

## Supporting Information

### Copper-Catalyzed Enantioselective 1,2-Reduction of Cycloalkenones

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## I. General Information

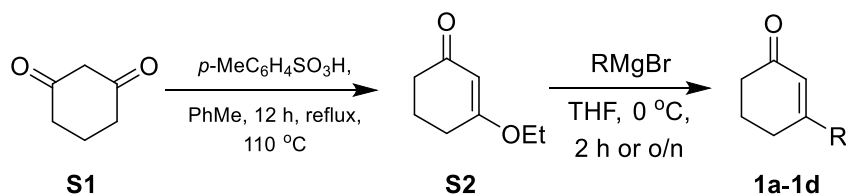
Unless otherwise mentioned, all experiments were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were dried with standard procedures and degassed with N<sub>2</sub>. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 300-400 mesh). NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz for <sup>1</sup>H NMR, 101 MHz for <sup>13</sup>C NMR, a Bruker DPX 500 spectrometer at 500 MHz for <sup>1</sup>H NMR, 126 MHz for <sup>13</sup>C NMR or a Bruker DPX 600 spectrometer at 600 MHz for <sup>1</sup>H NMR, 151MHz for <sup>13</sup>C NMR in CDCl<sub>3</sub> or CD<sub>3</sub>OD with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in ppm and coupling constants are given in Hz. Chemical shifts were reported relative to TMS (0.00 ppm) for <sup>1</sup>H NMR spectroscopy, and relative to CDCl<sub>3</sub> (77.00 ppm) or CD<sub>3</sub>OD (49.00 ppm) for <sup>13</sup>C NMR spectroscopy. Enantiomeric excesses were determined by chiral HPLC analysis using a Waters Analytical/Preparative HPLC system equipped with a 1525 Binary Pump, a 2707 Autosampler, and a variable wavelength Waters 2498 UV detector operated using Breeze 2 software or using a chiral stationary phase on Agilent Technologies 1260 Infinity II instrument in comparison with the authentic racemates. Optical rotations were obtained on Rudolph Autopol I polarimeter, serial number 35148. High resolution mass spectra (HRMS) were obtained on Thermo Scientific Q Exactive hybrid quadrupole-Orbitrap mass spectrometer at the Department of Chemistry, Southern University of Science and Technology or UPLC-ESI-MS (high resolution, positive) was recorded on a Thermo Scientific UltiMate 3000/Bruker maXis II system at the University of Hong Kong.

The C<sub>3</sub>\*-TunePhos series of ligands were synthesized according to reported literature.<sup>[1]</sup>

Hex = hexane; EA = ethyl acetate; DEMS= diethoxymethylsilane; DCM= dichloromethane; TMDS= tetramethyldisiloxane; rt = room temperature.

## II. General Procedures for the Synthesis of Substrates

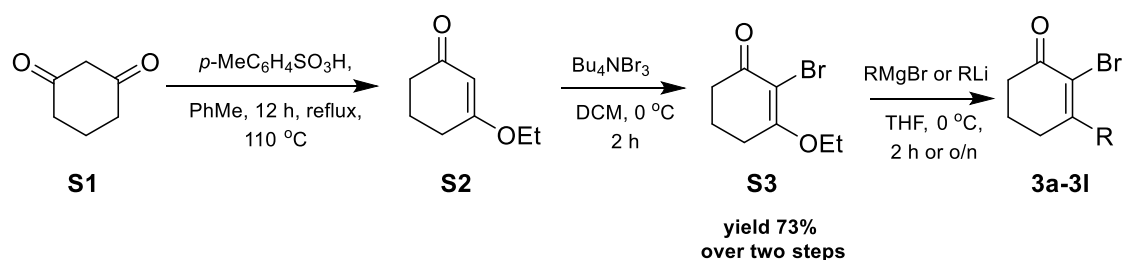
### General Procedure A:



**S2** was synthesized according to reported procedure.<sup>[2]</sup>

**S2** (0.70 g, 5.0 mmol) in 10 mL THF was added to PhMgBr (1 M in THF, 10 mmol) at  $0\text{ }^\circ\text{C}$  over 1 min. After addition was completed, the resulting mixture was allowed to stir 1 h at this temperature. It was allowed to warm to room temperature and stirred for an additional 2 h. 2 M HCl (10 mL) was added to the reaction with stirring for 5 min. An additional 20 mL of 2 M HCl were added. The resulting mixture was extracted with 2 x 20 mL EA. The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The volatiles were removed in vacuo. The residue was subjected to flash column chromatography on silica gel (eluent: EA/Hex=10%) to afford ketone **1a** as a white solid (1.25 g, 73% yield).

### General Procedure B:

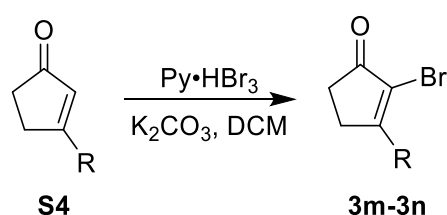


**S3** was synthesized according to reported procedure.<sup>[2]</sup>

**S3** (438 mg, 2.00 mmol) in 2 mL THF was added to PhMgBr (1.0 M in THF, 4 mmol) at  $0\text{ }^\circ\text{C}$  over 1 minute. After the addition was completed, the reaction was allowed to stir for 1 h at this temperature. It was then was allowed to warm to room

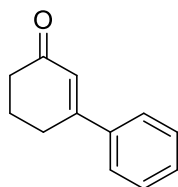
temperature and stirred for an additional 2 h. To the reaction was added 3 mL of 2 M HCl with stirring. After 5 min, an additional 10 mL of 2 M HCl were added. The resulting mixture was extracted with 2 x 20 mL EA. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the volatiles were removed in vacuo. The residue was subjected to flash column chromatography on silica gel (eluent: EA/Hex=10%) to afford **3a** as a pale yellow solid, (250 mg, 51% yield).

### General Procedure C:



**3m** and **3n** were synthesized according to a reported procedure.<sup>[3]</sup> K<sub>2</sub>CO<sub>3</sub> (3.45 g, 25 mmol) and Py·HBr<sub>3</sub> (3.19 g, 10 mmol) were added successively to a solution of **S4** (480 mg, 5 mmol) in 20 mL DCM at rt. The resulting mixture was continued to stir 5 h, then quenched by sat. NaHCO<sub>3</sub> solution, the organic layer was separated. The left water phase was extracted by 20 mL DCM twice. The organic layer was combined and dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed under vacuum. The residue was subjected to column chromatography on silica gel (eluent: EA/Hex=10%) to afford **3m** as a pale yellow solid, 368 mg, 42% yield.

### Individual Preparations and Characterization data of substrates

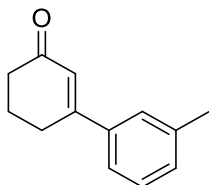


Chemical Formula: C<sub>12</sub>H<sub>12</sub>O  
 Exact Mass: 172.0888

### 5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (**1a**)

Prepared following **General procedure A**, using **S2** (1.4 g, 10 mmol). White solid, 1.25 g, 73% yield, obtained by the purification with flash column chromatography on

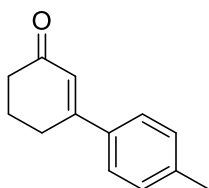
silica gel (eluent: EA/Hex=10%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.53 (dd,  $J$  = 6.6, 3.1 Hz, 2H), 7.48 – 7.38 (m, 3H), 6.42 (t,  $J$  = 1.4 Hz, 1H), 2.84 – 2.74 (m, 2H), 2.55 – 2.43 (m, 2H), 2.15 (p,  $J$  = 6.2 Hz, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  159.7, 129.9, 128.7, 126.0, 125.3, 37.2, 28.0, 22.7 ppm. The NMR data is consistent with that reported. <sup>[5]</sup>



Chemical Formula:  $\text{C}_{13}\text{H}_{14}\text{O}$   
Exact Mass: 186.1045

### 3'-methyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (1b)

Prepared following **General procedure A**, using **S2** (0.70 g, 5.0 mmol). Pale yellow solid, 0.71 g, 75% yield, obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.36 – 7.27 (m, 3H), 7.22 (d,  $J$  = 7.6 Hz, 1H), 6.41 (s, 1H), 2.76 (t,  $J$  = 6.7 Hz, 2H), 2.51 – 2.45 (m, 2H), 2.39 (s, 3H), 2.15 (p,  $J$  = 6.2 Hz, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  199.9, 160.0, 138.8, 138.3, 130.7, 128.6, 126.7, 125.3, 123.2, 37.2, 28.1, 22.8, 21.4 ppm. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{13}\text{H}_{15}\text{O}^+$ : 187.1117; Found: 187.1118.

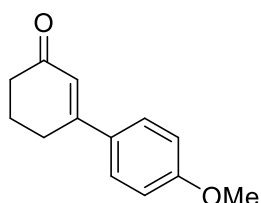


Chemical Formula:  $\text{C}_{13}\text{H}_{14}\text{O}$   
Exact Mass: 186.1045

### 4'-methyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (1c)

Prepared following **General procedure A**, using **S2** (0.70 g, 5.0 mmol). Pale yellow solid, 0.75 g, 80% yield, obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1\text{H}$  NMR (400 MHz, Chloroform-

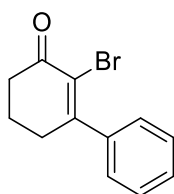
*d*)  $\delta$  7.44 (d,  $J$  = 8.3 Hz, 2H), 7.22 (d,  $J$  = 8.0 Hz, 2H), 6.41 (s, 1H), 2.76 (t,  $J$  = 6.7 Hz, 2H), 2.51 – 2.45 (m, 2H), 2.38 (s, 3H), 2.18 – 2.10 (m, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  199.9, 159.7, 140.3, 135.8, 129.4, 126.0, 124.6, 37.2, 27.9, 22.8, 21.2 ppm. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{13}\text{H}_{15}\text{O}^+$ : 187.1117; Found: 187.1117.



Chemical Formula:  $\text{C}_{13}\text{H}_{14}\text{O}_2$   
Exact Mass: 202.0994

#### 4'-methoxy-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (1d)

Prepared following **General procedure A**, using **S2** (0.70 g, 5.0 mmol). Pale yellow solid, 0.62 g, 61% yield, obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.52 (d,  $J$  = 8.9 Hz, 2H), 6.93 (d,  $J$  = 8.9 Hz, 2H), 6.39 (s, 1H), 3.84 (s, 3H), 2.75 (t,  $J$  = 6.6 Hz, 2H), 2.50 – 2.43 (m, 2H), 2.14 (p,  $J$  = 6.2 Hz, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  199.8, 161.2, 159.1, 130.7, 127.6, 123.6, 114.1, 55.3, 37.1, 27.8, 22.7 ppm. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{13}\text{H}_{15}\text{O}_2^+$ : 203.1067; Found: 203.1067.

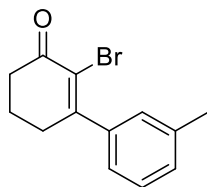


Chemical Formula:  $\text{C}_{12}\text{H}_{11}\text{BrO}$   
Exact Mass: 249.9993

#### 2-bromo-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (3a)

Prepared following **General procedure B**, using **S3** (438 mg, 2.00 mmol). Pale yellow solid, 250 mg, 51% yield, obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1\text{H}$  NMR (400 MHz, Chloroform-

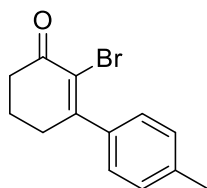
*d*)  $\delta$  7.45-7.32 (m, 5H), 2.79 (t,  $J$  = 6.0 Hz, 2H), 2.72 (t,  $J$  = 7.6 Hz, 2H), 2.20-2.13 (m, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  191.6, 160.7, 140.8, 128.8, 128.4, 126.8, 122.4, 37.8, 35.1, 22.3 ppm. The NMR data is consistent with that reported.<sup>[6]</sup>



Chemical Formula:  $\text{C}_{13}\text{H}_{13}\text{BrO}$   
Exact Mass: 264.0150

### 2-bromo-3'-methyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (3b)

Prepared following **General procedure B**, using **S3** (548 mg, 2.50 mmol). Pale yellow solid, 348 mg, 52% yield, obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.30 (t,  $J$  = 7.6 Hz, 1H), 7.19 (d,  $J$  = 7.6 Hz, 1H), 7.11 (d,  $J$  = 8.0 Hz, 2H), 2.76 (t,  $J$  = 6.0 Hz, 2H), 2.70 (t,  $J$  = 7.0 Hz, 2H), 2.38 (s, 3H), 2.17-2.12 (m, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  191.6, 161.0, 140.7, 138.0, 129.5, 128.2, 127.2, 123.8, 122.2, 37.7, 35.1, 22.2, 21.4 ppm. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{13}\text{H}_{14}\text{BrO}^+$ : 265.0223; Found: 265.0220.

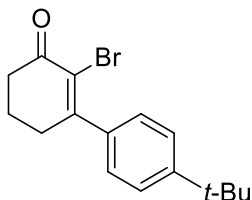


Chemical Formula:  $\text{C}_{13}\text{H}_{13}\text{BrO}$   
Exact Mass: 264.0150

### 2-bromo-4'-methyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (3c)

Prepared following **General procedure B**, using **S3** (548 mg, 2.50 mmol). Yellow oil, 450 mg, 68% yield, obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1\text{H}$  NMR (400MHz, Chloroform-*d*)  $\delta$  7.26-7.21 (m, 4H), 2.77 (t,  $J$  = 6.0 Hz, 2H), 2.70 (t,  $J$  = 6.4 Hz, 3H), 2.38 (s, 3H), 2.17-2.15 (m, 2H)

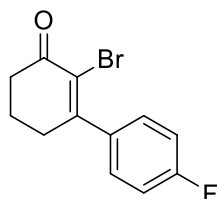
ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100MHz, Chloroform-*d*)  $\delta$  191.6, 160.8, 138.9, 137.8, 128.9, 126.9, 122.1, 37.7, 35.0, 22.2, 21.3 ppm. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{13}\text{H}_{14}\text{BrO}^+$ : 265.0223; Found: 265.0219.



Chemical Formula:  $\text{C}_{16}\text{H}_{19}\text{BrO}$   
Exact Mass: 306.0619

### 2-bromo-4'-(tert-butyl)-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (3d)

Prepared following **General procedure B**, using **S3** (548 mg, 2.50 mmol). Yellow oil, 421 mg, 54% yield, obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.44 (d,  $J = 8.4$  Hz, 2H), 7.30 (d,  $J = 8.4$  Hz, 2H), 2.79 (t,  $J = 6.0$  Hz, 2H), 2.71 (t,  $J = 6.8$  Hz, 2H), 2.18-2.12 (m, 2H), 1.35 (s, 9H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  191.7, 160.7, 152.2, 137.7, 126.9, 125.2, 122.2, 37.8, 35.1, 34.8, 31.2, 22.3 ppm. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{20}\text{BrO}^+$ : 307.0692; Found: 307.0690.

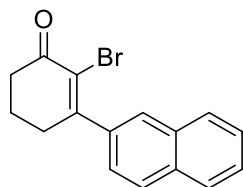


Chemical Formula:  $\text{C}_{12}\text{H}_{10}\text{BrFO}$   
Exact Mass: 267.9899

### 2-bromo-4'-fluoro-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (3e)

Prepared following **General procedure B**, using **S3** (219 mg, 1.00 mmol). Pale yellow solid, 147 mg, 55% yield, obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.40 – 7.30 (m, 2H), 7.19 – 7.07 (m, 2H), 2.77 (t,  $J = 6.0$  Hz, 2H), 2.72 (t,  $J = 7.5$  Hz, 2H), 2.17 (p,  $J = 6.0$  Hz, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$

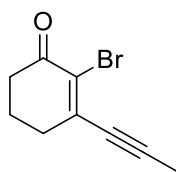
191.4, 164.0, 160.5 (d,  $J_{C-F} = 199.7$  Hz), 136.6 (d,  $J_{C-F} = 3.3$  Hz), 129.0 (d,  $J_{C-F} = 8.3$  Hz), 122.8, 115.5 (d,  $J_{C-F} = 21.8$  Hz), 37.7, 35.0, 22.2 ppm. HRMS (ESI),  $m/z$ :  $[M+H]^+$   
Calcd for  $C_{12}H_{11}BrFO^+$ : 268.9972; Found: 268.9969.



Chemical Formula:  $C_{16}H_{13}BrO$   
Exact Mass: 300.0150

### 2-bromo-3-(naphthalen-2-yl)cyclohex-2-en-1-one (3f)

Prepared following **General procedure B**, using **S3** (219 mg, 1.00 mmol). Pale yellow solid, 157 mg, 52% yield, obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1H$  NMR (400 MHz, Methanol- $d_4$ )  $\delta$  7.97 – 7.77 (m, 4H), 7.60 – 7.40 (m, 3H), 2.86 (t,  $J = 5.8$  Hz, 2H), 2.74 (t,  $J = 6.4$  Hz, 2H), 2.22-2.16 (m, 2H) ppm.  $^{13}C\{^1H\}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  191.5, 160.6, 138.1, 133.1, 132.8, 128.3, 128.0, 127.8, 126.9, 126.6, 126.3, 124.6, 122.7, 37.8, 35.2, 22.4 ppm. HRMS (ESI),  $m/z$ :  $[M+H]^+$  Calcd for  $C_{16}H_{14}BrO^+$ : 301.0223; Found: 301.0219.

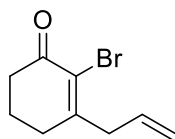


Chemical Formula:  $C_9H_9BrO$   
Exact Mass: 211.9837

### 2-bromo-3-(prop-1-yn-1-yl)cyclohex-2-en-1-one (3g)

Prepared following **General procedure B**, using **S3** (219 mg, 1.00 mmol). Yellow solid, 129 mg, 61% yield, obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1H$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  2.65 – 2.55 (m, 4H), 2.15 (s, 3H), 2.08 – 2.00 (m, 2H) ppm.  $^{13}C\{^1H\}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  190.8, 143.8, 126.7, 105.3, 79.9, 37.8, 33.6, 22.2, 5.4 ppm. HRMS (ESI),  $m/z$ :

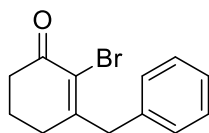
$[M+H]^+$  Calcd for  $C_9H_{10}BrO^+$ : 212.9910; Found: 212.9864.



Chemical Formula:  $C_9H_{11}BrO$   
Exact Mass: 213.9993

### 3-allyl-2-bromocyclohex-2-en-1-one (3h)

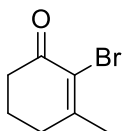
Prepared following **General procedure B**, using **S3** (219 mg, 1.00 mmol). Colorless oil, 171 mg, 79% yield, obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  5.85-5.75 (m, 1H), 5.25 – 5.13 (m, 2H), 3.25 (d,  $J$  = 6.7 Hz, 2H), 2.59 (t,  $J$  = 6.7 Hz, 2H), 2.51 (t,  $J$  = 6.0 Hz, 2H), 2.03-1.97 (m, 2H) ppm.  $^{13}C\{^1H\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  191.1, 160.8, 131.5, 123.1, 118.3, 43.3, 37.8, 32.1, 21.9 ppm. HRMS (ESI),  $m/z$ :  $[M+H]^+$  Calcd for  $C_9H_{12}BrO^+$ : 215.0066; Found: 215.0044. The NMR data is consistent with that reported.<sup>[6]</sup>



Chemical Formula:  $C_{13}H_{13}BrO$   
Exact Mass: 264.0150

### 3-benzyl-2-bromocyclohex-2-en-1-one (3i)

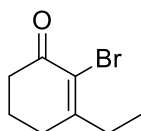
Prepared following **General procedure B**, using **S3** (679 mg, 3.10 mmol). Yellow oil, 208 mg, 25% yield, obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.40 – 7.28 (m, 3H), 7.26 – 7.22 (m, 2H), 3.89 (s, 2H), 2.63 – 2.55 (m, 2H), 2.40 (t,  $J$  = 6.0 Hz, 2H), 1.97 – 1.88 (m, 2H) ppm.  $^{13}C\{^1H\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  191.4, 161.6, 136.5, 128.8, 128.8, 127.1, 123.4, 44.8, 37.9, 31.9, 21.9 ppm. HRMS (ESI),  $m/z$ :  $[M+H]^+$  Calcd for  $C_{13}H_{14}BrO^+$ : 265.0223; Found: 265.0222.



Chemical Formula: C<sub>7</sub>H<sub>9</sub>BrO  
Exact Mass: 187.9837

### 2-bromo-3-methylcyclohex-2-en-1-one (3j)

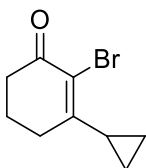
Prepared following **General procedure B**, using **S3** (438 mg, 2.00 mmol). Colorless oil, 187 mg, 50% yield, obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 2.62 – 2.55 (m, 2H), 2.52 (t, *J* = 5.3 Hz, 2H), 2.18 (s, 3H), 2.07 – 1.95 (m, 2H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*) δ 190.9, 160.3, 122.7, 37.6, 34.1, 25.8, 21.7 ppm. The NMR data is consistent with that reported.<sup>[2]</sup>



Chemical Formula: C<sub>8</sub>H<sub>11</sub>BrO  
Exact Mass: 201.9993

### 2-bromo-3-ethylcyclohex-2-en-1-one (3k)

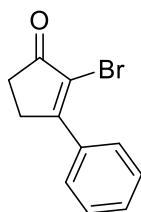
Prepared following **General procedure B**, using **S3** (219 mg, 1.00 mmol). Yellow oil, 89 mg, 44% yield, obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 2.58 (t, *J* = 6.7 Hz, 2H), 2.54-2.50 (m, 4H), 2.01 (p, *J* = 5.9 Hz, 2H), 1.14 (t, *J* = 7.6 Hz, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*) δ 191.1, 165.1, 121.8, 37.7, 32.3, 31.7, 21.9, 10.8 ppm. HRMS (ESI), *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>8</sub>H<sub>12</sub>BrO<sup>+</sup>: 203.0066; Found: 203.0021. The NMR data is consistent with that reported.<sup>[6]</sup>



Chemical Formula: C<sub>9</sub>H<sub>11</sub>BrO  
Exact Mass: 213.9993

### 2-bromo-3-phenylcyclopent-2-en-1-one (3l)

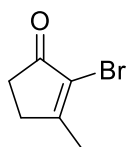
Prepared following **General procedure B**, using **S3** (219 mg, 1.00 mmol). Colorless oil, 110 mg, 52% yield, obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1\text{H}$  NMR (400 MHz, Methanol- $d_4$ )  $\delta$  2.58 (t,  $J$  = 6.3 Hz, 2H), 2.47 – 2.37 (m, 1H), 2.02 – 1.89 (m, 4H), 1.05 (q,  $J$  = 6.7 Hz, 2H), 0.87 (q,  $J$  = 6.8, 5.8 Hz, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  122.8, 38.1, 26.4, 21.6, 19.5, 7.7 ppm. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_9\text{H}_{12}\text{BrO}^+$ : 215.0066; Found: 215.0023.



Chemical Formula:  $\text{C}_{11}\text{H}_9\text{BrO}$   
Exact Mass: 235.9837

### 2-bromo-3-phenylcyclopent-2-en-1-one (3m)

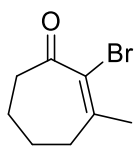
Prepared following **General procedure C**, using **S4** (316 mg, 2.00 mmol). Pale yellow solid, 149 mg, 63% yield, obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.92-7.89 (m, 2H), 7.6 – 7.4 (m, 3H), 3.1 (t,  $J$  = 4.8 Hz, 2H), 2.7 (t,  $J$  = 4.8 Hz, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  201.7, 167.5, 134.0, 131.0, 128.6, 127.7, 121.7, 32.5, 30.6 ppm. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{11}\text{H}_{10}\text{BrO}^+$ : 236.9910; Found: 236.9910. The NMR data is consistent with that reported.<sup>[7]</sup>



Chemical Formula:  $\text{C}_6\text{H}_7\text{BrO}$   
Exact Mass: 173.9680

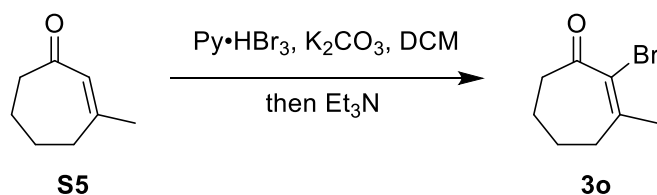
### 2-bromo-3-methylcyclopent-2-en-1-one (3n)

Prepared following **General procedure C**, using **S4** (480 mg, 5.00 mmol). Pale yellow solid, 368 mg, 42% yield, obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  2.67 (d,  $J$  = 4.8 Hz, 2H), 2.58 – 2.45 (m, 2H), 2.18 (d,  $J$  = 8.5 Hz, 3H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  201.4, 173.3, 123.2, 33.3, 32.2, 19.0 ppm. The NMR data is consistent with that reported.<sup>[8]</sup>



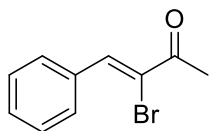
Chemical Formula:  $\text{C}_8\text{H}_{11}\text{BrO}$   
Exact Mass: 201.9993

### 2-bromo-3-methylcyclohept-2-en-1-one (**3o**)



**S5** was synthesized according to a reported procedure.<sup>[4]</sup>

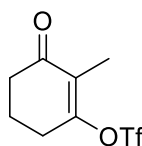
$\text{K}_2\text{CO}_3$  (1.38 g, 10 mmol) and  $\text{Py}\cdot\text{HBr}_3$  (1.28 g, 4 mmol) were added successively to a solution of **S5** (248 mg, 2 mmol) in 10 mL DCM at rt. The resulting mixture was stirred for 5 h, then 1.0 mL  $\text{Et}_3\text{N}$  was added and stirred for additional 12 h. The reaction was quenched by adding sat.  $\text{NaHCO}_3$  solution, the organic layer was separated. The aqueous layer was back-extracted using 10 mL DCM twice. The organic layers were combined, washed with brine (20 mL), dried over  $\text{Na}_2\text{SO}_4$ , and the solvent was removed under vacuum. The residue was subjected to column chromatography on silica gel (eluent: EA/Hex=5%) to afford **3o** as a yellow oil, 160 mg, 64% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  2.73 – 2.65 (m, 2H), 2.62 – 2.52 (m, 2H), 2.23 (s, 3H), 1.86 – 1.73 (m, 4H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  197.6, 155.5, 124.0, 40.4, 34.6, 28.7, 23.8, 20.9 ppm. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_8\text{H}_{12}\text{BrO}^+$ : 203.0066; Found: 203.0062.



Chemical Formula:  $C_{10}H_9BrO$   
Exact Mass: 223.9837

**(Z)-3-bromo-4-phenylbut-3-en-2-one (3p)**

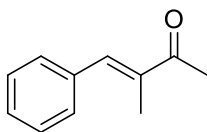
Substrate **3p** was synthesized according to a reported procedure.<sup>[9]</sup>



Chemical Formula:  $C_8H_9F_3O_4S$   
Exact Mass: 258.0174

**2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (3q)**

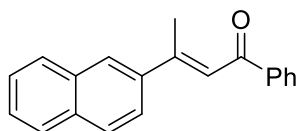
Compound **3q** was synthesized according to a reported procedure.<sup>[9]</sup>



Chemical Formula:  $C_{11}H_{12}O$   
Exact Mass: 160.0888

**(E)-3-methyl-4-phenylbut-3-en-2-one (3r)**

Compound **3r** was synthesized according to a reported procedure.<sup>[12]</sup>



Chemical Formula:  $C_{20}H_{16}O$   
Exact Mass: 272.1201

**(E)-3-(naphthalen-2-yl)-1-phenylbut-2-en-1-one (3s)**

Compound **3s** was synthesized according to a reported procedure.<sup>[13]</sup>

### III. Copper-catalyzed enantioselective 1,2-reductions of $\alpha$ , $\beta$ -unsaturated ketones

#### 3.1 Additional Conditions Examined

**Table S1. Optimizations for the reduction of 1a**

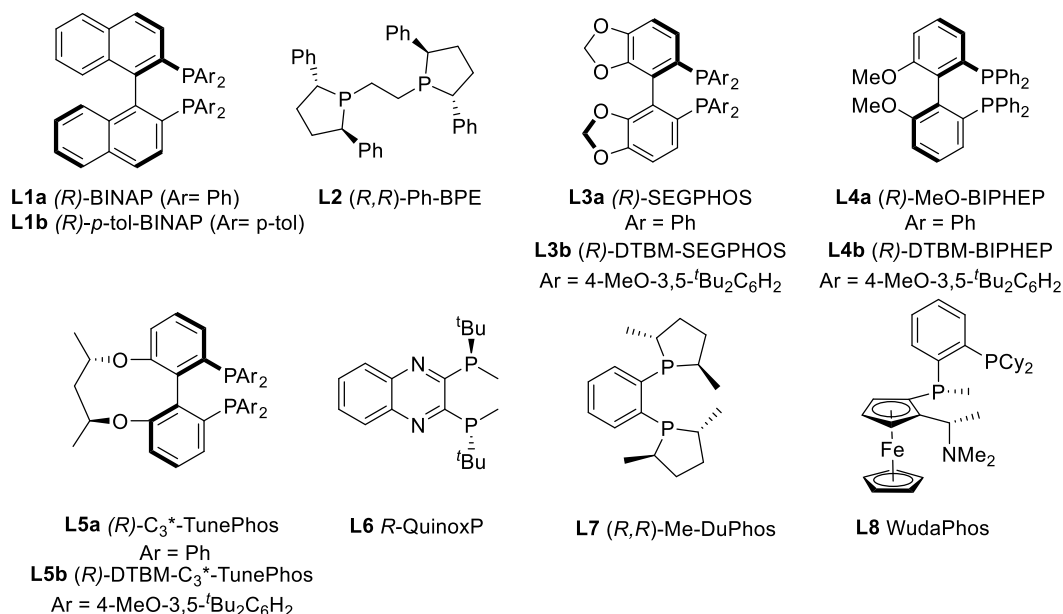
Reaction scheme showing the reduction of 1a (2-phenylcyclohex-2-en-1-one) to 2a (2-phenylcyclohex-2-en-1-ol) and 2a' (1-phenylcyclohexan-1-ol). The reaction conditions are: (1) 5% Ligand, 5% Cu(OAc)<sub>2</sub>, reductant, solvent, T; (2) sat. NH<sub>4</sub>F/MeOH work up.

Entry <sup>a</sup>	solvent	reductant	ligand	T/°C	conversion (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	THF	DEMS	<b>L3b</b>	25	<b>2a</b> : 47; <b>2a'</b> : 38	50
2	THF	Ph <sub>2</sub> SiH <sub>2</sub>	<b>L3b</b>	25	<b>2a</b> : 58; <b>2a'</b> : 42	50
3	THF	TMDS	<b>L3b</b>	25	<b>2a</b> : 43; <b>2a'</b> : 14	49
4	THF	PinBH	<b>L3b</b>	0	<b>2a</b> : 38; <b>2a'</b> : 58	53
5	THF	Ph <sub>2</sub> SiH <sub>2</sub>	<b>L3b</b>	-25	<b>2a</b> : 46; <b>2a'</b> : 28	N.D.
6	PhMe	Ph <sub>2</sub> SiH <sub>2</sub>	<b>L3b</b>	0	trace	N.D.
7	THF	PinBH	<b>L1b</b>	0	trace	N.D.
8	THF	PinBH	<b>L2</b>	0	trace	N.D.
9	THF	PinBH	<b>L3a</b>	0	trace	N.D.
10	THF	PinBH	<b>L4a</b>	0	20 <sup>d</sup>	30
11	THF	PinBH	<b>L5a</b>	0	81 <sup>d</sup>	65
12	THF	PinBH	<b>L6</b>	0	trace	N.D.
13	THF	PinBH	<b>L7</b>	0	trace	N.D.
14	THF	PinBH	<b>L8</b>	0	trace	N.D.
15	THF	PinBH	<b>L5b</b>	0	<b>2a</b> : 55; <b>2a'</b> : 8	68
16	THF	PinBH	<b>L4b</b>	0	<b>2a</b> : 35; <b>2a'</b> : 65	58
17 <sup>e</sup>	THF	PhSiH <sub>3</sub>	<b>L5b</b>	-25	<b>2a</b> : 99; <b>2a'</b> : 0	73

<sup>a</sup> Reaction conditions: **1a** (0.1 mmol), Ligand (5 mol%), Cu(OAc)<sub>2</sub> (5 mol%), reductant (0.15 mmol), solvent (0.5 mL), T, 12 h, b

Determined by <sup>1</sup>H NMR analysis. <sup>c</sup> The ee values were determined by HPLC using chiral columns. <sup>d</sup> isolated yield. <sup>e</sup> reaction time, 2

h.



**Table S2. Optimizations for the reduction of 3a**

Entry <sup>a</sup>	ligand	<i>T</i> /°C	conversion (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	<b>L1a</b>	rt	trace	-
2	<b>L2</b>	rt	8	56
3 <sup>d</sup>	<b>L3b</b>	0	99	93
4 <sup>d</sup>	<b>L5b</b>	0	99	95

<sup>a</sup> Reaction conditions: **3a** (0.1 mmol), Ligand (5 mol%), Cu(OAc)<sub>2</sub> (5 mol%), PhSiH<sub>3</sub> (0.15 mmol), THF (0.5 mL), *T*, 2 h. <sup>b</sup> Determined by <sup>1</sup>H NMR analysis. <sup>c</sup> The ee values were determined by HPLC using chiral columns. <sup>d</sup> Ligand (3.3 mol%), Cu(OAc)<sub>2</sub> (3 mol%), PhSiH<sub>3</sub> (0.12 mmol).

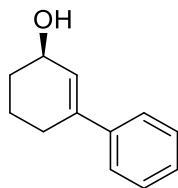
### 3.2 General Procedure for copper-catalyzed enantioselective 1,2-reduction of α, β-unsaturated ketones:

In an argon-filled glove box,\* an oven-dried 10 mL Schlenk tube containing a magnetic stir bar was charged with Cu(OAc)<sub>2</sub> (0.5 mg, 0.03 mmol), (*R*)-DTBM-C<sub>3</sub>\*-TunePhos (4.0 mg, 0.033 mol), and PPh<sub>3</sub> (0.8 mg, 0.03 mol). The Schenk tube was removed from the glove box. Degassed anhydrous THF (0.45 mL) was added and the mixture was stirred for 30 min. PhSiH<sub>3</sub> was added to the mixture and it was stirred for another 30

min for the generation of copper hydride, before being cooled to -25 °C. The substrate (0.1 mmol) was dissolved in 0.05 mL THF under argon and transferred to the resulting CuH solution at -25 °C *via* syringe. After stirring for 2 h, the reaction was allowed to warm to room temperature. Saturated NH<sub>4</sub>F in methanol (0.5 mL) was added and stirred for 10 min to quench the reaction. The resulting mixture was filtered *via* a short pad of celite to remove the precipitates. The filtrate was concentrated under vacuum and subjected to flash column chromatography on silica gel (eluent: EA/Hex=10%) to afford the corresponding products.

\*While we have stored and weighed out small quantities of Cu(OAc)<sub>2</sub> and (*R*)-DTBM-C<sub>3</sub>\*-TunePhos for small scale reactions in the glovebox due to the humid weather of our environs, the use of the glovebox is not absolutely necessary, particularly for the handling of larger quantities of materials.

### 3.3 Individual Experiments and Product Characterizations:

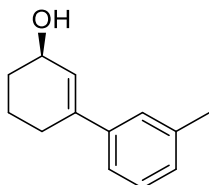


Chemical Formula: C<sub>12</sub>H<sub>14</sub>O  
Exact Mass: 174.1045

#### (*R*)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol (**2a**)

Following the General Procedure for reduction, **1a** (17.4 mg, 0.100 mmol) was reduced to give **2a** as a white solid, 17.1 mg, 98% yield, 73% ee, [ $\alpha$ ]<sub>D</sub><sup>23</sup> = +6.8 (c = 0.5, CHCl<sub>3</sub>), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.43 – 7.38 (m, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.29 – 7.23 (m, 1H), 6.15 – 6.10 (m, 1H), 4.39 (s, 1H), 2.52 – 2.30 (m, 2H), 2.00 – 1.86 (m, 2H), 1.79 – 1.63 (m, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  141.3, 140.1, 128.3, 127.4, 126.5, 125.4, 66.3, 31.6, 27.5, 19.4 ppm. HPLC: Chiracel OJ-3 Column (250 mm); detected at 210 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.8 mL/min; Retention time: 8.9 min (major), 11.0 min (minor). The NMR data is consistent with that reported.<sup>[10]</sup> The absolute configuration of **2a** was

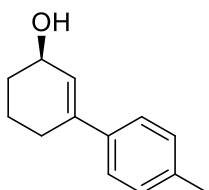
identified by comparison of its physical and spectroscopic data with the ones reported in the literature.<sup>[10]</sup> The absolute configuration of **2b-2d** was determined by comparing with **2a**.



Chemical Formula: C<sub>13</sub>H<sub>16</sub>O  
Exact Mass: 188.1201

#### (*R*)-3'-methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol (**2b**)

Following the General Procedure for reduction, **1b** (18.8 mg, 0.100 mmol) was reduced to give **2b** as a white solid, 17.3 mg, 92% yield, 71% ee,  $[\alpha]_D^{25} = +8.3$  ( $c = 1.0$ , CHCl<sub>3</sub>), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.25 – 7.18 (m, 3H), 7.11 – 7.06 (m, 1H), 6.14 – 6.06 (m, 1H), 4.38 (s, 1H), 2.52 – 2.41 (m, 1H), 2.40 – 2.30 (m, 4H), 1.99 – 1.85 (m, 2H), 1.80 – 1.61 (m, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  141.4, 140.3, 137.8, 128.2, 128.2, 126.4, 126.2, 122.5, 66.3, 31.7, 27.6, 21.5, 19.4 ppm. HRMS (ESI),  $m/z$ : [M+H-H<sub>2</sub>O]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>15</sub><sup>+</sup>: 171.1168, Found: 171.1168. HPLC: Chiracel OJ-3 Column (250 mm); detected at 210 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.8 mL/min; Retention time: 7.4 min (major), 8.3 min (minor).

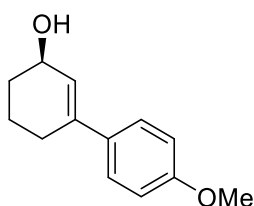


Chemical Formula: C<sub>13</sub>H<sub>16</sub>O  
Exact Mass: 188.1201

#### (*R*)-4'-methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol (**2c**)

Following the General Procedure for reduction, **1c** (18.8 mg, 0.100 mmol) was reduced to give **2c** as a white solid, 18.1 mg, 96% yield, 72% ee,  $[\alpha]_D^{25} = +2.9$  ( $c = 1.0$ , CHCl<sub>3</sub>), obtained by the purification with flash column chromatography on silica gel (eluent:

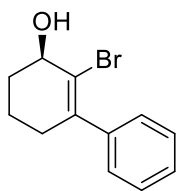
EA/Hex=10%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.31 (d,  $J$  = 8.2 Hz, 2H), 7.13 (d,  $J$  = 8.0 Hz, 2H), 6.13 – 6.08 (m, 1H), 4.38 (s, 1H), 2.50 – 2.41 (m, 1H), 2.34 (s, 4H), 1.99 – 1.85 (m, 2H), 1.80 – 1.62 (m, 3H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  140.0, 138.4, 137.2, 129.0, 125.7, 125.2, 66.3, 31.7, 27.5, 21.1, 19.4 ppm. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$  Calcd for  $\text{C}_{13}\text{H}_{15}^+$ : 171.1168, Found: 171.1168. HPLC: Chiracel AS-3 Column (250 mm); detected at 210 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.8 mL/min; Retention time: 7.4 min (major), 9.1 min (minor).



Chemical Formula:  $\text{C}_{13}\text{H}_{16}\text{O}_2$   
Exact Mass: 204.1150

#### **(*R*)-4'-methoxy-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol (2d)**

Following the General Procedure for reduction, **1d** (20.4 mg, 0.100 mmol) was reduced to give **2d** as a white solid, 17.5 mg, 86% yield, 77% ee,  $[\alpha]_D^{24} = -1.7$  ( $c = 0.5$ ,  $\text{CHCl}_3$ ), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.36 (d,  $J$  = 8.9 Hz, 2H), 6.86 (d,  $J$  = 8.9 Hz, 2H), 6.08 – 6.02 (m, 1H), 4.38 (s, 1H), 3.81 (s, 3H), 2.50 – 2.28 (m, 2H), 1.99 – 1.84 (m, 2H), 1.80 – 1.65 (m, 3H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  159.1, 139.5, 133.8, 126.4, 124.9, 113.6, 66.4, 55.3, 31.7, 27.5, 19.4 ppm. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$  Calcd for  $\text{C}_{13}\text{H}_{15}\text{O}^+$ : 187.1117, Found: 187.1117. HPLC: Chiracel OD-3 Column (250 mm); detected at 210 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.8 mL/min; Retention time: 10.1 min (minor), 12.4 min (major).



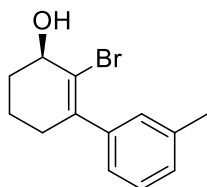
Chemical Formula: C<sub>12</sub>H<sub>13</sub>BrO

Exact Mass: 252.0150

**(R)-2-bromo-5,6-dihydro-[1,1'-biphenyl]-3(4H)-ol (4a)**

Following the General Procedure for reduction, **3a** (25.1 mg, 0.100 mmol) was reduced to give **4a** as a pale yellow solid, 23.9 mg, 95% yield, 97% ee,  $[\alpha]_D^{26} = +56.2$  ( $c = 1.0$ , CHCl<sub>3</sub>), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.39 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 7.25 – 7.20 (m, 2H), 4.43(s, 1H), 2.50 – 2.32 (m, 3H), 2.05 – 1.98 (m, 2H), 1.98 – 1.88 (m, 1H), 1.83 – 1.73 (m, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  142.2, 141.7, 128.2, 127.6, 127.4, 123.6, 71.1, 34.5, 31.7, 18.6 ppm. HPLC: Chiracel OD-3 Column (250 mm); detected at 210 nm; *n*-hexane / *i*-propanol = 90/10; flow = 1.0 mL/min; Retention time: 6.0 min (major), 6.5 min (minor). The absolute configuration of **4a** was identified by comparison of its physical and spectroscopic data with the ones reported in the literature.<sup>[6]</sup> The absolute configurations of **4b-4l** were designated in analogy to **4a**.

Following the General Procedure for reduction, with the exception that 2-MeTHF was used as solvent instead of THF, **3a** (25.1 mg, 0.100 mmol) was reduced to give **4a** as a pale yellow solid, 23.7 mg, 94% yield, 97% ee.



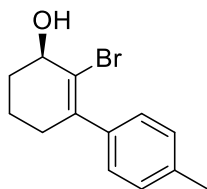
Chemical Formula: C<sub>13</sub>H<sub>15</sub>BrO

Exact Mass: 266.0306

**(R)-2-bromo-3'-methyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-ol (4b)**

Following the General Procedure for reduction, **3b** (26.6 mg, 0.100 mmol) was reduced

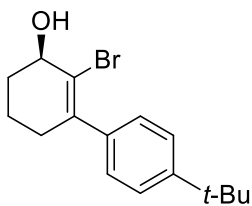
to give **4b** as a pale yellow solid, 26.7 mg, 99% yield, 95% ee,  $[\alpha]^{25}_{\text{D}} = +44.6$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.29 – 7.22 (m, 1H), 7.11 (d,  $J = 7.6$  Hz, 1H), 7.02 (d,  $J = 8.5$  Hz, 2H), 4.41 (t,  $J = 4.3$  Hz, 1H), 2.48 – 2.30 (m, 6H), 2.04 – 1.86 (m, 3H), 1.82 – 1.72 (m, 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  142.2, 141.8, 137.8, 128.2, 128.2, 128.1, 124.6, 123.4, 71.1, 34.5, 31.7, 21.4, 18.5 ppm. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$  Calcd for  $\text{C}_{13}\text{H}_{14}\text{Br}^+$ : 249.0273; Found: 249.0273. HPLC: Chiracel IC-3 Column (250 mm); detected at 210 nm;  $n$ -hexane /  $i$ -propanol = 95/5; flow = 1.0 mL/min; Retention time: 6.8 min (major), 8.4 min (minor).



Chemical Formula:  $\text{C}_{13}\text{H}_{15}\text{BrO}$   
Exact Mass: 266.0306

**(*R*)-2-bromo-4'-methyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-ol (4c)**

Following the General Procedure for reduction, **3c** (26.6 mg, 0.100 mmol) was reduced to give **4c** as a pale yellow solid, 25.9 mg, 97% yield, 93% ee,  $[\alpha]^{25}_{\text{D}} = +40.0$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.17 (d,  $J = 8.0$  Hz, 2H), 7.14 – 7.08 (m, 2H), 4.41 (t,  $J = 4.5$  Hz, 1H), 2.51 – 2.36 (m, 3H), 2.35 (s, 3H), 2.02 – 1.86 (m, 3H), 1.80 – 1.71 (m, 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  141.6, 139.3, 137.2, 128.8, 127.5, 123.4, 71.1, 34.5, 31.7, 21.2, 18.5 ppm. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$  Calcd for  $\text{C}_{13}\text{H}_{14}\text{Br}^+$ : 249.0273; Found: 249.0270. HPLC: Chiracel OD-3 Column (250 mm); detected at 210 nm;  $n$ -hexane /  $i$ -propanol = 98/2; flow = 1.0 mL/min; Retention time: 9.8 min (major), 10.4 min (minor).

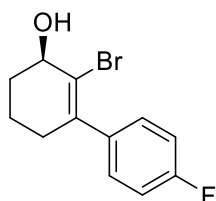


Chemical Formula: C<sub>16</sub>H<sub>21</sub>BrO

Exact Mass: 308.0776

**(*R*)-2-bromo-4'-(tert-butyl)-5,6-dihydro-[1,1'-biphenyl]-3(4H)-ol (4d)**

Following the General Procedure for reduction, **3d** (30.8 mg, 0.100 mmol) was reduced to give **4d** as a white solid, 29.3 mg, 95% yield, 96% ee,  $[\alpha]^{25}_D = +39.3$  ( $c = 1.0$ , CHCl<sub>3</sub>), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*)  $\delta$  7.37 (d,  $J = 8.2$  Hz, 2H), 7.16 (d,  $J = 8.2$  Hz, 2H), 4.41 (t,  $J = 4.4$  Hz, 1H), 2.50 (br, 1H), 2.46 – 2.40 (m, 1H), 2.39 – 2.32 (m, 1H), 2.03 – 1.96 (m, 2H), 1.95 – 1.87 (m, 1H), 1.79 – 1.73 (m, 1H), 1.33 (s, 9H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, Chloroform-*d*)  $\delta$  150.3, 141.5, 139.1, 127.3, 125.0, 123.2, 71.2, 34.4, 31.7, 31.3, 18.5 ppm. HRMS (ESI),  $m/z$ : [M+H-H<sub>2</sub>O]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>20</sub>Br<sup>+</sup>: 291.0743; Found: 291.0739. HPLC: Chiracel AS-3 Column (250 mm); detected at 210 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.8 mL/min; Retention time: 5.7 min (minor), 6.7 min (major).



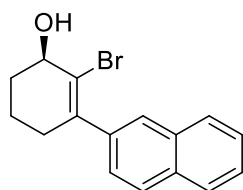
Chemical Formula: C<sub>12</sub>H<sub>12</sub>BrFO

Exact Mass: 270.0056

**(*R*)-2-bromo-4'-fluoro-5,6-dihydro-[1,1'-biphenyl]-3(4H)-ol (4e)**

Following the General Procedure for reduction, **3e** (27.0 mg, 0.100 mmol) was reduced to give **4e** as a white solid, 27.1 mg, 99% yield, 96% ee,  $[\alpha]^{25}_D = +47.4$  ( $c = 1.0$ , CHCl<sub>3</sub>), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.26 – 7.18 (m, 2H), 7.12 – 7.00 (m, 2H), 4.43 (t,  $J = 5.0$  Hz, 1H), 2.52 (br, 1H), 2.45 – 2.30 (m, 2H), 2.02–1.88 (m, 3H),

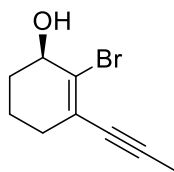
1.85 – 1.74 (m, 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  161.9 (d,  $J_{\text{C-F}} = 246.5$  Hz), 140.7, 138.0 (d,  $J_{\text{C-F}} = 3.3$  Hz), 129.4 (d,  $J_{\text{C-F}} = 8.1$  Hz), 124.0, 115.1 (d,  $J_{\text{C-F}} = 21.4$  Hz), 34.4, 31.6, 18.4 ppm. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$  Calcd for  $\text{C}_{12}\text{H}_{11}\text{BrF}^+$ : 253.0023; Found: 253.0019. HPLC: Chiracel AD-3 Column (250 mm); detected at 210 nm; *n*-hexane / *i*-propanol = 95/5; flow = 1.0 mL/min; Retention time: 10.9 min (minor), 12.2 min (major).



Chemical Formula:  $\text{C}_{16}\text{H}_{15}\text{BrO}$   
Exact Mass: 302.0306

**(*R*)-2-bromo-3-(naphthalen-2-yl)-cyclohex-2-en-1-ol (4f)**

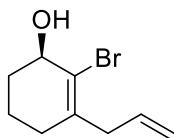
Following the General Procedure for reduction, **3f** (30.2 mg, 0.100 mmol) was reduced to give **4f** as a white solid, 27.6 mg, 91% yield, 96% ee,  $[\alpha]_{\text{D}}^{25} = +47.8$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.87 – 7.80 (m, 3H), 7.69 (s, 1H), 7.49-7.45 (m, 2H), 7.36 (dd,  $J = 8.5, 1.6$  Hz, 1H), 4.46 (t,  $J = 4.4$  Hz, 1H), 2.58 – 2.40 (m, 3H), 2.08 – 1.92 (m, 3H), 1.86 – 1.76 (m, 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  141.6, 139.6, 133.1, 132.5, 128.0, 127.8, 127.7, 126.5, 126.2, 126.1, 125.9, 124.0, 71.1, 34.6, 31.7, 18.6 ppm. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$  Calcd for  $\text{C}_{16}\text{H}_{14}\text{Br}^+$ : 285.0273; Found: 285.0270. HPLC: Chiracel AD-3 Column (250 mm); detected at 210 nm; *n*-hexane / *i*-propanol = 95/5; flow = 1.0 mL/min; Retention time: 12.1 min (minor), 15.4 min (major).



Chemical Formula:  $\text{C}_9\text{H}_{11}\text{BrO}$   
Exact Mass: 213.9993

**(R)-2-bromo-3-(prop-1-yn-1-yl)cyclohex-2-en-1-ol (4g)**

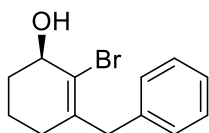
Following the General Procedure for reduction, **3g** (21.4 mg, 0.100 mmol) was reduced to give **4g** as a white solid, 20.6 mg, 96% yield, 93% ee,  $[\alpha]_D^{22} = +78.0$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  4.31 (s, 1H), 2.33 – 2.15 (m, 3H), 2.02 (s, 3H), 1.93 – 1.85 (m, 2H), 1.83 – 1.73 (m, 1H), 1.69 – 1.63 (m, 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  129.3, 125.5, 92.2, 79.3, 70.2, 32.7, 31.4, 17.9, 4.6 ppm. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$  Calcd for  $\text{C}_9\text{H}_{10}\text{Br}^+$ : 196.9960; Found: 199.9959. HPLC: Chiracel OJ-3 Column (250 mm); detected at 210 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.8 mL/min; Retention time: 12.1 min (minor), 13.6 min (major).



Chemical Formula:  $\text{C}_9\text{H}_{13}\text{BrO}$   
Exact Mass: 216.0150

**(R)-3-allyl-2-bromocyclohex-2-en-1-ol (4h)**

Following the General Procedure for reduction, **3h** (21.6 mg, 0.100 mmol) was reduced to give **4h** as a pale yellow solid, 20.0 mg, 92% yield, 96% ee,  $[\alpha]_D^{25} = +90.4$  ( $c = 1.5$ ,  $\text{CHCl}_3$ ), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  5.70-5.80 (m, 1H), 5.18 – 5.01 (m, 2H), 4.28 (t,  $J = 4.2$  Hz, 1H), 2.96 (d,  $J = 7.3$  Hz, 2H), 2.26 (s, 1H), 2.22 – 2.02 (m, 2H), 1.96 – 1.85 (m, 2H), 1.84 – 1.71 (m, 1H), 1.67-1.62 (m, 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  138.5, 133.6, 123.6, 116.6, 71.1, 41.6, 32.0, 31.2, 18.3 ppm. HPLC: Chiracel OD-3 Column (250 mm); detected at 210 nm; *n*-hexane / *i*-propanol = 95/5; flow = 1.0 mL/min; Retention time: 5.5 min (major), 6.0 min (minor). The NMR data is consistent with that reported.<sup>[6]</sup>

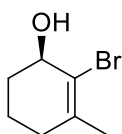


Chemical Formula: C<sub>13</sub>H<sub>15</sub>BrO

Exact Mass: 266.0306

**(R)-3-benzyl-2-bromocyclohex-2-en-1-ol (4i)**

Following the General Procedure for reduction, **3i** (26.6 mg, 0.100 mmol) was reduced to give **4i** as a pale yellow solid, 22.2 mg, 83% yield, 94% ee,  $[\alpha]_D^{25} = +55.5$  ( $c = 0.9$ , CHCl<sub>3</sub>), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.31 – 7.26 (m, 2H), 7.24 – 7.19 (m, 3H), 4.34 (t,  $J = 4.6$  Hz, 1H), 3.59 (s, 2H), 2.31 (s, 1H), 2.14 – 1.94 (m, 2H), 1.92 – 1.85 (m, 2H), 1.80 – 1.67 (m, 1H), 1.62 – 1.52 (m, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  139.5, 138.2, 128.6, 128.5, 126.4, 124.1, 71.2, 43.0, 32.0, 31.1, 18.3 ppm. HRMS (ESI),  $m/z$ :  $[M+H-H_2O]^+$  Calcd for C<sub>13</sub>H<sub>14</sub>Br<sup>+</sup>: 249.0273, Found: 249.0270. HPLC: Chiracel OJ-3 Column (250 mm); detected at 210 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.8 mL/min; Retention time: 9.7 min (major), 12.0 min (minor).



Chemical Formula: C<sub>7</sub>H<sub>11</sub>BrO

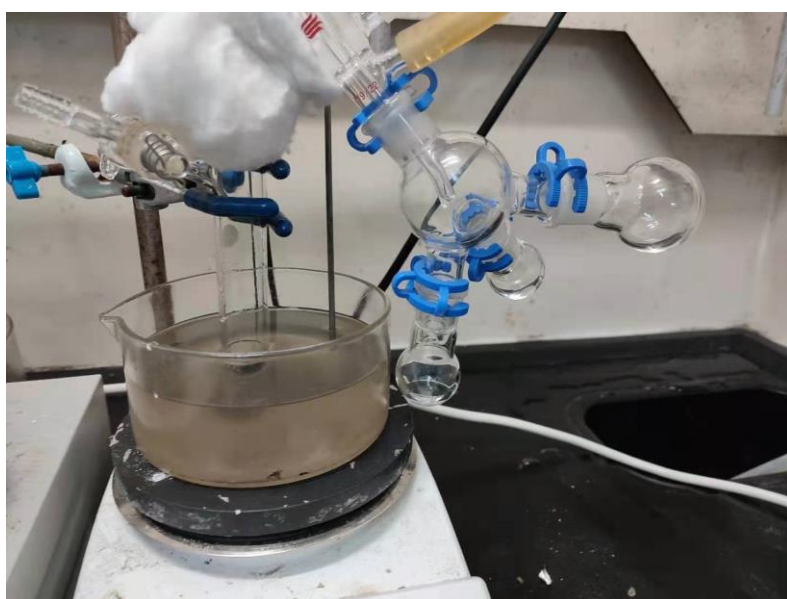
Exact Mass: 189.9993

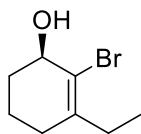
**(R)-2-bromo-3-methylcyclohex-2-en-1-ol (4j)**

Following the General Procedure for reduction, **3j** (19.0 mg, 0.100 mmol) was reduced to give **4j** as a white solid, 17.6 mg, 92% yield, 98% ee,  $[\alpha]_D^{26} = +62.4$  ( $c = 0.50$ , CHCl<sub>3</sub>), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  4.30 – 4.22 (m, 1H), 2.31 (d,  $J = 3.5$  Hz, 1H), 2.25 – 2.05 (m, 4H), 1.91 – 1.84 (m, 2H), 1.83 – 1.73 (m, 1H), 1.69 – 1.58 (m, 1H), 1.01 (t,  $J = 7.6$  Hz, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Chloroform-*d*)  $\delta$  137.1, 122.5, 71.0, 33.3, 31.9, 23.4, 18.2 ppm. HPLC: Chiracel OD-3 Column (250 mm);

detected at 210 nm; *n*-hexane / *i*-propanol = 95/5; flow = 1.0 mL/min; Retention time: 5.8 min (major), 6.2 min (minor). The NMR data is consistent with those reported for **4j**.<sup>[2]</sup>

An alternative workup procedure was developed that enabled the recovering and recycling of the THF used. Following the General procedure for reduction, **3j** (190 mg, 1.01 mmol) was treated with Cu(OAc)<sub>2</sub>, (*R*)-DTBM-C<sub>3</sub>\*-TunePhos, PPh<sub>3</sub> and PhSiH<sub>3</sub>. A total of 5.0 mL of degassed anhydrous THF was used in this reaction. After stirring for 2 h at –25 °C, the reaction was allowed to warm to room temperature. The reaction in the Schlenk tube was heated and THF was distilled off and collected (see photo), whereupon 4.2 mL (84%) of the THF used was collected and could be recycled. After distillation, 3.0 mL of MeOH was added to dilute the reaction. Then saturated NH<sub>4</sub>F in methanol (5.0 mL) was added and stirred for 10 min to quench the reaction. The resulting mixture was filtered through a short pad of celite to remove the precipitates. The filtrate was concentrated under vacuum and subjected to flash column chromatography on silica gel (eluent: EA/Hex=10%) to afford the corresponding **4j** (178 mg, 93% yield). Product **4j** obtained by this alternative procedure was checked to have 98% ee, ie. no decrease in ee was observed.

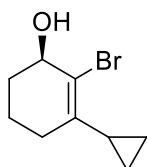




Chemical Formula: C<sub>8</sub>H<sub>13</sub>BrO  
Exact Mass: 204.0150

#### (*R*)-2-bromo-3-ethylcyclohex-2-en-1-ol (**4k**)

Following the General Procedure for reduction, **3k** (20.4 mg, 0.100 mmol) was reduced to give **4k** as a pale yellow solid, 16.6 mg, 81% yield, 96% ee,  $[\alpha]_D^{26} = +77.1$  ( $c = 0.9$ , CHCl<sub>3</sub>), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  4.3 – 4.2 (m, 1H), 2.3 (d,  $J = 3.5$  Hz, 1H), 2.2 – 2.0 (m, 4H), 1.9 – 1.8 (m, 2H), 1.8 – 1.7 (m, 1H), 1.7 – 1.6 (m, 1H), 1.0 (t,  $J = 7.6$  Hz, 3H) ppm. <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  142.1, 122.0, 71.1, 32.0, 30.8, 30.3, 18.3, 11.4 ppm. HPLC: Chiracel AD-3 Column (250 mm); detected at 210 nm; *n*-hexane / *i*-propanol = 99/1; flow = 1.0 mL/min; Retention time: 12.9 min (major), 16.1 min (minor). The NMR data is consistent with those reported for **4k**.<sup>[6]</sup>

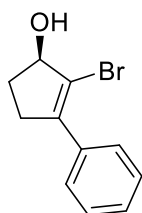


Chemical Formula: C<sub>9</sub>H<sub>13</sub>BrO  
Exact Mass: 216.0150

#### (*R*)-2-bromo-3-cyclopropylcyclohex-2-en-1-ol (**4l**)

Following the General Procedure for reduction, **3l** (43.2 mg, 0.200 mmol) was reduced to give **4l** as a colorless oil, 40.7 mg, 96% yield (0.2 mmol scale), 98% ee  $[\alpha]_D^{28} = +103.4$  ( $c = 1.5$ , CHCl<sub>3</sub>), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=10%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  4.29 (d,  $J = 3.5$  Hz, 1H), 2.29 (s, 1H), 2.06 – 1.96 (m, 1H), 1.88 (q,  $J = 7.2, 6.0$  Hz, 2H), 1.79 – 1.67 (m, 3H), 1.63 – 1.57 (m, 1H), 0.78 – 0.67 (m, 2H), 0.64 – 0.52 (m,

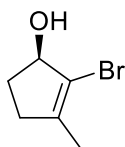
2H). ppm  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Methanol- $d_4$ )  $\delta$  140.7, 123.8, 72.1, 34.1, 27.3, 18.6, 18.0, 5.2, 4.4 ppm. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$  Calcd for  $\text{C}_9\text{H}_{12}\text{Br}^+$ : 199.0117; Found: 199.0115. HPLC: Chiracel OJ-3 Column (250 mm); detected at 210 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.8 mL/min; Retention time: 7.4 min (major), 8.7 min (minor).



Chemical Formula:  $\text{C}_{11}\text{H}_{11}\text{BrO}$   
Exact Mass: 237.9993

#### **(*R*)-2-bromo-3-phenylcyclopent-2-en-1-ol (4m)**

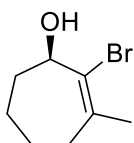
Following the General Procedure for reduction, **3m** (23.8 mg, 0.100 mmol) was reduced to give **4m** as a white solid, 20.9 mg, 88% yield, 96% ee,  $[\alpha]^{24}_{\text{D}} = +24.2$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=5%).  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.66 – 7.56 (m, 2H), 7.42 – 7.30 (m, 3H), 4.86 (t,  $J = 5.8$  Hz, 1H), 2.94 – 2.83 (m, 1H), 2.79 – 2.67 (m, 1H), 2.55 – 2.43 (m, 1H), 2.25 (s, 1H), 2.02 – 1.91 (m, 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  141.2, 135.0, 128.3, 128.2, 127.5, 120.4, 81.1, 33.8, 30.8 ppm. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$  Calcd for  $\text{C}_{11}\text{H}_{10}\text{Br}^+$ : 220.9960, Found: 220.9960. HPLC: Chiracel OD-3 Column (250 mm); detected at 210 nm; *n*-hexane / *i*-propanol = 95/5; flow = 0.8 mL/min; Retention time: 20.9 min (minor), 22.1 min (major).



