

Supporting Information

Bronsted Acid/Visible-Light-Promoted Markovnikov Hydroamination of Vinylarenes with Arylamines

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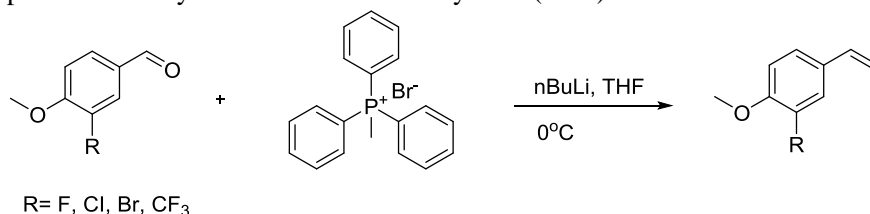
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I. General Methods

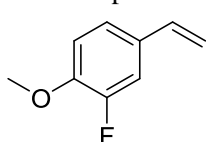
All reactions were carried out in flame-dried sealed tubes with magnetic stirring. Unless otherwise noted, all experiments were performed under argon atmosphere. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. Purifications of reaction products were carried out by flash chromatography using silica gel (300-400 mesh). Infrared spectra (IR) are reported as wavelength numbers (cm⁻¹). ¹H NMR and ¹³C NMR spectra were recorded with tetramethylsilane (TMS) as internal standard at ambient temperature unless otherwise indicated on a Bruker Avance DPX 600 fourier Transform spectrometer operating at 400 MHz or 500 MHz for ¹H NMR and 100 MHz or 125 MHz for ¹³C NMR. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), broad singlet (bs), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). Low resolution mass spectra were recorded using a Waters HPLC/ZQ4000 Mass Spectrometer. High resolution mass spectra (HR-MS) were recorded on an IF-TOF spectrometer (Micromass). Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS-QP5000 spectrometer.

II. Experimental procedures for the preparation of starting materials

1. General procedure for synthesis of substituted styrenes (1f-1i)¹

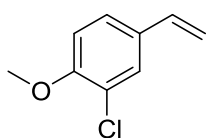


n-Butyl lithium (3.0 mmol, 2.5 M in THF) was added dropwise to a 0.12 M solution of methyltriphenylphosphonium bromide (1.07 g, 3.0 mmol) in THF under Ar atmosphere. The yellow solution was allowed to be stirred for 15 minutes before addition of aldehyde (3.0 mmol), upon which, the mixture turned white or pale yellow. After 2 hours (or observed completion of the reaction by TLC), saturated ammonium chloride was added and the mixture extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. Purification of the crude residue with column chromatography (ethyl acetate/petroleum ether or petroleum ether only was used as the eluent) afforded the substituted styrene.



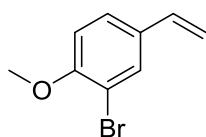
2-Fluoro-4-methoxy-1-vinylbenzene (1f)¹: This compound was prepared from 2-fluoro-4-methoxybenzaldehyde (0.46 g, 3 mmol) according to general procedure.¹ The crude residue was purified by silica gel chromatography (2% ethyl acetate/petroleum ether) to yield the alkene as colorless oil (0.23 g, 50%).

¹H NMR (400 MHz, CDCl₃) δ 7.20 (d, *J* = 12.5 Hz, 1H), 7.10 (d, *J* = 8.3 Hz, 1H), 6.92 (t, *J* = 8.5 Hz, 1H), 6.64 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.63 (d, *J* = 17.5 Hz, 1H), 5.21 (d, *J* = 10.8 Hz, 1H), 3.91 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.5 (d, *J* = 243.9 Hz), 147.4 (d, *J* = 11.0 Hz), 135.4 (d, *J* = 1.8 Hz), 131.2 (d, *J* = 6.4 Hz), 122.6 (d, *J* = 3.2 Hz), 113.3 (d, *J* = 9.4 Hz), 113.1 (d, *J* = 6.9 Hz), 113.0, 56.3; **MS(ESI)**: *m/z* = 152.1 [M⁺]



2-Chloro-1-methoxy-4-vinylbenzene (1g)¹: This compound was prepared from 3-chloro-4-methoxybenzaldehyde (0.51 g, 3 mmol) according to general procedure. The crude residue was purified by silica gel chromatography (2% ethyl acetate/petroleum ether) to yield the alkene as colorless oil (0.32 g, 64%).

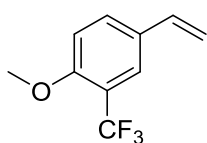
¹H NMR (400 MHz, CDCl₃) δ 7.35 (s, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.50 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.53 (d, *J* = 17.6 Hz, 1H), 5.08 (d, *J* = 10.9 Hz, 1H), 3.79 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 154.6, 135.1, 131.4, 127.7, 125.8, 122.7, 113.0, 111.9, 56.2; **MS(ESI)**: *m/z* = 168.0 [M⁺]



2-Bromo-1-methoxy-4-vinylbenzene (1h)¹: This compound was prepared from 3-bromo-4-methoxybenzaldehyde (0.65 g, 3 mmol) according to general procedure. The crude residue was purified by silica gel chromatography (2% ethyl acetate/petroleum ether) to yield the alkene as colorless oil (0.22 g, 35%).

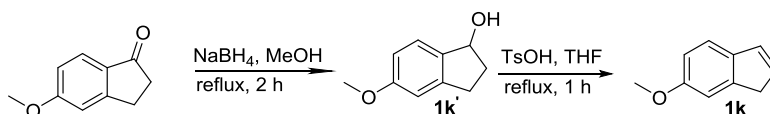
¹H NMR (400 MHz, CDCl₃) δ 7.64 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 6.87 (d, *J* =

8.5 Hz, 1H), 6.62 (dd, $J = 17.5, 10.9$ Hz, 1H), 5.64 (d, $J = 17.5$ Hz, 1H), 5.20 (d, $J = 10.9$ Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.5, 135.0, 131.9, 130.9, 126.5, 113.0, 111.9, 111.8, 56.3 (d, $J = 3$ Hz); **MS(ESI)**: $m/z=212.0$ [M^+].



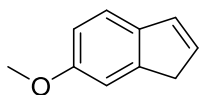
1-Methoxy-2-(trifluoromethyl)-4-vinylbenzene (1i)¹: This compound was prepared from 3-(trifluoromethyl)-4-methoxybenzaldehyde (0.61 g, 3 mmol) according to general procedure. The crude residue was purified by silica gel chromatography (2% ethyl acetate/petroleum ether) to yield the alkene as colorless oil (0.42 g, 70%). ^1H NMR (400 MHz, CDCl_3) δ 7.60 (s, 1H), 7.49 (t, $J = 12.0$ Hz, 1H), 6.94 (d, $J = 8.6$ Hz, 1H), 6.64 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.65 (d, $J = 17.6$ Hz, 1H), 5.21 (d, $J = 10.9$ Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.0, 135.1, 130.8, 130.0, 124.9 (q, $J = 5.2$ Hz), 122.3, 118.8 (q, $J = 30.5$ Hz), 113.3, 112.1, 56.0 (d, $J = 3.6$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -62.51; **MS(ESI)**: $m/z=202.1$ [M^+].

2. General procedure for the preparation of 6-methoxy-1H-indene (**1k**)²



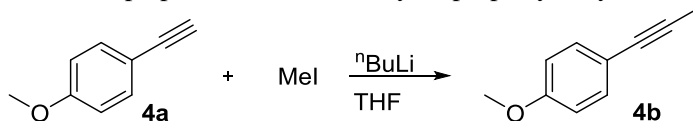
To a mixture of 5-methoxy-1-indanone **3** (0.49 g, 3 mmol) in methanol (12.0 mL) sodium borohydride (0.25 g, 6.6 mmol) was added, and the mixture was refluxed for 2 h. Most of the methanol was removed using a rotoevaporator, and 10 mL of water was added. This mixture was extracted with ethyl acetate (3 \times 20 mL). The ethyl acetate extracts were combined, and dried over magnesium sulfate, and the solvent was removed at reduced pressure to yield the crude 5-methoxy-1-indanol (**1k'**, 0.44 g), which could be directly used for preparing alkene **1k** without further purification.

A solution of the crude 5-methoxy-1-indanol (**1k'**, 0.44 g), *p*-toluenesulfonic acid monohydrate (0.01 g, 0.06 mmol) and tetrahydrofuran (10 mL) was stirred and heated at reflux temperature for one hour. The reaction solution was cooled, and 10 mL of bicarbonate (5%, weight/weight) was added. Most of the THF was removed under reduced pressure, 5.0 mL of water was added, and the mixture was extracted with diethyl ether (3 \times 20 mL). The ether extracts were combined and dried over magnesium sulfate. The solvent was removed at reduced pressure to yield 0.39 g of **1k** (88%).

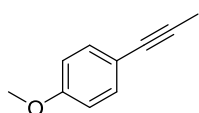


6-Methoxy-1H-indene (1k)²: ^1H NMR (400 MHz, CDCl_3) δ 7.28 (d, $J = 8.2$ Hz, 1H), 7.07 (s, 1H), 6.85 – 6.77 (m, 2H), 6.42 – 6.38 (m, 1H), 3.82 (s, 3H), 3.36 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.9, 145.6, 138.0, 132.0, 131.5, 121.1, 112.0, 110.3, 55.6, 39.2; **MS(ESI)**: $m/z=146.1$ [M^+].

3. General procedure for the preparation of 1-methoxy-4-(prop-1-yn-1-yl)benzene (**4b**)³

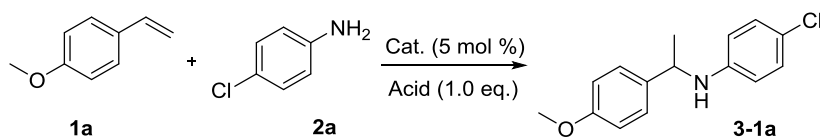


1-Methoxy-4-ethynylbenzene **4a** (500 mg, 3.78 mmol) dissolved in 15 mL of THF was treated with 1.5 mL (3.78 mmol, 2.5 M in hexane) *n*-BuLi at -20 $^\circ\text{C}$. The reaction mixture was stirred for 1 hour at low temperature and 0.6 mL (7.56 mmol) methyl iodide was added dropwise at -20 $^\circ\text{C}$. The solution was warmed to room temperature and stirred for 16 hours. The reaction was then quenched with a saturated NH_4Cl solution (30 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 \times 70 mL). The combined organic phases were dried over MgSO_4 and the solvent was removed in vacuo. After flash chromatography (hexane) the product was isolated as colorless oil (460.0 mg, 83%).



1-Methoxy-4-(prop-1-yn-1-yl)benzene (4b)³: ^1H NMR (400 MHz, CDCl_3) δ 7.36 (d, $J = 7.8$ Hz, 2H), 6.84 (d, $J = 7.9$ Hz, 2H), 3.81 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.0, 132.8, 116.2, 113.9, 84.1, 79.5, 55.2 (d, $J = 3.0$ Hz), 4.3; **MS(ESI)**: $m/z = 146.1$ [M^+].

III. Experimental Procedure for Optimizing the Reaction Conditions^a

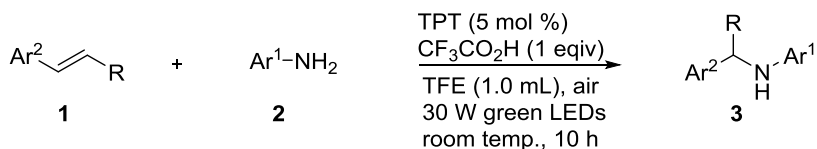


| Entry | Catalyst | Acid | Solvent | t (h) | A/B | Yield(%) ^b |
|-------|-------------------------------------------------------|-------------------|---------|-------|-----|-----------------------|
| 1 | eosinY | TFA | TFE | 10 | 1:1 | 57 |
| 2 | Ru(bpy) ₃ Cl ₂ (2%) | TFA | TFE | 10 | 1:1 | 41 |
| 3 | [Ir(dtbbpy)(ppy) ₂][PF ₆](1%) | TFA | TFE | 10 | 1:1 | 36 |
| 4 | CeCl ₃ | TFA | TFE | 10 | 1:1 | 28 |
| 5 | 9-Mesityl-10-methylacridinium perchlorate | TFA | TFE | 10 | 1:1 | 40 |
| 6 | HEH | TFA | TFE | 10 | 1:1 | 51 |
| 7 | TPT | TFA | TFE | 10 | 1:1 | 65 |
| 8 | TPT | TFA | DCE | 10 | 1:1 | 0 |
| 9 | TPT | TFA | MeCN | 10 | 1:1 | 0 |
| 10 | TPT | TFA | DMF | 10 | 1:1 | 0 |
| 11 | TPT | TFA | MeOH | 10 | 1:1 | 0 |
| 12 | TPT | TFA | THF | 10 | 1:1 | 0 |
| 13 | TPT | TFA | HFIP | 10 | 1:1 | 37 |
| 14 | TPT | TFA | TFE | 10 | 2:1 | 81 |
| 15 | TPT | TFA | TFE | 10 | 1:2 | 75 |
| 16 | TPT | TfOH | TFE | 10 | 2:1 | 58 |
| 17 | TPT | HBr | TFE | 10 | 2:1 | 38 |
| 18 | TPT | TsOH | TFE | 10 | 2:1 | 76 |
| 19 | TPT | TFBA ^c | TFE | 10 | 2:1 | 62 |
| 20 | TPT | No acid | TFE | 10 | 2:1 | 0 |
| 21 | TPT | TFA(0.2 equ.) | TFE | 10 | 2:1 | 16 |
| 22 | TPT | TFA(0.5 equ.) | TFE | 10 | 2:1 | 47 |
| 23 | TPT | TFA | TFE | 10 | 2:1 | 50 ^d |
| 24 | No PC | TFA | TFE | 10 | 2:1 | 49 |
| 25 | TPT no light | TFA | TFE | 10 | 2:1 | 57 |

^a Reaction conditions: 0.1 mmol of 4-methoxystyrene **1a**, 0.2 mmol of 4-chloroaniline **2a**, photo catalysts TPT (5 mol %), and CF₃CO₂H (0.1 mmol, 1.0 equiv) in TFE (1.0 mL) under an air atmosphere at room temperature for 10 h, green LED light. ^b Isolated yield. ^c TFBA = 2,3,4,5-tetrafluoro benzoic acids. ^d 30 W blue LED light was used.

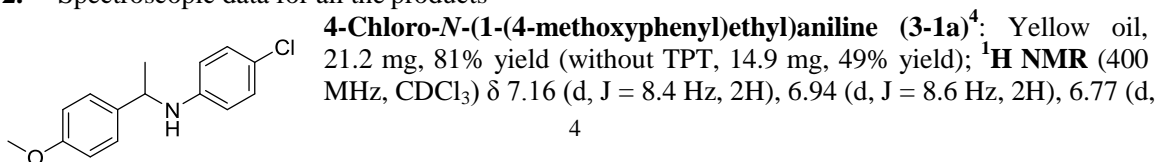
IV. Visible-Light-Promoted Markovnikov Hydroamination of Vinylarenes with Arylamines

- General procedure for the Visible-Light-Promoted Markovnikov Hydroamination of Vinylarenes with Arylamines

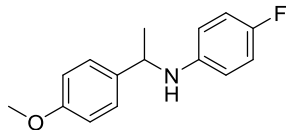


All of the products (**3-1a** ~ **3-2l**) were obtained according to the following procedure. To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added arylamines (0.20 mmol), vinylarenes (0.10 mmol), and CF₃CO₂H (0.10 mmol, 1.0 equiv) with photocatalyst TPT (5 mol %) in TFE (1.0 mL). The reaction mixture was irradiated with 30 W green LEDs at room temperature for 10 h under air atmosphere. Then, the solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel with ethyl acetate /petroleum as eluent to give the desired products **3-1a** ~ **3-2l**.

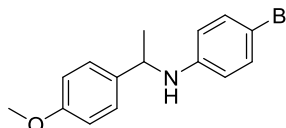
- Spectroscopic data for all the products



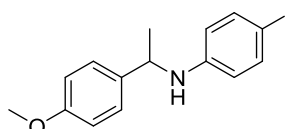
$J = 8.5$ Hz, 2H), 6.34 (d, $J = 8.6$ Hz, 2H), 4.31 (q, $J = 6.6$ Hz, 1H), 3.70 (s, 3H), 1.40 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 145.9, 136.7, 128.9, 126.9, 121.8, 114.5, 114.1, 55.3, 53.0, 24.9; **MS(ESI)**: $m/z=261.1$ [M^+], **IR (KBr)**: 3415, 2963, 2927, 2835, 1599, 1510, 1499, 1247, 1177, 815, 749 cm^{-1} .



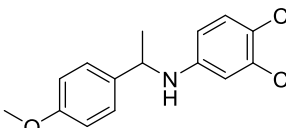
4-Fluoro-*N*-(1-(4-methoxyphenyl)ethyl)aniline (3-1b): Yellow oil, 17.4 mg, 71% yield (without TPT, 6 mg, 24% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.18 (d, $J = 8.1$ Hz, 2H), 6.78 (d, $J = 8.5$ Hz, 2H), 6.71 (t, $J = 8.7$ Hz, 2H), 6.35 (dd, $J = 8.8, 4.4$ Hz, 2H), 4.29 (q, $J = 6.6$ Hz, 1H), 3.70 (s, 3H), 1.40 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 156.8 (d, $J = 233.3$ Hz), 143.7, 137.1 (d, $J = 1.4$ Hz), 126.9, 115.6 (d, $J = 22.1$ Hz), 114.2 (d, $J = 7.3$ Hz), 114.1, 55.3, 53.5, 25.1; ^{19}F NMR (376 MHz, CDCl_3) δ -128.32; **HR-MS (ESI)** calcd for [$\text{M} + 1$] $^+$: $\text{C}_{15}\text{H}_{17}\text{FNO}$: 246.1289, found: 246.1289; **IR (KBr)**: 3423, 2963, 2836, 1612, 1510, 1276, 1245, 1219, 820, 764, 750 cm^{-1} .



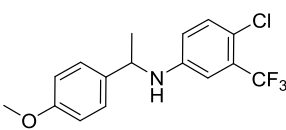
4-Bromo-*N*-(1-(4-methoxyphenyl)ethyl)aniline (3-1c)⁵: Yellow oil, 22.3 mg, 73% yield (without TPT, 7.6 mg, 25% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.15 (d, $J = 8.5$ Hz, 2H), 7.06 (d, $J = 8.7$ Hz, 2H), 6.77 (d, $J = 8.5$ Hz, 2H), 6.29 (d, $J = 8.7$ Hz, 2H), 4.30 (q, $J = 6.7$ Hz, 1H), 3.87 (s, 1H, NH), 3.69 (s, 3H), 1.39 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 146.3, 136.7, 131.8, 126.9, 115.0, 114.1, 108.8, 55.3, 52.9, 25.0; **MS(ESI)**: $m/z=305.0$ [M^+]; **IR (KBr)**: 3415, 2962, 2927, 2834, 1593, 1510, 1496, 1246, 1177, 811, 764, 750 cm^{-1} .



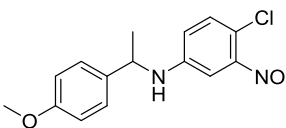
4-Iodo-*N*-(1-(4-methoxyphenyl)ethyl)aniline (3-1d): Yellow oil, 24.0 mg, 68% yield (without TPT, 19.4 mg, 55% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, $J = 7.5$ Hz, 2H), 7.23 (d, $J = 7.6$ Hz, 2H), 6.85 (d, $J = 7.5$ Hz, 2H), 6.28 (d, $J = 7.6$ Hz, 2H), 4.39 (q, $J = 6.6$ Hz, 1H), 3.78 (s, 3H), 1.48 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 146.8, 137.6, 136.6, 126.8, 115.6, 114.1, 77.8, 55.3, 52.8, 24.9; **HR-MS (ESI)** calcd for [$\text{M} + 1$] $^+$: $\text{C}_{15}\text{H}_{17}\text{INO}$: 354.0349, found: 354.0343; **IR (KBr)**: 2929, 2833, 1594, 1510, 1275, 1261, 1177, 832, 764, 750 cm^{-1} .



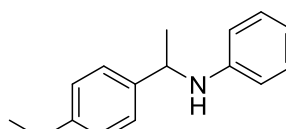
3,4-Dichloro-*N*-(1-(4-methoxyphenyl)ethyl)aniline (3-1e): Yellow oil, 21.9 mg, 74% yield (without TPT, 7 mg, 24% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.22 (d, $J = 8.1$ Hz, 2H), 7.08 (d, $J = 8.7$ Hz, 1H), 6.86 (d, $J = 8.1$ Hz, 2H), 6.57 (s, 1H), 6.32 (d, $J = 8.7$ Hz, 1H), 4.37 (q, $J = 6.5$ Hz, 1H), 4.07 (s, 1H, NH), 3.78 (s, 3H), 1.47 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.7, 146.8, 136.1, 132.6, 130.5, 126.8, 119.7, 114.5, 114.2, 112.9, 55.3, 52.9, 24.8; **HR-MS (ESI)** calcd for [$\text{M} + 1$] $^+$: $\text{C}_{15}\text{H}_{16}\text{Cl}_2\text{NO}$: 296.0603, found: 296.0606; **IR (KBr)**: 3419, 2963, 2928, 2835, 1597, 1511, 1492, 1320, 1244, 1175, 1132, 1036, 830, 808, 666 cm^{-1} .



4-Chloro-*N*-(1-(4-methoxyphenyl)ethyl)-3-(trifluoromethyl)aniline (3-1f): Yellow oil, 20.1 mg, 61% yield (without TPT, 17 mg, 52% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.27 (d, $J = 8.4$ Hz, 2H), 7.17 (d, $J = 8.7$ Hz, 1H), 6.93 – 6.85 (m, 3H), 6.54 (d, $J = 8.6$ Hz, 1H), 4.45 (q, $J = 6.2$ Hz, 1H), 4.26 (s, 1H, NH), 3.82 (s, 3H), 1.53 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.8, 145.8, 135.9, 131.9, 126.8, 121.6, 118.7 (d, $J = 2.2$ Hz), 116.5, 114.3, 112.2 (q, $J = 5.6$ Hz), 55.3, 53.0, 24.8; **HR-MS (ESI)** calcd for [$\text{M} + 1$] $^+$: $\text{C}_{16}\text{H}_{16}\text{ClF}_3\text{NO}$: 330.0867, found: 330.0864; **IR (KBr)**: 3412, 2964, 2930, 2838, 1612, 1511, 1487, 1341, 1247, 1174, 1133, 1025, 830, 814, 671 cm^{-1} .

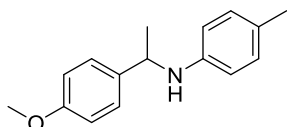


4-Chloro-*N*-(1-(4-methoxyphenyl)ethyl)-3-nitroaniline (3-1g): Yellow oil, 22.7 mg, 74% yield (without TPT, 15 mg, 49% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.21 (d, $J = 7.6$ Hz, 2H), 7.15 (d, $J = 8.7$ Hz, 1H), 6.95 (s, 1H), 6.86 (d, $J = 7.6$ Hz, 2H), 6.58 (d, $J = 8.8$ Hz, 1H), 4.41 (q, $J = 5.3$ Hz, 1H), 4.35 (s, 1H, NH), 3.78 (s, 3H), 1.51 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.0, 148.4, 146.5, 135.3, 131.9, 126.8, 117.7, 114.4, 113.5, 109.2, 55.3, 53.0, 24.6; **HR-MS (ESI)** calcd for [$\text{M} + \text{Na}$] $^+$: $\text{C}_{15}\text{H}_{16}\text{ClN}_2\text{NaO}_3$: 329.0663, found: 329.0665; **IR (KBr)**: 3412, 2964, 2929, 2836, 1611, 1533, 1511, 1332, 1246, 1176, 1035, 831, 817, 752, 685 cm^{-1} .

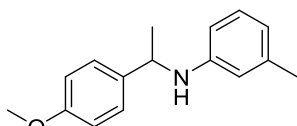


***N*-(1-(4-Methoxyphenyl)ethyl)aniline (3-1h)**⁶: Yellow oil, 15.2 mg, 67% yield (without TPT, 9.9 mg, 44% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.24 – 7.17 (m, 2H), 7.04 (t, $J = 7.4$ Hz, 2H), 6.77 (d, $J = 7.9$ Hz, 2H), 6.67 (t, $J = 6.9$ Hz, 1H), 6.57 (d, $J = 7.4$ Hz, 2H), 4.38 (q, $J =$

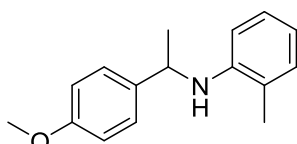
6.6 Hz, 1H), 3.70 (s, 3H), 1.49 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 147.4, 137.3, 129.1, 127.0, 117.3, 114.1, 113.4, 55.3, 52.9, 25.0; **MS(ESI)**: $m/z = 227.1$ [M^+]; **IR (KBr)**: 3407, 2960, 2923, 2835, 1603, 1508, 1244, 1178, 1034, 830, 750, 693 cm^{-1} .



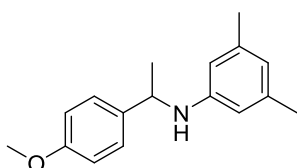
***N*-(1-(4-Methoxyphenyl)ethyl)-4-methylaniline (3-1i)**⁷: Yellow oil, 16.9 mg, 70% yield (without TPT, 7.5 mg, 31% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, $J = 8.5$ Hz, 2H), 6.96 (d, $J = 8.2$ Hz, 2H), 6.90 (d, $J = 8.6$ Hz, 2H), 6.50 (d, $J = 8.3$ Hz, 2H), 4.47 (q, $J = 6.6$ Hz, 1H), 3.83 (s, 3H), 2.24 (s, 3H), 1.53 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 145.1, 137.5, 129.6, 127.0, 126.4, 114.0, 113.6, 55.3, 53.1, 25.0, 20.4; **MS(ESI)**: $m/z = 241.2$ [M^+]; **IR (KBr)**: 3408, 2961, 2923, 2865, 2834, 1614, 1518, 1300, 1245, 1178, 1036, 830, 808, 750 cm^{-1} .



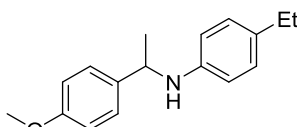
***N*-(1-(4-Methoxyphenyl)ethyl)-3-methylaniline (3-1j)**: Yellow oil, 15.9 mg, 66% yield (without TPT, 8.9 mg, 37% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, $J = 8.5$ Hz, 2H), 7.03 (t, $J = 7.7$ Hz, 1H), 6.91 (d, $J = 8.5$ Hz, 2H), 6.53 (d, $J = 7.4$ Hz, 1H), 6.42 (s, 1H), 6.37 (d, $J = 8.1$ Hz, 1H), 4.50 (q, $J = 6.6$ Hz, 1H), 3.83 (s, 3H), 2.27 (s, 3H), 1.53 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 147.4, 138.8, 137.4, 129.0, 127.0, 118.2, 114.3, 114.0, 110.4, 55.3, 52.8, 24.9, 21.6; **HR-MS (ESI)** calcd for [$\text{M} + 1$] $^+$: $\text{C}_{16}\text{H}_{20}\text{NO}$: 242.1539, found: 242.1535; **IR (KBr)**: 3403, 2961, 2924, 2834, 1607, 1587, 1510, 1488, 1244, 1176, 1036, 830, 769, 692 cm^{-1} .



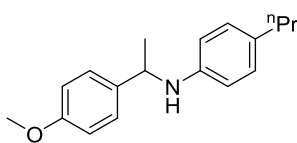
***N*-(1-(4-Methoxyphenyl)ethyl)-2-methylaniline (3-1k)**: Yellow oil, 7.0 mg, 29% yield (without TPT, trace yield); ^1H NMR (400 MHz, CDCl_3) δ 7.18 (d, $J = 7.6$ Hz, 2H), 6.95 (d, $J = 7.2$ Hz, 1H), 6.87 (t, $J = 7.7$ Hz, 1H), 6.76 (d, $J = 7.6$ Hz, 2H), 6.50 (t, $J = 7.3$ Hz, 1H), 6.30 (d, $J = 8.0$ Hz, 1H), 4.40 (q, $J = 6.3$ Hz, 1H), 3.71 (s, 1H, NH), 3.67 (s, 3H), 2.11 (s, 3H), 1.44 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 145.3, 137.4, 130.0, 127.0, 126.9, 121.6, 116.8, 114.1, 111.1, 55.3, 52.7, 25.3, 17.7; **HR-MS (ESI)** calcd for [$\text{M} + 1$] $^+$: $\text{C}_{16}\text{H}_{20}\text{NO}$: 242.1539, found: 242.1537; **IR (KBr)**: 3429, 2961, 2927, 2834, 1606, 1585, 1511, 1444, 1314, 1246, 1174, 1036, 829, 748 cm^{-1} .



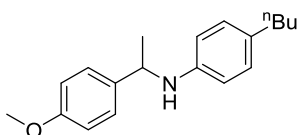
***N*-(1-(4-Methoxyphenyl)ethyl)-3,5-dimethylaniline (3-1l)**: Yellow oil, 19.2 mg, 75% yield (without TPT, 3.6 mg, 14% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.20 (d, $J = 8.1$ Hz, 2H), 6.77 (d, $J = 8.1$ Hz, 2H), 6.23 (s, 1H), 6.09 (s, 2H), 4.36 (q, $J = 6.4$ Hz, 1H), 3.70 (s, 3H), 2.09 (s, 6H), 1.39 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 147.5, 138.7, 137.5, 127.0, 119.3, 114.0, 111.3, 55.3, 52.7, 24.9, 21.5; **HR-MS (ESI)** calcd for [$\text{M} + 1$] $^+$: $\text{C}_{17}\text{H}_{22}\text{NO}$: 256.1696, found: 256.1692; **IR (KBr)**: 3401, 2960, 2922, 2856, 1603, 1510, 1338, 1244, 1180, 1035, 827, 749 cm^{-1} .



4-Ethyl-*N*-(1-(4-methoxyphenyl)ethyl)aniline (3-1m): Yellow oil, 16.8 mg, 66% yield (without TPT, 10 mg, 39% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, $J = 8.3$ Hz, 2H), 7.00 (d, $J = 8.1$ Hz, 2H), 6.92 (d, $J = 8.4$ Hz, 2H), 6.53 (d, $J = 8.1$ Hz, 2H), 4.48 (q, $J = 6.6$ Hz, 1H), 3.84 (s, 3H), 2.56 (q, $J = 7.6$ Hz, 2H), 1.54 (d, $J = 6.7$ Hz, 3H), 1.22 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 145.4, 137.6, 133.0, 128.5, 127.0, 114.0, 113.5, 55.3, 53.2, 27.9, 25.1, 15.9; **HR-MS (ESI)** calcd for [$\text{M} + 1$] $^+$: $\text{C}_{17}\text{H}_{22}\text{NO}$: 256.1696, found: 256.1694; **IR (KBr)**: 3407, 2961, 2928, 2869, 1614, 1517, 1300, 1245, 1179, 1036, 827 cm^{-1} .



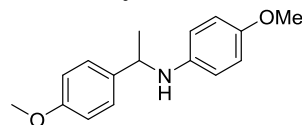
***N*-(1-(4-methoxyphenyl)ethyl)-4-propylaniline (3-1n)**: yellow oil, 17.8 mg, 66% yield (without TPT, 10.0 mg, 37% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.27 (d, $J = 7.9$ Hz, 2H), 6.90 (d, $J = 7.7$ Hz, 2H), 6.84 (d, $J = 8.0$ Hz, 2H), 6.44 (d, $J = 7.8$ Hz, 2H), 4.40 (q, $J = 6.5$ Hz, 1H), 3.76 (s, 3H), 2.42 (t, $J = 7.6$ Hz, 2H), 1.55 (dt, $J = 14.8, 7.4$ Hz, 2H), 1.46 (d, $J = 6.6$ Hz, 3H), 0.89 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 145.4, 137.6, 131.5, 129.1, 127.0, 114.0, 113.4, 55.3, 53.1, 37.2, 25.1, 24.9, 13.9; **HR-MS (ESI)** calcd for [$\text{M} + 1$] $^+$: $\text{C}_{18}\text{H}_{24}\text{NO}$: 270.1852, found: 270.1844; **IR (KBr)**: 3409, 2958, 2927, 2869, 1614, 1515, 1301, 1244, 1179, 1037, 829, 750 cm^{-1} .



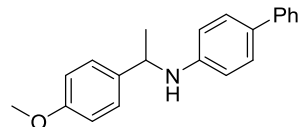
4-Butyl-*N*-(1-(4-methoxyphenyl)ethyl)aniline (3-1o): Yellow oil, 17.3 mg, 61% yield (without TPT, 9.6 mg, 34% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.28 (d, $J = 7.6$ Hz, 2H), 6.90 (d, $J = 7.5$ Hz, 2H), 6.84 (d, $J = 7.6$ Hz, 2H), 6.44 (d, $J = 7.4$ Hz, 2H), 4.40 (q, $J = 6.4$ Hz, 1H), 3.77 (s,

3H), 2.44 (t, $J = 7.5$ Hz, 2H), 1.55 – 1.44 (m, 5H), 1.35 – 1.24 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 145.3, 137.6, 131.6, 129.0, 127.0, 114.0, 113.4, 55.3, 53.1, 34.7, 34.0, 25.1, 22.4, 14.0; **HR-MS (ESI)** calcd for $[\text{M} + 1]^+$: $\text{C}_{19}\text{H}_{26}\text{NO}$: 284.2009, found: 284.2004; **IR (KBr)**: 3409, 2958, 2927, 2869, 1614, 1515, 1301, 1244, 1179, 1037, 829, 750 cm^{-1} .

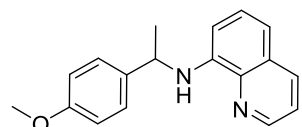
4-Methoxy-*N*-(1-(4-methoxyphenyl)ethyl)aniline (3-1p)⁸: Yellow oil, 19.0 mg, 74% yield (without TPT, 4.9 mg, 19% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, $J = 8.1$ Hz, 2H), 6.91 (d, $J = 8.2$ Hz, 2H), 6.75 (d, $J = 8.6$ Hz, 2H), 6.53 (d, $J = 8.5$ Hz, 2H), 4.43 (q, $J = 6.6$ Hz, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 1.52 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 152.0, 141.6, 137.5, 127.0, 114.8, 114.7, 114.0, 55.8, 55.3, 53.7, 25.1; **MS(ESI)**: m/z =257.1 $[\text{M}^+]$; **IR (KBr)**: 3397, 2959, 2931, 2833, 1611, 1511, 1241, 1177, 1037, 820, 758 cm^{-1} .



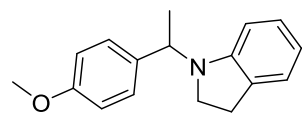
***N*-(1-(4-Methoxyphenyl)ethyl)-[1,1'-biphenyl]-4-amine (3-1q)**: Yellow oil, 17.6 mg, 58% yield (without TPT, 8.5 mg, 28% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 7.7$ Hz, 2H), 7.34 (t, $J = 7.0$ Hz, 4H), 7.28 (d, $J = 7.7$ Hz, 2H), 7.24 – 7.17 (m, 1H), 6.85 (d, $J = 7.7$ Hz, 2H), 6.56 (d, $J = 7.6$ Hz, 2H), 4.47 (q, $J = 6.5$ Hz, 1H), 4.06 (s, 1H, NH), 3.76 (s, 3H), 1.49 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 146.9, 141.3, 137.2, 130.1, 128.7, 127.9, 127.0, 126.3, 126.0, 114.1, 113.6, 55.3, 52.9, 25.1; **HR-MS (ESI)** calcd for $[\text{M} + 1]^+$: $\text{C}_{21}\text{H}_{22}\text{NO}$: 304.1696, found: 304.1683; **IR (KBr)**: 3409, 3025, 2962, 2928, 2834, 1612, 1524, 1511, 1489, 1322, 1299, 1245, 1177, 1036, 827, 763, 698 cm^{-1} .



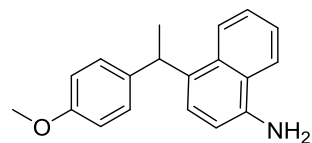
***N*-(1-(4-Methoxyphenyl)ethyl)quinolin-8-amine (3-1r)**: Yellow oil, 11.4 mg, 41% yield (without TPT, 2.5 mg, 9% yield); ^1H NMR (400 MHz, CDCl_3) δ 8.78 (d, $J = 2.1$ Hz, 1H), 8.07 (d, $J = 8.2$ Hz, 1H), 7.39 (t, $J = 9.0$ Hz, 3H), 7.26 (t, $J = 8.2$ Hz, 1H), 7.02 (d, $J = 8.1$ Hz, 1H), 6.88 (d, $J = 7.6$ Hz, 2H), 6.58 (s, 1H, NH), 6.46 (d, $J = 7.6$ Hz, 1H), 4.66 (m, 1H), 3.80 (s, 3H), 1.70 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 146.8, 143.7, 138.2, 137.2, 136.1, 128.6, 127.7, 126.9, 121.3, 114.0, 113.9, 106.2, 55.3, 52.7, 25.2; **HR-MS (ESI)** calcd for $[\text{M} + 1]^+$: $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}$: 279.1492, found: 279.1490; **IR (KBr)**: 3394, 2960, 2922, 2849, 1611, 1575, 1518, 1479, 1379, 1245, 1172, 1035, 830, 818, 791, 747 cm^{-1} .



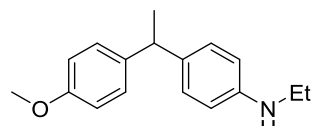
1-(1-(4-Methoxyphenyl)ethyl)indoline (3-1s): Yellow oil, 10.4 mg, 41% yield (without TPT, 7.3 mg, 29% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.36 (d, $J = 7.8$ Hz, 2H), 7.09 (d, $J = 7.1$ Hz, 1H), 7.04 (t, $J = 7.6$ Hz, 1H), 6.91 (d, $J = 7.7$ Hz, 2H), 6.64 (t, $J = 7.2$ Hz, 1H), 6.42 (d, $J = 7.8$ Hz, 1H), 4.74 (q, $J = 6.6$ Hz, 1H), 3.84 (s, 3H), 3.40 (q, $J = 9.0$ Hz, 1H), 3.31 (q, $J = 7.8$ Hz, 1H), 2.97 (t, $J = 8.4$ Hz, 2H), 1.55 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 151.5, 134.9, 130.2, 128.2, 127.2, 124.4, 116.9, 113.7, 107.2, 55.3, 53.8, 47.8, 28.2, 16.4; **HR-MS (ESI)** calcd for $[\text{M} + 1]^+$: $\text{C}_{17}\text{H}_{20}\text{NO}$: 254.1539, found: 254.1540; **IR (KBr)**: 2963, 2930, 2834, 1607, 1512, 1487, 1302, 1248, 1178, 1031, 832, 743 cm^{-1} .

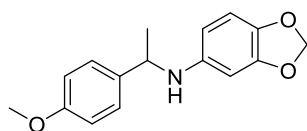


4-(1-(4-Methoxyphenyl)ethyl)naphthalen-1-amine (3-1t): Yellow oil, 20.0 mg, 72% yield (without TPT, 1.9 mg, 7% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.88 – 7.77 (m, 2H), 7.52 – 7.40 (m, 4H), 7.21 (d, $J = 8.0$ Hz, 2H), 6.87 (d, $J = 7.9$ Hz, 2H), 4.30 (q, $J = 7.0$ Hz, 1H), 4.11 (s, 2H, NH), 3.81 (s, 3H), 1.75 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.1, 138.8, 137.7, 133.1, 128.5, 125.8, 125.2, 124.9, 124.1, 123.8, 120.5, 118.4, 114.1, 55.3, 39.5, 21.9; **HR-MS (ESI)** calcd for $[\text{M} + 1]^+$: $\text{C}_{19}\text{H}_{20}\text{NO}$: 278.1539, found: 278.1540; **IR (KBr)**: 3460, 3387, 3057, 2963, 2930, 2834, 1621, 1509, 1400, 1245, 1178, 1031, 832, 803, 748 cm^{-1} .

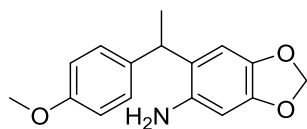


***N*-Ethyl-4-(1-(4-methoxyphenyl)ethyl)aniline (3-1u)**: Yellow oil, 14.0 mg, 55% yield (without TPT, 7.5 mg, 29% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.04 (d, $J = 8.5$ Hz, 2H), 6.93 (d, $J = 8.3$ Hz, 2H), 6.73 (d, $J = 8.5$ Hz, 2H), 6.47 (d, $J = 8.4$ Hz, 2H), 3.92 (q, $J = 7.2$ Hz, 1H), 3.70 (s, 1H, NH), 3.69 (s, 3H), 3.05 (q, $J = 7.1$ Hz, 2H), 1.48 (d, $J = 7.2$ Hz, 3H), 1.15 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.7, 146.5, 139.5, 135.8, 128.4, 128.3, 113.7, 112.9, 55.3, 43.1, 38.8, 22.3, 14.9; **HR-MS (ESI)** calcd for $[\text{M} + 1]^+$: $\text{C}_{17}\text{H}_{22}\text{NO}$: 256.1696, found: 256.1689; **IR (KBr)**: 2963, 2920, 1611, 1510, 1245, 1177, 1033, 831, 749 cm^{-1} .

