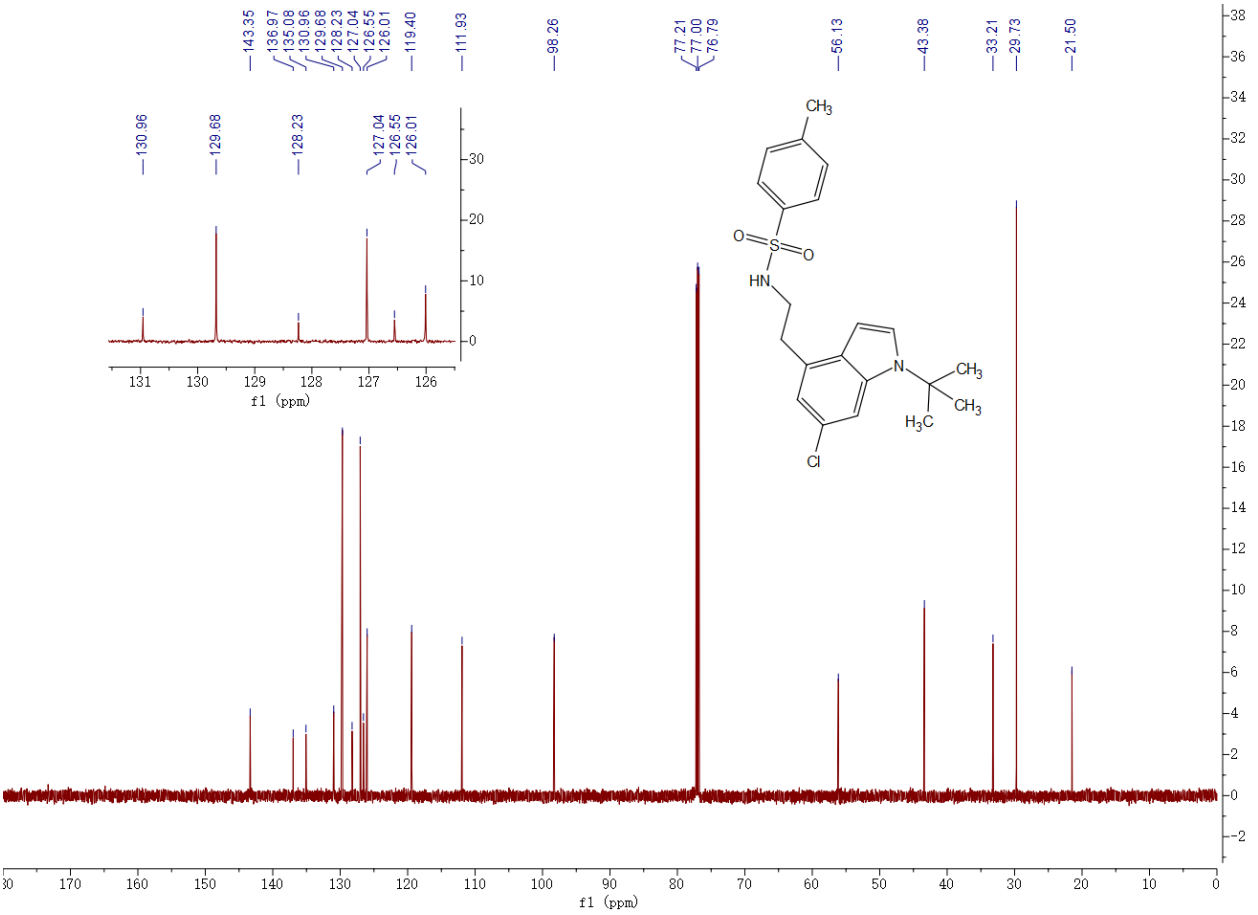


N-(2-(1-(tert-butyl)-6-chloro-1H-indol-4-yl)ethyl)-4-methylbenzenesulfonamide (3m)

^{1}H NMR (600 MHz, $CDCl_3$)

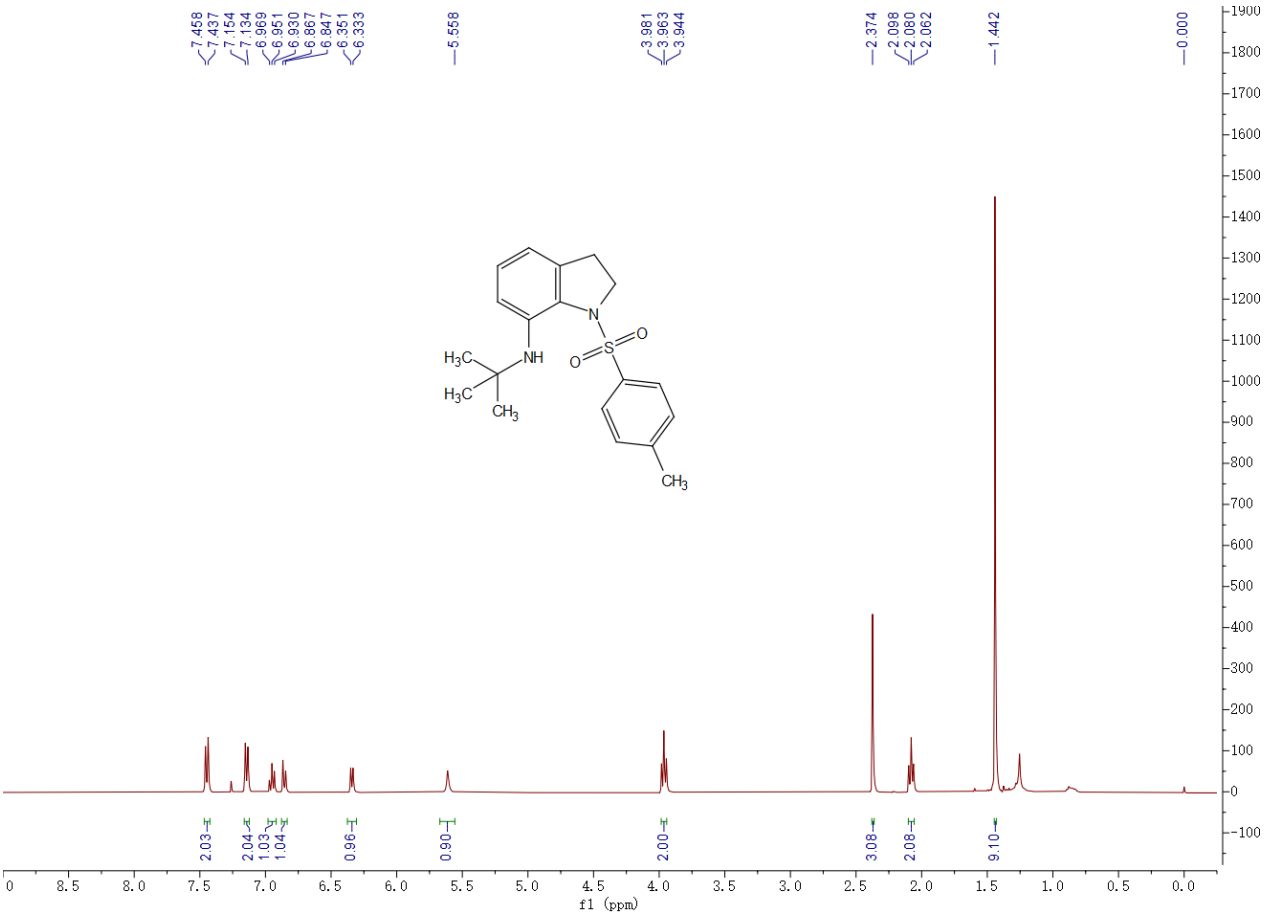


^{13}C NMR (151 MHz, $CDCl_3$)

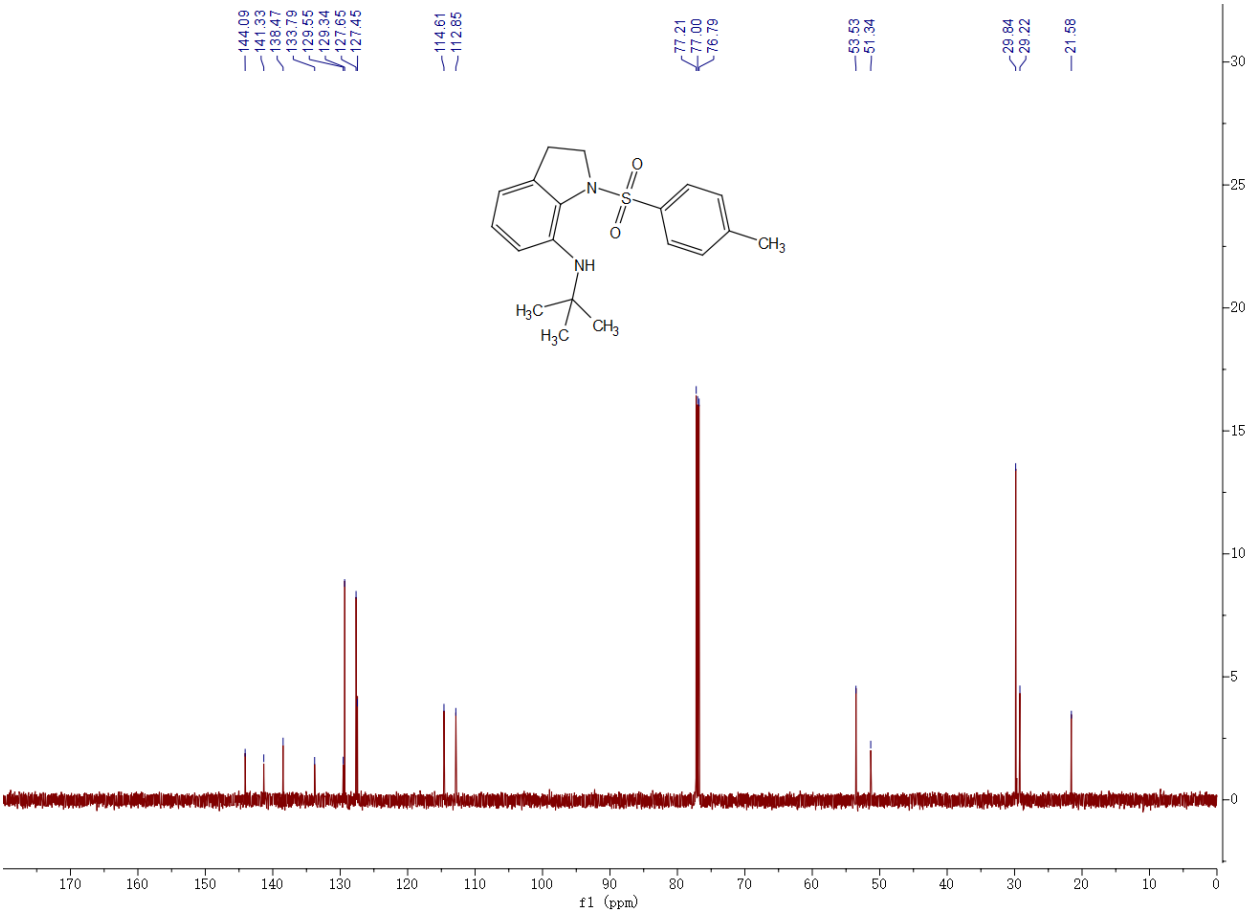


N-(tert-butyl)-1-tosylindolin-7-amine (4a)

^{1}H NMR (400 MHz, $CDCl_3$)

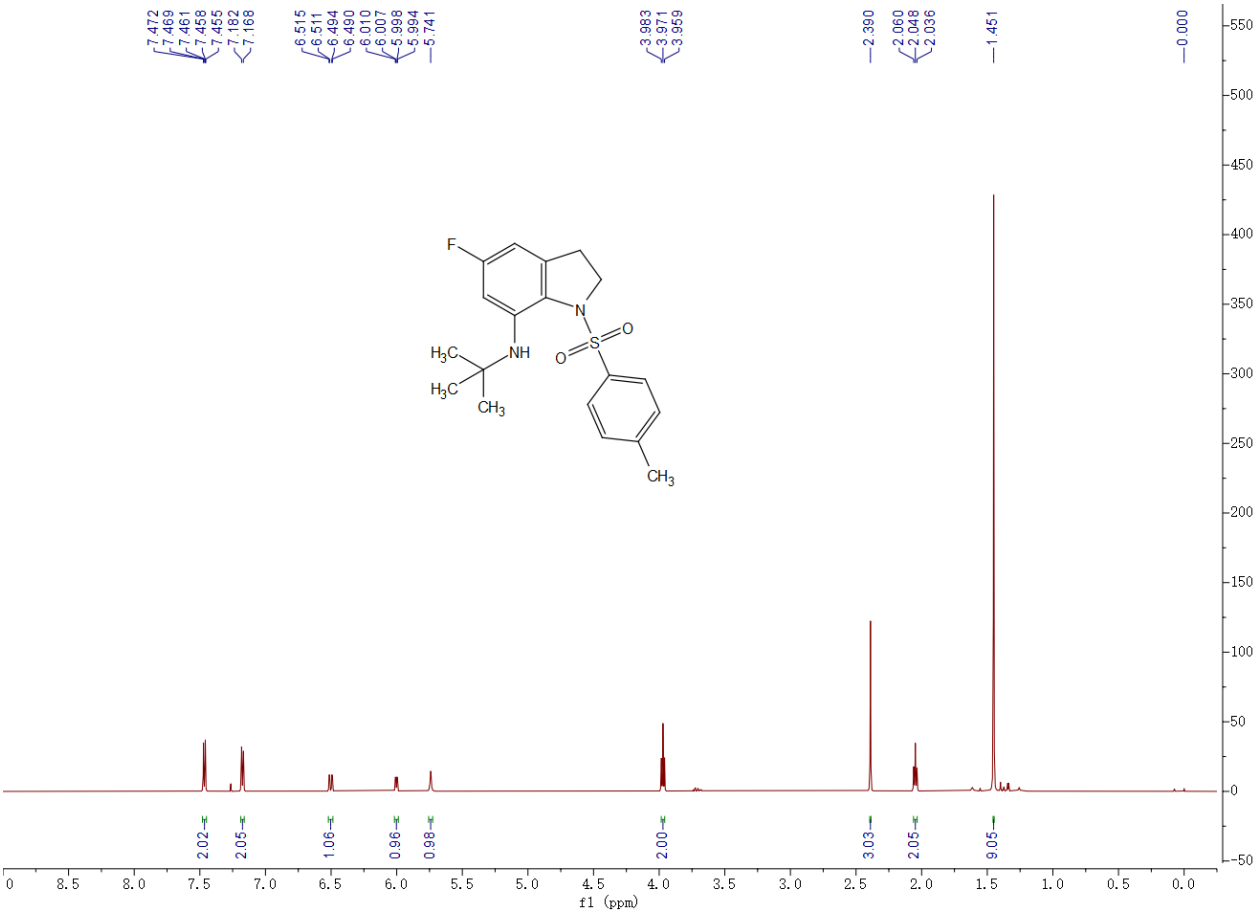


^{13}C NMR (151 MHz, $CDCl_3$)

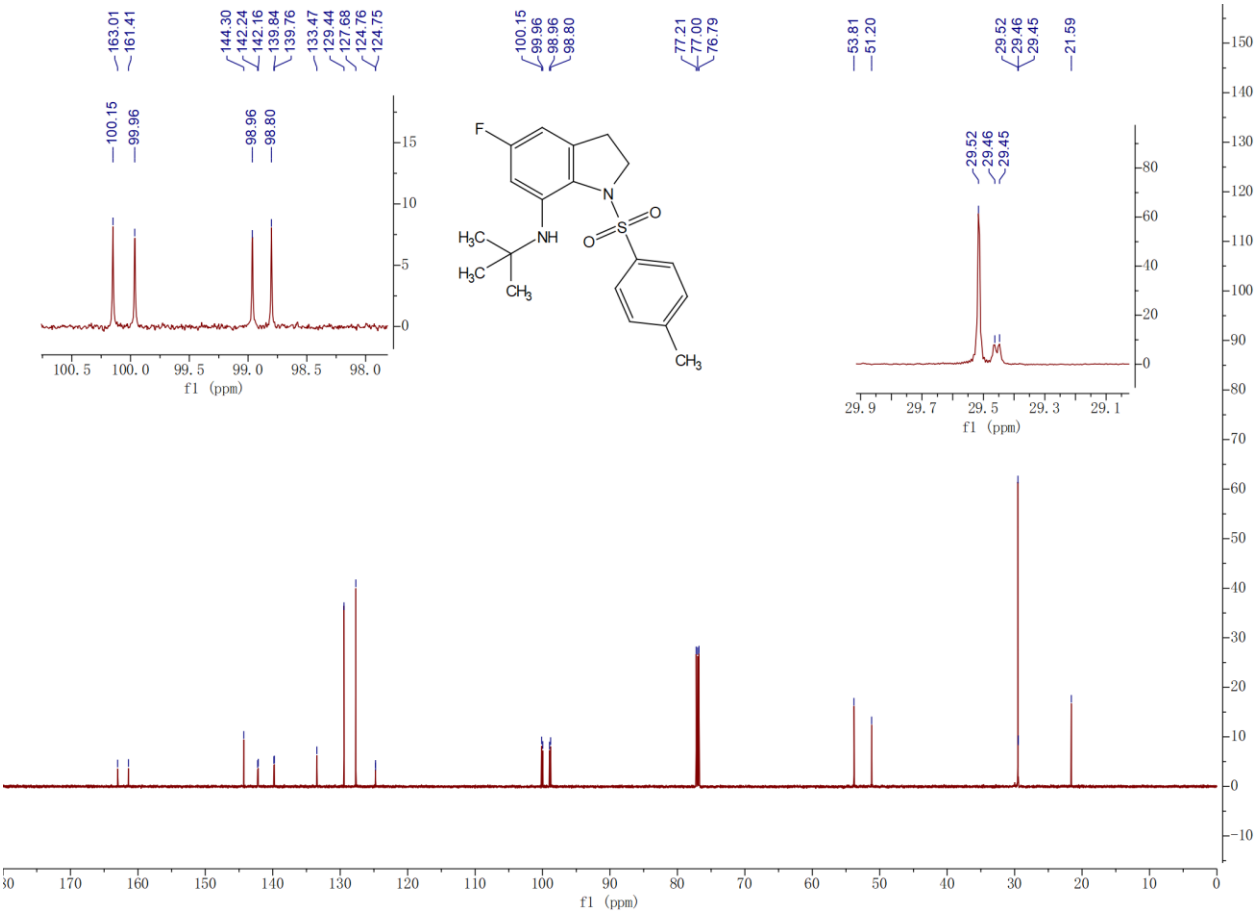


N-(tert-butyl)-5-fluoro-1-tosylindolin-7-amine (4b)

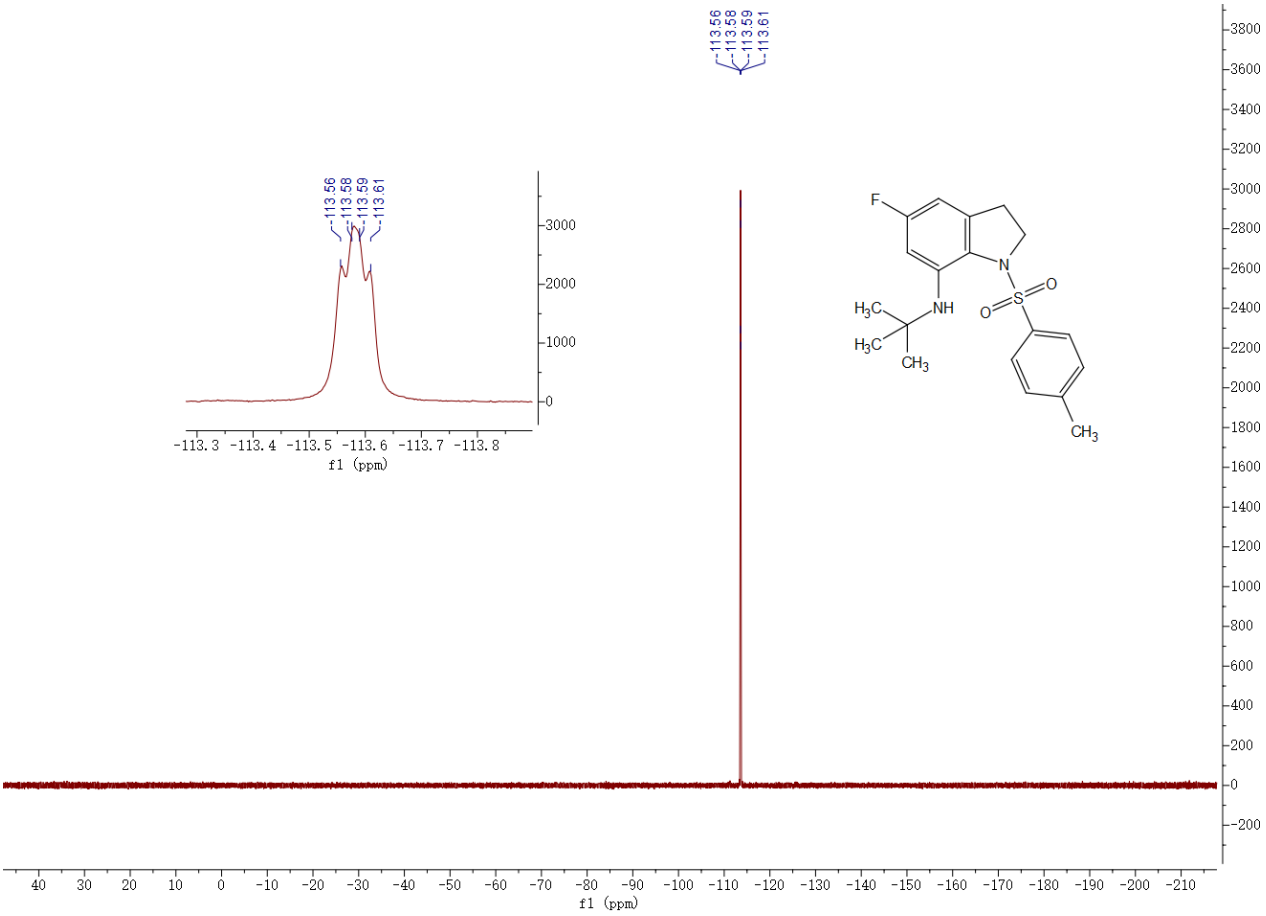
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

