Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Visible-Light-Mediated De-Aminative Alkylation of *N*-Arylamines with Alkyl Katritzky Salts.

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Contents

1. general information

Only if otherwise mentioned, all solvents and reagents were commercially available and utilized without any purification. Reactions were monitored by thin layer chromatography (TLC), and organic solutions were concentrated under reduced pressure on Eyela rotary evaporator. The products were obtained by column chromatography on silica gel (200-300 mesh).

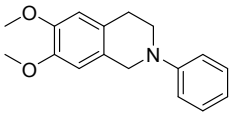
NMR spectra were acquired on Bruker 400 MHz NMR spectrometers. Chemical shifts were recorded relative to residual protiated solvents. Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a *J* value in Hz. HRMS was conducted with a Thermo LTQ Orbitrap XL instrument. The luminescence quenching experiments were performed using HITACHI F-2500.UV/vis absorption spectra were recorded on a SHIMADZU UV-2550.

2. General synthetic procedures

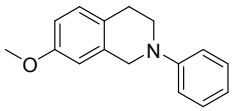
2.1 General procedure for the synthesis of *N*-aryl-tetrahydroisoquinolines[1]

***General procedure* A:** A dried flask equipped with a stirring bar was charged with BINAP (0.44 mmol, 5.5% mmol). It was purged thoroughly with N_2, toluene (20 ml) was added and heated at 100 °C, until a homogenous solution was obtained. The solution was cooled to room temperature before adding $Pd(OAc)_2$ (0.4 mmol, 5% mmol). The mixture was stirred for 5 min. Aryl bromide (9.6 mmol, 1.2 equiv), 1,2,3,4-tetrahydroisoquinoline (8 mmol, 1.0equiv) and potassium *tert*-butoxide (11.2 mmol, 1.4 equiv) were added sequentially and the mixture heated at 100 ℃. After the reaction was complete, the mixture was diluted with EtOAc and washed with water, and concentrated in vacuo. A crude product was purified by column chromatography.

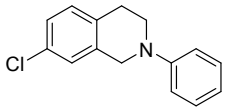
***General procedure* B:** CuI (1.6 mmol, 20% mmol), K_3PO_4 (16mmol, 2 equiv) were added to a dried flask which was purged thoroughly with N_2. Aryl iodide (8 mmol, 1equiv), tetrahydroisoquinoline (8 mmol, 1 equiv), ethylene glycol (32 mmol, 4 equiv) and 2-propanol (20 mL) were added. The mixture was refluxed for 24 h. After the reaction was complete, the mixture was diluted with EtOAc and washed with water, and concentrated in vacuo. A crude product was purified by column chromatography.



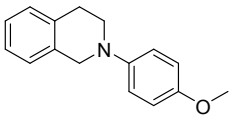
6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (1a).[2] Following the general procedure A. **Yield:** 65% (1.4 g). White solid. **Mp:** 92-94 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29 (t, *J* = 7.8 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.84 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 3.8 Hz, 2H), 4.34 (s, 2H), 3.87 (d, *J* = 3.0 Hz, 6H), 3.55 (t, *J* = 5.8 Hz, 2H), 2.90 (t, *J* = 5.6 Hz, 2H).



7-methoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (1b). Following the general procedure A. **Yield:** 33% (640 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.84 (t, *J* = 7.1 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.71 (s, 1H), 4.39 (s, 2H), 3.81 (s, 3H), 3.56 (t, *J* = 5.7 Hz, 2H), 2.92 (t, *J* = 5.6 Hz, 2H).

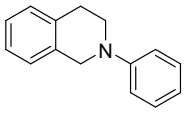


7-chloro-2-phenyl-1,2,3,4-tetrahydroisoquinoline (1c).[3] Following the general procedure A. **Yield:** 46% (900 mg). White solid. **Mp:** 32-37 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.15 (m, 2H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.86 (t, *J* = 7.2 Hz, 1H), 4.37 (s, 2H), 3.56 (t, *J* = 5.9 Hz, 2H), 2.94 (t, *J* = 5.9 Hz, 2H).

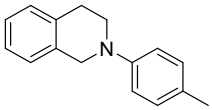


2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (1d).[4] Following the general procedure B. **Yield:** 26% (500 mg). Yellow solid. **Mp:** 92-94 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.16 (m, 4H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 4.31 (s, 2H), 3.79 (s, 3H), 3.46 (t, *J* = 5.7 Hz, 2H), 3.00 (t,

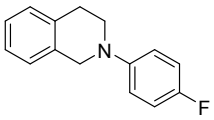
J = 5.7 Hz, 2H).



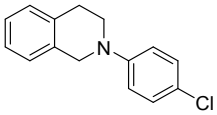
2-phenyl-1,2,3,4-tetrahydroisoquinoline (1e).[2] Following the general procedure B. **Yield:** 24% (500 mg). Yellow solid. **Mp:** 44-46 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29 (t, J = 8.0 Hz, 2H), 7.24 – 7.11 (m, 4H), 6.99 (d, J = 8.1 Hz, 2H), 6.83 (t, J = 7.3 Hz, 1H), 4.42 (s, 2H), 3.57 (t, J = 5.8 Hz, 2H), 2.99 (t, J = 5.9 Hz, 2H).



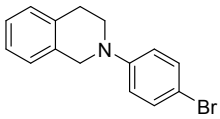
2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (1f).[2] Following the general procedure B. **Yield:** 34% (600 mg). Yellow solid. **Mp:** 40-42 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 – 7.08 (m, 6H), 6.94 (d, J = 8.1 Hz, 2H), 4.37 (s, 2H), 3.52 (t, J = 5.9 Hz, 2H), 3.00 (t, J = 6.0 Hz, 2H), 2.29 (s, 3H).



2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (1g).[4] Following the general procedure B. **Yield:** 9% (170 mg). Yellow solid. **Mp:** 72-73 °C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.17 (td, J = 10.6, 9.9, 4.0 Hz, 4H), 7.04 – 6.90 (m, 4H), 4.34 (s, 2H), 3.50 (t, J = 6.0 Hz, 2H), 3.00 (t, J = 6.0 Hz, 2H).



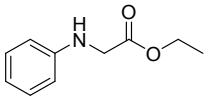
2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (1h).[4] Following the general procedure B. **Yield:** 13% (250 mg). White solid. **Mp:** 72-73 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.19 (m, 6H), 6.90 (d, J = 8.3 Hz, 2H), 4.38 (s, 2H), 3.54 (t, J = 5.9 Hz, 2H), 2.99 (t, J = 6.0 Hz, 2H).



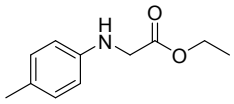
2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline (1i).[2] Following the general procedure B. **Yield:** 13% (300 mg). White solid. **Mp:** 77-79 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 (d, J = 8.5 Hz, 2H), 7.18 (m, 4H), 6.84 (d, J = 8.5 Hz, 2H), 4.38 (s, 2H), 3.54 (t, J = 5.9 Hz, 2H), 2.98 (t, J = 6.0 Hz, 2H).

2.2 General procedure for the synthesis of ethyl *N*-aryl glycine esters.[2]

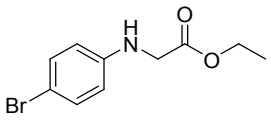
To the solution of ethyl bromoacetate (1 equiv) in EtOH was added substituted benzenamine (1 equiv) and NaOAc (1 equiv). The reaction mixture was heated to 85-90 °C. After the reaction was complete, the mixture was filtered, and the filtrate was concentrated in vacuo. A crude product was purified by column chromatography.



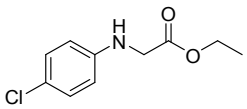
ethyl phenylglycinate (4a).[5] **Yield:** 70% (2.7 g). White solid. **Mp:** 48-50 °C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.20 (t, J = 7.9 Hz, 2H), 6.76 (t, J = 7.3 Hz, 1H), 6.63 (d, J = 7.9 Hz, 2H), 4.25 (m, 3H), 3.91 (s, 2H), 1.30 (t, J = 7.1 Hz, 3H).



ethyl *p*-tolylglycinate (4b).[2] Yield: 36% (1.3 g). Yellow solid. **Mp:** 56-58 °C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.02 (d, *J* = 7.9 Hz, 2H), 6.56 (d, *J* = 8.0 Hz, 2H), 4.25 (m, 3H), 3.89 (s, 2H), 2.25 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).

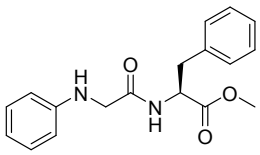


ethyl (4-bromophenyl)glycinate (4c).[5] Yield: 40% (1.2 g). White solid. **Mp:** 94-96 °C **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.20 (d, *J* = 8.3 Hz, 2H), 6.44 (d, *J* = 8.1 Hz, 2H), 4.17 (m, 3H), 3.79 (s, 2H), 1.22 (t, *J* = 7.1 Hz, 3H).



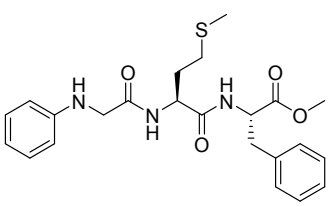
ethyl (4-chlorophenyl)glycinate (4d).[5] Yield: 36% (1.2 g). White solid. **Mp:** 86-88 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.14 (d, *J* = 8.1 Hz, 2H), 6.55 (d, *J* = 8.2 Hz, 2H), 4.24 m, 3H), 3.87 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H).

2.3 General procedure for the synthesis of methyl phenylglycyl-*L*-phenylalaninate(8)[6]



N-phenyl glycine (6.6 mmol, 1 equiv), methyl *L*-phenylalaninate hydrochloride (6.6 mmol, 1equiv) and DCM (30 mL) were added to a 100 mL round-bottom flask. At 0 ℃, DIPEA (16.5 mmol, 2.5 equiv), EDCI (7.26 mmol, 1.1 equiv) and HOBt (7.26 mmol, 1.1 equiv) were added. The reaction mixture was stirred at room temperature overnight, then washed with H_2O and brine, and concentrated in vacuo. A crude product was purified by column chromatography.(ethyl acetate/petroleum = 1:3) and the title compound was obtained as a white solid (1 g, 49%). Mp: 106-108 ℃. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.23 (d, *J* = 7.5 Hz, 2H), 7.16 (m, 3H), 6.94 (m, 3H), 6.74 (d, *J* = 7.8 Hz, 2H), 4.92 (q, *J* = 6.6 Hz, 1H), 3.86 (s, 2H), 3.69 (s, 3H), 3.07 (t, *J* = 5.2 Hz, 2H).

2.4 General procedure for the synthesis of methyl phenylglycyl-*L*-methionyl-*L*-phenylalaninate(9)[6]



Boc-*L*-methionine (20 mmol, 1 equiv) and methyl *L*-phenylalaninate hydrochloride (20 mmol, 1 equiv) and DCM (60 mL) were added to a 250 mL round-bottom flask. At 0 ℃, Et_3N (20 mmol, 1 equiv) and DIC (20 mmol, 1 equiv) were added The reaction mixture was stirred at room temperature overnight, then washed with H_2O and brine, and concentrated in vacuo. A crude product was purified by column

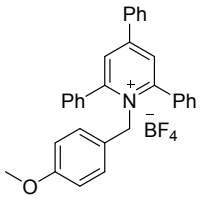
chromatography.(ethyl acetate/petroleum = 1:5-1:3) and the title compound was obtained as a white solid (4.1 g, 50%). Mp: 79-81 ℃. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 (m, 3H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.60 (m, 1H), 5.14 (s, 1H), 4.85 (q, *J* = 6.5 Hz, 1H), 4.26 (s, 1H), 3.72 (s, 3H), 3.12 (m, 2H), 2.53 (m, 2H), 2.05 (s, 3H), 2.00 (m, 1H), 1.86 (m, 1H), 1.43 (s, 9H).

The peptide (1.9 mmol, 1 equiv) was dissolved in 5 mL of DCM and 0.6 mL of TFA was added dropwise at 0 ℃. The reaction mixture was stirred at room temperature for 5 h, solvent was evaporated and the yellow oil was obtained. Then *N*-phenyl glycine (1.9 mmol, 1 equiv) and DCM (10 mL) were added. At 0 ℃, Et_3N (3.8 mmol, 2 equiv) and DIC (1.9 mmol, 1 equiv) were added. The reaction mixture was stirred at room temperature overnight, then washed with H_2O and brine, and concentrated in vacuo. A crude product was purified by column chromatography.(ethyl acetate/petroleum =1:3) and the title compound was obtained as a colorless oil (200 mg, 24%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 (m, 5H), 7.13 (d, *J* = 7.4 Hz, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.84 (t, *J* = 10.1 Hz, 2H), 4.82 (q, *J* = 6.8 Hz, 1H), 4.64 (q, *J* = 6.9 Hz, 1H), 3.90 (q, *J* = 17.1 Hz, 2H), 3.73 (s, 3H), 3.15 (dd, *J* = 13.7, 5.5 Hz, 1H), 3.04 (dd, *J* = 13.9, 7.1 Hz, 1H), 2.42 (t, *J* = 7.0 Hz, 2H), 2.04 – 1.79 (m, 5H).

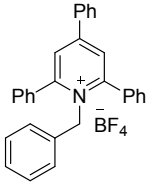
2.5 General procedure for the synthesis of pyridinium salts[7]

General procedure **A:** 2,4,6-Triphenylpyrylium tetrafluoroborate (500 mg, 1.3 mmol, 1.0 equiv.) was suspended in DCM (5 mL). The respective amine (2.0 equiv.) and acetic acid (50 μL, 0.9 mmol) was added and the mixture stirred at room temperature. After the reaction was complete, Et_2O (15 mL) was added, the resulting precipitate was collected by filtration, washed with Et_2O to afford pure product. If the product did not precipitated, concentrated in vacuo and the residue purified by column chromatography (DCM: MeOH=80:1).

General procedure **B:** 2,4,6-Triphenylpyrylium tetrafluoroborate (500 mg, 1.3 mmol, 1.0 equiv.) was suspended in EtOH (2 mL), then the respective amine (1.2 equiv.) was added. The reaction mixture was heated to 85-90 °C for 4 h. Subsequently, the mixture cooled to ambient temperature. Et_2O (15 mL) was added, the resulting precipitate was collected by filtration, washed with Et_2O to afford pure product. If the product did not precipitated, concentrated in vacuo and the residue purified by column chromatography (DCM: MeOH=80:1).

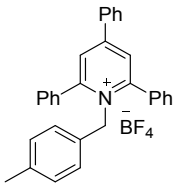


1-(4-methoxybenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2a).[8] Following the general procedure A. **Yield:** 77% (500 mg). White solid. **Mp:** 148-150 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (s, 2H), 7.80 (d, *J* = 7.1 Hz, 2H), 7.73 – 7.43 (m, 13H), 6.61 (d, *J* = 8.4 Hz, 2H), 6.35 (d, *J* = 8.3 Hz, 2H), 5.71 (s, 2H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.49, 157.53, 156.19, 133.83, 132.92, 132.34, 130.97, 129.79, 129.20, 129.14, 128.15, 127.81, 126.62, 126.02, 114.19, 57.89, 55.31.

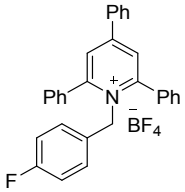


1-benzyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2b).[7] Following the general procedure B. **Yield:** 57% (350 mg). White solid. **Mp:** 187-189 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 (s, 2H), 7.85

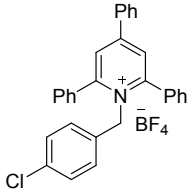
(d, *J* = 7.0 Hz, 2H), 7.76 – 7.42 (m, 13H), 7.16 (dd, *J* = 19.3, 7.4 Hz, 3H), 6.49 (d, *J* = 7.5 Hz, 2H), 5.80 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.57, 156.31, 134.07, 133.76, 132.75, 132.39, 130.96, 129.80, 129.16, 129.08, 128.83, 128.25, 128.17, 126.57, 126.24, 58.27.



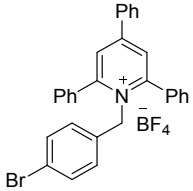
1-(4-methylbenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2c).[7] Following the general procedure B. **Yield:** 86% (440 mg). White solid. **Mp:** 134-136 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (s, 2H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 7.0 Hz, 4H), 7.60 – 7.39 (m, 9H), 6.89 (d, *J* = 7.6 Hz, 2H), 6.33 (d, *J* = 7.6 Hz, 2H), 5.71 (s, 2H), 2.23 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.56, 156.21, 138.22, 133.82, 132.80, 132.34, 131.10, 130.93, 129.79, 129.43, 129.13, 129.10, 128.16, 126.58, 126.14, 58.11, 21.03.



1-(4-fluorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2d).[7] Following the general procedure B. **Yield:** 95% (600 mg). White solid. **Mp:** 109-111 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (s, 2H), 7.79 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 4H), 7.62 – 7.43 (m, 9H), 6.78 (t, *J* = 8.3 Hz, 2H), 6.44 (dd, *J* = 8.2, 5.2 Hz, 2H), 5.76 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.31 (d, *J* = 248.7 Hz), 157.51 , 156.49 , 133.73 , 132.74 , 132.45 , 131.09 , 129.82 , 129.29 , 129.08 , 128.28 (d, *J* = 8.3 Hz), 128.17 , 115.86 (d, *J* = 21.9 Hz), 57.58 .

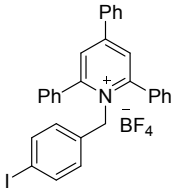


1-(4-chlorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2e).[7] Following the general procedure B. **Yield:** 76% (500 mg). White solid. **Mp:** 133-135 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (s, 2H), 7.79 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 7.3 Hz, 4H), 7.52 (m, 9H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.42 (d, *J* = 8.1 Hz, 2H), 5.74 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.51, 156.56, 134.33, 133.71, 132.63, 132.55, 132.48, 131.13, 129.82, 129.30, 129.07, 128.99, 128.18, 127.70, 126.66, 57.57.

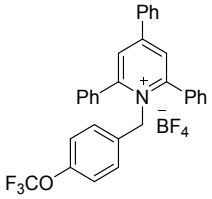


1-(4-bromobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate(2f).[9] Following the general procedure B. **Yield:** 84% (600 mg). White solid. **Mp:** 144-146 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 (s, 2H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 7.3 Hz, 4H), 7.60 – 7.40 (m, 9H), 7.21 (d, *J* = 8.0 Hz, 2H),

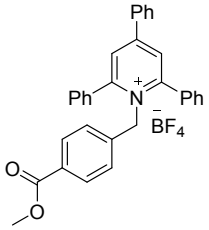
6.36 (d, *J* = 8.0 Hz, 2H), 5.71 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.45, 156.58, 133.72, 133.01, 132.64, 132.45, 131.95, 131.12, 129.80, 129.28, 129.09, 128.20, 127.99, 126.68, 122.37, 57.64.



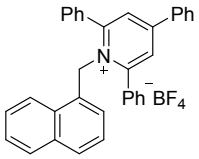
1-(4-iodobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2g).[9] Following the general procedure B. **Yield:** 77% (590 mg). White solid. **Mp:** 135-137 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (s, 2H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 7.3 Hz, 4H), 7.49 (m, 11H), 6.23 (d, *J* = 8.0 Hz, 2H), 5.71 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.49, 156.57, 137.88, 133.74, 133.71, 132.61, 132.47, 131.13, 129.81, 129.28, 129.07, 128.19, 128.09, 126.66, 93.84, 57.72.



2,4,6-triphenyl-1-(4-(trifluoromethoxy)benzyl)pyridin-1-ium tetrafluoroborate (2h). Following the general procedure A. **Yield:** 82% (590 mg). Red solid. **Mp:** 99-101 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (s, 2H), 7.73 (d, *J* = 7.0 Hz, 2H), 7.64 (d, *J* = 7.2 Hz, 4H), 7.46 (m, *J* = 14.5, 8.5, 7.3 Hz, 9H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.52 (d, *J* = 8.1 Hz, 2H), 5.76 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.39 , 157.37 , 156.62 , 148.82 , 133.73 , 132.75 , 132.62 , 132.39 , 131.06 , 129.75 , 129.24 , 129.09 , 128.20 , 128.17 , 126.71 , 121.30 , 120.24 (q, *J* = 257.8 Hz), 57.62 . **HRMS (ESI)** m/z: Calcd for $C_{31}H_{23}F_3NO$ $[M\text{-}BF_4^-]^+$: 482.1726, Found: 482.1716.

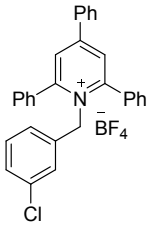


1-(4-(methoxycarbonyl)benzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2i).[9] Following the general procedure A. **Yield:** 80% (550 mg). White solid. **Mp:** 57-58 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 2.5 Hz, 2H), 7.83 (d, *J* = 7.5 Hz,21H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.69 – 7.39 (m, 13H), 6.59 (d, *J* = 8.0 Hz, 2H), 5.83 (s, 2H), 3.88 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.16, 157.57, 156.70, 138.97, 133.70, 132.53, 132.51, 131.16, 130.04, 130.00, 129.85, 129.29, 129.15, 128.27, 126.72, 126.24, 58.05, 52.32.

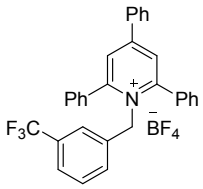


1-(naphthalen-2-ylmethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2j).[7] Following the general procedure A. **Yield:** 74% (500 mg). White solid. **Mp:** 182-184 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.96 (s, 2H), 7.83 – 7.77 (m, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.62 – 7.49 (m, 7H), 7.39 – 7.20 (m, 10H),

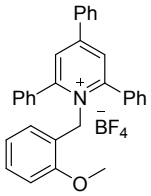
6.58 (d, *J* = 7.2 Hz, 1H), 6.14 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.88, 156.40, 133.85, 133.09, 132.42, 132.31, 131.00, 130.83, 129.83, 129.28, 129.02, 128.92, 128.79, 128.42, 128.20, 127.04, 126.66, 126.56, 124.57, 122.97, 121.89, 55.92.



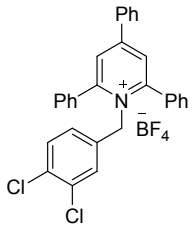
1-(3-chlorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2k).[10] Following the general procedure A. **Yield:** 90% (590 mg). White solid. **Mp:** 177-179 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 (s, 2H), 7.86 (d, *J* = 7.5 Hz, 2H), 7.69 (d, *J* = 7.3 Hz, 4H), 7.67 – 7.48 (m, 9H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.43 (d, *J* = 7.3 Hz, 2H), 5.79 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.49, 156.60, 135.84, 134.65, 133.66, 132.58, 132.52, 131.16, 130.25, 129.83, 129.31, 129.10, 128.53, 128.20, 126.65, 126.61, 124.64, 57.56.



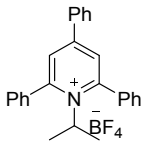
2,4,6-triphenyl-1-(3-(trifluoromethyl)benzyl)pyridin-1-ium tetrafluoroborate (2l).[7] Following the general procedure B. **Yield:** 57% (400 mg). Yellow solid. **Mp:** 86-88 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 (s, 2H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 7.1 Hz, 4H), 7.53 (m, 9H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.22 (m, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 6.59 (s, 1H), 5.85 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.50 , 156.83 , 134.82 , 133.76 , 132.77 , 132.58 , 131.31 , 130.97 (q, *J* = 32.7 Hz), 130.07 , 129.98 , 129.89 , 129.43 , 129.21 , 128.34 , 126.80 , 125.20 (q, *J* = 3.6 Hz), 123.79 (q, *J* = 3.9 Hz), 123.45 (q, *J* = 272.5 Hz), 57.80 .



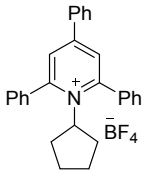
1-(2-methoxybenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2m).[10] Following the general procedure A. **Yield:** 91% (590 mg). White solid. **Mp:** 177-179 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (s, 2H), 7.79 (d, *J* = 7.4 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 4H), 7.48 (m, 9H), 7.10 (t, *J* = 7.9 Hz, 1H), 6.58 (m, 2H), 6.25 (d, *J* = 7.6 Hz, 1H), 5.72 (s, 2H), 3.45 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.98, 156.40, 155.89, 133.83, 133.18, 132.26, 130.80, 129.78, 129.09, 129.05, 128.58, 128.11, 126.13, 122.17, 120.52, 110.33, 55.74, 55.13.



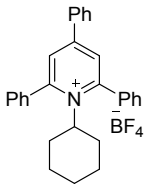
1-(3,4-dichlorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate(2n). Following the general procedure B. **Yield:** 69% (480 mg). White solid. **Mp:** 203-205 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.97 (s, 2H), 7.82 (d, *J* = 7.5 Hz, 2H), 7.67 (d, *J* = 7.3 Hz, 4H), 7.56 (m, 9H), 7.19 (d, *J* = 8.3 Hz, 1H), 6.48 (s, 1H), 6.38 (d, *J* = 8.3 Hz, 1H), 5.75 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.39, 156.76, 133.83, 133.62, 132.87, 132.73, 132.53, 131.27, 130.91, 129.82, 129.39, 129.12, 128.61, 128.22, 126.69, 125.94, 56.99. **HRMS (ESI)** m/z: Calcd for $C_{30}H_{22}Cl_2N$ $[M\text{-}BF_4^-]^+$: 466.1124, Found: 466.1124.



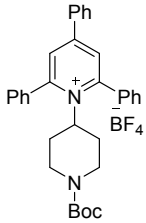
1-isopropyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2o).[11] Following the general procedure A. **Yield:** 82% (590 mg). White solid. **Mp:** 184-186°C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 – 7.70 (m, 8H), 7.68 – 7.40 (m, 9H), 5.13 (m, 1H), 1.36 (t, *J* = 6.2 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.01, 154.97, 134.05, 133.88, 131.83, 131.79, 130.80, 129.53, 129.50, 128.82, 128.24, 62.70, 23.34.



1-cyclopentyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2p).[11] Following the general procedure B. **Yield:** 43% (250 mg). White solid. **Mp:** 109-111 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 – 7.70 (m, 8H), 7.66 – 7.41 (m, 9H), 5.04 (m, 1H), 2.22 (m, 2H), 2.02 (m, 2H), 1.15 (m, 2H), 0.95 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.71, 154.88, 134.11, 134.00, 131.89, 130.75, 129.59, 129.57, 128.95, 128.23, 70.66, 33.74, 24.56.

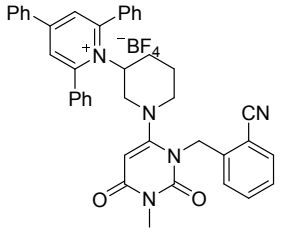


1-cyclohexyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2q).[11] Following the general procedure B. **Yield:** 33% (200 mg). White solid. **Mp:** 178-180 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 – 7.77 (m, 2H), 7.73 (d, *J* = 6.9 Hz, 6H), 7.66 – 7.39 (m, 9H), 4.61 (t, *J* = 11.9 Hz, 1H), 2.12 (d, *J* = 12.0 Hz, 2H), 1.62 – 1.52 (m, 2H), 1.47 (m, 2H), 1.34 (m, 1H), 0.67 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.06, 155.05, 134.08, 134.03, 131.84, 130.82, 129.55, 129.36, 128.78, 128.28, 71.93, 33.59, 26.51, 24.65.

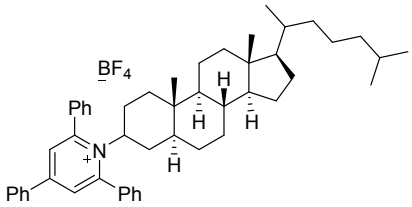


1-(1-(tert-butoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2r).[11] Following the general procedure B. **Yield:** 31% (225 mg). White solid. **Mp:** 136-138°C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 – 7.80 (m, 2H), 7.80 – 7.68 (m, 6H), 7.65 – 7.42 (m, 9H), 4.78 (t, *J* = 12.4 Hz, 1H), 3.93 (br, s, 2H), 2.13 (br, s, 4H), 1.73 (br, s, 2H), 1.31 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.15,

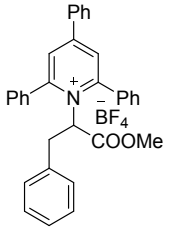
155.41, 154.19, 133.90, 133.71, 132.03, 131.08, 129.59, 129.31, 129.00, 128.29, 80.13, 69.92, 28.24.



1-(1-(3-(2-cyanobenzyl)-1-methyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-yl)piperidin-3-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2s).[12] Following the general procedure A. **Yield:** 35% (250 mg). Yellow solid. **Mp:** 156-158 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 10.3 Hz, 2H), 7.81 – 7.68 (m, 6H), 7.49 (m, 12H), 7.22 (d, *J* = 7.9 Hz, 1H), 5.06 – 4.68 (m, 4H), 3.66 (d, *J* = 11.2 Hz, 1H), 2.95 (m, 4H), 2.38 (d, *J* = 12.3 Hz, 2H), 2.05 (d, *J* = 10.8 Hz, 1H), 1.91 – 1.78 (m, 1H), 1.61 (d, *J* = 13.8 Hz, 1H), 1.31 – 1.14 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.64, 157.98, 156.67, 155.63, 151.49, 140.10, 133.93, 133.56, 133.11, 133.07, 132.01, 131.08, 130.09, 129.55, 129.28, 128.76, 128.45, 128.13, 117.09, 110.71, 90.53, 66.65, 55.18, 46.26, 31.77, 27.62, 24.79.



1-((5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-(6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2t).[9] Following the general procedure B. **Yield:** 29% (400 mg). Yeloow solid. **Mp:** 153-135 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 – 7.72 (m, 8H), 7.59 (m, 6H), 7.49 (m, 3H), 4.70 (m, 1H), 1.95 (m, 2H), 1.85 (m, 1H), 1.80 – 1.63 (m, 4H), 1.59 – 1.42 (m, 4H), 1.35 – 1.19 (m, 5H), 1.17 – 1.06 (m, 6H), 0.89 (m 14H), 0.67 (m, 2H), 0.53 (s, 3H), 0.49 – 0.29 (m, 2H), 0.10 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 156.25, 154.16, 133.21, 130.99, 129.90, 128.70, 127.99, 127.43, 70.78, 55.38, 55.31, 52.39, 46.26, 41.59, 38.88, 38.62, 37.23, 35.26, 34.89, 34.57, 34.29, 33.70, 30.64, 27.73, 27.31, 27.13, 23.24, 22.99, 21.95, 21.69, 20.04, 17.74, 11.04, 10.85.



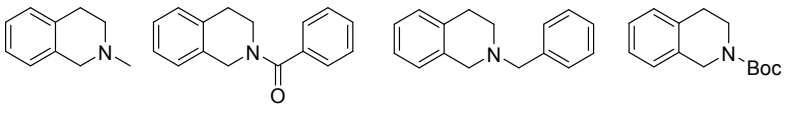
1-(1-methoxy-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2u).[7] Following the general procedure A. **Yield:** 69% (385 mg). Yellow solid. **Mp:** 130-132 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 – 7.90 (m, 2H), 7.82 (m, 4H), 7.67 – 7.37 (m, 11H), 7.09 (m, 3H), 6.77 (d, *J* = 6.9 Hz, 2H), 5.71 – 5.58 (m, 1H), 3.69 (s, 3H), 3.55 – 3.40 (m, 1H), 3.01 – 2.83 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.03, 167.93, 157.07, 156.90, 136.40, 136.32, 133.77, 132.44, 132.32, 131.56, 131.54, 129.73, 129.14, 129.00, 128.63, 128.61, 128.58, 127.93, 127.25, 127.22, 70.24, 53.77, 53.73, 37.75.

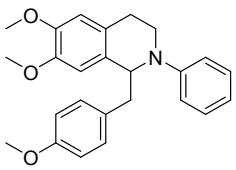
2.6 General procedure for the alkylation of *N*-arylamines.

A glass reaction tube equipped with a stirring bar was charged with $[Ir(dtbbpy)(ppy)_2]PF_6$ (3.6 mg, 4 μmol, 2.0 mol%), amine (0.2 mmol, 1eq.) and alkyl 2,4,6-triphenylpyridinium tetrafluoroborate (if benzyl: 0.24 mmol, 1.2 eq; if secondary alkyl: 0.4 mmol, 2 eq.). DMA (2 ml) and H_2O (180 μl) were added, then the resulting mixture was degassed by three freeze-thaw cycles and backfilled with argon. The reaction mixture was stirred at room temperature with the irradiation of a 10 W blue LED (if benzyl: 6 h; if secondary alkyl: 30 h.). After the reaction was complete, the mixture was diluted with EtOAc and washed with water, and concentrated in vacuo. A crude product was purified by column chromatography. **Without phtocatalyst:** A glass reaction tube equipped with a stirring bar was charged with amine (0.2 mmol, 1eq.) and alkyl 2,4,6-triphenylpyridinium tetrafluoroborate (if benzyl: 0.3 mmol, 1.5 eq; if secondary alkyl: 0.4 mmol, 2 eq.). DMA (2 ml) and H_2O (180 μl) were added, then the resulting mixture was degassed by three freeze-thaw cycles and backfilled with argon. The reaction mixture was stirred for 9 h at room temperature with the irradiation of a 40 W blue LED. After the reaction was complete, the mixture was diluted with EtOAc and washed with water, and concentrated in vacuo. A crude product was purified by column chromatography.

Figure S1. Reaction setup of alkylation of *N*-arylamines.

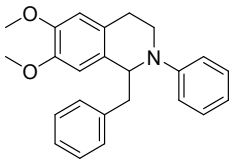
THIQs bearing other protecting groups are not suitable for the system.



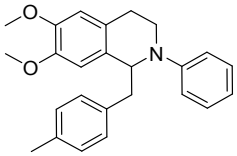


6,7-dimethoxy-1-(4-methoxybenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3aa). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 91% (71 mg); without photocatalyst,77% (60 mg). White solid. **Mp:** 83-85 °C. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.15 (t, J = 7.5 Hz, 2H), 7.06 (d, J = 7.8

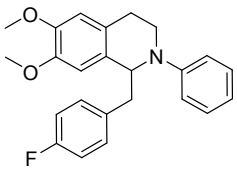
Hz, 2H), 6.88 (d, *J* = 8.1 Hz, 2H), 6.80 (d, *J* = 7.8 Hz, 2H), 6.71 (s, 1H), 6.63 (t, *J* = 7.2 Hz, 1H), 6.44 (s, 1H), 4.88 (t, *J* = 6.8 Hz, 1H), 3.75 (d, *J* = 8.3 Hz, 6H), 3.68 – 3.62 (m, 2H), 3.60 (s, 3H), 3.16 (m, 1H), 3.06 – 2.88 (m, 3H), 2.71 – 2.61 (m, 1H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 158.33, 149.80, 148.14, 147.13, 131.34, 130.68, 129.75, 128.96, 126.88, 116.99, 114.07, 113.40, 111.78, 111.66, 60.81, 55.13, 55.05, 54.54, 41.26, 40.78, 26.29. **HRMS (ESI)** m/z: Calcd for $C_{25}H_{28}NO_3$ $[M+H]^+$: 390.2069, Found: 390.2054.



1-benzyl-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ab). **Eluent:** petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 82% (59 mg); without photocatalyst, 69% (50 mg). White solid. **Mp:** 115-117 °C. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.30 – 7.12 (m, 7H), 6.90 (d, *J* = 8.2 Hz, 2H), 6.73 (s, 1H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.43 (s, 1H), 4.95 (t, *J* = 6.9 Hz, 1H), 3.78 (s, 3H), 3.72 – 3.64 (m, 2H), 3.59 (s, 3H), 3.25 (dd, *J* = 13.3, 6.8 Hz, 1H), 3.06 (dd, *J* = 13.4, 7.1 Hz, 1H), 2.95 (dt, *J* = 15.3, 7.4 Hz, 1H), 2.70 (dt, *J* = 16.0, 5.0 Hz, 1H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 149.76, 148.17, 147.13, 139.52, 129.79, 129.63, 128.97, 127.99, 126.85, 125.98, 117.09, 114.14, 111.80, 111.59, 60.74, 55.14, 55.01, 41.66, 41.26, 26.28. **HRMS (ESI)** m/z: Calcd for $C_{24}H_{26}NO_2$ $[M+H]^+$: 360.1958, Found: 360.1955.

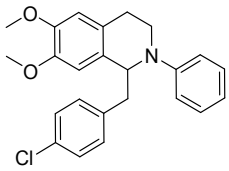


6,7-dimethoxy-1-(4-methylbenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ac). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 81% (60 mg); without photocatalyst, 54% (40 mg). White solid. **Mp:** 101-103 °C. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.15 (t, *J* = 7.6 Hz, 2H), 7.05 (m, 4H), 6.89 (d, *J* = 8.2 Hz, 2H), 6.70 (s, 1H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.41 (s, 1H), 4.90 (t, *J* = 7.0 Hz, 1H), 3.76 (s, 3H), 3.65 (m, 2H), 3.57 (s, 3H), 3.18 (dd, *J* = 13.3, 6.7 Hz, 1H), 2.95 (m, 2H), 2.72 – 2.62 (m, 1H), 2.27 (s, 3H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 149.79, 148.15, 147.11, 136.39, 135.25, 129.71, 129.67, 128.97, 128.61, 126.84, 117.04, 114.13, 111.79, 111.65, 60.73, 55.14, 54.97, 41.25, 41.23, 26.28, 20.16. **HRMS (ESI)** m/z: Calcd for $C_{25}H_{28}NO_2$ $[M+H]^+$: 374.2120, Found: 374.2124.

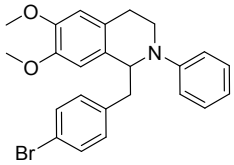


1-(4-fluorobenzyl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ad). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 79% (60 mg); without photocatalyst, 66% (50 mg). Yellow solid. **Mp:** 90-91 °C. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.16 (m, 4H), 6.98 (t, *J* = 8.5 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.71 (s, 1H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.53 (s, 1H), 4.92 (t, *J* = 6.9 Hz, 1H), 3.76 (s, 3H), 3.64 m, 5H), 3.20 (dd, *J* = 13.5, 7.2 Hz, 1H), 3.07 (dd, *J* = 13.6, 6.6 Hz, 1H), 2.92 (dt, *J* = 15.3, 7.4 Hz, 1H), 2.64 (dt, *J* = 16.0, 4.9 Hz, 1H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 161.52 (d, *J* = 242.1 Hz), 149.75 , 148.24 , 147.29 , 135.56 (d, *J* = 3.2 Hz), 131.44 (d, *J* = 7.8 Hz), 129.55 , 128.98 , 126.98 , 117.16 , 114.52 (d, *J* = 21.0 Hz), 114.14 , 111.86 , 111.54 , 60.64 , 55.16 , 55.13 , 41.24 , 40.82 , 26.15 . **^{19}F NMR (376 MHz, Acetone-d_6)** δ -118.80. **HRMS (ESI)** m/z: Calcd for $C_{24}H_{25}FNO_2$ $[M+H]^+$:

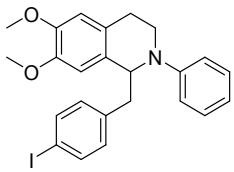
278.1864, Found:378.1860.



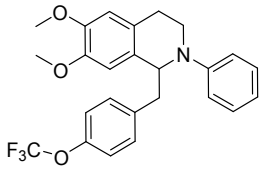
1-(4-chlorobenzyl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ae). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 67% (53 mg); without photocatalyst, 40% (30 mg). Yellow oil. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.25 (d, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 2H), 6.85 (d, *J* = 8.1 Hz, 2H), 6.71 (s, 1H), 6.63 (t, *J* = 7.2 Hz, 1H), 6.55 (s, 1H), 4.94 (t, *J* = 6.8 Hz, 1H), 3.76 (s, 3H), 3.64 (m, 5H), 3.22 (dd, *J* = 13.4, 7.3 Hz, 1H), 3.08 (dd, *J* = 13.4, 6.4 Hz, 1H), 2.92 (dt, *J* = 15.3, 7.4 Hz, 1H), 2.64 (dt, *J* = 15.9, 4.5 Hz, 1H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 149.75, 148.27, 147.32, 138.48, 131.48, 131.38, 129.46, 128.97, 127.91, 126.98, 117.24, 114.25, 111.87, 111.51, 60.46, 55.15, 55.10, 41.22, 40.98, 26.06. **HRMS (ESI)** m/z: Calcd for $C_{24}H_{25}ClNO_2$ $[M+H]^+$: 394.1568, Found: 394.1550.



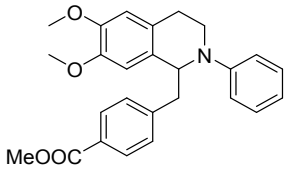
1-(4-bromobenzyl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3af). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 57% (50 mg); without photocatalyst, 57% (50 mg). Yellow solid. **Mp:** 93-95 °C. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.15 (m, 4H), 6.88 (d, *J* = 8.2 Hz, 2H), 6.72 (s, 1H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.56 (s, 1H), 4.96 (t, *J* = 6.8 Hz, 1H), 3.78 (s, 3H), 3.66 (m, 5H),3.22 (dd, *J* = 13.5, 7.3 Hz, 1H), 3.08 (dd, *J* = 13.4, 6.5 Hz, 1H), 2.93 (m, 1H), 2.65 (dt, *J* = 16.0, 4.9 Hz, 1H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 149.73, 148.26, 147.31, 138.94, 131.89, 130.91, 129.42, 128.99, 126.97, 119.45, 117.27, 114.26, 111.86, 111.50, 60.40, 55.16, 55.10, 41.24, 41.03, 26.07. **HRMS (ESI)** m/z: Calcd for $C_{24}H_{25}BrNO_2$ $[M+H]^+$: 438.1063, Found: 438.1068.



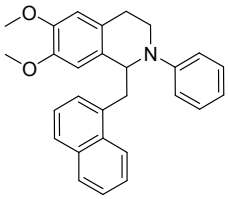
1-(4-iodobenzyl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ag). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 52% (50 mg); without photocatalyst, 57% (55 mg). Yellow solid. **Mp:** 114-116 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.55 (d, *J* = 7.8 Hz, 2H), 7.31 – 7.21 (m, 2H), 6.88 (d, *J* = 8.1 Hz, 2H), 6.77 (d, *J* = 7.8 Hz, 3H), 6.62 (s, 1H), 6.06 (s, 1H), 4.81 – 4.73 (m, 1H), 3.86 (d, *J* = 1.2 Hz, 3H), 3.64 – 3.50 (m, 5H), 3.21 – 3.14 (m, 1H), 2.98 – 2.84 (m, 2H), 2.71 – 2.62 (m, 1H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 149.74, 148.26, 147.29, 139.50, 136.99, 132.17, 129.41, 128.98, 126.95, 117.26, 114.28, 111.87, 111.52, 90.72, 60.40, 55.15, 55.09, 41.25, 41.12, 26.07. **HRMS (ESI)** m/z: Calcd for $C_{24}H_{25}INO_2$ $[M+H]^+$: 486.0924, Found: 486.0924.



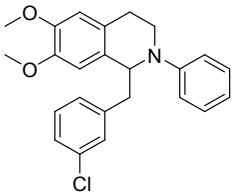
6,7-dimethoxy-2-phenyl-1-(4-(trifluoromethoxy)benzyl)-1,2,3,4-tetrahydroisoquinoline (3ah). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 62% (55 mg); without photocatalyst, 78% (60 mg). colorless oil. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.31 (d, *J* = 8.1 Hz, 2H), 7.19 (m, 4H), 6.93 (d, *J* = 7.9 Hz, 2H), 6.74 (s, 1H), 6.70 (t, *J* = 7.0 Hz, 1H), 6.51 (s, 1H), 4.99 (t, *J* = 6.8 Hz, 1H), 3.78 (s, 3H), 3.69 (m, 2H), 3.62 (s, 3H), 3.31 (dd, *J* = 13.3, 6.9 Hz, 1H), 3.14 (dd, *J* = 13.4, 6.8 Hz, 1H), 2.95 (m, 1H), 2.73 (m, 1H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 149.40, 148.30, 147.51 (q, *J* = 1.9 Hz), 147.29, 138.92, 131.43, 129.16, 129.01, 126.83, 120.61, 120.58 (q, *J* = 254.9 Hz), 117.78, 114.61, 111.86, 111.43, 60.77, 55.15, 55.00, 41.71, 40.84, 26.10. **^{19}F NMR (376 MHz, Acetone-d_6)** δ -58.59. **HRMS (ESI)** m/z: Calcd for $C_{25}H_{25}F_3NO_3$ $[M+H]^+$: 444.1781, Found: 444.1777.



methyl 4-((6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)methyl)benzoate (3ai). Eluent: petroleum ether/ethyl acetate=30/1-5/1. **Yield:** 36% (30 mg); without photocatalyst, 18% (15 mg). Yellow oil. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.88 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.7 Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.71 (s, 1H), 6.63 (t, *J* = 7.2 Hz, 1H), 6.58 (s, 1H), 5.02 (t, *J* = 6.9 Hz, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 3.72 – 3.64 (m, 2H), 3.62 (s, 3H), 3.30 (dd, *J* = 13.2, 7.5 Hz, 1H), 3.18 (dd, *J* = 13.3, 6.4 Hz, 1H), 2.92 (m, 1H), 2.69 – 2.58 (m, 1H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 166.33, 149.72, 148.29, 147.35, 145.28, 129.99, 129.45, 129.02, 128.97, 128.10, 126.96, 117.30, 114.30, 111.88, 111.43, 60.43, 55.15, 55.12, 51.28, 41.70, 41.17, 26.00. **HRMS (ESI)** m/z: Calcd for $C_{26}H_{28}NO_4$ $[M+H]^+$: 418.2013, Found: 418.2010.

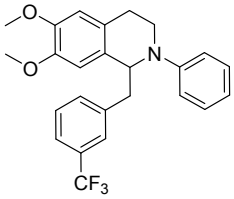


6,7-dimethoxy-1-(naphthalen-1-ylmethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3aj). **Eluent:** petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 37% (30 mg); without photocatalyst, 43% (35 mg). White solid. **Mp:** 97-99 °C. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.45 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.0 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 2H), 6.85 (d, *J* = 8.1 Hz, 2H), 6.70 (s, 1H), 6.64 (t, *J* = 7.2 Hz, 1H), 6.17 (s, 1H), 5.10 (t, *J* = 6.9 Hz, 1H), 3.83 – 3.72 (m, 4H), 3.71 – 3.64 (m, 1H), 3.60 (d, *J* = 6.9 Hz, 2H), 3.38 (s, 3H), 2.94 (m, 1H), 2.71 (dt, *J* = 15.9, 4.2 Hz, 1H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 149.91, 148.32, 147.10, 135.61, 133.94, 132.59, 129.64, 128.96, 128.56, 128.26, 126.83, 126.71, 125.69, 125.33, 123.93, 117.46, 114.74, 112.03, 111.66, 60.32, 55.22, 54.90, 41.16, 38.10, 26.27. **HRMS (ESI)** m/z: Calcd for $C_{28}H_{28}NO_2$ $[M+H]^+$: 410.2115, Found: 410.2129.

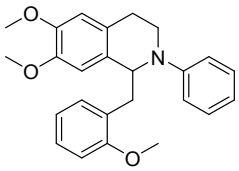


1-(3-chlorobenzyl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ak). Eluent:

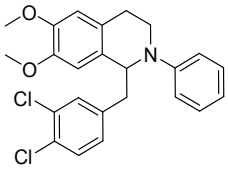
petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 51% (40 mg); without photocatalyst, 63% (50 mg). Yellow solid. **Mp:** 83-84 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.26 (m, 2H), 7.16 (d, *J* = 7.0 Hz, 2H), 7.05 (s, 1H), 6.90 (t, *J* = 7.4 Hz, 3H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.63 (s, 1H), 6.10 (s, 1H), 4.79 (t, *J* = 6.5 Hz, 1H), 3.86 (s, 3H), 3.60 (d, *J* = 13.9 Hz, 5H), 3.21 (dd, *J* = 13.2, 5.3 Hz, 1H), 2.93 (m, 2H), 2.70 (dt, *J* = 15.9, 5.4 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.42, 147.81, 146.63, 141.19, 133.92, 129.92, 129.41, 129.30, 128.99, 128.14, 126.83, 126.38, 117.85, 114.46, 111.27, 110.87, 60.96, 55.90, 55.73, 42.08, 41.74, 27.15. **HRMS (ESI)** m/z: Calcd for $C_{24}H_{25}ClNO_2$ $[M+H]^+$: 394.1568, Found: 394.1554.



6,7-dimethoxy-2-phenyl-1-(3-(trifluoromethyl)benzyl)-1,2,3,4-tetrahydroisoquinoline (3al). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 53% (45 mg); without photocatalyst, 68% (50 mg). Yellow oil. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.43 – 7.26 (m, 4H), 6.98 (t, *J* = 7.7 Hz, 2H), 6.72 (d, *J* = 8.2 Hz, 2H), 6.57 (s, 1H), 6.50 (d, *J* = 8.4 Hz, 2H), 4.89 (t, *J* = 7.0 Hz, 1H), 3.62 (s, 3H), 3.55 (dt, *J* = 11.5, 5.4 Hz, 2H), 3.50 (s, 3H), 3.19 (dd, *J* = 13.5, 7.7 Hz, 1H), 3.09 (dd, *J* = 13.5, 6.2 Hz, 1H), 2.78 (ddd, *J* = 15.5, 9.1, 6.0 Hz, 1H), 2.48 (dt, *J* = 16.0, 4.8 Hz, 1H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 149.75, 148.32, 147.46, 140.93, 133.74, 129.63 (q, *J* = 31.7 Hz), 129.38, 128.95, 128.71, 127.00, 126.40 (q, *J* = 3.8 Hz), 124.57 (q, *J* = 271.6 Hz), 122.71 (q, *J* = 4.0 Hz), 117.38, 114.41, 111.97, 111.42, 60.23, 55.19, 55.10, 41.38, 41.26, 25.95. **^{19}F NMR (376 MHz, Acetone-d_6)** δ -62.87. **HRMS (ESI)** m/z: Calcd for $C_{25}H_{25}F_3NO_2$ $[M+H]^+$: 428.1832, Found: 428.1829.

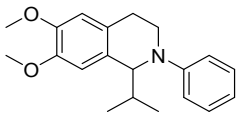


6,7-dimethoxy-1-(2-methoxybenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3am). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 77% (60 mg); without photocatalyst, 71% (55 mg). White solid. **Mp:** 133-135 °C. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.17 (m, 3H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 7.2 Hz, 1H), 6.78 – 6.72 (m, 2H), 6.61 (t, *J* = 7.1 Hz, 1H), 6.11 (s, 1H), 4.98 (t, *J* = 7.2 Hz, 1H), 3.94 (s, 3H), 3.75 (s, 3H), 3.72 (m, 1H), 3.59 (m, 1H), 3.46 (s, 3H), 3.37 – 3.29 (m, 1H), 3.04 – 2.84 (m, 3H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 158.00, 149.73, 148.02, 146.81, 131.74, 130.00, 128.90, 127.58, 127.56, 126.87, 120.11, 116.53, 113.45, 111.71, 111.64, 110.26, 58.61, 55.15, 54.92, 54.85, 41.52, 37.02, 26.64. **HRMS (ESI)** m/z: Calcd for $C_{25}H_{28}NO_3$ $[M+H]^+$:390.2064, Found: 390.2063.

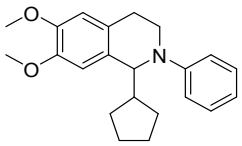


1-(3,4-dichlorobenzyl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3an). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 64% (55 mg); without photocatalyst, 53% (45 mg). Yellow oil. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.41 (m, 2H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.13 (t, *J* = 7.5

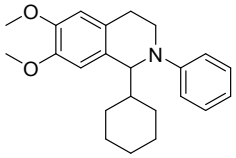
Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.70 (d, *J* = 10.8 Hz, 2H), 6.64 (t, *J* = 7.2 Hz, 1H), 4.99 (t, *J* = 6.9 Hz, 1H), 3.76 (s, 3H), 3.69 (m, 5H), 3.23 (dd, *J* = 13.5, 7.9 Hz, 1H), 3.13 (dd, *J* = 13.5, 5.9 Hz, 1H), 2.92 (dt, *J* = 15.5, 7.6 Hz, 1H), 2.63 (dt, *J* = 16.0, 4.3 Hz, 1H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 149.76, 148.35, 147.47, 140.73, 131.76, 131.10, 129.92, 129.32, 129.30, 128.98, 127.01, 117.48, 114.51, 111.95, 111.46, 60.16, 55.18, 41.15, 40.75, 25.84. **HRMS (ESI)** m/z: Calcd for $C_{24}H_{24}Cl_2NO_2$ $[M+H]^+$: 428.1179, Found: 428.1179.



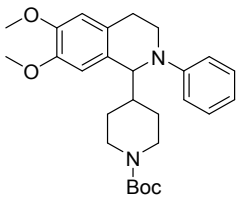
1-isopropyl-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ao). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 64% (40 mg). Yellow oil. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.14 (t, *J* = 7.6 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 6.83 (s, 1H), 6.73 (s, 1H), 6.61 (t, *J* = 7.2 Hz, 1H), 4.40 (d, *J* = 8.3 Hz, 1H), 3.77 (m, 6H), 3.70 (m, 1H), 3.53 (m, 1H), 2.93 (d, *J* = 6.9 Hz, 1H), 2.89 – 2.79 (m, 1H), 2.11 (s, 1H), 1.06 d, *J* = 6.8 Hz 3H), 1.00 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 150.39, 148.26, 146.92, 129.84, 127.28, 116.41, 113.64, 112.86, 112.09, 63.80, 55.43, 55.19, 42.25, 34.13, 26.00, 20.14, 19.67. **HRMS (ESI)** m/z: Calcd for $C_{20}H_{26}NO_2$ $[M+H]^+$: 312.1958, Found: 312.1953.



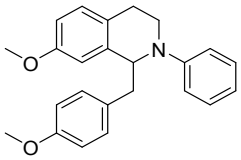
1-cyclopentyl-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ap). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 44% (30 mg); without photocatalyst, %. Yellow oil. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.13 (t, *J* = 7.7 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 2H), 6.85 (s, 1H), 6.67 (s, 1H), 6.60 (t, *J* = 7.3 Hz, 1H), 4.52 (d, *J* = 9.0 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.70 (dd, *J* = 8.0, 5.0 Hz, 2H), 2.94 (dt, *J* = 16.0, 8.0 Hz, 1H), 2.72 (dt, *J* = 16.3, 5.0 Hz, 1H), 2.34 m, 1H), 1.83 (m, 1H), 1.75 – 1.42 (m, 7H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 150.33, 148.21, 147.07, 131.00, 128.90, 126.68, 116.70, 114.21, 112.31, 112.04, 62.18, 55.41, 55.17, 47.11, 41.26, 30.89, 30.51, 25.44, 25.08, 24.18. **HRMS (ESI)** m/z: Calcd for $C_{22}H_{28}NO_2$ $[M+H]^+$: 338.2115, Found: 338.2114.



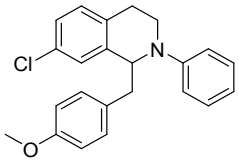
1-cyclohexyl-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3aq). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 50% (35 mg). Yellow solid. **Mp:** 168-170 °C. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.14 (t, *J* = 7.4 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 2H), 6.80 (s, 1H), 6.74 (s, 1H), 6.59 (t, *J* = 7.1 Hz, 1H), 4.44 (d, *J* = 8.3 Hz, 1H), 3.77 (m, 6H), 3.71 (dt, *J* = 12.6, 6.4 Hz, 1H), 3.52 (dt, *J* = 12.7, 6.4 Hz, 1H), 2.93 (m, 2H), 1.99 (m, 1H), 1.76 (m, 4H), 1.67 – 1.58 (m, 1H), 1.18 (m, 5H). **^{13}C NMR (100 MHz, MeOD)** δ 150.28, 147.80, 146.39, 129.92, 128.56, 127.57, 116.30, 113.49, 112.51, 111.81, 63.07, 55.33, 55.10, 43.98, 42.28, 30.80, 30.54, 26.36, 26.20, 25.91. **HRMS (ESI)** m/z: Calcd for $C_{23}H_{30}NO_2$ $[M+H]^+$: 352.2277, Found: 352.2272.



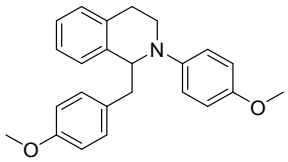
***tert*-butyl 4-(6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)piperidine-1-carboxylate (3ar). Eluent:** petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 74% (63 mg). White solid. **Mp:** 168-170 °C. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.14 (t, *J* = 7.7 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 6.82 (s, 1H), 6.74 (s, 1H), 6.61 (t, *J* = 7.2 Hz, 1H), 4.49 (d, *J* = 8.7 Hz, 1H), 4.11 (m, 2H), 3.77 (m, 6H), 3.75 – 3.67 (m, 1H), 3.56 (m, 1H), 3.02 – 2.83 (m, 2H), 2.02 – 1.87 (m, 2H), 1.66 (m, 1H), 1.42 (s, 9H), 1.28 (m, 2H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 154.04, 150.27, 148.38, 146.94, 129.17, 128.92, 127.18, 116.60, 113.73, 112.86, 112.24, 78.25, 62.24, 55.45, 55.20, 43.73, 42.28, 42.05, 29.89, 27.72, 25.76. **HRMS (ESI)** m/z: Calcd for $C_{27}H_{37}N_2O_4$ $[M+H]^+$: 453.2753, Found: 453.2747.



