

Supporting information

**Activation of Chromium Catalysts by Photoexcited  
Hantzsch ester for Decarboxylative Allylation of  
Aldehydes with Butadiene**

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## S1 General Information

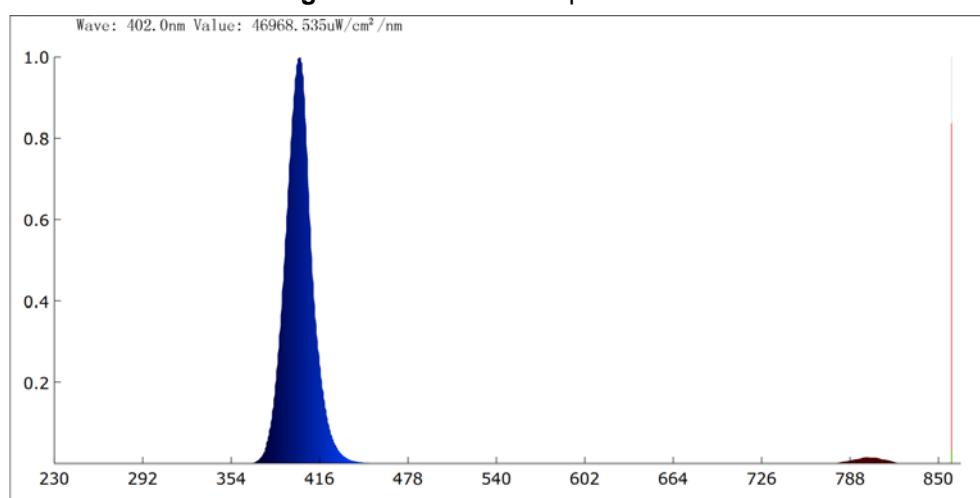
Unless otherwise noted, all reactions of substrates preparation were conducted in flame-dried glassware under a nitrogen atmosphere using anhydrous solvent passed through an activated alumina column (Innovative Technology). Commercially available reagents were used without further purification. Thin layer chromatography (TLC) was performed using Shanghai TLC silica gel plates HSG F254 and visualized using UV light, anisaldehyde or potassium permanganate. The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP-TEC-1020L) with 10W LED.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  on a Bruker 400M spectrometer. Chemical shifts in  $^1\text{H}$  NMR spectra were reported in parts per million (ppm) on the  $\delta$  scale from an internal standard of residual  $\text{CDCl}_3$  (7.26 ppm). Data for  $^1\text{H}$  NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz) and integration. Data for  $^{13}\text{C}$  NMR spectra were reported in terms of chemical shift in ppm from the central peak of  $\text{CDCl}_3$  (77.00 ppm). ESI mass spectra were obtained from an HPLC-Q-Tof mass spectrometer using acetonitrile as the mobile phase. HP 8453 spectrometer was used as the light source for the quantum yield measurements and the UV-Vis data. The fluorescence emission spectra were collected on an Edinburgh FS920. High performance liquid chromatography (HPLC) was carried out with Agress 1100 HPLC gradient system on a D1100 UV spectrophotometric detector (ELITE).

## S2 Picture of Reaction Set-Up

The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP-TEC-1020L).

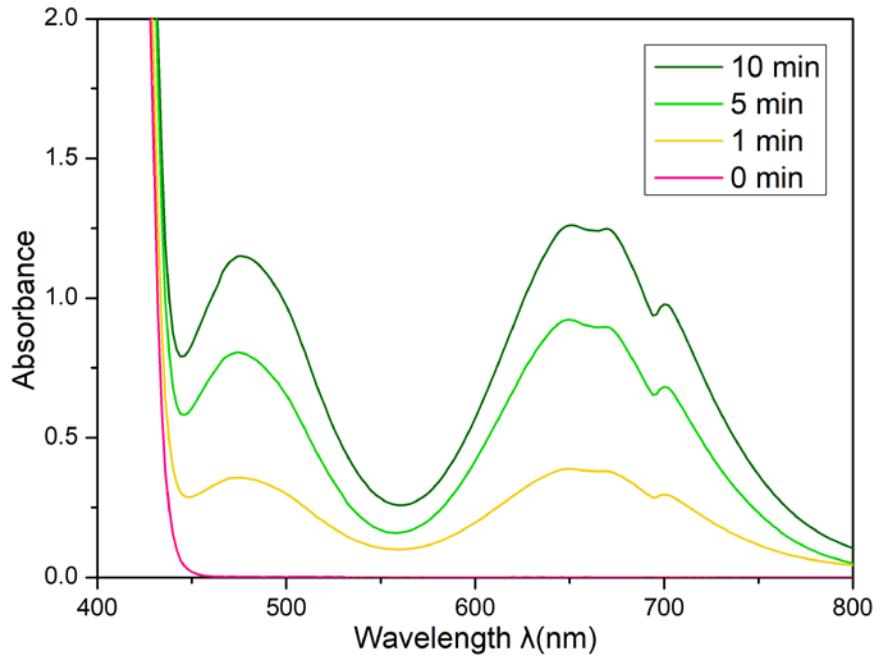


**Figure S1** Picture of the photoreactor



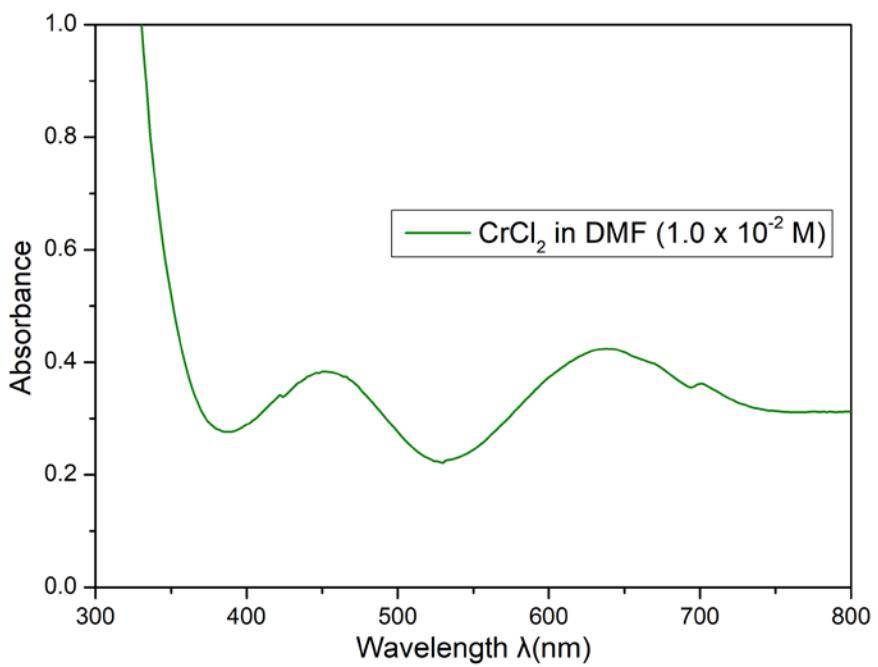
**Figure S2** Emission spectra of the 10 W blue LED lamp (maximum emission at  $\lambda = 402$  nm). Wave length: 395 nm-405 nm Quartz glass was used as reaction vessel. Distance between light source and quartz tube was approximately 0.5 cm and no filter was used for the reaction

### S3 UV/vis Absorption Spectroscopy

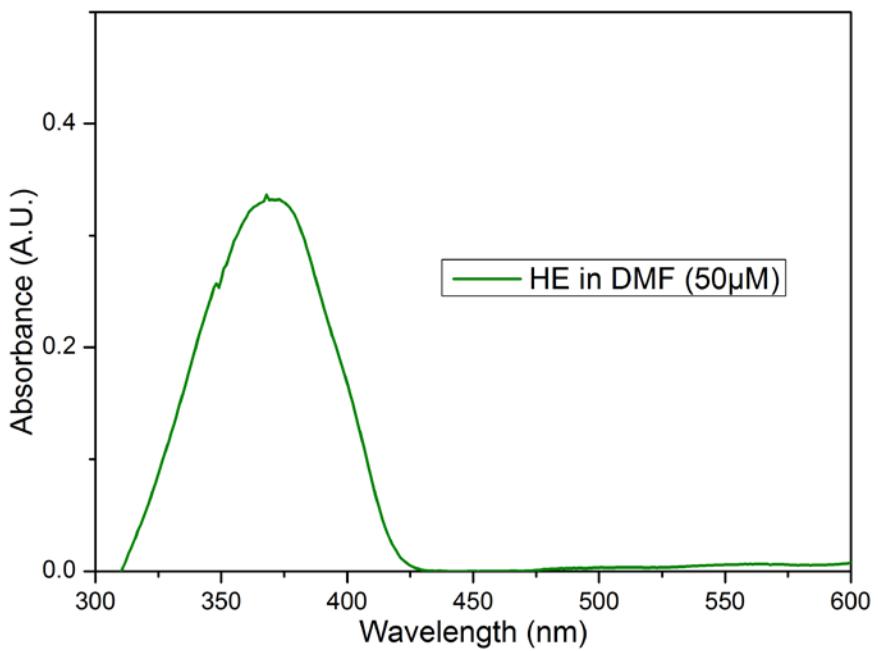


**Figure S3** UV-vis spectra showing the reduction of  $\text{CrCl}_3$  by HE upon photoirradiation in DMF; the peak at 700, 670, 652 and 476nm corresponds to  $\text{CrCl}_2$ .

In a  $\text{N}_2$ -filled glovebox, an oven-dried 20 mL Schlenk tube equipped with a magnetic stir bar was charged with  $\text{CrCl}_3$  (24.6 mg, 0.2 mmol, 1 eq.,  $2 \times 10^{-2}$  M), HE (101.3 mg, 0.4 mmol, 2 eq.) in 10 ml DMF. Then the mixture was stirred and irradiated under 10w 400-405 nm LED. UV-Vis spectrum is taken from 400 to 800 nm for 0 min, 1 min, 5 min and 10 min.



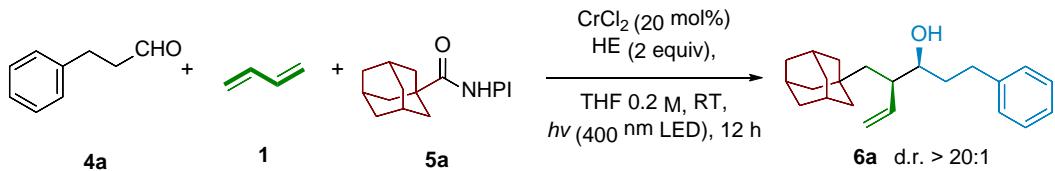
**Figure S4** UV-vis spectrum of the CrCl<sub>2</sub> in DMF.



**Figure S5** UV-vis absorption spectra of 50 mM HE.

#### S4 Condition-based Sensitivity Screen

Procedure and Results of Sensitivity Assessment of Reaction:



Standard conditions:  $n$  (**4a**) = 0.1 mmol,  $c$  = 0.1 M,  $V$  = 1.0 mL, inert atmosphere,  $T$  = 25 °C, 10 W 400-nm LED.

Stock solution:  $n$  (**4a**) = 0.1 mmol,  $c$  = 0.111 M,  $V$  = 0.9 mL, **4a**: 13.5 mg, **5a**: 65.1 mg, 1,3-Butadiene in THF: 0.9 mL,  $\text{CrCl}_2$ : 2.5 mg, HE: 50.6 mg.

Stock solution 'big scale':  $n$  (**5a**) = 2.0 mmol,  $c$  = 0.1 M,  $V$  = 20.0 mL, **4a**: 270 mg, **5a**: 1.30 g, 1,3-Butadiene in THF: 20.0 mL,  $\text{CrCl}_2$ : 49.2 mg, HE: 1.01 g, 4-CzIPN, 15.8 mg, 10W 450 nm Blue LED.

**Table S1.** Preparation of sensitivity assessment of reaction.

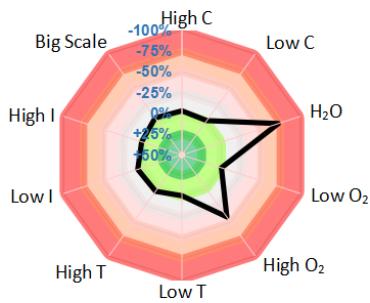
| Number | Experiment  | Preparation  |
|--------|-------------|--|
| 1      | High $c$    | 0.9 mL stock sol.                                  |
| 2      | Low $c$     | 0.9 mL stock sol. + 0.2 mL THF                     |
| 3      | High $H_2O$ | 0.9 mL stock sol. + 0.1 mL THF + 10 $\mu$ L $H_2O$ |
| 4      | Low $O_2$   | 0.9 mL stock sol. + 0.1 mL THF + degassed          |
| 5      | High $O_2$  | 0.9 mL stock sol. + 0.1 mL THF + 10 mL air         |
| 6      | Low $T$     | 0.9 mL stock sol. + 0.1 mL THF, $T$ = 15 °C        |
| 7      | High $T$    | 0.9 mL stock sol. + 0.1 mL THF, $T$ = 35 °C        |
| 8      | Low $I$     | 0.9 mL stock sol. + 0.1 mL THF, $I$ = 1 W LED      |
| 9      | High $I$    | 0.9 mL stock sol. + 0.1 mL THF, $I$ = 10 W LED     |
| 10     | Control     | 0.9 mL stock sol. + 0.1 mL THF                     |
| 11     | Big scale   | 20 mL stock solution 'big scale'                   |

## Results

**Table S2.** Results of sensitivity assessment of reaction.

| Number | Experiment            | Yield 1 / % | Yield 2 / % | Average Y. / % | Deviation / % |
|--------|-----------------------|-------------|-------------|----------------|---------------|
| 1      | High c                | 89          | 90          | 89             | -3            |
| 2      | Low c                 | 92          | 90          | 91             | -1            |
| 3      | High H <sub>2</sub> O | 17          | 23          | 20             | -72           |
| 4      | Low O <sub>2</sub>    | 93          | 91          | 92             | 0             |
| 5      | High O <sub>2</sub>   | 45          | 55          | 50             | -42           |
| 6      | Low T                 | 91          | 90          | 90             | -2            |
| 7      | High T                | 87          | 89          | 88             | -4            |
| 8      | Low I                 | 84          | 88          | 86             | -6            |
| 9      | High I                | 90          | 93          | 91             | -1            |
| 10     | Control               | 91          | 93          | 92             |               |
| 11     | Big scale             | 86          | 89          | 87             | -5            |
| 12     | Control 2             | 91          | 92          | 91             |               |

Radar diagram:



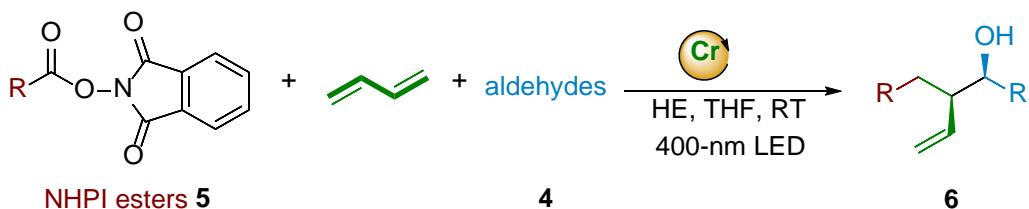
Condition-based sensitivity screening revealed that the reaction is sensitive toward H<sub>2</sub>O and high oxygen concentration.

## References:

- 1) L. Pitzer, F. Schäfers, F. Glorius, *Angew. Chem., Int. Ed.* **2019**, *58*, 8572.

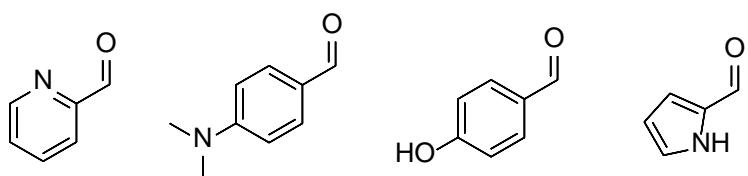
## S5 General procedure of Allylation

### a) Procedure 1: General procedure of allylation for aldehydes, condition A



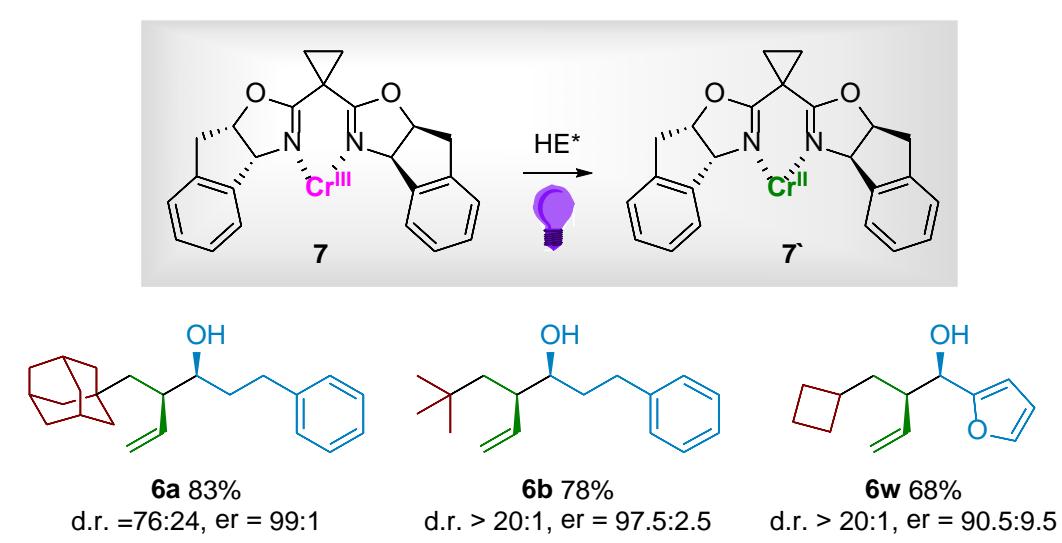
To an oven-dried 15.0 mL reaction tube containing a magnetic stir bar were added HE (253 mg, 1 mol, 2 eq.) and the respective carbonyl substrate (if solid, 0.5 mmol, 1 eq.). The tube was transferred to an argon-filled glovebox and  $\text{CrCl}_2$  (12.3 mg, 0.1 mmol, 20 mol%) was added. After putting the reaction tube in the working unit and removing the unit from the glovebox, the 1,3-diene in THF (1.0 mL), the respective carbonyl substrate (if liquid, 0.5 mmol, 1 eq.) and THF (2 mL) were added. The reaction mixture was stirred and irradiated with 400-405 nm LEDs (10W), then The solution of NHPI esters (1.0 mmol, 2 eq.) and 2.0 mL THF was added very slowly for 20 h. The reaction was quenched by opening the work unit and stirring under air atmosphere for 5 minutes. The reaction mixture was concentrated under reduced pressure and purified by column chromatography on silica gel with the specified solvent system to afford the title compounds.

Unsuccessful aldehydes



**b) Procedure 2: Procedure for the enantioselective three-component NHK allylation**

Ee was determined by HPLC-UV analysis equipped with a HPLC Column CHIRALPAK® AD-H column (25 cm x 0.46 cm, 5 µm).

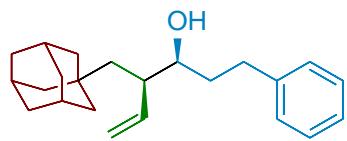


To an oven-dried 15 mL reaction tube containing a magnetic stir bar was added bisoxazoline ligand (7.2 mg, 0.02 mmol, 20 mol%). The reaction tube was transferred to an argon-filled glovebox and  $\text{CrCl}_2$  (2.5 mg, 0.02 mmol, 20 mol%) and THF (0.3 mL) were added. The catalyst solution was stirred for 2 h at rt. Then, HE (76 mg, 0.2 mmol, 3 eq.) and the aldehyde (0.1 mmol, 1 eq.) were added. After putting the reaction tube in the working unit and removing the unit from the glovebox, the 1,3-diene in THF (0.7 mL) were added. The reaction mixture was stirred and irradiated with 400-405 nm blue LEDs (10W). The solution of NHPI esters (0.2 mmol, 2 eq.) and 0.5 mL THF was added very slowly for 8 h. Then the reaction was quenched by opening the screw-cap and stirring under air atmosphere for 5 minutes. The reaction mixture was concentrated under reduced pressure and purified by column chromatography on silica gel with the specified solvent system to afford the title compounds. The ee was determined by chiral HPLC analysis of the isolated products.

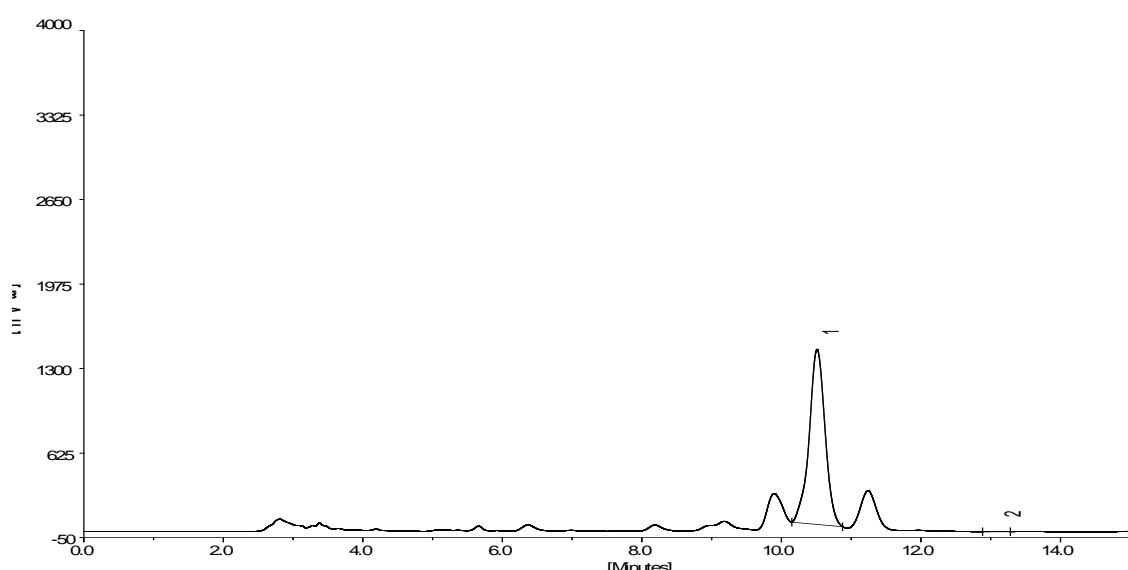
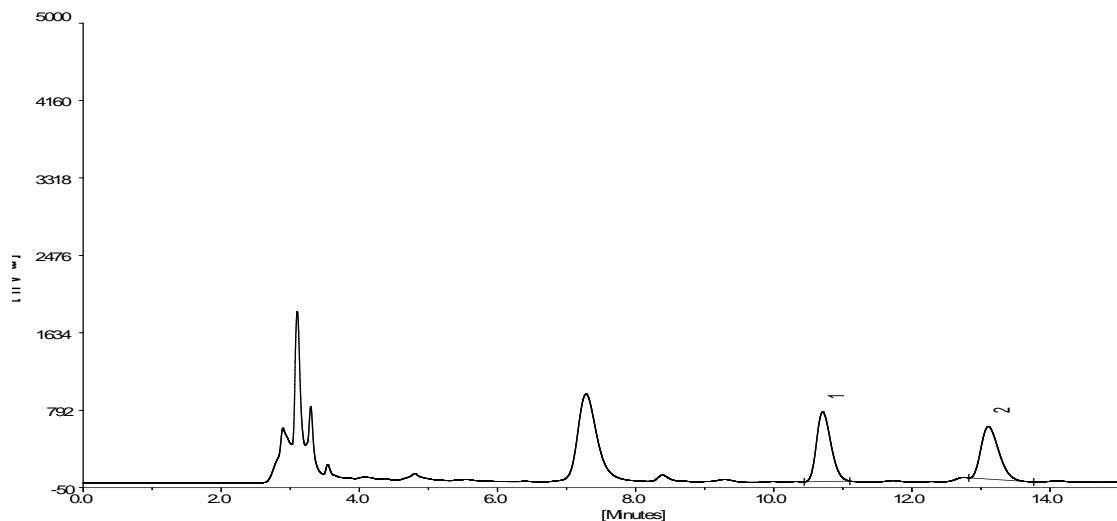
**6a:**  $[\alpha]_D^{20} = -21.0$ , ( $c = 0.22$ ,  $\text{CHCl}_3$ ).

**6b:**  $[\alpha]_D^{22} = -21.5$ , ( $c = 0.41$ ,  $\text{CHCl}_3$ ).

**6w:**  $[\alpha]_D^{21} = 24.5$ , ( $c = 0.23$ ,  $\text{CHCl}_3$ ).

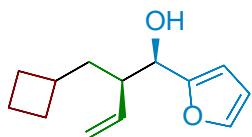


**6a er = 99:1**

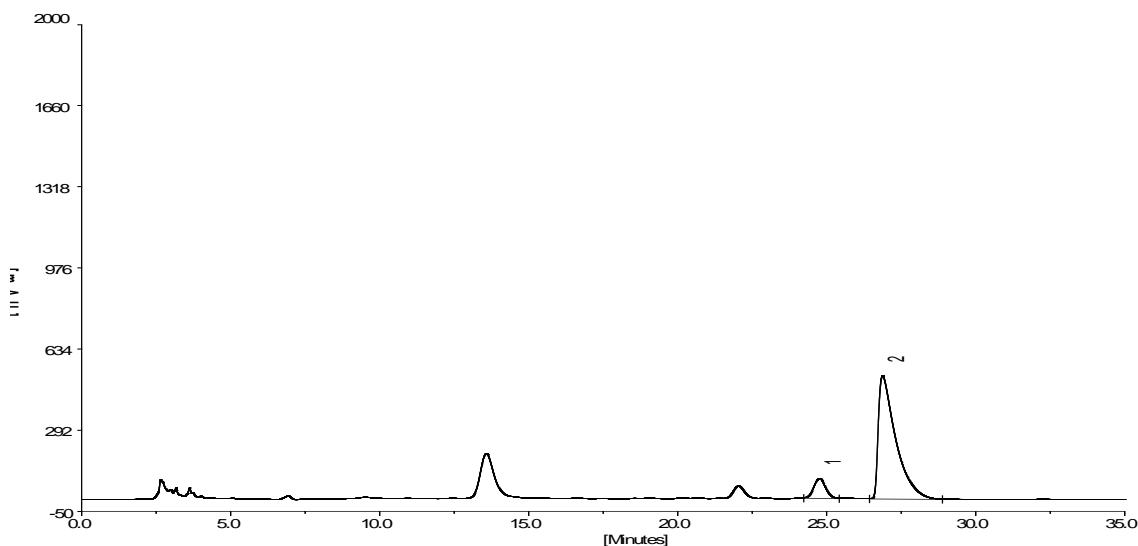
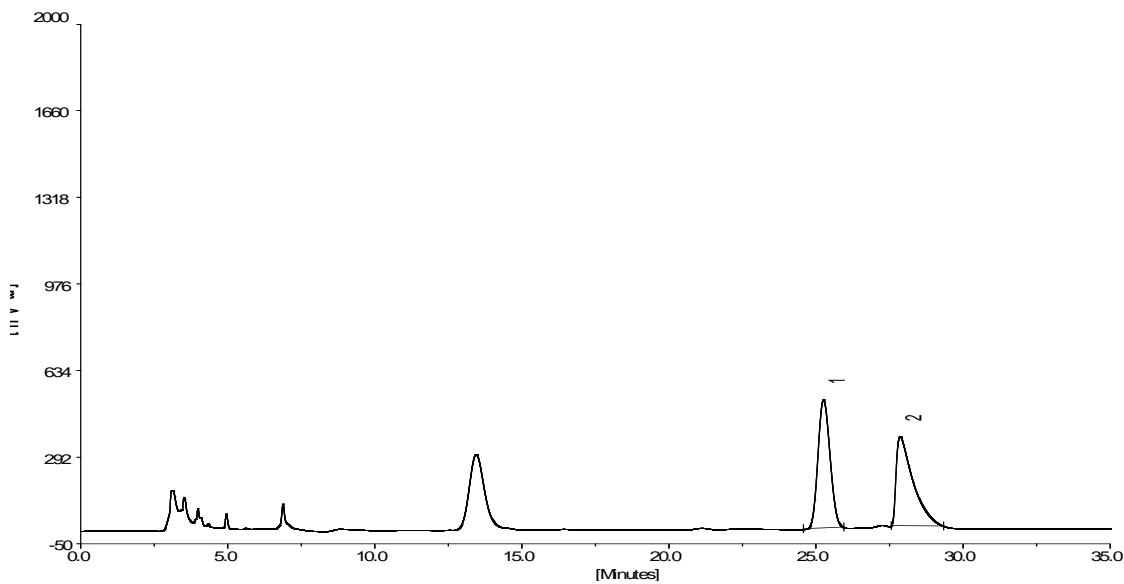


**Chiral HPLC** (hexane/*i*-PrOH = 99/1, 1.0 mL/min, 208 nm)  $t_R$  (major) 10.5 min,  $t_R$  (minor) 13.1 min, 99.9/0.1 er.

$[\alpha]_D^{20} = -21.0$ , ( $c = 0.22$ ,  $\text{CHCl}_3$ ).

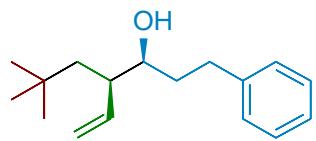


**6w** er = 90.5:9.5

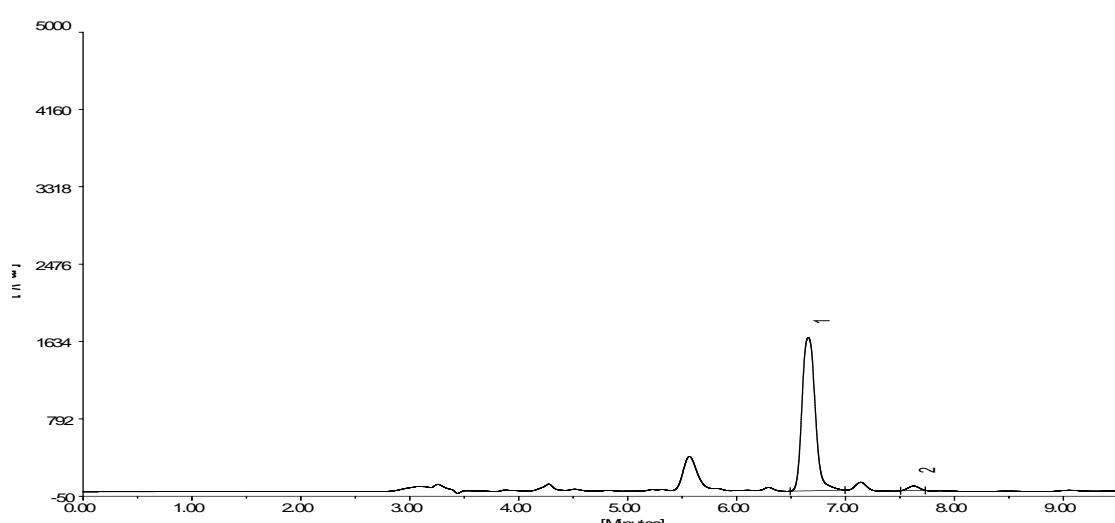
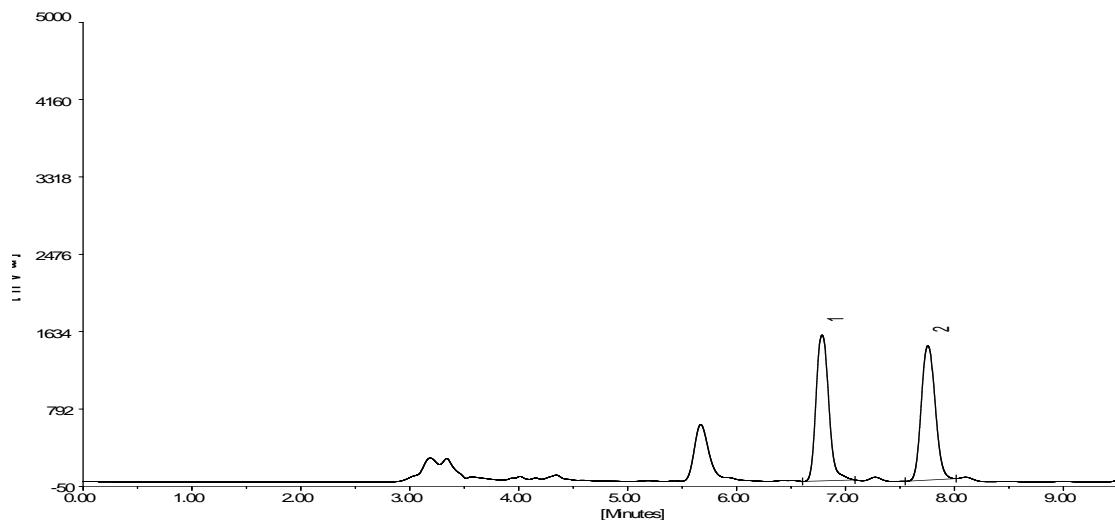


**Chiral HPLC** (hexane/*i*-PrOH = 99.5/0.5, 1.0 mL/min, 208 nm)  $t_R$  (major) 26.9 min,  $t_R$  (minor), 24.8 min, 90.5/9.5 er.

$[\alpha]_D^{21} = 24.5$ , ( $c = 0.23$ ,  $\text{CHCl}_3$ ).



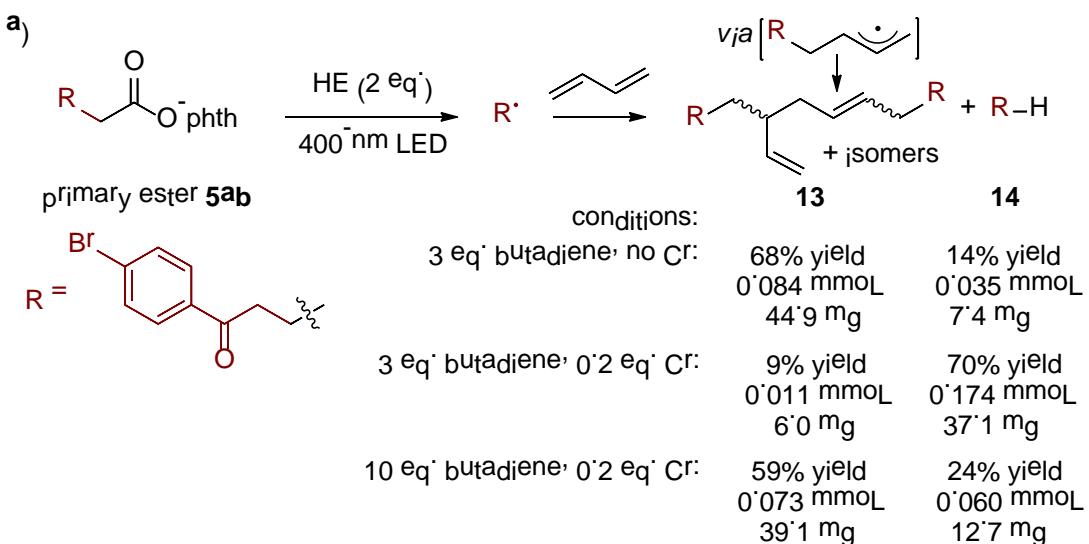
**6b er = 97.5:2.5**



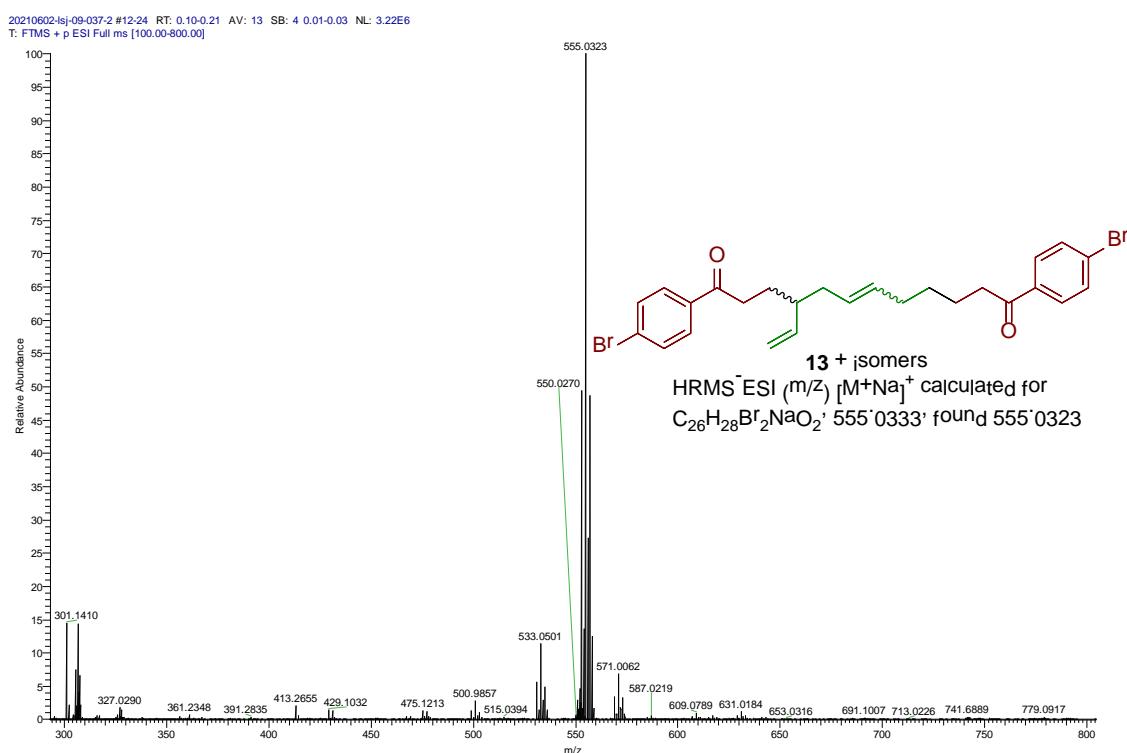
**Chiral HPLC** (hexane/i-PrOH = 98/2, 1.0 mL/min, 208 nm)  $t_R$  (major) 6.6min,  $t_R$  (minor) 7.6 min, 97.5/2.5 er.

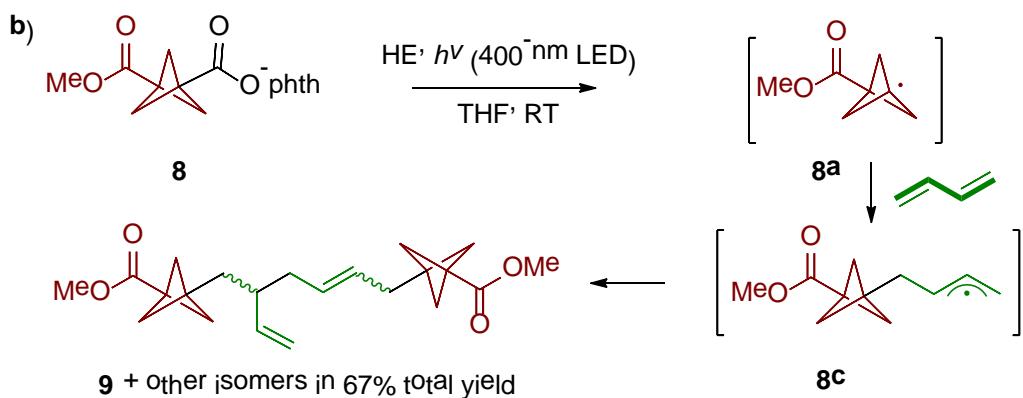
$[\alpha]_D^{22} = -21.5$ , ( $c = 0.41$ ,  $\text{CHCl}_3$ ).

c) Procedure 3 for dimerization

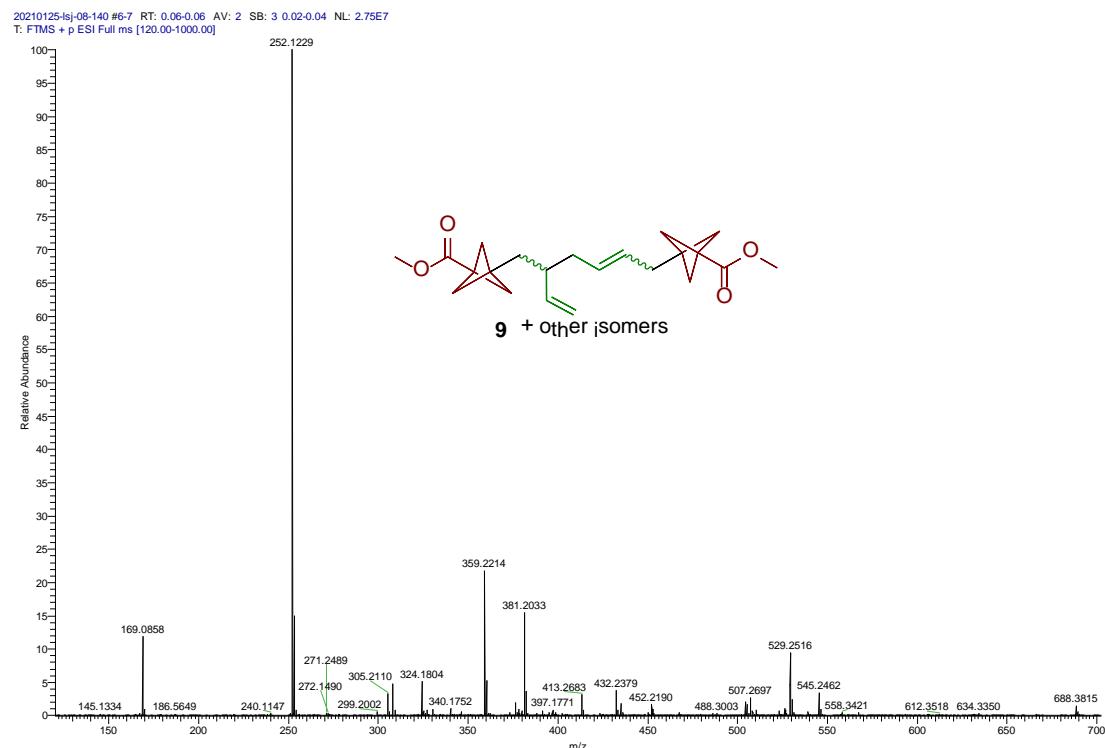


To an oven-dried 15.0 mL reaction tube containing a magnetic stir bar were added HE (126mg, 0.50 mol, 2.0 eq.), the primary ester **5ab** (100 mg, 0.25 mmol, 1.0 eq.). After putting the reaction tube in the working unit and replace the air of the unit with the N<sub>2</sub>, the 1,3-diene (2M in THF) ( 0.75 mmol, 0.38 mL, 3.0 eq. or 2.5 mmol, 1.25 mL, 10.0 eq.), CrCl<sub>2</sub> ( 0.05 mmol, 6.1 mg, 0.2eq.) and THF ( 1 mL ) were added. The reaction mixture was stirred and irradiated with 400-405 nm blue LEDs (10W) for 12 h. The reaction mixture was concentrated under reduced pressure and purified by column chromatography on silica gel to obtain **13** and **14**.