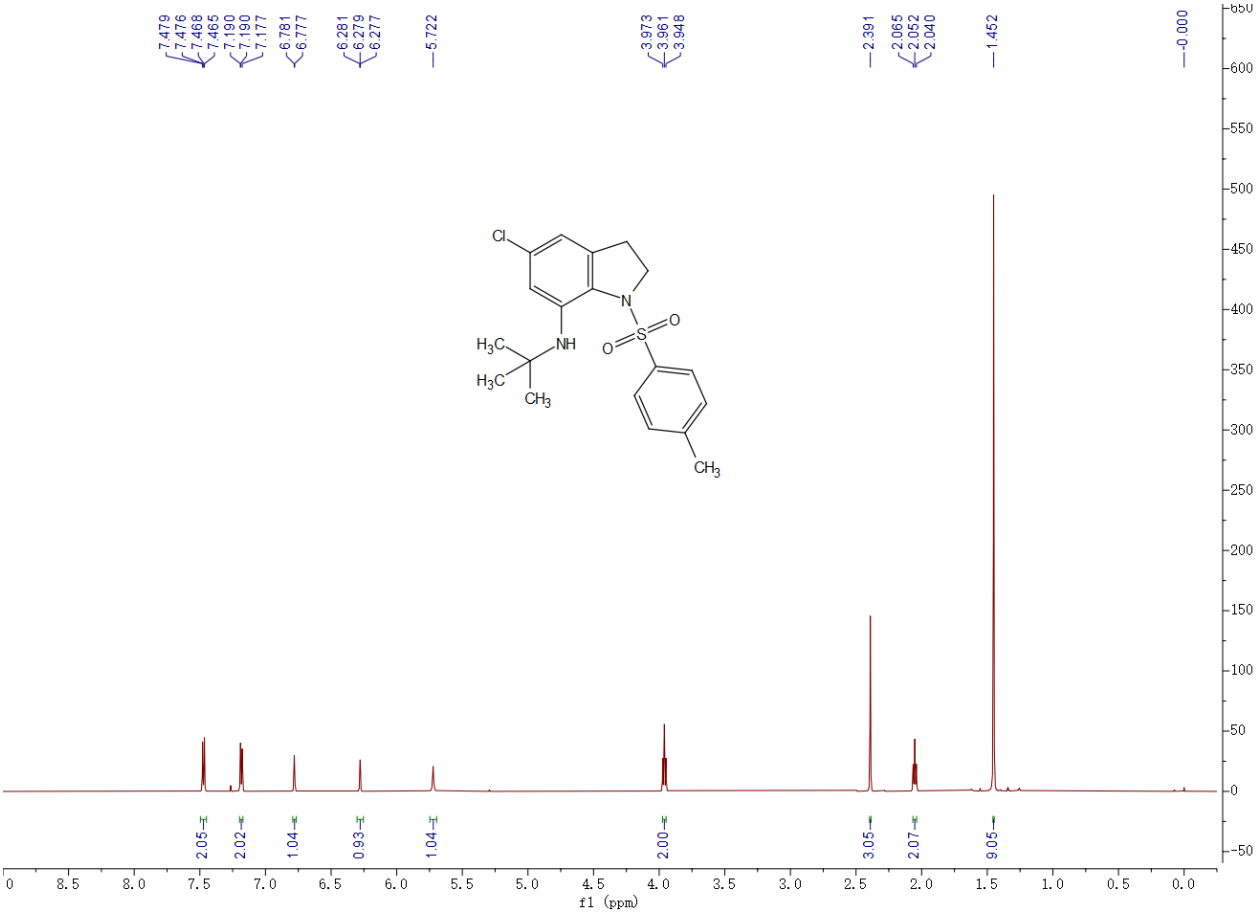


^{19}F NMR (376 MHz, $CDCl_3$)

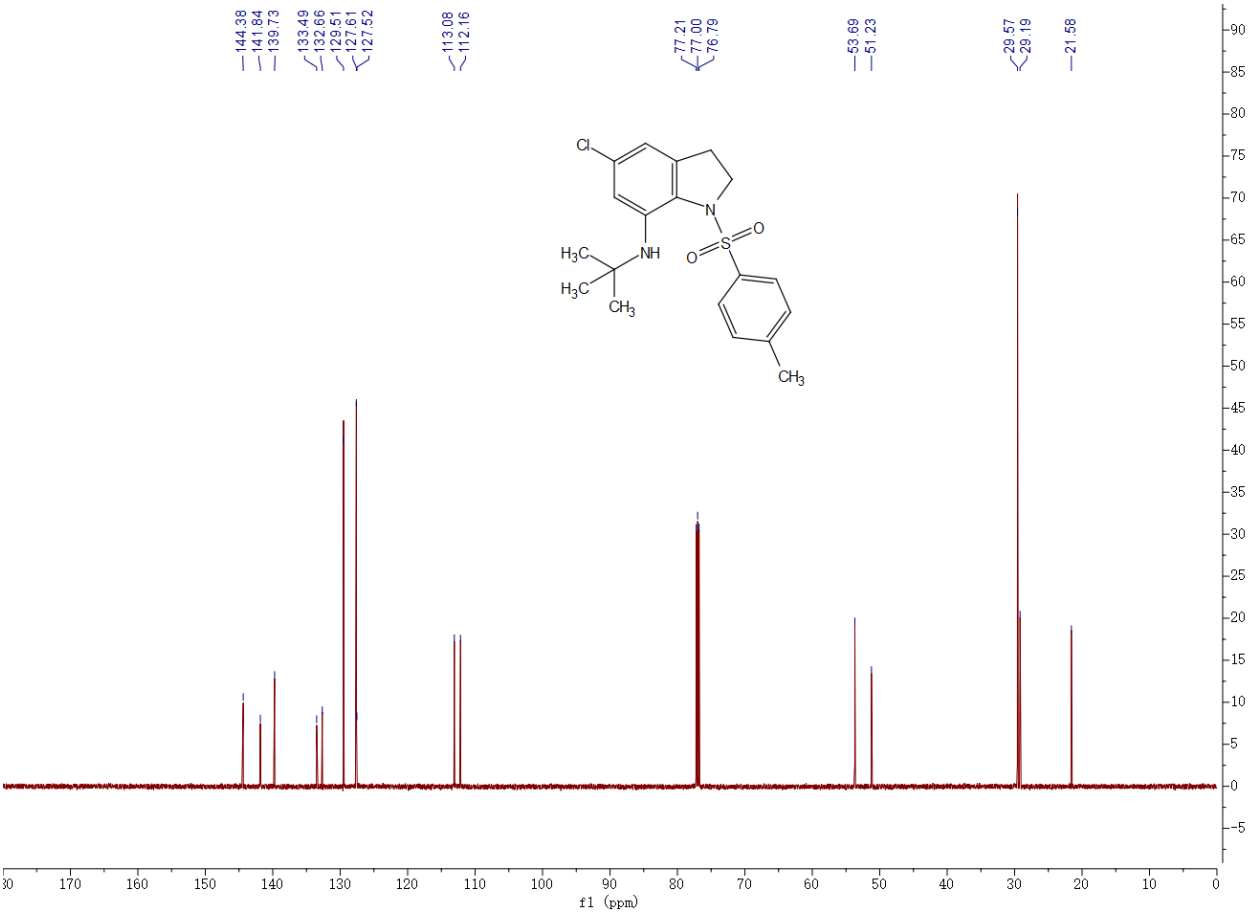


N-(tert-butyl)-5-chloro-1-tosylindolin-7-amine (4c)

^{1}H NMR (600 MHz, $CDCl_3$)

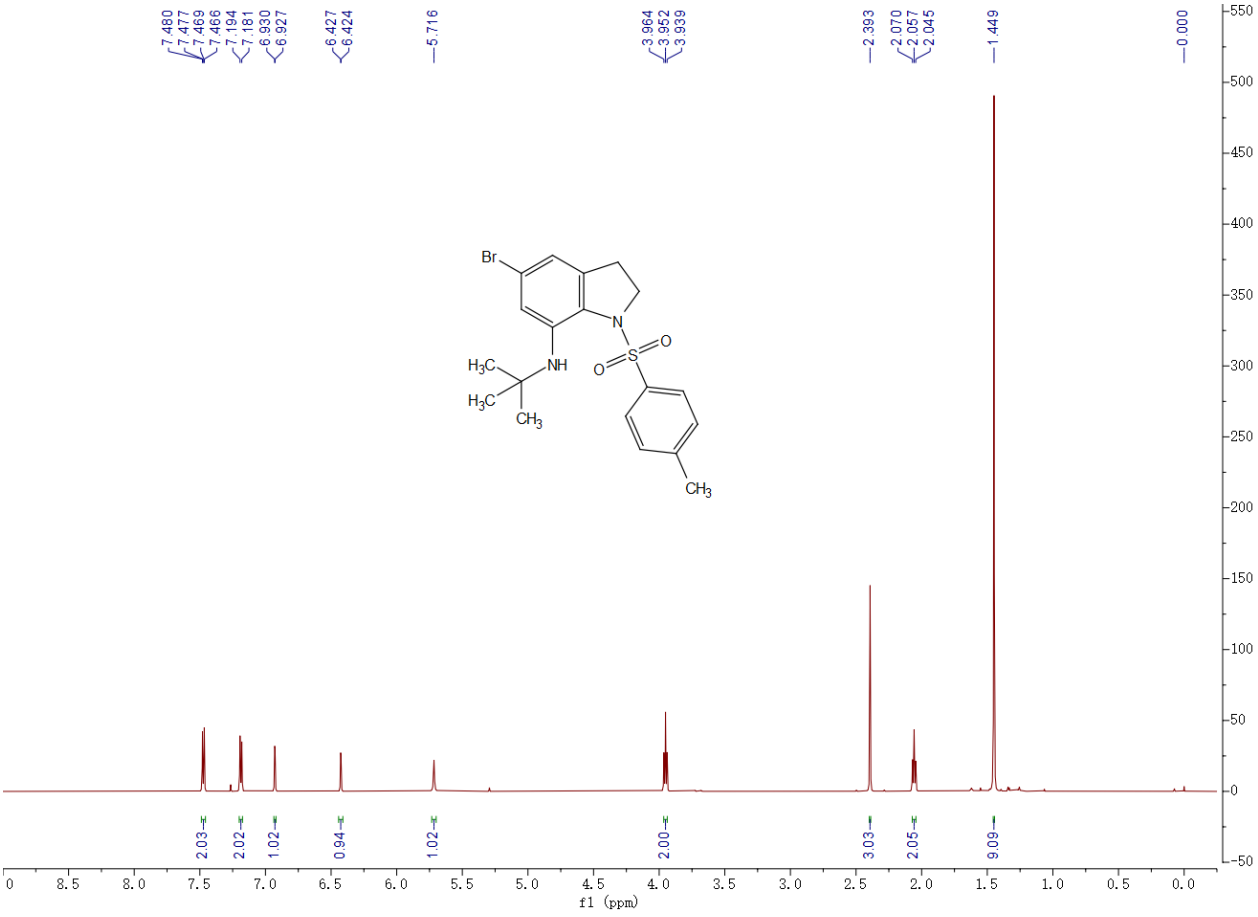


^{13}C NMR (151 MHz, $CDCl_3$)

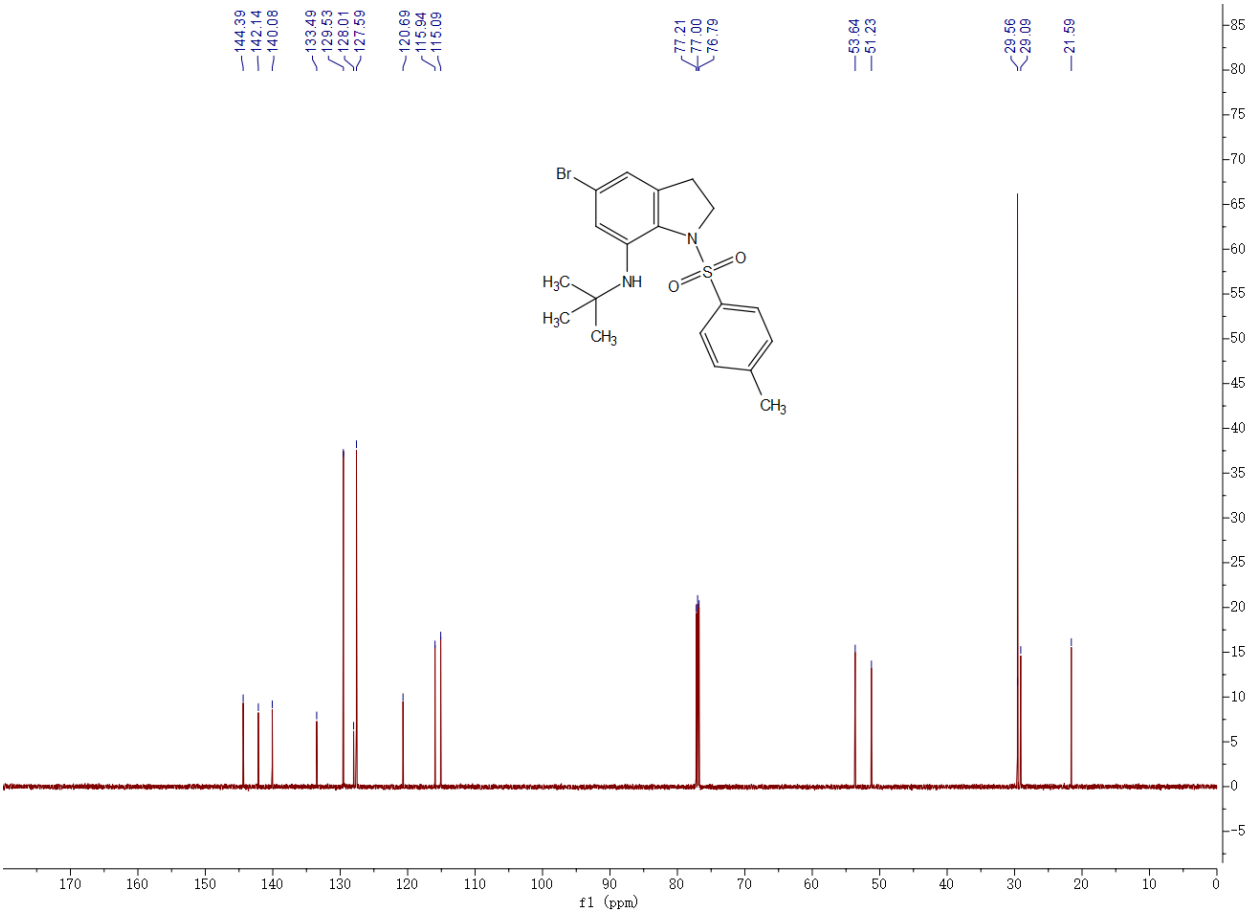


5-bromo-N-(tert-butyl)-1-tosylindolin-7-amine (4d)

^{1}H NMR (600 MHz, $CDCl_3$)

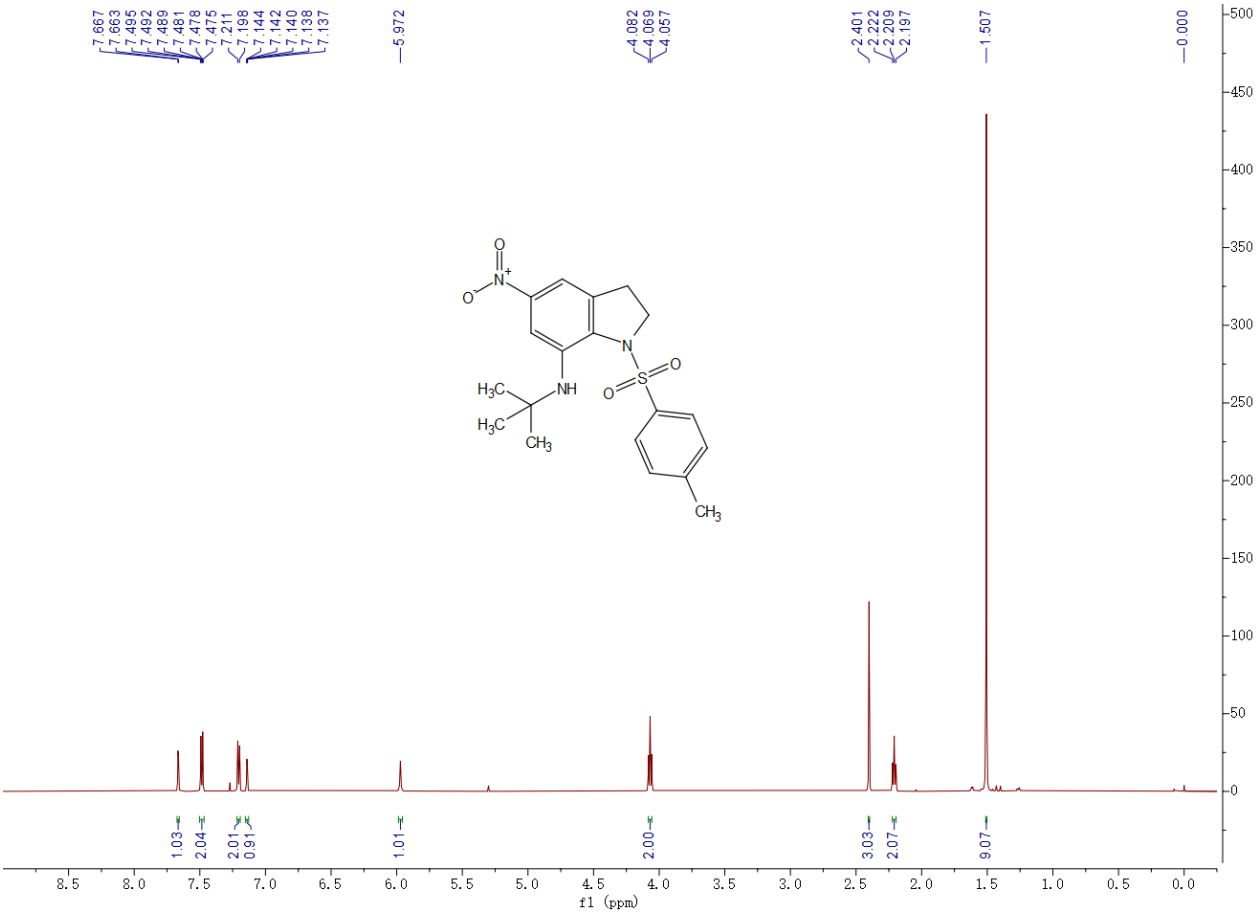


^{13}C NMR (151 MHz, $CDCl_3$)

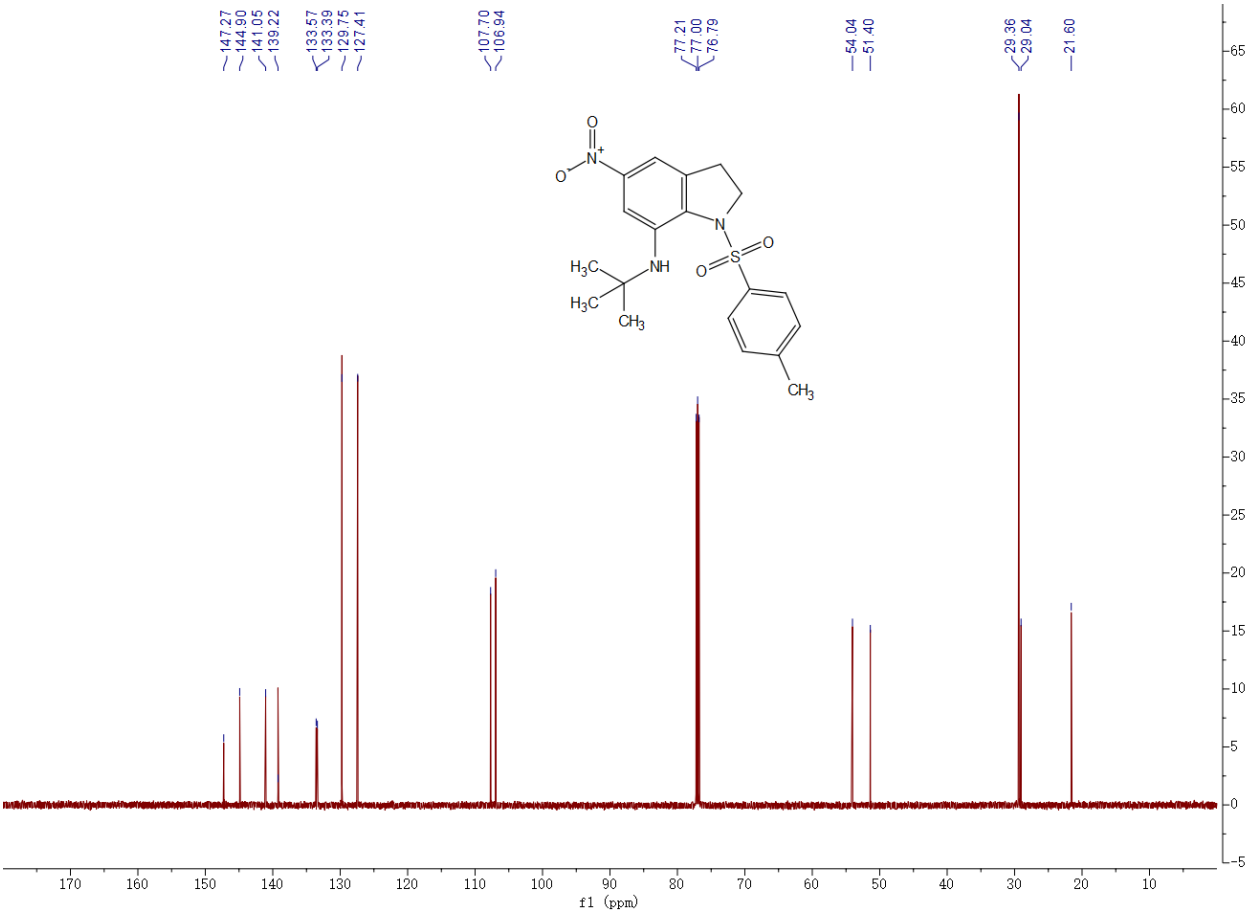


N-(tert-butyl)-5-nitro-1-tosylindolin-7-amine (4e)

