*Supporting Information for*

# $BF_3 \cdot Et_2O$ as a metal-free catalyst for direct reductive amination of aldehydes with amines using formic acid as a reductant

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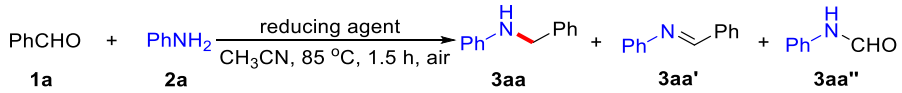
## 1. General information:

Unless otherwise noted, all experiments were carried out in air, and all commercially available chemicals including organic solvents were used as received from Aldrich, Acros or Strem without further purification. $^{1}$H NMR, $^{13}$C NMR, $^{11}$B NMR and $^{19}$F NMR spectra were recorded on a Bruker Model Avance DMX 400, 500 and 600 Spectrometer ($^{1}$H 400 MHz, $^{13}$C 101 MHz, $^{1}$H 500 MHz, $^{13}$C 126 MHz, $^{1}$H 600 MHz, $^{13}$C 151 MHz, $^{11}$B 193 MHz and $^{19}$F 565 MHz respectively). Chemical shifts (δ) are given in ppm and are referenced to residual solvent peaks. High resolution mass spectra (HRMS) were performed on a VG Autospec-3000 spectrometer. HPLC analyses were performed on a Varian Prostar 210 liquid chromatograph. Column chromatography was performed with silica gel (200-300 me sh). Ethyl (*E*)-3-(2-formylphenyl)acrylate (**6b**) was synthesized according to published literature method.[1]

## 2. Determination of the optimal reaction conditions

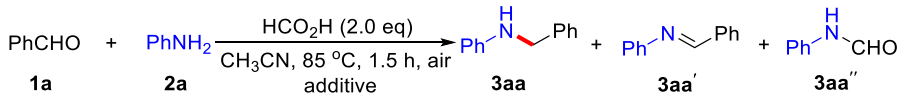
**Table S1.** The effect of different reducing agents.[a]




| entry | reducing agent (equiv) | **3aa** (%)[b] | **3aa′** (%)[b] | **3aa″**(%)[b] |
|---|---|---|---|---|
| 1 | $HCO_2Na$ (4) | 0 | >99 | 0 |
| 2 | $HCO_2NH_4$ (4) | 4 | 93 | 0 |
| 3 | $HCO_2Et$ (4) | 0 | >99 | 0 |
| 4 | $HCO_2H$ (4) | 34 | 20 | 45 |
| 5 | $HCO_2H/NEt_3$ (5/2) (4) | 32 | 31 | 36 |
| 6 | $HCO_2H$ (3) | 34 | 26 | 37 |
| 7 | $HCO_2H$ (2) | 34 | 33 | 31 |
| 8 | $HCO_2H$ (1) | 18 | 55 | 26 |

[a] Reaction Conditions: **1a** (1.0 mmol), **2a** (1.1 mmol), reducing agent, $CH_3CN$ (2.0 mL), 85 °C, 1.5 h, air. [b] Determined by $^{1}$H NMR with $CH_2Br_2$ as an internal standard.

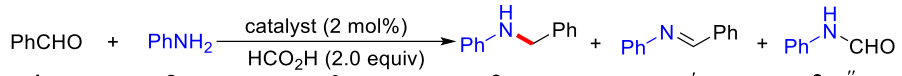
**Table S2.** The effect of additives.[a]




| entry | Additive | **3aa** (%)[b] | **3aa′** (%)[b] | **3aa″**(%)[b] |
|---|---|---|---|---|
| 1 | 3Å MS | 34 | 32 | 33 |
| 2 | 4Å MS | 32 | 34 | 31 |
| 3 | 5Å MS | 33 | 32 | 33 |
| 4 | anhydrous $Na_2SO_4$ | 32 | 34 | 32 |
| 5 | trimethyl orthoformate | 34 | 32 | 31 |

[a] Reaction Conditions: **1a** (1.0 mmol), **2a** (1.1 mmol), $HCO_2H$ (2.0 eq), $CH_3CN$ (2.0 mL), additive (100 mg), 85 °C, 1.5 h, air. [b] Determined by $^{1}$H NMR with $CH_2Br_2$ as an internal standard.

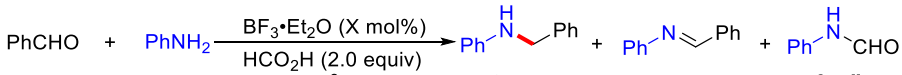
**Table S3.** The effect of different catalysts.[a]




| entry | catalyst | **3aa** (%)[b] | **3aa′** (%)[b] | **3aa′′**(%)[b] |
|---|---|---|---|---|
| 1 | $AlCl_3$ | 62 | 34 | 2 |
| 2 | $FeCl_3$ | 50 | 23 | 15 |
| 3 | $MnBr_2$ | 35 | 37 | 26 |
| 4 | $InI_3$ | 43 | 32 | 23 |
| 5 | $CoCl_2$ | 40 | 37 | 19 |
| 6 | $SnCl_4$ | 51 | 32 | 15 |
| 7 | $Sn(OTf)_2$ | 57 | 27 | 13 |
| 8 | AgOAc | 50 | 30 | 17 |
| 9 | AgOTf | 55 | 28 | 15 |
| 10 | $Zn(OTf)_2$ | 36 | 37 | 23 |
| 11 | $Ni(OTf)_2$ | 60 | 17 | 20 |
| 12 | $Cu(OTf)_2$ | 39 | 34 | 25 |
| 13 | $Yb(OTf)_3$ | 48 | 31 | 18 |
| 14 | $Sc(OTf)_3$ | 36 | 44 | 16 |
| 15 | $Bi(OTf)_3$ | 36 | 37 | 23 |
| 16 | $Ti(O\mathit{i}Pr)_4$ | 72 | 21 | 2 |
| 17 | $Si(OEt)_4$ | 50 | 25 | 22 |
| 18 | $B(OH)_3$ | 43 | 31 | 22 |
| 19 | $B(OMe)_3$ | 77 | 9 | 13 |
| 20 | $BEt_3$ | 93 | 2 | 4 |
| 21 | $BPh_3$ | 82 | 8 | 8 |
| 22 | $BF_3{\cdot}Et_2O$ | >99 | 0 | 0 |
| 23 | $B(C_6F_5)_3$ | >99 | 0 | 0 |
| 24 | 2-aminoquinazolin-4(3*H*)-one | 15 | 56 | 27 |
| 25 | Benzoic acid | 34 | 31 | 30 |
| 26 | Phenylboronic acid | 30 | 39 | 28 |
| 27 | Benzenesulfonic acid | 44 | 42 | 11 |
| 28 | $CF_3CO_2H$ | 26 | 49 | 20 |
| 29 | CSA | 61 | 23 | 14 |
| 30 | TfOH | 81 | 15 | 3 |
| 31 | 1,1′-binaphthyl-2,2'-diyl hydrogenphosphate | 32 | 39 | 28 |

[a] Reaction Conditions: **1a** (1.0 mmol), **2a** (1.1 mmol), catalyst (2.0 mol%), $HCO_2H$ (2.0 mmol), $CH_3CN$ (2.0 mL), 85 °C, 1.5 h, air. [b] Determined by $^1H$ NMR with $CH_2Br_2$ as an internal standard. CSA: Camphorsulfonic acid.

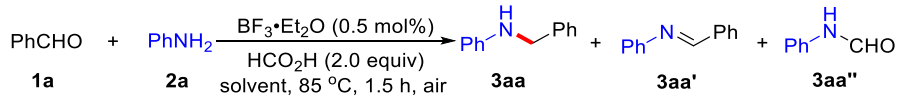
**Table S4.** The effect of $BF_3{\cdot}Et_2O$ loading.[a]




| entry | $BF_3{\cdot}Et_2O$ (mol%) | **3aa** (%)[b] | **3aa′** (%)[b] | **3aa′′**(%)[b] |
|---|---|---|---|---|
| 1 | 2 | >99 | 0 | 0 |
| 2 | 1.5 | >99 | 0 | 0 |
| 3 | 1.0 | >99 | 0 | 0 |
| 4 | 0.5 | >99 | 0 | 0 |
| 5[c] | 0.5 | 0 | >99 | 0 |
| 6[d] | 0.5 | 0 | >99 | 0 |
| 7[e] | 0.5 | 16 | 83 | 0 |
| 8[f] | 0.5 | 79 | 20 | 0 |
| 9 | 0.4 | 95 | <1 | 3 |

[a] Reaction Conditions: **1a** (1.0 mmol), **2a** (1.1 mmol), $BF_3 \cdot Et_2O$, $HCO_2H$ (2.0 mmol), $CH_3CN$ (2.0 mL), 85 °C, 1.5 h, air. [b] Determined by $^1H$ NMR with $CH_2Br_2$ as an internal standard. [c] $HCO_2Et$ (2.0 mmol) was used to replace $HCO_2H$. [d] $HCO_2Na$ (2.0 mmol) was used to replace $HCO_2H$. [e] $HCO_2NH_4$ (2.0 mmol) was used to replace $HCO_2H$. [f] $HCO_2H/NEt_3$ (5/2, 2.0 mmol) was used to replace $HCO_2H$.

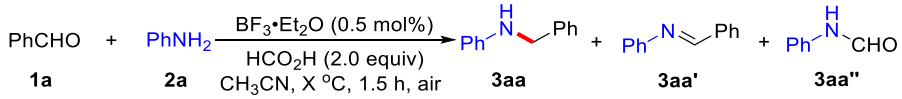
**Table S5.** The effect of solvents.[a]




| Entry | Solvent | **3aa** (%)[b] | **3aa′**(%)[b] | **3aa′′** (%)[b] |
|---|---|---|---|---|
| 1 | toluene | 23 | 48 | 28 |
| 2 | PhCl | 19 | 47 | 31 |
| 3 | THF | 15 | 54 | 30 |
| 4 | ethyl acetate | 23 | 45 | 30 |
| 5 | 1,4-dioxane | 20 | 44 | 35 |
| 6 | DCE | 25 | 43 | 23 |
| 7 | sulfolane | 68 | 26 | 0 |
| 8 | $CH_3CN$ | >99 | 0 | 0 |
| 9[c] | $CH_3CN$ | 96 | 0 | 3 |
| 10 | DMF | 27 | 60 | 5 |
| 11 | DMSO | 77 | 0 | 0 |
| 12 | MeOH | 3 | 68 | 26 |
| 13 | EtOH | 3 | 67 | 25 |
| 14 | *i*-PrOH | 0 | 68 | 23 |
| 15 | $H_2O$ | 0 | 0 | 36 |

[a] Reaction Conditions: **1a** (1.0 mmol), **2a** (1.1 mmol), $BF_3 \cdot Et_2O$ (0.5 mol%), $HCO_2H$ (2.0 mmol), solvent (2.0 mL), 85 °C, 1.5 h, air. [b] Determined by $^1H$ NMR with $CH_2Br_2$ as an internal standard. [c] $CH_3CN$ (1.0 mL).

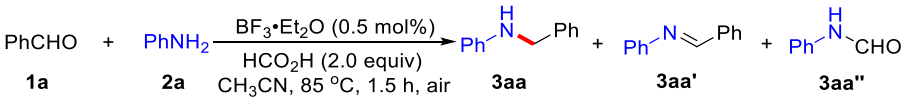
**Table S6.** The effect of temperature.[a]




| Entry | Temperature (°C) | **3aa** (%)[b] | **3aa′** (%)[b] | **3aa′′**(%)[b] |
|---|---|---|---|---|
| 1 | 100 | >99 | 0 | 0 |
| 2 | 90 | >99 | 0 | 0 |
| 3 | 85 | >99(93)[c] | 0 | 0 |
| 4 | 80 | 89 | 10 | 0 |

[a] Reaction Conditions: **1a** (1.0 mmol), **2a** (1.1 mmol), $BF_3 \cdot Et_2O$ (0.5 mol%), $HCO_2H$ (2.0 mmol), $CH_3CN$ (2.0 mL), 1.5 h, air. [b] Determined by $^1H$ NMR with $CH_2Br_2$ as an internal standard. [c] Isolated yield.

**Table S7.** The effect of the amount of **2a**.[a]




| Entry | **2a** (equiv) | **3aa** (%)[b] | **3aa′** (%)[b] | **3aa′′**(%)[b] |
|---|---|---|---|---|
| 1 | 1.0 | 95 | 0 | 0 |
| 2 | 1.1 | >99 | 0 | 0 |
| 3 | 1.2 | >99 | 0 | 0 |

[a] Reaction Conditions: **1a** (1.0 mmol), **2a**, $BF_3 \cdot Et_2O$ (0.5 mol%), $HCO_2H$ (2.0 mmol), $CH_3CN$ (2.0 mL), 85 °C, 1.5 h, air. [b] Determined by $^1H$ NMR with $CH_2Br_2$ as an internal standard.

## 3. General procedure for DRA of Aldehydes with Amines

### (1) General procedure for DRA of aldehydes with primary amines

To an oven-dried screw-capped pressure tube was sequentially added aldehyde **1** (1 mmol), primary amine **2** (1.1 mmol), $BF_3 \cdot Et_2O$ (0.71 mg, 0.005 mmol), $CH_3CN$ (2 mL), and $HCO_2H$ (92 mg, 2 mmol). The tube was sealed, and the mixture was then stired at 85 °C for 1.5 h. After being cooled to room temperature, the resulting mixture was basified with saturated aqueous $NaHCO_3$ solution (10 mL), and extracted with $CH_2Cl_2$ (3 × 10 mL). The organic layers were combined, washed with brine (20 mL), dried over anhydrous $Na_2SO_4$ and filtered. The filtrate was concentrated in *vacuo* to obtain the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane (1:20 to 1:10, 1% $NEt_3$ was used) to obtain the pure product **3**.

### (2) General procedure for DRA of alkyl aldehydes and primary alkyl amines

To an oven-dried screw-capped pressure tube was sequentially added alkyl aldehyde **4** (1 mmol), primary alkyl amine **2** (1.1 mmol), $BF_3 \cdot Et_2O$ (2.84 mg, 0.02 mmol), $CH_3CN$ (2 mL) and $HCO_2H$ (92 mg, 2 mmol). The tube was sealed, and the mixture was stirred at 85 °C for 5 h. After being cooled to room temperature, the resulting mixture was basified with saturated aqueous $NaHCO_3$ (10 mL) solution and extracted with $CH_2Cl_2$ (3 × 10 mL). The organic layers were combined, washed with brine (20 mL), dried over anhydrous $Na_2SO_4$ and filtered. The filtrate was concentrated in *vacuo* to obtain the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane (1:20 to 1:10, 1% $NEt_3$ was used) to obtain the pure product.

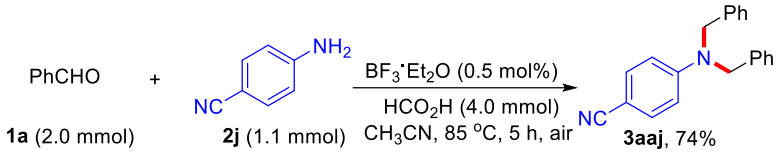
### (3) General procedure for DRA of the aldehydes with secondary amines

To an oven-dried screw-capped pressure tube was sequentially added aldehyde **1** or **4** (1 mmol), secondary amine **8** (1.1 mmol), $BF_3 \cdot Et_2O$ (0.71 mg, 0.005 mmol), $CH_3CN$ (2 mL) and $HCO_2H$ (92 mg, 2 mmol). The tube was sealed, and the mixture was stirred at 85 °C for 5 h. After being cooled to room temperature, the mixture was concentrated in *vacuo* to afford a crude mixture. The resulting solution was basified with saturated aqueous $NaHCO_3$ solution (10 mL) and extracted with $CH_2Cl_2$ (3 × 10 mL). The organic layers were combined, washed with brine (20 mL), dried over anhydrous $Na_2SO_4$ and

filtered. The filtrate was concentrated in *vacuo* to obtain the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane (1:20 to 1:10, 1% $NEt_3$ was used) to obtain the pure product.

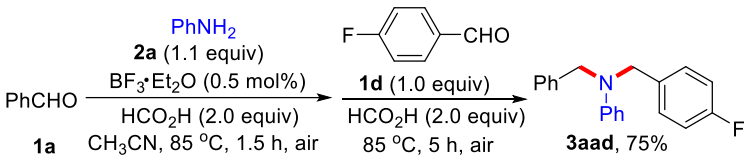
**(4) General procedure for N,N-dialkylation of amine**

**(a) Synthesis of 3aaj**




To an oven-dried screw-capped pressure tube was sequentially added benzaldehyde **1a** (2 mmol), 4-aminobenzonitrile **2j** (1.1 mmol), $BF_3 \cdot Et_2O$ (0.71 mg, 0.005 mmol), $CH_3CN$ (2 mL) and $HCO_2H$ (184 mg, 4 mmol). The tube was sealed, and the mixture was stirred at 85 °C for 5 h. After being cooled to room temperature, the mixture was basified with saturated aqueous $NaHCO_3$ (20 mL) solution and extracted with $CH_2Cl_2$ (3 × 10 mL). The organic layers were combined, washed with brine (20 mL), dried over anhydrous $Na_2SO_4$ and filtered. The filtrate was concentrated in *vacuo* to obtain the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane (1:10 to 1:5) to obtain the pure product **3aaj** (220.8 mg, 74% yield).

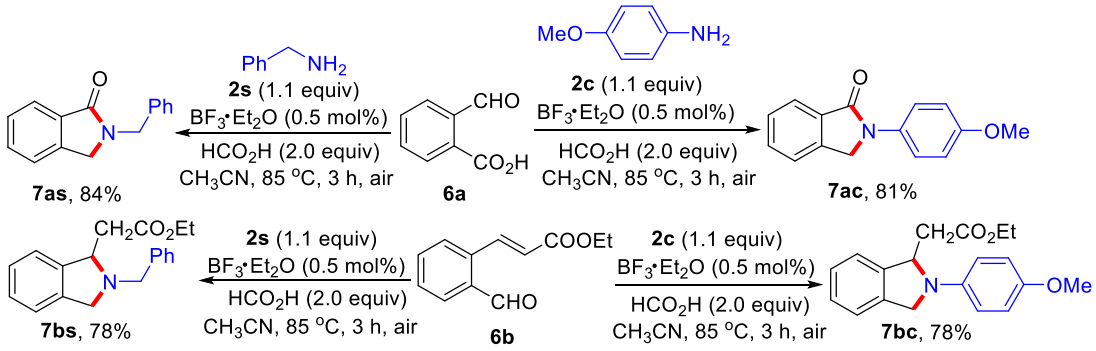
**(b) Synthesis of 3aad**




To an oven-dried screw-capped pressure tube was sequentially added benzaldehyde **1a** (1 mmol), aniline **2a** (1.1 mmol), $BF_3 \cdot Et_2O$ (0.71 mg, 0.005 mmol), $CH_3CN$ (2 mL), and $HCO_2H$ (92 mg, 2 mmol). The tube was sealed, and the mixture was stirred at 85 °C for 1.5 h. After being cooled to room temperature, the tube was opened to air, and 4-fluorobenzaldehyde **1d** (1.0 mmol) and $HCO_2H$ (92 mg, 2 mmol) was added. Then the tube was sealed, and the mixture was stirred at 85 °C for 5 h. After being cooled to room temperature, the mixture was basified with saturated aqueous $NaHCO_3$ (20 mL) solution and extracted with $CH_2Cl_2$ (3 × 10 mL). The organic layers were combined, washed with brine (20 mL), dried over anhydrous $Na_2SO_4$ and filtered. The filtrate was

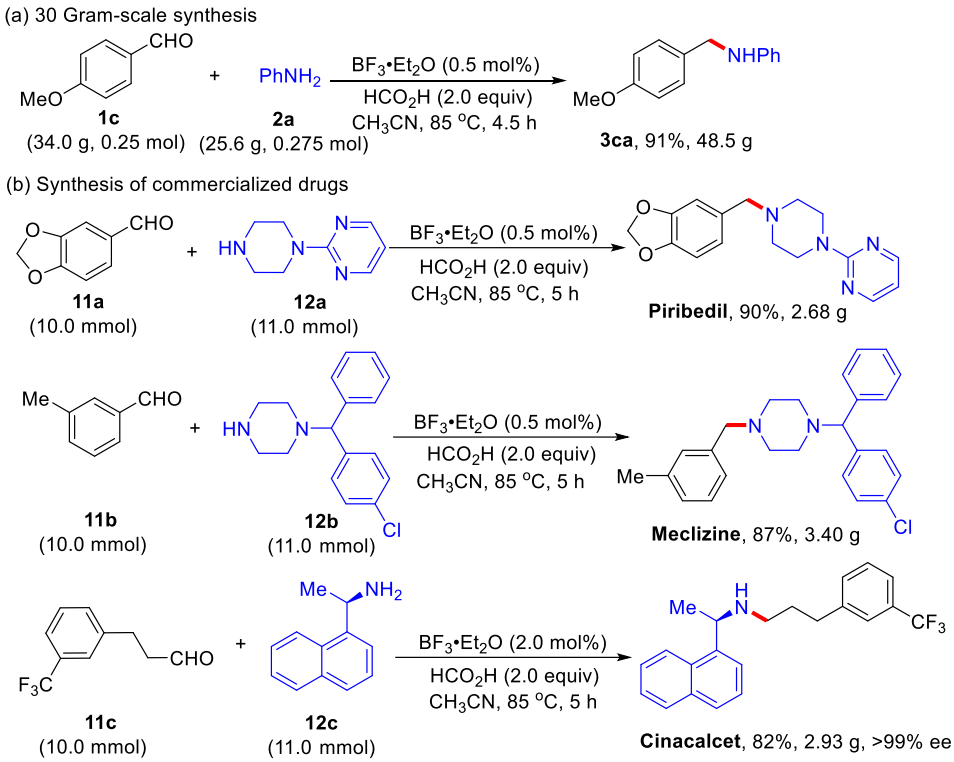
concentrated in *vacuo* to obtain the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane (1:20 to 1:10) to obtain the pure product **3aad** (218.5 mg, 75% yield).

**(5) Synthesis of isoindolinones and isoindolines**



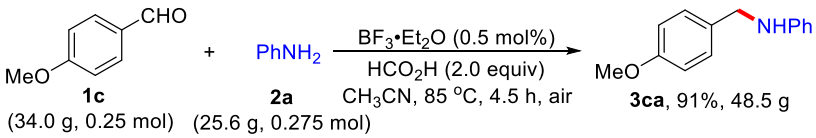

To an oven-dried screw-capped pressure tube was sequentially added 2-formylbenzoic acid **6a** (1 mmol) or ethyl (*E*)-3-(2-formylphenyl)acrylate **6b** (1 mmol), 4-methoxyaniline **2c** (1.1 mmol) or phenylmethanamine **2s** (1.1 mmol), $BF_3 \cdot Et_2O$ (0.71 mg, 0.005 mmol), $CH_3CN$ (2 mL), and $HCO_2H$ (92 mg, 2 mmol). The tube was sealed, and the mixture was stirred at 85 °C for 3 h. After being cooled to room temperature, the mixture was basified with saturated aqueous $NaHCO_3$ (10 mL) solution and extracted with $CH_2Cl_2$ (3 × 10 mL). The organic layers were combined, washed with brine (20 mL), dried over anhydrous $Na_2SO_4$ and filtered. The filtrate was concentrated in *vacuo* to obtain the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane (1:20 to 1:10, 1% $NEt_3$ was used) to obtain the pure products.

## 4. Synthetic Applications




**Scheme S1.** Synthetic Applications

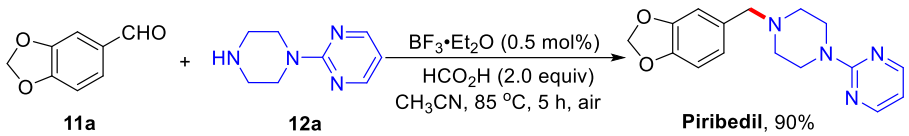
### (a) 30 Gram-scale synthesis of 3ca




To a 1.0 L round-bottom flask equipped with a reflux condenser was charged 4-methoxybenzaldehyde **1c** (34.0 g, 0.25 mol), aniline **2a** (25.6 g, 0.275 mol), $BF_3{\cdot}OEt_2$ (177.4 mg, 0.00125 mol), $CH_3CN$ (0.5 L), then $HCO_2H$ (23.3 g, 0.5 mol) was added slowly. The mixture was refluxed in air at 85 °C for 4.5 h. After being cooled to room temperature, the mixture was basified with saturated aqueous $NaHCO_3$ (100 mL) solution and extracted with $CH_2Cl_2$ (3 × 100 mL). The organic layers were combined, washed with brine (200 mL), dried over anhydrous $Na_2SO_4$ and filtered. The filtrate was concentrated in *vacuo* to obtain the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane (1:20 to 1:10, 1% $NEt_3$ was used) to obtain pure **3ca** as a yellow oil (48.5 g, 91% yield).

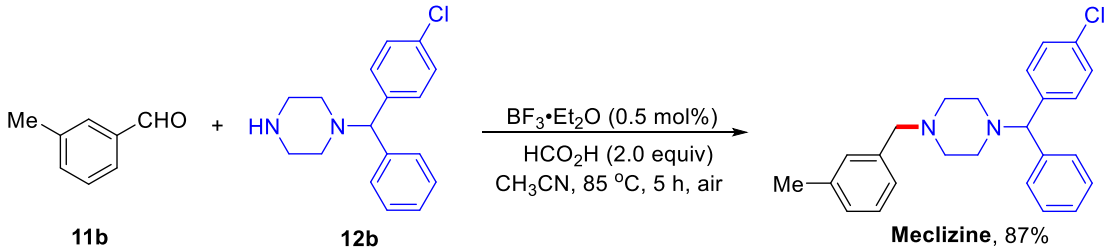
### (b) Synthesis of commercialized drugs.

### (i) Synthesis of Piribedil




To a 100 mL round-bottom flask equipped with a reflux condenser was charged benzo[d][1,3]dioxole-5-carbaldehyde **11a** (1.5 g, 10 mmmol), 2-(piperazin-1-yl)pyrimidine **12a** (1.8 g, 11 mmol), $BF_3 \cdot OEt_2$ (7.1 mg, 0.05 mmol), $CH_3CN$ (20 mL), and $HCO_2H$ (0.9 g, 20 mmol). The mixture was refluxed in air at 85 °C for 5.0 h. After being cooled to room temperature, the mixture was basified with saturated aqueous $NaHCO_3$ (20 mL) solution and extracted with methylene dichloride (3 × 20 mL). The organic layers were combined, washed with brine (20 mL), dried over anhydrous $Na_2SO_4$ and filtered. The filtrate was concentrated in *vacuo* to obtain the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane (1:10 to 1:5, 1% $NEt_3$ was used) to obtain pure Piribedil as a colorless oil (2.68 g, 90% yield).[2] $^1$H NMR (600 MHz, $CDCl_3$) δ 8.29 (d, $J$ = 4.7 Hz, 2H), 6.89 (s, 1H), 6.76 (s, 2H), 6.46 (t, $J$ = 4.7 Hz, 1H), 5.94 (s, 2H), 3.85-3.79 (m, 4H), 3.45 (s, 2H), 2.48 (t, $J$ = 5.1 Hz, 4H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 161.75, 157.78, 147.76, 146.75, 131.99, 122.32, 109.81, 109.58, 107.99, 101.00, 62.98, 52.95, 43.79. HRMS (ESI) calcd. for $C_{16}H_{19}N_4O_2^+$ $[M+H]^+$: 299.1503, found: 299.1509.

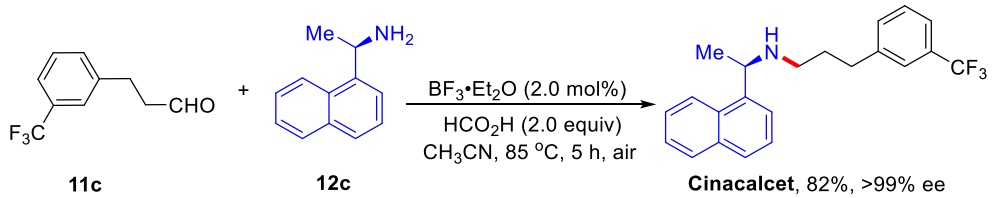
**(ii) Synthesis of Meclizine**




To a 100 mL round-bottom flask equipped with a reflux condenser was charged 3-methylbenzaldehyde **11b** (1.2 g, 10 mmol), 1-((4-chlorophenyl)(phenyl)methyl)piperazine **12b** (3.15 g, 11 mmol), $BF_3 \cdot OEt_2$ (7.1 mg, 0.05 mmol), $CH_3CN$ (20 mL), and $HCO_2H$ (0.9 g, 20 mmol). The mixture was refluxed in air at 85 °C for 5.0 h. After being cooled to room temperature, the mixture was basified with saturated aqueous $NaHCO_3$ (20 mL) solution and extracted with methylene dichloride (3 × 20 mL). The organic layers were combined, washed with brine (20 mL), dried over anhydrous $Na_2SO_4$ and filtered. The filtrate was concentrated in *vacuo* to obtain the crude product, which was purified by silica gel column

chromatography using a mixture of ethyl acetate and hexane (1:10 to 1:5, 1% $NEt_3$ was used) to obtain pure Meclizine as a white solid (3.4 g, 87% yield).[3] $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43-7.39 (m, 4H), 7.33-7.21 (m, 6H), 7.18-7.10 (m, 3H), 4.27 (s, 1H), 3.54 (s, 2H), 2.54 (s, 8H), 2.38 (s, 3H, $-CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 142.29, 141.51, 137.99, 137.79, 132.55, 130.04, 129.31, 128.67, 128.61, 128.12, 127.97, 127.83, 127.17, 126.43, 75.52, 63.17, 53.43, 51.88, 21.49. HRMS (ESI) calcd. for $C_{25}H_{28}ClN_2^+$ $[M+H]^+$: 391.1936, found: 391.1940.

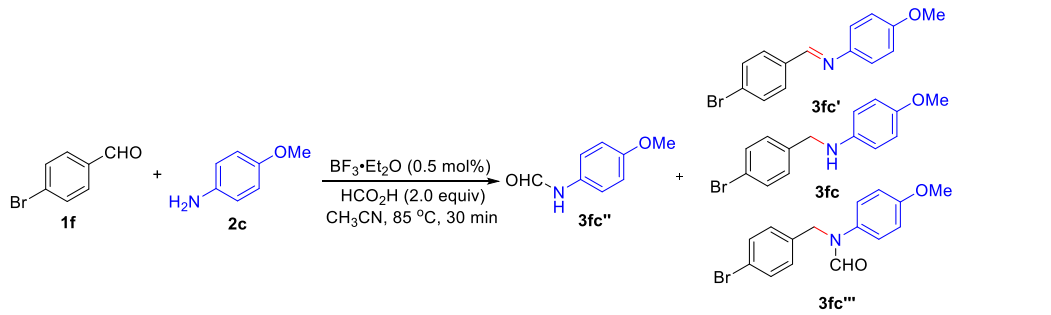
**(iii) Synthesis of Cinacalcet**

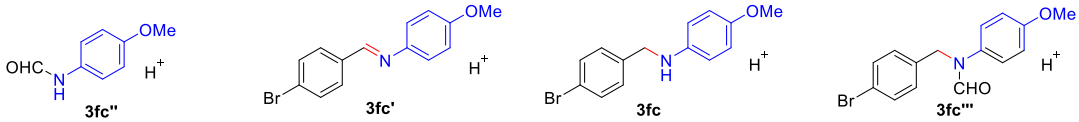



To a 100 mL round-bottom flask equipped with a reflux condenser was charged 3-(3-(trifluoromethyl)phenyl)propanal **11c** (2.02 g, 10 mmol), **(*R*)**-1-(naphthalen-1-yl)ethan-1-amine **12c** (1.88 g, 11 mmol), $BF_3{\cdot}OEt_2$ (28.4 mg, 0.2 mmol), $CH_3CN$ (20 mL), and $HCO_2H$ (0.9 g, 20 mmol). The mixture was refluxed in air at 85 °C for 5.0 h. After being cooled to room temperature, the mixture was basified with saturated aqueous $NaHCO_3$ (20 mL) solution and extracted with $CH_2Cl_2$ (3 × 20 mL). The organic layers were combined, washed with brine (20 mL), dried over anhydrous $Na_2SO_4$ and filtered. The filtrate was concentrated in *vacuo* to obtain the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane (1:10 to 1:5, 1% $NEt_3$ was used) to obtain pure Cinacalcet as a colorless oil (2.93 g, 82% yield, >99% ee).[2] $^1$H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, $J$ = 8.2 Hz, 1H), 8.01 (d, $J$ = 7.6 Hz, 1H), 7.89 (d, $J$ = 8.1 Hz, 1H), 7.79 (d, $J$ = 7.1 Hz, 1H), 7.63 (q, $J$ = 8.3, 7.7 Hz, 5H), 7.34 (d, $J$ = 7.9 Hz, 2H), 4.75 (q, $J$ = 6.6 Hz, 1H), 2.77 (tdd, $J$ = 25.6, 12.7, 6.8 Hz, 4H), 1.95 (p, $J$ = 7.4 Hz, 2H), 1.64 (d, $J$ = 6.6 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 146.45, 141.37, 134.10, 131.42, 129.08, 128.73, 128.30, 127.98, 127.27, 125.83, 125.77, 125.41, 125.25 (q, $J$ = 3.9 Hz), 123.05, 122.77, 53.89, 47.35, 33.52, 31.87, 23.73. HRMS (ESI) calcd. for $C_{22}H_{23}F_3N^+$ $[M+H]^+$: 358.1777, found: 358.1779.

## 5. The mechanistic study

### (1) ESI-MS Study



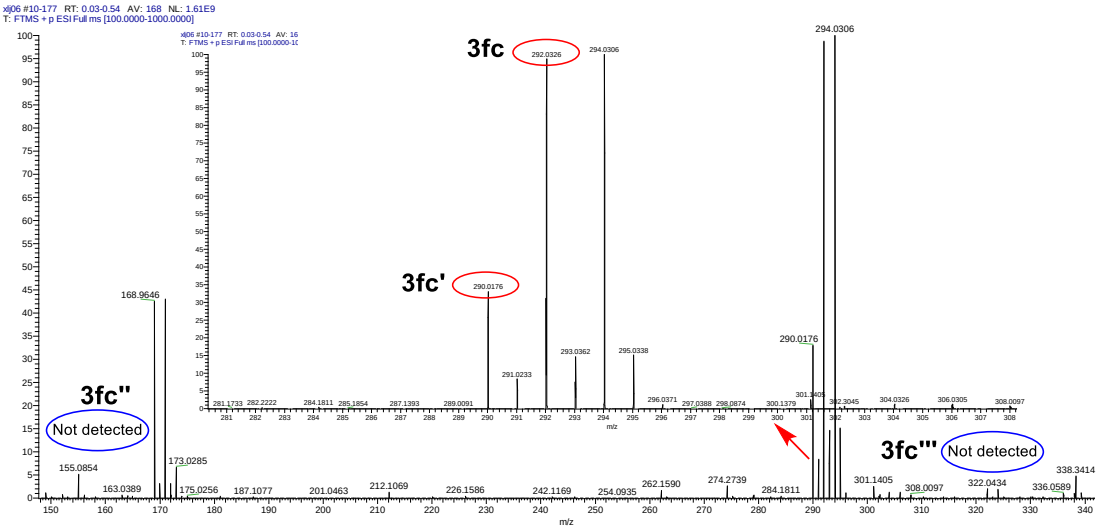




Chemical Formula: $C_8H_{10}NO_2^+$
Exact Mass: 152.0706

Chemical Formula: $C_{14}H_{13}BrNO^+$
Exact Mass: 290.0175

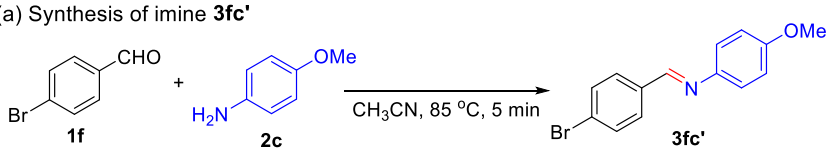
Chemical Formula: $C_{14}H_{15}BrNO^+$
Exact Mass: 292.0332

Chemical Formula: $C_{15}H_{15}BrNO_2^+$
Exact Mass: 320.0281



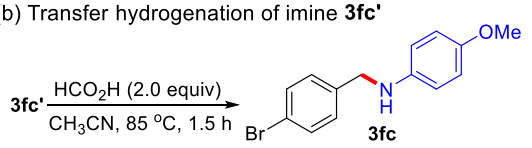

## (2) Control experiments

(a) Synthesis of imine **3fc'**



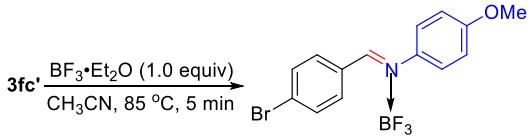

without $BF_3$•$Et_2O$, 67%
with $BF_3$•$Et_2O$ (0.5 mol%), 99%

(b) Transfer hydrogenation of imine **3fc'**

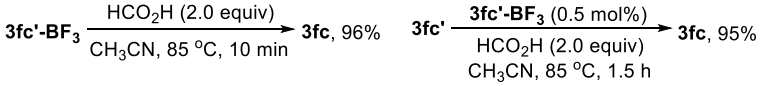



without $BF_3$•$Et_2O$, 38%
with $BF_3$•$Et_2O$ (0.5 mol%), 99%

(c) Synthesis and application of **3fc'-BF$_3$** adduct




**3fc'-BF$_3$**, 99%



**Scheme S2**. Control experiments performed

**(a) Synthsis of imine 3fc′**

A mixture of 4-bromobenzaldehyde (**1f**) (185.0 mg, 1.0 mmol), 4-methoxyaniline (**2c**) (135.4 mg, 1.1 mmol) in $CH_3CN$ (2.0 mL) with or without $BF_3 \cdot Et_2O$ (0.7 mg, 0.005 mmol) in an oven-dried screw-capped pressure tube was stirred at 85 °C for 5 min. After being cooled to ambient temperature, the reaction mixture was concentrated in *vacuo* to obtain the crude product, which was purified by silica gel column chromatography (ethyl acetate/hexane = 1:10-1:5, 1% $NEt_3$ was used) to obtain product **3fc'** as a grey solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.77-7.74 (m, 2H), 7.641-7.58 (m, 2H), 7.26-7.22 (m, 2H), 6.95-6.92 (m, 2H), 3.83 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 158.63, 156.83, 144.55, 135.51, 132.08, 130.03, 125.53, 122.36, 114.55, 55.62.

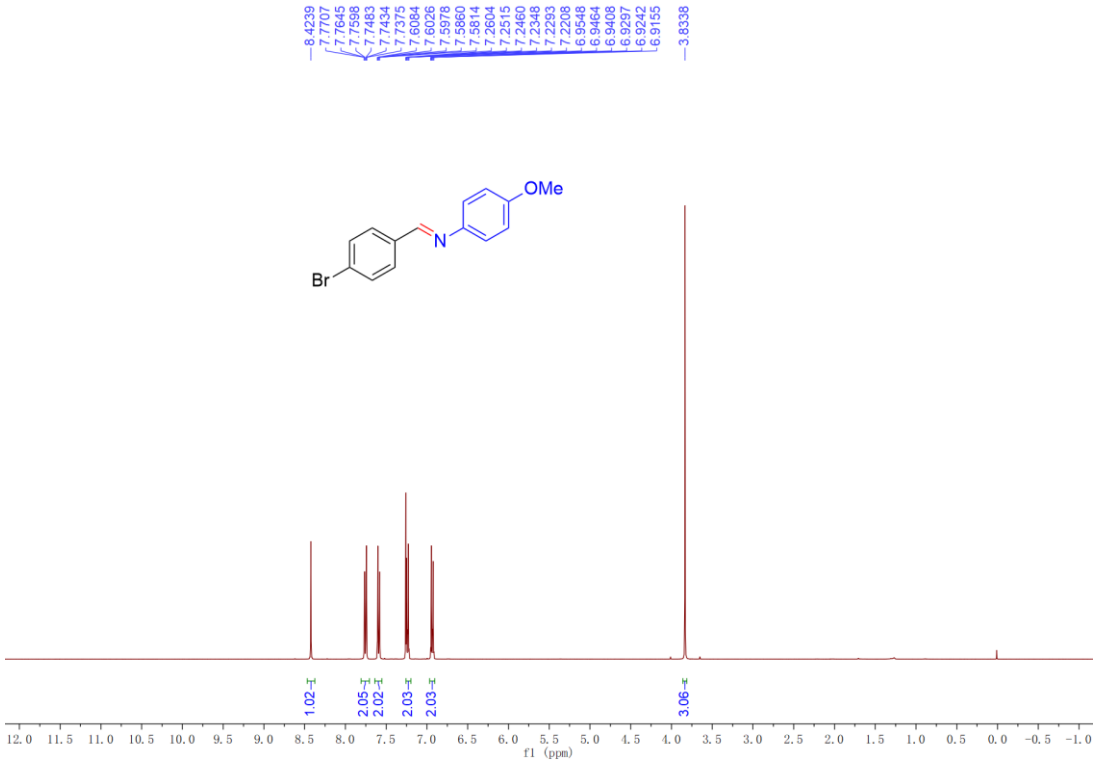



**Figure S1**. $^1$H NMR spectra of **3fc'** (400 MHz, Chloroform-*d*)

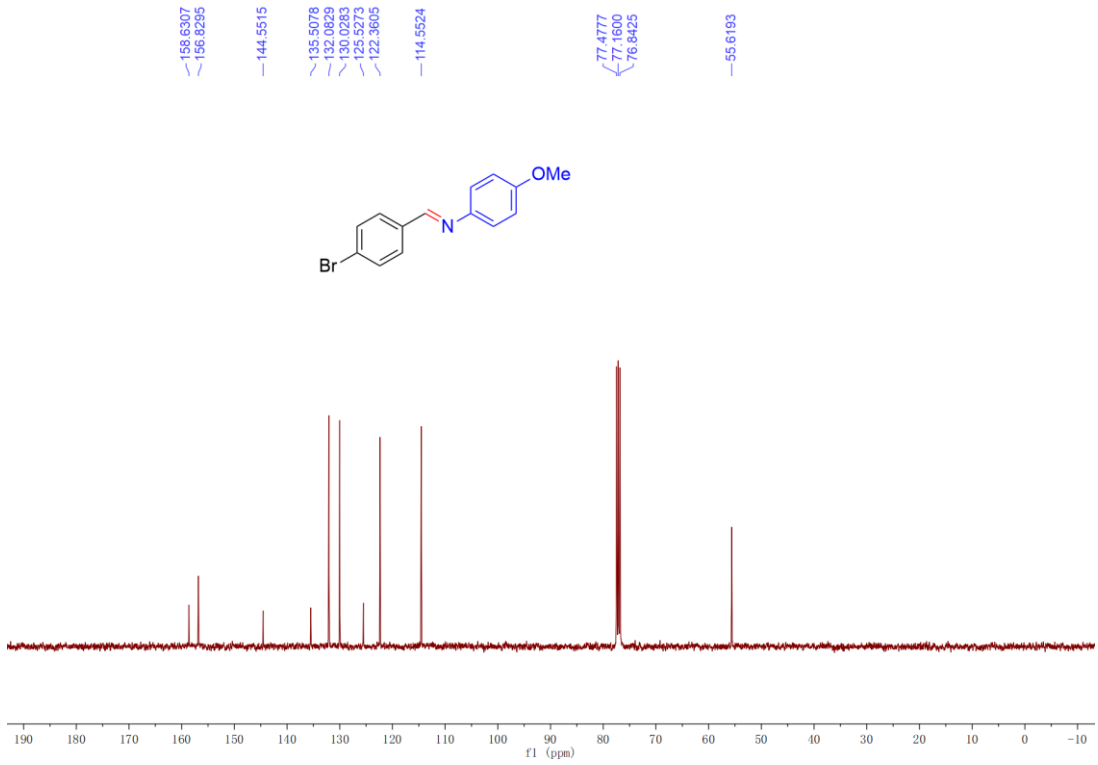



**Figure S2**. $^{13}$C NMR spectra of **3fc'** (101 MHz, Chloroform-*d*)

**(b) Transfer hydrogenation of imine 3fc'**

A mixture of (*E*)-1-(4-bromophenyl)-N-(4-methoxyphenyl)methanimine **3fc'** (80.0 mg, 1.0 mmol), $HCO_2H$ (2.0 mmol) with or without $BF_3{\cdot}Et_2O$ (0.7 mg, 0.005 mmol) in $CH_3CN$ (2.0 mL) in an oven-dried screw-capped pressure tube was stirred at 85 °C for 1.5 h. After being cooled to ambient temperature, the reaction mixture was concentrated in *vacuo* to obtain the crude product, which was purified by silica gel column chromatography (ethyl acetate/hexane = 1:10-1:5, 1% $NEt_3$ was used) to obtain product **3fc** as a light-yellow solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 2H), 7.32-7.28 (m, 2H), 6.86-6.82 (m, 2H), 6.65-6.61 (m, 2H), 4.30 (s, 2H), 3.88 (s, 1H), 3.80 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 152.35, 142.11, 138.90, 131.68, 129.16, 120.87, 114.97, 114.21, 55.82, 48.57.

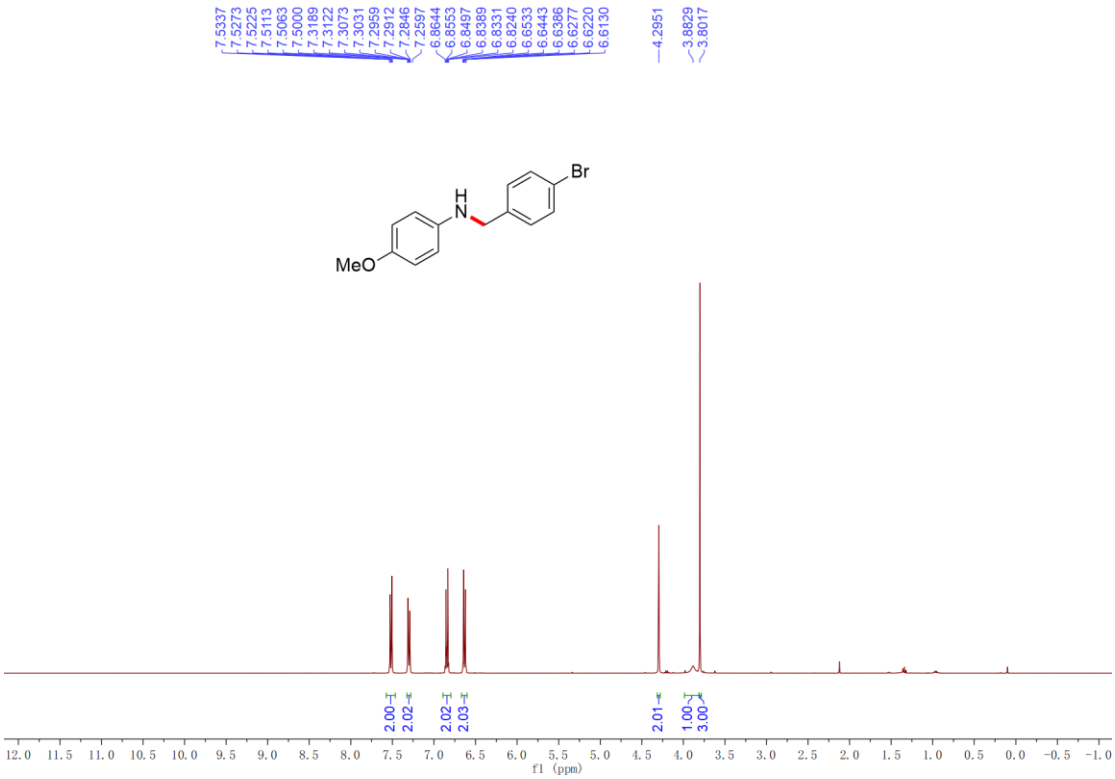



**Figure S3**. $^{1}$H NMR spectra of **3fc** (400 MHz, Chloroform-*d*)

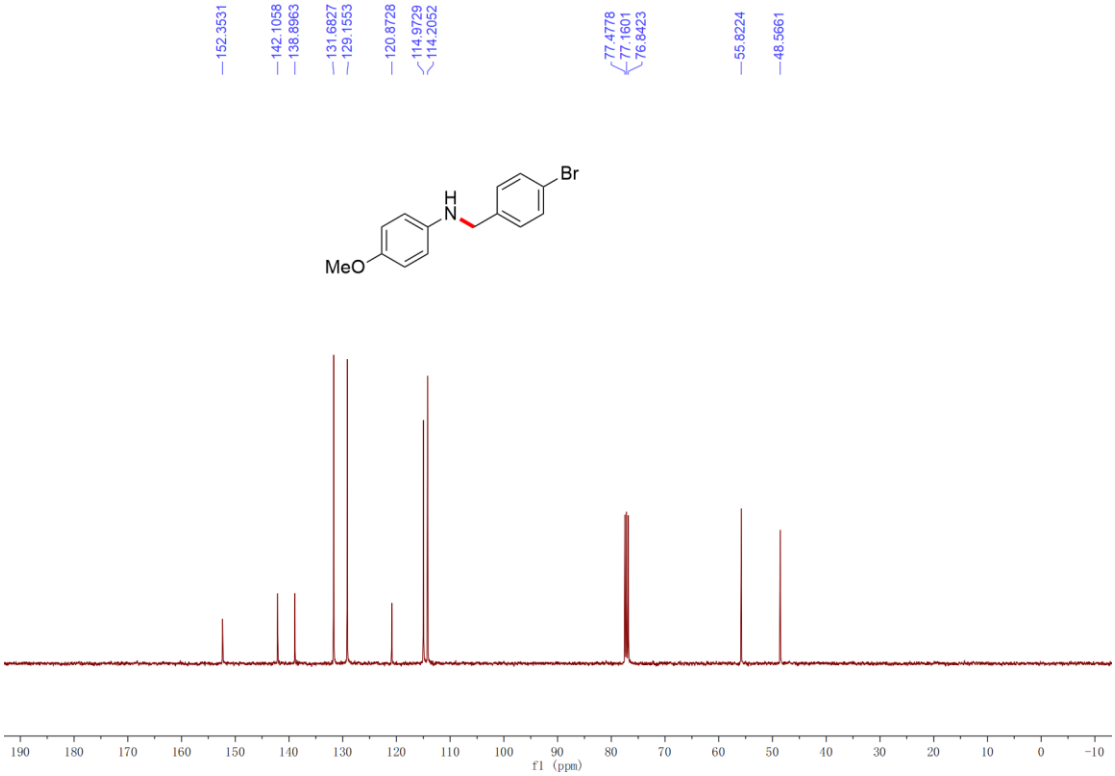
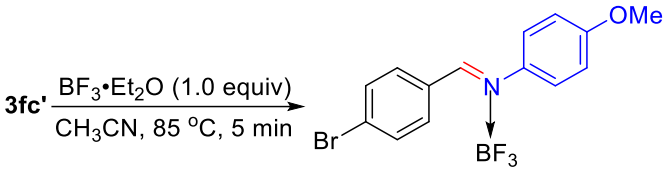



**Figure S4**. $^{13}$C NMR spectra of **3fc** (101 MHz, Chloroform-*d*)

## (c) Synthesis and application of 3fc'-$BF_3$ adduct




**3fc'-BF$_3$**, 99%

To an oven-dried tube was sequentially added **3fc'** (580.3 mg, 2 mmol) and $BF_3 \cdot Et_2O$ (283.8 mg, 2 mmol) in $CH_3CN$ (4.0 mL). The reaction mixture was stirred at 85 °C for 5 min. After being cooled at 0 °C for 1 h, the resulting solution was filtered to give **3fc'-BF$_3$** as a yellow solid (708 mg, 99% yield). $^1$H NMR (600 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.86 (s, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 166.91, 160.34, 134.55, 132.99, 132.64, 132.22, 131.27, 127.14, 124.96, 115.59, 114.56, 55.65. $^{11}$B NMR (193 MHz, Chloroform-*d*) δ -2.74. $^{19}$F NMR (565 MHz, $CDCl_3$) δ -152.08.

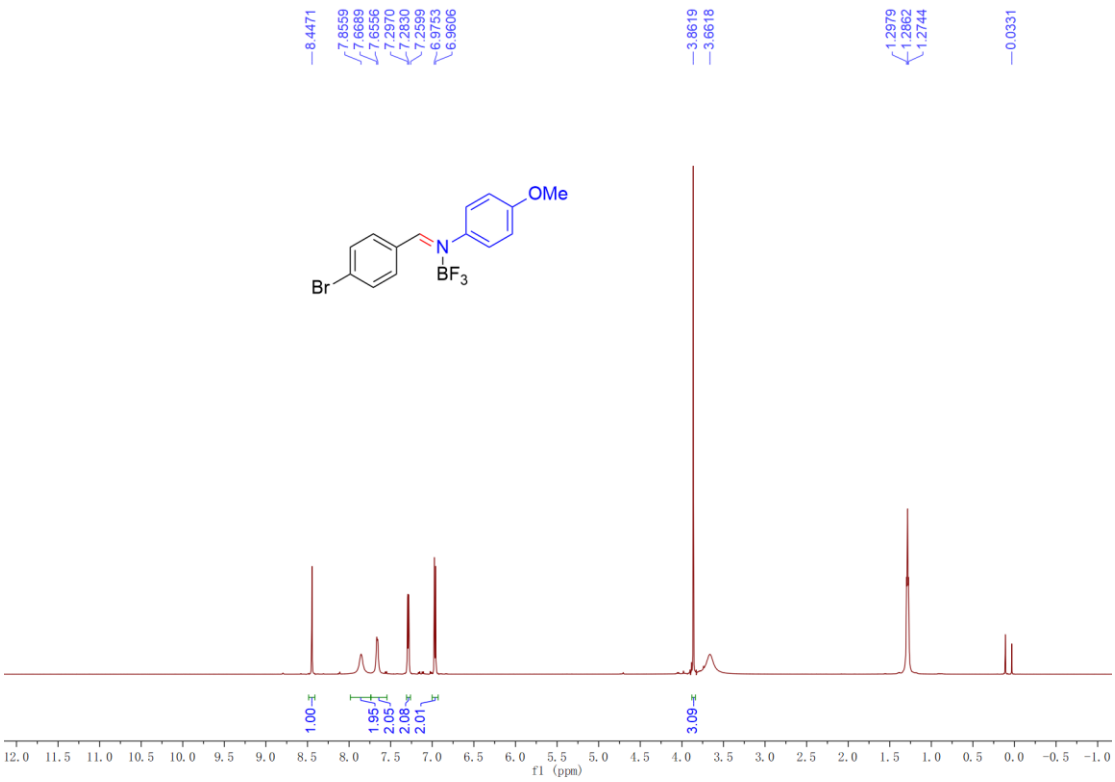



**Figure S5**. $^1$H NMR spectra of **3fc'-BF$_3$** (600 MHz, Chloroform-*d*)

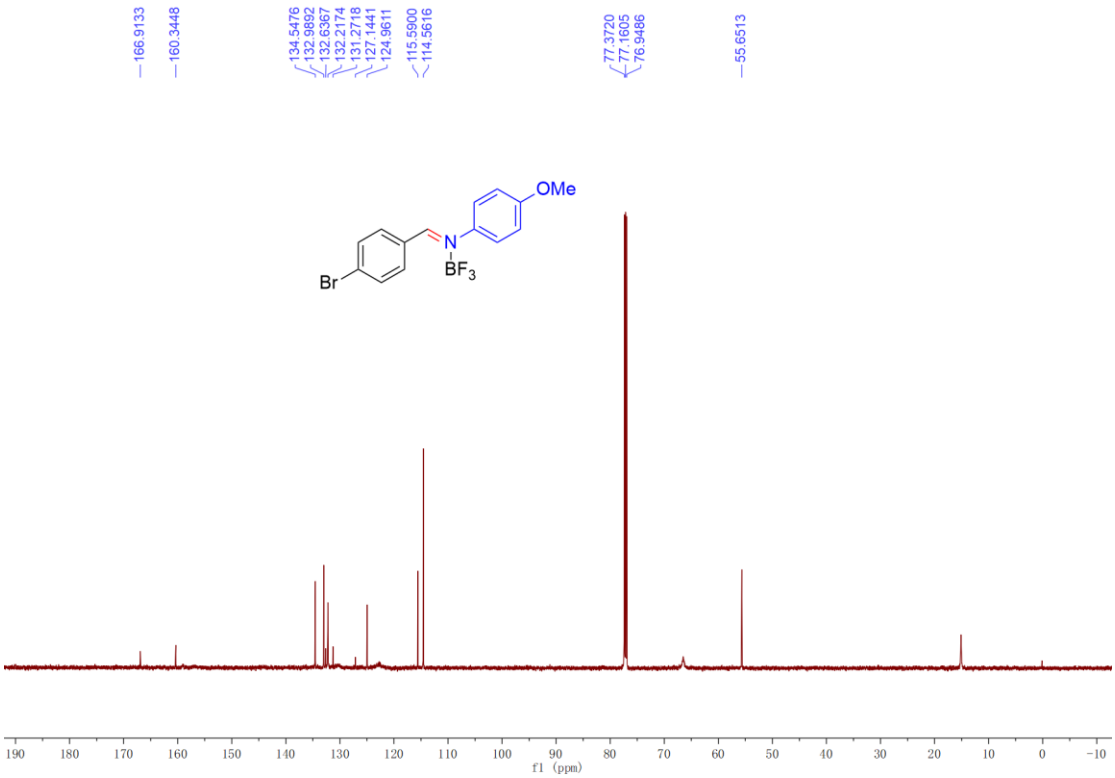



**Figure S6**. $^{13}$C NMR spectra of **3fc'-BF$_3$** (151 MHz, Chloroform-*d*)

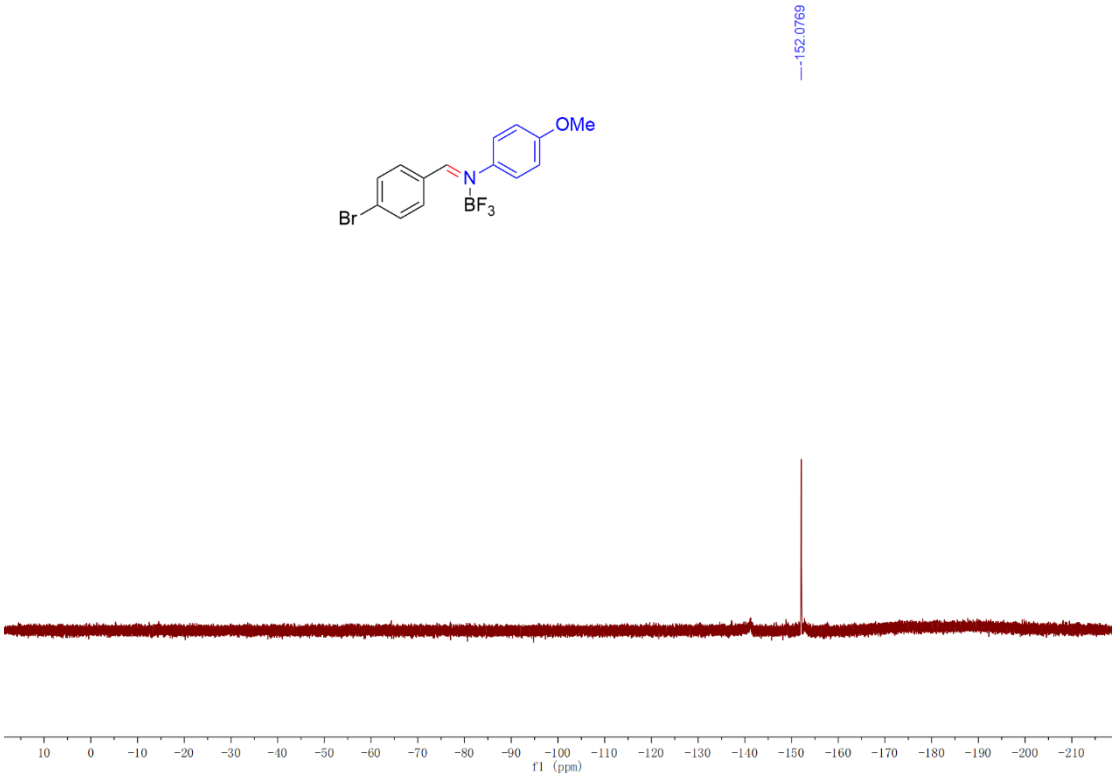



**Figure S7**. $^{11}$B NMR spectra of **3fc'-BF$_3$** (193 MHz, Chloroform-*d*)

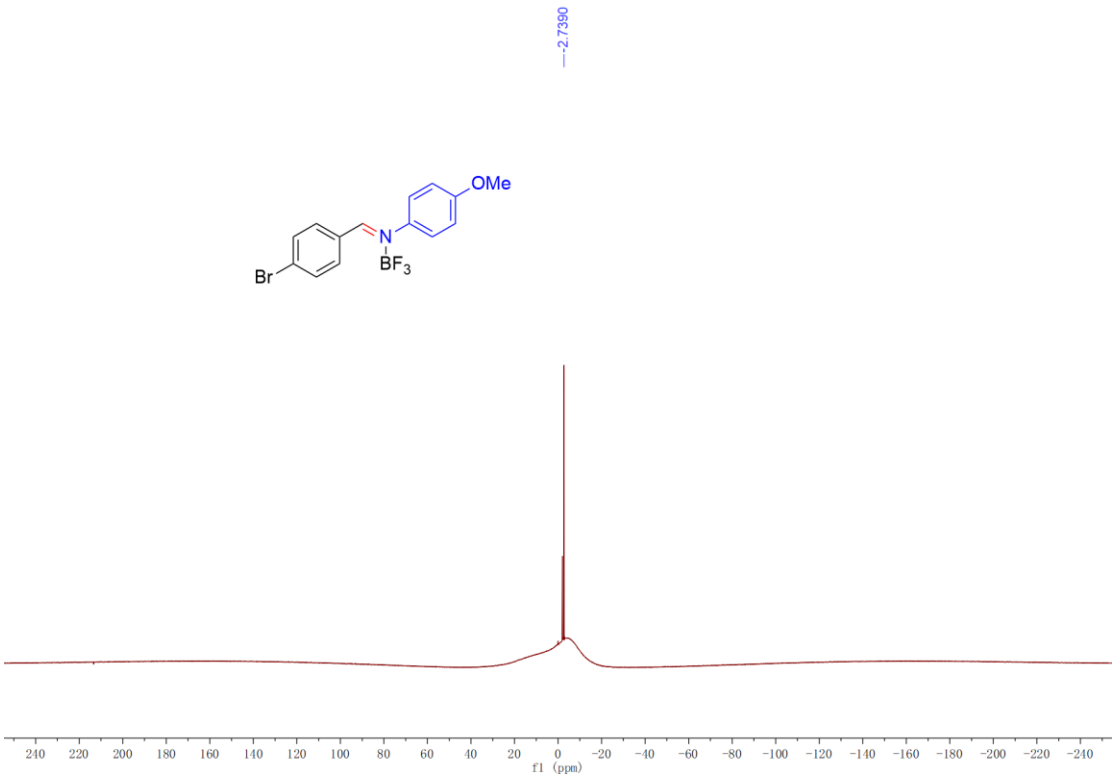
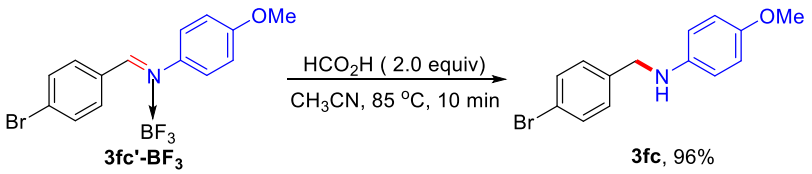
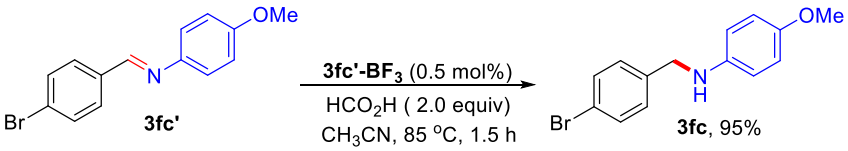



**Figure S8**. $^{19}$F NMR spectra of **3fc'-BF$_3$** (565 MHz, Chloroform-*d*)




To an oven-dried screw-capped pressure tube was sequentially added **3fc'-BF$_3$** (358 mg, 1 mmol) and $HCO_2H$ (92 mg, 2 mmol) in $CH_3CN$ (2.0 mL). The reaction mixture was stirred at 85 °C for 10 min. After being cooled to ambient temperature, the resulting solution was basified with saturated aqueous $NaHCO_3$ (10 mL) solution and extracted with $CH_2Cl_2$ (3 × 10 mL). The combined organic phases were dried over anhydrous $Na_2SO_4$ and filtered. The filtrate was concentrated in *vacuo* to afford a crude product, which was purified by silica gel column chromatography (ethyl acetate/hexane = 1:10-1:5, 1% $NEt_3$ was used) to obtain product **3fc** (280.5 mg, 96% yield).




To an oven-dried screw-capped pressure tube was sequentially added **3fc'** (290.1 mg, 1mmol), **3fc'-BF$_3$** (1.8 mg, 0.005 mmol) and $HCO_2H$ (92 mg, 2 mmol) in $CH_3CN$ (2.0 mL). The reaction mixture was stirred at 85 °C for 10 min. After being cooled to

ambient temperature, the resulting solution was basified with saturated aqueous $NaHCO_3$ (10 mL) solution and extracted with $CH_2Cl_2$ (3 × 10 mL). The combined organic phases were dried over anhydrous $Na_2SO_4$ and filtered. The filtrate was concentrated in *vacuo* to afford a crude product, which was purified by silica gel column chromatography (ethyl acetate/hexane = 1:10-1:5, 1% $NEt_3$ was used) to obtain product **3fc** (277.6 mg, 95% yield).

**(3) Reaction profile of the DRA**

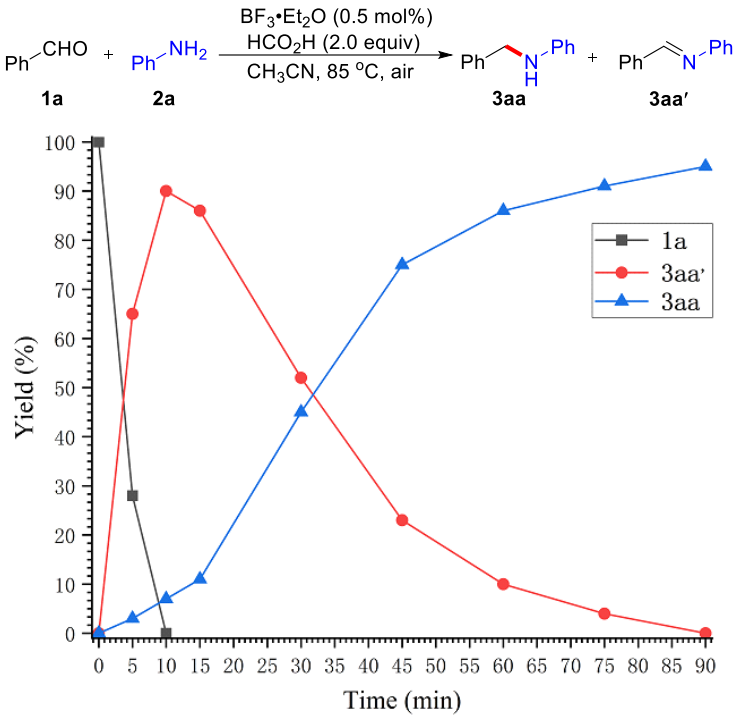
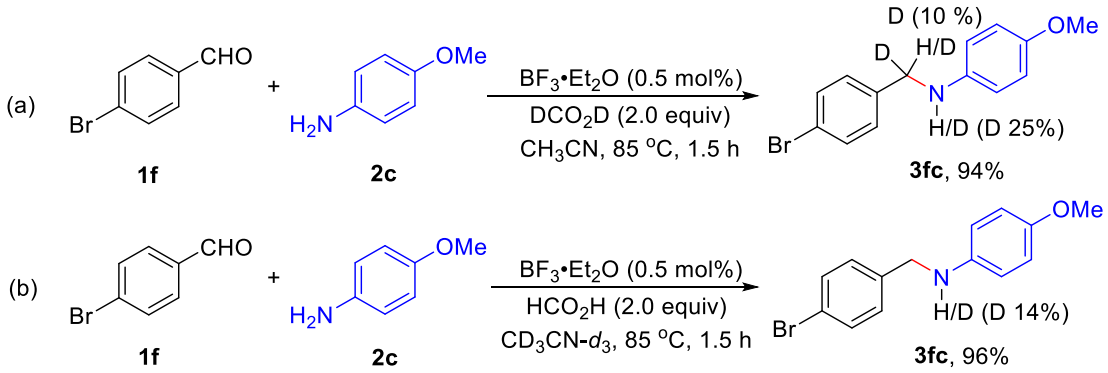



**Figure S9**. Reaction profile of the DRA with catalyst $BF_3{\cdot}Et_2O$. Conditions: **1a** (1.0 mmol), **2a** (1.1 mmol), $BF_3{\cdot}Et_2O$ (0.005 mmol), $HCO_2H$ (2 mmol), $CH_3CN$ (2 mL) at 85 °C, air. Yields were determined by $^1$H NMR with $CH_2Br_2$ as an internal standard.

**(4) Deuterium labelling experiments**



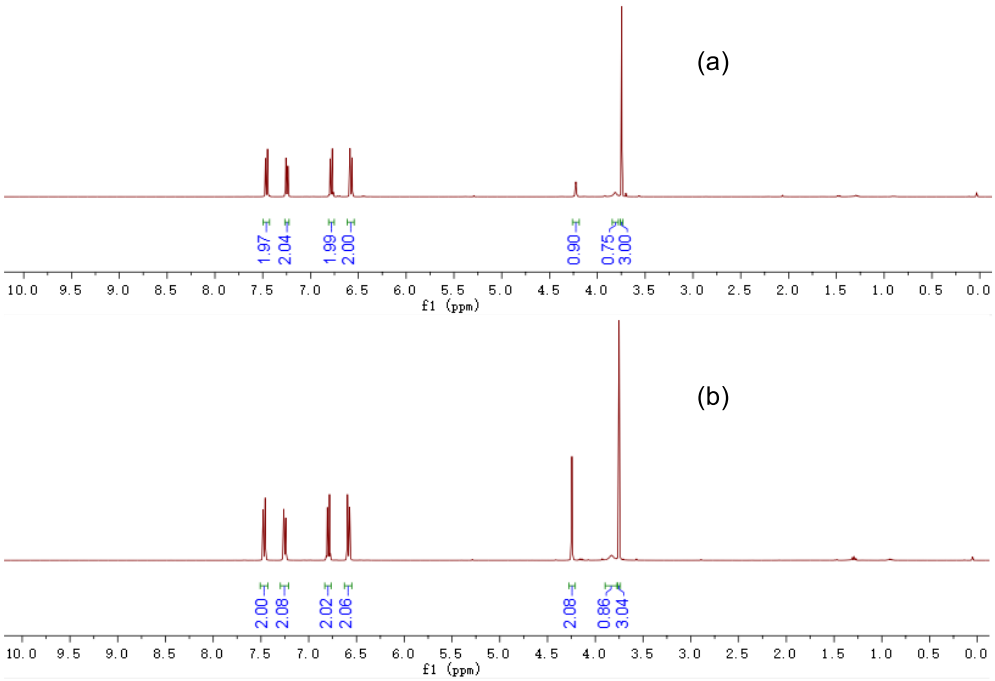
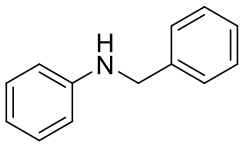



**Figure S10**. Deuterium labelling experiments: (a) **1f** (1.0 mmol), **2c** (1.1 mmol), $BF_3 \cdot Et_2O$ (0.7 mg, 0.005 mmol) and $DCO_2D$ (2.0 mmol) in $CH_3CN$ (2.0 mL), 85 °C for 1.5 h. (b) **1f** (1.0 mmol), **2c** (1.1 mmol), $BF_3 \cdot Et_2O$ (0.7 mg, 0.005 mmol) and $HCO_2H$ (2.0 mmol) in $CD_3CN$-$d_3$ (2.0 mL), 85 °C for 1.5 h.

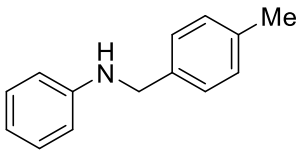
## 6. Characterization of the products

### N-Benzylaniline (3aa)[3]



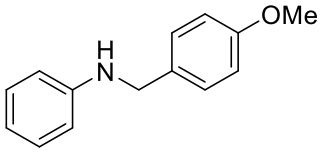
Colorless oil, 170.4 mg, 93% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.43-7.38 (m, 4H), 7.36-7.32 (m, 1H), 7.28-7.23 (m, 2H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 2H), 4.34 (s, 2H), 4.00 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 148.15, 139.49, 129.25, 128.60, 127.46, 127.18, 117.49, 112.83, 48.20. HRMS (ESI) calcd. for $C_{13}H_{14}N^+$ $[M+H]^+$: 184.1121, found: 184.1124.

### N-(4-Methylbenzyl)aniline (3ba)[4]



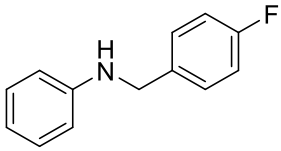
Colorless oil, 185.4 mg, 94% yield. $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.8 Hz, 2H), 7.45-7.41 (m, 4H), 6.99 (t, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 2H), 4.48 (s, 2H), 4.14 (s, 1H), 2.62 (s, 3H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 148.21, 136.70, 136.41, 129.27, 129.21, 127.46, 117.39, 112.81, 47.94, 21.09. HRMS (ESI) calcd. for $C_{14}H_{16}N^+$ $[M+H]^+$: 198.1277, found: 198.1278.

**N-(4-Methoxybenzyl)aniline (3ca)[4]**



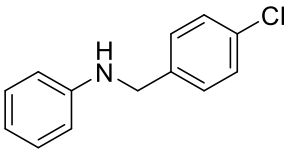
Colorless oil, 192.0 mg, 90% yield. $^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 8.5 Hz, 2H), 7.15 (t, *J* = 7.8 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.9 Hz, 2H), 4.21 (s, 2H), 3.91 (s, 1H), 3.76 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 158.96, 148.31, 131.54, 129.31, 128.85, 117.56, 114.12, 112.93, 55.34, 47.85. HRMS (ESI) calcd. for $C_{14}H_{16}NO^{+}$ $[M+H]^{+}$: 214.1226, found: 214.1228.

**N-(4-Fluorobenzyl)aniline (3da)[3]**



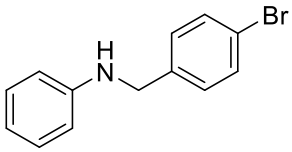
Yellow oil, 175.1 mg, 87% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.51-7.47 (m, 2H), 7.40-7.35 (m, 2H), 7.23-7.17 (m, 2H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 2H), 4.44 (s, 2H), 4.16 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 162.16 (d, *J* = 244.7 Hz, C-F), 148.11, 135.32, 129.46, 129.17, 129.10, 117.84, 115.67, 115.45, 113.02, 47.65. HRMS (ESI) calcd. for $C_{13}H_{13}FN^{+}$ $[M+H]^{+}$: 202.1027, found: 202.1027.

**N-(4-Chlorobenzyl)aniline (3ea)[3]**



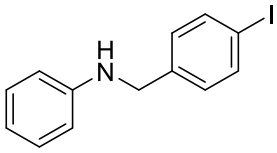
Yellow solid, mp: 76-77 °C, 195.9 mg, 90% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.22-7.09 (m, 6H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 7.9 Hz, 2H), 4.16 (s, 2H), 3.90 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 147.82, 138.04, 132.71, 129.28, 128.67, 128.65, 117.71, HRMS (ESI) calcd. for $C_{13}H_{13}ClN^{+}$ $[M+H]^{+}$: 218.0731, found: 218.0731.

**N-(4-Bromobenzyl)aniline (3fa)[4]**



Yellow solid, mp: 50-51 °C, 225.4 mg, 86% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.19-7.12 (m, 4H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 7.9 Hz, 2H), 4.22 (s, 2H), 3.98 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 147.75, 138.53, 131.60, 129.27, 128.99, 120.80, 117.70, 112.83, 47.46. HRMS (ESI) calcd. for $C_{13}H_{13}BrN^{+}$ $[M+H]^{+}$: 262.0226, found: 262.0229.

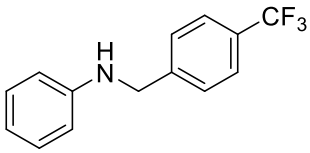
**N-(4-Iodobenzyl)aniline (3ga)[5]**



Light yellow solid, mp: 54-55 °C, 259.7 mg, 84% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.30-7.23 (m, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 6.82 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 2H), 4.32 (s, 2H), 4.09 (s, 1H). $^{13}$C NMR (101 MHz,

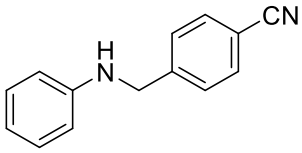
Chloroform-*d*) δ 147.77, 139.25, 137.62, 129.32, 117.78, 112.88, 92.46, 47.65. HRMS (ESI) calcd. for $C_{13}H_{13}IN^+$ $[M+H]^+$: 310.0087, found: 310.0089.

**N-(4-(Trifluoromethyl)benzyl)aniline (3ha)[6]**



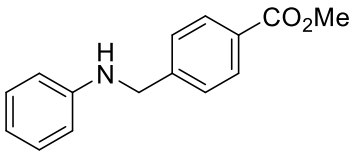

Yellow oil, 206.0 mg, 82% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.40-7.35 (m, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 2H), 4.55 (s, 2H), 4.29 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 147.82, 143.92, 129.62, 129.46, 129.30, 127.53, 125.64 (q, *J* = 3.8 Hz, C-F), 123.03, 118.02, 113.00, 47.79. HRMS (ESI) calcd. for $C_{14}H_{13}F_3N^+$ $[M+H]^+$: 252.0995, found: 252.0995.

**4-((Phenylamino)methyl)benzonitrile (3ia)[5]**



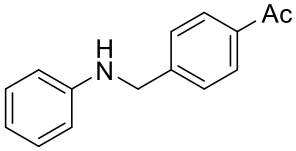

Yellow solid, mp: 86 ºC, 172.9 mg, 83% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.21 (t, *J* = 7.9 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 2H), 4.44 (s, 2H), 4.36 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 147.40, 145.47, 132.28, 129.25, 127.60, 118.92, 117.83, 112.77, 110.55, 47.54. HRMS (ESI) calcd. for $C_{14}H_{13}N_2^+$ $[M+H]^+$: 209.1073, found: 209.1075.

**Methyl 4-((phenylamino)methyl)benzoate (3ja)[7]**



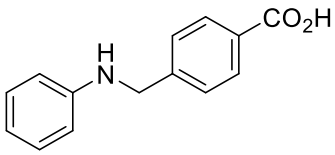

Yellow solid, mp: 71-72 ºC, 200.3 mg, 83% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 2H), 4.40 (s, 2H), 4.22 (s, 1H), 3.92 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 166.95, 147.83, 145.08, 129.94, 129.31, 129.05, 127.14, 117.79, 112.91, 52.08, 47.94. HRMS (ESI) calcd. for $C_{15}H_{16}NO_2^+$ $[M+H]^+$: 242.1176, found: 242.1178.

**1-(4-((Phenylamino)methyl)phenyl)ethan-1-one (3ka)[8]**



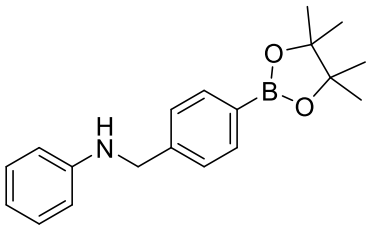

Yellow solid, mp: 77-78 ºC, 180.2 mg, 80% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 7.7 Hz, 2H), 4.42 (s, 2H), 4.20 (s, 1H), 2.60 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 197.78, 147.77, 145.33, 136.08, 129.29, 128.71, 127.25, 117.76, 112.88, 47.82, 26.62. HRMS (ESI) calcd. for $C_{15}H_{16}NO^+$ $[M+H]^+$: 226.1226, found: 226.1229.

**4-((Phenylamino)methyl)benzoic acid (3la)[16]**



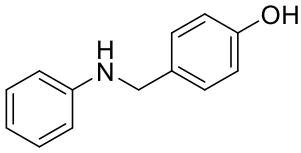
White solid, mp: 196-198 °C, 177.3 mg, 78% yield. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.84 (s, 1H), 7.88 (d, $J$ = 7.9 Hz, 2H), 7.44 (d, $J$ = 7.9 Hz, 2H), 7.01 (t, $J$ = 7.7 Hz, 2H), 6.50 (dd, $J$ = 18.8, 7.7 Hz, 3H), 6.31 (s, 1H), 4.31 (s, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 167.69, 148.89, 146.30, 129.84, 129.66, 129.31, 127.58, 116.38, 112.75, 46.68. HRMS (ESI) calcd. for $C_{14}H_{14}NO_2^+$ $[M+H]^+$: 228.1019, found: 228.1019.

**N-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)aniline (3ma)[7]**



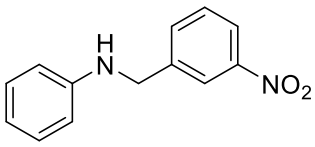
Yellow solid, mp: 103-104 °C, 228.8 mg, 74% yield. $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.78 (d, $J$ = 7.6 Hz, 2H), 7.33 (d, $J$ = 7.7 Hz, 2H), 7.12 (t, $J$ = 7.7 Hz, 2H), 6.67 (t, $J$ = 7.4 Hz, 1H), 6.56 (d, $J$ = 7.9 Hz, 2H), 4.27 (s, 2H), 4.02 (s, 1H), 1.31 (s, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 148.09, 142.84, 135.18, 129.26, 126.74, 117.55, 112.89, 83.78, 48.32, 24.93. HRMS (ESI) calcd. for $C_{19}H_{25}BNO_2^+$ $[M+H]^+$: 310.1973, found: 310.1975.

**4-((Phenylamino)methyl)phenol (3na)[9]**



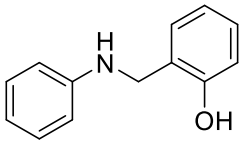
Yellow oil, 167.4 mg, 84% yield. $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.25-7.16 (m, 4H), 6.83-6.63 (m, 5H), 4.82 (brs, 1H), 4.24 (s, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 154.86, 148.19, 131.53, 129.40, 129.16, 117.89, 115.59, 113.21, 48.02. HRMS (ESI) calcd. for $C_{13}H_{14}NO^+$ $[M+H]^+$: 200.1070, found: 200.1071.

**N-(3-Nitrobenzyl)aniline (3oa)[12]**



Dark yellow oil, 184.9 mg, 81% yield. $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.27 (s, 1H), 8.12 (d, $J$ = 8.1 Hz, 1H), 7.74 (d, $J$ = 7.6 Hz, 1H), 7.49 (t, $J$ = 7.9 Hz, 1H), 7.25 (t, $J$ = 7.9 Hz, 2H), 6.81 (t, $J$ = 7.3 Hz, 1H), 6.68 (d, $J$ = 7.9 Hz, 2H), 4.45 (s, 2H), 4.42 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 148.21, 147.35, 142.03, 133.19, 129.36, 129.18, 121.92, 121.77, 117.77, 112.77, 47.11. HRMS (ESI) calcd. for $C_{13}H_{13}N_2O_2^+$ $[M+H]^+$: 229.0972, found: 229.0977.

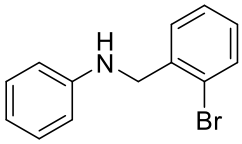
**2-((Phenylamino)methyl)phenol (3pa)[9]**



White solid, mp: 114 °C, 181.3 mg, 91% yield. $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.56 (s, 1H), 7.31-7.18 (m, 4H), 6.99-6.86 (m, 5H), 4.42 (s, 2H), 3.99 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 156.71, 147.27, 129.41, 129.22, 128.79, 123.09, 120.77, 120.14,

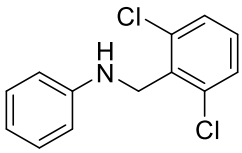
116.63, 115.90, 48.61. HRMS (ESI) calcd. for $C_{13}H_{14}NO^+$ $[M+H]^+$: 200.1070, found: 200.1070.

**N-(2-Bromobenzyl)aniline (3qa)[8]**



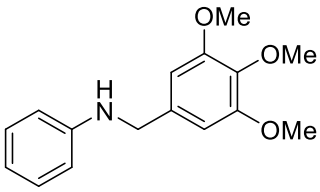
Yellow oil, 220.2 mg, 84% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.32-7.16 (m, 4H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 2H), 4.45 (s, 2H), 4.22 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 147.74, 138.23, 132.84, 129.35, 129.18, 128.72, 127.61, 123.29, 117.79, 112.97, 48.44. HRMS (ESI) calcd. for $C_{13}H_{13}BrN^+$ $[M+H]^+$: 262.0226, found: 262.0227.

**N-(2,6-Dichlorobenzyl)aniline (3ra)[17]**



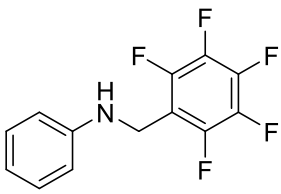
Colorless oil, 181.5 mg, 72% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.29 (q, *J* = 7.8, 7.0 Hz, 2H), 7.25-7.17 (m, 1H), 6.86 (d, *J* = 7.7 Hz, 3H), 4.67 (s, 2H), 4.06 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 147.78, 136.12, 134.63, 129.39, 129.28, 128.56, 118.13, 113.52, 43.96. HRMS (ESI) calcd. for $C_{13}H_{12}Cl_2N^+$ $[M+H]^+$: 252.0341, found: 252.0346.

**N-(3,4,5-Trimethoxybenzyl)aniline (3sa)[18]**



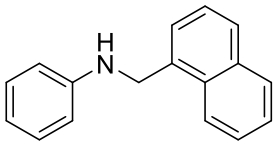
White solid, mp: 135 ºC, 259.7 mg, 95% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.24-7.16 (m, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 2H), 6.63 (s, 2H), 4.27 (s, 2H), 4.06 (s, 1H), 3.87 (s, 3H), 3.85 (s, 6H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 153.42, 148.21, 136.99, 135.27, 129.27, 117.70, 112.92, 104.31, 60.87, 56.10, 48.78. HRMS (ESI) calcd. for $C_{16}H_{20}NO_3^+$ $[M+H]^+$: 274.1438, found: 274.1439.

**N-((Perfluorophenyl)methyl)aniline (3ta)[19]**



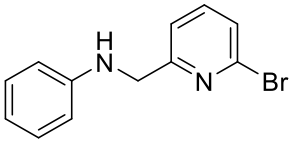
White solid, mp: 94-96 ºC, 199.4 mg, 73% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.27-7.16 (m, 2H), 6.84-6.66 (m, 3H), 4.51 (d, *J* = 6.8 Hz, 2H), 4.09 (t, *J* = 7.2 Hz, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 146.73, 146.56, 144. 28, 138.91, 136.40, 129.56, 118.87, 113.24, 112.89, 36.11. HRMS (ESI) calcd. for $C_{13}H_9F_5N^+$ $[M+H]^+$: 274.0650, found: 274.0650.

**N-(Naphthalen-1-ylmethyl)aniline (3ua)[4]**



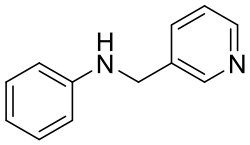
White solid, mp: 156-158 °C, 210.0 mg, 90% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.11-8.08 (m, 1H), 7.92 (dt, *J* = 7.4, 2.5 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.54 (td, *J* = 6.1, 3.3 Hz, 3H), 7.45 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.26-7.22 (m, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.72 (s, 2H), 4.75 (s, 2H), 3.95 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 148.28, 134.40, 133.93, 131.60, 129.40, 128.85, 128.23, 126.40, 126.08, 125.92, 125.63, 123.67, 117.62, 112.79, 46.43. HRMS (ESI) calcd. for $C_{17}H_{16}N^+$ $[M+H]^+$: 234.1277, found: 234.1282.

**N-((6-Bromopyridin-2-yl)methyl)aniline (3va)[20]**



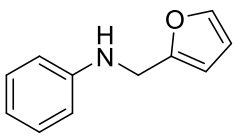
Colorless oil. 239.5 mg, 91% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.34 (s, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 2H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.60 (d, *J* = 7.9 Hz, 2H), 4.29 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 149.20, 147.26, 140.59, 137.72, 134.57, 129.29, 127.90, 118.06, 112.89, 44.87. HRMS (ESI) calcd. for $C_{12}H_{12}BrN_2^+$ $[M+H]^+$: 263.0178, found: 263.0179.

**N-(Pyridin-3-ylmethyl)aniline (3wa)[4]**



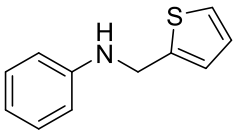
Yellow oil, 167.7 mg, 91% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.60 (s, 1H), 8.50 (d, *J* = 4.1 Hz, 1H), 7.67 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.24 (dt, *J* = 7.8, 3.9 Hz, 1H), 7.18 (ddd, *J* = 8.4, 5.6, 1.8 Hz, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 2H), 4.32 (s, 2H), 4.29 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 149.17, 148.69, 147.68, 135.09, 134.95, 129.35, 123.55, 117.96, 112.94, 45.74. HRMS (ESI) calcd. for $C_{12}H_{13}N_2^+$ $[M+H]^+$: 185.1073, found: 185.1079.

**N-(Furan-2-ylmethyl)aniline (3xa)[3]**



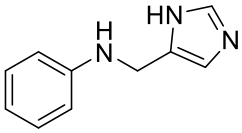
Light yellow oil, 155.9 mg, 90% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.41 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.26-7.22 (m, 2H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 2H), 6.36 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.27 (dd, *J* = 3.2, 0.9 Hz, 1H), 4.35 (s, 2H), 4.05 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 152.84, 147.71, 141.98, 129.31, 118.08, 113.22, 110.43, 107.06, 41.50. HRMS (ESI) calcd. for $C_{11}H_{12}NO^+$ $[M+H]^+$: 174.0913, found: 174.0917.

**N-(Thiophen-2-ylmethyl)aniline (3ya)[5]**



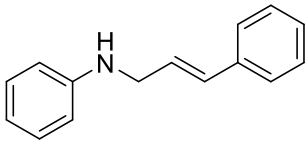
Yellow oil, 168.4 mg, 89% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.32-7.26 (m, 3H), 7.11-7.05 (m, 2H), 6.86 (t, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 2H), 4.57 (s, 2H), 4.11 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 147.65, 143.04, 129.32, 126.90, 125.05, 124.60, 118.10, 113.21, 43.50. HRMS (ESI) calcd. for $C_{11}H_{12}NS^{+}$ $[M+H]^{+}$: 190.0685, found: 190.0685.

**N-((1H-Imidazol-5-yl)methyl)aniline (3za)[12]**



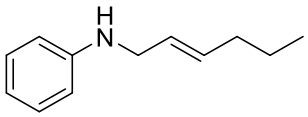
Yellow solid, mp: 116-117 °C, 148.9 mg, 86% yield. $^{1}$H NMR (400 MHz, Methanol-$d_4$) δ 7.60 (s, 1H), 7.09 (t, *J* = 7.7 Hz, 2H), 6.94 (s, 1H), 6.68-6.60 (m, 3H), 4.24 (s, 2H). $^{13}$C NMR (101 MHz, Methanol-$d_4$) δ 149.88, 136.14, 129.94, 118.36, 117.77, 114.33, 41.82. HRMS (ESI) calcd. for $C_{10}H_{12}N_3^{+}$ $[M+H]^{+}$: 174.1026, found: 174.1026.

**N-Cinnamylaniline (5aa)[4]**



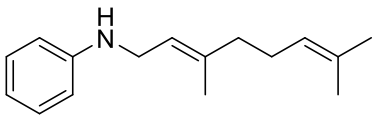
Yellow oil, 196.7 mg, 94% yield. $^{1}$H NMR (600 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.41 (dt, *J* = 15.5, 7.6 Hz, 3H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 2H), 6.78 (d, *J* = 15.9 Hz, 1H), 6.47 (dt, *J* = 15.9, 5.7 Hz, 1H), 4.05 (d, *J* = 5.7 Hz, 2H), 3.94 (s, 1H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 148.04, 136.87, 131.36, 129.27, 128.58, 127.51, 127.08, 126.34, 117.54, 113.01, 46.09. HRMS (ESI) calcd. for $C_{15}H_{16}N^{+}$ $[M+H]^{+}$: 210.1277, found: 210.1278.

**(*E*)-N-(Hex-2-en-1-yl)aniline (5ba)[13]**



Yellow oil, 152.5 mg, 87% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.27 (td, *J* = 7.4, 1.9 Hz, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 2H), 5.83-5.76 (m, 1H), 5.69-5.63 (m, 1H), 3.78 (d, *J* = 5.7 Hz, 2H), 3.75 (s, 1H), 2.13 (q, *J* = 7.0 Hz, 2H), 1.51 (h, *J* = 7.4 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 148.30, 133.16, 129.20, 127.03, 117.36, 113.01, 46.11, 34.48, 22.46, 13.74. HRMS (ESI) calcd. for $C_{12}H_{18}N^{+}$ $[M+H]^{+}$: 176.1434, found: 176.1438.

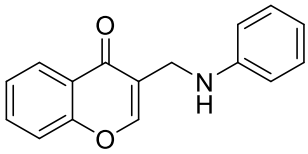
**(*E*)-N-(3,7-Dimethylocta-2,6-dien-1-yl)aniline (5ca)[13]**



Yellow oil, 199.5 mg, 87% yield (*E*/*Z* = 11.5:1). $^{1}$H NMR (600 MHz, Chloroform-*d*) δ 7.23 (t, *J* = 7.3 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 2H), 5.39 (t, *J* = 6.6 Hz, 1H), 5.16 (t, *J* = 6.9 Hz, 1H), 3.75 (d, *J* = 6.6 Hz, 2H), 3.62 (s, 1H),

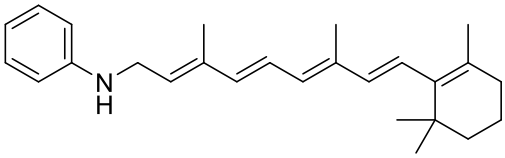
2.17 (q, $J$ = 6.9 Hz, 2H), 2.11-2.03 (m, 2H), 1.76 (s, 3H), 1.75 (s, 3H), 1.67 (s, 3H). $^{13}$C NMR (151 MHz, Chloroform-$d$) δ 148.54, 139.03, 131.75, 129.27, 124.05, 121.67, 117.34, 112.97, 42.06, 26.55, 25.81, 16.47. HRMS (ESI) calcd. for $C_{16}H_{24}N^+$ $[M+H]^+$: 230.1903, found: 230.1905.

**3-((Phenylamino)methyl)-4H-chromen-4-one (5da)[14]**



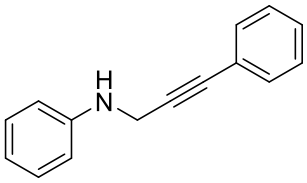
Colorless oil, 221.1 mg, 88% yield. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.24 (s, 1H), 8.08 (d, $J$ = 7.7 Hz, 1H), 7.77 (t, $J$ = 7.4 Hz, 1H), 7.58 (d, $J$ = 8.3 Hz, 1H), 7.47 (t, $J$ = 7.4 Hz, 1H), 7.07 (t, $J$ = 7.3 Hz, 2H), 6.63 (d, $J$ = 7.7 Hz, 2H), 6.54 (t, $J$ = 7.0 Hz, 1H), 5.87 (t, $J$ = 5.9 Hz, 1H), 4.10 (d, $J$ = 6.1 Hz, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 176.96, 156.36, 154.65, 148.66, 134.54, 129.38, 125.81, 125.38, 123.64, 121.58, 118.83, 116.63, 112.86, 38.81. HRMS (ESI) calcd. for $C_{16}H_{14}NO_2^+$ $[M+H]^+$: 252.1019, found: 252.1020.

**N-((2E,4E,6E,8E)-3,7-Dimethyl-9-(2,6,6-trimethylcyclohex-1-en-1-yl)nona-2,4,6,8-tetraen-1-yl)aniline (5ea)**



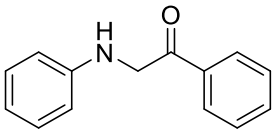
Yellow oil, 296.5 mg, 82% yield. $^1$H NMR (600 MHz, Chloroform-$d$) δ 7.19 (t, $J$ = 7.8 Hz, 1H), 6.74-6.60 (m, 4H), 6.30-6.09 (m, 5H), 5.65-5.61 (m, 1H), 3.89 (d, $J$ = 6.6 Hz, 2H), 3.70 (s, 1H), 2.02 (t, $J$ = 7.8 Hz, 2H), 1.97 (s, 3H), 1.91 (d, $J$ = 9.1 Hz, 3H), 1.72 (s, 3H), 1.64-1.60 (m, 2H), 1.47 (t, $J$ = 6.1 Hz, 2H), 1.03 (s, 6H). $^{13}$C NMR (151 MHz, Chloroform-$d$) δ 148.27, 139.26, 137.81, 136.92, 136.45, 136.09, 135.91, 130.26, 130.07, 129.38, 129.12, 125.94, 117.67, 113.11, 61.45, 42.40, 39.75, 34.40, 33.21, 29.10, 21.89, 19.41, 12.87. HRMS (ESI) calcd. for $C_{26}H_{36}N^+$ $[M+H]^+$: 362.2842, found: 362.2843.

**N-(3-Phenylprop-2-yn-1-yl)aniline (5fa)[15]**



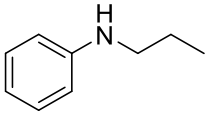
Yellow oil, 167.9 mg, 81% yield. $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.59-7.54 (m, 2H), 7.42-7.35 (m, 5H), 6.94 (t, $J$ = 7.3 Hz, 1H), 6.85 (d, $J$ = 7.6 Hz, 2H), 4.23 (s, 2H), 4.05 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 147.14, 131.70, 129.22, 128.28, 128.22, 122.90, 118.40, 113.55, 86.59, 83.26, 34.47. HRMS (ESI) calcd. for $C_{15}H_{14}N^+$ $[M+H]^+$: 208.1121, found: 208.1126.

**1-Phenyl-2-(phenylamino)ethan-1-one (5ga)[21]**



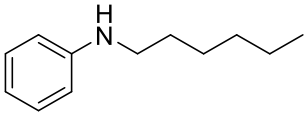
Yellow solid, mp: 70-71 °C, 173.2 mg, 82% yield. $^{1}$H NMR (600 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 2H), 6.79-6.73 (m, 3H), 5.02 (s, 1H), 4.63 (s, 2H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 195.13, 147.10, 134.02, 129.52, 129.03, 127.90, 118.05, 113.25, 50.52. HRMS (ESI) calcd. for $C_{14}H_{14}NO^{+}$ $[M+H]^{+}$: 212.1070, found: 212.1073.

**N-Propylaniline (5ha)[22]**



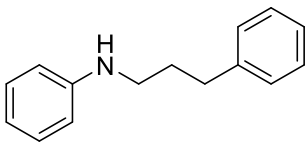
Yellow oil, 100.1 mg, 74% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.15 (t, *J* = 7.8 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 2H), 3.58 (s, 1H), 3.05 (t, *J* = 7.1 Hz, 2H), 1.61 (h, *J* = 7.3 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 148.61, 129.29, 117.13, 112.77, 45.87, 22.82, 11.73. HRMS (ESI) calcd. for $C_{9}H_{14}N^{+}$ $[M+H]^{+}$: 136.1121, found: 136.1121.

**N-Hexylaniline (5ia)[22]**



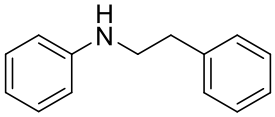
Colorless oil, 133.0 mg, 75% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.07 (t, *J* = 7.7 Hz, 2H), 6.59 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 2), 3.45 (s, 1H), 2.99 (t, *J* = 7.1 Hz, 2H), 1.50 (p, *J* = 7.1 Hz, 2H), 1.39-1.13 (m, 6H), 0.91-0.74 (m, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 148.63, 129.27, 117.10, 112.75, 44.07, 31.76, 29.65, 26.96, 22.74, 14.14. HRMS (ESI) calcd. for $C_{12}H_{20}N^{+}$ $[M+H]^{+}$: 178.1590, found: 178.1590.

**N-(3-Phenylpropyl)aniline (5ja)[22]**



Colorless oil, 181.7 mg, 86% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.57 (t, *J* = 7.4 Hz, 2H), 7.47 (q, *J* = 8.3, 7.5 Hz, 5H), 6.99 (t, *J* = 7.3 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 2H), 3.76 (s, 1H), 3.35 (t, *J* = 7.1 Hz, 2H), 2.96 (t, *J* = 7.6 Hz, 2H), 2.15 (p, *J* = 7.3 Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 148.33, 141.66, 129.17, 128.38, 128.36, 125.90, 117.09, 112.68, 43.28, 33.33, 30.96. HRMS (ESI) calcd. for $C_{15}H_{18}N^{+}$ $[M+H]^{+}$: 212.1434, found: 212.1434.

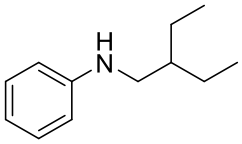
**N-Phenethylaniline (5ka)[22]**



Light yellow oil, 175.6 mg, 89% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.40 (t, *J* = 7.2 Hz, 2H), 7.34-7.24 (m, 5H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 7.7 Hz, 2H), 3.73 (s, 1H), 3.46 (t, *J* = 7.0 Hz, 2H), 2.98 (t, *J* = 7.0 Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-*d*)

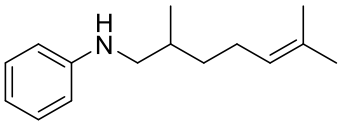
δ 148.10, 139.41, 129.37, 128.88, 128.69, 126.51, 117.54, 113.08, 45.12, 35.62. HRMS (ESI) calcd. for $C_{14}H_{16}N^+$ $[M+H]^+$: 198.1277, found: 198.1279.

**N-(2-Ethylbutyl)aniline (5la)[22]**



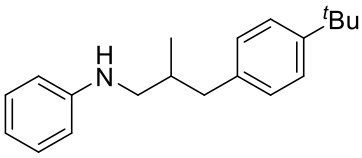
Light yellow oil, 147.2 mg, 83% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.30-7.25 (m, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.70 (dt, *J* = 7.7, 1.1 Hz, 2H), 3.69 (s, 1H), 3.12 (d, *J* = 6.1 Hz, 2H), 1.64-1.47 (m, 5H), 1.03 (t, *J* = 7.4 Hz, 6H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 148.80, 129.26, 116.93, 112.64, 46.69, 40.64, 24.08, 11.04. HRMS (ESI) calcd. for $C_{12}H_{20}N^+$ $[M+H]^+$: 178.1590, found: 178.1593.

***N*-(2,6-Dimethylhept-5-en-1-yl)aniline (5ma)[23]**



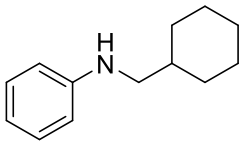
Yellow oil, 176.1 mg, 81% yield (*E*/*Z* = 19:1). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.28-7.22 (m, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 2H), 5.27-5.15 (m, 1H), 3.73 (s, 1H), 3.13 (dd, *J* = 12.2, 5.9 Hz, 1H), 2.96 (dd, *J* = 12.2, 7.3 Hz, 1H), 2.14 (ddd, *J* = 27.5, 15.1, 7.7 Hz, 2H), 1.85 (dt, *J* = 13.1, 6.6 Hz, 1H), 1.79 (s, 3H), 1.71 (s, 3H), 1.59-1.52 (m, 1H), 1.36-1.28 (m, 1H), 1.07 (d, *J* = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 148.71, 131.58, 129.29, 124.63, 117.00, 112.71, 50.34, 34.97, 32.63, 25.84, 25.56, 18.11, 17.80. HRMS (ESI) calcd. for $C_{15}H_{24}N^+$ $[M+H]^+$: 218.1903, found: 218.1904.

**N-(3-(4-(*tert*-Butyl)phenyl)-2-methylpropyl)aniline (5na)[24]**



Light yellow oil, 244.9 mg, 87% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.39 (dd, *J* = 8.5, 2.2 Hz, 2H), 7.26-7.17 (m, 4H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.6 Hz, 2H), 3.71 (s, 1H), 3.16 (dd, *J* = 12.5, 6.0 Hz, 1H), 3.02 (dd, *J* = 12.4, 6.9 Hz, 1H), 2.78 (dd, *J* = 13.5, 6.6 Hz, 1H), 2.57 (dd, *J* = 13.5, 7.6 Hz, 1H), 2.13 (dq, *J* = 13.5, 6.7 Hz, 1H), 1.41 (s, 9H), 1.06 (d, *J* = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 148.85, 148.56, 137.52, 129.28, 128.90, 125.27, 117.12, 112.81, 50.00, 41.04, 35.14, 34.48, 31.55, 18.40. HRMS (ESI) calcd. for $C_{20}H_{28}N^+$ $[M+H]^+$: 282.2216, found: 282.2217.

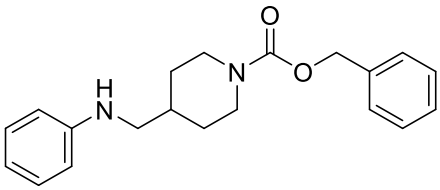
**N-(Cyclohexylmethyl)aniline (5oa)[22]**



Light yellow oil, 157.1 mg, 83% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.18 (td, *J* = 7.4, 1.9 Hz, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 2H), 3.71 (s, 1H), 2.97 (d, *J* = 6.7 Hz, 2H), 1.85-1.69 (m, 5H), 1.63-1.56 (m, 1H), 1.32-1.18 (m, 3H), 1.04-0.96 (m, 2H). $^{13}$C

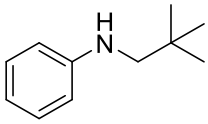
NMR (101 MHz, Chloroform-*d*) δ 148.70, 129.24, 116.88, 112.64, 50.63, 37.63, 31.38, 26.67, 26.06. HRMS (ESI) calcd. for $C_{13}H_{20}N^+$ $[M+H]^+$: 190.1590, found: 190.1592.

**Benzyl 4-((phenylamino)methyl)piperidine-1-carboxylate (5pa)[12]**



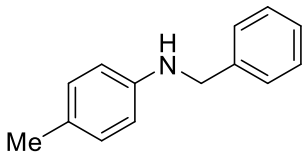
Light yellow oil, 275.8 mg, 85% yield. (New compound), $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.41-7.32 (m, 5H), 7.21 (t, *J* = 7.8 Hz, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.9 Hz, 2H), 5.18 (s, 2H), 4.25 (s, 2H), 3.78 (s, 1H), 3.04 (d, *J* = 6.3 Hz, 2H), 2.80 (t, *J* = 12.6 Hz, 2H), 1.84-1.74 (m, 3H), 1.34-1.16 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 155.26, 148.20, 136.90, 129.30, 128.50, 127.97, 127.86, 117.22, 112.63, 67.02, 49.58, 43.97, 35.87, 30.11, 29.98. HRMS (ESI) calcd. for $C_{20}H_{25}N_2O_2^+$ $[M+H]^+$: 325.1911, found: 325.1913.

**N-Neopentylaniline (5qa)[22]**



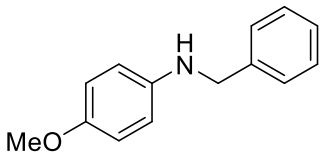
Light yellow oil, 138.8 mg, 85% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.23 (td, *J* = 7.4, 1.9 Hz, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 7.7 Hz, 2H), 3.68 (s, 1H), 2.96 (s, 2H), 1.06 (s, 9H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 149.22, 129.31, 117.01, 112.75, 55.96, 31.97, 27.78. HRMS (ESI) calcd. for $C_{11}H_{18}N^+$ $[M+H]^+$: 164.1434, found: 164.1434.

**N-Benzyl-4-methylaniline (3ab)[4]**



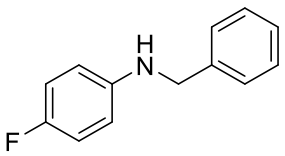
White solid, mp: 82-83 $^o$C, 185.4 mg, 94% yield. $^1$H NMR (600 MHz, DMSO-$d_6$) δ 8.10 (s, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.31-7.23 (m, 5H), 3.97 (s, 2H), 2.39 (s, 3H). $^{13}$C NMR (151 MHz, DMSO-$d_6$) δ 143.02, 138.33, 138.17, 130.06, 128.68, 128.03, 127.58, 127.02, 46.61, 21.43. HRMS (ESI) calcd. for $C_{14}H_{16}N^+$ $[M+H]^+$: 198.1277, found: 198.1278.

**N-Benzyl-4-methoxyaniline (3ac)[7]**



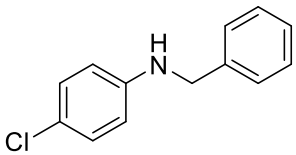
Colorless oil, 202.6 mg, 95% yield. $^1$H NMR (500 MHz, Chloroform-*d*) δ 7.43-7.37 (m, 4H), 7.32 (t, *J* = 6.9 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.65 (d, *J* = 8.7 Hz, 2H), 4.32 (s, 2H), 3.82 (s, 1H), 3.78 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 152.48, 142.75, 139.99, 128.82, 127.77, 127.38, 115.21, 114.37, 56.05, 49.50. HRMS (ESI) calcd. for $C_{14}H_{16}NO^+$ $[M+H]^+$: 214.1226, found: 214.1226.

**N-Benzyl-4-fluoroaniline (3ad)[4]**



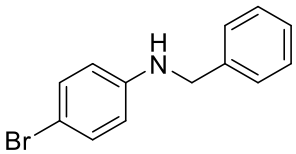
Yellow oil, 171.1 mg, 85% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.45-7.35 (m, 5H), 7.00-6.94 (m, 2H), 6.65-6.50 (m, 2H), 4.33 (s, 2H), 4.09 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 155.92 (d, *J* = 235.0 Hz, C-F), 144.57, 139.34, 128.73, 127.54, 127.36, 115.83, 115.61, 113.73, 113.66, 48.93. HRMS (ESI) calcd. for $C_{13}H_{13}FN^{+}$ $[M+H]^{+}$: 202.1027, found: 202.1029.

**N-Benzyl-4-chloroaniline (3ae)[7]**



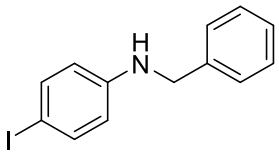
Yellow solid, mp: 44-45 °C, 191.6 mg, 88% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 4.4 Hz, 4H), 7.36-7.30 (m, 1H), 7.17-7.12 (m, 2H), 6.59-6.55 (m, 2H), 4.32 (s, 2H), 4.09 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 146.74, 139.03, 129.16, 128.80, 127.50, 127.46, 122.16, 114.01, 48.42. HRMS (ESI) calcd. for $C_{13}H_{13}ClN^{+}$ $[M+H]^{+}$: 218.7035, found: 218.7035.

