

## Supplementary information

### Iodine-catalyzed isomerization of enamides

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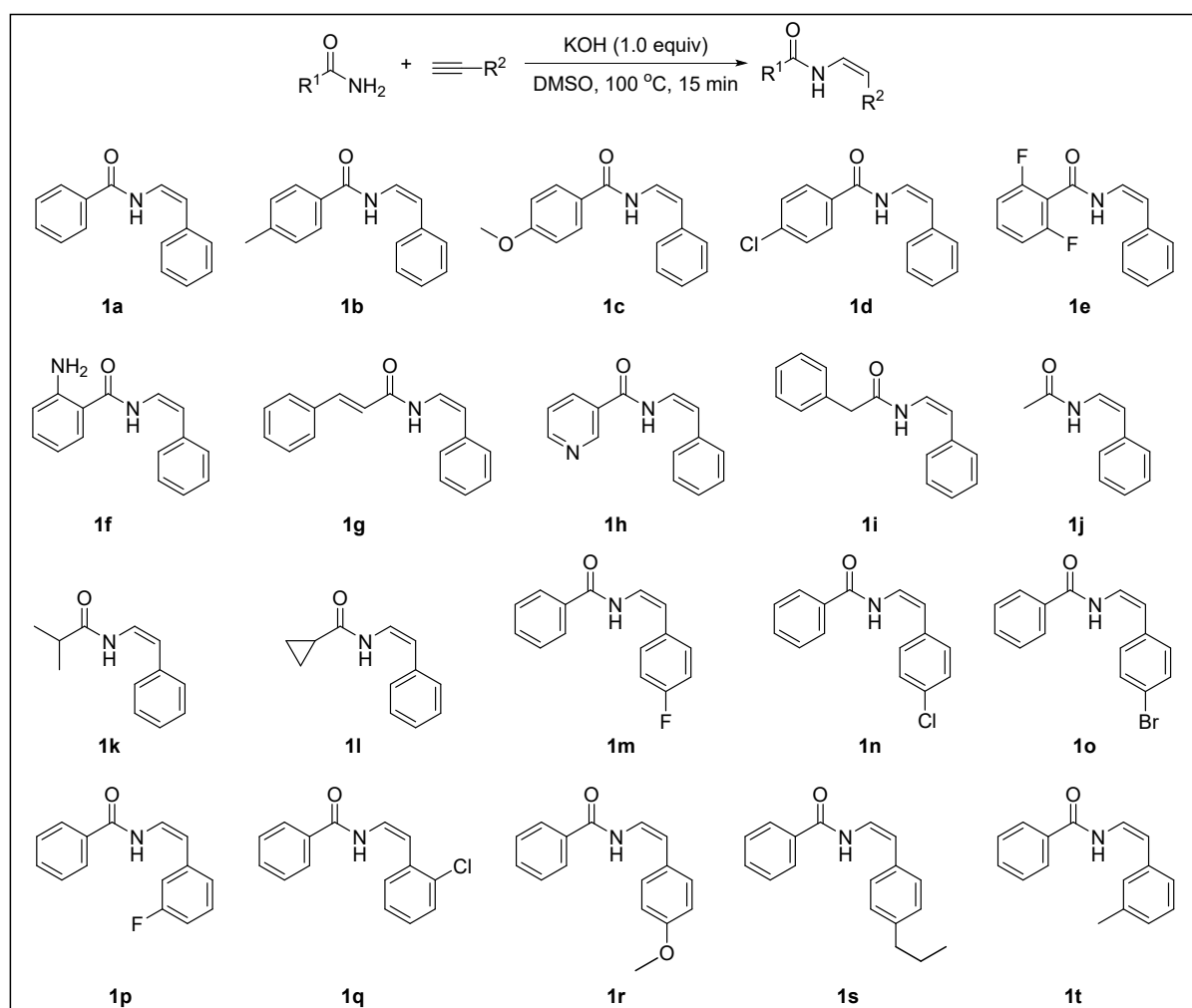
## 1. General Information

All the chemicals and solvents were purchased from commercial suppliers and used as received unless otherwise noted. The primary amides and alkynes were purchased from Aladdin (<https://www.aladdin-e.com/>). The amino acids (L-valine and L-phenylalanine) and drugs (fenofibric acid and ibuprofen) were purchased from Bide Pharmatech Ltd. (<https://www.bidepharm.com/>). Other substrates, catalysts, and ligands were obtained from Shanghai Yansu Technology Co., Ltd (Shanghai, China; [mall.shiyanjia.com](http://mall.shiyanjia.com)). All reactions were carried out in air without extra protection. Reactions were monitored by thin layer chromatography (TLC). Visualization was achieved under a UV lamp (254 nm and 365 nm). For column chromatography, silica gel (refined type, 200-300 mesh) was used as the stationary phase. Petroleum ether (PE) and ethyl acetate (EA) were used as the moving phase. Melting points were recorded on a Thermocouple digital melting point apparatus and were uncorrected.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were measured on a 300 MHz or 400 MHz Bruker AVANCE spectrometer, using  $\text{DMSO-}d_6$  or  $\text{CDCl}_3$  as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts were reported in ppm.  $^1\text{H}$  NMR spectra were referenced to  $\text{CDCl}_3$  (7.26 ppm) or  $\text{DMSO-}d_6$  (2.50 ppm), and  $^{13}\text{C}$  NMR spectra were referenced to  $\text{CDCl}_3$  (77.0 ppm) or  $\text{DMSO-}d_6$  (39.5 ppm). Peak multiplicities were designated by the following abbreviations: s = singlet; d = doublet; t = triplet; m = multiplet; q = quartet. All coupling constants ( $J$  values) were reported in Hertz (Hz). Analysis of crude reaction mixture was done on the Shimadzu GCMS QP-2000. and Thermo Scientific Q Exactive UHMR Hybrid Quadrupole Orbitrap mass spectrometer. High-resolution mass spectrometry (HRMS) was performed with a TOF MS instrument with an ESI source.

## 2. Synthesis and Analytical Data of Substrates 1

### 2.1 Synthesis of secondary *Z*-enamides 1a-1t

**Method A:**<sup>[1]</sup> A 25 mL round bottom flask was charged with primary amide (5 mmol), alkyne (5 mmol), KOH (5 mmol) and DMSO (10 mL). The mixture was stirred at 100 °C for 15 minutes. The progress of the reaction was monitored by TLC. After the reaction was complete, ice water was added to the reaction mixture and was extracted with EtOAc (20 mL × 3). The combined organic phase was washed with water, dried over anhydrous sodium sulfat, filtered and evaporated in vacuo. The crude product was purified by column chromatography (silica gel, petroleum ether: ethyl acetate = 9:1) to give the desired *Z*-enamides **1a-1t**.



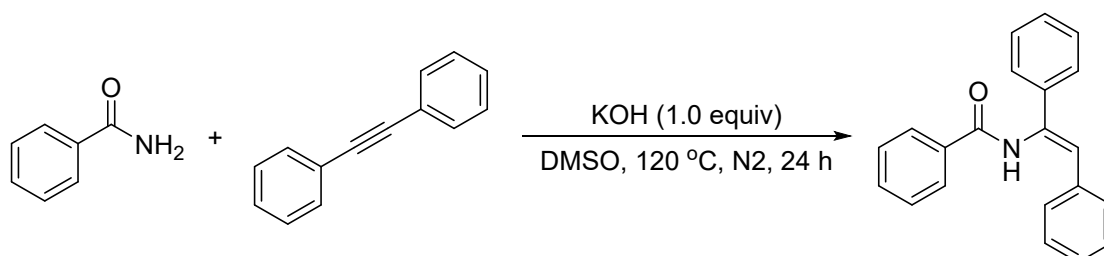
**Figure S1:** Substrates synthesized according to Method A.

**1a**,<sup>[1]</sup> **1b**,<sup>[2]</sup> **1c-1h**,<sup>[1]</sup> **1i-1j**,<sup>[2]</sup> **1k**,<sup>[3]</sup> **1l**,<sup>[4]</sup> **1m**,<sup>[1]</sup> **1n**,<sup>[3]</sup> **1o-1q**,<sup>[1]</sup> **1r**,<sup>[2]</sup> and **1s-1t**<sup>[1]</sup> are known compounds, their physical and spectral data are in well accordance with literature data.

## 2.2 Synthesis of (*Z*)-*N*-(1,2-diphenylvinyl)benzamide

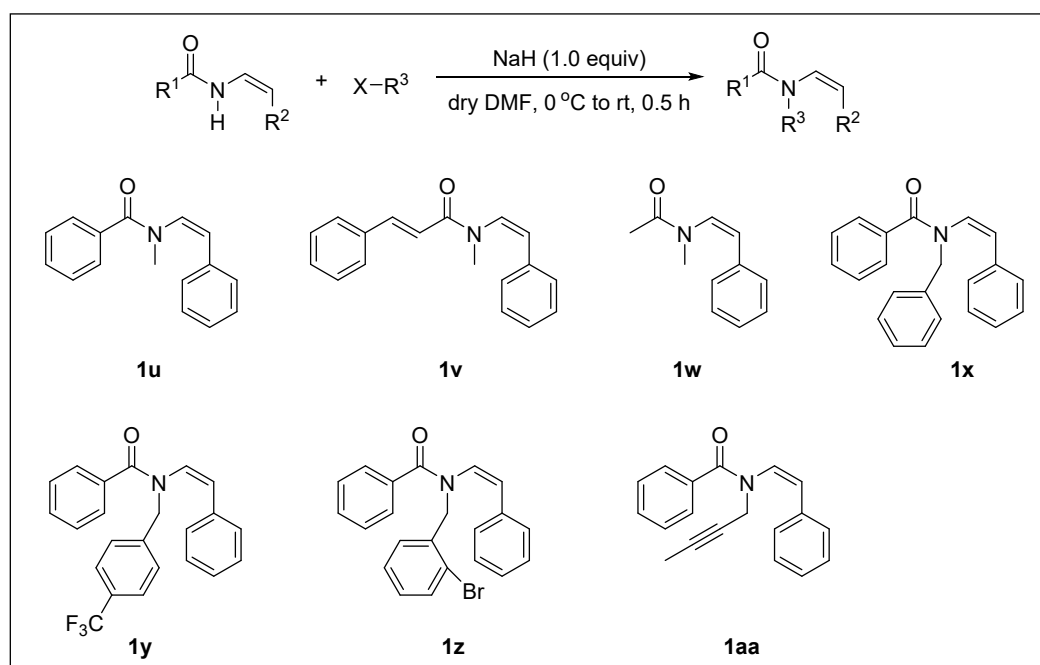
A 25 mL round bottom flask was charged with benzamide (5 mmol), 1,2-diphenylethyne (5 mmol), KOH (5 mmol) and DMSO (10 mL). The mixture was stirred at 120 °C for 24 hours under N<sub>2</sub> atmosphere. The progress of the reaction was monitored by TLC. After the reaction was complete, ice water was added to the reaction mixture and was extracted with EtOAc (20 mL × 3). The combined organic phase was washed with water, dried over anhydrous sodium sulfat, filtered and evaporated in vacuo. The crude product was purified by column chromatography (silica gel, petroleum ether: ethyl acetate = 9:1) to give the desired (*Z*)-*N*-(1,2-diphenylvinyl)benzamide in 60% yield.

(*Z*)-*N*-(1,2-diphenylvinyl)benzamide is a known compound, its spectroscopic data match those previously reported in the literature.<sup>[5]</sup>



## 2.3 Synthesis and analytical data of tertiary *Z*-enamides **1u-1aa**

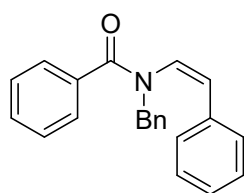
**Method B:**<sup>[1]</sup> To a well stirred solution of secondary *Z*-enamide (1 mmol) in dry *N,N*-dimethylformamide (3 mL) at 0 °C was added sodium hydride (1 mmol). After 15 minutes, alkyl halide (methyl iodide, benzyl bromide or 1-bromobut-2-yne, 1 mmol) was added to the reaction mixture. The reaction was continuously kept on stirring for further 30 minutes. After the reaction was complete as indicated by TLC, ice water was added to the reaction mixture and was extracted with EtOAc (10 mL × 3). The combined organic phase was washed with water, dried over anhydrous sodium sulfate, filtered and evaporated in vacuo. The crude product was purified by column chromatography (silica gel, petroleum ether: ethyl acetate = 20:1) to give the desired tertiary *Z*-enamides **1u-1aa**.



**Figure S2:** Substrates synthesized according to Method B.

**1u**,<sup>[2]</sup> **1v**,<sup>[1]</sup> and **1w**<sup>[2]</sup> are known compounds, their physical and spectral data are in well accordance with literature data.

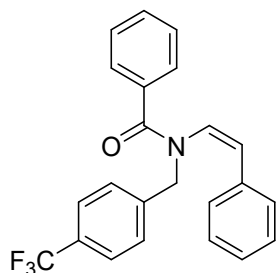
### (*Z*)-*N*-benzyl-*N*-styrylbenzamide (**1x**)



Compound **1x** (284.9 mg, 0.91 mmol, 91%) was prepared from **1a** (223.0 mg, 1.00 mmol) and benzyl bromide (1.0 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **1x** as a yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39-7.46 (m, 2H), 7.33-7.17 (m, 11H), 7.17-7.10 (m, 2H), 6.09 (d, *J* = 9.0 Hz, 1H), 5.86 (d, *J* = 9.0 Hz, 1H), 4.84 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.0, 137.3, 135.8,

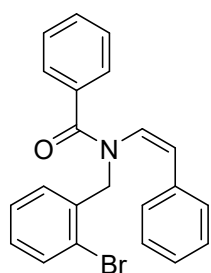
134.9, 130.4, 129.1, 128.7, 128.6, 128.5, 128.3, 127.9, 127.8, 127.6, 123.4, 49.8; GC-MS (EI, 70 eV)  $m/z$ :  $[M]^+$  Calcd for  $C_{22}H_{19}NO$  313; Found 313, 222, 105, 91, 77.

#### (Z)-N-styryl-N-(4-(trifluoromethyl)benzyl)benzamide (1y)



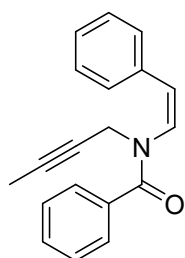
Compound **1y** (354.2 mg, 0.93 mmol, 93%) was prepared from **1a** (223.0 mg, 1.00 mmol) and *p*-trifluoromethylbenzyl bromide (1.0 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **1y** as a yellow oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.56-7.51 (m, 4H), 7.43-7.26 (m, 8H), 7.25-7.16 (m, 2H), 6.15 (d,  $J$  = 9 Hz, 1H), 5.94 (d,  $J$  = 8.9 Hz, 1H), 4.88 (s, 2H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  171.1, 135.3, 134.7, 130.8, 129.9, 129.5, 128.8, 128.7, 128.4, 128.3, 128.1, 128.0, 127.1, 125.5, 125.4, 125.4, 125.4, 125.3, 122.8, 122.7, 49.2;  $^{19}F$  NMR (377 MHz,  $CDCl_3$ )  $\delta$  -62.5; GC-MS (EI, 70 eV)  $m/z$ :  $[M]^+$  Calcd for  $C_{23}H_{18}F_3NO$  381; Found 381, 105, 77.

#### (Z)-N-(2-bromobenzyl)-N-styrylbenzamide(1z)



Compound **1z** (321.5 mg, 0.82 mmol, 82%) was prepared from **1a** (223.0 mg, 1.00 mmol) and *o*-bromobenzyl bromide (1.0 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **1z** as a yellow oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.52 (d,  $J$  = 8.1 Hz 1H), 7.47-7.41 (m, 2H), 7.36 (t,  $J$  = 7.4 Hz 1H), 7.32-7.22 (m, 7H), 7.20-7.09 (m, 3H), 6.20 (d,  $J$  = 7.0 Hz, 1H), 5.90 (d,  $J$  = 7.9 Hz, 1H), 4.98 (s, 2H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  168.9, 135.9, 135.6, 133.0, 130.4, 129.9, 129.9, 129.0, 128.8, 128.6, 128.4, 128.1, 127.9, 127.8, 127.4, 124.1, 124.0, 50.4; GC-MS (EI, 70 eV)  $m/z$ :  $[M]^+$  Calcd for  $C_{22}H_{18}BrNO$  391; Found 393, 391, 312, 105, 77.

#### (Z)-N-(but-2-yn-1-yl)-N-styrylbenzamide(1aa)



Compound **1aa** (244.8 mg, 0.89 mmol, 89%) was prepared from **1a** (223.0 mg, 1.00 mmol) and 1-bromobut-2-yne (1.0 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **1y** as a yellow oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.45 (d,  $J$  = 7.8 Hz, 2H), 7.38 (m, 1H), 7.34-7.23 (m, 7H), 6.31 (d,  $J$  = 8.5 Hz, 1H), 6.04 (d,  $J$  = 7.8 Hz, 1H), 4.36 (s, 2H), 1.83 (t,  $J$  = 2.4 Hz, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  170.6, 135.1, 134.6, 130.4, 128.7, 128.6, 128.36, 128.32, 127.8, 127.7, 123.8, 79.6, 74.0, 36.8, 3.6; GC-MS (EI, 70 eV)  $m/z$ :  $[M]^+$  Calcd for  $C_{19}H_{17}NO$  275; Found 275, 170, 105, 77.

## 2.4 Synthesis of biorelevant substrates 1ab-1ae

### Method C:<sup>[3]</sup>

Step 1: A dried 50 mL round bottom flask was charged with the carboxylic acid (10 mmol, 1.0 equiv.) and 1,1'-carbonyldiimidazole (CDI) (10 mmol, 1.0 equiv.). Subsequently, EtOAc (20 mL) were added. The resulting mixture was stirred for 2 h at room temperature, then, ammonia water (8.0 mL) was added slowly under vigorous stirring. The mixture was stirred for 2 h at 45 °C. The resulting mixture was extracted with EtOAc (20 mL × 3). The combined organic layers were washed with water and brine, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the volatiles were removed under vacuo. The residue was used for step 2 without further purification.

Step2: A 100 mL schlenk flask was charged with amide (1.2 equiv.), copper(I) iodide (0.5 equiv.), and Cs<sub>2</sub>CO<sub>3</sub> (2.0 equiv.). The flask was backfilled with argon, and closed with a rubber bung. Styryl bromide (1.0 equiv.) and *N,N*- dimethylethylenediamine (1.0 equiv.) in dry and degassed THF (25 mL) were next added. The mixture was stirred at 65 °C overnight. The reaction mixture was cooled to room temperature, filtered, the solution layer was extracted with EtOAc and concentrated under vacuo. The crude residue was purified by flash chromatography on silica gel to give the desired enamides **1ab-1ae**. Physical and spectral data are in accordance with literature data.<sup>[3]</sup>

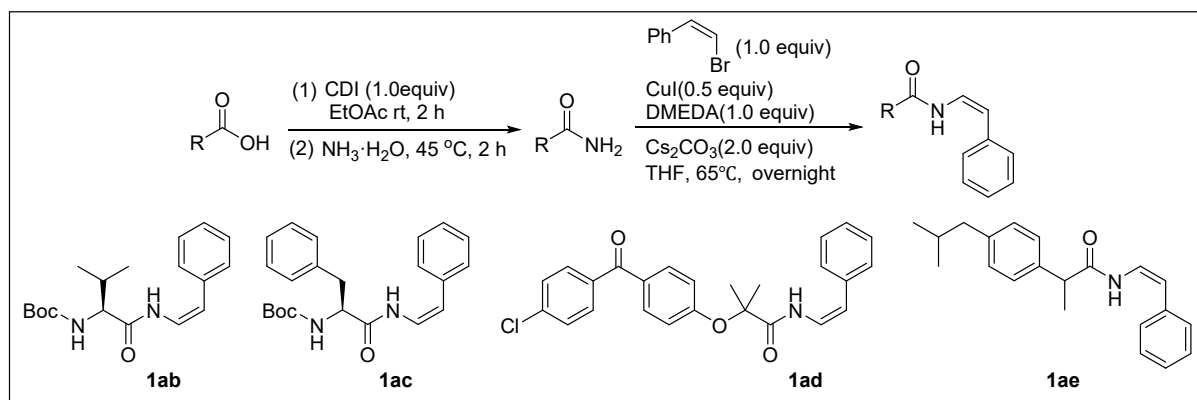
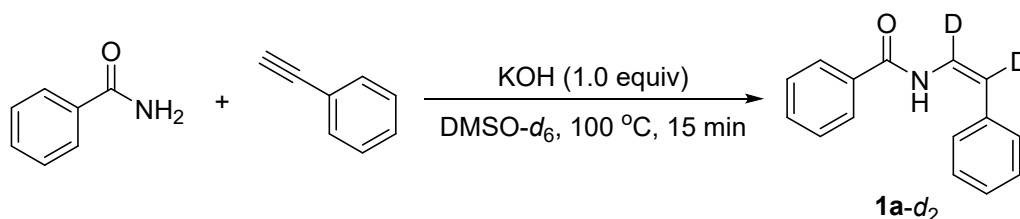


Figure S3: Substrates synthesized according to Method C.

## 2.5 Synthesis of dideuterated *Z*-enamide **1a-d<sub>2</sub>**

A 25 mL round bottom flask was charged with benzamide (1 mmol), ethynylbenzene (1 mmol), KOH (1 mmol) and deuterated DMSO-*d*<sub>6</sub> (2 mL). The mixture was stirred at 100 °C for 15 minutes. The progress of the reaction was monitored by TLC. After the reaction was complete, ice water was added to the reaction mixture and was extracted with EtOAc (10 mL × 3). The combined organic phase was washed with water, dried over anhydrous sodium sulfat, filtered and evaporated in vacuo. The crude product was purified by column chromatography (silica gel, petroleum ether: ethyl acetate = 9:1) to give the desired dideuterated *Z*-enamide **1a-d<sub>2</sub>**.



**1a-d<sub>2</sub>** is a known compound<sup>[1]</sup>, its analytical data is in well accordance with literature data.

## 3. General procedure for the *Z*-to-*E* isomerization of enamides

To a stirred solution of **1** (1.0 mmol) in ethyl acetate (3 mL) was added I<sub>2</sub> (10 mol%). The resulting mixture was stirred for 10 min at rt. After completion of the reaction as indicated by thin layer chromatography (TLC), the reaction mixture was quenched with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.1 M, 5 mL) and extracted with EtOAc (10 mL × 3). The combined organic phase was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated *in vacuo*. The resulting crude product was purified by column chromatography on silica gel (200–300 mesh) using ethyl acetate/petroleum ether as eluent to afford the pure *E*-enamide **2**.

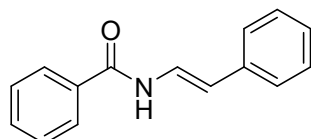
## 4. Gram-Scale Synthesis Product **2a**

To a stirred solution of **1a** (10 mmol) in ethyl acetate (20 mL) was added I<sub>2</sub> (10 mol%). The resulting mixture was stirred for 10 min at rt. After completion of the reaction as indicated by thin layer chromatography (TLC), the reaction mixture was quenched with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.1 M, 20 mL) and extracted with EtOAc (20 mL × 3). The combined organic phase was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated in vacuo. The resulting crude product was purified by column chromatography on silica gel (200–300 mesh) using ethyl acetate/petroleum ether as eluent to afford the pure *E*-enamide **2a** (97%, 2.15g).

## 5. Analytical Data of Products 2

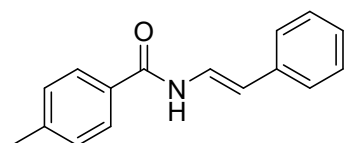
**2a-2b**,<sup>[3]</sup> **2c**,<sup>[6]</sup> **2d**,<sup>[3]</sup> **2e**,<sup>[7]</sup> **2g**,<sup>[3]</sup> **2h**,<sup>[8]</sup> **2i**,<sup>[7]</sup> **2j**,<sup>[9]</sup> **2k**,<sup>[3]</sup> **2l**,<sup>[4]</sup> **2m-2r**,<sup>[3]</sup> **2t**,<sup>[4]</sup> **2u**,<sup>[6]</sup> **2v**,<sup>[10]</sup> **2w**,<sup>[11]</sup> **2x**,<sup>[12]</sup> and **2ab-2ae**<sup>[3]</sup> are known compounds, their physical and spectral data are in well accordance with literature data.

### (*E*)-*N*-styrylbenzamide (**2a**)



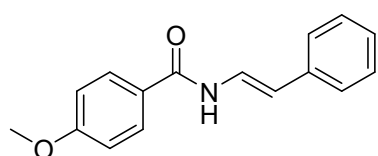
Compound **2a** (218.7 mg, 0.98 mmol, 98%) was prepared from **1a** (223.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2a** as a white solid, mp 179 – 180 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.65 (d, *J* = 9.9 Hz, 1H), 7.97 (d, *J* = 6.7 Hz, 2H), 7.74-7.47 (m, 4H), 7.40 (d, *J* = 7.0 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 14.8 Hz, 1H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 164.5, 137.0, 133.8, 132.3, 129.1, 128.9, 128.1, 126.7, 125.7, 124.6, 113.4; GC-MS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>15</sub>H<sub>13</sub>NO: 223, found: 223, 105, 77.

### (*E*)-4-methyl-*N*-styrylbenzamide (**2b**)



Compound **2b** (228.7 mg, 0.96 mmol, 96%) was prepared from **1b** (237.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2b** as a white solid, mp 198 – 199 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.57 (d, *J* = 9.9 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.65 (dd, *J*<sub>1</sub> = 14.7 Hz, *J*<sub>2</sub> = 9.9 Hz, 1H), 7.45-7.26 (m, 6H), 7.23-7.12 (m, 1H), 6.45 (d, *J* = 14.7 Hz, 1H), 2.38 (s, 3H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 164.3, 142.4, 137.1, 130.9, 129.4, 129.1, 128.1, 126.6, 125.6, 124.6, 113.0, 21.4; GC-MS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>16</sub>H<sub>15</sub>NO: 237, found: 237, 119, 91, 65.

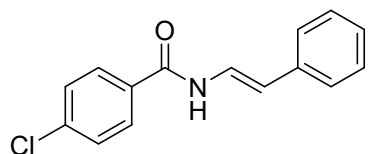
### (*E*)-4-methoxy-*N*-styrylbenzamide (**2c**)



Compound **2c** (240.5 mg, 0.95 mmol, 95%) was prepared from **1c** (253.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2c** as a white solid, mp 194 – 195 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.51 (d, *J* = 9.9 Hz, 1H), 8.02-7.91 (m, 2H), 7.65 (dd, *J*<sub>1</sub> = 14.7 Hz, *J*<sub>2</sub> = 4.8 Hz, 1H), 7.45-7.25 (m, 4H), 7.21-7.12 (m, 1H), 7.10-7.03 (m, 2H), 6.43 (d, *J*<sub>1</sub> = 14.8 Hz, 1H), 3.84 (s, 3H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 163.9, 162.5, 137.1, 130.0, 129.1, 126.5, 125.8,

125.6, 124.8, 114.1, 112.7, 55.8; GC-MS (EI, 70 eV)  $m/z$ :  $[M]^+$  calcd for  $C_{16}H_{15}NO_2$ : 253, found: 253, 135, 107, 77.

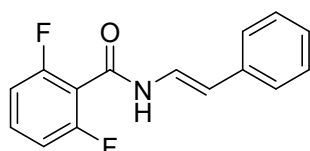
#### (E)-4-chloro-N-styrylbenzamide (2d)



Compound **2d** (249.6 mg, 0.97 mmol, 97%) was prepared from **1d** (257.0 mg, 1.00 mmol) following the general procedure.

Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2d** as a white solid, mp 222 – 223 °C;  $^1H$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.73 (d,  $J$  = 9.9 Hz, 1H), 8.01 (d,  $J$  = 9.5 Hz, 2H), 7.70-7.57 (m, 3H), 7.41 (d,  $J$  = 7.2 Hz, 2H), 7.32 (t,  $J$  = 7.4 Hz, 2H), 7.23-7.12 (m, 1H), 6.47 (d,  $J$  = 14.7 Hz, 1H);  $^{13}C$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  163.1, 136.9, 136.6, 132.1, 129.6, 128.8, 128.7, 126.4, 125.4, 124.1, 113.4; GC-MS (EI, 70 eV)  $m/z$ :  $[M]^+$  calcd for  $C_{15}H_{12}ClNO$ : 257, found: 257, 141, 139, 113, 111.

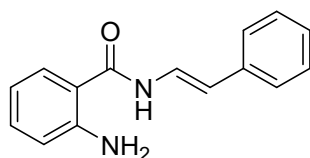
#### (E)-2,6-difluoro-N-styrylbenzamide (2e)



Compound **2e** (238.3 mg, 0.92 mmol, 92%) was prepared from **1e** (259.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc =

20:1) afforded **2e** as a white solid, mp 167 - 169 °C;  $^1H$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.97 (d,  $J$  = 10.4 Hz, 1H), 7.65-7.54 (m, 1H), 7.54-7.44 (m, 1H), 7.43-7.35 (m, 2H), 7.34-7.11 (m, 5H), 6.28 (d,  $J$  = 14.7 Hz, 1H);  $^{13}C$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  161.10, 161.00, 157.85, 157.80, 157.70, 136.40, 132.95, 132.82, 132.69, 129.17, 127.10, 125.97, 123.21, 115.17, 114.88, 114.51, 113.97, 112.71, 112.64, 112.48, 112.41; GC-MS (EI, 70 eV)  $m/z$ :  $[M]^+$  calcd for  $C_{15}H_{11}F_2NO$ : 259, found: 259, 141, 113.

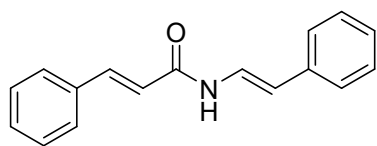
#### (E)-2-amino-N-styrylbenzamide (2f)



Compound **2f** (182.5 mg, 0.80 mmol, 80%) was prepared from **1f** (228.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc =

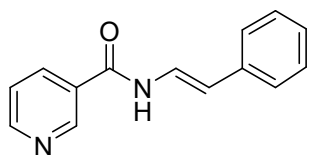
20:1) afforded **2f** as a white solid, mp 209 - 210 °C;  $^1H$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.37 (d,  $J$  = 9.8 Hz, 1H), 7.71-7.54 (m, 2H), 7.42-7.33 (m, 2H), 7.32-7.25 (m, 2H), 7.24-7.11 (m, 2H), 6.74 (d,  $J$  = 8.3 Hz, 1H), 6.65-6.50 (m, 3H), 6.40 (d,  $J$  = 14.8 Hz, 1H);  $^{13}C$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  166.5, 150.6, 137.0, 132.7, 128.8, 128.5, 126.2, 125.2, 124.3, 116.7, 114.7, 113.1, 112.1; GC-MS (EI, 70 eV)  $m/z$ :  $[M]^+$  calcd for  $C_{15}H_{14}N_2O$ : 238, found: 238, 120, 92, 65.

### ***N*-((*E*-styryl)cinnamamide (2g)**



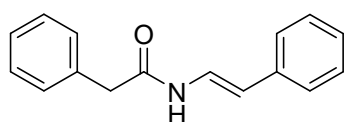
Compound **2g** (239.1 mg, 0.96 mmol, 96%) was prepared from **1g** (249.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2g** as a yellow solid, mp 226 - 228 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.50 (d, *J* = 10.3 Hz, 1H), 7.72-7.51 (m, 4H), 7.50-7.35 (m, 5H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 15.8 Hz, 1H), 6.25 (d, *J* = 14.7 Hz, 1H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 163.0, 141.0, 136.9, 135.0, 130.3, 129.8, 129.1, 128.2, 126.6, 125.6, 124.1, 121.3, 112.6; GC-MS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>17</sub>H<sub>15</sub>NO: 249, found: 249, 131, 119, 103, 77.

### **(*E*)-*N*-styrylnicotinamide (2h)**



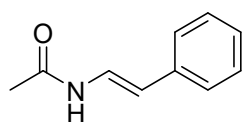
Compound **2h** (210.7 mg, 0.94 mmol, 94%) was prepared from **1h** (224.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2h** as a white solid, mp 146 - 147 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.65 (d, *J* = 9.8 Hz, 1H), 9.12 (d, *J* = 9.5 Hz, 1H), 8.77 (dd, *J*<sub>1</sub> = 4.8 Hz, *J*<sub>2</sub> = 1.7 Hz, 1H), 8.30 (dt, *J*<sub>1</sub> = 8.1 Hz, *J*<sub>2</sub> = 2.1 Hz, 1H), 7.52-7.72 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 8.3 Hz, 2H), 7.19 (m, 1H), 6.48 (d, *J* = 14.7 Hz, 1H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 162.8, 151.7, 148.4, 136.4, 134.5, 129.1, 128.4, 126.5, 123.8, 122.4, 113.7; GC-MS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O: 224, found: 224, 106, 78.

### **(*E*)-2-phenyl-*N*-styrylacetamide (2i)**



Compound **2i** (215.6 mg, 0.91 mmol, 91%) was prepared from **1i** (237.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2i** as a white solid, mp 163 - 165 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.37 (d, *J* = 10.6 Hz, 1H), 7.45-7.19 (m, 10H), 7.16-7.05 (m, 1H), 6.17 (d, *J* = 14.7 Hz, 1H); 3.54 (s, 2H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 168.7, 136.9, 135.6, 129.5, 129.1, 128.7, 127.0, 126.5, 125.6, 124.0, 112.1, 42.7; GC-MS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>16</sub>H<sub>15</sub>NO: 237, found: 237, 119, 91, 65.

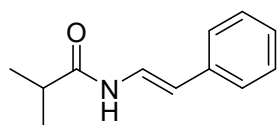
### **(*E*)-*N*-styrylacetamide (2j)**



Compound **2j** (148.8 mg, 0.92 mmol, 92%) was prepared from **1j** (161.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2j**

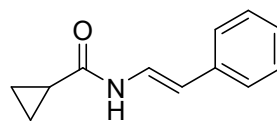
as a white solid, mp 119 – 120 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.17 (d, *J* = 10.0 Hz, 1H), 7.40 (dd, *J*<sub>1</sub> = 14.7 Hz, *J*<sub>2</sub> = 10.2 Hz, 1H), 7.35-7.23(m, 4H), 7.17-7.10 (m, 1H), 6.11 (d, *J* = 14.8 Hz, 1H), 1.97 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 168.3, 135.9, 128.4, 126.4, 125.3, 122.5, 113.0, 22.5; GC-MS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>10</sub>H<sub>11</sub>NO: 161, found: 161, 119, 91.

**(*E*)-*N*-styrylisobutyramide (2k)**



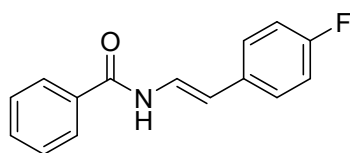
Compound **2k** (178.3 mg, 0.94 mmol, 94%) was prepared from **1k** (189.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2k** as a white solid, mp 189 – 190 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.07 (d, *J* = 10.0 Hz, 1H), 7.395 (dd, *J*<sub>1</sub> = 14.7 Hz, *J*<sub>2</sub> = 10.2 Hz, 1H), 7.36-7.30 (m, 2H), 7.30-7.23 (m, 2H), 7.18-7.09 (m, 1H), 6.15 (d, *J* = 14.7 Hz, 1H), 2.50-2.36 (m, 1H), 1.07 (d, *J* = 6.81 Hz, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 174.9, 136.1, 128.5, 126.3, 125.3, 122.8, 112.7, 35.4, 19.3; GC-MS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>12</sub>H<sub>15</sub>NO: 189, found: 189, 119, 91, 71.

**(*E*)-*N*-styrylcyclopropanecarboxamide (2l)**



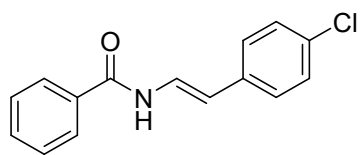
Compound **2l** (173.9 mg, 0.93 mmol, 93%) was prepared from **1l** (187.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2l** as a white solid, mp 149 – 150 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.40 (d, *J* = 10.1 Hz, 1H), 7.45-7.20 (m, 5H), 7.17-7.09 (m, 1H), 6.10 (d, *J* = 14.7 Hz, 1H), 1.71-1.53 (m, 1H), 0.77 (d, *J* = 2.6 Hz, 4H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 172.0, 136.3, 128.6, 126.5, 125.4, 122.9, 112.3, 14.8, 8.2; GC-MS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>12</sub>H<sub>13</sub>NO: 187, found: 187, 119, 91, 69.