^{1}H NMR (600 MHz, $CDCl_3$)

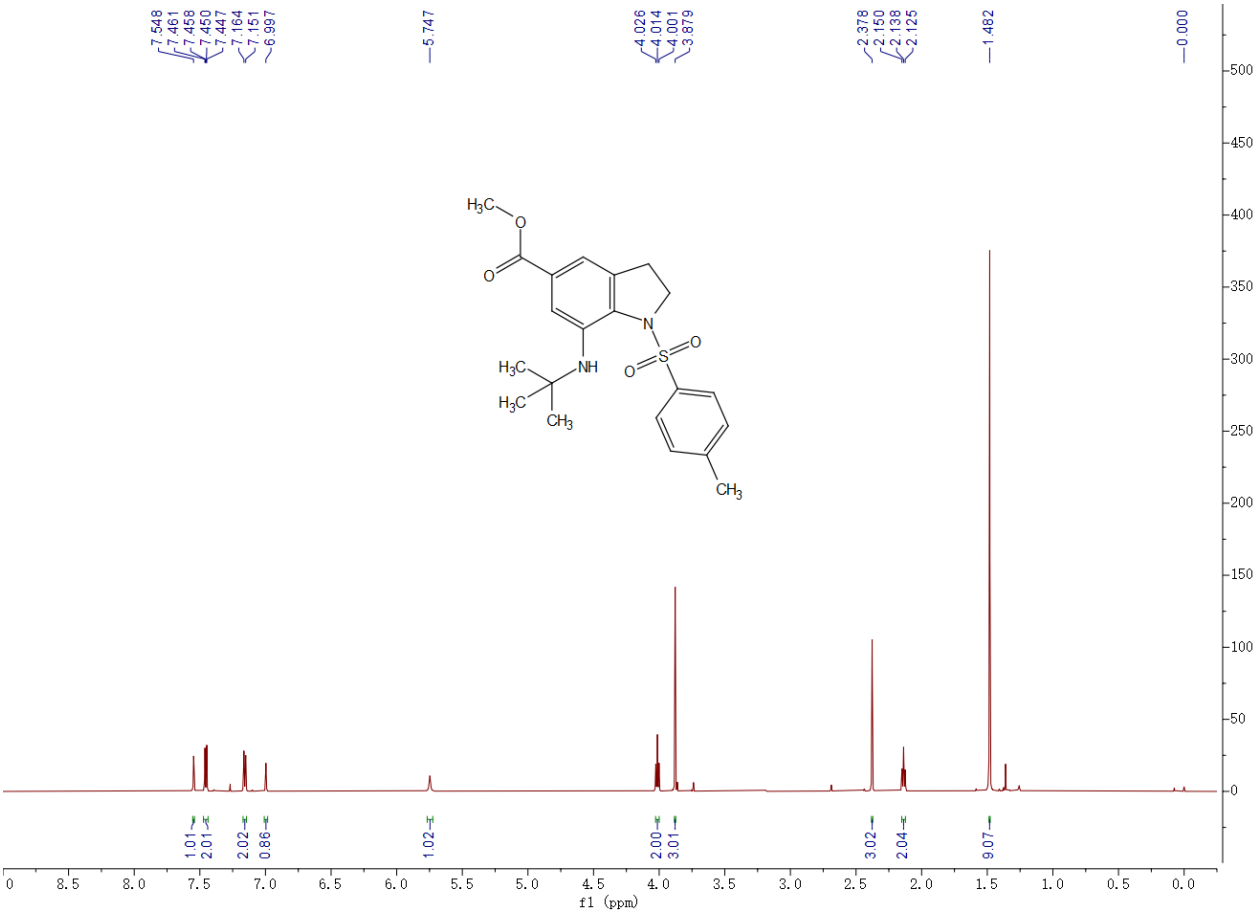


^{13}C NMR (151 MHz, $CDCl_3$)

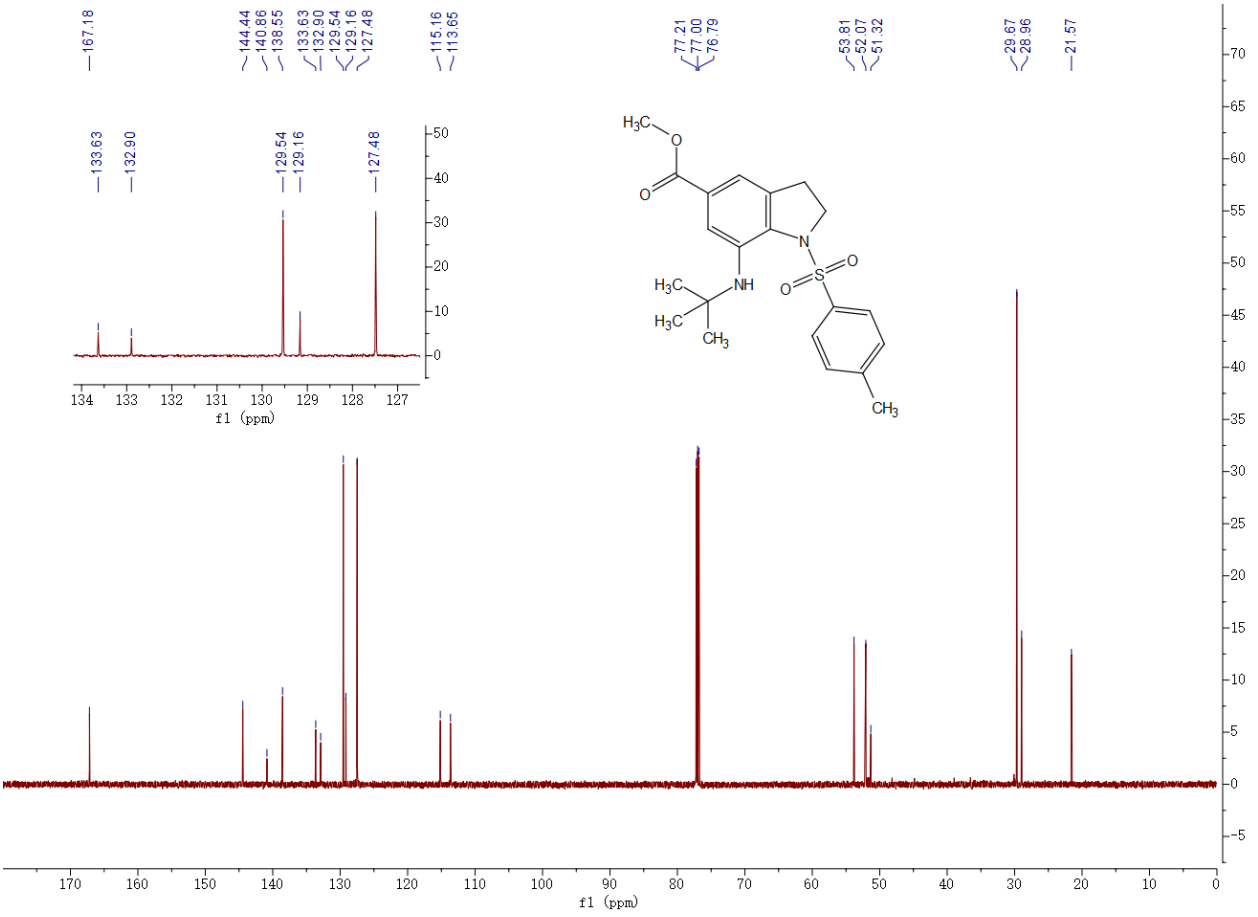


methyl 7-(tert-butylamino)-1-tosylindoline-5-carboxylate (4f)

^{1}H NMR (600 MHz, $CDCl_3$)

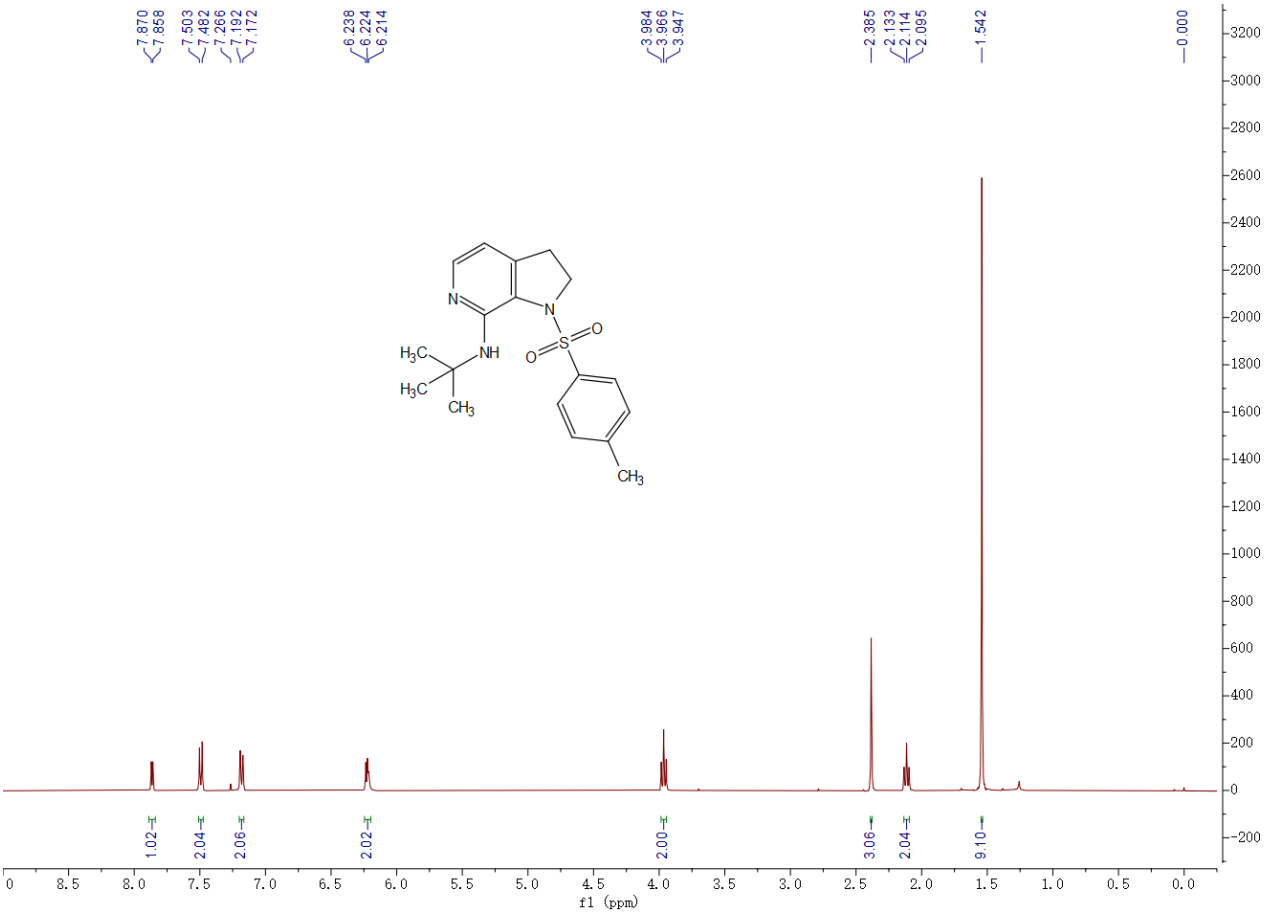


^{13}C NMR (151 MHz, $CDCl_3$)

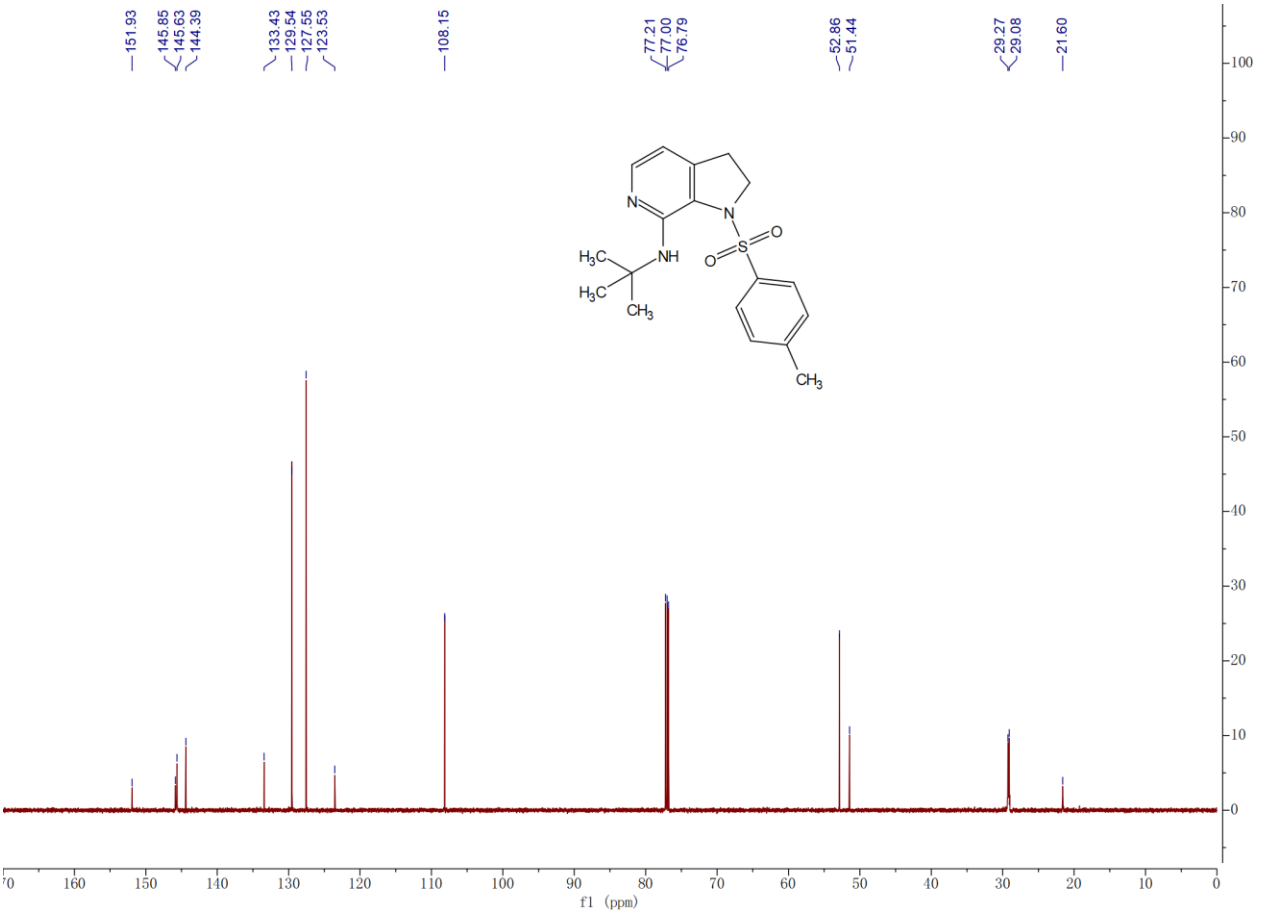


N-(tert-butyl)-1-tosyl-2,3-dihydro-1H-pyrrolo[2,3-c]pyridin-7-amine (4g)

^{1}H NMR (400 MHz, $CDCl_3$)

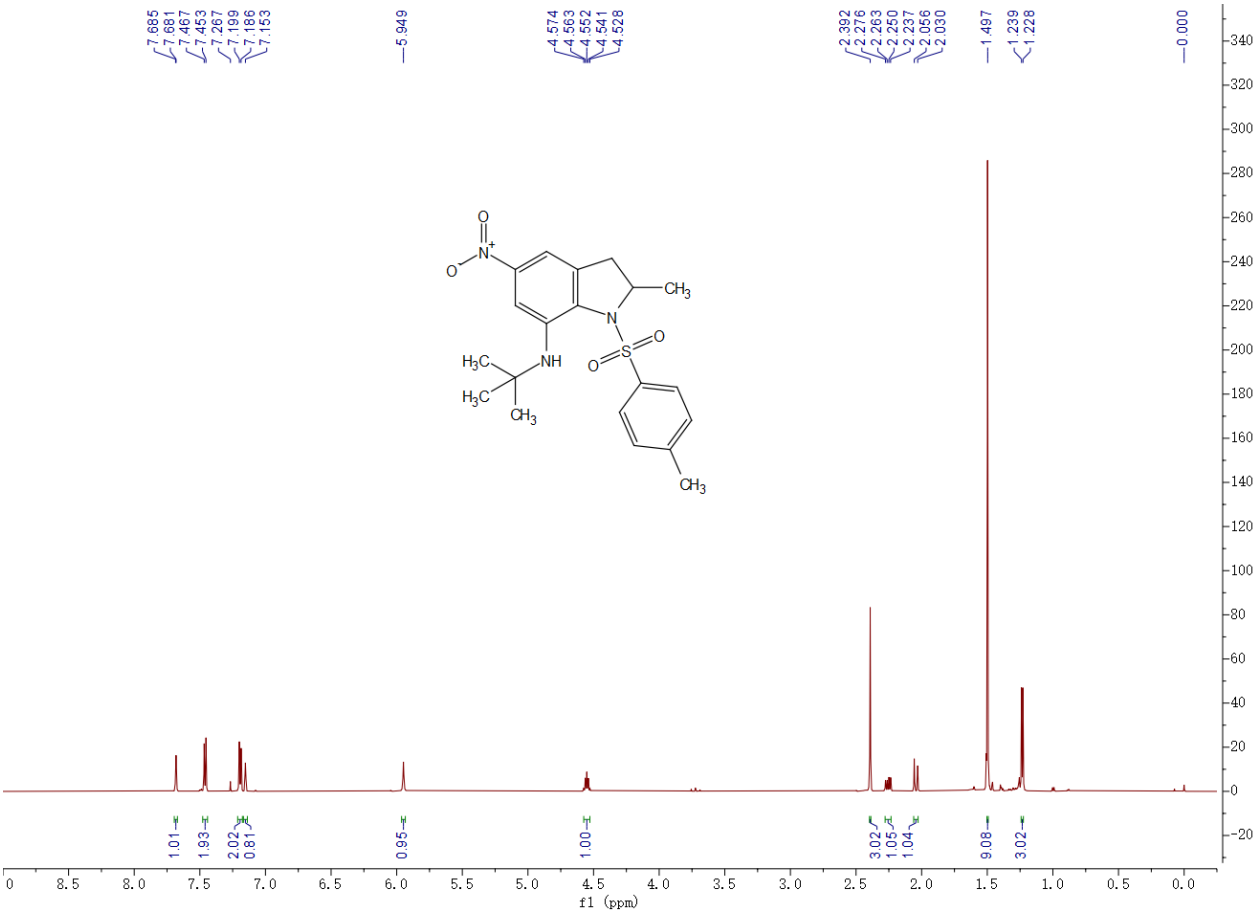


^{13}C NMR (151 MHz, $CDCl_3$)

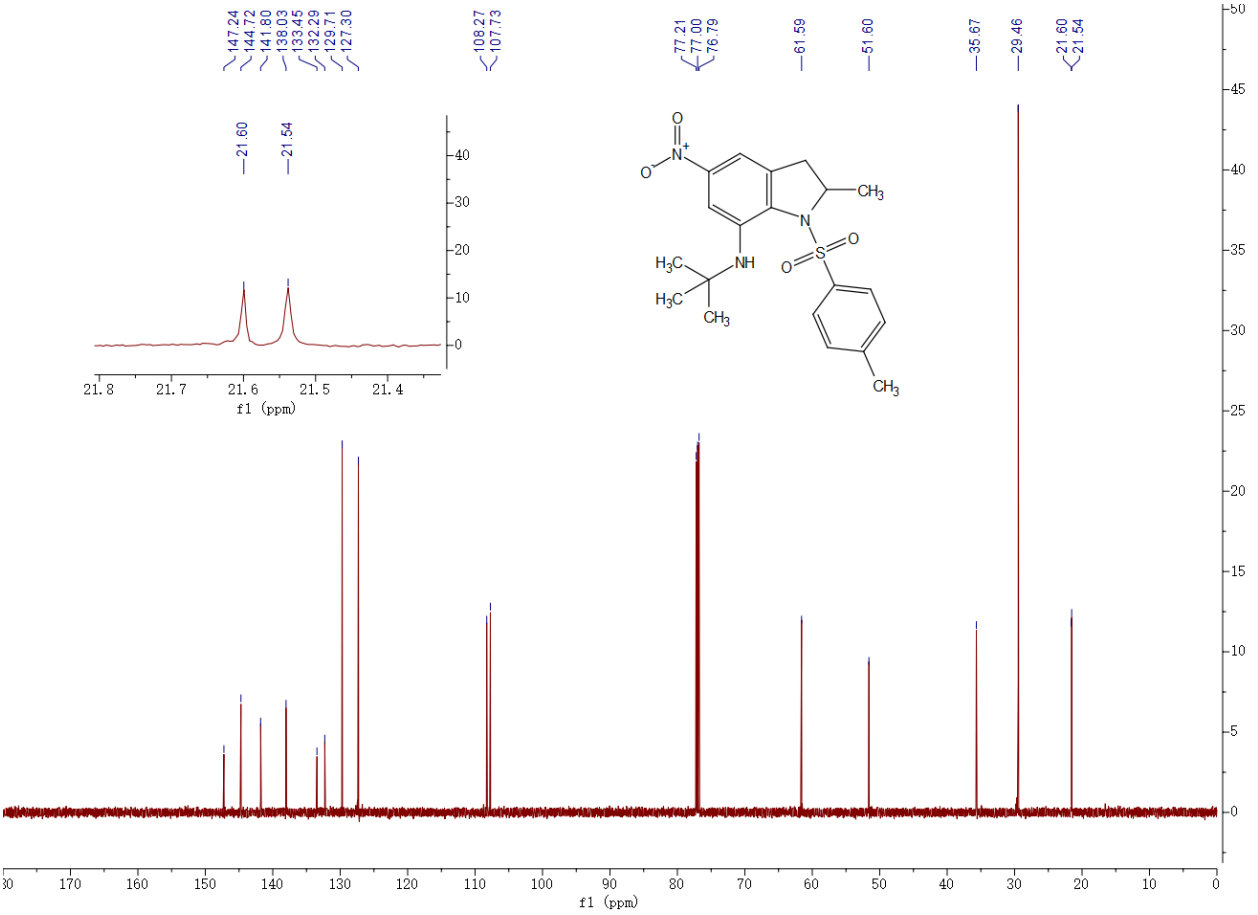


N-(tert-butyl)-2-methyl-5-nitro-1-tosylindolin-7-amine (4h)