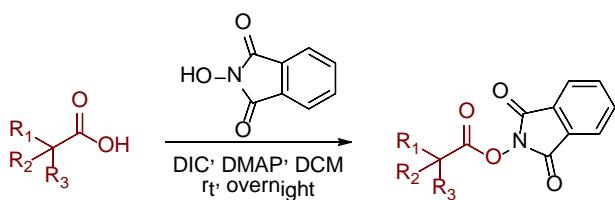




To an oven-dried 15.0 mL reaction tube containing a magnetic stir bar were added HE (127 mg, 0.5 mol, 1.0 eq.), the NHPI esters **8** (165 mg, 0.5 mmol, 1.0 eq.). After putting the reaction tube in the working unit and replace the air of the unit with the N<sub>2</sub>, the 1,3-diene in THF (2M in THF) (1.0 mL) were added. The reaction mixture was stirred and irradiated with 400-405 nm blue LEDs (10W) for 12 h. The reaction mixture was concentrated under reduced pressure and purified by column chromatography on silica gel to obtain **9**, 60 mg, yield 67%. HRMS-ESI (m/z) [M+H]<sup>+</sup> calculated for C<sub>22</sub>H<sub>31</sub>O<sub>4</sub>, 359.2222, found 359.2214.



**d) General Procedures for the Preparation of N-hydroxyphthalimide (NHPI) esters**

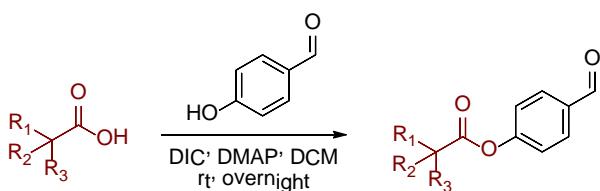


N-hydroxyphthalimide (NHPI) esters were prepared according to the known Procedures.<sup>[2]</sup> N-Hydroxyphthalimide (1.0 eq.), DMAP (0.1 eq.) and, if solid, carboxylic acid (1.0 eq.) was added to a round-bottomed flask. Dichloromethane (0.2 M) and, if liquid, carboxylic acid (1.0 eq) were then added, followed by DIC (1.0 eq.). The reaction mixture was allowed to stir at room temperature overnight. The solution was washed with water three times and the organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>. Then the reaction mixture was concentrated under reduced pressure and purified by column chromatography on silica gel with the specified solvent system to afford the title compounds. If solid and not pure, the NHPI ester can be recrystallized from DCM/MeOH or EtOAc to give pure material.

**References:**

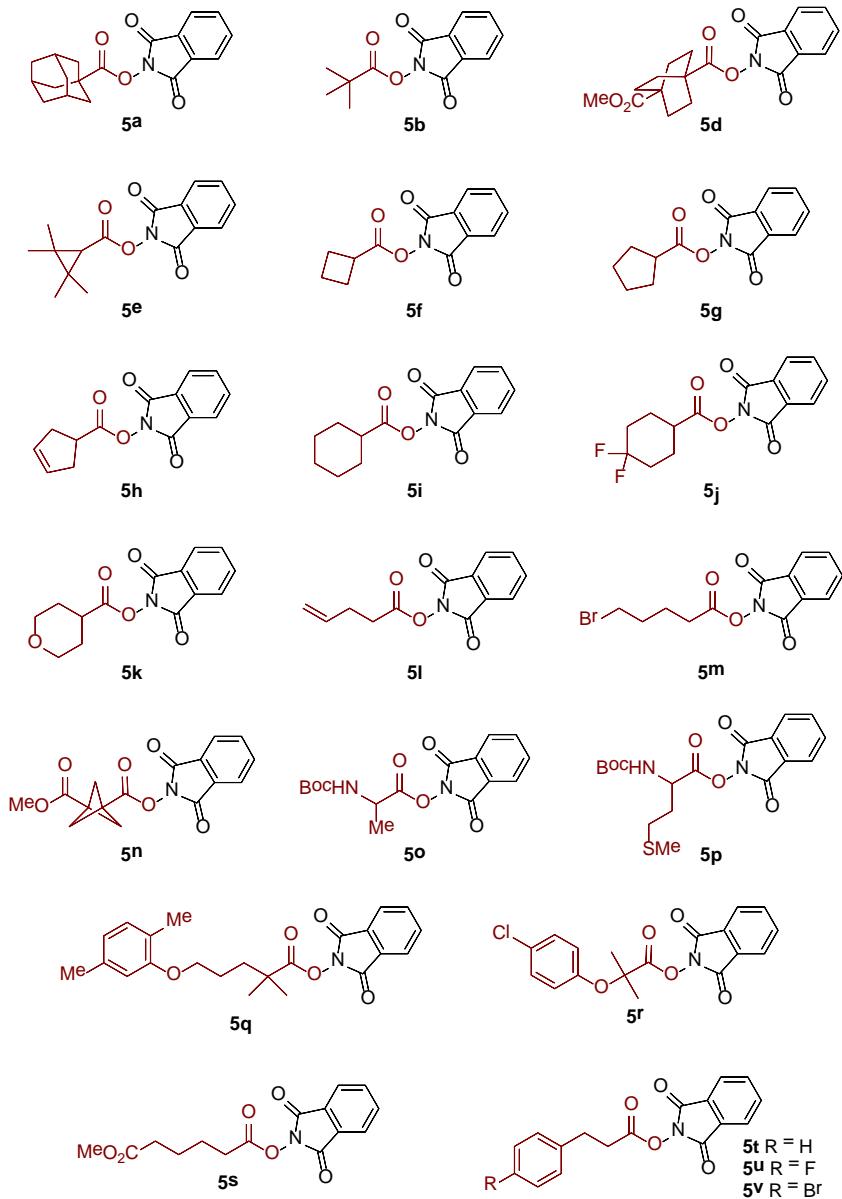
- 2) A. Fawcett, J. Pradeilles, Y. Wang, T. Mutsuga, E. L. Myers, V. K. Aggarwal, *Science*. **2017**, 357(6348), 283-286.

**e) General Procedures for the Preparation of aldehydes.**



Some special aldehydes were prepared according to the same Procedures.<sup>[2]</sup> 4-Hydroxybenzaldehyde (1.0 eq.), DMAP (0.1 eq.) and, if solid, carboxylic acid (1.0 eq.) was added to a round-bottomed flask. Dichloromethane (0.2 M) and, if liquid, carboxylic acid (1.0 eq) were then added, followed by DIC (1.0 eq.). The reaction mixture was allowed to stir at room temperature overnight. The solution was washed with water three times and the organic layer was dried with  $\text{Na}_2\text{SO}_4$ . Then the reaction mixture was concentrated under reduced pressure and purified by column chromatography on silica gel with the specified solvent system to afford the title compounds.

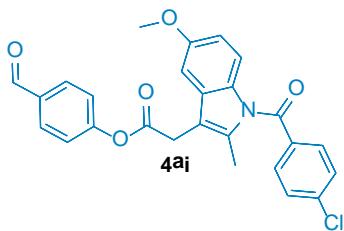
## S6 Characterization of Products



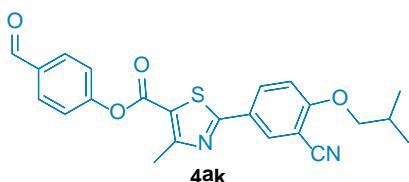
These N-hydroxyphthalimide (NHPI) esters were synthesized according to the reported methods<sup>3</sup>. Most of the aldehydes used are commercially available.

### References:

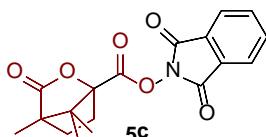
- 3) a) A. Fawcett, J. Pradeilles, Y. Wang, T. Mutsuga, E. L. Myers, V. K. Aggarwal, *Science*. **2017**, 357(6348), 283-286. b) C. Chan, Q. Xing, Y. Chow, S. Hung, W. Yu, *Organic Letters*. **2019**, 21(19), 8037-8043. c) L. Ren, H. Cong, *Organic Letters*. **2018**, 20(11), 3225-3228. d) F. Toriyama, J. Cornella, L. Wimmer, T. Chen, D. D. Dixon, G. Creech, P. S. Baran, *Journal of the American Chemical Society*. **2016**, 138(35), 11132-11135. e) Y. Zhang, L. Yang, J. Wu, C. Zhu, P. Wang, *Organic Letters*. **2018**, 22(19), 7768-7772. f) S. Ni, N. M. Padial, C. Kingston, J. C. Vantourout, D. C. Schmitt, J. T. Edwards, M. M. Kruszyk, R. R. Merchant, P. K. Mykhailiuk, B. B. Sanchez, S. Yang, M. A. Perry, G. M. Gallego, J. J. Mousseau, M. I. R. Collins, R. J. Cherney, P. S. Lebed, J. S. Chen, T. Qin, P. S. Baran, *Journal of the American Chemical Society*. **2019**, 141(16), 6726-6739.



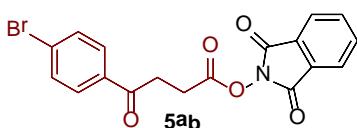
**4ai**, RF=0.6 (EA:PE=1:2), column solvent: hexane/EtOAc = 10/1, (7.29 mmol, 3.36 g) 73%, white solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.90 (s, 1H), 7.85 – 7.79 (m, 2H), 7.66 – 7.56 (m, 2H), 7.46 – 7.37 (m, 2H), 7.23 – 7.10 (m, 2H), 6.97 (d, *J* = 2.5 Hz, 1H), 6.81 (d, *J* = 9.0 Hz, 1H), 6.63 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.87 (s, 2H), 3.77 (s, 3H), 2.40 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.8, 168.5, 168.2, 156.1, 155.2, 139.4, 136.3, 134.0, 133.6, 131.1, 131.1, 130.8, 130.3, 129.1, 122.1, 115.0, 111.7, 111.4, 101.1, 55.7, 30.5, 13.3. HRMS-ESI (m/z) [M+Na]<sup>+</sup> calculated for C<sub>26</sub>H<sub>20</sub>CINaO<sub>5</sub>, 484.0928, found 484.0919.



**4ak**, RF=0.7 (EA:PE=1:2), column solvent: hexane/EtOAc = 10/1, (7.23 mmol, 3.04 g) 72%, white solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.03 (s, 1H), 8.23 (d, *J* = 2.3 Hz, 1H), 8.14 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.99 (d, *J* = 2.0 Hz, 1H), 7.97 (d, *J* = 2.0 Hz, 1H), 7.47 – 7.35 (m, 2H), 7.04 (d, *J* = 8.9 Hz, 1H), 3.92 (d, *J* = 6.5 Hz, 2H), 2.83 (s, 3H), 2.21 (dp, *J* = 13.2, 6.6 Hz, 1H), 1.10 (d, *J* = 6.7 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.8, 168.6, 163.8, 162.8, 159.6, 154.8, 134.28, 132.7, 132.3, 131.3, 125.6, 122.4, 119.9, 115.2, 112.7, 103.1, 75.7, 28.1, 19.0, 17.8. HRMS-ESI (m/z) [M+H]<sup>+</sup> calculated for C<sub>23</sub>H<sub>21</sub>N<sub>2</sub>O<sub>4</sub>S, 421.1222, found 421.1206.

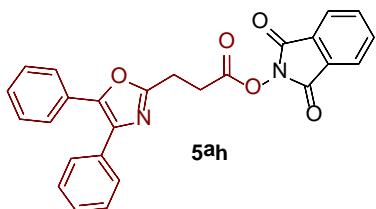


**5c**, RF=0.5 (EA:PE=1:2), column solvent: hexane/EtOAc = 10/1, (5.78 mmol, 1.98 g) 58%, white solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.81 (dd, *J* = 5.5, 3.1 Hz, 2H), 2.60 (ddd, *J* = 13.5, 10.8, 4.2 Hz, 1H), 2.28 (ddd, *J* = 13.7, 9.3, 4.6 Hz, 1H), 2.02 (ddd, *J* = 13.2, 10.8, 4.6 Hz, 1H), 1.78 (ddd, *J* = 13.4, 9.3, 4.2 Hz, 1H), 1.18 (s, 3H), 1.17 (s, 3H), 1.16 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 177.1, 164.1, 161.3, 134.9, 128.7, 124.1, 89.8, 55.4, 54.7, 30.7, 28.8, 16.4, 16.3, 9.7. HRMS-ESI (m/z) [M+Na]<sup>+</sup> calculated for C<sub>18</sub>H<sub>17</sub>NNaO<sub>6</sub>, 366.0954, found 366.0944.

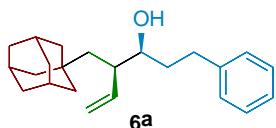


**5ab**, RF=0.6 (EA:PE=1:2), column solvent: hexane/EtOAc = 5/1, (6.81 mmol, 2.73 g) 68%, white solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 – 7.82 (m, 4H), 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.64 – 7.55 (m, 2H), 3.42 (t, *J* = 6.8 Hz, 2H), 3.13 (t, *J* = 6.8 Hz, 2H). <sup>13</sup>C NMR (101 MHz,

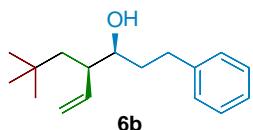
$\text{CDCl}_3$ )  $\delta$  195.4, 169.1, 161.7, 134.7, 134.7, 131.9, 129.5, 128.8, 128.6, 123.9, 33.0, 25.3. HRMS-ESI (m/z) [M+Na] $^+$ calculated for  $\text{C}_{18}\text{H}_{12}\text{BrNNaO}_5$ , 423.9797, found 423.9788.



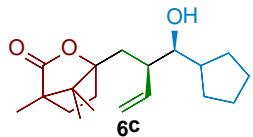
**5ah**, RF=0.4 (EA:PE=1:2), column solvent: hexane/EtOAc = 10/1, (6.24 mmol, 2.73 g) 62%, white solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (dd,  $J$  = 5.5, 3.1 Hz, 2H), 7.77 (dd,  $J$  = 5.5, 3.1 Hz, 2H), 7.72 – 7.64 (m, 2H), 7.64 – 7.56 (m, 2H), 7.43 – 7.29 (m, 6H), 3.33 (s, 4H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.3, 161.6, 160.3, 145.7, 135.1, 134.7, 132.2, 128.7, 128.7, 128.5, 128.50, 128.4, 128.0, 127.8, 126.4, 123.9, 28.0, 23.0. HRMS-ESI (m/z) [M+Na] $^+$ calculated for  $\text{C}_{26}\text{H}_{18}\text{N}_2\text{NaO}_5$ , 461.1113, found 461.1096.



**6a**, RF=0.6 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.47 mmol, 150.9 mg) 93%, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 (dd,  $J$  = 13.0, 5.6 Hz, 2H), 7.12 (dd,  $J$  = 15.2, 7.2 Hz, 3H), 5.60 (dt,  $J$  = 17.3, 9.8 Hz, 1H), 5.08 (dd,  $J$  = 10.3, 1.5 Hz, 1H), 5.03 (d,  $J$  = 17.4 Hz, 1H), 3.29 (s, 1H), 2.82 – 2.72 (m, 1H), 2.59 (ddd,  $J$  = 13.7, 10.1, 6.5 Hz, 1H), 2.17 (td,  $J$  = 11.2, 5.7 Hz, 1H), 1.84 (s, 3H), 1.76 (ddd,  $J$  = 13.7, 6.7, 3.5 Hz, 1H), 1.66 – 1.56 (m, 5H), 1.52 (d,  $J$  = 12.2 Hz, 3H), 1.40 (q,  $J$  = 12.1 Hz, 6H), 1.14 (d,  $J$  = 5.6 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.3, 141.6, 128.5, 128.3, 125.7, 117.2, 74.1, 45.5, 44.9, 43.1, 37.1, 36.2, 33.1, 32.4, 28.7. HRMS-ESI (m/z) [M-OH] $^+$ calculated for  $\text{C}_{23}\text{H}_{31}$ , 307.2420, found 307.2421.

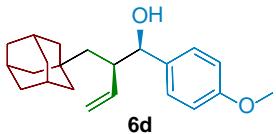


**6b**, RF=0.6 (EA:PE=1:3), column solvent: hexane/EtOAc = 20/1, (0.42 mmol, 102.7 mg) 84%, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (td,  $J$  = 7.2, 3.3 Hz, 2H), 7.26 – 7.18 (m, 3H), 5.71 (ddd,  $J$  = 17.3, 10.2, 9.4 Hz, 1H), 5.19 (dd,  $J$  = 10.3, 1.9 Hz, 1H), 5.16 – 5.11 (m, 1H), 3.46 – 3.36 (m, 1H), 2.87 (ddd,  $J$  = 13.9, 10.3, 5.3 Hz, 1H), 2.69 (ddd,  $J$  = 13.7, 10.1, 6.5 Hz, 1H), 2.28 – 2.16 (m, 1H), 1.87 (qt,  $J$  = 17.8, 7.3 Hz, 1H), 1.77 – 1.64 (m, 2H), 1.42 – 1.37 (m, 2H), 0.92 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.3, 141.2, 128.4, 128.3, 125.7, 117.4, 74.0, 47.1, 44.7, 36.2, 32.3, 31.1, 30.1. HRMS-ESI (m/z) [M-OH] $^+$ calculated for  $\text{C}_{17}\text{H}_{25}$ , 229.1951, found 229.1953.

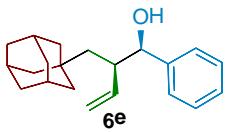


**6c**, RF=0.4 (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, (0.43 mmol, 132.7 mg) 87%, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.83 (dt,  $J$  = 17.3, 10.0 Hz, 1H), 5.11 (dd,  $J$  = 15.9,

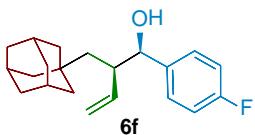
9.3 Hz, 2H), 3.38 (dd,  $J$  = 16.8, 5.0 Hz, 1H), 2.49 (dd,  $J$  = 13.4, 6.5 Hz, 1H), 2.01 (dt,  $J$  = 12.1, 6.0 Hz, 1H), 1.95 – 1.77 (m, 3H), 1.77 – 1.64 (m, 5H), 1.60 (dd,  $J$  = 12.6, 6.7 Hz, 3H), 1.56 – 1.49 (m, 2H), 1.37 – 1.26 (m, 1H), 1.11 (dd,  $J$  = 18.1, 6.6 Hz, 1H), 1.07 (s, 3H), 0.87 (s, 3H), 0.82 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  180.5, 138.4, 117.0, 94.8, 78.9, 53.5, 52.2, 44.2, 43.6, 31.3, 30.3, 30.0, 29.0, 28.6, 25.5, 25.3, 16.5, 16.2, 9.9. HRMS-ESI (m/z) [M+H] $^+$  calculated for  $\text{C}_{19}\text{H}_{31}\text{O}_3$ , 307.2273, found 307.2265.



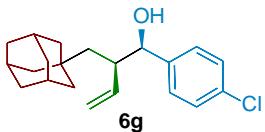
**6d**, RF=0.5 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.42 mmol, 135.6 mg) 83%, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 – 7.22 (m, 2H), 6.89 – 6.85 (m, 2H), 5.71 (ddd,  $J$  = 17.1, 10.3, 9.2 Hz, 1H), 5.23 (dd,  $J$  = 5.6, 1.6 Hz, 1H), 5.20 (dd,  $J$  = 12.5, 1.6 Hz, 1H), 4.19 (dd,  $J$  = 8.2, 1.8 Hz, 1H), 3.81 (s, 3H), 2.49 (qd,  $J$  = 9.1, 2.1 Hz, 1H), 2.35 (d,  $J$  = 2.0 Hz, 1H), 1.85 (s, 3H), 1.63 (d,  $J$  = 14.0 Hz, 3H), 1.53 (d,  $J$  = 11.4 Hz, 3H), 1.33 (d,  $J$  = 2.4 Hz, 6H), 1.09 (dd,  $J$  = 14.0, 9.1 Hz, 1H), 1.00 (dd,  $J$  = 14.0, 2.2 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9, 142.5, 134.2, 128.5, 117.9, 113.4, 76.3, 55.2, 47.3, 44.8, 42.8, 36.9, 32.8, 28.6. HRMS-ESI (m/z) [M-OH] $^+$  calculated for  $\text{C}_{22}\text{H}_{29}\text{O}$ , 309.2213, found 309.2206.



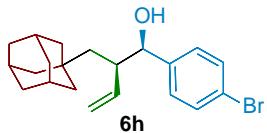
**6e**, RF=0.6 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.39 mmol, 115.3 mg) 78%, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.30 (m, 4H), 7.30 – 7.25 (m, 1H), 5.71 (ddd,  $J$  = 17.2, 10.2, 9.2 Hz, 1H), 5.26 – 5.17 (m, 2H), 4.26 (dd,  $J$  = 7.9, 1.8 Hz, 1H), 2.52 (qd,  $J$  = 9.2, 2.2 Hz, 1H), 2.35 (d,  $J$  = 2.1 Hz, 1H), 1.85 (s, 3H), 1.61 (t,  $J$  = 10.5 Hz, 3H), 1.53 (d,  $J$  = 11.3 Hz, 3H), 1.33 (d,  $J$  = 2.3 Hz, 6H), 1.13 (dd,  $J$  = 14.1, 9.1 Hz, 1H), 1.04 (dd,  $J$  = 14.1, 2.3 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.1, 128.0, 127.5, 127.3, 118.0, 76.9, 47.2, 44.8, 42.8, 37.0, 32.9, 28.6. HRMS-ESI (m/z) [M-OH] $^+$  calculated for  $\text{C}_{21}\text{H}_{27}$ , 279.2107, found 279.2106.



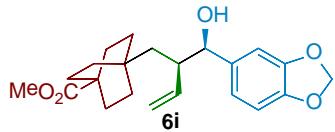
**6f**, RF=0.6 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.41 mmol, 129.8 mg) 83%, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 – 7.31 (m, 2H), 7.30 – 7.25 (m, 2H), 5.76 – 5.65 (m, 1H), 5.26 (dd,  $J$  = 10.2, 1.7 Hz, 1H), 5.23 – 5.17 (m, 1H), 4.25 (d,  $J$  = 7.8 Hz, 1H), 2.48 (td,  $J$  = 9.4, 2.0 Hz, 1H), 2.26 (s, 1H), 1.88 (s, 3H), 1.65 (d,  $J$  = 11.9 Hz, 3H), 1.56 (d,  $J$  = 11.3 Hz, 3H), 1.35 (d,  $J$  = 2.3 Hz, 6H), 1.14 (dd,  $J$  = 14.0, 9.3 Hz, 1H), 1.02 (dd,  $J$  = 14.0, 2.1 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.8, 140.7, 133.1, 128.7, 128.2, 118.4, 76.2, 47.3, 44.7 – 44.7 (m), 42.8, 36.9, 32.8, 28.5. HRMS-ESI (m/z) [M+Cl] $^+$  calculated for  $\text{C}_{21}\text{H}_{27}\text{ClFO}$ , 349.1734, found 349.1740.



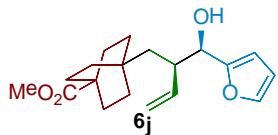
**6g**, RF=0.6 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.41 mmol, 134.3 mg) 81%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 – 7.30 (m, 2H), 7.29 – 7.25 (m, 2H), 5.69 (ddt, J = 13.5, 8.6, 6.8 Hz, 1H), 5.25 (dd, J = 10.2, 1.7 Hz, 1H), 5.20 (dd, J = 17.3, 1.3 Hz, 1H), 4.25 (d, J = 7.8 Hz, 1H), 2.48 (td, J = 9.4, 2.0 Hz, 1H), 2.39 (s, 1H), 1.89 (s, 3H), 1.66 (d, J = 12.0 Hz, 3H), 1.56 (d, J = 11.4 Hz, 3H), 1.36 (d, J = 2.3 Hz, 6H), 1.14 (dd, J = 14.0, 9.3 Hz, 1H), 1.02 (dd, J = 14.0, 2.1 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.7, 140.7, 133.1, 128.7, 128.2, 118.3, 76.2, 47.2, 44.7, 42.8, 36.9, 32.8, 28.5. HRMS-ESI (m/z) [M-H]<sup>+</sup> calculated for C<sub>21</sub>H<sub>26</sub>ClO, 329.1678, found 329.1676.



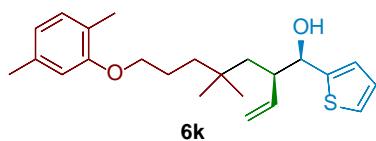
**6h**, RF=0.6 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.44 mmol, 164.4 mg) 88%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48 – 7.43 (m, 2H), 7.22 – 7.17 (m, 2H), 5.67 (ddd, J = 17.2, 10.1, 9.2 Hz, 1H), 5.23 (dd, J = 10.2, 1.7 Hz, 1H), 5.17 (dd, J = 17.3, 1.2 Hz, 1H), 4.22 (d, J = 7.8 Hz, 1H), 2.45 (td, J = 9.4, 2.1 Hz, 1H), 2.38 (s, 1H), 1.86 (s, 3H), 1.63 (d, J = 12.0 Hz, 3H), 1.54 (d, J = 11.4 Hz, 3H), 1.33 (d, J = 2.3 Hz, 6H), 1.12 (dd, J = 14.0, 9.3 Hz, 1H), 1.00 (dd, J = 14.0, 2.1 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.7, 141.3, 131.2, 129.1, 121.3, 118.4, 76.3, 47.3, 44.8, 42.9, 37.0, 32.9, 28.6. HRMS-ESI (m/z) [M-H]<sup>+</sup> calculated for C<sub>21</sub>H<sub>26</sub>BrO, 375.1152, found 375.1153.



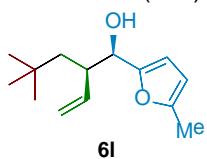
**6i**, RF=0.5 (EA:PE=1:2), column solvent: hexane/EtOAc = 10/1, (0.41 mmol, 154.2 mg) 83%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.81 (s, 1H), 6.77 – 6.70 (m, 2H), 5.95 (dd, J = 4.7, 1.3 Hz, 2H), 5.71 – 5.58 (m, 1H), 5.24 (dd, J = 10.2, 1.6 Hz, 1H), 5.19 (dd, J = 17.2, 1.5 Hz, 1H), 4.13 (d, J = 8.1 Hz, 1H), 3.59 (s, 3H), 2.41 – 2.28 (m, 2H), 1.68 (dd, J = 17.4, 9.7 Hz, 6H), 1.33 – 1.22 (m, 6H), 1.10 (qd, J = 14.2, 5.9 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 178.4, 147.5, 146.9, 141.8, 136.0, 121.0, 118.5, 107.7, 107.3, 100.9, 76.5, 51.5, 48.5, 41.6, 38.8, 30.9, 30.8, 28.4. HRMS-ESI (m/z) [M+Na]<sup>+</sup> calculated for C<sub>22</sub>H<sub>28</sub>NaO<sub>5</sub>, 395.1834, found 395.1823.



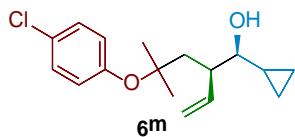
**6j**, RF=0.3 (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, (0.34 mmol, 109.2 mg) 69%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 (d, J = 1.1 Hz, 1H), 6.32 (dd, J = 3.2, 1.8 Hz, 1H), 6.25 (d, J = 3.2 Hz, 1H), 5.65 (ddd, J = 16.8, 10.5, 9.3 Hz, 1H), 5.26 – 5.18 (m, 2H), 4.30 (dd, J = 8.1, 3.4 Hz, 1H), 3.60 (s, 3H), 2.65 (td, J = 9.3, 1.8 Hz, 1H), 2.27 (d, J = 3.4 Hz, 1H), 1.69 (dd, J = 9.7, 6.2 Hz, 6H), 1.32 (dd, J = 9.6, 6.3 Hz, 6H), 1.20 (dd, J = 14.2, 9.2 Hz, 1H), 1.08 (dd, J = 14.2, 2.0 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 178.4, 154.3, 141.9, 141.2, 118.6, 110.0, 108.0, 70.4, 51.5, 45.5, 41.8, 38.8, 31.0, 30.7, 28.4. HRMS-ESI (m/z) [M-OH]<sup>+</sup> calculated for C<sub>19</sub>H<sub>25</sub>O<sub>3</sub>, 301.1798, found 301.1797.



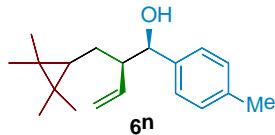
**6k**, RF=0.4 (EA:PE=1:5), column solvent: hexane/EtOAc = 15/1, (0.41 mmol, 152.9 mg) 82%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.27 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 7.01 (dt, *J* = 4.2, 2.1 Hz, 1H), 6.98 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 1H), 6.64 (s, 1H), 5.77 (dt, *J* = 17.8, 9.5 Hz, 1H), 5.32 (d, *J* = 1.7 Hz, 1H), 5.29 (dd, *J* = 4.2, 1.5 Hz, 1H), 4.60 (d, *J* = 7.8 Hz, 1H), 3.87 (qd, *J* = 6.2, 2.5 Hz, 2H), 2.64 – 2.46 (m, 2H), 2.35 (s, 3H), 2.22 (s, 3H), 1.72 – 1.62 (m, 1H), 1.61 – 1.51 (m, 1H), 1.42 – 1.35 (m, 2H), 1.35 – 1.29 (m, 2H), 0.86 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 157.1, 146.0, 141.5, 136.4, 130.3, 126.2, 125.5, 124.9, 123.6, 120.6, 119.0, 112.0, 73.0, 68.5, 49.8, 41.8, 38.4, 33.2, 27.9, 24.0, 21.5, 15.9. HRMS-ESI (m/z) [M-OH]<sup>+</sup> calculated for C<sub>23</sub>H<sub>31</sub>OS, 355.2090, found 355.2085.



**6l**, RF=0.5 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.37 mmol, 81.7 mg) 74%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.14 (d, *J* = 3.0 Hz, 1H), 5.92 – 5.84 (m, 1H), 5.77 – 5.62 (m, 1H), 5.25 (ddd, *J* = 10.1, 2.1, 1.2 Hz, 2H), 4.22 (d, *J* = 8.6 Hz, 1H), 2.66 (qd, *J* = 8.9, 2.1 Hz, 1H), 2.27 (d, *J* = 0.7 Hz, 4H), 1.25 (dd, *J* = 13.9, 8.8 Hz, 1H), 1.16 (dd, *J* = 14.0, 2.2 Hz, 1H), 0.81 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.2, 151.6, 141.8, 118.5, 109.1, 105.8, 70.3, 46.4, 44.3, 31.0, 29.9, 13.5. HRMS-ESI (m/z) [M-OH]<sup>+</sup> calculated for C<sub>14</sub>H<sub>21</sub>O, 205.1587, found 205.1599.

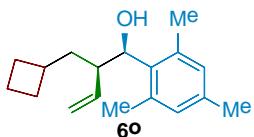


**6m**, RF=0.4 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.43 mmol, 127.8 mg) 87%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.23 – 7.17 (m, 2H), 6.93 – 6.87 (m, 2H), 5.93 – 5.82 (m, 1H), 5.16 (d, *J* = 0.7 Hz, 1H), 5.14 – 5.11 (m, 1H), 2.88 – 2.79 (m, 1H), 2.60 (ddd, *J* = 13.1, 8.6, 4.2 Hz, 1H), 2.13 (dd, *J* = 14.4, 4.1 Hz, 1H), 1.98 (s, 1H), 1.77 (dd, *J* = 14.4, 8.3 Hz, 1H), 1.27 (d, *J* = 4.7 Hz, 6H), 1.01 – 0.89 (m, 1H), 0.60 – 0.47 (m, 2H), 0.36 – 0.27 (m, 1H), 0.27 – 0.20 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.6, 140.5, 128.8, 128.4, 125.2, 116.4, 81.3, 79.5, 46.7, 43.1, 27.5, 26.2, 15.0, 3.3, 2.7. HRMS-ESI (m/z) [M+Na]<sup>+</sup> calculated for C<sub>17</sub>H<sub>23</sub>ClNaO<sub>2</sub>, 317.1284, found 317.1278.

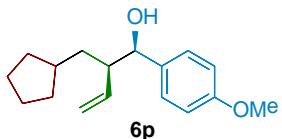


**6n**, RF=0.6 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.36 mmol, 97.5 mg) 72%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.21 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.69 (ddd, *J* = 17.1, 10.1, 9.4 Hz, 1H), 5.25 (dd, *J* = 10.2, 2.0 Hz, 1H), 5.18 (dd, *J* = 17.3, 1.7 Hz, 1H), 4.39 (d, *J* = 7.8 Hz, 1H), 2.34 (s, 3H), 2.28 (ddd, *J* = 17.2, 9.3, 4.8 Hz, 1H), 2.12 (d, *J* =

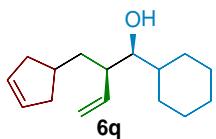
1.4 Hz, 1H), 1.24 – 1.10 (m, 2H), 0.98 (d,  $J$  = 2.4 Hz, 6H), 0.78 (s, 3H), 0.72 (s, 3H), 0.08 – 0.03 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.6, 139.6, 137.1, 128.8, 126.7, 118.3, 76.3, 53.6, 31.6, 26.5, 23.7, 23.6, 21.1, 20.7, 20.5, 17.1, 16.7. HRMS-ESI (m/z) [M-OH] $^+$  calculated for  $\text{C}_{19}\text{H}_{27}$ , 255.2107, found 255.2111.



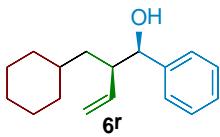
**6o**, RF=0.6 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.43 mmol, 127.8 mg) 72%, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.83 (s, 2H), 5.72 – 5.61 (m, 1H), 5.26 (dd,  $J$  = 10.2, 2.0 Hz, 1H), 5.22 (dd,  $J$  = 17.2, 1.9 Hz, 1H), 4.79 (d,  $J$  = 10.0 Hz, 1H), 2.66 (ddd,  $J$  = 21.1, 9.8, 3.0 Hz, 1H), 2.41 (s, 6H), 2.25 (d,  $J$  = 7.4 Hz, 3H), 2.22 – 2.14 (m, 1H), 1.96 (s, 1H), 1.95 – 1.85 (m, 2H), 1.81 – 1.69 (m, 1H), 1.68 – 1.59 (m, 1H), 1.51 – 1.41 (m, 1H), 1.36 – 1.22 (m, 2H), 1.02 (ddd,  $J$  = 13.0, 9.8, 3.0 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.9, 136.8, 136.5, 134.2, 130.1, 129.9, 118.4, 72.6, 48.6, 37.7, 33.9, 28.8, 27.9, 21.1, 20.7, 18.3. HRMS-ESI (m/z) [M-OH] $^+$  calculated for  $\text{C}_{18}\text{H}_{25}$ , 241.1951, found 241.1946.



**6p**, RF=0.5 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.40 mmol, 105.6 mg) 81%, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (dd,  $J$  = 9.2, 2.4 Hz, 2H), 6.88 (d,  $J$  = 8.6 Hz, 2H), 5.72 – 5.60 (m, 1H), 5.29 – 5.16 (m, 2H), 4.30 (dd,  $J$  = 8.1, 1.4 Hz, 1H), 3.81 (s, 3H), 2.33 (ddd,  $J$  = 11.4, 9.1, 3.5 Hz, 1H), 2.16 (d,  $J$  = 2.0 Hz, 1H), 1.80 – 1.61 (m, 3H), 1.54 – 1.39 (m, 3H), 1.33 (ddd,  $J$  = 15.0, 11.0, 3.9 Hz, 1H), 1.16 (ddd,  $J$  = 17.8, 17.1, 12.4 Hz, 1H), 0.97 (tdd,  $J$  = 16.8, 11.2, 5.8 Hz, 2H), 0.86 – 0.72 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9, 139.8, 134.5, 128.1, 118.5, 113.5, 76.3, 55.1, 52.1, 37.4, 36.8, 33.3, 31.5, 25.0, 24.9. HRMS-ESI (m/z) [M+Na] $^+$  calculated for  $\text{C}_{17}\text{H}_{24}\text{NaO}_2$ , 283.1674, found 283.1670.

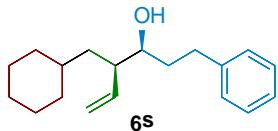


**6q**, RF=0.6 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.31 mmol, 73.0 mg) 62%, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.73 – 5.62 (m, 3H), 5.17 (dd,  $J$  = 10.3, 2.0 Hz, 1H), 5.10 (dd,  $J$  = 17.2, 1.6 Hz, 1H), 3.16 (dd,  $J$  = 10.5, 5.4 Hz, 1H), 2.45 (dt,  $J$  = 14.8, 8.3 Hz, 2H), 2.33 – 2.20 (m, 2H), 2.00 – 1.88 (m, 2H), 1.85 – 1.71 (m, 3H), 1.65 (d,  $J$  = 10.3 Hz, 2H), 1.57 – 1.47 (m, 2H), 1.45 (d,  $J$  = 4.5 Hz, 1H), 1.43 – 1.35 (m, 1H), 1.29 – 1.00 (m, 5H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.8, 130.0, 129.7, 117.5, 77.7, 45.7, 40.2, 39.5, 38.2, 37.8, 35.2, 29.8, 27.33, 26.4, 26.3, 26.0. HRMS-ESI (m/z) [M+H] $^+$  calculated for  $\text{C}_{16}\text{H}_{27}\text{O}$ , 235.2062, found 235.2053.

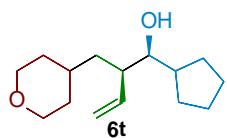


**6r**, RF=0.6 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.34 mmol, 82.7 mg) 68%,

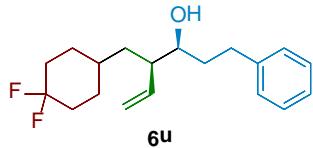
colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.23 (m, 5H), 5.67 (ddd,  $J$  = 17.1, 10.1, 9.4 Hz, 1H), 5.28 (dd,  $J$  = 10.3, 1.9 Hz, 1H), 5.21 (dd,  $J$  = 17.2, 1.5 Hz, 1H), 4.36 (d,  $J$  = 7.8 Hz, 1H), 2.47 (td,  $J$  = 11.2, 3.8 Hz, 1H), 2.21 (s, 1H), 1.74 – 1.50 (m, 5H), 1.31 – 1.03 (m, 5H), 0.95 (ddd,  $J$  = 13.6, 9.8, 3.6 Hz, 1H), 0.84 (ddd,  $J$  = 24.0, 12.5, 3.3 Hz, 1H), 0.60 (qd,  $J$  = 12.4, 3.2 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.4, 139.5, 128.2, 127.5, 126.9, 118.6, 76.8, 49.7, 38.0, 34.6, 34.4, 31.7, 26.5, 26.3, 26.0. HRMS-ESI (m/z) [M-OH] $^+$  calculated for  $\text{C}_{17}\text{H}_{23}$ , 227.1794, found 227.1794.