Chemical Formula:  $\text{C}_6\text{H}_9\text{BrO}$   
Exact Mass: 175.9837

#### **(*R*)-2-bromo-3-methylcyclopent-2-en-1-ol (4n)**

Following the General Procedure for reduction, **3n** (17.6 mg, 0.100 mmol) was reduced to give **4n** as a pale yellow solid, 11.8 mg, 67% yield, 98% ee,  $[\alpha]_D^{27} = +47.4$  ( $c = 0.5$ ,  $\text{CHCl}_3$ ), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=5%).  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  4.71 (s, 1H), 2.50 – 2.43 (m, 1H), 2.39 – 2.32 (m, 1H), 2.28 – 2.21 (m, 1H), 2.14 (br, 1H), 1.88 – 1.80 (m, 1H), 1.78 (s, 3H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  141.5, 120.1, 79.9, 34.3, 31.2, 15.9 ppm. HPLC: Chiracel AD-3 Column (250 mm); detected at 210 nm;  $n$ -hexane /  $i$ -propanol = 98/2; flow = 1.0 mL/min; Retention time: 11.4 min (major), 13.5 min (minor). The NMR data is consistent with that reported.<sup>[11]</sup> The absolute configuration of **2n** was identified by comparison of its physical and spectroscopic data with the ones reported in the literature.<sup>[11]</sup> The absolute configuration of **4m** was determined by comparing with **4n**.

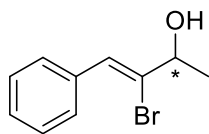


Chemical Formula:  $\text{C}_8\text{H}_{13}\text{BrO}$

Exact Mass: 204.0150

#### **(R)-2-bromo-3-methylcyclohept-2-en-1-ol (4o)**

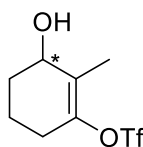
Following the General Procedure for reduction, **3o** (21.1 mg, 0.105 mmol) was reduced to give **4o** as a white solid, 17.8 mg, 84% yield, 98% ee,  $[\alpha]_D^{24} = -27.0$  ( $c = 0.5$ ,  $\text{CHCl}_3$ ), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=3%).  $^1\text{H}$  NMR (400 MHz, Methanol- $d_4$ )  $\delta$  4.55 (dd,  $J = 7.8, 2.7$  Hz, 1H), 2.55 – 2.38 (m, 1H), 2.27 – 2.15 (m, 1H), 2.03 – 1.86 (m, 4H), 1.84 – 1.69 (m, 2H), 1.66 – 1.52 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Methanol- $d_4$ )  $\delta$  140.0, 126.2, 77.2, 34.6, 33.4, 27.5, 26.1, 25.1. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$  Calcd for  $\text{C}_8\text{H}_{12}\text{Br}^+$ : 187.0117, Found: 187.0115. HPLC: Chiracel AS-3 Column (250 mm); detected at 220 nm;  $n$ -hexane /  $i$ -propanol = 98/2; flow = 0.6 mL/min; Retention time: 14.2 min (major), 16.8 min (minor). The absolute configuration of **4o** was determined by comparing with **4n** and **4a**.



Chemical Formula: C<sub>10</sub>H<sub>11</sub>BrO  
Exact Mass: 225.9993

### (Z)-3-bromo-4-phenylbut-3-en-2-ol (**4p**)

Following the General Procedure for reduction, **3p** (22.6 mg, 0.100 mmol) was reduced to give **4p** as a light yellow oil, 18.3 mg, 81% yield, 86% ee,  $[\alpha]^{21}_{\text{D}} = +3.6$  ( $c = 0.5$ , CHCl<sub>3</sub>), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=3%). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*)  $\delta$  7.60 (d,  $J = 7.5$  Hz, 2H), 7.38 – 7.28 (m, 3H), 7.07 (s, 1H), 4.48 (p,  $J = 6.1$  Hz, 1H), 2.19 (d,  $J = 5.6$  Hz, 1H), 1.47 (d,  $J = 6.3$  Hz, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, Chloroform-*d*)  $\delta$  135.1, 131.4, 129.1, 128.1, 128.1, 126.9, 73.6, 22.5 ppm. HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; *n*-hexane / *i*-propanol = 95/5; flow = 0.8 mL/min; Retention time: 13.0 min (major), 14.6 min (minor). The NMR data is consistent with those reported for **4p**.<sup>[9]</sup>

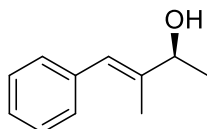


Chemical Formula: C<sub>8</sub>H<sub>11</sub>F<sub>3</sub>O<sub>4</sub>S  
Exact Mass: 260.0330

### 3-hydroxy-2-methylcyclohex-1-en-1-yl trifluoromethanesulfonate (**4q**)

Following the General Procedure for reduction, **3q** (25.8 mg, 0.100 mmol) was reduced to give **4q** as a colorless oil, 25.2 mg, 97% yield, 92% ee,  $[\alpha]^{25}_{\text{D}} = +0.6$  ( $c = 0.5$ , CHCl<sub>3</sub>), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=5%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  4.21 (s, 1H), 2.42 – 2.26 (m, 2H), 1.94 – 1.79 (m, 6H), 1.77 – 1.70 (m, 2H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  146.5, 128.1, 118.3 (q,  $J_{\text{C-F}} = 319.5$  Hz), 69.3, 31.0, 27.8, 18.5, 13.8 ppm. HPLC: Chiracel ID Column (250 mm); detected at 210 nm; *n*-hexane / *i*-propanol = 98/2; flow

= 0.8 mL/min; Retention time: 8.3 min (minor), 8.9 min (major). The NMR data is consistent with that reported.<sup>[9]</sup>

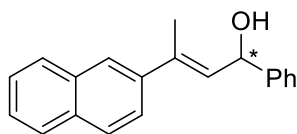


Chemical Formula: C<sub>11</sub>H<sub>14</sub>O

Exact Mass: 162.1045

#### **(*S,E*)-3-methyl-4-phenylbut-3-en-2-ol (4r)**

Following the General Procedure for reduction, **3r** (32.0 mg, 0.200 mmol) was reduced to give **4r** as a light yellow oil, 30.1 mg, 93% yield, 90% ee,  $[\alpha]^{25}_{\text{D}} = +9.6$  ( $c = 0.5$ , CHCl<sub>3</sub>), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=3%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.37 – 7.29 (m, 2H), 7.29 – 7.24 (m, 2H), 7.24 – 7.18 (m, 1H), 6.51 (s, 1H), 4.37 (q,  $J = 6.4$  Hz, 1H), 1.88 (d,  $J = 1.4$  Hz, 3H), 1.36 (d,  $J = 6.5$  Hz, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  141.6, 137.6, 128.9, 128.1, 126.4, 124.3, 73.6, 21.7, 13.4 ppm. HPLC: Chiracel OD-3 Column (250 mm); detected at 254 nm; *n*-hexane / *i*-propanol = 95/5; flow = 0.8 mL/min; Retention time: 10.8 min (minor), 12.4 min (major). The NMR data is consistent with that reported.<sup>[9]</sup>



Chemical Formula: C<sub>20</sub>H<sub>18</sub>O

Exact Mass: 274.1358

#### **(*E*)-3-(naphthalen-2-yl)-1-phenylbut-2-en-1-ol (4s)**

Following the General Procedure for reduction, **3s** (27.2 mg, 0.100 mmol) was reduced to give **4s** as a white solid, 26.8 mg, 98% yield, 54% ee,  $[\alpha]^{24}_{\text{D}} = +27.2$  ( $c = 0.5$ , CHCl<sub>3</sub>), obtained by the purification with flash column chromatography on silica gel (eluent: EA/Hex=3%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.84 – 7.74 (m, 4H), 7.58 (dd,  $J = 8.6, 1.9$  Hz, 1H), 7.51 – 7.42 (m, 4H), 7.41 – 7.36 (m, 2H), 7.32 – 7.26 (m, 1H), 6.16

(dd,  $J = 8.6, 1.4$  Hz, 1H), 5.71 (d,  $J = 8.5$  Hz, 1H), 2.30 (d,  $J = 1.3$  Hz, 3H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  143.6, 139.8, 137.0, 133.3, 132.7, 130.6, 128.6, 128.1, 127.8, 127.6, 127.5, 126.2, 126.1, 125.8, 124.7, 124.2, 71.2, 16.5 ppm. HRMS (ESI),  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{20}\text{H}_{17}^+$ : 257.1325, Found: 257.1320. HPLC: Chiracel AS-3 Column (250 mm); detected at 254 nm;  $n$ -hexane /  $i$ -propanol = 95/5; flow = 0.8 mL/min; Retention time: 15.1 min (minor), 17.3 min (major).

### 3.4 TON experiments:

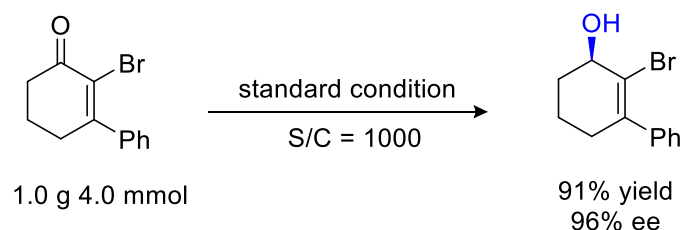
S/C = 500 experiment: In a argon-filled glove box, an oven-dried 4 mL screw-cap vial containing a magnetic stir bar was charged with  $\text{Cu}(\text{OAc})_2$  (1.8 mg, 0.01 mmol), ( $R$ )-DTBM- $\text{C}_3^*$ -TunePhos (13.1 mg, 0.011 mol), and  $\text{PPh}_3$  (2.6 mg, 0.01 mol). The vial was removed from the glove box. Degassed anhydrous THF (2.0 mL) was added and the mixture was stirred for 30 min. The resulting solution (0.2 mL) was transferred to a 10 mL Schleck tube with 0.2 mL THF.  $\text{PhSiH}_3$  (1.2 equiv) was added to the mixture and stirred for another 30 min to generate the copper hydride, before being cooled to  $-25^\circ\text{C}$ . Substrate **3j** (0.5 mmol, 89.5 mg) was dissolved in 0.1 mL THF under argon and transferred to the resulting CuH solution at  $-25^\circ\text{C}$  *via* syringe. After stirring for 2 h, the reaction was allowed to warm to room temperature. Saturated  $\text{NH}_4\text{F}$  in methanol (2.5 mL) was added with stirring for 10 min to quench the reaction. The resulting mixture was filtered *via* a short pad of celite to remove the precipitates. The filtrate was concentrated under vacuum and subjected to flash column chromatography on silica gel (eluent: EA/Hex=10%) to afford **4j**.

**Table S3. Results of TON experiments**

	<b>3j</b>	S/C	total solvent	yield of <b>4j</b>	ee
1	0.1 mmol	100	0.5 mL	96%	98%
2	0.5 mmol	500	0.5 mL	96%	98%
3	1.0 mmol	1000	0.5 mL	95%	98%

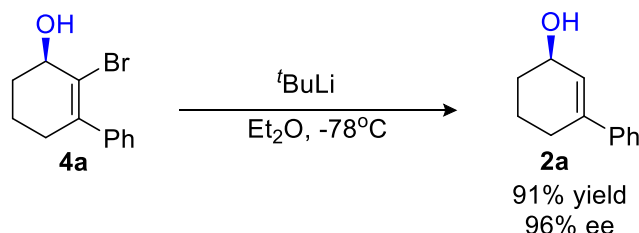
## IV. Gram-scale reaction and derivatization Reactions

### 4.1 Gram-scale reaction:



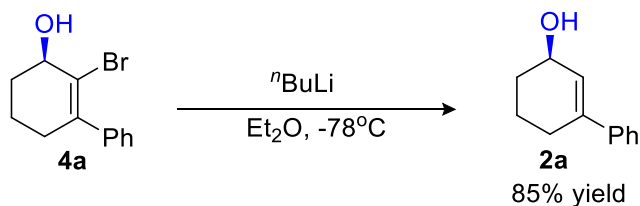
An Ar filled and oven-dried 25 mL screw-cap vial containing a magnetic stir bar was charged with  $\text{Cu}(\text{OAc})_2$  (0.8 mg, 0.004 mmol), *R*-DTBM- $\text{C}_3^*$ -TunePhos (5.2 mg, 0.0044 mol), and  $\text{PPh}_3$  (1.1 mg, 0.0042 mol). Degassed anhydrous THF (4 mL) was added and the mixture was stirred for 30 min, and a pale blue solution is formed. The reaction was added  $\text{PhSiH}_3$  (0.6 mL, 4.8 mmol) and the resultant pale yellow solution was stirred for another 30 min to generate copper hydride, before being cooled to  $-25^\circ\text{C}$ . Substrate **3a** (1.0 g, 4.0 mmol) was dissolved in 2 mL THF under argon and transferred to the resulting  $\text{CuH}$  solution at  $-25^\circ\text{C}$  via syringe. After stirring for 3 h, the reaction allowed to warm to room temperature, Saturated  $\text{NH}_4\text{F}$  in methanol (5 mL) was added and stirred for 10 min to quench the reaction. Saturated aqueous  $\text{NH}_4\text{Cl}$  (10 mL) was then added. The organic layer was separated, the aqueous layer was extracted with 3 x 10 mL EA. The combined organics were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , concentrated under vacuum. The residue was subjected to column chromatography on silica gel (eluent: EA/Hex=10%) to afford **4a** (0.91 g, 91% yield).

### 4.2 Debromination reaction:



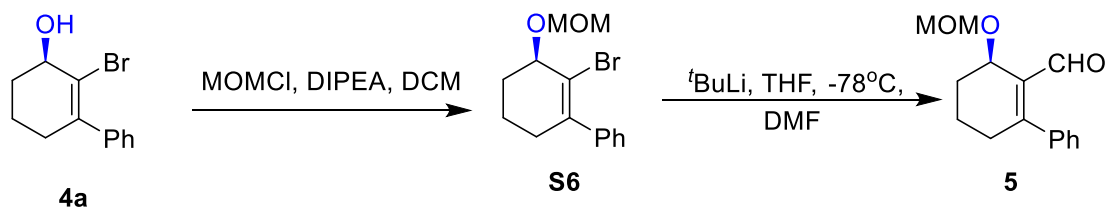
To a solution of **4a** (110 mg, 0.435 mmol) in THF (5 mL) was added *t*-BuLi (1.1 M, 2.3 mL, 2.1 mmol) at  $-78^\circ\text{C}$ . The reaction was stirred for 1 h, then warmed to room

temperature. It was quenched by the addition of saturated aqueous  $\text{NH}_4\text{Cl}$ . The organic layer was separated, and the aqueous layer was extracted with 2 x 10 mL EA. The combined organics were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated. The residue was subjected to flash column chromatography on silica gel (eluent: EA/Hex=10%) to afford **2a** (69 mg, 91% yield),  $[\alpha]^{27}_{\text{D}} = +9.6$  ( $c = 0.5$ ,  $\text{CHCl}_3$ ).



**Alternative debromination using *n*-BuLi:** To a solution of **4a** (25.3 mg, 0.100 mmol) in THF (1 mL) was added *n*-BuLi (1.6 M, 0.35 mL, 0.56 mmol) at  $-78^\circ\text{C}$ . The reaction was stirred for 2 h, then warmed to room temperature and continued to stir for 12 h. It was quenched by the addition of saturated aqueous  $\text{NH}_4\text{Cl}$ . The organic layer was separated, and the aqueous layer was extracted with 2 x 5 mL EA. The combined organics were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated. The residue was subjected to flash column chromatography on silica gel (eluent: EA/Hex=10%) to afford **2a** (14.8 mg, 85% yield).

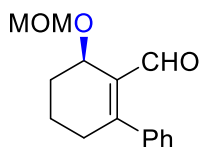
### 4.3 Formylation:



To a solution of **4a** (253 mg, 1.00 mmol) in 1.5 mL DCM at room temperature was added DIPEA (258 mg, 2.00 mmol) and MOMCl (0.22 mL, 2.6 mmol). The reaction was stirred for 12 h at room temperature. Then saturated aqueous  $\text{NH}_4\text{Cl}$  (4 mL) was added to quench the reaction. The organic layer was separated, and the aqueous layer

was extracted with 2 x 4 mL DCM. The combined organics were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was subjected to flash column chromatography on silica gel (eluent: EA/Hex=5%) to afford **S6** (244 mg, 82% yield).

To **S6** (33.8 mg, 0.110 mmol) in 1 mL THF under Ar at - 78°C was added *t*-BuLi (2.5 mL, 1.3 M; 0.19 mmol) dropwise. The reaction was stirred for 0.5 h at this temperature. Then DMF (15.5 mg, 0.210 mmol) was added. The reaction mixture was stirred for 0.5 h at - 78°C. Saturated aqueous NH<sub>4</sub>Cl (3 mL) was added to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with 2 x 3 mL EA. The combined organics were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was subjected to flash column chromatography on silica gel (eluent: EA/Hex=5%) to afford **5** as a white solid, 29.2 mg, 97% yield.



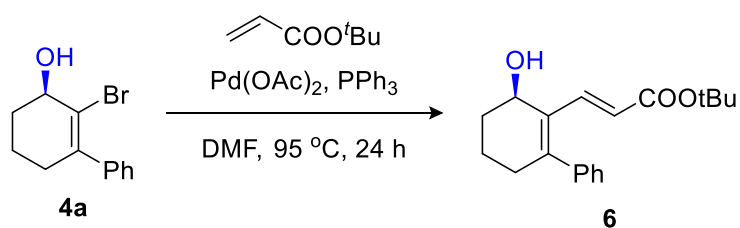
Chemical Formula: C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>

Exact Mass: 246.1256

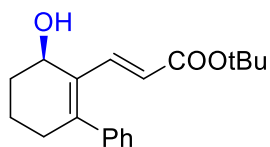
#### **(R)-3-(methoxymethoxy)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carbaldehyde (5)**

White solid, 29.2 mg, 80% yield over two steps,  $[\alpha]_D^{27} = +118.6$  (c = 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 9.41 (s, 1H), 7.36 – 7.28 (m, 3H), 7.20 – 7.15 (m, 2H), 4.83 (d, *J* = 6.8 Hz, 1H), 4.65 (d, *J* = 7.0 Hz, 2H), 3.35 (s, 3H), 2.59 (dd, *J* = 20.1, 5.3 Hz, 1H), 2.45 – 2.33 (m, 1H), 2.11 (d, *J* = 14.0 Hz, 1H), 2.03 – 1.89 (m, 1H), 1.80 – 1.70 (m, 1H), 1.46 (t, *J* = 14.0 Hz, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, Chloroform-*d*) δ 192.7, 161.9, 138.5, 135.5, 128.8, 128.5, 128.3, 96.9, 66.6, 55.7, 33.8, 27.8, 16.9 ppm. HRMS (ESI), *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>Na<sup>+</sup>: 269.1148; Found:269.1153.

#### **4.4 Heck reaction:**



Pd(OAc)<sub>2</sub> (9.0 mg, 0.040 mmol), PPh<sub>3</sub> (31 mg, 0.12 mmol) and **4a** (48.5 mg, 0.190 mmol) were dissolved in 3 mL DMF under Ar, and stirred for 10 min. Et<sub>3</sub>N (0.28 mL) and *tert*-butyl acrylate (64 mg, 0.50 mmol) was then added to the mixture. The reaction was heated to 100 °C with stirring for 24 h. The reaction was cooled to room temperature and the mixture was poured into MTBE (10 mL) and H<sub>2</sub>O (10 mL). The organic layer was separated and the aqueous layer was extracted with 2 x 10 mL MTBE. The combined organics were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was subjected to flash column chromatography on silica gel (eluent: EA/Hex=5%) to afford **6** (49.7 mg, 83% yield).



Chemical Formula: C<sub>19</sub>H<sub>24</sub>O<sub>3</sub>

Exact Mass: 300.1725

***tert*-butyl (*R*, *E*)-3-(3-hydroxy-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)acrylate (**6**)**

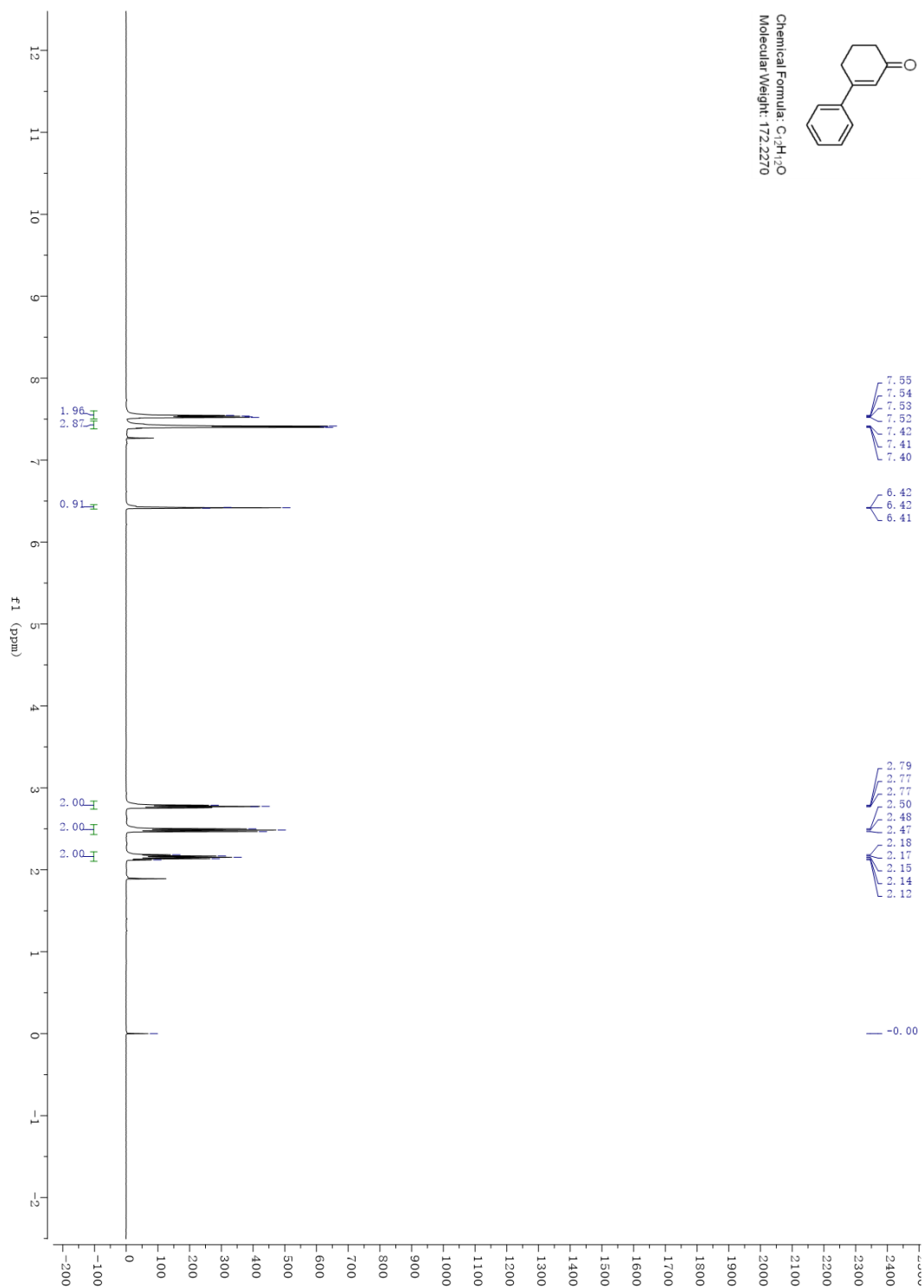
White solid,  $[\alpha]_D^{28} = +147.5$  ( $c = 0.5$ , CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.39 – 7.24 (m, 5H), 7.16 – 7.12 (m, 2H), 6.09 (d,  $J = 16.0$  Hz, 1H), 4.64 (s, 1H), 2.53 (dd,  $J = 19.3, 7.2$  Hz, 1H), 2.49 – 2.38 (m, 1H), 2.09 – 2.01 (m, 1H), 1.98 – 1.88 (m, 1H), 1.81 – 1.67 (m, 3H), 1.42 (s, 9H) ppm. <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  166.8, 149.9, 141.9, 141.1, 131.1, 128.2, 128.2, 127.7, 118.7, 80.0, 63.6, 33.7, 30.9, 28.1, 17.0 ppm. HRMS (ESI),  $m/z$ : [M+Na]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>24</sub>O<sub>3</sub>Na<sup>+</sup>: 323.1618; Found: 323.1613.

## V. References

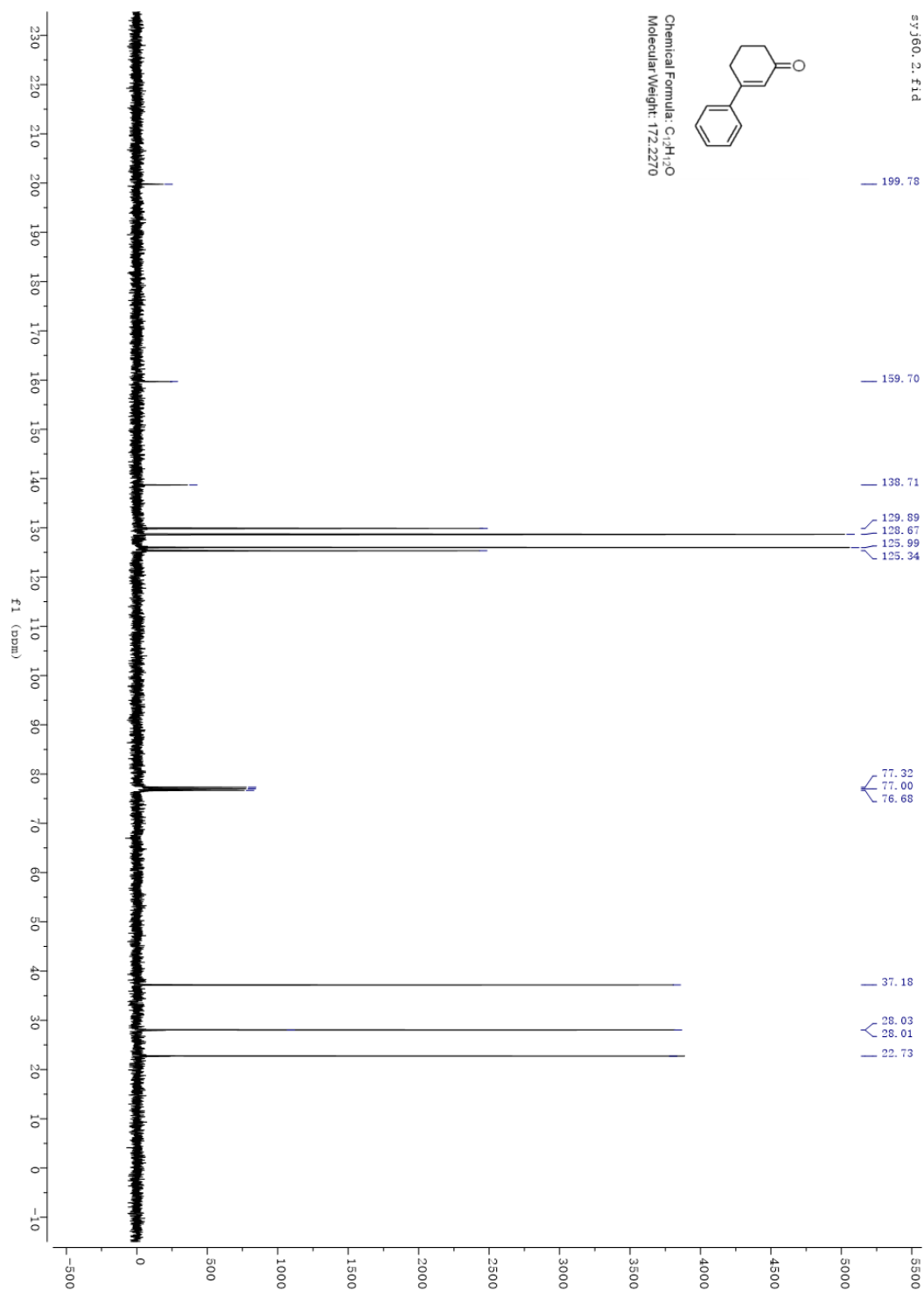
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## VI. NMR spectra

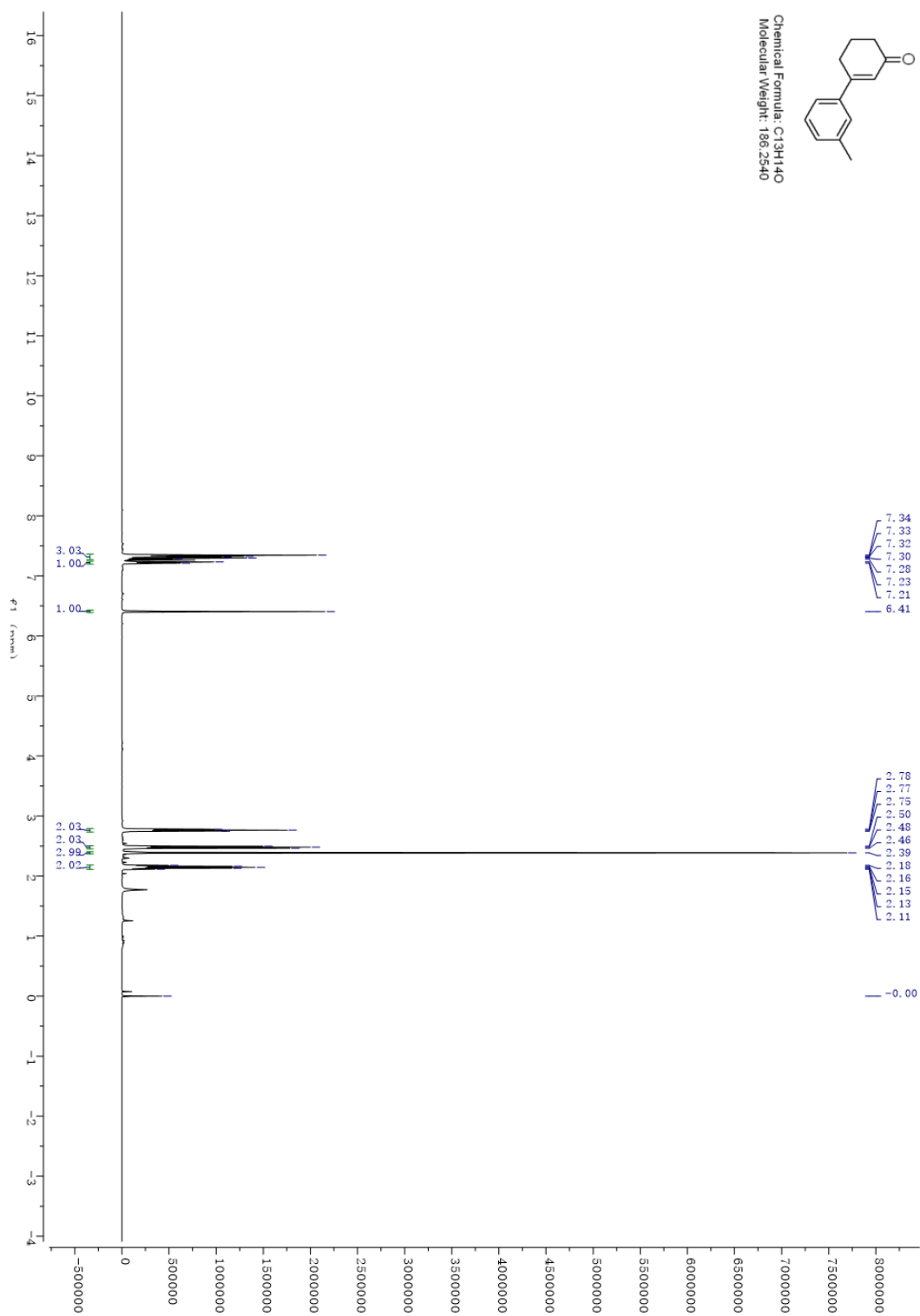
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **1a**



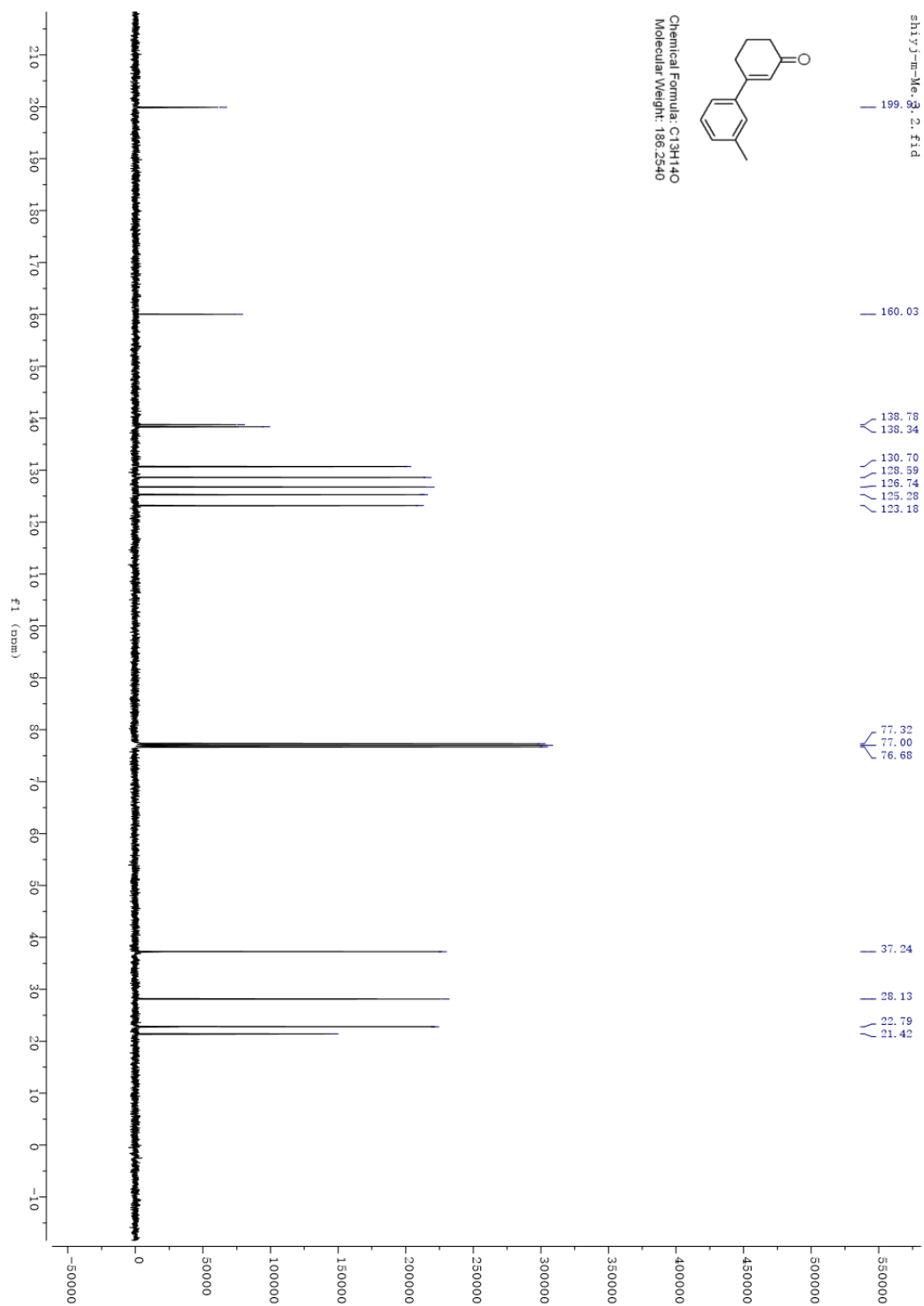
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **1a**



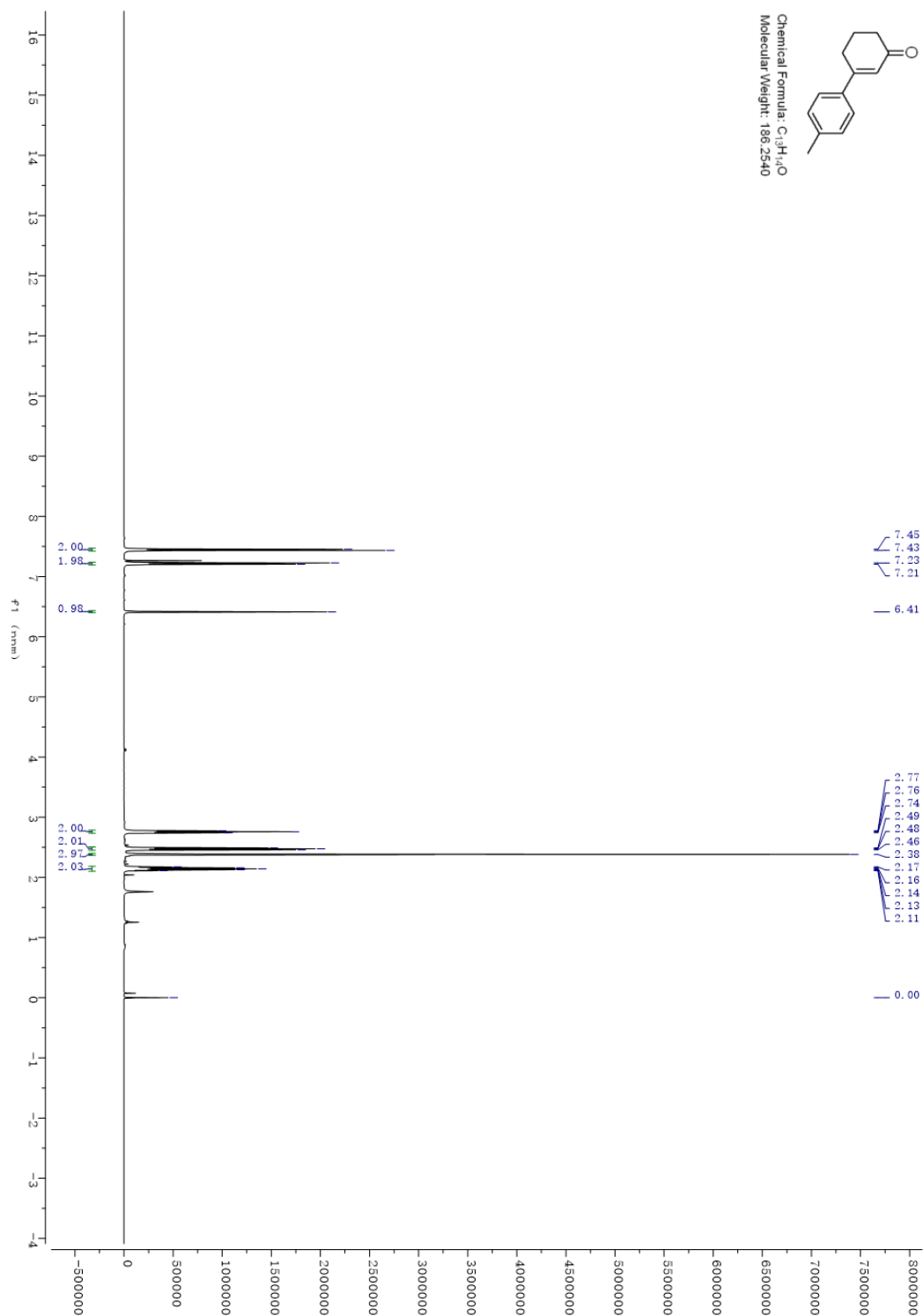
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **1b**



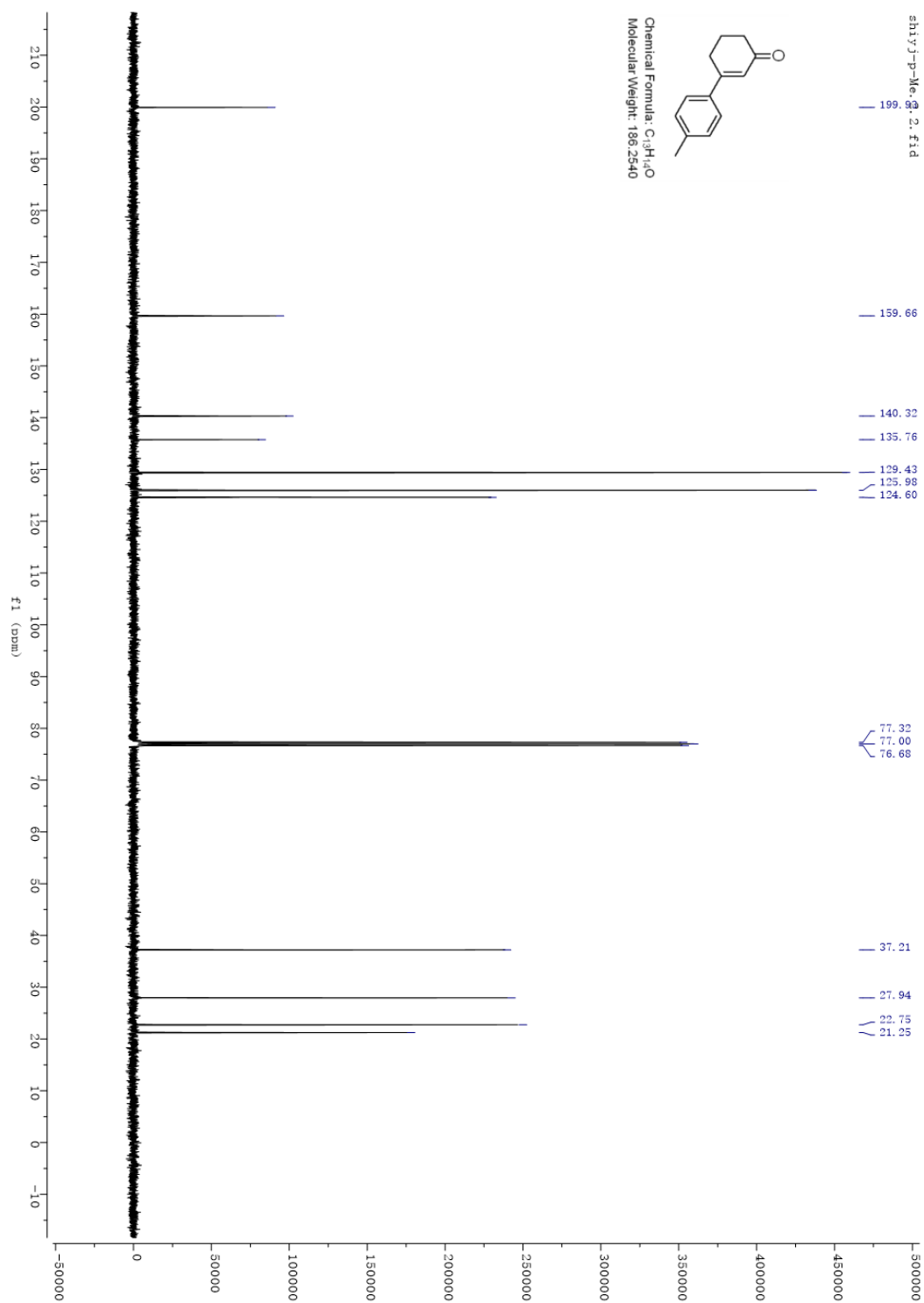
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **1b**



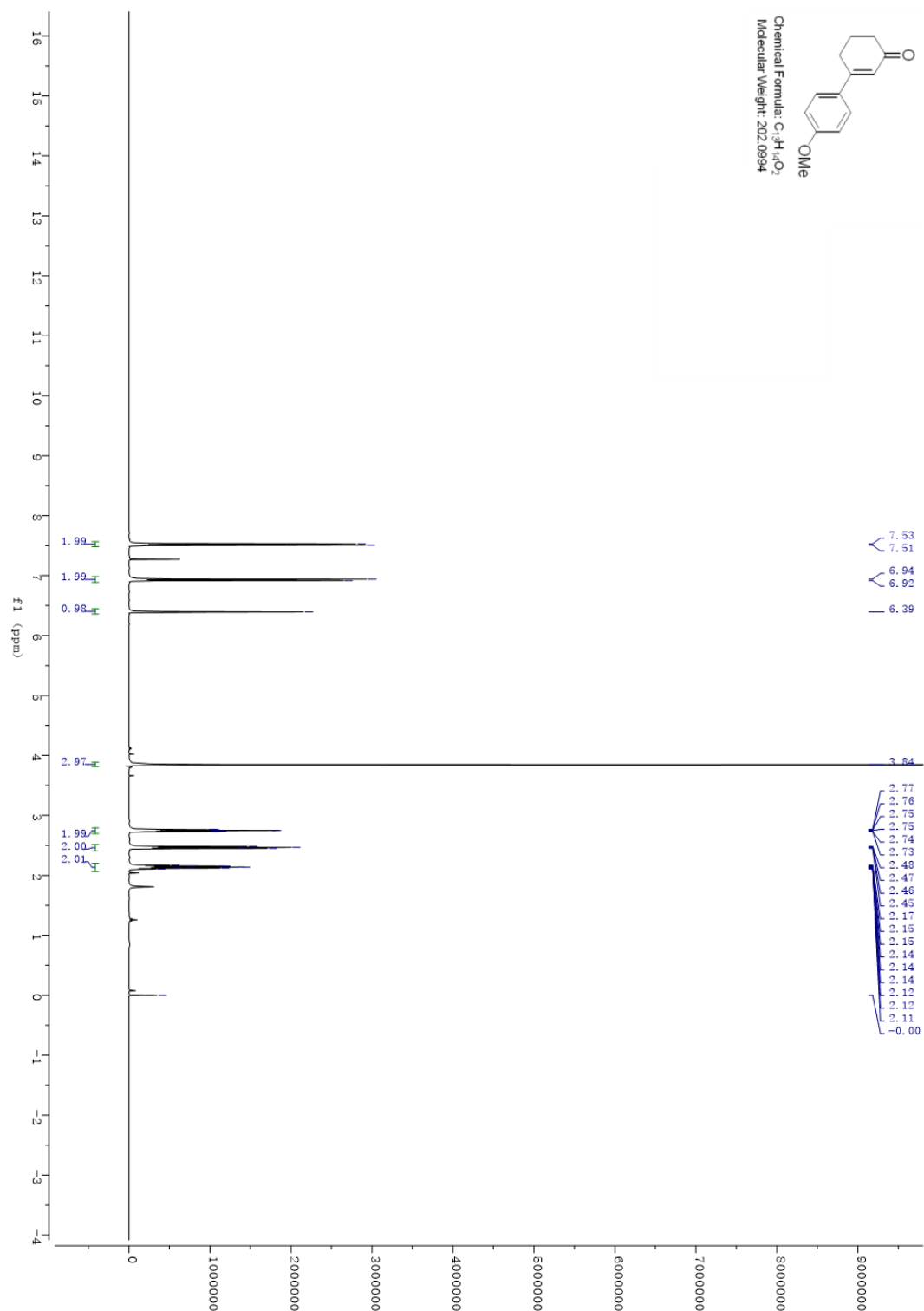
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **1c**



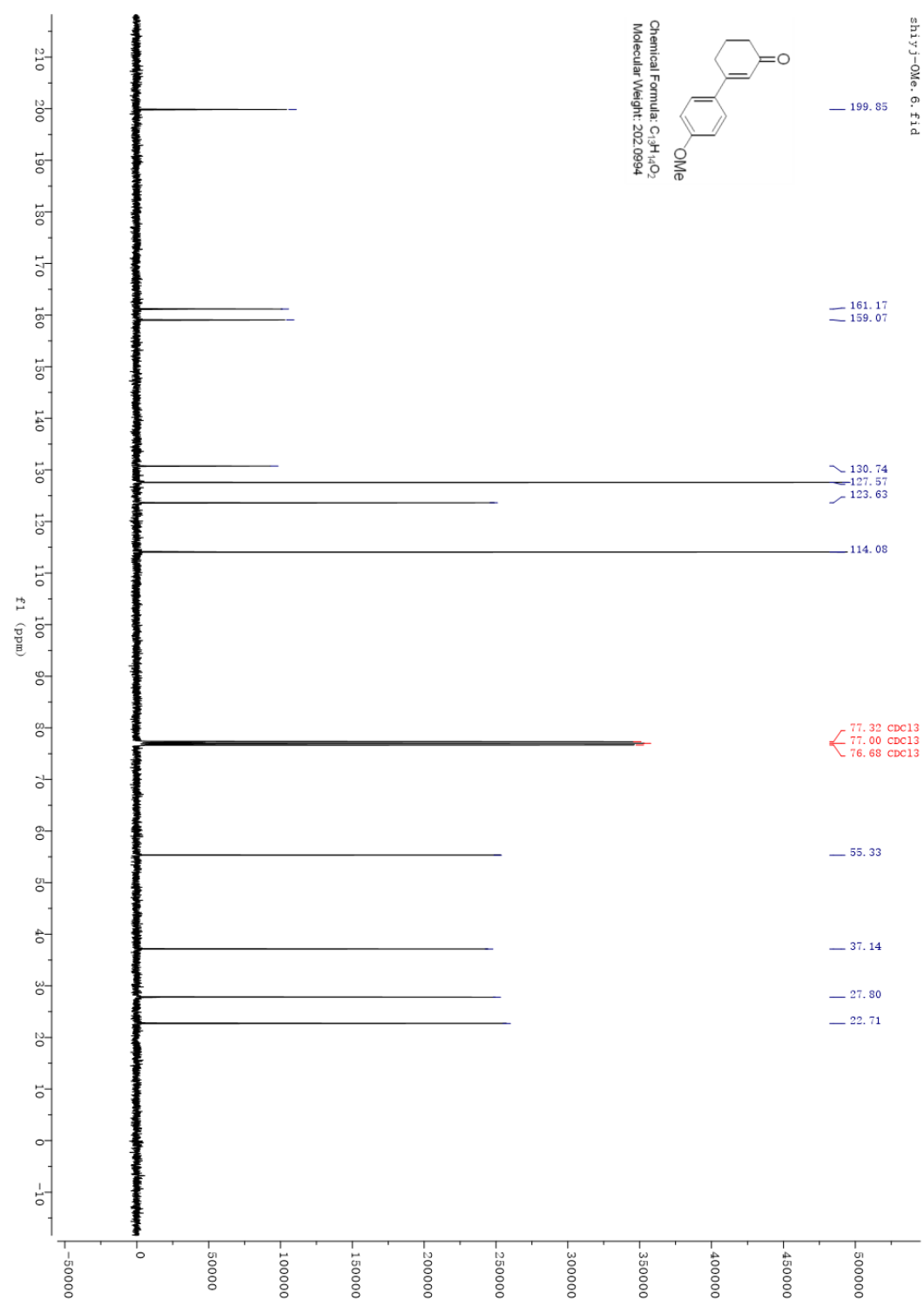
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **1c**



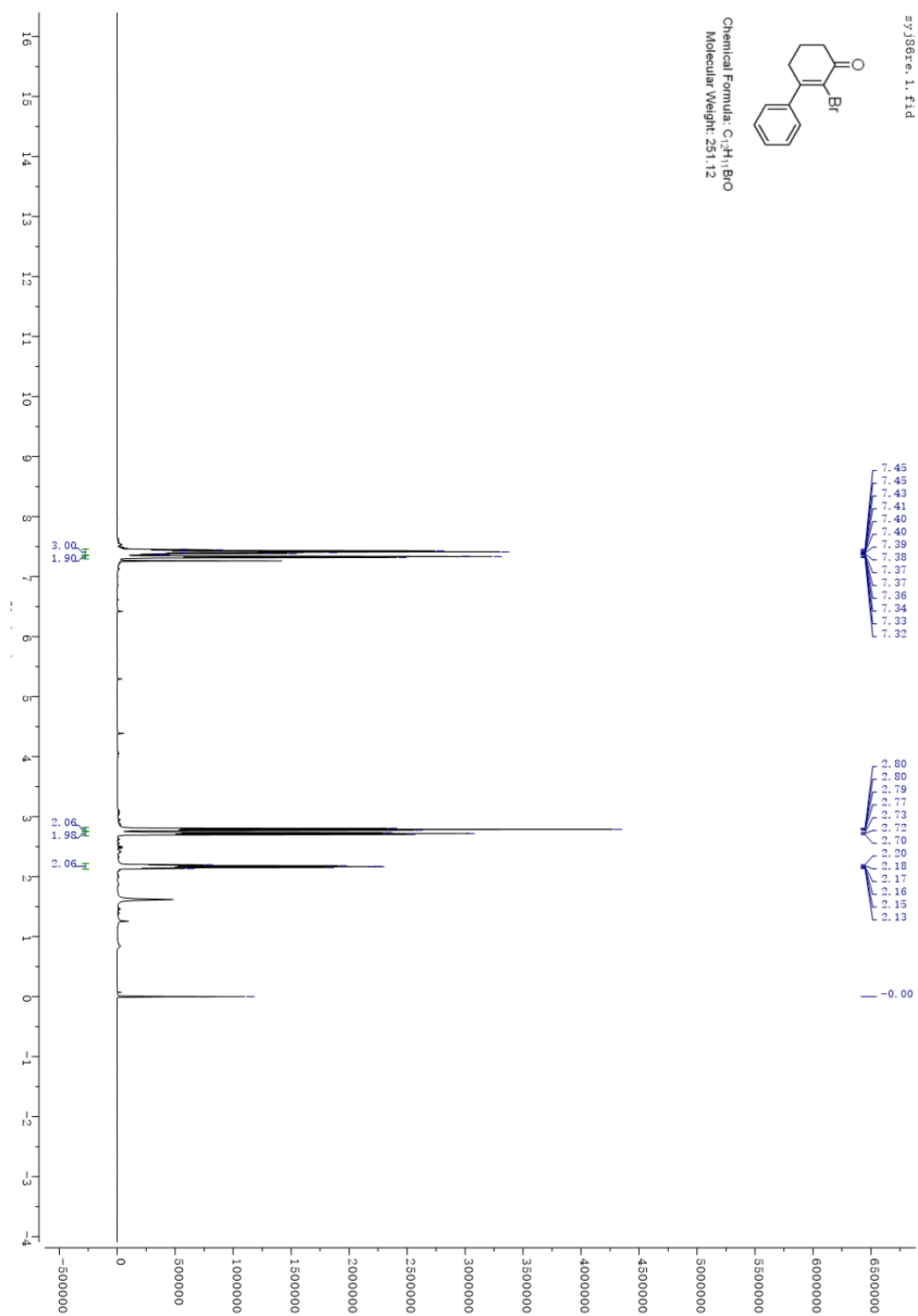
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **1d**



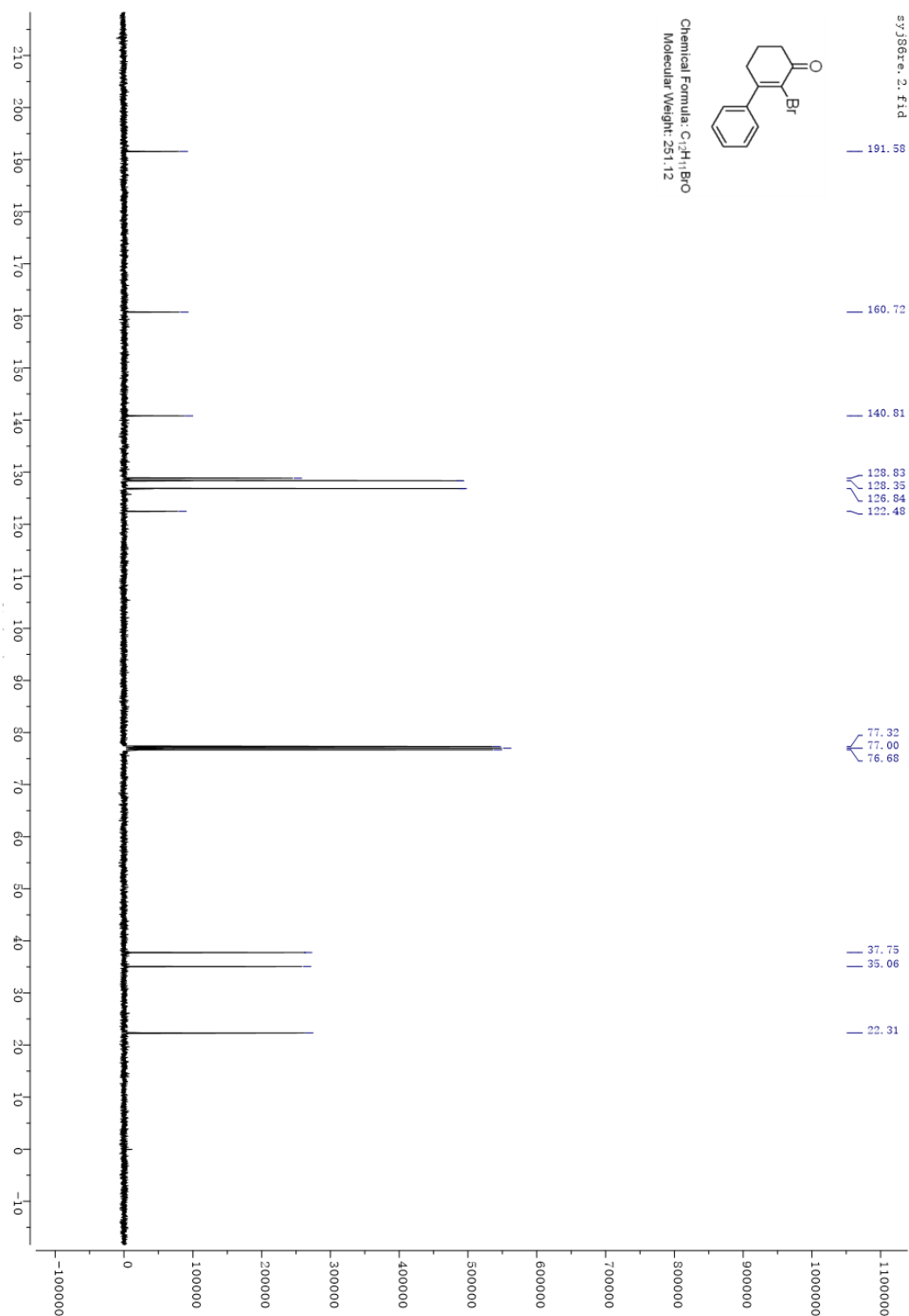
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-d) of compound **1d**



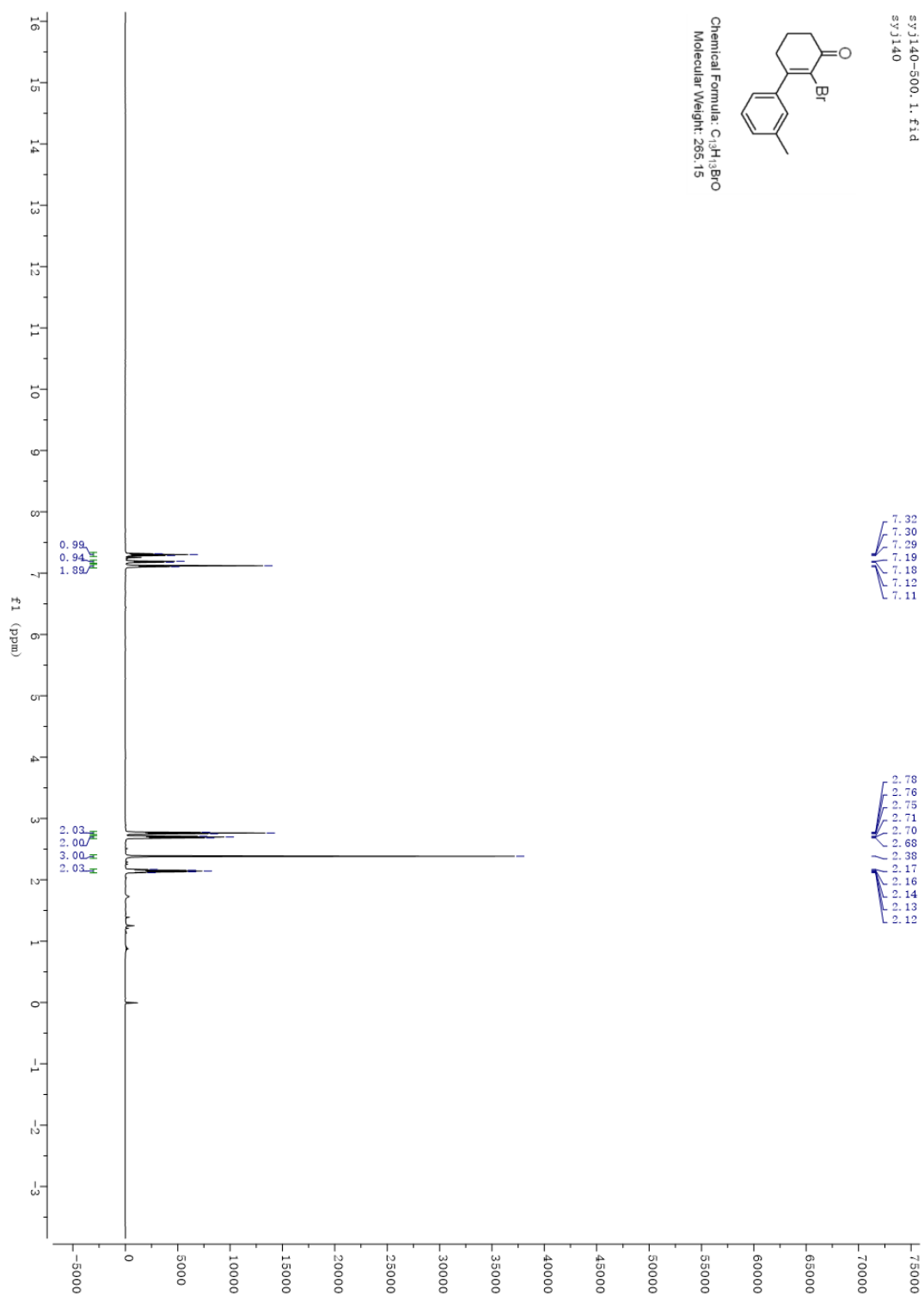
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **3a**



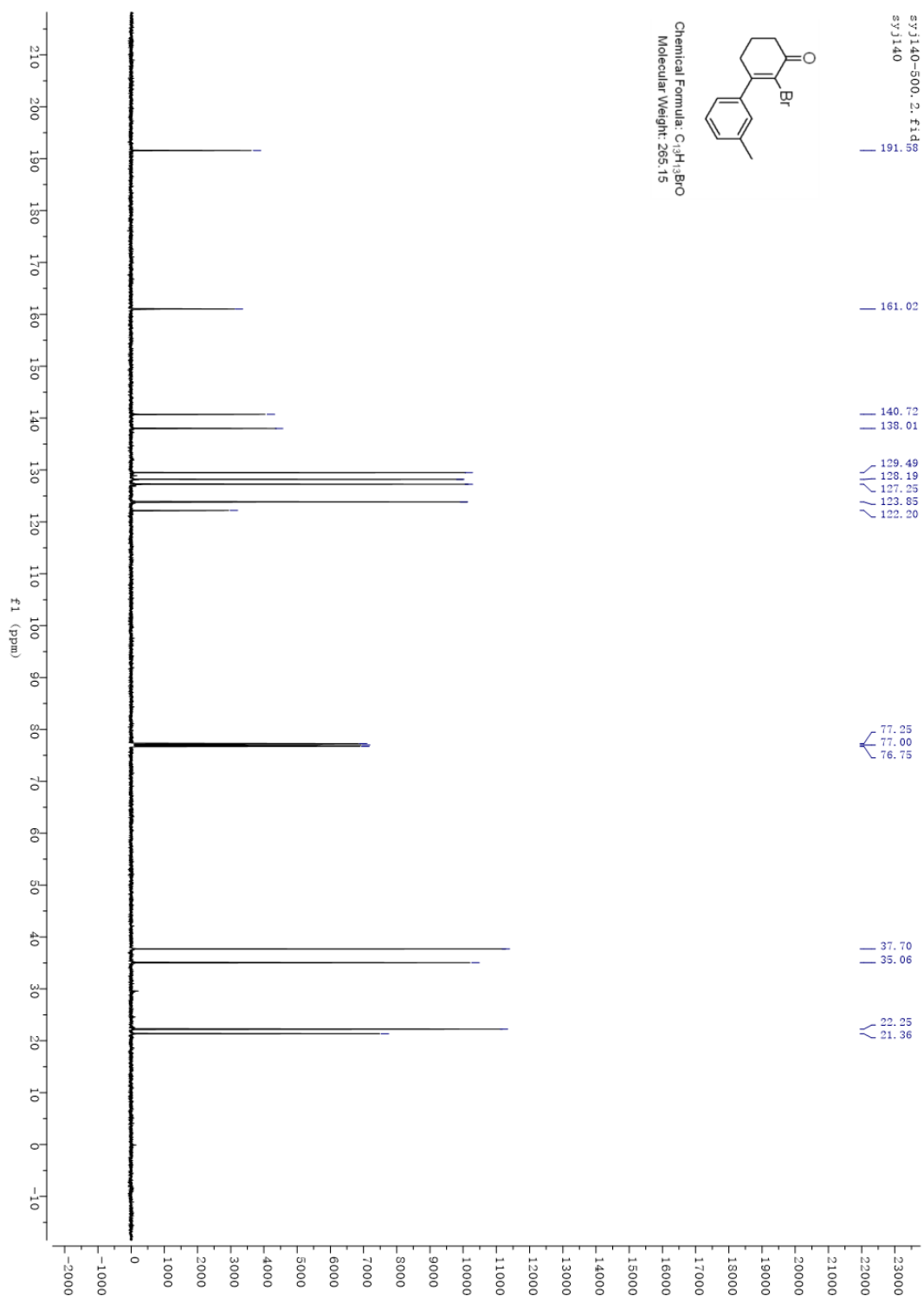
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **3a**