^{1}H NMR (600 MHz, $CDCl_3$)

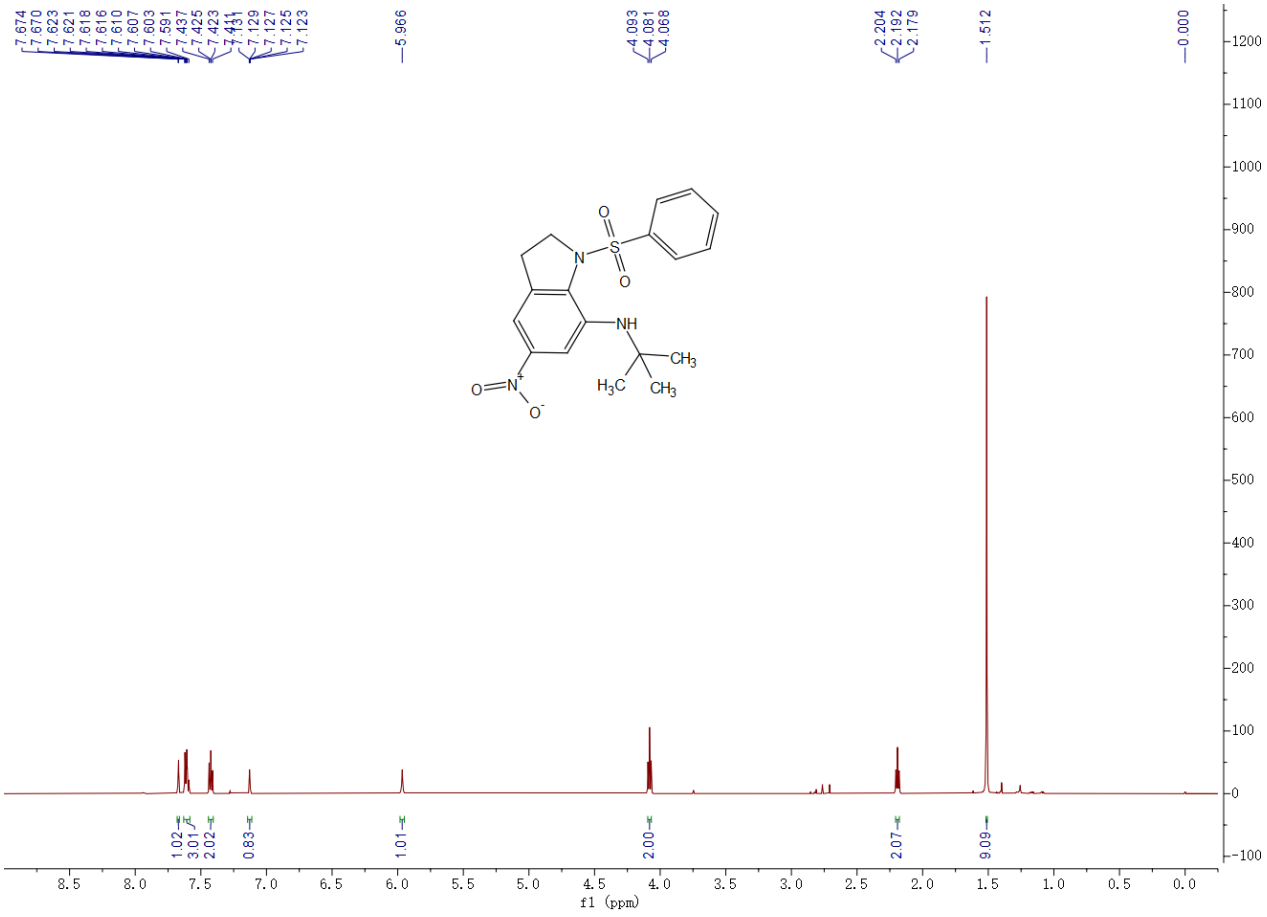


^{13}C NMR (151 MHz, $CDCl_3$)

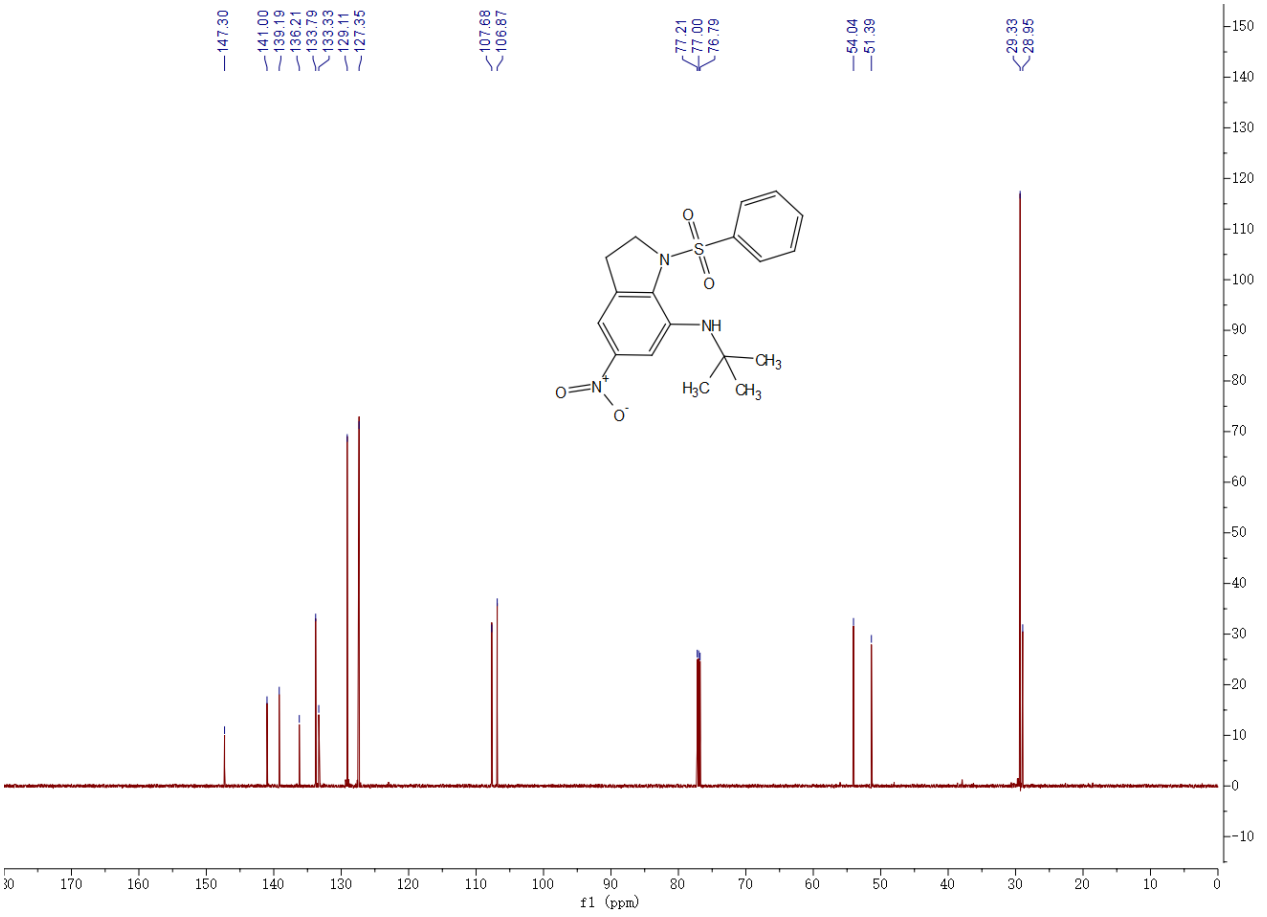


N-(tert-butyl)-5-nitro-1-(phenylsulfonyl)indolin-7-amine (4i)

^{1}H NMR (600 MHz, $CDCl_3$)

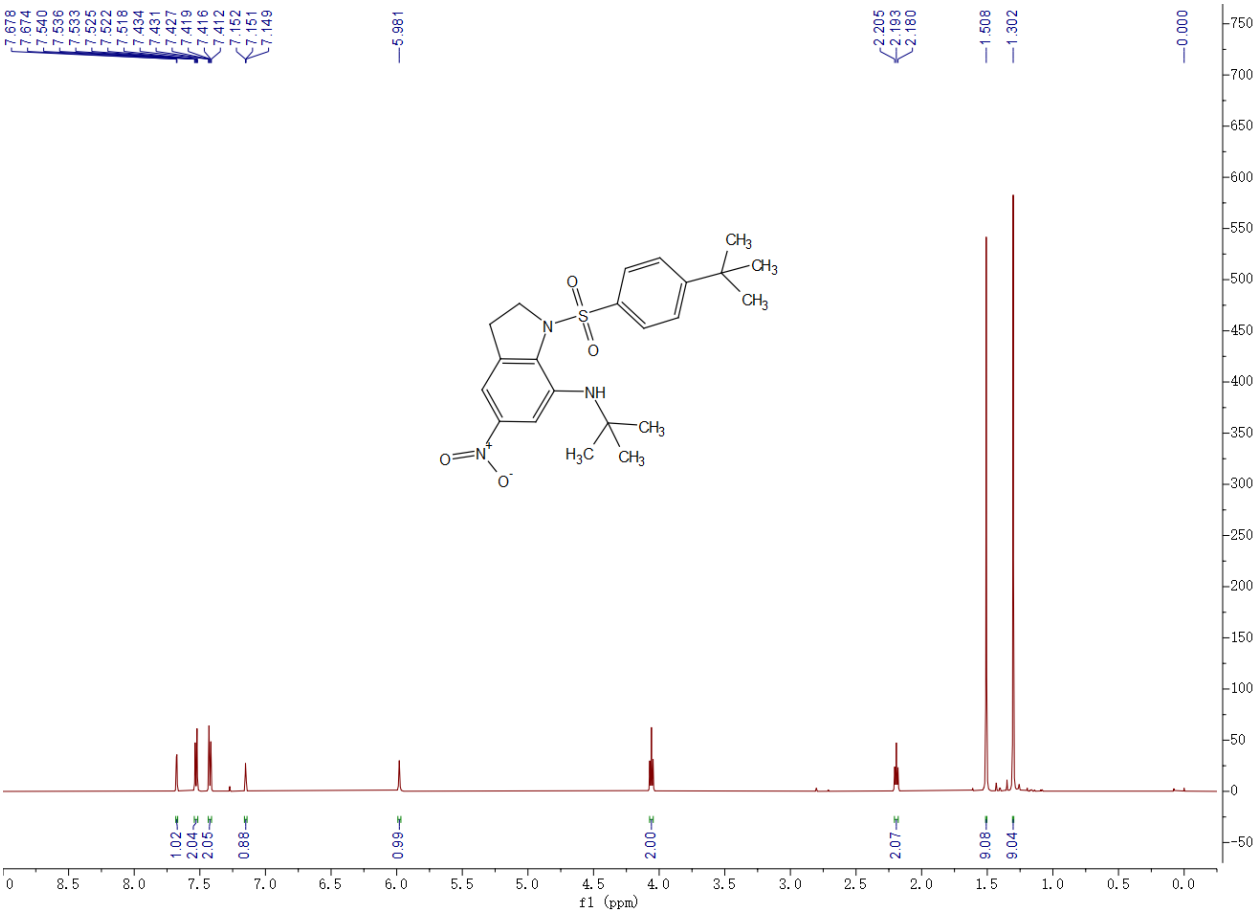


^{13}C NMR (151 MHz, $CDCl_3$)

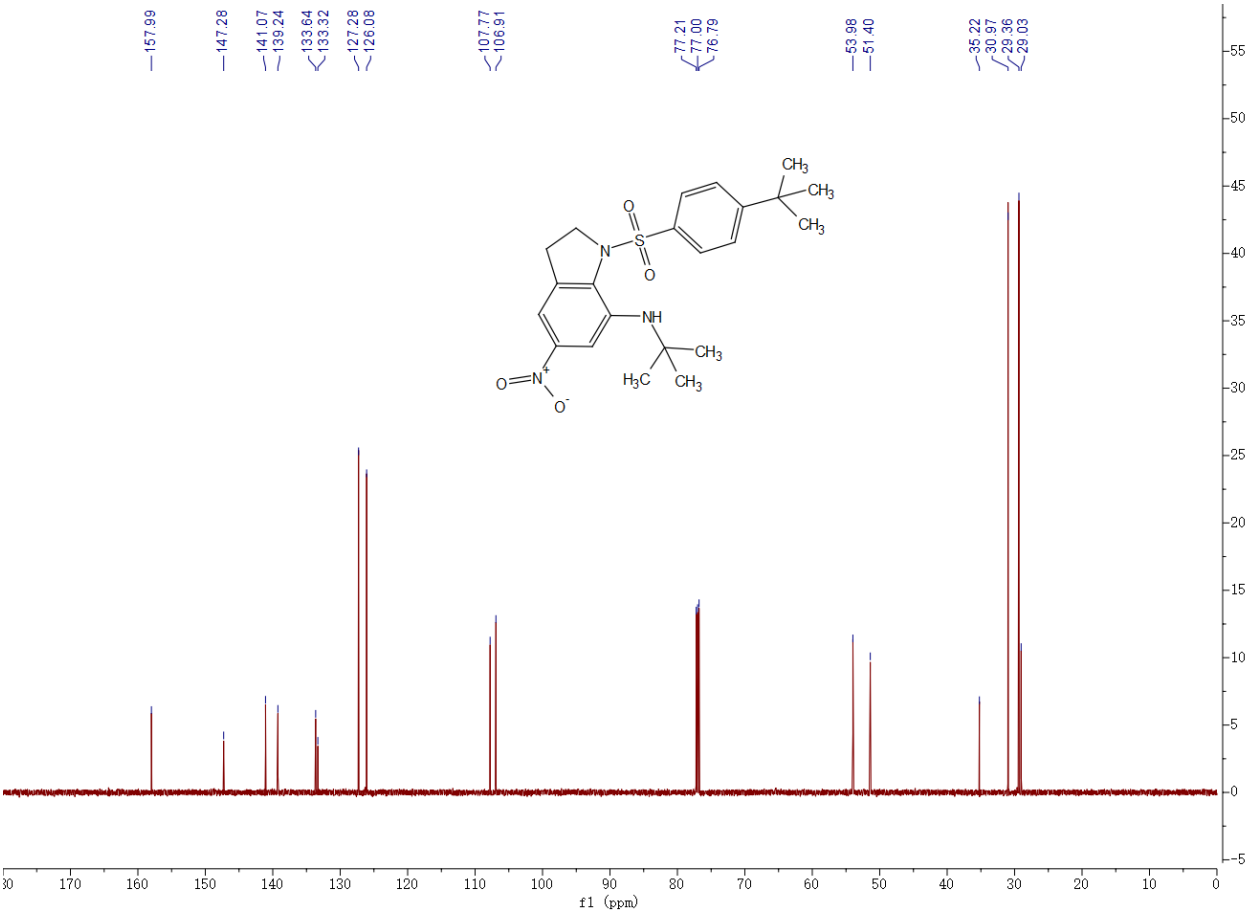


N-(tert-butyl)-1-((4-(tert-butyl)phenyl)sulfonyl)-5-nitroindolin-7-amine (4j)

^{1}H NMR (600 MHz, $CDCl_3$)

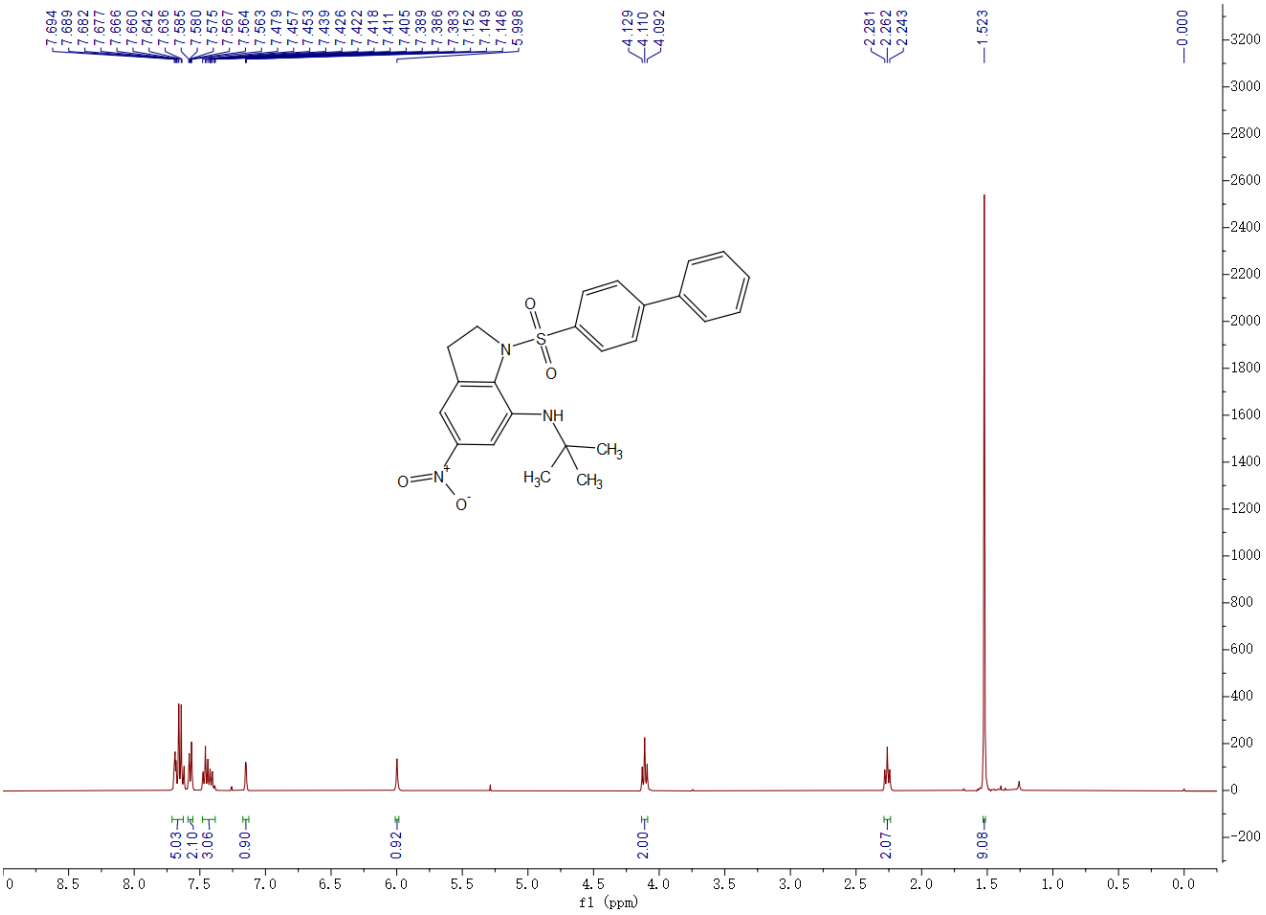


^{13}C NMR (151 MHz, $CDCl_3$)

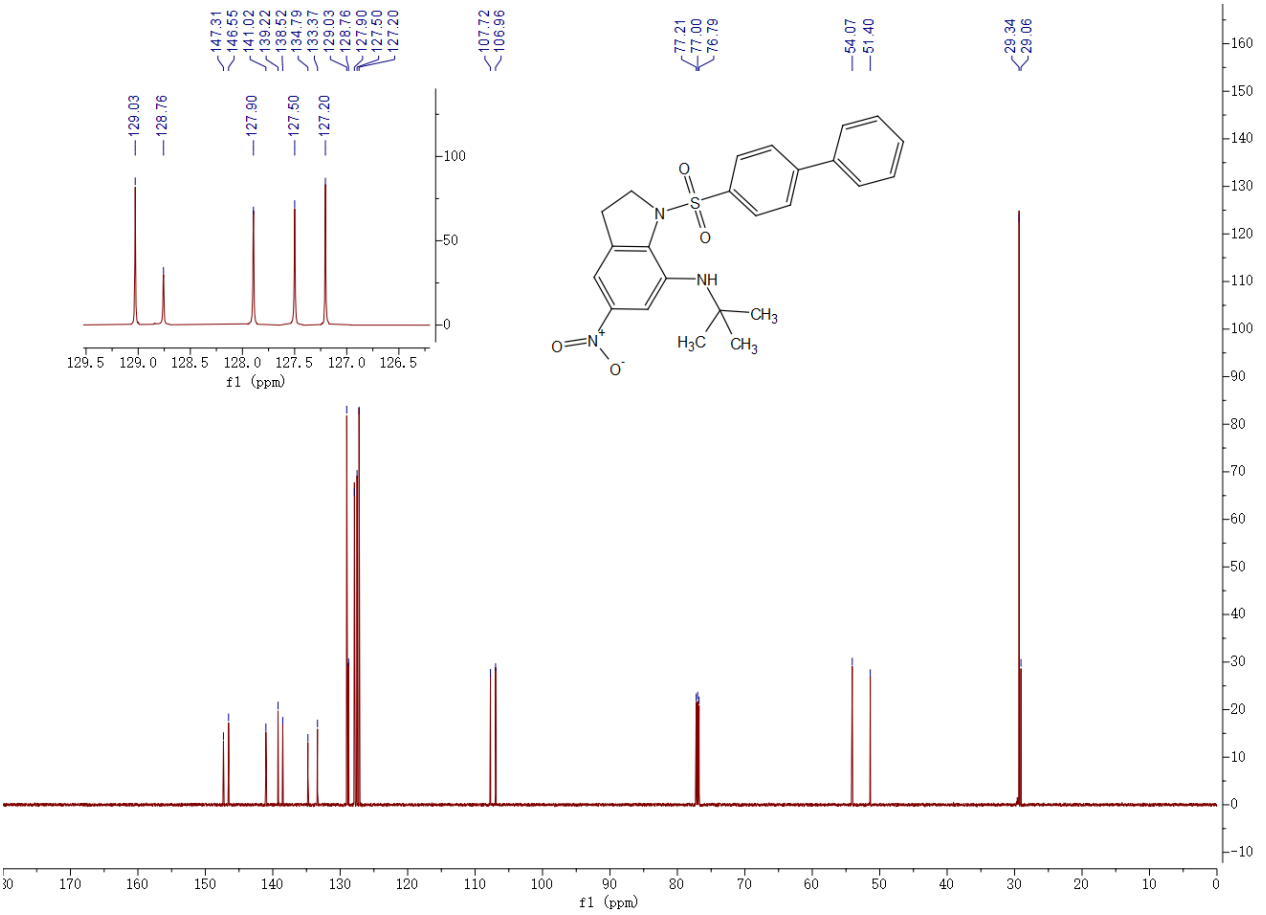


1-([1,1'-biphenyl]-4-ylsulfonyl)-N-(tert-butyl)-5-nitroindolin-7-amine (4k)

