Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Fluoroamide-Driven Intermolecular Hydrogen Atom Transfer Enabled Intermolecular 1,2-Difunctionalization of Alkenes

Chaozhihui Cheng,[ab] De Chen,[a] Yang Li,*[ab] Jian-Nan Xiang,*[a] and Jin-Heng Li*[abcd]

[a.] *State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, China. E-mail: liyang8825490@126.com, jnxiang@hnu.edu.cn, and jhli@hnu.edu.cn*

[b.] *State Key Laboratory Base of Eco-Chemical Engineering, College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China.*

[c.] *State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China.*

[d.] *School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China.*

List of Contents

(A) **General Experimental Procedures**

(a) General Information

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker 500 MHz advance spectrometer at room temperature in $CDCl_3$ with tetramethylsilane as internal standard. High-resolution mass spectra (HRMS) were recorded on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. All products were identified by ^{1}H and ^{13}C NMR, HRMS.

Unless otherwise noted, all reactions were carried out using standard Schlenk techniques. Olefins **1** were purchased commercially or prepared according to the literatures,[1] and the other starting materials and solvents were commercially available and were used without further purification. Column chromatography was performed on silica gel (300-400 mesh) using petroleum ether/ethyl acetate.

(b) General Procedure for Synthesis of the carbazates:[2]

A round-bottom flask was charged with isopropyl alcohol (1.0 ml, 10.0 mmol, 1 equiv), followd by the addition of DCM (10 ml) and pyridine (1.20 g, 15 mmol, 1.5 equiv), The solution was cooled to 0 °C, A solution of phenyl chloroformate (1.38 mL, 11 mmol, 1.1 equiv) in dichloromethane (10 mL) was added. then cooled to room temperature and allowed to stir for overnight. The reaction was quenched with 1M hydrochloric acid. The aqueous layer was washed with methylene chloride, dried over Na_2SO_4 and concentrated in vacuo to afford the crude product carbonate. Next, hydrazine hydrate (2.0 equiv) was added to the solution of the corresponding carbonate in EtOH (20 mL) and then stirred for about 1 h at 80 ºC. Once complete, the reaction was quenched with 1M Sodium hydroxide solution. and extracted with EtOAc (50 mL × 3), the organic solvent was dried over Na_2SO_4. The solvent was evaporated under reduced pressure. The corresponding carbazate was purified by silica gel column chromatography. (eluent: petroleum ether/ethyl acetate = 1:1).

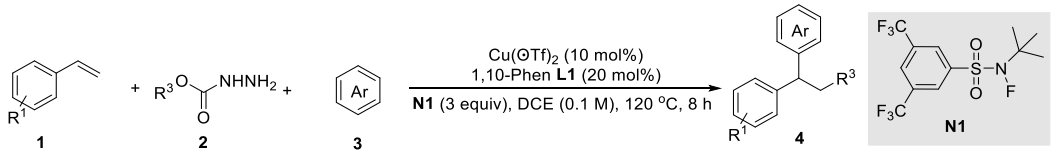
(c) Synthesis of *N*-fluoro-*N*-alkyl sulfonamides According to the literature procedure:[3]

An amine (1.0-1.2 equiv) was added to a mixture of pyridine or Et_3N (3.16 g, 40.0 mmol) in dry DCM (16 mL) and cooled to 0 °C. A sulfonyl chloride or benzoyl chloride (20.0 mmol) dissolved in dry DCM (12 mL) was added and the mixture was allowed to stir at 0 °C or room temperature until full conversion, as monitored by TLC. The mixture was diluted with Et_2O/pentane (1:1) and extracted with a 1 M HCl

solution (40 mL). The layers were separated and the aqueous phase was extracted with Et_2O/pentane (1:1; 40 mL). The organic layers were washed with a 1 M aqueous solution of HCl (2 × 40 mL) and water (3 × 40 mL), dried over Na_2SO_4, and concentrated.

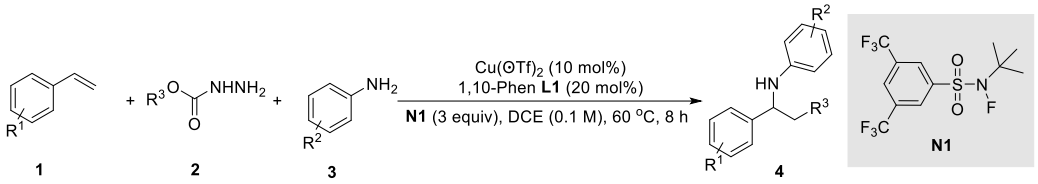
The crude product was purified by column chromatography or recrystallization. to a suspension of potassium hydride (3.52 g, 90.0 mmol) in DCM (60 mL) was added N-alkyl sulfonamide (15.0 mmol) and stirred at room temperature for 30 min. Then NFSI (14.19 g, 45.0 mmol) in DCM (60 mL) was added and the reaction mixture was allowed to stir at room temperature for 4 h. The reaction mixture was cooled to 0 °C and quenched by dropwise addition of water. The mixture was diluted with a NaOH-NH_4OH solution (300 mL, 20 g NH_4OH and 65 g NaOH in 1000 mL H_2O) and extracted with Et2O. The organic layers were washed with a NaOH-NH_4OH solution (200 mL), a 2 M aqueous solution of HCl (2 × 200 mL), and brine (200 mL). The organic layers were dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography.

(c) Typical Experimental Procedure for the Synthesis of Compounds 4:



To a Schlenk tube were added $Cu(OTf)_2$ (7.22 mg; 0.02 mmol; 10 mol%), 1,10-Phen **L1** (7.20 mg; 0.04 mmol; 20 mol%), alkenes **1** (0.2 mmol; 1.0 equiv), carbazates **2** (0.6 mmol; 3.0 equiv), indole **3** (0.8 mmol; 4.0 equiv), **N1** (0.3 mmol; 3.0 equiv) and DCE (2 mL). Then the tube was charged with argon three times, and was stirred at 120 °C for 8 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the combined organic extracts were dried over Na_2SO_4 and the concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (EtOAc/hexanes = 1:50) to afford the desired product **4.**

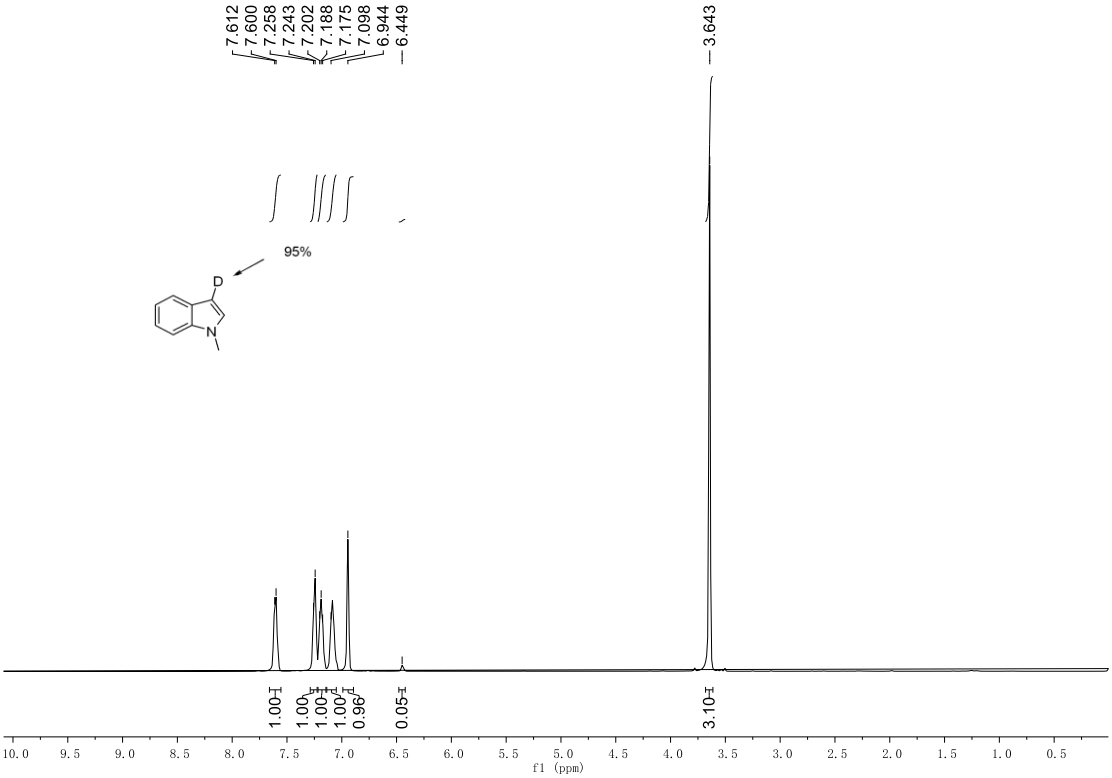
(d) Typical Experimental Procedure for the Alkene Alkylamination:

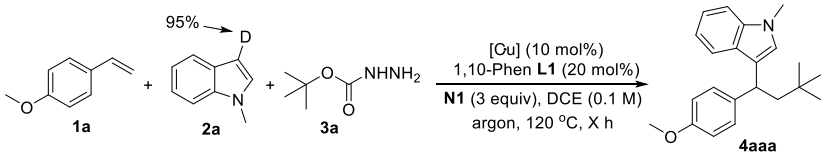


To a Schlenk tube were added $Cu(OTf)_2$ (7.22 mg; 0.02 mmol; 10 mol%), 1,10-Phen **L1** (7.20 mg; 0.04 mmol; 20 mol%), alkenes **1** (0.2 mmol; 1.0 equiv), carbazates **2** (0.6 mmol; 3.0 equiv), amine **3** (0.8 mmol; 4.0 equiv), **N1** (0.3 mmol; 3.0 equiv) and DCE (2 mL). Then the tube was charged with argon three times, and was stirred at 60 ºC for 8 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the combined organic extracts were dried over Na_2SO_4 and the concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (EtOAc/hexanes = 1:50) to afford the desired product **4**.

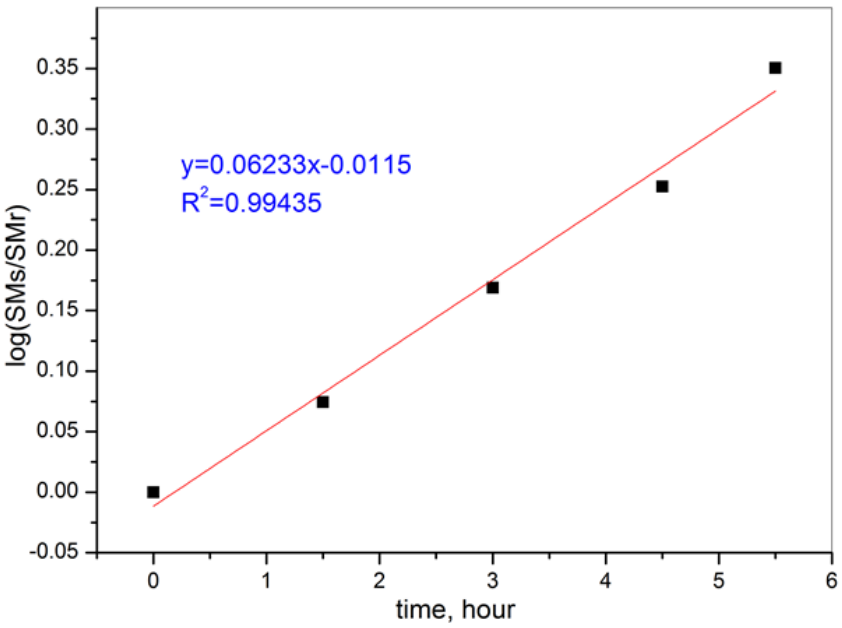
(e) The Kinetic Isotope Effect (KIE) Experiments:[4]

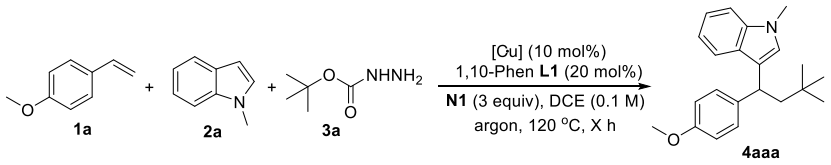
3-deuterated-1-methyl indole (2a-D1)



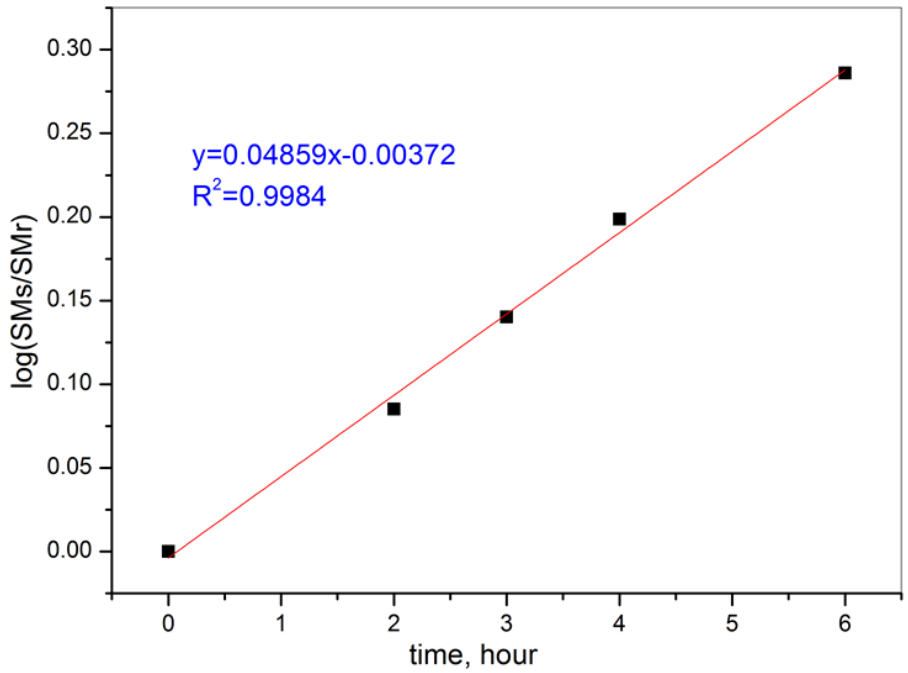


1-methyl-1H-indole (3-D)			
t, hour	SMs	SMr	log（SMs/SMr）
0	0.1060	0.1060	0
1.5	0.1097	0.0944	0.07444
3.0	0.1082	0.0733	0.1689
4.5	0.1112	0.0622	0.2525
5.5	0.1075	0.0479	0.3505





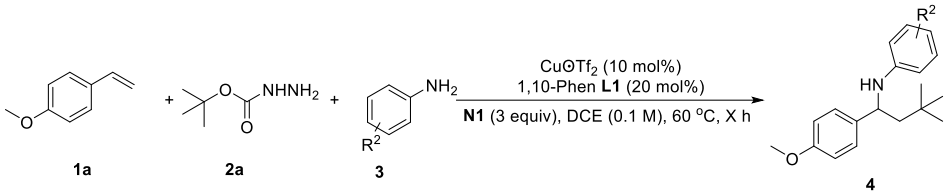
1-methyl-1*H*-indole (3-H)			
t, hour	SMs	SMr	log（SMs/SMr）
0	0.1104(14.8)	0.1104	0
2.0	0.1067(14.3)	0.0877	0.0852
3.0	0.1127(15.1)	0.0816	0.1402
4.0	0.1097(14.7)	0.0694	0.1988
6.0	0.1090(14.6)	0.0547	0.2861



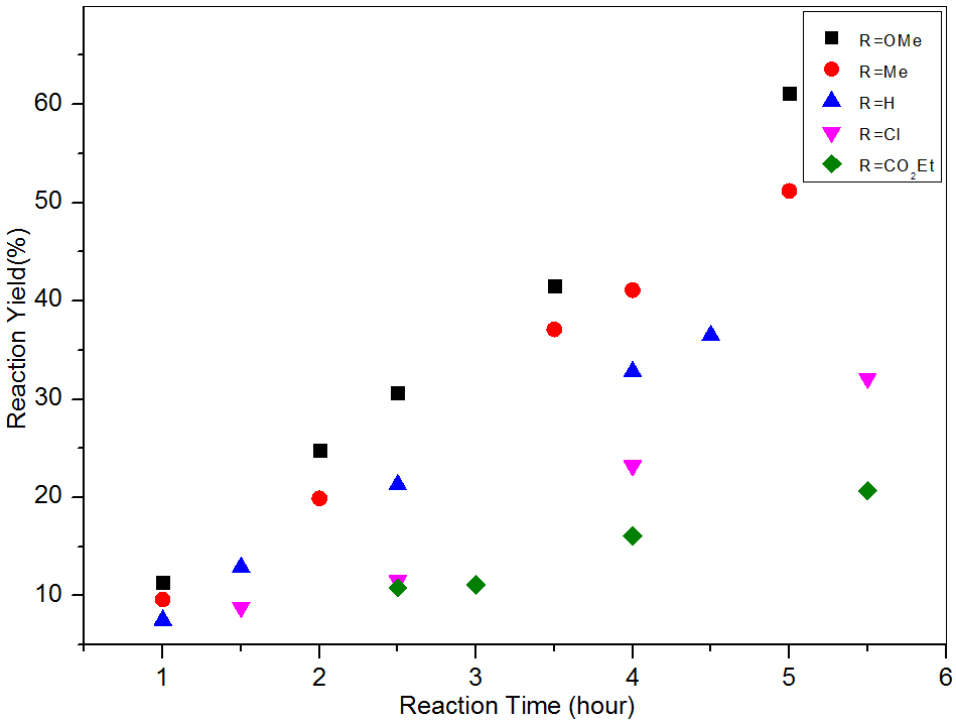
Calculation: k_H/k_D=0.04859/0.06233=0.78

Figure S1: The kinetic isotope effect (KIE) experiments of 3-deuterated 1-methy-1H-lindole (2a-1D) and 1-methy-1H-lindole 3a

(f) Hammett Studies of the Reaction (Substitution Effect of amine)



To a schlenk tube were added $Cu(OTf)_2$ (0.01 mmol; 10 mol%), 1,10-Phen **L1** (0.02 mmol; 20 mol%), 1-methoxy-4-vinylbenzene **1a** (0.1 mmol; 1.0 equiv), *tert*-butyl hydrazinecarboxylate **2a** (0.3 mmol; 3.0 equiv), amine **3** (0.4 mmol; 4.0 equiv), **N1** (0.3 mmol; 3.0 equiv) and DCE (1 mL). Then the tube was charged with argon three times, was stirred at 60 °C, six groups were carried out in parallel and stop the one of reaction every one hour. After the reaction was finished, the combined organic extracts were dried over Na_2SO_4 and the concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (EtOAc/hexanes = 1:50) to afford the desired products **.**



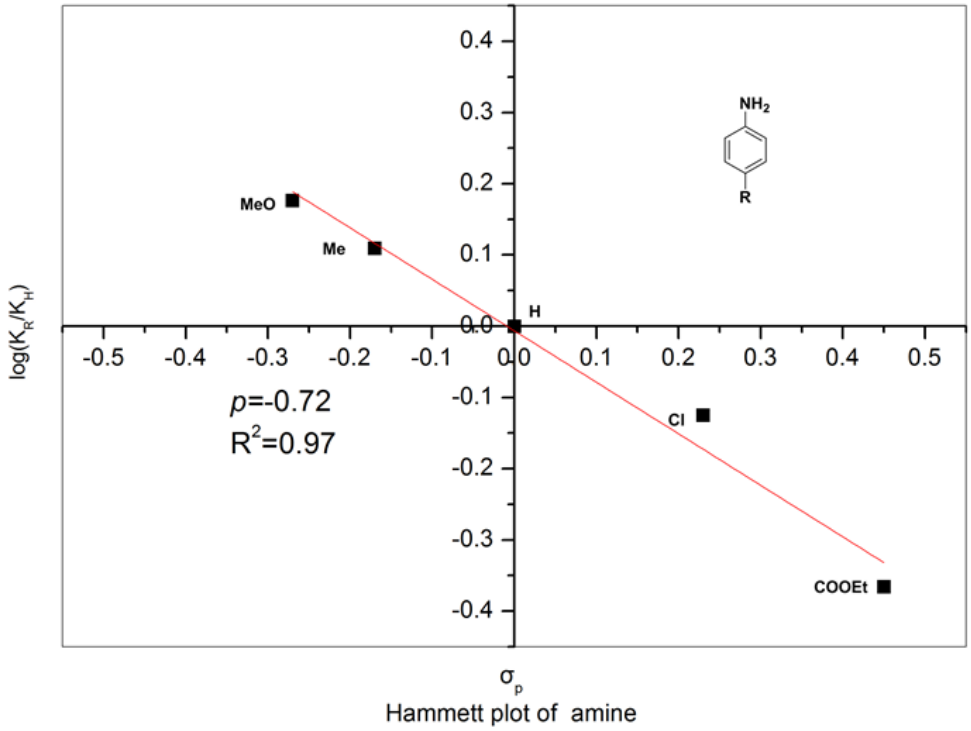


Figure S2: The electronic effect of amine for the reaction (TOP: Time course of reaction; Bottom: Hammett plot, log(kR/kH) vs σ).

(g) EPR experiments

To a Schlenk tube were added $Cu(OTf)_2$ (7.22 mg; 0.02 mmol; 10 mol%), 1,10-Phen **L1** (7.20 mg; 0.04 mmol; 20 mol%), carbazates **2** (0.8 mmol; 4.0 equiv), and DCE (2 mL). Then the tube was charged with argon three times. After 20 mins, DMPO (80 μL) was added and stir for 1 min. Then, the solution sample was taken out into a small tube and analyzed by EPR. A mixture signal of sp^2 carbon radicals (g = 2.006, A_N = 14.6 G, A_H = 21.3 G) and sp^3 carbon radicals (g = 2.006, A_N = 14.6 G, A_H = 16.8 G) was identified, and the ratio of alkyl radical (a) to ester radical (b) is 3:5.

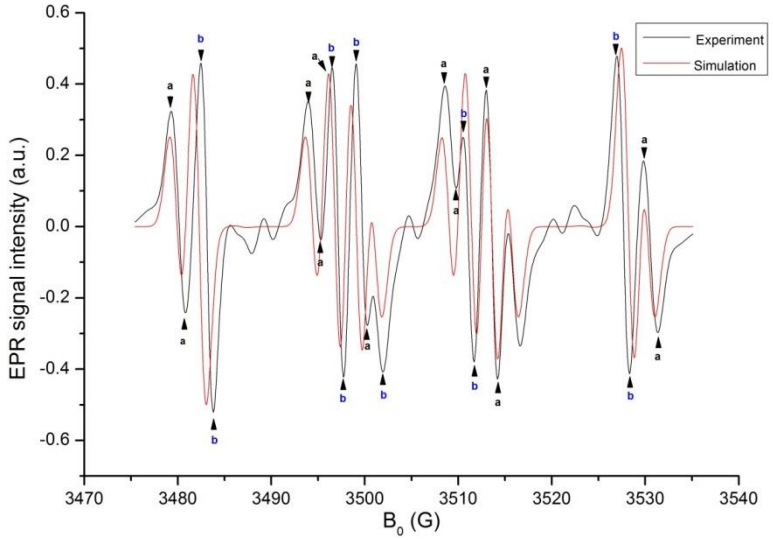
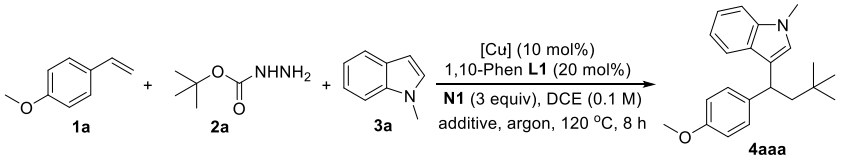


Figure S3. EPR spectra (X band, 9.8 GHz, room temperature) for reaction mixtures in the presence of (1) the radical trap DMPO (2.5×10^{-2} M)

(h) Control Experiments with Radical Inhibitors.

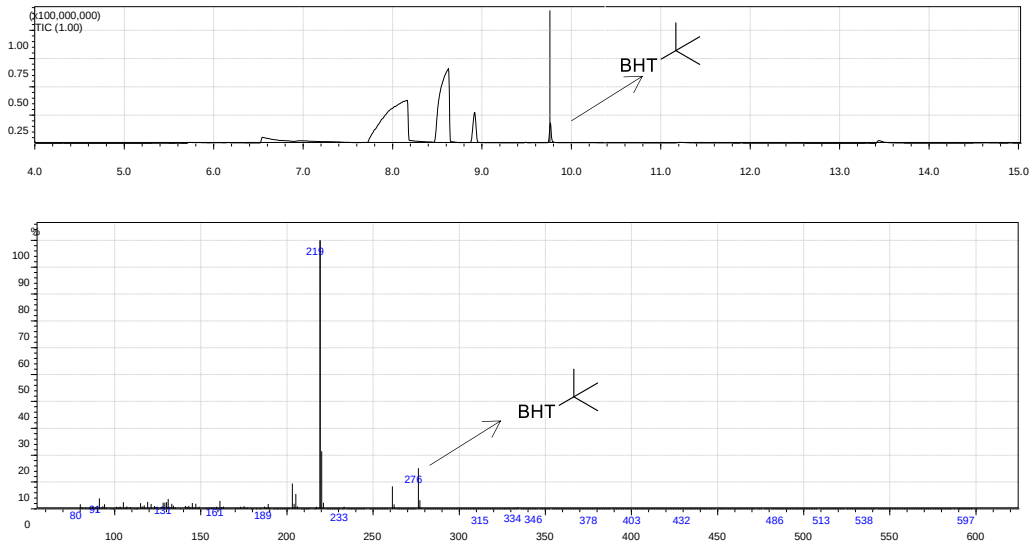


Entry	Additive	Yield[b]
1	air	27%
2	TEMPO	trace
3	BQ	trace
4	BHT	18%

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), **3** (0.8 mmol), $Cu(OTf)_2$ (10 mol%), **L1** (20 mol%), additive (3 equiv), **N1** (3 equiv), DCE (2 mL), argon, 120 °C and 8 h. [b] Yield of isolated product.

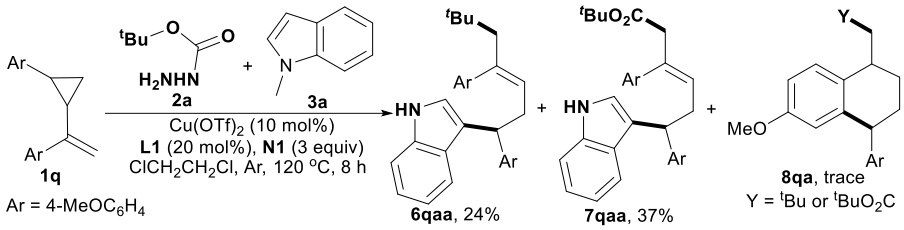
Addition of radical scavenger to the reaction system obviously inhibited the desired pathway.

As shown in run 1, to a Schlenk tube were added $Cu(OTf)_2$ (0.02 mmol; 10 mol%), 1,10-Phen **L1** (0.04 mmol; 20 mol%), 1-methoxy-4-vinylbenzene **1a** (0.2 mmol; 1.0 equiv), *tert*-butyl carbazate **2a** (0.6 mmol; 3.0 equiv), *N*-methyl indole **3a** (0.8 mmol; 3.0 equiv), radical scavenger (0.6 mmol, 3.0 equiv), **N1** (0.6 mmol; 3.0 equiv), and DCM (2 mL). Then the tube was charged with argon three times, and was stirred at 120 °C for 8 h until complete. After the reaction was finished, the combined organic extracts were dried over Na_2SO_4 and the concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (EtOAc/hexanes = 1:50) to afford the desired product.



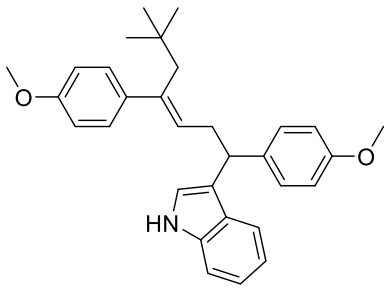
# of Peaks 507
Raw Spectrum 9.760 (scan : 1153)
Background No Background Spectrum
Base Peak m/z 219.20 (Inten : 6,324,650)
Event# 1

m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity
214.00	2634	0.04	221.20	142889	2.26	273.10	46	
215.15	3712	0.06	222.20	10924	0.17	274.10	1514	
216.15	1010	0.02	223.10	719	0.01	275.25	5494	0.09
217.15	49796	0.79	269.20	78		**276.25**	**958541**	**15.16**
218.25	23822	0.38	270.20	31		277.20	205974	3.26
219.20	**6324650**	**100.00**	271.20	65		278.20	23170	0.37
220.20	1357433	21.46	272.20	11				



As shown in run 1, to a Schlenk tube were added $Cu(OTf)_2$ (0.02 mmol; 10 mol%), 1,10-Phen **L1** (0.04 mmol; 20 mol%), 1-methoxy-4-(1-(2-(4-methoxyphenyl)-cyclopropyl)vinyl)benzene **1q** (0.2 mmol; 1.0 equiv), tert-butyl carbazate **2a** (0.6 mmol; 3.0 equiv), *N*-methyl indole **3a** (0.8 mmol; 4.0 equiv), **N1** (0.6 mmol; 3.0 equiv), and DCM (2 mL). Then the tube was charged with argon three times, and was stirred at 120 °C for 8 h until complete. After the reaction was finished, the combined organic extracts were dried over Na_2SO_4 and the concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (EtOAc/hexanes = 1:20) to afford the desired products **6qaa** and **7qaa**.

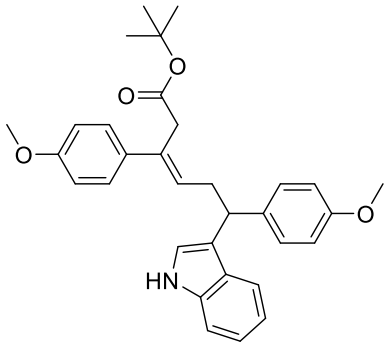
3-(1,4-Bis(4-methoxyphenyl)-6,6-dimethylhept-3-en-1-yl)-1*H*-indole (6qaa):



Following the typical experimental procedure on 0.2 mmol scale, compound **6qaa** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 30:1, v/v). 21.7 mg, 24% yield. Yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.42

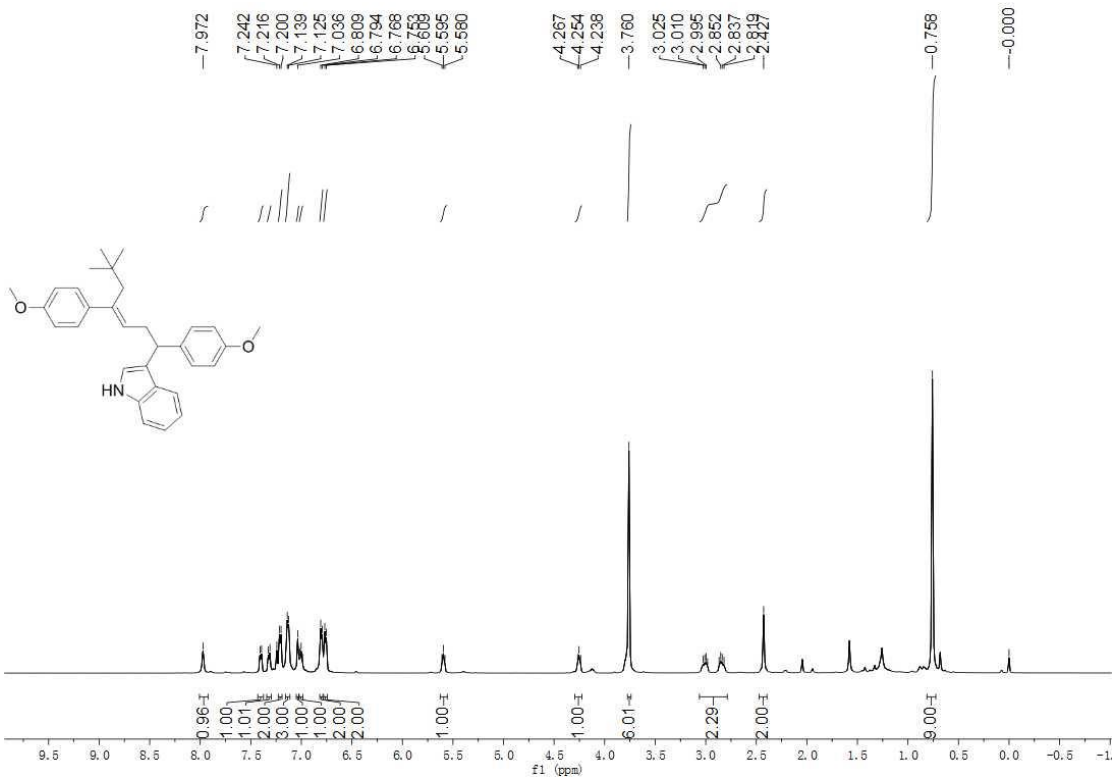
(d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 7.1 Hz, 3H), 7.05 (s, 1H), 7.02 (t, *J* = 7.1 Hz, 1H), 6.82 (d, *J* = 7.1 Hz, 2H), 6.78 (d, *J* = 7.4 Hz, 2H), 5.61 (t, *J* = 7.4 Hz, 1H), 4.27 (t, *J* = 7.3 Hz, 1H), 3.78 (s, 6H), 3.04 - 2.83 (m, 2H), 2.45 (s, 2H), 0.78 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.08, 157.74, 139.15, 138.57, 137.17, 136.50, 129.55, 128.88, 127.65, 127.04, 121.92, 121.29, 120.14, 119.59, 119.17, 113.59, 113.23, 110.96, 55.17, 42.81, 42.31, 36.24, 33.07, 30.45. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{36}NO_2$ 454.2741, Found 454.2743.

Tert-butyl-6-(1*H*-indol-3-yl)-3,6-bis(4-methoxyphenyl)hex-3-enoate (7qaa)：

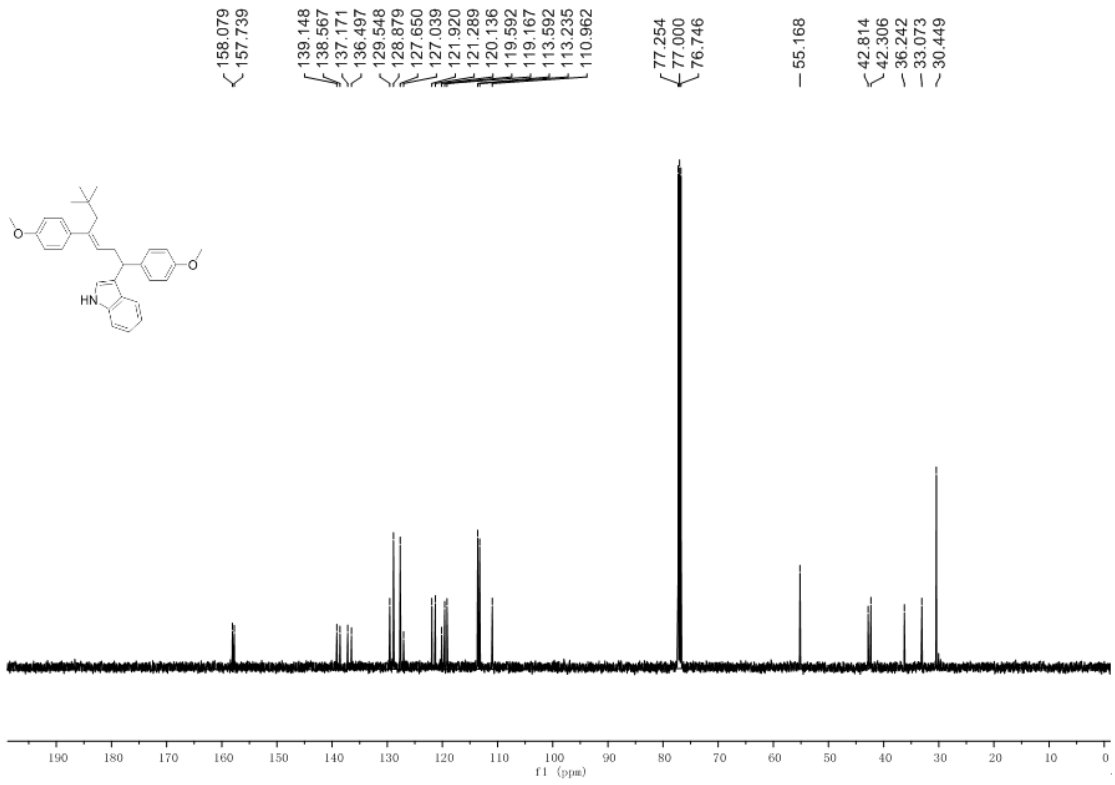


Following the typical experimental procedure on 0.2 mmol scale, compound **7qaa** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 36.8 mg, 37% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 6.8 Hz, 3H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.10 (s, 1H), 7.01 (t, *J* = 6.2 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 4H), 5.86 (t, *J* = 6.4 Hz, 1H), 4.34 (t, *J* = 7.3 Hz, 1H), 3.78 (s, 6H), 3.38 (q, *J* = 15.5 Hz, 2H), 3.09-2.86 (m, 2H), 1.49 (s, 2H), 1.38 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.77, 158.52, 157.82, 136.98, 136.54, 134.94, 132.99, 129.07, 128.85, 127.07, 121.89, 121.55, 119.70, 119.59, 119.15, 113.64, 113.47, 110.99, 80.61, 55.18, 42.10, 37.58, 35.76, 28.12, 27.94. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{36}NO_4$ 498.2639, Found 498.2635.

3-(1,4-bis(4-methoxyphenyl)-6,6-dimethylhept-3-en-1-yl)-1*H*-indole (6qaa):

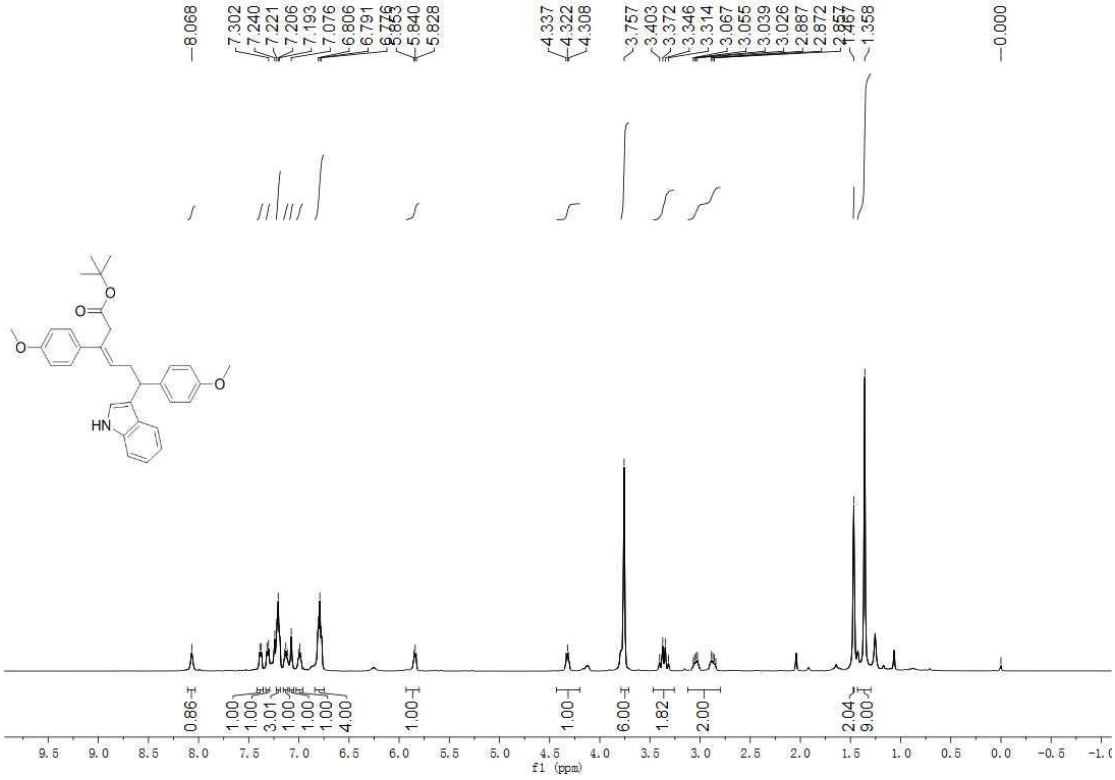


^{1}H-NMR (500 MHz, $CDCl_3$)

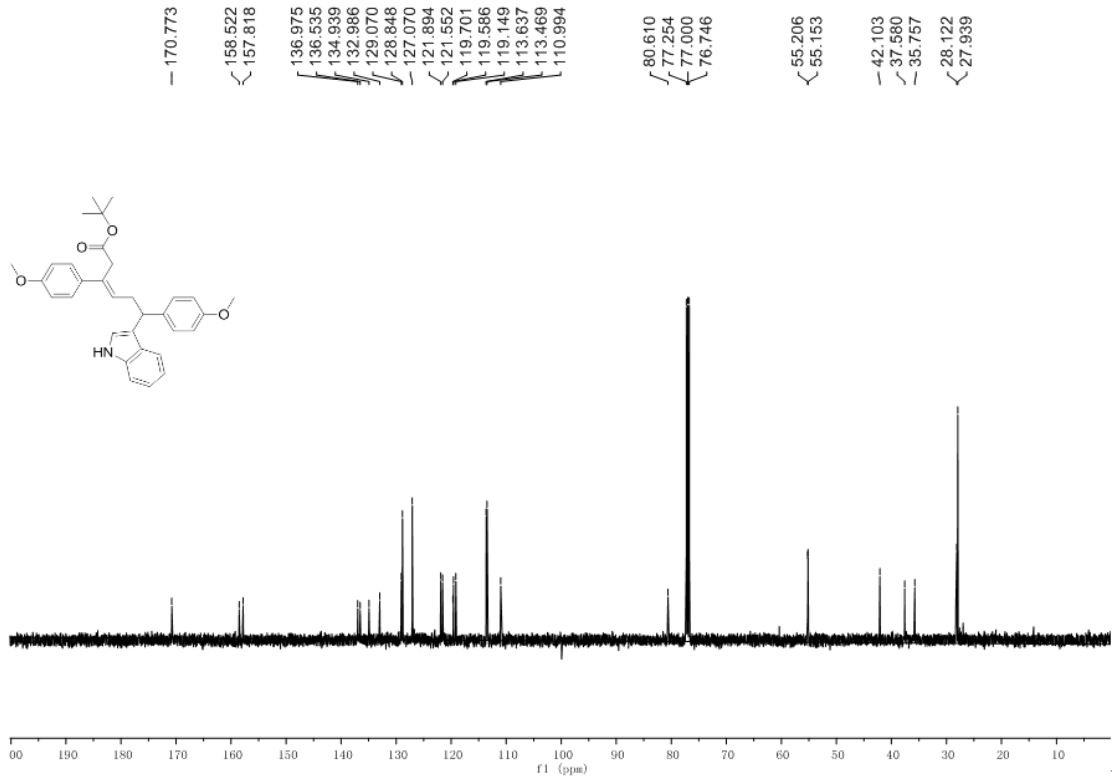


^{13}C-NMR (125 MHz, $CDCl_3$)

Tert-butyl-6-(1*H*-indol-3-yl)-3,6-bis(4-methoxyphenyl)hex-3-enoate (7qaa)：



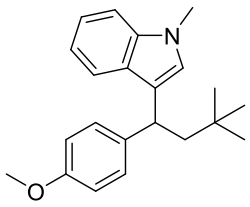
^{1}H-NMR (500 MHz, $CDCl_3$)



^{13}C-NMR (125 MHz, $CDCl_3$)

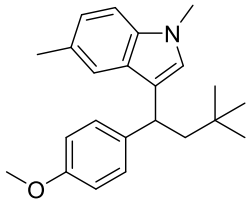
(B) Analytical data

3-(1-(4-Methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole (4aaa):



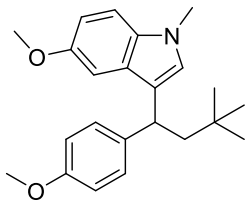
Following the typical experimental procedure on 0.2 mmol scale, compound **4aaa** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 46.2 mg, 72% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.25 (d, *J* = 6.3 Hz, 1H), 7.13 (d, *J* = 3.9 Hz, 2H), 6.85 - 6.79 (m, 3H), 4.26 - 4.19 (m, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 2.13 - 2.00 (m, 2H), 0.87 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.70, 138.69, 135.62, 128.73, 128.00, 127.14, 124.47, 121.73, 120.87, 118.78, 113.75, 110.19, 55.21, 50.01, 38.40, 32.85, 31.54, 30.29. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}NO$ 322.2165, Found 322.2167.

3-(1-(4-Methoxyphenyl)-3,3-dimethylbutyl)-1,6-dimethyl-1*H*-indole (4aab):



Following the typical experimental procedure on 0.2 mmol scale, compound **4aab** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 38.2 mg, 57% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.82 (t, *J* = 9.1 Hz, 2H), 6.71 (s, 1H), 4.33-4.21 (m, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 2.46 (s, 3H), 2.18 - 2.01 (m, 2H), 0.89 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.49, 139.15, 135.62, 128.78, 127.64, 127.17, 125.94, 123.02, 120.52, 118.93, 113.57, 108.79, 55.16, 50.09, 38.44, 32.63, 31.51, 30.29, 21.58. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{30}NO$ 336.2322, Found 336.2319.

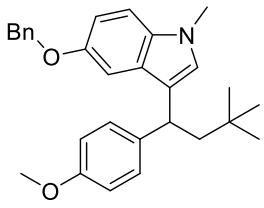
5-Methoxy-3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole (4aac):



Following the typical experimental procedure on 0.2 mmol scale, compound **4aac** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 39.3 mg, 51% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 1H), 7.03 (d, *J* = 2.0 Hz, 1H), 6.87 - 6.84 (m, 1H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.71 (s, 1H), 4.25 - 4.22 (m, *J* = 8.0, 4.9 Hz, 1H),

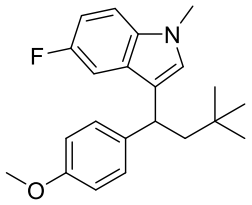
3.83 (s, 3H), 3.78 (s, 3H), 3.68 (s, 3H), 2.16 - 2.01 (m, 2H), 0.89 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.55, 153.37, 138.91, 132.69, 128.84, 127.22, 126.54, 120.56, 113.59, 111.22, 109.78, 101.68, 55.94, 55.17, 49.82, 38.54, 32.77, 31.49, 30.28. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{30}NO_2$ 352.2271, Found 352.2280.

5-(Benzyloxy)-3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole (4aad):



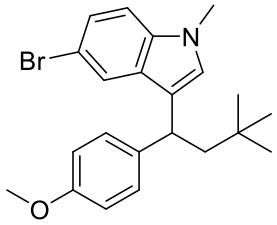
Following the typical experimental procedure on 0.2 mmol scale, compound **4aad** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 43.5 mg, 51% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.44 (m, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.30 (s, 1H), 7.23-7.19 (m, 2H), 7.13-7.05 (m, 2H), 6.94-6.87 (m, 1H), 6.80 (d, *J* = 6.4 Hz, 2H), 6.68 (s, 1H), 5.07 (s, 2H), 4.18 (t, *J* = 7.4 Hz, 1H), 3.75 (s, 3H), 3.64 (s, 3H), 2.10-1.98 (m, 2H), 0.84 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.54, 152.52, 138.91, 137.80, 132.85, 128.79, 128.46, 127.67, 127.52, 127.16, 126.54, 120.61, 113.60, 112.16, 109.76, 103.40, 71.04, 55.15, 49.78, 38.54, 32.73, 31.46, 30.26. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{34}NO_2$ 428.2584, Found 428.2583.

5-Fluoro-3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole (4aae):



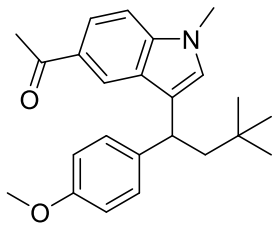
Following the typical experimental procedure on 0.2 mmol scale, compound **4aae** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 33.9 mg, 50% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.23 (m, 2H), 7.20-7.19 (m, 1H), 7.12 (d, *J* = 5.5 Hz, 1H), 6.91 (s, 1H), 6.82-6.79 (m, 3H), 4.26-4.14 (m, 1H), 3.76 (s, 3H), 3.68 (s, 3H), 2.11-2.02 (m, 2H), 0.86 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.66, 157.38 (d, *J* = 233.3 Hz), 138.70, 133.87, 128.74, 127.42, 127.15 (d, *J* = 9.7 Hz), 121.02, 113.69, 109.77 (d, *J* = 10.2 Hz), 109.62 (d, *J* = 6.4 Hz), 104.23 (d, *J* = 23.2 Hz), 55.16, 49.81, 38.53, 32.87, 31.47, 30.24. ^{19}F NMR (471 MHz, $CDCl_3$) δ -125.66 (s). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}FNO$ 340.2071, Found 340.2079.

5-Bromo-3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole (4aaf):



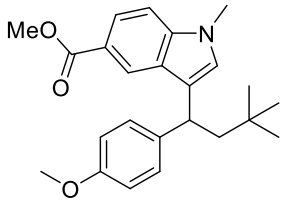
Following the typical experimental procedure on 0.2 mmol scale, compound **4aaf** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 41.5 mg, 52% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 5.5 Hz, 1H), 7.24-7.22 (m, 3H), 7.11-7.06 (m, 1H), 6.83-6.75 (m, 3H), 4.25-4.19 (m, 1H), 3.76 (s, 3H), 3.67 (s, 3H), 2.09-2.01 (m, 2H), 0.86 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.68, 138.64, 135.83, 128.67, 126.94, 124.25, 121.82, 120.80, 113.72, 112.06, 110.61, 55.17, 50.02, 38.33, 32.78, 31.49, 30.24. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}BrNO$ 400.1271, Found 400.1265.

1-(3-(1-(4-Methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indol-5-yl)ethan-1-one (4aag):



Following the typical experimental procedure on 0.2 mmol scale, compound **4aag** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 31.9 mg, 44% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 1H), 7.62 (d, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.05 (s, 1H), 6.82 (d, *J* = 8.9 Hz, 3H), 4.29 (t, *J* = 6.3 Hz, 1H), 3.94 (s, 3H), 3.81 (s, 3H), 3.77 (s, 3H), 2.15 - 2.01 (m, 2H), 0.88 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.11, 157.62, 138.63, 134.33, 129.69, 129.19, 128.73, 124.79, 123.56, 121.31, 117.76, 115.77, 113.64, 55.14, 52.00, 49.98, 38.12, 37.05, 31.47, 30.24. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{30}NO_2$ 364.2271, Found 364.2276.

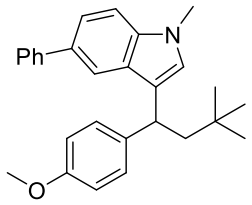
Methyl-3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole-5-carboxylate (4aah):



Following the typical experimental procedure on 0.2 mmol scale, compound **4aah** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 44.7 mg, 59% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 1H), 7.62 (d, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 9.4 Hz, 2H), 7.05 (t, *J* = 7.7 Hz, 1H), 6.85 - 6.77 (m, 3H), 4.33 - 4.23 (m, 1H), 3.94 (s, 3H), 3.81 (s, 3H),

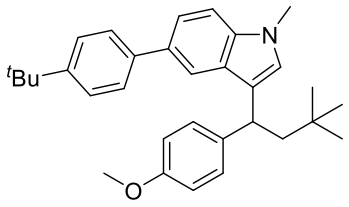
3.77 (s, 3H), 2.15 - 2.00 (m, 2H), 0.88 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.11, 157.61, 138.62, 134.32, 129.68, 129.20, 128.73, 124.79, 123.56, 121.30, 117.76, 115.76, 113.63, 55.15, 52.02, 49.98, 38.11, 37.07, 31.48, 30.25. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{30}NO_3$ 380.2220, Found 380.2227.

3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-5-phenyl-1*H*-indole (4aai):



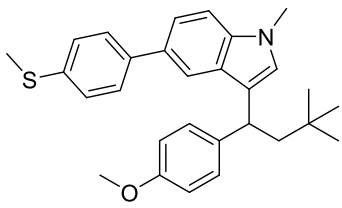
Following the typical experimental procedure on 0.2 mmol scale, compound **4aai** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 41.3 mg, 52% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 5.0 Hz, 1H), 7.61 (d, *J* = 5.5 Hz, 2H), 7.46-7.39 (m, 3H), 7.31-7.26 (m, 4H), 6.82-6.81 (m Hz, 2H), 6.75 (s, 1H), 4.38-4.28 (m, 1H), 3.73 (s, 3H), 3.67 (s, 3H), 2.18-2.06 (m, 2H), 0.88 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.61, 142.82, 138.92, 136.77, 132.09, 128.81, 128.61, 127.46, 127.34, 126.48, 126.12, 121.63, 121.30, 117.89, 113.66, 109.36, 55.14, 50.06, 38.52, 32.66, 31.53, 30.31. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{30}NO_3$ 398.2478, Found 398.2474.

5-(4-(Tert-butyl)phenyl)-3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole (4aaj):



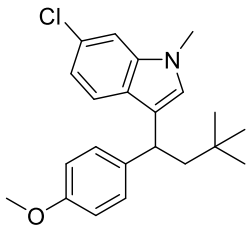
Following the typical experimental procedure on 0.2 mmol scale, compound **4aaj** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 51.6 mg, 57% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 5.0 Hz, 1H), 7.56 (d, *J* = 5.5 Hz, 2H), 7.49-7.41 (m, 3H), 7.28 (t, *J* = 9.7 Hz, 3H), 6.81 (d, *J* = 4.7 Hz, 2H), 6.74 (s, 1H), 4.36-4.29 (m, 1H), 3.75 (s, 3H), 3.69 (s, 3H), 2.12 (m, 2H), 1.37 (s, 9H), 0.88 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.59, 149.00, 139.93, 138.96, 136.67, 131.95, 128.82, 128.67, 127.43, 126.96, 126.41, 125.57, 121.60, 121.28, 117.75, 113.66, 109.28, 55.17, 50.05, 38.54, 34.43, 32.69, 31.54, 31.43, 30.31. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{40}NO$ 454.3104, Found 454.3106.

3-(1-(4-Methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-5-(4-(methylthio)phenyl)-1*H*-indole (4aak):



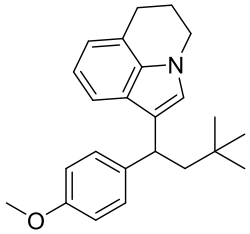
Following the typical experimental procedure on 0.2 mmol scale, compound **4aak** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 30:1, v/v). 40.7 mg, 46% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.57 (d, *J* = 7.1 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 3H), 6.84 (d, *J* = 7.3 Hz, 2H), 6.79 (s, 1H), 4.39 - 4.29 (m, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 2.55 (s, 3H), 2.22-2.06 (m, 2H), 0.91 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.58, 139.87, 138.87, 136.73, 135.94, 131.37, 128.80, 127.69, 127.46, 127.27, 126.54, 121.60, 121.01, 117.60, 113.64, 109.41, 55.16, 50.02, 38.48, 32.71, 31.53, 30.29, 16.24. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{34}NOS$ 444.2356, Found 444.2361.

6-Chloro-3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole (4aal):



Following the typical experimental procedure on 0.2 mmol scale, compound **4aal** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 37.6 mg, 53% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 2H), 6.72 (s, 1H), 4.32 - 4.25 (m, 1H), 3.75 (s, 3H), 3.69 (s, 3H), 2.17-2.01 (m, 2H), 0.87 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.59, 139.05, 137.24, 128.87, 127.03, 125.89, 121.44, 121.21, 119.41, 118.56, 113.64, 109.14, 55.21, 50.01, 38.58, 32.65, 31.55, 30.32. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}ClNO$ 356.1776, Found 356.1771.

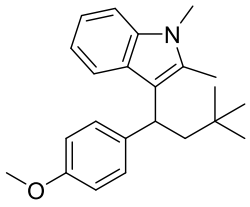
1-(1-(4-Methoxyphenyl)-3,3-dimethylbutyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-ij]quinoline (4aam):



Following the typical experimental procedure on 0.2 mmol scale, compound **4aam** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 43.7 mg, 63% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 9.5 Hz, 2H), 6.97-6.91 (m, 1H), 6.86-6.77 (m, 3H), 6.71 (s, 1H), 4.30-4.22 (m, 1H), 4.08-3.99 (m, 2H), 3.75 (s, 3H), 2.97-2.88 (m,

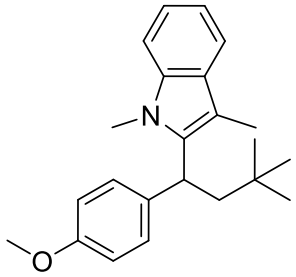
2H), 2.20-2.02 (m, 4H), 0.86 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.52, 139.16, 134.69, 128.86, 124.43, 123.09, 121.54, 121.42, 118.91, 118.29, 117.01, 113.57, 55.15, 49.92, 43.80, 39.05, 31.50, 30.28, 24.68, 22.83.