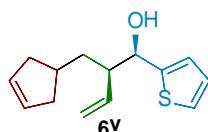
**6s**, RF=0.6 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.40 mmol, 110.0 mg) 81%, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 – 7.27 (m, 2H), 7.26 – 7.18 (m, 3H), 5.63 (ddd,  $J$  = 17.2, 10.2, 9.5 Hz, 1H), 5.22 (dd,  $J$  = 10.3, 2.0 Hz, 1H), 5.13 (dd,  $J$  = 17.2, 1.6 Hz, 1H), 3.45 (ddd,  $J$  = 9.0, 5.6, 3.6 Hz, 1H), 2.85 (ddd,  $J$  = 13.8, 10.3, 5.4 Hz, 1H), 2.69 (ddd,  $J$  = 13.7, 10.1, 6.4 Hz, 1H), 2.24 – 2.15 (m, 1H), 1.90 – 1.81 (m, 1H), 1.80 – 1.59 (m, 7H), 1.32 – 1.11 (m, 6H), 0.94 (td,  $J$  = 12.5, 6.4 Hz, 1H), 0.77 (dt,  $J$  = 12.5, 7.9 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.3, 138.9, 128.4, 128.3, 125.7, 73.1, 47.5, 38.4, 36.5, 34.7, 34.5, 32.2, 32.1, 26.6, 26.3, 26.1. HRMS-ESI (m/z) [M+H] $^+$  calculated for  $\text{C}_{19}\text{H}_{29}\text{O}$ , 273.2218, found 273.2210.



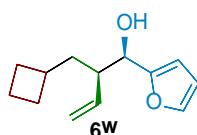
**6t**, RF=0.5 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.35 mmol, 84.4 mg) 71%, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.70 (ddd,  $J$  = 17.3, 10.2, 9.5 Hz, 1H), 5.16 (dd,  $J$  = 10.3, 2.0 Hz, 1H), 5.06 (dd,  $J$  = 17.3, 2.0 Hz, 1H), 3.98 – 3.87 (m, 2H), 3.35 (qd,  $J$  = 11.6, 2.2 Hz, 2H), 3.25 (dd,  $J$  = 7.8, 3.8 Hz, 1H), 2.29 – 2.20 (m, 1H), 2.00 – 1.87 (m, 1H), 1.81 – 1.71 (m, 1H), 1.69 – 1.58 (m, 4H), 1.58 – 1.48 (m, 4H), 1.48 – 1.41 (m, 2H), 1.39 – 1.27 (m, 3H), 1.24 – 1.11 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.2, 117.3, 78.4, 68.0, 68.0, 44.8, 43.9, 38.6, 33.8, 32.4, 32.0, 28.9, 28.7, 25.5, 25.5. HRMS-ESI (m/z) [M+H] $^+$  calculated for  $\text{C}_{15}\text{H}_{27}\text{O}_2$ , 239.2011, found 239.2001.



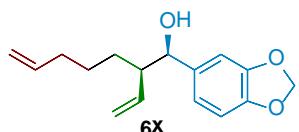
**6u**, RF=0.6 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.38 mmol, 116.1 mg) 75%, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 – 7.28 (m, 2H), 7.23 (t,  $J$  = 7.7 Hz, 3H), 5.65 (dt,  $J$  = 17.3, 9.8 Hz, 1H), 5.24 (dd,  $J$  = 10.2, 1.7 Hz, 1H), 5.15 (d,  $J$  = 17.2 Hz, 1H), 3.50 – 3.43 (m, 1H), 2.90 – 2.79 (m, 1H), 2.75 – 2.65 (m, 1H), 2.16 (td,  $J$  = 9.6, 5.2 Hz, 1H), 2.07 (d,  $J$  = 6.7 Hz, 2H), 1.85 (ddt,  $J$  = 16.5, 13.0, 5.1 Hz, 2H), 1.78 – 1.57 (m, 5H), 1.36 (dt,  $J$  = 14.0, 7.6 Hz, 4H), 1.22 – 1.08 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.0, 138.3, 128.4, 128.3, 125.8, 118.3, 73.1, 47.8, 36.7 (d,  $J$  = 2.0 Hz), 36.5, 33.3 (dd,  $J$  = 46.4, 21.1 Hz), 32.9, 32.1, 30.0 (d,  $J$  = 9.4 Hz), 27.7 (d,  $J$  = 9.5 Hz). HRMS-ESI (m/z) [M+H] $^+$  calculated for  $\text{C}_{19}\text{H}_{27}\text{F}_2\text{O}$ , 309.2030, found 309.2020.



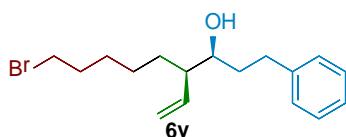
**6v**, RF=0.4 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.39 mmol, 90.9 mg) 78%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.27 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.00 – 6.94 (m, 2H), 5.69 (ddd, *J* = 17.0, 10.2, 9.4 Hz, 1H), 5.64 – 5.58 (m, 2H), 5.32 – 5.23 (m, 2H), 4.67 (d, *J* = 7.9 Hz, 1H), 2.50 – 2.30 (m, 4H), 2.29 – 2.17 (m, 1H), 1.92 – 1.76 (m, 2H), 1.44 (ddd, *J* = 13.4, 10.8, 4.6 Hz, 1H), 1.33 – 1.25 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.2, 138.9, 129.9, 129.7, 126.3, 125.2, 124.9, 119.3, 72.7, 52.5, 39.5, 37.9, 37.3, 35.1. HRMS-ESI (m/z) [M-OH]<sup>+</sup> calculated for C<sub>14</sub>H<sub>17</sub>S, 217.1045, found 217.1042.



**6w**, RF=0.5 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.32 mmol, 65.7 mg) 64%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38 (dd, *J* = 8.3, 7.3 Hz, 1H), 6.33 (dt, *J* = 12.6, 6.4 Hz, 1H), 6.26 (d, *J* = 3.2 Hz, 1H), 5.61 (dq, *J* = 16.3, 9.8 Hz, 1H), 5.31 – 5.11 (m, 2H), 4.43 (dd, *J* = 7.8, 3.8 Hz, 1H), 2.47 (ddd, *J* = 17.6, 9.5, 4.1 Hz, 1H), 2.27 (tt, *J* = 16.5, 8.3 Hz, 1H), 2.13 (d, *J* = 3.9 Hz, 1H), 1.97 (dtd, *J* = 11.1, 8.3, 3.0 Hz, 2H), 1.86 – 1.66 (m, 2H), 1.60 – 1.43 (m, 2H), 1.37 (ddd, *J* = 13.4, 9.9, 5.9 Hz, 1H), 1.27 (ddd, *J* = 13.3, 9.2, 4.1 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.9, 141.9, 138.8, 118.5, 110.0, 107.3, 70.0, 48.1, 37.8, 33.7, 28.7, 28.0, 18.3. HRMS-ESI (m/z) [M-OH]<sup>+</sup> calculated for C<sub>13</sub>H<sub>17</sub>O, 189.1274, found 189.1275.

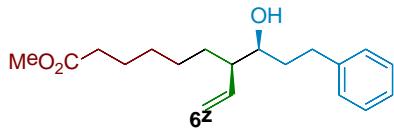


**6x**, RF=0.3 (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, (0.38 mmol, 99.4 mg) 76%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.84 (s, 1H), 6.76 (s, 2H), 5.95 (dd, *J* = 2.7, 1.4 Hz, 2H), 5.77 – 5.67 (m, 1H), 5.67 – 5.59 (m, 1H), 5.27 (dd, *J* = 10.3, 1.9 Hz, 1H), 5.20 (dd, *J* = 17.1, 1.6 Hz, 1H), 4.96 – 4.85 (m, 2H), 4.29 (d, *J* = 8.1 Hz, 1H), 2.23 (qd, *J* = 8.8, 4.6 Hz, 1H), 2.15 (s, 1H), 2.04 – 1.94 (m, 1H), 1.89 (ddd, *J* = 14.7, 10.7, 6.7 Hz, 1H), 1.44 – 1.32 (m, 1H), 1.28 – 1.21 (m, 1H), 1.20 – 1.14 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.6, 147.0, 139.3, 138.6, 136.4, 120.5, 118.9, 114.3, 107.8, 107.1, 100.9, 76.5, 52.7, 33.5, 29.9, 26.4. HRMS-ESI (m/z) [M+Na]<sup>+</sup> calculated for C<sub>16</sub>H<sub>20</sub>NaO<sub>3</sub>, 283.1310, found 283.1304.

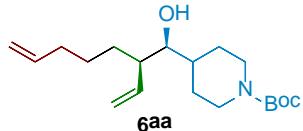


**6y**, RF=0.6 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.33 mmol, 108.5 mg) 67%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32 – 7.26 (m, 2H), 7.23 – 7.16 (m, 3H), 5.63 (ddd, *J* = 17.2, 10.2, 9.4 Hz, 1H), 5.20 (dd, *J* = 10.3, 2.0 Hz, 1H), 5.11 (dd, *J* = 17.2, 1.9 Hz, 1H), 3.48 (ddd, *J* = 8.9, 5.3, 3.7 Hz, 1H), 3.39 (t, *J* = 6.8 Hz, 2H), 2.88 – 2.77 (m, 1H), 2.67 (ddd, *J* = 13.7, 9.8, 6.6 Hz, 1H), 2.07 – 1.98 (m, 1H), 1.89 – 1.78 (m, 3H), 1.77 – 1.67 (m, 1H), 1.58 (s, 1H),

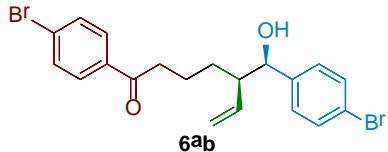
1.50 – 1.41 (m, 2H), 1.40 – 1.28 (m, 3H), 1.23 (tdd,  $J$  = 9.1, 6.2, 3.0 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.2, 138.4, 128.4, 128.3, 125.7, 118.2, 72.9, 50.4, 36.5, 33.8, 32.6, 32.1, 30.4, 28.0, 26.4. HRMS-ESI (m/z)  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{17}\text{H}_{26}\text{BrO}$ , 325.1167, found 325.1152.



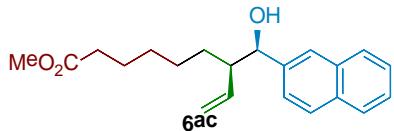
**6z**, RF=0.3 (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, (0.30 mmol, 91.0 mg) 60%, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.25 (m, 2H), 7.19 (m, 3H), 5.68 – 5.54 (m, 1H), 5.19 (dd,  $J$  = 10.3, 2.0 Hz, 1H), 5.09 (dd,  $J$  = 17.2, 1.5 Hz, 1H), 3.66 (s, 3H), 3.47 (ddd,  $J$  = 8.9, 5.4, 3.6 Hz, 1H), 2.86 – 2.78 (m, 1H), 2.66 (ddd,  $J$  = 13.7, 9.9, 6.6 Hz, 1H), 2.29 (t,  $J$  = 7.5 Hz, 2H), 2.05 – 1.96 (m, 1H), 1.87 – 1.77 (m, 1H), 1.76 – 1.65 (m, 1H), 1.64 – 1.54 (m, 3H), 1.43 (dd,  $J$  = 12.9, 4.9 Hz, 1H), 1.26 (ddt,  $J$  = 12.6, 9.2, 6.6 Hz, 5H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 142.2, 138.6, 128.4, 128.3, 125.7, 118.1, 72.9, 51.4, 50.4, 36.5, 34.0, 32.1, 30.4, 29.0, 26.9, 24.8. HRMS-ESI (m/z)  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{19}\text{H}_{28}\text{NaO}_3$ , 327.1936, found 327.1930.



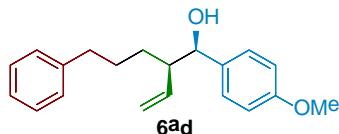
**6aa**, RF=0.2 (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, (0.41 mmol, 134.1 mg) 83%, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.77 (ddt,  $J$  = 16.9, 10.2, 6.7 Hz, 1H), 5.66 (dt,  $J$  = 17.3, 9.9 Hz, 1H), 5.17 (dd,  $J$  = 10.3, 1.8 Hz, 1H), 5.07 (dd,  $J$  = 17.2, 1.7 Hz, 1H), 4.98 (dd,  $J$  = 17.1, 1.7 Hz, 1H), 4.93 (d,  $J$  = 10.2 Hz, 1H), 4.11 (s, 2H), 3.19 (dd,  $J$  = 11.1, 4.9 Hz, 1H), 2.63 (s, 2H), 2.22 – 2.10 (m, 1H), 2.10 – 1.95 (m, 2H), 1.76 (dd,  $J$  = 29.0, 15.1 Hz, 1H), 1.59 (d,  $J$  = 4.9 Hz, 1H), 1.56 – 1.48 (m, 2H), 1.44 (s, 9H), 1.42 – 1.33 (m, 3H), 1.33 – 1.20 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.7, 138.6, 138.0, 117.8, 114.5, 79.2, 76.8, 46.4, 44.1 – 43.4 (m), 39.0, 33.6, 30.5, 28.4, 27.3 – 27.0 (m), 26.5. HRMS-ESI (m/z)  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{19}\text{H}_{33}\text{NNaO}_3$ , 346.2358, found 346.2350.



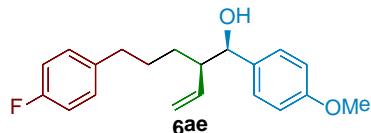
**6ab**, RF=0.2 (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, (0.38 mmol, 173.4 mg) 77%, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J$  = 8.4 Hz, 2H), 7.58 (d,  $J$  = 8.4 Hz, 2H), 7.45 (d,  $J$  = 8.3 Hz, 2H), 7.19 (d,  $J$  = 8.3 Hz, 2H), 5.65 (dt,  $J$  = 17.2, 9.7 Hz, 1H), 5.27 (dd,  $J$  = 10.1, 1.0 Hz, 1H), 5.19 (d,  $J$  = 17.3 Hz, 1H), 4.41 (dd,  $J$  = 7.4, 1.5 Hz, 1H), 2.91 – 2.72 (m, 2H), 2.33 – 2.21 (m, 2H), 1.76 (qd,  $J$  = 14.4, 6.5 Hz, 1H), 1.53 (dt,  $J$  = 14.3, 8.0 Hz, 1H), 1.34 – 1.19 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.8, 141.2, 138.2, 135.5, 131.8, 131.3, 129.4, 128.5, 128.1, 121.4, 119.5, 75.8, 52.6, 38.2, 29.9, 21.8. HRMS-ESI (m/z)  $[\text{M}-\text{OH}]^+$  calculated for  $\text{C}_{20}\text{H}_{19}\text{Br}_2\text{O}$ , 432.9797, found 432.9796.



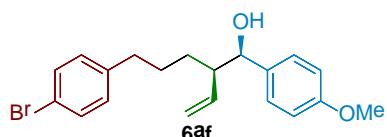
**6ac**, RF=0.4 (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, (0.30 mmol, 99.1 mg) 61%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 (d, *J* = 9.0 Hz, 3H), 7.75 (s, 1H), 7.54 – 7.40 (m, 3H), 5.75 – 5.62 (m, 1H), 5.27 (dt, *J* = 8.2, 4.1 Hz, 1H), 5.21 (dd, *J* = 17.1, 1.5 Hz, 1H), 4.55 (dd, *J* = 7.8, 2.0 Hz, 1H), 3.62 (s, 3H), 2.45 – 2.36 (m, 1H), 2.34 (d, *J* = 2.3 Hz, 1H), 2.21 (t, *J* = 7.5 Hz, 2H), 1.58 – 1.45 (m, 2H), 1.36 – 1.26 (m, 1H), 1.26 – 1.17 (m, 3H), 1.17 – 1.10 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.1, 139.8, 139.1, 133.1, 133.0, 128.0, 127.9, 127.6, 126.0, 126.0, 125.7, 124.6, 118.9, 76.7, 52.5, 51.3, 33.9, 30.2, 28.8, 26.8, 24.7. HRMS-ESI (m/z) [M-OH]<sup>+</sup> calculated for C<sub>21</sub>H<sub>25</sub>O<sub>2</sub>, 309.1849, found 309.1848.



**6ad**, RF=0.4 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.36 mmol, 106.6 mg) 72%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.24 (dd, *J* = 13.7, 5.3 Hz, 4H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 7.0 Hz, 2H), 6.91 – 6.86 (m, 2H), 5.71 – 5.60 (m, 1H), 5.26 (dd, *J* = 10.3, 1.9 Hz, 1H), 5.20 (dd, *J* = 17.1, 1.7 Hz, 1H), 4.33 (d, *J* = 8.1 Hz, 1H), 3.82 (s, 3H), 2.59 – 2.49 (m, 1H), 2.46 – 2.36 (m, 1H), 2.30 (ddd, *J* = 17.5, 8.9, 5.1 Hz, 1H), 2.12 (s, 1H), 1.70 – 1.52 (m, 1H), 1.44 (ddt, *J* = 13.3, 9.5, 6.2 Hz, 1H), 1.30 – 1.14 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.1, 142.4, 139.4, 134.5, 128.3, 128.2, 128.0, 125.6, 118.8, 113.6, 76.2, 55.2, 52.7, 35.6, 30.1, 29.1. HRMS-ESI (m/z) [M-OH]<sup>+</sup> calculated for C<sub>20</sub>H<sub>23</sub>O, 279.1743, found 279.1742.

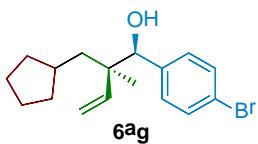


**6ae**, RF=0.4 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.37 mmol, 117.6 mg) 75%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.25 – 7.20 (m, 2H), 7.03 – 6.96 (m, 2H), 6.94 – 6.85 (m, 4H), 5.71 – 5.59 (m, 1H), 5.27 (dd, *J* = 10.2, 1.9 Hz, 1H), 5.20 (dd, *J* = 17.1, 1.5 Hz, 1H), 4.32 (d, *J* = 8.1 Hz, 1H), 3.82 (s, 3H), 2.54 – 2.45 (m, 1H), 2.37 (ddd, *J* = 13.9, 10.3, 5.7 Hz, 1H), 2.28 (ddd, *J* = 17.4, 8.8, 5.4 Hz, 1H), 2.13 (s, 1H), 1.65 – 1.50 (m, 1H), 1.41 (ddt, *J* = 13.2, 9.4, 7.9 Hz, 1H), 1.22 – 1.12 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.1 (d, *J* = 243.2 Hz), 159.1, 139.3, 137.9, 134.4, 129.5 (d, *J* = 7.8 Hz), 128.0, 118.9, 114.8 (d, *J* = 21.1 Hz), 113.6, 76.2, 55.2, 52.7, 34.7, 29.8, 29.1. HRMS-ESI (m/z) [M-OH]<sup>+</sup> calculated for C<sub>20</sub>H<sub>22</sub>FO, 297.1649, found 297.1643.

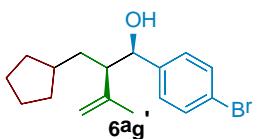


**6af**, RF=0.4 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.37 mmol, 138.5 mg) 74%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 – 7.31 (m, 2H), 7.25 – 7.20 (m, 2H), 6.93 (m, 2H), 6.90 – 6.85 (m, 2H), 5.70 – 5.58 (m, 1H), 5.26 (dd, *J* = 10.2, 1.9 Hz, 1H), 5.20 (dd, *J* = 17.1, 1.6 Hz, 1H), 4.32 (d, *J* = 8.1 Hz, 1H), 3.82 (s, 3H), 2.53 – 2.44 (m, 1H), 2.41 – 2.33 (m, 1H), 2.31 – 2.23 (m, 1H), 2.14 (s, 1H), 1.61 – 1.51 (m, 1H), 1.47 – 1.36 (m, 1H), 1.22 – 1.14 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.1, 141.3, 139.3, 134.4, 131.2, 130.1, 128.1, 119.3,

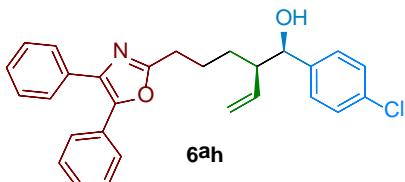
118.9, 113.7, 76.2, 55.3, 52.7, 34.9, 29.8, 28.8. HRMS-ESI (m/z) [M-OH]<sup>+</sup> calculated for C<sub>20</sub>H<sub>22</sub>BrO, 357.0849, found 357.0846.



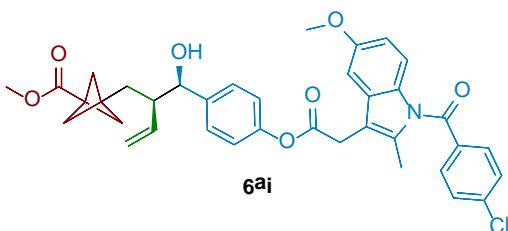
**6ag**, RF=0.6 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.17 mmol, 56.4 mg) 35%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 (p, J = 4.8, 4.2 Hz, 2H), 7.17 (dt, J = 8.6, 4.5 Hz, 2H), 5.86 (ddt, J = 16.3, 8.8, 4.2 Hz, 1H), 5.34 – 5.21 (m, 1H), 5.08 (dt, J = 17.6, 4.3 Hz, 1H), 4.40 – 4.27 (m, 1H), 2.09 (s, 1H), 1.73 (tdd, J = 21.6, 10.3, 5.5 Hz, 3H), 1.55 (dtp, J = 13.6, 9.2, 5.1, 4.1 Hz, 3H), 1.48 – 1.38 (m, 2H), 1.28 (ddt, J = 13.5, 9.2, 3.9 Hz, 1H), 1.07 (t, J = 4.7 Hz, 1H), 1.00 (ddq, J = 11.1, 7.1, 3.4, 3.0 Hz, 1H), 0.91 (t, J = 4.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.4, 139.3, 130.5, 129.8, 121.2, 115.8, 79.6, 46.3, 44.1, 36.3, 35.0, 34.7, 25.0, 25.0, 16.6. HRMS-ESI (m/z) [M-H]<sup>-</sup> calculated for C<sub>17</sub>H<sub>22</sub>BrO, 321.0854, found 321.0874.



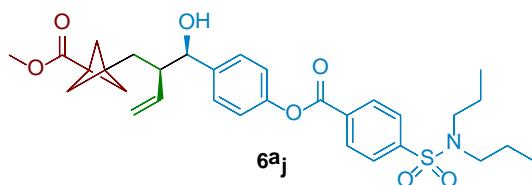
**6ag'**, RF=0.6 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.12 mmol, 37.6 mg) 23%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 5.08 (t, J = 1.8 Hz, 1H), 4.99 (d, J = 2.1 Hz, 1H), 4.32 (d, J = 9.4 Hz, 1H), 2.34 (ddt, J = 12.3, 9.4, 4.2 Hz, 1H), 2.30 (s, 1H), 1.74 (s, 3H), 1.66 – 1.52 (m, 3H), 1.44 (dddt, J = 15.4, 12.4, 6.7, 3.6 Hz, 5H), 0.93 (q, J = 8.0, 7.2 Hz, 1H), 0.73 (ddt, J = 12.5, 6.2, 3.0 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.7, 141.7, 131.3, 128.9, 121.4, 116.4, 74.7, 55.4, 37.4, 35.0, 33.42, 31.4, 25.0, 24.9, 17.9. HRMS-ESI (m/z) [M-H]<sup>-</sup> calculated for C<sub>17</sub>H<sub>22</sub>BrO, 321.0854, found 321.0879.



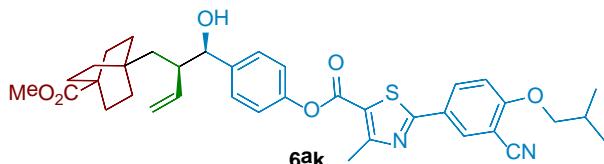
**6ah**, RF=0.5 (EA:PE=1:2), column solvent: hexane/EtOAc = 10/1, (0.40 mmol, 179.4 mg) 81%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.56 (m, 2H), 7.54 – 7.49 (m, 2H), 7.40 – 7.26 (m, 6H), 7.26 – 7.20 (m, 4H), 5.63 (dt, J = 17.2, 9.7 Hz, 1H), 5.25 (dd, J = 10.2, 1.4 Hz, 1H), 5.18 (d, J = 17.2 Hz, 1H), 4.40 (d, J = 7.4 Hz, 1H), 2.73 (dd, J = 11.0, 4.0 Hz, 2H), 2.43 (s, 1H), 2.30 (td, J = 14.2, 8.9 Hz, 1H), 1.92 – 1.79 (m, 1H), 1.74 – 1.60 (m, 1H), 1.40 – 1.28 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.1, 145.0, 140.7, 138.3, 134.9, 133.2, 132.4, 129.0, 128.6, 128.5, 128.3, 128.3, 128.2, 127.9, 127.8, 126.3, 119.4, 75.7, 52.2, 29.7, 27.8, 24.6. HRMS-ESI (m/z) [M+H]<sup>+</sup> calculated for C<sub>28</sub>H<sub>27</sub>CINO<sub>2</sub>, 444.1730, found 444.1721.



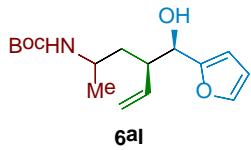
**6ai**, RF=0.4 (EA:PE=1:2), column solvent: hexane/EtOAc = 10/1, (0.36 mmol, 231.8 mg) 72%, white solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 – 7.64 (m, 2H), 7.49 – 7.45 (m, 2H), 7.31 – 7.25 (m, 2H), 7.05 (t,  $J$  = 5.6 Hz, 3H), 6.92 – 6.86 (m, 1H), 6.69 (dd,  $J$  = 9.0, 2.5 Hz, 1H), 5.66 – 5.55 (m, 1H), 5.24 (dd,  $J$  = 10.3, 1.6 Hz, 1H), 5.18 (dd,  $J$  = 17.2, 1.2 Hz, 1H), 4.37 (dd,  $J$  = 7.2, 1.9 Hz, 1H), 3.90 (s, 2H), 3.83 (s, 3H), 3.62 (s, 3H), 2.45 (s, 3H), 2.34 (dd,  $J$  = 8.7, 7.3 Hz, 1H), 2.28 (d,  $J$  = 2.1 Hz, 1H), 1.86 (s, 6H), 1.44 (d,  $J$  = 7.0 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.4, 169.2, 168.2, 156.0, 150.0, 139.6, 139.3, 139.0, 136.1, 133.7, 131.1, 130.7, 130.4, 129.1, 127.8, 121.1, 119.2, 114.9, 111.9, 111.7, 101.1, 75.7, 55.6, 52.2, 51.4, 50.4, 39.1, 38.4, 31.7, 30.5, 13.3. HRMS-ESI (m/z) [M+Na] $^+$  calculated for  $\text{C}_{37}\text{H}_{36}\text{ClNNaO}_7$ , 664.2078, found 664.2076.



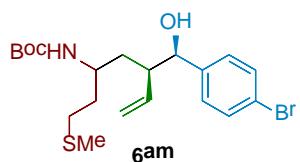
**6aj**, RF=0.3 (EA:PE=1:2), column solvent: hexane/EtOAc = 5/1, (0.37 mmol, 207.4 mg) 73%, white solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.31 (d,  $J$  = 8.4 Hz, 2H), 7.94 (d,  $J$  = 8.4 Hz, 2H), 7.37 (d,  $J$  = 8.5 Hz, 2H), 7.20 (d,  $J$  = 8.6 Hz, 2H), 5.64 (dt,  $J$  = 17.3, 9.9 Hz, 1H), 5.27 (dd,  $J$  = 10.3, 1.2 Hz, 1H), 5.21 (d,  $J$  = 17.2 Hz, 1H), 4.43 (dd,  $J$  = 7.0, 1.6 Hz, 1H), 3.63 (s, 3H), 3.16 – 3.08 (m, 4H), 2.44 – 2.34 (m, 1H), 2.32 – 2.28 (m, 1H), 1.88 (s, 6H), 1.62 – 1.52 (m, 4H), 1.50 (t,  $J$  = 6.2 Hz, 2H), 0.88 (t,  $J$  = 7.4 Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5, 163.8, 150.0, 144.97, 140.0, 139.1, 132.8, 130.7, 128.1, 127.2, 121.2, 119.4, 75.8, 52.3, 51.5, 50.5, 49.9, 39.2, 38.5, 31.8, 21.9, 11.1. HRMS-ESI (m/z) [M+Na] $^+$  calculated for  $\text{C}_{31}\text{H}_{39}\text{NNaO}_7\text{S}$ , 592.2345, found 592.2329.



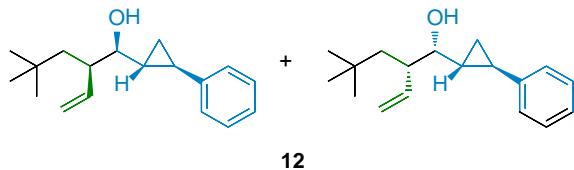
**6ak**, RF=0.4 (EA:PE=1:2), column solvent: hexane/EtOAc = 5/1, (0.29 mmol, 188.7 mg) 59%, white solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.20 (d,  $J$  = 2.3 Hz, 1H), 8.11 (dd,  $J$  = 8.8, 2.3 Hz, 1H), 7.35 (d,  $J$  = 8.5 Hz, 2H), 7.18 (d,  $J$  = 8.5 Hz, 2H), 7.02 (d,  $J$  = 8.9 Hz, 1H), 5.66 (dt,  $J$  = 17.3, 9.8 Hz, 1H), 5.23 (dd,  $J$  = 10.2, 1.5 Hz, 1H), 5.17 (d,  $J$  = 17.2 Hz, 1H), 4.29 (t,  $J$  = 6.7 Hz, 1H), 3.90 (d,  $J$  = 6.5 Hz, 2H), 3.59 (s, 3H), 2.81 (s, 3H), 2.48 – 2.37 (m, 2H), 2.20 (dp,  $J$  = 13.3, 6.7 Hz, 1H), 1.73 – 1.63 (m, 6H), 1.34 – 1.23 (m, 6H), 1.16 (dd,  $J$  = 11.4, 5.7 Hz, 2H), 1.11 – 1.03 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.4, 168.0, 162.9, 162.6, 160.2, 149.5, 141.3, 140.1, 132.6, 132.1, 128.3, 125.8, 121.1, 120.6, 118.5, 115.2, 112.6, 103.0, 76.4, 75.7, 51.4, 48.3, 41.5, 38.8, 31.0, 30.8, 28.4, 28.1, 18.9, 17.6. HRMS-ESI (m/z) [M+H] $^+$  calculated for  $\text{C}_{37}\text{H}_{43}\text{N}_2\text{O}_6\text{S}$ , 643.2842, found 643.2838.



**6al**, RF=0.5 (EA:PE=1:2), column solvent: hexane/EtOAc = 10/1, (0.33 mmol, 99.5 mg) 67%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35 (dt, *J* = 6.1, 3.0 Hz, 1H), 6.30 (dq, *J* = 7.4, 2.7 Hz, 1H), 6.28 – 6.15 (m, 1H), 5.77 – 5.57 (m, 1H), 5.28 – 5.13 (m, 2H), 4.51 (dh, *J* = 8.8, 5.0 Hz, 1H), 4.32 (d, *J* = 28.5 Hz, 1H), 3.64 (s, 1H), 2.66 (d, *J* = 11.1 Hz, 1H), 2.61 – 2.41 (m, 1H), 1.61 – 1.47 (m, 1H), 1.41 (d, *J* = 6.2 Hz, 9H), 1.22 – 1.12 (m, 1H), 1.05 (dp, *J* = 11.9, 6.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.2, 155.0, 154.7, 154.6, 141.9, 141.8, 137.8, 137.7, 119.1, 118.9, 110.0, 110.0, 107.4, 107.4, 78.9, 69.9, 67.1, 47.0, 46.5, 44.4, 44.2, 37.8, 37.8, 28.3, 22.0, 20.2. HRMS-ESI (m/z) [M+Na]<sup>+</sup> calculated for C<sub>16</sub>H<sub>25</sub>NNaO<sub>4</sub>, 318.1681, found 318.1679.

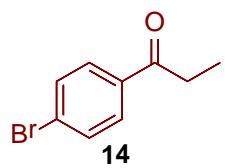


**6am**, RF=0.6 (EA:PE=1:2), column solvent: hexane/EtOAc = 10/1, (0.31 mmol, 140.9 mg) 63%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 5.68 (dt, *J* = 18.1, 9.5 Hz, 1H), 5.19 (d, *J* = 10.3 Hz, 1H), 5.08 (d, *J* = 17.2 Hz, 1H), 4.58 (d, *J* = 5.9 Hz, 1H), 4.34 (d, *J* = 9.5 Hz, 1H), 3.76 (d, *J* = 11.0 Hz, 1H), 2.41 (dd, *J* = 31.5, 22.2, 12.8, 6.4 Hz, 4H), 2.06 (s, 3H), 1.83 – 1.68 (m, 1H), 1.42 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.5, 141.4, 137.5, 131.1, 128.3, 121.2, 118.7, 79.3, 74.6, 48.8, 48.0, 36.3, 34.3, 30.4, 28.3, 15.6. HRMS-ESI (m/z) [M+Na]<sup>+</sup> calculated for C<sub>20</sub>H<sub>30</sub>BrNNaO<sub>3</sub>S, 466.1027, found 466.1020.

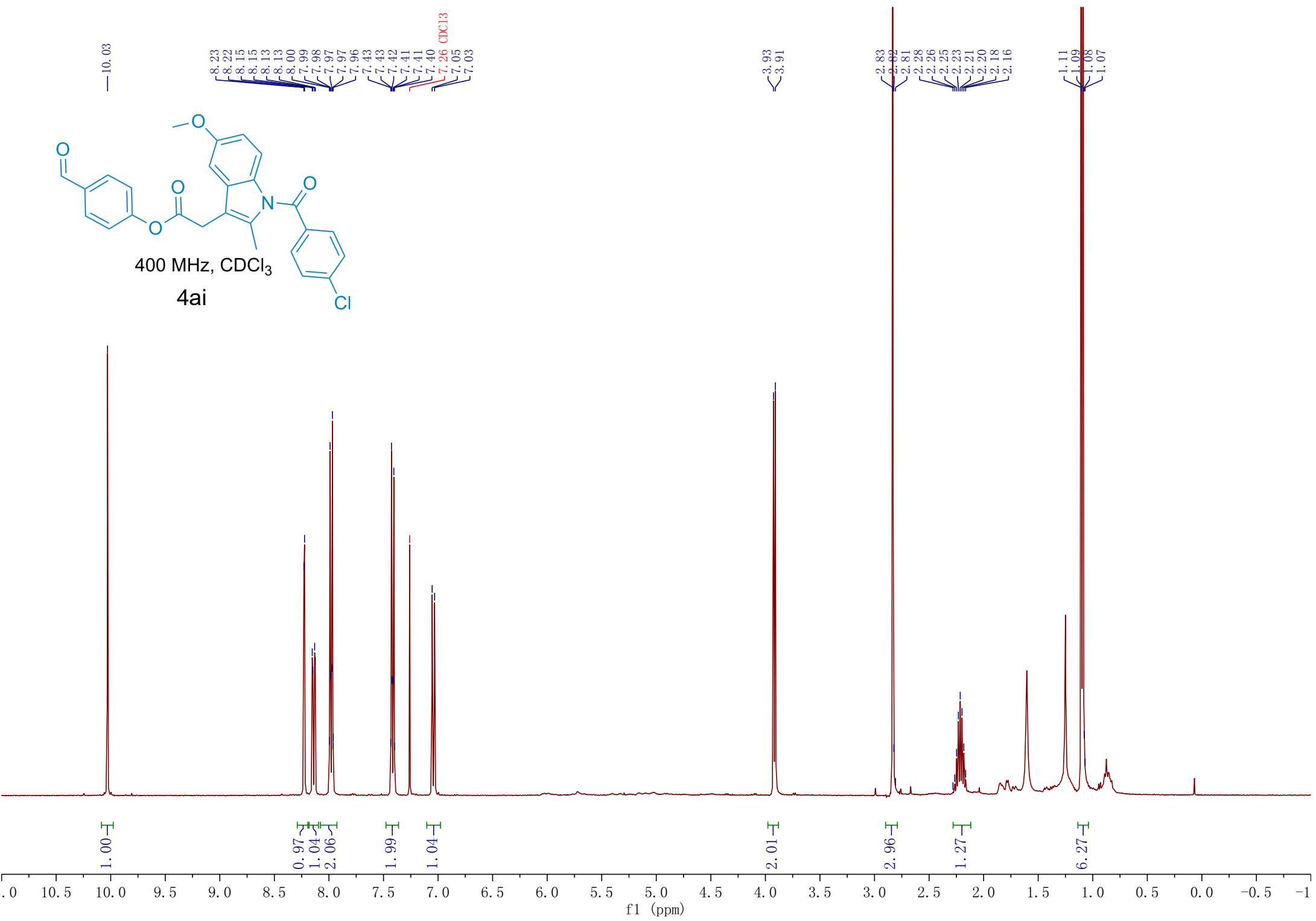


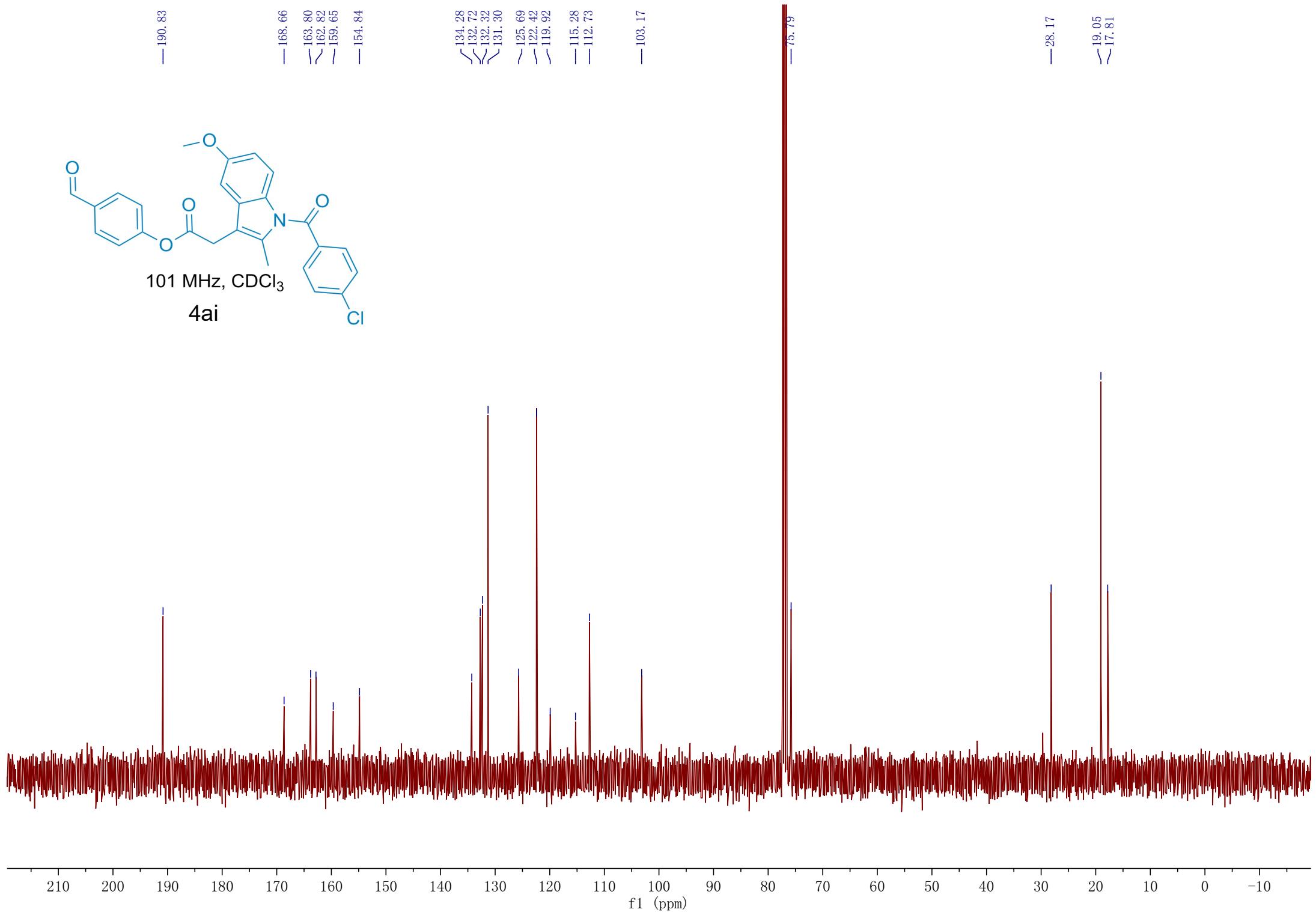
**Minor isomer of 12**, RF=0.6 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.18 mmol, 46.1 mg) 36%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.22 (t, *J* = 7.5 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 2H), 5.84 – 5.68 (m, 1H), 5.13 (s, 1H), 5.09 (dt, *J* = 6.3, 3.1 Hz, 1H), 2.94 (s, 1H), 2.39 – 2.31 (m, 1H), 1.94 – 1.88 (m, 1H), 1.73 (t, *J* = 4.6 Hz, 1H), 1.55 (dd, *J* = 13.9, 2.6 Hz, 1H), 1.40 (dd, *J* = 14.0, 9.0 Hz, 1H), 1.24 (tt, *J* = 8.3, 5.7 Hz, 1H), 1.00 – 0.91 (m, 2H), 0.89 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.7, 141.3, 128.2, 125.8, 125.4, 116.8, 79.0, 47.3, 44.4, 31.1, 30.1, 27.2, 20.8, 14.2. HRMS-ESI (m/z) [M+Na]<sup>+</sup> calculated for C<sub>18</sub>H<sub>26</sub>NaO, 281.1881, found 281.1879.