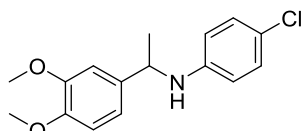




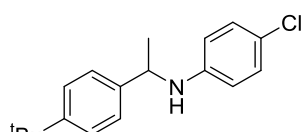
N-(1-(4-Methoxyphenyl)ethyl)benzo[d][1,3]dioxol-5-amine (3-1v): Yellow oil, 7.6 mg, 28% yield (without TPT, 8.9 mg, 37% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.25 (d, $J = 7.6$ Hz, 2H), 6.85 (d, $J = 8.0$ Hz, 2H), 6.56 (d, $J = 8.3$ Hz, 1H), 6.14 (s, 1H), 5.94 (d, $J = 8.3$ Hz, 1H), 5.78 (s, 2H), 4.34 (q, $J = 6.4$ Hz, 1H), 3.77 (s, 3H), 1.45 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 148.1, 143.1, 139.4, 137.3, 126.9, 114.0, 108.5, 105.2, 100.5, 96.4, 55.3, 53.7, 25.1; **HR-MS (ESI)** calcd for $[\text{M} + 1]^+$: $\text{C}_{16}\text{H}_{18}\text{NO}_3$: 272.1281, found: 272.1287; **IR (KBr)**: 3410, 2961, 2921, 2850, 1633, 1611, 1504, 1488, 1285, 1244, 1210, 1178, 1038, 934, 831, 813, 789 cm^{-1} .



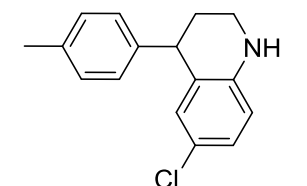
6-(1-(4-Methoxyphenyl)ethyl)benzo[d][1,3]dioxol-5-amine (3-1w): Yellow oil, 14.1 mg, 52% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.10 (d, $J = 7.9$ Hz, 2H), 6.85 – 6.77 (m, 3H), 6.24 (s, 1H), 5.85 (s, 2H), 3.96 (q, $J = 7.0$ Hz, 1H), 3.76 (s, 3H), 3.24 (s, 2H, NH), 1.53 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.1, 146.2, 140.6, 138.6, 137.8, 128.3, 122.8, 114.1, 107.4, 100.6, 98.6, 55.3, 39.1, 22.2; **HR-MS (ESI)** calcd for $[\text{M} + 1]^+$: $\text{C}_{16}\text{H}_{18}\text{NO}_3$: 272.1281, found: 272.1281; **IR (KBr)**: 3442, 3367, 2962, 2929, 2835, 1633, 1609, 1507, 1485, 1244, 1172, 1037, 932, 831, 750 cm^{-1} .



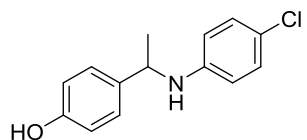
4-Chloro-N-(1-(3,4-dimethoxyphenyl)ethyl)aniline (3-2a): Yellow oil, 21.3 mg, 73% yield (without TPT, 14.9 mg, 51% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.02 (d, $J = 7.5$ Hz, 2H), 6.87 (d, $J = 10.3$ Hz, 2H), 6.81 (d, $J = 8.0$ Hz, 1H), 6.42 (d, $J = 7.5$ Hz, 2H), 4.36 (q, $J = 6.5$ Hz, 1H), 4.02 (s, 1H, NH), 3.84 (s, 6H), 1.48 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.3, 148.0, 145.9, 137.4, 128.9, 121.8, 117.7, 114.5, 111.4, 109.0, 55.9, 53.4, 25.0; **HR-MS (ESI)** calcd for $[\text{M} + 1]^+$: $\text{C}_{16}\text{H}_{19}\text{ClNO}_2$: 292.1099, found: 292.1091; **IR (KBr)**: 3404, 2961, 2932, 2834, 1599, 1515, 1499, 1316, 1256, 1169, 1027, 814, 764 cm^{-1} .



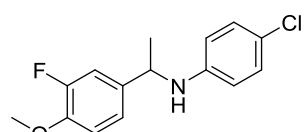
N-(1-(4-(tert-Butyl)phenyl)ethyl)-4-chloroaniline (3-2b): Yellow oil, 22.2 mg, 77% yield (without TPT, 3.5 mg, 12% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, $J = 7.3$ Hz, 2H), 7.31 (d, $J = 7.6$ Hz, 2H), 7.09 (d, $J = 7.6$ Hz, 2H), 6.49 (d, $J = 7.7$ Hz, 2H), 4.48 (q, $J = 6.5$ Hz, 1H), 4.08 (s, 1H, NH), 1.55 (d, $J = 6.5$ Hz, 3H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.9, 146.0, 141.6, 129.0, 125.6, 125.5, 121.7, 114.4, 53.2, 34.5, 31.5, 24.8; **HR-MS (ESI)** calcd for $[\text{M} + 1]^+$: $\text{C}_{18}\text{H}_{23}\text{ClN}$: 288.1441, found: 288.1429; **IR (KBr)**: 3418, 3023, 2962, 2903, 2867, 1600, 1497, 1316, 1295, 1252, 1177, 1091, 1015, 832, 814, 677, 576 cm^{-1} .



6-Chloro-4-(p-tolyl)-1,2,3,4-tetrahydroquinoline (3-2c): Yellow oil, 7.7 mg, 30% yield (without TPT, 2.5 mg, 9% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.14 (d, $J = 7.7$ Hz, 2H), 7.03 (d, $J = 7.7$ Hz, 2H), 6.97 (d, $J = 8.3$ Hz, 1H), 6.75 (s, 1H), 6.48 (d, $J = 8.5$ Hz, 1H), 4.08 (t, $J = 6.0$ Hz, 1H), 3.34 – 3.21 (m, 2H), 2.36 (s, 3H), 2.23 – 2.14 (m, 1H), 2.08 – 1.99 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.4, 142.8, 136.0, 129.9, 129.2, 128.5, 127.2, 125.2, 121.5, 115.3, 42.3, 39.1, 30.7, 21.0; **HR-MS (ESI)** calcd for $[\text{M} + 1]^+$: $\text{C}_{16}\text{H}_{17}\text{ClN}$: 258.1044, found: 258.1036; **IR (KBr)**: 3415, 2922, 2851, 1601, 1496, 1353, 1297, 1263, 1084, 809, 765 cm^{-1} .

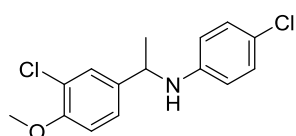


4-(1-((4-Chlorophenyl)amino)ethyl)phenol (3-2d): Yellow oil, 9.9 mg, 40% yield (without TPT, 2.5 mg, 10% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.17 (d, $J = 7.8$ Hz, 2H), 7.02 (d, $J = 8.0$ Hz, 2H), 6.76 (d, $J = 7.9$ Hz, 2H), 6.41 (d, $J = 8.0$ Hz, 2H), 4.54 (s, 1H, NH), 4.37 (q, $J = 6.6$ Hz, 1H), 1.46 (d, $J = 6.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.5, 145.8, 136.9, 128.9, 127.1, 121.8, 115.6, 114.5, 53.0, 25.0; **HR-MS (ESI)** calcd for $[\text{M} + 1]^+$: $\text{C}_{14}\text{H}_{15}\text{ClNO}$: 248.0837, found: 248.0836; **IR (KBr)**: 3589, 3450, 3022, 2965, 2925, 2868, 1612, 1598, 1512, 1497, 1316, 1252, 1176, 1092, 1012, 832, 816, 739 cm^{-1} .



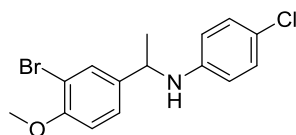
4-Chloro-N-(1-(3-fluoro-4-methoxyphenyl)ethyl)aniline (3-2e): Yellow oil, 19.0 mg, 68% yield (without TPT, trace yield); ^1H NMR (400 MHz, CDCl_3) δ 7.09 – 7.00 (m, 4H), 6.90 (t, $J = 8.5$ Hz, 1H), 6.40 (d, $J = 8.5$ Hz, 2H), 4.36 (q, $J = 6.5$ Hz, 1H), 4.00 (s, 1H, NH), 3.86 (s, 3H), 1.47 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.4 (d, $J = 10.7$ Hz), 145.6, 138.0 (d, $J = 4.9$ Hz), 129.0, 122.1, 121.3 (d, $J = 3.1$ Hz), 114.4, 113.7 (d, $J = 1.0$ Hz), 113.6, 113.5, 56.4, 52.8, 25.0; **HR-MS (ESI)** calcd for $[\text{M} + 1]^+$:

C₁₅H₁₆ClFNO: 280.0899, found: 280.0896; **IR (KBr)**: 3412, 2964, 2928, 2850, 1600, 1518, 1499, 1295, 1274, 1133, 1028, 815, 761 cm⁻¹.



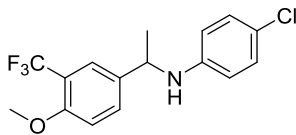
4-Chloro-N-(1-(3-chloro-4-methoxyphenyl)ethyl)aniline (3-2f):

Yellow oil, 12.7 mg, 43% yield (without TPT, 2.8 mg, 9% yield); **¹H NMR** (400 MHz, CDCl₃) δ 7.33 (s, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.40 (d, *J* = 8.5 Hz, 2H), 4.35 (q, *J* = 6.6 Hz, 1H), 3.99 (s, 1H, NH), 3.86 (s, 3H), 1.45 (d, *J* = 9.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 154.0, 145.6, 138.0, 129.0, 127.7, 125.0, 122.7, 122.0, 114.5, 112.3, 56.2, 52.8, 25.0; **HR-MS (ESI)** calcd for [M + 1]⁺: C₁₅H₁₆Cl₂NO: 296.0603, found: 296.0606; **IR (KBr)**: 3417, 2965, 2927, 2838, 1600, 1503, 1316, 1290, 1256, 1202, 1178, 1091, 1063, 1021, 814, 739 cm⁻¹.



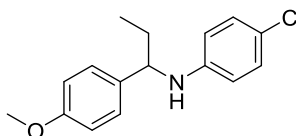
N-(1-(3-Bromo-4-methoxyphenyl)ethyl)-4-chloroaniline (3-2g):

Yellow oil, 14.0 mg, 41% yield (without TPT, 8 mg, 24% yield); **¹H NMR** (400 MHz, CDCl₃) δ 7.51 (d, *J* = 1.9 Hz, 1H), 7.22 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.40 (d, *J* = 8.8 Hz, 2H), 4.35 (q, *J* = 6.6 Hz, 1H), 3.99 (s, 1H, NH), 3.86 (s, 3H), 1.47 (d, *J* = 6.7 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 154.9, 145.6, 138.5, 130.8, 129.0, 125.7, 122.1, 114.5, 112.2, 112.0, 56.3, 52.7, 25.0; **HR-MS (ESI)** calcd for [M + 1]⁺: C₁₅H₁₆BrClNO: 340.0098, found: 340.0081; **IR (KBr)**: 3415, 2963, 2927, 2838, 1600, 1497, 1315, 1286, 1255, 1053, 1020, 814, 736, 680, 552 cm⁻¹.



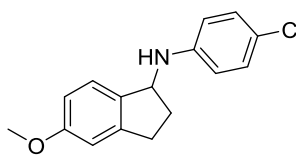
4-Chloro-N-(1-(4-methoxy-3-trifluoromethyl)phenyl)ethyl)aniline (3-2h):

Yellow oil, 18.8 mg, 57% yield (without TPT, 11.5 mg, 35% yield); **¹H NMR** (400 MHz, CDCl₃) δ 7.45 (s, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.32 (d, *J* = 8.8 Hz, 2H), 4.33 (q, *J* = 6.6 Hz, 1H), 3.94 (s, 1H, NH), 3.80 (s, 3H), 1.41 (d, *J* = 6.7 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 156.5 (q, *J* = 1.7 Hz), 145.5, 136.5, 130.4, 129.0, 124.6 (q, *J* = 5.2 Hz), 122.2, 119.1, 114.5, 112.4, 56.0, 52.9, 25.0; **¹⁹F NMR** (376 MHz, CDCl₃) δ -62.30; **HR-MS (ESI)** calcd for [M + 1]⁺: C₁₆H₁₆ClF₃NO: 330.0867, found: 330.0867; **IR (KBr)**: 3422, 2967, 2931, 2843, 1620, 1599, 1504, 1324, 1277, 1258, 1129, 1057, 1024, 817, 677 cm⁻¹.



4-Chloro-N-(1-(4-methoxyphenyl)propyl)aniline (3-2i):

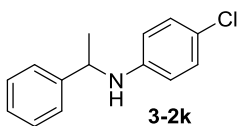
Yellow oil, 12.4 mg, 45% yield (without TPT, 5.5 mg, 20% yield); **¹H NMR** (400 MHz, CDCl₃) δ 7.21 (d, *J* = 8.1 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 8.1 Hz, 2H), 6.42 (d, *J* = 8.3 Hz, 2H), 4.12 (t, *J* = 6.4 Hz, 1H), 4.04 (s, 1H, NH), 3.78 (s, 3H), 1.88 – 1.70 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 158.6, 146.1, 135.3, 128.9, 127.5, 121.6, 114.4, 114.0, 59.3, 55.3, 31.6, 10.8; **HR-MS (ESI)** calcd for [M + 1]⁺: C₁₆H₁₉ClNO: 276.1150, found: 276.1155; **IR (KBr)**: 3430, 2960, 2920, 2850, 1608, 1509, 1497, 1302, 1245, 1175, 1090, 1032, 814, 749 cm⁻¹.



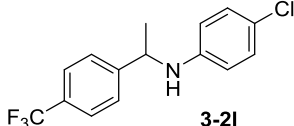
N-(4-Chlorophenyl)-5-methoxy-2,3-dihydro-1H-inden-1-amine (3-2j):

Yellow oil, 6.8 mg, 25% yield (without TPT, 0% yield); **¹H NMR** (500 MHz, CDCl₃) δ 7.24 (d, *J* = 8.3 Hz, 1H), 7.16 – 7.14 (m, 1H), 7.13 – 7.11 (m, 1H), 6.81 (d, *J* = 2.0 Hz, 1H), 6.76 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.63 – 6.61 (m, 1H), 6.61 – 6.59 (m, 1H), 4.90 (t, *J* = 6.3 Hz, 1H), 3.86 (s, 1H, NH), 3.80 (s, 3H), 3.04 – 2.95 (m, 1H), 2.91 – 2.81 (m, 1H), 2.60 – 2.50 (m, 1H), 1.96 – 1.86 (m, 1H); **¹³C NMR** (125 MHz, CDCl₃) δ 160.1, 145.4, 136.2, 129.2, 124.9, 114.3, 112.9, 110.0, 58.1, 55.5, 33.9, 30.4; **HR-MS (ESI)** calcd for [M + 1]⁺: C₁₆H₁₇ClNO: 274.0985, found: 274.1000; **IR (KBr)**: 3444, 2955, 2921, 2849, 1645, 1494, 1467, 1399, 1303, 1256, 1176, 1089, 1032, 814, 747 cm⁻¹.

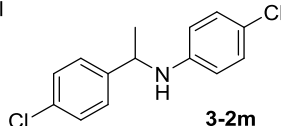
Note:



3-2k

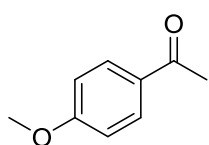


3-2l

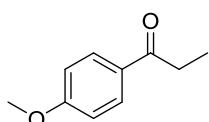


3-2m

4-Chloro-N-(1-phenylethyl)aniline (3-2k), 4-Chloro-N-(1-(4-(trifluoromethyl)phenyl)ethyl)aniline (3-2l) and 4-Chloro-N-(1-(4-chlorophenyl)ethyl)aniline (3-2m) could not be obtained under our reaction conditions.



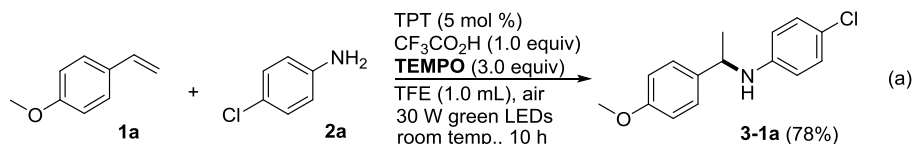
1-(4-Methoxyphenyl)ethan-1-one (5a)⁹: To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added 4-chloroaniline (0.20 mmol), 1-ethynyl-4-methoxybenzene (0.10 mmol), and CF₃CO₂H (1.0 equiv) with photocatalyst TPT (5 mol %) in TFE (1.0 mL). The reaction mixture was irradiated with 30 W green LEDs at room temperature for 10 h under air atmosphere. Then, the solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel with ethyl acetate /petroleum as eluent to give the desired products. yellow oil, 12.5 mg, 83% yield (without TPT, 7 mg, 47% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 2H), 3.87 (s, 3H), 2.55 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 196.8, 163.5, 130.6, 130.4, 113.7, 55.5, 26.3; **MS(ESI):** *m/z* = 150.1 [M⁺]; **IR (KBr):** 3339, 3003, 2960, 2932, 2840, 1676, 1599, 1576, 1510, 1358, 1258, 1172, 1028, 957, 834, 806, 592, 577, 564 cm⁻¹.



1-(4-Methoxyphenyl)propan-1-one (5b)⁹: To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added 4-chloroaniline (0.20 mmol), 1-methoxy-4-(prop-1-yn-1-yl)benzene (0.10 mmol), and CF₃CO₂H (1.0 equiv) with photocatalyst TPT (5 mol %) in TFE (1.0 mL). The reaction mixture was irradiated with 30 W green LEDs at room temperature for 10 h under air atmosphere. Then, the solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel with ethyl acetate /petroleum as eluent to give the desired products. yellow oil, 8.0 mg, 49% yield (without TPT, 4 mg, 15% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.2 Hz, 2H), 3.86 (s, 3H), 2.95 (q, *J* = 7.0 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 199.6, 163.3, 130.2, 130.0, 113.7, 55.4, 31.4, 8.5; **MS(ESI):** *m/z* = 164.1 [M⁺]; **IR (KBr):** 3339, 3004, 2963, 2934, 2850, 1676, 1600, 1576, 1510, 1417, 1359, 1258, 1170, 1028, 959, 832, 807, 590, 578, 560 cm⁻¹.

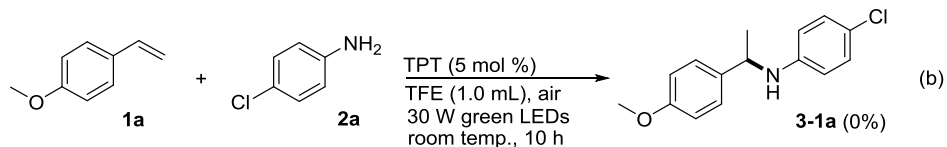
V. Control Experiments for Mechanism Studies

1. The effect of TEMPO on the intermolecular hydroamination of alkene **1a** with 4-chloroaniline **2a**



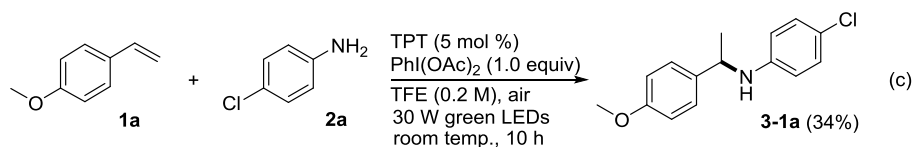
To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added 1-methoxy-4-vinylbenzene **1a** (0.10 mmol), 4-chloroaniline **2a** (0.20 mmol), TEMPO (0.3 mmol, 3 eq.) and CF₃CO₂H (1.0 equiv) with photocatalyst TPT (5 mol %) in TFE (1.0 mL). The reaction mixture was irradiated with 30 W green LEDs at room temperature for 10 h under air atmosphere. Then, the solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel with ethyl acetate /petroleum as eluent. The product **3-1a** was obtained in 78% yield.

2. Visible-light-promoted Markovnikov hydroamination of 4-methoxystyrene (**1a**) with 4-chloroaniline (**2a**) in the absence of CF₃CO₂H



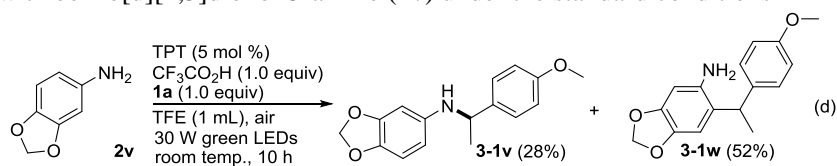
To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added 1-methoxy-4-vinylbenzene **1a** (0.10 mmol), 4-chloroaniline **2a** (0.20 mmol), and photocatalyst TPT (5 mol %) in TFE (1.0 mL). The reaction mixture was irradiated with 30 W green LEDs at room temperature for 10 h under air atmosphere. Then, the solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel with ethyl acetate /petroleum as eluent. No product **3-1b** was detected by TLC.

3. Visible-light-promoted Markovnikov hydroamination of 4-methoxystyrene (**1a**) with 4-chloroaniline (**2a**) in the presence of PhI(OAc)₂



To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added 1-methoxy-4-vinylbenzene **1a** (0.10 mmol), 4-chloroaniline **2a** (0.20 mmol), and PhI(OAc)₂ (0.10 mmol, 1.0 equiv) with photocatalyst TPT (5 mol %) in TFE (1.0 mL). The reaction mixture was irradiated with 30 W green LEDs at room temperature for 10 h under air atmosphere. Then, the solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel with ethyl acetate /petroleum as eluent. The product **3-1a** was obtained in 34% yield.

4. Visible-light-promoted hydroamination of 4-methoxystyrene (**1a**) with benzo[d][1,3]dioxol-5-amine (**2v**) with benzo[d][1,3]dioxol-5-amine (**2v**) under the standard conditions



To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added 1-methoxy-4-vinylbenzene **1a** (0.10 mmol), benzo[d][1,3]dioxol-5-amine **2v** (0.20 mmol), and CF₃CO₂H (1.0 equiv) with photocatalyst TPT (5 mol %) in TFE (1.0 mL). The reaction mixture was irradiated with 30 W green LEDs at room temperature for 10 h under air atmosphere. Then, the solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel with ethyl acetate /petroleum as eluent. The product **3-1v** was obtained in 28% yield, and the product **3-1w** was obtained in 52% yield.

5. Stern-Volmer fluorescence quenching experiments

Fluorescence spectra were collected on Agilent Cary Eclipse fluorescence spectrophotometer. Experimental procedures: All the TPT solutions were excited at 410 nm and the emission intensity was collected at 470 nm. A screw-top quartz cuvette was charged with a 5 μ M solution of TPT in dry MeCN (2.0 mL) and the initial emission was collected. Another two series of samples, 5 μ M TPT in dry MeCN with 4-chloroaniline and trifluoroacetic acid or 4-methoxystyrene (**1a**) as quencher in gradient concentrations (2.5 μ M, 5 μ M, 7.5 μ M, 1 μ M, 1.25 μ M, 1.5 μ M), were tested and the emissions were collected.

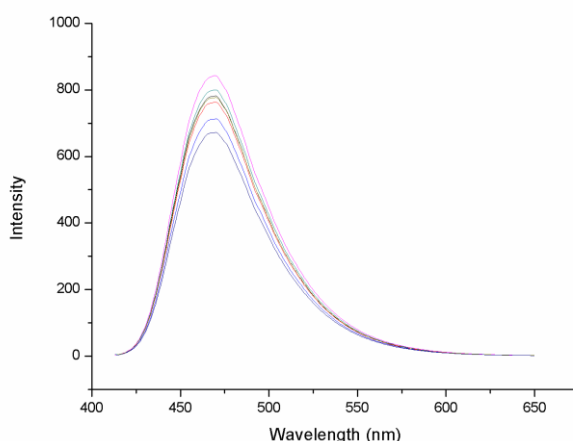


Figure. S-1 Luminescence quenching of TPT with excitation at 410 nm by *p*-chloroaniline (10⁻⁶ M) in the presence of trifluoroacetic acid (using CH₃CN as solvent)

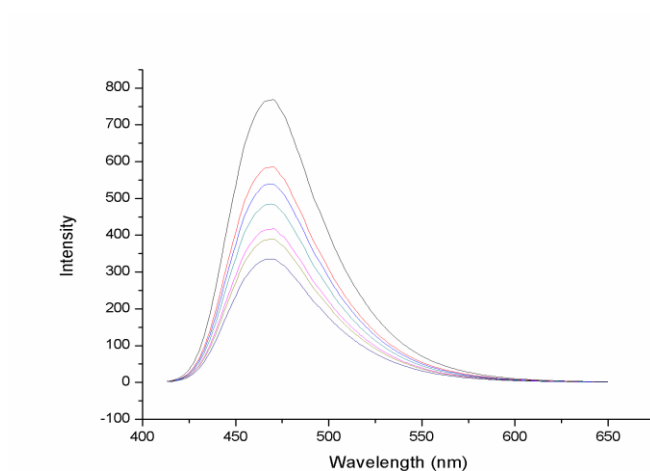


Figure. S-2 Luminescence quenching of TPT with excitation at 410 nm by 4-methoxystyrene (10^{-6} M) (using CH_3CN as solvent)

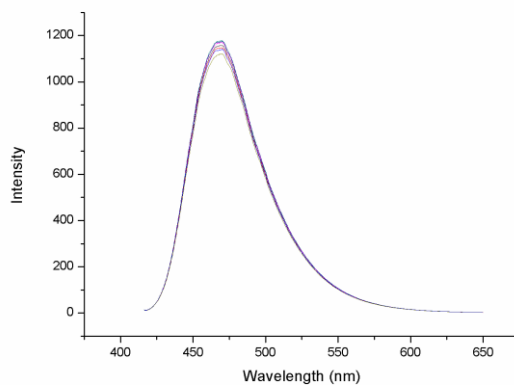


Figure. S-3 Luminescence quenching of TPT with excitation at 410 nm by $\text{CF}_3\text{CO}_2\text{H}$ (10^{-6} M) (using CH_3CN as solvent)

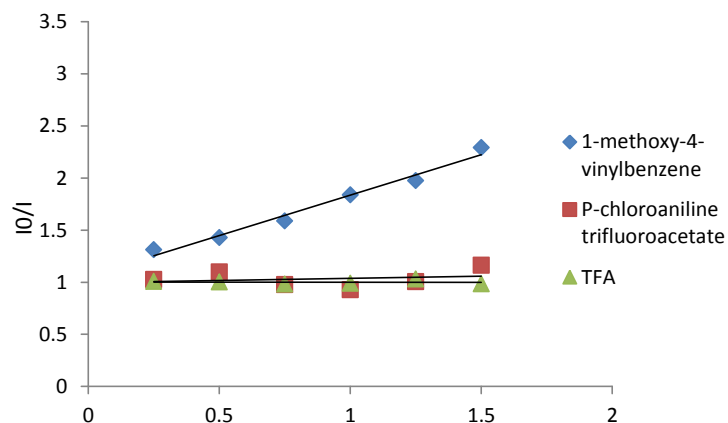


Figure. S-4 The Stern-Volmer plot about the luminescence quenching of TPT by 4-chloroaniline, 4-methoxystyrene, and $\text{CF}_3\text{CO}_2\text{H}$.

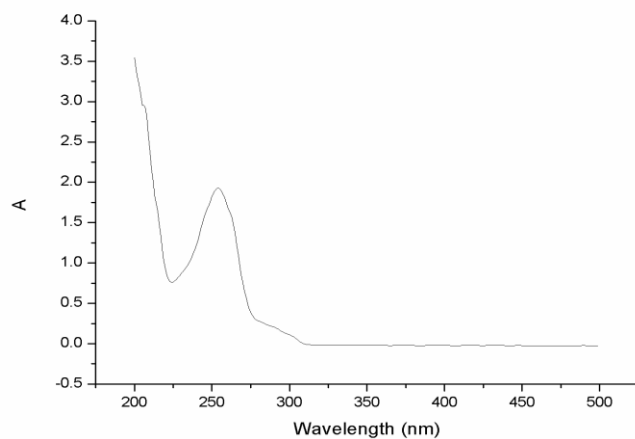


Figure. S-5 UV-vis absorption spectrum of TPT (1×10^{-5} M) in TFE.

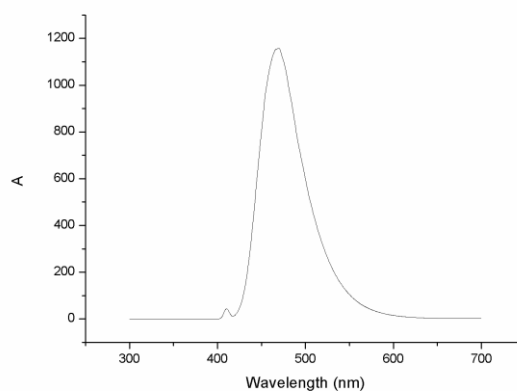


Figure. S-6 The emission spectrum of TPT (5 μ M) photocatalyst irradiated by 410 nm light (using CH_3CN as solvent).

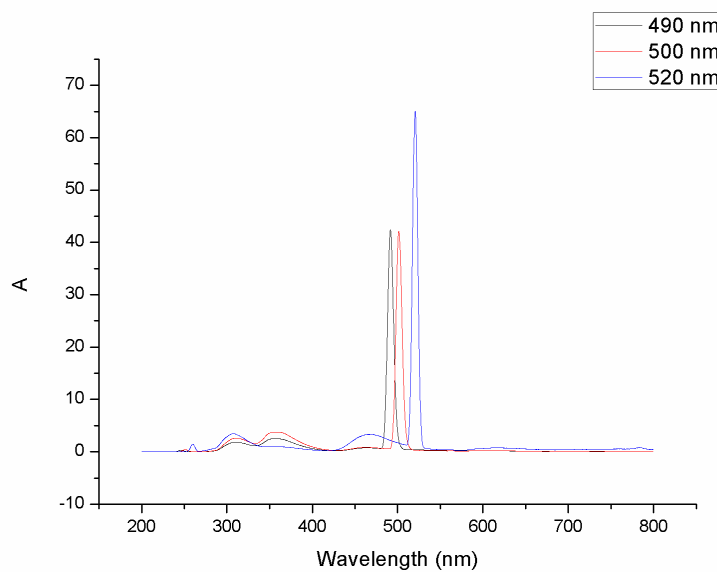


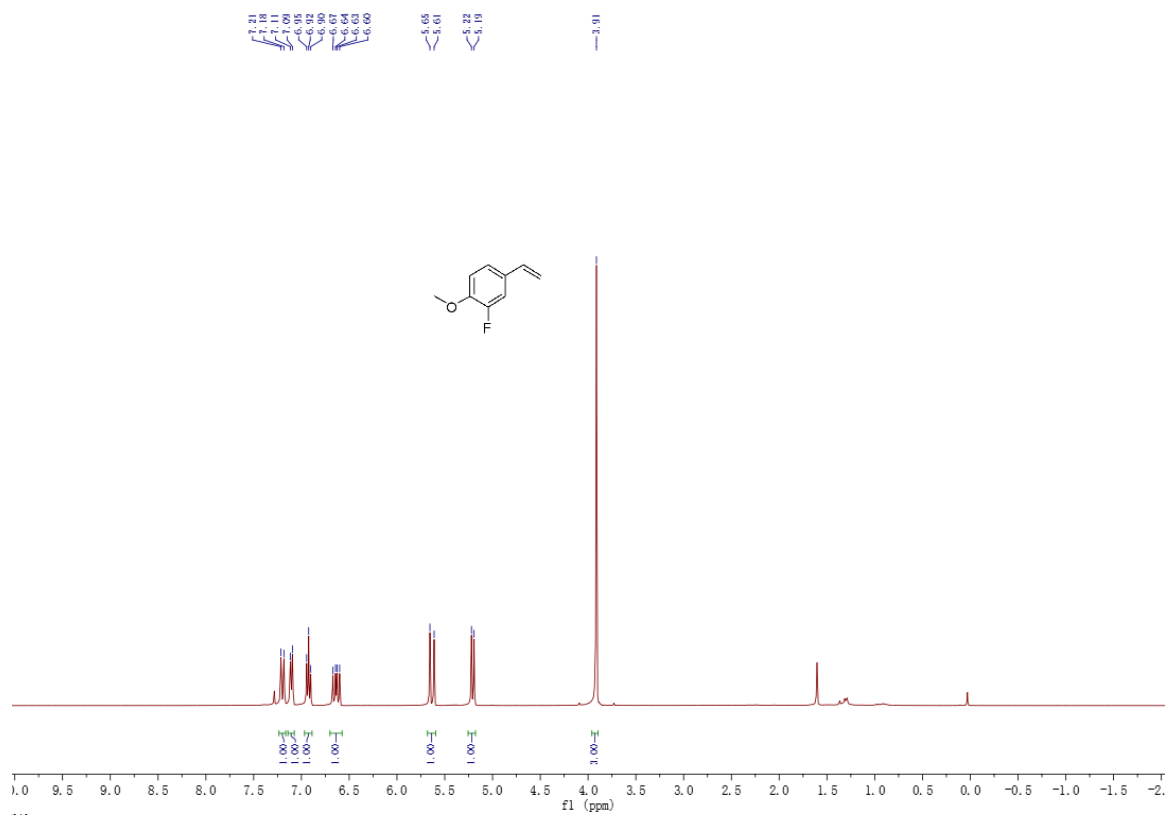
Figure. S-7 The emission spectrum of TPT (5 μ M) photocatalyst irradiated by 490 nm, 500 nm and 520 nm light (using CH_3CN as solvent).

VI. References

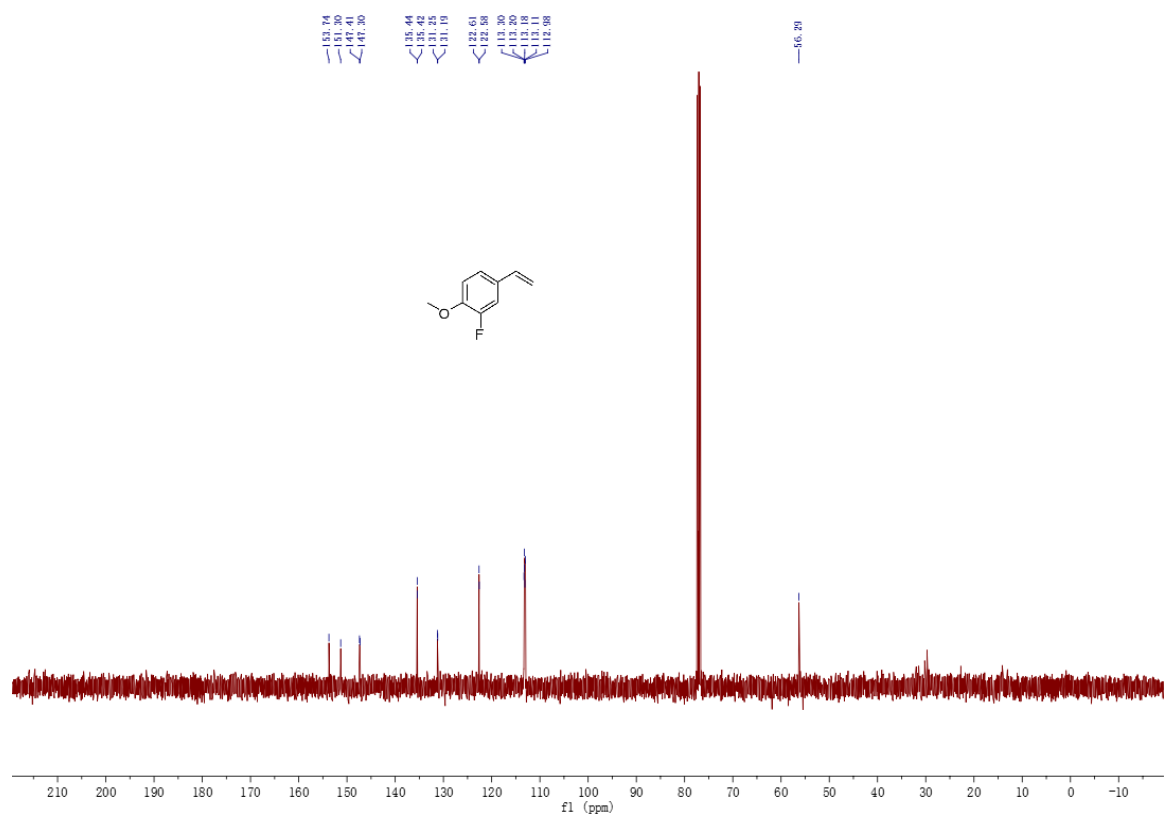
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VII. Spectral Copies of ^1H and ^{13}C NMR of Compounds Obtained in This Study

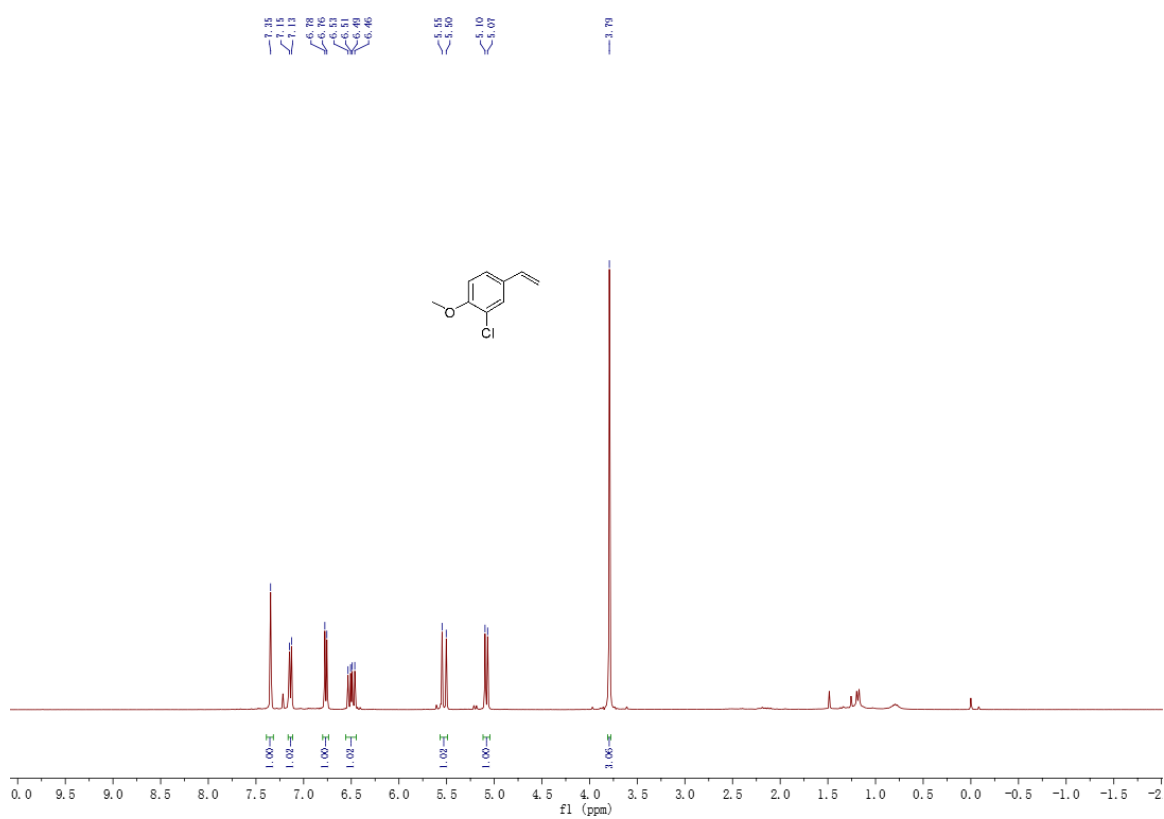
^1H NMR spectrum (400 MHz, CDCl_3) of **1f**



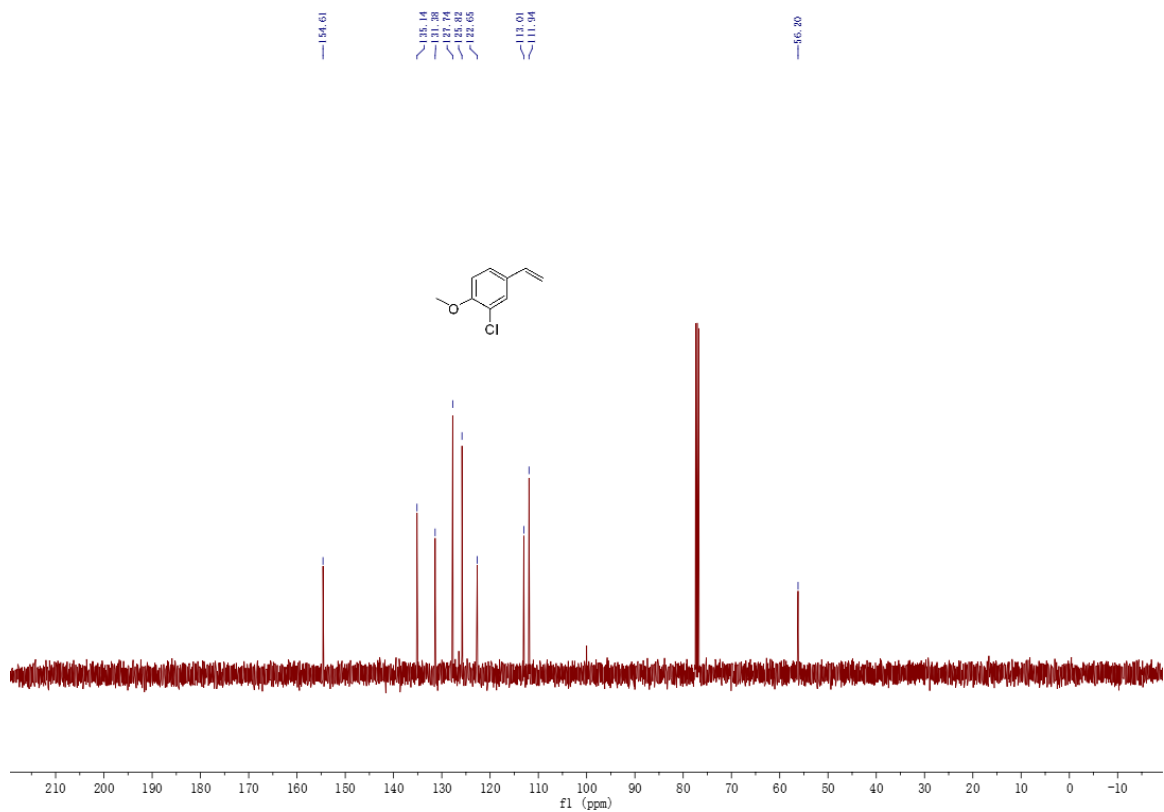
^{13}C NMR spectrum (100 MHz, CDCl_3) of **1f**