**(*E*)-*N*-(4-fluorostyryl)benzamide (2m)**



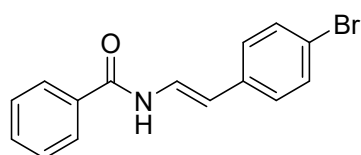
Compound **2m** (224.9 mg, 0.93 mmol, 93%) was prepared from **1m** (241.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2m** as a white solid, mp 187 – 188 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.65 (d, *J* = 9.9 Hz, 1H), 8.01-7.93 (m, 2H), 7.66-7.40 (m, 6H), 7.19-7.09 (m, 2H), 6.45 (d, *J* = 14.7 Hz, 1H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 164.5, 162.9, 159.6 (*J*<sub>1</sub> = 241.8 Hz) 133.7, 133.5, 133.5 (*J*<sub>3</sub> = 3.2 Hz) 132.3, 128.9, 128.0, 127.4, 127.3, 124.6, 124.5 (*J*<sub>4</sub> = 2.2 Hz) 116.0, 115.8 (*J*<sub>2</sub> = 21.2 Hz), 112.3; GC-MS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>15</sub>H<sub>12</sub>FNO: 241, found: 241, 105, 77.

**(E)-N-(4-chlorostyryl)benzamide (2n)**



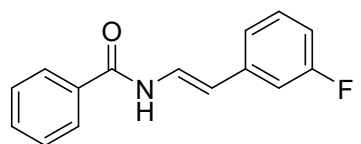
Compound **2n** (246.1 mg, 0.96 mmol, 96%) was prepared from **1n** (257.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2n** as a white solid, mp 216 – 217 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.70 (d, *J* = 9.8 Hz, 1H), 7.97 (d, *J* = 6.9 Hz, 2H), 7.73-7.49 (m, 4H), 7.48-7.31 (m, 4H), 6.45 (d, *J* = 14.8 Hz, 1H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 164.5, 136.0, 133.7, 132.3, 130.8, 129.0, 128.9, 128.1, 127.3, 125.4, 112.0; GC-MS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>15</sub>H<sub>12</sub>ClNO: 257, found: 257, 105, 77.

**(E)-N-(4-bromostyryl)benzamide (2o)**



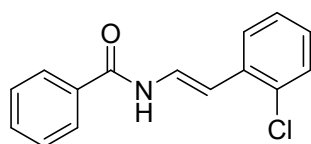
Compound **2o** (284.5 mg, 0.94 mmol, 94%) was prepared from **1o** (302.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2o** as a white solid, mp 224 – 225 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.71 (d, *J* = 10.0 Hz, 1H), 8.02-7.92 (m, 2H) 7.70 (dd, *J*<sub>1</sub>=14.7 Hz, *J*<sub>2</sub>=9.9 Hz, 1H) 7.64-7.57 (m, 1H), 7.57-7.50 (m, 2H), 7.50-7.45 (m, 2H), 7.41-7.34 (m, 2H), 6.43 (d, *J* = 14.7 Hz, 1H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 164.5, 136.4, 133.6, 132.4, 131.9, 128.9, 128.1, 127.6, 125.5, 119.2, 112.0; GC-MS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>15</sub>H<sub>12</sub>BrNO: 303, found: 303, 301, 105, 77.

**(E)-N-(3-fluorostyryl)benzamide (2p)**



Compound **2p** (229.2 mg, 0.95 mmol, 95%) was prepared from **1p** (241.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2p** as a white solid, mp 209 – 210 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.73(d, *J* = 9.9 Hz, 1H), 8.04-7.93(m, 2H), 7.72 (dd, *J*<sub>1</sub>=14.7 Hz, *J*<sub>2</sub>=9.9 Hz, 1H), 7.65-7.50 (m, 3H), 7.39-7.20 (m, 3H), 6.99 (td, *J*<sub>1</sub>=8.2 Hz, *J*<sub>2</sub>=1.8 Hz, 1H), 6.46 (d, *J* = 14.7 Hz, 1H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 164.4, 164.3, 161.2 (*J*<sub>1</sub> = 241.8Hz), 139.6, 139.5(*J*<sub>3</sub> = 8.0Hz), 133.3, 132.1, 130.6, 130.5(*J*<sub>3</sub> = 8.6Hz), 128.6, 127.8, 125.7, 121.5, 121.5(*J*<sub>4</sub> = 2.6Hz), 113.0, 112.7(*J*<sub>2</sub> = 21.2Hz), 111.9, 111.9, (*J*<sub>4</sub> = 2.8Hz)111.9, 111.6(*J*<sub>2</sub> = 23.6Hz); GC-MS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>15</sub>H<sub>12</sub>FNO:241, found:241, 105, 77.

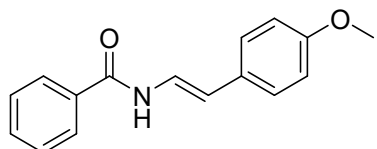
**(E)-N-(2-chlorostyryl)benzamide (2q)**



Compound **2q** (232.4 mg, 0.90 mmol, 90%) was prepared from **1q** (257.0 mg, 1.00 mmol) following the general procedure. Purification

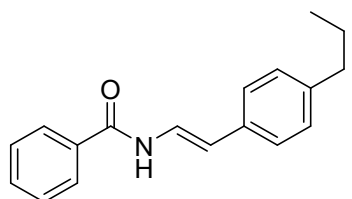
by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2q** as a white solid, mp 152 – 153 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.81 (d, *J* = 10.0Hz, 1H), 8.03-7.91(m, 2H), 7.77-7.63(m, 2H), 7.62-7.46(m, 3H), 7.44-7.36(m, 1H), 7.28 (t, *J* = 7.7Hz, 1H), 7.18 (t, *J* = 7.7Hz, 1H), 6.80 (d, *J* = 14.6Hz, 1H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 164.3, 134.6, 133.2, 132.2, 131.2, 129.7, 128.6, 127.8, 127.7, 127.6, 126.7, 125.6, 108.6; GC-MS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>15</sub>H<sub>12</sub>ClNO: 257, found: 257, 222, 105, 77.

**(*E*)-*N*-(4-methoxystyryl)benzamide (2r)**



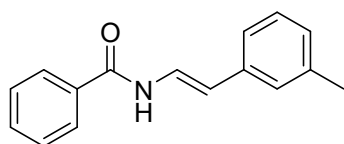
Compound **2r** (240.3 mg, 0.95 mmol, 95%) was prepared from **1r** (253.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2r** as a white solid, mp 190 – 191 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.52 (d, *J* = 9.7 Hz, 1H), 7.94 (d, *J* = 8.9 Hz, 2H), 7.66-7.45 (m, 4H), 7.30 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.40 (d, *J* = 14.7Hz, 1H), 3.71 (s, 3H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 164.2, 158.4, 133.9, 132.2, 129.4, 128.8, 128.0, 126.8, 122.7, 114.6, 113.2, 55.4; GC-MS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub>: 253, found: 253, 150, 105, 77.

**(*E*)-*N*-(4-propylstyryl)benzamide (2s)**



Compound **2s** (246.9 mg, 0.93 mmol, 93%) was prepared from **1s** (265.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2s** as a white solid, mp 188 – 189 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.61 (d, *J* = 9.8 Hz, 1H), 8.02-7.92 (m, 2H), 7.67-7.49 (m, 4H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.13(d, *J* = 8.3 Hz, 2H), 6.43 (d, *J* = 14.3 Hz, 1H), 2.60-2.52 (m, 2H), 1.65-1.47(m, 2H), 0.89 (t, 3H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 164.3, 140.2, 134.4, 133.8, 132.2, 129.1, 128.9, 128.0, 125.6, 123.8, 113.4, 37.3, 24.5, 14.0; GC-MS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>18</sub>H<sub>19</sub>NO: 265, found: 265, 105, 77.

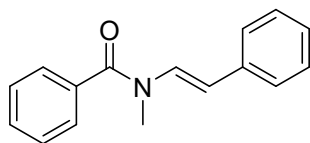
**(*E*)-*N*-(3-methylstyryl)benzamide (2t)**



Compound **2t** (225.2 mg, 0.95 mmol, 95%) was prepared from **1t** (237.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2t** as a white solid, mp 191 – 192 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.64 (d, *J* = 9.8 Hz, 1H), 8.00-7.94 (m, 2H), 7.70-7.48 (m, 4H), 7.26-7.13 (m, 3H), 7.03-6.95 (m, 1H), 6.42(d, *J* = 14.8 Hz, 1H), 2.30 (s, 3H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>)

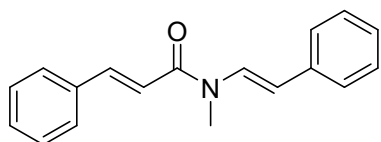
$\delta$  164.5, 138.2, 136.9, 133.8, 132.3, 129.0, 128.9, 128.1, 127.4, 126.2, 124.4, 122.9, 113.4, 21.4; GC-MS (EI, 70 eV)  $m/z$ :  $[M]^+$  calcd for  $C_{16}H_{15}NO$ : 237, found: 237, 105, 77.

#### (*E*)-*N*-methyl-*N*-styrylbenzamide (**2u**)



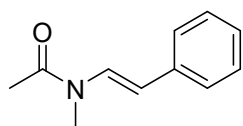
Compound **2u** (233.9 mg, 0.99 mmol, 99%) was prepared from **1u** (237.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2u** as a white solid, mp 109 – 110 °C;  $^1H$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.71-7.36 (m, 6H), 7.35-7.02(m, 5H), 6.20(d,  $J$  = 14.6 Hz, 1H), 3.26(s, 3H);  $^{13}C$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  169.9, 137.0, 135.6, 130.8, 129.2, 129.0, 128.1, 126.7, 125.7, 111.0, 31.0; GC-MS (EI, 70 eV)  $m/z$ :  $[M]^+$  calcd for  $C_{16}H_{15}NO$ : 237, found: 237, 105, 77.

#### *N*-methyl-*N*-((*E*)-styryl)cinnamamide (**2v**)



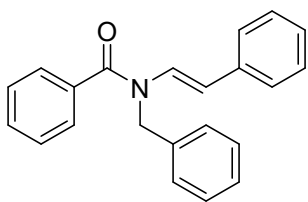
Compound **2v** (258.0 mg, 0.98 mmol, 98%) was prepared from **1v** (263.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2v** as a white solid, mp 117 – 118 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ) rotameric mixture :  $\delta$  8.23 and 7.59-7.45 (d,  $J$ =15.1Hz and m, 3H, rotamer), 7.73 (d,  $J$  = 15.1Hz, 1H), 7.42-7.25 (m, 7H), 7.20-7.10 (m, 1H), 7.06-6.86 (m, 1H), 5.98(d,  $J$  = 14.5Hz, 1H), 3.26(s, 1H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ) rotameric mixture resonances for rotamer in parenthesis:  $\delta$  165.9(165.2), 144.3(144.1), 136.8 (136.6), 135.0, 130.1, 128.9, 128.8, 128.5, 128.1, 126.6, 125.7, 117.1, 112.3 (111.7), 32.6 (30.8); GC-MS (EI, 70 eV)  $m/z$ :  $[M]^+$  calcd for  $C_{18}H_{17}NO$ : 263, found: 263, 131, 103,77.

#### (*E*)-*N*-methyl-*N*-styrylacetamide (**2w**)



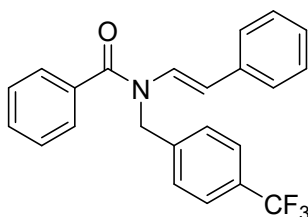
Compound **2w** (168.4 mg, 0.96 mmol, 96%) was prepared from **1w** (175.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2w** as a white solid, mp 79 – 80 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ) rotameric mixture:  $\delta$  8.09 and 7.35 (d,  $J_1$  = 15.0 Hz and d,  $J_2$  = 9.5 Hz, 1H, rotamer), 7.33 - 7.21 (m, 4H), 7.21 - 7.09 (m, 1H),  $\delta$  5.94 and 5.80 (d,  $J_1$  = 14.1 Hz and d,  $J_2$  = 14.9 Hz, 1H, rotamer),, 3.18 and 3.17 (2 s, 3H, rotamer), 2.28 and 2.22 (2 s, 3H, rotamer);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ) rotameric mixture, resonances for minor rotamer in parenthesis:  $\delta$  169.4 (169.2), 136.6 (136.8), 128.8 (129.0), 128.6 (127.1), 126.5 (126.4), 125.4 (125.7), 111.1 (110.8), 29.49 (33.0), 22.0 (22.7); GC-MS (EI, 70 eV)  $m/z$ :  $[M]^+$  calcd for  $C_{11}H_{13}NO$ :175, found:175, 133, 117, 104, 91,77.

#### (*E*)-*N*-benzyl-*N*-styrylbenzamide (**2x**)



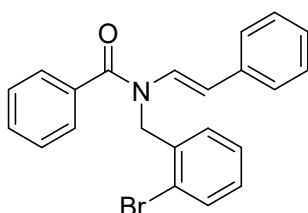
Compound **2x** (298.1 mg, 0.95 mmol, 95%) was prepared from **1x** (313.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2x** as a white solid, mp 153 – 154 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.66 (s, 2H), 7.59-7.29 (m, 9H), 7.29-7.00 (m, 5H) 5.86 (d, *J* = 14.7 Hz, 1H), 5.22 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.9, 136.7, 136.3, 135.1, 130.8, 129.6, 128.8, 128.7, 128.6, 128.3, 127.3, 126.7, 126.6, 125.5, 111.8, 47.4; GC-MS (EI, 70 eV) *m/z*: [M]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>19</sub>NO: 313; Found: 313, 222, 105, 91, 77.

**(E)-N-styryl-N-(4-(trifluoromethyl)phenyl)benzamide (2y)**



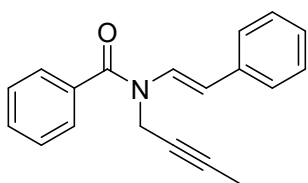
Compound **2x** (358.2 mg, 0.94 mmol, 94%) was prepared from **1x** (381.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2x** as a white solid, mp 156 – 157 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63 (d, *J* = 8.3 Hz, 3H), 7.60-7.26 (m, 7H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.16-6.95 (m, 3H), 5.91 (d, *J* = 14.5 Hz, 1H), 5.21 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.8, 140.8, 135.9, 134.6, 131.0, 129.8, 129.5, 129.2, 128.7, 128.3, 127.0, 126.7, 125.9, 125.8, 125.8, 125.7, 125.5, 125.4, 122.7, 111.9, 47.1; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -62.4; HRMS (ESI) calcd for C<sub>23</sub>H<sub>18</sub>F<sub>3</sub>NONa [M+Na]<sup>+</sup>: 404.1233, found: 404.1232.

**(E)-N-(2-bromophenyl)-N-styrylbenzamide (2z)**



Compound **2z** (377.8 mg, 0.96 mmol, 96%) was prepared from **1z** (392.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2z** as a white solid, mp 161 – 162 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75-7.40 (m, 6H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24-6.94 (m, 7H), 5.83 (d, *J* = 14.5 Hz, 1H), 5.21 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.7, 136.1, 135.0, 134.8, 132.9, 130.8, 128.7, 128.6, 128.6, 128.3, 127.8, 127.1, 126.6, 125.5, 112.0, 47.6; HRMS (ESI) calcd for C<sub>22</sub>H<sub>18</sub>BrNONa [M+Na]<sup>+</sup>: 414.0464, found: 414.0466.

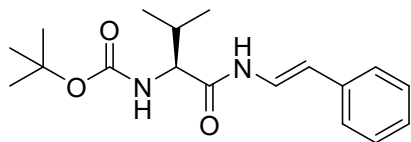
**(E)-N-(but-2-yn-1-yl)-N-styrylbenzamide (2aa)**



Compound **2aa** (253.8 mg, 0.92 mmol, 92%) was prepared from **1aa** (275.0 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2aa** as a white solid, mp 161 – 162 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59 (d, *J* = 7.7 Hz, 2H), 7.53-7.43 (m, 3H), 7.42-7.05 (m, 6H), 6.25 (d, *J* = 14.4

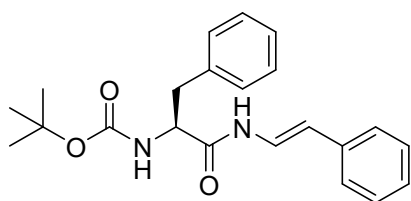
Hz, 1H), 4.63 (s, 2H), 1.85 (t,  $J=2.5$ Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.8, 136.5, 134.7, 130.8, 128.6, 128.5, 128.2, 126.6, 125.6, 112.6, 73.5, 33.3, 3.7; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{18}\text{NO}$   $[\text{M}+\text{H}]^+$ :276.1383, found: 276.1389.

***tert*-Butyl (*S*, *E*)-(3-methyl-1-oxo-1-(styrylamino)butan-2-yl)carbamate (**2ab**)**



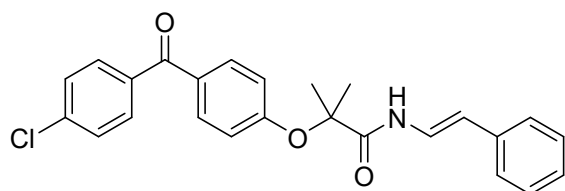
Compound **2ab** (274.7 mg, 0.86 mmol, 86%) was prepared from **1ab** (318 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2ab** as a white solid, mp 153 – 154°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.05 (d,  $J = 10.8$  Hz, 1H), 7.42 (dd,  $J_1 = 14.8$  Hz,  $J_2 = 10.5$  Hz, 1H), 7.32-7.13 (m, 4H), 6.10 (d,  $J = 14.8$  Hz, 1H), 5.55 (d,  $J = 8.9$  Hz, 1H), 4.10 (t,  $J = 8.0$  Hz, 1H), 2.23-2.01 (m, 1H), 1.47 (s, 9H), 1.01 (d,  $J = 6.8$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.0, 156.5, 136.1, 128.5, 126.5, 125.5, 122.4, 113.8, 80.2, 60.4, 30.9, 28.4, 19.3, 18.5; HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_{27}\text{N}_2\text{O}_3$   $[\text{M}+\text{H}]^+$ :319.2016, found: 319.2018.

***tert*-butyl (*S*,*E*)-(1-oxo-3-phenyl-1-(styrylamino)propan-2-yl)carbamate (**2ac**)**



Compound **2ac** (305.1 mg, 0.83 mmol, 83%) was prepared from **1ac** (366 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2ac** as a white solid, mp 148 – 149°C;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  10.31 (d,  $J = 10.1$ Hz, 1H), 7.42-7.33 (m, 3H), 7.32-7.25 (m, 6H), 7.22-7.12 (m, 3H), 6.21 (d,  $J = 14.8$  Hz, 1H), 4.26-4.18 (m, 1H), 2.96 (dd,  $J_1 = 13.6$  Hz,  $J_2 = 4.7$  Hz, 1H), 2.79 (dd,  $J_1 = 13.6$  Hz,  $J_2 = 10.2$  Hz, 1H), 1.32 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO}-d_6$ )  $\delta$  170.5, 155.9, 138.4, 136.9, 129.6, 129.1, 128.5, 126.7, 126.6, 125.6, 123.9, 112.5, 78.5, 56.5, 37.6, 28.6; HRMS (ESI) calcd for  $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ : 389.1836, found: 389.1832.

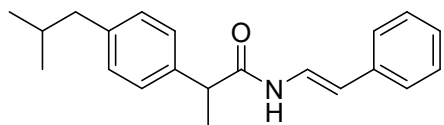
**(*E*)-2-(4-(4-chlorobenzoyl)phenoxy)-2-methyl-*N*-styrylpropanamide (**2ad**)**



Compound **2ad** (403.1 mg, 0.96 mmol, 96%) was prepared from **1ad** (419 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded **2ad** as a white solid, mp 132 – 133°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 (d,  $J = 11.2$  Hz, 1H), 7.77 (d,  $J = 8.5$  Hz, 2H), 7.72 (d,  $J = 8.3$  Hz, 2H), 7.60-7.39 (m, 3H), 7.38-7.11 (m, 6H), 7.01 (d,  $J = 8.4$  Hz, 2H), 6.18 (d,  $J = 14.7$  Hz, 1H), 1.64 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.2, 171.5, 158.1, 138.7, 135.9, 135.7, 132.1, 132.0,

131.2, 128.7, 128.6, 126.9, 125.6, 121.9, 120.1, 114.2, 81.9, 25.0; HRMS (ESI) calcd for  $C_{25}H_{22}NO_3ClNa$   $[M+Na]^+$ :442.1180, found: 442.1183.

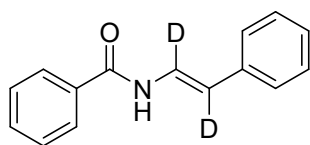
**(E)-2-(4-isobutylphenyl)-N-styrylpropanamide (2ae)**



Compound **2ae** (292.8 mg, 0.95 mmol, 95%) was prepared from **1ae** (307 mg, 1.00 mmol) following the general procedure. Purification by column chromatography on

silica gel (petroleum ether/EtOAc = 20:1) afforded **2ae** as a white solid, mp 144 – 145 °C;  $^1H$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.27 (d,  $J$  = 10.3 Hz, 1H), 7.36 (dd,  $J_1$  = 14.8 Hz,  $J_2$  = 10.2 Hz, 1H), 7.32-7.22 (m, 6H), 7.17-7.07 (m, 3H), 6.15 (d,  $J$  = 14.7 Hz, 1H), 3.67 (q,  $J$  = 6.8 Hz, 1H), 2.40 (d,  $J$  = 7.1 Hz, 2H), 1.89-1.70 (m, 1H), 1.37 (d,  $J$  = 7.0 Hz, 3H), 0.85 (d,  $J$  = 6.6 Hz, 6H);  $^{13}C$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  171.9, 140.0, 139.2, 137.0, 129.3, 129.0, 127.4, 126.4, 125.5, 124.2, 112.0, 45.3, 44.6, 30.0, 22.5, 18.9; GC-MS (EI, 70 eV)  $m/z$ :  $[M]^+$ calcd for  $C_{21}H_{25}NO$ : 307, found: 307, 161, 119.

**(E)-N-(2-phenylvinyl-1,2- $d_2$ )benzamide (2a- $d_2$ )**



Compound **2a- $d_2$**  (108.1 mg, 0.48 mmol, 96%) was prepared from **1a- $d_2$**  (113 mg, 0.50 mmol) following the general procedure. Purification by column chromatography on silica gel (petroleum

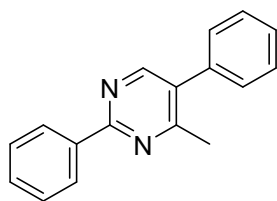
ether/EtOAc = 20:1) afforded **2a- $d_2$**  as a white solid, mp 170 – 171 °C;  $^1H$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.60 (s, 1H), 7.95 (d,  $J$  = 8.13 Hz, 2H), 7.69-7.44(m, 3H), 7.44-7.33 (m, 2H), 7.32-7.22 (m, 2H), 7.14 (t,  $J$  = 8.9Hz, 1H). GC-MS (EI, 70 eV)  $m/z$ :  $[M]^+$ calcd for  $C_{15}H_{11}D_2NO$ : 225, found: 225, 105, 77.

## 6. Synthesis and Analytical Data of pyrimidine derivative 3

General procedure:<sup>[13]</sup> Under argon atmosphere, a 10 mL Schlenk tube equipped with a teflon-coated magnetic stir bar was charged with (*Z*)-*N*-styrylbenzamide or (*E*)-*N*-styrylbenzamide (223 mg, 1 mmol, 1.0 equiv), acetonitrile (520.0  $\mu$ L, 5.0 mmol, 5.0 equiv), 2-chloropyridine (115.0  $\mu$ L, 1.2 mmol, 1.2 equiv) and anhydrous DCM (5.0 mL). The reaction mixture was cooled to -78 °C.  $\text{TiF}_3$  (185.0  $\mu$ L, 1.1 mmol, 1.1 equiv) was added via syringe over 1 min to reaction mixture at -78 °C. After 10 min, the reaction mixture was placed in an ice-water bath and warmed to 0 °C. After 10 min, the resulting solution was allowed to warm to ambient temperature for 5 minutes. The reaction vessel was placed into a preheated oil bath at 45 °C and maintained at that temperature. After 1 h, the reaction vessel was allowed to cool to ambient temperature and aqueous sodium hydroxide solution (1.0 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. DCM (3.0 mL) was added to dilute the mixture and the layers were separated. The aqueous layer was washed with DCM ( $2 \times 3.0$  mL). The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and concentrated in vacuo. The residual was purified by prep-TLC on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) to afford 4-methyl-2,5-diphenylpyrimidine **3** as a white solid.

Product **3** is a known compound, its physical and spectral data are in well accordance with literature data.<sup>[6]</sup>

### 4-methyl-2,5-diphenylpyrimidine (3)



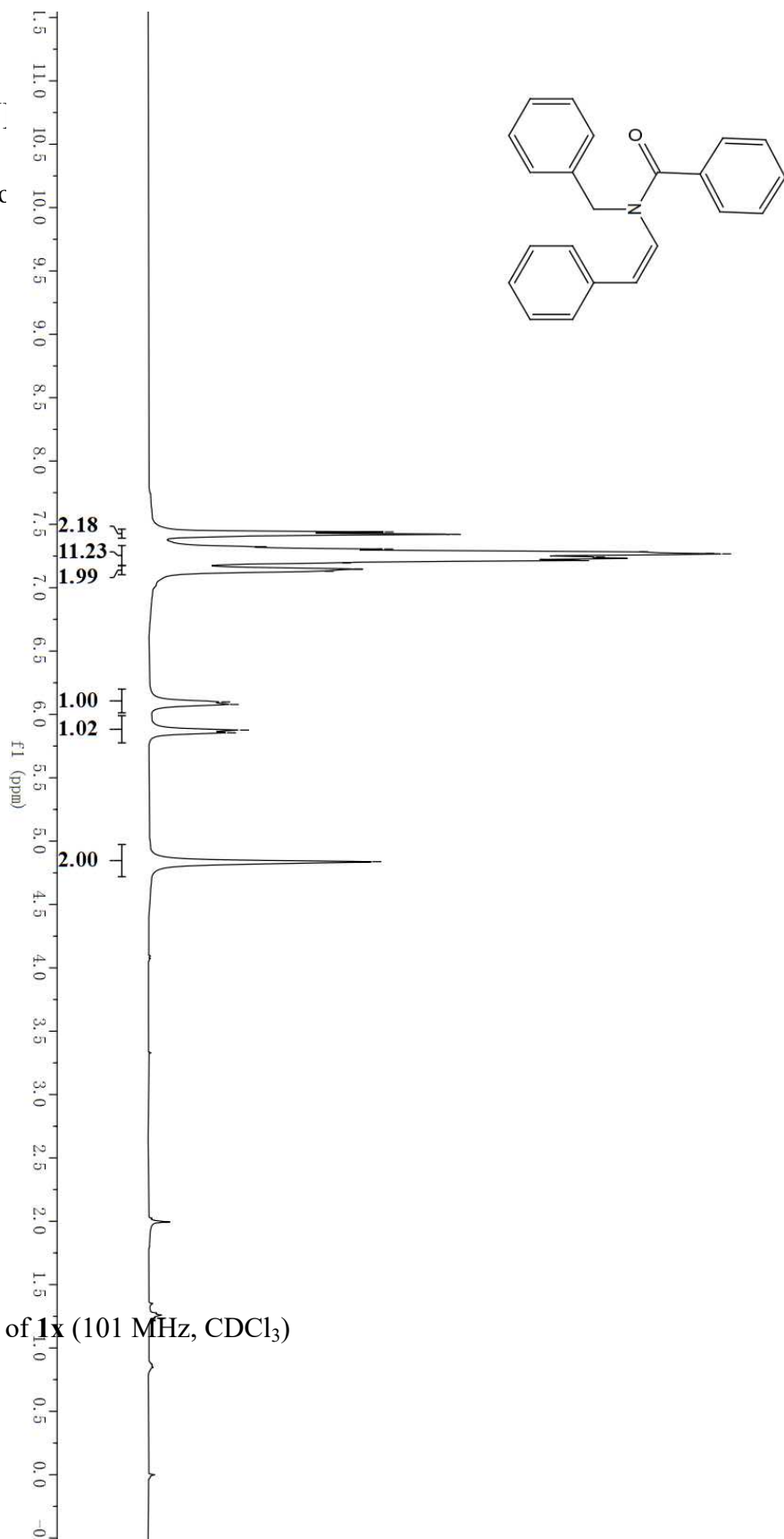
Following the general procedure, using 20/1 petroleum ether/ EtOAc as the eluent afforded the title compound as a white solid, mp 83 – 84°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.62 (s, 1H), 8.52-8.46 (m, 2H), 7.55-7.46 (m, 5H), 7.46-7.41 (m, 1H), 7.40-7.35 (m, 2H), 2.59 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.5, 163.0, 156.7, 137.6, 136.2, 132.3, 130.5, 129.1, 128.7, 128.5, 128.1, 128.1, 23.2; HRMS (ESI) calcd for  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{Na}$   $[\text{M}+\text{Na}]^+$ :269.1049, found: 269.1047.

## 7. References

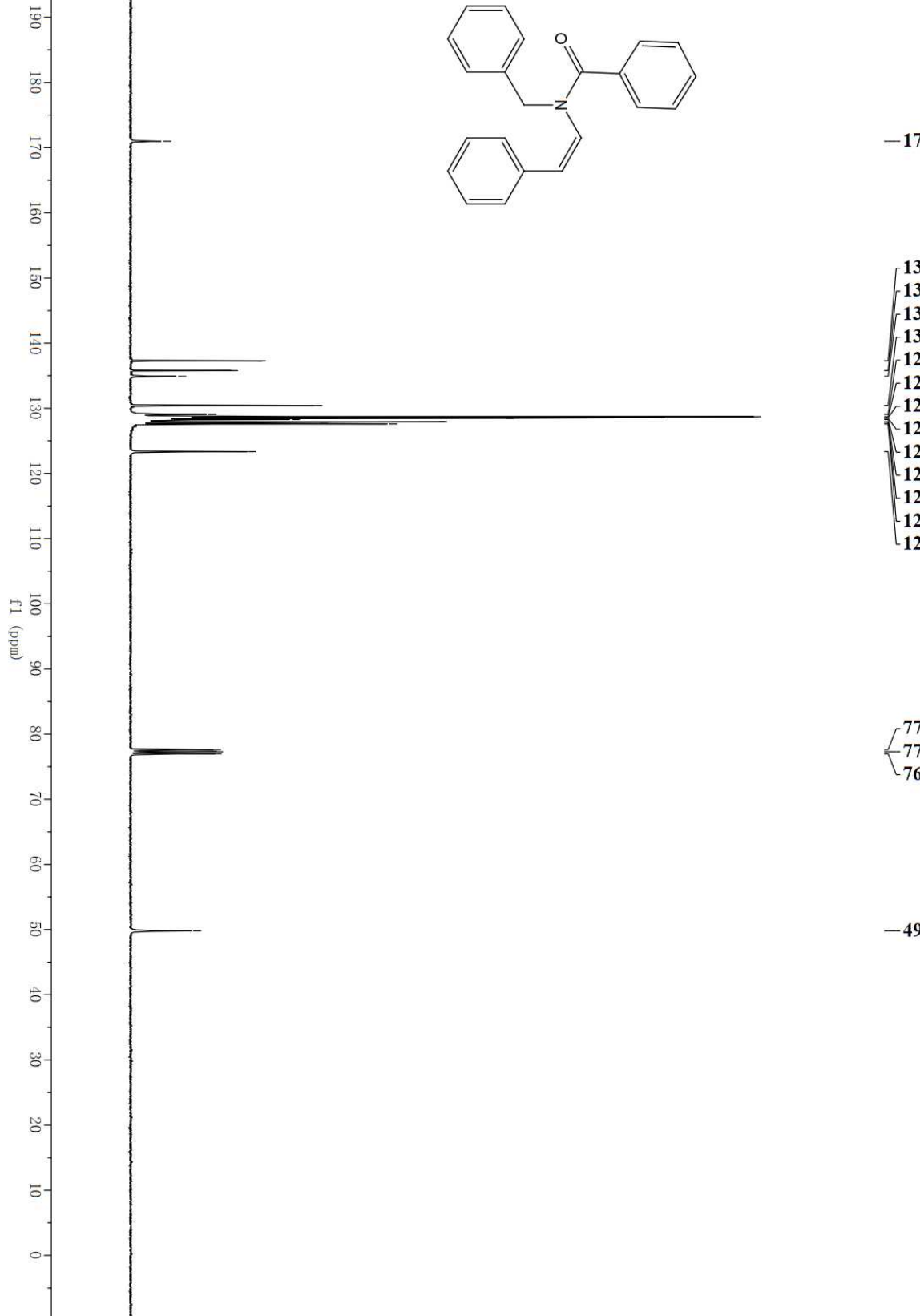
- [1] S. A. Bhat, Q. N. Ahmed, K. A. Bhat, *Chem. Commun.* **2024**, *60*, 114-117.
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# 8. Copies of N