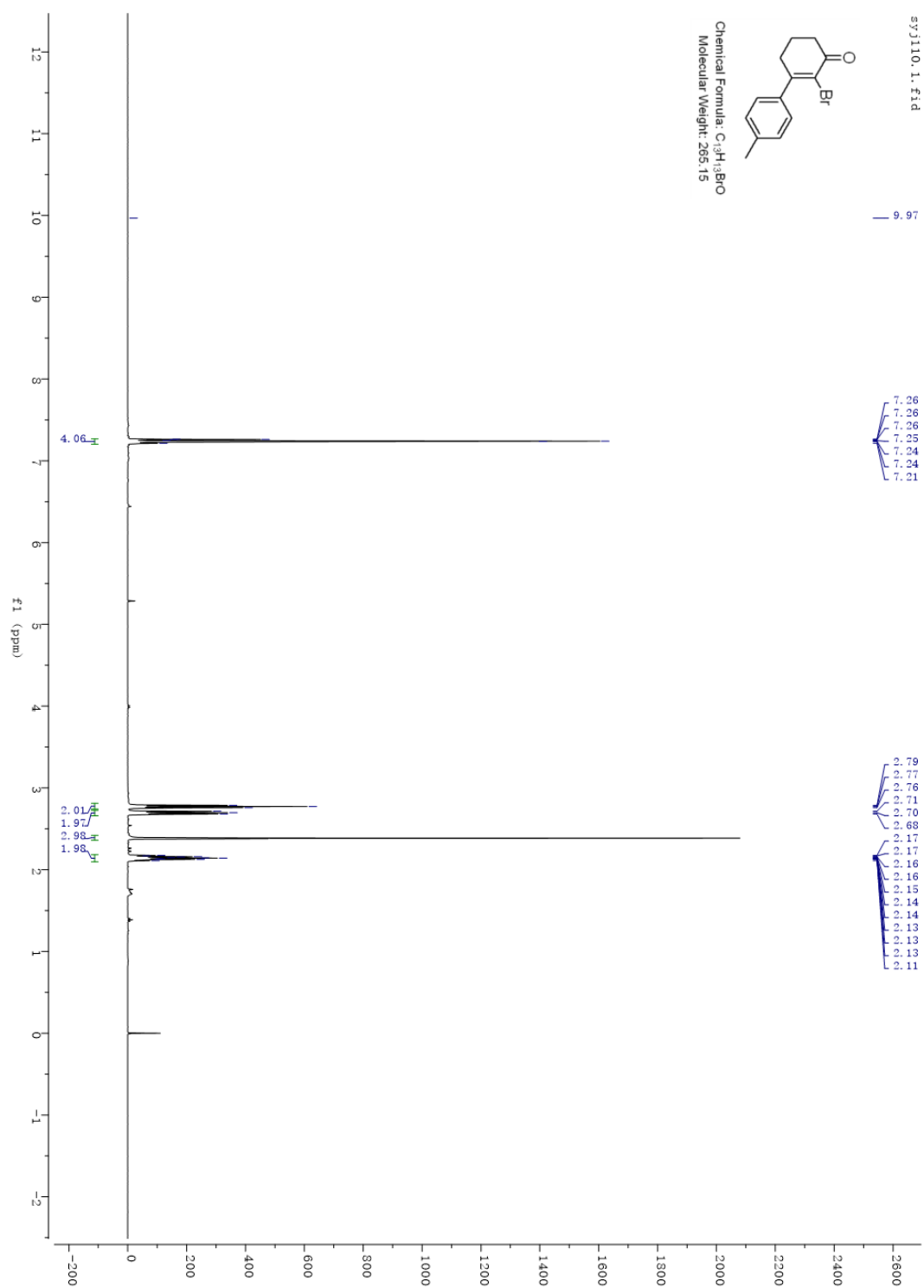
$^1\text{H}$  NMR (500 MHz, Chloroform- $d$ ) of compound **3b**



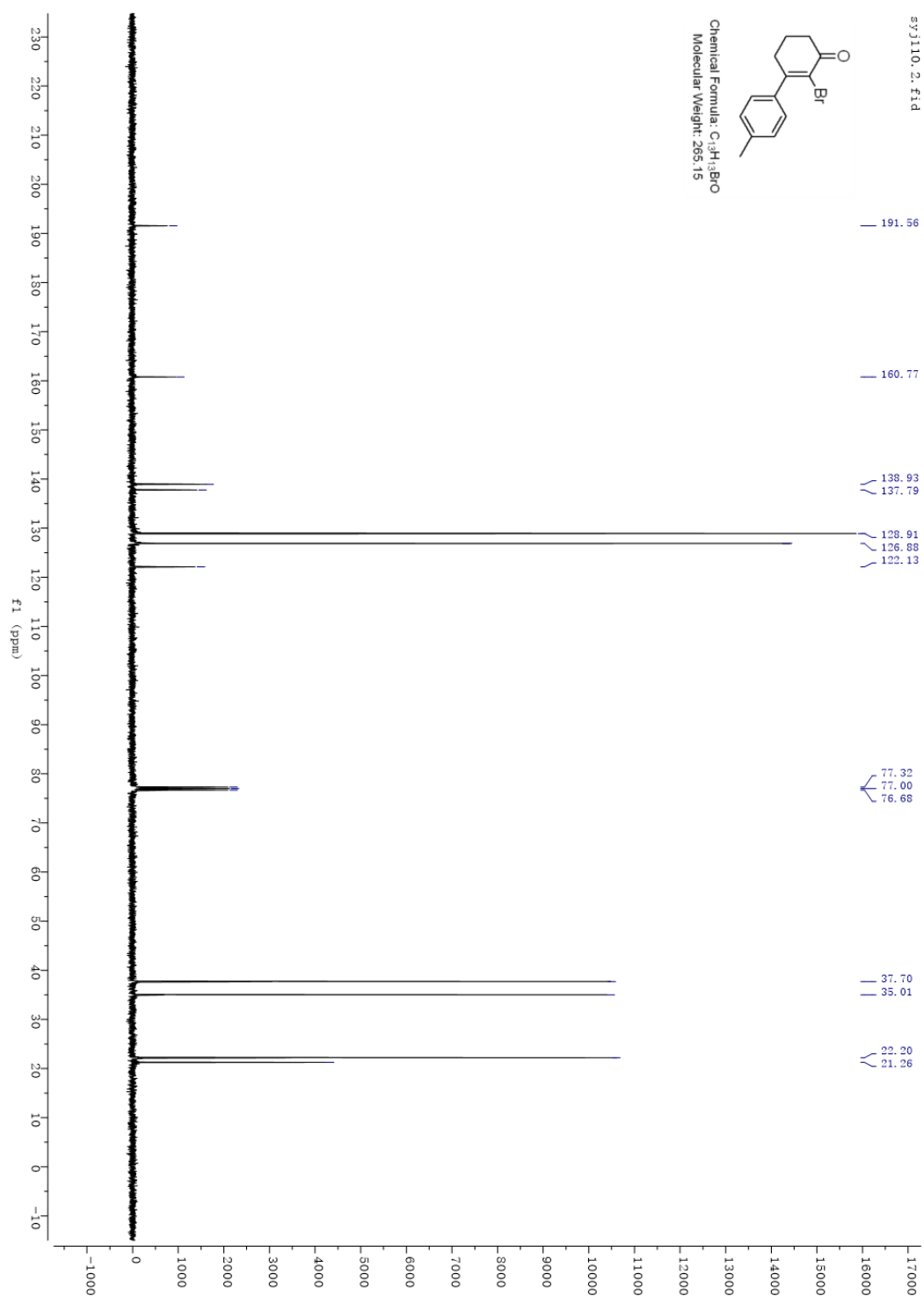
$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, Chloroform- $d$ ) of compound **3b**



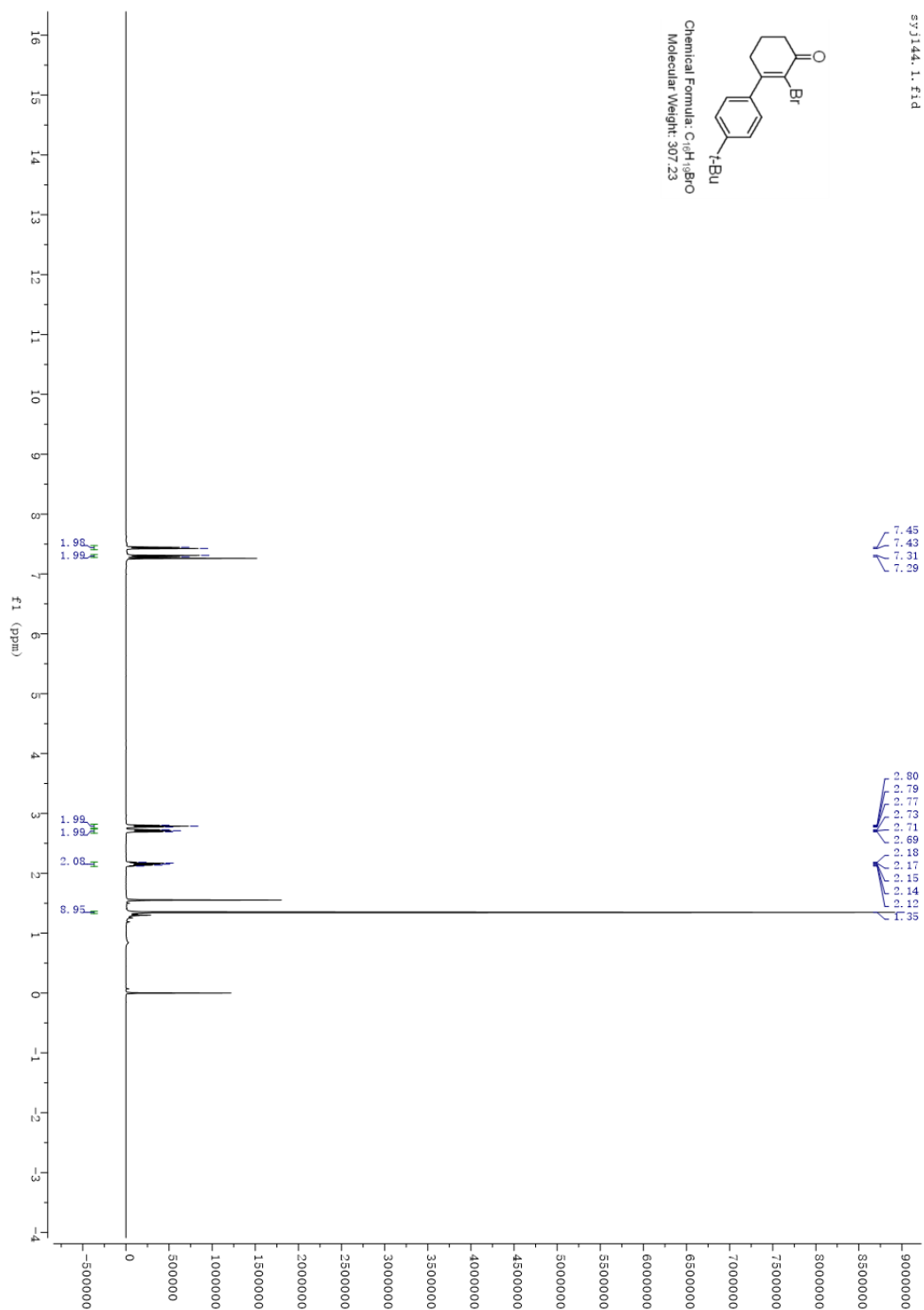
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **3c**



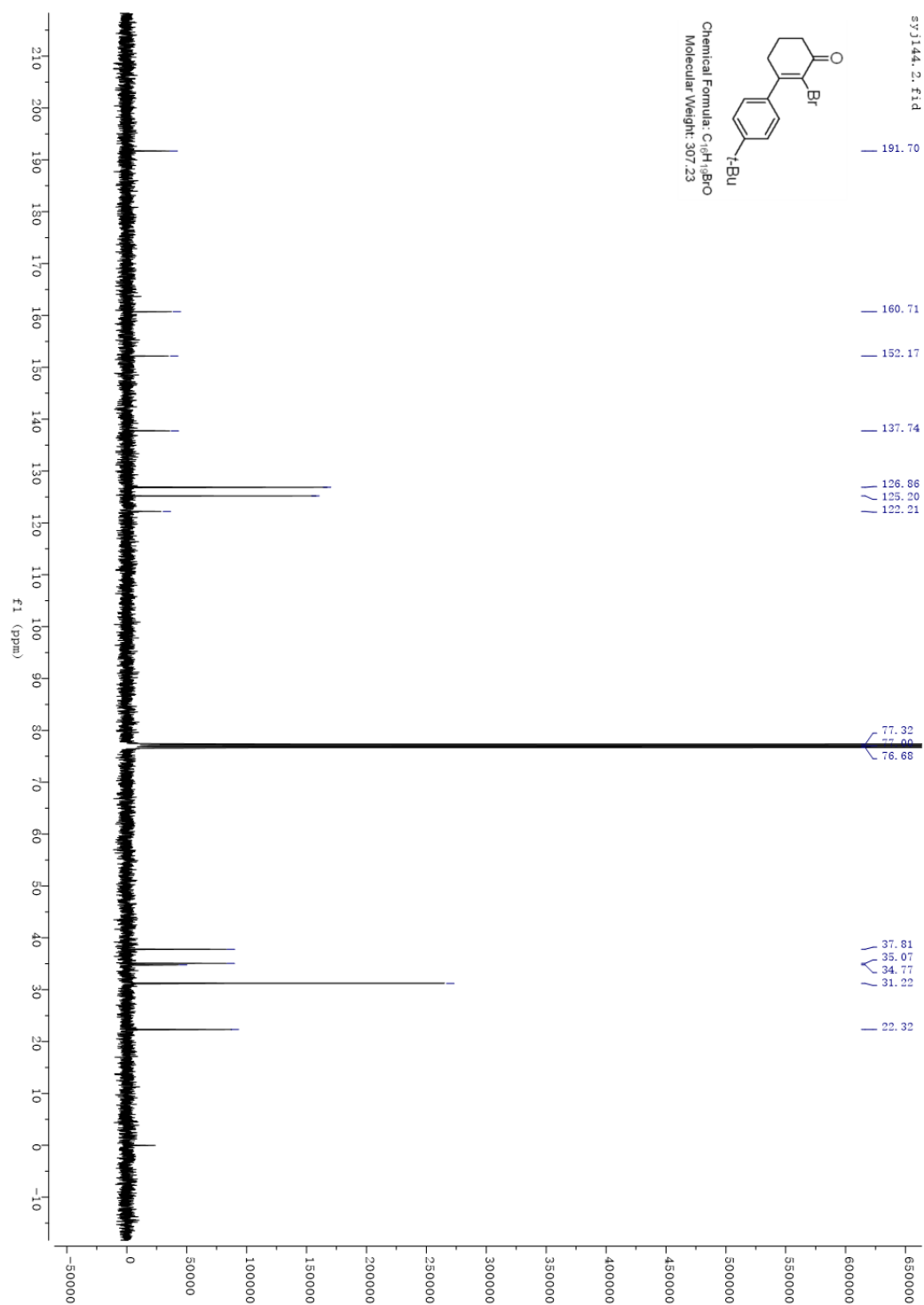
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **3c**



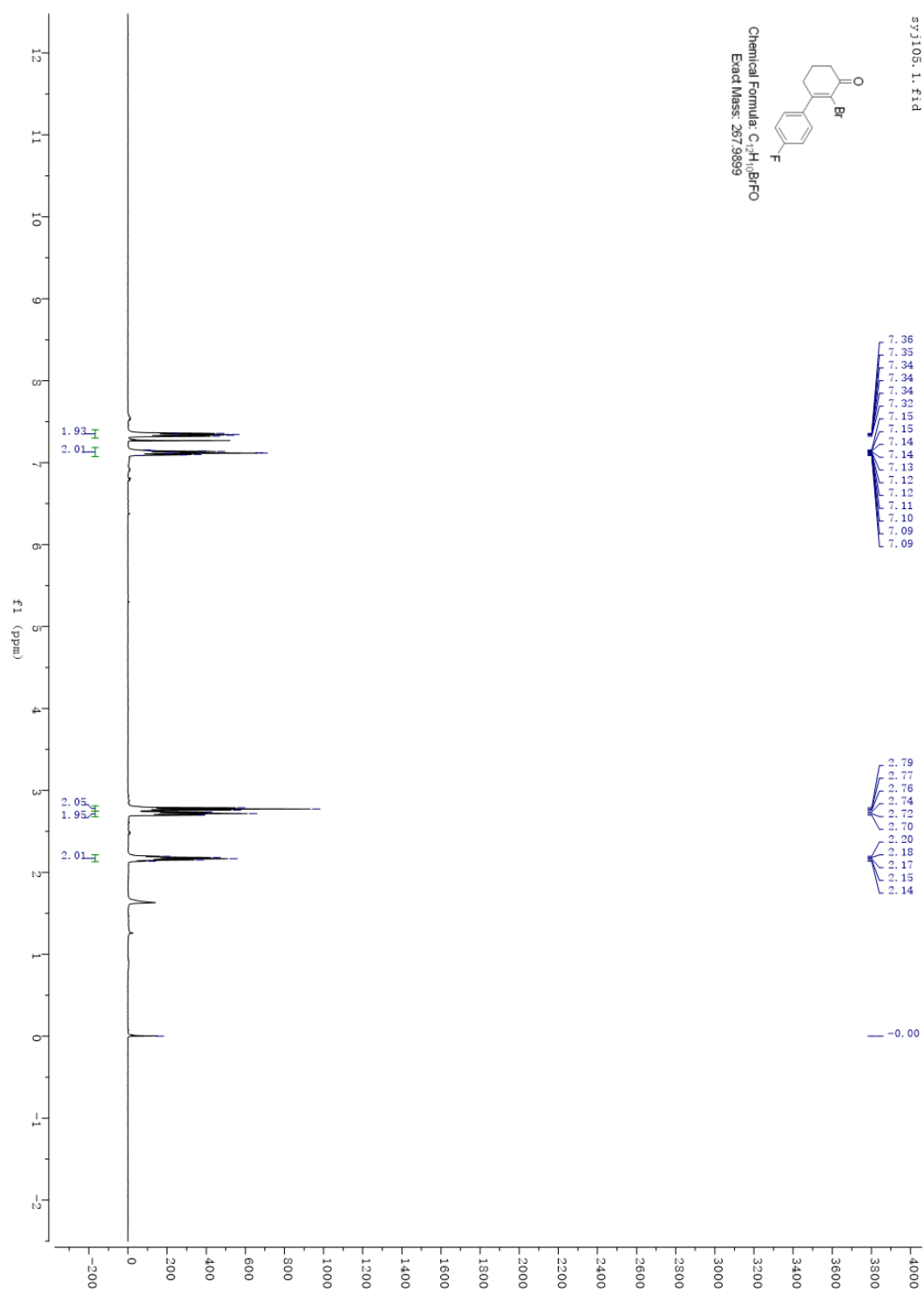
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **3d**



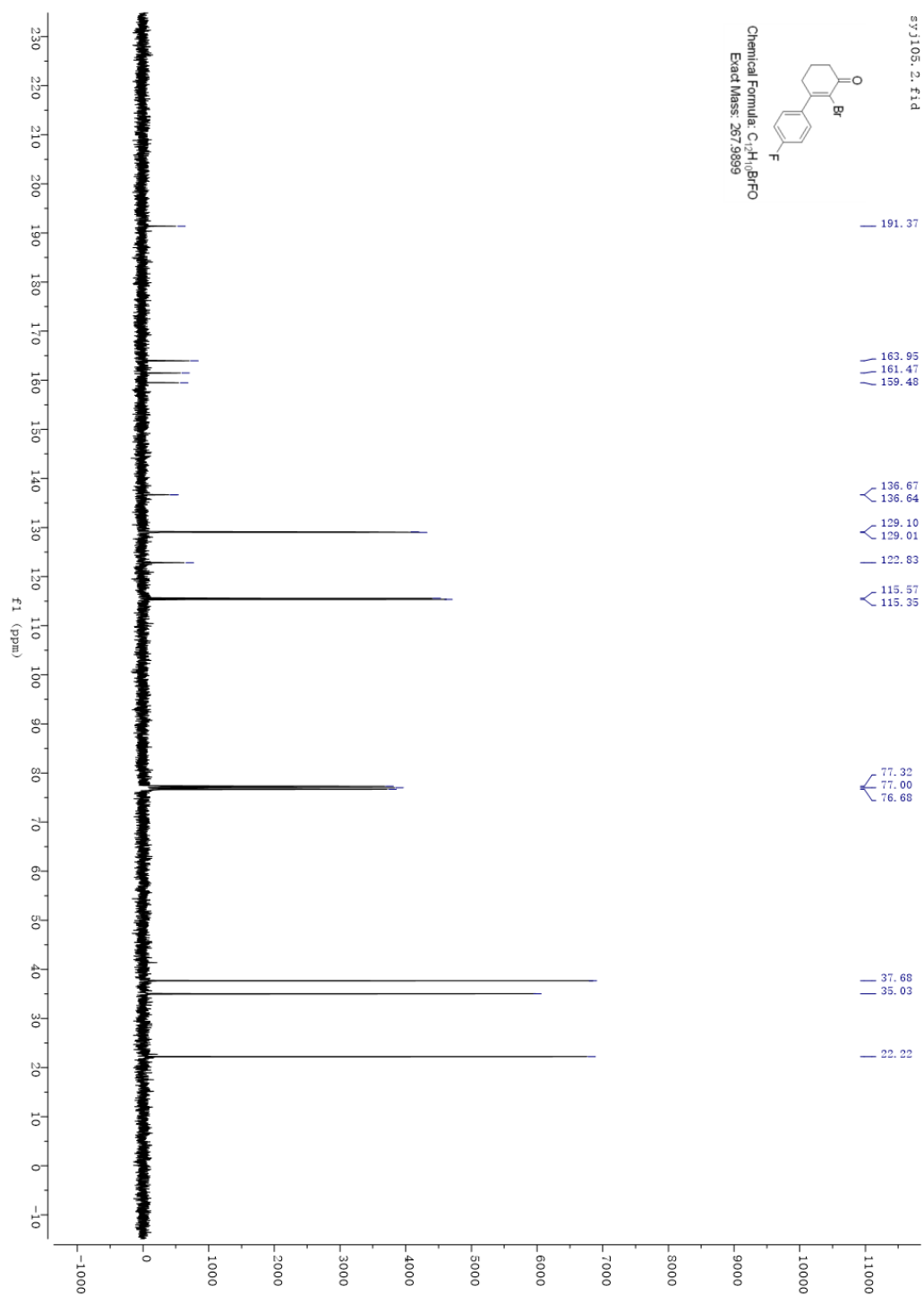
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **3d**



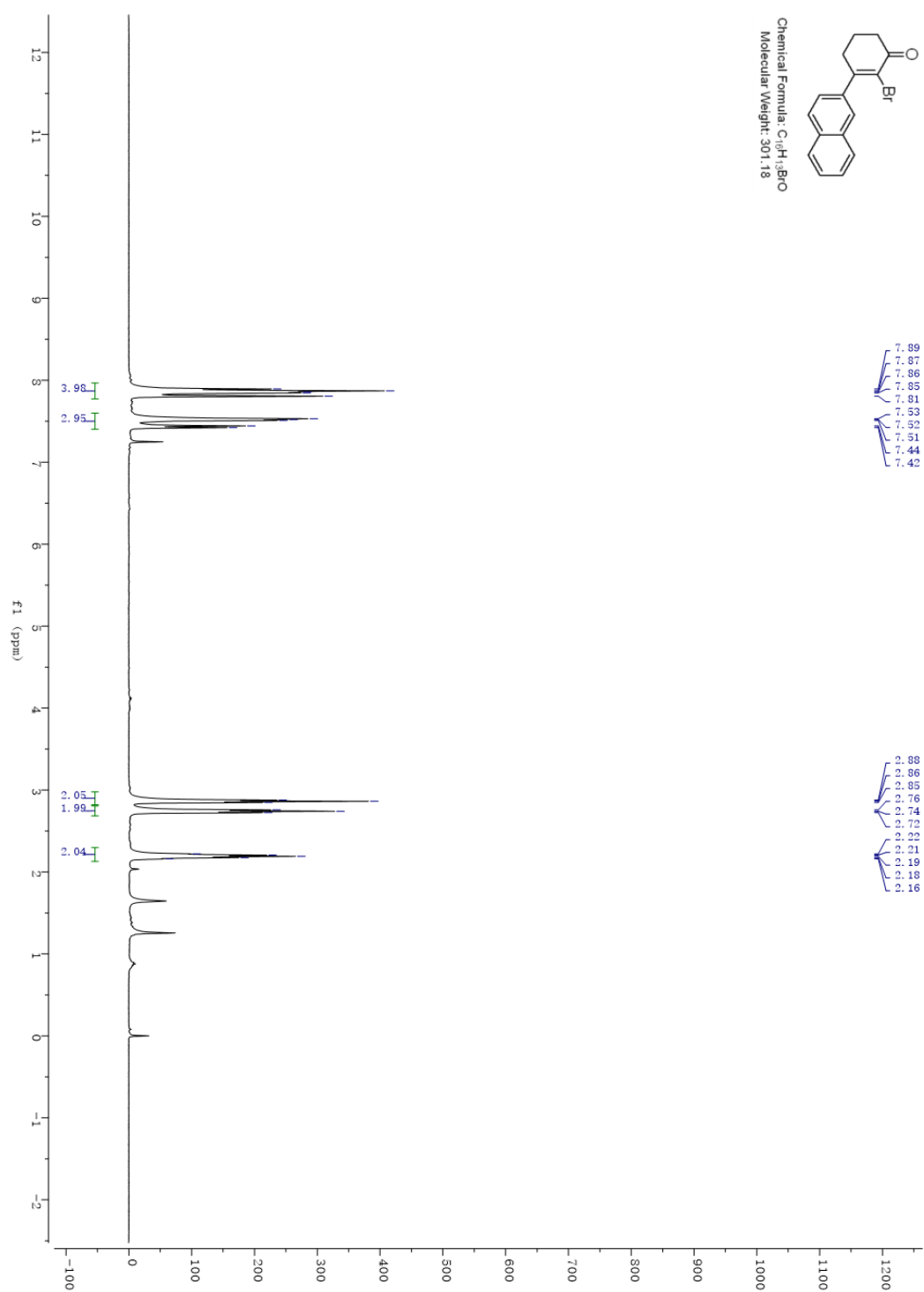
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **3e**



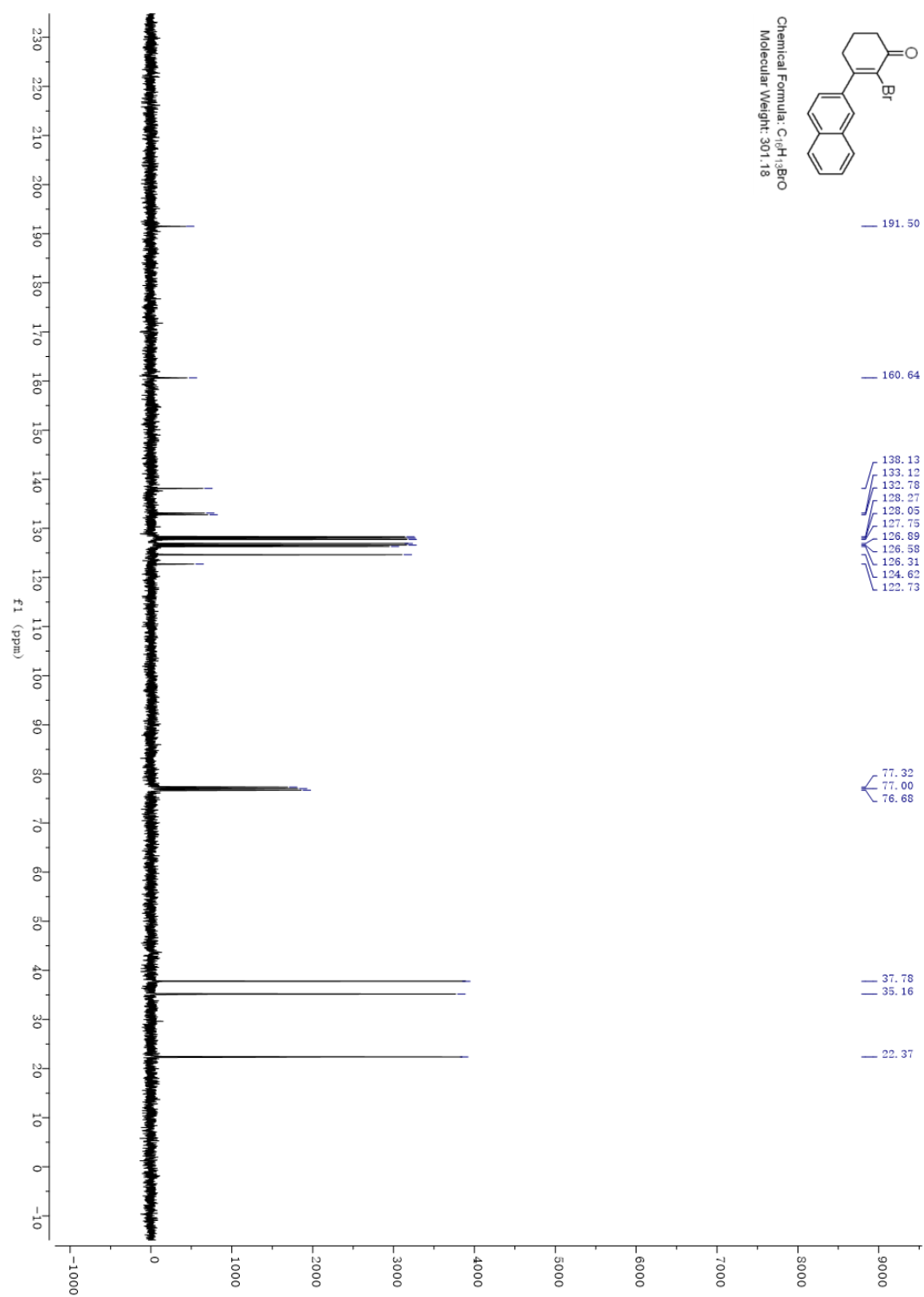
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **3e**



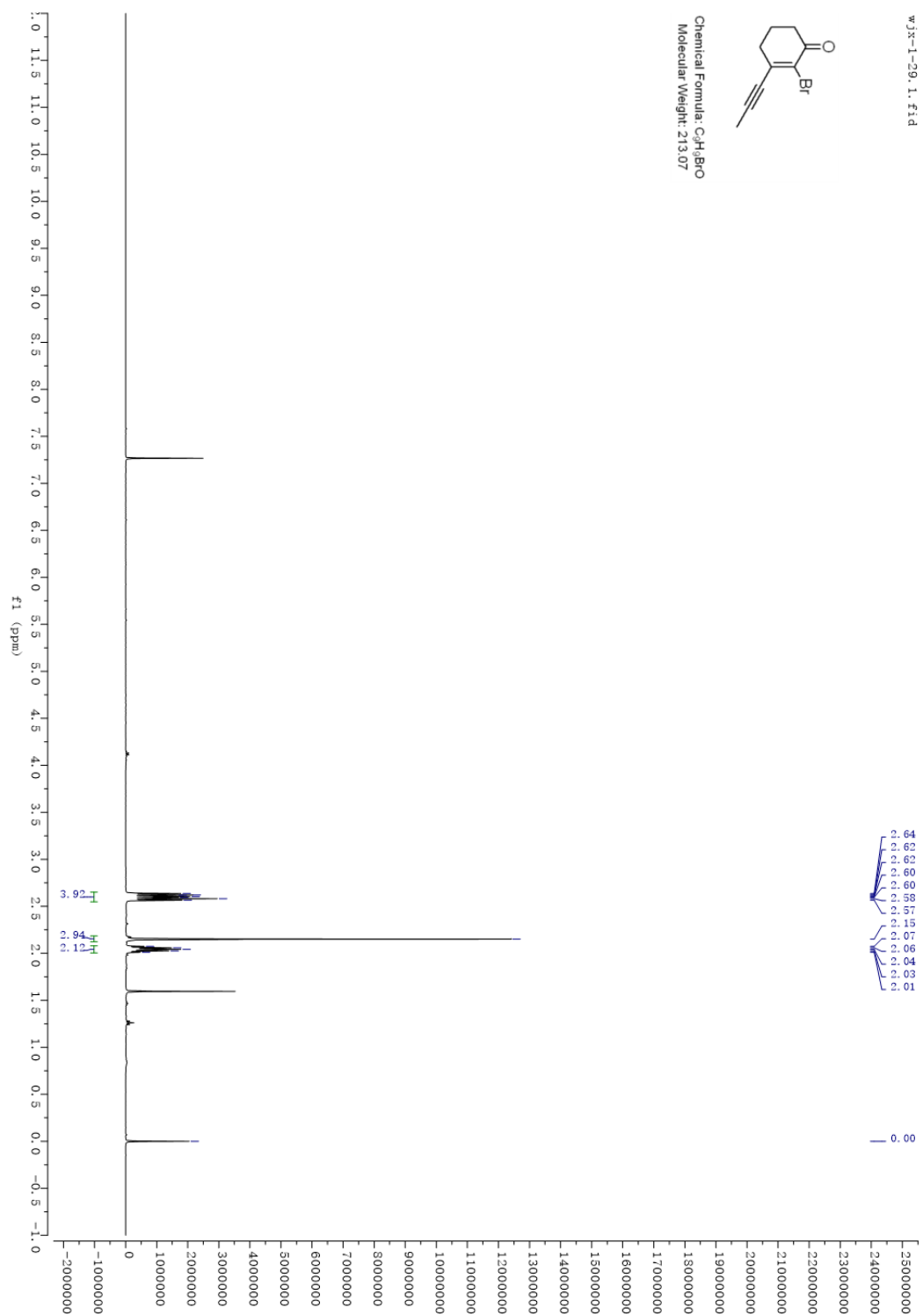
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **3f**



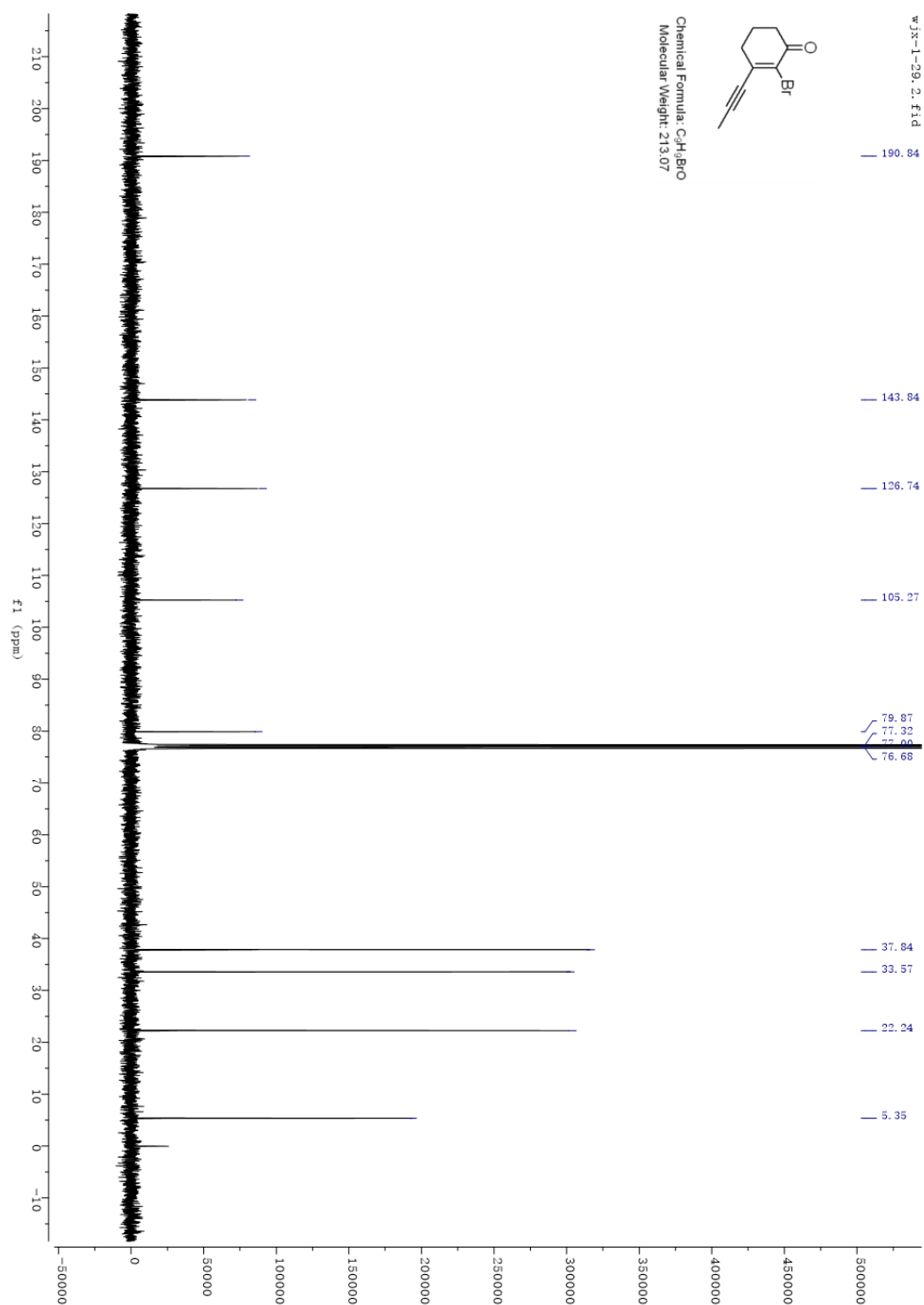
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **3f**



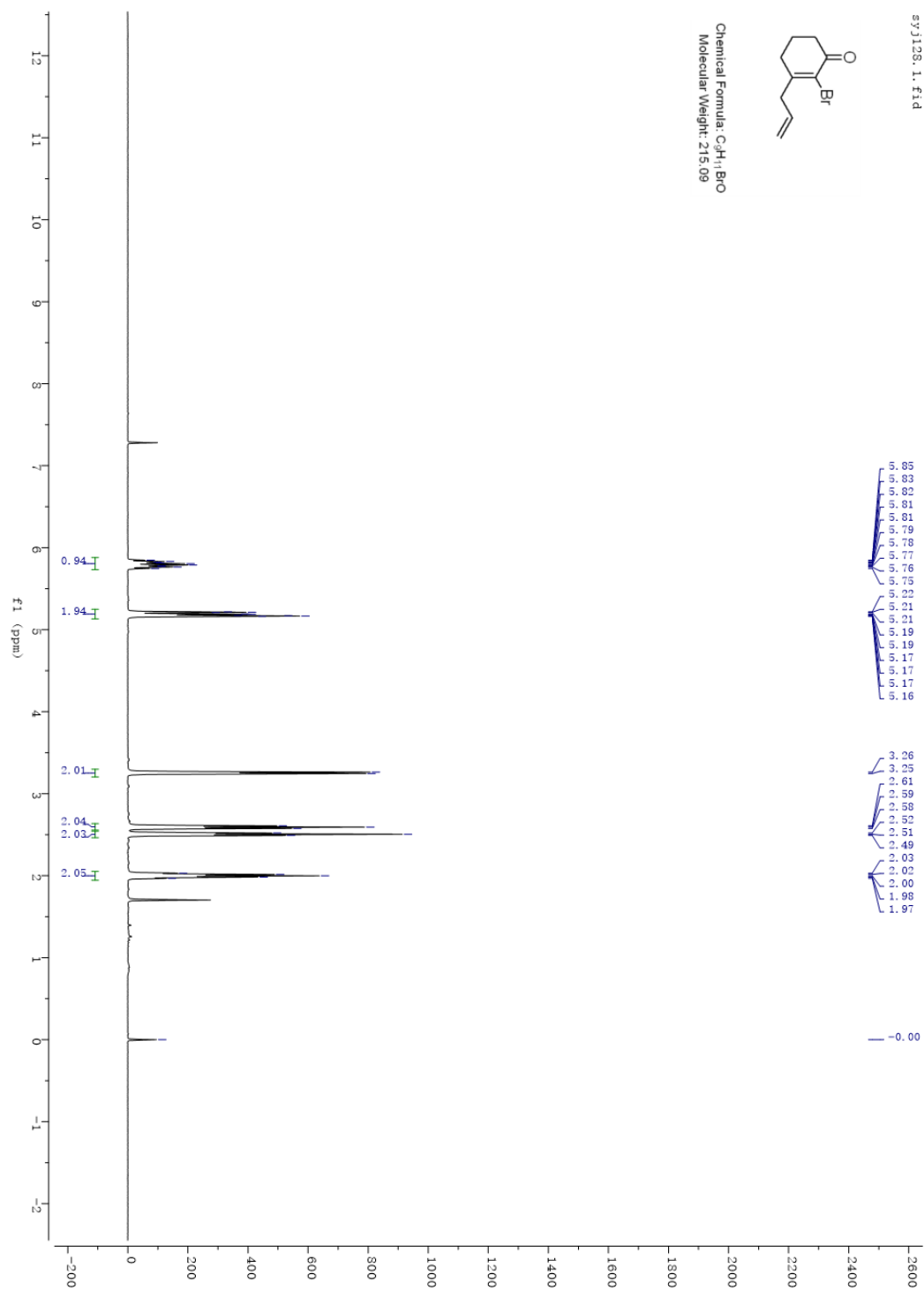
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **3g**



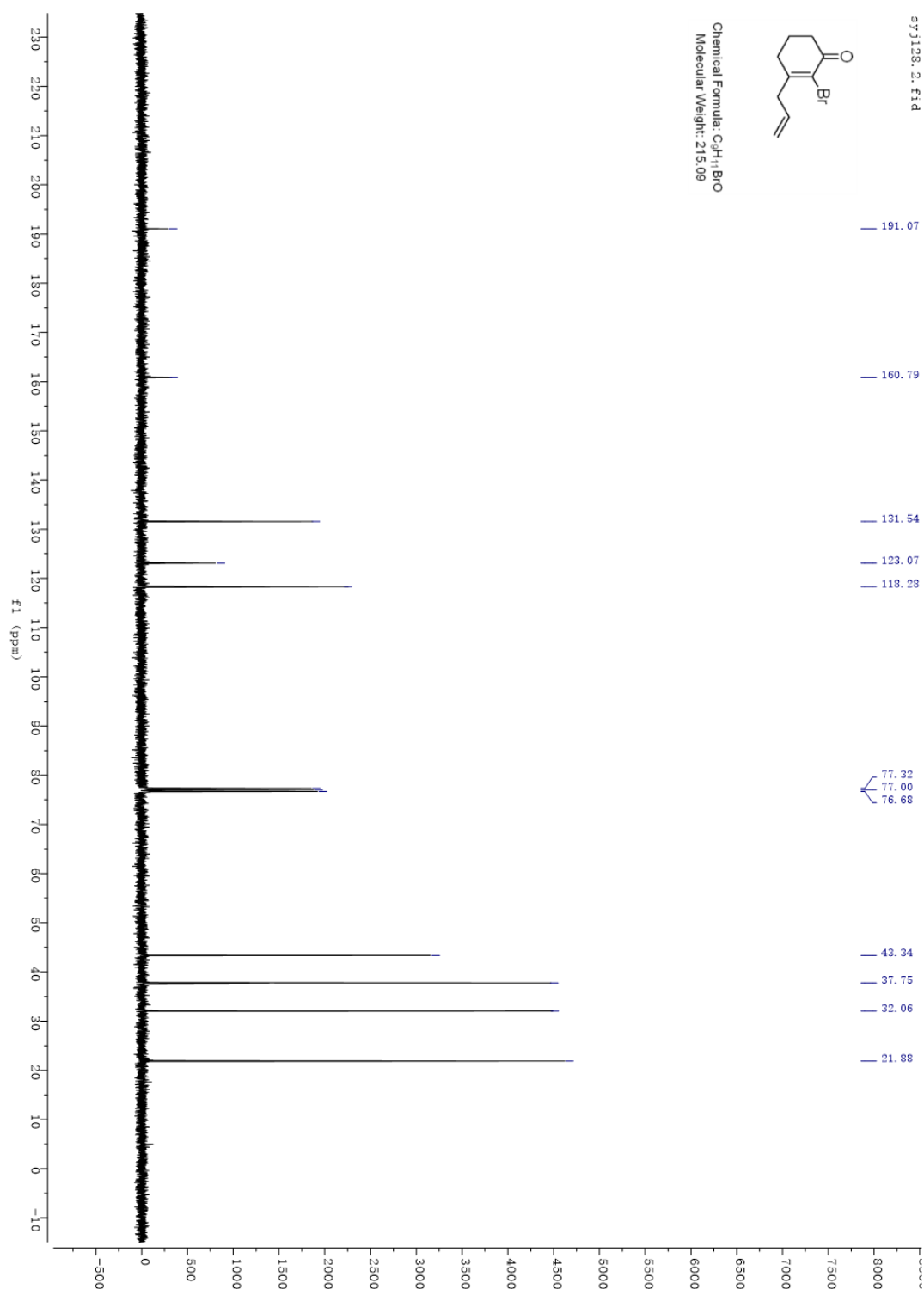
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **3g**



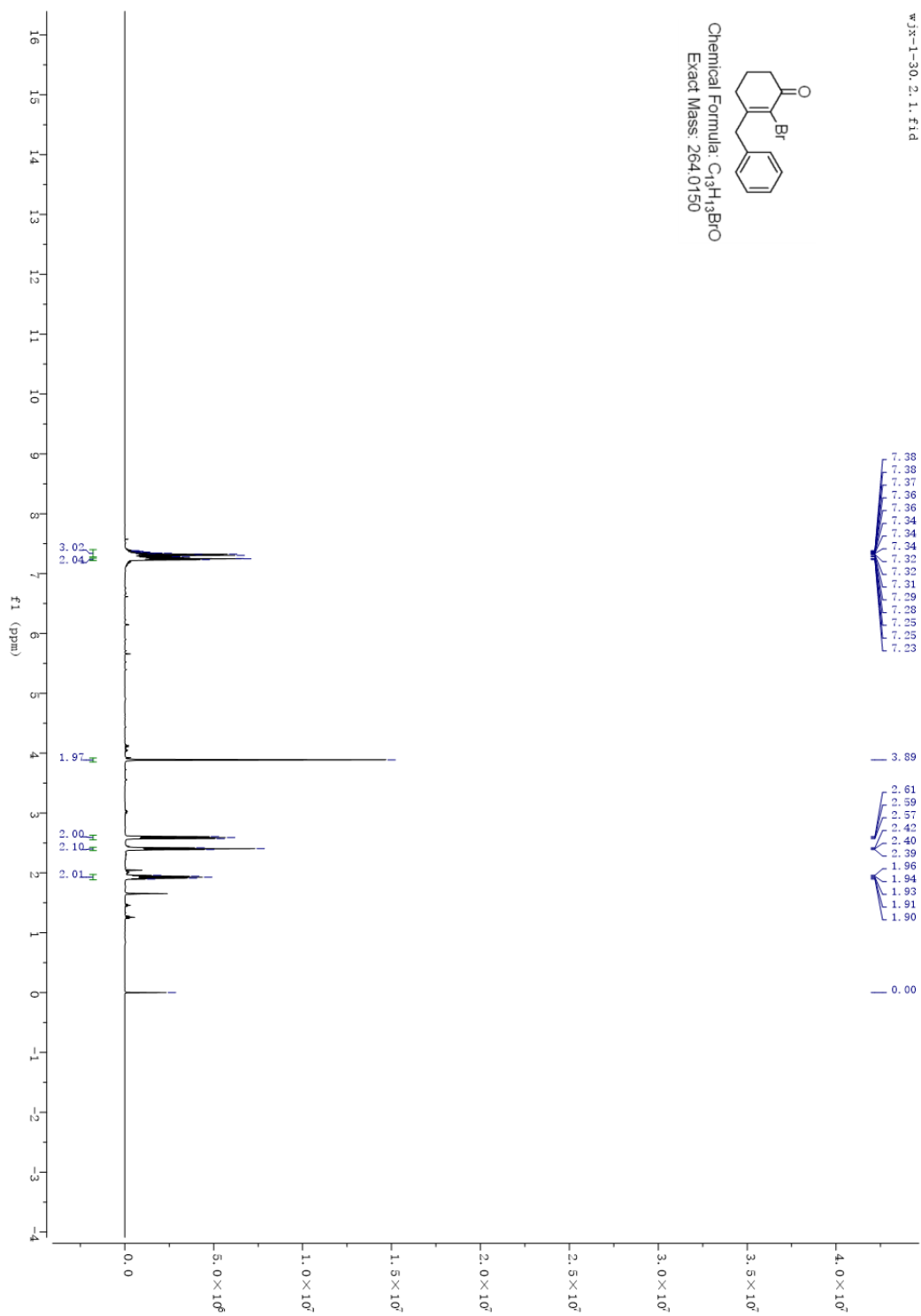
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **3h**



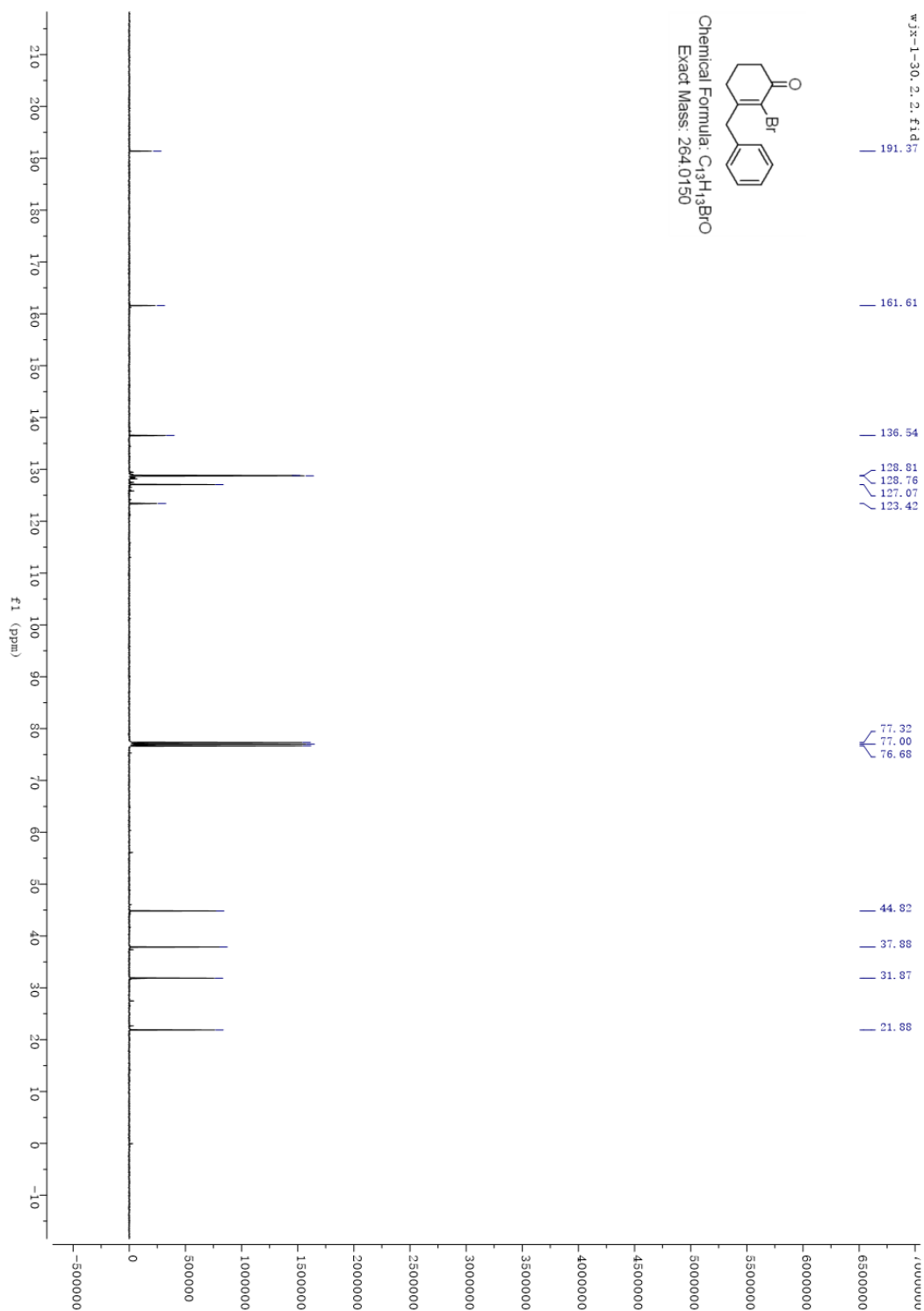
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **3h**



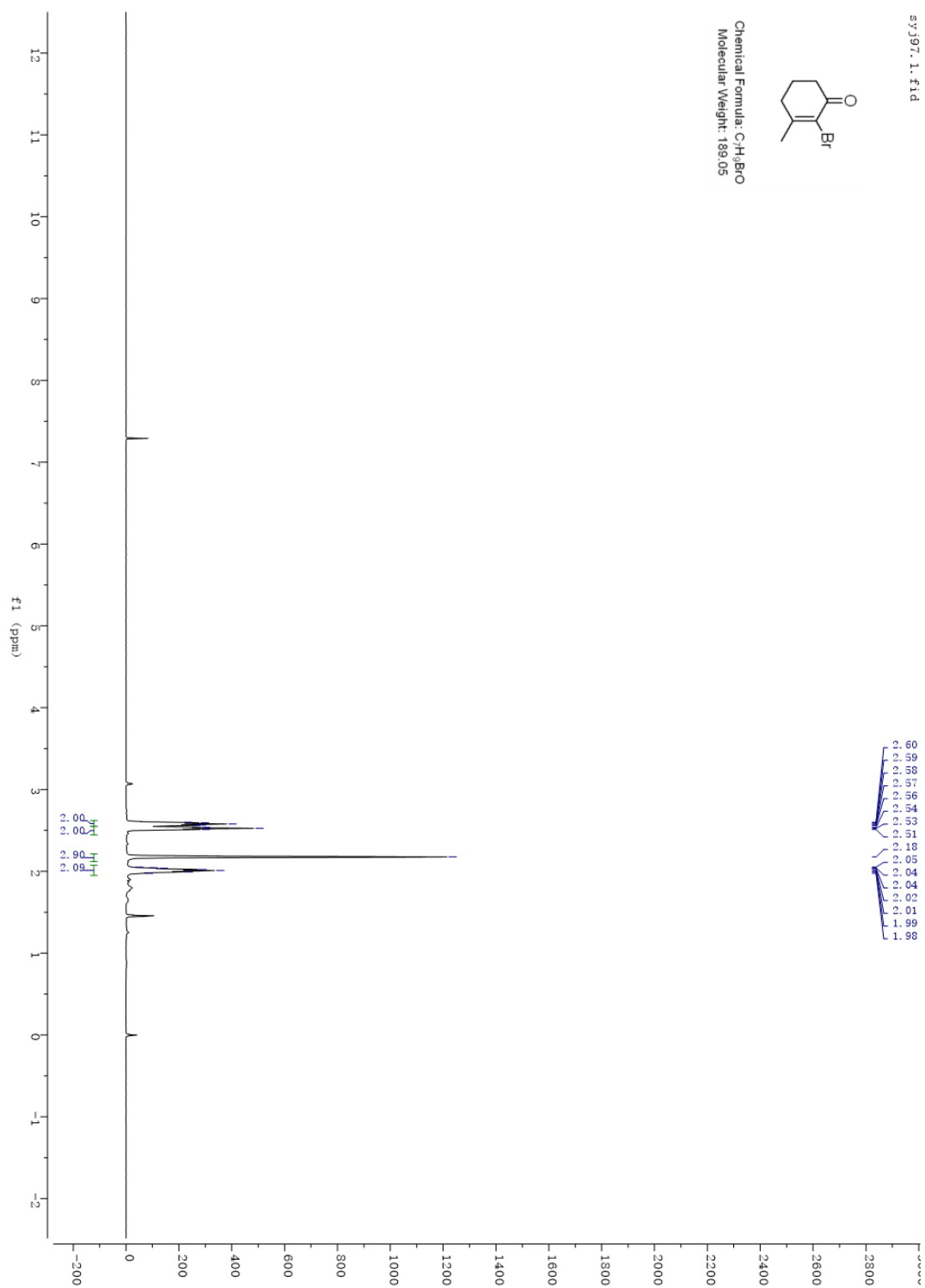
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **3i**



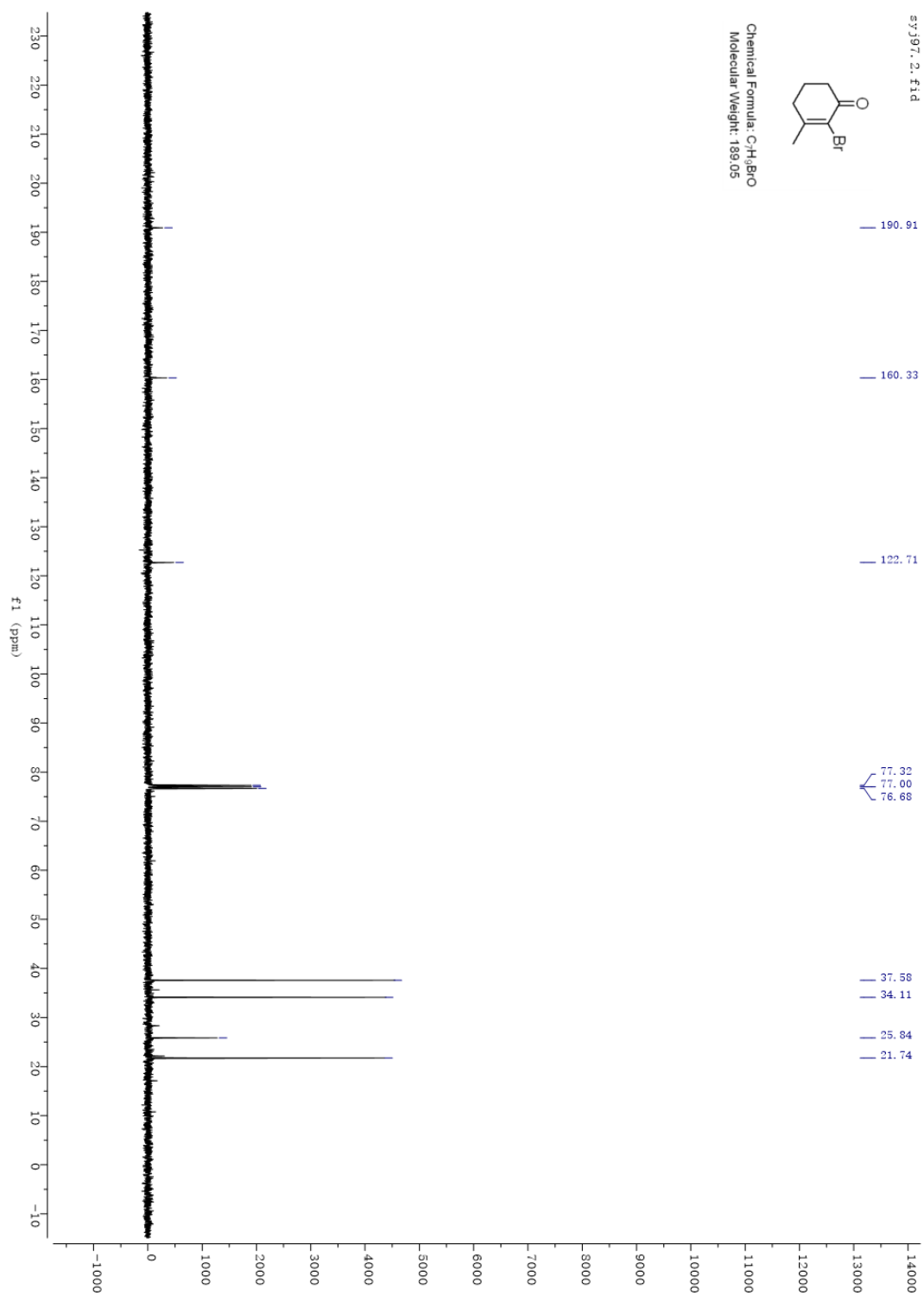
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **3i**