**N-Benzyl-4-bromoaniline (3af)[7]**



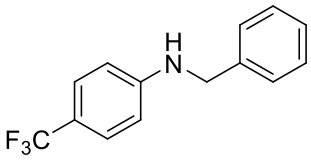
Yellow solid, mp: 52-53 °C, 225.4 mg, 86% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.47-7.38 (m, 5H), 7.35-7.31 (m, 2H), 6.57- 6.54 (m, 2H), 4.34 (d, *J* = 5.3 Hz, 2H), 4.13 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 147.06, 138.89, 131.92, 128.71, 127.39, 114.44, 109.04, 48.15. HRMS (ESI) calcd. for $C_{13}H_{13}BrN^{+}$ $[M+H]^{+}$: 262.0226, found: 262.0226.

**N-Benzyl-4-iodoaniline(3ag)[7]**



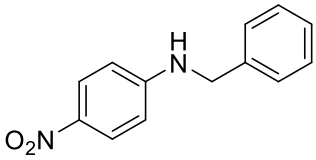
Yellow solid, mp: 55-56 °C, 265.9 mg, 86% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.51-7.36 (m, 7H), 6.48-6.45 (m, 2H), 4.35 (s, 2H), 4.14 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 147.56, 138.79, 137.72, 128.68, 127.35, 115.08, 78.12, 47.94. HRMS (ESI) calcd. for $C_{13}H_{13}IN^{+}$ $[M+H]^{+}$: 310.0087, found: 310.0089.

**N-Benzyl-4-(trifluoromethyl)aniline (3ah)[7]**



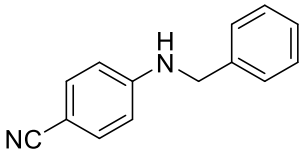
Yellow oil, 201.0 mg, 80% yield. $^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.38-7.35 (m, 4H), 7.33-7.29 (m, 1H), 6.64 (d, *J* = 8.4 Hz, 2H), 4.38 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 150.47, 138.46, 128.79, 127.53, 127.36, 126.63 (q, *J* = 3.9 Hz), 123.89, 119.21, 118.95, 111.98, 47.82. HRMS (ESI) calcd. for $C_{14}H_{13}F_{3}N^{+}$ $[M+H]^{+}$: 252.0995, found: 252.0995.

**N-Benzyl-4-nitroaniline (3ai)[7]**



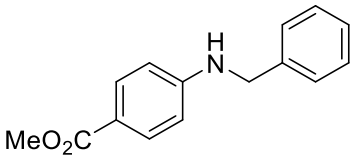
Yellow soild, mp: 149 °C, 178.0 mg, 78% yield. $^{1}$H NMR (600 MHz, DMSO-$d_6$) δ 7.98 (d, $J$ = 9.0 Hz, 2H), 7.85 (t, $J$ = 6.1 Hz, 1H), 7.34 (d, $J$ = 4.4 Hz, 4H), 7.26 (h, $J$ = 4.1 Hz, 1H), 6.68 (d, $J$ = 8.9 Hz, 2H), 4.42 (d, $J$ = 6.0 Hz, 2H). $^{13}$C NMR (151 MHz, DMSO-$d_6$) δ 154.87, 138.98, 136.41, 128.97, 127.70, 127.54, 126.62, 46.33. HRMS (ESI) calcd. for $C_{13}H_{13}N_2O_2^+$ $[M+H]^+$: 229.0972, found: 229.0973.

**4-(Benzylamino)benzonitrile (3aj)[10]**



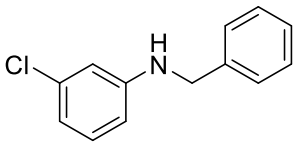
Yellow solid, mp: 66-67 °C, 166.6 mg, 80% yield. $^{1}$H NMR (600 MHz, Chloroform-$d$) δ 7.42-7.29 (m, 7H), 6.60-6.59 (m, 2H), 4.84 (s, 1H), 4.38 (d, $J$ = 5.5 Hz, 2H). $^{13}$C NMR (151 MHz, Chloroform-$d$) δ 151.30, 137.96, 133.72, 128.89, 127.67, 127.32, 120.63, 112.47, 98.73, 47.41. HRMS (ESI) calcd. for $C_{14}H_{13}N_2^+$ $[M+H]^+$: 209.1073, found: 209.1075.

**Methyl 4-(benzylamino)benzoate (3ak)[7]**



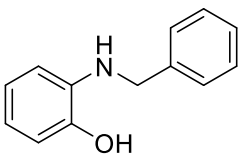
Colorless oil, 195.4 mg, 81% yield. $^{1}$H NMR (600 MHz, Chloroform-$d$) δ 7.87 (d, $J$ = 8.7 Hz, 2H), 7.37-7.34 (m, 4H), 7.31-7.28 (m, 1H), 6.59 (d, $J$ = 8.7 Hz, 2H), 4.54 (s, 1H), 4.39 (s, 2H), 3.85 (s, 3H). $^{13}$C NMR (151 MHz, Chloroform-$d$) δ 167.38, 151.86, 138.48, 131.66, 128.89, 127.63, 127.51, 118.75, 111.75, 51.66, 47.77. HRMS (ESI) calcd. for $C_{15}H_{16}NO_2^+$ $[M+H]^+$: 242.1176, found: 242.1179.

**N-Benzyl-3-chloroaniline (3al)[10]**



Colorless oil, 187.2 mg, 86% yield. $^{1}$H NMR (600 MHz, Chloroform-$d$) δ 7.41-7.32 (m, 5H), 7.10 (t, $J$ = 8.0 Hz, 1H), 6.72 (dd, $J$ = 7.9, 1.9 Hz, 1H), 6.65 (s, 1H), 6.52 (dd, $J$ = 8.2, 2.3 Hz, 1H), 4.33 (s, 2H), 4.12 (s, 1H). $^{13}$C NMR (151 MHz, Chloroform-$d$) δ 149.30, 138.83, 135.09, 130.31, 128.82, 127.55, 127.53, 117.48, 112.57, 111.21, 48.15. HRMS (ESI) calcd. for $C_{13}H_{13}ClN^+$ $[M+H]^+$: 218.0731, found: 218.0731.

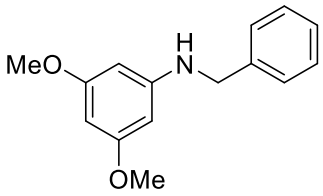
**2-(Benzylamino)phenol (3am)[9]**



Yellow oil, 169.4 mg, 85% yield. $^{1}$H NMR (600 MHz, Chloroform-$d$) δ 7.41 (d, $J$ = 7.3 Hz, 2H), 7.36 (t, $J$ = 7.6 Hz, 2H), 7.30 (t, $J$ = 7.2 Hz, 1H), 6.86 (t, $J$ = 7.5 Hz, 1H), 6.70 (d, $J$ = 7.7 Hz, 2H), 6.65 (t, $J$ = 7.5 Hz, 1H), 4.74 (brs, 2H), 4.36 (s, 2H). $^{13}$C NMR (151 MHz, Chloroform-$d$) δ 143.54, 139.47, 137.05, 128.72, 127.69, 127.32, 121.83, 117.97,

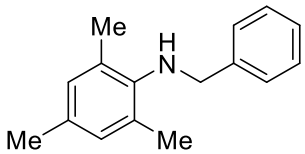
114.50, 112.65, 48.69. HRMS (ESI) calcd. for $C_{13}H_{14}NO^+$ $[M+H]^+$: 200.1070, found: 200.1071.

**N-Benzyl-3,5-dimethoxyaniline (3an)**



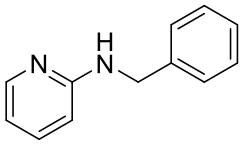

Colorless oil, 228.7 mg, 94% yield. $^1$H NMR (500 MHz, Chloroform-*d*) δ 7.37-7.31 (m, 4H), 7.28-7.24 (m, 1H), 5.89 (t, *J* = 2.1 Hz, 1H), 5.83 (d, *J* = 2.2 Hz, 2H), 4.29 (s, 2H), 4.04 (s, 1H), 3.72 (s, 6H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 161.87, 150.23, 139.40, 128.77, 127.67, 127.39, 91.90, 90.09, 55.27, 48.49. HRMS (ESI) calcd. for $C_{15}H_{18}NO_2^+$ $[M+H]^+$: 244.1332, found: 244.1335.

**N-Benzyl-2,4,6-trimethylaniline (3ao)**



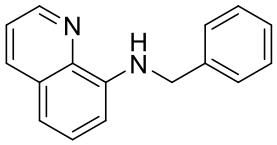

Yellow oil, 189.3 mg, 84% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.56-7.42 (m, 5H), 7.01 (s, 2H), 4.23 (s, 2H), 3.25 (s, 1H), 2.42 (s, 9H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 143.34, 140.59, 131.65, 130.16, 129.52, 128.59, 128.06, 127.28, 53.22, 20.70, 18.34. HRMS (ESI) calcd. for $C_{16}H_{20}N^+$ $[M+H]^+$: 226.1590, found: 226.1592.

**N-Benzylpyridin-2-amine (3ap)[4]**



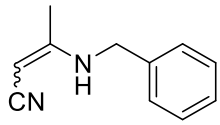

White solid, mp: 92-93 ºC, 158.4 mg, 86% yield. $^1$H NMR (600 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 4.8 Hz, 1H), 7.41-7.33 (m, 5H), 7.28 (d, *J* = 7.0 Hz, 1H), 6.59 (t, *J* = 6.0 Hz, 1H), 6.37 (d, *J* = 8.4 Hz, 1H), 4.98 (s, 1H), 4.51 (d, *J* = 5.8 Hz, 2H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 158.77, 148.34, 139.31, 137.56, 128.74, 127.52, 127.34, 113.25, 106.89, 46.44. HRMS (ESI) calcd. for $C_{12}H_{13}N_2^+$ $[M+H]^+$: 185.1073, found: 185.1077.

**N-Benzylquinolin-8-amine (3aq)[11]**



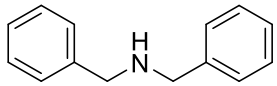

Colorless oil, 210.9 mg, 90% yield. $^1$H NMR (600 MHz, Chloroform-*d*) δ 8.80 (d, *J* = 6.0 Hz, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.47-7.38 (m, 4H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 1H), 6.73 (d, *J* = 7.4 Hz, 2H), 4.62 (d, *J* = 5.8 Hz, 2H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 147.02, 144.70, 139.36, 138.35, 136.10, 128.73, 127.89, 127.52, 127.25, 121.52, 114.26, 105.25, 47.79. HRMS (ESI) calcd. for $C_{16}H_{15}N_2^+$ $[M+H]^+$: 235.1230, found: 235.1234.

**3-(Benzylamino)but-2-enenitrile (3ar)[25]**



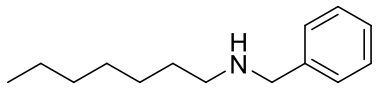
White solid, mp: 126-127 ºC. 117.1 mg, 68% yield. $^{1}$H NMR (600 MHz, Chloroform-*d*) δ 7.41-7.21 (m, 5H), 4.82 (s, 1H), 4.13 (d, *J* = 5.2 Hz, 2H), 3.83 (s, 1H), 2.12 (s, 3H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 159.97, 136.48, 128.95, 128.00, 127.66, 121.85, 61.52, 47.84, 20.24. HRMS (ESI) calcd. for $C_{11}H_{13}N_2^+$ $[M+H]^+$: 173.1073, found: 173.1073.

**Dibenzylamine (3as)[4]**



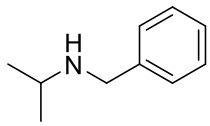
Colorless oil, 165.7 mg, 84% yield. $^{1}$H NMR (600 MHz, Chloroform-*d*) δ 7.30 (td, *J* = 8.0, 5.9 Hz, 8H), 7.23-7.20 (m, 2H), 3.76 (s, 4H), 1.56 (s, 1H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 140.39, 128.40, 128.15, 126.94, 53.18. HRMS (ESI) calcd. for $C_{14}H_{16}N^+$ $[M+H]^+$: 198.1277, found: 198.1277.

**N-Benzylheptan-1-amine (3at)[4]**



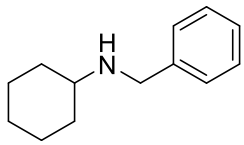
Colorless oil, 156.1 mg, 76% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 4.4 Hz, 4H), 7.25 (ddd, *J* = 8.8, 5.0, 3.8 Hz, 1H), 3.79 (s, 2H), 2.68-2.60 (m, 2H), 1.52 (q, *J* = 7.2 Hz, 2H), 1.37-1.27 (m, 8H), 1.22 (s, 1H), 0.90 (t, *J* = 6.8 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 140.68, 128.35, 128.09, 126.82, 54.17, 49.59, 31.88, 30.21, 29.30, 27.38, 22.67, 14.13. HRMS (ESI) calcd. for $C_{14}H_{24}N^+$ $[M+H]^+$: 206.1903, found: 206.1906.

**N-Benzylpropan-2-amine (3au)[22]**



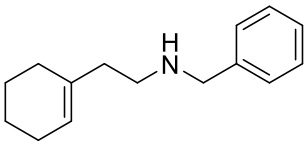
Colorless oil, 108.9 mg, 73% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.33-7.29 (m, 4H), 7.27-7.21 (m, 1H), 3.78 (s, 2H), 2.86 (hept, *J* = 6.2 Hz, 1H), 1.16 (s, 1H), 1.11 (d, *J* = 6.4 Hz, 6H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 140.75, 128.26, 127.97, 126.68, 51.55, 47.98, 22.87. HRMS (ESI) calcd. for $C_{10}H_{16}N^+$ $[M+H]^+$: 150.1277, found: 150.1279.

**N-Benzylcyclohexanamine (3av)[22]**



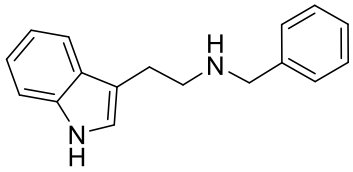
Colorless oil, 142.0 mg, 75% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.34-7.30 (m, 4H), 7.26-7.22 (m, 1H), 3.82 (s, 2H), 2.53-2.46 (m, 1H), 1.95-1.91 (m, 2H), 1.77-1.73 (m, 2H), 1.65-1.61 (m, 1H), 1.32-1.09 (m, 6H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 141.05, 128.35, 128.06, 126.74, 56.19, 51.08, 33.60, 26.24, 25.03. HRMS (ESI) calcd. for $C_{13}H_{20}N^+$ $[M+H]^+$: 190.1590, found: 190.1595.

**N-Benzyl-2-(cyclohex-1-en-1-yl)ethan-1-amine (3aw)[26]**



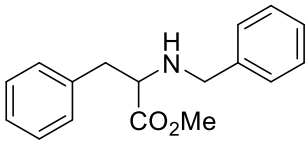
Colorless oil, 155.0 mg, 72% yield. $^{1}$H NMR (600 MHz, Chloroform-*d*) δ 7.37-7.23 (m, 5H), 5.46 (tt, *J* = 3.6, 1.7 Hz, 1H), 3.79 (s, 2H), 2.69 (t, *J* = 7.0 Hz, 2H), 2.16 (t, *J* = 7.0 Hz, 2H), 1.98 (dh, *J* = 6.4, 2.1 Hz, 2H), 1.88 (td, *J* = 6.0, 2.5 Hz, 2H), 1.62-1.58 (m, 2H), 1.56-1.52 (m, 2H), 1.44 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 140.56, 135.44, 128.36, 128.09, 126.84, 122.75, 53.92, 46.95, 38.32, 28.13, 25.28, 22.98, 22.52. HRMS (ESI) calcd. for $C_{15}H_{22}N^{+}$ $[M+H]^{+}$: 216.1747, found: 216.1747.

**N-Benzyl-2-(1H-indol-3-yl)ethan-1-amine (3ax)[9]**



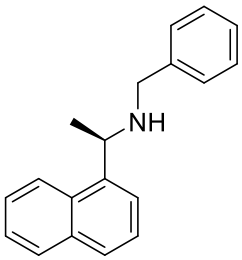
Colorless oil, 187.7 mg, 75% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.82 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.48-7.19 (m, 8H), 6.95 (d, *J* = 2.3 Hz, 1H), 3.94 (s, 2H), 3.14 (s, 4H), 1.65 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 140.16, 136.43, 128.41, 128.15, 127.42, 126.94, 122.18, 121.83, 119.10, 118.83, 113.46, 111.26, 53.83, 49.37, 25.72. HRMS (ESI) calcd. for $C_{17}H_{19}N_2^{+}$ $[M+H]^{+}$: 251.1543, found: 251.1545.

**Methyl benzylphenylalaninate (3ay)[4]**



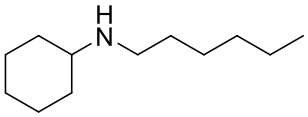
Colorless oil, 218.2 mg, 81% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.31-7.16 (m, 10H), 3.82 (d, *J* = 13.2 Hz, 1H), 3.66-3.63 (m, 4H), 3.55 (t, *J* = 6.9 Hz, 1H), 2.97 (d, *J* = 8.3 Hz, 2H), 1.85 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 174.95, 139.60, 137.31, 129.20, 128.35, 128.30, 128.09, 126.98, 126.64, 62.03, 51.96, 51.57, 39.73. HRMS (ESI) calcd. for $C_{17}H_{20}NO_2^{+}$ $[M+H]^{+}$: 270.1489, found: 270.1489.

**(*R*)-N-Benzyl-1-(naphthalen-1-yl)ethan-1-amine (3az)[11]**



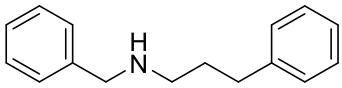
Colorless oil, 222.1 mg, 85% yield, >99% ee. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 9.3 Hz, 1H), 8.04-8.00 (m, 1H), 7.95-7.90 (m, 2H), 7.67-7.61 (m, 3H), 7.47-7.38 (m, 5H), 4.83 (q, *J* = 6.6 Hz, 1H), 3.94-3.83 (m, 2H), 1.84 (s, 1H), 1.67 (d, *J* = 6.6 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 141.10, 140.78, 134.09, 131.46, 129.01, 128.42, 128.23, 127.29, 126.92, 125.82, 125.75, 125.35, 123.10, 122.97, 53.14, 51.95, 23.77. HRMS (ESI) calcd. for $C_{19}H_{20}N^{+}$ $[M+H]^{+}$: 262.1590, found: 262.1593.

**N-hexylcyclohexanamine (5iv)[4]**



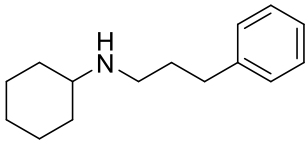
Colorless oil, 118.5 mg, 70% yield. $^{1}$H NMR (600 MHz, Chloroform-*d*) δ 3.01-2.97 (m, 1H), 2.94-2.86 (m, 2H), 2.22 (d, *J* = 11.5 Hz, 2H), 1.95-1.88 (m, 2H), 1.80 (d, *J* = 10.7 Hz, 2H), 1.63 (q, *J* = 10.4, 8.9 Hz, 3H), 1.43-1.03 (m, 10H), 0.82 (t, *J* = 6.9 Hz, 3H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 57.51, 44.69, 31.20, 29.03, 26.67, 25.89, 24.77, 24.56, 22.46, 13.95. HRMS (ESI) calcd. for $C_{12}H_{26}N^{+}$ $[M+H]^{+}$: 184.2060, found: 184.2063.

**N-Benzyl-3-phenylpropan-1-amine (5js)[10]**



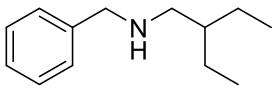
Colorless oil, 182.5 mg, 81% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.40-7.19 (m, 10H), 3.82 (s, 2H), 2.70 (q, *J* = 8.2 Hz, 4H), 2.27 (s, 1H), 1.89 (p, *J* = 7.5 Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 141.88, 139.20, 128.47, 128.39, 128.36, 127.21, 125.83, 53.59, 48.50, 33.52, 31.20. HRMS (ESI) calcd. for $C_{16}H_{20}N^{+}$ $[M+H]^{+}$: 226.1590, found: 226.1591.

**N-(3-Phenylpropyl)cyclohexanamine (5jv)[13]**



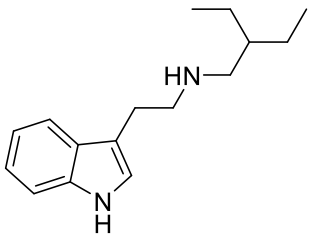
Colorless oil, 160.8 mg, 74% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.22 (dd, *J* = 31.6, 7.3 Hz, 5H), 2.65 (t, *J* = 7.5 Hz, 4H), 2.44-2.33 (m, 1H), 1.90-1.65 (m, 6H), 1.34-0.94 (m, 7H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 142.30, 128.43, 128.36, 125.78, 56.94, 46.68, 33.90, 33.83, 32.25, 26.31, 25.20. HRMS (ESI) calcd. for $C_{15}H_{24}N^{+}$ $[M+H]^{+}$: 218.1903, found: 218.1903.

**N-Benzyl-2-ethylbutan-1-amine (5is)[5]**



Colorless oil, 143.5 mg, 75% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.38-7.32 (m, 4H), 7.28-7.25 (m, 1H), 3.81 (s, 2H), 2.55 (d, *J* = 5.4 Hz, 2H), 1.38 (tdd, *J* = 13.6, 6.7, 4.0 Hz, 6H), 0.89 (t, *J* = 7.2 Hz, 6H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 140.83, 128.36, 128.10, 126.83, 54.35, 52.22, 40.99, 24.10, 11.02. HRMS (ESI) calcd. for $C_{13}H_{22}N^{+}$ $[M+H]^{+}$: 192.1747, found: 192.1747.

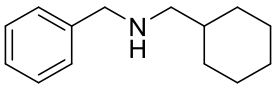
**N-(2-(1H-Indol-3-yl)ethyl)-2-ethylbutan-1-amine (5lx)**



Light yellow oil, 210.2 mg, 86% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.85 (s, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.00 (s, 1H), 3.08-3.00 (m, 4H), 2.61 (d, *J* = 6.2 Hz, 2H), 1.46-1.30 (m, 5H), 1.27 (brs, 1H), 0.88 (t, *J* = 7.4 Hz,

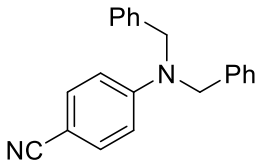
6H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 136.52, 127.54, 122.06, 121.86, 119.11, 118.91, 113.85, 111.25, 52.80, 50.39, 40.90, 25.82, 24.11, 10.96. HRMS (ESI) calcd. for $C_{16}H_{25}N_2^+$ $[M+H]^+$: 245.2012, found: 245.2013.

**N-Benzyl-1-cyclohexylmethanamine (5os)[11]**



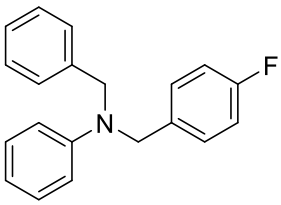
Colorless oil, 158.6 mg, 78% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.38-7.32 (m, 4H), 7.29-7.24 (m, 1H), 3.83 (s, 1H), 3.80 (s, 2H), 2.49 (d, *J* = 6.7 Hz, 2H), 1.75 (q, *J* = 14.8 Hz, 5H), 1.56-1.47 (m, 1H), 1.23 (dt, *J* = 25.1, 12.3 Hz, 3H), 0.98-0.90 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 140.72, 128.30, 128.02, 126.76, 56.26, 54.18, 38.04, 31.48, 26.73, 26.11. HRMS (ESI) calcd. for $C_{14}H_{22}N^+$ $[M+H]^+$: 204.1747, found: 204.1749.

**4-(Dibenzylamino)benzonitrile (3aaj)[6]**



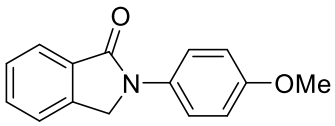
White solid, mp: 132-133 °C, 220.8 mg, 74% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.43-7.30 (m, 8H), 7.22-7.19 (m, 4H), 6.73-6.70 (m, 2H), 4.72 (s, 4H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 151.93, 136.89, 133.77, 129.07, 127.55, 126.41, 112.18, 98.63, 54.24. HRMS (ESI) calcd. for $C_{21}H_{19}N_2^+$ $[M+H]^+$: 299.1543, found: 299.1544.

**N-Benzyl-N-(4-fluorobenzyl)aniline (3aad)**



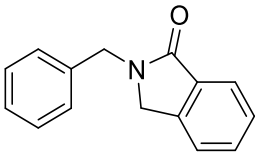
Yellow oil, 218.5 mg, 75% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.46-7.42 (m, 4H), 7.36 (t, *J* = 6.6 Hz, 6H), 6.99-6.93 (m, 2H), 6.78-6.74 (m, 2H), 4.71 (s, 4H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 155.6 (d, *J* = 235.3 Hz, C-F), 145.82, 138.59, 128.76, 127.08, 126.83, 115.75, 115.53, 114.00, 113.93, 55.12. HRMS (ESI) calcd. for $C_{20}H_{19}FN^+$ $[M+H]^+$: 292.1496, found: 292.1497.

**2-(4-Methoxyphenyl)isoindolin-1-one (7ac)[7]**



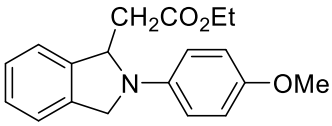
Yellow oil, 193.8 mg, 81% yield. $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.79-7.68 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.49 (dt, *J* = 7.2, 3.4 Hz, 2H), 7.01-6.89 (m, 2H), 4.79 (s, 2H), 3.81 (s, 3H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 167.31, 156.69, 140.24, 133.39, 132.76, 131.90, 128.40, 124.09, 122.66, 121.53, 114.42, 55.60, 51.25. HRMS (ESI) calcd. for $C_{15}H_{14}NO_2^+$ $[M+H]^+$: 240.1019, found: 240.1022.

**2-Benzylisoindolin-1-one (7as)[7]**



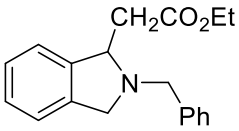
Yellow oil, 187.5 mg, 84% yield. $^{1}$H NMR (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.33-7.24 (m, 5H), 4.78 (s, 2H), 4.23 (s, 2H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 168.39, 141.22, 137.01, 132.57, 131.32, 128.75, 128.11, 127.97, 127.63, 123.76, 122.77, 49.38, 46.32. HRMS (ESI) calcd. for $C_{15}H_{14}NO^{+}$ $[M+H]^{+}$: 224.1070, found: 224.1073.

**Ethyl 2-(2-(4-methoxyphenyl)isoindolin-1-yl)acetate (7bc)[4]**



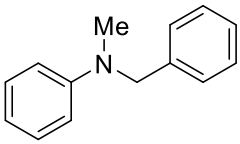
Yellow oil, 242.9 mg, 78% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.43-7.34 (m, 4H), 7.07-7.02 (m, 2H), 6.84-6.80 (m, 2H), 5.56-5.53 (m, 1H), 4.84 (d, *J* = 13.0 Hz, 1H), 4.58 (d, *J* = 13.0 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 3.20 (dd, *J* = 15.5, 3.0 Hz, 1H), 2.59 (dd, *J* = 15.5, 8.9 Hz, 1H), 1.36 (t, *J* = 7.2 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 171.70, 151.44, 141.64, 140.23, 137.50, 127.59, 127.27, 122.54, 122.47, 115.28, 113.21, 60.54, 60.34, 55.83, 54.24, 38.75, 14.23. HRMS (ESI) calcd. for $C_{19}H_{22}NO_3^{+}$ $[M+H]^{+}$: 312.1594, found: 312.1594.

**Ethyl 2-(2-benzylisoindolin-1-yl)acetate (7bs)[11]**



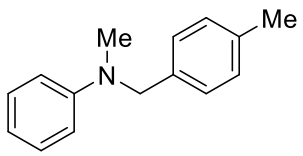
Yellow oil, 230.4 mg, 78% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.44-7.14 (m, 9H), 4.54 (t, *J* = 5.9 Hz, 1H), 4.25-4.13 (m, 3H), 4.12 (dd, *J* = 13.4, 1.9 Hz, 1H), 3.69 (d, *J* = 13.2 Hz, 2H), 2.91-2.79 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 172.17, 142.64, 139.47, 128.76, 128.44, 127.28, 127.12, 126.98, 122.40, 122.37, 65.68, 60.56, 58.55, 58.20, 40.63, 14.31. HRMS (ESI) calcd. for $C_{19}H_{22}NO_2^{+}$ $[M+H]^{+}$: 296.1645, found: 296.1647.

**N-Benzyl-N-methylaniline (9aa)[11]**



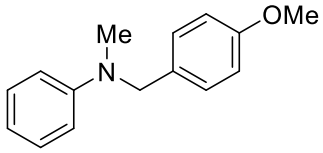
Yellow oil. 177.6 mg, 90% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.54-7.50 (m, 2H), 7.44 (td, *J* = 7.2, 2.2 Hz, 5H), 6.95 (dd, *J* = 15.4, 7.7 Hz, 3H), 4.72 (s, 2H), 3.20 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 149.98, 139.26, 129.42, 128.79, 127.09, 126.97, 116.80, 112.61, 56.83, 38.69. HRMS (ESI) calcd. for $C_{14}H_{16}N^{+}$ $[M+H]^{+}$: 198.1277, found: 198.1279.

**N-Methyl-N-(4-methylbenzyl)aniline (9ba)[11]**



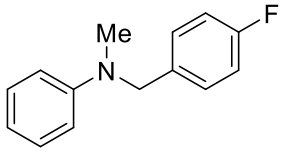

Yellow oil, 194.4 mg, 92% yield. $^{1}$H NMR (600 MHz, Chloroform-*d*) δ 7.23 (t, *J* = 7.8 Hz, 2H), 7.13 (s, 4H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 4.49 (s, 2H), 2.99 (s, 3H), 2.34 (s, 3H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 150.02, 136.58, 136.12, 129.45, 129.38, 126.95, 116.68, 112.60, 56.54, 38.59, 21.30. HRMS (ESI) calcd. for $C_{15}H_{18}N^{+}$ $[M+H]^{+}$: 212.1434, found: 212.1435.

**N-(4-Methoxybenzyl)-N-methylaniline (9ca)[11]**



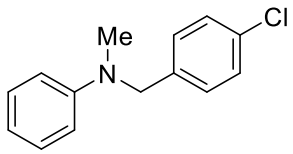

Yellow oil, 204.6 mg, 90% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.45 (t, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.98 (dd, *J* = 13.0, 7.9 Hz, 3H), 4.66 (s, 2H), 3.95 (s, 3H), 3.17 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 158.59, 149.79, 130.83, 129.15, 127.95, 116.52, 113.92, 112.48, 55.93, 55.11, 38.21. HRMS (ESI) calcd. for $C_{15}H_{18}NO^{+}$ $[M+H]^{+}$: 228.1383, found: 228.1384.

**N-(4-Fluorobenzyl)-N-methylaniline (9da)[11]**



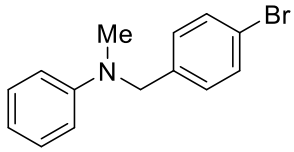

Yellow oil, 187.3 mg, 87% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.31-7.22 (m, 4H), 7.07-7.01 (m, 2H), 6.81-6.77 (m, 3H), 4.54 (s, 2H), 3.04 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 162.01 (d, *J* = 244.5 Hz, C-F), 149.78, 134.73, 129.33, 128.44, 128.36, 116.94, 115.59, 115.38, 112.66, 56.20, 38.54. HRMS (ESI) calcd. for $C_{14}H_{15}FN^{+}$ $[M+H]^{+}$: 216.1183, found: 216.1185.

**N-(4-Chlorobenzyl)-N-methylaniline (9ea)[11]**




Yellow oil, 210.9 mg, 91% yield. $^{1}$H NMR (600 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 3H), 4.55 (s, 2H), 3.07 (s, 3H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 149.58, 137.63, 132.60, 129.32, 128.78, 128.20, 116.94, 112.53, 56.22, 38.63. HRMS (ESI) calcd. for $C_{14}H_{15}ClN^{+}$ $[M+H]^{+}$: 232.0888, found: 232.0889.

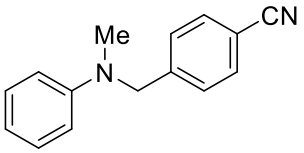
**N-(4-Bromobenzyl)-N-methylaniline (9fa)[11]**




Yellow oil, 245.8 mg, 89% yield. $^{1}$H NMR (600 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 6.81 (t, *J* = 9.0 Hz, 3H), 4.53 (s, 2H), 3.07 (s, 3H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 149.54, 138.16, 131.71, 129.32,

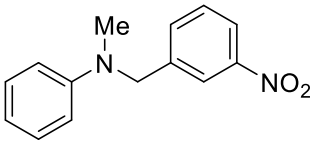
128.57, 120.65, 116.94, 112.51, 56.26, 38.65. HRMS (ESI) calcd. for $C_{14}H_{15}BrN^+$ $[M+H]^+$: 276.0382, found: 276.0382.

**4-((Methyl(phenyl)amino)methyl)benzonitrile (9ia)[11]**



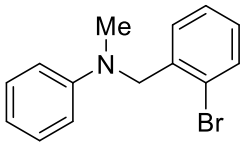

Yellow oil, 184.5 mg, 83% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.33-7.25 (m, 2H), 6.86-6.72 (m, 3H), 4.62 (s, 2H), 3.10 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 149.03, 144.90, 132.26, 129.18, 127.25, 118.80, 117.02, 112.27, 110.53, 56.39, 38.73. HRMS (ESI) calcd. for $C_{15}H_{15}N_2^+$ $[M+H]^+$: 223.1230, found: 223.1231.

**N-Methyl-N-(3-nitrobenzyl)aniline (9oa)[11]**



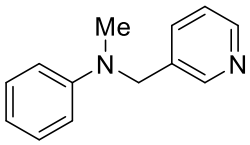

Dark yellow oil, 196.2 mg, 81% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.17 (s, 1H), 8.13 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 1H), 7.33-7.26 (m, 2H), 6.86-6.76 (m, 3H), 4.65 (s, 2H), 3.12 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 149.20, 148.55, 141.68, 132.82, 129.57, 129.30, 122.04, 121.61, 117.30, 112.56, 56.36, 38.85. HRMS (ESI) calcd. for $C_{14}H_{15}N_2O_2^+$ $[M+H]^+$: 243.1128, found: 243.1130.

**N-(2-Bromobenzyl)-N-methylaniline (9qa)[11]**



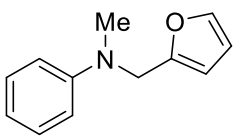

Light yellow oil, 229.2 mg, 83% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.30-7.25 (m, 3H), 7.21-7.14 (m, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 2H), 4.60 (s, 2H), 3.14 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 149.27, 137.46, 132.90, 129.34, 128.47, 127.99, 127.63, 122.83, 116.72, 112.03, 57.47, 38.86. HRMS (ESI) calcd. for $C_{14}H_{15}BrN^+$ $[M+H]^+$: 276.0382, found: 276.0382.

**N-Methyl-N-(pyridin-3-ylmethyl)aniline (9wa)**



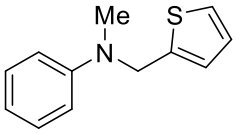

Light yellow oil, 158.6 mg, 80% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.53 (s, 1H), 8.50 (d, *J* = 3.7 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.25-7.21 (m, 3H), 6.77-6.73 (m, 3H), 4.53 (s, 2H), 3.00 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 149.48, 148.78, 148.46, 134.72, 134.52, 129.35, 123.58, 117.30, 112.80, 54.52, 38.66. HRMS (ESI) calcd. for $C_{13}H_{15}N_2^+$ $[M+H]^+$: 199.1230, found: 199.1230.

**N-(Furan-2-ylmethyl)-N-methylaniline (9xa)[3]**



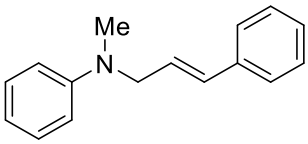
Light yellow oil, 153.5 mg, 82% yield. $^{1}$H NMR (600 MHz, Chloroform-*d*) δ 7.35 (s, 1H), 7.25 (t, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.30 (dd, *J* = 3.2, 1.7 Hz, 1H), 6.14 (d, *J* = 3.2 Hz, 1H), 4.46 (s, 2H), 2.99 (s, 3H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 152.44, 149.46, 141.94, 129.21, 117.23, 113.14, 110.28, 107.32, 49.96, 38.41. HRMS (ESI) calcd. for $C_{12}H_{14}NO^{+}$ $[M+H]^{+}$: 188.1070, found: 188.1070.

**N-Methyl-N-(thiophen-2-ylmethyl)aniline (9ya)** [5]



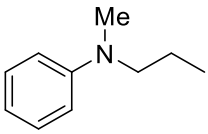
Light yellow oil, 170.8 mg, 84% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.34-7.29 (m, 2H), 7.22 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.01-6.96 (m, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.83 (t, *J* = 7.3 Hz, 1H), 4.72 (s, 2H), 3.04 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 149.36, 142.25, 129.27, 126.79, 124.99, 124.37, 117.42, 113.32, 52.19, 38.26. HRMS (ESI) calcd. for $C_{12}H_{14}NS^{+}$ $[M+H]^{+}$: 204.0841, found: 204.0844.

**N-Cinnamyl-N-methylaniline (10aa)**



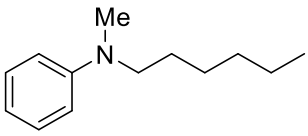
Yellow oil, 203.2 mg, 91% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.42-7.24 (m, 7H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.30 (dt, *J* = 15.9, 5.5 Hz, 1H), 4.13 (d, *J* = 5.4 Hz, 2H), 3.03 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 149.70, 137.03, 131.39, 129.31, 128.65, 127.52, 126.44, 125.89, 116.72, 112.76, 55.02, 38.14. HRMS (ESI) calcd. for $C_{16}H_{18}N^{+}$ $[M+H]^{+}$: 224.1434, found: 224.1434.

**N-Methyl-N-propylaniline (10ha)**[7]



Yellow oil, 105.9 mg, 71% yield. $^{1}$H NMR (600 MHz, Chloroform-*d*) δ 7.33 (t, *J* = 7.8 Hz, 2H), 6.79 (dd, *J* = 16.9, 7.9 Hz, 3H), 3.41-3.32 (m, 2H), 3.02 (s, 3H), 1.71 (h, *J* = 7.4 Hz, 2H), 1.03 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 149.50, 129.21, 115.88, 112.14, 54.63, 38.39, 20.05, 11.63. HRMS (ESI) calcd. for $C_{10}H_{16}N^{+}$ $[M+H]^{+}$: 150.1277, found: 150.1277.

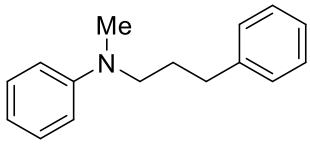
**N-Hexyl-N-methylaniline (10ia)**[8]



Yellow oil, 137.7 mg, 72% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.28-7.24 (m, 2H), 6.74-6.69 (m, 3H), 3.33 (t, *J* = 6.5 Hz, 2H), 2.96 (s, 3H), 1.64-1.57 (m, 2H), 1.39-1.34 (m, 6H), 0.94 (t, *J* = 6.5 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 149.51,

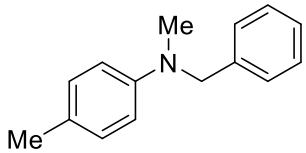
129.24, 115.91, 112.21, 52.97, 38.38, 31.90, 27.01, 26.77, 22.82, 14.19. HRMS (ESI) calcd. for $C_{13}H_{22}N^+$ $[M+H]^+$: 192.1747, found: 192.1747.

**N-Methyl-N-(3-phenylpropyl)aniline (10ja)[7]**



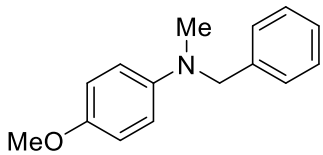
Yellow oil, 166.7 mg, 74% yield. $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.46 (dd, *J* = 8.6, 6.5 Hz, 2H), 7.41-7.35 (m, 5H), 6.86 (dd, *J* = 18.5, 7.7 Hz, 3H), 3.52-3.48 (m, 2H), 3.07 (s, 3H), 2.82 (t, *J* = 7.8 Hz, 2H), 2.08 (p, *J* = 7.5 Hz, 2H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 149.36, 141.83, 129.20, 128.43, 128.39, 125.93, 116.09, 112.27, 52.26, 38.32, 33.39, 28.24. HRMS (ESI) calcd. for $C_{16}H_{20}N^+$ $[M+H]^+$: 226.1590, found: 226.1590.

**N-Benzyl-N,4-dimethylaniline (9ab)[11]**



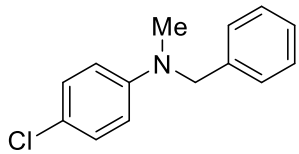
White solid, mp: 72-74 $^o$C, 192.3 mg, 91% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.22-7.11 (m, 7H), 3.98 (s, 2H), 2.43 (s, 3H), 2.31 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 143.54, 135.79, 134.46, 129.83, 128.69, 128.44, 127.94, 127.57, 54.22, 34.41, 21.60. HRMS (ESI) calcd. for $C_{15}H_{18}N^+$ $[M+H]^+$: 212.1434, found: 212.1434.

**N-Benzyl-4-methoxy-N-methylaniline (9ac)[11]**



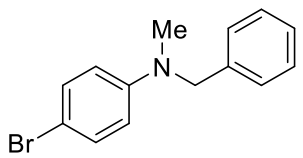
Light yellow oil, 213.7 mg, 94% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.33-7.11 (m, 5H), 6.78 (d, *J* = 9.0 Hz, 2H), 6.69 (d, *J* = 9.0 Hz, 2H), 4.35 (s, 2H), 3.67 (s, 3H), 2.85 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 151.80, 144.78, 139.26, 128.47, 127.11, 126.85, 114.73, 114.54, 57.95, 55.64, 39.02. HRMS (ESI) calcd. for $C_{15}H_{18}NO^+$ $[M+H]^+$: 228.1383, found: 228.1384.

**N-Benzyl-4-chloro-N-methylaniline (9ad)[3]**



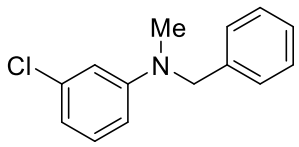
Light yellow oil, 213.2 mg, 92% yield. $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.3 Hz, 1H), 7.17-7.15 (m, 2H), 7.11-7.10 (m, 2H), 6.61-6.59 (m, 2H), 4.46 (s, 2H), 2.96 (s, 3H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 148.32, 138.55, 128.72, 127.09, 126.70, 121.36, 113.54, 56.72, 38.84. HRMS (ESI) calcd. for $C_{14}H_{15}ClN^+$ $[M+H]^+$: 232.0888, found: 232.0888.

**N-Benzyl-4-bromo-N-methylaniline (9ae)[3]**



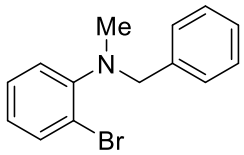
Light yellow oil, 243.0 mg, 88% yield. $^{1}$H NMR (600 MHz, Chloroform-*d*) δ 7.43 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 8.7 Hz, 3H), 7.31 (d, *J* = 7.6 Hz, 2H), 6.70 (d, *J* = 9.0 Hz, 2H), 4.60 (s, 2H), 3.10 (s, 3H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 148.61, 138.42, 131.83, 128.69, 127.06, 126.64, 113.97, 108.40, 56.54, 38.76. HRMS (ESI) calcd. for $C_{14}H_{15}BrN^{+}$ $[M+H]^{+}$: 276.0382, found: 276.0384.

**N-Benzyl-3-chloro-N-methylaniline (9af)[11]**



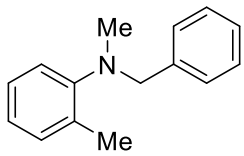
Light yellow oil, 197.0 mg, 85% yield. $^{1}$H NMR (600 MHz, Chloroform-*d*) δ 7.41-7.32 (m, 5H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.72 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.65 (s, 1H), 6.52 (dd, *J* = 8.2, 2.3 Hz, 1H), 4.33 (s, 2H), 4.12 (s, 1H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 149.30, 138.83, 135.09, 130.31, 128.82, 127.55, 127.53, 117.48, 112.57, 111.21, 48.15. HRMS (ESI) calcd. for $C_{14}H_{15}ClN^{+}$ $[M+H]^{+}$: 232.0888, found: 232.0888.

**N-Benzyl-2-bromo-N-methylaniline (9ag)[11]**



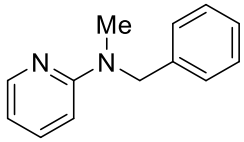
Light yellow oil, 223.7 mg, 81% yield. $^{1}$H NMR (600 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.37-7.30 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 4.26 (s, 2H), 2.74 (s, 3H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 151.18, 138.31, 133.96, 128.58, 128.32, 128.11, 127.19, 124.33, 120.17, 60.58, 40.51. HRMS (ESI) calcd. for $C_{14}H_{15}BrN^{+}$ $[M+H]^{+}$: 276.0382, found: 276.0383.

**N-Benzyl-N,2-dimethylaniline (9ah)[11]**



Light yellow oil, 181.7 mg, 86% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.36-7.23 (m, 3H), 7.17 (d, *J* = 6.9 Hz, 1H), 7.07 (t, *J* = 7.3 Hz, 1H), 4.12 (s, 2H), 2.67 (s, 3H), 2.50 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 152.51, 139.21, 132.98, 131.25, 128.46, 128.39, 127.08, 126.58, 123.15, 120.17, 60.91, 41.02, 18.53. HRMS (ESI) calcd. for $C_{15}H_{18}N^{+}$ $[M+H]^{+}$: 212.1434, found: 212.1434.

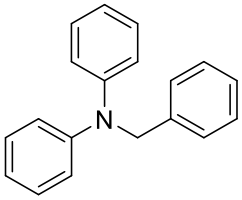
**N-Benzyl-N-methylpyridin-2-amine (9ai)[27]**



Yellow oil, 158.6 mg, 80% yield. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 4.8 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.30-7.27 (m, 2H), 7.21 (d, *J* = 7.6 Hz, 3H), 6.54 (t, *J* = 5.9 Hz, 1H), 6.48 (d, *J* = 8.6 Hz, 1H), 4.79 (s, 2H), 3.05 (s, 3H). $^{13}$C NMR (151 MHz,

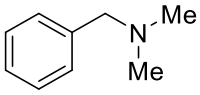
Chloroform-*d*) δ 158.96, 148.05, 138.79, 137.35, 128.58, 127.07, 126.94, 111.88, 105.73, 53.25, 36.21. HRMS (ESI) calcd. for $C_{13}H_{15}N_2^+$ $[M+H]^+$: 199.1230, found: 199.1230.

**N-Benzyl-N-phenylaniline (9aj)[11]**



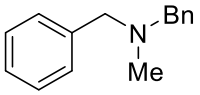
Light yellow oil, 212.7 mg, 82% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.37 (ddd, *J* = 9.6, 5.8, 2.1 Hz, 5H), 7.23 (d, *J* = 7.9 Hz, 4H), 7.07 (t, *J* = 7.3 Hz, 2H), 5.14 (s, 2H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 148.13, 139.26, 129.35, 128.64, 126.86, 126.59, 121.46, 120.75, 56.37. HRMS (ESI) calcd. for $C_{19}H_{18}N^+$ $[M+H]^+$: 260.1434, found: 260.1434.

**N,N-Dimethyl-1-phenylmethanamine (9ak)[4]**



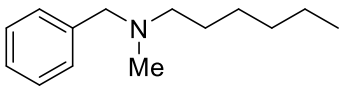
Colorless oil, 100.1 mg, 74% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.37-7.16 (m, 5H), 3.41 (s, 2H), 2.23 (s, 6H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 139.01, 129.18, 128.31, 127.11, 64.53, 45.49. HRMS (ESI) calcd. for $C_9H_{14}N^+$ $[M+H]^+$: 136.1121, found: 136.1123.

**N-Benzyl-N-methyl-1-phenylmethanamine (9al)[4]**



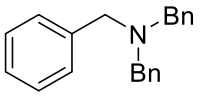
Colorless oil, 179.6 mg, 85% yield. $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.8 Hz, 4H), 7.48 (t, *J* = 7.6 Hz, 4H), 7.40 (t, *J* = 7.4 Hz, 2H), 3.69 (s, 4H), 2.35 (s, 3H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 139.42, 128.96, 128.29, 126.99, 61.95, 42.32. HRMS (ESI) calcd. for $C_{15}H_{18}N^+$ $[M+H]^+$: 212.1434, found: 212.1435.

**N-benzyl-N-methylhexan-1-amine (9am)[10]**



Colorless oil, 145.4 mg, 76% yield. $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.29 (q, *J* = 7.5 Hz, 4H), 7.21 (t, *J* = 6.7 Hz, 1H), 3.45 (s, 2H), 2.34 (t, *J* = 6.7 Hz, 2H), 2.16 (s, 3H), 1.50 (p, *J* = 7.3 Hz, 2H), 1.28 (tdd, *J* = 15.5, 7.9, 3.5 Hz, 6H), 0.88 (t, *J* = 6.9 Hz, 3H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 139.46, 129.06, 128.19, 126.86, 62.46, 57.72, 42.33, 31.93, 27.53, 27.23, 22.76, 14.16. HRMS (ESI) calcd. for $C_{14}H_{24}N^+$ $[M+H]^+$: 206.1903, found: 206.1905.

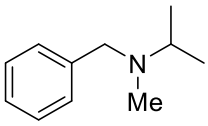
**Tribenzylamine (9an)[4]**



Colorless oil, 235.7 mg, 82% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.4 Hz, 5H), 7.33 (t, *J* = 7.5 Hz, 5H), 7.24 (d, *J* = 7.6

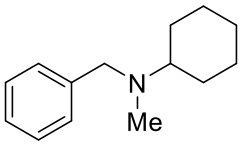
Hz, 5H), 3.57 (s, 6H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 139.79, 128.87, 128.35, 126.98, 58.07. HRMS (ESI) calcd. for $C_{21}H_{22}N^+$ $[M+H]^+$: 288.1747, found: 288.1747.

**N-Benzyl-N-methylpropan-2-amine (9ao)[4]**



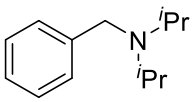
Colorless oil, 122.4 mg, 75% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.50-7.27 (m, 5H), 3.61 (s, 2H), 3.00 (pd, *J* = 6.6, 1.8 Hz, 1H), 2.26 (s, 3H), 1.18 (d, *J* = 6.6 Hz, 6H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 140.27, 128.73, 128.14, 126.66, 57.58, 53.07, 36.83, 17.88. HRMS (ESI) calcd. for $C_{11}H_{18}N^+$ $[M+H]^+$: 164.1434, found: 164.1435.

**N-Benzyl-N-methylcyclohexanamine (9ap)[4]**



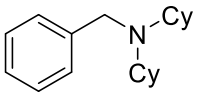
Colorless oil, 156.6 mg, 77% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 6.0 Hz, 3H), 7.24 (d, *J* = 13.2 Hz, 2H), 3.56 (s, 2H), 2.43 (t, *J* = 10.6 Hz, 1H), 2.19 (s, 3H), 1.88 (d, *J* = 11.2 Hz, 2H), 1.80 (d, *J* = 11.7 Hz, 2H), 1.63 (d, *J* = 12.4 Hz, 1H), 1.31-1.09 (m, 5H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 140.58, 128.94, 128.29, 126.77, 62.68, 57.98, 37.86, 28.87, 26.60, 26.19. HRMS (ESI) calcd. for $C_{14}H_{22}N^+$ $[M+H]^+$: 204.1747, found: 204.1747.

**N-Benzyl-N-isopropylpropan-2-amine (9aq)[4]**



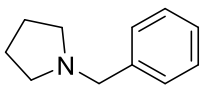
Colorless oil, 133.9 mg, 70% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 1H), 3.69 (s, 2H), 3.07 (p, *J* = 6.6 Hz, 2H), 1.07 (d, *J* = 6.7 Hz, 12H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 143.39, 128.09, 128.01, 126.27, 49.06, 47.92, 20.92. HRMS (ESI) calcd. for $C_{13}H_{22}N^+$ $[M+H]^+$: 192.1747, found: 192.1748.

**N-Benzyl-N-cyclohexylcyclohexanamine (9ar)[4]**



Colorless oil, 192.7 mg, 71% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 7.4 Hz, 1H), 3.84 (s, 2H), 2.62 (tt, *J* = 11.3, 3.3 Hz, 2H), 1.92-1.76 (m, 8H), 1.66 (dd, *J* = 12.6, 3.7 Hz, 2H), 1.41-1.21 (m, 8H), 1.17-1.07 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 143.81, 128.00, 127.81, 126.12, 57.87, 50.14, 32.11, 26.63, 26.46. HRMS (ESI) calcd. for $C_{19}H_{30}N^+$ $[M+H]^+$: 272.2373, found: 272.2374.

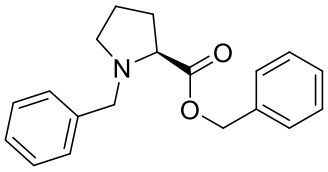
**1-Benzylpyrrolidine (9as)[7]**



Colorless oil, 119.3 mg, 74% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.38-7.22 (m, 5H), 3.62 (s, 2H), 2.56-2.47 (m, 4H), 1.78 (p, *J* =

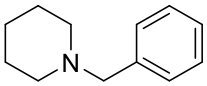
3.1 Hz, 4H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 139.49, 129.04, 128.33, 126.98, 60.88, 23.60. HRMS (ESI) calcd. for $C_{11}H_{16}N^+$ $[M+H]^+$: 162.1277, found: 162.1277.

**Benzyl benzyl-L-prolinate (9at)[7]**



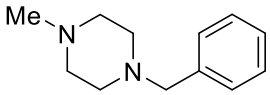
Colorless oil, 209.7 mg, 71% yield, >99% ee. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.43-7.19 (m, 10H), 5.20-5.07 (m, 2H), 3.95 (d, *J* = 12.8 Hz, 1H), 3.58 (d, *J* = 12.8 Hz, 1H), 3.34 (dd, *J* = 8.9, 6.1 Hz, 1H), 3.06 (ddd, *J* = 8.9, 7.6, 3.1 Hz, 1H), 2.43 (q, *J* = 8.3 Hz, 1H), 2.22-2.09 (m, 1H), 2.07-1.70 (m, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 173.89, 138.54, 136.05, 129.13, 128.52, 128.23, 128.17, 127.04, 66.19, 65.14, 58.52, 53.14, 29.32, 23.09. HRMS (ESI) calcd. for $C_{19}H_{22}NO_2^+$ $[M+H]^+$: 296.1645, found: 296.1645.

**1-Benzylpiperidine (9au)[22]**



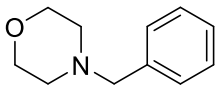
Colorless oil, 140.2 mg, 80% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.37-7.25 (m, 5H), 3.51 (s, 2H), 2.43-2.40 (m, 4H), 1.61 (p, *J* = 5.6 Hz, 4H), 1.47 (p, J = 5.8 Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 138.76, 129.24, 128.14, 126.86, 63.98, 54.59, 26.10, 24.51. HRMS (ESI) calcd. for $C_{12}H_{18}N^+$ $[M+H]^+$: 176.1434, found: 176.1434.

**1-Benzyl-4-methylpiperazine (9av)[22]**



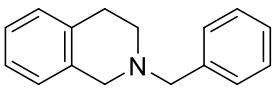
Colorless oil, 154.1 mg, 81% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.36-7.17 (m, 5H), 3.49 (s, 2H), 2.44 (s, 8H), 2.26 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 138.25, 129.25, 128.25, 127.07, 63.12, 55.22, 53.16, 46.12. HRMS (ESI) calcd. for $C_{12}H_{19}N_2^+$ $[M+H]^+$: 191.1543, found: 191.1544.

**4-Benzylmorpholine (9aw)[9]**



Colorless oil, 145.3 mg, 82% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.39-7.20 (m, 5H), 3.72-3.70 (m, 4H), 3.50 (s, 2H), 2.44 (t, *J* = 4.6 Hz, 4H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 137.78, 129.14, 128.22, 127.10, 66.98, 63.44, 53.62. HRMS (ESI) calcd. for $C_{11}H_{16}NO^+$ $[M+H]^+$: 178.1226, found: 178.1226.

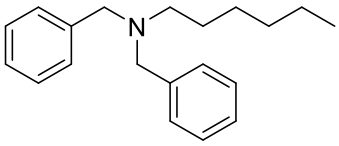
**2-Benzyl-1,2,3,4-tetrahydroisoquinoline (9ax)[22]**



Colorless oil, 187.6 mg, 84% yield. $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.21 (dd, *J* = 12.8, 5.9 Hz, 3H), 7.07 (d, *J* = 7.6 Hz, 1H),

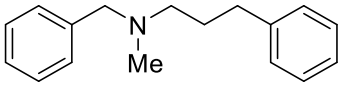
3.77 (s, 2H), 3.73 (s, 2H), 2.99 (t, $J$ = 5.9 Hz, 2H), 2.83 (t, $J$ = 5.9 Hz, 2H). $^{13}$C NMR (151 MHz, Chloroform-d) δ 138.54, 135.03, 134.48, 129.14, 128.77, 128.37, 127.17, 126.68, 126.15, 125.63, 62.90, 56.24, 50.74, 29.29. HRMS (ESI) calcd. for $C_{16}H_{18}N^+$ $[M+H]^+$: 224.1434, found: 224.1438.

***N,N*-Dibenzylhexan-1-amine (10in)[12]**



Yellow oil, 205.5 mg, 73% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, $J$ = 7.1 Hz, 4H), 7.38 (t, $J$ = 7.4 Hz, 4H), 7.30 (t, $J$ = 7.2 Hz, 2H), 3.63 (s, 4H), 2.52-2.44 (m, 2H), 1.59 (p, $J$ = 7.2 Hz, 2H), 1.39-1.23 (m, 6H), 0.94 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 140.23, 128.88, 128.23, 126.81, 58.45, 53.57, 31.87, 27.13, 27.09, 22.82, 14.23. HRMS (ESI) calcd. for $C_{20}H_{28}N^+$ $[M+H]^+$: 282.2216, found: 282.2219.

**N-Benzyl-N-methyl-3-phenylpropan-1-amine (10jl)[11]**



Yellow oil, 169.9 mg, 71% yield. $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.36-7.18 (m, 7H), 7.16 (d, $J$ = 7.6 Hz, 3H), 3.46 (s, 2H), 2.67-2.58 (m, 2H), 2.40 (t, $J$ = 7.2 Hz, 2H), 2.17 (s, 3H), 1.82 (p, $J$ = 7.4 Hz, 2H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 142.55, 139.44, 129.13, 128.55, 128.39, 128.30, 126.98, 125.79, 62.43, 57.02, 42.30, 33.69, 29.37. HRMS (ESI) calcd. for $C_{17}H_{22}N^+$ $[M+H]^+$: 240.1747, found: 240.1747.

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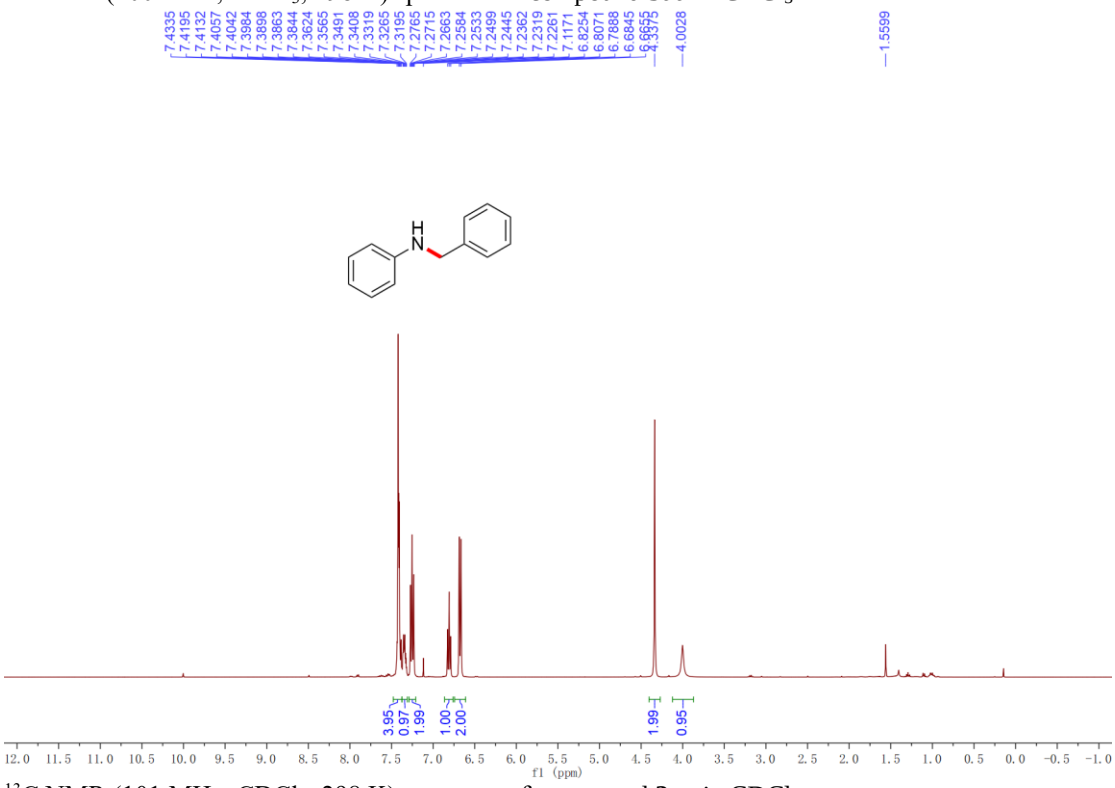
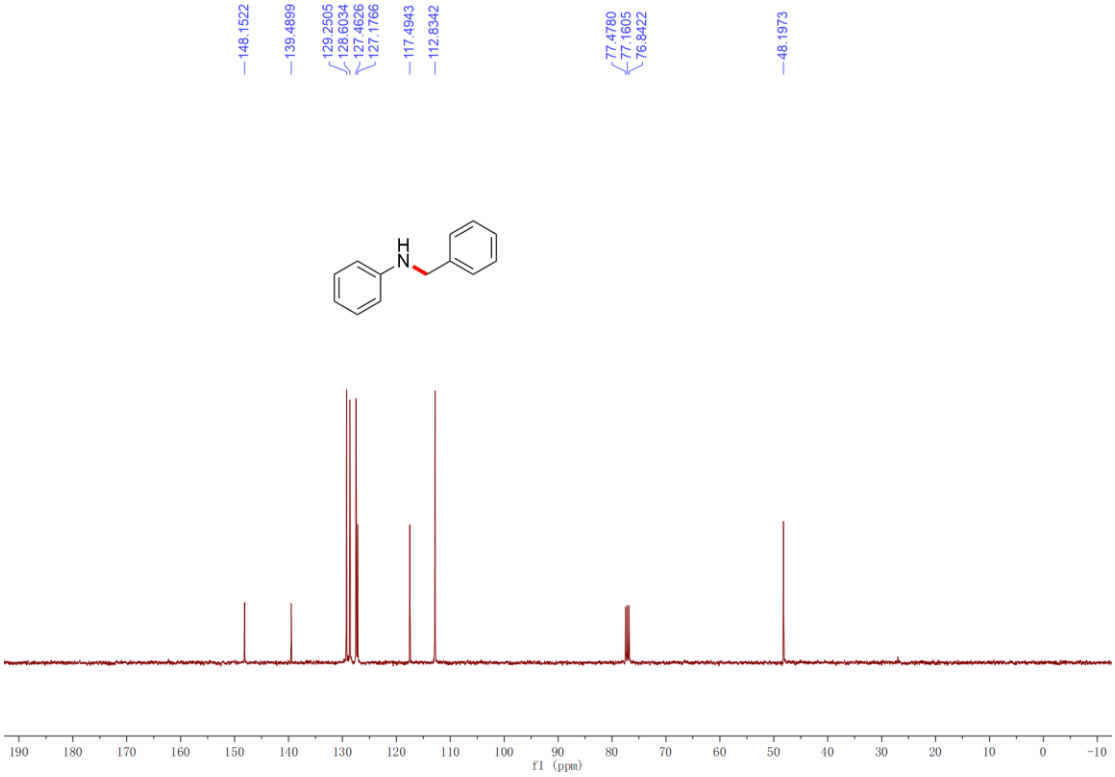
## 8. The spectra of $^{1}H$ and $^{13}C$ NMR and HPLC

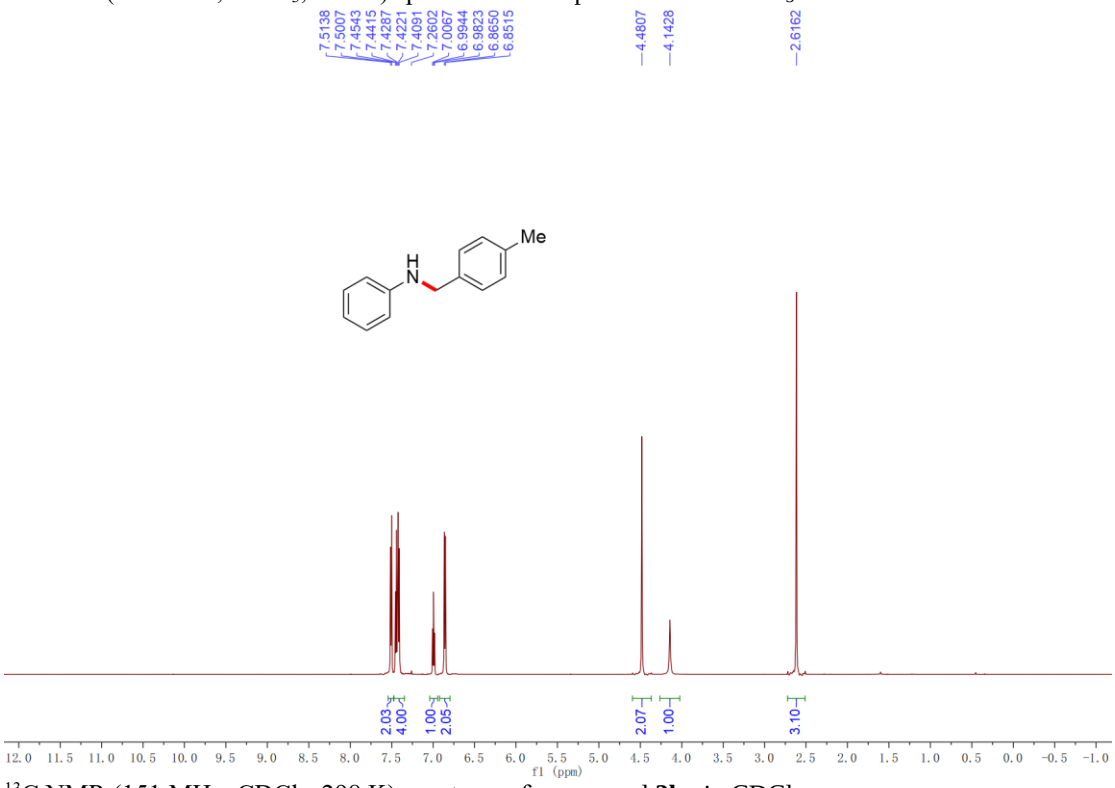
$^{1}H$ NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3aa** in $CDCl_3$.



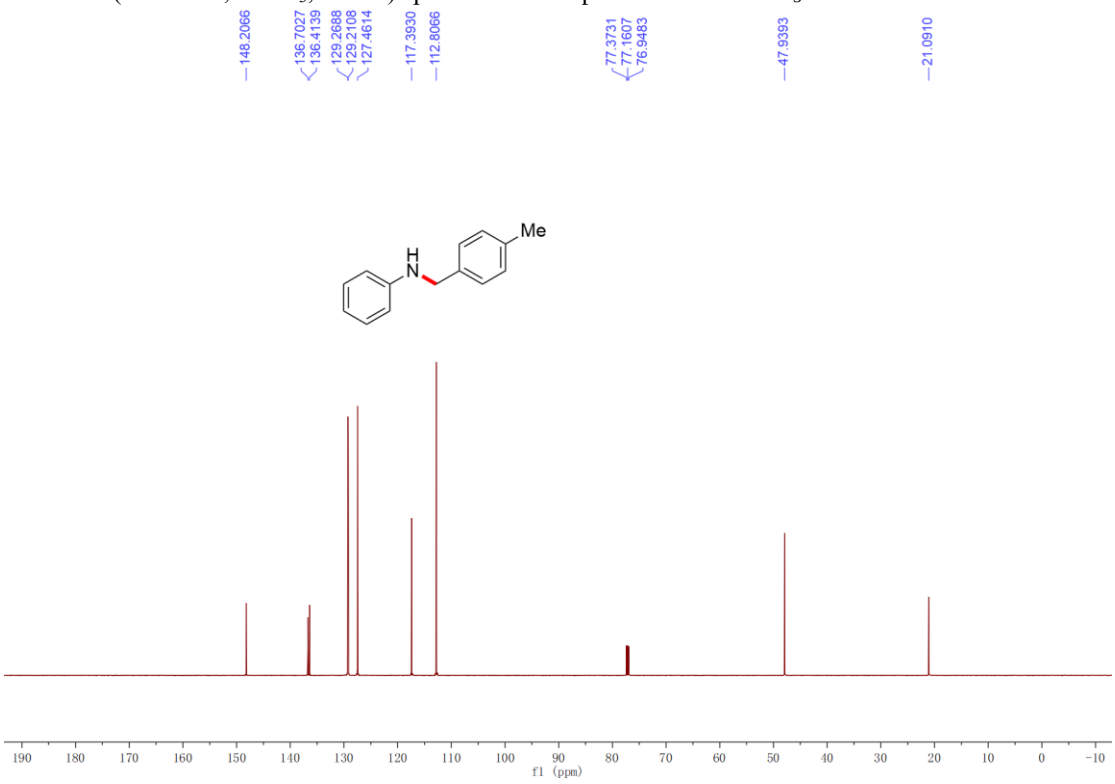

$^{13}C$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3aa** in $CDCl_3$.



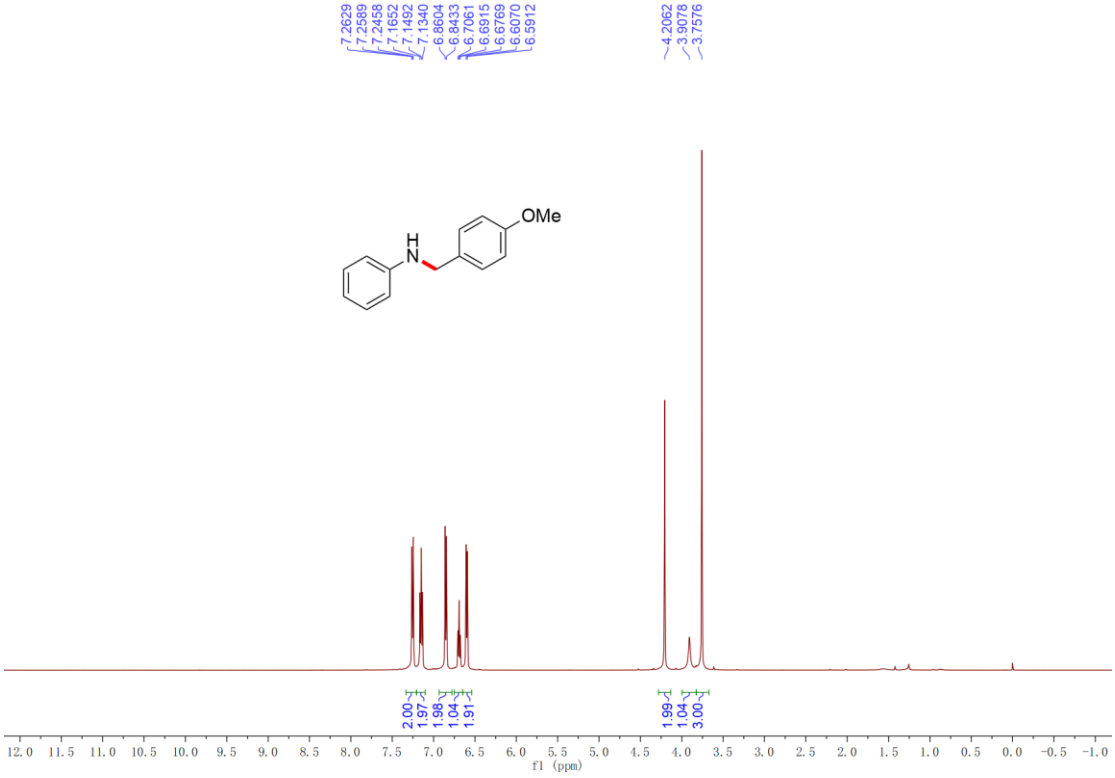
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **3ba** in $CDCl_3$.



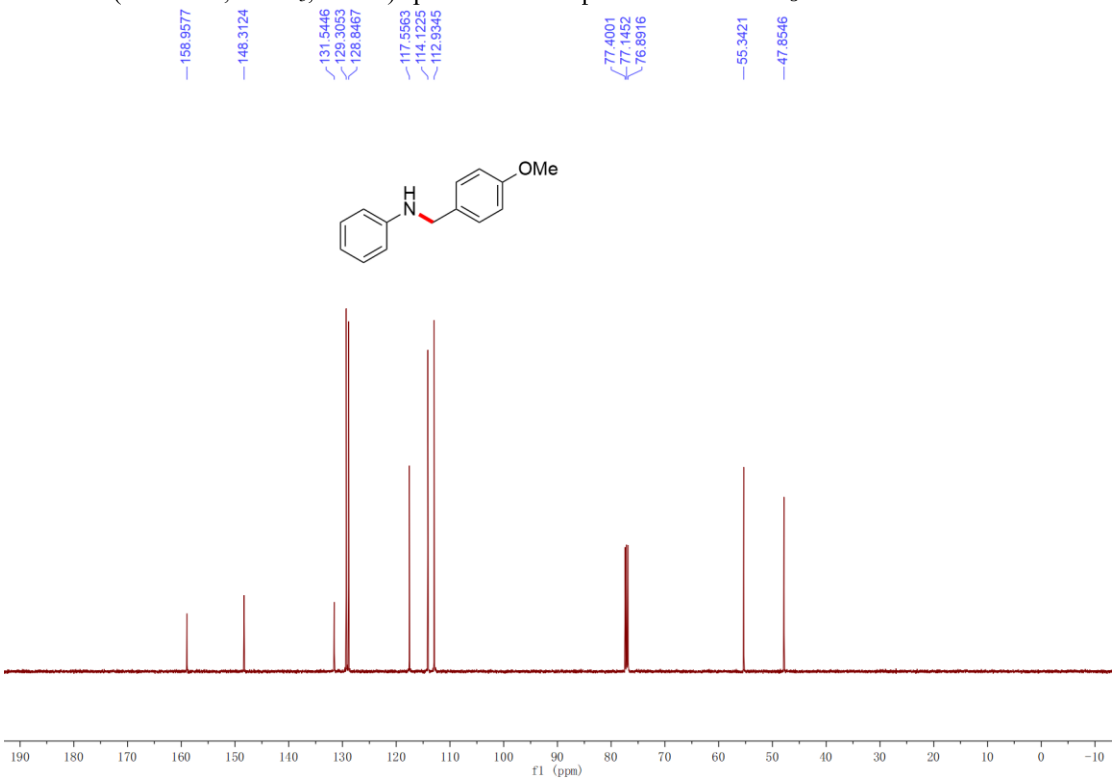

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **3ba** in $CDCl_3$.



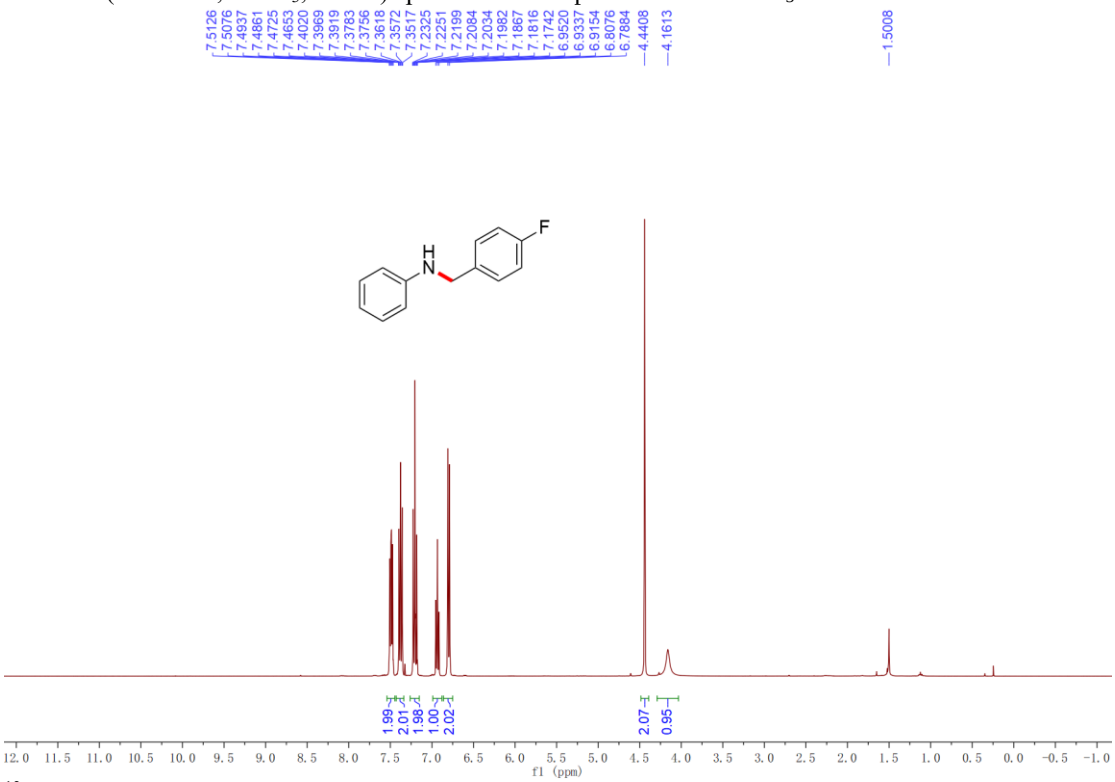
$^{1}$H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of compound **3ca** in $CDCl_3$.



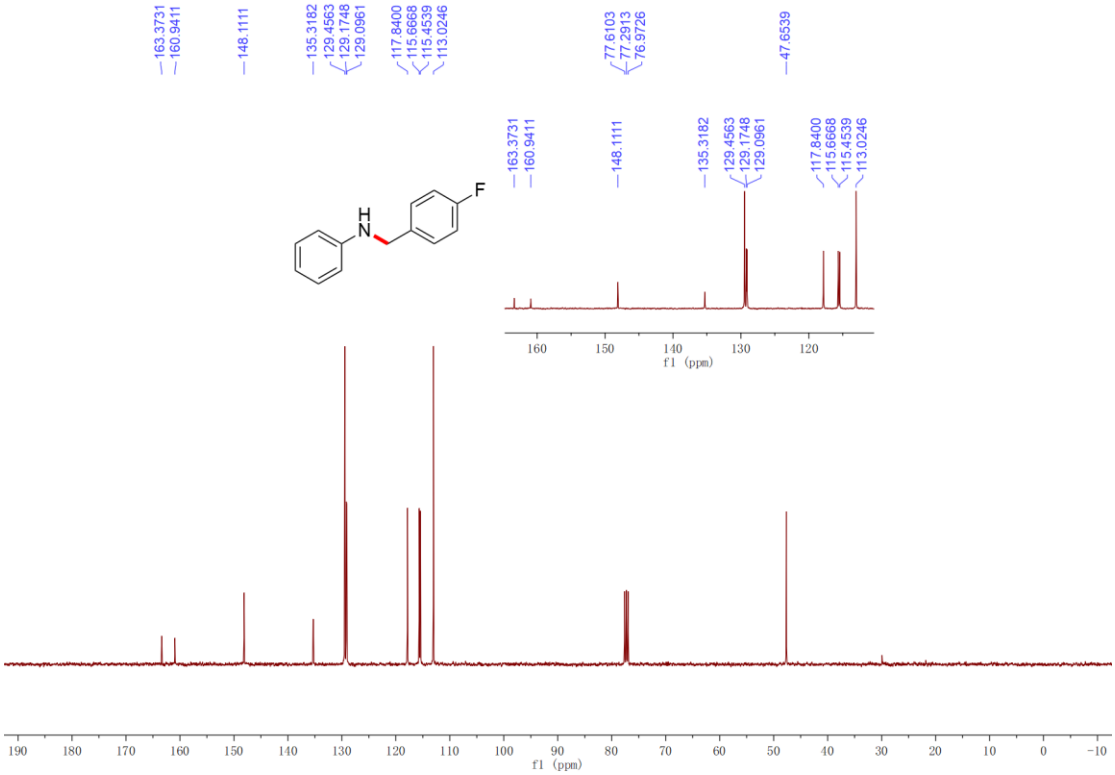

$^{13}$C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of compound **3ca** in $CDCl_3$.



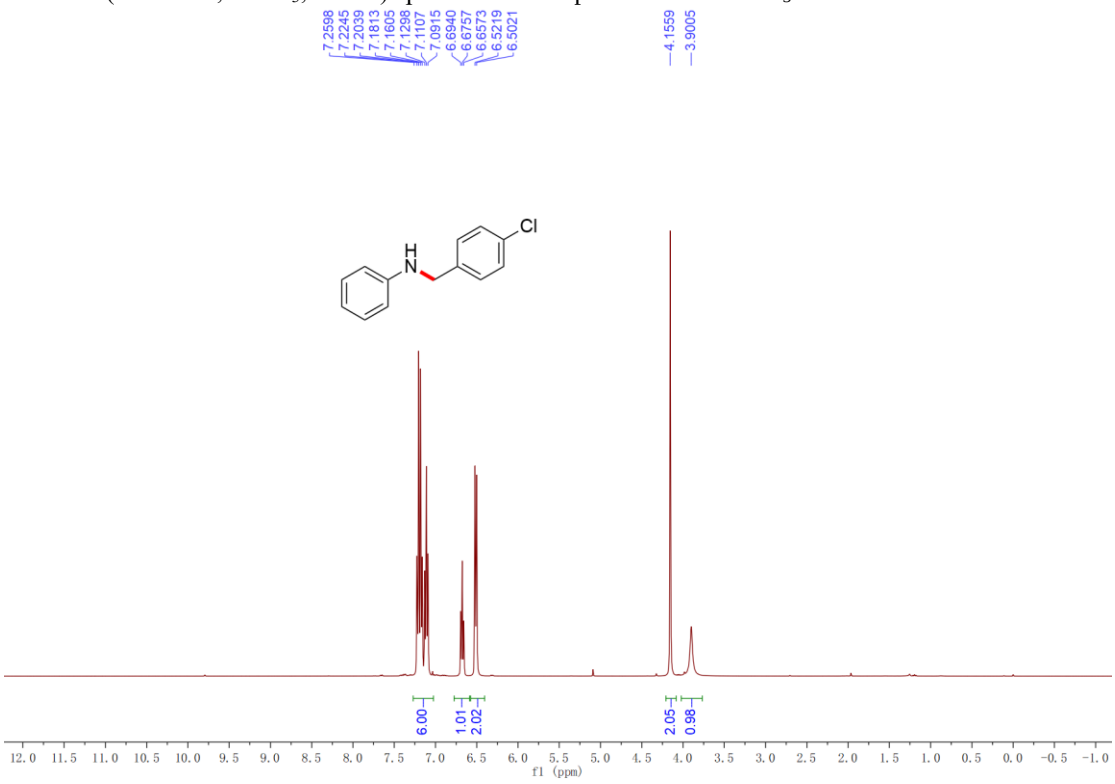
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3da** in $CDCl_3$.



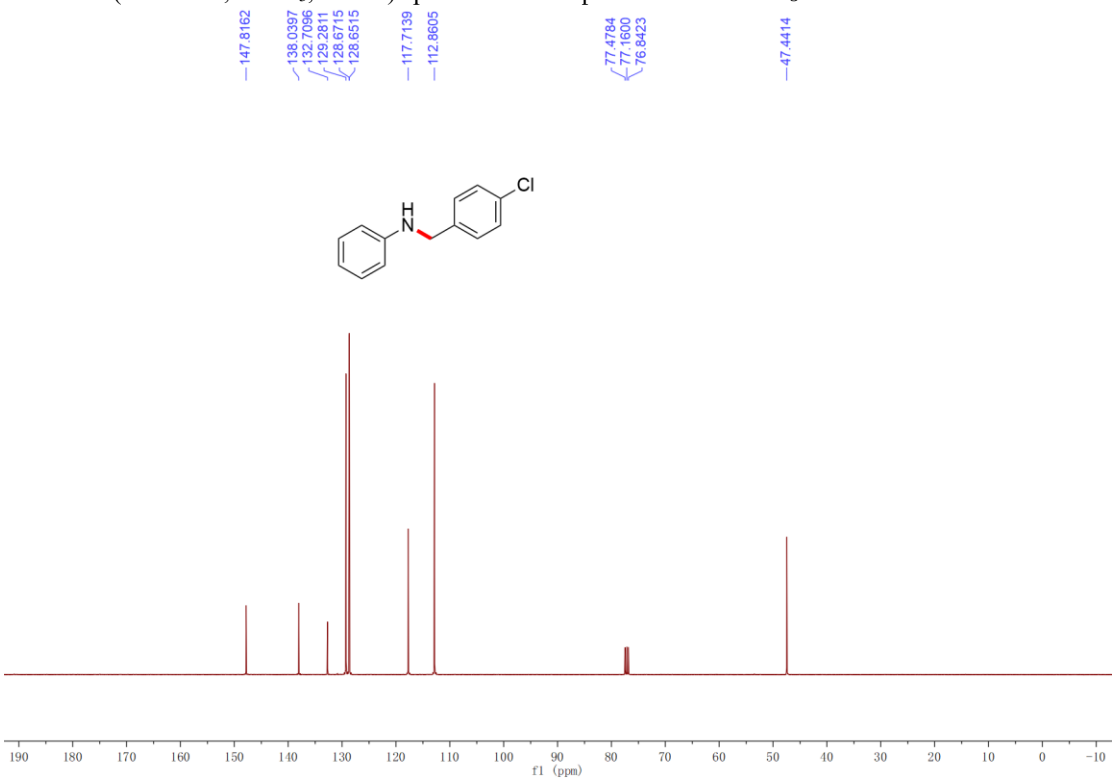

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3da** in $CDCl_3$.



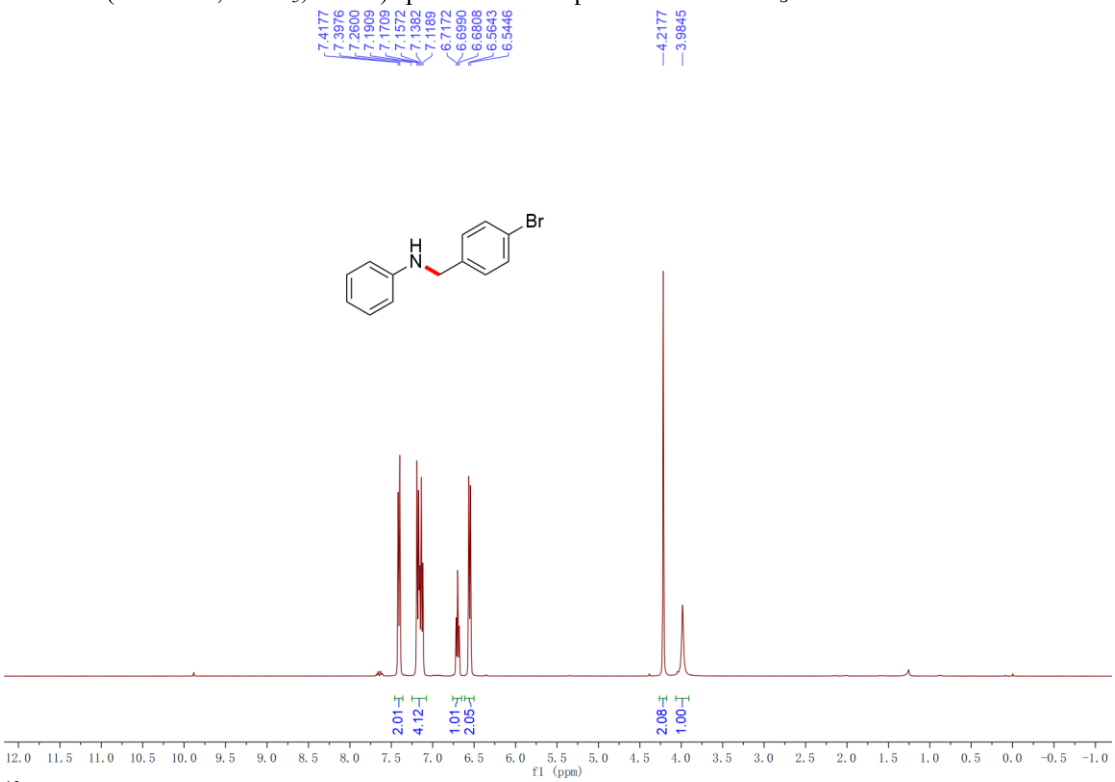
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3ea** in $CDCl_3$.



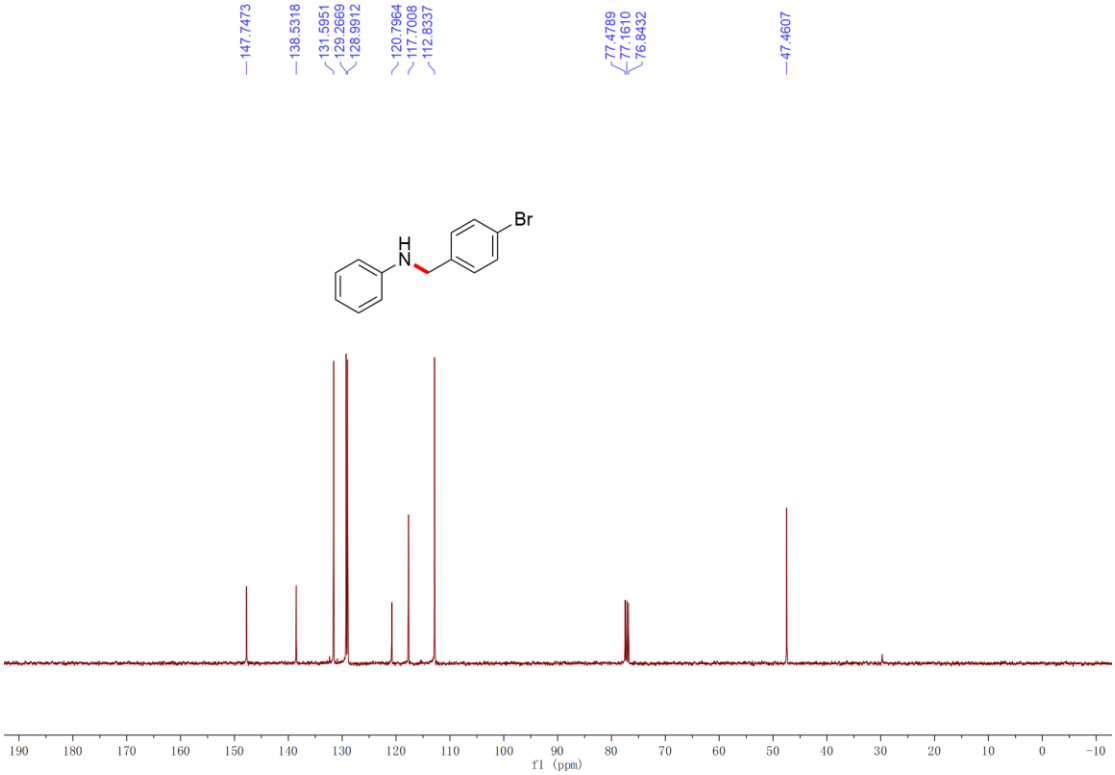

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3ea** in $CDCl_3$.



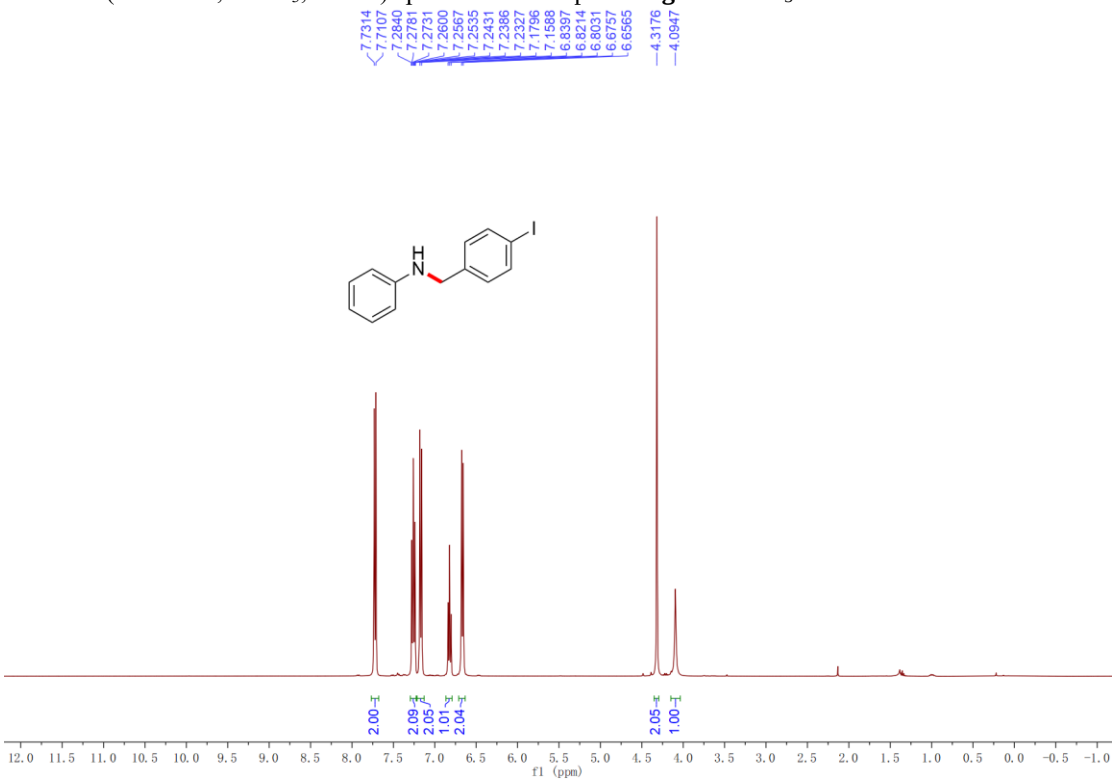
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3fa** in $CDCl_3$.



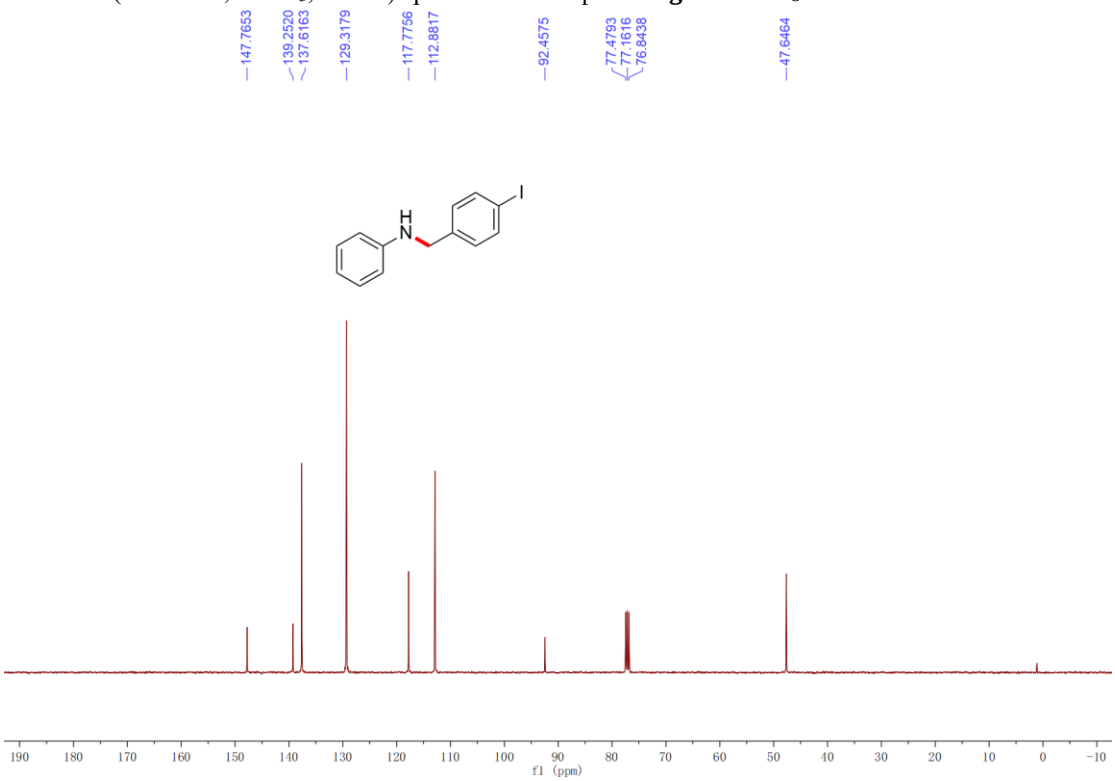

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3fa** in $CDCl_3$.



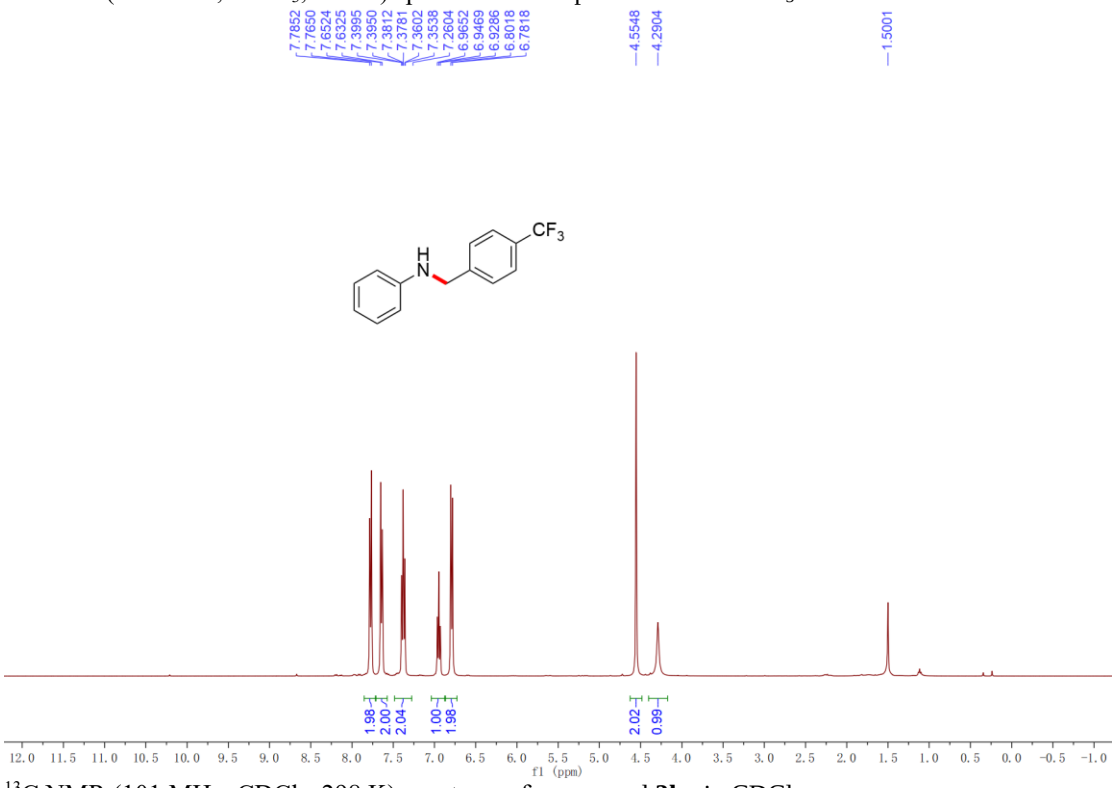
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3ga** in $CDCl_3$.



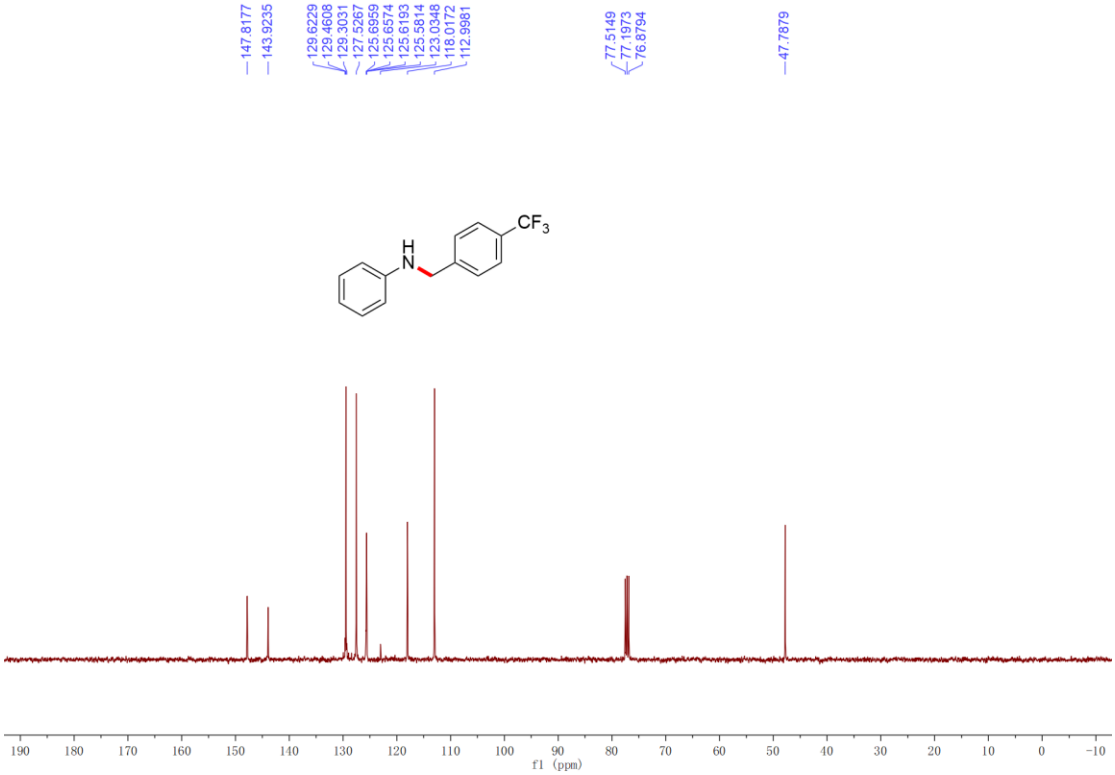

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3ga** in $CDCl_3$.



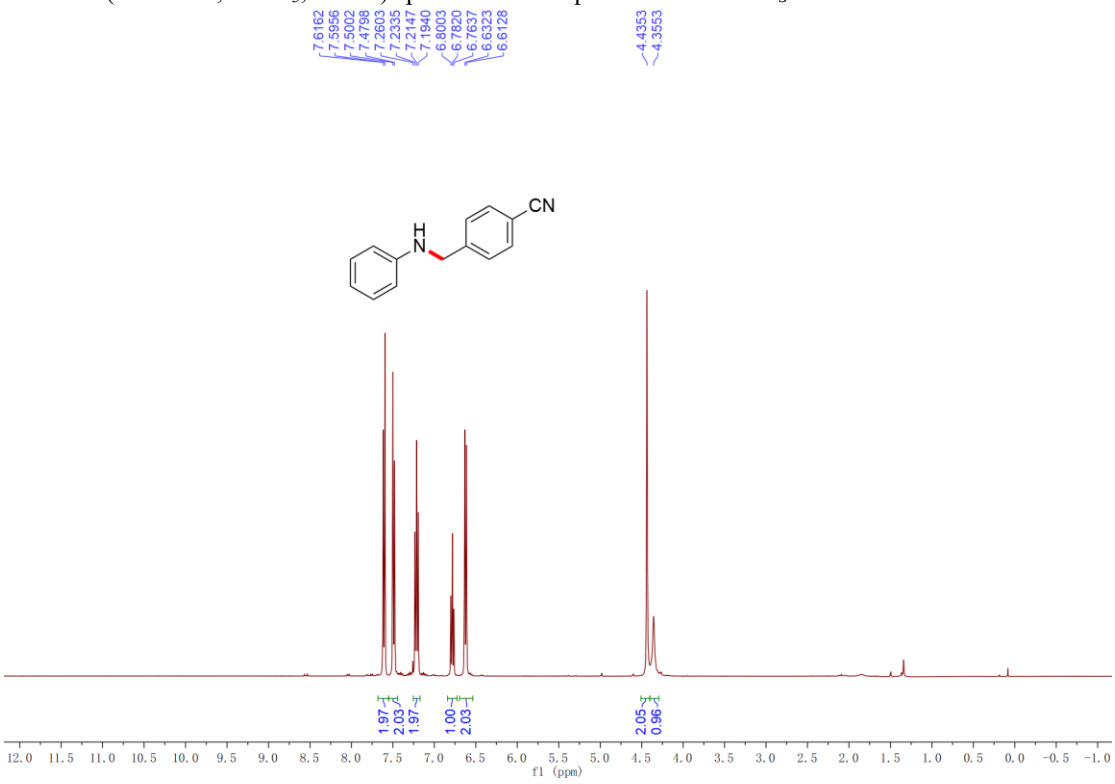
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3ha** in $CDCl_3$.



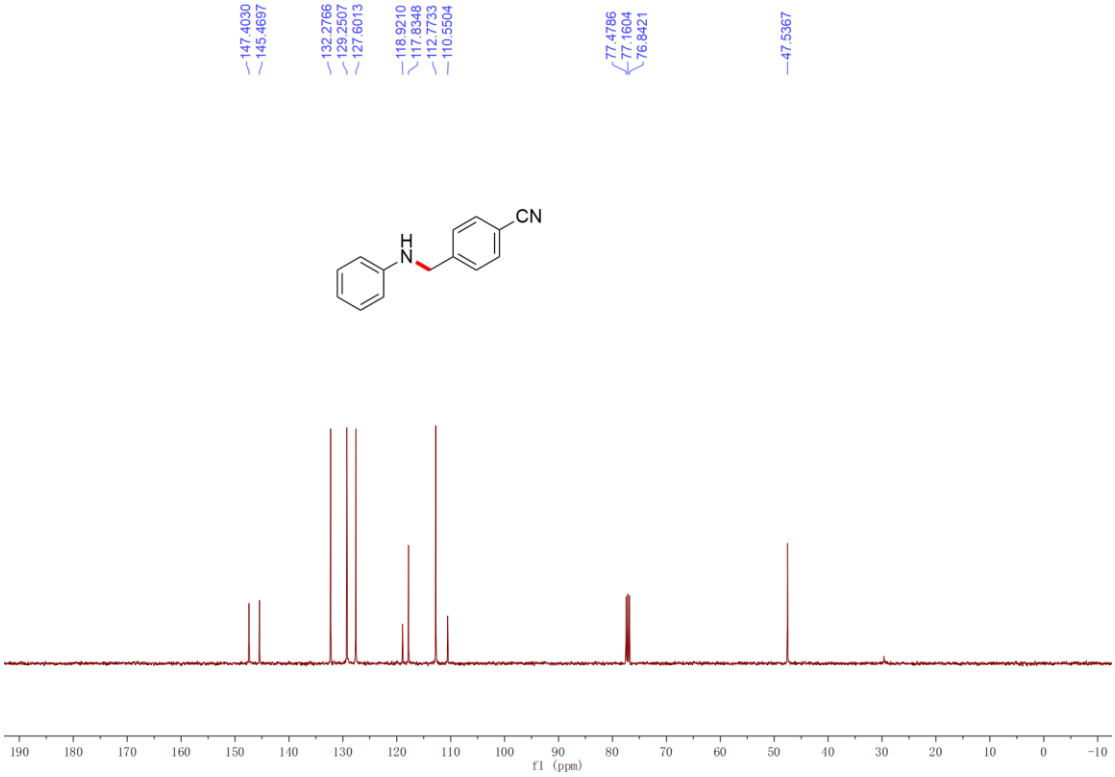

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3ha** in $CDCl_3$.



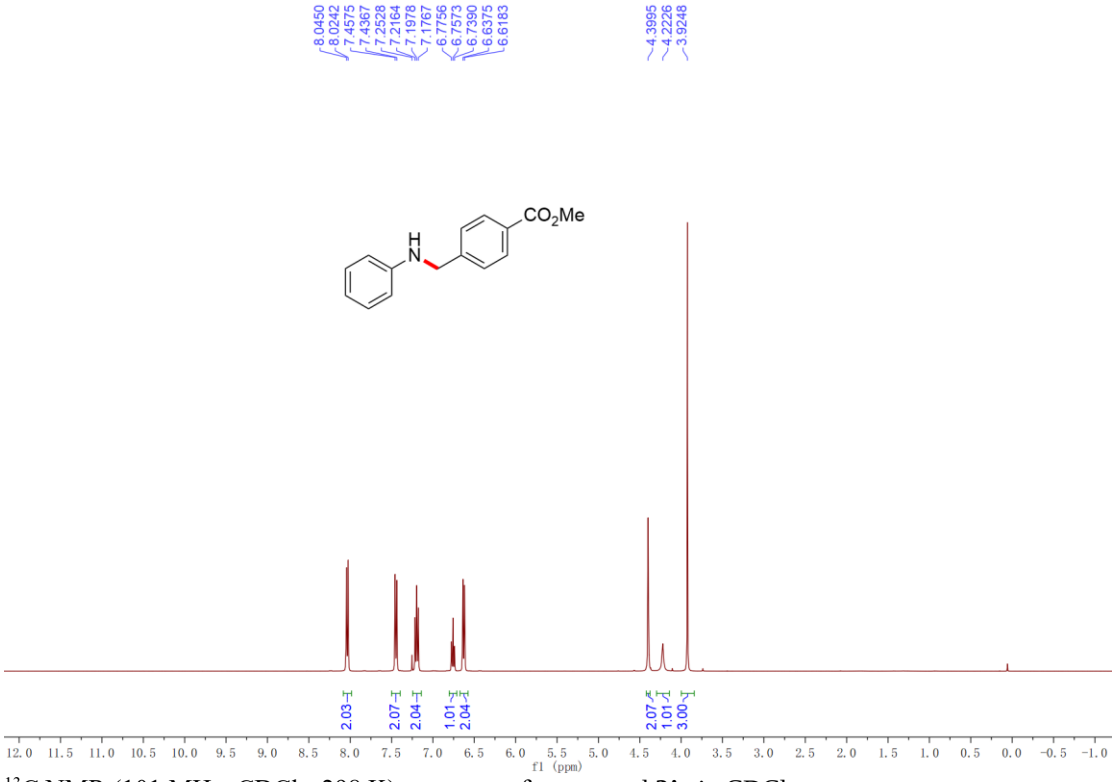
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3ia** in $CDCl_3$.