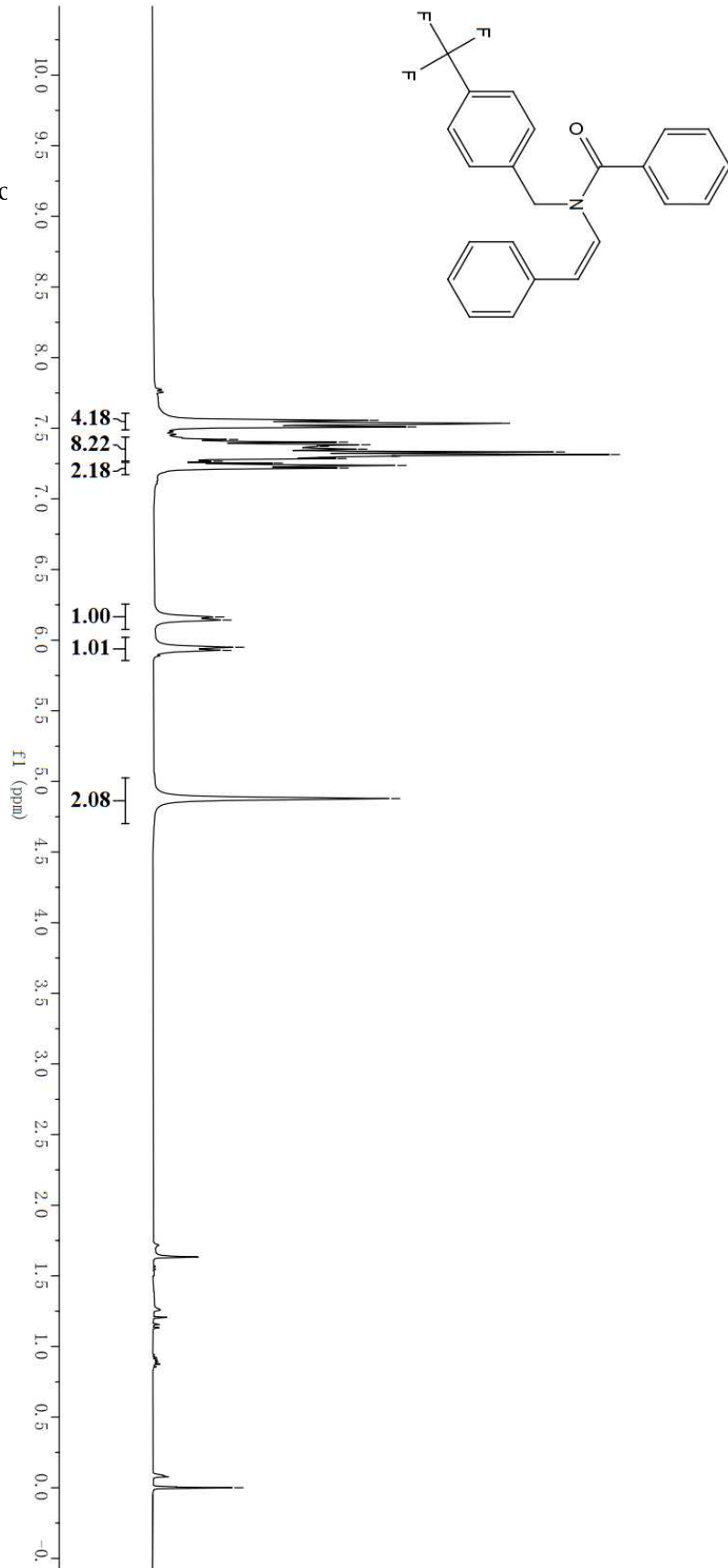
<sup>1</sup>H NMR spectrum c



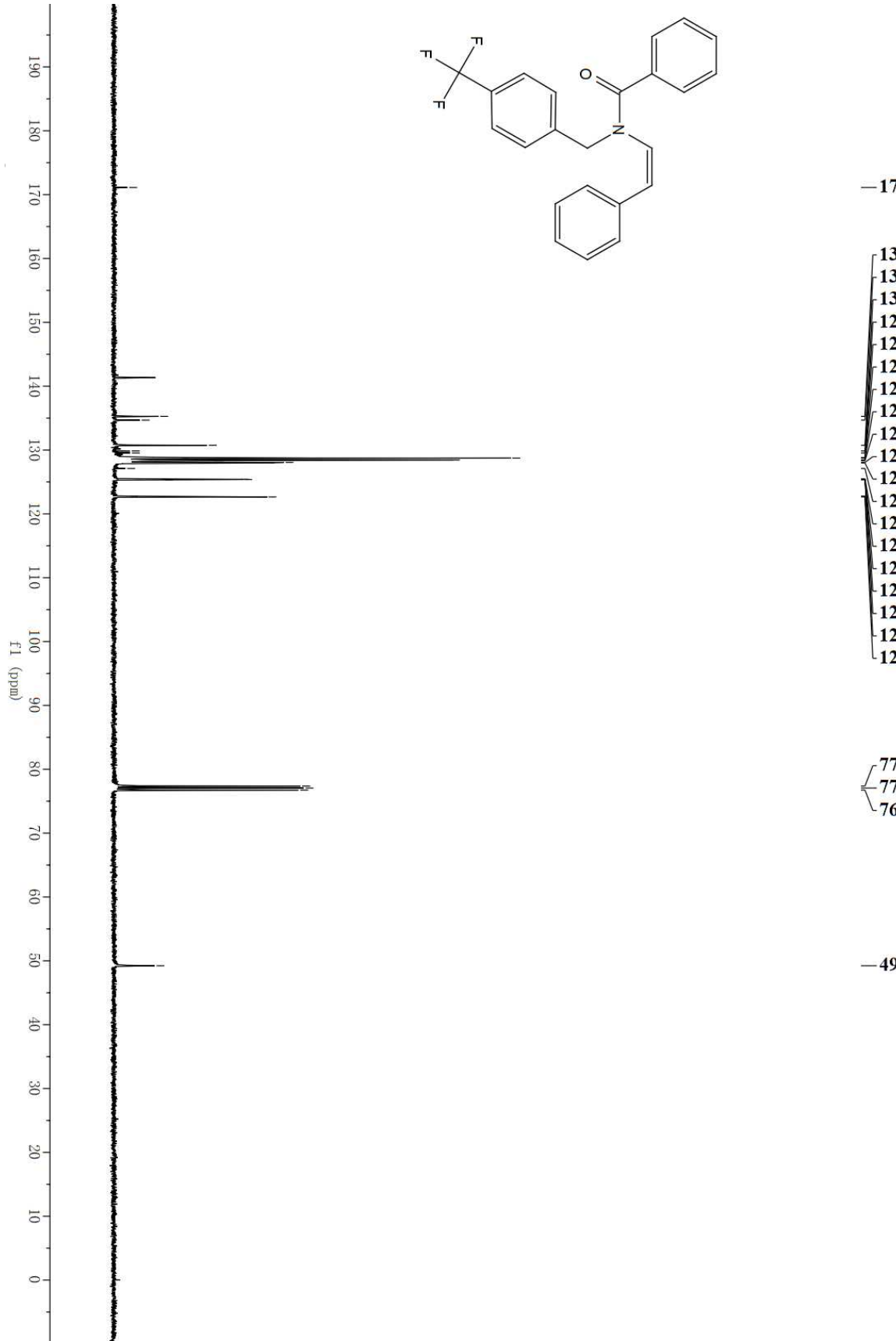
<sup>13</sup>C NMR spectrum of **1x** (101 MHz, CDCl<sub>3</sub>)



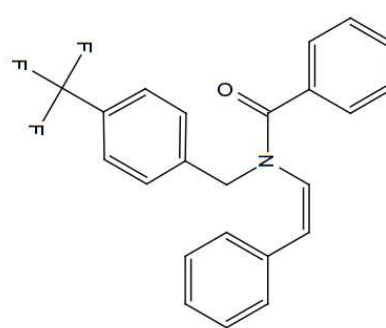
<sup>1</sup>H NMR spectrum c



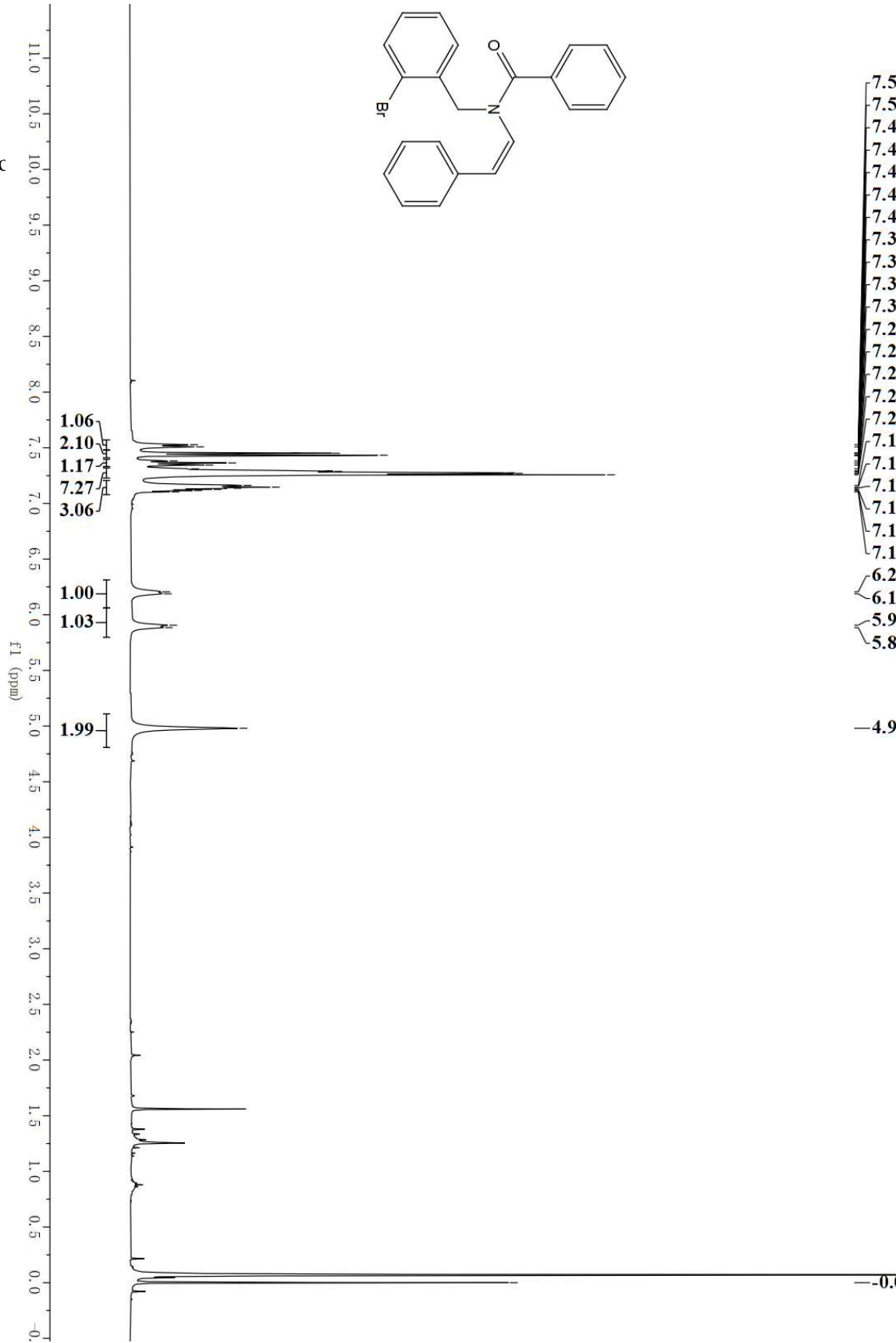
<sup>13</sup>C NMR spectrum



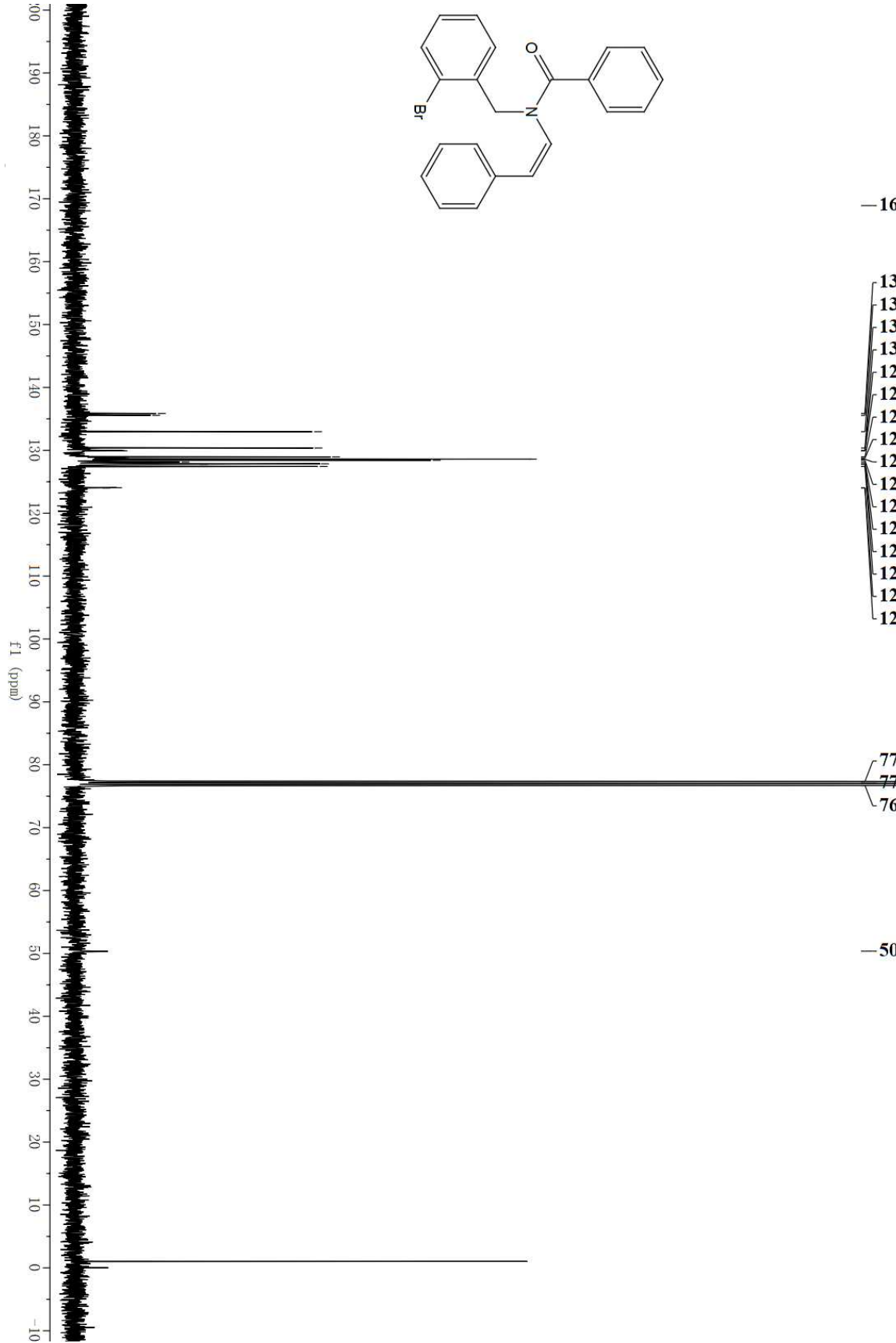
$^{19}\text{F}$  NMR spectrum



<sup>1</sup>H NMR spectrum c

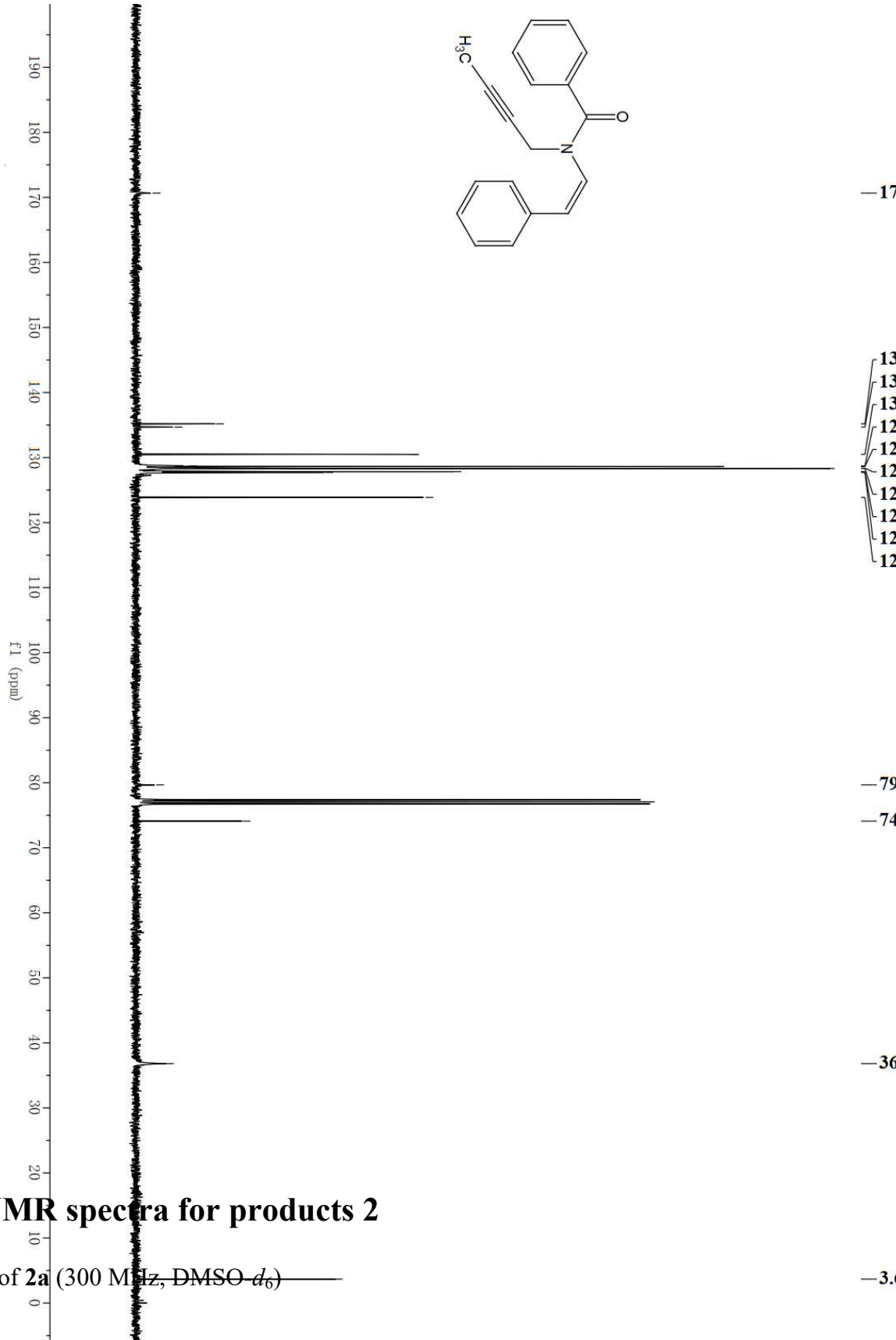


<sup>13</sup>C NMR spectrum





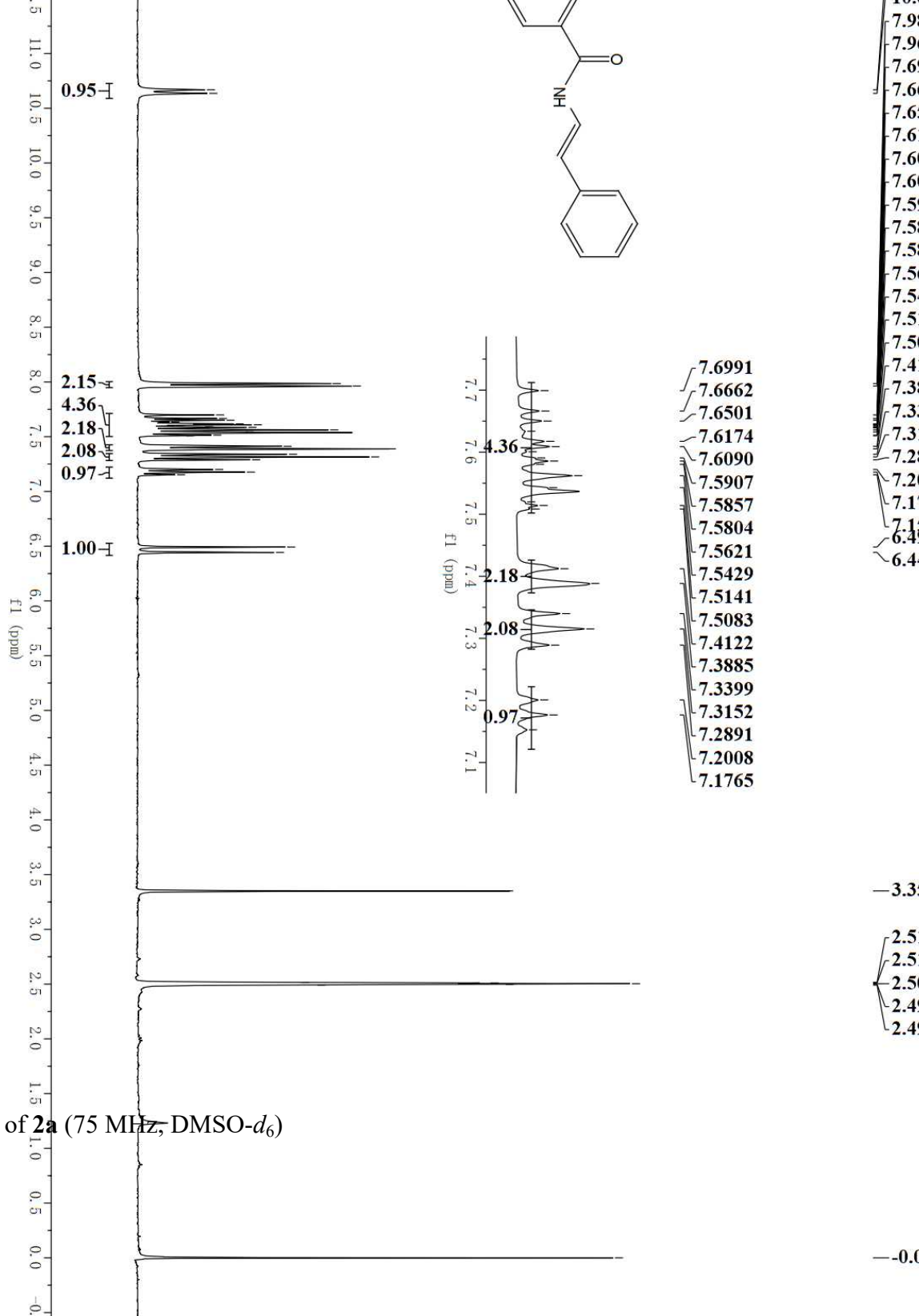
$^{13}\text{C}$  NMR spectrum



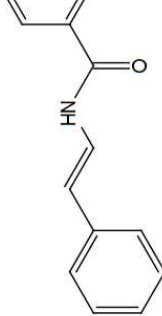
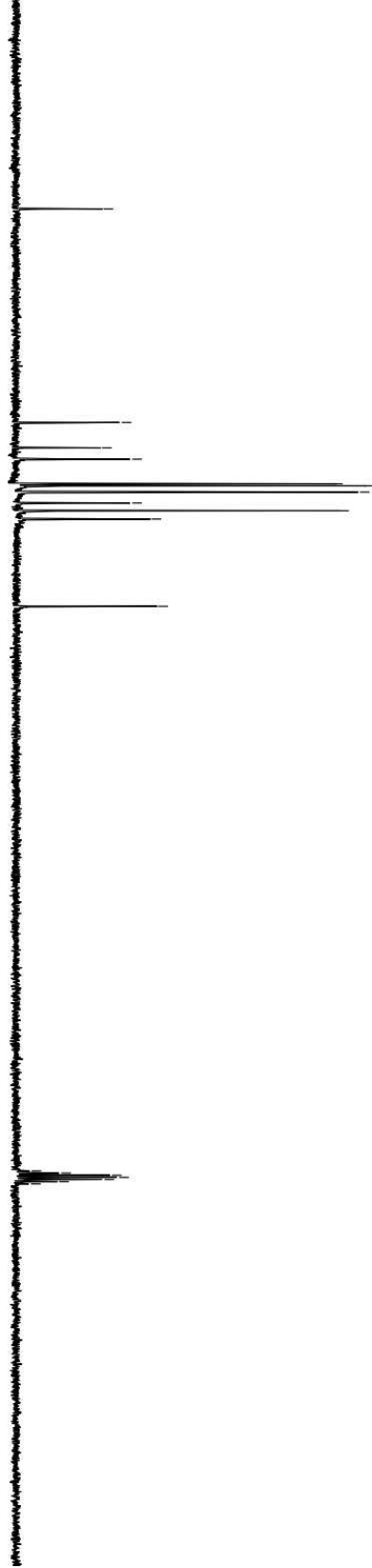
## 9. Copies of NMR spectra for products 2

$^1\text{H}$  NMR spectrum of **2a** (300 MHz,  $\text{DMSO-}d_6$ )

$^{13}\text{C}$  NMR spectrum of **2a** (75 MHz,  $\text{DMSO-}d_6$ )



F1 (ppm)

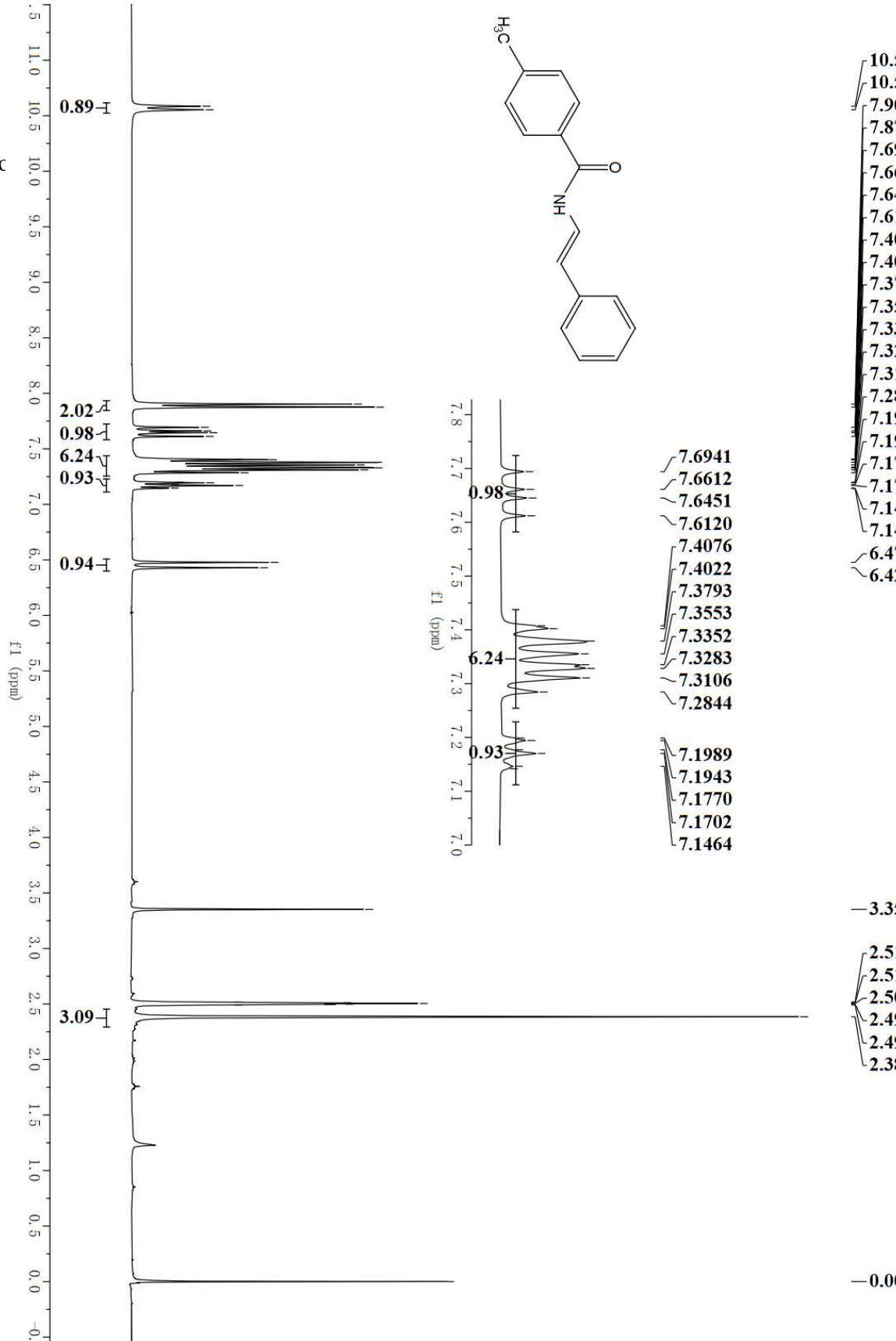


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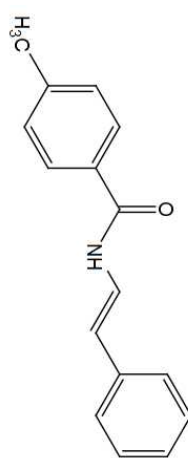
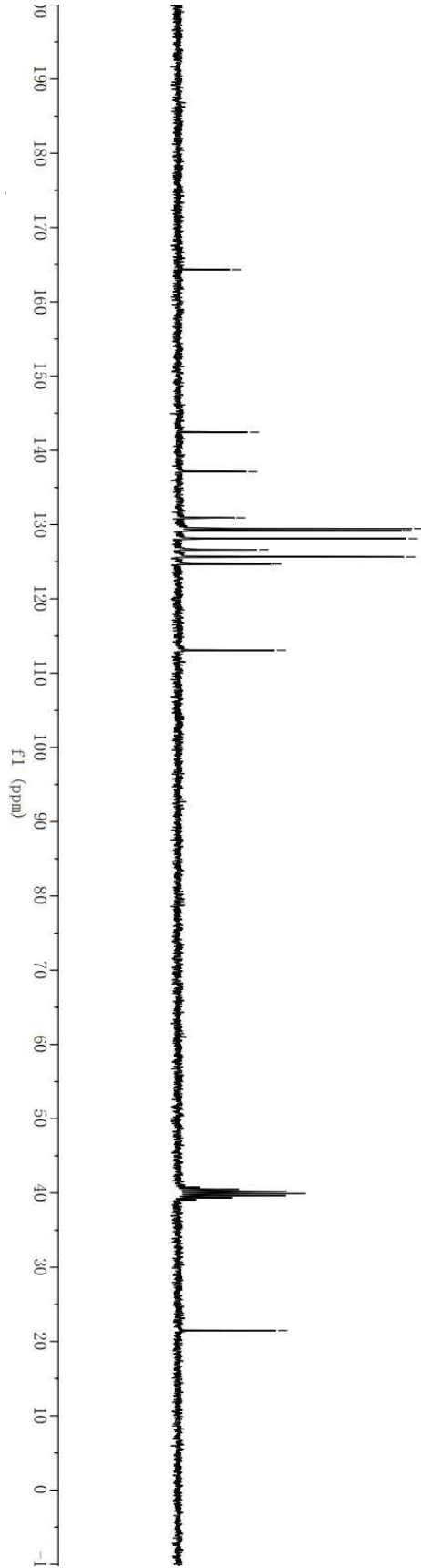
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39

<sup>1</sup>H NMR spectrum c



<sup>13</sup>C NMR spectrum



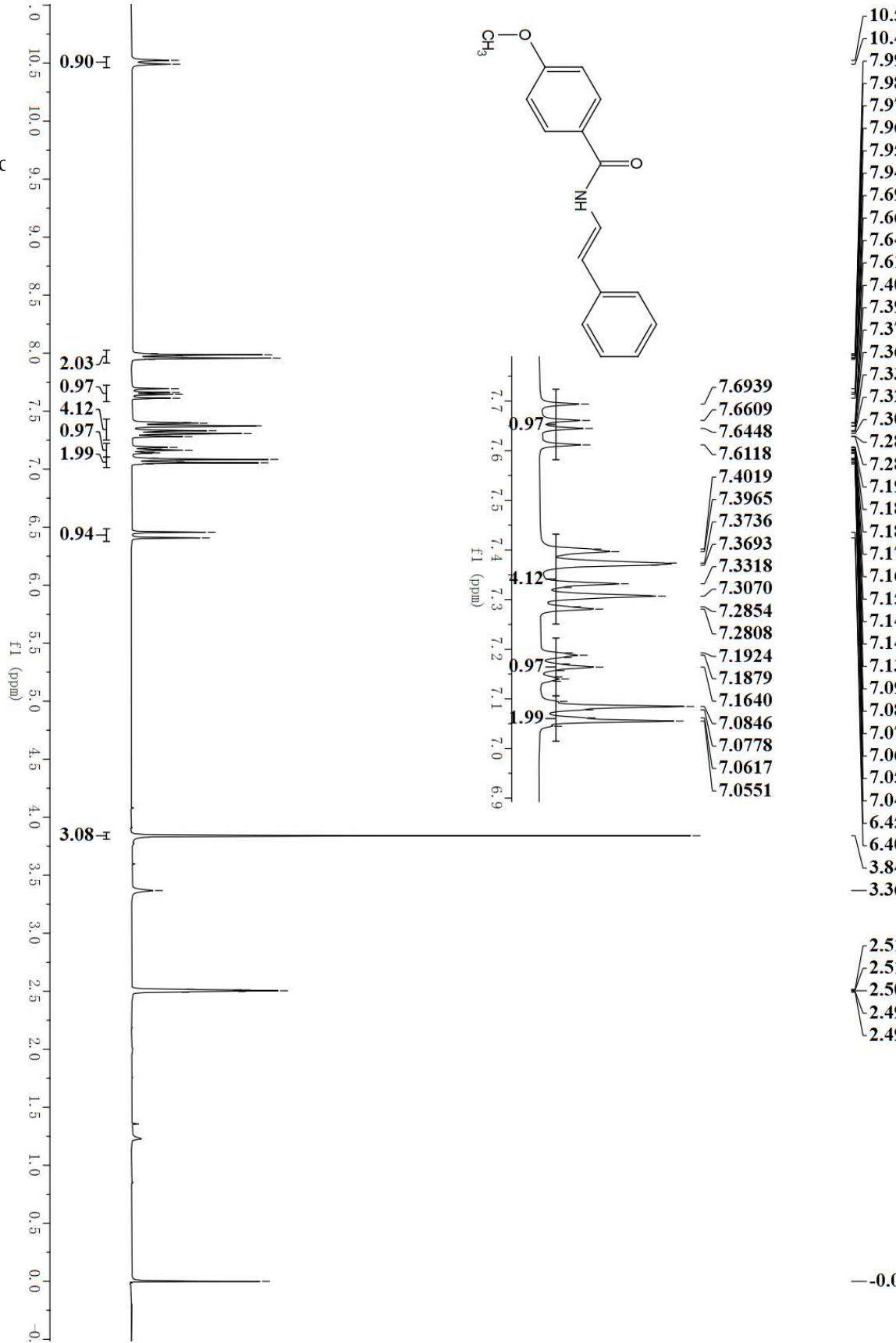
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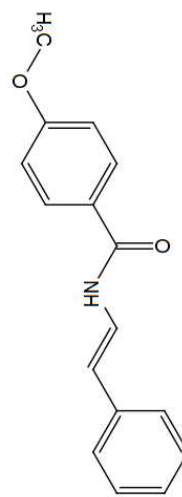
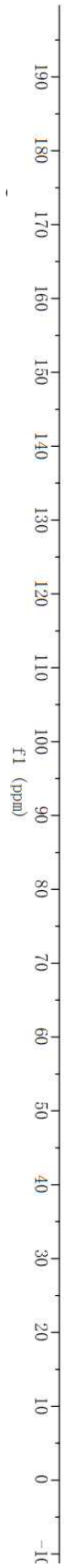
- 11

- 21

<sup>1</sup>H NMR spectrum c



<sup>13</sup>C NMR spectrum



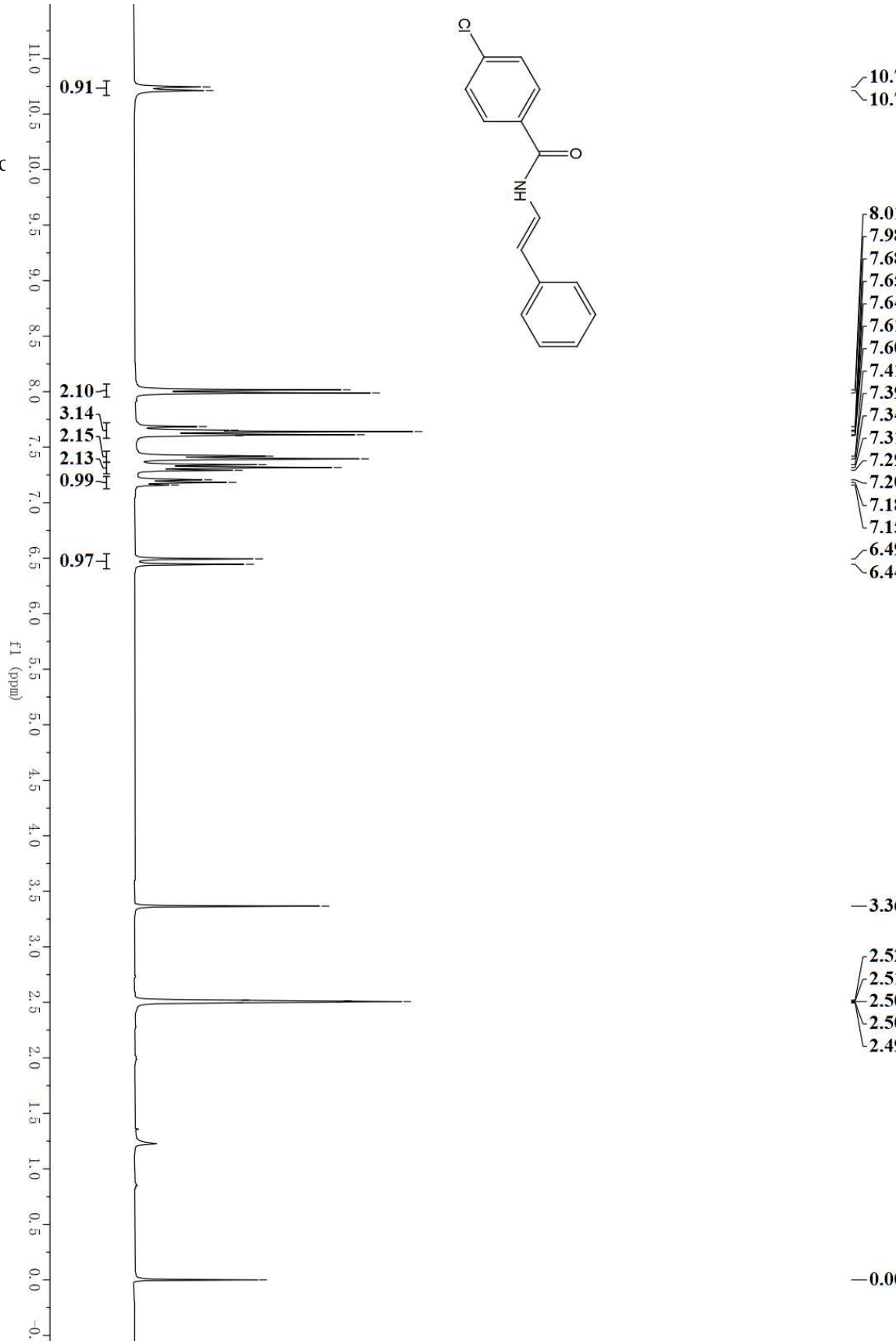
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~16