7-methoxy-1-(4-methoxybenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline(3ba). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 42% (30 mg); without photocatalyst, 0%. White solid. **Mp:** 108-110 °C. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.15 (t, *J* = 7.6 Hz, 2H), 7.05 (m, 3H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 8.3 Hz, 1H), 6.63 (t, *J* = 7.2 Hz, 1H), 6.52 (s, 1H), 4.93 (t, *J* = 6.8 Hz, 1H), 3.73 (s, 3H), 3.63 (m, 5H), 3.18 (dd, *J* = 13.6, 6.9 Hz, 1H), 3.01 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.92 (m, 1H), 2.73 – 2.61 (m, 1H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 158.35, 157.47, 149.68, 138.97, 131.14, 130.63, 129.17, 128.98, 126.86, 116.99, 113.92, 113.40, 112.93, 112.35, 61.32, 54.52, 54.47, 41.58, 40.93, 25.90. **HRMS (ESI)** m/z: Calcd for $C_{24}H_{26}NO_2$ $[M+H]^+$: 360.1960, Found: 360.1960.

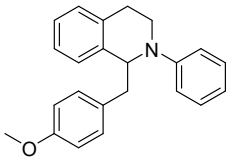


7-chloro-1-(4-methoxybenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ca). Eluent: petroleum ether/ethyl acetate=200/1-30/1. **Yield:** 21% (15 mg); without photocatalyst, 0%. Colorless oil. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.23 – 7.03 (m, 7H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.64 (t, *J* = 7.2 Hz, 1H), 5.00 (t, *J* = 6.8 Hz, 1H), 3.74 (s, 3H), 3.72 – 3.64 (m, 2H), 3.18 (dd, *J* = 13.6, 7.4 Hz, 1H), 3.00 (m, 2H), 2.72 (dt, *J* = 16.3, 4.7 Hz, 1H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 158.42, 149.51, 140.27, 134.02, 130.76, 130.59, 130.40, 130.13, 129.00, 127.43, 126.36, 117.35, 114.18, 113.44, 60.73, 54.52, 40.84, 40.71, 25.92. **HRMS (ESI)** m/z: Calcd for $C_{23}H_{23}ClNO$ $[M+H]^+$: 364.1463, Found: 364.1466.

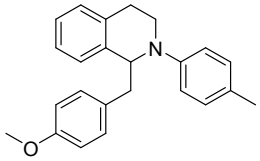


1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline(3da). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 81% (58 mg); without photocatalyst, 77% (55 mg). Colorless oil. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.18 – 7.02 (m, 5H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.86 – 6.65 (m, 6H),

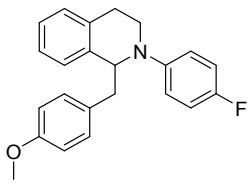
4.79 (t, *J* = 6.8 Hz, 1H), 3.69 (s, 3H), 3.63 (s, 3H), 3.56 (m, 2H), 3.04 (m, 1H), 2.94 – 2.80 (m, 2H), 2.63 (m, 1H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 158.01, 152.04, 144.28, 138.54, 135.03, 131.62, 130.83, 129.01, 127.95, 126.69, 125.76, 116.51, 114.93, 113.82, 61.45, 55.66, 55.36, 41.37, 41.02, 26.14. **HRMS (ESI)** m/z: Calcd for $C_{24}H_{26}NO_2$ $[M+H]^+$: 360.1958, Found: 360.1967.



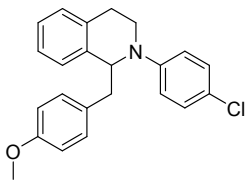
1-(4-methoxybenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline(3ea).[13] Eluent: petroleum ether/ethyl acetate=200/1-30/1. **Yield:** 80% (53 mg); without photocatalyst, 30% (20 mg). Yellow oil. **^{1}H NMR (400 MHz, Acetone-*d*$_6$)** δ 7.14 (m, 4H), 7.04 (m, 3H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.63 (t, *J* = 7.2 Hz, 1H), 4.97 (t, *J* = 6.7 Hz, 1H), 3.73 (s, 3H), 3.67 (m, 1H), 3.60 (m, 1H), 3.22 – 3.13 (m, 1H), 3.06 – 2.93 (m, 2H), 2.74 (dt, *J* = 16.1, 5.2 Hz, 1H). **^{13}C NMR (100 MHz, Acetone)** δ 158.33, 149.59, 138.03, 135.17, 131.03, 130.59, 128.99, 128.33, 127.63, 126.43, 125.39, 116.93, 113.75, 113.37, 61.12, 54.49, 41.37, 41.05, 26.73.



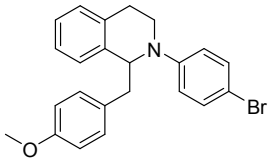
1-(4-methoxybenzyl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (3fa). Eluent: petroleum ether/ethyl acetate=200/1-30/1. **Yield:** 66% (55 mg); without photocatalyst, 0%. Colorless oil. **^{1}H NMR (400 MHz, Acetone-*d*$_6$)** δ 7.12 (d, *J* = 3.6 Hz, 2H), 7.09 – 7.00 (m, 3H), 6.96 (m, 3H), 6.81 – 6.74 (m, 4H), 4.91 (t, *J* = 6.7 Hz, 1H), 3.73 (s, 3H), 3.67 (m, 1H), 3.58 (m, 1H), 3.14 (m, 1H), 2.97 (m, 2H), 2.70 (dt, *J* = 16.2, 5.0 Hz, 1H), 2.16 (s, 3H). **^{13}C NMR (100 MHz, Acetone-*d*$_6$)** δ 158.28, 147.64, 138.15, 135.13, 131.21, 130.56, 129.49, 128.39, 127.61, 126.33, 125.97, 125.33, 114.36, 113.33, 61.31, 54.48, 41.43, 41.00, 26.60, 19.42. **HRMS (ESI)** m/z: Calcd for $C_{24}H_{26}NO$ $[M+H]^+$: 344.2009, Found: 344.2010.



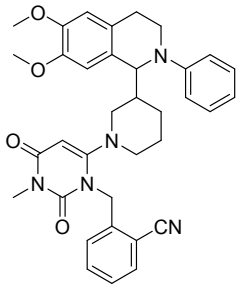
2-(4-fluorophenyl)-1-(4-methoxybenzyl)-1,2,3,4-tetrahydroisoquinoline (3ga). Eluent: petroleum ether/ethyl acetate=200/1-30/1. **Yield:** 58% (40 mg); without photocatalyst, 0%. Yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.15 (m, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.93 (m, 4H), 6.78 (m, 5H), 4.77 (t, *J* = 6.5 Hz, 1H), 3.78 (s, 3H), 3.68 – 3.56 (m, 1H), 3.51 (m, 1H), 3.16 (m, 1H), 2.97 (m, 2H), 2.73 (m, 1H). **^{13}C NMR (100 MHz, Acetone-*d*$_6$)** δ 158.33 , 155.60 (d, *J* = 234.3 Hz), 146.47 , 137.88 , 134.92 , 131.03 , 130.57 , 128.45 , 127.60 , 126.45 , 125.45 , 115.61 (d, *J* = 7.3 Hz), 115.17 (d, *J* = 22.1 Hz), 113.39 , 61.75 , 54.50 , 41.90 , 40.99 , 26.48. **^{19}F NMR (376 MHz, Acetone-*d*$_6$)** δ -129.60. **HRMS (ESI)** m/z: Calcd for $C_{23}H_{23}FNO_2$ $[M+H]^+$: 348.1758, Found: 348.1760.



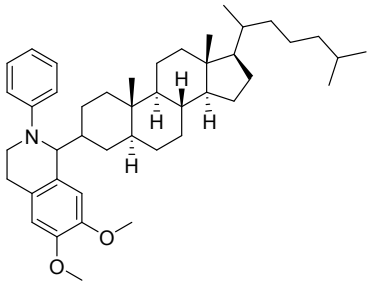
2-(4-chlorophenyl)-1-(4-methoxybenzyl)-1,2,3,4-tetrahydroisoquinoline (3ha). Eluent: petroleum ether/ethyl acetate=200/1-30/1. **Yield:** 62% (45 mg) ; without photocatalyst, 0%. Yellow oil. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.19 – 7.07 (m, 5H), 7.02 (m, 3H), 6.84 (d, *J* = 8.3 Hz, 2H), 6.78 (d, *J* = 7.7 Hz, 2H), 4.97 (t, *J* = 6.7 Hz, 1H), 3.74 (s, 3H), 3.73 – 3.67 (m, 1H), 3.63-3.57 (m, 1H), 3.21 – 3.12 (m, 1H), 3.06-3.92 (m, 2H), 2.79 – 2.72 (m, 1H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 158.39, 148.31, 137.73, 135.00, 130.76, 130.60, 128.66, 128.33, 127.61, 126.55, 125.51, 120.85, 114.81, 113.41, 61.10, 54.50, 41.48, 40.96, 26.65. **HRMS (ESI)** m/z: Calcd for $C_{23}H_{23}ClNO$ $[M+H]^+$: 364.1463, Found: 364.1460.



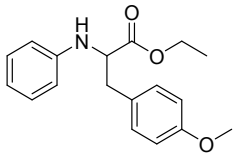
2-(4-bromophenyl)-1-(4-methoxybenzyl)-1,2,3,4-tetrahydroisoquinoline (3ia). Eluent: petroleum ether/ethyl acetate=200/1-30/1 **Yield:** 49% (40 mg); without photocatalyst, 0%. White solid. **Mp:** 108-109 °C. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.29 – 7.22 (d, *J* = 8.3 Hz, 2H), 7.14 (m, 2H), 7.08 (m, 1H), 7.00 (m, 3H), 6.78 (m, 4H), 4.95 (t, *J* = 6.8 Hz, 1H), 3.73 (s, 3H), 3.67 (m, 1H), 3.57 (m, 1H), 3.15 (m, 1H), 2.99 (mz, 2H), 2.74 (m, 1H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 158.40, 148.64, 137.68, 135.01, 131.58, 130.72, 130.61, 128.32, 127.61, 126.58, 125.53, 115.24, 113.42, 107.93, 61.01, 54.51, 41.45, 40.93, 26.67. **HRMS (ESI)** m/z: Calcd for $C_{23}H_{23}NO$ $[M+H]^+$: 408.0958, Found: 408.0958.



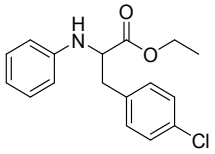
2-((6-(3-(6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)piperidin-1-yl)-3-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)methyl)benzonitrile (3as). Eluent: petroleum ether/ethyl acetate=2/1. **Yield:** 68% (80 mg). White solid. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.77 (d, *J* = 7.6 Hz, 0.64H), 7.65 (d, *J* = 7.6 Hz, 0.37H), 7.46 m, 2H), 7.27 – 7.08 (m, 3H), 6.90 – 6.78 (m, 2.64H), 6.70 (m, 1.36H), 6.62 (t, *J* = 7.1 Hz, 1H), 5.37 – 5.16 (m, 3H), 4.47 (m, 1H), 3.83 – 3.71 (m, 6H), 3.51 (m, 2.65H), 3.15 (m, 4.41H), 2.89 (m, 1H), 2.79 – 2.53 (m, 3H), 2.11 (m, 1.3H), 1.78 (m, 1.68H), 1.64 – 1.27 (m, 2H). **^{13}C NMR (101 MHz, Acetone-d_6)** δ 162.31, 162.28, 160.54, 160.41, 152.59, 152.38, 150.16, 150.04, 148.51, 148.45, 147.07, 146.90, 141.66, 141.35, 133.21, 133.00, 132.87, 132.80, 128.95, 128.91, 128.44, 128.27, 127.66, 127.64, 127.23, 127.14, 126.61, 126.43, 117.21, 117.02, 116.92, 114.45, 113.99, 112.86, 112.33, 112.28, 112.06, 110.41, 110.10, 90.43, 90.01, 60.66, 60.31, 55.80, 55.50, 55.48, 55.40, 55.17, 55.14, 52.07, 51.64, 45.98, 45.93, 42.27, 42.09, 41.72, 41.68, 28.29, 28.19, 26.92, 26.85, 25.73, 25.17, 24.96, 24.85. **HRMS (ESI)** m/z: Calcd for $C_{35}H_{38}N_5O_4$ $[M+H]^+$:592.2918, Found: 592.2911.



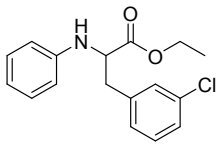
1-((5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-(6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3at). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 55% (70 mg). White solid. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.14 m, 2H), 6.97 (m, 2H), 6.85 (m, 1H), 6.78 – 6.66 (m, 1H), 6.61 (t, *J* = 7.3 Hz, 1H), 4.96 (d, *J* = 10.9 Hz, 0.3H), 4.49 (m, 0.7H), 3.84 – 3.67 (m, 7H), 3.57 (m, 1H), 3.02 – 2.83 (m, 2H), 1.93 – 1.73 (m, 3H), 1.66 – 1.02 (m, 26H), 0.89 (m, 15H), 0.71 (m, 3H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ150.75, 150.42, 150.37, 148.27, 146.84, 146.82, 146.64, 131.00, 130.41, 129.90, 128.96, 128.88, 127.18, 127.15, 126.63, 116.90, 116.70, 116.33, 116.28, 114.70, 114.41, 113.64, 113.55, 113.09, 113.00, 112.71, 112.62, 112.18, 112.14, 42.51, 42.06, 41.27, 41.11, 40.38, 40.27, 40.14, 40.09, 39.37, 38.65, 38.61, 37.73, 37.46, 36.29, 36.17, 36.08, 35.78, 35.74, 35.62, 35.54, 34.26, 33.82, 33.00, 32.94, 32.12, 32.07, 28.06, 27.81, 26.24, 26.16, 25.99, 25.89, 24.90, 24.63, 23.98, 23.71, 23.66, 22.59, 22.37, 22.22, 21.97, 20.93, 20.72, 18.25, 11.94, 11.89, 11.69, 11.63, 11.61. **HRMS (ESI)** m/z: Calcd for $C_{44}H_{66}NO_2$ $[M+H]^+$: 640.5088, Found: 640.5087.



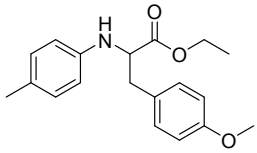
ethyl 3-(4-methoxyphenyl)-2-(phenylamino)propanoate (5aa). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 65% (39 mg); without photocatalyst, 0%. Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.18 (t, *J* = 7.6 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 2H), 4.31 (t, *J* = 6.1 Hz, 1H), 4.12 (q, *J* = 6.4 Hz, 2H), 3.79 (s, 3H), 3.09 (t, *J* = 7.0 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.99, 158.63, 146.01, 130.34, 129.35, 128.23, 118.74, 113.99, 113.92, 61.14, 58.17, 55.25, 37.65, 14.17. **HRMS (ESI)** m/z: Calcd for $C_{18}H_{22}NO_3$ $[M+H]^+$: 300.1600, Found: 300.1598.



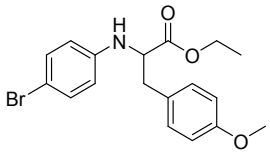
ethyl 3-(4-chlorophenyl)-2-(phenylamino)propanoate (5ae). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 66% (40 mg). Colorless oil. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.31 (s, 4H), 7.09 (t, *J* = 7.6 Hz, 2H), 6.65 (dd, *J* = 15.4, 7.7 Hz, 3H), 5.17 (d, *J* = 7.5 Hz, 1H), 4.34 (q, *J* = 7.3 Hz, 1H), 4.05 (d, *J* = 7.0 Hz, 2H), 3.11 (dd, *J* = 6.3, 4.0 Hz, 2H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 172.69, 147.35, 136.39, 131.95, 131.08, 128.98, 128.19, 117.41, 113.15, 60.41, 57.63, 37.57, 13.57. **HRMS (ESI)** m/z: Calcd for $C_{17}H_{19}ClNO_2$ $[M+H]^+$: 304.1099, Found: 304.1101



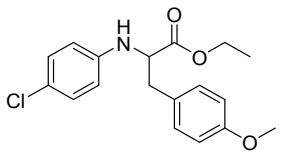
ethyl 3-(2-chlorophenyl)-2-(phenylamino)propanoate (5ak). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 61% (37 mg). White solid. **Mp:** 45-47 °C. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.40 – 7.22 (m, 4H), 7.10 (t, *J* = 7.5 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 5.21 (d, *J* = 9.0 Hz, 1H), 4.37 (q, *J* = 7.3 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.19 – 3.08 (m, 2H), 1.13 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 172.68, 147.36, 139.97, 133.47, 129.83, 129.35, 128.98, 127.90, 126.61, 117.44, 113.17, 60.41, 57.59, 37.89, 13.56. **HRMS (ESI)** m/z: Calcd for $C_{17}H_{19}ClNO_2$ $[M+H]^+$: 304.1009, Found: 304.1104.



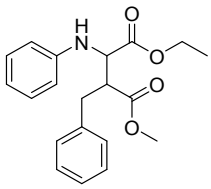
ethyl 3-(4-methoxyphenyl)-2-(p-tolylamino)propanoate (5ba).[14] Eluent: petroleum ether/ethyl acetate=30/1-10/1. Yield: 64% (40 mg). Yellow solid. **Mp:** 59-61 °C. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.04 (d, *J* = 7.9 Hz, 2H), 6.77 (d, *J* = 7.9 Hz, 2H), 6.70 (d, *J* = 7.8 Hz, 2H), 6.43 (d, *J* = 7.7 Hz, 2H), 4.74 (d, *J* = 9.2 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 1H), 3.91 (q, *J* = 6.7 Hz, 2H), 3.61 (s, 3H), 2.88 (d, *J* = 6.7 Hz, 2H), 2.02 (s, 3H), 0.98 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 173.08, 158.64, 145.20, 130.29, 129.44, 129.18, 126.08, 113.59, 113.31, 60.18, 58.34, 54.54, 37.61, 19.55, 13.61.



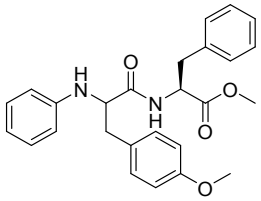
ethyl 2-((4-bromophenyl)amino)-3-(4-methoxyphenyl)propanoate (5ca). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 66% (40 mg). Yellow solid. **Mp:** 54-56 °C. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.20 (m, 4H), 6.84 (d, *J* = 7.9 Hz, 2H), 6.63 (d, *J* = 8.1 Hz, 2H), 5.35 (d, *J* = 9.0 Hz, 1H), 4.27 (q, *J* = 7.3 Hz, 1H), 4.07 (q, *J* = 6.9 Hz, 2H), 3.75 (s, 3H), 3.05 (m, 2H), 1.13 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 172.58, 158.69, 146.83, 131.63, 130.29, 128.93, 114.85, 113.64, 108.21, 60.41, 57.96, 54.56, 37.36, 13.60. **HRMS (ESI)** m/z: Calcd for $C_{18}H_{21}BrNO_3$ $[M+H]^+$: 378.0705, Found: 378.0704.



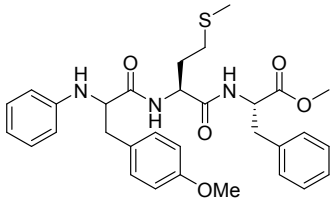
ethyl 2-((4-chlorophenyl)amino)-3-(4-methoxyphenyl)propanoate (5da). Eluent: petroleum ether/ethyl acetate=30/1-10/1. **Yield:** 60% (40 mg); without photocatalyst, 0%. Yellow solid. **Mp:** 57-59 °C. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.19 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 7.8 Hz, 2H), 6.67 (d, *J* = 8.1 Hz, 2H), 5.33 (d, *J* = 8.8 Hz, 1H), 4.27 (q, *J* = 7.3 Hz, 1H), 4.07 (q, *J* = 7.0 Hz, 2H), 3.76 (s, 3H), 3.05 (h, *J* = 6.6 Hz, 2H), 1.13 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 172.63, 158.69, 146.44, 130.29, 128.95, 128.72, 121.19, 114.34, 113.64, 60.38, 58.07, 54.55, 37.39, 13.59. **HRMS (ESI)** m/z: Calcd for $C_{18}H_{21}ClNO_3$ $[M+H]^+$: 334.1204, Found: 334.1210.



4-ethyl 1-methyl 2-benzyl-3-(phenylamino)succinate (5au) Eluent: petroleum ether/ethyl acetate=30/1-10/1. **A: Yield:** 29% (20 mg). White solid. **Mp:** 58-60 °C. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.31 – 7.18 (m, 5H), 7.13 (m, 2H), 6.70 (m, 3H), 5.14 (d, *J* = 10.3 Hz, 1H), 4.32 (dd, *J* = 10.2, 6.0 Hz, 1H), 4.14 (m, 2H), 3.58 (s, 3H), 3.09 – 2.91 (m, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 172.54, 171.55, 147.23, 138.73, 129.01, 128.91, 128.40, 126.50, 118.03, 113.67, 60.81, 57.49, 51.20, 49.63, 34.30, 13.57. **B: Yield:** 26% (18 mg). White solid. **Mp:** 48-50 °C. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.25 (m, 5H), 7.11 (t, *J* = 7.6 Hz, 2H), 6.72 – 6.62 (m, 3H), 5.32 (d, *J* = 9.9 Hz, 1H), 4.36 – 4.29 (m, 1H), 4.11 (q, *J* = 6.8, 6.4 Hz, 2H), 3.58 (s, 3H), 3.27 – 3.05 (m, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 172.21, 171.48, 147.27, 138.90, 129.10, 129.01, 128.31, 126.43, 117.81, 113.44, 60.77, 57.35, 51.09, 50.23, 34.29, 13.56. **HRMS (ESI)** m/z: Calcd for $C_{20}H_{24}NO_4$ $[M+H]^+$:342.1700, Found: 342.1702.



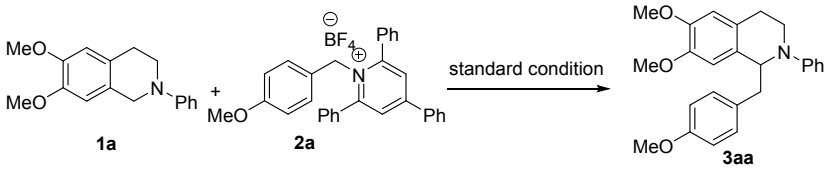
methyl (3-(4-methoxyphenyl)-2-(phenylamino)propanoyl)-L-phenylalaninate (6). Eluent: petroleum ether/ethyl acetate=20/1-2/1. **Yield:** 69% (60 mg). Yellow oil. **^{1}H NMR (400 MHz, Acetone-d_6)** δ 7.58 (d, *J* = 7.8 Hz, 0.45H), 7.49 (d, *J* = 8.2 Hz, 0.40H), 7.31 – 7.03 (m, 8H), 6.95 (d, *J* = 5.8 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 2H), 6.70 – 6.54 (m, 3H), 5.01 (d, *J* = 6.2 Hz, 0.49H), 4.90 (d, *J* = 6.3 Hz, 0.46H), 4.76 (m, 1H), 4.03 (m, 1H), 3.73 (s, 3H), 3.65 (s, 1.54H), 3.59 (s, 1.41H), 3.11 (m, 3H), 2.91 – 2.80 (m,1H). **^{13}C NMR (100 MHz, Acetone-d_6)** δ 172.57, 172.37, 171.44, 171.42, 158.56, 158.54, 147.64, 147.51, 136.97, 136.52, 130.16, 130.15, 129.71, 129.29, 129.27, 128.96, 128.85, 128.30, 128.28, 128.00, 126.63, 126.60, 117.60, 117.58, 113.68, 113.49, 113.46, 113.29, 60.00, 59.84, 54.53, 53.26, 52.92, 51.43, 51.35, 37.89, 37.86, 37.51, 37.30. **HRMS (ESI)** m/z: Calcd for $C_{26}H_{29}N_2O_4$ $[M+H]^+$: 433.2127, Found: 433.2119.



methyl (3-(4-methoxyphenyl)-2-(phenylamino)propanoyl)-L-methionyl-L-phenylalaninate (7). Eluent: petroleum ether/ethyl acetate=5/1-2/1. **Yield:** 62% (70 mg). Yellow solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.49 – 7.18 (m, 5H), 7.17 – 7.05 (m, 3H), 7.02 – 6.87 (m, 2H), 6.87 – 6.56 (m, 4H), 4.76 (m, 1H), 4.57 – 4.49 (m, 1H), 4.05 (m, 1H), 3.74 (m, 6H), 3.20 (m, 1H), 3.16 – 2.99 (m, 2H), 2.82 (m, 1H), 2.25 (m, 2H), 2.04 – 1.67 (m, 5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.92, 172.83, 171.59, 170.48, 170.17, 158.88, 158.79, 146.11, 145.82, 135.88, 135.71, 130.18, 129.98, 129.63, 129.46, 129.38, 129.23, 129.13, 128.70, 128.60, 128.18, 127.98, 127.22, 127.10, 124.97, 119.79, 114.41, 114.29, 114.20, 60.45, 60.12, 55.28, 55.26, 53.43, 53.40, 53.31, 52.39, 52.36, 52.16, 51.75, 37.84, 37.72, 37.51, 30.80,

30.53, 29.80, 29.70, 29.66, 14.99, 14.86. **HRMS (ESI)** m/z: Calcd for $C_{31}H_{38}N_3O_5S$ $[M+H]^+$: 564.2527, Found: 564.2531.

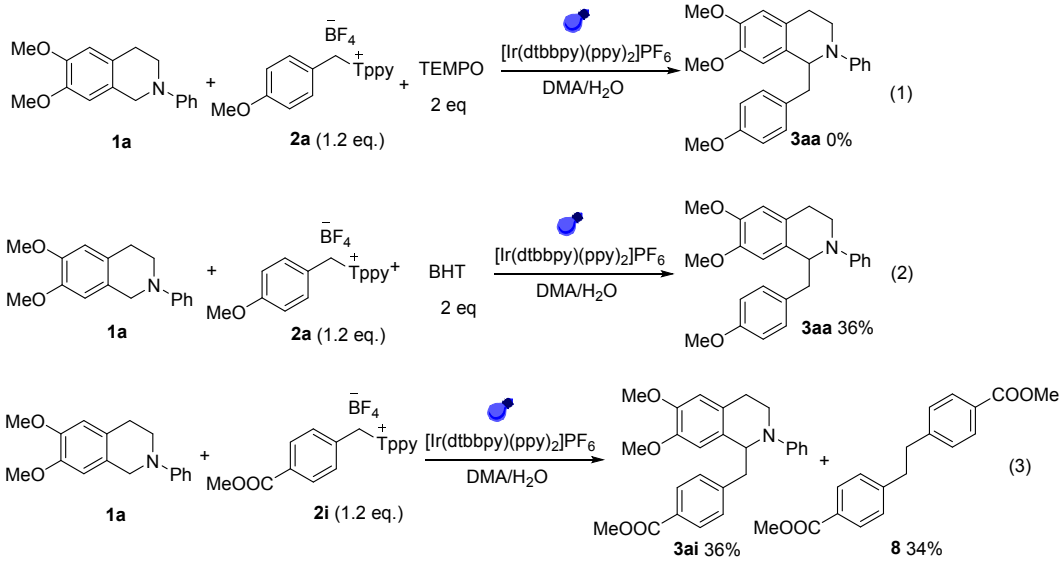
3 Representative procedure for large-scale general procedure for the alkylation of *N*-arylamines.



A glass reaction tube equipped with a stirring bar was charged with $[Ir(dtbbpy)(ppy)_2]PF_6$ (34 mg, 37μmol, 2.0 mol%), 6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline **1a** (1g, 3.7 mmol) and alkyl 2,4,6-triphenylpyridinium tetrafluoroborate **2a** (2.3 g, 4.5 mmol.). DMA (36 ml) and H_2O (3.3 ml) were added, then the resulting mixture was degassed by three freeze-thaw cycles and backfilled with argon. The reaction mixture was stirred at room temperature with the irradiation of a 10 W blue LED. After the reaction was complete, the mixture was diluted with EtOAc and washed with water, and concentrated in vacuo. A crude product was purified by column chromatography (30:1-10:1). The desired product **3aa** was isolated as a white solid (1.24 g, 86%).

4 The mechanistic considerations

4.1 Radical trapping experiments



Scheme S1. Radical trapping experiments

Procedure of (1) or (2)

A glass reaction tube equipped with a stirring bar was charged with $[Ir(dtbbpy)(ppy)_2]PF_6$ (1.8 mg, 2 μmol), **1a** (0.1 mmol, 27 mg), **2a** (0.12 mmol, 62 mg) and TEMPO (0.2 mmol, 36 mg) or BHT (0.2 mmol, 44 mg). DMA (1 ml) and H_2O (90 μl) were added, then the resulting mixture was degassed by three freeze-thaw cycles and backfilled with argon. The reaction mixture was stirred at room temperature

with the irradiation of a 10 W blue LED. After the reaction was complete, the mixture was diluted with EtOAc and washed with water, and concentrated in vacuo. A crude product was purified by column chromatography. **Yield:** (1): 0, (2): 36%.

Procedure of (3)

A glass reaction tube equipped with a stirring bar was charged with $[Ir(dtbbpy)(ppy)_2]PF_6$ (3.6 mg, 4 µmol), **1a** (0.2 mmol, 54 mg), **2a** (0.24 mmol, 130 mg). DMA (2 ml) and H_2O (180 µl) were added, then the resulting mixture was degassed by three freeze-thaw cycles and backfilled with argon. The reaction mixture was stirred at room temperature with the irradiation of a 10 W blue LED. After the reaction was complete, the mixture was diluted with EtOAc and washed with water, and concentrated in vacuo. A crude product was purified by column chromatography. **Yield: 3ai** (36%, 30 mg), **8 (**34%, 20 mg**).** ^1H NMR of **8** (400 MHz, $CDCl_3$)[15] δ 7.93 (d, *J* = 7.6 Hz, 4H), 7.19 (d, *J* = 7.8 Hz, 4H), 3.90 (s, 6H), 2.99 (s, 4H).

4.2 Stern-Volmer quenching experiments

$[Ir(dtbbpy)(ppy)_2]PF_6$was dissolved in DMA (c = $3.0 \cdot 10^{-5}$ M) and subsequently degassed by purging with argon for 30 minutes. In a typical experiment appropriate amount of potential quencher (**1d, 2b**) was added to the solution placed in a quartz screw-top cuvette (final volume - 1 mL) equipped with PTFE/silicone septum. After adding variable concentrations of quncher, the resulting mixture was additionally degassed for 2 minutes. The solutions were irradiated at 420 nm and luminescence was observed at 560 nm.

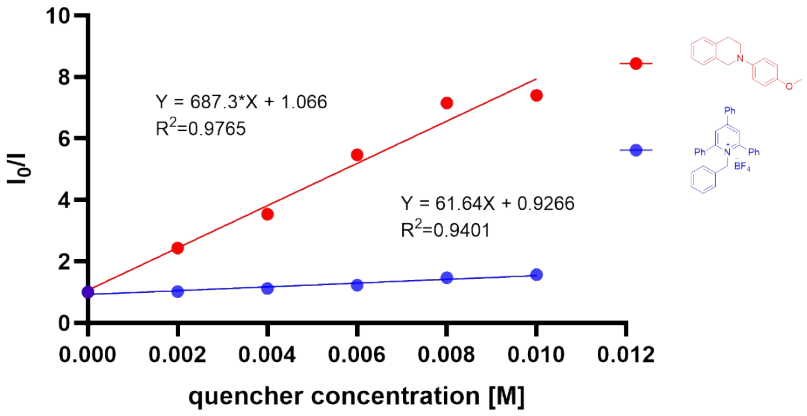


Figure S2. Stern- Volmer plot of components of the reaction mixture.

4.3 UV/vis absorption

UV/vis absorption spectra of *N*-phenyl tetrahydroisoquinoline **1a** (0.05 M) and Katritzky salts **2b** (0.05 M) in 1 ml DMA were recorded using UV/vis spectrometer.

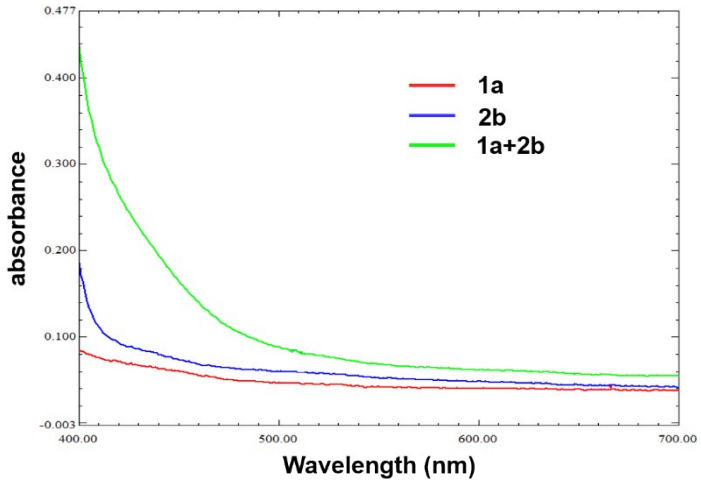


Figure S3. The UV/vis absorption spectra of **1a** and **2b**.

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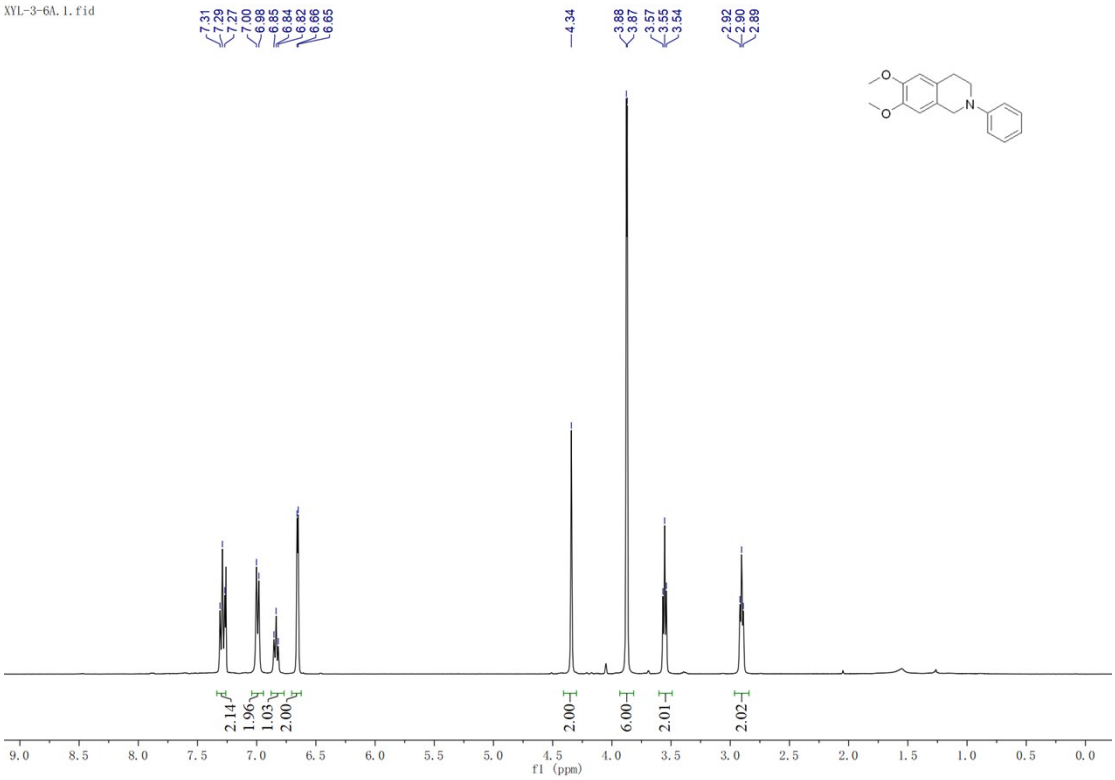
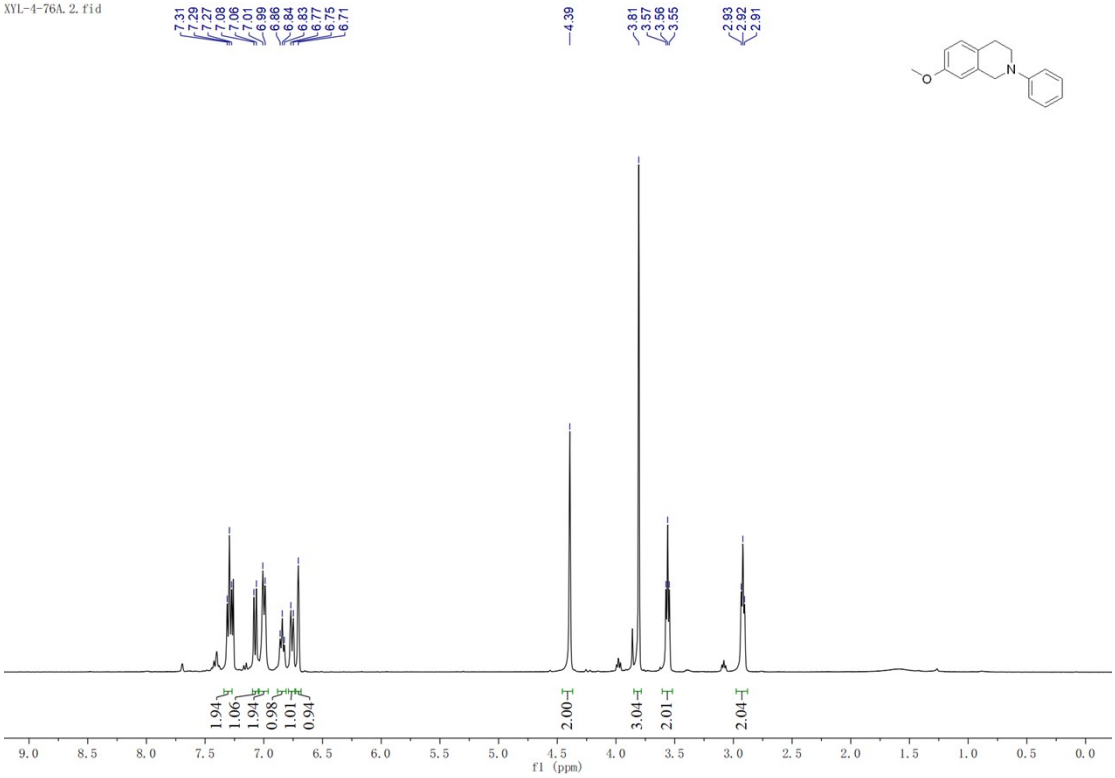
6 NMR Spectra

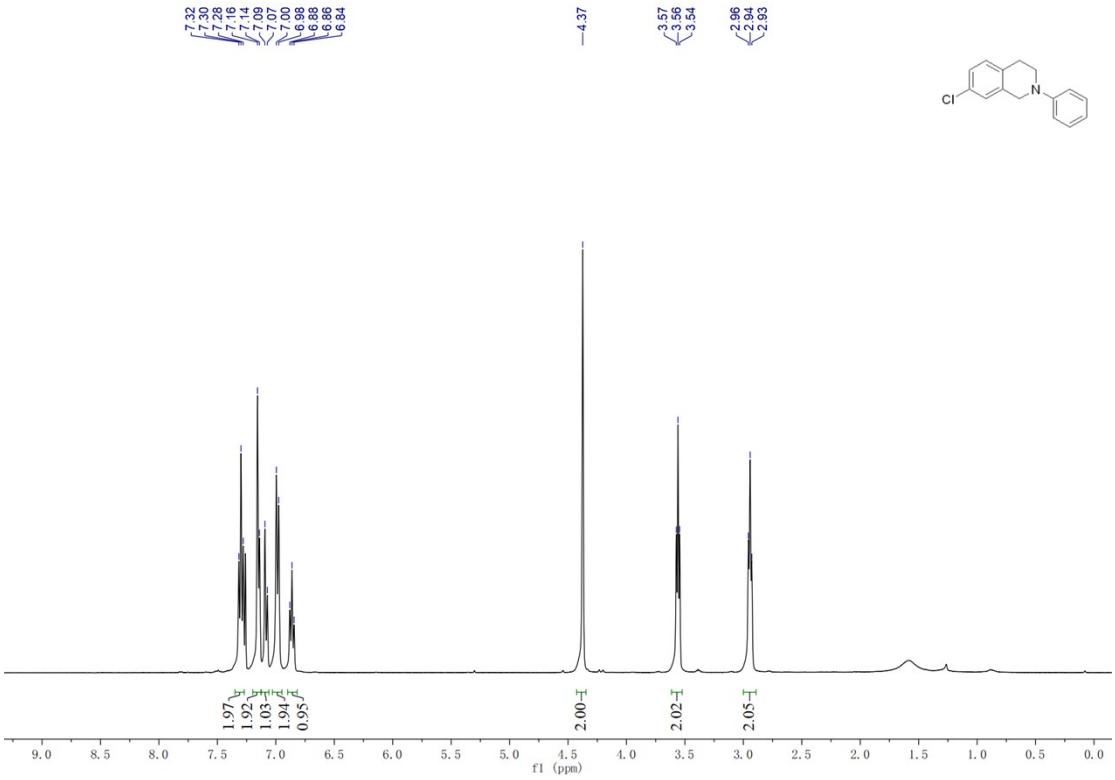
^{1}H NMR spectrum of **6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (1a).**



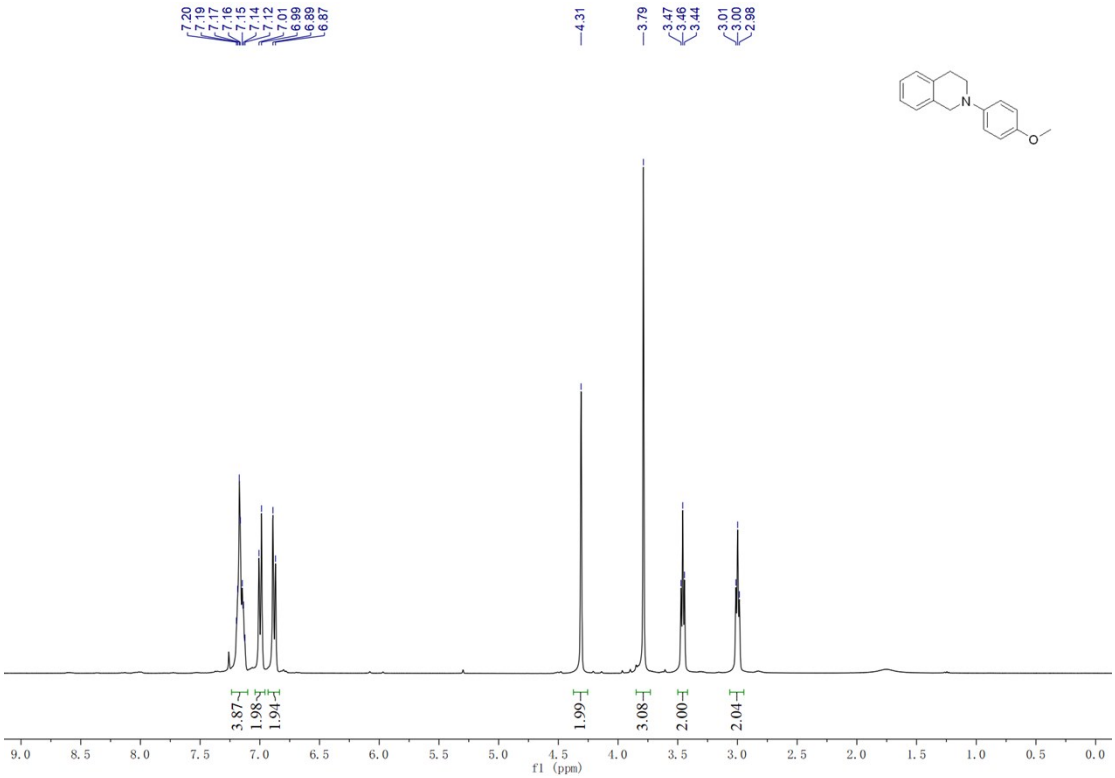
^{1}H NMR spectrum of **7-methoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (1b).**



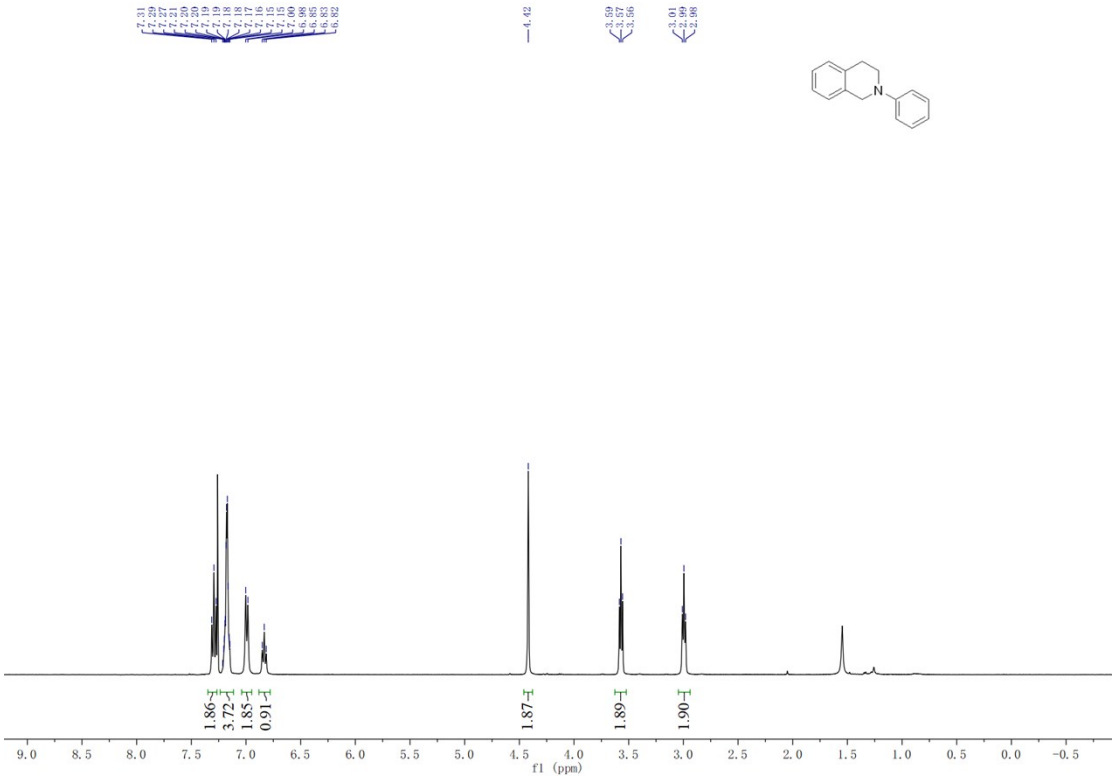
^{1}H NMR spectrum of **7-chloro-2-phenyl-1,2,3,4-tetrahydroisoquinoline (1c).**



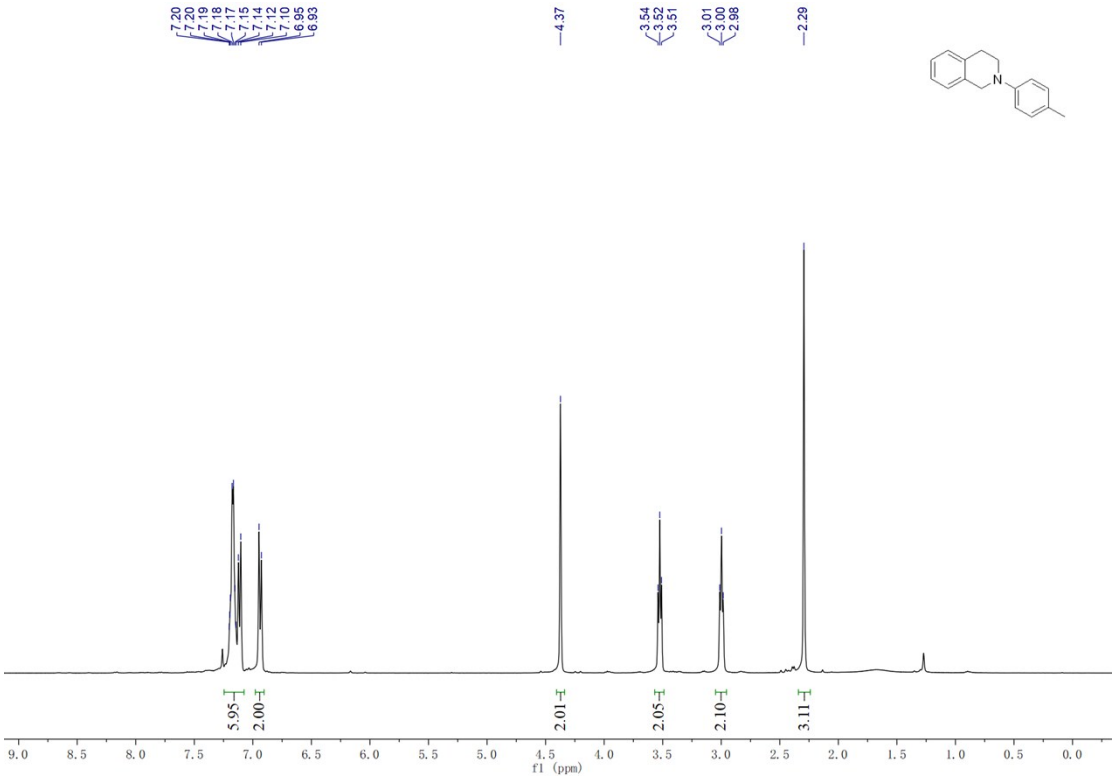
^{1}H NMR spectrum of **2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (1d).**



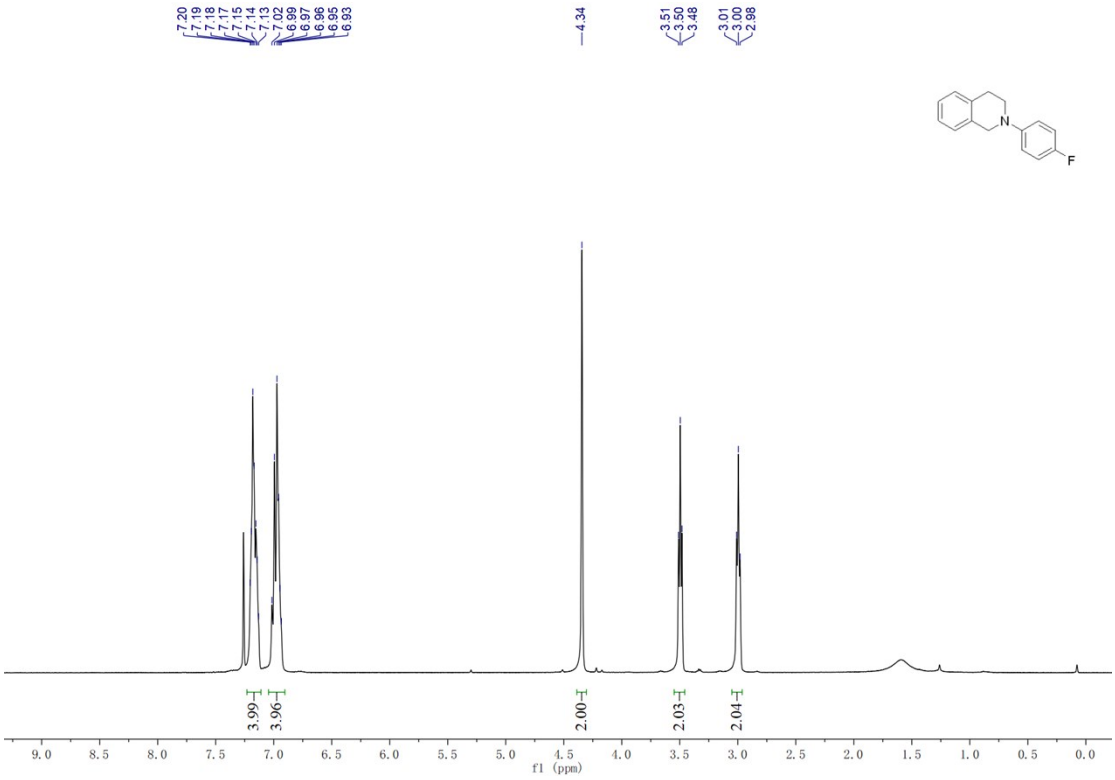
^{1}H NMR spectrum of **2-phenyl-1,2,3,4-tetrahydroisoquinoline (1e).**



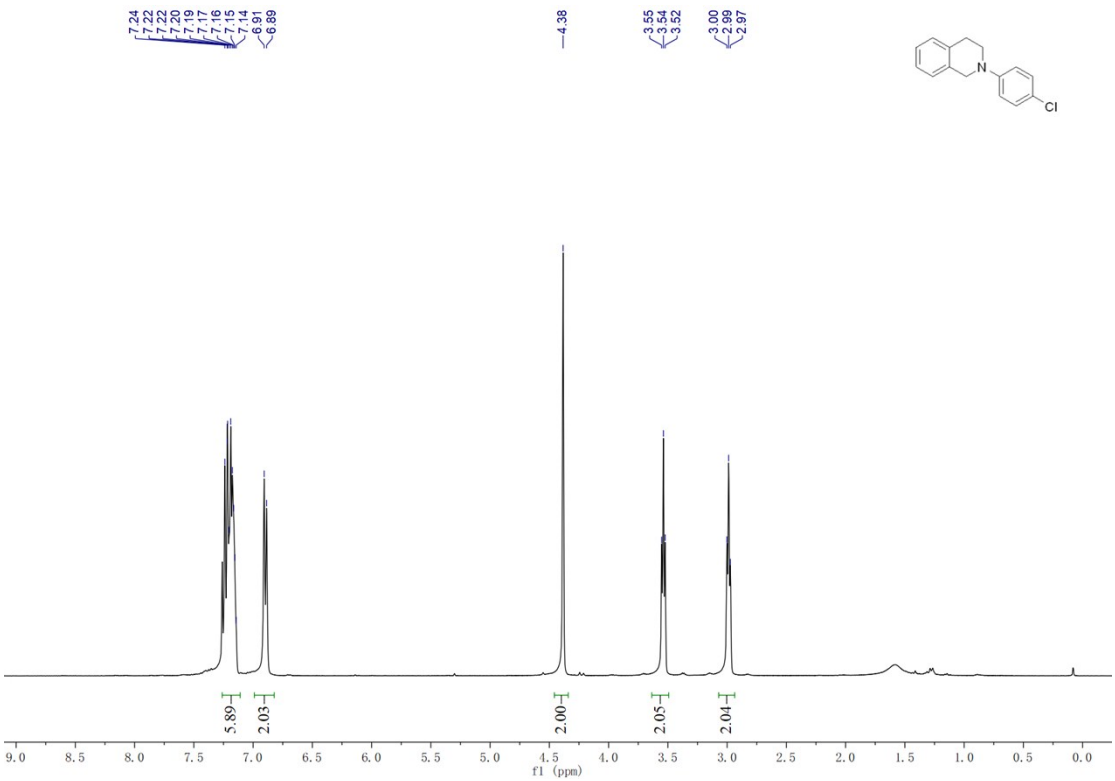
^{1}H NMR spectrum of **2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (1f).**



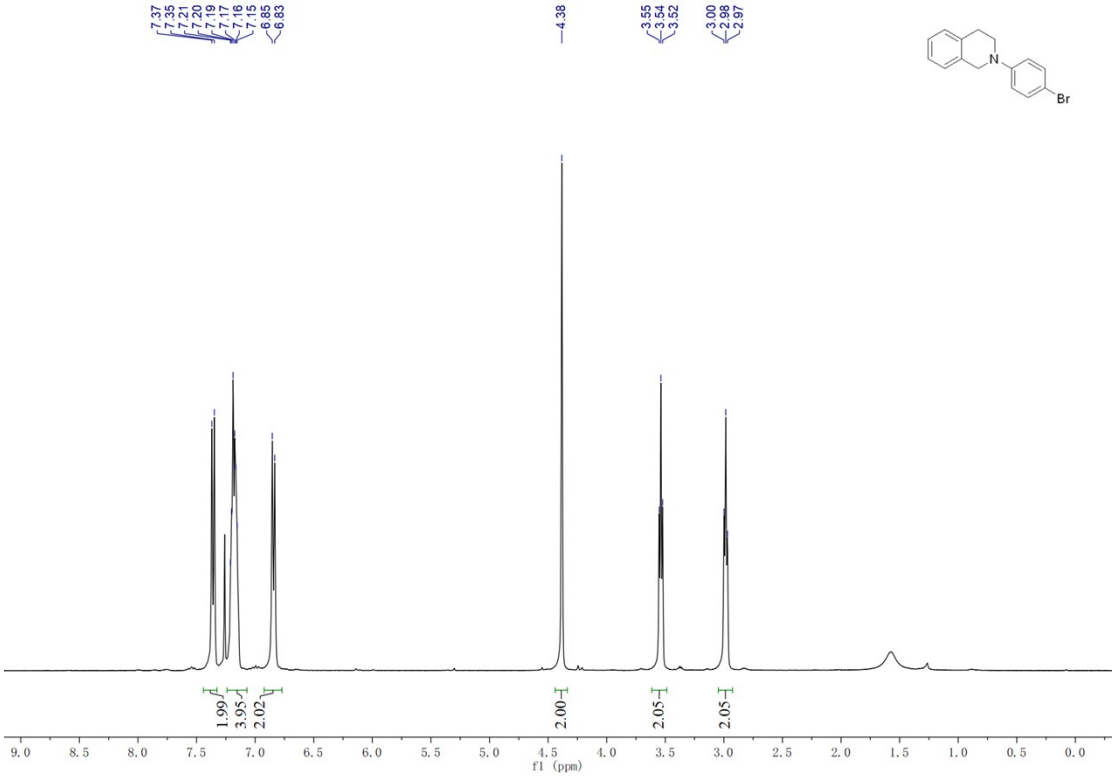
^{1}H NMR spectrum of **2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (1g).**