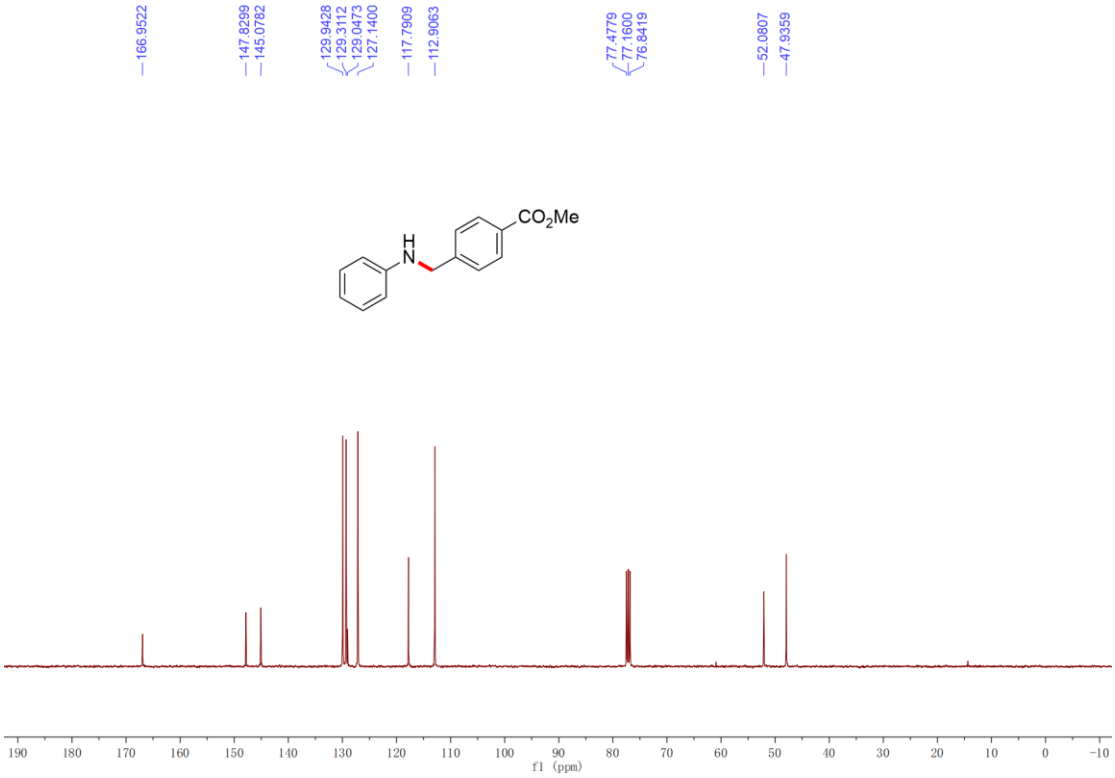

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3ia** in $CDCl_3$.



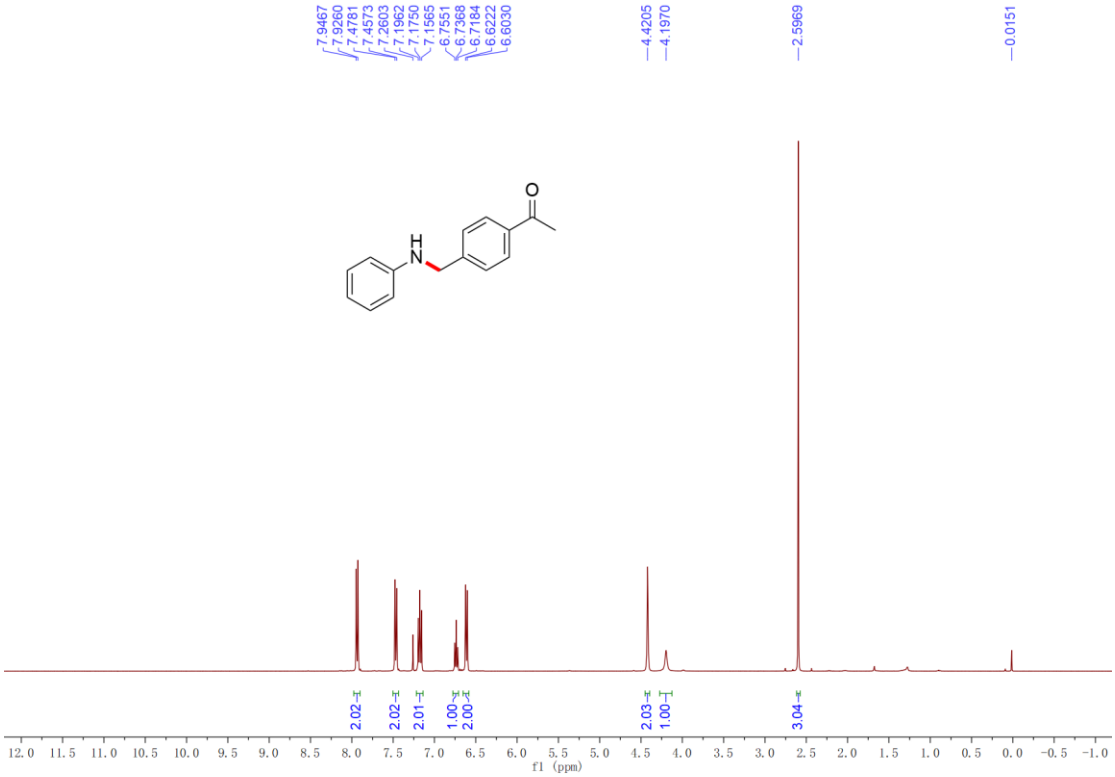
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3ja** in $CDCl_3$.



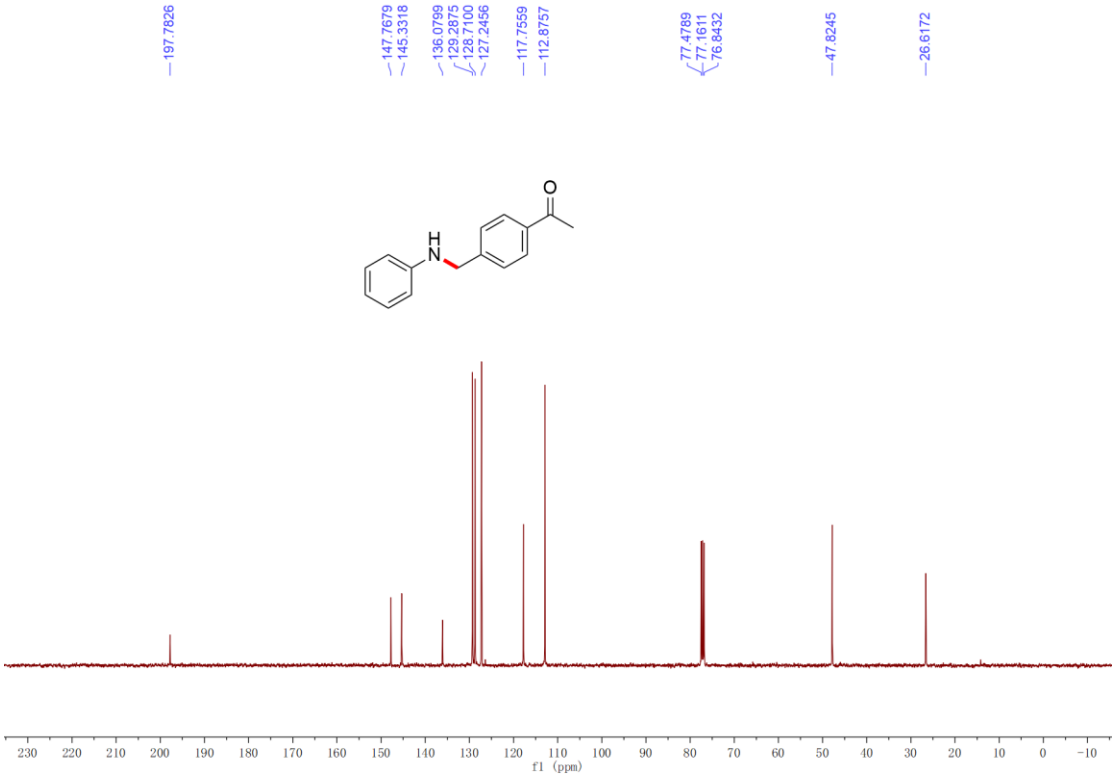

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3ja** in $CDCl_3$.



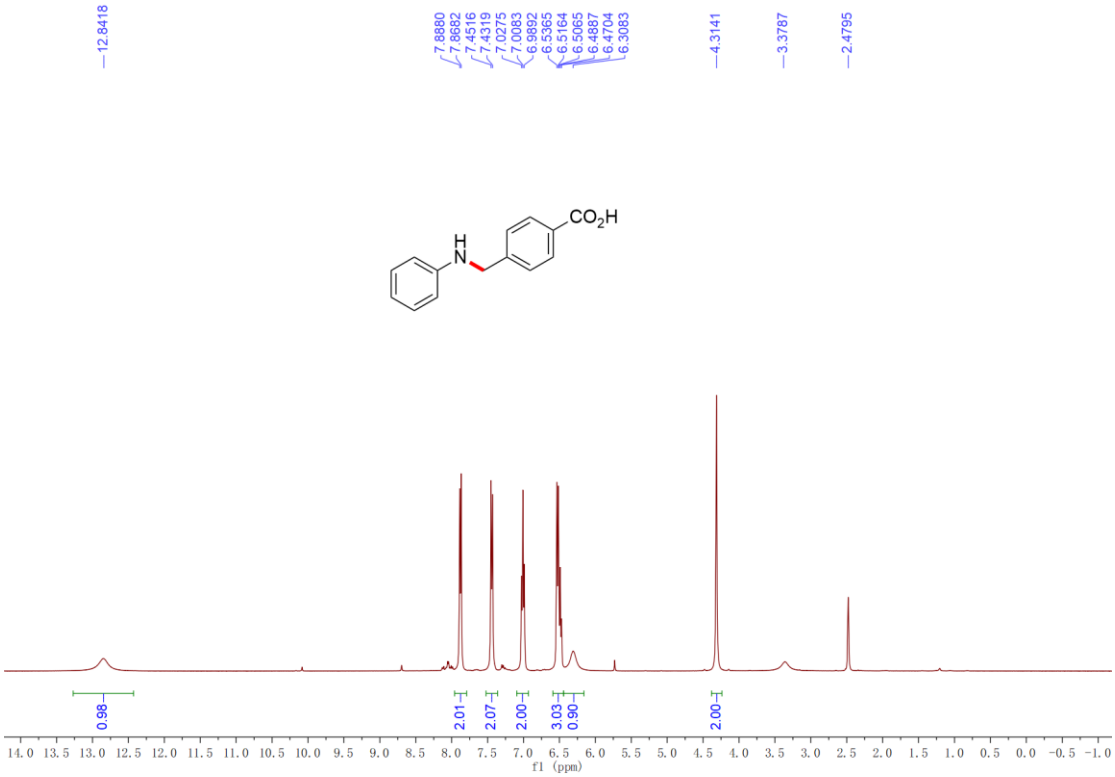
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3ka** in $CDCl_3$.



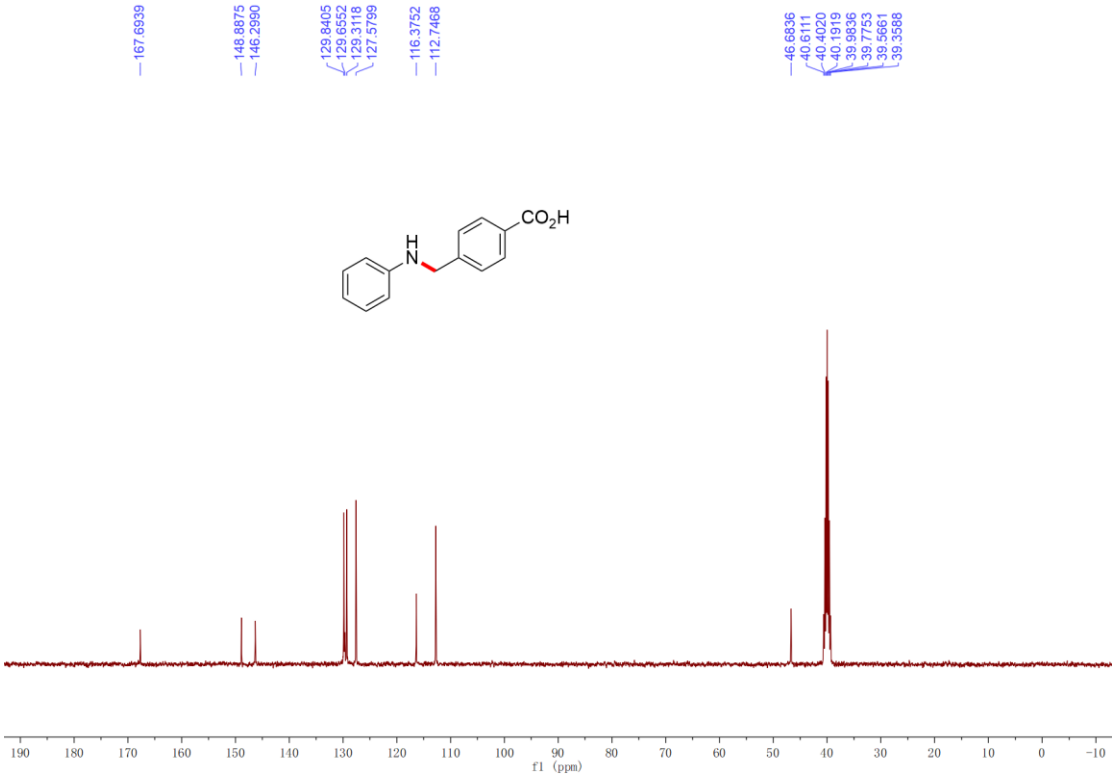

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3ka** in $CDCl_3$.



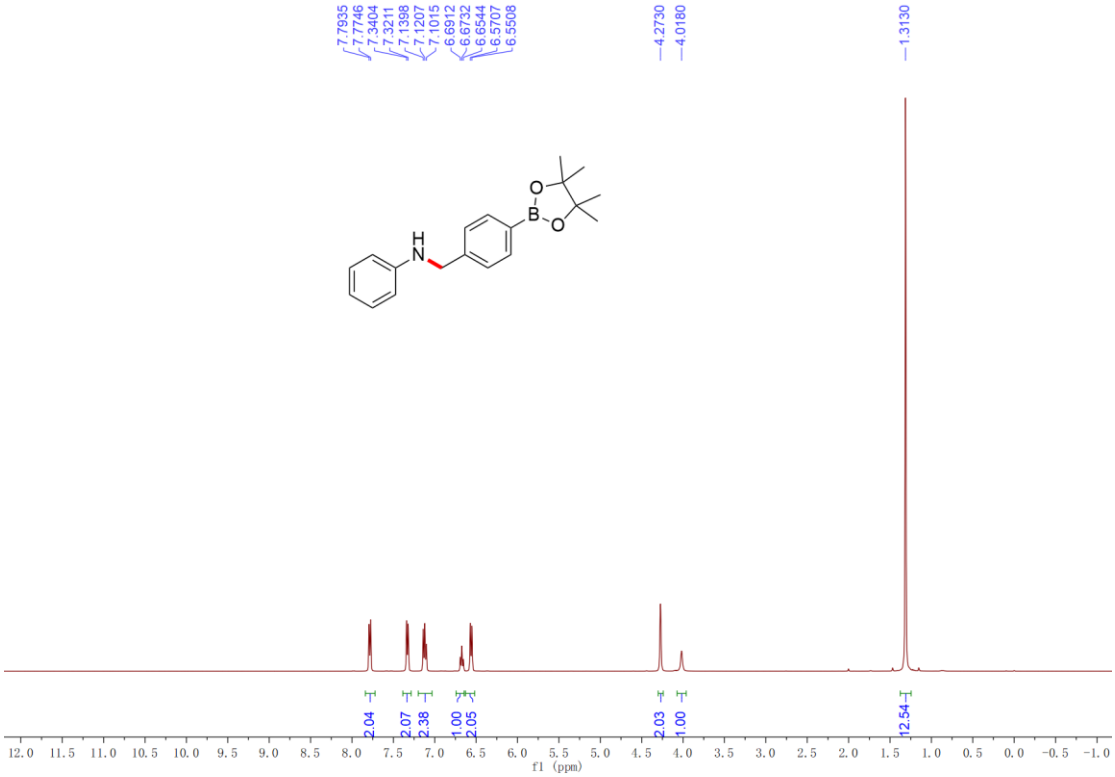
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3la** in DMSO-$d_6$.



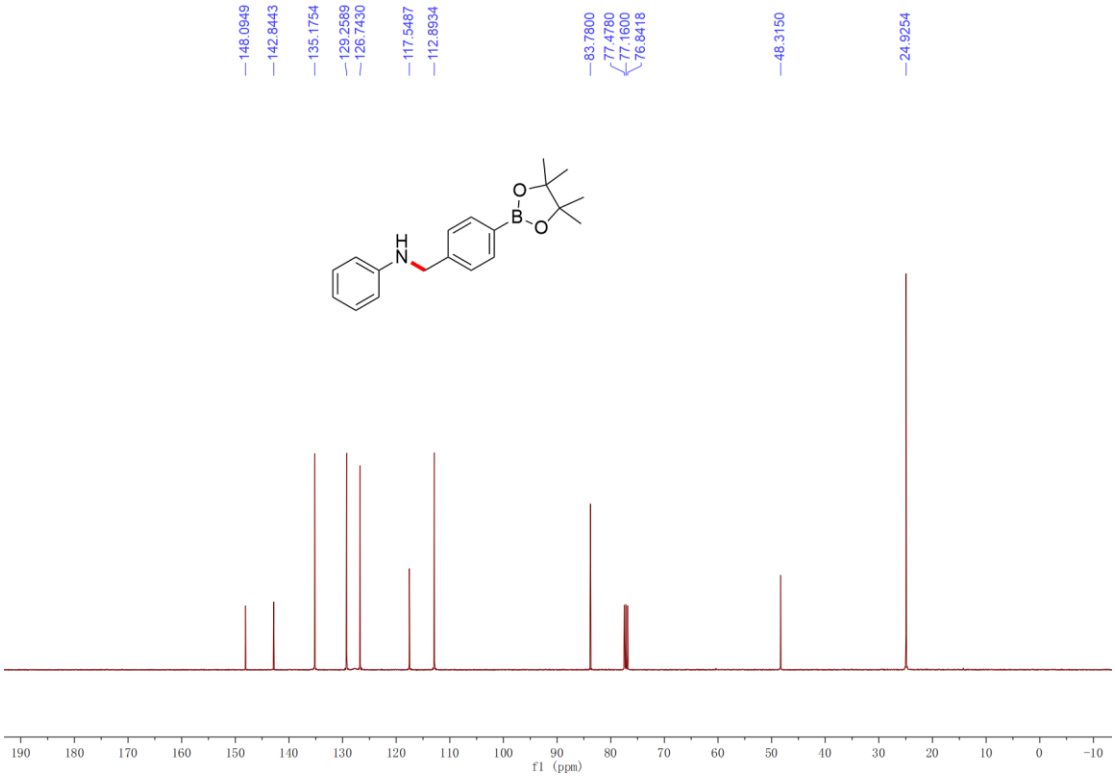

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3la** in DMSO-$d_6$.



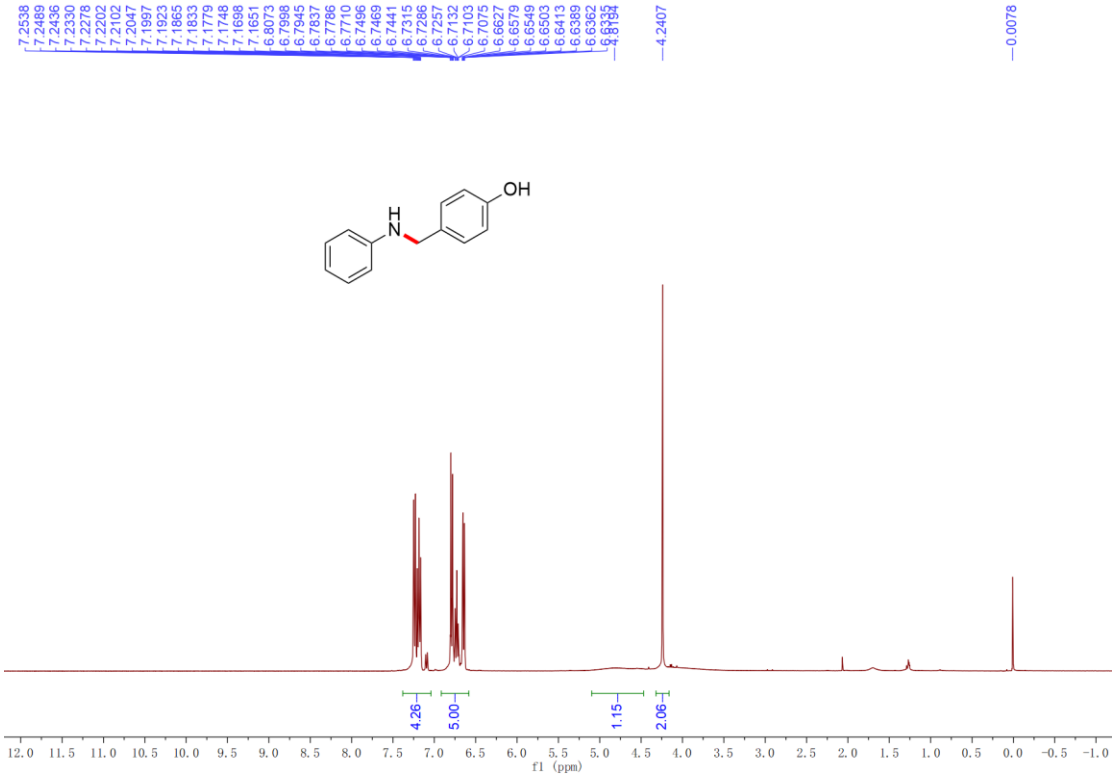
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3ma** in $CDCl_3$.



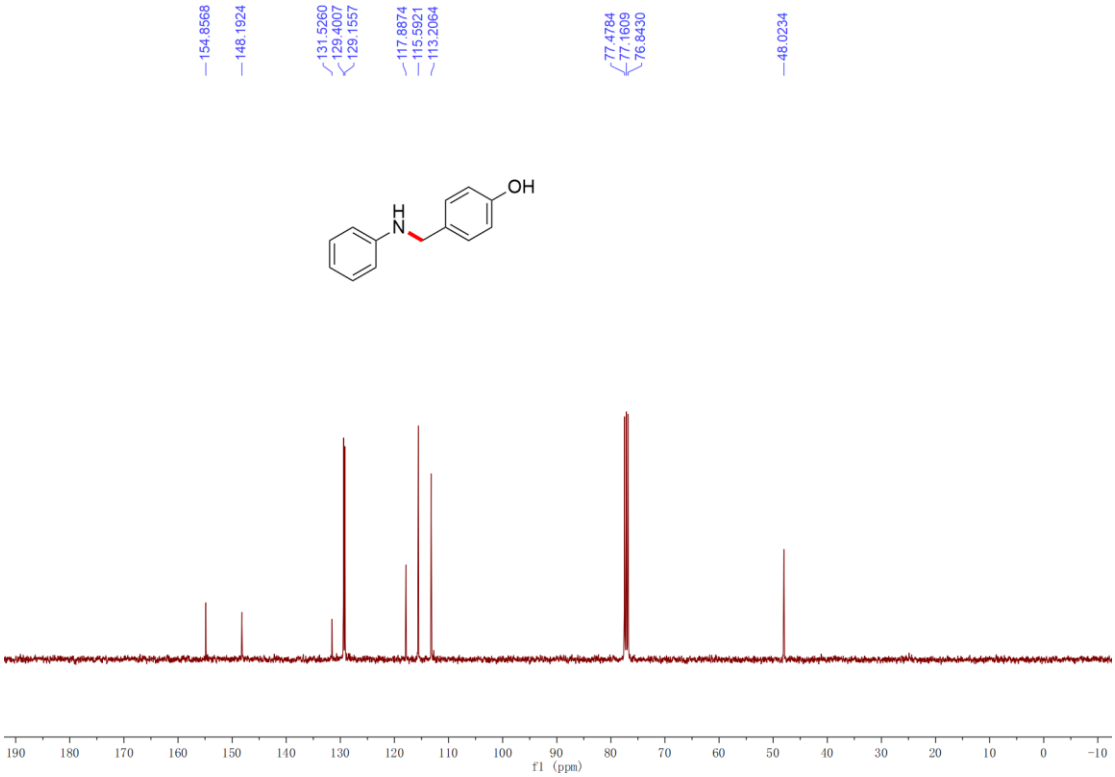

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3ma** in $CDCl_3$.



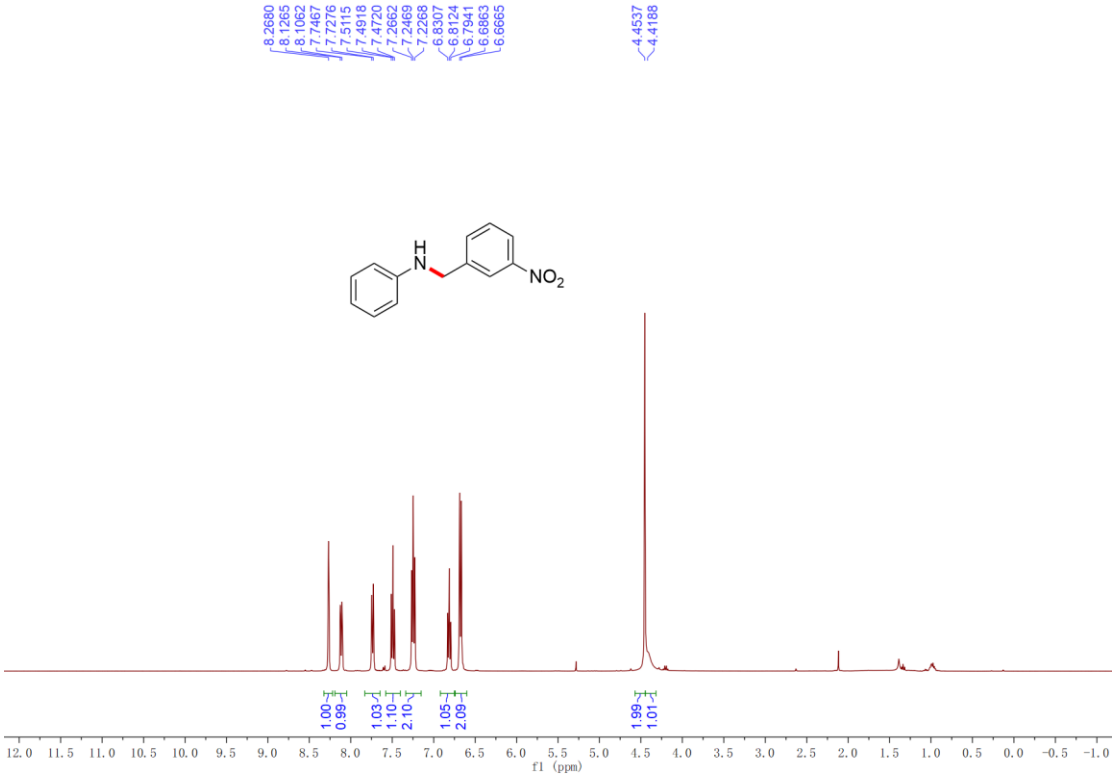
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3na** in $CDCl_3$.



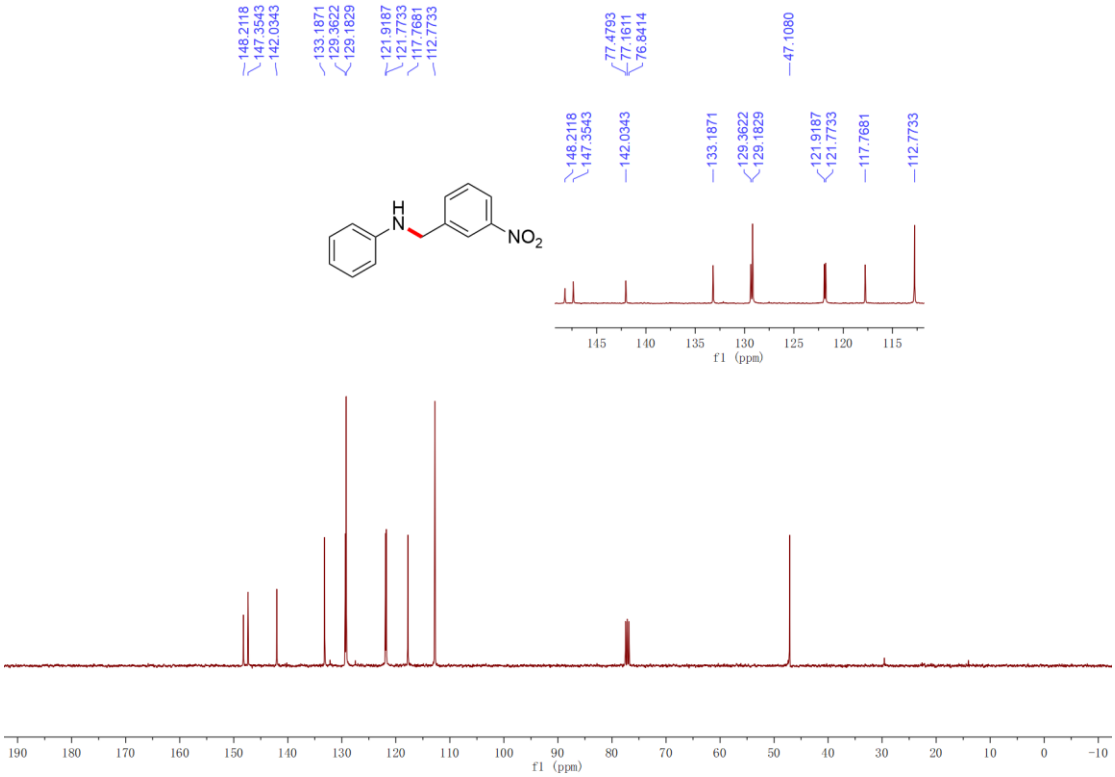

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3na** in $CDCl_3$.



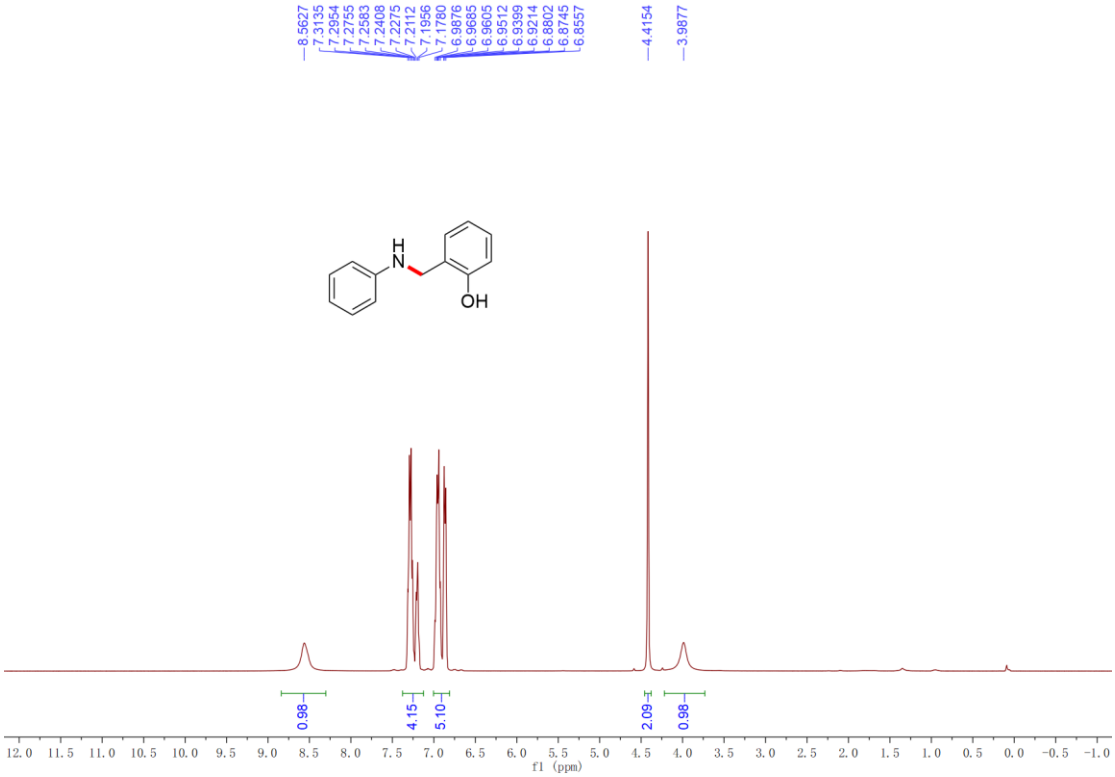
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3oa** in $CDCl_3$.



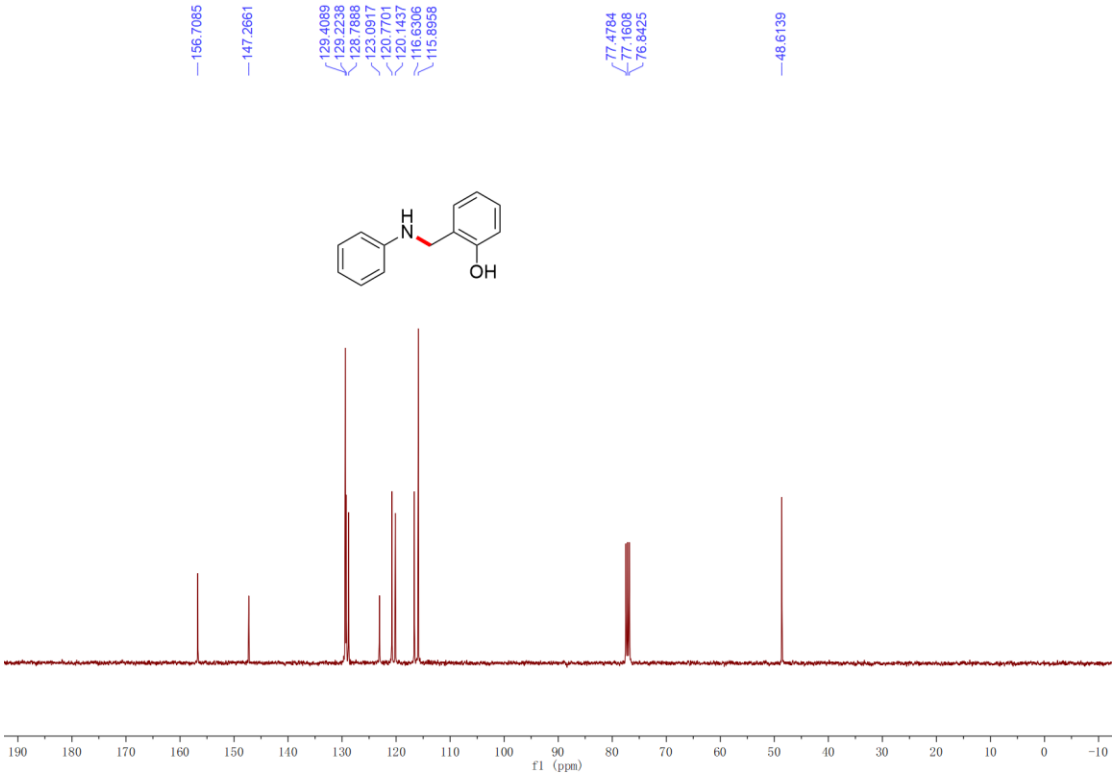

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3oa** in $CDCl_3$.



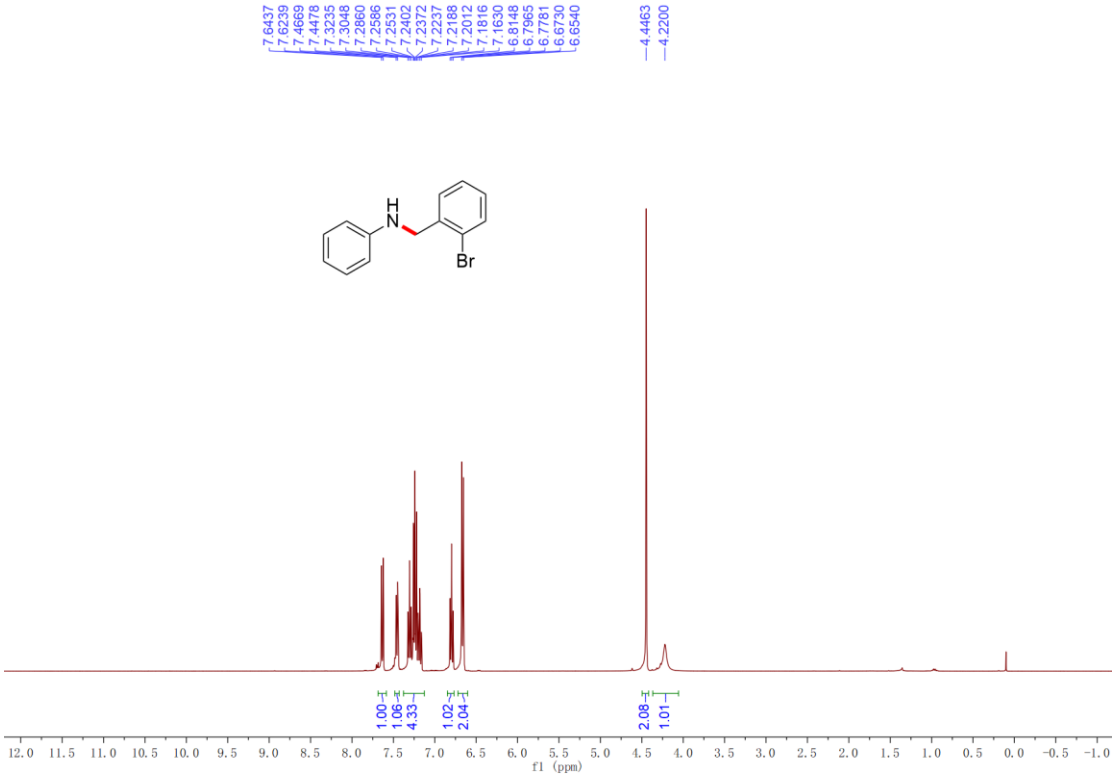
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3pa** in $CDCl_3$.



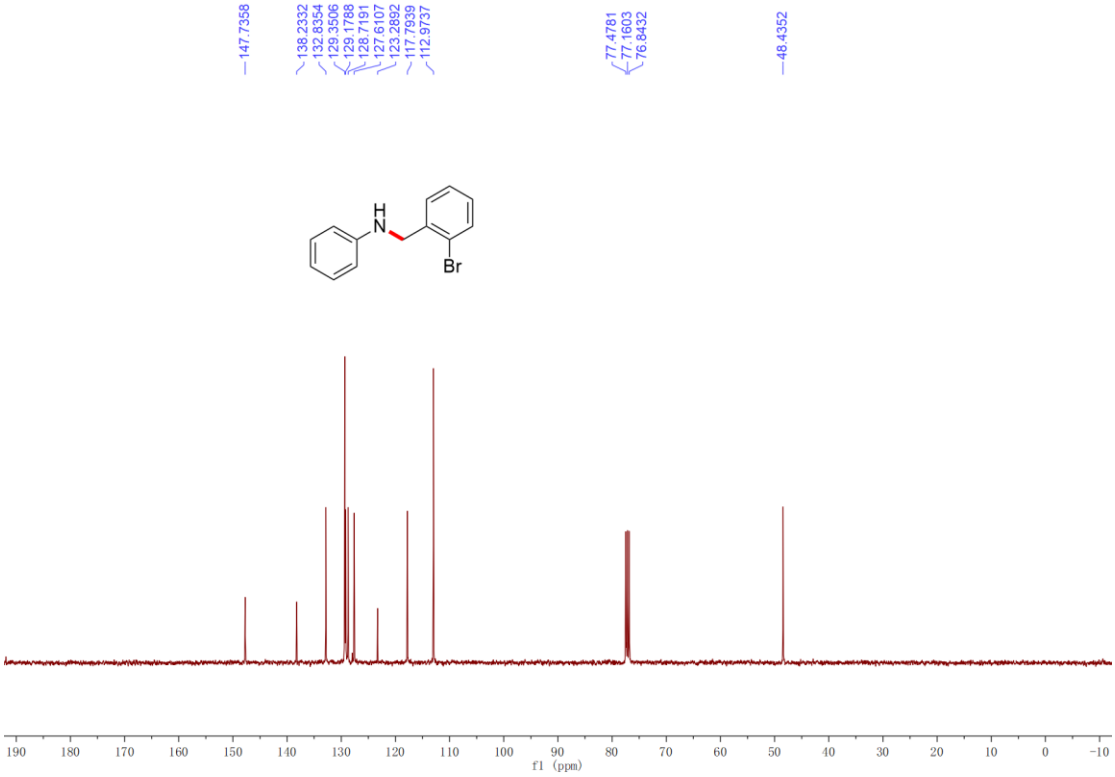

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3pa** in $CDCl_3$.



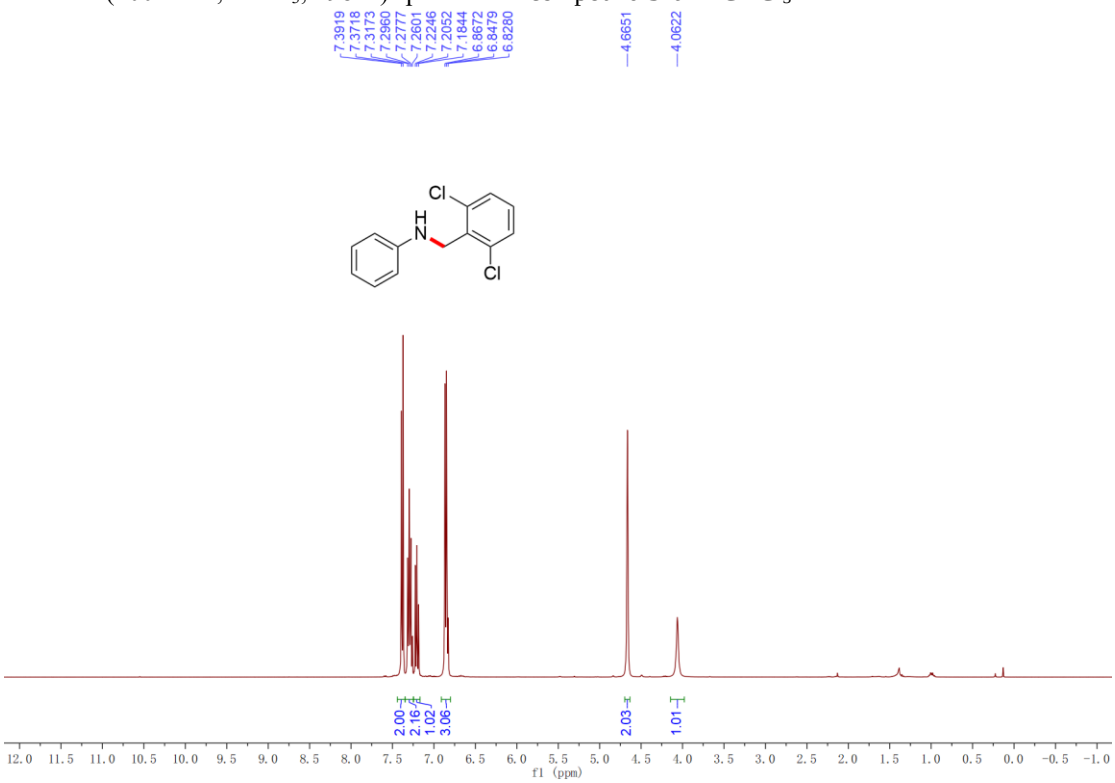
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3qa** in $CDCl_3$.



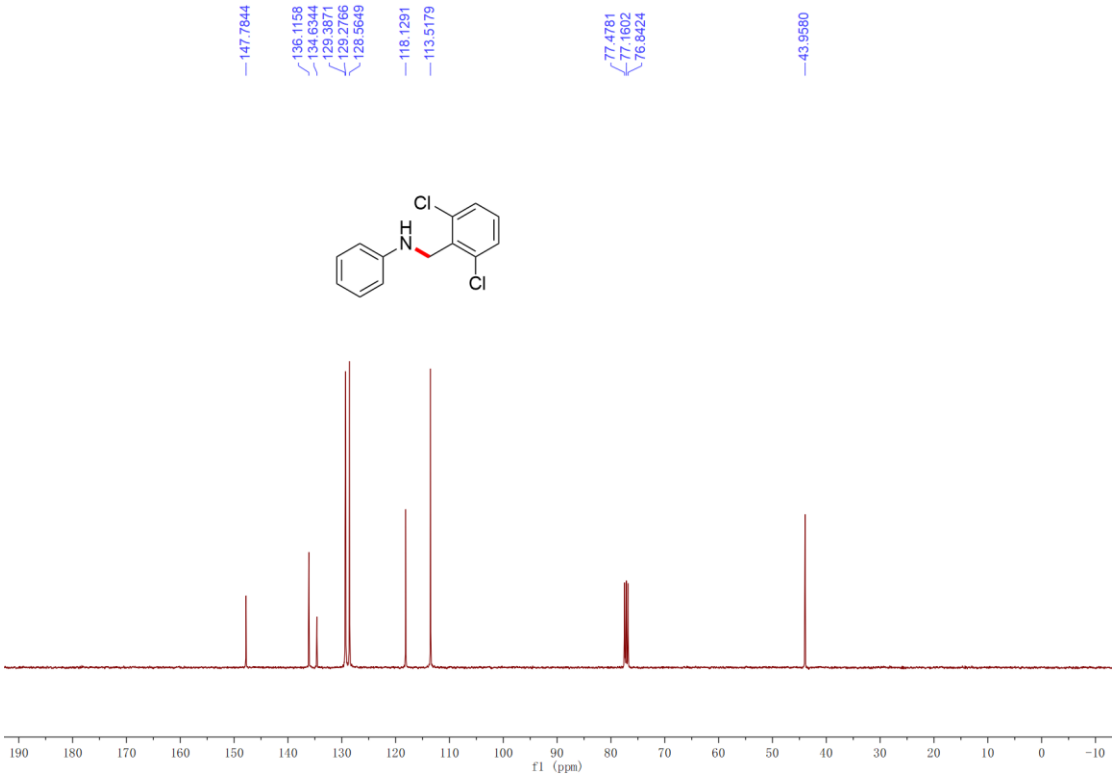

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3qa** in $CDCl_3$.



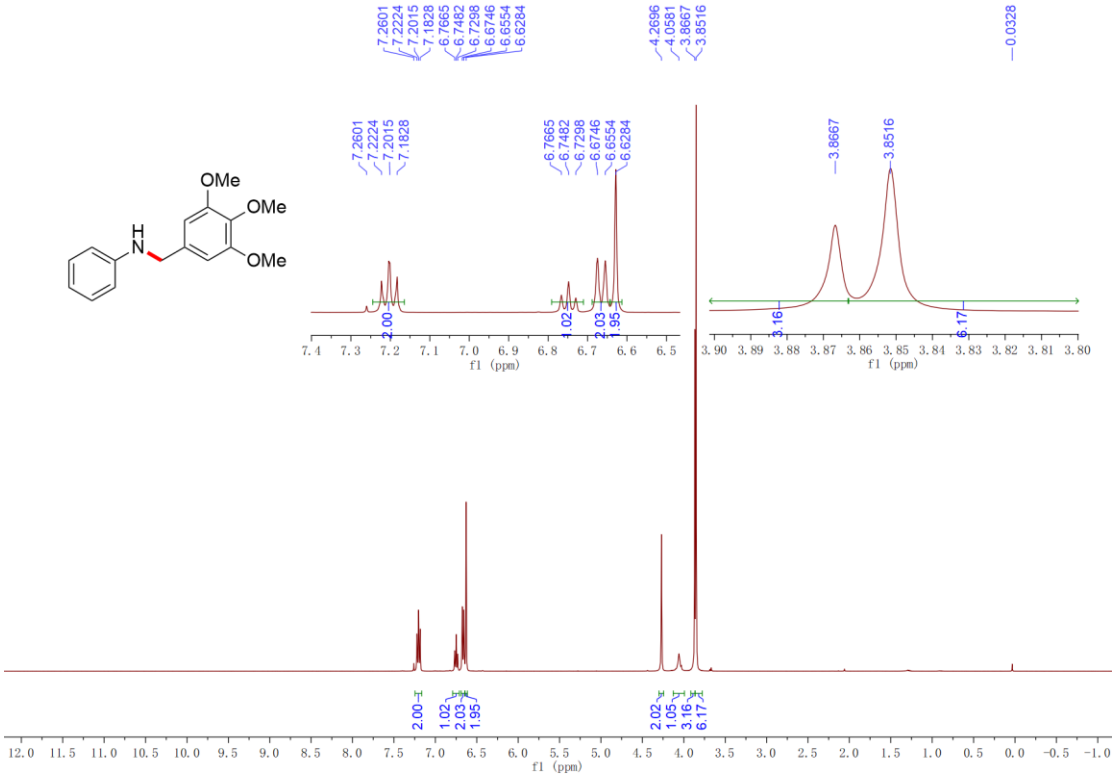
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3ra** in $CDCl_3$.



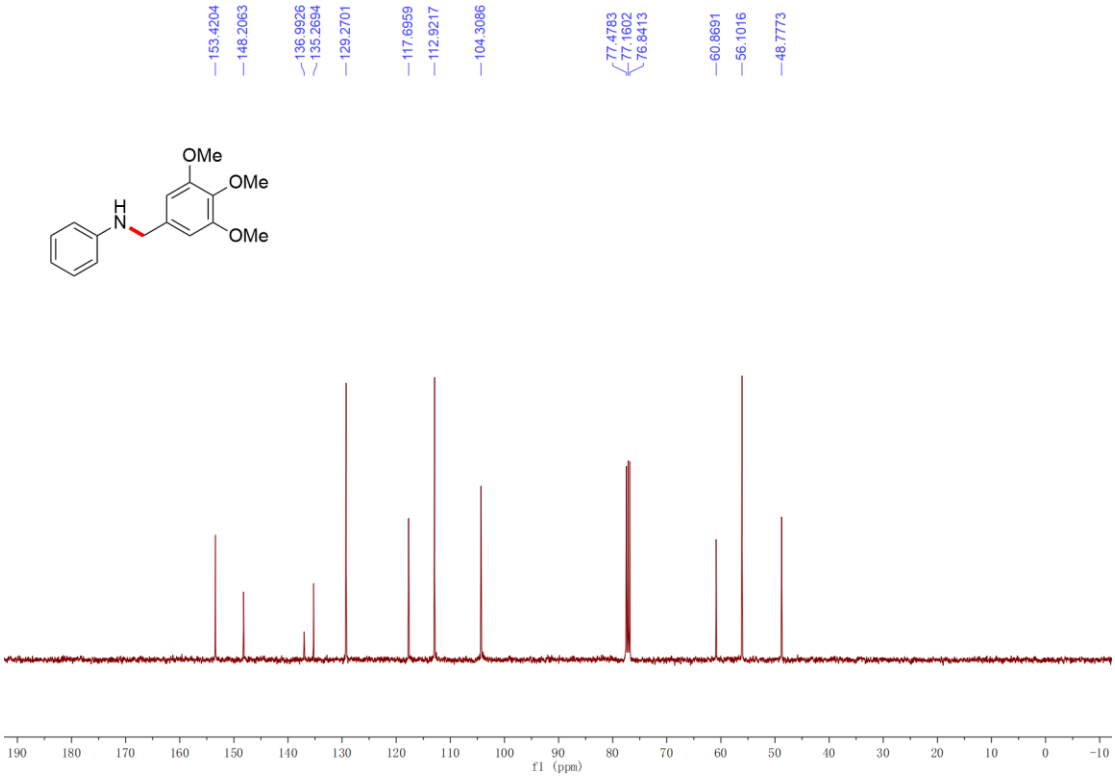

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3ra** in $CDCl_3$.



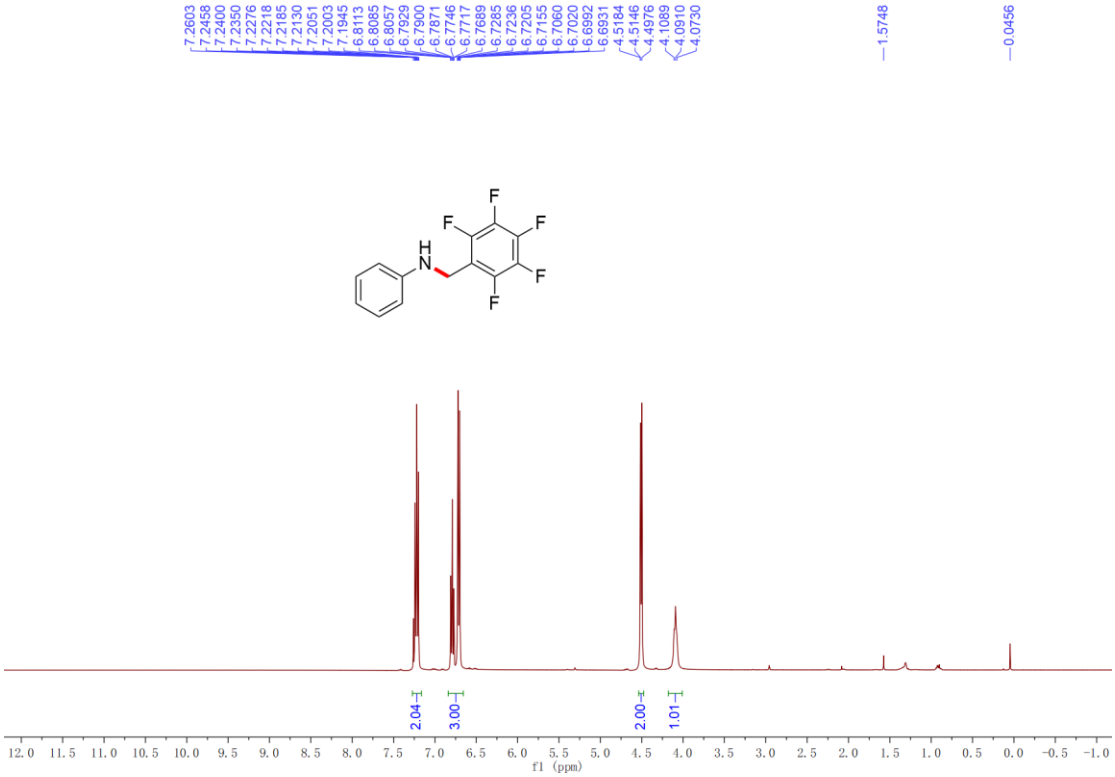
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3sa** in $CDCl_3$.



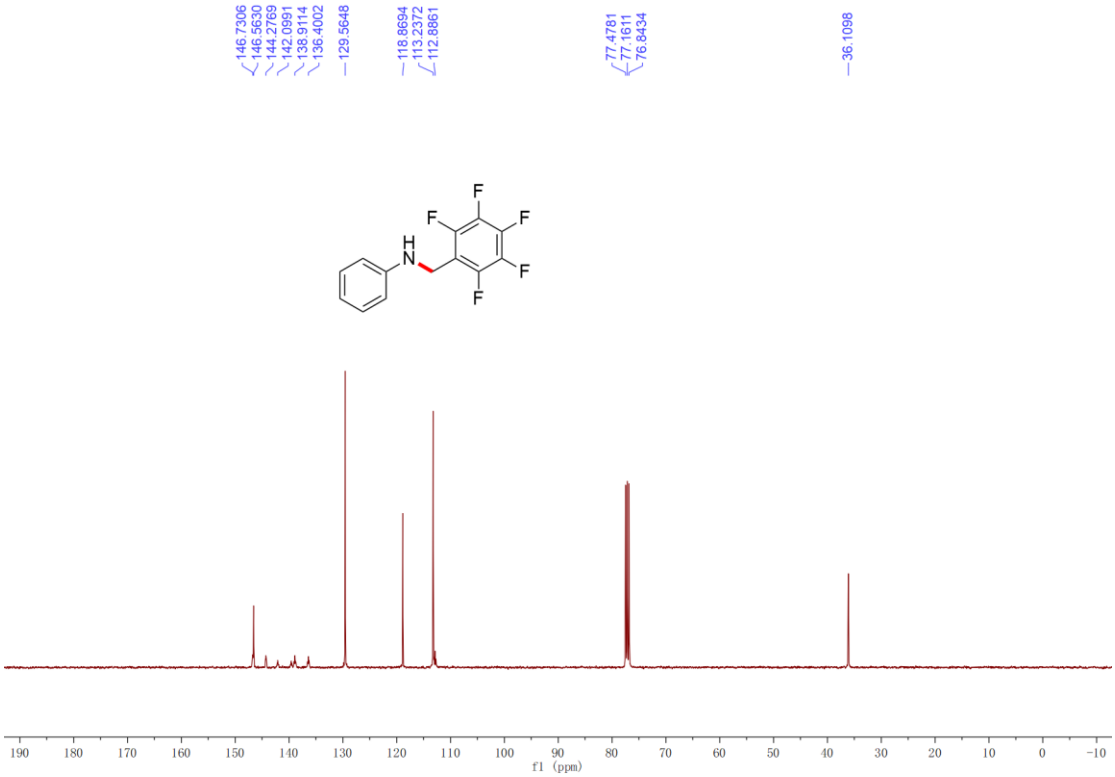

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3sa** in $CDCl_3$.



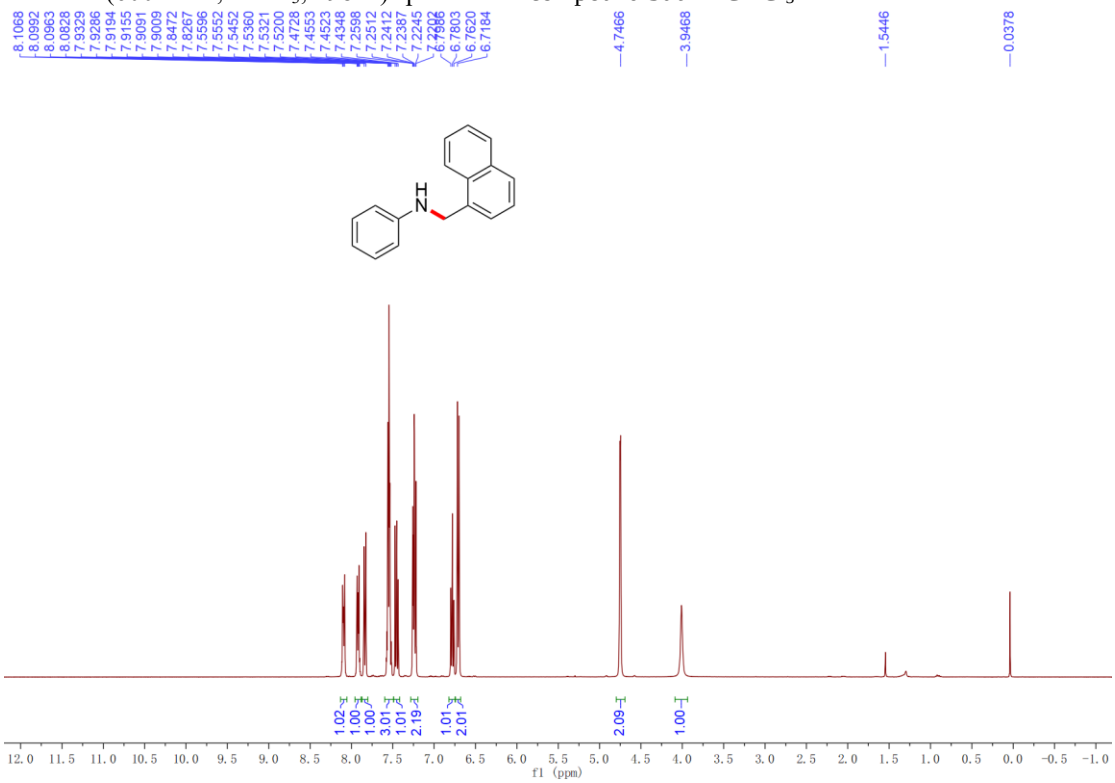
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3ta** in $CDCl_3$.



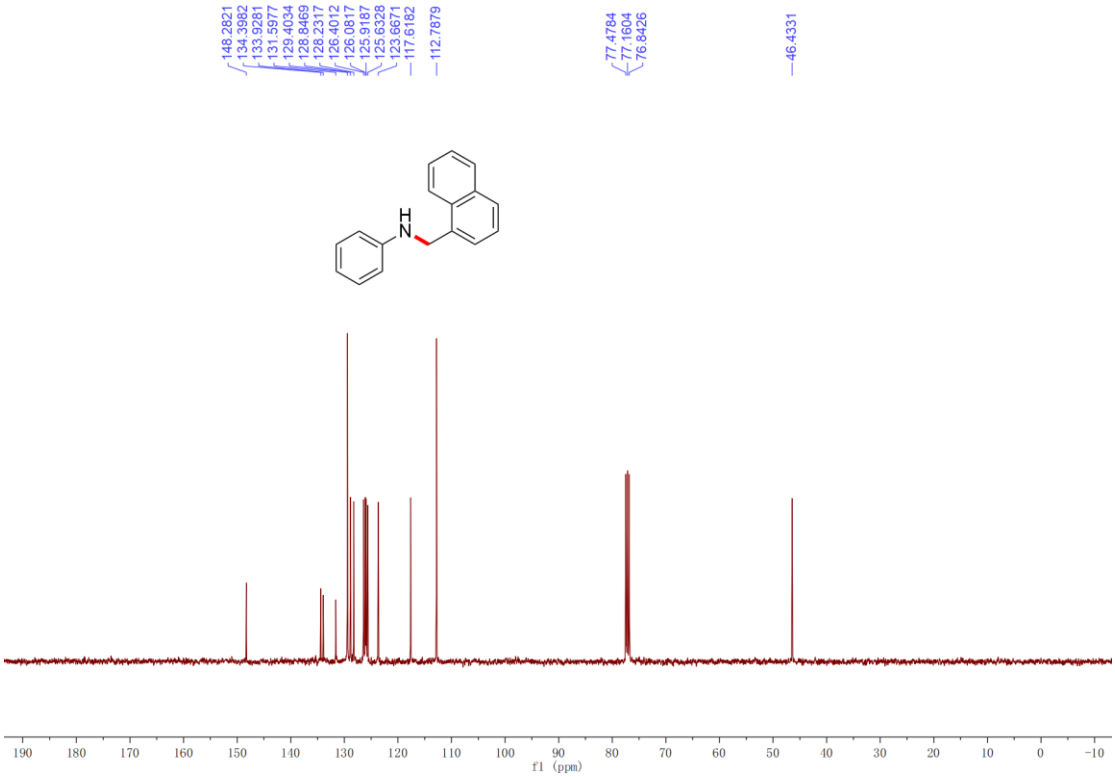

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3ta** in $CDCl_3$.



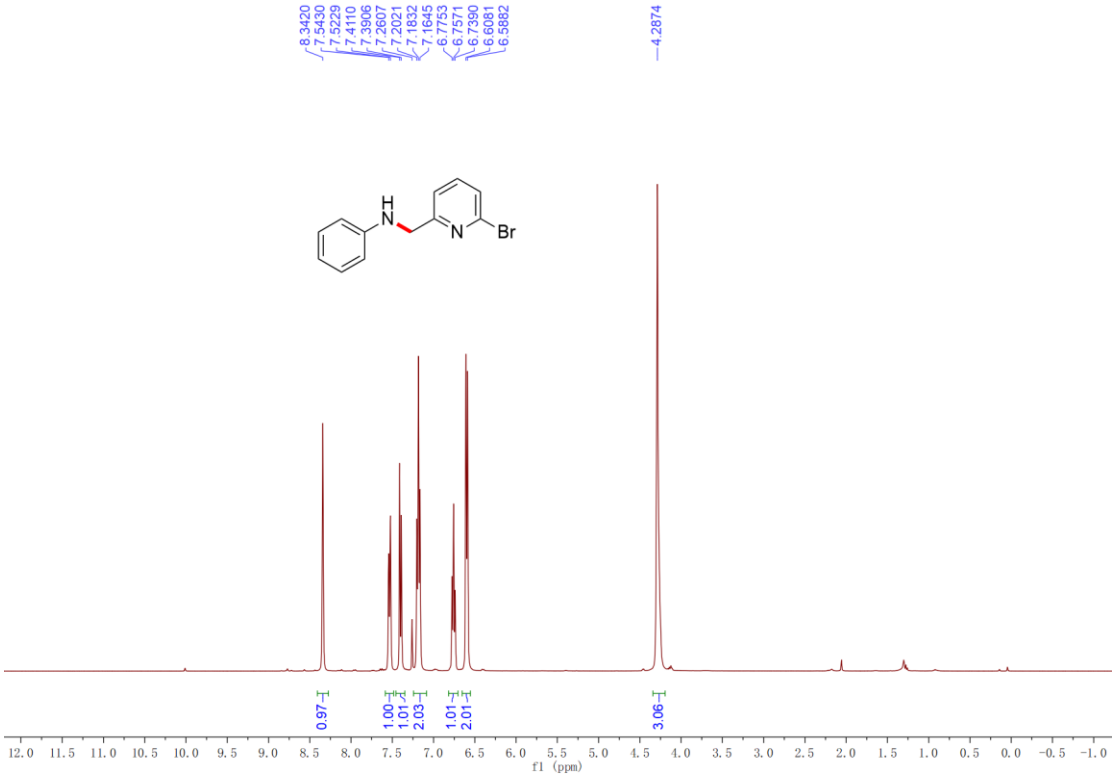
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **3ua** in $CDCl_3$.



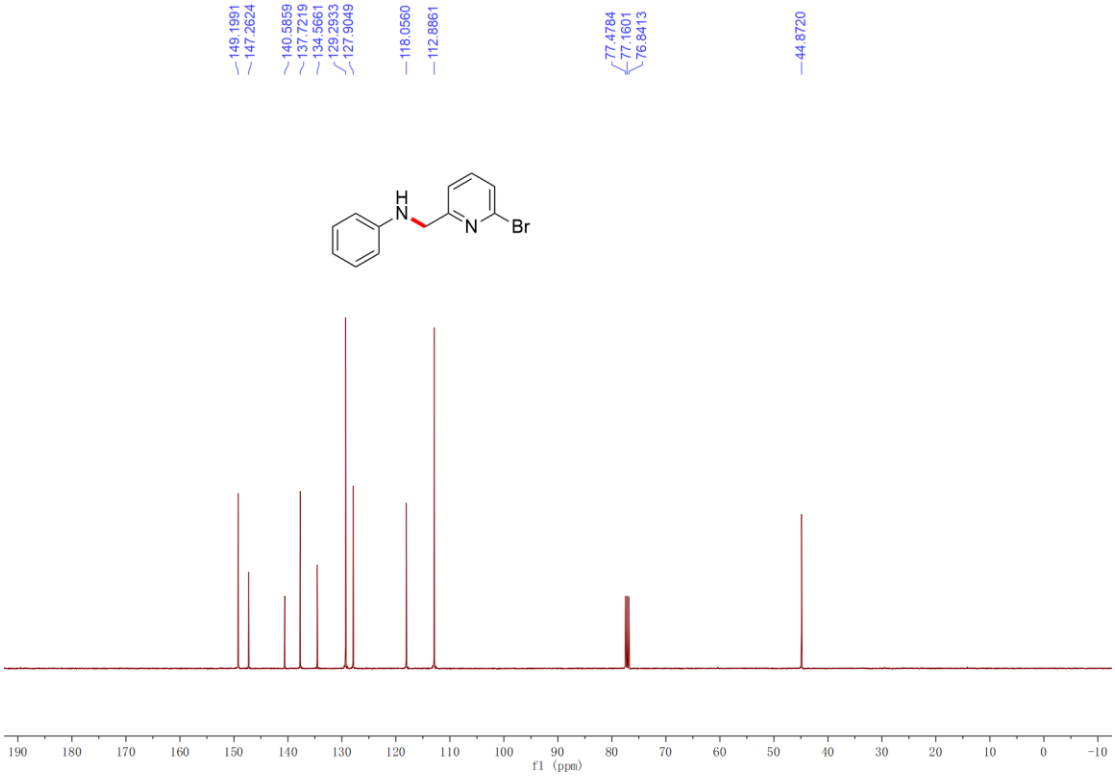

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **3ua** in $CDCl_3$.



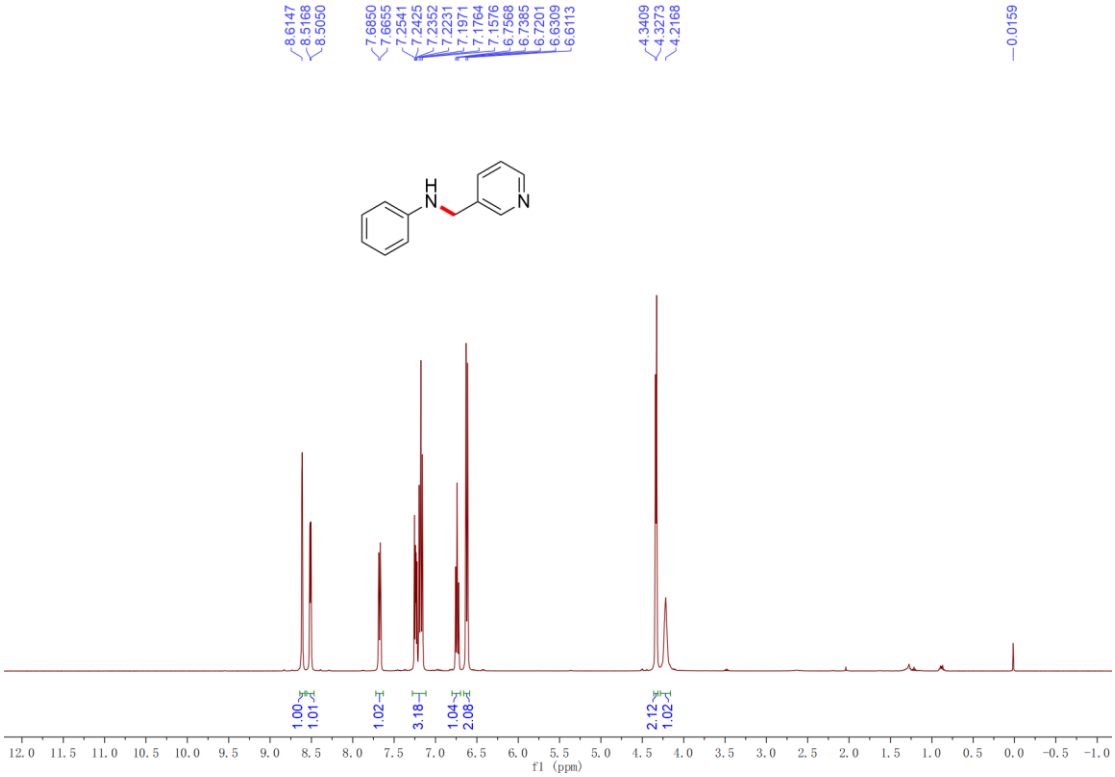
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3va** in $CDCl_3$.



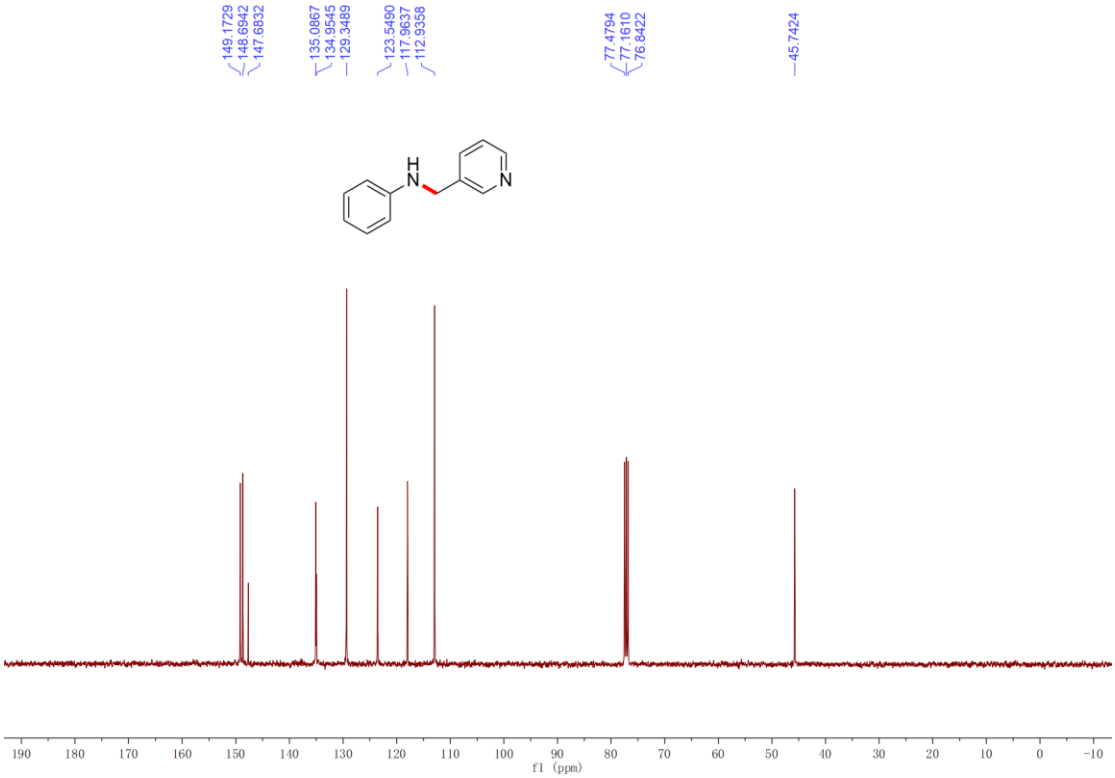

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3va** in $CDCl_3$.



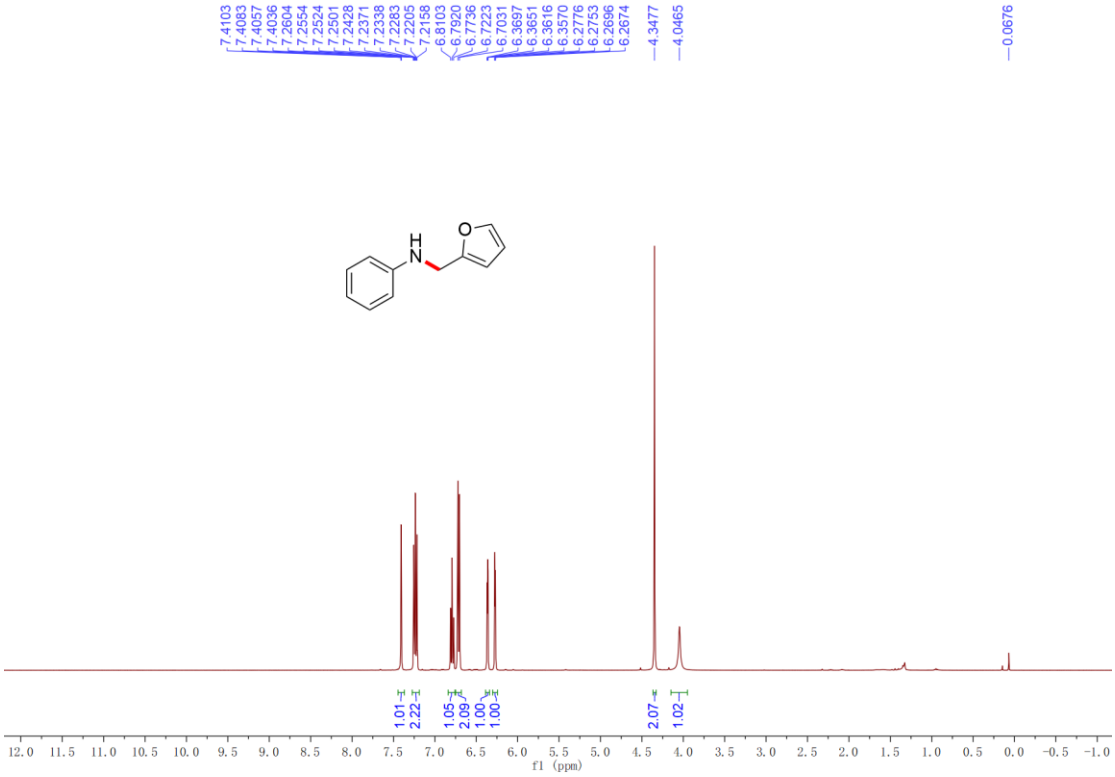
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3wa** in $CDCl_3$.



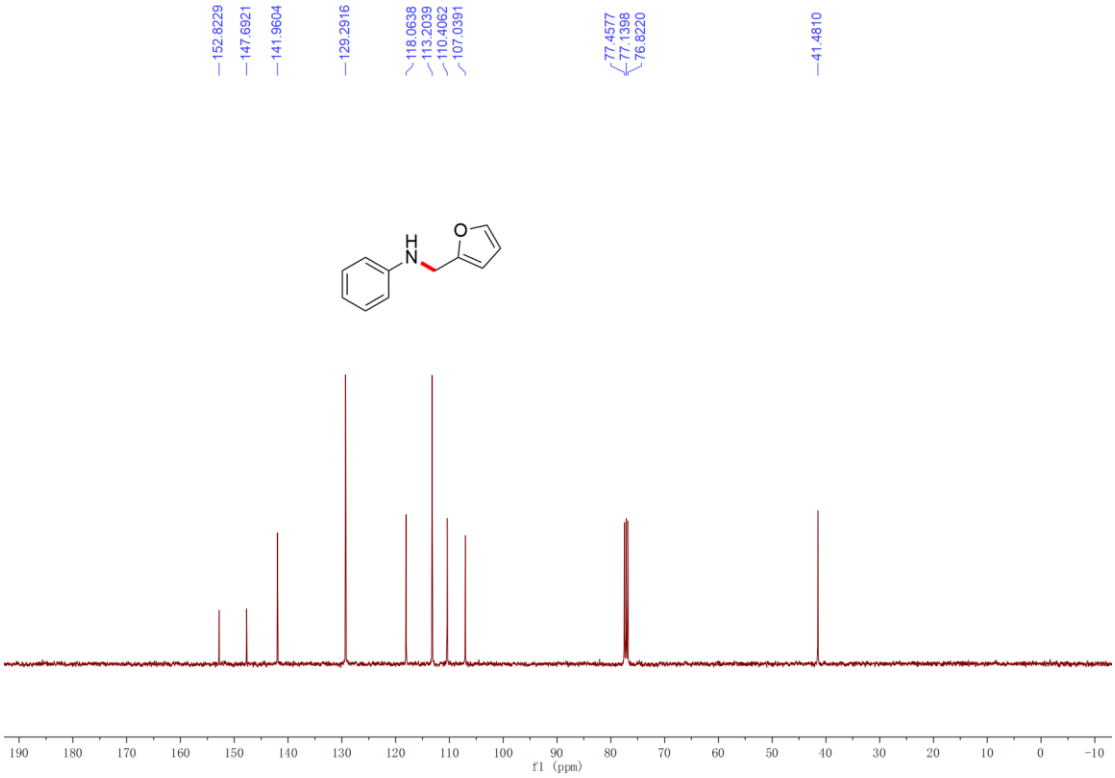

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3wa** in $CDCl_3$.



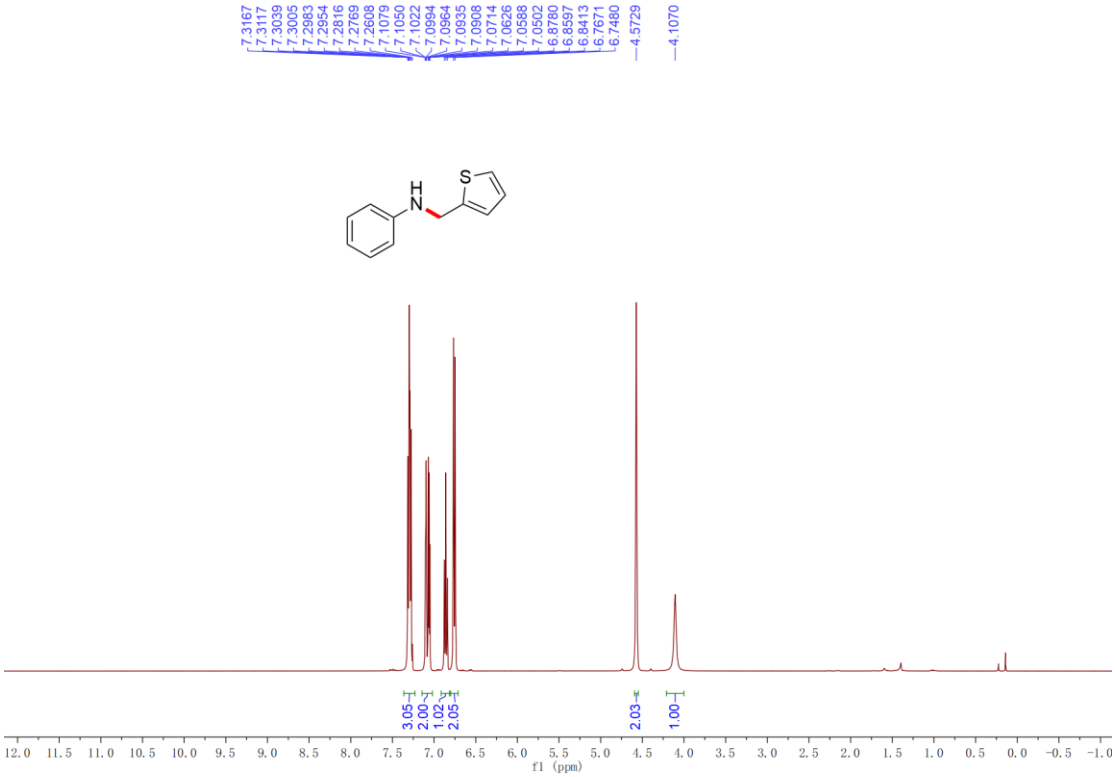
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3xa** in $CDCl_3$.



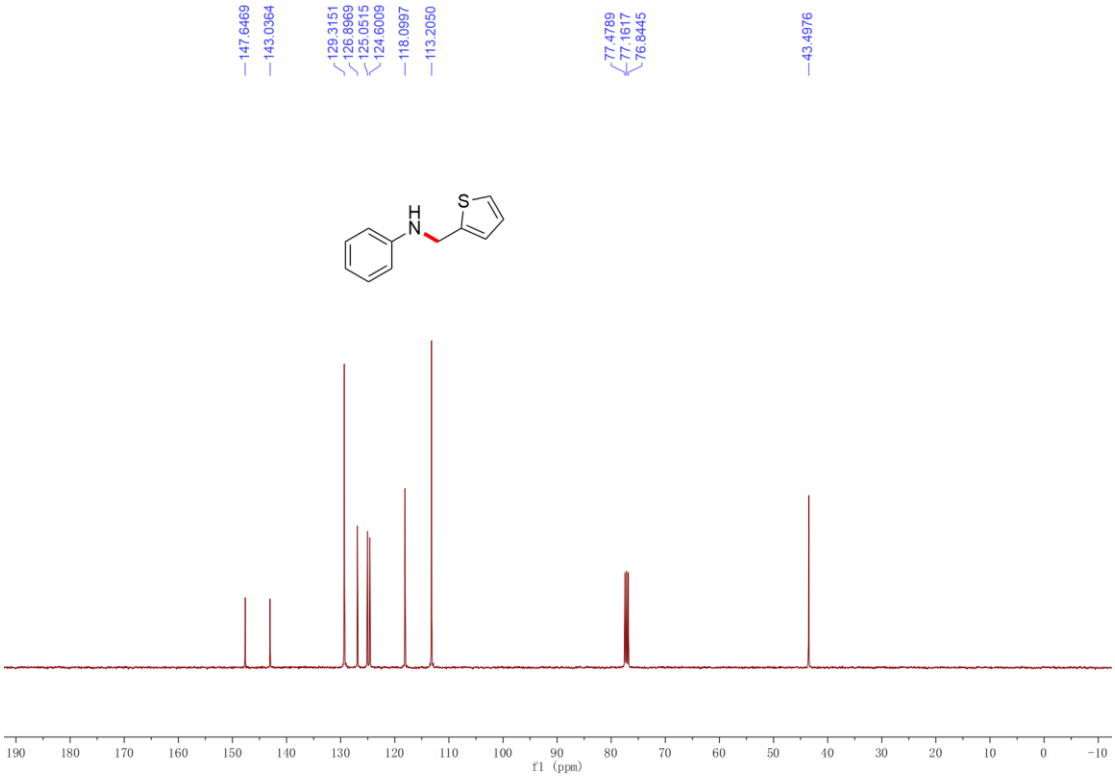

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3xa** in $CDCl_3$.



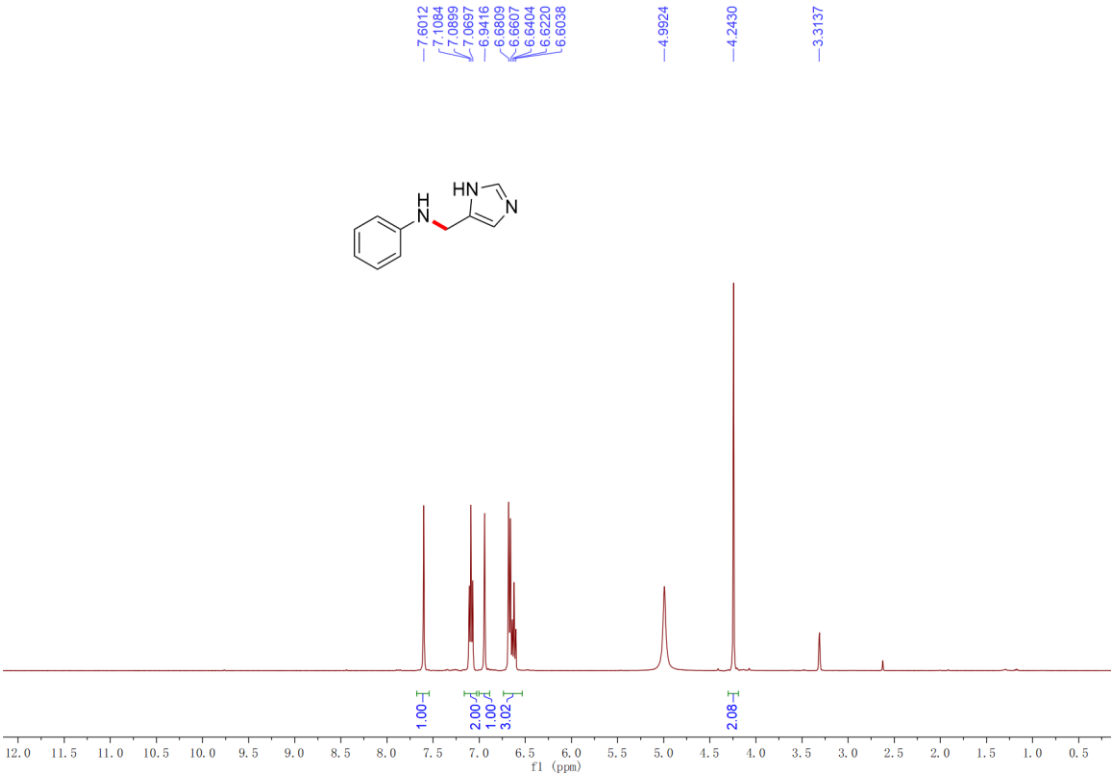
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3ya** in $CDCl_3$.



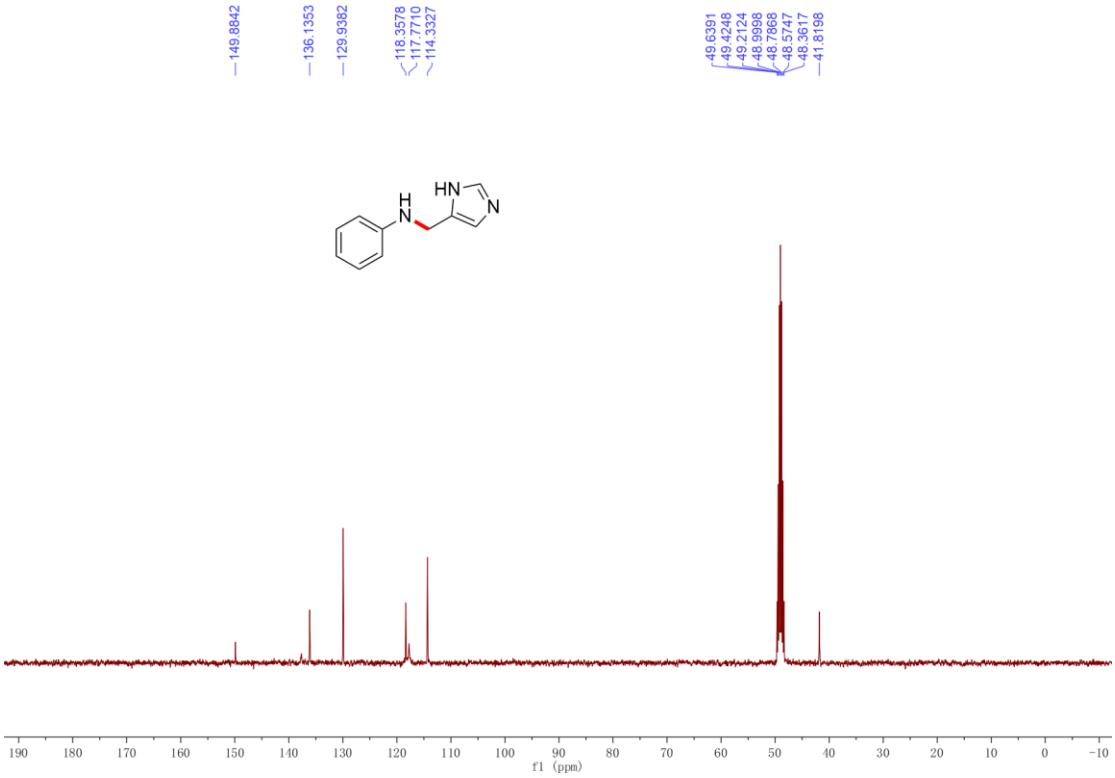

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3ya** in $CDCl_3$.



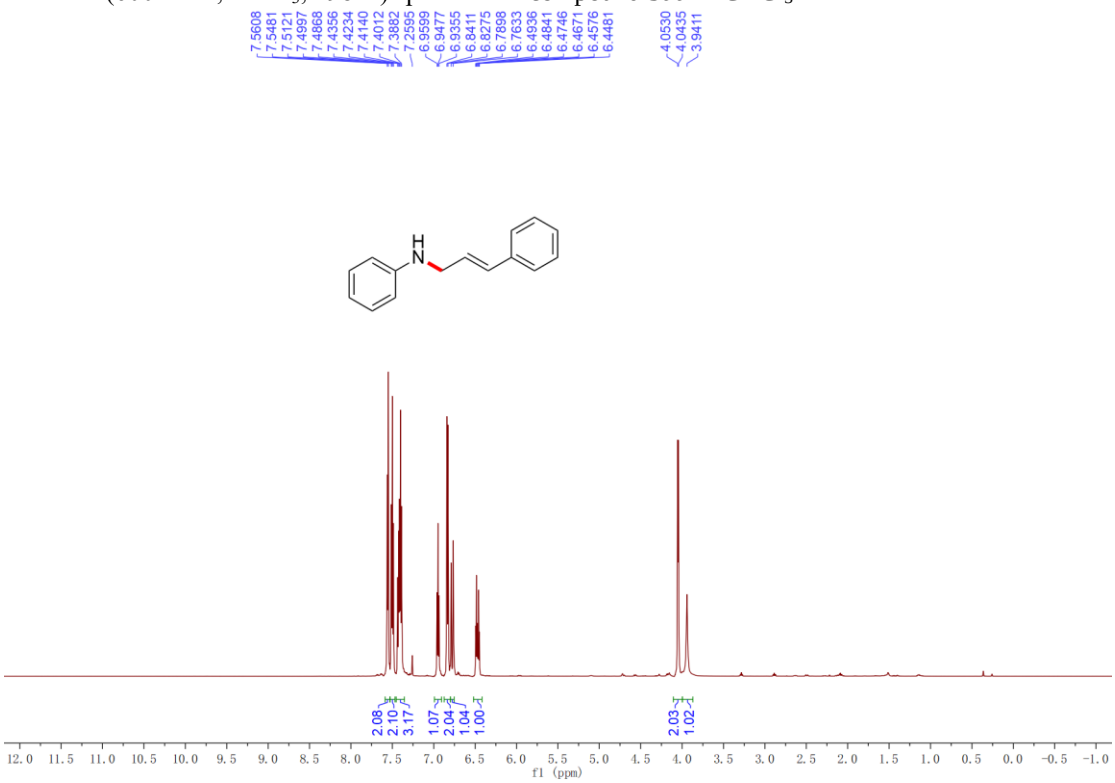
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3za** in Methanol-$d_4$.



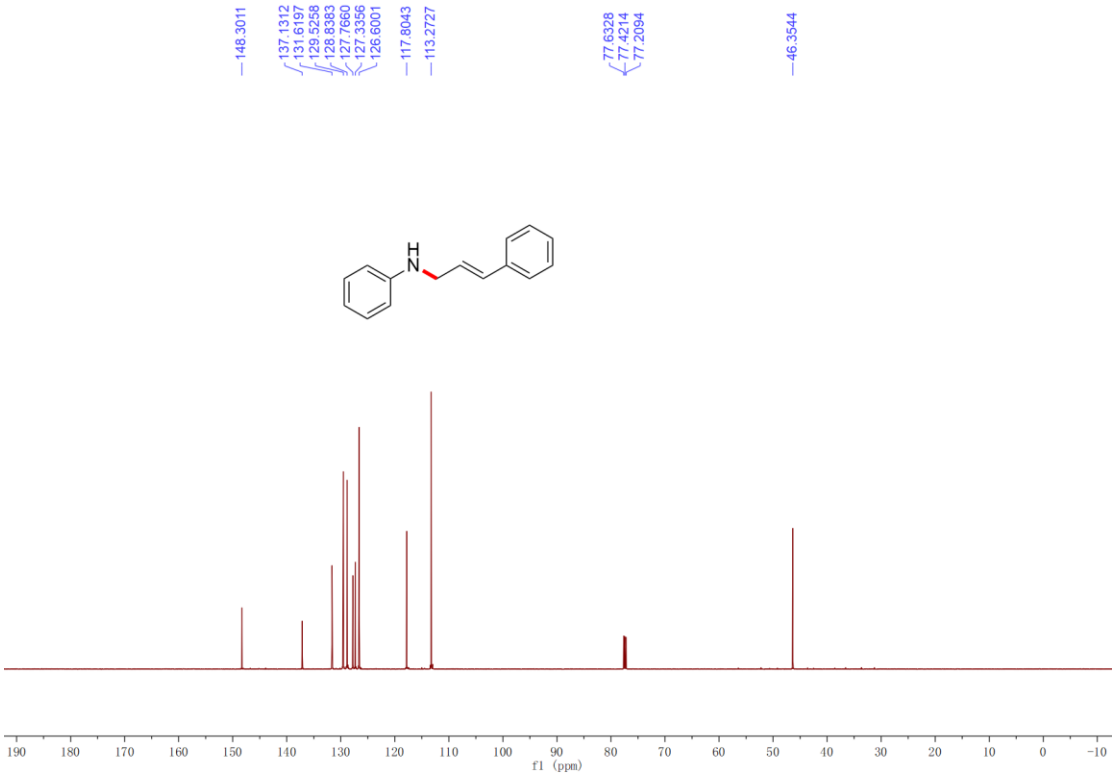

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3za** in Methanol-$d_4$.



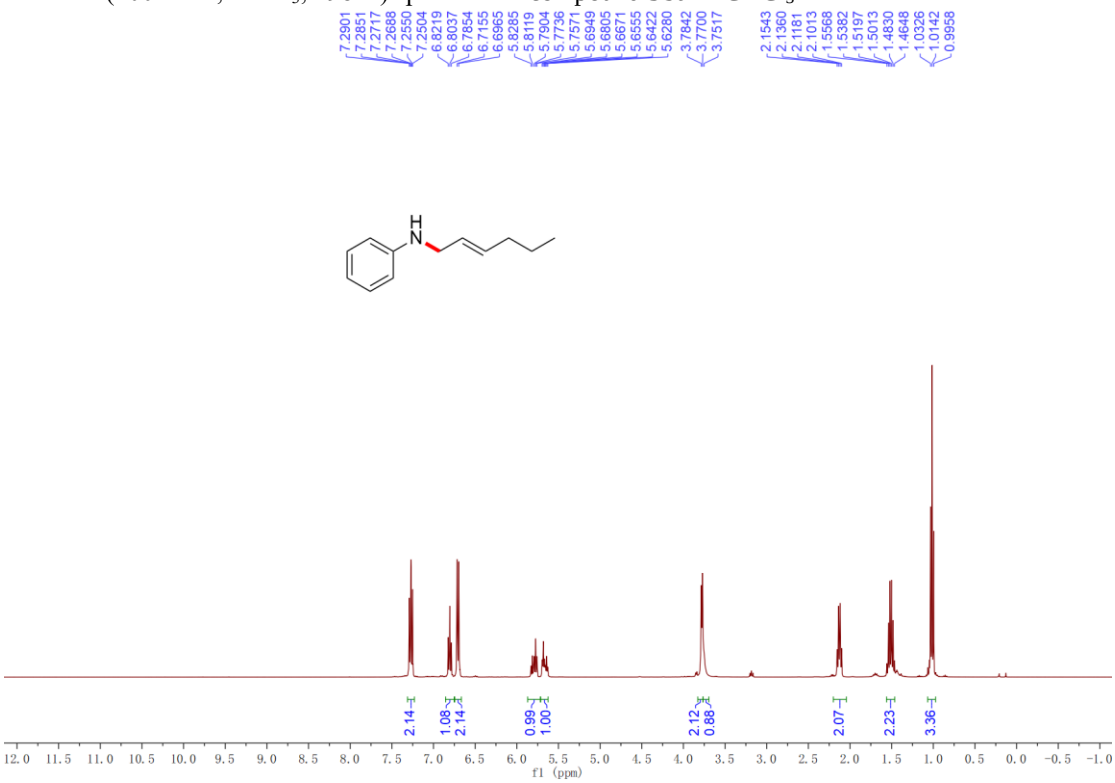
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **5aa** in $CDCl_3$.



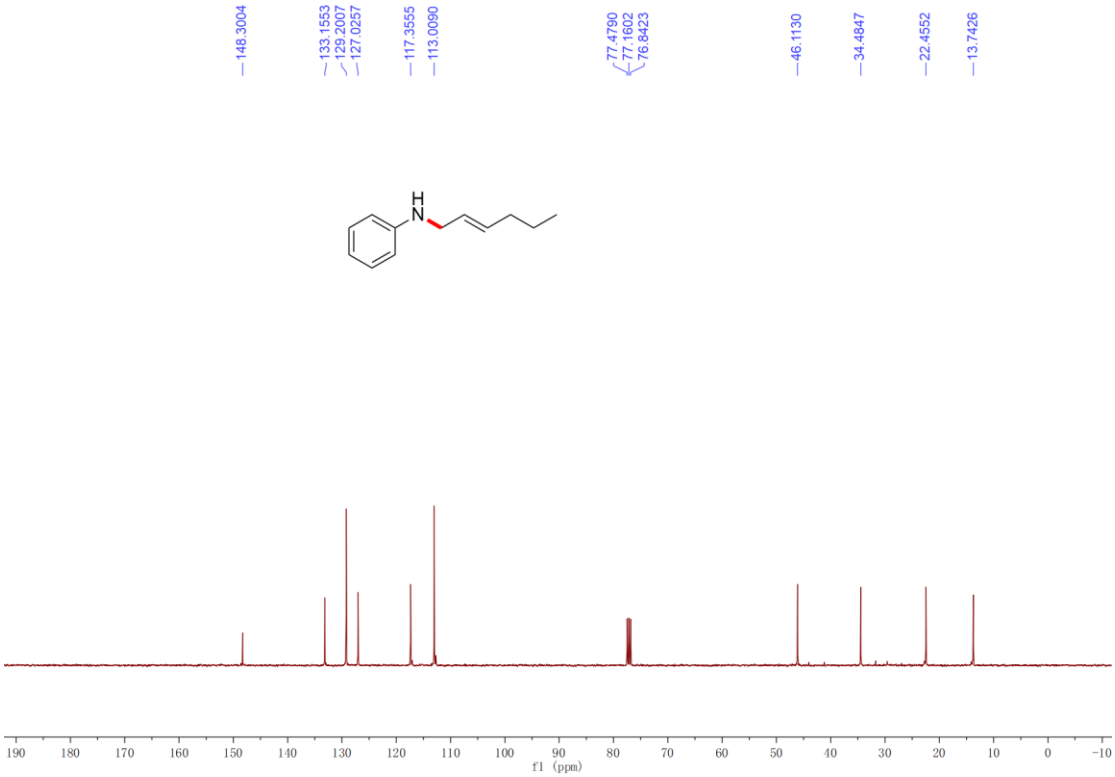

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **5aa** in $CDCl_3$.



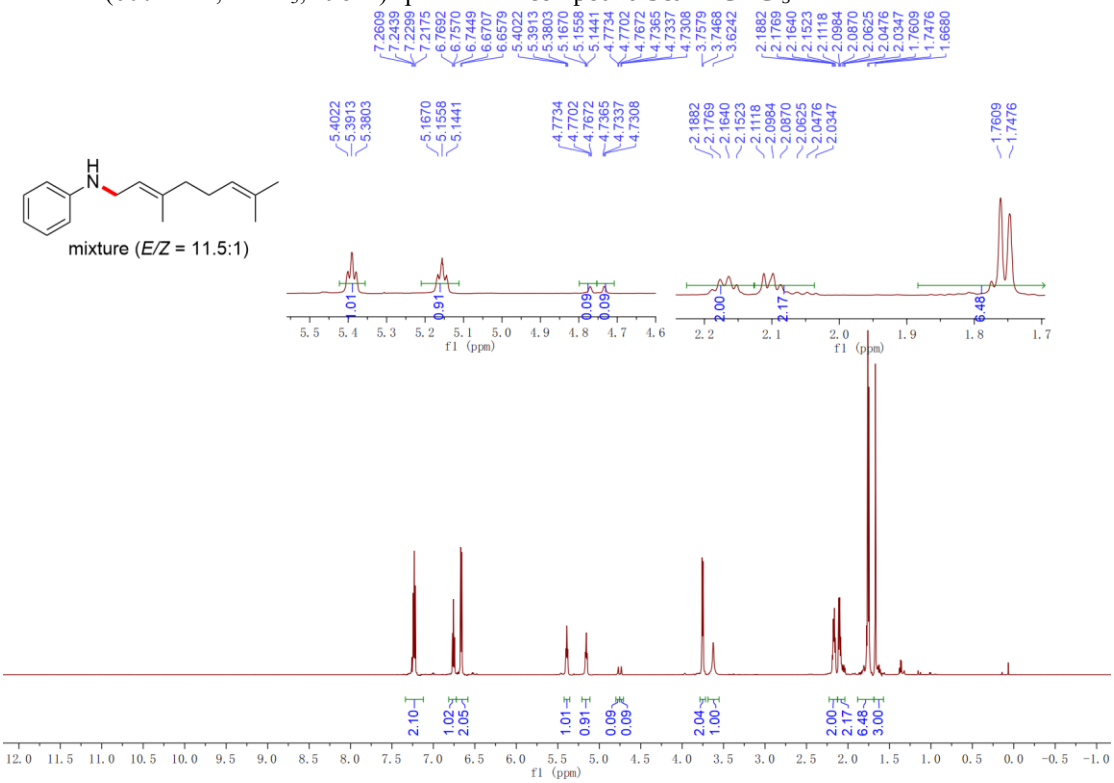
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **5ba** in $CDCl_3$.



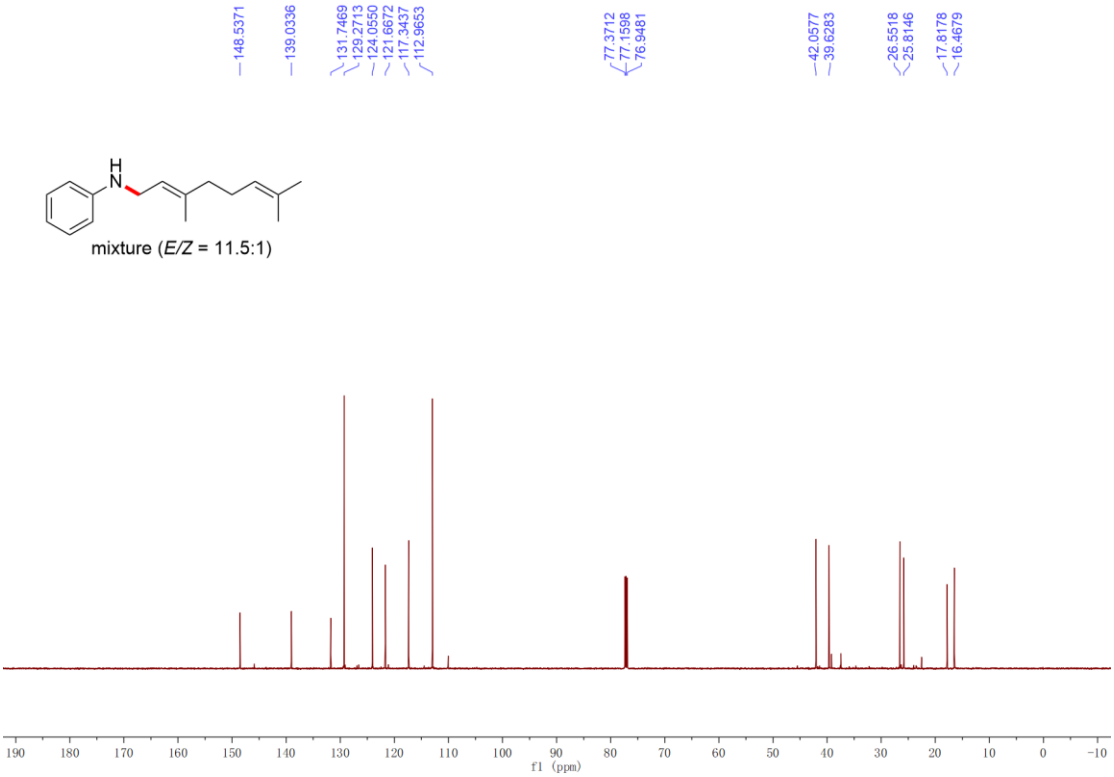

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **5ba** in $CDCl_3$.



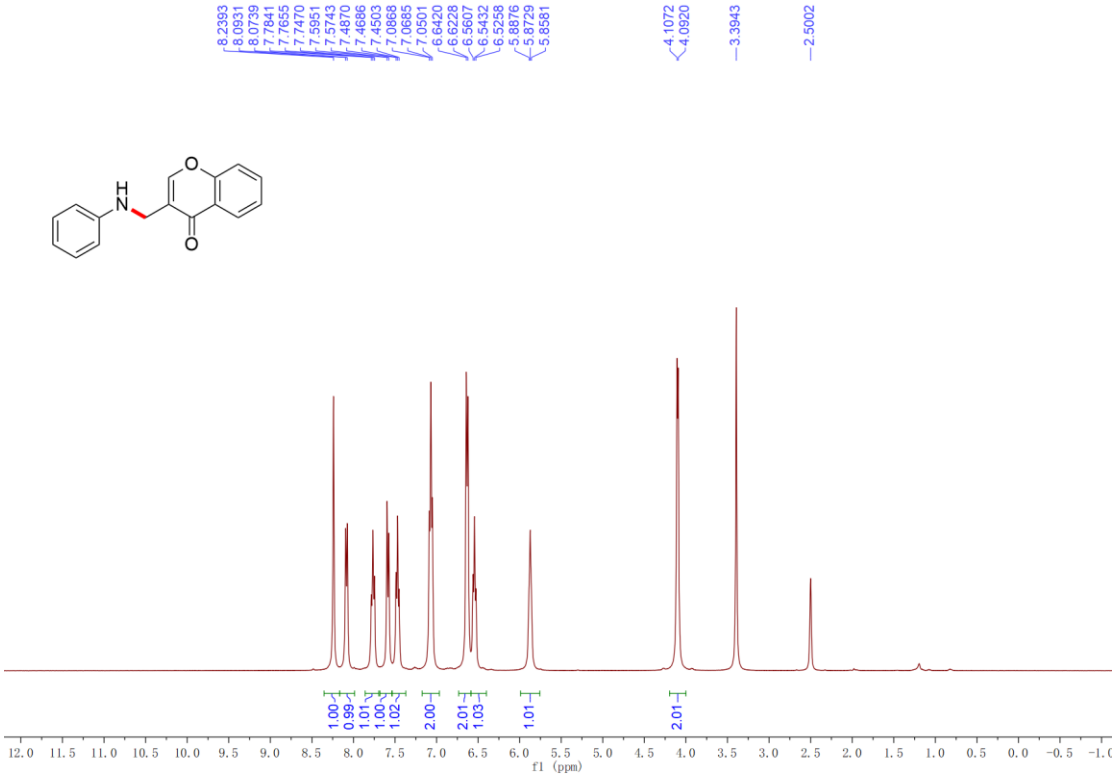
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **5ca** in $CDCl_3$.



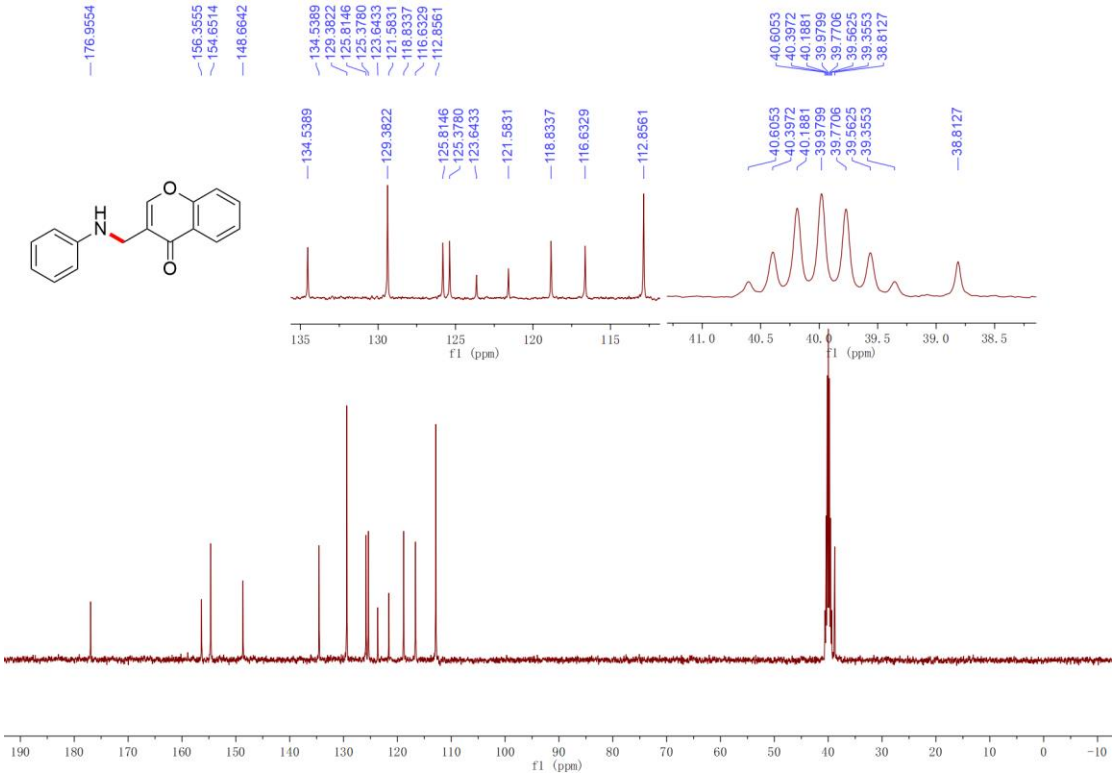

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **5ca** in $CDCl_3$.