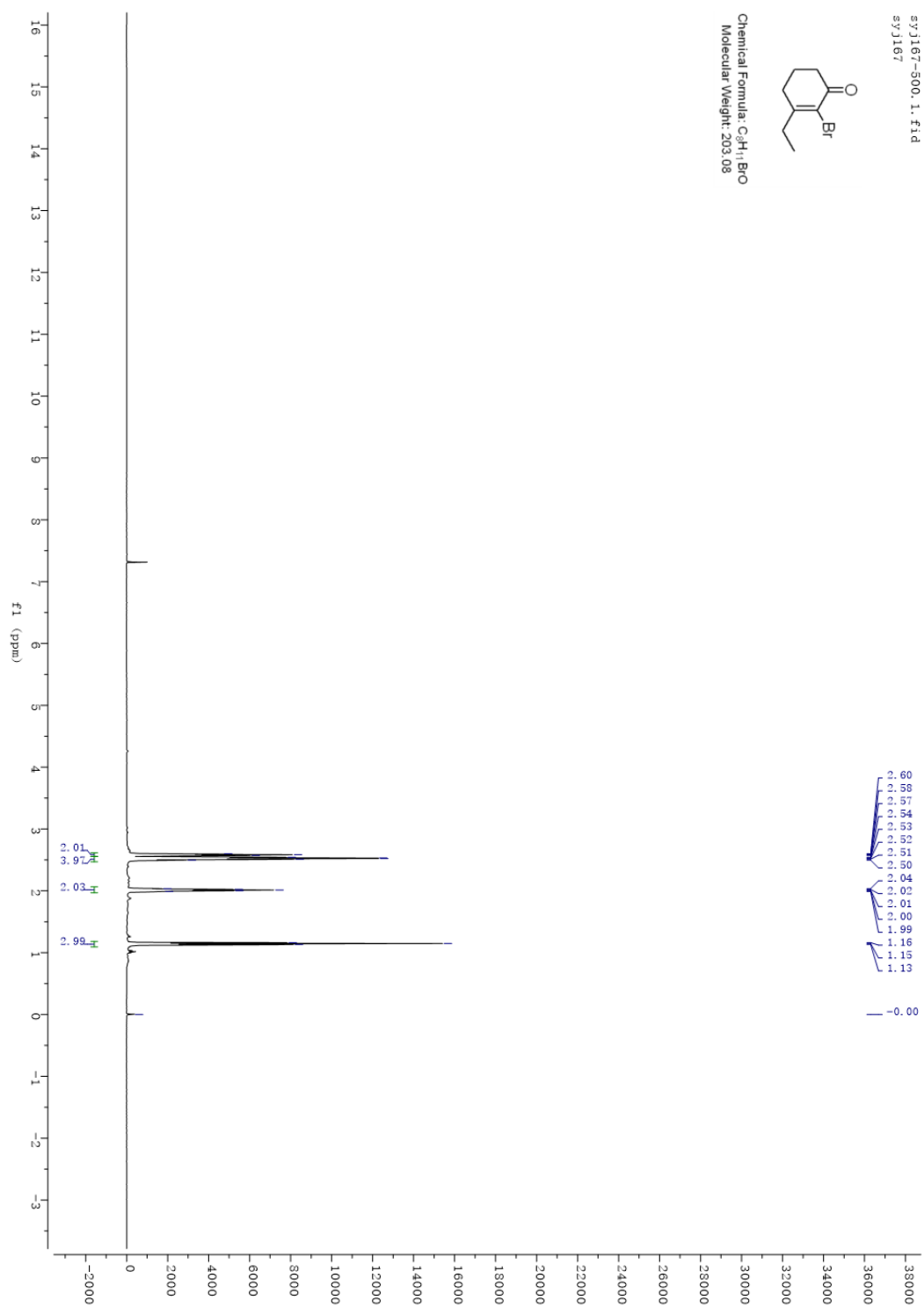
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **3j**



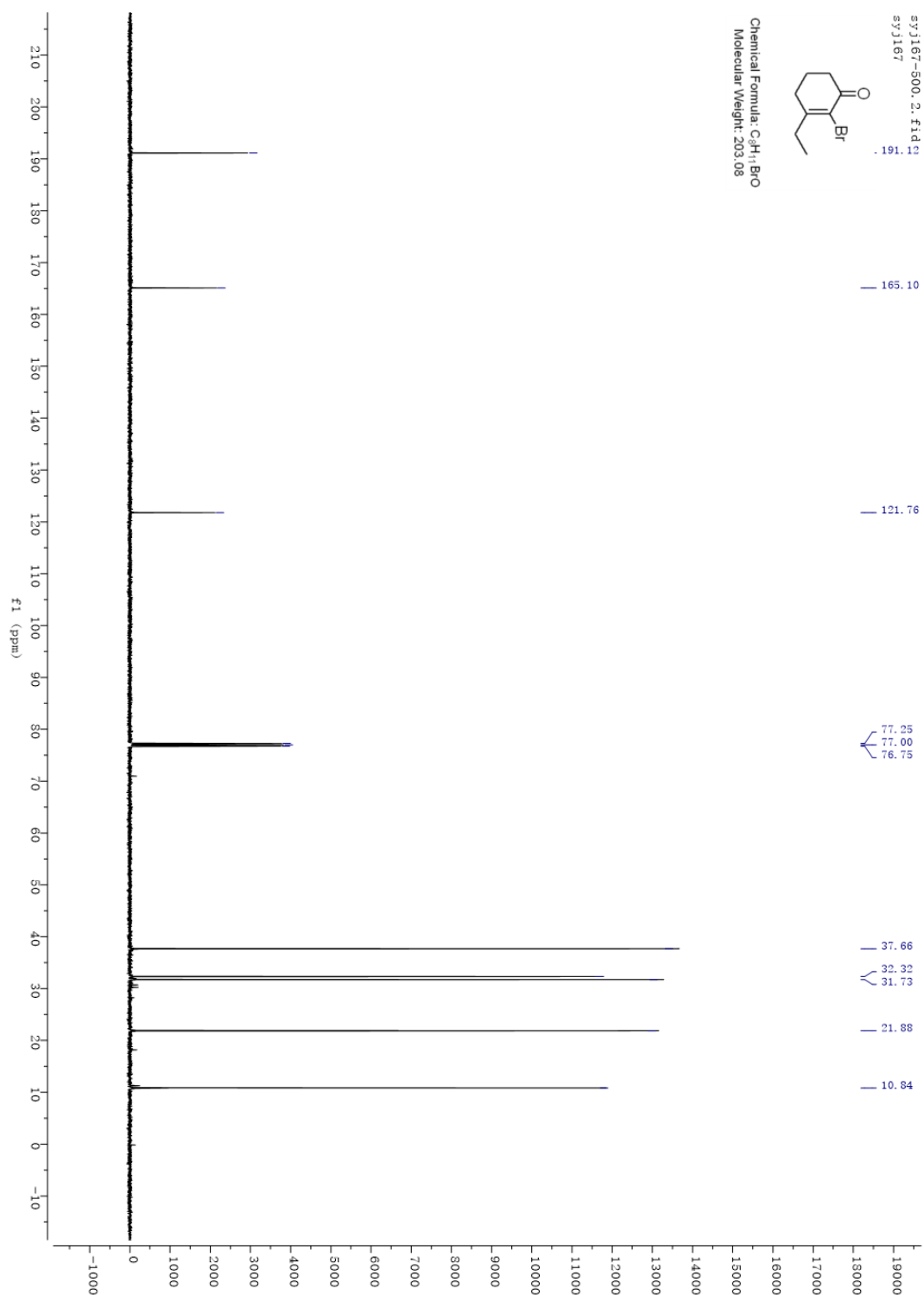
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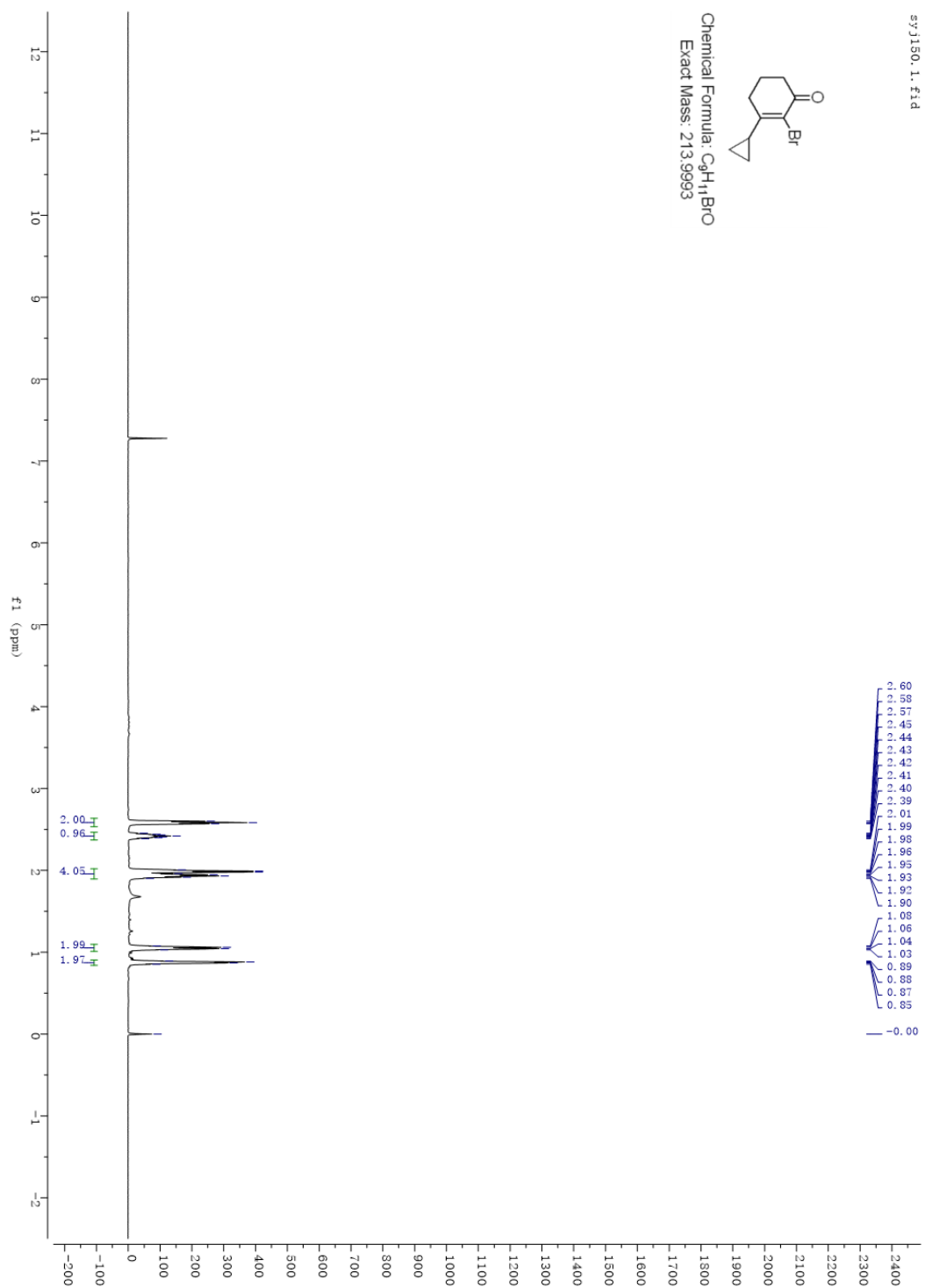
$^1\text{H}$  NMR (500 MHz, Chloroform- $d$ ) of compound **3k**



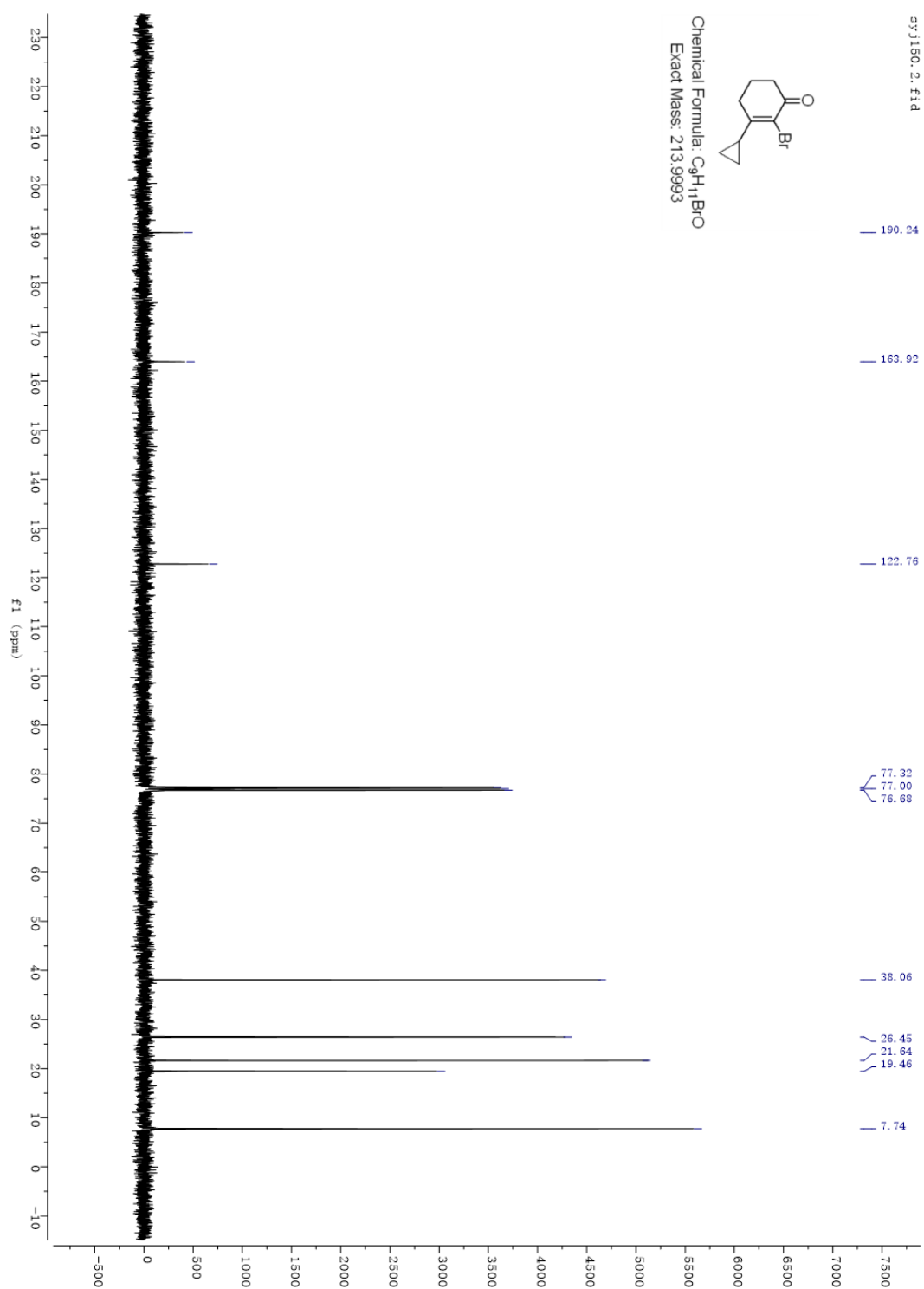
$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, Chloroform- $d$ ) of compound **3k**



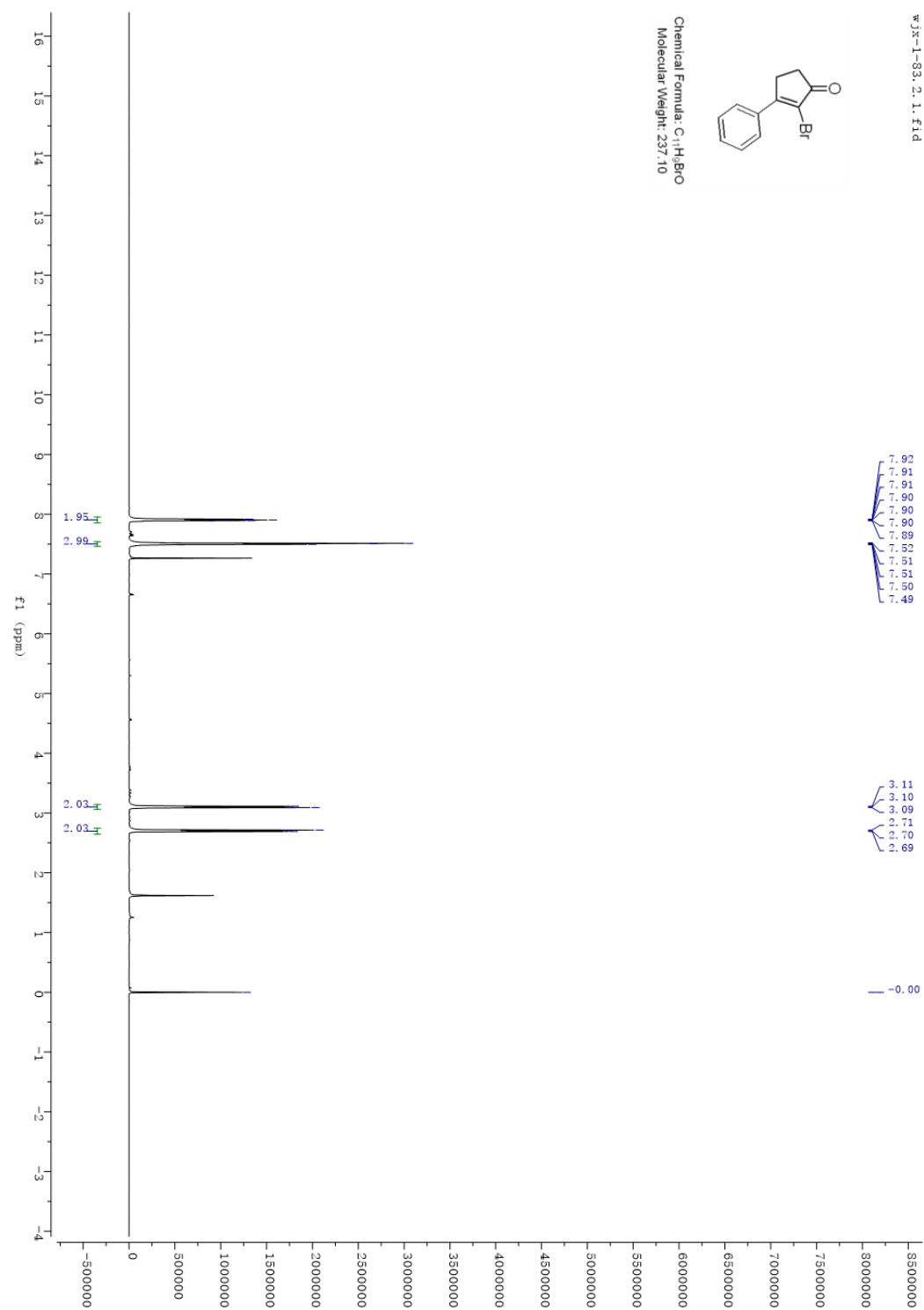
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **3l**



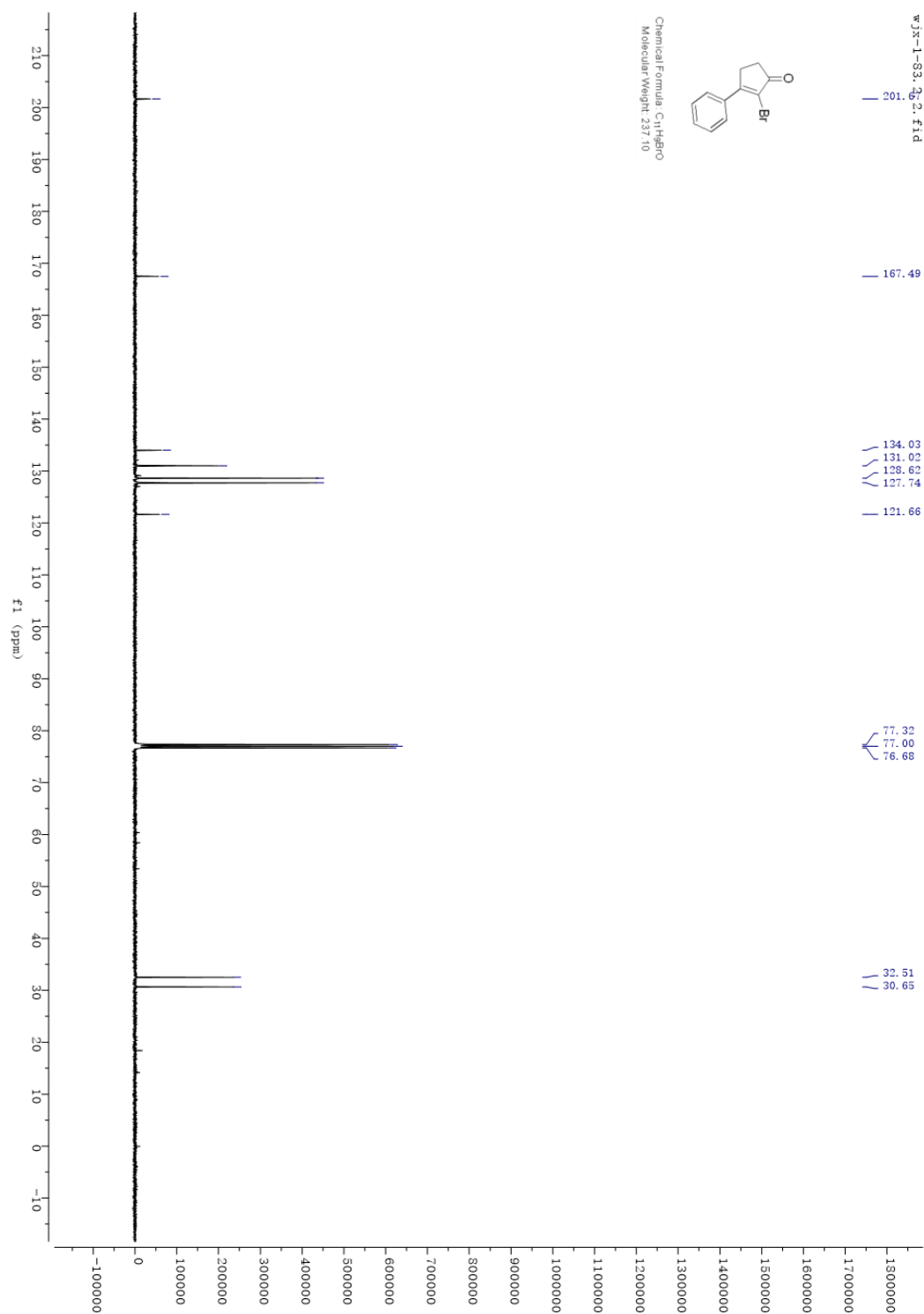
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **31**



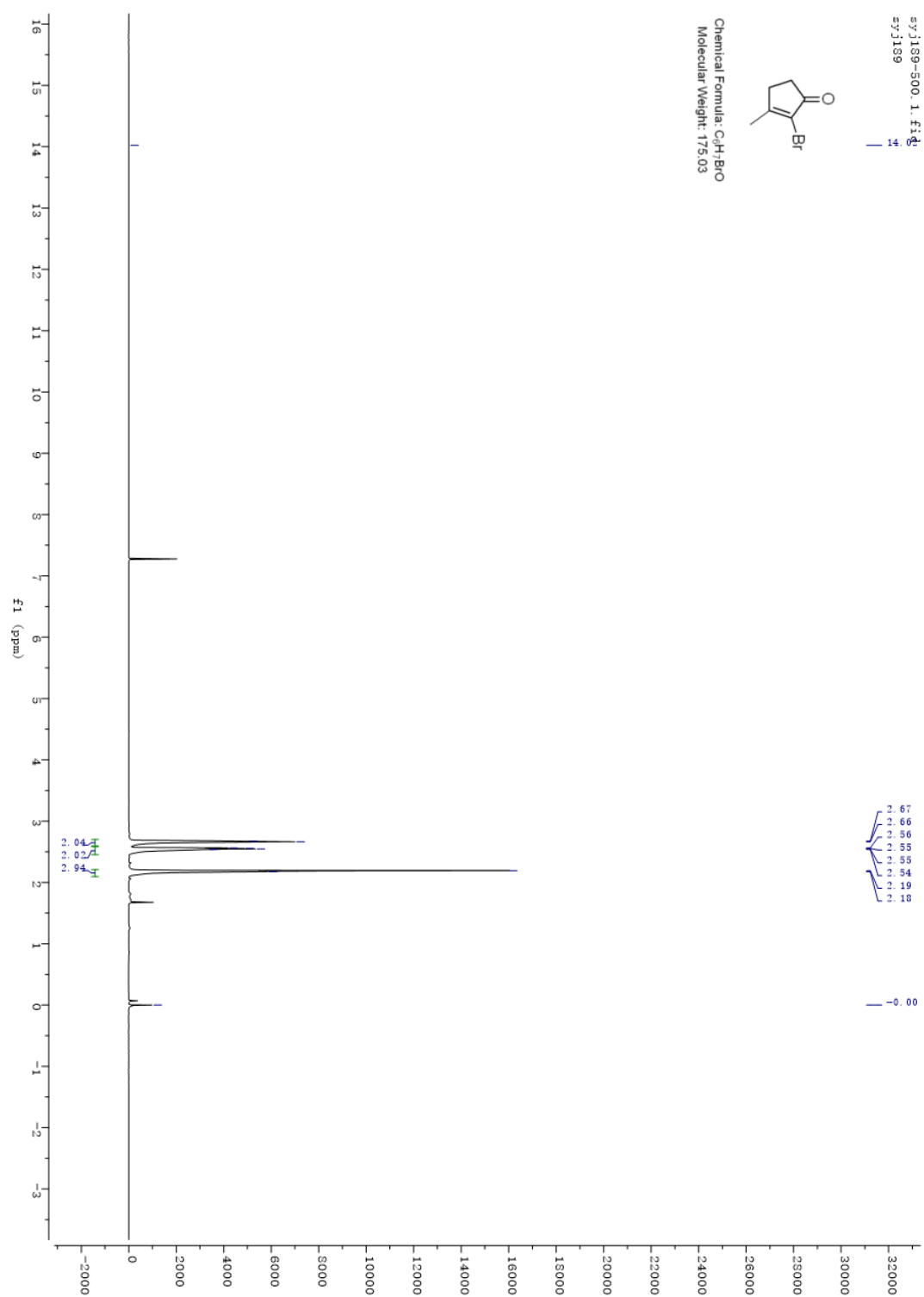
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **3m**



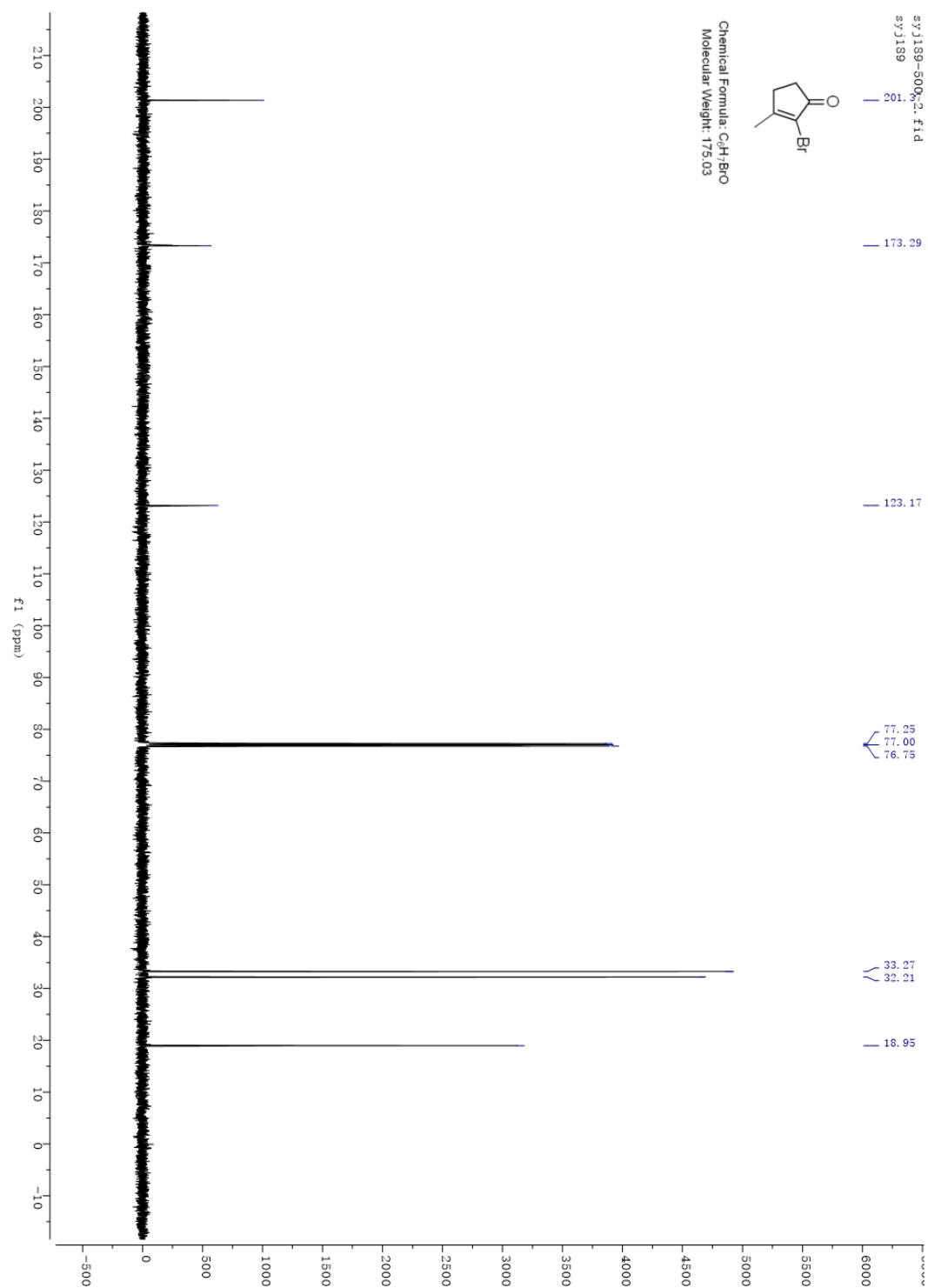
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **3m**



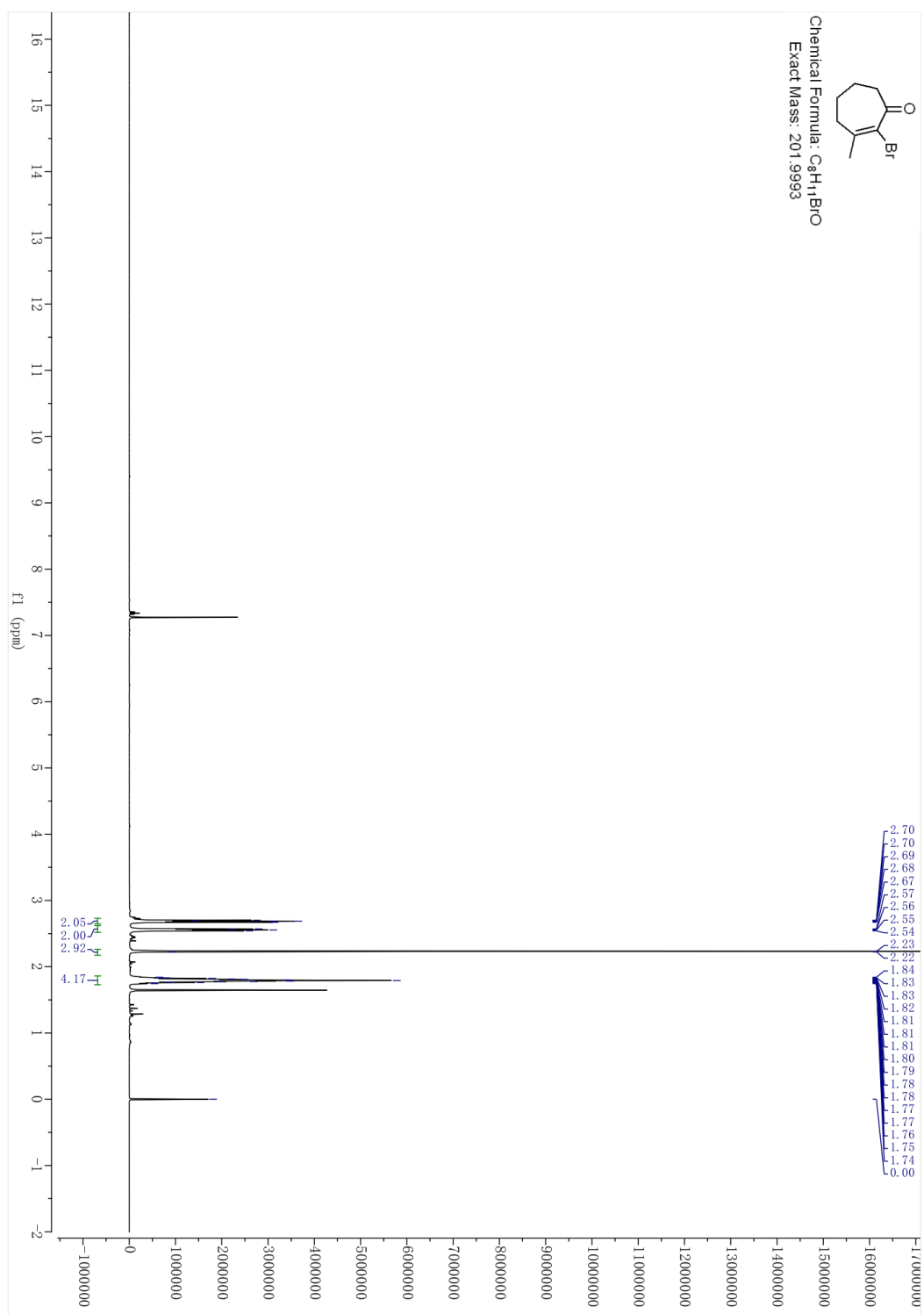
$^1\text{H}$  NMR (500 MHz, Chloroform- $d$ ) of compound **3n**



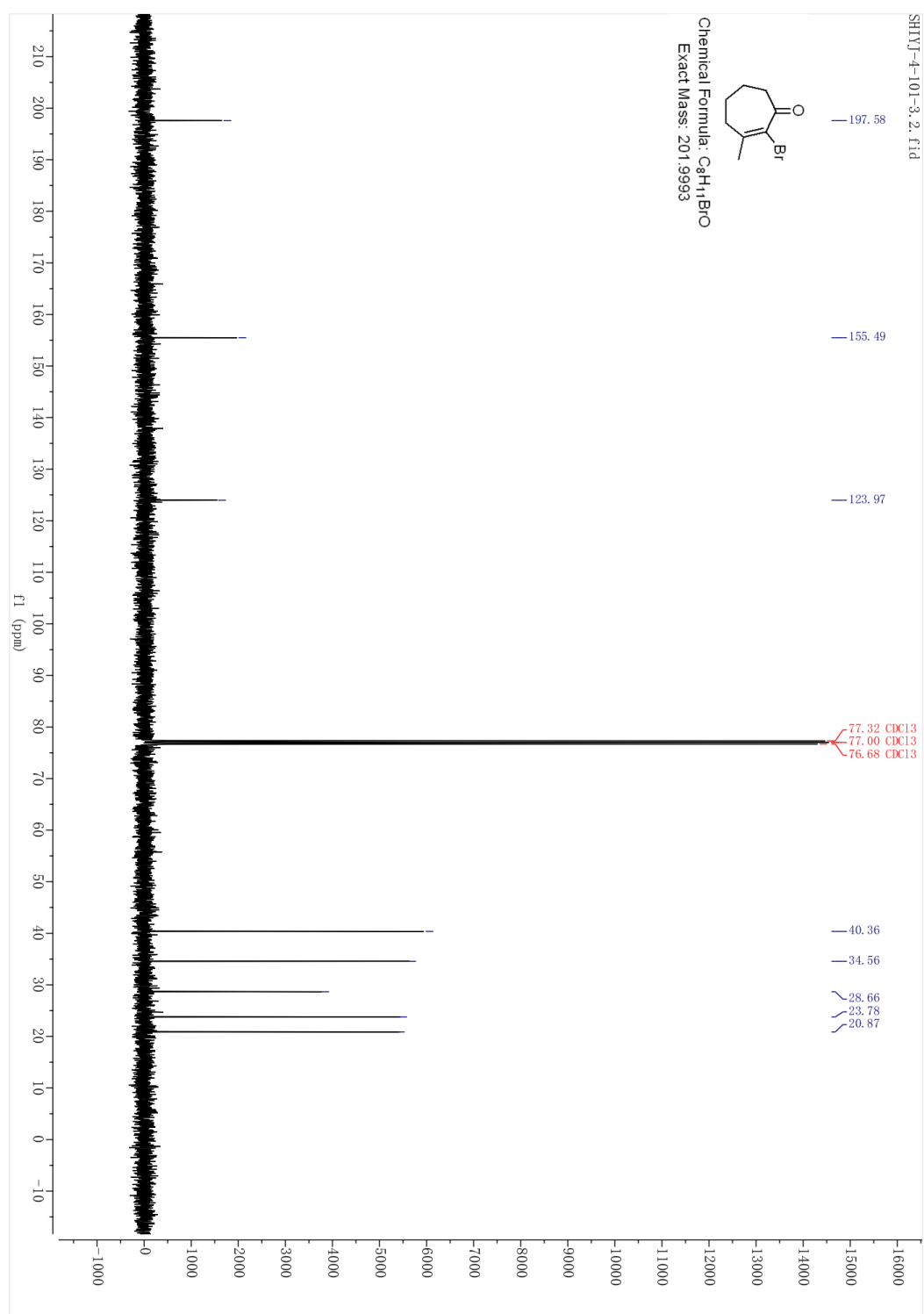
$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, Chloroform- $d$ ) of compound **3n**



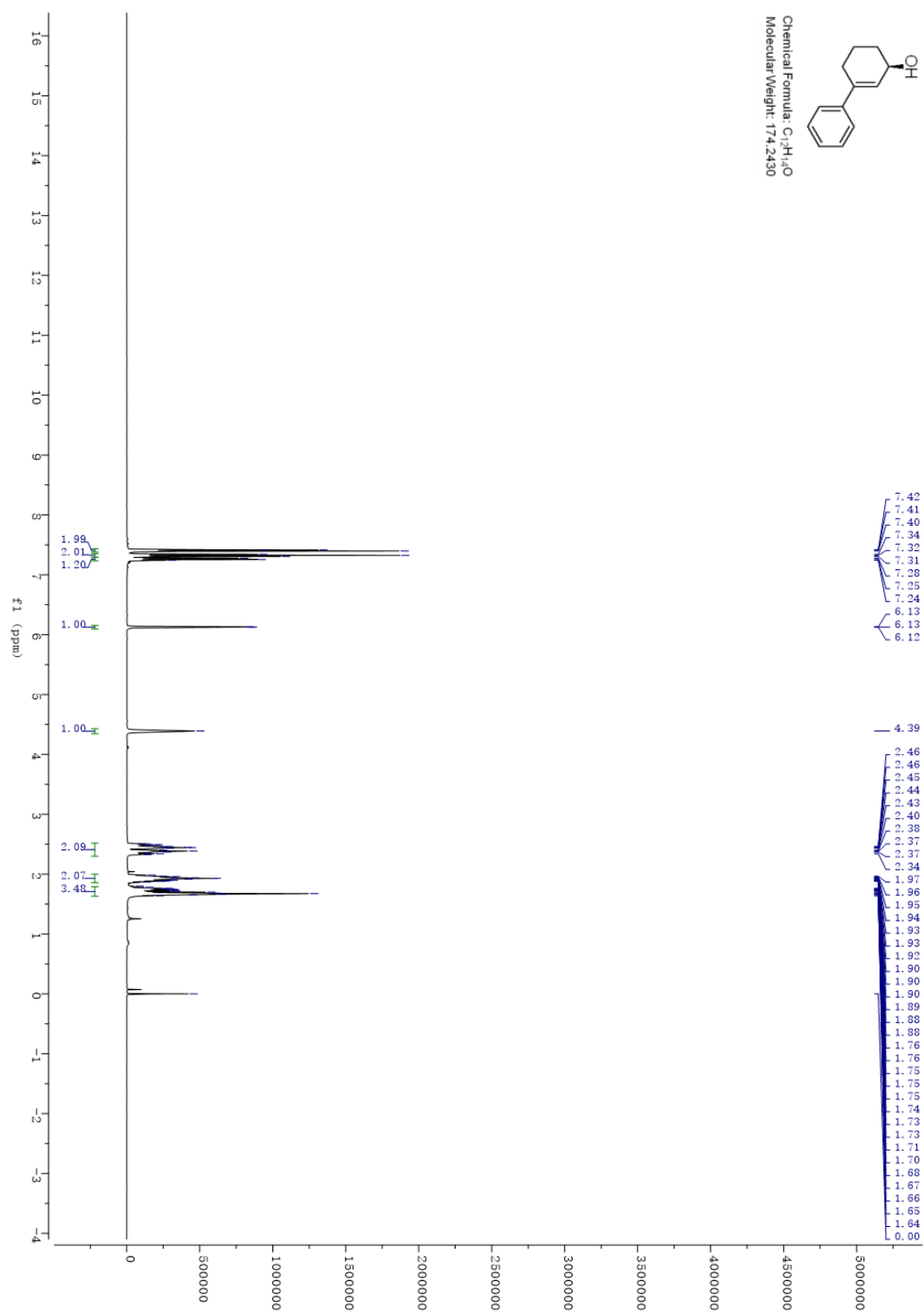
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*) of compound **3o**



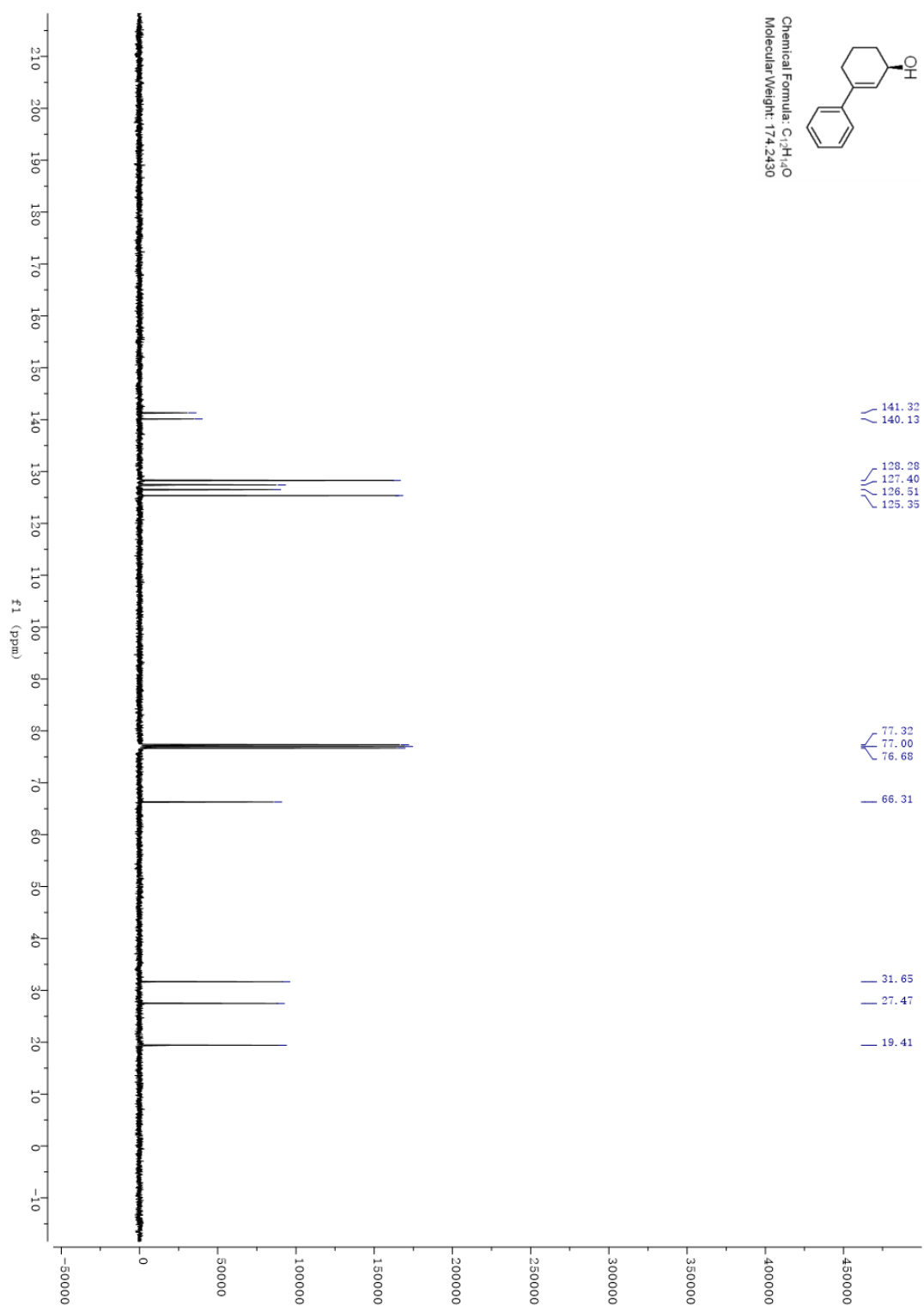
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of compound **3o**



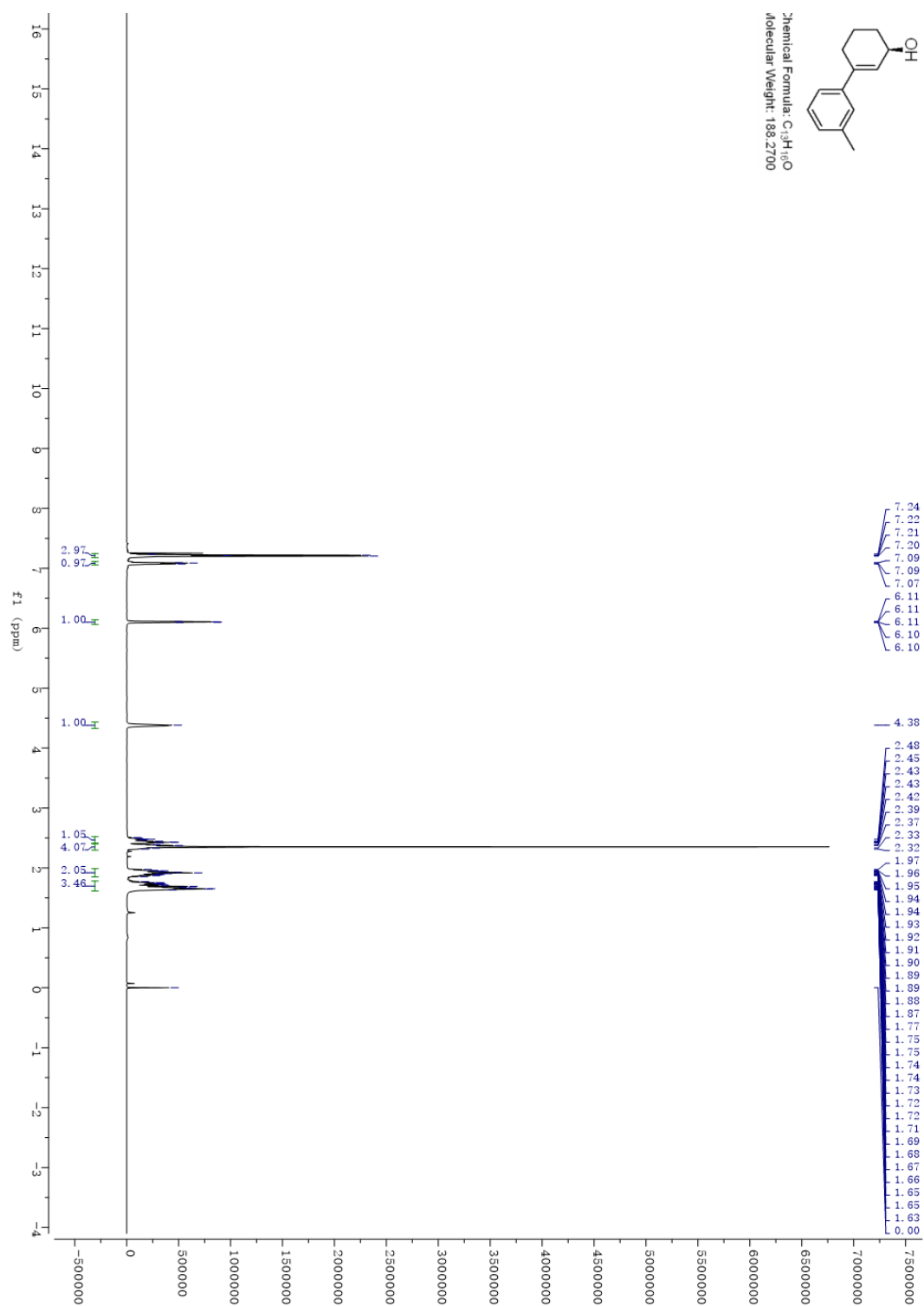
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **2a**



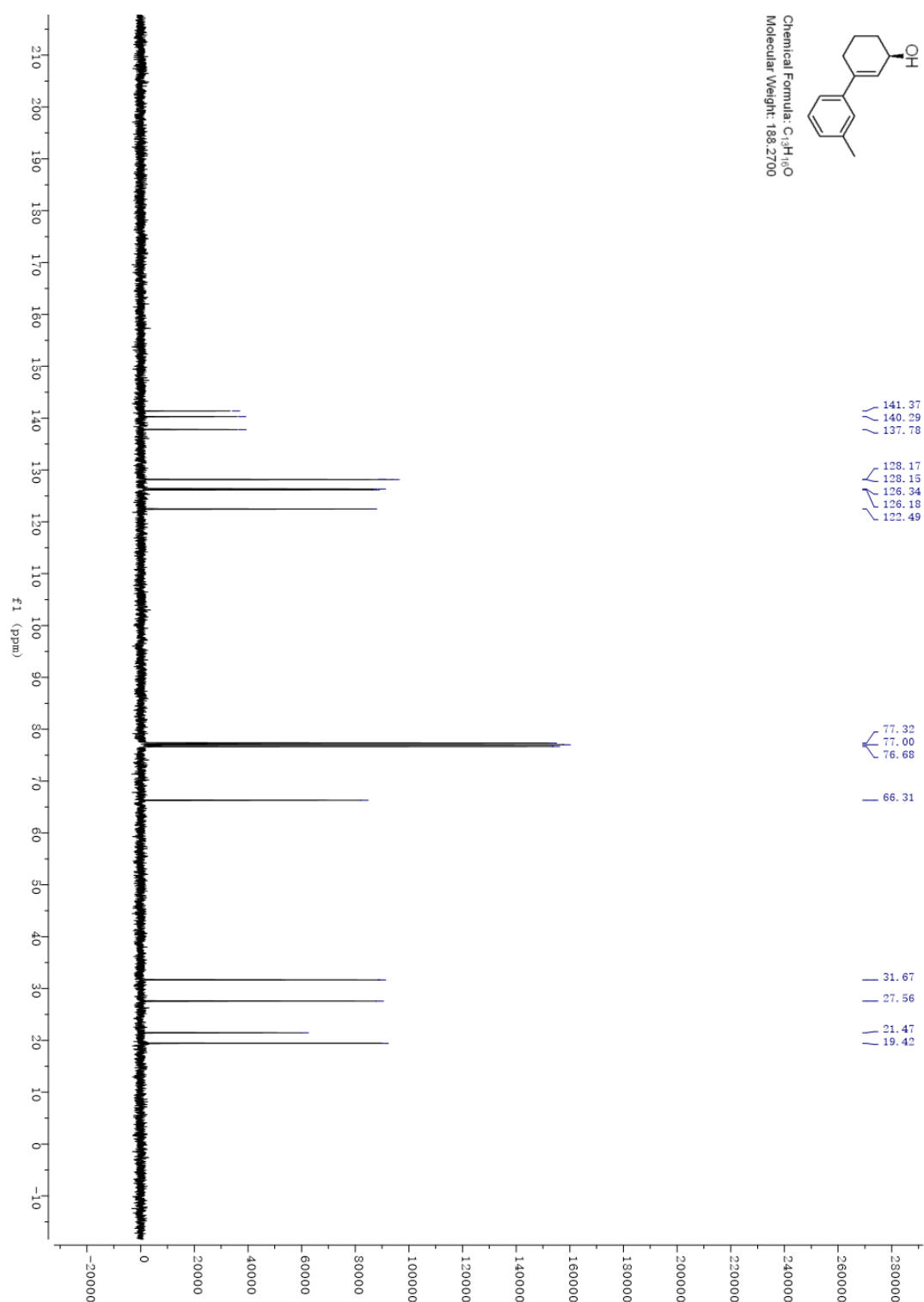
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **2a**



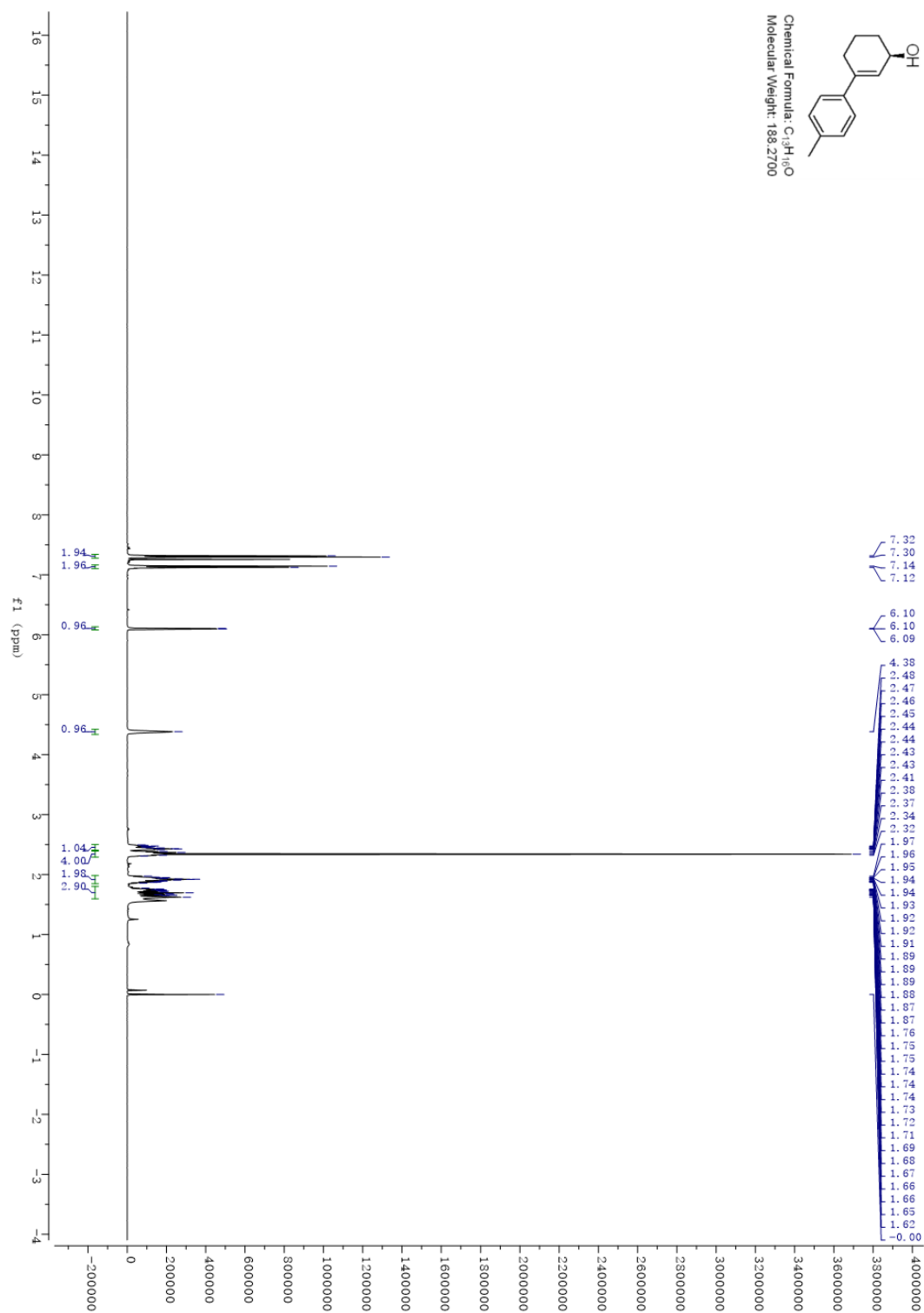
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **2b**



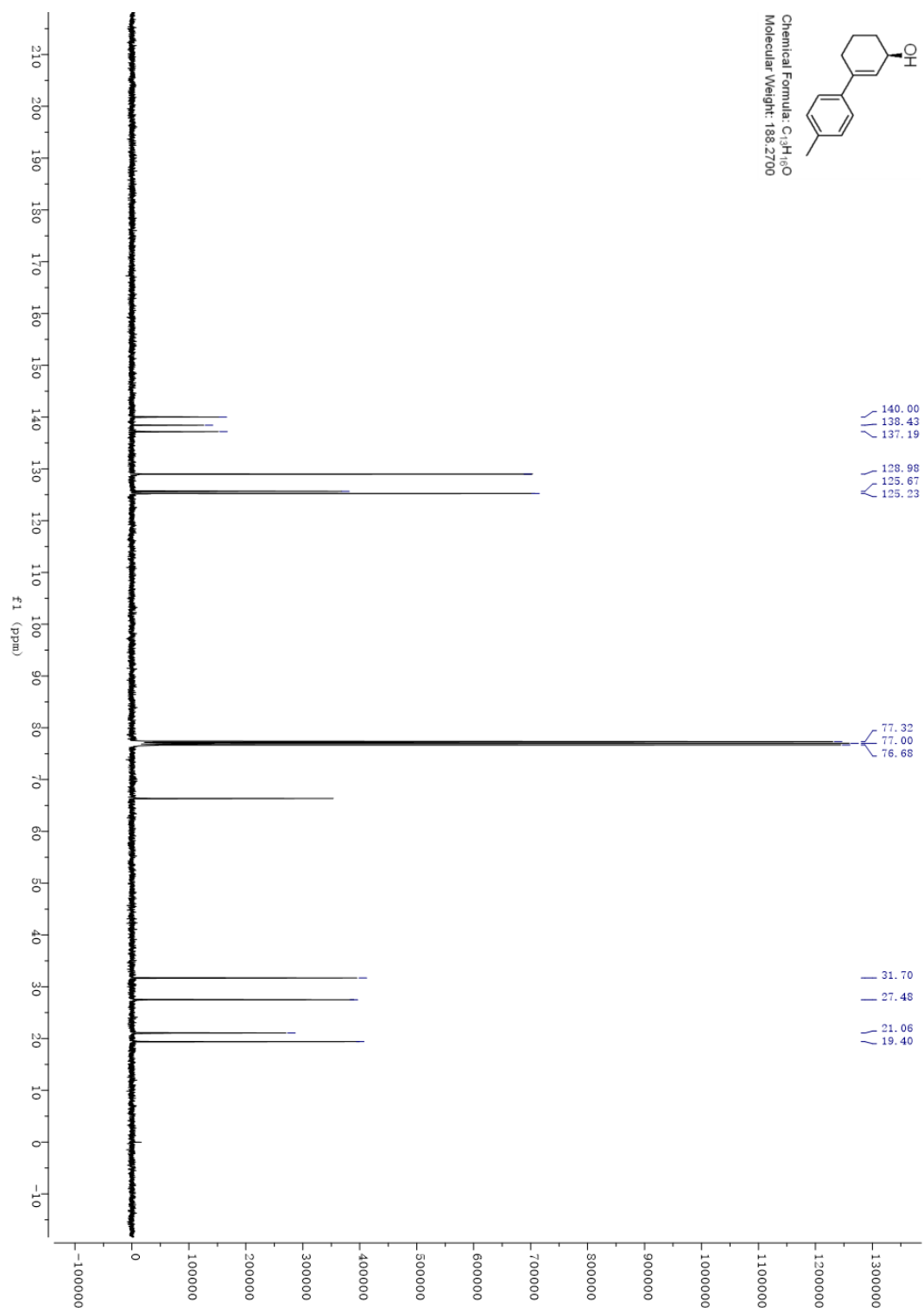
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **2b**



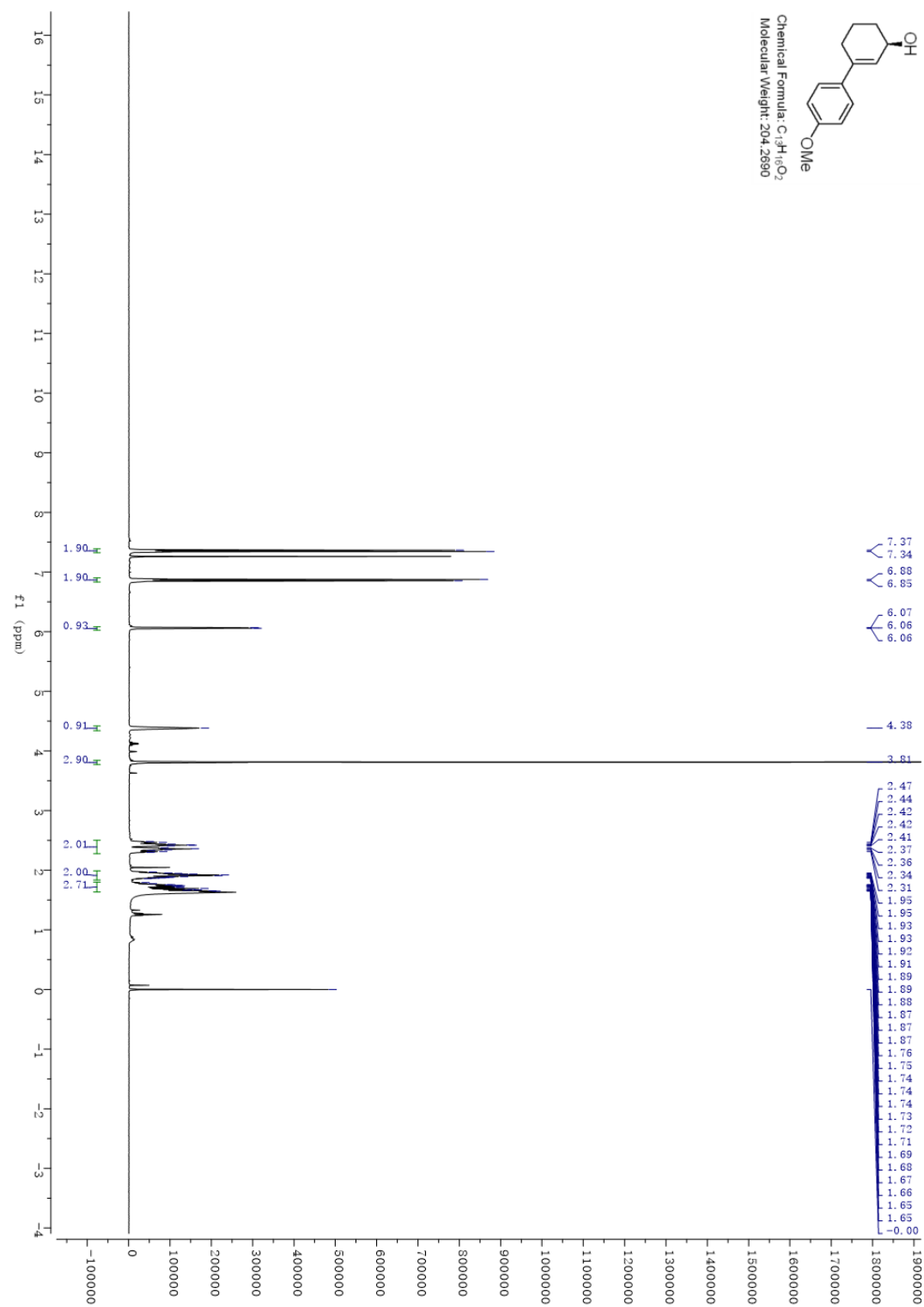
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **2c**