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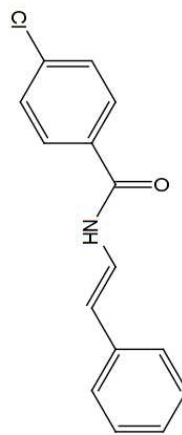
~11  
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<sup>1</sup>H NMR spectrum c



<sup>13</sup>C NMR spectrum

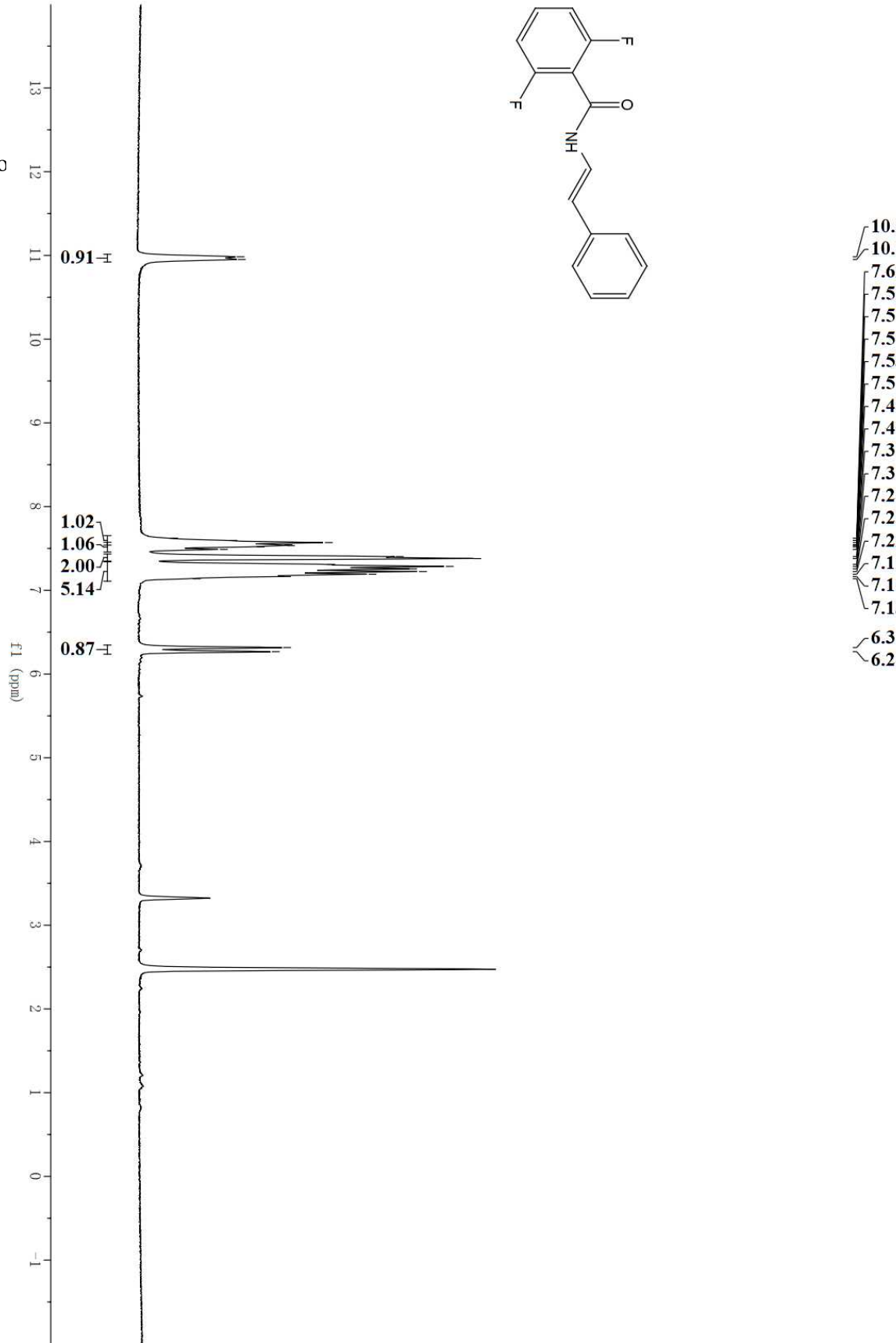


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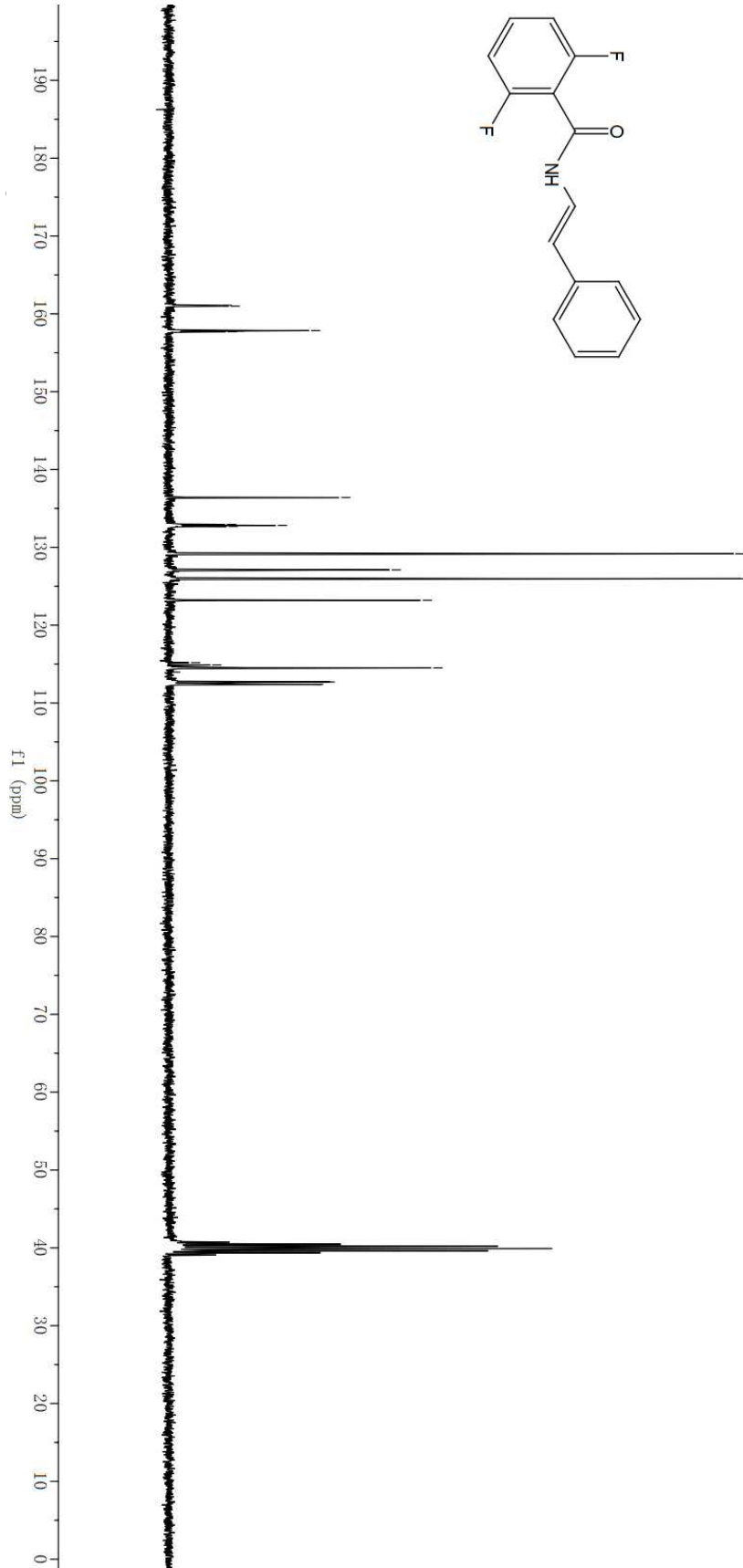
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38

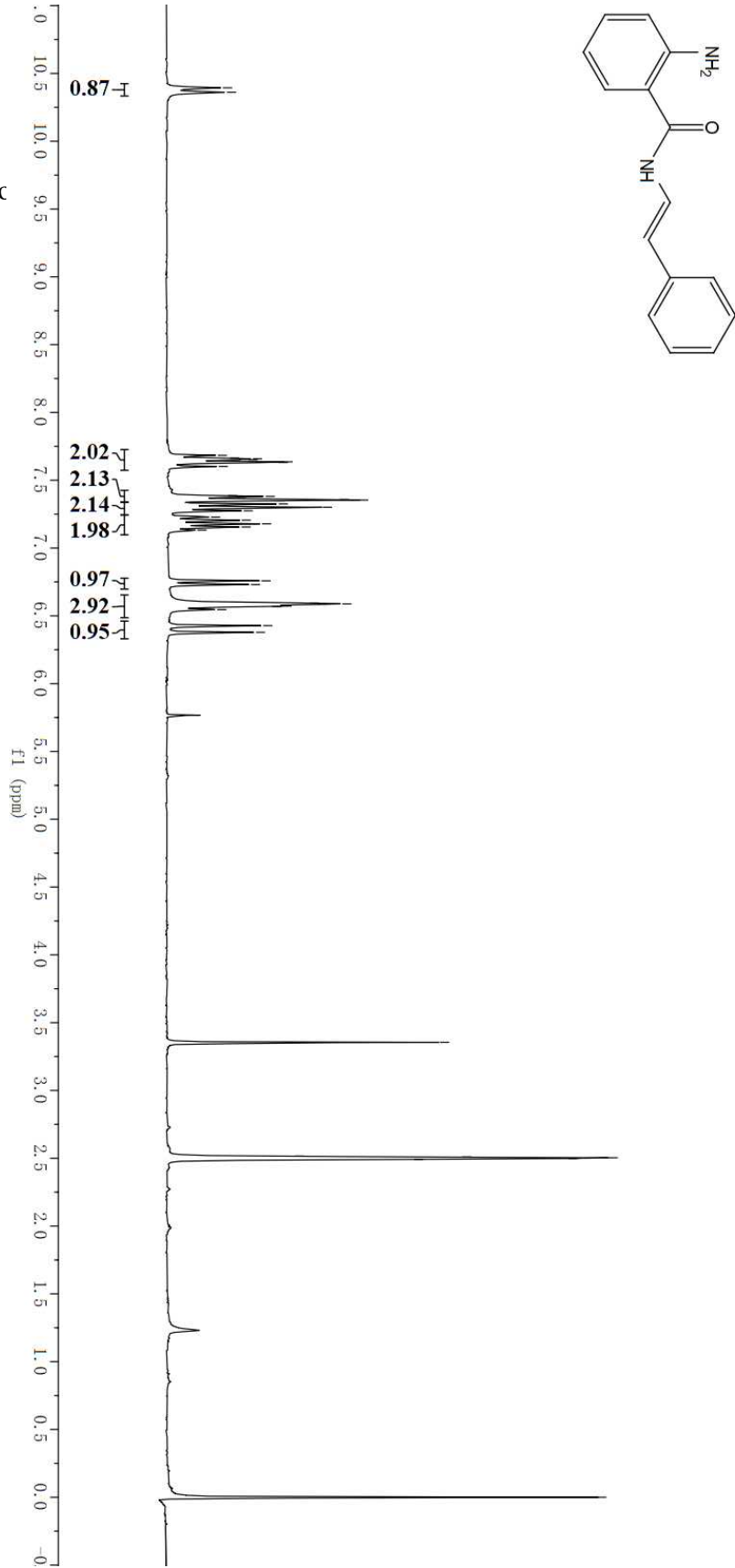
<sup>1</sup>H NMR spectrum of



<sup>13</sup>C NMR spectrum

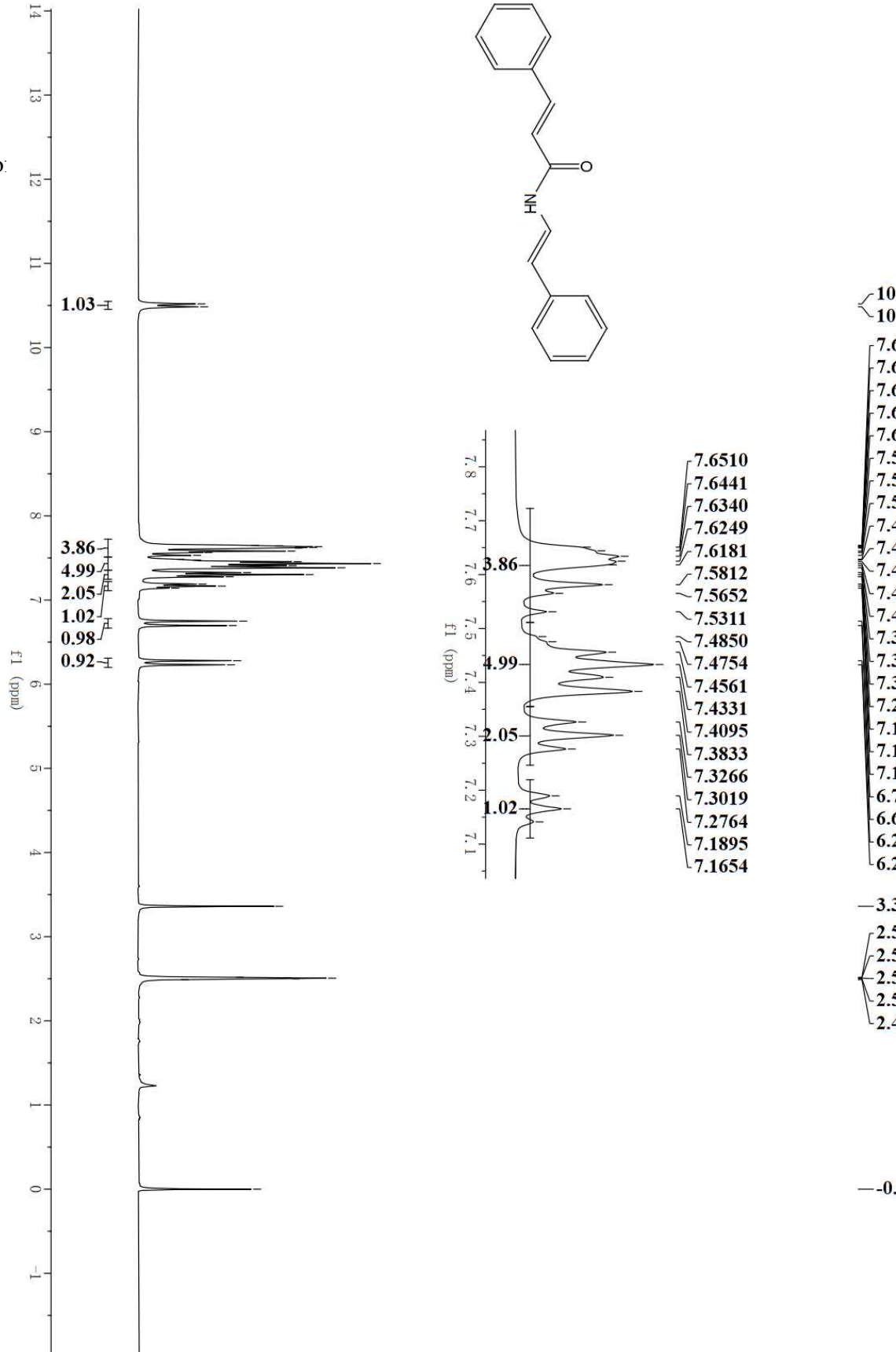


<sup>1</sup>H NMR spectrum c

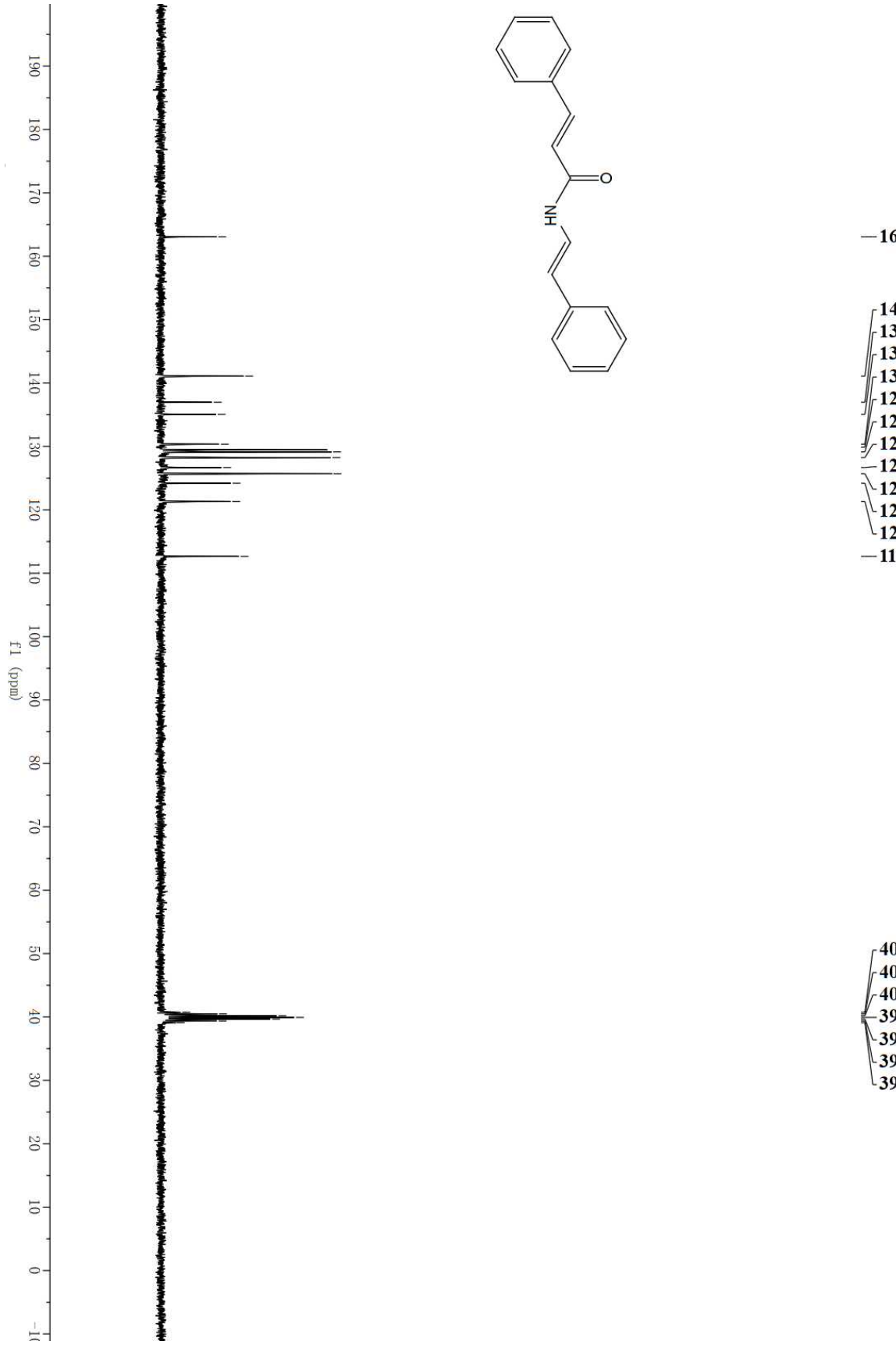




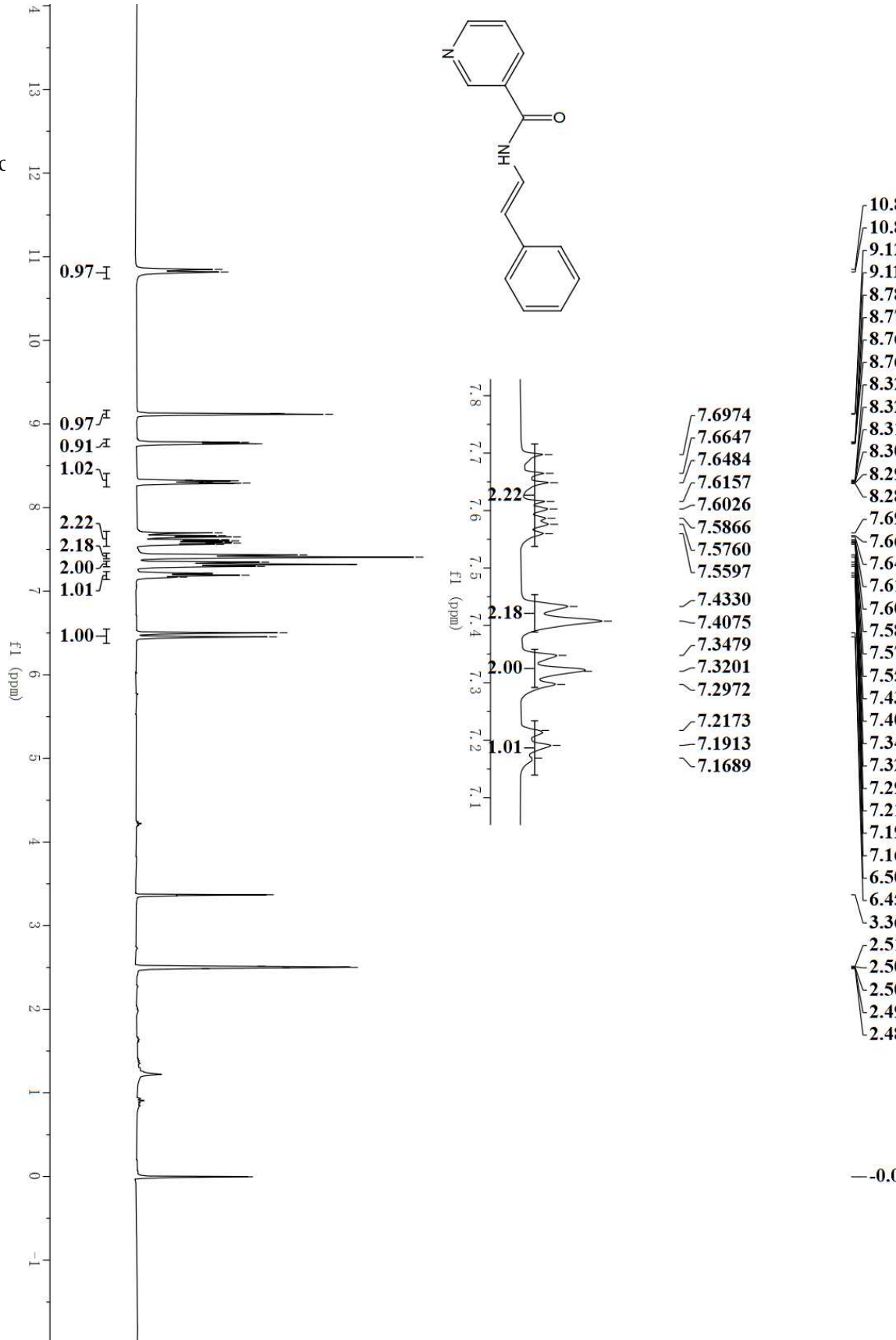
<sup>1</sup>H NMR spectrum of:



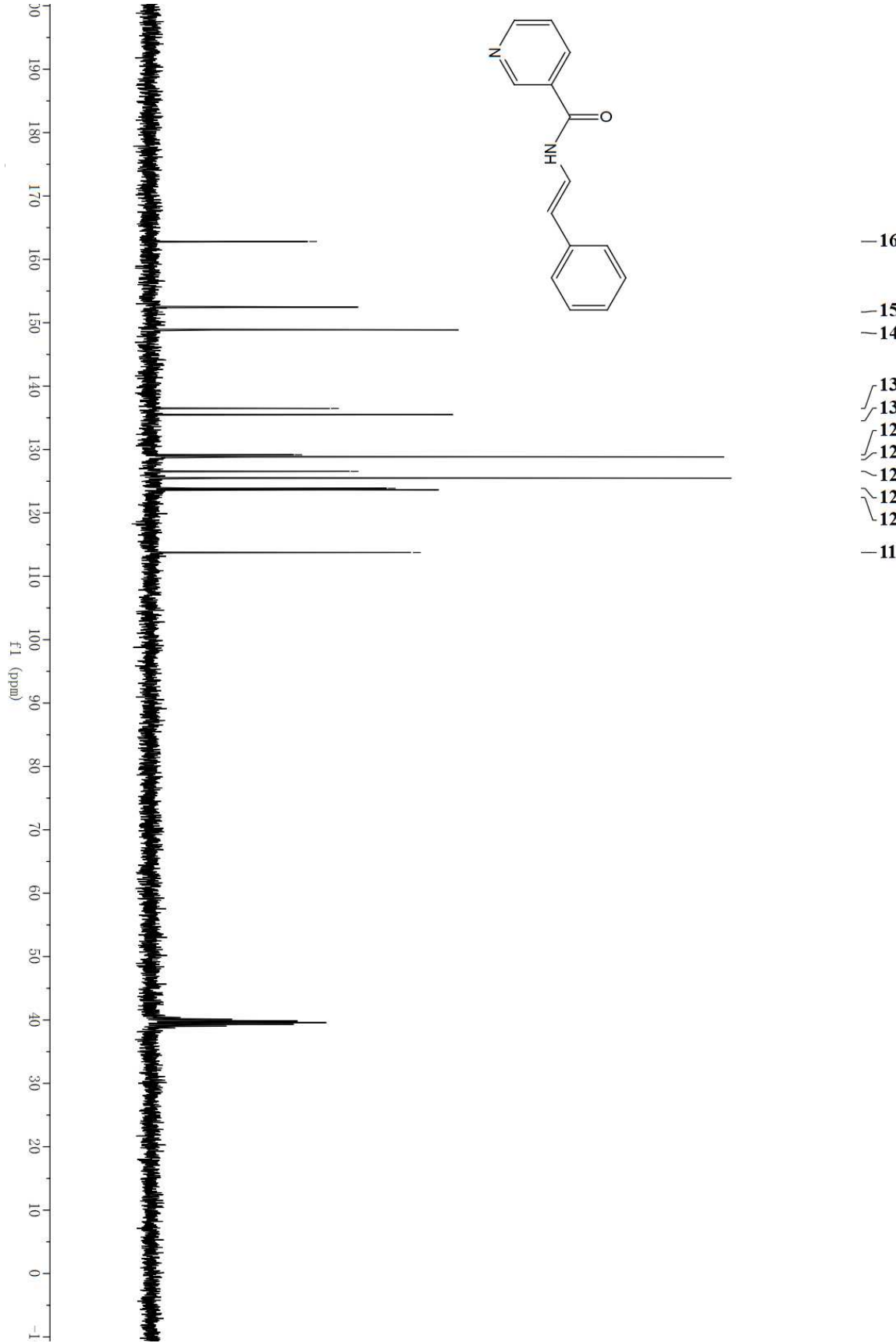
<sup>13</sup>C NMR spectrum



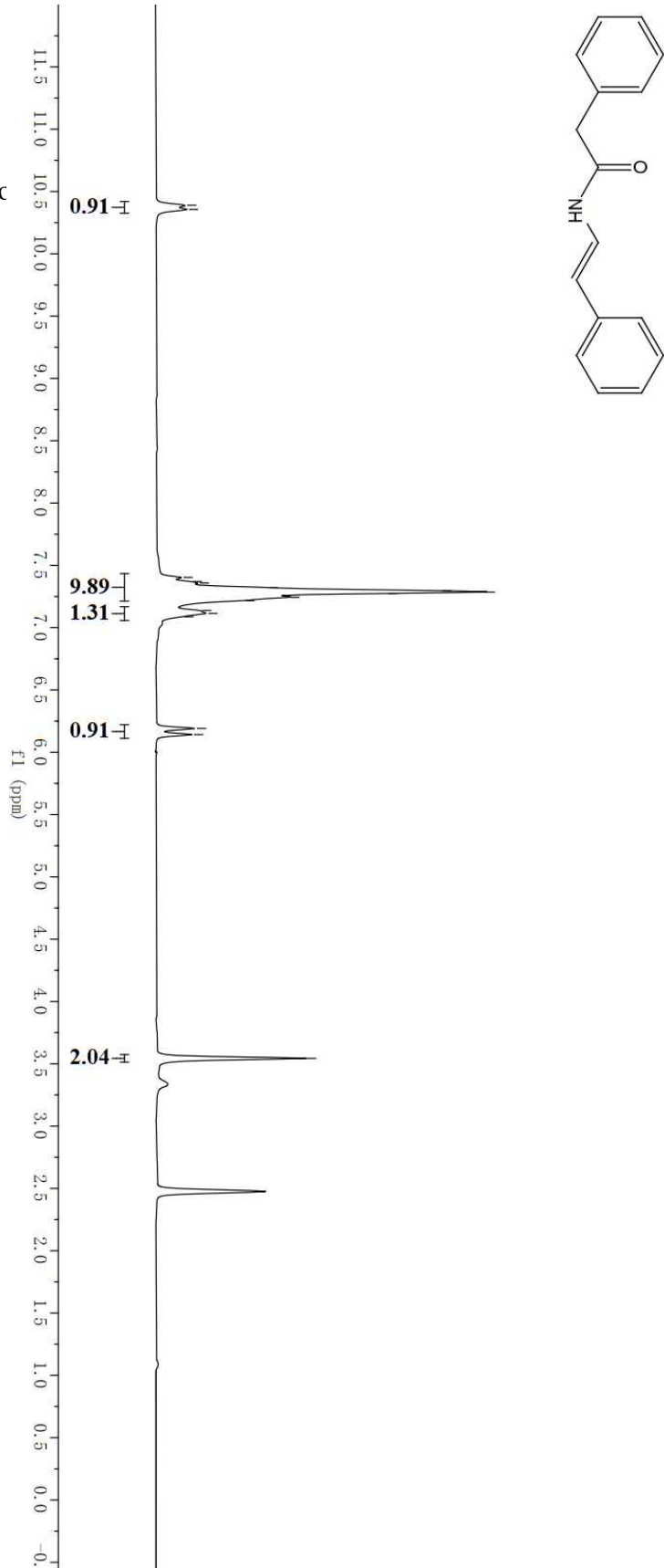
<sup>1</sup>H NMR spectrum c



<sup>13</sup>C NMR spectrum



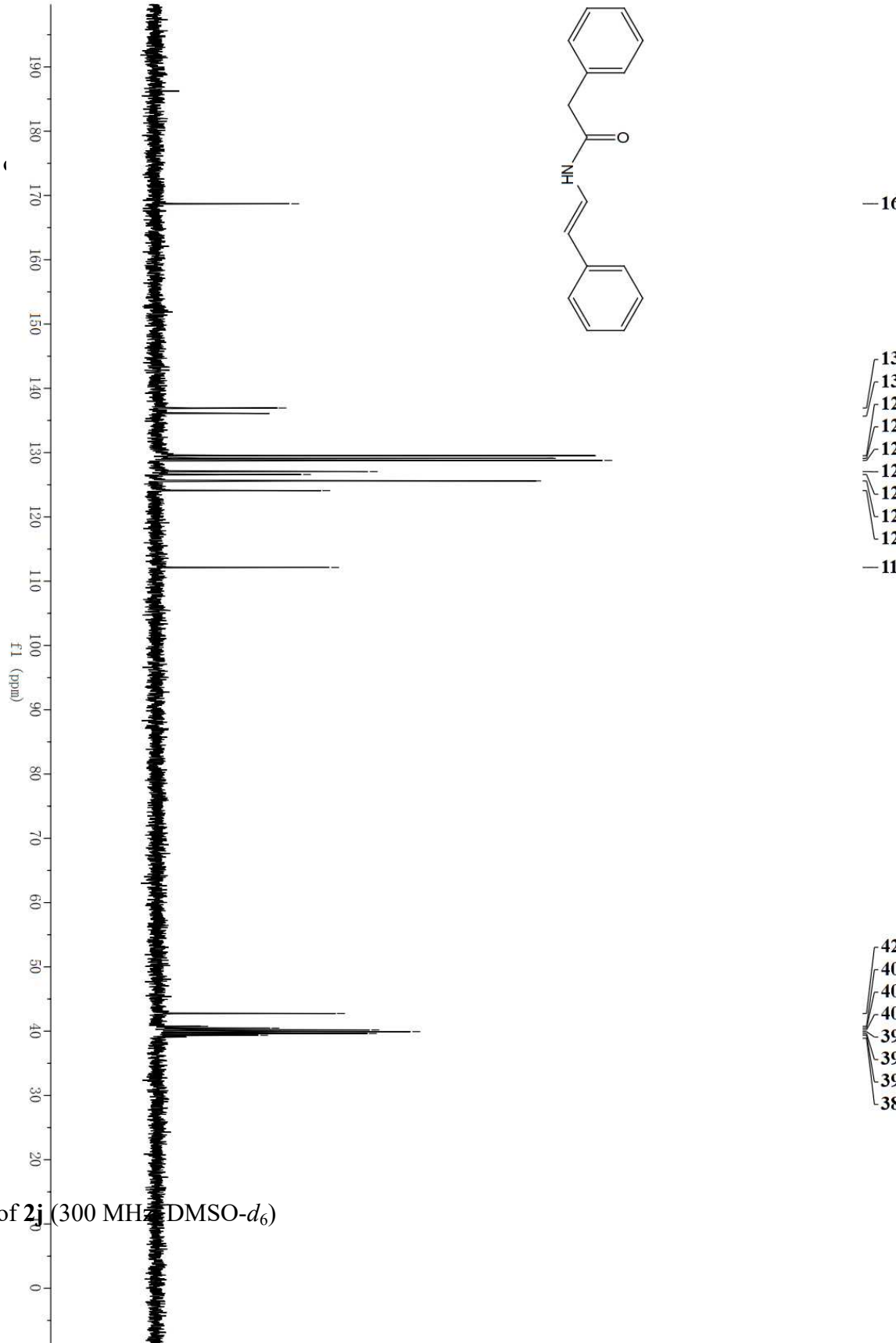
<sup>1</sup>H NMR spectrum c



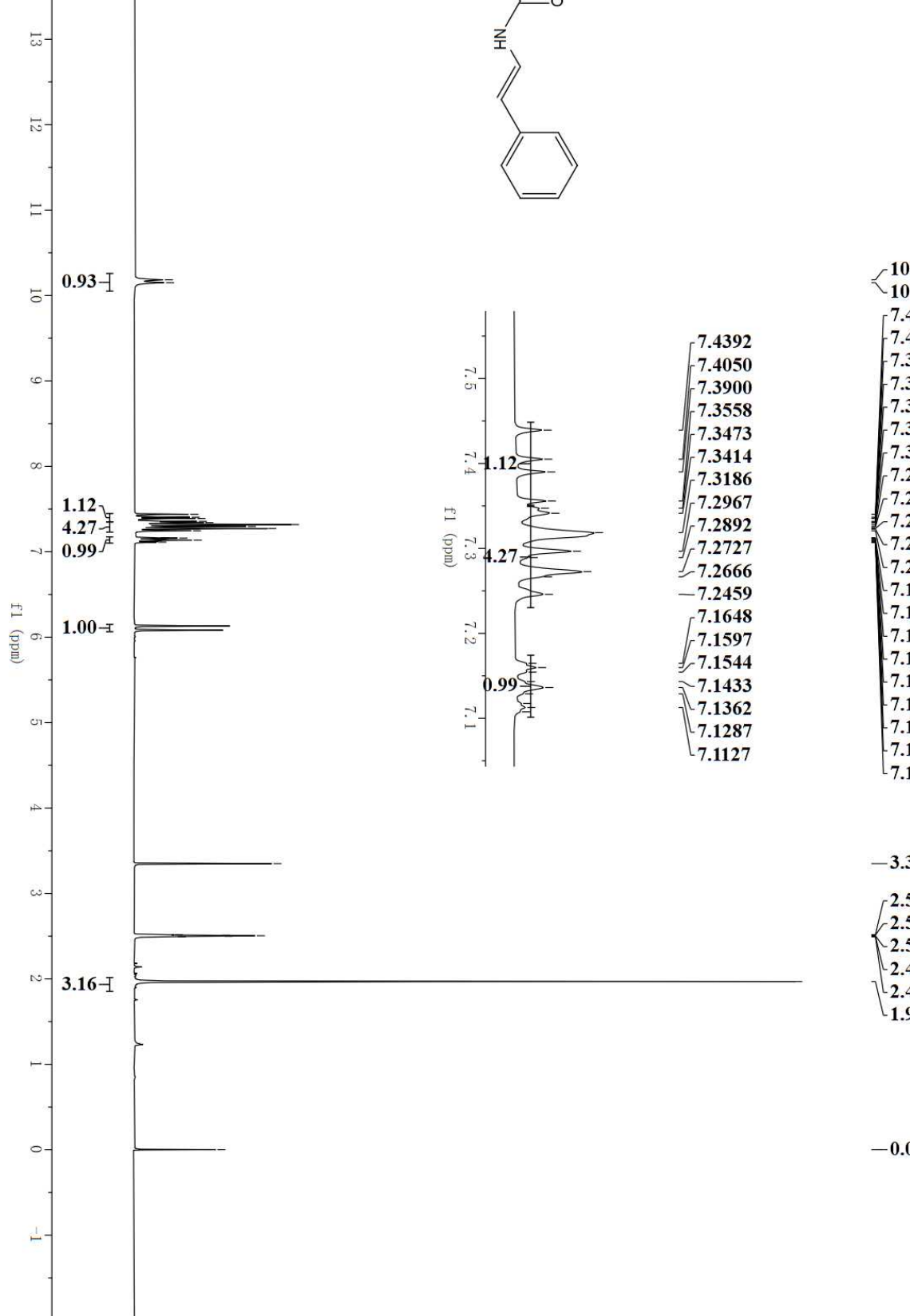
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7.1  
7.0  
6.1  
6.1