3-(1-(4-Methoxyphenyl)-3,3-dimethylbutyl)-1,2-dimethyl-1*H*-indole (4aan):



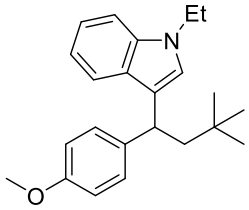
Following the typical experimental procedure on 0.2 mmol scale, compound **4aan** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 28.2 mg, 42% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.19-7.12 (m, 2H), 7.10 (s, 1H), 7.06 (d, *J* = 5.7 Hz, 1H), 6.76 - 6.69 (m, 2H), 4.37 - 4.18 (m, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 2.18 (s, 3H), 2.15 - 1.99 (m, 2H), 0.87 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.72, 138.59, 137.17, 130.27, 127.04, 126.11, 125.82, 121.34, 119.37, 118.47, 109.61, 109.05, 55.24, 50.04, 38.48, 32.60, 31.52, 30.28, 16.39. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{30}NO$ 336.2322, Found 336.2317.

2-(1-(4-Methoxyphenyl)-3,3-dimethylbutyl)-1,3-dimethyl-1H-indole (4aao):



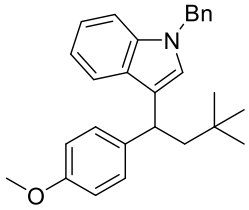
Following the typical experimental procedure on 0.2 mmol scale, compound **4aao** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 25.5mg, 38% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.86 - 6.81 (m, 2H), 6.77 (s, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 4.24 - 4.21 (m, 1H), 4.19 (s, 3H), 3.70 (s, 3H), 2.14 - 1.97 (m, 2H), 0.87 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.10, 141.39, 140.50, 137.13, 126.99, 125.77, 121.38, 120.91, 120.82, 119.33, 118.51, 116.81, 116.46 , 109.06, 64.36 , 64.25, 50.01, 38.60, 32.60, 31.50, 30.23. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{30}NO$ 336.2322, Found 336.2313.

1-Ethyl-3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1*H*-indole (4aap):



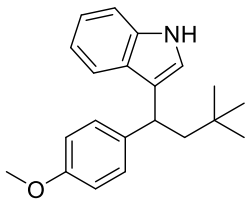
Following the typical experimental procedure on 0.2 mmol scale, compound **4aap** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 46.2 mg, 69% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 7.7 Hz, 3H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 7.1 Hz, 1H), 6.80 (d, *J* = 4.4 Hz, 3H), 4.32 - 4.26 (m, 1H), 4.07 (q, *J* = 7.5 Hz, 2H), 3.75 (s, 3H), 2.18-2.00 (m, 2H), 1.39 (t, *J* = 7.2 Hz, 3H), 0.86 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.52, 139.04, 136.20, 128.85, 127.18, 124.08, 121.23, 121.08, 119.47, 118.45, 113.56, 109.15, 55.15, 49.98, 40.75, 38.57, 31.49, 30.28, 15.50. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{30}NO$ 336.2322, Found 322.2333.

1-Benzyl-3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1*H*-indole (4aaq):



Following the typical experimental procedure on 0.2 mmol scale, compound **4aaq** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 48.4mg, 61% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 6.9 Hz, 1H), 7.28-7.22 (m, 5H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 6.2 Hz, 1H), 7.04 (d, *J* = 2.7 Hz, 3H), 6.87 (s, 1H), 6.79 (d, *J* = 6.9 Hz, 2H), 5.24 (s, 2H), 4.31 (s, 1H), 3.74 (d, *J* = 1.2 Hz, 3H), 2.22 - 1.94 (m, 2H), 0.86 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.60, 139.11, 137.95, 136.92, 128.86, 128.71, 127.44, 126.54, 125.37, 121.68, 119.58, 118.88, 113.66, 109.66, 55.22, 50.06, 49.91, 38.56, 31.57, 30.34. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{32}NO$ 398.2478, Found 398.2475.

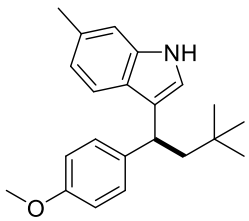
3-(1-(4-Methoxyphenyl)-3,3-dimethylbutyl)-1*H*-indole (4aas):



Following the typical experimental procedure on 0.2 mmol scale, compound **4aas** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1, v/v). 42.3mg, 70% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.25 (s, 2H), 7.12 (s, 1H), 7.05 (s, 1H), 6.84 (s, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 4.29 (s, 1H), 3.73 (s, 3H), 2.26 - 1.96 (m, 2H), 0.86 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.52, 138.93, 136.47, 128.82, 126.64, 122.43,

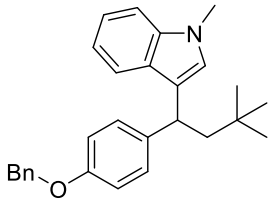
121.81, 120.97, 119.28, 119.07, 113.58, 111.04, 55.13, 49.79, 38.50, 31.46, 30.25. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}NO$ 308.2009, Found 322.2012.

3-(1-(4-Methoxyphenyl)-3,3-dimethylbutyl)-6-methyl-1*H*-indole (4aat)：



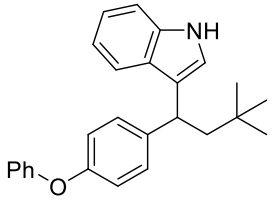
Following the typical experimental procedure on 0.2 mmol scale, compound **4aat** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 48.1 mg, 75% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.44 (s, 1H), 7.24 (s, 2H), 7.17 (s, 1H), 6.97 (d, *J* = 3.4 Hz, 1H), 6.93 (s, 1H), 6.84 (s, 1H), 6.78 (d, *J* = 2.9 Hz, 2H), 4.28 (s, 1H), 3.71 (s, 3H), 2.39 (d, *J* = 12.3 Hz, 3H), 2.24 – 1.96 (m, 2H), 0.87 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.48, 139.00, 136.01, 128.79, 126.17, 122.95, 122.37, 120.69, 120.13, 119.31, 117.05, 113.57, 55.12, 49.80, 38.61, 31.46, 30.25, 16.48. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{28}NO$ 322.2165, Found 322.2164.

3-(1-(4-(Benzyloxy)phenyl)-3,3-dimethylbutyl)-1-methyl-1H-indole (4baa)：



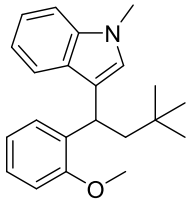
Following the typical experimental procedure on 0.2 mmol scale, compound **4baa** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 44.5 mg, 56% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 6.7 Hz, 2H), 7.36 (t, *J* = 7.0 Hz, 2H), 7.31 (d, *J* = 6.8 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 6.6 Hz, 1H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 2H), 6.73 (s, 1H), 5.00 (s, 2H), 4.29 (s, 1H), 3.69 (s, 3H), 2.19 - 1.99 (m, 2H), 0.87 (s, 10H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.91, 139.39, 137.29, 137.23, 128.89, 128.56, 127.89, 127.58, 127.04, 125.90, 121.46, 121.14, 119.42, 118.58, 114.60, 109.14, 70.07, 50.04, 38.59, 32.66, 31.56, 30.33. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{32}NO$ 398.2478, Found 398.2481.

3-(3,3-dimethyl-1-(4-phenoxyphenyl)butyl)-1-methyl-1*H*-indole (4caa):



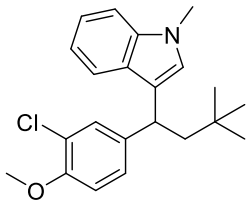
Following the typical experimental procedure on 0.2 mmol scale, compound **4caa** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1, v/v). 45.7 mg, 62% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.33 - 7.25 (m, 4H), 7.23 (d, *J* = 5.1 Hz, 1H), 7.19 (d, *J* = 7.1 Hz, 1H), 7.05 (dd, *J* = 15.7, 7.7 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 2H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.78 (s, 1H), 4.36 - 4.30 (m, 1H), 3.71 (s, 3H), 2.19 - 2.02 (m, 2H), 0.88 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.62, 154.80, 142.02, 137.16, 129.58, 129.14, 127.00, 125.82, 122.79, 121.48, 120.75, 119.34, 118.90, 118.58, 118.44, 109.14, 50.05, 38.73, 32.64, 31.53, 30.27. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{28}NO$ 370.2165, Found 370.2154.

3-(1-(2-Methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole (4daa):



Following the typical experimental procedure on 0.2 mmol scale, compound **4daa** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 44.9 mg, 70% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70-7.56 (m, 1H), 7.34-7.25 (m, 1H), 7.20-6.98 (m, 4H), 6.83-6.78 (m, 3H), 5.00-4.80 (m, 1H), 3.85 (s, 3H), 3.67 (s, 3H), 2.11-2.02 (m, 2H), 0.85 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.40, 137.13, 135.52, 128.61, 127.57, 126.49, 126.21, 121.34, 120.84, 120.44, 119.66, 118.46, 110.63, 108.99, 55.47, 49.74, 32.67, 31.69, 30.38, 30.26. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}NO$ 322.2165, Found 322.2144.

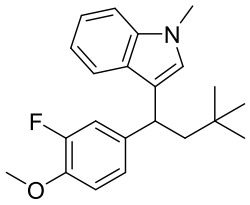
3-(1-(3-Chloro-4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole (4eaa):



Following the typical experimental procedure on 0.2 mmol scale, compound **4eaa** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 38.3 mg, 54% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.87 (s, 1H), 6.84 (d, *J* = 1.9 Hz, 1H), 6.80 (s, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 4.25 - 4.21 (m, 1H), 4.21 (s, 3H), 3.72 (s, 3H), 2.13 - 2.02 (m, 2H), 0.89 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.10, 141.39, 140.50, 137.13, 126.99, 125.77,

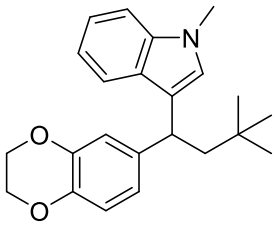
121.38, 120.91, 120.82, 119.33, 118.51, 116.81, 116.46, 109.06, 64.36, 64.25, 50.01, 38.60, 32.60, 31.50, 30.23. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}ClNO$ 356.1776, Found 356.1780.

3-(1-(3-Fluoro-4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole (4faa):



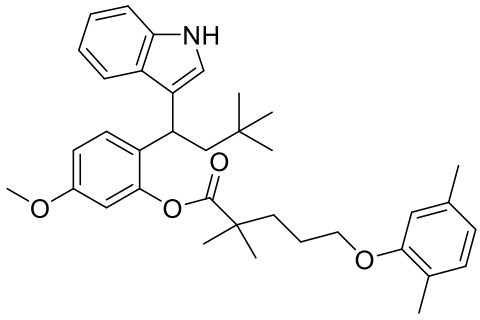
Following the typical experimental procedure on 0.2 mmol scale, compound **4faa** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 40.0 mg, 59% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.18 (t, *J* = 7.0 Hz, 1H), 7.06 (d, *J* = 11.0 Hz, 3H), 6.84 (t, *J* = 8.5 Hz, 1H), 6.75 (s, 1H), 4.46 - 4.12 (m, 1H), 3.82 (s, 3H), 3.70 (s, 3H), 2.16 - 1.97 (m, 2H), 0.87 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.27, 151.32, 145.43 (d, *J* = 10.8 Hz), 140.25 (d, *J* = 5.4 Hz), 137.17, 126.84, 125.74, 123.37 (d, *J* = 3.0 Hz), 121.54, 120.41, 119.20, 118.64, 115.46 (d, *J* = 18.1 Hz), 113.16, 109.17, 56.24, 49.82, 38.51, 32.62, 31.47, 30.22. ^{19} F NMR (471 MHz, $CDCl_3$) δ -140.80. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}FNO$ 340.2071, Found 340.2070.

3-(1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole (4gaa):



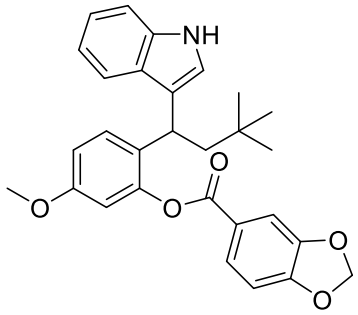
Following the typical experimental procedure on 0.2 mmol scale, compound **4gaa** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 35.5 mg, 51% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.24 (s, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.90 - 6.83 (m, 2H), 6.80 (s, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 4.25 (d, *J* = 7.1 Hz, 1H), 4.21 (s, 4H), 3.72 (s, 3H), 2.17 - 1.99 (m, 2H), 0.89 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.10, 141.39, 140.50, 137.13, 126.99, 125.77, 121.38, 120.91, 120.82, 119.33, 118.51, 116.81, 116.46, 109.06, 64.36, 64.25, 50.01, 38.60, 32.60, 31.50, 30.23. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{28}NO_2$ 350.2115, Found 350.2119.

2-(1-(1*H*-indol-3-yl)-3,3-dimethylbutyl)-5-methoxyphenyl-5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (4has)：



Following the typical experimental procedure on 0.2 mmol scale, compound **4has** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 10:1, v/v). 66.6 mg, 60% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 6.5 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 6.65 (d, *J* = 6.5 Hz, 1H), 6.57 (s, 1H), 6.52 (d, *J* = 6.0 Hz, 2H), 4.62-4.49 (m, 1H), 3.75 (s, 3H), 3.68 (t, *J* = 8.0 Hz, 2H), 2.30 (s, 3H), 2.12 (d, *J* = 8.7 Hz, 4H), 2.07 - 2.01 (m, 1H), 1.82 - 1.69 (m, 2H), 1.63 (s, 2H), 1.32 (s, 3H), 1.31 (s, 3H), 0.89 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.08, 158.04, 156.89, 148.90, 136.62, 136.38, 130.21, 129.32, 129.26, 126.36, 123.51, 121.91, 121.71, 121.50, 120.61, 119.03, 118.92, 111.95, 111.72, 111.18, 107.96, 67.62, 55.35, 48.61, 42.52, 37.06, 31.50, 30.85, 30.32, 25.38, 24.98, 24.95, 21.37, 15.74. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{36}H_{46}NO_4$ 556.3421, Found 556.3425.

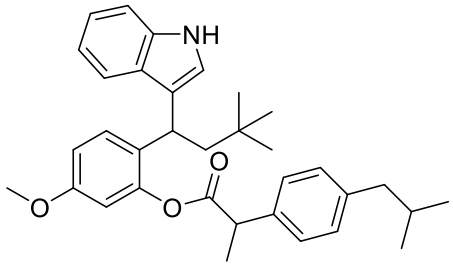
2-(1-(1*H*-indol-3-yl)-3,3-dimethylbutyl)-5-methoxyphenyl benzo[d][1,3]dioxole-5-Carboxylate (4ias):



Following the typical experimental procedure on 0.2 mmol scale, compound **4ias** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 10:1, v/v). 43.3 mg, 46% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.82 (s, 1H), 7.61 (s, 1H), 7.57 (d, *J* = 3.6 Hz, 1H), 7.35 (d, *J* = 5.3 Hz, 1H), 7.32-7.18 (m, 2H), 7.12 (s, 1H), 7.03 (s, 1H), 6.88 (d, *J* = 9.8 Hz, 2H), 6.74 (d, *J* = 6.9 Hz, 1H), 6.68 (s, 1H), 6.07 (s, 2H), 4.55 (s, 1H), 3.74 (s, 3H), 2.14-1.93 (m, 2H), 0.81 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.41, 158.10, 152.22, 148.57, 147.97, 136.42, 130.72, 129.41, 126.76, 126.26, 123.50, 121.85, 121.56, 121.12, 119.26, 119.15, 112.39, 111.04, 109.98, 108.24, 107.96, 102.00,

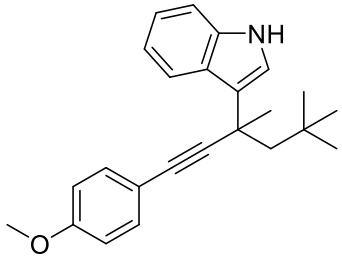
55.42, 49.13, 31.49, 31.35, 30.27. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{30}NO_5$ 472.2118, Found 472.2115.

2-(1-(1*H*-indol-3-yl)-3,3-dimethylbutyl)-5-methoxyphenyl-2-(4-isobutylphenyl)propanoate (4jas):



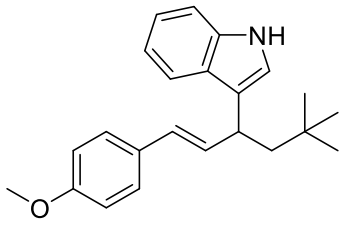
Following the typical experimental procedure on 0.2 mmol scale, compound **4jas** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 10:1, v/v). 62.3 mg, 61% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.58 - 7.47 (m, 1H), 7.34 - 7.29 (m, 1H), 7.24 (s, 3H), 7.13 (s, 1H), 7.08 (s, 3H), 6.71 (s, 1H), 6.61 (d, *J* = 21.1 Hz, 1H), 6.48 (s, 1H), 4.37 (s, 1H), 3.95 - 3.89 (m, 1H), 3.70 (s, 3H), 2.45 (s, 2H), 2.10 - 1.89 (m, 2H), 1.68 - 1.47 (m, 4H), 0.89 (s, 6H), 0.78 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.98, 157.92, 148.67, 140.79, 137.08, 136.44, 129.99, 129.52, 129.07, 127.38, 126.51, 121.72, 121.65, 121.32, 119.25, 119.04, 111.79, 111.00, 107.77, 55.32, 48.69, 45.34, 45.04, 31.32, 31.02, 30.18, 30.14, 22.38, 18.60. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{42}NO_3$ 512.3159, Found 512.3165.

3-(1-(4-Methoxyphenyl)-3,5,5-trimethylhex-1-yn-3-yl)-1*H*-indole (4las)：



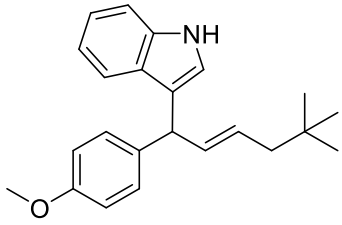
Following the typical experimental procedure on 0.2 mmol scale, compound **4las** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 30:1, v/v). 35.8 mg, 52% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.4 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.29 (s, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 6.9 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 2H), 3.82 (s, 3H), 2.33 (d, *J* = 14.3 Hz, 1H), 1.96 (d, *J* = 14.3 Hz, 1H), 1.86 (s, 3H), 0.95 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.03, 137.30, 132.60, 125.41, 122.50, 121.79, 121.53, 121.16, 118.97, 116.53, 113.84, 111.37, 95.66, 82.31, 55.27, 53.64, 35.27, 32.38, 32.12, 30.91. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{28}NO$ 346.2165, Found 346.2170.

3-(1-(4-Methoxyphenyl)-5,5-dimethylhex-1-en-3-yl)-1*H*-indole (4mas)：



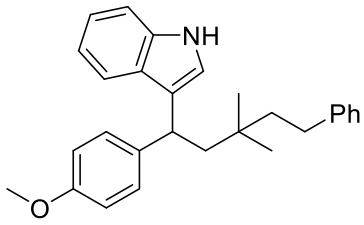
Following the typical experimental procedure on 0.2 mmol scale, compound **4mas** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 20.6 mg, 31% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.17 (t, *J* = 7.0 Hz, 1H), 7.10 (t, *J* = 6.0 Hz, 1H), 6.97 (s, 1H), 6.80 (d, *J* = 7.0 Hz, 2H), 6.39 - 6.25 (m, 2H), 3.91 - 3.87 (m, 1H), 3.76 (s, 3H), 1.99 - 1.79 (m, 2H), 0.96 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.57, 136.49, 134.08, 130.78, 127.57, 127.09, 126.52, 121.85, 121.12, 120.52, 119.55, 119.10, 113.82, 111.12, 55.25, 49.38, 37.17, 31.41, 30.22. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{28}NO$ 334.2165, Found 334.2162.

3-(1-(4-Methoxyphenyl)-5,5-dimethylhex-2-en-1-yl)-1*H*-indole (4mas)：



Following the typical experimental procedure on 0.2 mmol scale, compound **4mas** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 24.6 mg, 37% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.41 (d, *J* = 6.6 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.1 Hz, 2H), 7.17 (d, *J* = 7.0 Hz, 1H), 7.04 (d, *J* = 5.9 Hz, 1H), 6.89 – 6.83 (m, 3H), 5.92 (dd, *J* = 14.5, 6.7 Hz, 1H), 5.62-5.50 (m, 1H), 4.91 (d, *J* = 6.0 Hz, 1H), 3.80 (s, 3H), 1.97 (d, *J* = 6.2 Hz, 2H), 0.90 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.81, 136.63, 136.33, 134.77, 129.19, 128.22, 126.79, 122.20, 121.89, 119.96, 119.71, 119.14, 113.59, 110.97, 55.18, 47.05, 45.25, 31.06, 29.37. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{28}NO$ 334.2165, Found 334.2167.

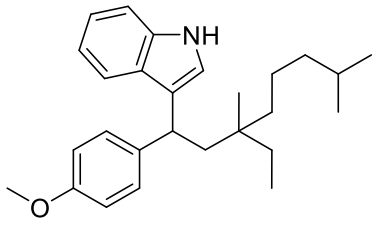
3-(1-(4-Methoxyphenyl)-3,3-dimethyl-5-phenylpentyl)-1*H*-indole (4abs)：



Following the typical experimental procedure on 0.2 mmol scale, compound **4abs** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 56.3 mg, 71% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.28 (d, *J* =

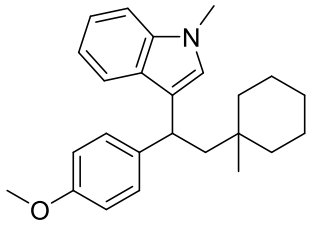
7.3 Hz, 2H), 7.21 (d, *J* = 7.3 Hz, 2H), 7.13 (t, *J* = 7.1 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 1H), 7.01 (d, *J* = 6.3 Hz, 2H), 6.91 (s, 1H), 6.80 (d, *J* = 7.3 Hz, 2H), 4.33 (t, *J* = 6.2 Hz, 1H), 3.73 (s, 3H), 2.49 (d, *J* = 6.1 Hz, 2H), 2.29 - 2.07 (m, 2H), 1.53 - 1.48 (m, 2H), 0.93 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.61, 143.37, 138.93, 136.47, 128.83, 128.25, 128.18, 126.61, 125.42, 122.40, 121.88, 120.91, 119.33, 119.16, 113.68, 111.06, 55.16, 47.42, 44.87, 38.13, 34.12, 30.65, 28.00, 27.95. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{32}NO$ 398.2478, Found 398.2472.

3-(3-Ethyl-1-(4-methoxyphenyl)-3,7-dimethyloctyl)-1*H*-indole (4acs):



Following the typical experimental procedure on 0.2 mmol scale, compound **4acs** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 52.3 mg, 67% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.58 (d, *J* = 6.8 Hz, 1H), 7.26 (d, *J* = 7.2 Hz, 3H), 7.12 (t, *J* = 6.5 Hz, 1H), 7.04 (t, *J* = 7.7 Hz, 1H), 6.95 (s, 1H), 6.78 (d, *J* = 7.0 Hz, 2H), 4.26 (s, 1H), 3.73 (s, 3H), 2.15 - 2.01 (m, 2H), 1.47-1.39 (m, 1H), 1.27-1.21 (m, 2H), 1.12 (d, *J* = 16.7 Hz, 4H), 0.97 (s, 2H), 0.81 (d, *J* = 2.0 Hz, 6H), 0.73 (t, *J* = 6.1 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.47, 139.29, 136.44, 128.82, 126.68, 122.69, 121.79, 120.78, 119.38, 119.07, 113.55, 111.00, 55.15, 45.13, 39.90, 39.31, 37.73, 36.26, 32.08, 27.96, 25.16, 22.68, 21.27, 8.06. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{38}NO$ 392.2948, Found 392.2942.

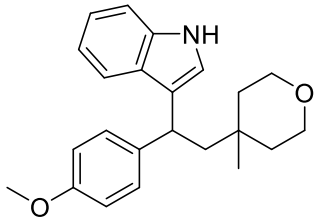
3-(1-(4-Methoxyphenyl)-2-(1-methylcyclohexyl)ethyl)-1-methyl-1*H*-indole (4ads)：



Following the typical experimental procedure on 0.2 mmol scale, compound **4ads** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 38.3 mg, 53% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 7.3 Hz, 2H), 7.22 (d, *J* = 5.9 Hz, 1H), 7.16 (t, *J* = 7.1 Hz, 1H), 7.04 (t, *J* = 7.0 Hz, 1H), 6.79 (d, *J* = 7.3 Hz, 2H), 6.75 (s, 1H), 4.35 - 4.29 (m, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 2.18 - 2.03 (m, 2H), 1.42 - 1.26 (m, 8H), 1.17 (s, 2H), 0.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.47, 139.30, 137.15, 128.81, 126.97, 125.86, 121.36, 121.32, 119.40, 118.49, 113.54, 109.07, 55.14, 38.72,

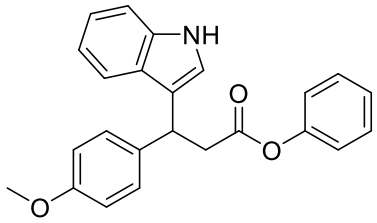
38.37, 37.48, 33.89, 32.59, 26.45, 22.10, 22.02. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{32}NO$ 362.2478, Found 362.2471.

3-(1-(4-Methoxyphenyl)-2-(4-methyltetrahydro-2H-pyran-4-yl)ethyl)-1*H*-indole (4aes)：



Following the typical experimental procedure on 0.2 mmol scale, compound **4aes** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 46.0 mg, 66% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.62 (d, *J* = 7.4 Hz, 1H), 7.30 (s, 3H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.09 (t, *J* = 6.4 Hz, 1H), 6.93 (s, 1H), 6.83 (d, *J* = 7.5 Hz, 2H), 4.39 (t, *J* = 6.7 Hz, 1H), 3.78 (s, 3H), 3.73 - 3.51 (m, 4H), 2.31 - 2.13 (m, 2H), 1.58 (t, *J* = 11.3 Hz, 1H), 1.45 (t, *J* = 11.4 Hz, 1H), 1.31 (d, *J* = 13.3 Hz, 1H), 1.19 (d, *J* = 13.5 Hz, 1H), 1.06 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.63, 138.50, 136.47, 128.76, 126.45, 121.99, 121.89, 121.01, 119.16, 119.13, 113.67, 111.10, 63.89, 63.84, 55.14, 49.04, 38.49, 38.20, 37.33, 31.68, 23.72. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{28}NO_2$ 350.2115, Found 350.2119.

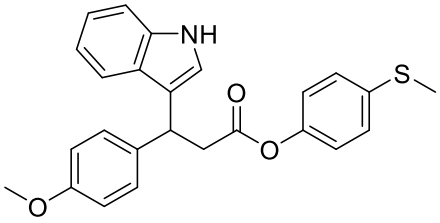
Phenyl-3-(1H-indol-3-yl)-3-(4-methoxyphenyl)propanoate (4ags)：



Following the typical experimental procedure on 0.2 mmol scale, compound **4ags** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 60.8 mg, 82% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.43 (d, *J* = 6.6 Hz, 1H), 7.32 - 7.20 (m, 5H), 7.13 (s, 2H), 7.01 (s, 1H), 6.94 (s, 1H), 6.80 (s, 4H), 4.86 (t, *J* = 8.0 Hz, 1H), 3.72 (s, 3H), 3.22 - 3.17 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.88, 158.11, 150.46, 136.44, 135.26, 129.28, 128.71, 126.37, 125.73, 122.05, 121.43, 121.12, 119.30, 118.38, 113.79, 111.15, 55.11, 41.55, 38.67. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{22}NO_3$ 372.1594, Found 372.1595.

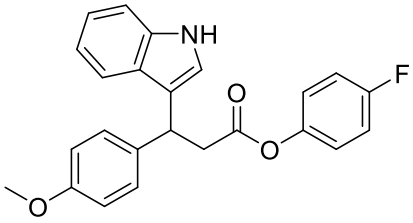
4-(Methylthio)phenyl 3-(1*H*-indol-3-yl)-3-(4-methoxyphenyl)propanoate (4ahs):

Following the typical experimental procedure on 0.2 mmol scale, compound **4ahs** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1,



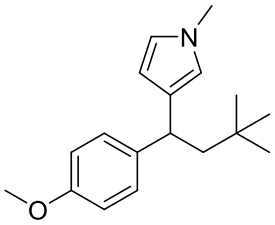
v/v). 68.3 mg, 74% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 9.7 Hz, 3H), 7.19 (d, *J* = 7.5 Hz, 3H), 7.10 - 7.02 (m, 2H), 6.86 (d, *J* = 7.7 Hz, 2H), 6.75 (d, *J* = 7.9 Hz, 2H), 4.88 (t, *J* = 7.3 Hz, 1H), 3.79 (s, 3H), 3.42 - 3.19 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.76, 158.25, 148.29, 136.53, 135.54, 135.24, 128.75, 127.90, 126.49, 122.23, 121.95, 121.11, 119.47, 118.70, 113.88, 111.11, 55.21, 41.61, 38.74, 16.44. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{24}NO_3S$ 418.1471, Found 418.1458.

4-Fluorophenyl 3-(1*H*-indol-3-yl)-3-(4-methoxyphenyl)propanoate (4ais):



Following the typical experimental procedure on 0.2 mmol scale, compound **4ais** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1, v/v). 50.5 mg, 65% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.37 - 7.29 (m, 3H), 7.19 (t, *J* = 6.7 Hz, 1H), 7.10 - 7.04 (m, 2H), 6.98 (t, *J* = 7.5 Hz, 2H), 6.86 (d, *J* = 7.5 Hz, 2H), 6.81 - 6.72 (m, 2H), 4.88 (t, *J* = 7.3 Hz, 1H), 3.79 (s, 3H), 3.41 - 3.22 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.81 , 160.12 (d, *J* = 244.1 Hz), 158.24 , 146.31 , 136.51 , 135.16 , 128.73 , 126.44 , 122.86 (d, *J* = 8.5 Hz), 122.25 , 121.09 , 119.45 (d, *J* = 9.1 Hz), 118.64 , 115.93 (d, *J* = 23.5 Hz), 113.87 , 111.13 , 55.20 , 41.52 , 38.73. ^{19}F NMR (471 MHz, $CDCl_3$) δ -117.03. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{21}FNO$ 390.1500, Found 390.1522.

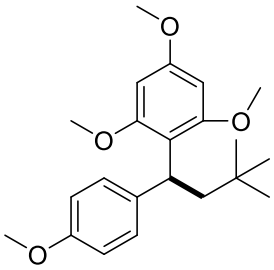
3-(1-(4-Methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-pyrrole (4aau)：



Following the typical experimental procedure on 0.2 mmol scale, compound **4aau** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 29.2 mg, 54% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, *J* = 4.6 Hz, 2H), 6.79 (d, *J* = 6.1 Hz, 2H), 6.47 (s, 1H), 6.07 (d, *J* = 12.1 Hz, 2H), 3.95 (s, 1H), 3.76 (s, 3H), 3.39 (s, 3H), 2.12-1.84 (m, 2H), 0.85 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.67, 137.59, 137.08, 128.86, 121.15, 113.73, 106.08,

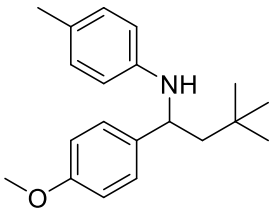
105.60, 55.19, 50.02, 38.82, 33.86, 31.21, 30.15. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{26}NO$ 272.2009, Found 272.2006.

1,3,5-Trimethoxy-2-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)benzene (4aav):



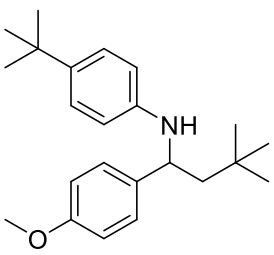
Following the typical experimental procedure on 0.2 mmol scale, compound **4aav** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1, v/v). 42.2 mg, 59% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.7 Hz, 2H), 6.74 (d, *J* = 7.7 Hz, 2H), 6.09 (s, 2H), 4.71 - 4.65 (m, 1H), 3.78 (s, 1H), 3.76 (s, 1H), 3.74 (s, 3H), 2.30 - 1.99 (m, 2H), 0.81 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.14, 156.96, 139.43, 128.91, 128.13, 116.10, 113.94, 112.88, 55.15, 55.12, 45.93, 34.89, 31.42, 29.88. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{31}O_4$ 359.2217, Found 359.2221.

***N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-4-methylaniline (4aaw):**



Following the typical experimental procedure on 0.2 mmol scale, compound **4aaw** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 38.1 mg, 64% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.6 Hz, 3H), 6.89 (d, *J* = 8.1 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.41 (d, *J* = 8.2 Hz, 2H), 4.33 (t, *J* = 5.9 Hz, 1H), 3.76 (s, 3H), 2.17 (s, 3H), 1.66 (d, *J* = 6.1 Hz, 2H), 0.98 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.22, 144.95, 138.19, 129.57, 127.09, 126.02, 113.92, 113.16, 55.20, 53.65, 31.01, 30.19, 20.30. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{28}NO$ 298.2165, Found 298.2168.

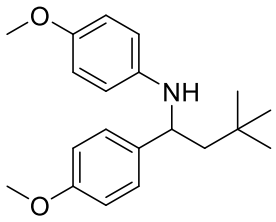
4-(Tert-butyl)-*N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)aniline (4aax):



Following the typical experimental procedure on 0.2 mmol scale, compound **4aax** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 48.8 mg, 72% yield. Yellow oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, J = 6.9 Hz, 2H), 7.16 (d, J = 6.9 Hz, 2H), 6.89 (d, J = 7.0 Hz, 2H), 6.51 (d, J = 7.0 Hz, 2H), 4.40 (s, 1H), 3.81 (s, 3H), 1.73 (d, J = 4.2 Hz, 2H), 1.29 (s, 9H), 1.04 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.23, 144.75, 139.54,

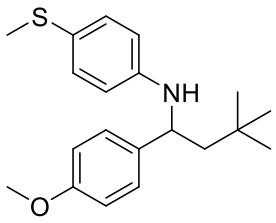
138.24, 127.15, 125.78, 113.89, 112.75, 55.35, 55.14, 53.56, 33.71, 31.48, 30.98, 30.18. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{34}NO$ 340.2635, Found 340.2629.

4-Methoxy-*N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)aniline (4aay):



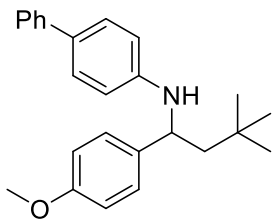
Following the typical experimental procedure on 0.2 mmol scale, compound **4aay** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 45.7 mg, 73% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 8.7 Hz, 2H), 6.44 (d, *J* = 8.7 Hz, 2H), 4.27 (t, *J* = 5.8 Hz, 1H), 3.75 (s, 3H), 3.67 (s, 3H), 1.66 (d, *J* = 5.9 Hz, 2H), 0.98 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.21, 151.62, 141.59, 138.23, 127.12, 114.72, 114.19, 113.88, 55.90, 55.65, 55.13, 53.55, 30.95, 30.16. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{28}NO_2$ 314.2115, Found 314.2108.

***N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-4-(methylthio)aniline (4aaz):**



Following the typical experimental procedure on 0.2 mmol scale, compound **4aaz** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 30.2 mg, 46% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.3 Hz, 2H), 6.43 (d, *J* = 8.3 Hz, 2H), 4.38 - 4.29 (m, 1H), 3.76 (s, 3H), 2.35 (s, 3H), 1.70 - 1.63 (m, 2H), 0.98 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.31, 146.02, 137.58, 131.41, 127.03, 123.60, 113.95, 113.64, 55.16, 55.05, 53.52, 30.95, 30.14, 19.09. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{28}NOS$ 330.1886, Found 330.1900.

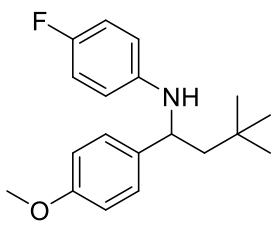
***N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-[1,1'-biphenyl]-4-amine (4aaaa):**



Following the typical experimental procedure on 0.2 mmol scale, compound **4aaaa** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 45.2 mg, 63% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.1 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 4H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.55 (d, *J* = 8.3 Hz, 2H), 4.45 - 4.35 (m, 1H), 3.74 (s, 3H), 1.68 (d, *J* = 4.1 Hz, 2H), 0.99 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ

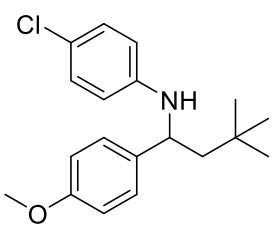
158.29, 146.53, 141.21, 137.74, 129.76, 128.51, 127.73, 127.05, 126.13, 125.84, 113.96, 113.27, 55.13, 55.02, 53.56, 30.96, 30.16. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{30}NO$ 360.2322, Found 360.2249.

4-Fluoro-*N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)aniline (4aaab):



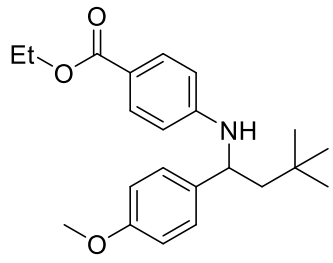
Following the typical experimental procedure on 0.2 mmol scale, compound **4aaab** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 36.1 mg, 60% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.3 Hz, 2H), 6.77 (t, *J* = 8.6 Hz, 2H), 6.41 – 6.38 (m, 2H), 4.28 (t, *J* = 5.7 Hz, 1H), 3.75 (s, 3H), 1.66 (d, *J* = 5.1 Hz, 2H), 0.98 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.43, 155.56 (d, *J* = 234.3 Hz), 143.71, 137.85, 127.18, 115.55 (d, *J* = 22.2 Hz), 114.07, 113.86 (d, *J* = 7.3 Hz), 55.82, 55.25, 53.68, 31.06, 30.25. ^{19}F NMR (471 MHz, $CDCl_3$) δ -128.61. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{25}FNO$ 302.1915, Found 302.1908.

4-Chloro-*N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)aniline (4aaac):



Following the typical experimental procedure on 0.2 mmol scale, compound **4aaac** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 32.3 mg, 51% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.39 (d, *J* = 8.6 Hz, 2H), 4.31 - 4.29 (m, 1H), 3.75 (s, 3H), 1.66 (d, *J* = 3.7 Hz, 2H), 0.97 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.35, 145.68, 137.33, 128.86, 127.01, 121.42, 114.10, 113.98, 55.17, 55.15, 53.50, 30.93, 30.12. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{25}ClNO$ 318.1619, Found 318.1621.

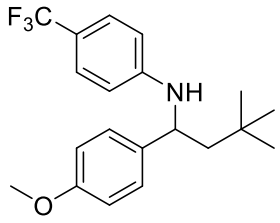
Ethyl-4-((1-(4-methoxyphenyl)-3,3-dimethylbutyl)amino)benzoate (4aaad):



Following the typical experimental procedure on 0.2 mmol scale, compound **4aaad** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 29.1 mg, 41% yield. Yellow oil. ^{1}H NMR (500

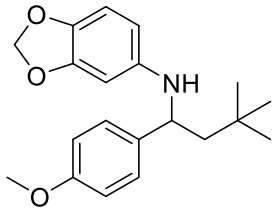
MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.49 (s, 2H), 4.46 - 4.44 (m, 2H), 4.29 (q, *J* = 7.0 Hz, 2H), 3.77 (s, 3H), 1.71 (d, *J* = 6.8 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.99 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.76, 158.41, 150.70, 136.76, 131.30, 126.98, 118.37, 114.00, 111.88, 60.01, 55.14, 54.54, 53.21, 30.89, 30.05, 14.35. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{30}NO_3$ 356.2220, Found 356.2249.

***N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-4-(trifluoromethyl)aniline (4aaae):**



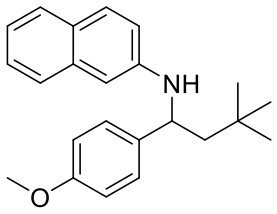
Following the typical experimental procedure on 0.2 mmol scale, compound **4aaae** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 40.7 mg, 58% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.49 (d, *J* = 8.3 Hz, 2H), 4.43 - 4.35 (m, 1H), 3.74 (s, 3H), 1.69 (d, *J* = 4.0 Hz, 2H), 0.98 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.61, 149.62, 136.96, 127.10, 126.55 (q, *J* = 3.6 Hz), 118.47 (q, *J* = 32.5 Hz), 114.20, 112.31, 77.36, 77.11, 76.85, 55.24, 54.85, 53.53, 31.03, 30.17. ^{19}F NMR (471 MHz, $CDCl_3$) δ -60.78. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{25}F_3NO$ 352.1883, Found 352.1884.

***N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)benzo[d][1,3]dioxol-5-amine (4aaaf):**



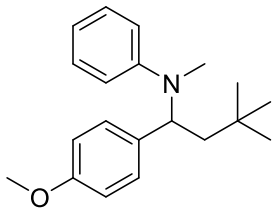
Following the typical experimental procedure on 0.2 mmol scale, compound **4aaaf** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 34.0 mg, 52% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.1 Hz, 2H), 6.85 (d, *J* = 8.1 Hz, 2H), 6.57 (d, *J* = 8.3 Hz, 1H), 6.13 (s, 1H), 5.92 (d, *J* = 8.1 Hz, 1H), 5.79 (d, *J* = 3.7 Hz, 2H), 4.27 (t, *J* = 5.8 Hz, 1H), 3.78 (s, 3H), 1.66 (d, *J* = 5.9 Hz, 2H), 0.99 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.34, 148.16, 143.15, 139.19, 138.09, 127.13, 114.01, 108.60, 104.81, 100.44, 96.07, 56.06, 55.25, 53.65, 31.04, 30.23. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{26}NO_3$ 328.1907, Found 328.1908.

***N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)naphthalen-2-amine (4aaag):**



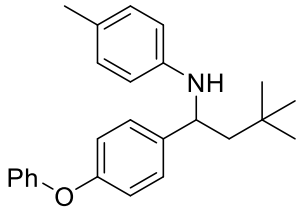
Following the typical experimental procedure on 0.2 mmol scale, compound **4aaag** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 33.3 mg, 50% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 3H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 3H), 6.63 (s, 1H), 4.50 (t, *J* = 5.9 Hz, 1H), 3.77 (s, 3H), 1.75 (d, *J* = 5.8 Hz, 2H), 1.02 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.35, 144.72, 137.60, 135.08, 128.76, 127.52, 127.25, 127.14, 126.12, 125.87, 121.73, 117.94, 114.01, 105.19, 55.22, 55.11, 53.53, 31.06, 30.21. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{28}NO$ 334.2165, Found 334.2181.

***N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-*N*-methylaniline (4aaai):**



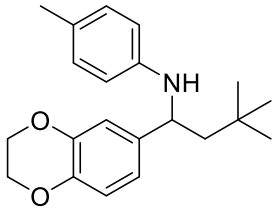
Following the typical experimental procedure on 0.2 mmol scale, compound **4aaai** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 30.3 mg, 51% yield. Yellow oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 6.1 Hz, 2H), 7.07 (d, *J* = 6.7 Hz, 2H), 6.78 (d, *J* = 4.3 Hz, 2H), 6.52 (d, *J* = 6.1 Hz, 2H), 3.96 – 3.84 (m, 1H), 3.74 (s, 3H), 2.77 (s, 3H), 2.00 (s, 2H), 0.82 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.44, 147.28, 139.84, 136.04, 128.48, 128.31, 113.65, 112.51, 55.16, 49.79, 46.50, 31.39, 30.88, 30.24. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{28}NO$ 298.2165, Found 298.2168.

***N*-(3,3-dimethyl-1-(4-phenoxyphenyl)butyl)-4-methylaniline (4caw):**



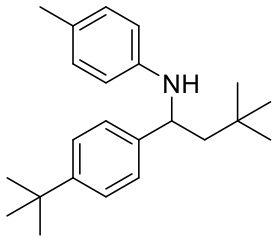
Following the typical experimental procedure on 0.2 mmol scale, compound **4caw** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 50.2 mg, 70% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 - 7.24 (m, 4H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.93 - 6.89 (m, 4H), 6.41 (d, *J* = 8.0 Hz, 2H), 4.35 (s, 1H), 2.18 (s, 3H), 1.73 - 1.63 (m, 2H), 0.99 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.36, 155.66, 144.84, 141.07, 129.62, 129.60, 127.34, 126.12, 122.99, 118.99, 118.67, 113.12, 55.39, 53.70, 31.04, 30.18, 20.31. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{30}NO$ 360.2322, Found 360.2313.

***N*-(1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-3,3-dimethylbutyl)-4-methylaniline (4gaw):**



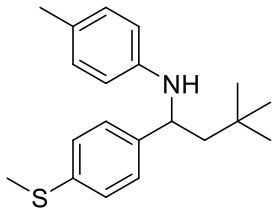
Following the typical experimental procedure on 0.2 mmol scale, compound **4gaw** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 44.2 mg, 68% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (d, *J* = 8.0 Hz, 2H), 6.85 (s, 1H), 6.81 (s, 2H), 6.43 (d, *J* = 8.1 Hz, 2H), 4.29 - 4.26 (m, 1H), 4.23 (s, 4H), 2.20 (s, 3H), 1.67 (d, *J* = 4.1 Hz, 2H), 1.00 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.96, 143.54, 142.13, 139.78, 129.62, 126.05, 118.98, 117.27, 114.81, 113.18, 64.40, 64.30, 55.34, 53.71, 31.07, 30.22, 20.36. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{28}NO_2$ 326.2115, Found 326.2137.

***N*-(1-(4-(tert-butyl)phenyl)-3,3-dimethylbutyl)-4-methylaniline (4naw):**



Following the typical experimental procedure on 0.2 mmol scale, compound **4naw** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 40.1 mg, 62% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.42 (d, *J* = 8.0 Hz, 2H), 4.36 - 4.33 (m, 1H), 2.18 (s, 3H), 1.68 - 1.67 (m, 2H), 1.29 (s, 9H), 1.00 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.26, 145.06, 143.08, 129.61, 125.91, 125.66, 125.43, 113.06, 55.44, 53.68, 34.39, 31.42, 31.11, 30.22, 20.34. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{34}N$ 324.2686, Found 324.2681.

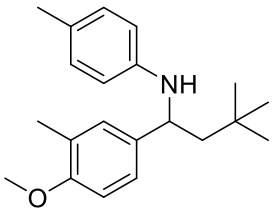
***N*-(3,3-dimethyl-1-(4-(methylthio)phenyl)butyl)-4-methylaniline (4oaw):**



Following the typical experimental procedure on 0.2 mmol scale, compound **4oaw** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 47.6 mg, 76% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 6.88 (d, *J* = 6.4 Hz, 2H), 6.39 (d, *J* = 3.7 Hz, 2H), 4.34 - 4.31 (m, 1H), 2.42 (s, 3H), 2.17 (s, 3H), 1.67 - 1.61 (m, 2H), 0.99 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.90, 143.44, 136.21, 129.70, 127.19,

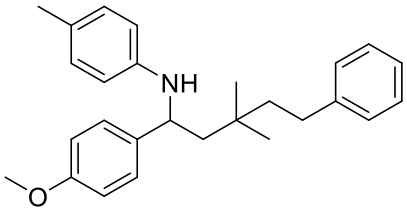
126.76, 126.25, 113.26, 55.61, 53.74, 31.17, 30.29, 20.43, 16.15. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{28}NS$ 314.1937, Found 314.1924.

***N*-(1-(4-methoxy-3-methylphenyl)-3,3-dimethylbutyl)-4-methylaniline (4paw):**



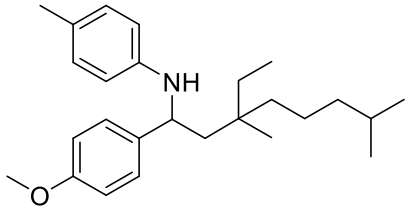
Following the typical experimental procedure on 0.2 mmol scale, compound **4paw** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 32.9 mg, 53% yield. Yellow oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.73 (t, *J* = 7.7 Hz, 1H), 6.60 (t, *J* = 7.7 Hz, 1H), 6.38 (d, *J* = 7.8 Hz, 1H), 5.29 (s, 2H), 4.39 - 4.36 (m, 1H), 3.89 (s, 3H), 3.79 (s, 3H), 1.89 - 1.71 (m, 2H), 1.02 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.19, 146.56, 138.18, 137.26, 127.08, 121.14, 115.80, 113.86, 110.55, 109.24, 55.51, 55.16, 54.84, 53.64, 30.90, 30.14. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{30}NO$ 312.2322, Found 312.2320.

***N*-(1-(4-methoxyphenyl)-3,3-dimethyl-5-phenylpentyl)-4-methylaniline (4abw):**



Following the typical experimental procedure on 0.2 mmol scale, compound **4abw** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 51.1 mg, 66% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 6.5 Hz, 4H), 7.15 - 7.09 (m, 3H), 6.88 (d, *J* = 6.7 Hz, 2H), 6.82 (d, *J* = 7.5 Hz, 2H), 6.40 (d, *J* = 6.2 Hz, 2H), 4.38 (d, *J* = 2.0 Hz, 1H), 3.72 (s, 3H), 2.60 - 2.49 (m, 2H), 2.16 (s, 3H), 1.73 (s, 2H), 1.62 - 1.53 (m, 2H), 1.03 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.23, 144.76, 142.94, 138.01, 129.52, 128.27, 128.22, 127.07, 125.99, 125.56, 113.92, 113.19, 55.09, 54.77, 51.32, 44.97, 33.58, 30.62, 27.80, 27.72, 20.26. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{34}NO$ 388.2635; Found 388.2632.

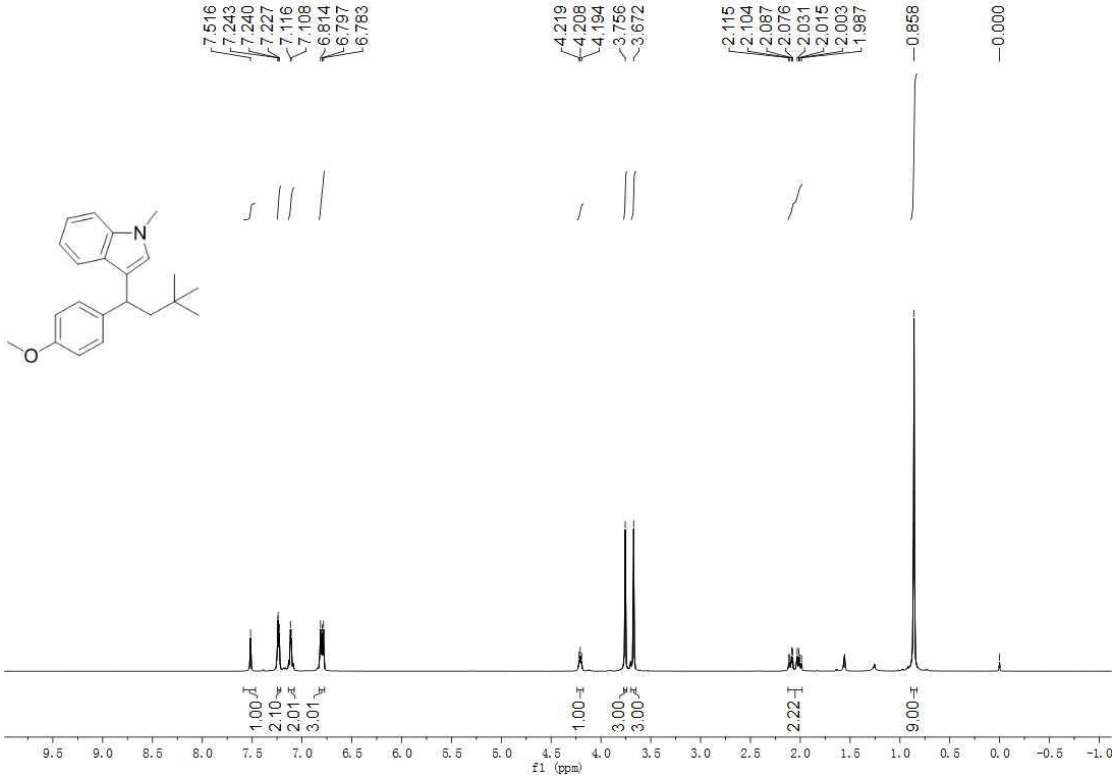
***N*-(3-ethyl-1-(4-methoxyphenyl)-3,7-dimethyloctyl)-4-methylaniline (4acw):**



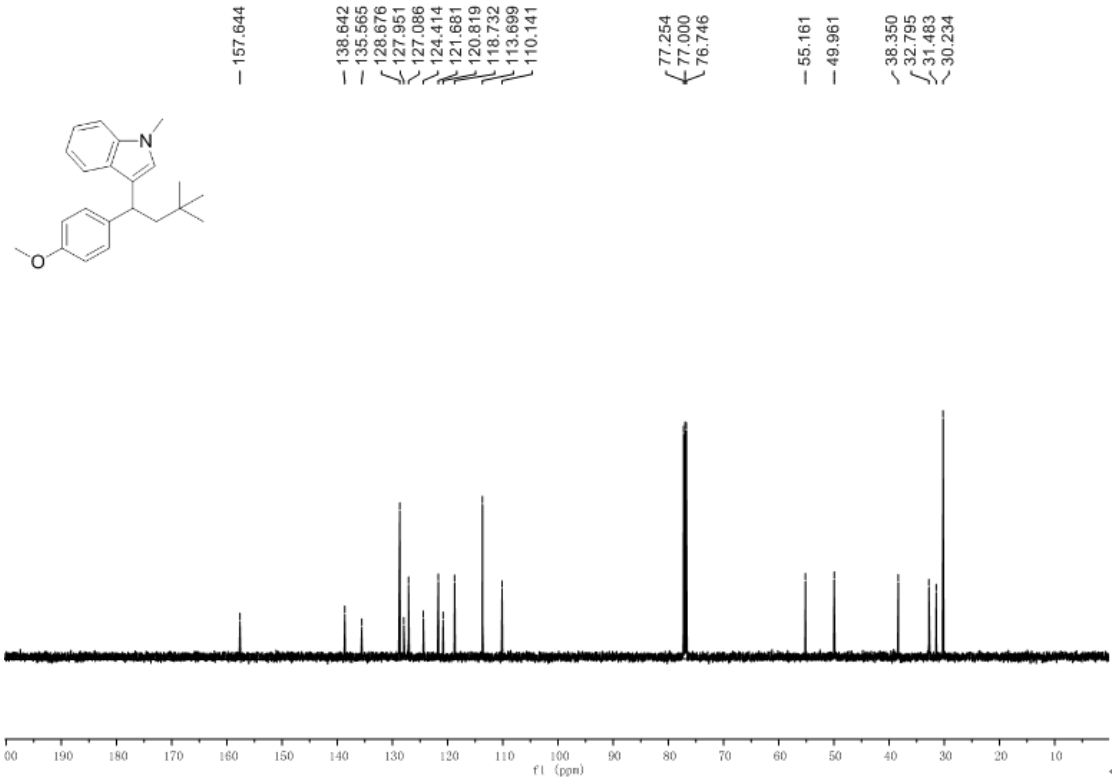
Following the typical experimental procedure on 0.2 mmol scale, compound **4acw** was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v). 46.5 mg, 61% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 6.0 Hz, 2H), 6.89 (d, *J* = 7.0 Hz, 2H), 6.83 (d, *J* = 7.0 Hz, 2H), 6.39 (d, *J* = 7.5 Hz, 2H), 4.37-4.27 (m, 1H), 3.76 (s, 3H), 2.17 (s, 3H), 1.64-1.63 (m, 2H), 1.53-1.50 (m, 1H), 1.34-1.31 (m, 2H), 1.25-1.16 (m, 4H), 1.14-1.07 (m, 2H), 0.91 (s, 3H), 0.87 (d, *J* = 5.0 Hz, 6H), 0.83-0.78 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.19, 144.92, 138.47, 129.55, 127.03, 125.94, 113.91, 113.14, 55.17, 54.56, 49.19, 49.10, 39.91, 39.60, 39.33, 35.87, 32.10, 31.88, 27.98, 25.25, 25.16, 22.71, 22.65, 21.34, 21.28, 20.30, 8.08. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{40}NO$ 382.3104, Found 382.3107.