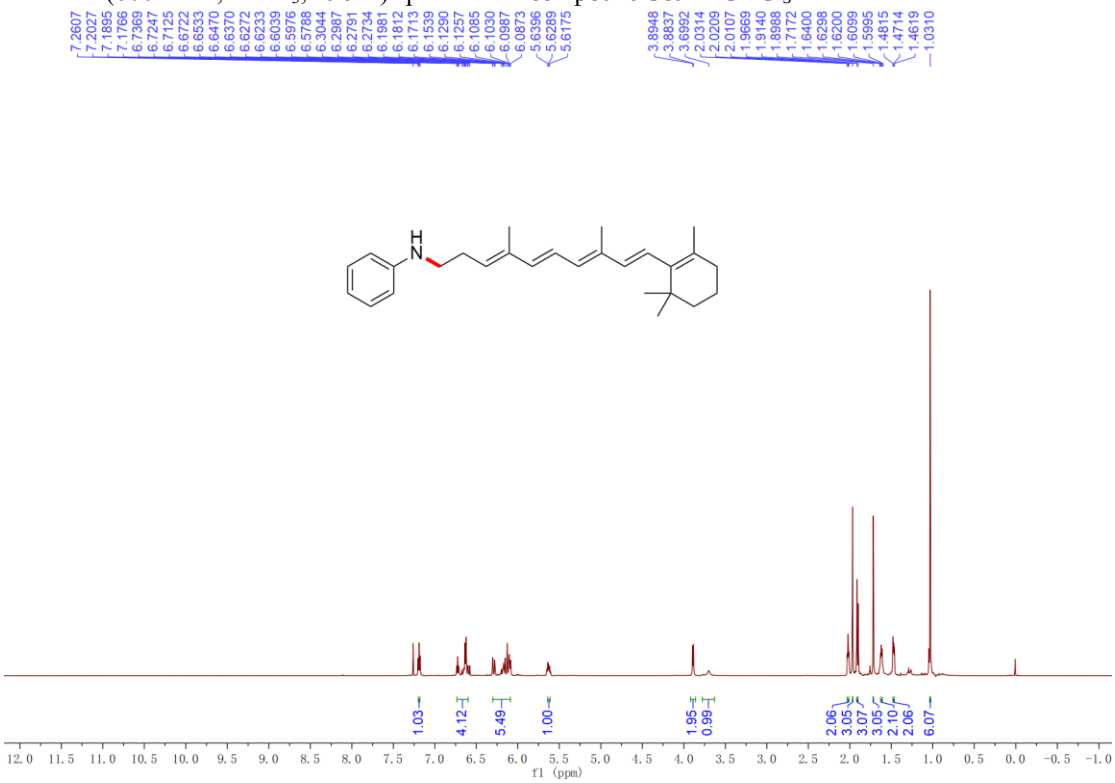
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **5da** in DMSO-$d_6$.



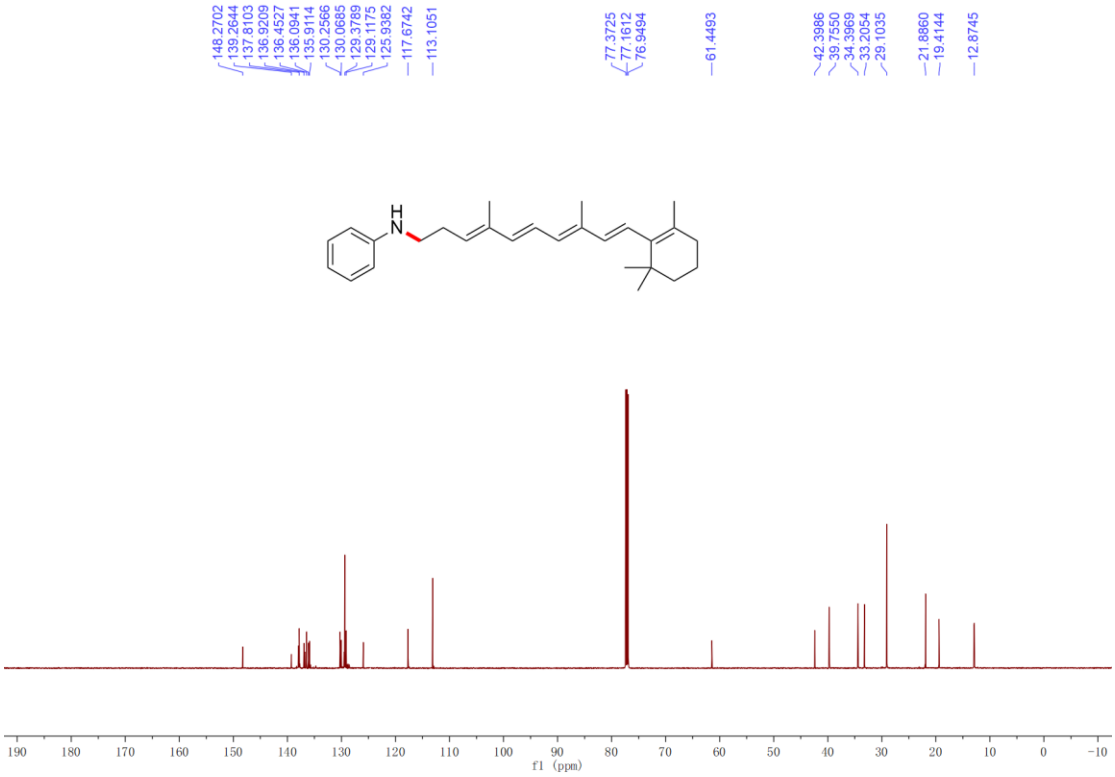

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **5da** in DMSO-$d_6$.



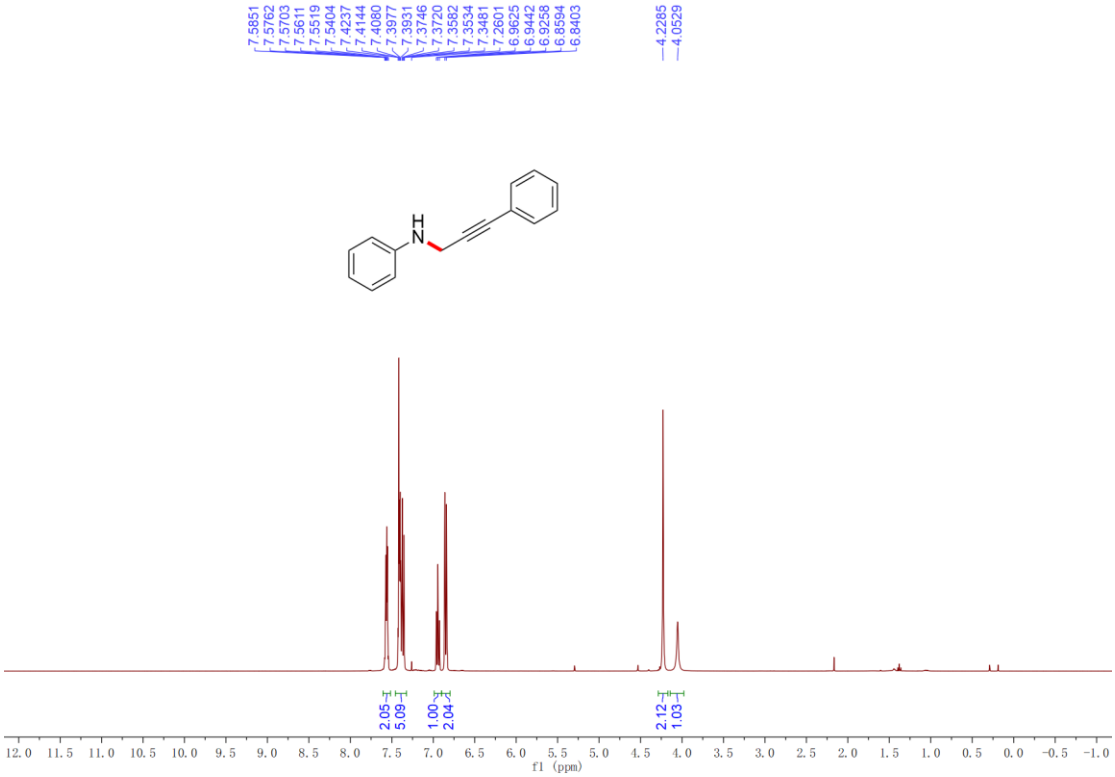
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **5ea** in $CDCl_3$.



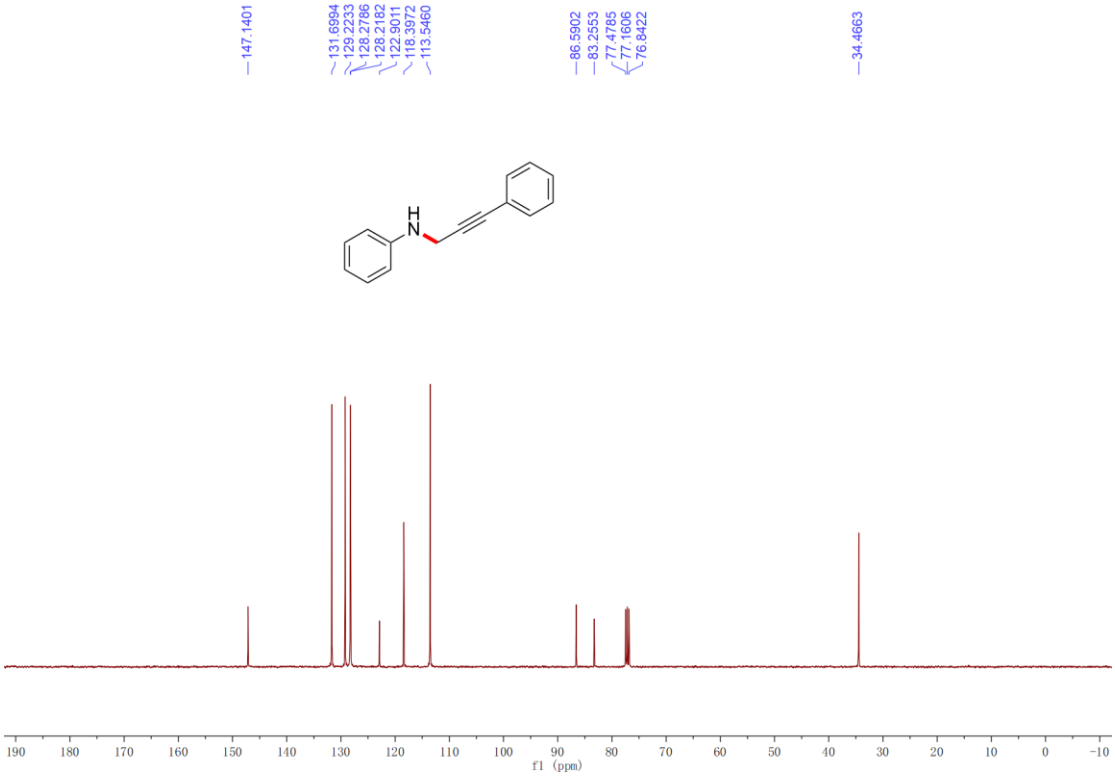

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **5ea** in $CDCl_3$.



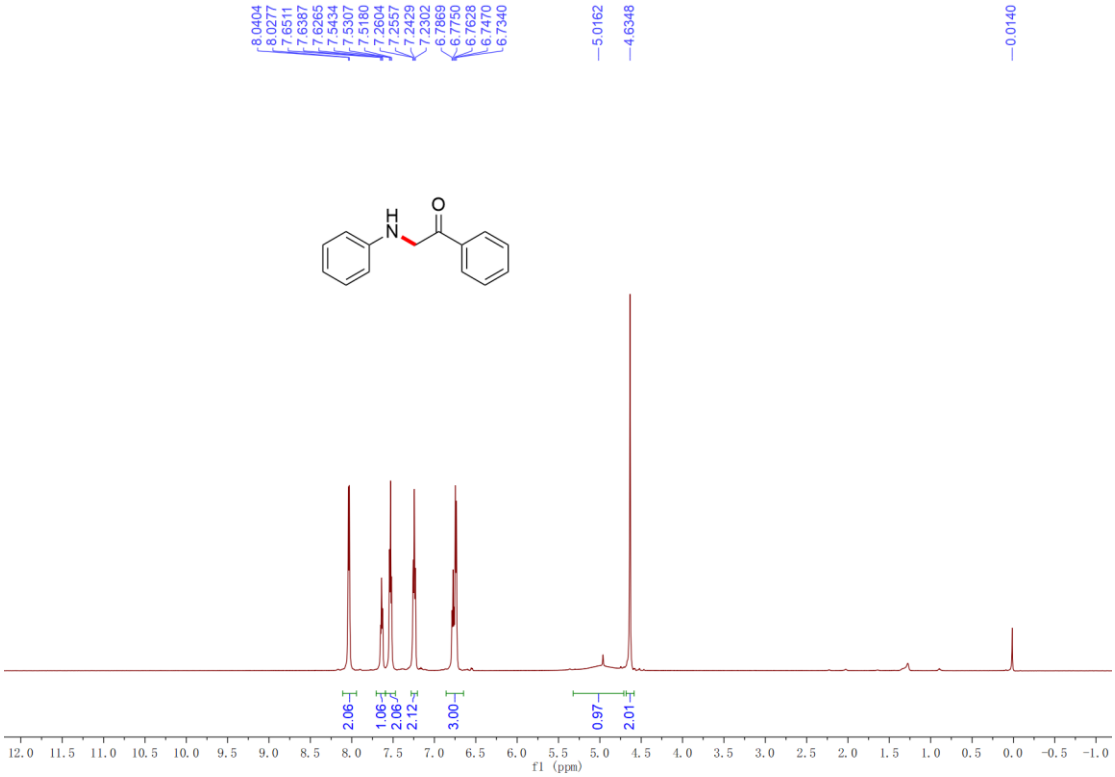
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **5fa** in $CDCl_3$.



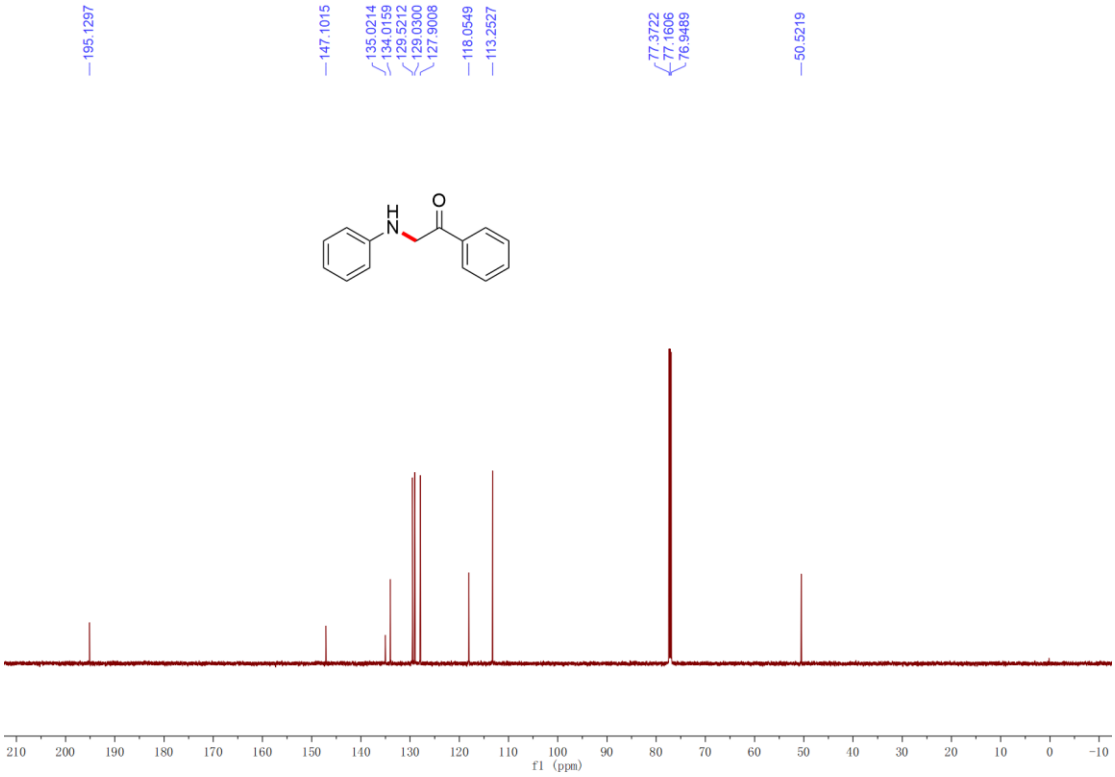

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **5fa** in $CDCl_3$.



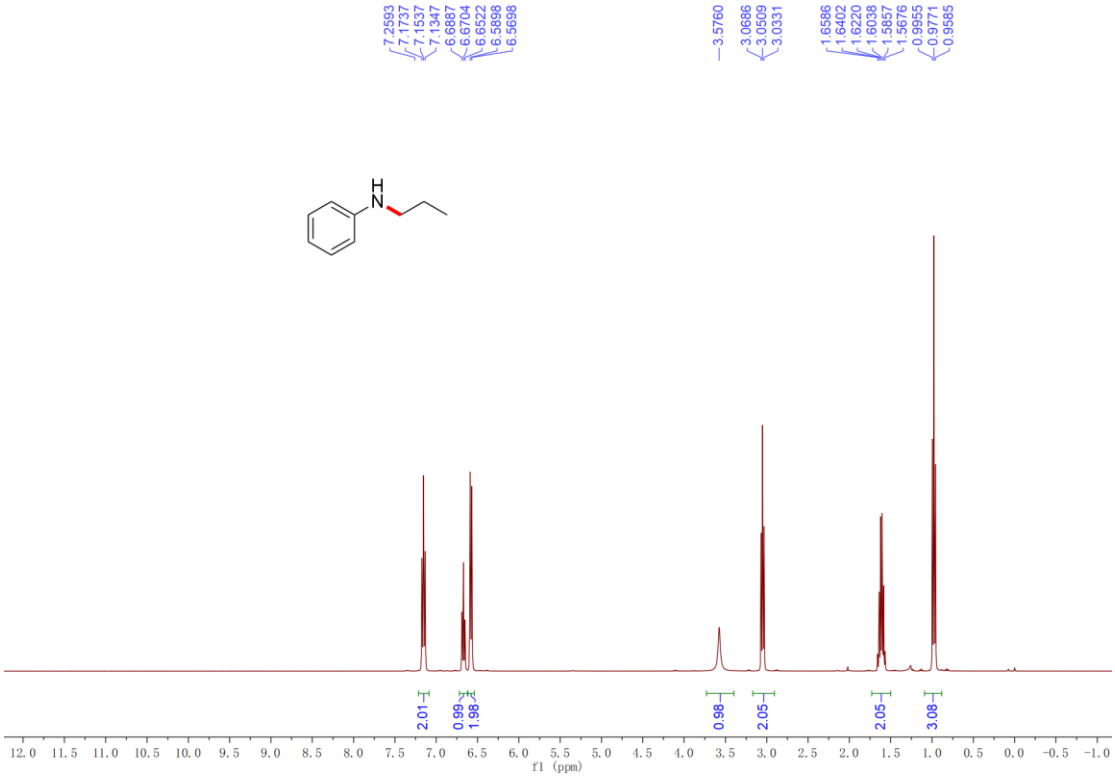
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **5ga** in $CDCl_3$.



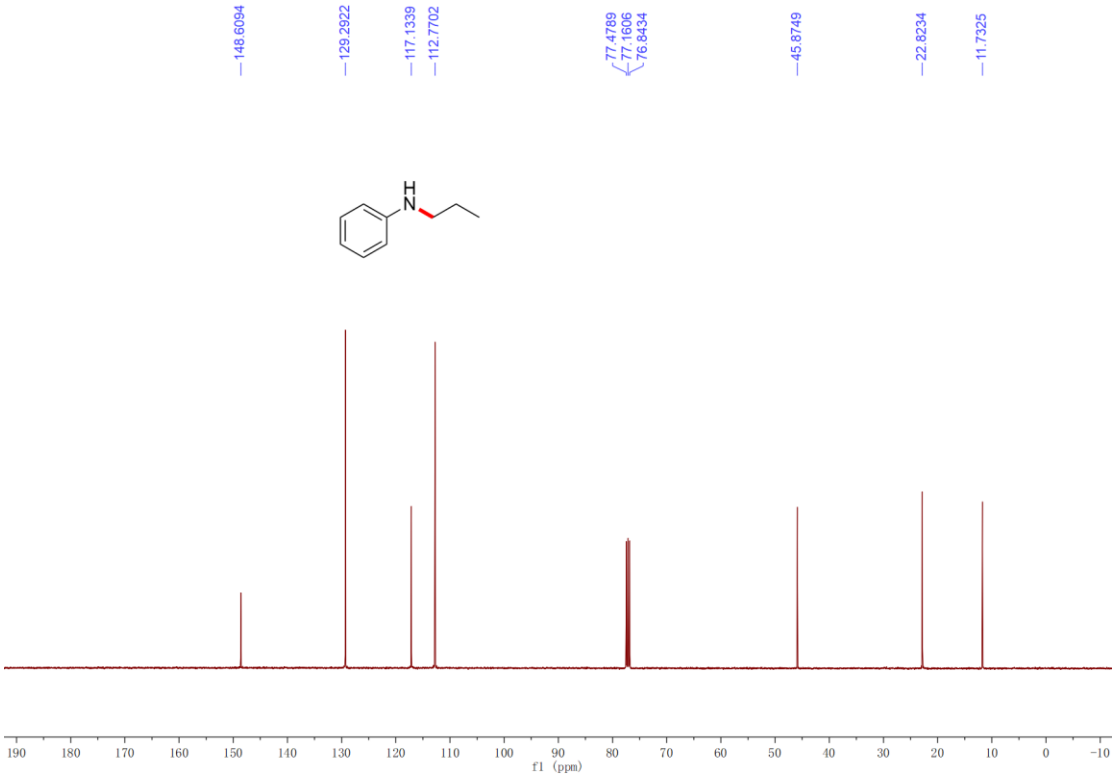

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **5ga** in $CDCl_3$.



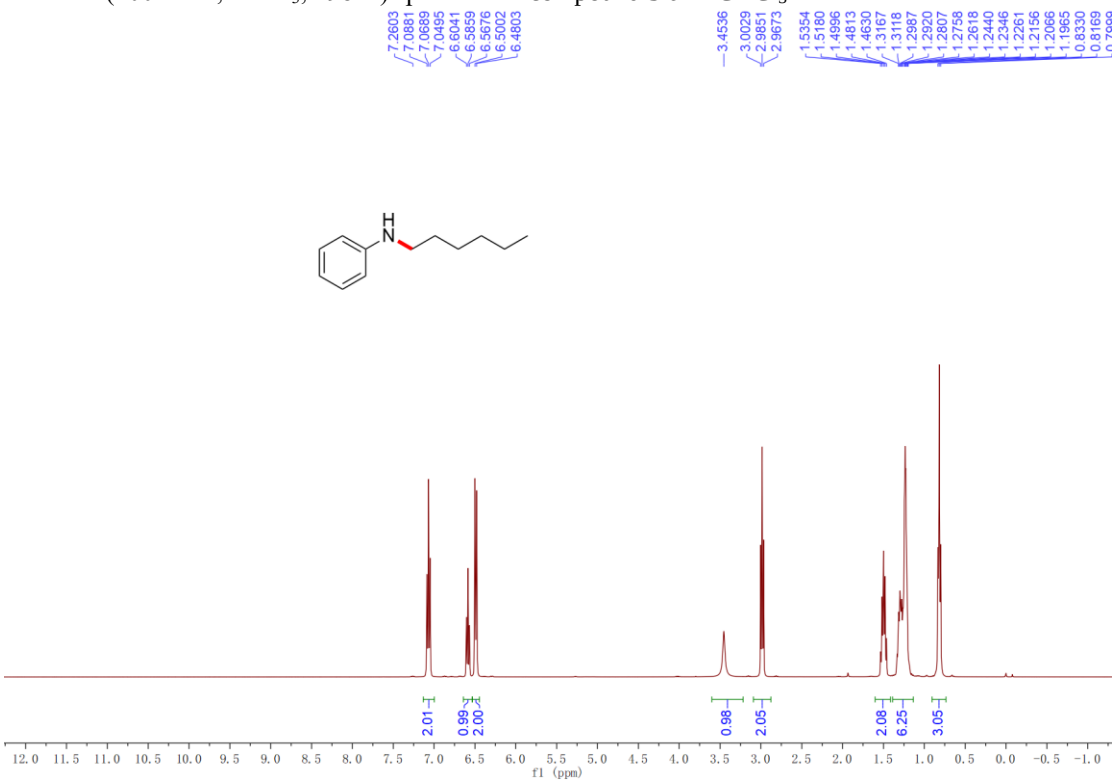
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **5ha** in $CDCl_3$.



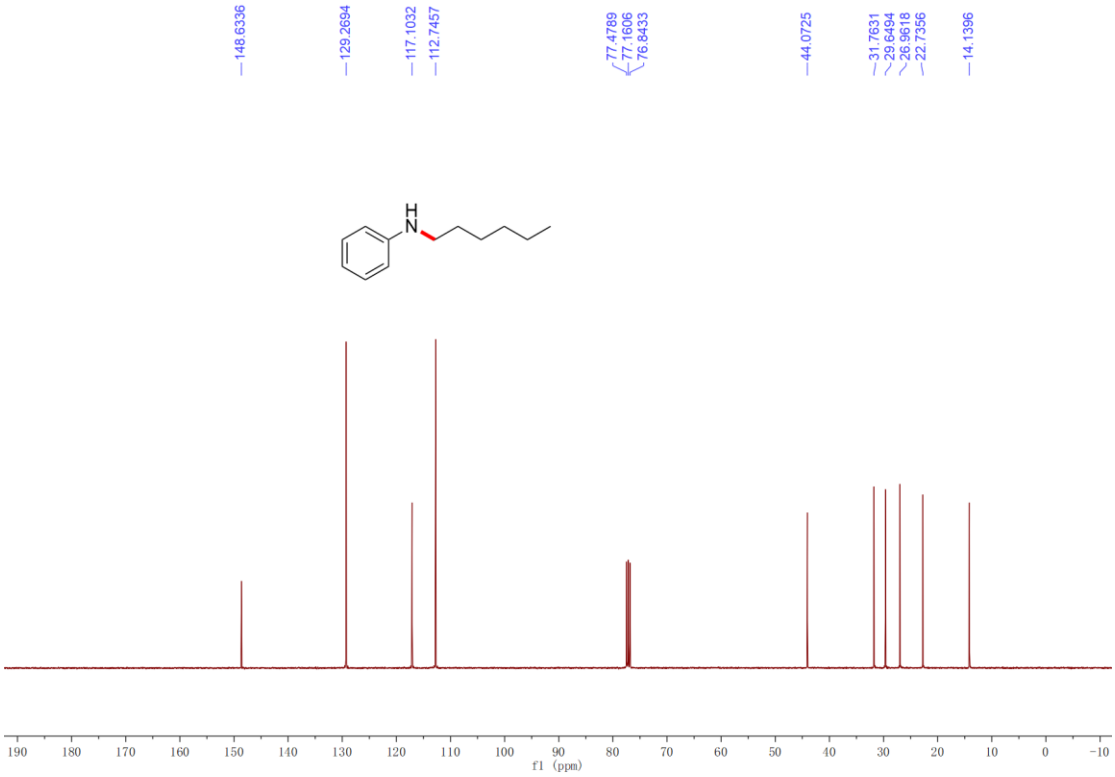

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **5ha** in $CDCl_3$.



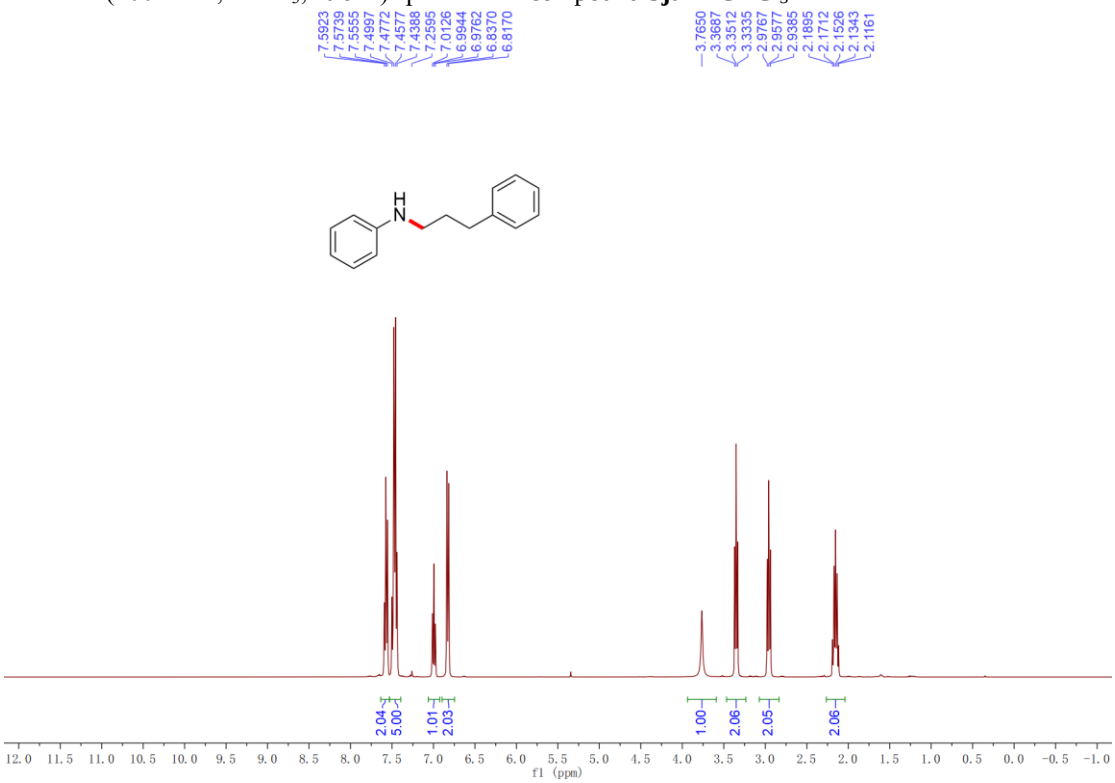
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **5ia** in $CDCl_3$.



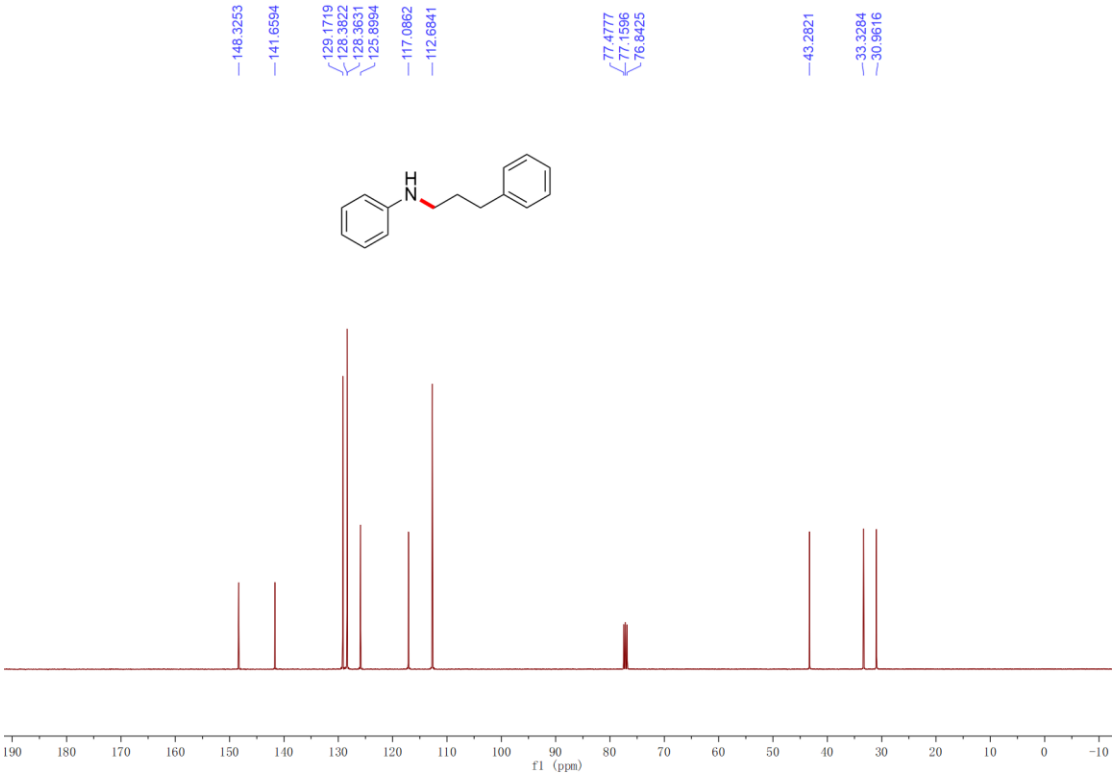

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **5ia** in $CDCl_3$.



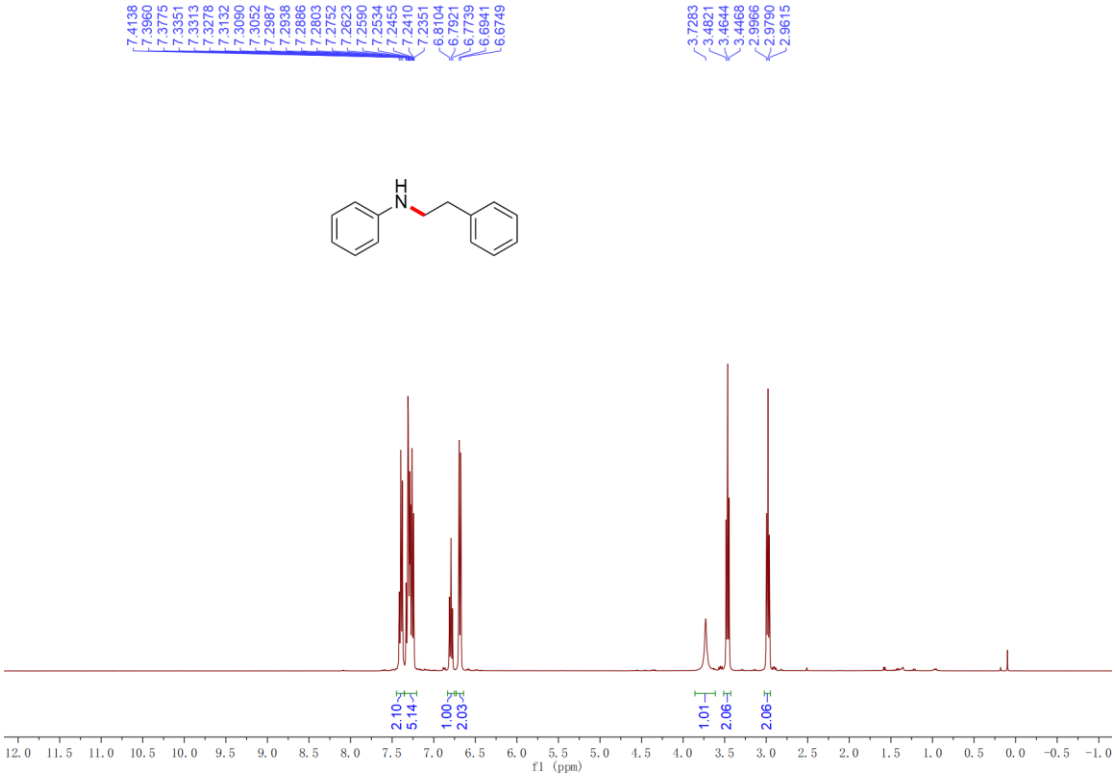
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **5ja** in $CDCl_3$.



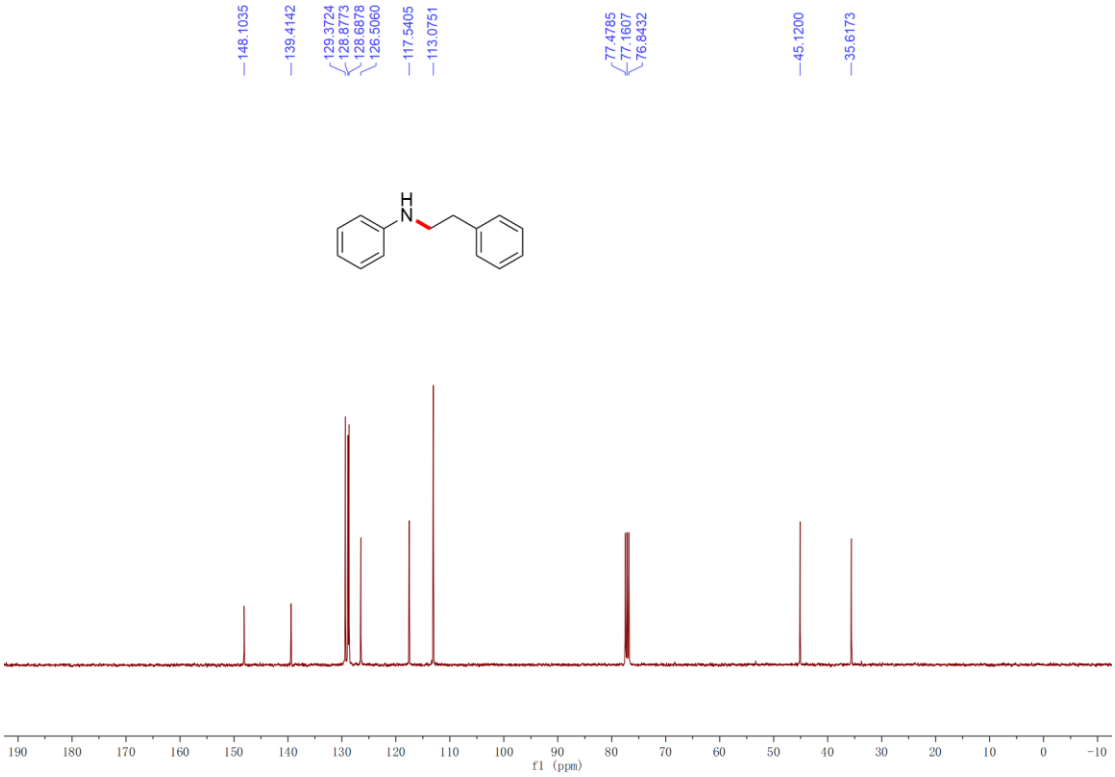

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **5ja** in $CDCl_3$.



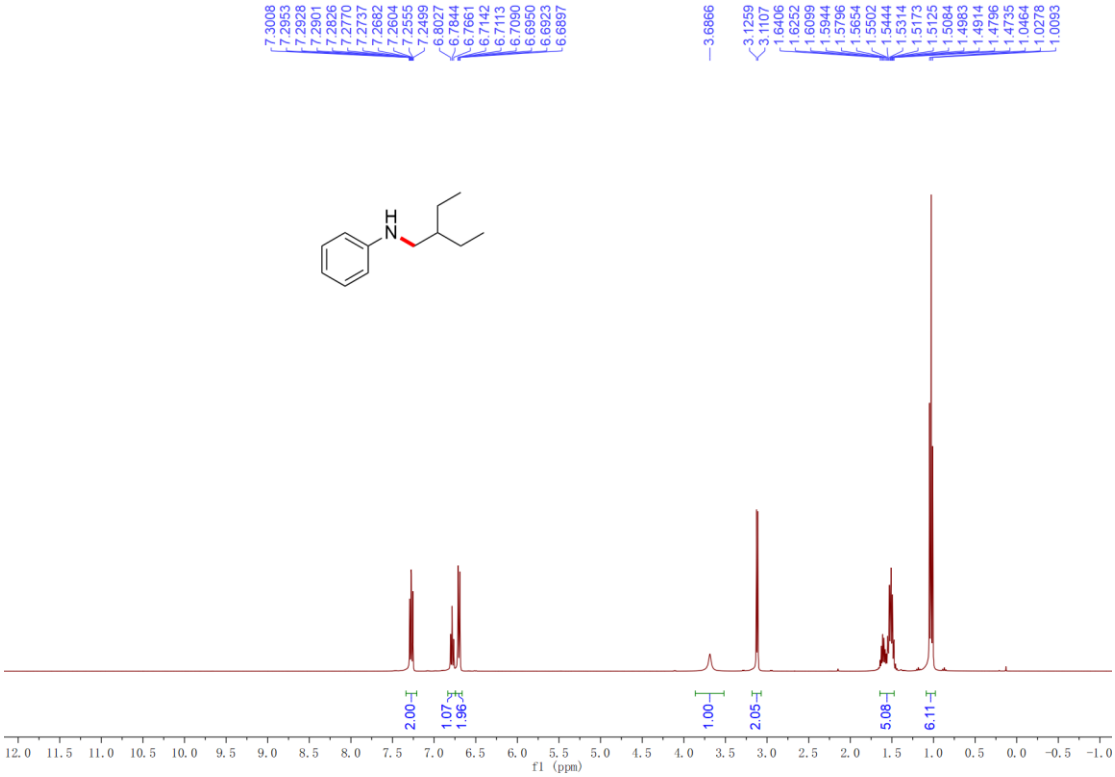
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **5ka** in $CDCl_3$.



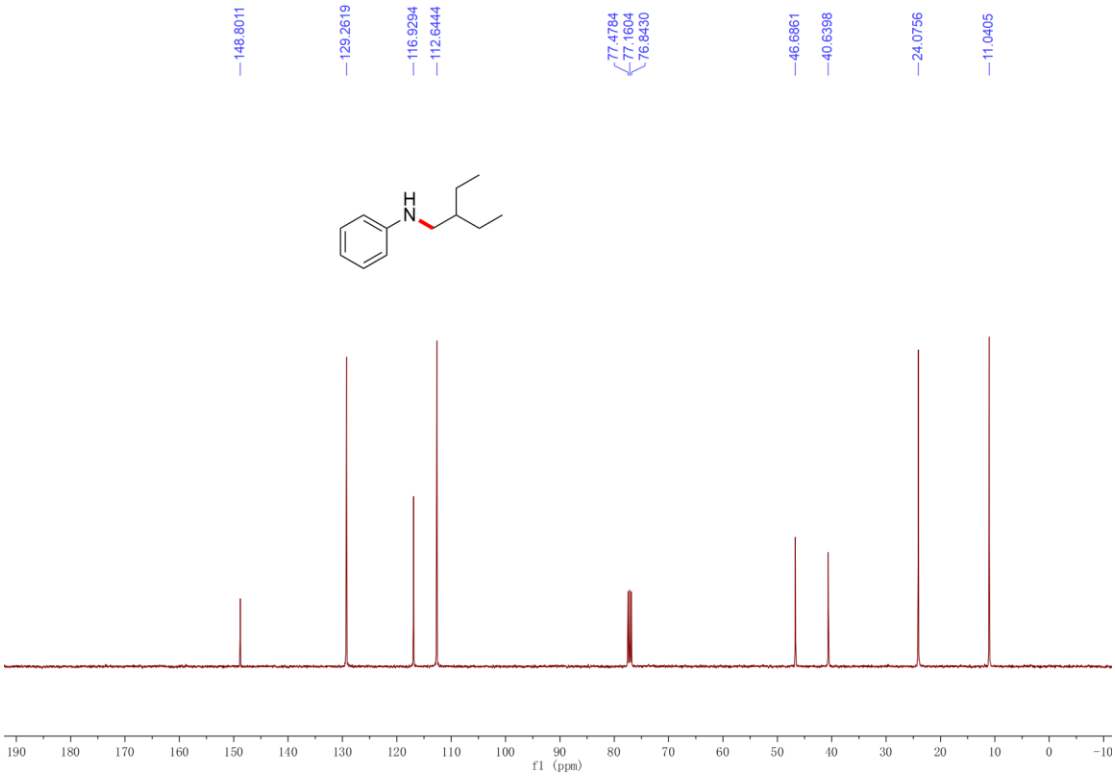

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **5ka** in $CDCl_3$.



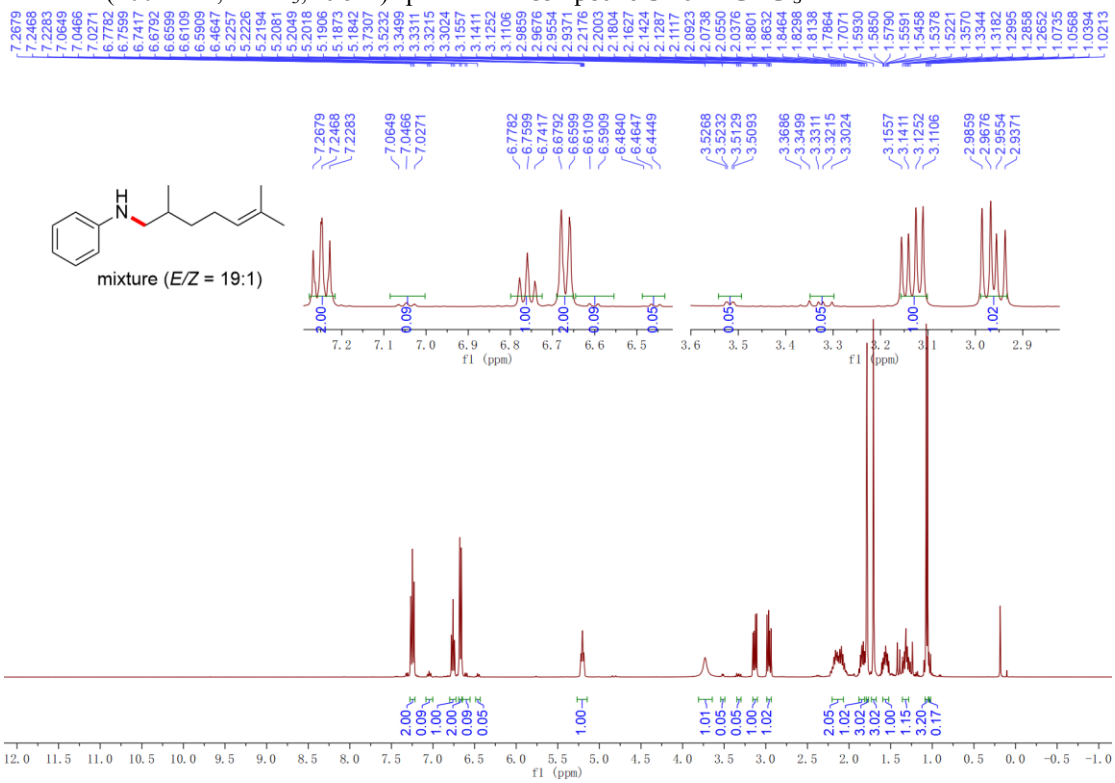
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **5la** in $CDCl_3$.



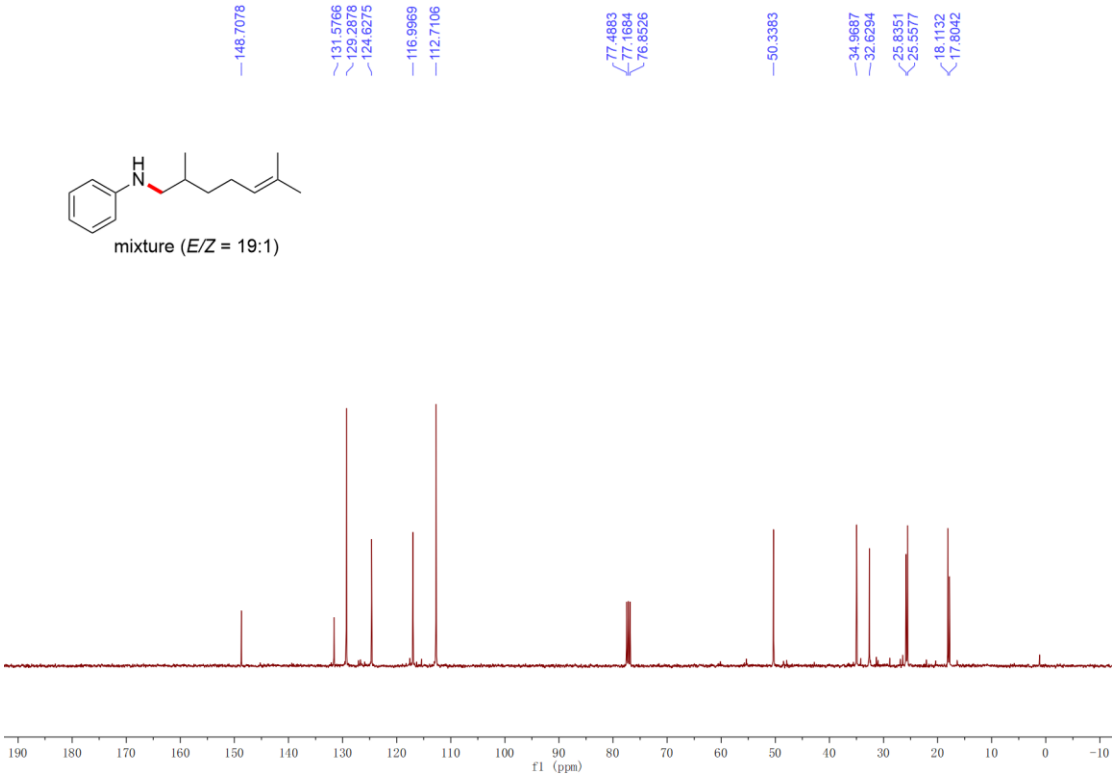

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **5la** in $CDCl_3$.



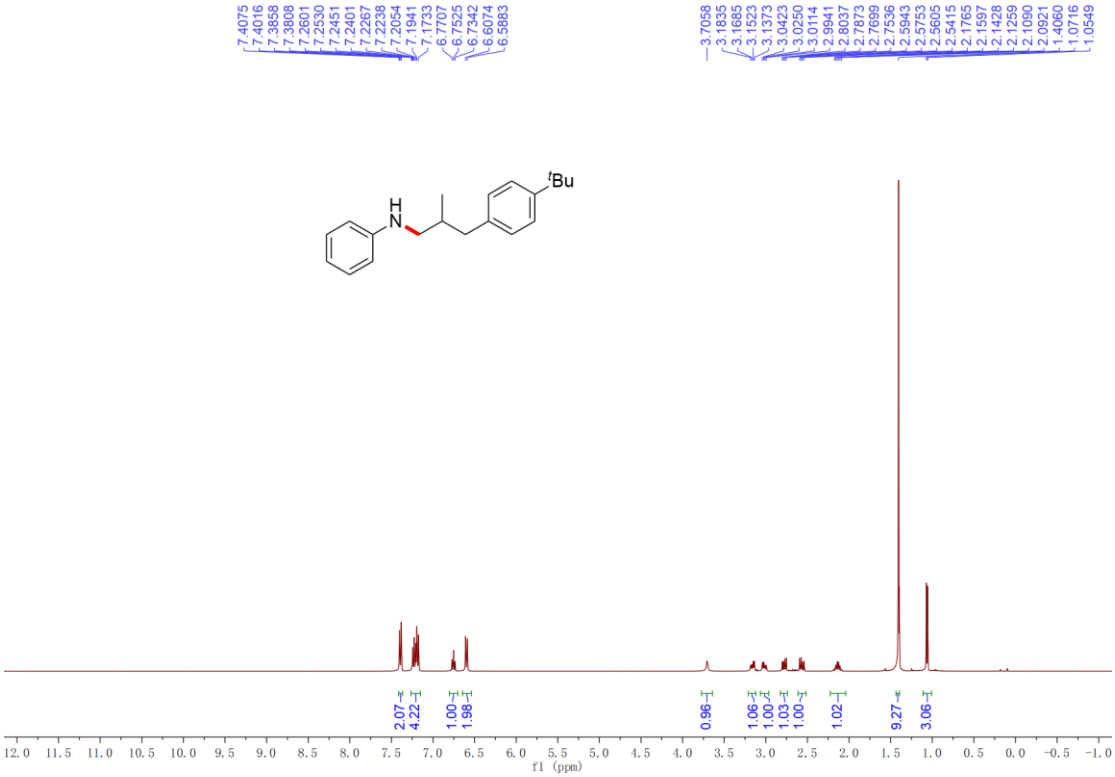
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **5ma** in $CDCl_3$.



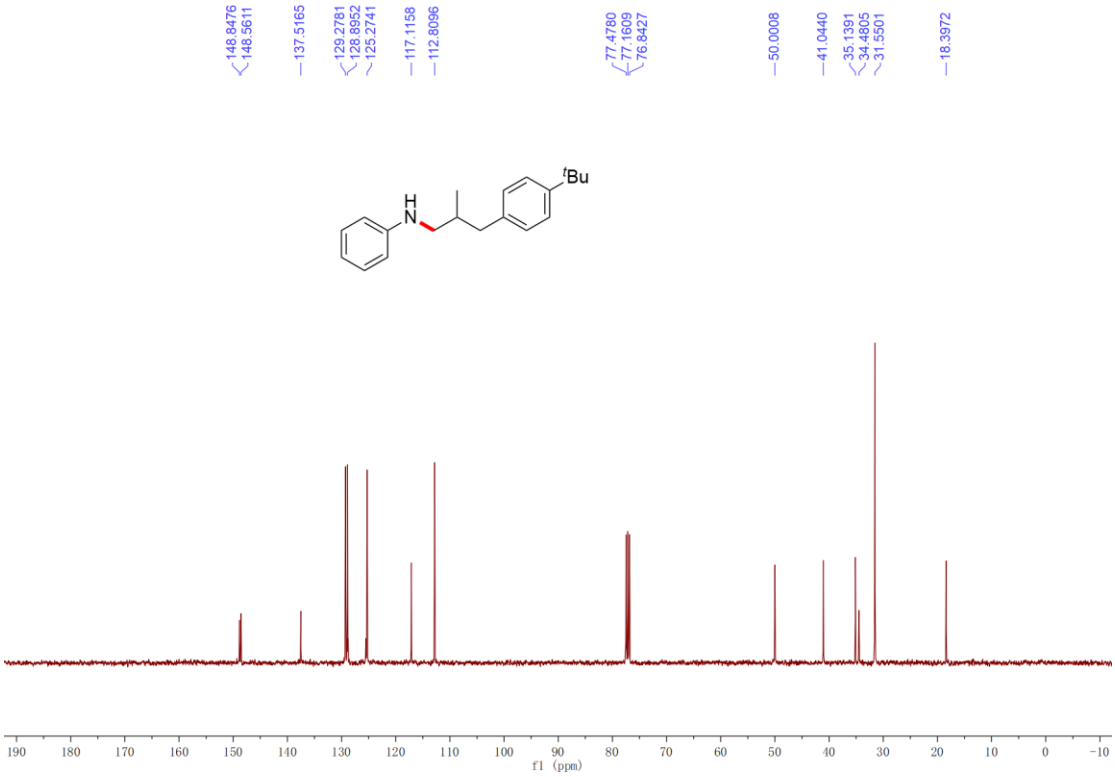

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **5ma** in $CDCl_3$.



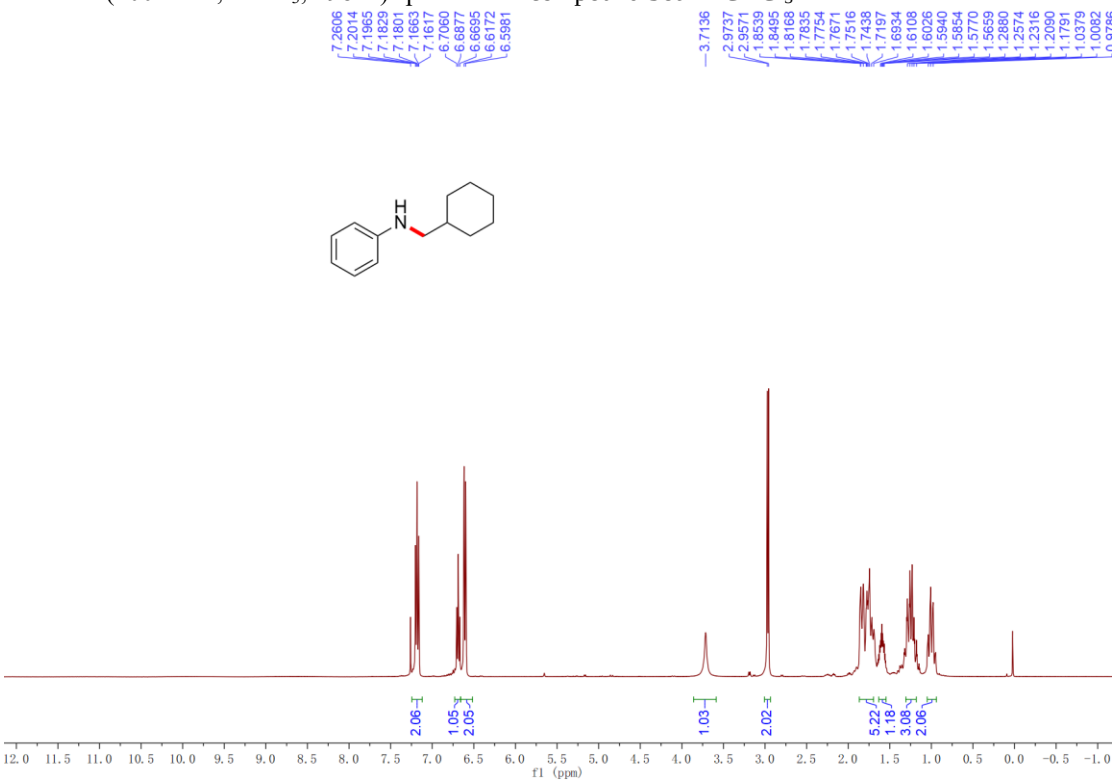
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **5na** in $CDCl_3$.



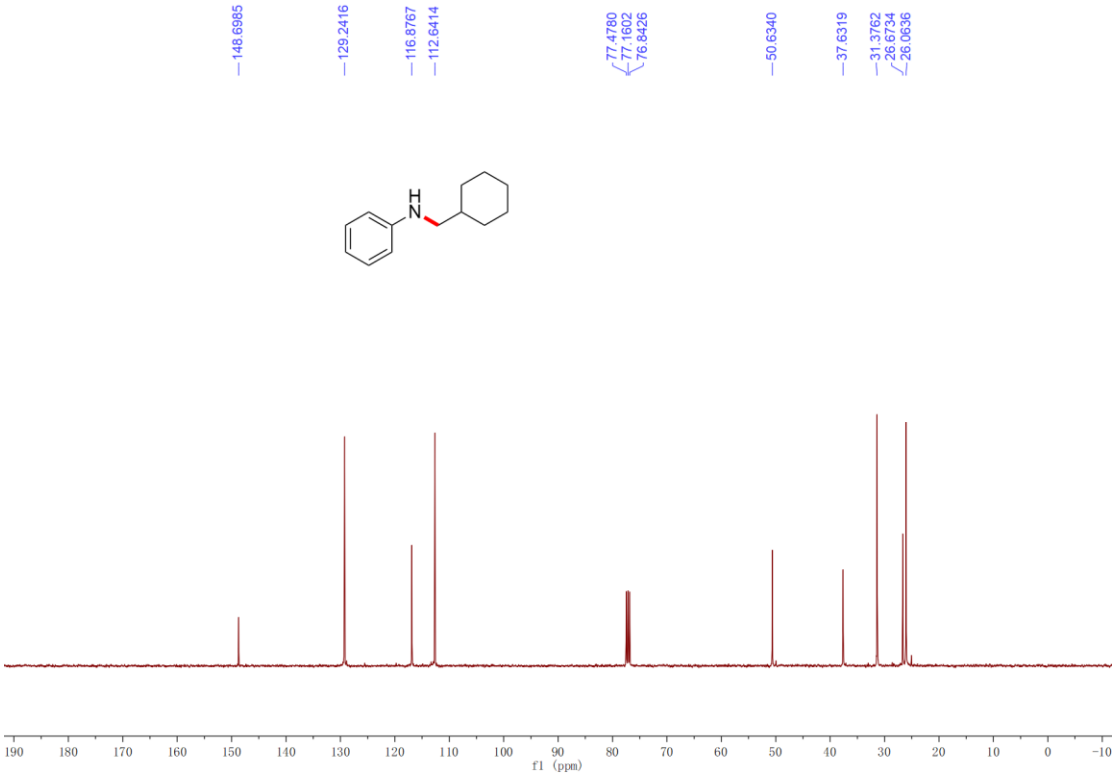

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **5na** in $CDCl_3$.



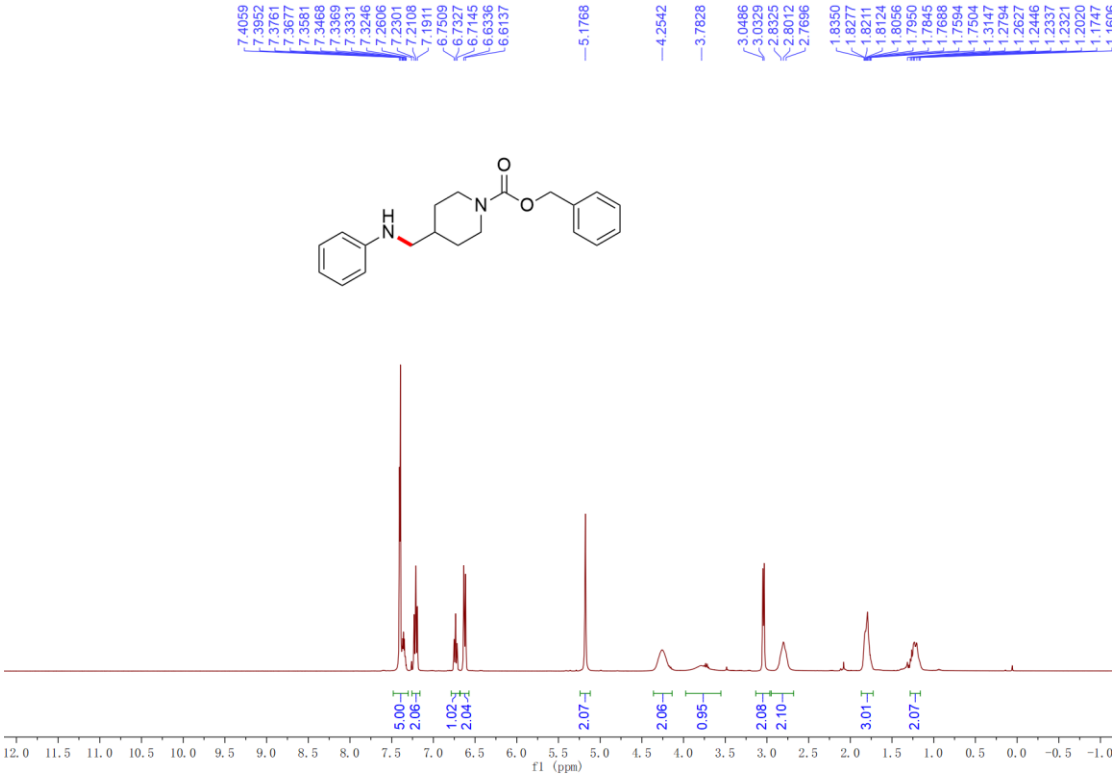
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **5oa** in $CDCl_3$.



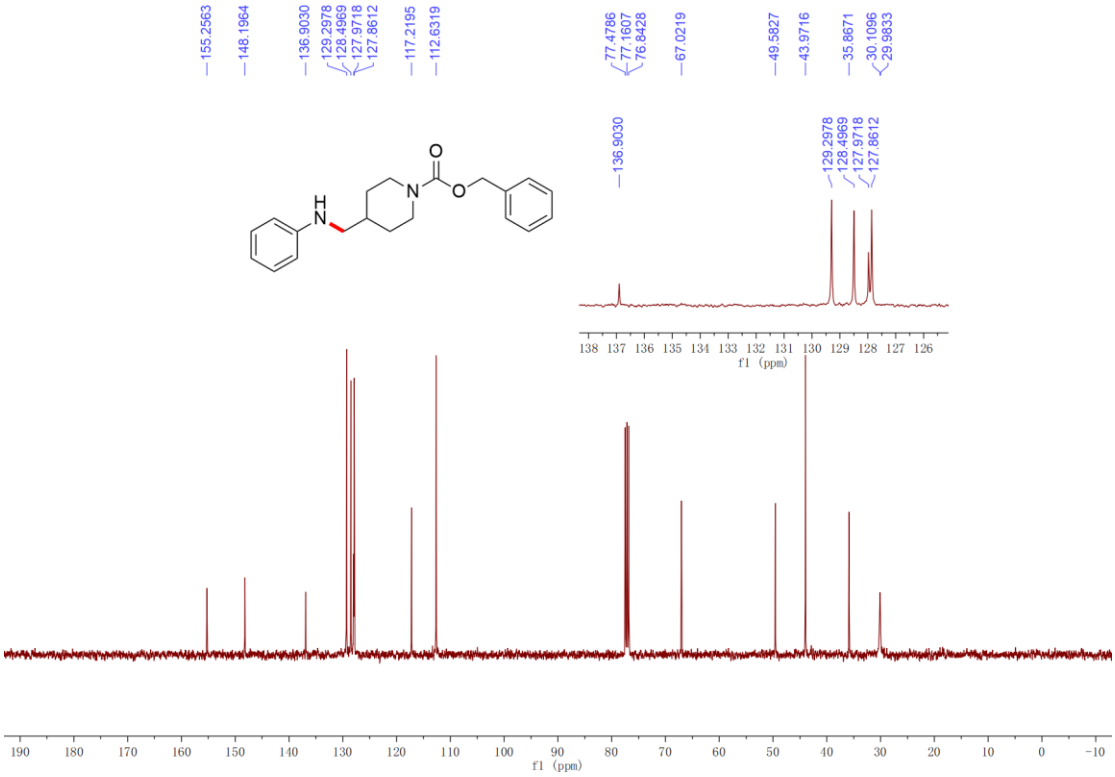

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **5oa** in $CDCl_3$.



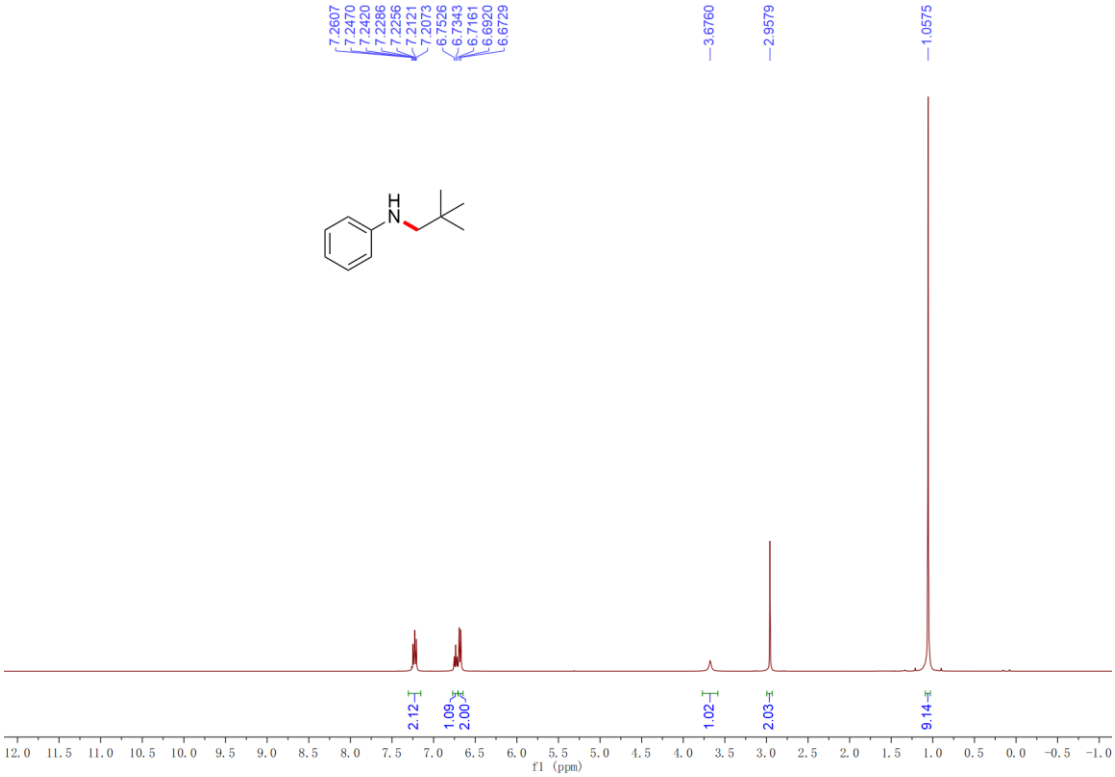
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **5pa** in $CDCl_3$.



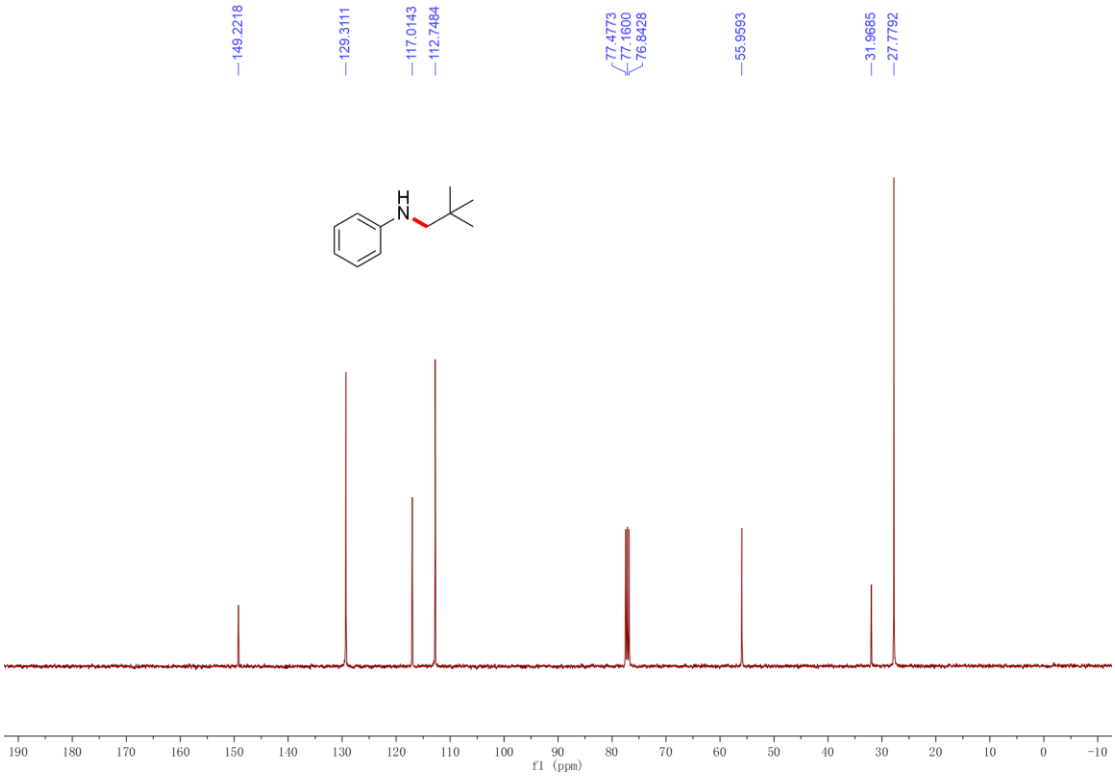

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **5pa** in $CDCl_3$.



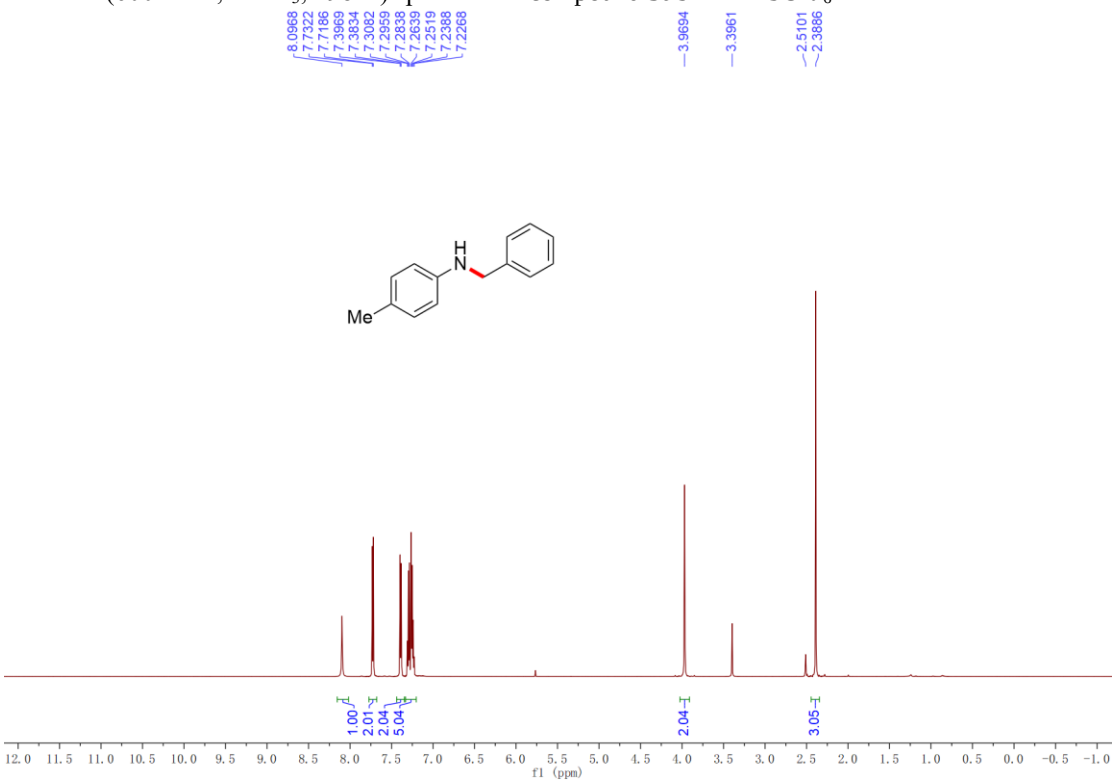
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **5qa** in $CDCl_3$.



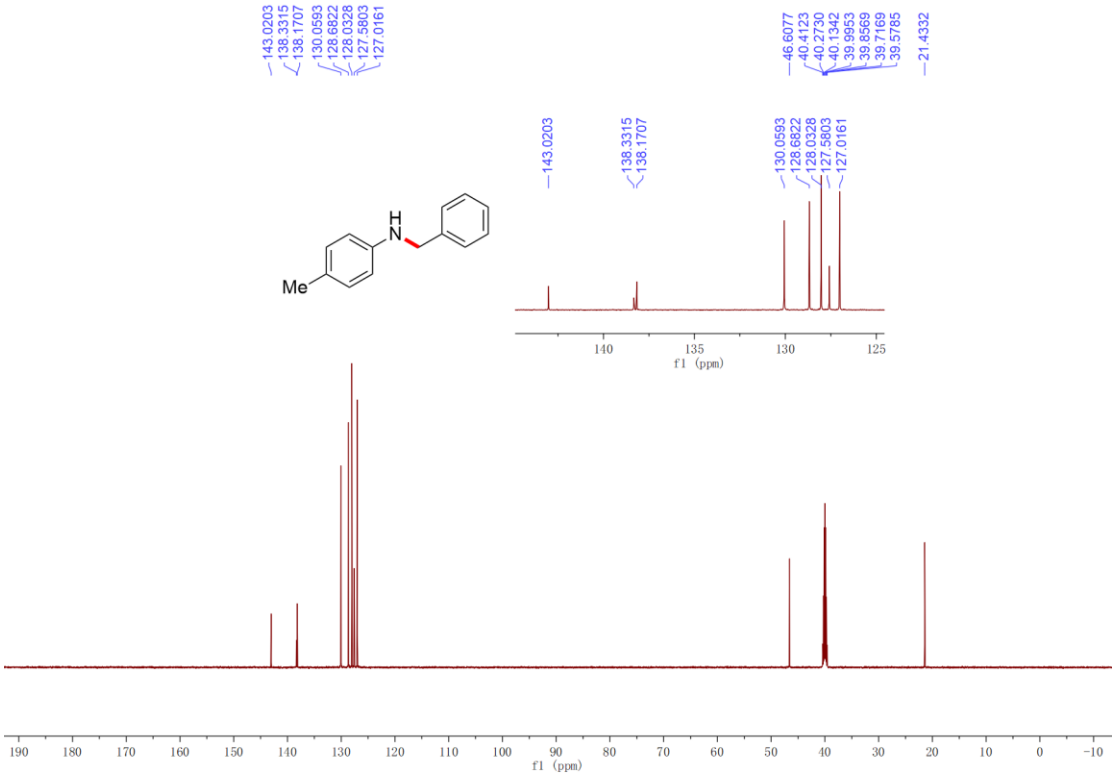

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **5qa** in $CDCl_3$.



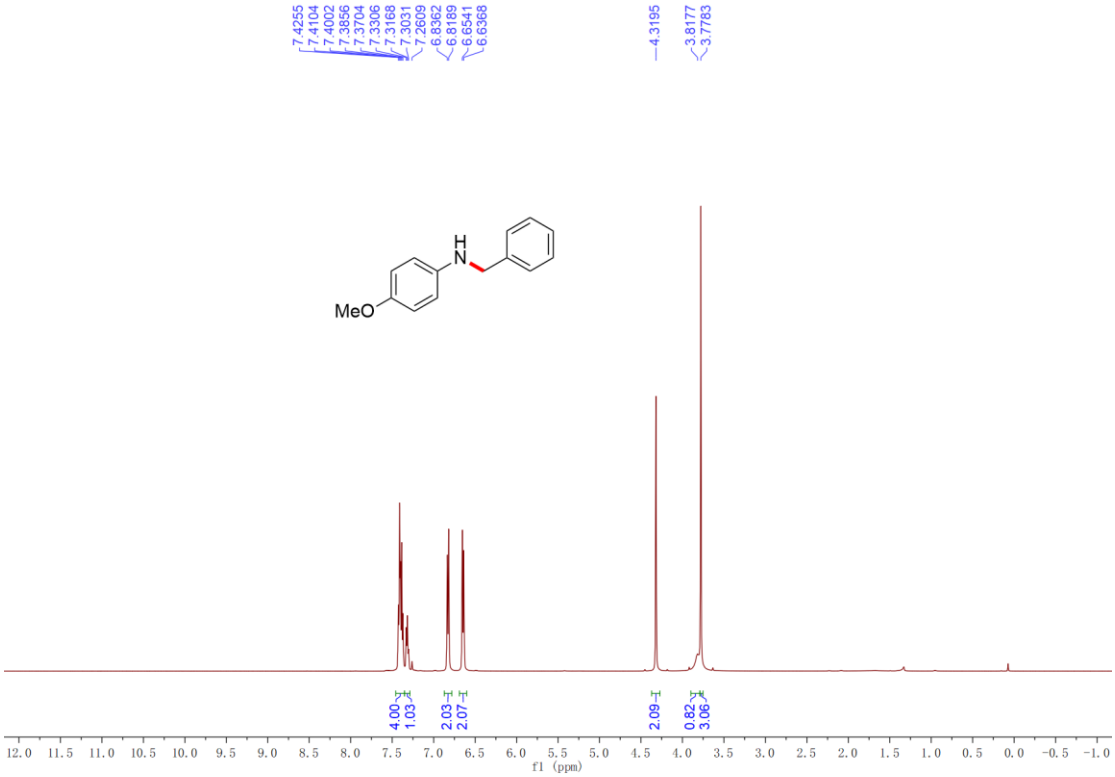
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **3ab** in DMSO-$d_6$.



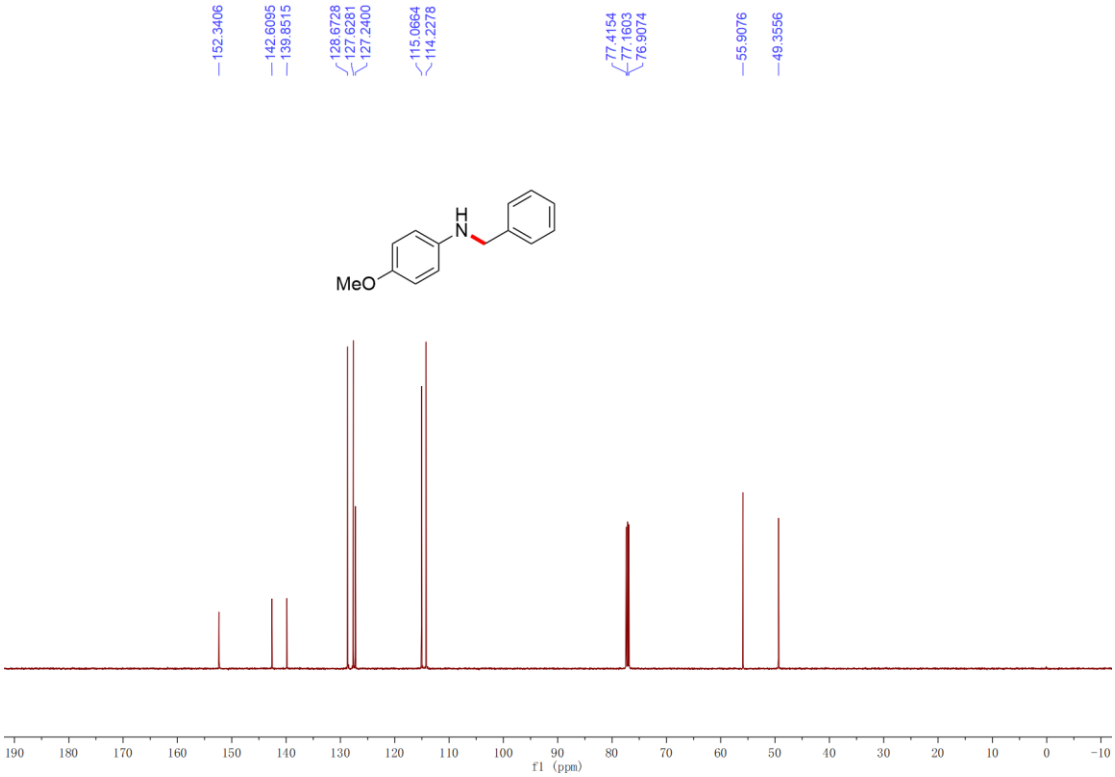

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **3ab** in DMSO-$d_6$.



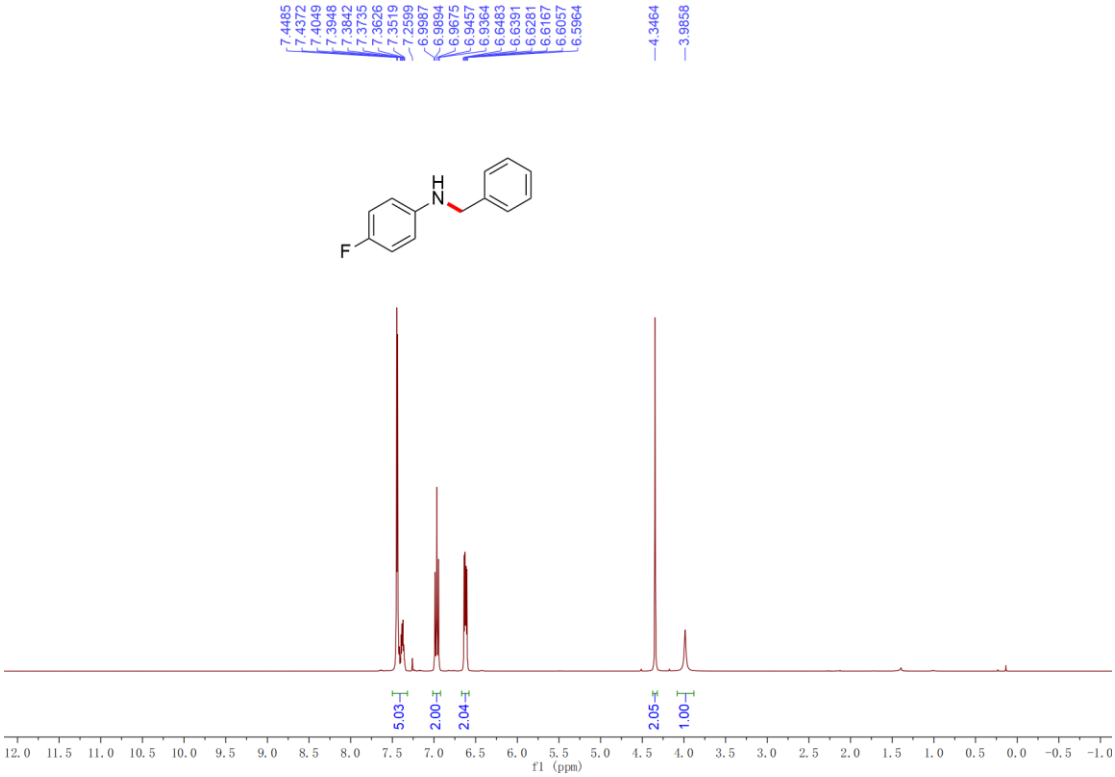
$^{1}$H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of compound **3ac** in $CDCl_3$.



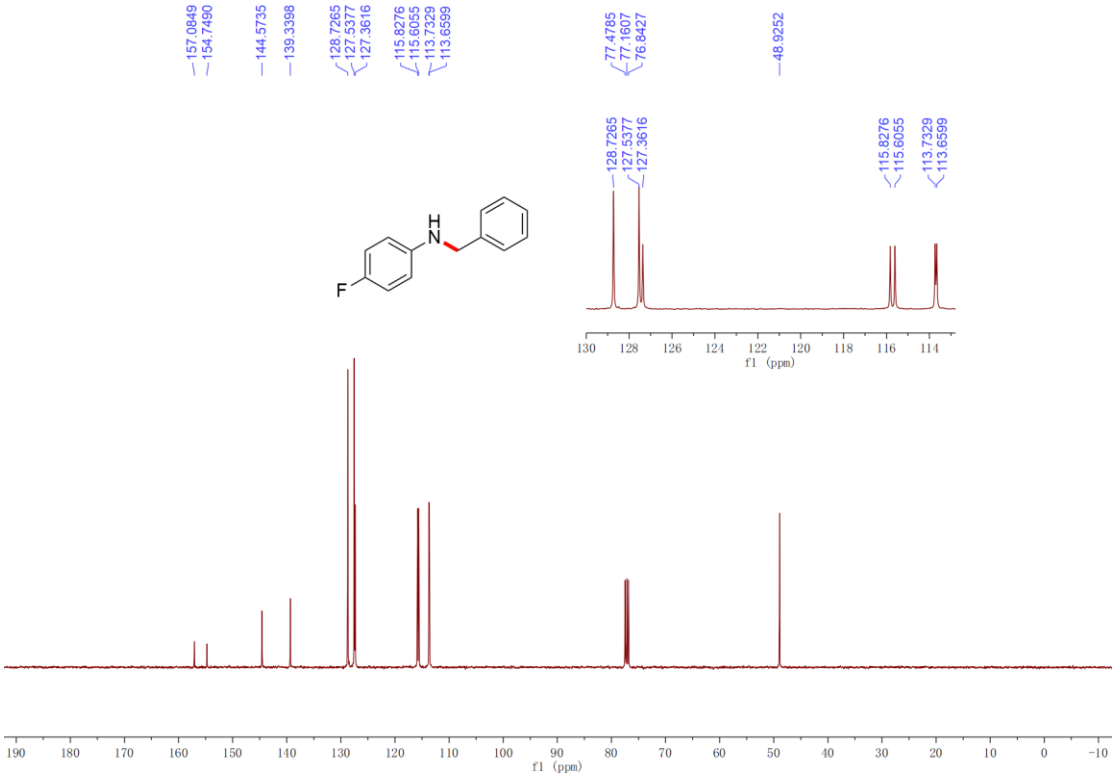

$^{13}$C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of compound **3ac** in $CDCl_3$.



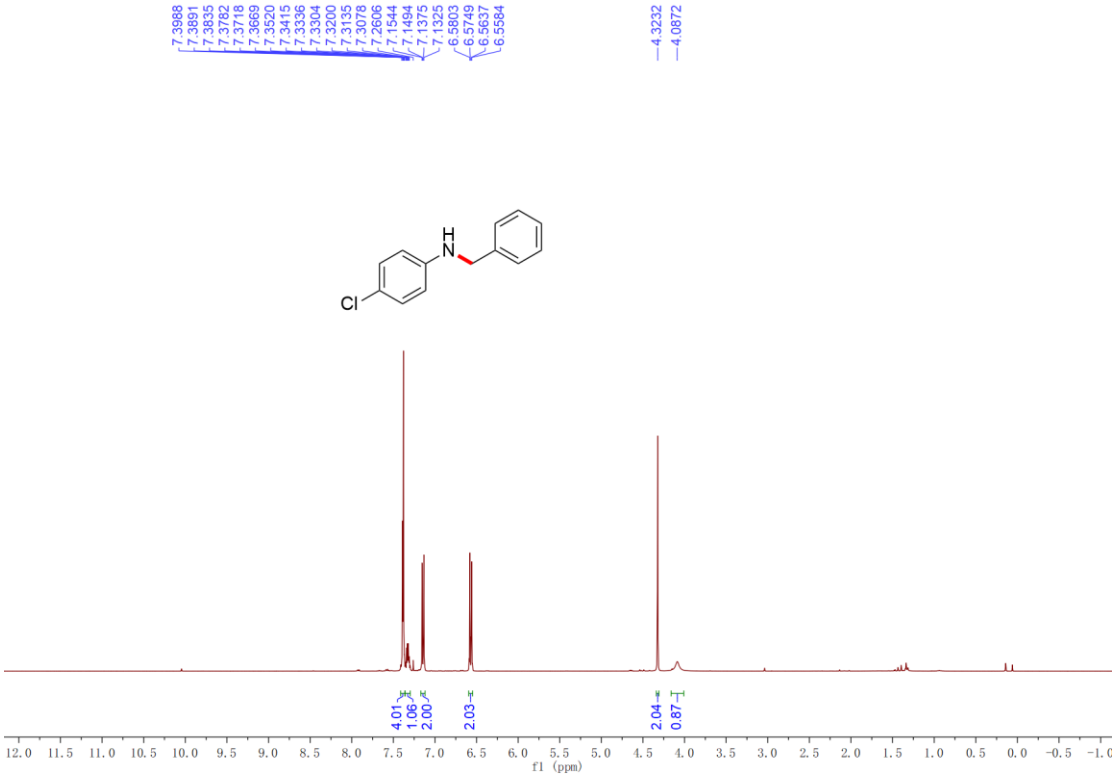
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3ad** in $CDCl_3$.



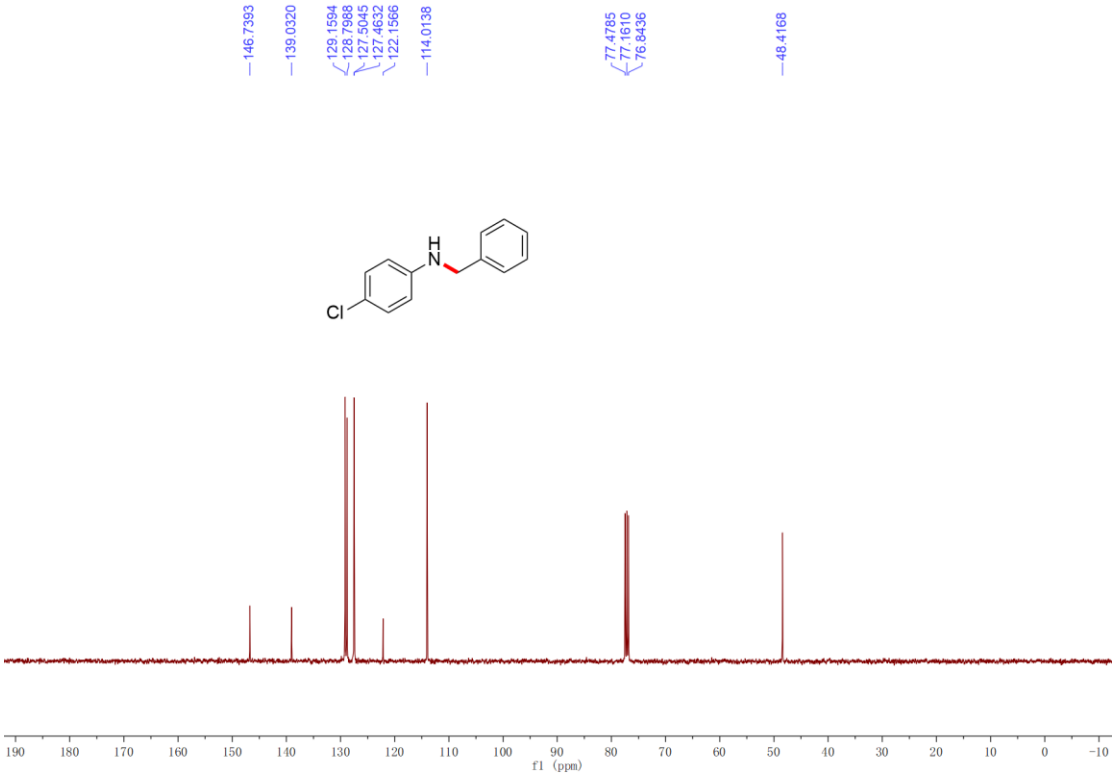

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3ad** in $CDCl_3$.



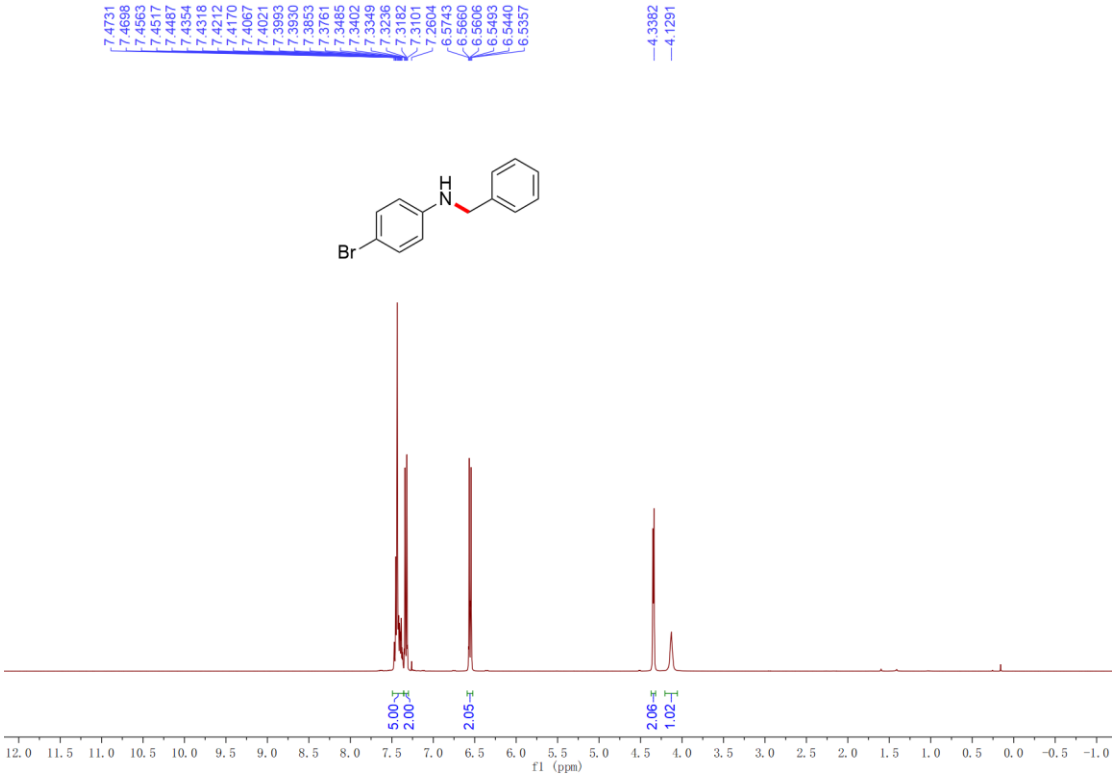
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3ae** in $CDCl_3$.



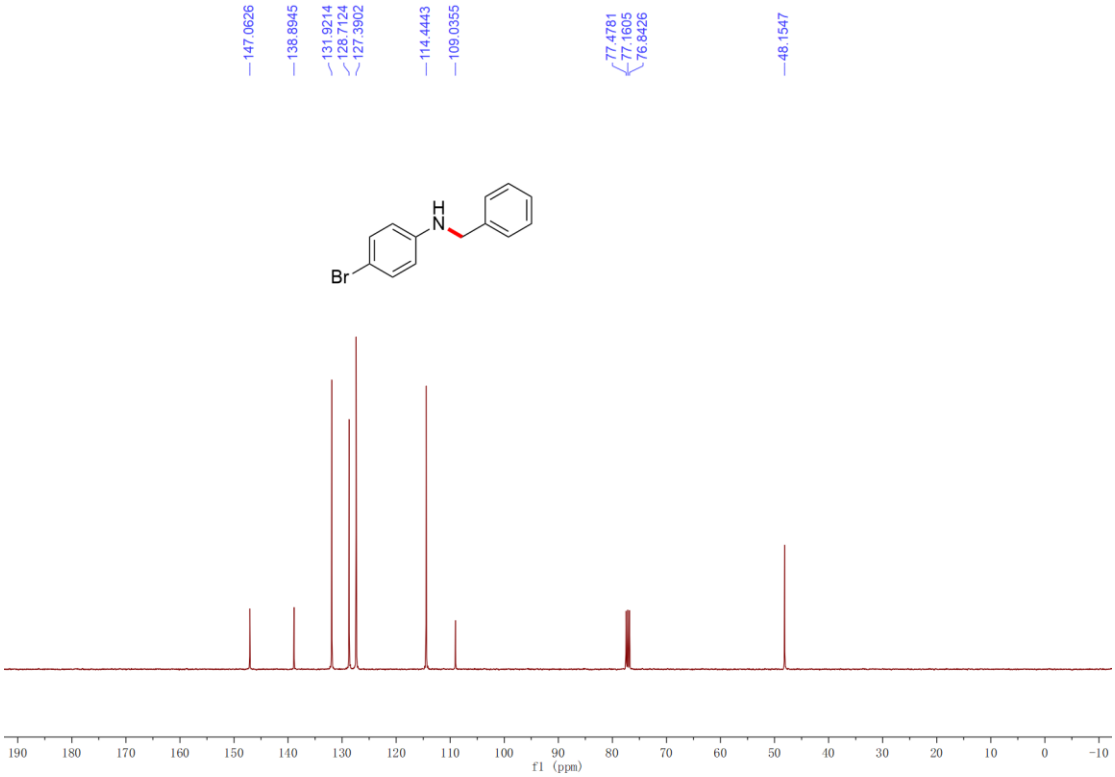

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3ae** in $CDCl_3$.



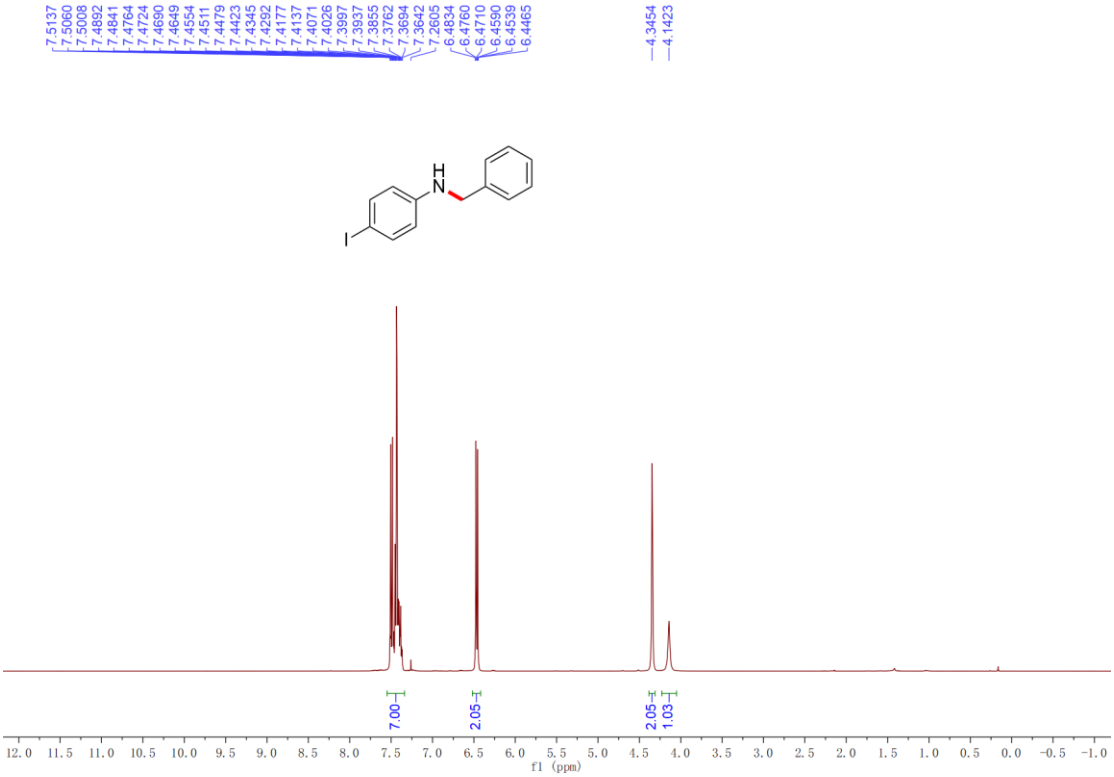
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3af** in $CDCl_3$.



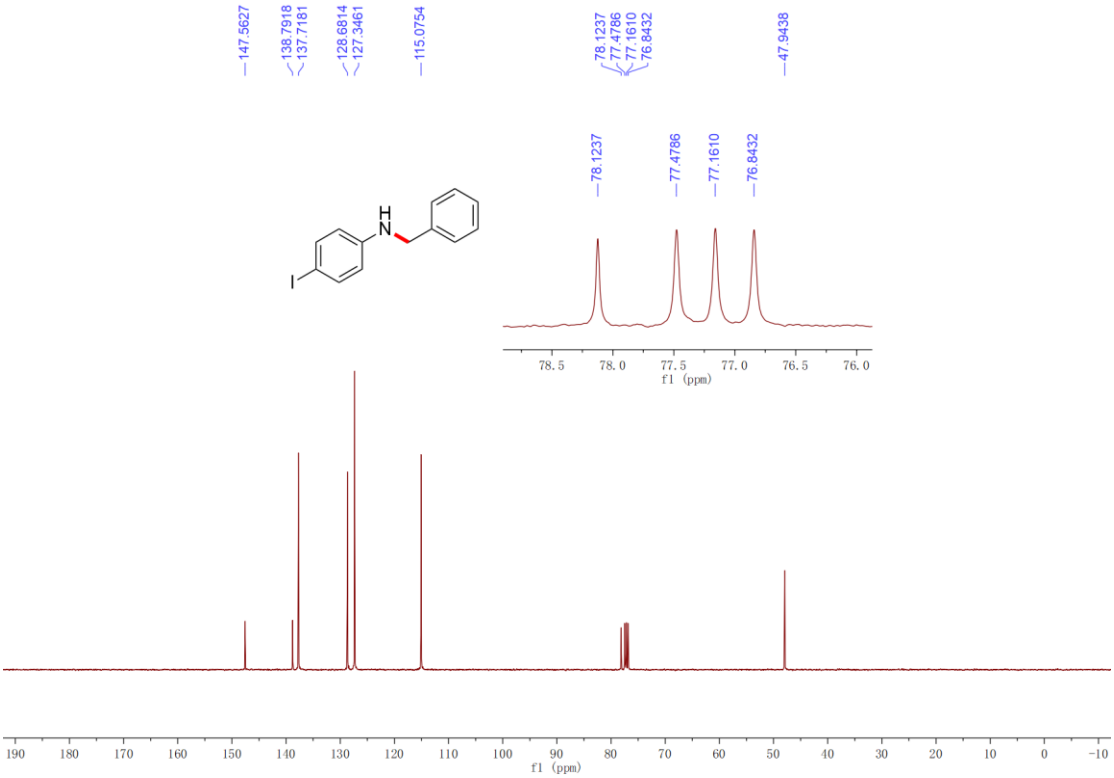

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3af** in $CDCl_3$.



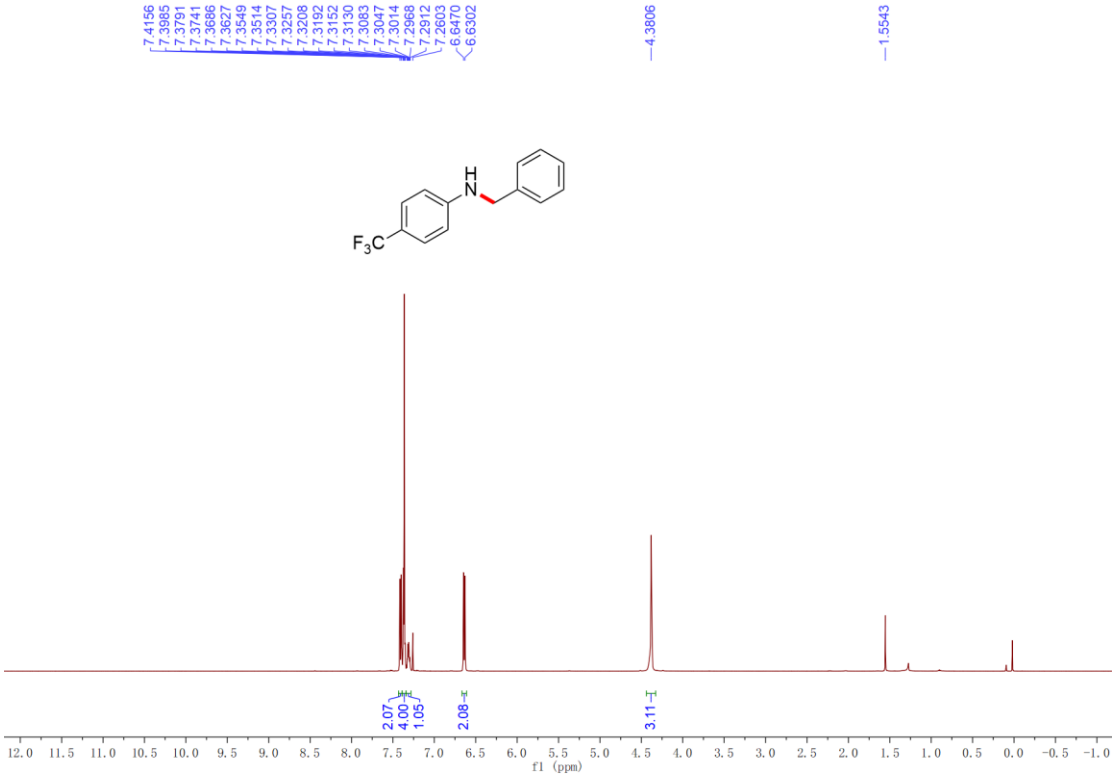
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3ag** in $CDCl_3$.



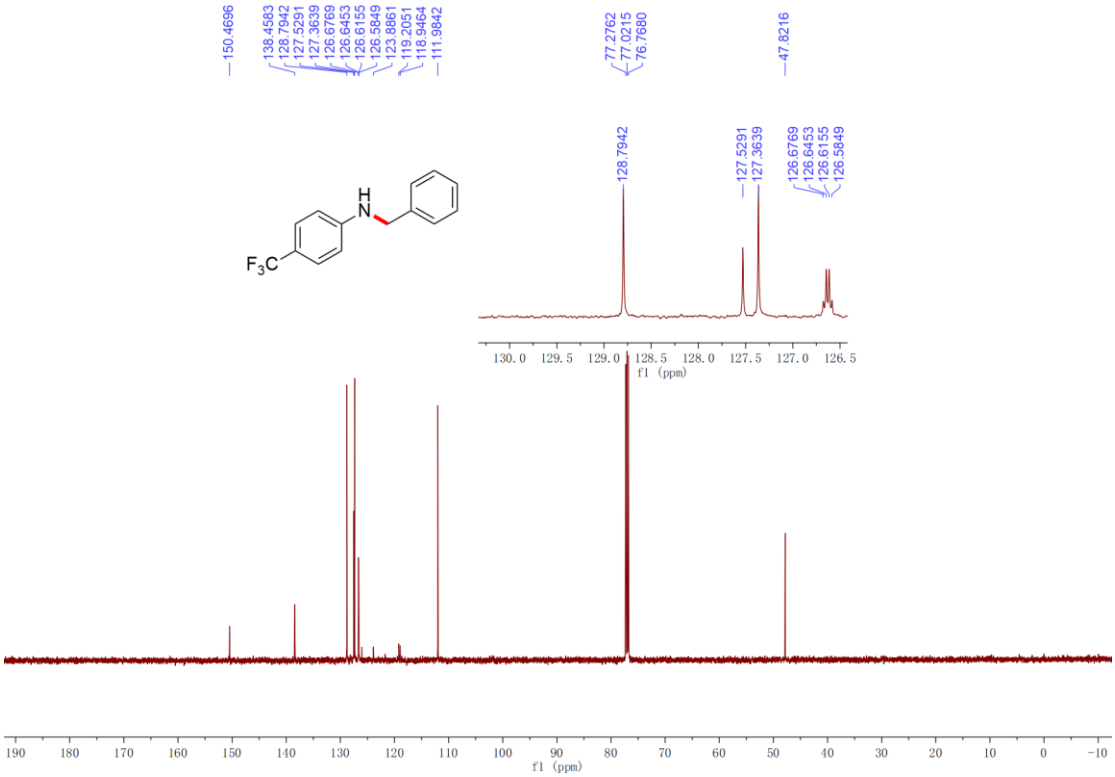

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3ag** in $CDCl_3$.