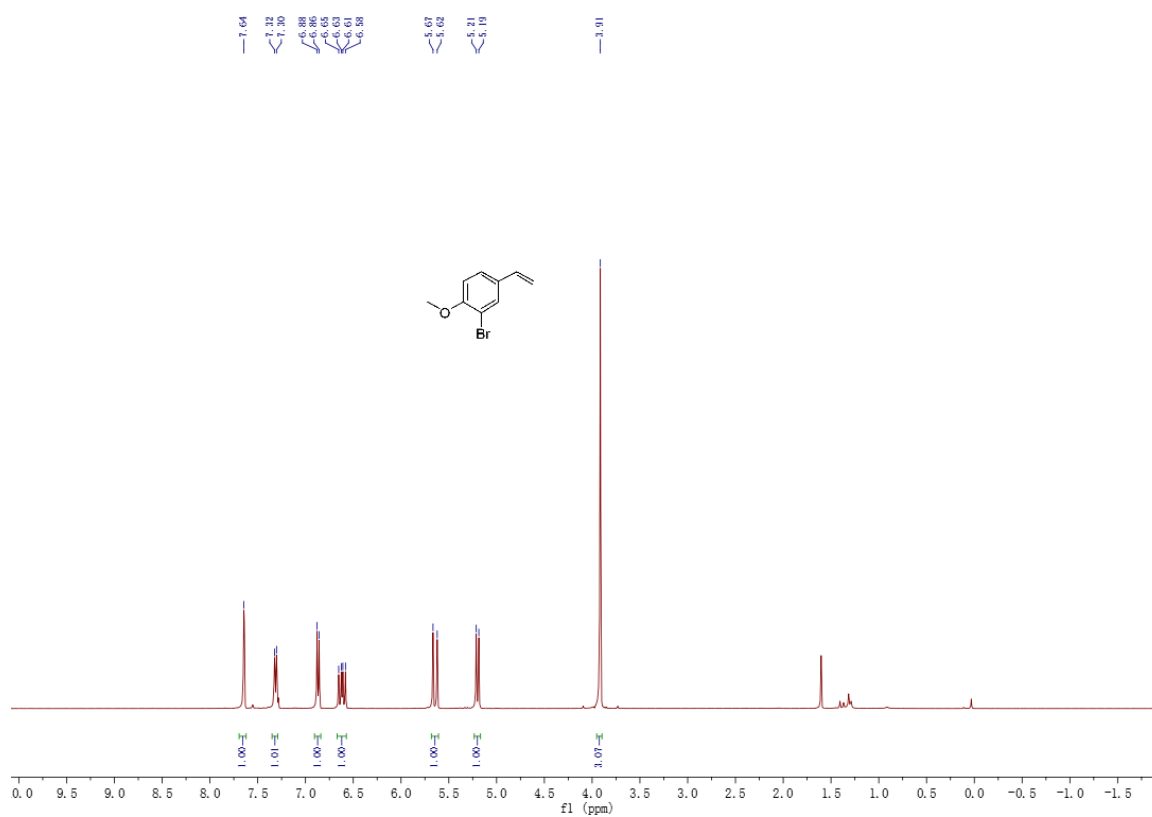
^1H NMR spectrum (400 MHz, CDCl_3) of **1g**



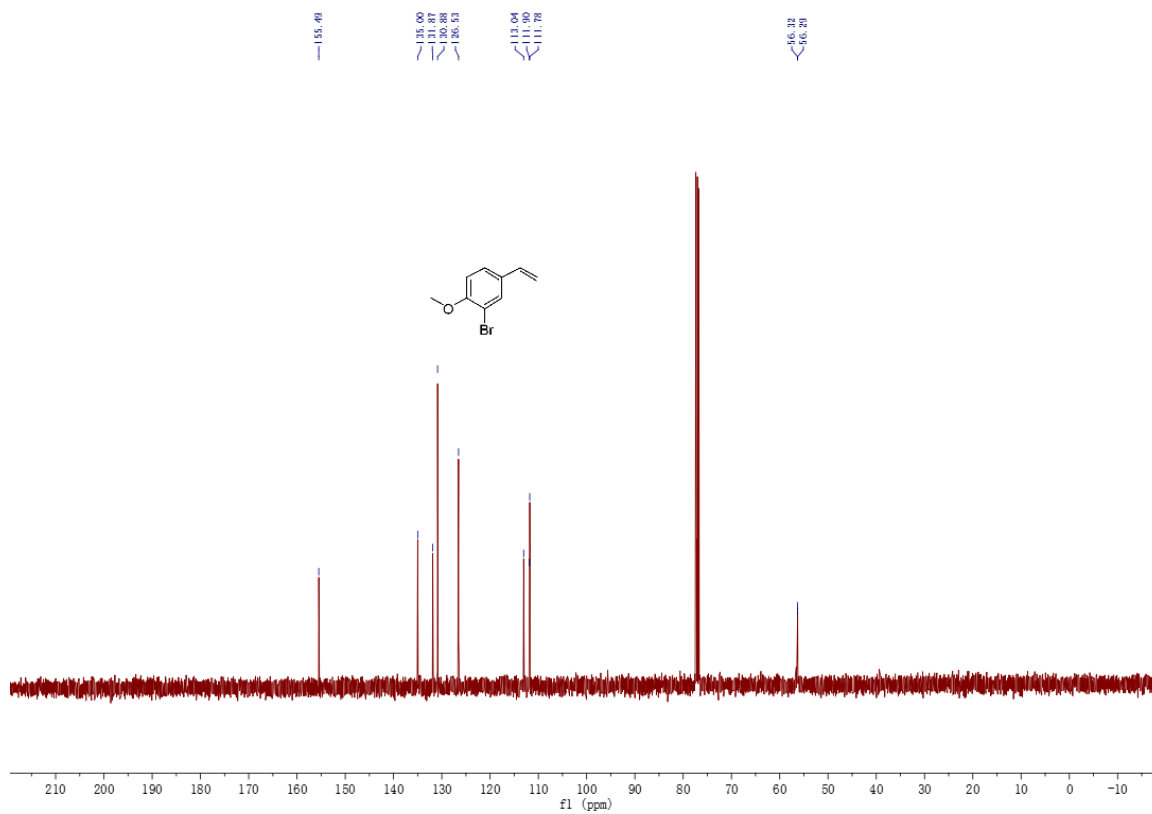
^{13}C NMR spectrum (100 MHz, CDCl_3) of **1g**



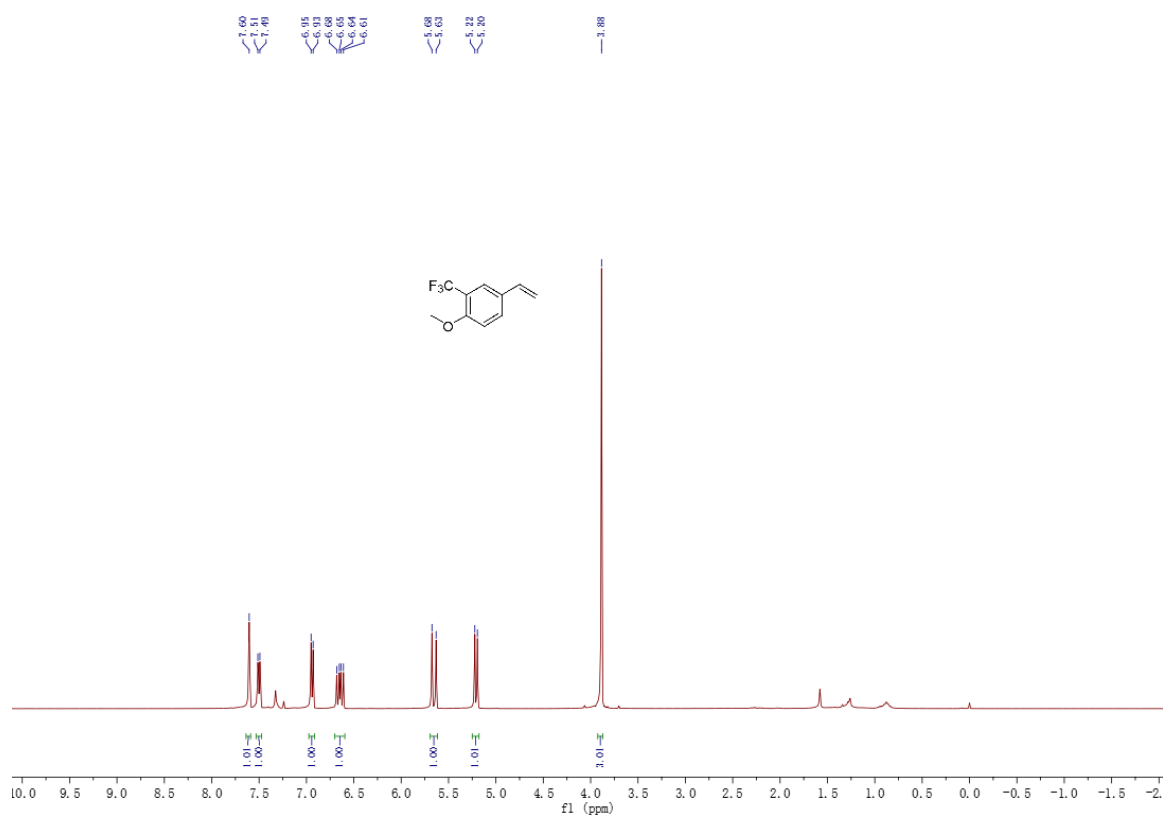
^1H NMR spectrum (400 MHz, CDCl_3) of **1h**



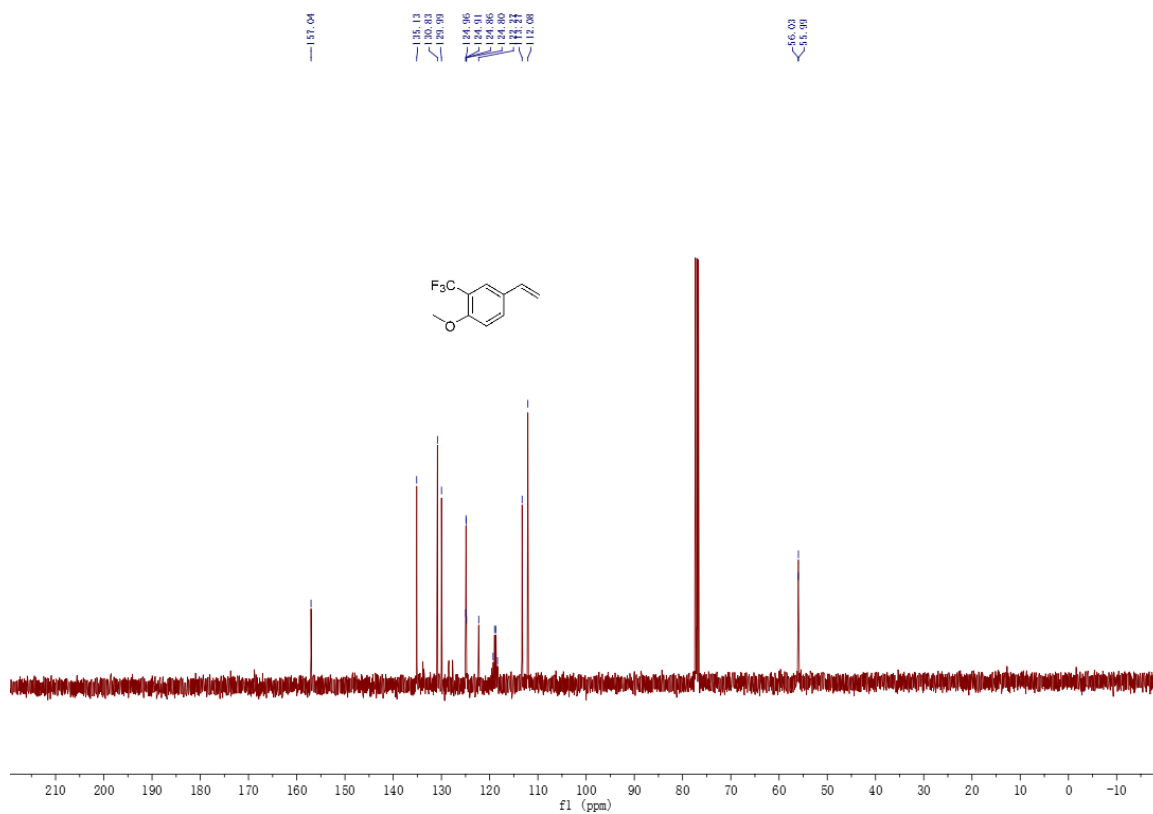
^{13}C NMR spectrum (100 MHz, CDCl_3) of **1h**



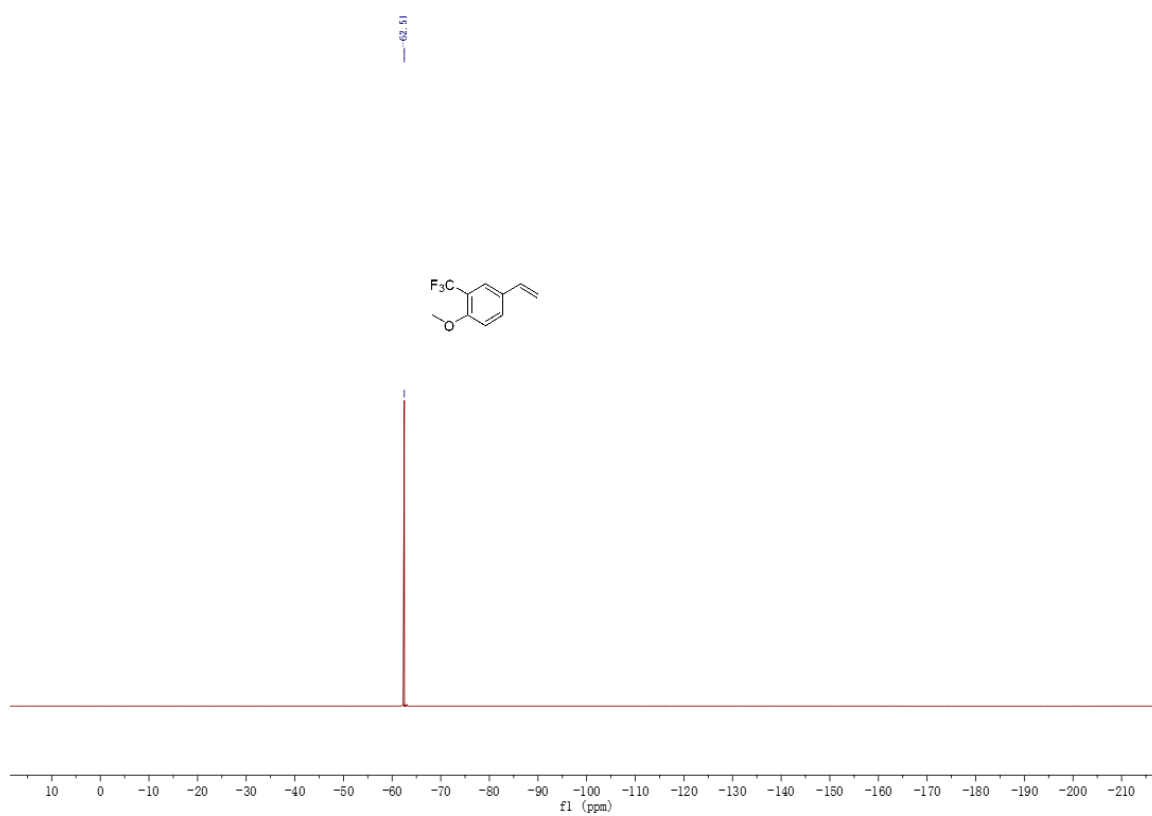
^1H NMR spectrum (400 MHz, CDCl_3) of **1i**



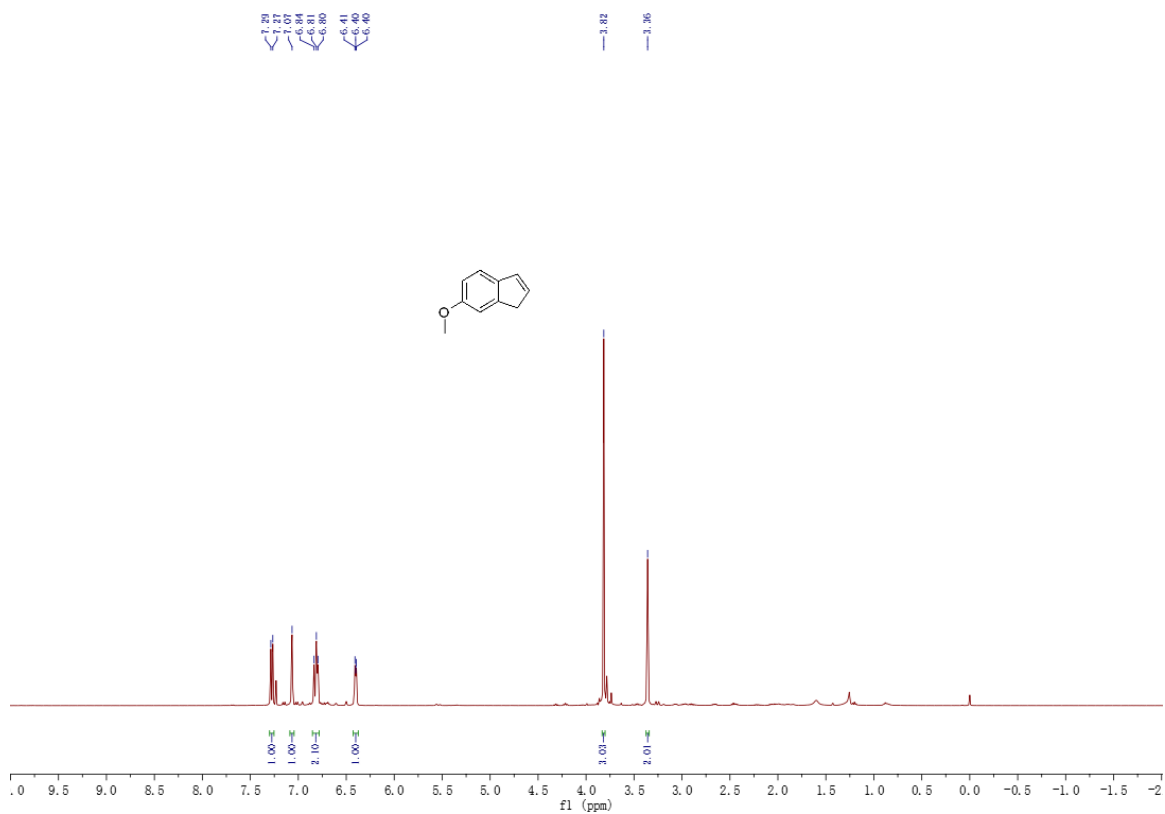
^{13}C NMR spectrum (100 MHz, CDCl_3) of **1i**



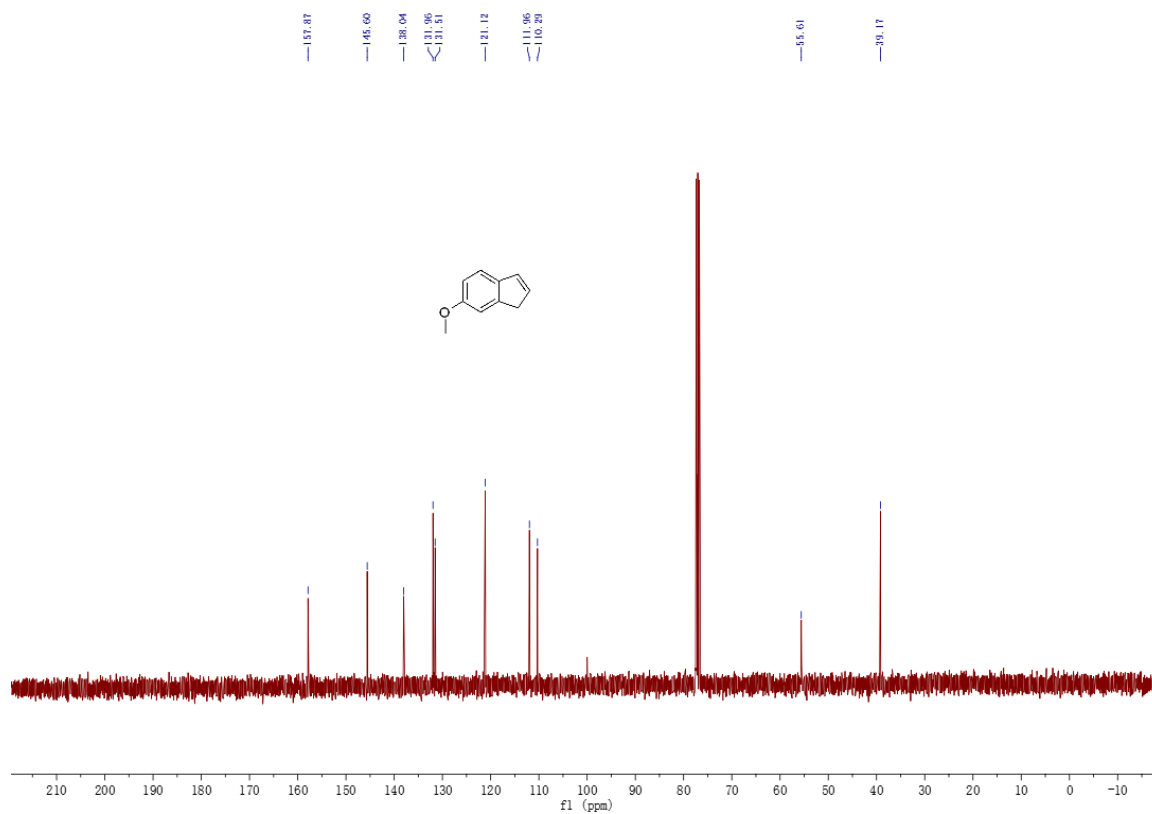
^{19}F NMR spectrum (376 MHz, CDCl_3) of **1i**



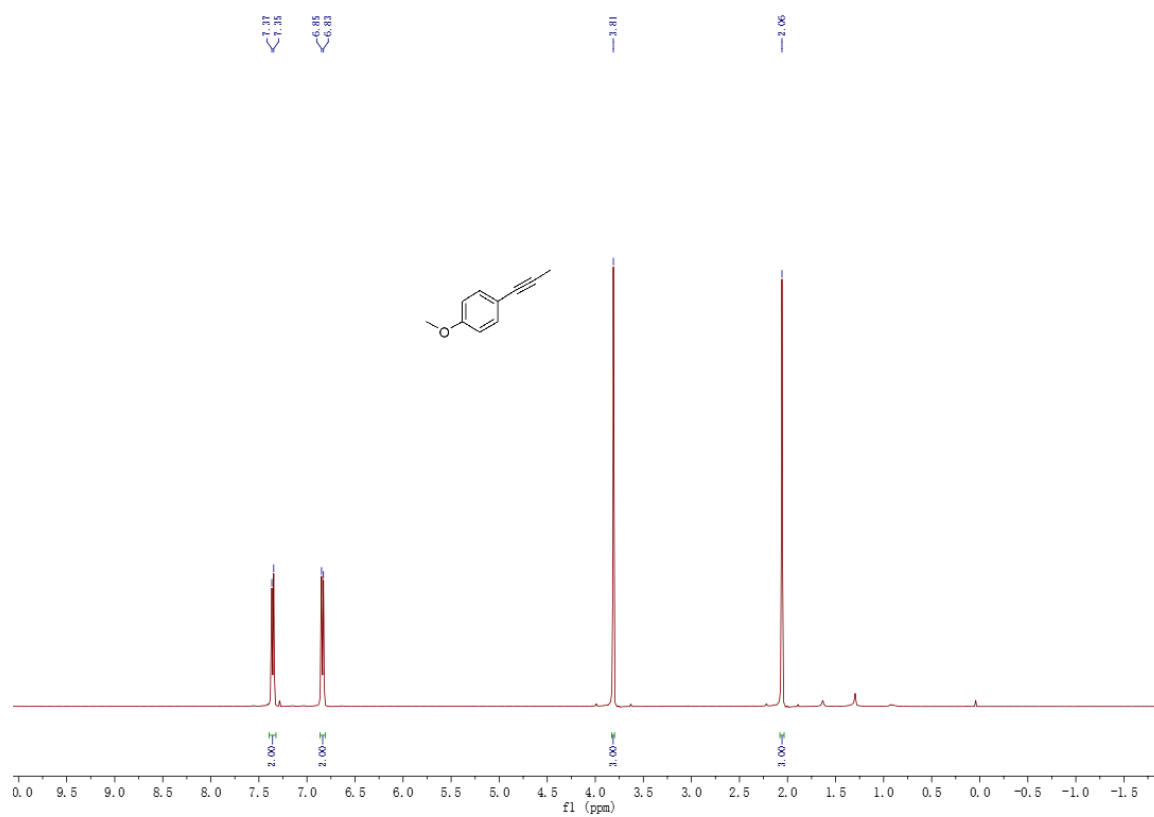
^1H NMR spectrum (400 MHz, CDCl_3) of **1k**



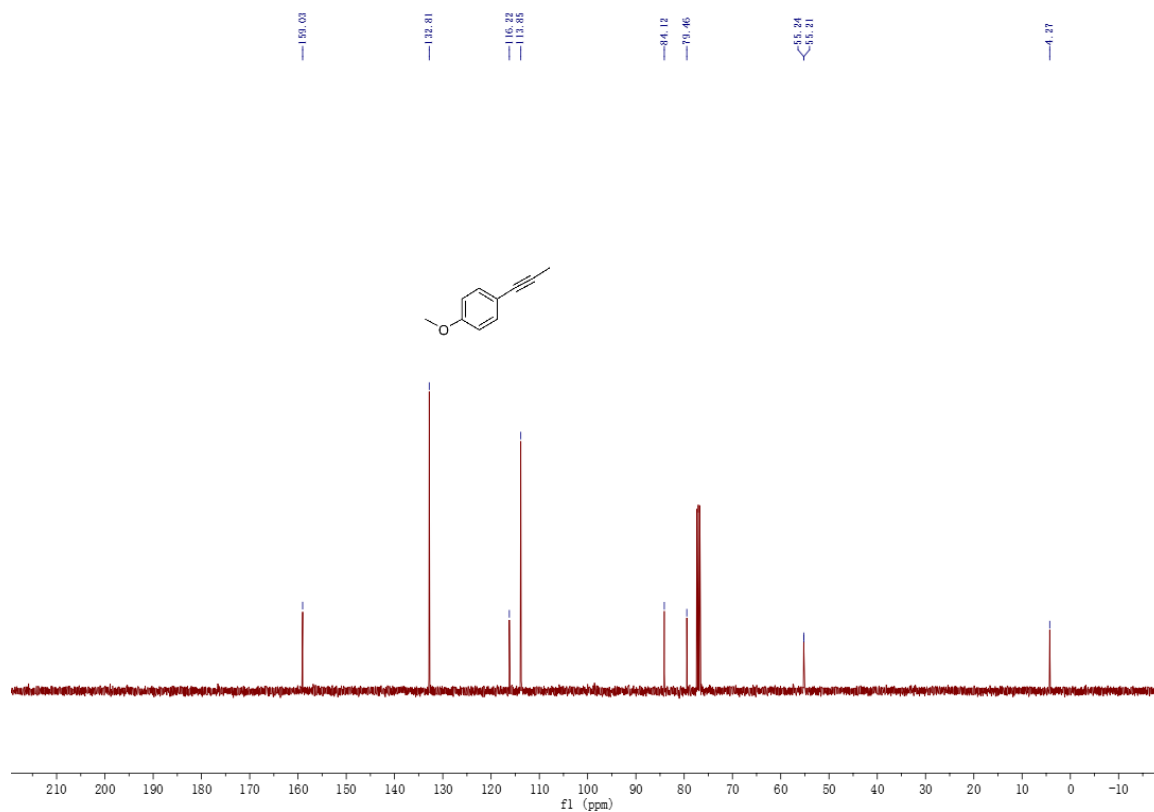
^{13}C NMR spectrum (100 MHz, CDCl_3) of **1k**



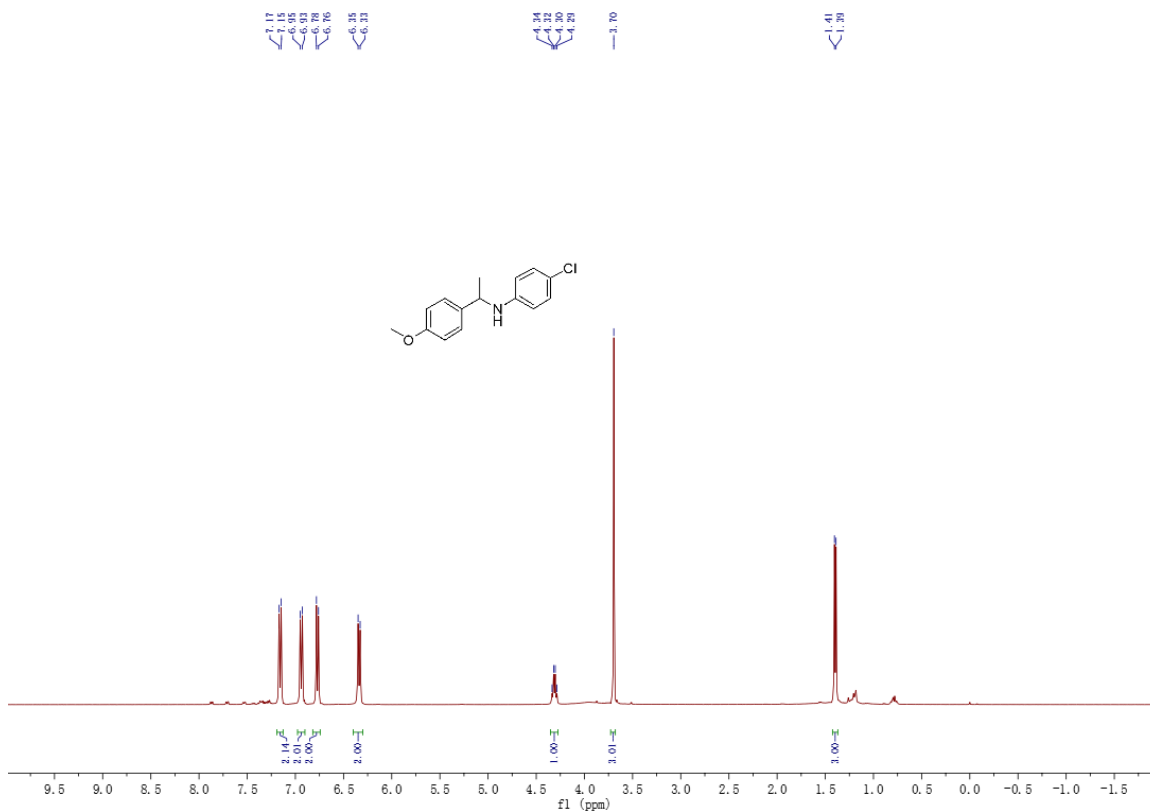
^1H NMR spectrum (400 MHz, CDCl_3) of **4b**



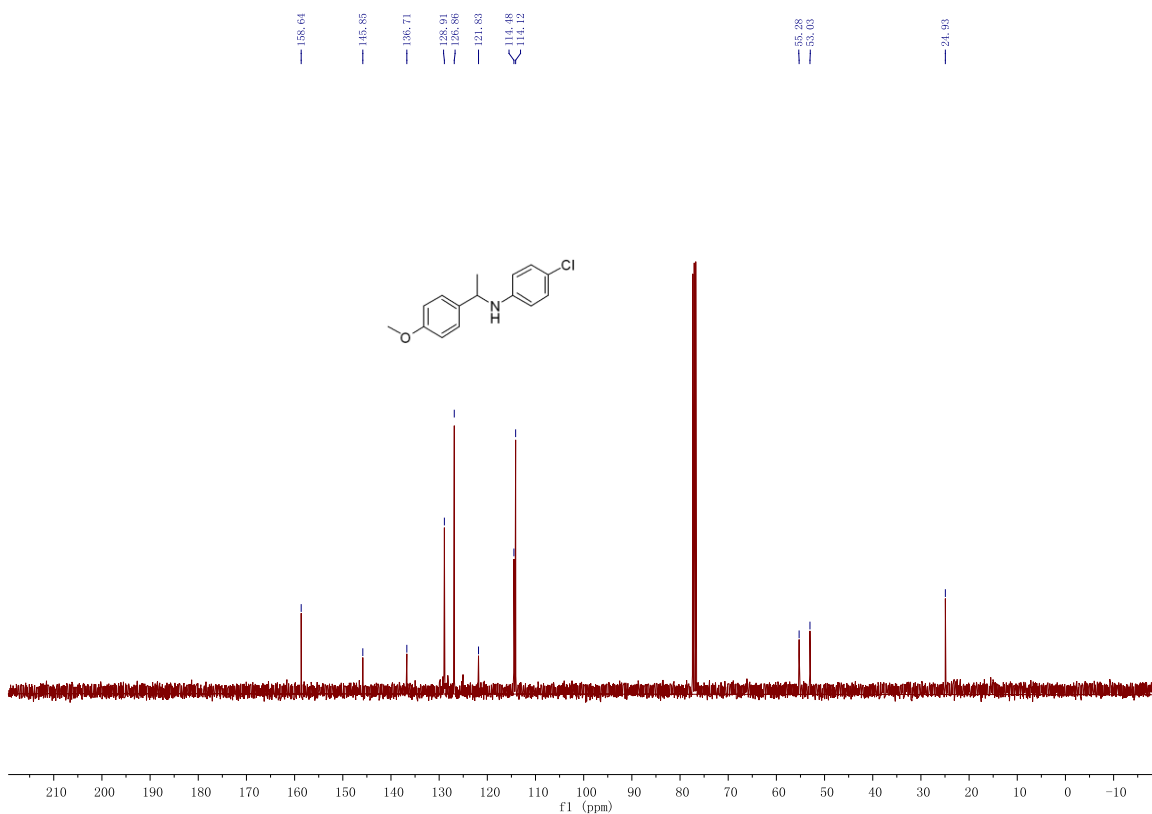
^{13}C NMR spectrum (100 MHz, CDCl_3) of **4b**



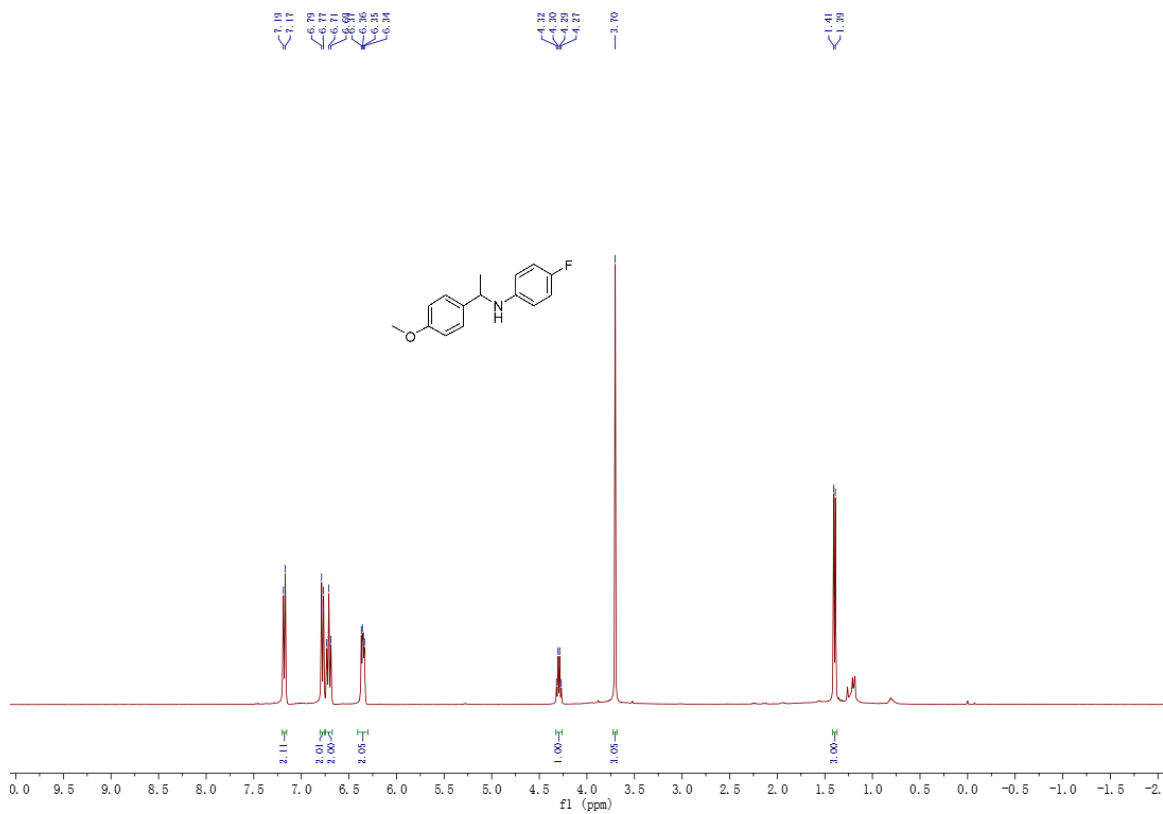
^1H NMR spectrum (400 MHz, CDCl_3) of **3-1a**



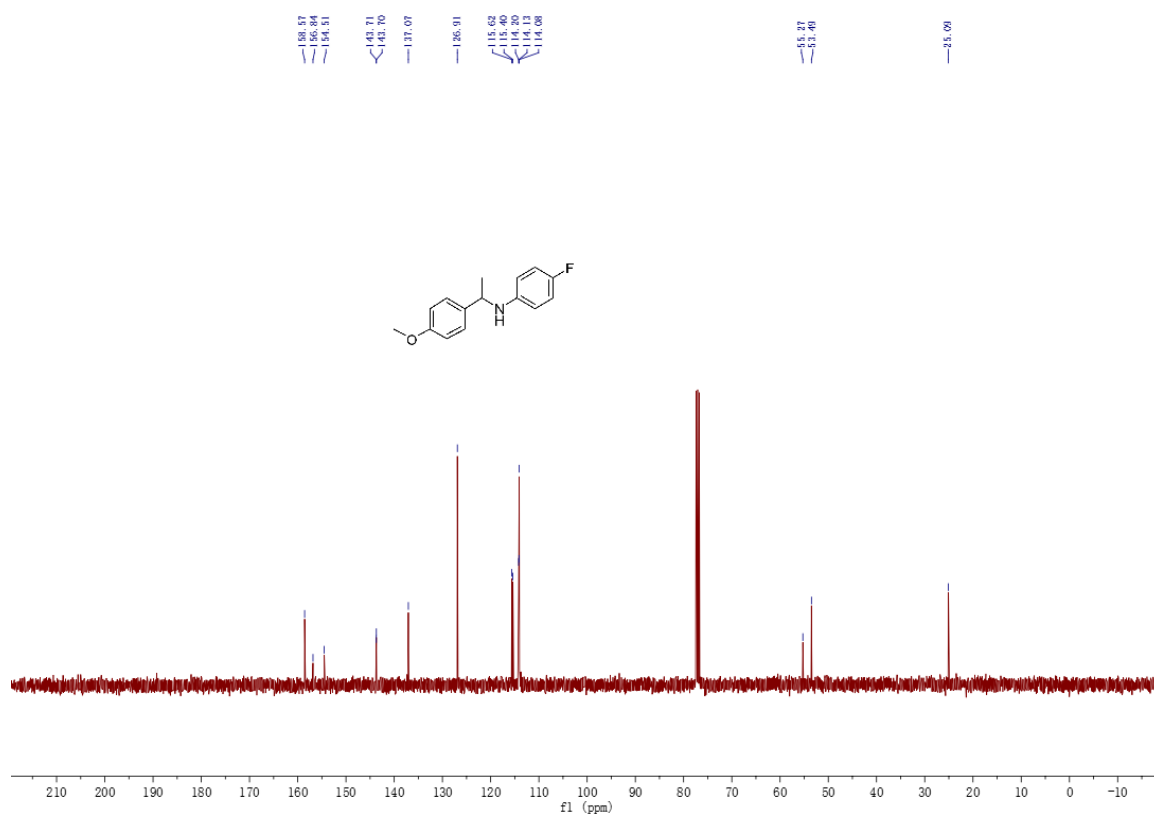
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3-1a**