^{1}H NMR (400 MHz, $CDCl_3$)

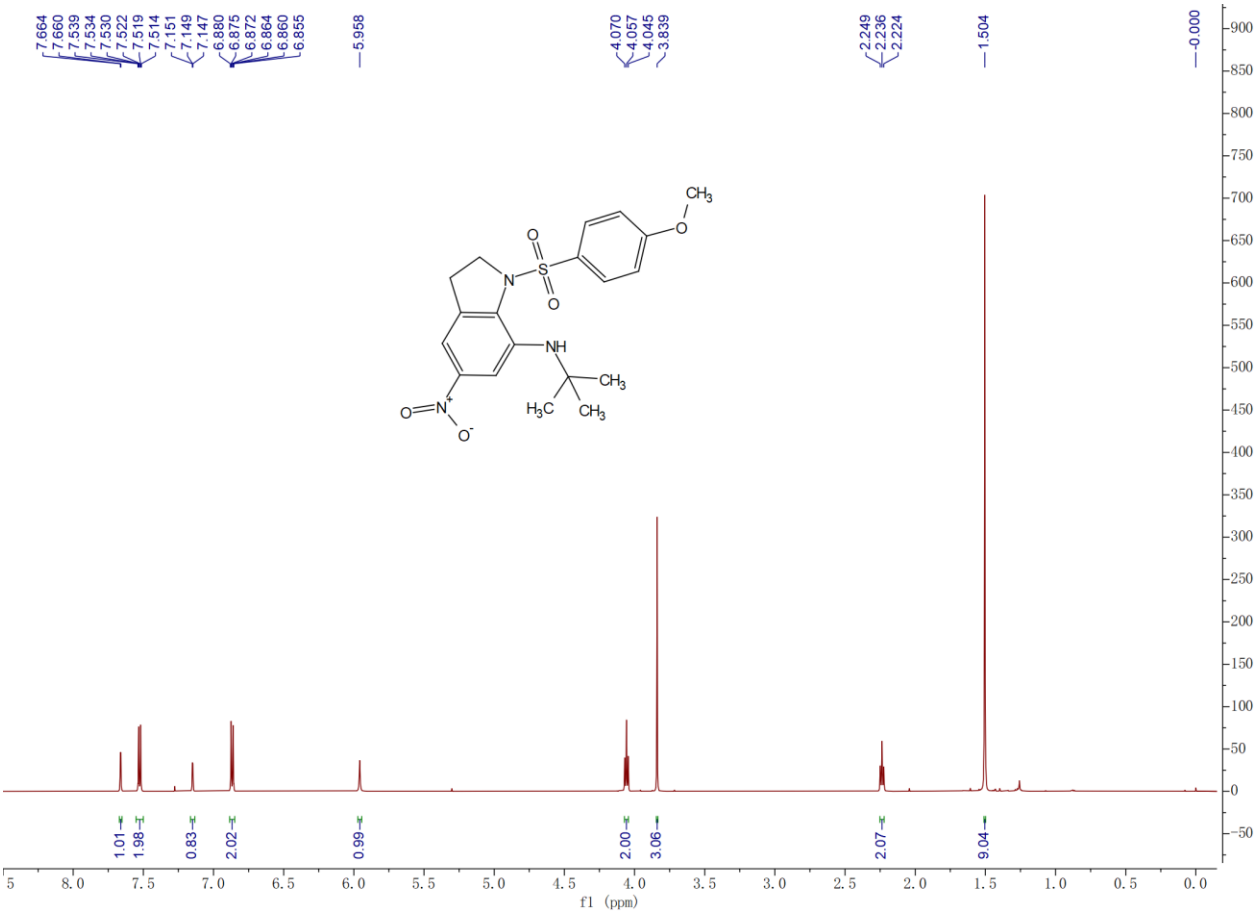


^{13}C NMR (151 MHz, $CDCl_3$)

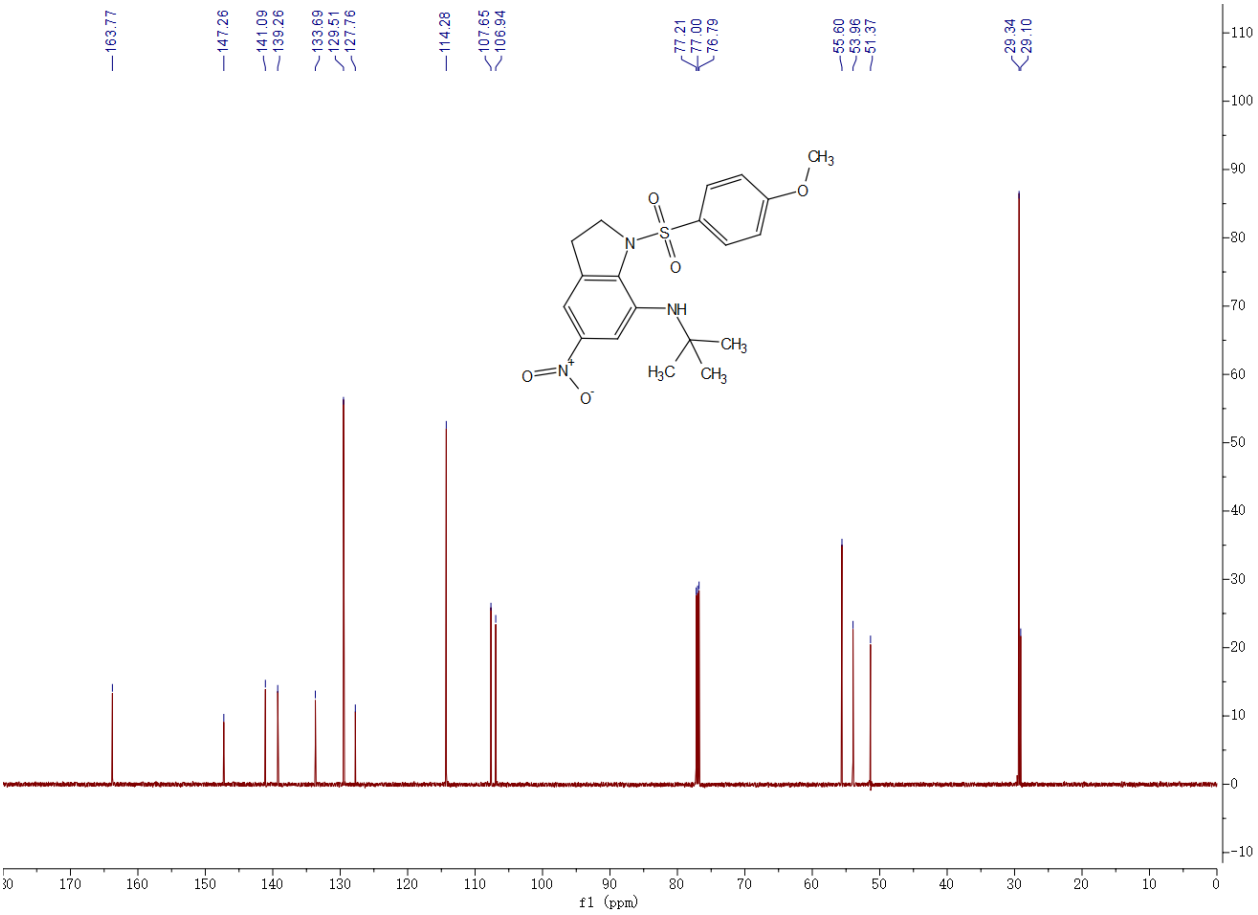


N-(tert-butyl)-1-((4-methoxyphenyl)sulfonyl)-5-nitroindolin-7-amine (4l)

^{1}H NMR (600 MHz, $CDCl_3$)

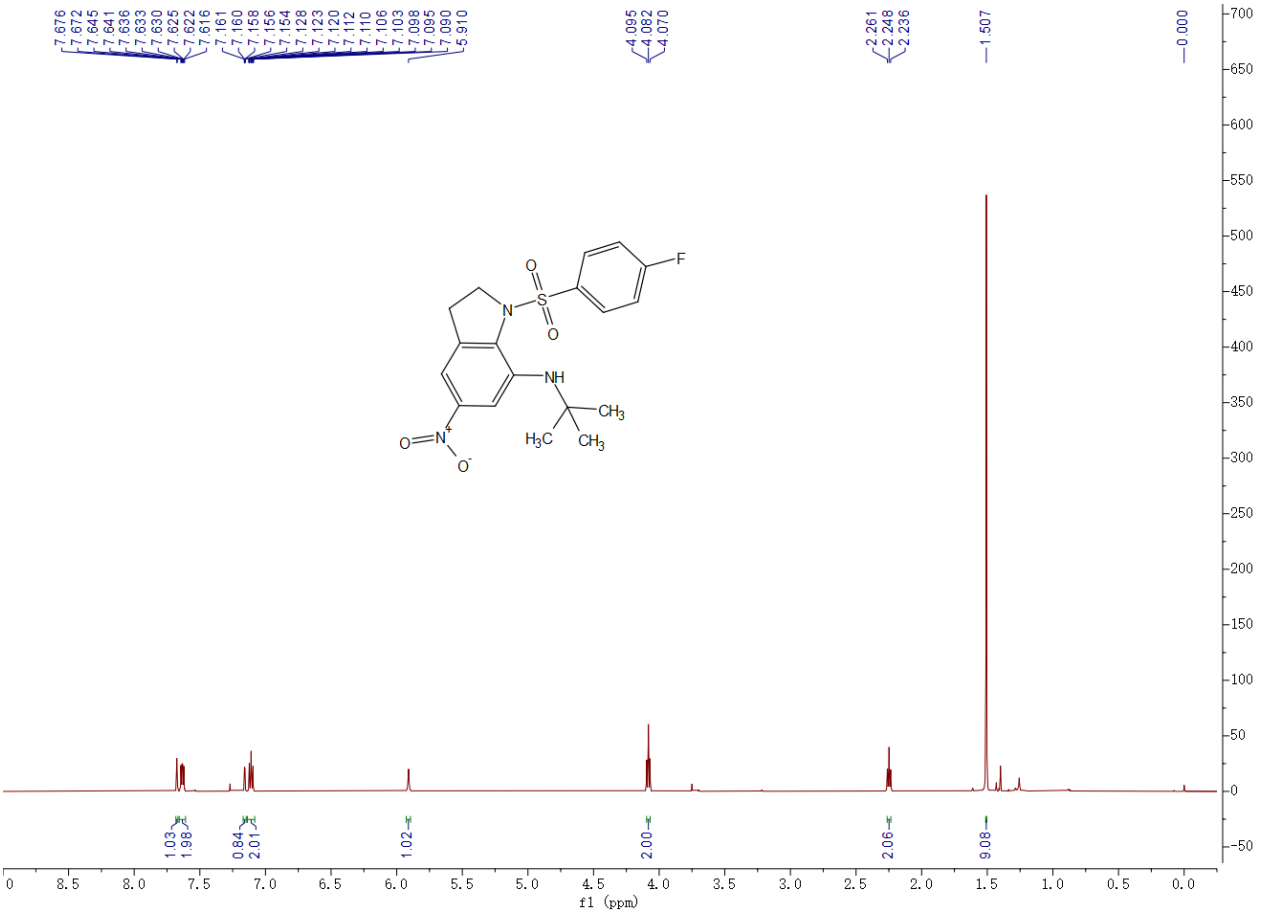


^{13}C NMR (151 MHz, $CDCl_3$)

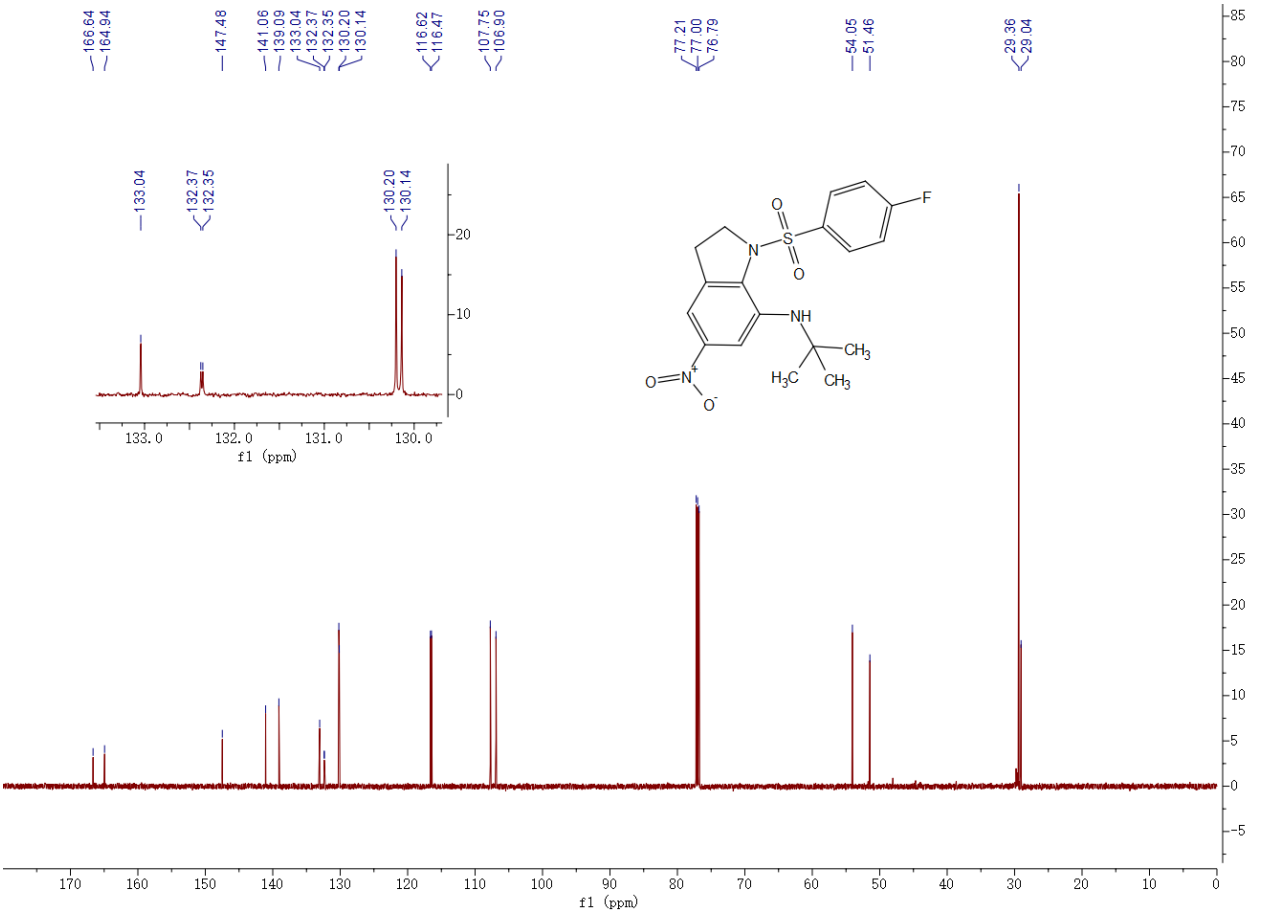


N-(tert-butyl)-1-((4-fluorophenyl)sulfonyl)-5-nitroindolin-7-amine (4m)

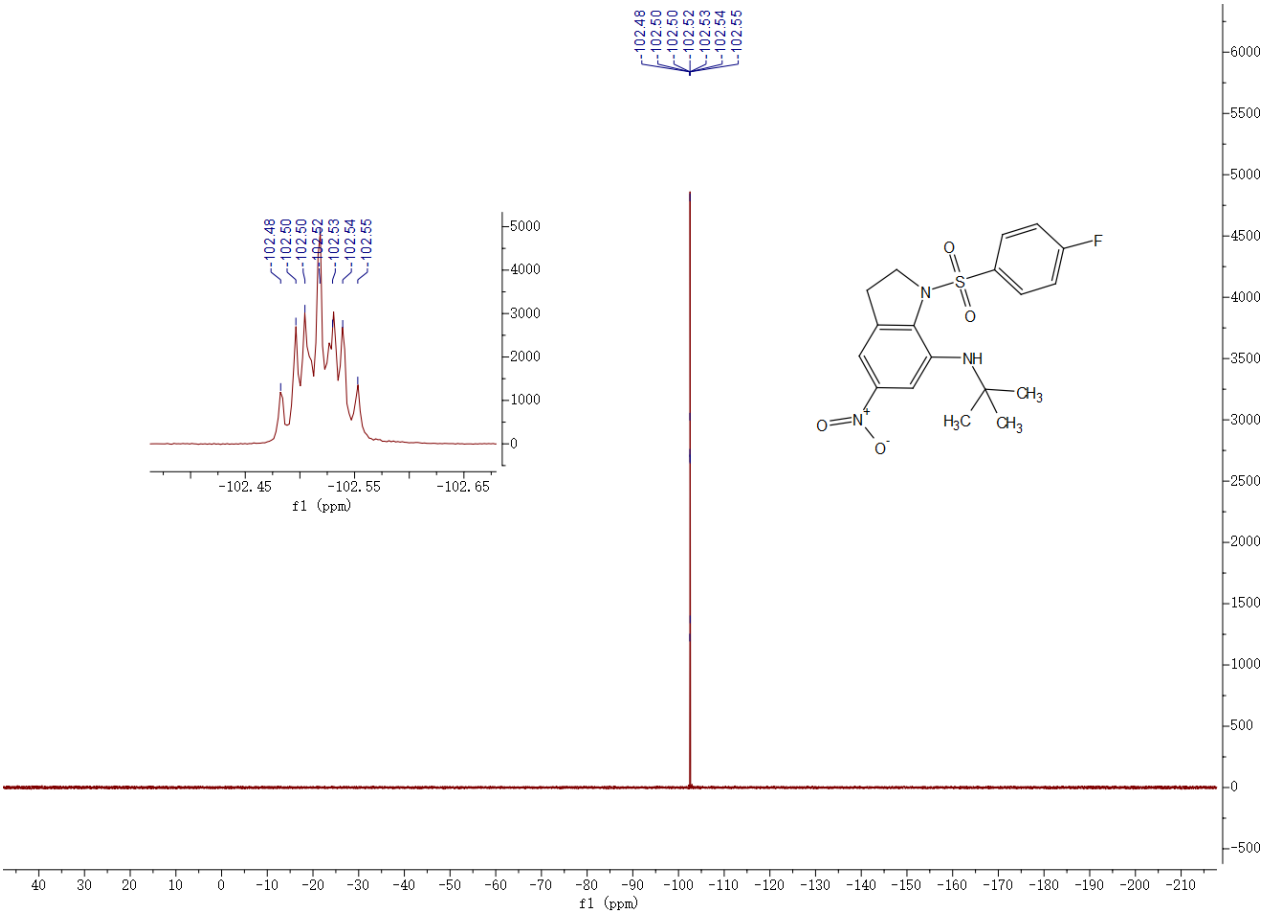
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