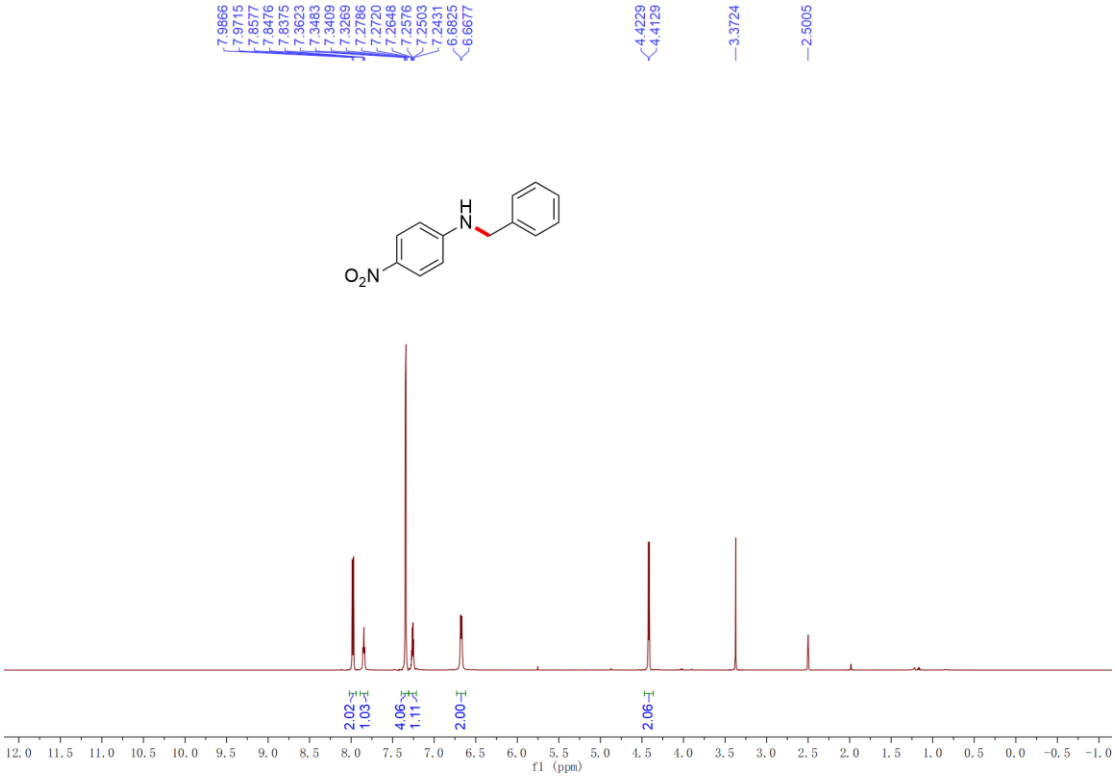
$^{1}$H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of compound **3ah** in $CDCl_3$.



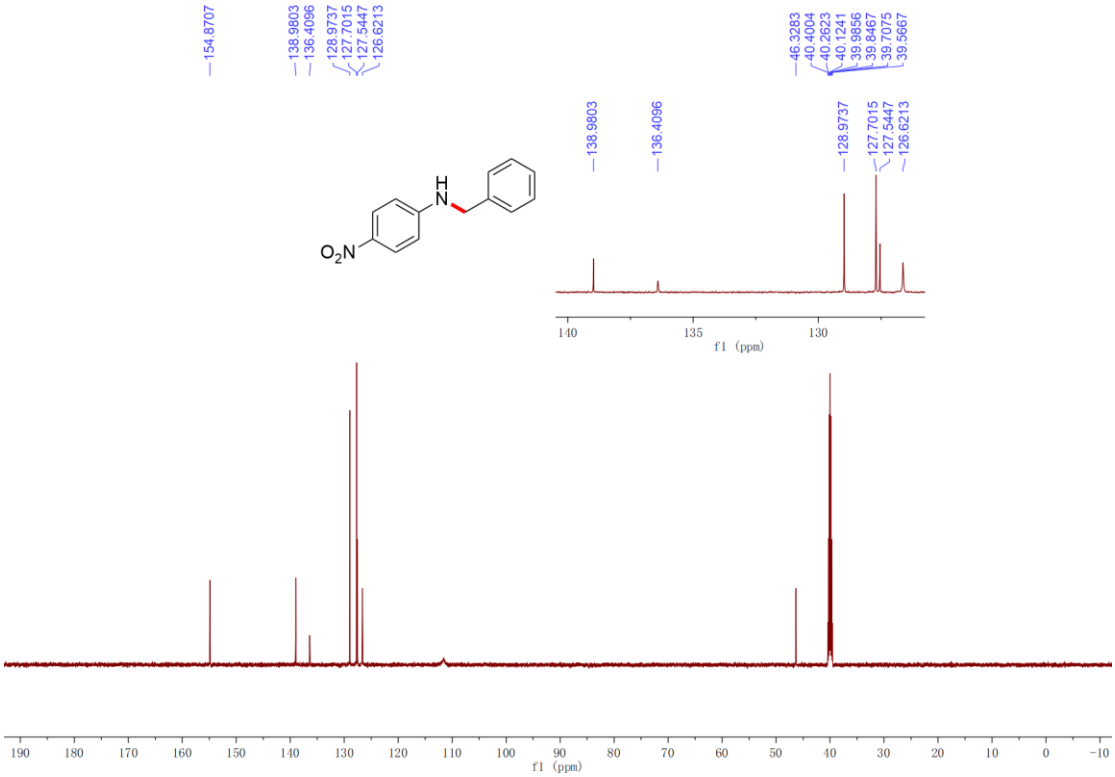

$^{13}$C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of compound **3ah** in $CDCl_3$.



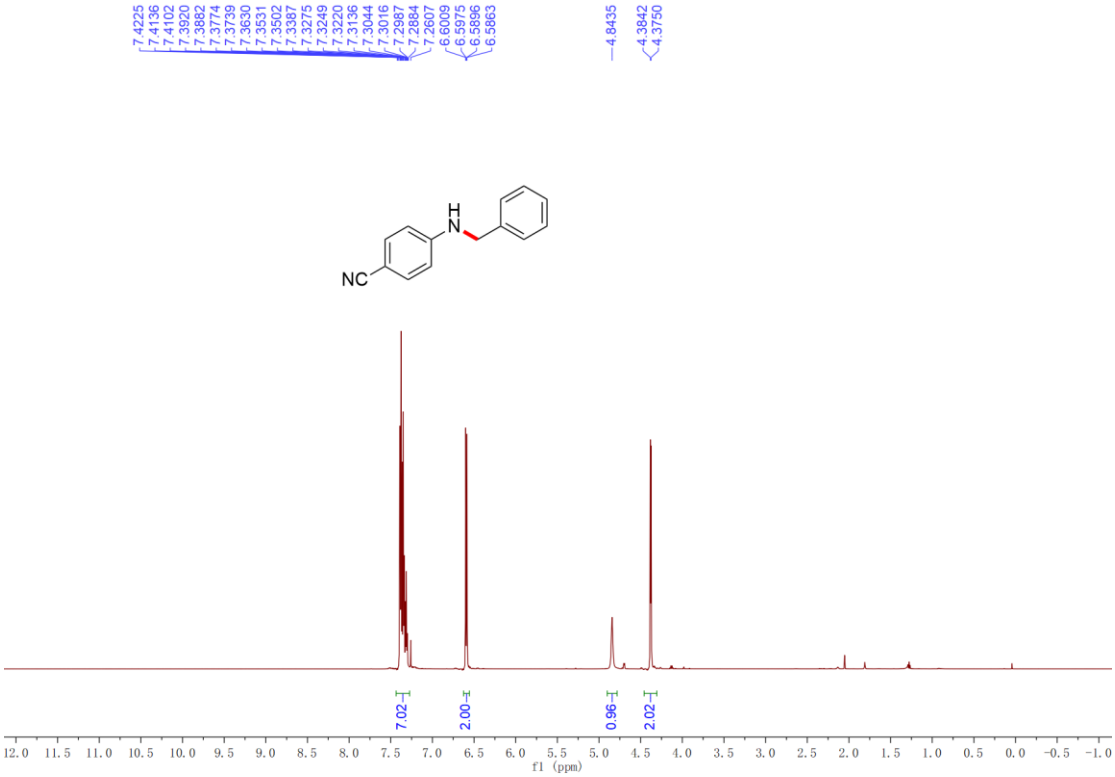
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **3ai** in DMSO-$d_6$.



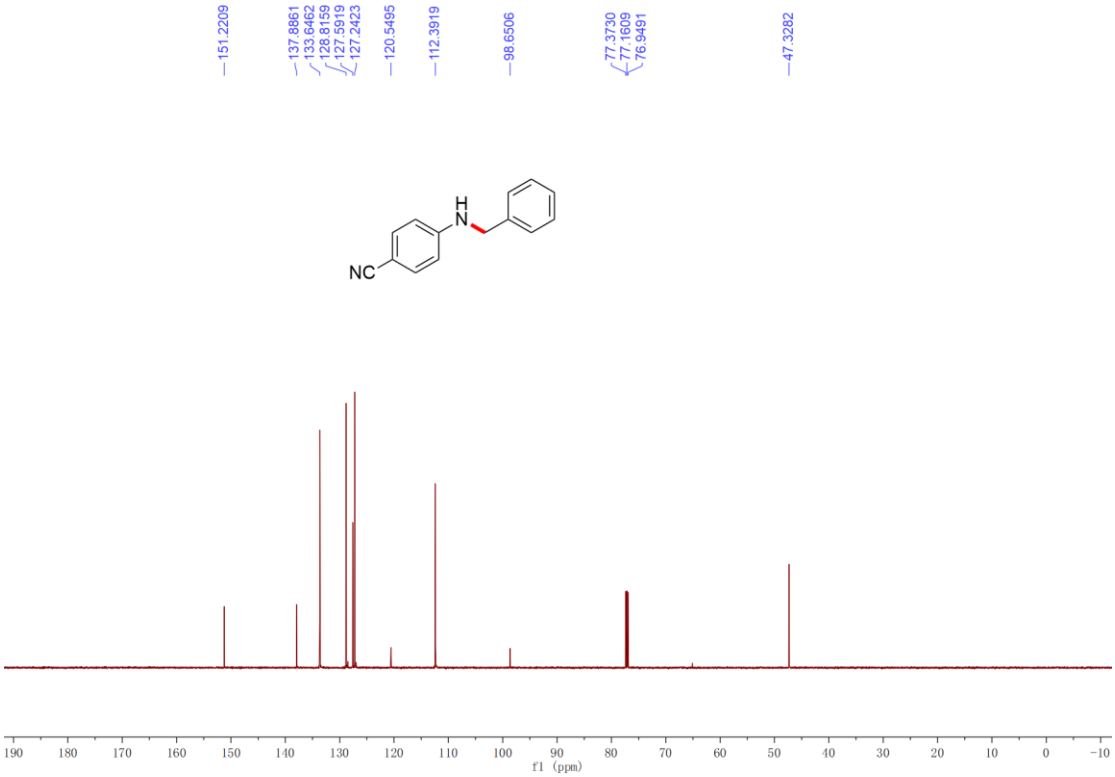

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **3ai** in DMSO-$d_6$.



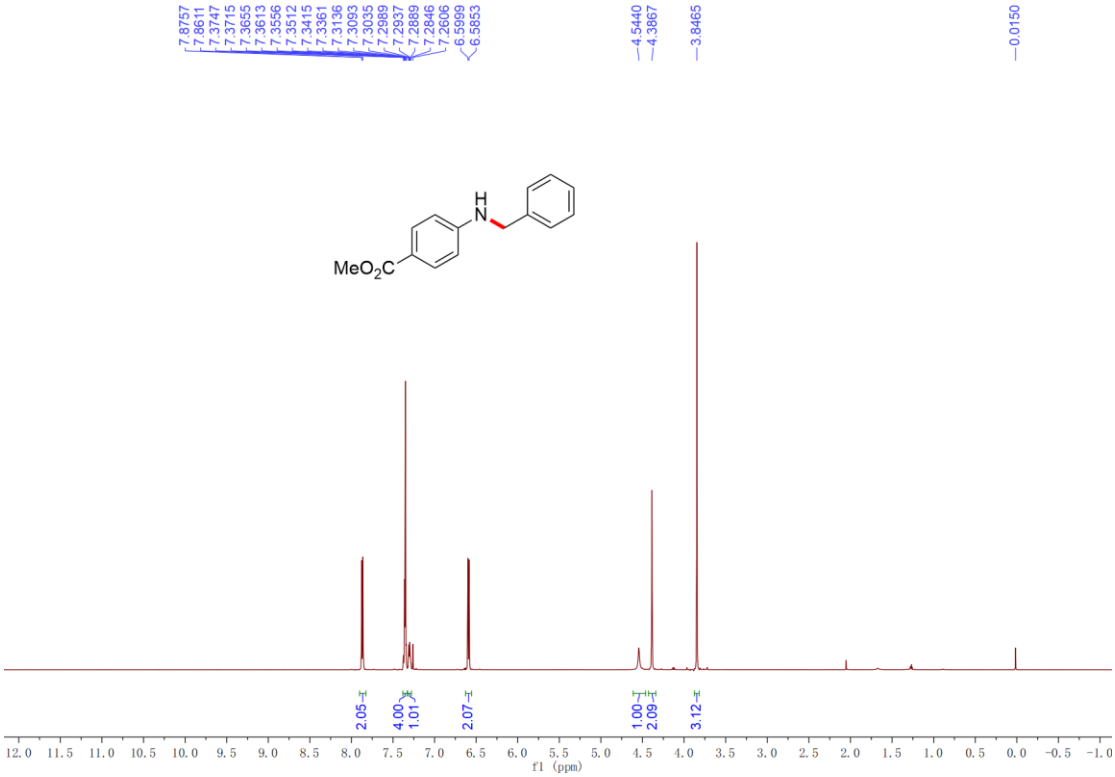
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **3aj** in $CDCl_3$.



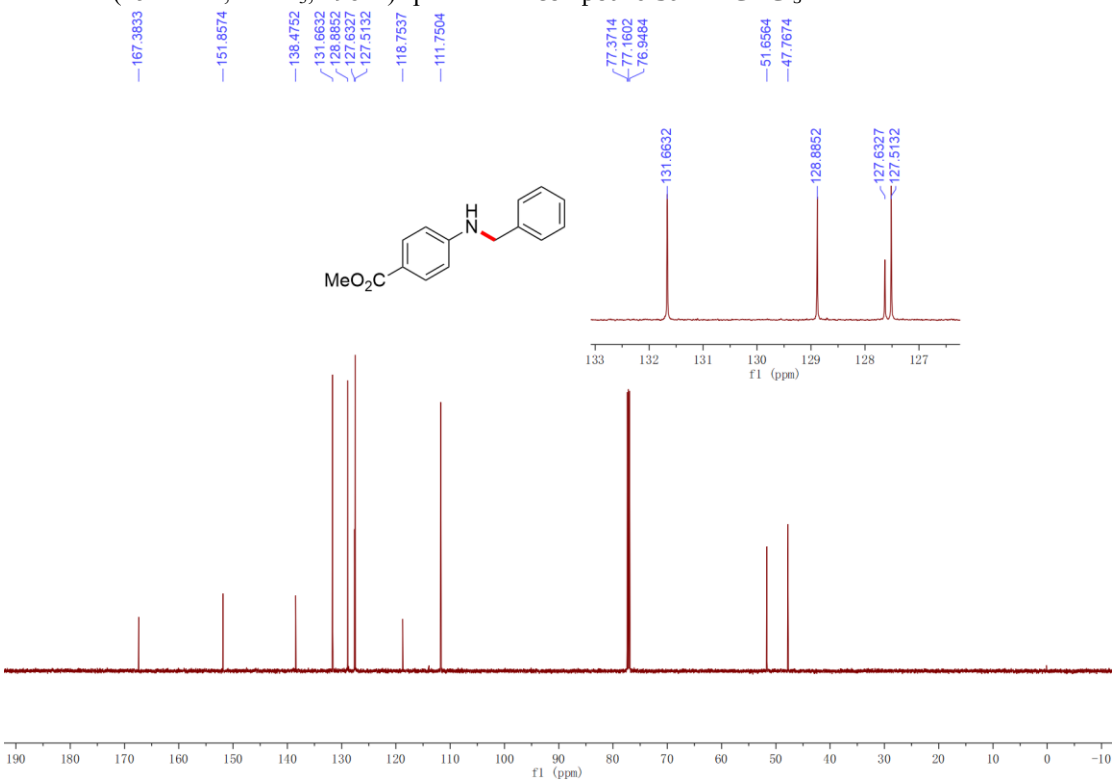

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **3aj** in $CDCl_3$.



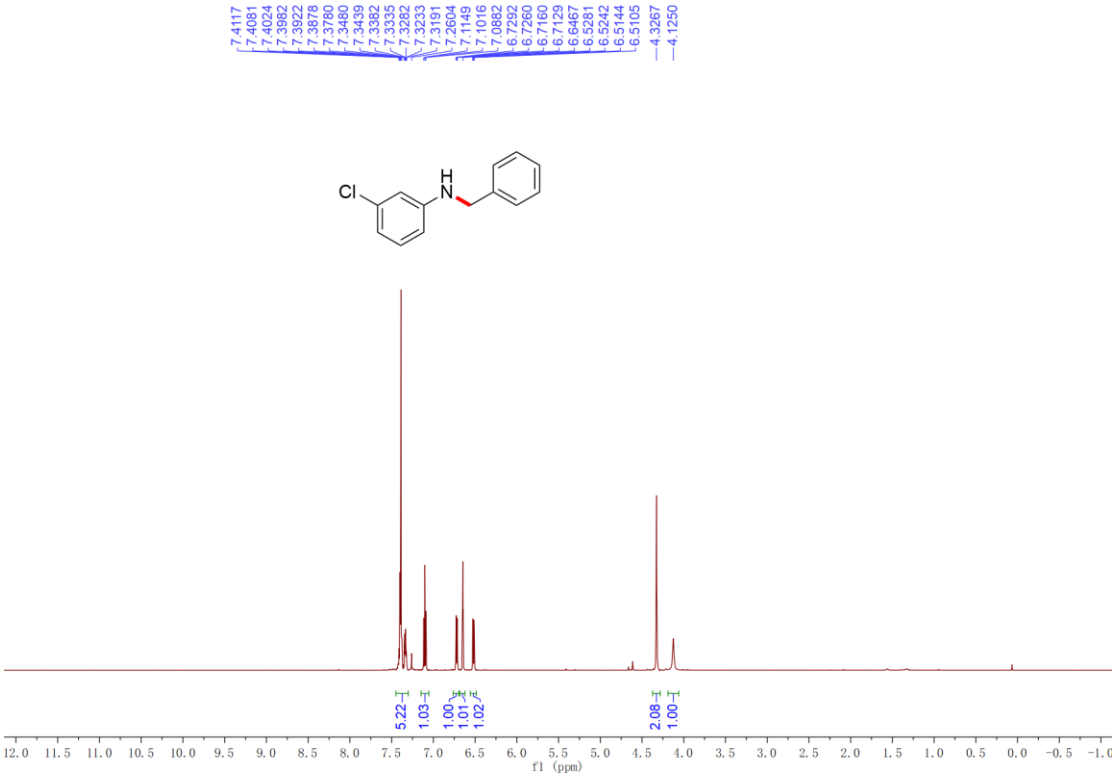
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **3ak** in $CDCl_3$.



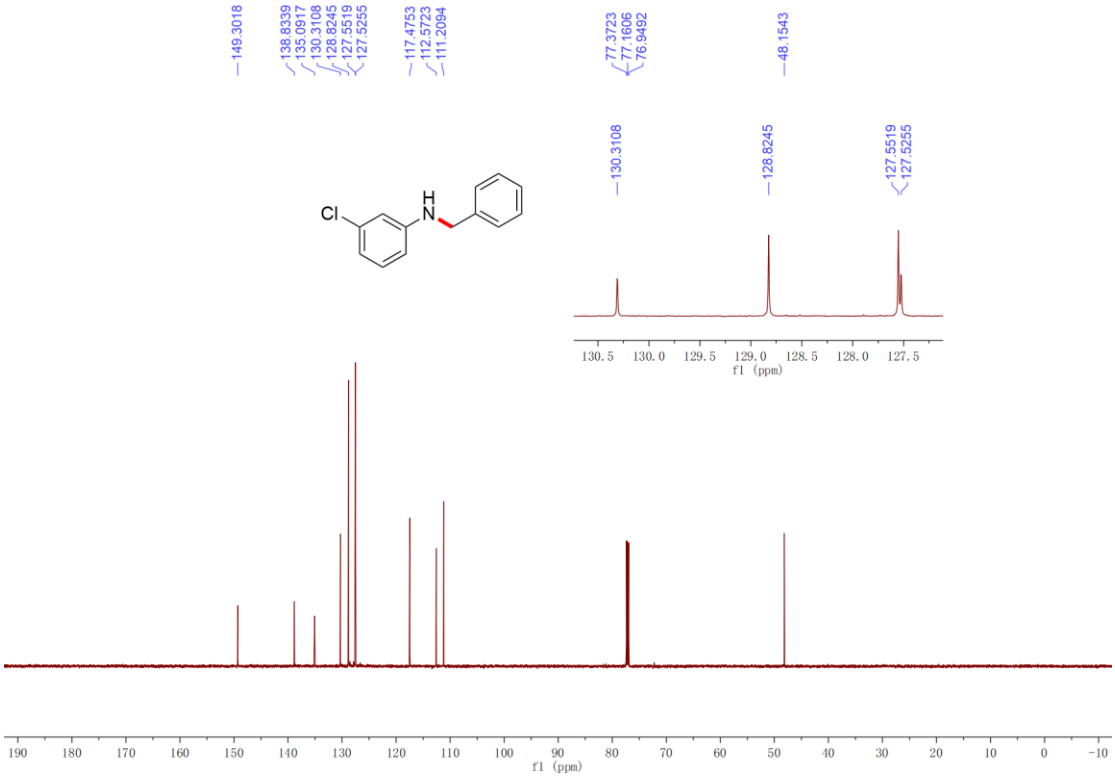

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **3ak** in $CDCl_3$.



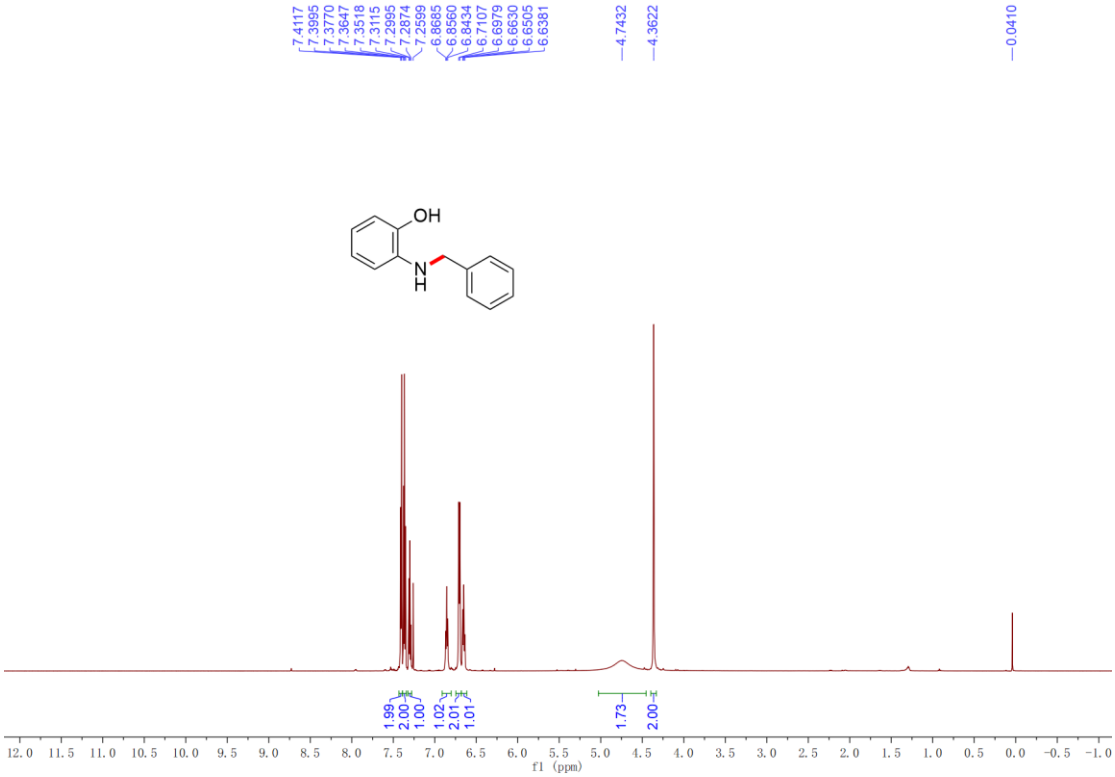
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **3al** in $CDCl_3$.



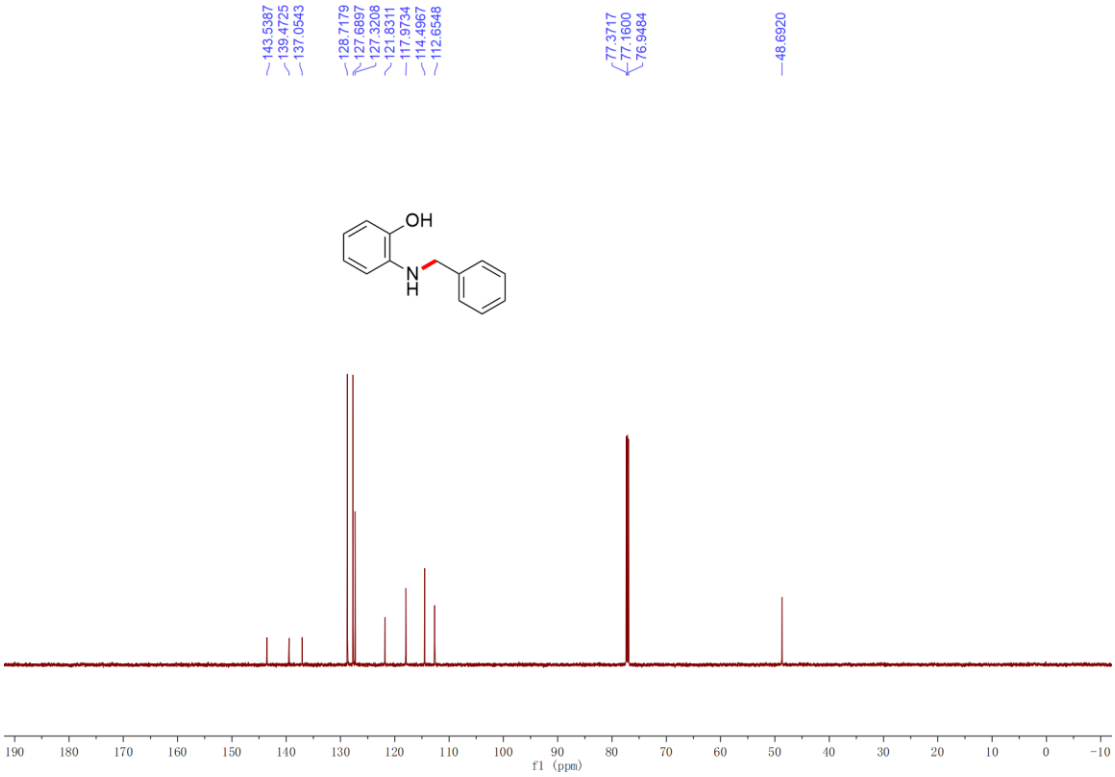

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **3al** in $CDCl_3$.



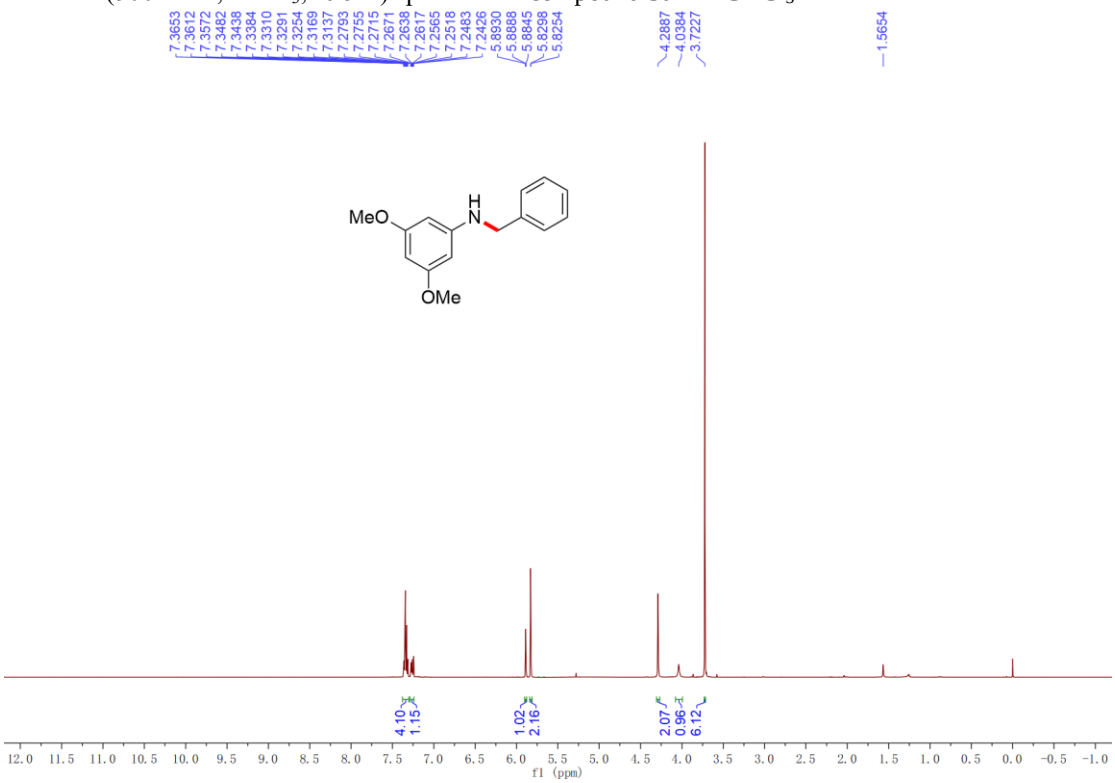
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **3am** in $CDCl_3$.



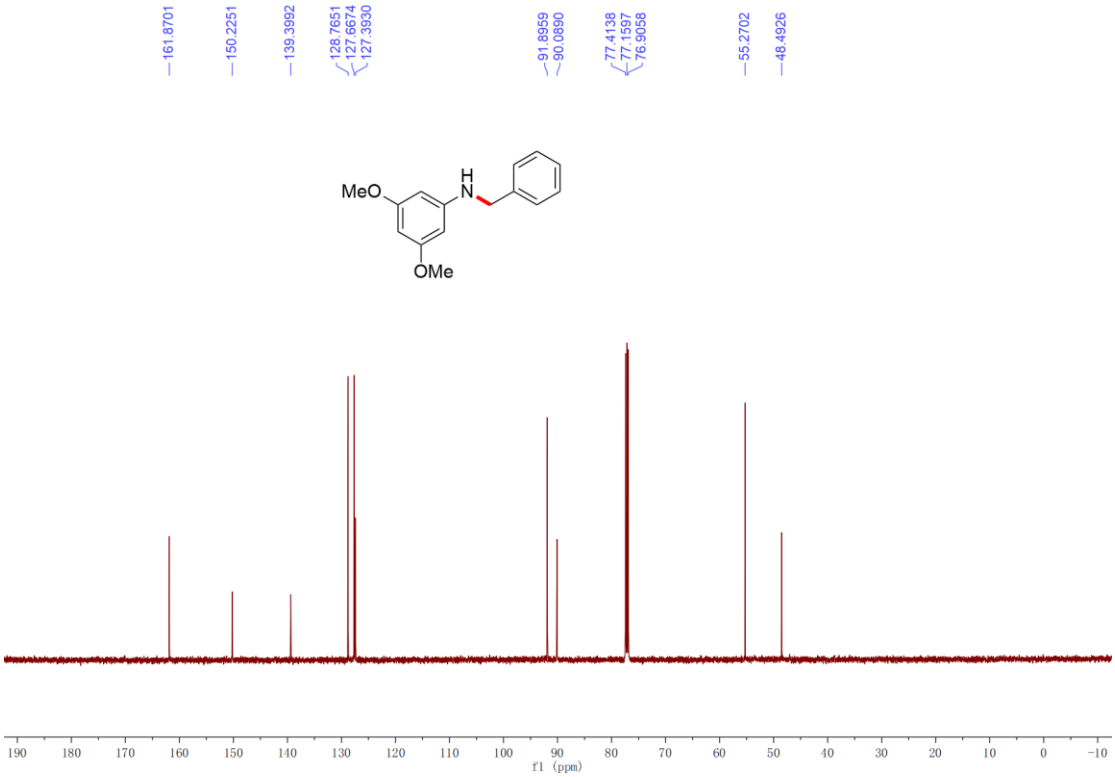

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **3am** in $CDCl_3$.



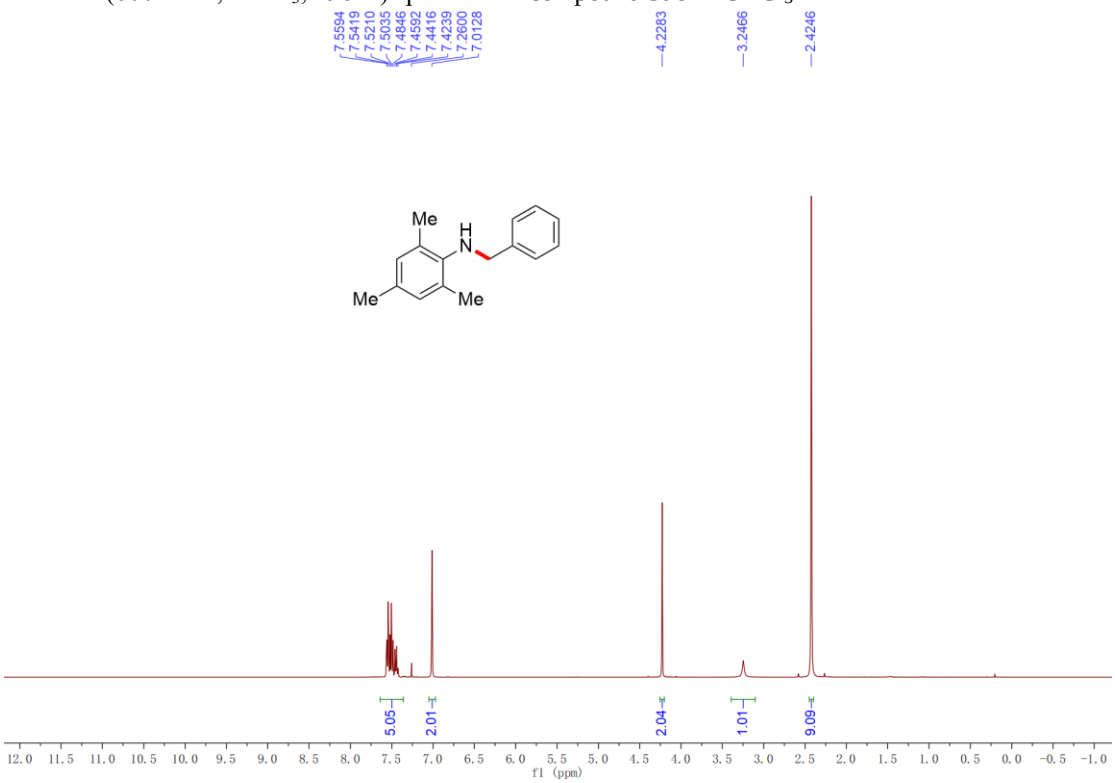
$^{1}$H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of compound **3an** in $CDCl_3$.



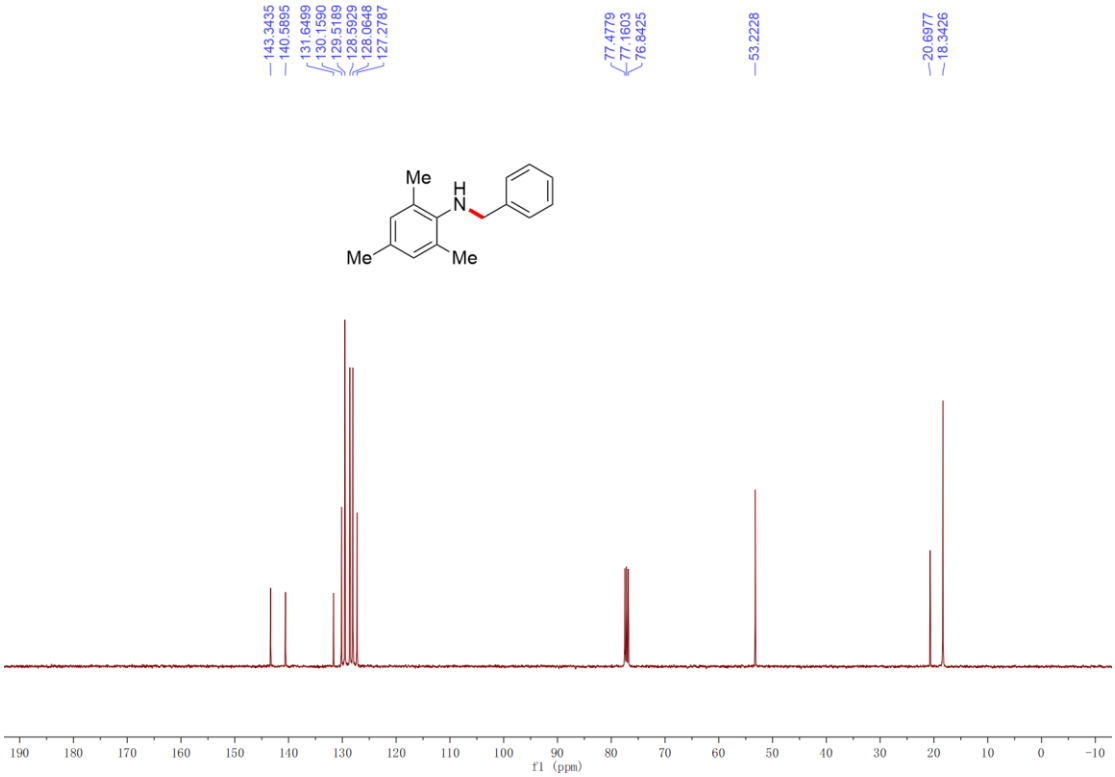

$^{13}$C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of compound **3an** in $CDCl_3$.



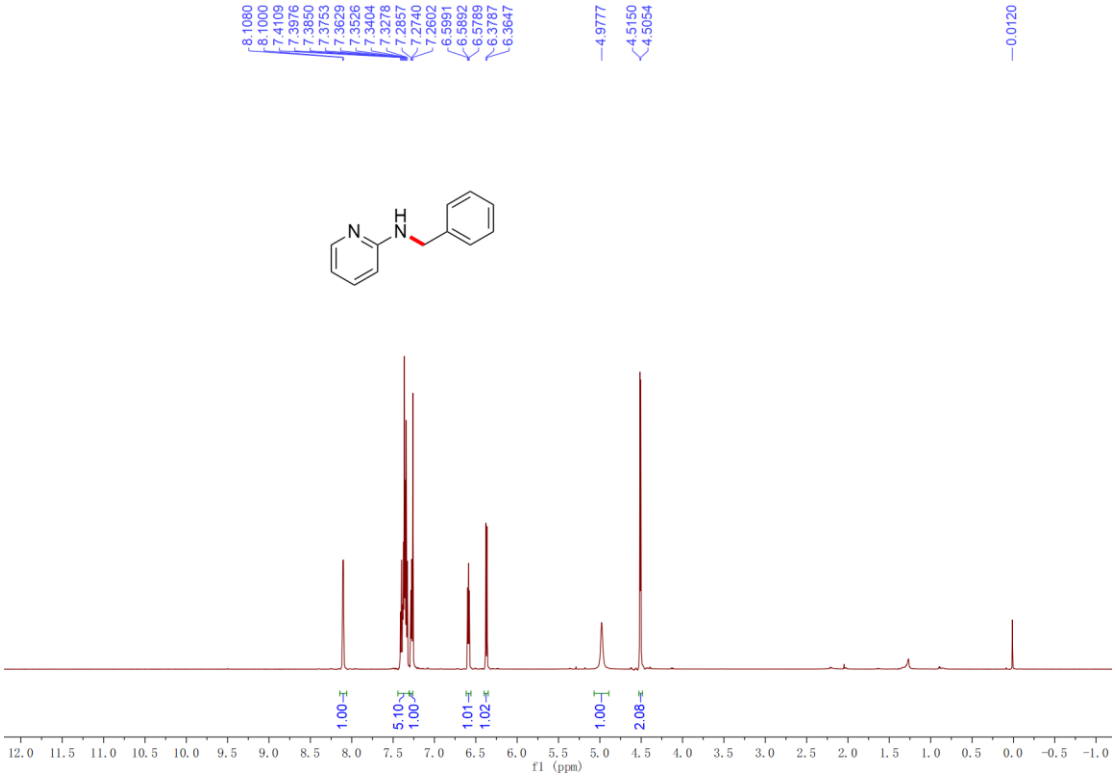
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **3ao** in $CDCl_3$.



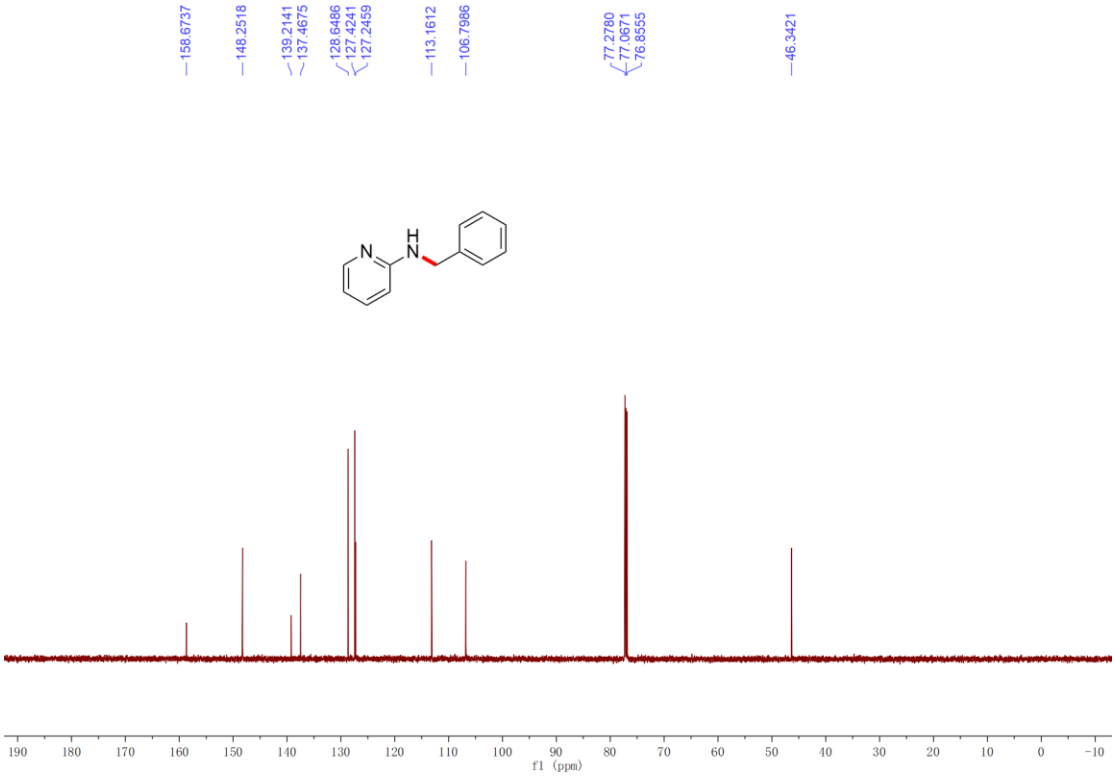

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **3ao** in $CDCl_3$.



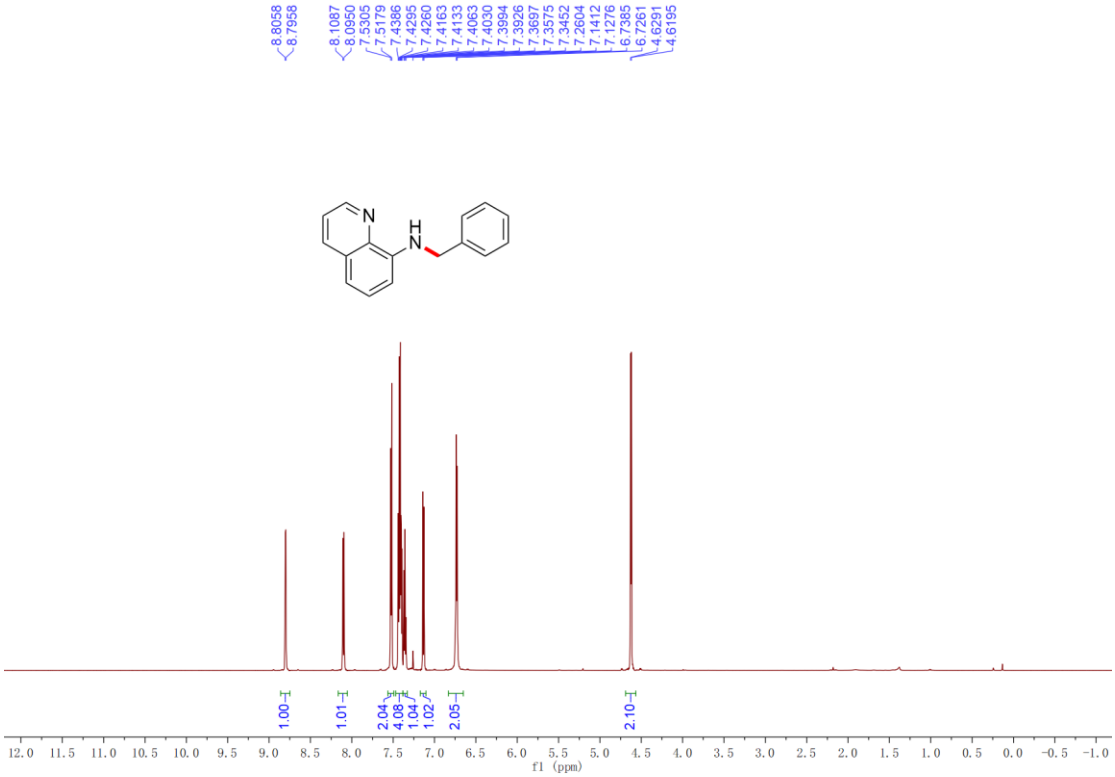
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **3ap** in $CDCl_3$.



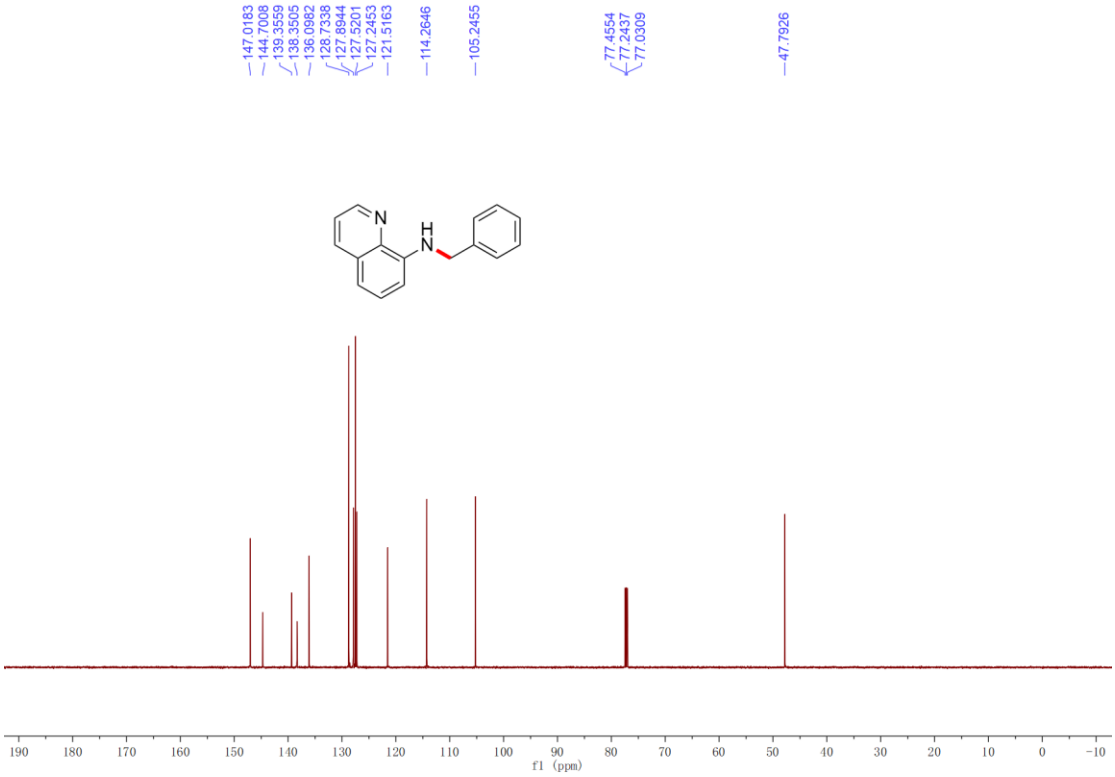

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **3ap** in $CDCl_3$.



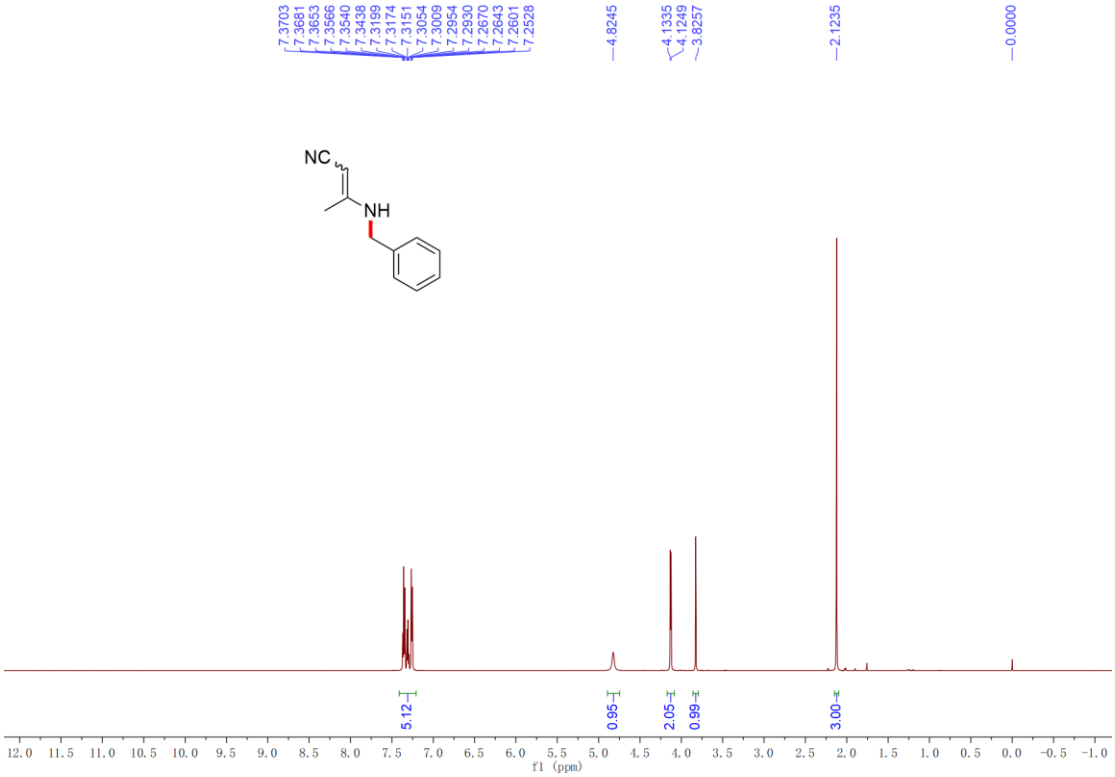
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **3aq** in $CDCl_3$.



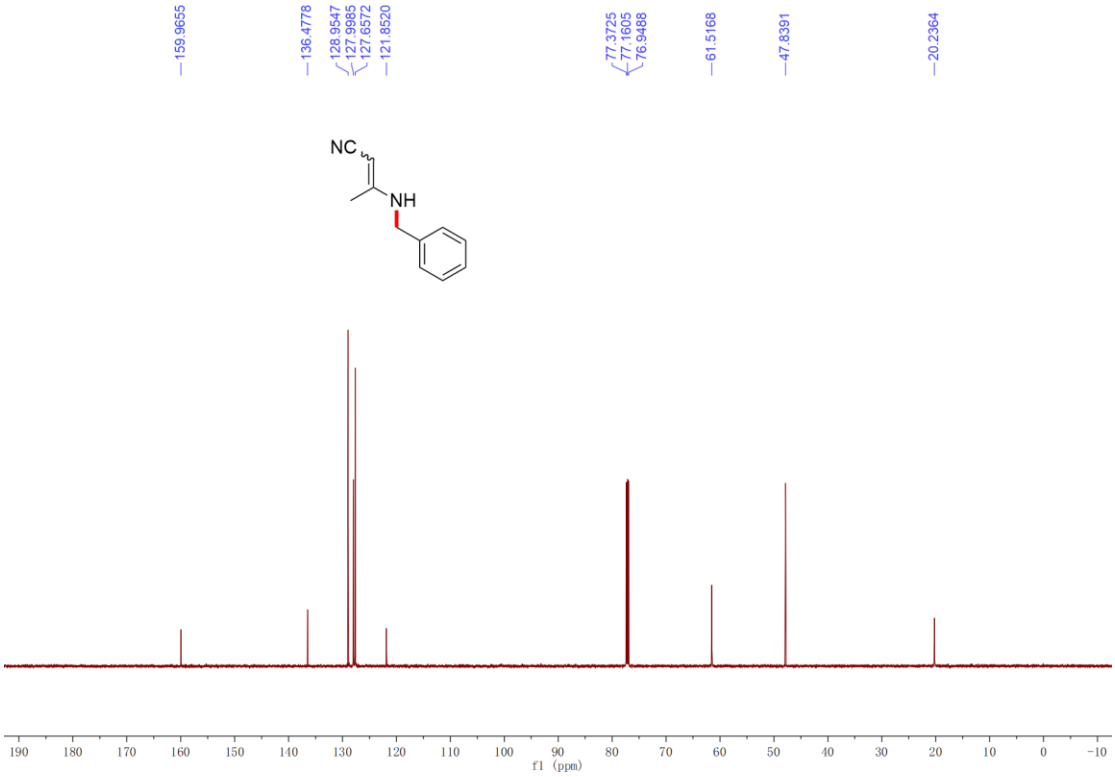

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **3aq** in $CDCl_3$.



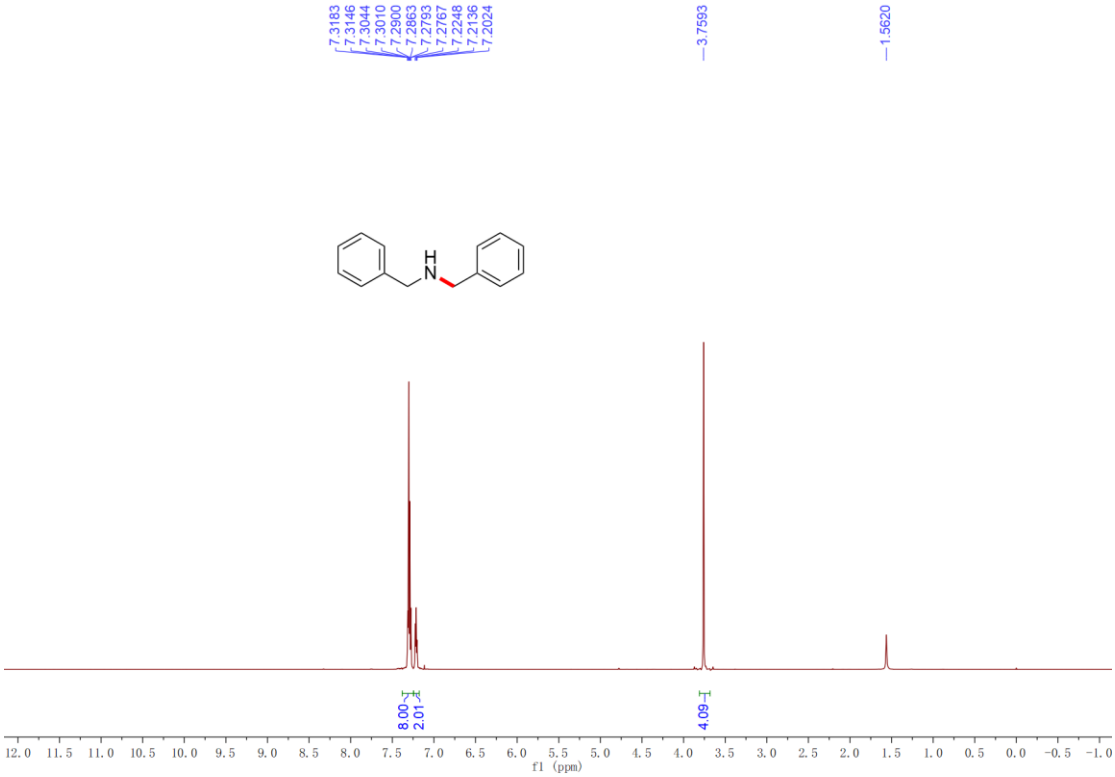
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **3ar** in $CDCl_3$.



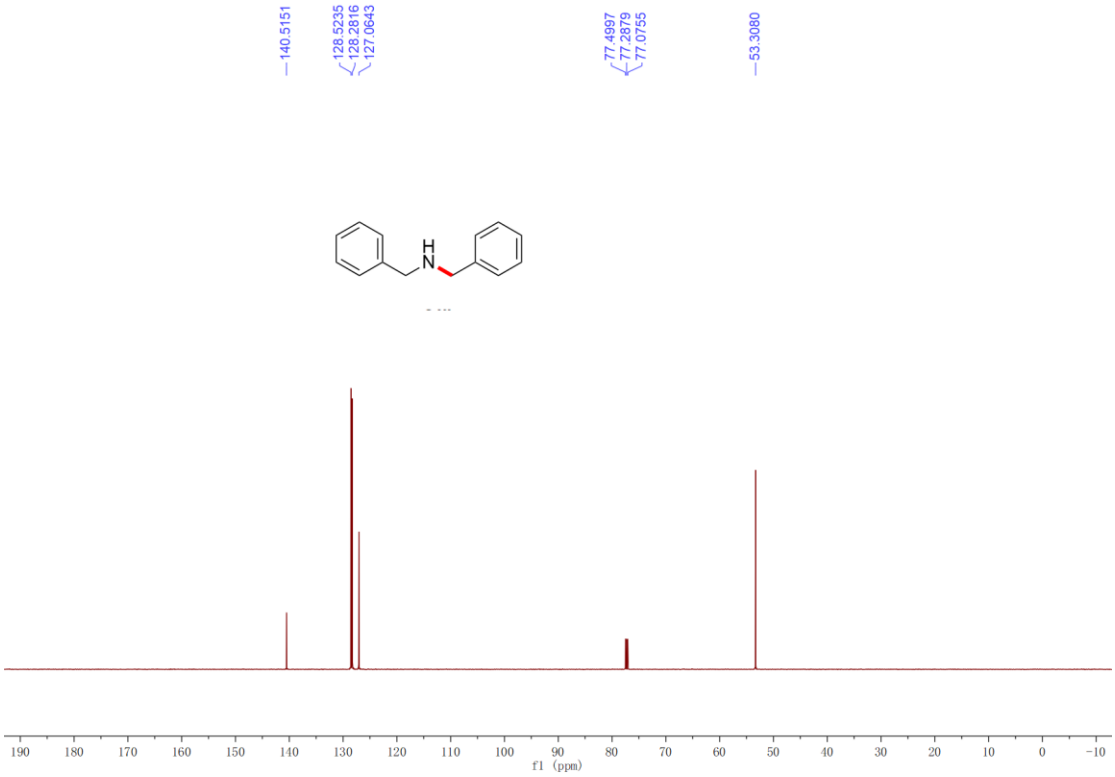

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **3ar** in $CDCl_3$.



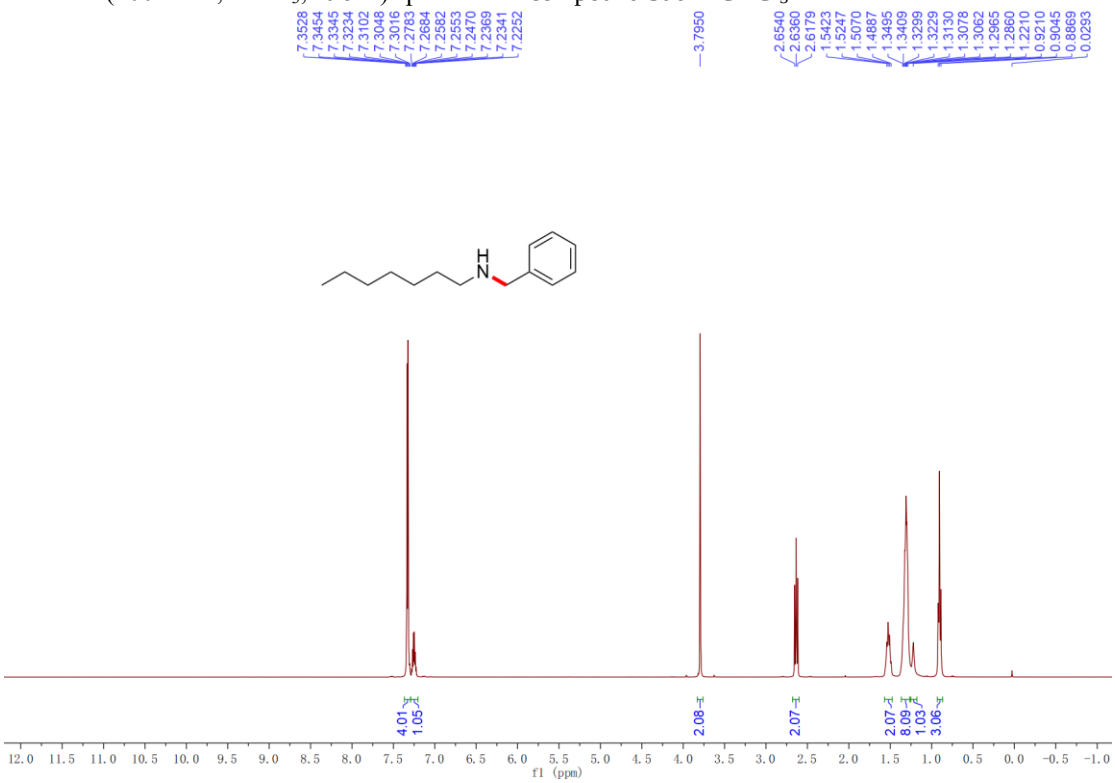
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **3as** in $CDCl_3$.



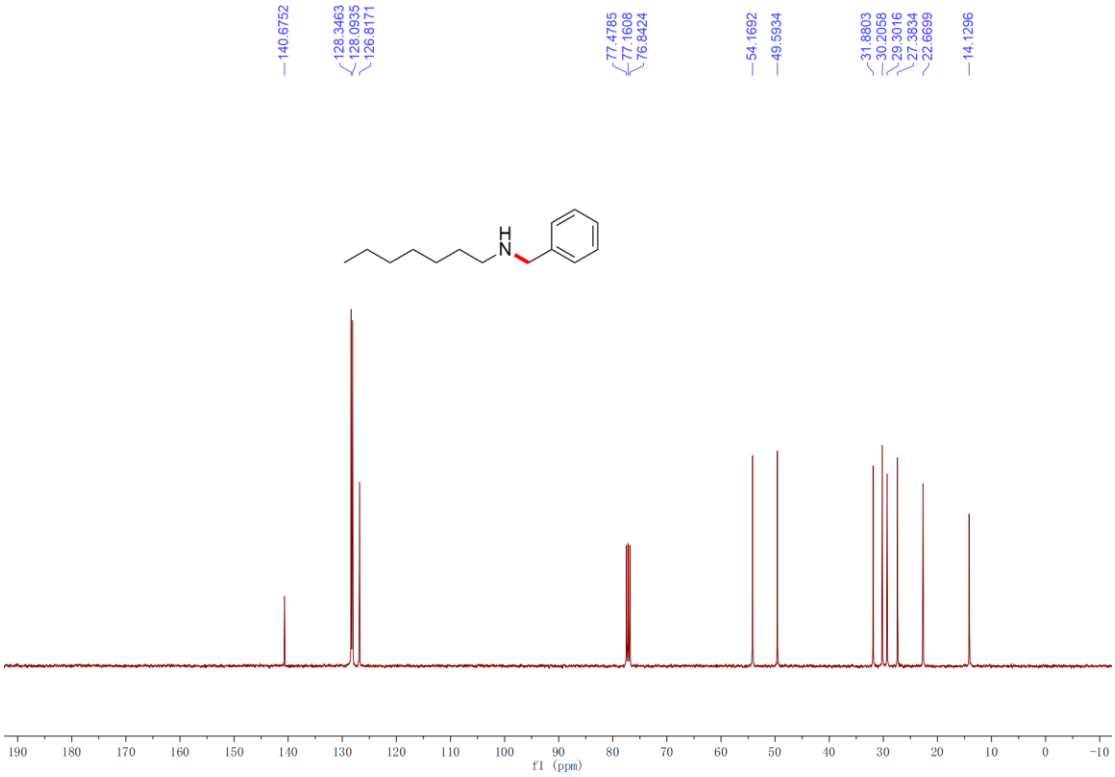

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **3as** in $CDCl_3$.



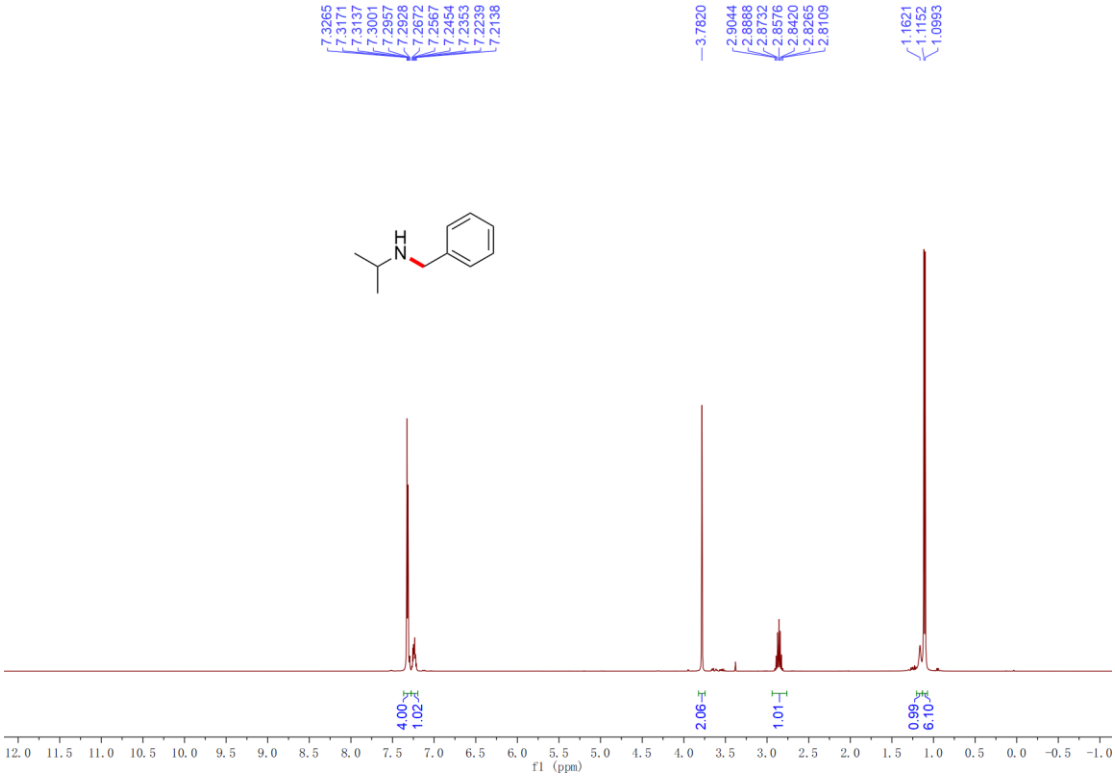
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3at** in $CDCl_3$.



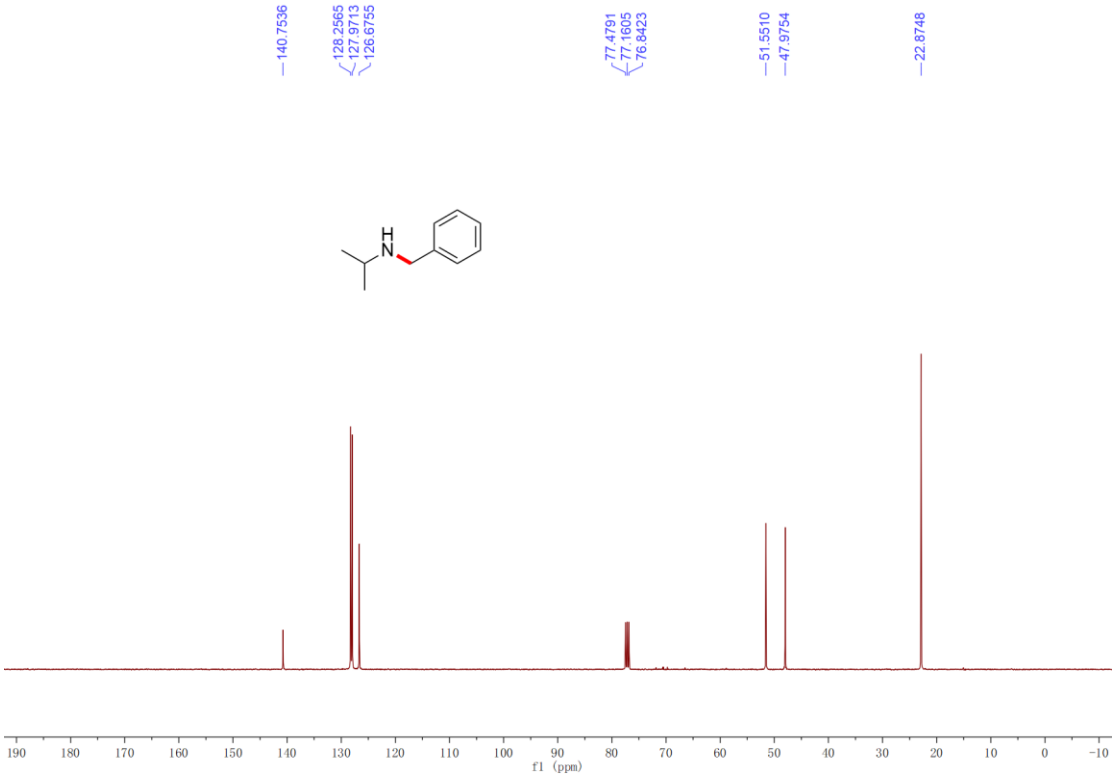

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3at** in $CDCl_3$.



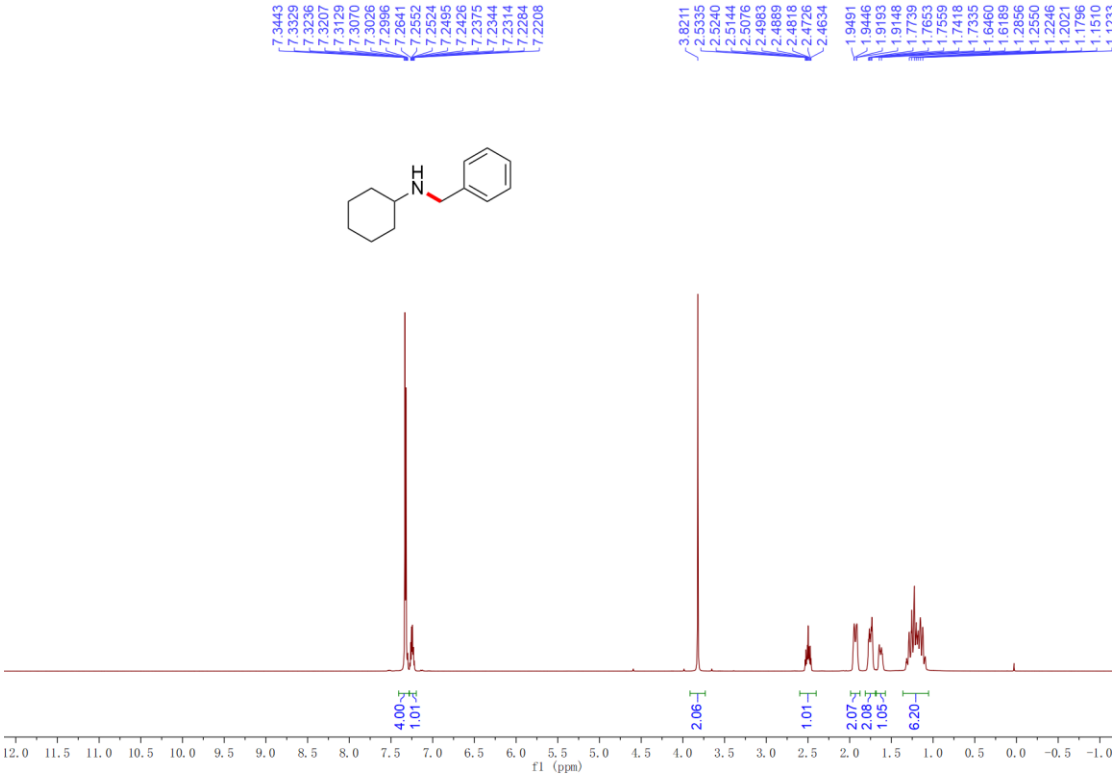
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3au** in $CDCl_3$.



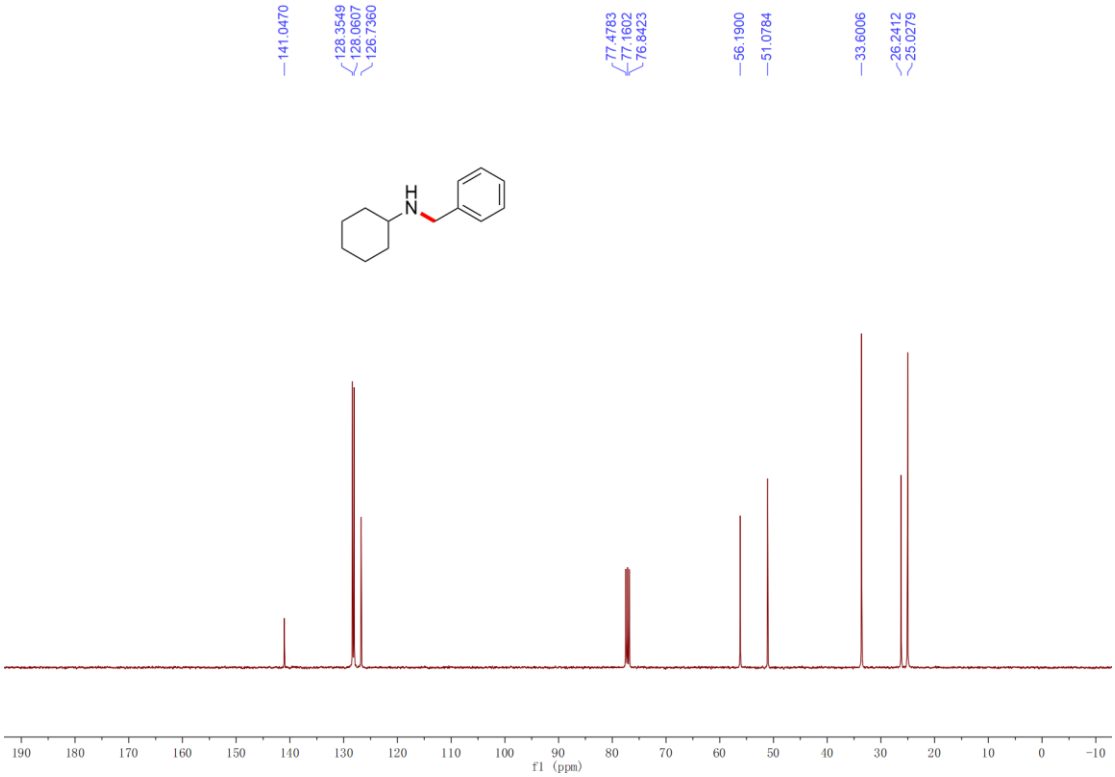

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3au** in $CDCl_3$.



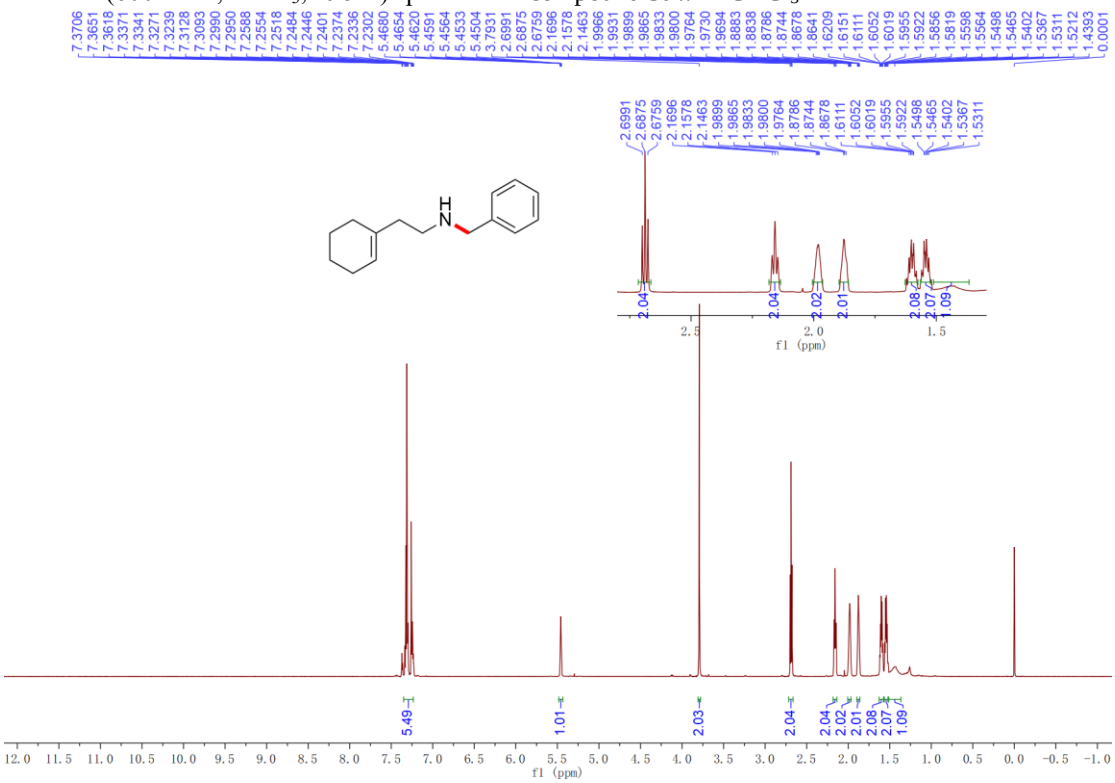
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3av** in $CDCl_3$.



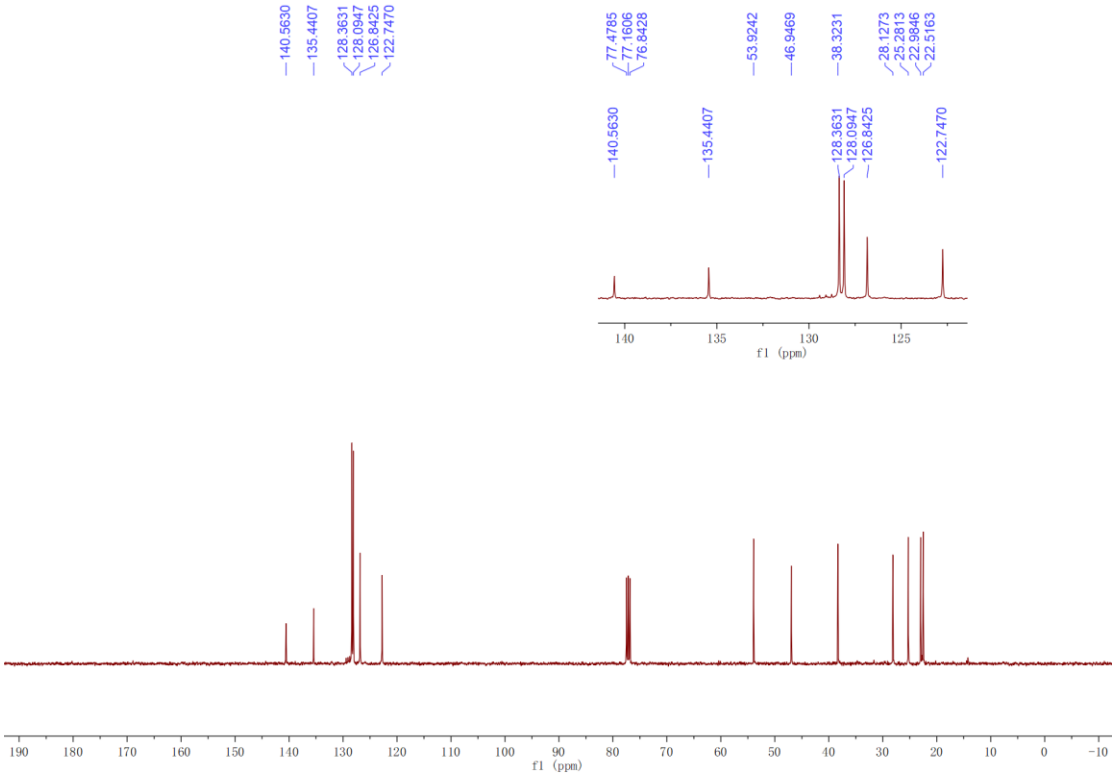

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3av** in $CDCl_3$.



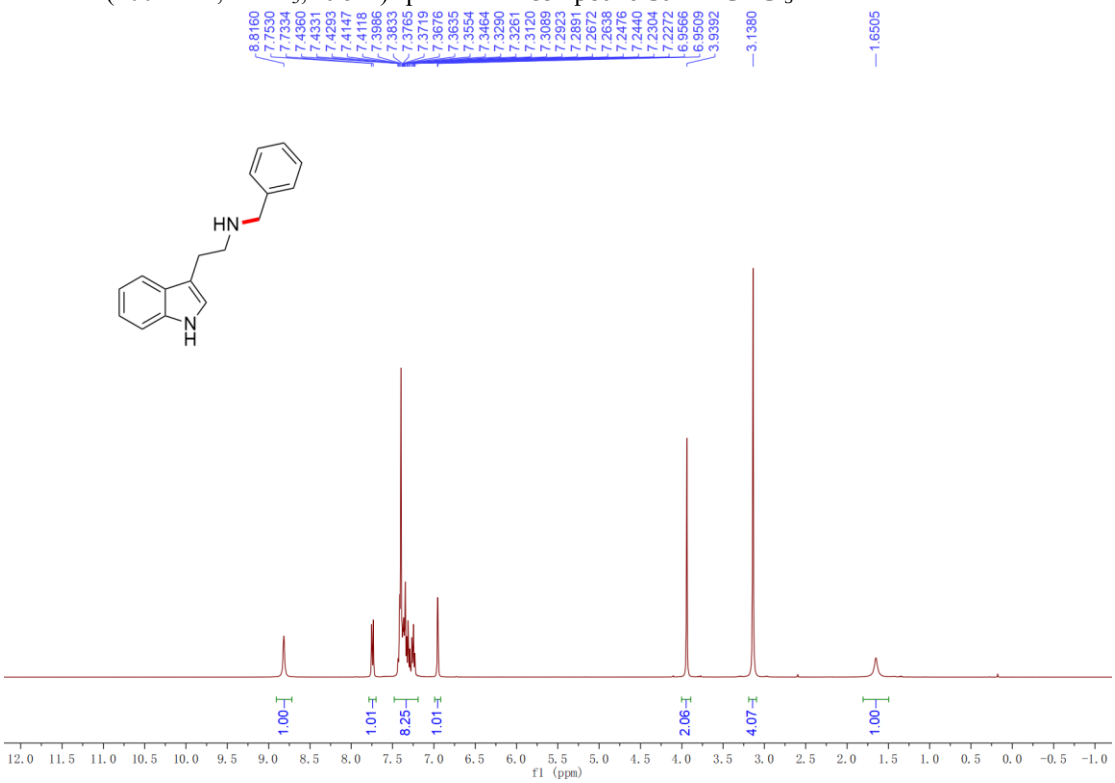
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **3aw** in $CDCl_3$.



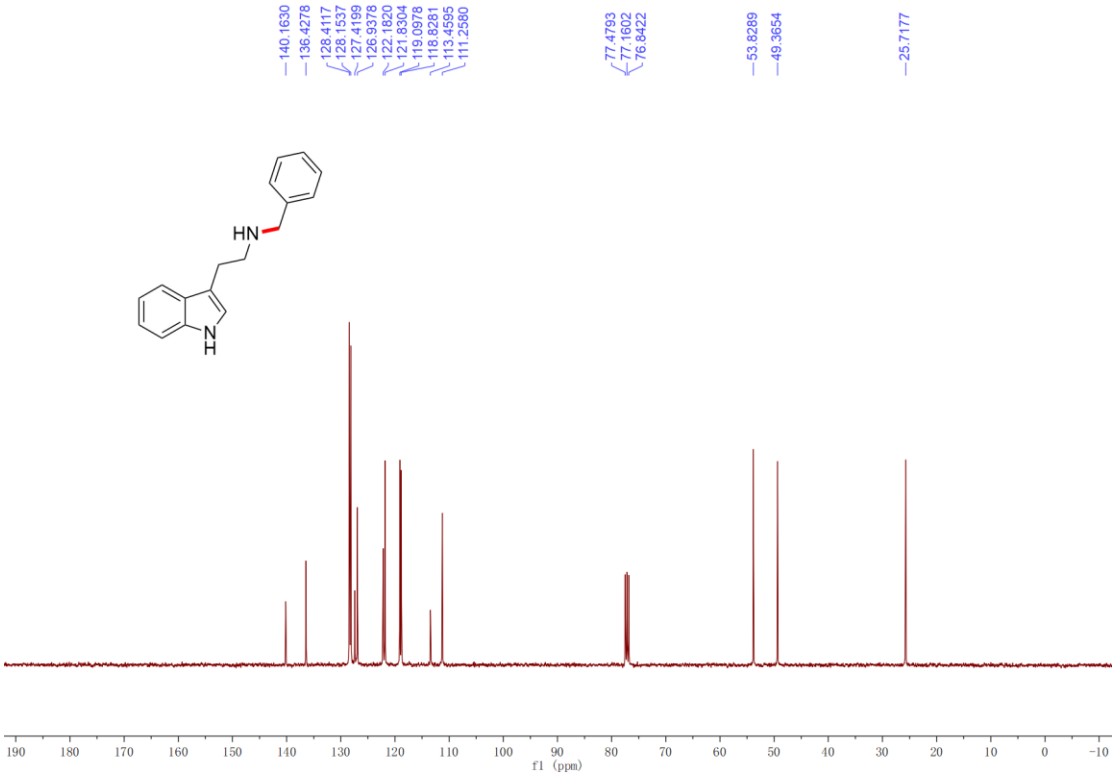
$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3aw** in $CDCl_3$.



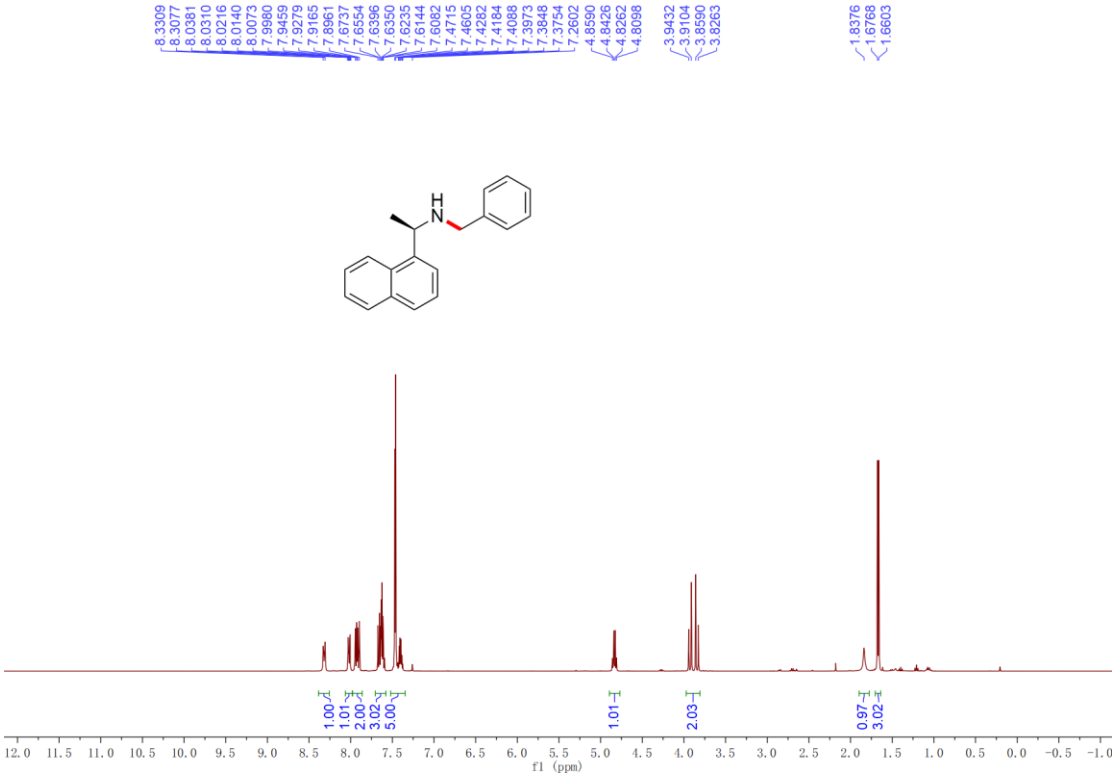
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3ax** in $CDCl_3$.



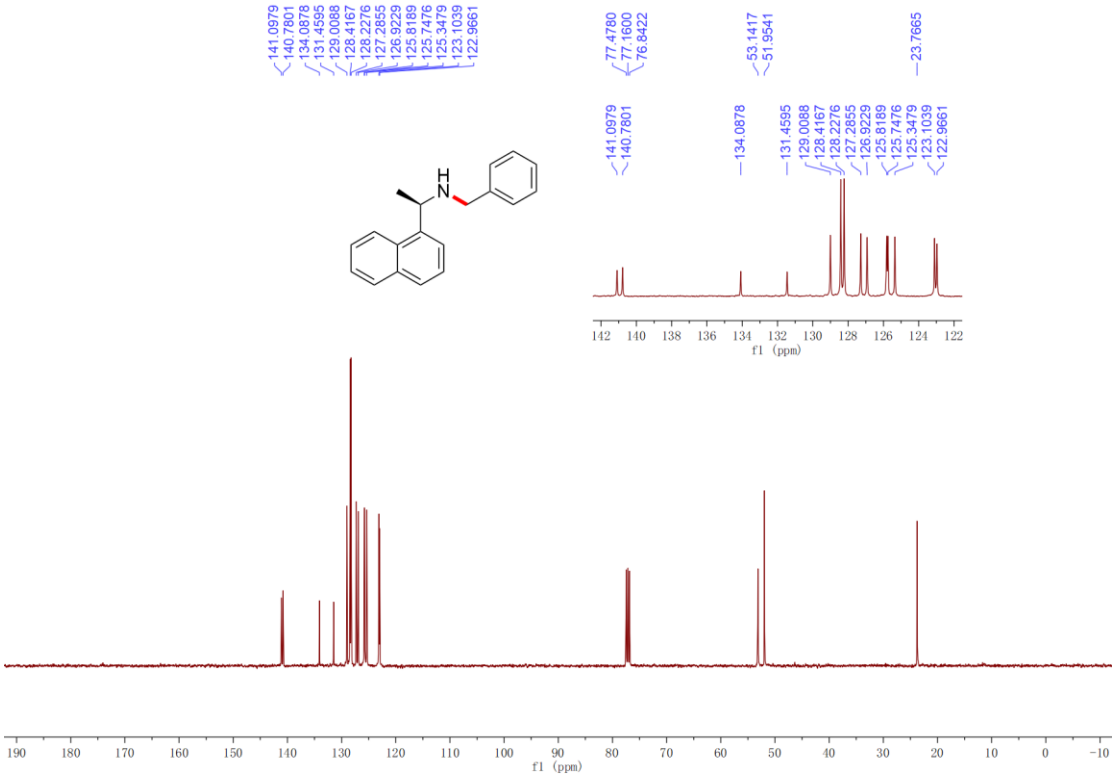

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3ax** in $CDCl_3$.



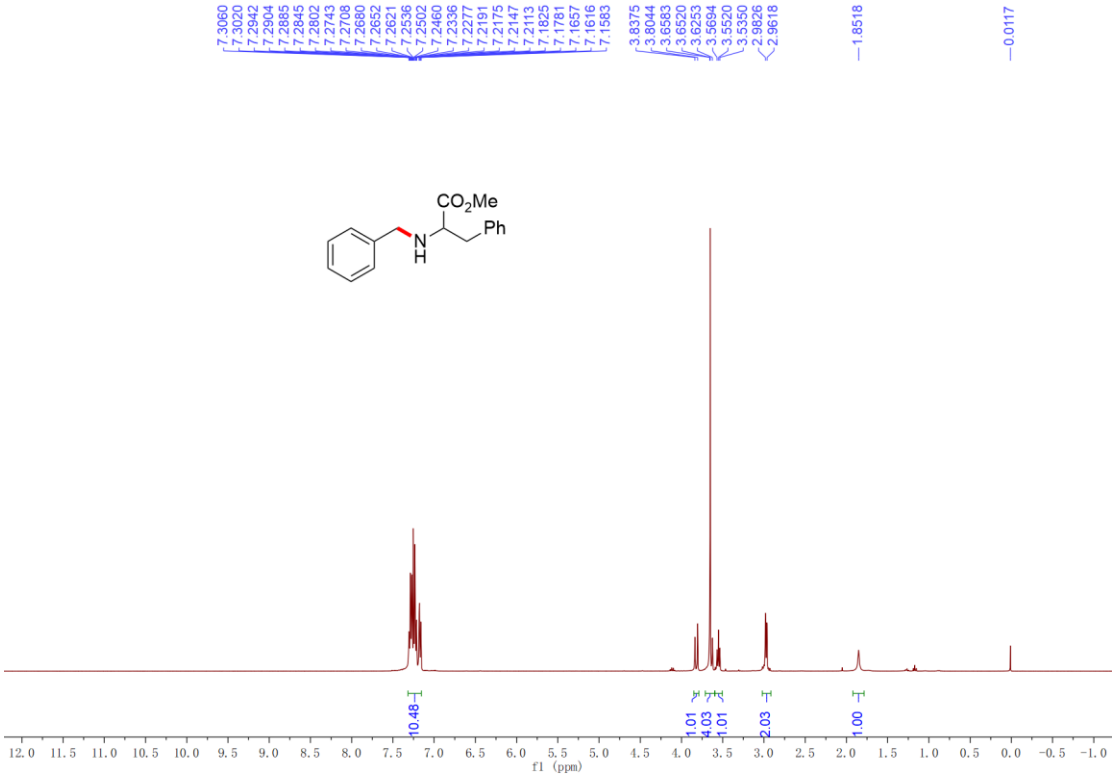
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3ay** in $CDCl_3$.



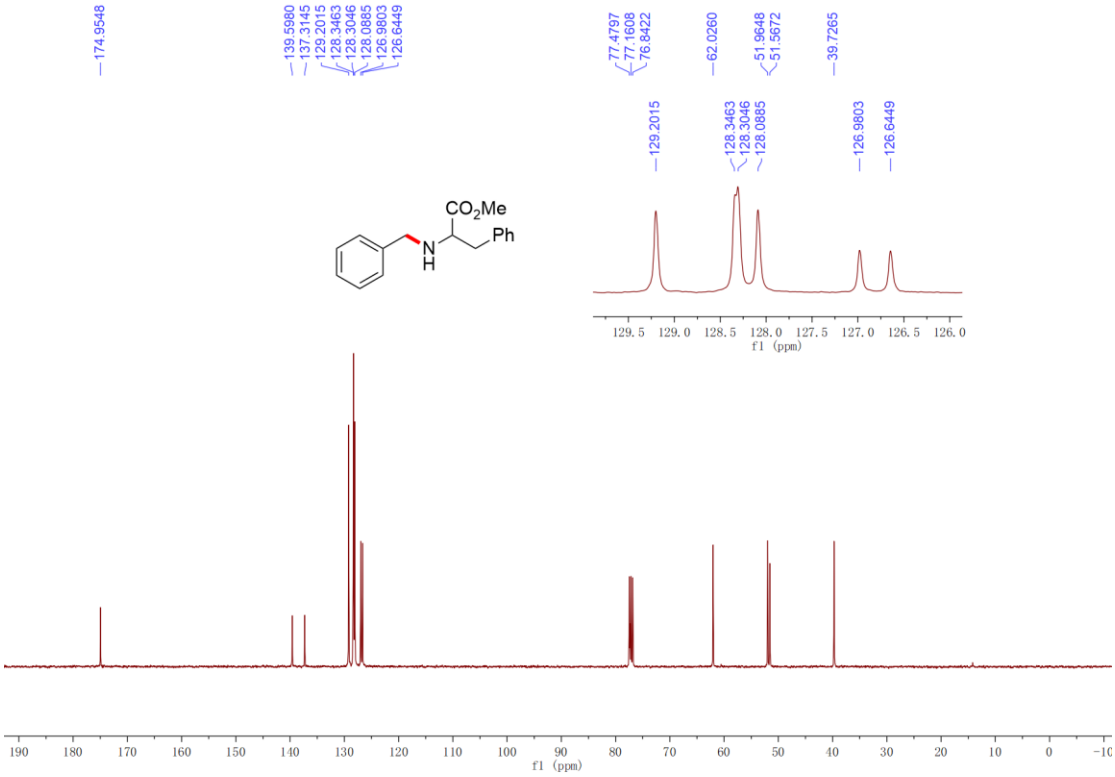

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3ay** in $CDCl_3$.



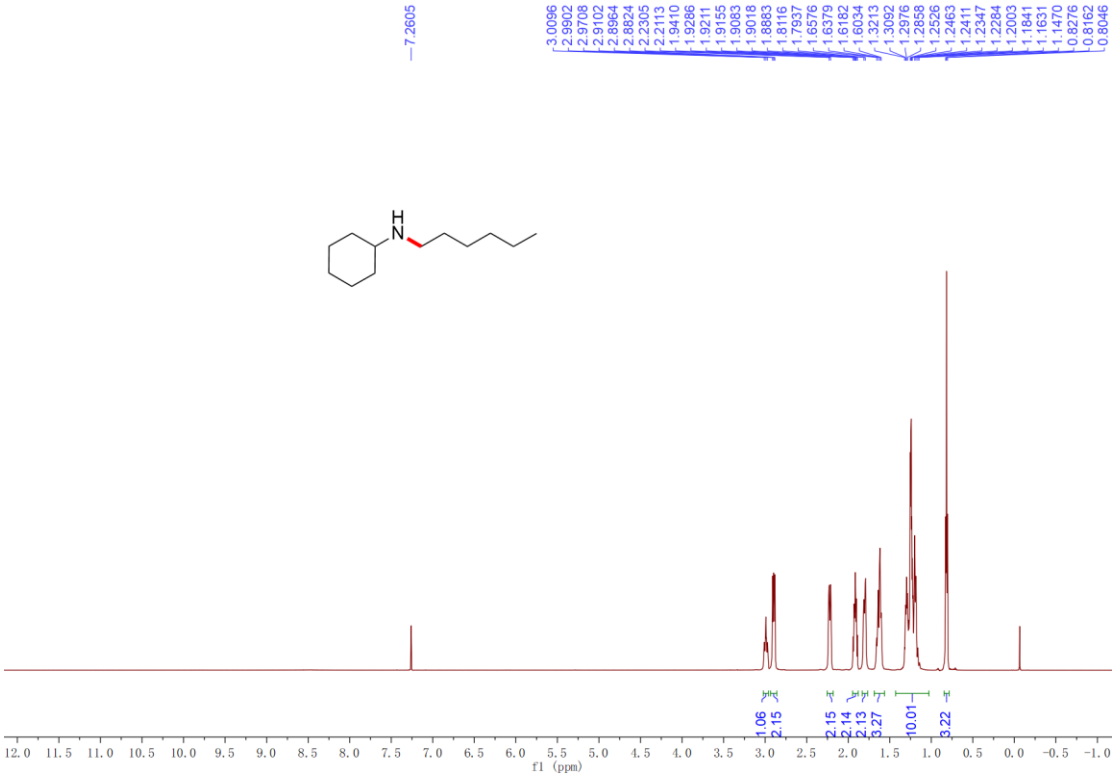
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3az** in $CDCl_3$.



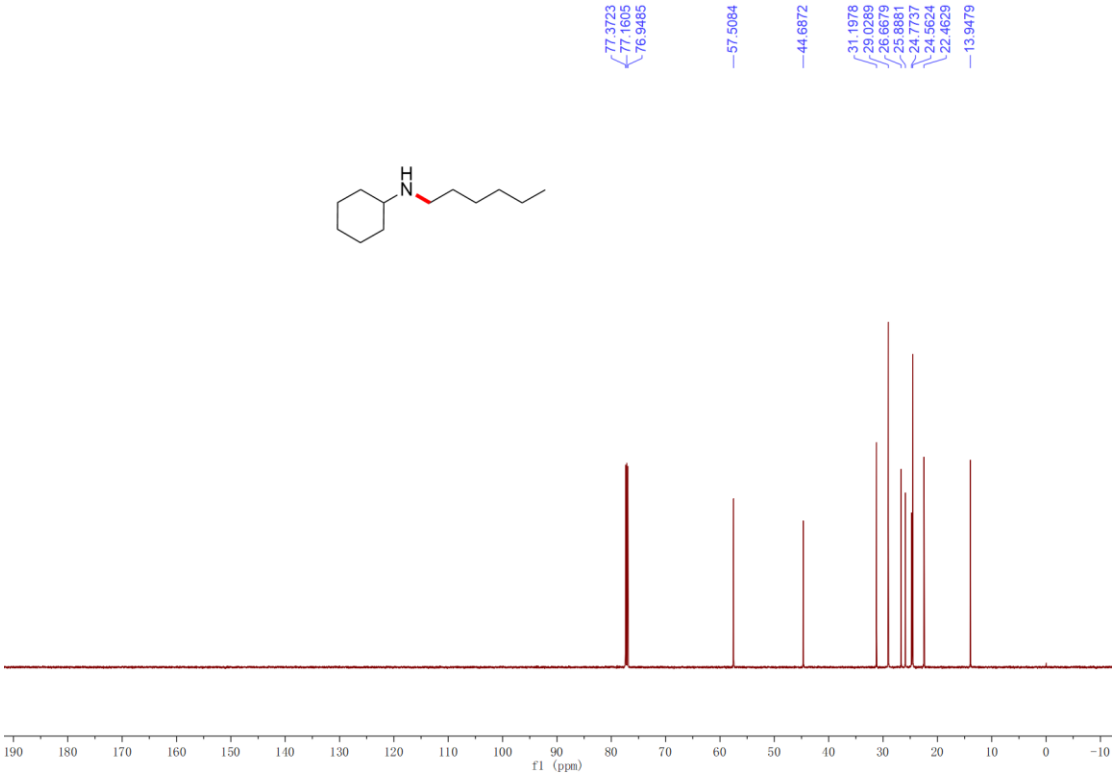

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3az** in $CDCl_3$.



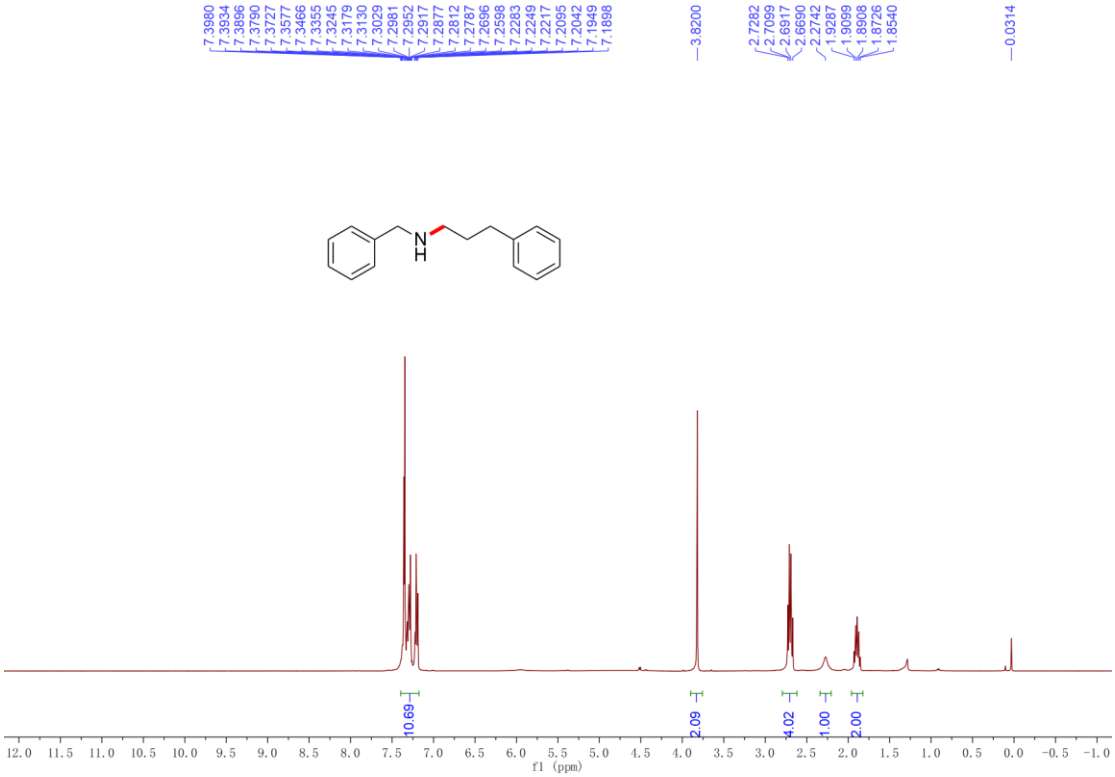
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **5iv** in $CDCl_3$.



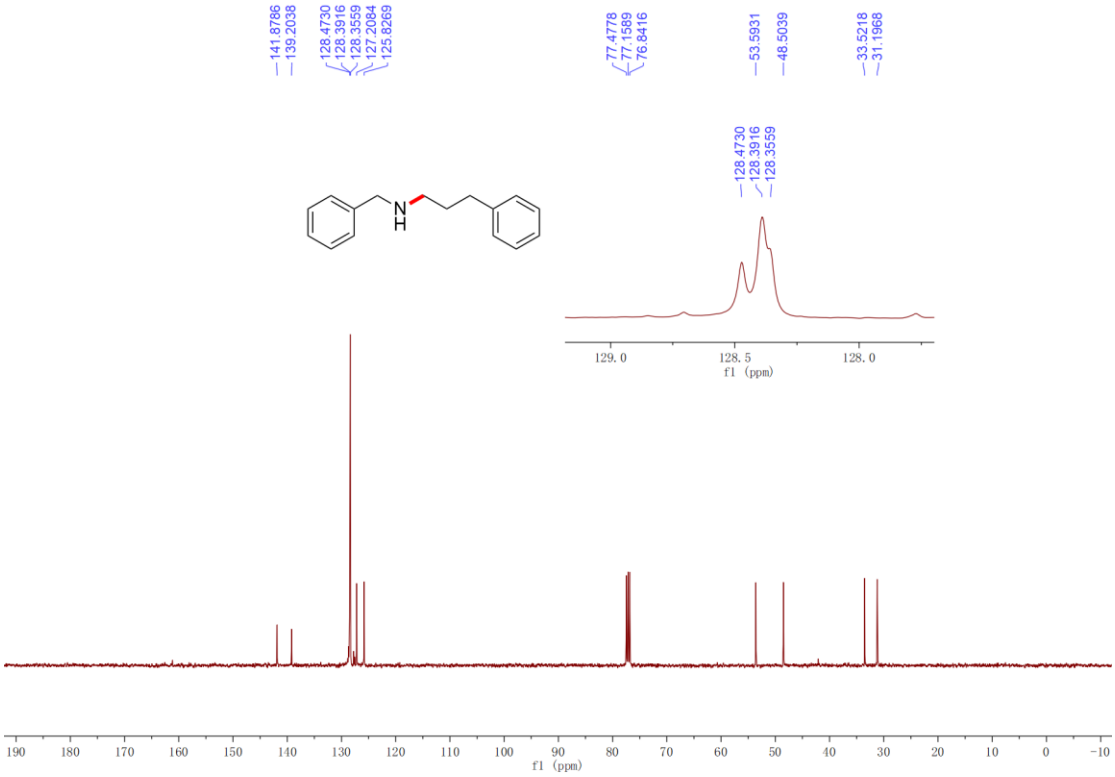

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **5iv** in $CDCl_3$.



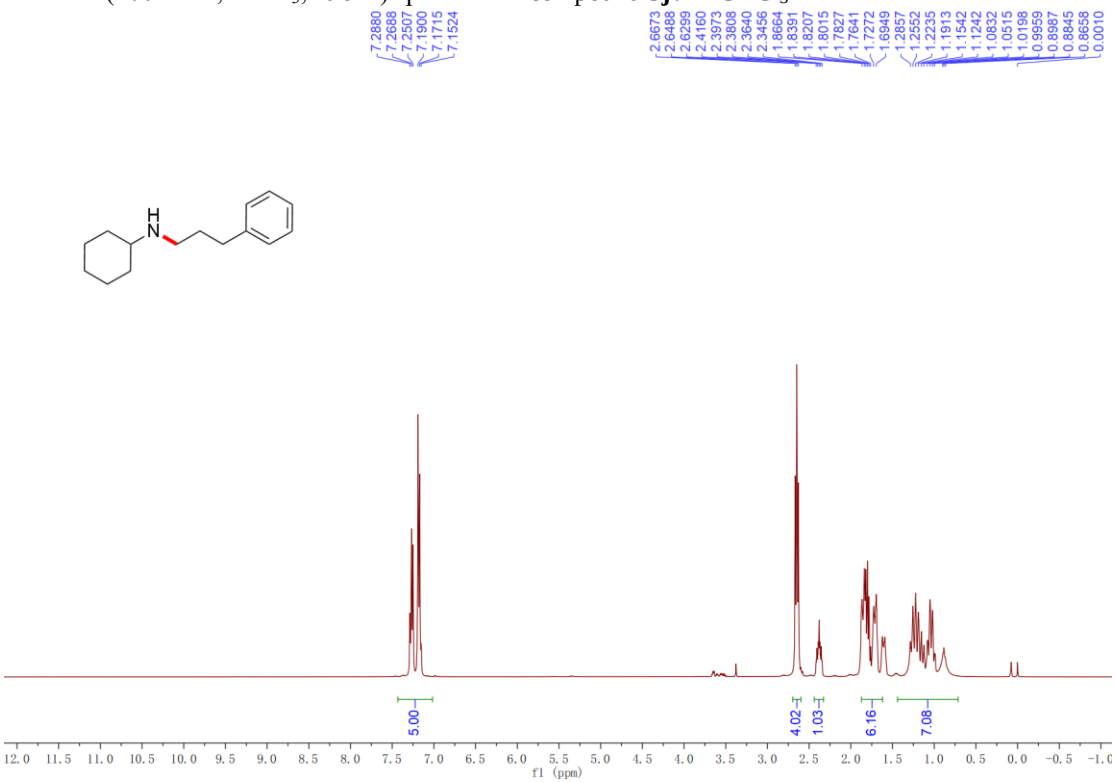
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **5js** in $CDCl_3$.