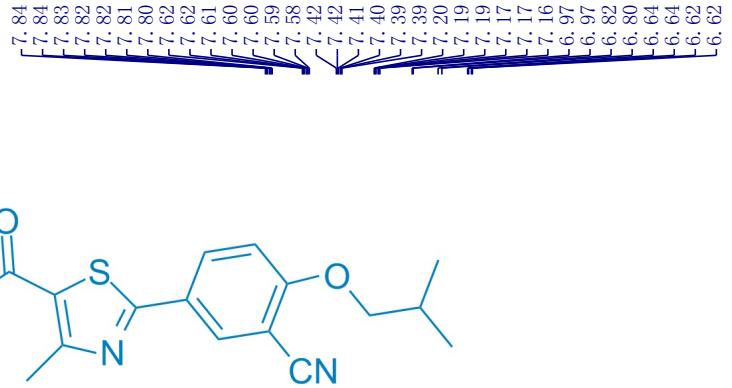
**Major isomer of 12**, RF=0.5 (EA:PE=1:5), column solvent: hexane/EtOAc = 20/1, (0.23 mmol, 58.5 mg) 45%, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.25 (dd, *J* = 9.7, 5.4 Hz, 2H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 2H), 5.74 (dt, *J* = 17.3, 9.8 Hz, 1H), 5.12 (dd, *J* = 10.2, 1.5 Hz, 1H), 5.10 – 5.02 (m, 1H), 2.95 (t, *J* = 6.8 Hz, 1H), 2.35 (ddd, *J* = 14.9, 8.8, 2.1 Hz, 1H), 1.88 – 1.81 (m, 1H), 1.79 (s, 1H), 1.58 (dd, *J* = 13.9, 2.2 Hz, 1H), 1.36 (dd, *J* = 13.9, 9.2 Hz, 1H), 1.25 (tt, *J* = 8.3, 5.3 Hz, 1H), 1.02 (dt, *J* = 8.9, 5.3 Hz, 1H), 0.96 (dt, *J* = 8.6, 5.1 Hz, 1H), 0.84 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.2, 141.7, 128.2, 125.7, 125.5, 117.1, 78.5, 47.9, 44.1, 31.0, 30.0, 27.1, 22.1, 13.0. HRMS-ESI (m/z) [M+Na]<sup>+</sup> calculated for C<sub>18</sub>H<sub>26</sub>NaO, 281.1881, found 281.1880.



**14**, RF=0.7 (EA:PE=1:5), column solvent: hexane/EtOAc = 30/1, white solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.87 – 7.76 (m, 2H), 7.66 – 7.51 (m, 2H), 2.96 (q, *J* = 7.2 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 199.68, 135.59, 131.83, 129.49, 127.95, 31.75, 8.10. HRMS-ESI (m/z) [M+H]<sup>+</sup> calculated for C<sub>9</sub>H<sub>10</sub>BrO 212.9915, found 212.9910.

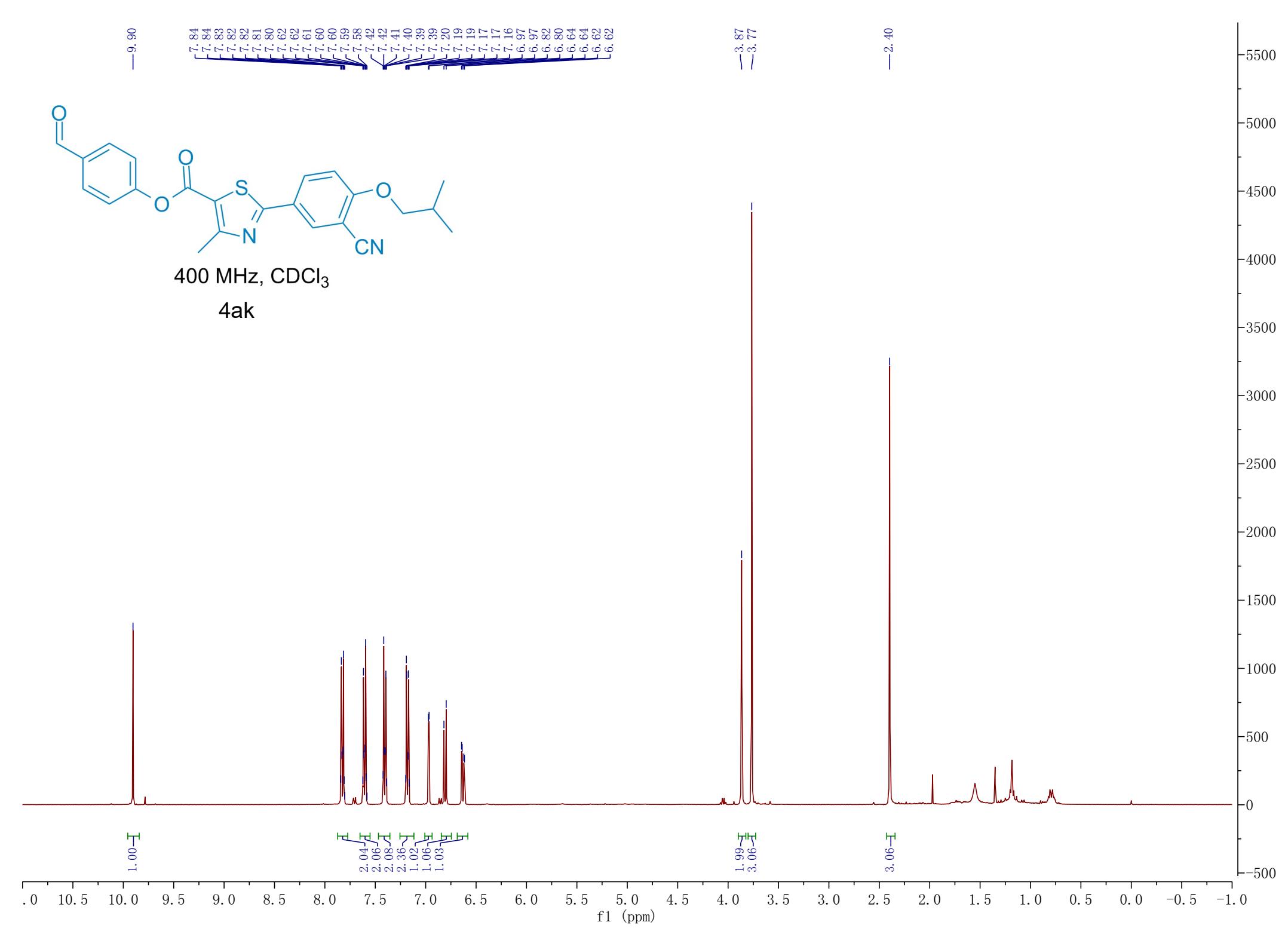


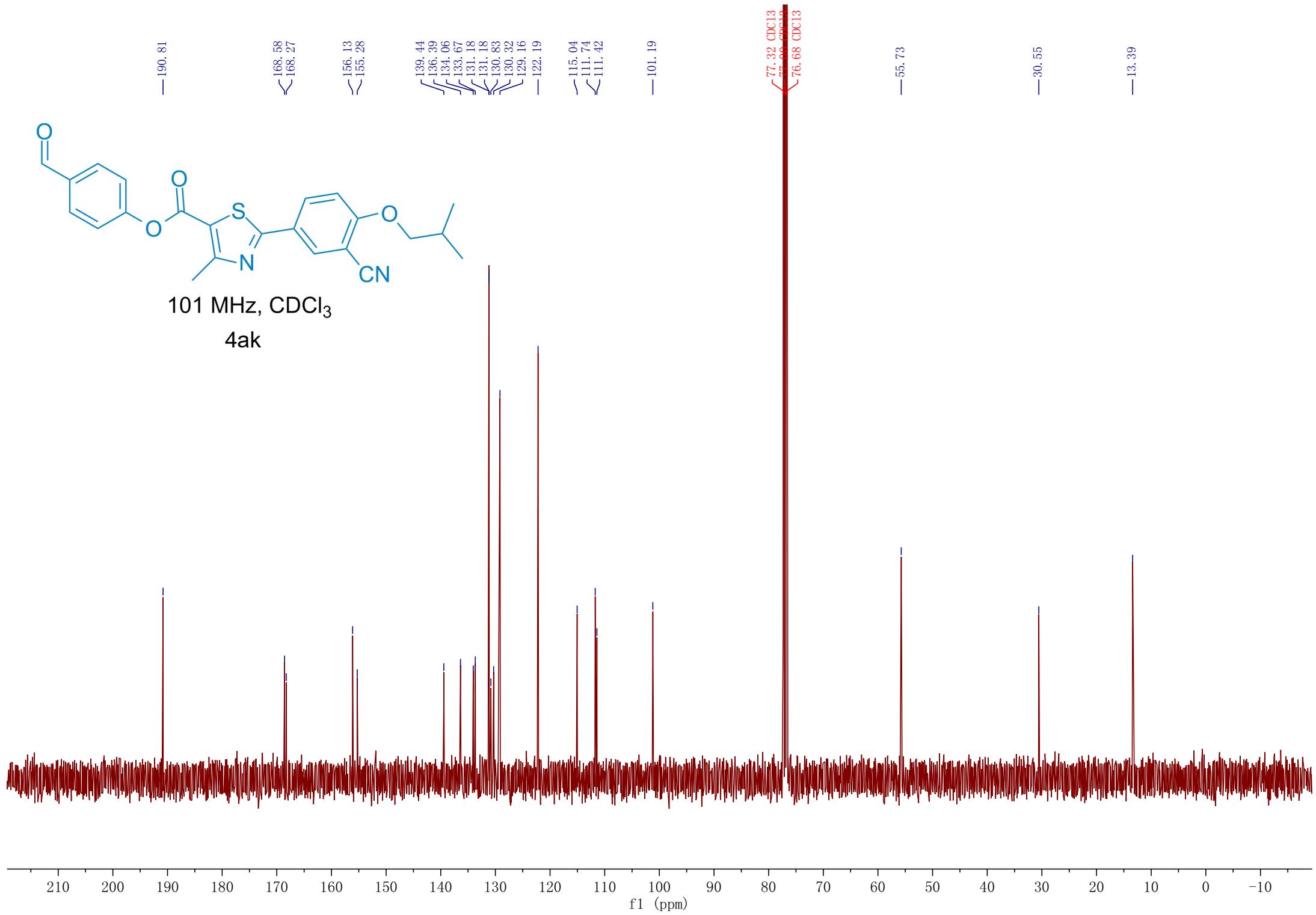


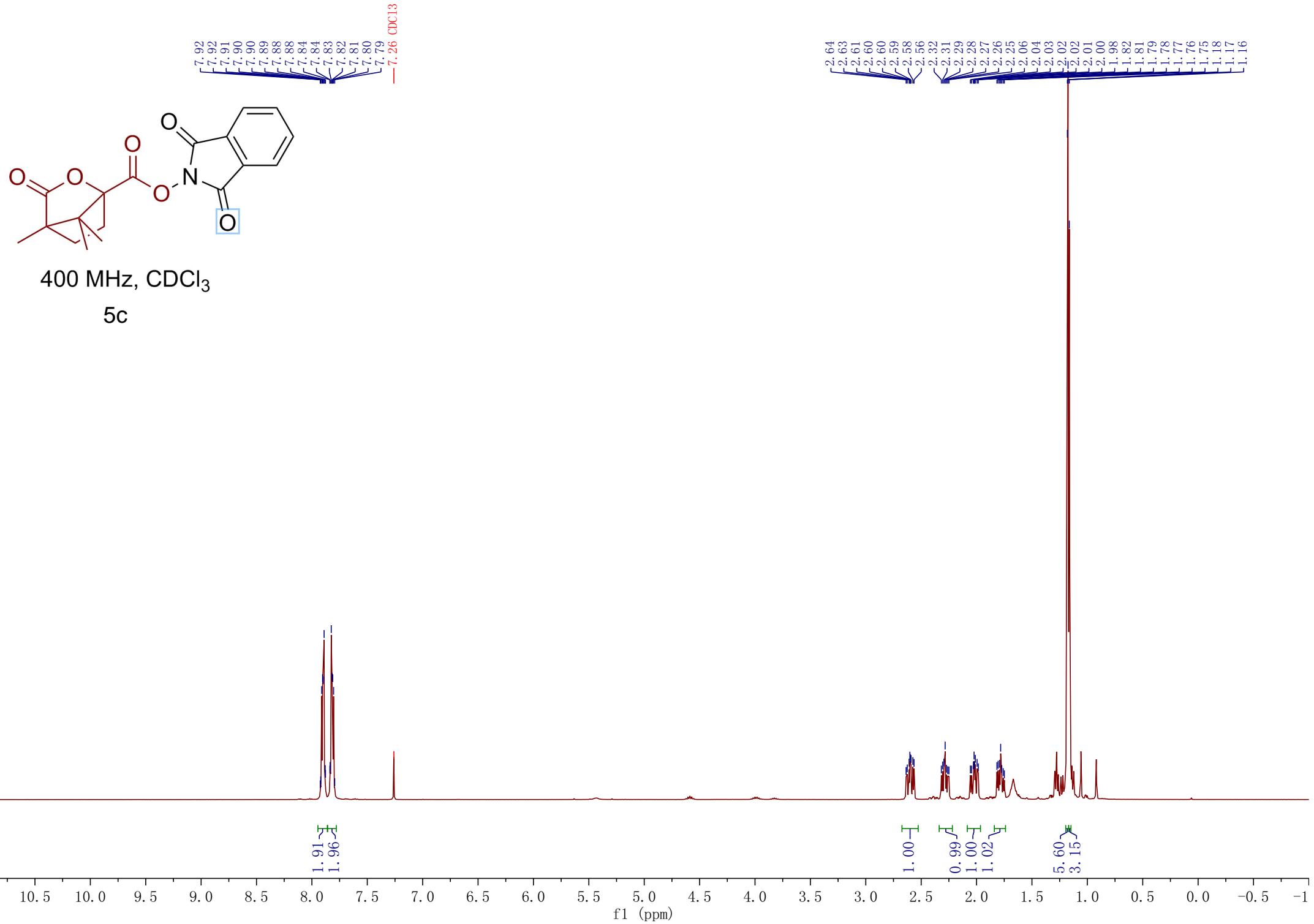


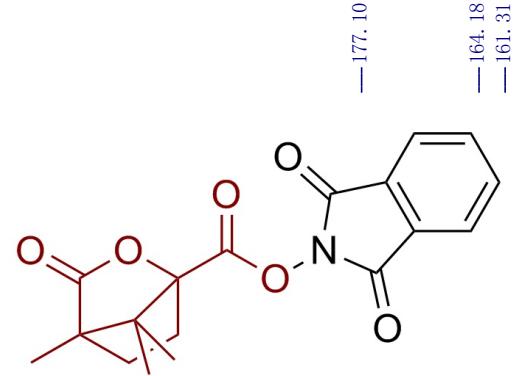
400 MHz,  $\text{CDCl}_3$

**4ak**



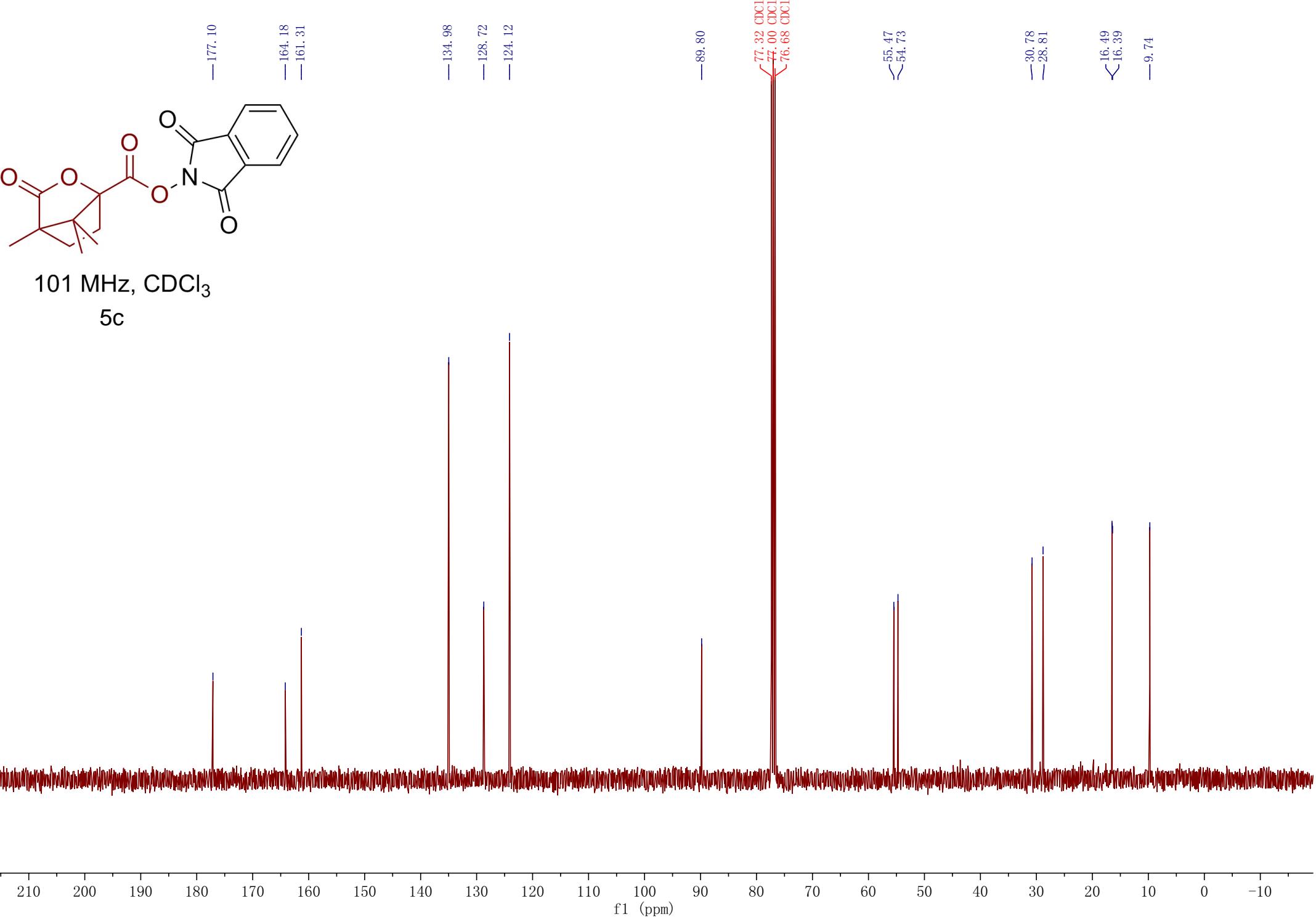


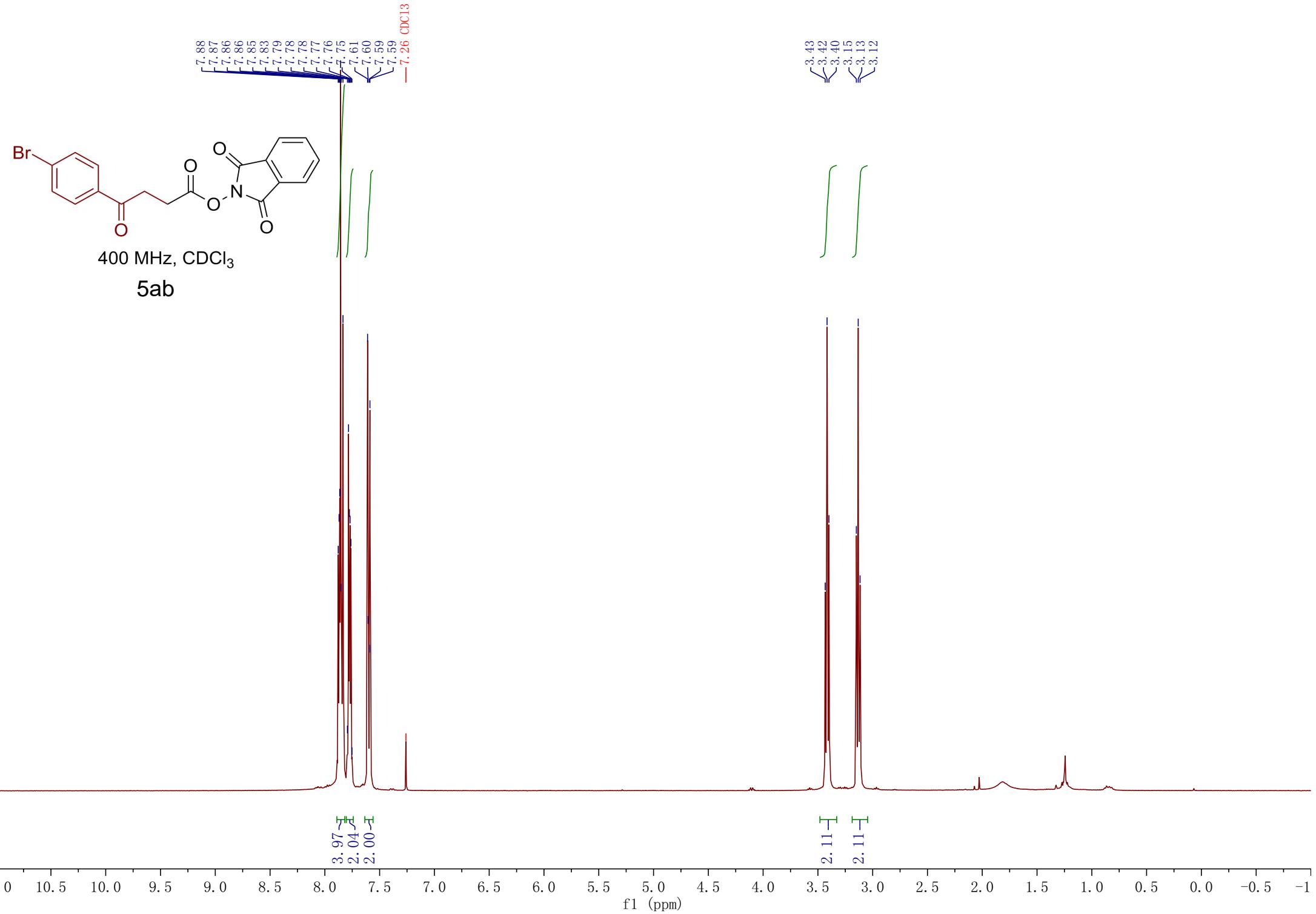




101 MHz, CDCl<sub>3</sub>

5c

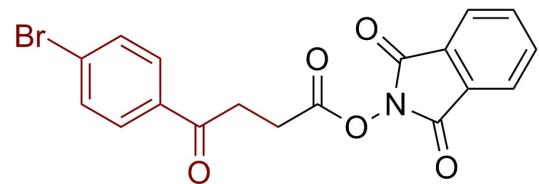




— 195.46

— 169.16

— 161.71



101 MHz,  $\text{CDCl}_3$

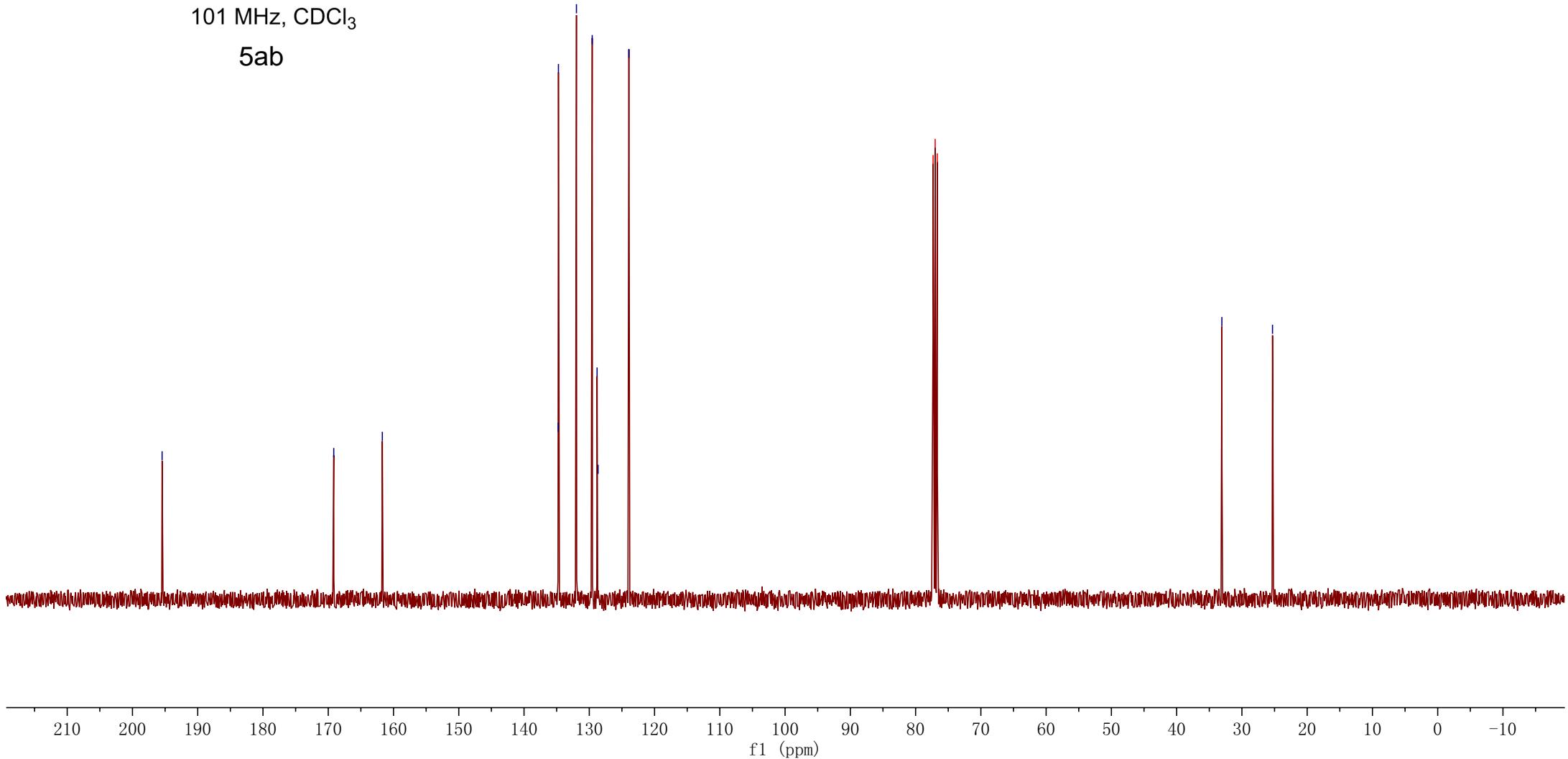
5ab

— 134.76  
— 134.73  
— 131.97  
— 129.55  
— 128.81  
— 128.66  
— 123.93

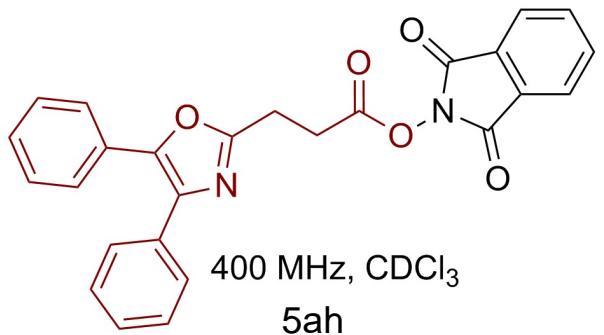
— 77.32  $\text{CDCl}_3$   
— 77.00  $\text{CDCl}_3$   
— 76.68  $\text{CDCl}_3$

— 33.07

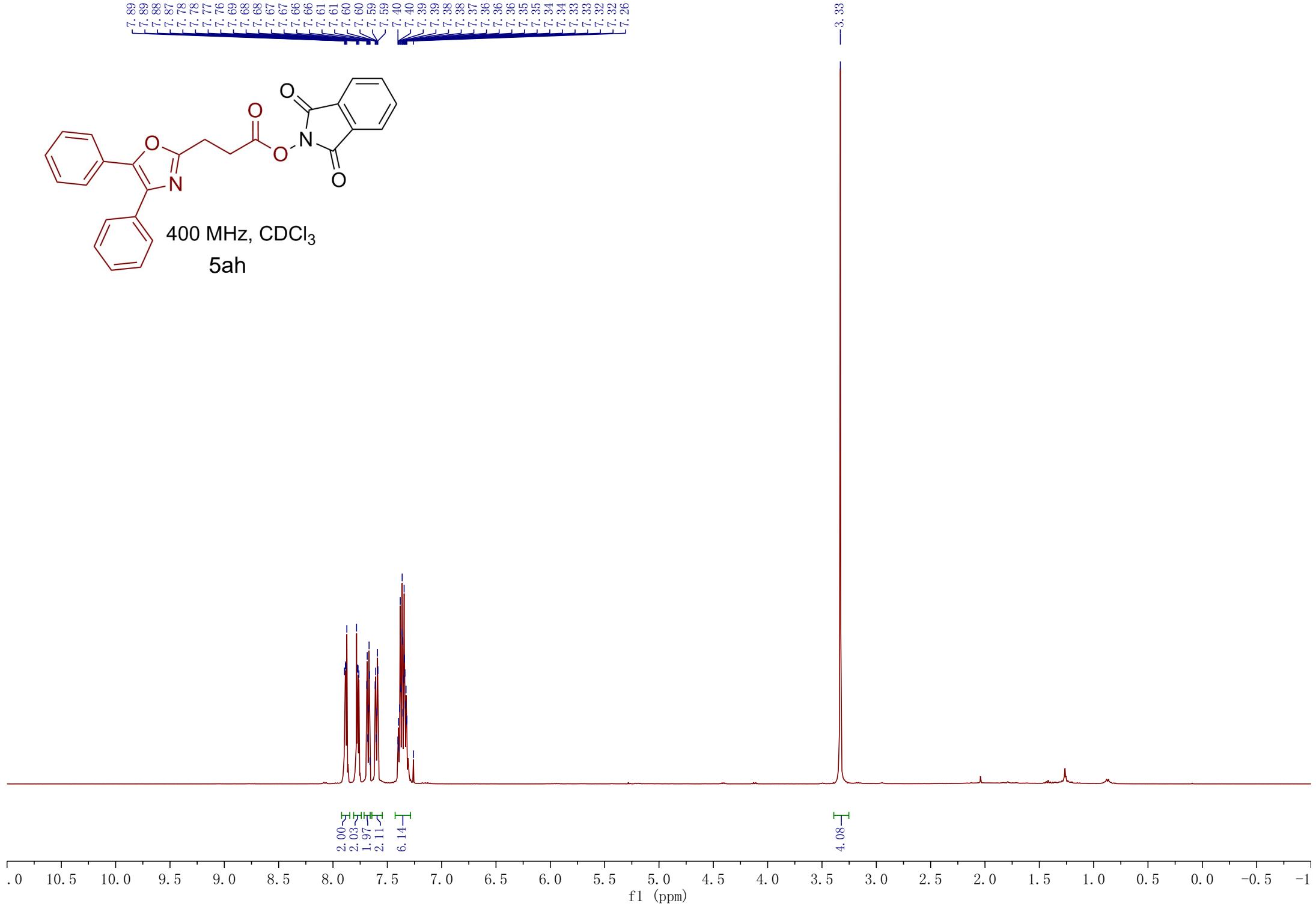
— 25.31

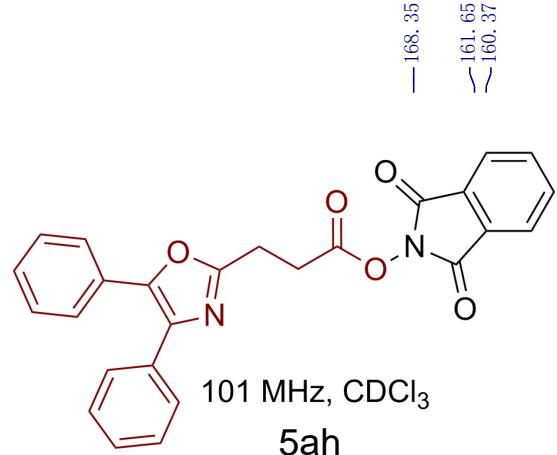


7.89  
7.88  
7.87  
7.78  
7.77  
7.76  
7.69  
7.68  
7.68  
7.67  
7.67  
7.66  
7.66  
7.61  
7.61  
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7.59  
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7.39  
7.39  
7.38  
7.38  
7.37  
7.36  
7.36  
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7.35  
7.35  
7.34  
7.34  
7.33  
7.33  
7.32  
7.32