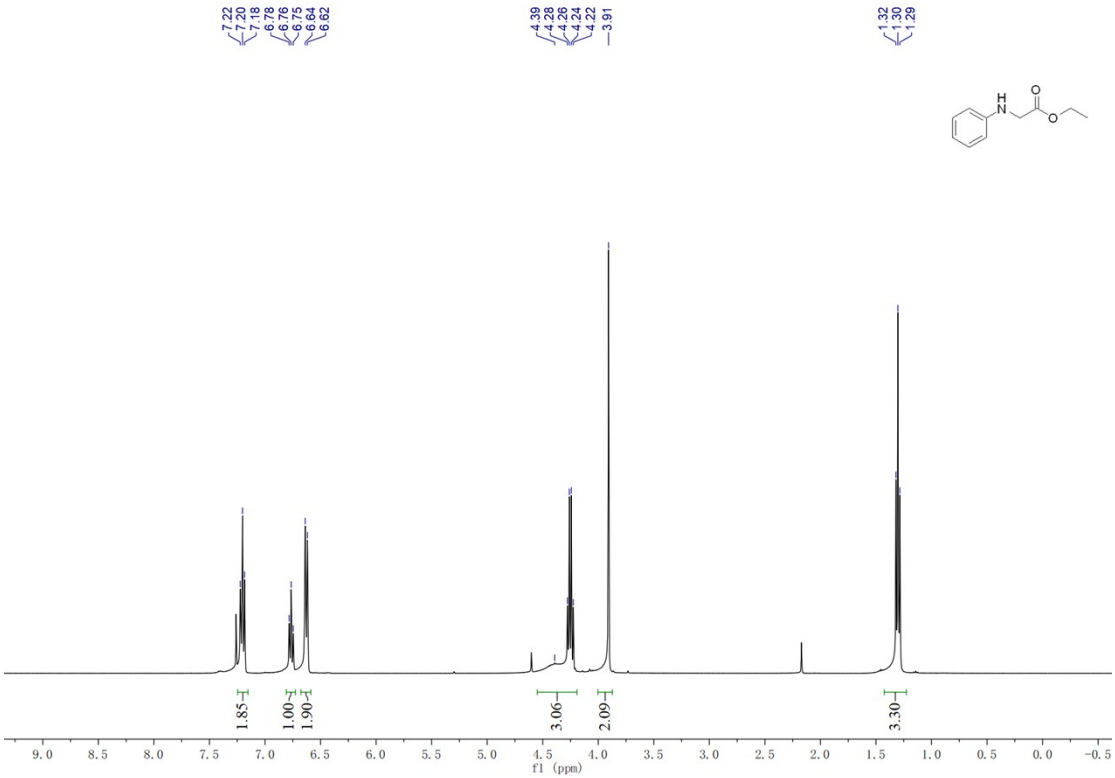
^{1}H NMR spectrum of **2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (1h).**



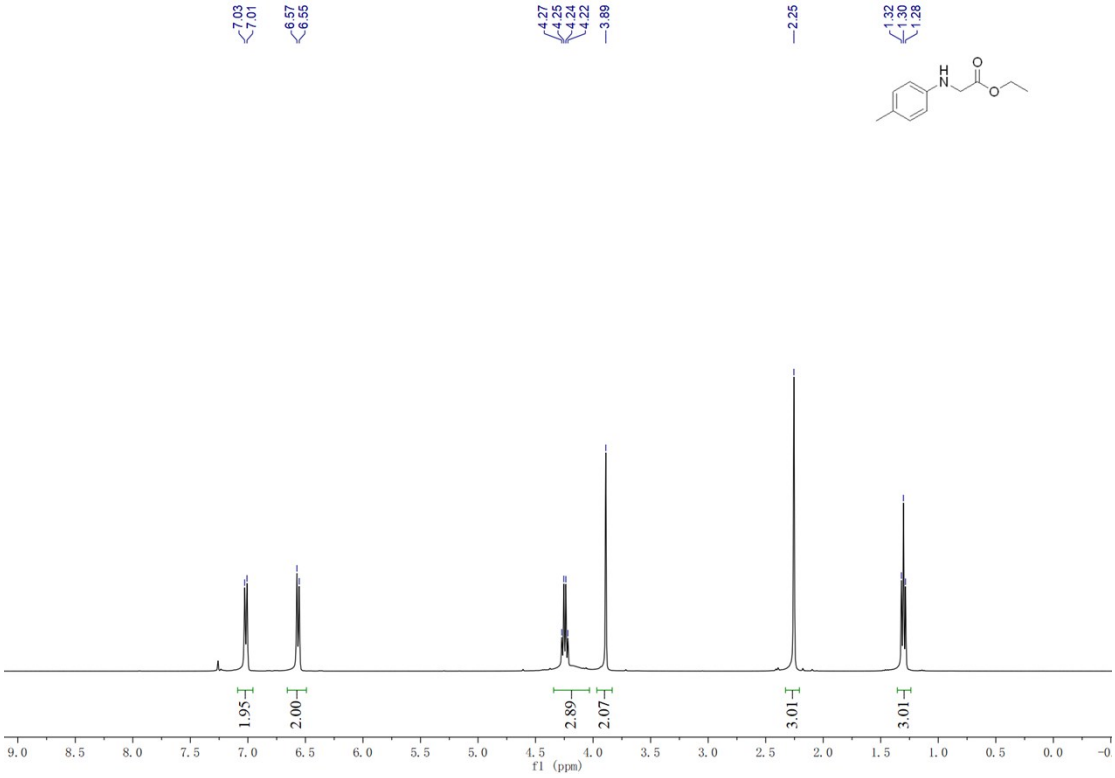
^{1}H NMR spectrum of **2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline (1i).**



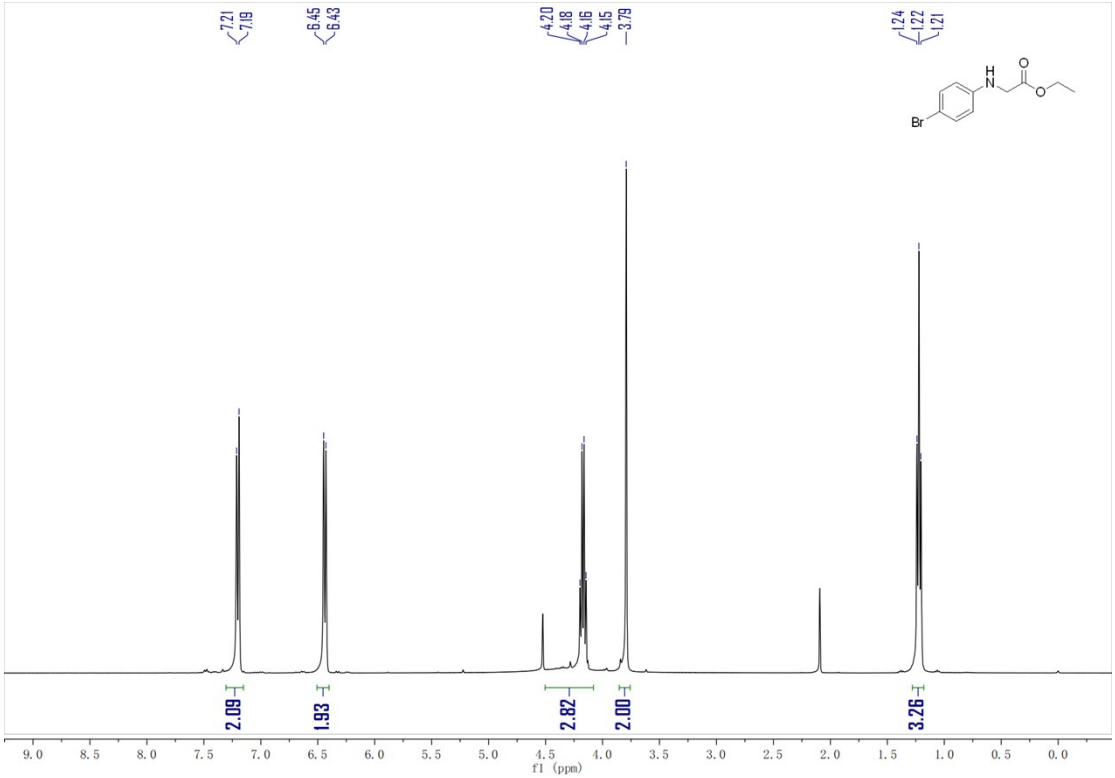
^{1}H NMR spectrum of **ethyl phenylglycinate (4a).**



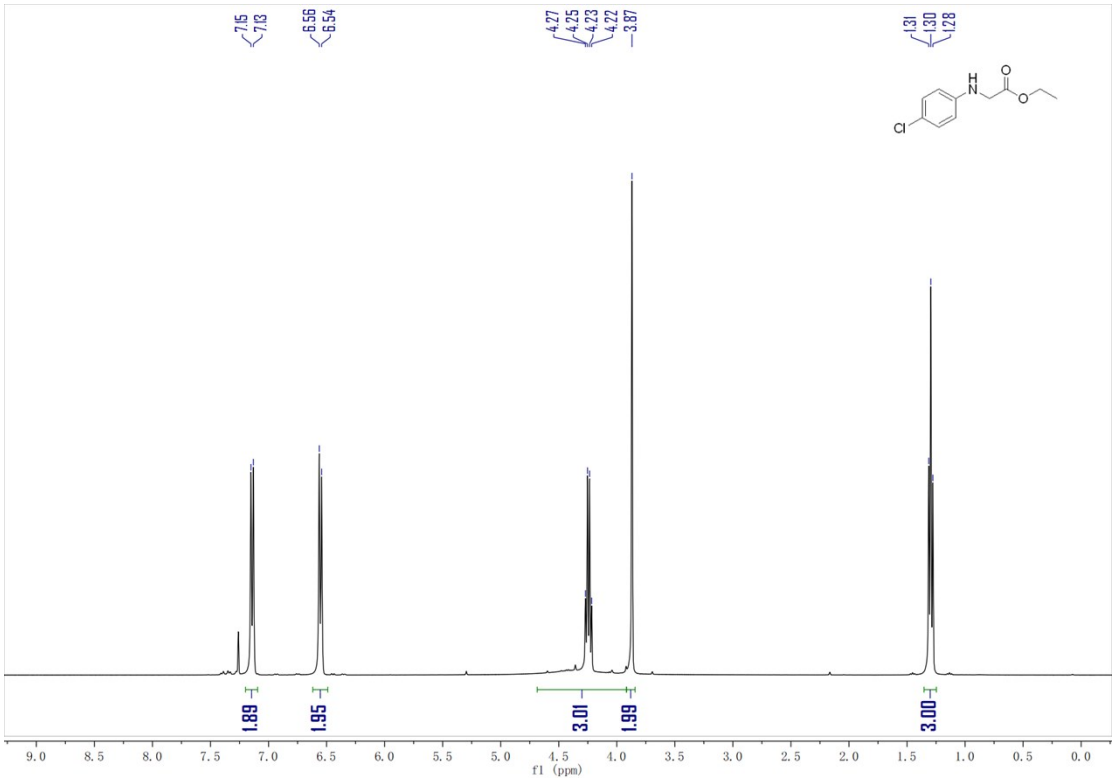
^{1}H NMR spectrum of **ethyl p-tolylglycinate (4b).**



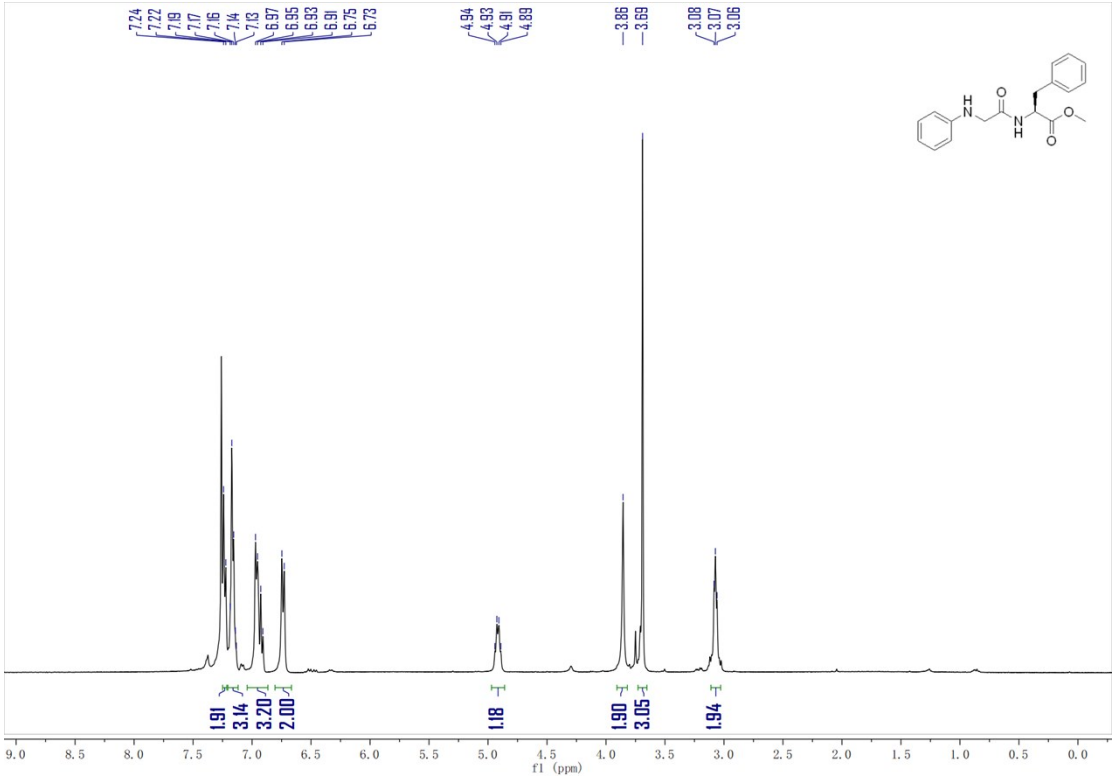
^{1}H NMR spectrum of **ethyl (4-bromophenyl)glycinate (4c).**



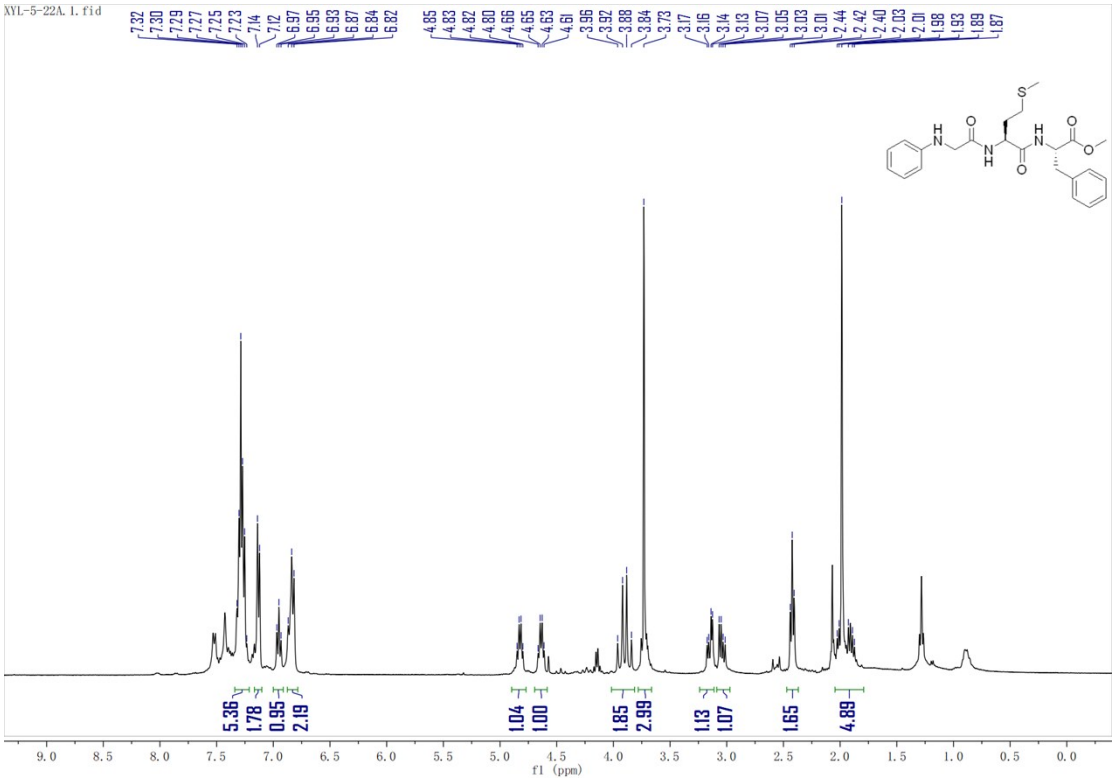
^{1}H NMR spectrum of **ethyl (4-chlorophenyl)glycinate (4d).**



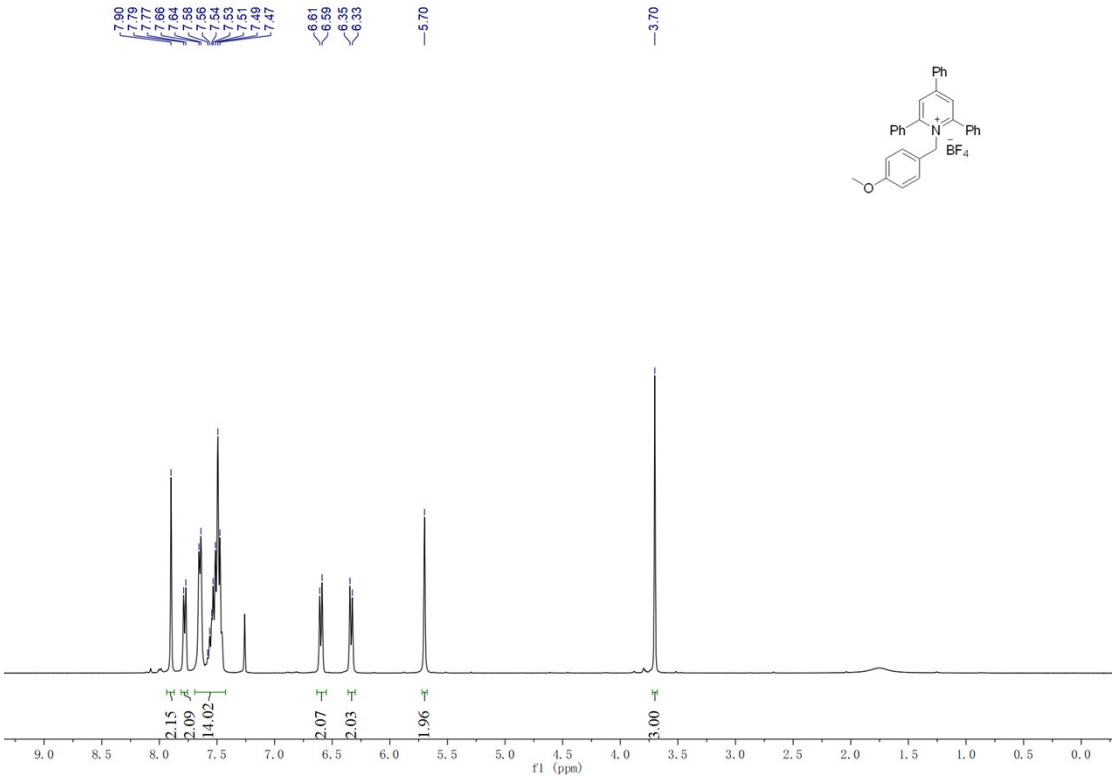
^{1}H NMR spectrum of **methyl phenylglycyl-L-phenylalaninate (8).**



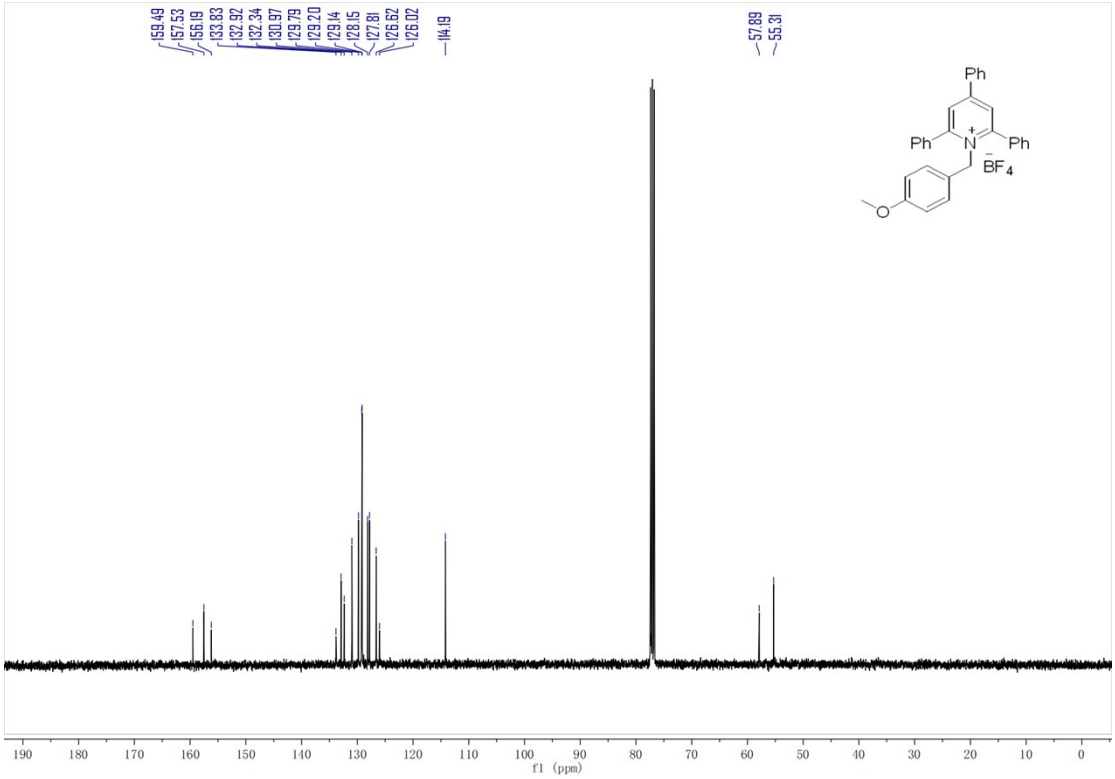
^{1}H NMR spectrum of **methyl phenylglycyl-L-methionyl-L-phenylalaninate (9).**



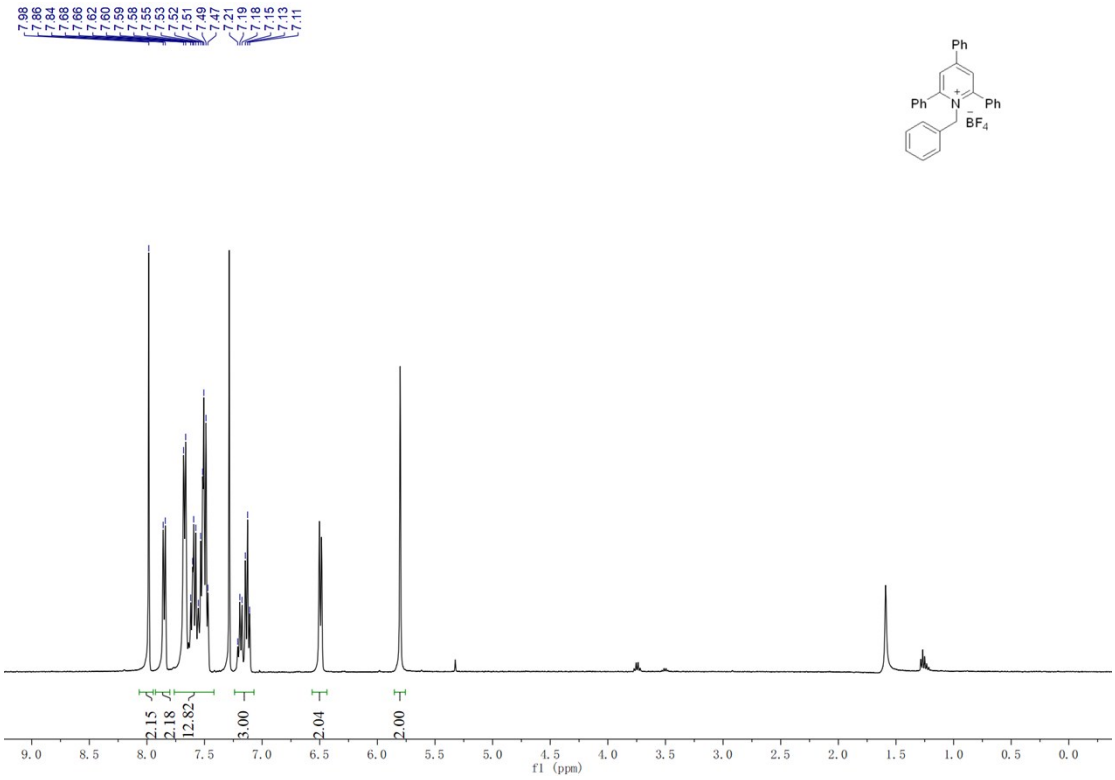
^{1}H NMR spectrum of **1-(4-methoxybenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2a).**



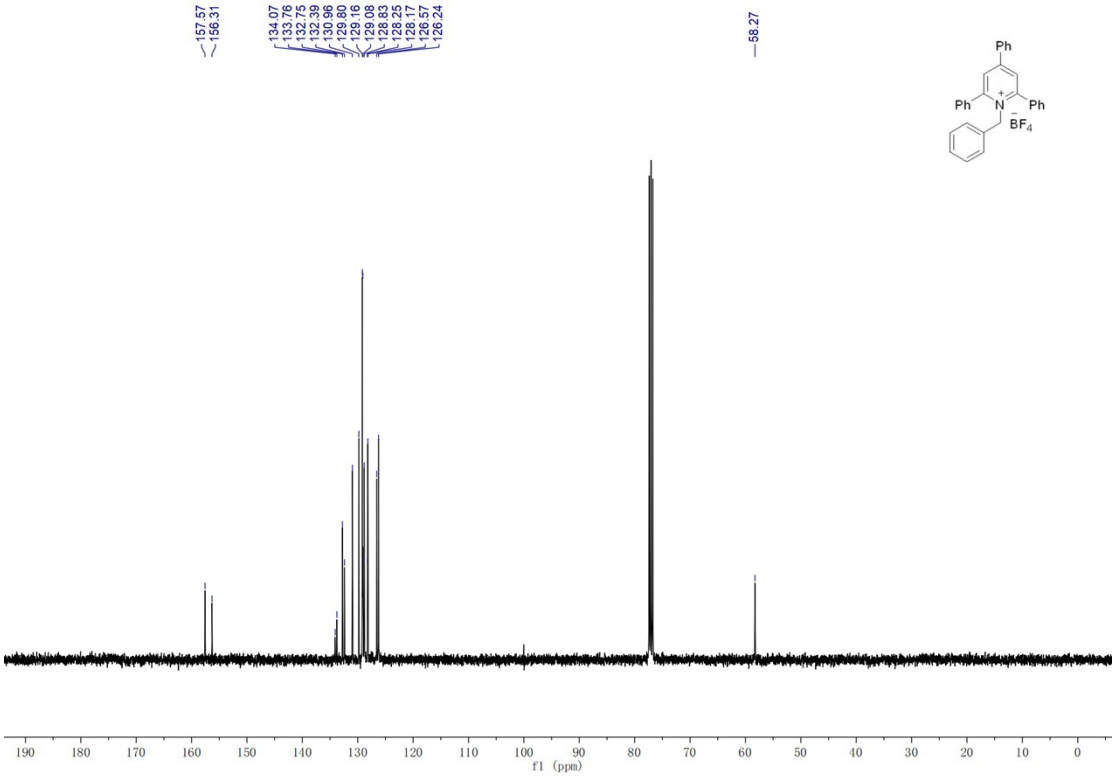
^{13}C NMR spectrum of **1-(4-methoxybenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2a).**



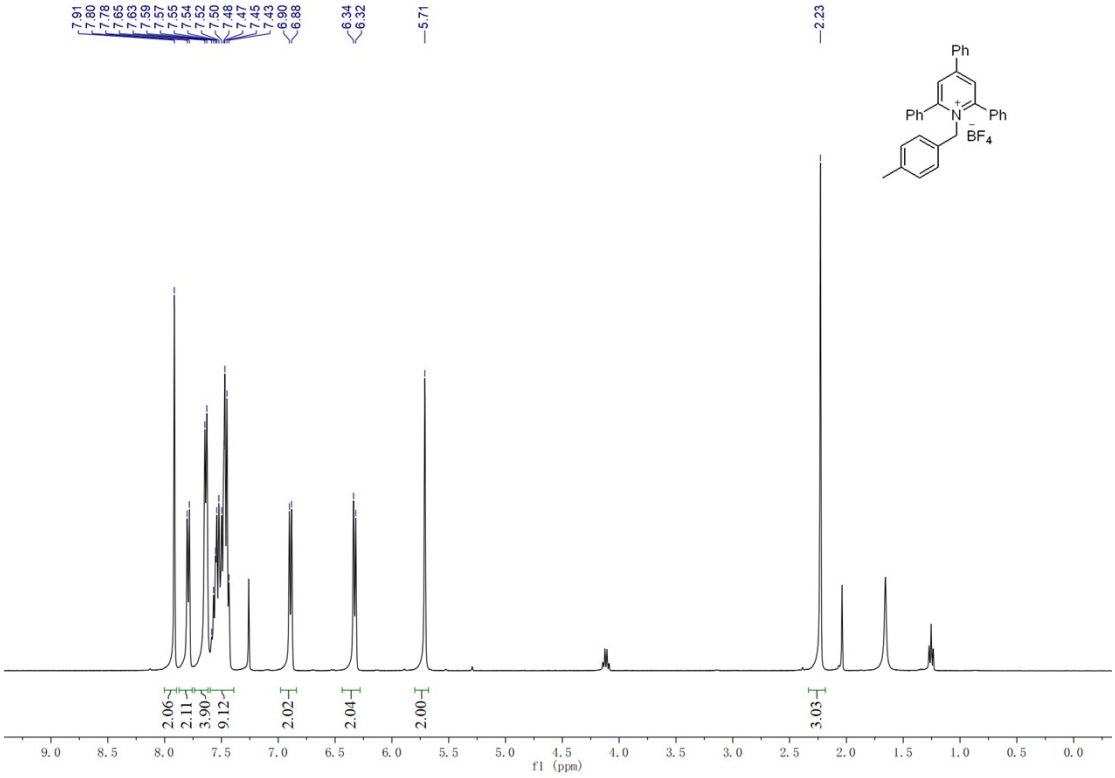
^{1}H NMR spectrum of **1-benzyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2b).**



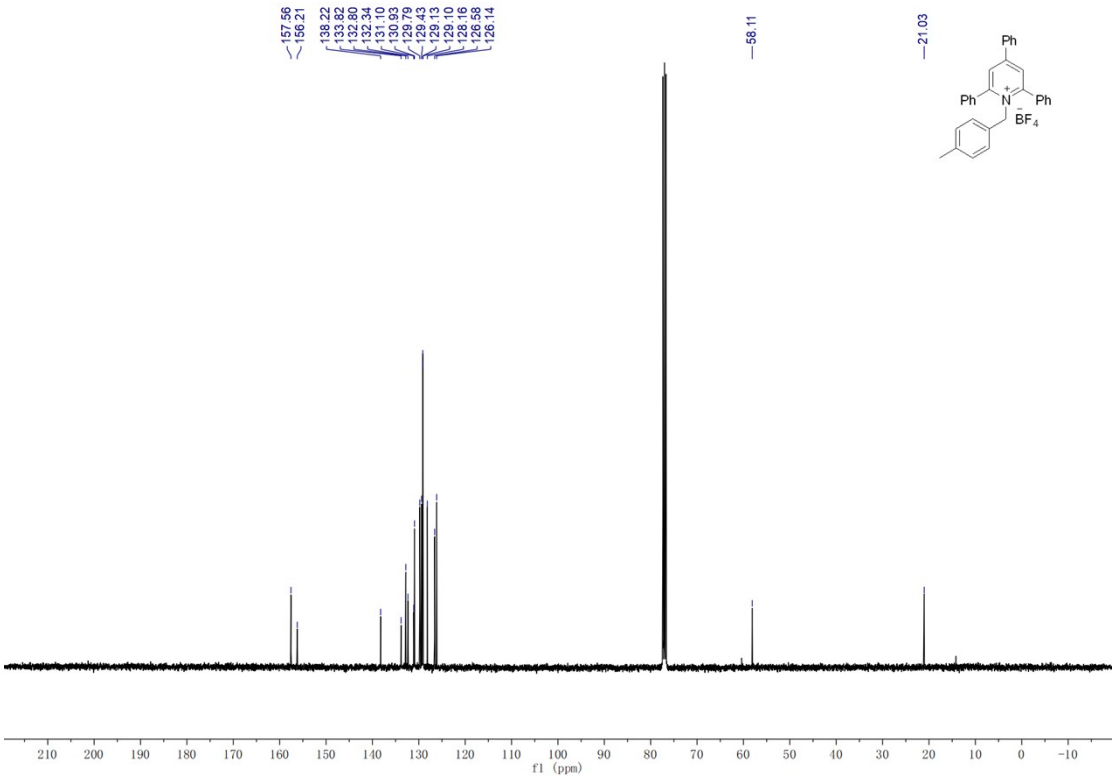
^{13}C NMR spectrum of **1-benzyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2b).**



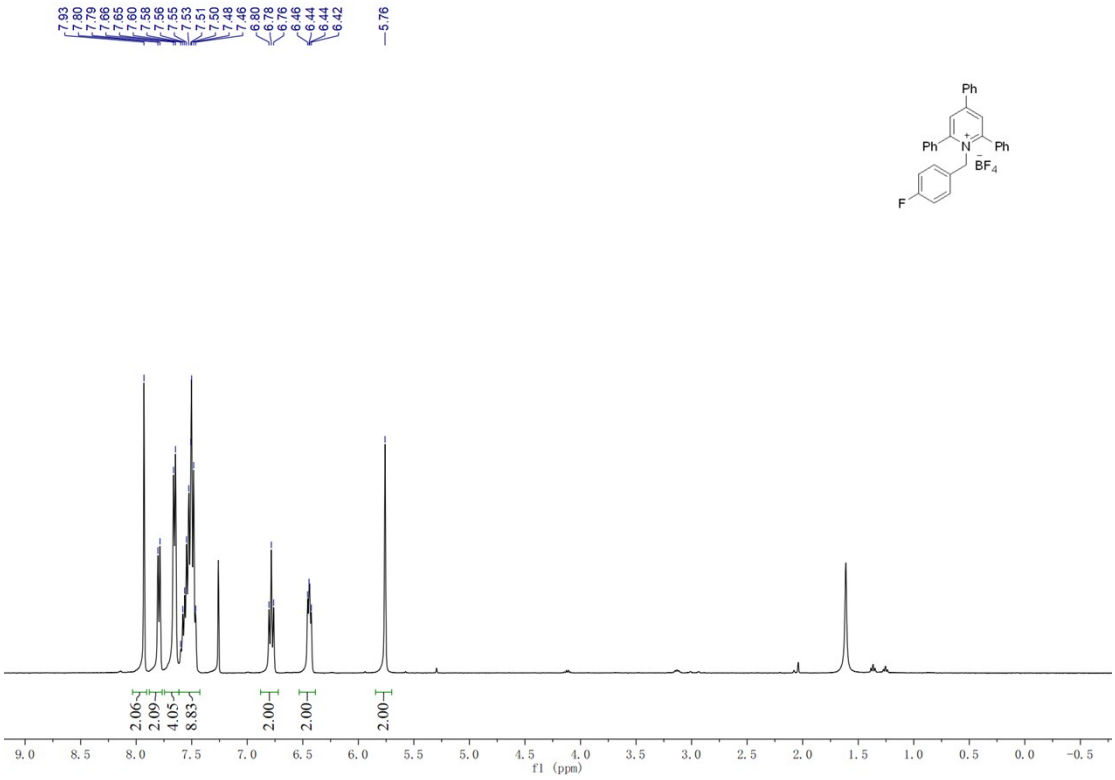
^{1}H NMR spectrum of **1-(4-methylbenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2c).**



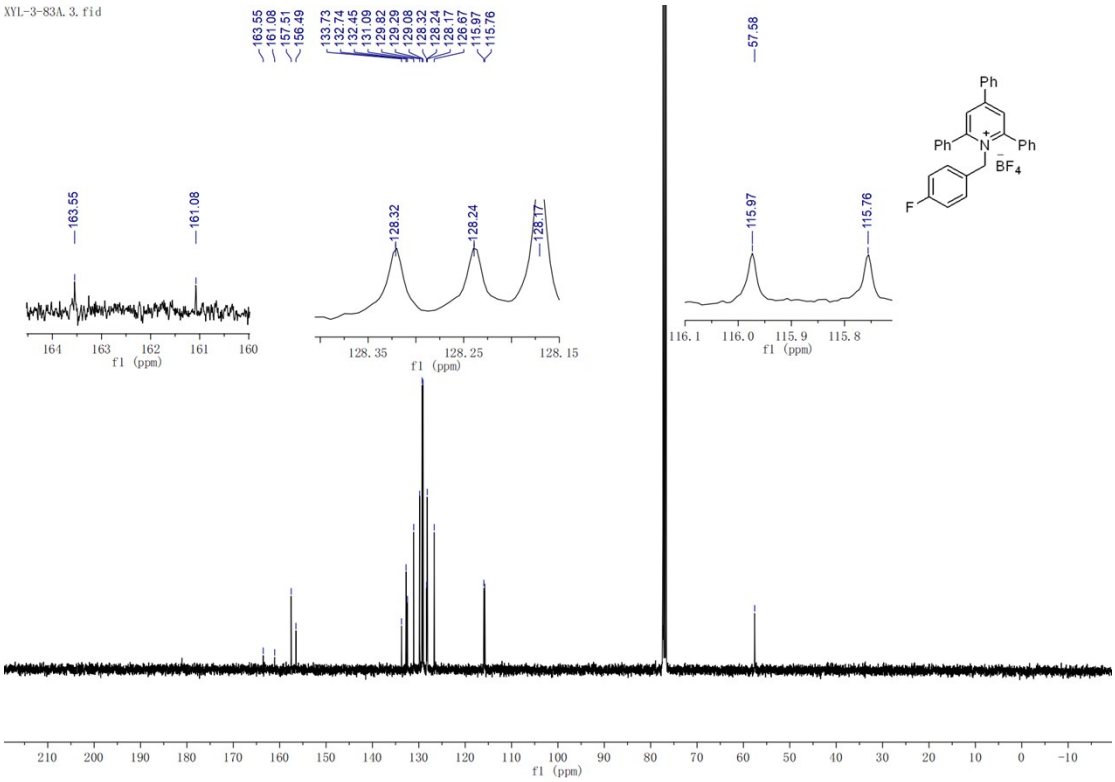
^{13}C NMR spectrum of **1-(4-methylbenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2c).**



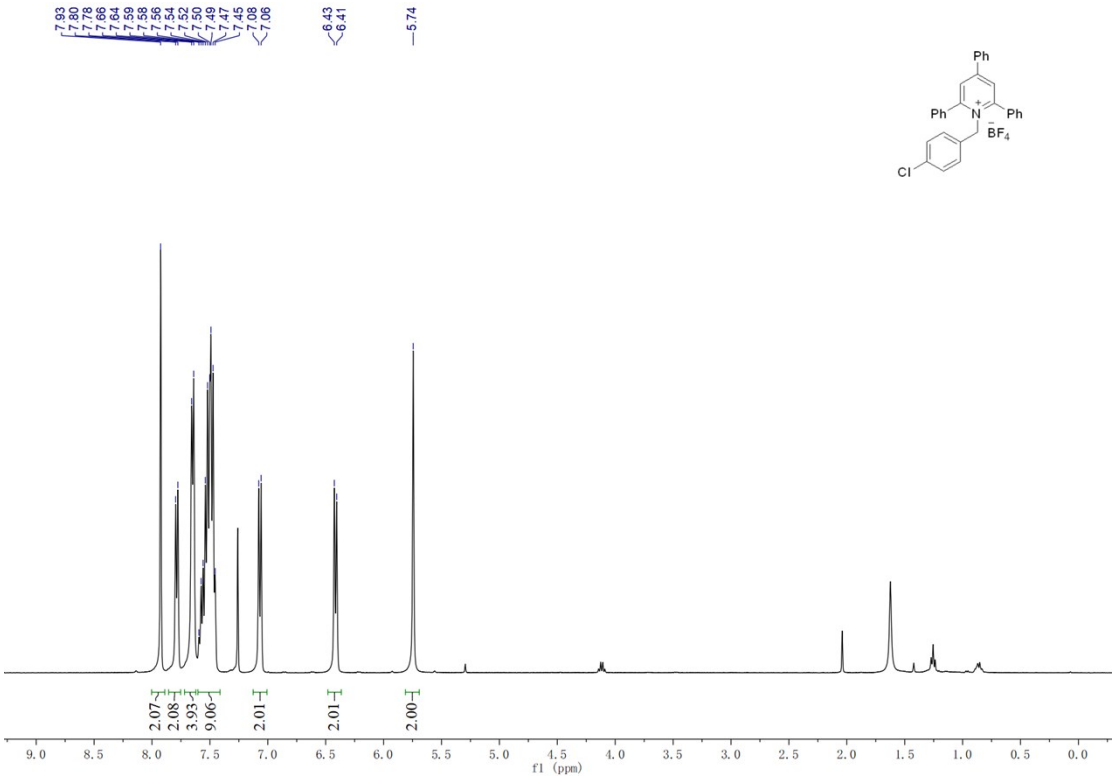
^{1}H NMR spectrum of **1-(4-fluorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2d).**



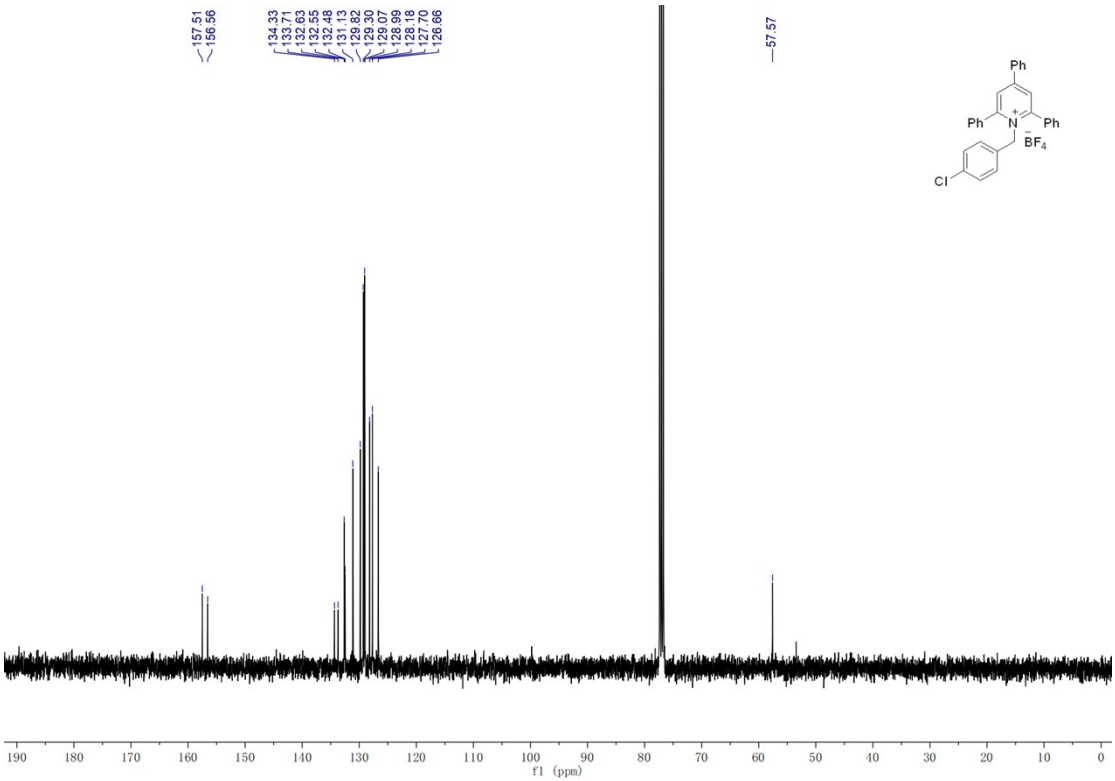
^{13}C NMR spectrum of **1-(4-fluorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2d).**



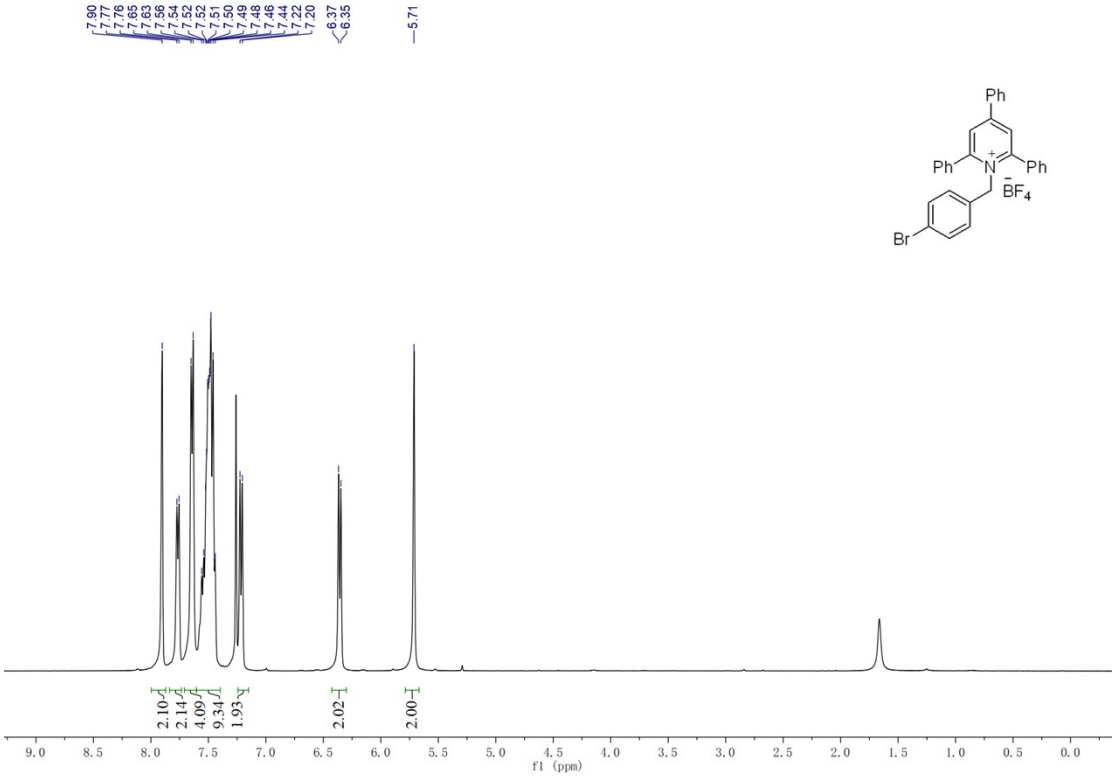
[1]H NMR spectrum of **1-(4-fluorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2e).**



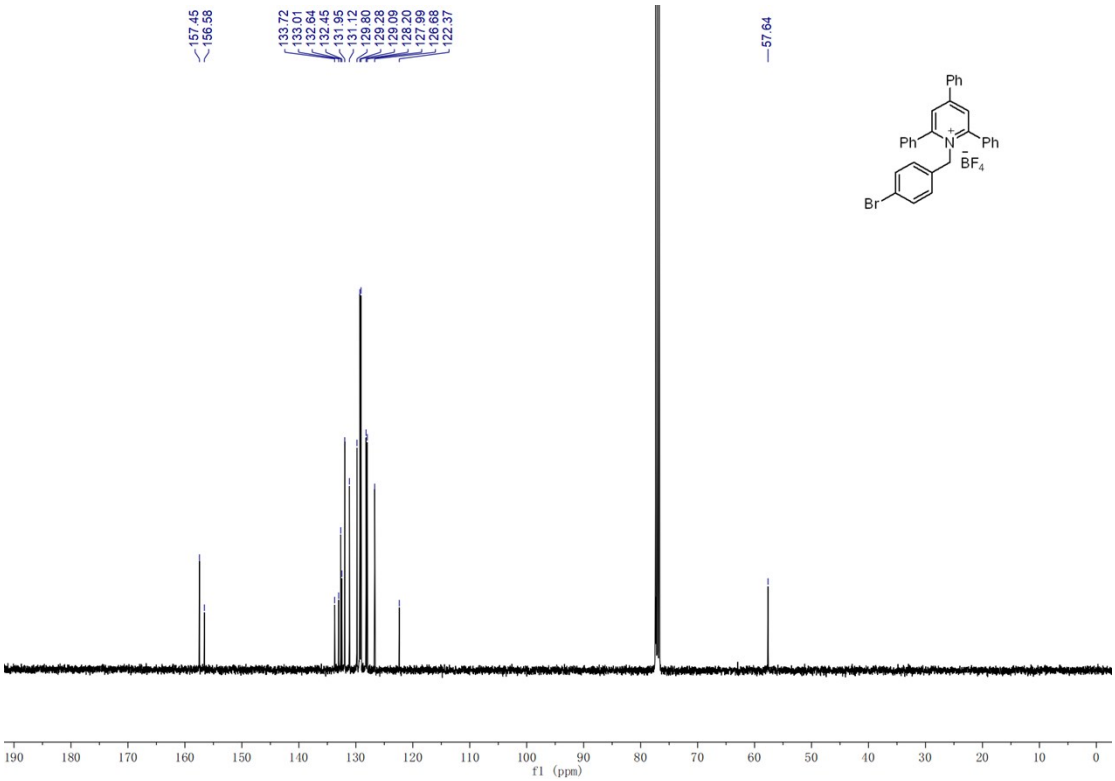
[13]C NMR spectrum of **1-(4-fluorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2e).**



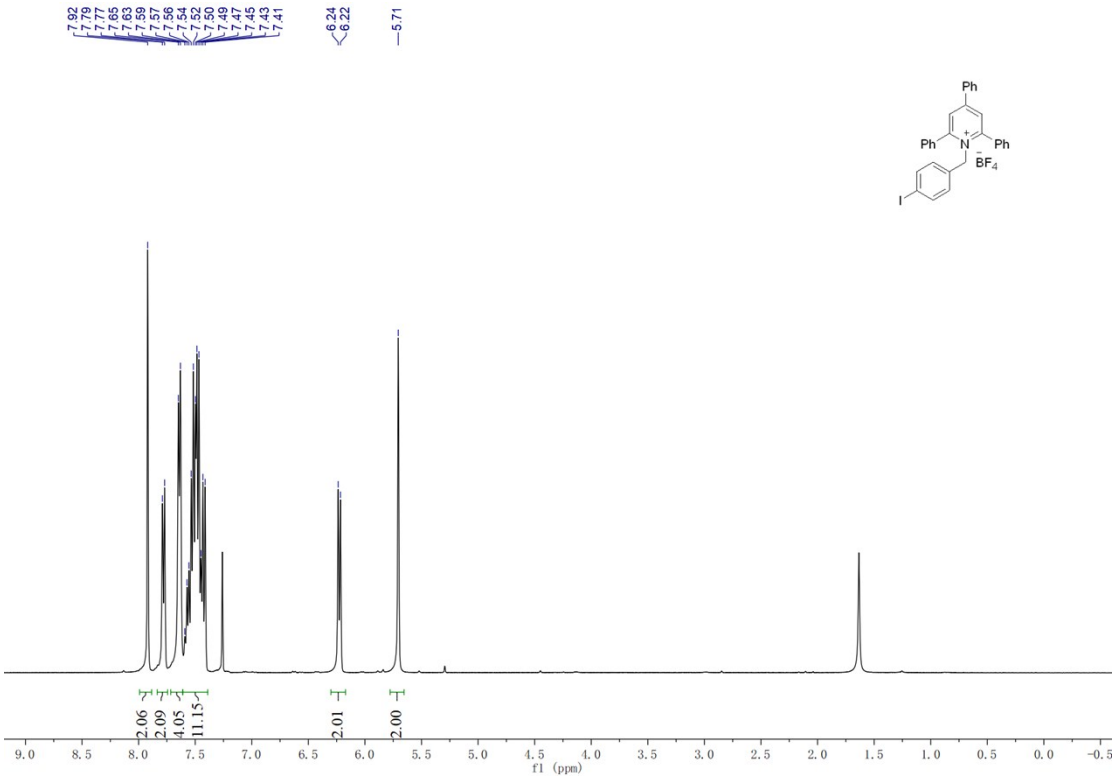
^{1}H NMR spectrum of **1-(4-bromobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2f).**



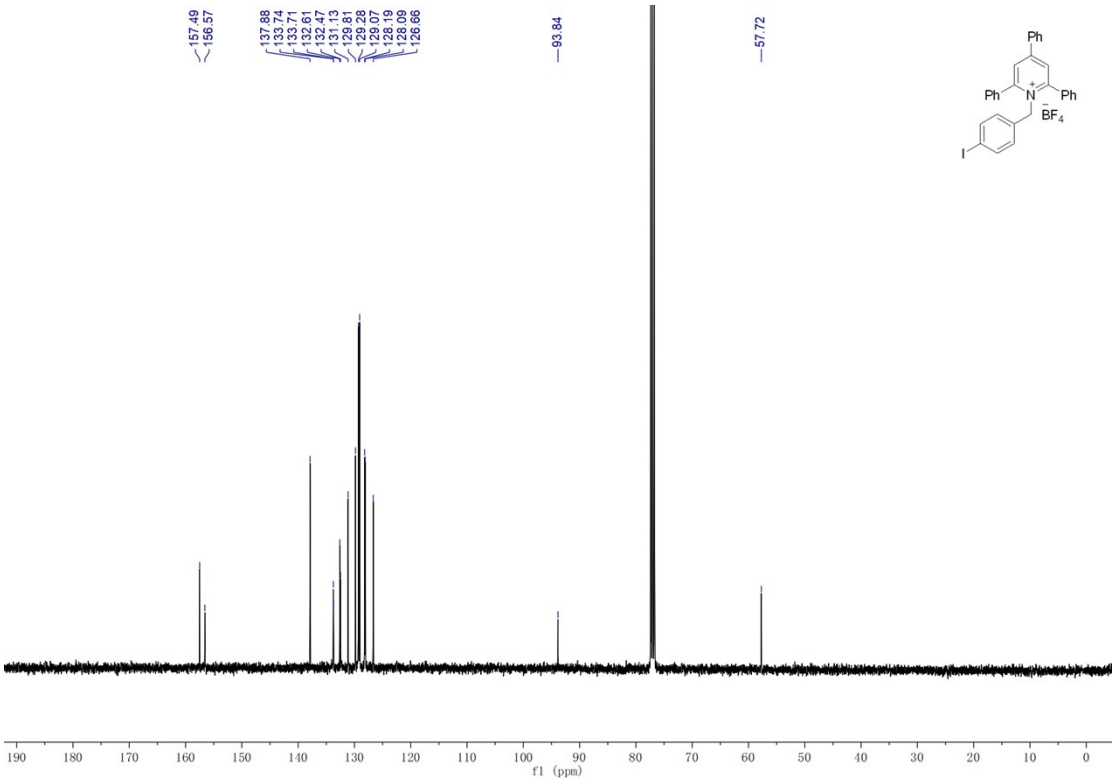
^{13}C NMR spectrum of **1-(4-bromobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2f).**



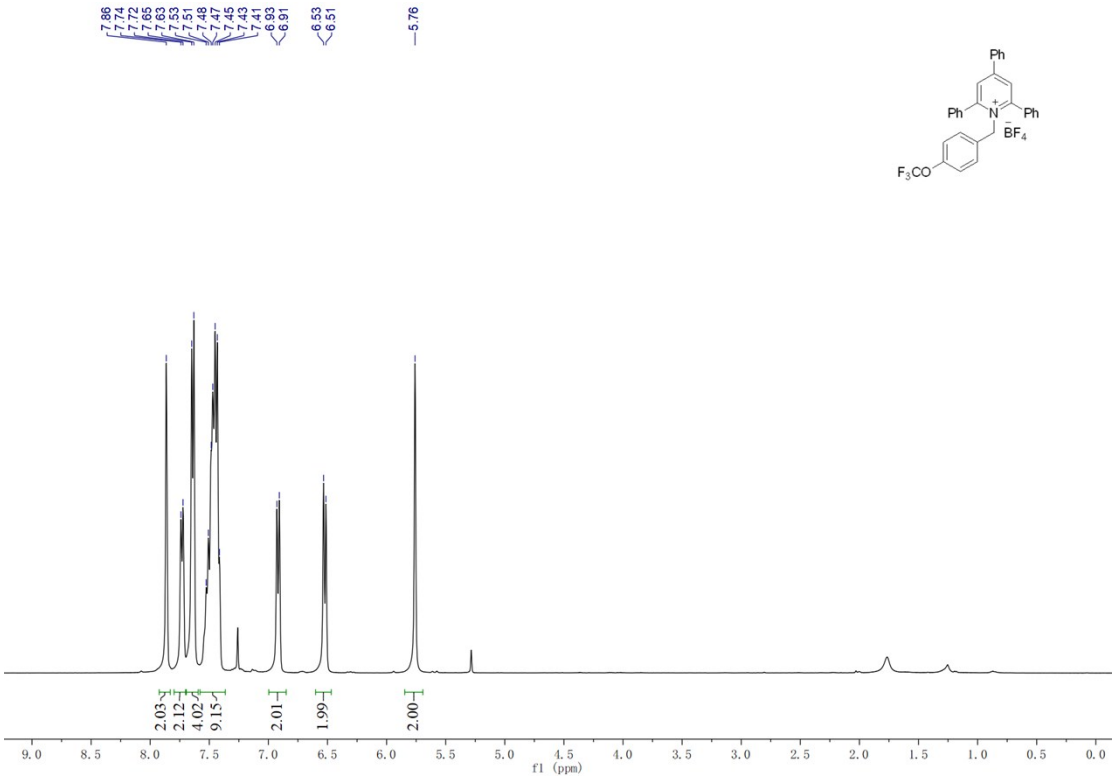
^{1}H NMR spectrum of **1-(4-iodobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2g).**