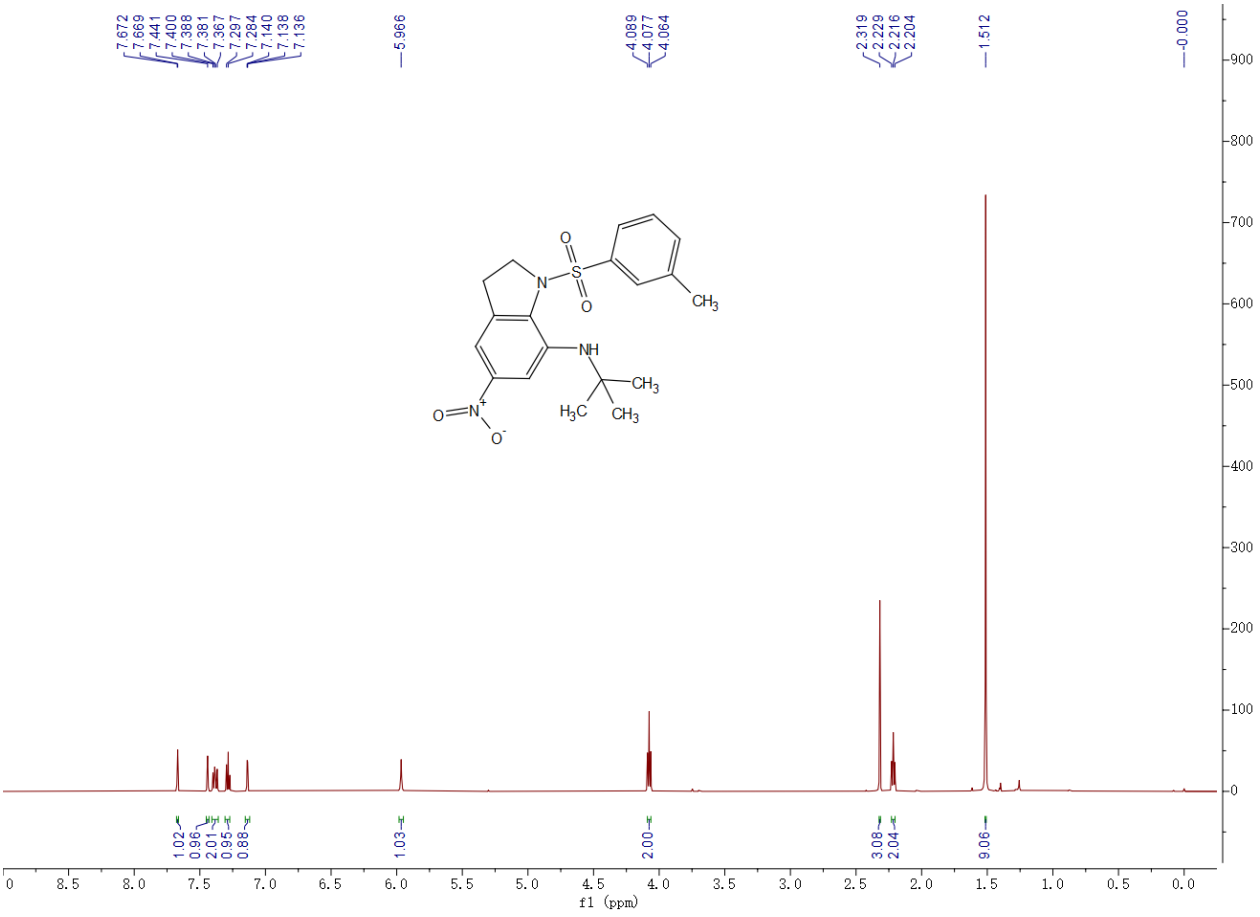


^{19}F NMR (376 MHz, $CDCl_3$)

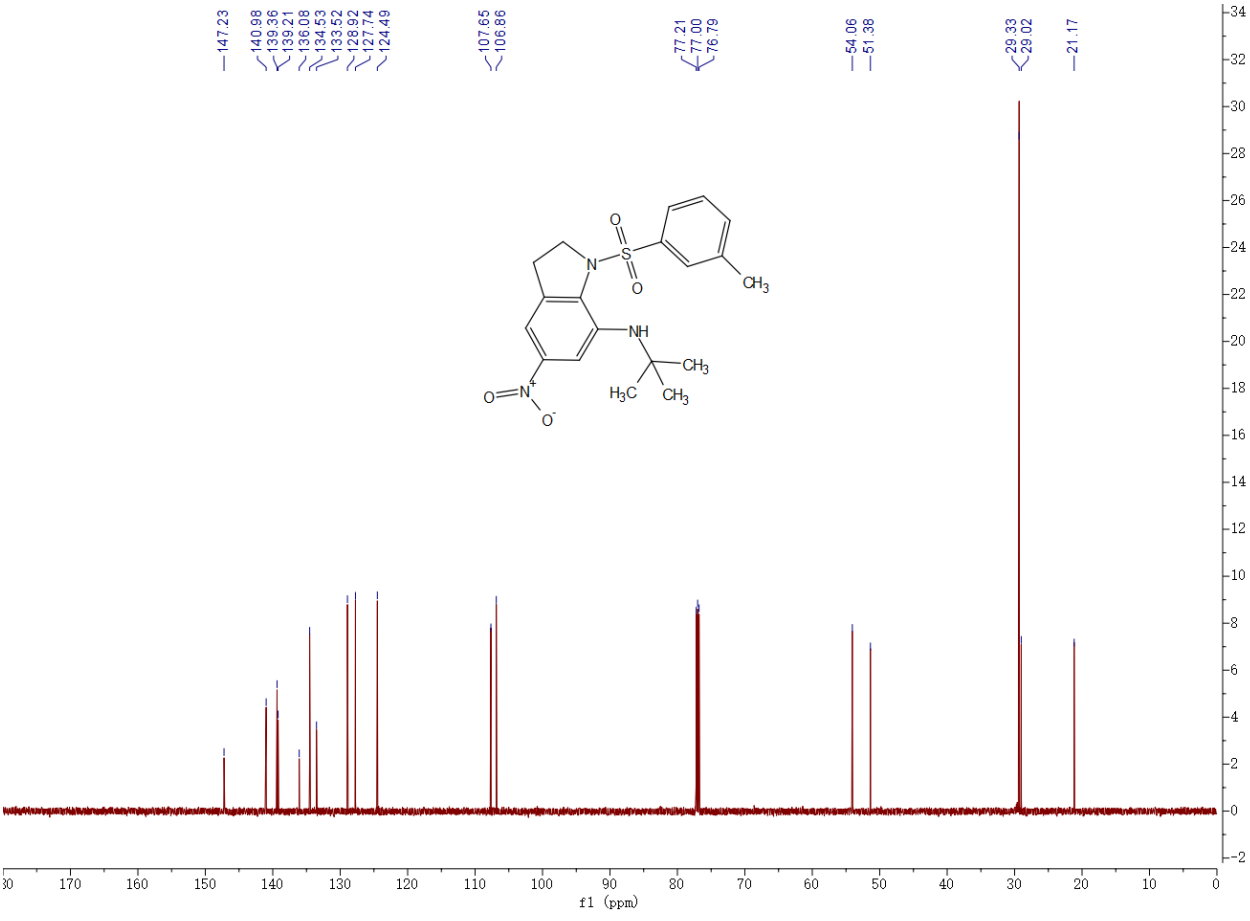


N-(tert-butyl)-5-nitro-1-(m-tolylsulfonyl)indolin-7-amine (4n)

^{1}H NMR (600 MHz, $CDCl_3$)

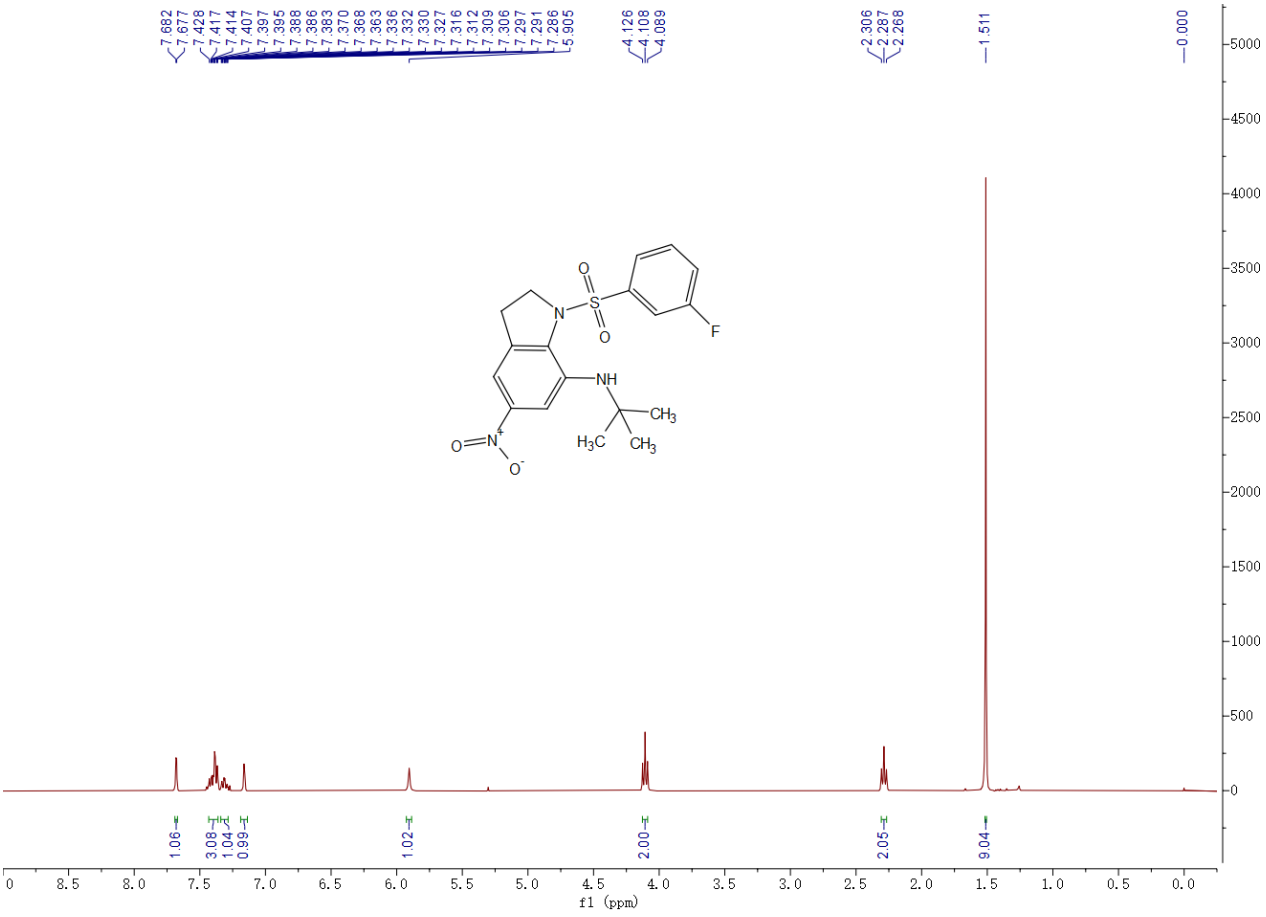


^{13}C NMR (151 MHz, $CDCl_3$)

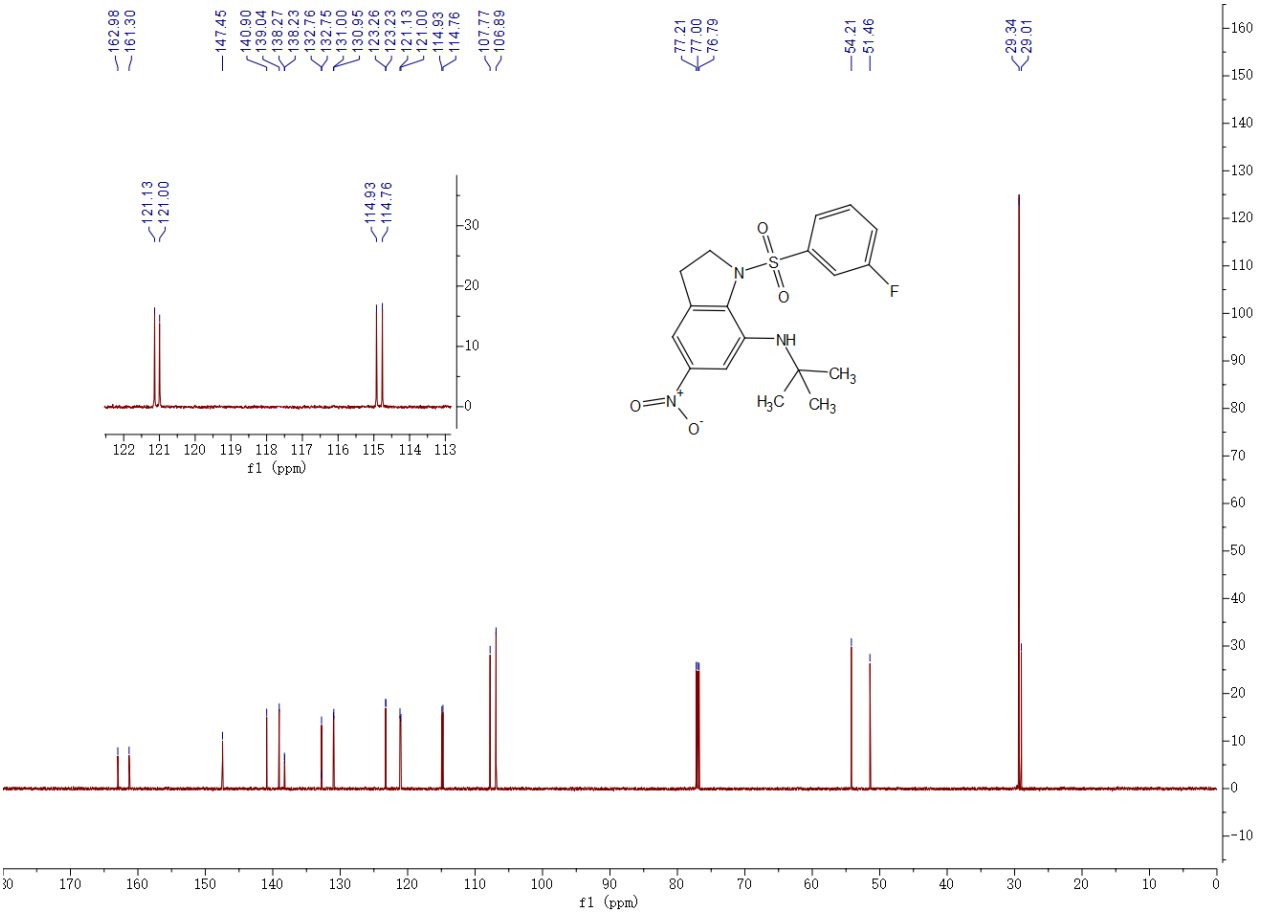


N-(tert-butyl)-1-((3-fluorophenyl)sulfonyl)-5-nitroindolin-7-amine (4o)

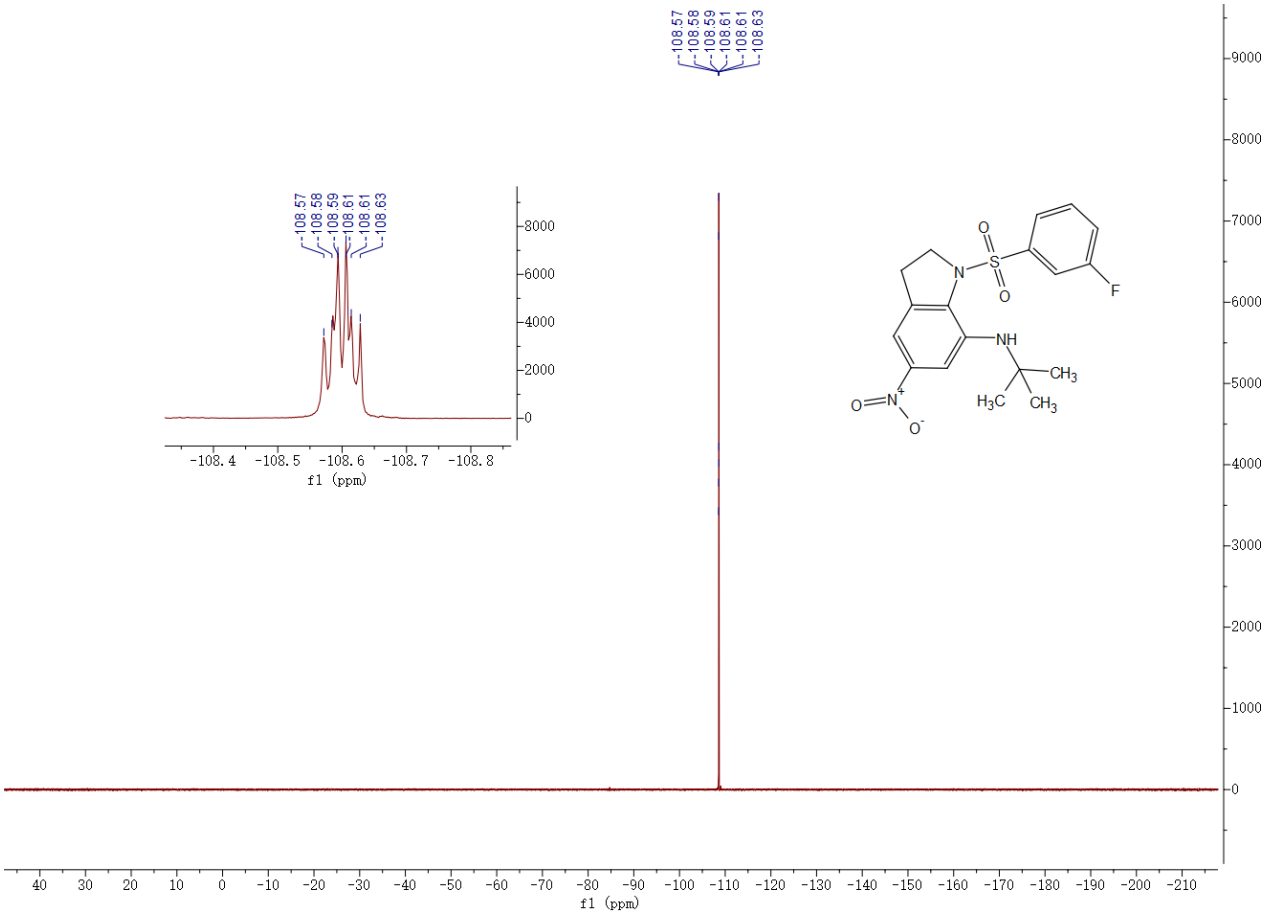
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

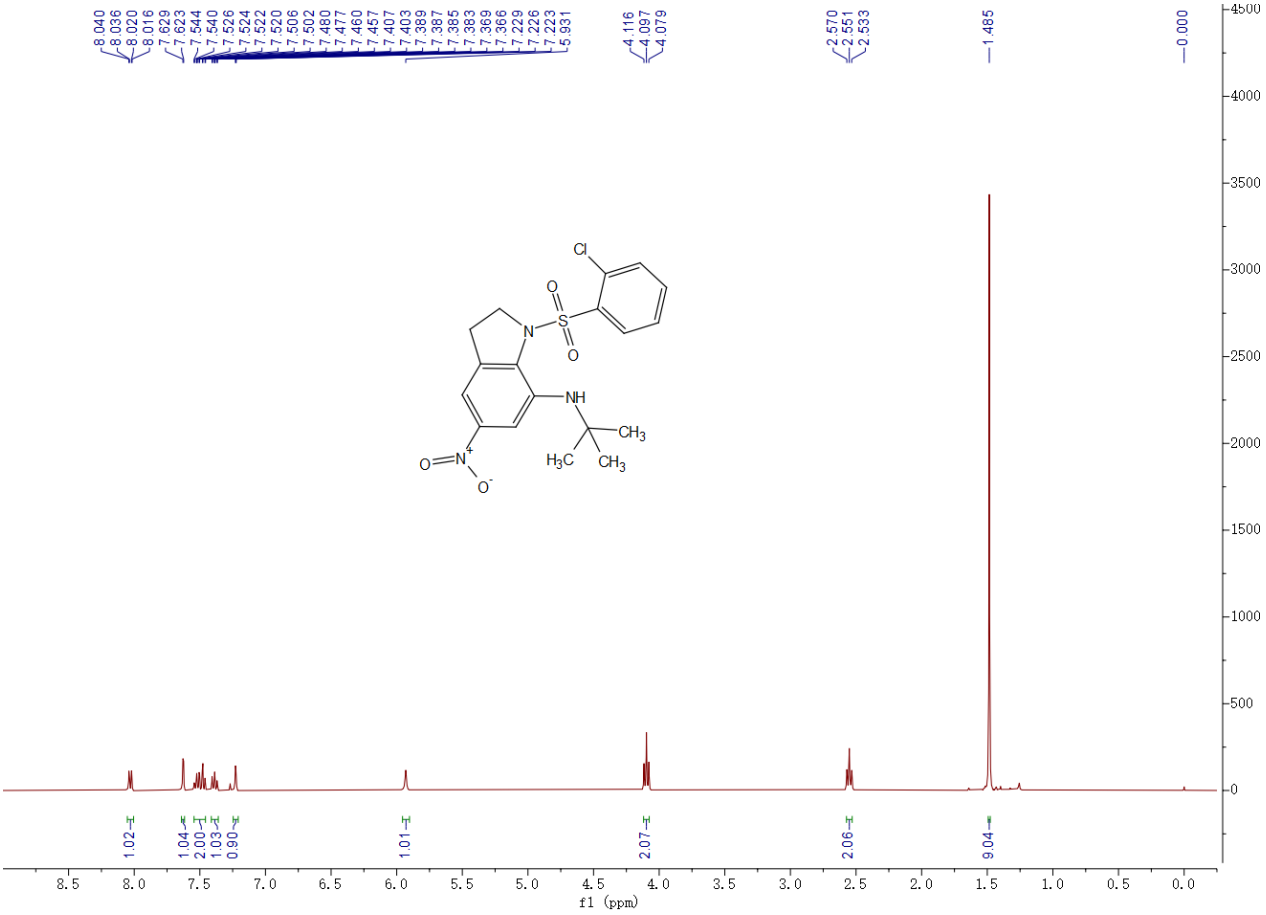


^{19}F NMR (376 MHz, $CDCl_3$)