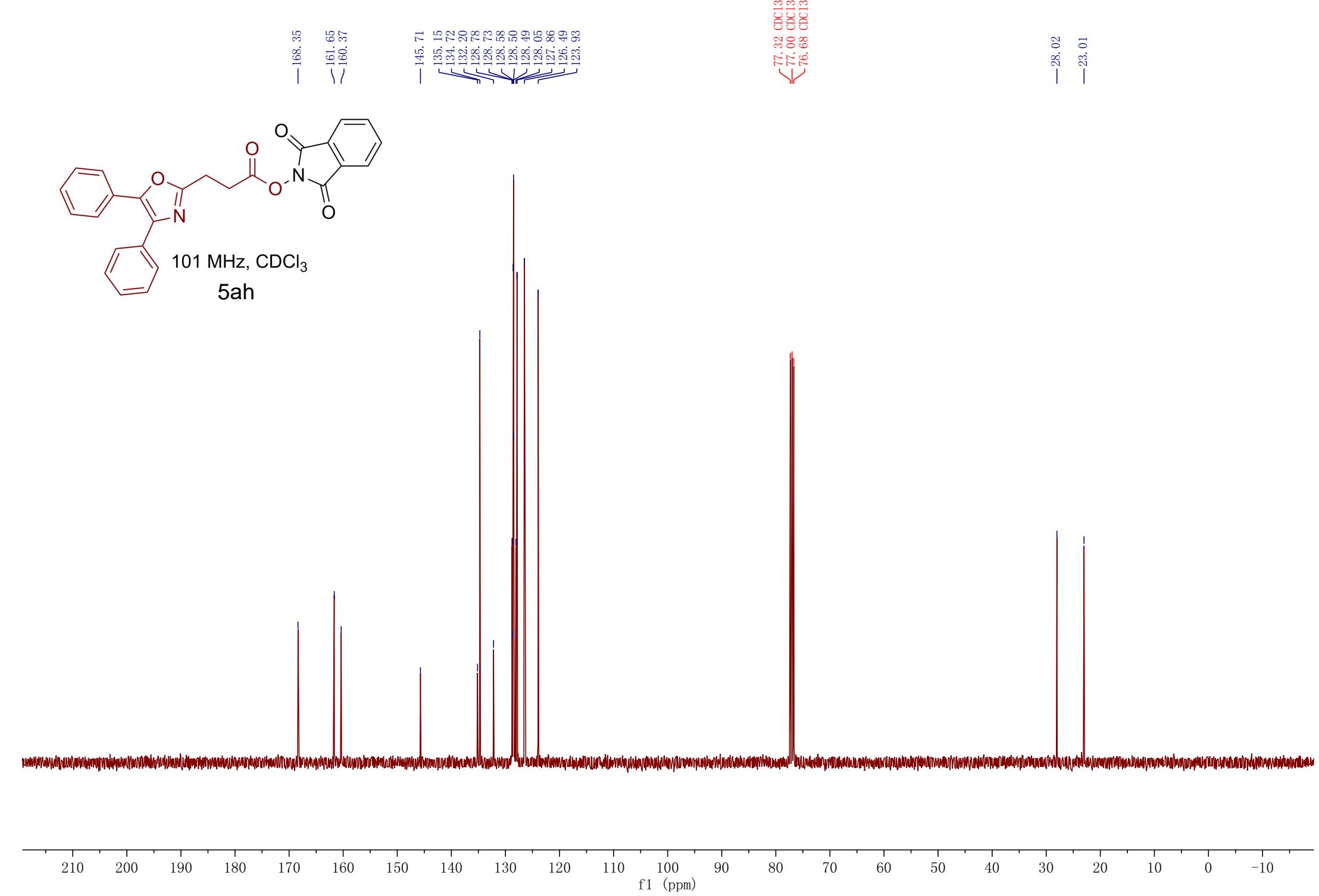


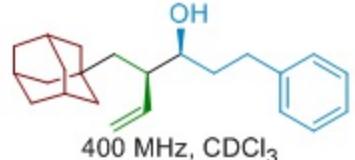
400 MHz, CDCl<sub>3</sub>  
5ah



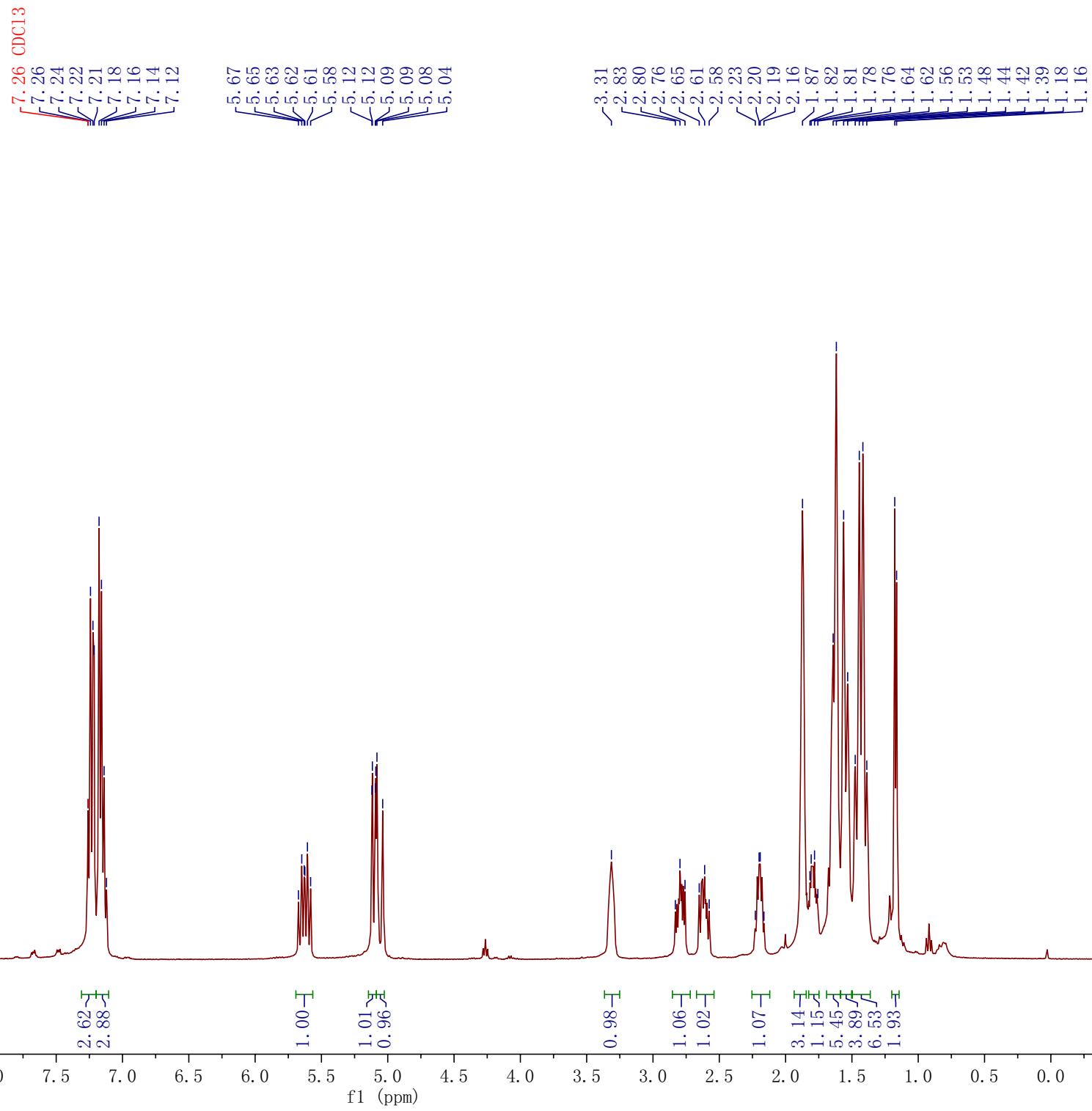


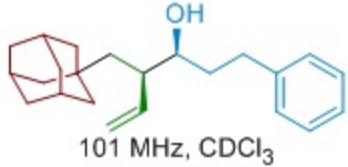
101 MHz, CDCl<sub>3</sub>  
**5ah**





6a





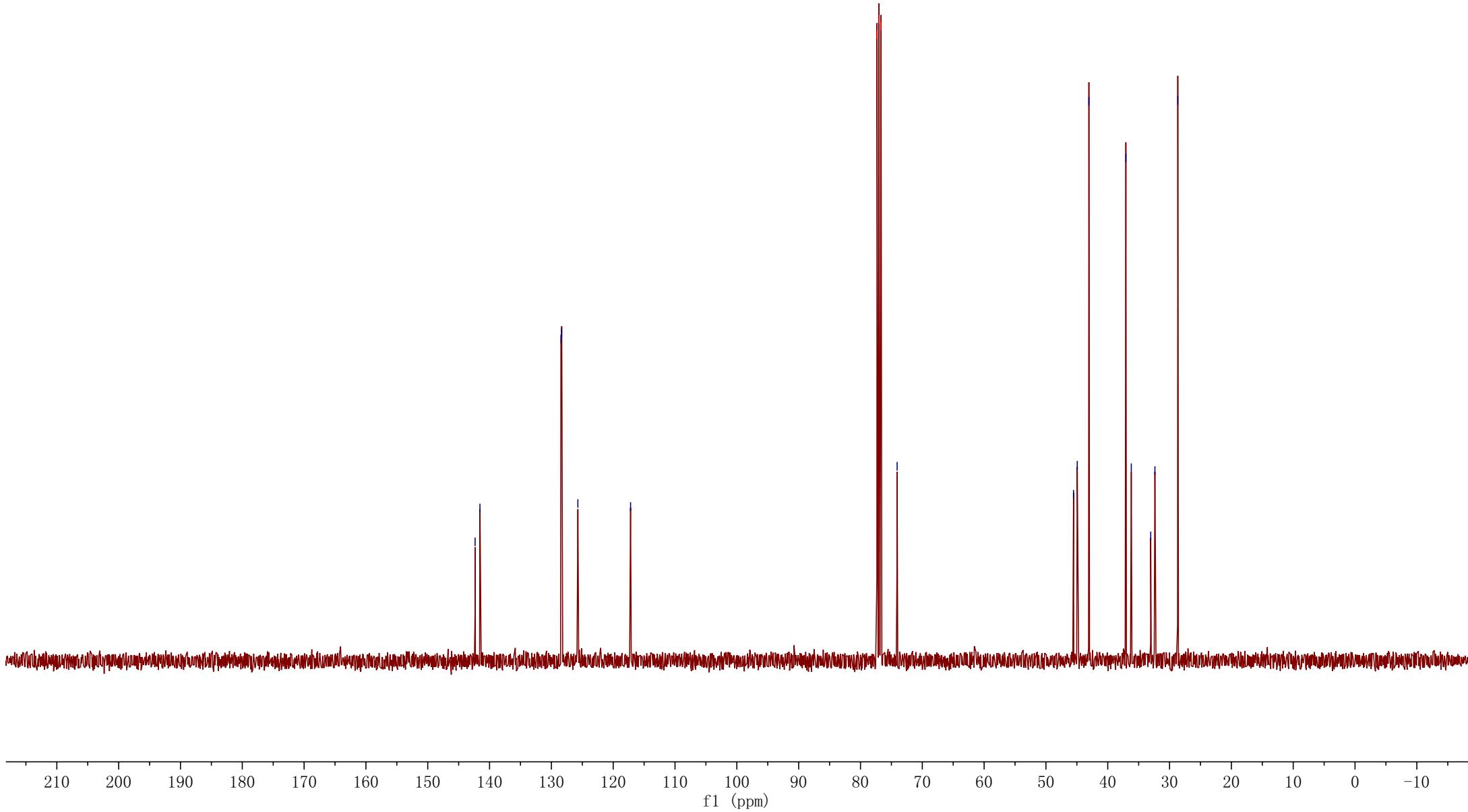
101 MHz, CDCl<sub>3</sub>

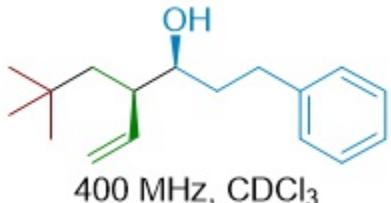
6a

~142.34  
~141.56  
~128.45  
~128.33  
~125.72  
-117.19

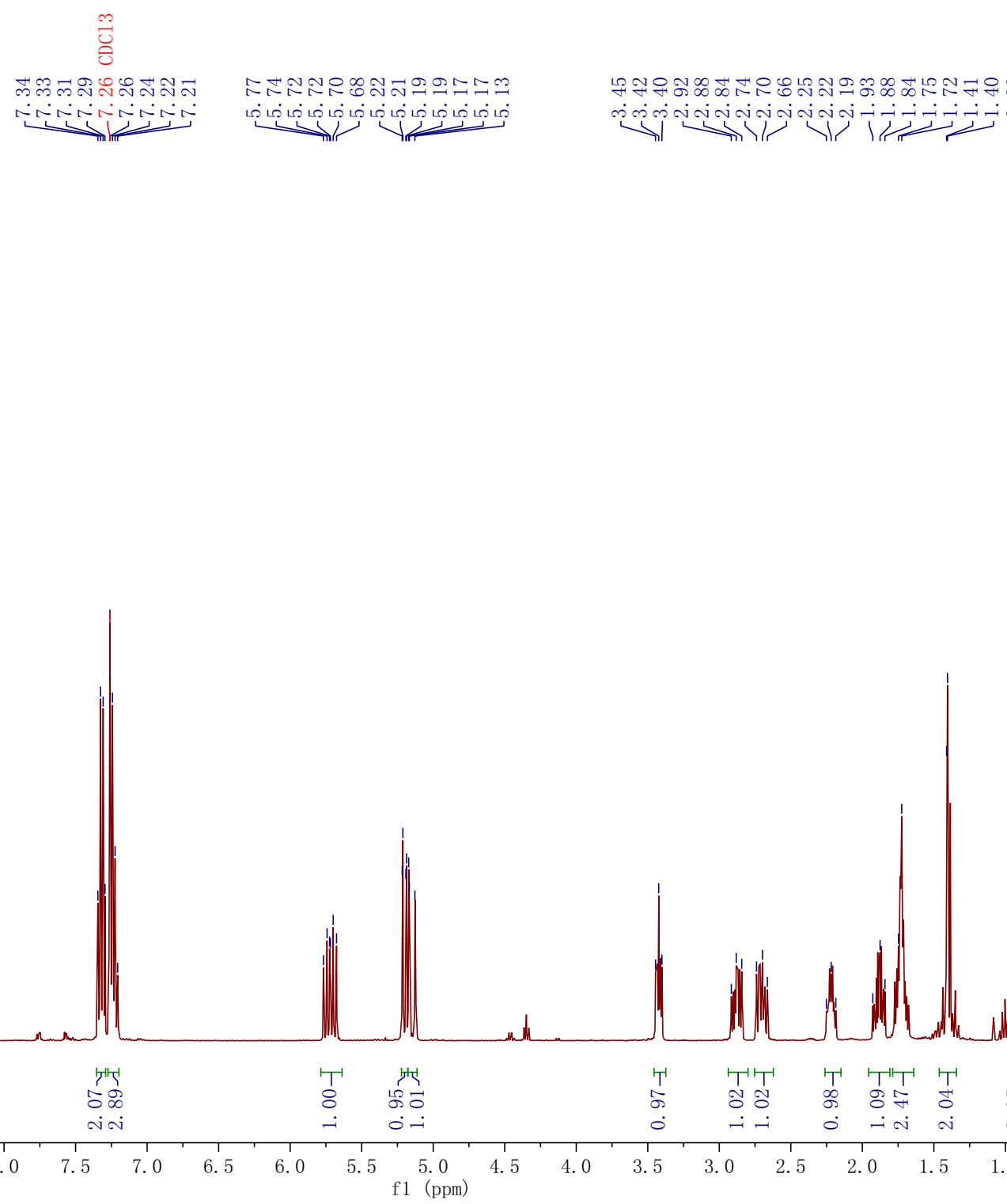
77.32 CDCl<sub>3</sub>  
77.00 CDCl<sub>3</sub>  
76.68 CDCl<sub>3</sub>  
74.07

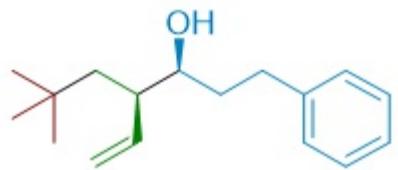
45.54  
44.94  
43.05  
37.06  
36.19  
33.05  
32.37  
28.67





**6b**



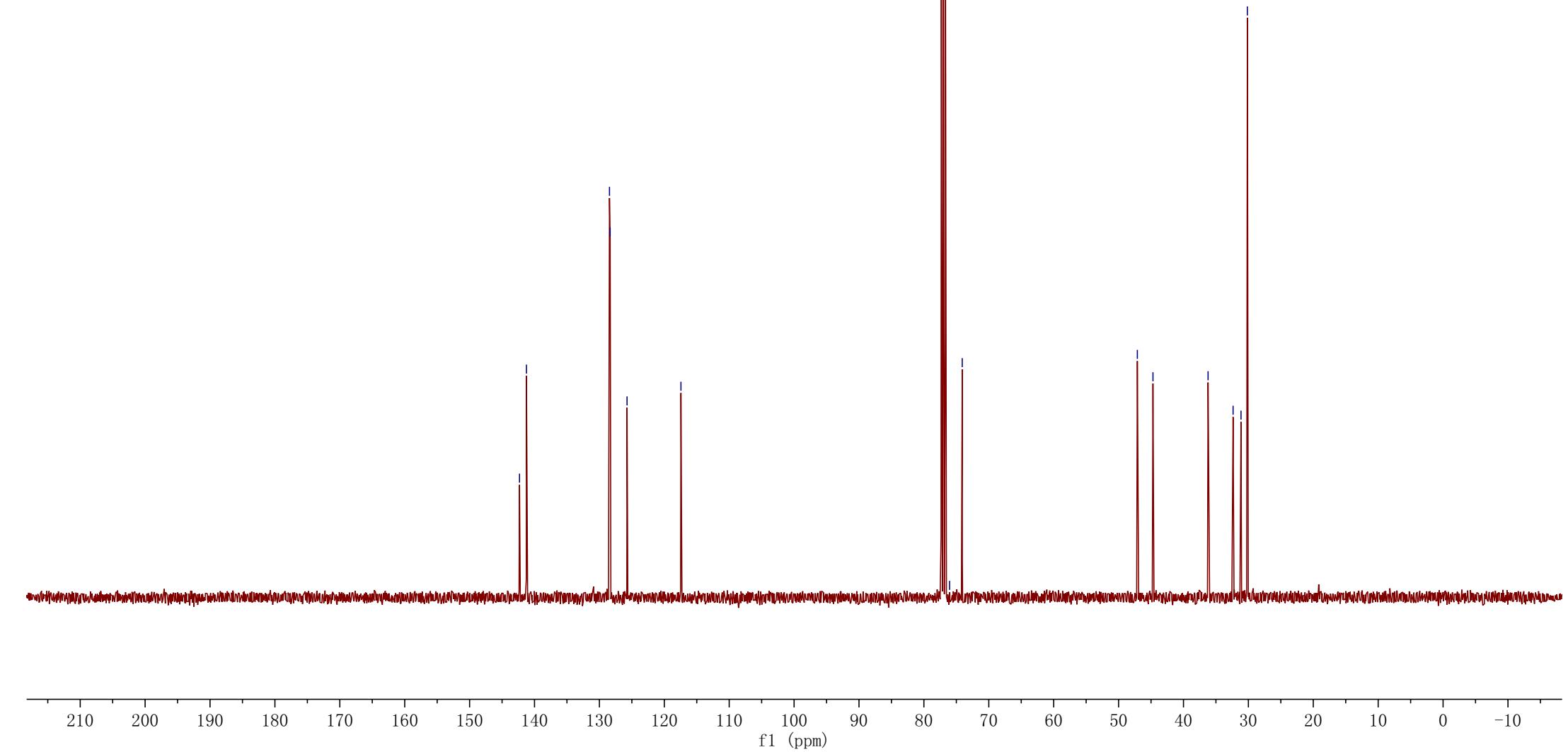


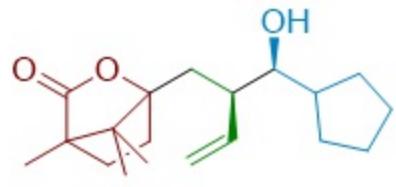
101 MHz, CDCl<sub>3</sub>  
6b

— 142.3  
— 141.2  
— 128.4  
— 128.3  
— 125.7  
— 117.4

— 77.3 CDCl<sub>3</sub>  
— 77.0 CDCl<sub>3</sub>  
— 76.7 CDCl<sub>3</sub>  
— 76.0  
— 74.1

— 47.1  
— 44.7  
— 36.2  
— 32.4  
— 31.1  
— 30.2

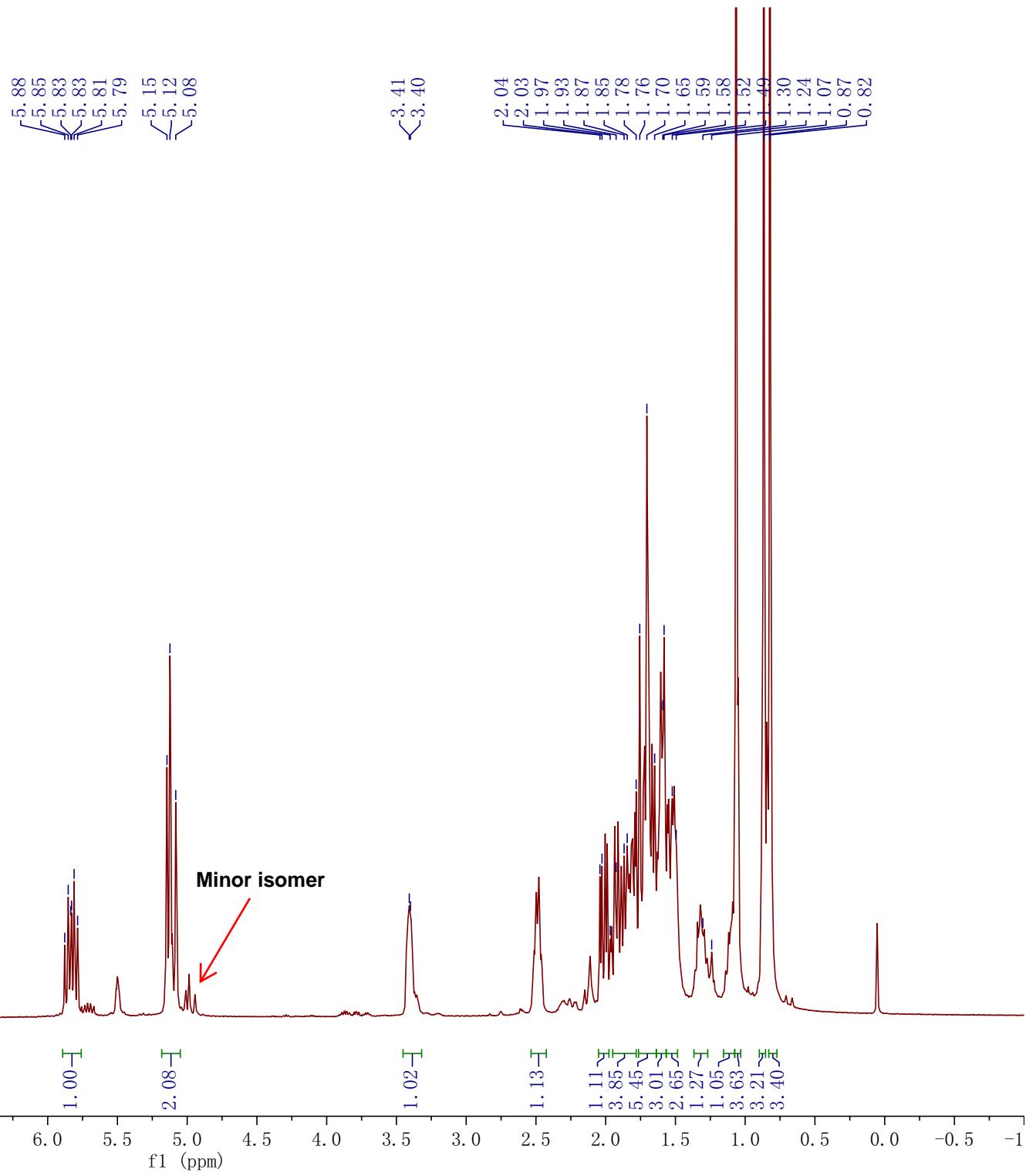


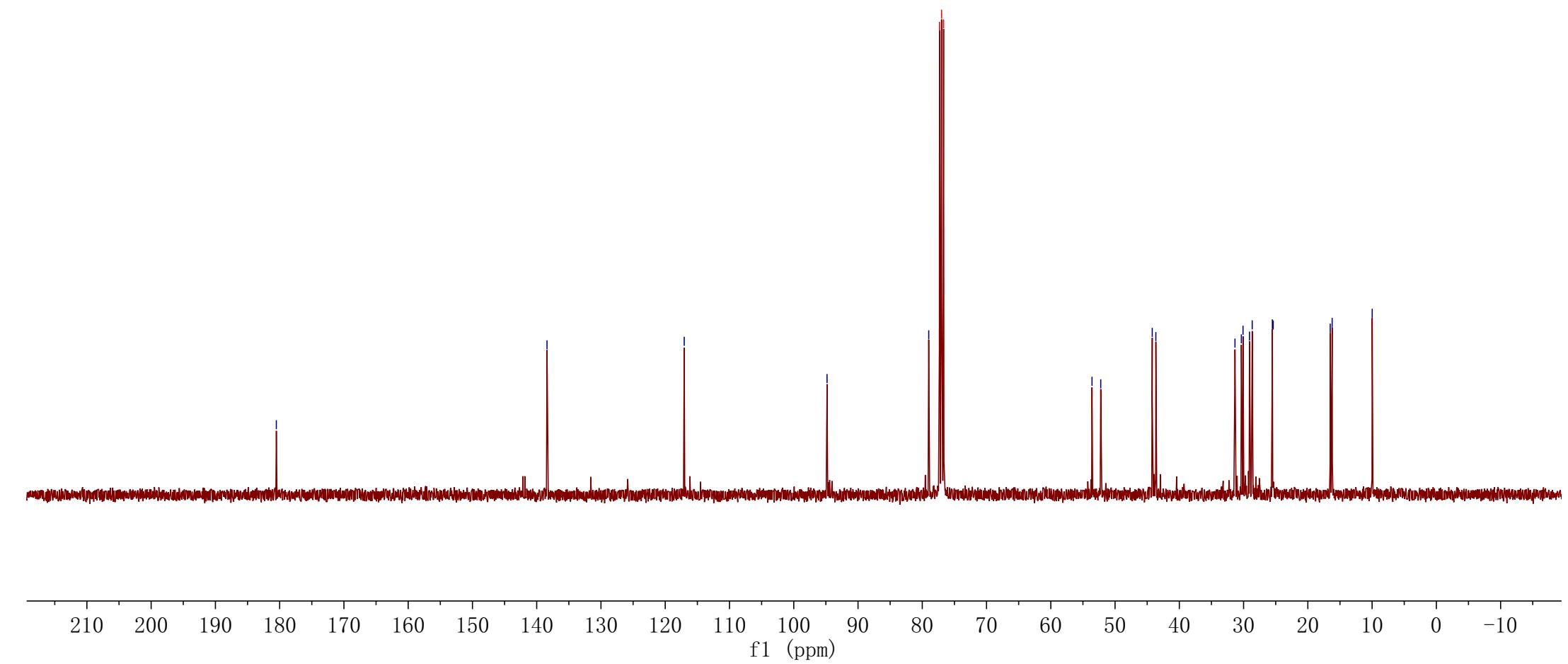
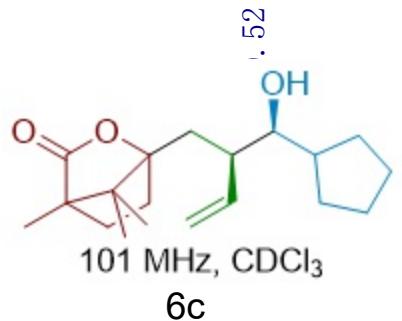


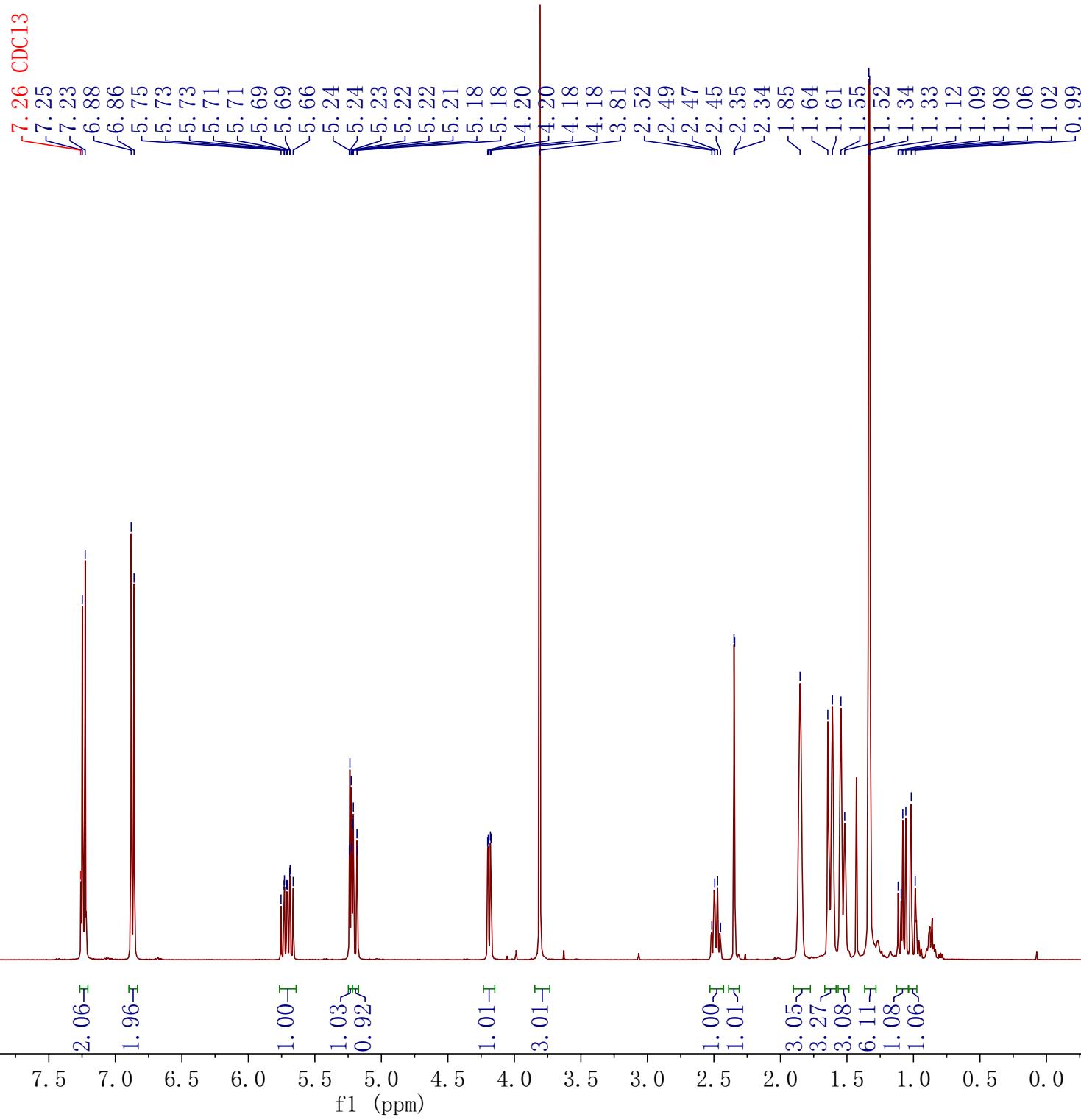
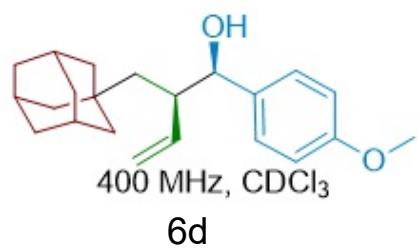
400 MHz, CDCl<sub>3</sub>

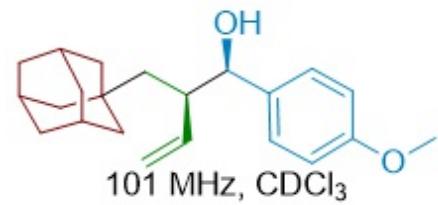
**6c**

-7.26 CDCl<sub>3</sub>









6d

-158. 96

-142. 53

-134. 29

-128. 50

-117. 97

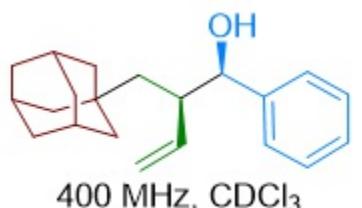
-113. 47

77. 32  $\text{CDCl}_3$   
77. 00  $\text{CDCl}_3$   
76. 68  $\text{CDCl}_3$   
76. 37

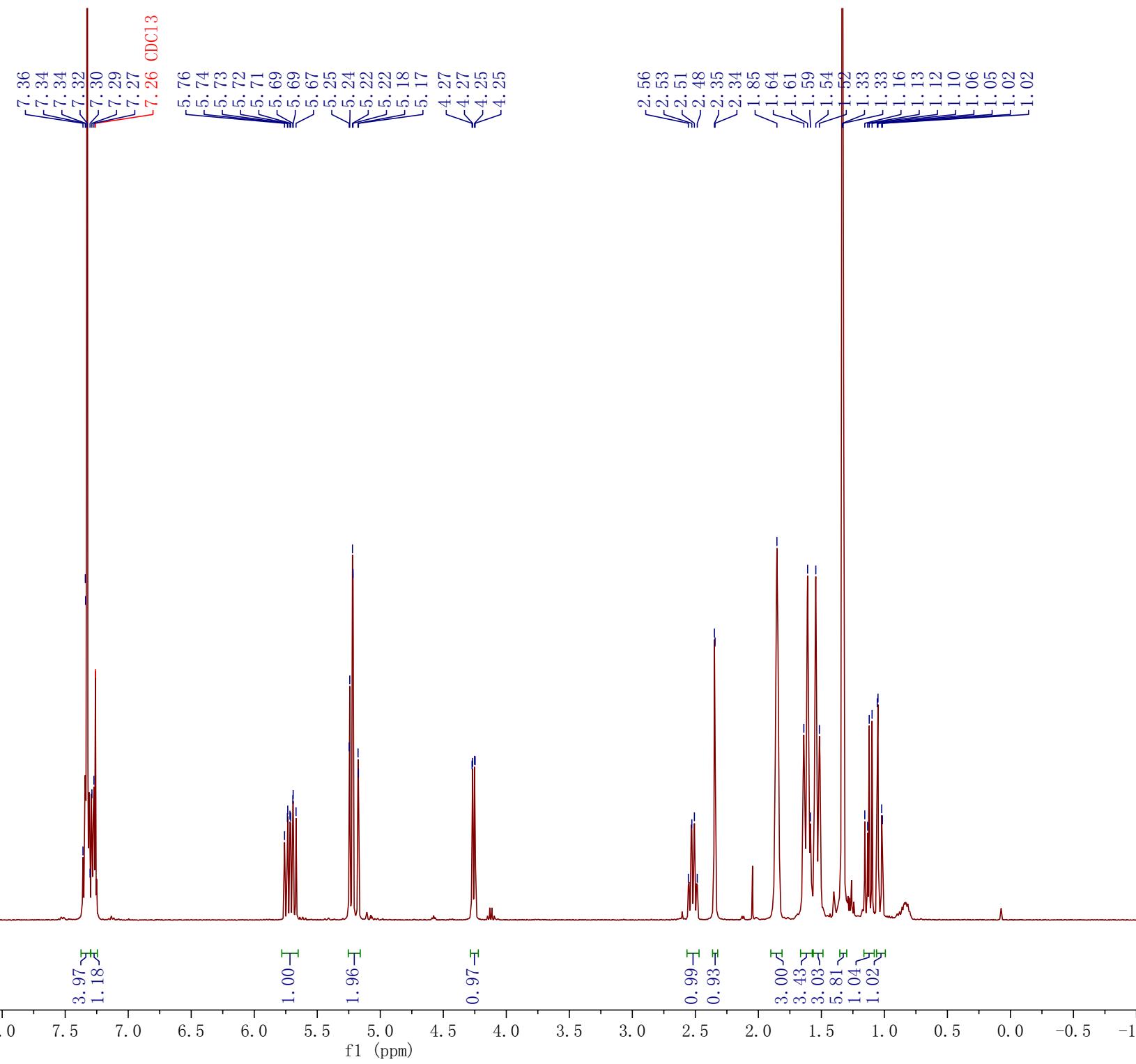
-55. 20

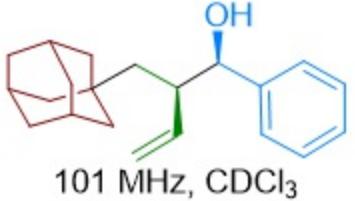
-47. 33  
-44. 86  
-42. 86  
-36. 98  
-32. 87  
-28. 60

f1 (ppm)



6e





6e

— 142.18

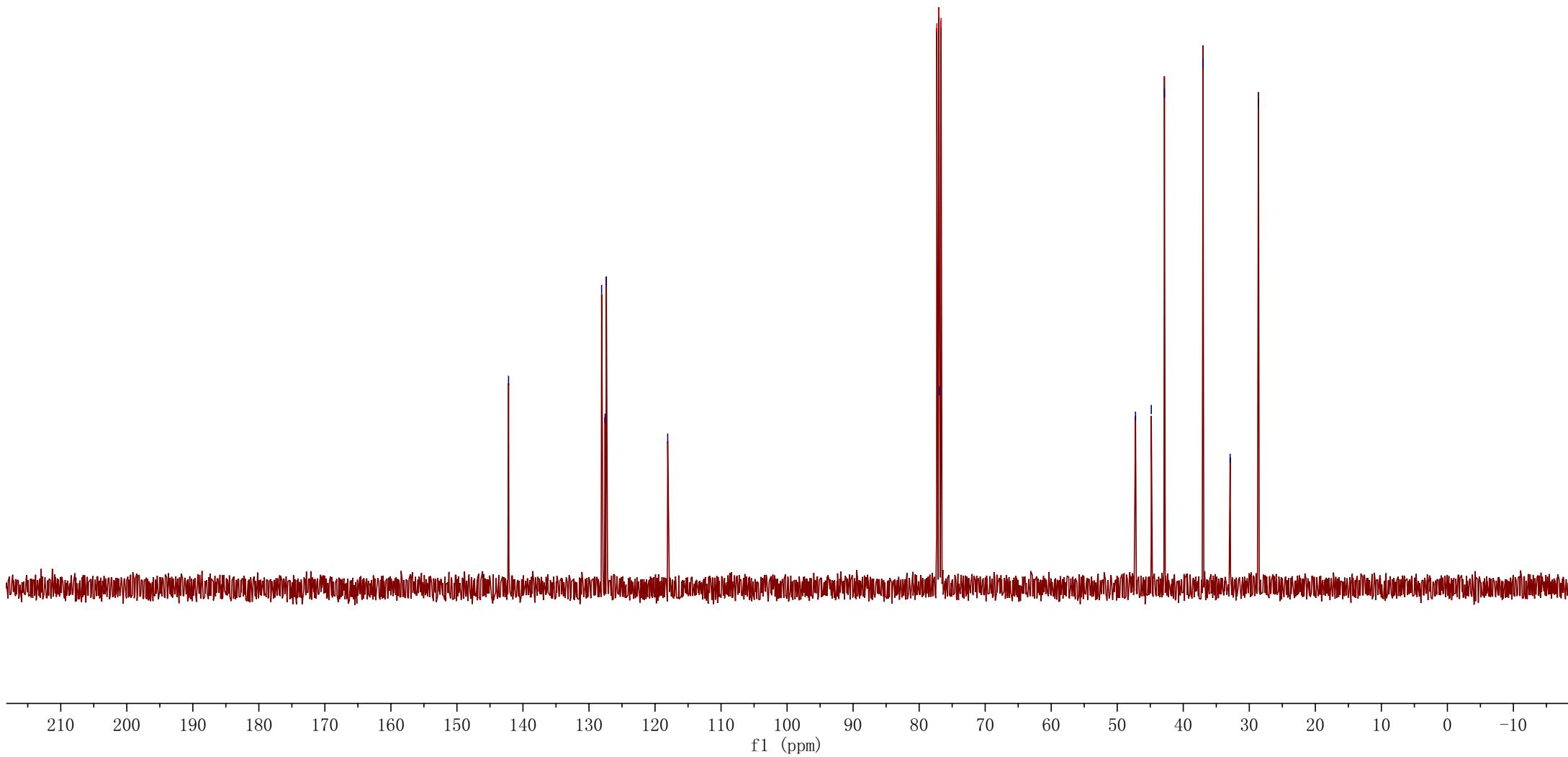
128.09  
127.57  
127.37

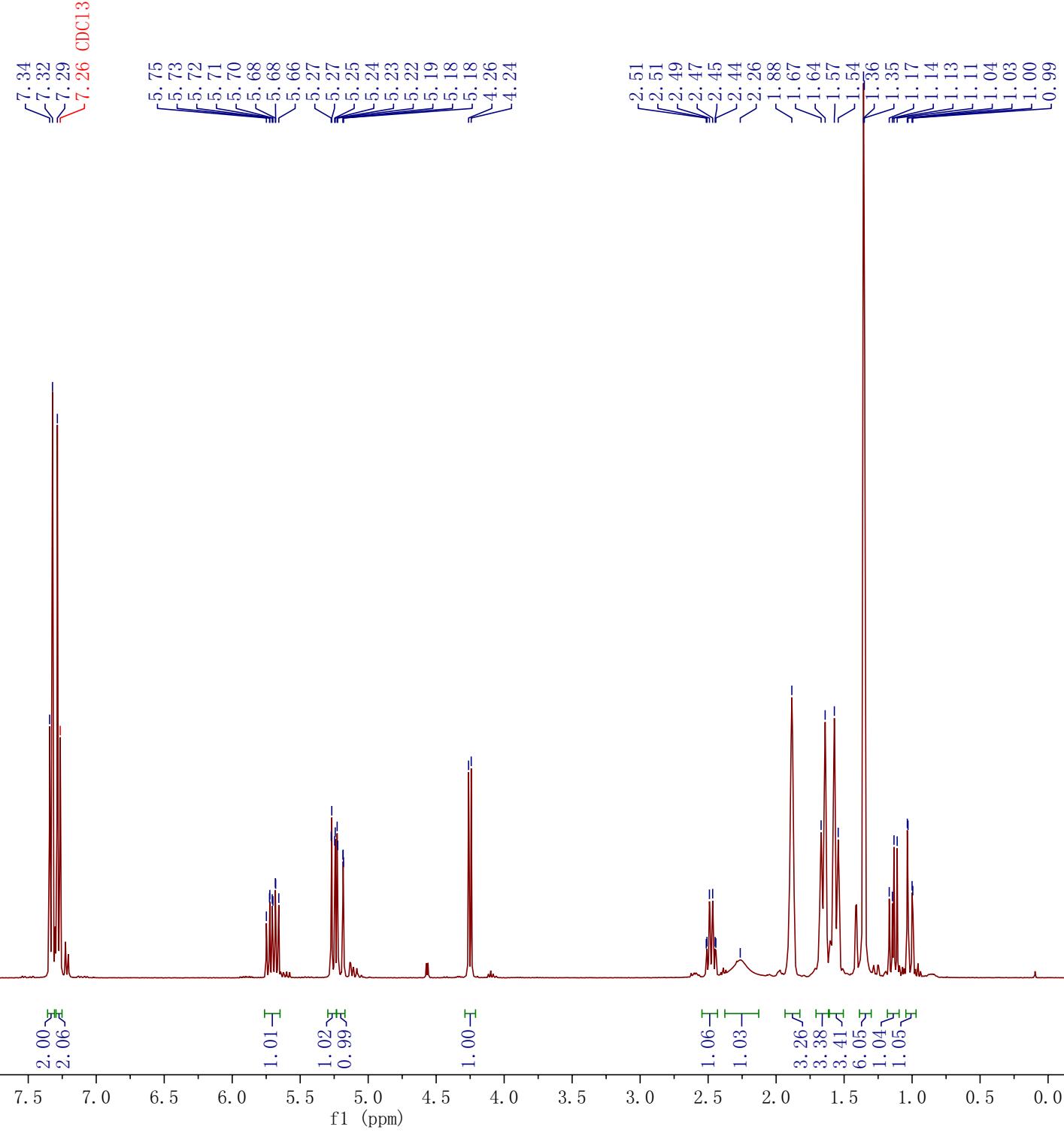
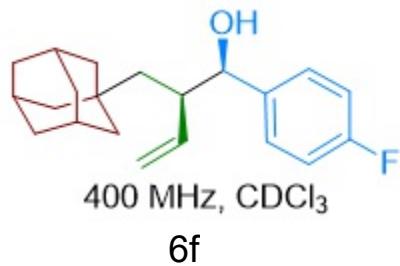
— 118.08

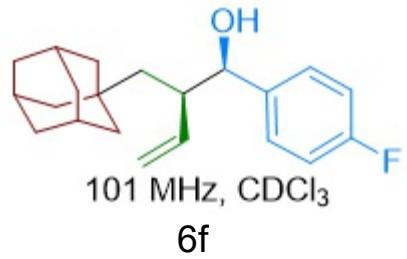
77.32 CDCl<sub>3</sub>  
77.00 CDCl<sub>3</sub>  
76.91  
76.68 CDCl<sub>3</sub>