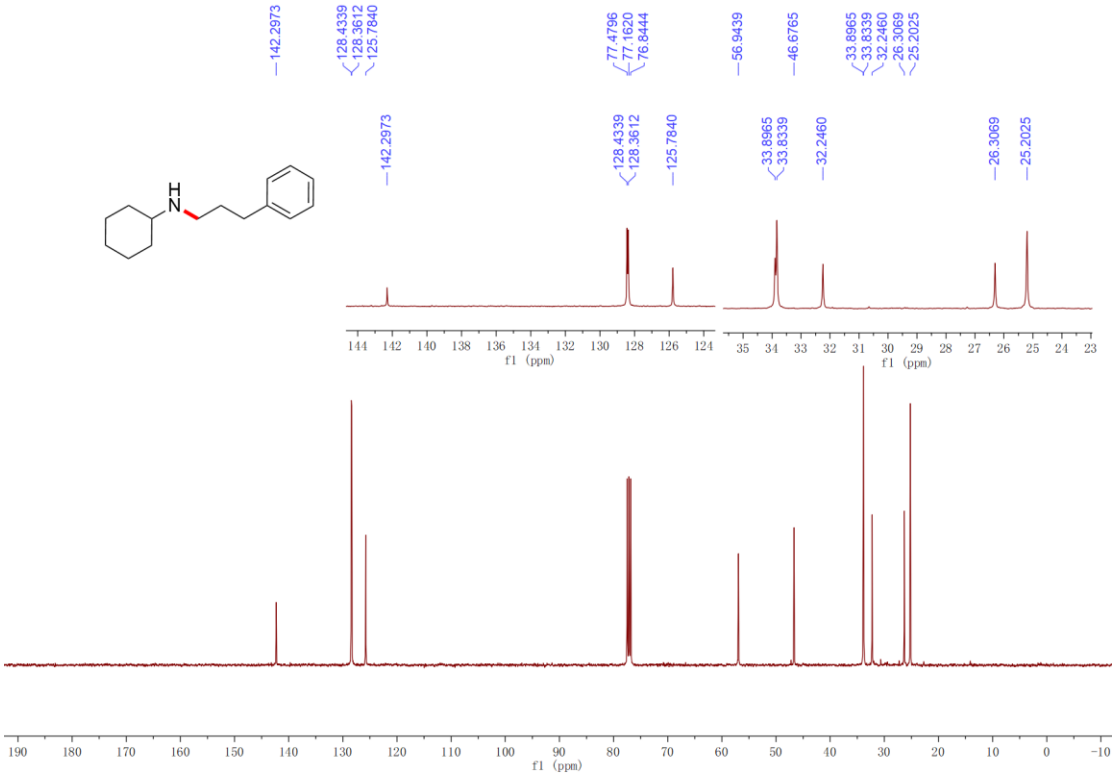

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **5js** in $CDCl_3$.



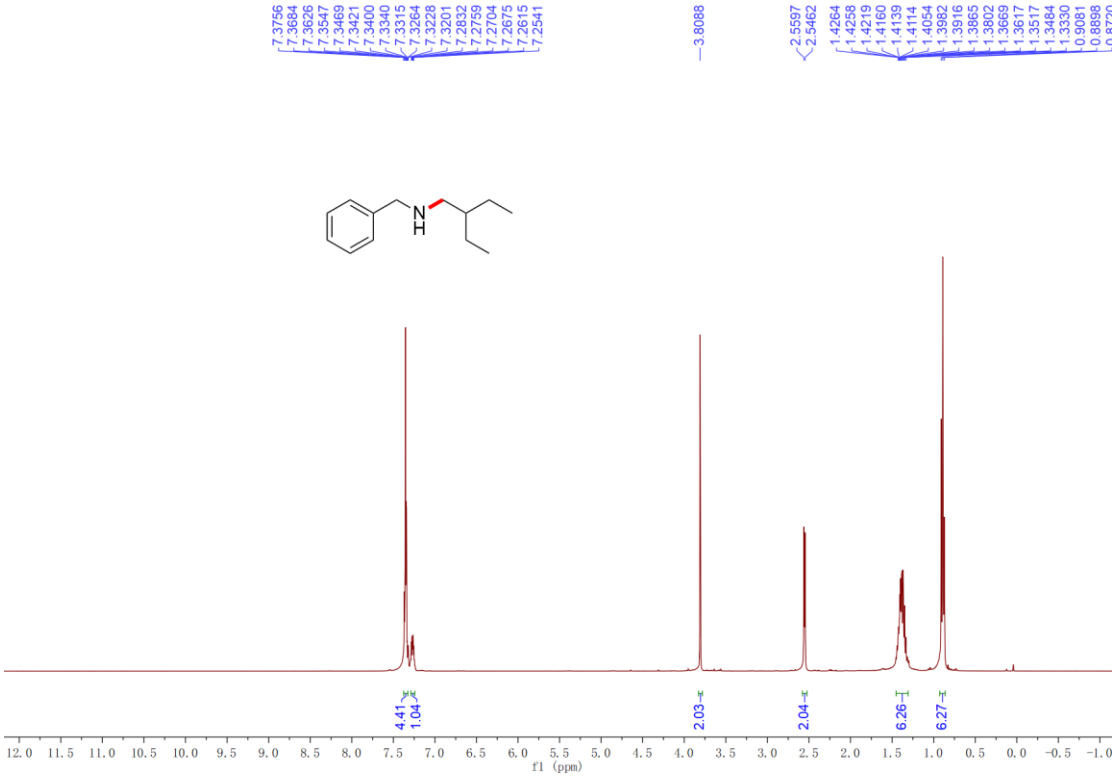
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **5jv** in $CDCl_3$.



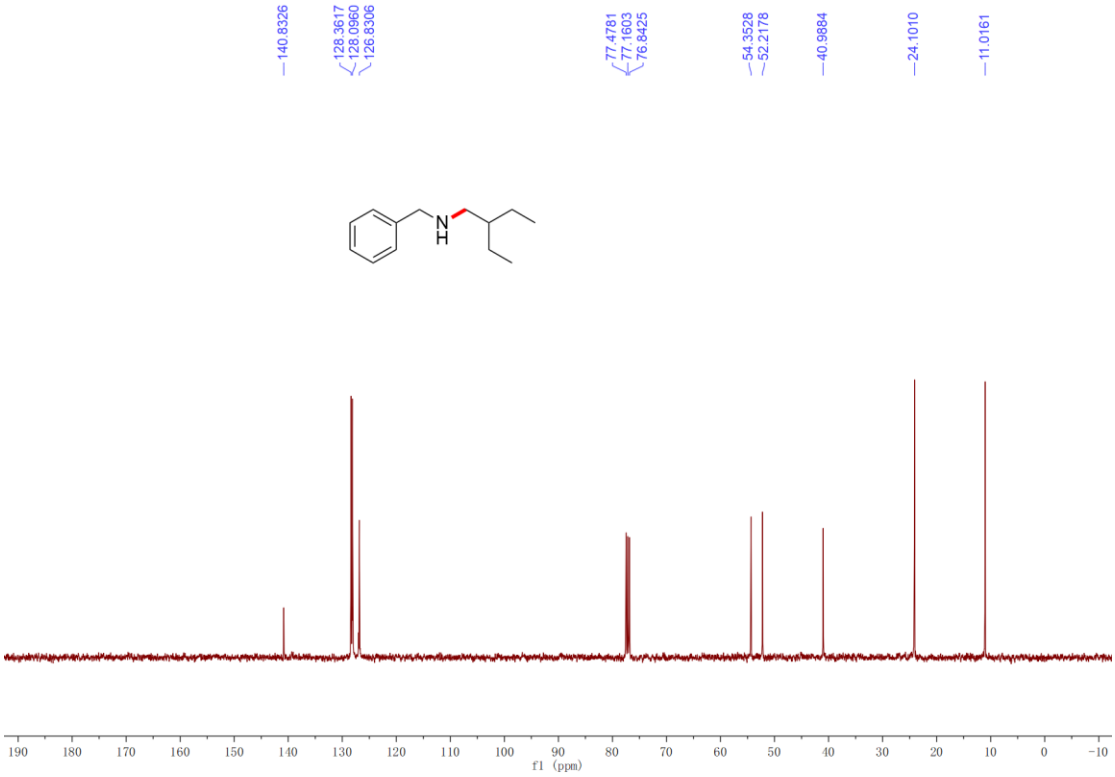

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **5jv** in $CDCl_3$.



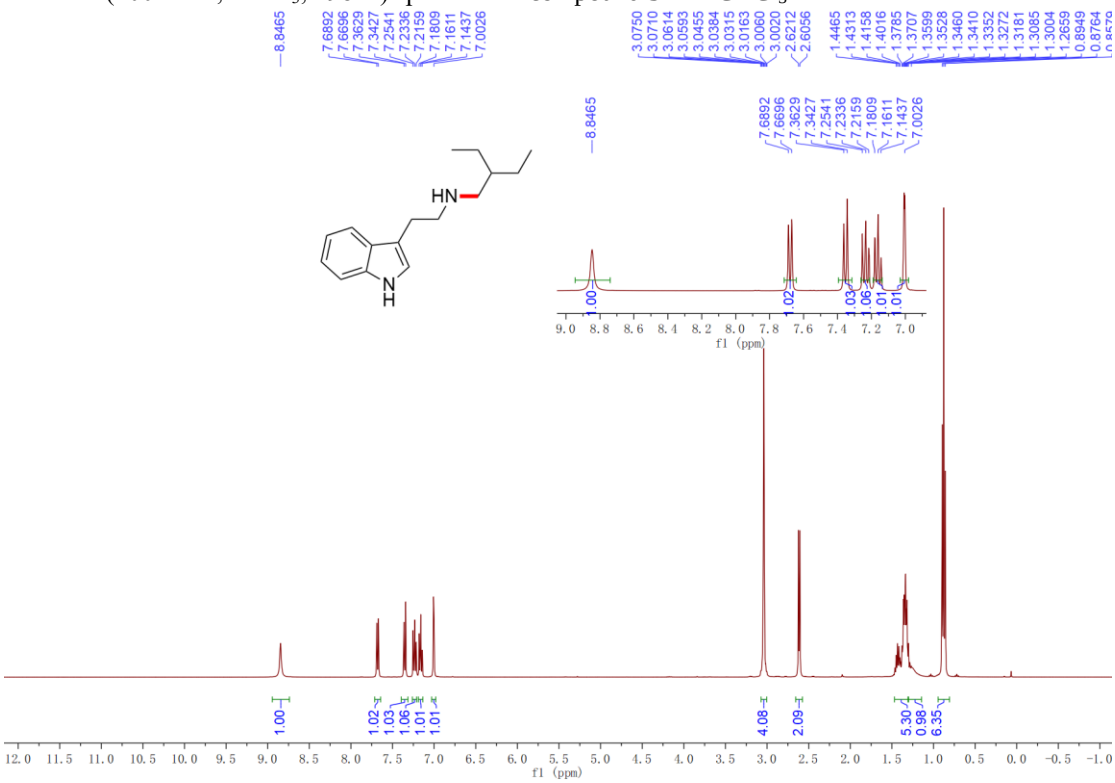
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **5ls** in $CDCl_3$.



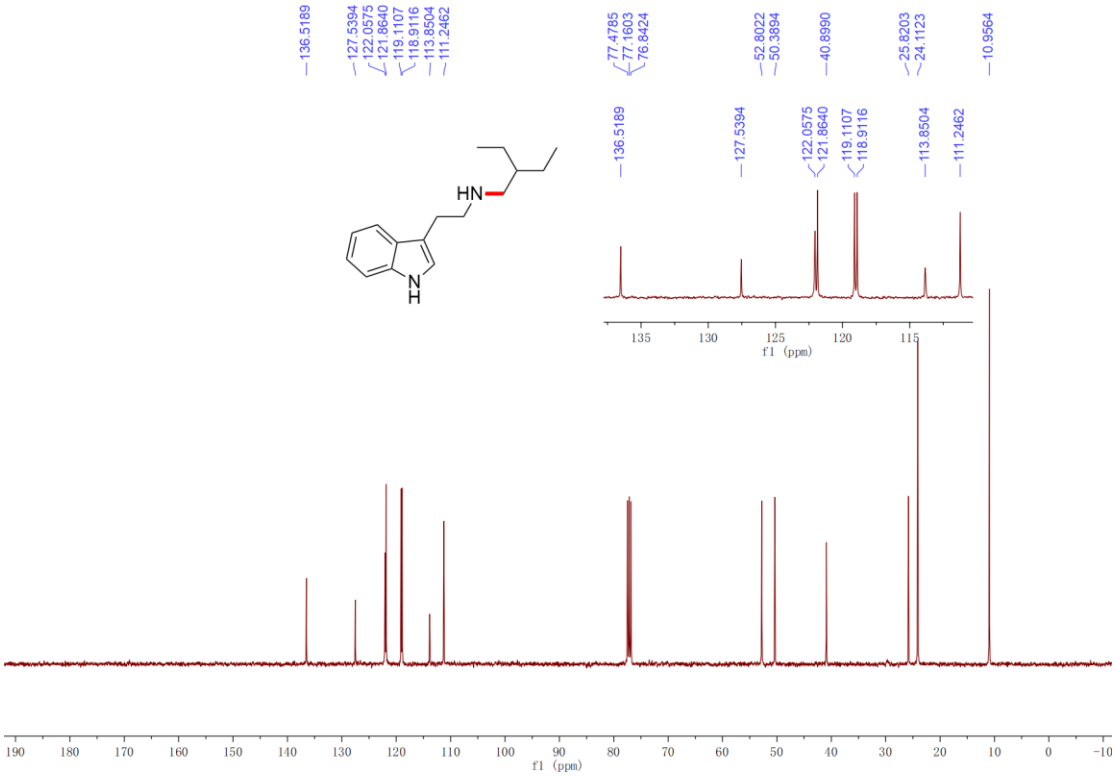

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **5ls** in $CDCl_3$.



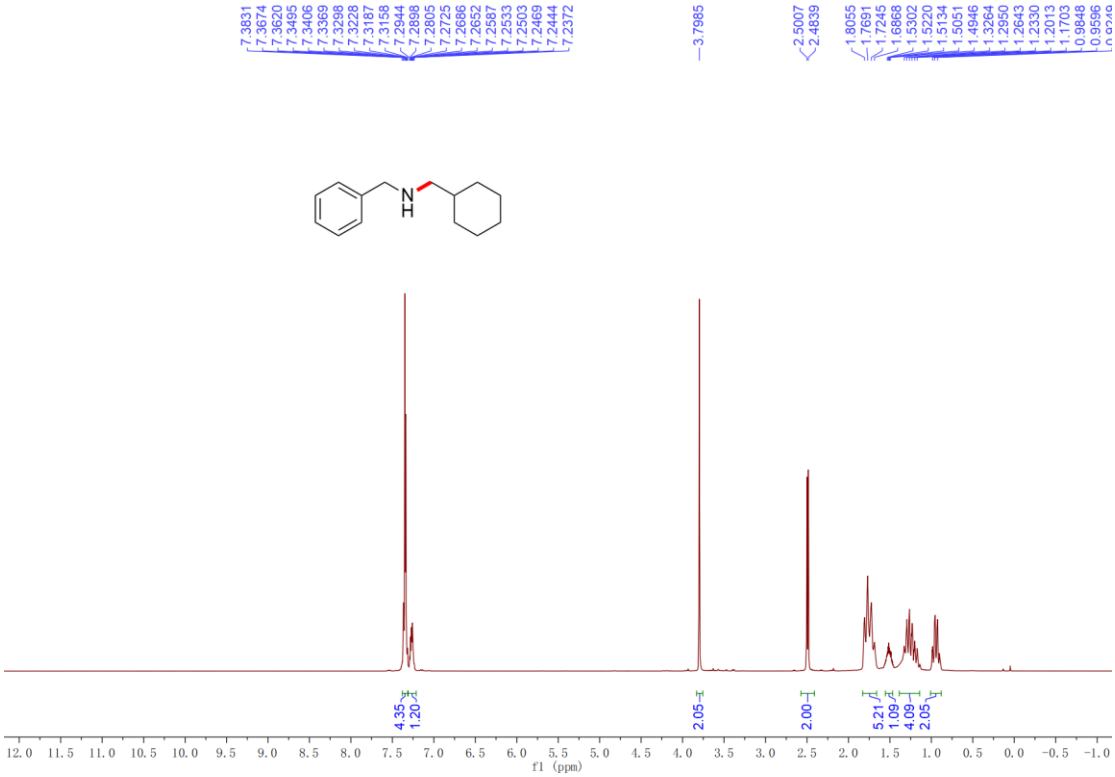
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **5lx** in $CDCl_3$.



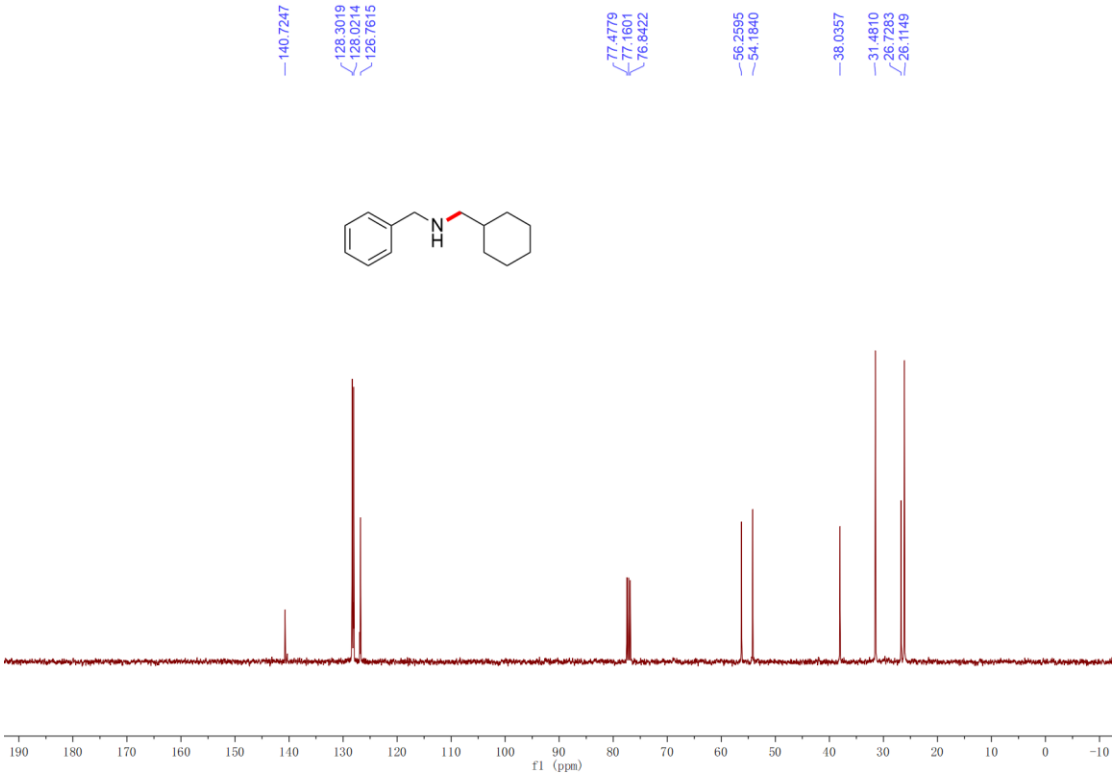

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **5lx** in $CDCl_3$.



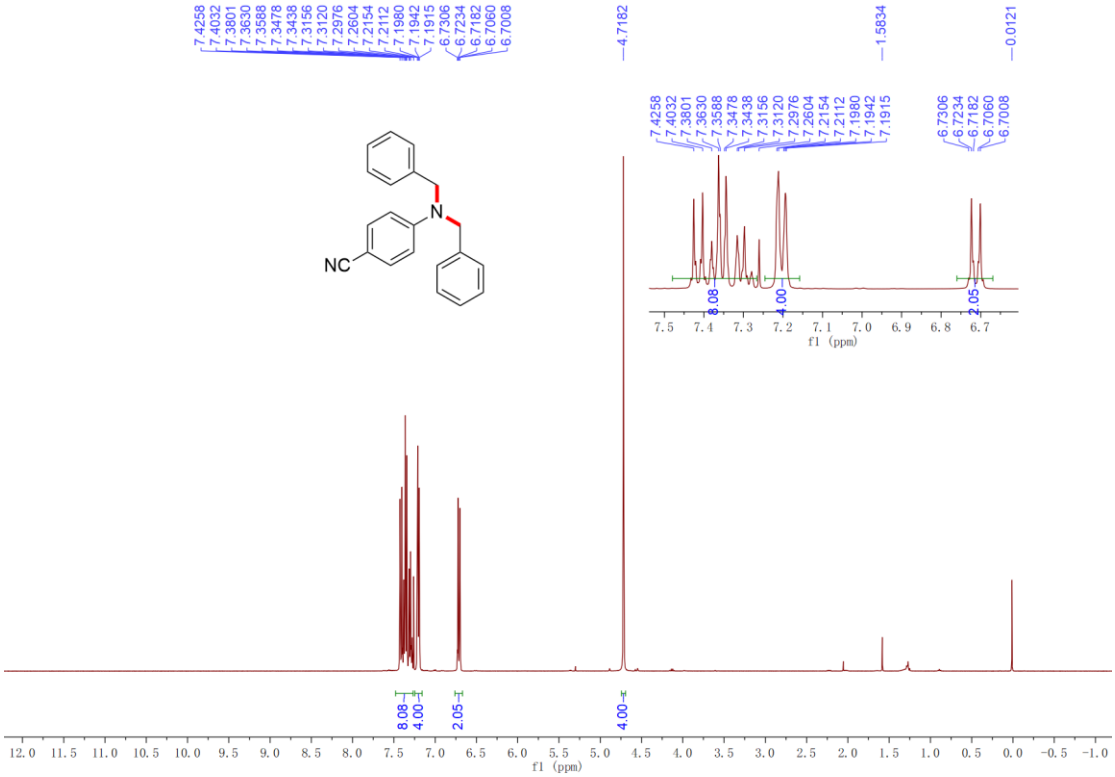
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **5os** in $CDCl_3$.



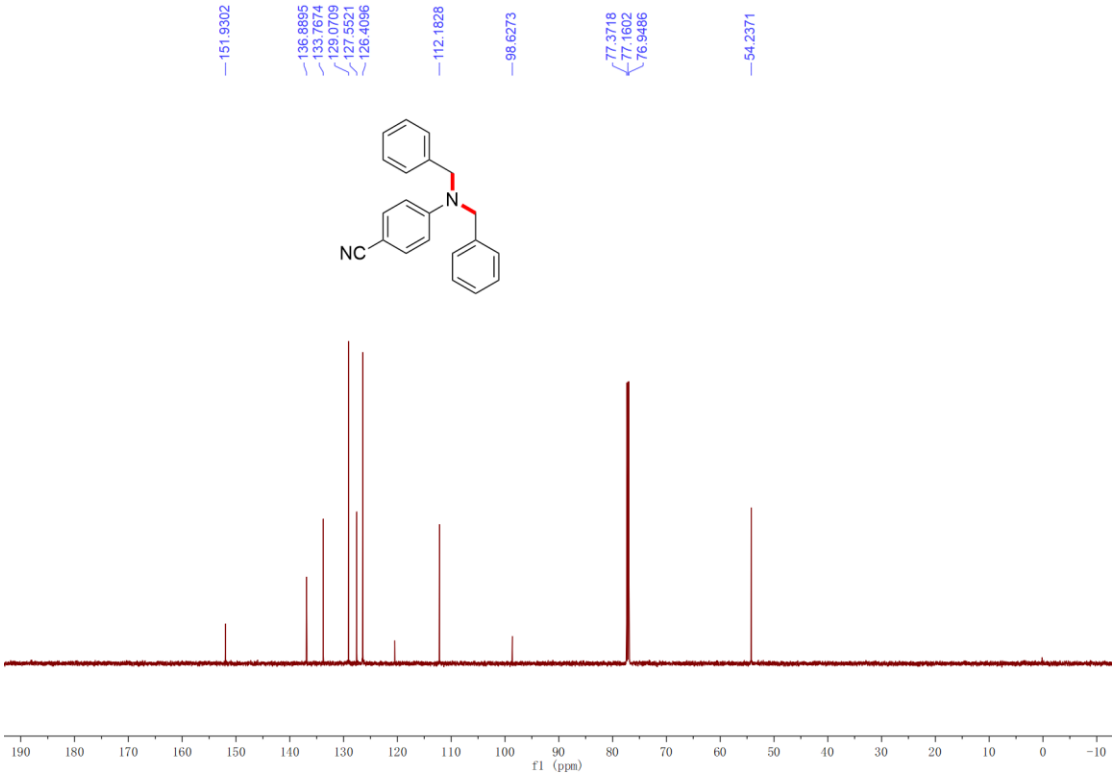

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **5os** in $CDCl_3$.



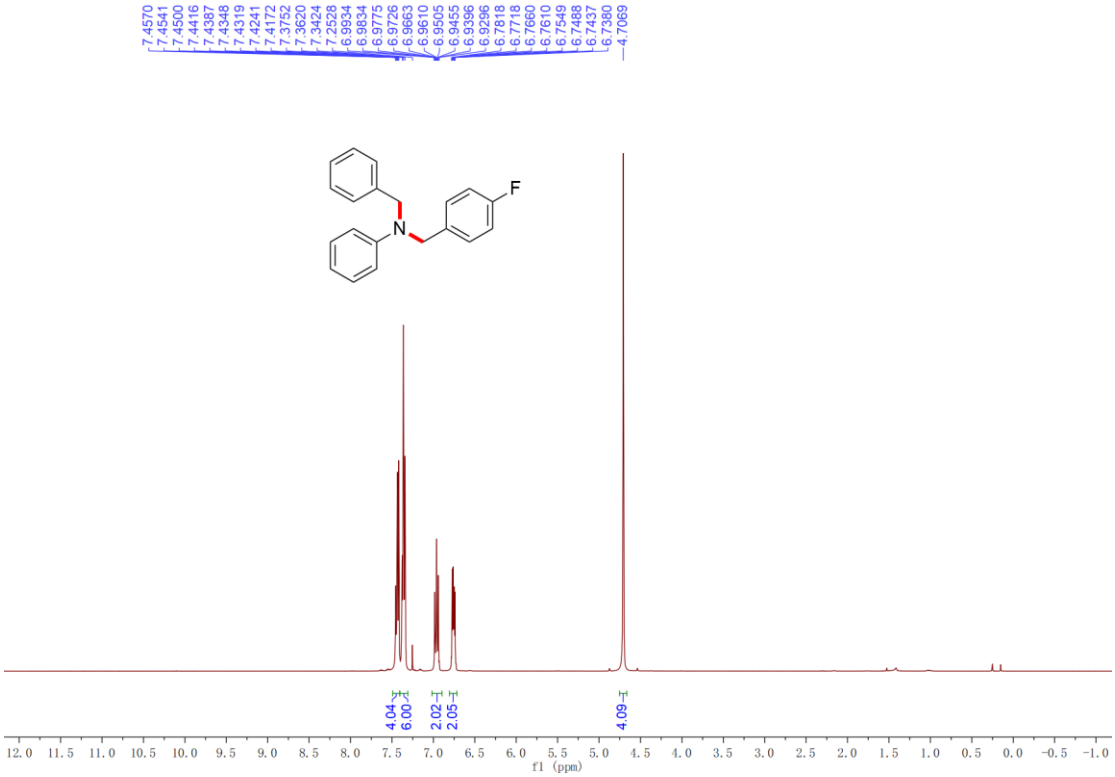
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3aaj** in $CDCl_3$.



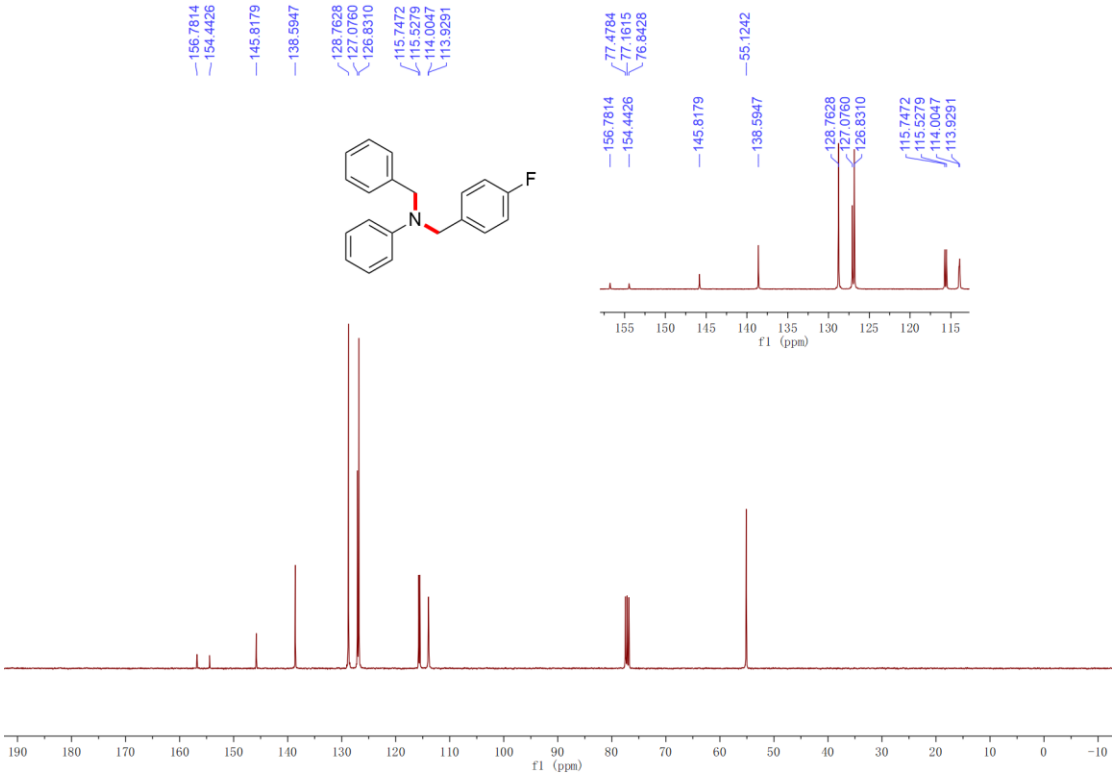

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3aaj** in $CDCl_3$.



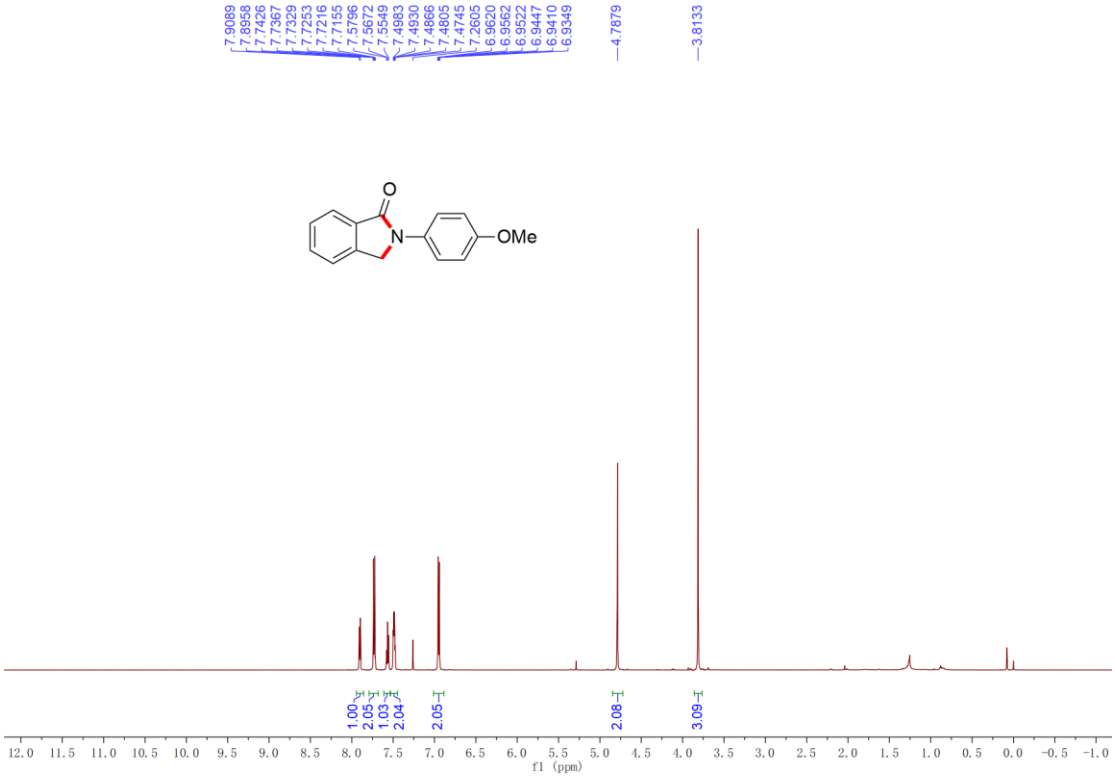
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3aad** in $CDCl_3$.



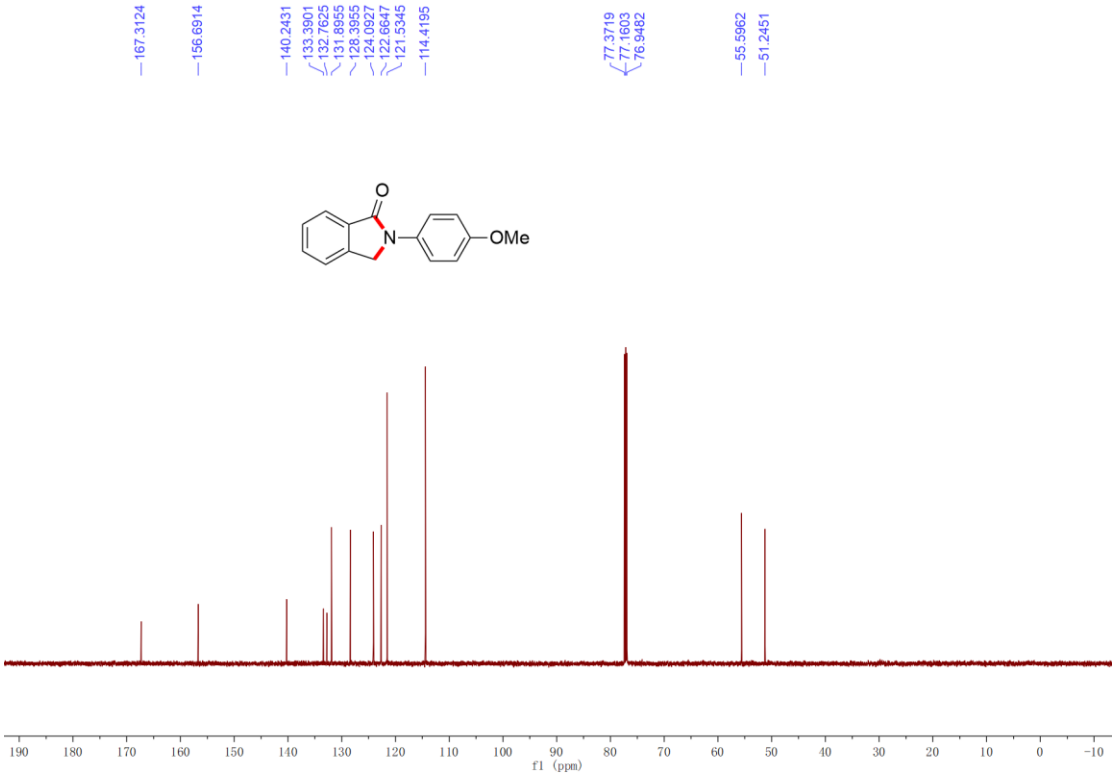

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **3aad** in $CDCl_3$.



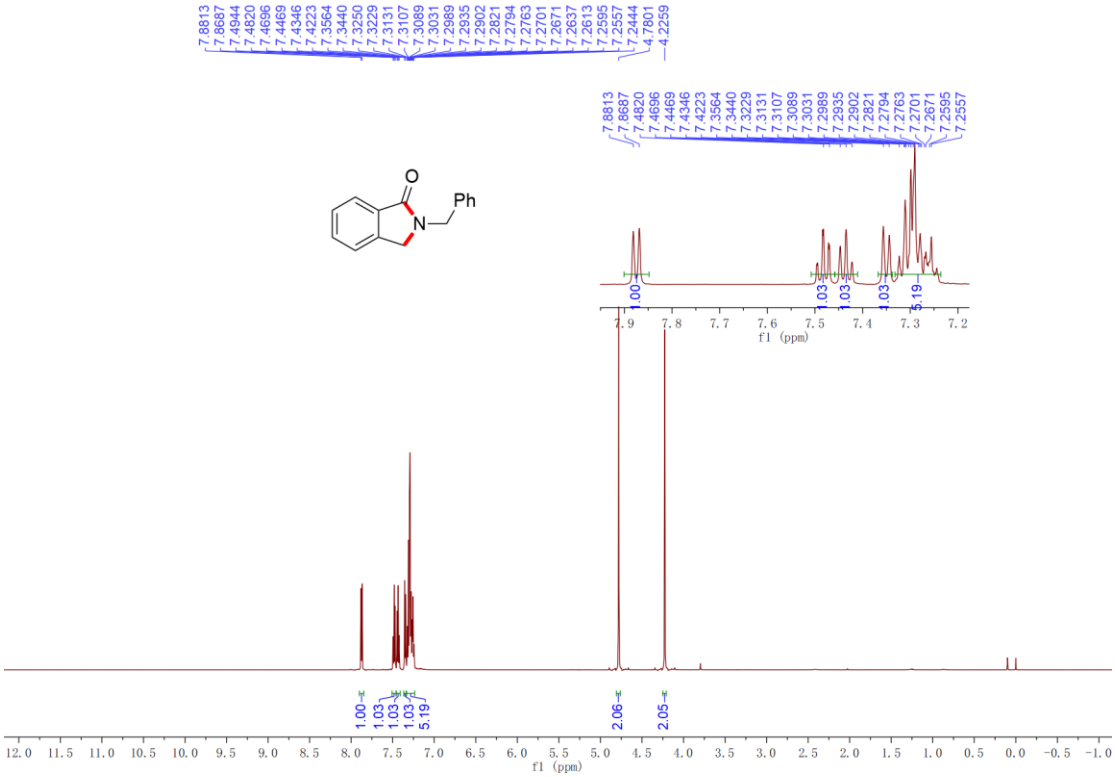
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **7ac** in $CDCl_3$.



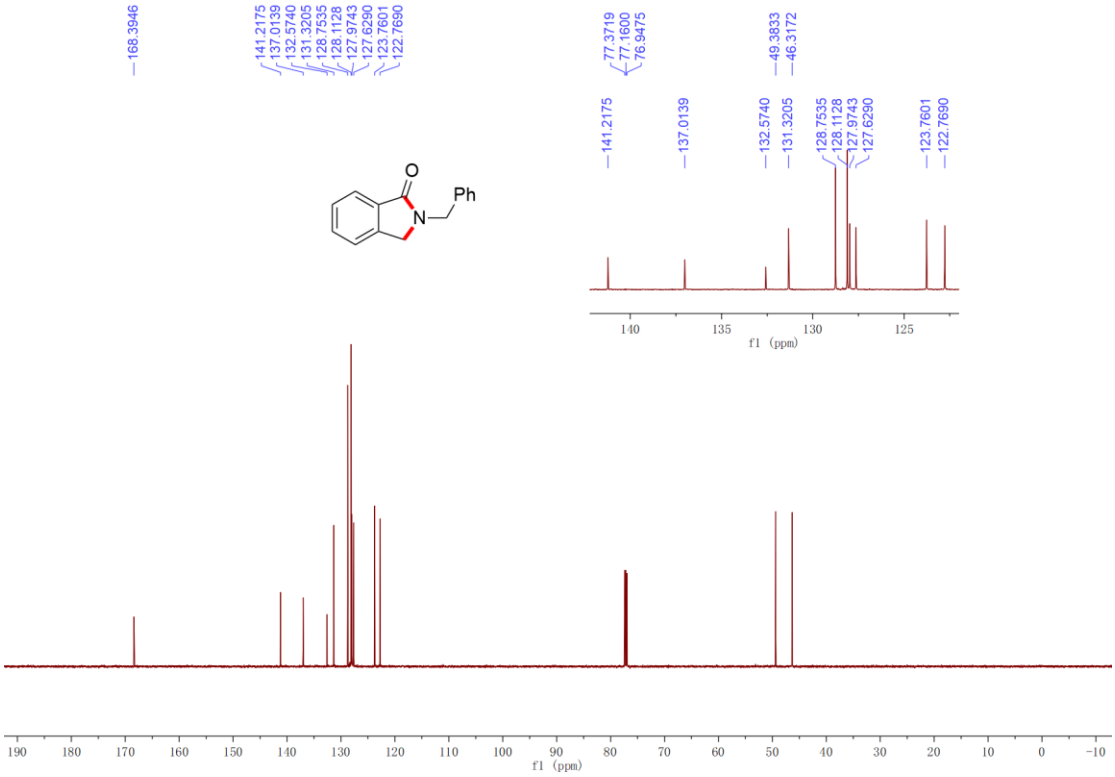

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **7ac** in $CDCl_3$.



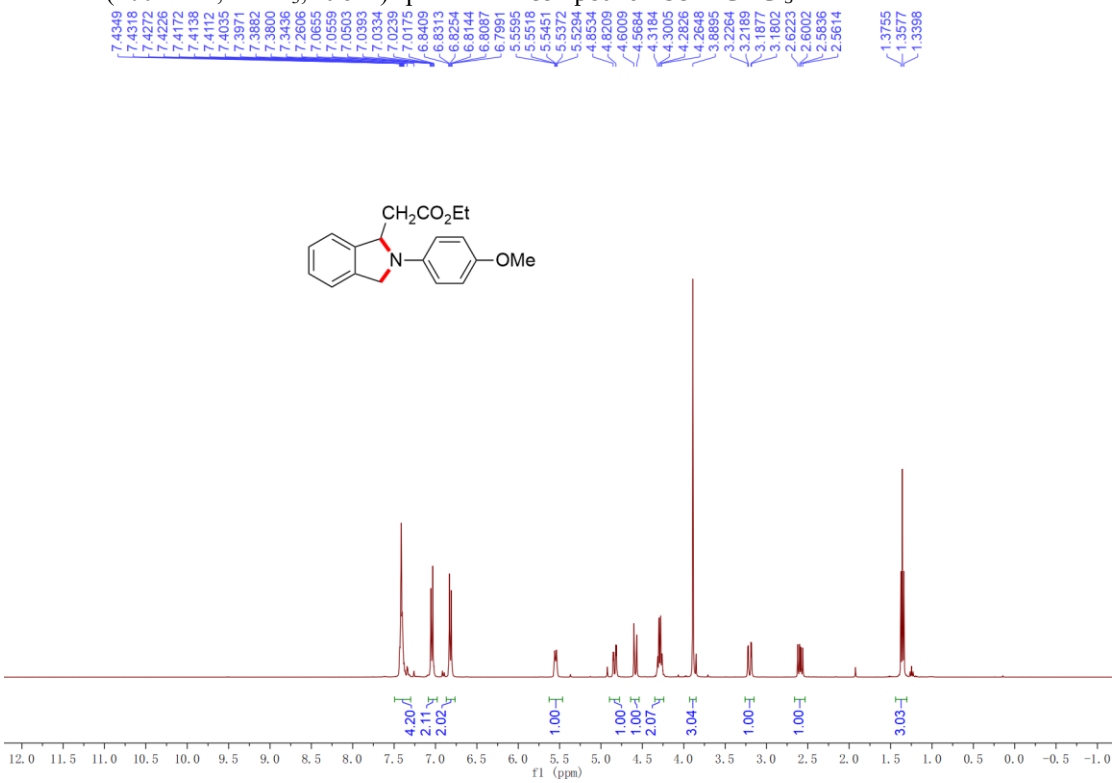
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **7as** in $CDCl_3$.



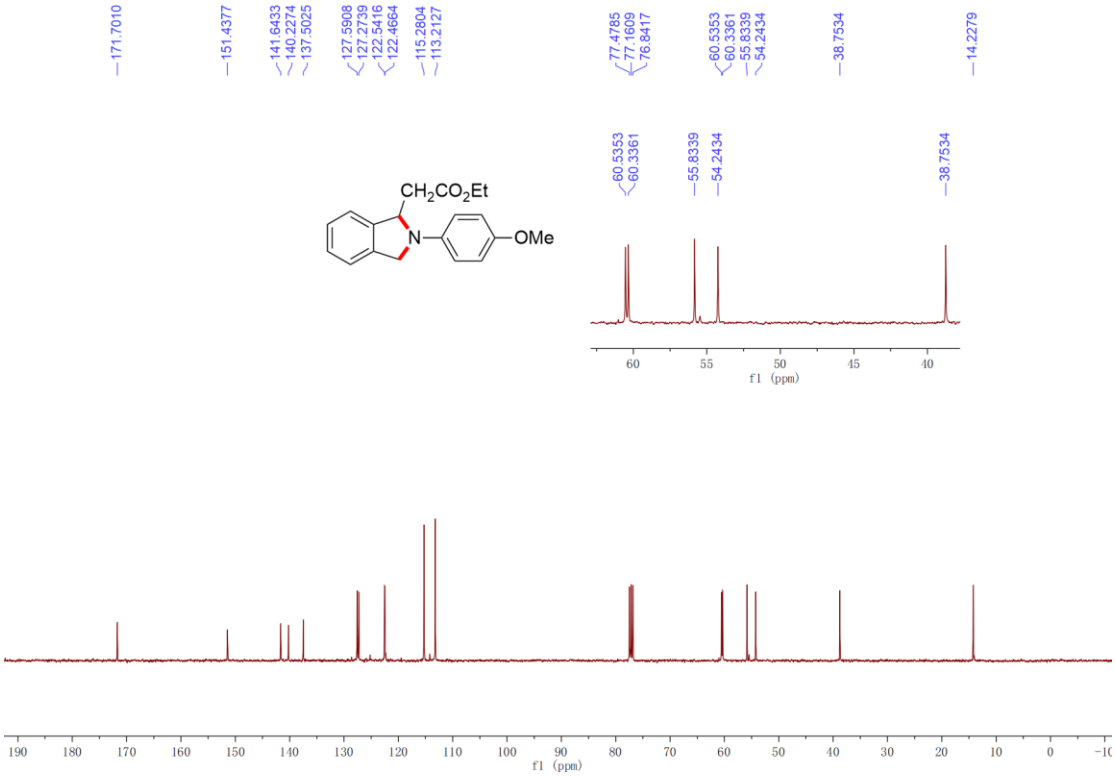

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **7as** in $CDCl_3$.



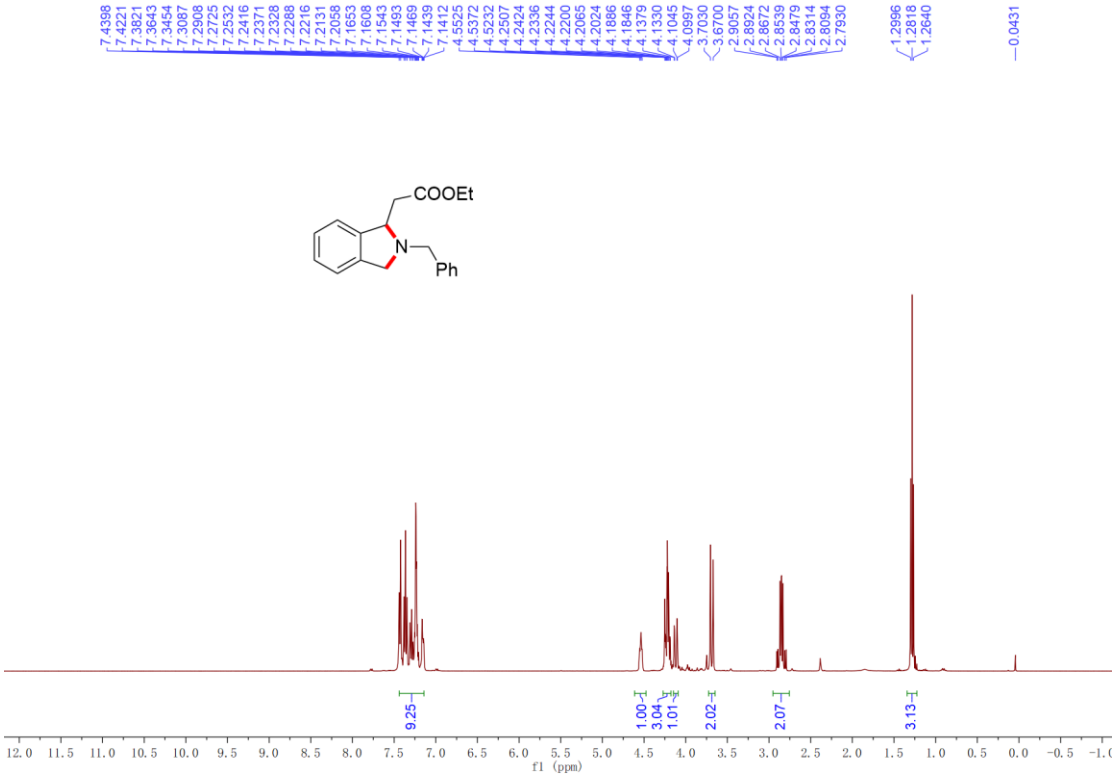
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **7bc** in $CDCl_3$.



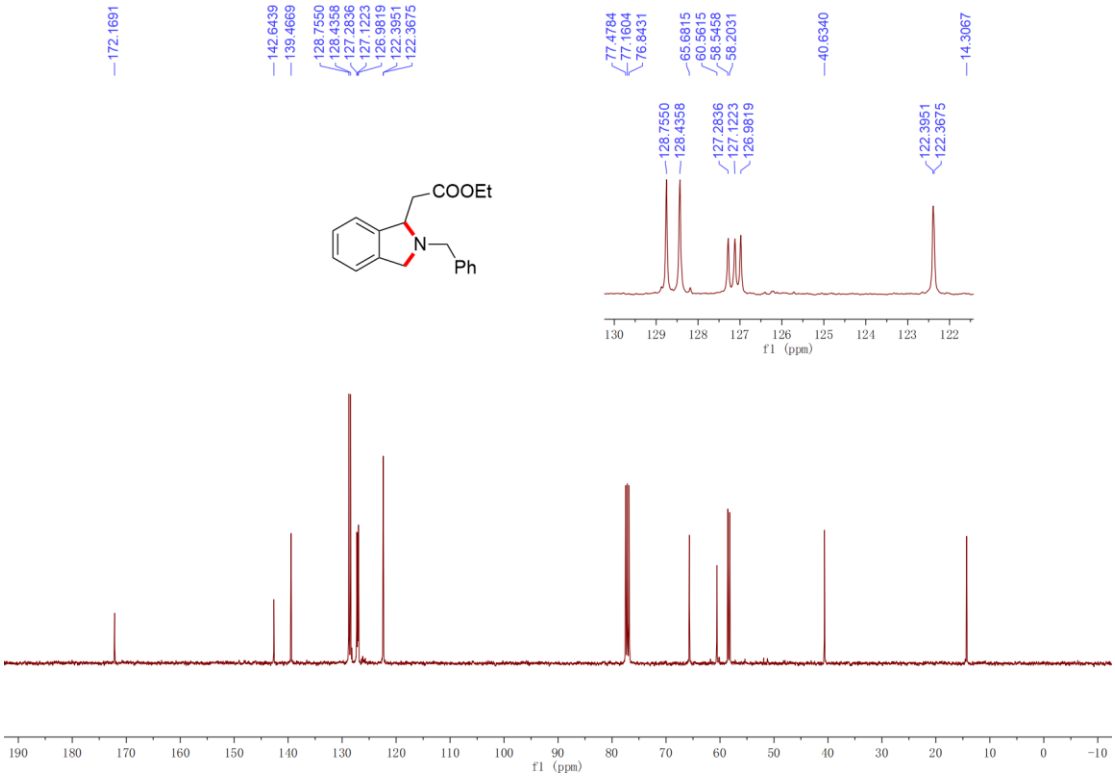

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **7bc** in $CDCl_3$.



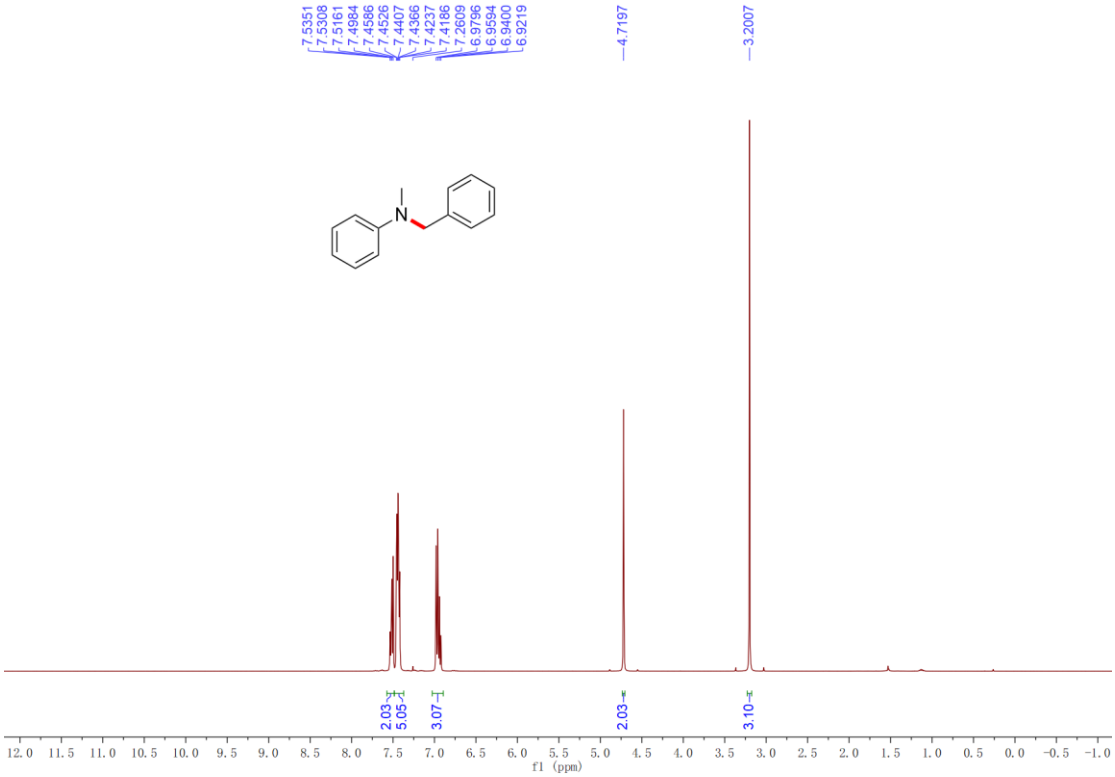
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **7bs** in $CDCl_3$.



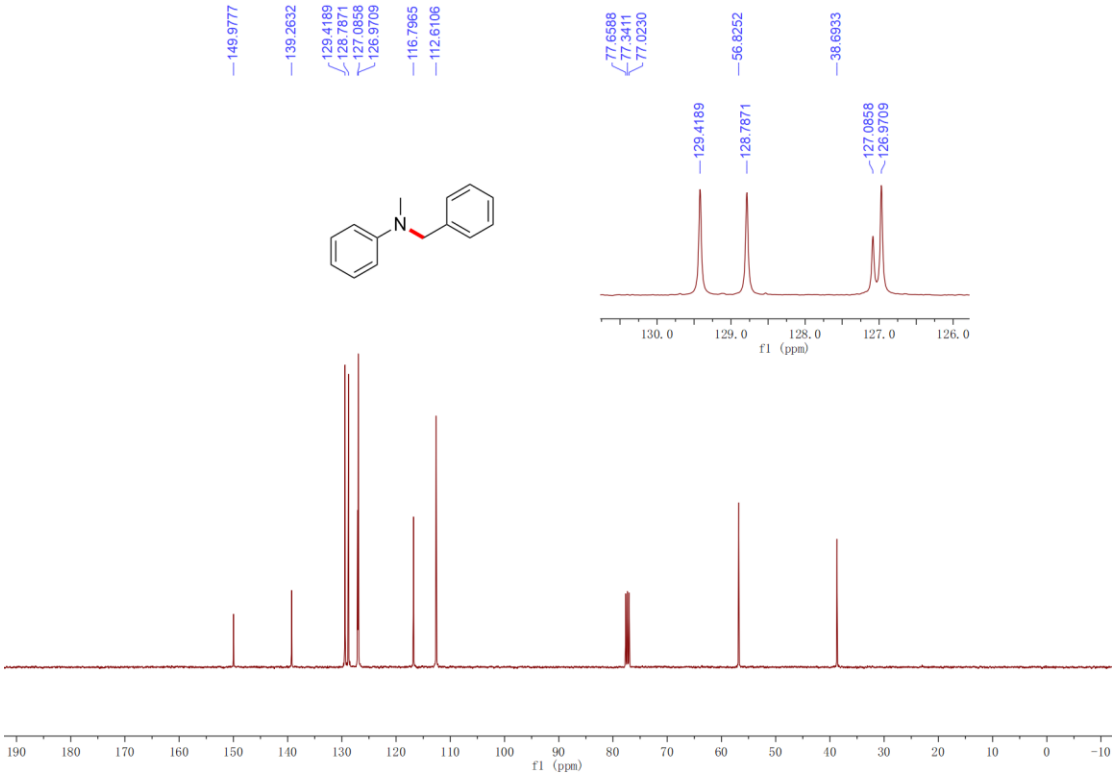

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **7bs** in $CDCl_3$.



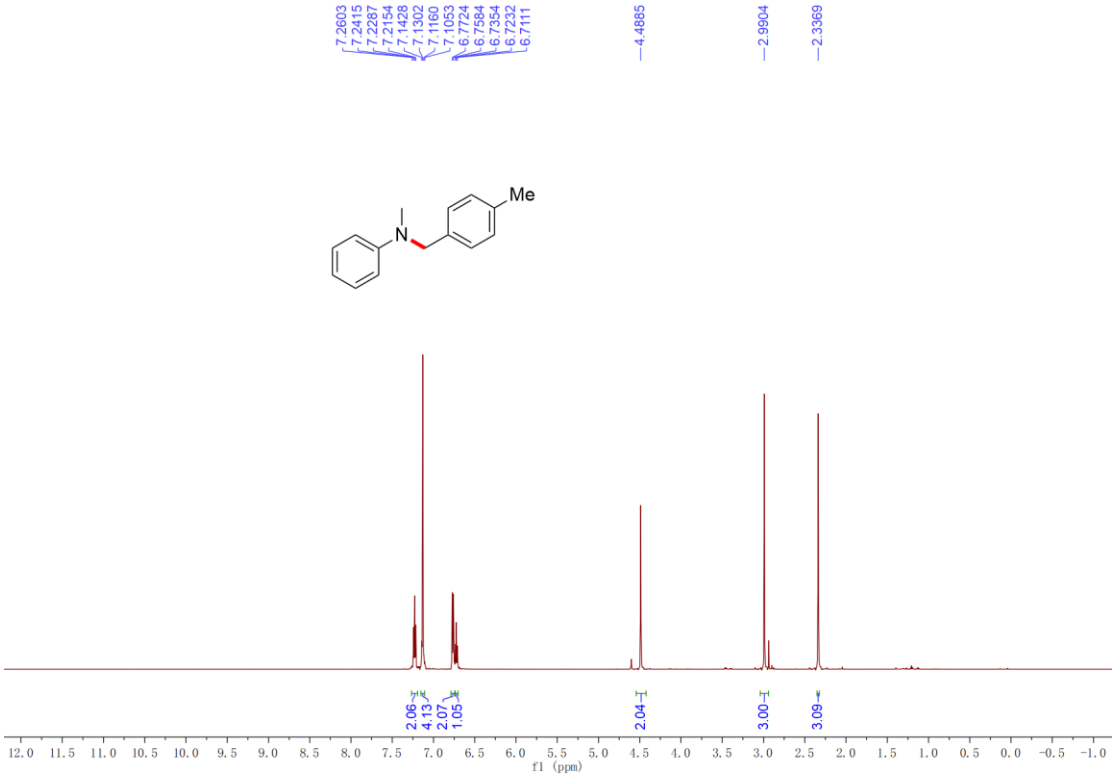
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9aa** in $CDCl_3$.



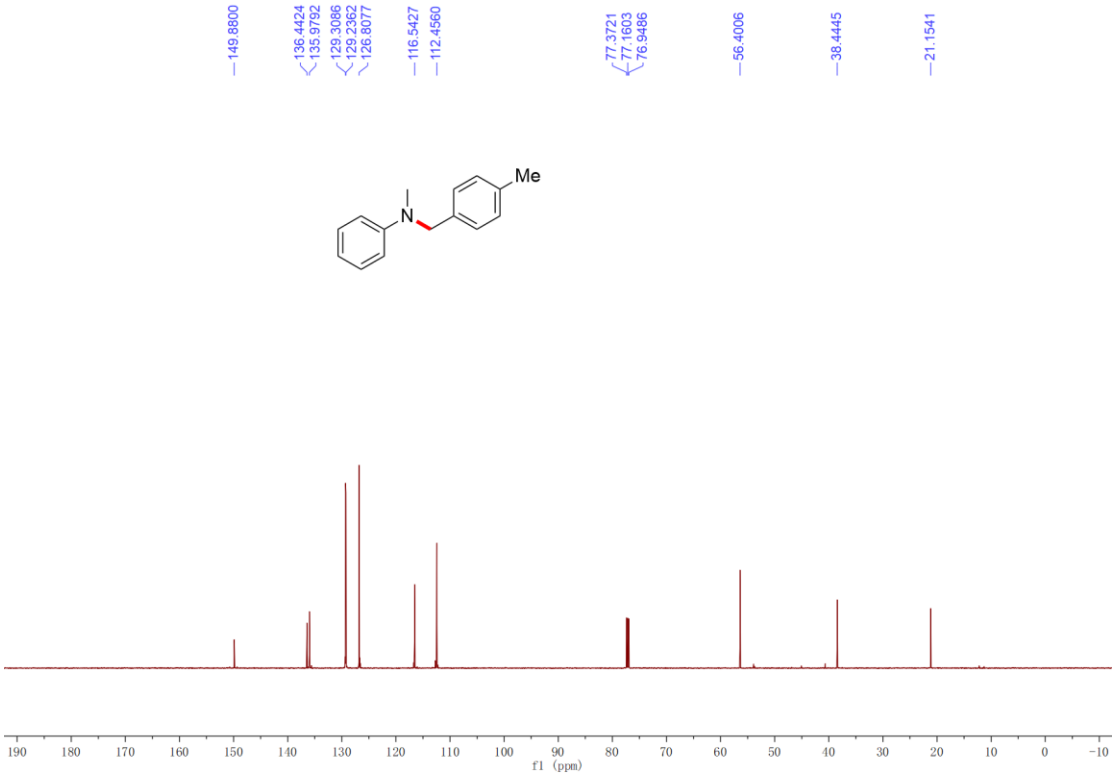

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9aa** in $CDCl_3$.



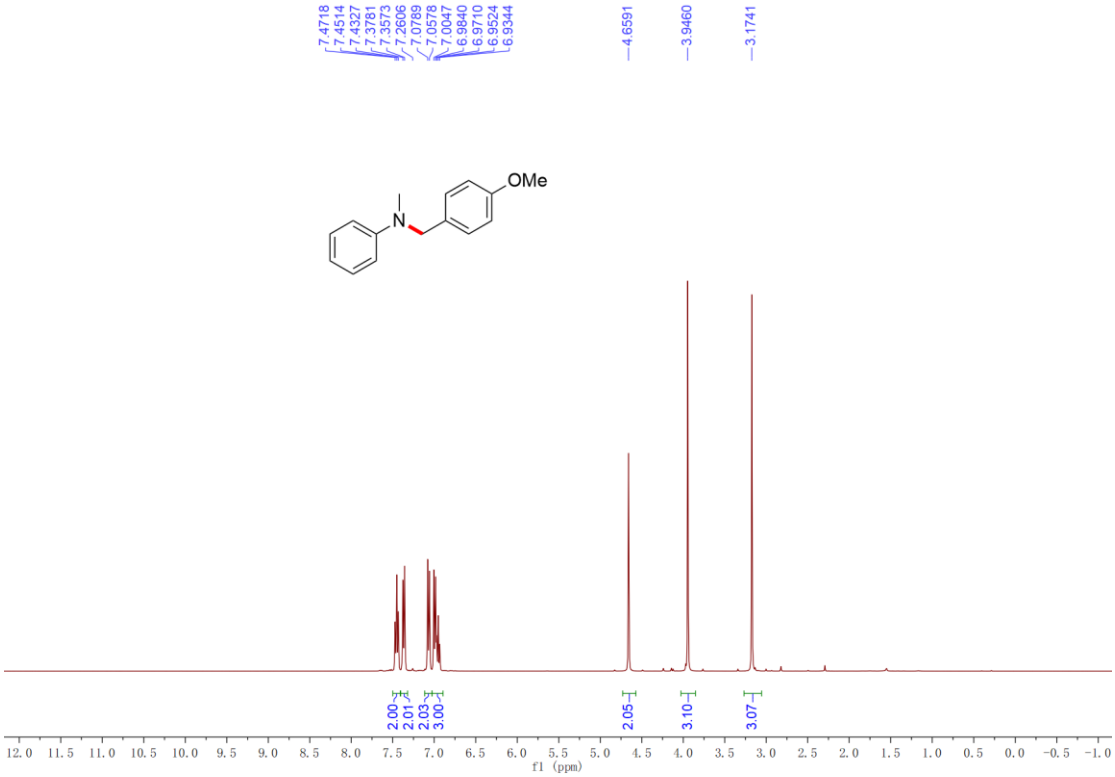
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **9ba** in $CDCl_3$.



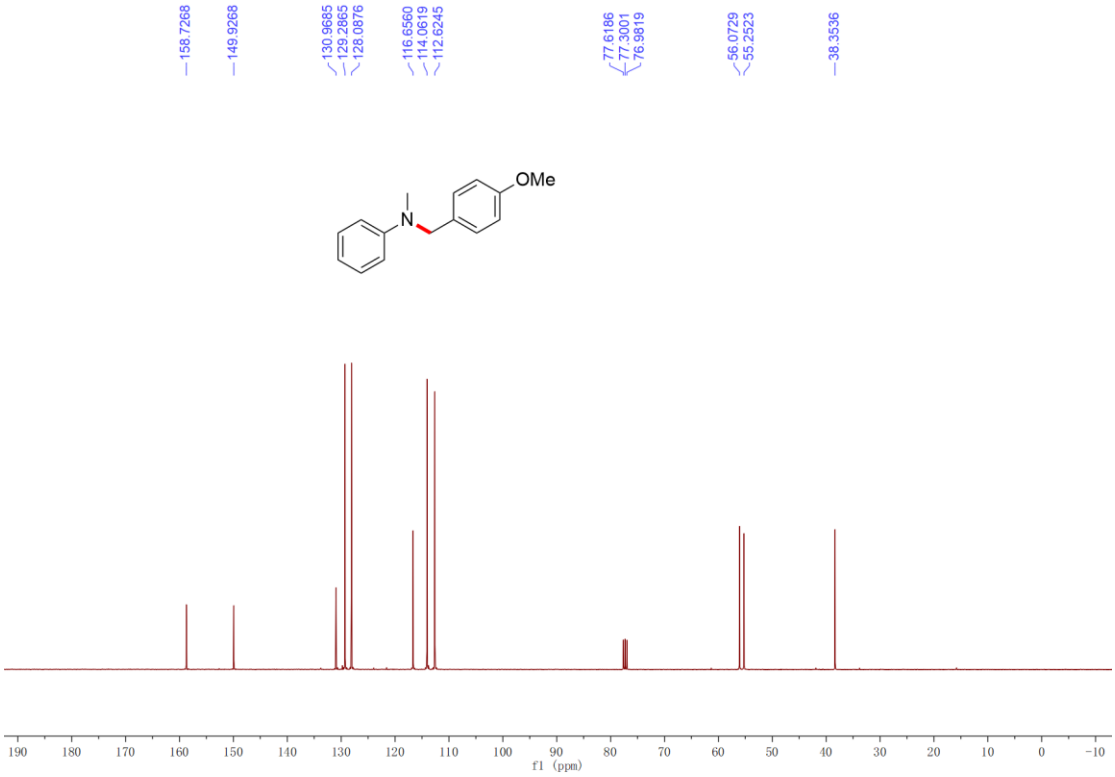

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **9ba** in $CDCl_3$.



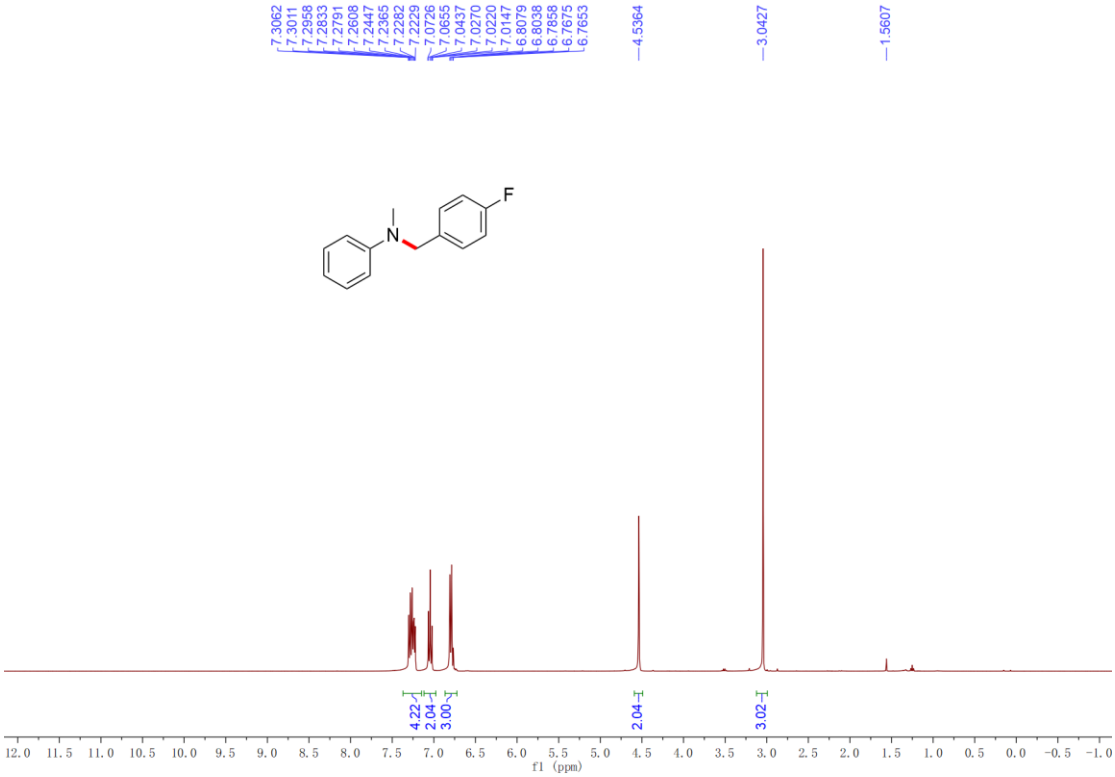
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ca** in $CDCl_3$.



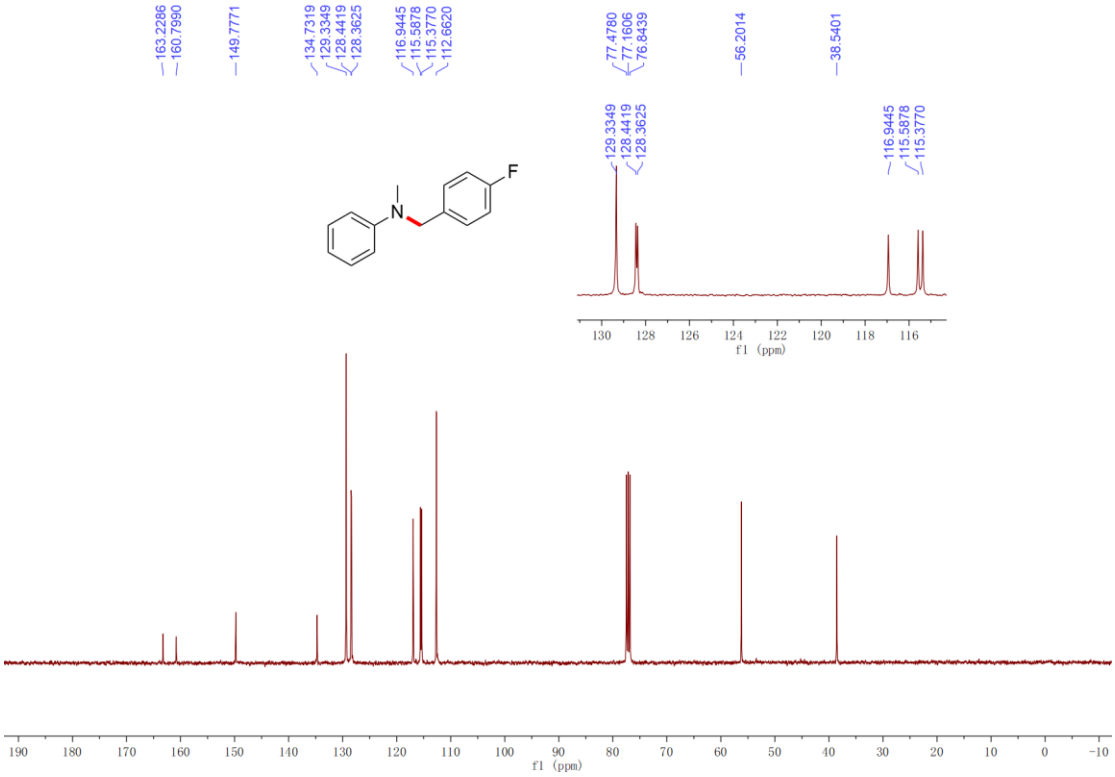

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ca** in $CDCl_3$.



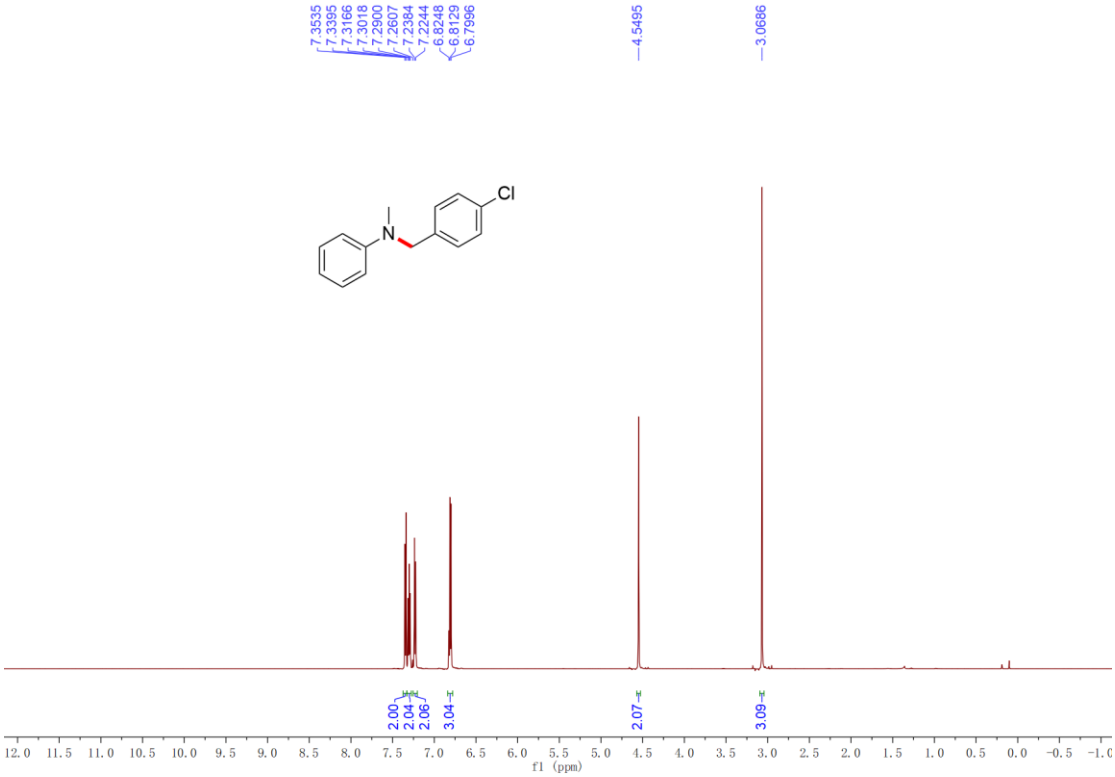
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9da** in $CDCl_3$.



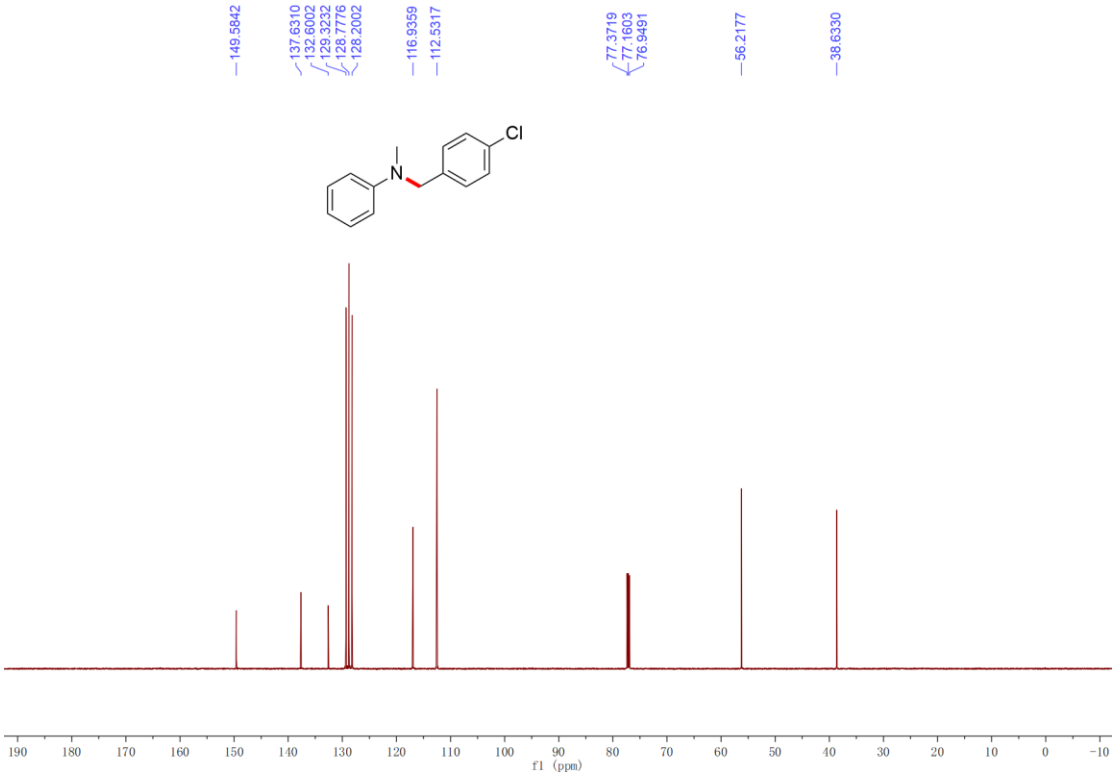

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9da** in $CDCl_3$.



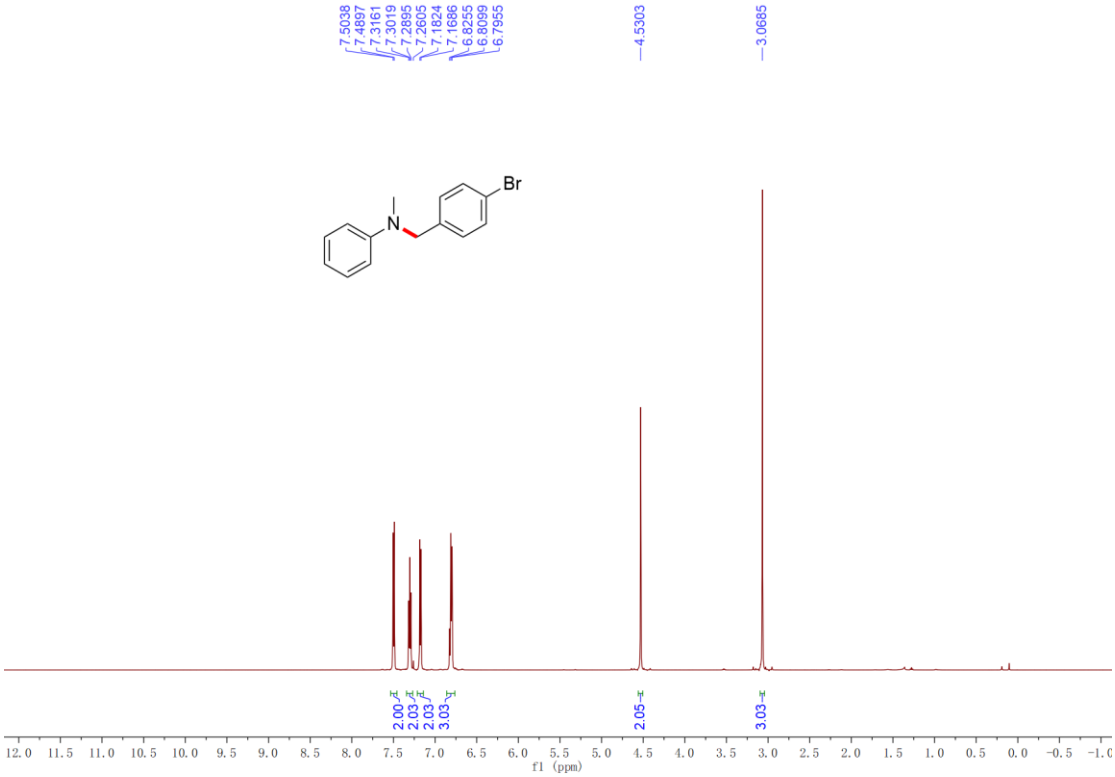
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **9ea** in $CDCl_3$.



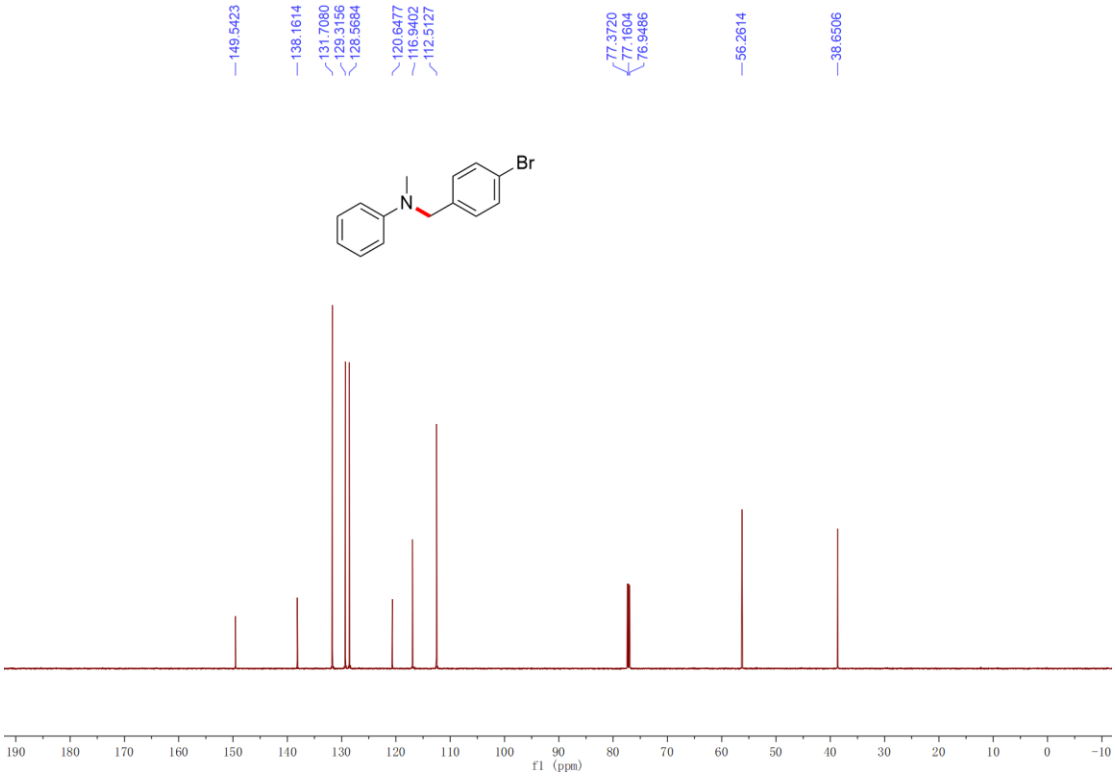

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **9ea** in $CDCl_3$.



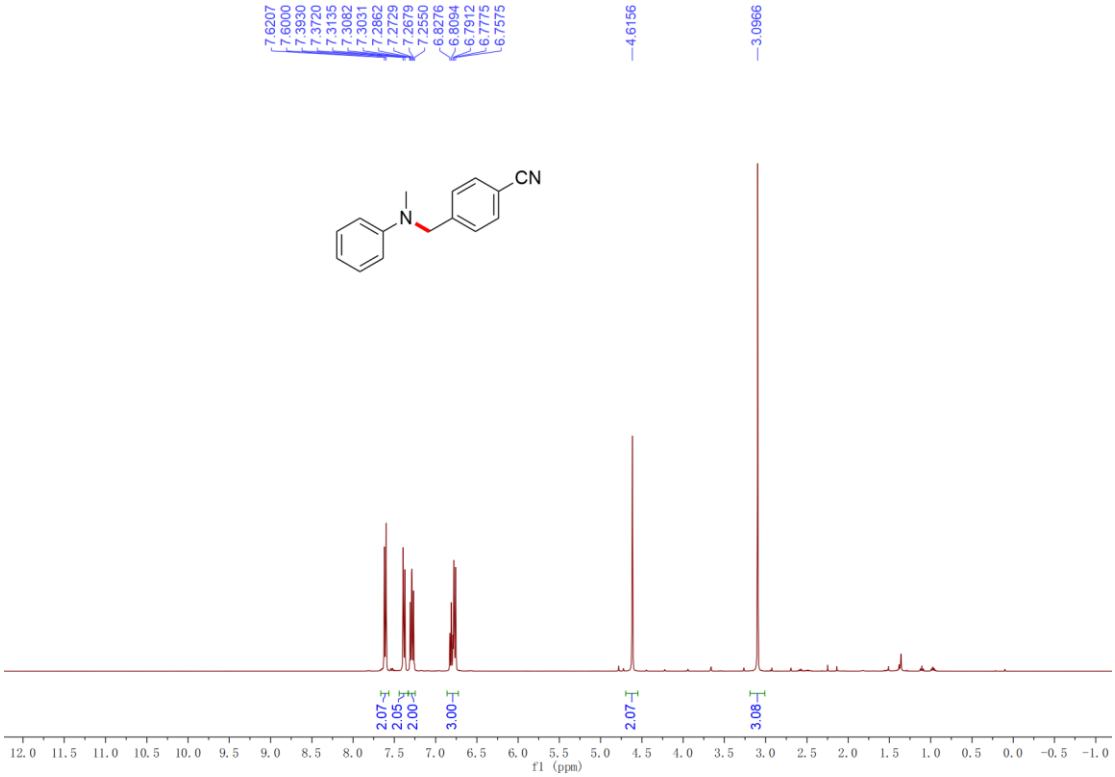
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **9fa** in $CDCl_3$.



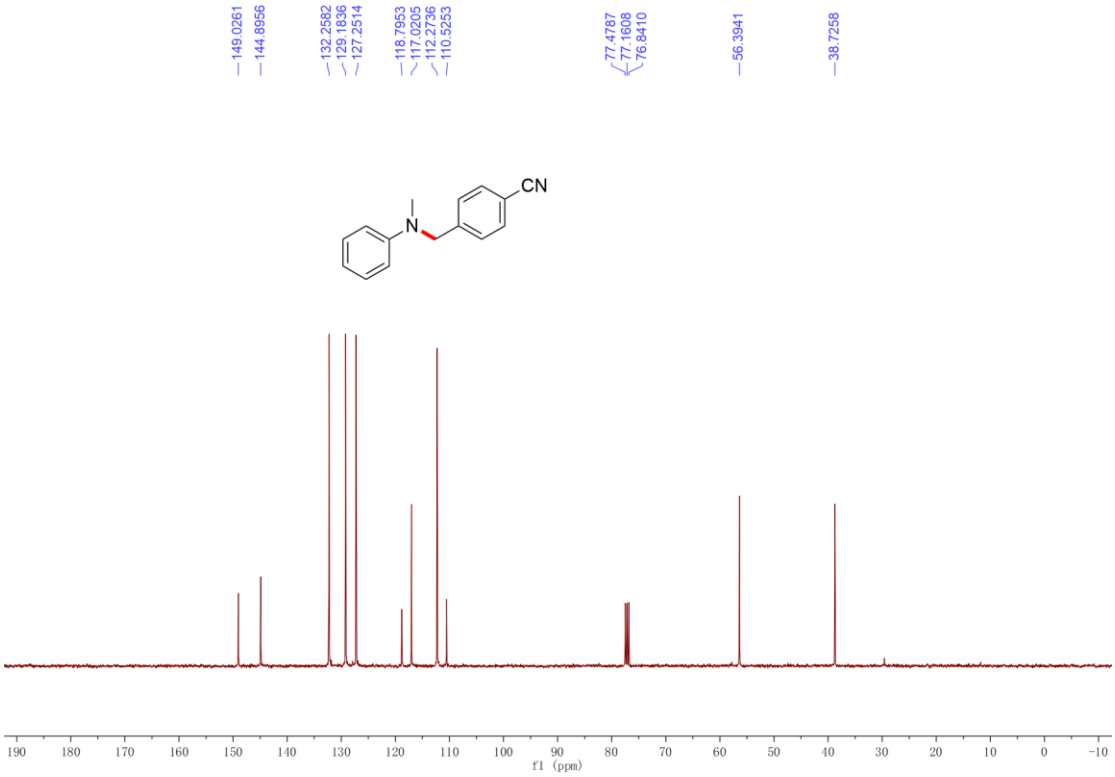

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **9fa** in $CDCl_3$.



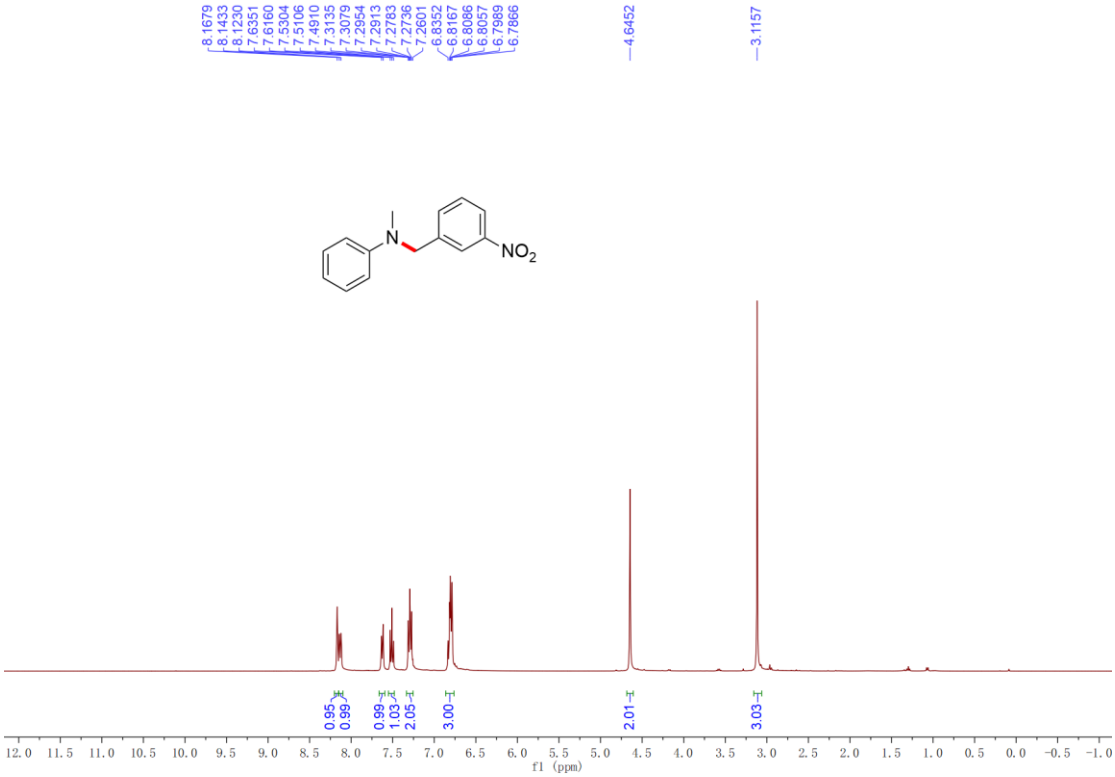
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ia** in $CDCl_3$.



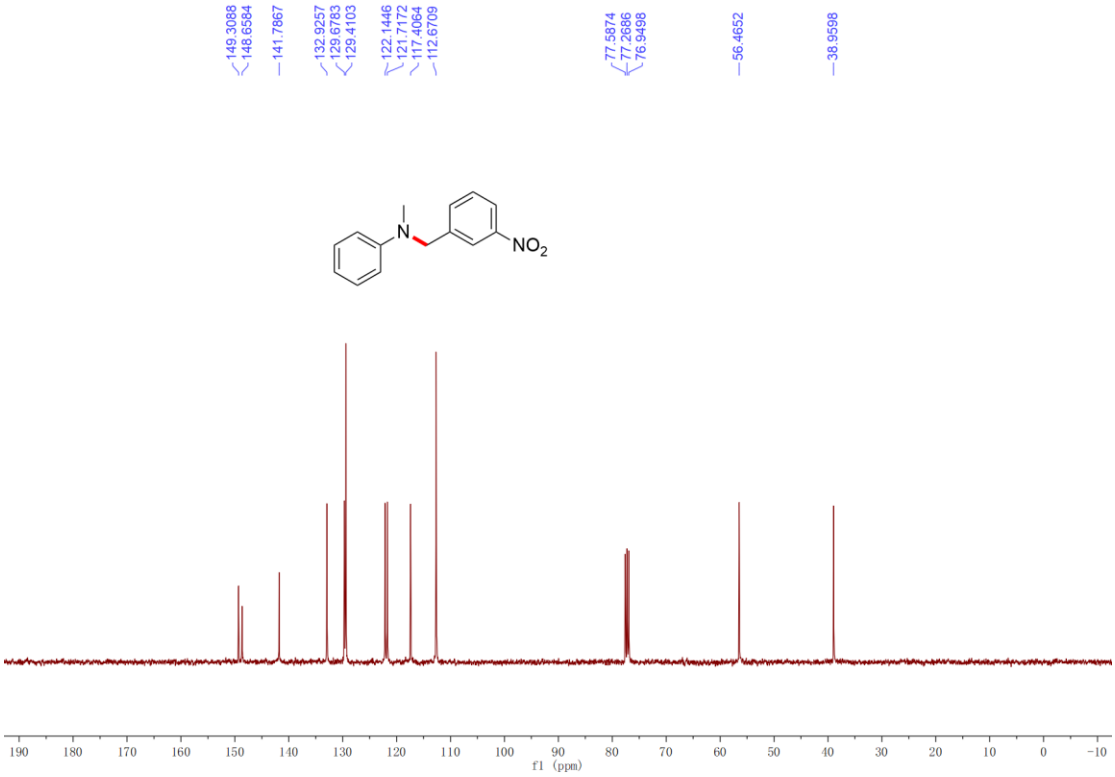

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ia** in $CDCl_3$.



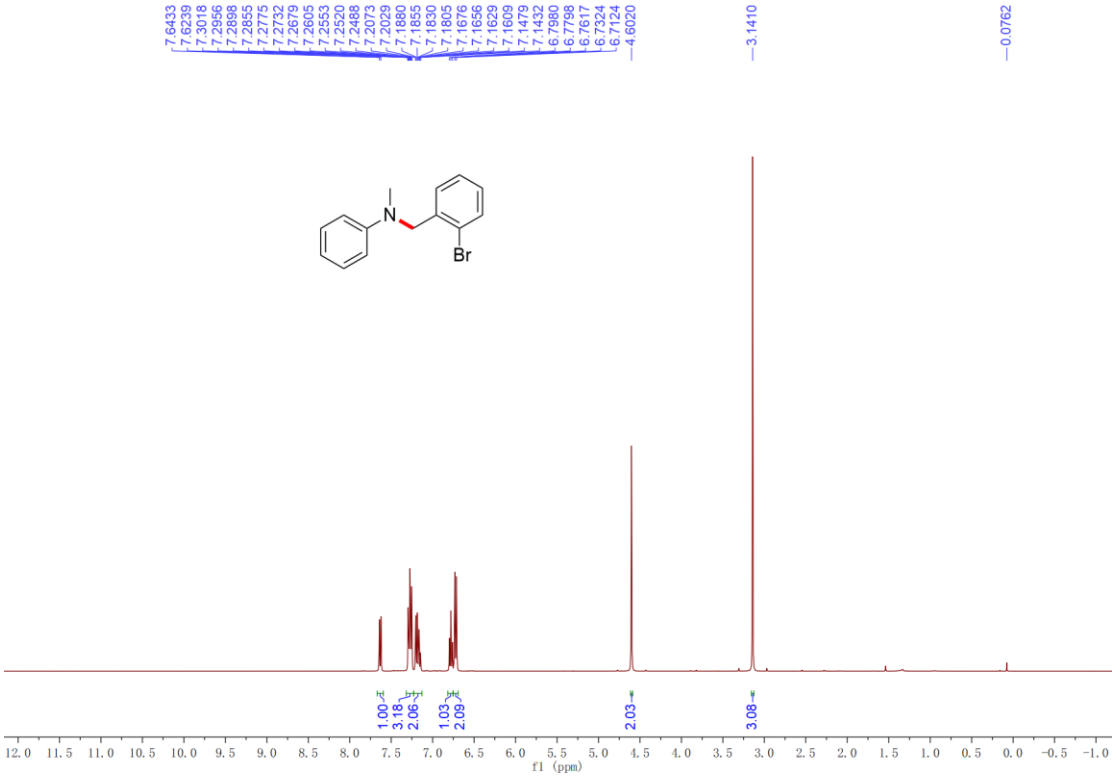
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9pa** in $CDCl_3$.



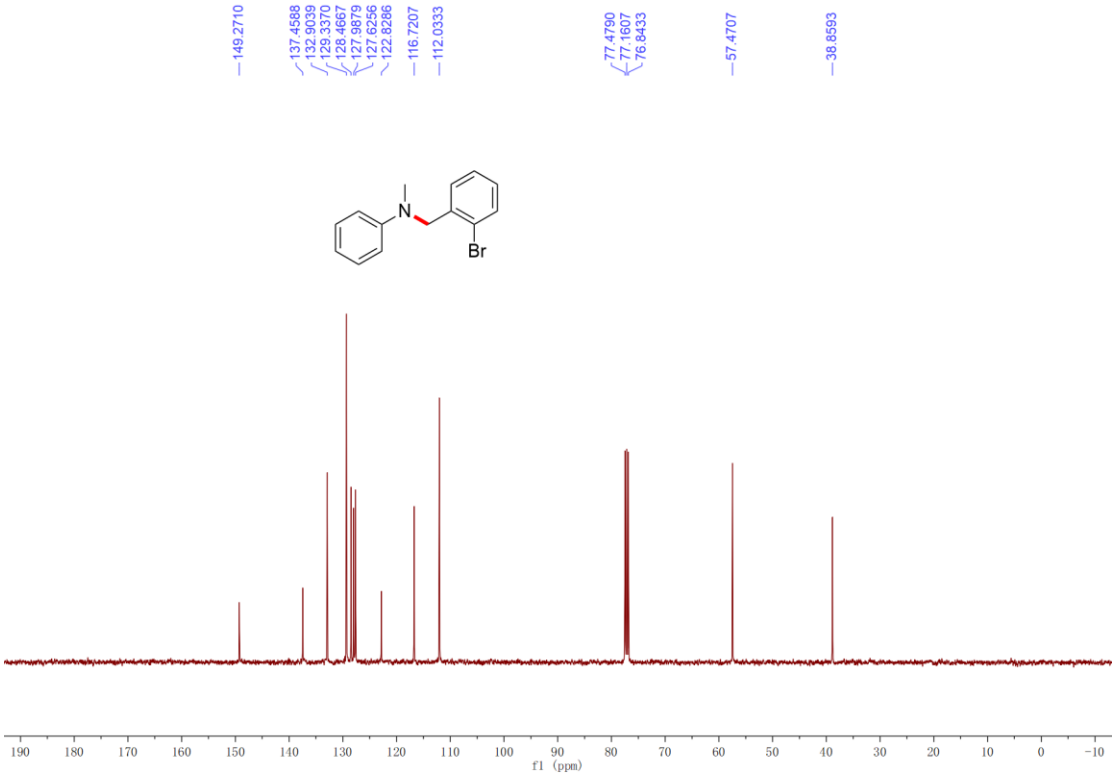

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9pa** in $CDCl_3$.



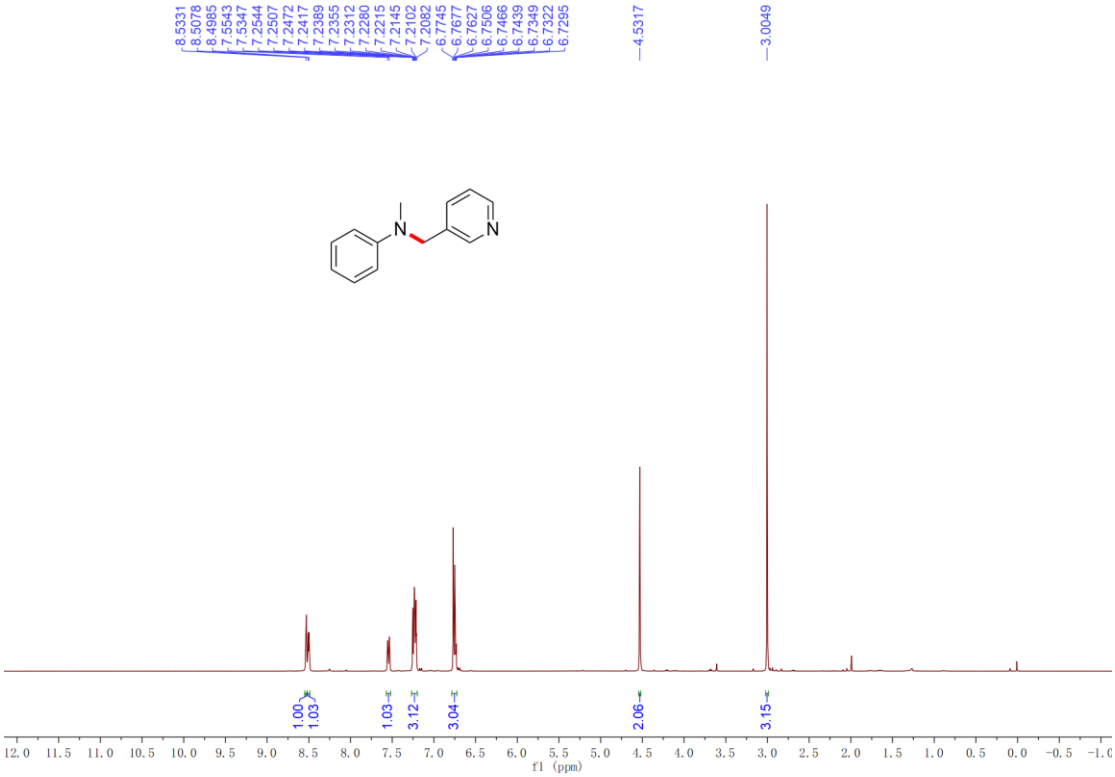
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9qa** in $CDCl_3$.



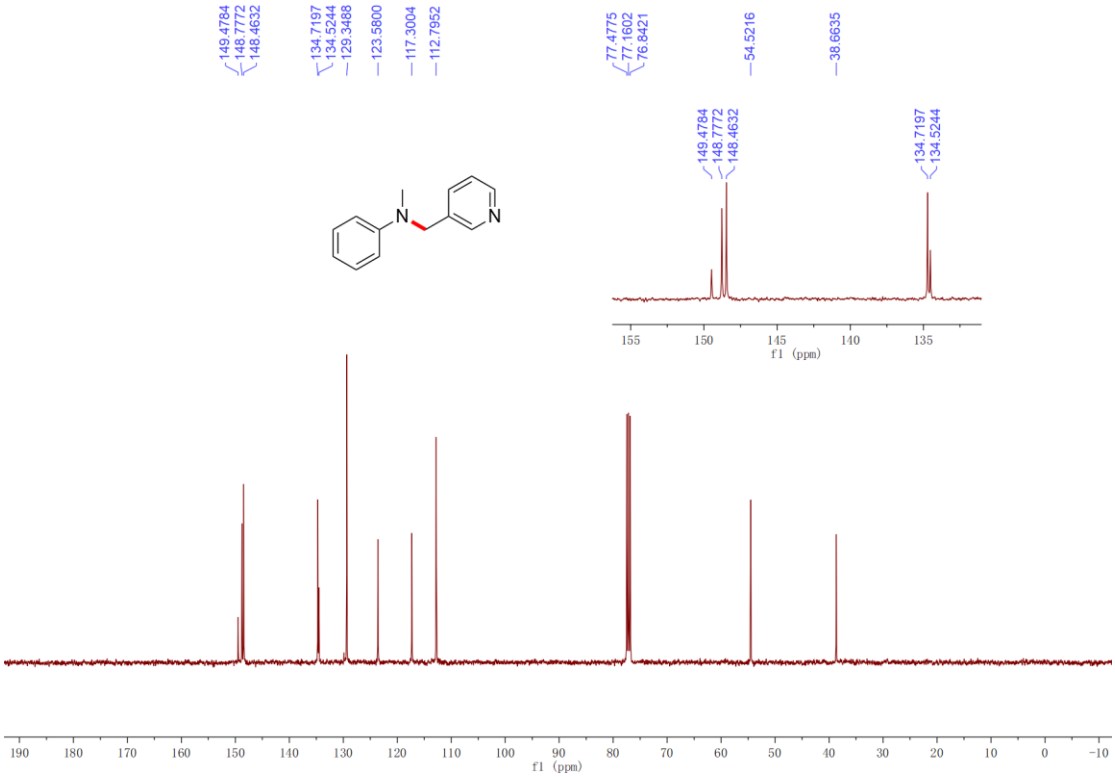

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9qa** in $CDCl_3$.



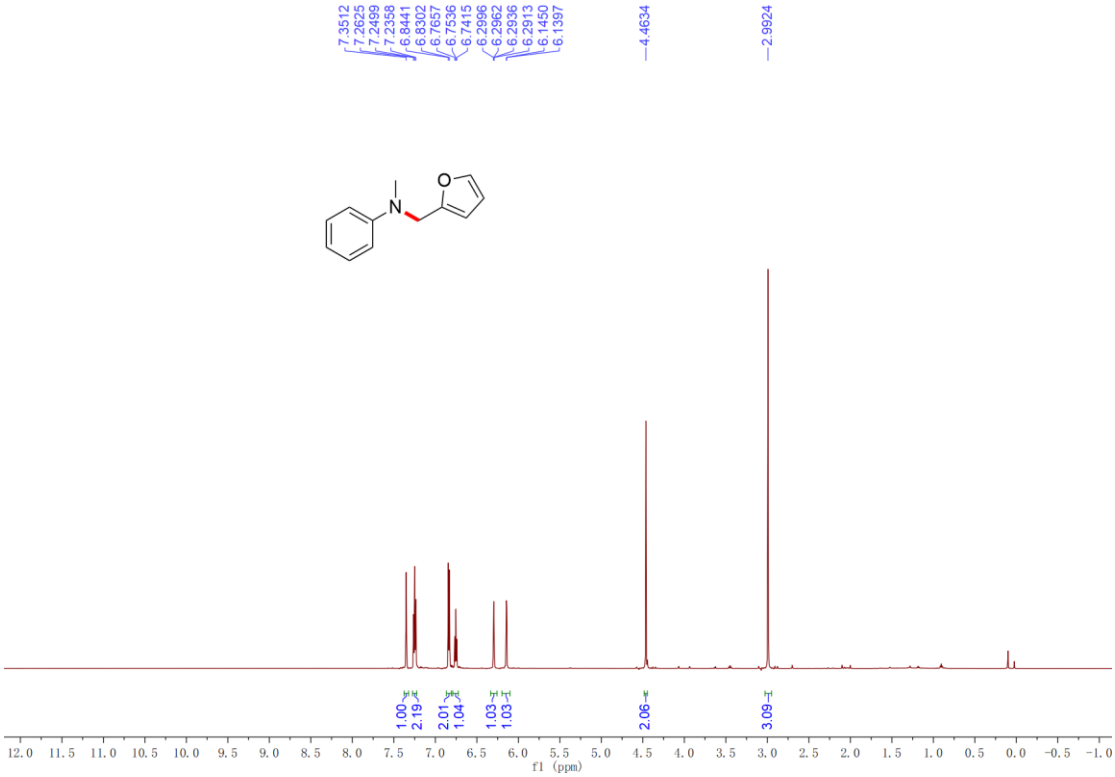
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9wa** in $CDCl_3$.