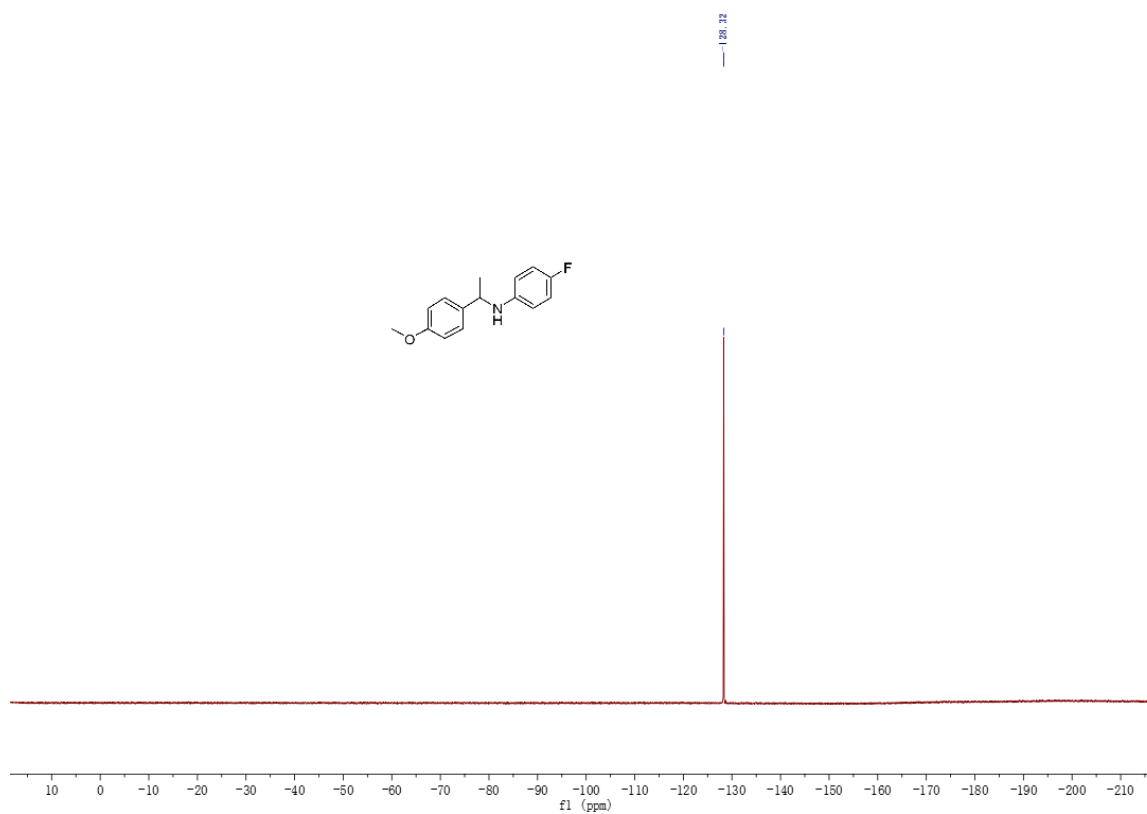
^1H NMR spectrum (400 MHz, CDCl_3) of **3-1b**



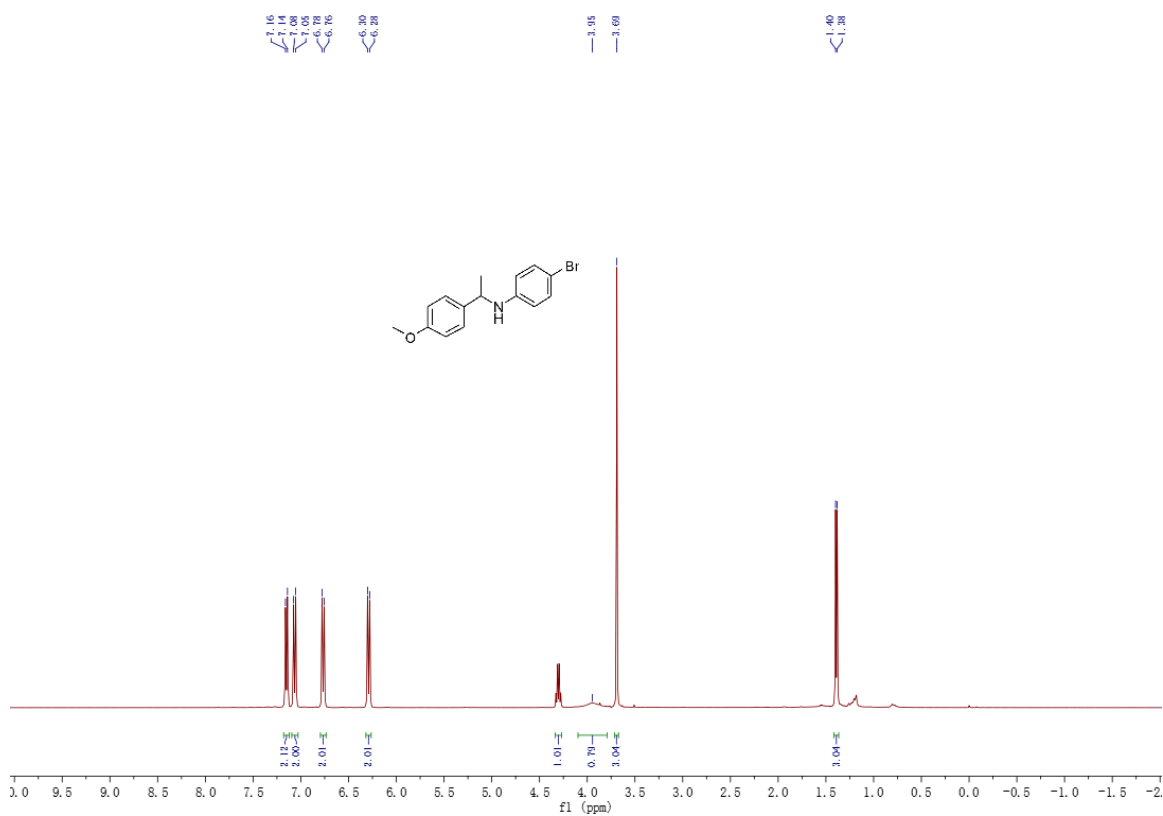
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3-1b**



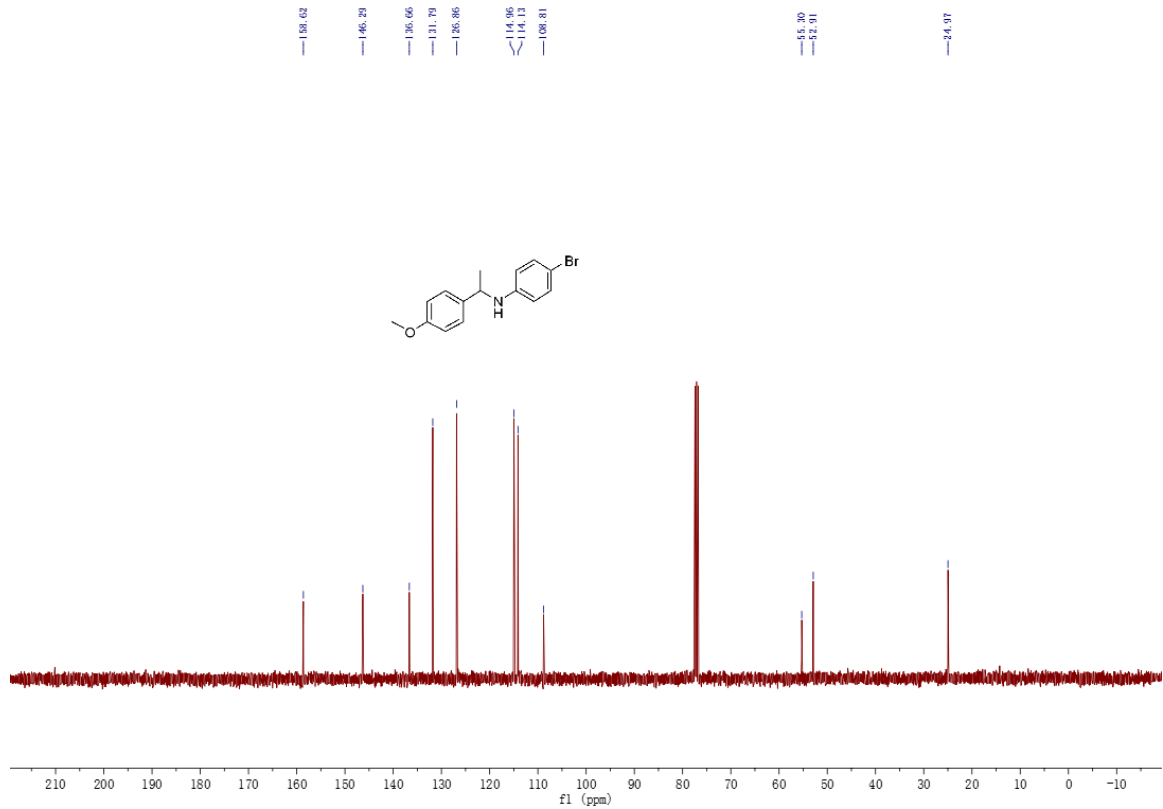
^{19}F NMR spectrum (376 MHz, CDCl_3) of **3-1b**



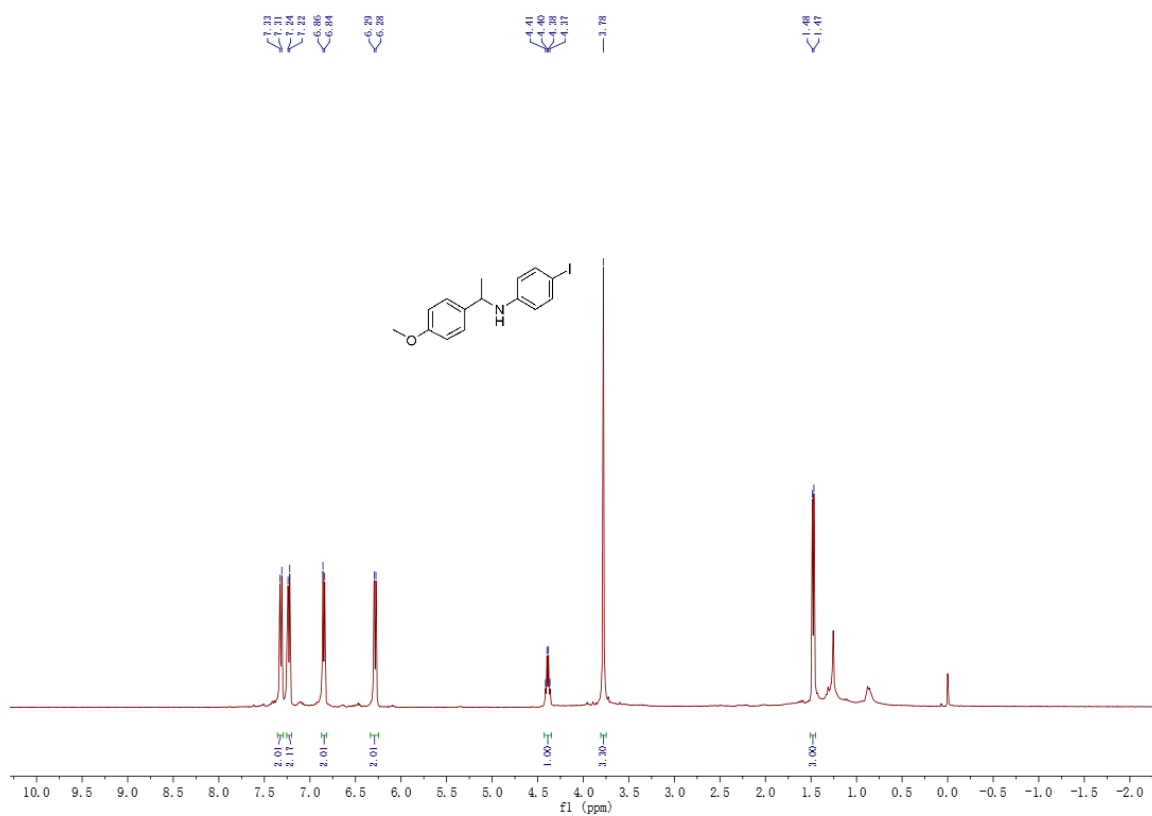
^1H NMR spectrum (400 MHz, CDCl_3) of **3-1c**



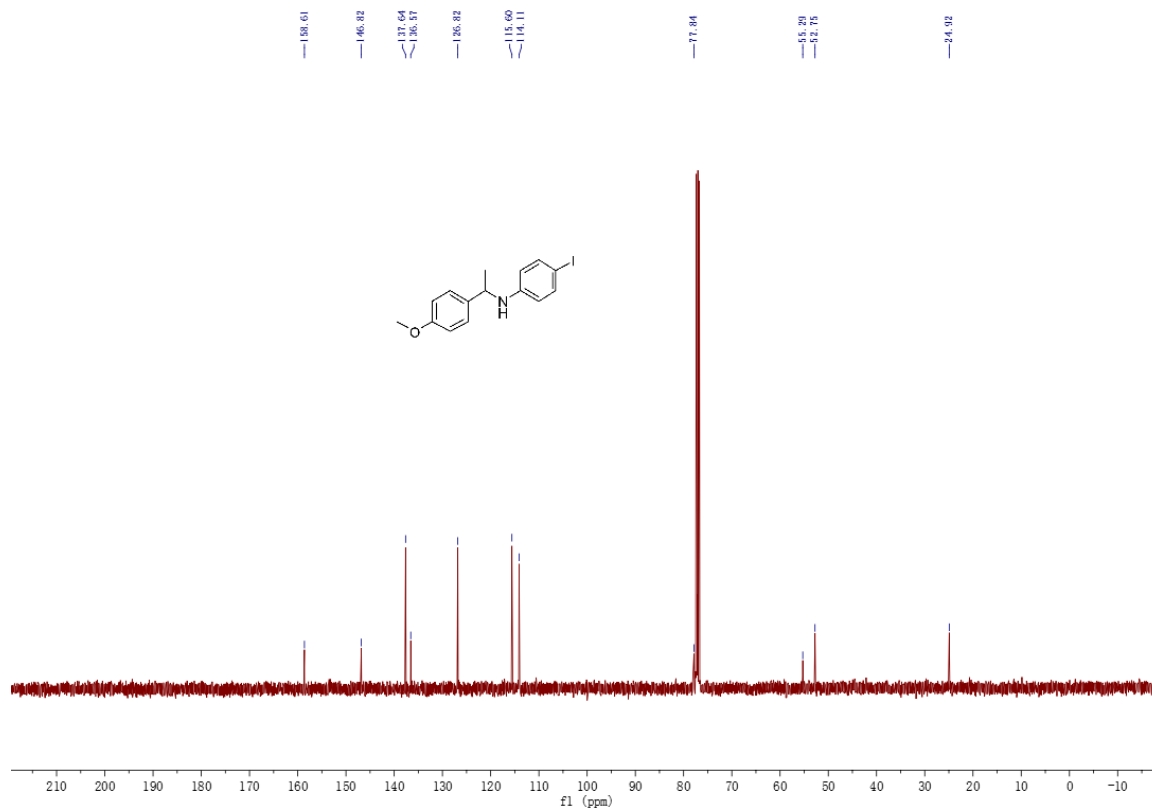
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3-1c**



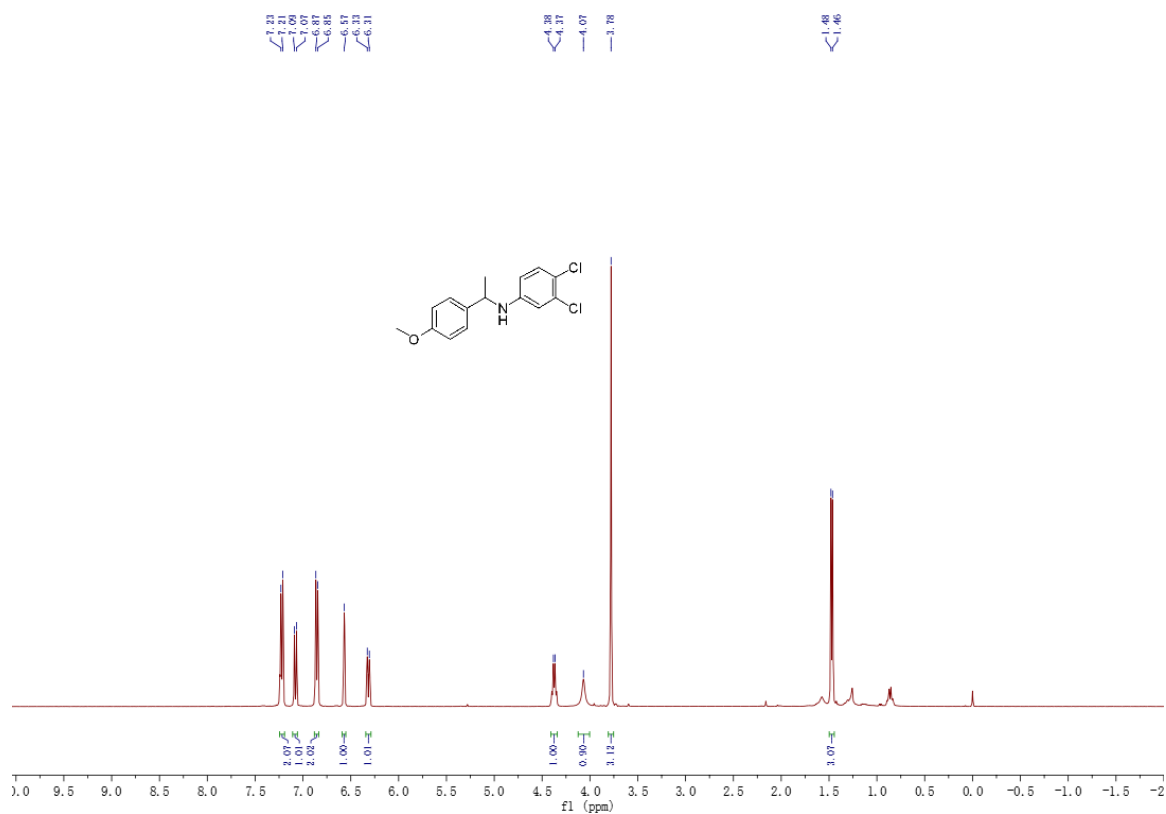
^1H NMR spectrum (400 MHz, CDCl_3) of **3-1d**