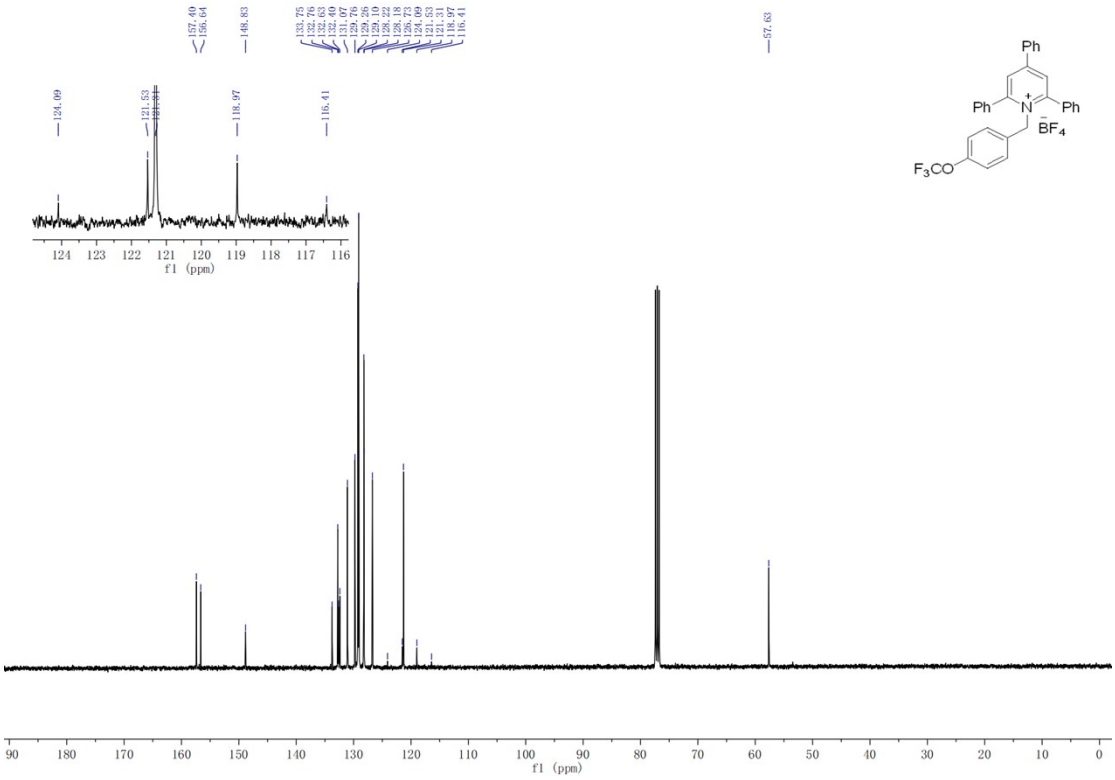
^{13}C NMR spectrum of **1-(4-iodobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2g).**



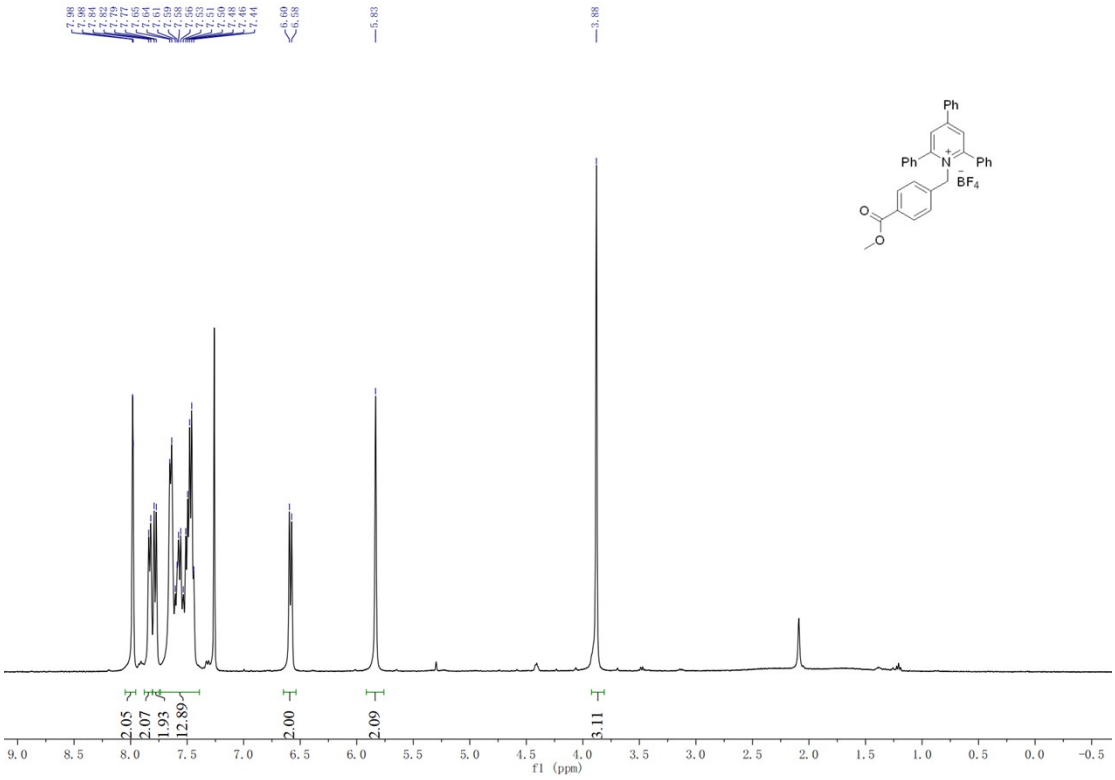
^{1}H NMR spectrum of **2,4,6-triphenyl-1-(4-(trifluoromethoxy)benzyl)pyridin-1-ium tetrafluoroborate (2h).**



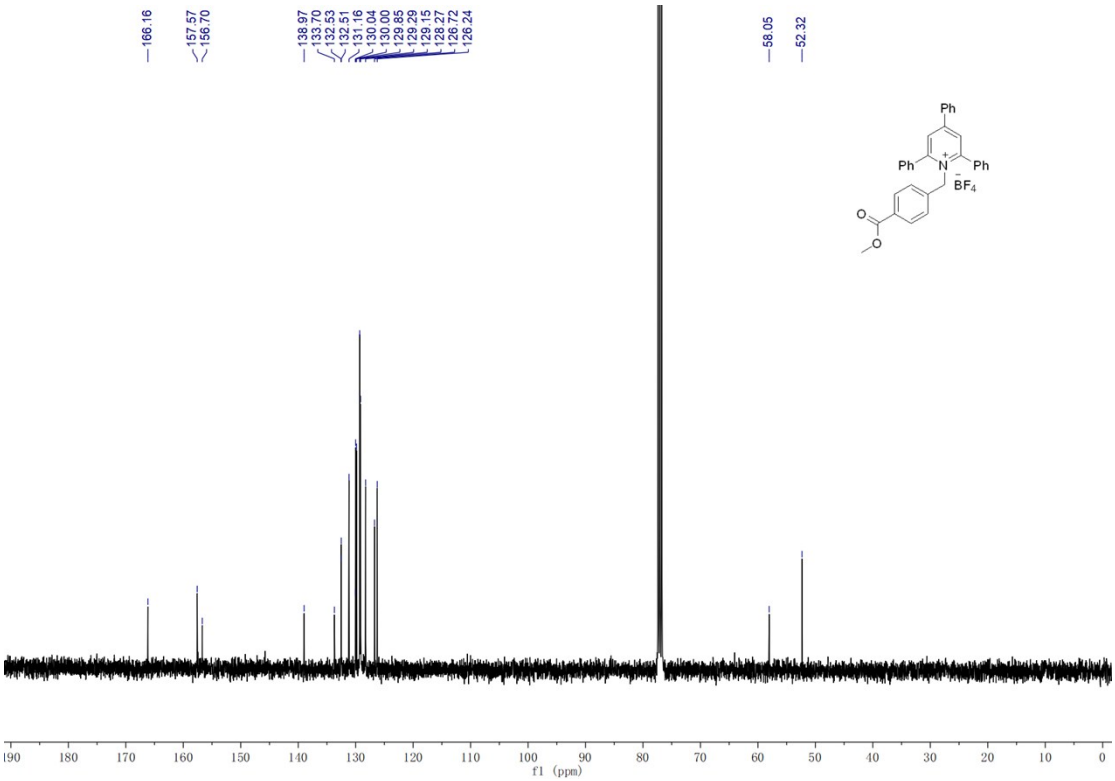
^{13}C NMR spectrum of **2,4,6-triphenyl-1-(4-(trifluoromethoxy)benzyl)pyridin-1-ium tetrafluoroborate (2h).**



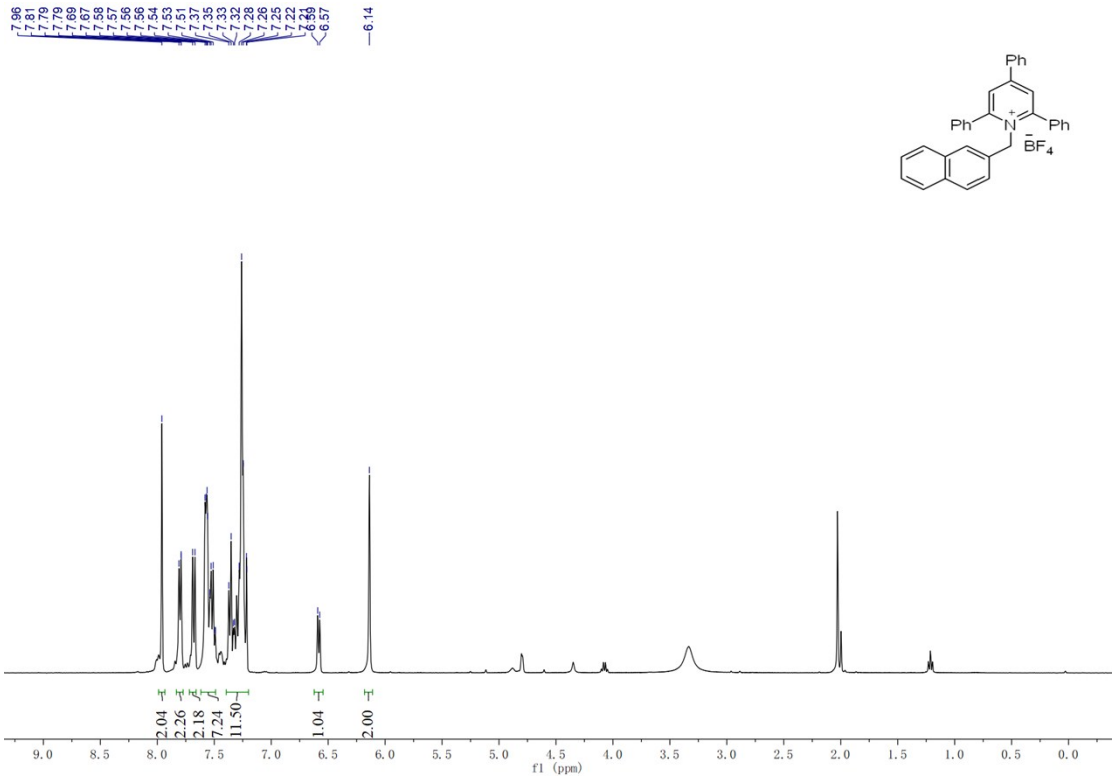
^{1}H NMR spectrum of **1-(4-(methoxycarbonyl)benzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2i).**



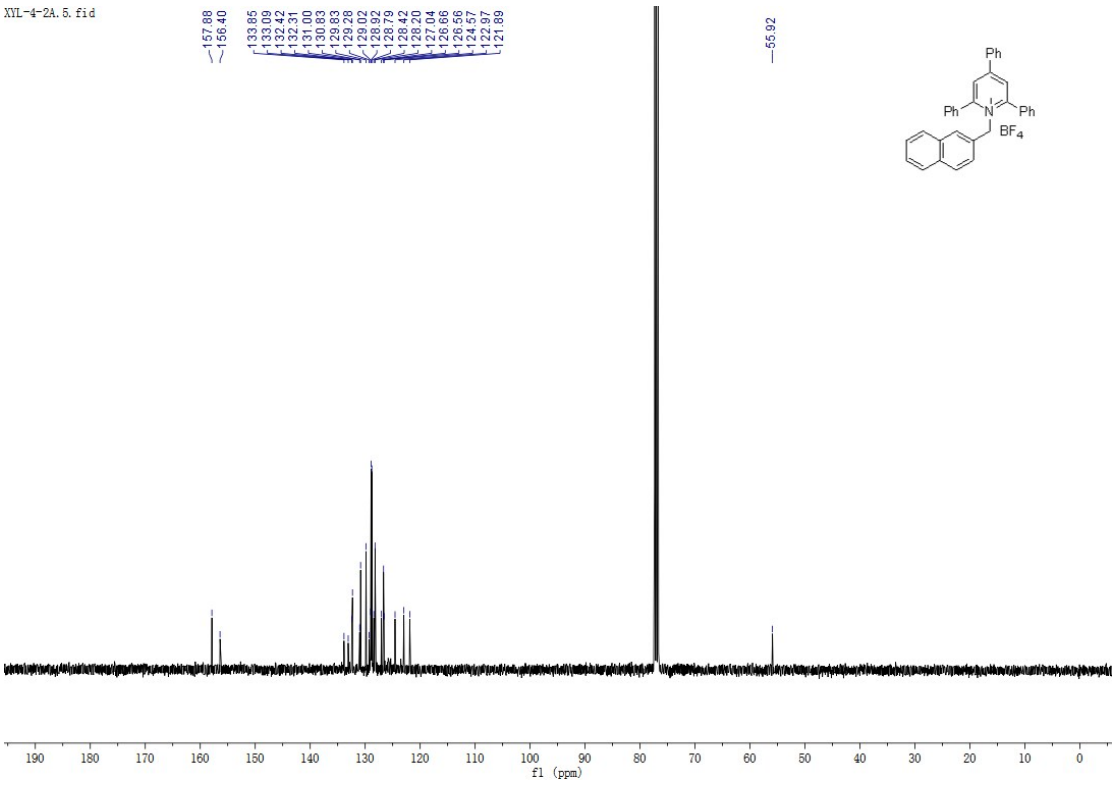
^{13}C NMR spectrum of **1-(4-(methoxycarbonyl)benzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2i).**



^{1}H NMR spectrum of **1-(naphthalen-2-ylmethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2j).**



^{13}C NMR spectrum of **1-(naphthalen-2-ylmethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2j).**



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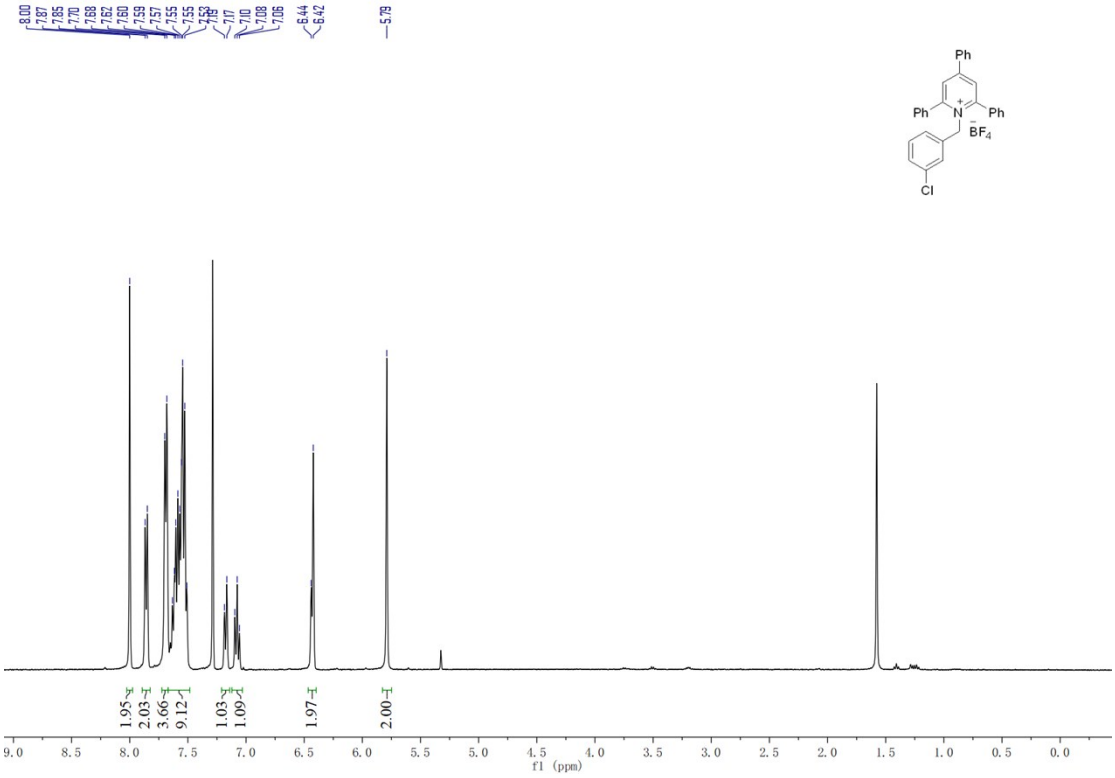
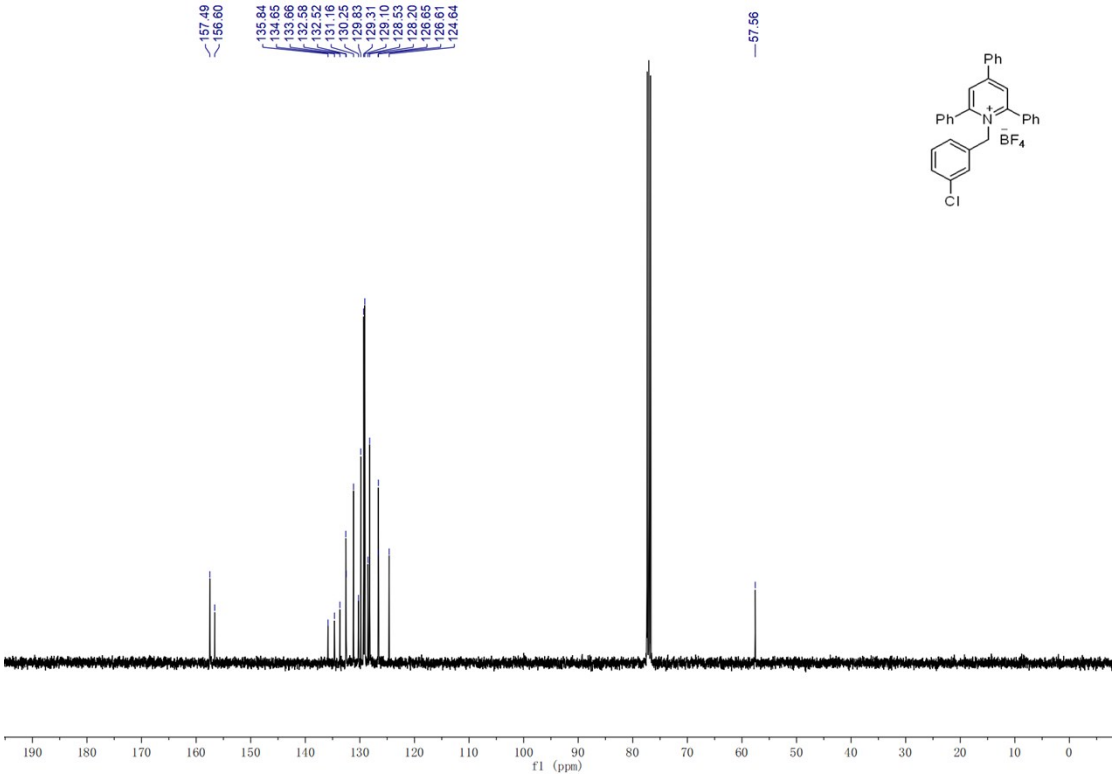
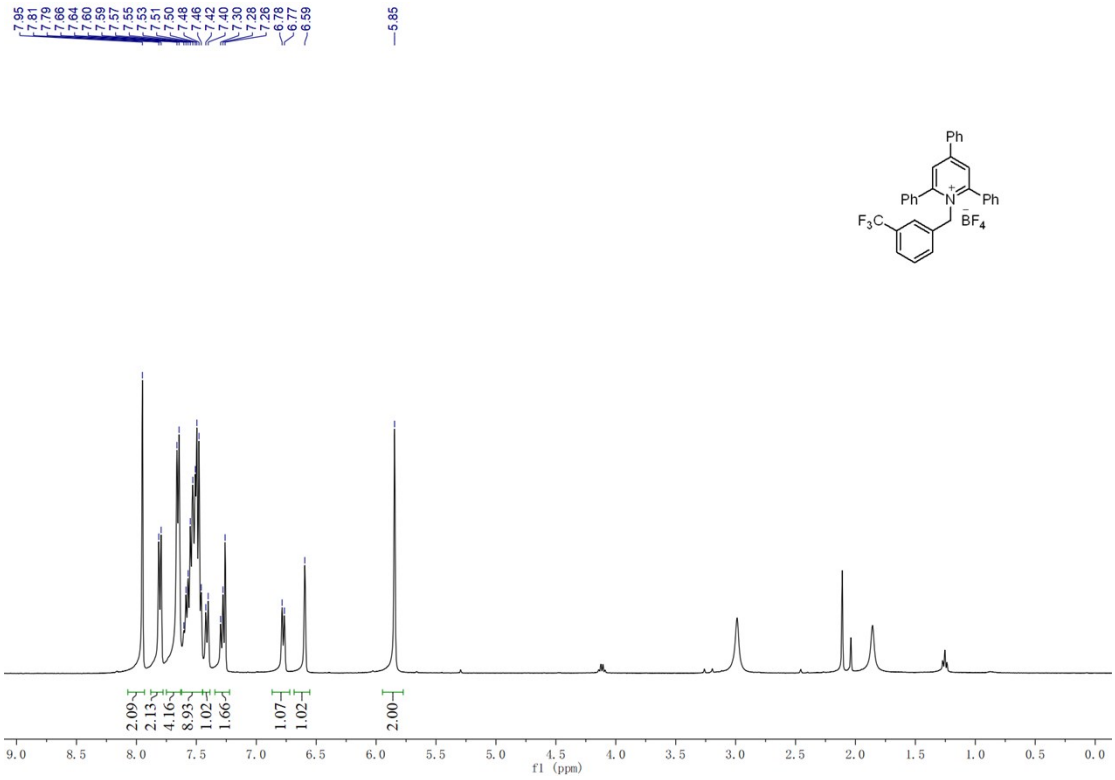


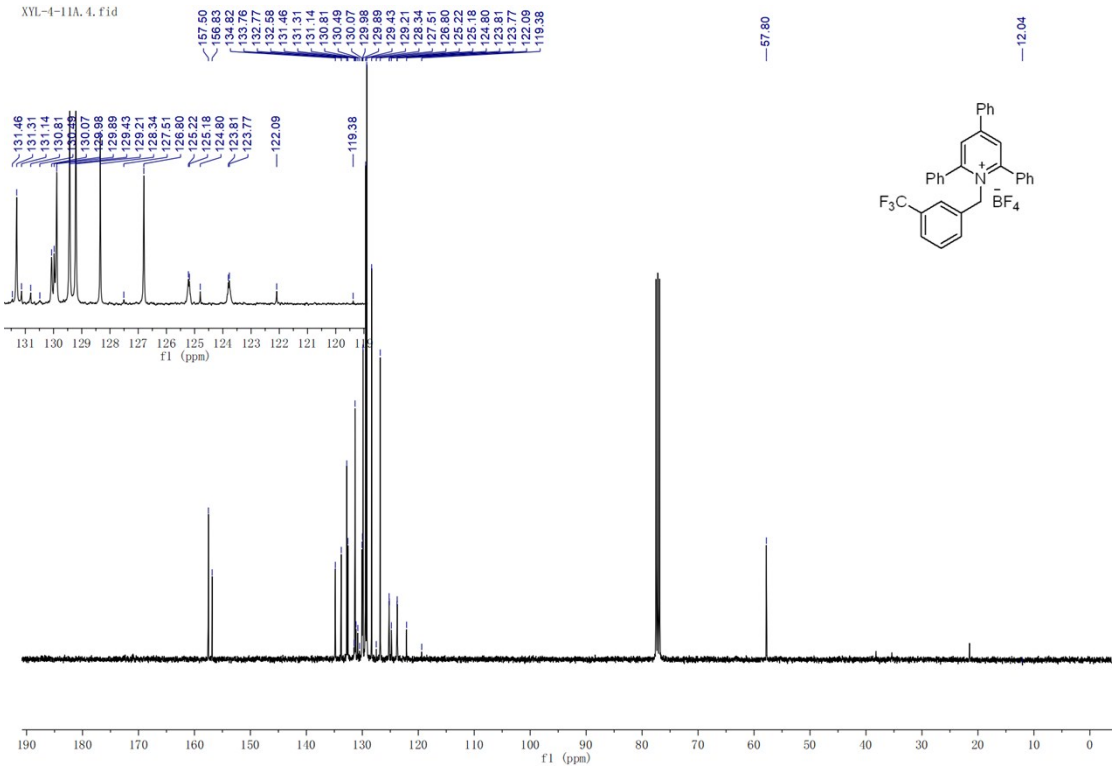
^{13}C NMR spectrum of **1-(3-chlorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2k).**



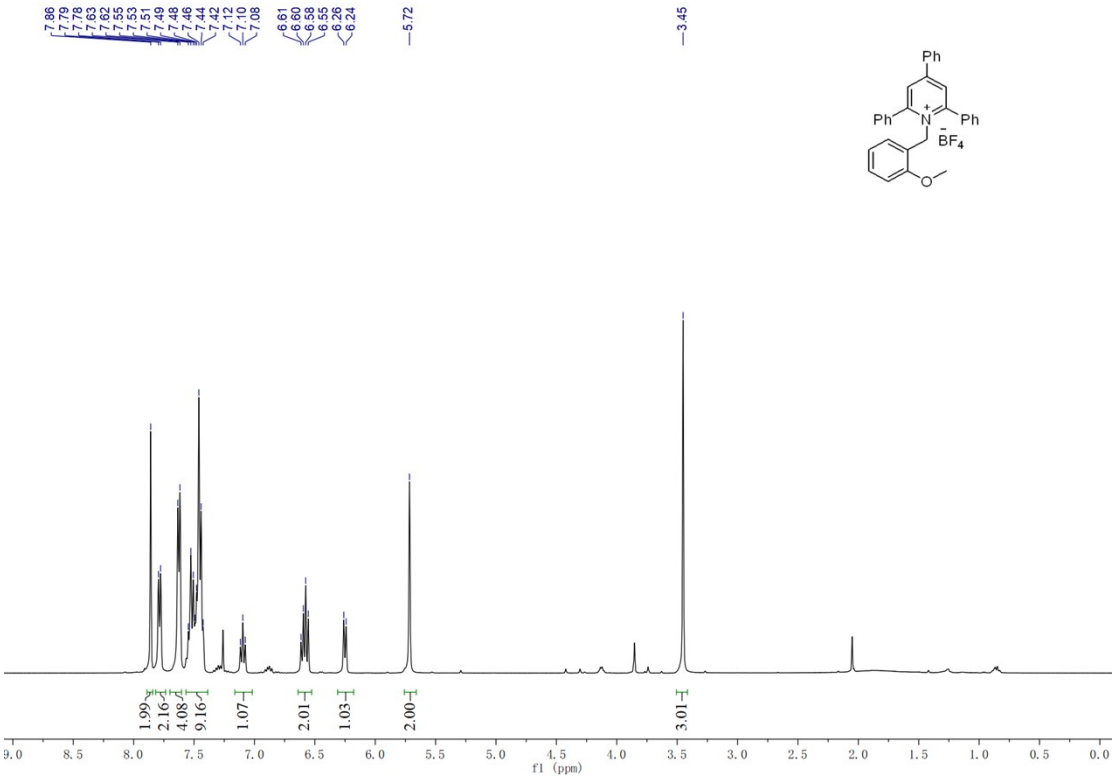
^{1}H NMR spectrum of **2,4,6-triphenyl-1-(3-(trifluoromethyl)benzyl)pyridin-1-ium tetrafluoroborate (2l).**



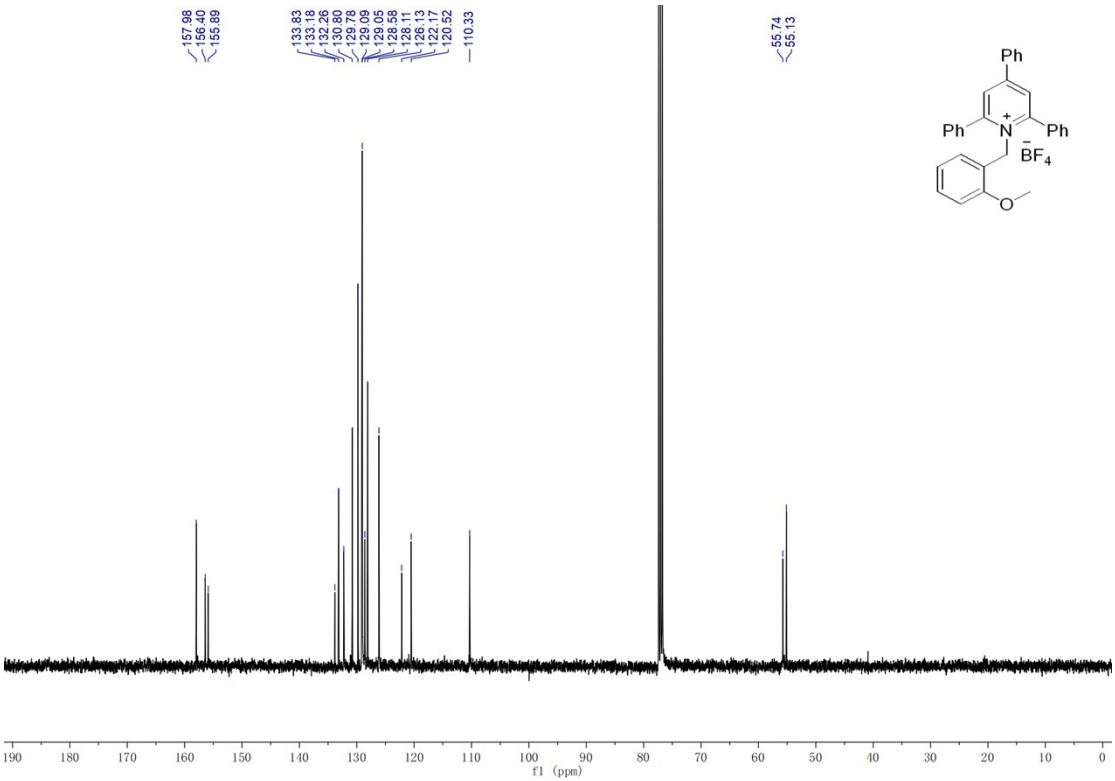
^{13}C NMR spectrum of **2,4,6-triphenyl-1-(3-(trifluoromethyl)benzyl)pyridin-1-ium tetrafluoroborate (2l).**



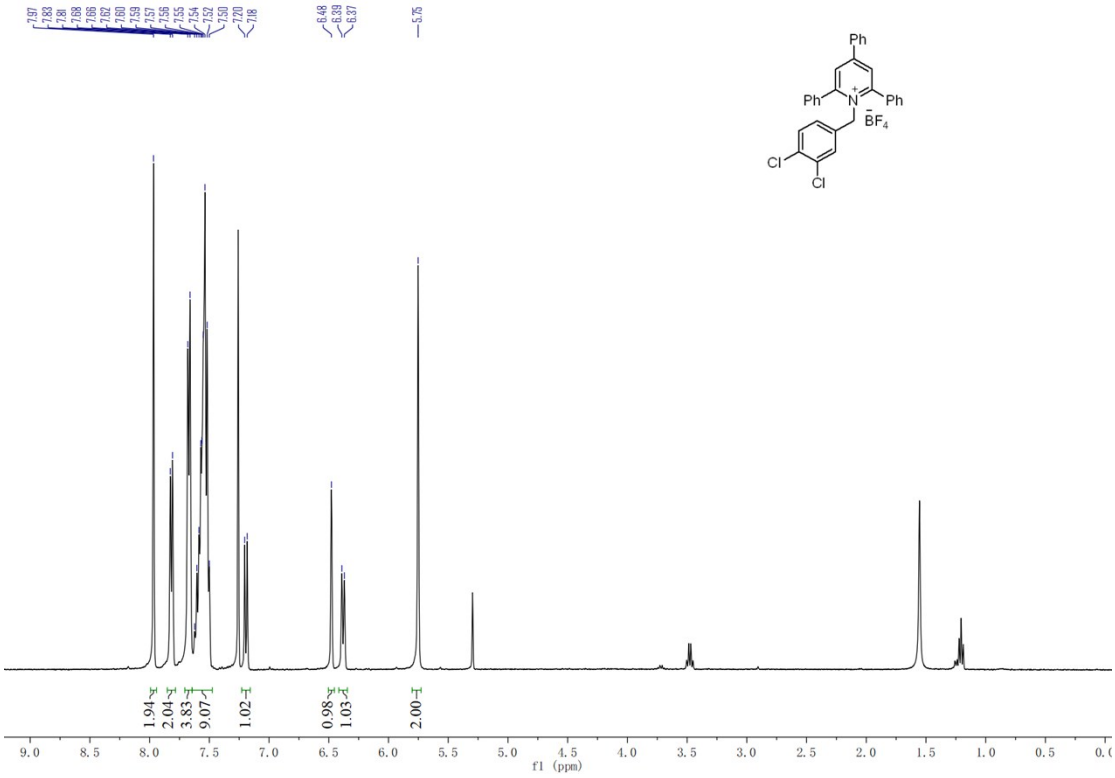
^{1}H NMR spectrum of **1-(2-methoxybenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2m).**



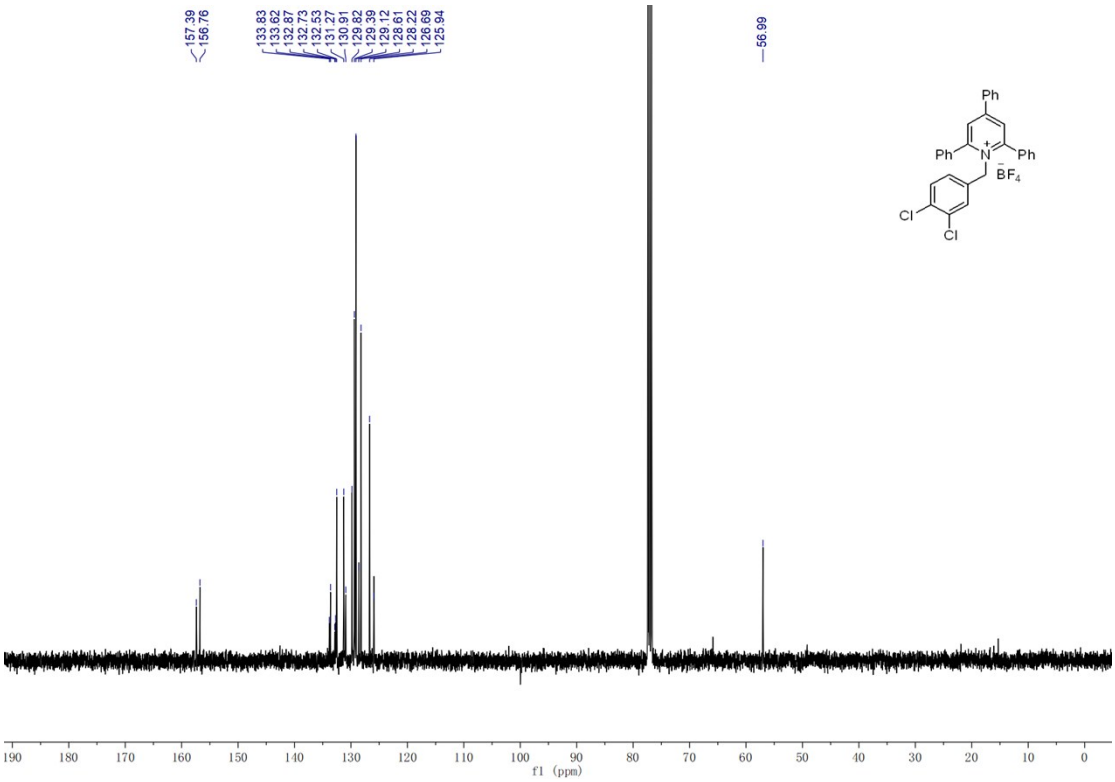
^{1}H NMR spectrum of **1-(2-methoxybenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2m).**



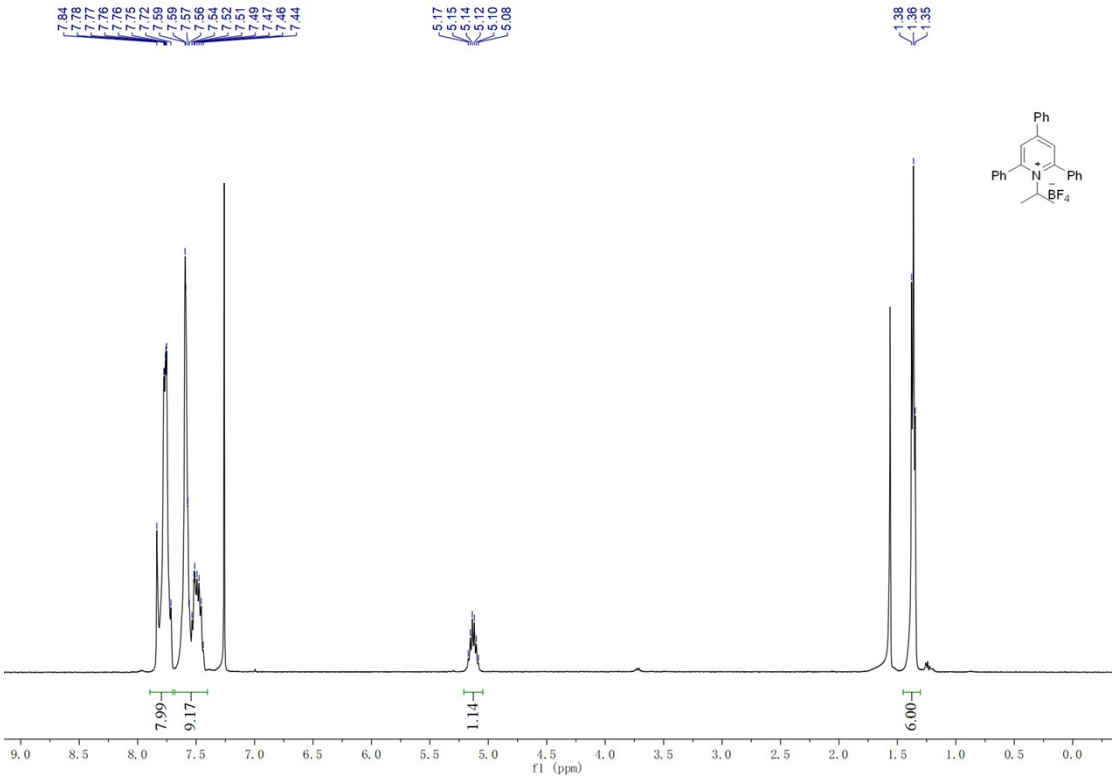
^{1}H NMR spectrum of **1-(3,4-dichlorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2n).**



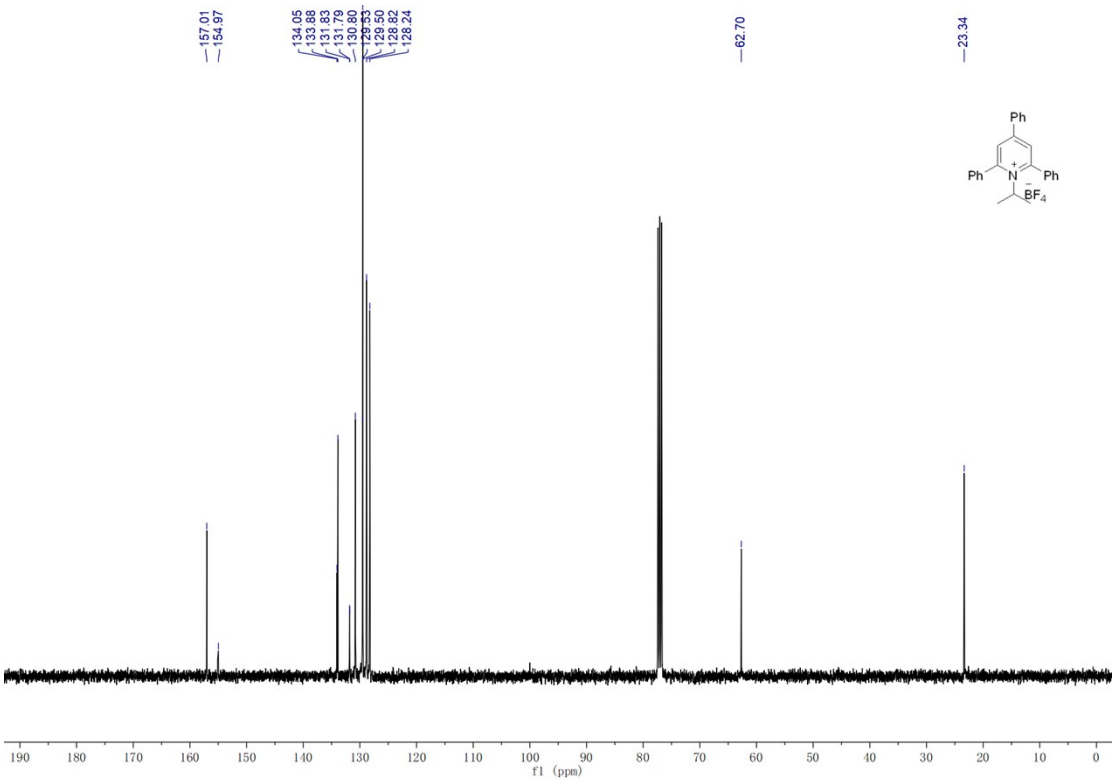
^{13}C NMR spectrum of **1-(3,4-dichlorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2n).**



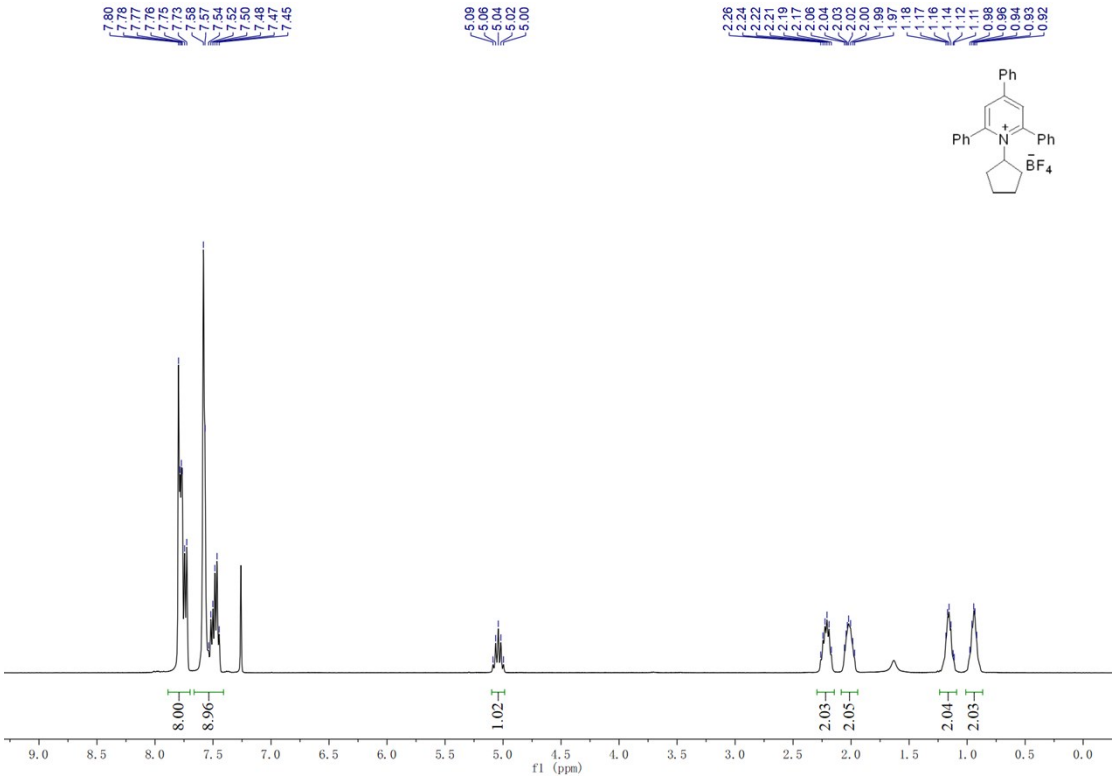
^{1}H NMR spectrum of **1-isopropyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2o).**



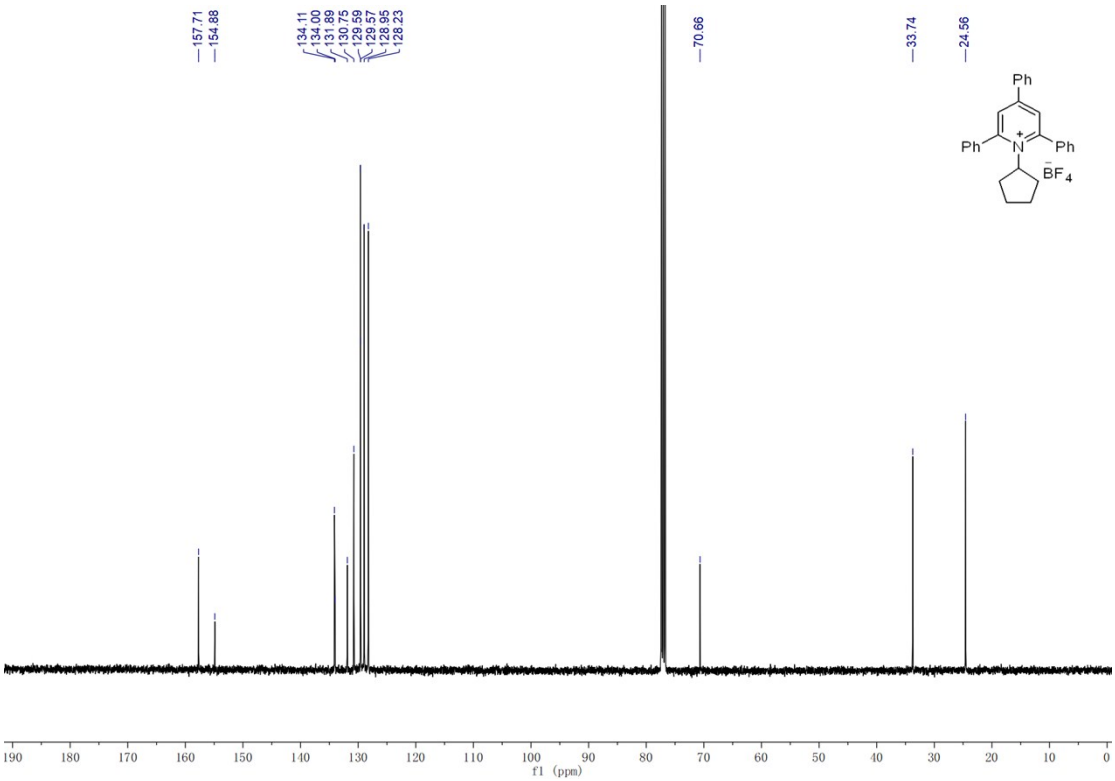
^{13}C NMR spectrum of **1-isopropyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2o).**



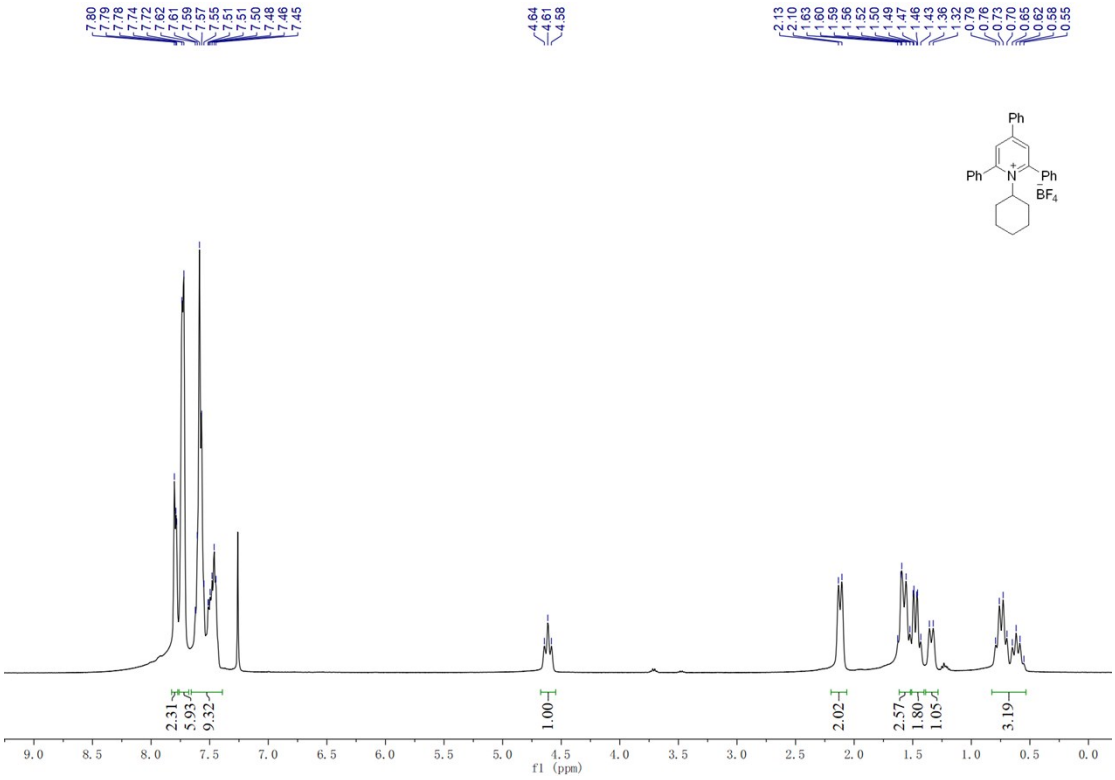
^{1}H NMR spectrum of **1-cyclopentyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2p).**



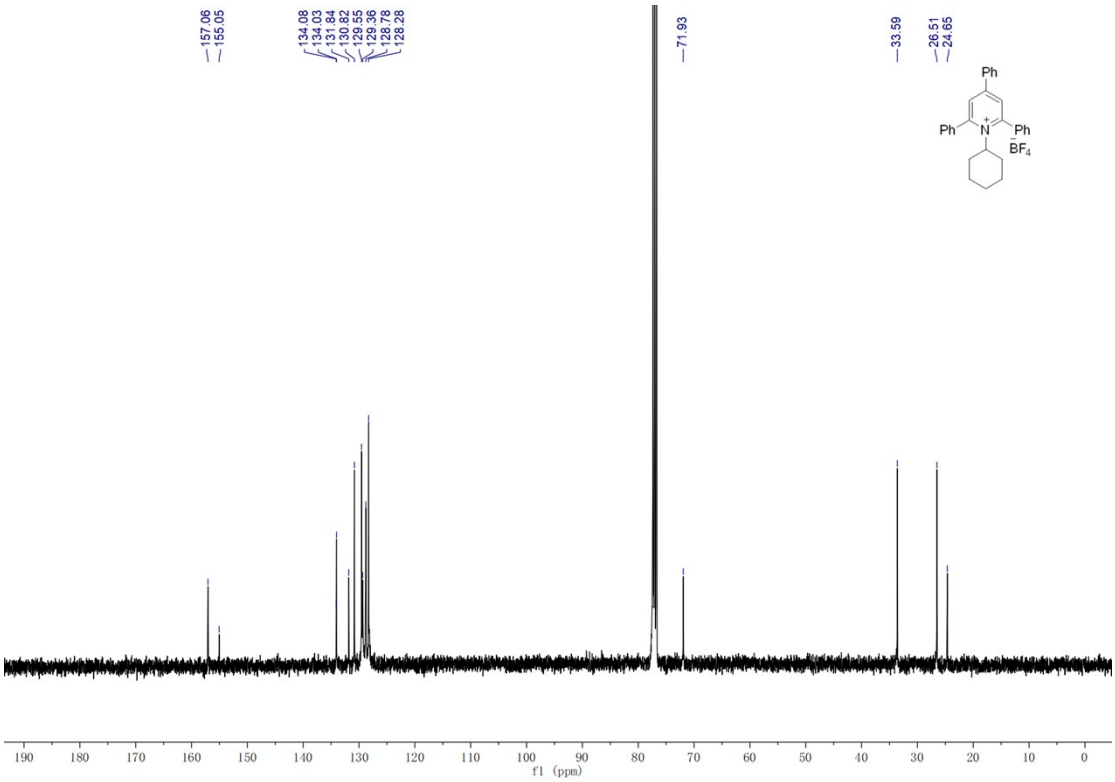
^{13}C NMR spectrum of **1-cyclopentyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2p).**



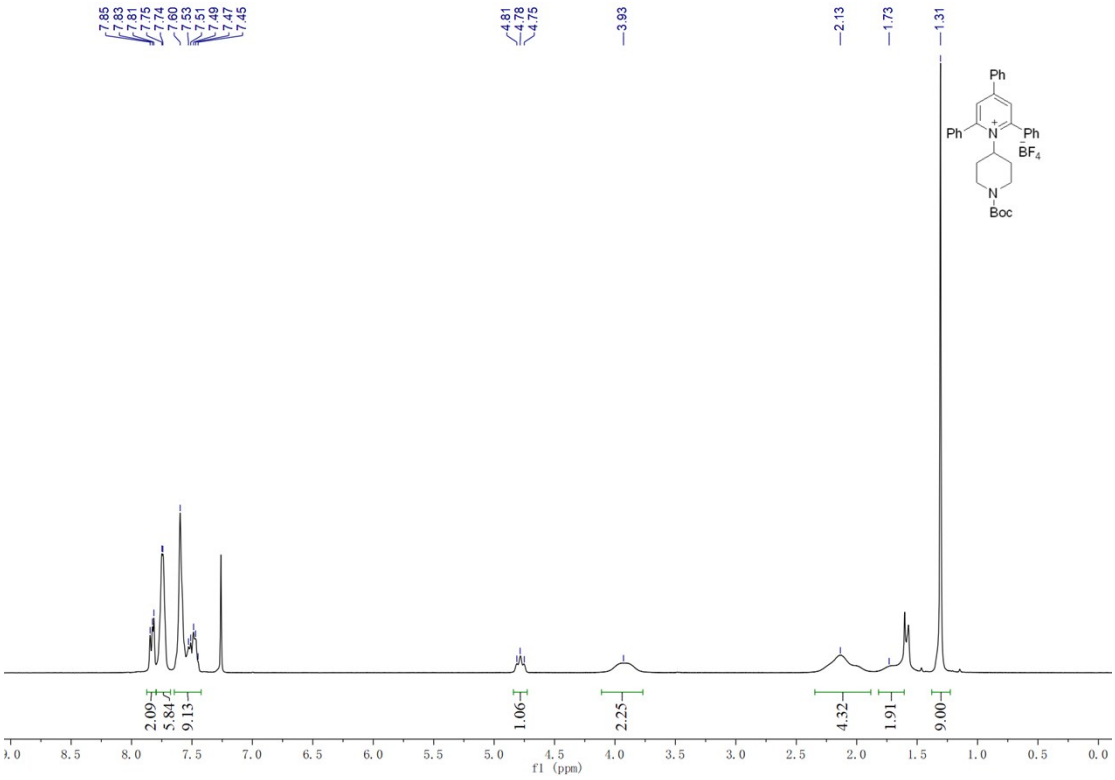
^{1}H NMR spectrum of **1-cyclohexyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2q).**