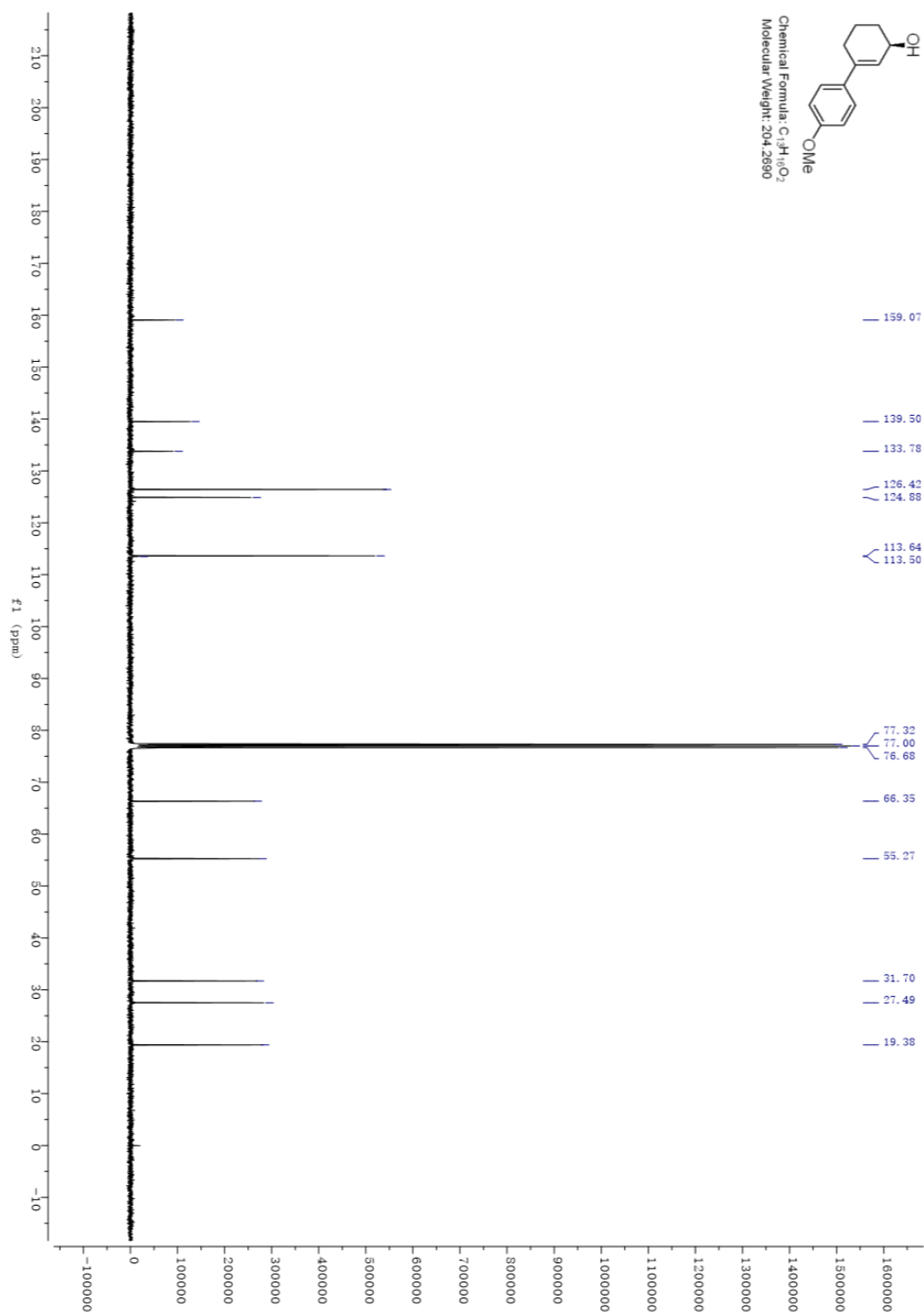
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **2c**



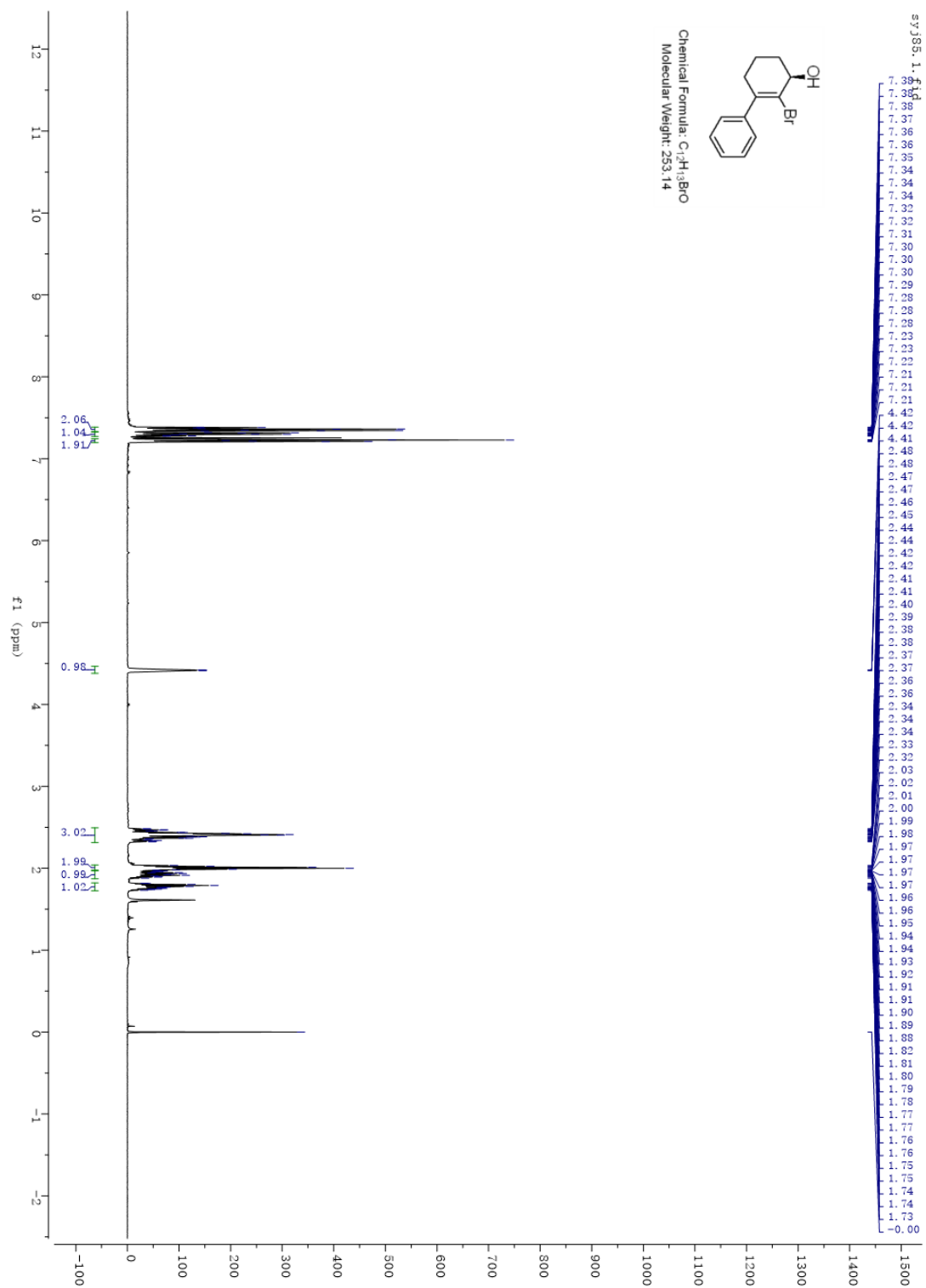
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **2d**



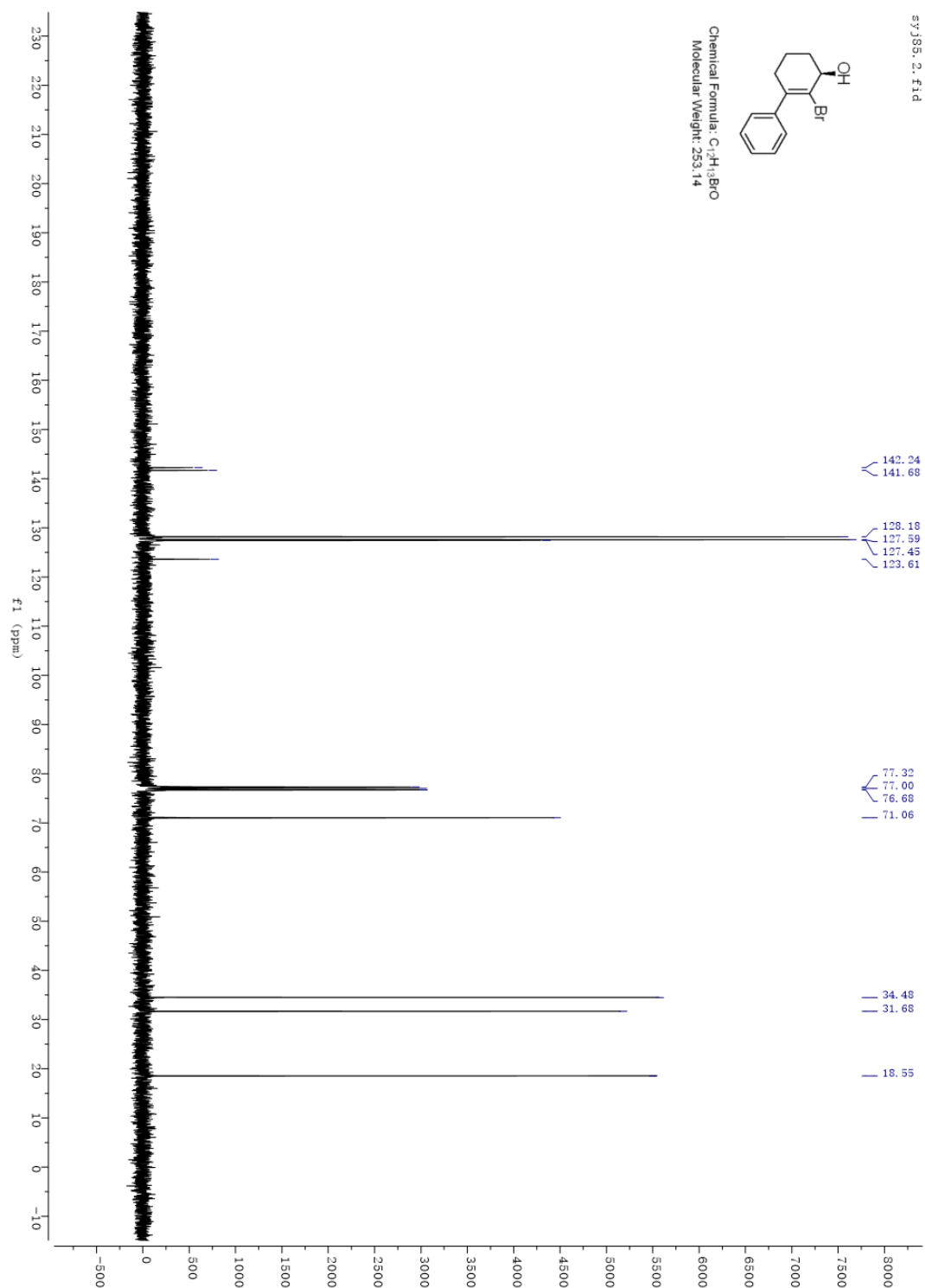
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **2d**



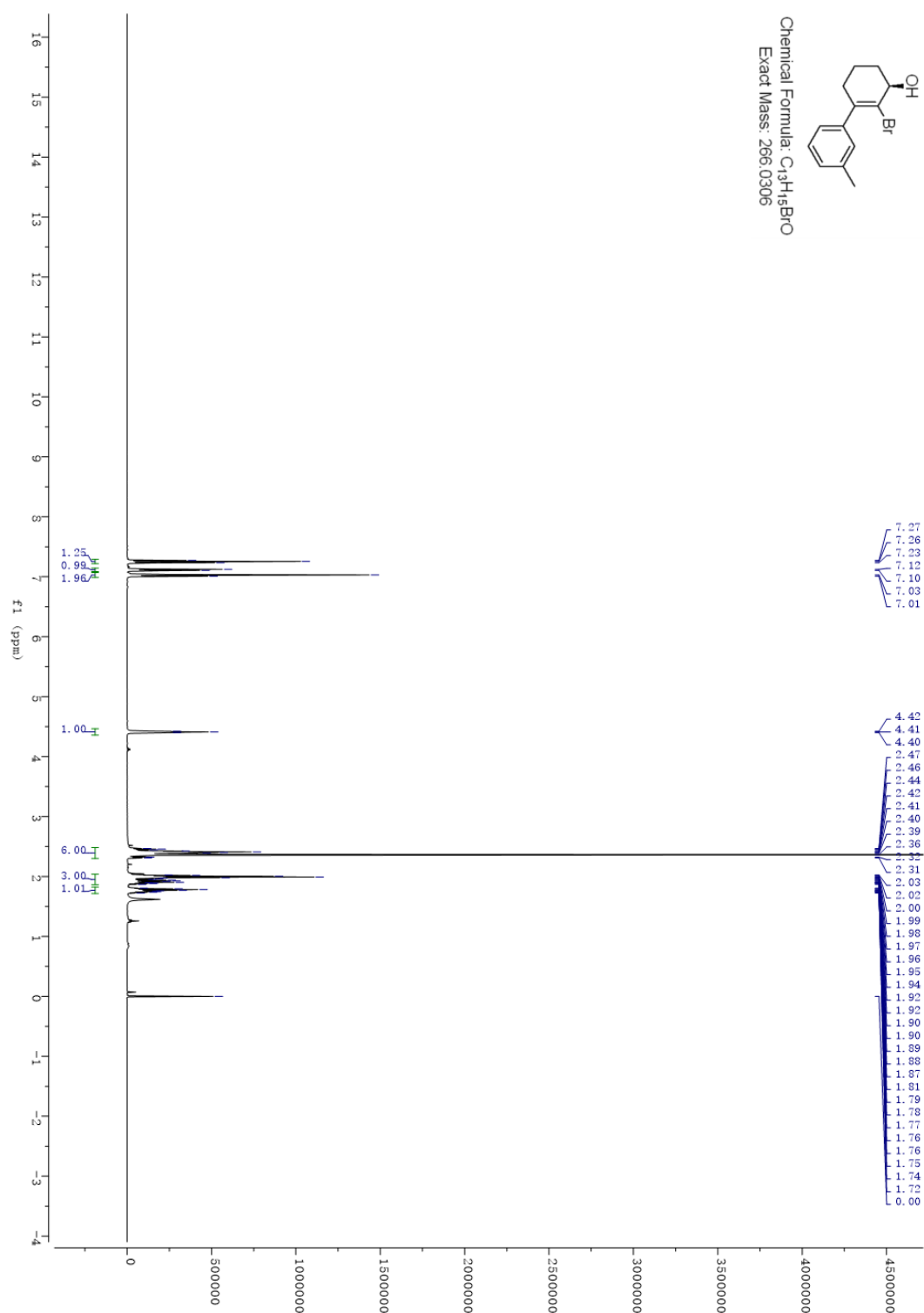
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **4a**



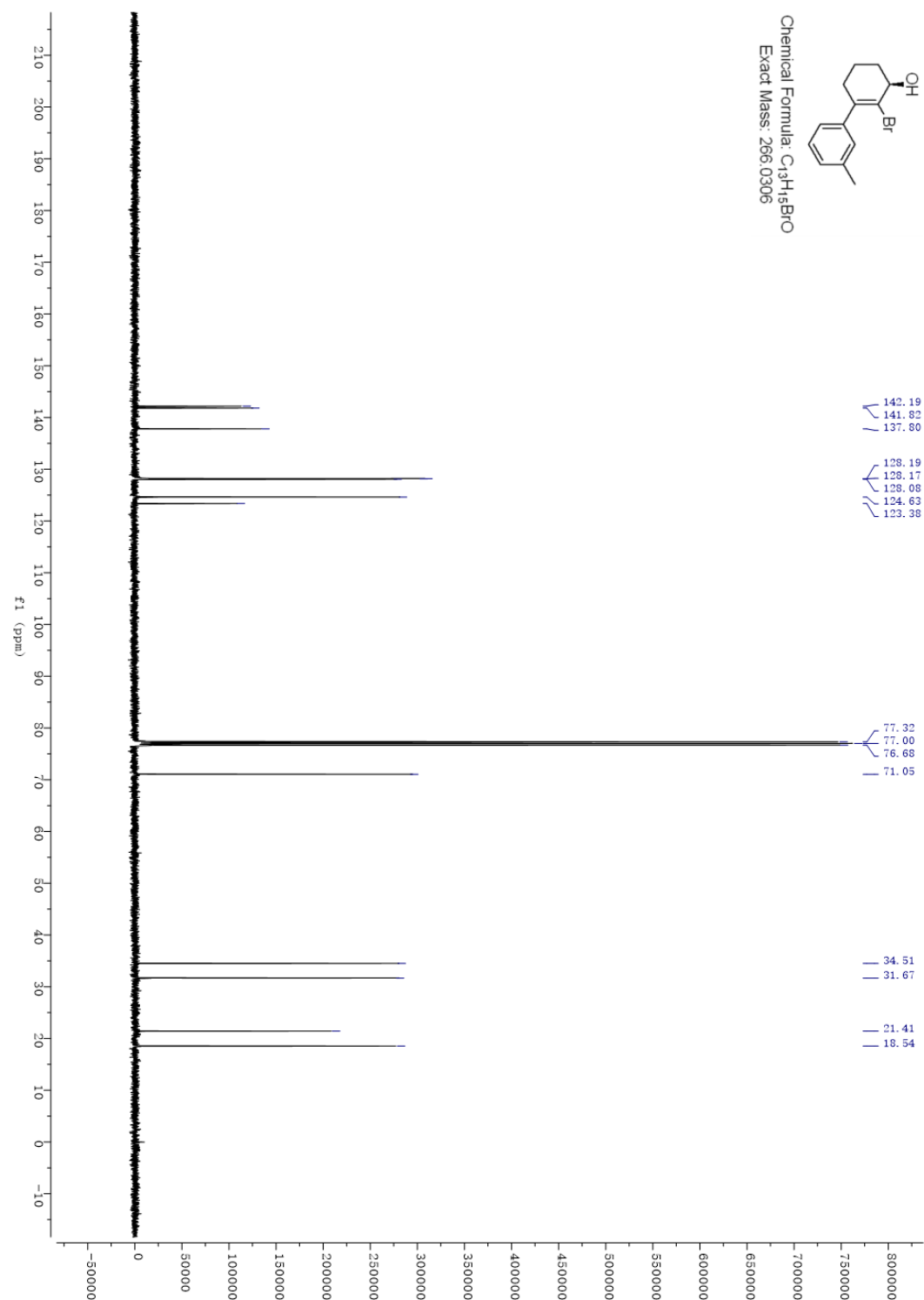
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-d) of compound **4a**



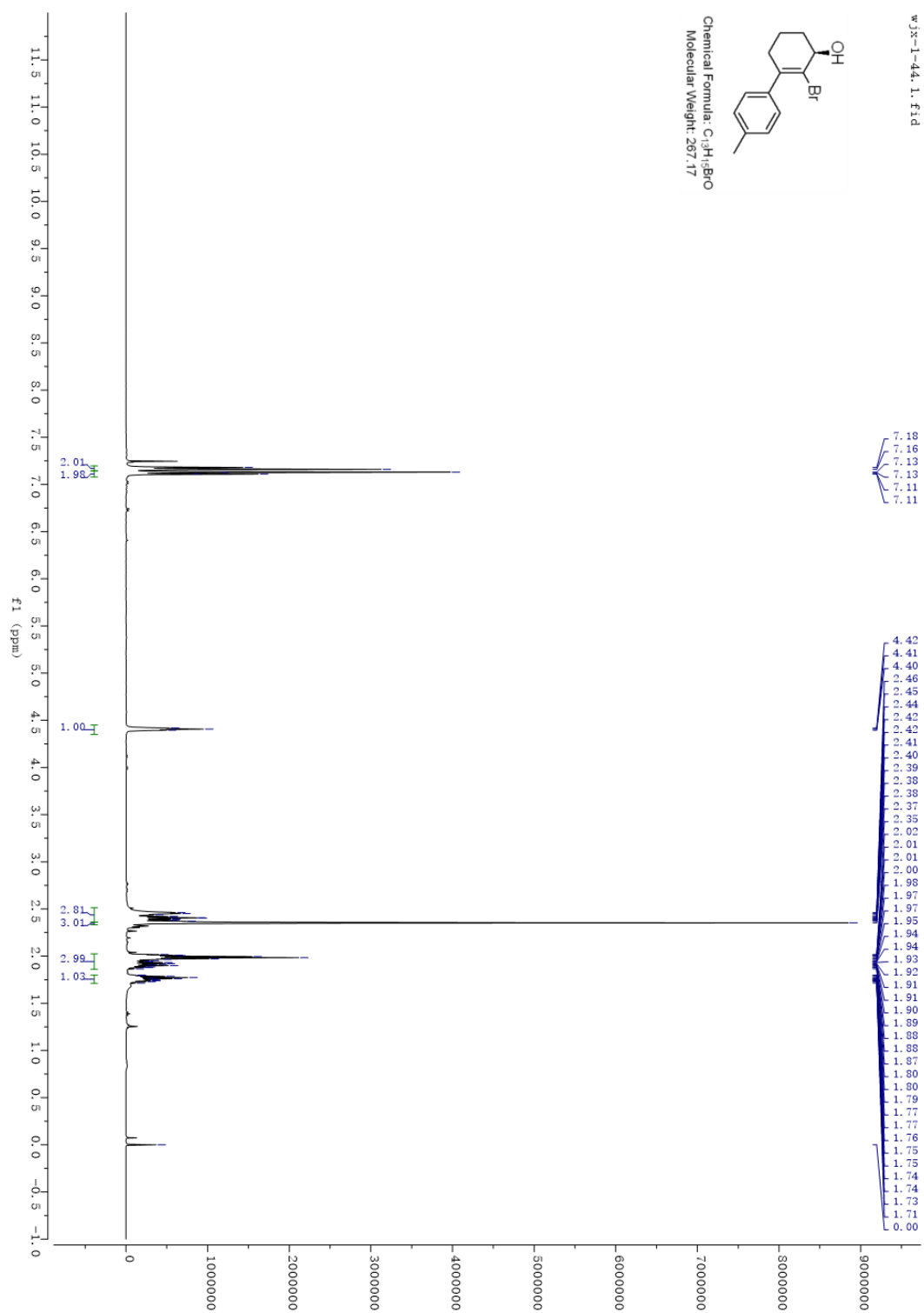
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **4b**



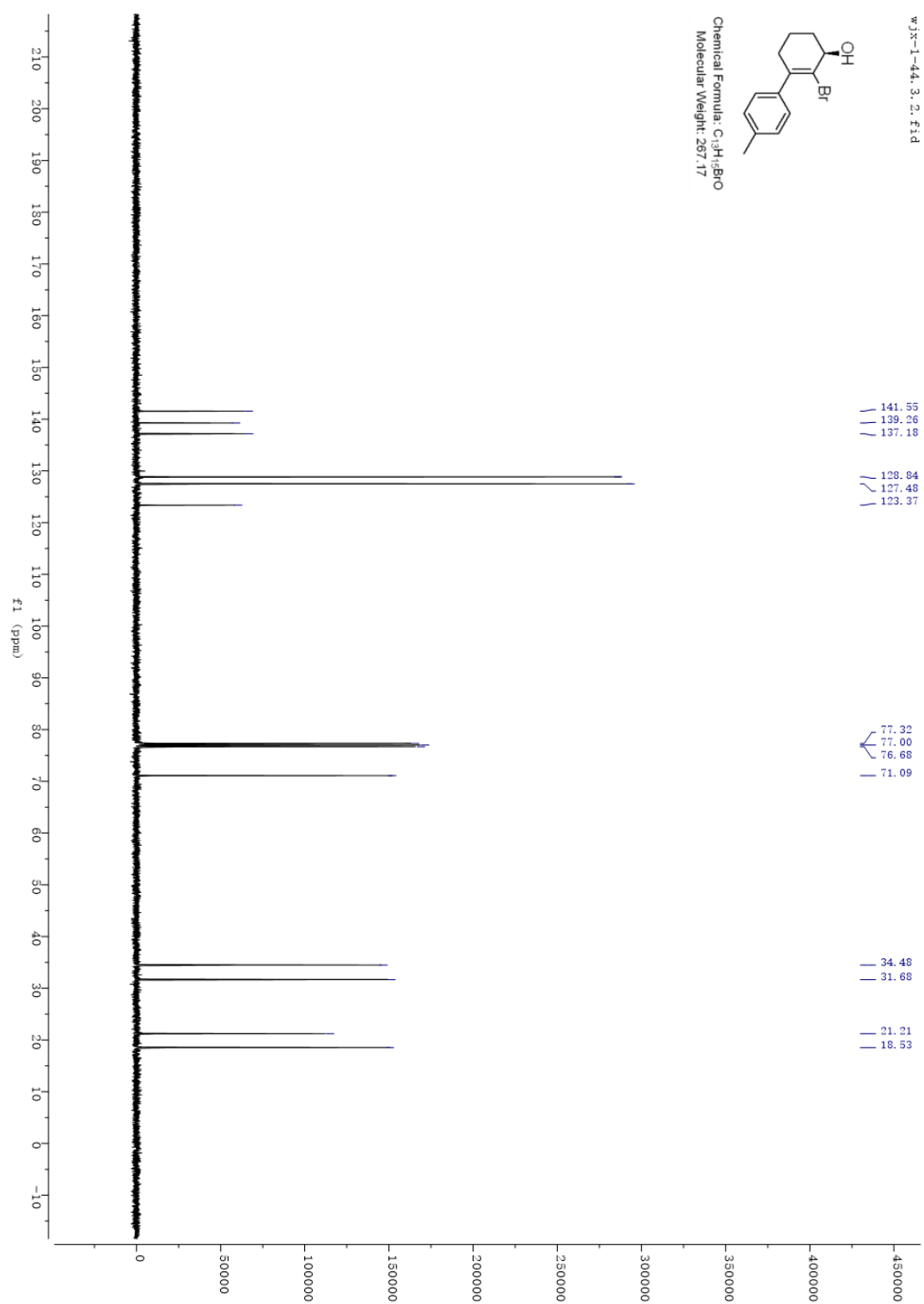
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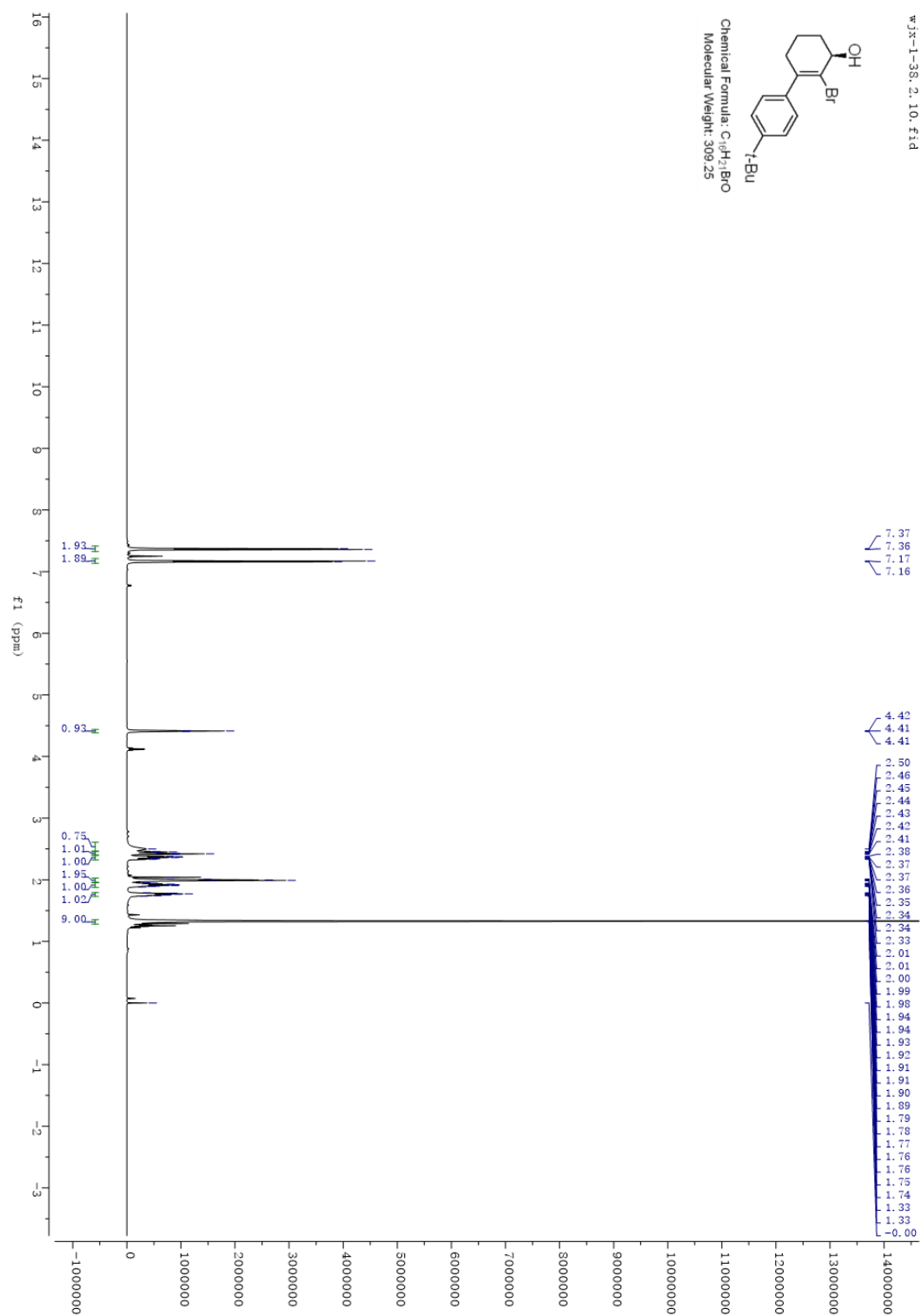
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **4c**



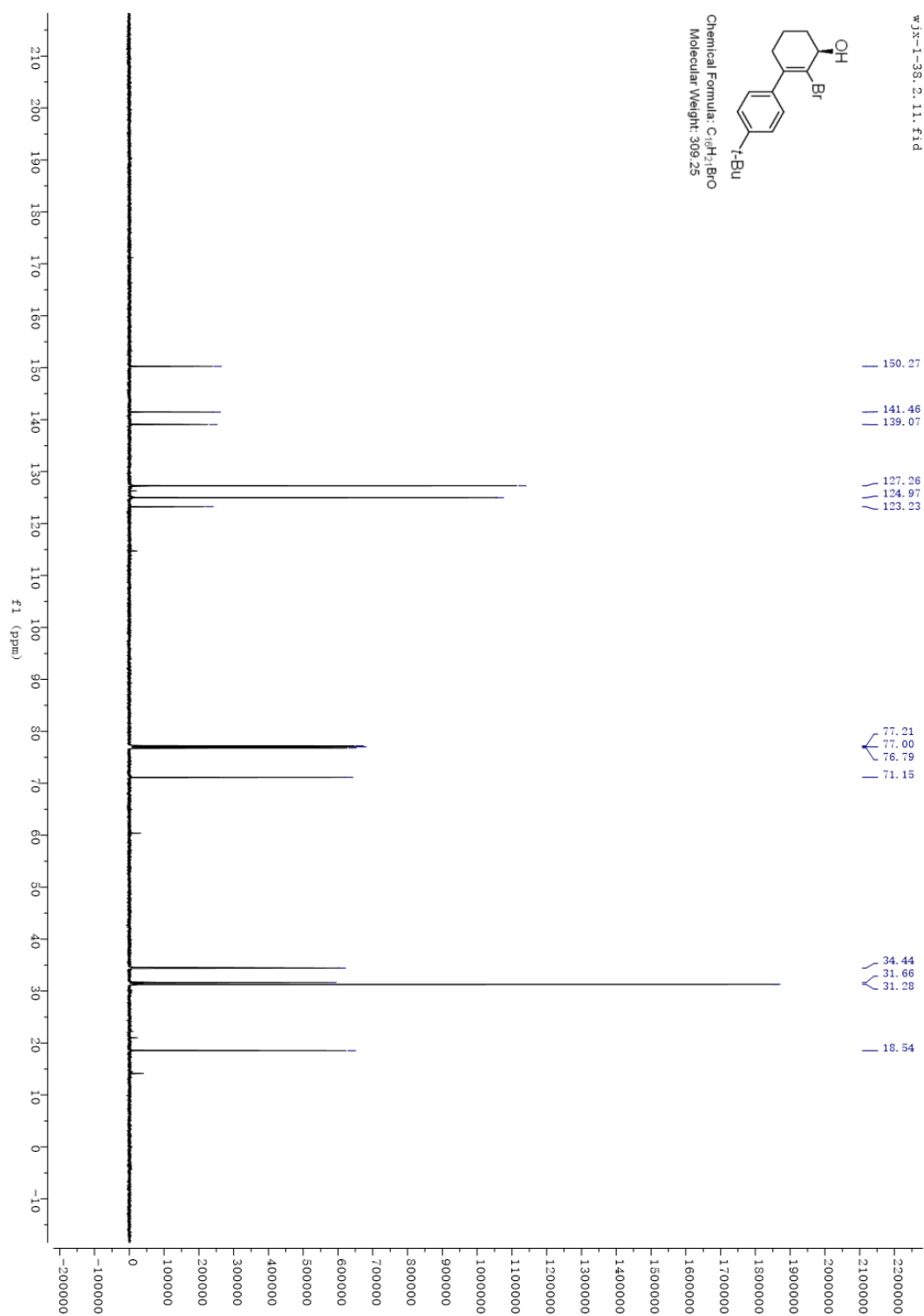
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **4c**



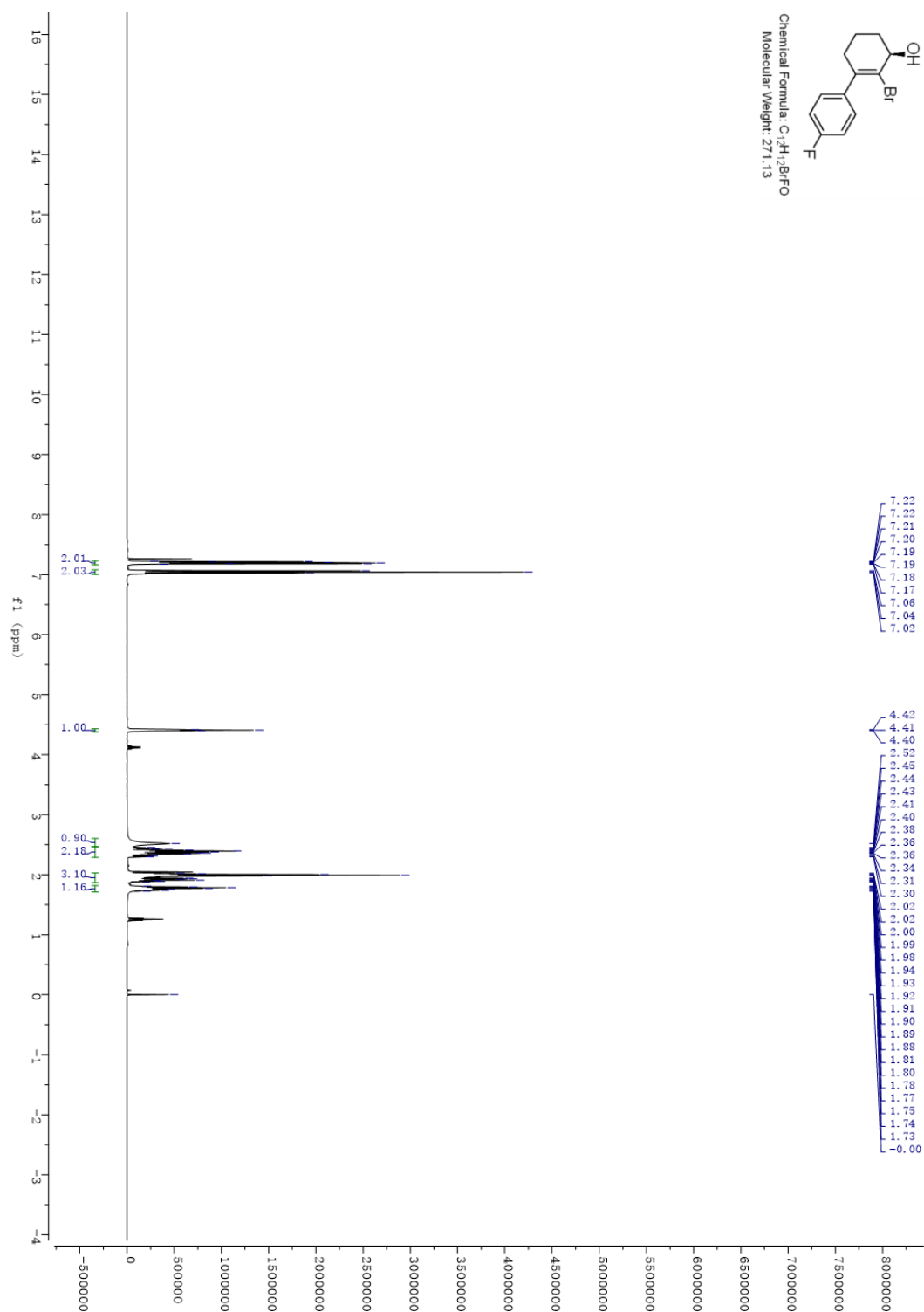
$^1\text{H}$  NMR (600 MHz, Chloroform- $d$ ) of compound **4d**



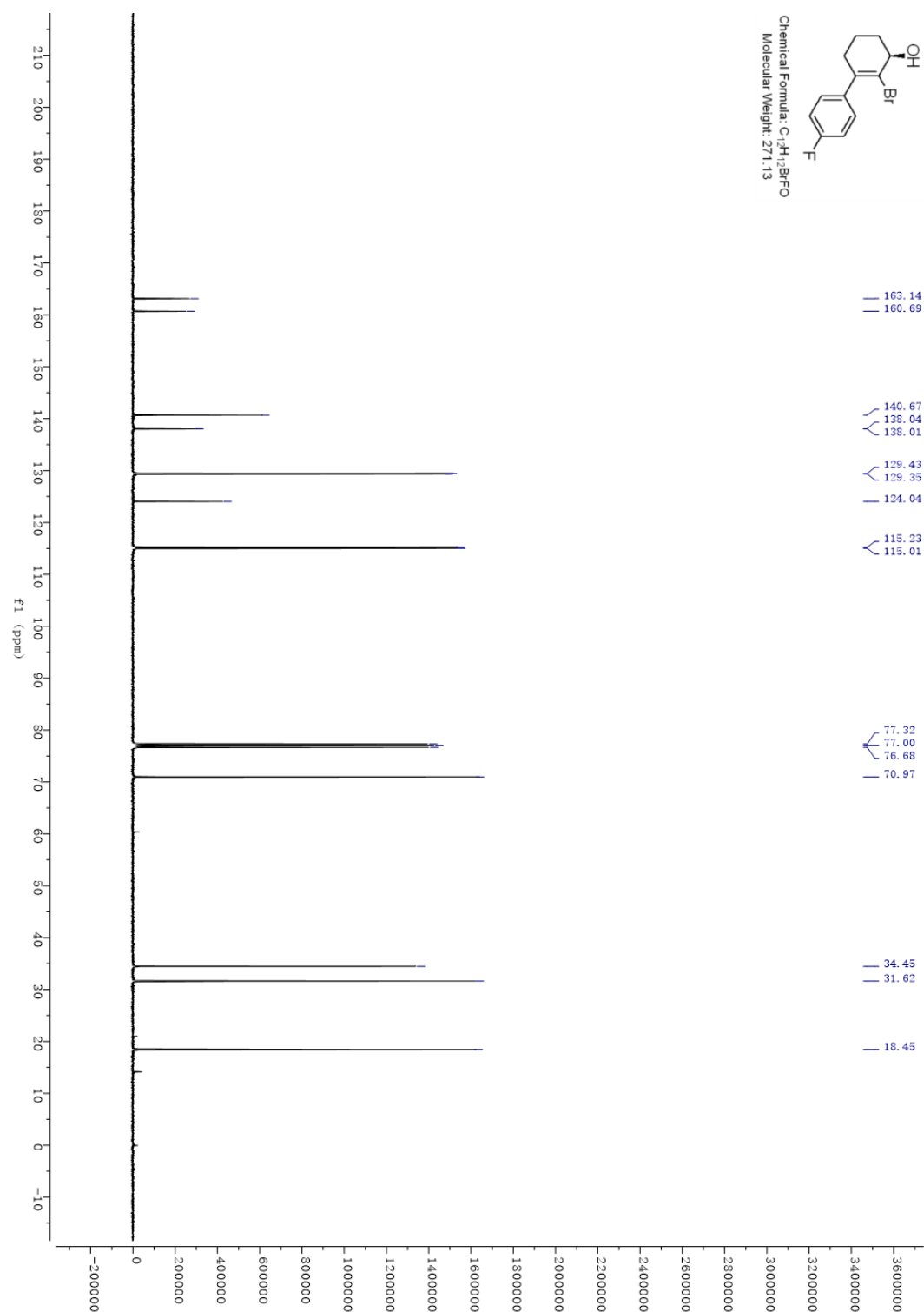
$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform- $d$ ) of compound **4d**



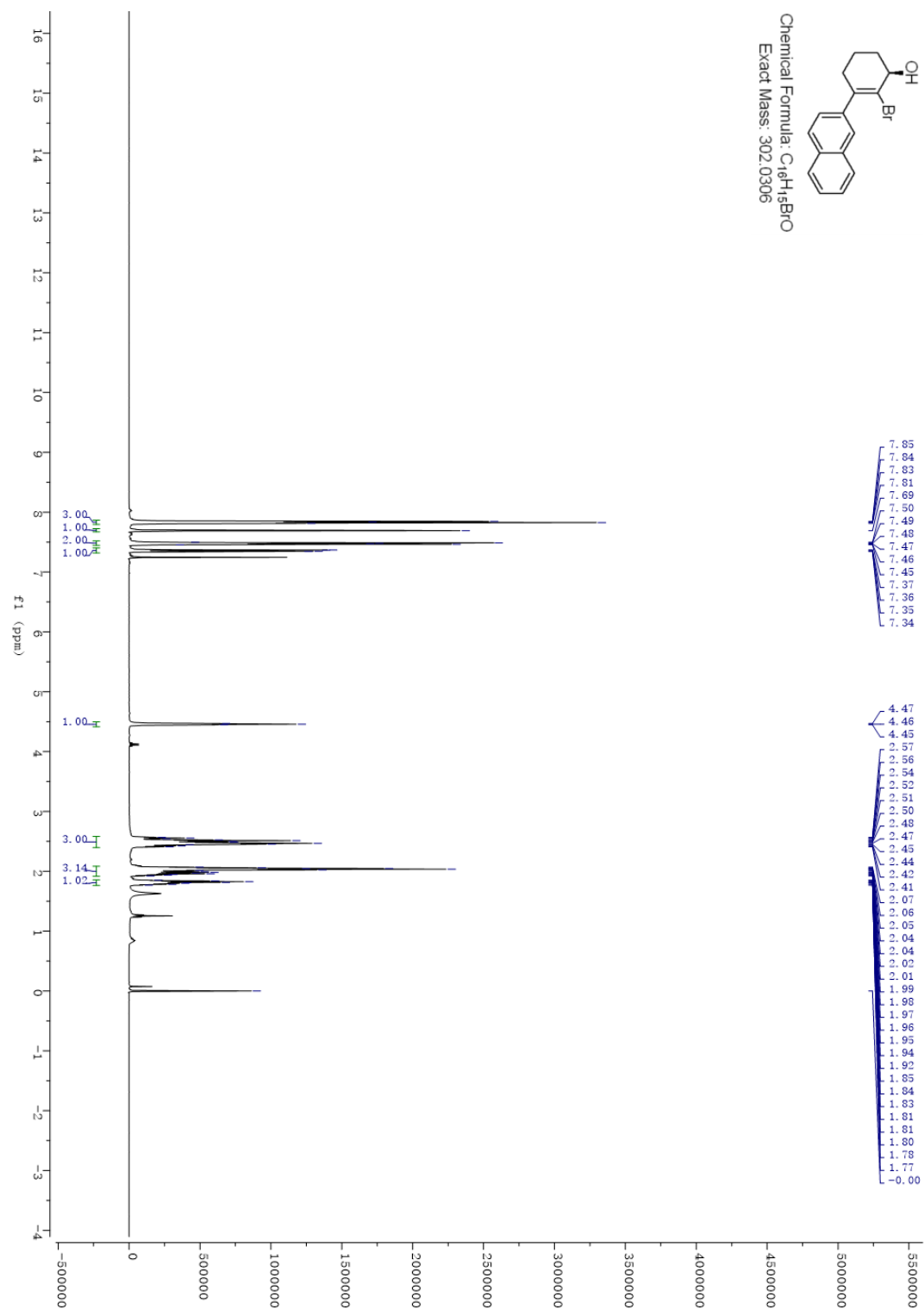
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **4e**



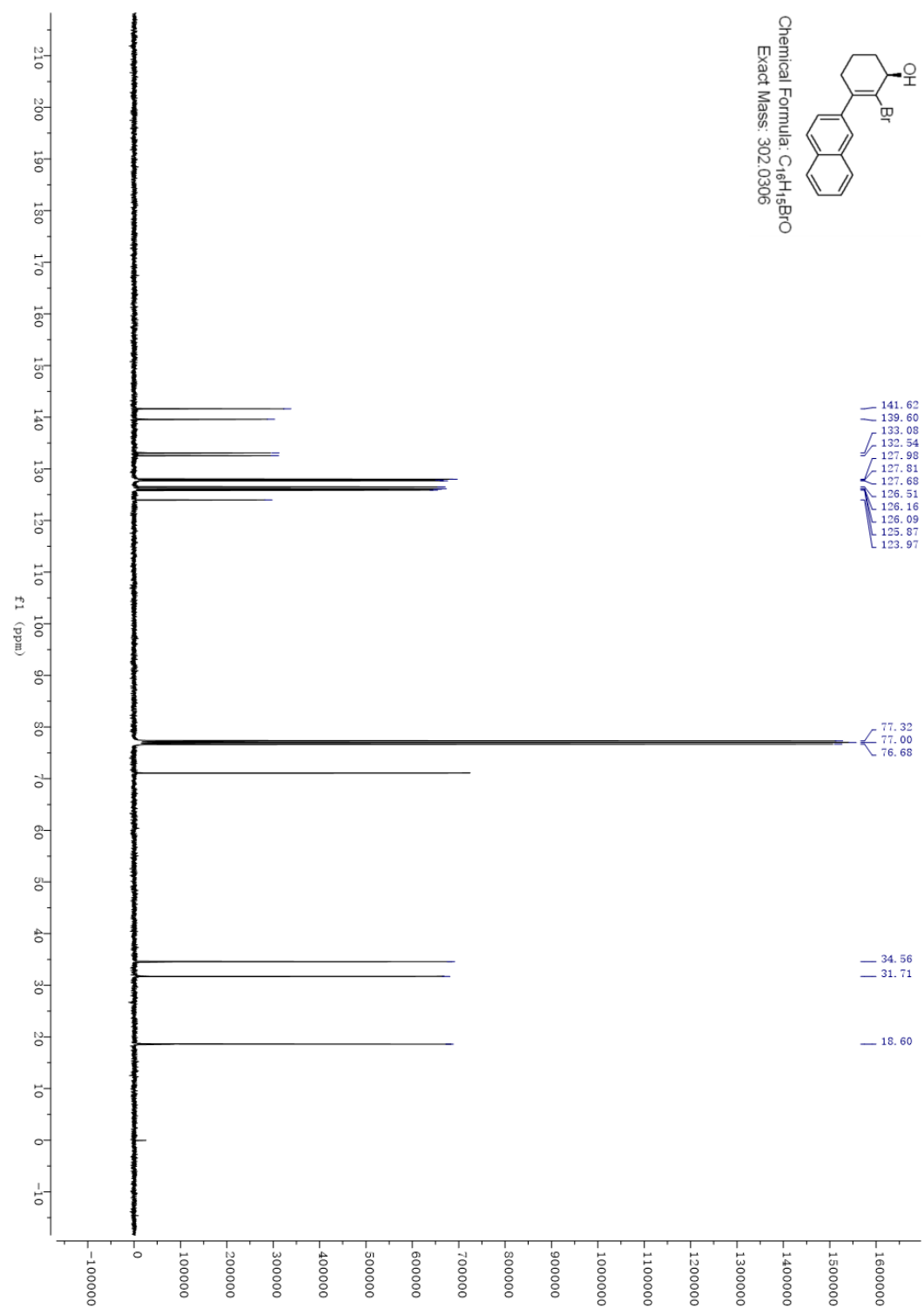
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **4e**



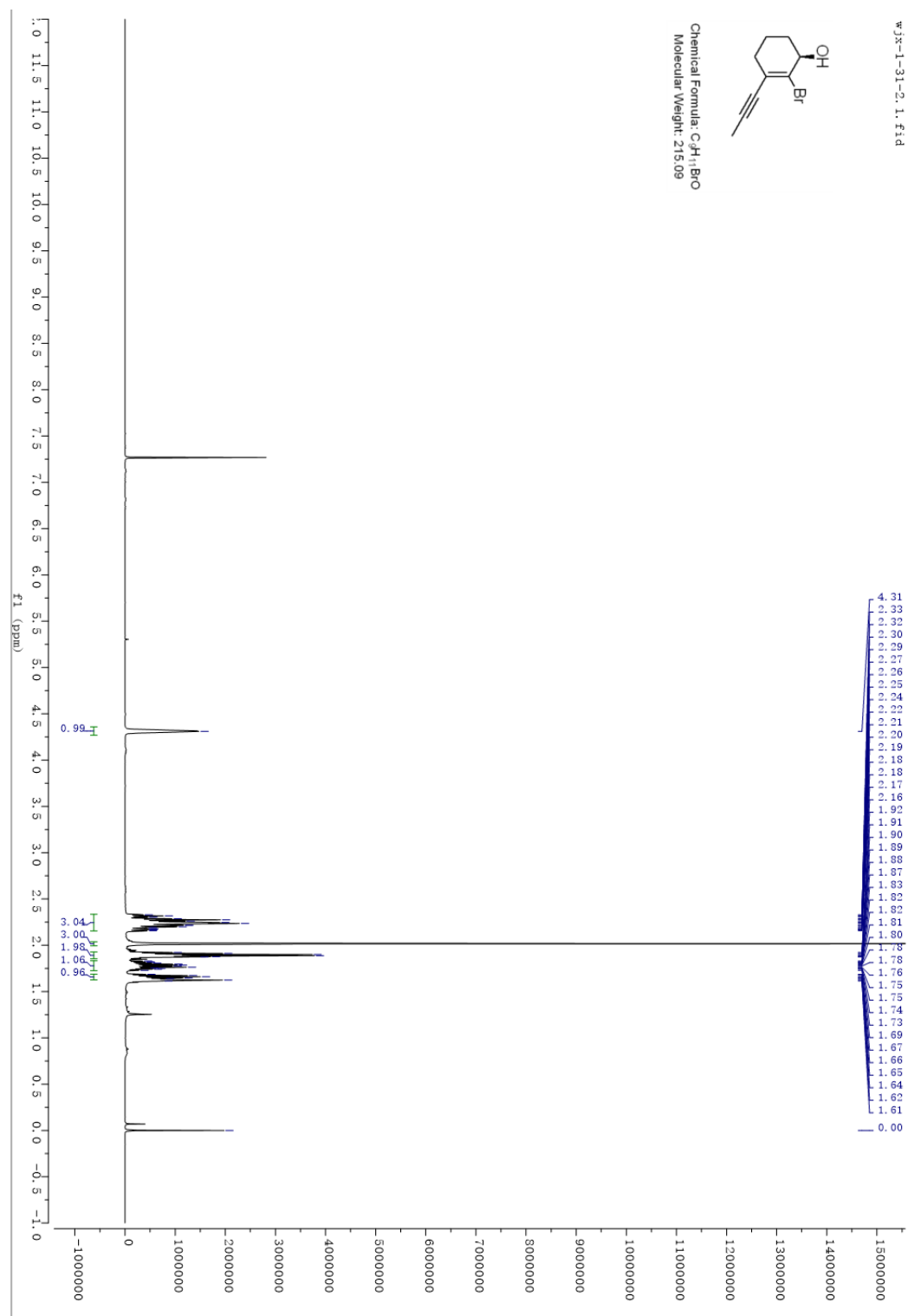
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **4f**



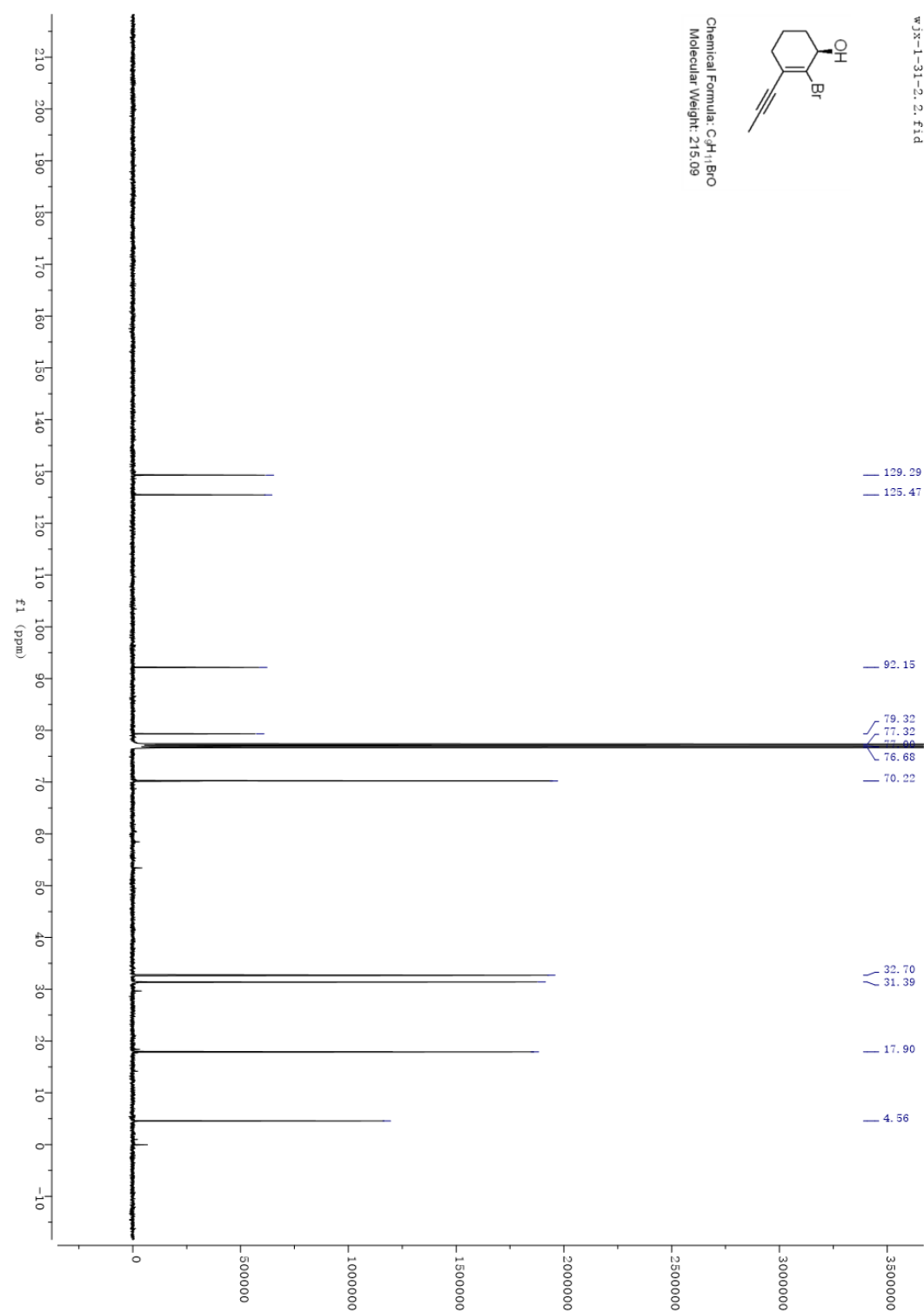
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **4f**



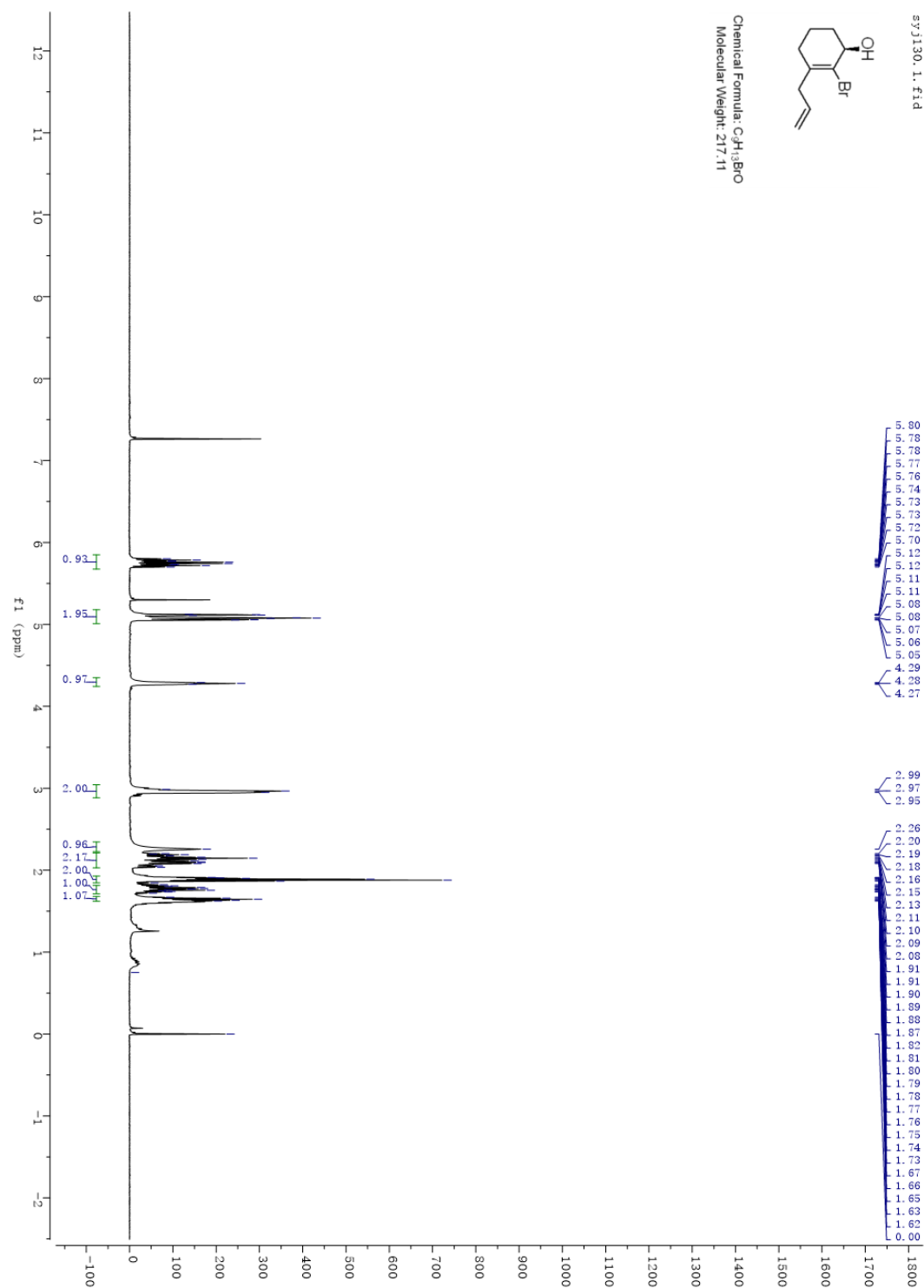
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **4g**



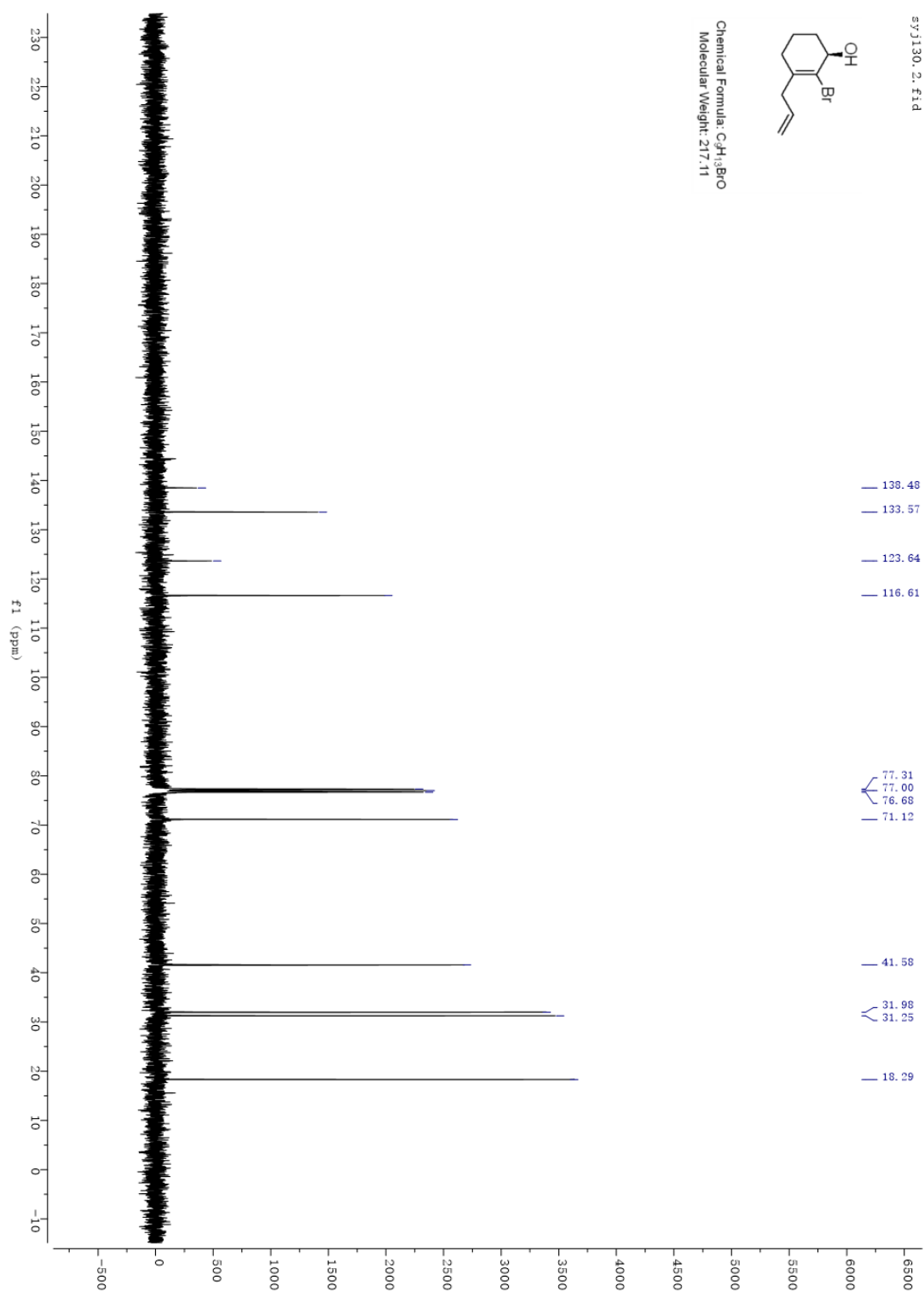
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **4g**