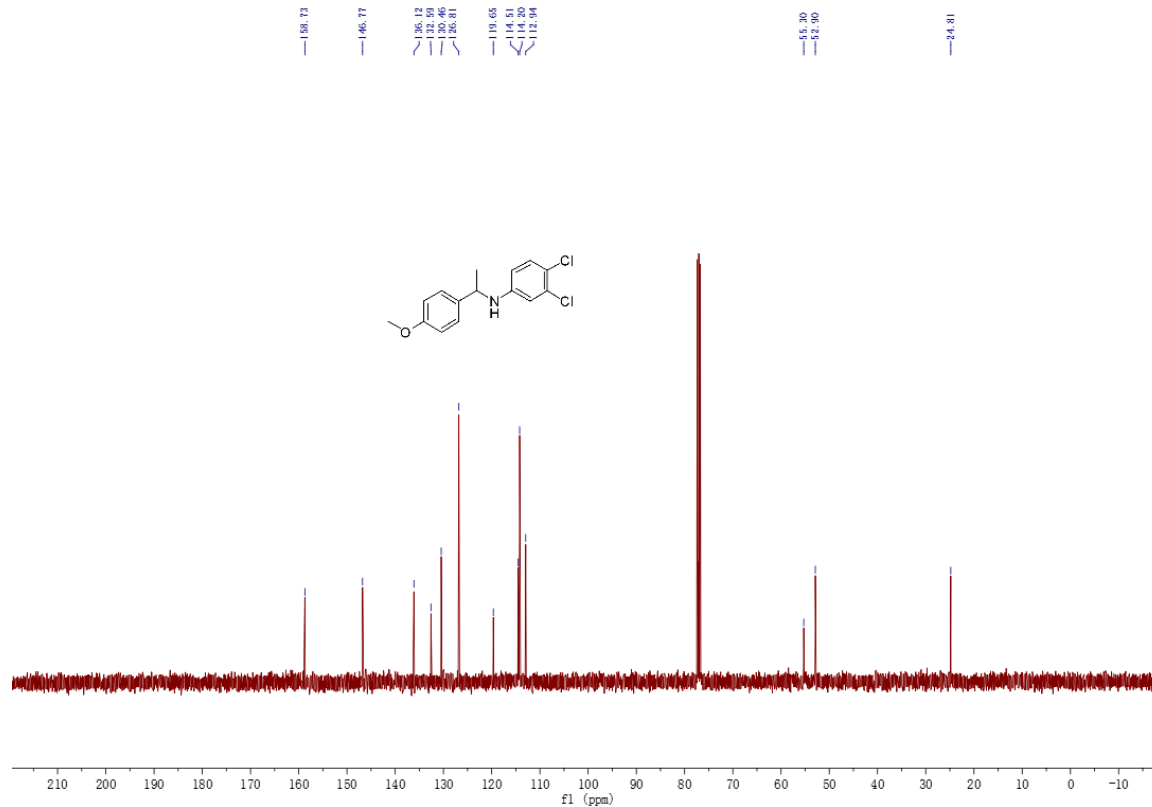
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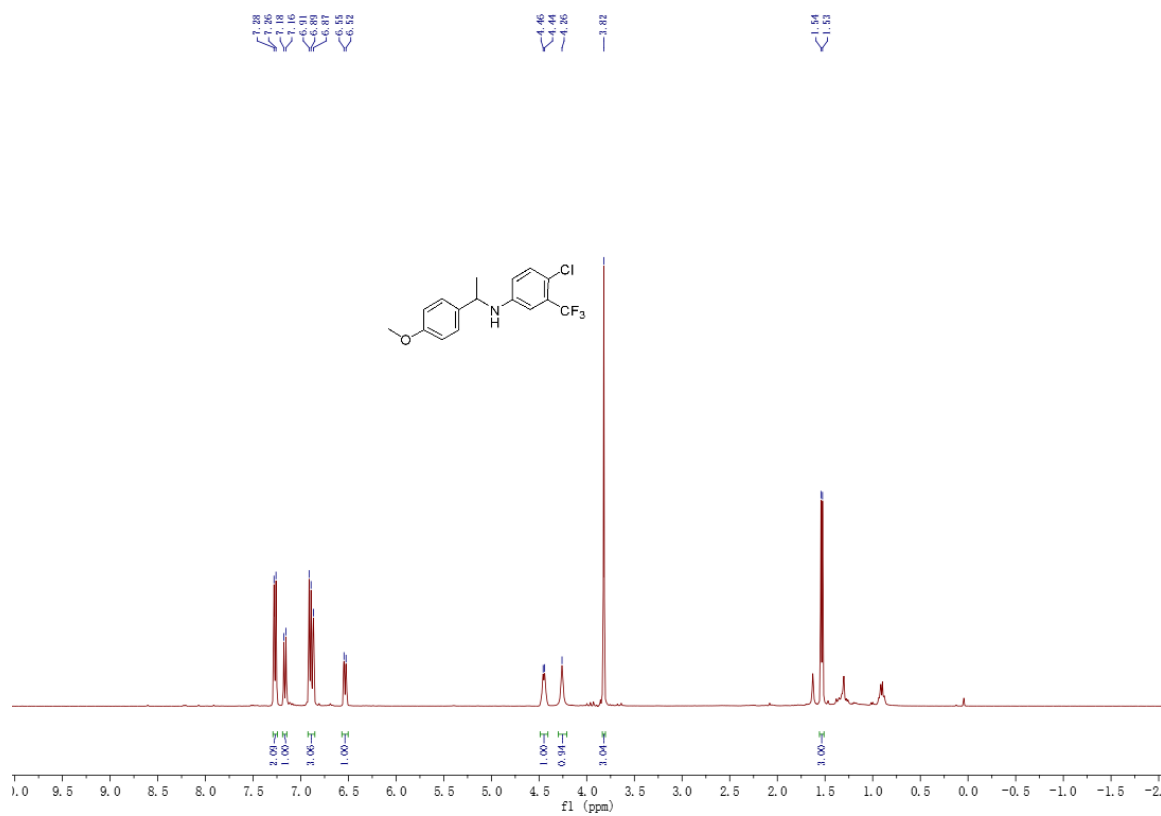
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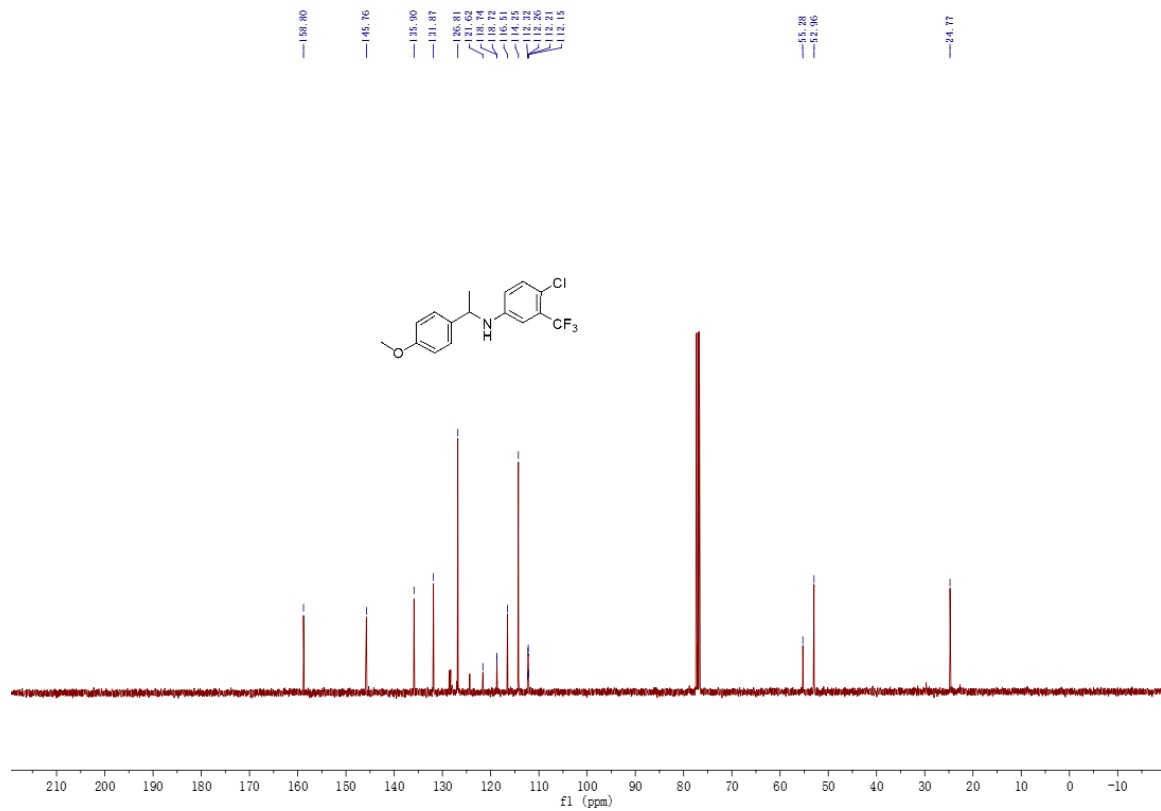
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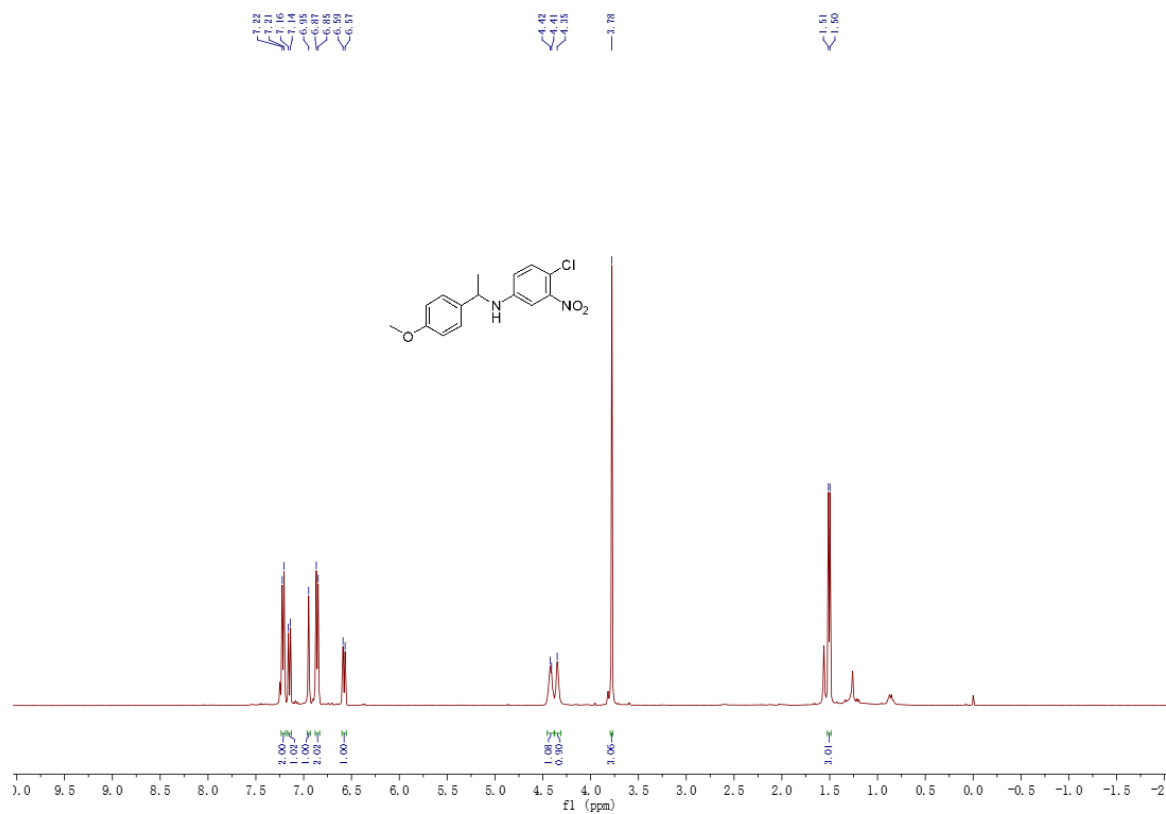
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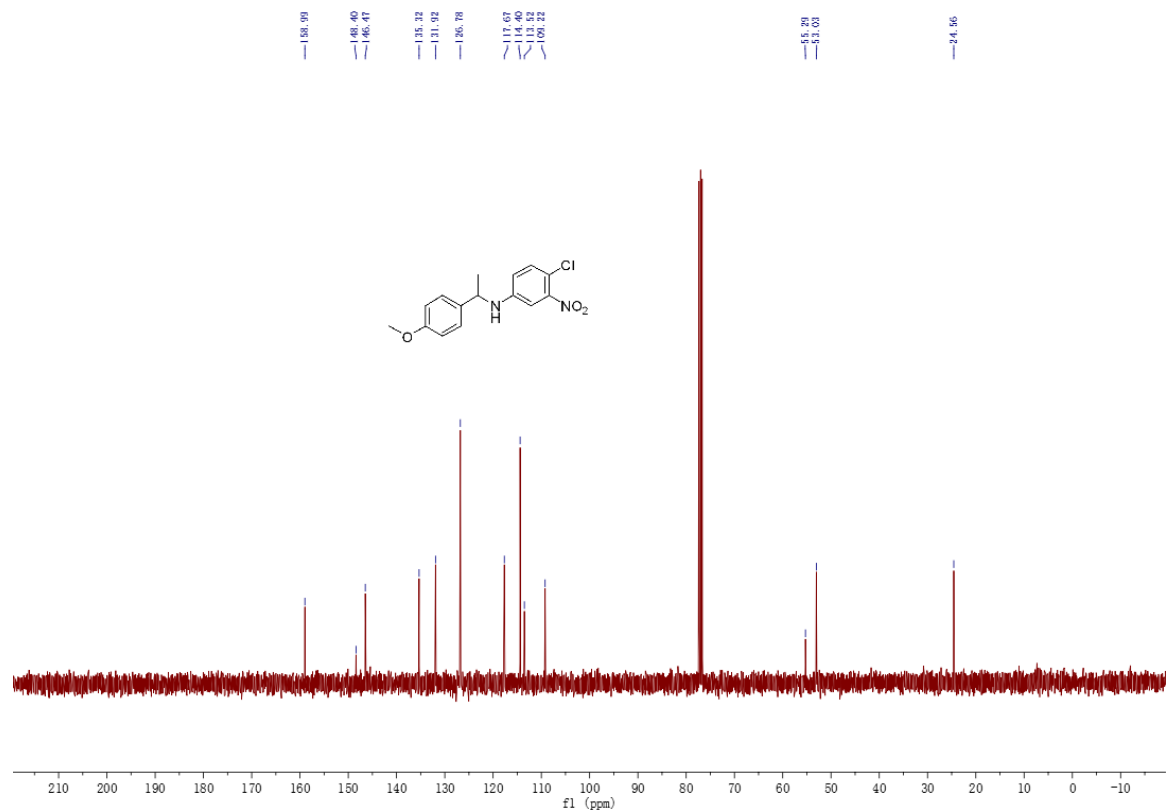
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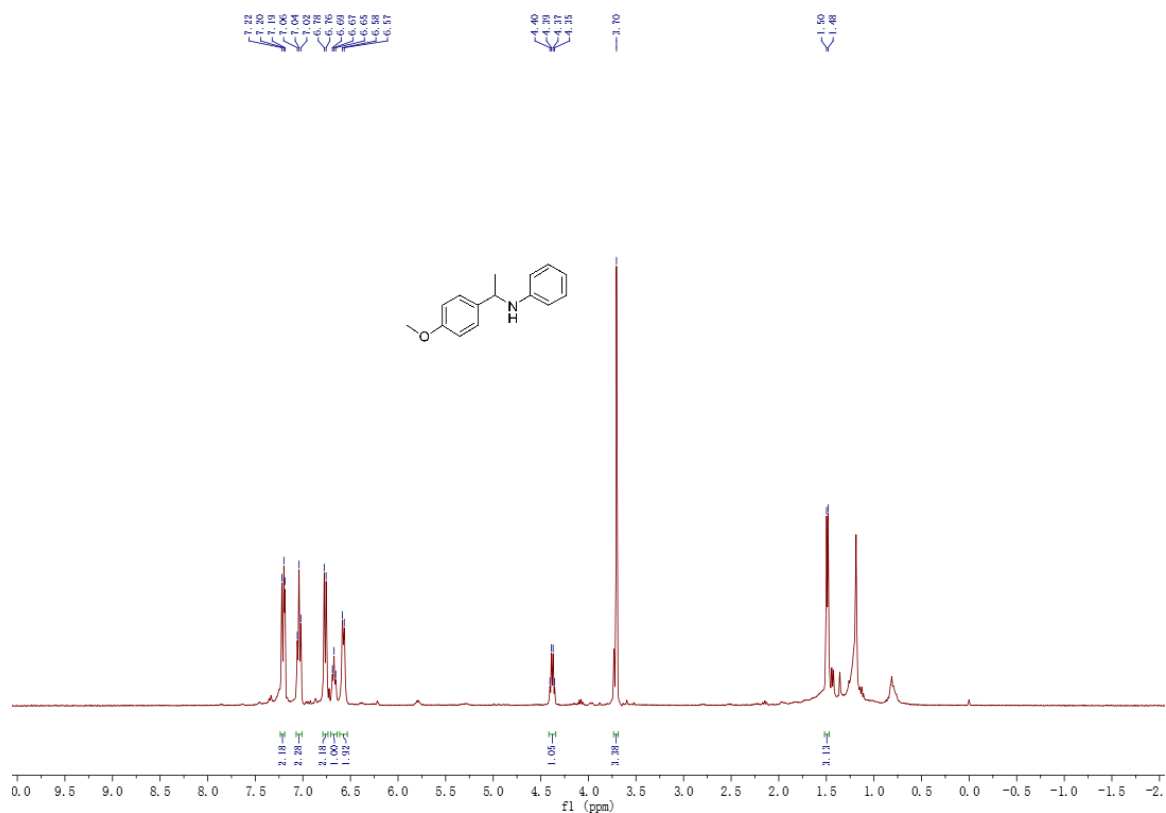
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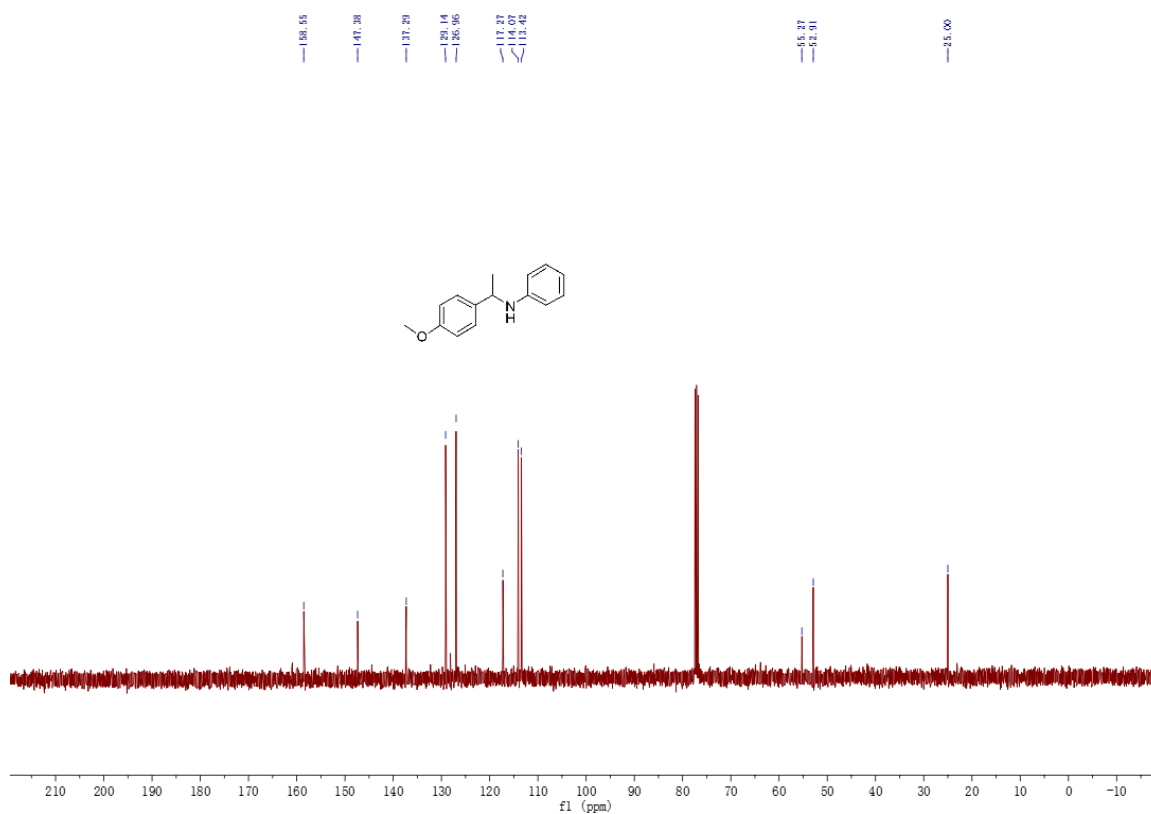
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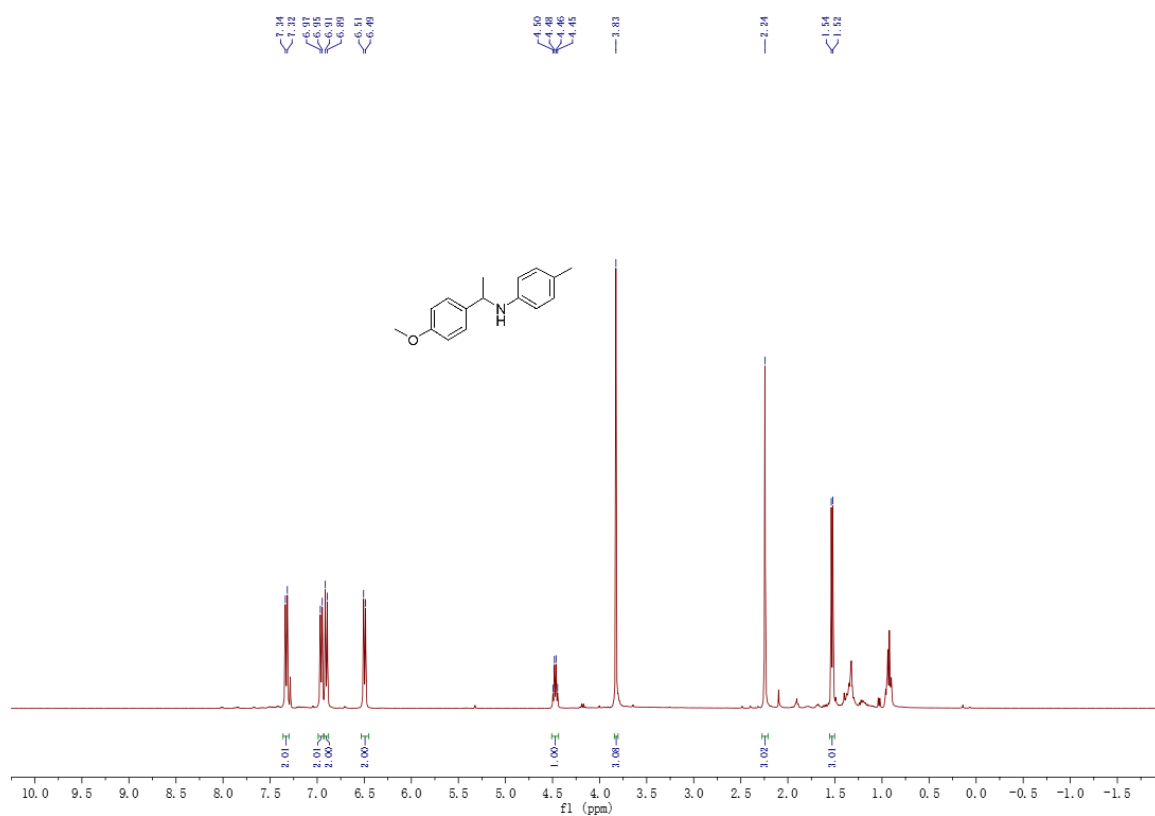
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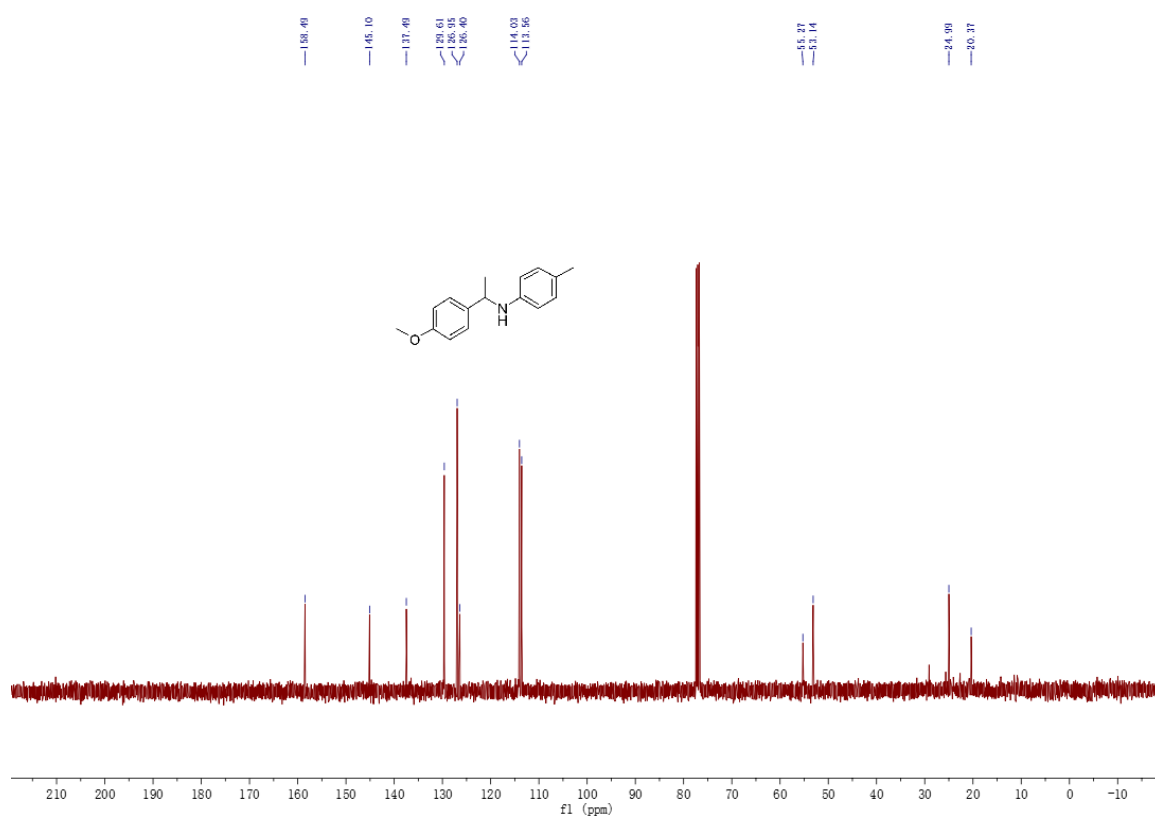
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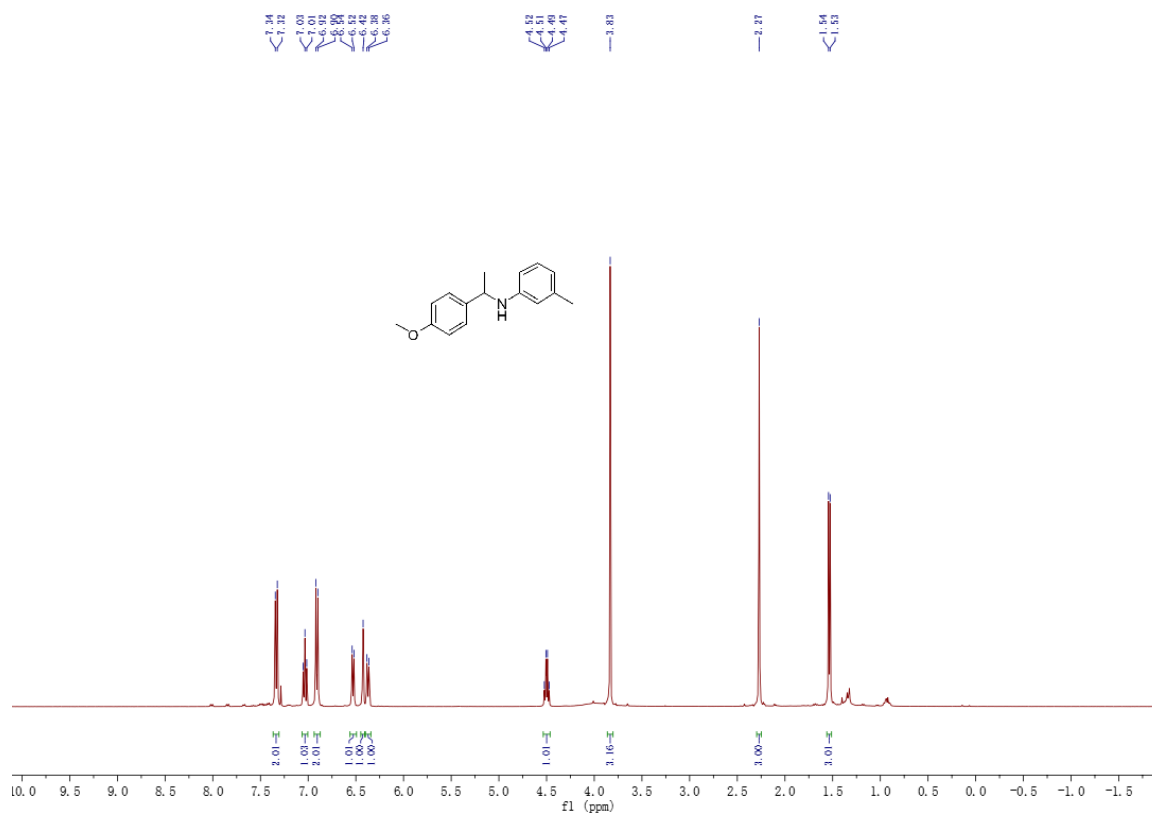
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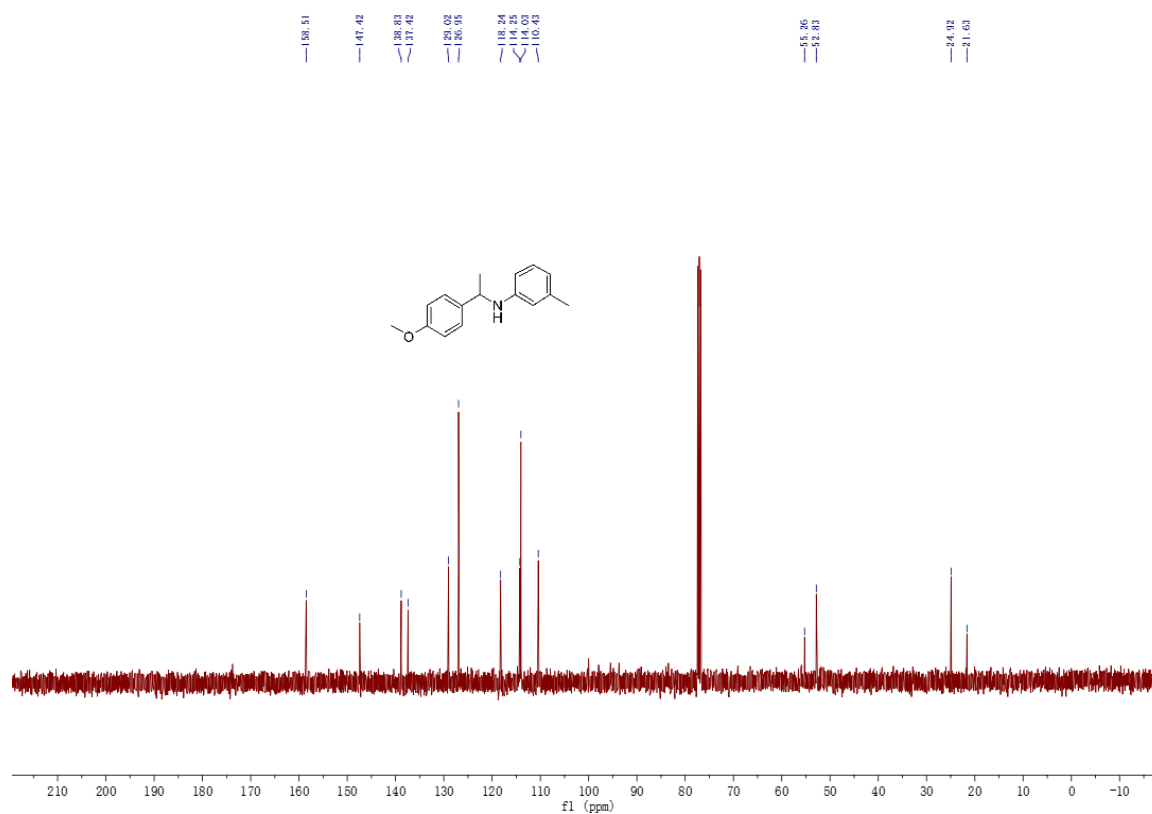
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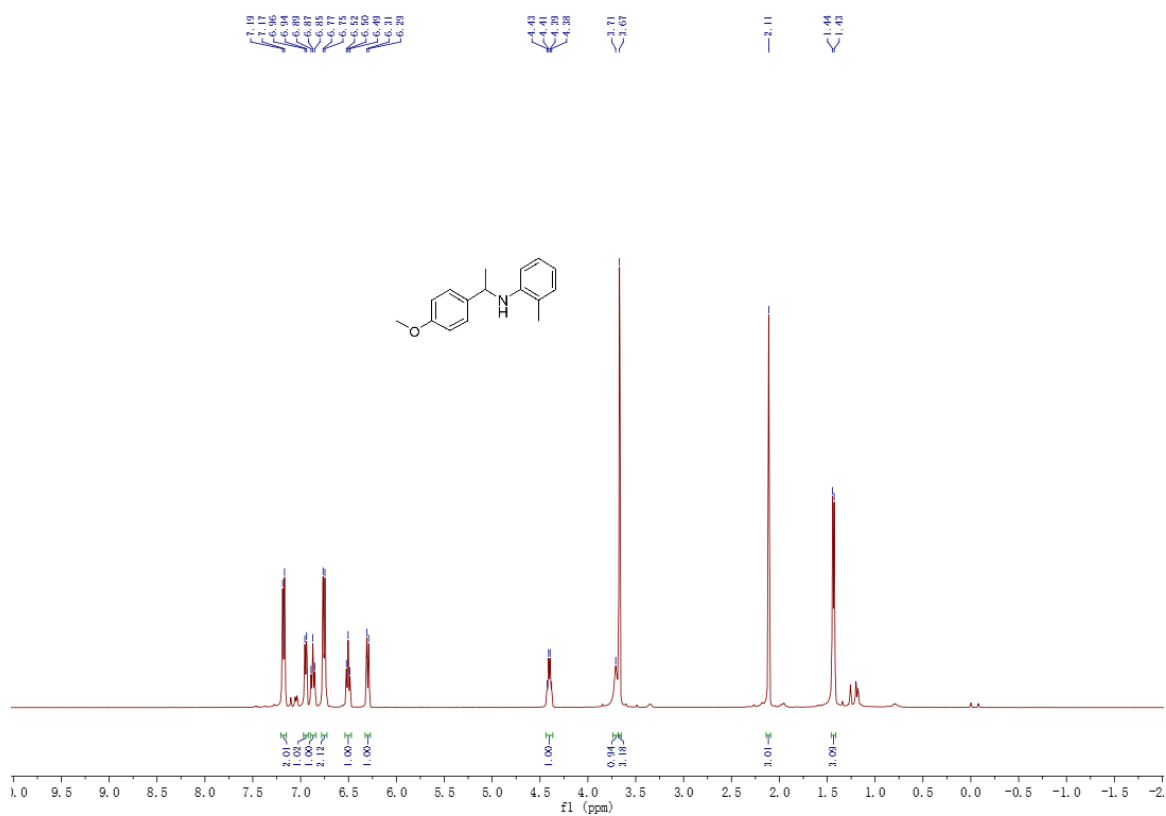
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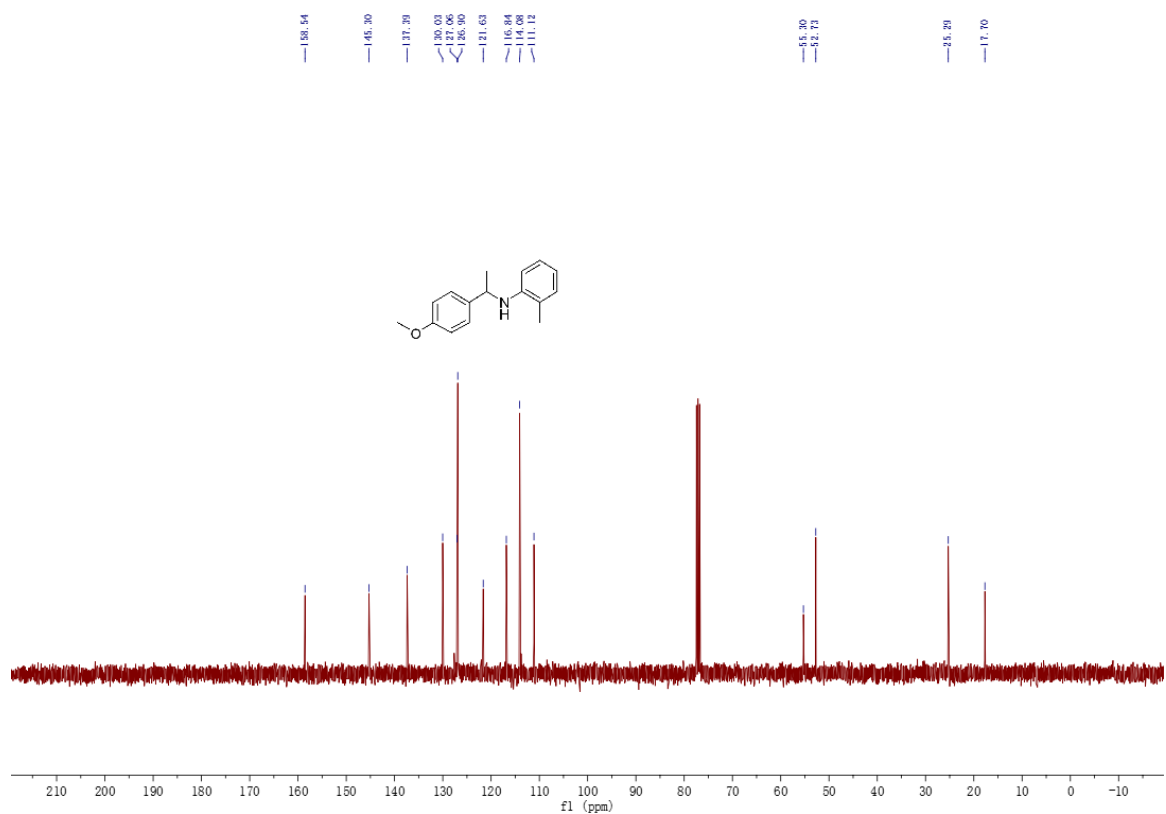
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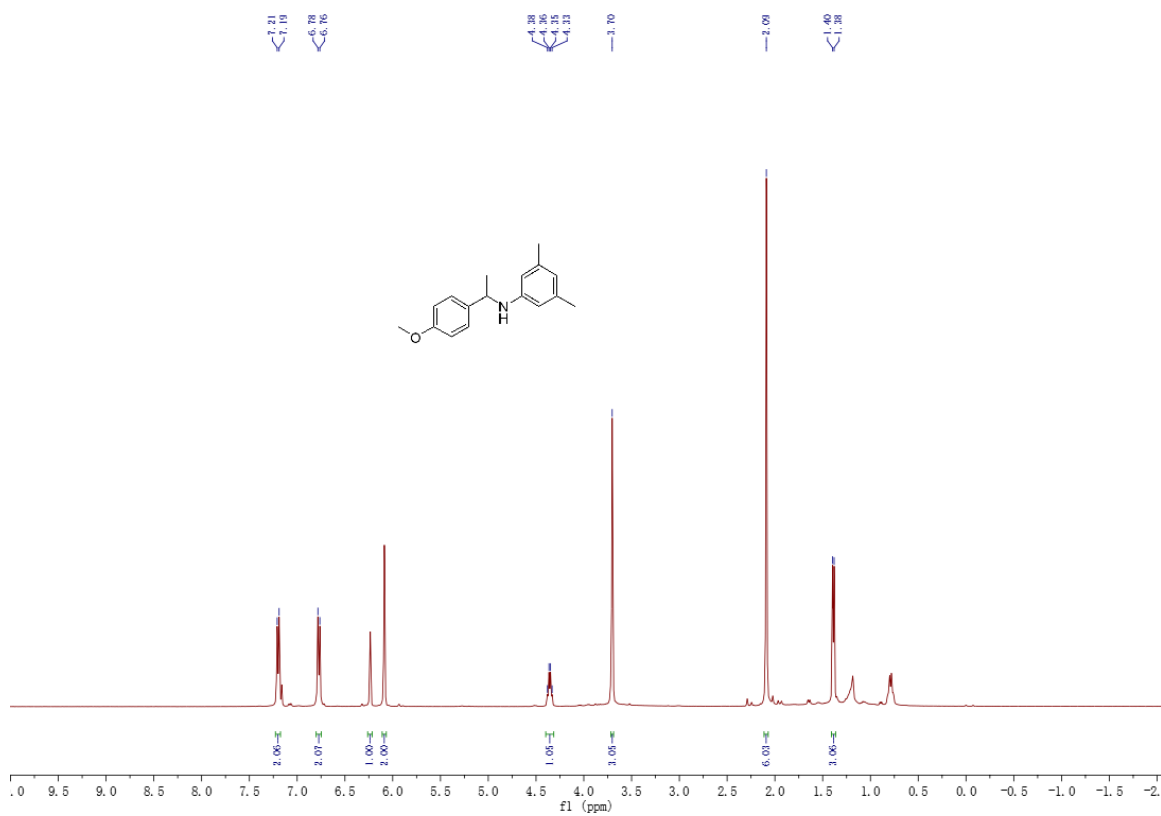
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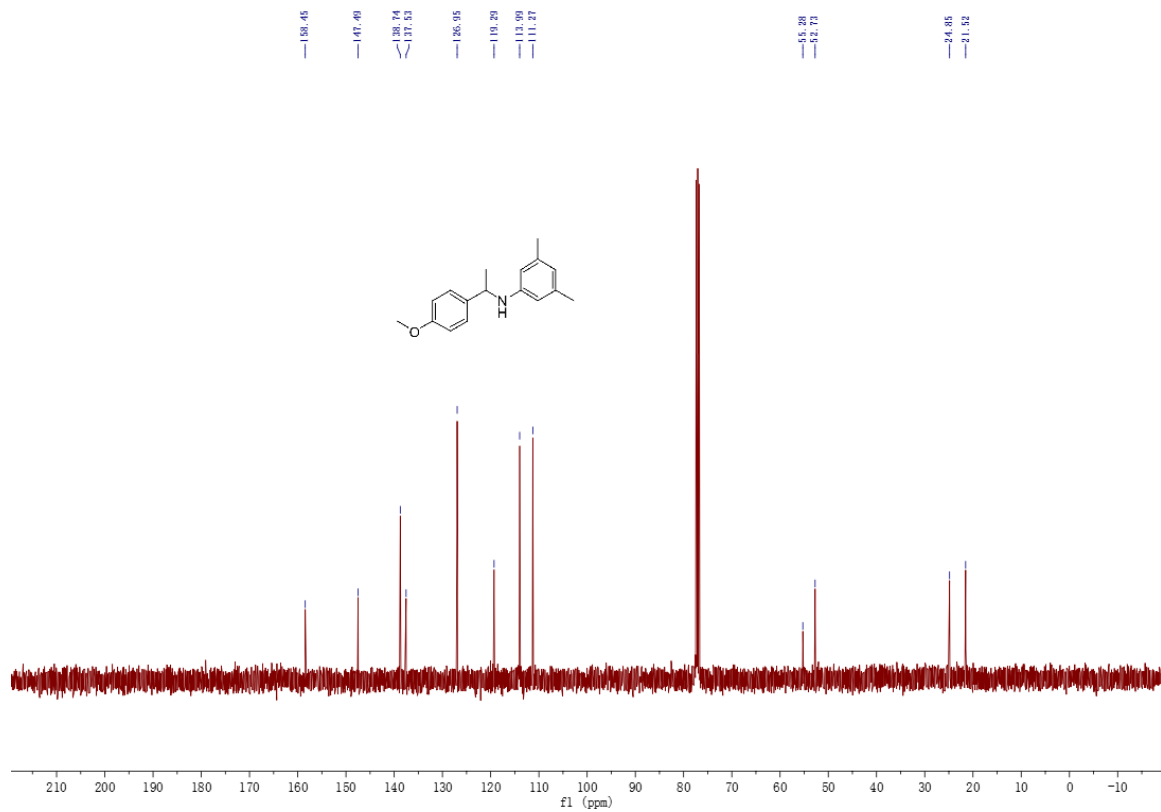
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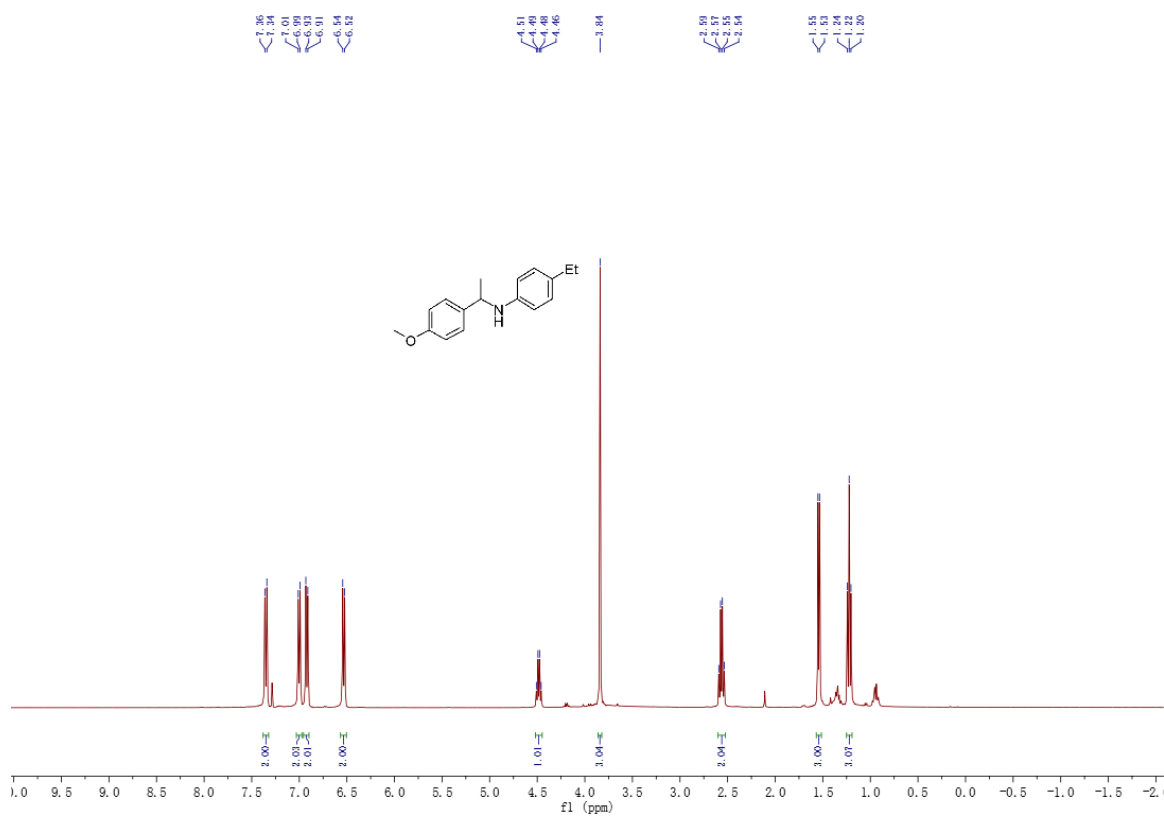
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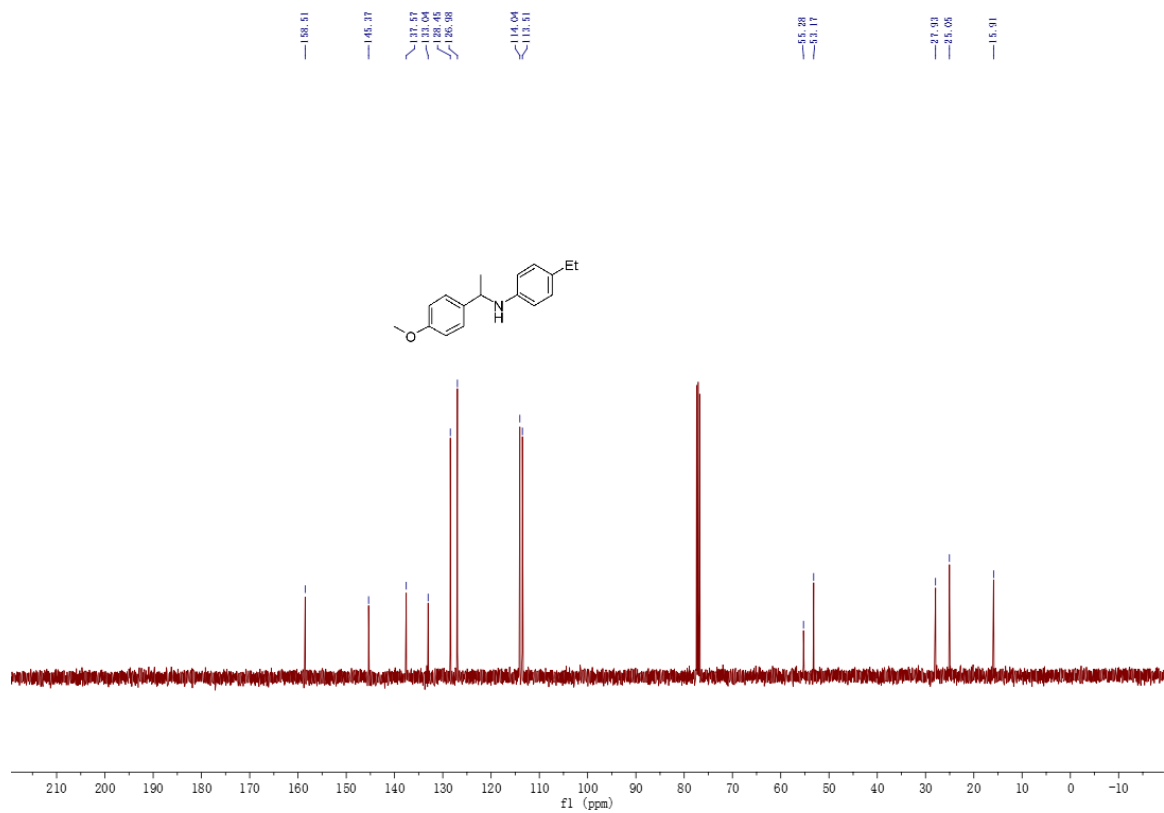
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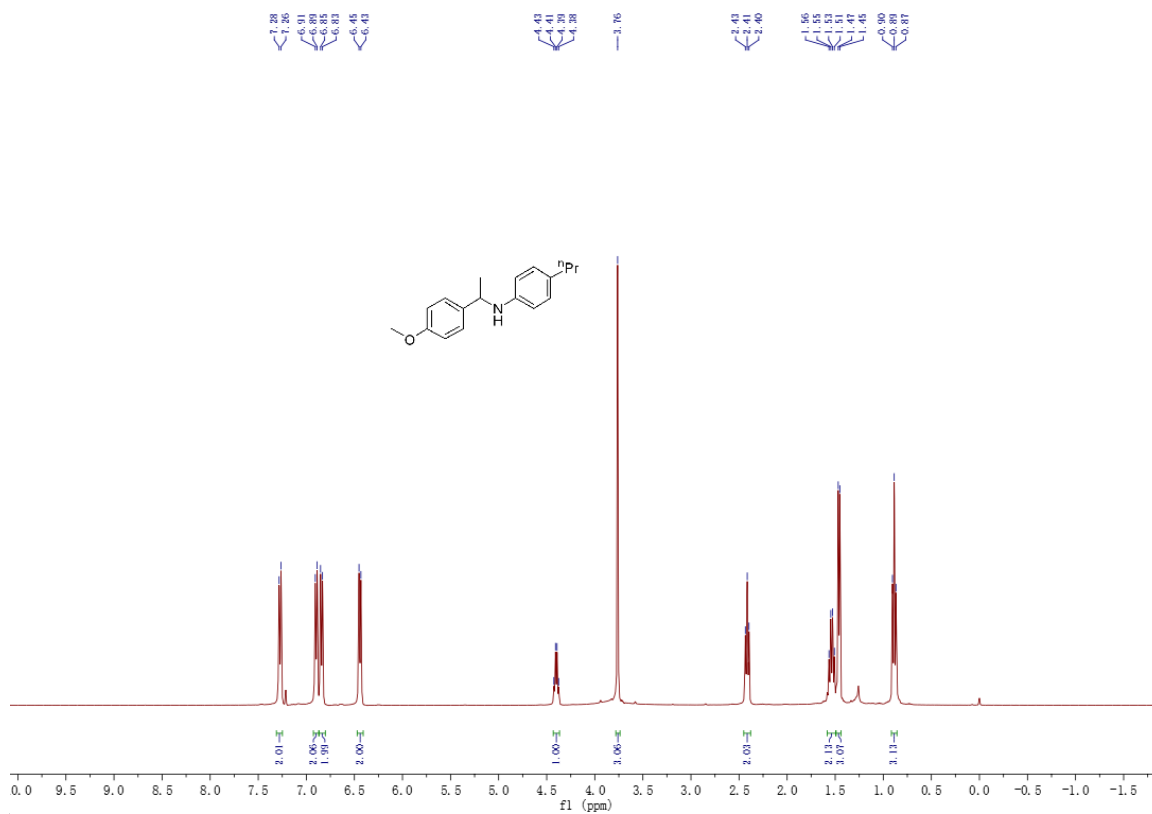
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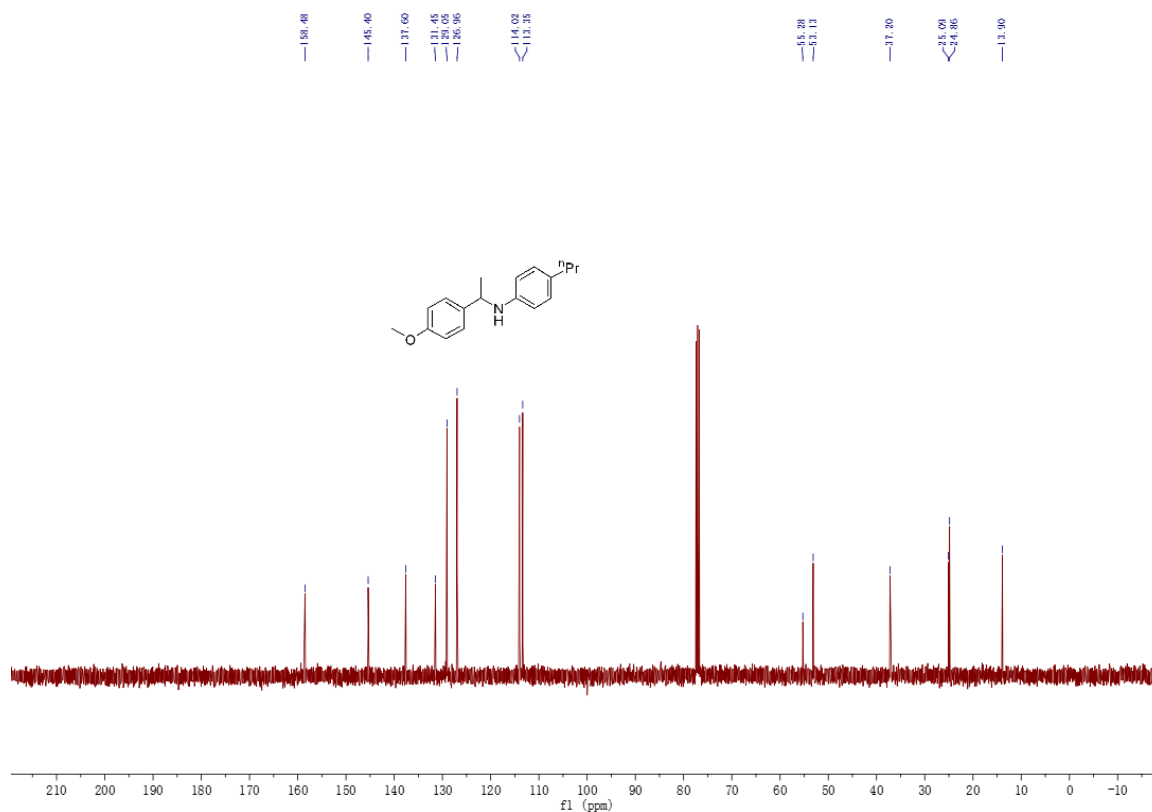
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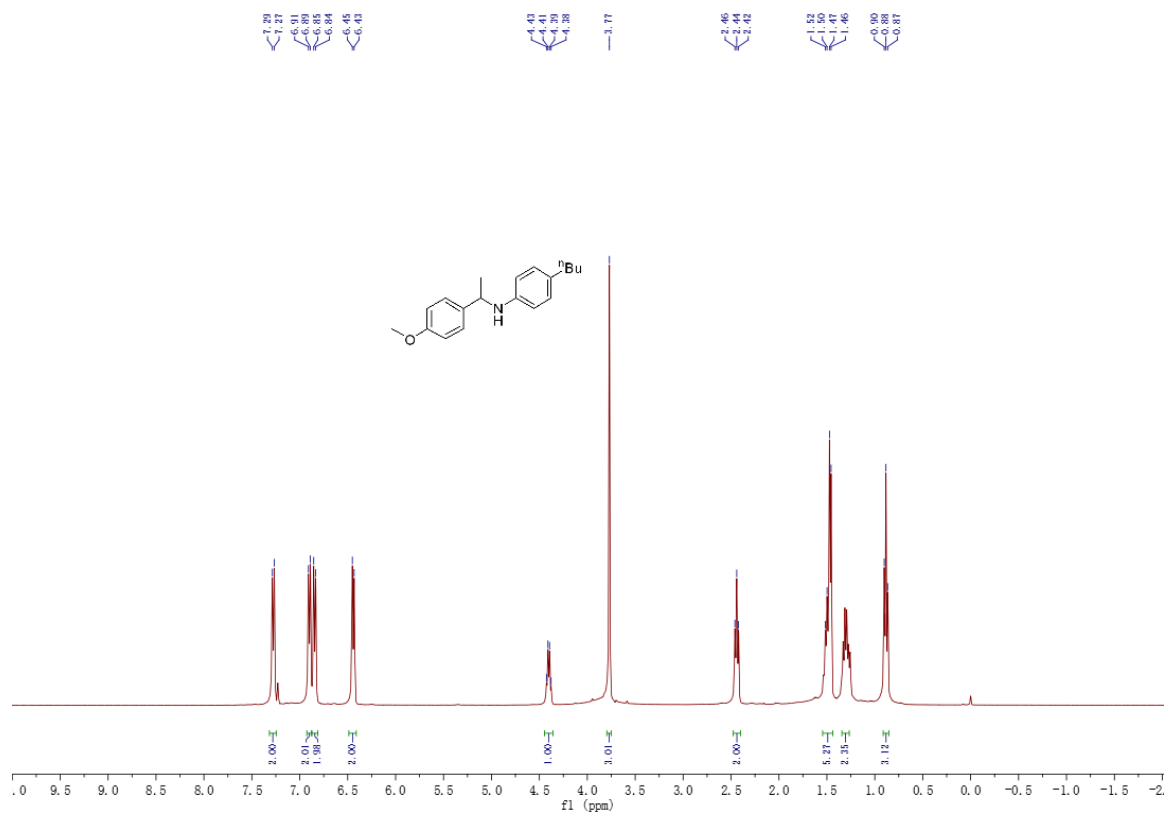
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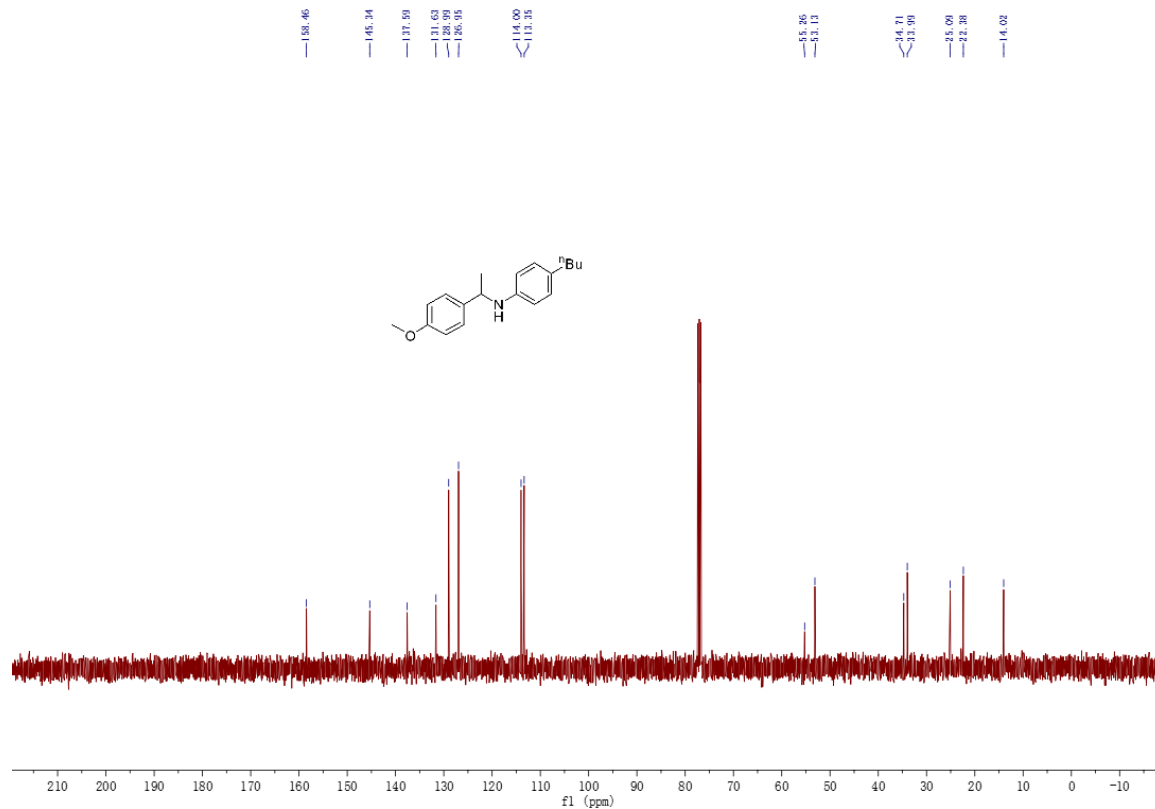
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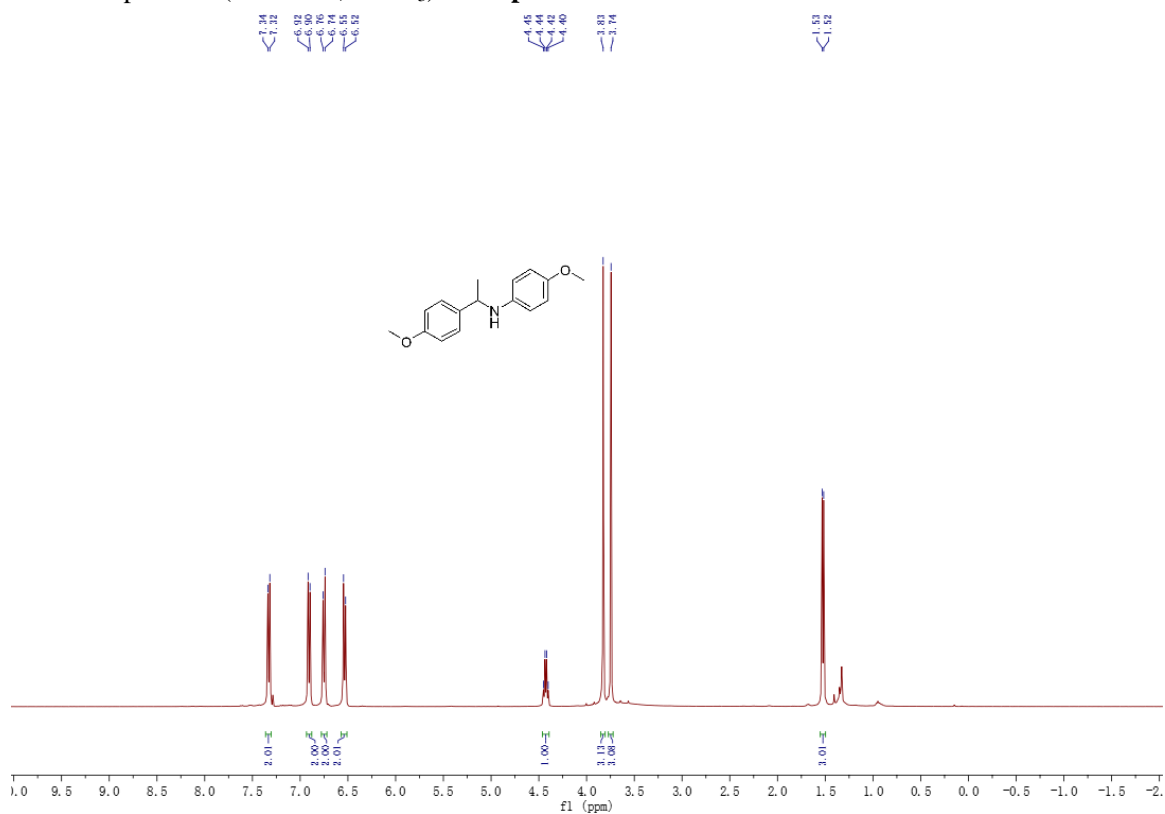
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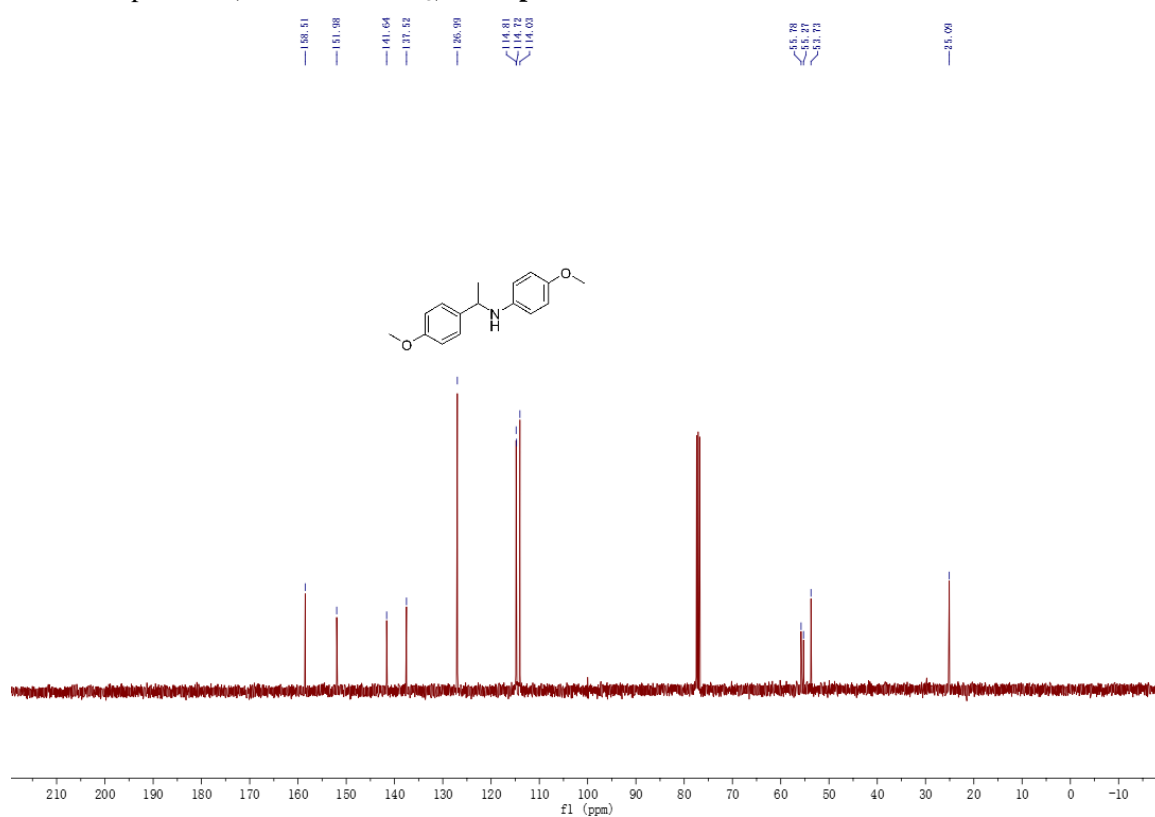
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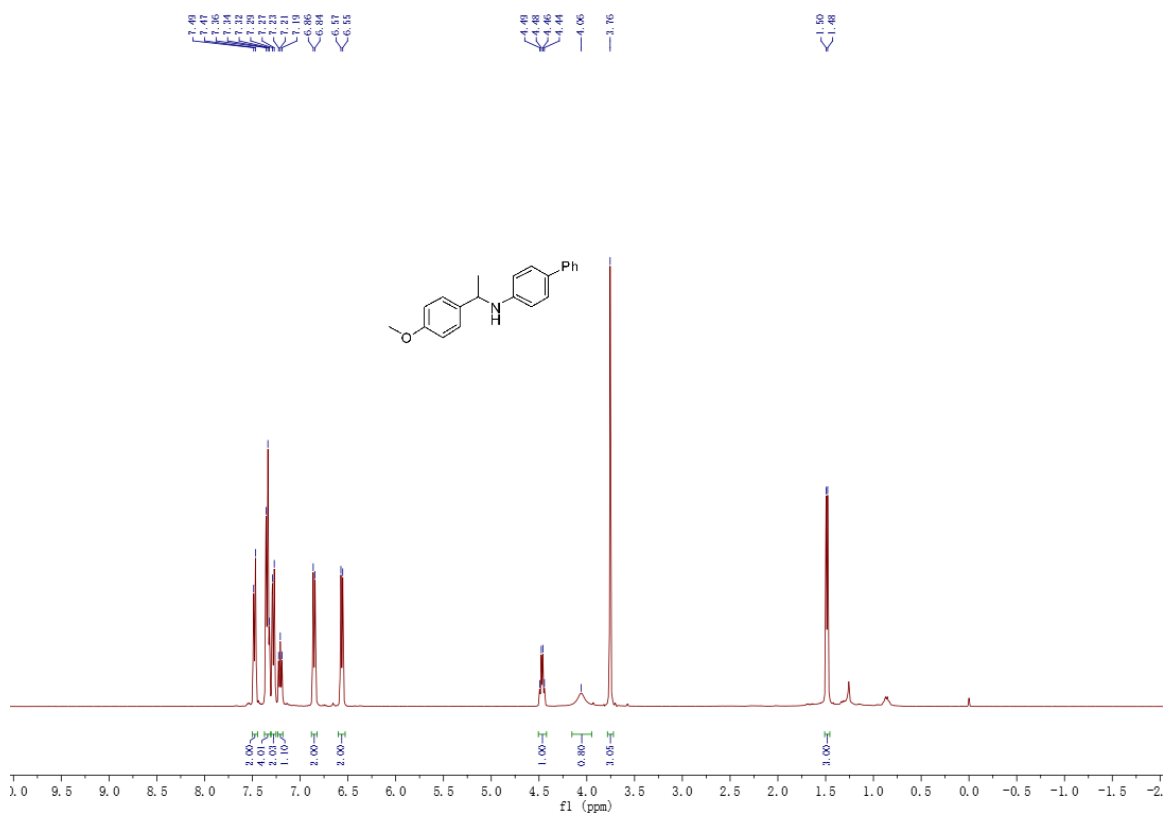
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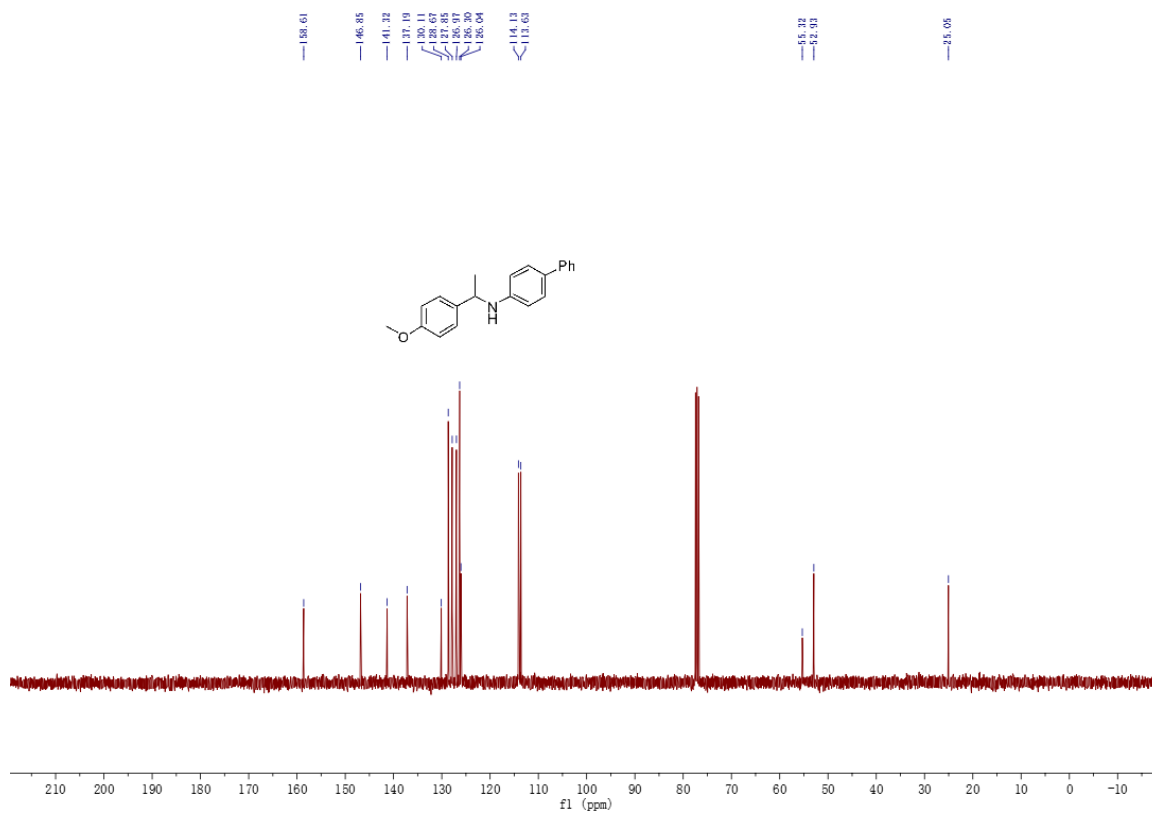
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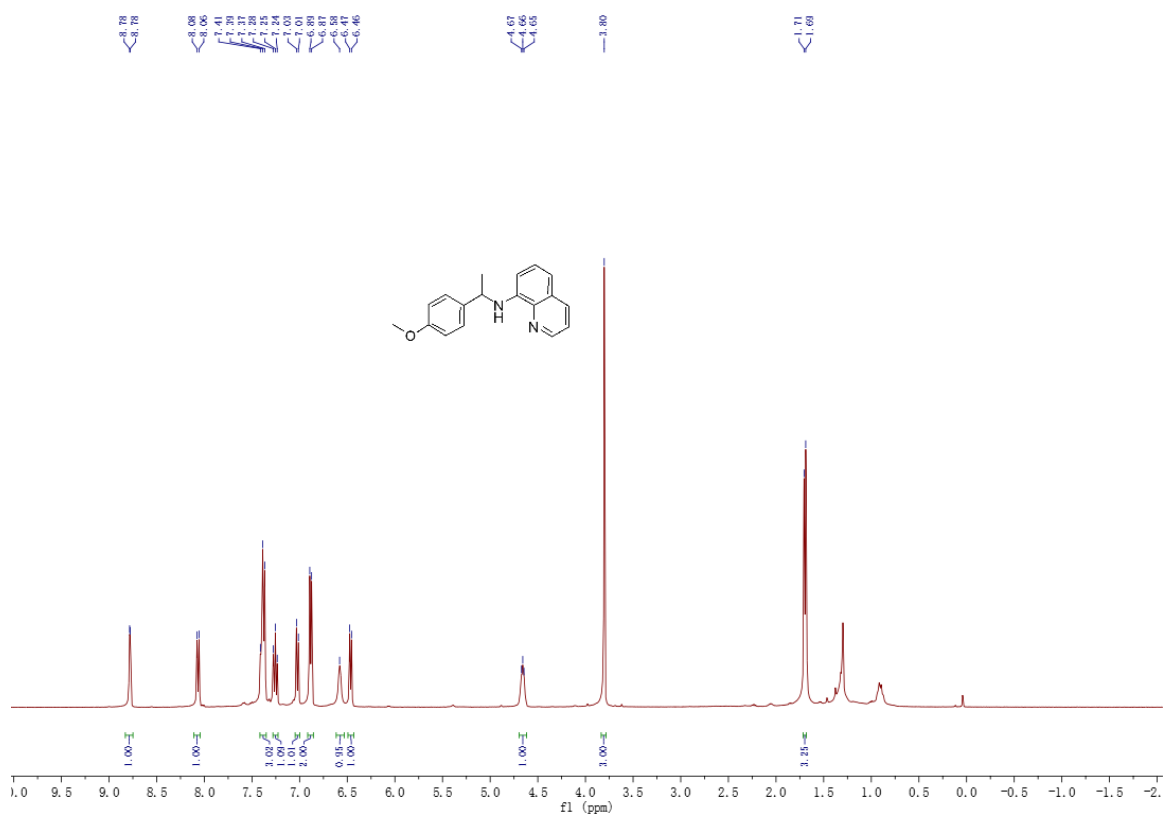
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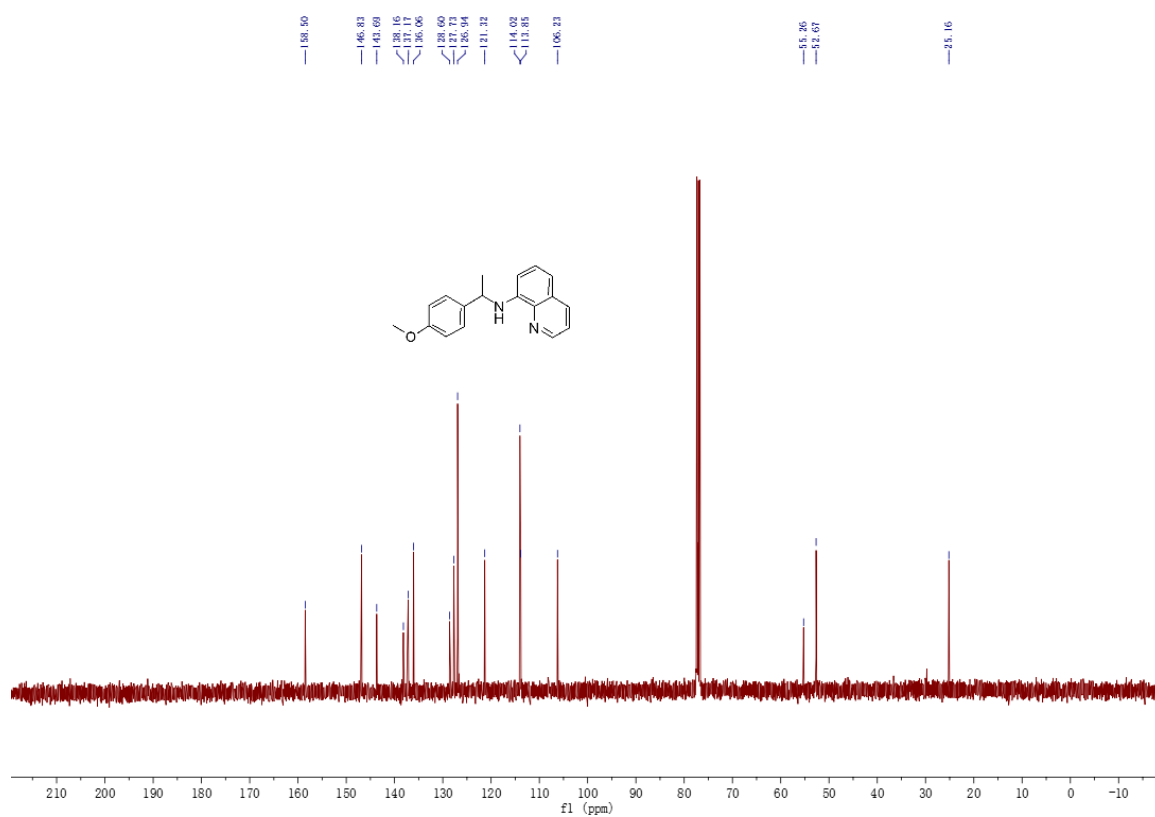
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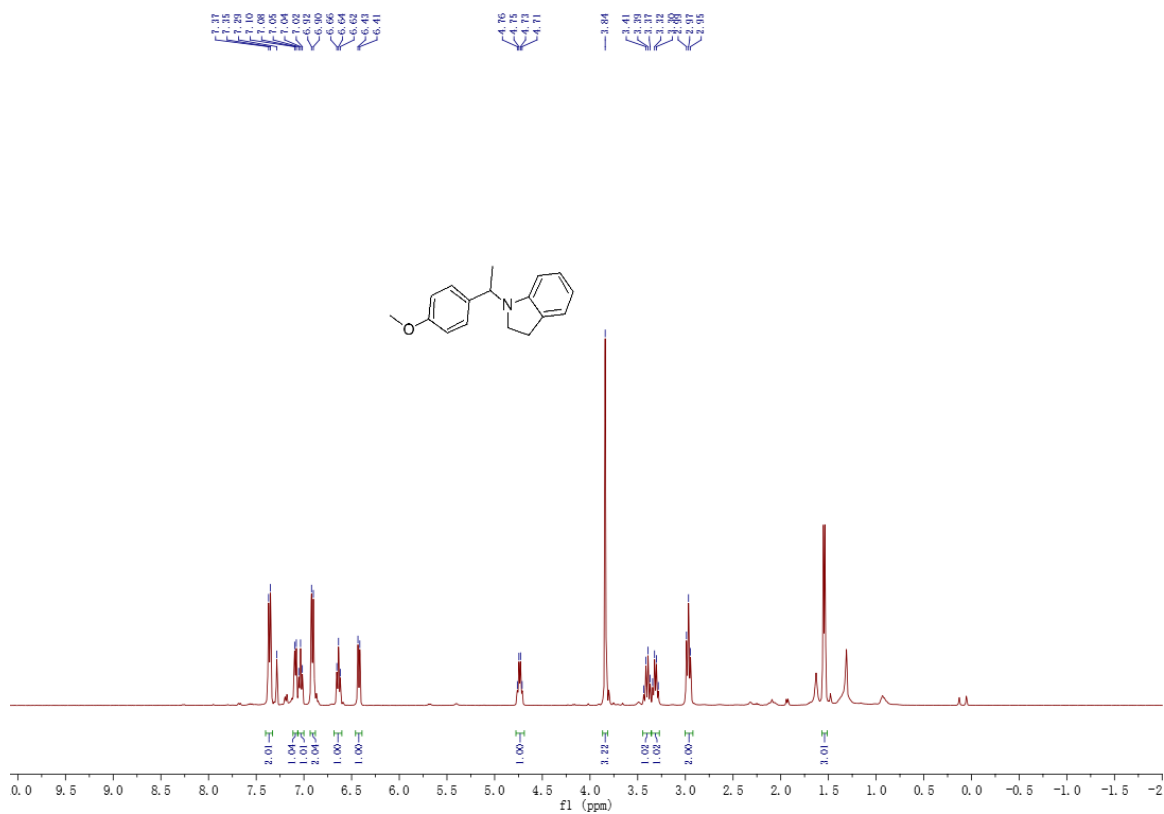
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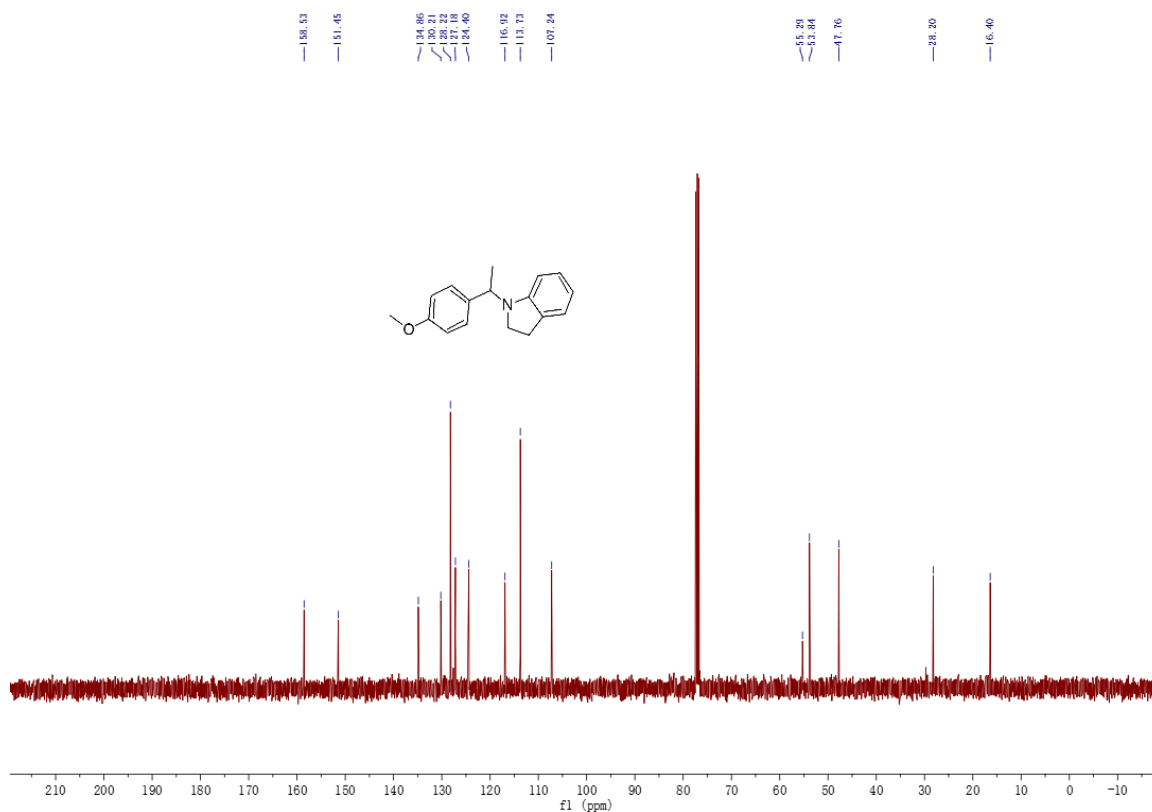
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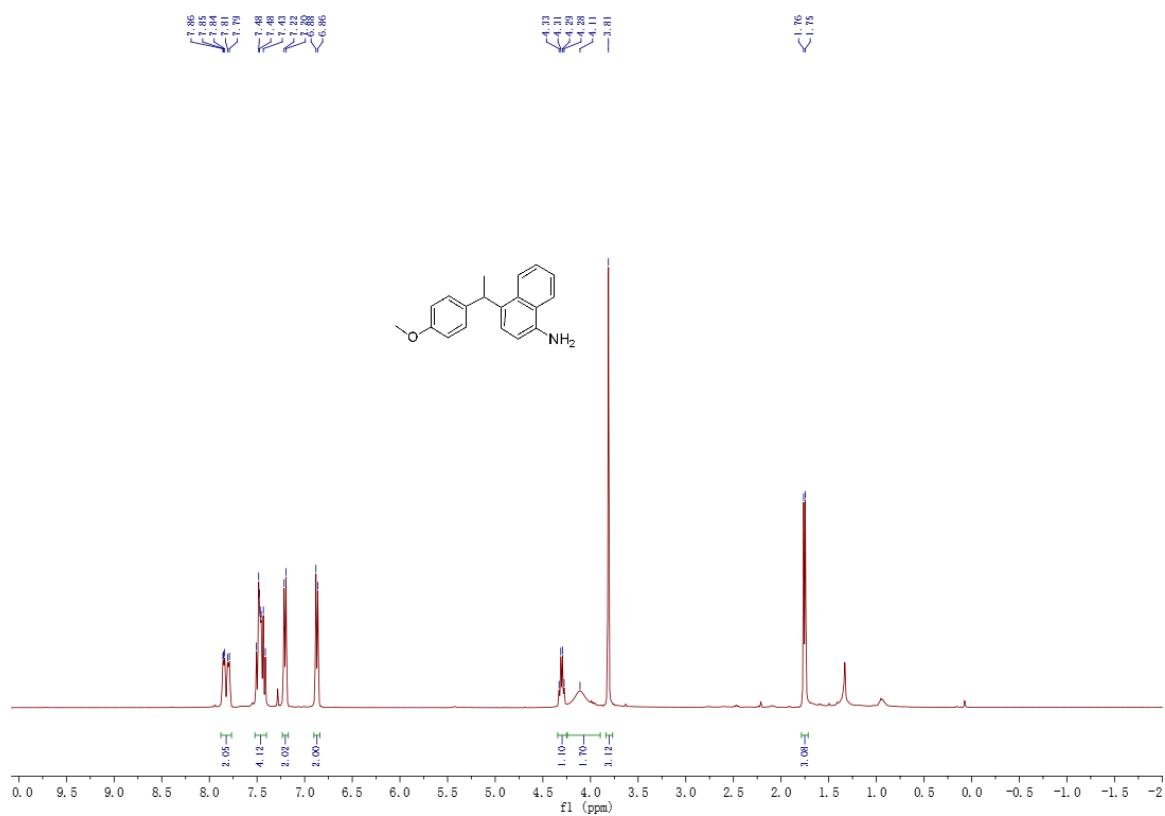
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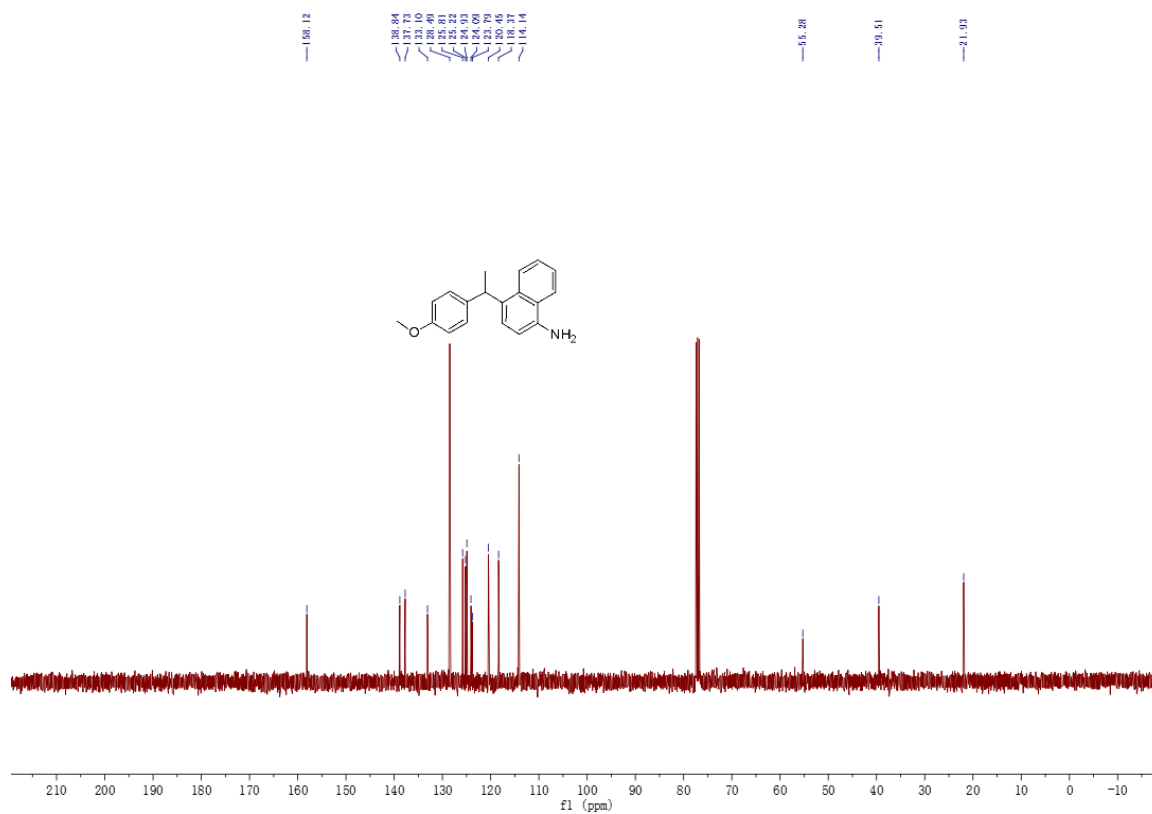
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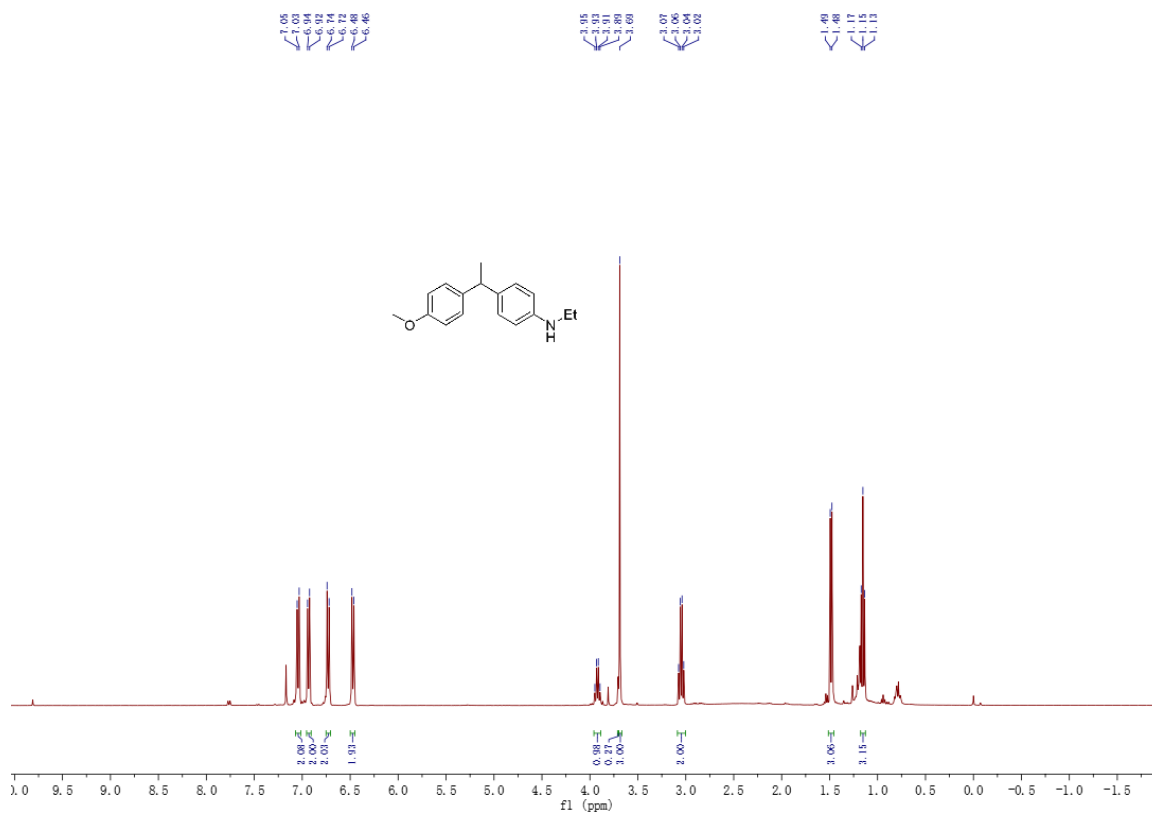
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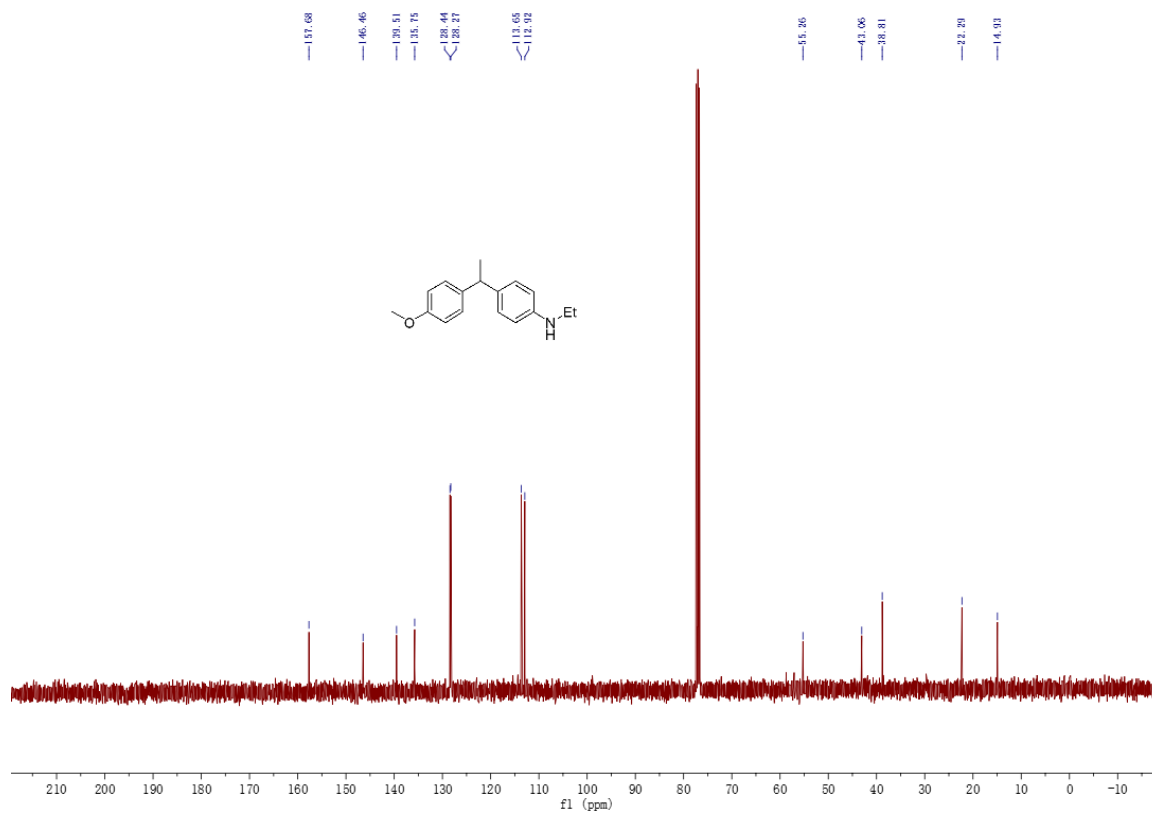
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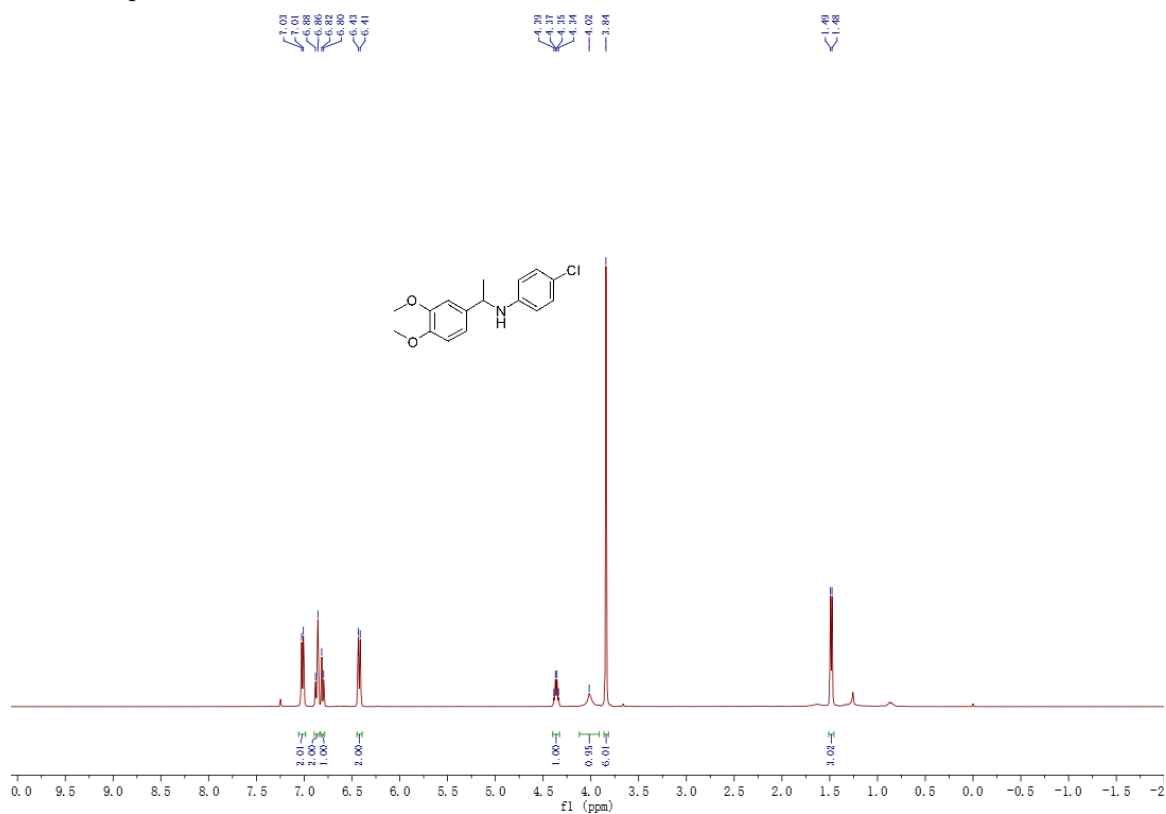
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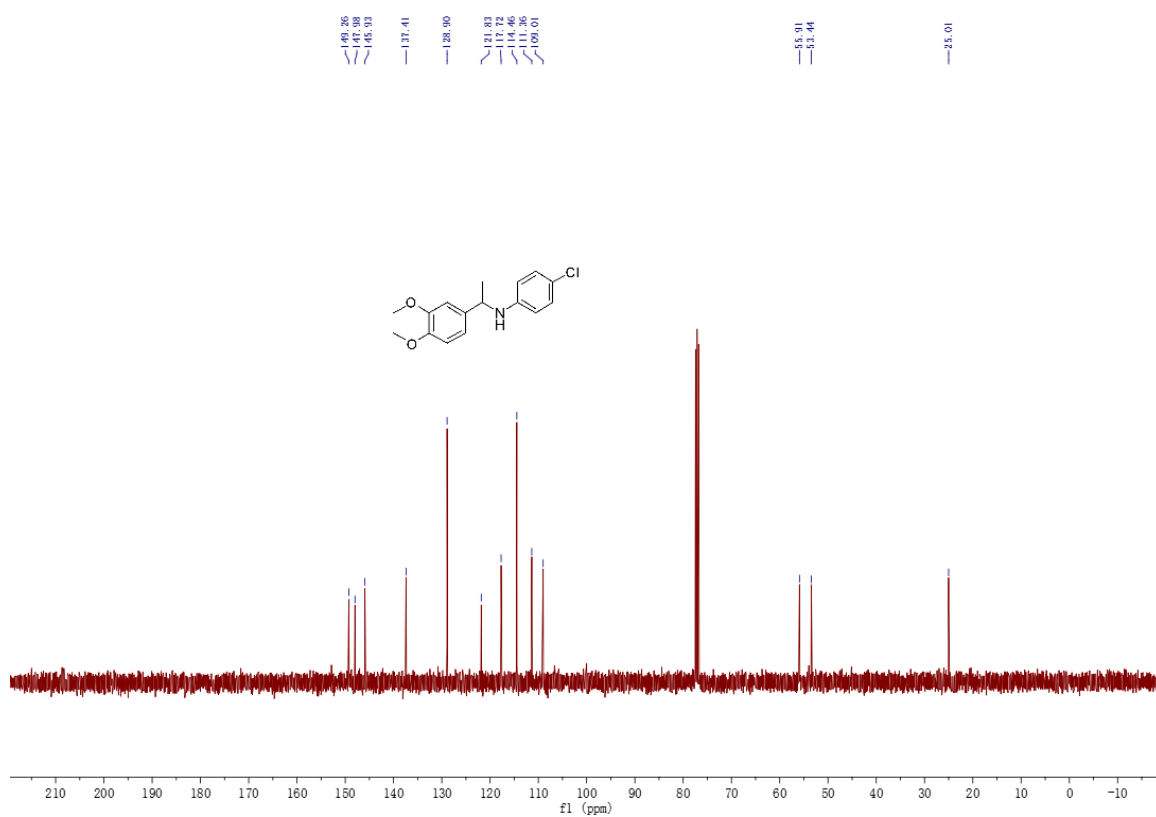
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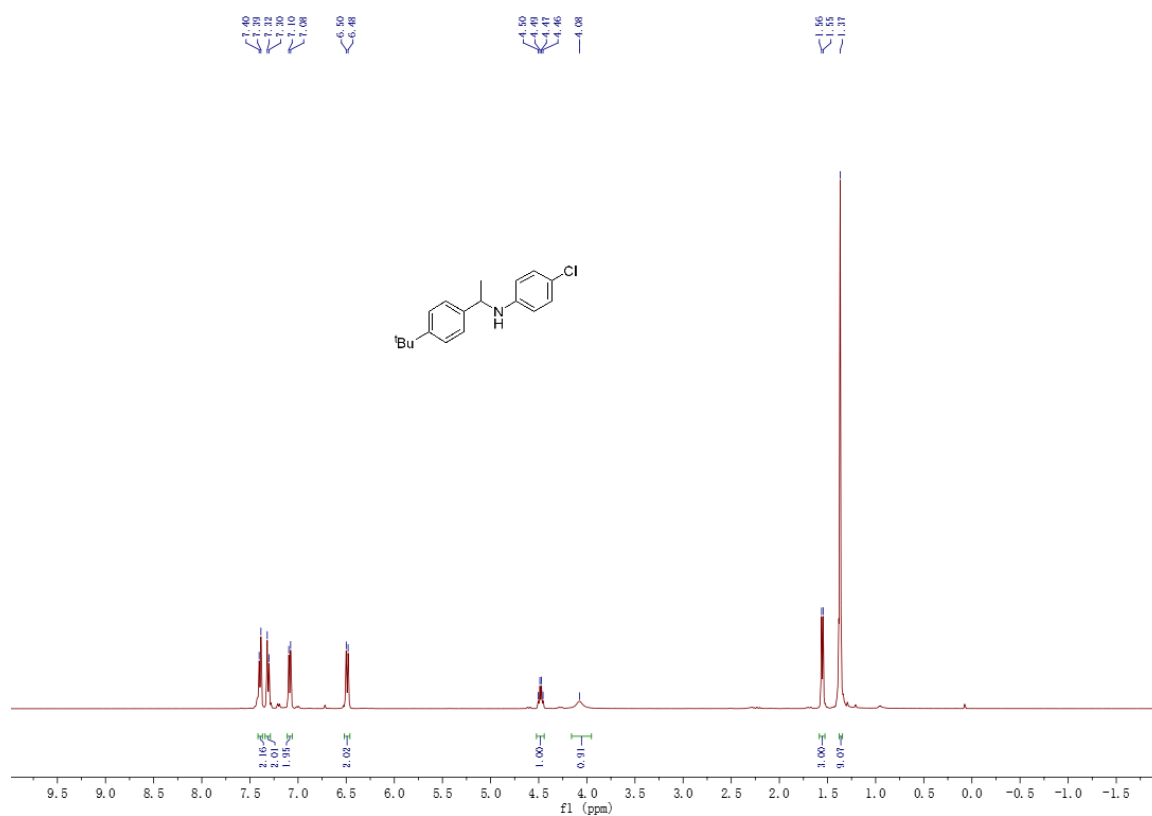
^1H NMR spectrum (400 MHz, CDCl_3) of **3-2a**