(C) Spectra

3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole(4aaa):

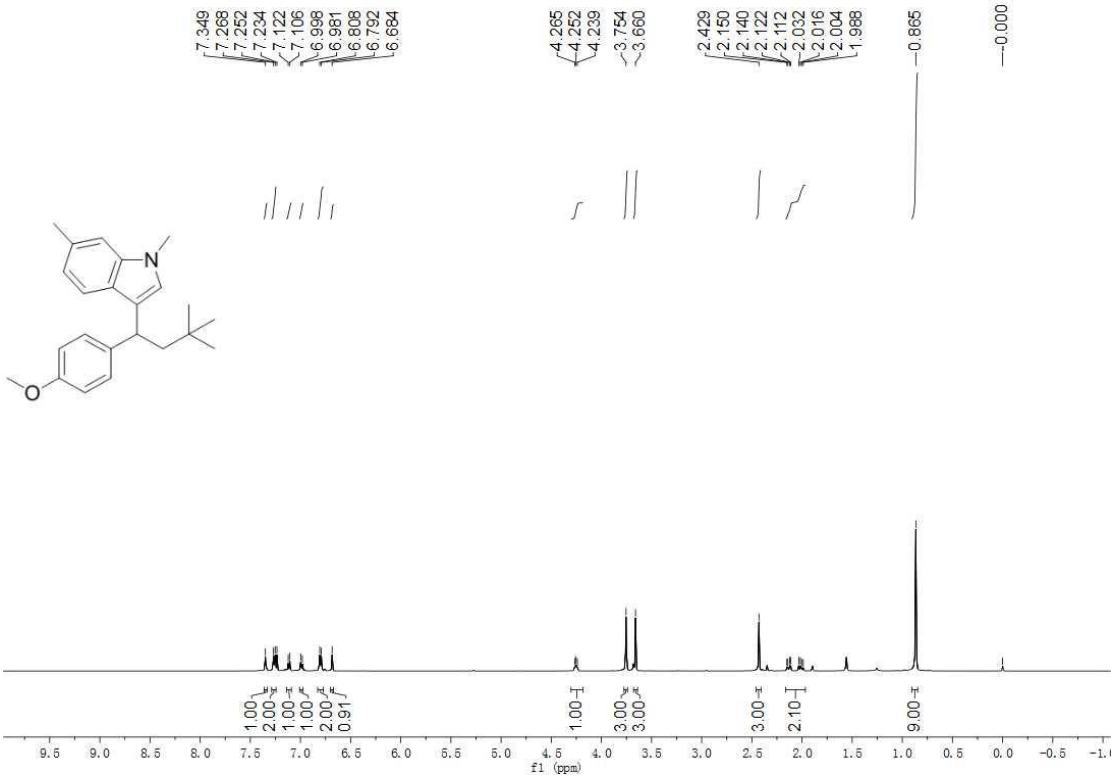


^{1}H-NMR (500 MHz, $CDCl_3$)

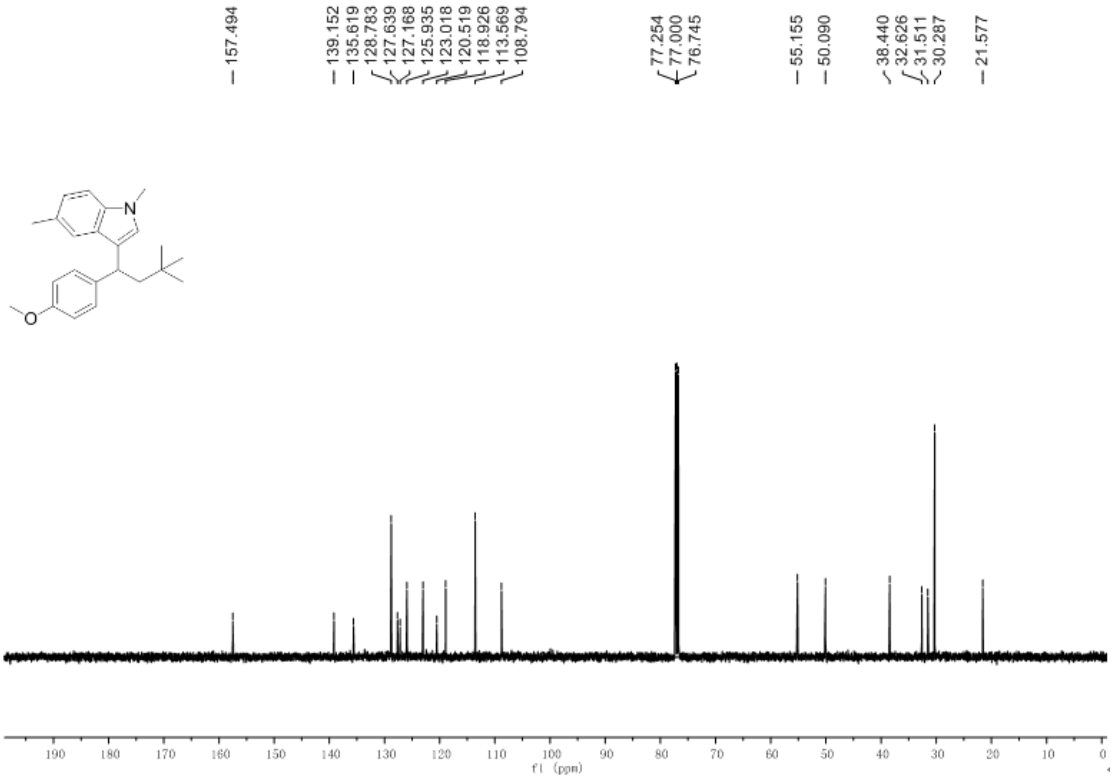


^{13}C-NMR (125 MHz, $CDCl_3$)

3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1,6-dimethyl-1*H*-indole (4aab):

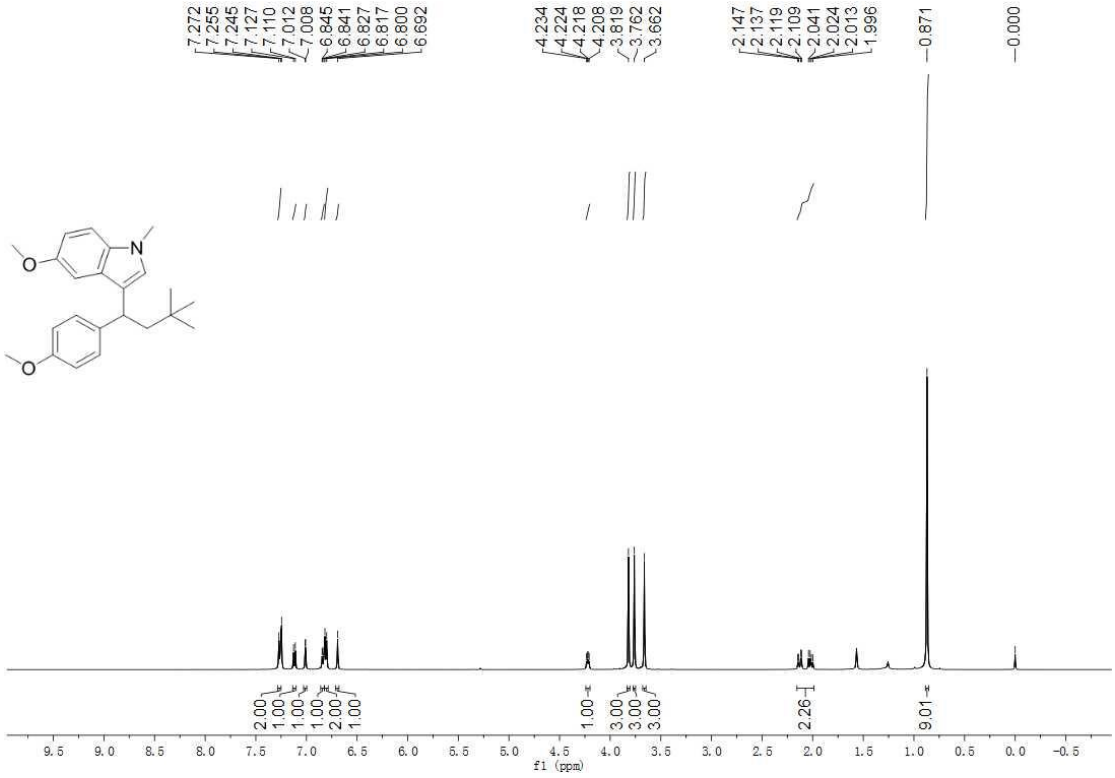


^{1}H-NMR (500 MHz, $CDCl_3$)

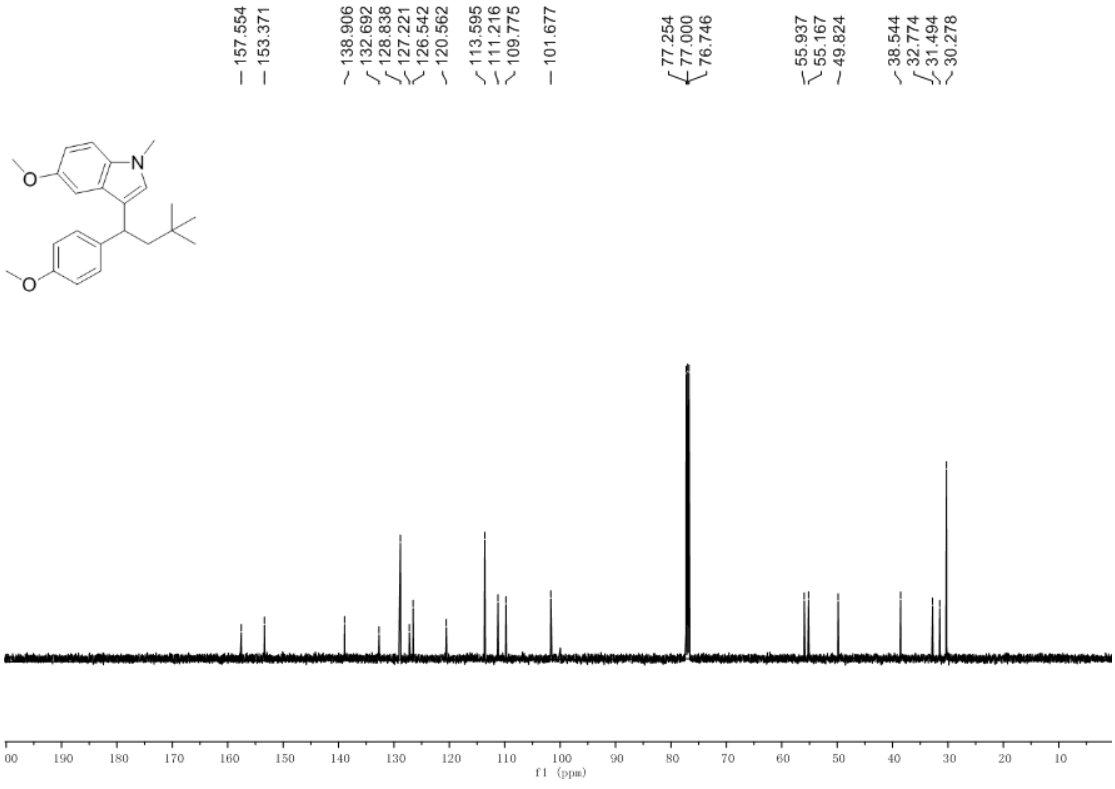


^{13}C-NMR (125 MHz, $CDCl_3$)

5-methoxy-3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole (4aac):

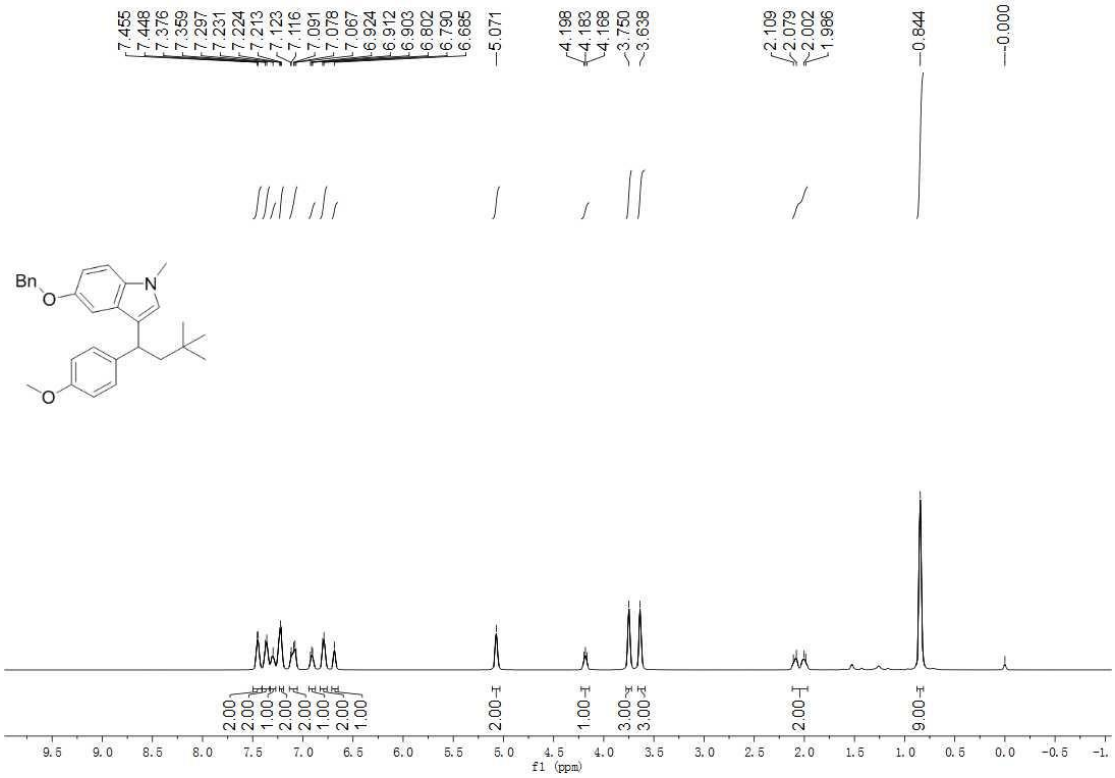


^{1}H-NMR (500 MHz, $CDCl_3$)

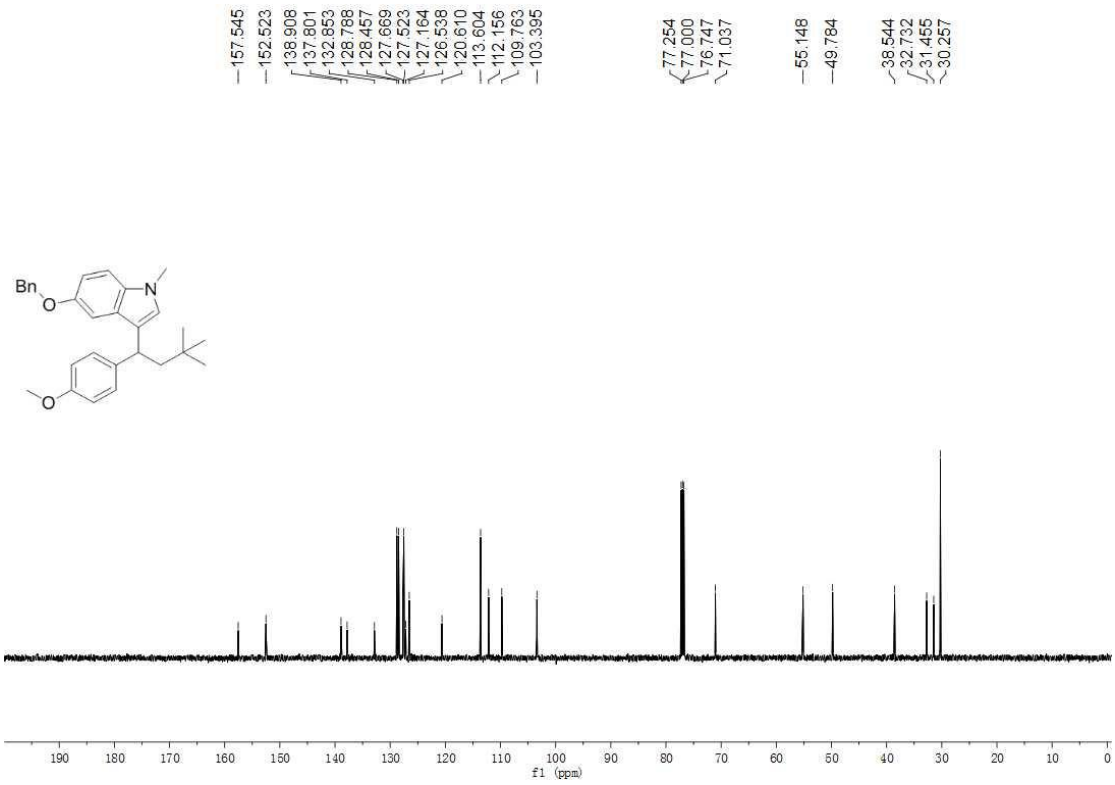


^{13}C-NMR (125 MHz, $CDCl_3$)

5-(benzyloxy)-3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole(4aad):

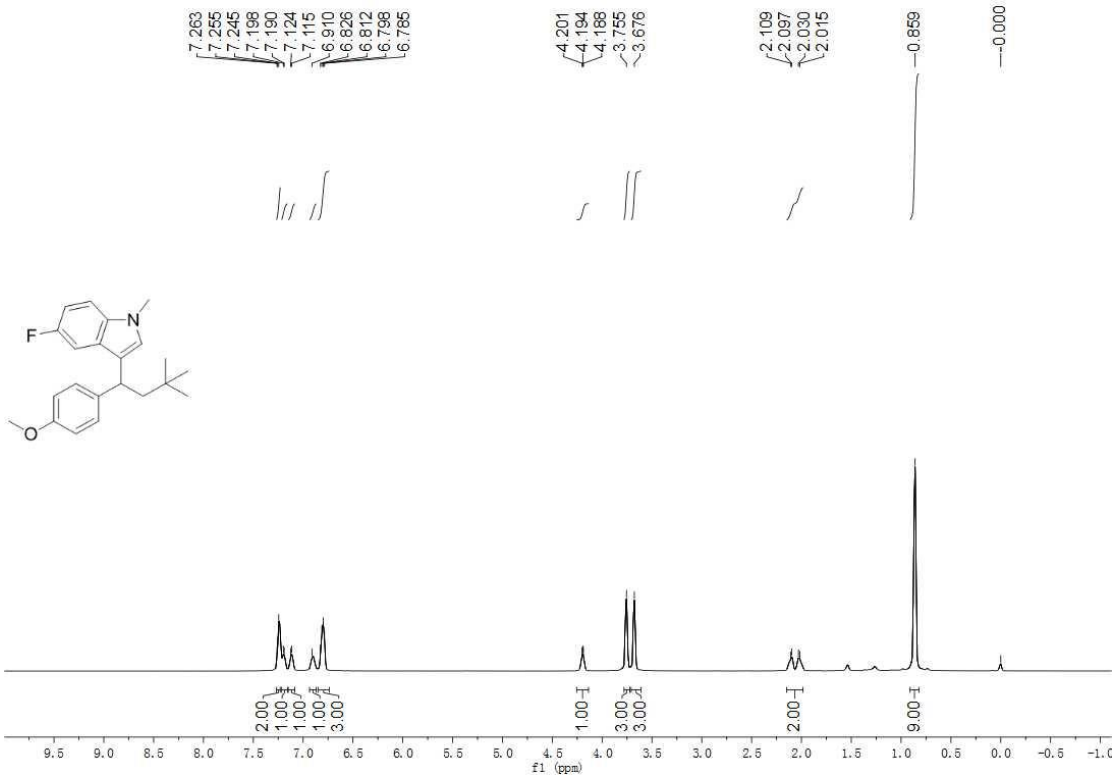


^{1}H-NMR (500 MHz, $CDCl_3$)

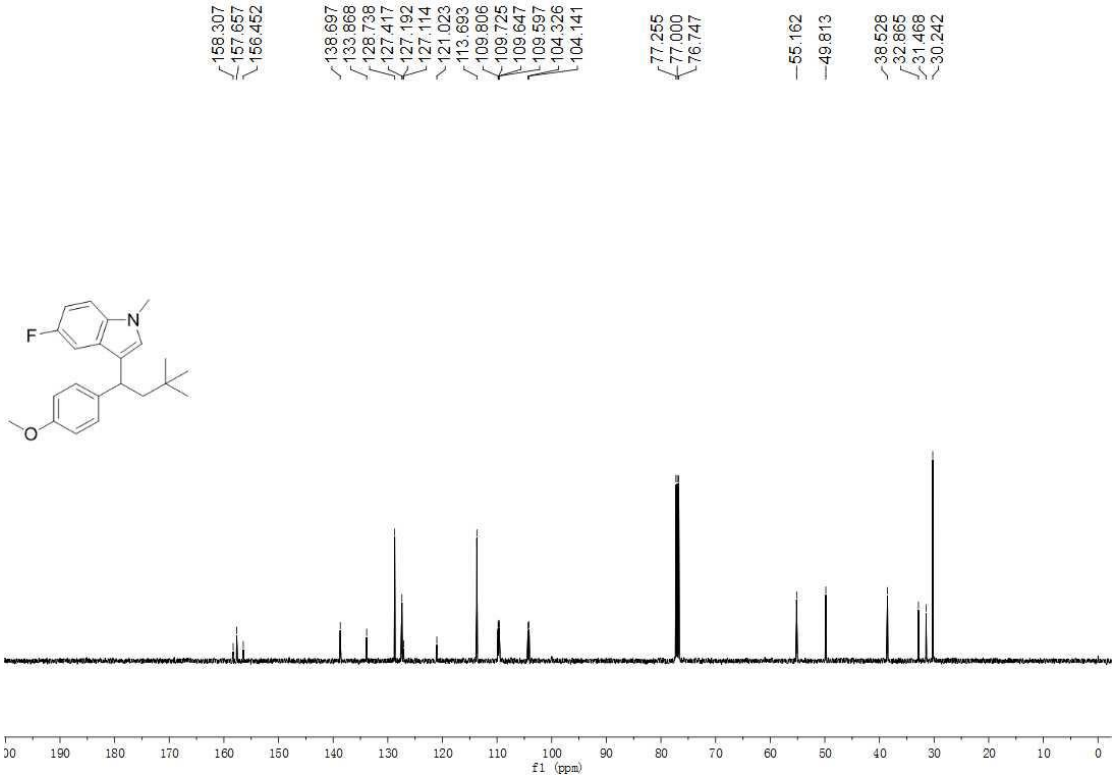


^{13}C-NMR (125 MHz, $CDCl_3$)

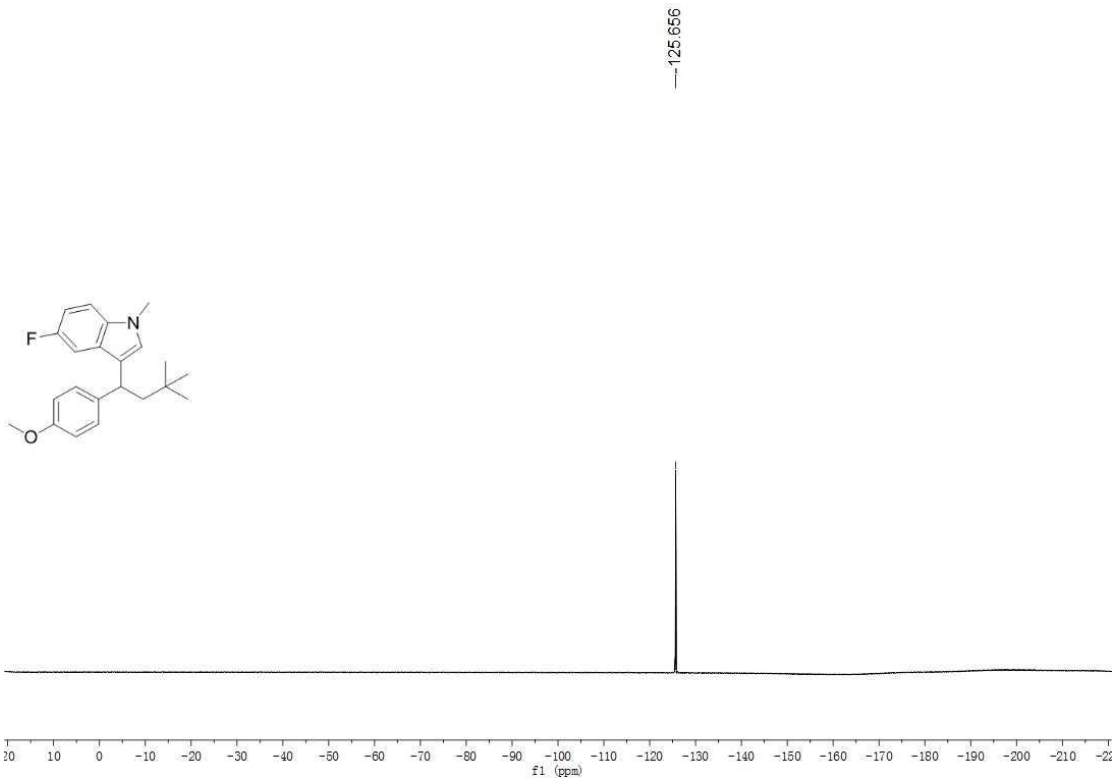
5-fluoro-3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole (4aae):



^{1}H-NMR (500 MHz, $CDCl_3$)

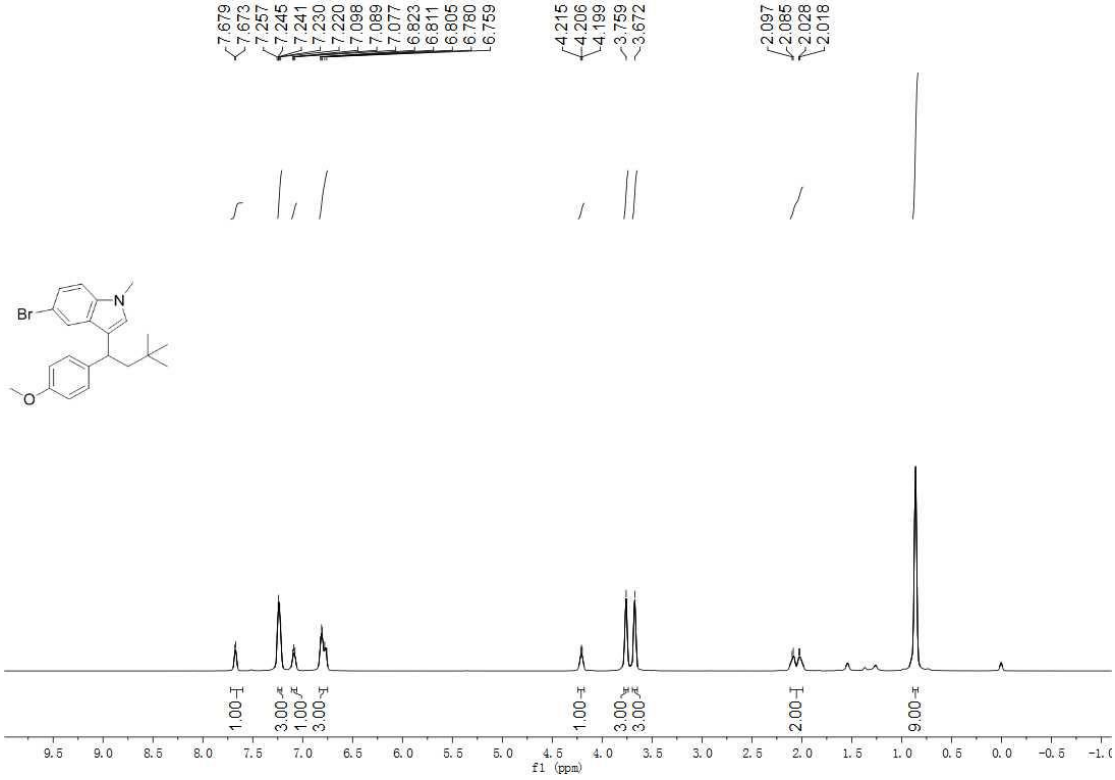


^{13}C-NMR (125 MHz, $CDCl_3$)

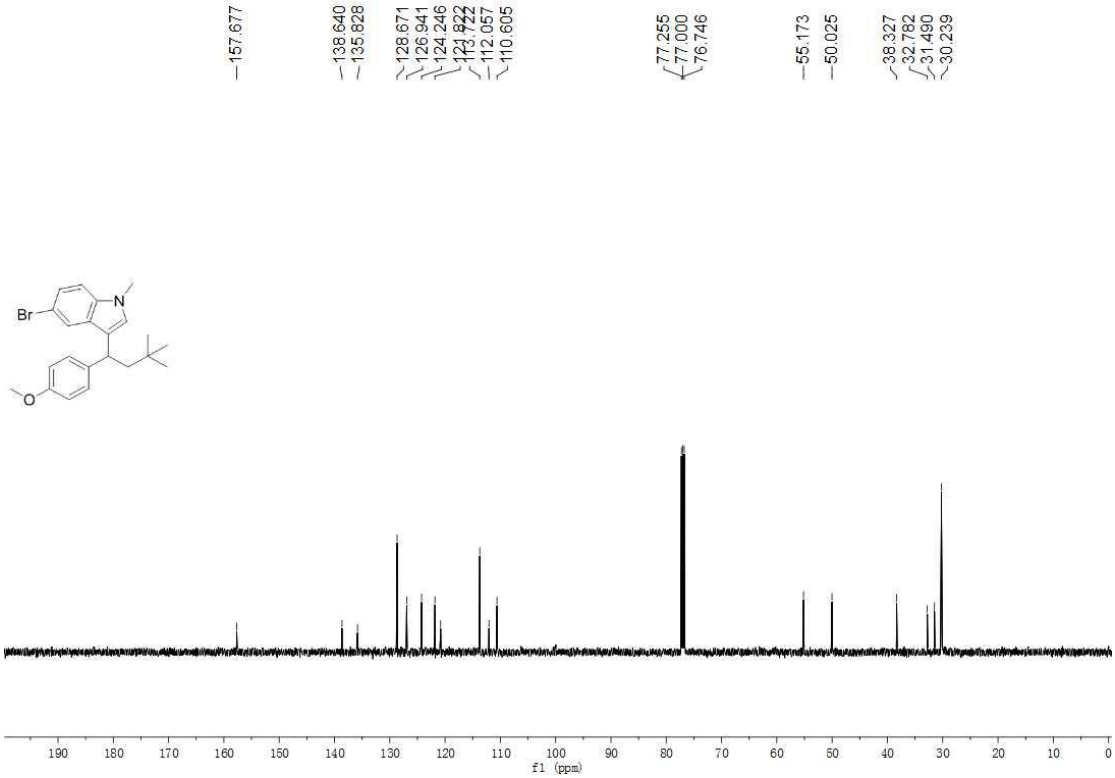


^{19}F NMR (471 MHz, $CDCl_3$)

5-bromo-3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole (4aaf):

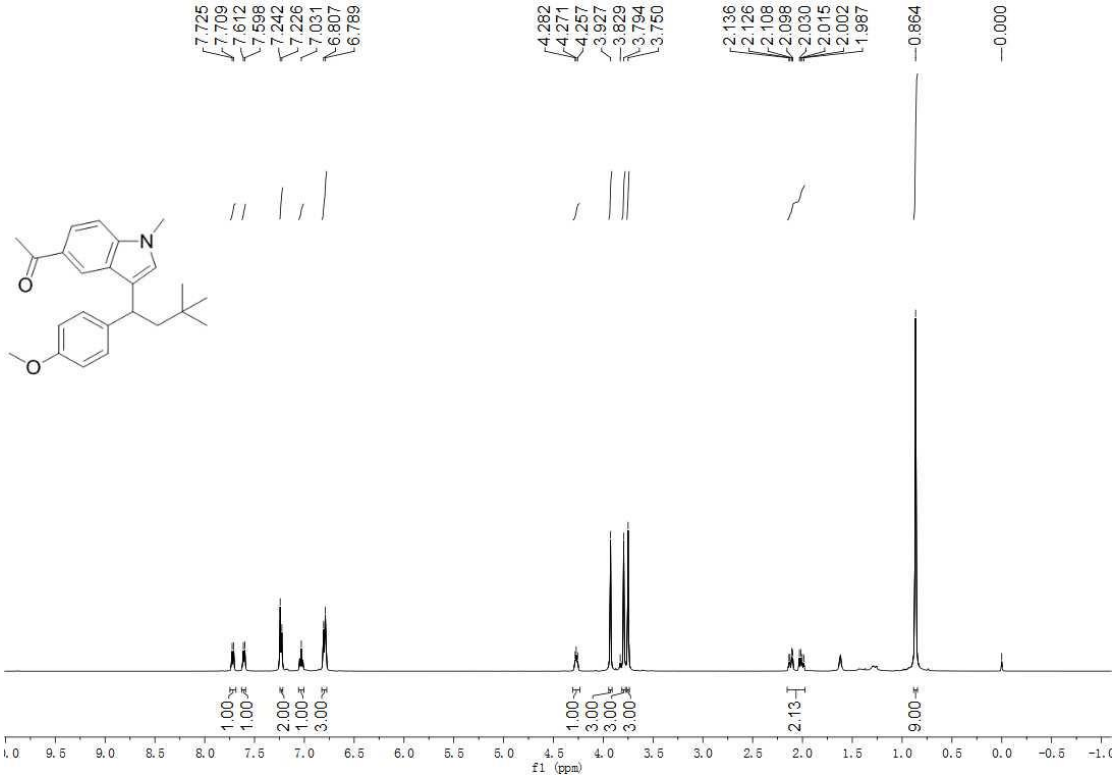


^{1}H-NMR (500 MHz, $CDCl_3$)

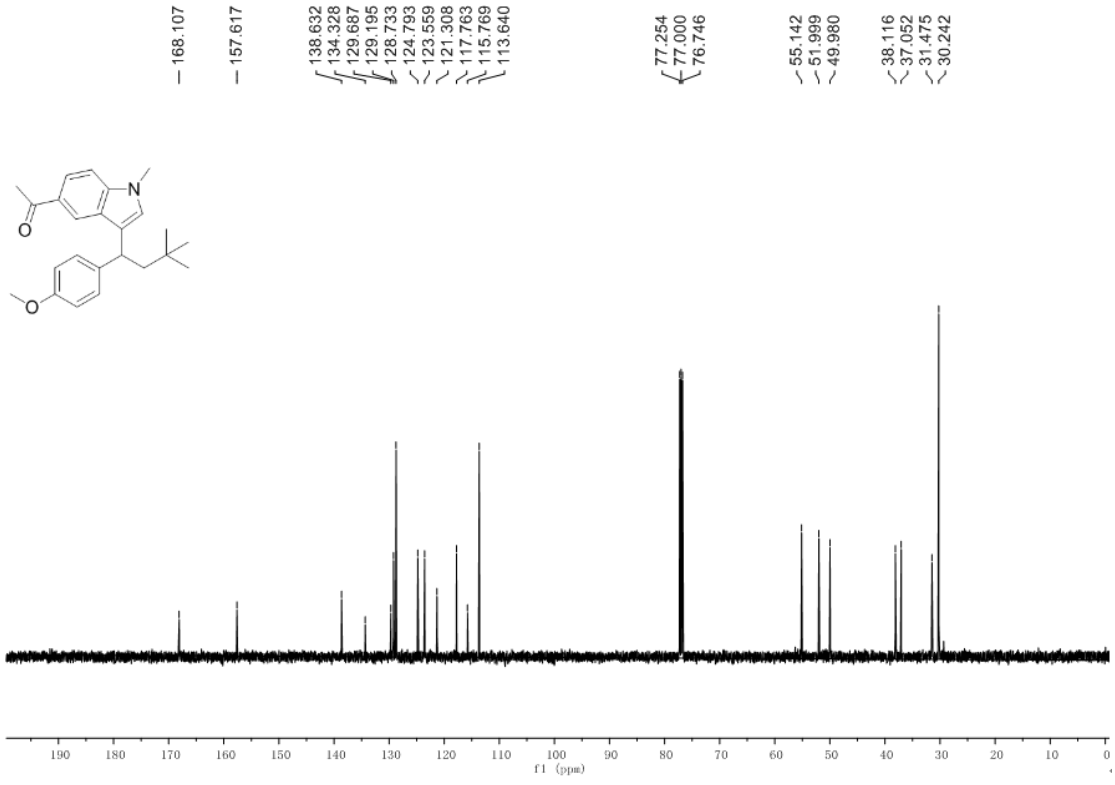


^{13}C-NMR (125 MHz, $CDCl_3$)

1-(3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indol-5-yl)ethan-1-one (4aag):

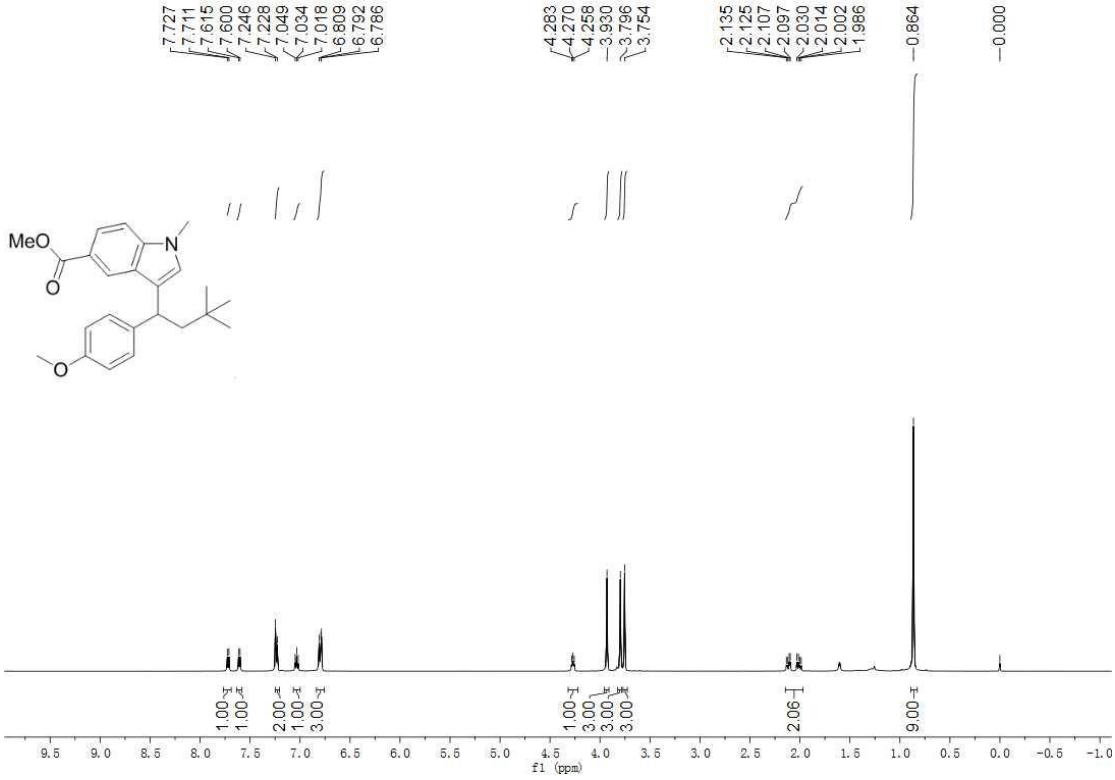


^{1}H-NMR (500 MHz, $CDCl_3$)

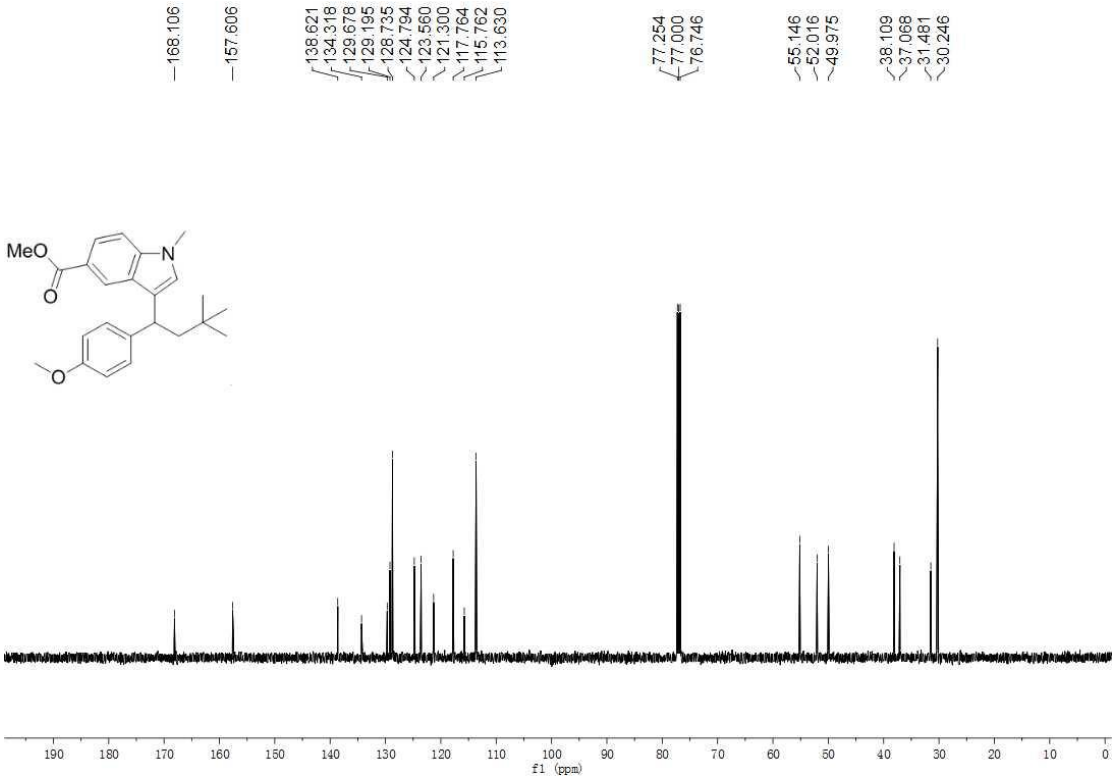


^{13}C-NMR (125 MHz, $CDCl_3$)

Methyl-3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole-5-carboxylate (4aah):

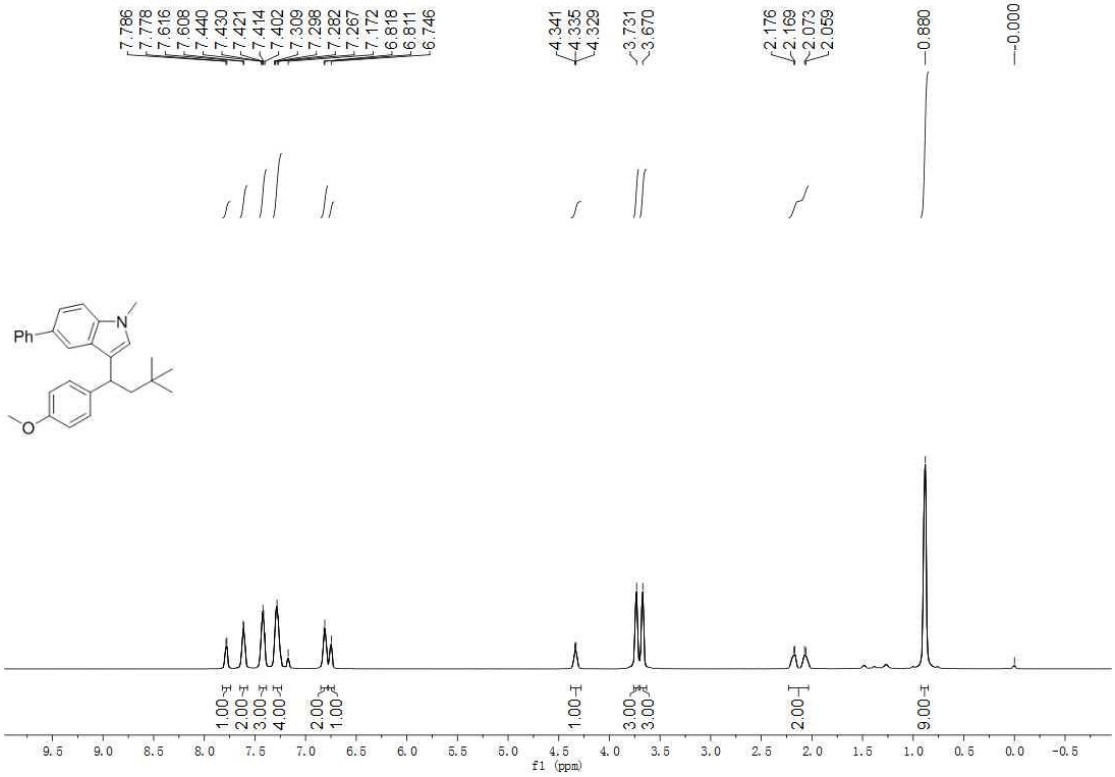


^{1}H-NMR (500 MHz, $CDCl_3$)

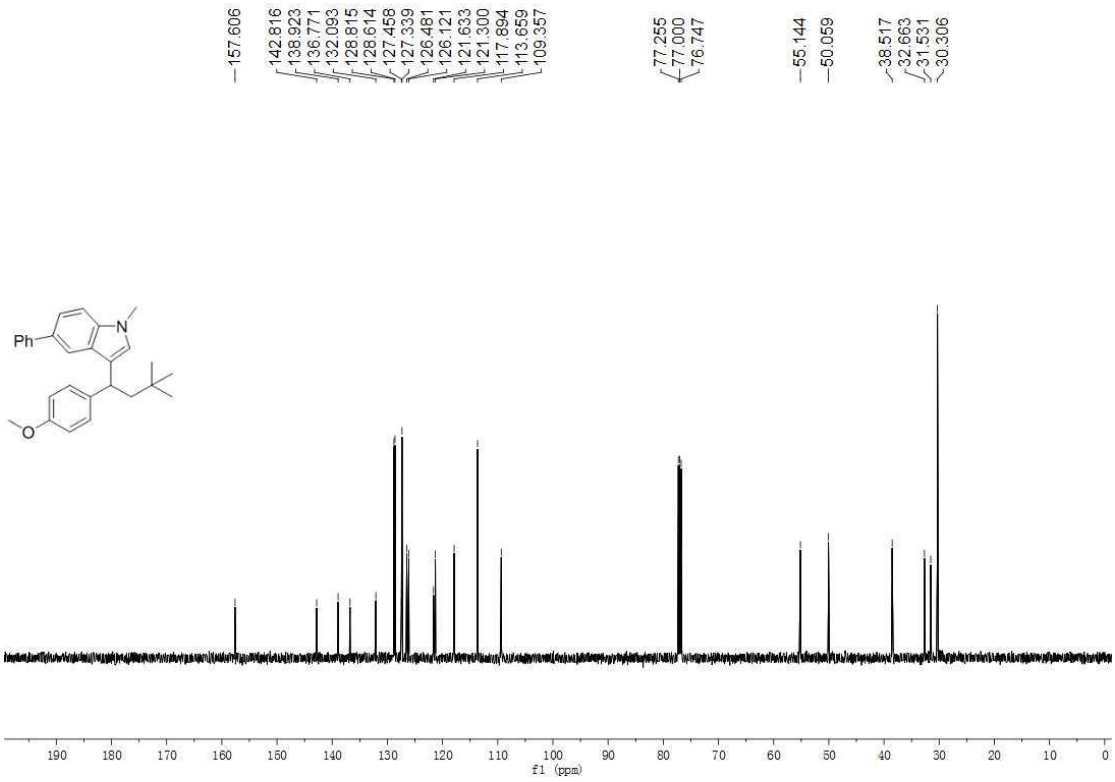


^{13}C-NMR (125 MHz, $CDCl_3$)

3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-5-phenyl-1*H*-indole (4aai):

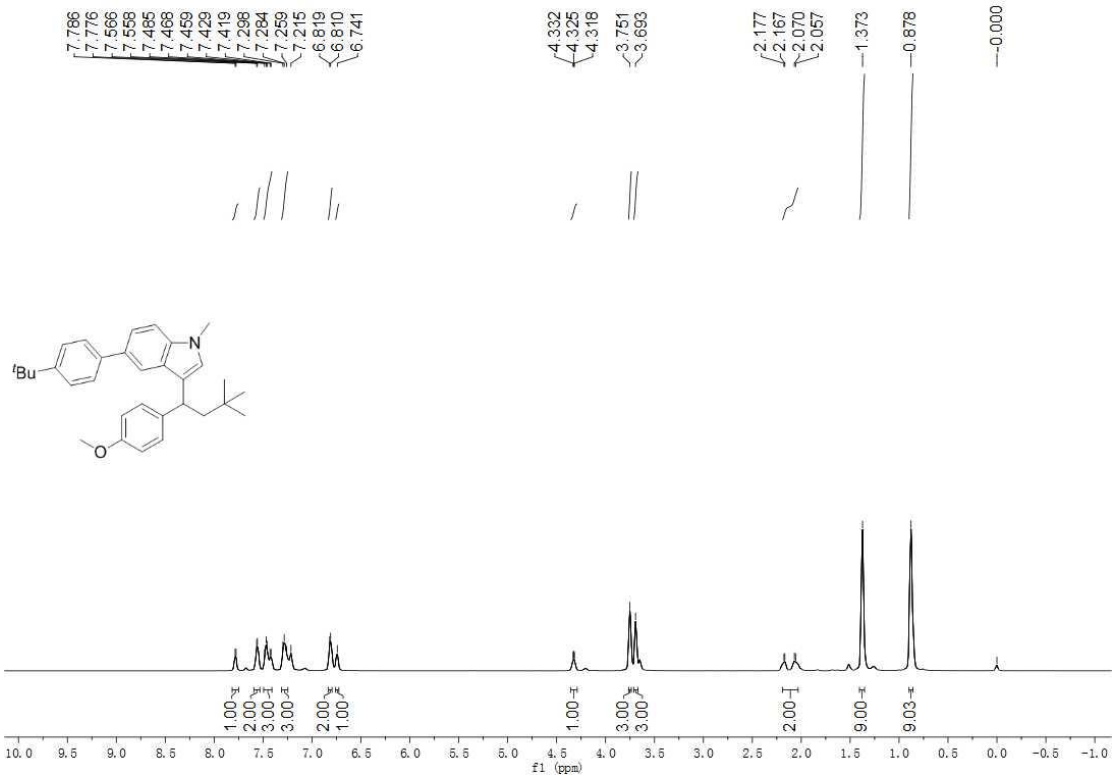


^{1}H-NMR (500 MHz, $CDCl_3$)

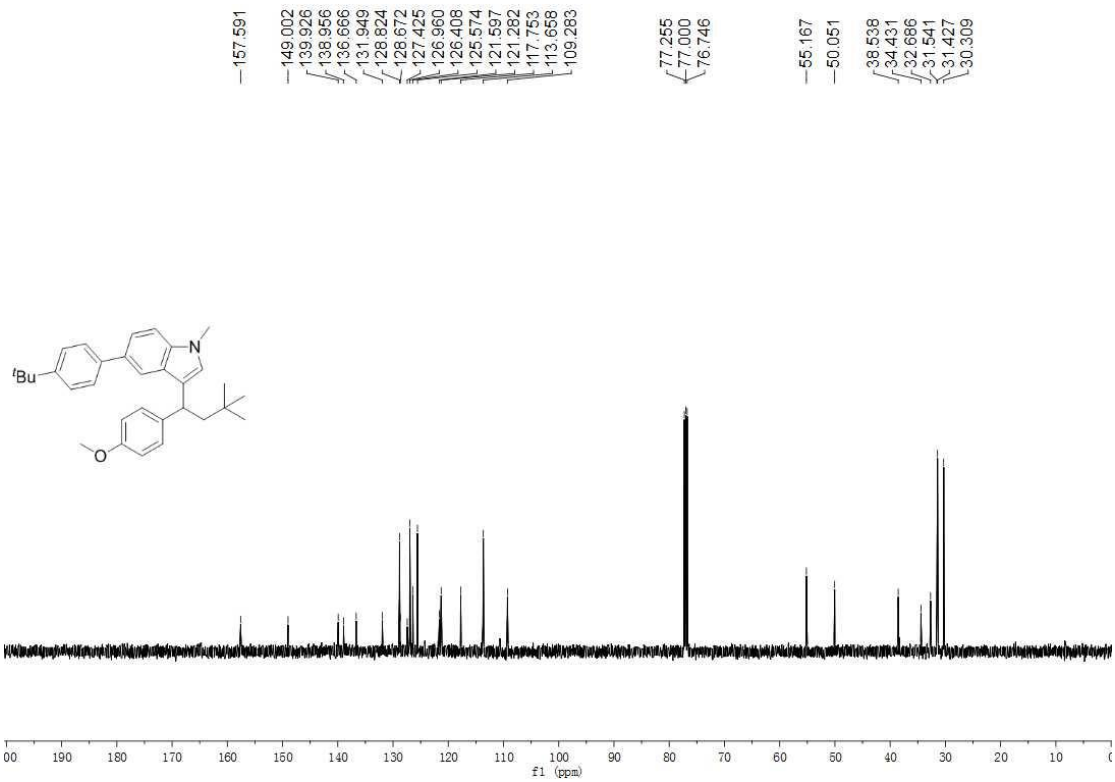


^{13}C-NMR (125 MHz, $CDCl_3$)

5-(4-(tert-butyl)phenyl)-3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole (4aaj):

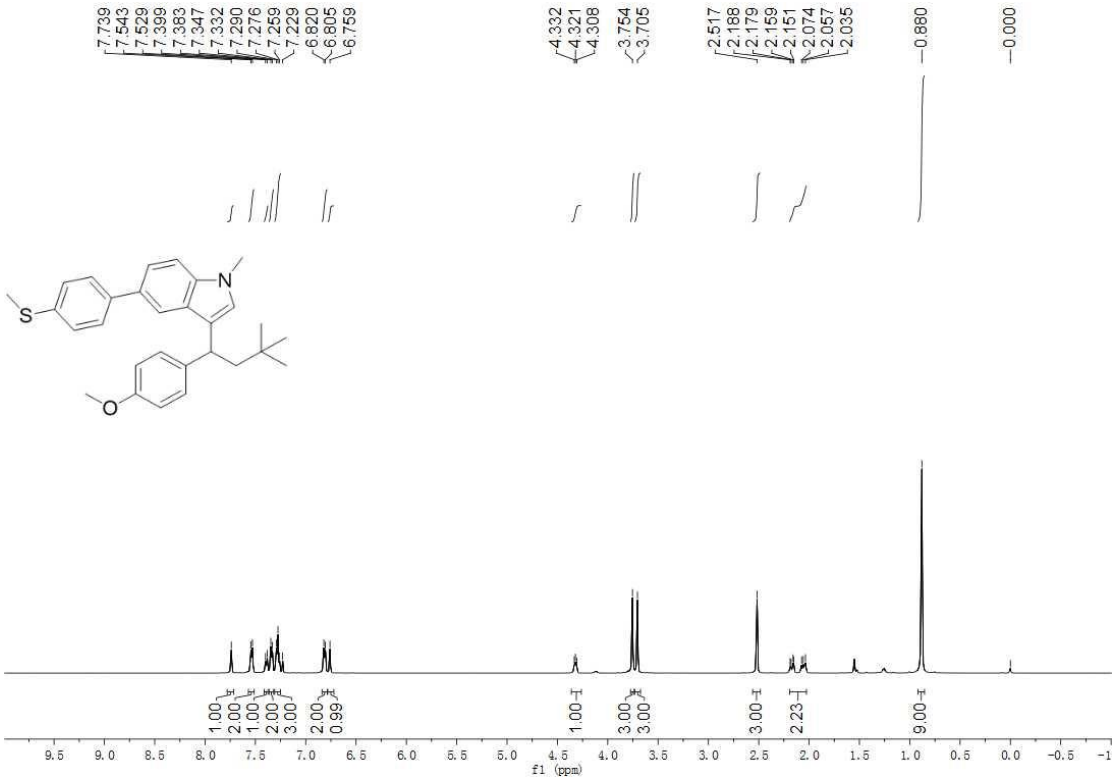


^{1}H-NMR (500 MHz, $CDCl_3$)

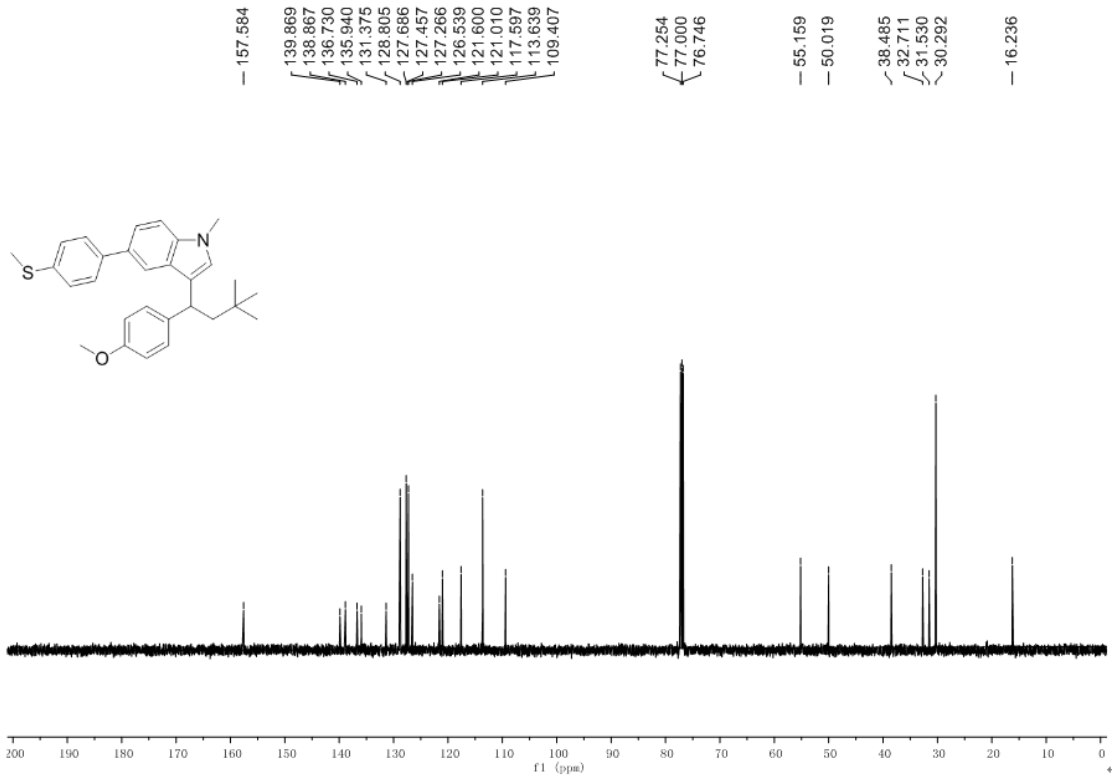


^{13}C-NMR (125 MHz, $CDCl_3$)