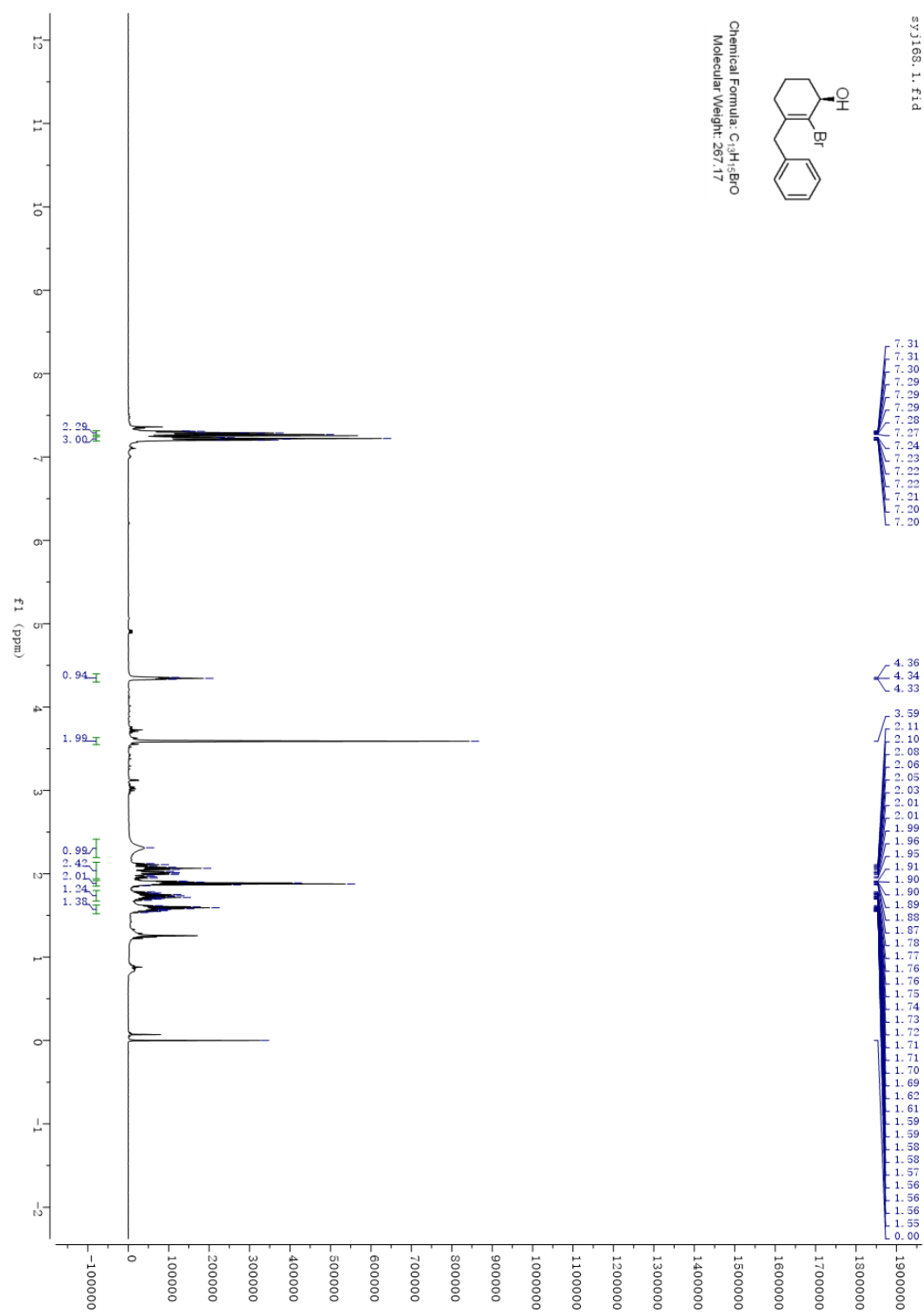
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **4h**



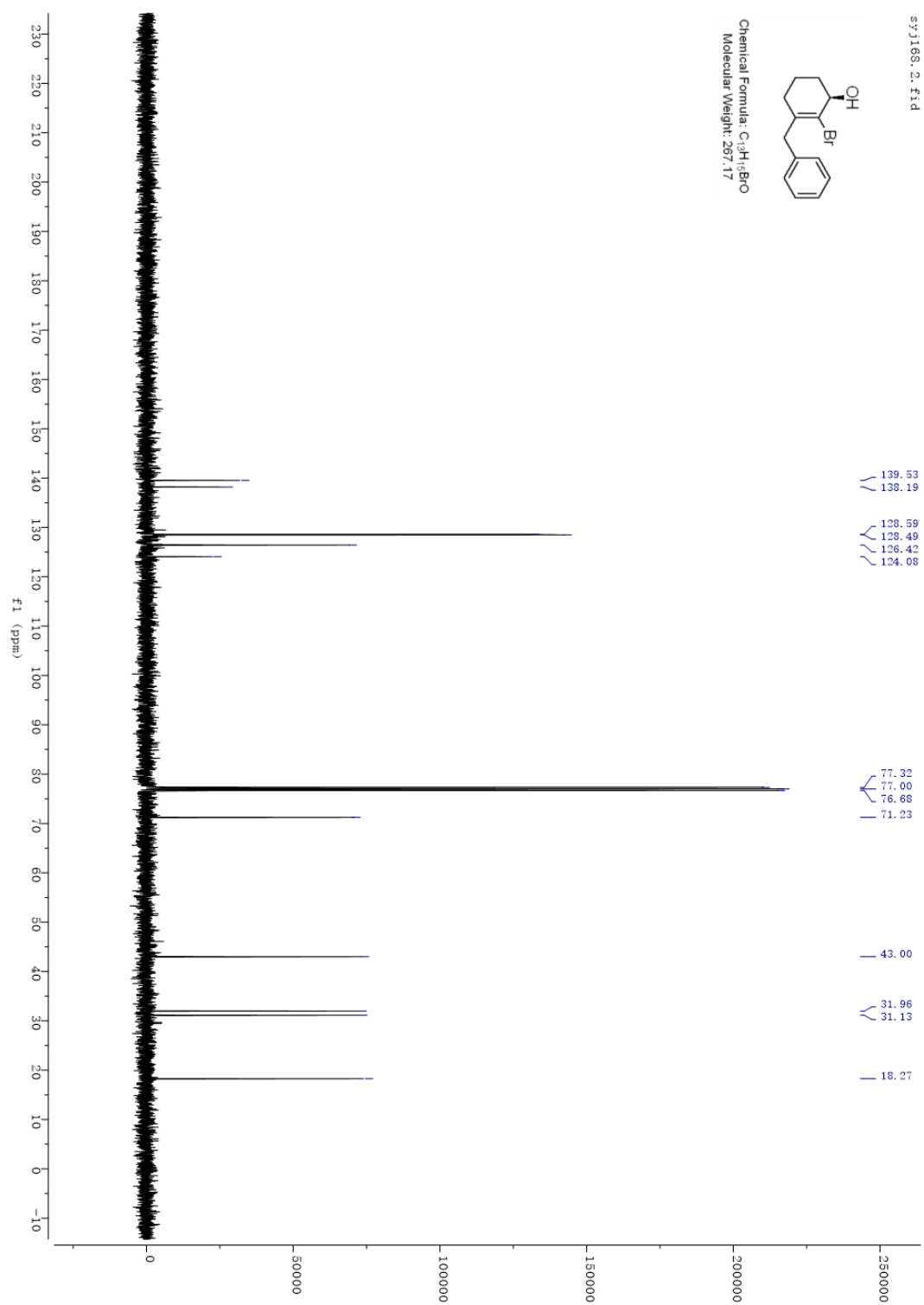
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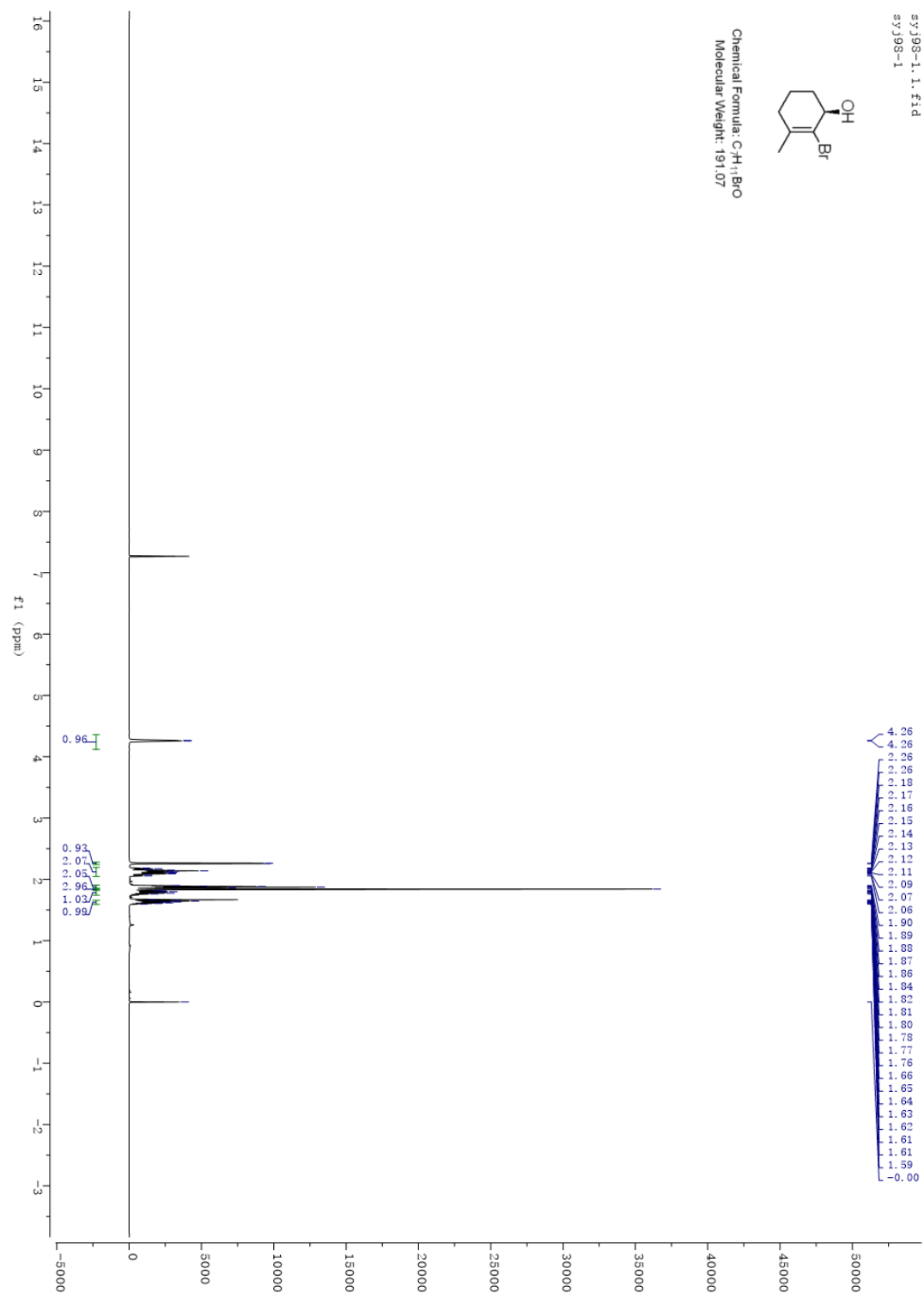
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **4i**



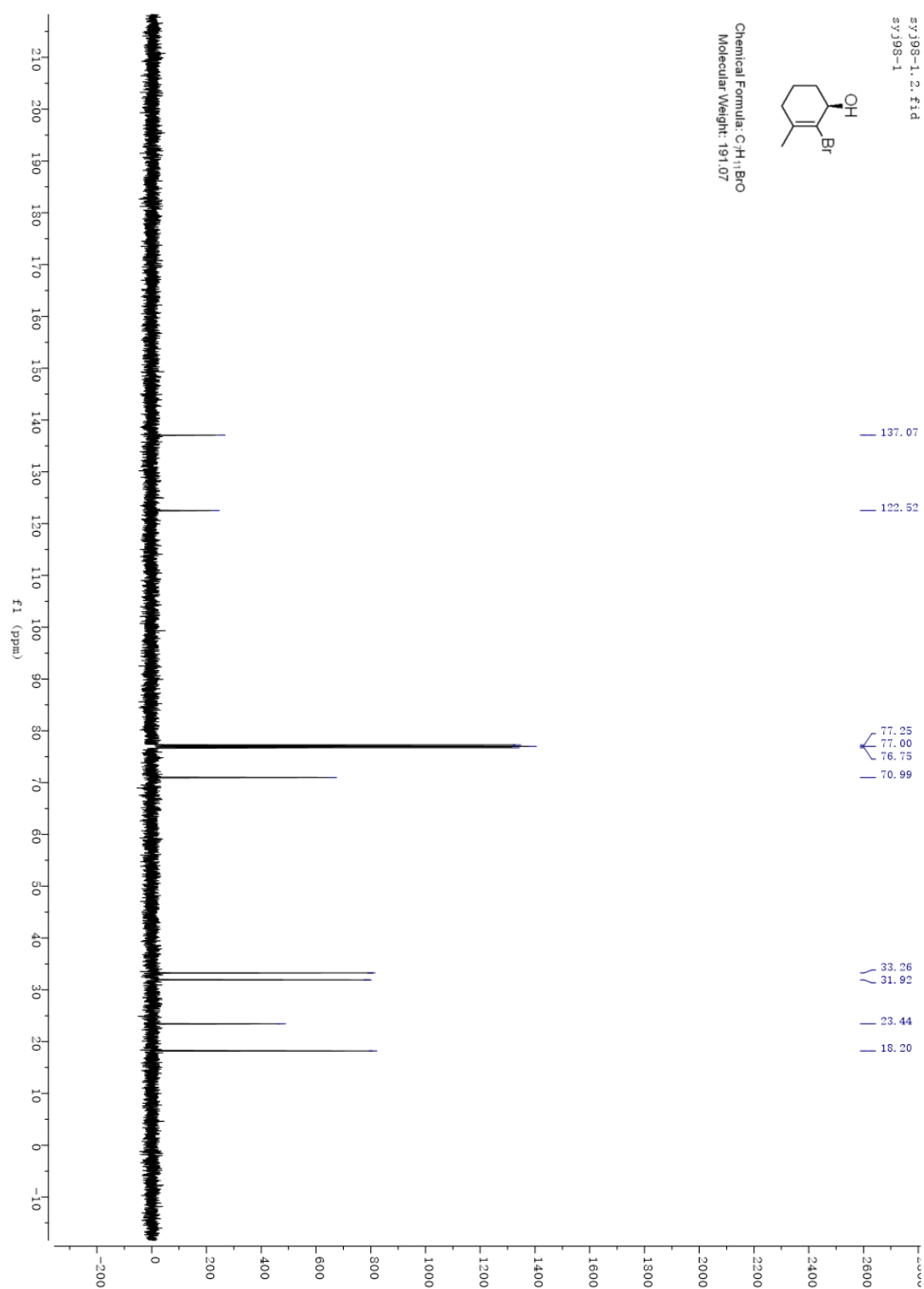
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **4i**

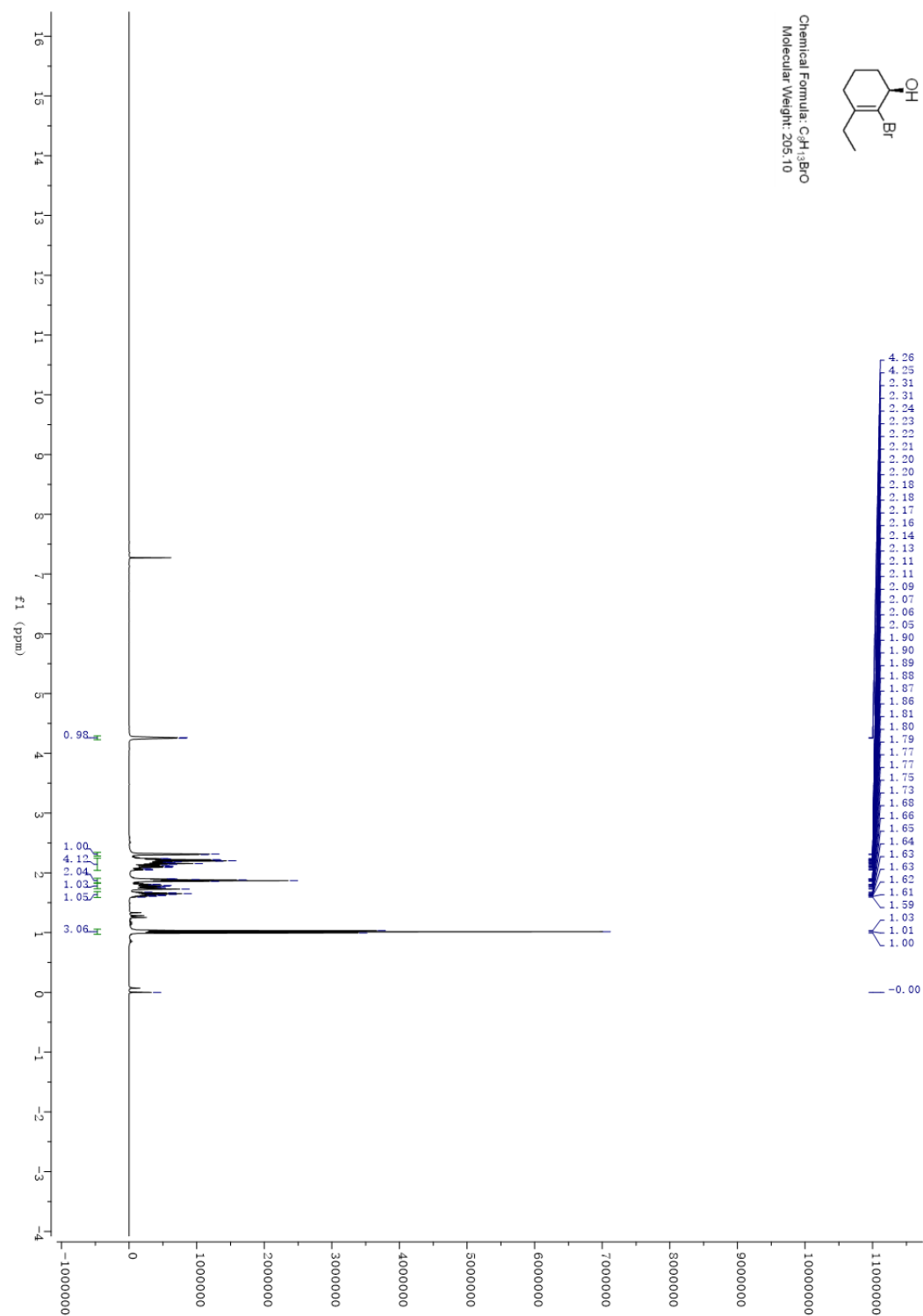


<sup>1</sup>H NMR (400 MHz, Chloroform-d) of compound **4j**

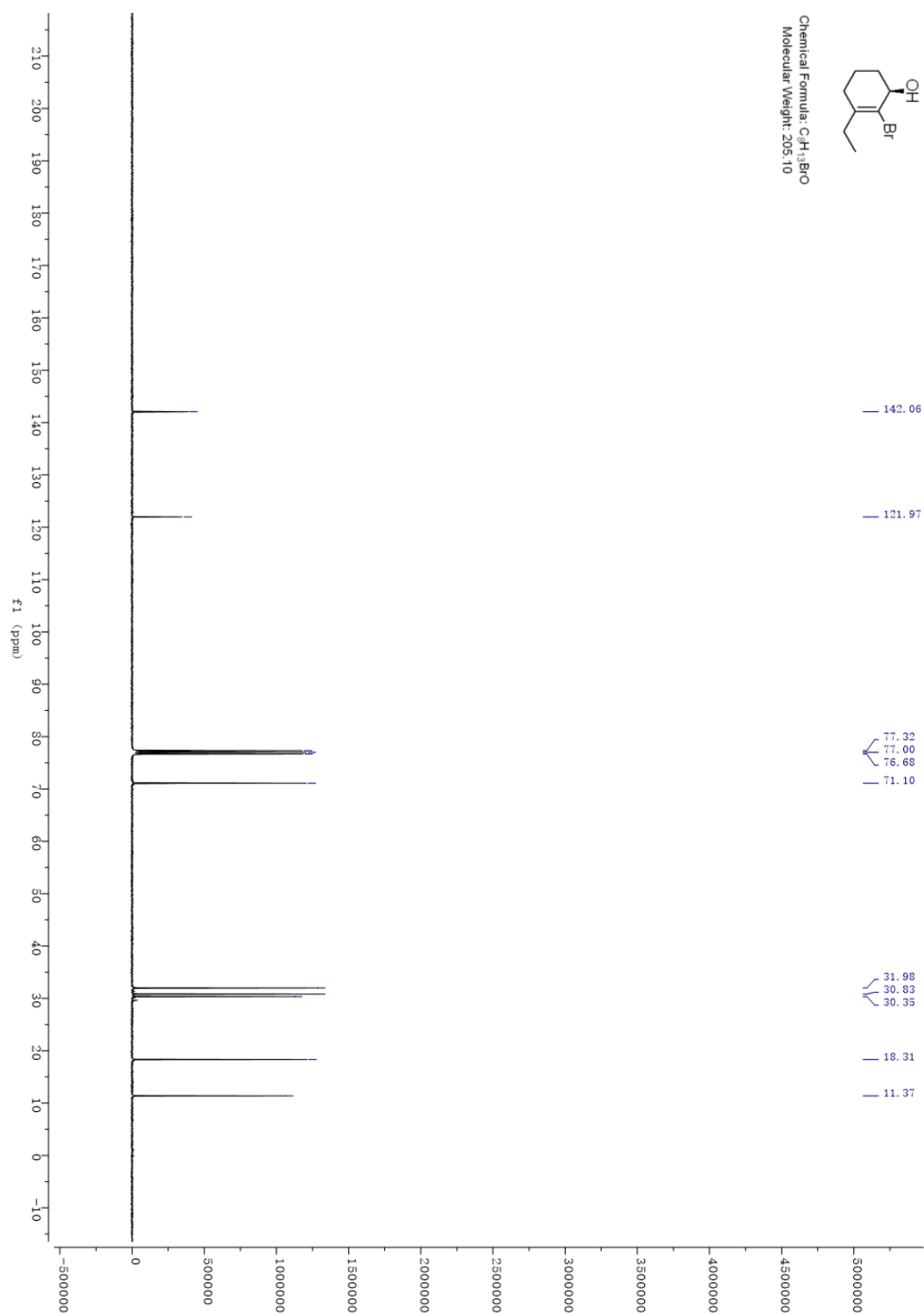


$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-d) of compound **4j**

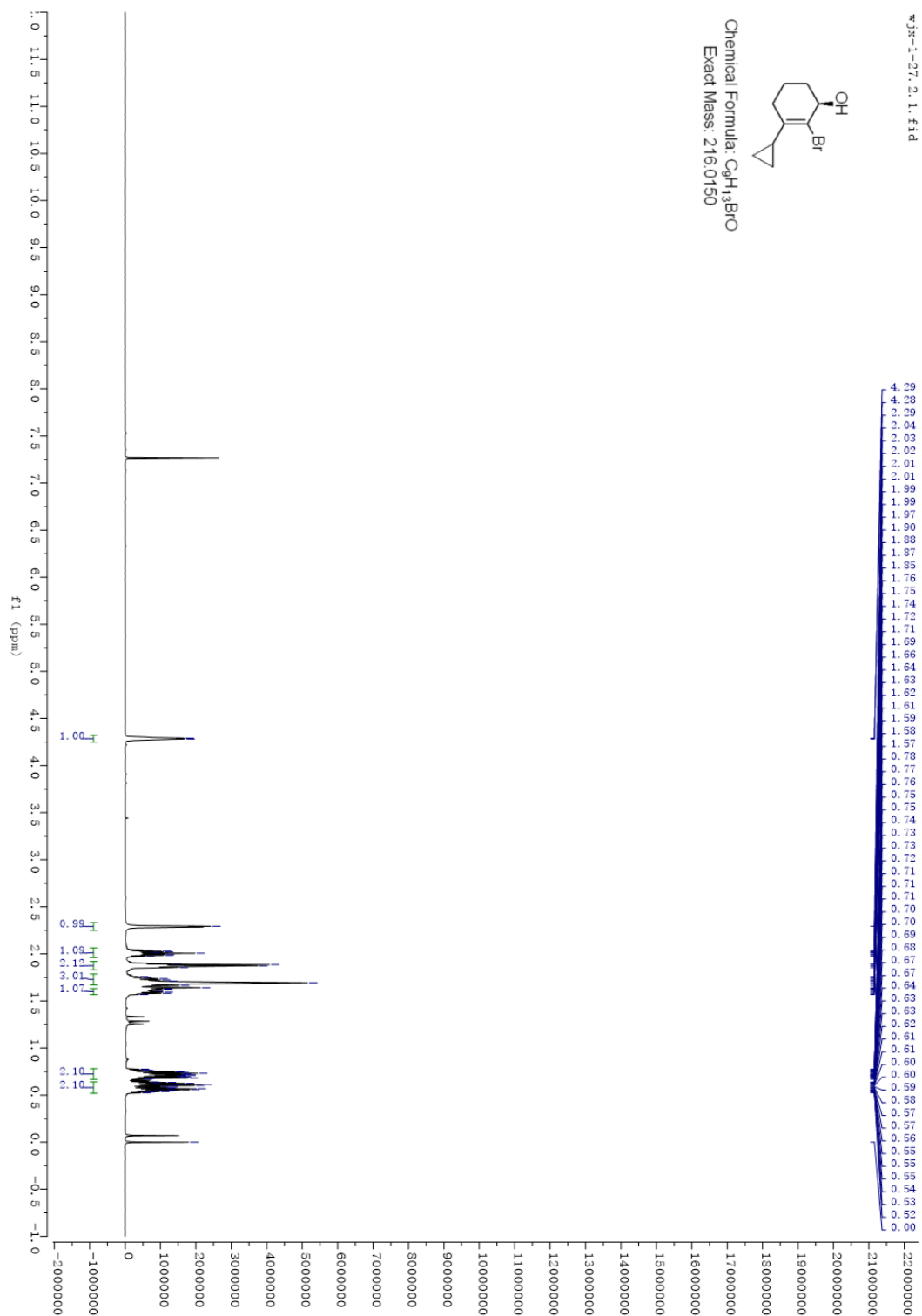


<sup>1</sup>H NMR (400 MHz, Chloroform-d) of compound **4k**

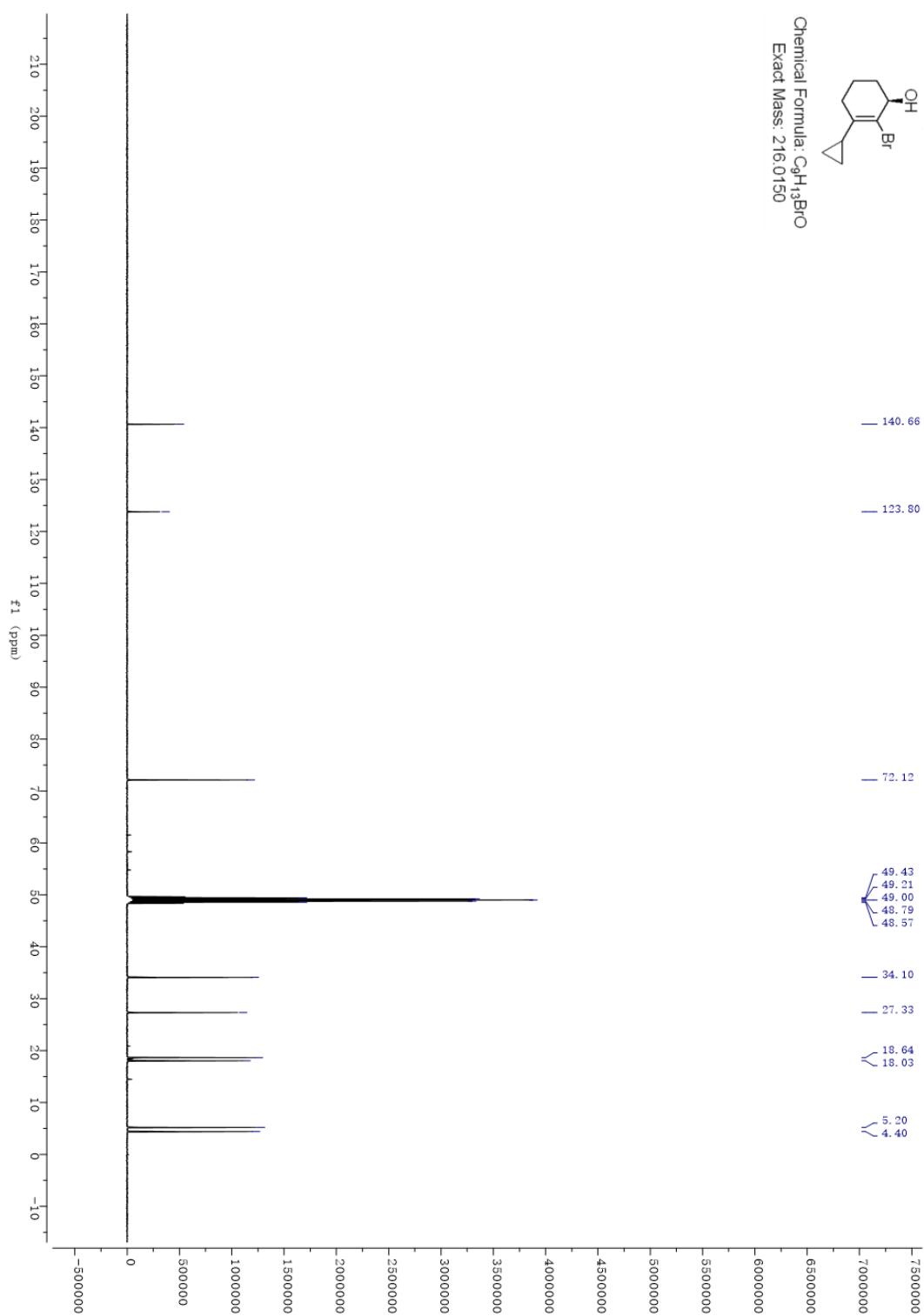
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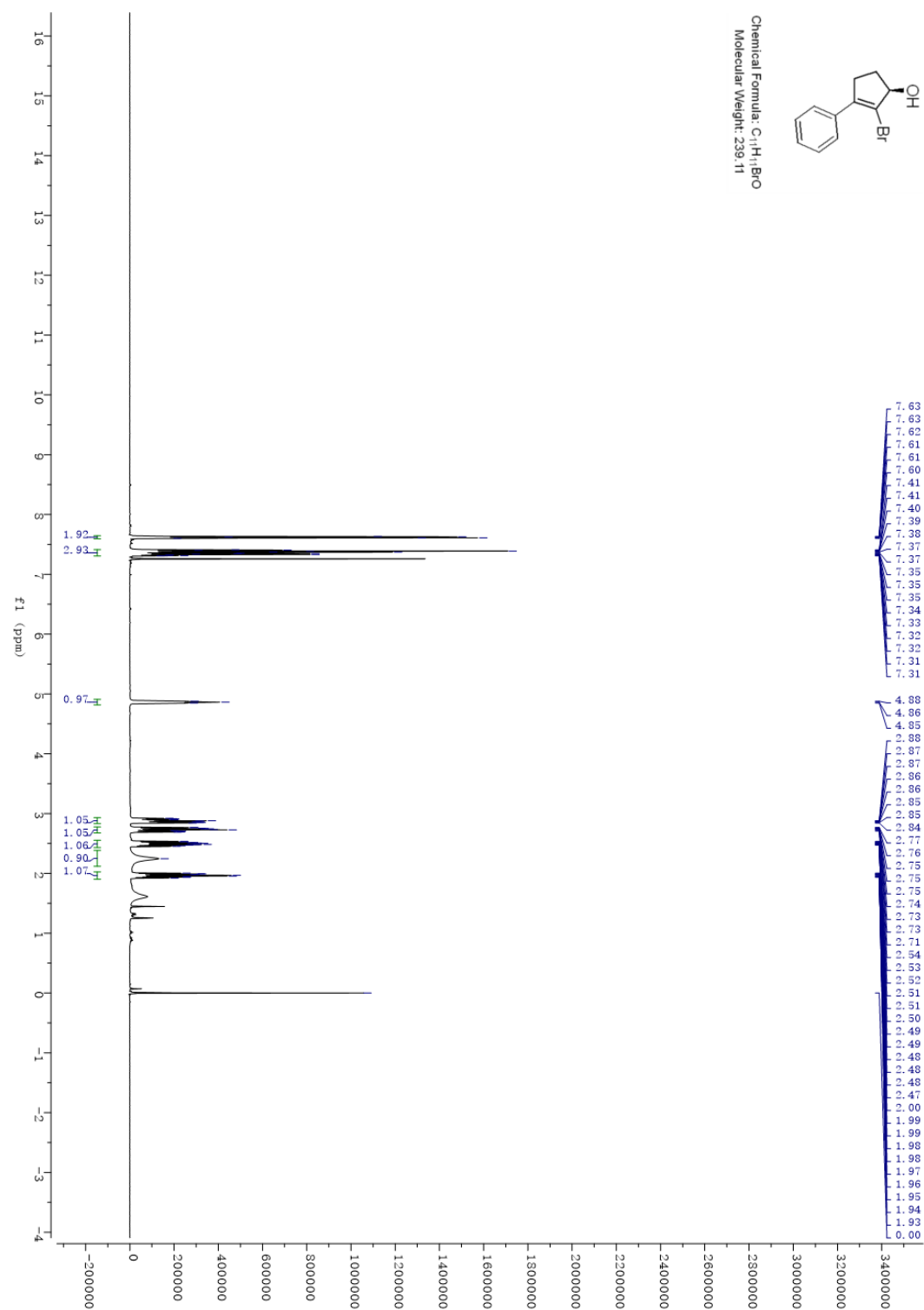
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **4l**



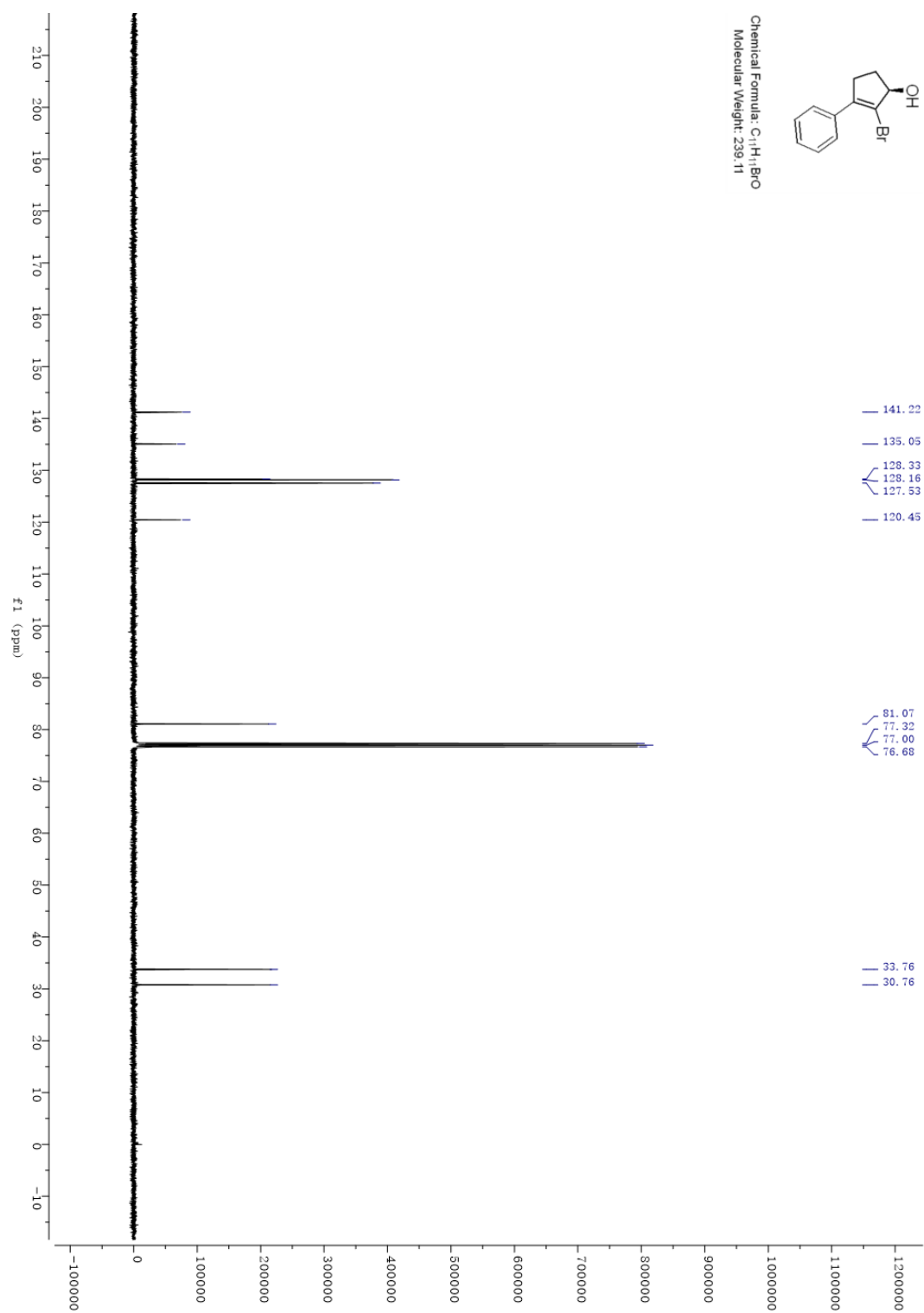
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-d) of compound **4l**

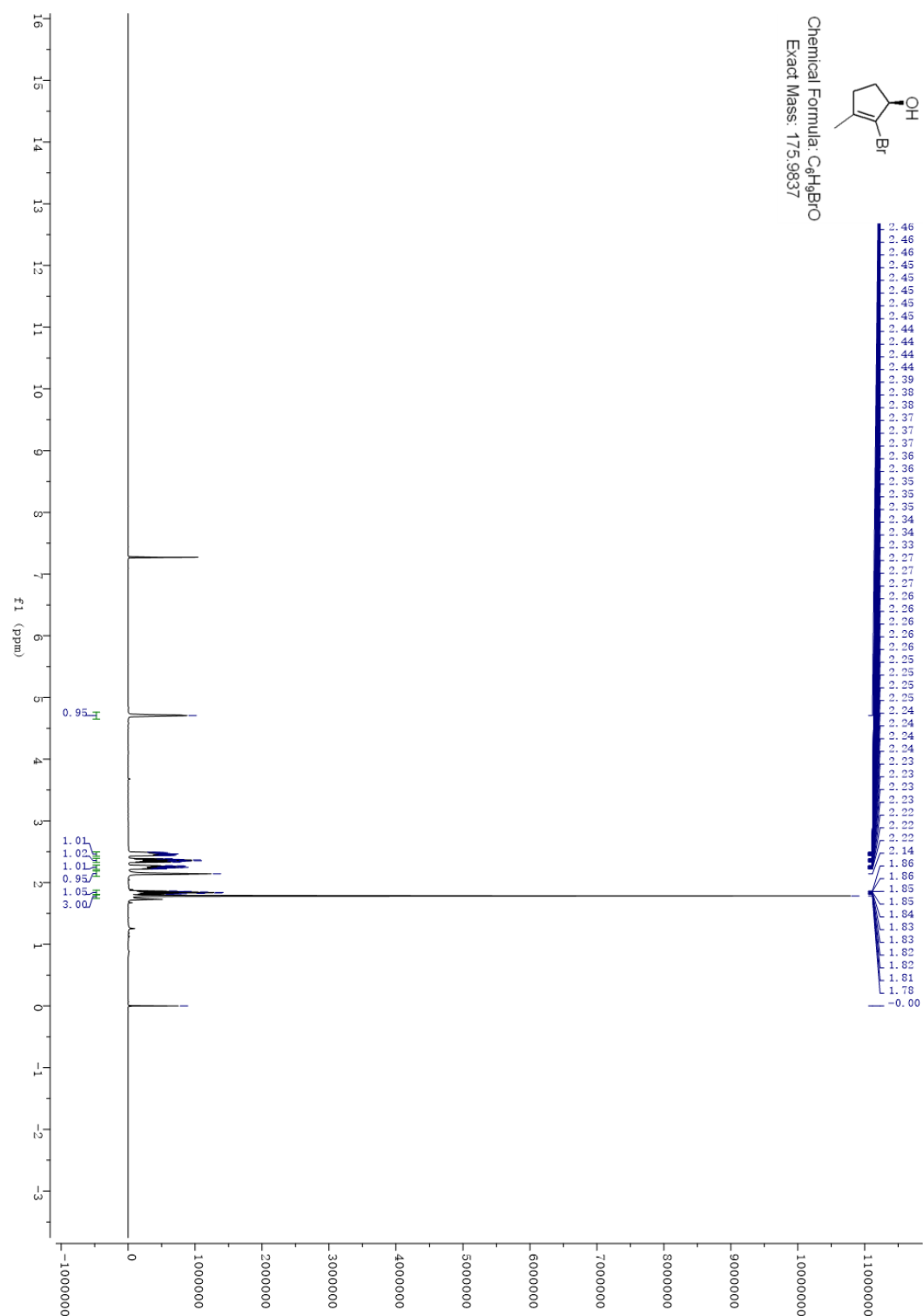


$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **4m**

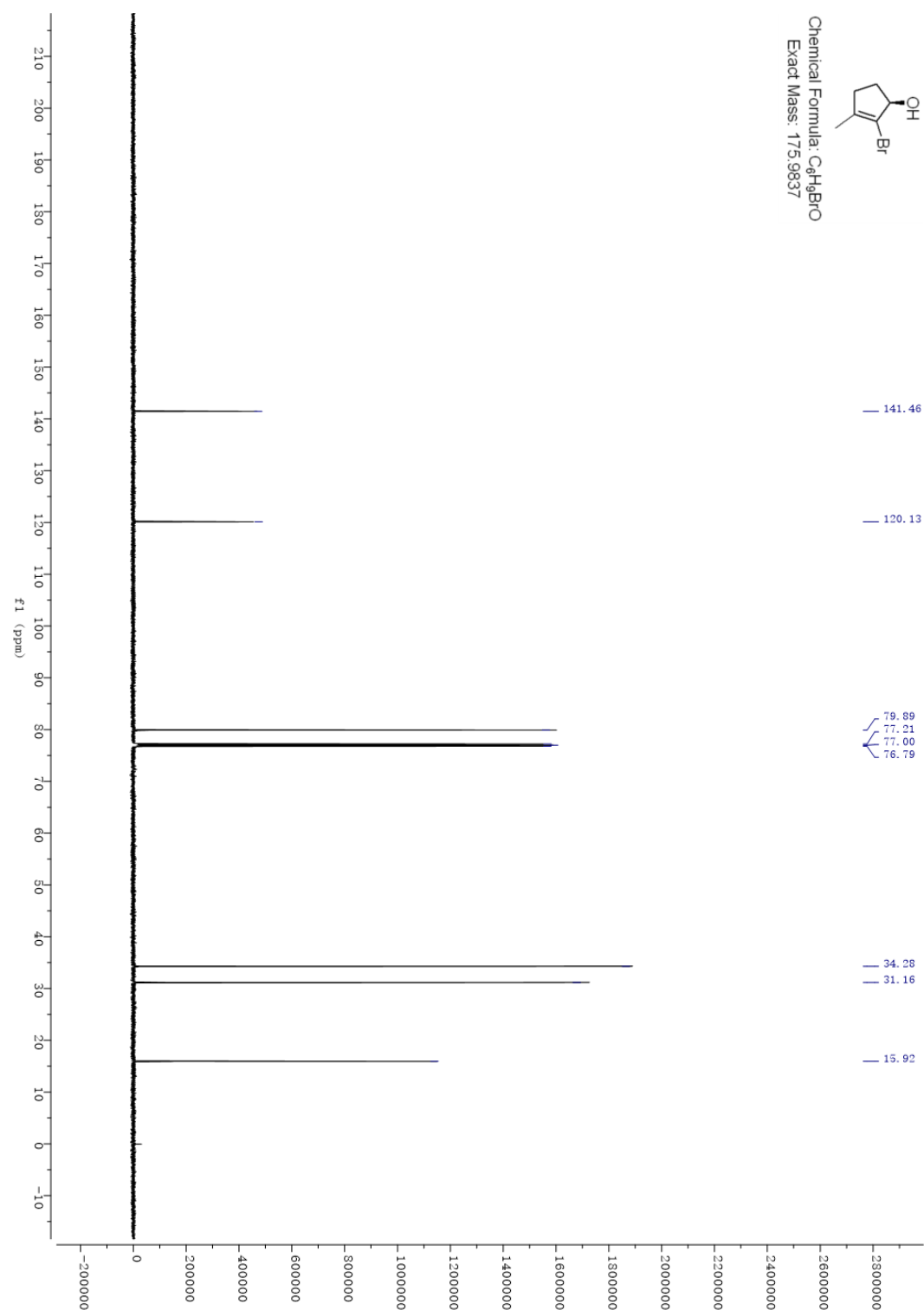


$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **4m**

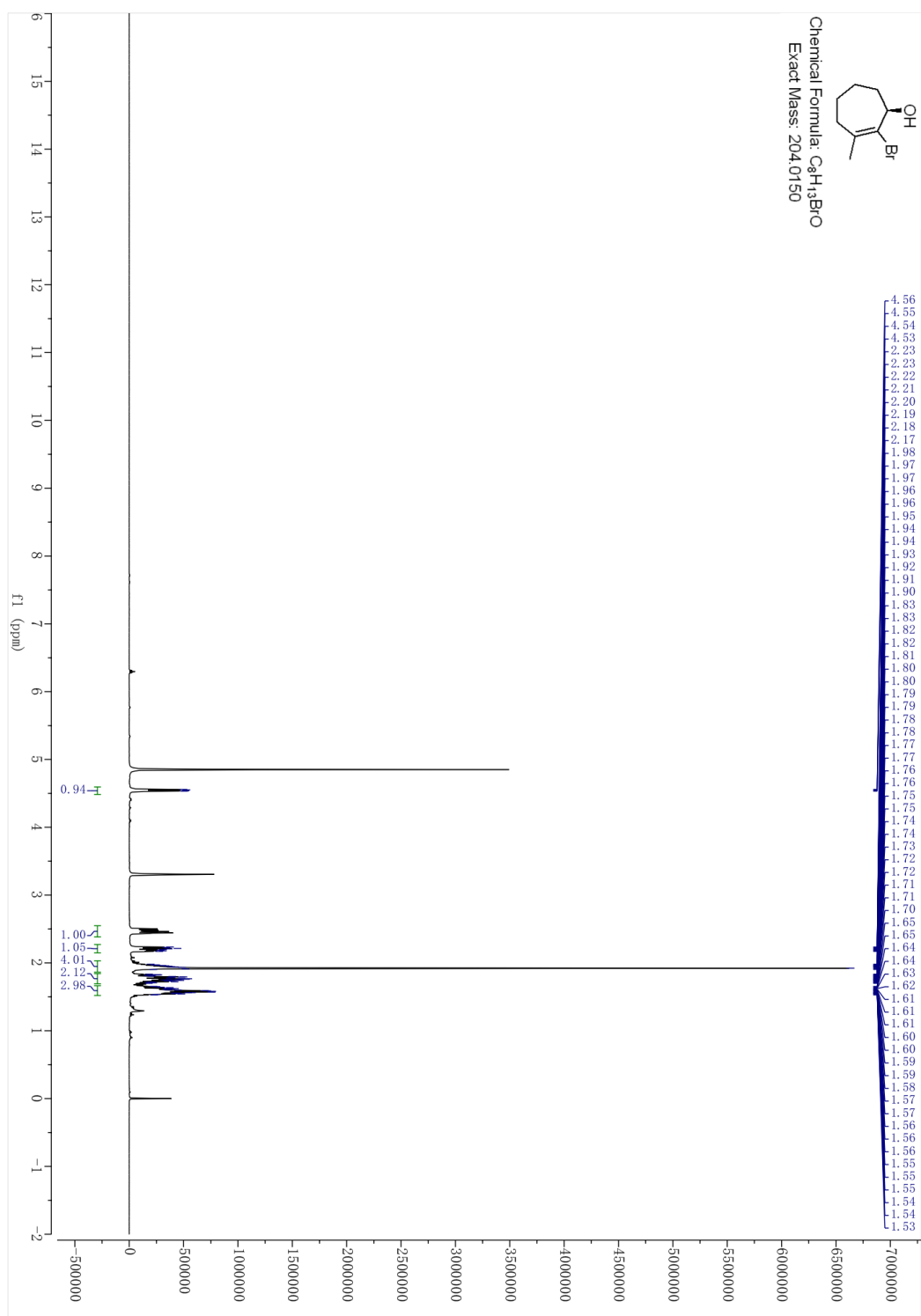


<sup>1</sup>H NMR (500 MHz, Chloroform-d) of compound **4n**

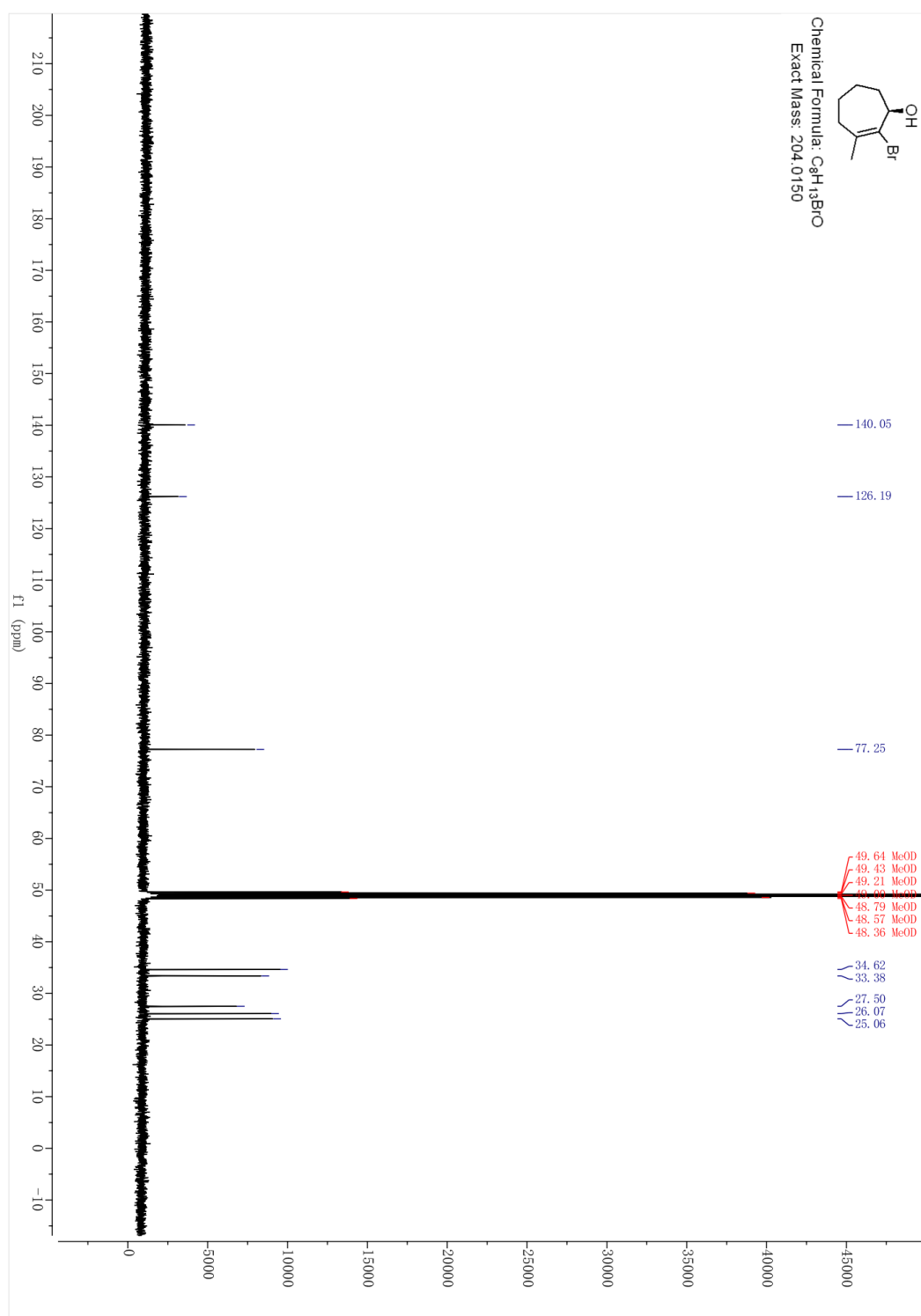
$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, Chloroform- $d$ ) of compound **4n**



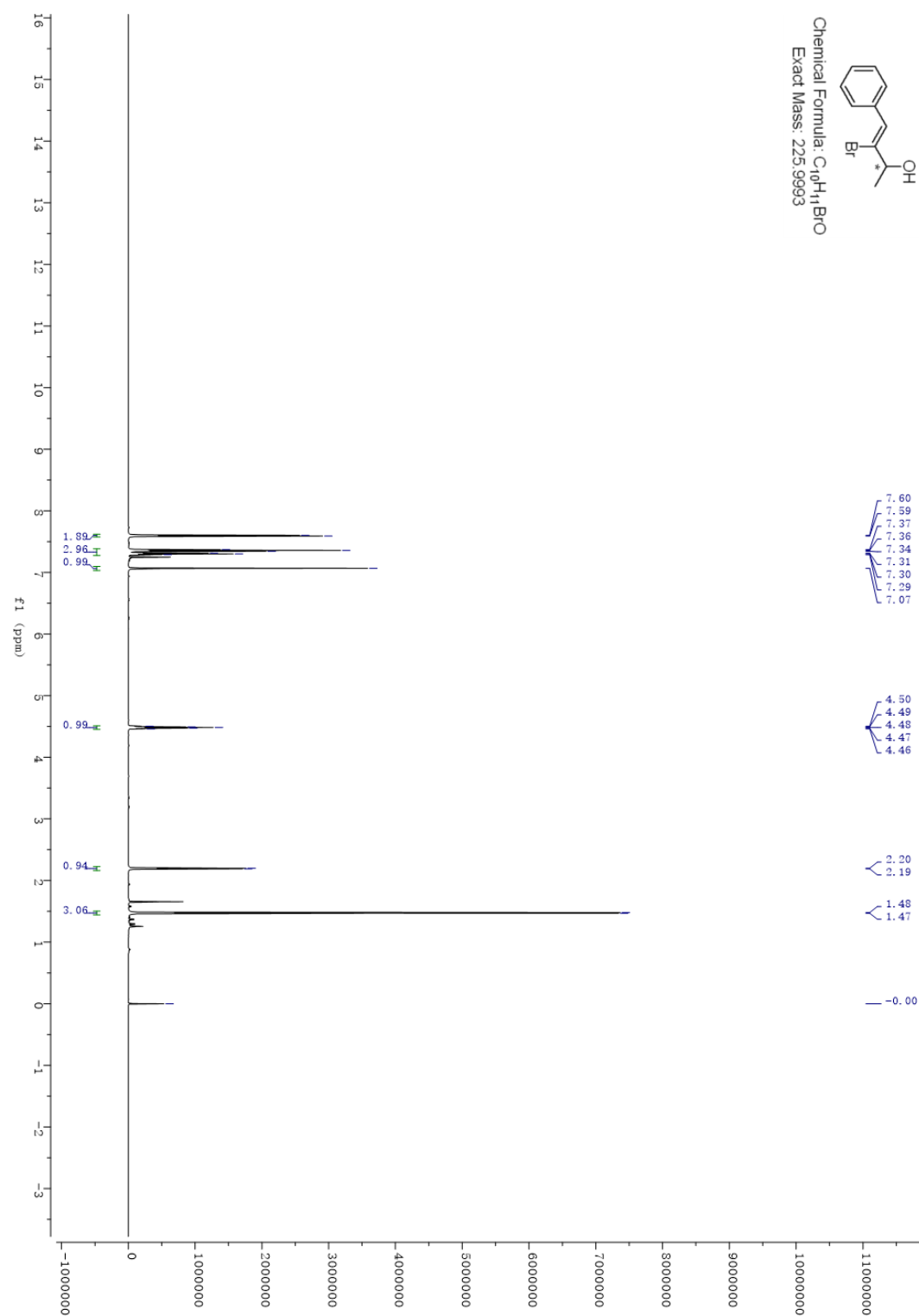
$^1\text{H}$  NMR (400 MHz, Methanol- $d_4$ ) of compound **4o**



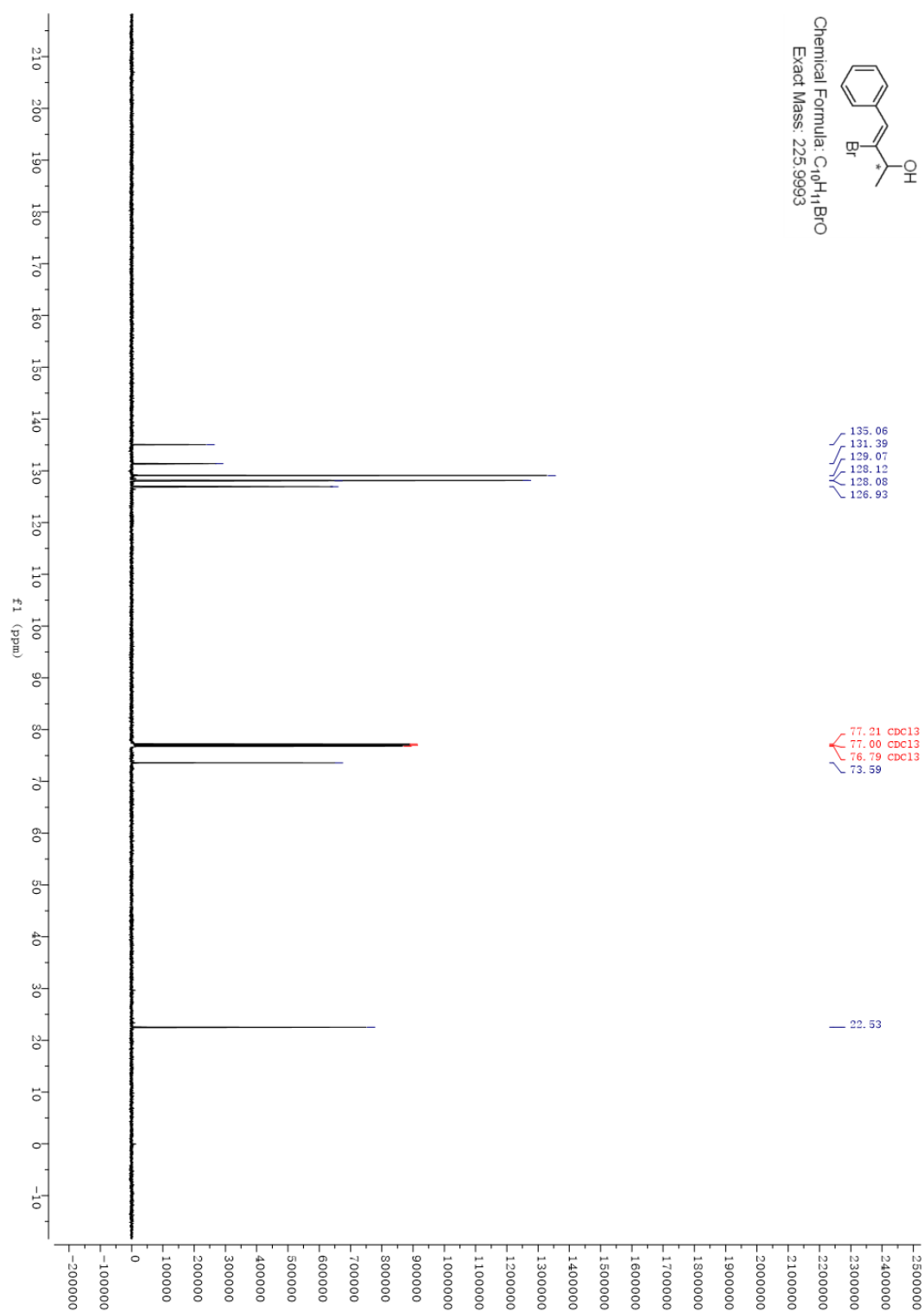
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Methanol- $d_4$ ) of compound **4o**



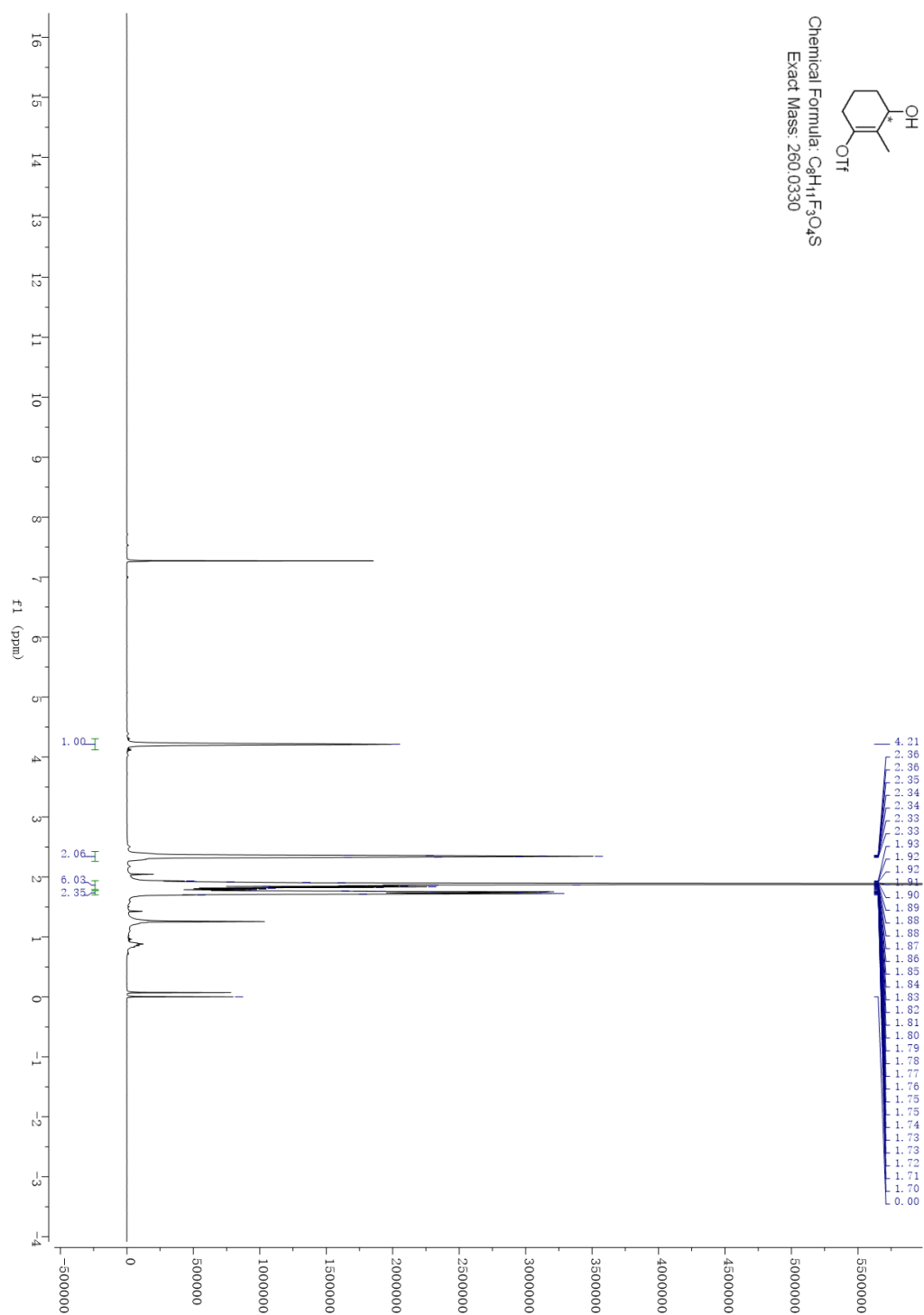
$^1\text{H}$  NMR (600 MHz, Chloroform- $d$ ) of compound **4p**