— 47.23  
— 44.84  
— 42.85

~ 37.00  
— 32.90  
— 28.61





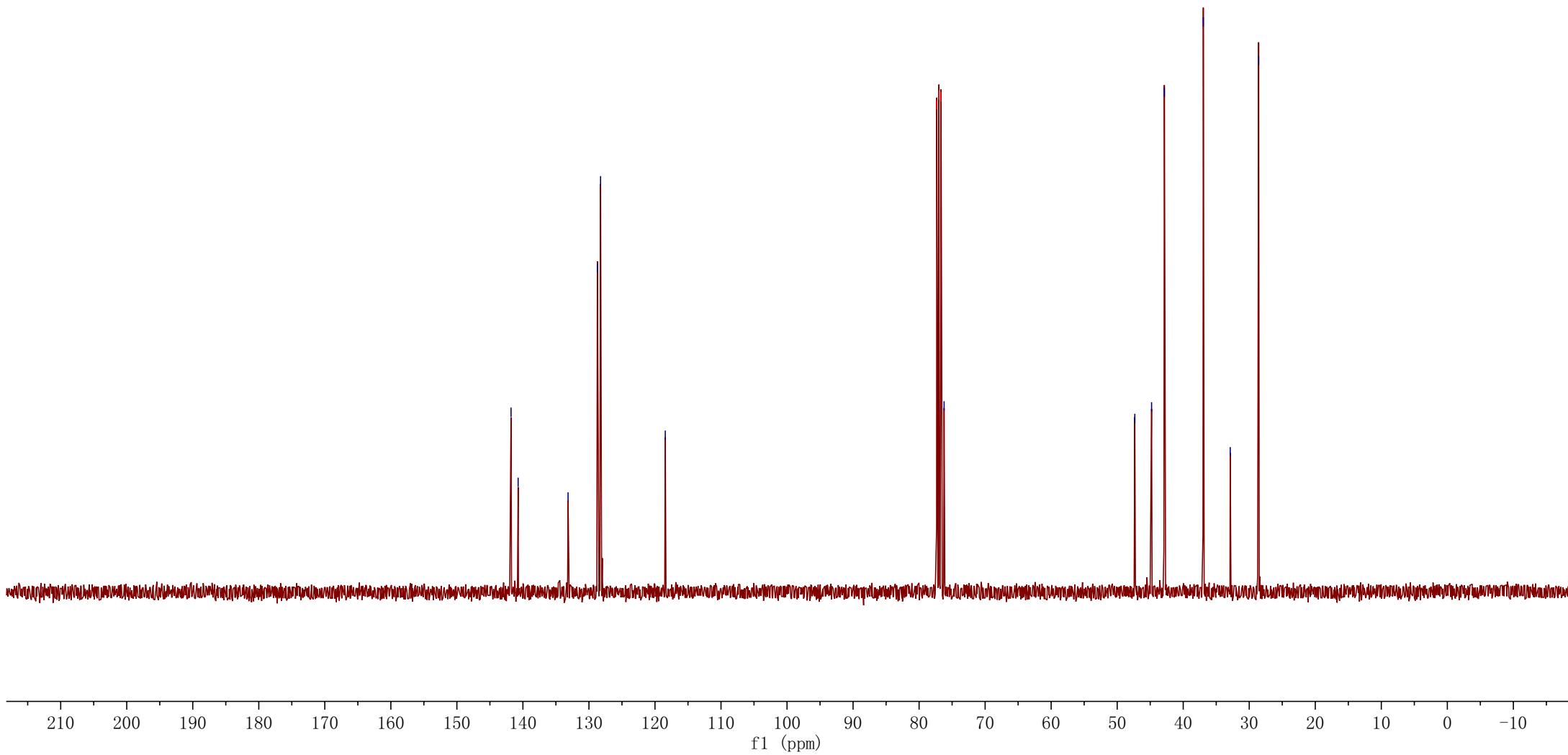


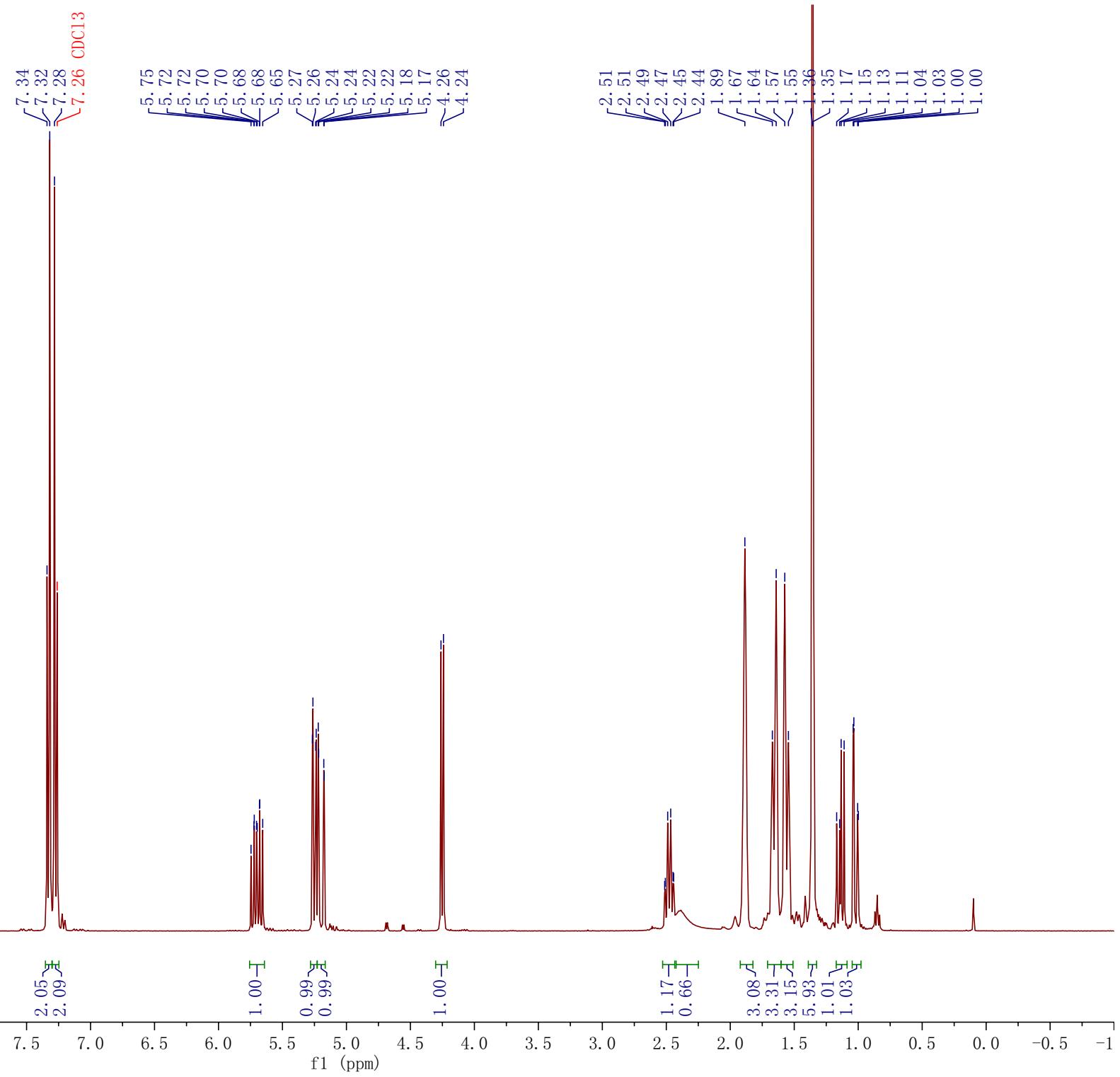
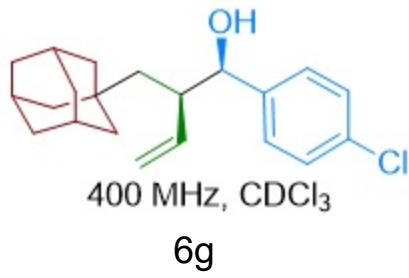
— 141.80  
— 140.72  
— 133.16  
— 128.73  
— 128.24  
— 118.44

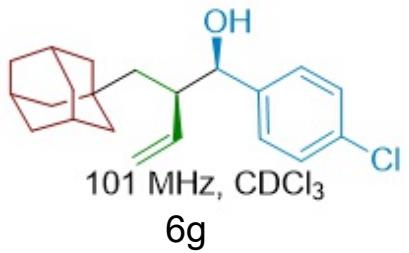
77.32 CDCl<sub>3</sub>  
77.00 CDCl<sub>3</sub>  
76.68 CDCl<sub>3</sub>  
76.21 CDCl<sub>3</sub>

— 47.33  
— 44.79  
— 42.85

— 36.96  
— 32.88  
— 28.58





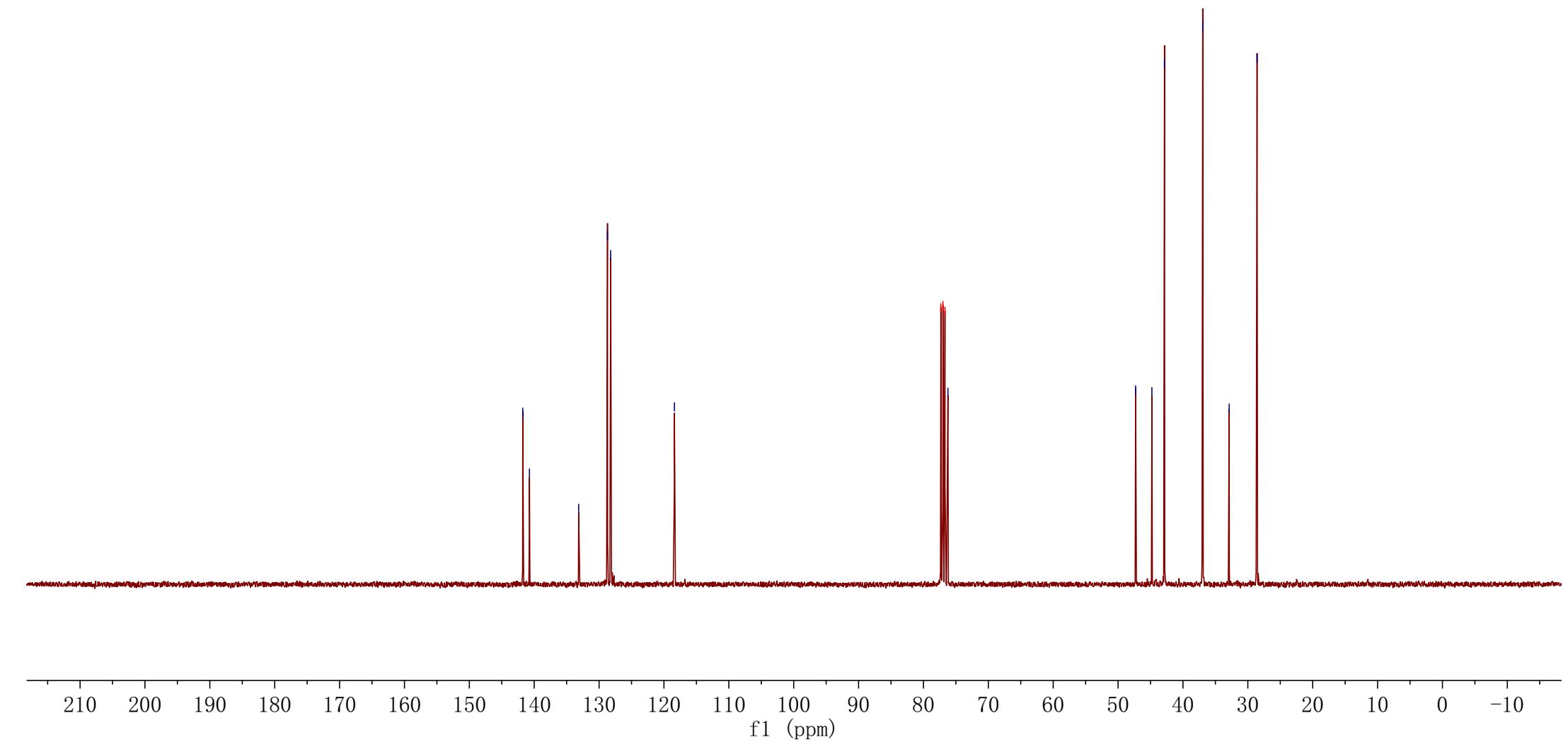


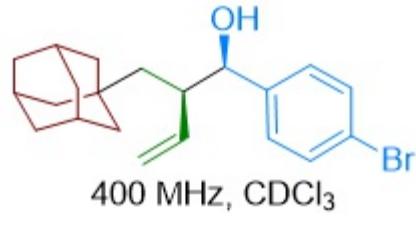
~141.77  
~140.73  
~133.14  
~128.70  
~128.22

-118.39

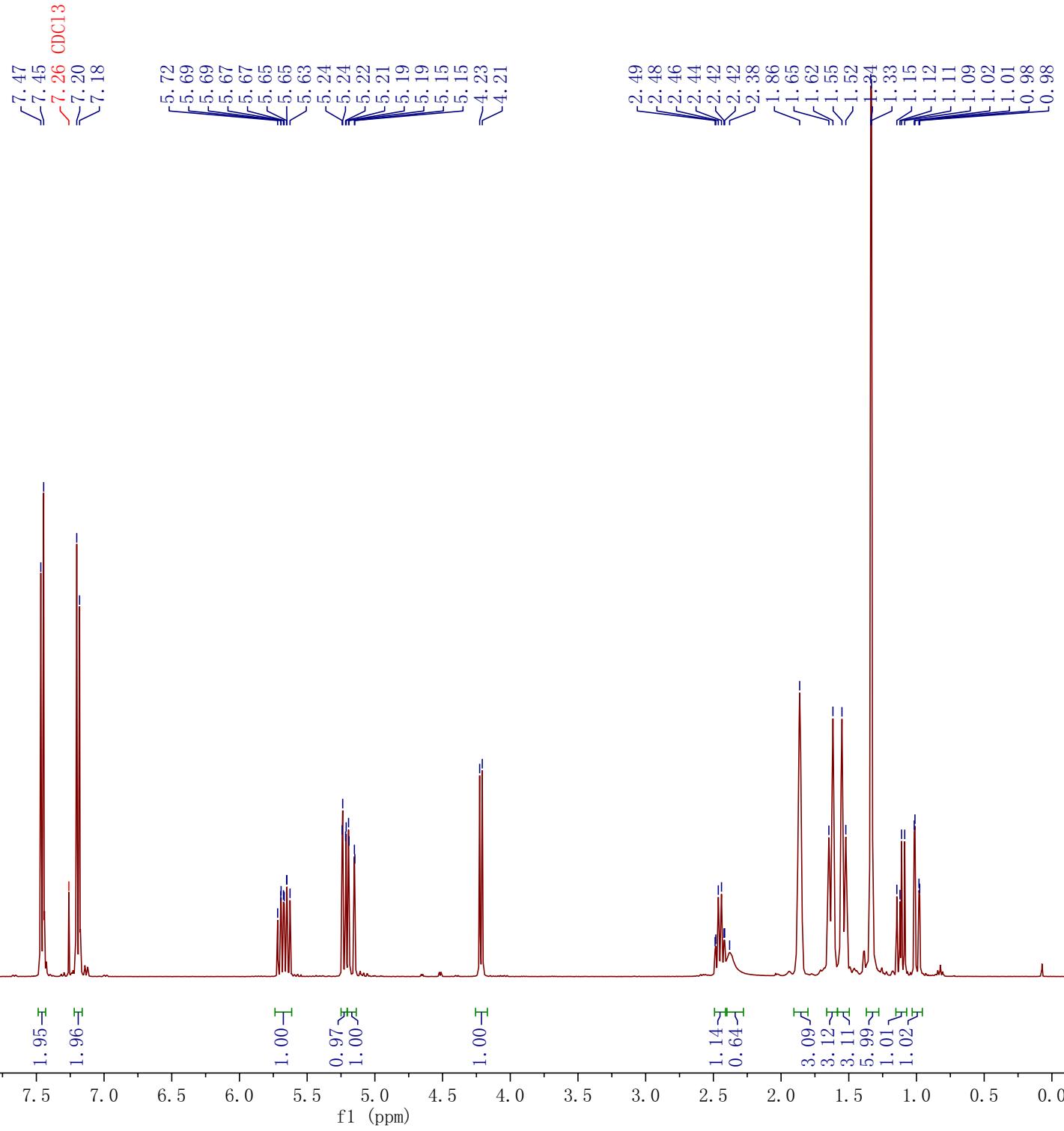
77.32 CDCl<sub>3</sub>  
77.00 CDCl<sub>3</sub>  
76.68 CDCl<sub>3</sub>  
76.23

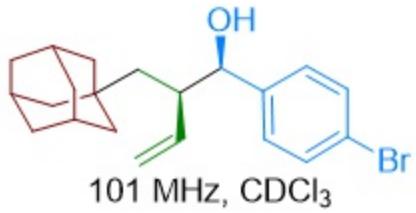
~47.29  
~44.79  
~42.85  
~36.95  
~32.87  
~28.57





**6h**





101 MHz, CDCl<sub>3</sub>

**6h**

141.78  
141.32

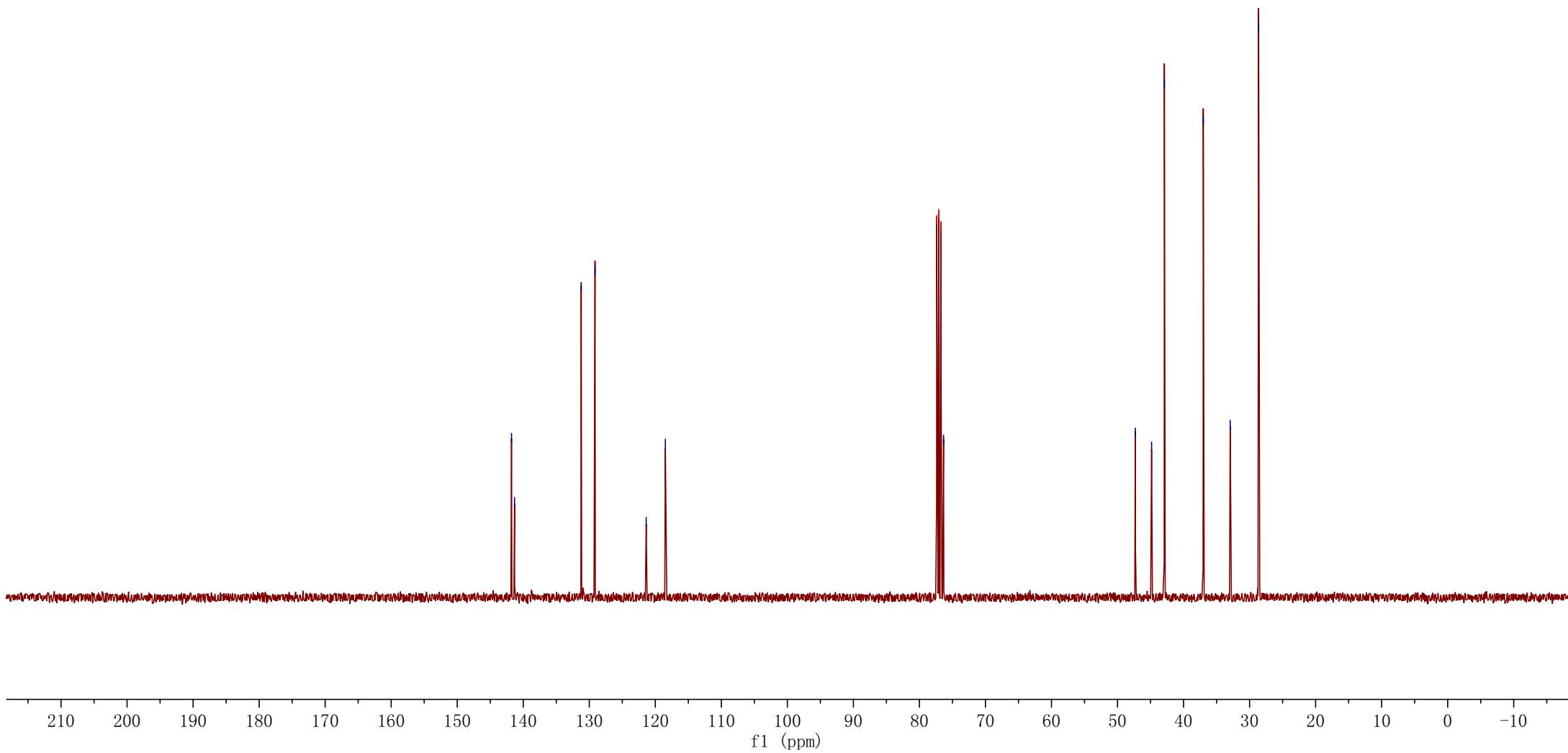
131.22  
129.13

121.38  
118.48

77.38 CDCl<sub>3</sub>  
77.06 CDCl<sub>3</sub>  
76.74 CDCl<sub>3</sub>  
76.35

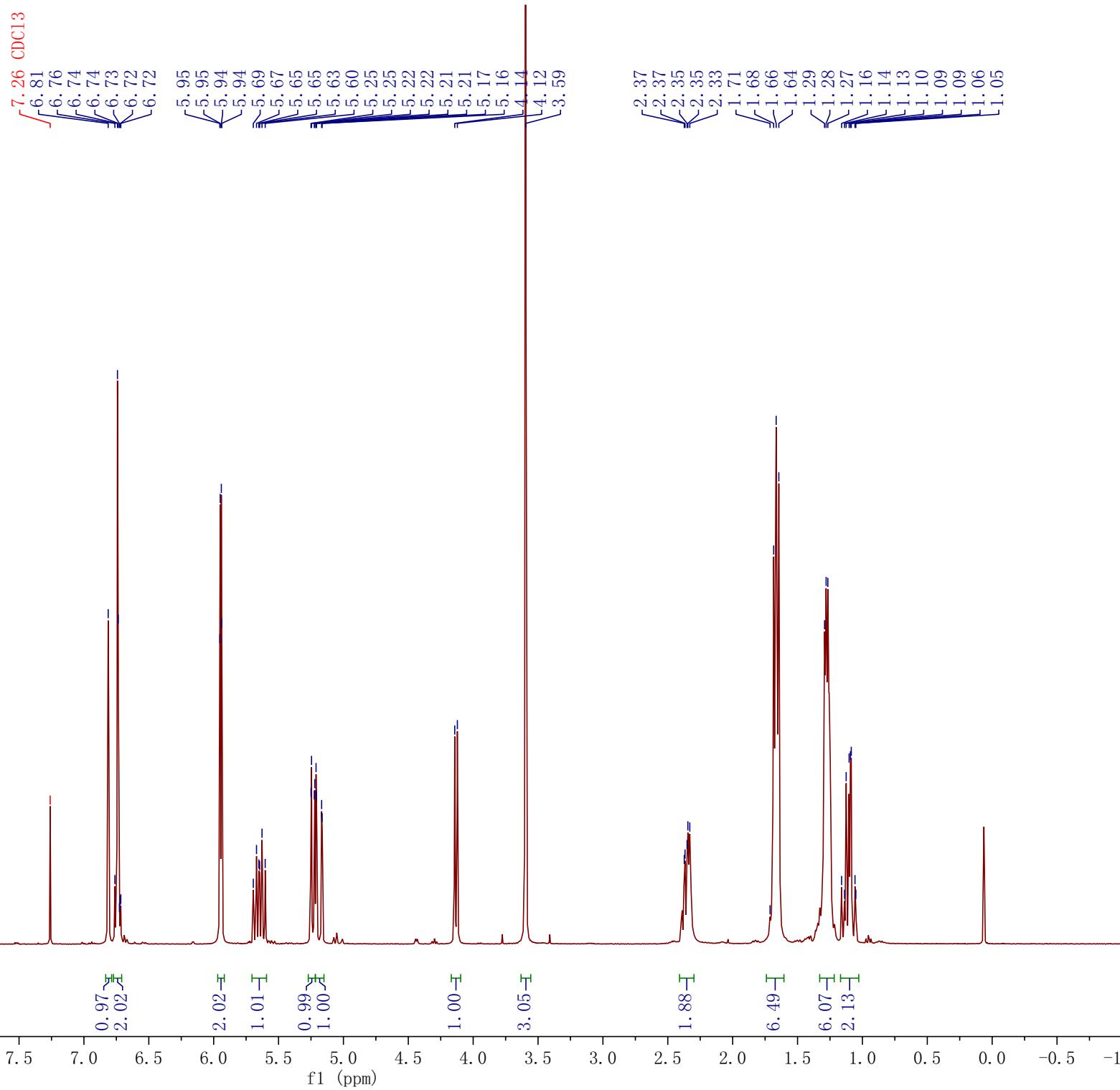
47.30  
44.84  
42.91

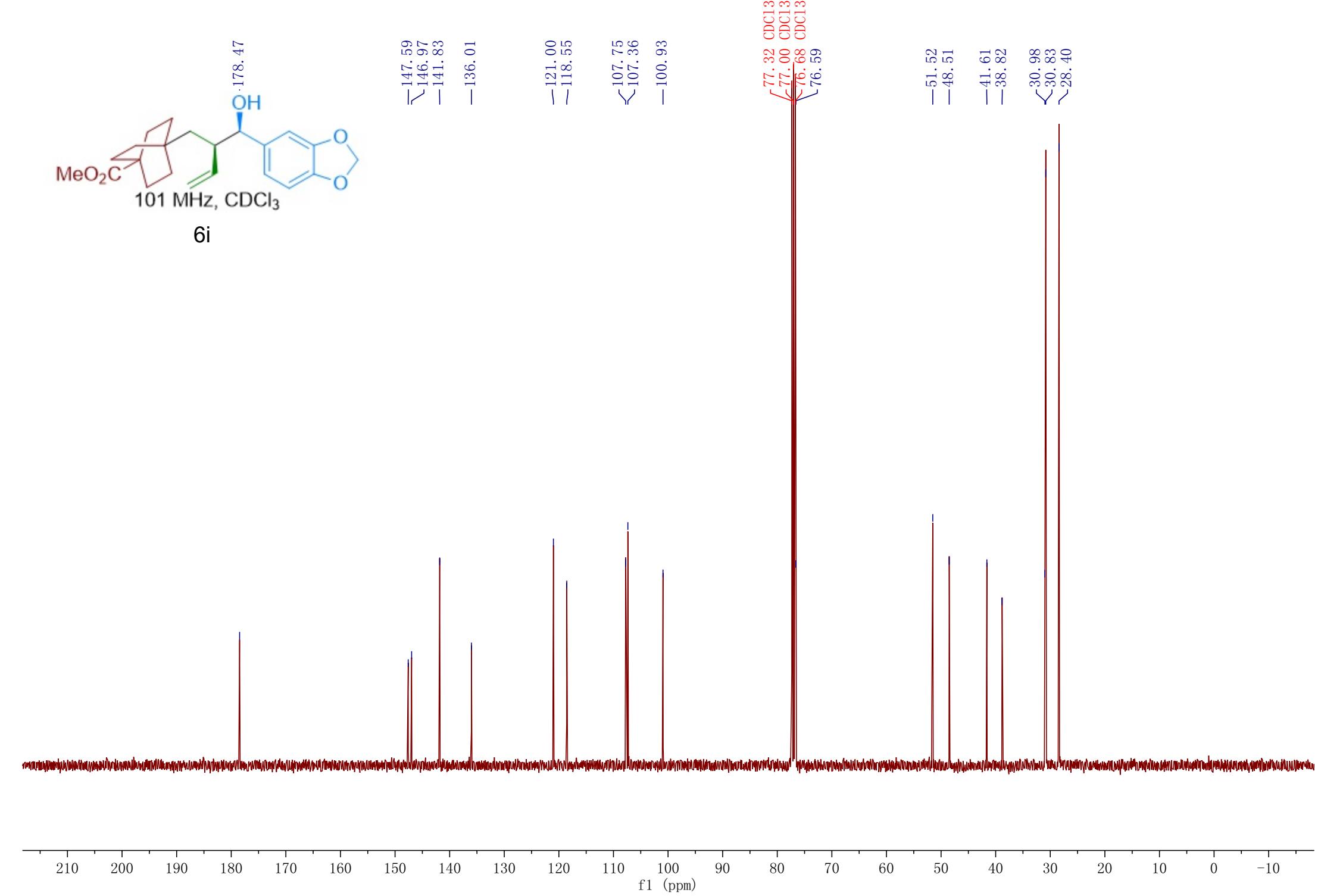
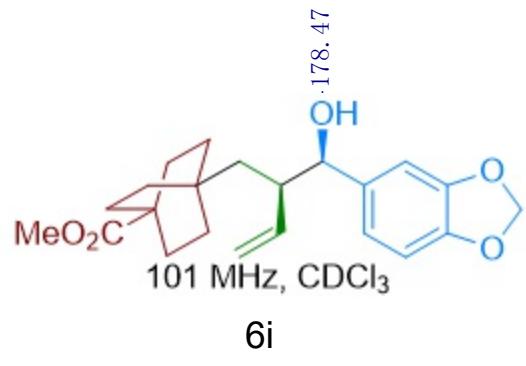
37.01  
32.94  
28.63

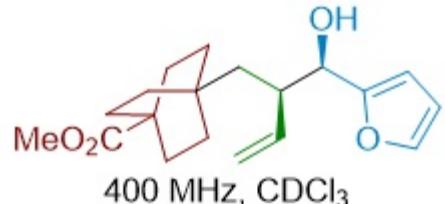




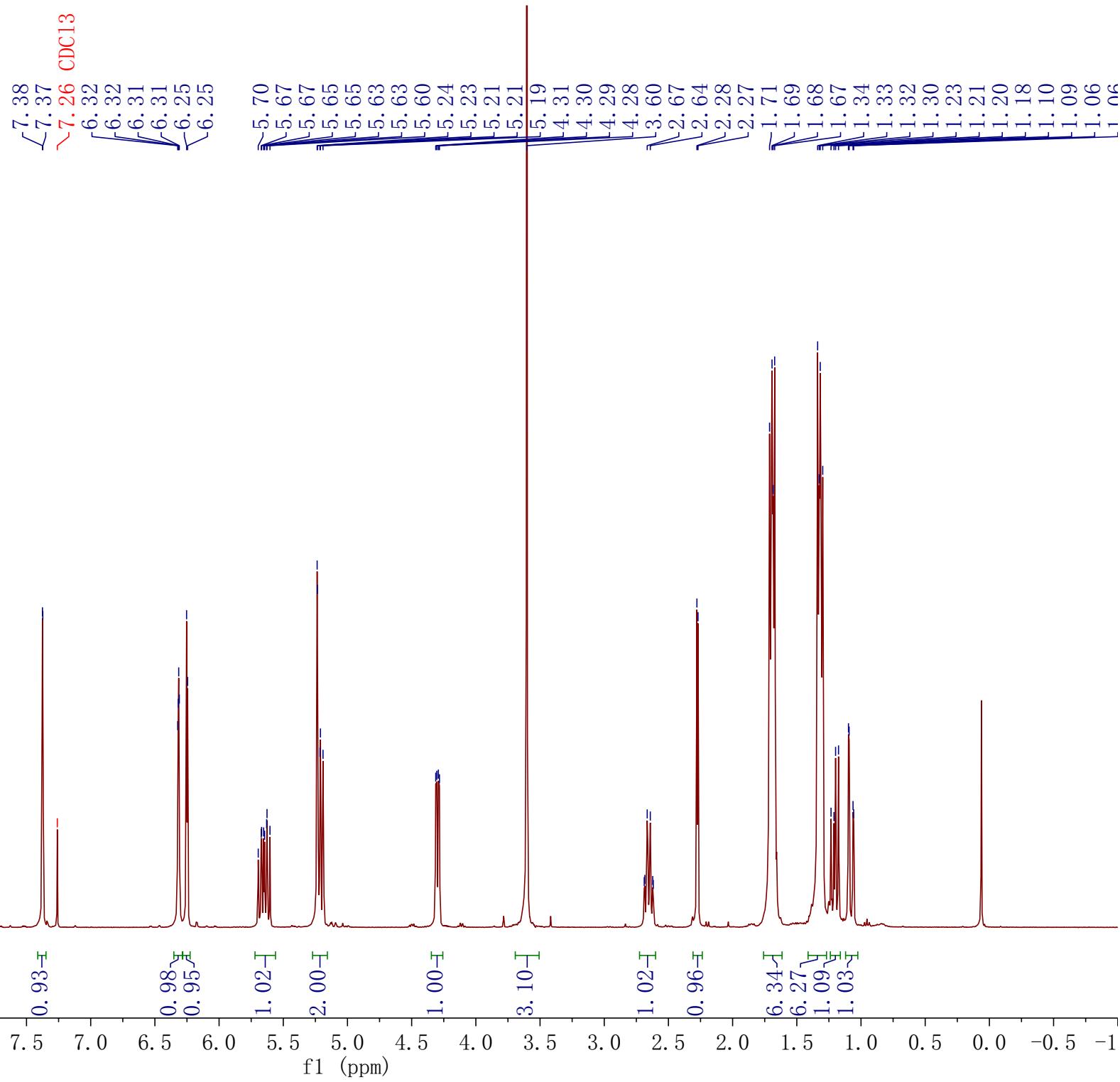
6i

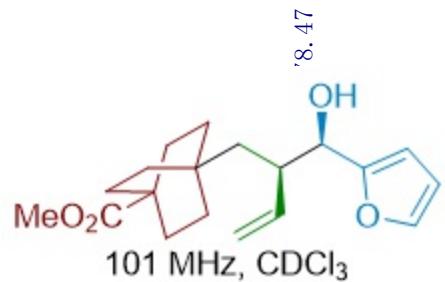




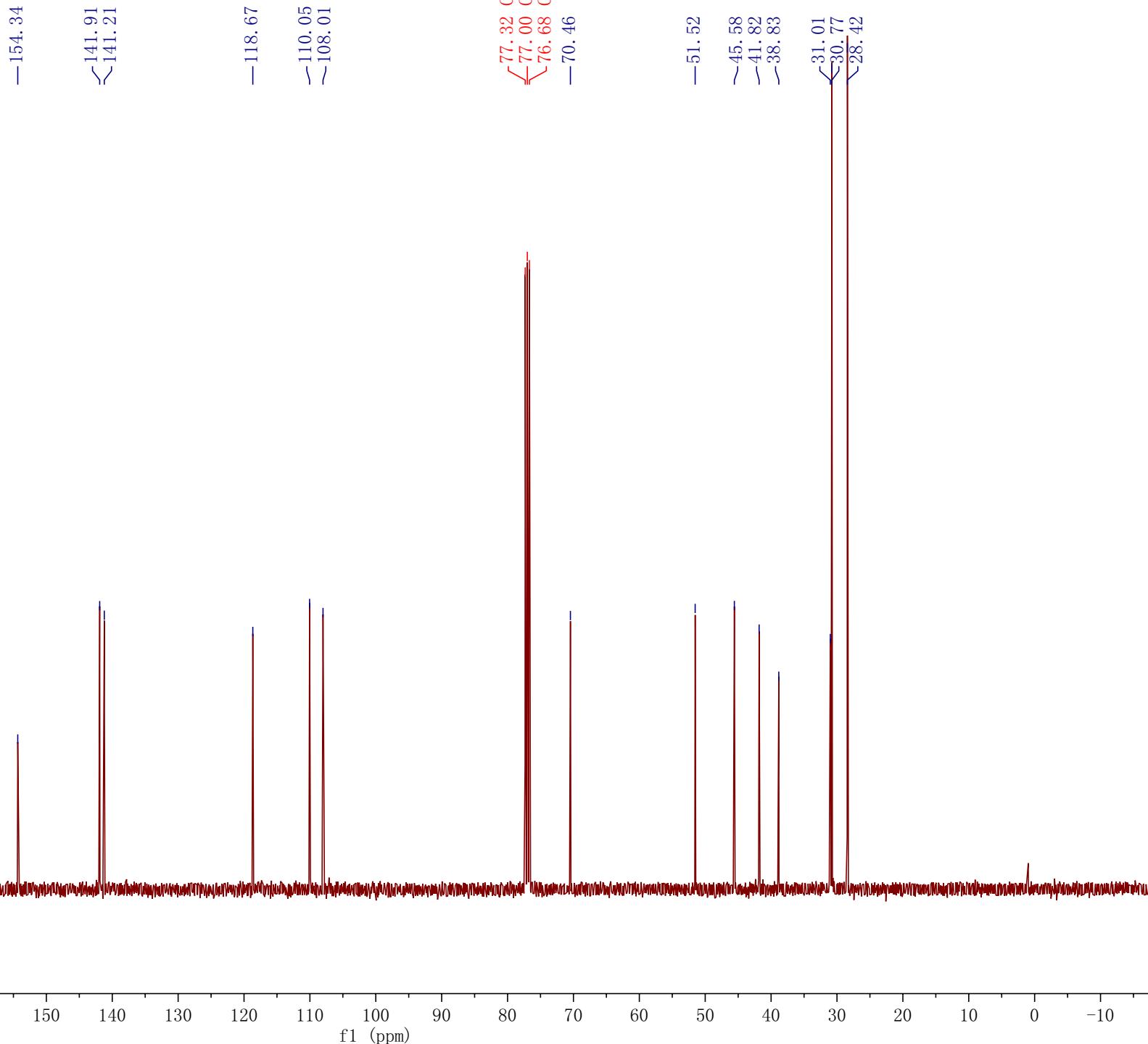


**6j**





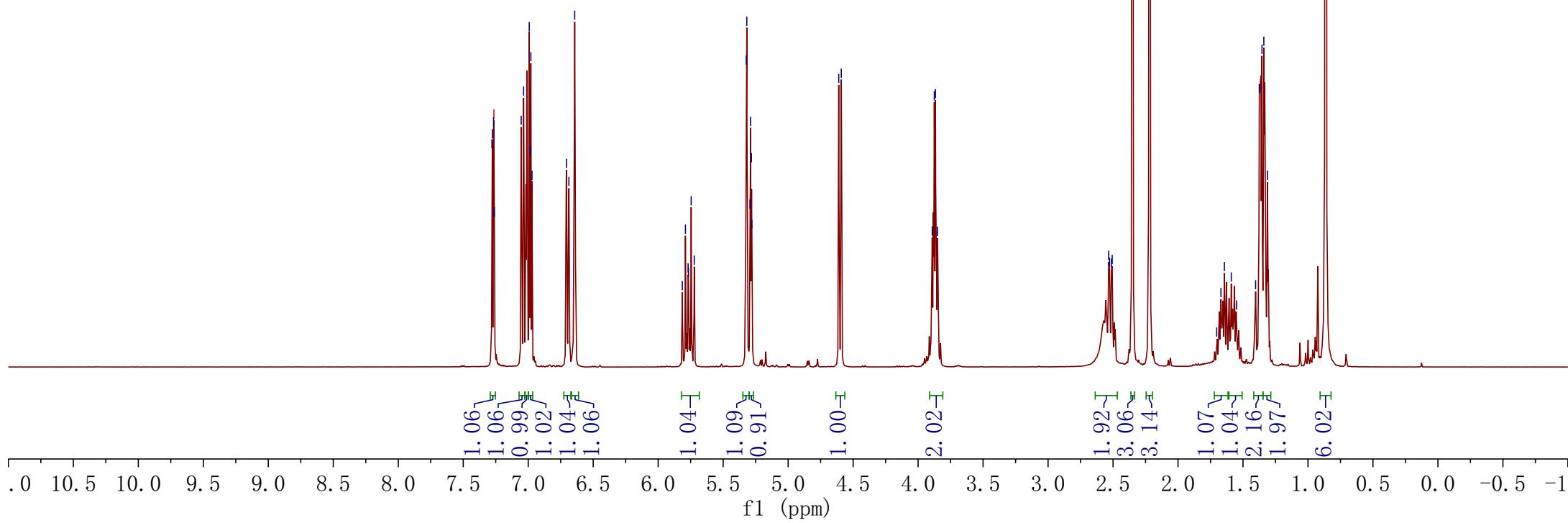
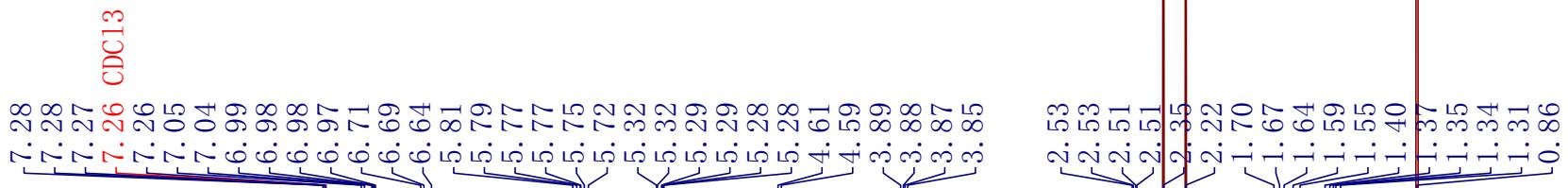
**6j**