3.5

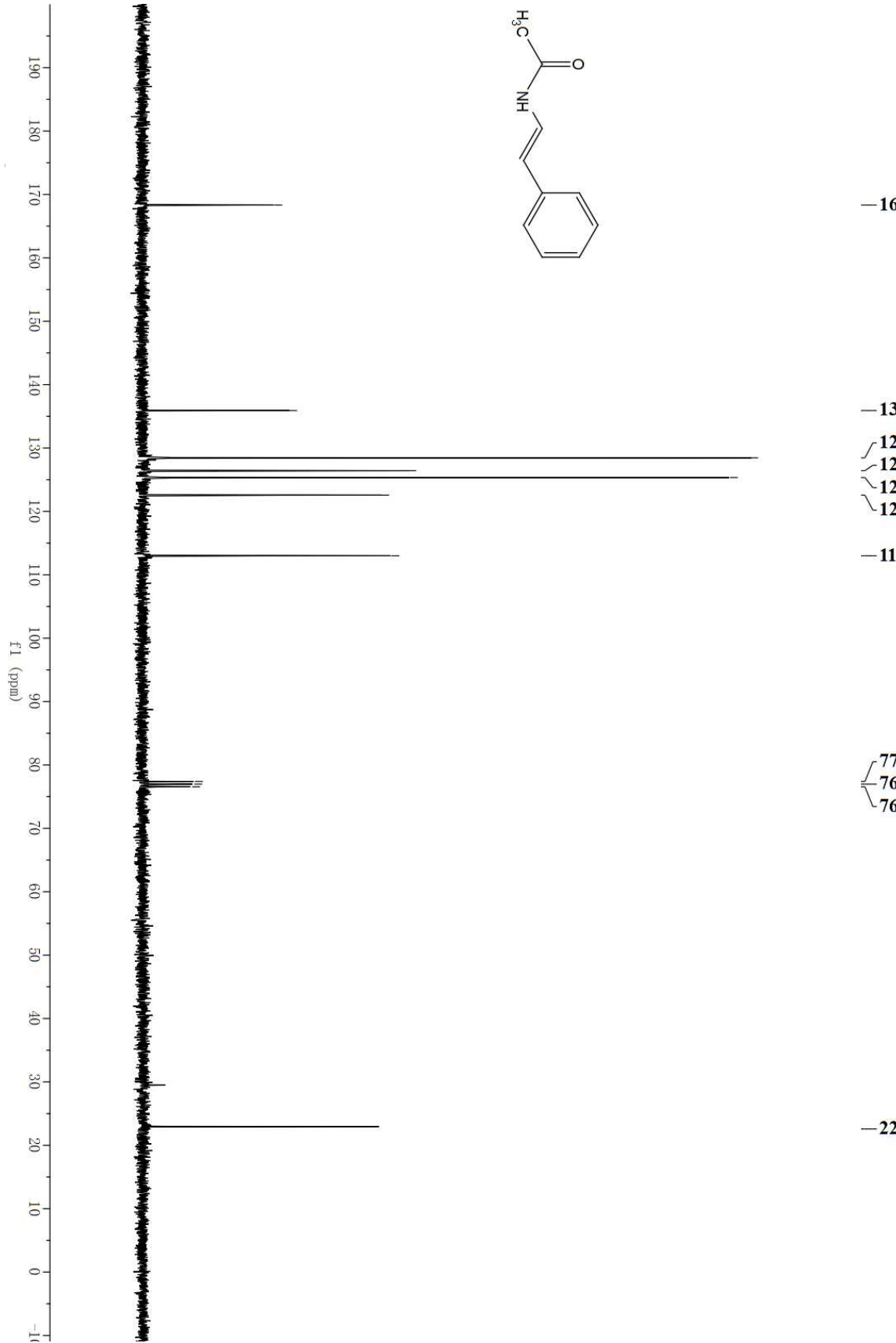
$^{13}\text{C}$  NMR spectrum of



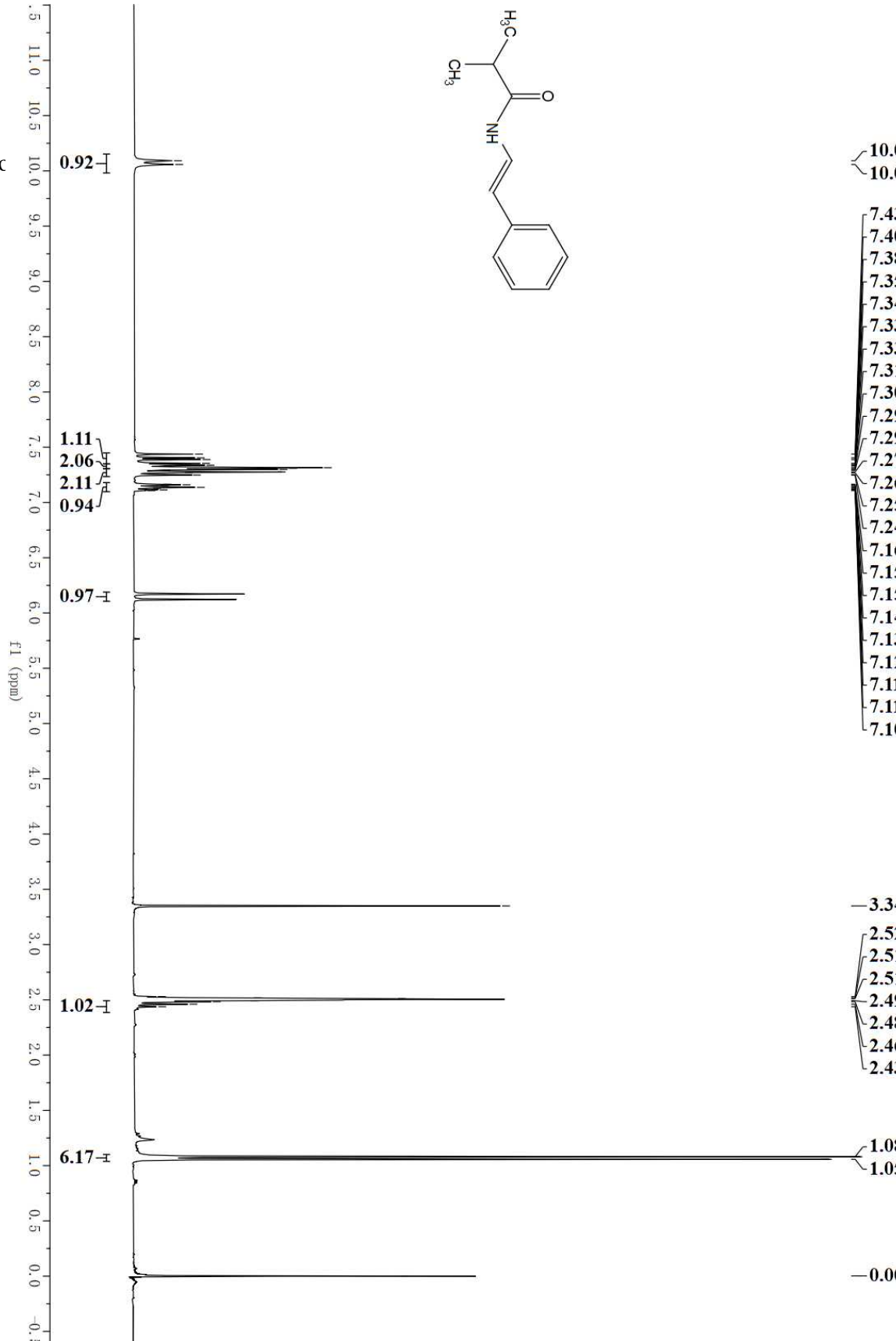
$^1\text{H}$  NMR spectrum of **2j** (300 MHz,  $\text{DMSO-}d_6$ )