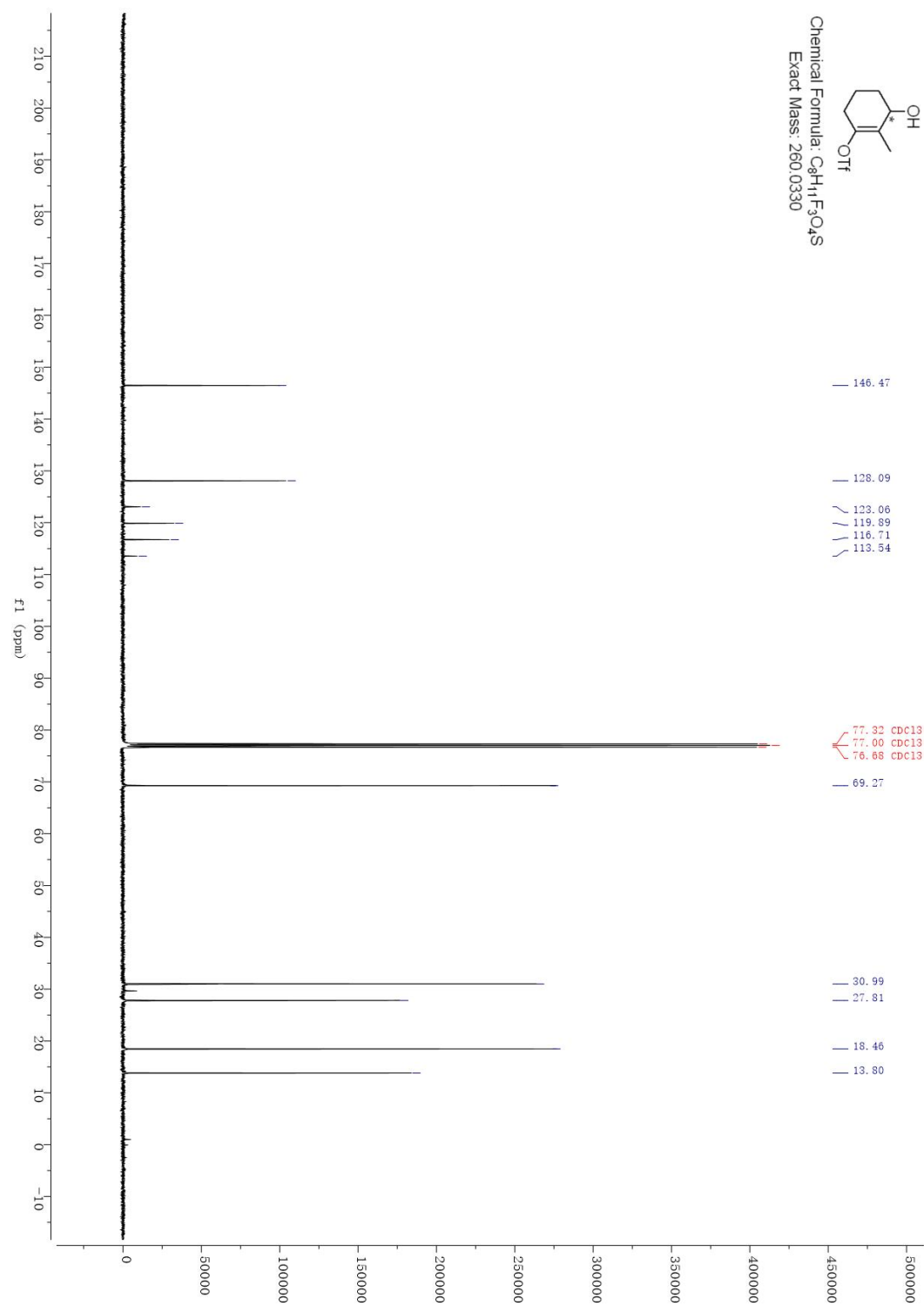
$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform- $d$ ) of compound **4p**



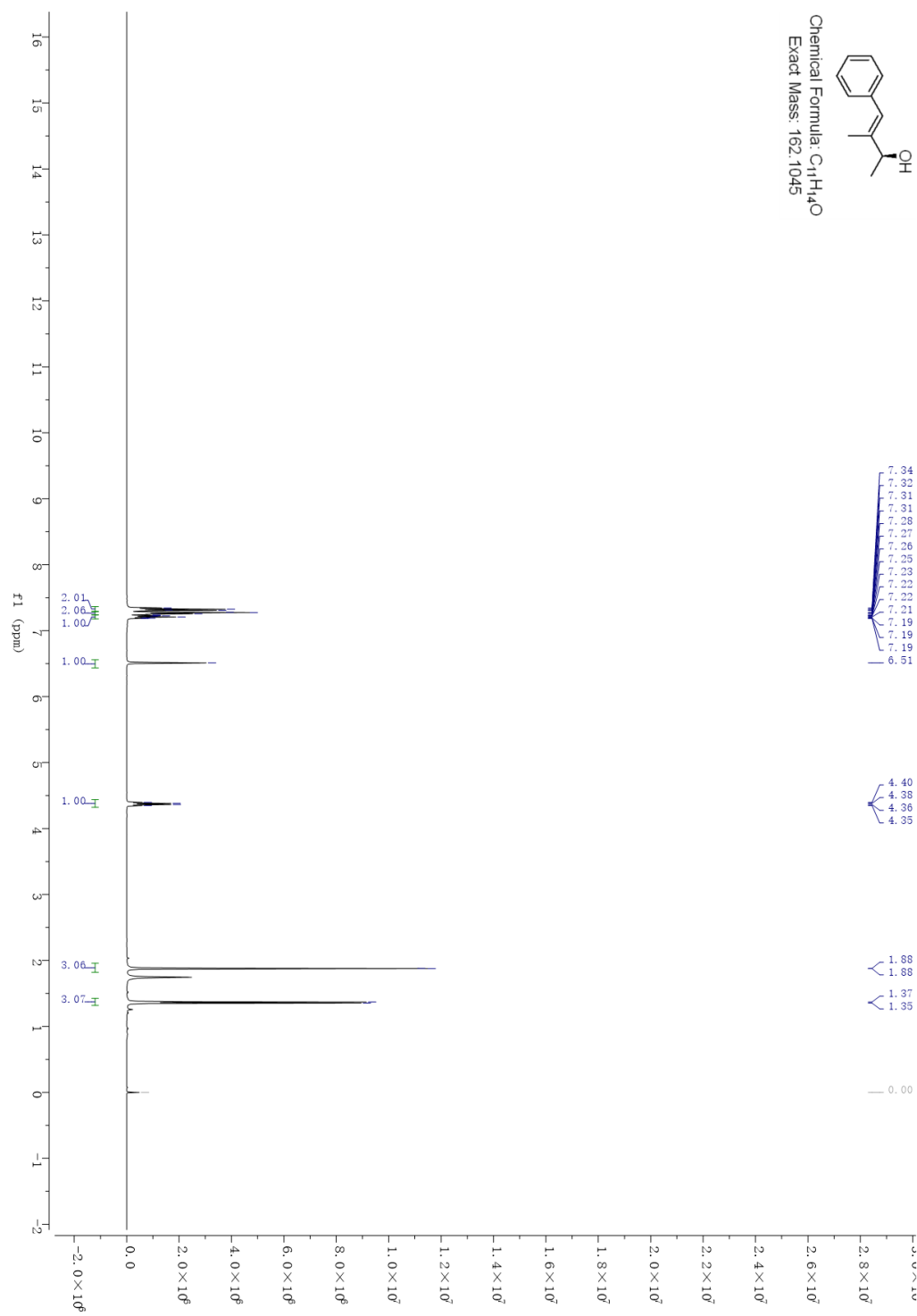
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **4q**



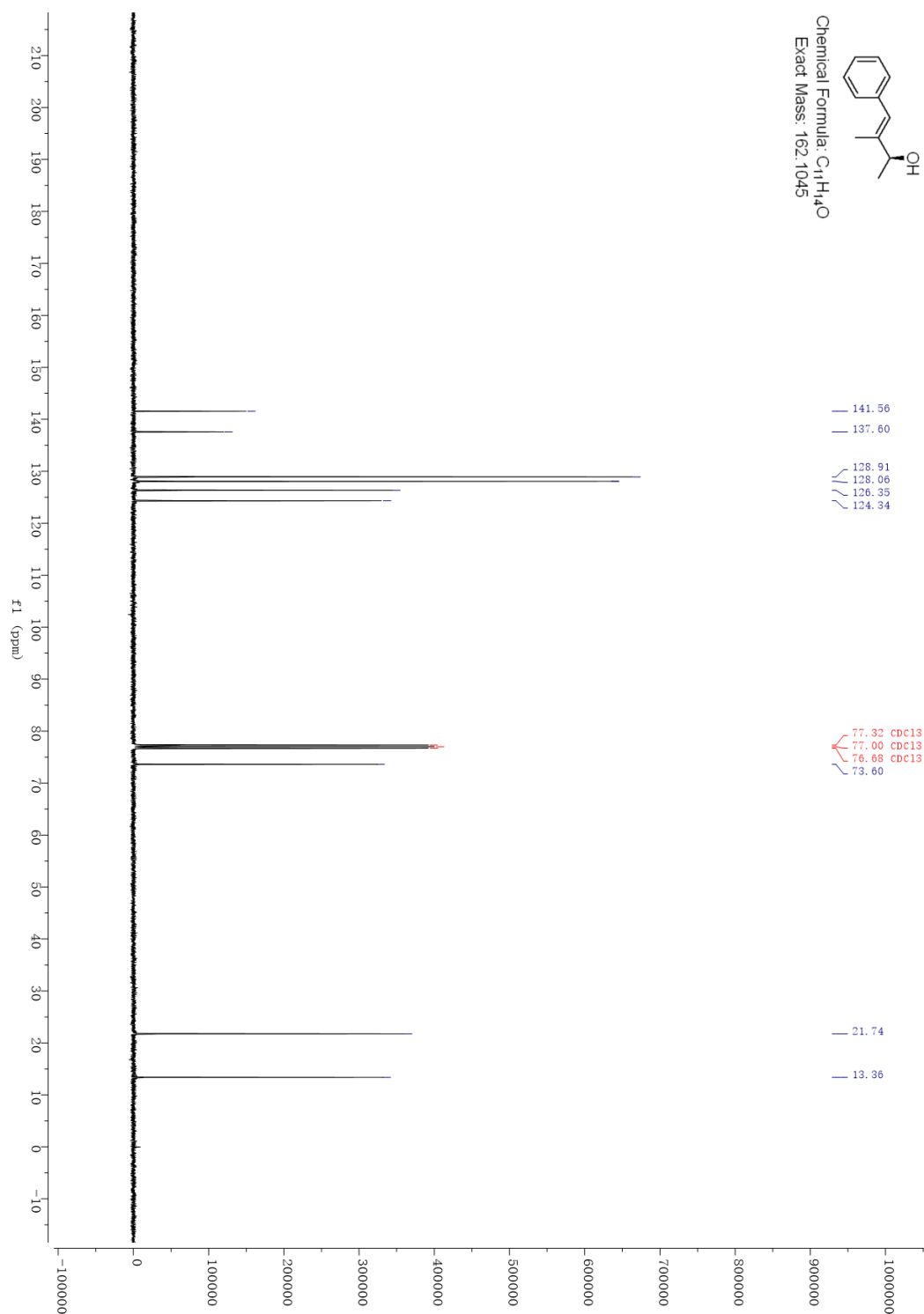
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **4q**



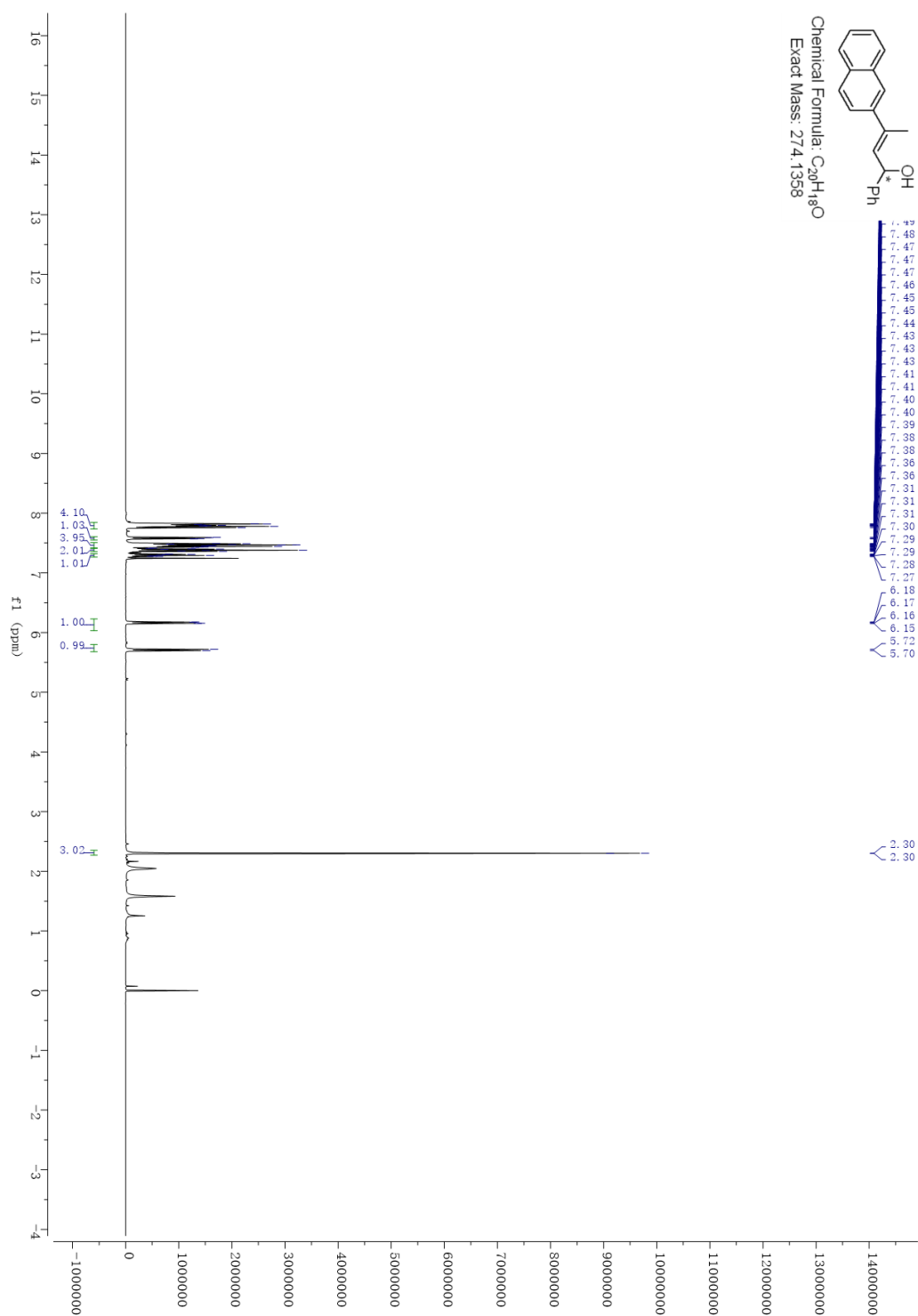
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **4r**



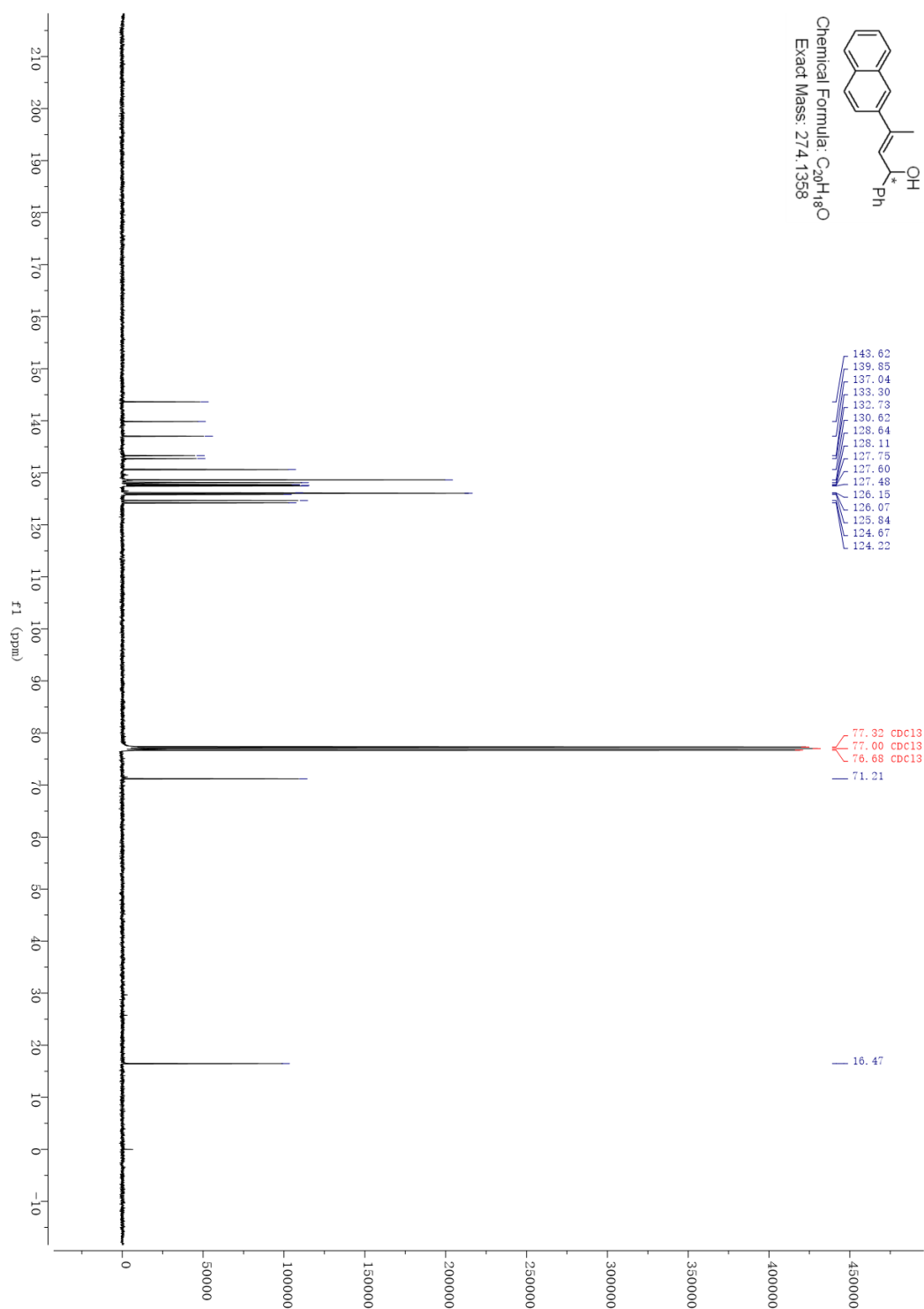
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **4r**



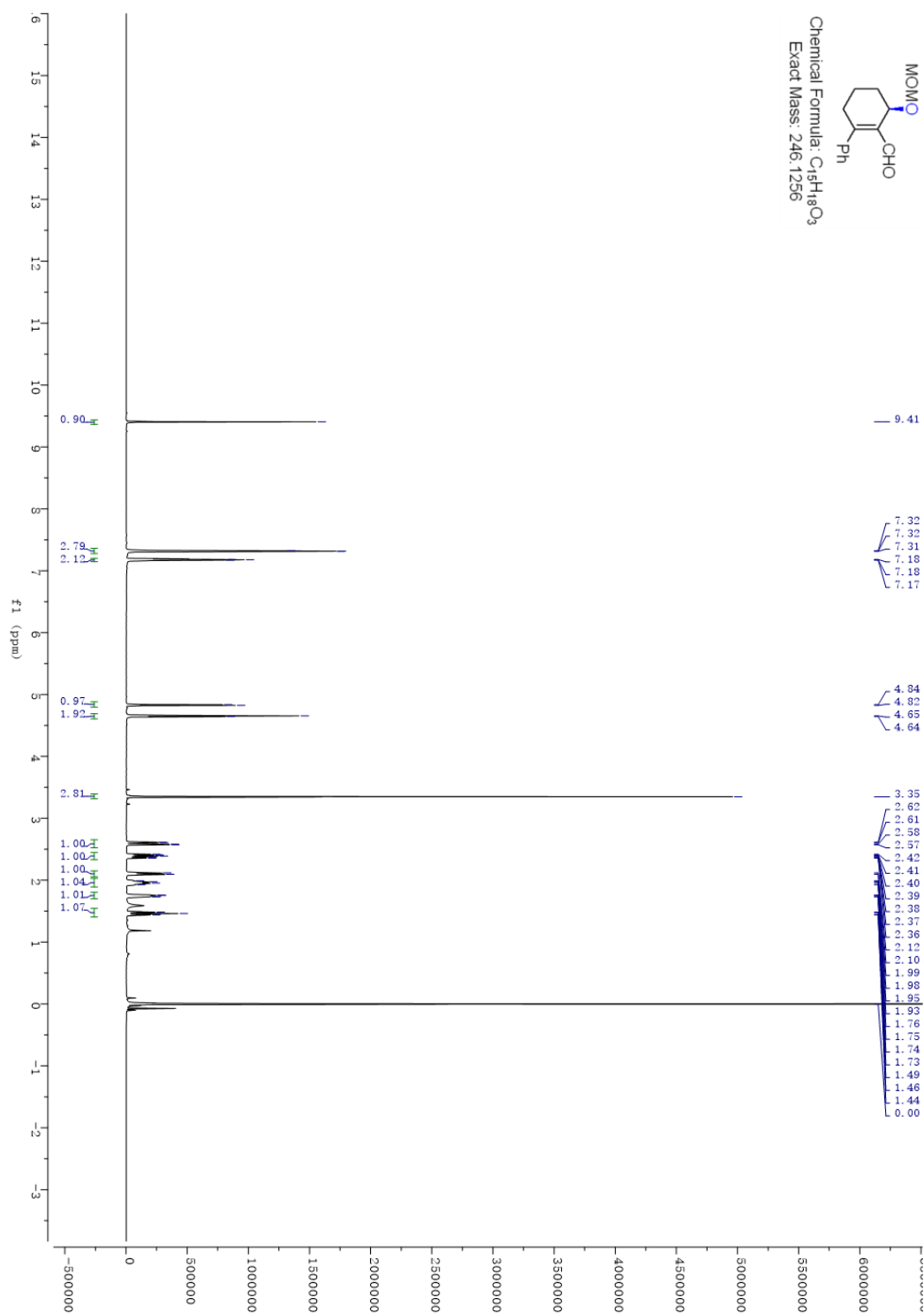
$^1\text{H}$  NMR (400 MHz, Chloroform-d) of compound **4s**



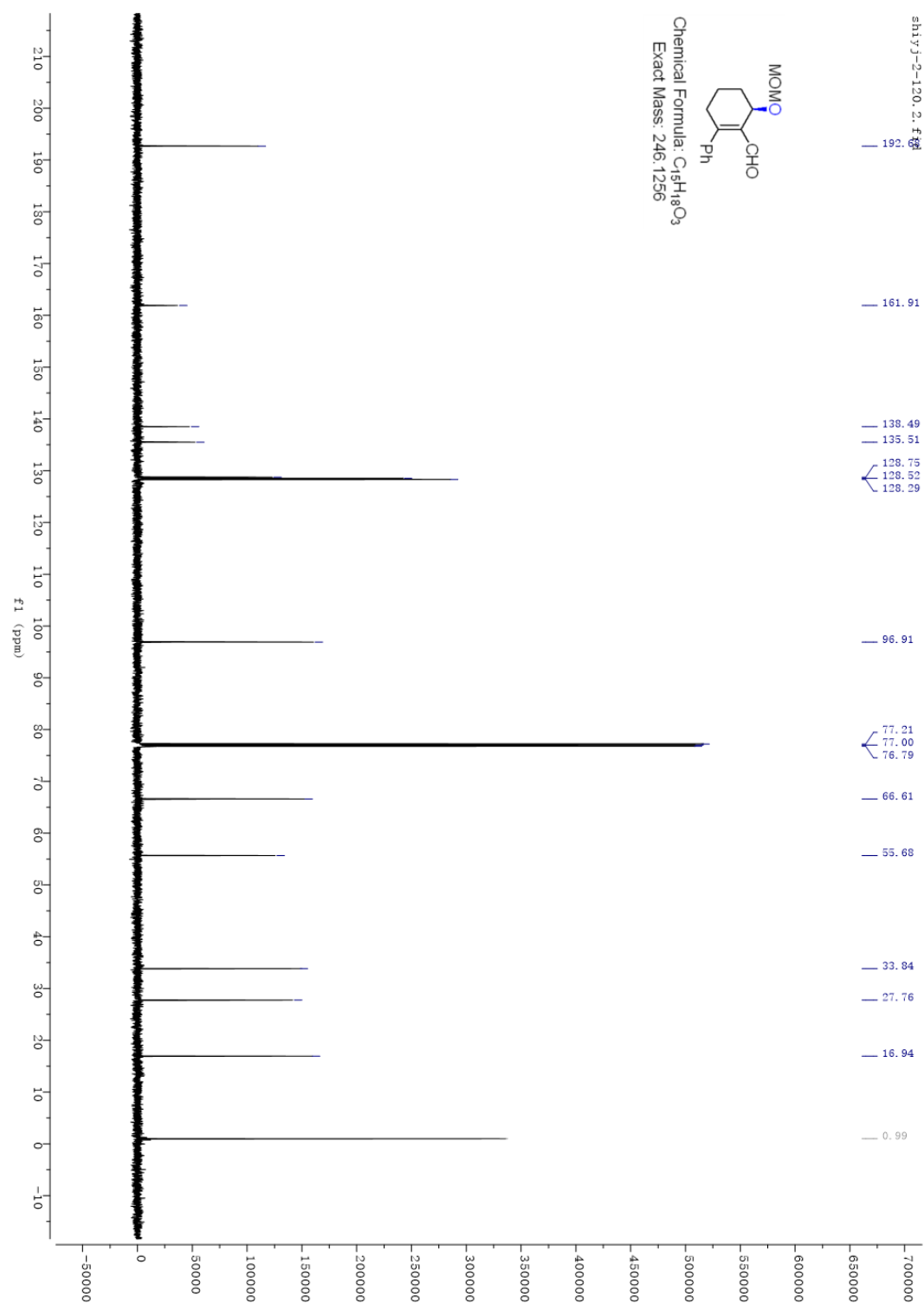
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-d) of compound **4s**



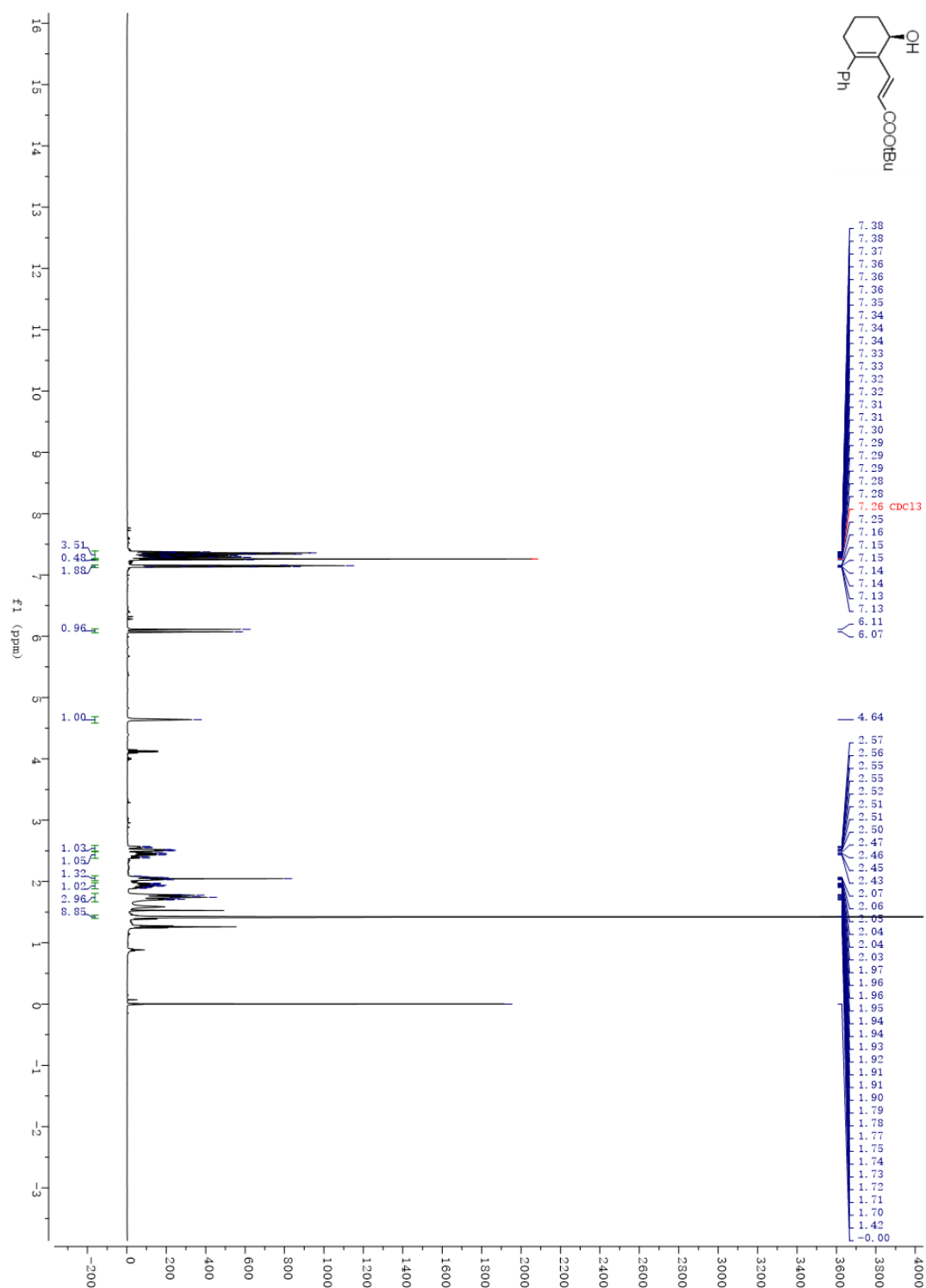
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **5**



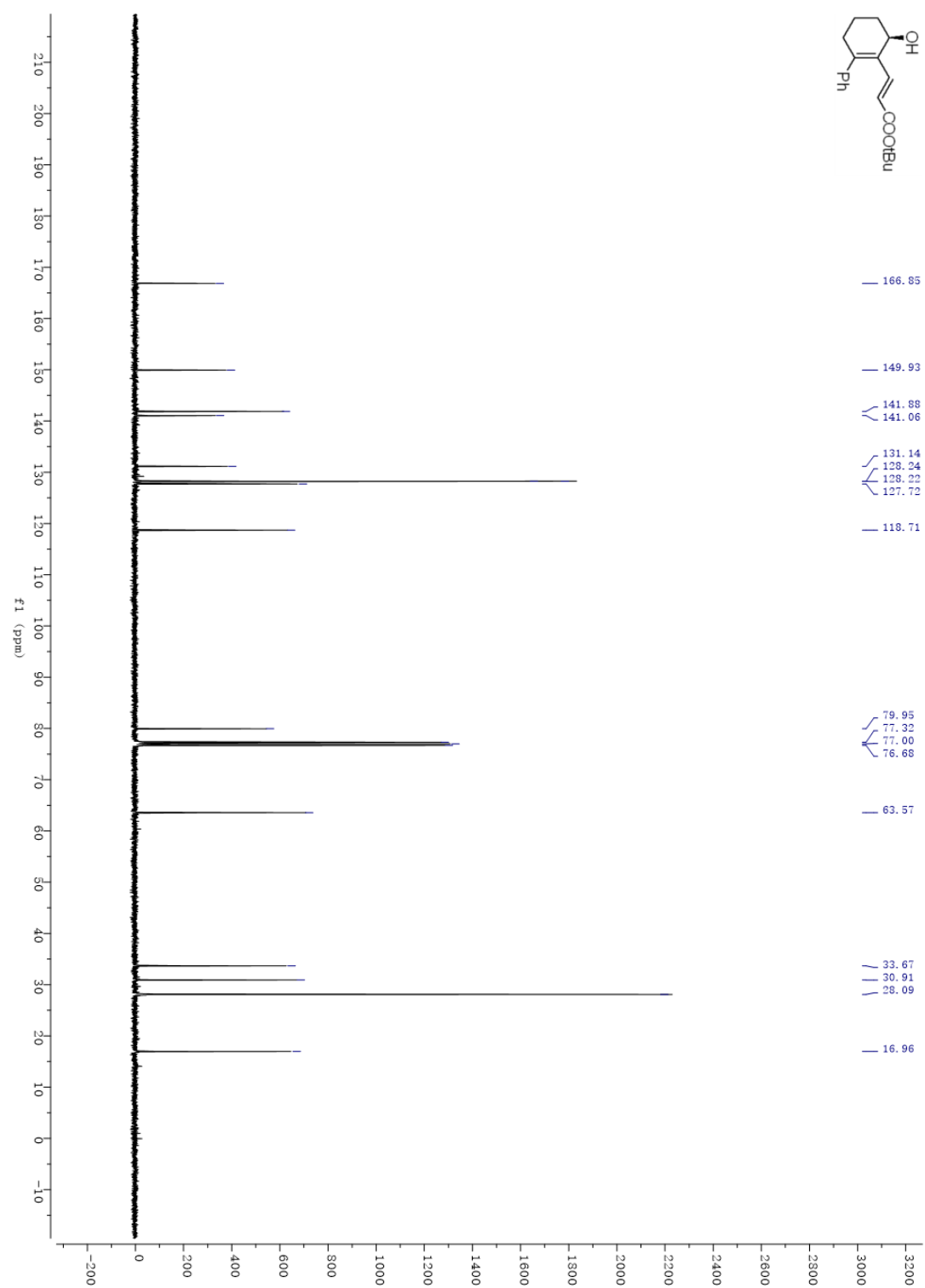
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of compound **5**



$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) of compound **6**

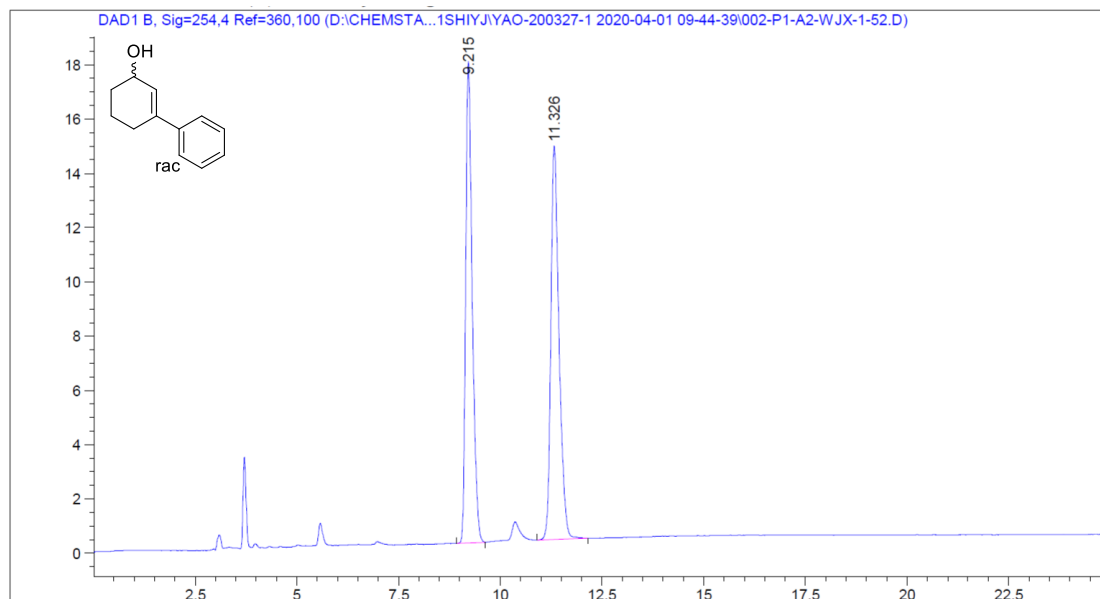


$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-d) of compound **6**



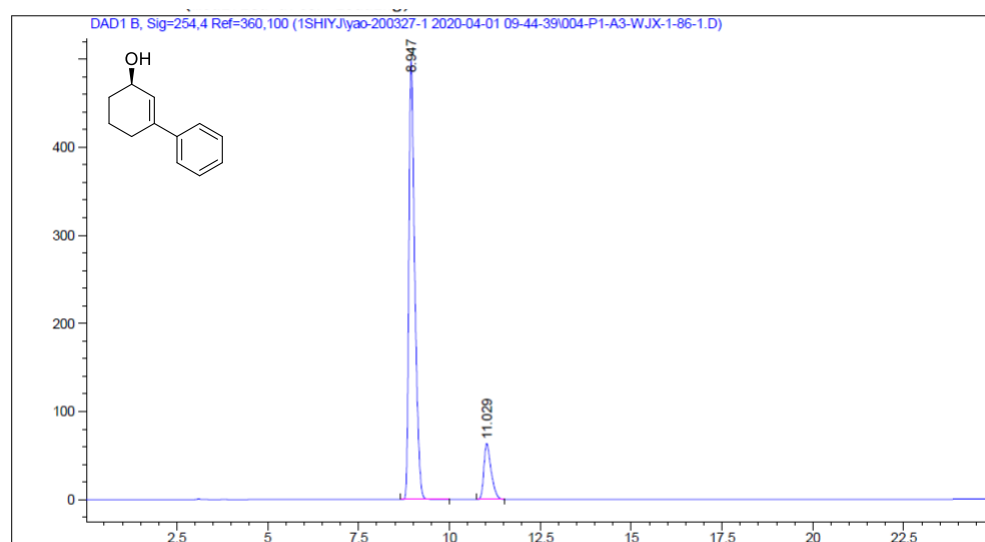
## VII. HPLC Chromatograms

### (*R*)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol (2a)



Signal 1: DAD1 B, Sig=254,4 Ref=360,100

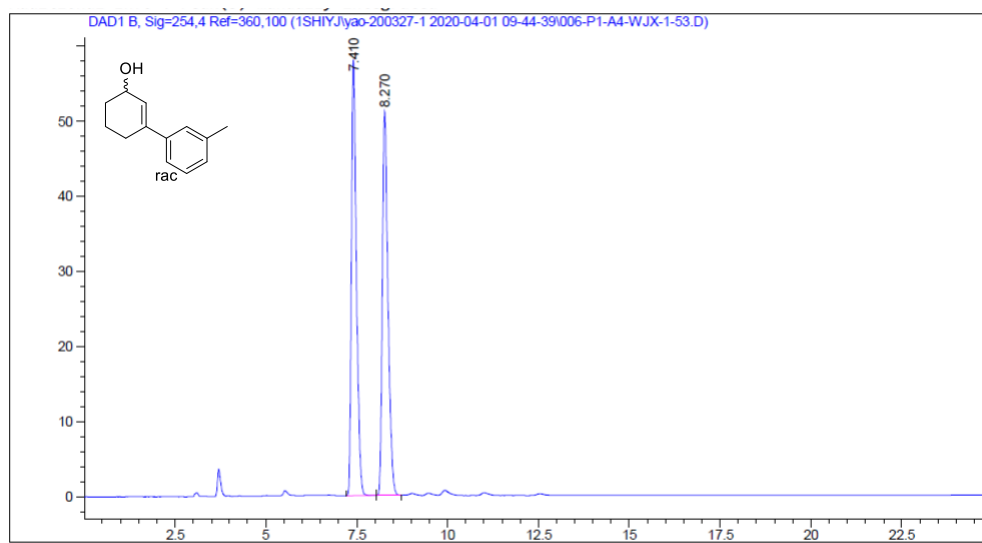
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.215	BB	0.1661	198.08331	17.76459	49.4165
2	11.326	BB	0.2092	202.76144	14.49681	50.5835



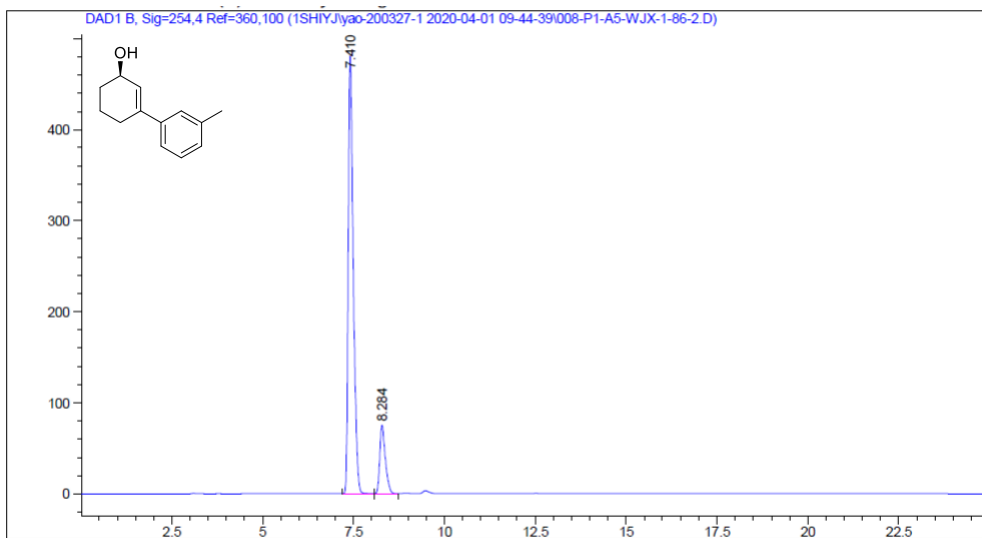
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.947	BB	0.1703	5640.93457	497.48322	86.6093
2	11.029	BB	0.2067	872.14569	63.32018	13.3907

**(R)-3'-methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol (2b)**

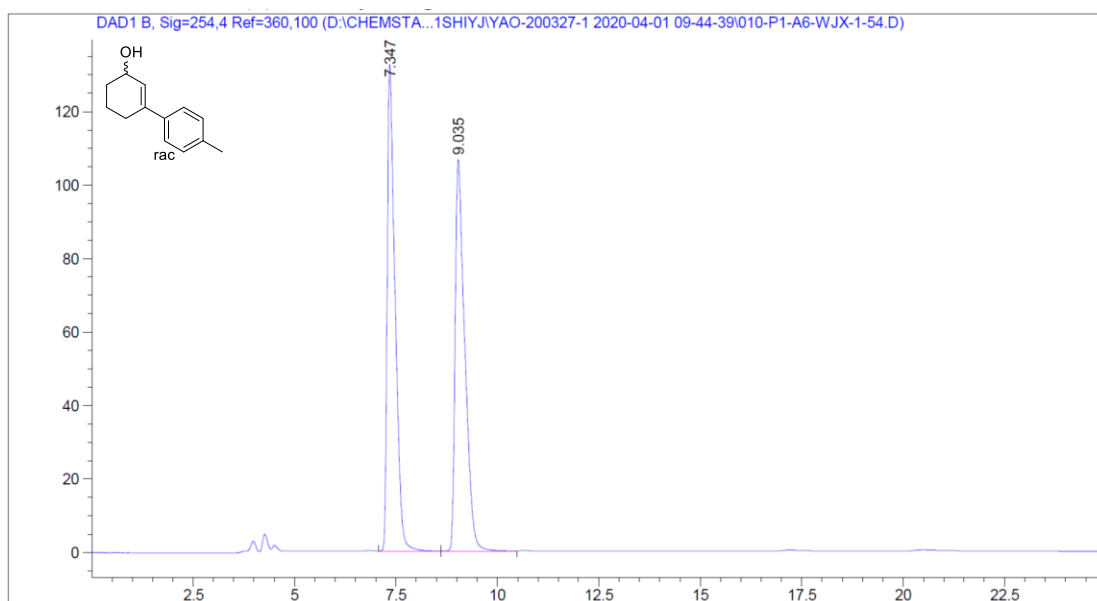


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.410	BB	0.1403	549.00989	58.08640	50.0517
2	8.270	BB	0.1590	547.87500	51.11688	49.9483



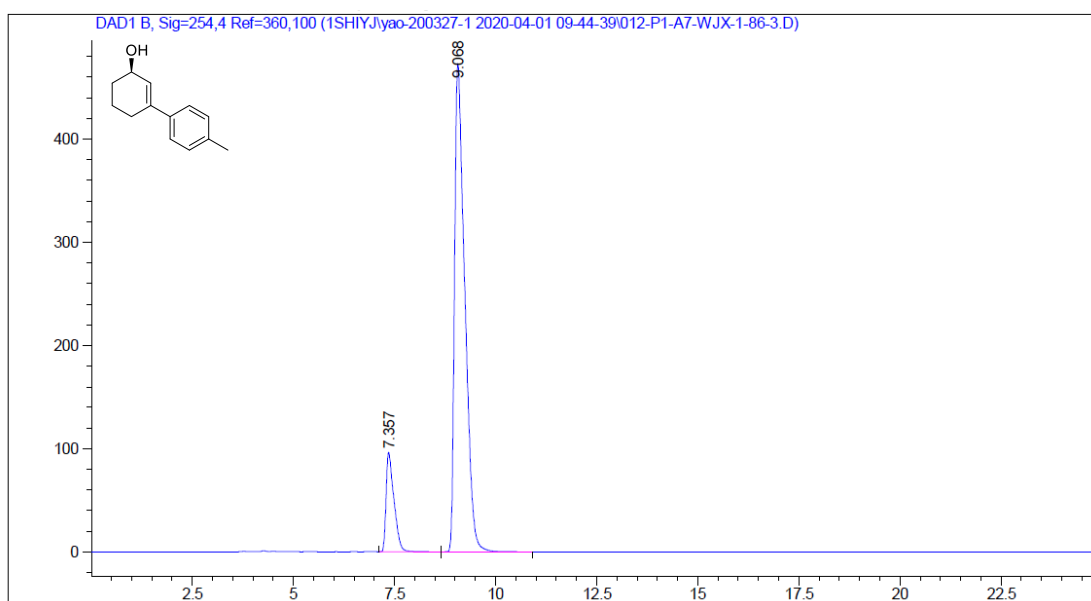
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.410	BB	0.1418	4608.12207	481.08047	85.2803
2	8.284	BB	0.1574	795.37720	75.22758	14.7197

**(R)-4'-methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol (2c)**



Signal 1: DAD1 B, Sig=254,4 Ref=360,100

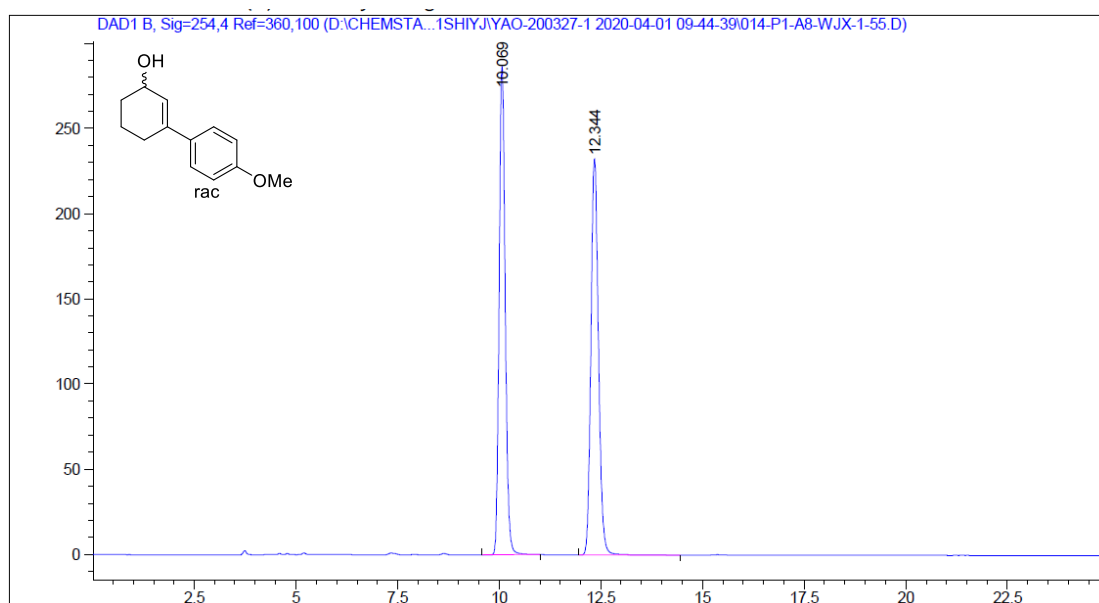
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.347	BB	0.1914	1765.56946	132.52914	50.0557
2	9.035	BB	0.2369	1761.64160	106.53366	49.9443



Signal 1: DAD1 B, Sig=254,4 Ref=360,100

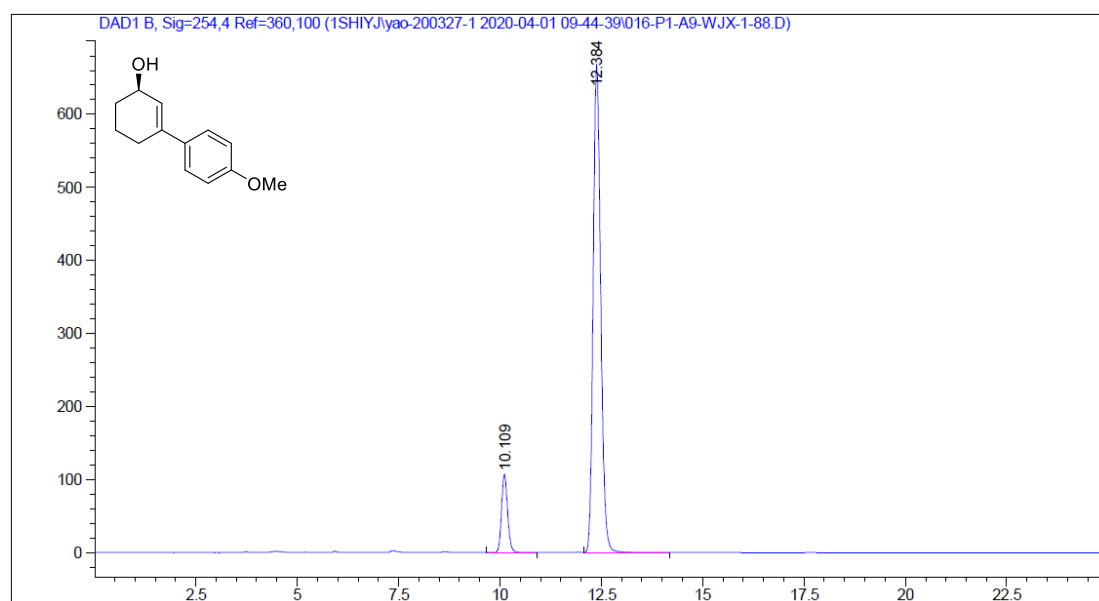
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.357	BB	0.1941	1303.72925	96.19120	13.5278
2	9.068	BB	0.2560	8333.69727	472.06473	86.4722

**(R)-4'-methoxy-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol (2d)**



Signal 1: DAD1 B, Sig=254,4 Ref=360,100

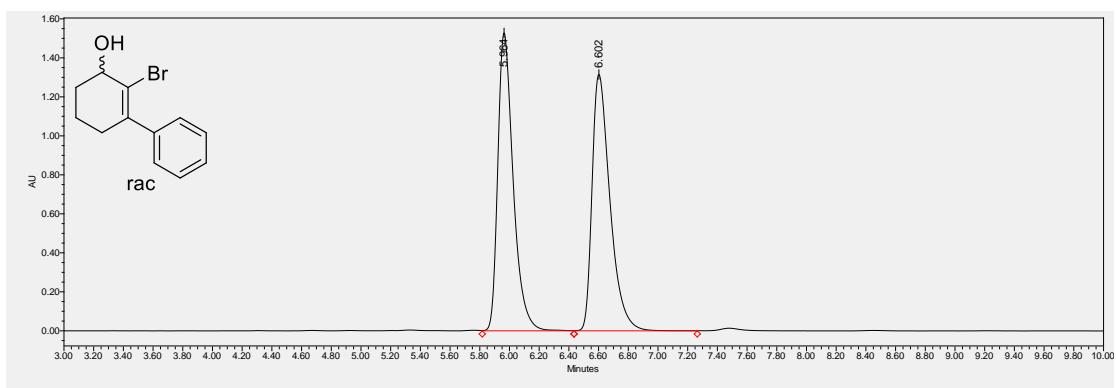
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.069	BB	0.1611	2983.14819	287.33865	49.8389
2	12.344	BB	0.1985	3002.43140	232.67932	50.1611



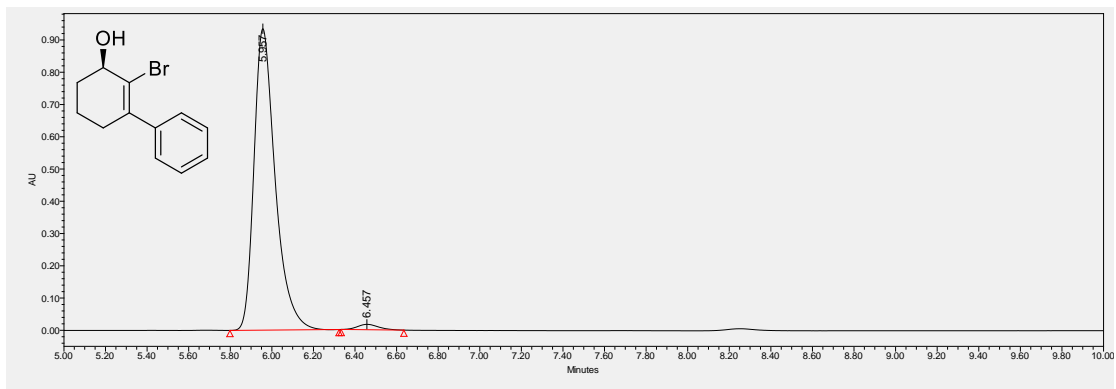
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.109	BB	0.1601	1119.66943	106.95674	11.4555
2	12.384	BB	0.1992	8654.39746	667.62903	88.5445

**(R)-2-bromo-5,6-dihydro-[1,1'-biphenyl]-3(4H)-ol (4a)**

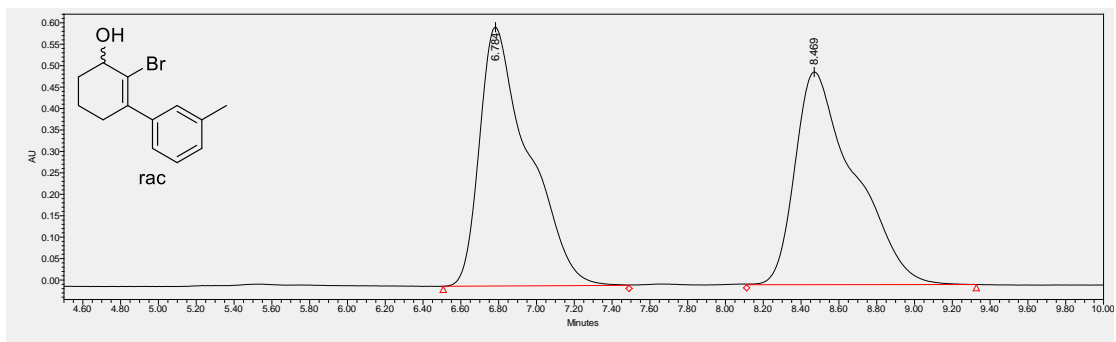


	Channel Description	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	2998 Ch1 254nm@1.2nm	5.964	10988571	49.94	1528144
2	2998 Ch1 254nm@1.2nm	6.602	11016654	50.06	1315341

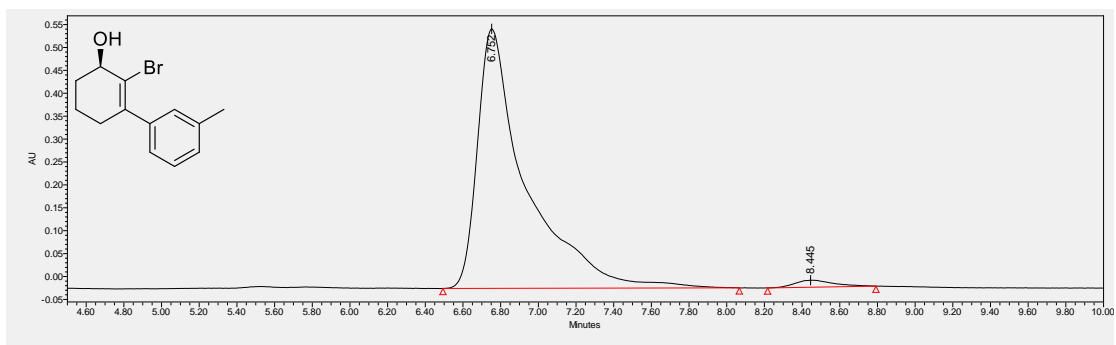


	Channel Description	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	2998 Ch1 254nm@1.2nm	5.957	6627766	98.25	934334
2	2998 Ch1 254nm@1.2nm	6.457	118375	1.75	16661

**(R)-2-bromo-3'-methyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-ol (4b)**

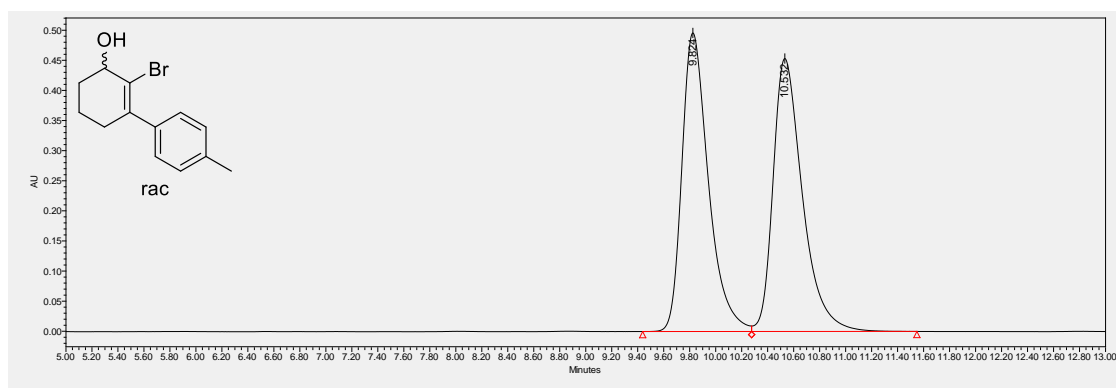


	Channel Description	RT (min)	Area ( $\mu\text{V}\cdot\text{sec}$ )	% Area	Height ( $\mu\text{V}$ )
1	2998 Ch1 254nm@1.2nm	6.784	1846763	49.63	103283
2	2998 Ch1 254nm@1.2nm	8.471	1874026	50.37	85373

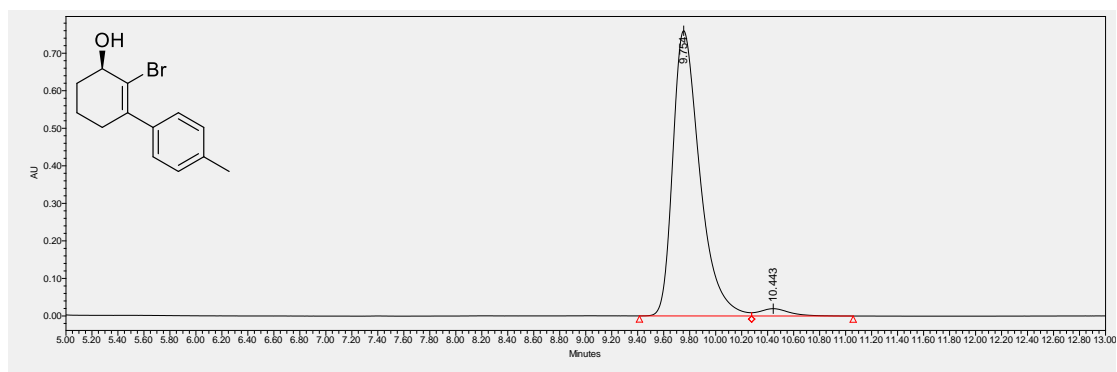


	Channel Description	RT (min)	Area ( $\mu\text{V}\cdot\text{sec}$ )	% Area	Height ( $\mu\text{V}$ )
1	2998 Ch2 210nm@1.2nm	6.752	10147099	97.87	566541
2	2998 Ch2 210nm@1.2nm	8.445	220576	2.13	15357

**(R)-2-bromo-4'-methyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-ol (4c)**

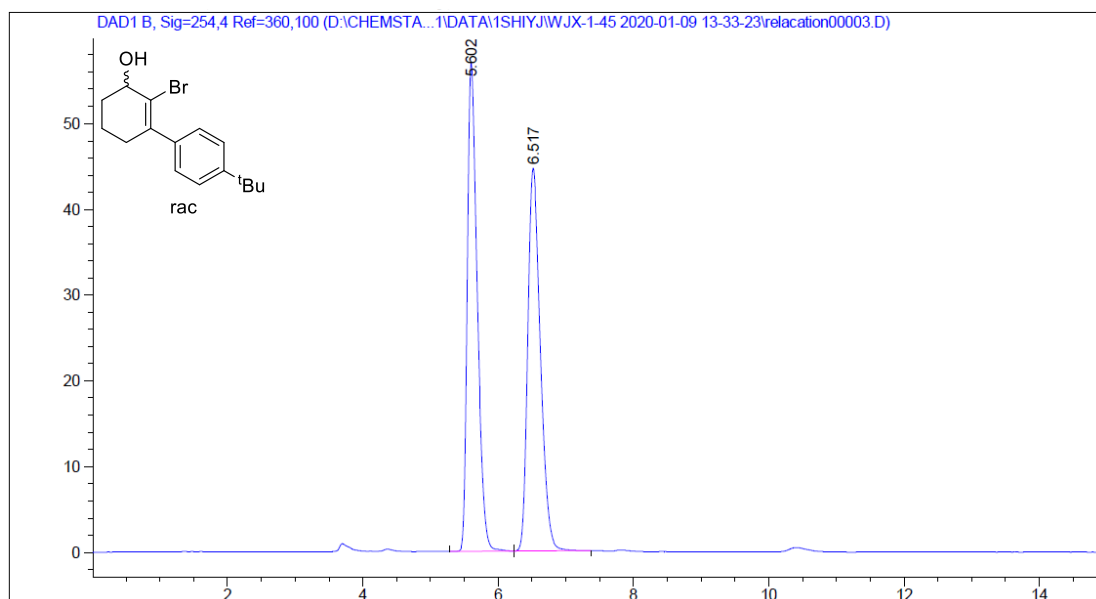


	Channel Description	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	2998 Ch1 254nm@1.2nm	9.824	7032804	49.71	495891
2	2998 Ch1 254nm@1.2nm	10.532	7116104	50.29	453344