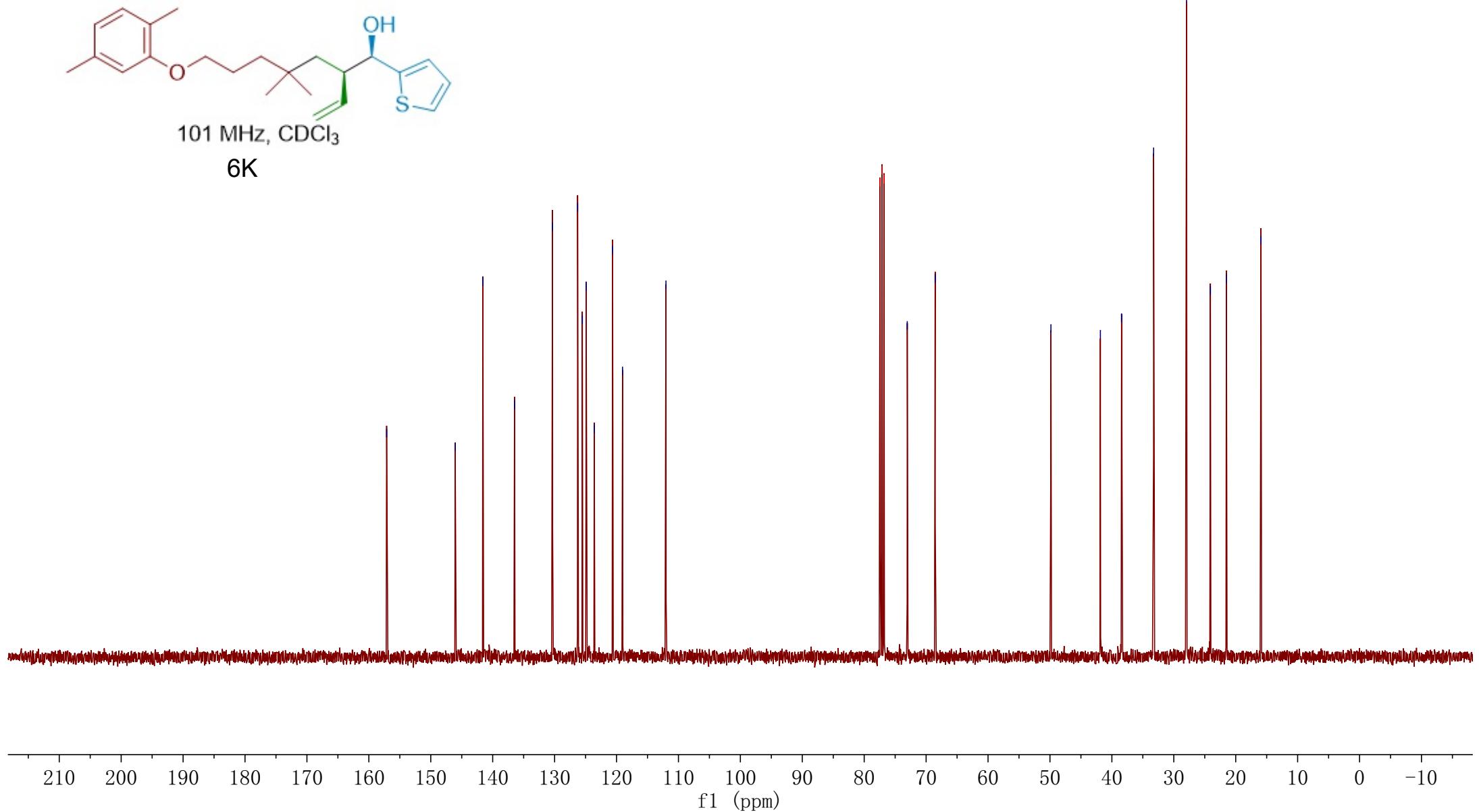


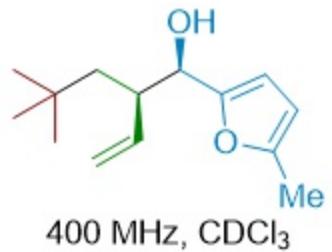


400 MHz, CDCl<sub>3</sub>

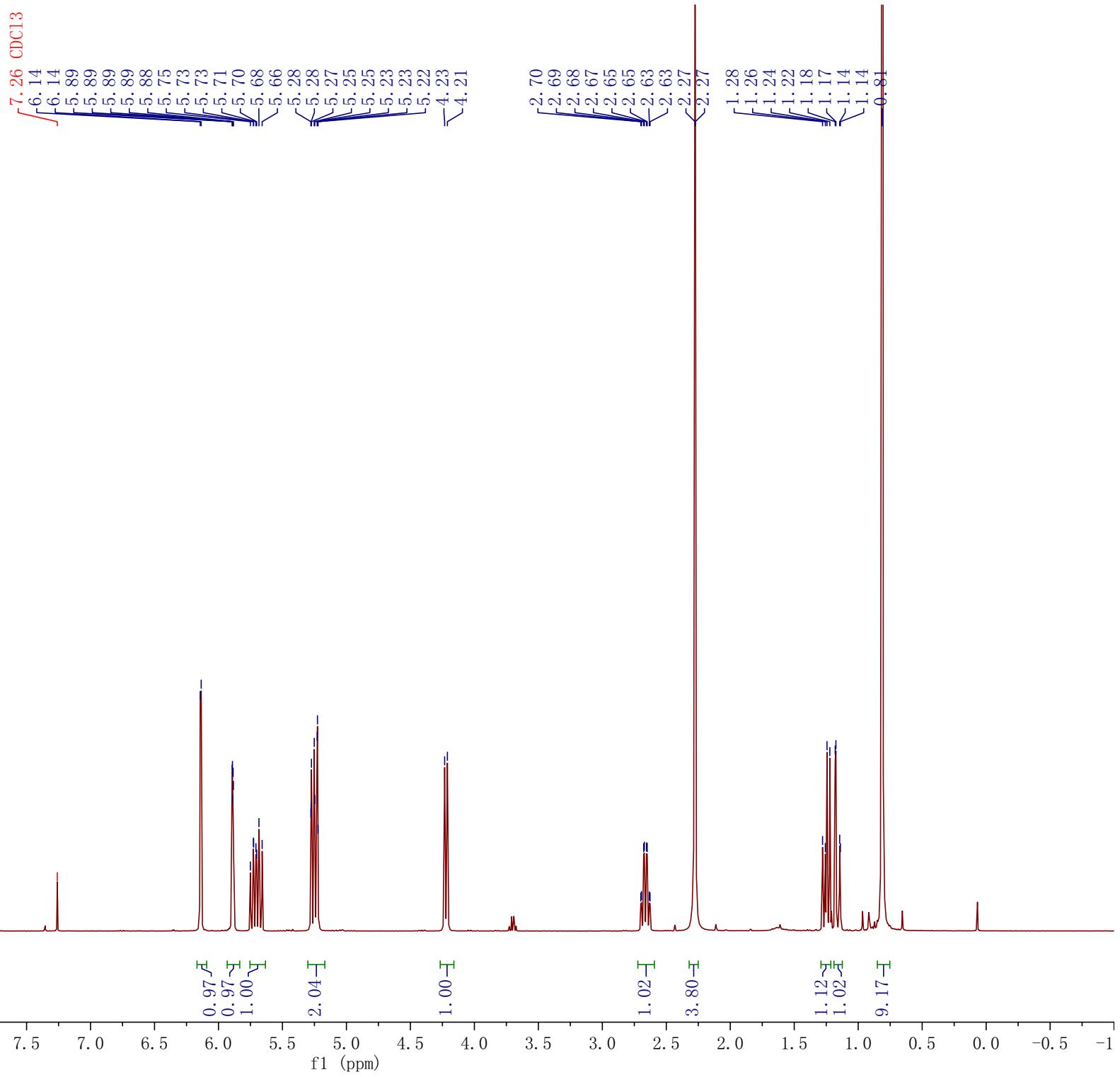
6K

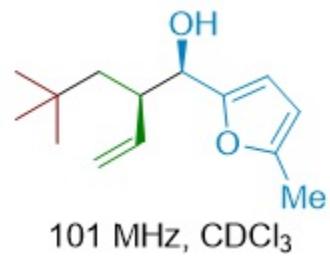






**6l**

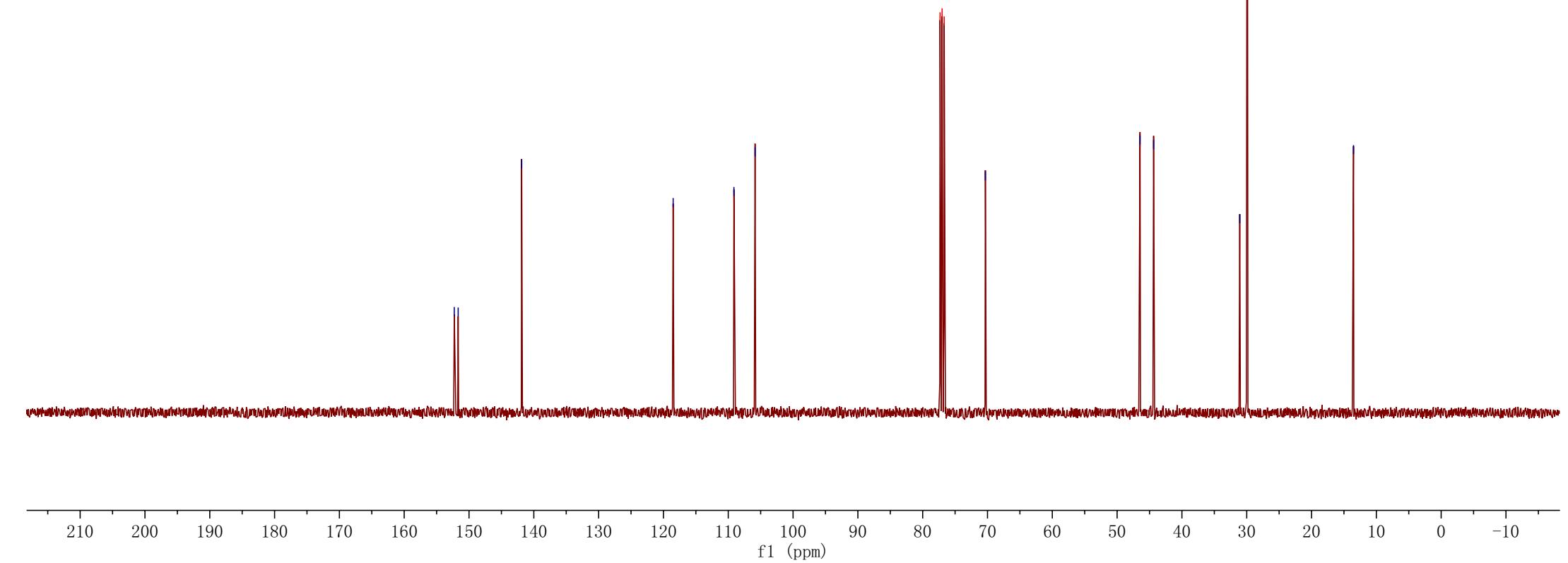


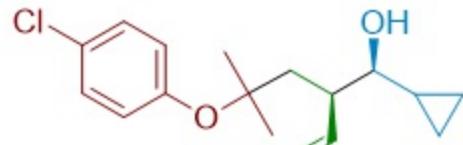


101 MHz, CDCl<sub>3</sub>

**6l**

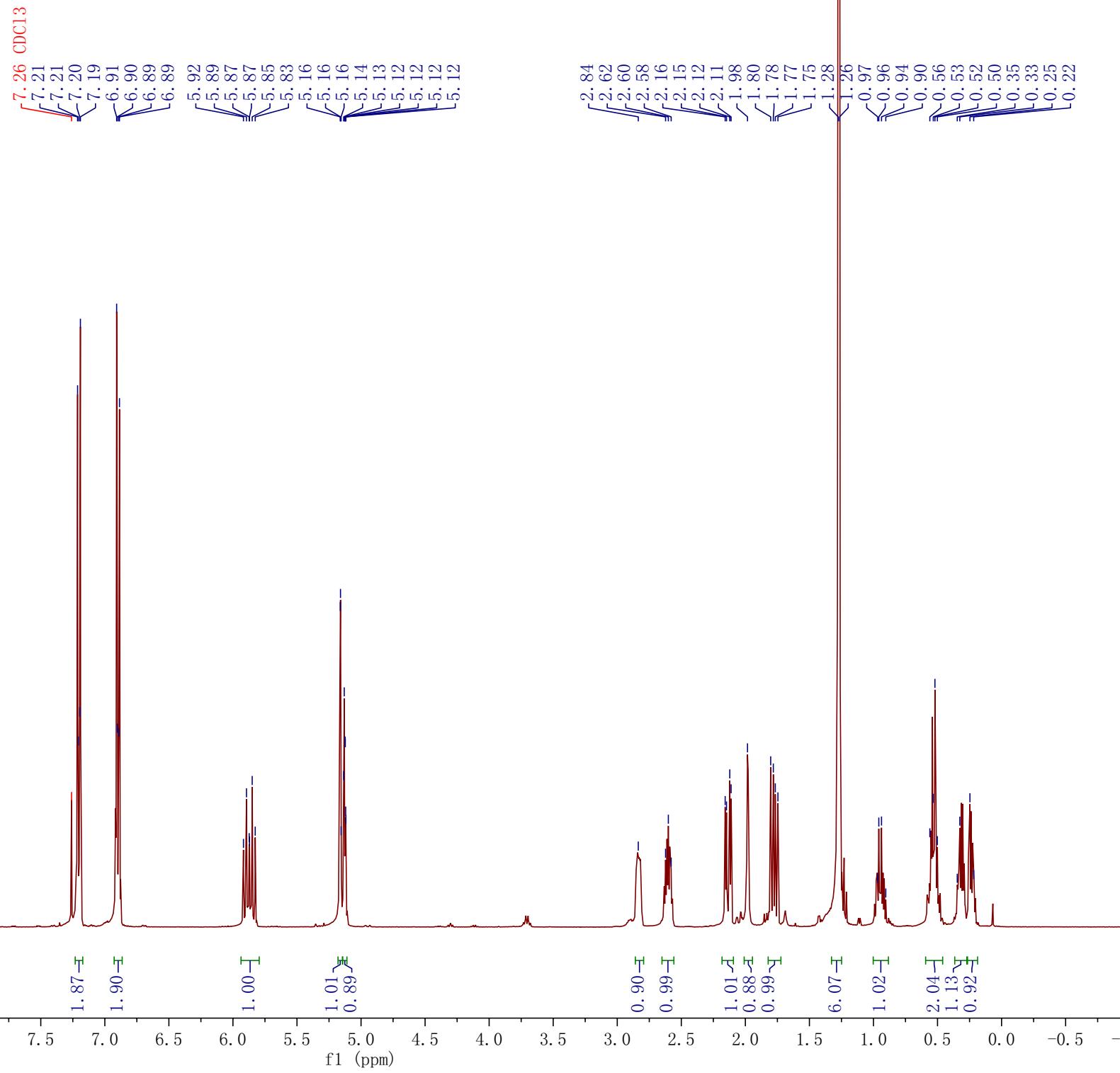
—152.28  
—151.67  
—141.88  
—118.50  
—109.12  
—105.86  
—70.33  
—46.46  
—44.37  
—31.08  
—29.92  
—13.52

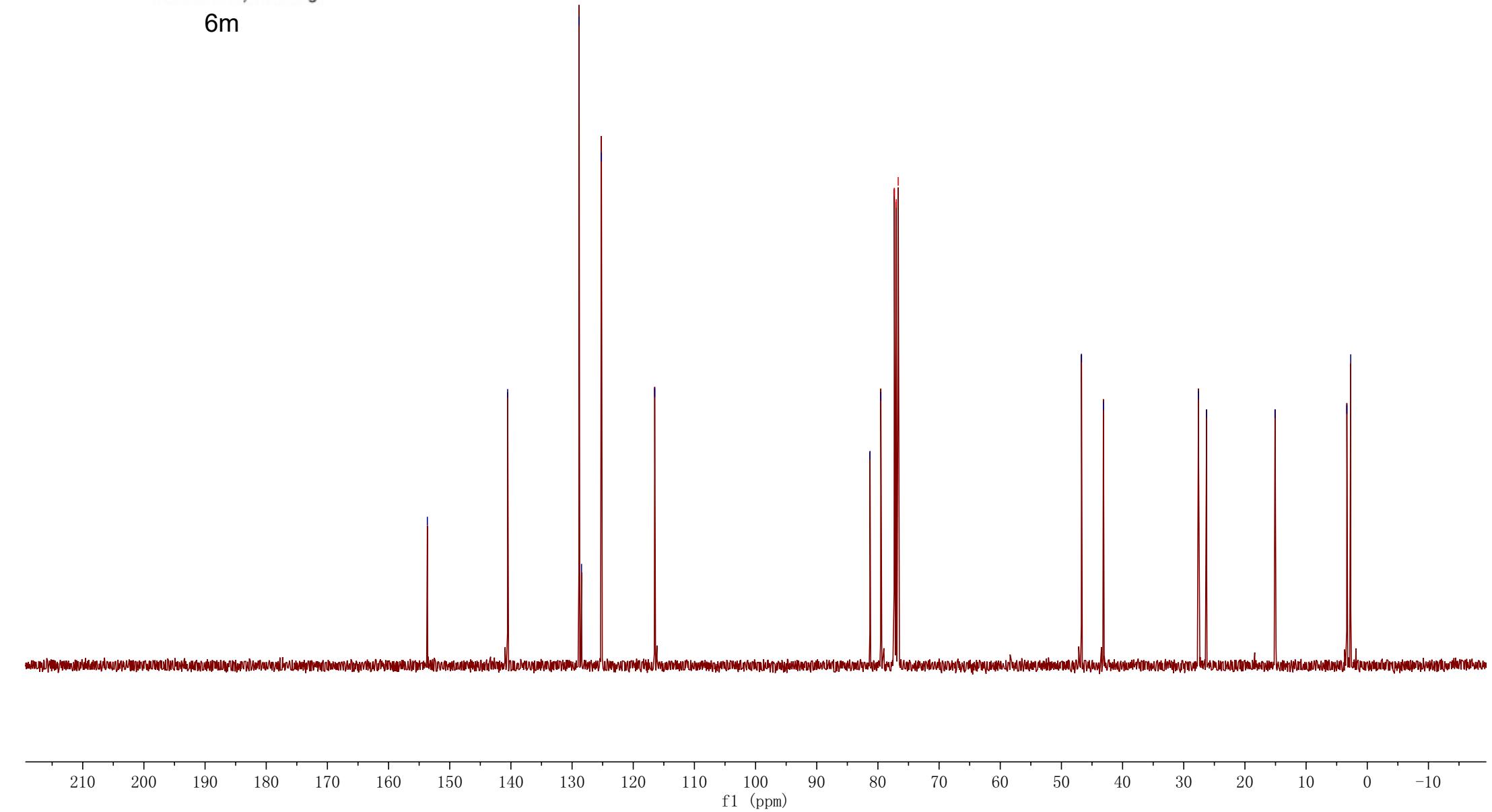
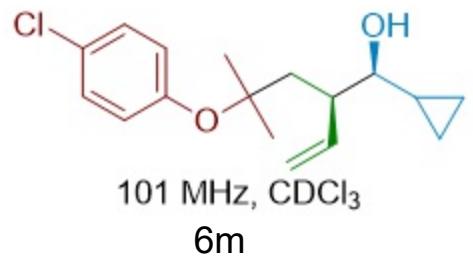


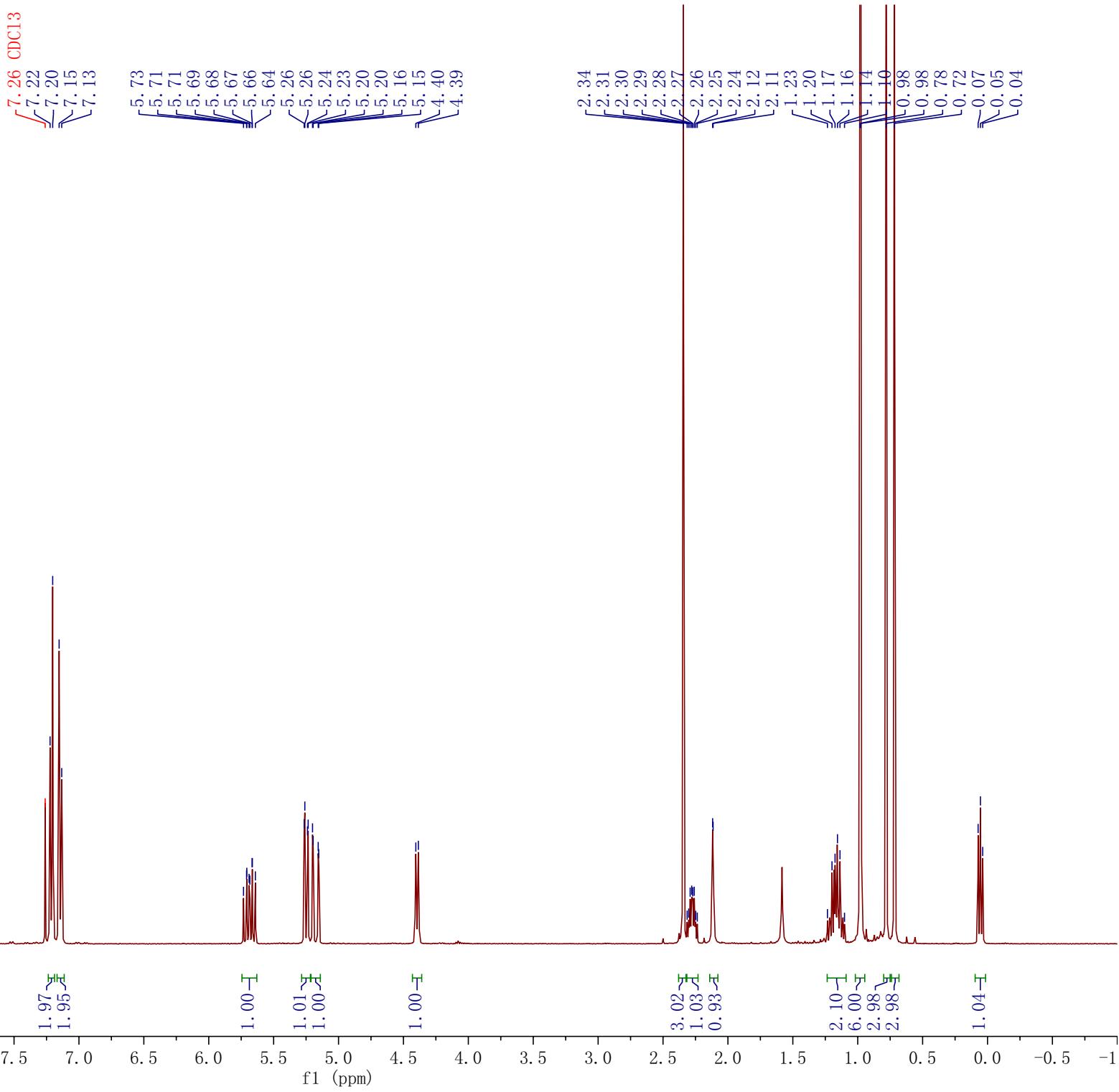
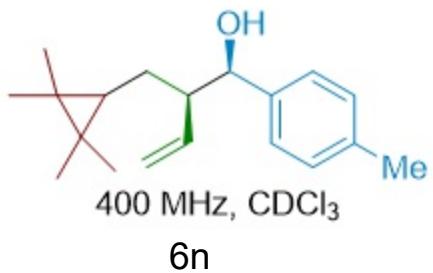


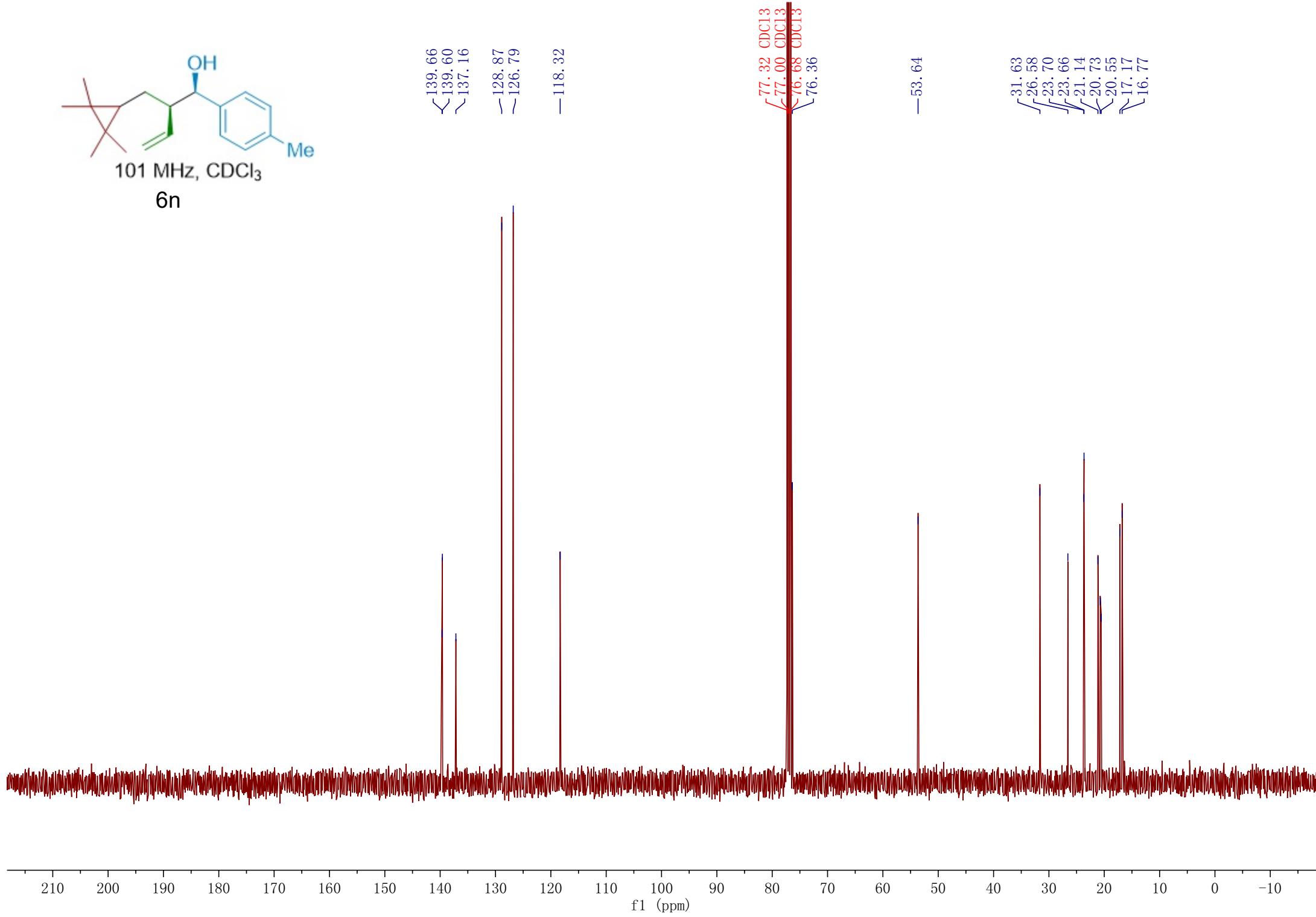
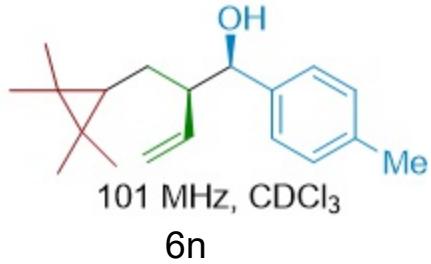
400 MHz, CDCl<sub>3</sub>

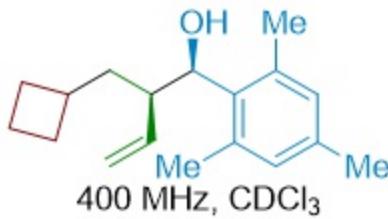
6m



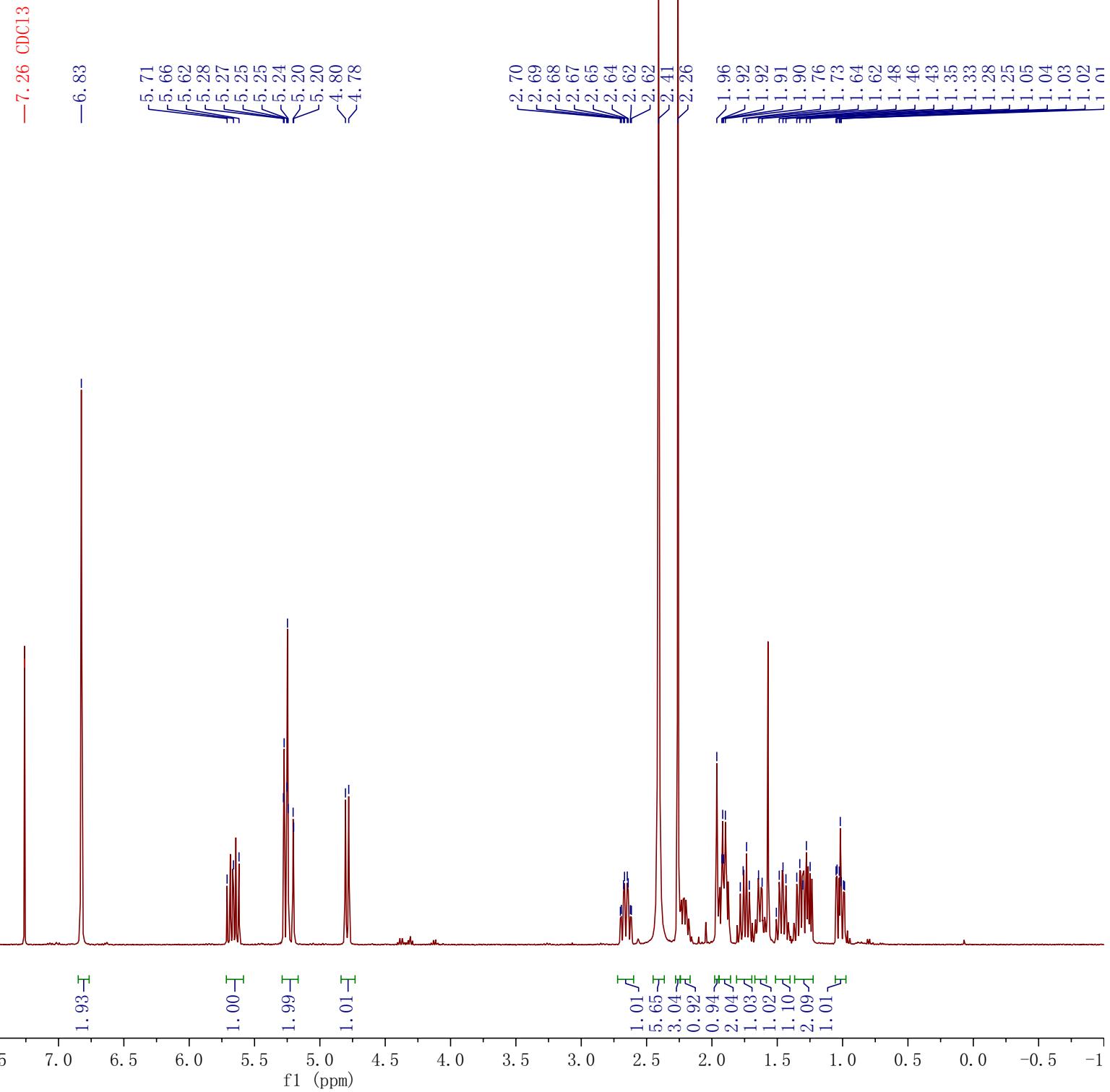








6o





**6o**

—140.97  
—136.87  
—136.59  
—134.26  
—130.17

—118.42

—77.32 CDCl<sub>3</sub>  
—77.00 CDCl<sub>3</sub>  
—76.68 CDCl<sub>3</sub>  
—72.60

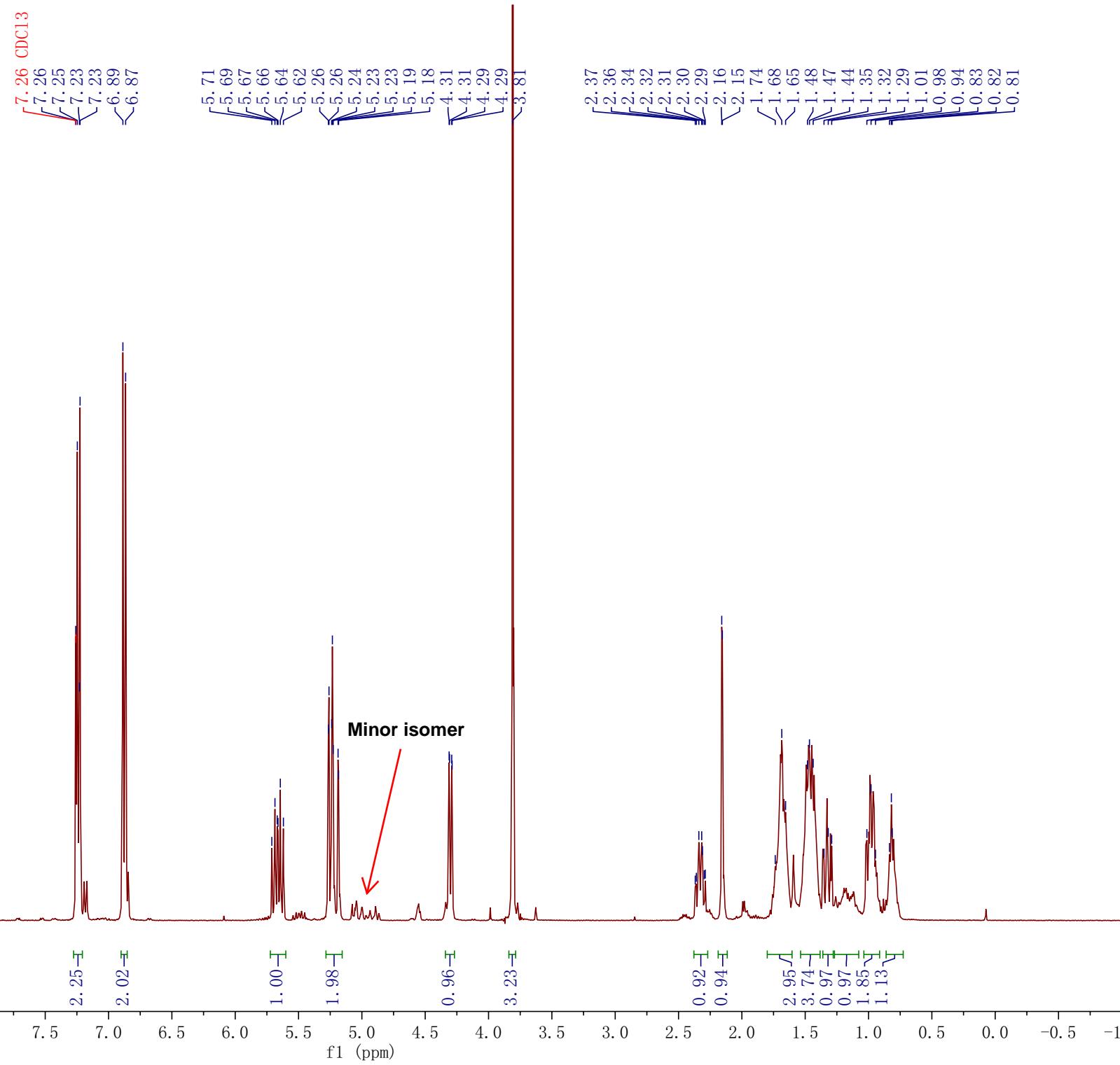
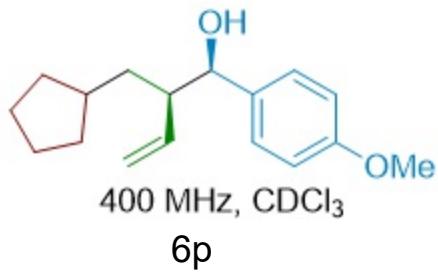
—48.62

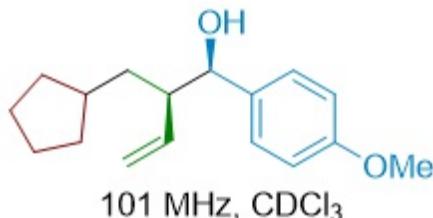
—37.71  
—33.97  
—28.81  
—27.94

—21.10  
—20.78  
—18.32

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)





101 MHz, CDCl<sub>3</sub>

**6p**

—158.99

—139.83

—134.56

—128.12

—118.50

—113.58

77.32 CDCl<sub>3</sub>  
77.00 CDCl<sub>3</sub>  
76.68 CDCl<sub>3</sub>  
76.37 CDCl<sub>3</sub>

—55.19

—52.12

~37.49

~36.87

~33.38

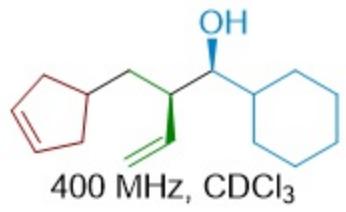
~31.56

~25.01

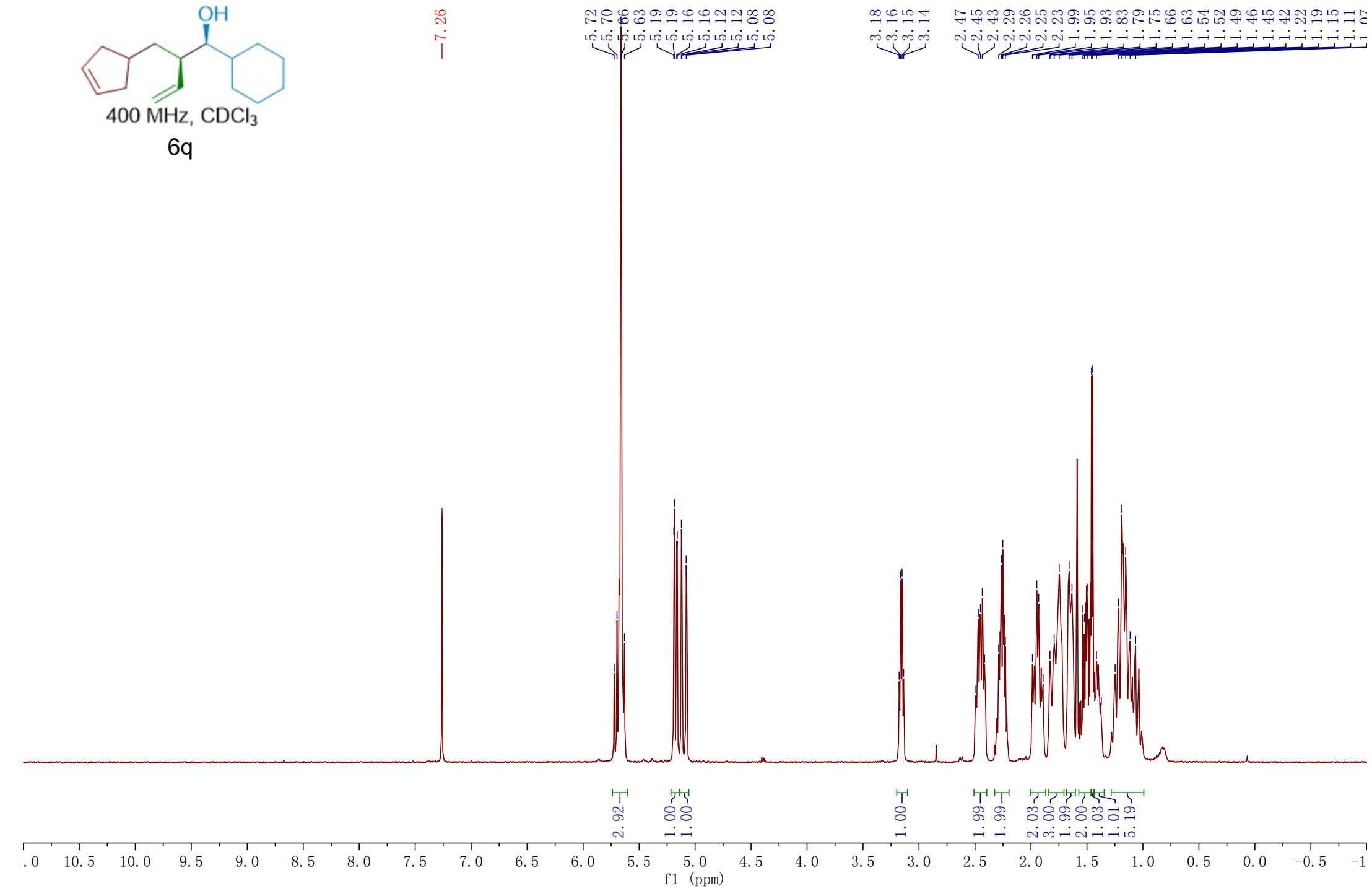
~24.97

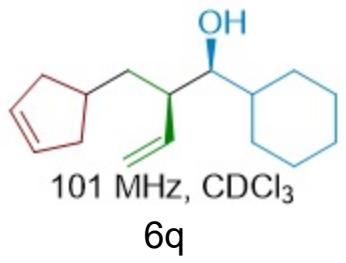
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