3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-5-(4-(methylthio)phenyl)-1*H*-indole (4aak):

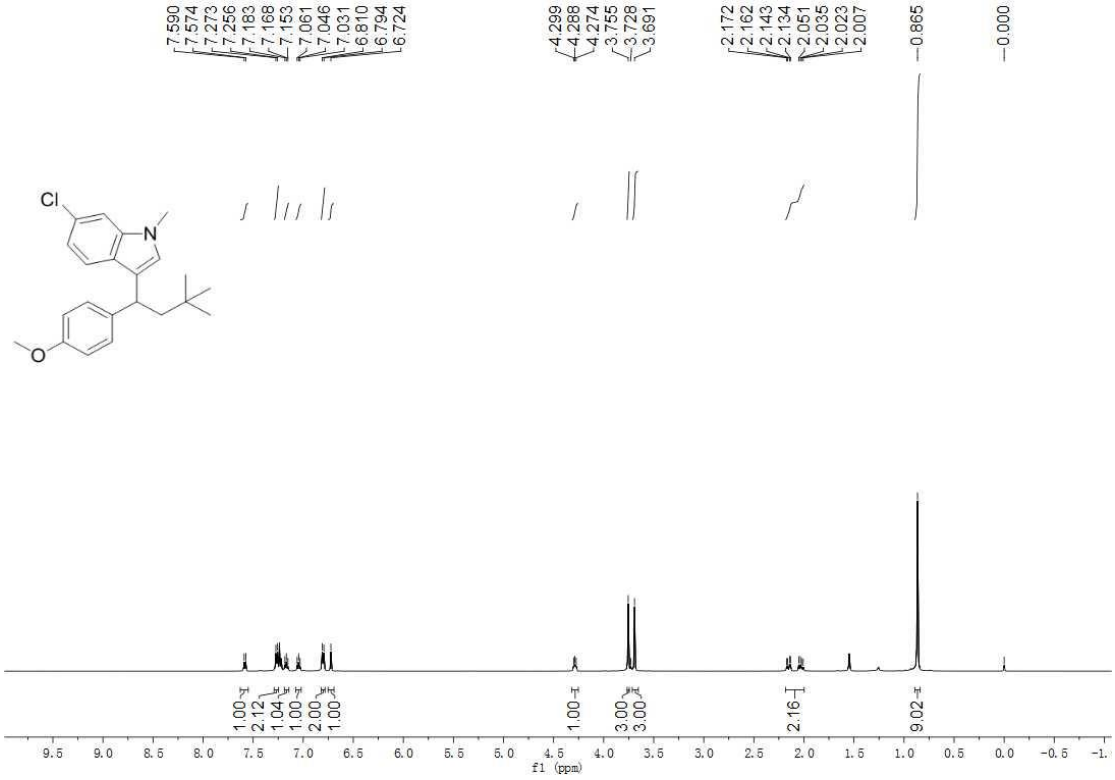


^{1}H-NMR (500 MHz, $CDCl_3$)

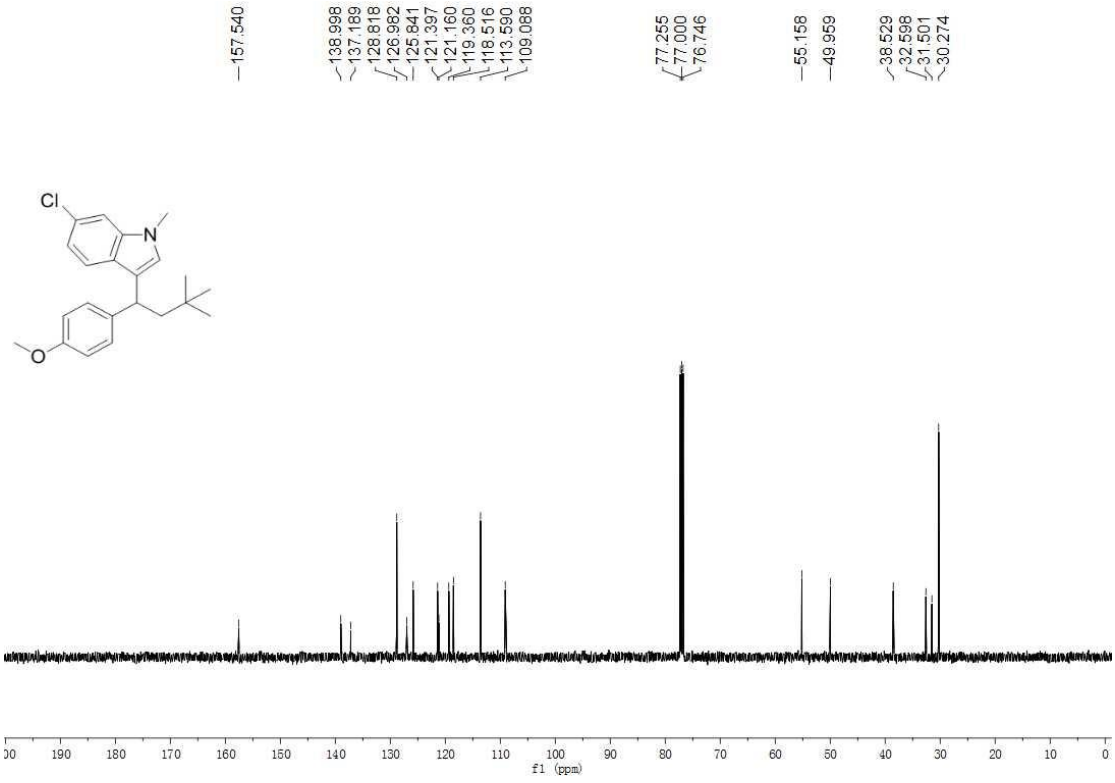


^{13}C-NMR (125 MHz, $CDCl_3$)

6-chloro-3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole (4aal):

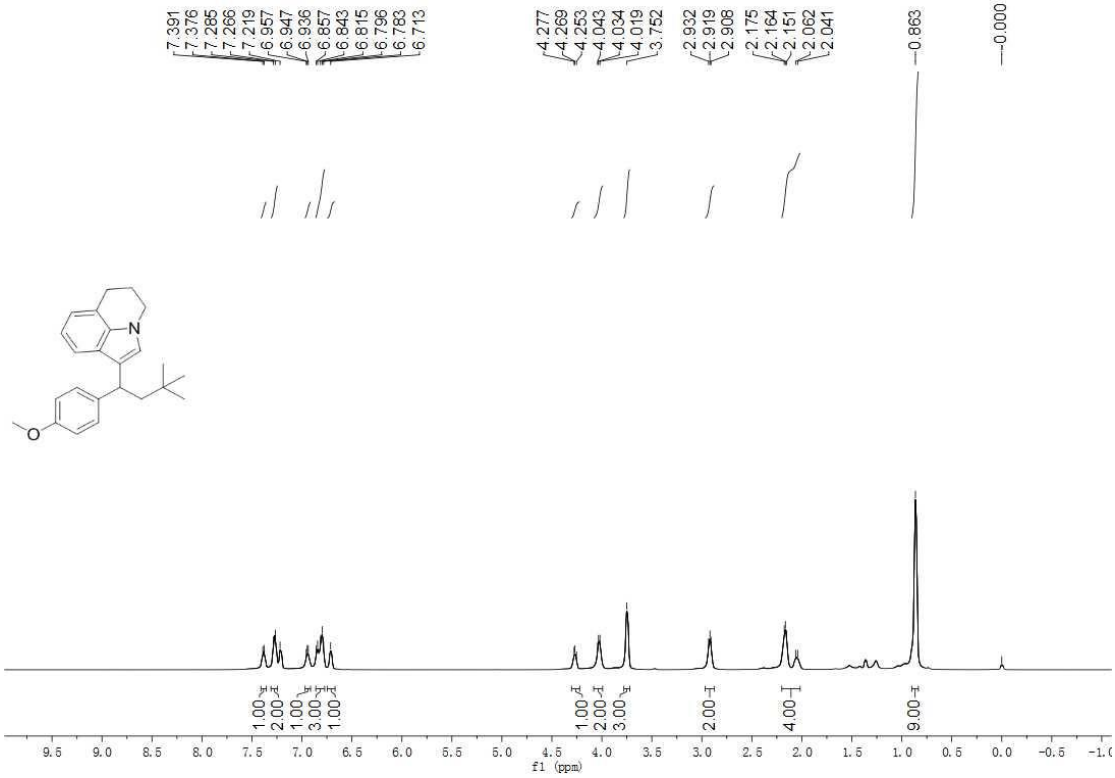


^{1}H-NMR (500 MHz, $CDCl_3$)

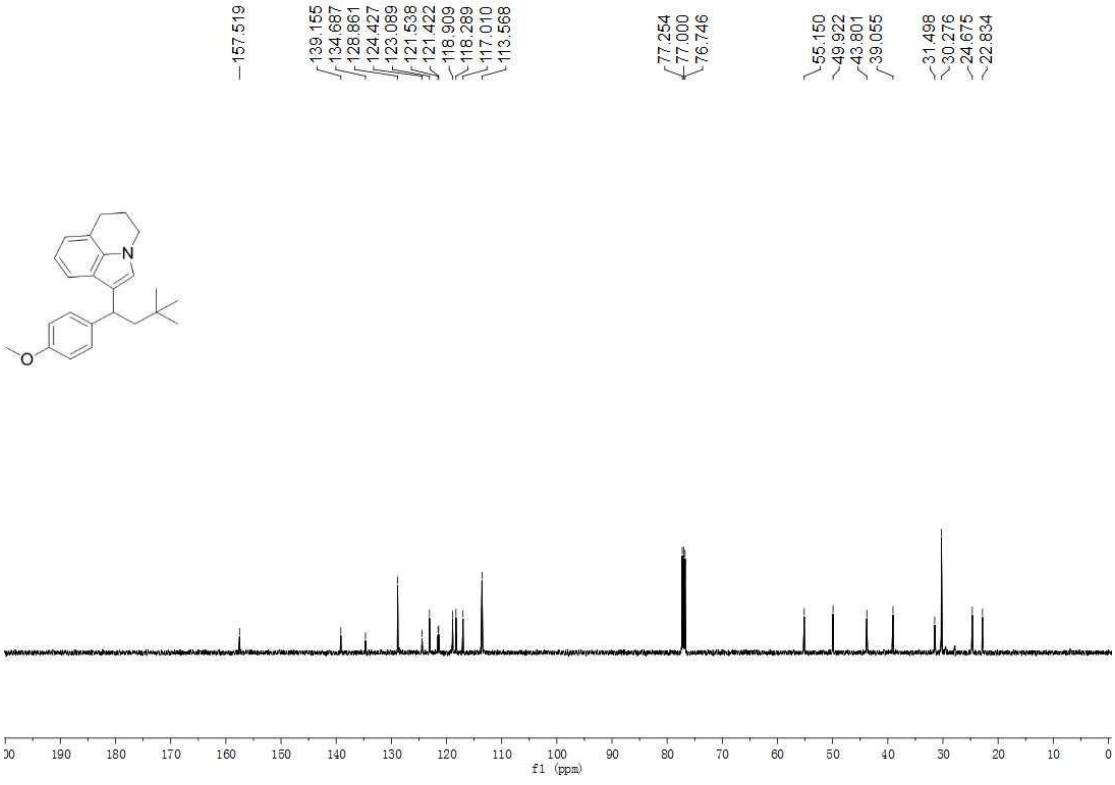


^{13}C-NMR (125 MHz, $CDCl_3$)

1-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-ij]quinoline (4aam):

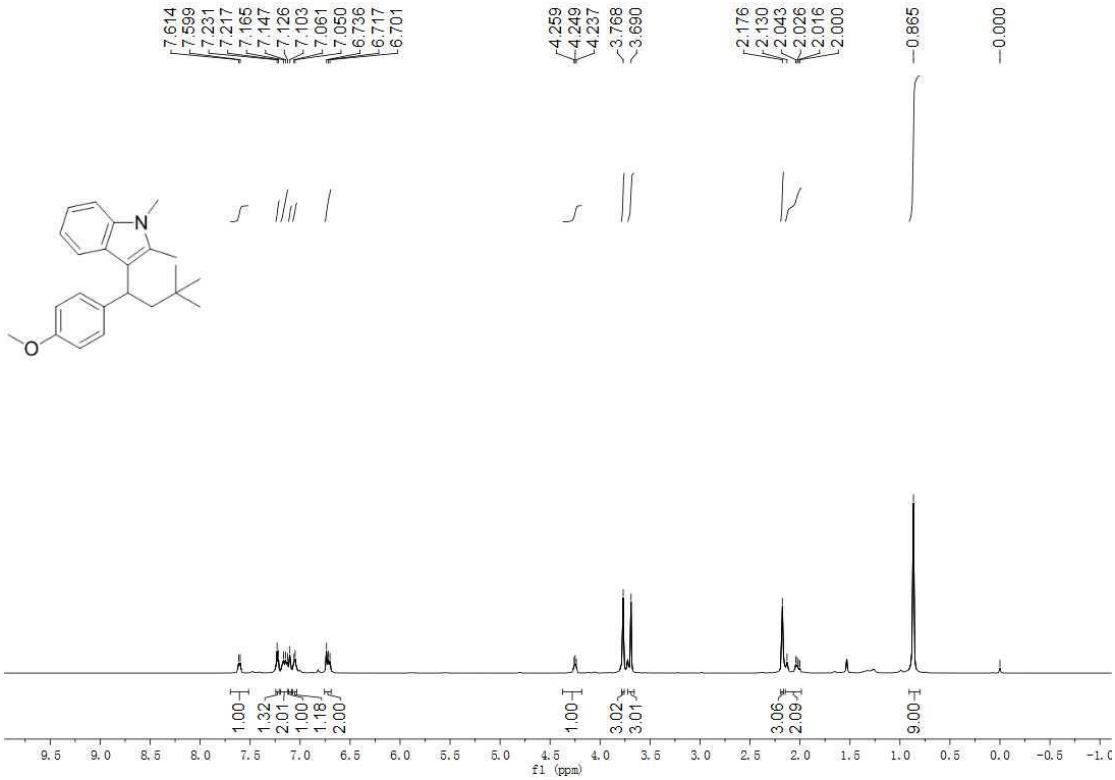


^{1}H-NMR (500 MHz, $CDCl_3$)

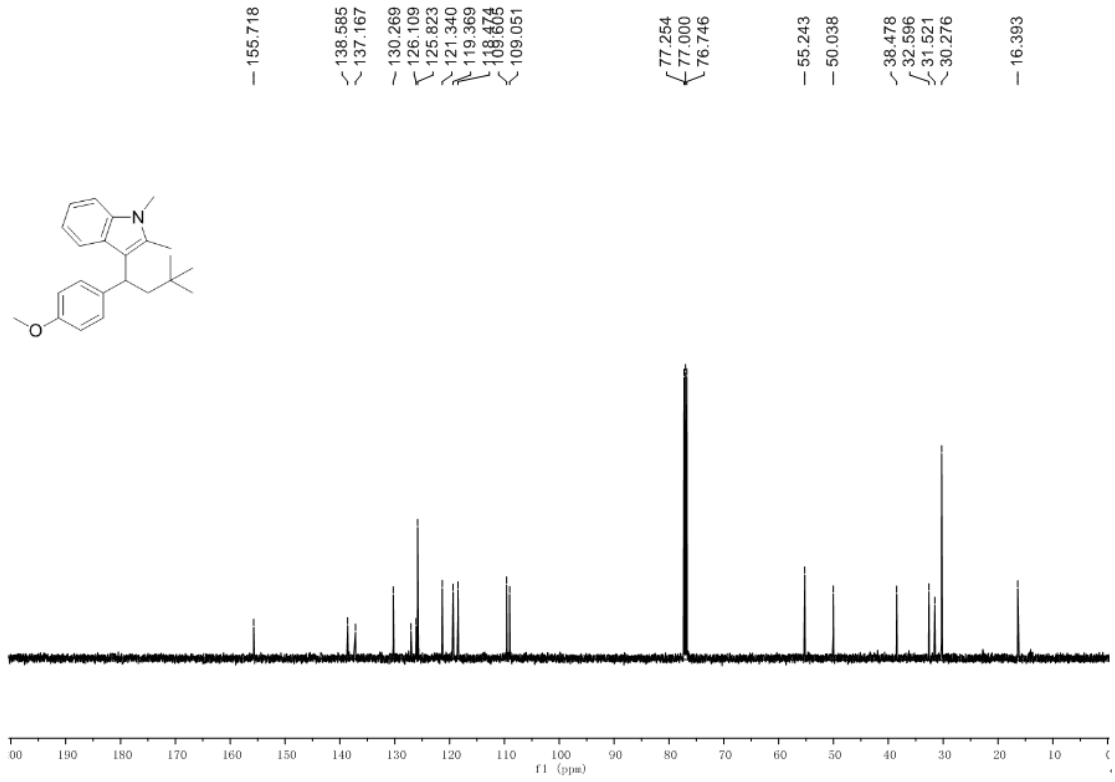


^{13}C-NMR (125 MHz, $CDCl_3$)

3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1,2-dimethyl-1*H*-indole (4aan):

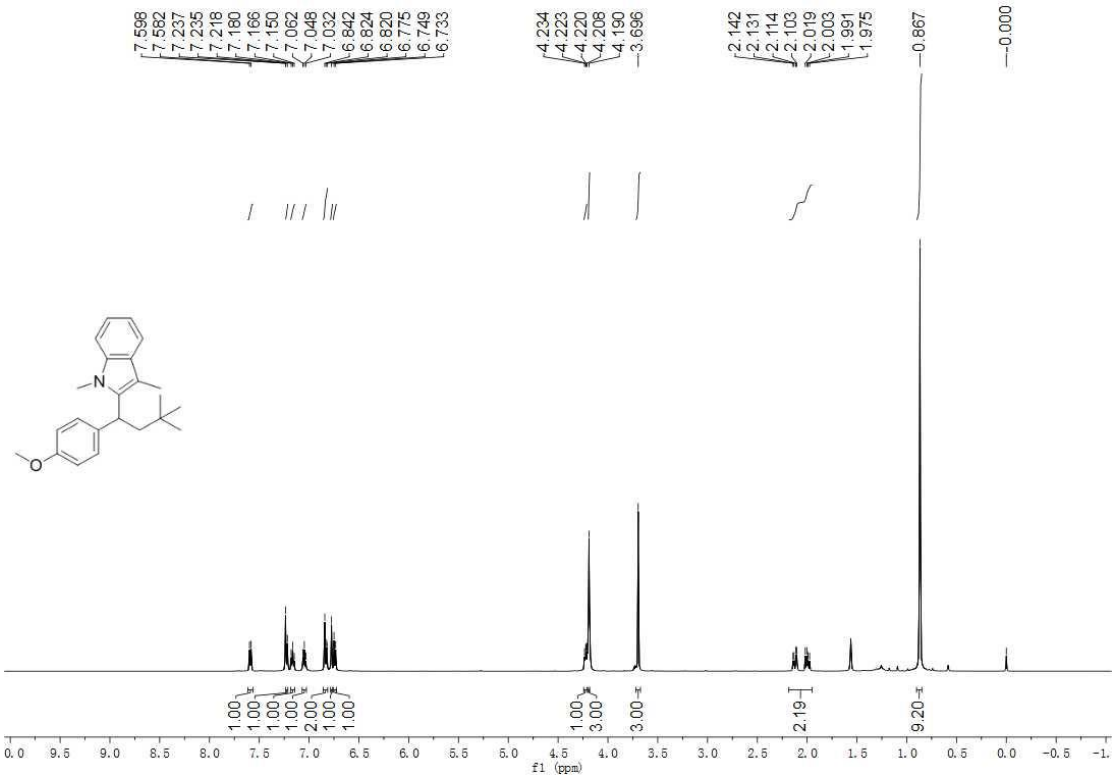


^{1}H-NMR (500 MHz, $CDCl_3$)

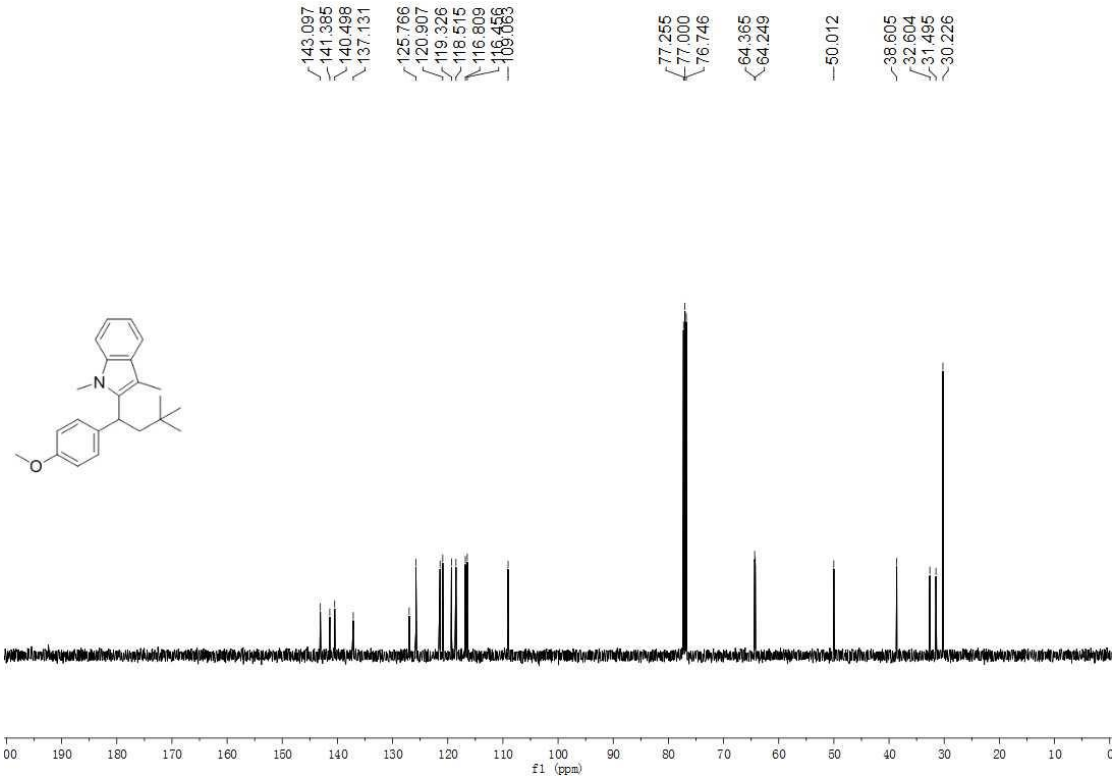


^{13}C-NMR (125 MHz, $CDCl_3$)

2-(1-(4-Methoxyphenyl)-3,3-dimethylbutyl)-1,3-dimethyl-1H-indole (4aao):

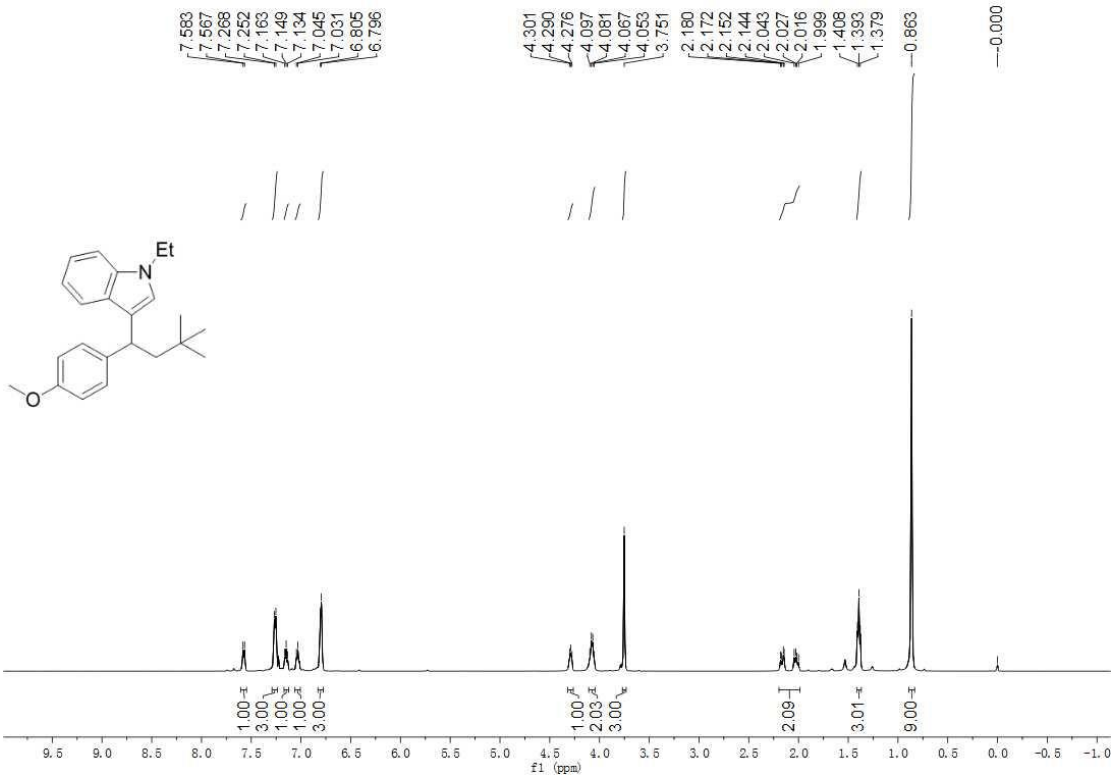


^{1}H-NMR (500 MHz, $CDCl_3$)

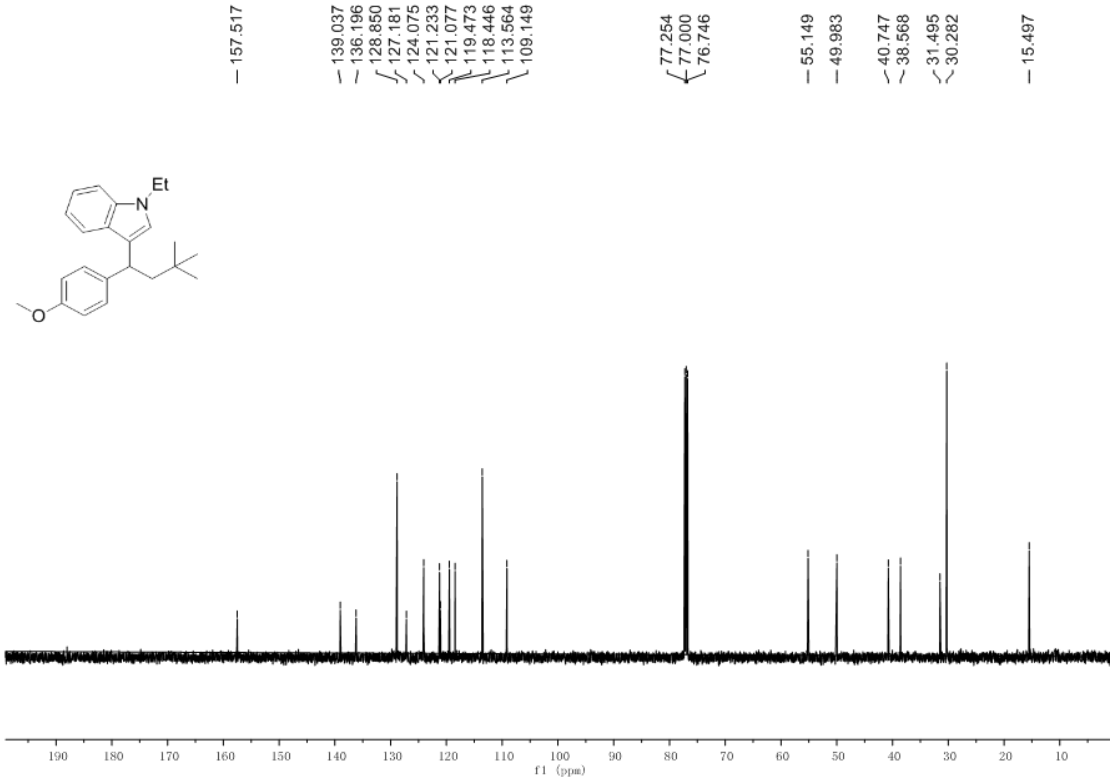


^{13}C-NMR (125 MHz, $CDCl_3$)

1-ethyl-3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1*H*-indole (4aap):

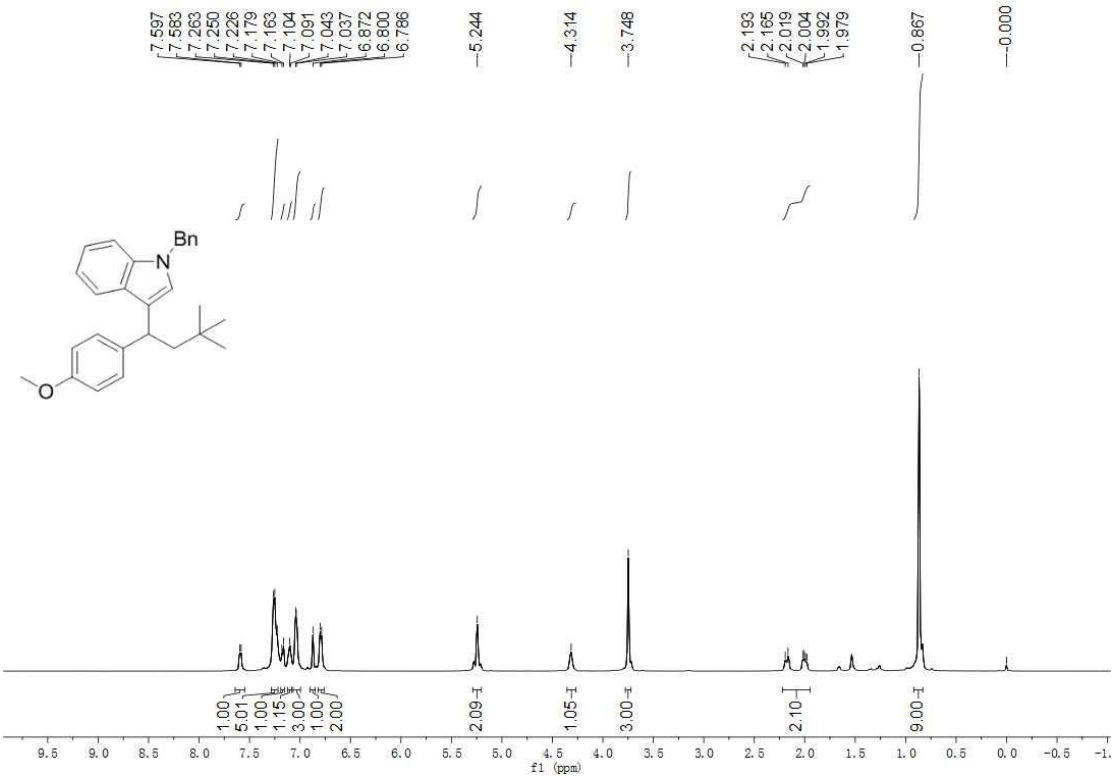


^{1}H-NMR (500 MHz, $CDCl_3$)

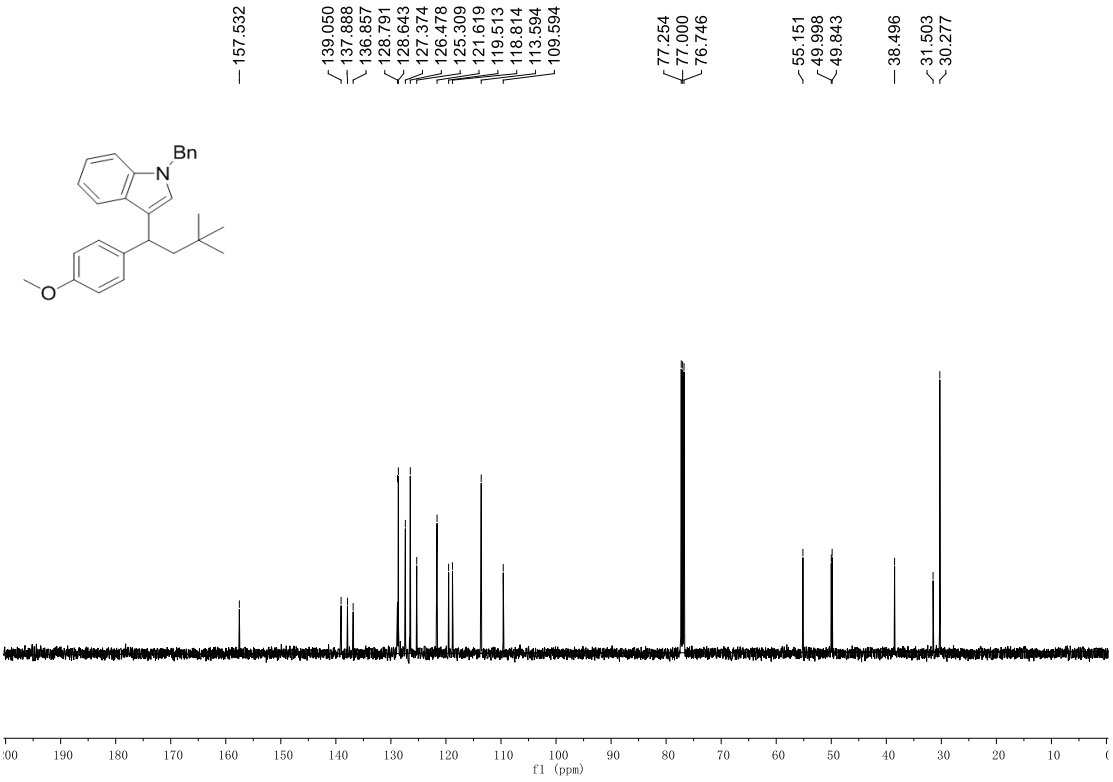


^{13}C-NMR (125 MHz, $CDCl_3$)

1-benzyl-3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1*H*-indole (4aaq):

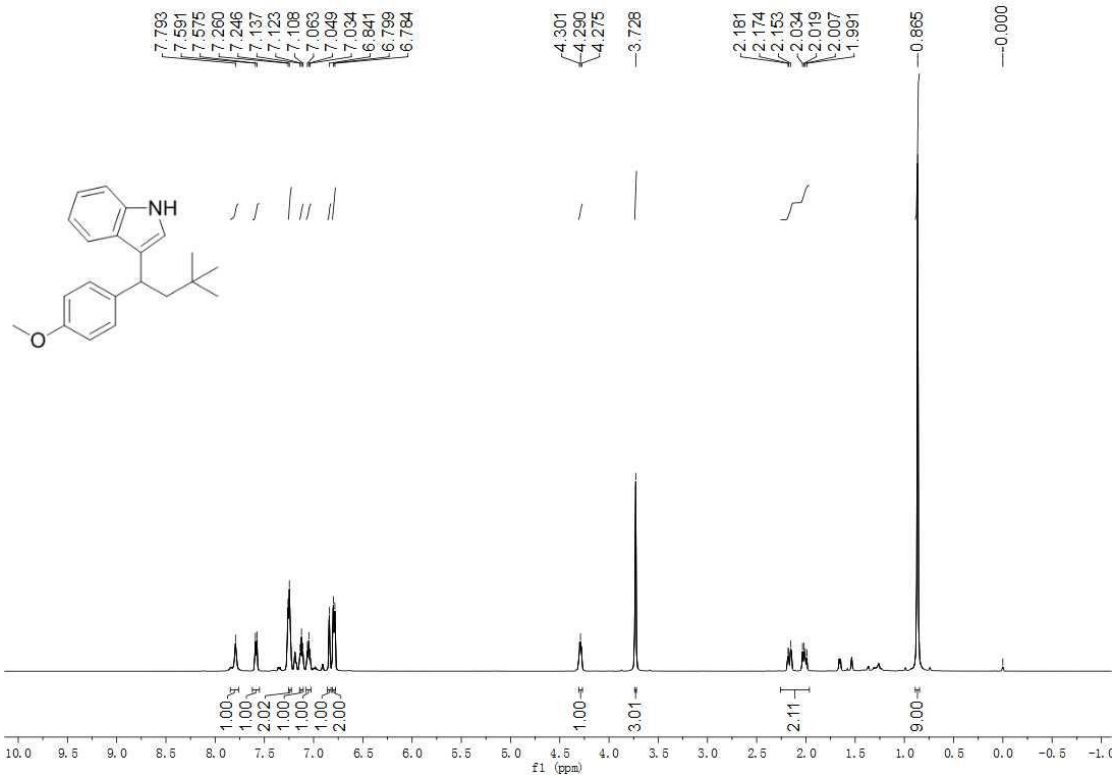


^{1}H-NMR (500 MHz, $CDCl_3$)

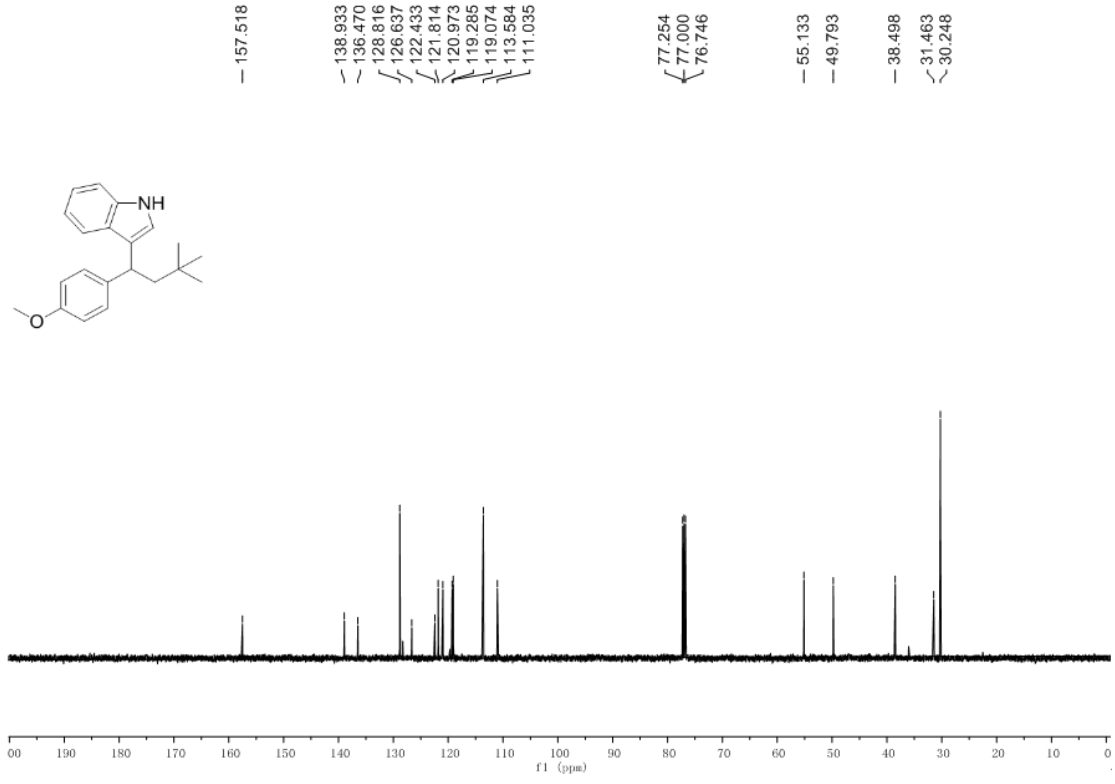


^{13}C-NMR (125 MHz, $CDCl_3$)

3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1*H*-indole (4aas):

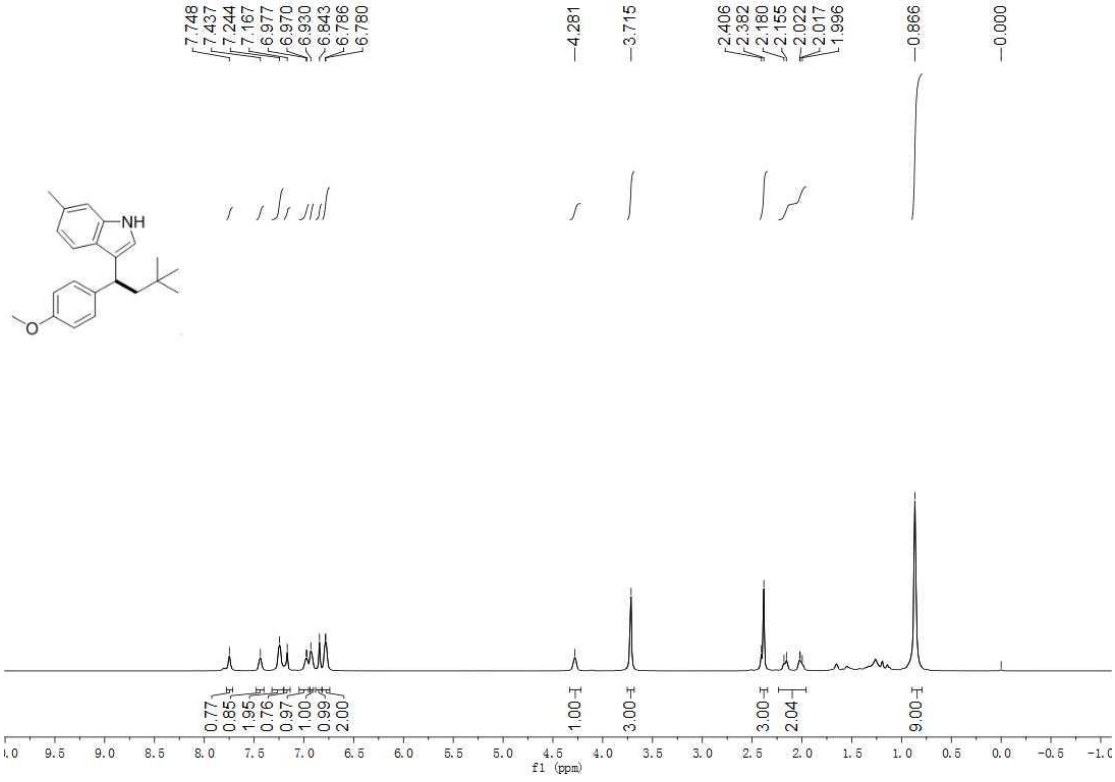


^{1}H-NMR (500 MHz, $CDCl_3$)

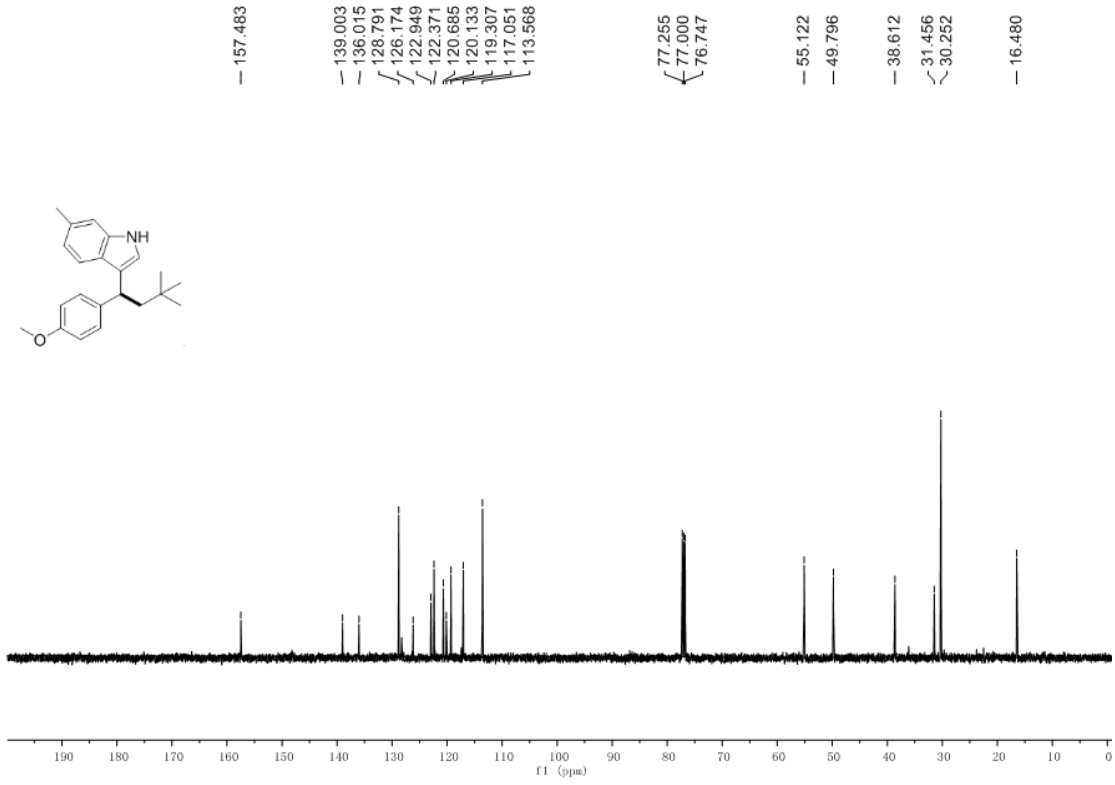


^{13}C-NMR (125 MHz, $CDCl_3$)

3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-6-methyl-1*H*-indole (4aat)：

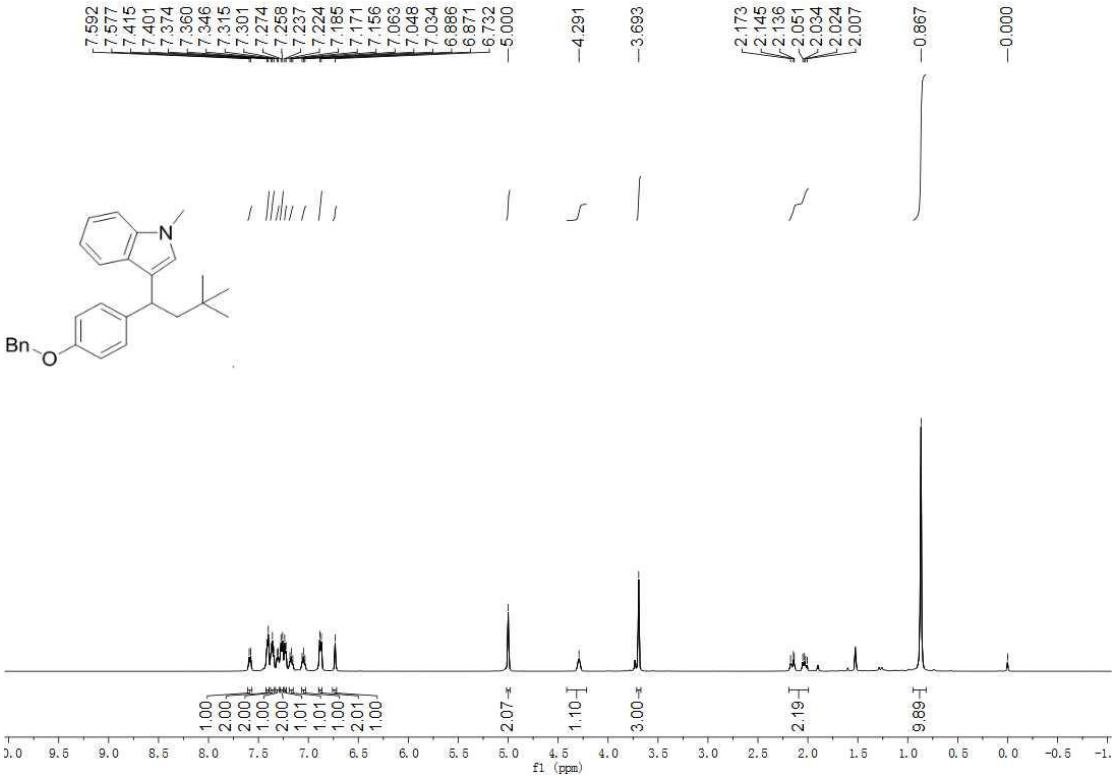


^{1}H-NMR (500 MHz, $CDCl_3$)

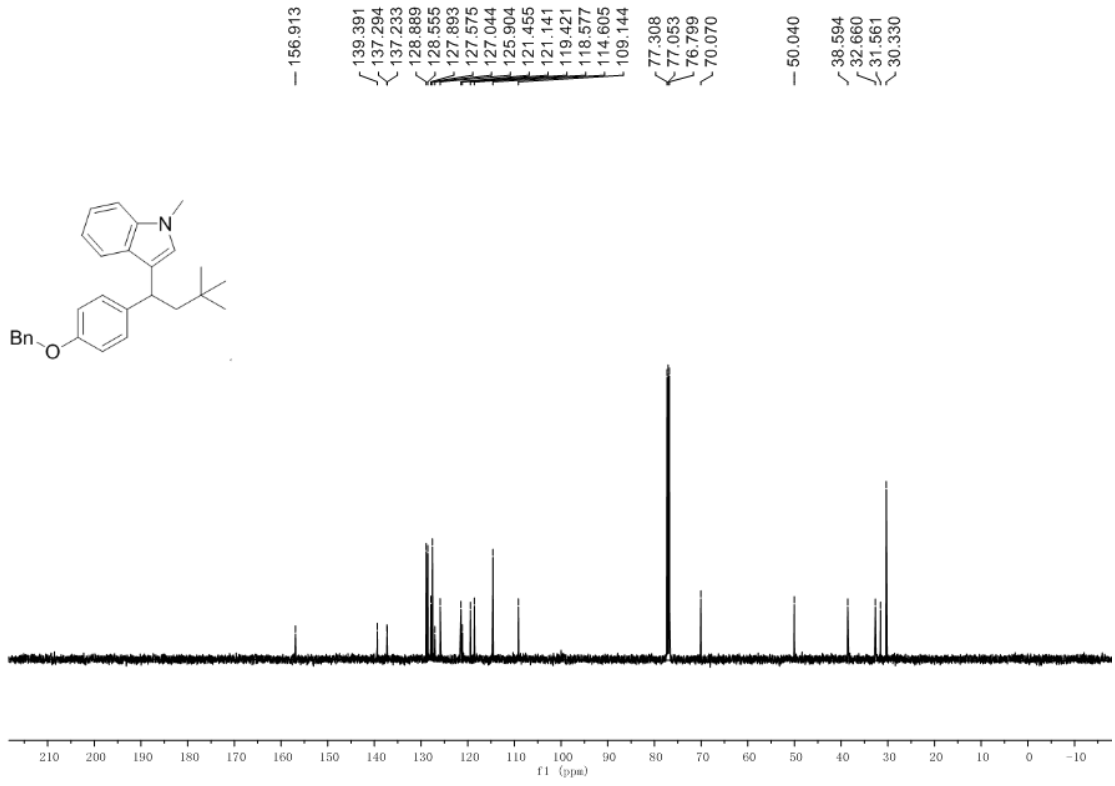


^{13}C-NMR (125 MHz, $CDCl_3$)

3-(1-(4-(benzyloxy)phenyl)-3,3-dimethylbutyl)-1-methyl-1H-indole (4baa)：

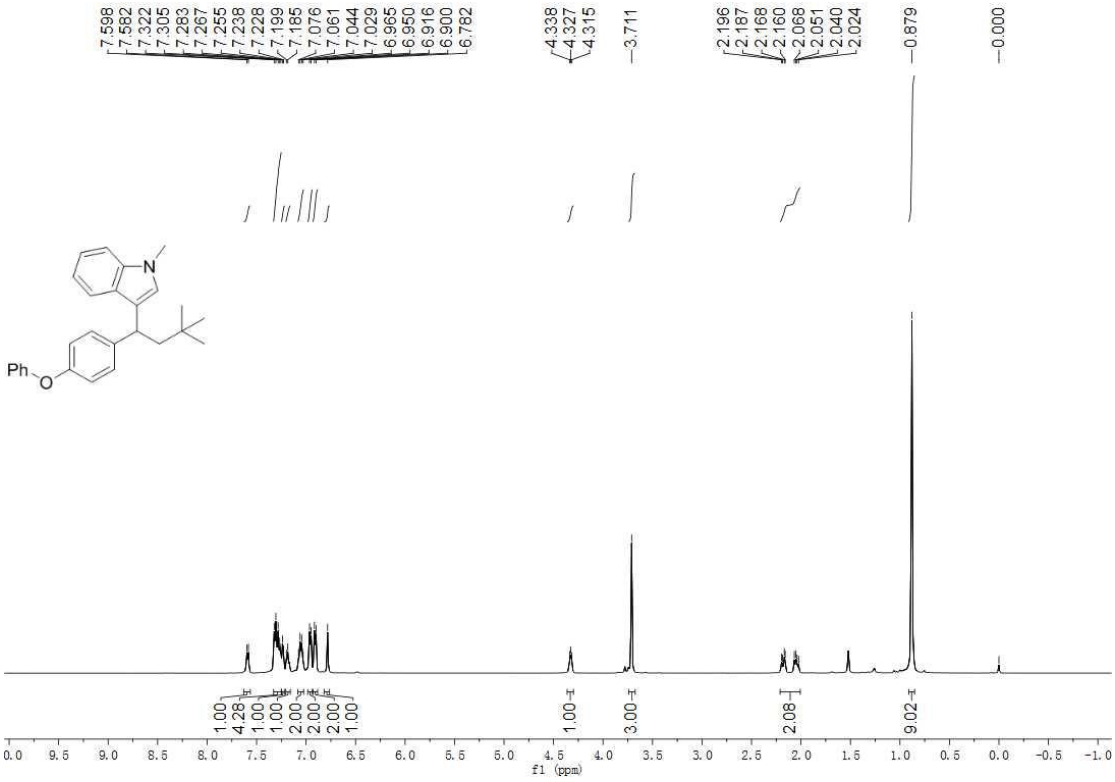


^{1}H-NMR (500 MHz, $CDCl_3$)

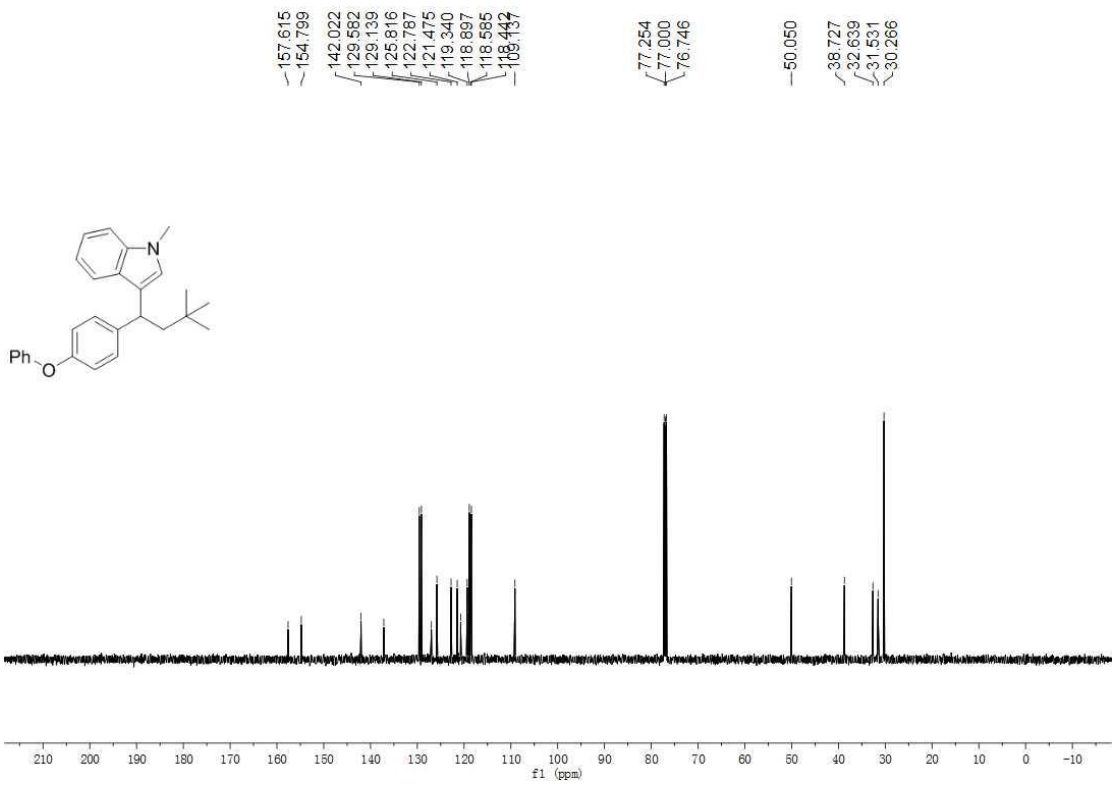


^{13}C-NMR (125 MHz, $CDCl_3$)

3-(3,3-dimethyl-1-(4-phenoxyphenyl)butyl)-1-methyl-1*H*-indole (4caa):