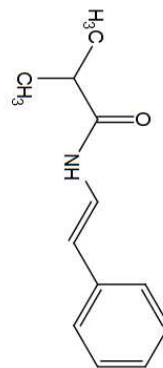
$^{13}\text{C}$  NMR spectrum



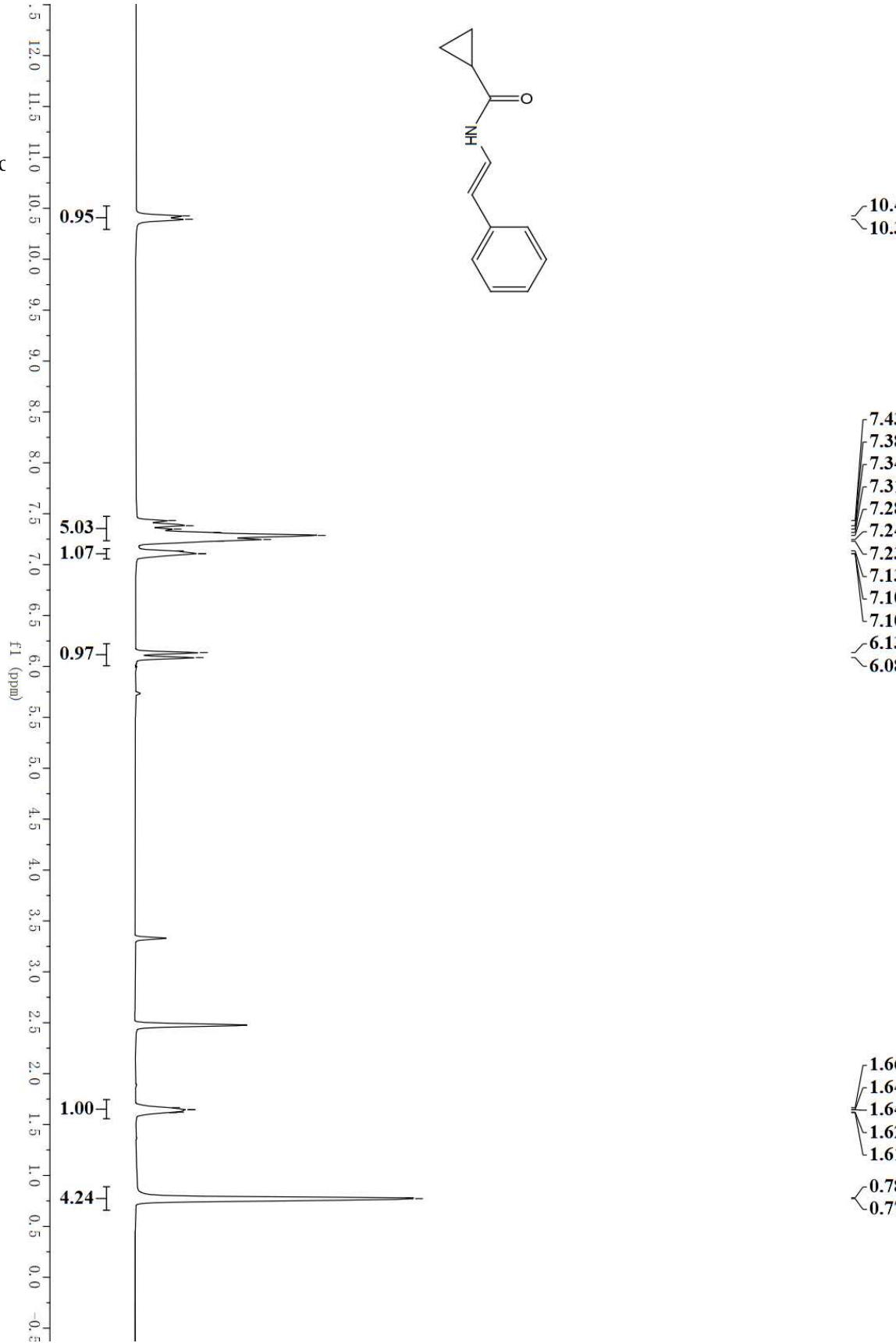
<sup>1</sup>H NMR spectrum c



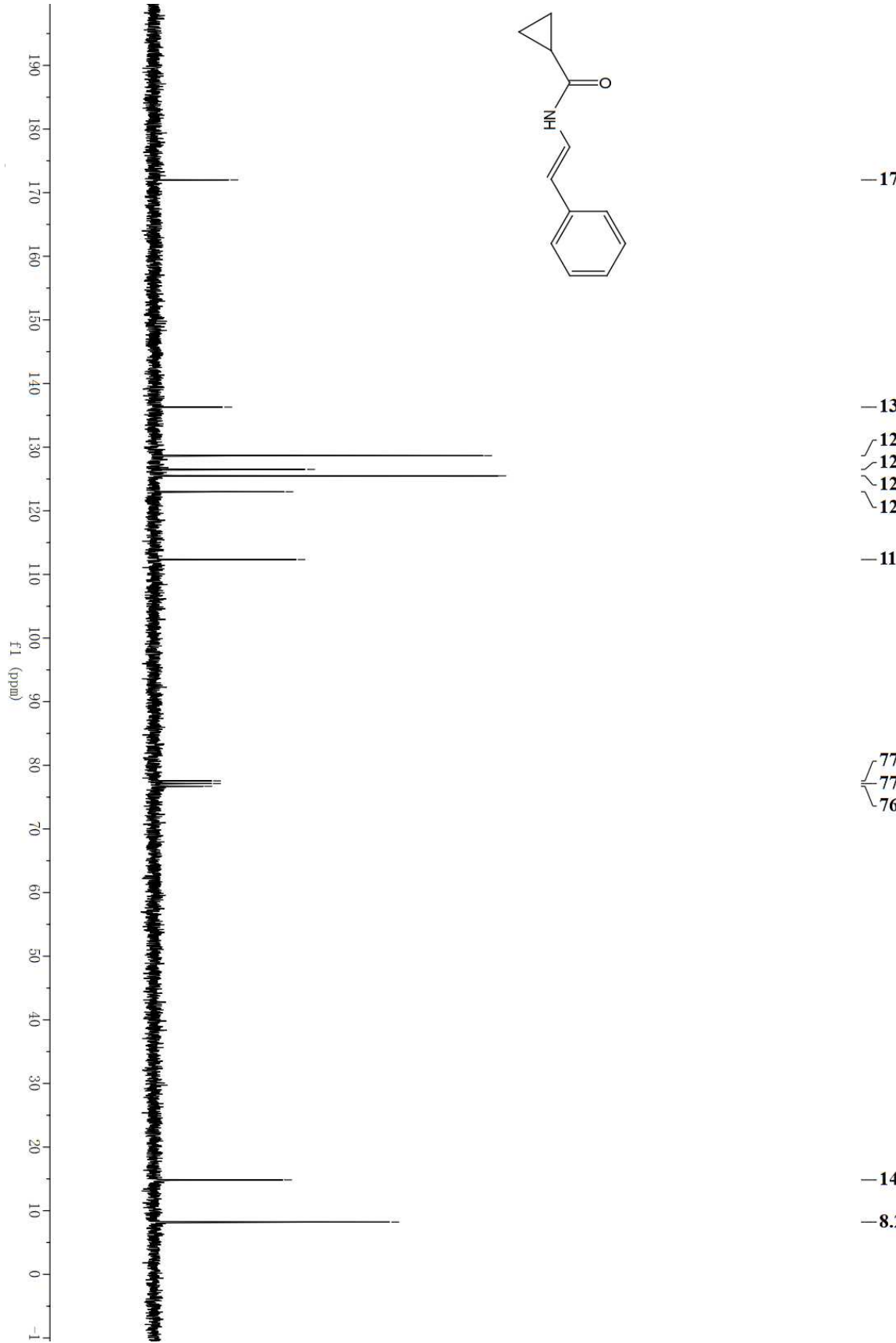
$^{13}\text{C}$  NMR spectrum



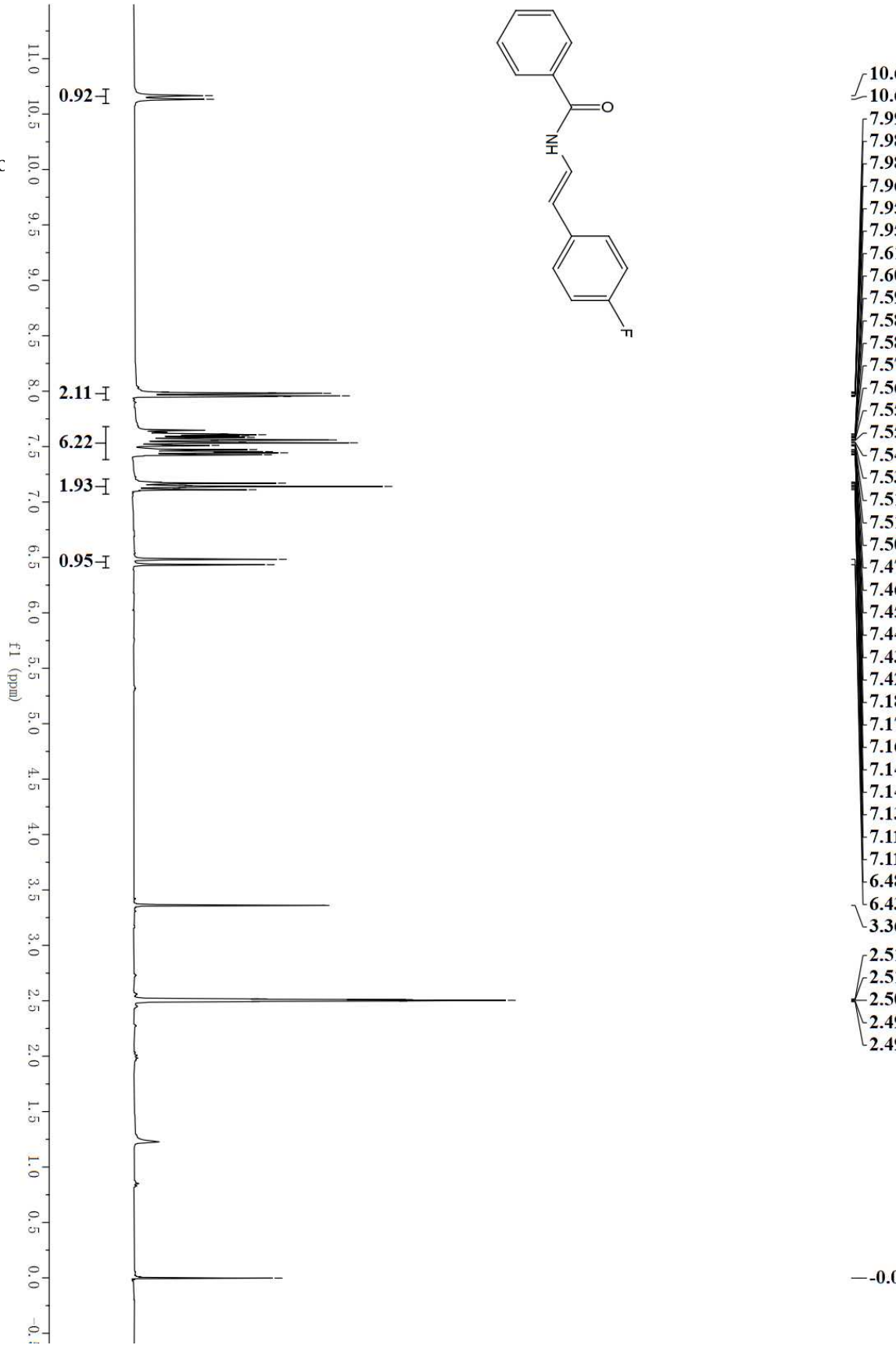
<sup>1</sup>H NMR spectrum c



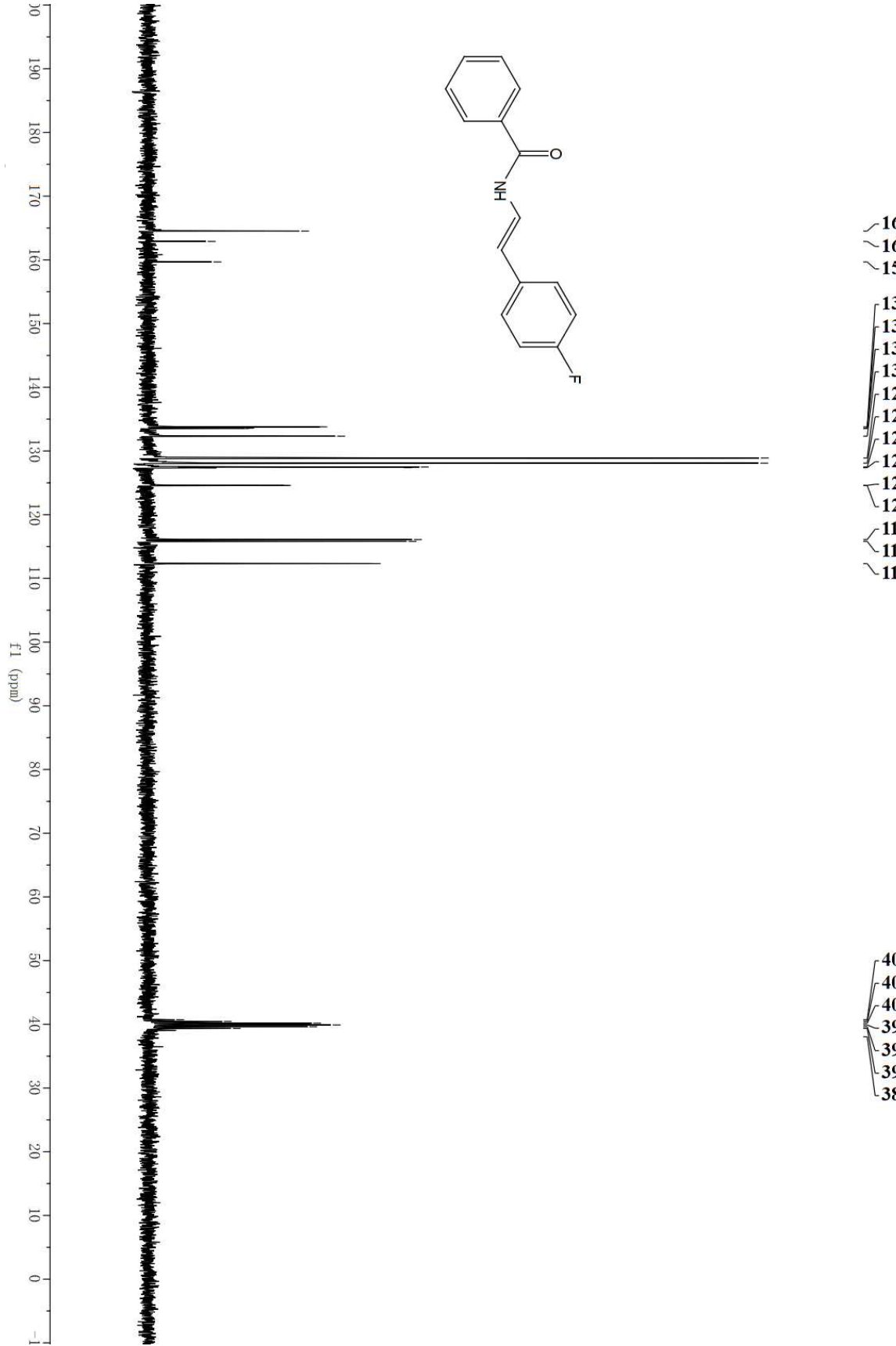
$^{13}\text{C}$  NMR spectrum



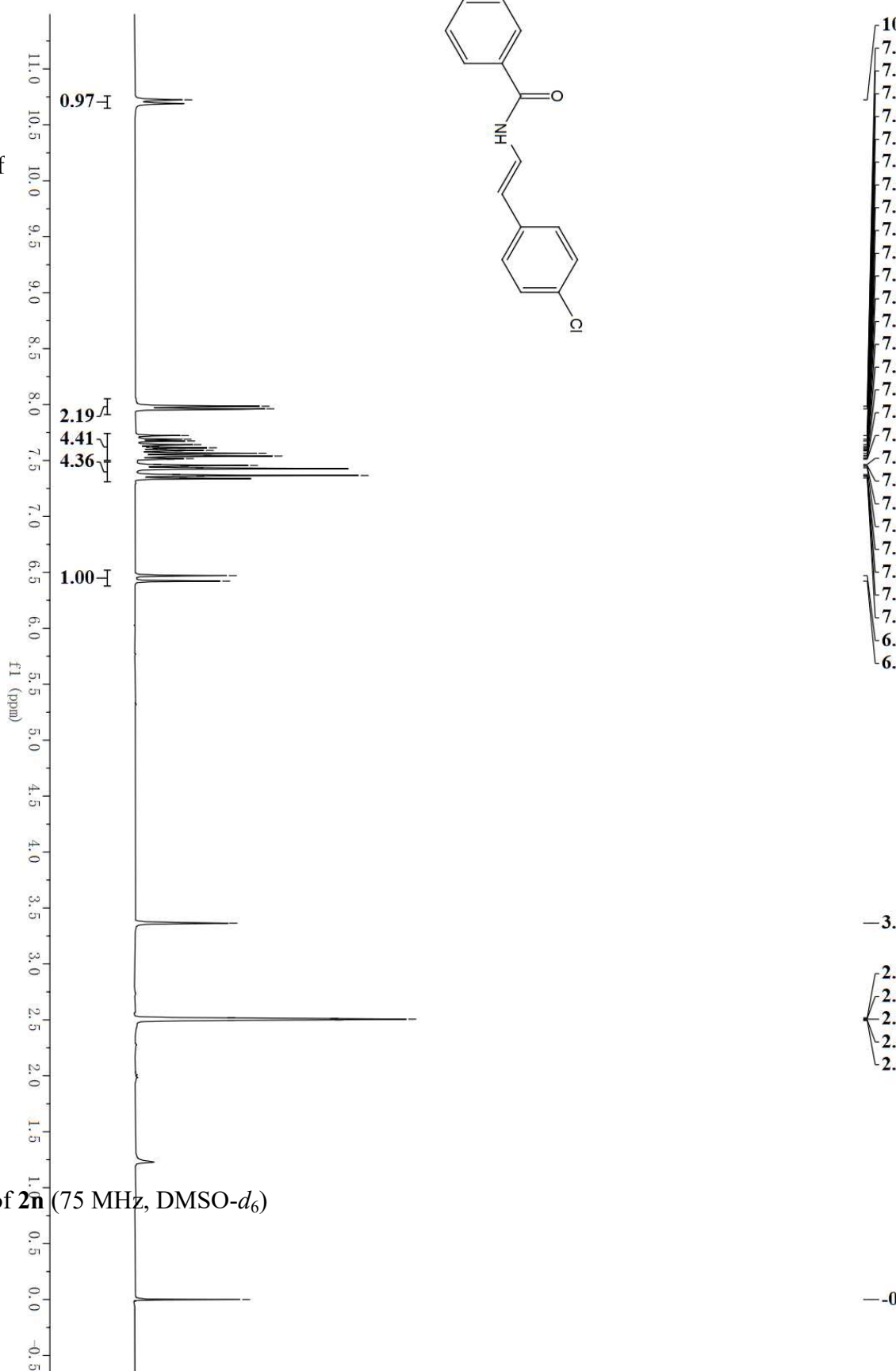
<sup>1</sup>H NMR spectrum c

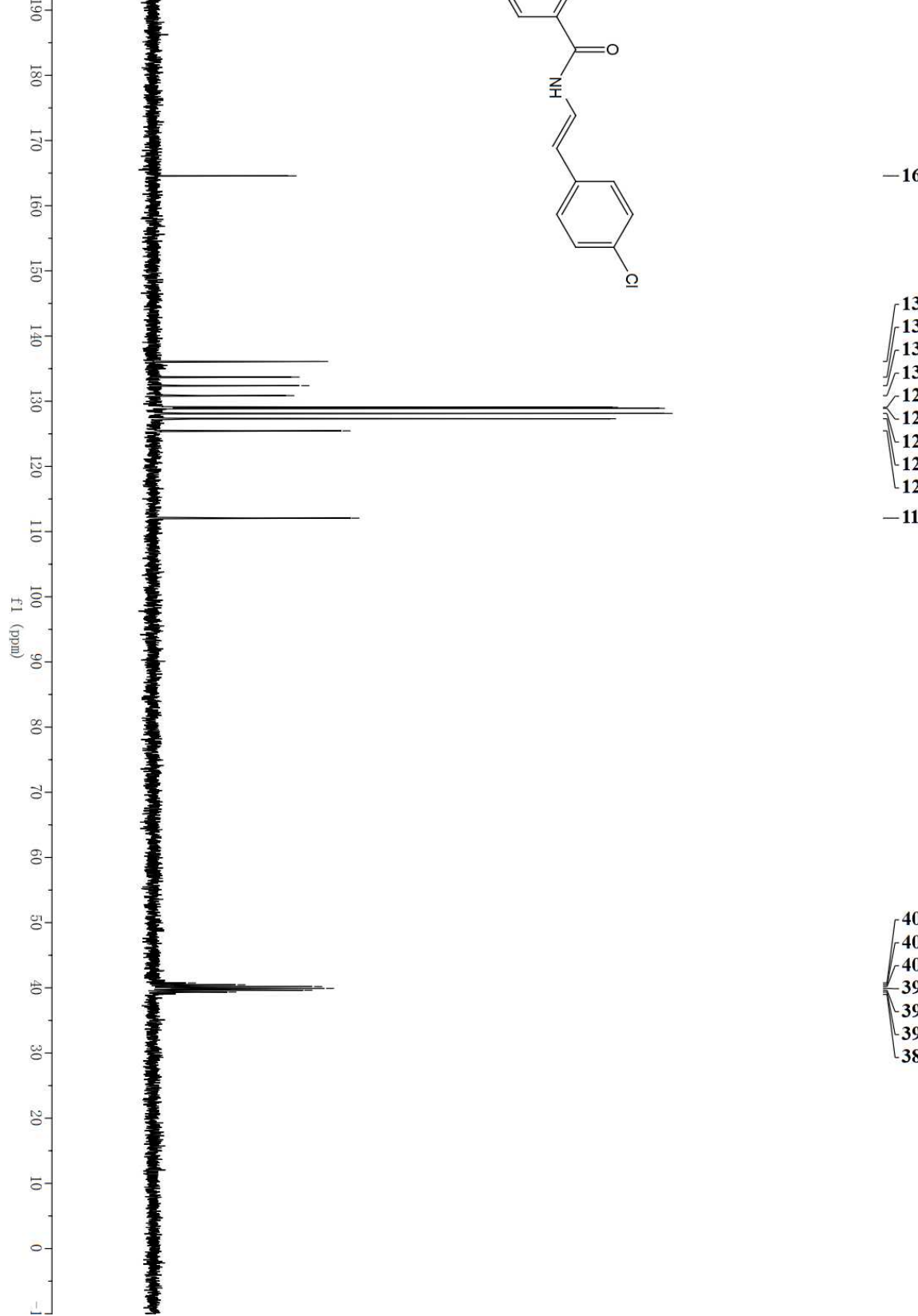


<sup>13</sup>C NMR spectrum

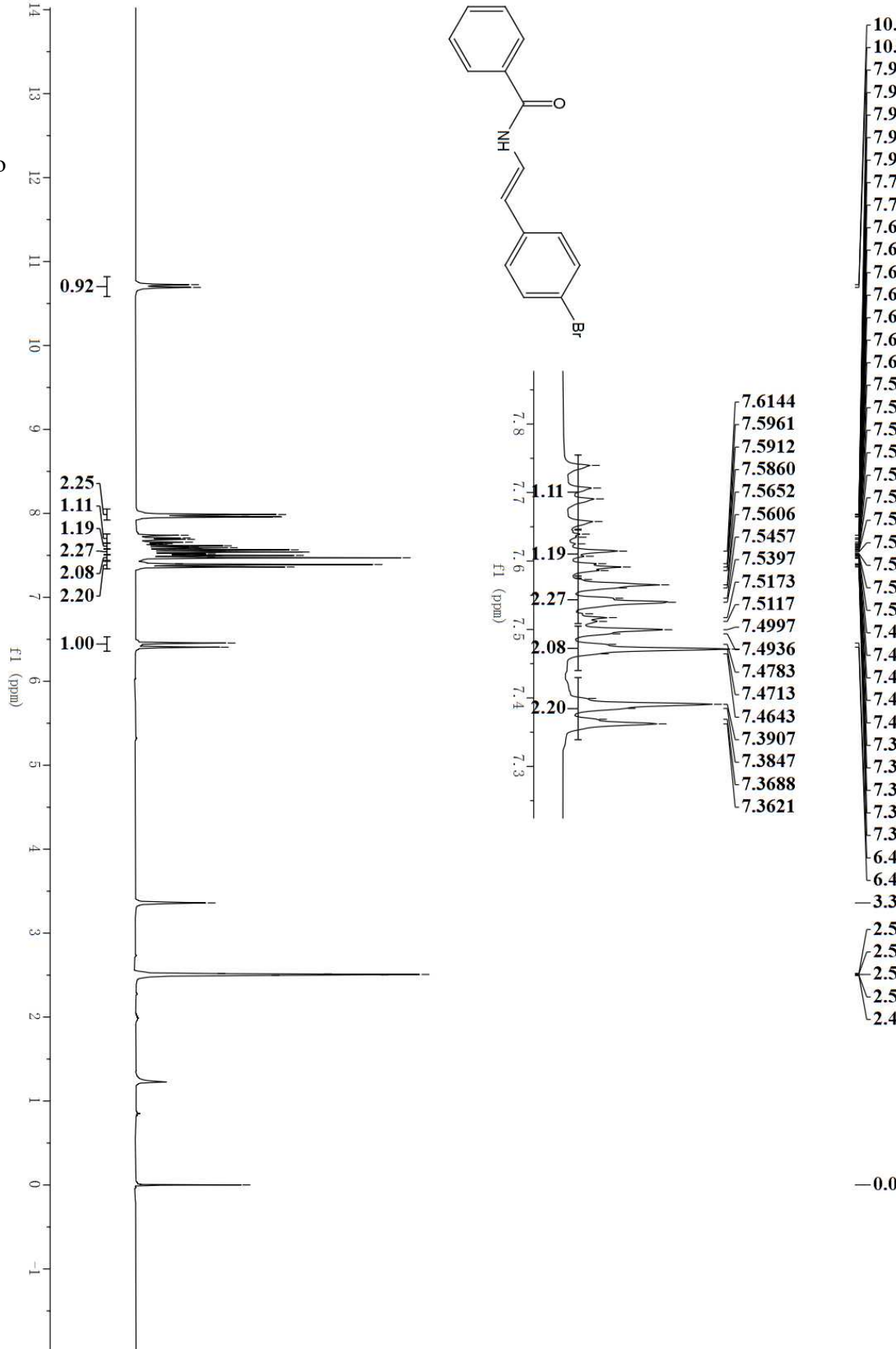


$^1\text{H}$  NMR spectrum of

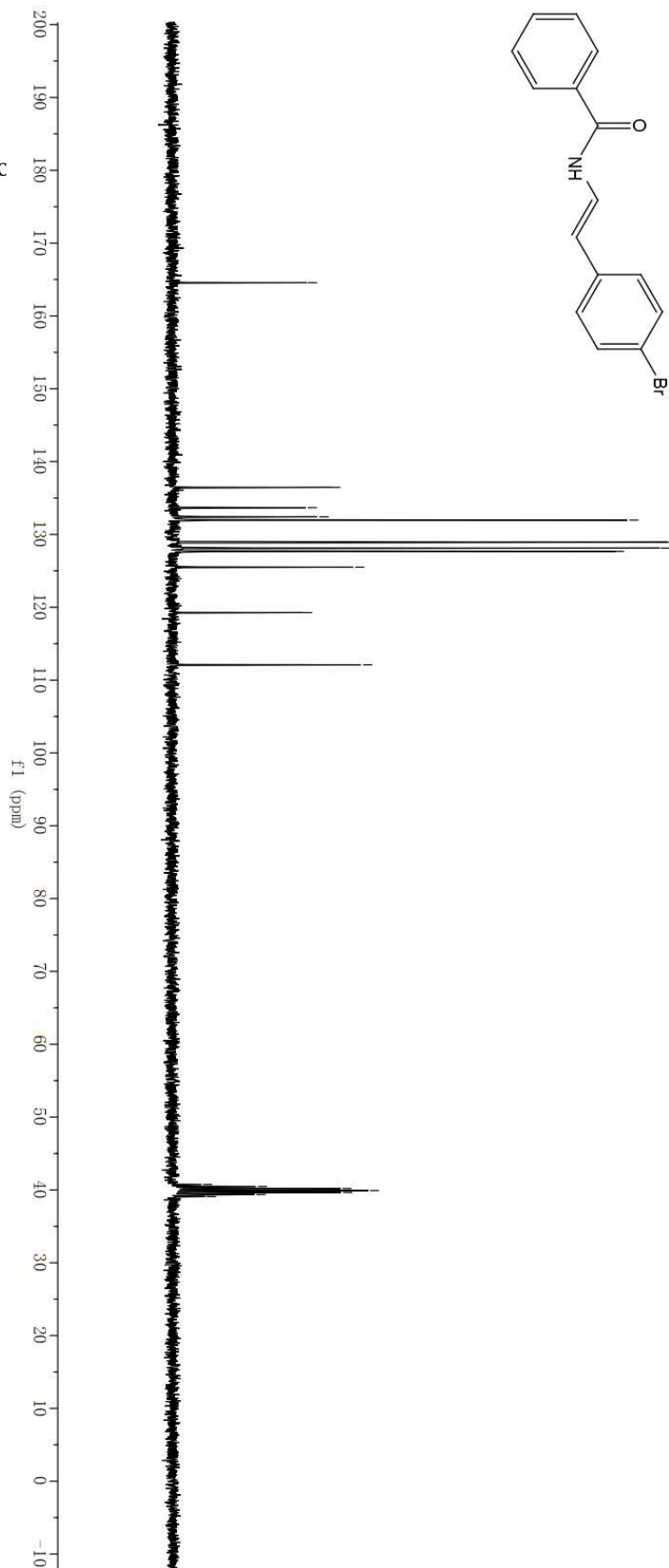




<sup>1</sup>H NMR spectrum of



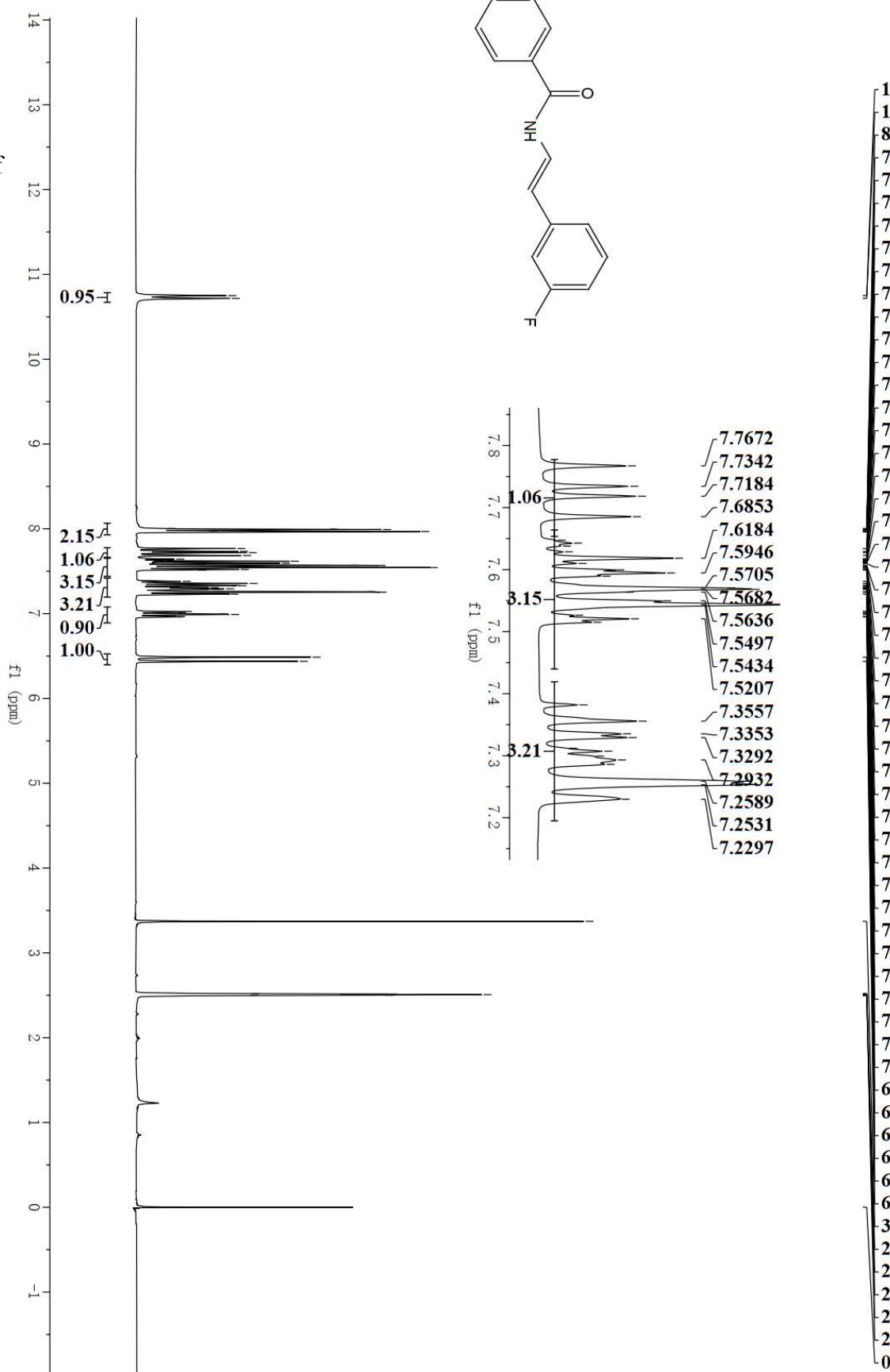
$^{13}\text{C}$  NMR spectrum c



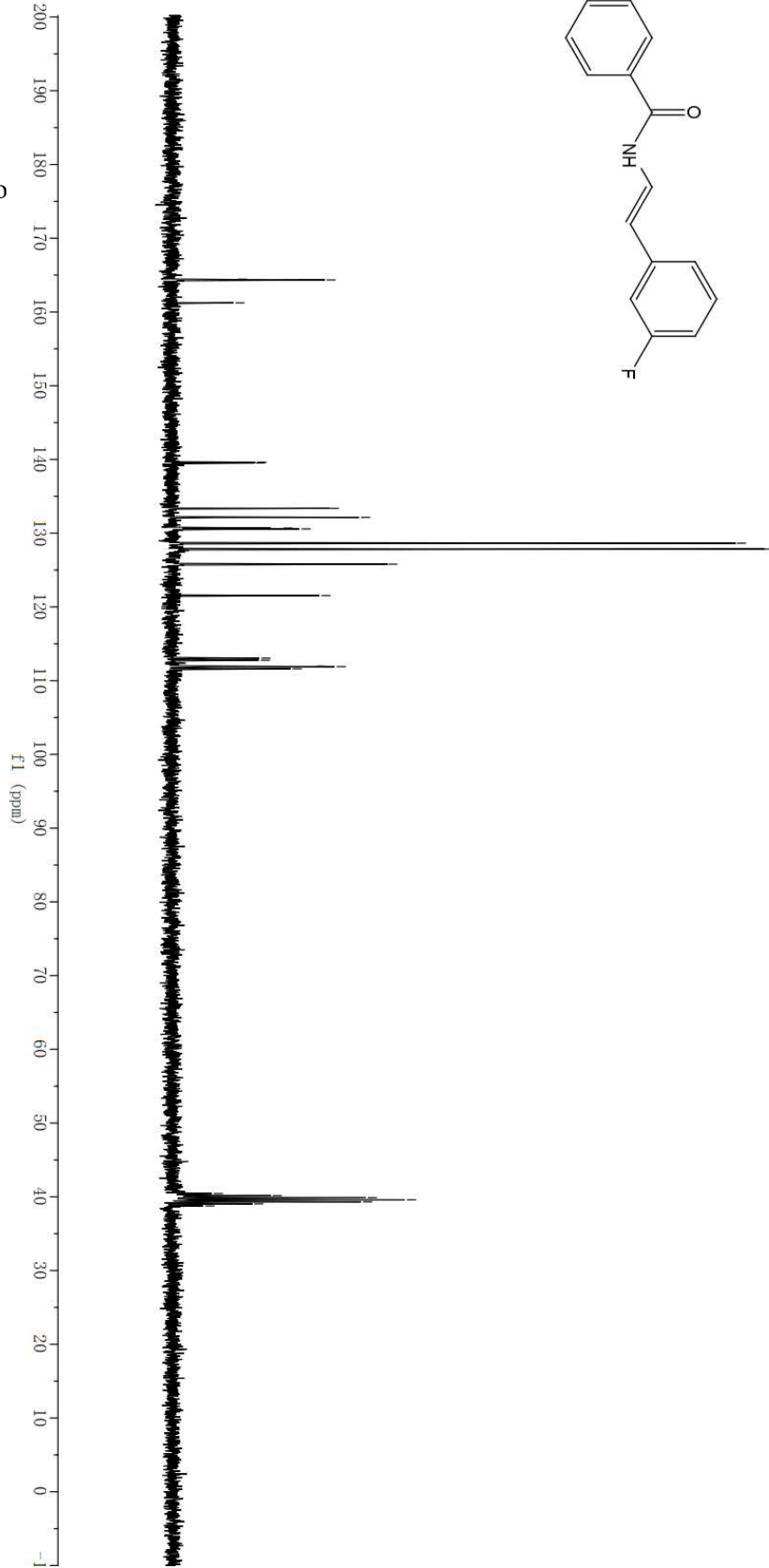
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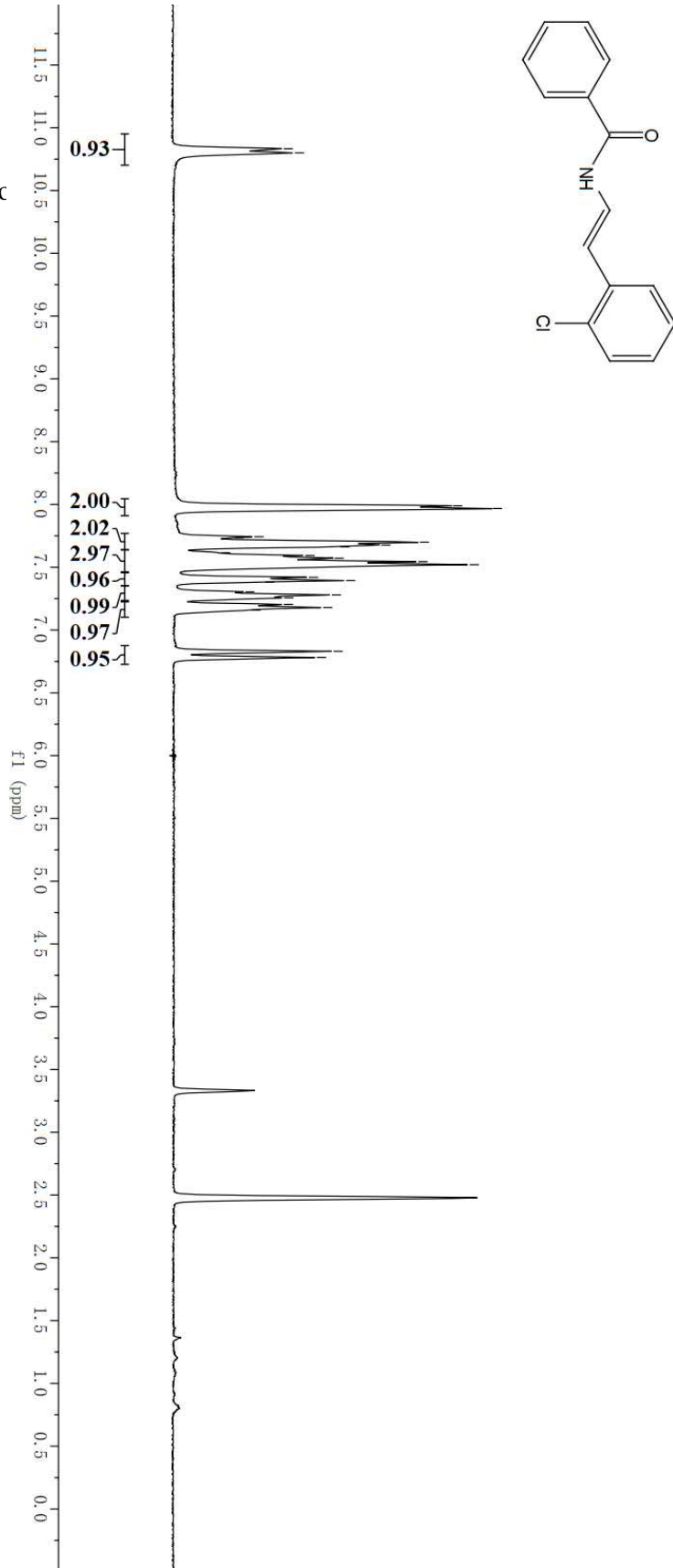
<sup>1</sup>H NMR spectrum of



$^{13}\text{C}$  NMR spectrum of

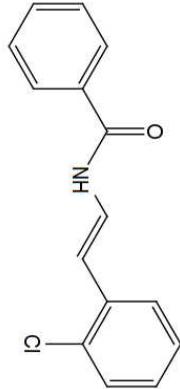


<sup>1</sup>H NMR spectrum c



10.3  
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7.6  
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7.5  
7.5  
7.5  
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7.2  
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7.1  
6.8  
6.7

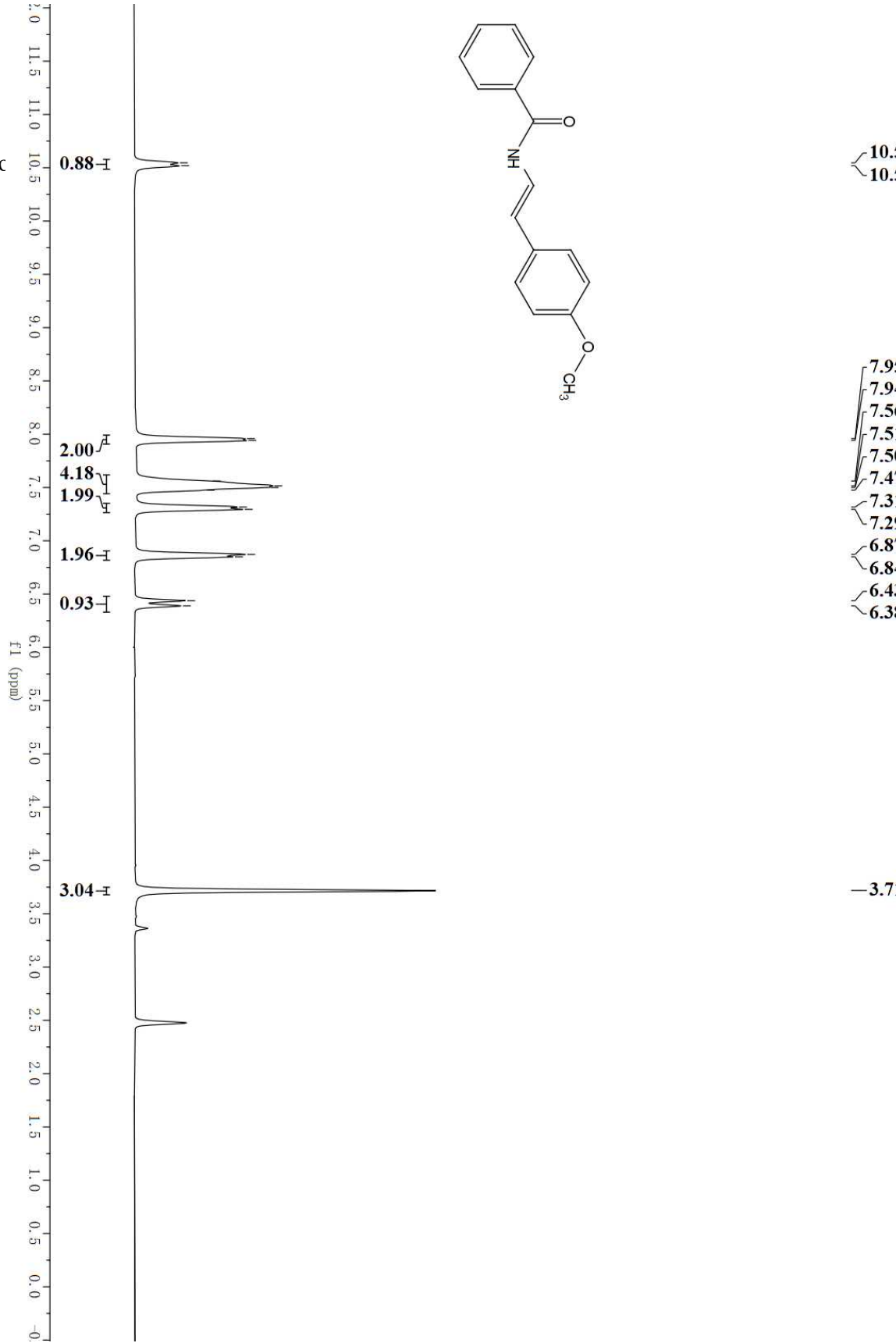
$^{13}\text{C}$  NMR spectrum c



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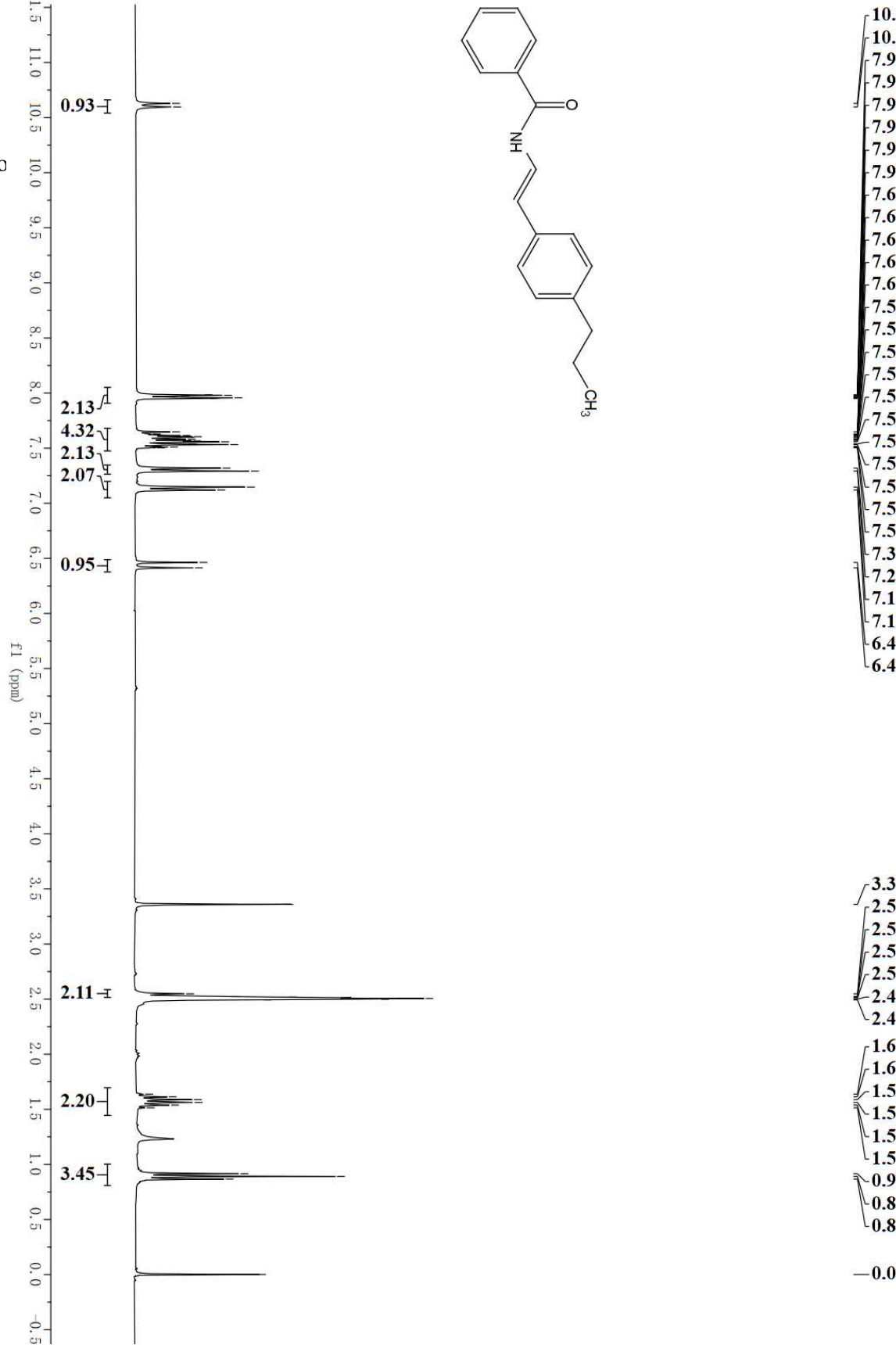
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<sup>1</sup>H NMR spectrum c

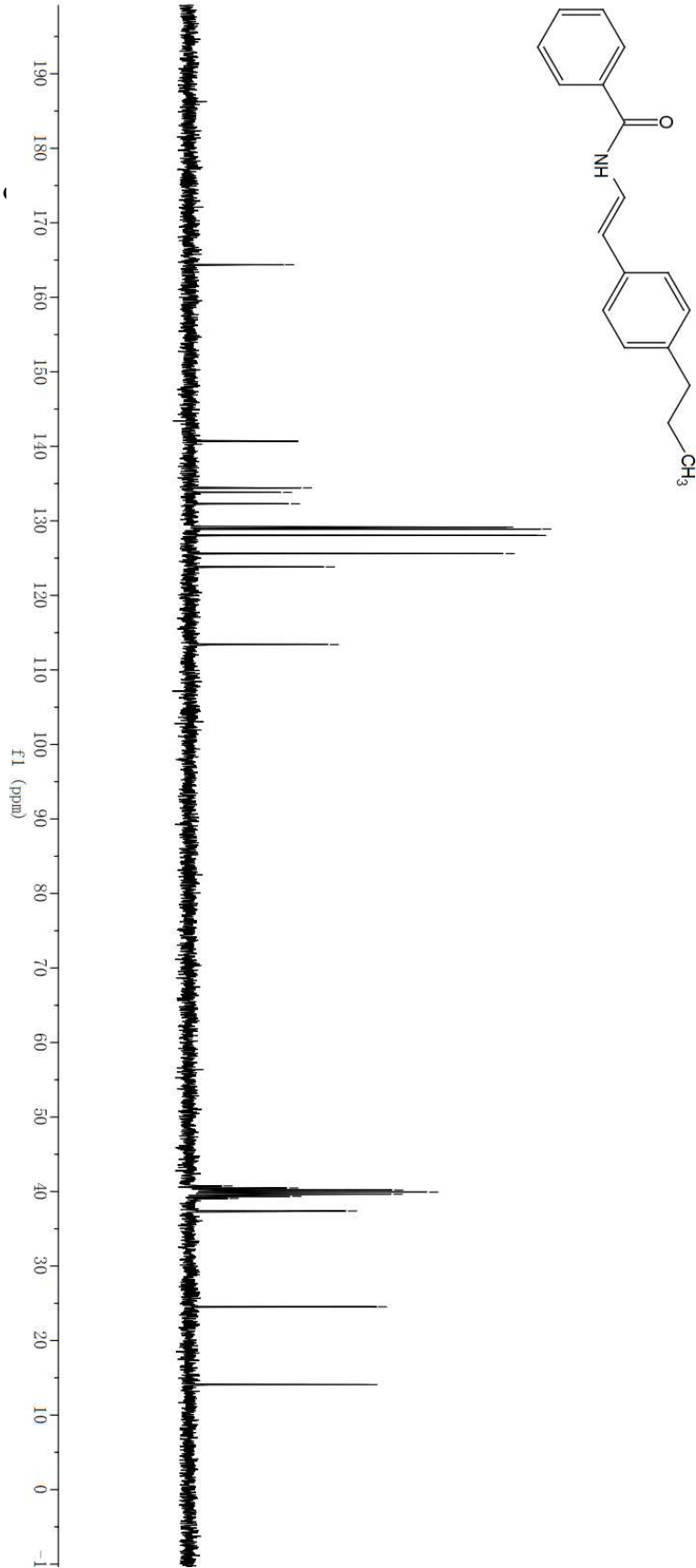




<sup>1</sup>H NMR spectrum of



<sup>13</sup>C NMR spectrum



- 10

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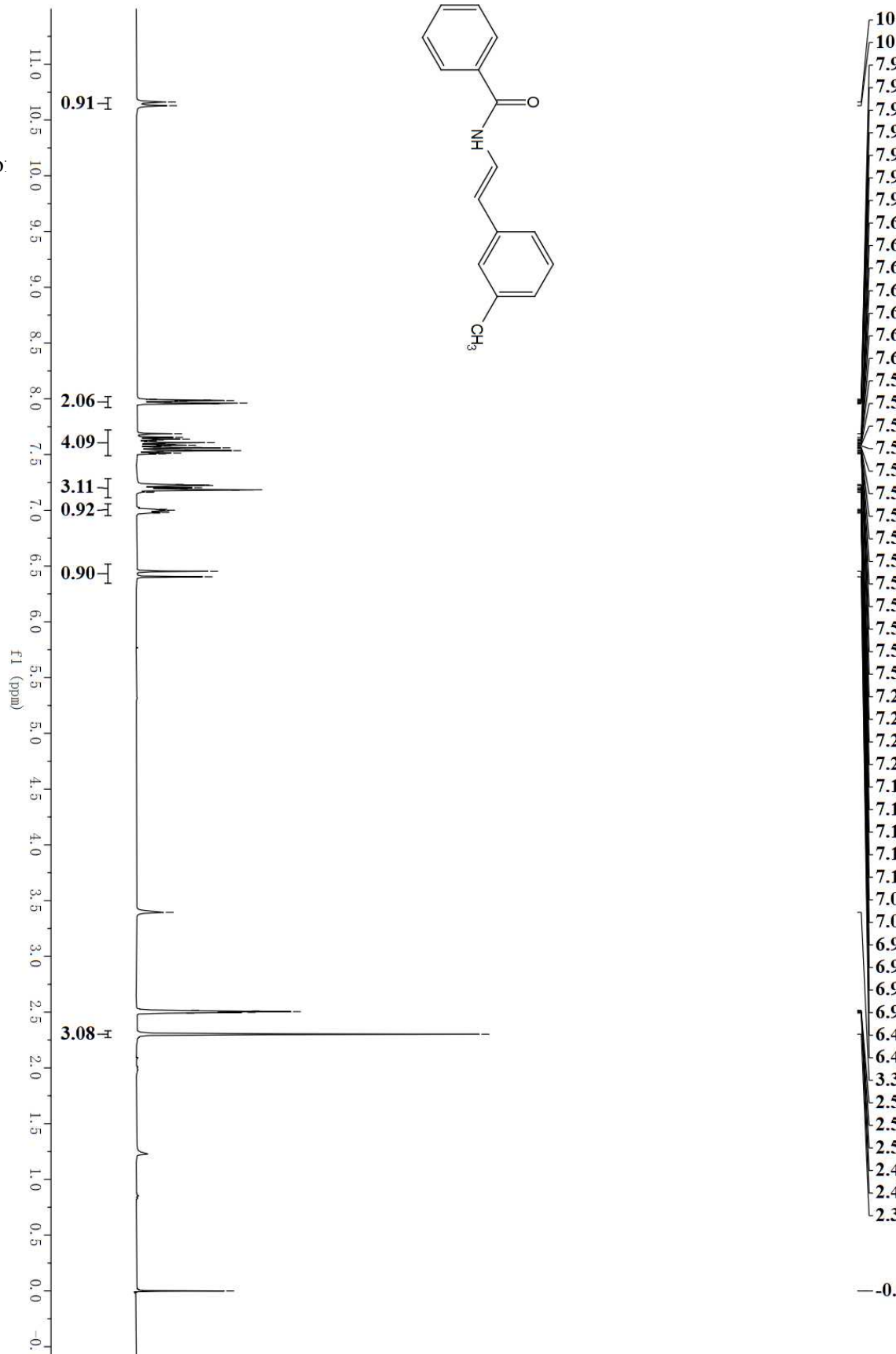
- 11

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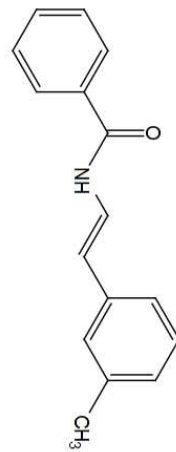
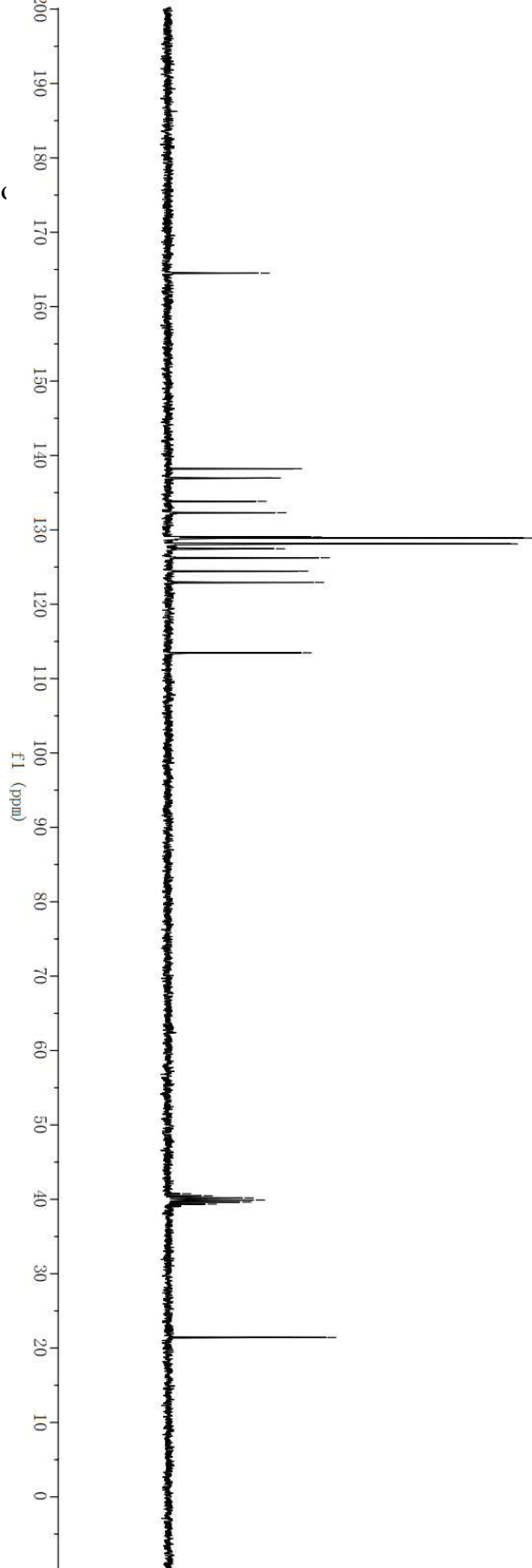
- 24

- 14

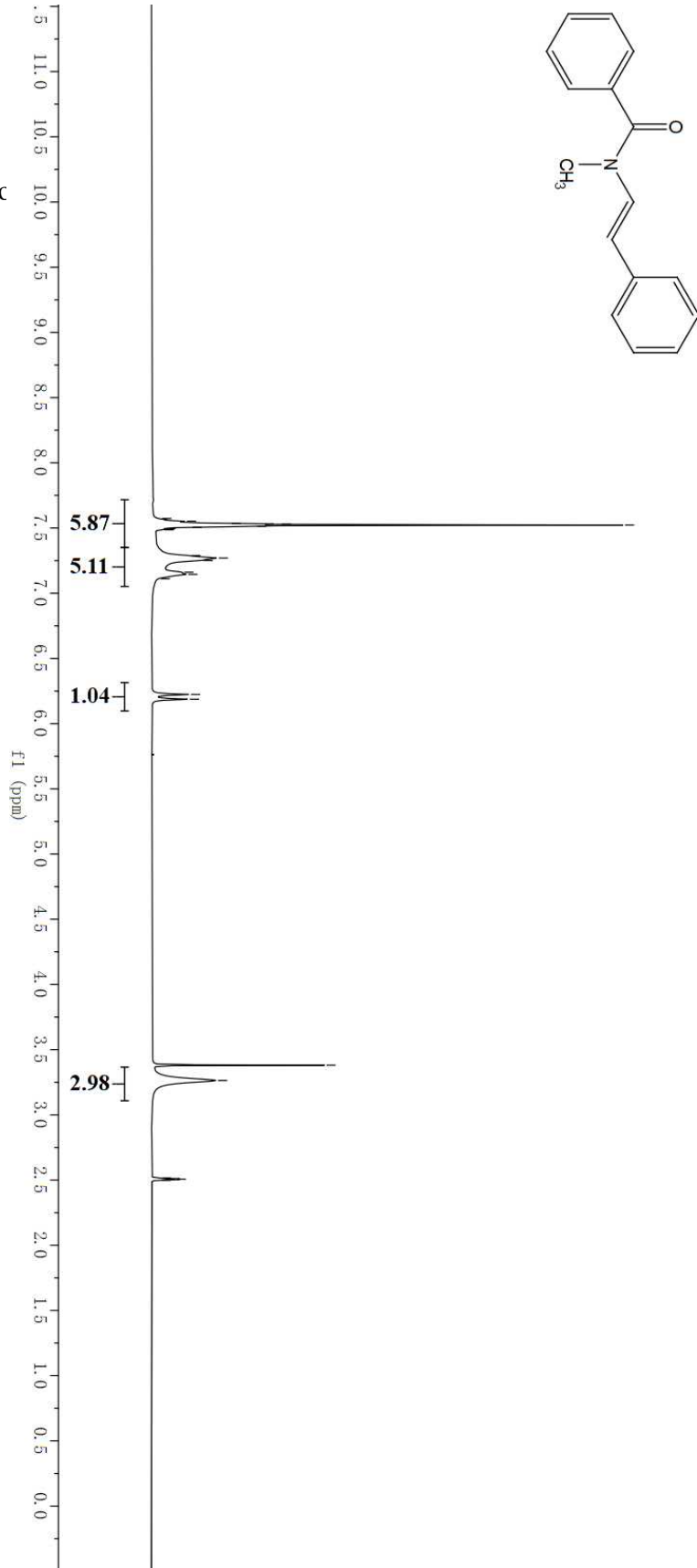
$^1\text{H}$  NMR spectrum of:



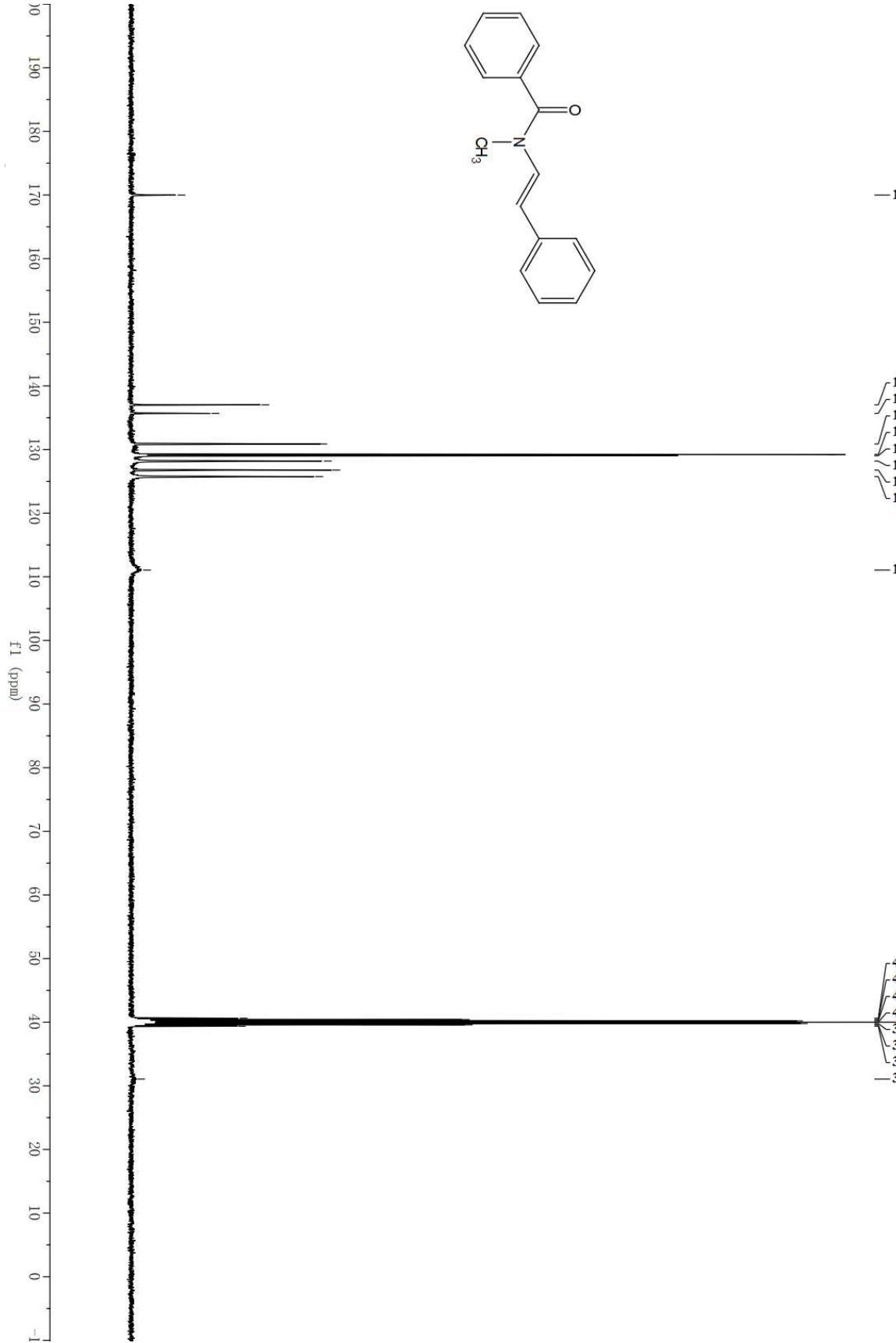
<sup>13</sup>C NMR spectrum (



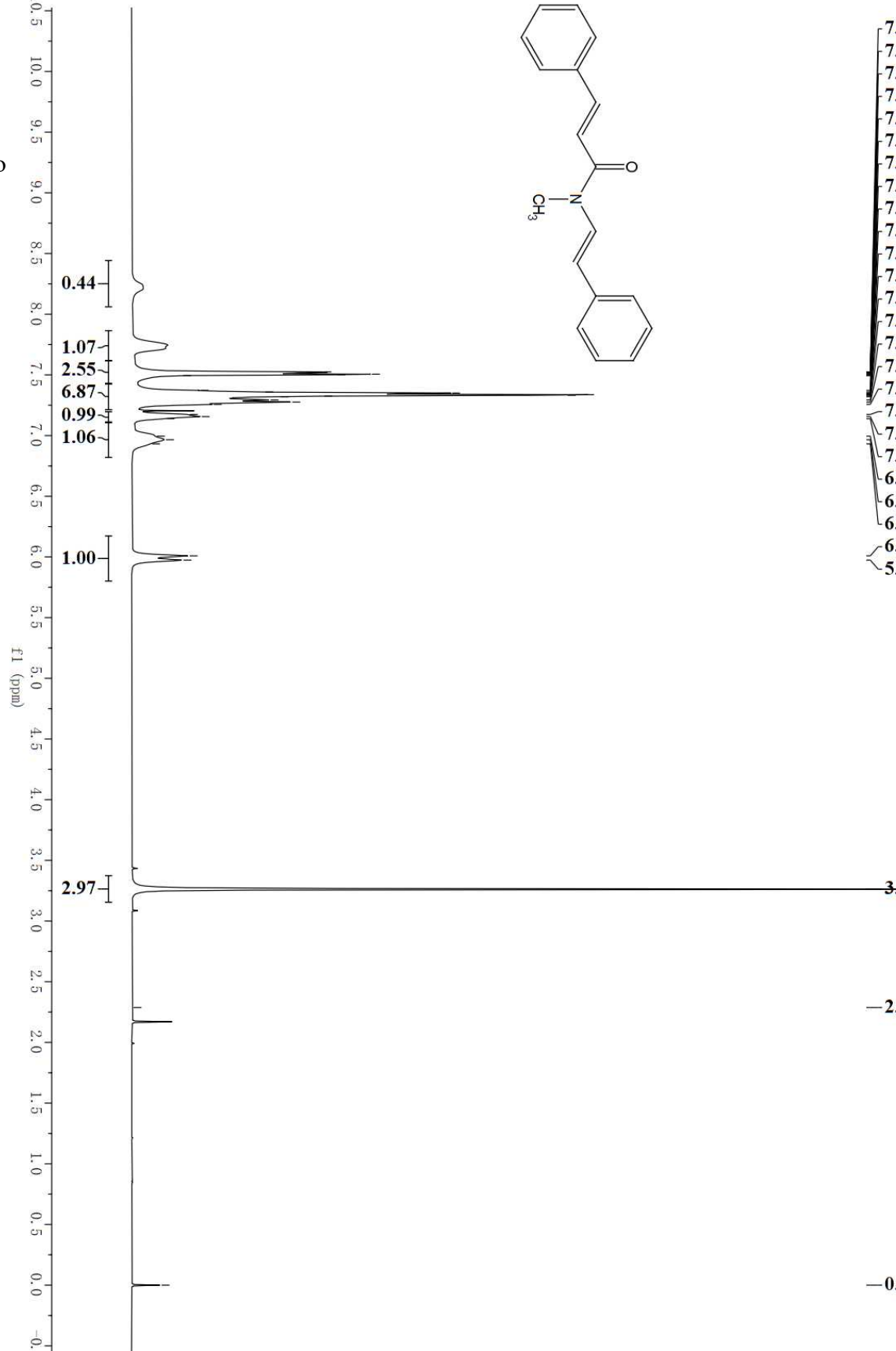
<sup>1</sup>H NMR spectrum c



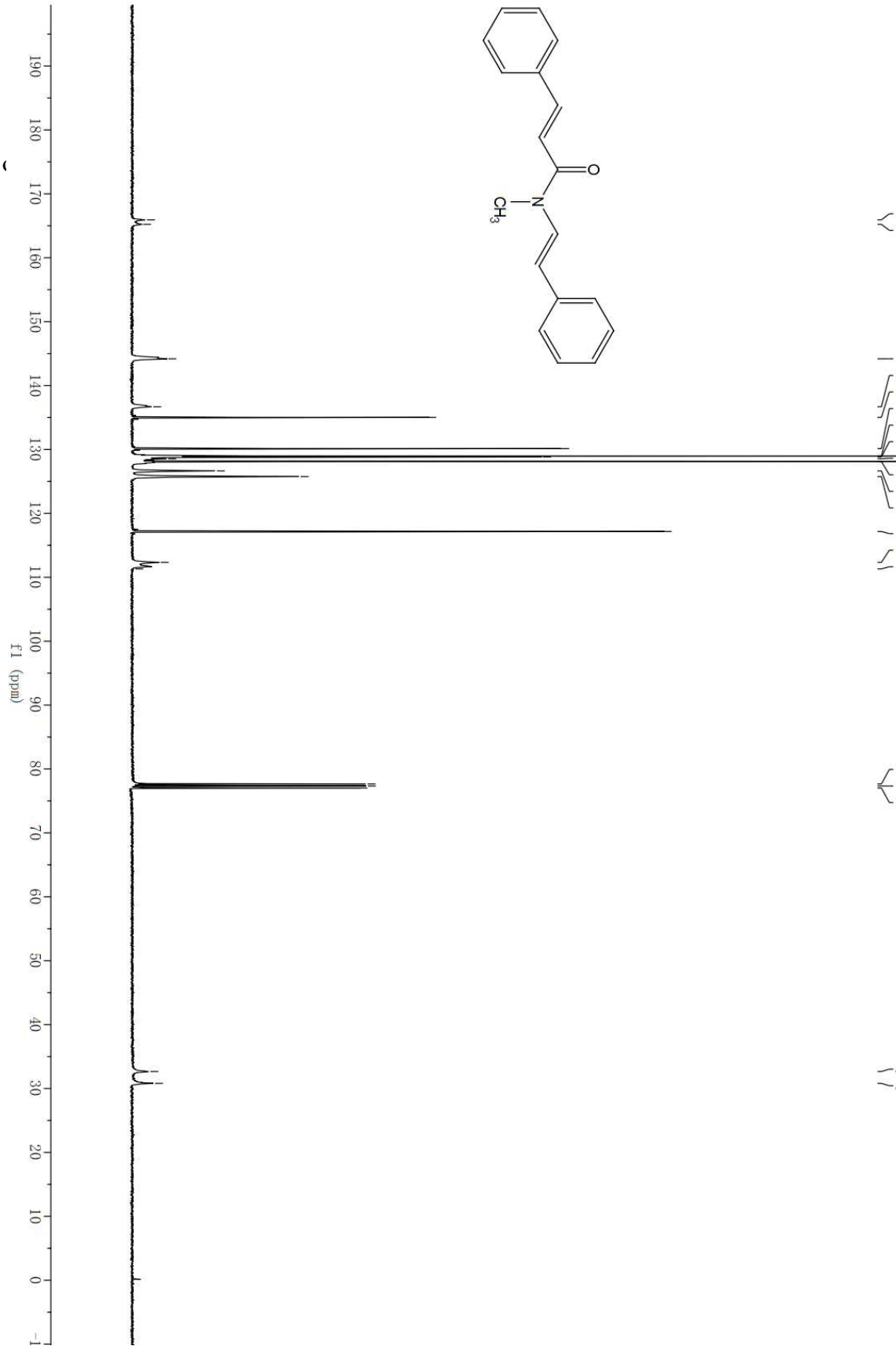
$^{13}\text{C}$  NMR spectrum



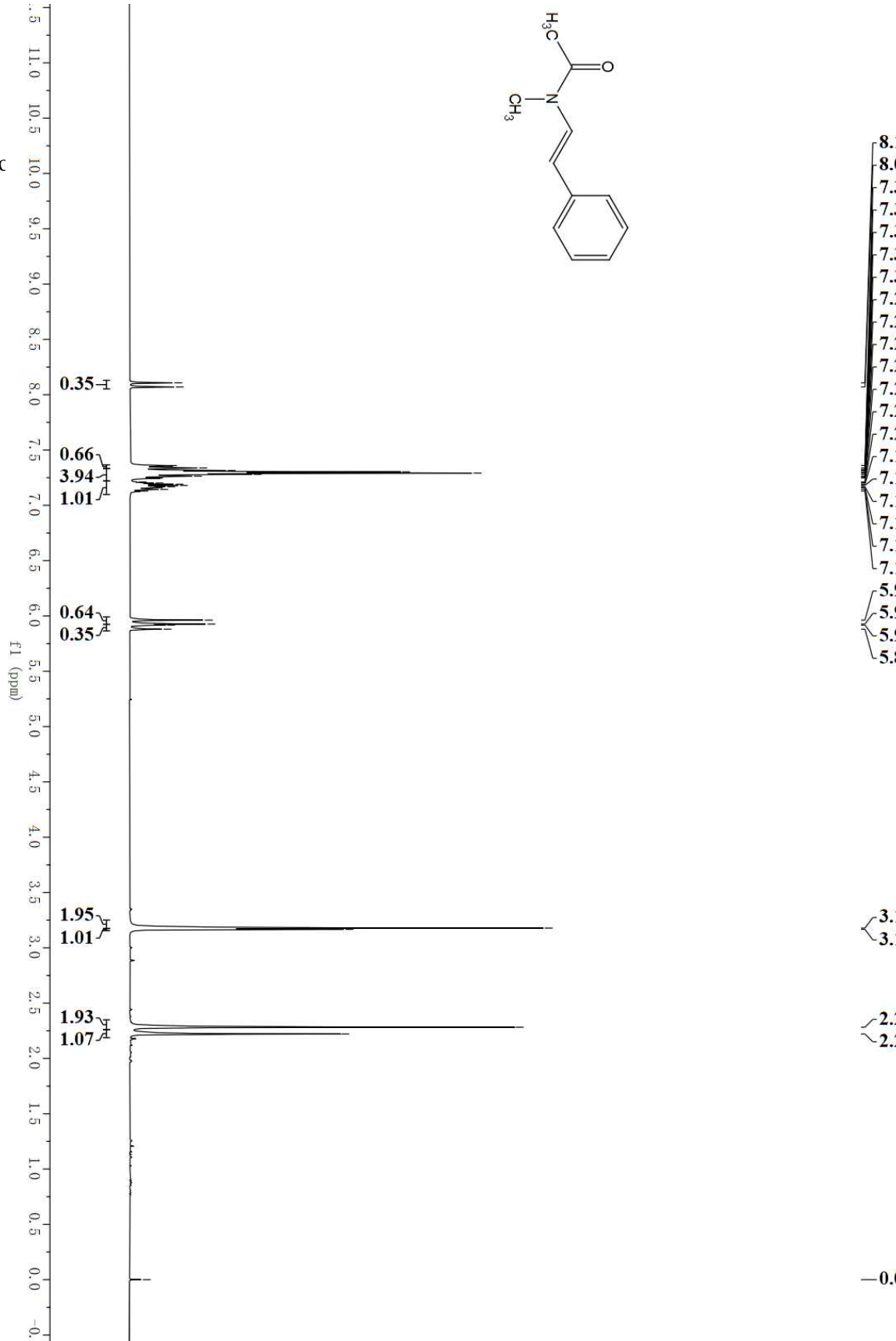
<sup>1</sup>H NMR spectrum of



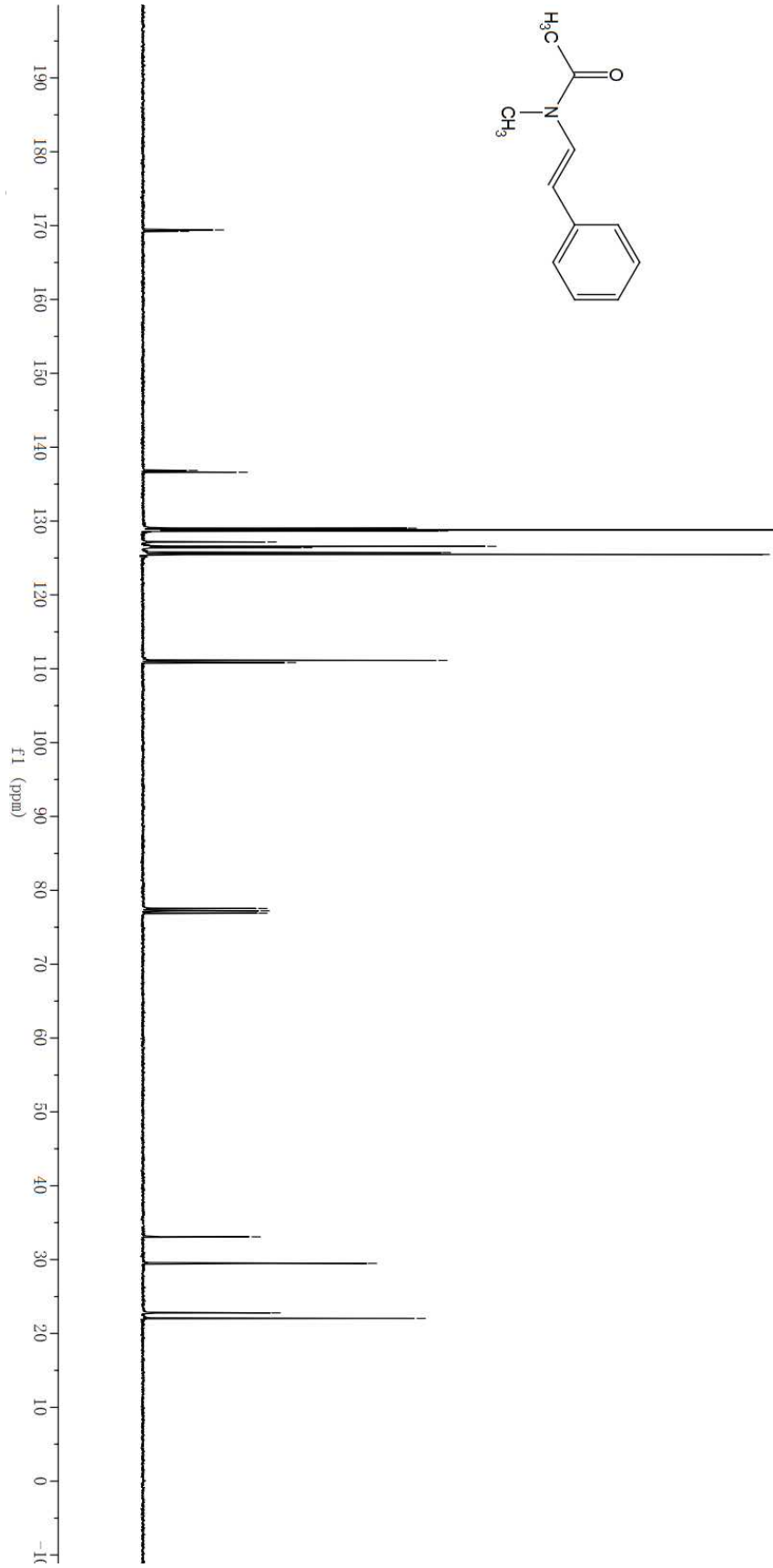
$^{13}\text{C}$  NMR spectrum (



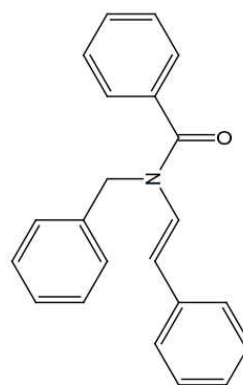
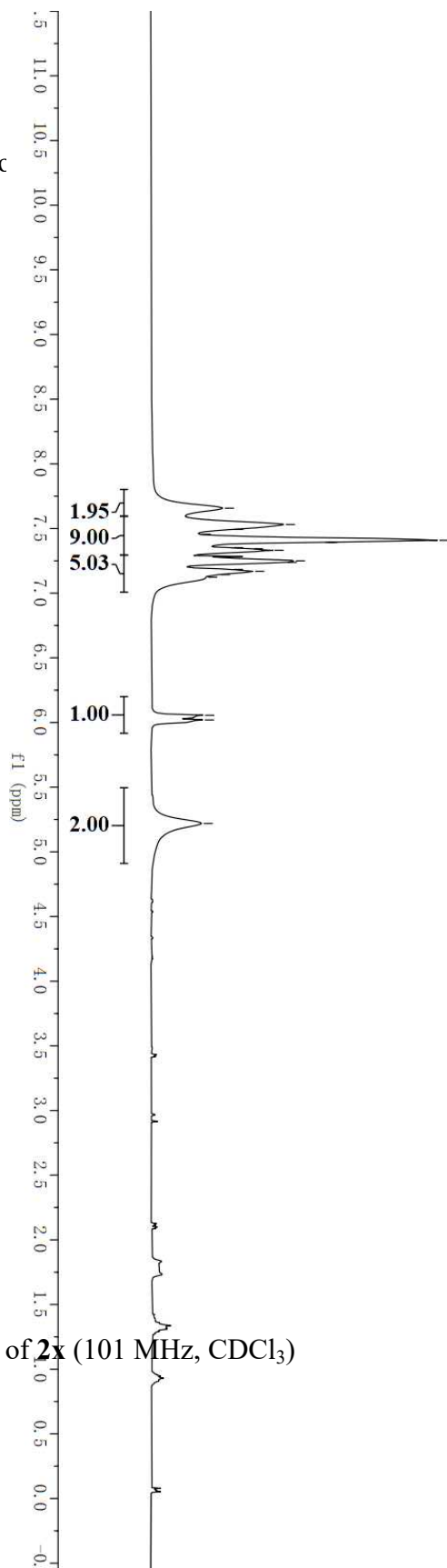
<sup>1</sup>H NMR spectrum c



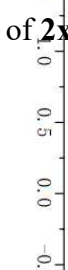
$^{13}\text{C}$  NMR spectrum

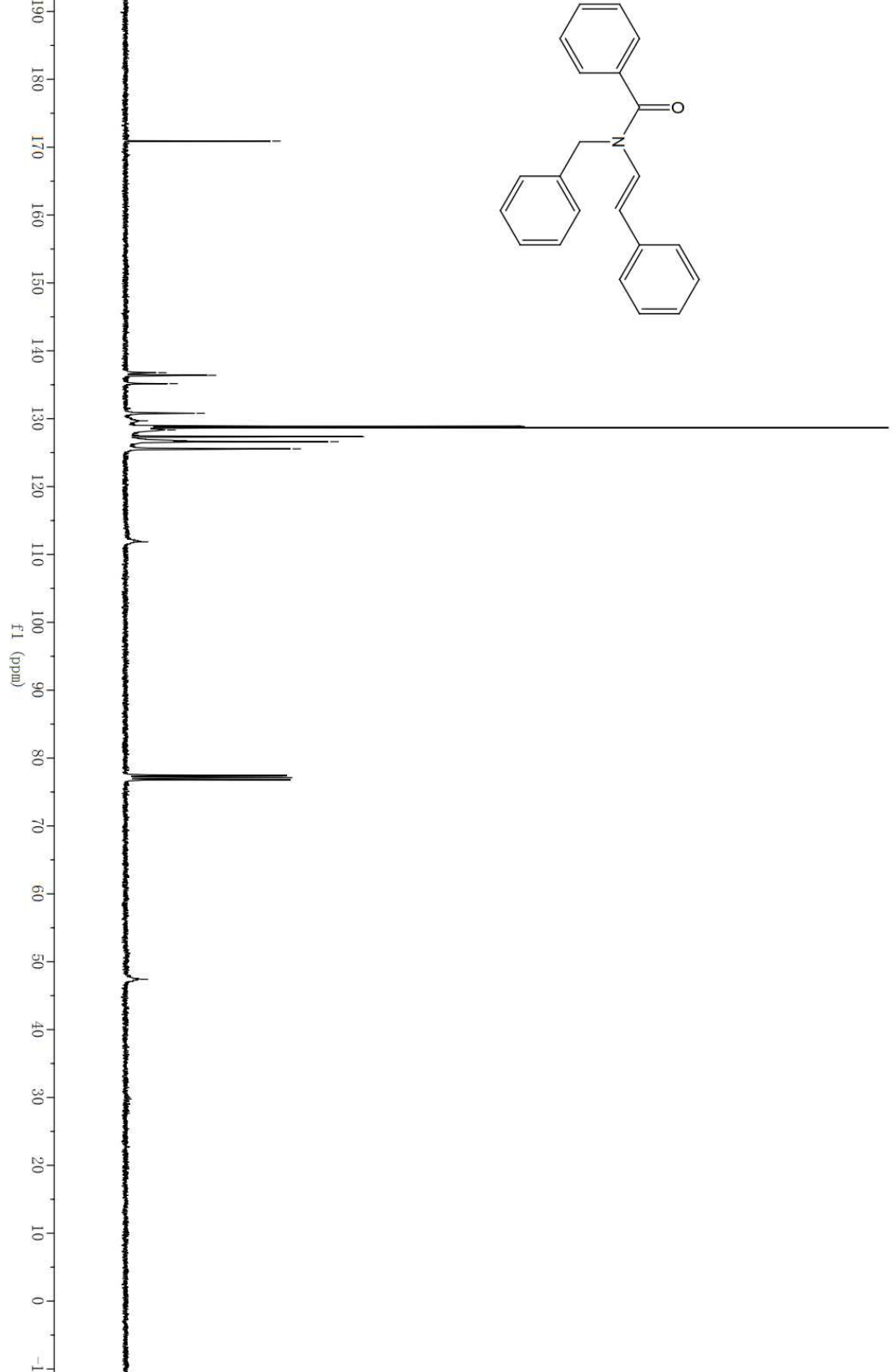


$^1\text{H}$  NMR spectrum c

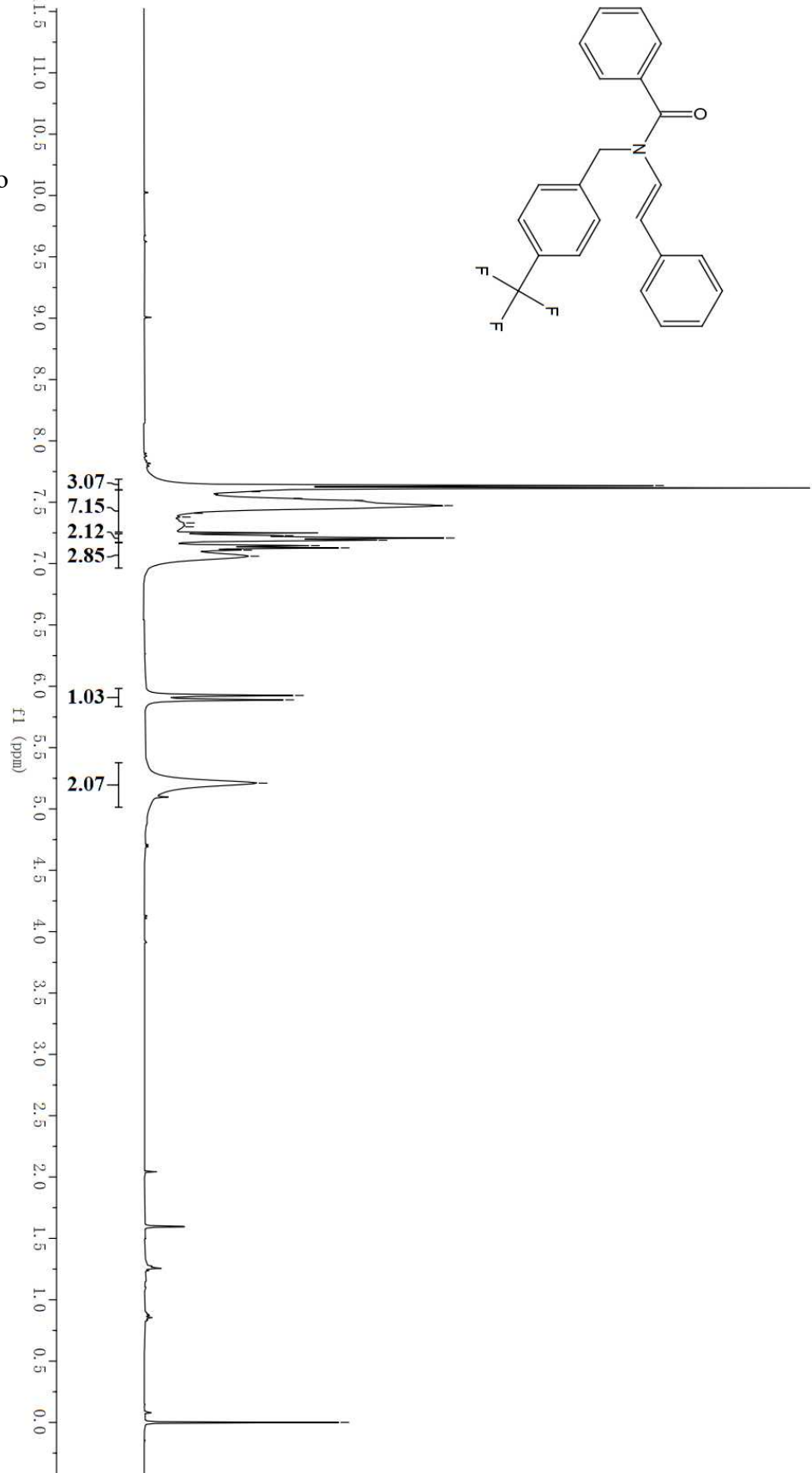


$^{13}\text{C}$  NMR spectrum of **2x** (101 MHz,  $\text{CDCl}_3$ )