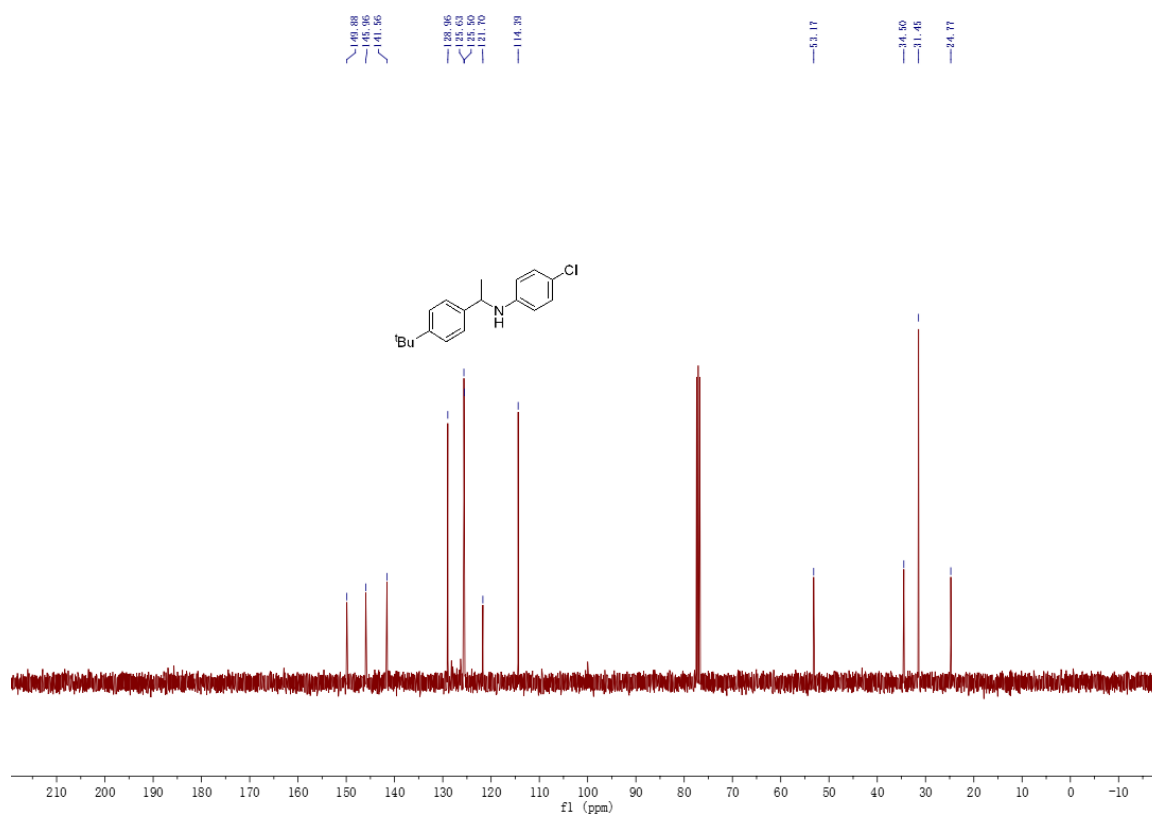
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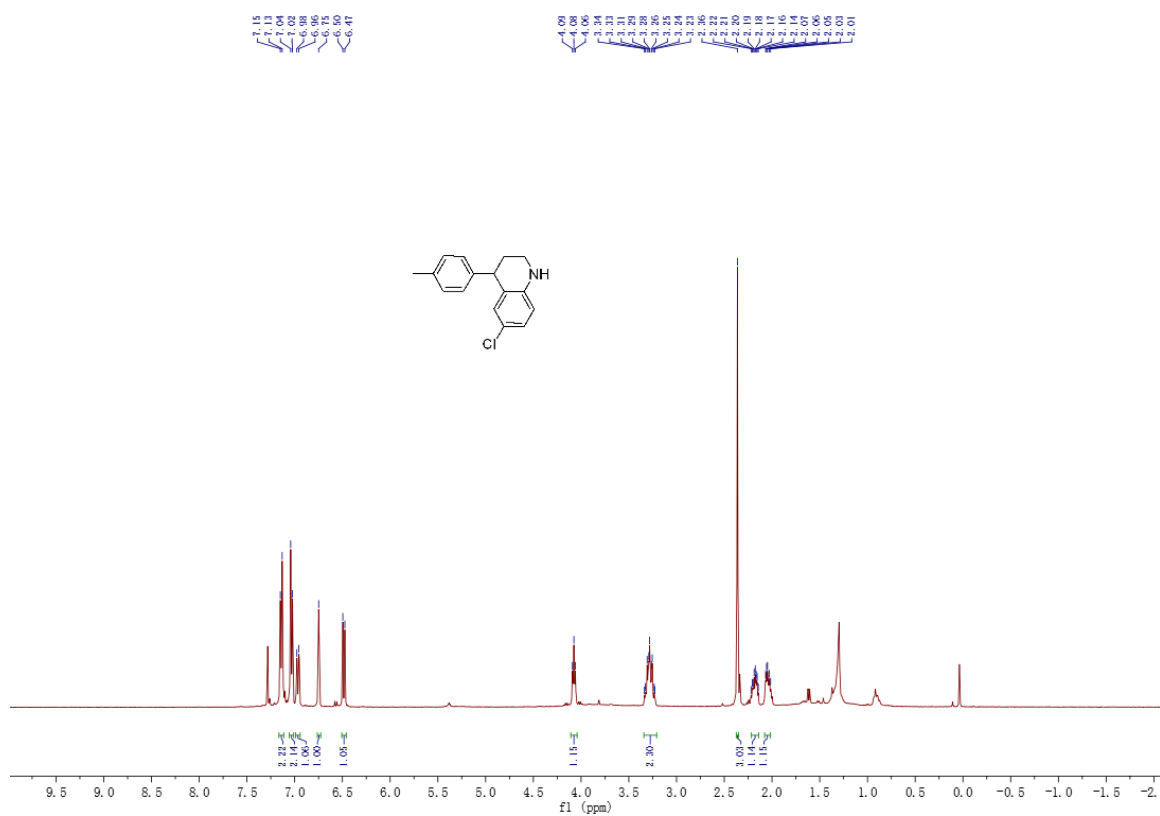
^1H NMR spectrum (400 MHz, CDCl_3) of **3-2b**