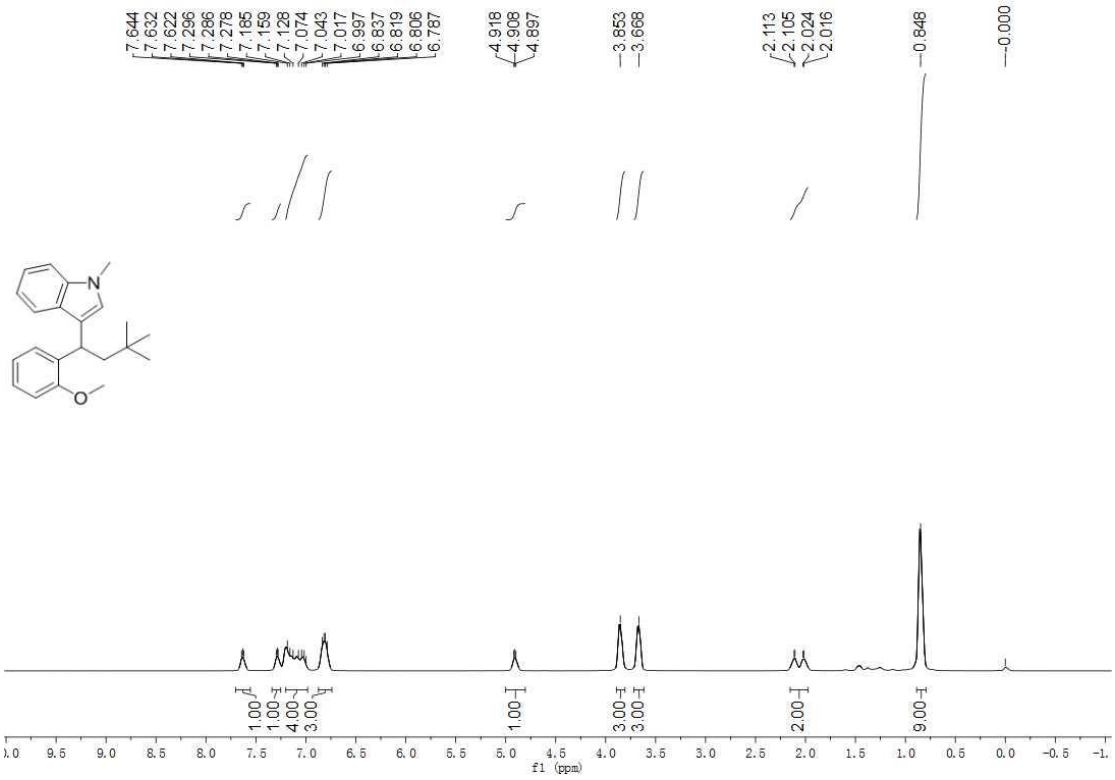


^{1}H-NMR (500 MHz, $CDCl_3$)

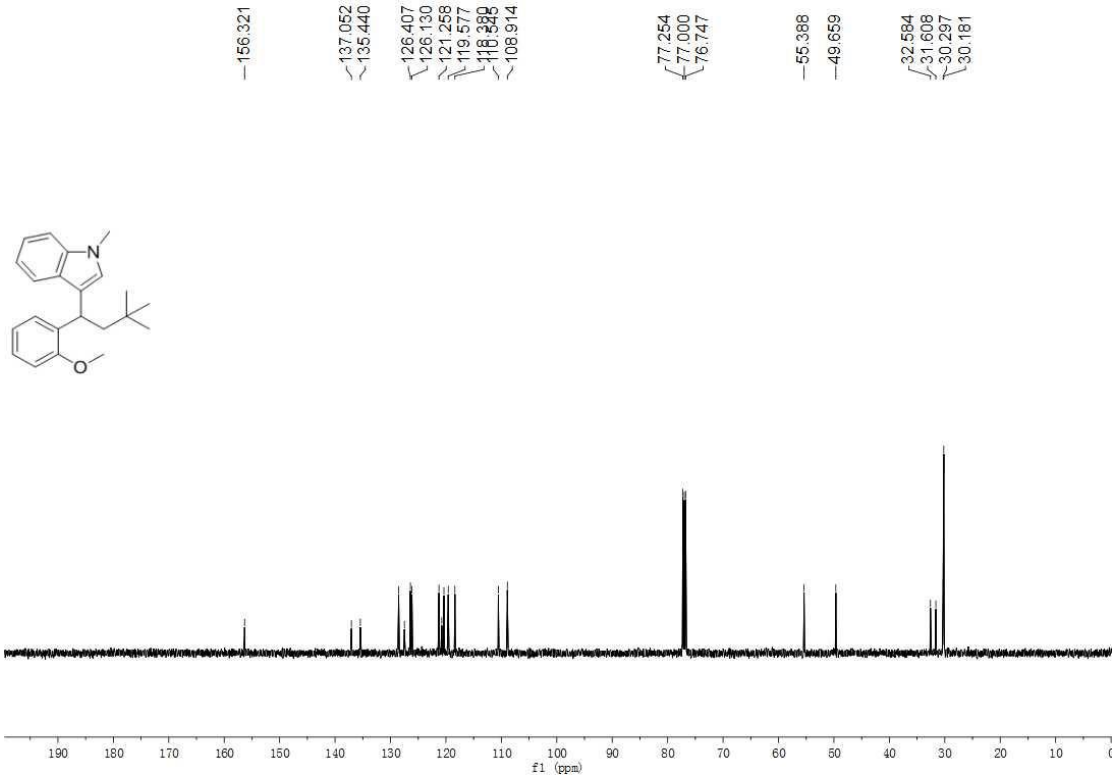


^{13}C-NMR (125 MHz, $CDCl_3$)

3-(1-(2-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole (4daa):

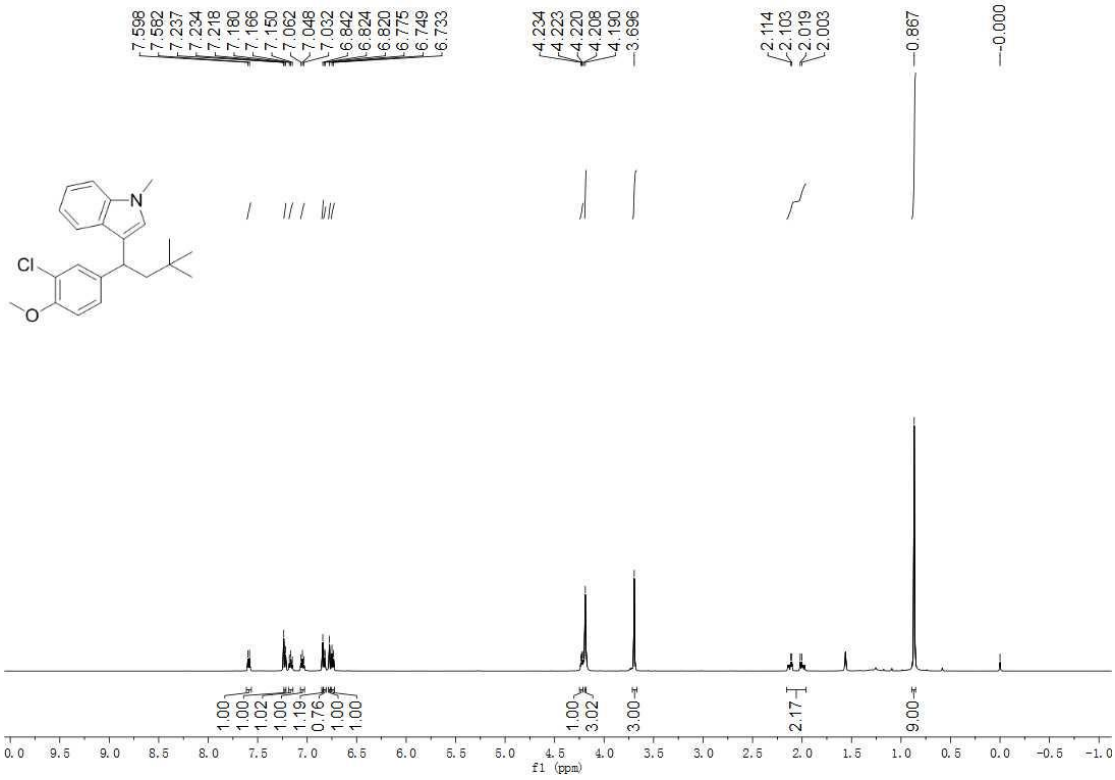


^{1}H-NMR (500 MHz, $CDCl_3$)

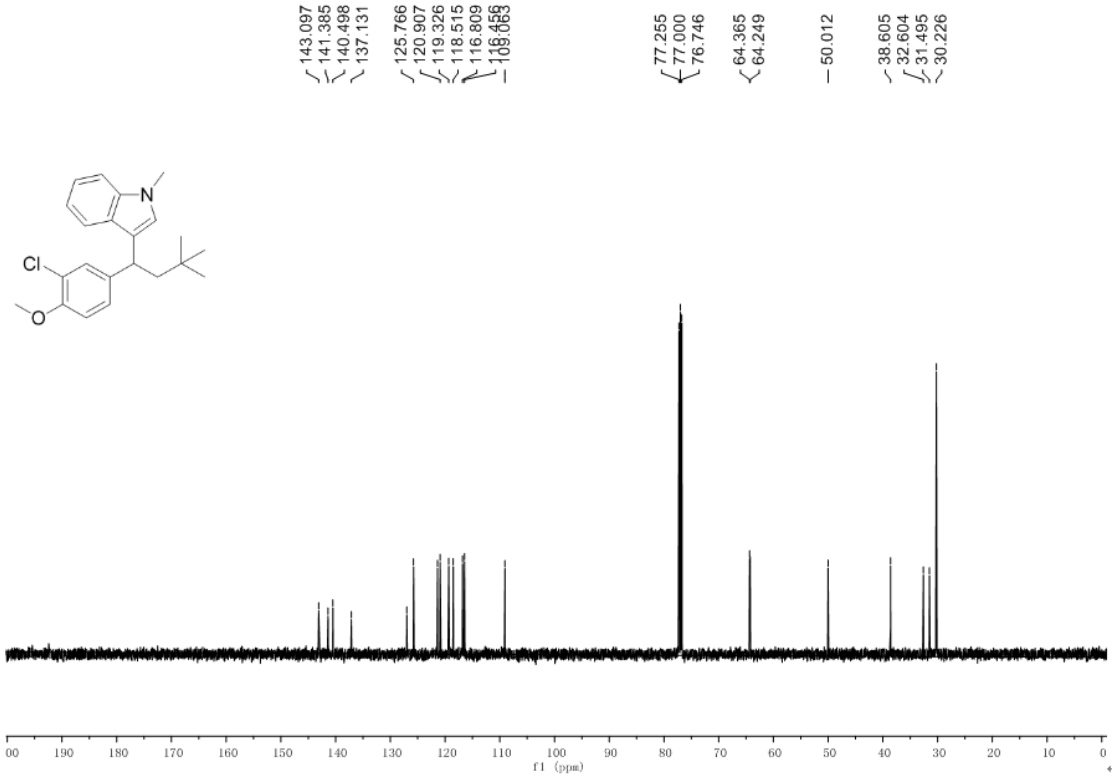


^{13}C-NMR (125 MHz, $CDCl_3$)

3-(1-(3-chloro-4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole (4eaa):

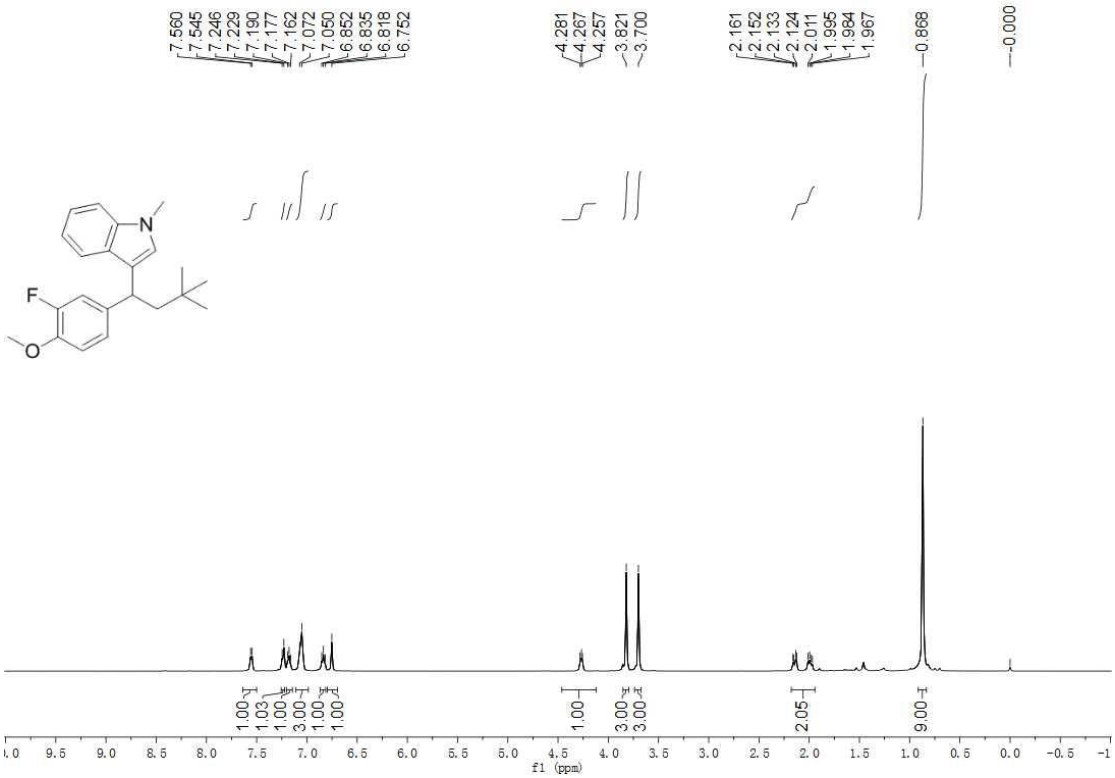


^{1}H-NMR (500 MHz, $CDCl_3$)

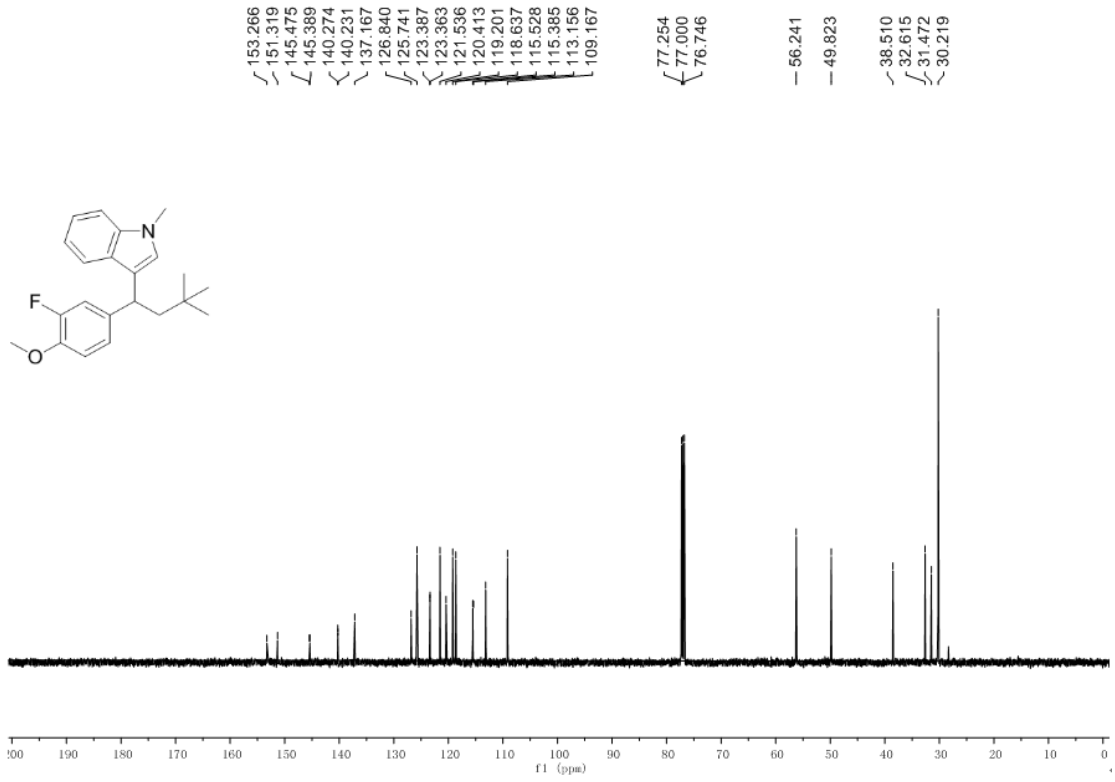


^{13}C-NMR (125 MHz, $CDCl_3$)

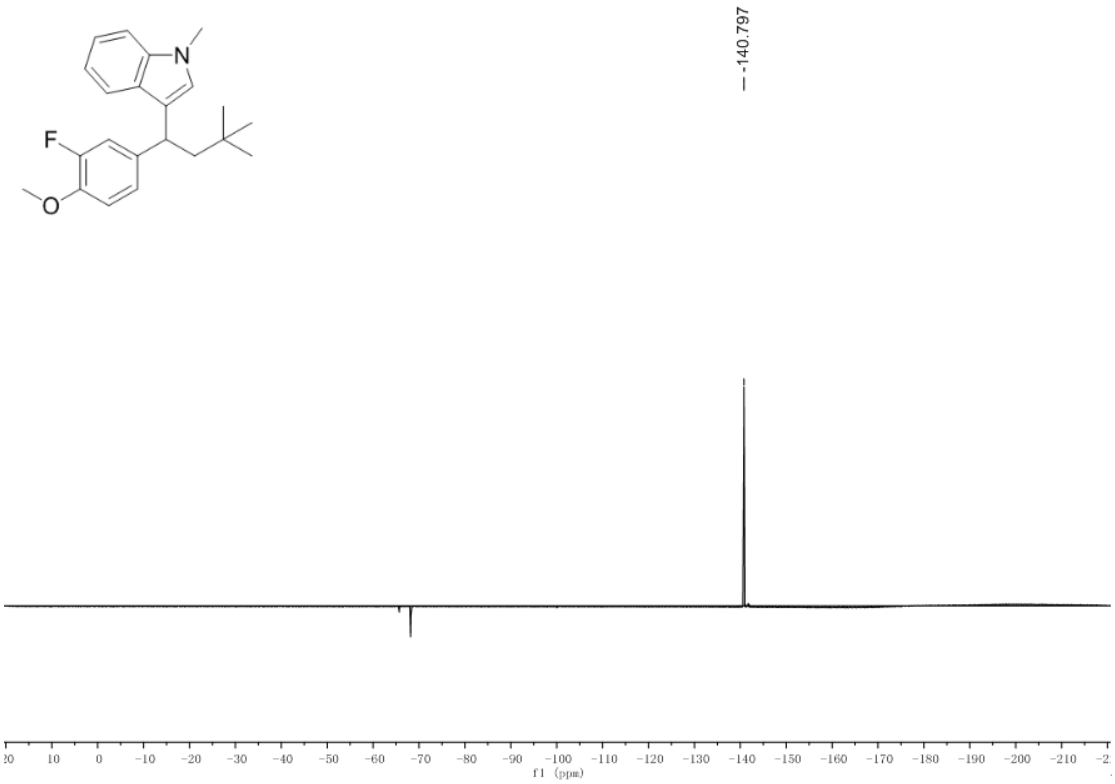
3-(1-(3-fluoro-4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-indole (4faa):



^{1}H-NMR (500 MHz, $CDCl_3$)

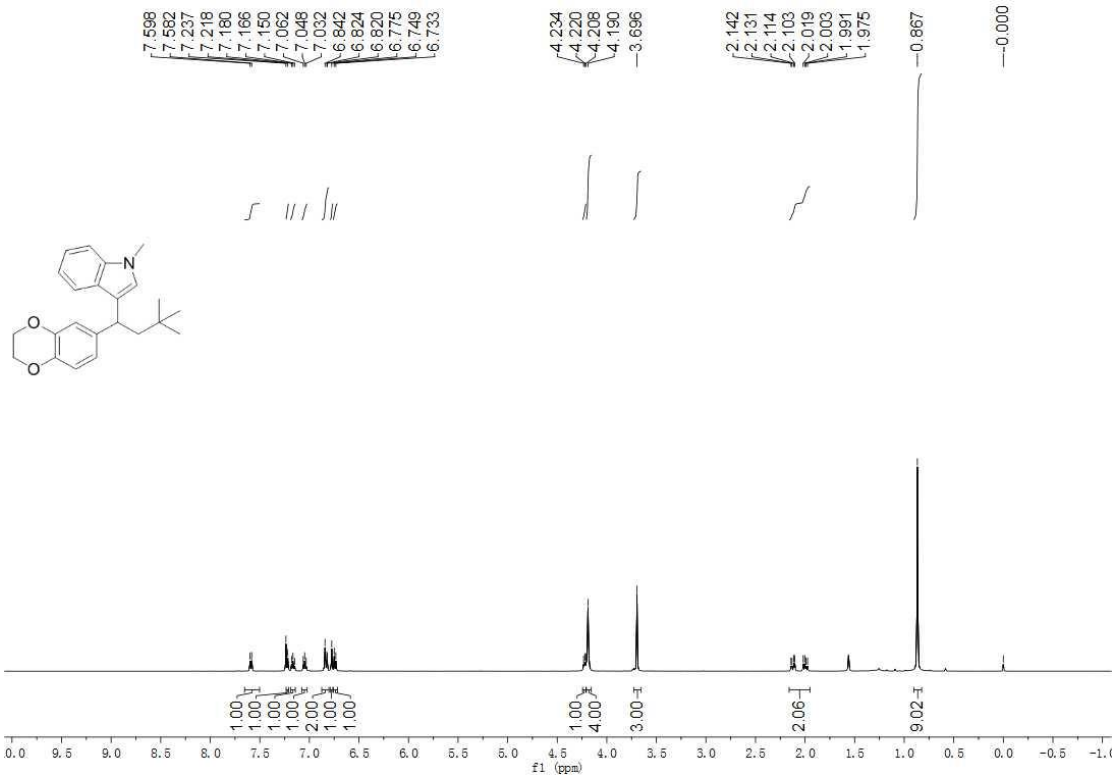


^{13}C-NMR (125 MHz, $CDCl_3$)

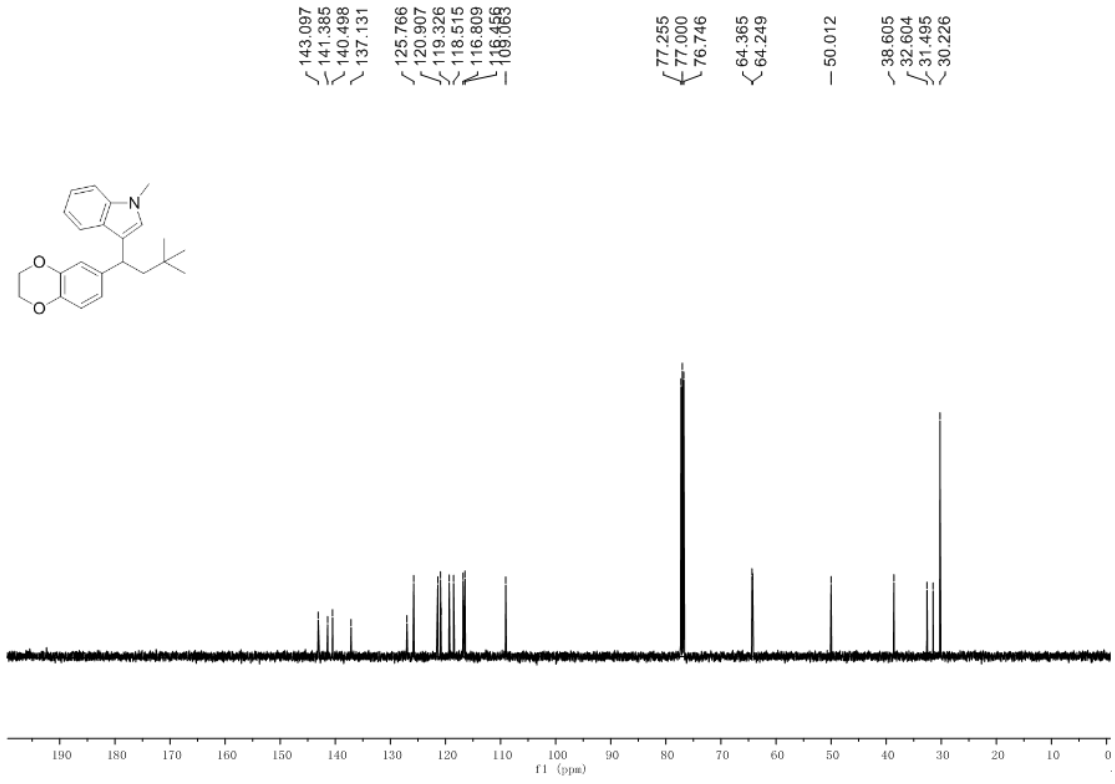


^{19}F NMR (471 MHz, $CDCl_3$)

3-(1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-3,3-dimethylbutyl)-1-methyl-1H-indole (4gaa):

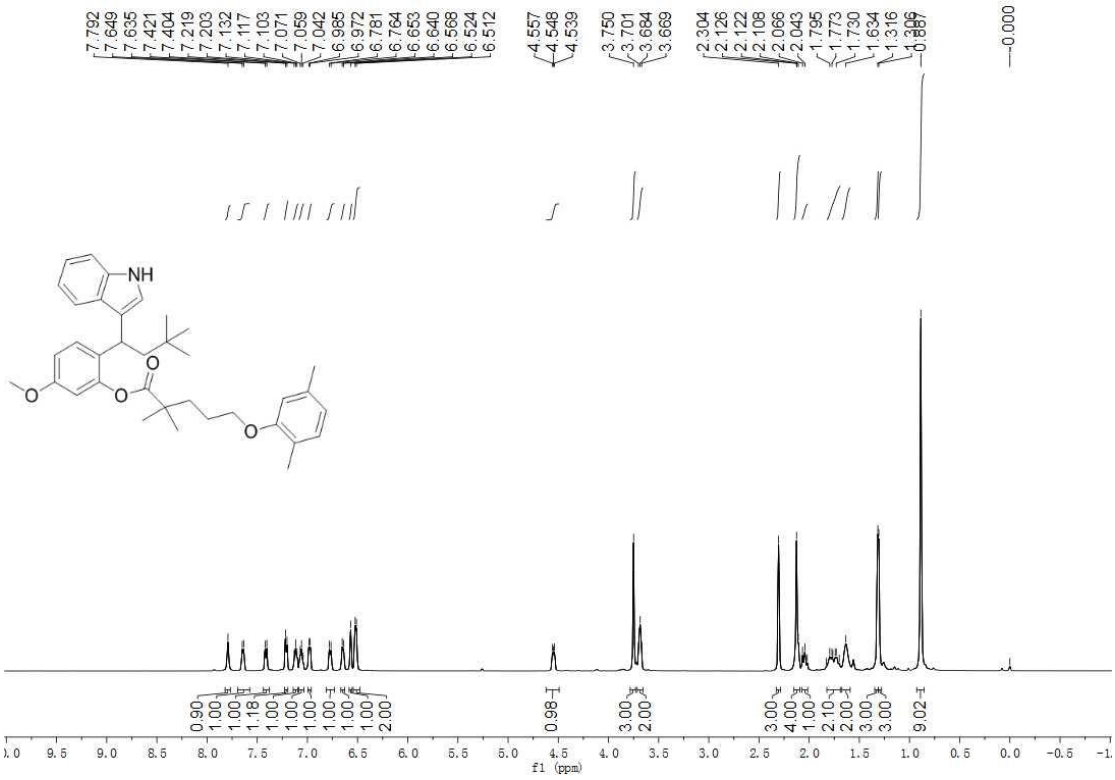


^{1}H-NMR (500 MHz, $CDCl_3$)

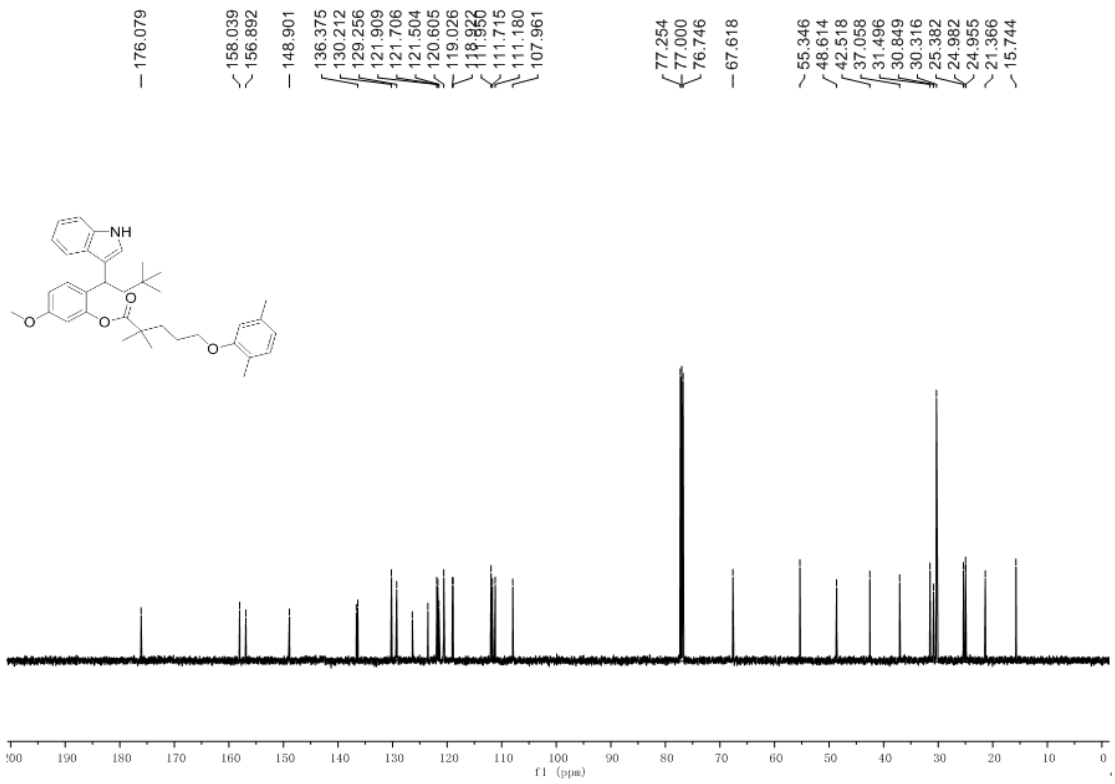


^{13}C-NMR (125 MHz, $CDCl_3$)

2-(1-(1*H*-indol-3-yl)-3,3-dimethylbutyl)-5-methoxyphenyl-5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (4has)：

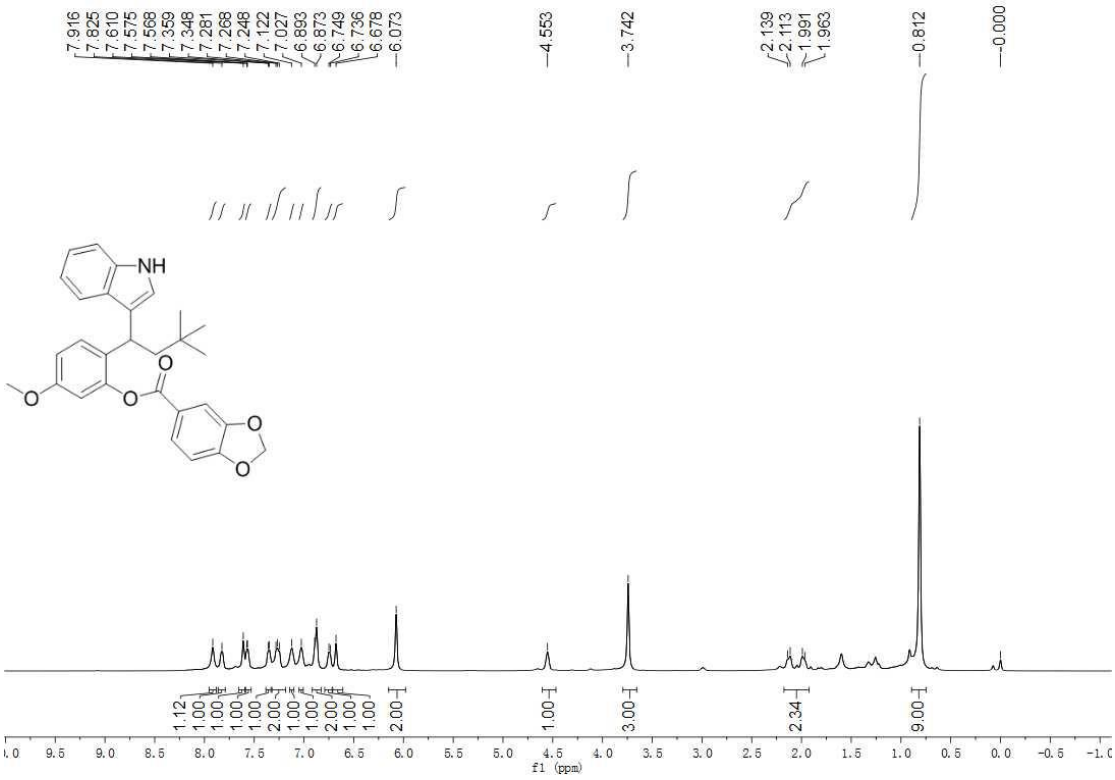


^{1}H-NMR (500 MHz, $CDCl_3$)

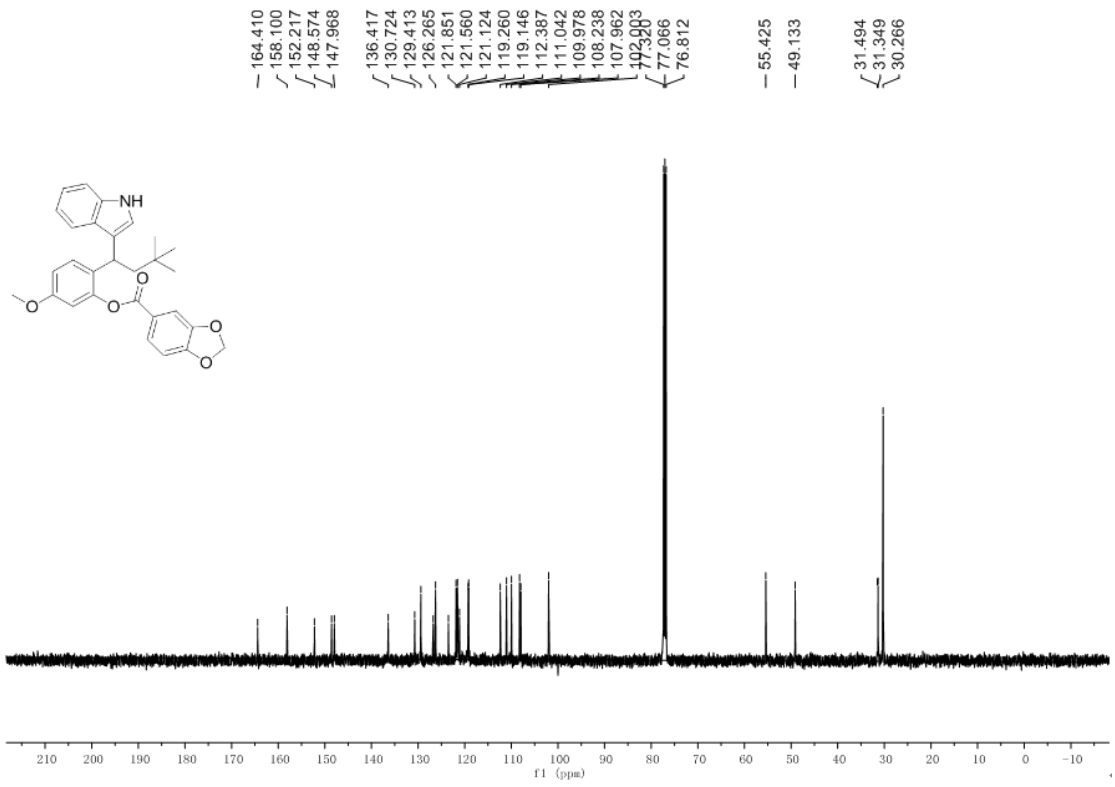


^{13}C-NMR (125 MHz, $CDCl_3$)

2-(1-(1*H*-indol-3-yl)-3,3-dimethylbutyl)-5-methoxyphenyl benzo[d][1,3]dioxole-5-Carboxylate (4ias):

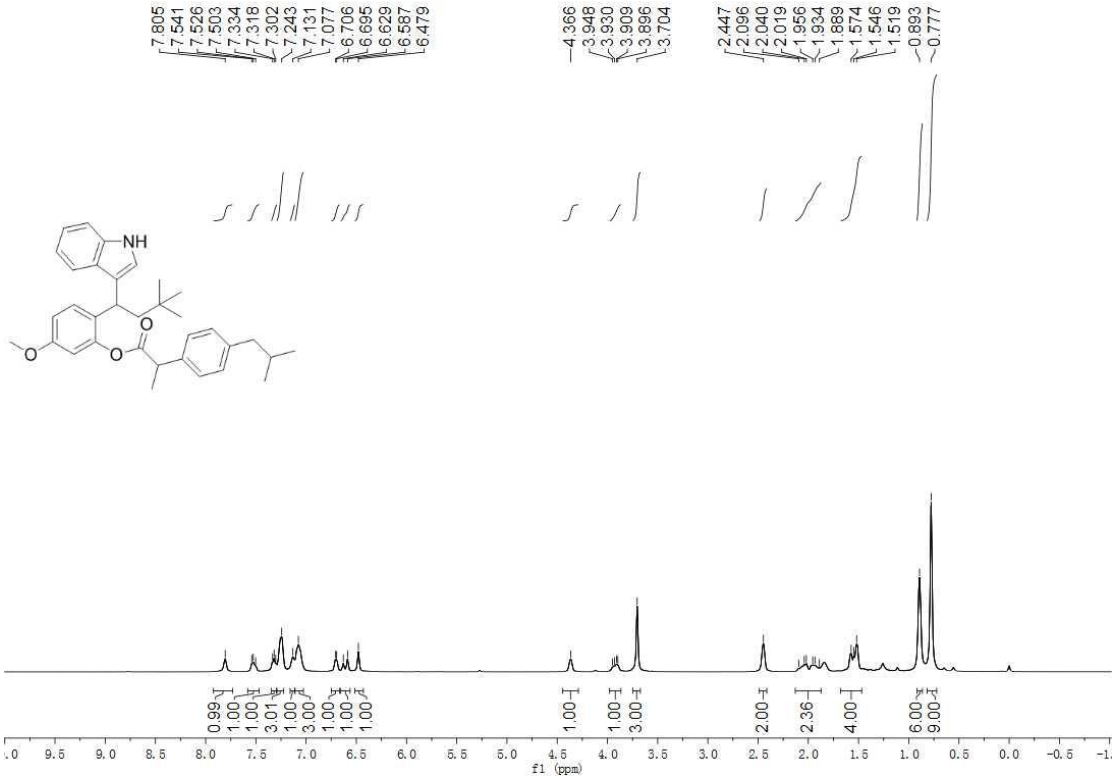


^{1}H-NMR (500 MHz, $CDCl_3$)

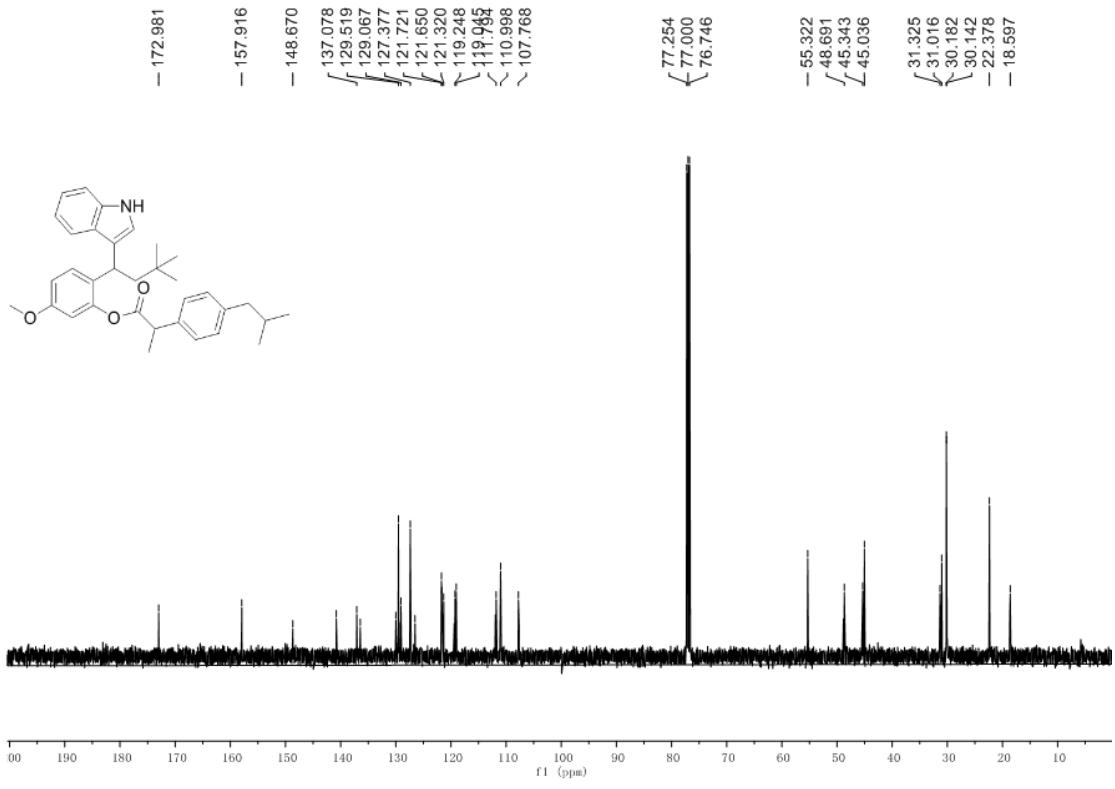


^{13}C-NMR (125 MHz, $CDCl_3$)

2-(1-(1*H*-indol-3-yl)-3,3-dimethylbutyl)-5-methoxyphenyl-2-(4-isobutylphenyl)propanoate (4jas):

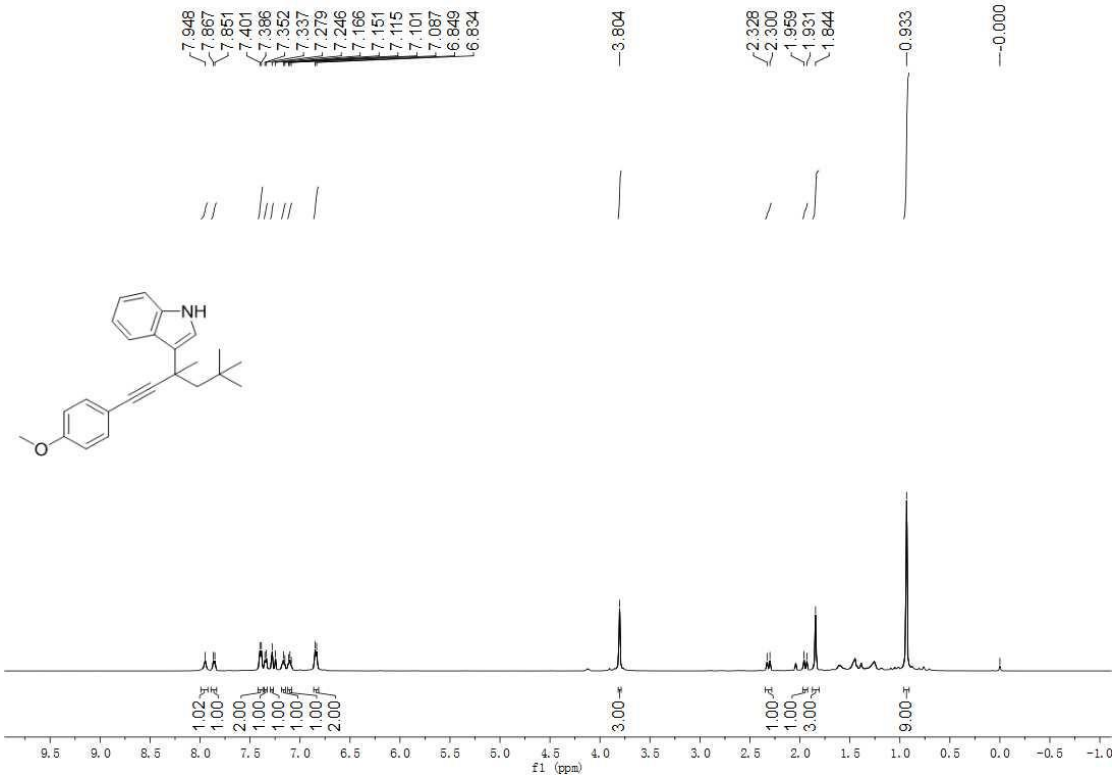


^{1}H-NMR (500 MHz, $CDCl_3$)

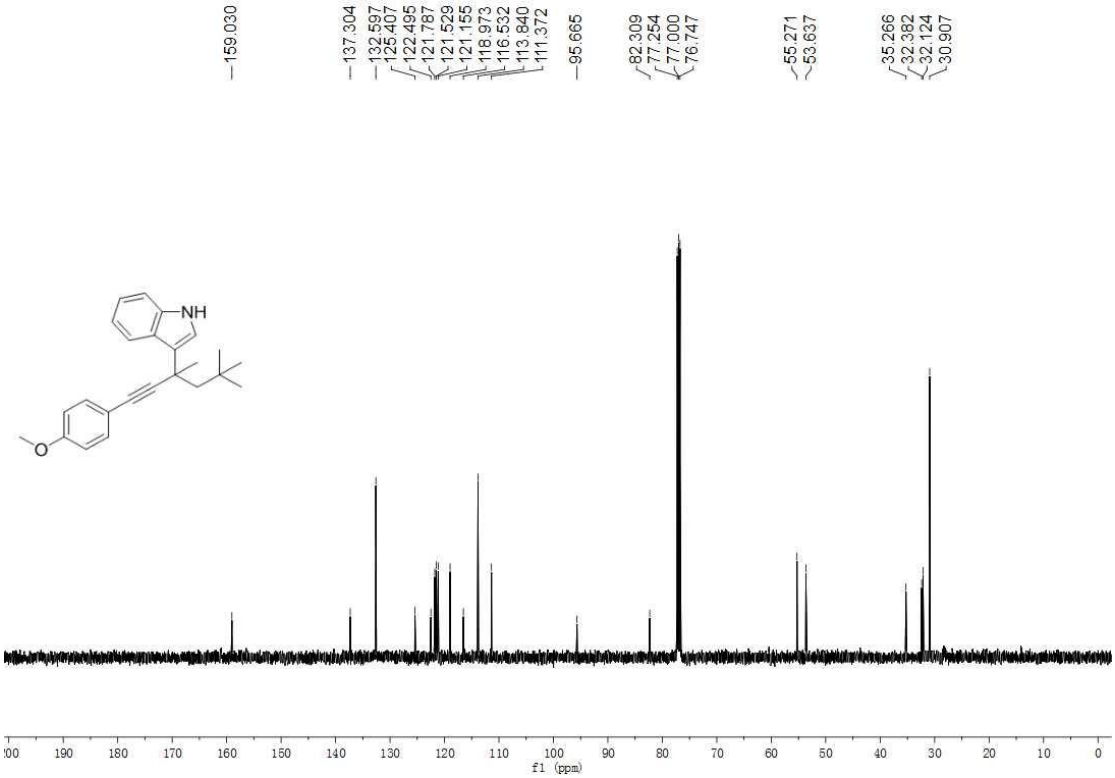


^{13}C-NMR (125 MHz, $CDCl_3$)

3-(1-(4-methoxyphenyl)-3,5,5-trimethylhex-1-yn-3-yl)-1*H*-indole (4las)：

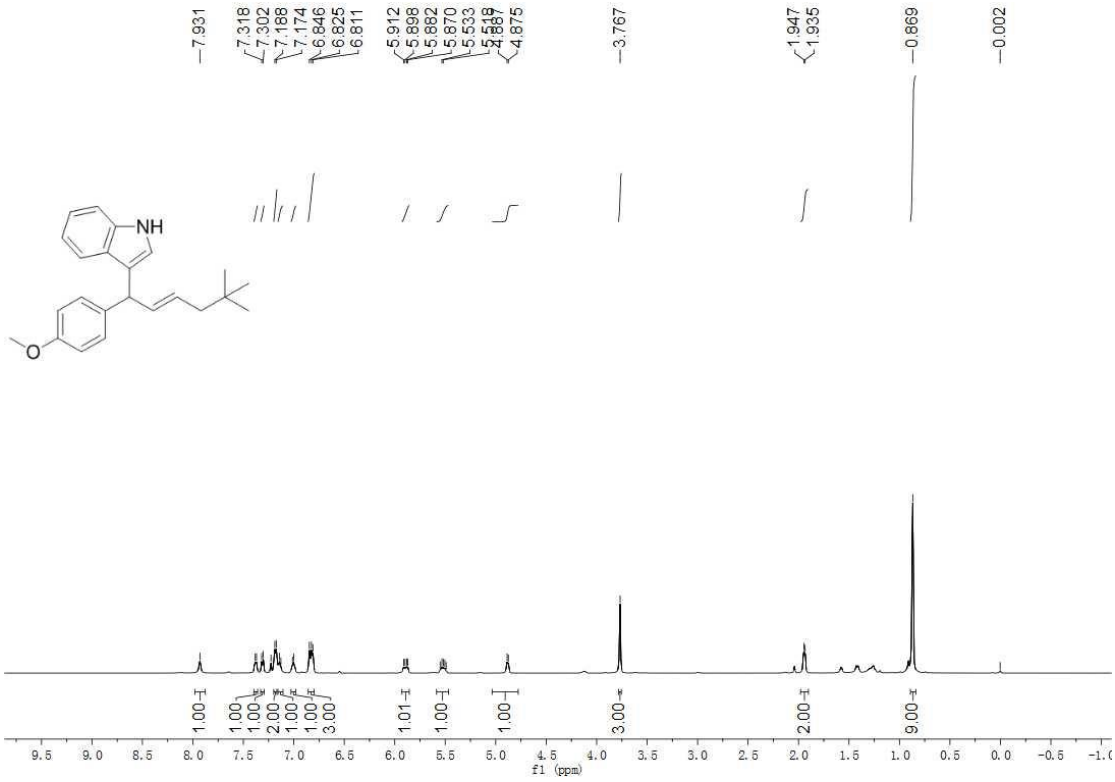


^{1}H-NMR (500 MHz, $CDCl_3$)

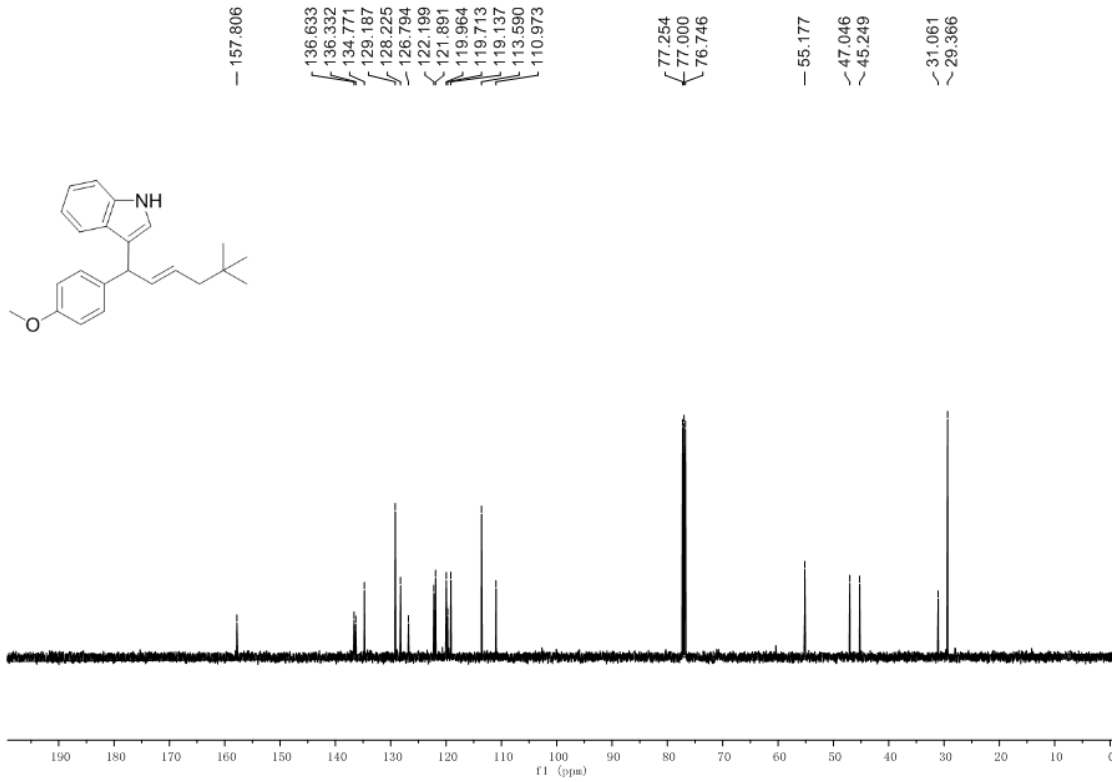


^{13}C-NMR (125 MHz, $CDCl_3$)

3-(1-(4-methoxyphenyl)-5,5-dimethylhex-2-en-1-yl)-1*H*-indole (4mas)：

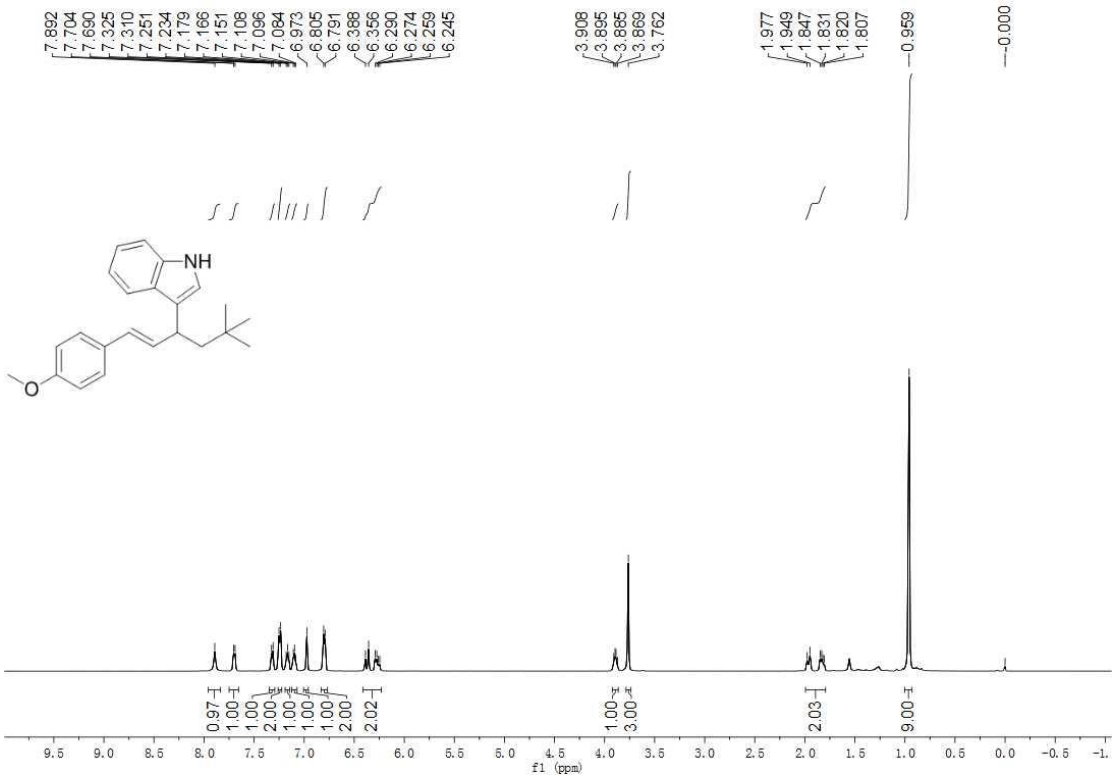


^{1}H-NMR (500 MHz, $CDCl_3$)