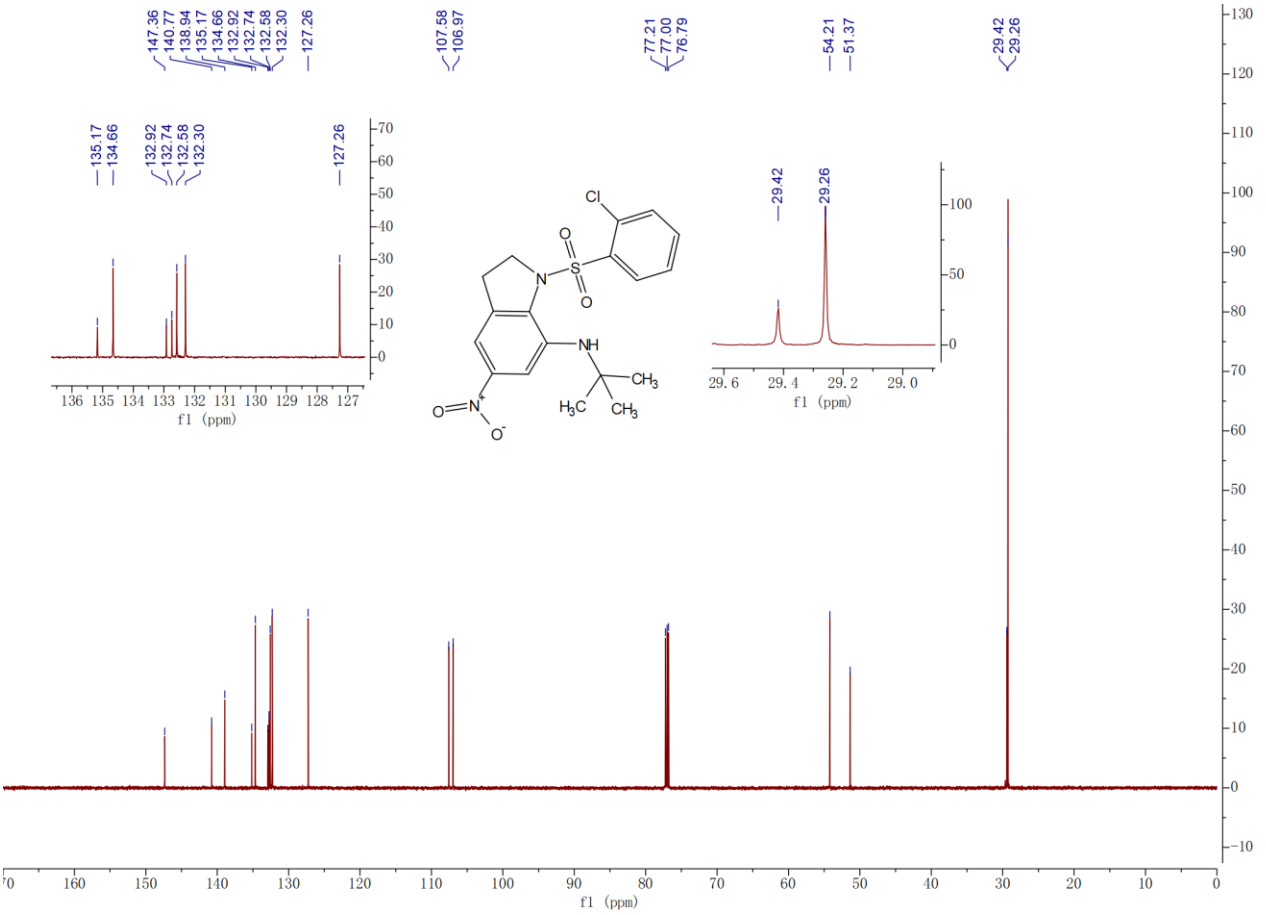


N-(tert-butyl)-1-((2-chlorophenyl)sulfonyl)-5-nitroindolin-7-amine (4p)

^{1}H NMR (400 MHz, $CDCl_3$)

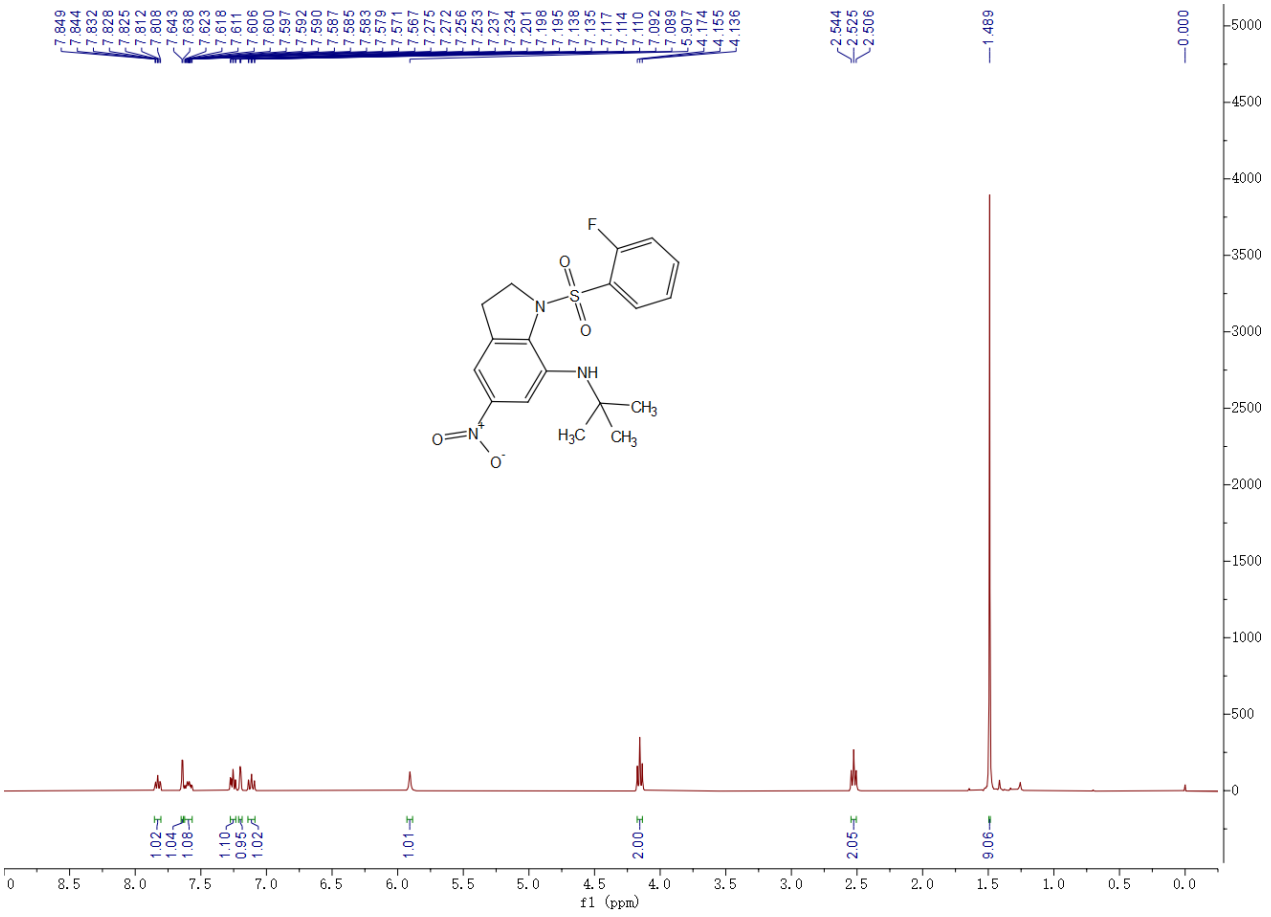


^{13}C NMR (151 MHz, $CDCl_3$)

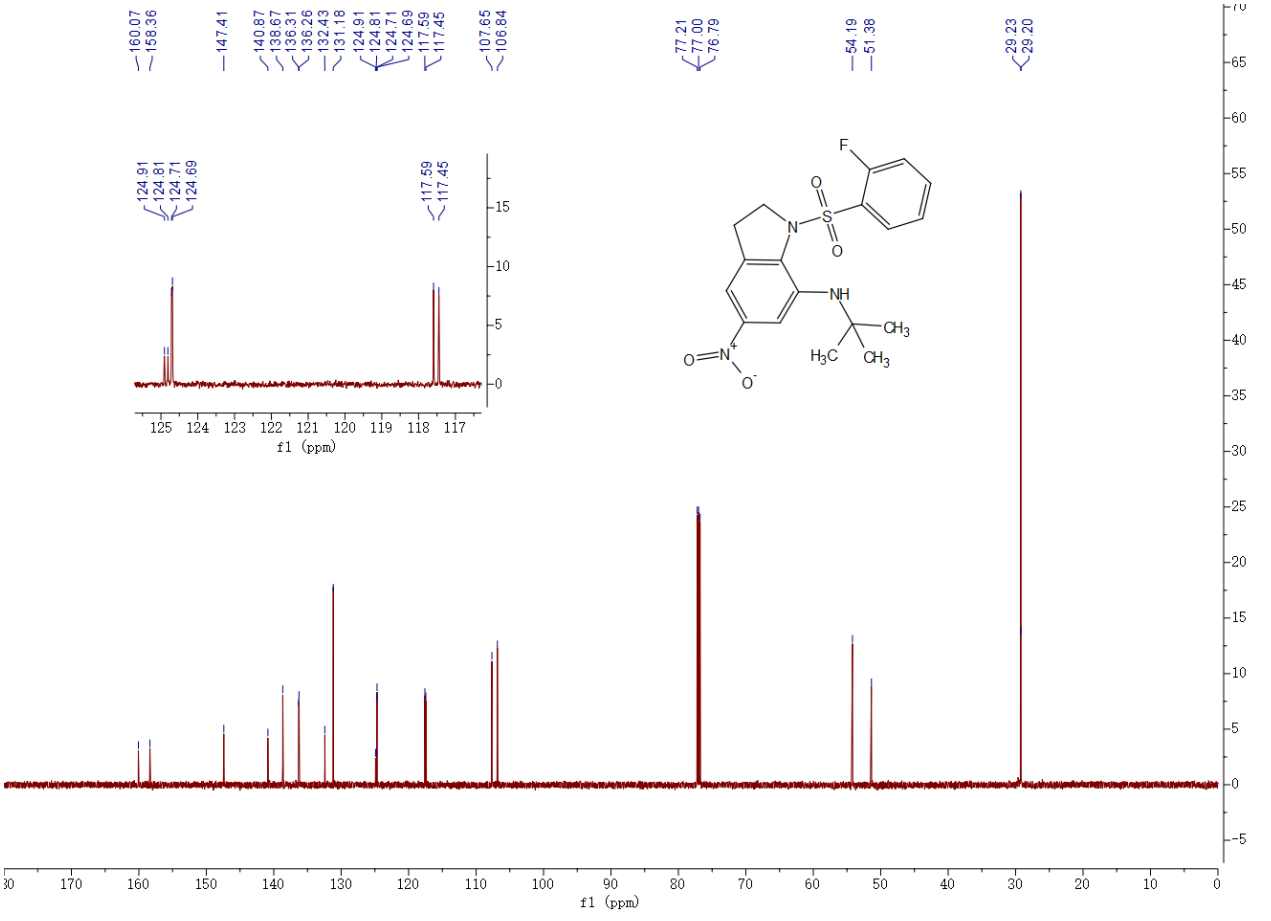


N-(tert-butyl)-1-((2-fluorophenyl)sulfonyl)-5-nitroindolin-7-amine (4q)

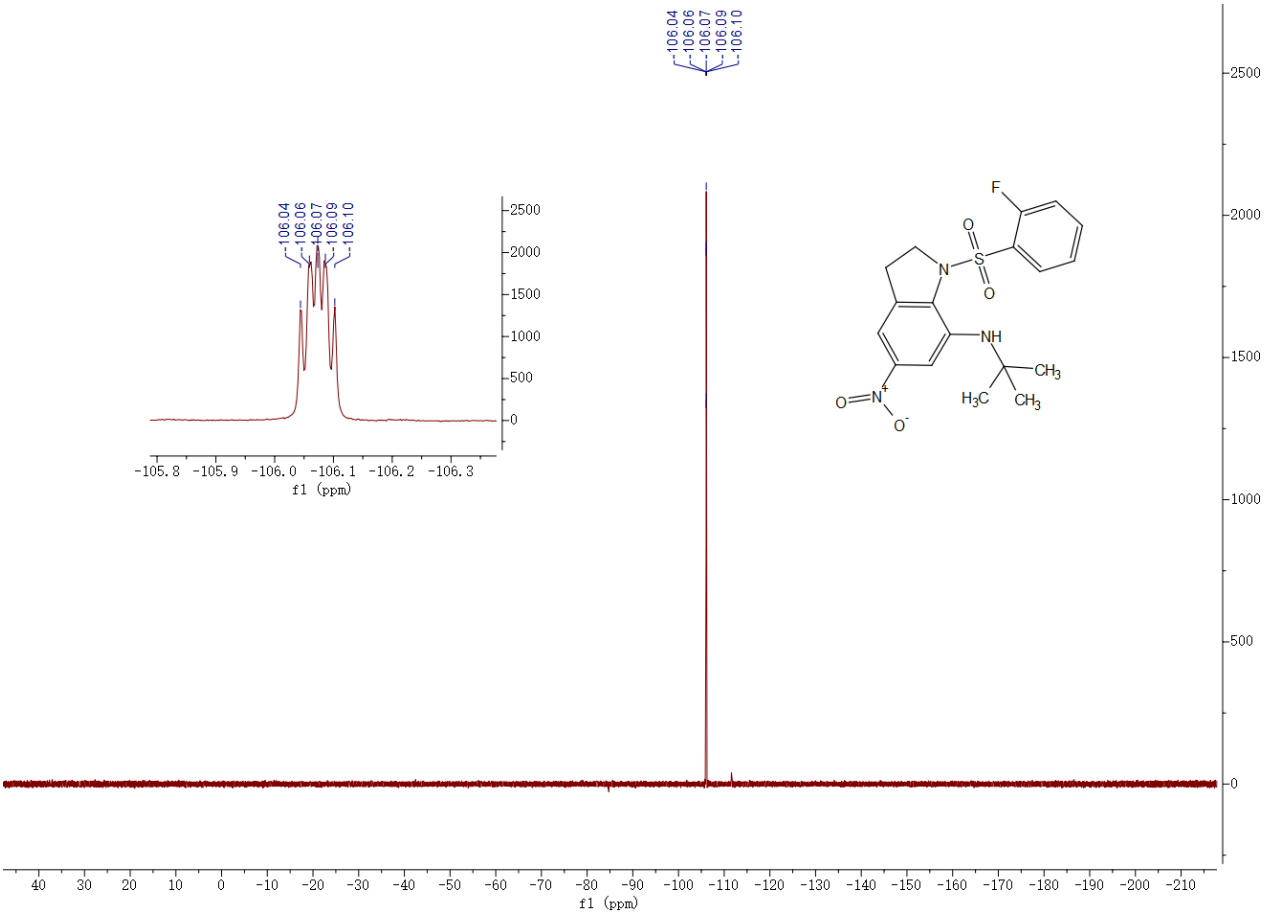
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

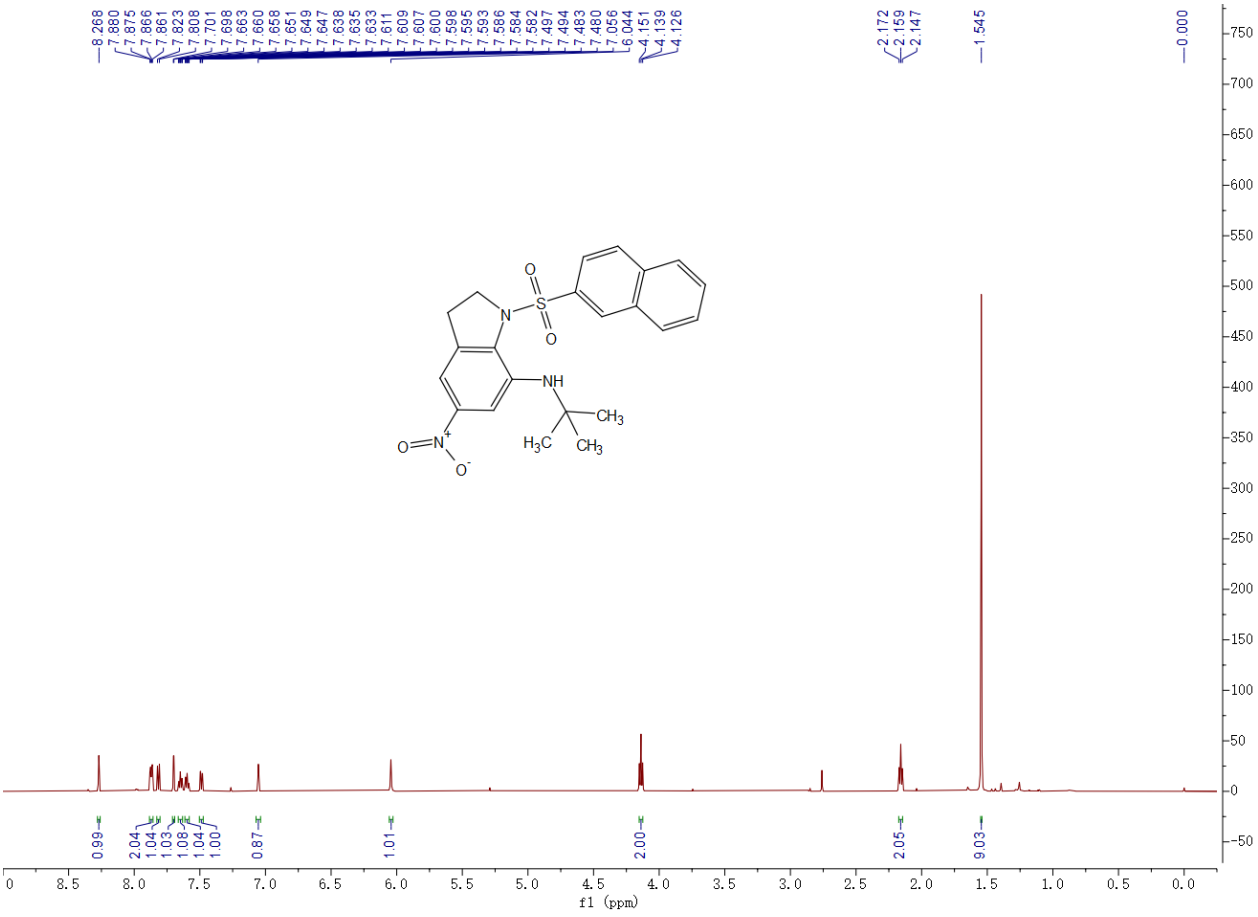


^{19}F NMR (376 MHz, $CDCl_3$)

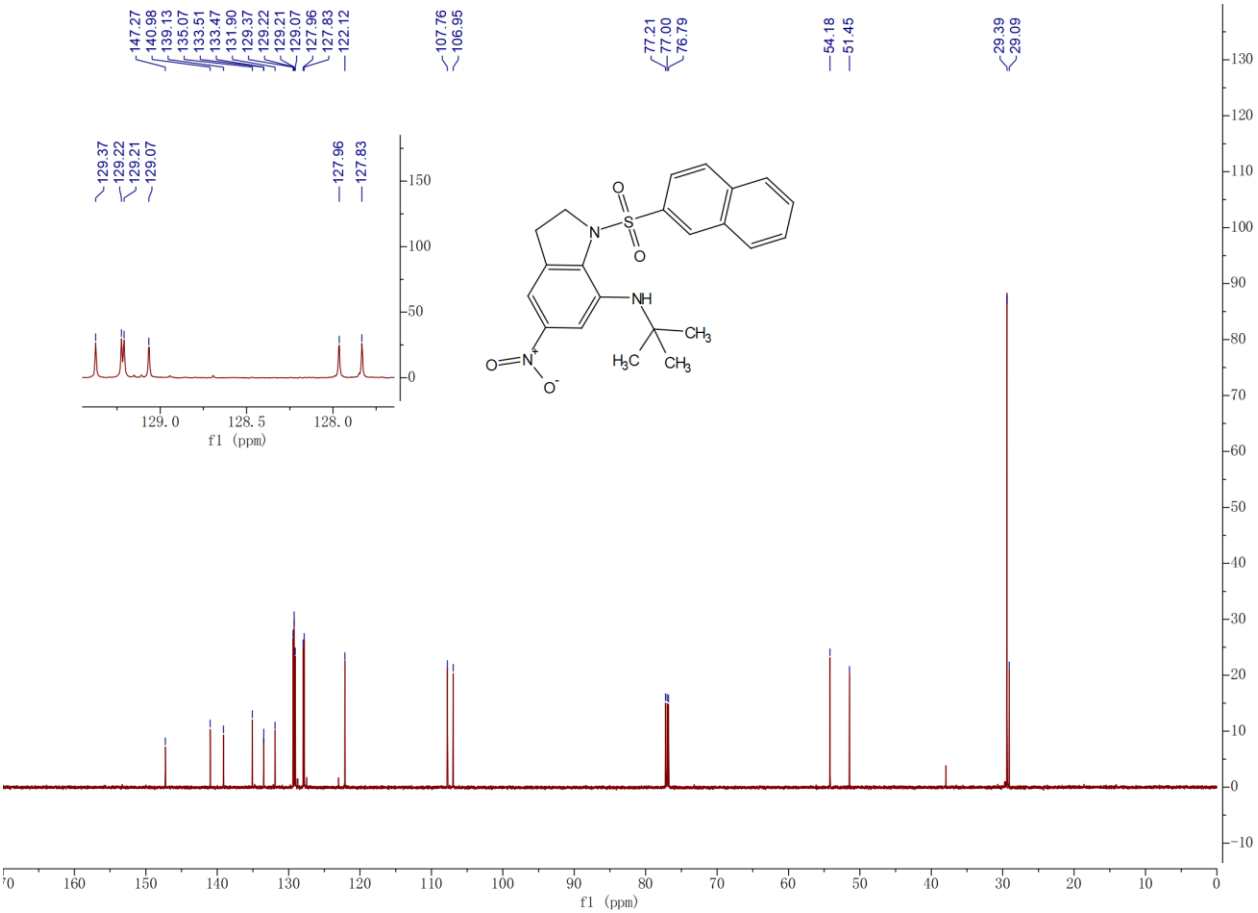


N-(tert-butyl)-1-(naphthalen-2-ylsulfonyl)-5-nitroindolin-7-amine (4r)

^{1}H NMR (600 MHz, $CDCl_3$)