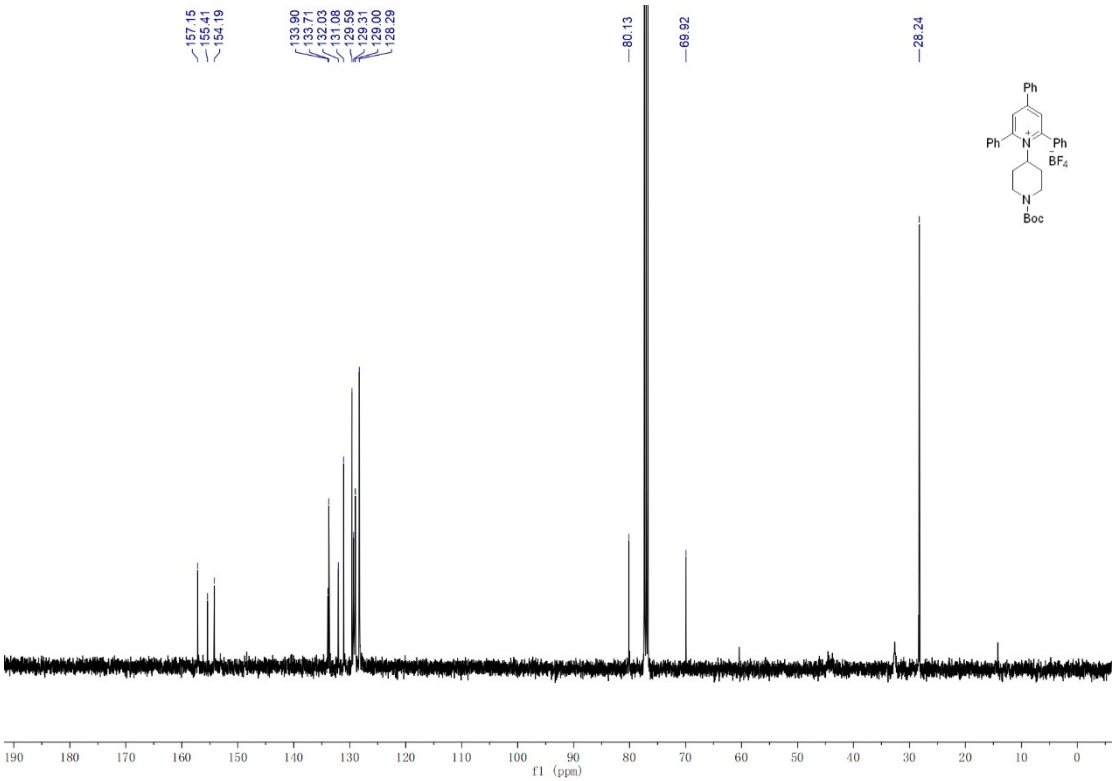
^{13}C NMR spectrum of **1-cyclohexyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2q).**



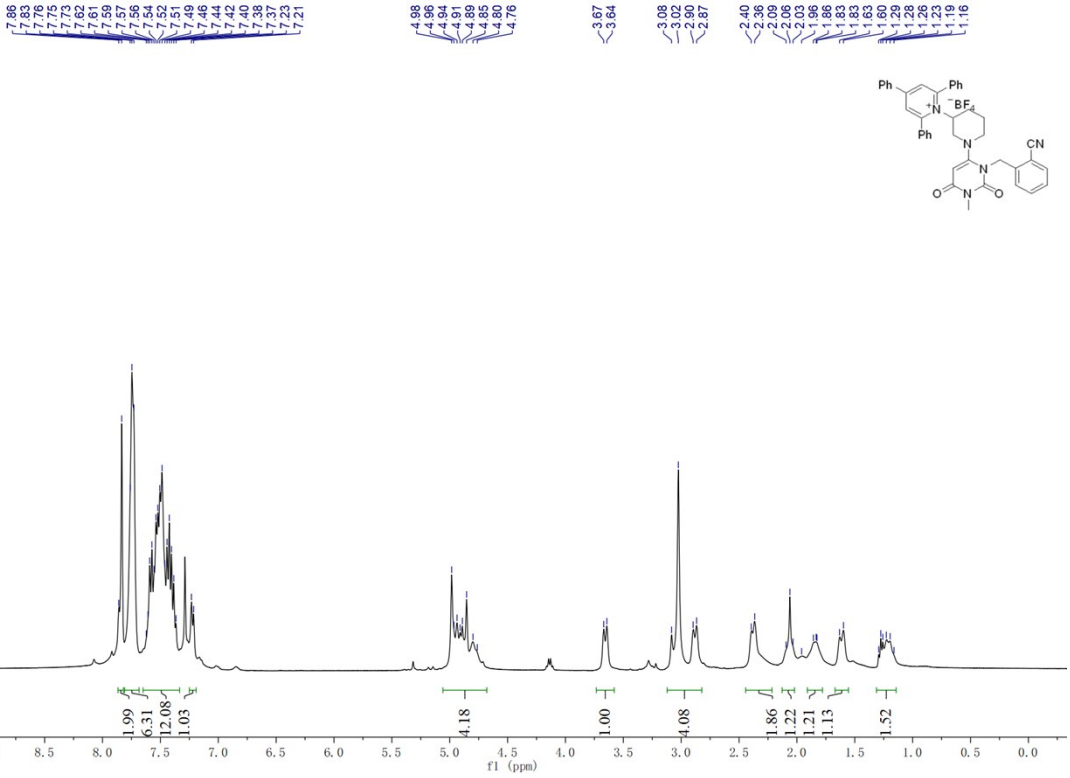
^{1}H NMR spectrum of **1-(1-(tert-butoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2r).**



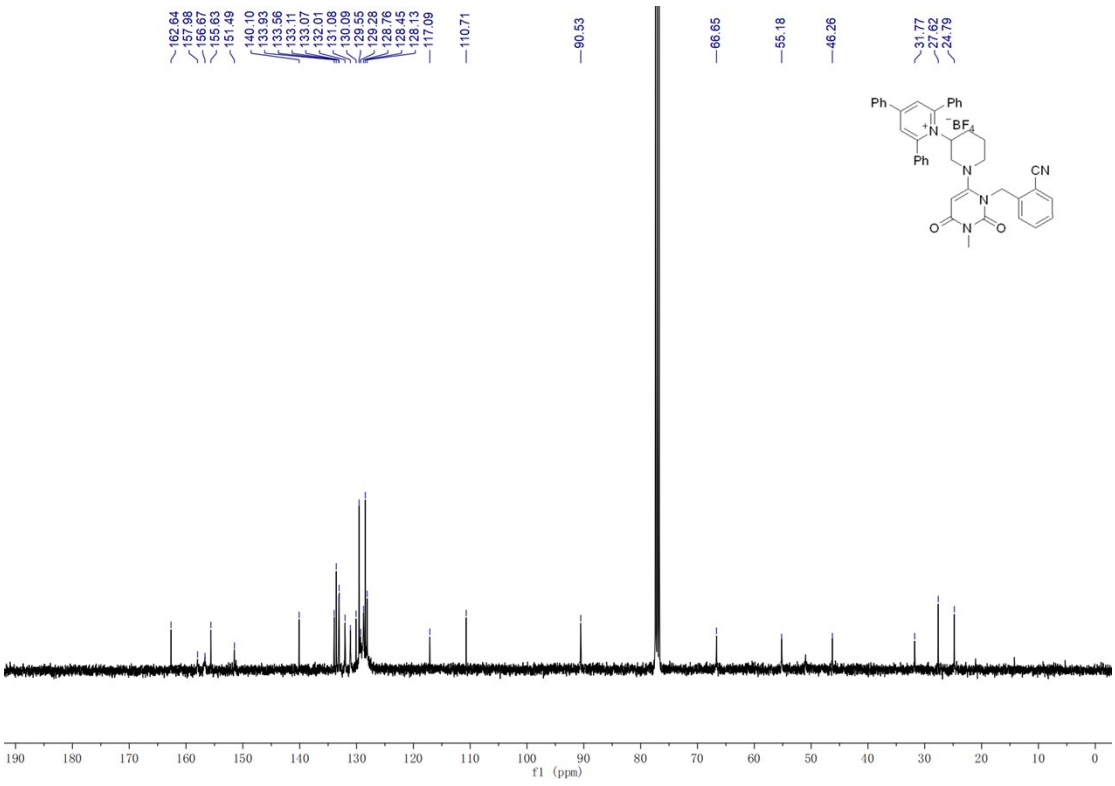
^{13}C NMR spectrum of **1-(1-(tert-butoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2r).**



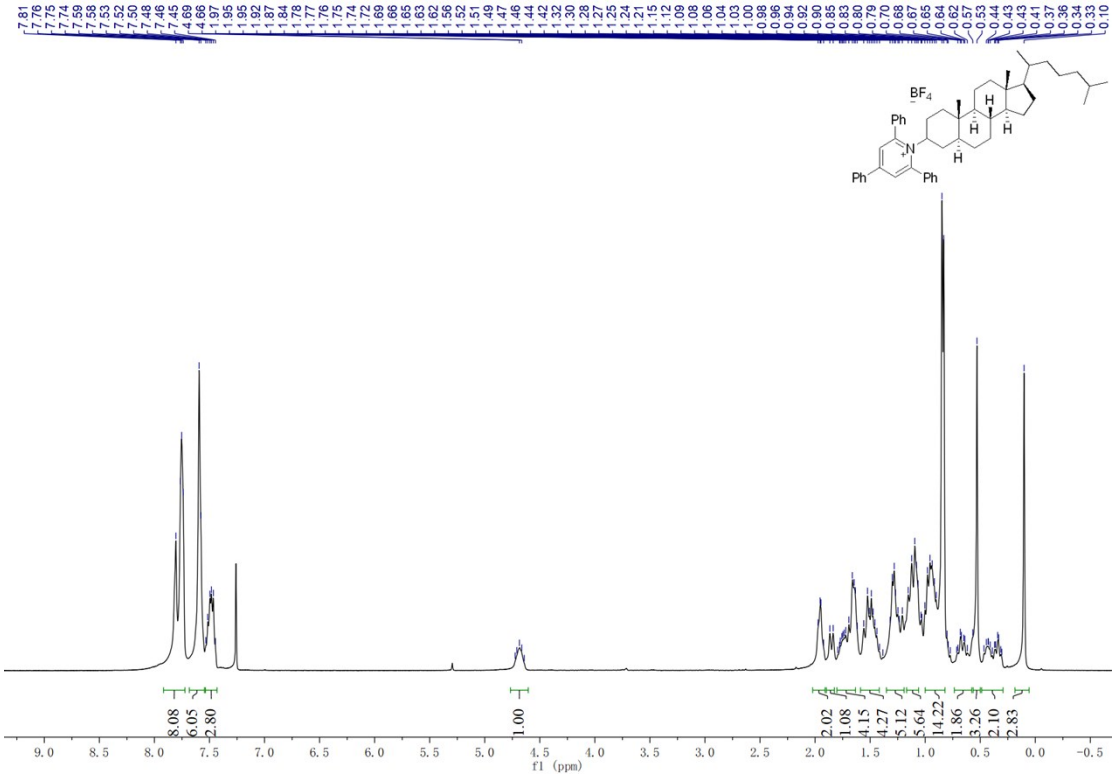
^{1}H NMR spectrum of **1-(1-(3-(2-cyanobenzyl)-1-methyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-yl) piperidin-3-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2s).**



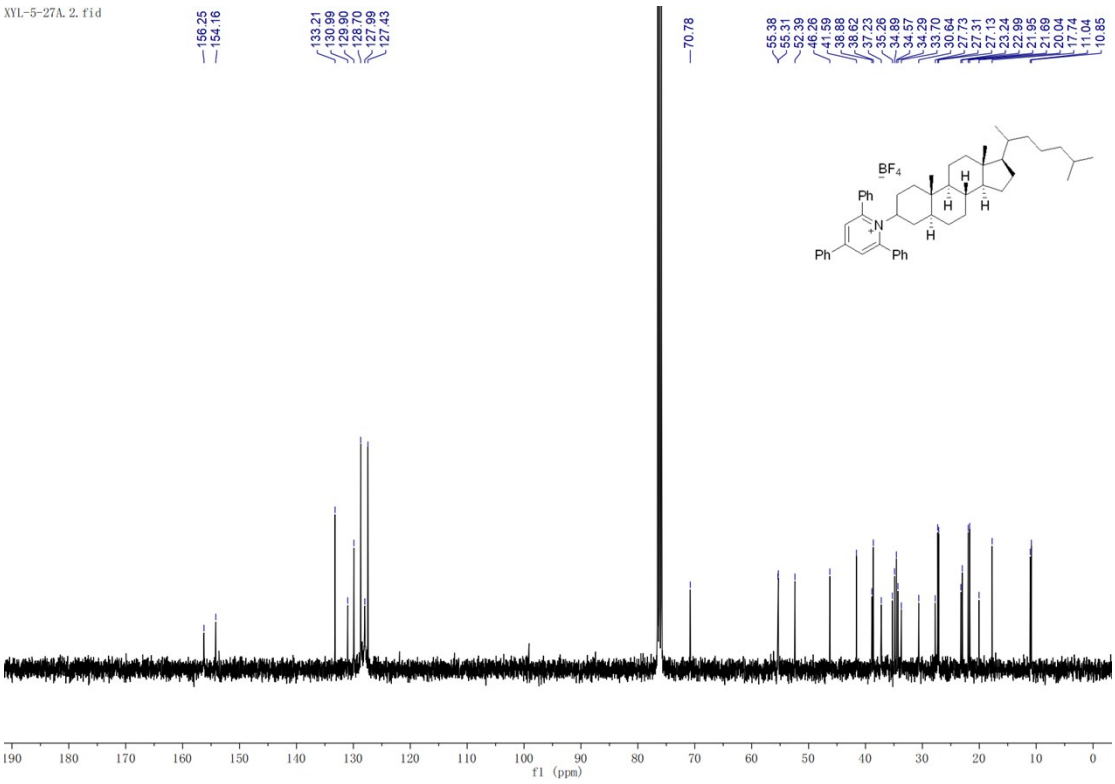
^{13}C NMR spectrum of **1-(1-(3-(2-cyanobenzyl)-1-methyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-y -l)piperidin-3-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2s)**



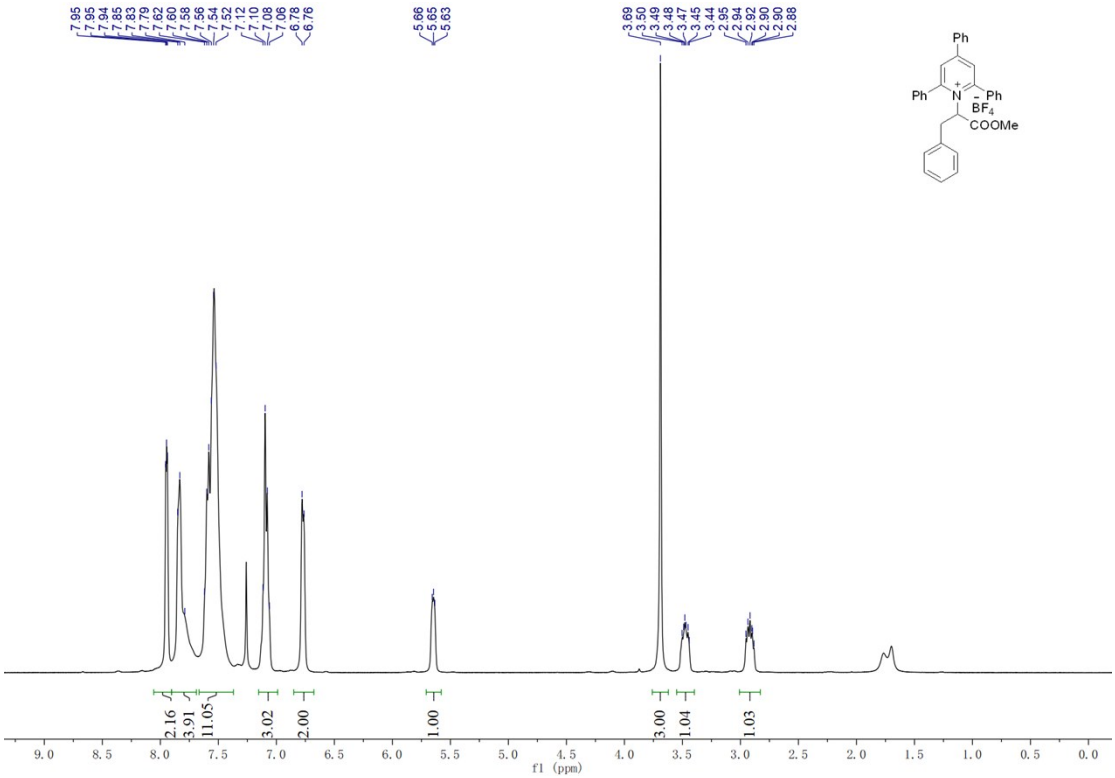
^{1}H NMR spectrum of **1-((5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-(6-methylheptan-2-yl) hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)-2,4,6-triphenylpyridin-1-ium tetrafluorobor - ate (2t).**



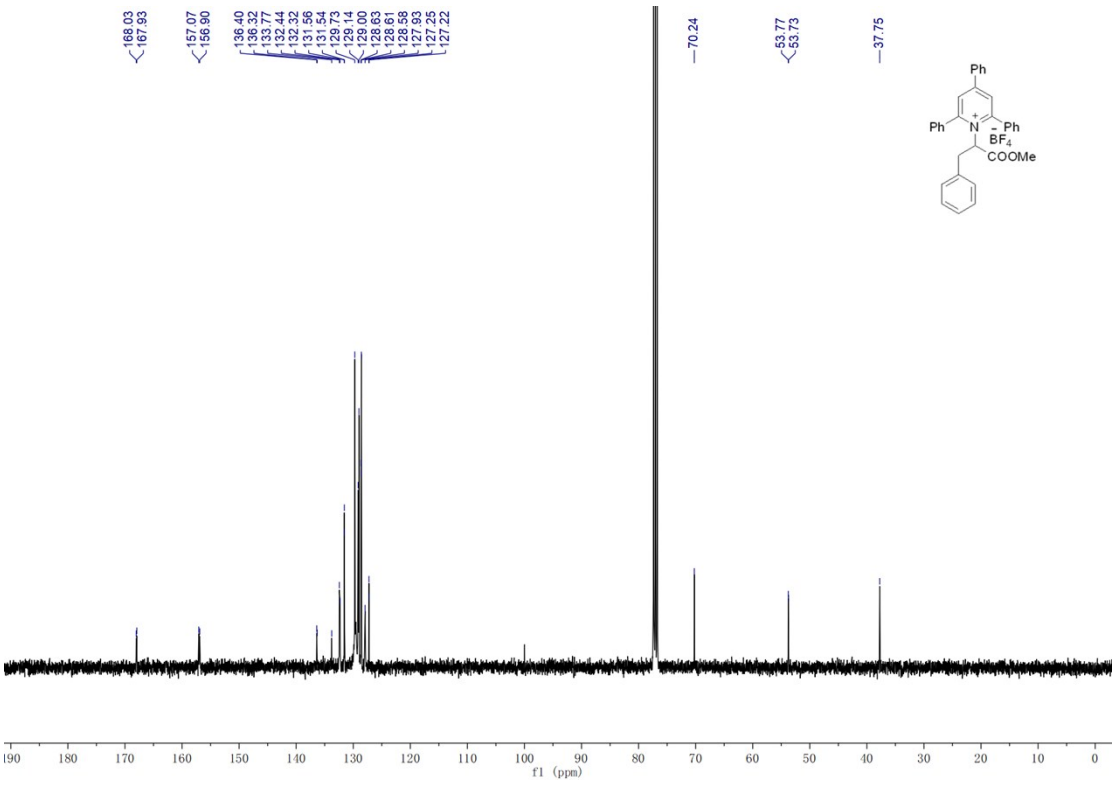
^{13}C NMR spectrum of **1-((5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-(6-methylheptan-2-yl) hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)-2,4,6-triphenylpyridin-1-ium tetrafluorobor - ate (2t).**



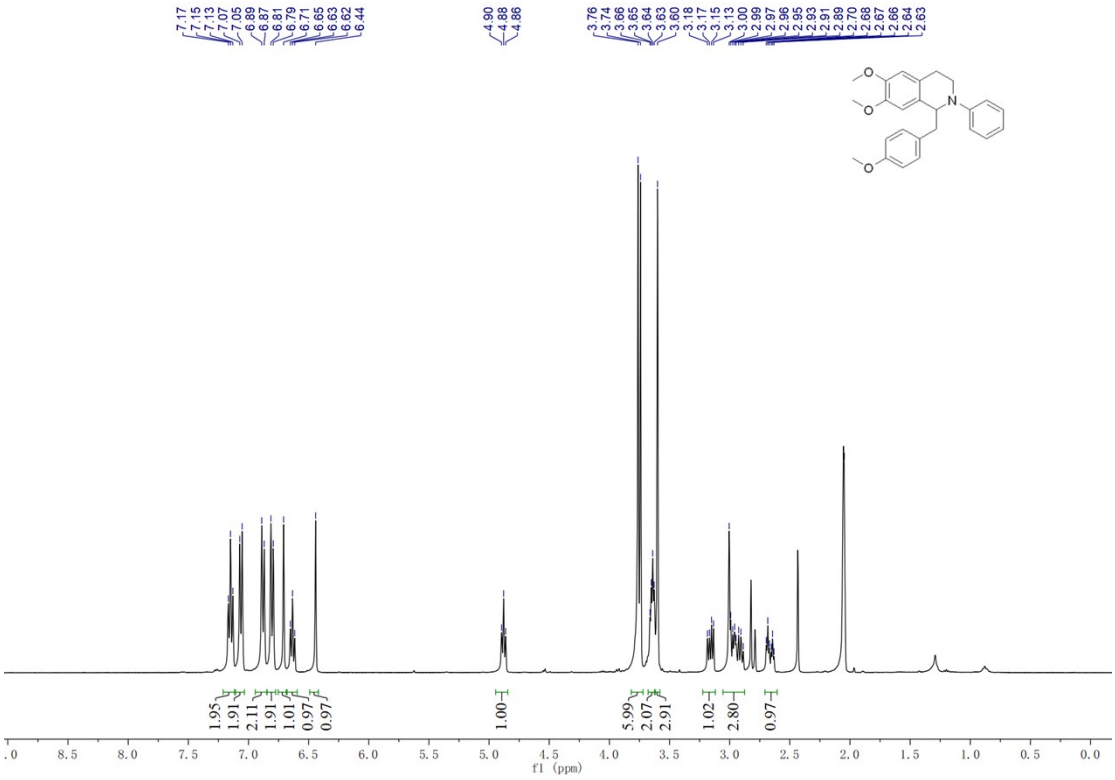
^{1}H NMR spectrum of **1-(1-methoxy-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2u).**



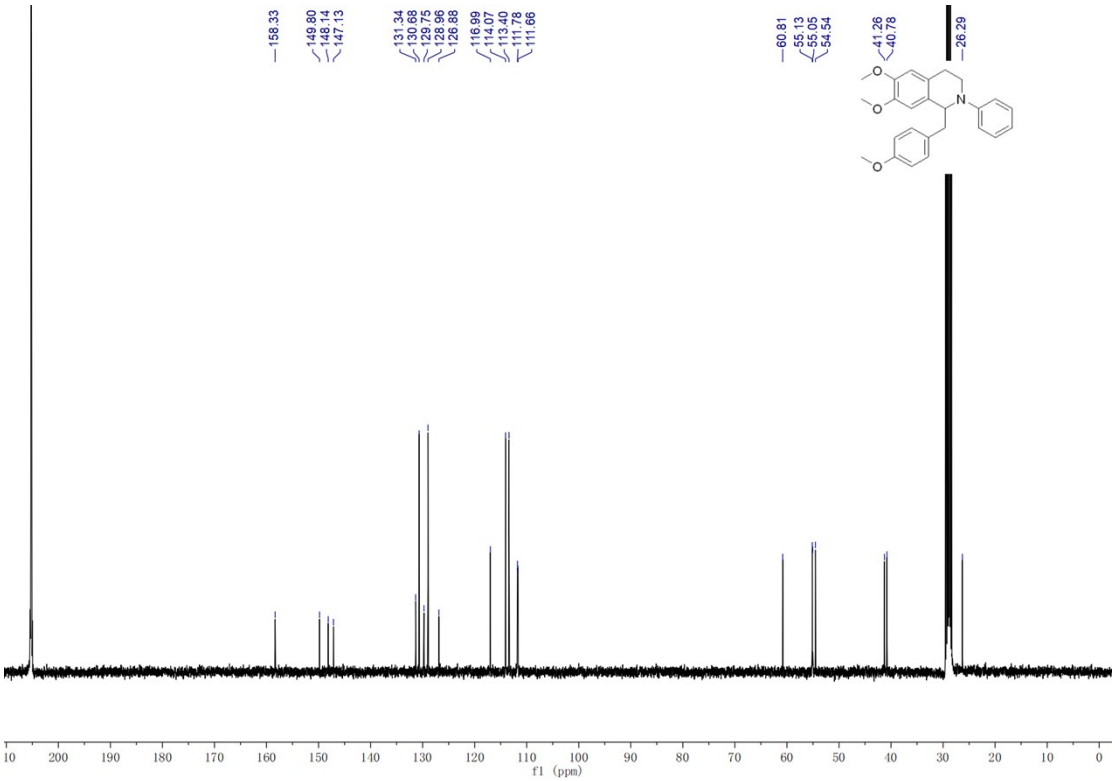
^{13}C NMR spectrum of **1-(1-methoxy-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2u).**



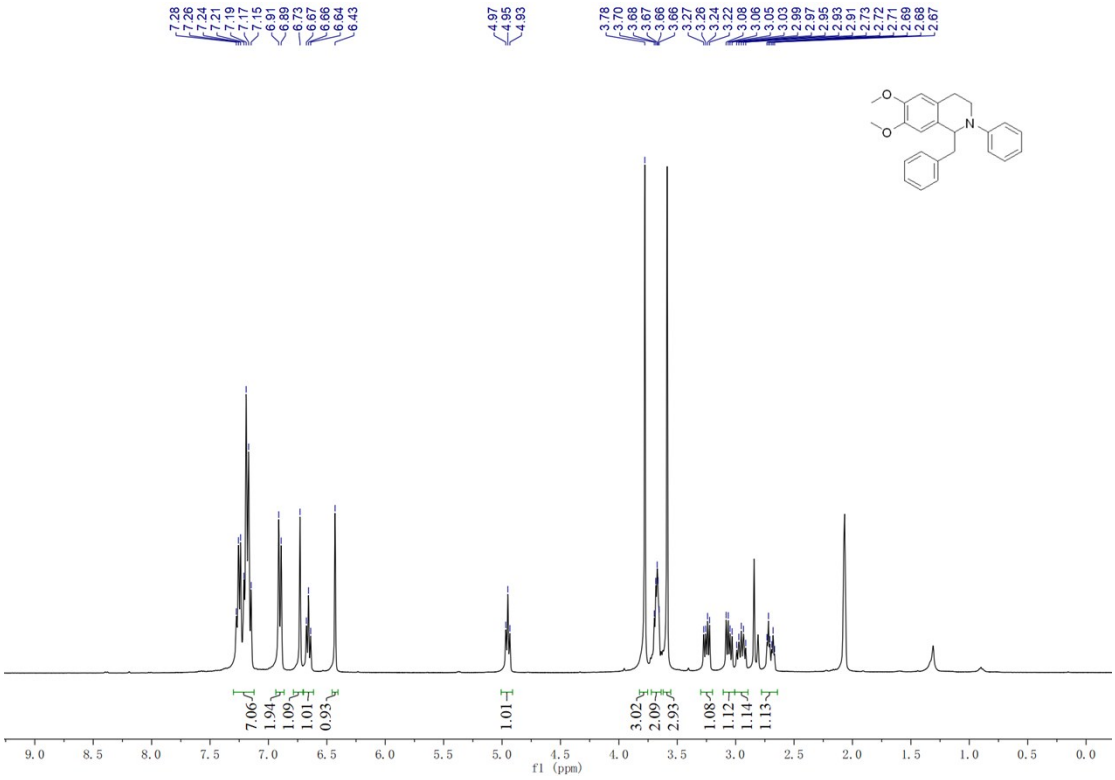
^{1}H NMR spectrum of **6,7-dimethoxy-1-(4-methoxybenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3aa).**



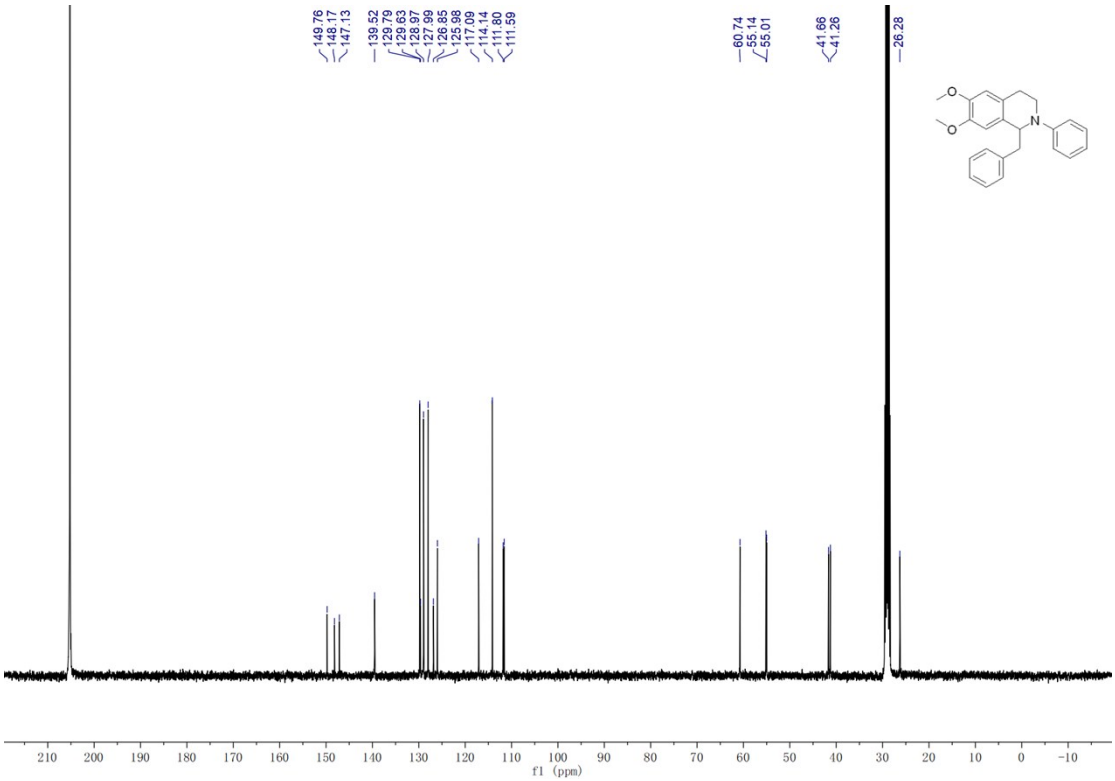
^{13}C NMR spectrum of **6,7-dimethoxy-1-(4-methoxybenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3aa).**



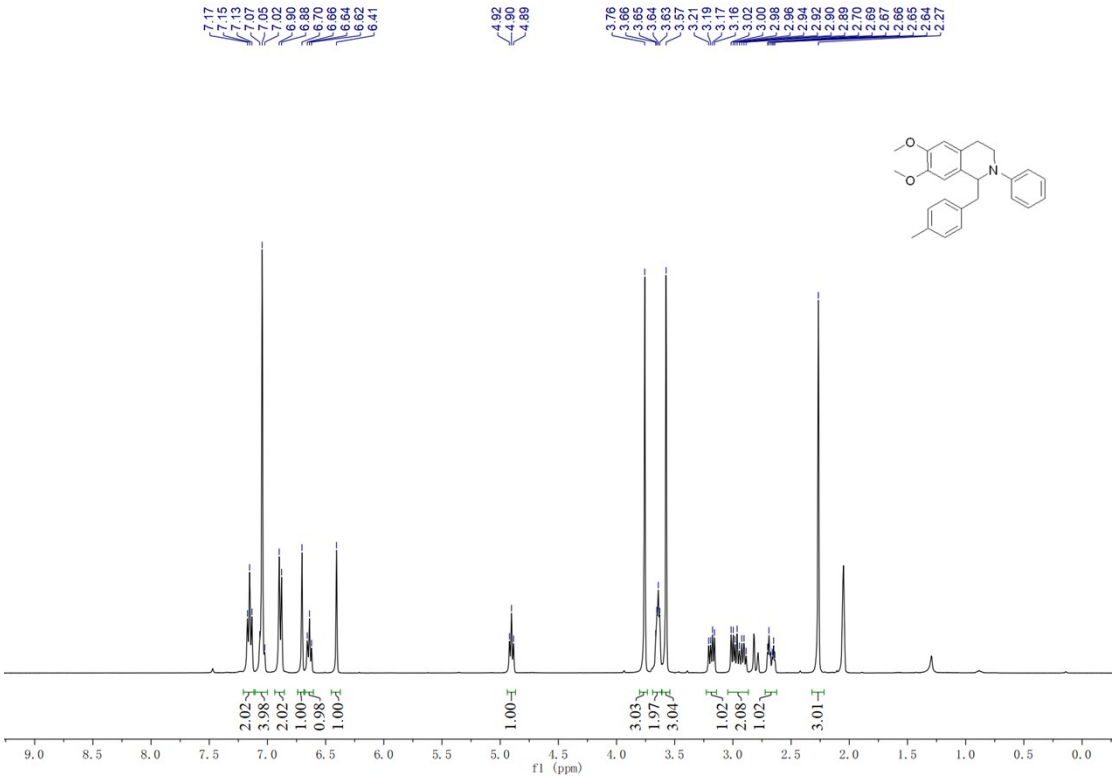
^{1}H NMR spectrum of **1-benzyl-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ab).**



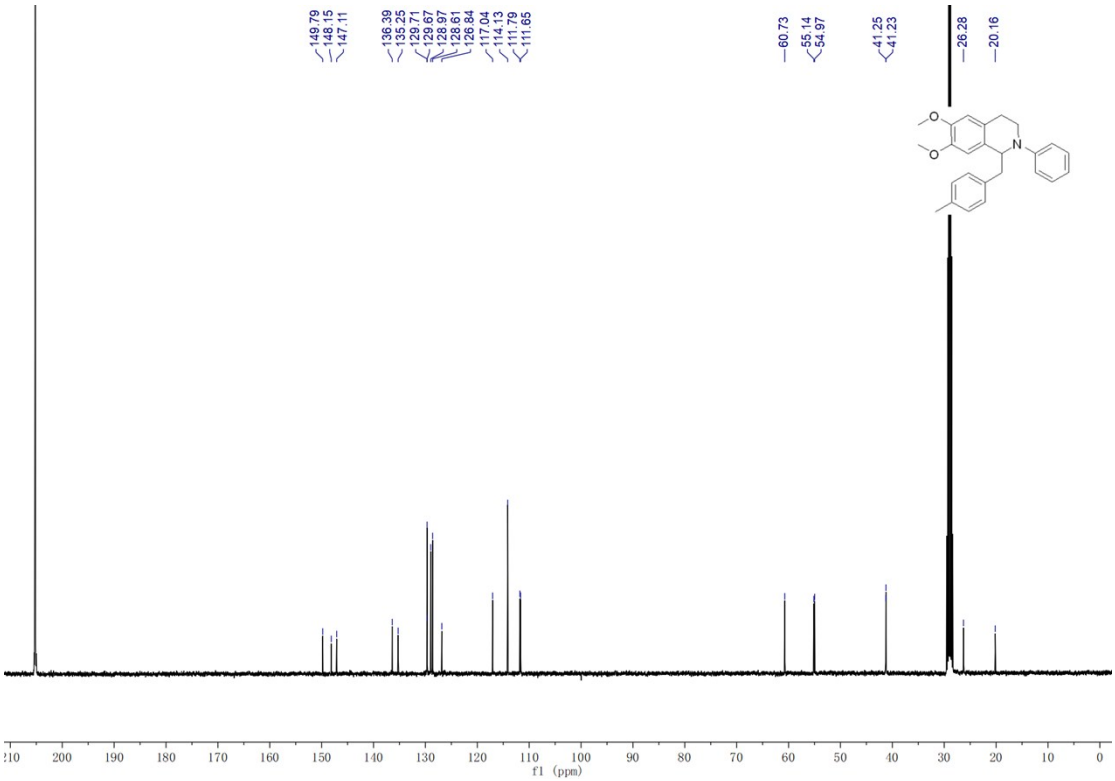
^{1}H NMR spectrum of **1-benzyl-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ab).**



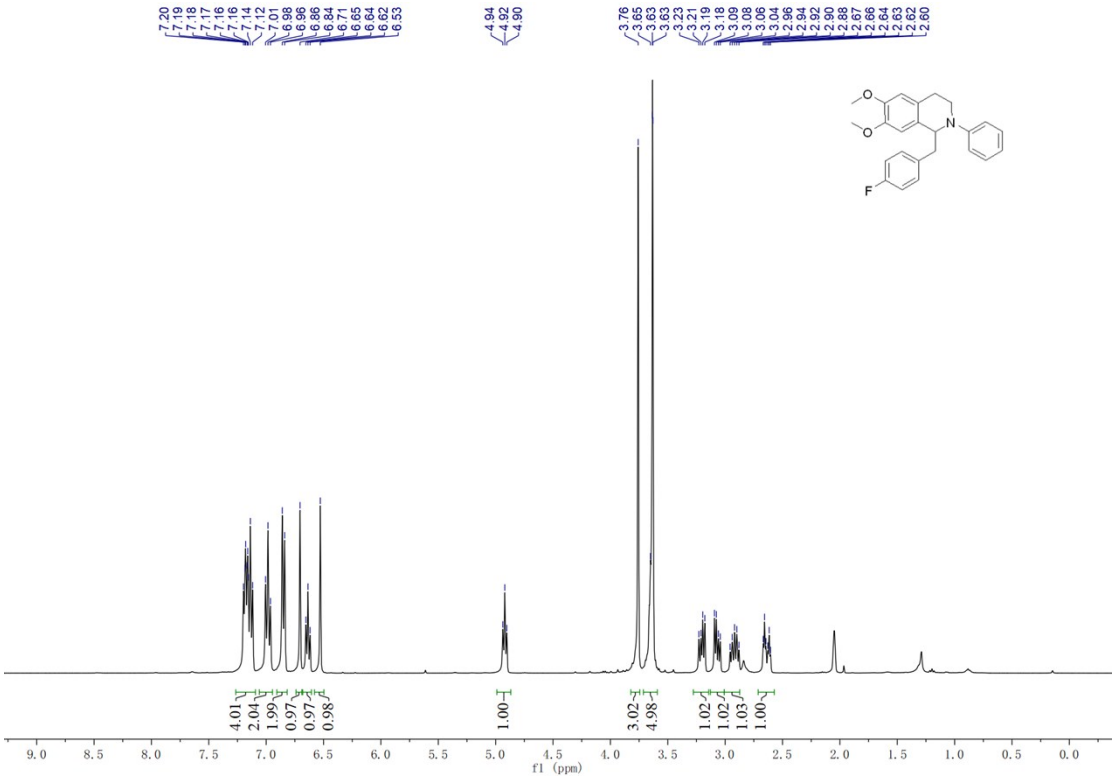
^{1}H NMR spectrum of **6,7-dimethoxy-1-(4-methylbenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ac).**



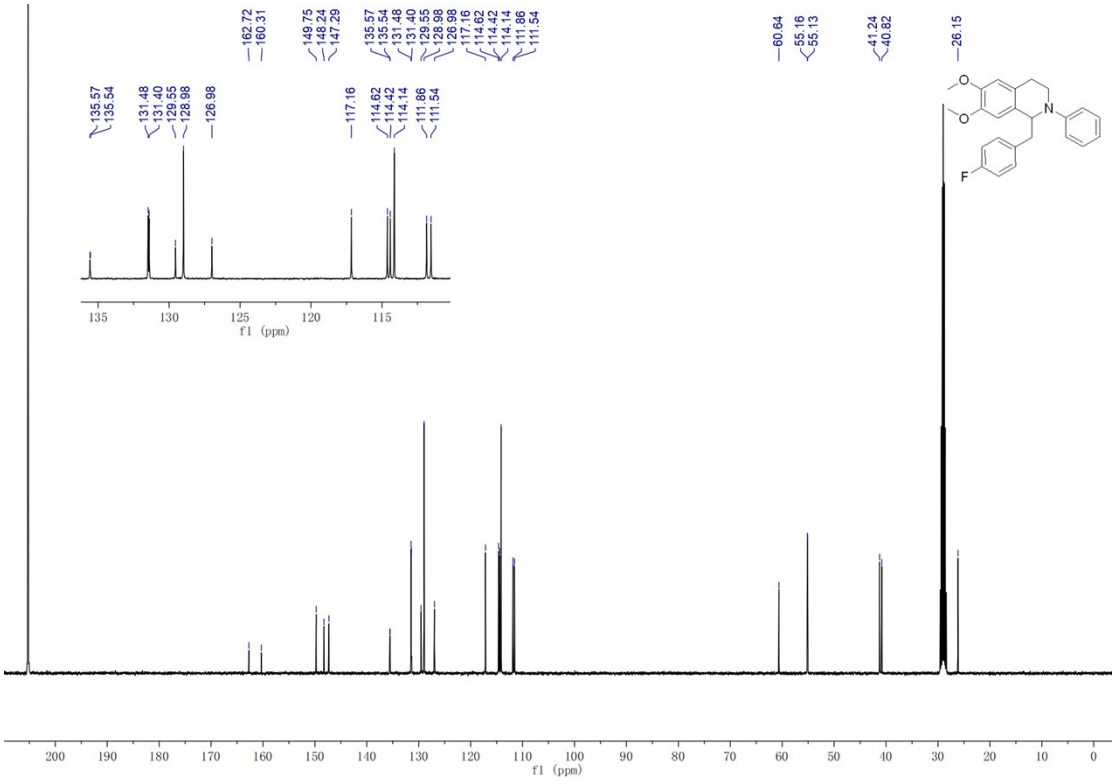
^{13}H NMR spectrum of **6,7-dimethoxy-1-(4-methylbenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ac).**



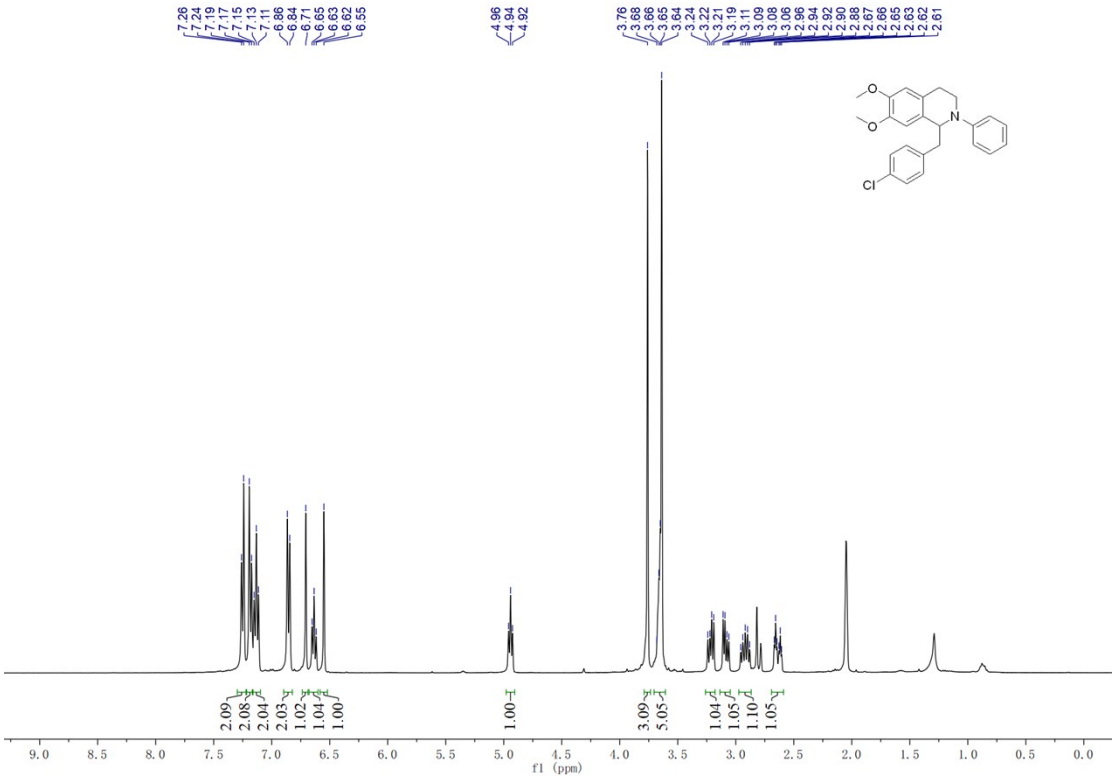
^{1}H NMR spectrum of **1-(4-fluorobenzyl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ad).**



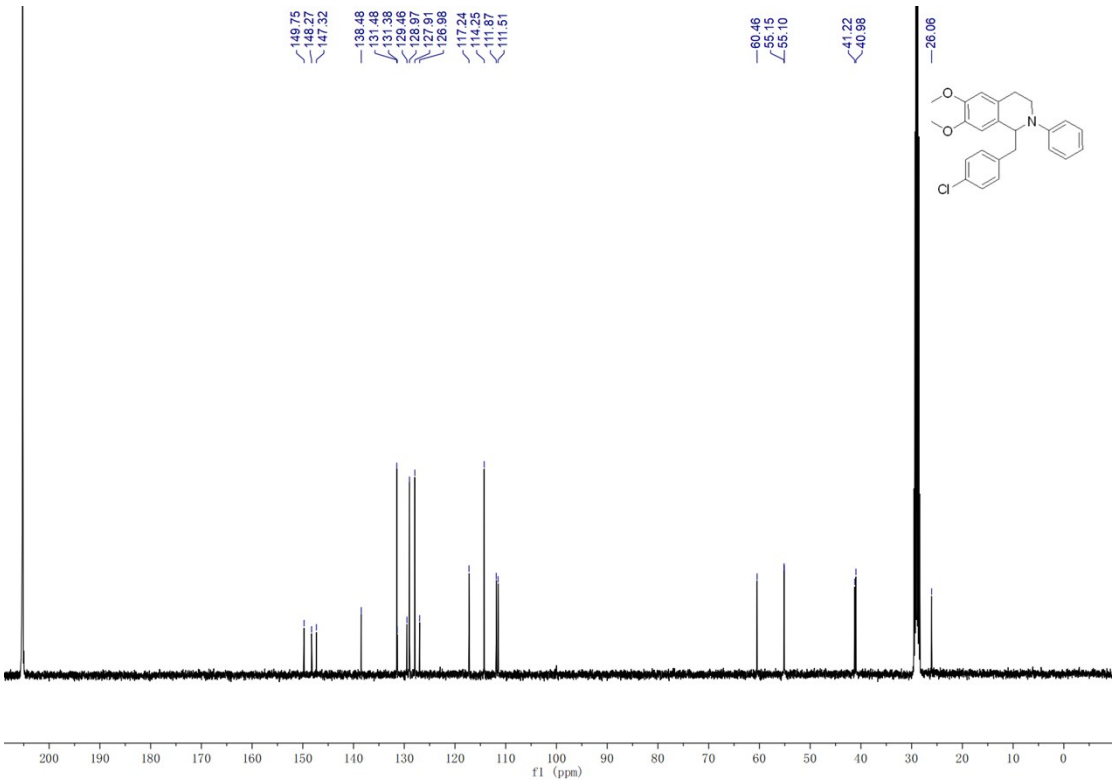
^{13}C NMR spectrum of **1-(4-fluorobenzyl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ad).**



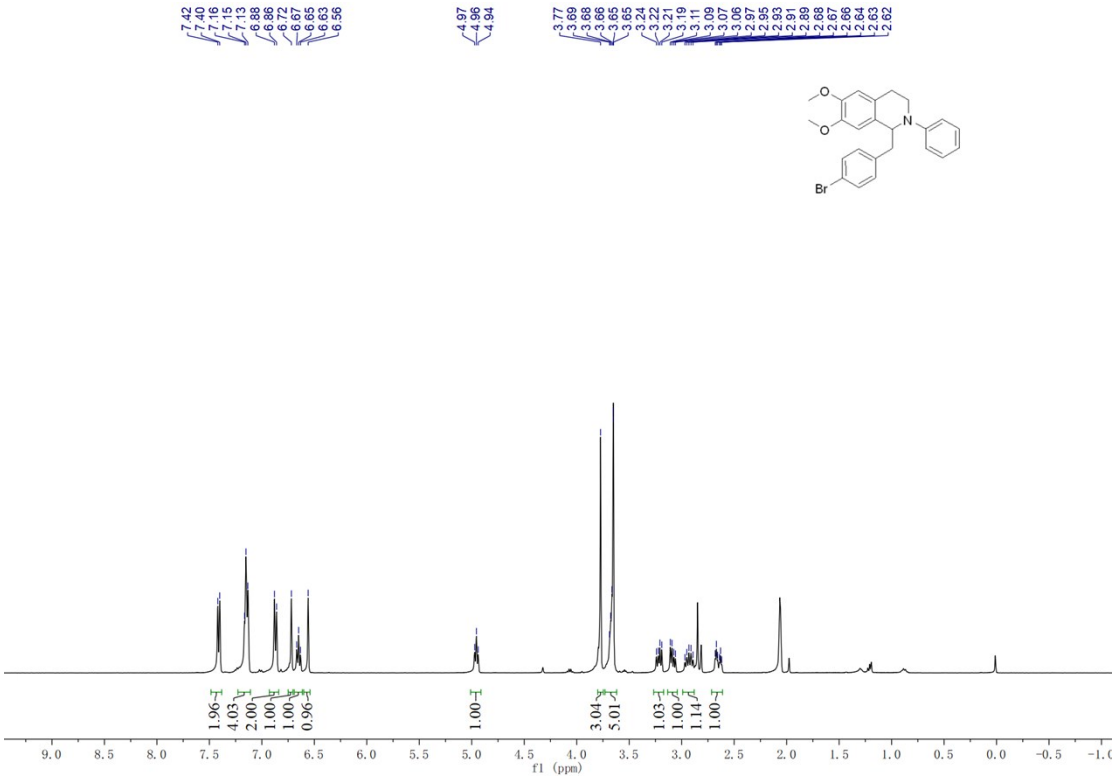
^{1}H NMR spectrum of **1-(4-chlorobenzyl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ae).**



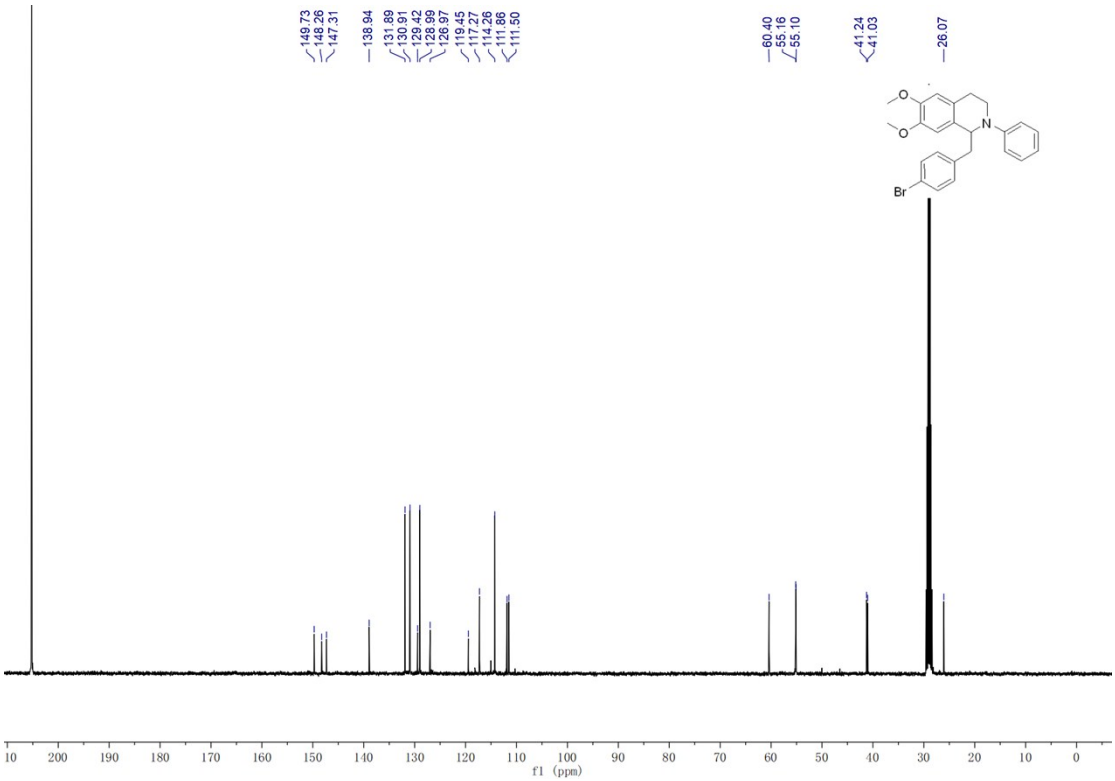
^{13}C NMR spectrum of **1-(4-chlorobenzyl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ae).**



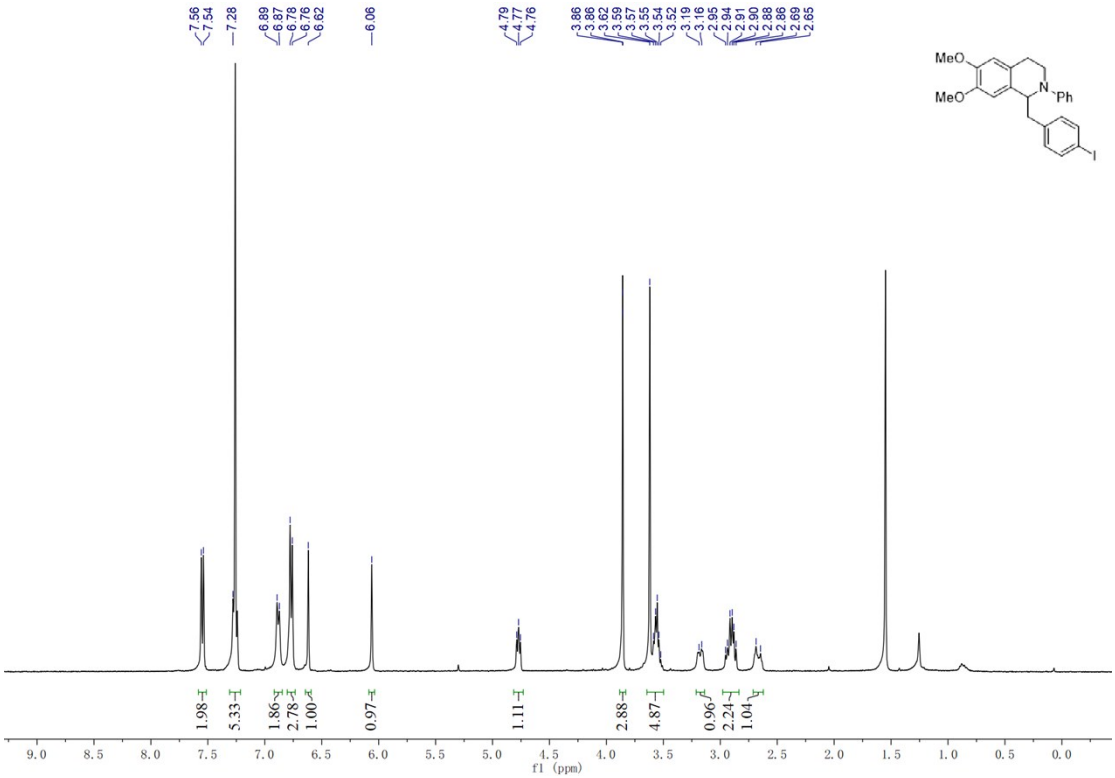
^{1}H NMR spectrum of **1-(4-chlorobenzyl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3af).**



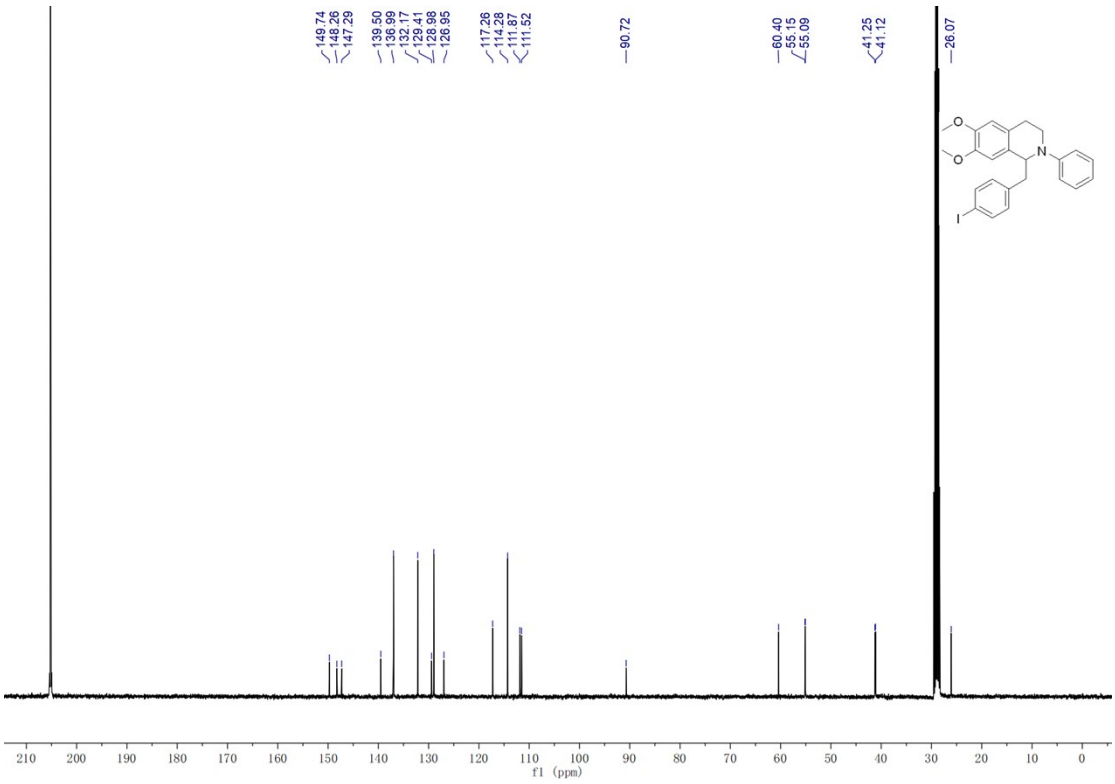
^{13}C NMR spectrum of **1-(4-chlorobenzyl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3af).**