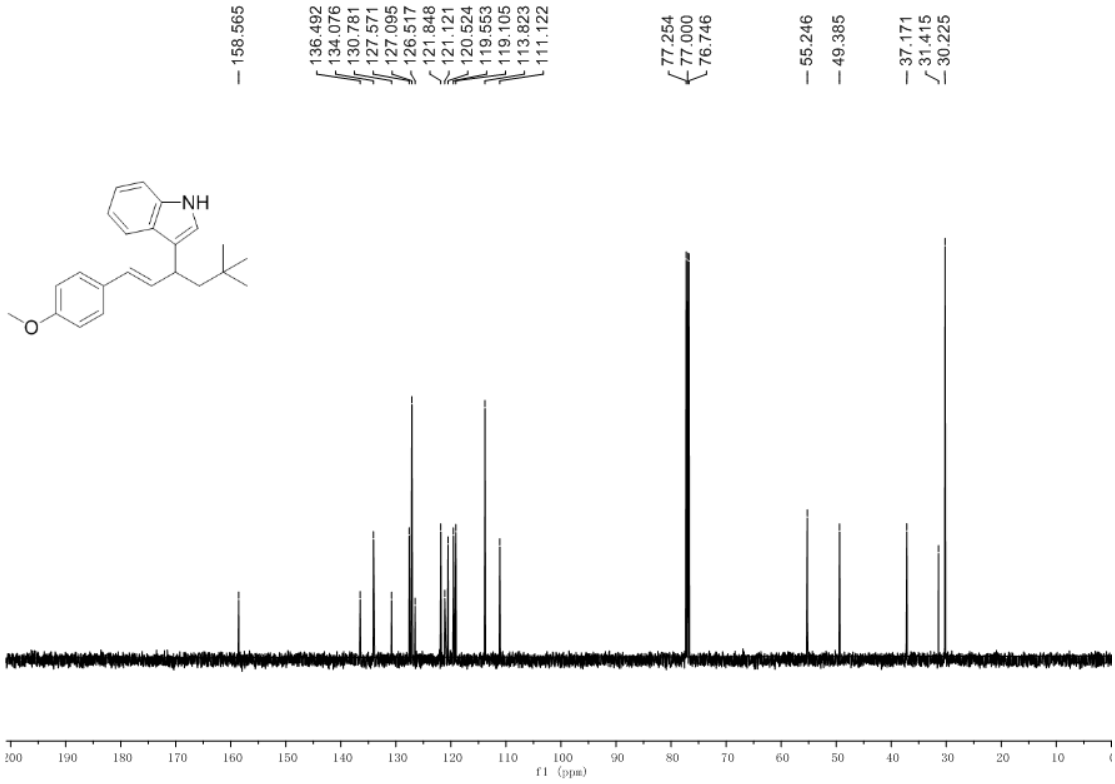


^{13}C-NMR (125 MHz, $CDCl_3$)

3-(1-(4-methoxyphenyl)-5,5-dimethylhex-1-en-3-yl)-1*H*-indole (4mas)：

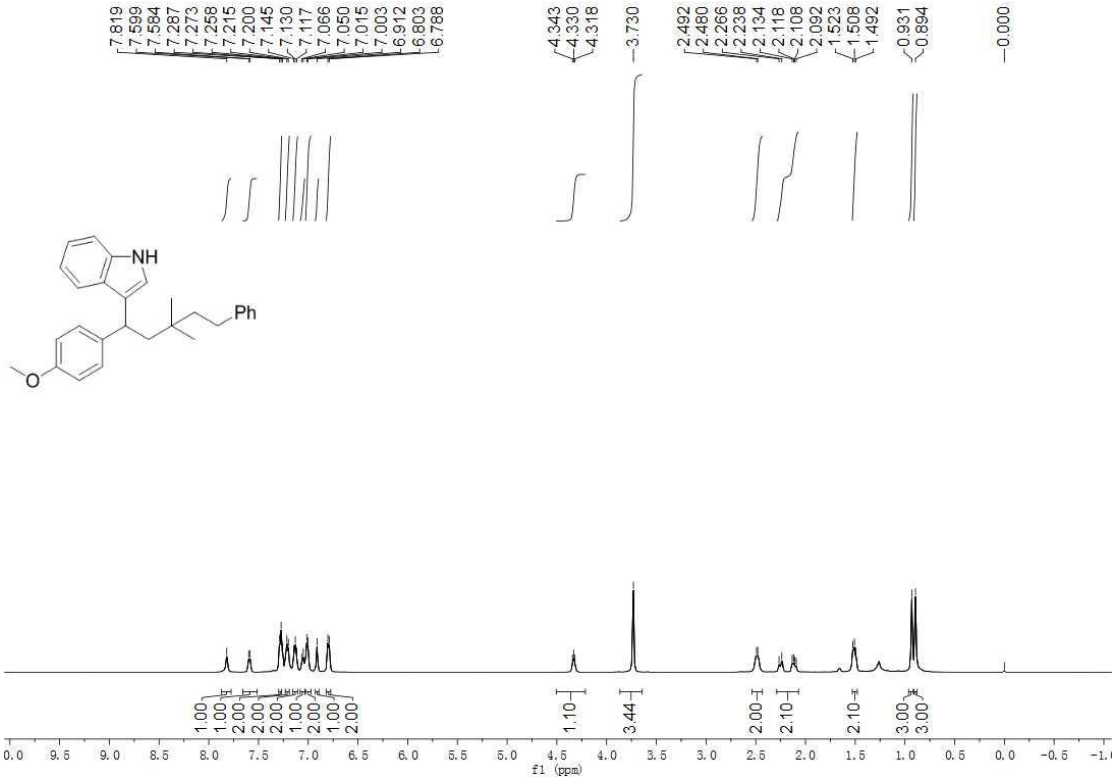


^{1}H-NMR (500 MHz, $CDCl_3$)

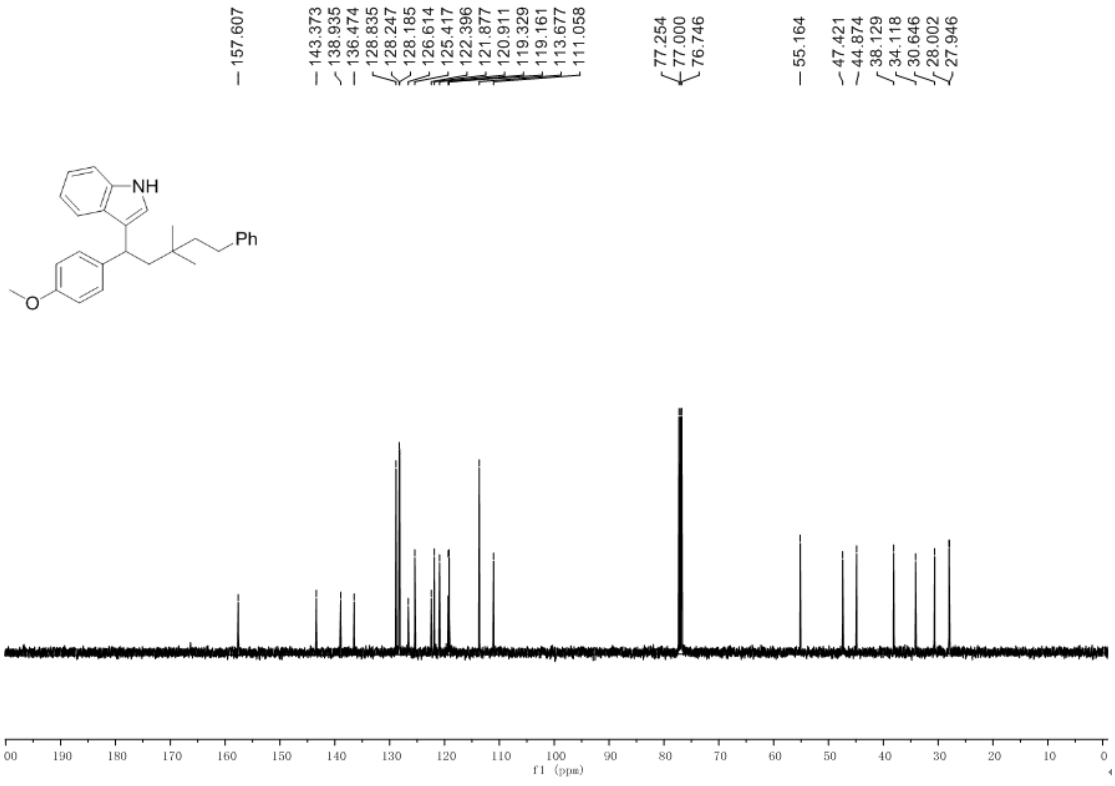


^{13}C-NMR (125 MHz, $CDCl_3$)

3-(1-(4-methoxyphenyl)-3,3-dimethyl-5-phenylpentyl)-1*H*-indole (4abs)：

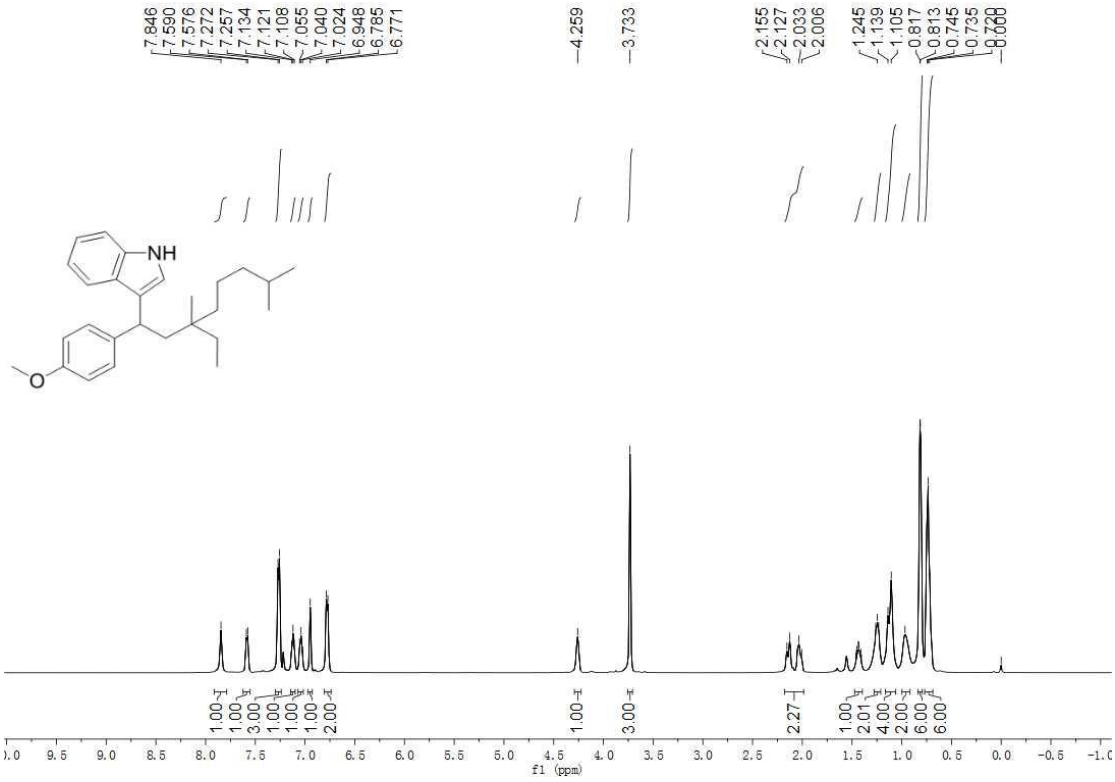


^{1}H-NMR (500 MHz, $CDCl_3$)

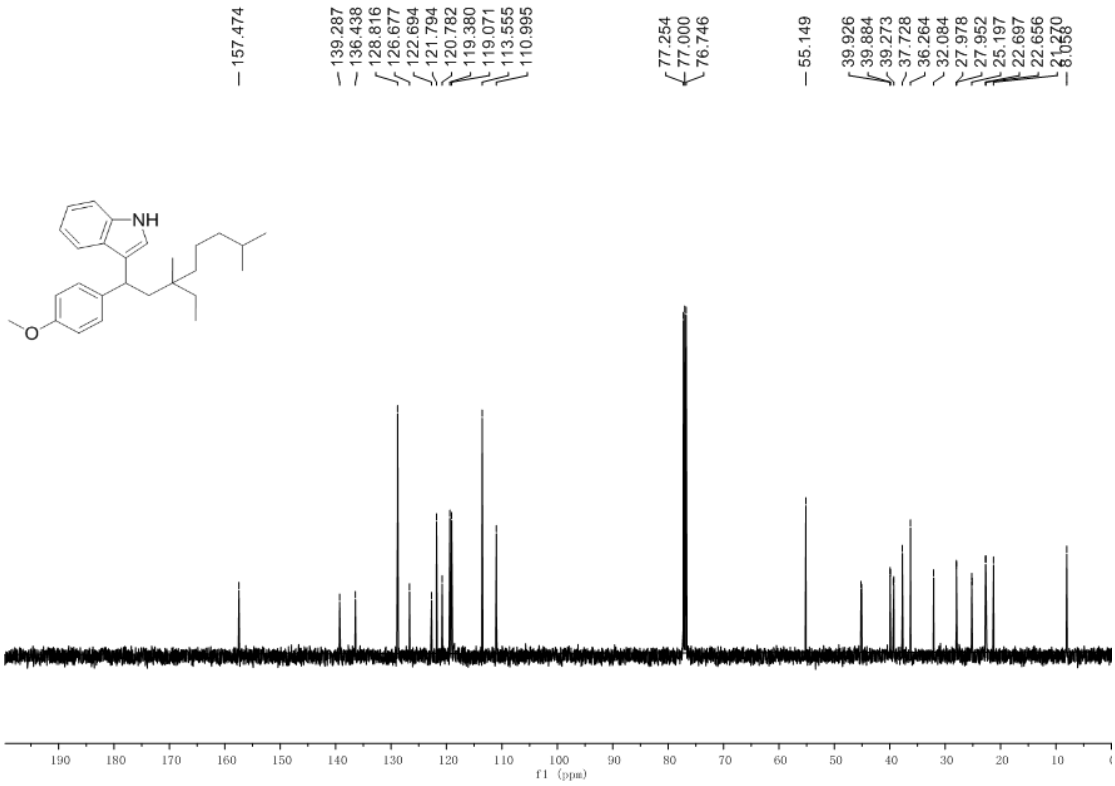


^{13}C-NMR (125 MHz, $CDCl_3$)

3-(3-ethyl-1-(4-methoxyphenyl)-3,7-dimethyloctyl)-1*H*-indole (4acs):

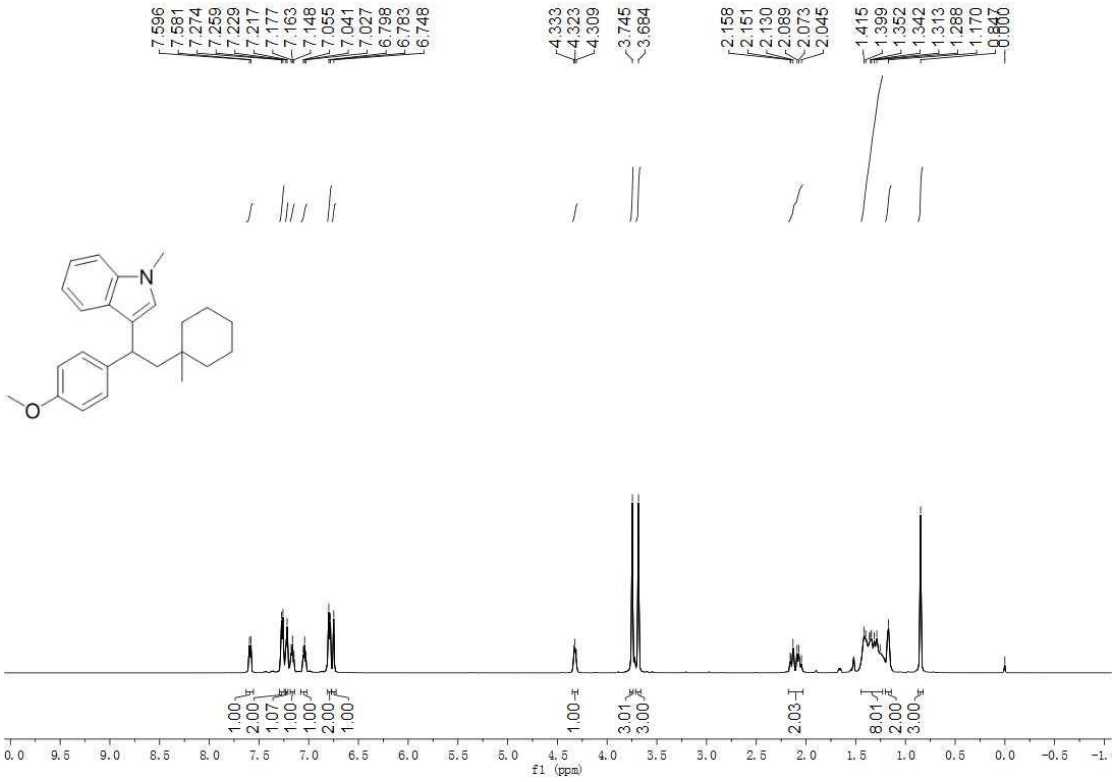


^{1}H-NMR (500 MHz, $CDCl_3$)

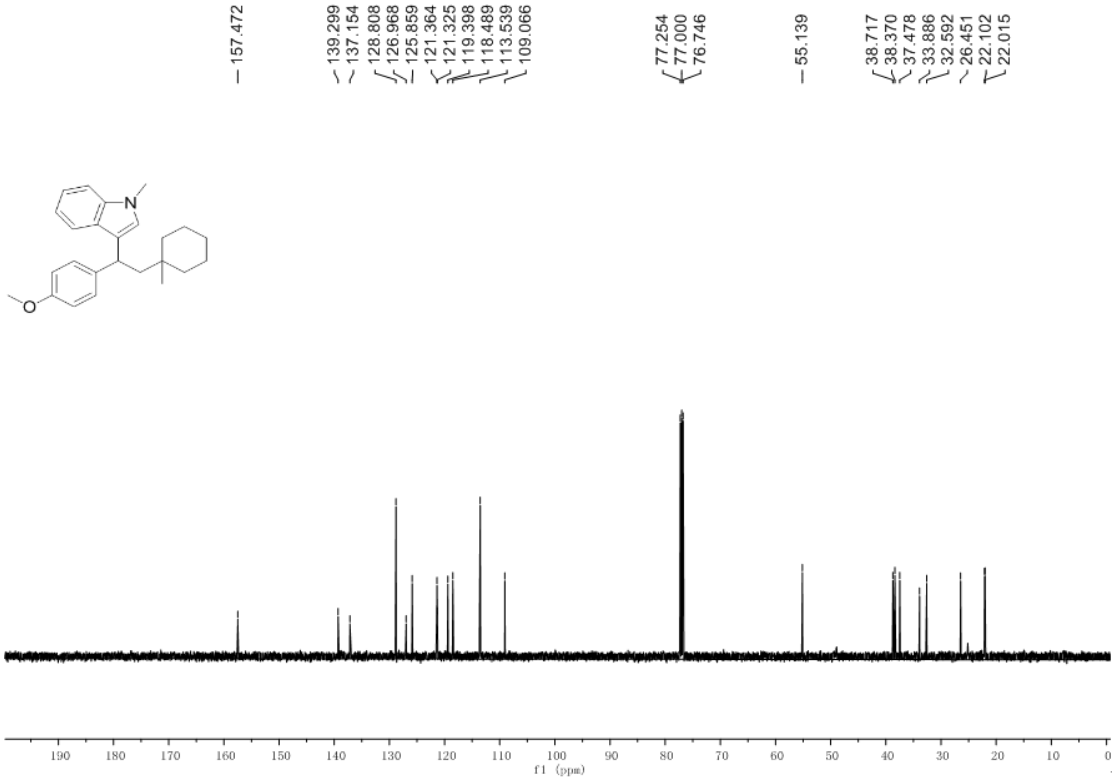


^{13}C-NMR (125 MHz, $CDCl_3$)

3-(1-(4-methoxyphenyl)-2-(1-methylcyclohexyl)ethyl)-1-methyl-1*H*-indole (4ads)：

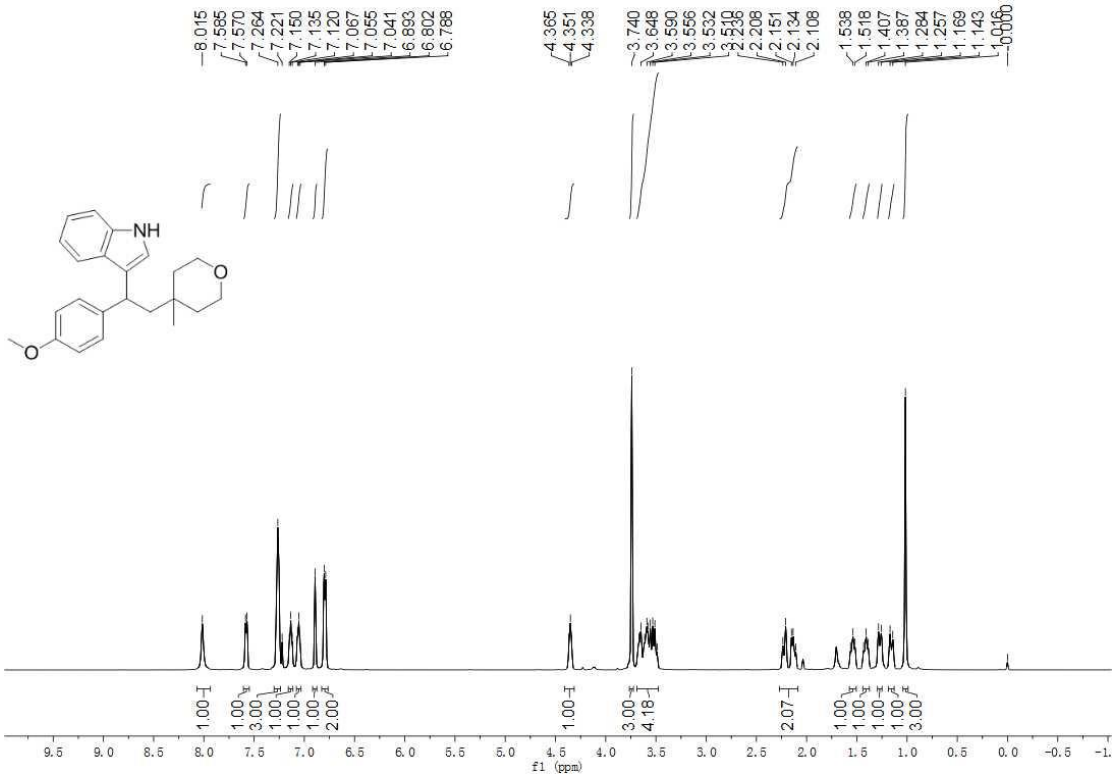


^{1}H-NMR (500 MHz, $CDCl_3$)

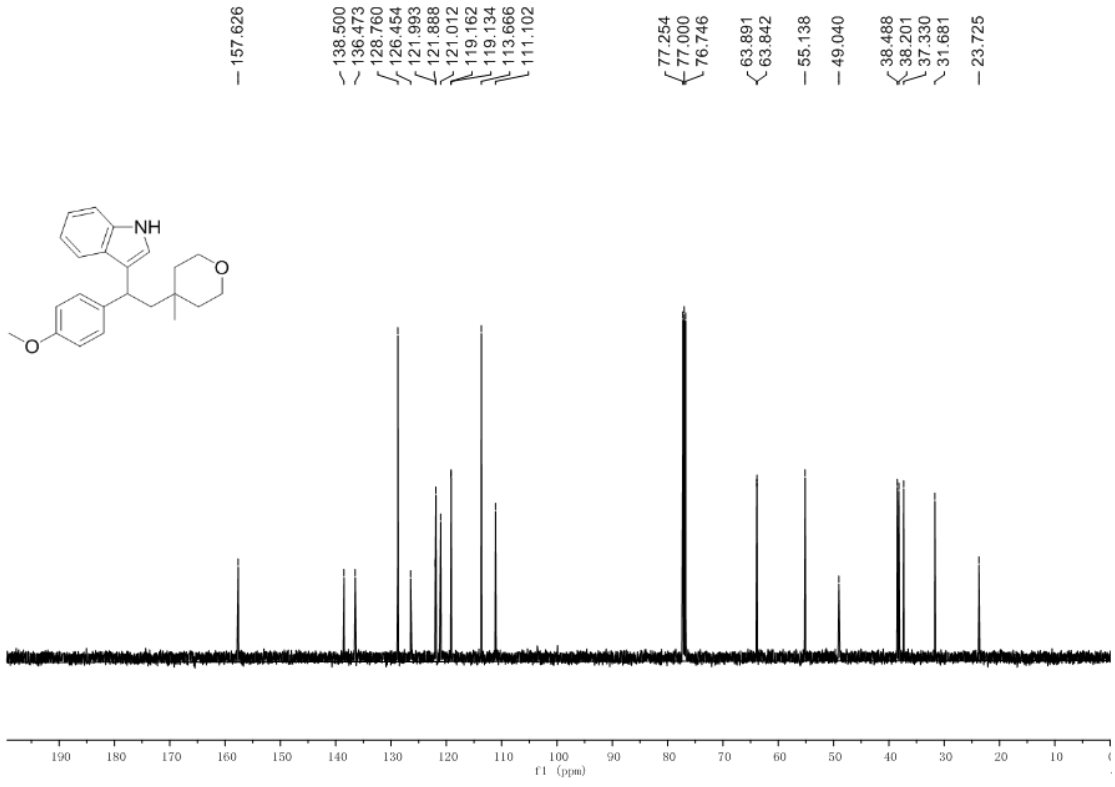


^{13}C-NMR (125 MHz, $CDCl_3$)

3-(1-(4-methoxyphenyl)-2-(4-methyltetrahydro-2H-pyran-4-yl)ethyl)-1*H*-indole (4aes)：

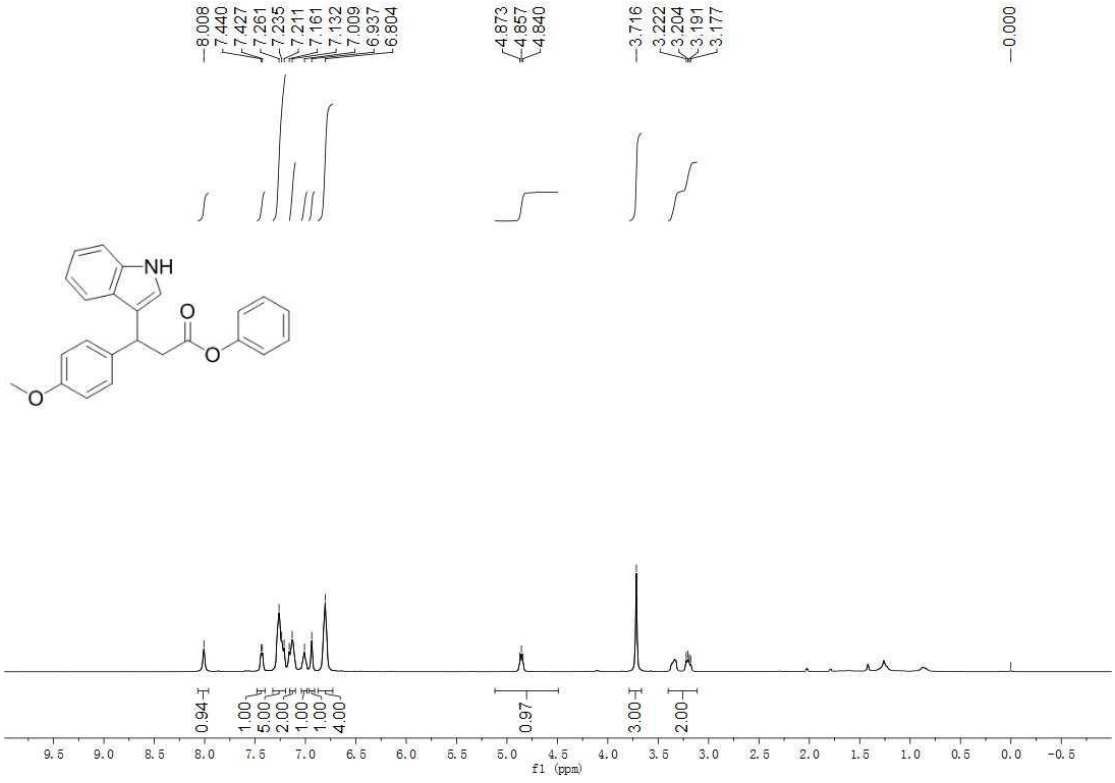


^{1}H-NMR (500 MHz, $CDCl_3$)

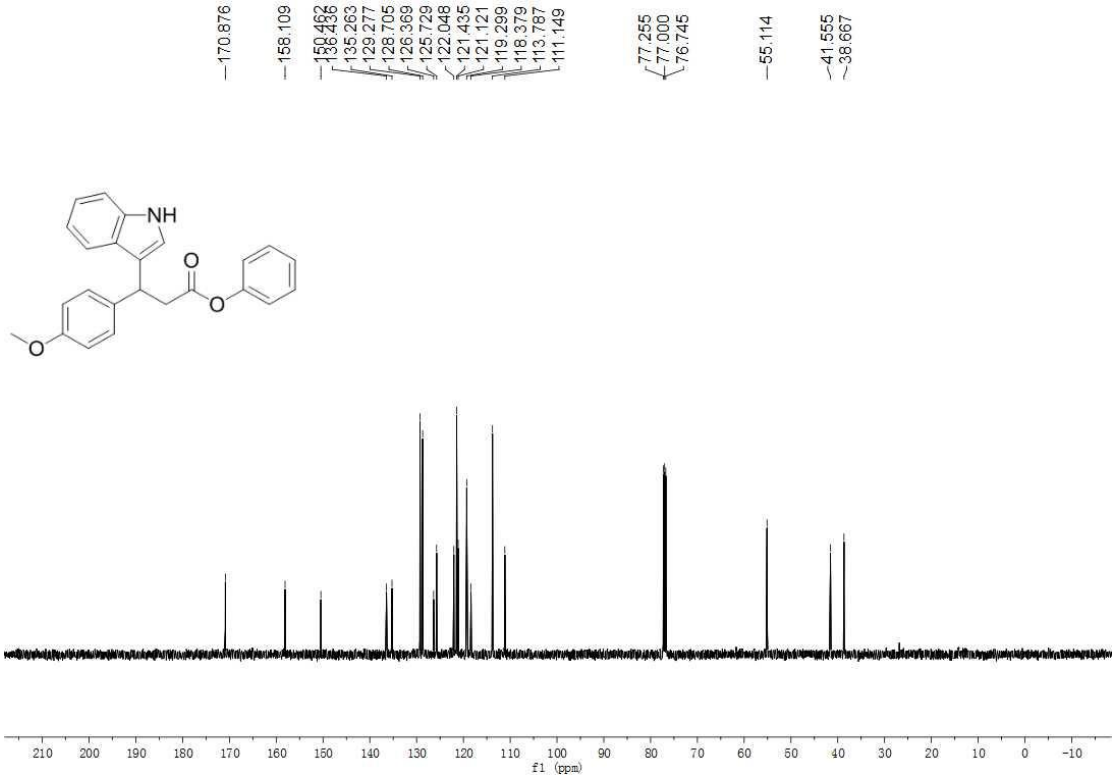


^{13}C-NMR (125 MHz, $CDCl_3$)

Phenyl-3-(1H-indol-3-yl)-3-(4-methoxyphenyl)propanoate (4ags)：

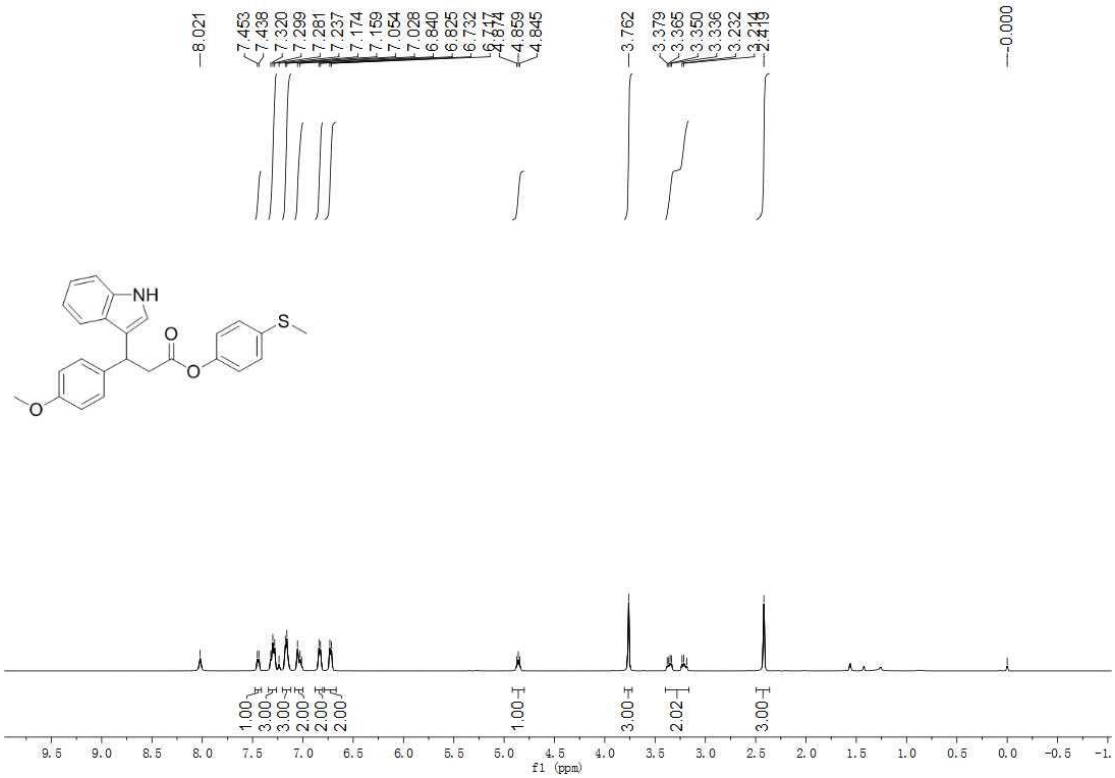


^{1}H-NMR (500 MHz, $CDCl_3$)

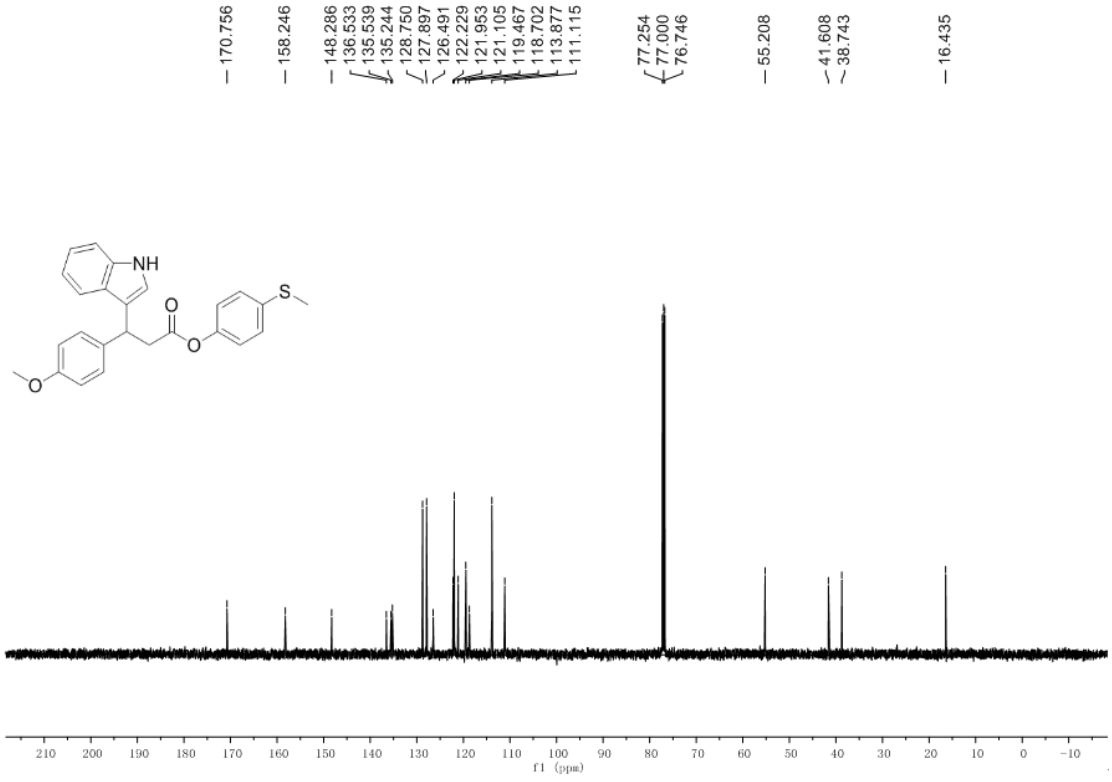


^{13}C-NMR (125 MHz, $CDCl_3$)

4-(methylthio)phenyl 3-(1*H*-indol-3-yl)-3-(4-methoxyphenyl)propanoate (4ahs):

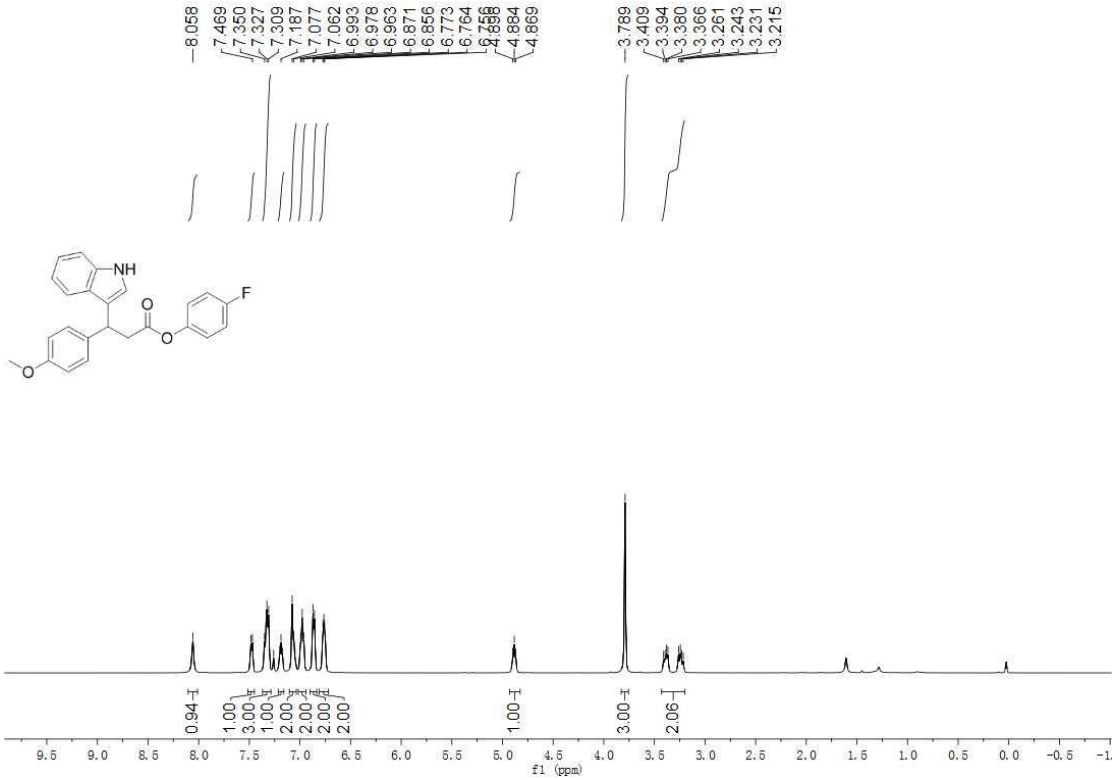


^{1}H-NMR (500 MHz, $CDCl_3$)

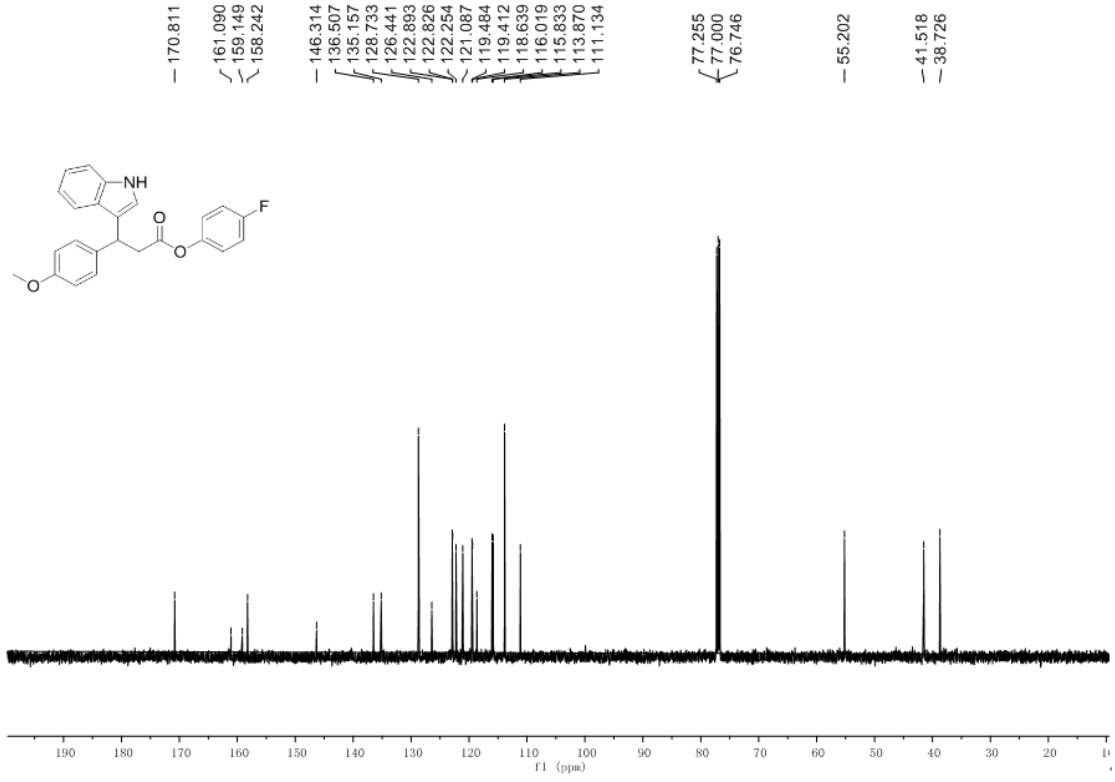


^{13}C-NMR (125 MHz, $CDCl_3$)

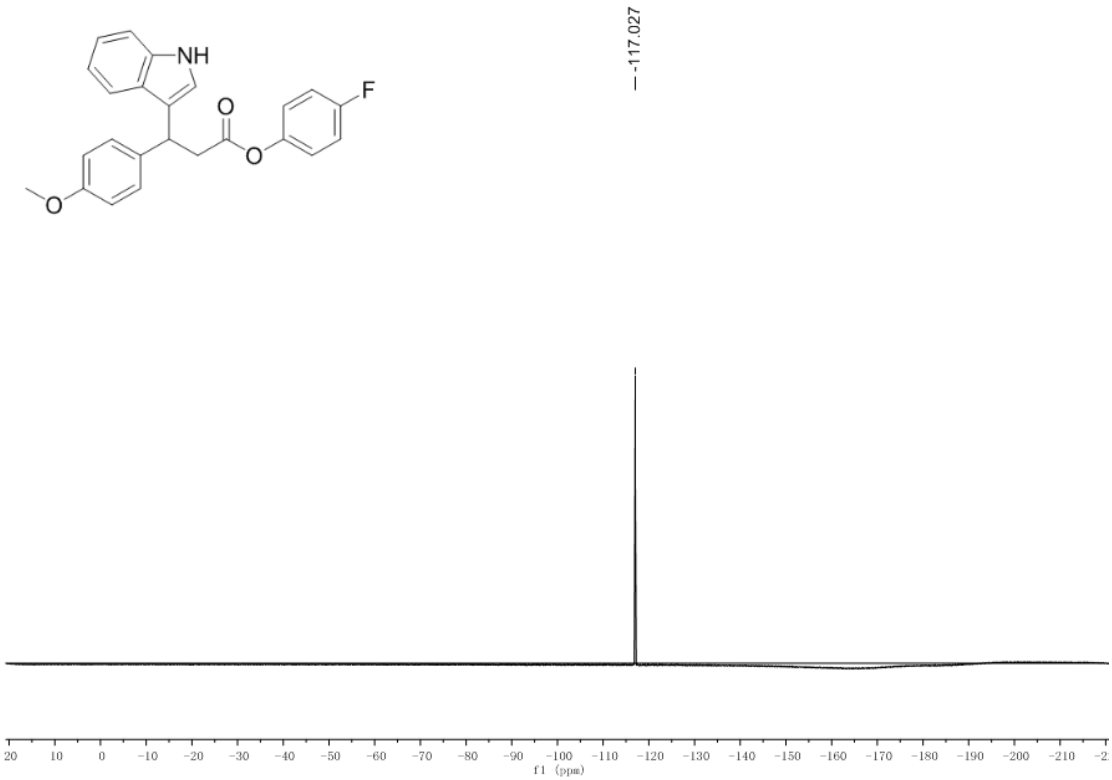
4-fluorophenyl 3-(1*H*-indol-3-yl)-3-(4-methoxyphenyl)propanoate (4ais):



^{1}H-NMR (500 MHz, $CDCl_3$)

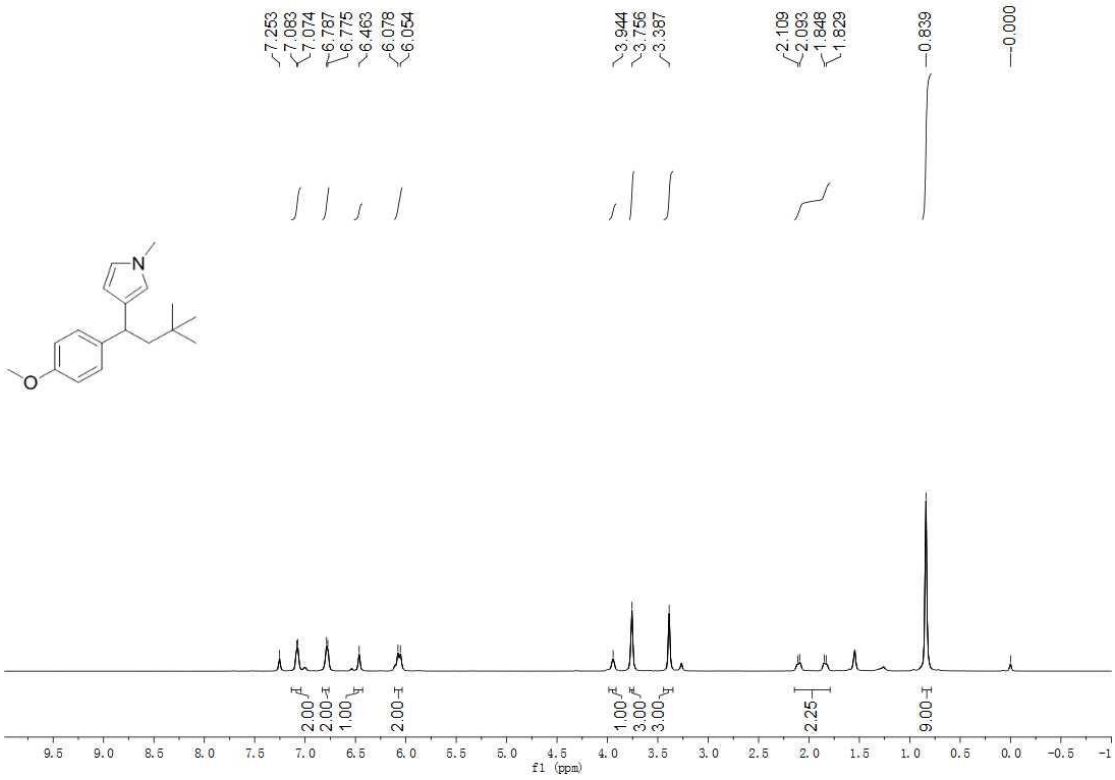


^{13}C-NMR (125 MHz, $CDCl_3$)

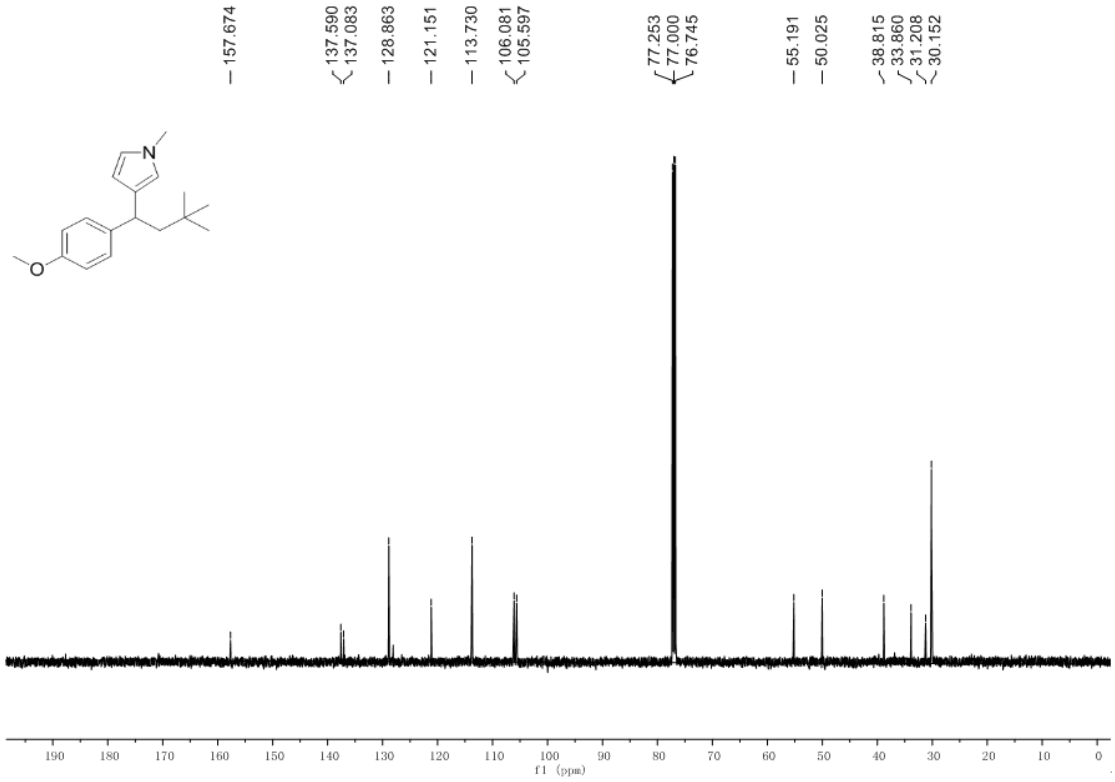


^{19}F NMR (471 MHz, $CDCl_3$)

3-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1-methyl-1*H*-pyrrole (4aau)：

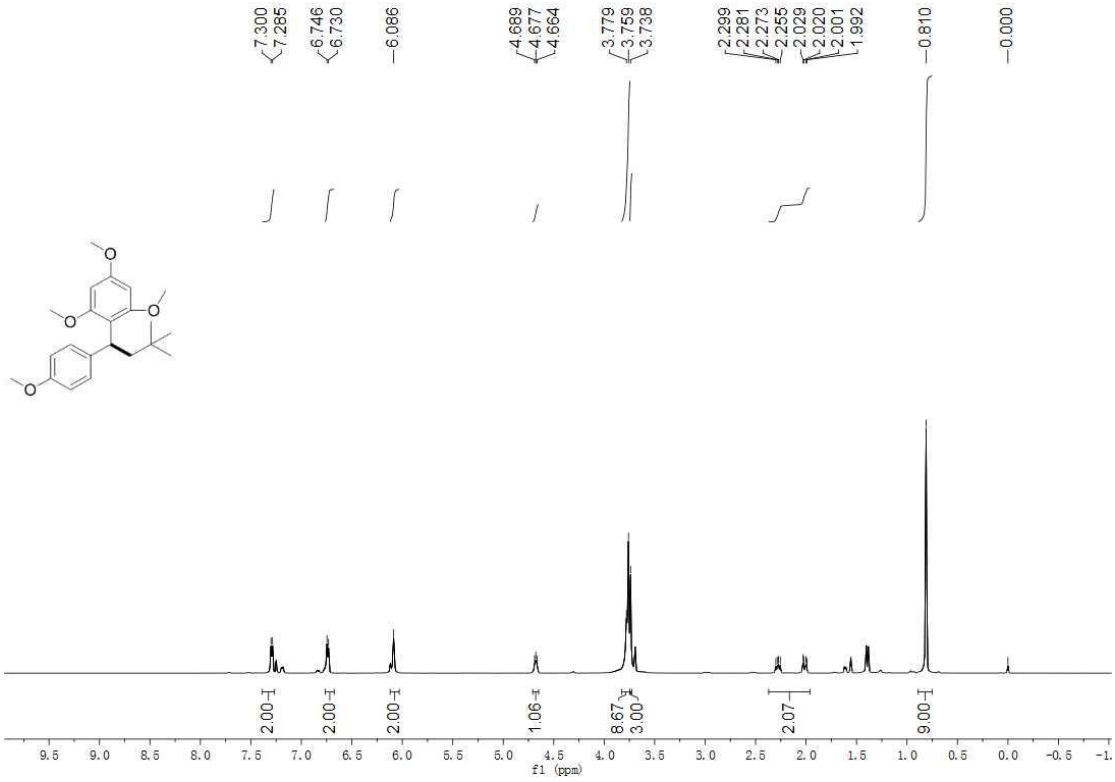


^{1}H-NMR (500 MHz, $CDCl_3$)

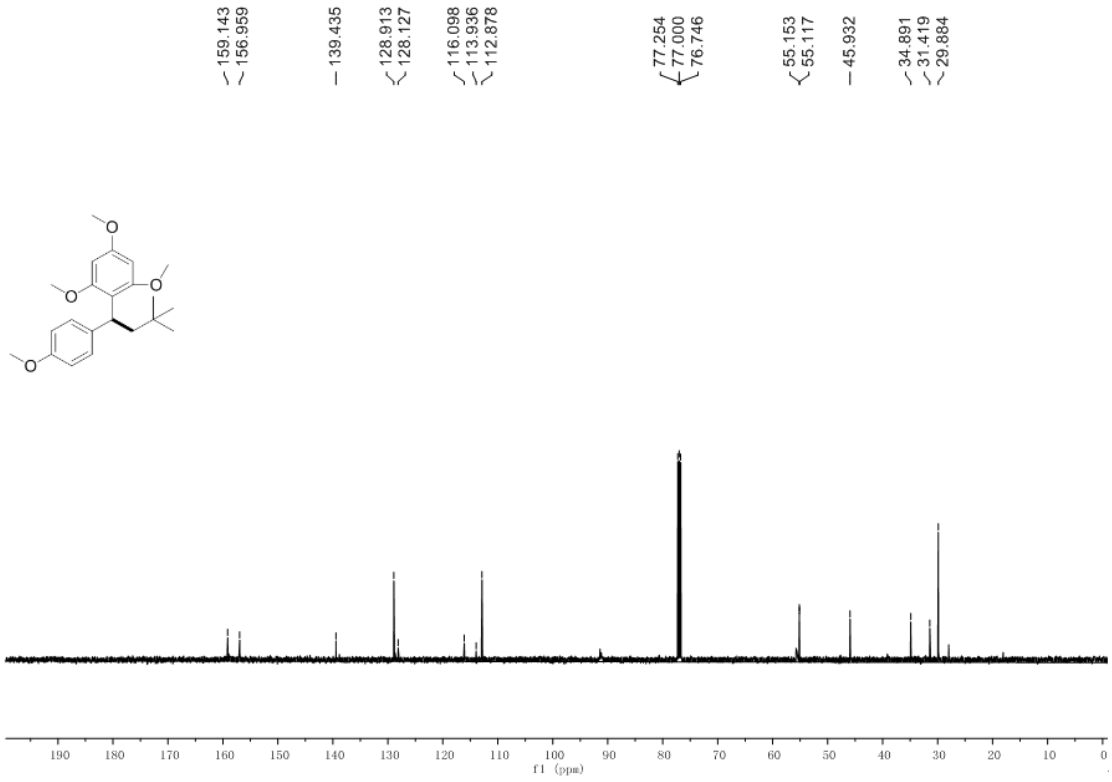


^{13}C-NMR (125 MHz, $CDCl_3$)

1,3,5-trimethoxy-2-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)benzene (4aav)：