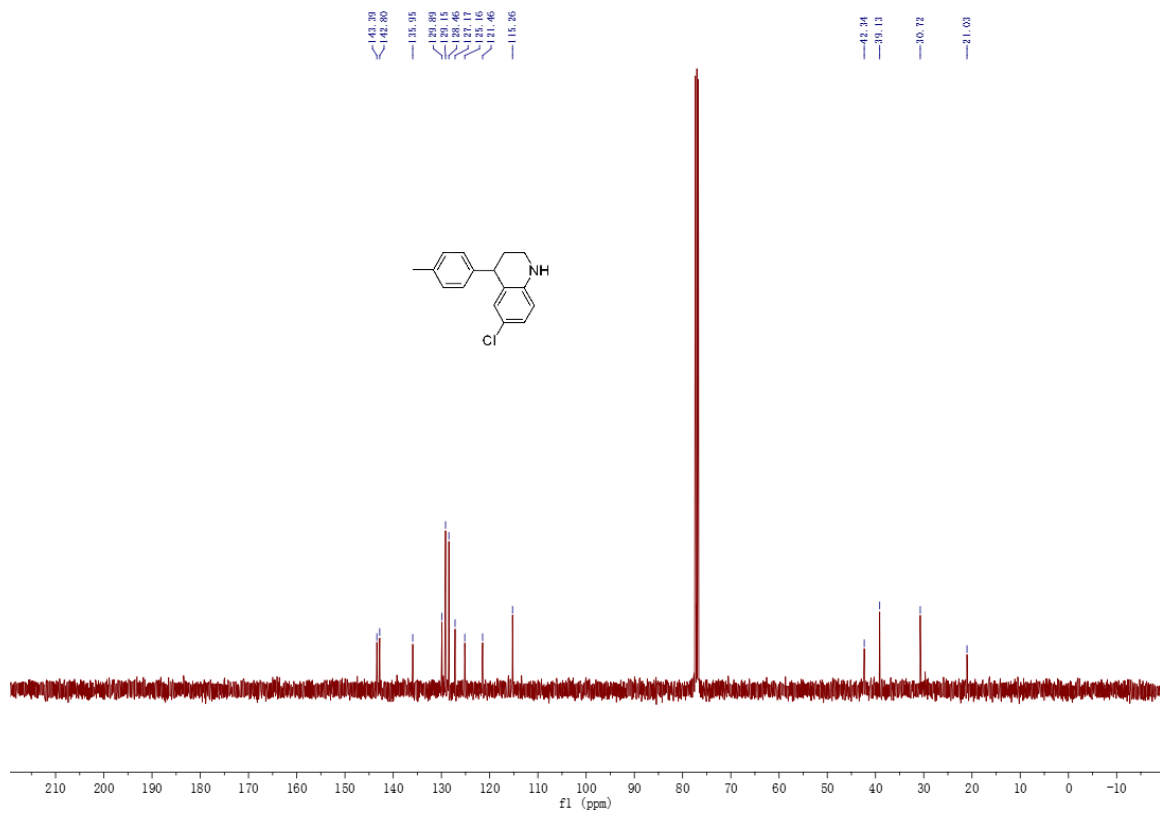
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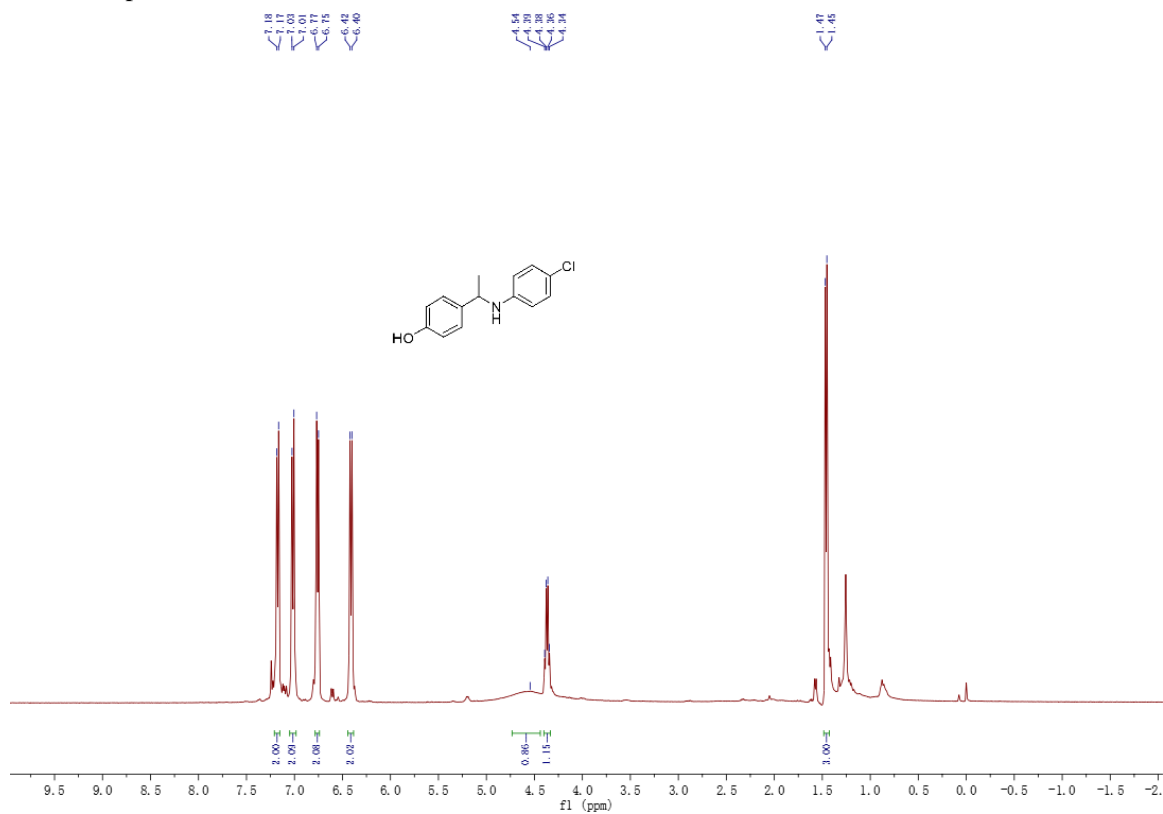
^1H NMR spectrum (400 MHz, CDCl_3) of **3-2c**



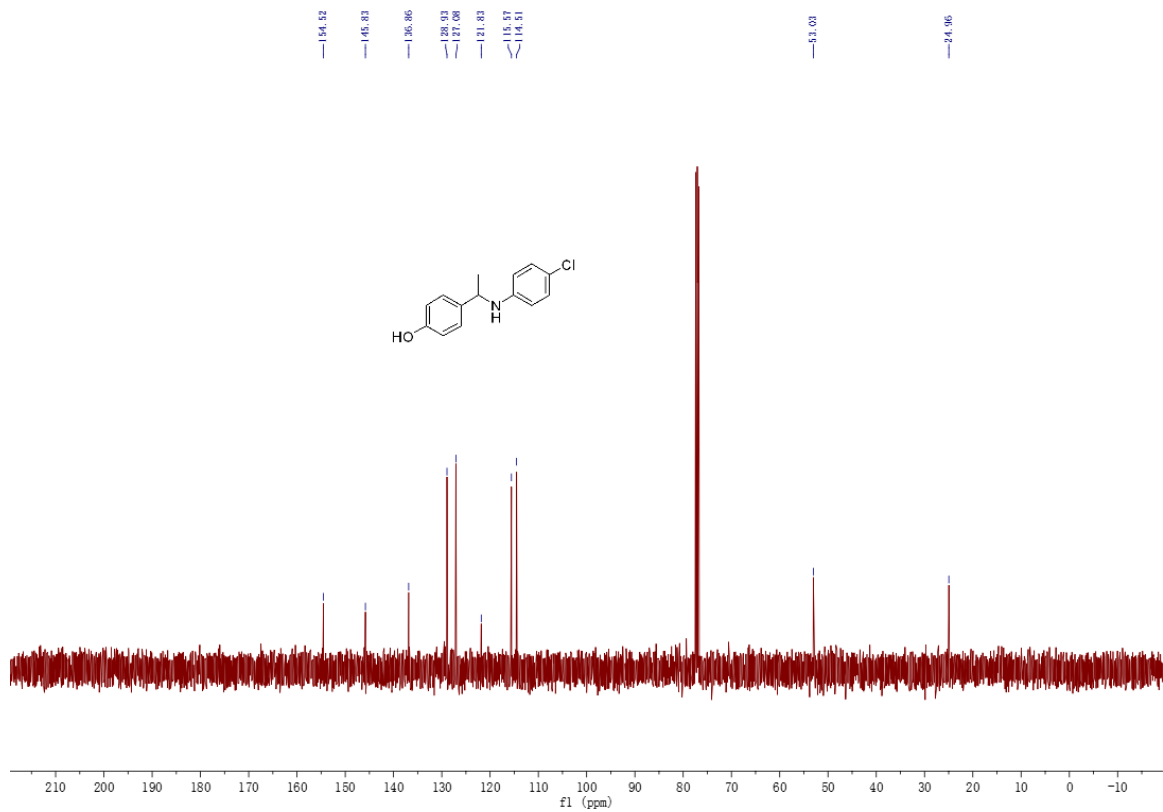
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3-2c**



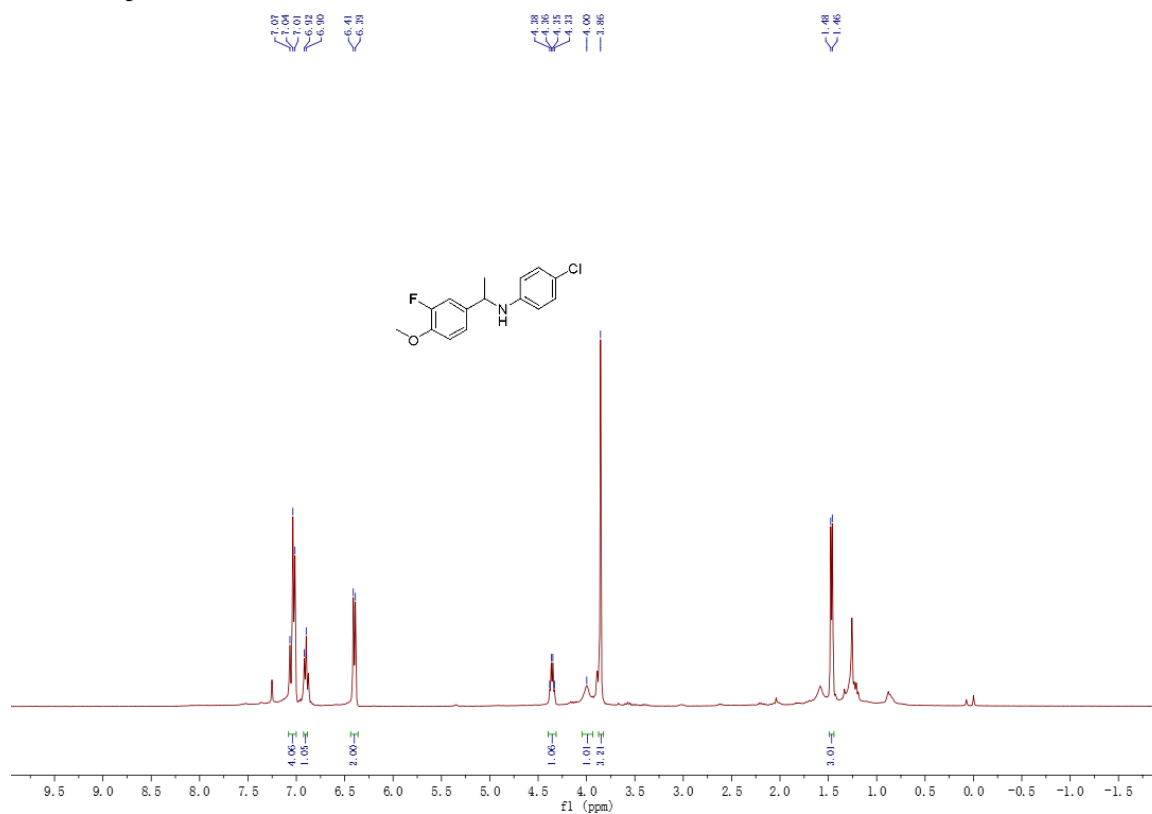
^1H NMR spectrum (400 MHz, CDCl_3) of **3-2d**



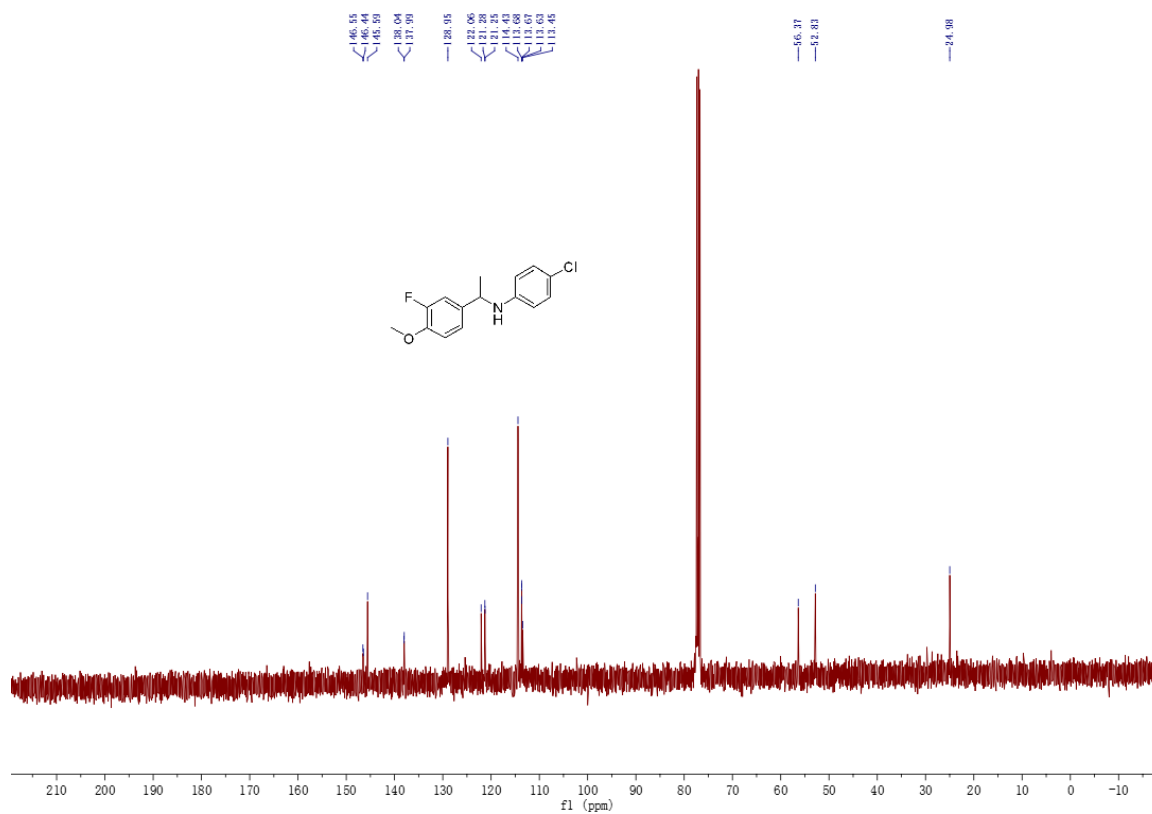
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3-2d**



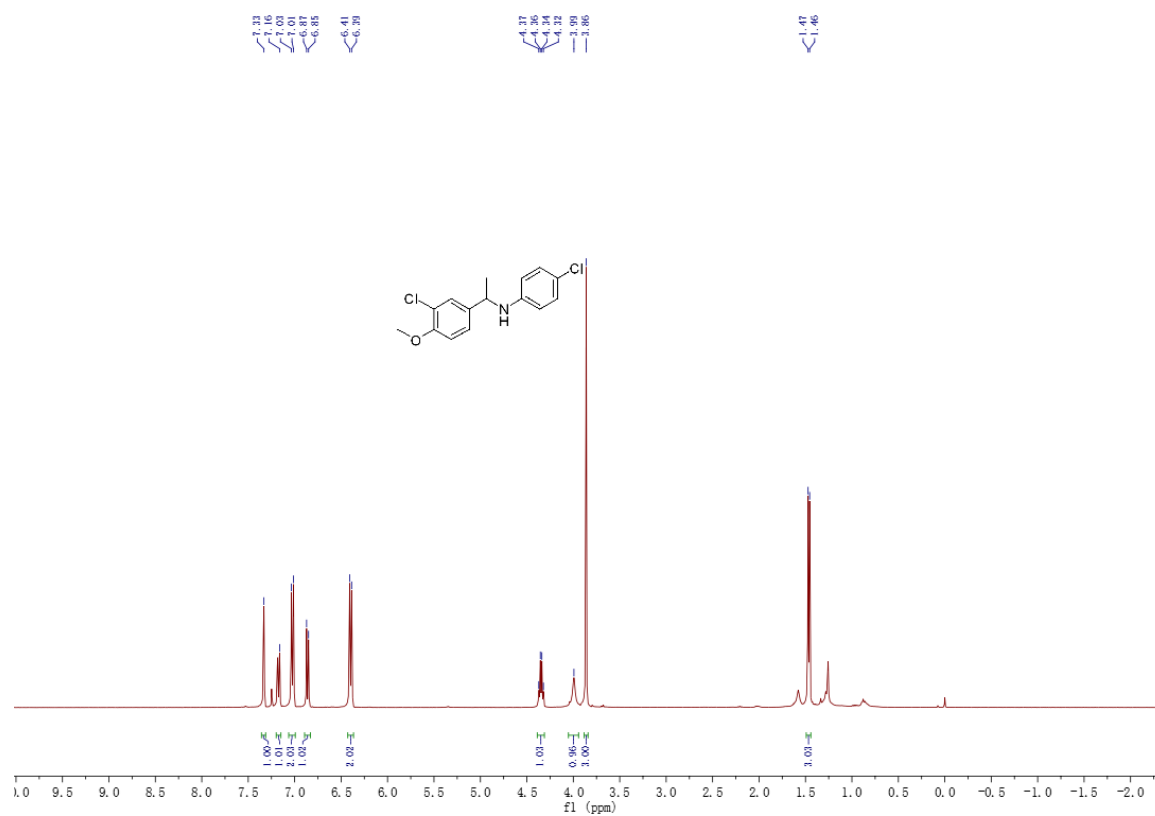
^1H NMR spectrum (400 MHz, CDCl_3) of **3-2e**



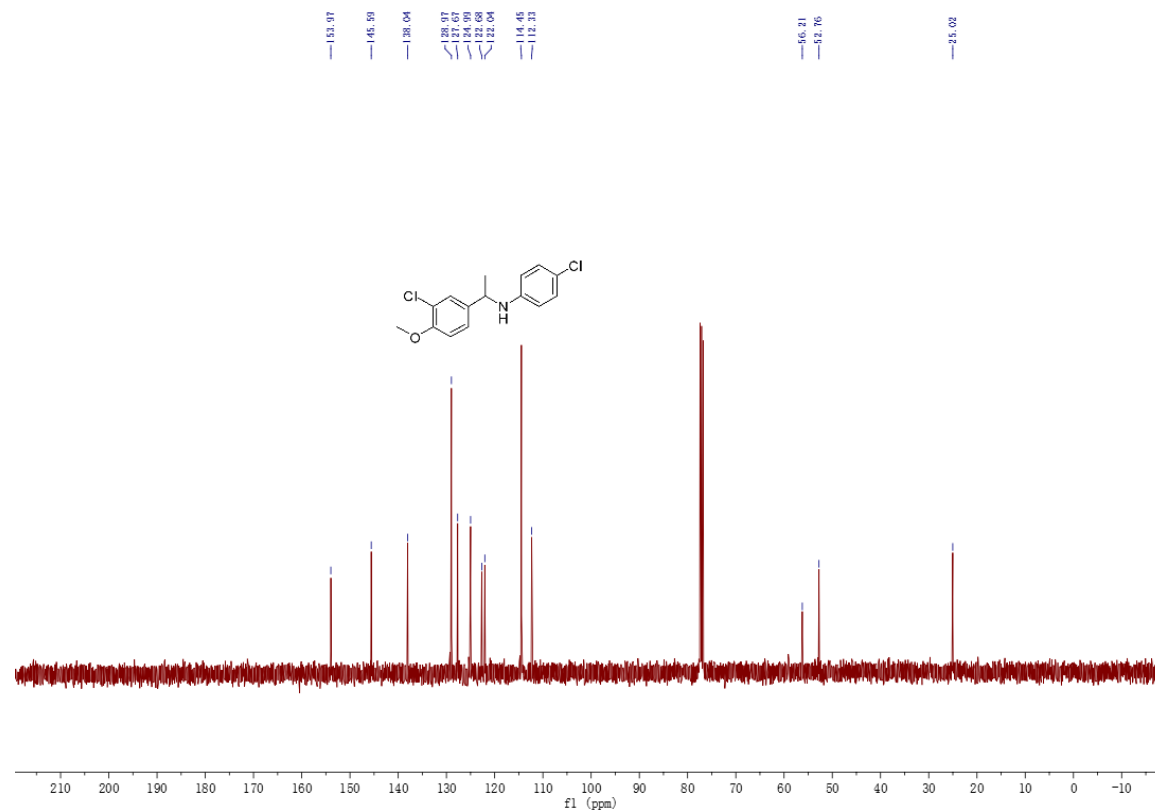
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3-2e**



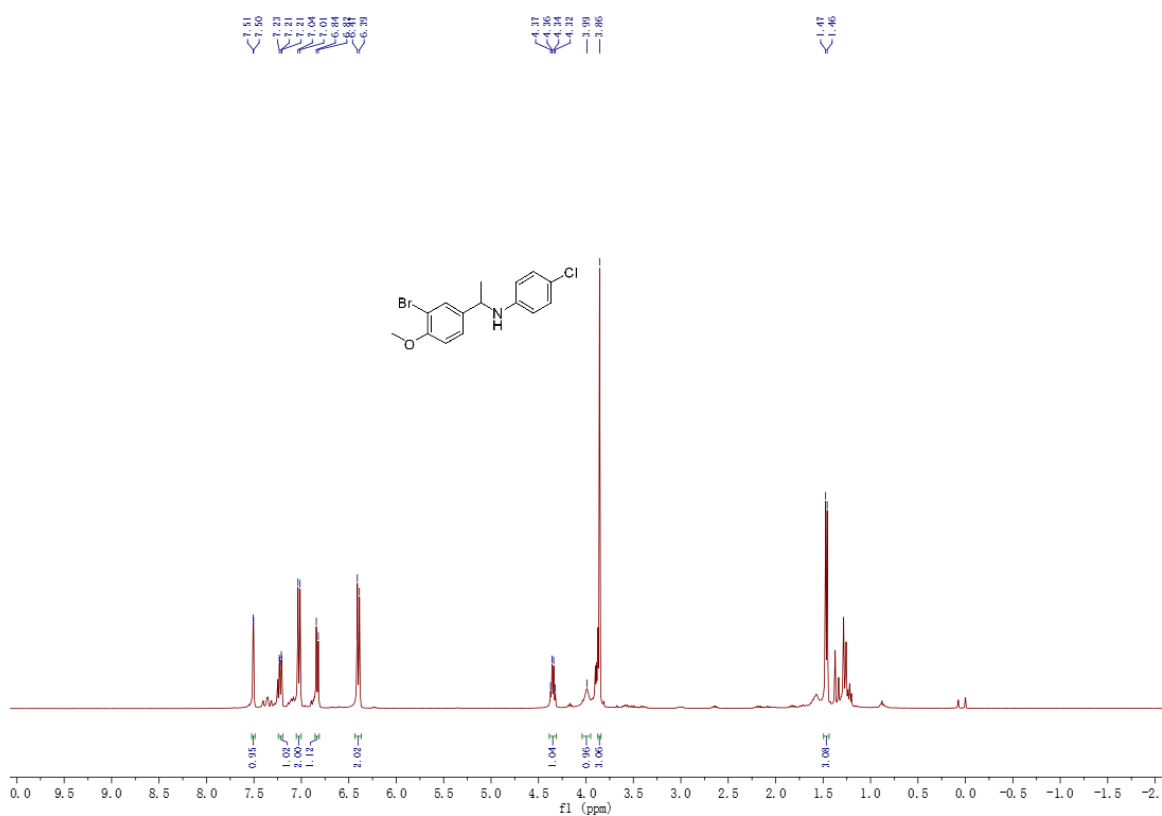
^1H NMR spectrum (400 MHz, CDCl_3) of **3-2f**



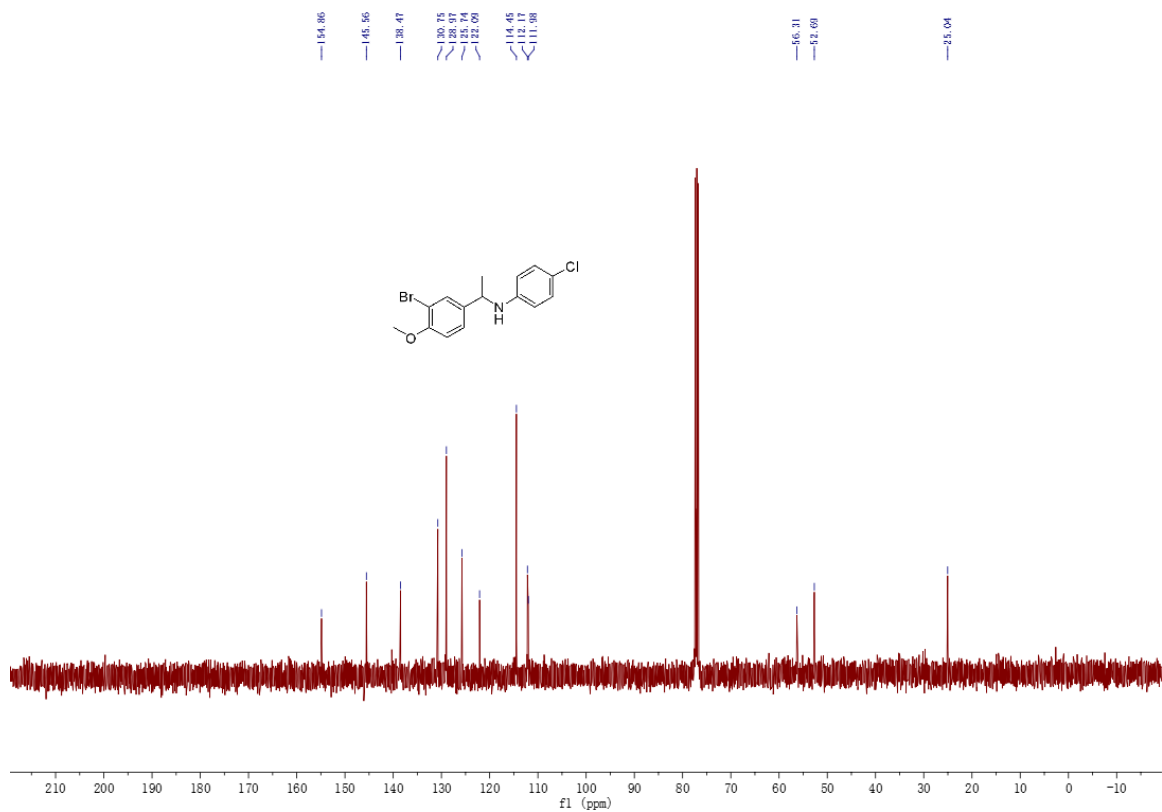
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3-2f**



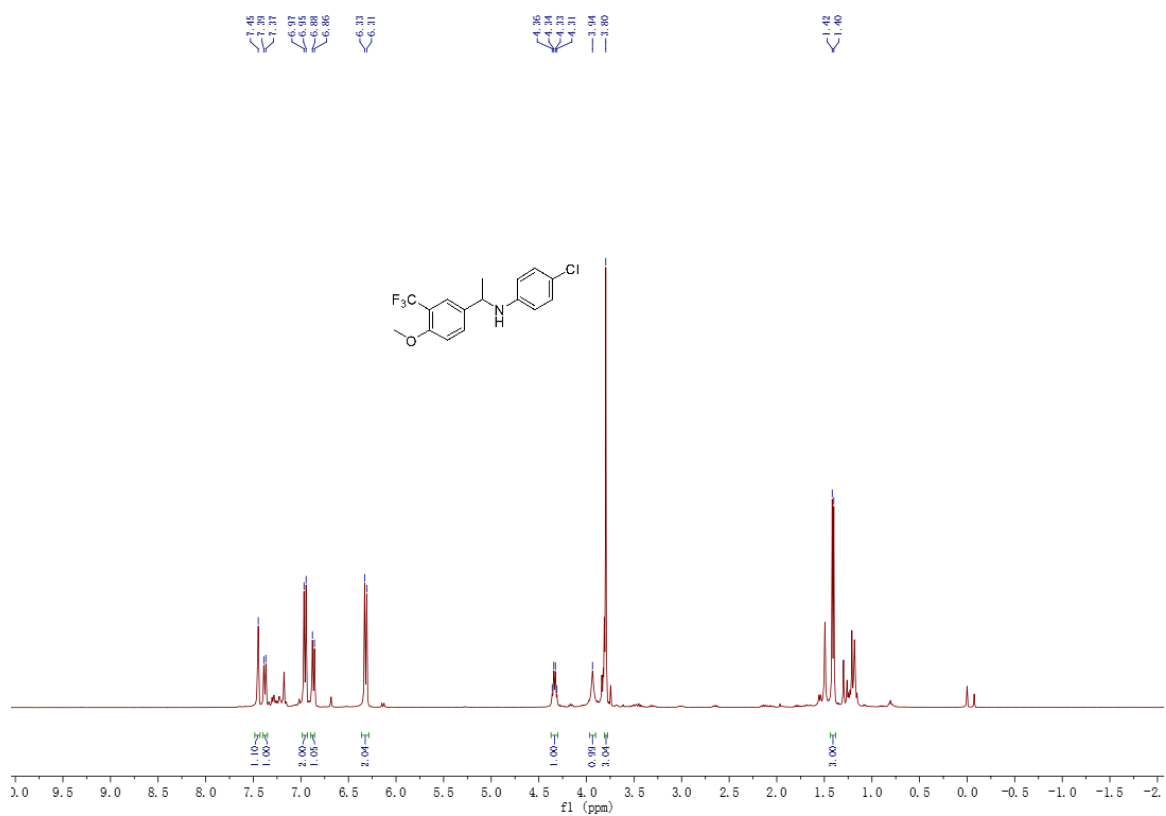
^1H NMR spectrum (400 MHz, CDCl_3) of **3-2g**



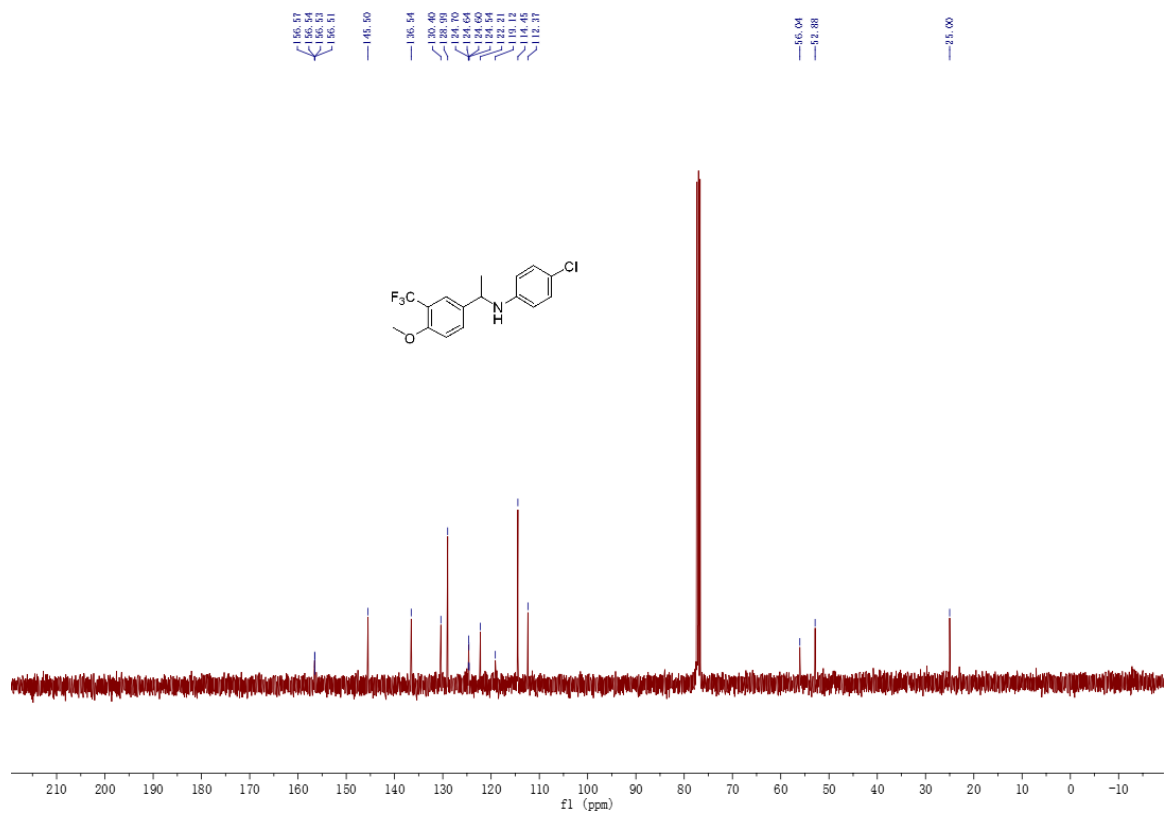
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3-2g**