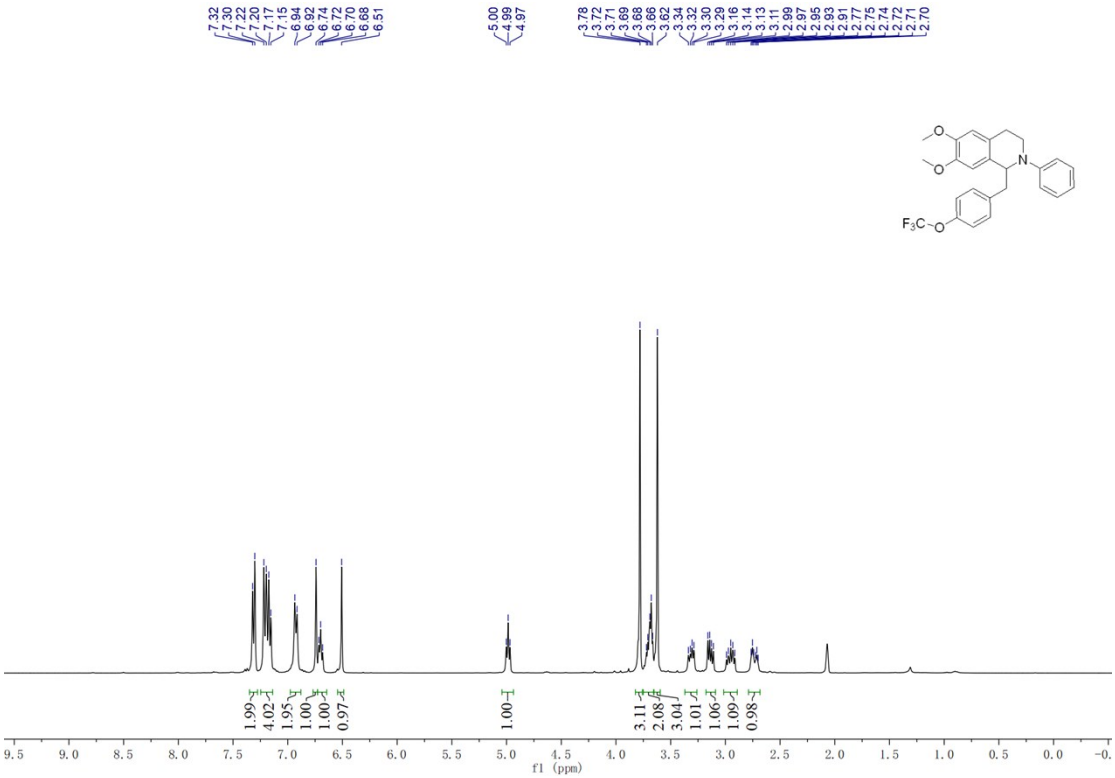
^{1}H NMR spectrum of **1-(4-iodobenzyl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ag).**



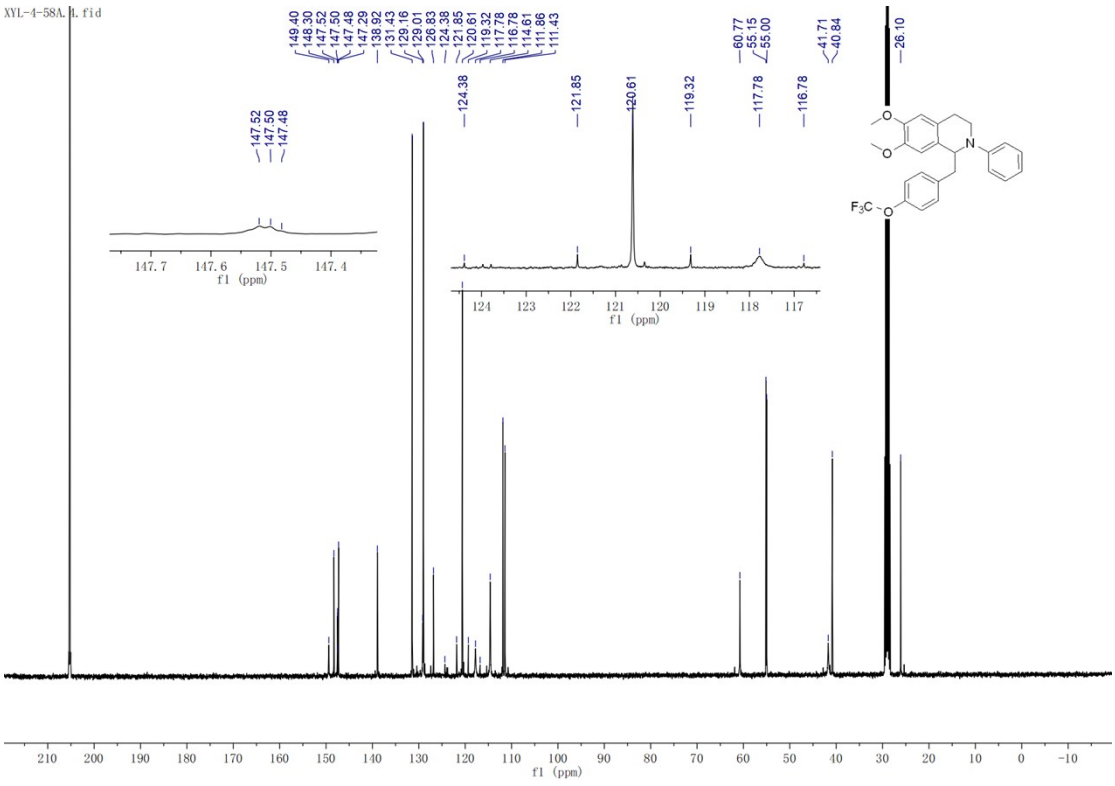
^{13}C NMR spectrum of **1-(4-iodobenzyl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ag).**



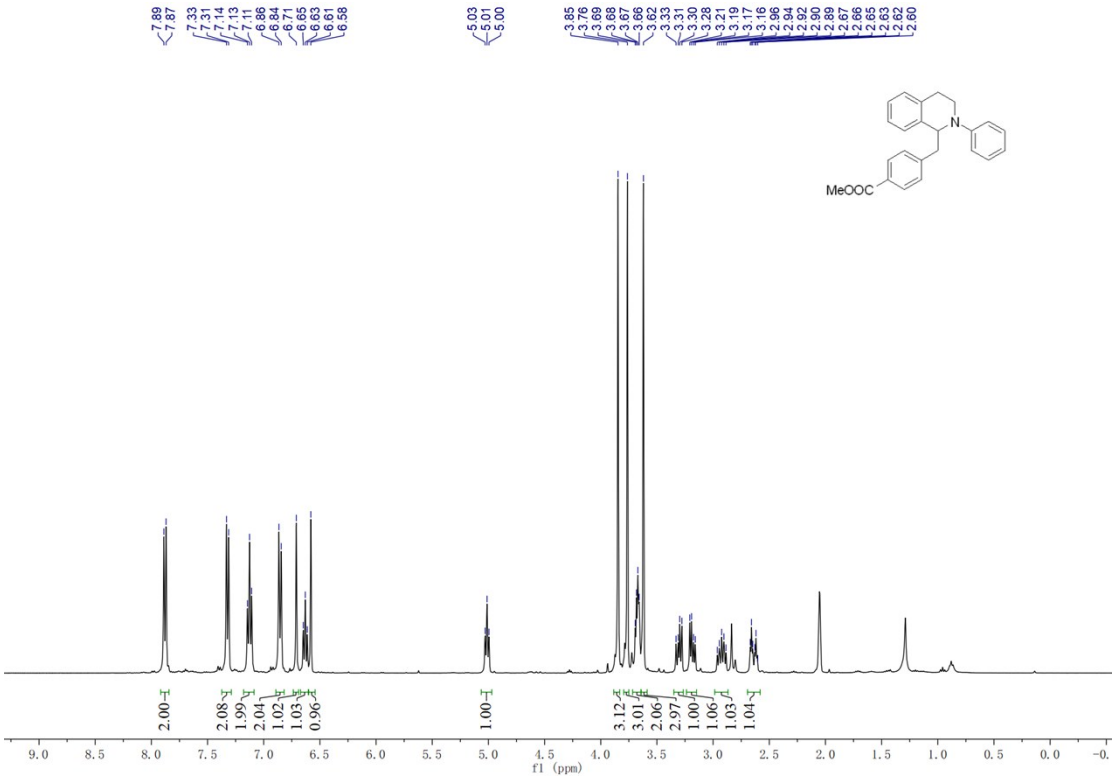
^{1}H NMR spectrum of **6,7-dimethoxy-2-phenyl-1-(4-(trifluoromethoxy)benzyl)-1,2,3,4-tetrahydroisoquinoline (3ah).**



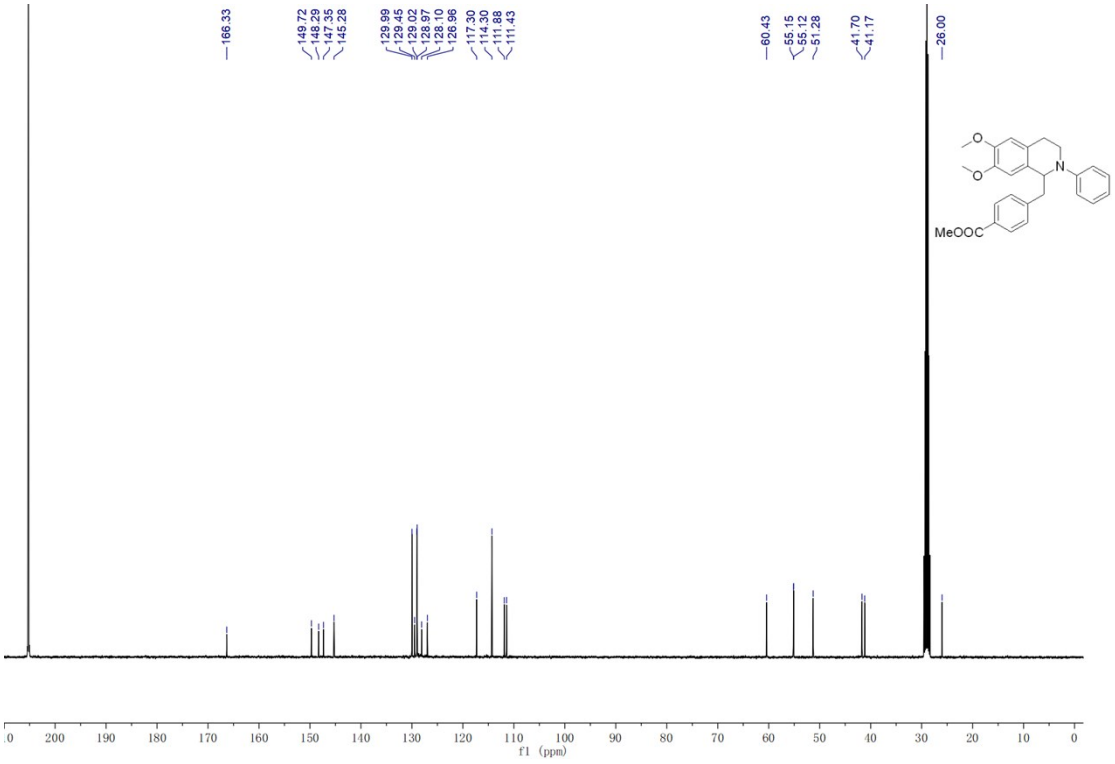
^{13}C NMR spectrum of **6,7-dimethoxy-2-phenyl-1-(4-(trifluoromethoxy)benzyl)-1,2,3,4-tetrahydroisoquinoline (3ah).**



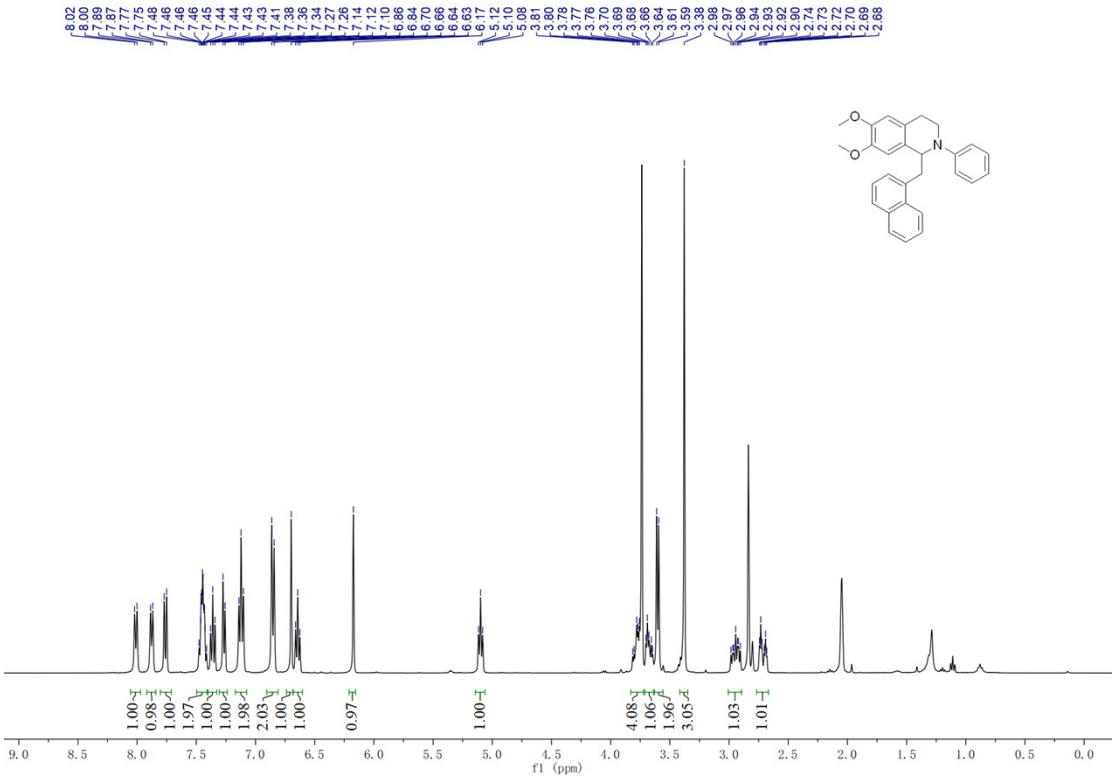
^{1}H NMR spectrum of **methyl 4-((6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin -1-yl)methyl)benzoate (3ai).**



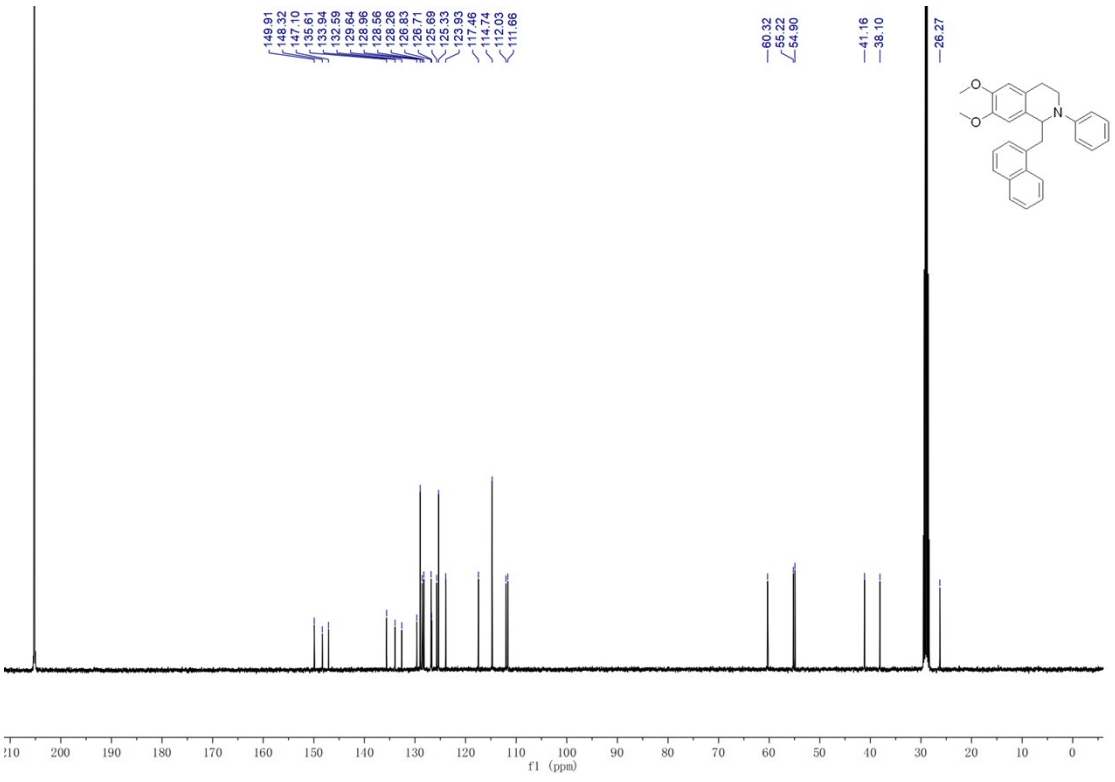
^{13}C NMR spectrum of **methyl 4-((6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin -1-yl)methyl)benzoate (3ai).**



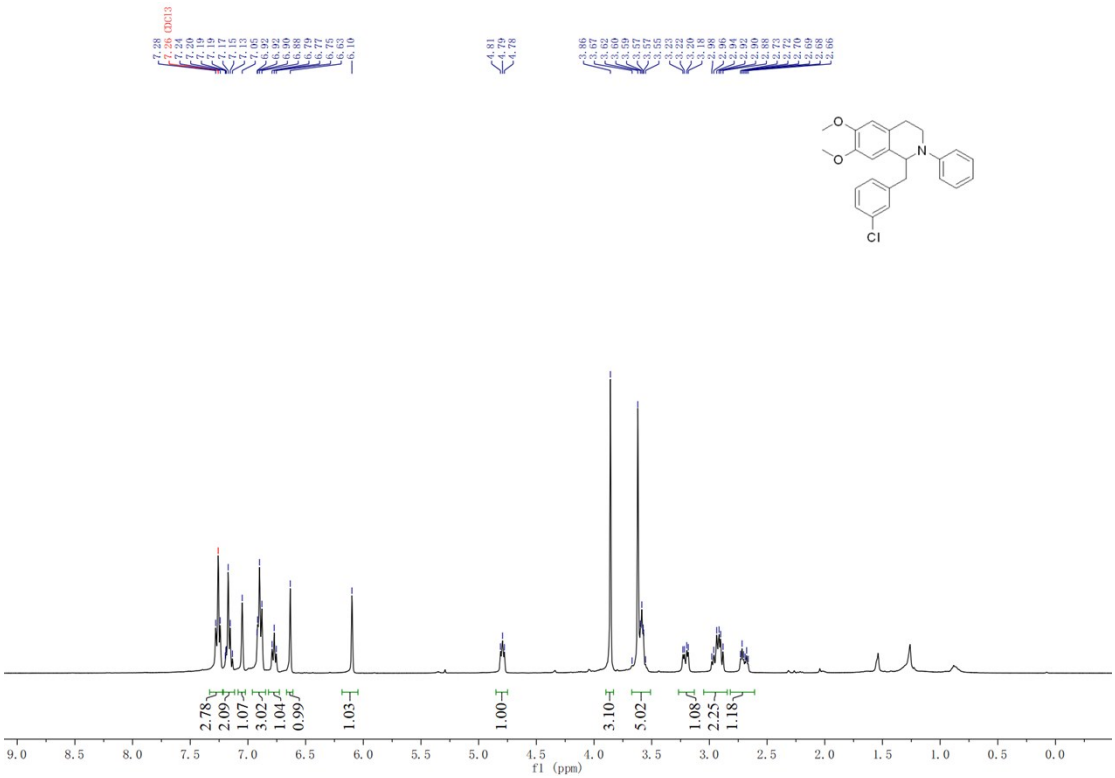
^{1}H NMR spectrum of **6,7-dimethoxy-1-(naphthalen-1-ylmethyl)-2-phenyl-1,2,3,4 -tetrahydroisoquinoline (3aj).**



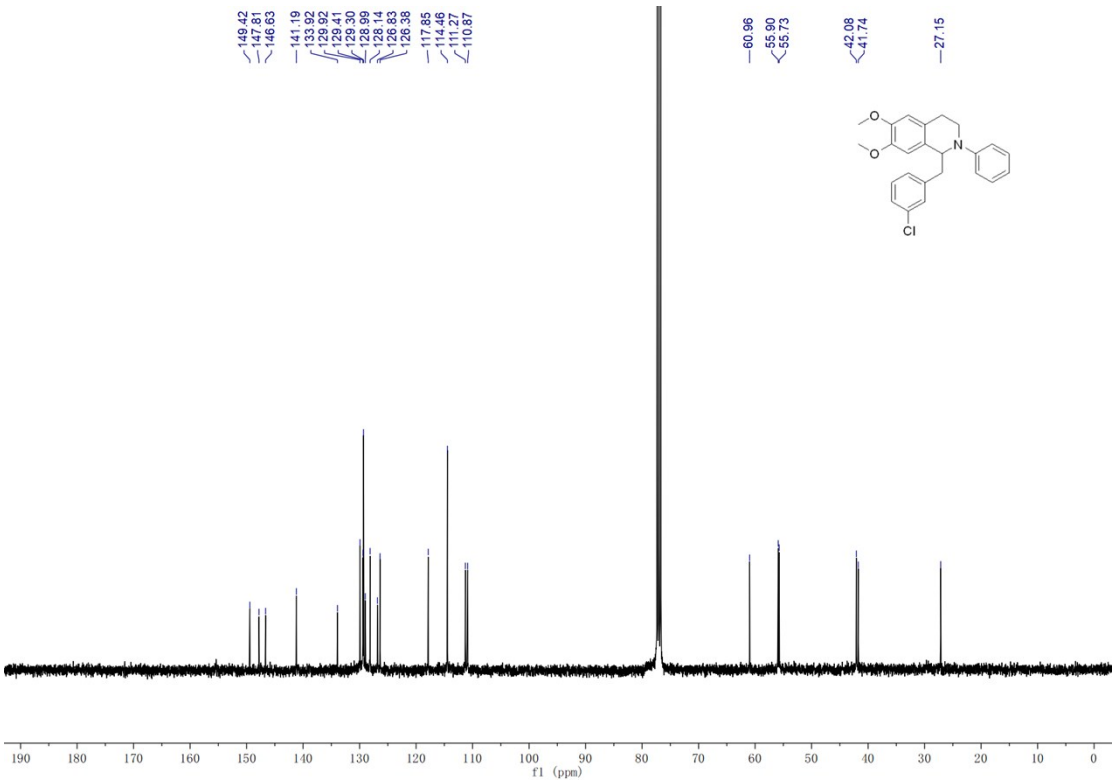
^{13}C NMR spectrum of **6,7-dimethoxy-1-(naphthalen-1-ylmethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3aj).**



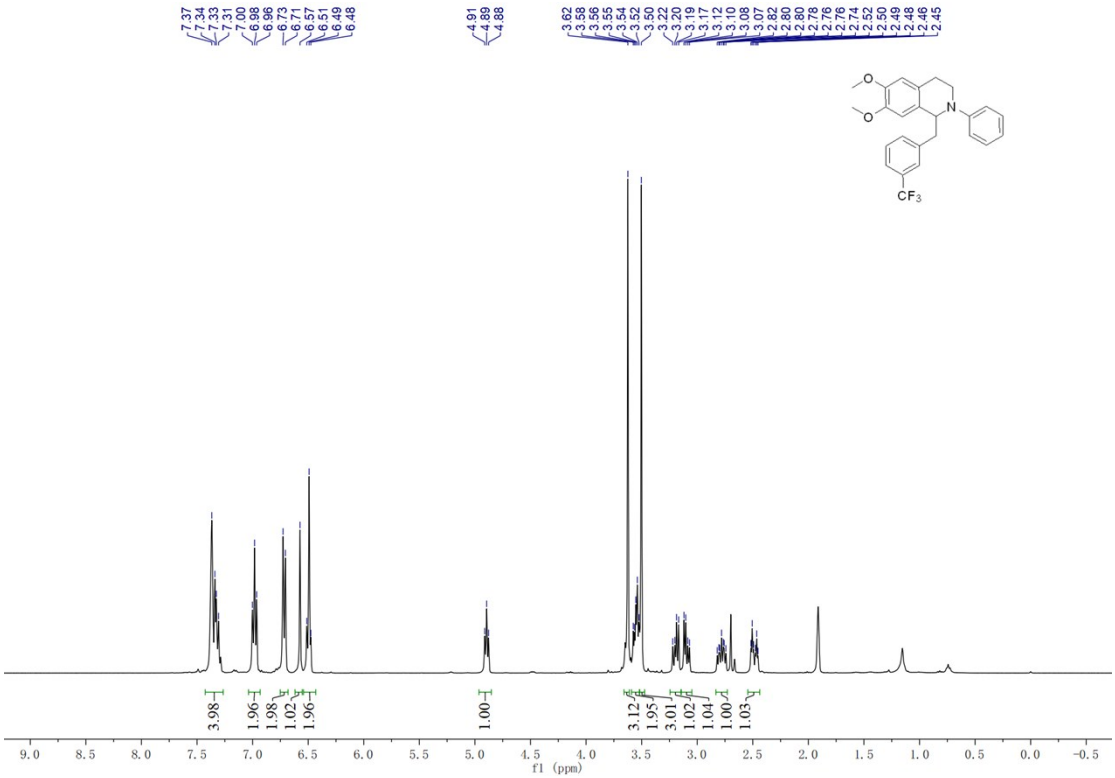
^{1}H NMR spectrum of **1-(3-chlorobenzyl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ak).**



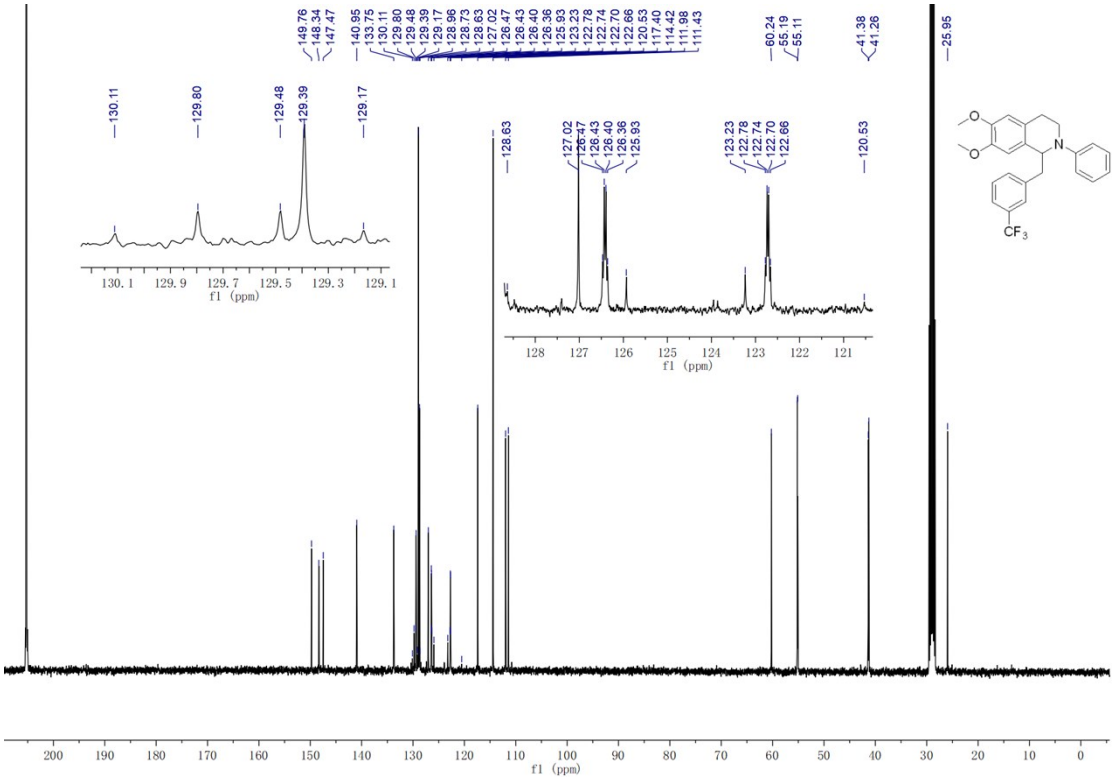
^{13}C NMR spectrum of **1-(3-chlorobenzyl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ak).**



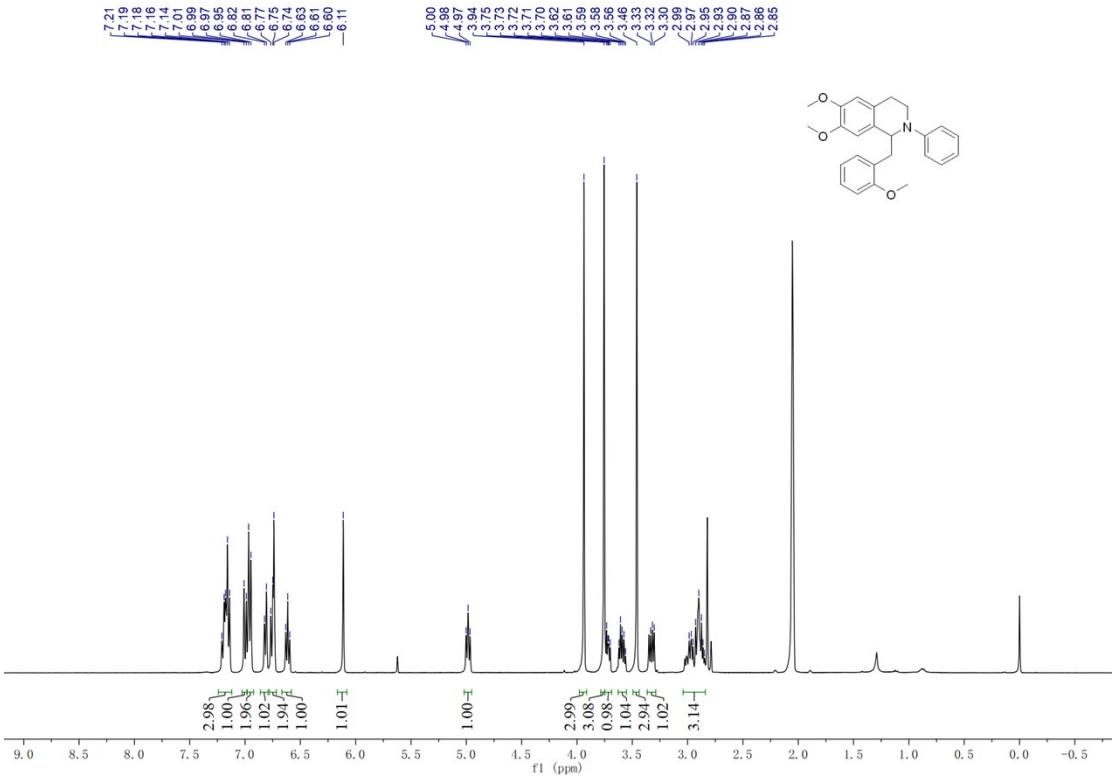
^{1}H NMR spectrum of **6,7-dimethoxy-2-phenyl-1-(3-(trifluoromethyl)benzyl)-1,2,3,4- t etrahydroisoquinoline (3al).**



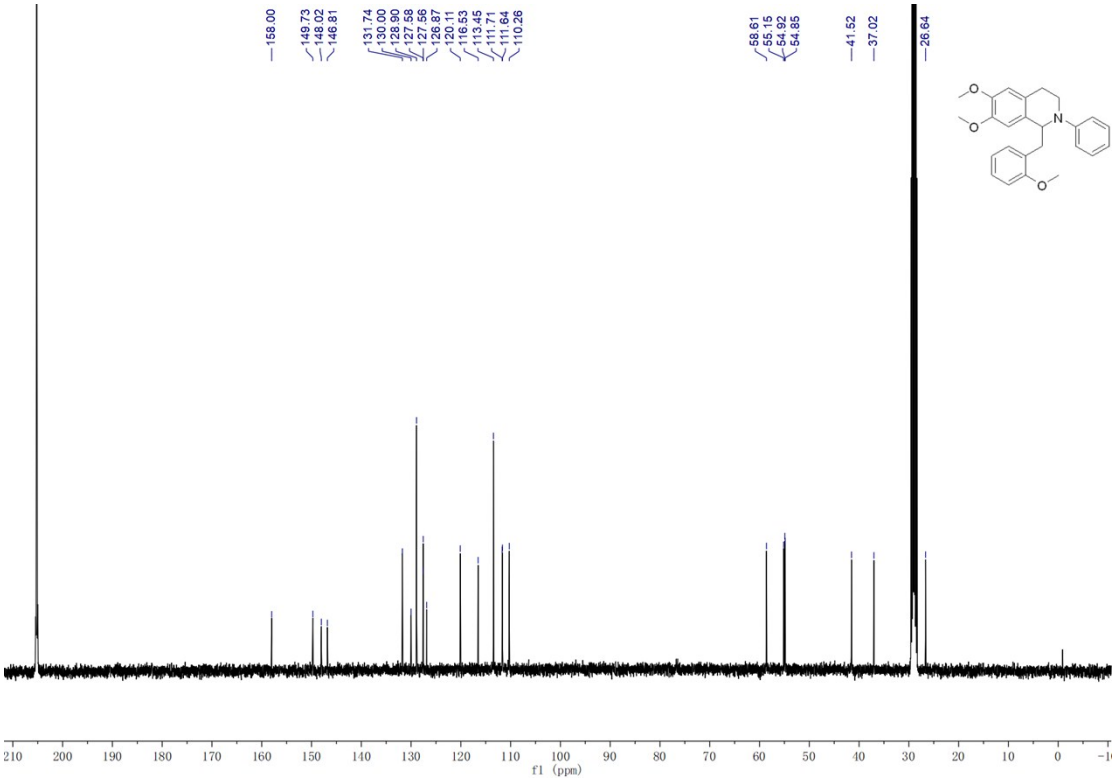
^{13}C NMR spectrum of **6,7-dimethoxy-2-phenyl-1-(3-(trifluoromethyl)benzyl)-1,2,3,4- t etrahydroisoquinoline (3al).**



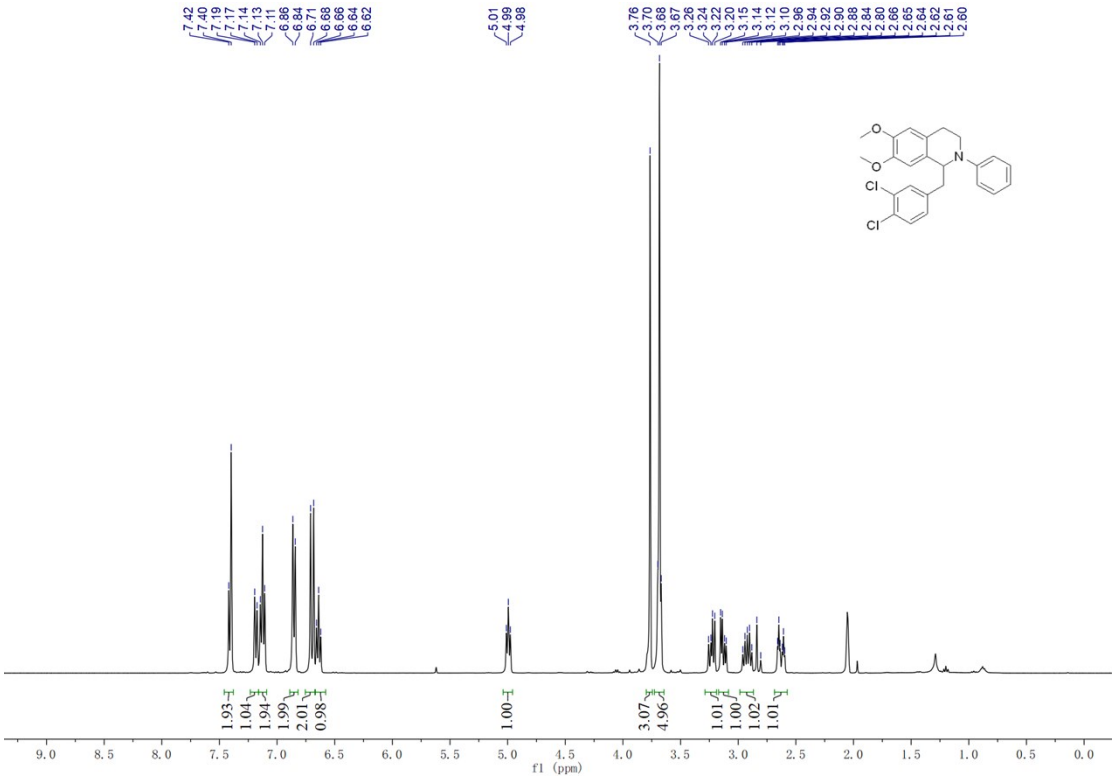
^{1}H NMR spectrum of **6,7-dimethoxy-1-(2-methoxybenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3am).**



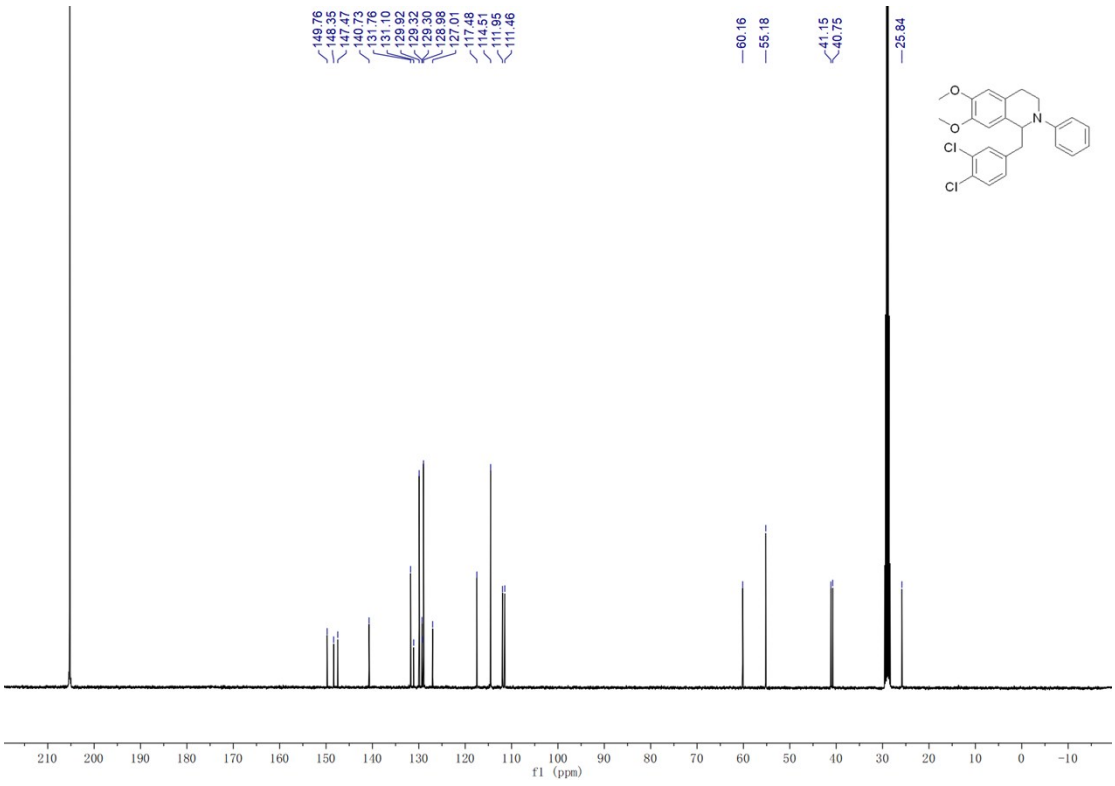
^{13}C NMR spectrum of **6,7-dimethoxy-1-(2-methoxybenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3am).**



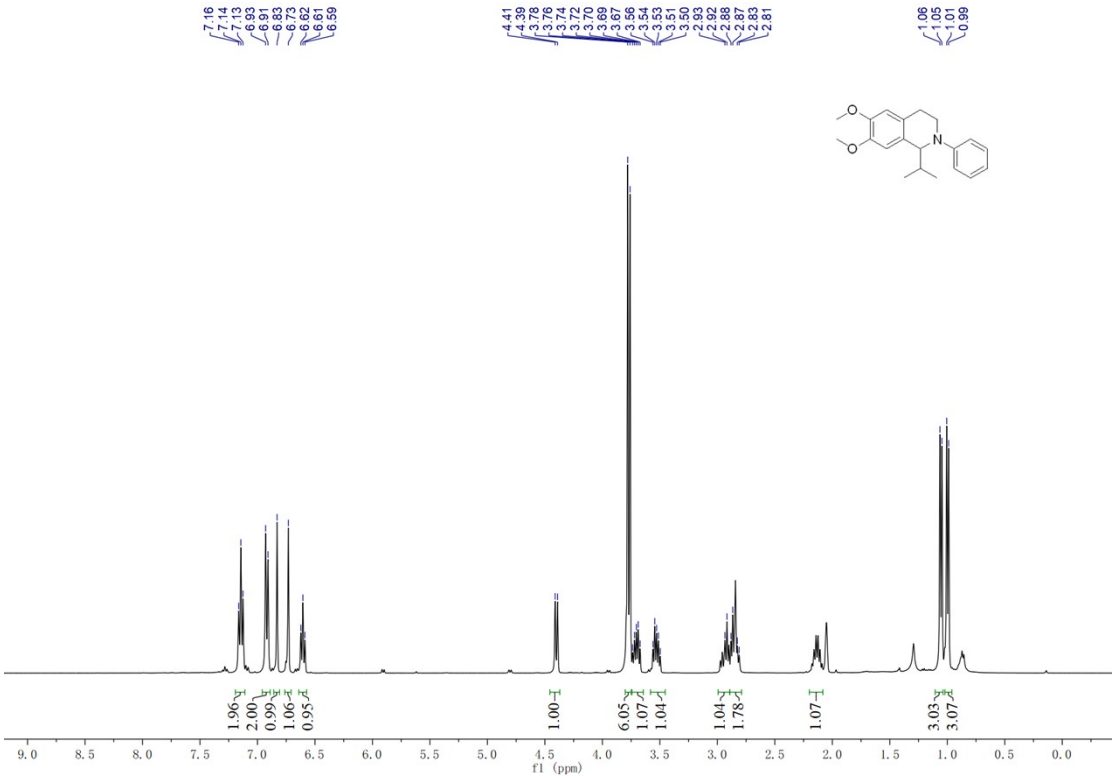
^{1}H NMR spectrum of **1-(3,4-dichlorobenzyl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3an).**



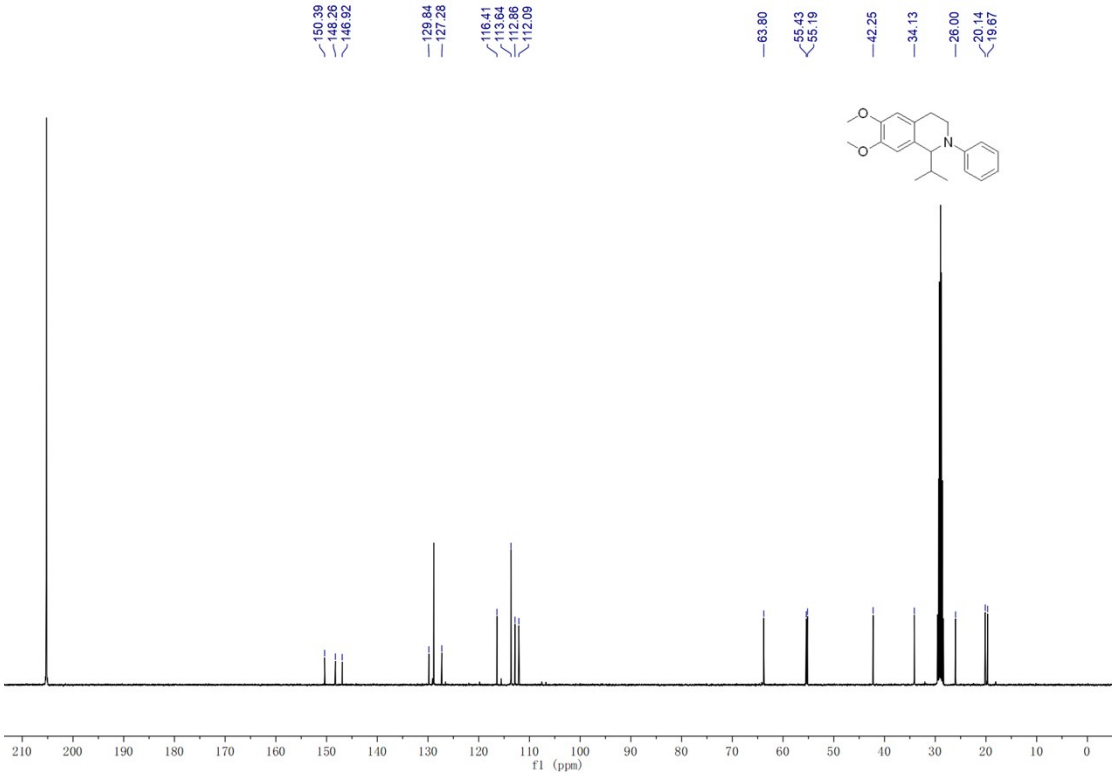
^{13}C NMR spectrum of **1-(3,4-dichlorobenzyl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3an).**



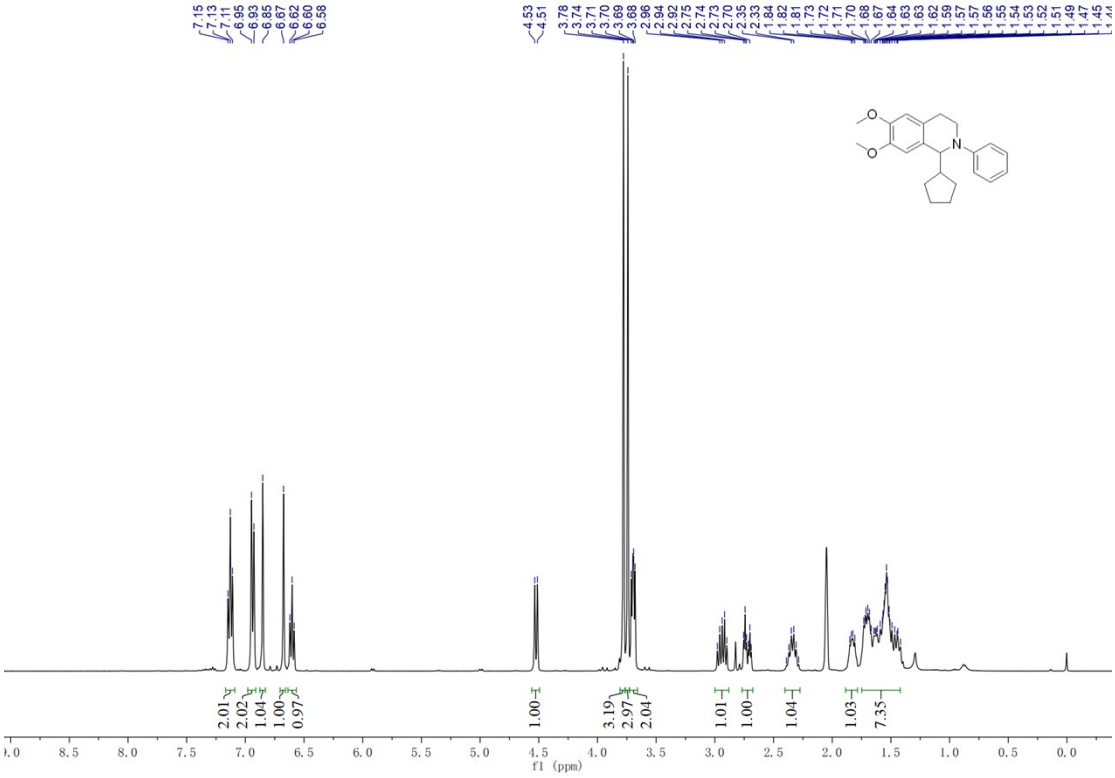
^{1}H NMR spectrum of **1-isopropyl-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ao).**



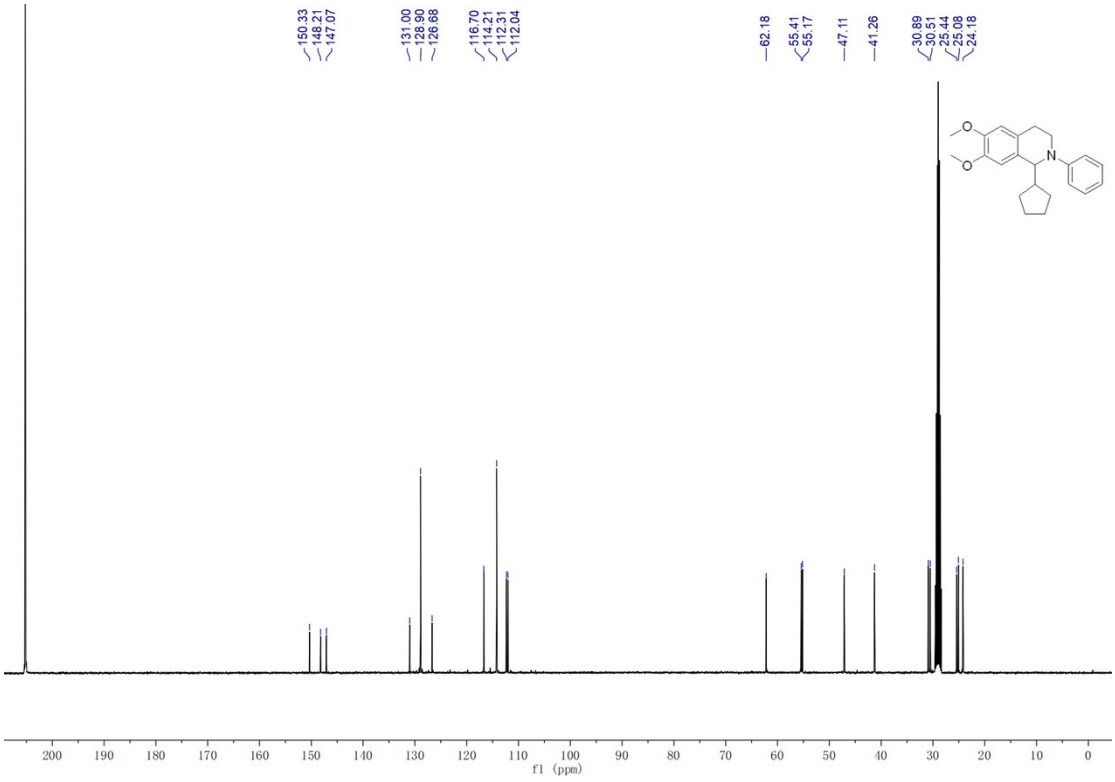
^{13}C NMR spectrum of **1-isopropyl-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ao).**



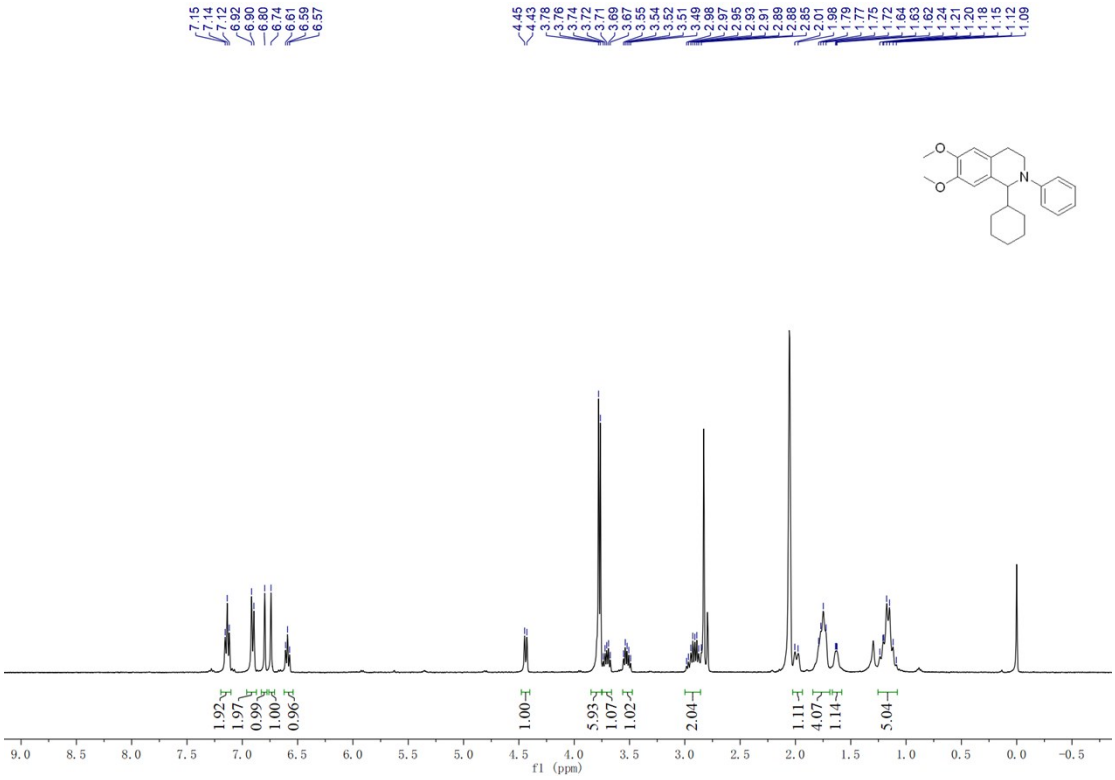
^{1}H NMR spectrum of **1-cyclopentyl-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ap).**



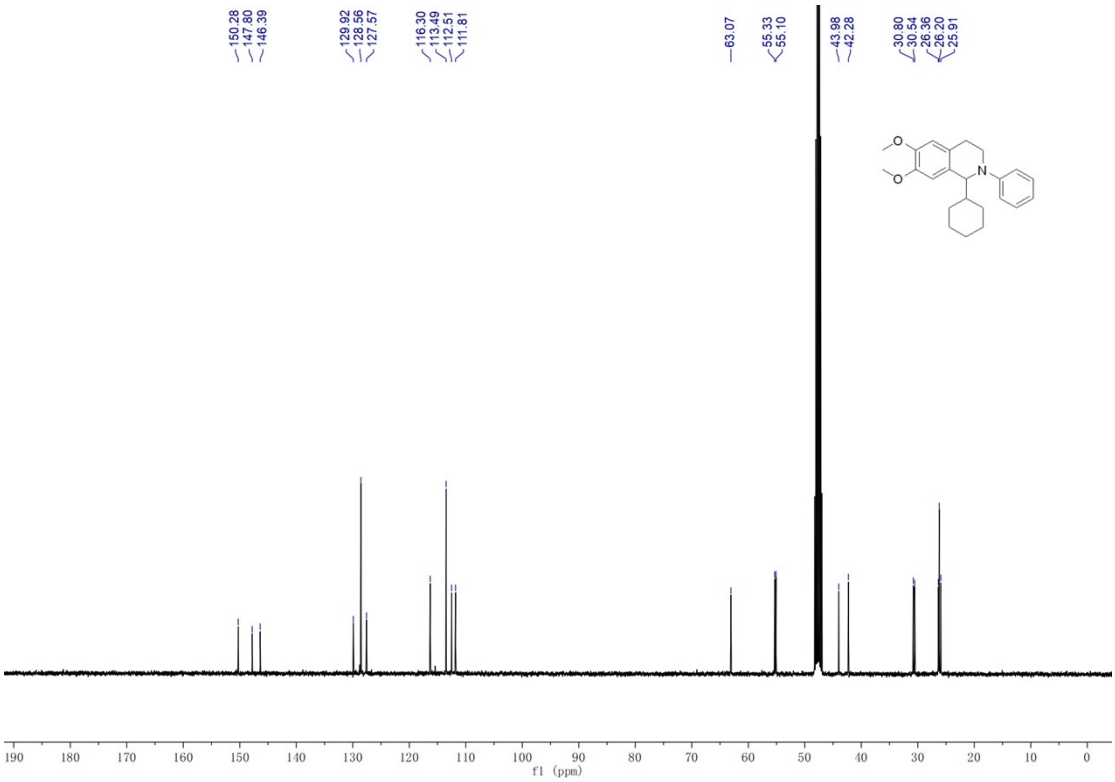
^{13}C NMR spectrum of **1-cyclopentyl-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ap).**