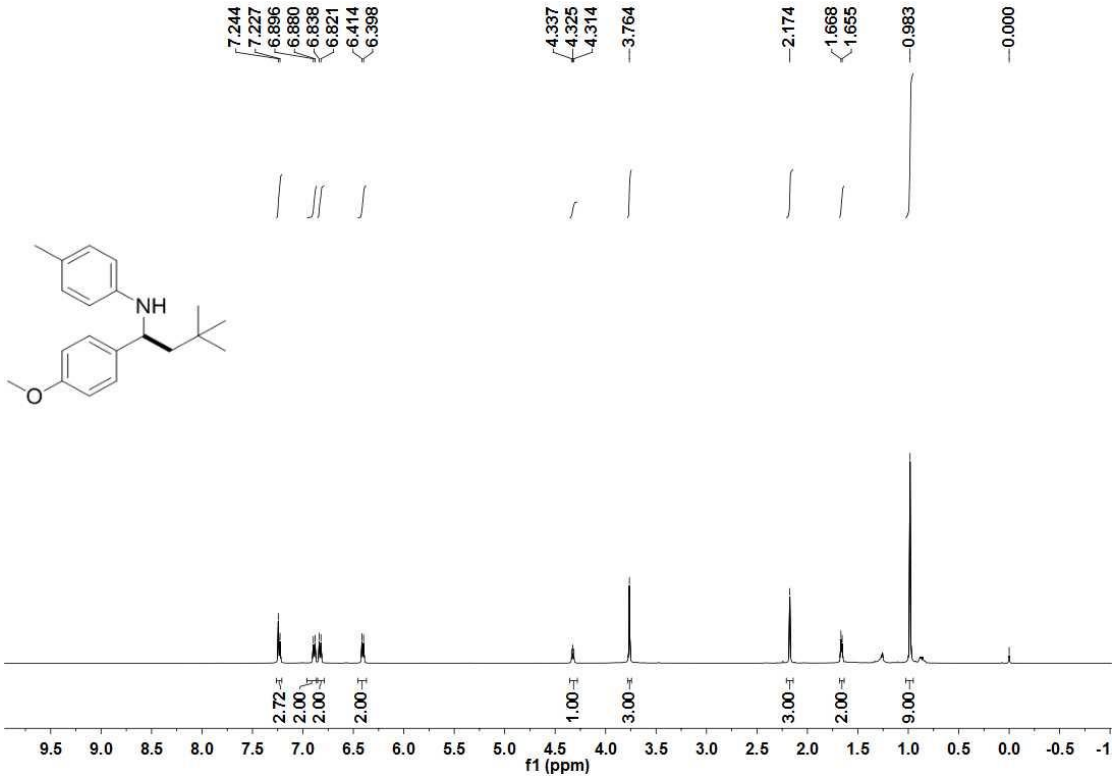


^{1}H-NMR (500 MHz, $CDCl_3$)

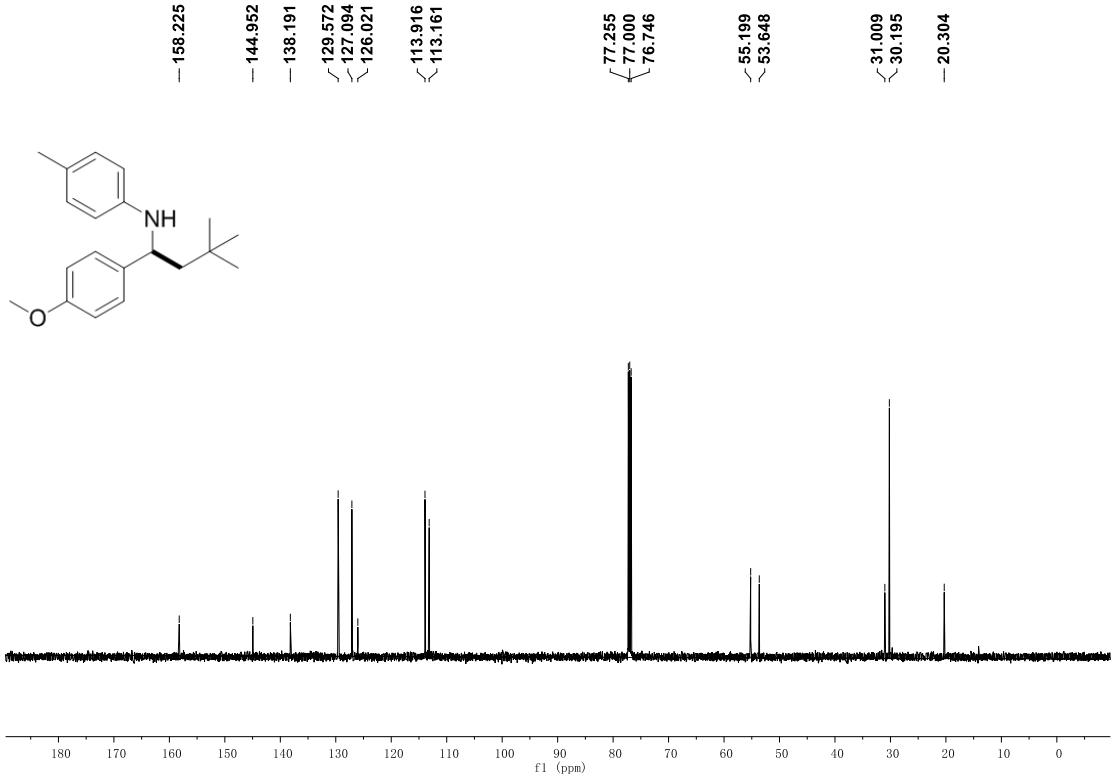


^{13}C-NMR (125 MHz, $CDCl_3$)

***N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-4-methylaniline (4aaw):**

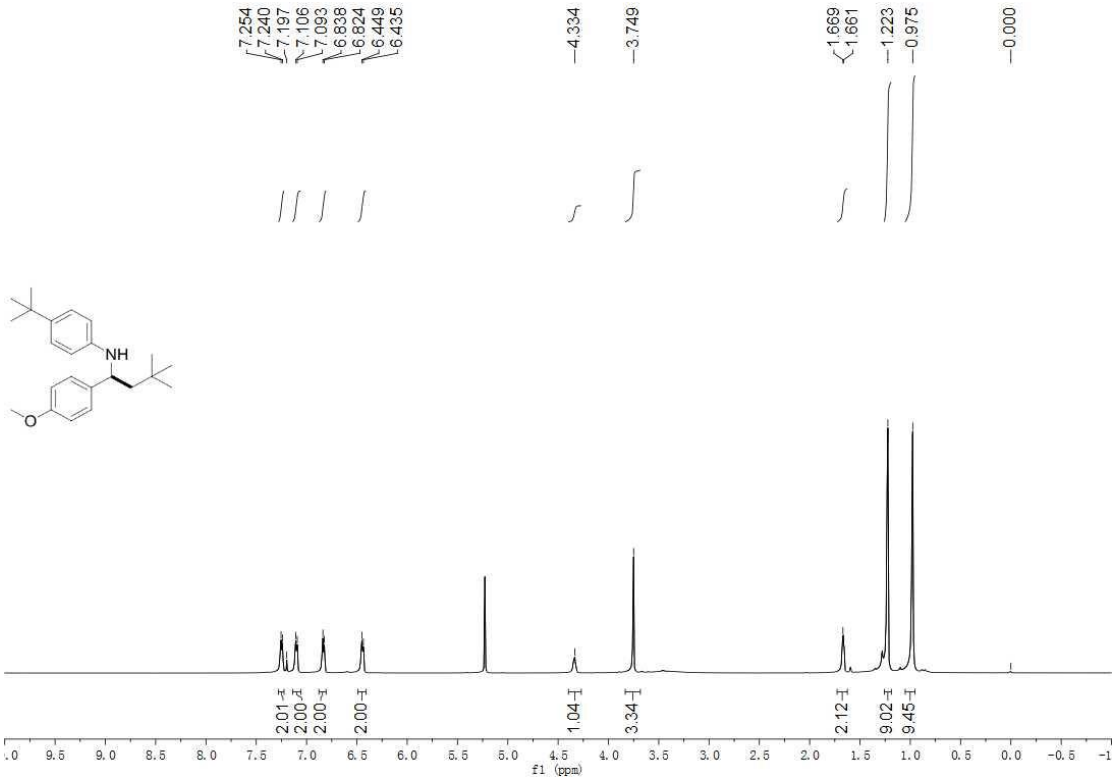


^{1}H-NMR (500 MHz, $CDCl_3$)

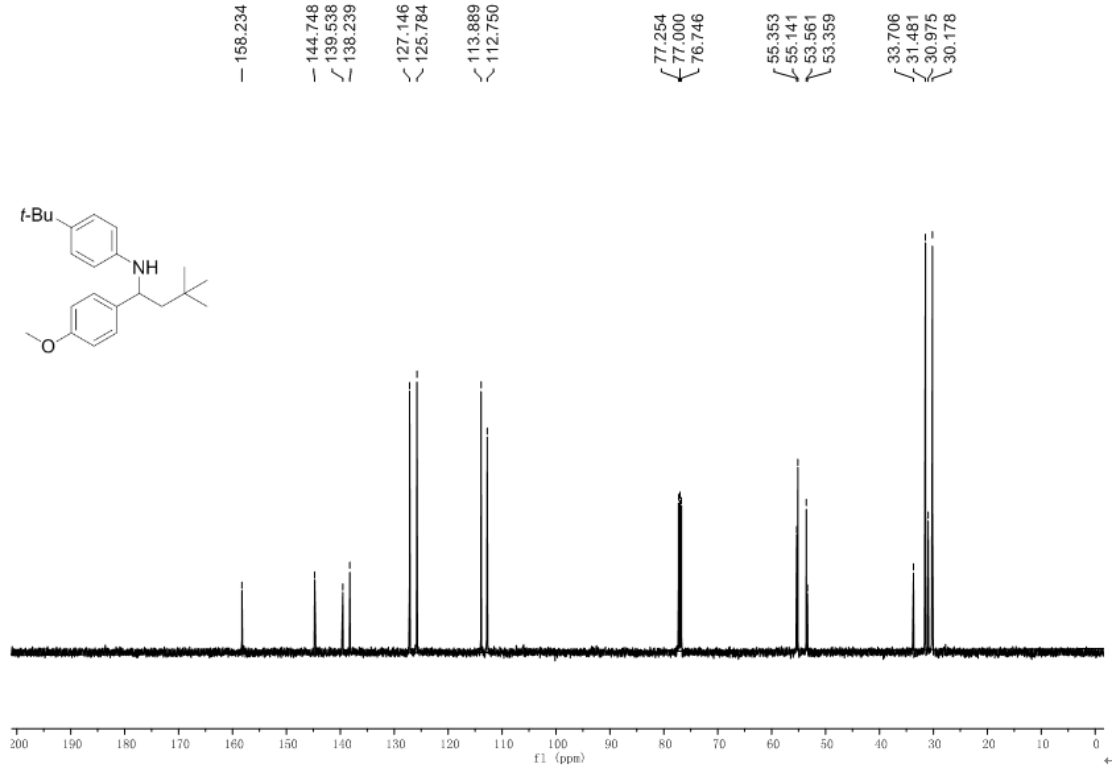


^{13}C-NMR (125 MHz, $CDCl_3$)

4-(Tert-butyl)-*N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)aniline (4aax):

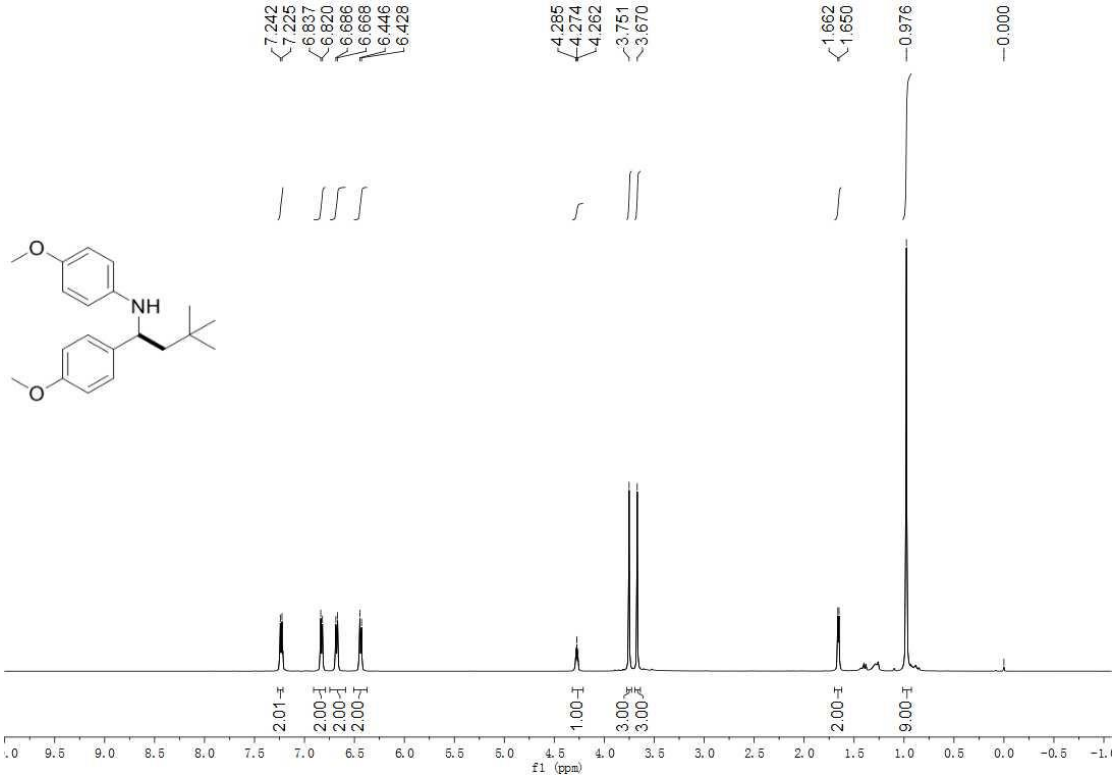


^{1}H-NMR (500 MHz, $CDCl_3$)

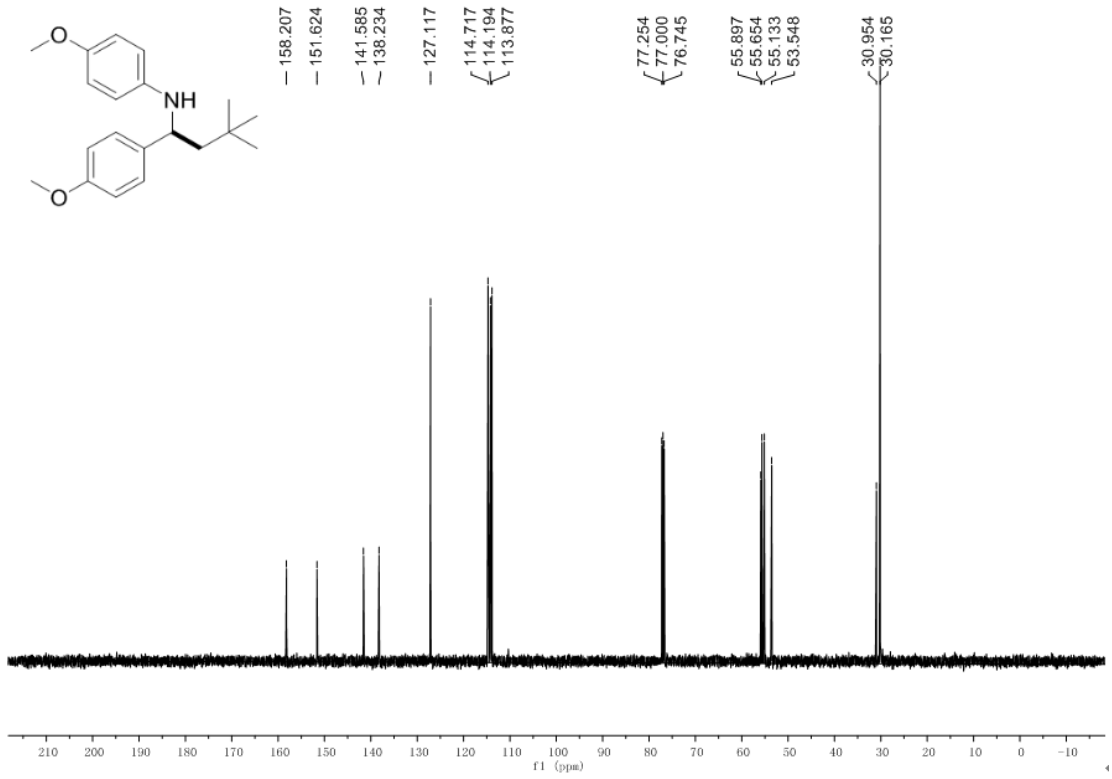


^{13}C-NMR (125 MHz, $CDCl_3$)

4-methoxy-*N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)aniline (4aay)：

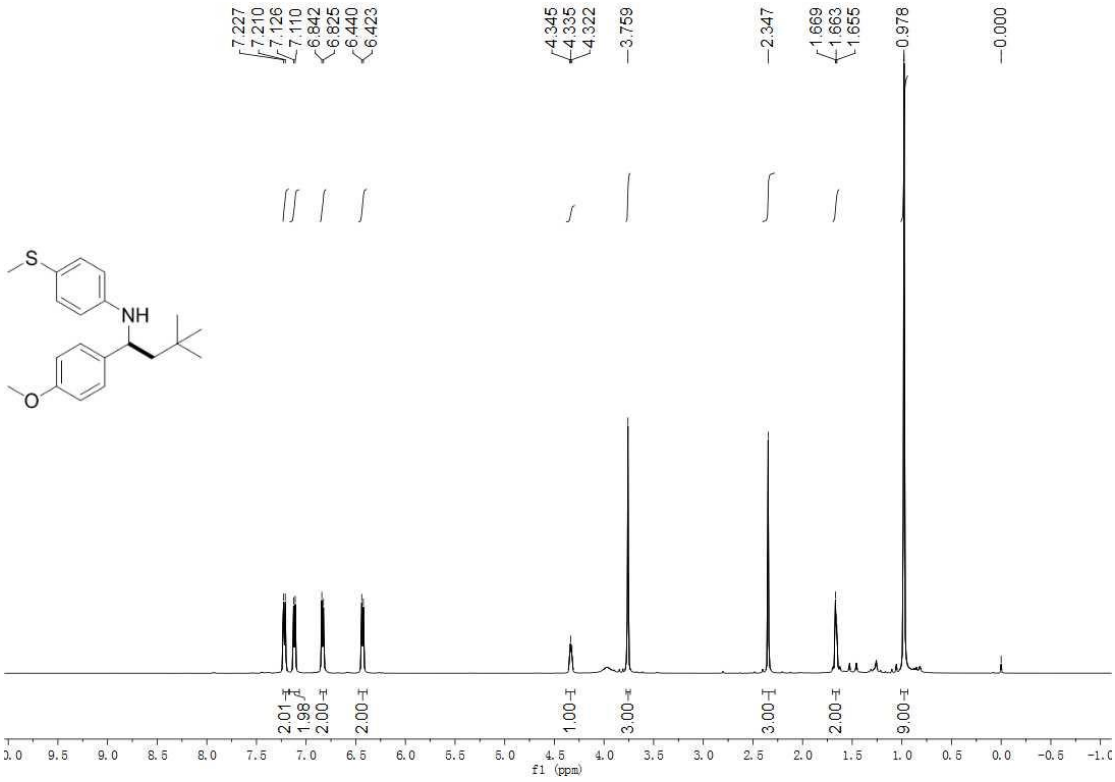


^{1}H-NMR (500 MHz, $CDCl_3$)

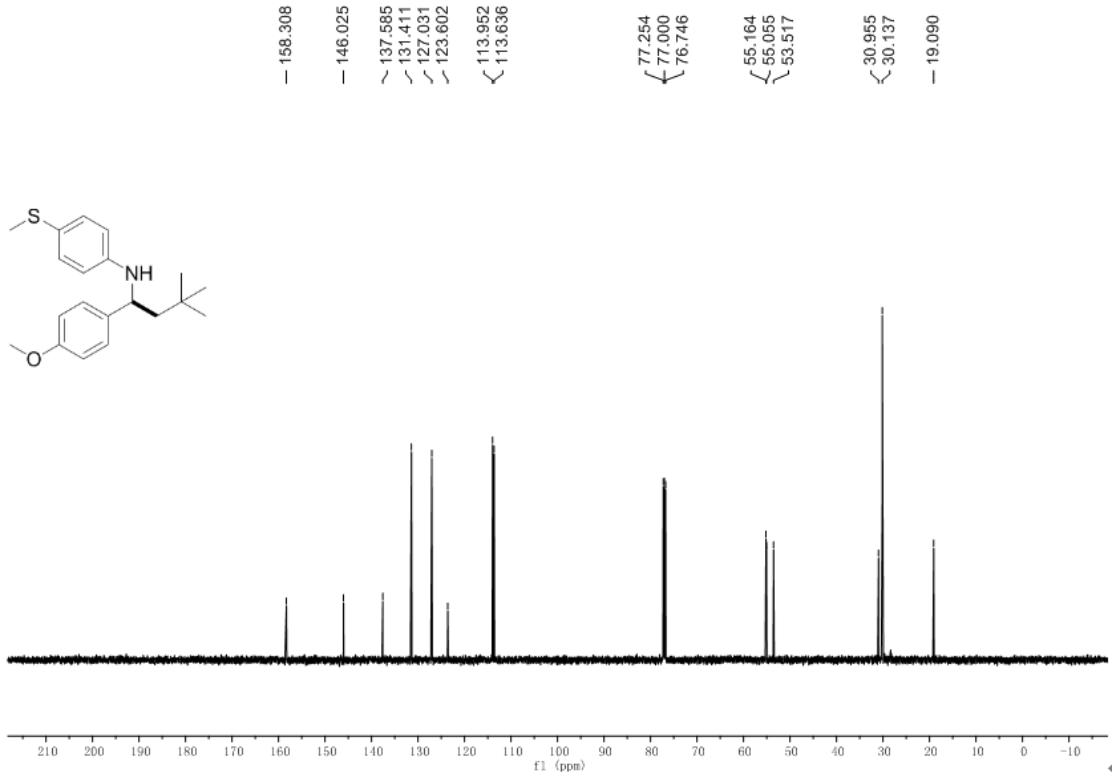


^{13}C-NMR (125 MHz, $CDCl_3$)

***N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-4-(methylthio)aniline (4aaz):**

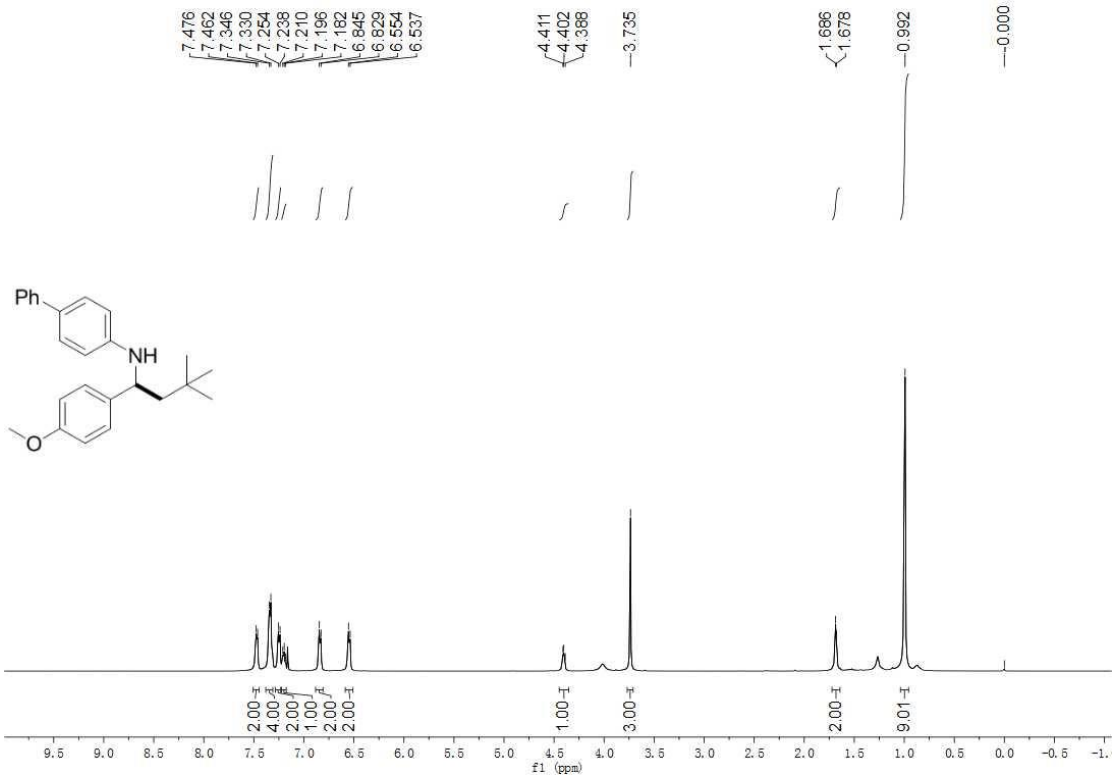


^{1}H-NMR (500 MHz, $CDCl_3$)

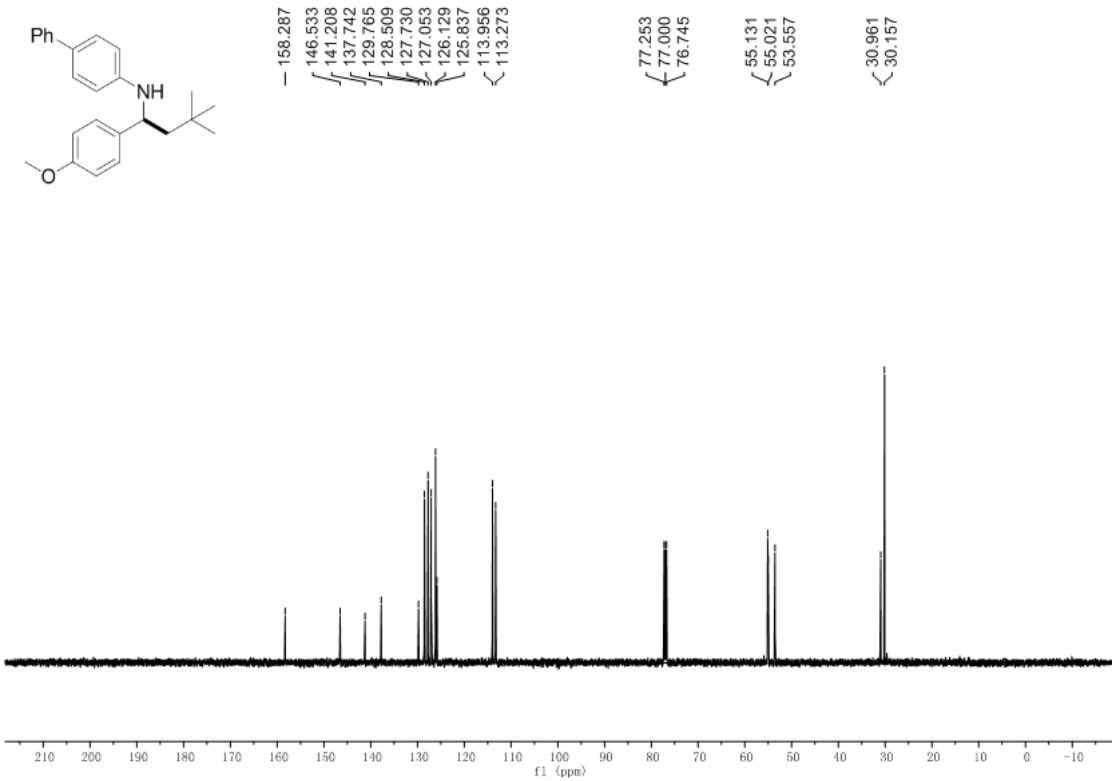


^{13}C-NMR (125 MHz, $CDCl_3$)

***N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-[1,1'-biphenyl]-4-amine (4aaaa):**

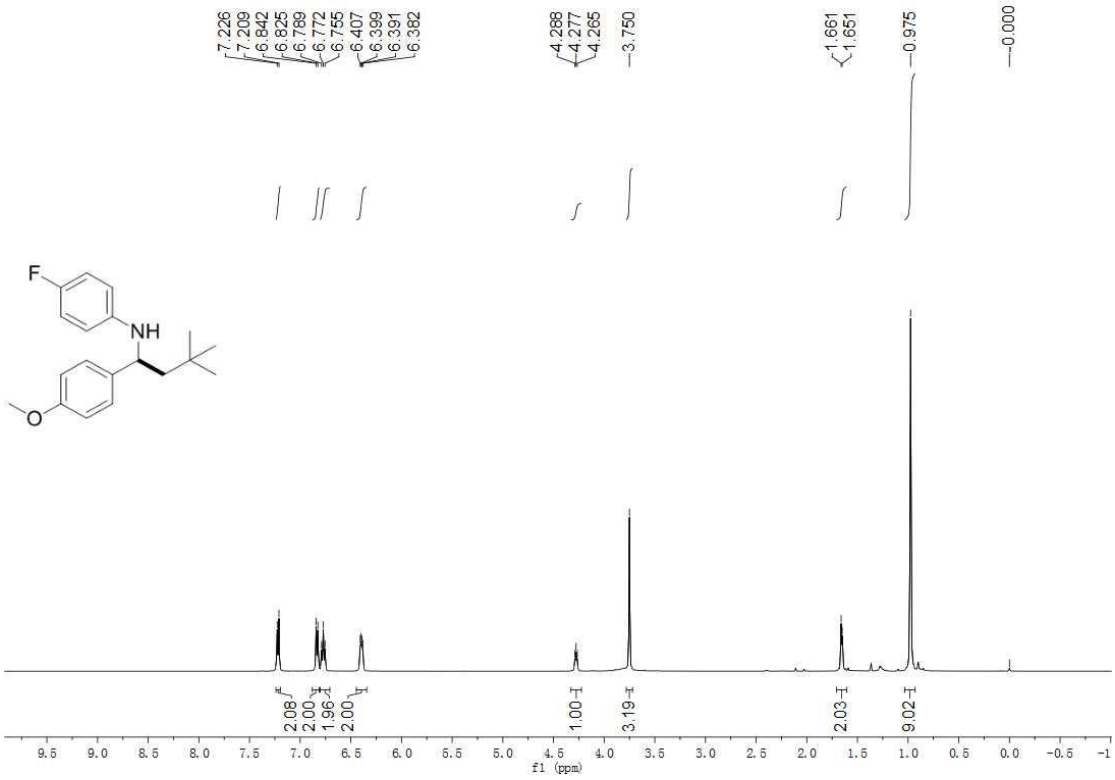


^{1}H-NMR (500 MHz, $CDCl_3$)

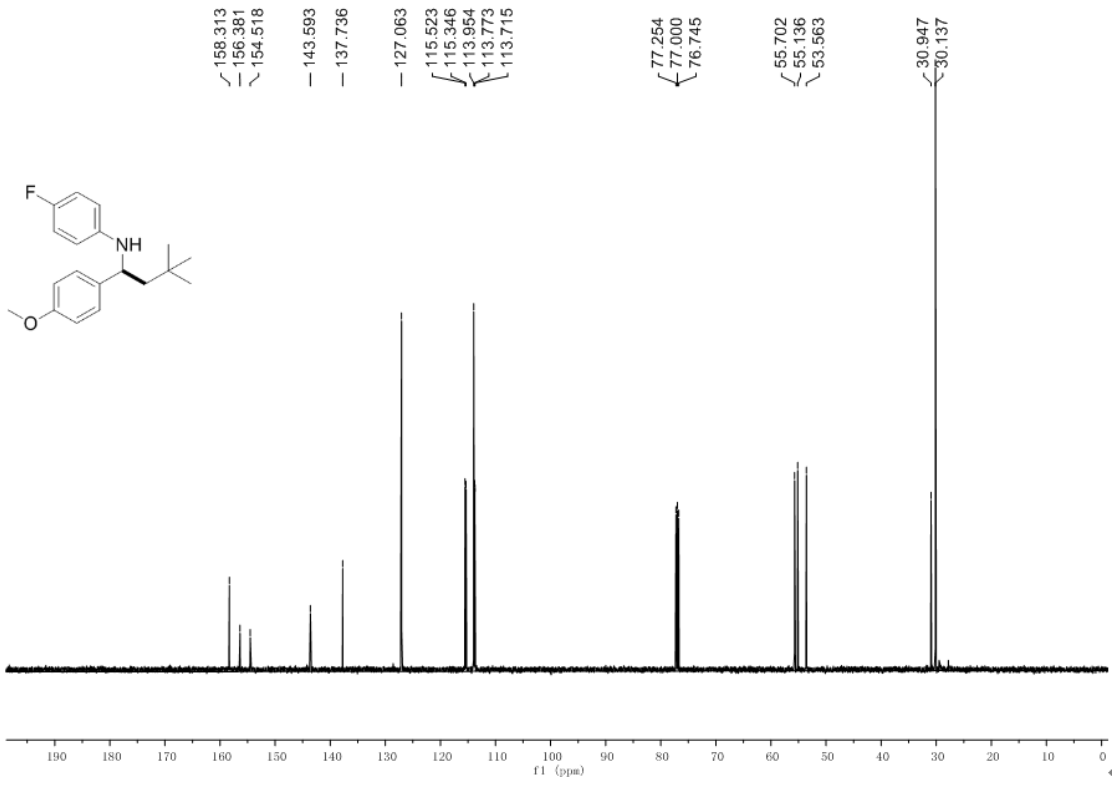


^{13}C-NMR (125 MHz, $CDCl_3$)

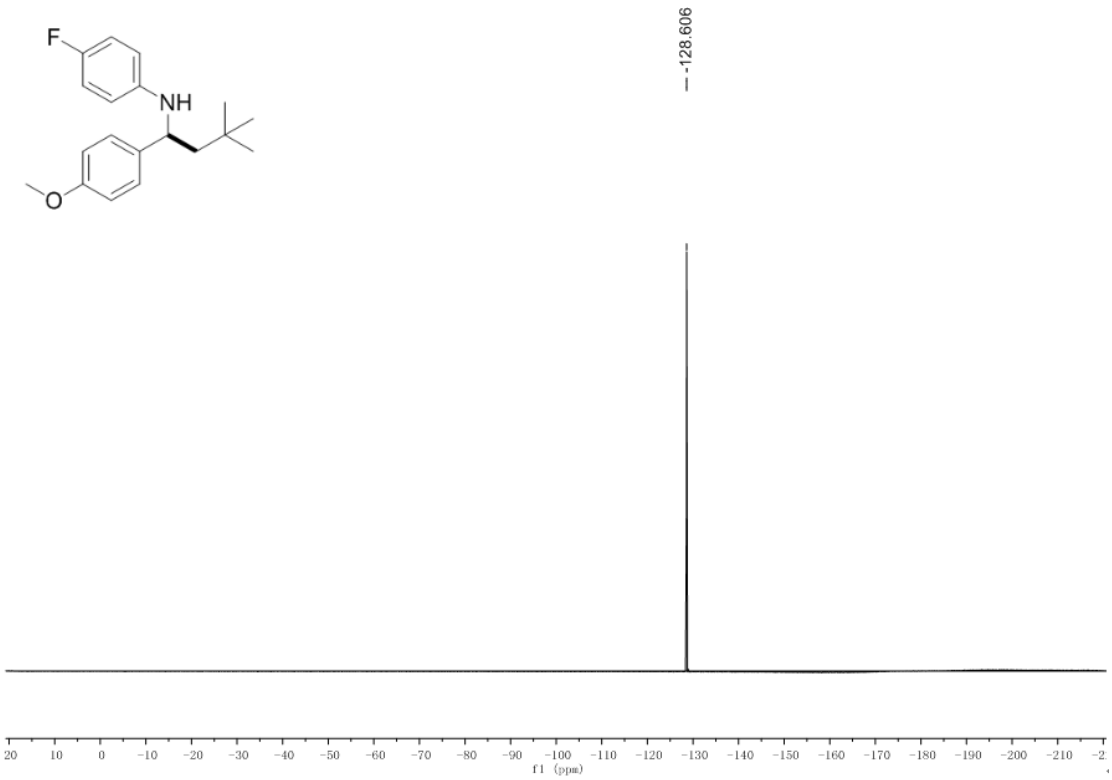
4-fluoro-*N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)aniline (4aaab)：



^{1}H-NMR (500 MHz, $CDCl_3$)

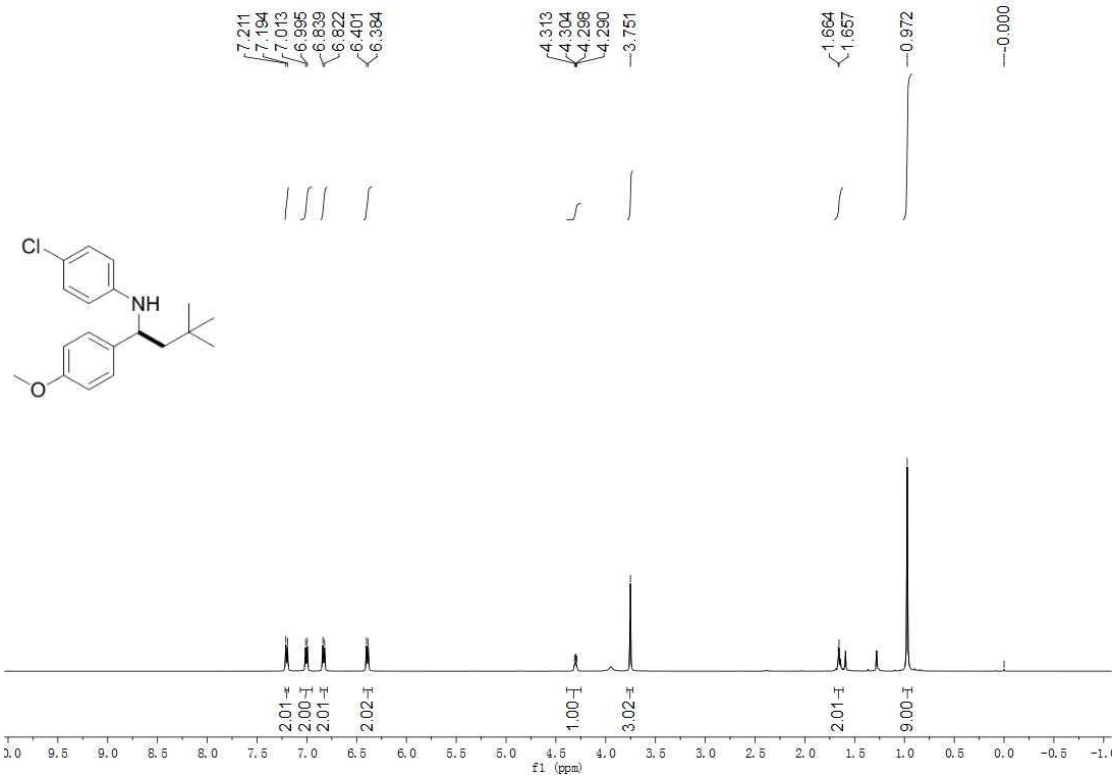


^{13}C-NMR (125 MHz, $CDCl_3$)

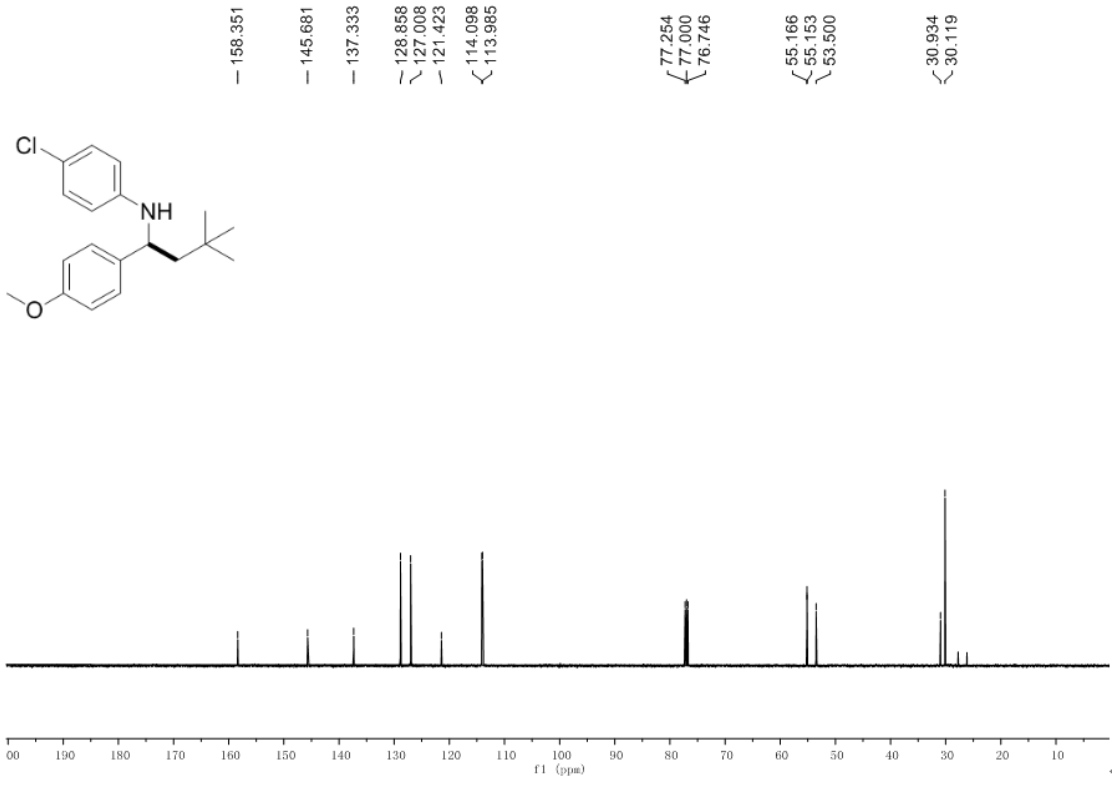


^{19}F NMR (471 MHz, $CDCl_3$)

4-chloro-*N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)aniline (4aaac):

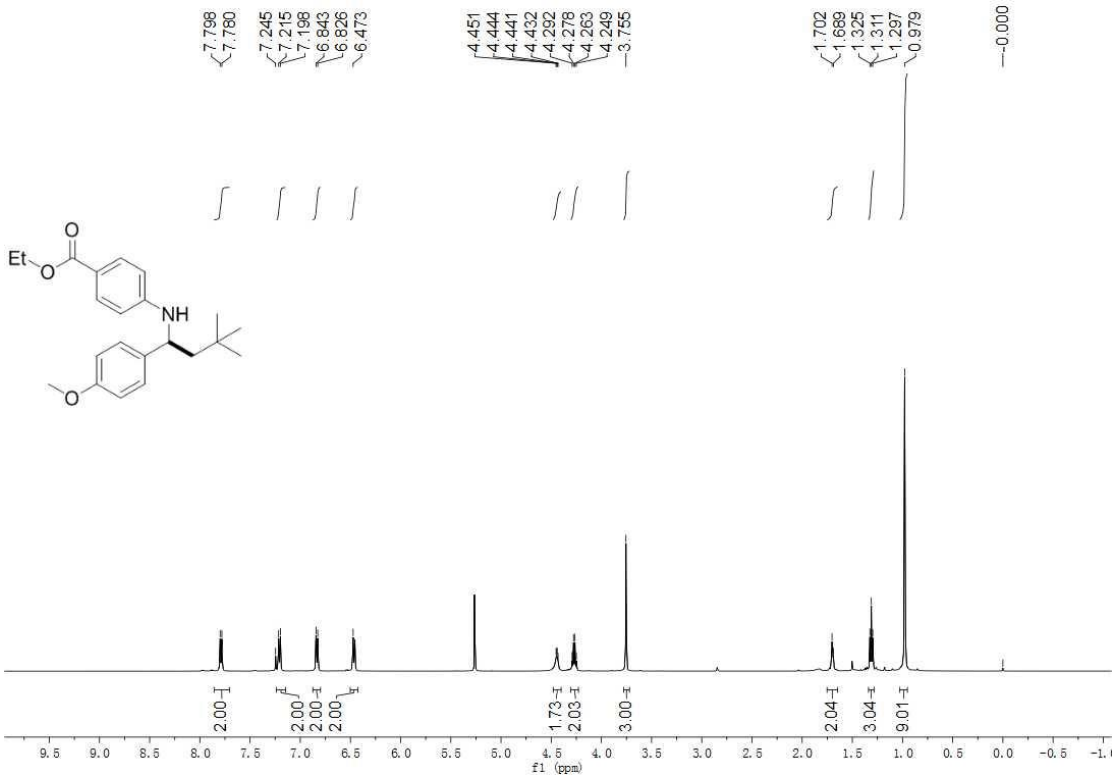


^{1}H-NMR (500 MHz, $CDCl_3$)

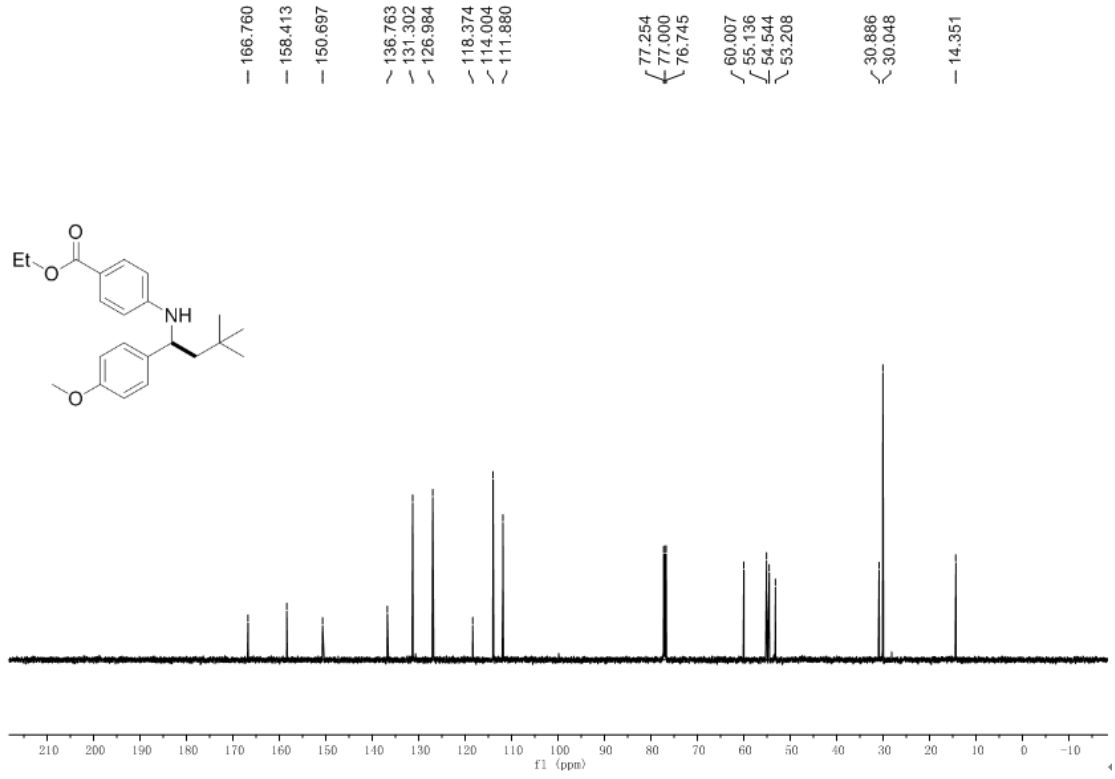


^{13}C-NMR (125 MHz, $CDCl_3$)

Ethyl-4-((1-(4-methoxyphenyl)-3,3-dimethylbutyl)amino)benzoate (4aaad)：

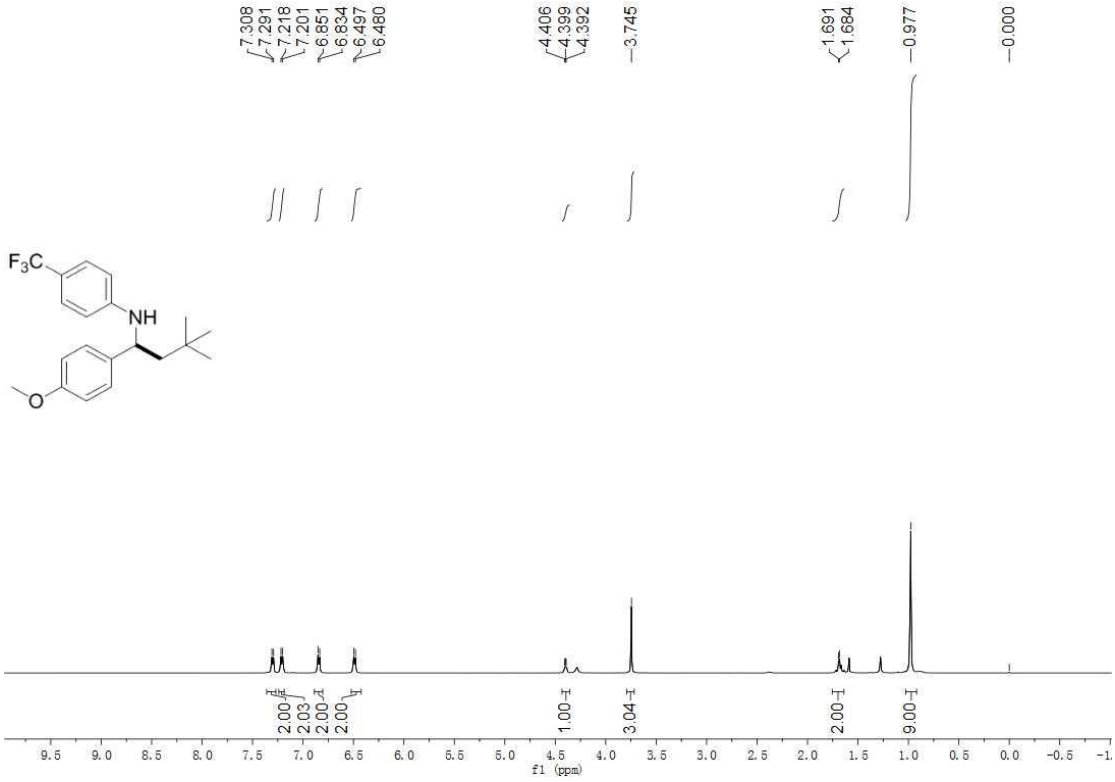


^{1}H-NMR (500 MHz, $CDCl_3$)

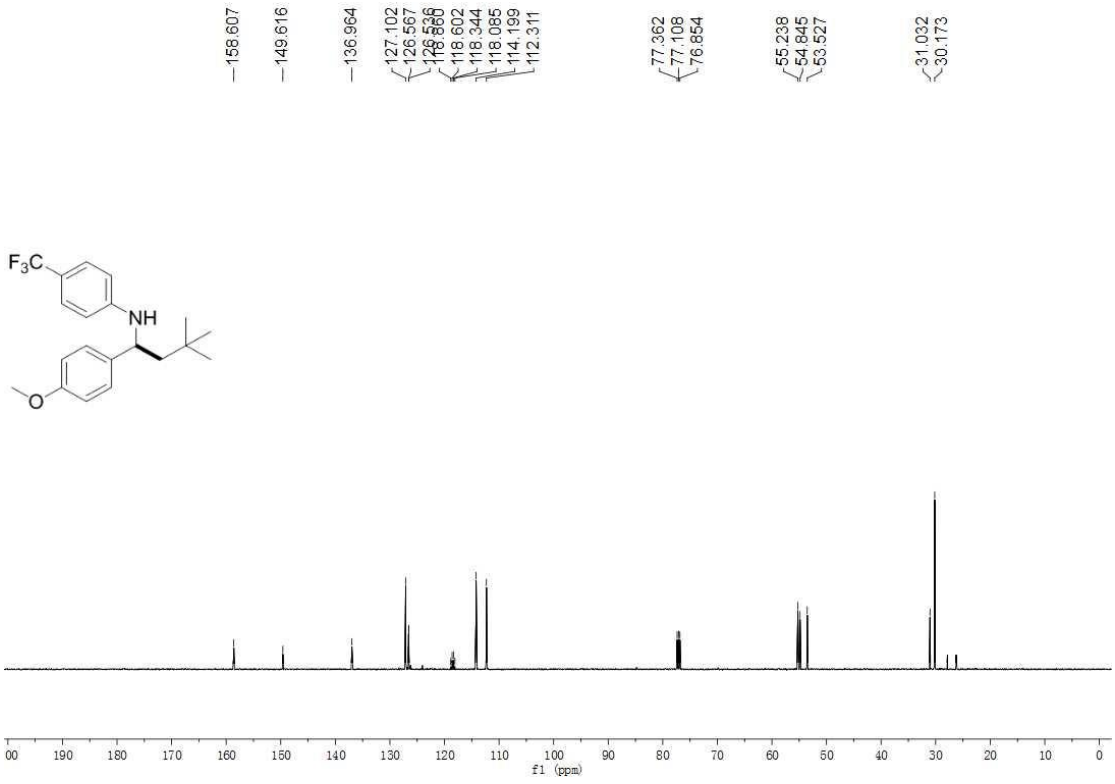


^{13}C-NMR (125 MHz, $CDCl_3$)

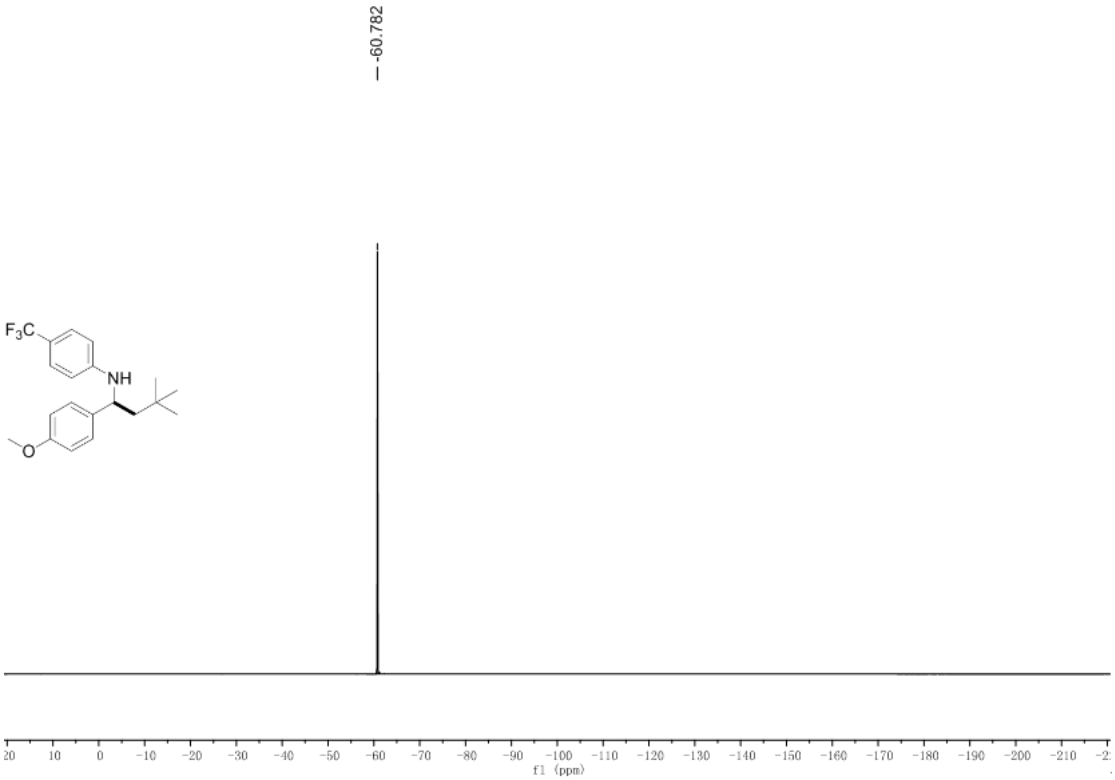
***N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-4-(trifluoromethyl)aniline (4aaae)：**



^{1}H-NMR (500 MHz, $CDCl_3$)

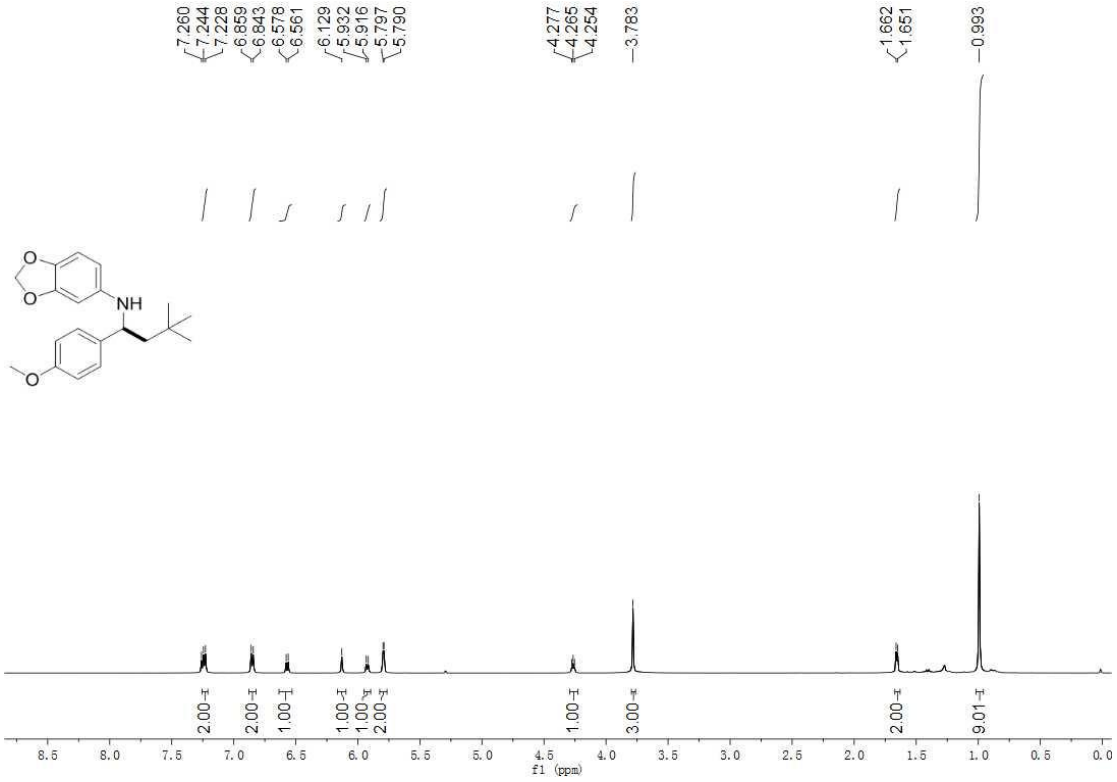


^{13}C-NMR (125 MHz, $CDCl_3$)