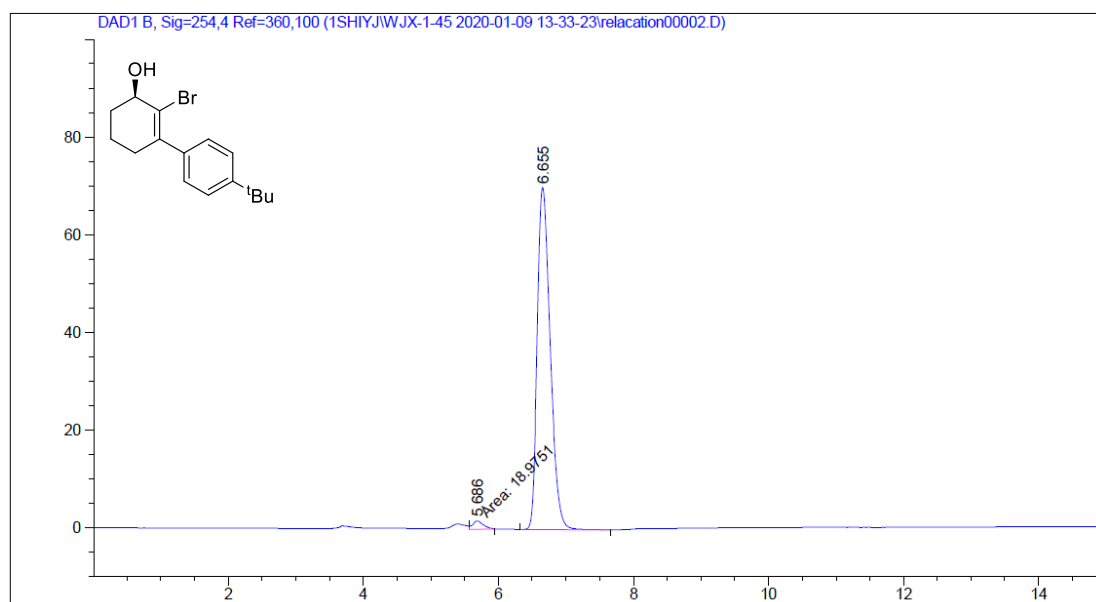
	Channel Description	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	2998 Ch2 254nm@1.2nm	9.754	10948459	97.22	759615
2	2998 Ch2 254nm@1.2nm	10.443	313592	2.78	19486

**(R)-2-bromo-4'-(tert-butyl)-5,6-dihydro-[1,1'-biphenyl]-3(4H)-ol (4d)**



Signal 1: DAD1 B, Sig=254,4 Ref=360,100

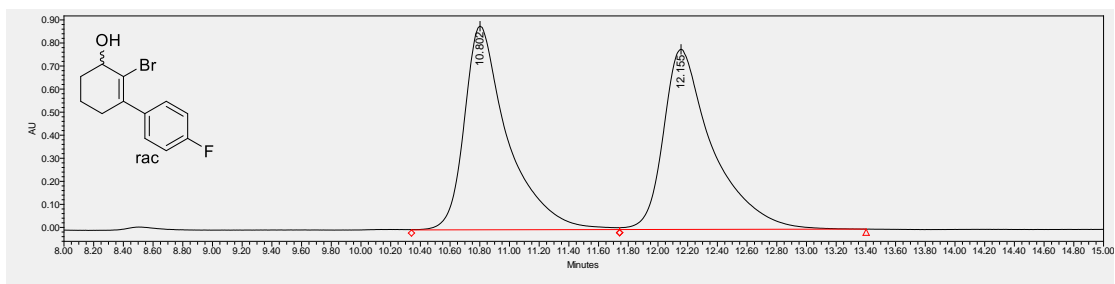
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.602	BB	0.1513	572.63300	56.95068	49.7735
2	6.517	BB	0.1991	577.84540	44.62836	50.2265



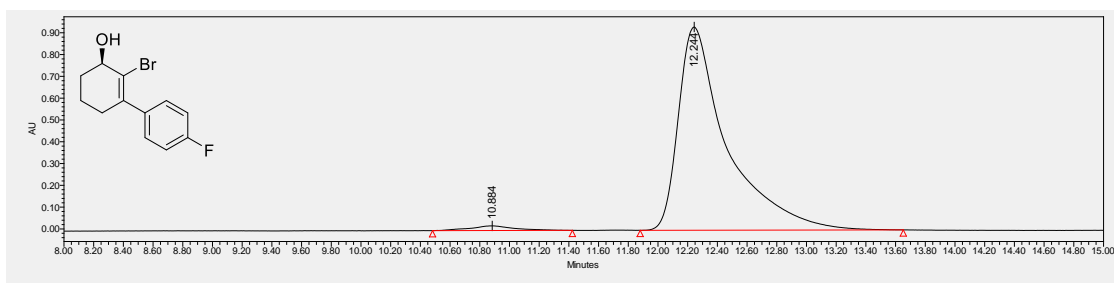
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.686	MM	0.1865	18.97507	1.69528	2.0018
2	6.655	BB	0.2046	928.92151	70.09771	97.9982

**(R)-2-bromo-4'-fluoro-5,6-dihydro-[1,1'-biphenyl]-3(4H)-ol (4e)**

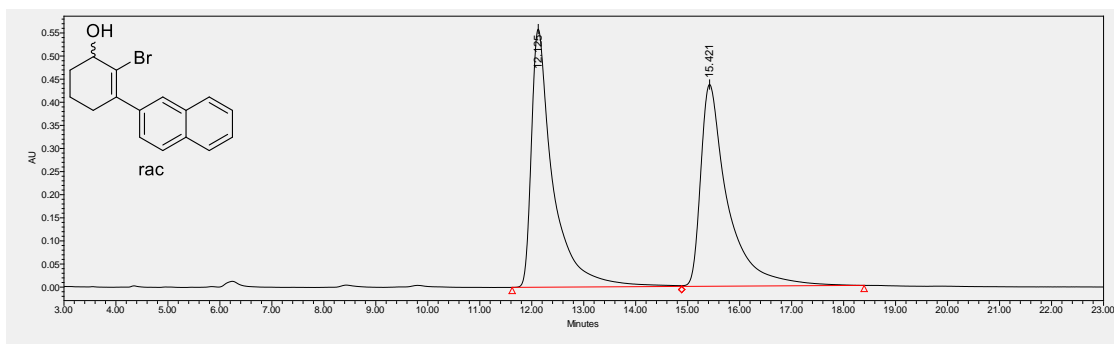


	Channel Description	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	2998 Ch2 210nm@1.2nm	10.802	17942494	50.05	882950
2	2998 Ch2 210nm@1.2nm	12.155	17909499	49.95	781090

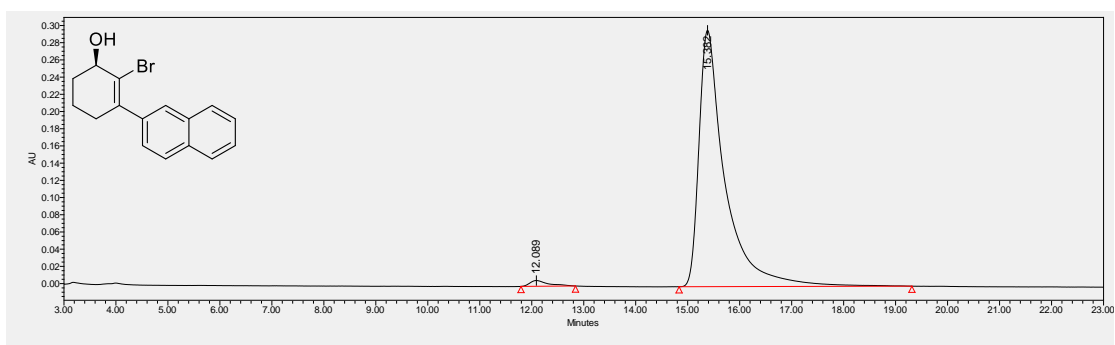


	Channel Description	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	2998 Ch2 210nm@1.2nm	10.884	444869	2.05	21315
2	2998 Ch2 210nm@1.2nm	12.244	21220791	97.95	932412

**(R)-2-bromo-3-(naphthalen-2-yl)-cyclohex-2-en-1-ol (4f)**

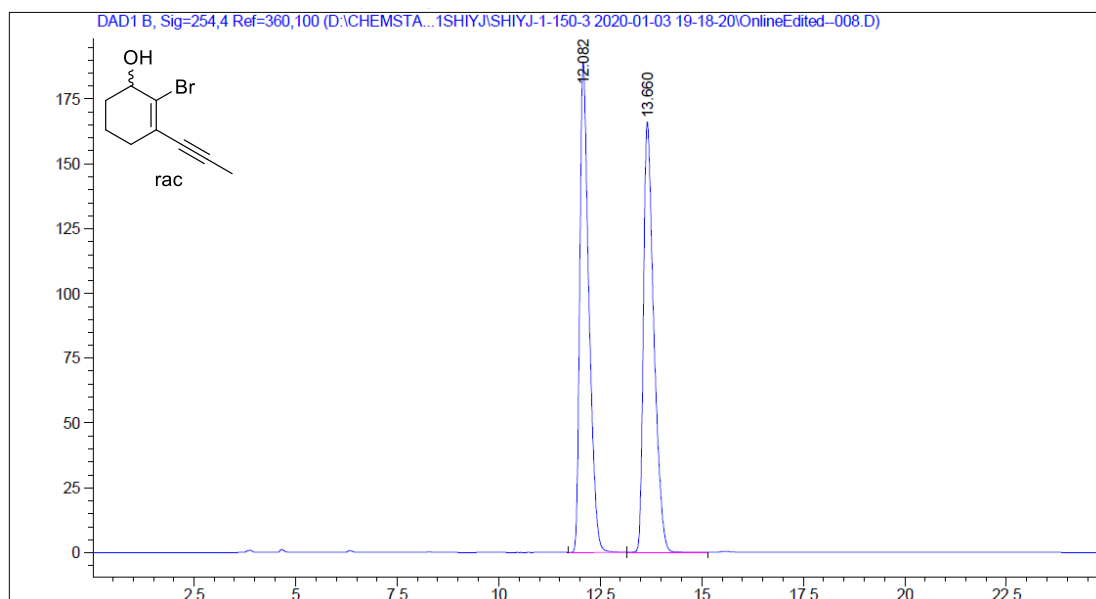


	Channel Description	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	2998 Ch1 254nm@1.2nm	12.125	16127855	50.67	558484
2	2998 Ch1 254nm@1.2nm	15.421	15704295	49.33	436639



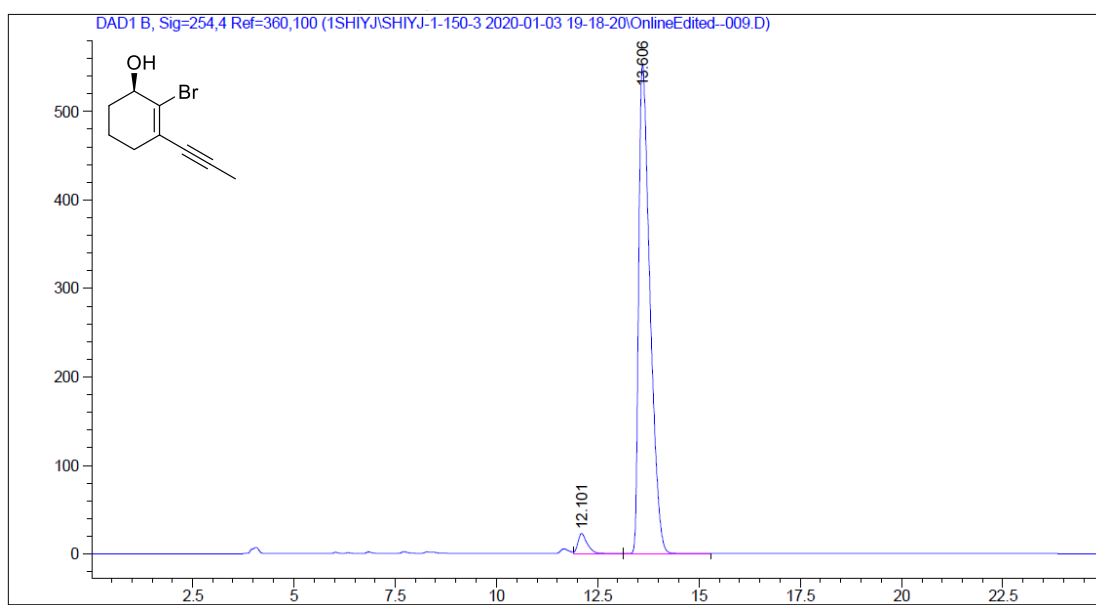
	Channel Description	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	2998 Ch1 254nm@1.2nm	12.089	164835	1.56	6686
2	2998 Ch1 254nm@1.2nm	15.382	10384980	98.44	298021

**(R)-2-bromo-3-(prop-1-yn-1-yl)cyclohex-2-en-1-ol (4g)**



Signal 1: DAD1 B, Sig=254,4 Ref=360,100

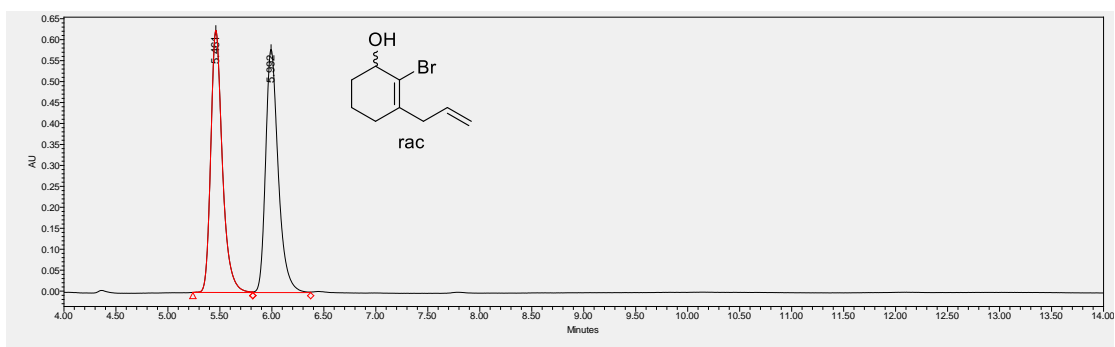
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.082	BB	0.2333	2968.27783	188.93820	50.0429
2	13.660	BB	0.2662	2963.18457	166.02328	49.9571



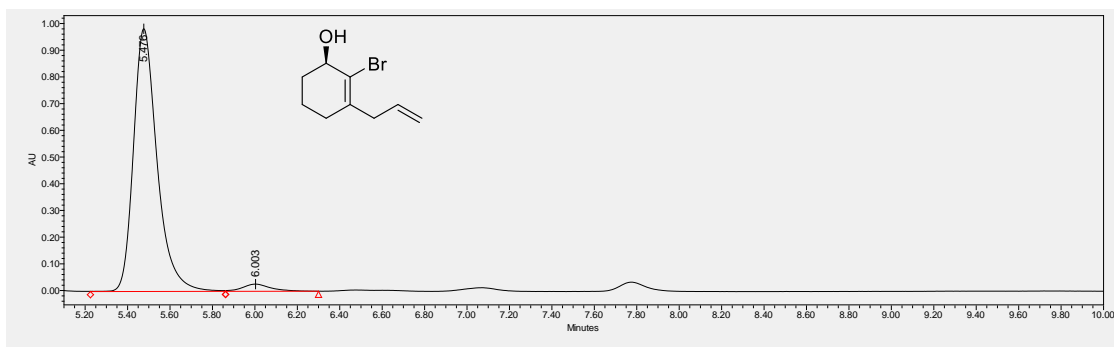
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.101	VB	0.2352	366.05594	22.81298	3.3028
2	13.606	BB	0.2943	1.07170e4	552.61218	96.6972

**(R)-3-allyl-2-bromocyclohex-2-en-1-ol (4h)**

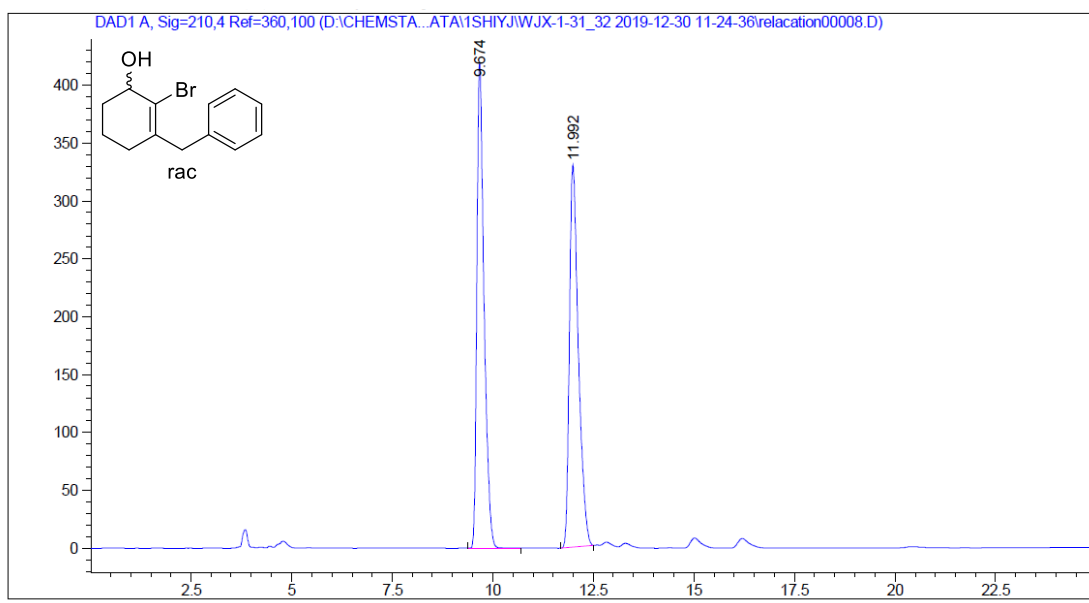


	Channel Description	RT (min)	Area (μV*sec)	%Area	Height (μV)
1	2998 Ch3 220nm@1.2nm	5.461	4854603	49.77	625460
2	2998 Ch3 220nm@1.2nm	5.992	4899800	50.23	580255



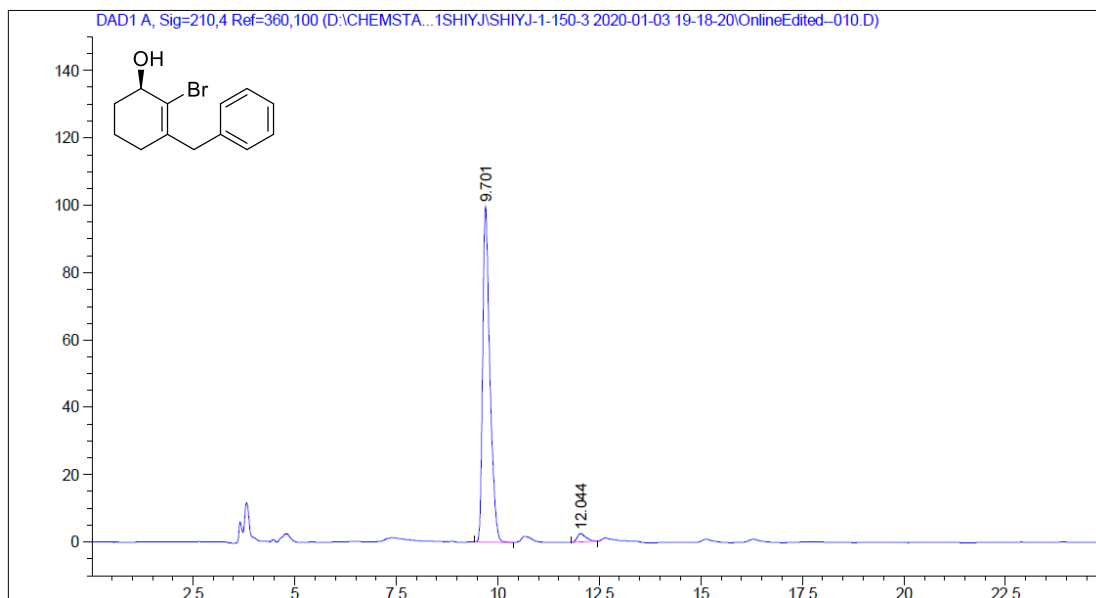
	Channel Description	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	2998 Ch3 220nm@1.2nm	5.476	7563104	97.38	982422
2	2998 Ch3 220nm@1.2nm	6.003	203649	2.62	24952

**(R)-3-benzyl-2-bromocyclohex-2-en-1-ol (4i)**



Signal 1: DAD1 A, Sig=210,4 Ref=360,100

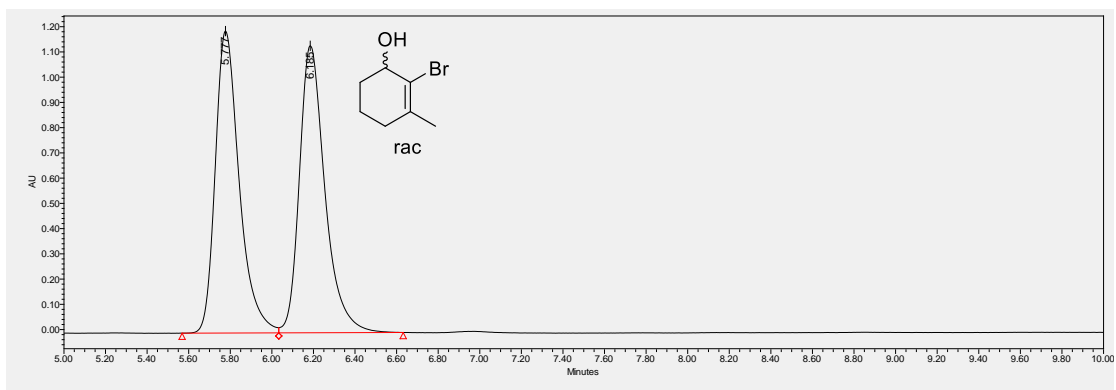
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.674	BB	0.1824	5186.69531	419.05200	50.3619
2	11.992	BB	0.2304	5112.15625	330.56192	49.6381



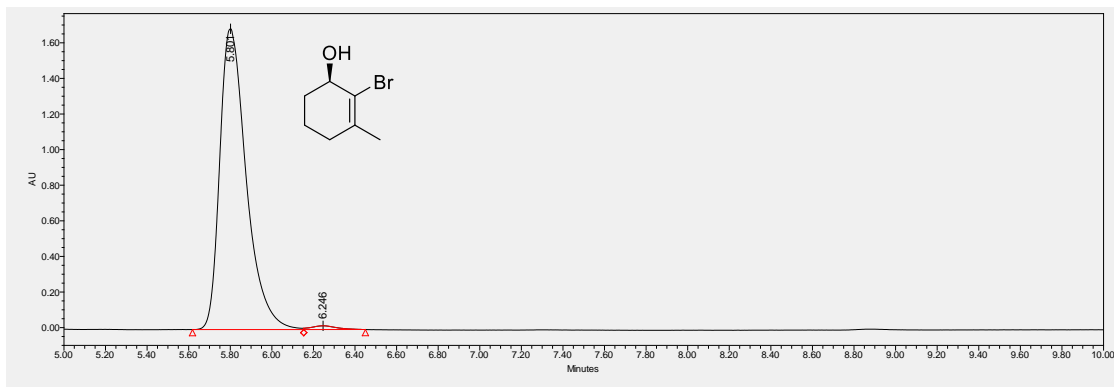
Signal 1: DAD1 A, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.701	BB	0.1815	1226.41772	99.73952	97.0175
2	12.044	BB	0.2268	37.70187	2.48796	2.9825

**(R)-2-bromo-3-methylcyclohex-2-en-1-ol (4j)**

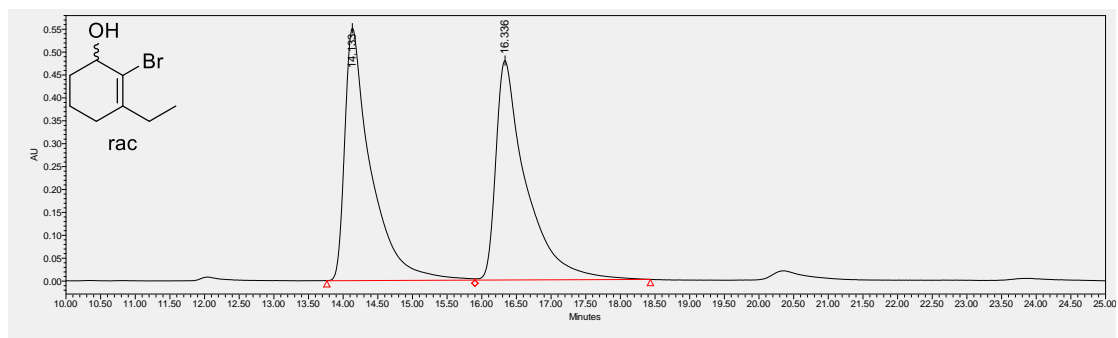


	Channel Description	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	2998 Ch2 210nm@1.2nm	5.777	9558936	49.81	1195564
2	2998 Ch2 210nm@1.2nm	6.185	9633053	50.19	1135230

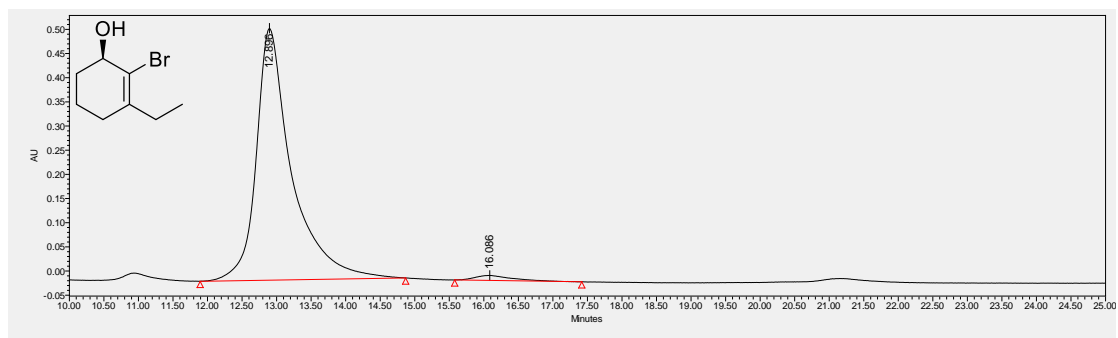


	Channel Description	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	2998 Ch2 210nm@1.2nm	5.801	14954088	98.85	1689489
2	2998 Ch2 210nm@1.2nm	6.246	174244	1.15	20781

**(R)-2-bromo-3-ethylcyclohex-2-en-1-ol (4k)**

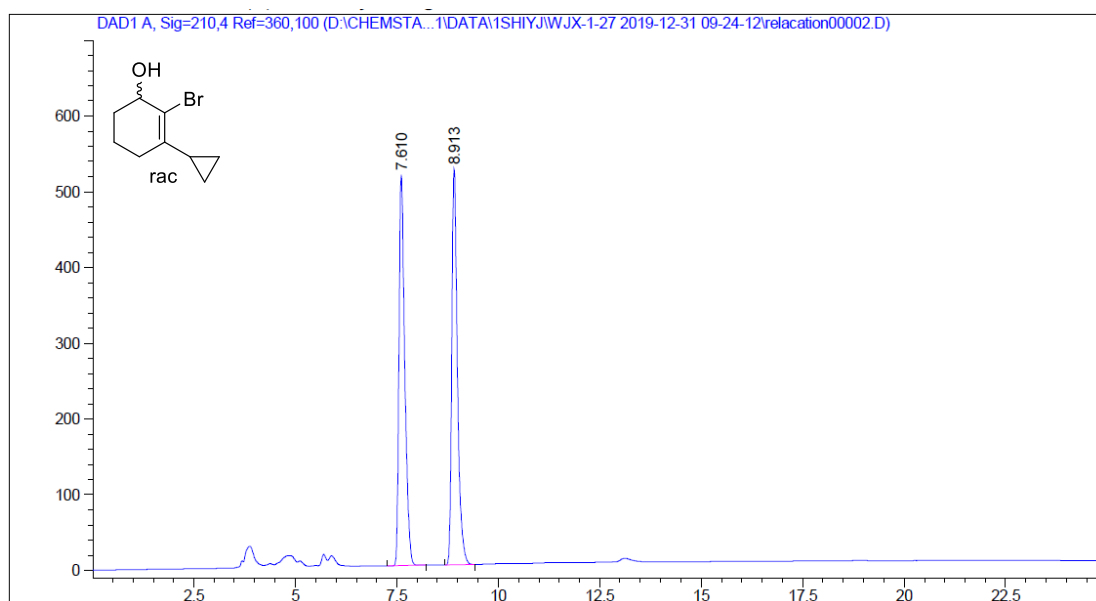


	Channel Description	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	2998 Ch2 210nm@1.2nm	2.913	105933	0.36	10550
2	2998 Ch2 210nm@1.2nm	14.133	14455917	49.75	551082
3	2998 Ch2 210nm@1.2nm	16.336	14494320	49.88	479192



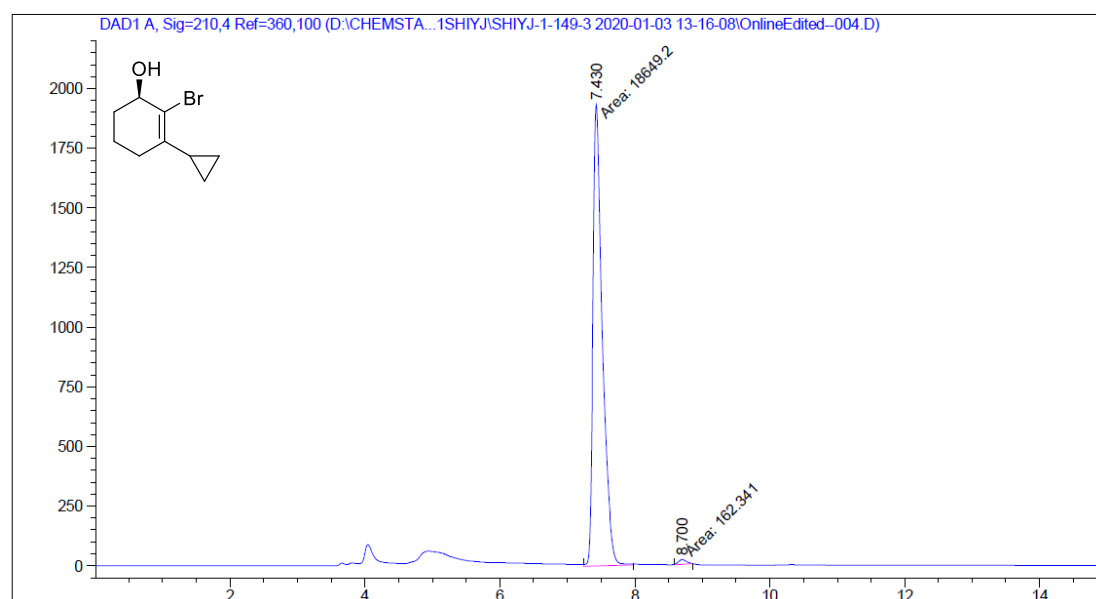
	Channel Description	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	2998 Ch2 210nm@1.2nm	12.896	18583036	98.57	521210
2	2998 Ch2 210nm@1.2nm	16.086	269082	1.43	9270

**(R)-2-bromo-3-cyclopropylcyclohex-2-en-1-ol (4l)**



Signal 1: DAD1 A, Sig=210,4 Ref=360,100

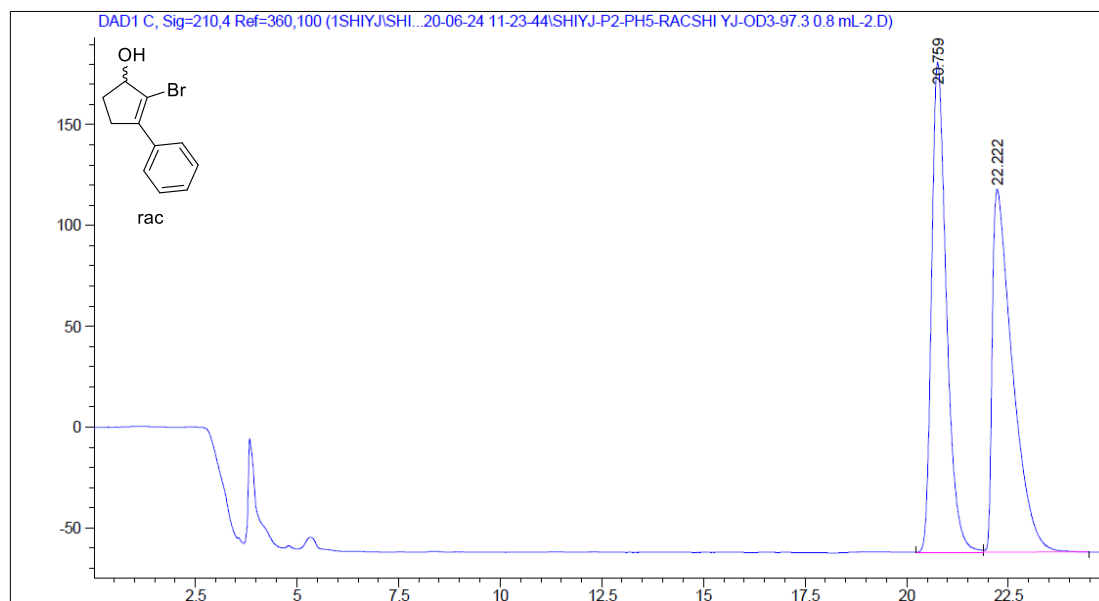
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.610	BB	0.1472	5097.41797	516.21954	50.0126
2	8.913	BB	0.1497	5094.85840	522.77856	49.9874



Signal 1: DAD1 A, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.430	MM	0.1607	1.86492e4	1934.00952	99.1370
2	8.700	MM	0.1330	162.34131	20.34279	0.8630

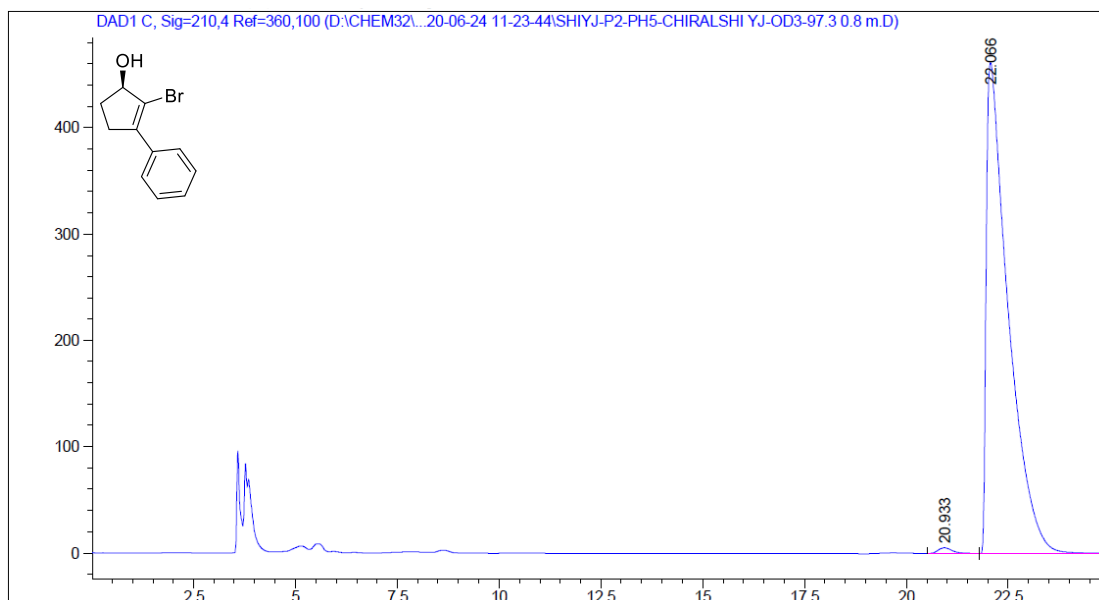
**(R)-2-bromo-3-phenylcyclopent-2-en-1-ol (4m)**



Signal 1: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.759	BV	0.3863	6170.28906	242.96638	49.8183
2	22.222	VB	0.5029	6215.29004	179.98018	50.1817

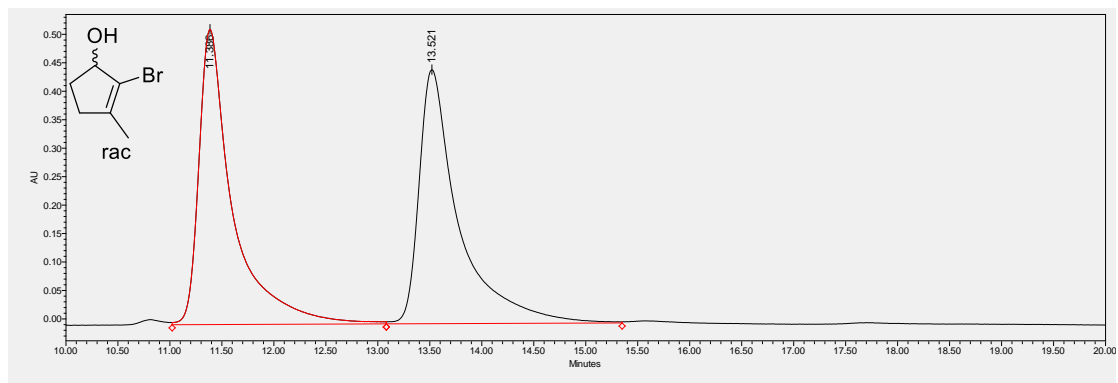
Totals : 1.23856e4 422.94656



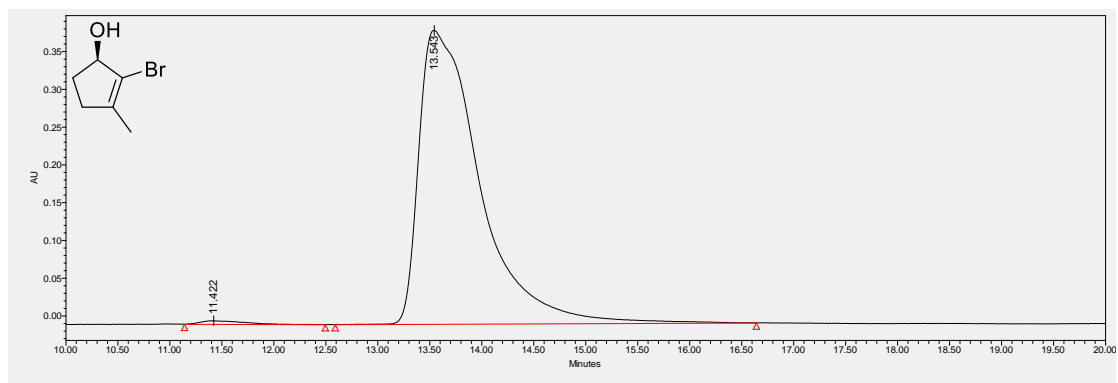
Signal 1: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.933	BV	0.3712	141.51633	5.59315	0.8127
2	22.066	VBA	0.5261	1.72707e4	461.97781	99.1873

**(R)-2-bromo-3-methylcyclopent-2-en-1-ol (4n)**

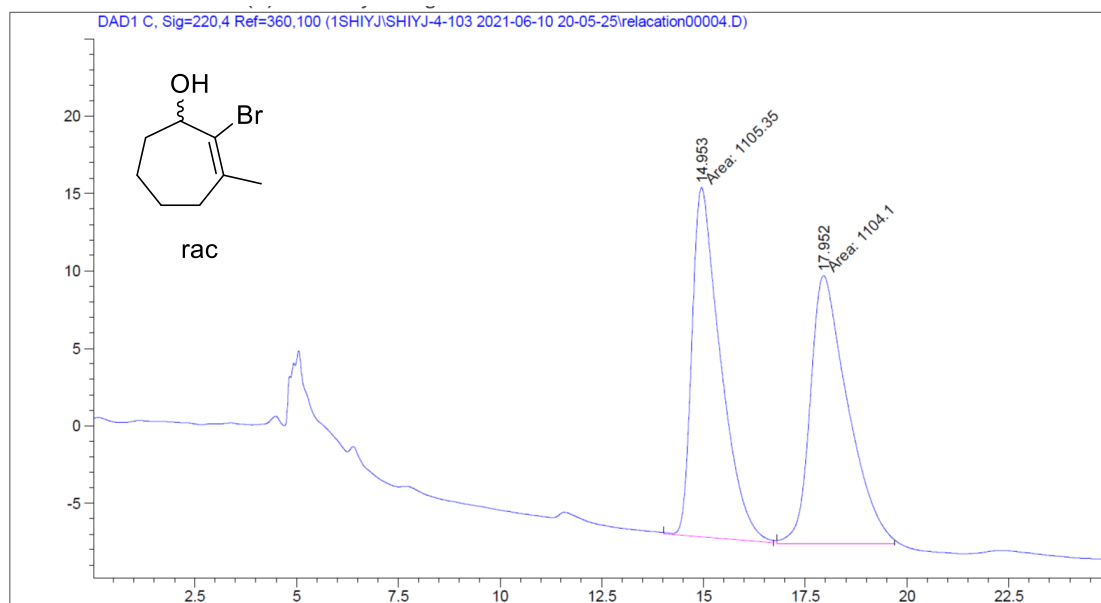


	Channel Description	RT (min)	Area ( $\mu\text{V}\cdot\text{sec}$ )	% Area	Height ( $\mu\text{V}$ )
1	2998 Ch1 210nm@1.2nm	11.386	11779960	49.92	518708
2	2998 Ch1 210nm@1.2nm	13.521	11818265	50.08	446479



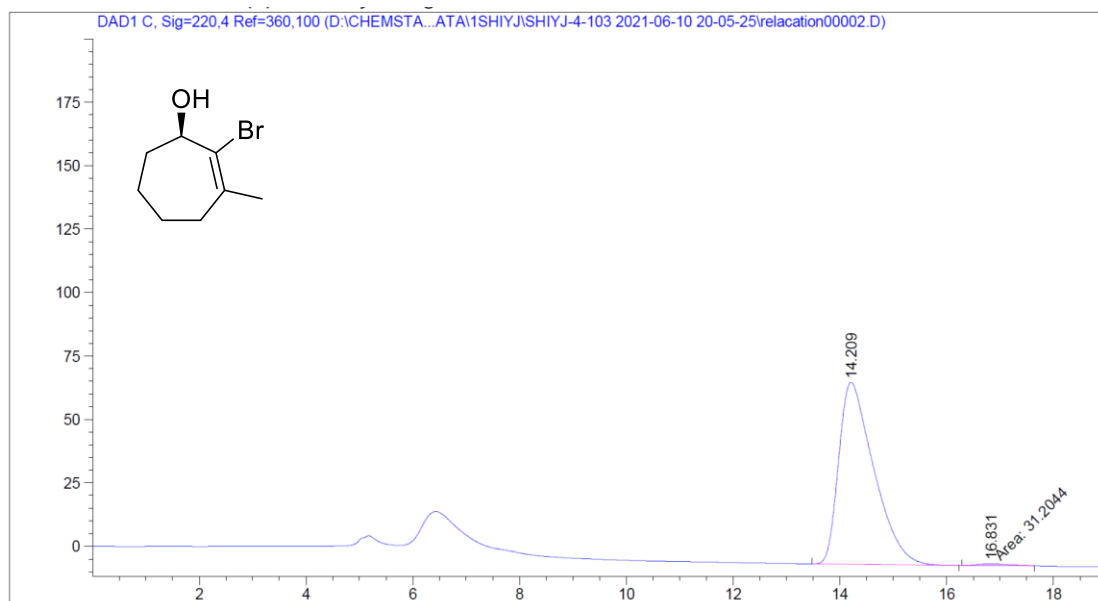
	Channel Description	RT (min)	Area ( $\mu\text{V}\cdot\text{sec}$ )	% Area	Height ( $\mu\text{V}$ )
1	2998 Ch1 210nm@1.2nm	11.422	146746	0.92	4816
2	2998 Ch1 210nm@1.2nm	13.543	15868201	99.08	389016

**(R)-2-bromo-3-methylcyclohept-2-en-1-ol (4o)**



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

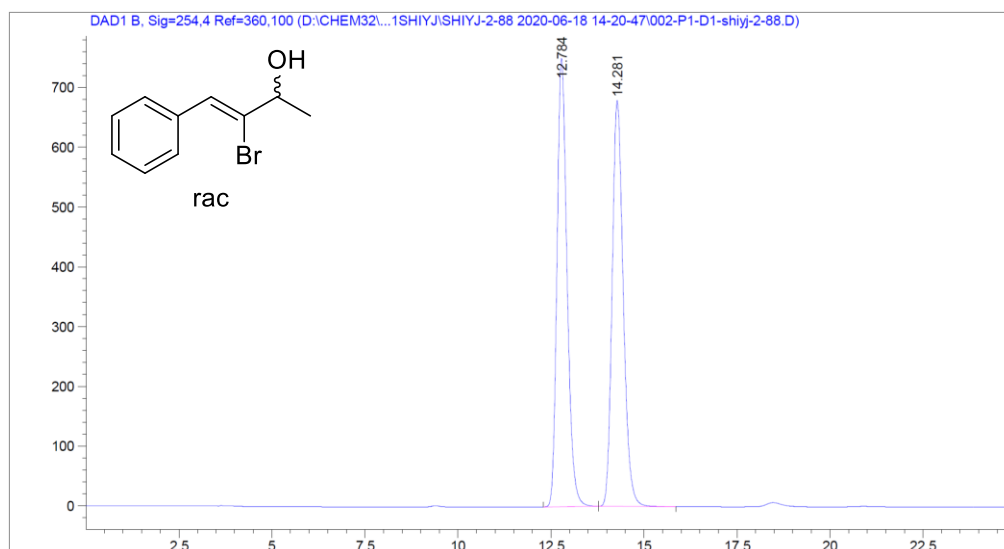
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.953	MM	0.8166	1105.35425	22.56133	50.0284
2	17.952	MM	1.0636	1104.10132	17.30142	49.9716



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.209	BB	0.6689	3272.86694	71.65337	99.0556
2	16.831	MM	0.7352	31.20444	7.07412e-1	0.9444

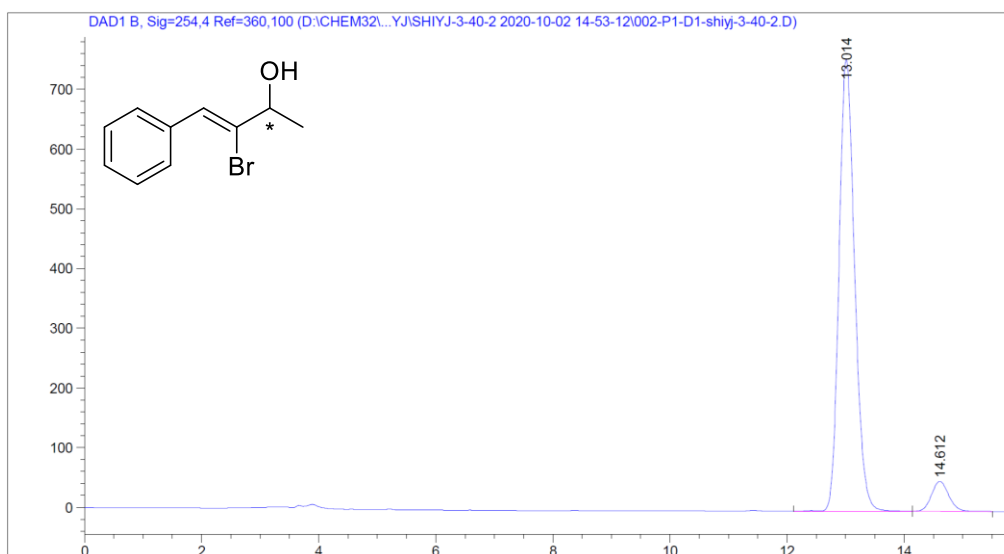
**(Z)-3-bromo-4-phenylbut-3-en-2-ol (4p)**



Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.784	BB	0.2870	1.40716e4	749.76166	49.9806
2	14.281	BB	0.3200	1.40825e4	679.02972	50.0194

Totals : 2.81541e4 1428.79138

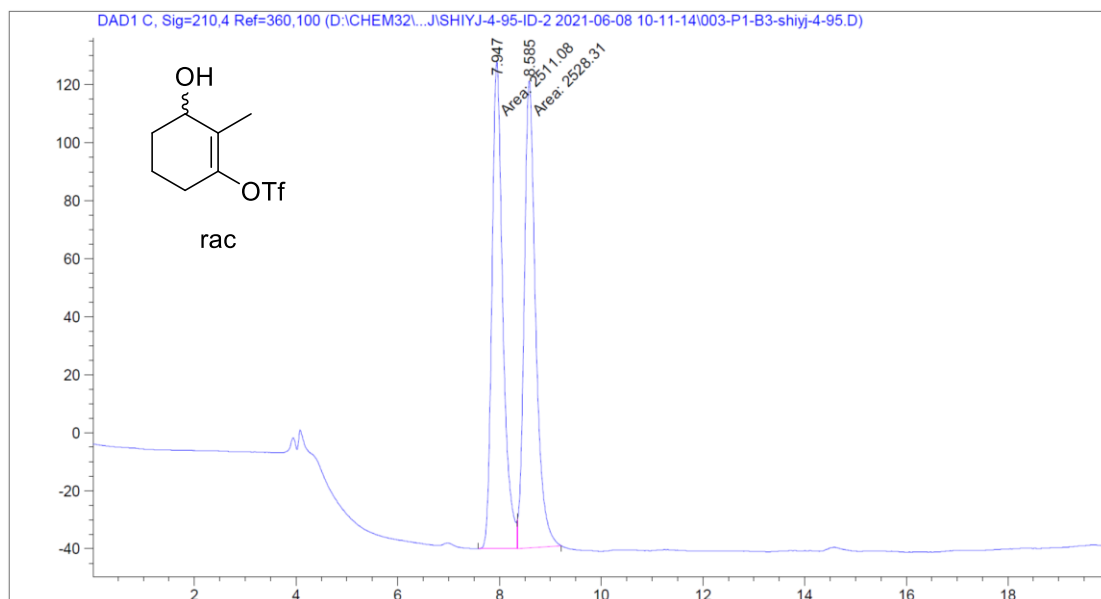


Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.014	VB R	0.2860	1.40156e4	756.11426	93.2163
2	14.612	BB	0.3147	1019.96344	50.27044	6.7837

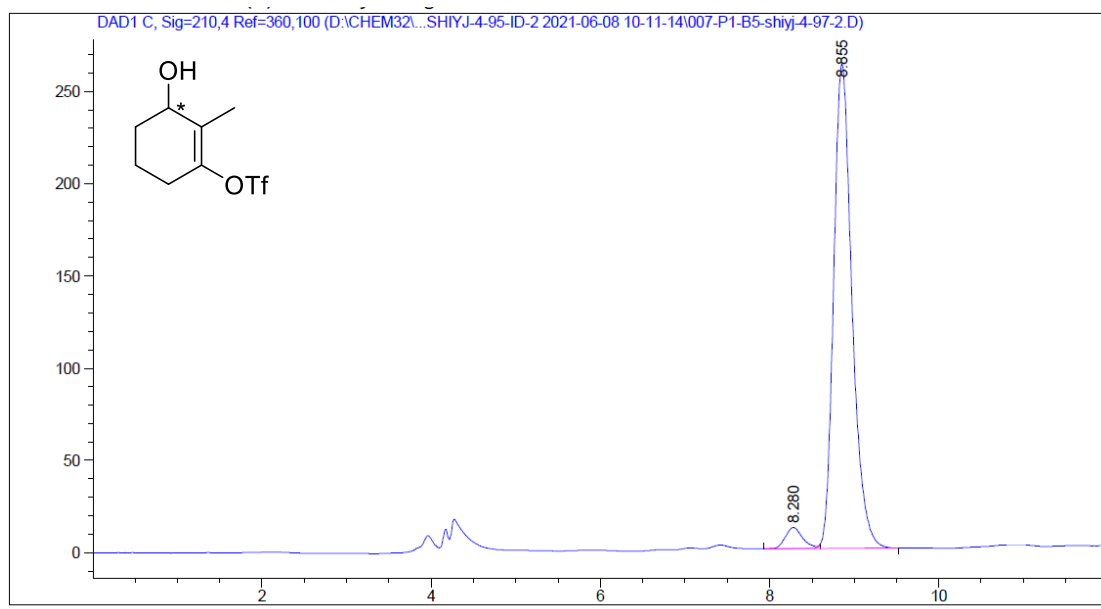
Totals : 1.50356e4 806.38469

### 3-hydroxy-2-methylcyclohex-1-en-1-yl trifluoromethanesulfonate (4q)



Signal 1: DAD1 C, Sig=210,4 Ref=360,100

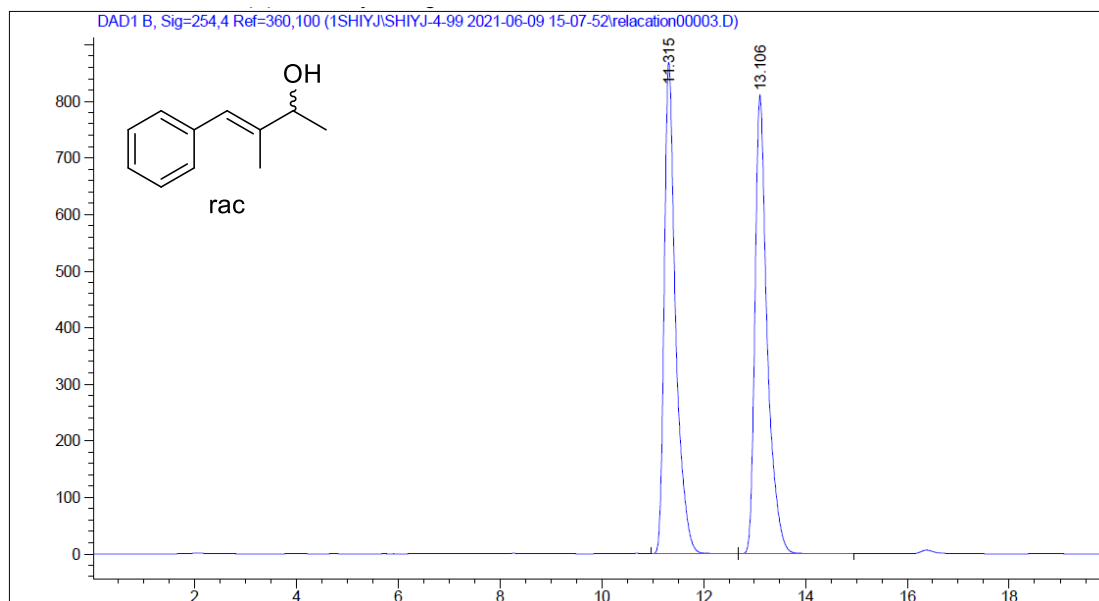
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.947	MM	0.2494	2511.08179	167.77930	49.8291
2	8.585	MM	0.2618	2528.30884	160.93854	50.1709



Signal 1: DAD1 C, Sig=210,4 Ref=360,100

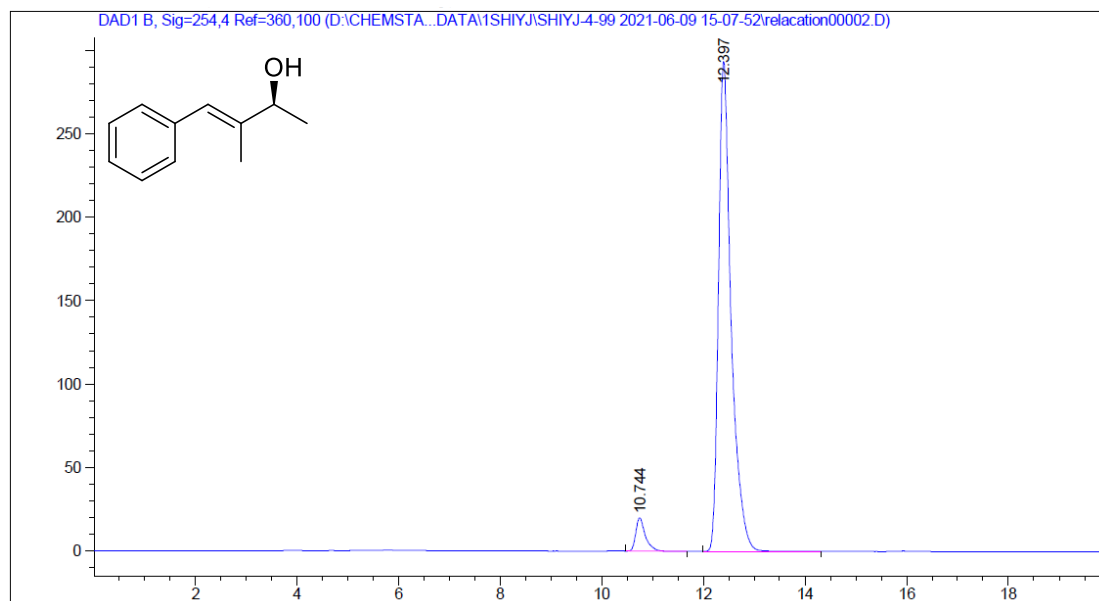
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.280	BV E	0.2148	161.47171	11.43172	3.9310
2	8.855	VB R	0.2293	3946.12646	262.65872	96.0690

**(*S,E*)-3-methyl-4-phenylbut-3-en-2-ol (4r)**



Signal 1: DAD1 B, Sig=254,4 Ref=360,100

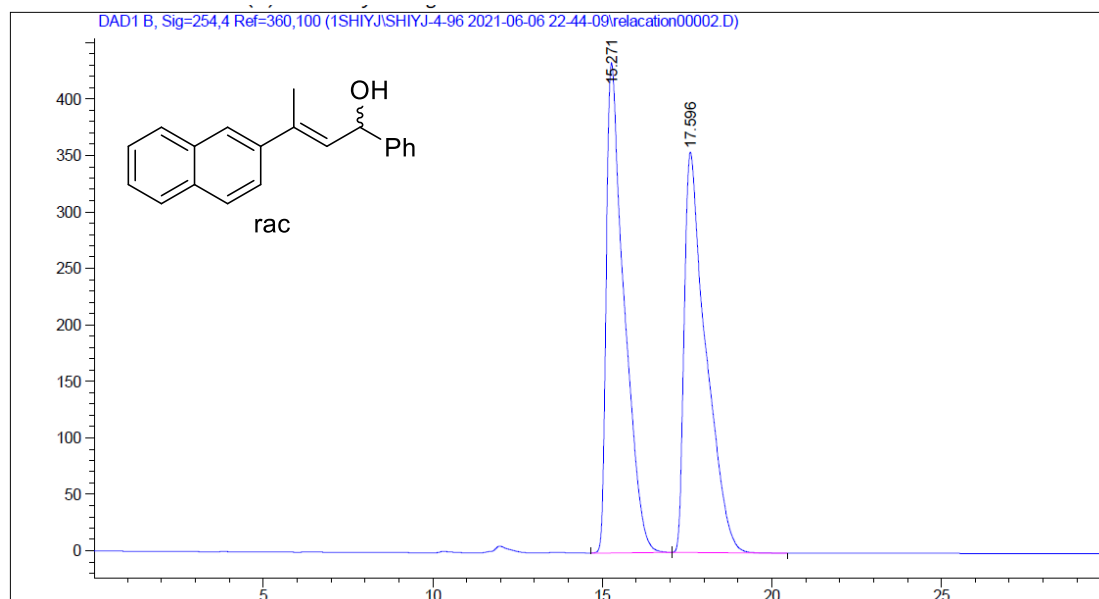
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.315	VB	0.2320	1.35498e4	868.64685	49.9448
2	13.106	BB	0.2474	1.35798e4	810.73889	50.0552



Signal 1: DAD1 B, Sig=254,4 Ref=360,100

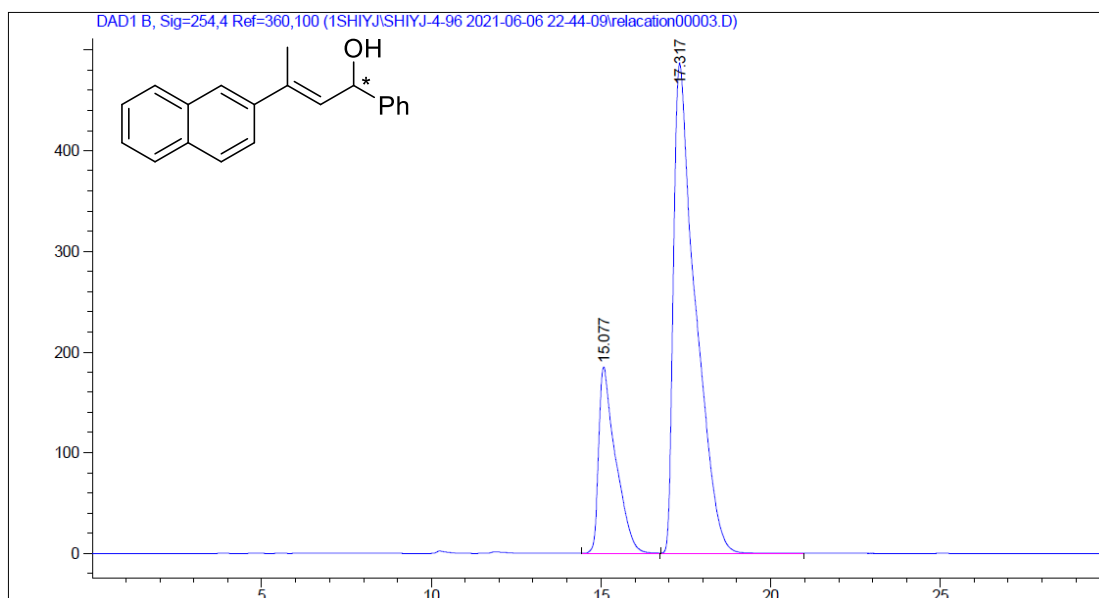
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.744	BB	0.1941	261.74890	20.07481	4.9096
2	12.397	BB	0.2554	5069.57813	293.72095	95.0904

**(E)-3-(naphthalen-2-yl)-1-phenylbut-2-en-1-ol (4s)**



Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.271	BB	0.5187	1.58601e4	433.67978	50.2610
2	17.596	BB	0.6244	1.56954e4	354.56549	49.7390



Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.077	BB	0.4900	6437.38770	184.99539	22.8217
2	17.317	BB	0.6320	2.17699e4	486.51770	77.1783