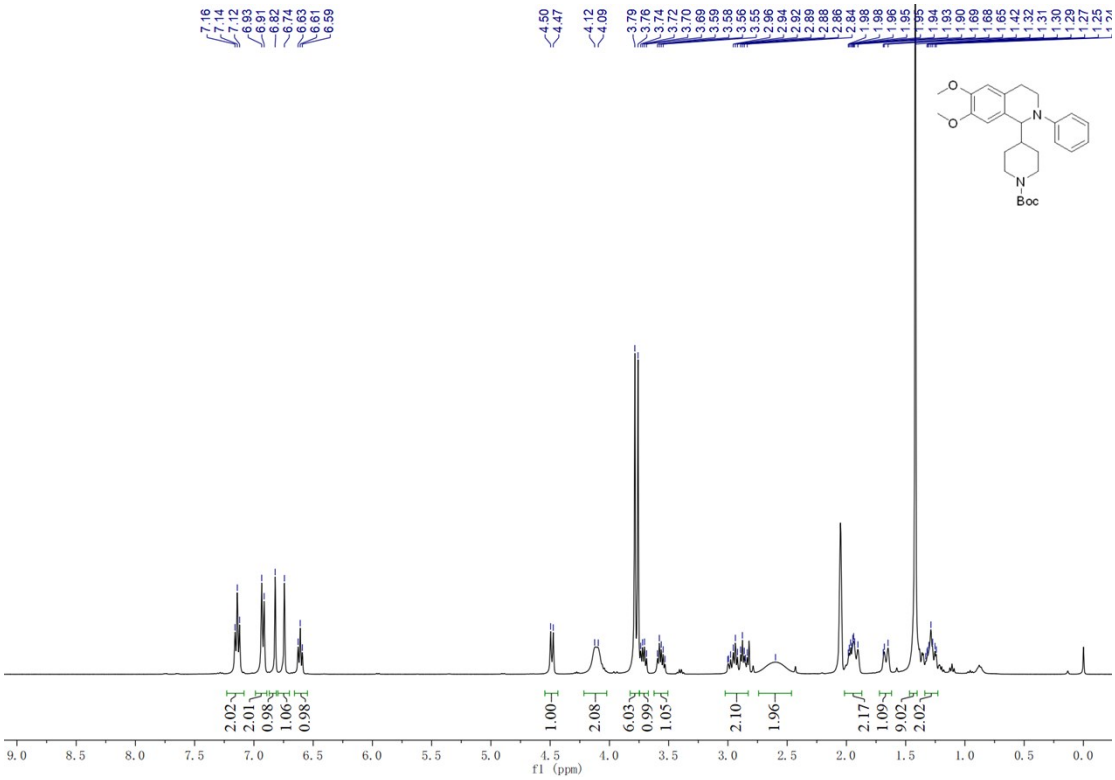
^{1}H NMR spectrum of **1-cyclohexyl-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3aq).**



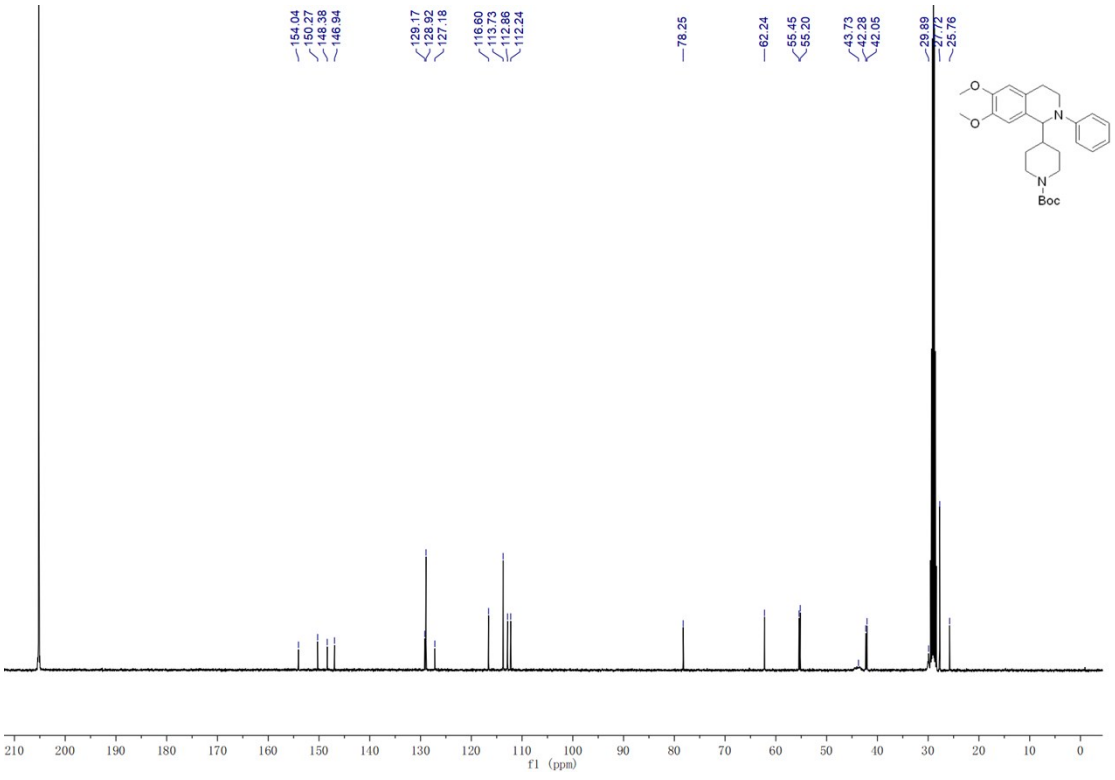
^{13}C NMR spectrum of **1-cyclohexyl-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3aq).**



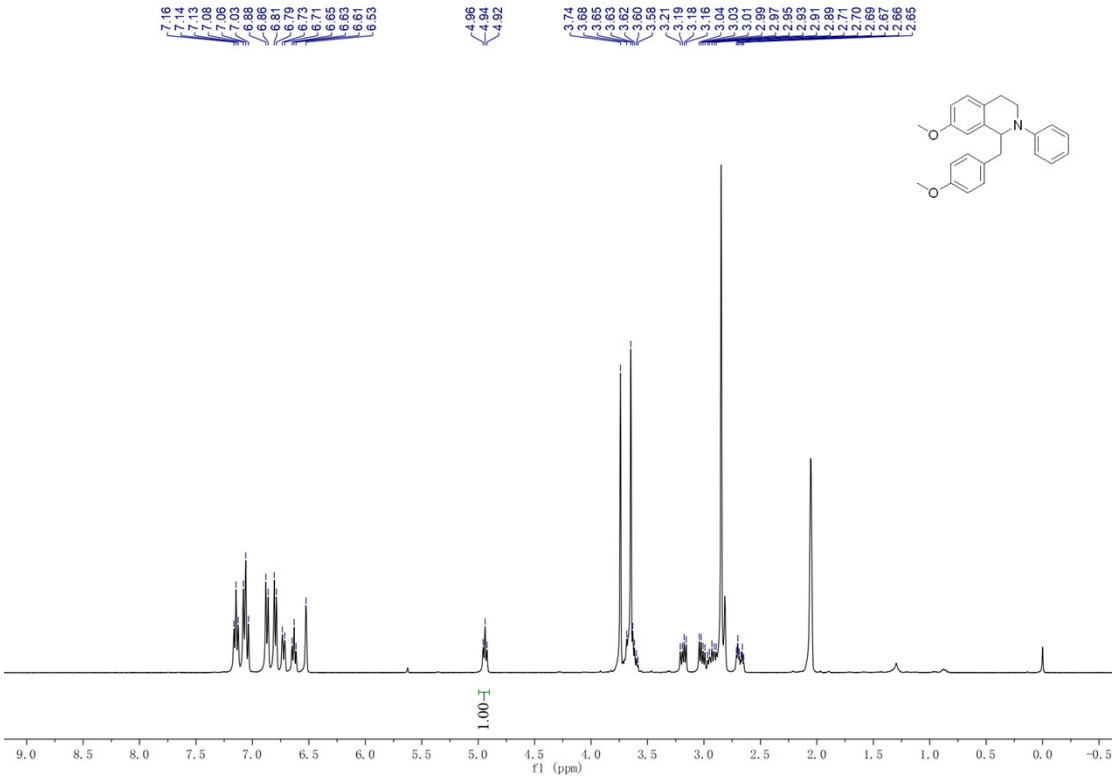
^{1}H NMR spectrum of ***tert*-butyl 4-(6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1 -yl)piperidine-1-carbox ylate (3ar).**



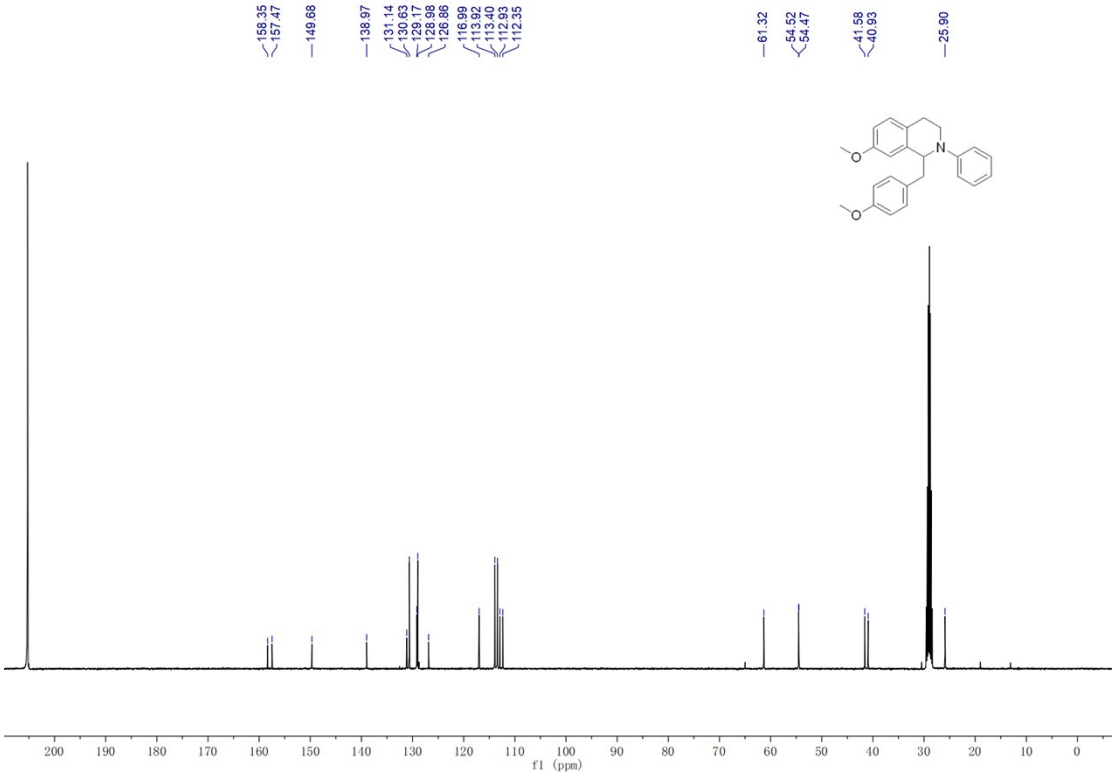
^{1}H NMR spectrum of ***tert*-butyl 4-(6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1 -yl)piperidine-1-carbox ylate (3ar)**



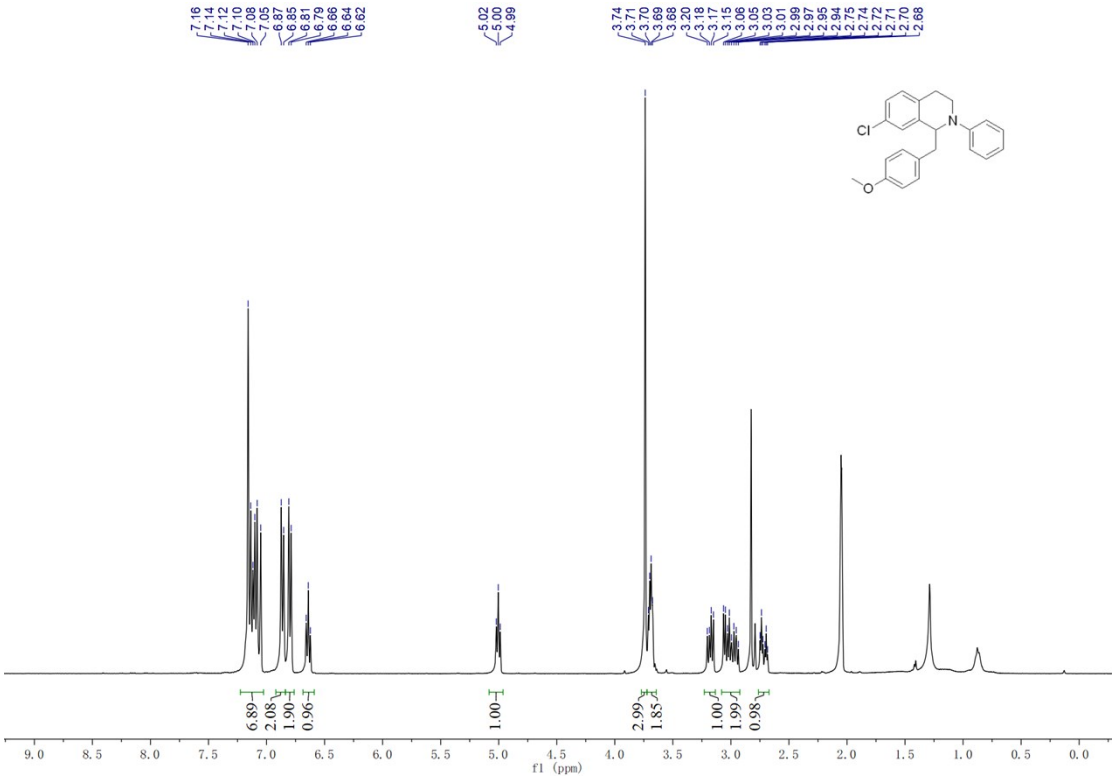
^{1}H NMR spectrum of **7-methoxy-1-(4-methoxybenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ba).**



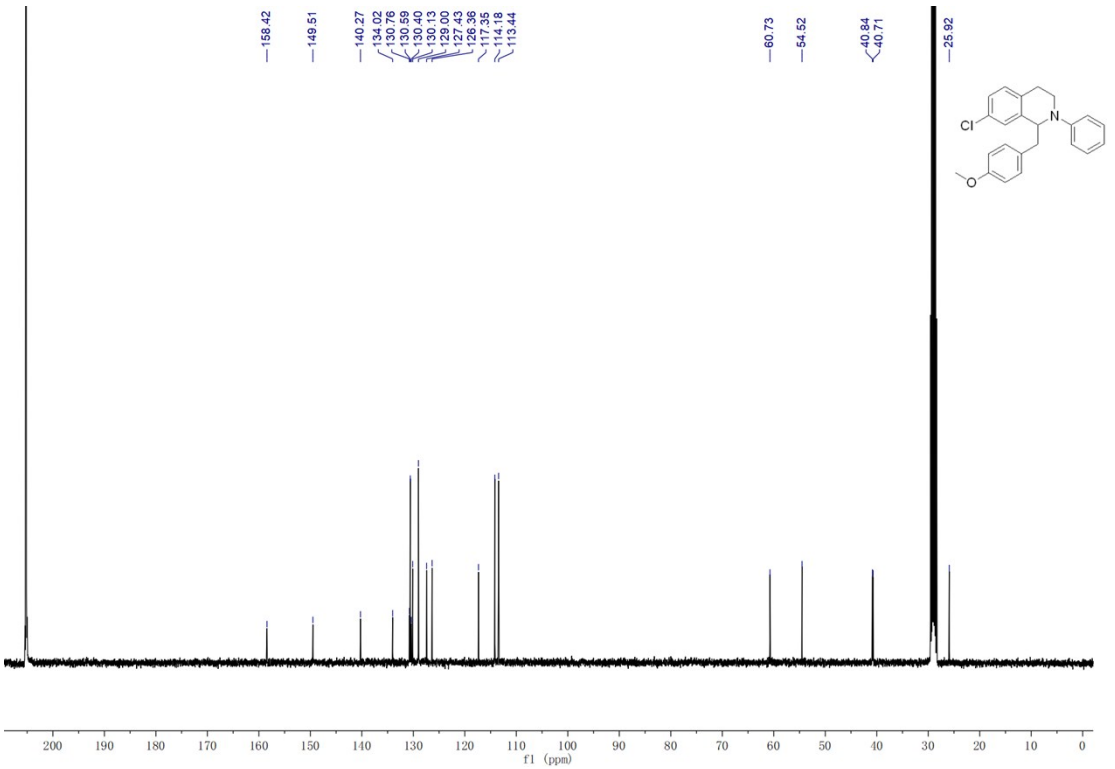
^{13}C NMR spectrum of **7-methoxy-1-(4-methoxybenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ba).**



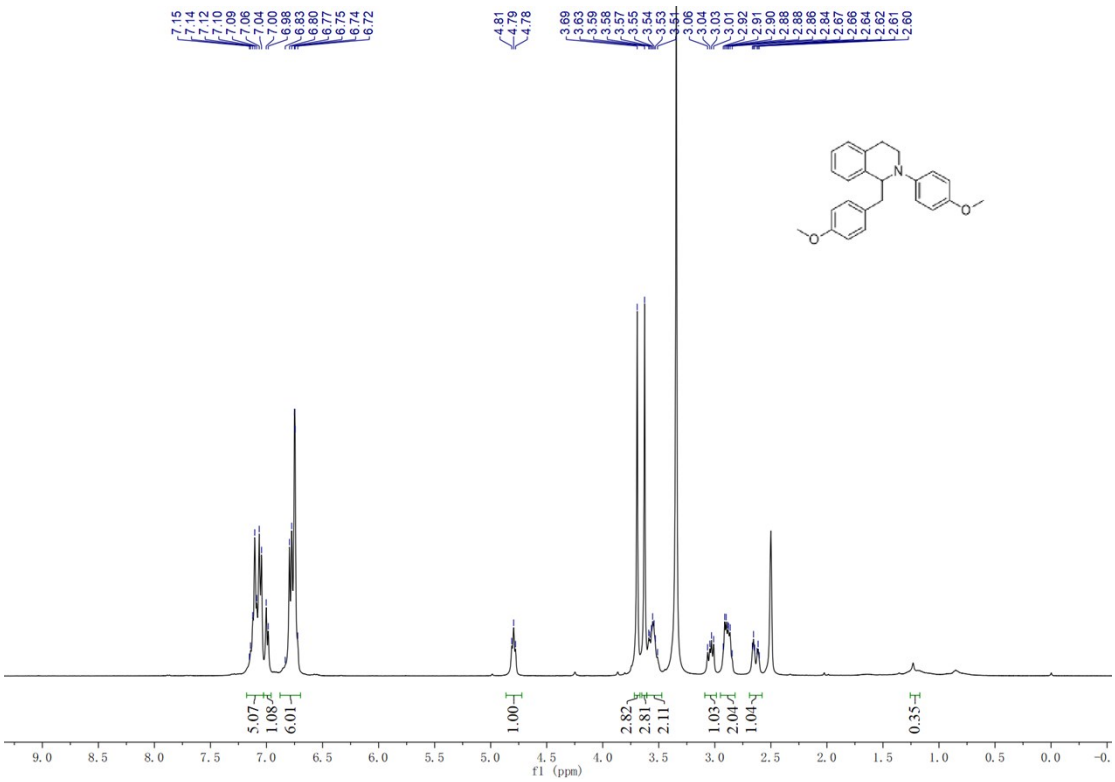
^{1}H NMR spectrum of **7-chloro-1-(4-methoxybenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ca).**



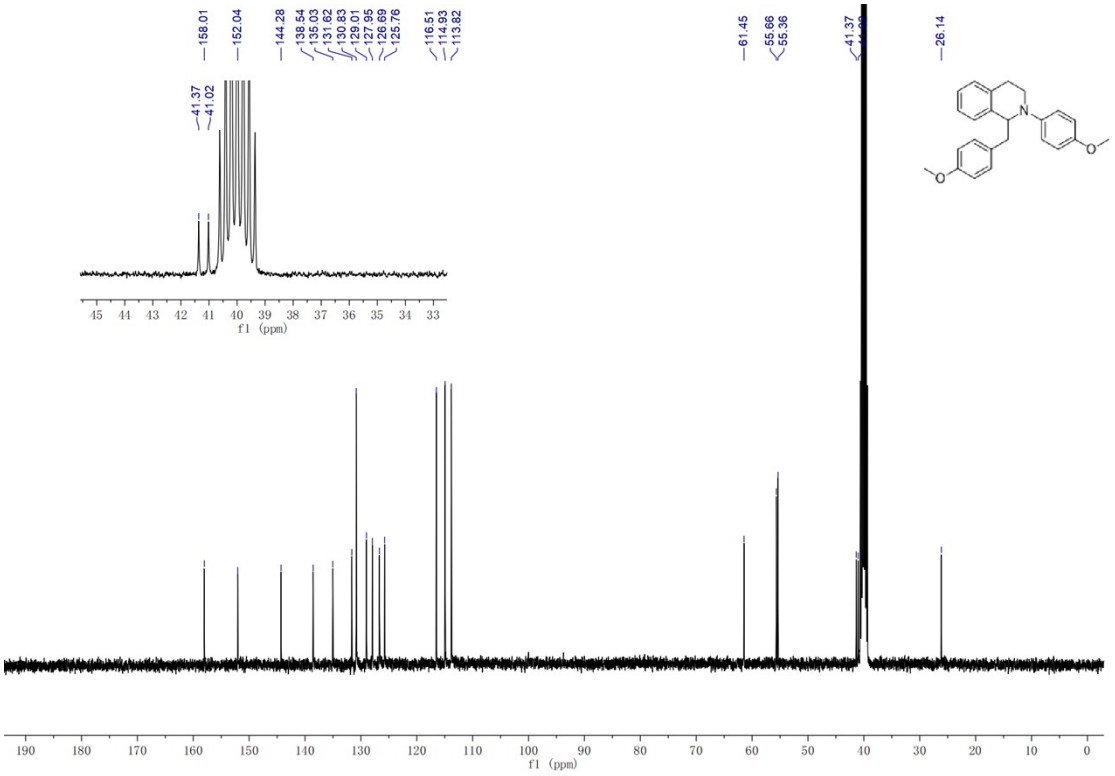
^{13}C NMR spectrum of **7-chloro-1-(4-methoxybenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ca).**



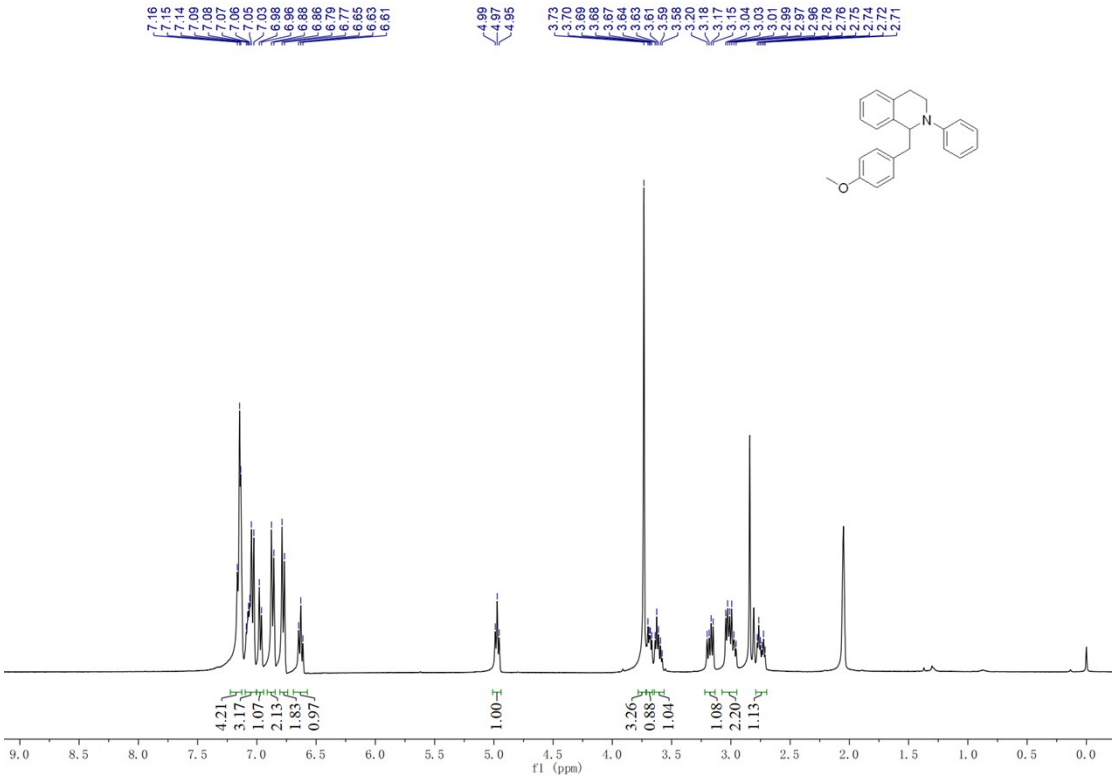
^{1}H NMR spectrum of **1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (3da).**



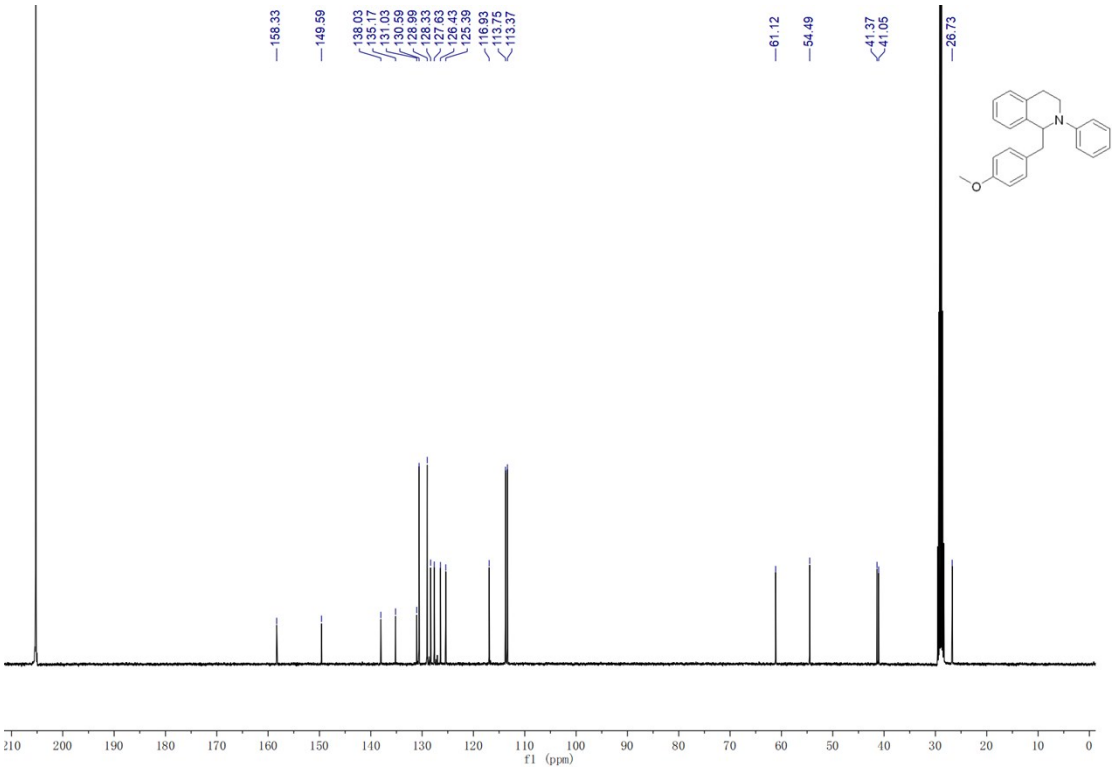
^{13}C NMR spectrum of **1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (3da).**



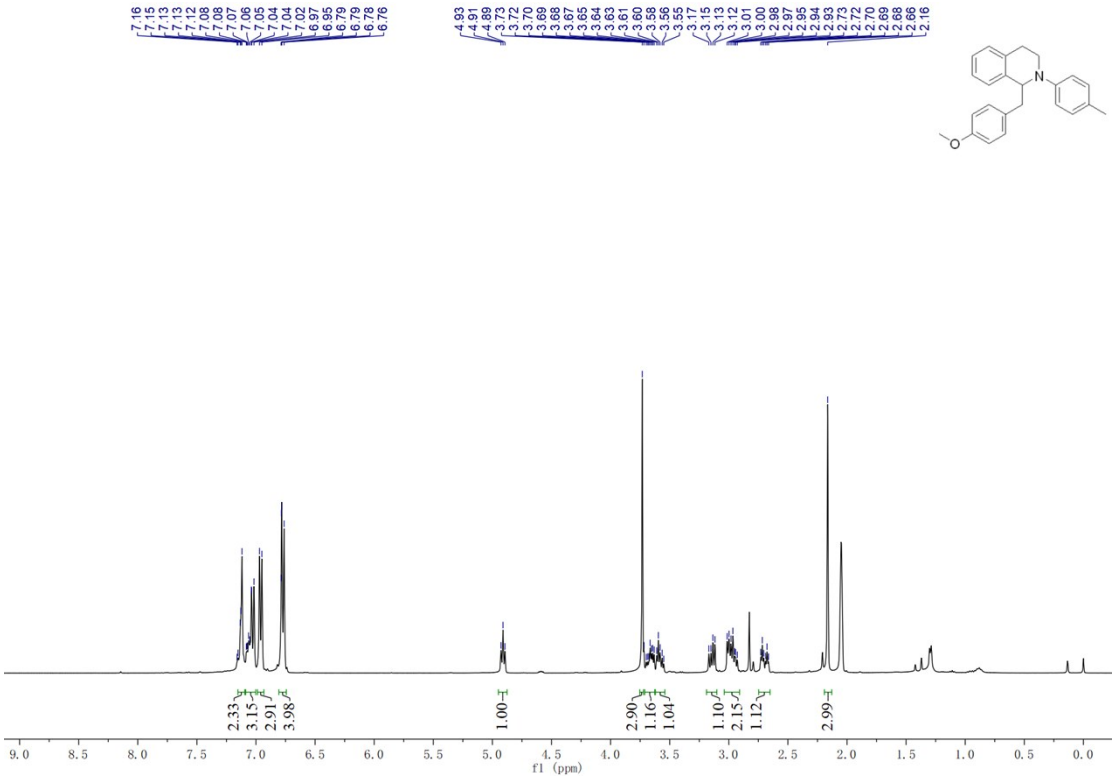
^{1}H NMR spectrum of **1-(4-methoxybenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ea).**



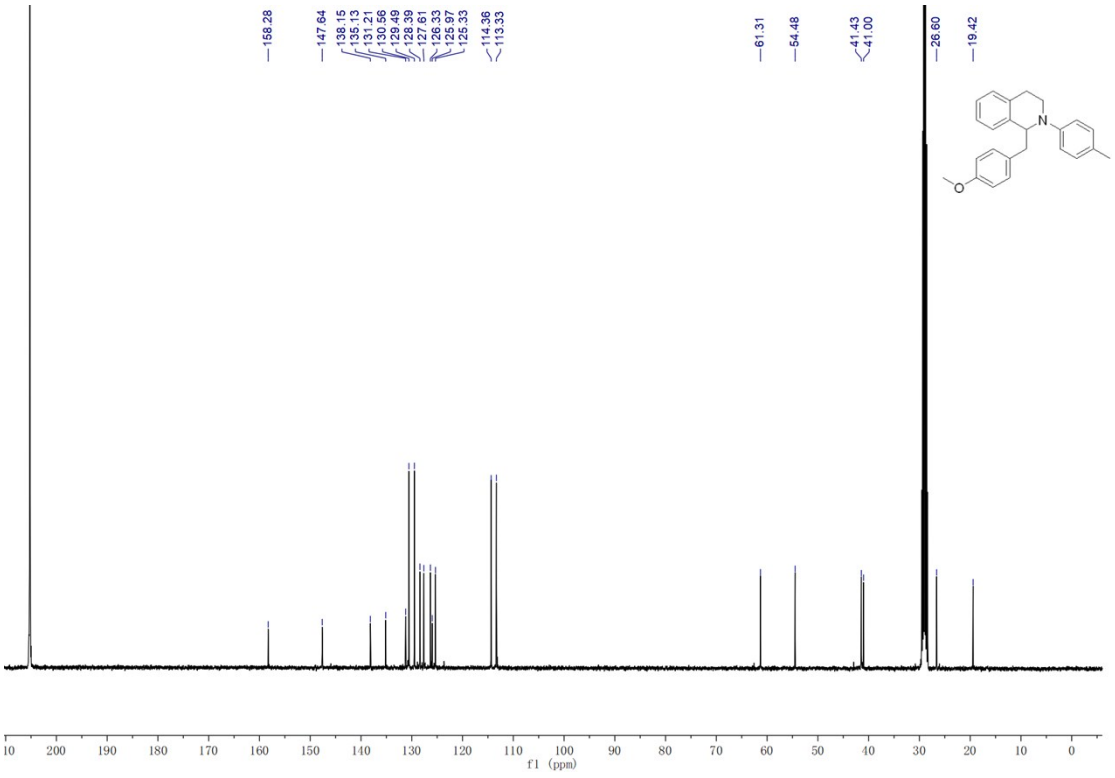
^{13}H NMR spectrum of **1-(4-methoxybenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ea).**



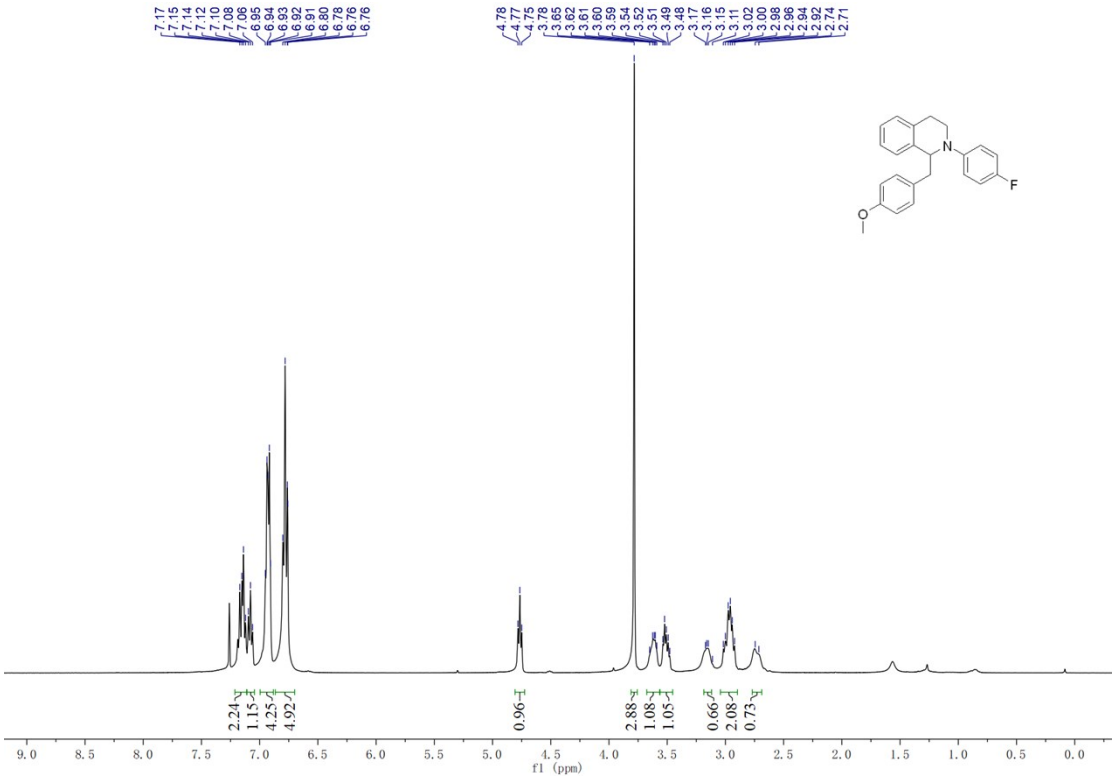
^{1}H NMR spectrum of **1-(4-methoxybenzyl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (3fa).**



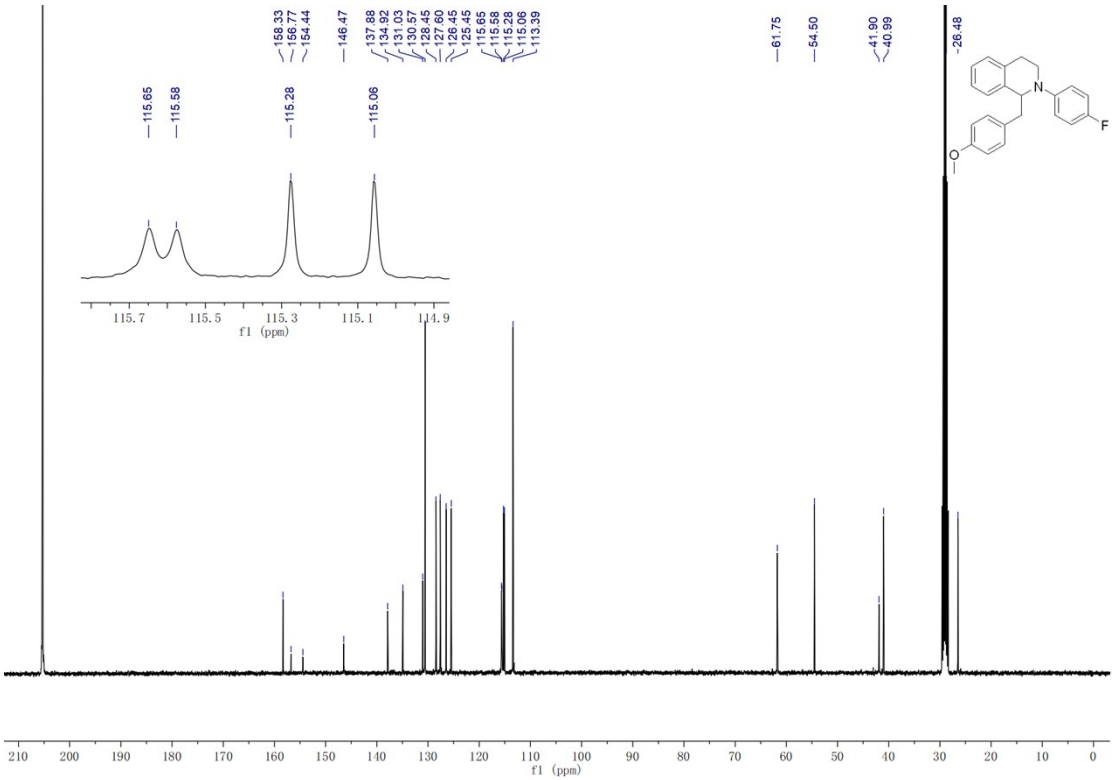
^{13}C NMR spectrum of **1-(4-methoxybenzyl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (3fa).**



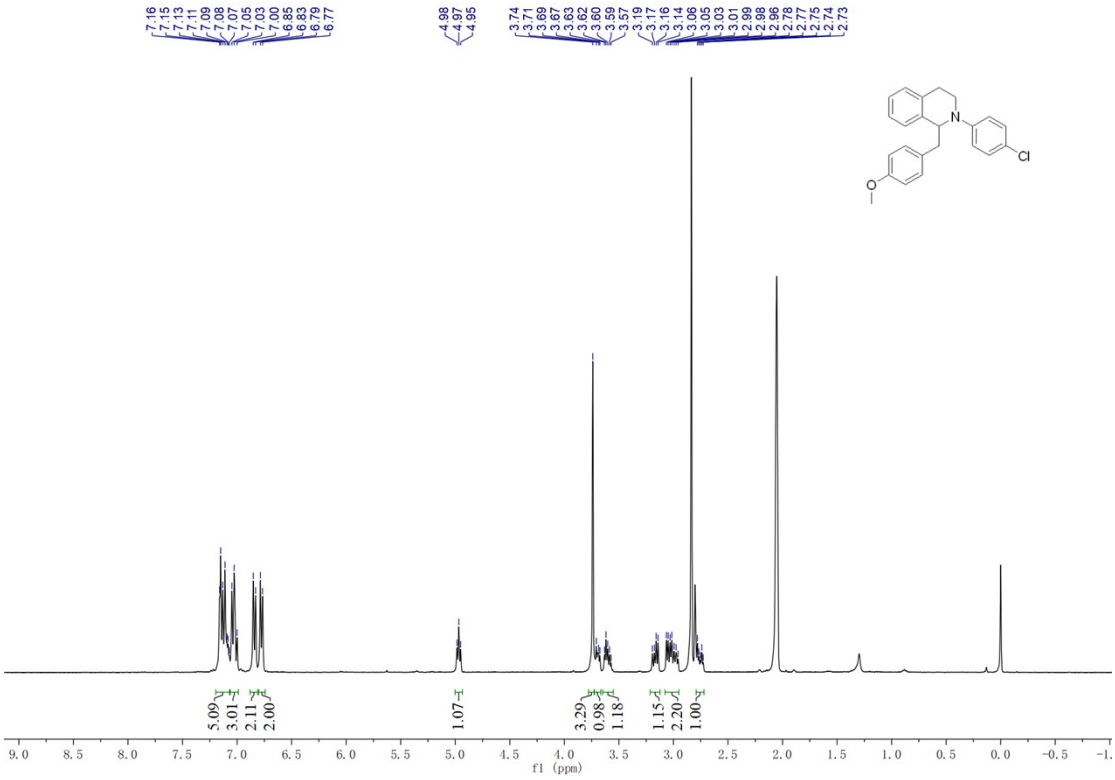
^{1}H NMR spectrum of **2-(4-fluorophenyl)-1-(4-methoxybenzyl)-1,2,3,4-tetrahydroisoquinoline (3ga).**



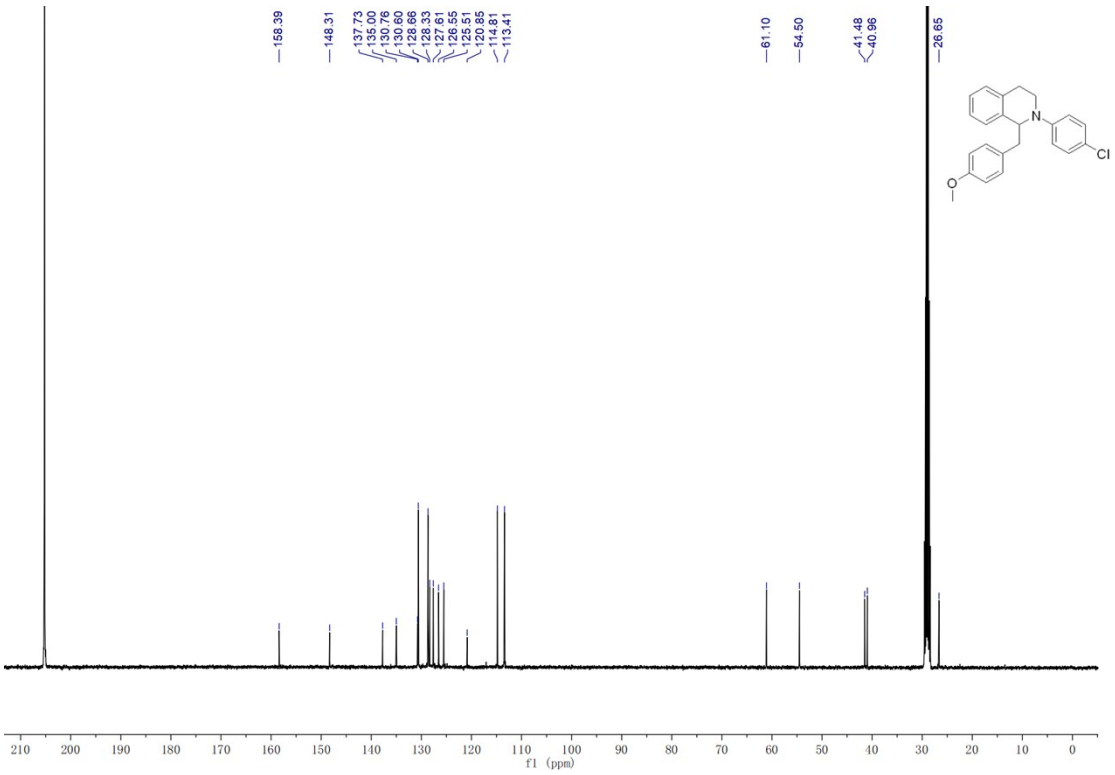
^{13}C NMR spectrum of **2-(4-fluorophenyl)-1-(4-methoxybenzyl)-1,2,3,4-tetrahydroisoquinoline (3ga).**



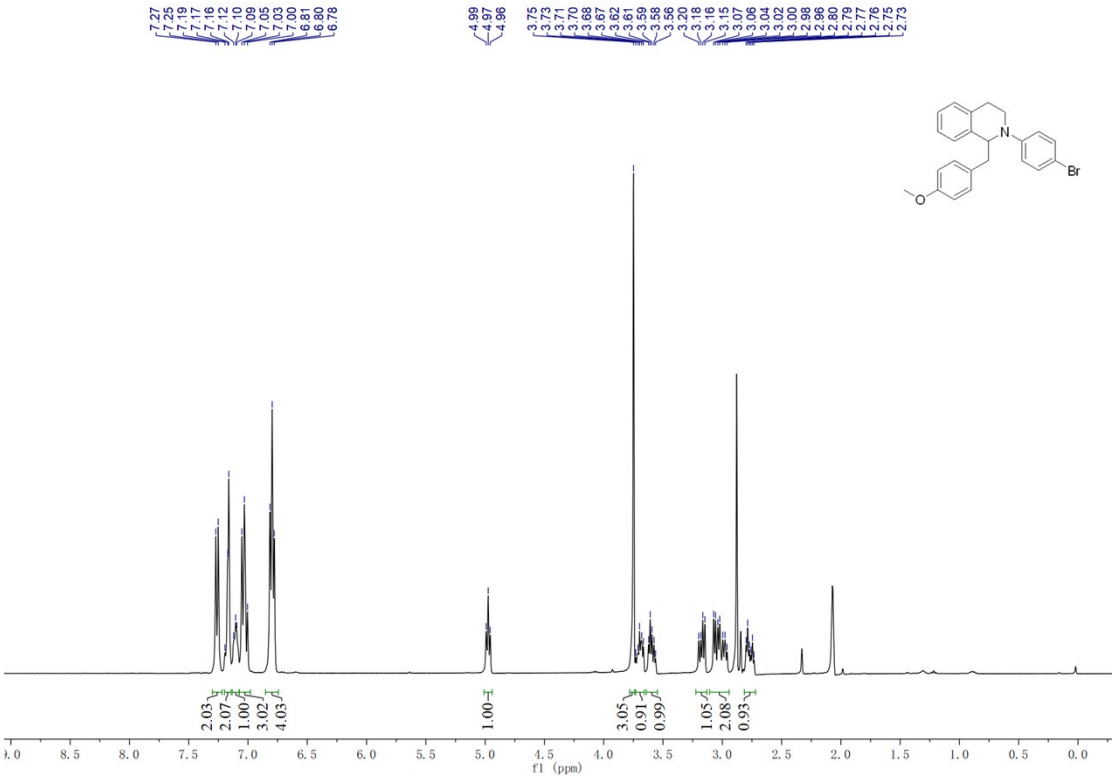
^{1}H NMR spectrum of **2-(4-chlorophenyl)-1-(4-methoxybenzyl)-1,2,3,4-tetrahydroisoquinoline (3ha).**



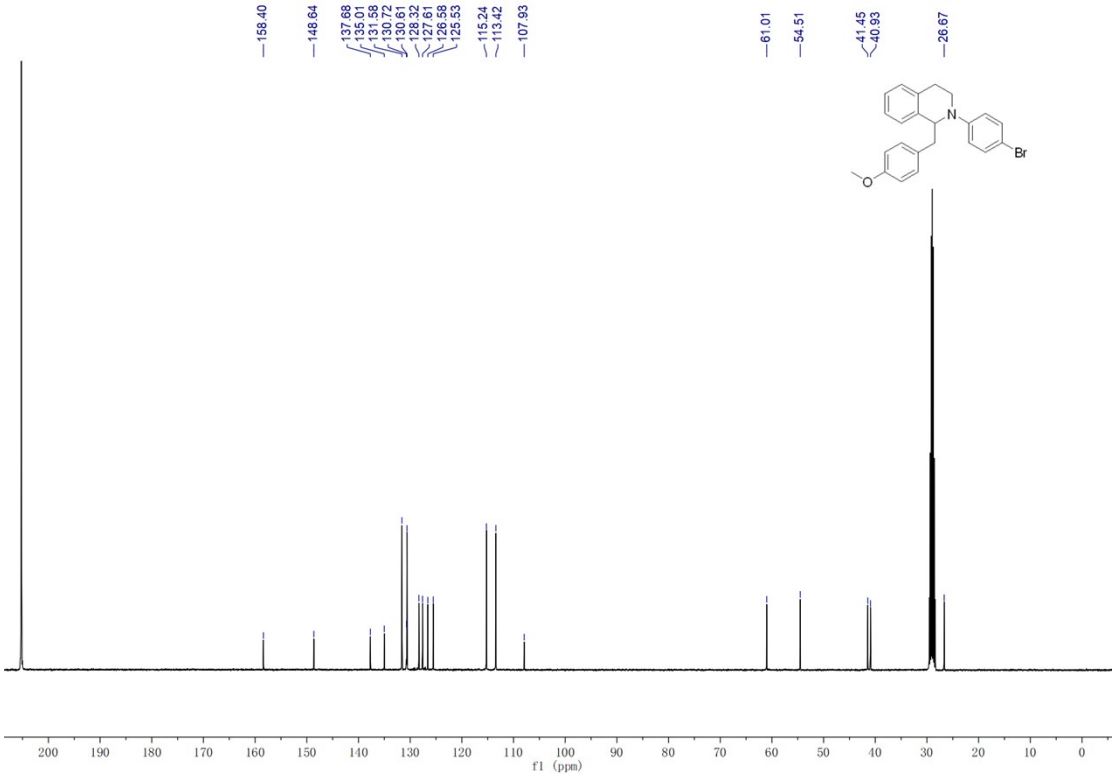
^{13}C NMR spectrum of **2-(4-chlorophenyl)-1-(4-methoxybenzyl)-1,2,3,4-tetrahydroisoquinoline (3ha).**



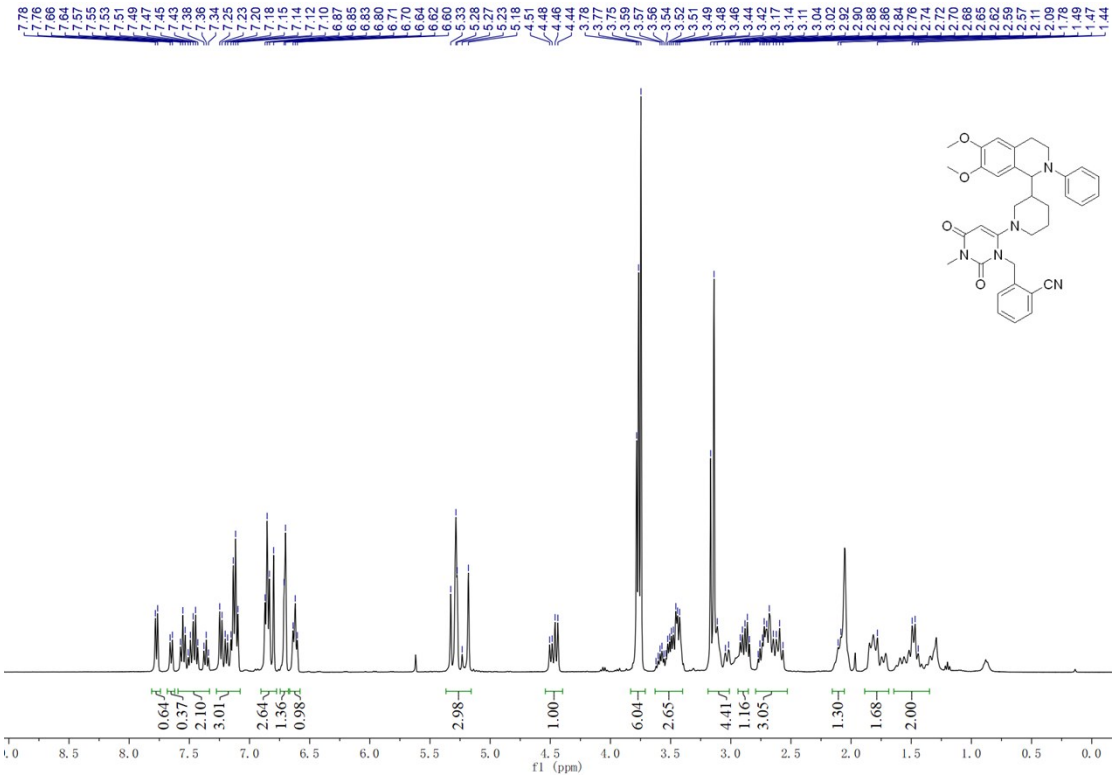
^{1}H NMR spectrum of **2-(4-bromophenyl)-1-(4-methoxybenzyl)-1,2,3,4-tetrahydroisoquinoline (3ia).**



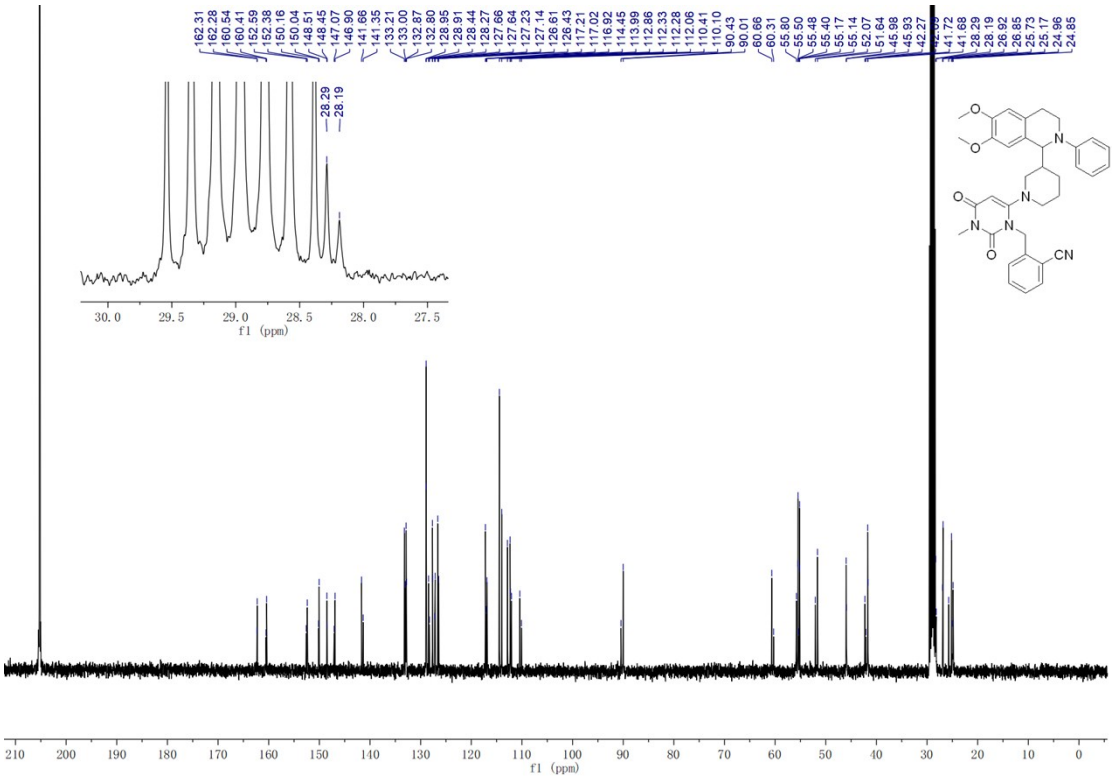
^{13}C NMR spectrum of **2-(4-bromophenyl)-1-(4-methoxybenzyl)-1,2,3,4-tetrahydroisoquinoline (3ia).**



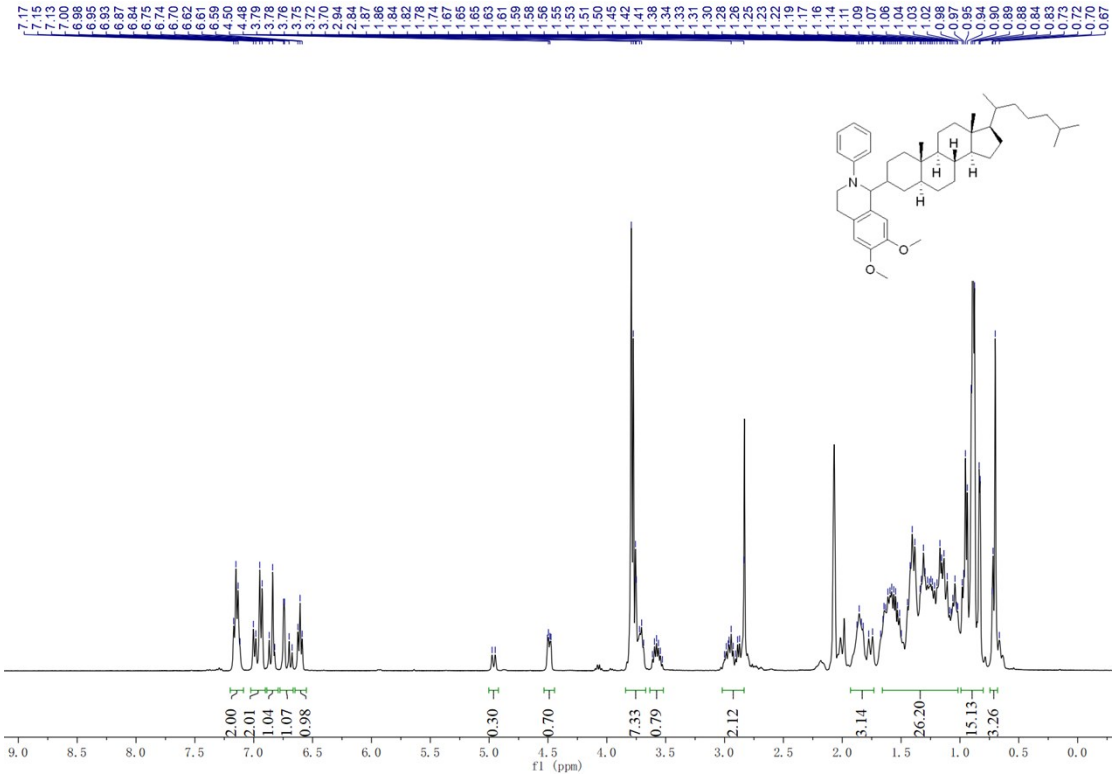
^{1}H NMR spectrum of **2-((6-(3-(6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl) piperidin-1-yl)-3-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)methyl)benzonitrile (3as).**