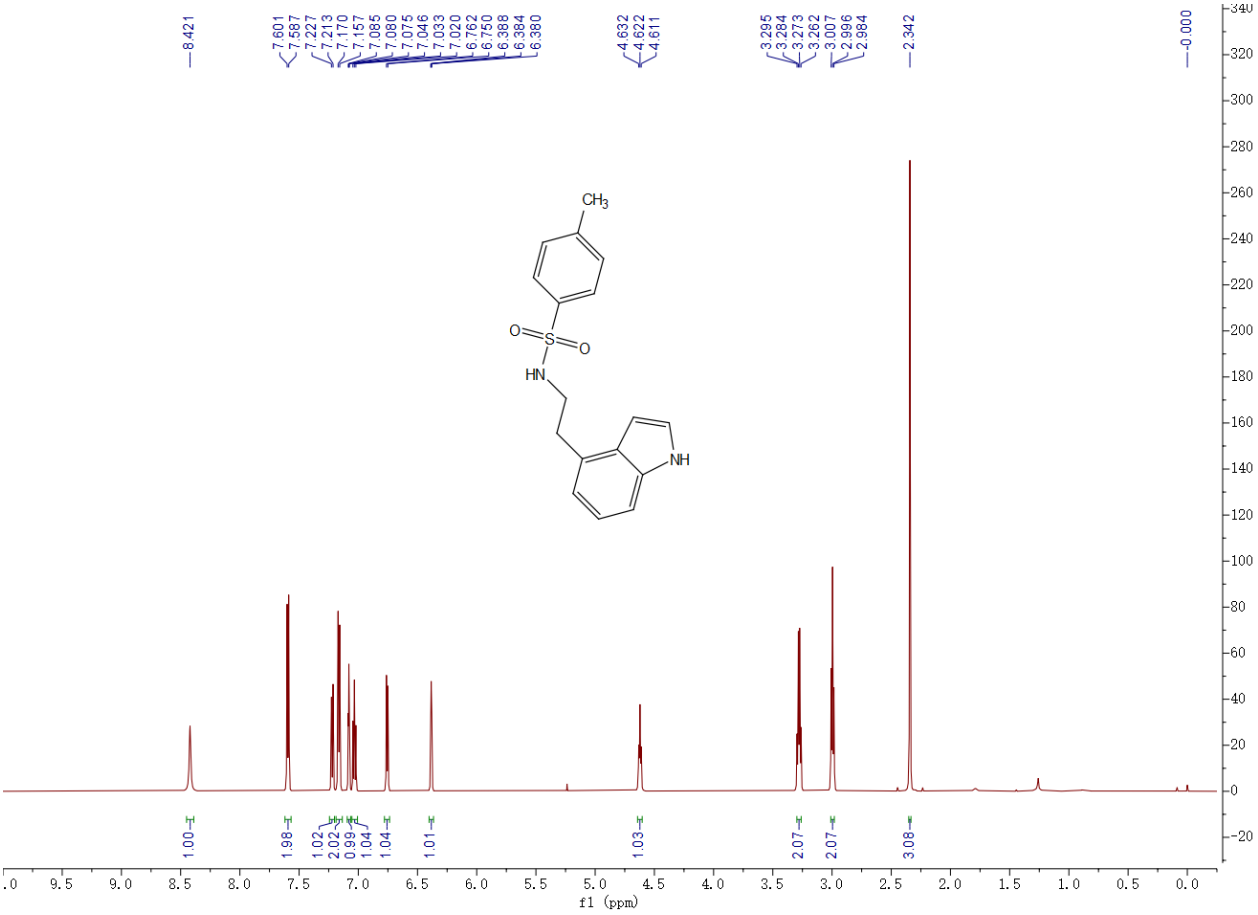


^{13}C NMR (151 MHz, $CDCl_3$)

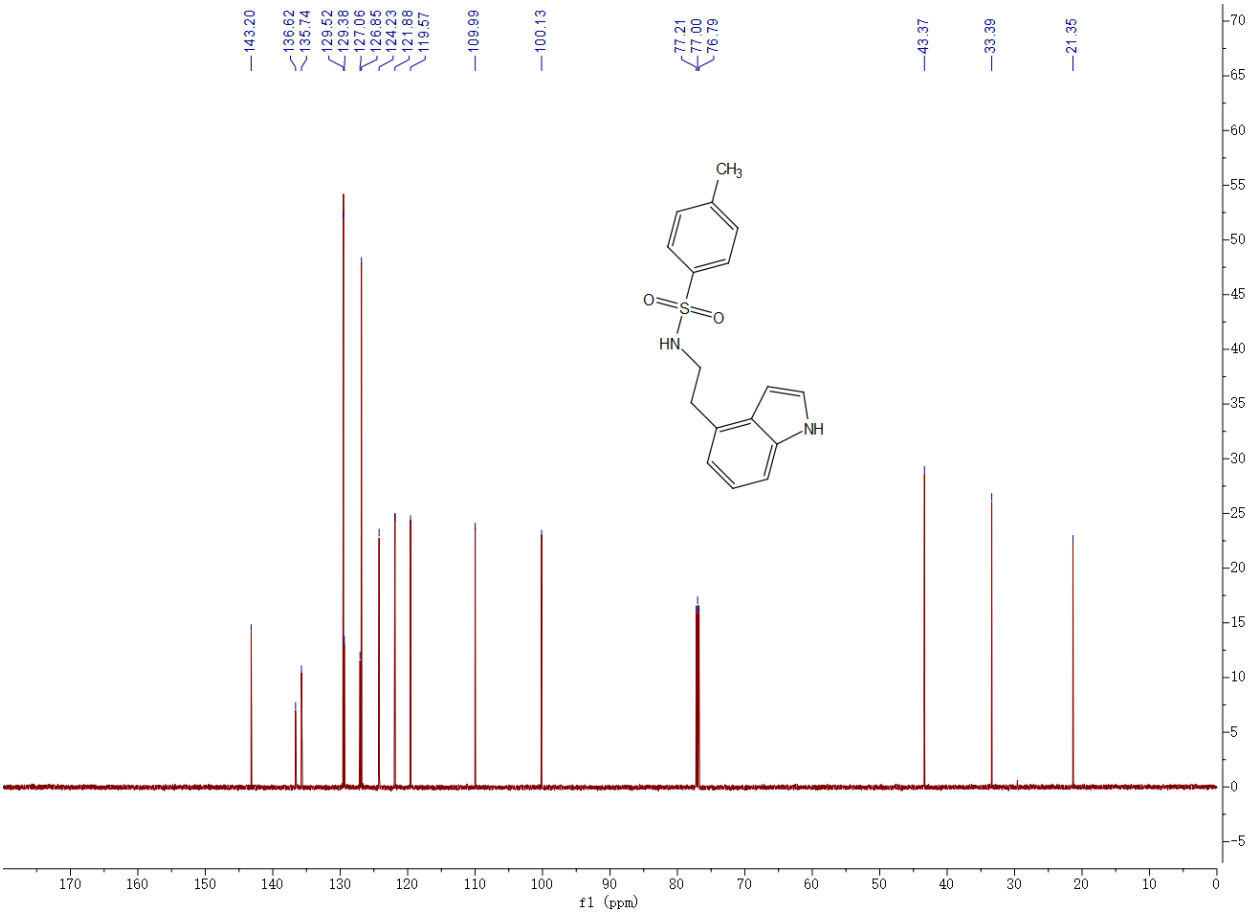


N-(2-(1H-indol-4-yl)ethyl)-4-methylbenzenesulfonamide (5)

^{1}H NMR (600 MHz, $CDCl_3$)

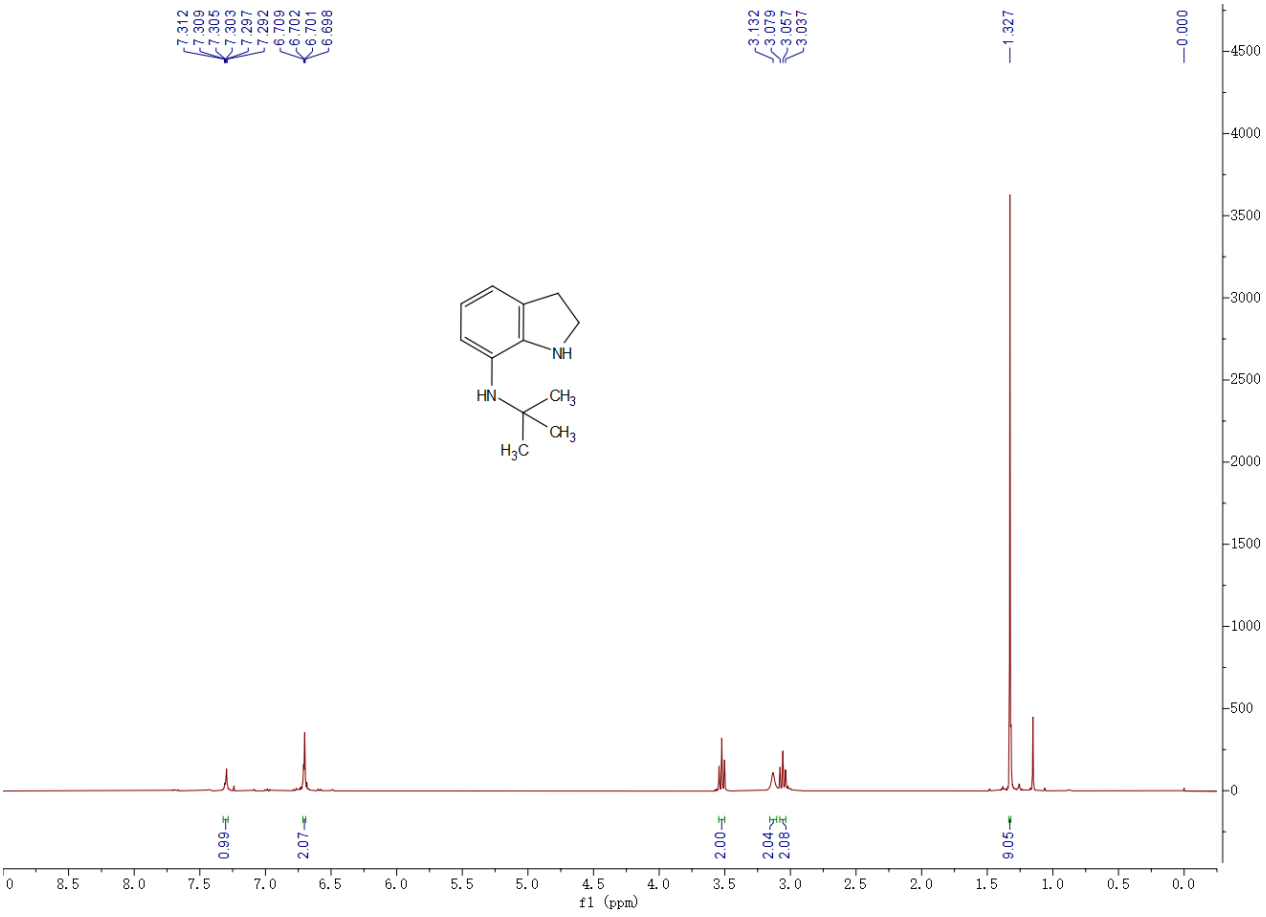


^{13}C NMR (151 MHz, $CDCl_3$)

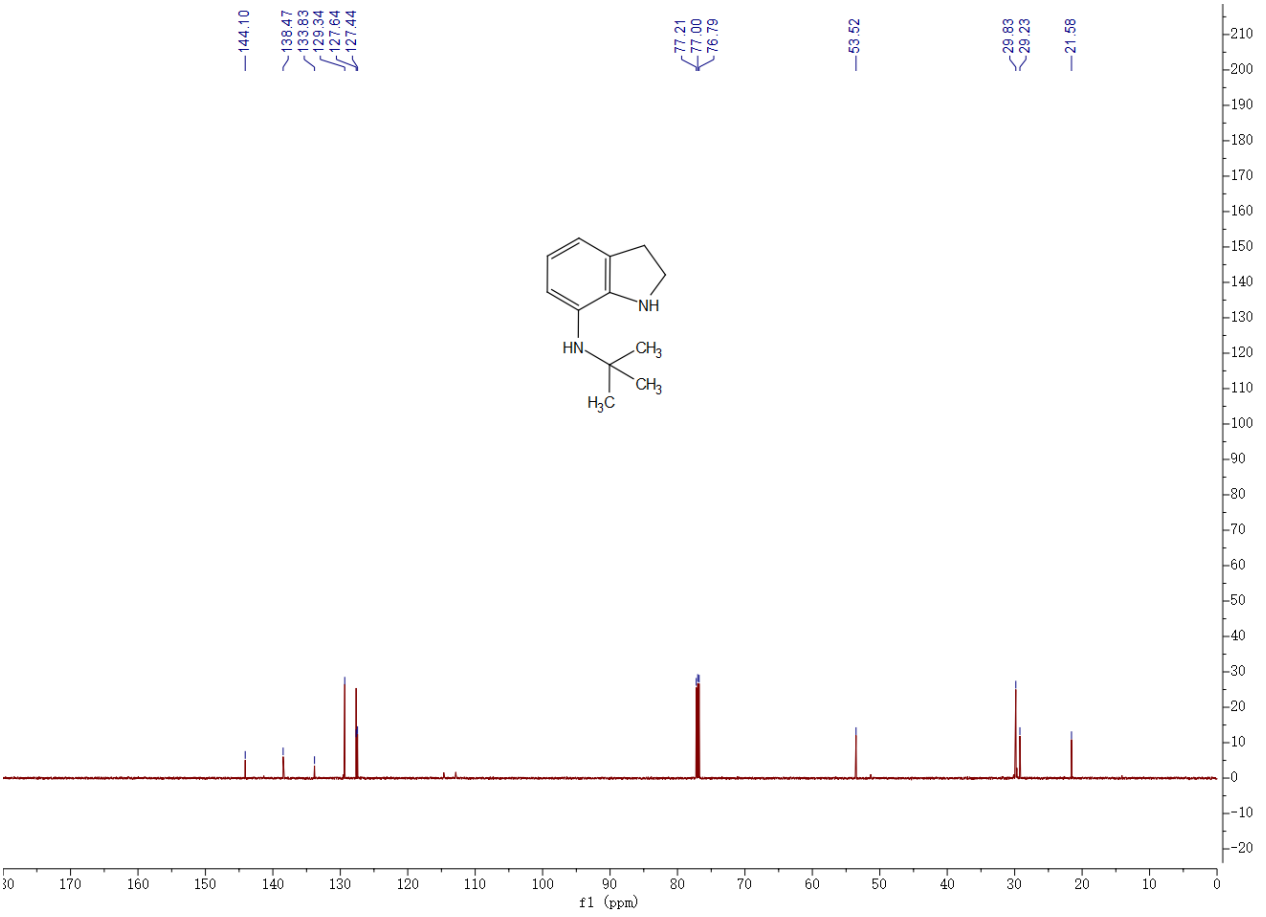


N-(2-(1H-indol-4-yl)ethyl)-4-methylbenzenesulfonamide (6)

^{1}H NMR (400 MHz, $CDCl_3$)

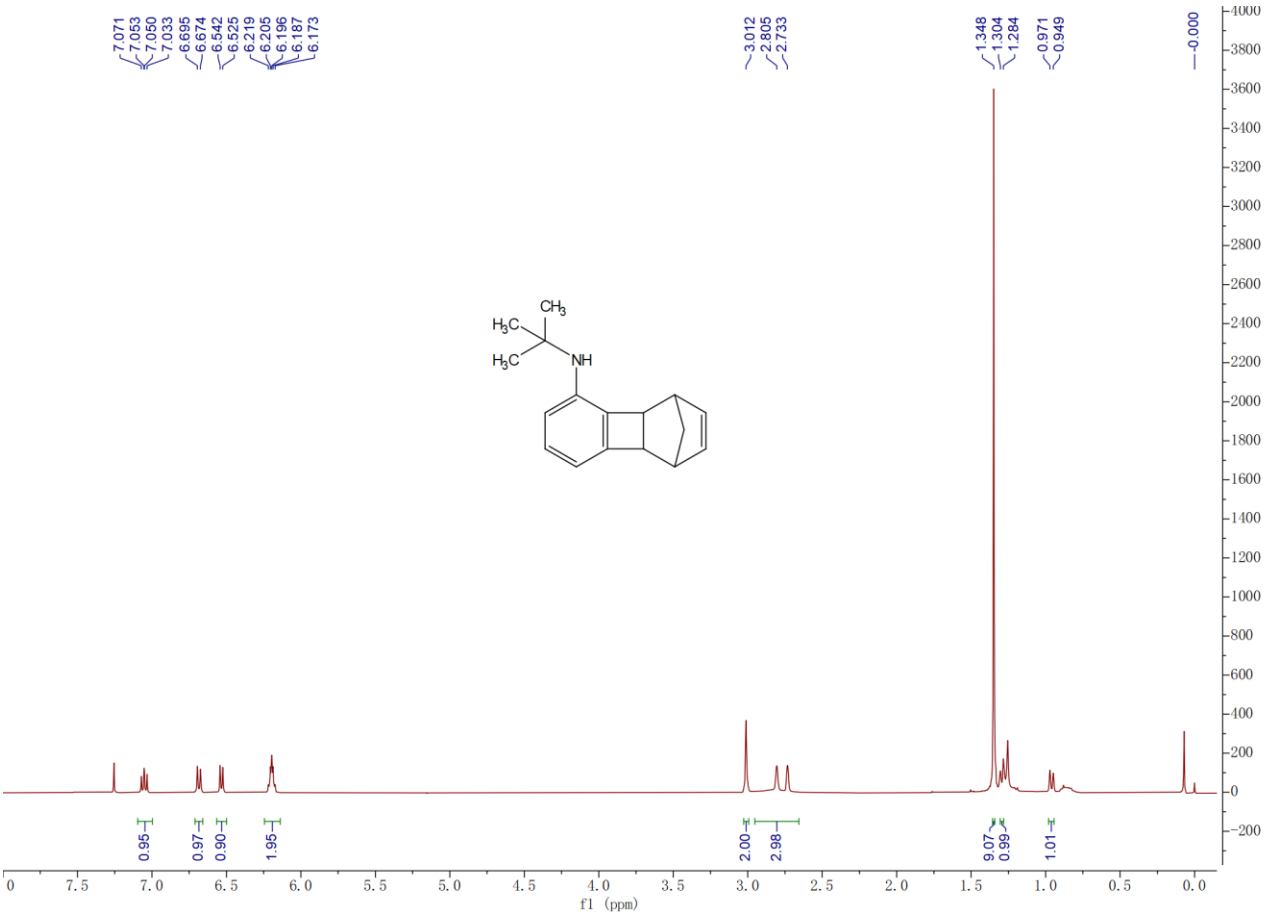


^{13}C NMR (151 MHz, $CDCl_3$)

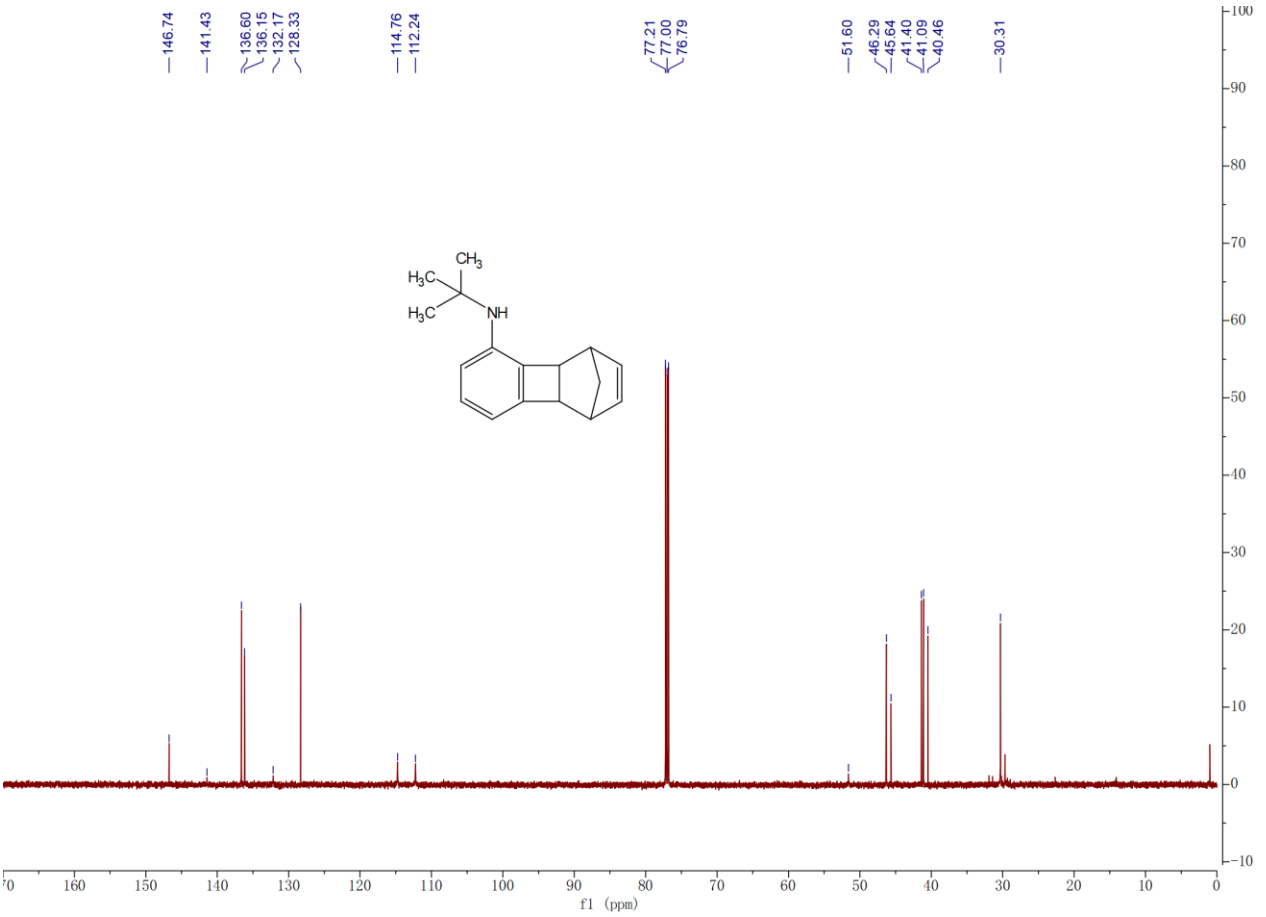


N-(tert-butyl)-1,4,4a,8b-tetrahydro-1,4-methanobiphenylen-5-amine (II')

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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