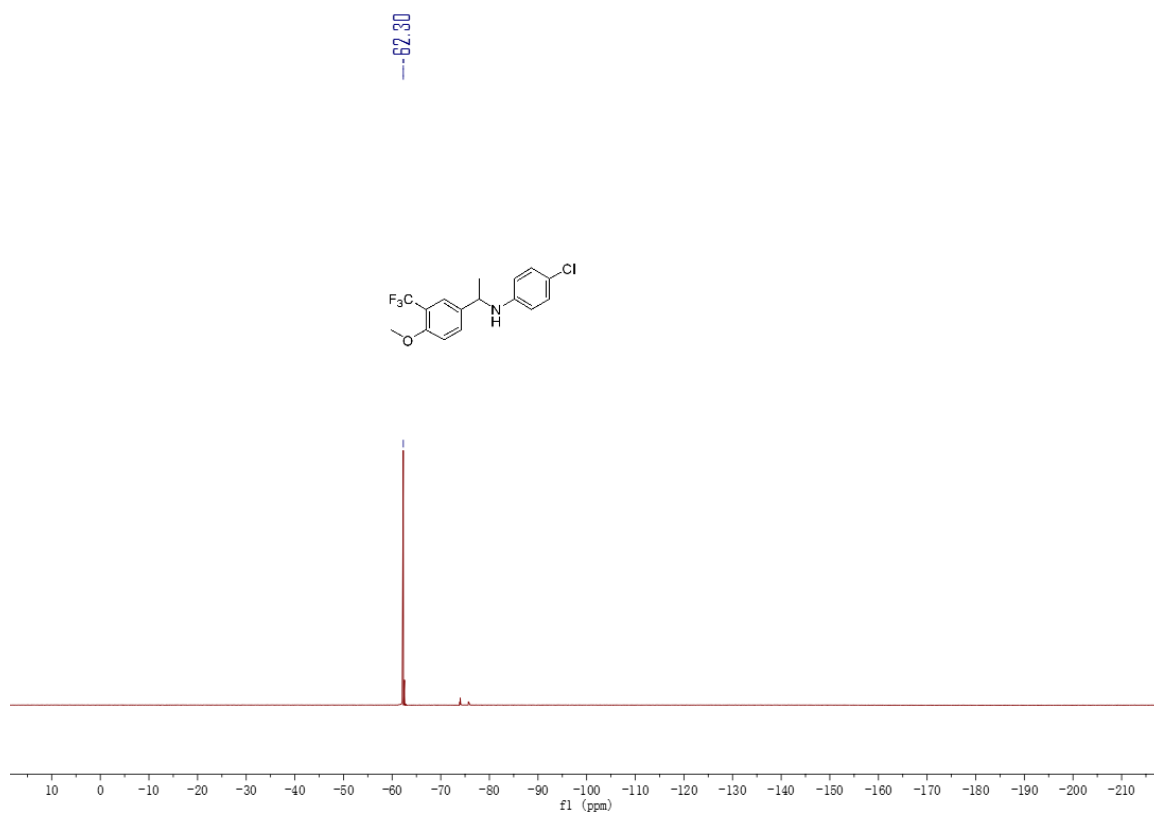
^1H NMR spectrum (400 MHz, CDCl_3) of **3-2h**



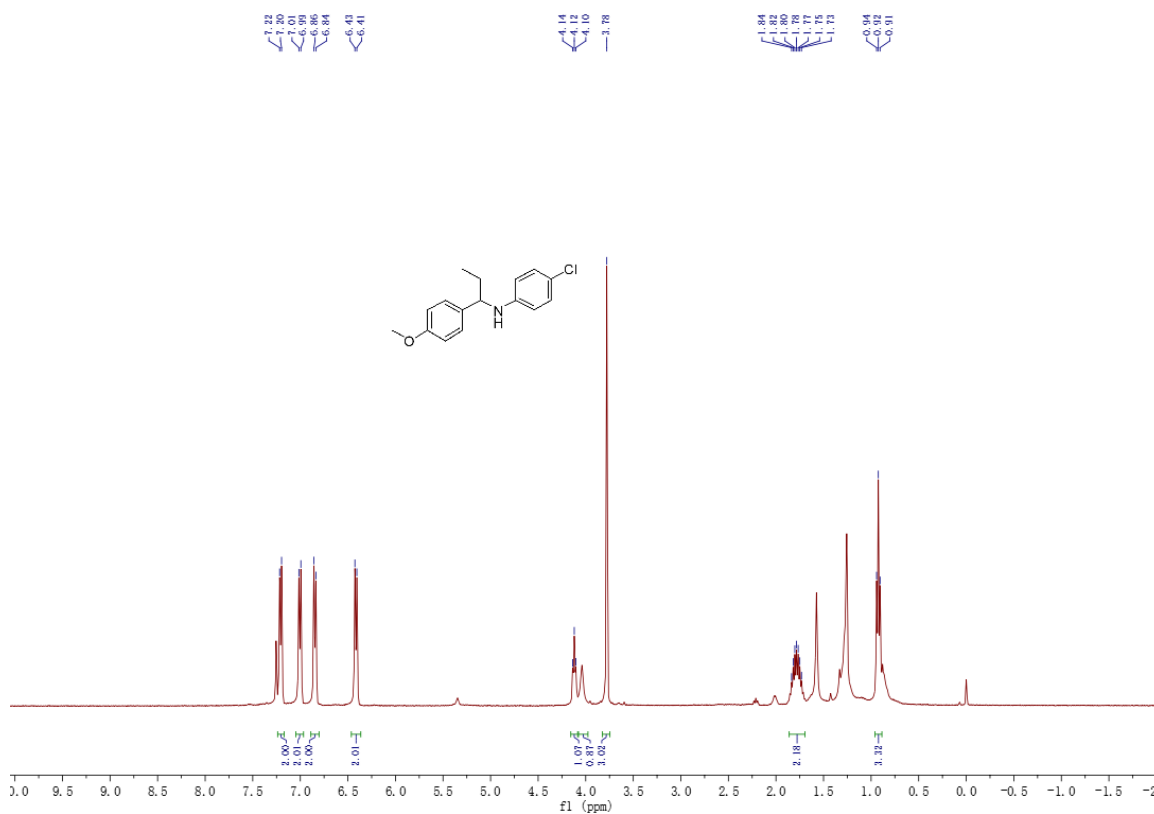
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3-2h**



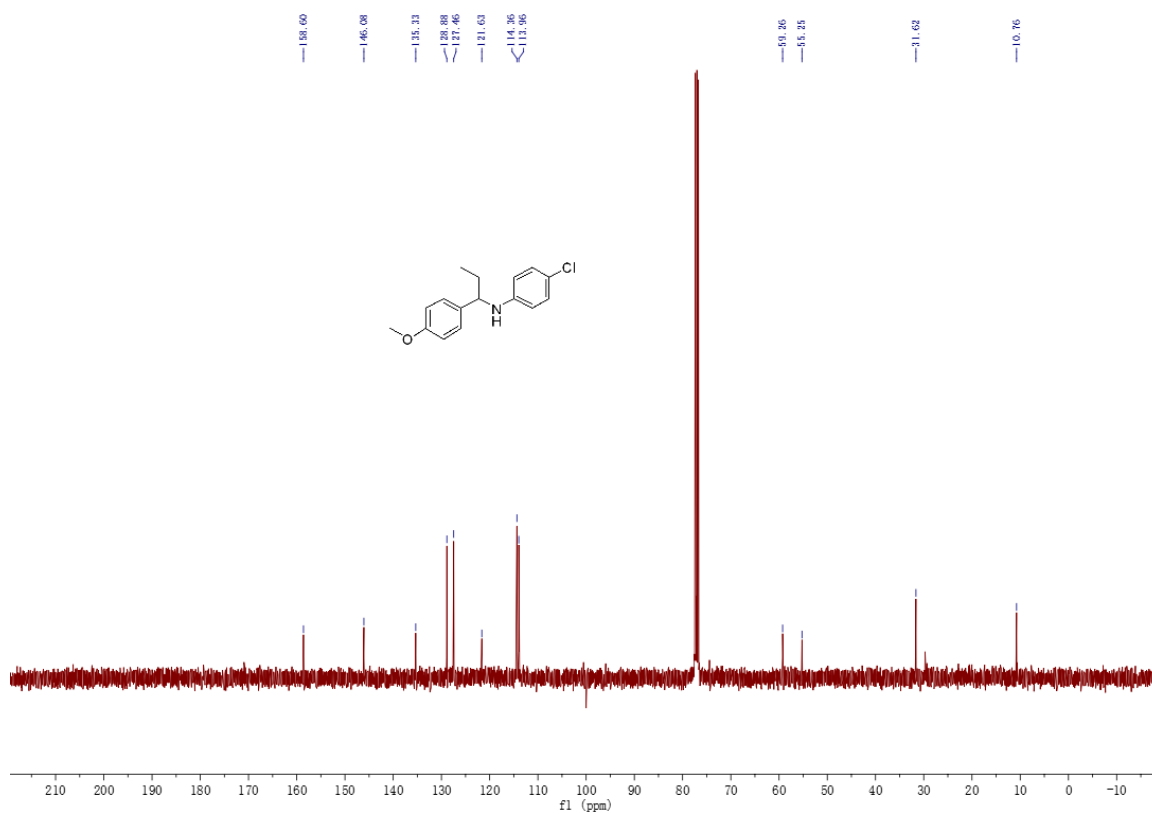
^{19}F NMR spectrum (400 MHz, CDCl_3) of **3-2h**



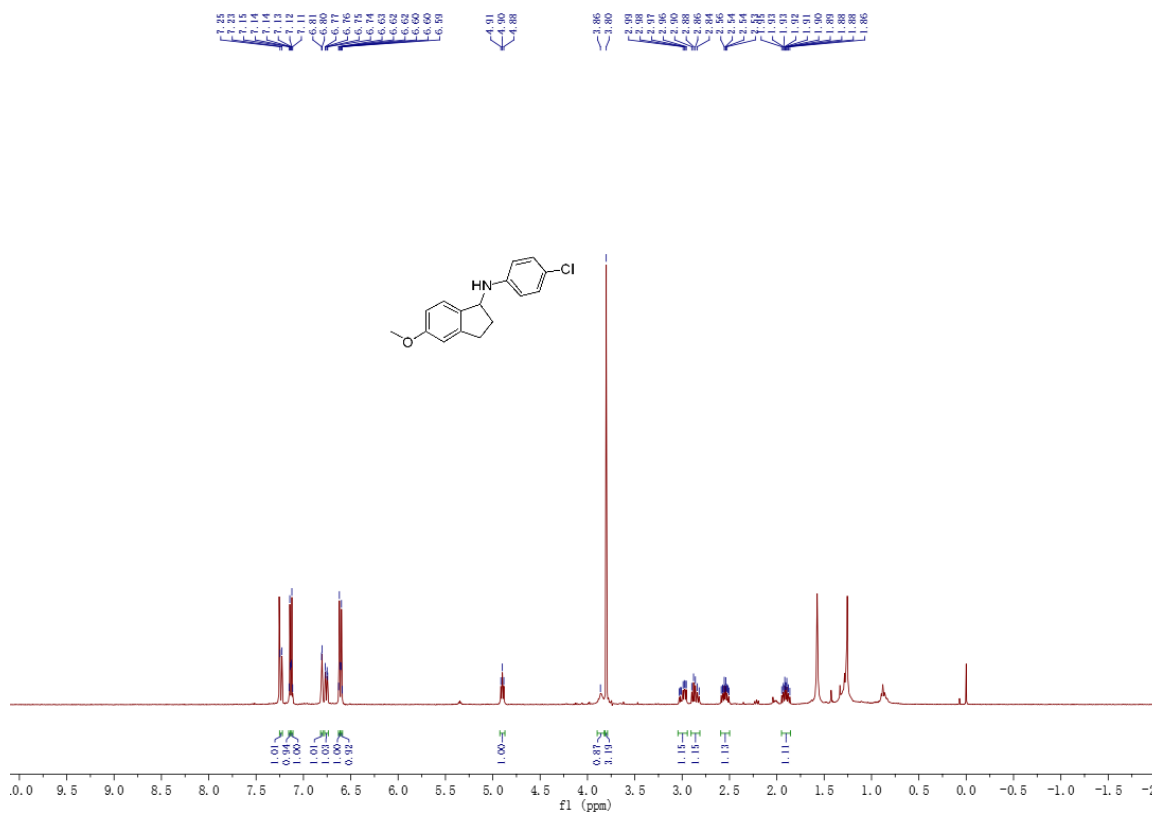
^1H NMR spectrum (400 MHz, CDCl_3) of **3-2i**



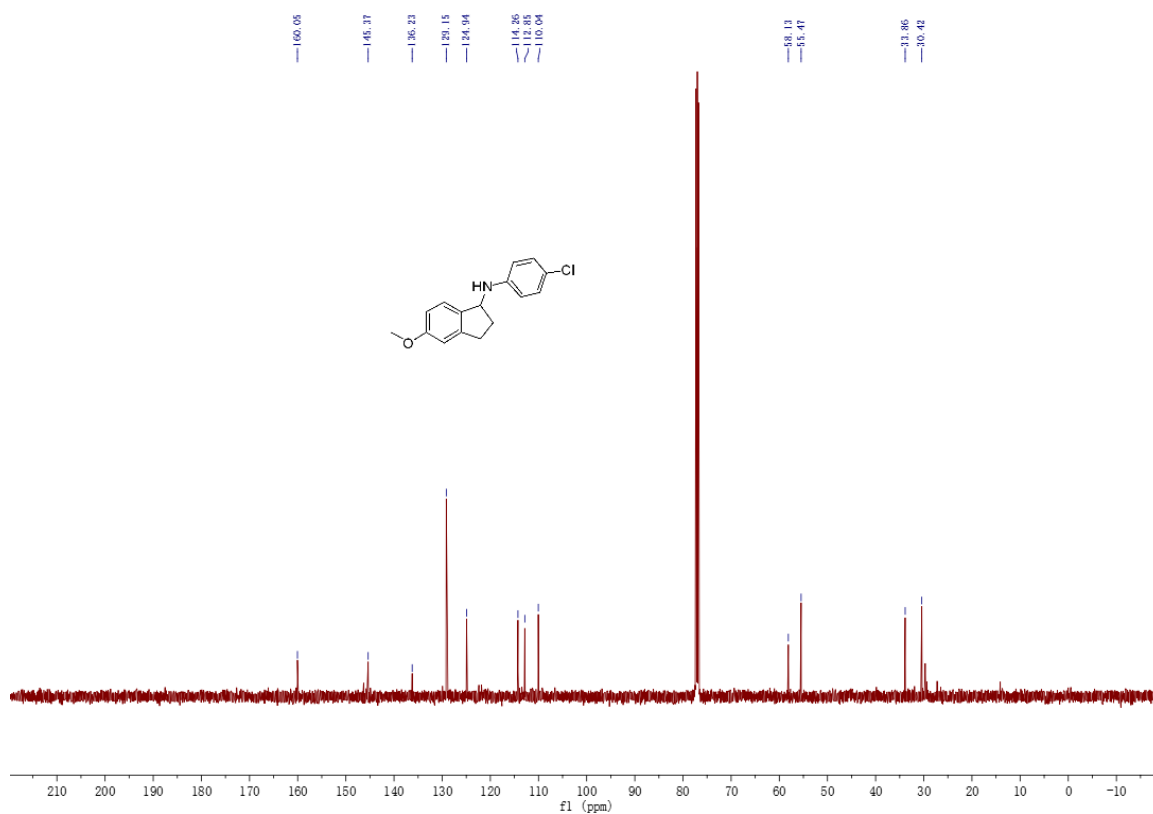
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3-2i**



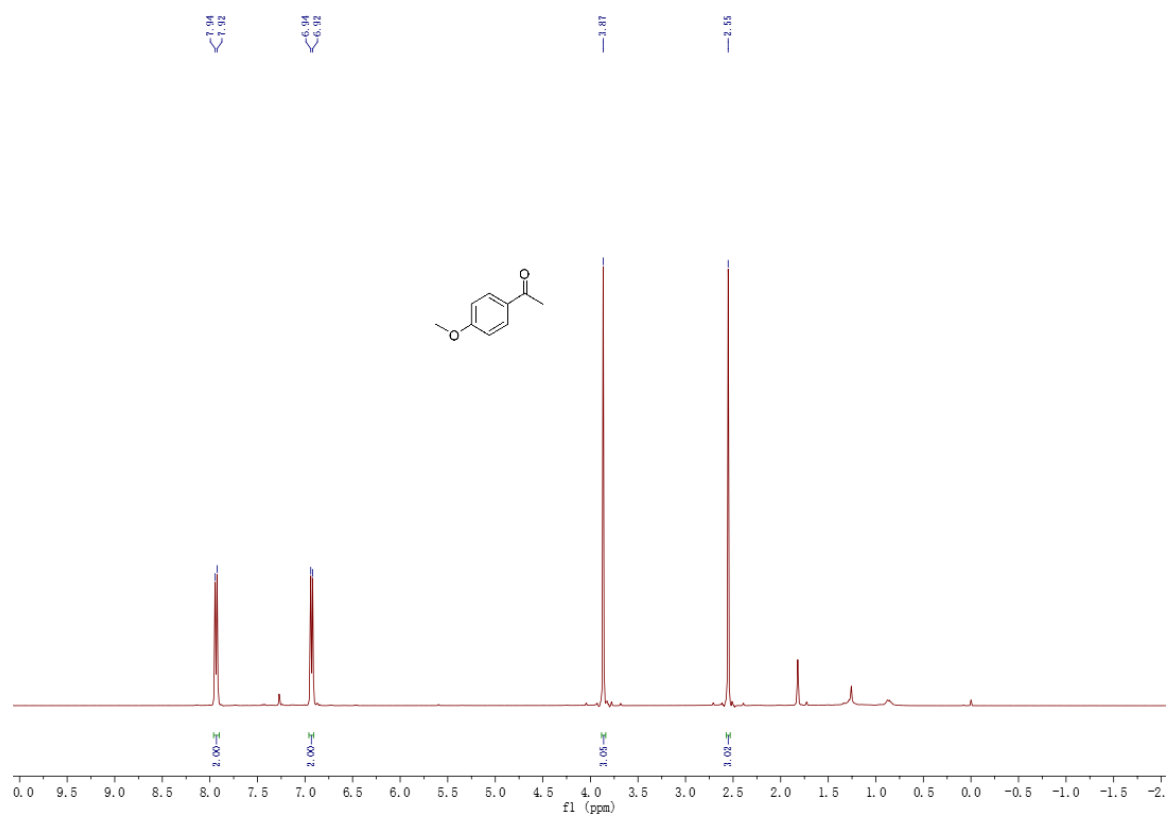
^1H NMR spectrum (400 MHz, CDCl_3) of **3-2j**



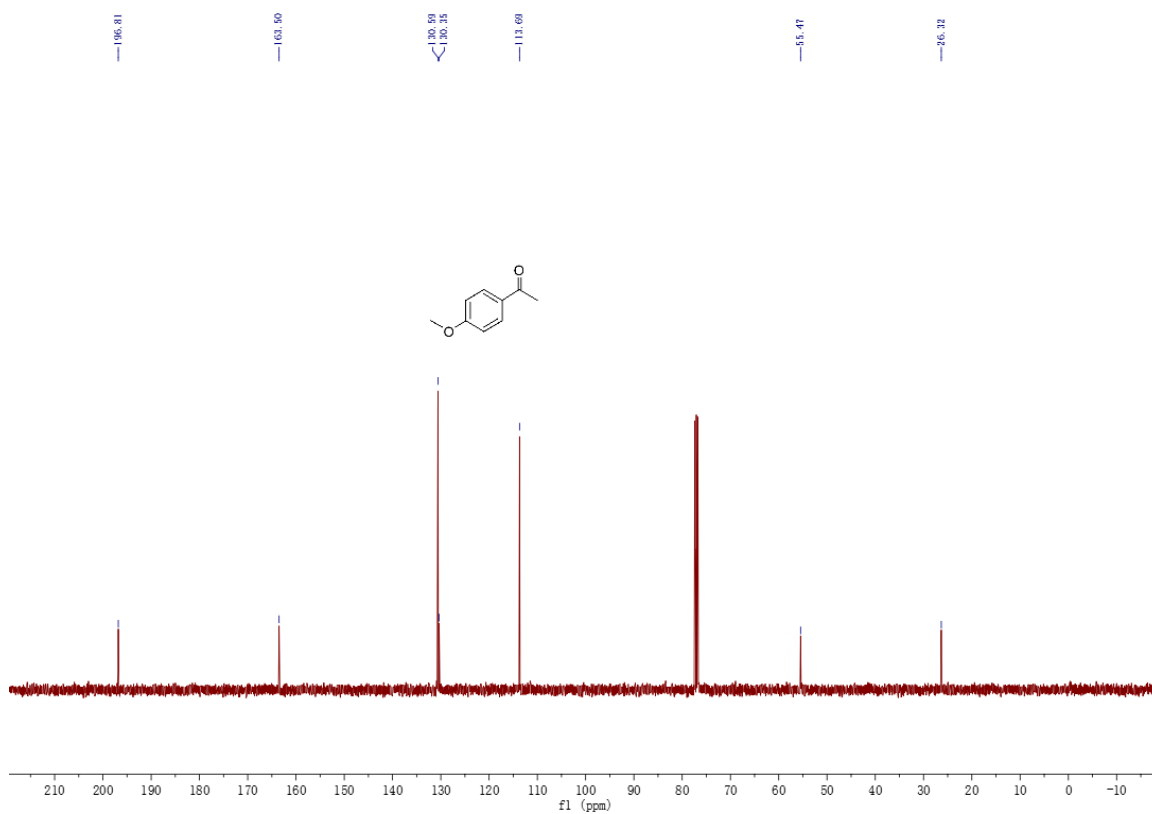
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3-2j**



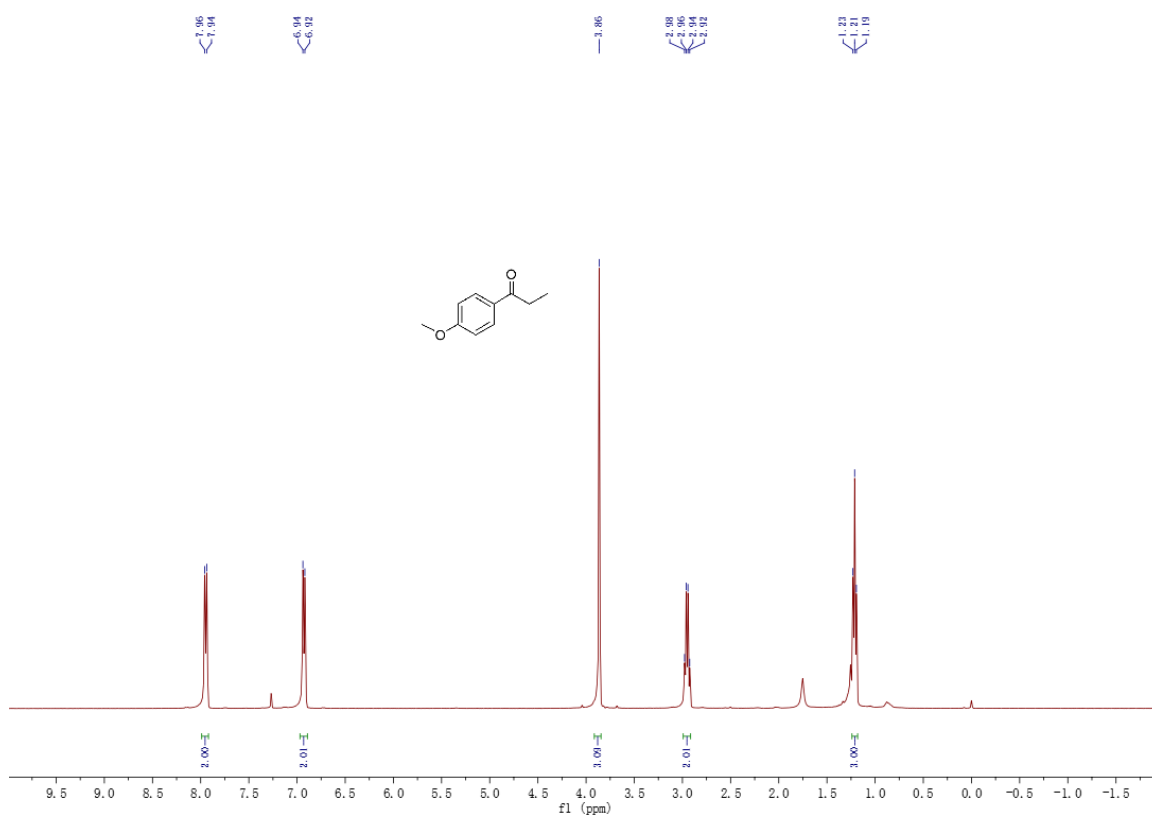
^1H NMR spectrum (400 MHz, CDCl_3) of **5a**



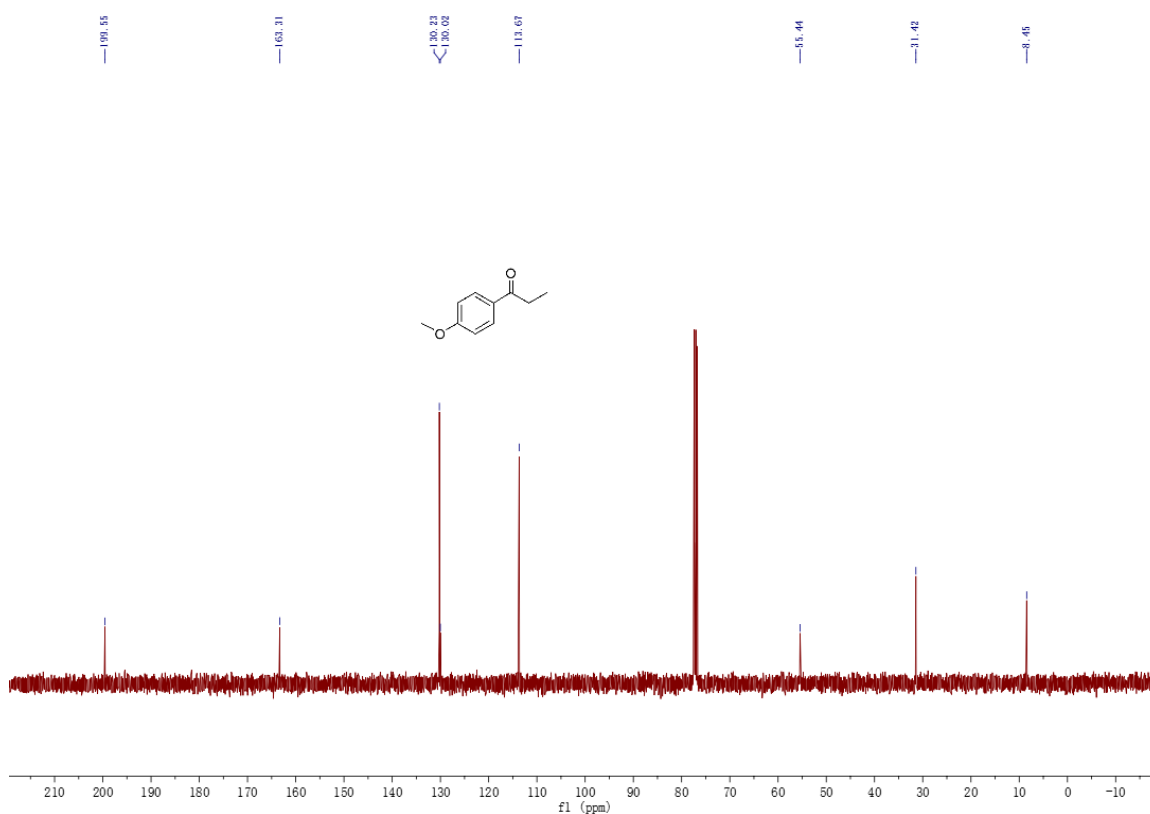
^{13}C NMR spectrum (100 MHz, CDCl_3) of **5a**



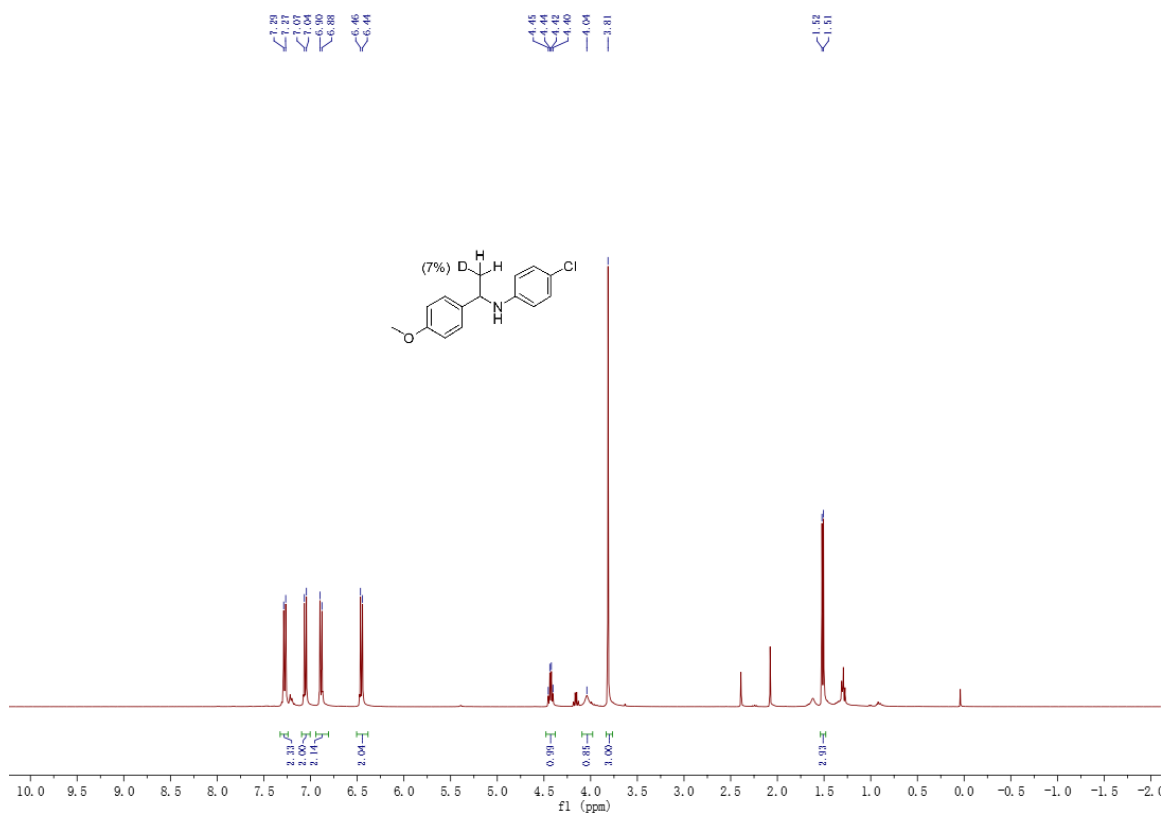
^1H NMR spectrum (400 MHz, CDCl_3) of **5b**



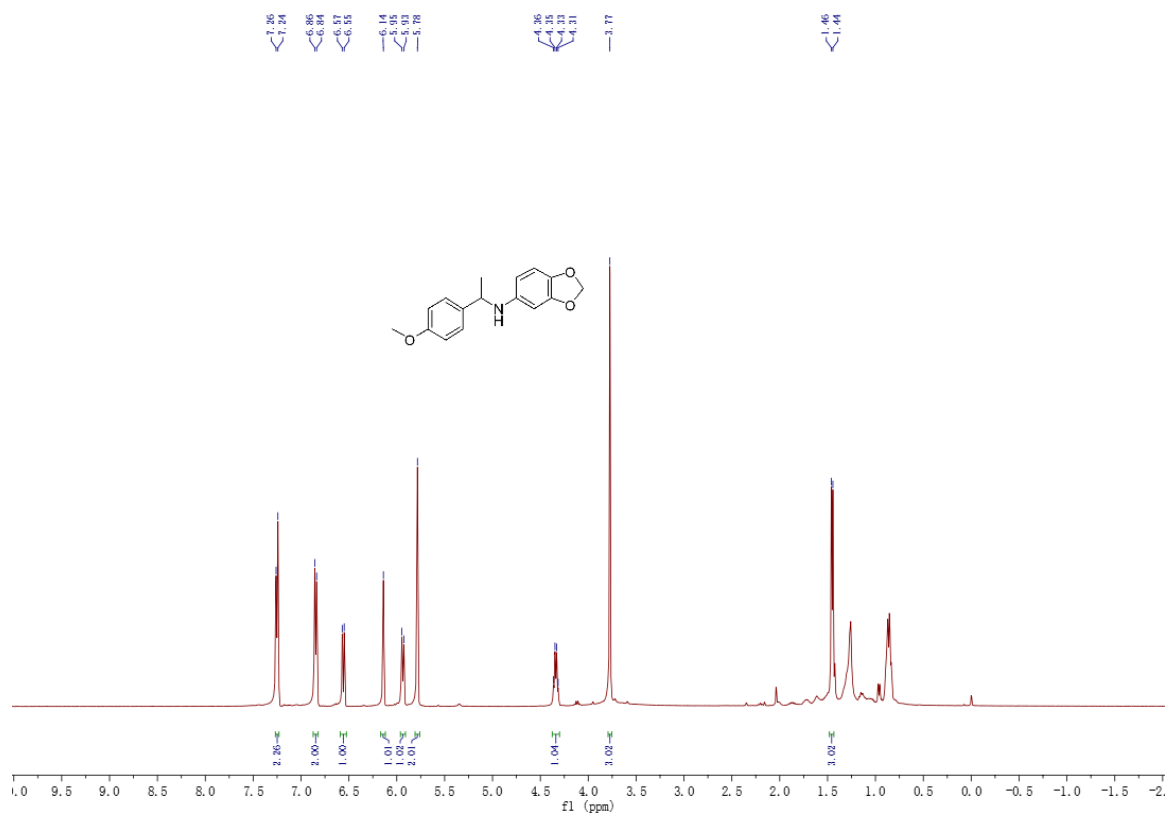
^{13}C NMR spectrum (100 MHz, CDCl_3) of **5b**



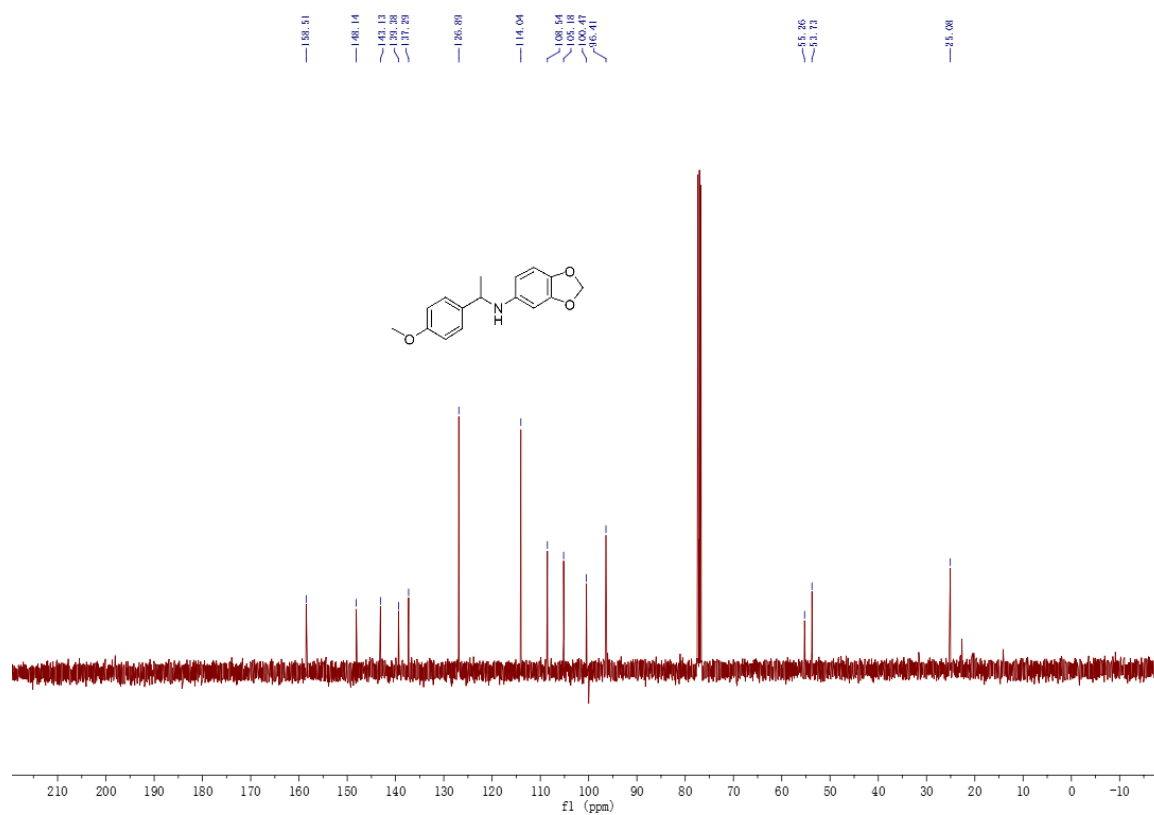
^1H NMR spectrum (400 MHz, CDCl_3) of d1-**3-1a**



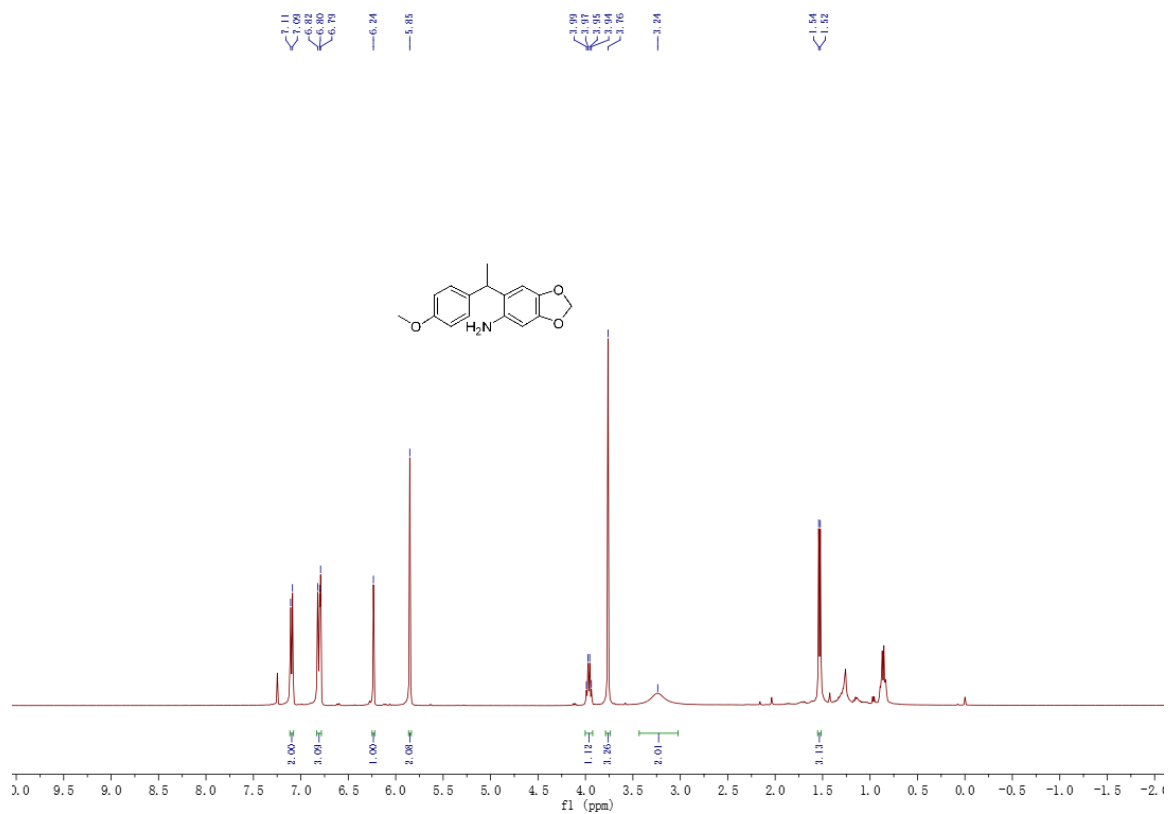
^1H NMR spectrum (400 MHz, CDCl_3) of **3-1v**



^{13}C NMR spectrum (100 MHz, CDCl_3) of **3-1v**



^1H NMR spectrum (400 MHz, CDCl_3) of **3-1w**



^{13}C NMR spectrum (100 MHz, CDCl_3) of **3-1w**