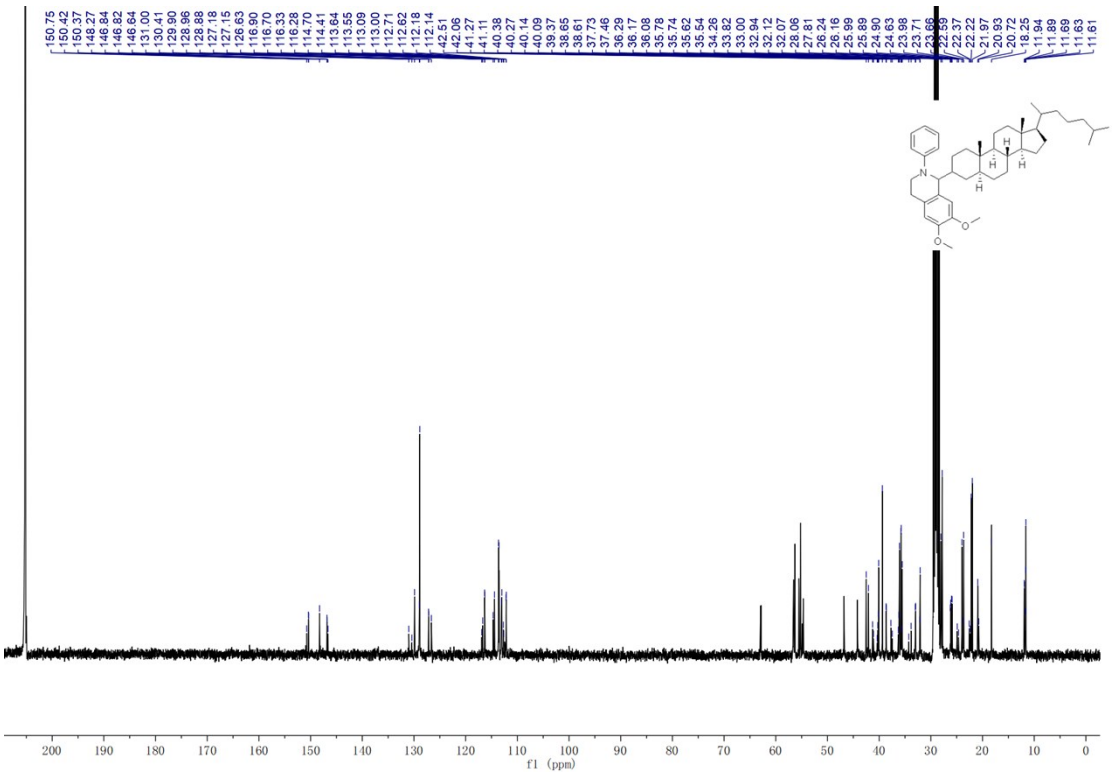
^{13}C NMR spectrum of **2-((6-(3-(6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl) piperidin-1-yl)-3-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)methyl)benzonitrile (3as).**



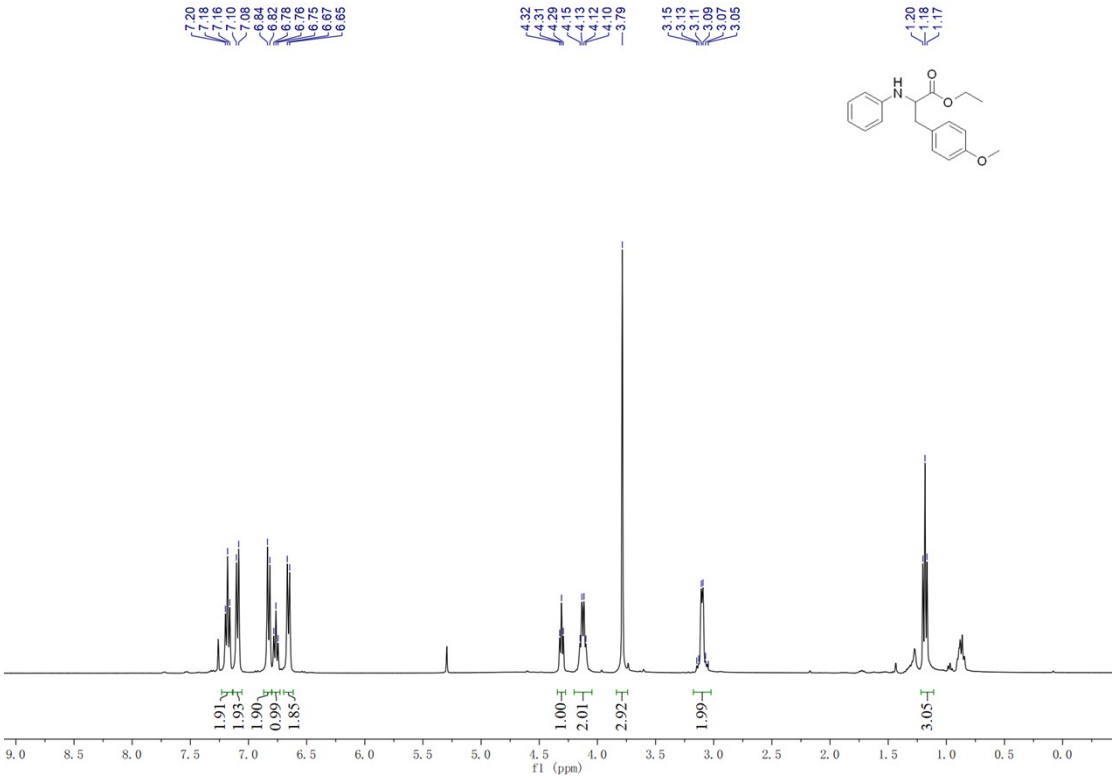
^{1}H NMR spectrum of **1-((5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-(6-methylheptan-2-yl) hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3at).**



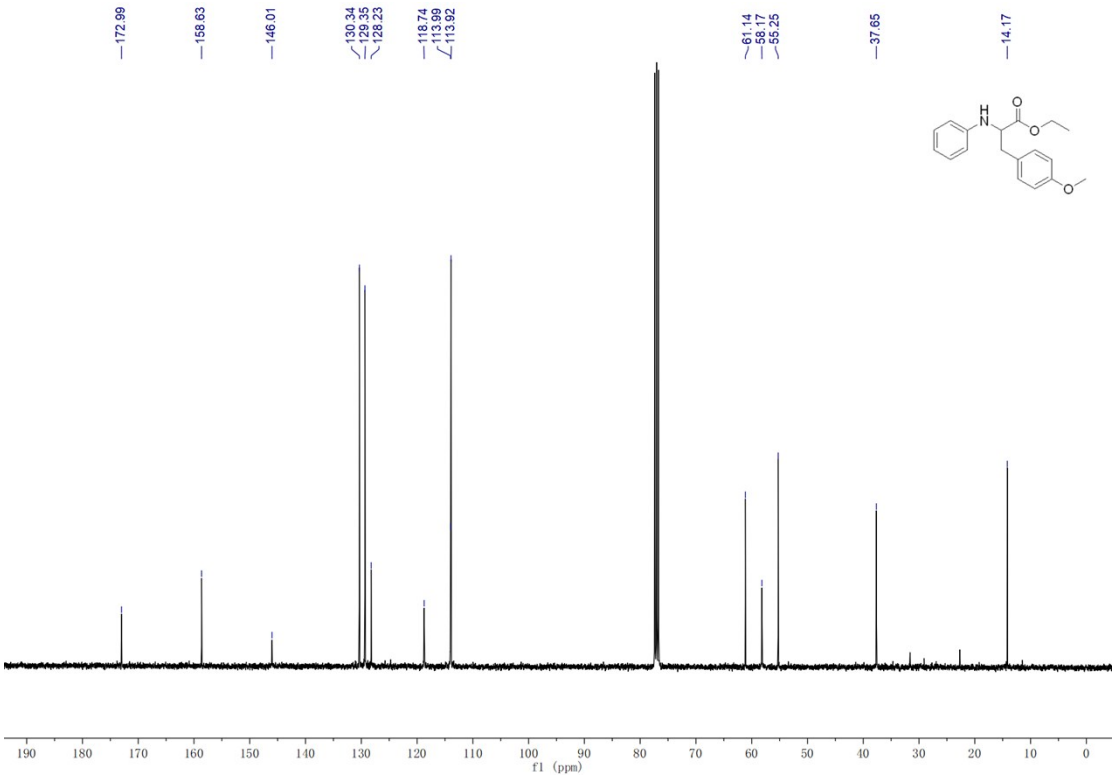
^{13}C NMR spectrum of **1-((5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-(6-methylheptan-2-yl) hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3at).**



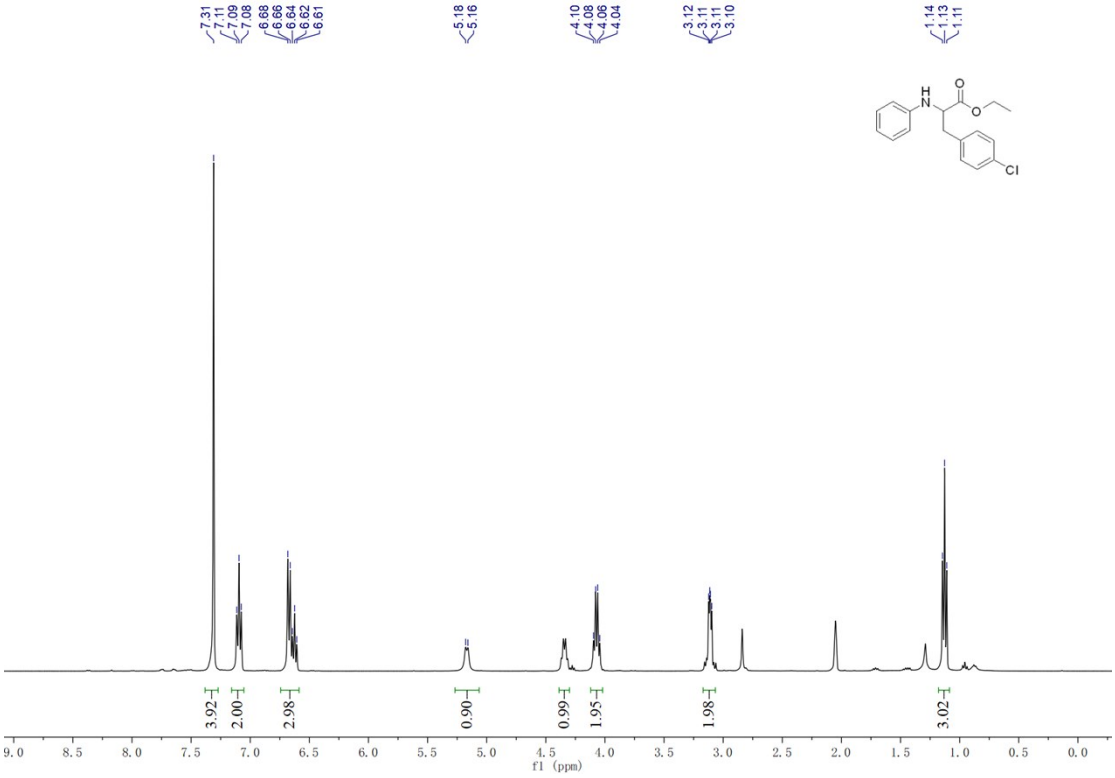
^{1}H NMR spectrum of **ethyl 3-(4-methoxyphenyl)-2-(phenylamino)propanoate (5aa).**



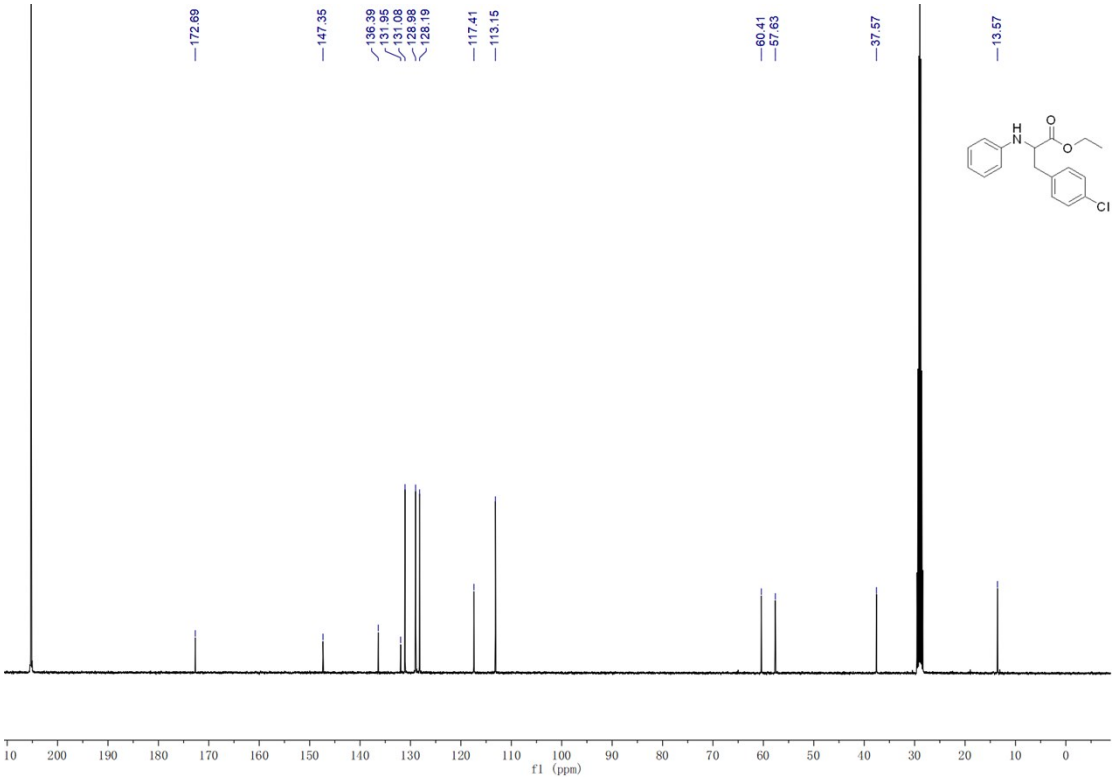
^{13}C NMR spectrum of **ethyl 3-(4-methoxyphenyl)-2-(phenylamino)propanoate (5aa).**



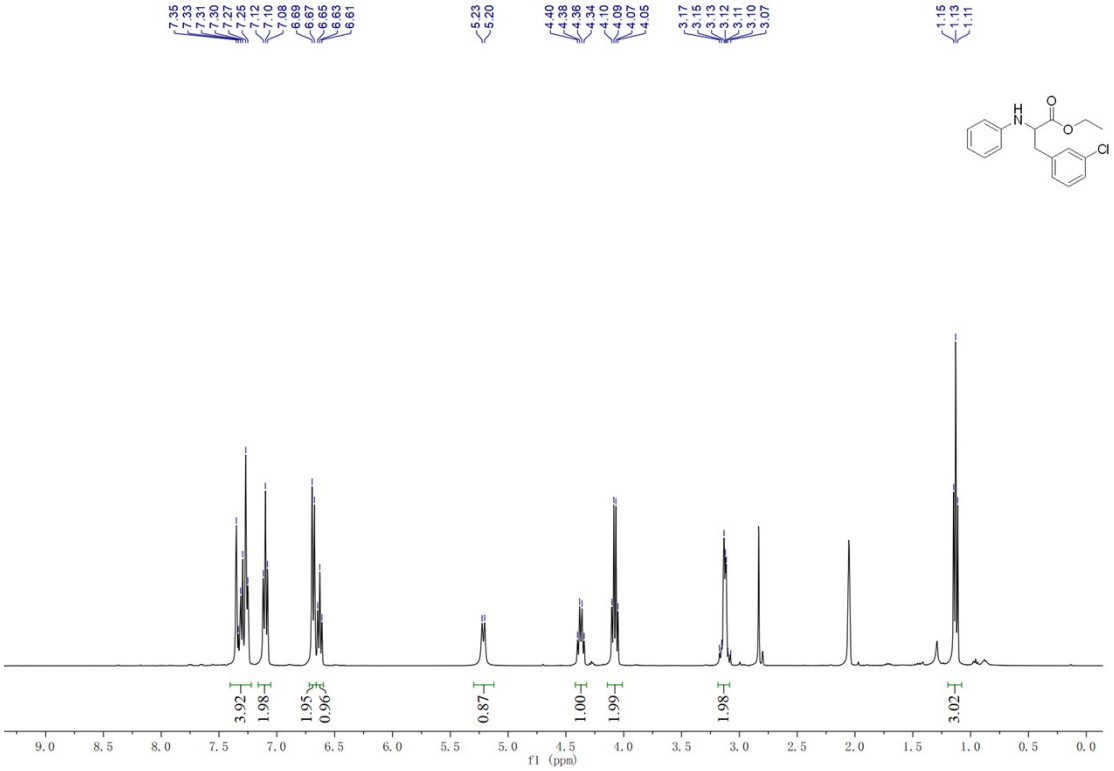
^{1}H NMR spectrum of **ethyl 3-(4-chlorophenyl)-2-(phenylamino)propanoate (5ae).**



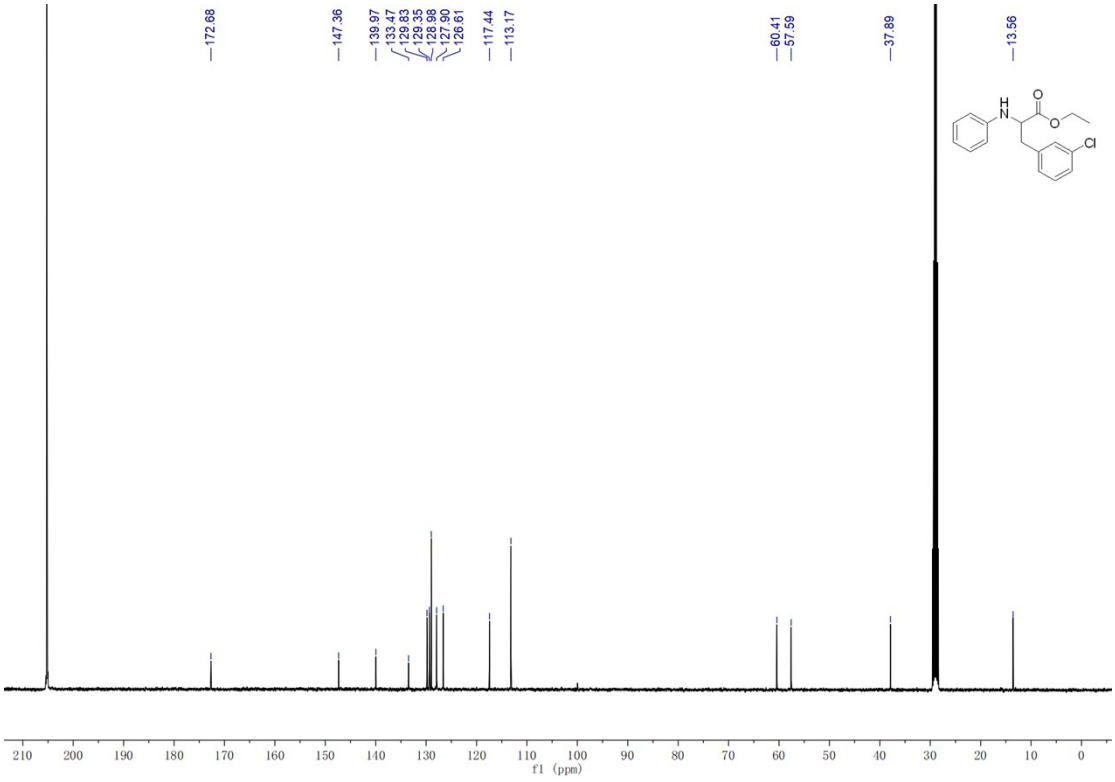
^{13}C NMR spectrum of **ethyl 3-(4-chlorophenyl)-2-(phenylamino)propanoate (5ae).**



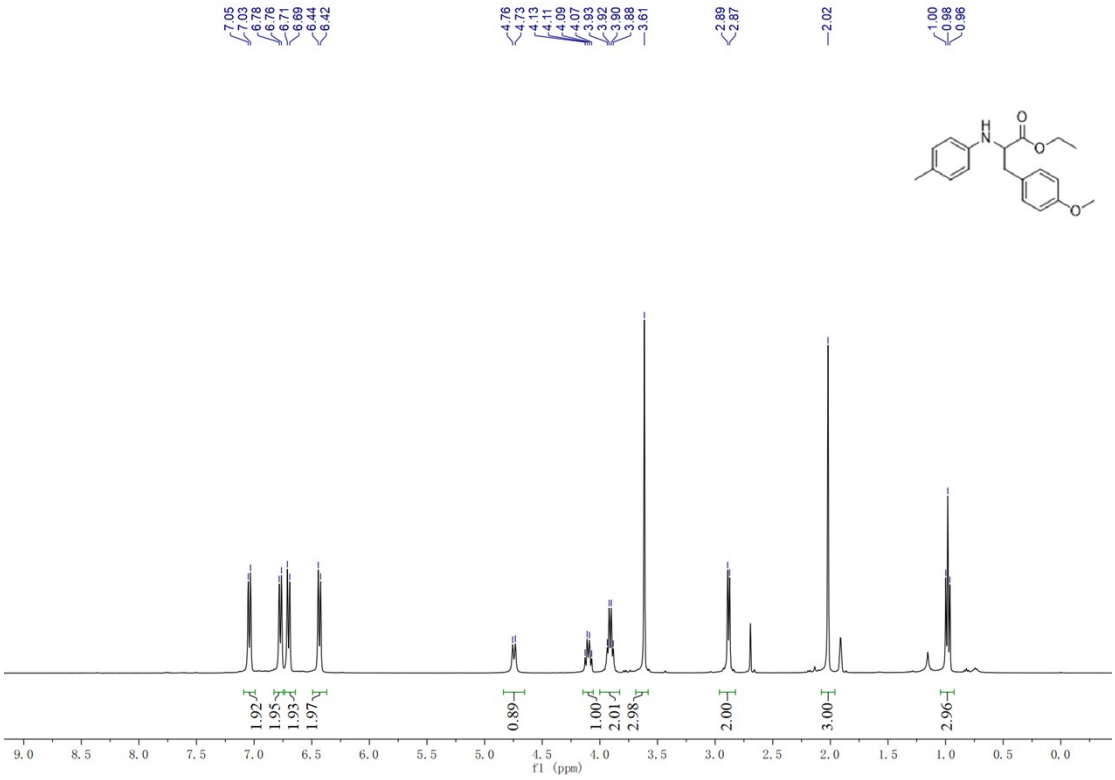
^{1}H NMR spectrum of **ethyl 3-(2-chlorophenyl)-2-(phenylamino)propanoate (5ak).**



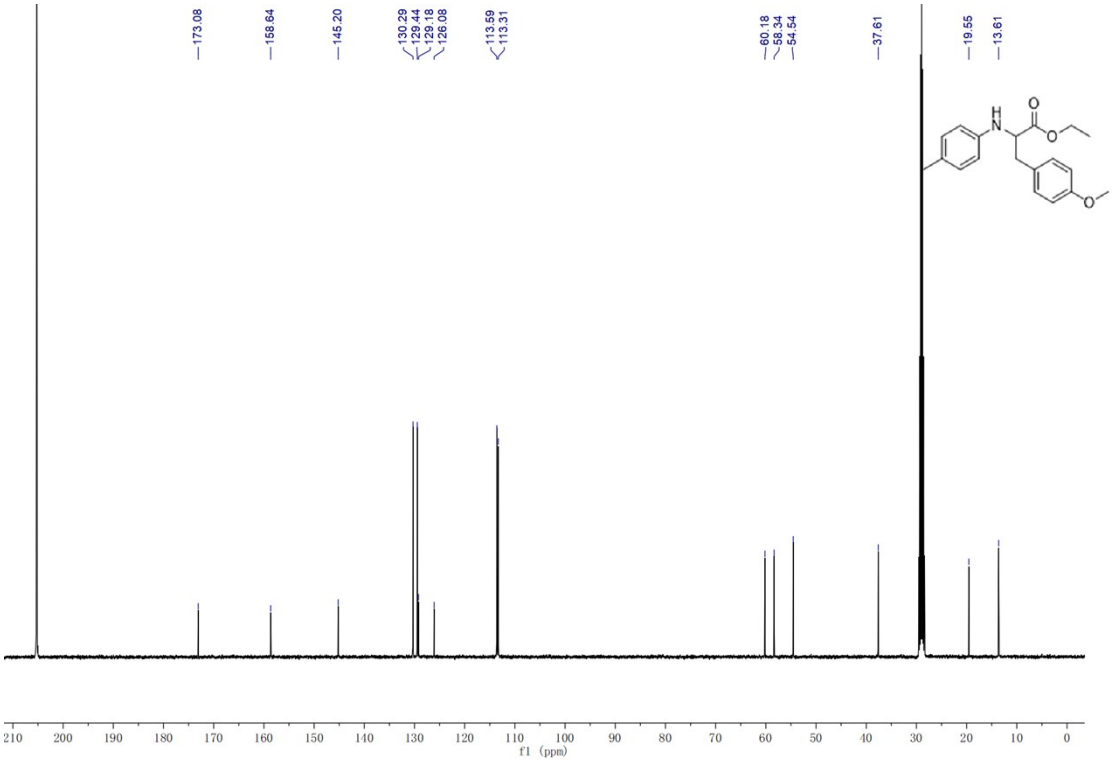
^{13}C NMR spectrum of **ethyl 3-(2-chlorophenyl)-2-(phenylamino)propanoate (5ak).**



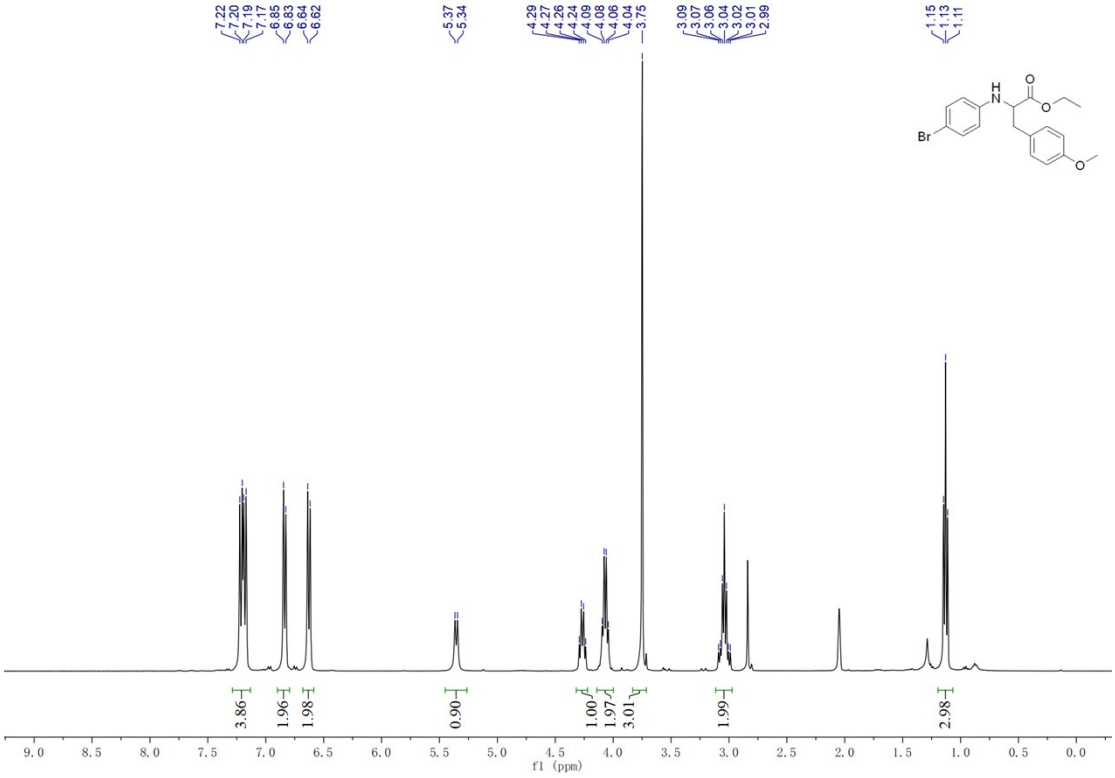
^{1}H NMR spectrum of **ethyl 3-(4-methoxyphenyl)-2-(p-tolylamino)propanoate (5ba).**



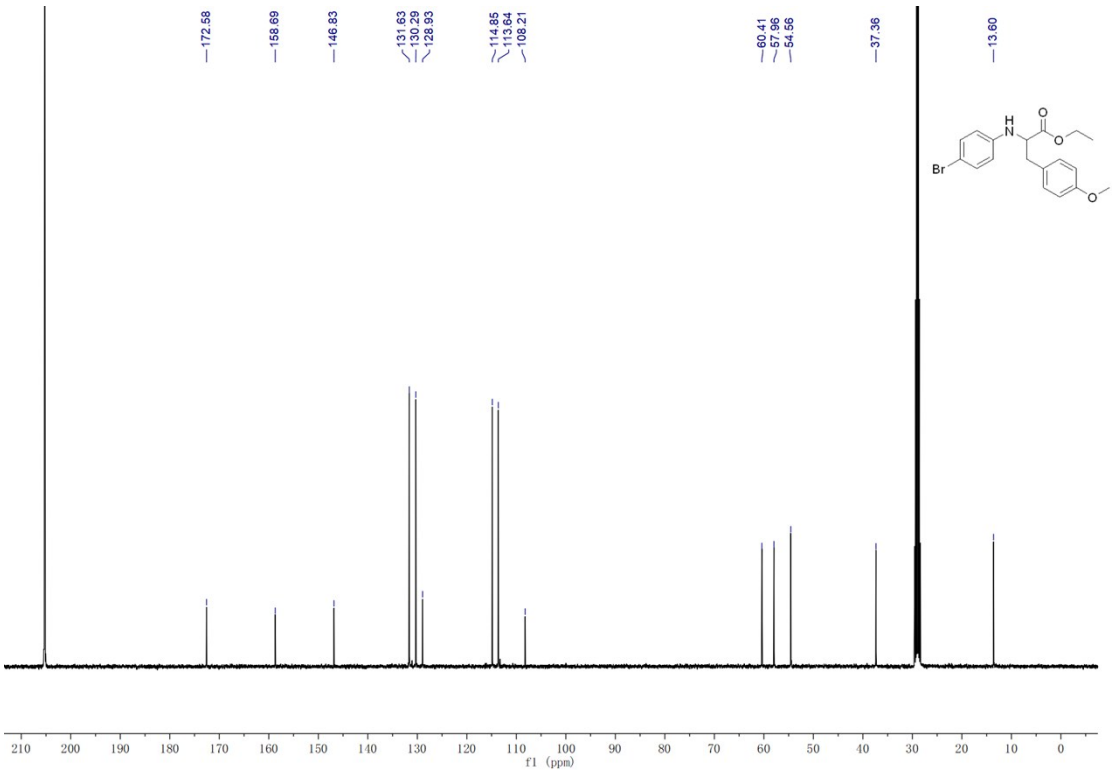
^{13}C NMR spectrum of **ethyl 3-(4-methoxyphenyl)-2-(p-tolylamino)propanoate (5ba).**



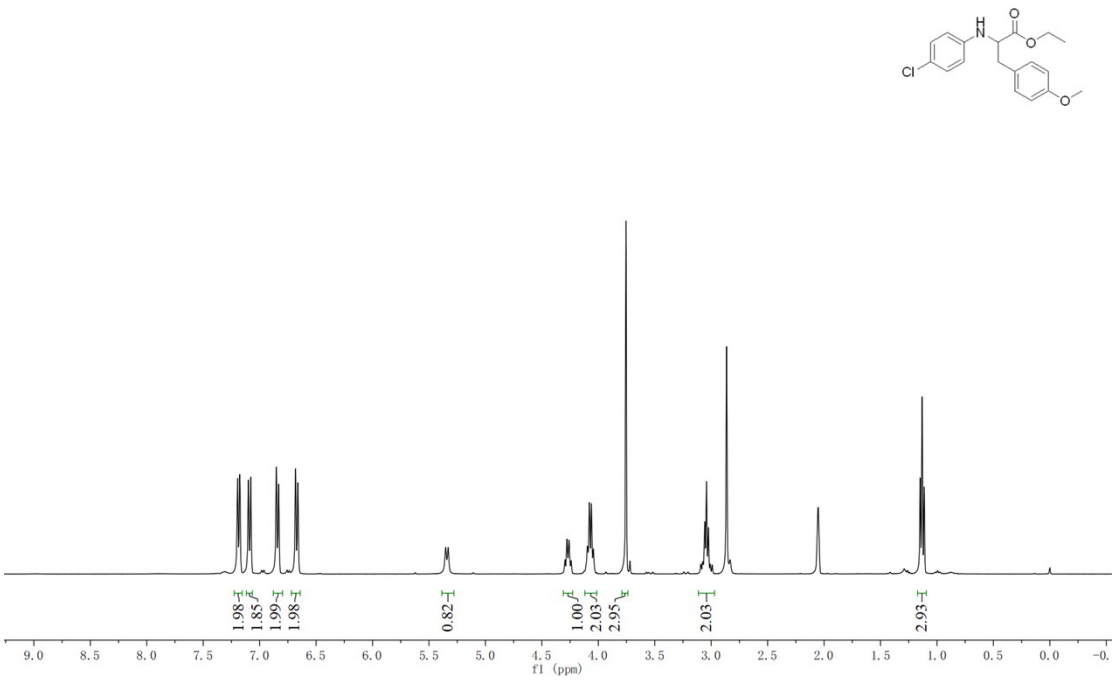
^{1}H NMR spectrum of **ethyl 2-((4-bromophenyl)amino)-3-(4-methoxyphenyl)propanoate (5ca).**



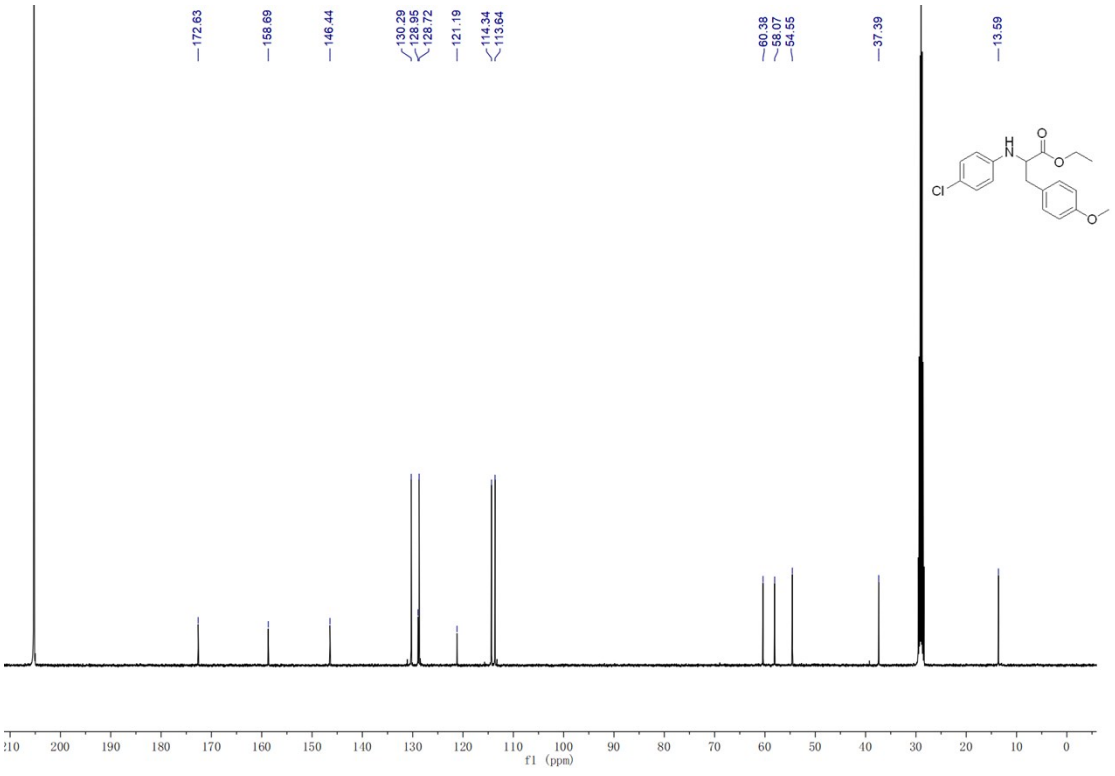
^{1}H NMR spectrum of **ethyl 2-((4-bromophenyl)amino)-3-(4-methoxyphenyl)propanoate (5ca).**



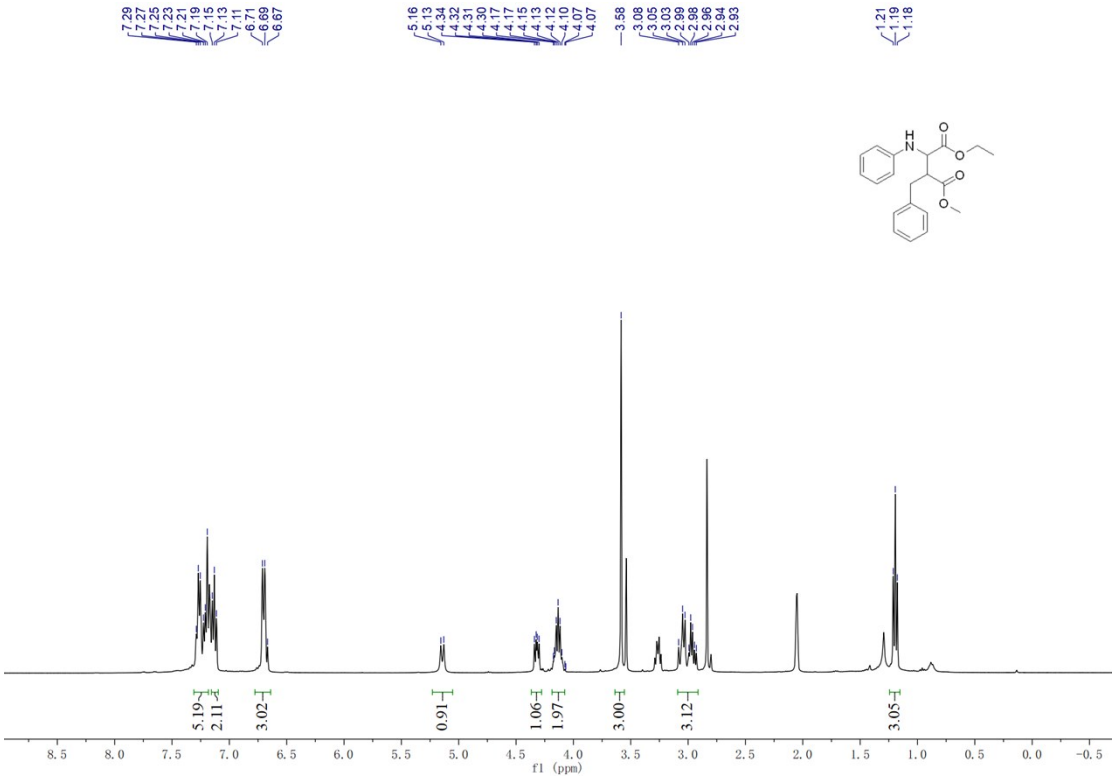
^{1}H NMR spectrum of **ethyl 2-((4-chlorophenyl)amino)-3-(4-methoxyphenyl)propanoate (5da).**



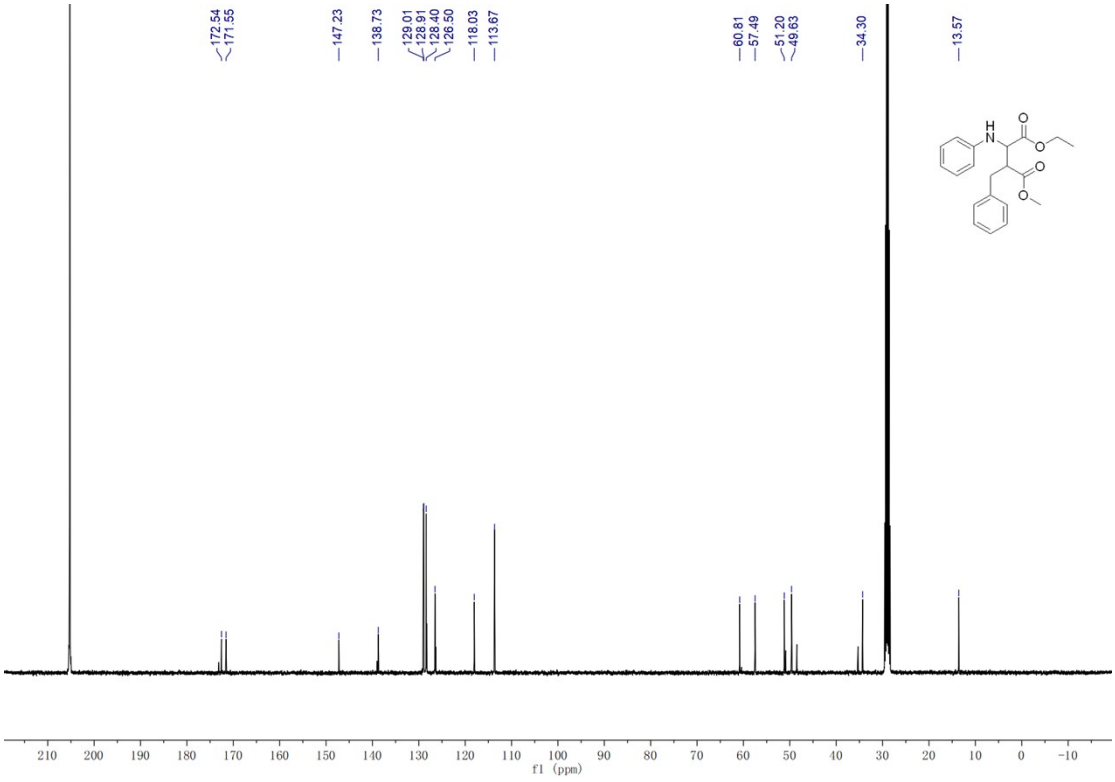
^{13}C NMR spectrum of **ethyl 2-((4-chlorophenyl)amino)-3-(4-methoxyphenyl)propanoate (5da)**



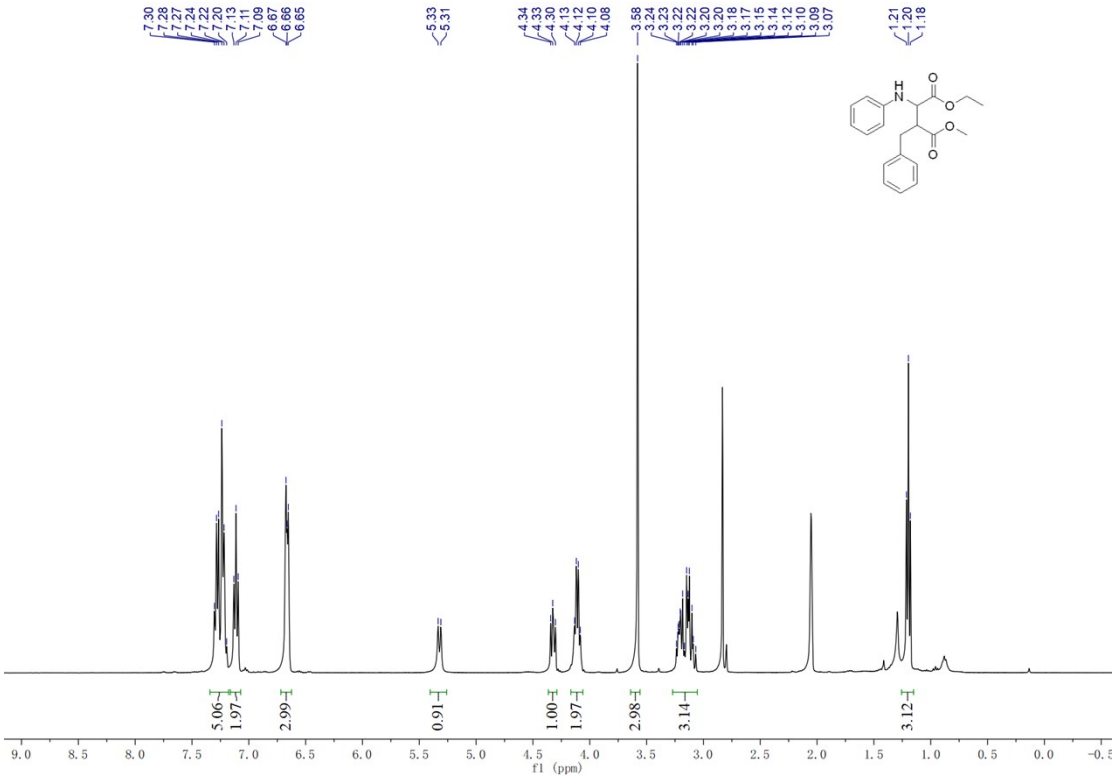
^{1}H NMR spectrum of **4-ethyl 1-methyl 2-benzyl-3-(phenylamino)succinate (5au A).**



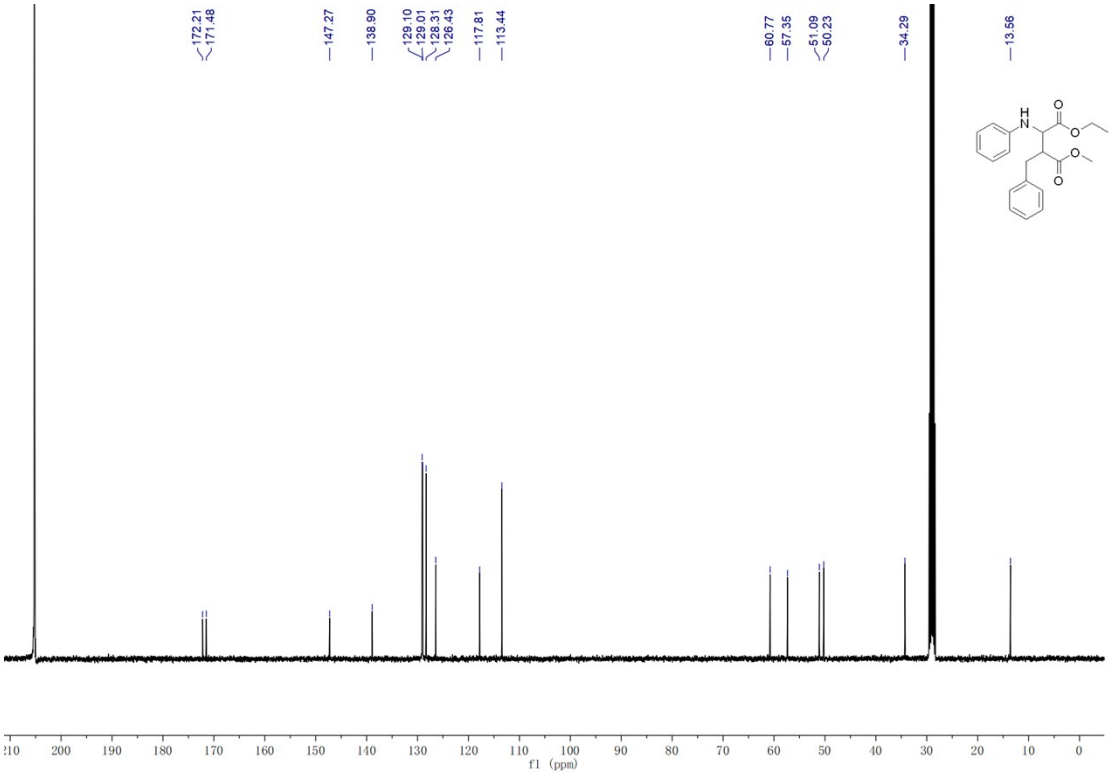
^{13}C NMR spectrum of **4-ethyl 1-methyl 2-benzyl-3-(phenylamino)succinate (5au A).**



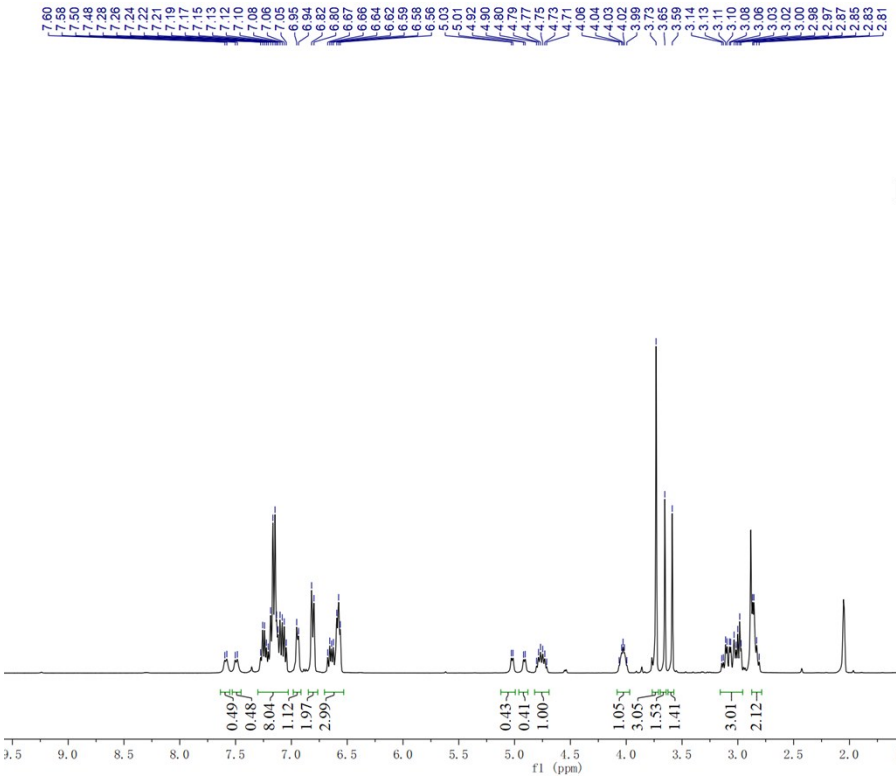
^{1}H NMR spectrum of **4-ethyl 1-methyl 2-benzyl-3-(phenylamino)succinate (5au B).**



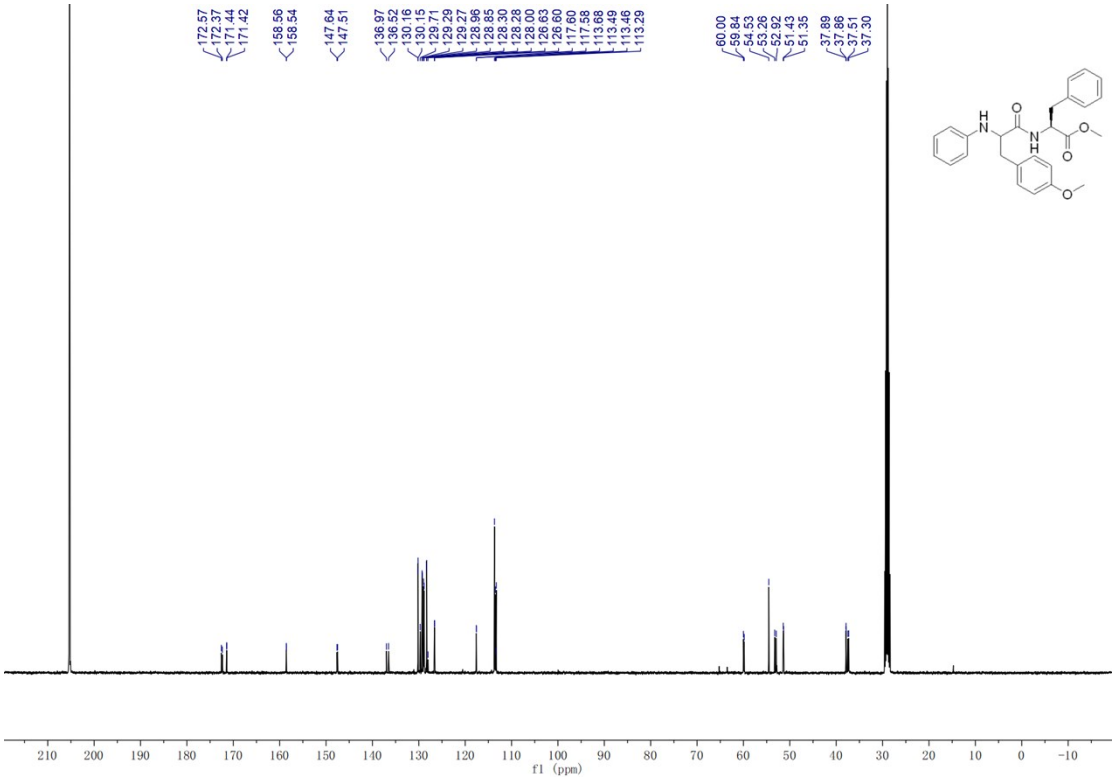
^{13}C NMR spectrum of **4-ethyl 1-methyl 2-benzyl-3-(phenylamino)succinate (5au B).**



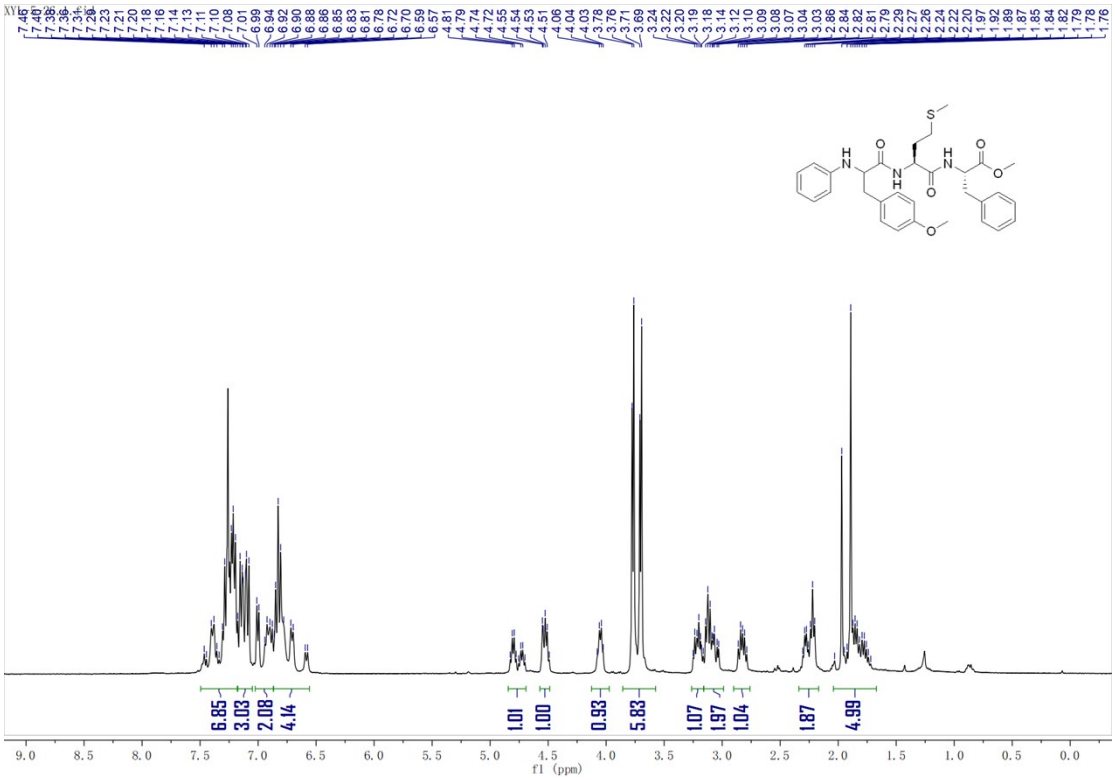
^{1}H NMR spectrum of **methyl (3-(4-methoxyphenyl)-2-(phenylamino)propanoyl)-L-phenylalaninate (6).**



^{13}C NMR spectrum of **methyl (3-(4-methoxyphenyl)-2-(phenylamino)propanoyl)-L-phenylalaninate (6).**



^{1}H NMR spectrum of **methyl (3-(4-methoxyphenyl)-2-(phenylamino)propanoyl)-L-methionyl -L-phenylalaninate (7).**



^{13}C NMR spectrum of **methyl (3-(4-methoxyphenyl)-2-(phenylamino)propanoyl)-L-methionyl -L-phenylalaninate (7).**