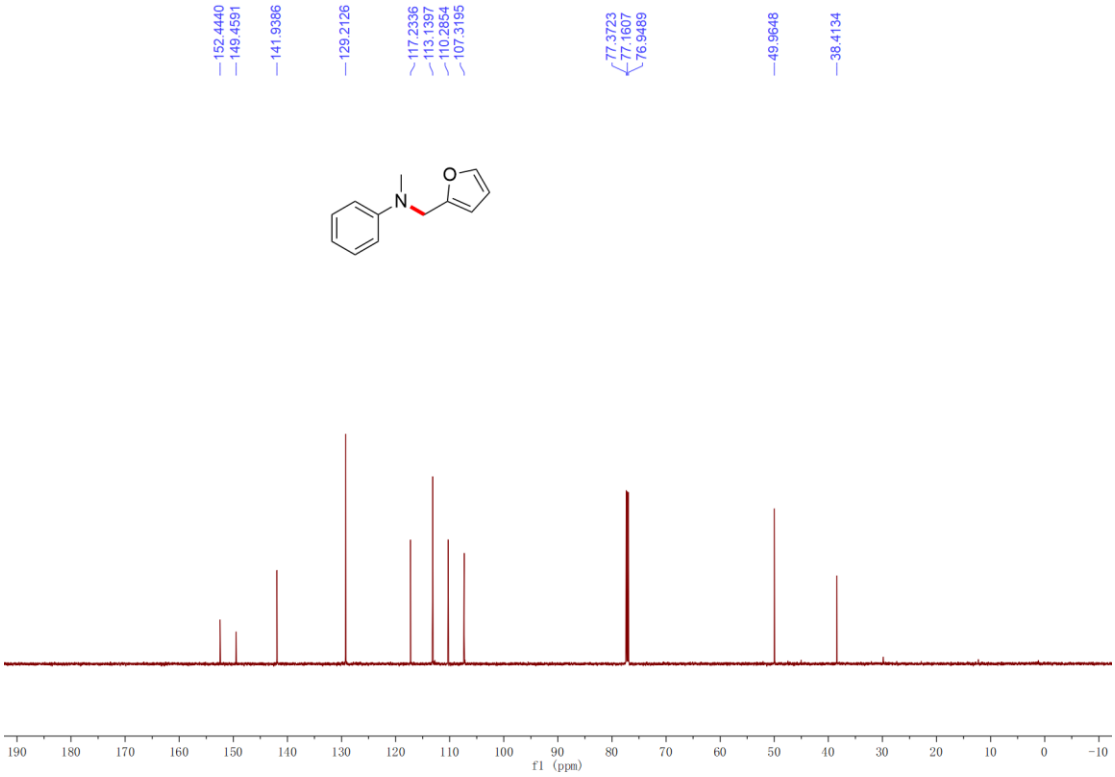

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9wa** in $CDCl_3$.



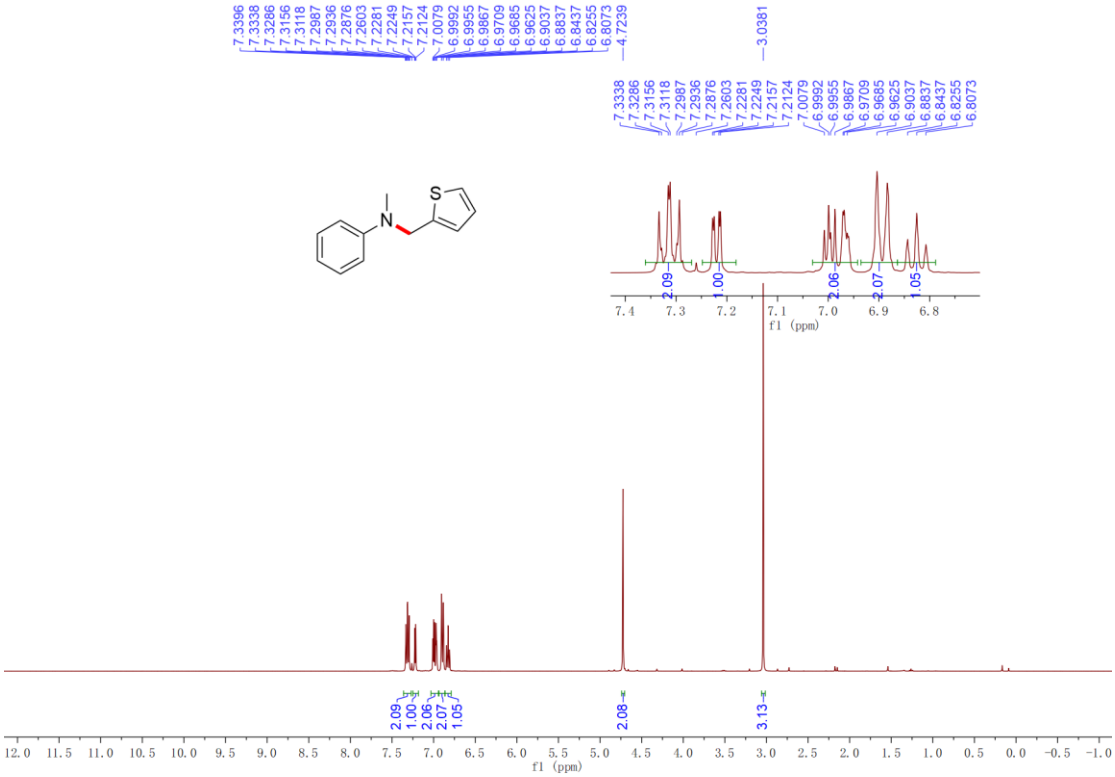
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **9xa** in $CDCl_3$.



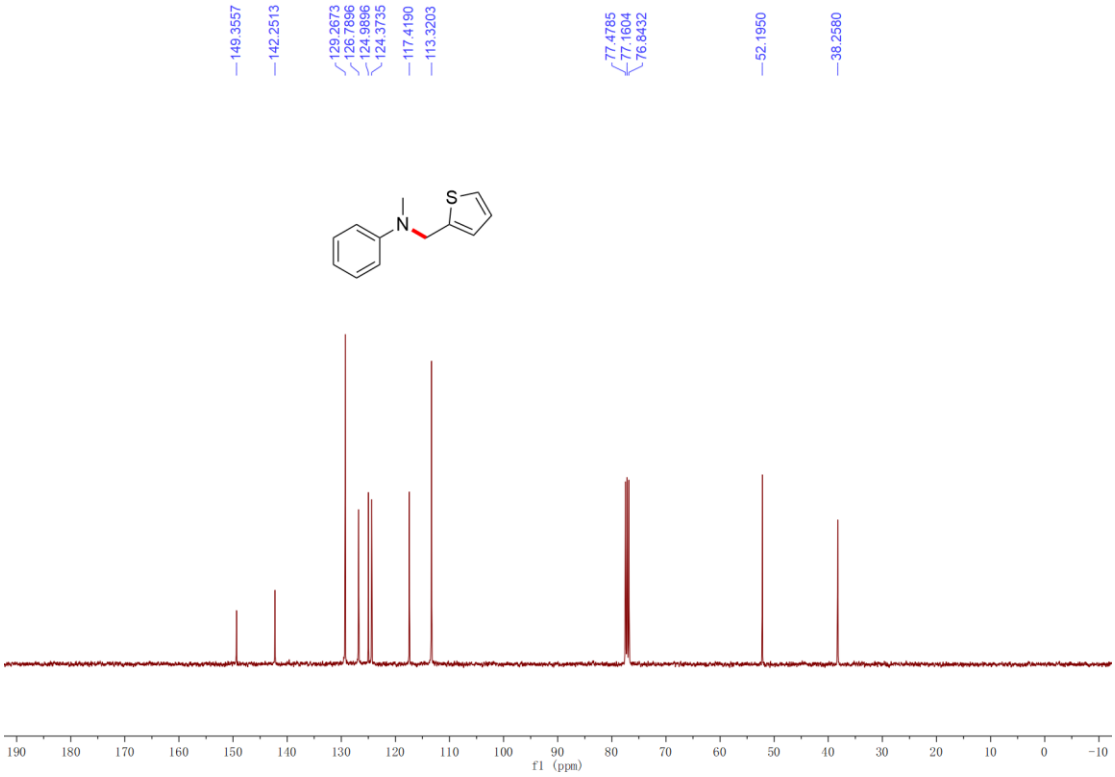

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **9xa** in $CDCl_3$.



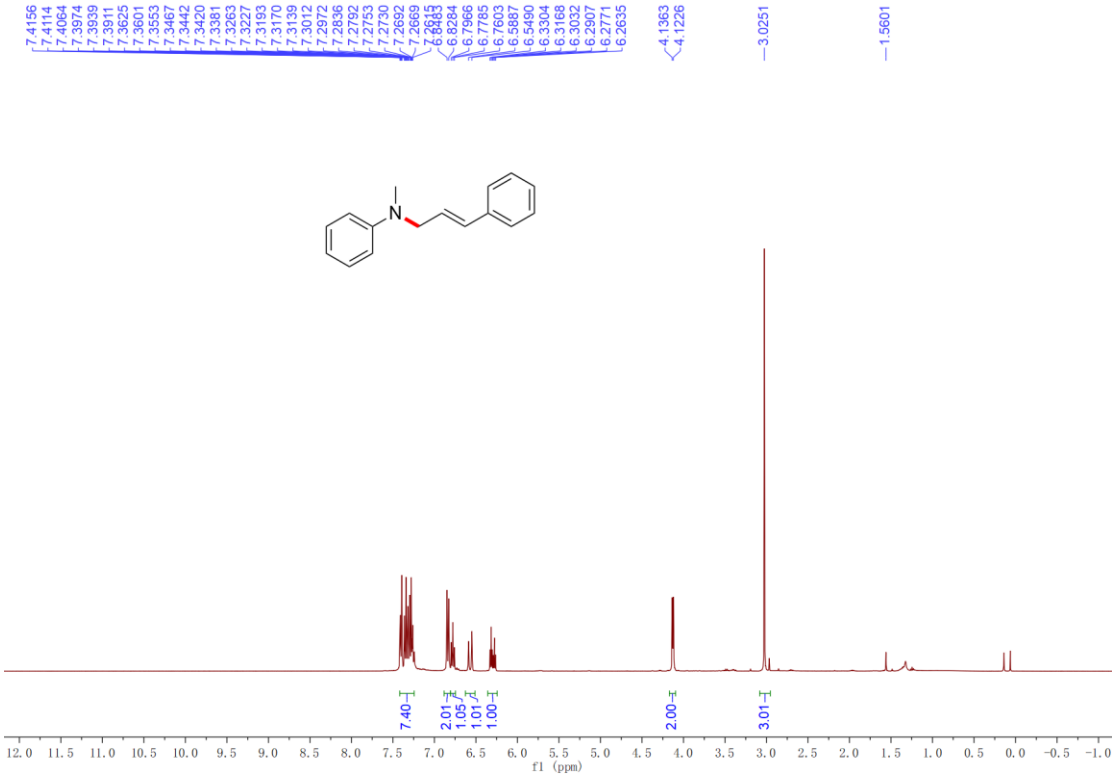
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ya** in $CDCl_3$.



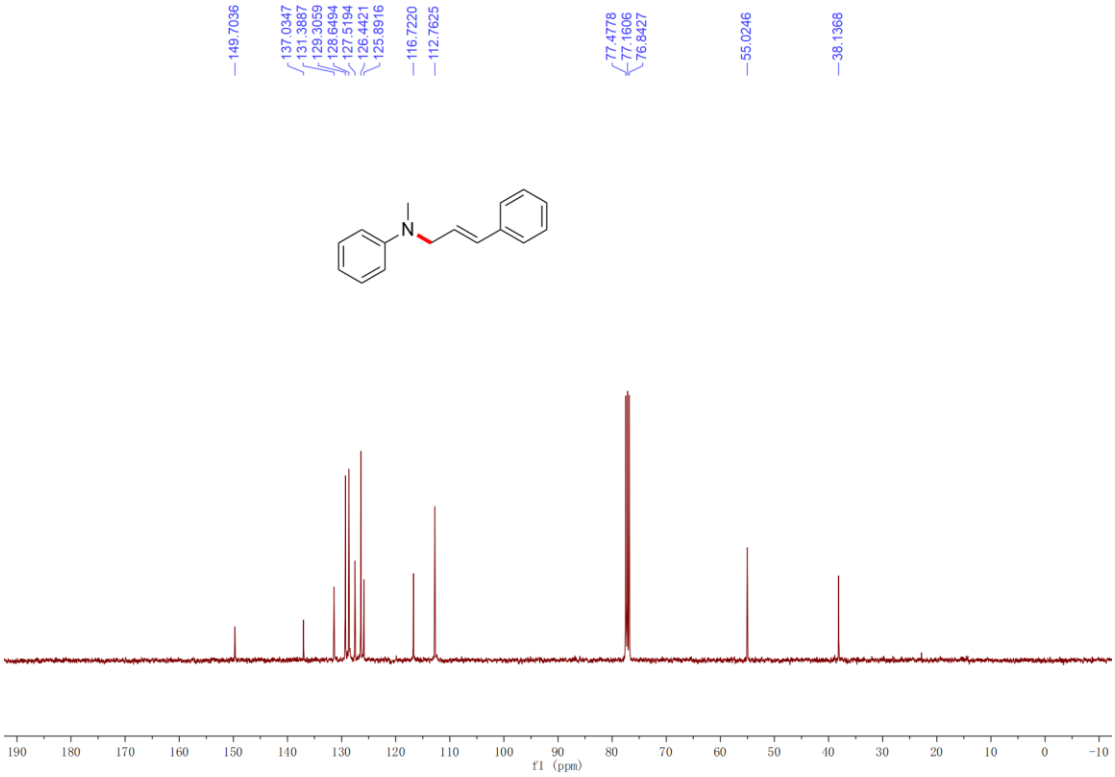

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ya** in $CDCl_3$.



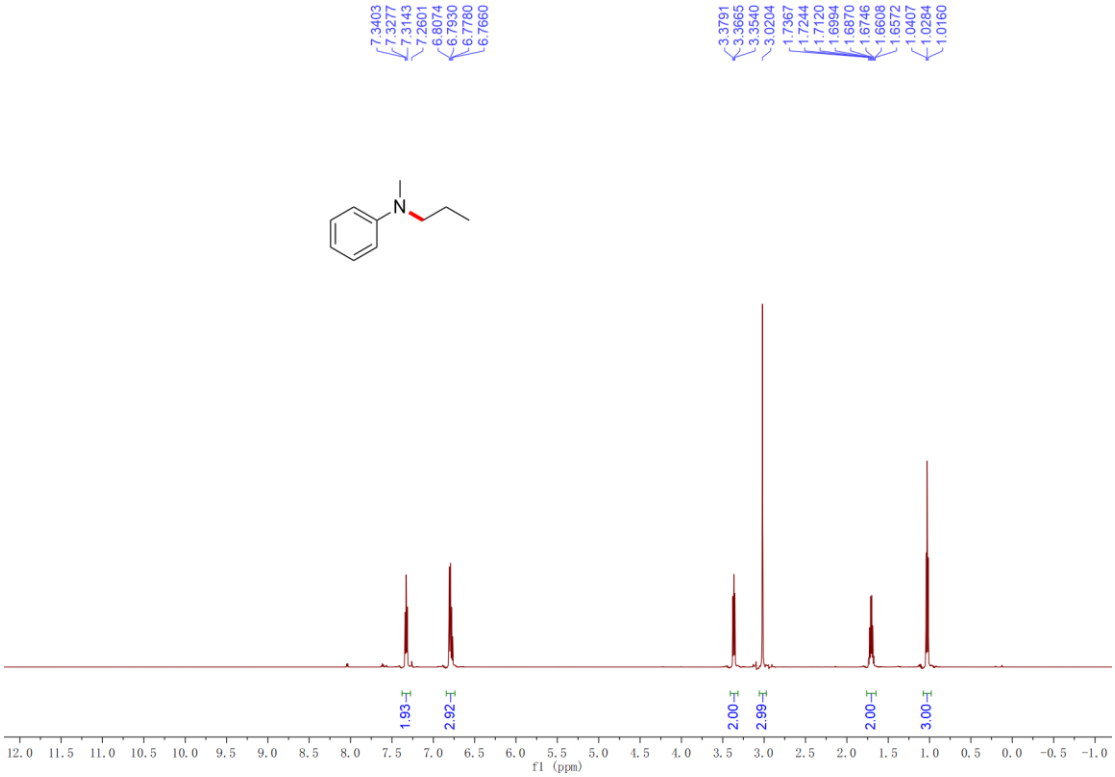
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **10aa** in $CDCl_3$.



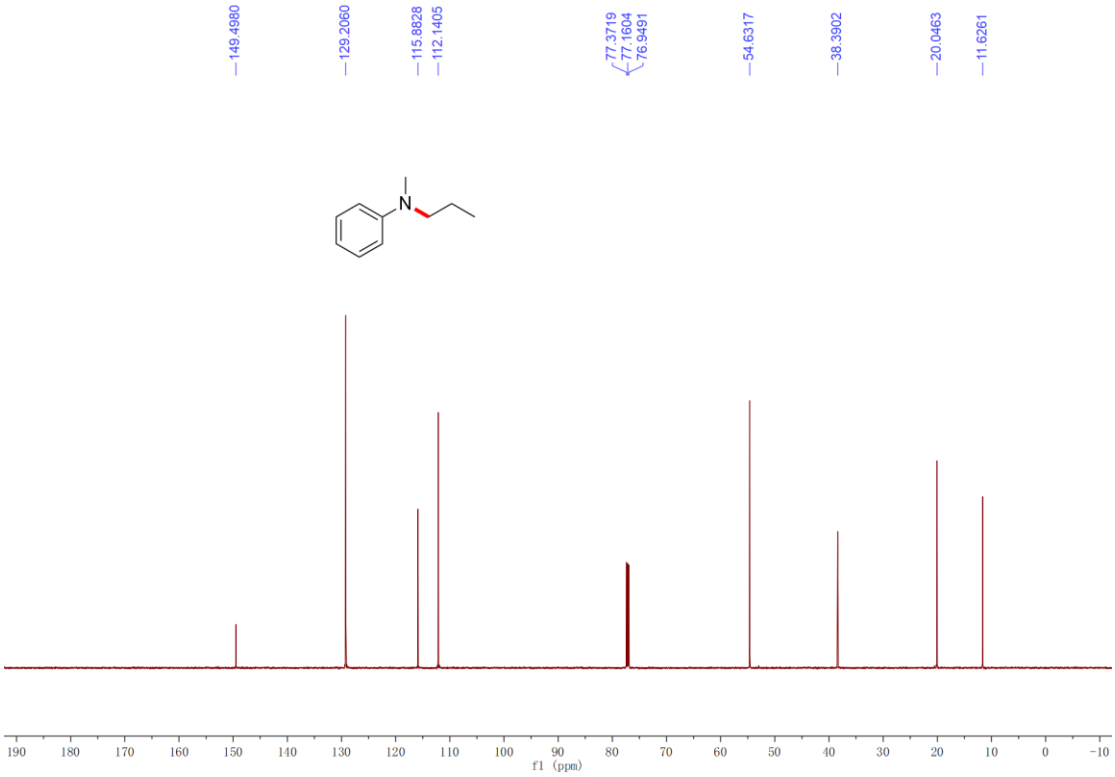

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **10aa** in $CDCl_3$.



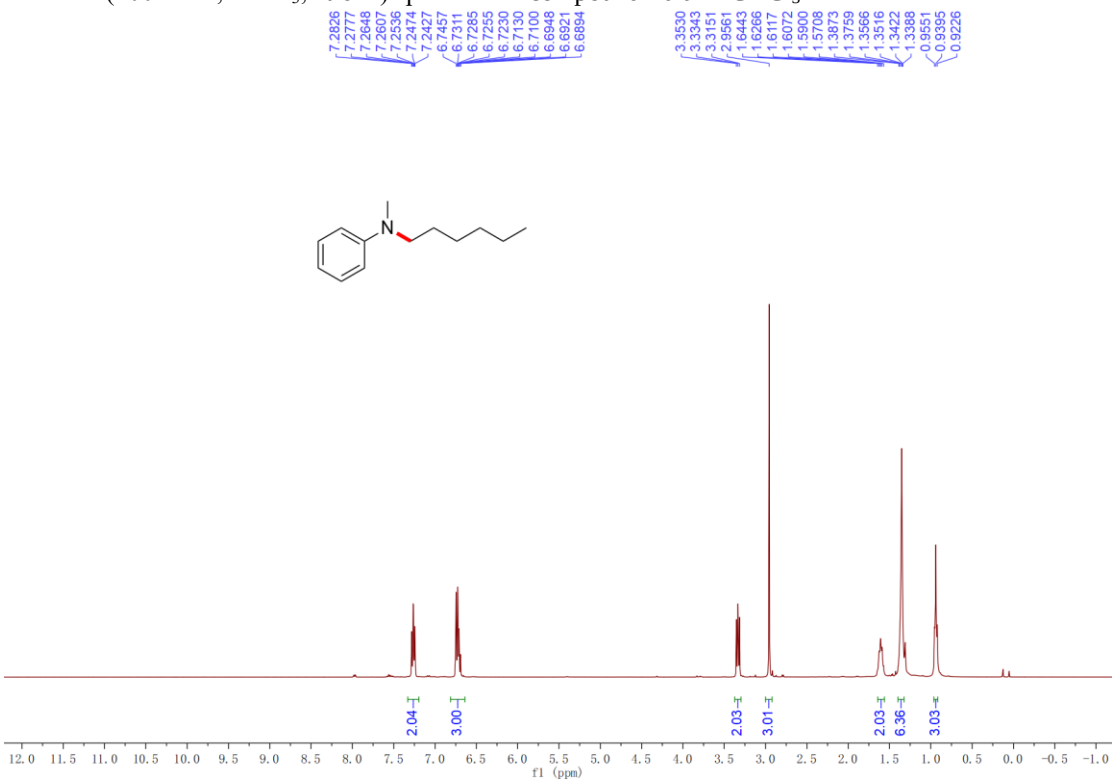
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **10ha** in $CDCl_3$.



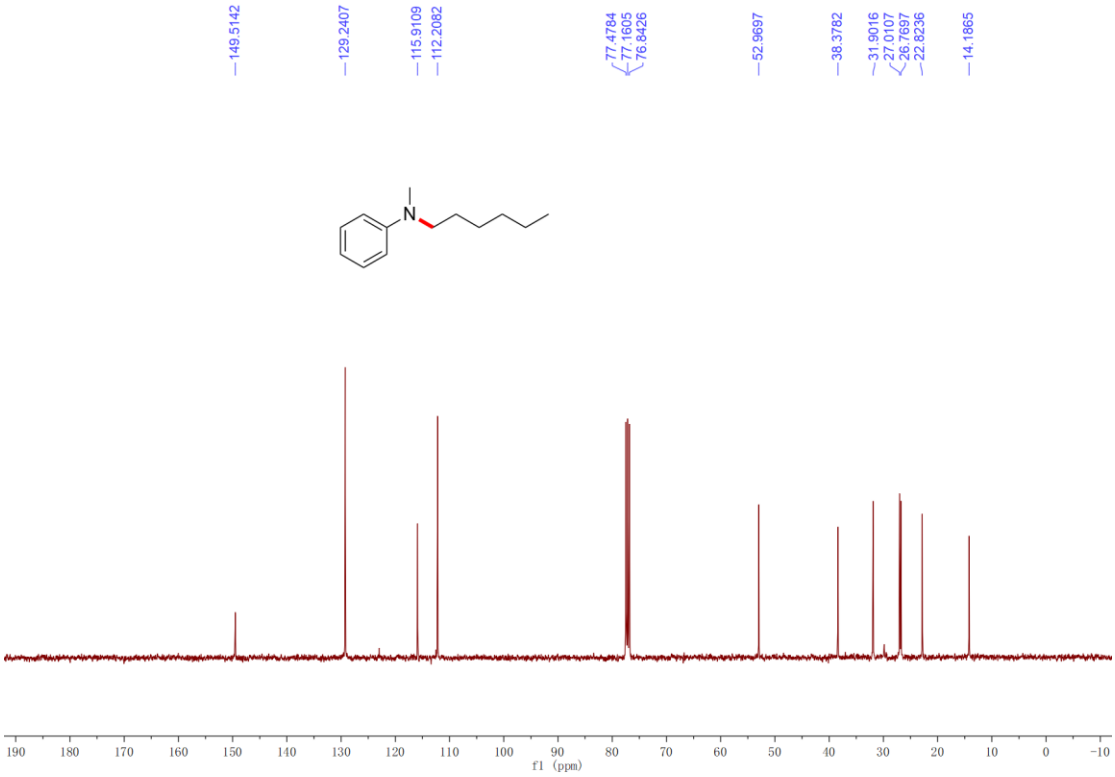

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **10ha** in $CDCl_3$.



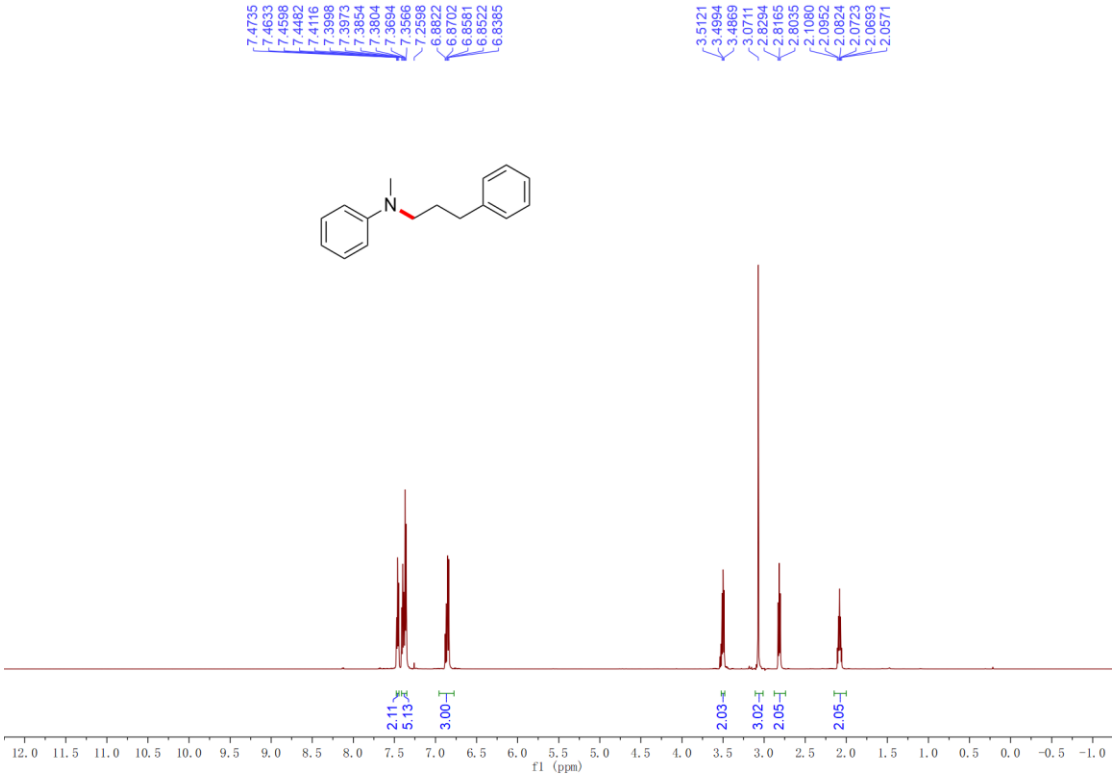
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **10ia** in $CDCl_3$.



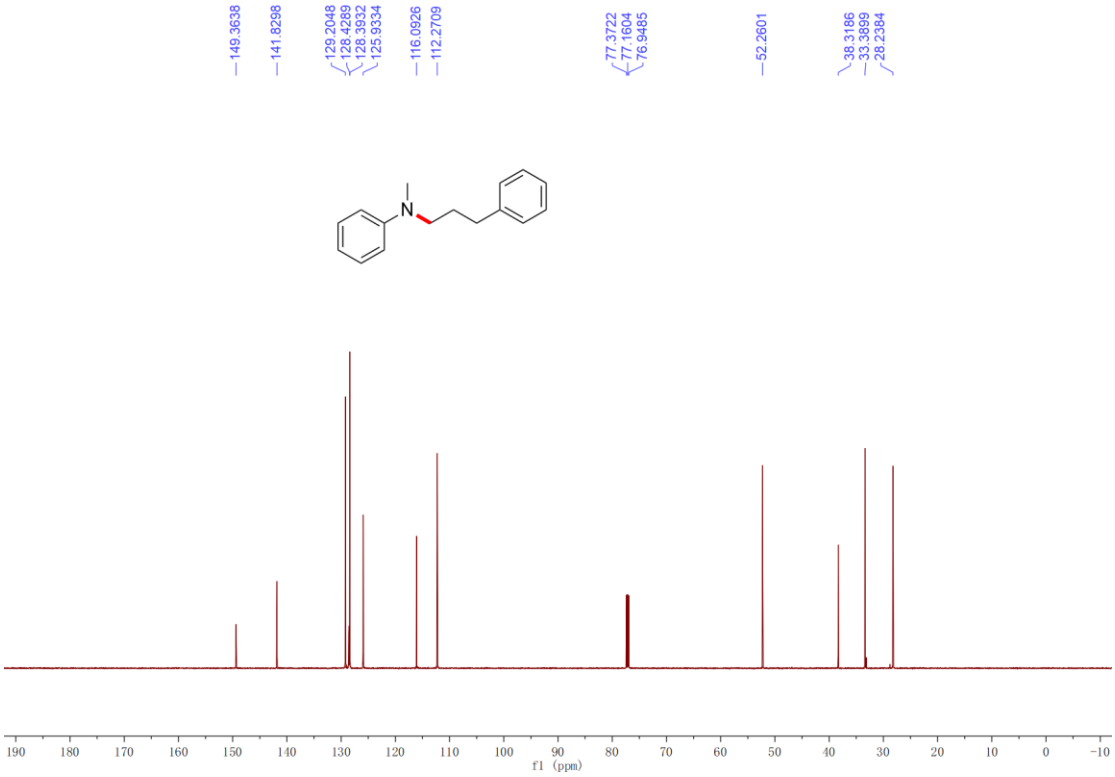

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **10ia** in $CDCl_3$.



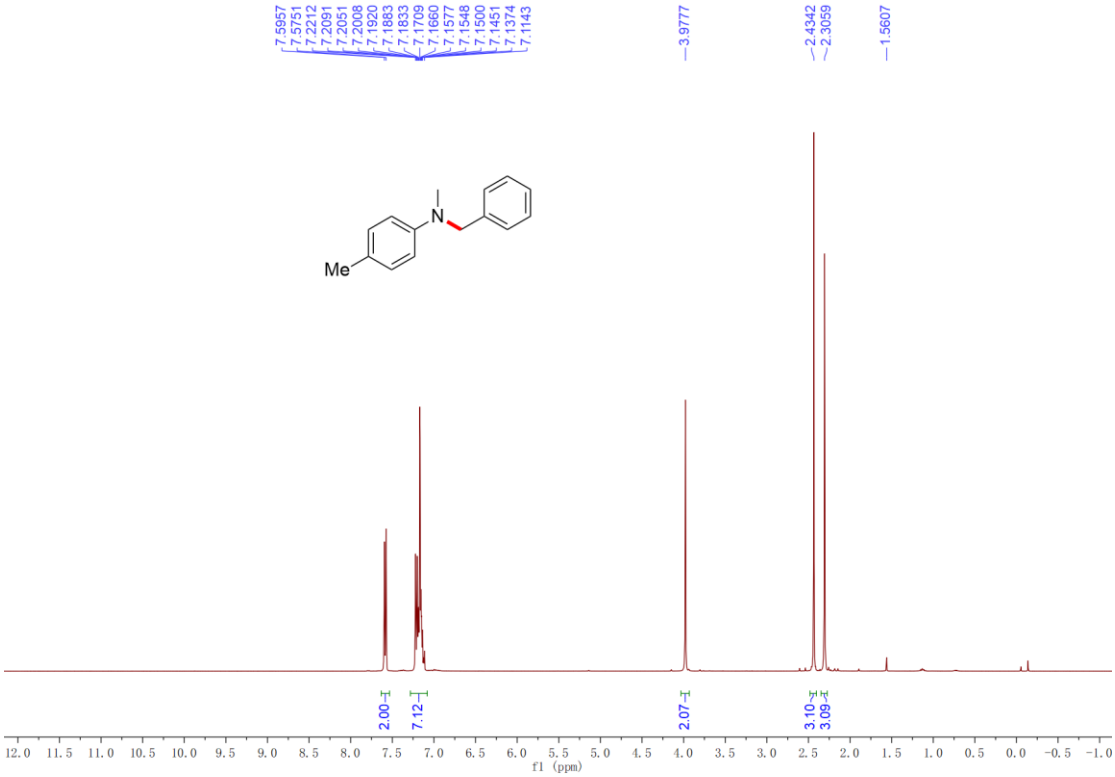
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **10ja** in $CDCl_3$.



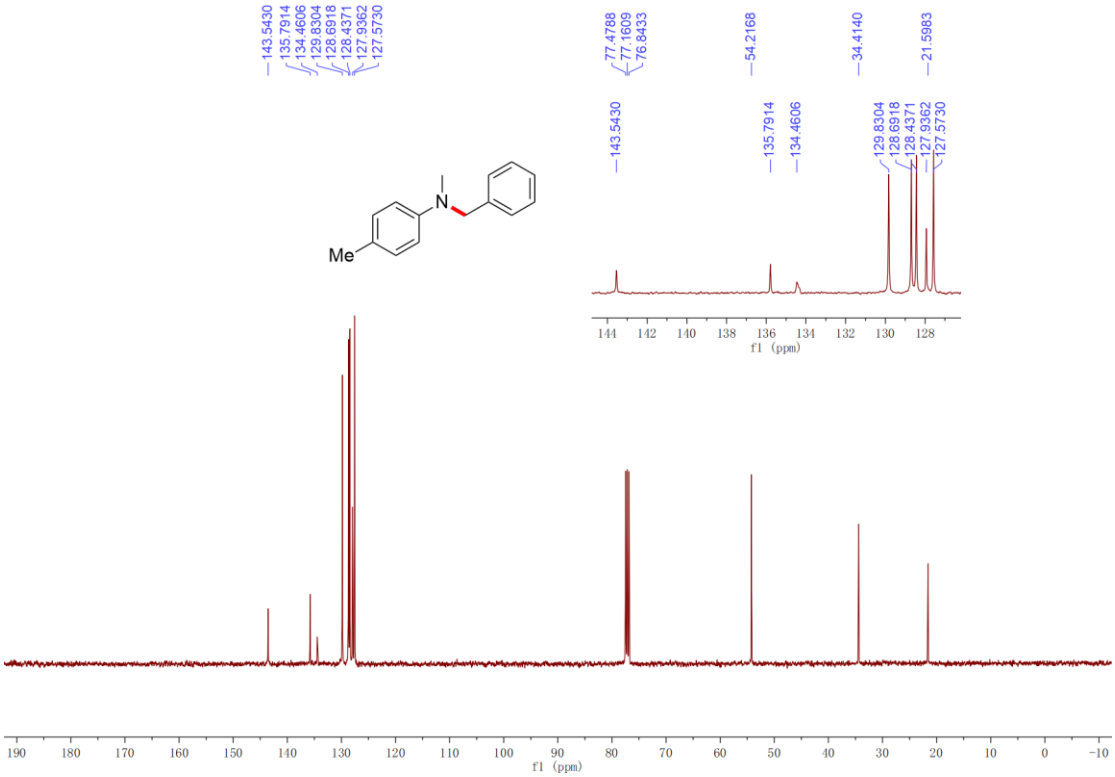

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **10ja** in $CDCl_3$.



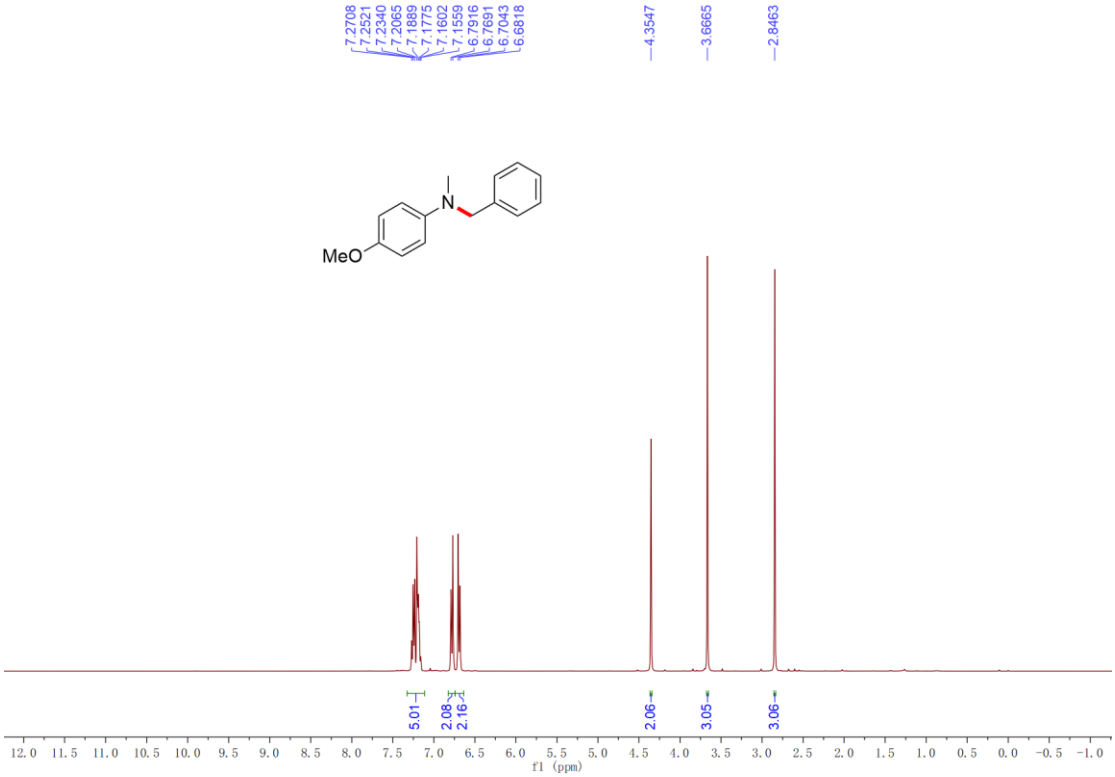
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ab** in $CDCl_3$.



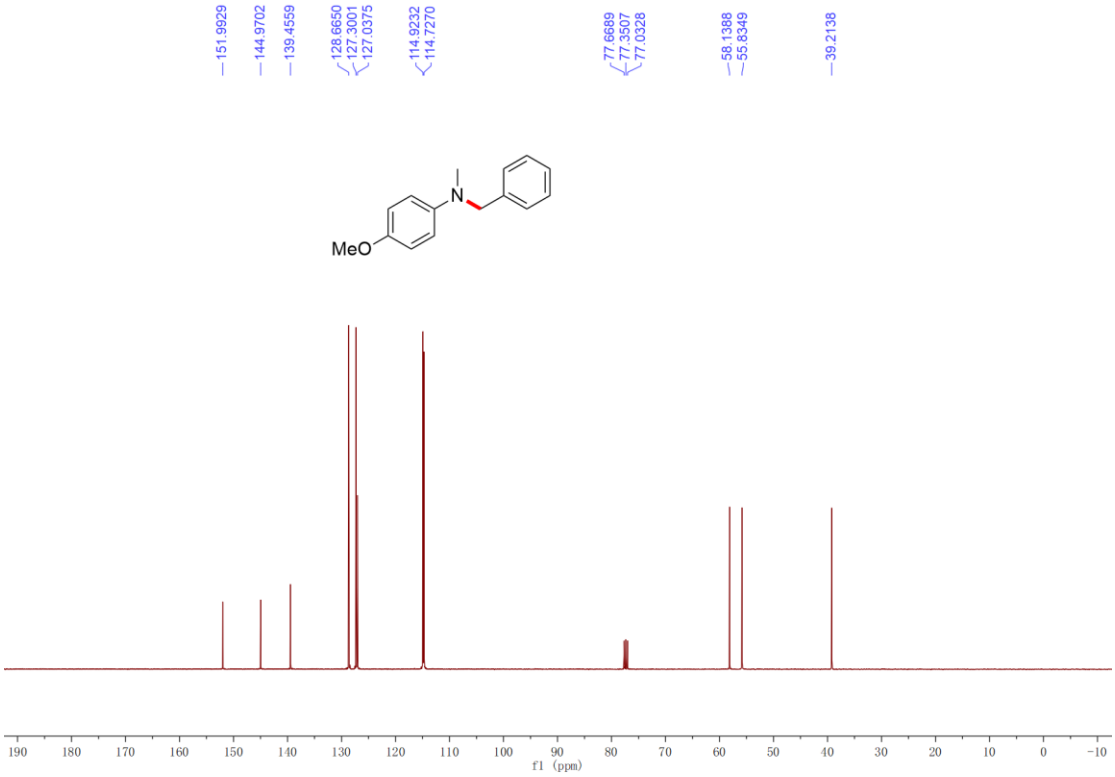

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ab** in $CDCl_3$.



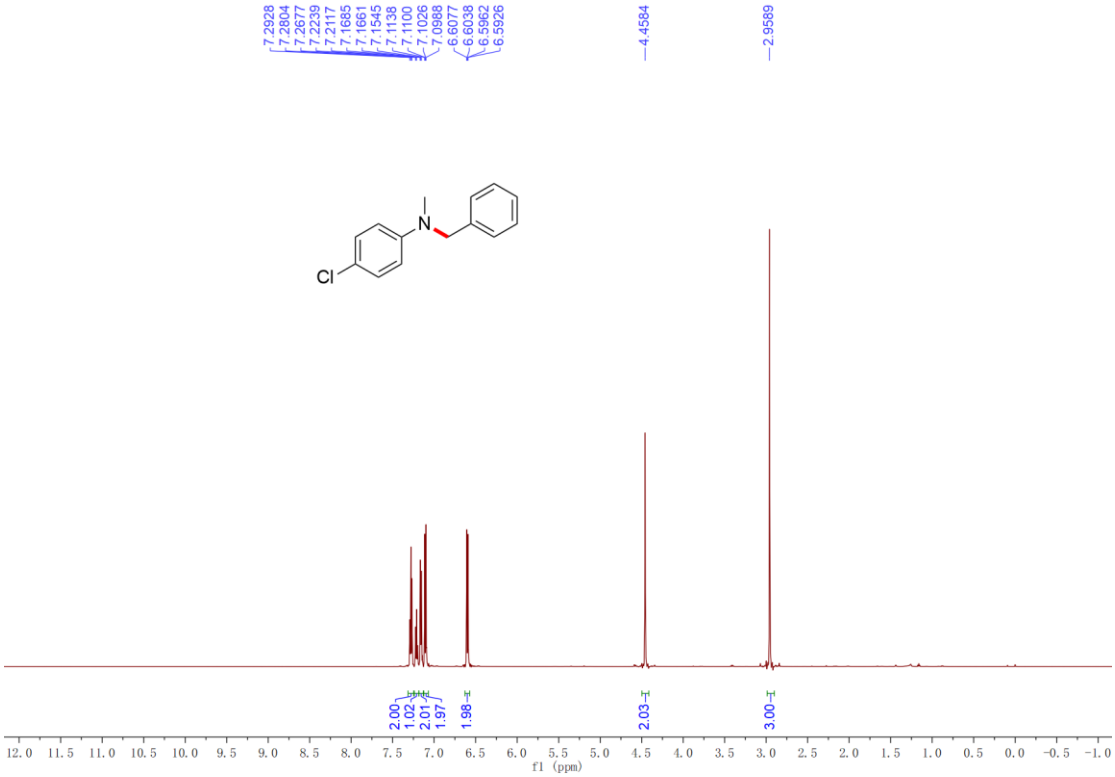
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ac** in $CDCl_3$.



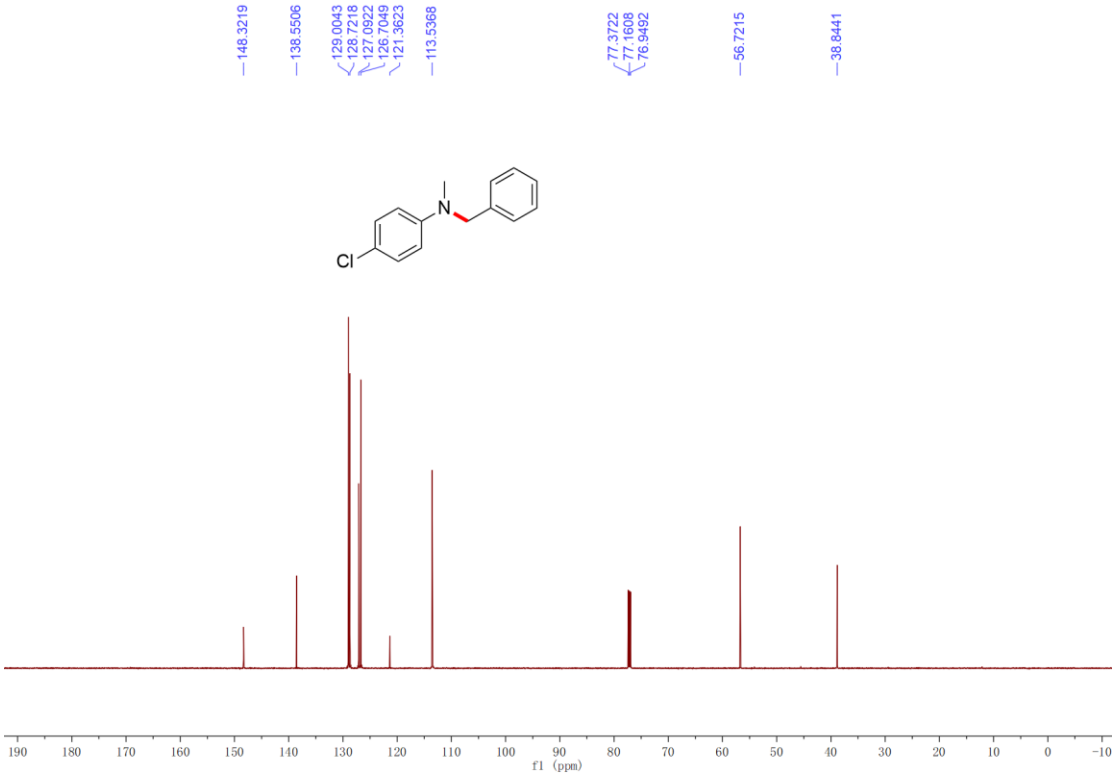

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ac** in $CDCl_3$.



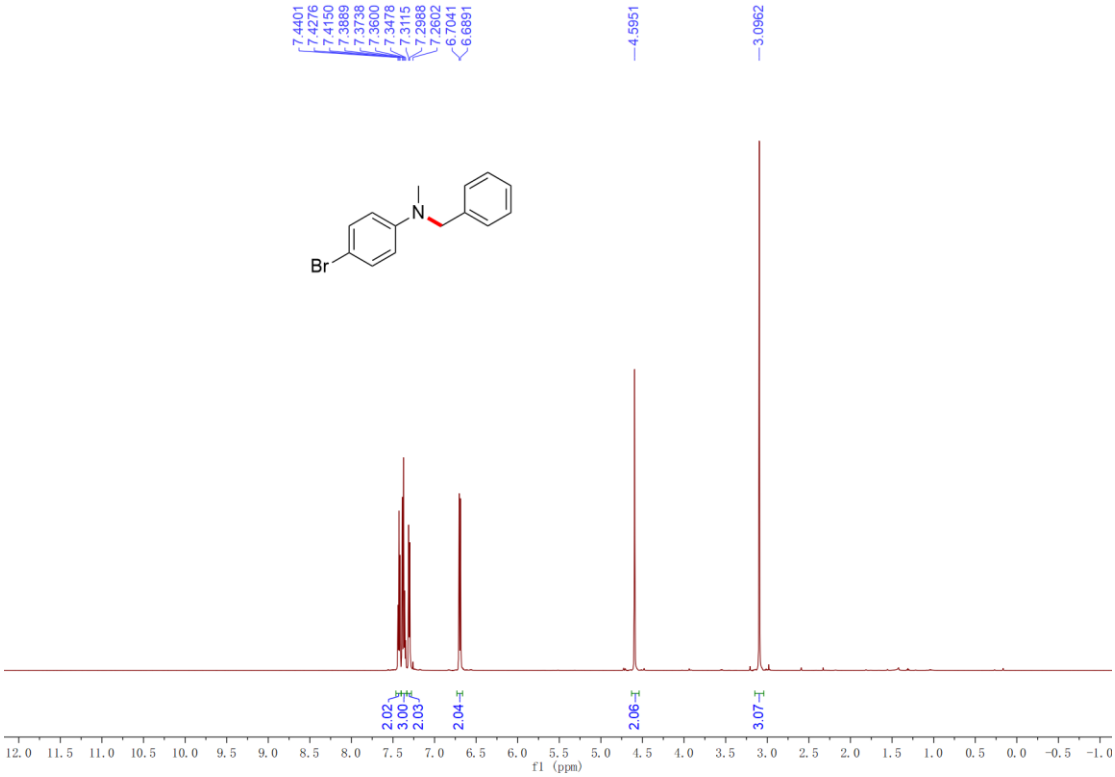
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **9ad** in $CDCl_3$.



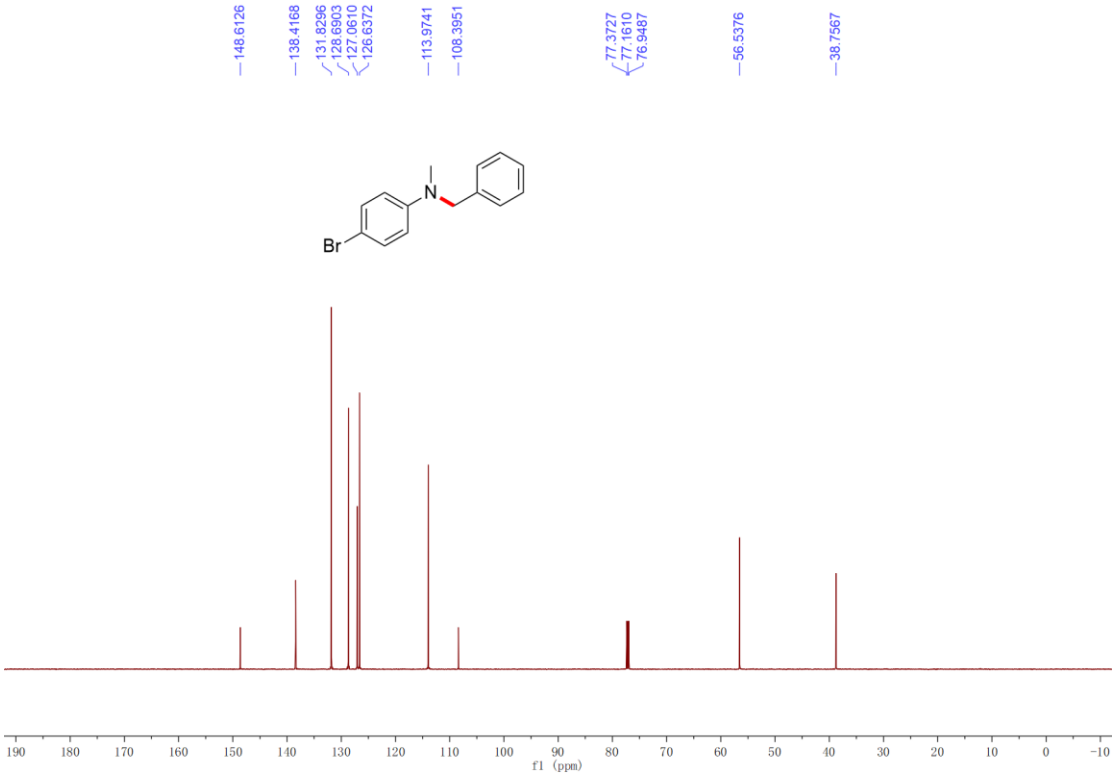

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **9ad** in $CDCl_3$.



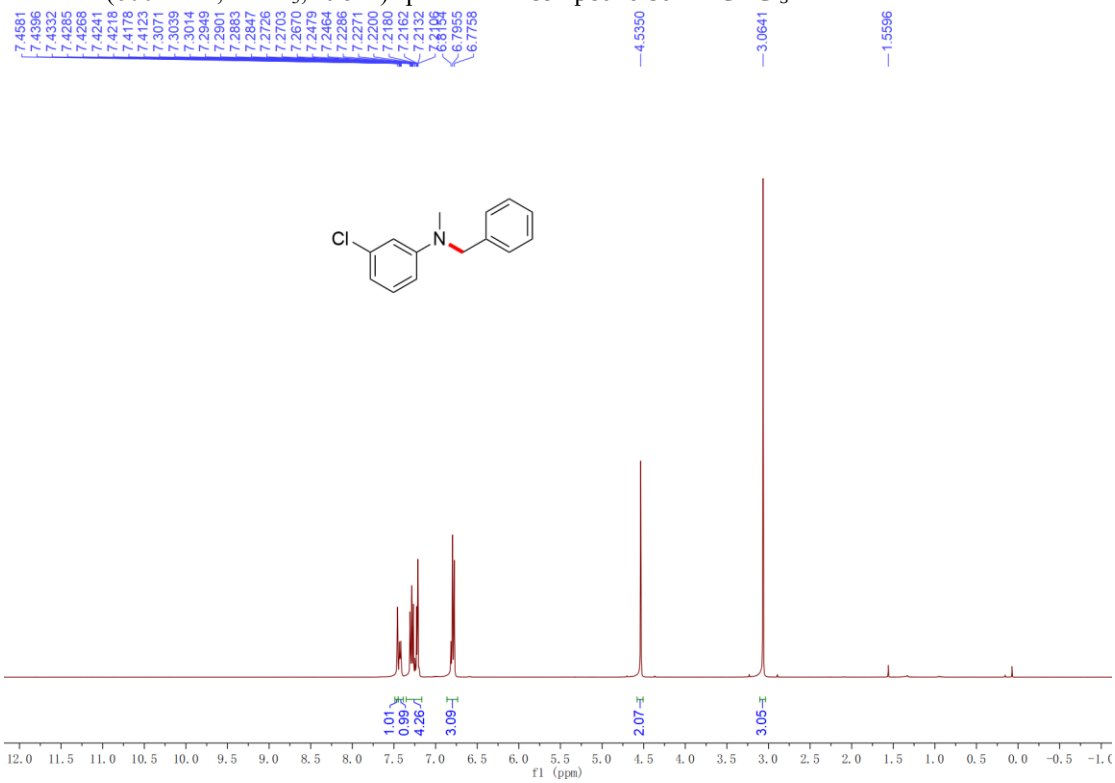
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **9ae** in $CDCl_3$.



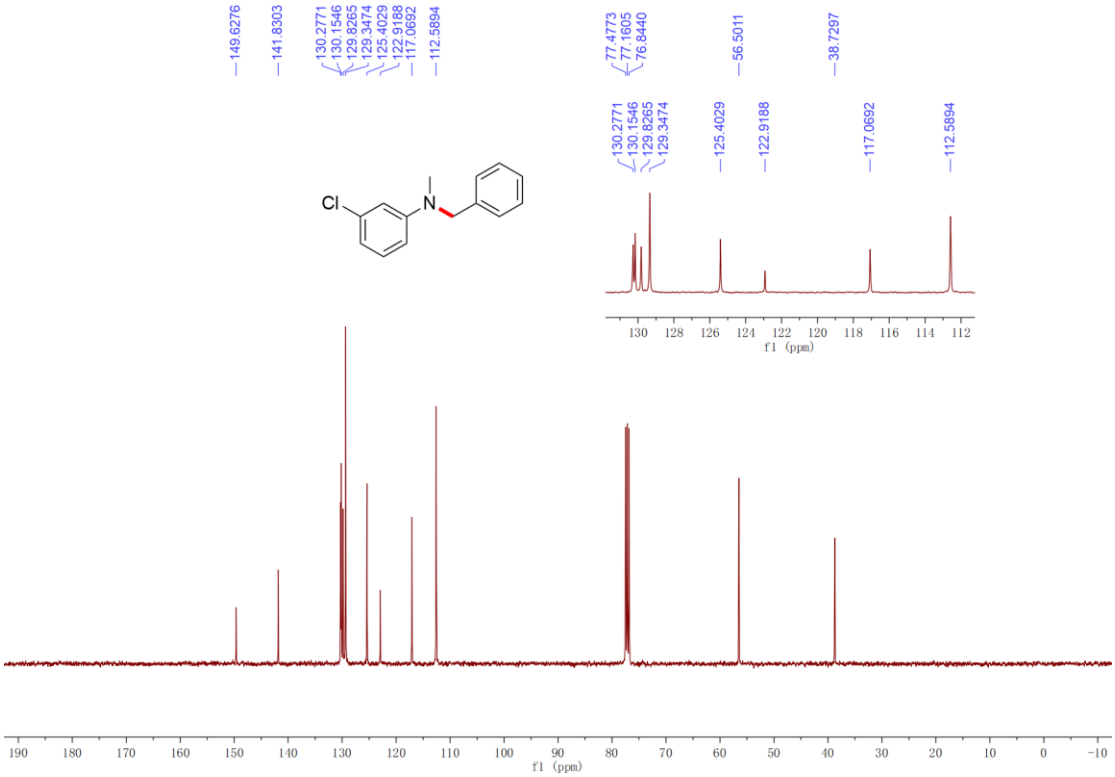

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **9ae** in $CDCl_3$.



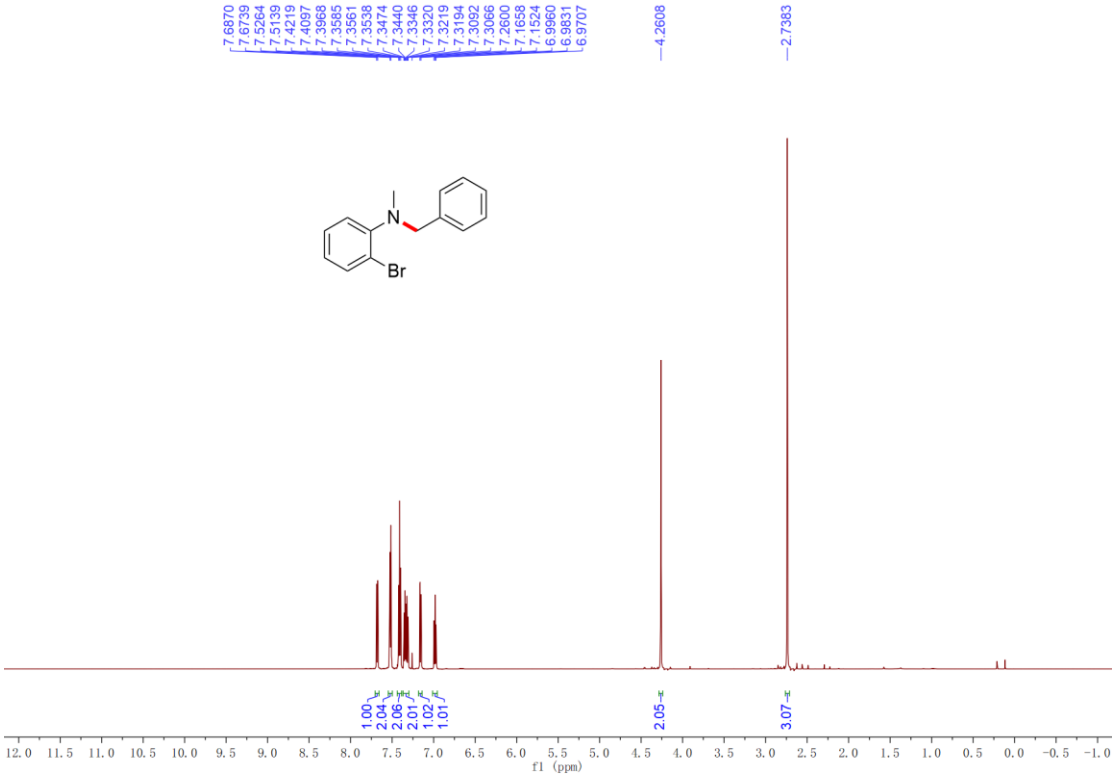
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **9af** in $CDCl_3$.



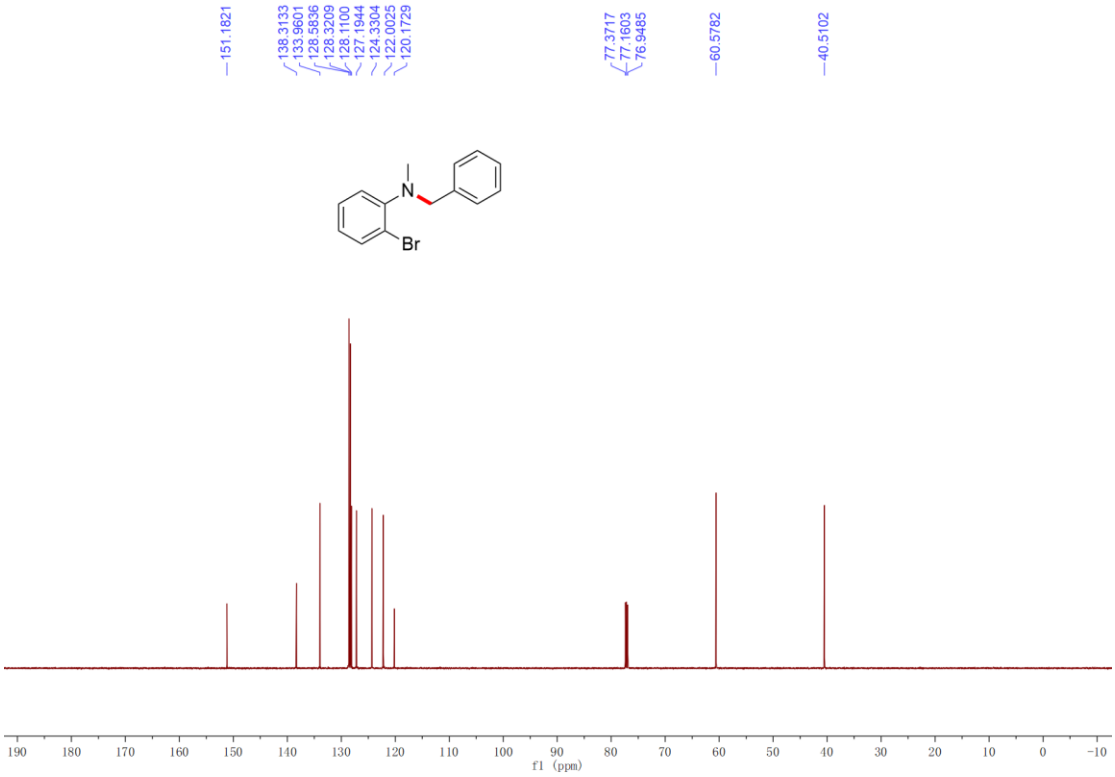

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **9af** in $CDCl_3$.



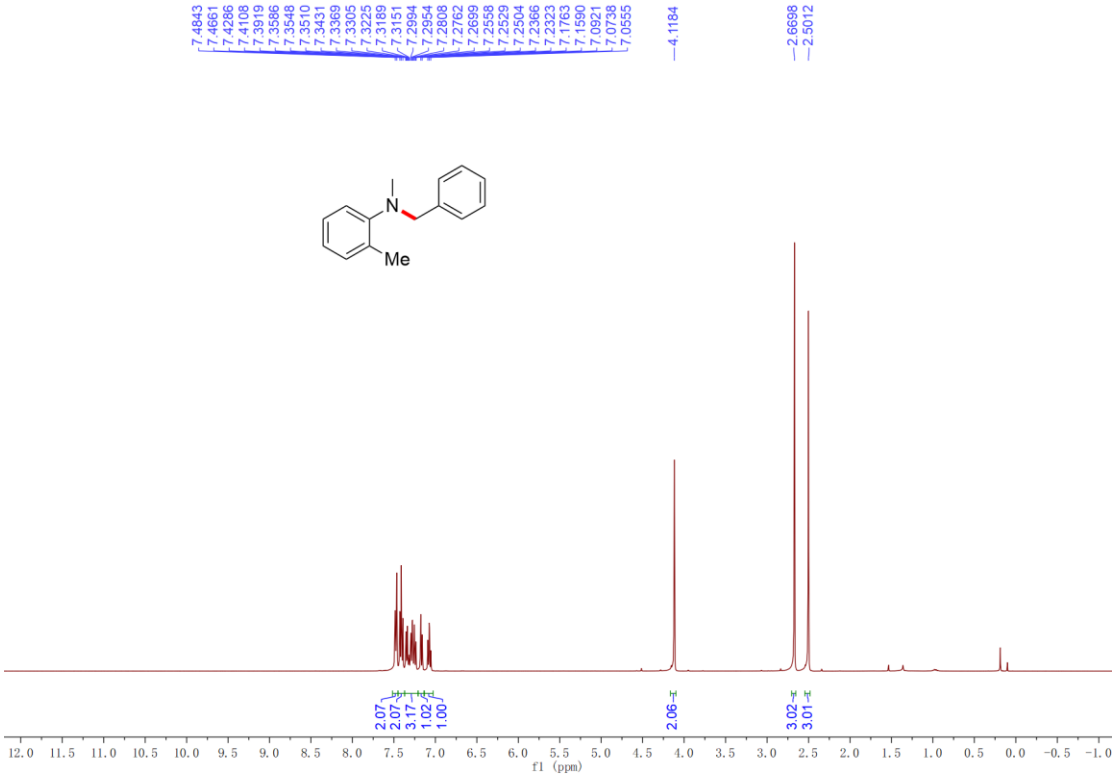
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **9ag** in $CDCl_3$.



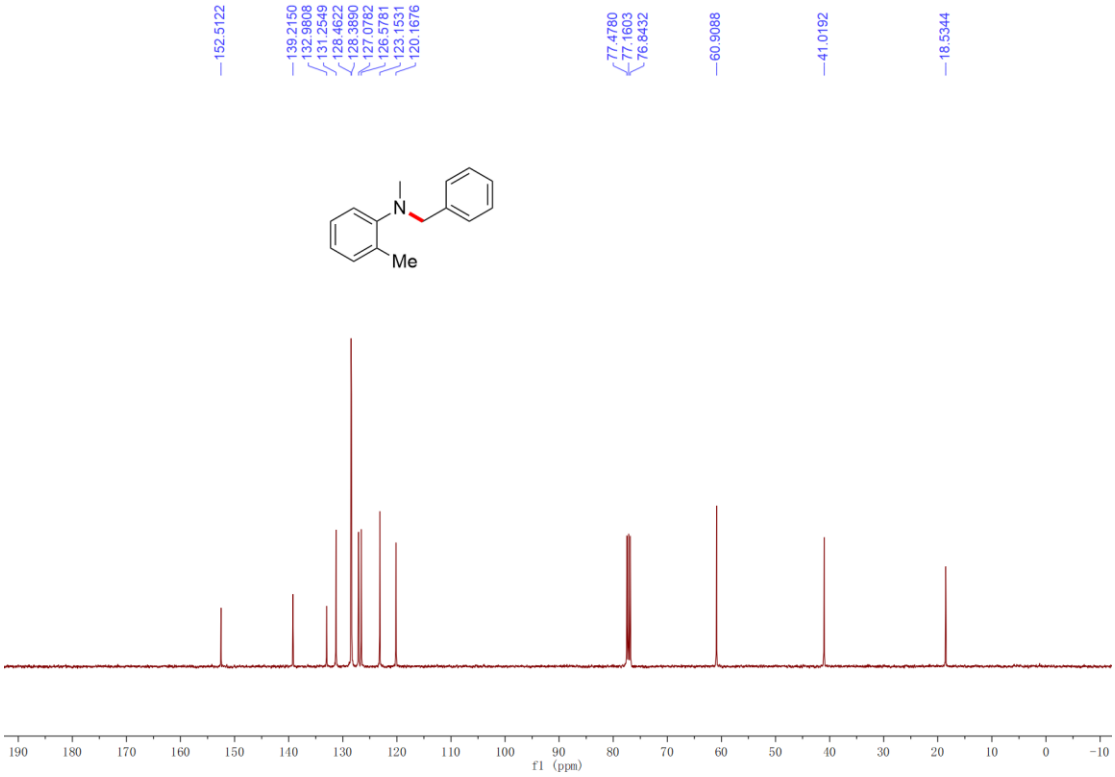

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **9ag** in $CDCl_3$.



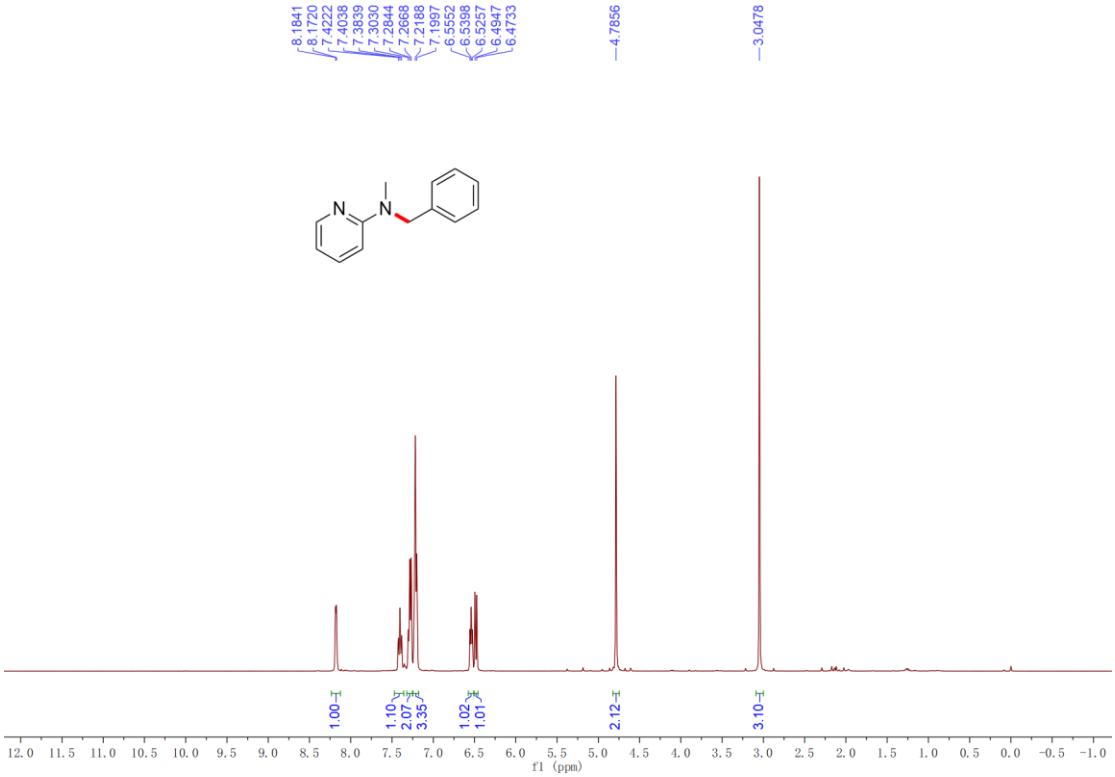
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ah** in $CDCl_3$.



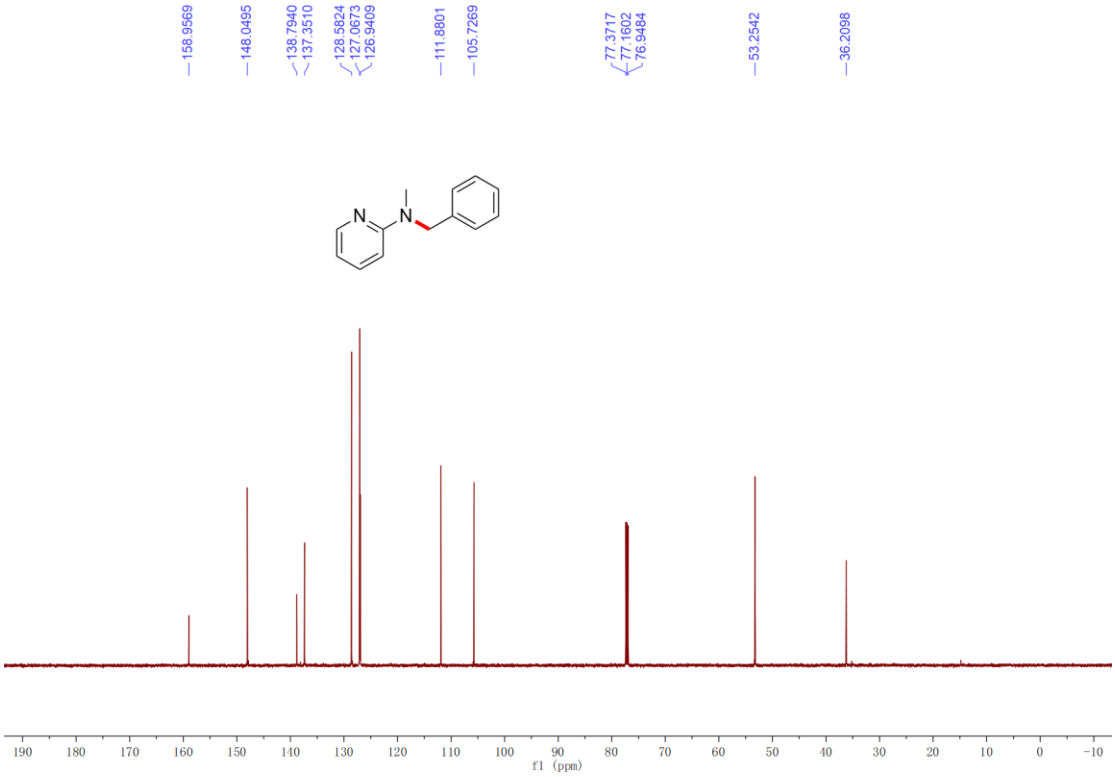

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ah** in $CDCl_3$.



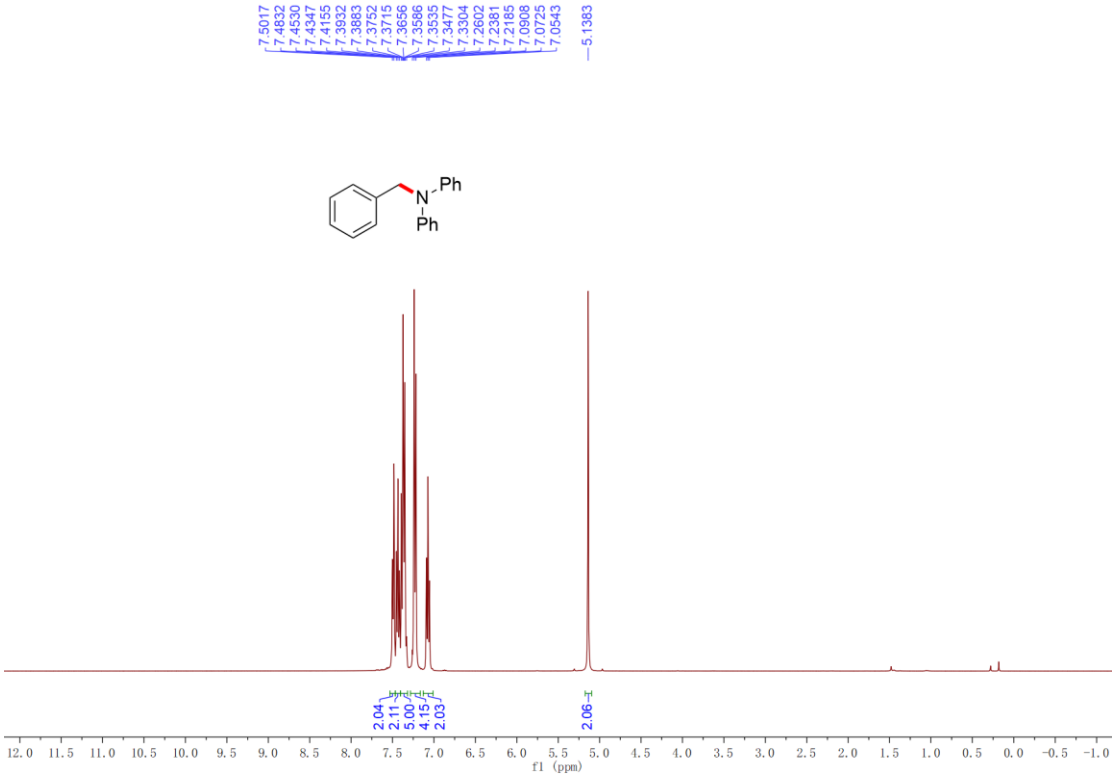
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ai** in $CDCl_3$.



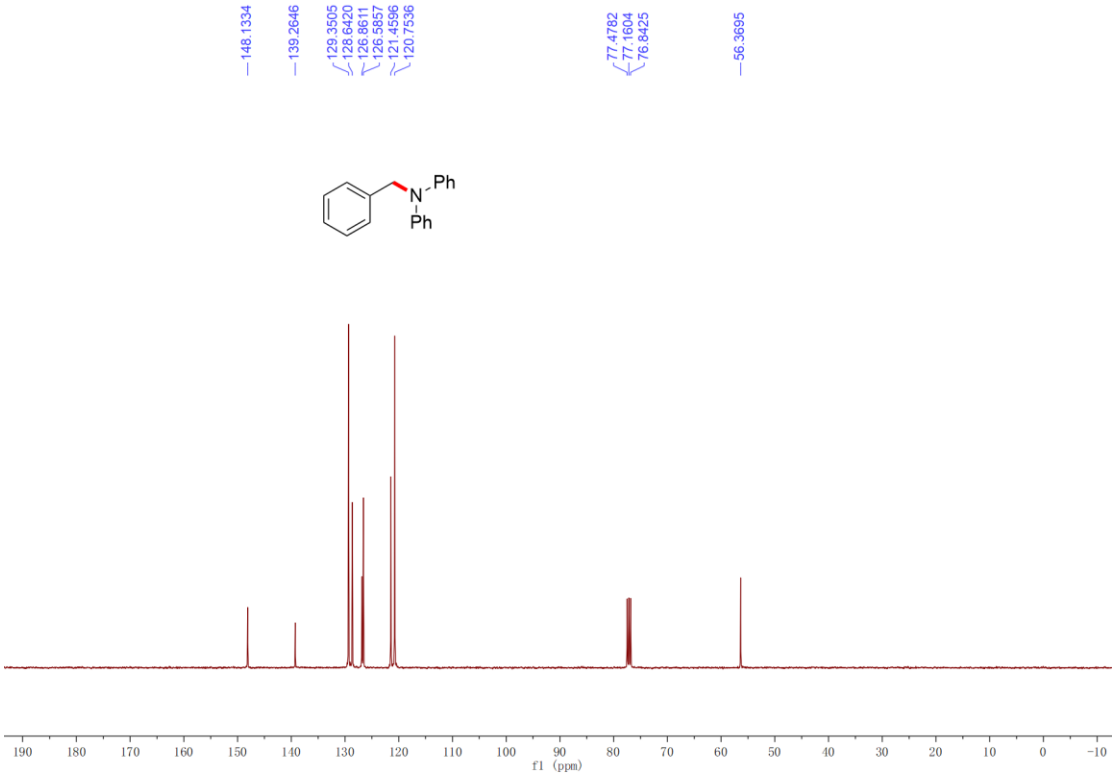

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ai** in $CDCl_3$.



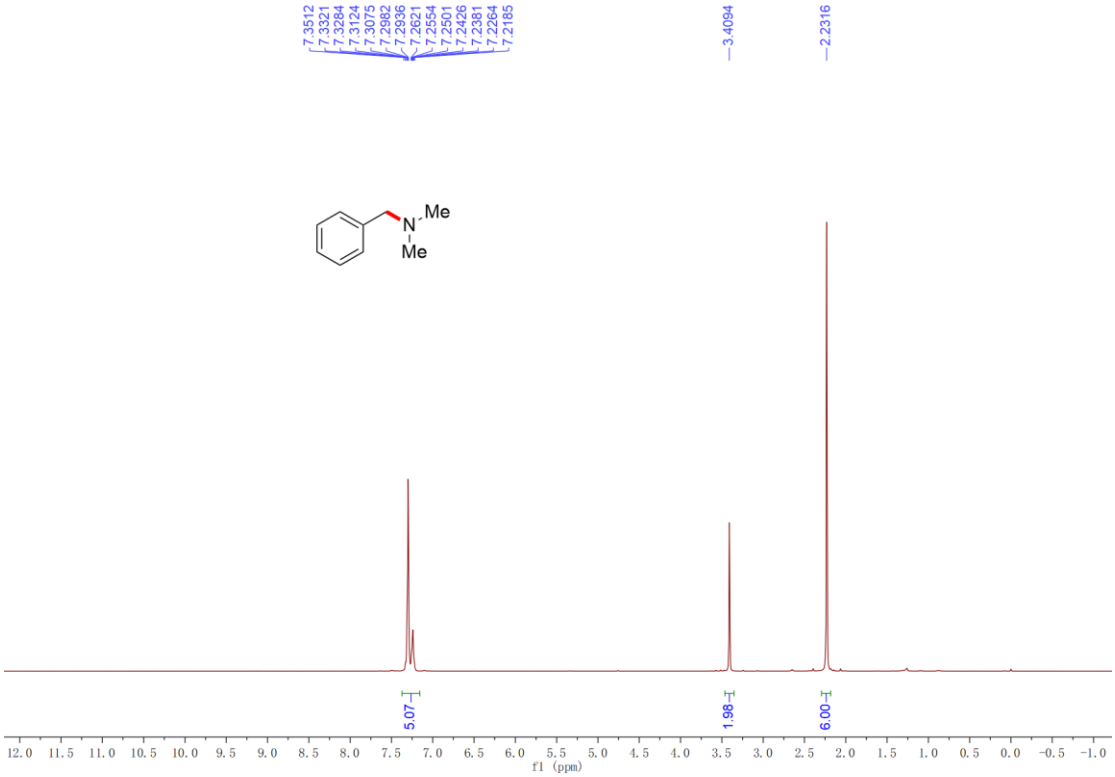
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9aj** in $CDCl_3$.



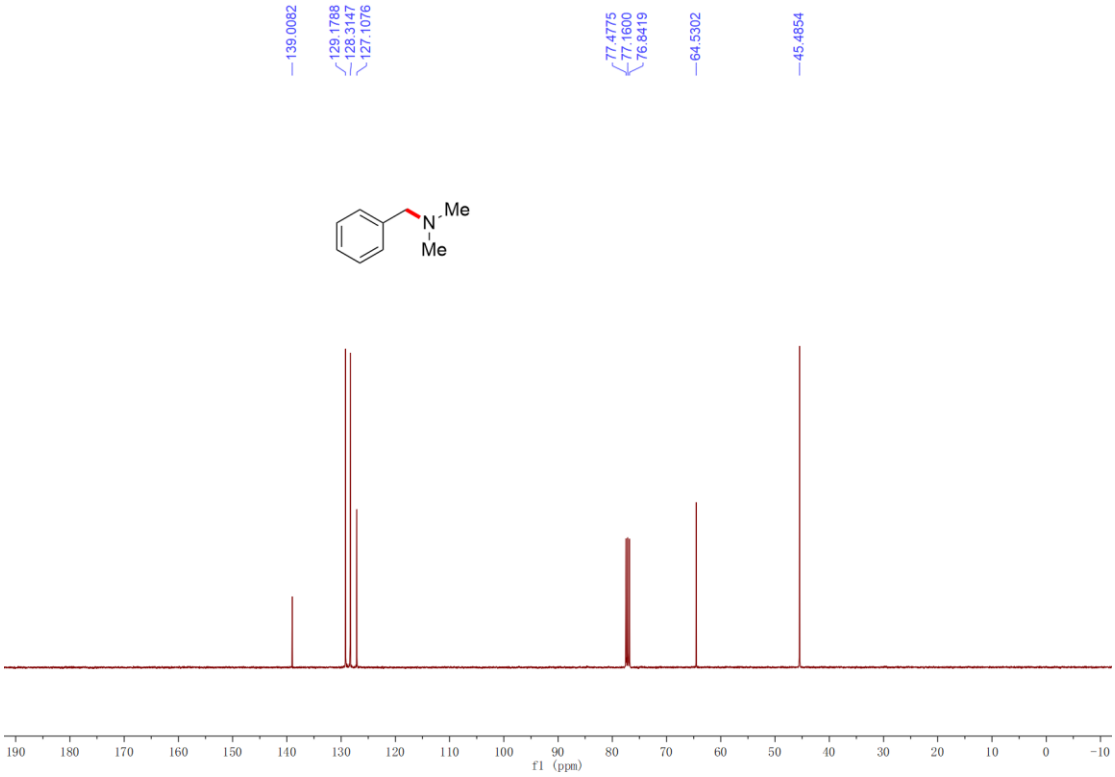

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9aj** in $CDCl_3$.



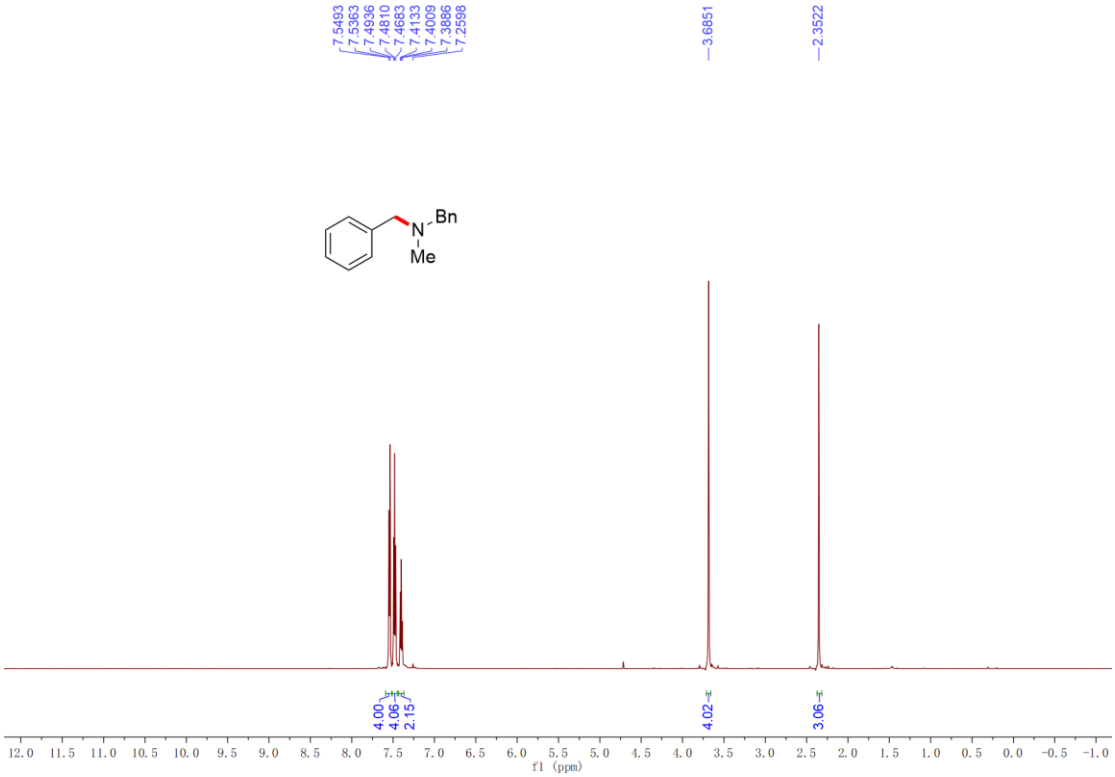
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ak** in $CDCl_3$.



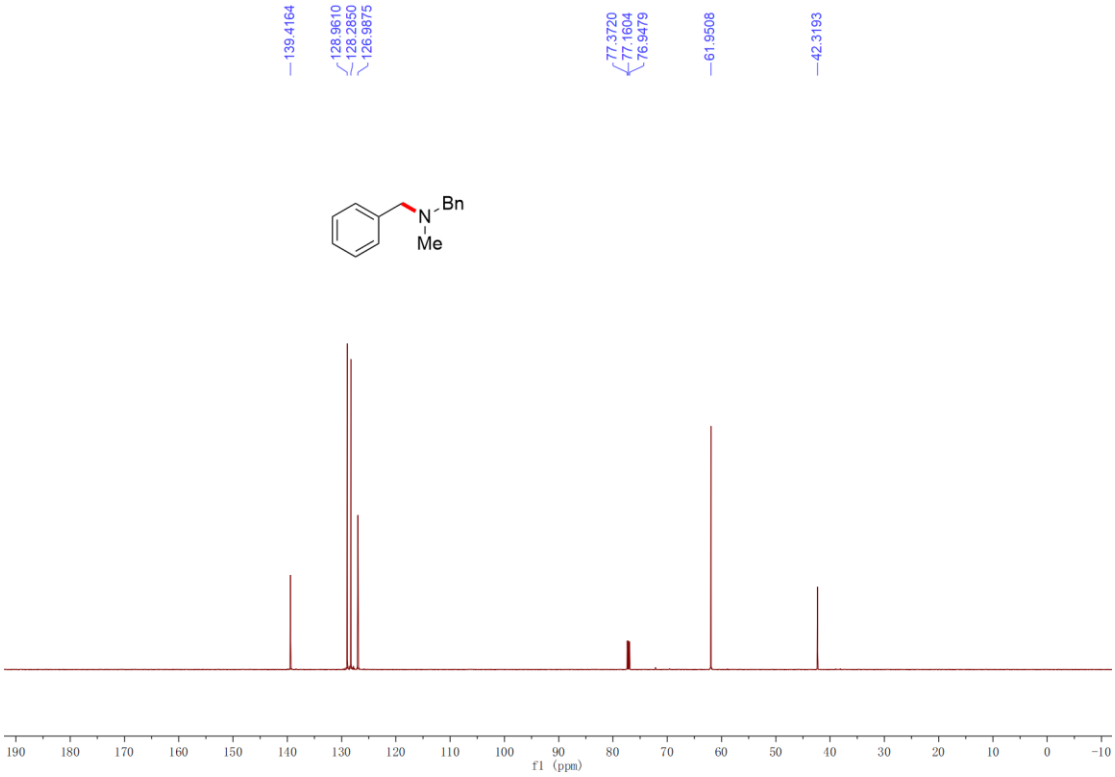

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ak** in $CDCl_3$.



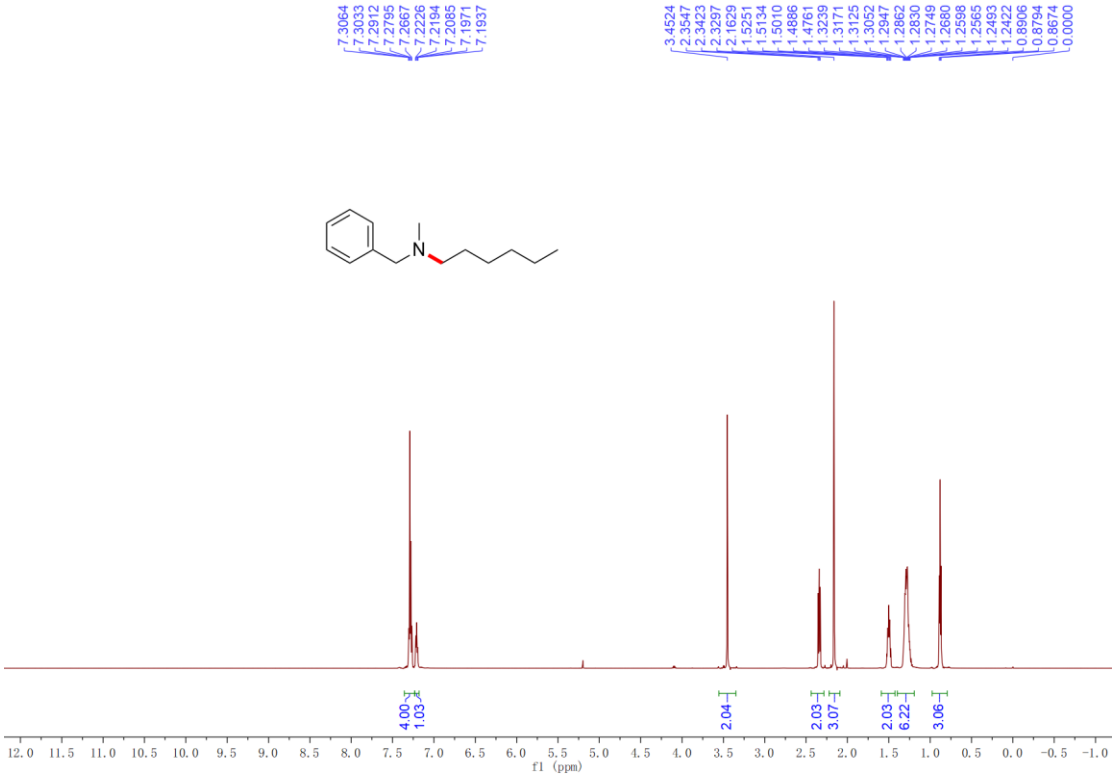
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **9al** in $CDCl_3$.



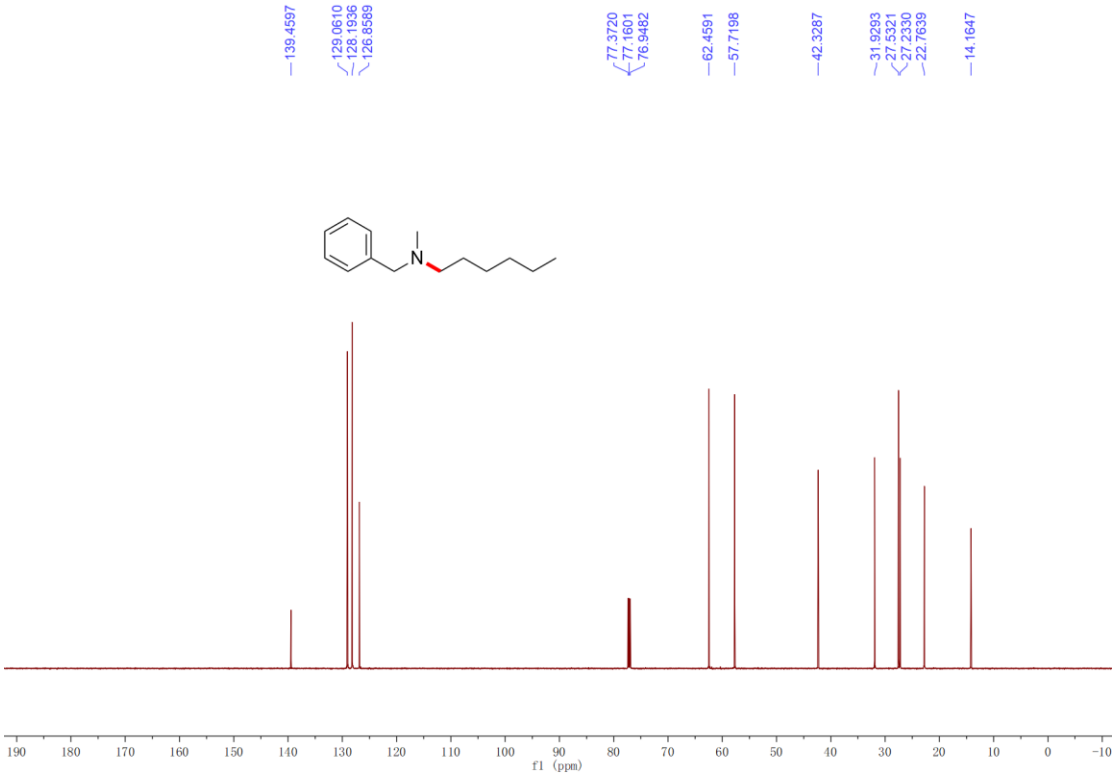

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **9al** in $CDCl_3$.



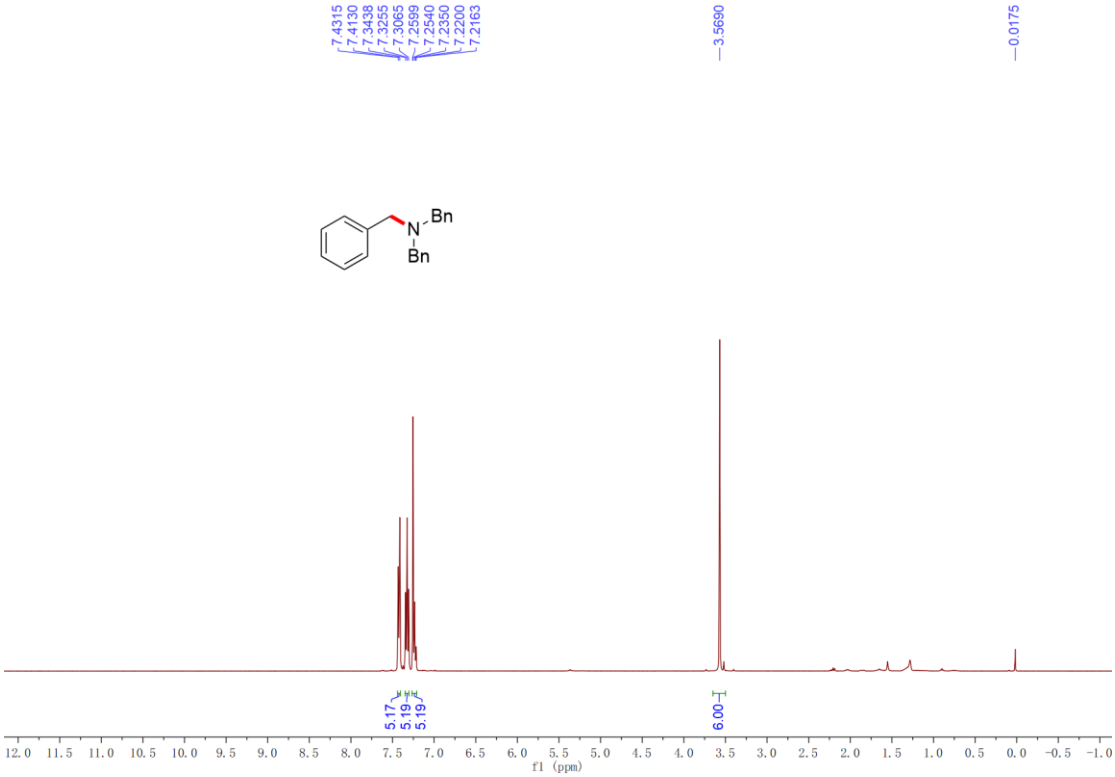
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9am** in $CDCl_3$.



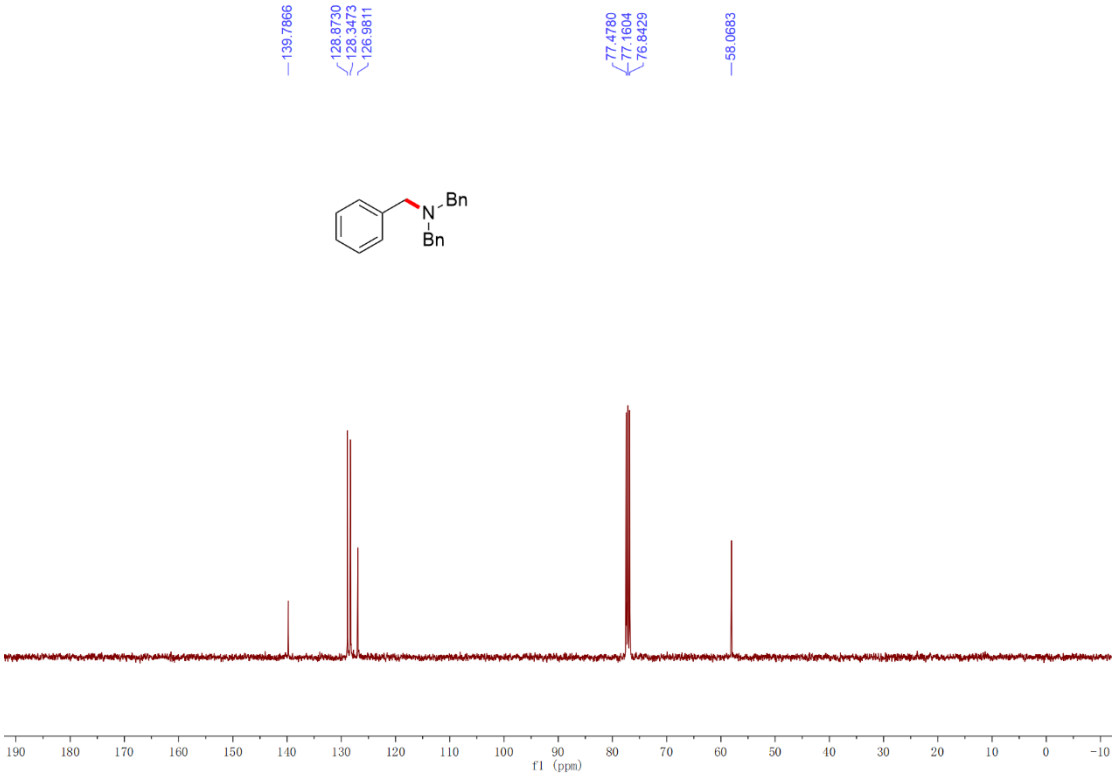

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9am** in $CDCl_3$.



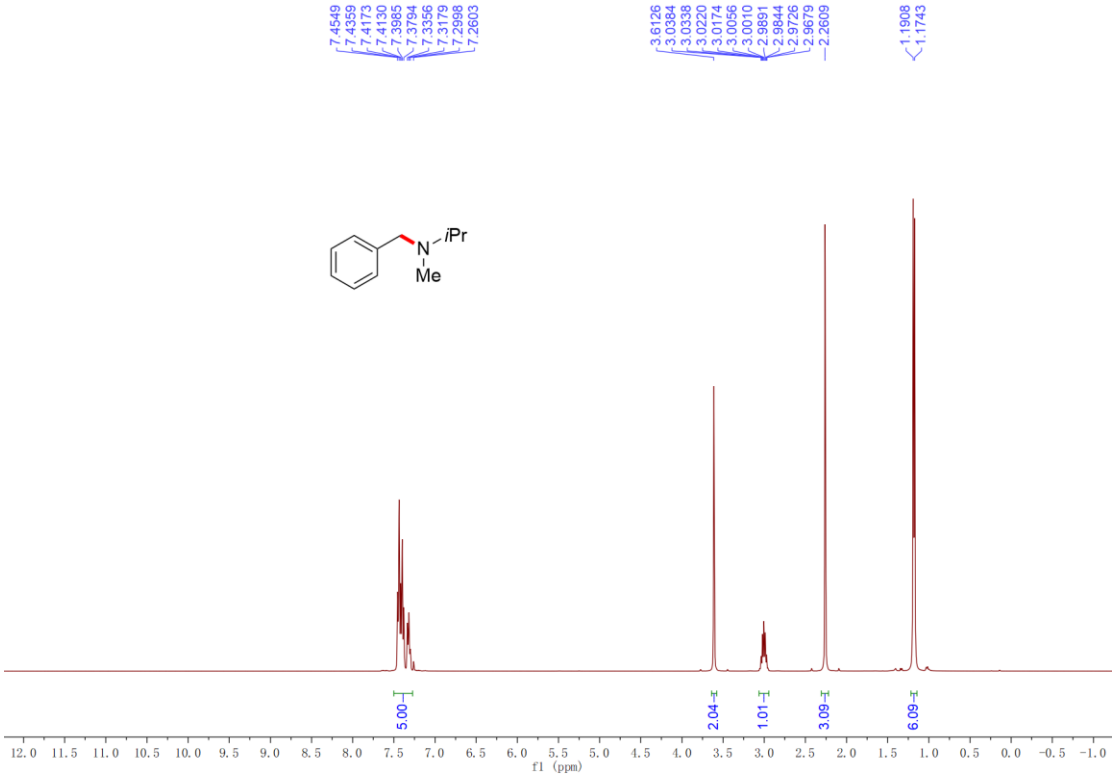
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9an** in $CDCl_3$.



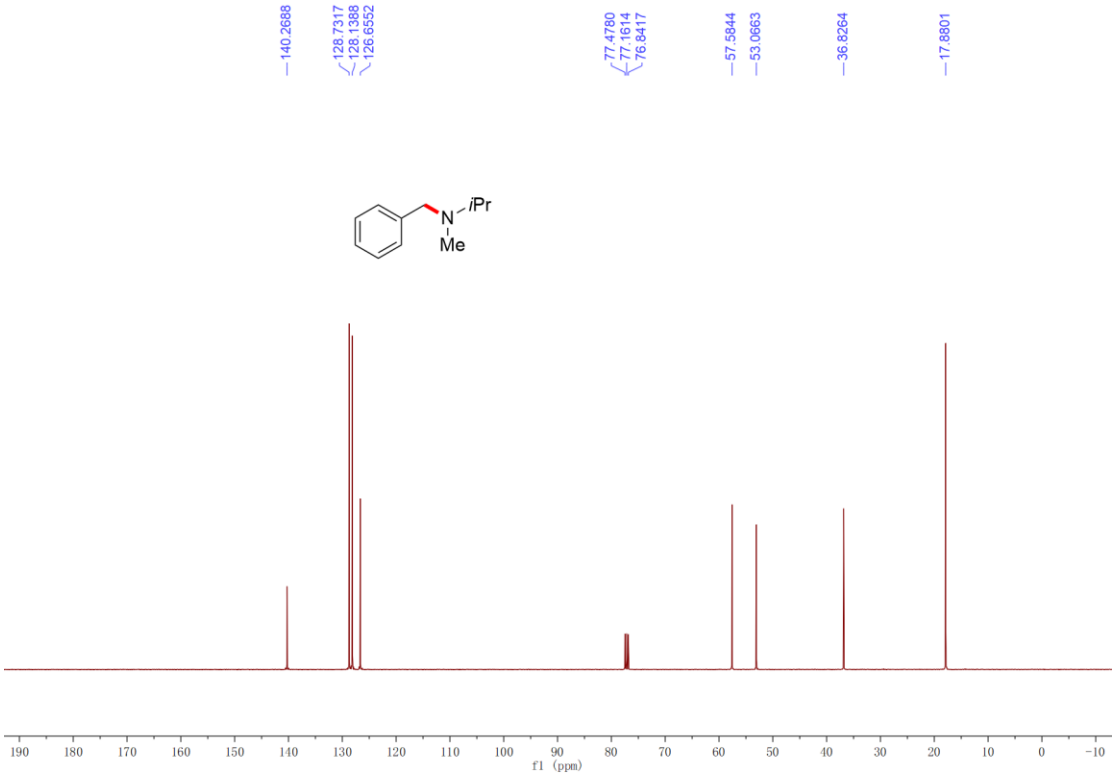

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9an** in $CDCl_3$.



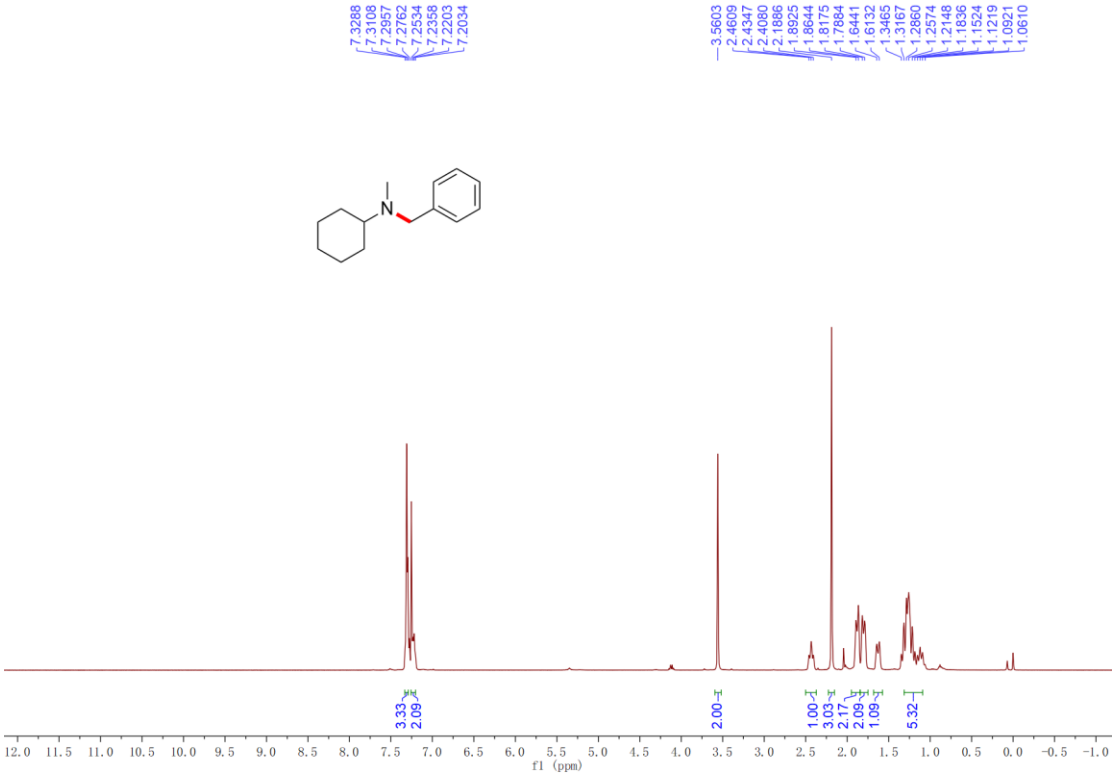
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ao** in $CDCl_3$.



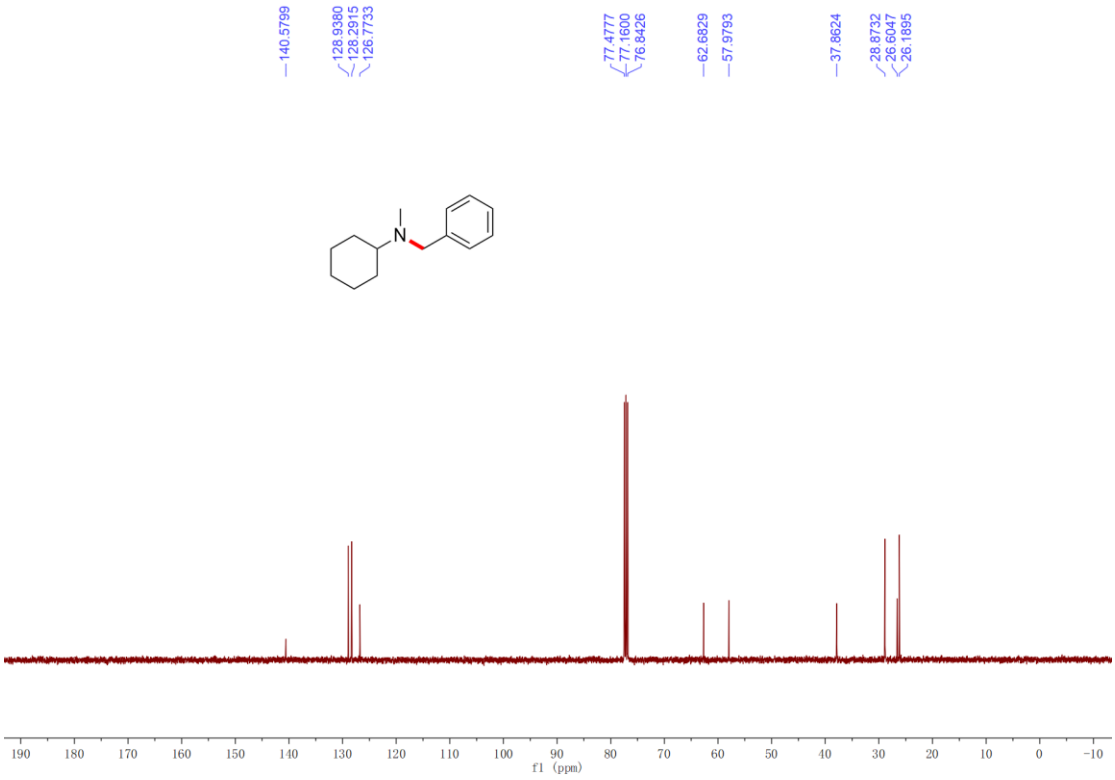

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ao** in $CDCl_3$.