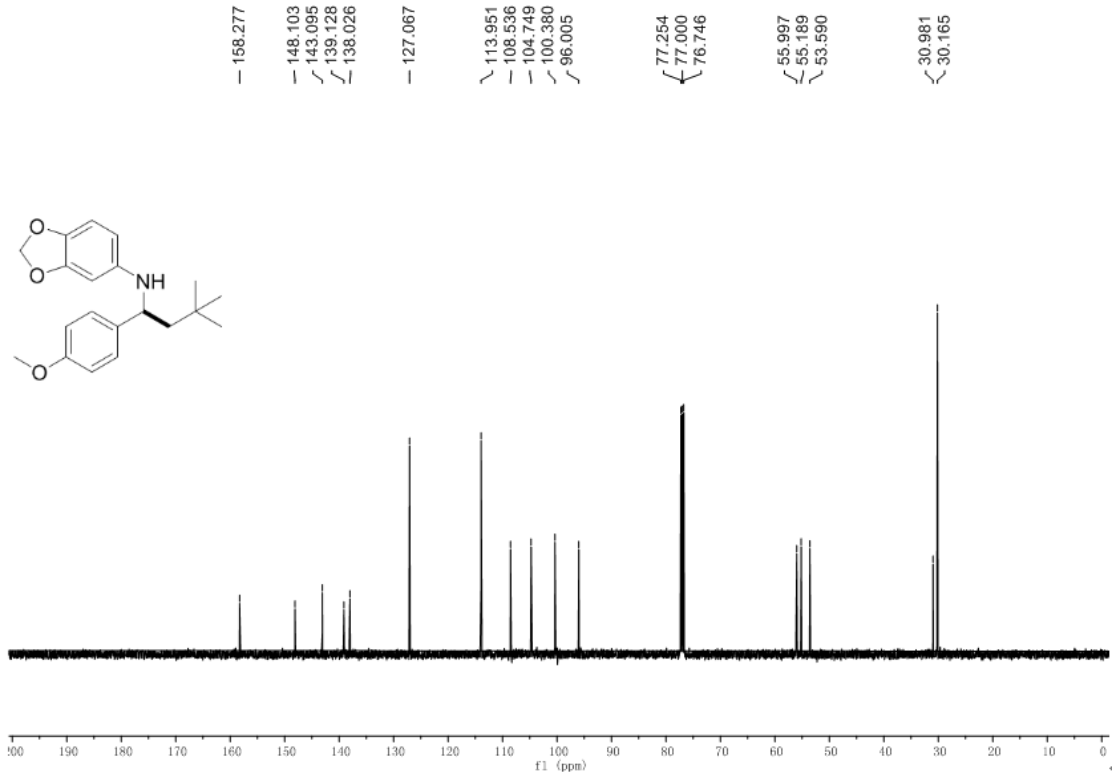


^{19}F NMR (471 MHz, $CDCl_3$)

***N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)benzo[d][1,3]dioxol-5-amine (4aaaf)：**

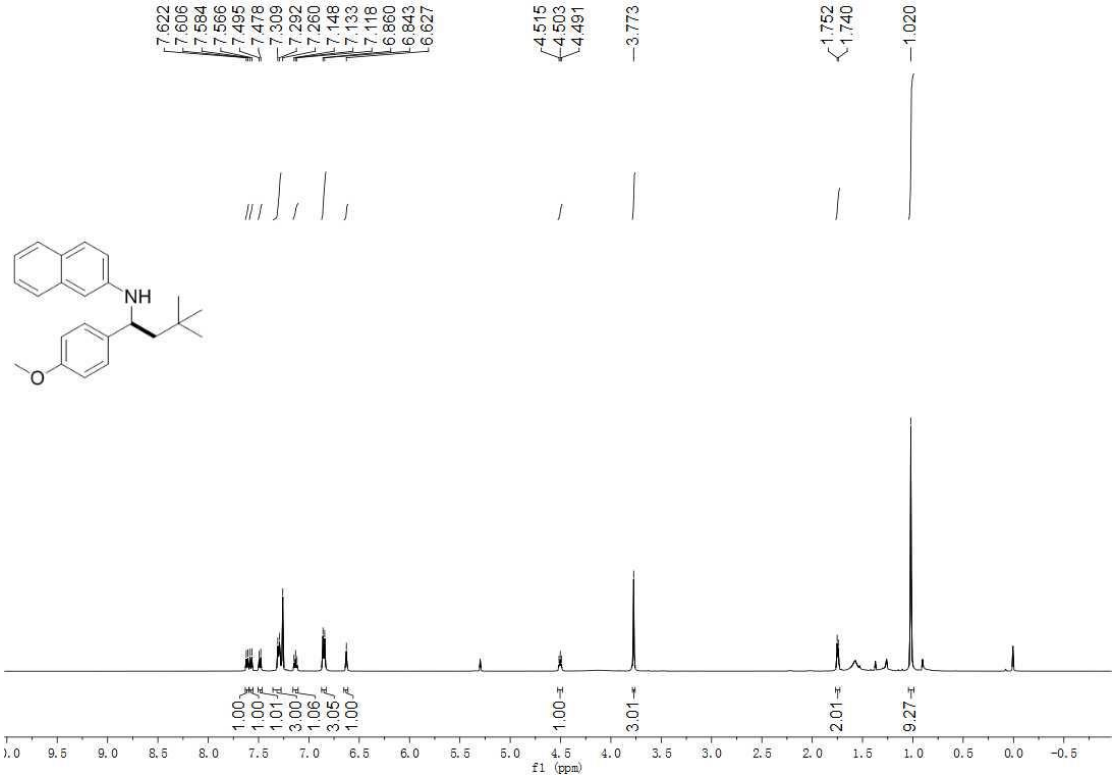


^{1}H-NMR (500 MHz, $CDCl_3$)

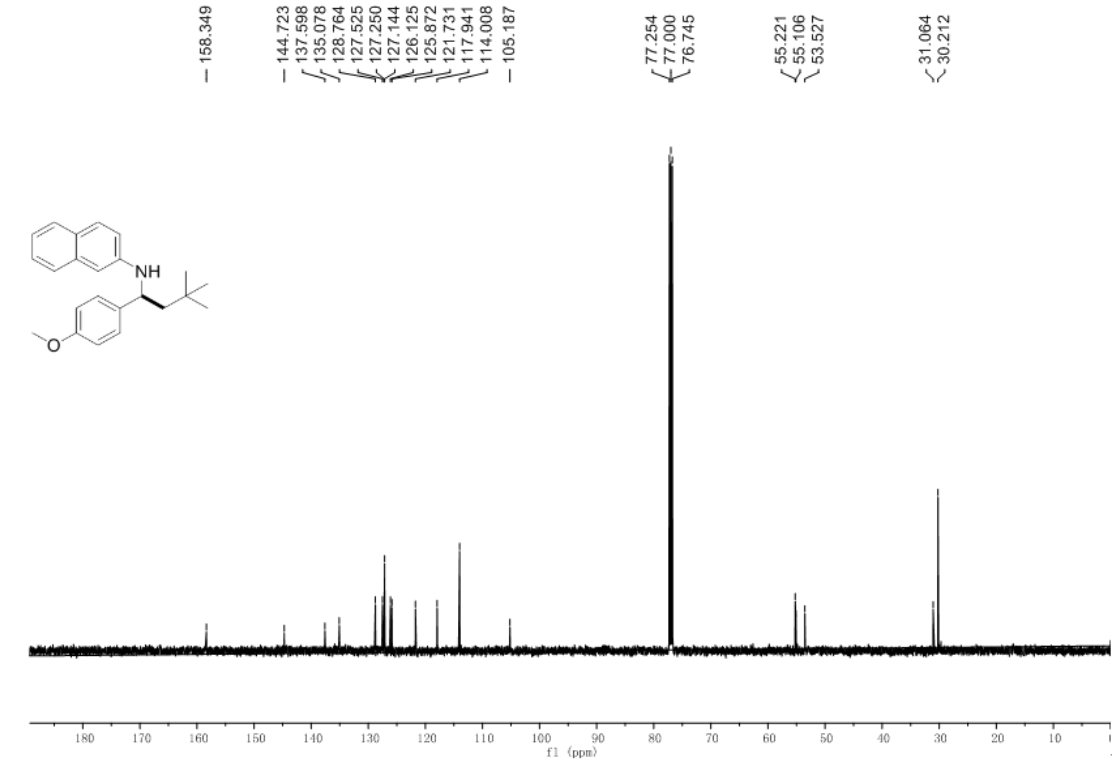


^{13}C-NMR (125 MHz, $CDCl_3$)

***N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)naphthalen-2-amine (4aaag)：**

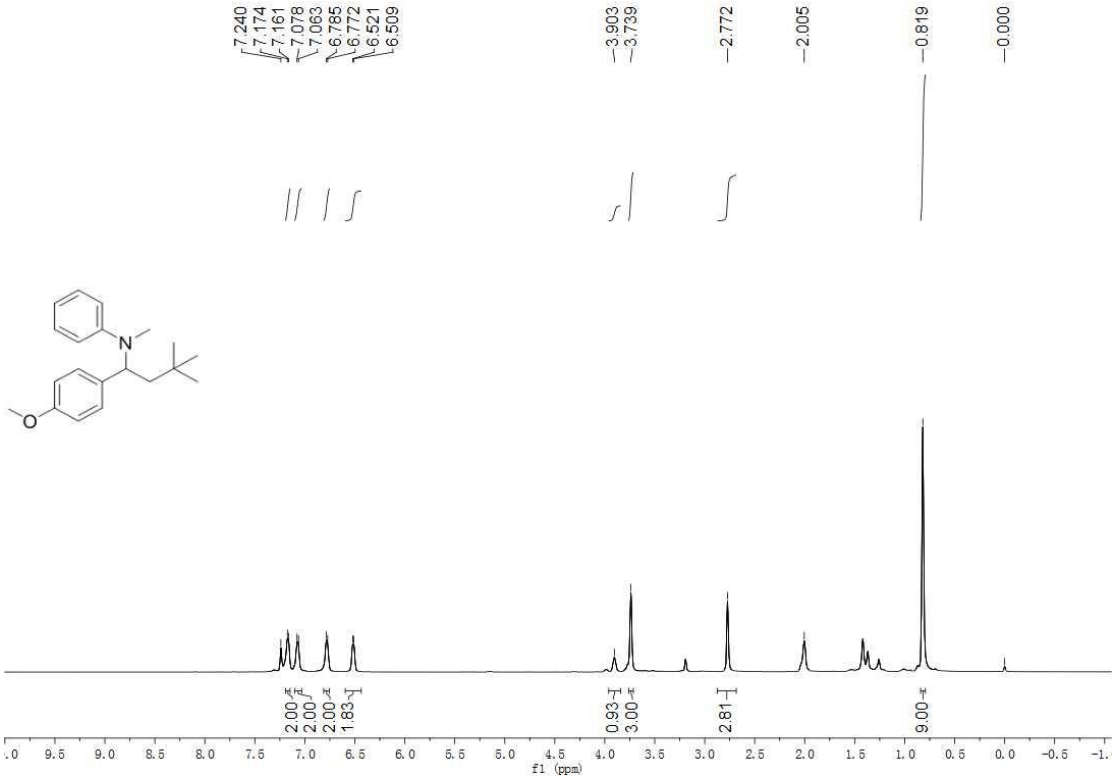


^{1}H-NMR (500 MHz, $CDCl_3$)

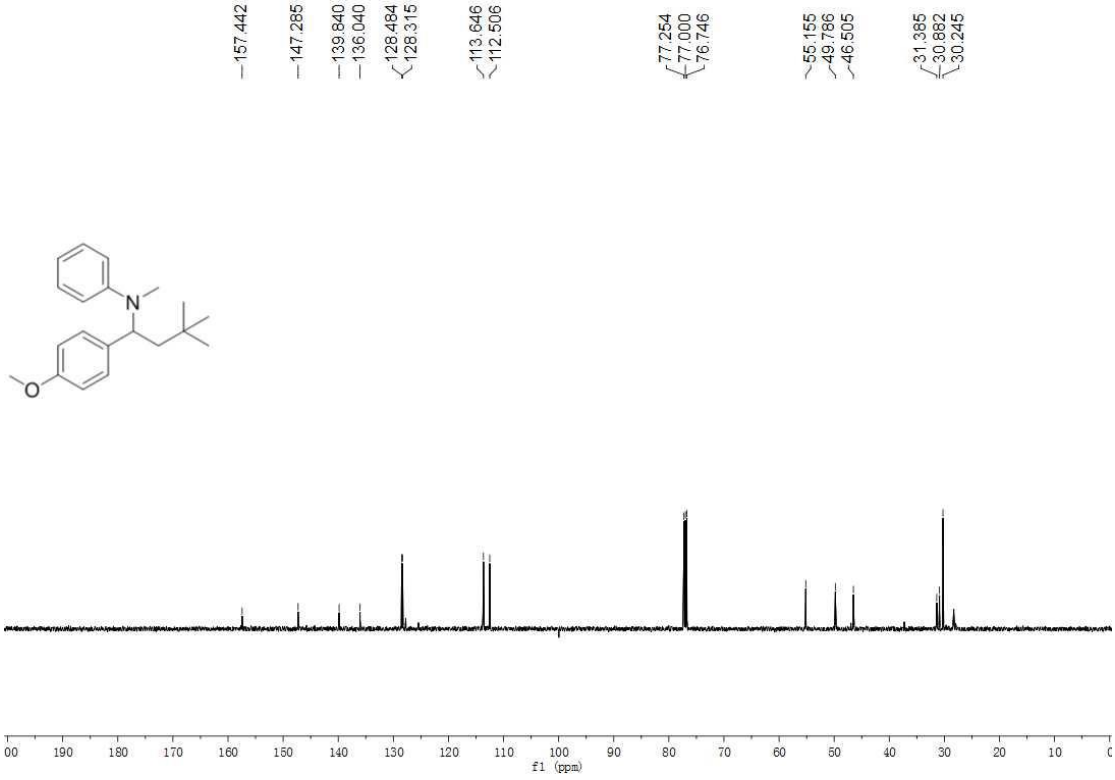


^{13}C-NMR (125 MHz, $CDCl_3$)

***N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-*N*-methylaniline (4aaai)：**

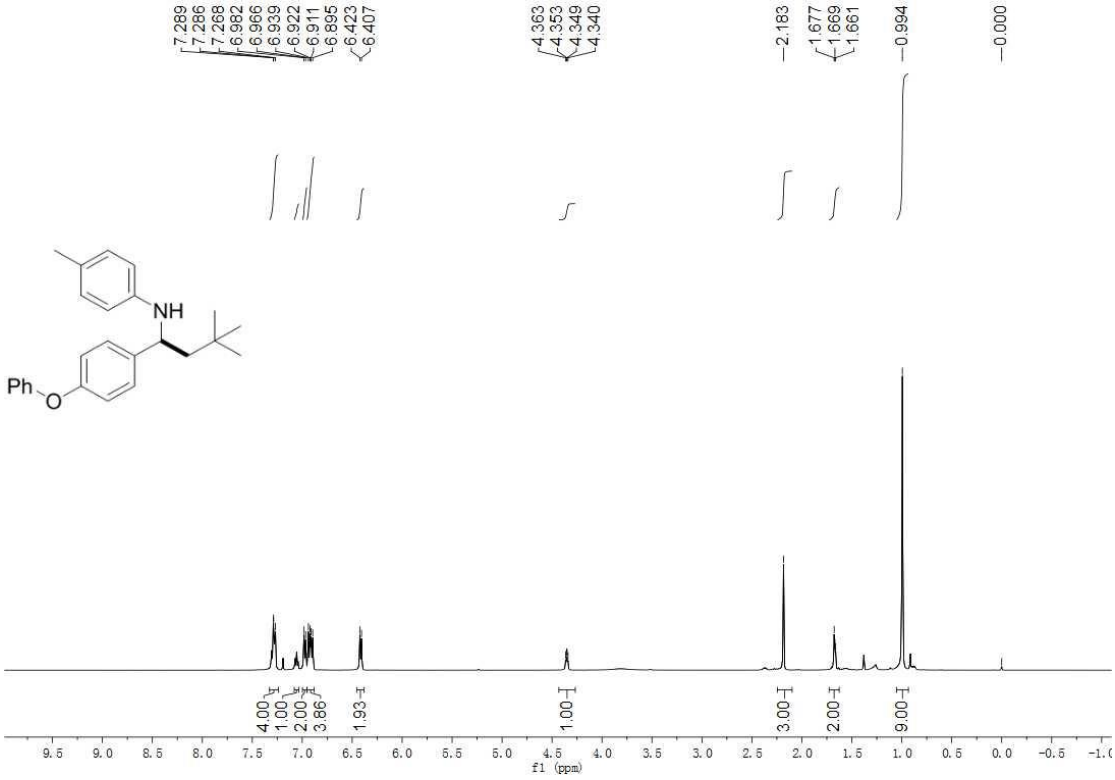


^{1}H-NMR (500 MHz, $CDCl_3$)

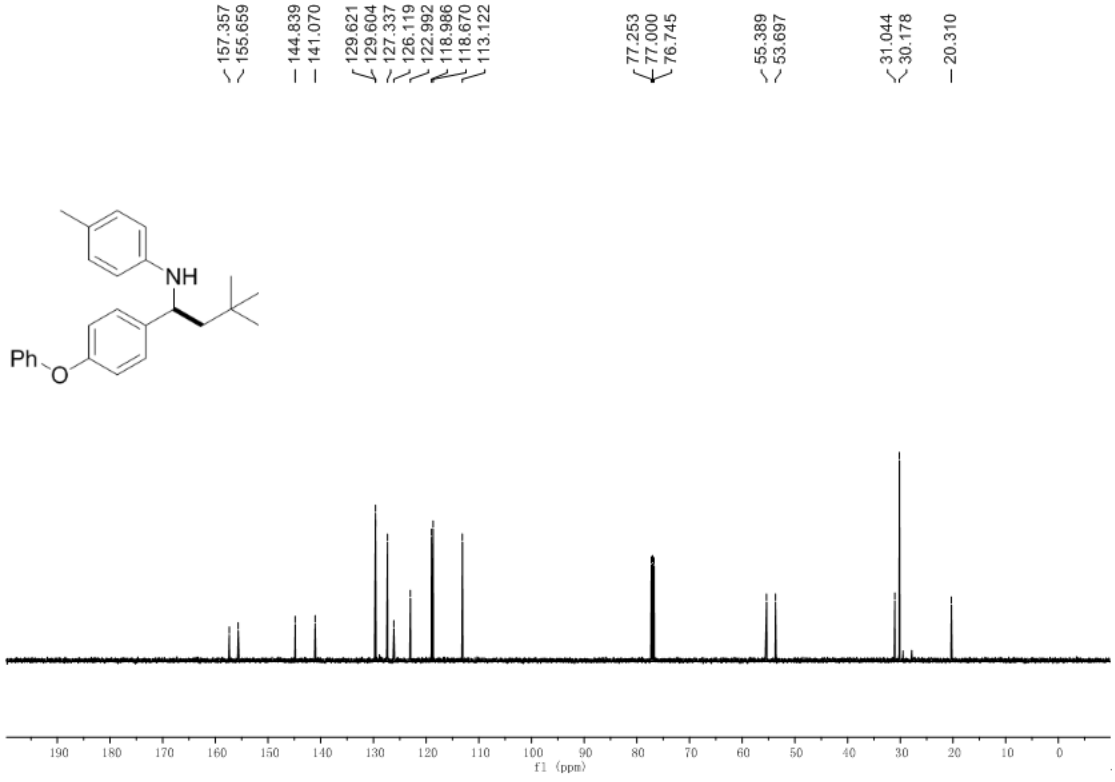


^{13}C-NMR (125 MHz, $CDCl_3$)

***N*-(3,3-dimethyl-1-(4-phenoxyphenyl)butyl)-4-methylaniline (4caw):**

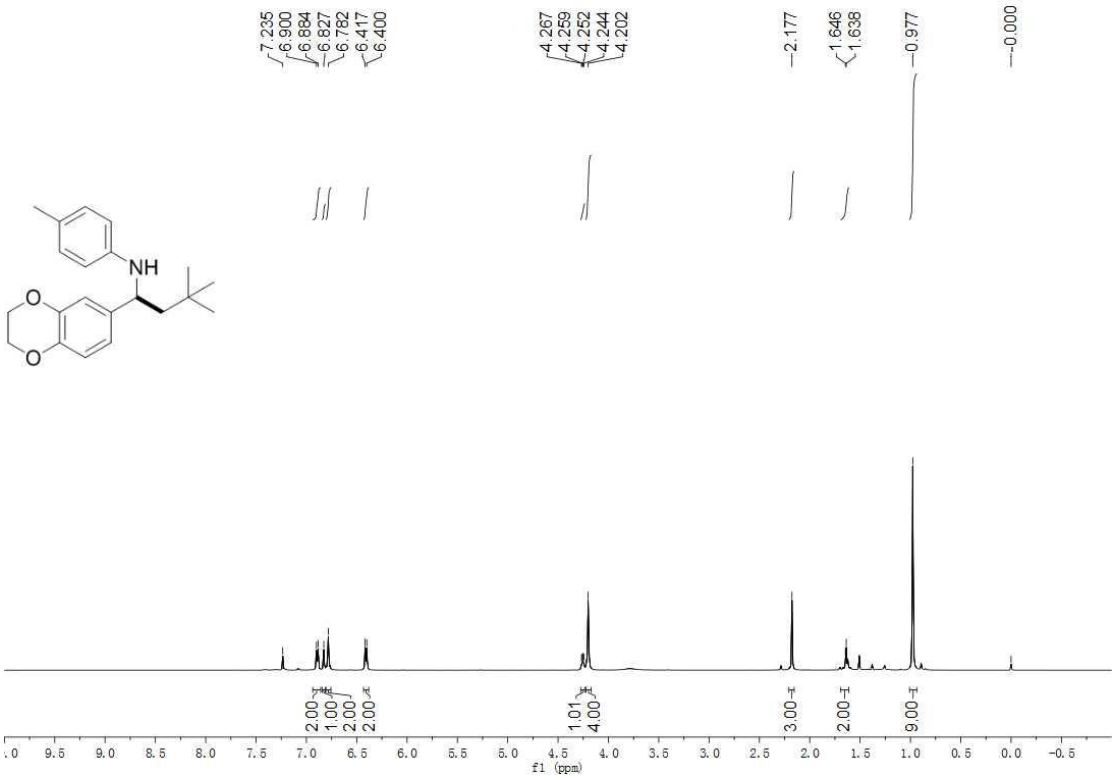


^{1}H-NMR (500 MHz, $CDCl_3$)

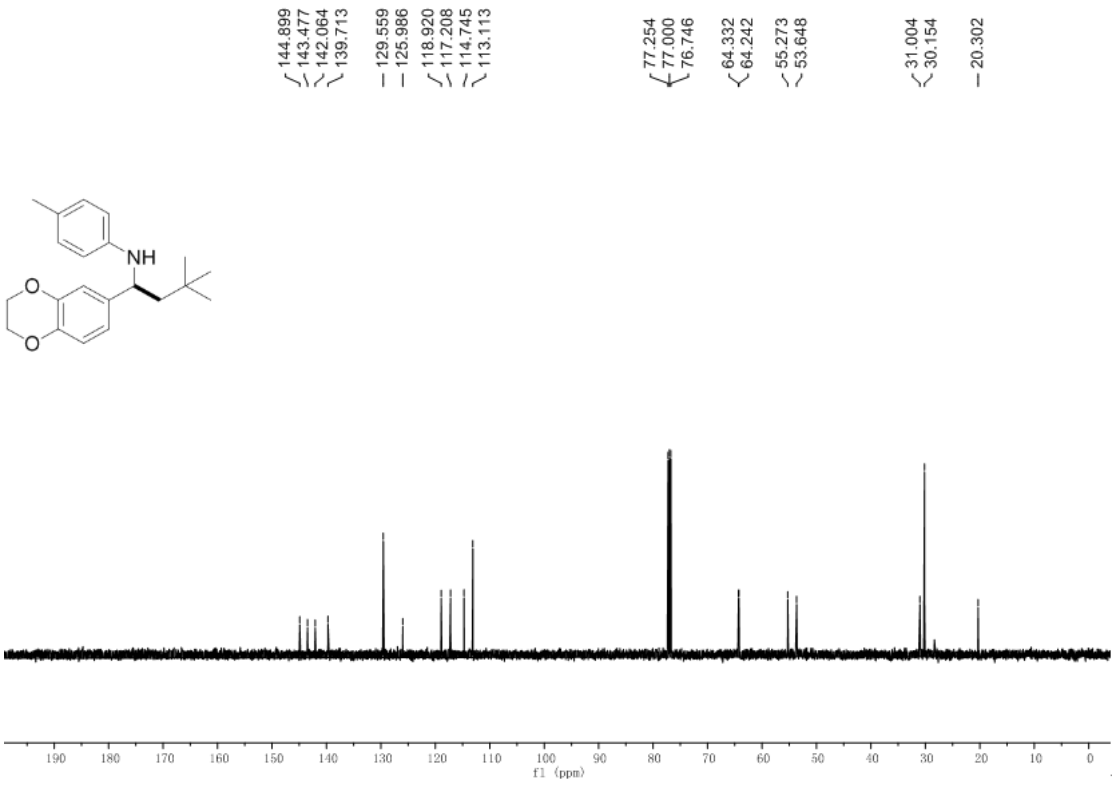


^{13}C-NMR (125 MHz, $CDCl_3$)

***N*-(1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-3,3-dimethylbutyl)-4-methylaniline (4gaw):**

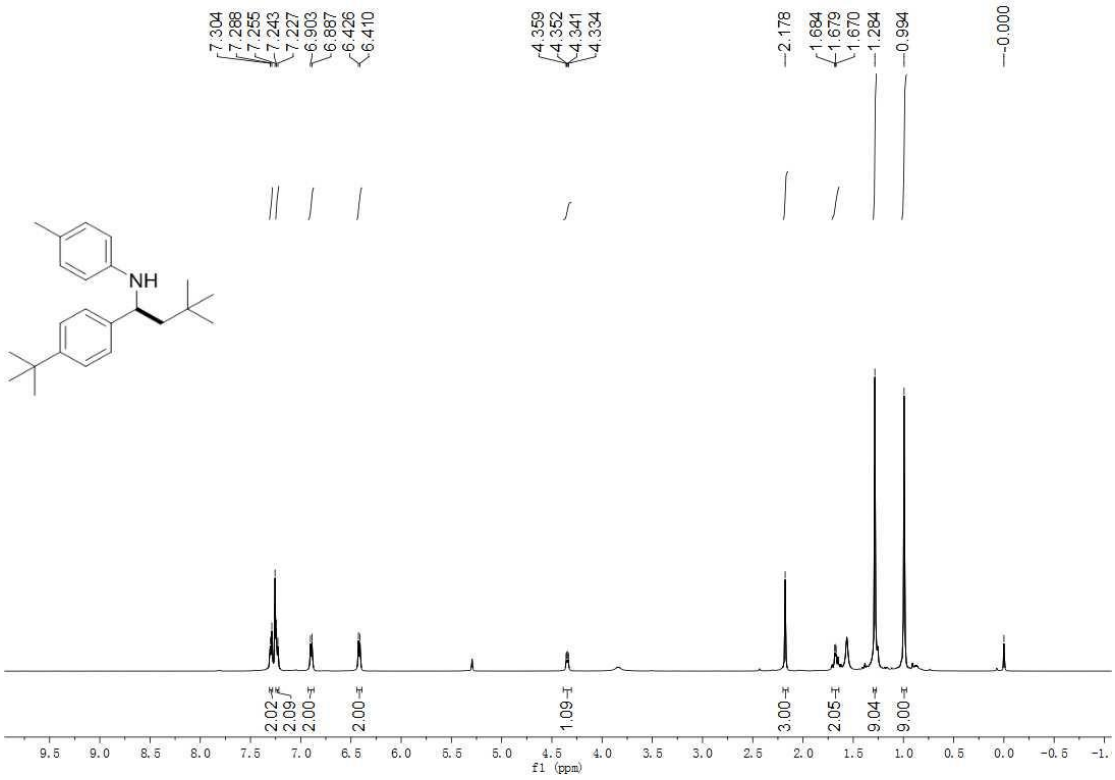


^{1}H-NMR (500 MHz, $CDCl_3$)

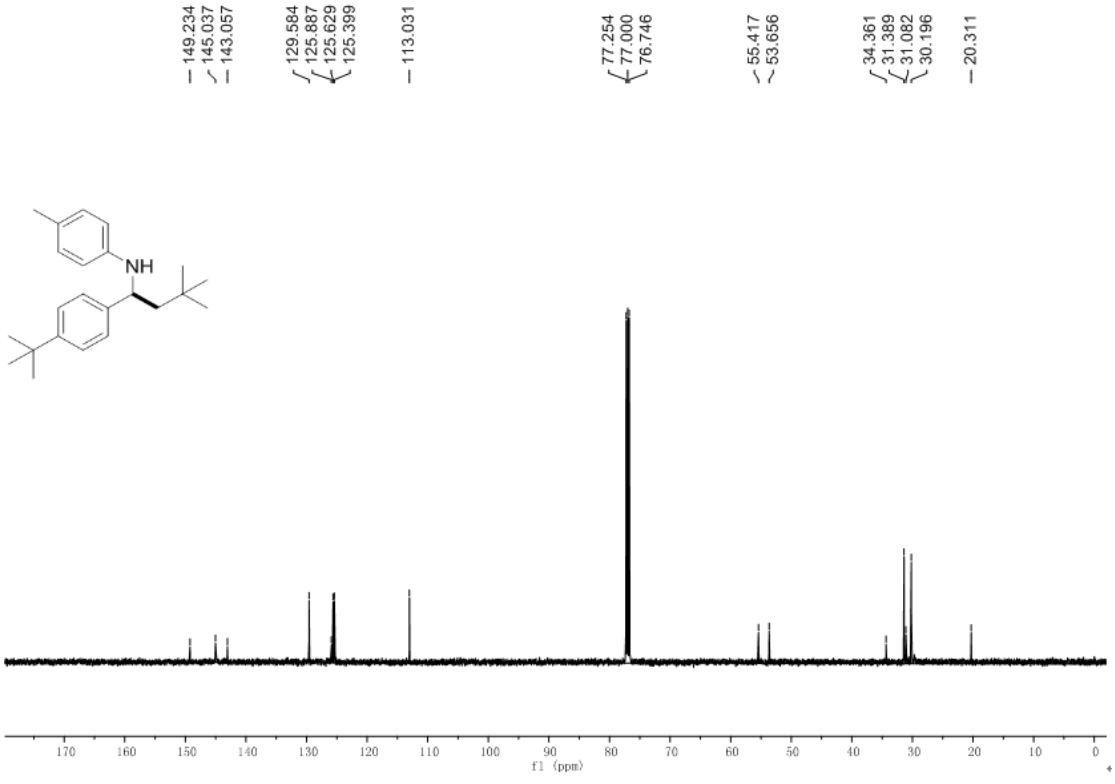


^{13}C-NMR (125 MHz, $CDCl_3$)

***N*-(1-(4-(tert-butyl)phenyl)-3,3-dimethylbutyl)-4-methylaniline (4naw)：**

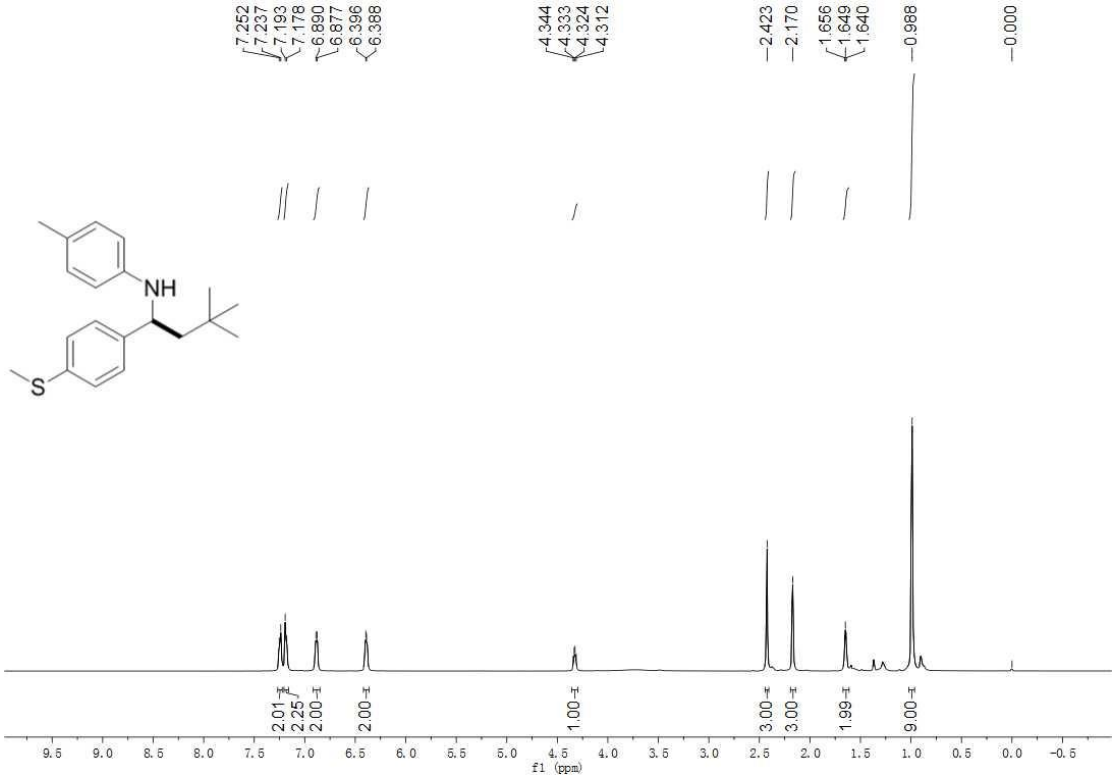


^{1}H-NMR (500 MHz, $CDCl_3$)

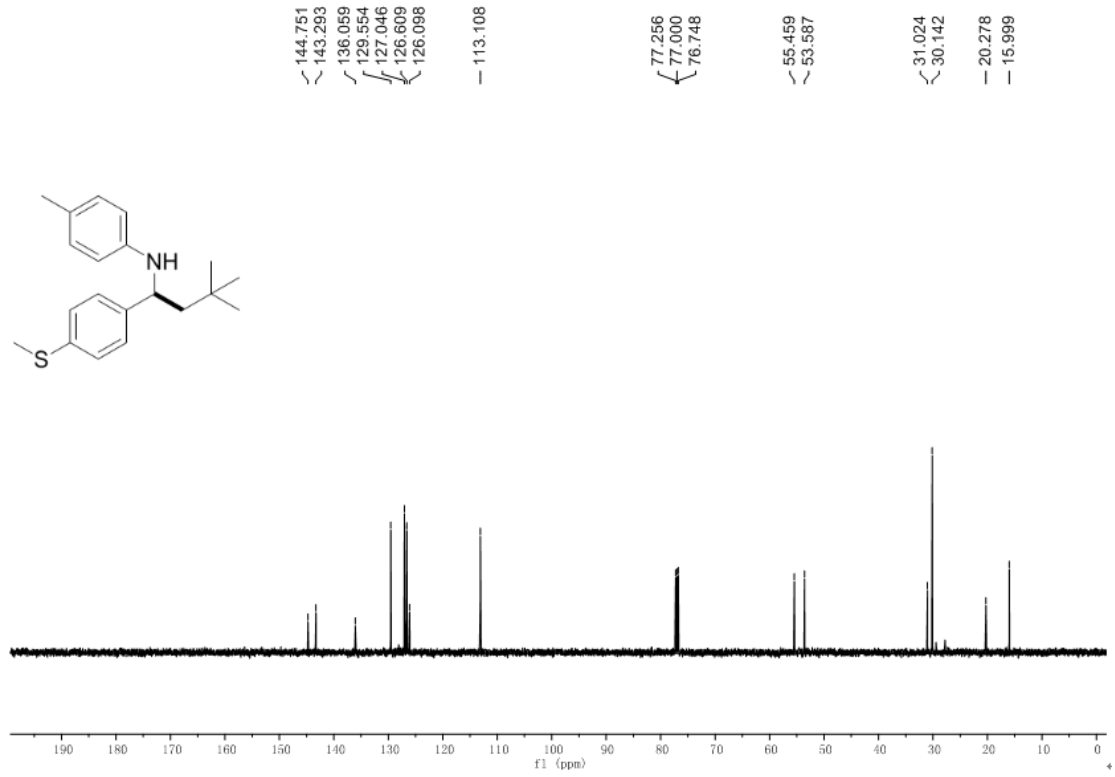


^{13}C-NMR (125 MHz, $CDCl_3$)

***N*-(3,3-dimethyl-1-(4-(methylthio)phenyl)butyl)-4-methylaniline (4oaw):**

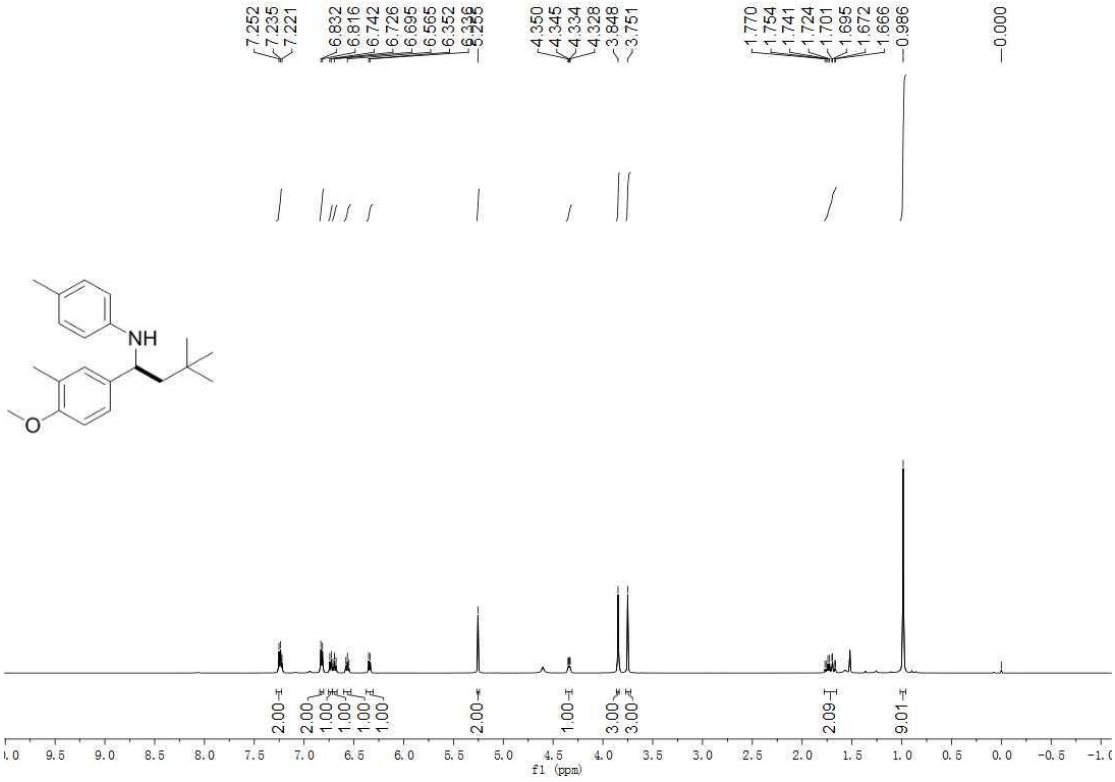


^{1}H-NMR (500 MHz, $CDCl_3$)

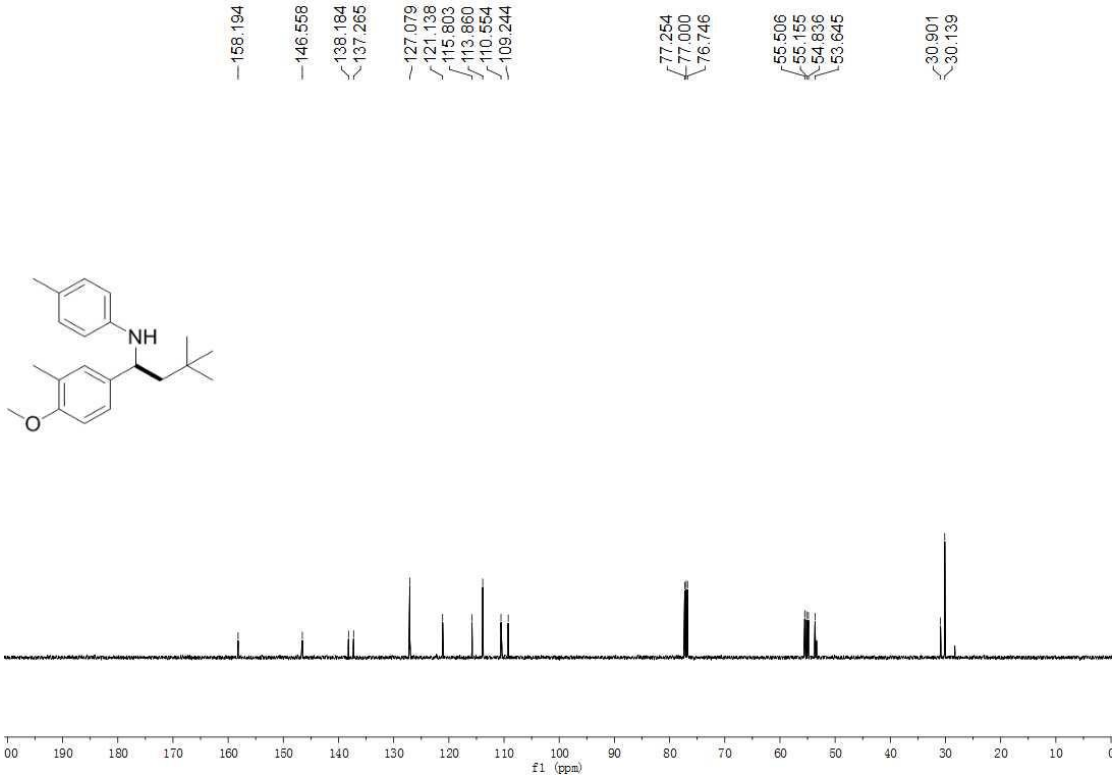


^{13}C-NMR (125 MHz, $CDCl_3$)

***N*-(1-(4-methoxy-3-methylphenyl)-3,3-dimethylbutyl)-4-methylaniline (4paw)：**

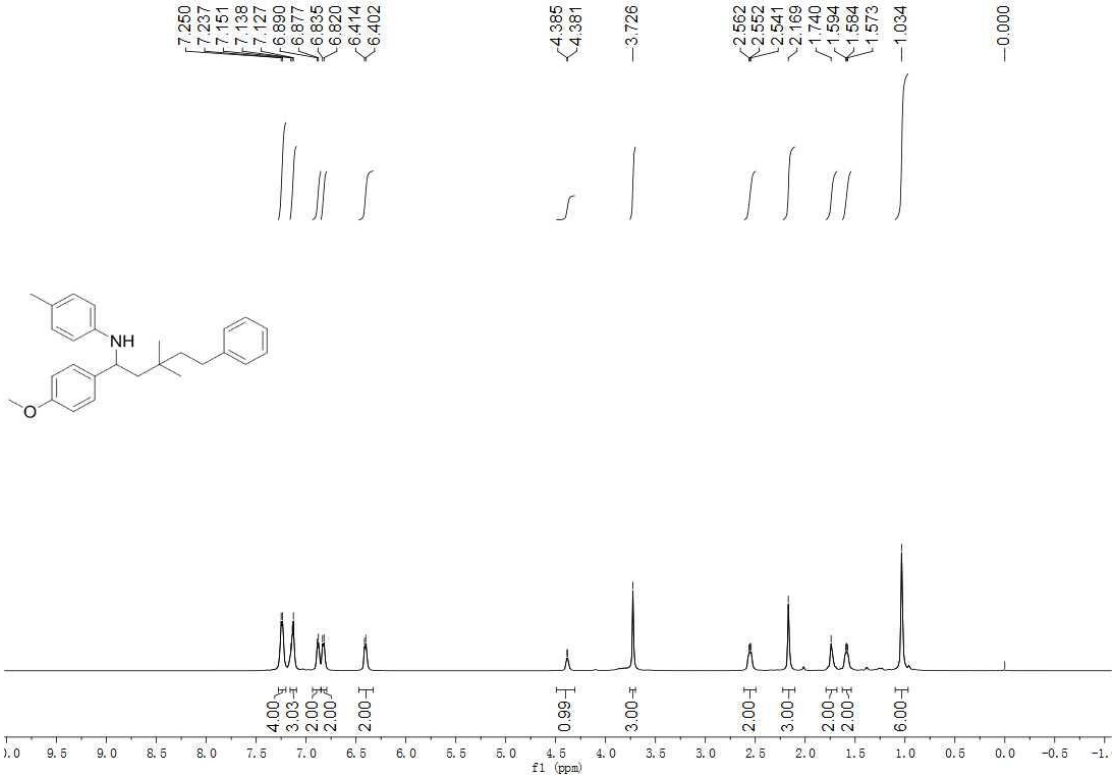


^{1}H-NMR (500 MHz, $CDCl_3$)

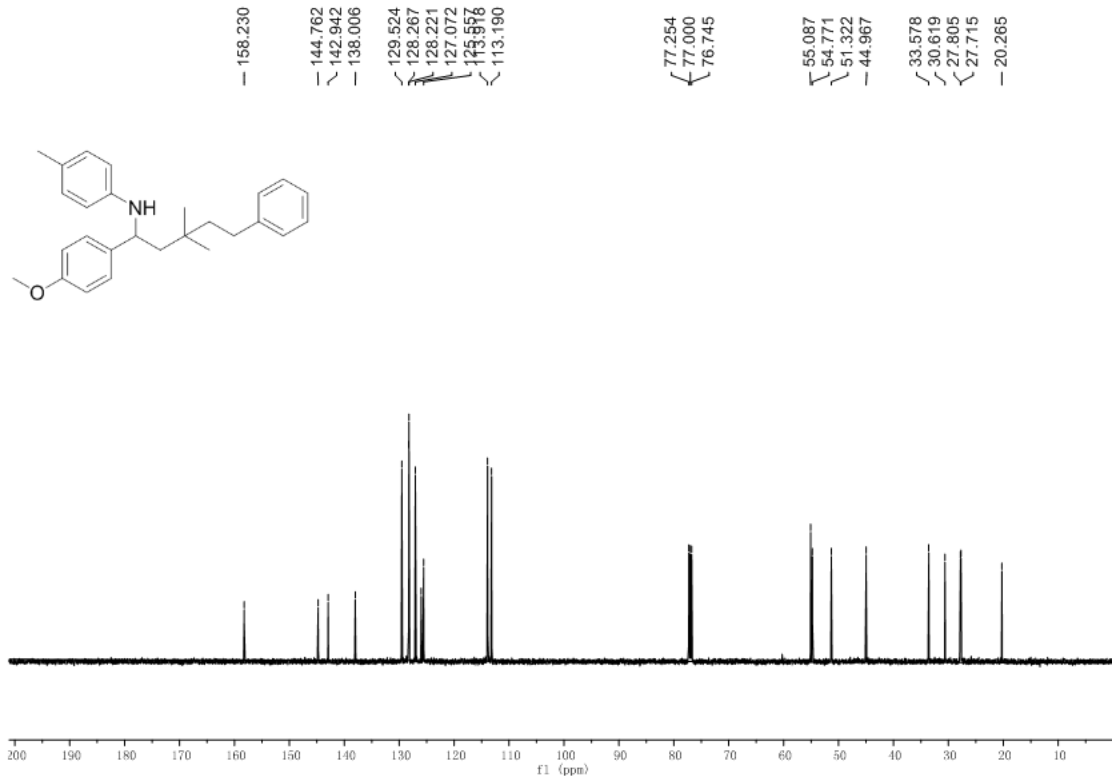


^{13}C-NMR (125 MHz, $CDCl_3$)

***N*-(1-(4-methoxyphenyl)-3,3-dimethyl-5-phenylpentyl)-4-methylaniline (4abw):**

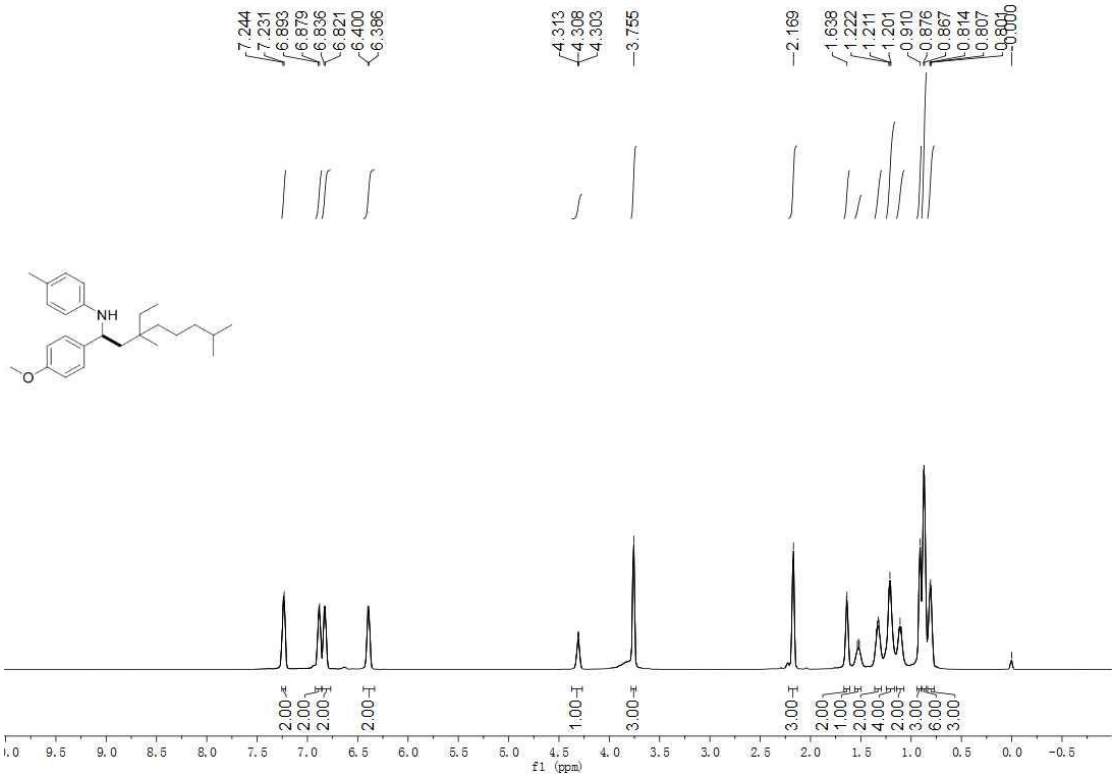


^{1}H-NMR (500 MHz, $CDCl_3$)

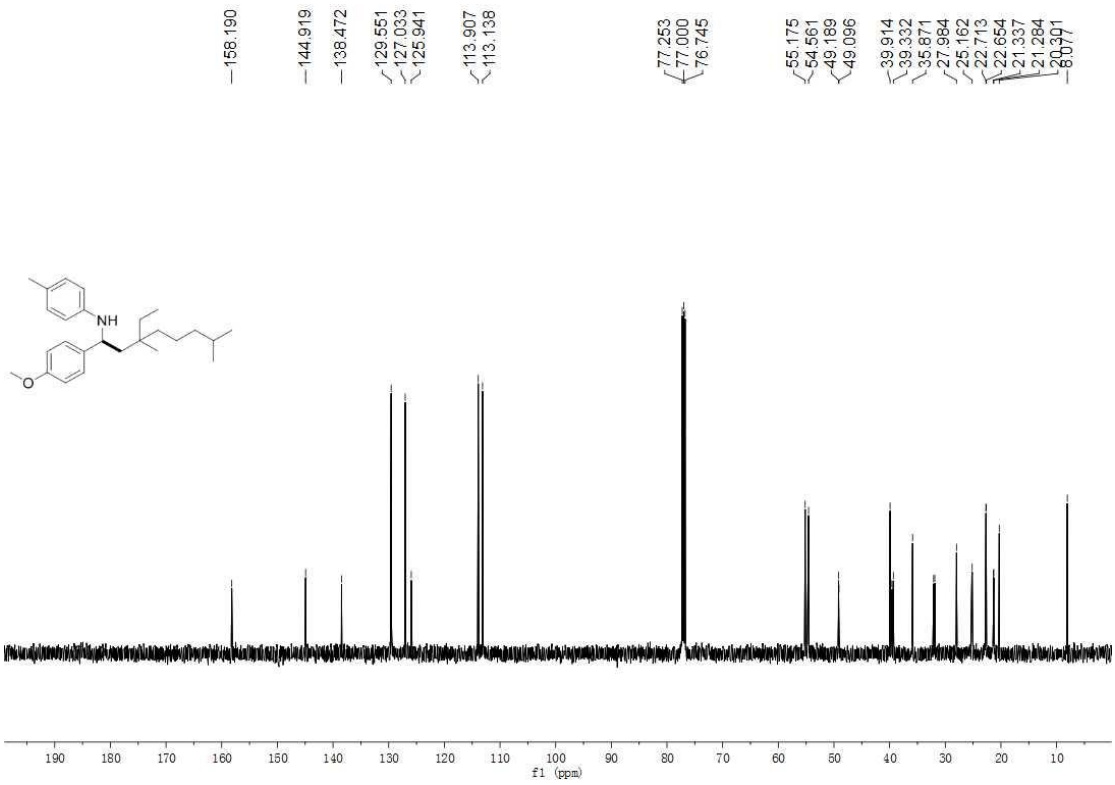


^{13}C-NMR (125 MHz, $CDCl_3$)

***N*-(3-ethyl-1-(4-methoxyphenyl)-3,7-dimethyloctyl)-4-methylaniline (4acw):**



^{1}H-NMR (500 MHz, $CDCl_3$)



^{13}C-NMR (125 MHz, $CDCl_3$)

(D) References

1 C. H. Xu, Z. -Q. Xiong, Y. Li, Y. P. Zhu and J. -H. Li, Copper-Catalyzed Oxidative Phosphonoheteroarylation of Alkenes with Phosphonates and *N*-Heteroarenes via P-H/C-H Functionalization. *Org. Chem. Front.,* 2022, **9**, 476-480.

2 D. Meyer, H. Jangra, F. Walther, H. Zipse and P. Renaud, A Third Generation of Radical Fluorinating Agents Based on *N*-Fluoro-*N*-arylsulfonamides. *Nat. Commun.,* 2018, **9**, 4888.

3 Y. Gao, Z. Wu, L. Yu, Y. Wang and Y. Pan, Alkyl Carbazates for Electrochemical Deoxygenative Functionalization of Heteroarenes. *Angew. Chem. Int. Ed.,* 2020, **132**, 10951-10955.

4 (*a*) M.-J. Kang, W. J. Song, A.-R. Han, Y. S. Choi, H. G. Jang and W. Nam, Mechanistic Insight into the Aromatic Hydroxylation by High-valent Iron (IV)-oxo Porphyrin π-Cation Radical Complexes. *J. Org.Chem*., 2007, **72**, 6301-6304; (*b*) S. P. de. Visser, K. Oh, A.-R. Han and W. Nam Combined Experimental and Theoretical Study on Aromatic Hydroxylation by Mononuclear Nonheme Iron (IV)-Oxo Complexes., *Inorg. Chem*., 2007, **46**, 4632-4641; (*c*) B. S. Lane, M. A. Brown and D. Sames, Direct Palladium-Catalyzed C-2 and C-3 Arylation of Indoles: a Mechanistic Rationale for Regioselectivity. *J. Am. Chem. Soc*., 2005, **127**, 8050-8057; (d) H. A. Chiong and O. Daugulis, Palladium-Catalyzed Arylation of Electron-rich Heterocycles with Aryl Chlorides. *Org. Lett*., 2007, **9**, 1449-1451; (*e*) X.-H. Ouyang, R.-J. Song, M. Hu, Y. Yang and J.-H. Li, Silver-Mediated Intermolecular 1, 2-Alkylarylation of Styrenes with α-Carbonyl Alkyl Bromides and Indoles. *Angew. Chem. Int. Ed*., 2016, **55**, 3187-3191; (*f*) J.-H. Qin, M.-J. Luo, D.-L. An and J.-H. Li, Electrochemical 1, 2-Diarylation of Alkenes Enabled by Direct Dual C-H Functionalizations of Electron-Rich Aromatic Hydrocarbons. *Angew. Chem. Int. Ed.,* 2021, **60**, 1861-1868; (g) L. -J. Zhong, Z. -Q. Xiong, X. -H. Ouyang, Y. Li, R.-J. Song, Q. Sun, X. Lu and J. -H. Li, Intermolecular 1,2-Difunctionalization of Alkenes Enabled by Fluoroamide-Directed Remote Benzyl C(sp^3)-H Functionalization, *J. Am. Chem. Soc*., 2021, **144**, 339-348.