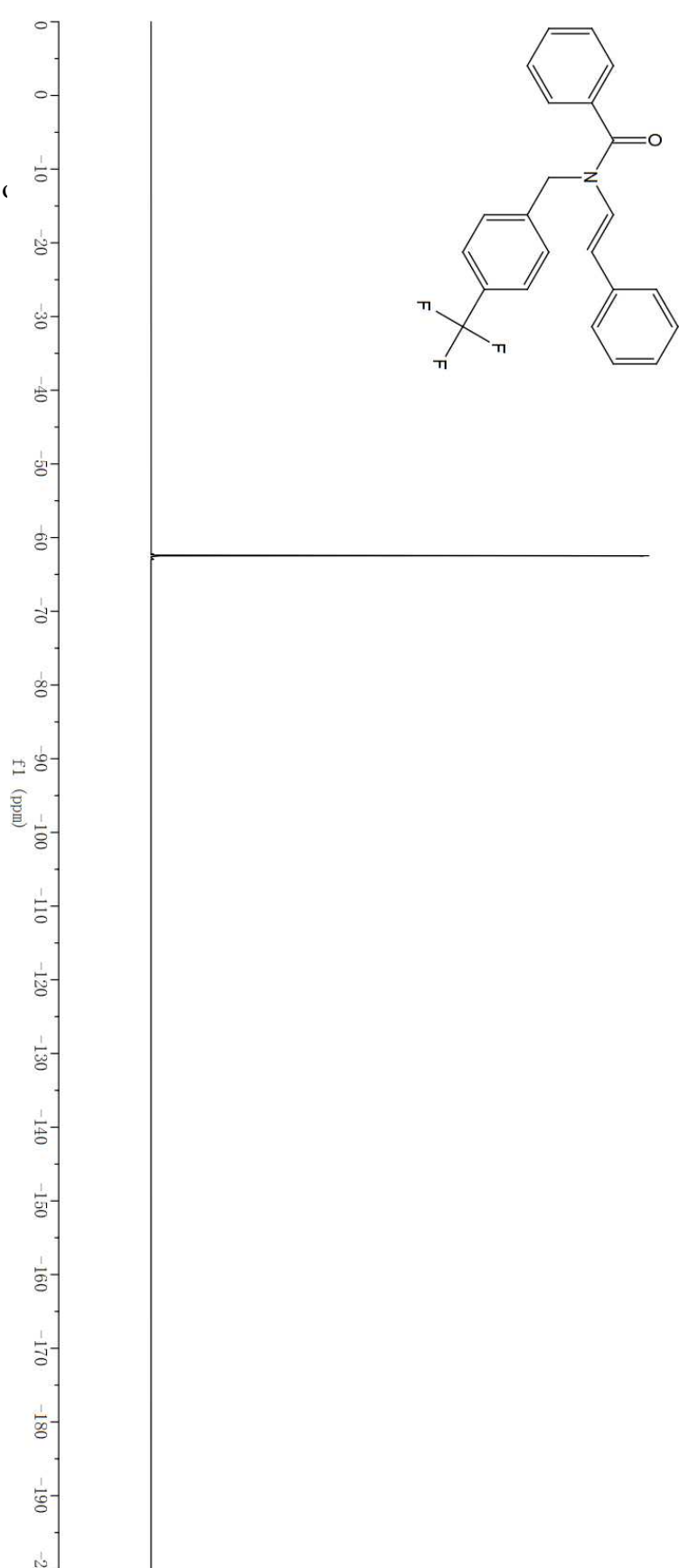


<sup>1</sup>H NMR spectrum of



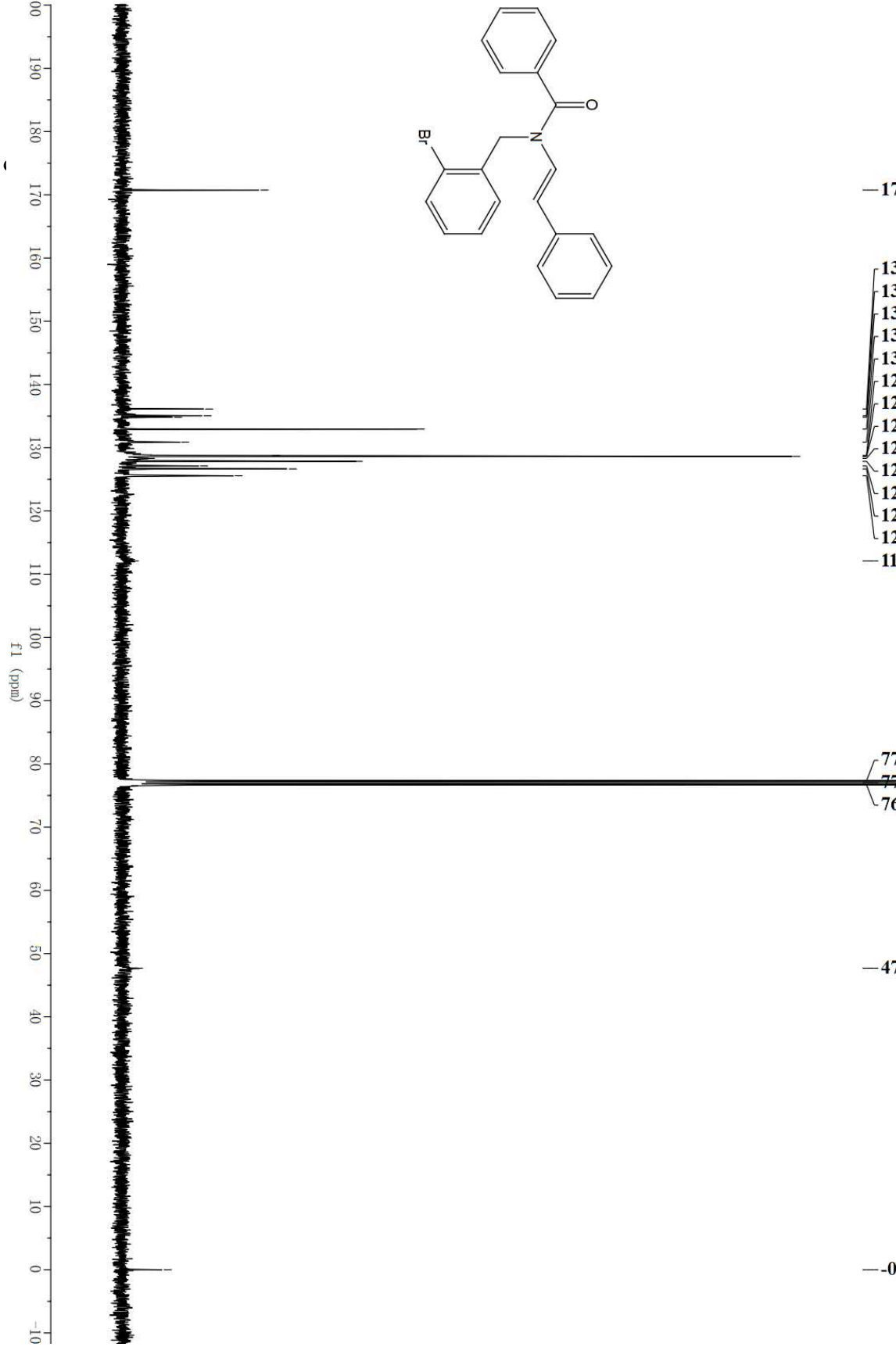


$^{19}\text{F}$  NMR spectrum (

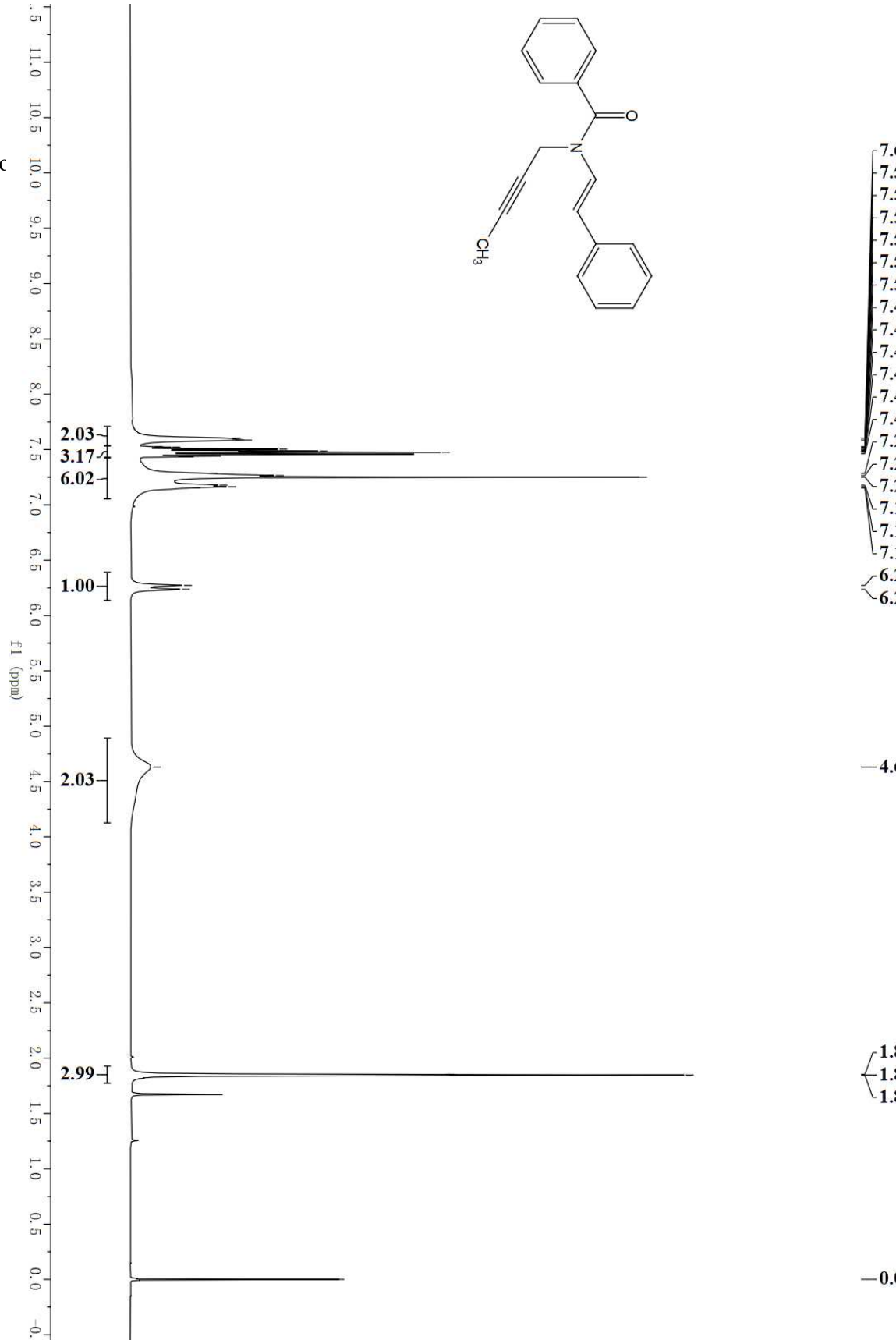




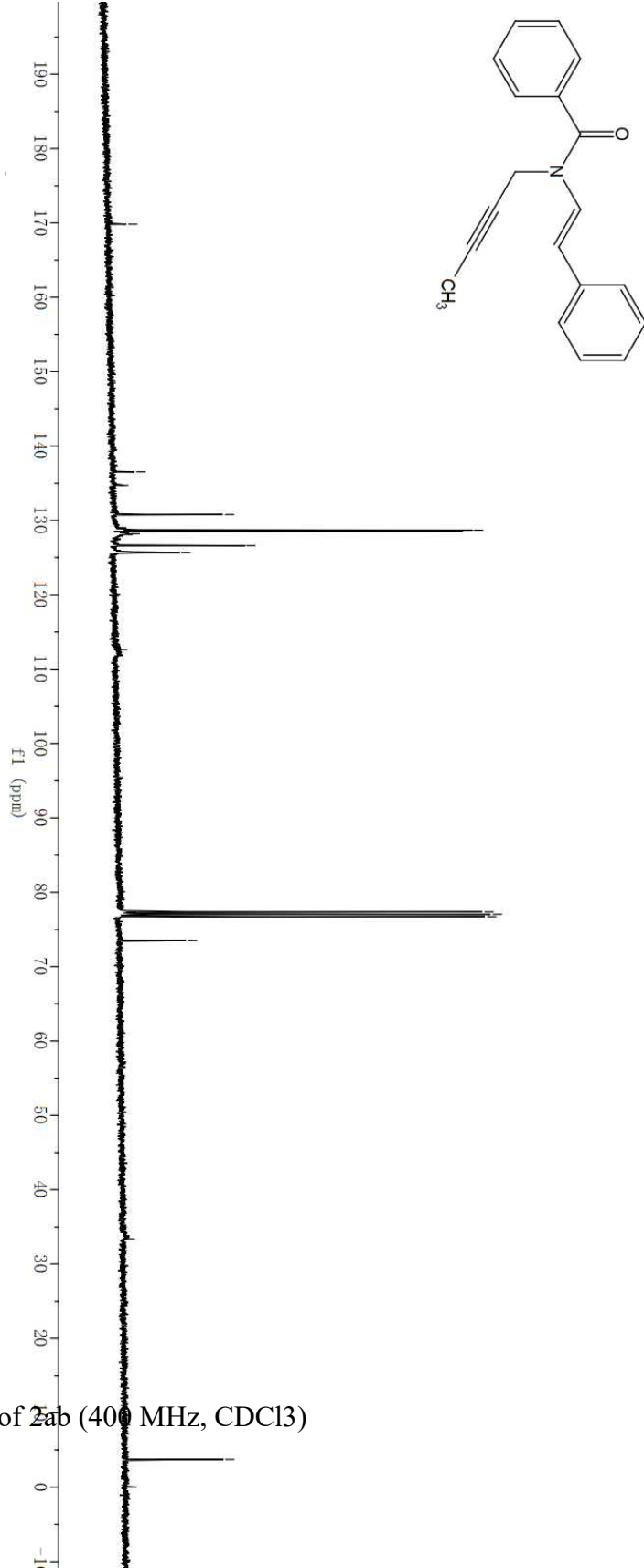
$^{13}\text{C}$  NMR spectrum



<sup>1</sup>H NMR spectrum c

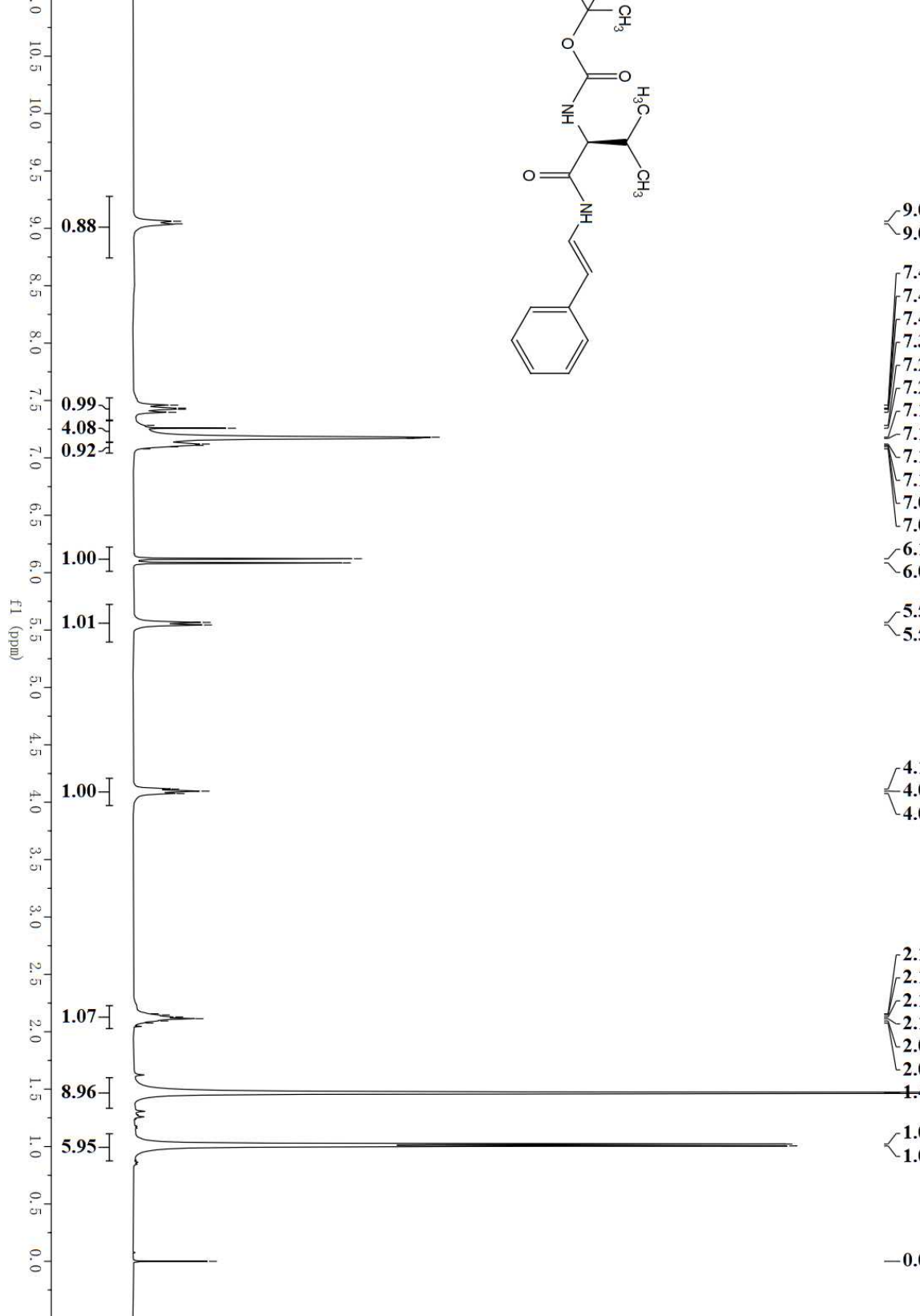


$^{13}\text{C}$  NMR spectrum

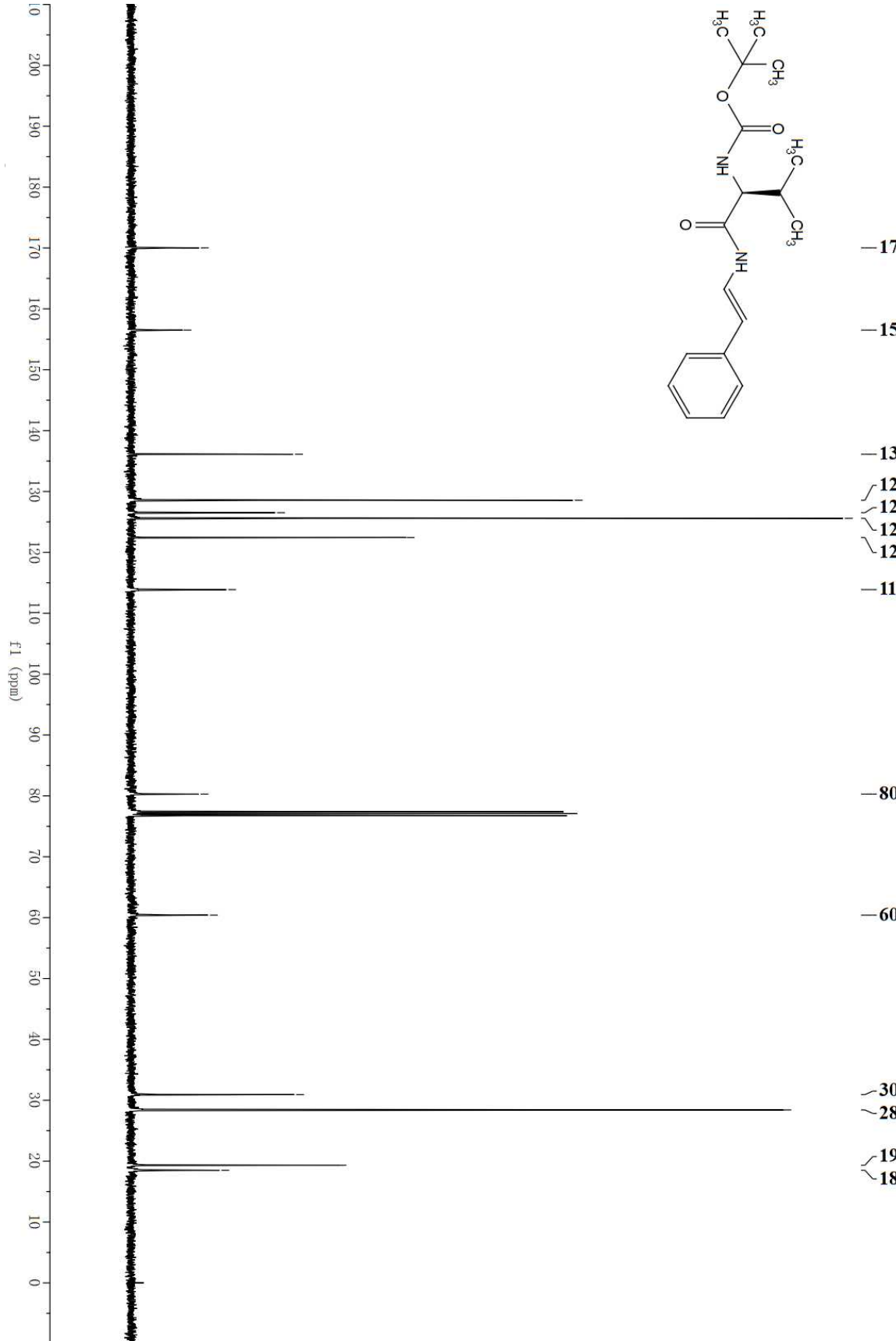


$^1\text{H}$  NMR spectrum of 2ab (400 MHz, CDCl<sub>3</sub>)

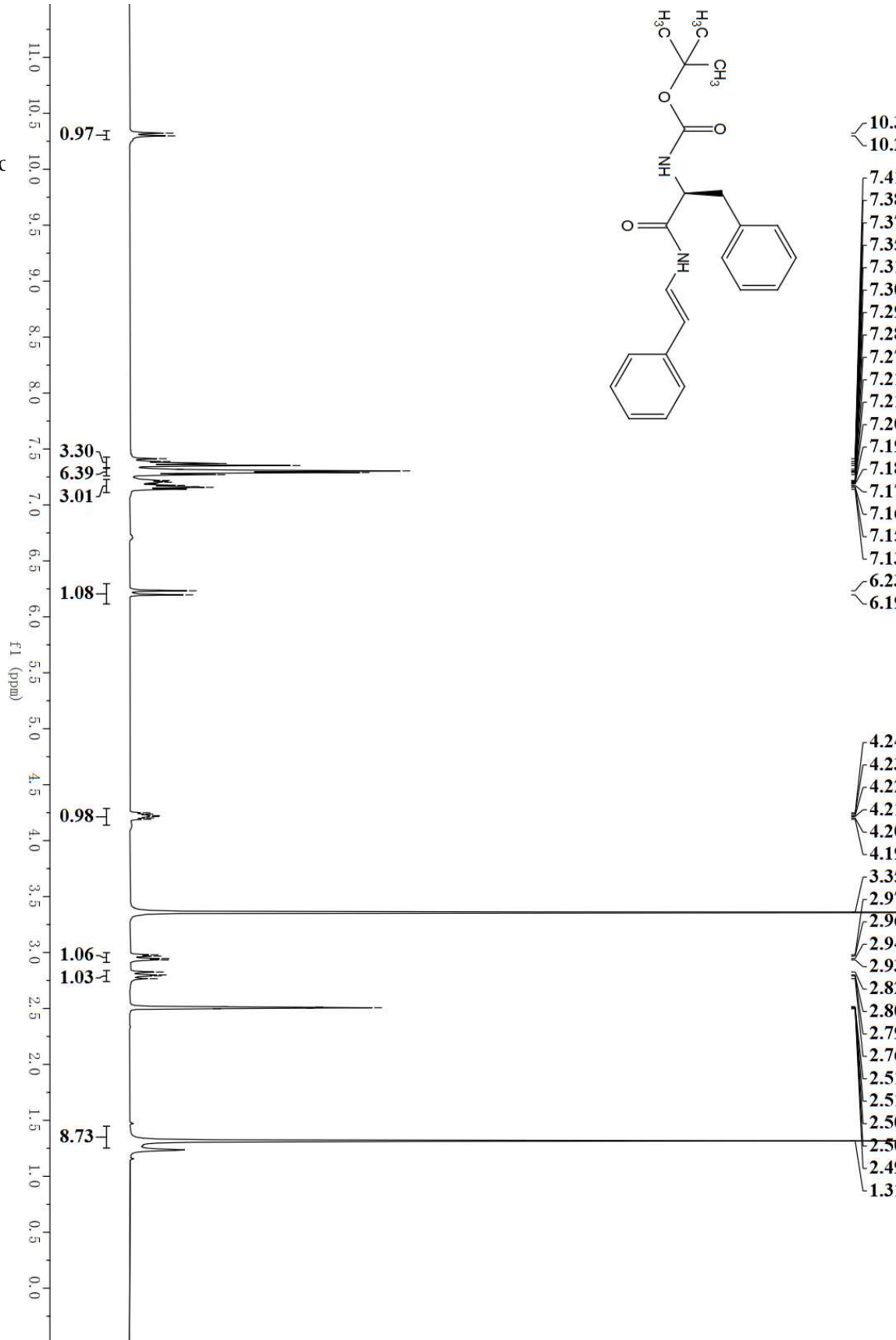




<sup>13</sup>C NMR spectrum

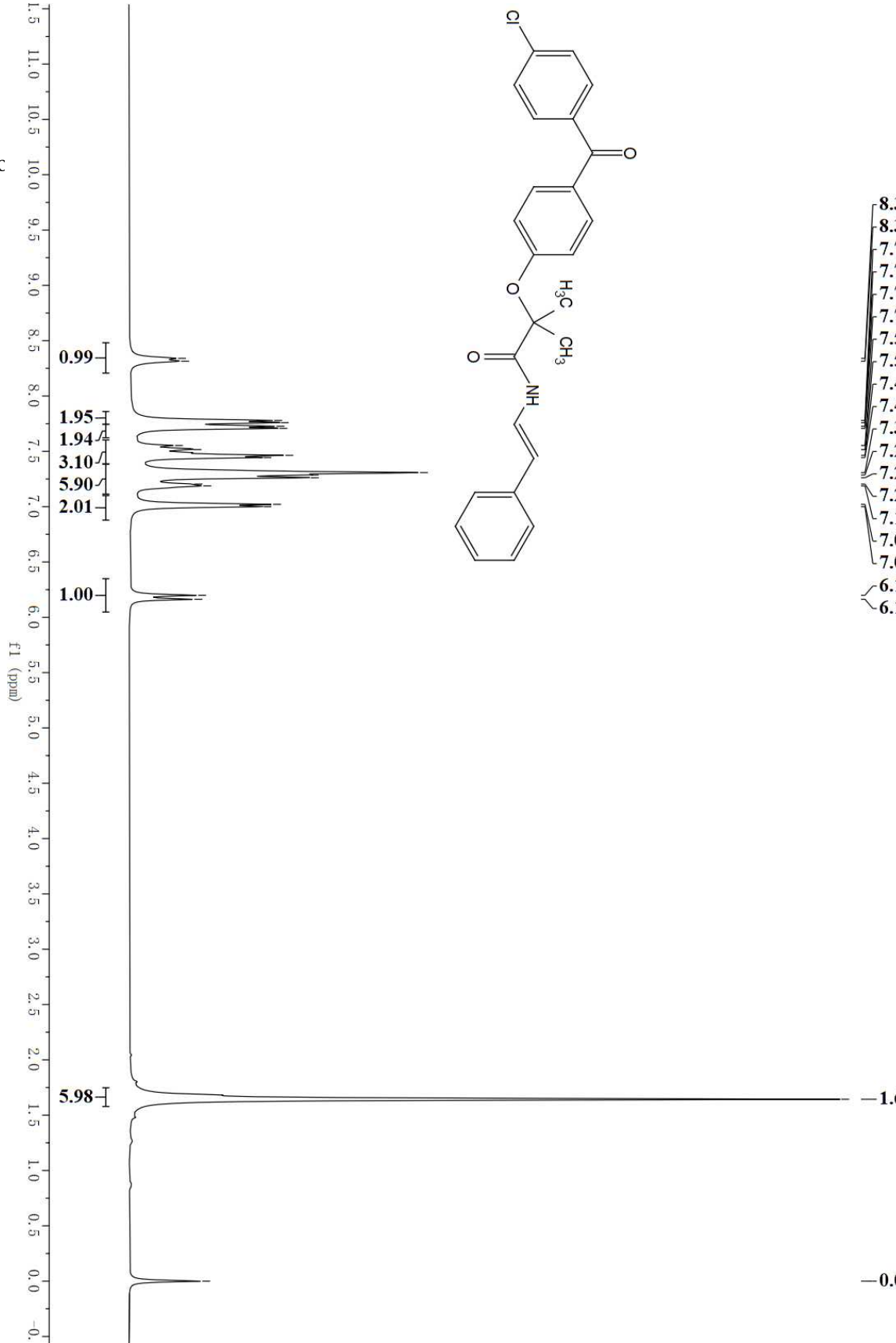


<sup>1</sup>H NMR spectrum c

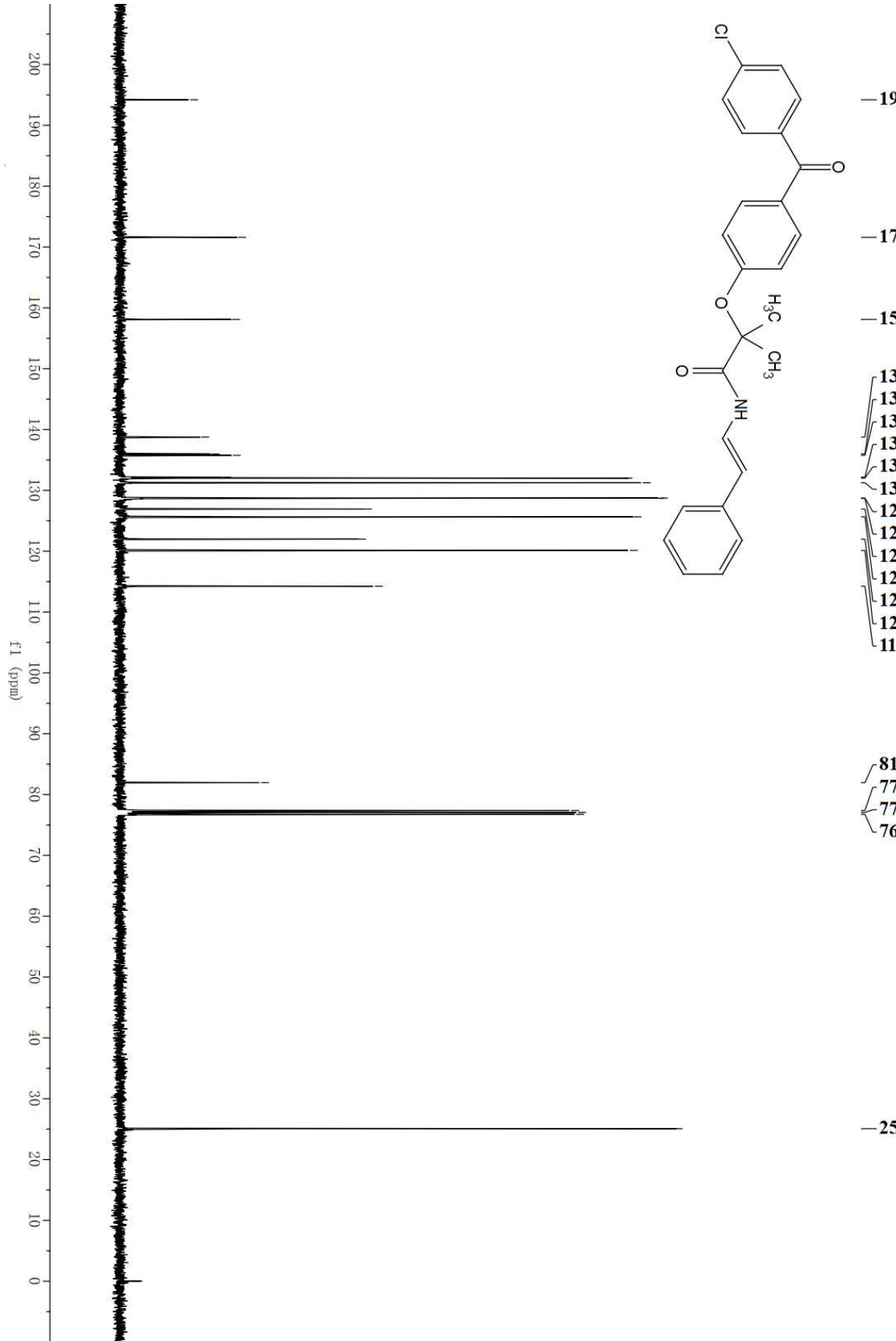




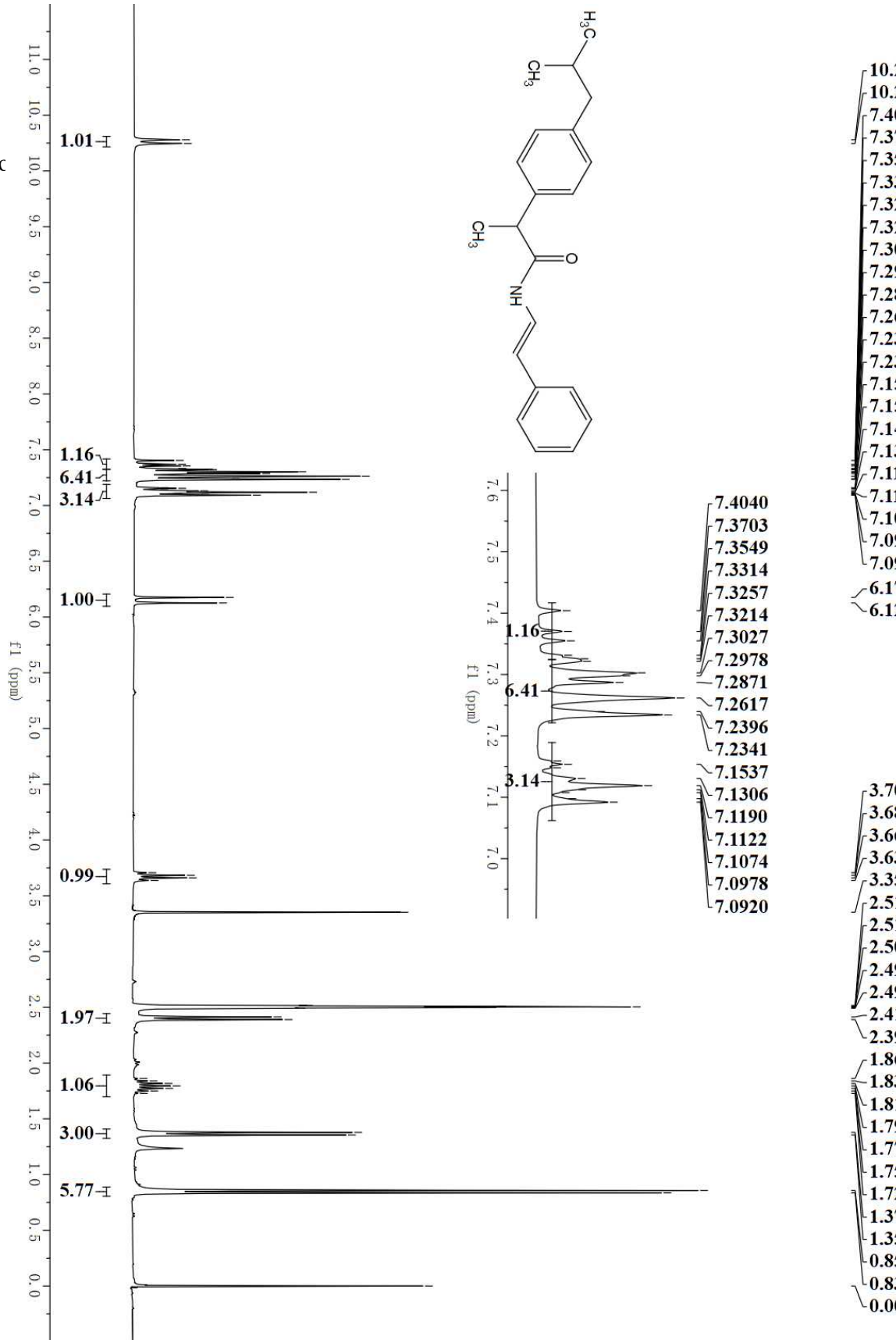
<sup>1</sup>H NMR spectrum c



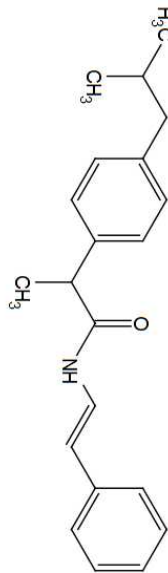
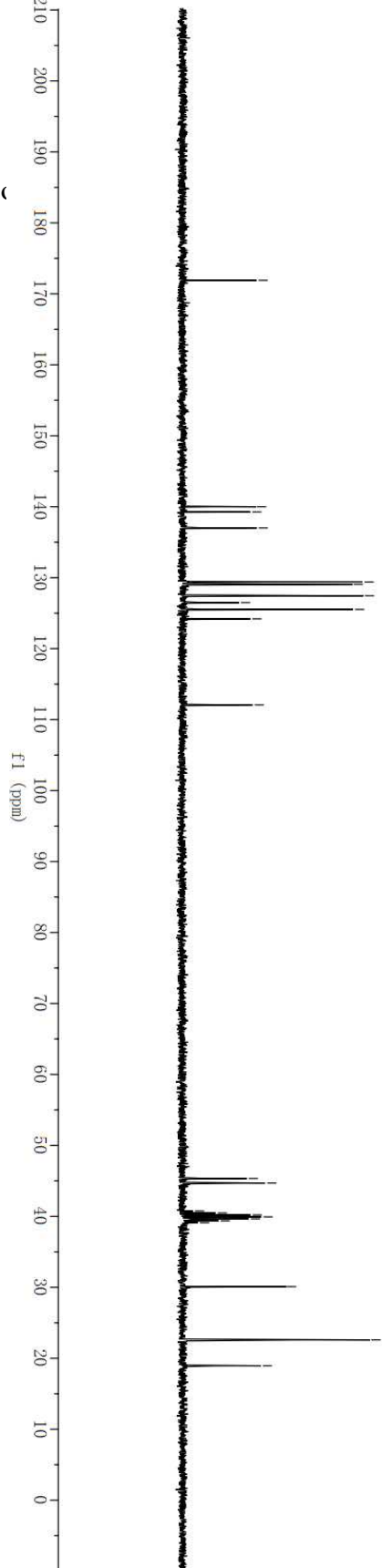
<sup>13</sup>C NMR spectrum



<sup>1</sup>H NMR spectrum c



$^{13}\text{C}$  NMR spectrum (



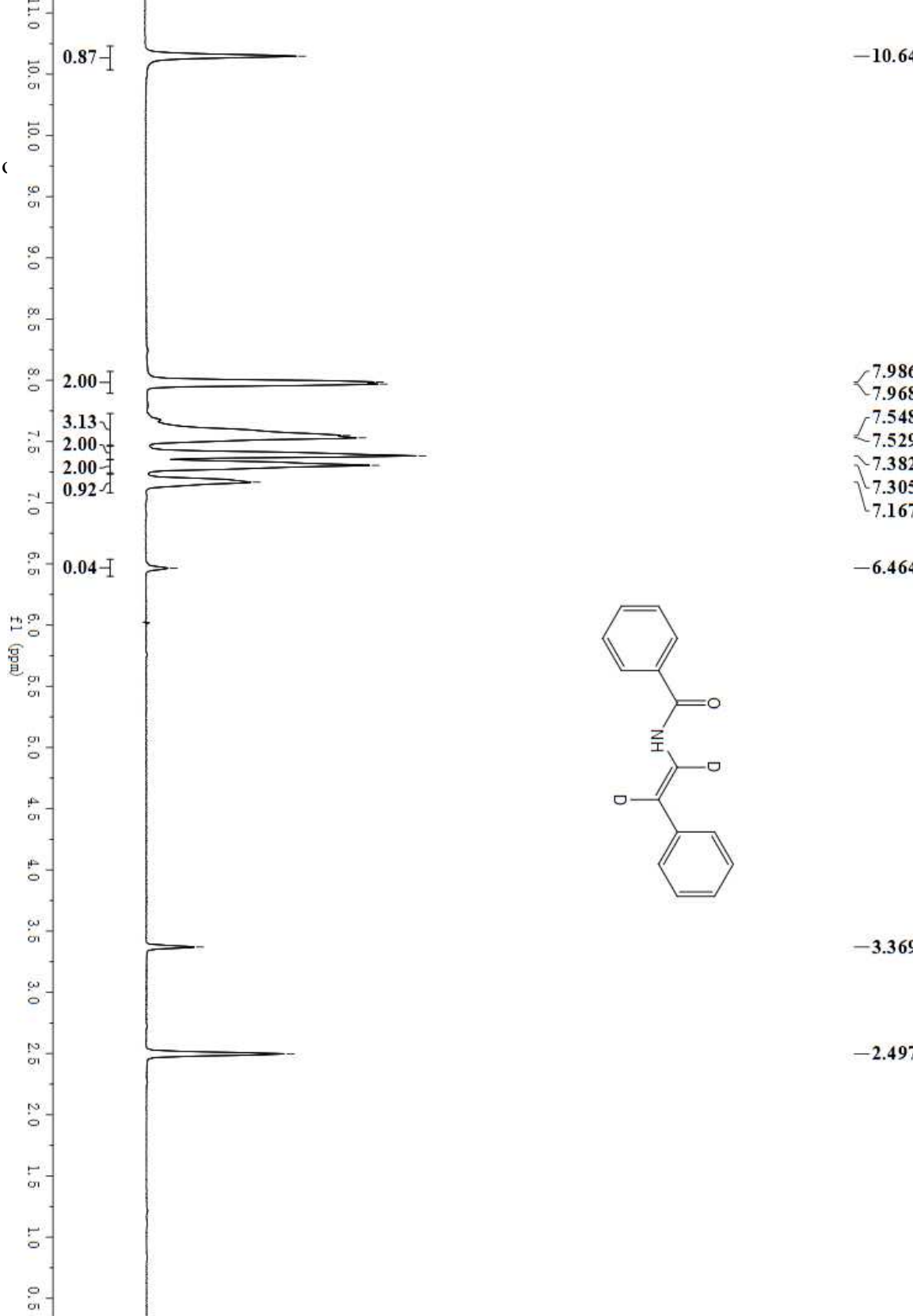
-1

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<sup>1</sup>H NMR spectrum (



# 10. Copies of $^1\text{H}$

$^1\text{H}$  NMR spectrum c