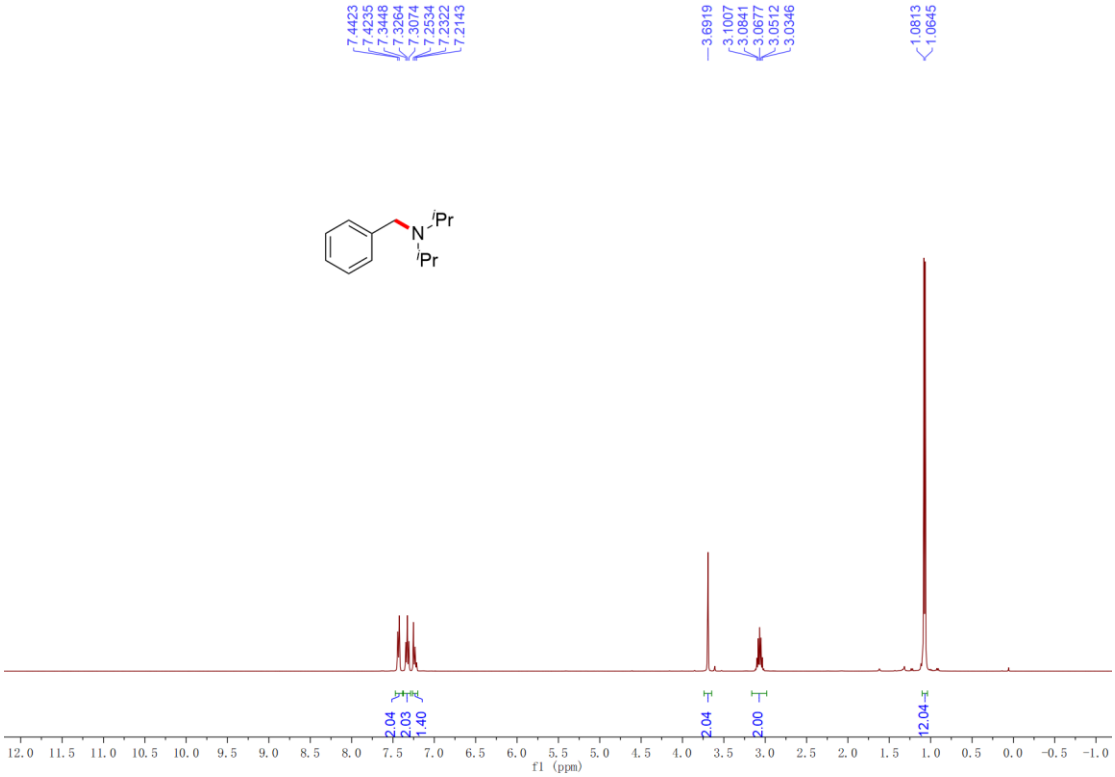
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ap** in $CDCl_3$.



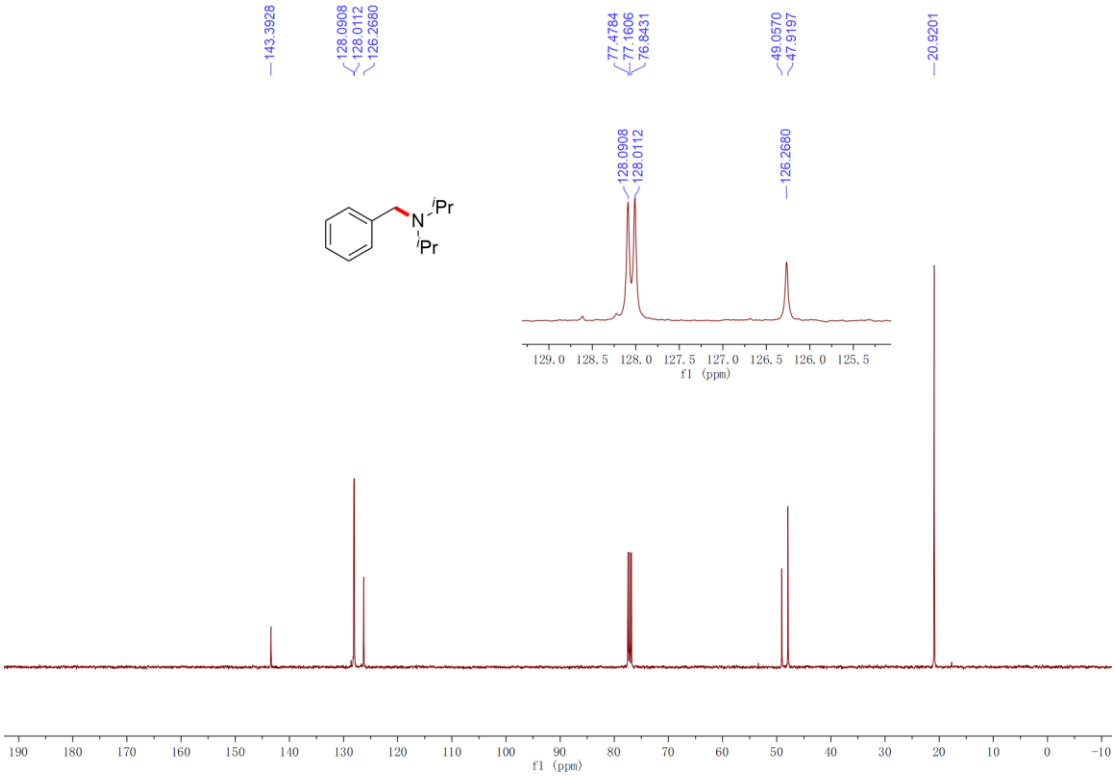

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ap** in $CDCl_3$.



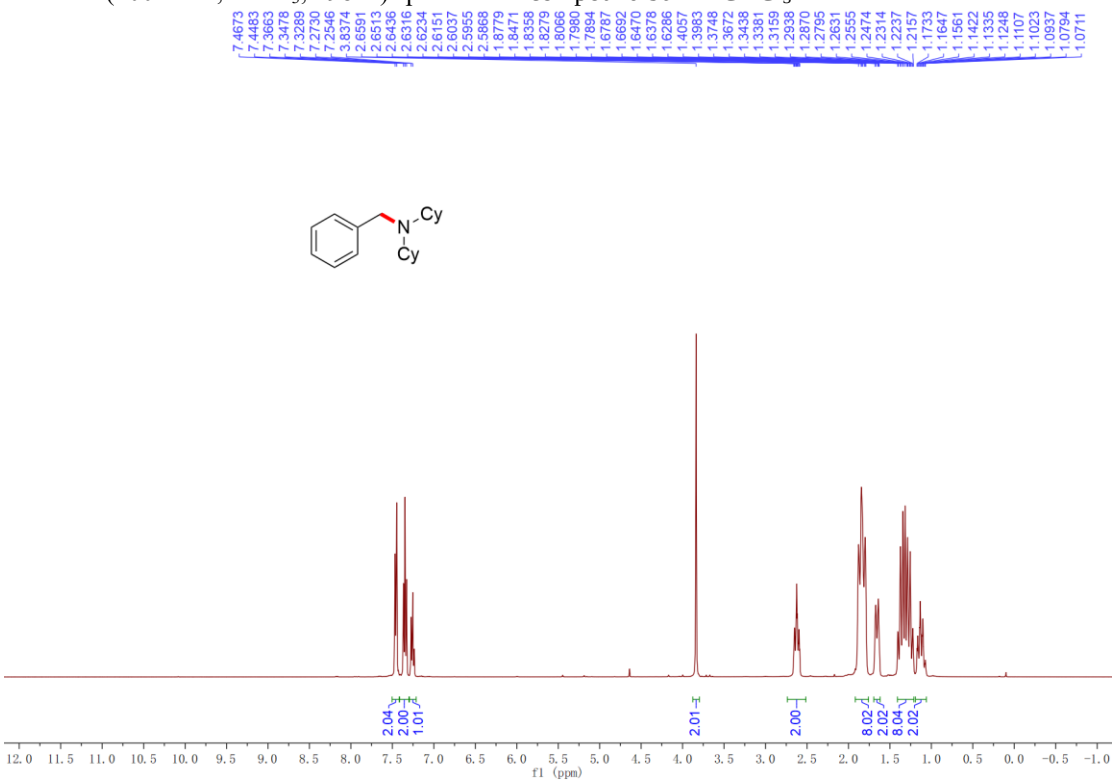
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9aq** in $CDCl_3$.



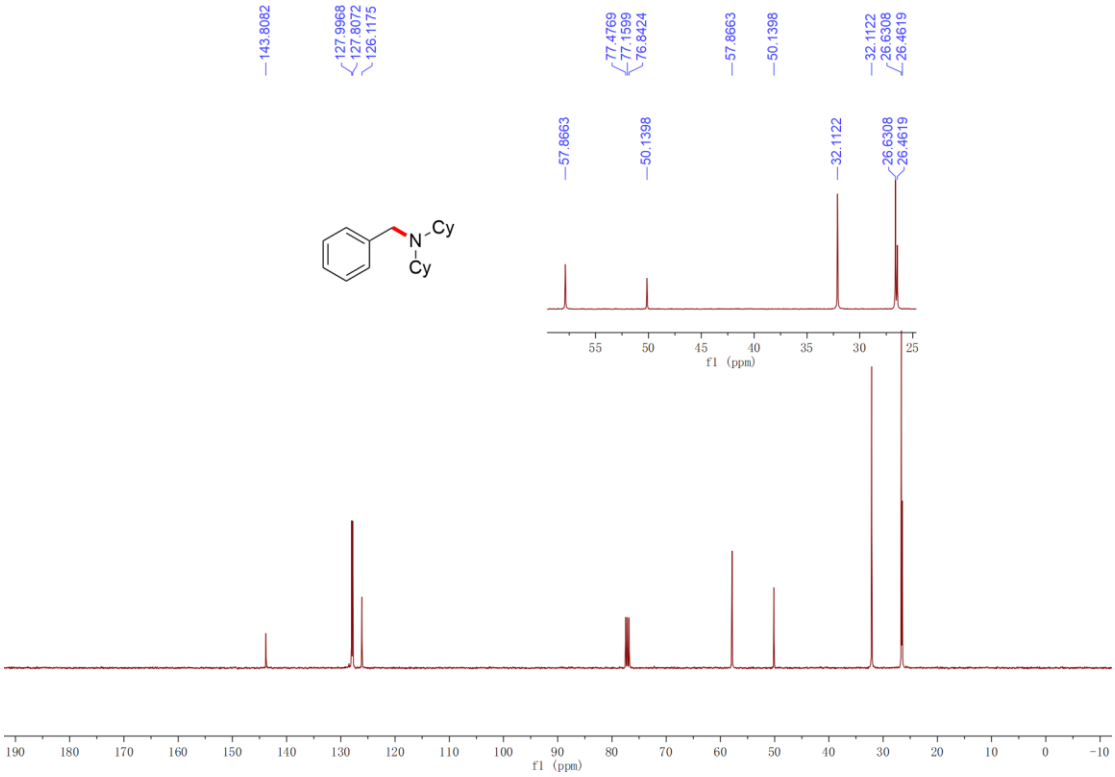

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9aq** in $CDCl_3$.



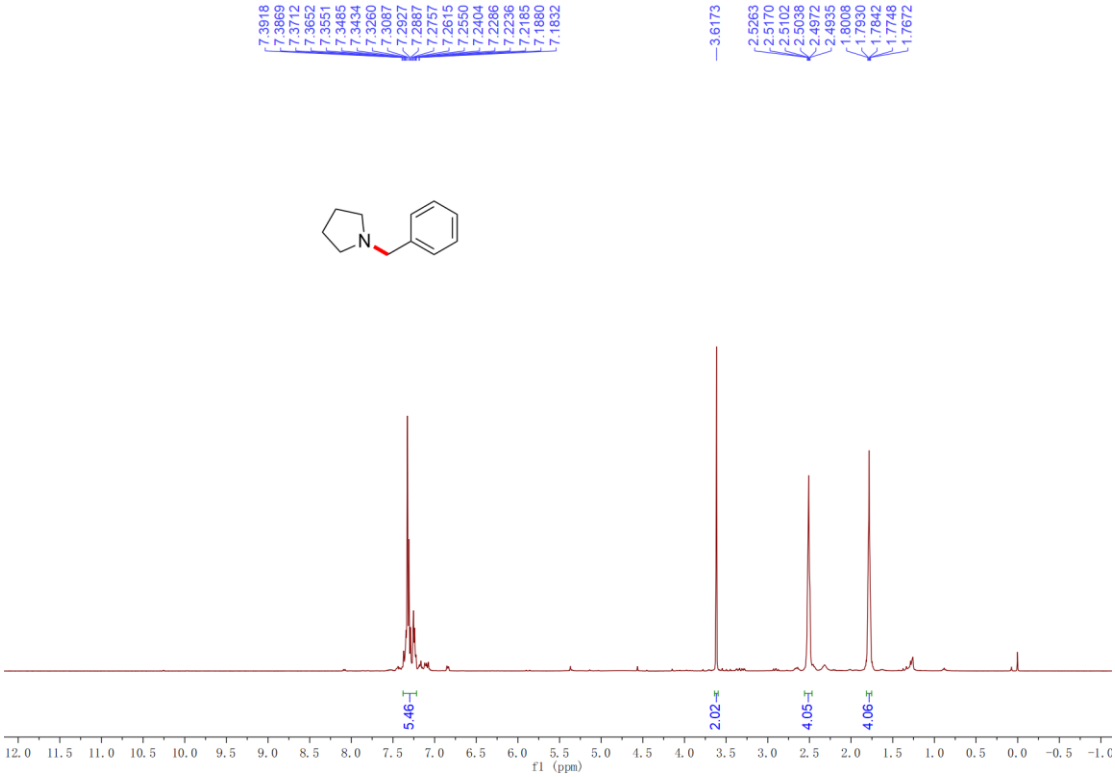
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ar** in $CDCl_3$.



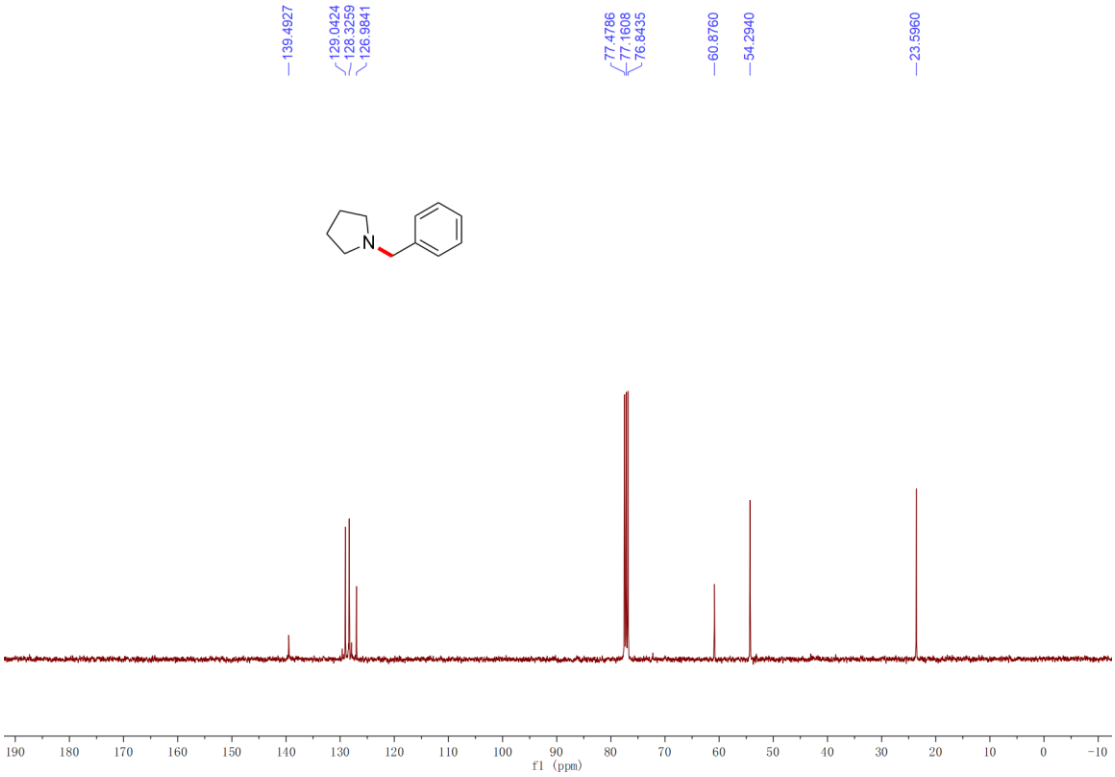

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ar** in $CDCl_3$.



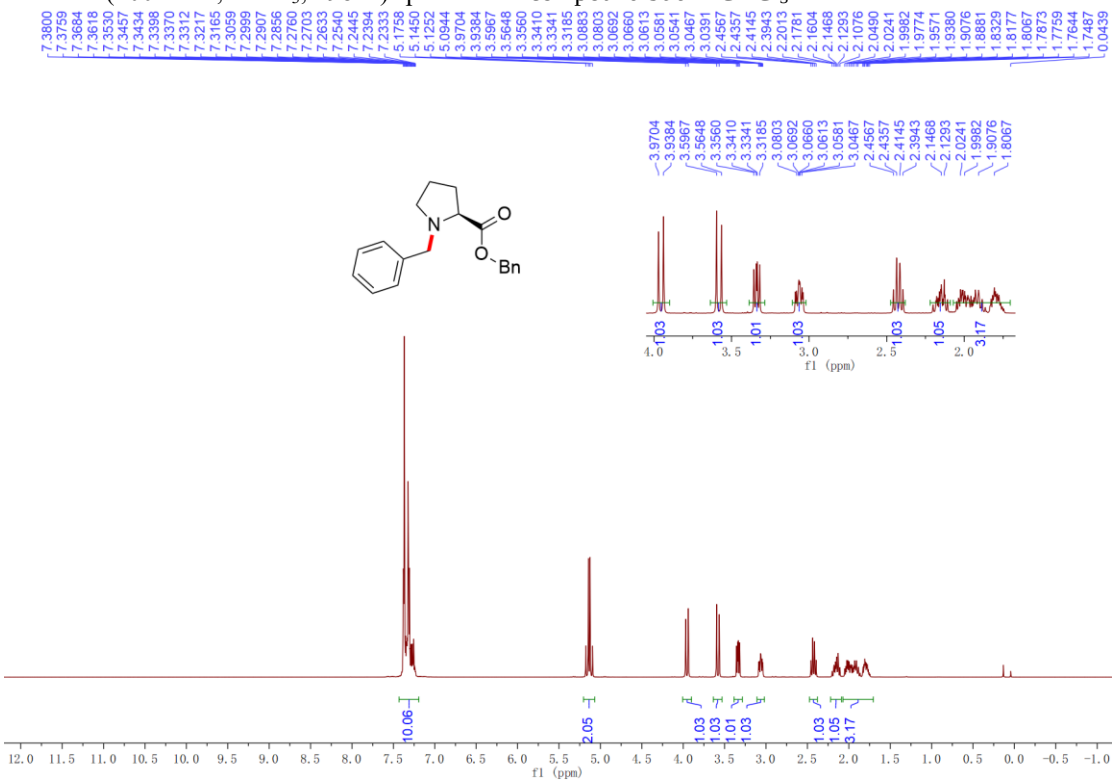
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9as** in $CDCl_3$.



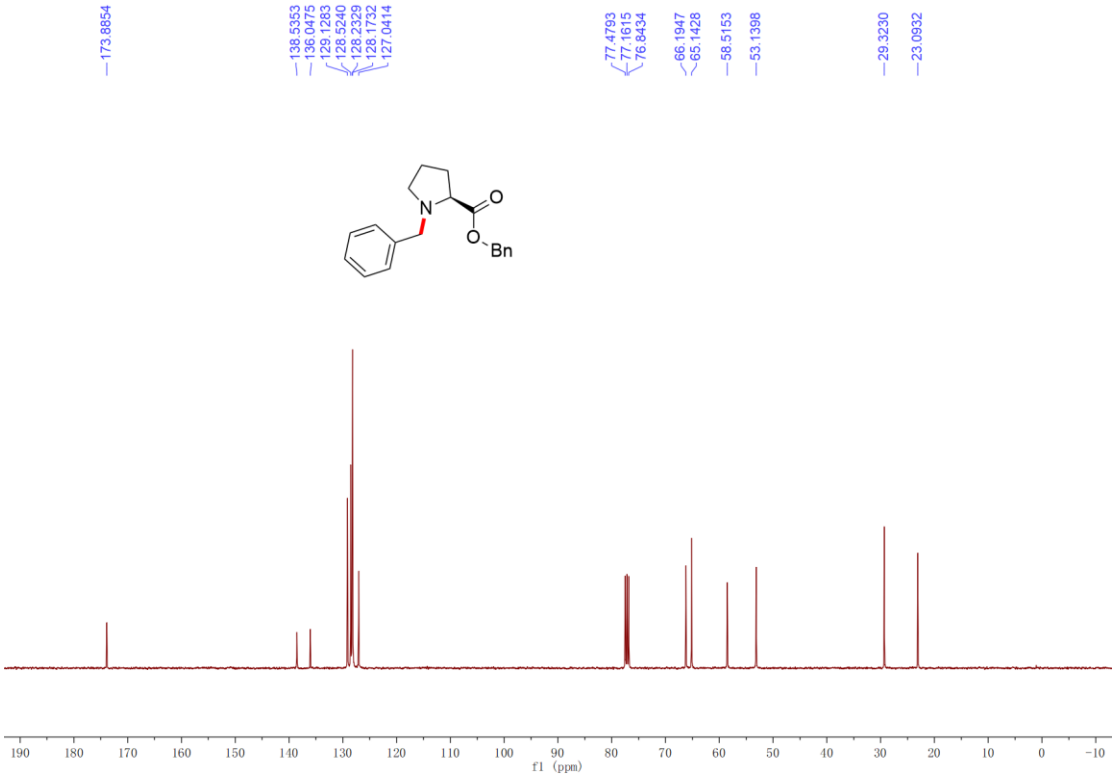

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9as** in $CDCl_3$.



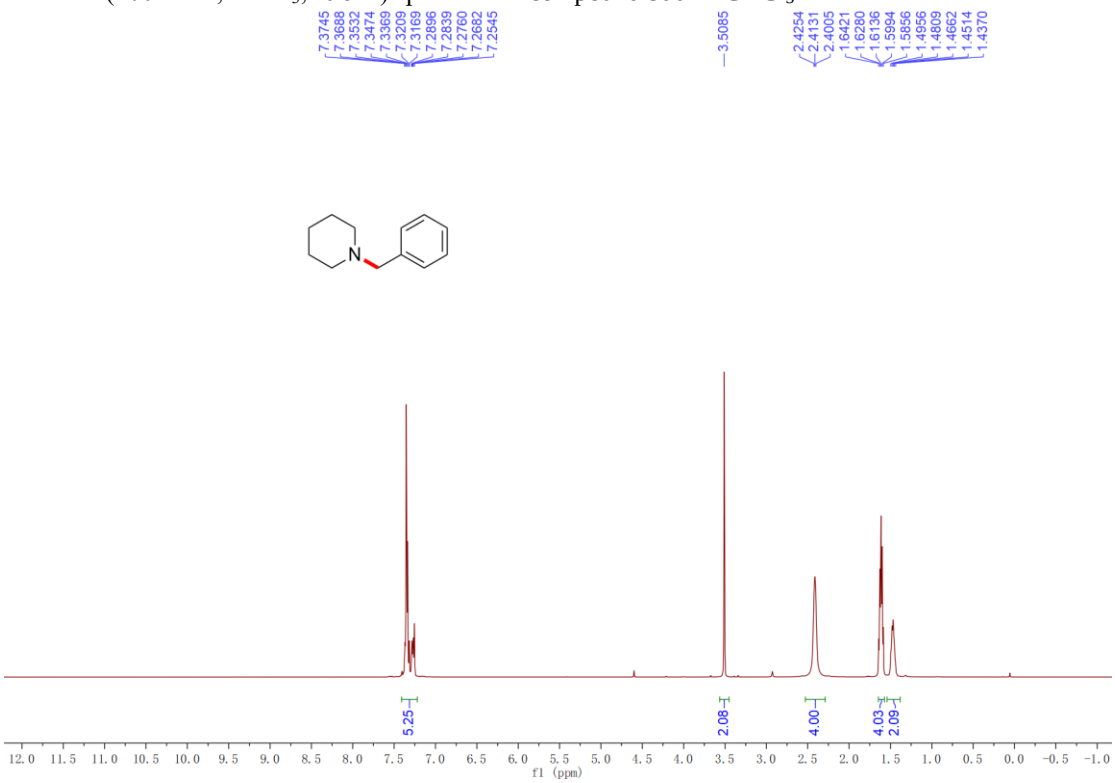
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9at** in $CDCl_3$.



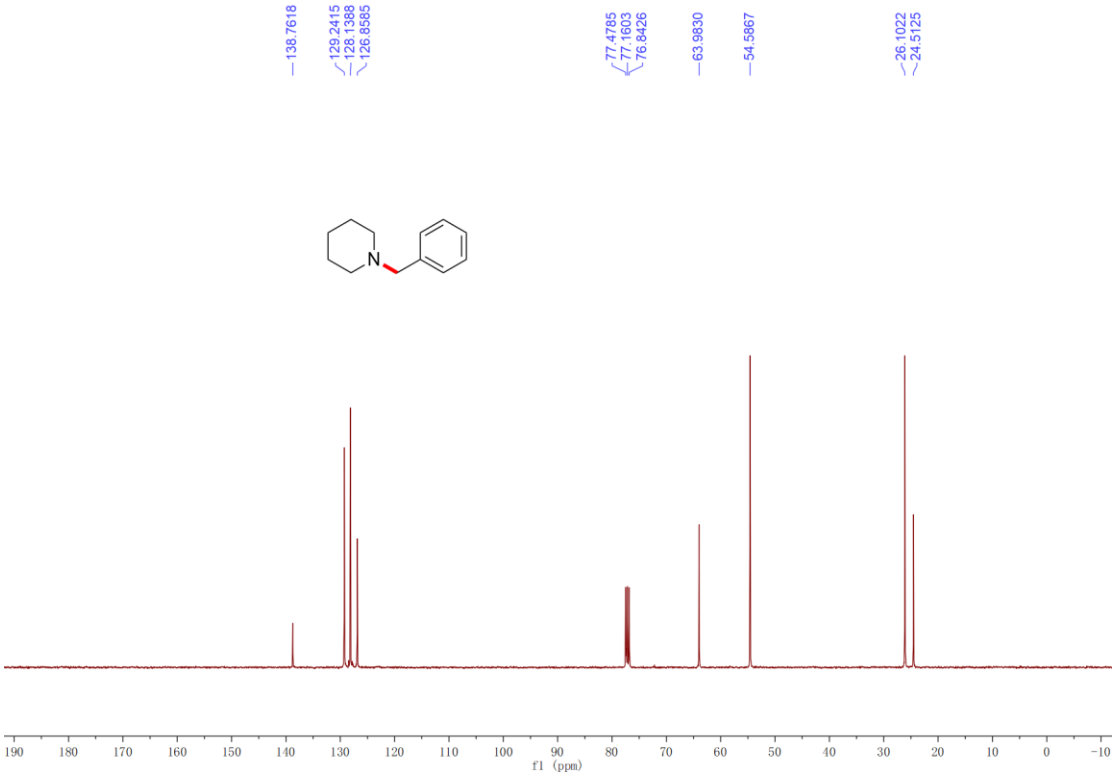

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9at** in $CDCl_3$.



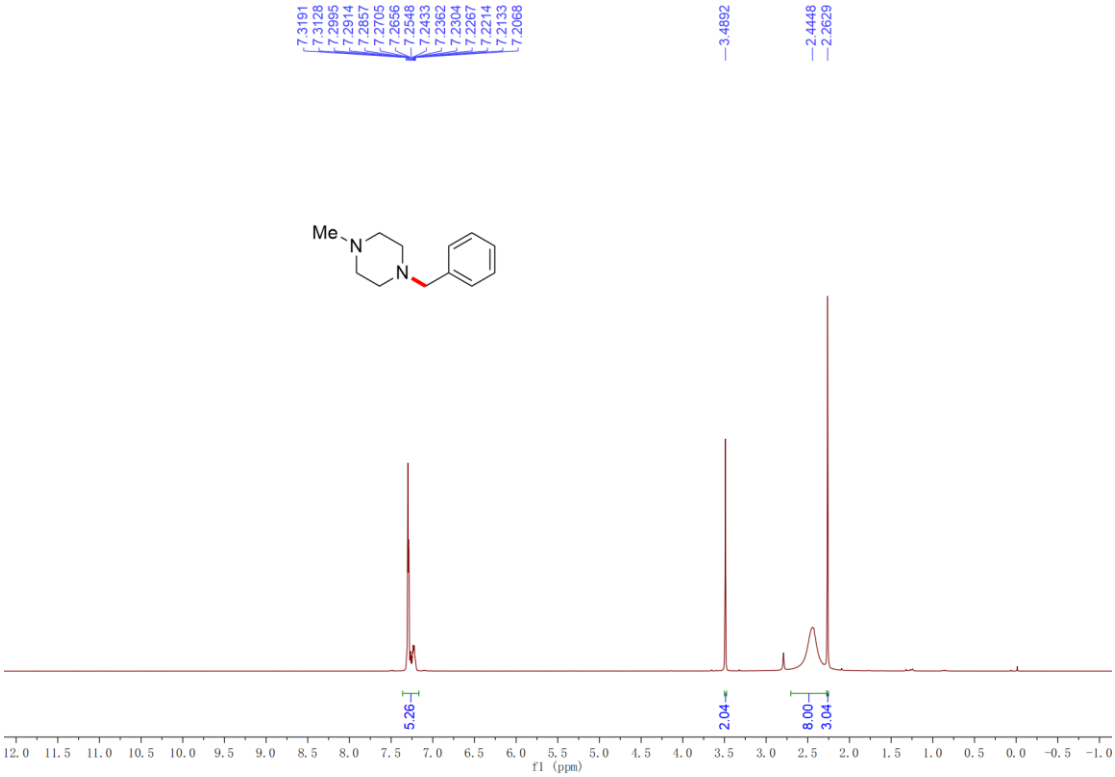
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9au** in $CDCl_3$.



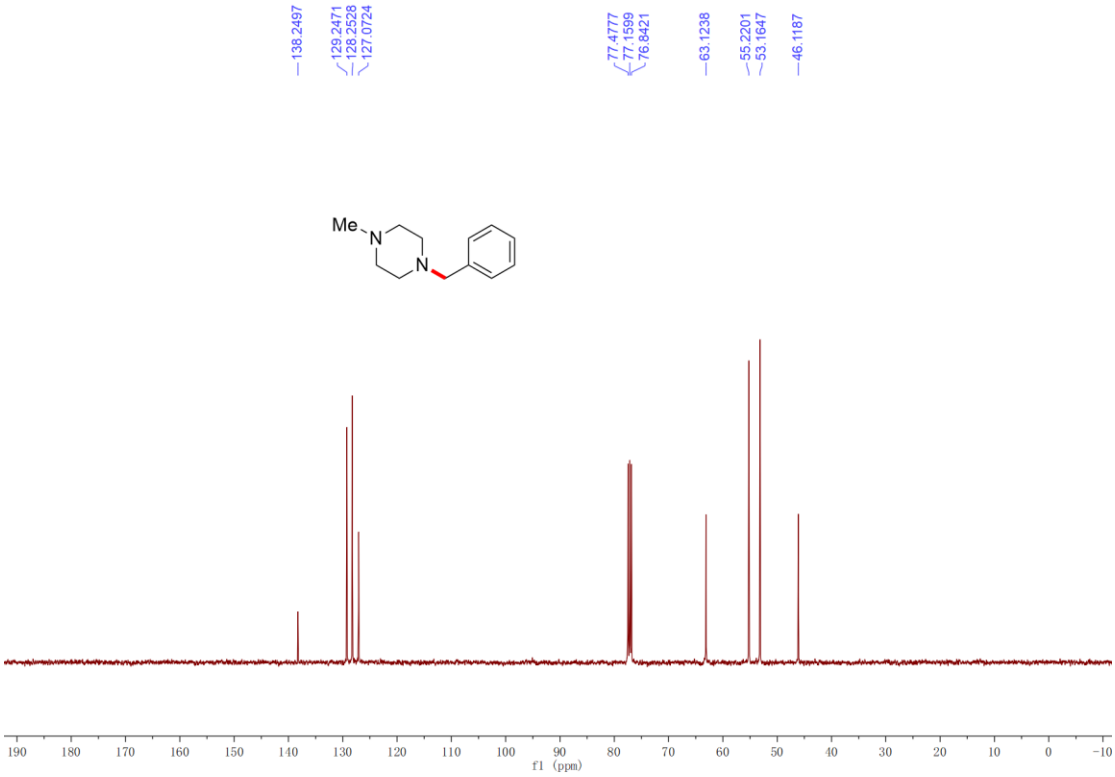

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9au** in $CDCl_3$.



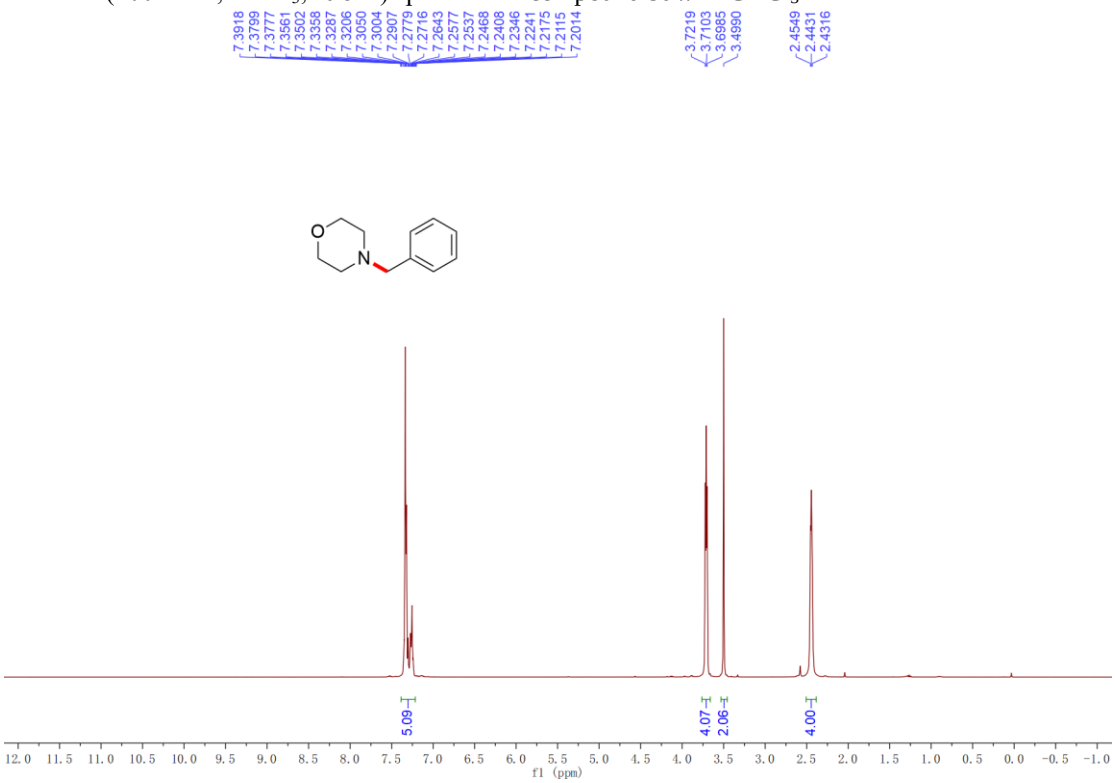
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9av** in $CDCl_3$.



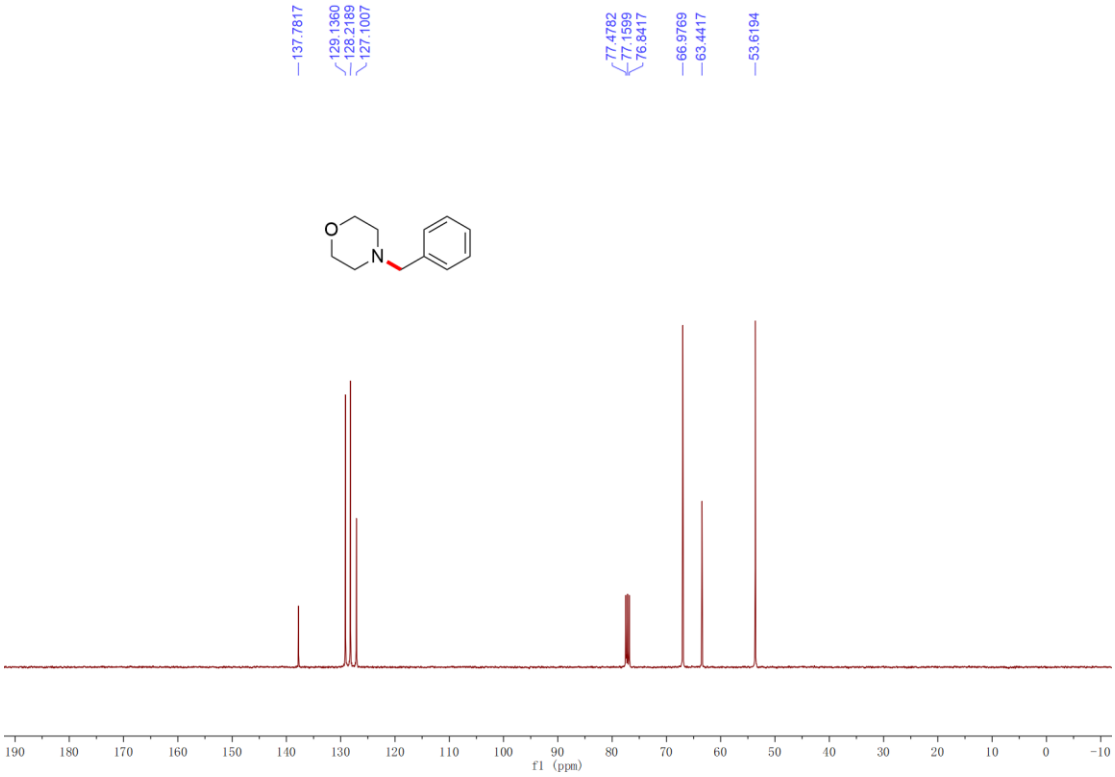

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9av** in $CDCl_3$.



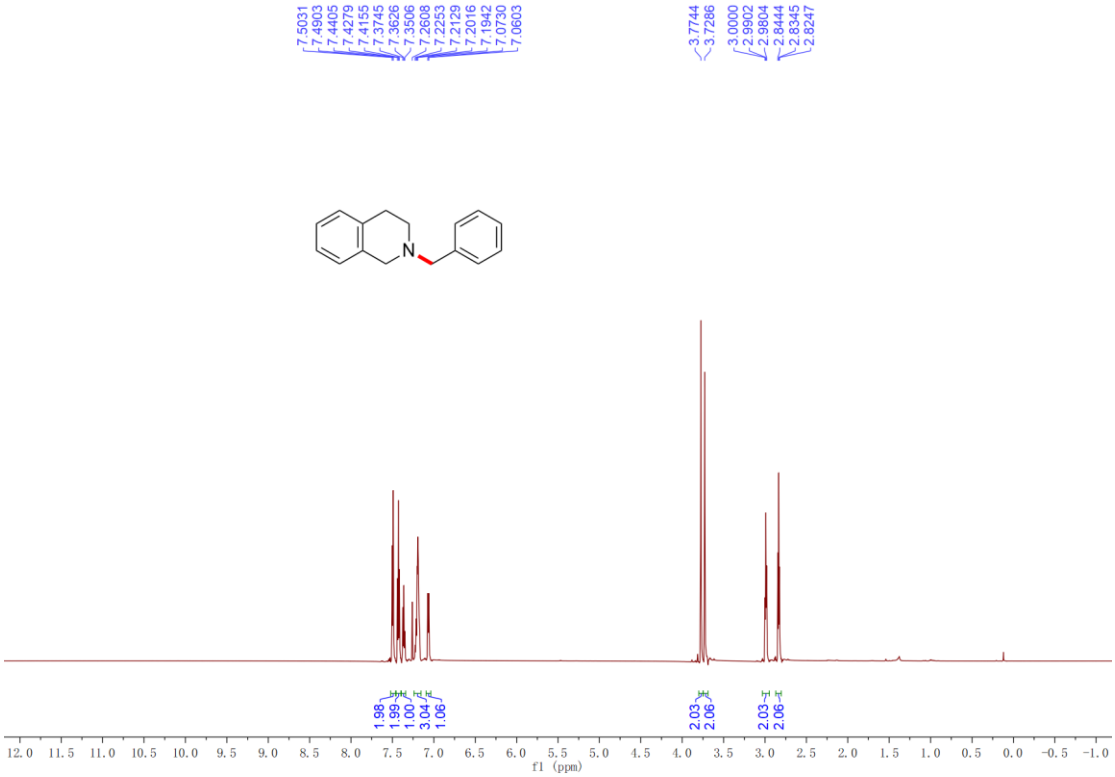
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9aw** in $CDCl_3$.



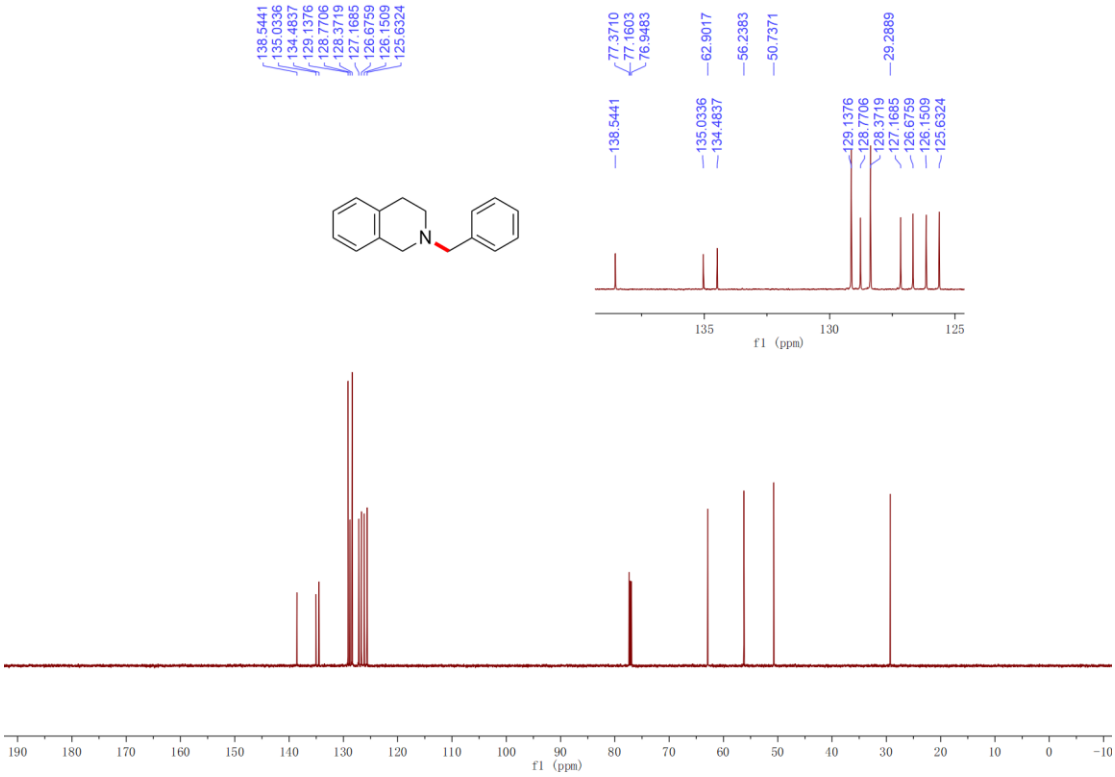

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9aw** in $CDCl_3$.



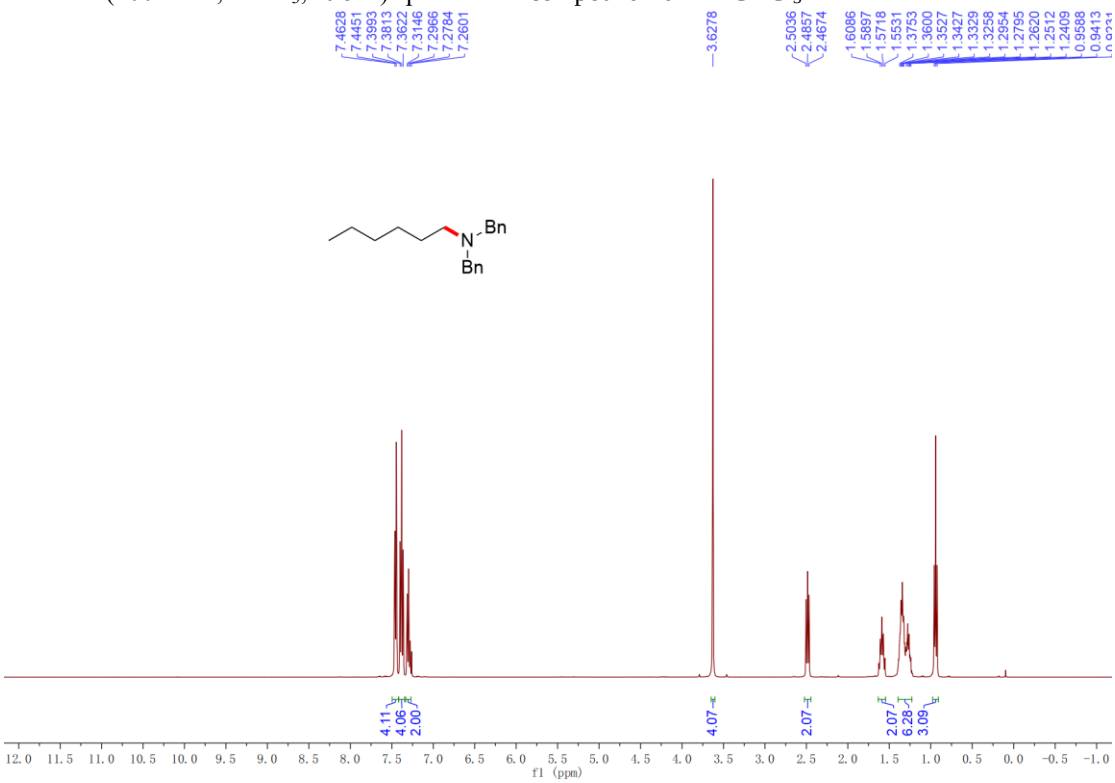
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **9ax** in $CDCl_3$.



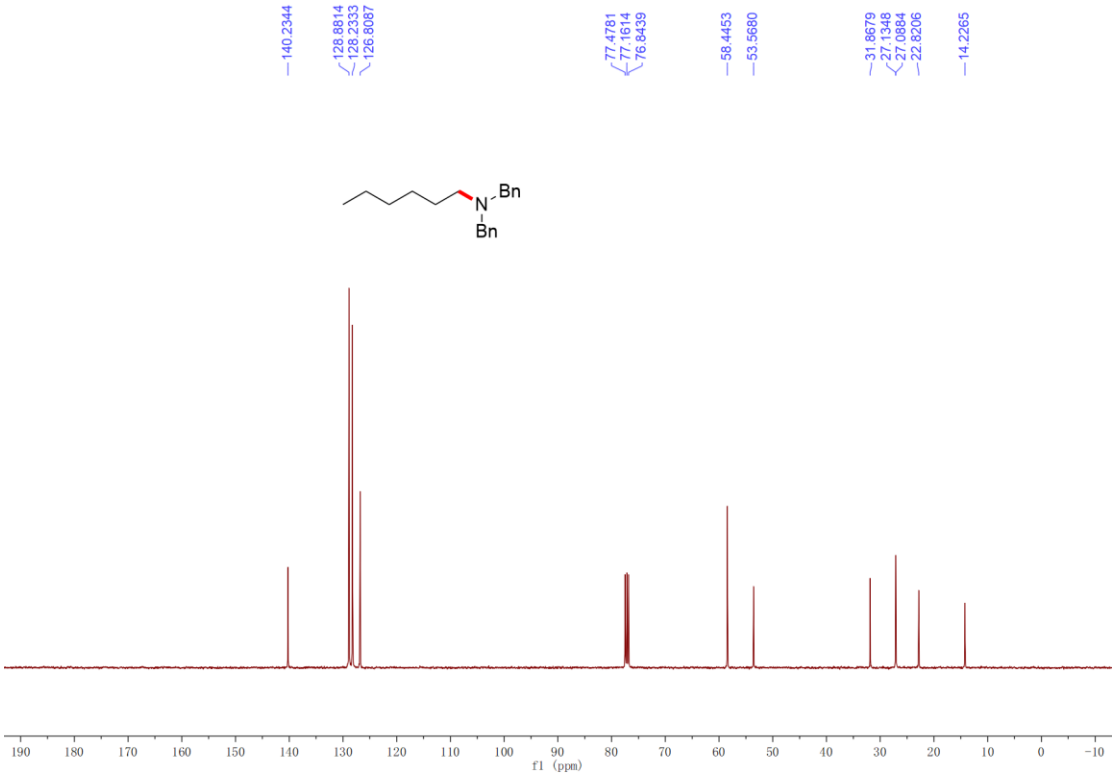

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **9ax** in $CDCl_3$.



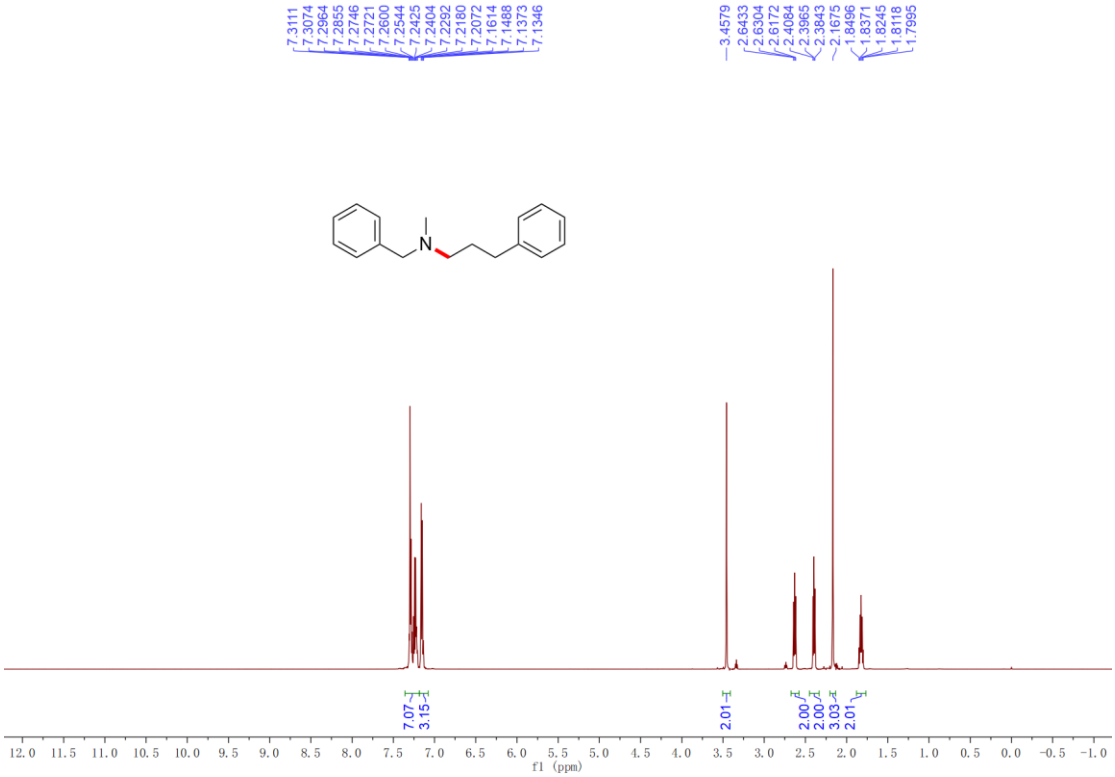
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **10in** in $CDCl_3$.



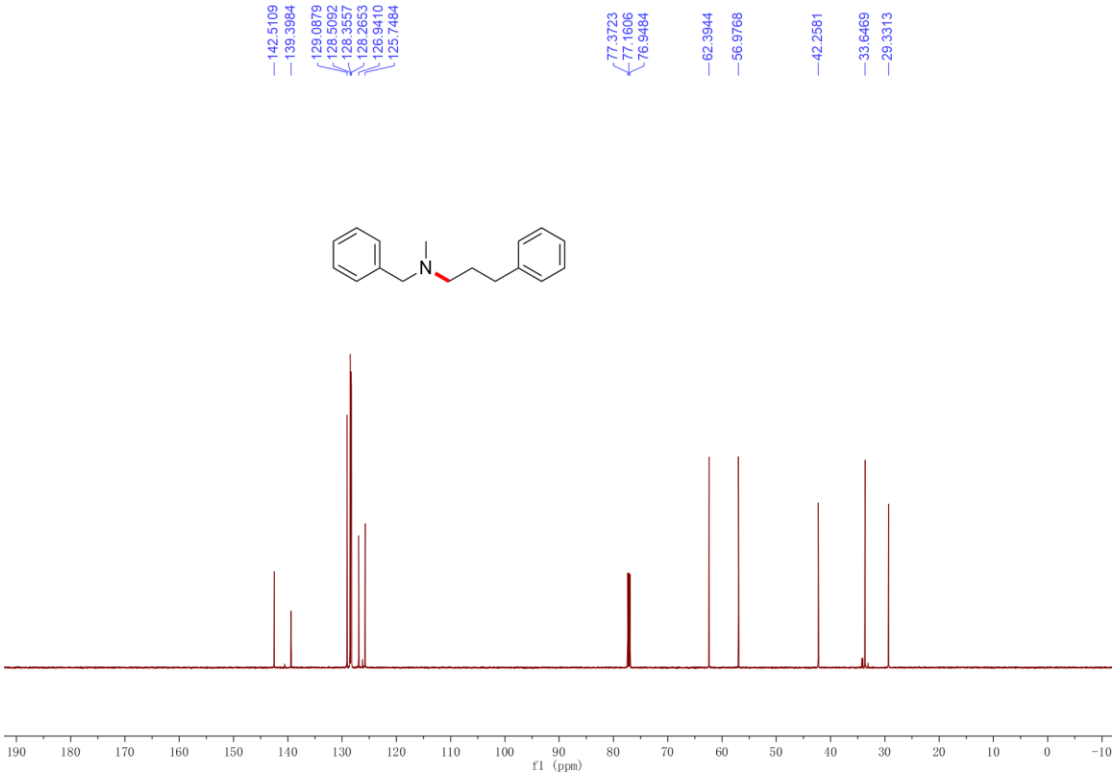

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **10in** in $CDCl_3$.



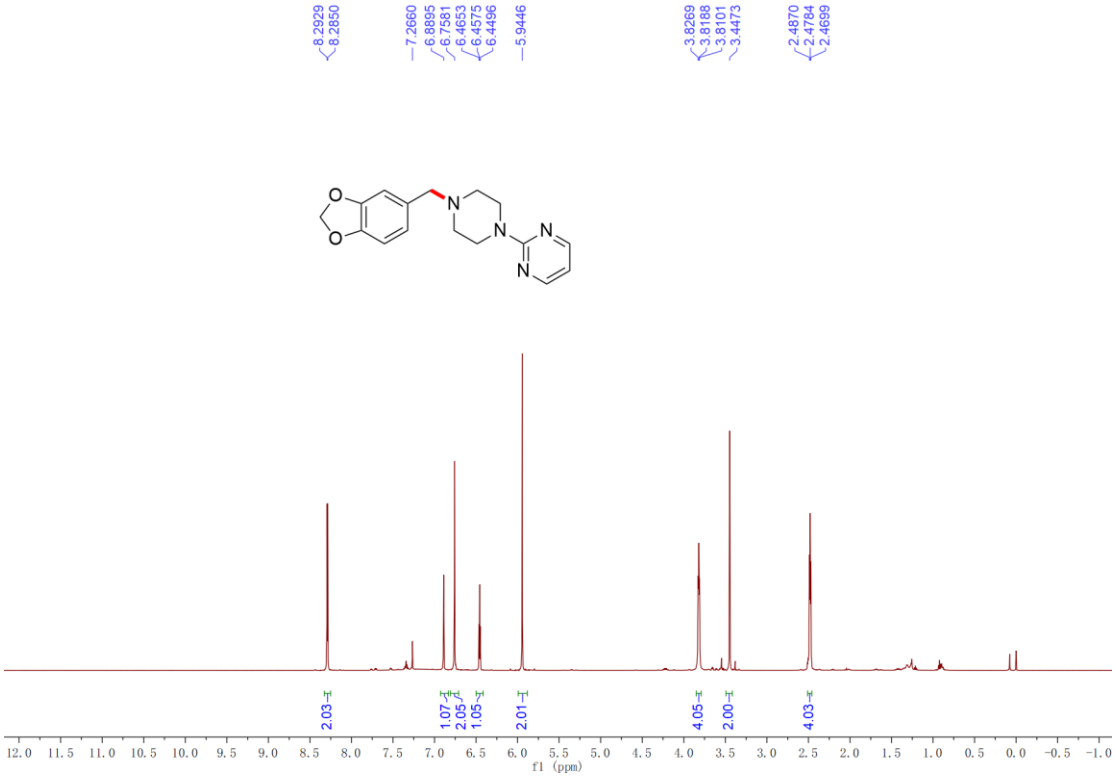
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **10jl** in $CDCl_3$.



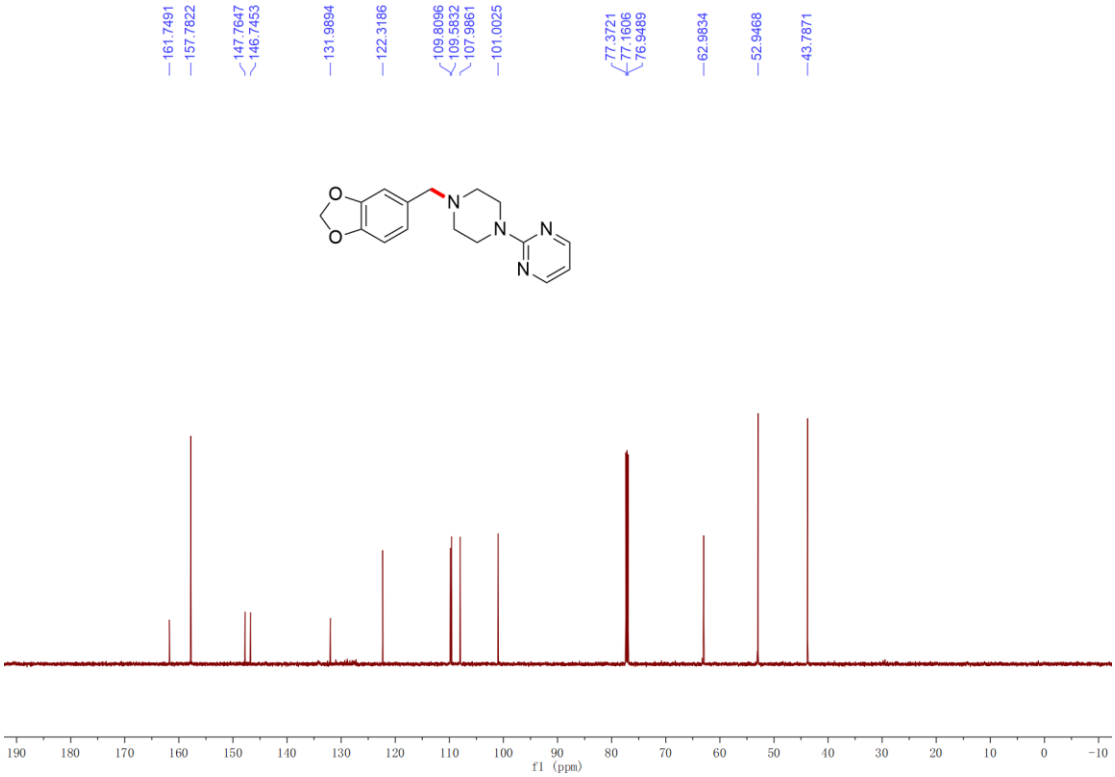

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **10jl** in $CDCl_3$.



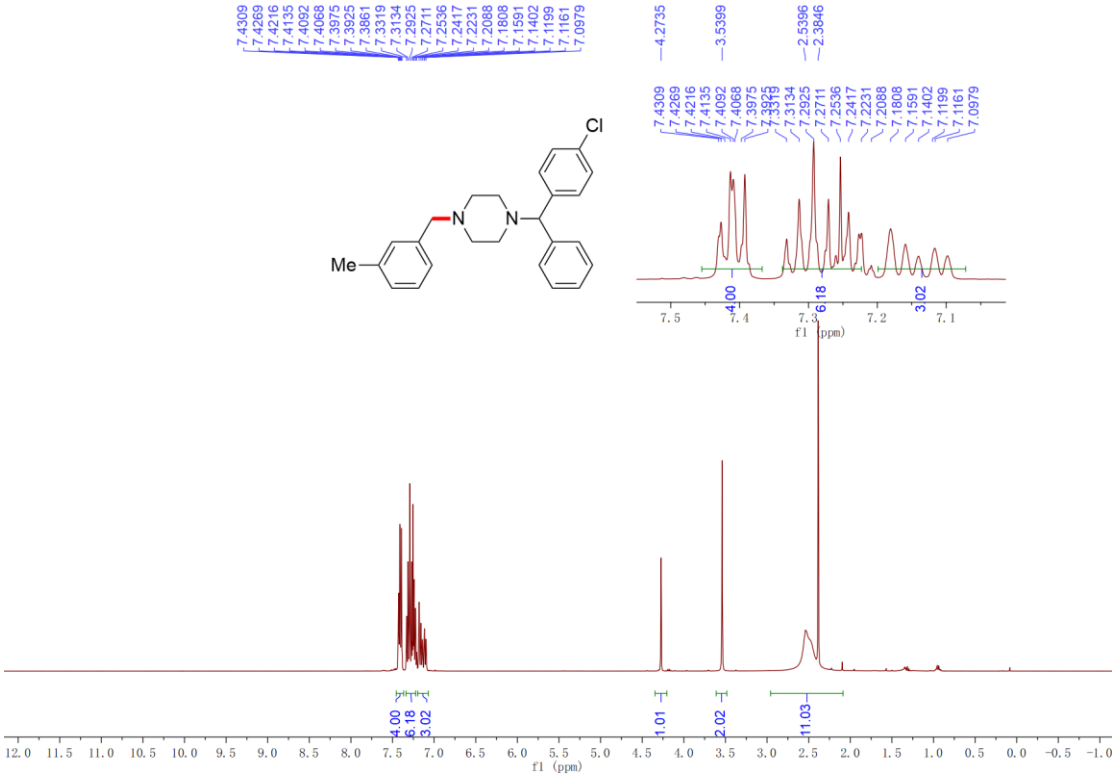
$^{1}$H NMR (600 MHz, $CDCl_3$, 298 K) spectrum of compound **Piribedil** in $CDCl_3$.



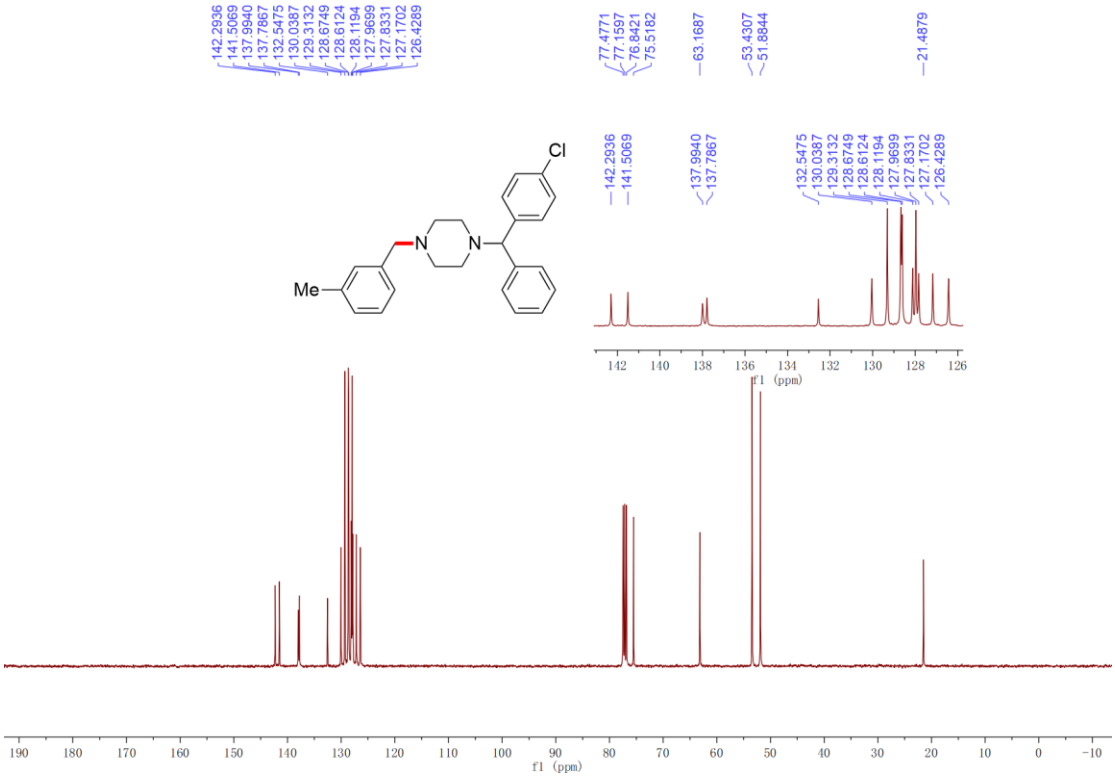

$^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) spectrum of compound **Piribedil** in $CDCl_3$.



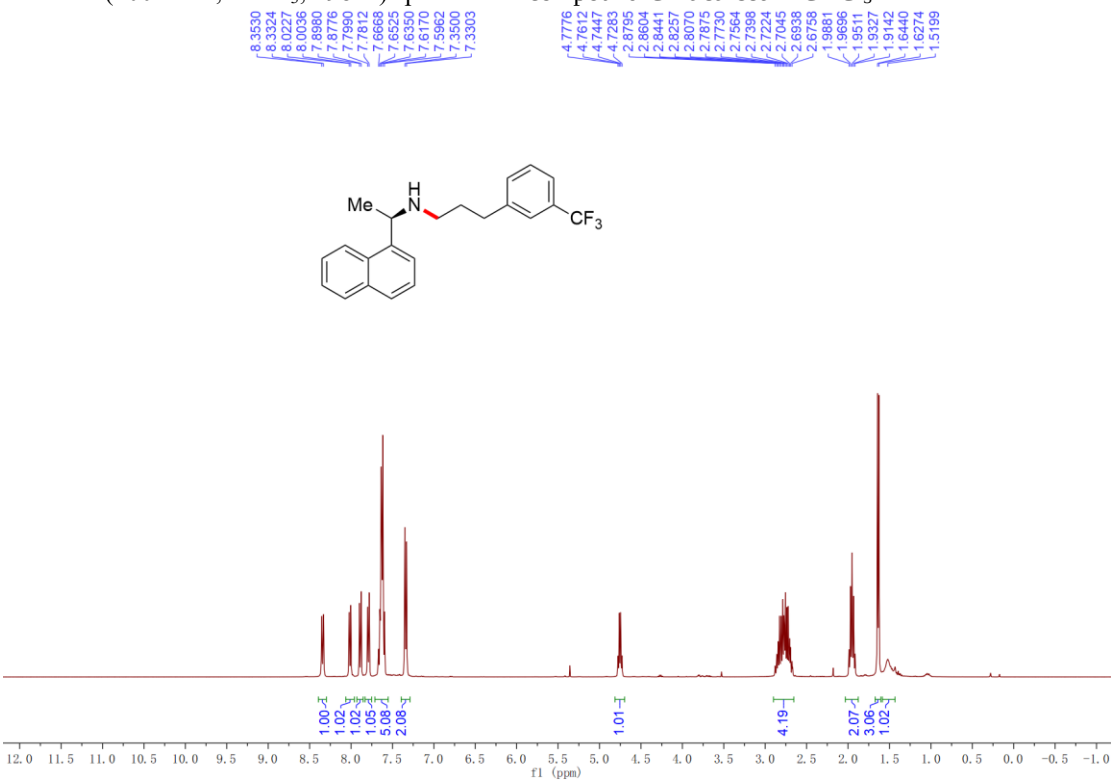
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **Meclizine** in $CDCl_3$.



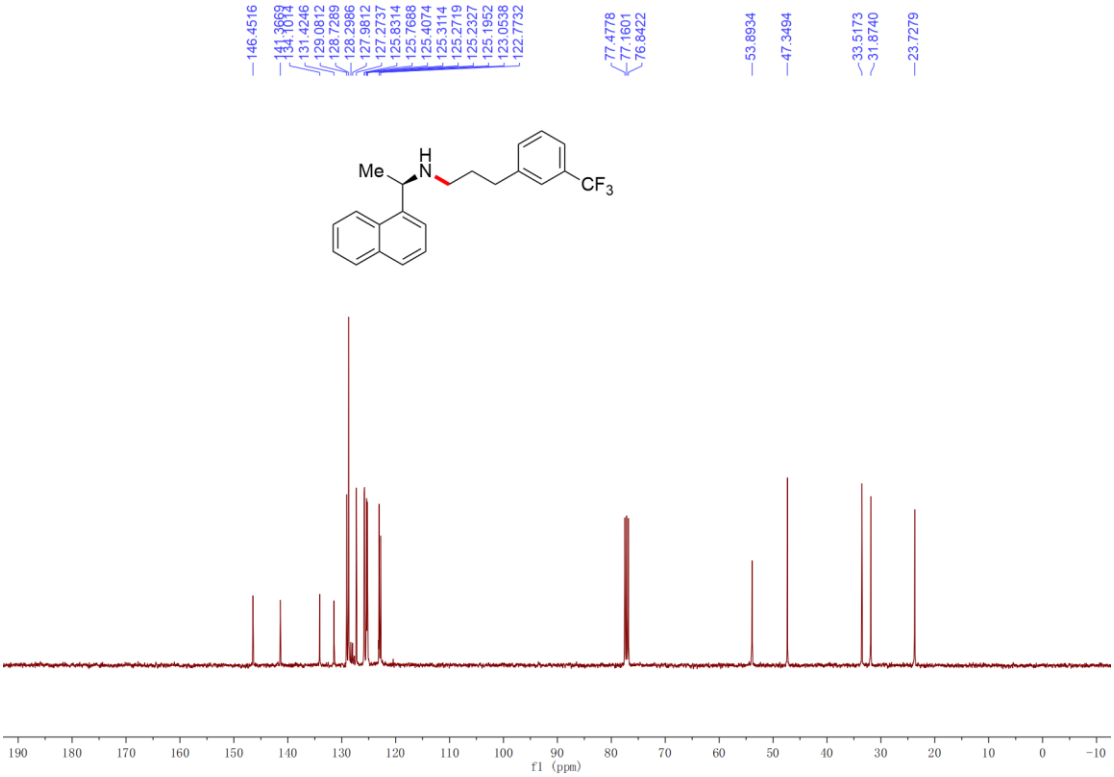

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **Meclizine** in $CDCl_3$.

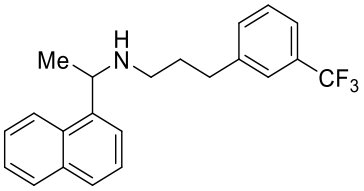


$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **Cinacalcet** in $CDCl_3$.



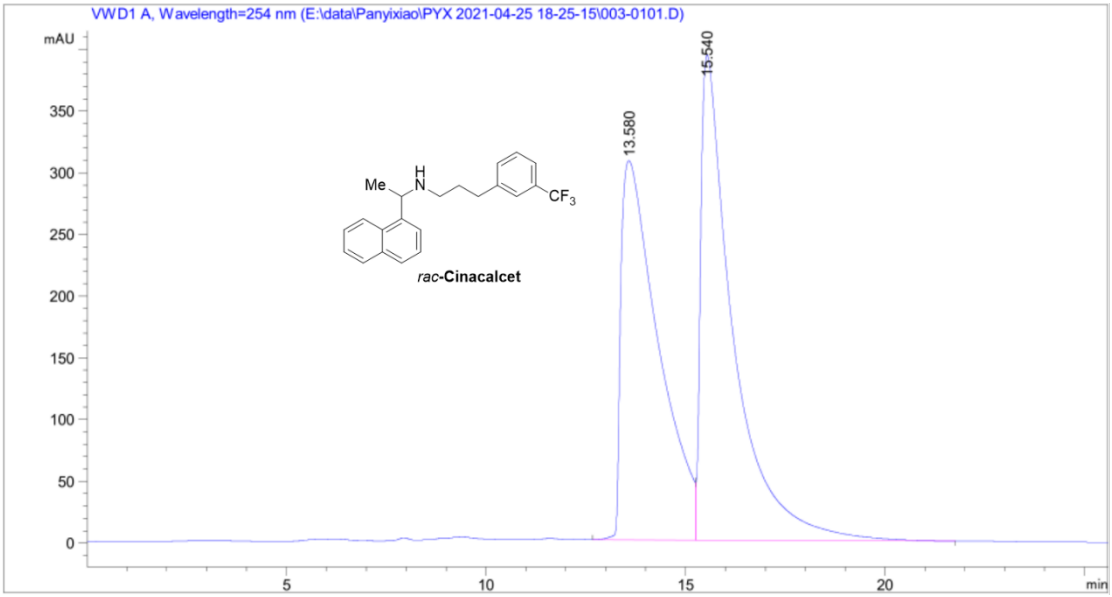

$^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **Cinacalcet** in $CDCl_3$.



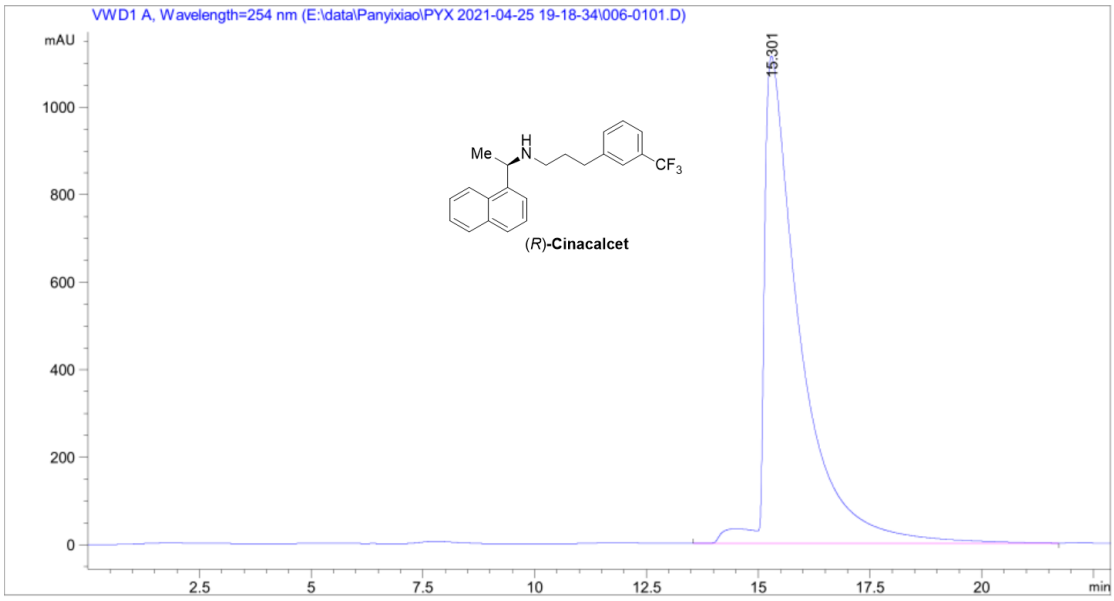



**Cinacalcet**

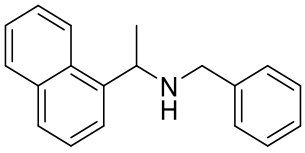
**HPLC Conditions:** The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane/isopropanol = 95/5, flowing rate = 0.5 mL/min, 25 ºC, UV 254 nm), $t_{R1}$ = 15.3 min (major); $[\alpha]_D^{20}$ = +17.5 (c = 0.62, $CH_2Cl_2$).




| Peak | Ret. Time | Type | Width | Area | Height | Area% |
|---|---|---|---|---|---|---|
| 1 | 13.580 | BV | 0.9385 | 1.99513e4 | 307.26288 | 47.2770 |
| 2 | 15.540 | VB | 0.7824 | 2.22497e4 | 393.06583 | 52.7230 |

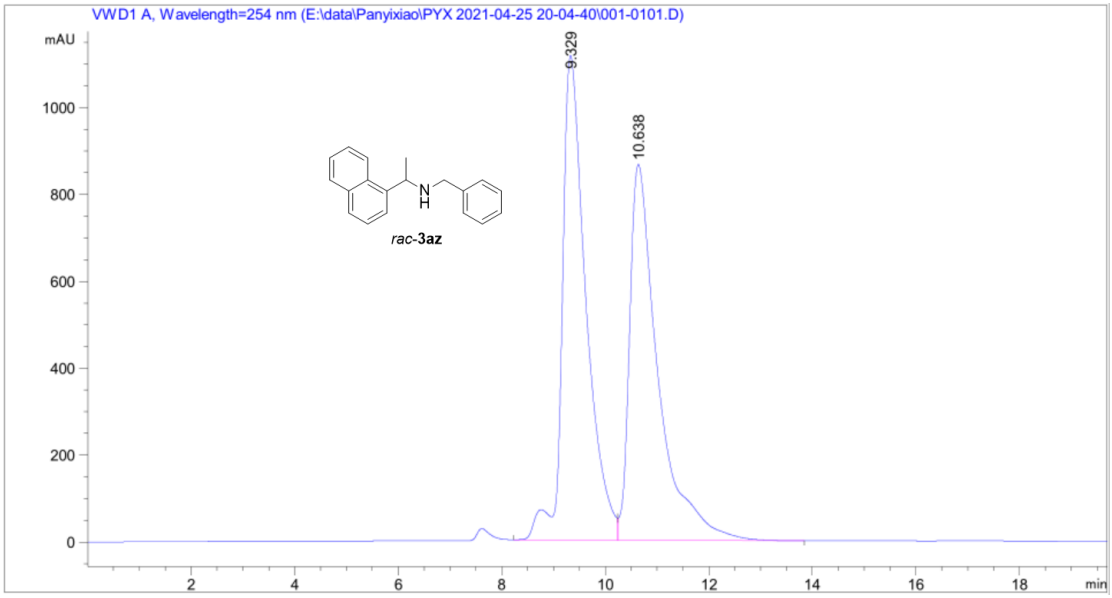



| Peak | Ret. Time | Type | Width | Area | Height | Area% |
|---|---|---|---|---|---|---|
| 1 | 15.301 | VB R | 0.7614 | 6.18200e4 | 1113.37878 | 100.0000 |

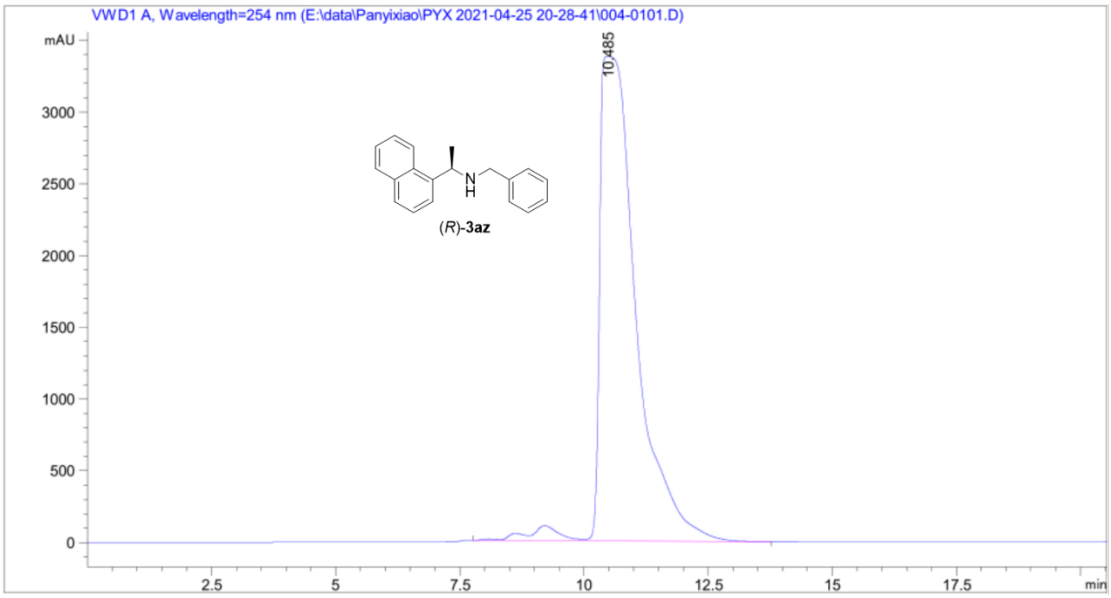


**3az**

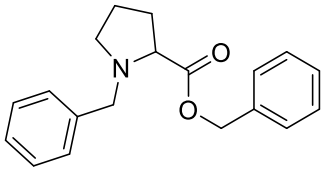
**HPLC Conditions:** The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane/isopropanol = 955, flowing rate = 0.5 mL/min, 25 ºC, UV 254 nm), $t_{R1}$ = 10.5 min (major); $[\alpha]_D^{20}$ = +6.5 (c = 0.44, MeOH).




| Peak | Ret. Time | Type | Width | Area | Height | Area% |
|---|---|---|---|---|---|---|
| 1 | 9.329 | VV R | 0.4498 | 3.56983e4 | 1114.84509 | 51.9253 |
| 2 | 10.638 | VB | 0.5527 | 3.30511e4 | 865.09796 | 48.0747 |

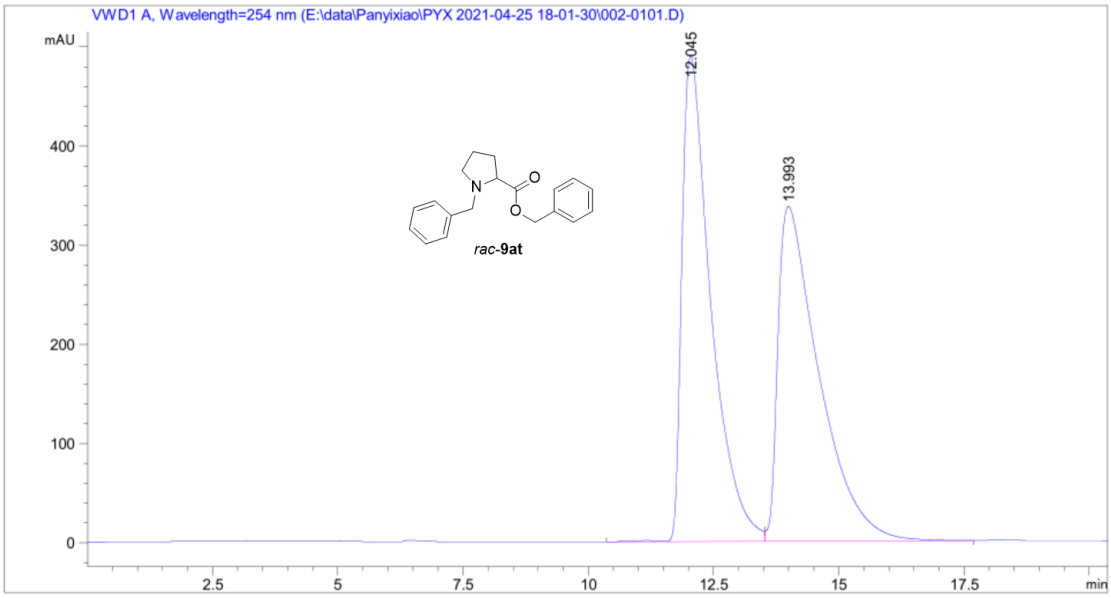



| Peak | Ret. Time | Type | Width | Area | Height | Area% |
|---|---|---|---|---|---|---|
| 1 | 10.485 | VB R | 0.6656 | 1.74737e5 | 3379.13599 | 100.0000 |

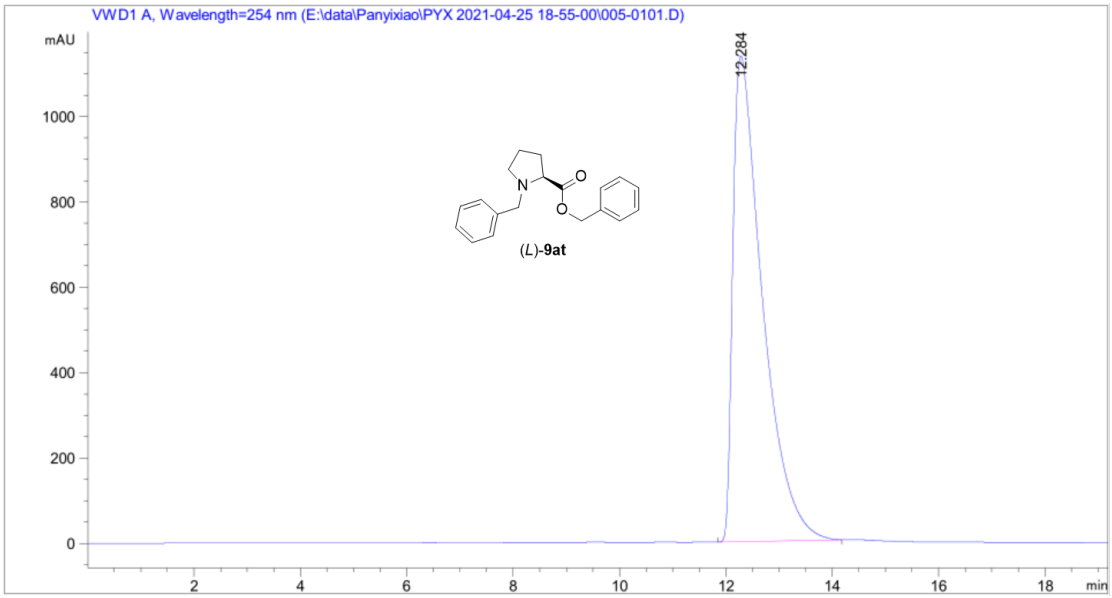


**9at**

**HPLC Conditions:** The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane/isopropanol = 95/5, flowing rate = 0.5 mL/min, 25 ºC, UV 254 nm), $t_{R1}$ = 12.3 min (major); $[\alpha]_D^{20}$ = +9.6 (c = 0.75, MeOH).




| Peak | Ret. Time | Type | Width | Area | Height | Area% |
|---|---|---|---|---|---|---|
| 1 | 12.045 | VV R | 0.5917 | 1.96726e4 | 489.64050 | 50.5714 |
| 2 | 13.993 | VB | 0.8314 | 1.92281e4 | 337.63345 | 49.4286 |




| Peak | Ret. Time | Type | Width | Area | Height | Area% |
|---|---|---|---|---|---|---|
| 1 | 12.284 | BB | 0.5760 | 4.3983e4 | 1137.72510 | 100.0000 |

## 9. Single crystal X-ray structure of 3aaj

## X-ray of 3aaj, CCDC 2070767

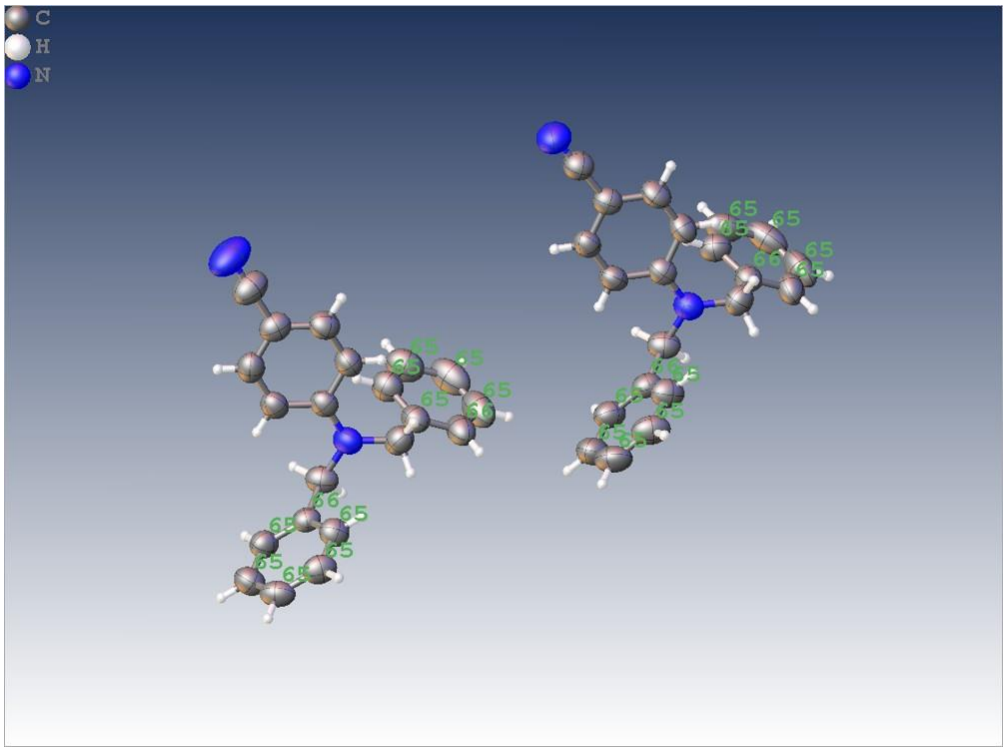



**Table 1 Crystal data and structure refinement for** exp_3044**.**

| | |
|---|---|
| Identification code | exp_3044 |
| Empirical formula | $C_{42}H_{36}N_4$ |
| Formula weight | 596.75 |
| Temperature/K | 272(1) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 15.6432(3) |
| b/Å | 13.2799(2) |
| c/Å | 17.6411(4) |
| α/° | 90 |
| β/° | 114.078(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 3345.90(12) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.185 |
| μ/mm$^{-1}$ | 0.537 |
| F(000) | 1264.0 |
| Crystal size/mm$^3$ | 0.300 × 0.200 × 0.150 |
| Radiation | ? (λ = 1.54184) |
| 2Θ range for data collection/° | 8.63 to 151.896 |
| Index ranges | $-19 \leq h \leq 18$, $-10 \leq k \leq 16$, $-22 \leq l \leq 21$ |
| Reflections collected | 22664 |
| Independent reflections | 6695 [$R_{int}$ = 0.0257, $R_{sigma}$ = 0.0267] |
| Data/restraints/parameters | 6695/0/415 |
| Goodness-of-fit on $F^2$ | 1.027 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0447, $wR_2$ = 0.1198 |

Final R indexes [all data] $R_1$ = 0.0559, $wR_2$ = 0.1279 Largest diff. peak/hole / e $Å^{-3}$ 0.11/-0.16

**Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for exp_3044.** Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| N001 | 8723.8(8) | 4696.0(9) | 3550.8(7) | 70.8(3) |
| N002 | 6241.7(8) | 3478.8(9) | 6500.5(8) | 71.4(3) |
| C003 | 5508.0(8) | 3340.5(9) | 7518.4(8) | 58.6(3) |
| C004 | 7687.1(10) | 3528.7(10) | 3892.3(8) | 66.7(3) |
| C005 | 9405.3(9) | 4535.3(10) | 2494.2(8) | 64.8(3) |
| C006 | 4623.2(9) | 3139.8(11) | 6914.7(9) | 69.5(3) |
| C007 | 5585.2(10) | 3615.4(10) | 8296.9(9) | 69.2(3) |
| C008 | 6300.2(8) | 4451.8(10) | 6270.4(8) | 61.7(3) |
| C009 | 8708.7(8) | 5694.1(10) | 3749.8(8) | 61.5(3) |
| C00A | 8658.6(9) | 7749.2(11) | 4127.3(8) | 66.0(3) |
| C00B | 8737.3(9) | 6453.0(10) | 3208.1(8) | 65.4(3) |
| C00C | 8708.8(9) | 7449.8(11) | 3390.7(8) | 67.2(3) |
| C00D | 6350.8(9) | 5261.8(10) | 6798.2(9) | 66.4(3) |
| C00E | 6925.0(10) | 4161.1(12) | 3538.1(10) | 76.1(4) |
| C00F | 7094.1(10) | 2183.8(10) | 6051.2(9) | 70.4(3) |
| C00G | 8655.0(10) | 6005.6(11) | 4492.8(8) | 69.2(3) |
| C00H | 9280.0(11) | 4624.7(11) | 1678.5(10) | 78.0(4) |
| C00I | 6326.6(10) | 4682.8(11) | 5499.4(9) | 70.8(3) |
| C00J | 7919.9(11) | 2722.4(13) | 6375.3(10) | 81.5(4) |
| C00K | 7536.2(13) | 2552.1(12) | 4074.5(9) | 82.7(4) |
| C00L | 4802.0(11) | 3717.3(13) | 8468.9(10) | 80.5(4) |
| C00M | 6426.2(9) | 6233.6(11) | 6570.4(10) | 72.6(4) |
| C00N | 6446.9(10) | 6450.5(11) | 5806.9(10) | 74.7(4) |
| C00O | 8563.0(10) | 4414.0(12) | 2700.5(9) | 74.3(4) |
| C00P | 8636.6(10) | 7007.2(11) | 4675.5(8) | 71.8(3) |
| N00Q | 8550.7(13) | 9641.7(12) | 4388.2(11) | 106.1(5) |
| C00R | 6375.9(10) | 3231.8(12) | 7346.2(9) | 72.6(4) |
| C00S | 10308.7(10) | 4545.0(12) | 3099.1(10) | 80.3(4) |
| C00T | 3843.9(9) | 3232.3(12) | 7091.5(10) | 76.5(4) |
| C00U | 3933.4(10) | 3527.1(12) | 7861.6(10) | 78.6(4) |
| C00V | 8671.4(10) | 3882.0(11) | 4078.9(10) | 75.2(4) |
| C00W | 7111.4(14) | 1209.9(12) | 5776.0(10) | 84.1(4) |
| C00X | 6394.3(10) | 5656.2(12) | 5278.2(9) | 76.2(4) |
| C00Y | 8603.9(11) | 8796.8(13) | 4287.8(10) | 78.8(4) |

| | | | | |
|---|---|---|---|---|
| C00Z | 6169.7(10) | 2629.9(11) | 5957.9(11) | 77.3(4) |
| C010 | 10038.1(14) | 4746.7(14) | 1476.2(12) | 93.5(5) |
| C011 | 6630.8(17) | 2226.5(16) | 3901.8(11) | 102.1(6) |
| C012 | 6032.1(12) | 3831.7(16) | 3373.0(12) | 93.8(5) |
| C013 | 7919.2(18) | 790.8(15) | 5807.2(13) | 104.4(6) |
| C014 | 5887.0(15) | 2863.2(19) | 3551.6(12) | 104.9(6) |
| C015 | 11065.0(11) | 4660.7(14) | 2893.0(12) | 91.3(5) |
| C016 | 8744.5(13) | 2296.8(17) | 6409.6(12) | 100.5(5) |
| C017 | 10931.6(13) | 4775.4(14) | 2088.4(13) | 95.2(5) |
| C018 | 8734.2(17) | 1327.3(19) | 6120.3(14) | 111.9(7) |
| C019 | 6534.0(13) | 7469.3(14) | 5579.4(12) | 98.0(5) |
| N01A | 6608.2(17) | 8281.3(15) | 5405.8(14) | 142.3(8) |

**Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for exp_3044. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.**

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| N001 | 71.4(7) | 73.2(7) | 71.6(7) | -6.9(5) | 33.0(6) | -5.9(5) |
| N002 | 77.0(7) | 71.5(7) | 77.7(7) | 3.3(5) | 43.9(6) | 5.5(5) |
| C003 | 57.4(6) | 55.6(6) | 62.5(7) | 10.3(5) | 24.2(5) | 1.2(5) |
| C004 | 76.1(8) | 68.5(7) | 58.3(7) | -3.0(6) | 30.4(6) | -1.3(6) |
| C005 | 63.8(7) | 60.9(7) | 68.8(8) | -11.7(6) | 26.0(6) | 4.0(5) |
| C006 | 63.6(7) | 78.4(8) | 61.7(7) | 5.3(6) | 20.7(6) | 2.9(6) |
| C007 | 64.1(7) | 74.0(8) | 65.8(8) | 0.4(6) | 22.6(6) | -7.6(6) |
| C008 | 51.6(6) | 72.3(8) | 64.9(7) | -0.2(6) | 27.6(5) | 4.5(5) |
| C009 | 50.0(6) | 75.4(8) | 57.2(7) | -2.7(6) | 20.0(5) | -3.2(5) |
| C00A | 57.7(7) | 74.9(8) | 63.8(7) | -5.3(6) | 23.3(6) | -2.4(6) |
| C00B | 62.9(7) | 80.1(8) | 59.0(7) | -0.8(6) | 30.8(6) | 4.0(6) |
| C00C | 62.0(7) | 78.6(8) | 66.6(8) | 6.3(6) | 32.0(6) | 3.6(6) |
| C00D | 59.6(7) | 80.2(9) | 65.1(7) | -4.1(6) | 31.4(6) | -0.5(6) |
| C00E | 71.6(8) | 77.1(9) | 82.3(9) | -7.0(7) | 34.3(7) | -0.1(7) |
| C00F | 81.6(9) | 69.3(8) | 67.3(8) | 5.2(6) | 37.6(7) | 7.9(6) |
| C00G | 73.9(8) | 79.9(9) | 52.5(7) | 0.1(6) | 24.7(6) | -8.4(6) |
| C00H | 73.3(9) | 84.8(9) | 72.8(9) | -6.3(7) | 26.6(7) | 13.9(7) |
| C00I | 74.0(8) | 78.8(9) | 62.3(8) | -4.4(6) | 30.7(6) | 1.3(6) |
| C00J | 76.9(9) | 85.3(10) | 86.8(10) | 1.8(8) | 37.9(8) | 10.0(7) |
| C00K | 110.4(12) | 77.3(9) | 62.8(8) | 3.4(7) | 37.8(8) | -6.1(8) |
| C00L | 84.8(10) | 92.2(10) | 73.1(9) | 3.3(7) | 41.0(8) | 1.0(8) |
| C00M | 62.2(7) | 76.2(9) | 79.6(9) | -12.1(7) | 29.2(7) | -2.3(6) |
| C00N | 62.0(8) | 76.4(9) | 78.0(9) | 7.4(7) | 20.6(7) | -0.8(6) |
| C00O | 67.4(8) | 81.8(9) | 73.0(9) | -17.0(7) | 27.8(7) | -6.8(6) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C00P | 74.4(8) | 88.0(9) | 51.5(7) | -8.9(6) | 24.2(6) | -7.2(7) |
| N00Q | 136.5(14) | 85.5(10) | 103.0(11) | -11.0(8) | 55.7(10) | 5.9(9) |
| C00R | 62.5(7) | 80.7(9) | 77.5(9) | 15.0(7) | 31.7(7) | 8.9(6) |
| C00S | 67.1(8) | 97.3(11) | 71.7(9) | -10.5(8) | 23.5(7) | 4.3(7) |
| C00T | 53.6(7) | 84.3(9) | 81.9(10) | 12.5(7) | 17.8(6) | -1.1(6) |
| C00U | 67.8(8) | 86.9(10) | 91.1(10) | 20.3(8) | 42.5(8) | 7.7(7) |
| C00V | 69.3(8) | 71.9(8) | 79.2(9) | 4.8(7) | 25.1(7) | 6.2(6) |
| C00W | 115.8(13) | 70.6(8) | 75.2(9) | 6.7(7) | 48.5(9) | 11.5(8) |
| C00X | 75.1(8) | 88.4(10) | 61.9(8) | 7.0(7) | 24.6(7) | -0.5(7) |
| C00Y | 81.1(9) | 83.0(10) | 72.4(9) | -6.3(7) | 31.4(7) | -0.4(7) |
| C00Z | 75.8(9) | 69.1(8) | 92.0(10) | -5.0(7) | 39.3(8) | -4.0(6) |
| C010 | 103.1(13) | 105.1(12) | 86.0(11) | 1.1(9) | 52.7(10) | 20.0(10) |
| C011 | 142.5(18) | 103.4(13) | 75.9(10) | -11.4(9) | 60.4(12) | -49.5(13) |
| C012 | 74.9(10) | 119.9(14) | 95.7(12) | -22.6(10) | 44.0(9) | -6.9(9) |
| C013 | 143.1(18) | 88.9(12) | 96.7(13) | 15.1(10) | 64.7(13) | 40.7(12) |
| C014 | 97.7(13) | 148.4(19) | 86.0(12) | -29.1(12) | 55.1(11) | -40.7(13) |
| C015 | 62.3(8) | 106.0(12) | 101.1(13) | -21.2(10) | 28.8(8) | 4.8(8) |
| C016 | 80.6(11) | 126.0(15) | 99.1(12) | 16.7(11) | 41.0(9) | 18.9(10) |
| C017 | 85.2(11) | 100.8(12) | 117.6(15) | -14.1(10) | 59.7(11) | 6.9(9) |
| C018 | 122.1(17) | 126.8(17) | 106.6(14) | 31.7(12) | 66.7(13) | 62.4(14) |
| C019 | 94.5(12) | 84.0(11) | 96.8(12) | 11.4(9) | 20.1(10) | -9.0(9) |
| N01A | 162.9(19) | 93.9(12) | 136.7(16) | 23.9(11) | 27.1(14) | -25.1(11) |

**Table 4 Bond Lengths for exp_3044.**

| Atom Atom | Length/Å | Atom Atom | Length/Å |
|---|---|---|---|
| N001 C009 | 1.3738(17) | C00D C00M | 1.371(2) |
| N001 C00O | 1.4649(18) | C00E C012 | 1.377(2) |
| N001 C00V | 1.4510(19) | C00F C00J | 1.380(2) |
| N002 C008 | 1.3686(17) | C00F C00W | 1.386(2) |
| N002 C00R | 1.4566(18) | C00F C00Z | 1.508(2) |
| N002 C00Z | 1.4533(19) | C00G C00P | 1.372(2) |
| C003 C006 | 1.3850(18) | C00H C010 | 1.380(2) |
| C003 C007 | 1.3779(19) | C00I C00X | 1.367(2) |
| C003 C00R | 1.5143(18) | C00J C016 | 1.387(2) |
| C004 C00E | 1.382(2) | C00K C011 | 1.391(3) |
| C004 C00K | 1.379(2) | C00L C00U | 1.367(2) |
| C004 C00V | 1.512(2) | C00M C00N | 1.391(2) |
| C005 C00H | 1.376(2) | C00N C00X | 1.388(2) |
| C005 C00O | 1.5119(19) | C00N C019 | 1.433(2) |
| C005 C00S | 1.380(2) | N00Q C00Y | 1.144(2) |
| C006 C00T | 1.382(2) | C00S C015 | 1.381(2) |

| | | | |
|---|---|---|---|
| C007 C00L | 1.384(2) | C00T C00U | 1.365(2) |
| C008 C00D | 1.4036(18) | C00W C013 | 1.361(3) |
| C008 C00I | 1.4112(19) | C010 C017 | 1.375(3) |
| C009 C00B | 1.4020(19) | C011 C014 | 1.365(3) |
| C009 C00G | 1.4093(18) | C012 C014 | 1.365(3) |
| C00A C00C | 1.3914(19) | C013 C018 | 1.365(3) |
| C00A C00P | 1.391(2) | C015 C017 | 1.356(3) |
| C00A C00Y | 1.429(2) | C016 C018 | 1.383(3) |
| C00B C00C | 1.3673(19) | C019 N01A | 1.140(2) |

**Table 5 Bond Angles for exp_3044.**

| Atom Atom Atom | Angle/° | Atom Atom Atom | Angle/° |
|---|---|---|---|
| C009 N001 C00O | 119.64(12) | C00W C00F C00Z | 118.90(14) |
| C009 N001 C00V | 122.92(12) | C00P C00G C009 | 121.20(13) |
| C00V N001 C00O | 115.84(12) | C005 C00H C010 | 120.64(15) |
| C008 N002 C00R | 121.15(12) | C00X C00I C008 | 121.13(13) |
| C008 N002 C00Z | 122.25(12) | C00F C00J C016 | 120.24(17) |
| C00Z N002 C00R | 116.10(12) | C004 C00K C011 | 119.81(17) |
| C006 C003 C00R | 121.59(12) | C00U C00L C007 | 119.72(14) |
| C007 C003 C006 | 118.11(12) | C00D C00M C00N | 121.17(14) |
| C007 C003 C00R | 120.27(12) | C00M C00N C019 | 120.61(16) |
| C00E C004 C00V | 121.61(13) | C00X C00N C00M | 118.36(14) |
| C00K C004 C00E | 118.60(14) | C00X C00N C019 | 121.03(16) |
| C00K C004 C00V | 119.79(13) | N001 C00O C005 | 114.63(11) |
| C00H C005 C00O | 119.64(13) | C00G C00P C00A | 120.98(12) |
| C00H C005 C00S | 118.15(14) | N002 C00R C003 | 114.68(11) |
| C00S C005 C00O | 122.20(13) | C005 C00S C015 | 120.96(16) |
| C00T C006 C003 | 120.42(13) | C00U C00T C006 | 120.56(13) |
| C003 C007 C00L | 121.27(13) | C00T C00U C00L | 119.89(13) |
| N002 C008 C00D | 121.29(12) | N001 C00V C004 | 114.24(11) |
| N002 C008 C00I | 121.53(12) | C013 C00W C00F | 121.20(19) |
| C00D C008 C00I | 117.18(12) | C00I C00X C00N | 121.13(14) |
| N001 C009 C00B | 120.72(12) | N00Q C00Y C00A | 177.67(17) |
| N001 C009 C00G | 122.31(12) | N002 C00Z C00F | 114.81(12) |
| C00B C009 C00G | 116.96(12) | C017 C010 C00H | 120.37(16) |
| C00C C00A C00Y | 119.61(13) | C014 C011 C00K | 120.69(18) |
| C00P C00A C00C | 118.27(13) | C014 C012 C00E | 120.03(18) |
| C00P C00A C00Y | 122.09(13) | C00W C013 C018 | 120.08(19) |
| C00C C00B C009 | 121.48(12) | C012 C014 C011 | 119.78(17) |
| C00B C00C C00A | 121.09(13) | C017 C015 C00S | 120.36(16) |
| C00M C00D C008 | 121.02(13) | C018 C016 C00J | 119.52(19) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C012 | C00E | C004 | 121.09(16) | C015 | C017 | C010 | 119.48(16) |
| C00J | C00F | C00W | 118.69(14) | C013 | C018 | C016 | 120.25(17) |
| C00J | C00F | C00Z | 122.37(13) | N01A | C019 | C00N | 179.4(3) |

**Table 6 Torsion Angles for exp_3044.**

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| N001 | C009 | C00B | C00C | 179.01(12) | C00I | C008 | C00D | C00M | -0.23(18) |
| N001 | C009 | C00G | C00P | -179.70(12) | C00J | C00F | C00W | C013 | -1.2(2) |
| N002 | C008 | C00D | C00M | 178.82(12) | C00J | C00F | C00Z | N002 | -22.7(2) |
| N002 | C008 | C00I | C00X | -179.35(13) | C00J | C016 | C018 | C013 | -0.4(3) |
| C003 | C006 | C00T | C00U | 0.3(2) | C00K | C004 | C00E | C012 | 0.4(2) |
| C003 | C007 | C00L | C00U | 1.1(2) | C00K | C004 | C00V | N001 | 153.13(13) |
| C004 | C00E | C012 | C014 | -0.7(3) | C00K | C011 | C014 | C012 | -0.4(3) |
| C004 | C00K | C011 | C014 | 0.1(2) | C00M | C00N | C00X | C00I | -0.2(2) |
| C005 | C00H | C010 | C017 | 0.3(3) | C00O | N001 | C009 | C00B | -13.39(18) |
| C005 | C00S | C015 | C017 | 0.5(3) | C00O | N001 | C009 | C00G | 165.96(12) |
| C006 | C003 | C007 | C00L | -1.8(2) | C00O | N001 | C00V | C004 | -74.78(16) |
| C006 | C003 | C00R | N002 | 33.65(18) | C00O | C005 | C00H | C010 | 179.31(14) |
| C006 | C00T | C00U | C00L | -1.1(2) | C00O | C005 | C00S | C015 | -179.77(14) |
| C007 | C003 | C006 | C00T | 1.1(2) | C00P | C00A | C00C | C00B | -0.09(19) |
| C007 | C003 | C00R | N002 | -148.35(13) | C00R | N002 | C008 | C00D | -9.68(18) |
| C007 | C00L | C00U | C00T | 0.4(2) | C00R | N002 | C008 | C00I | 169.33(12) |
| C008 | N002 | C00R | C003 | 84.64(16) | C00R | N002 | C00Z | C00F | -81.81(16) |
| C008 | N002 | C00Z | C00F | 90.16(17) | C00R | C003 | C006 | C00T | 179.14(13) |
| C008 | C00D | C00M | C00N | 0.6(2) | C00R | C003 | C007 | C00L | -179.86(13) |
| C008 | C00I | C00X | C00N | 0.5(2) | C00S | C005 | C00H | C010 | -1.7(2) |
| C009 | N001 | C00O | C005 | 79.79(16) | C00S | C005 | C00O | N001 | 22.6(2) |
| C009 | N001 | C00V | C004 | 90.73(16) | C00S | C015 | C017 | C010 | -1.9(3) |
| C009 | C00B | C00C | C00A | 0.6(2) | C00V | N001 | C009 | C00B | -178.38(12) |
| C009 | C00G | C00P | C00A | 0.8(2) | C00V | N001 | C009 | C00G | 0.98(19) |
| C00B | C009 | C00G | C00P | -0.32(19) | C00V | N001 | C00O | C005 | -114.19(14) |
| C00C | C00A | C00P | C00G | -0.6(2) | C00V | C004 | C00E | C012 | -179.83(14) |
| C00D | C008 | C00I | C00X | -0.3(2) | C00V | C004 | C00K | C011 | -179.91(14) |
| C00D | C00M | C00N | C00X | -0.3(2) | C00W | C00F | C00J | C016 | 1.1(2) |
| C00D | C00M | C00N | C019 | -179.46(14) | C00W | C00F | C00Z | N002 | 159.59(13) |
| C00E | C004 | C00K | C011 | -0.1(2) | C00W | C013 | C018 | C016 | 0.2(3) |
| C00E | C004 | C00V | N001 | -26.7(2) | C00Y | C00A | C00C | C00B | -178.28(13) |
| C00E | C012 | C014 | C011 | 0.7(3) | C00Y | C00A | C00P | C00G | 177.54(13) |
| C00F | C00J | C016 | C018 | -0.3(3) | C00Z | N002 | C008 | C00D | 178.74(12) |
| C00F | C00W | C013 | C018 | 0.6(3) | C00Z | N002 | C008 | C00I | -2.2(2) |
| C00G | C009 | C00B | C00C | -0.37(18) | C00Z | N002 | C00R | C003 | -103.29(14) |

| | | | |
|---|---|---|---|
| C00H C005 C00O N001 | -158.38(13) | C00Z C00F C00J C016 | -176.70(15) |
| C00H C005 C00S C015 | 1.2(2) | C00Z C00F C00W C013 | 176.63(15) |
| C00H C010 C017 C015 | 1.4(3) | C019 C00N C00X C00I | 178.92(15) |