-7.26 CDCl<sub>3</sub>





101 MHz, CDCl<sub>3</sub>

**6q**

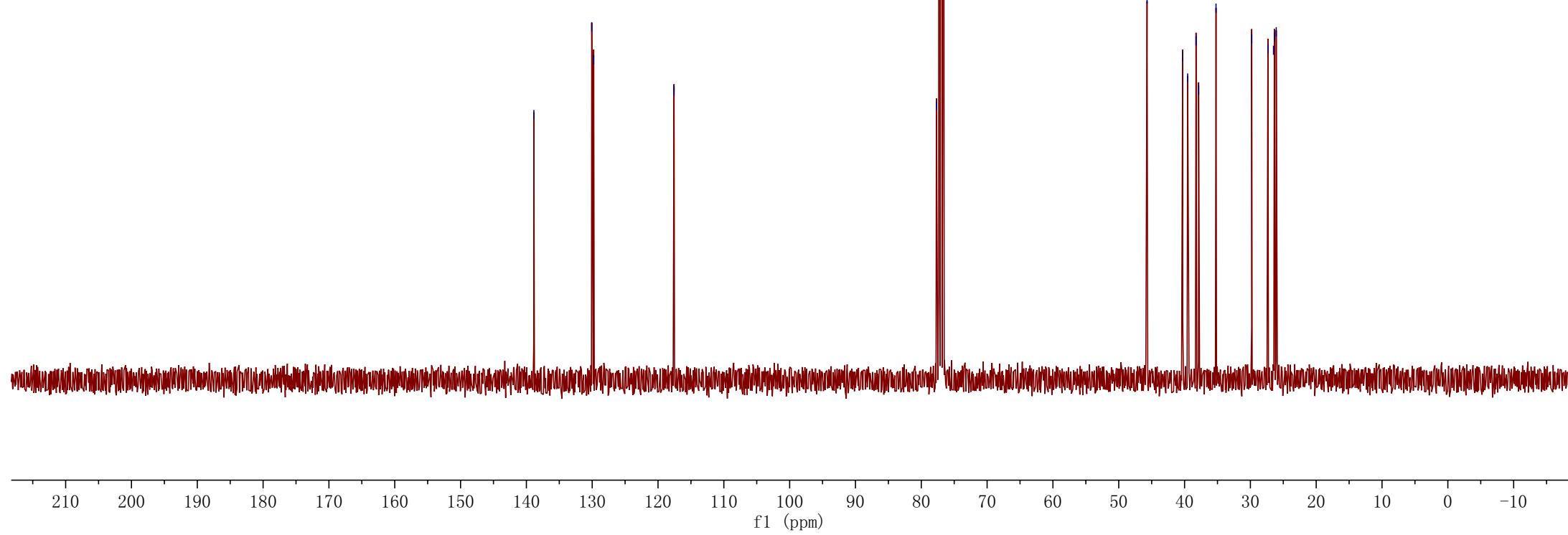
—138.86

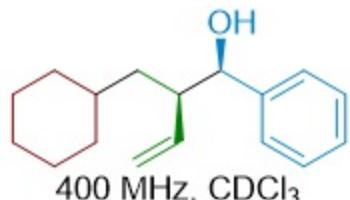
130.07  
129.77

—117.56

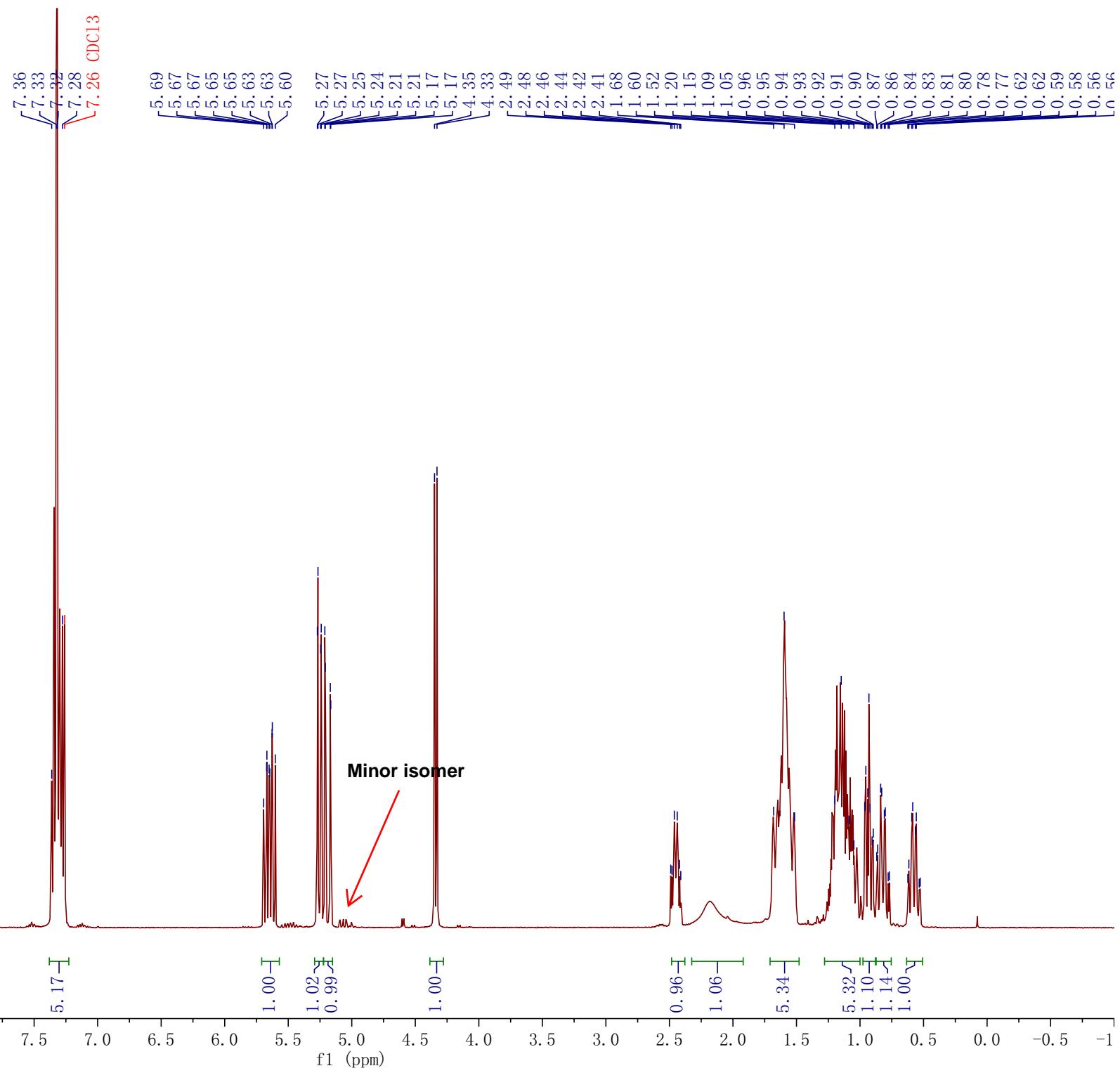
77.70  
77.32 CDCl<sub>3</sub>  
77.00 CDCl<sub>3</sub>  
76.68 CDCl<sub>3</sub>

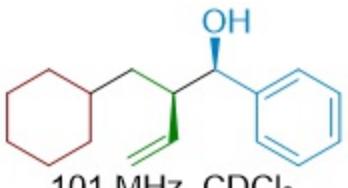
45.70  
40.29  
39.53  
38.26  
37.86  
35.22  
29.80  
27.33  
26.49  
26.36  
26.07





6r





101 MHz, CDCl<sub>3</sub>

6r

—142.42  
—139.56

128.20  
127.59  
126.99

—118.62

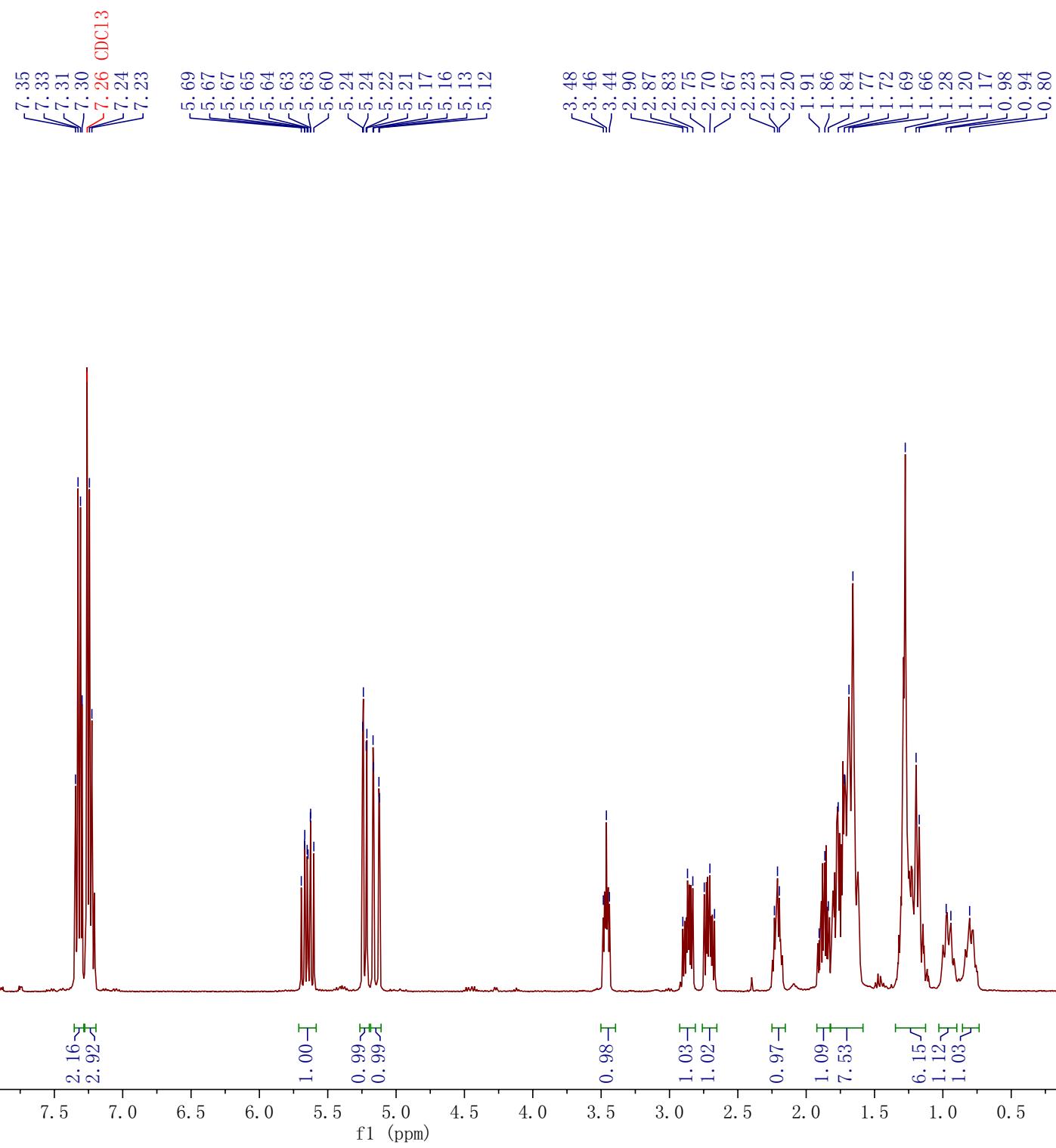
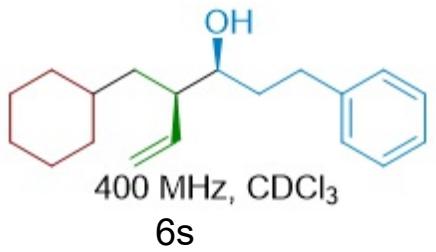
77.32 CDCl<sub>3</sub>  
77.00 CDCl<sub>3</sub>  
76.87  
76.68 CDCl<sub>3</sub>

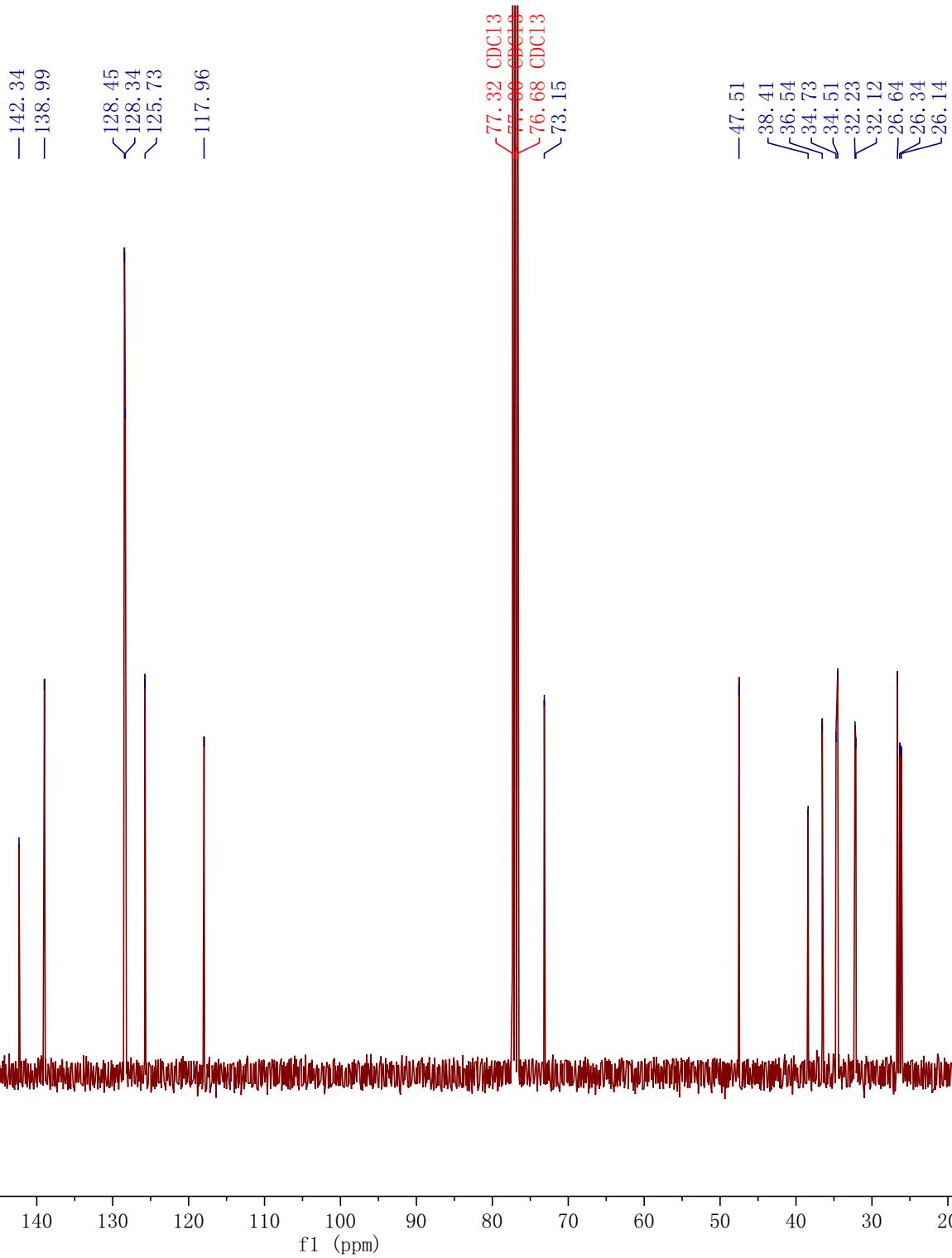
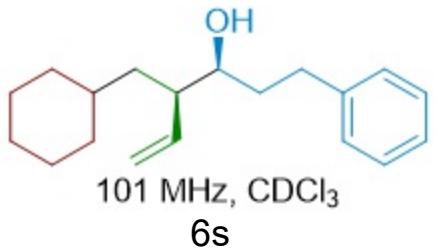
—49.76

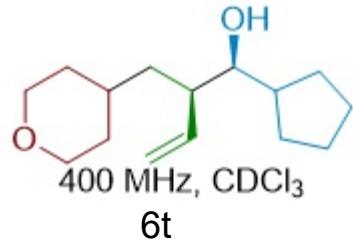
38.09  
34.64  
34.42  
—31.79  
26.55  
26.30  
26.03

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

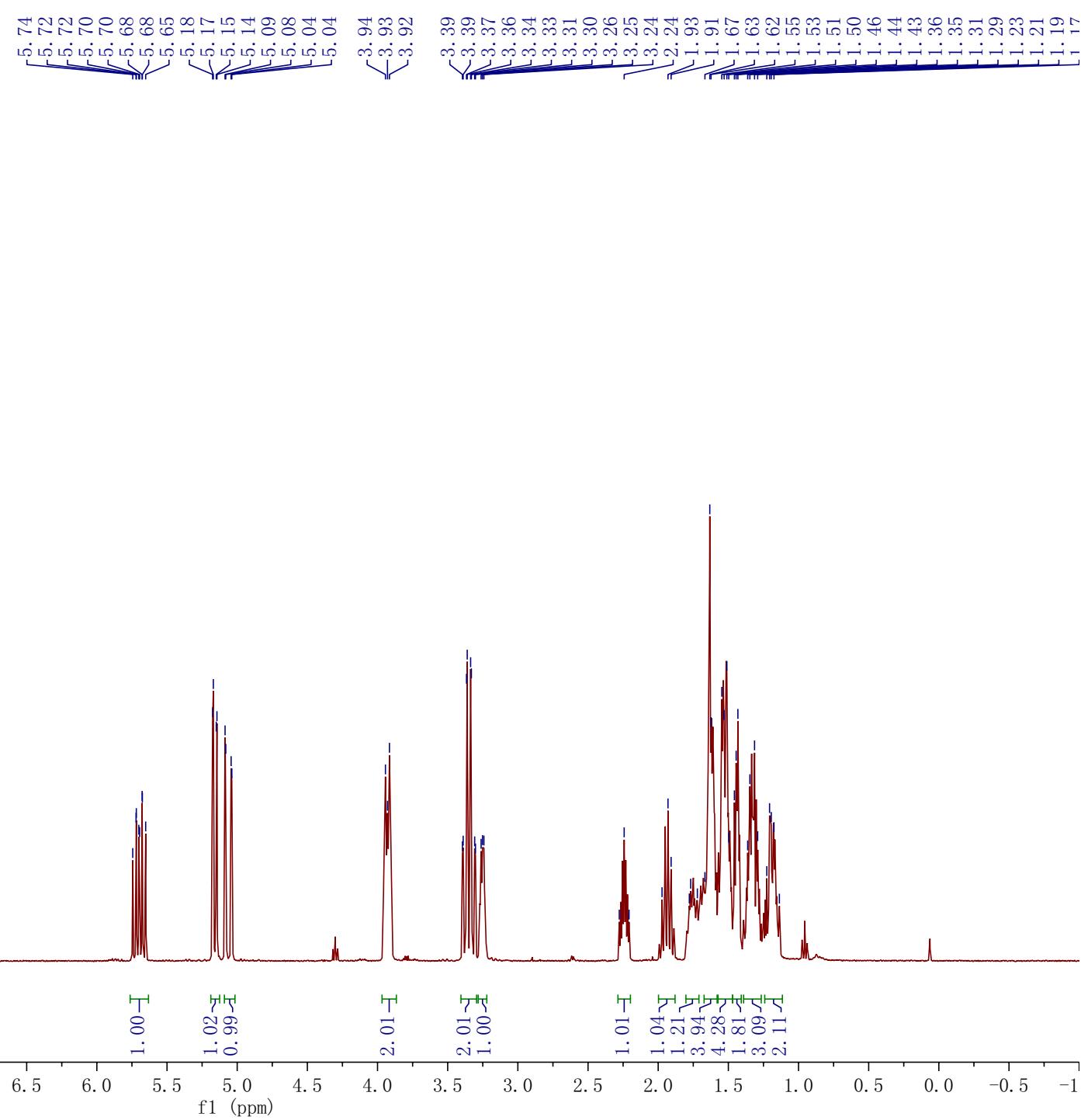
f1 (ppm)

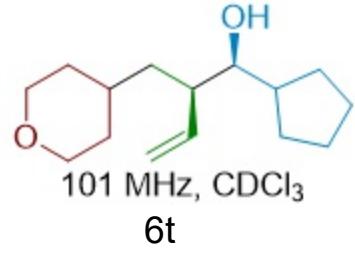






—7.26 CDCl<sub>3</sub>



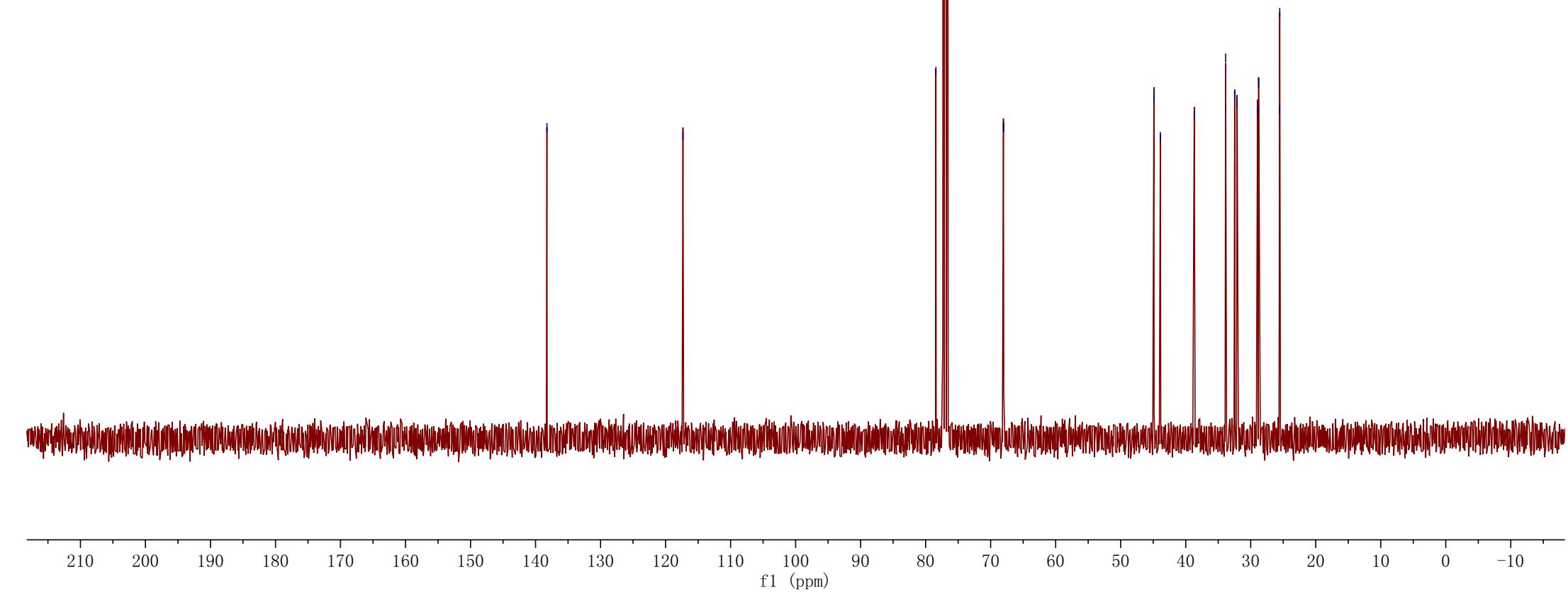


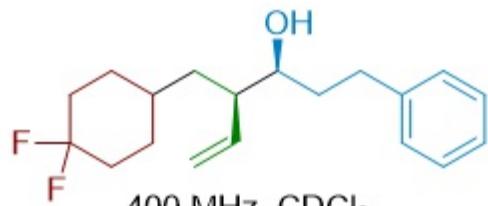
—138.25

—117.32

78.42  
77.32 CDCl<sub>3</sub>  
77.00 CDCl<sub>3</sub>  
76.68 CDCl<sub>3</sub>  
68.04  
68.00

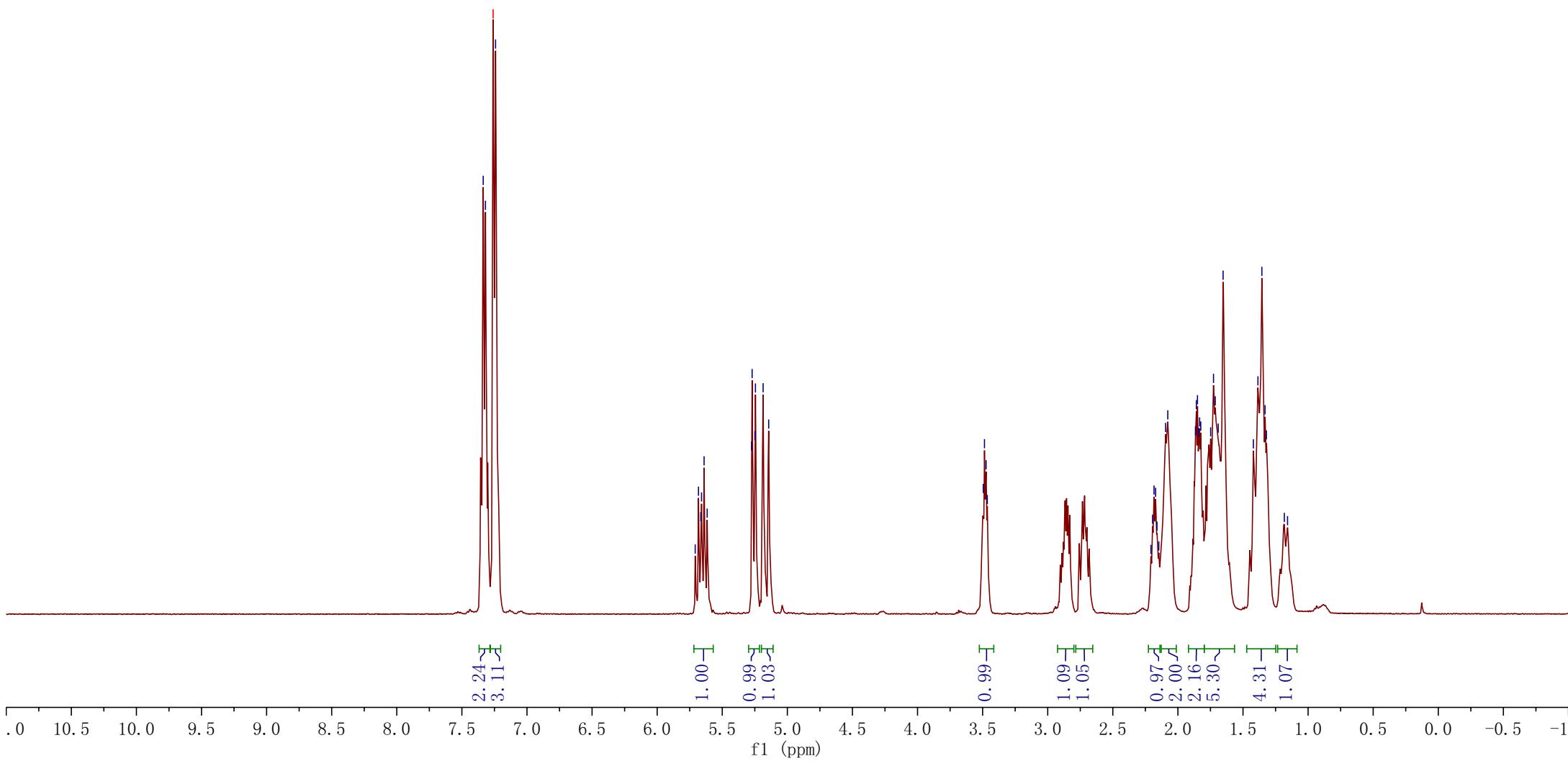
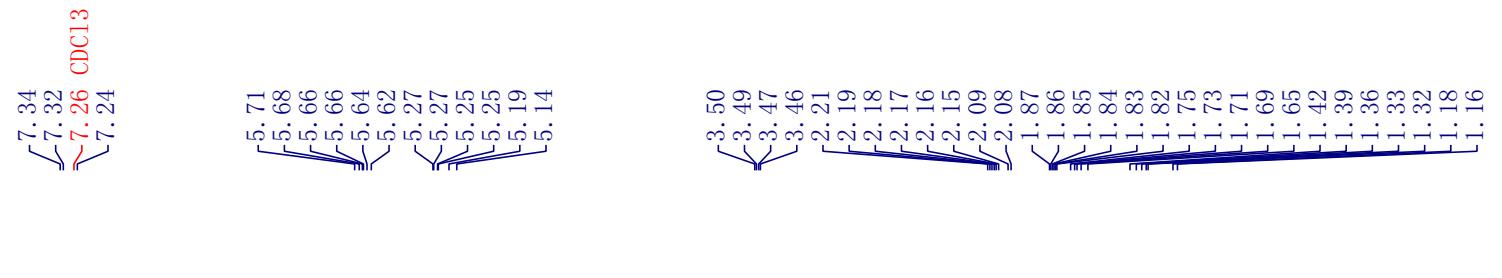
44.89  
43.90  
38.68  
33.86  
32.47  
32.09  
28.95  
28.79  
25.58  
25.54

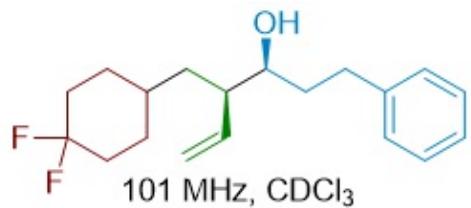




400 MHz, CDCl<sub>3</sub>

6u





**6u**

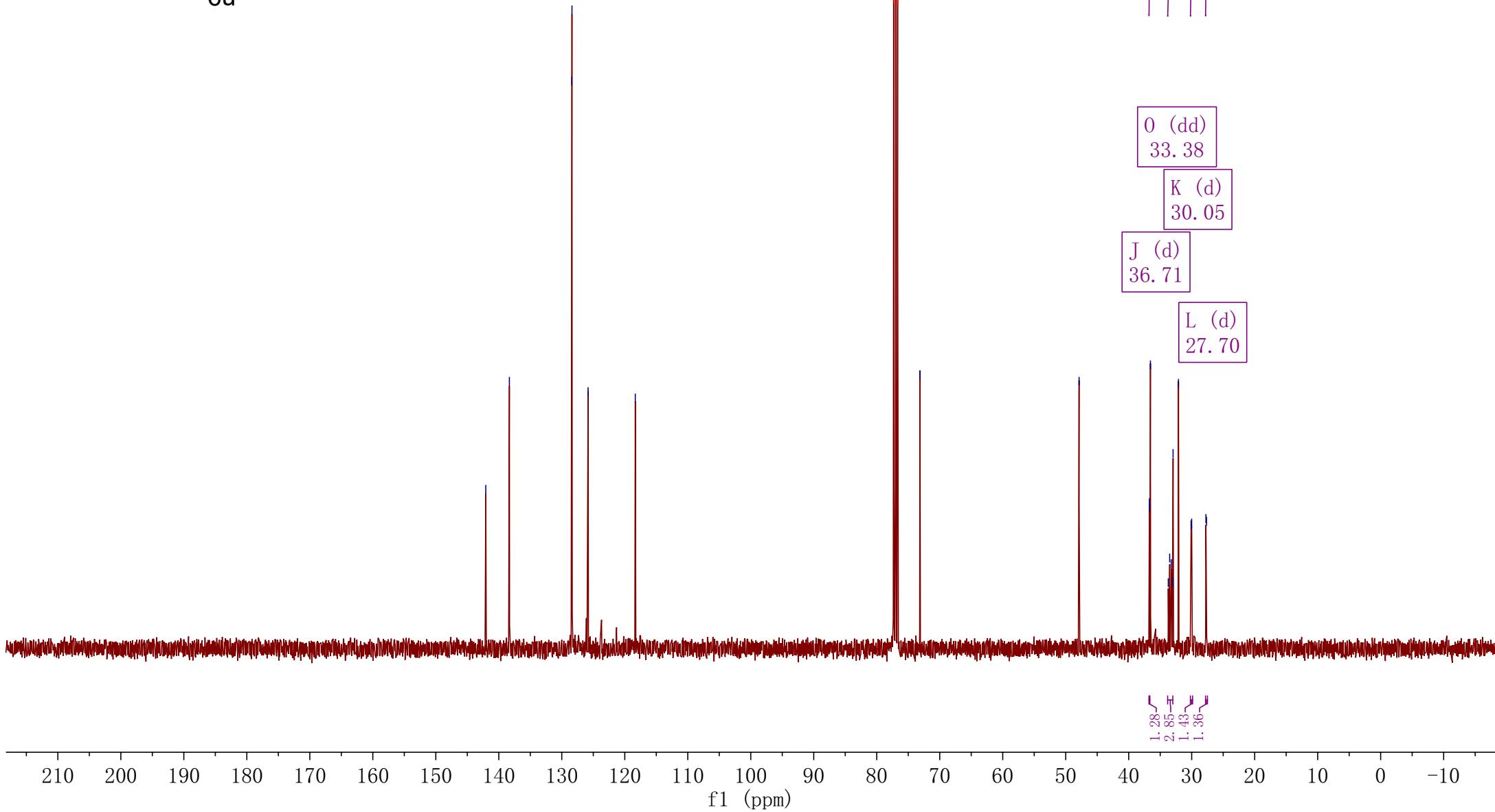
-142.07  
-138.32  
  
<128.42  
<128.38  
<125.82  
-118.33

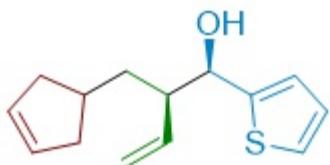
77.32 CDCl<sub>3</sub>  
77.00 CDCl<sub>3</sub>  
76.68 CDCl<sub>3</sub>  
73.14

-47.88  
36.72  
36.70  
36.55  
33.72  
33.50  
33.25  
33.05  
32.96  
32.10  
30.10  
30.00  
27.74  
27.65

0 (dd)  
33.38  
  
K (d)  
30.05  
  
J (d)  
36.71  
  
L (d)  
27.70

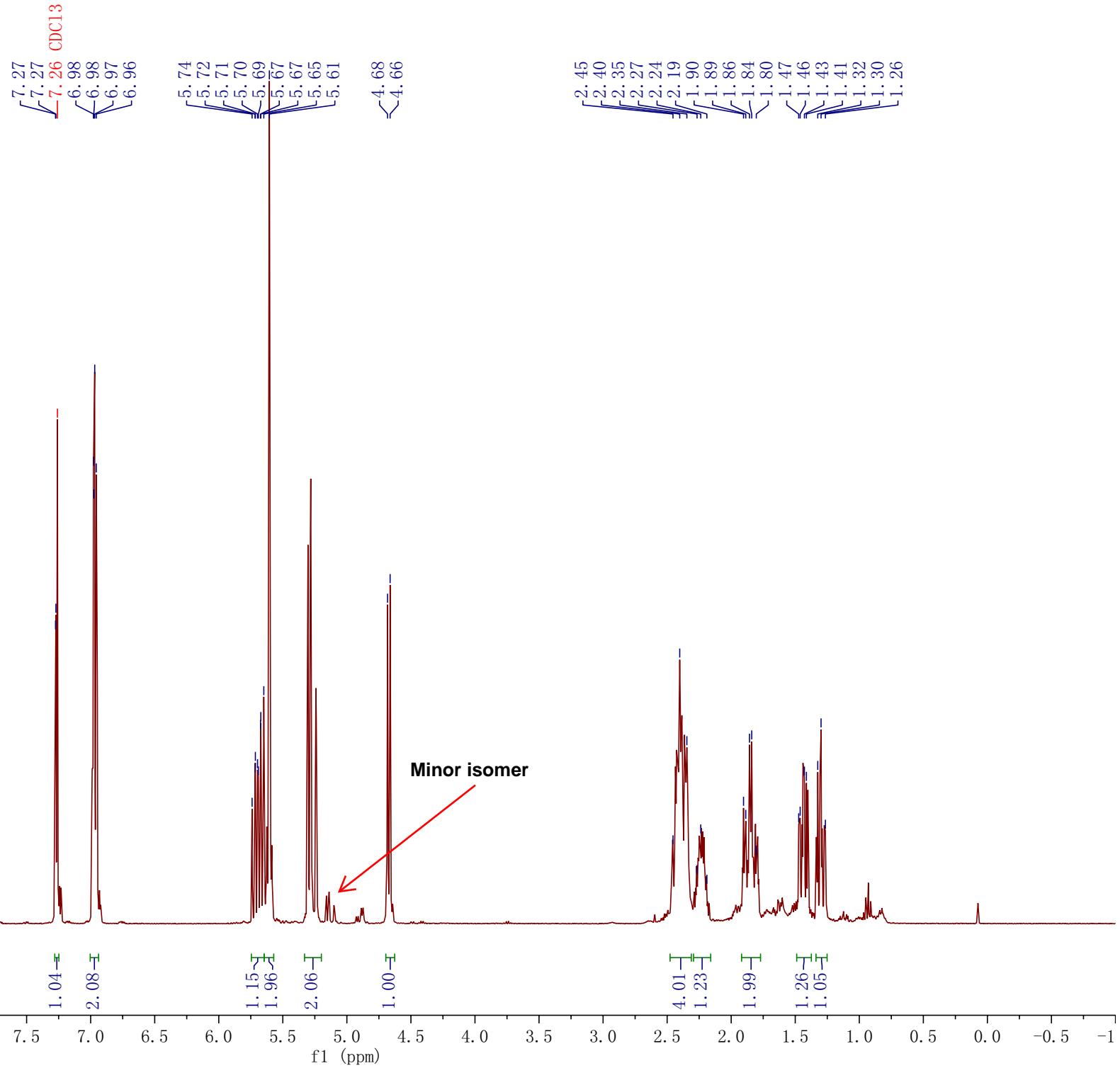
1.28  
2.85  
1.43  
1.36

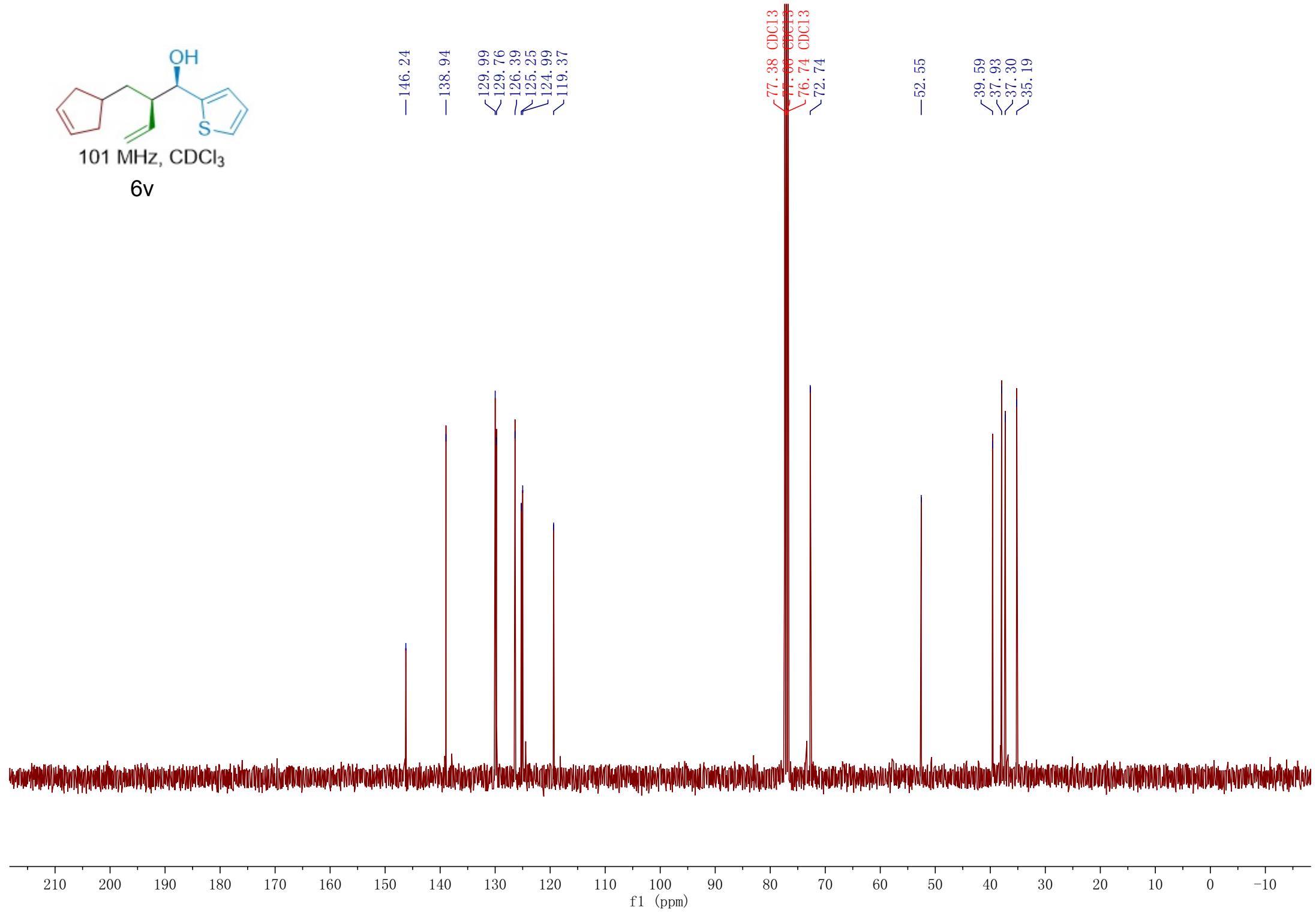
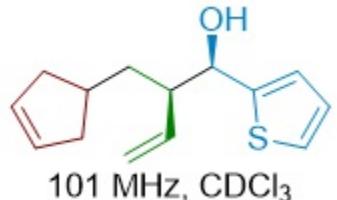


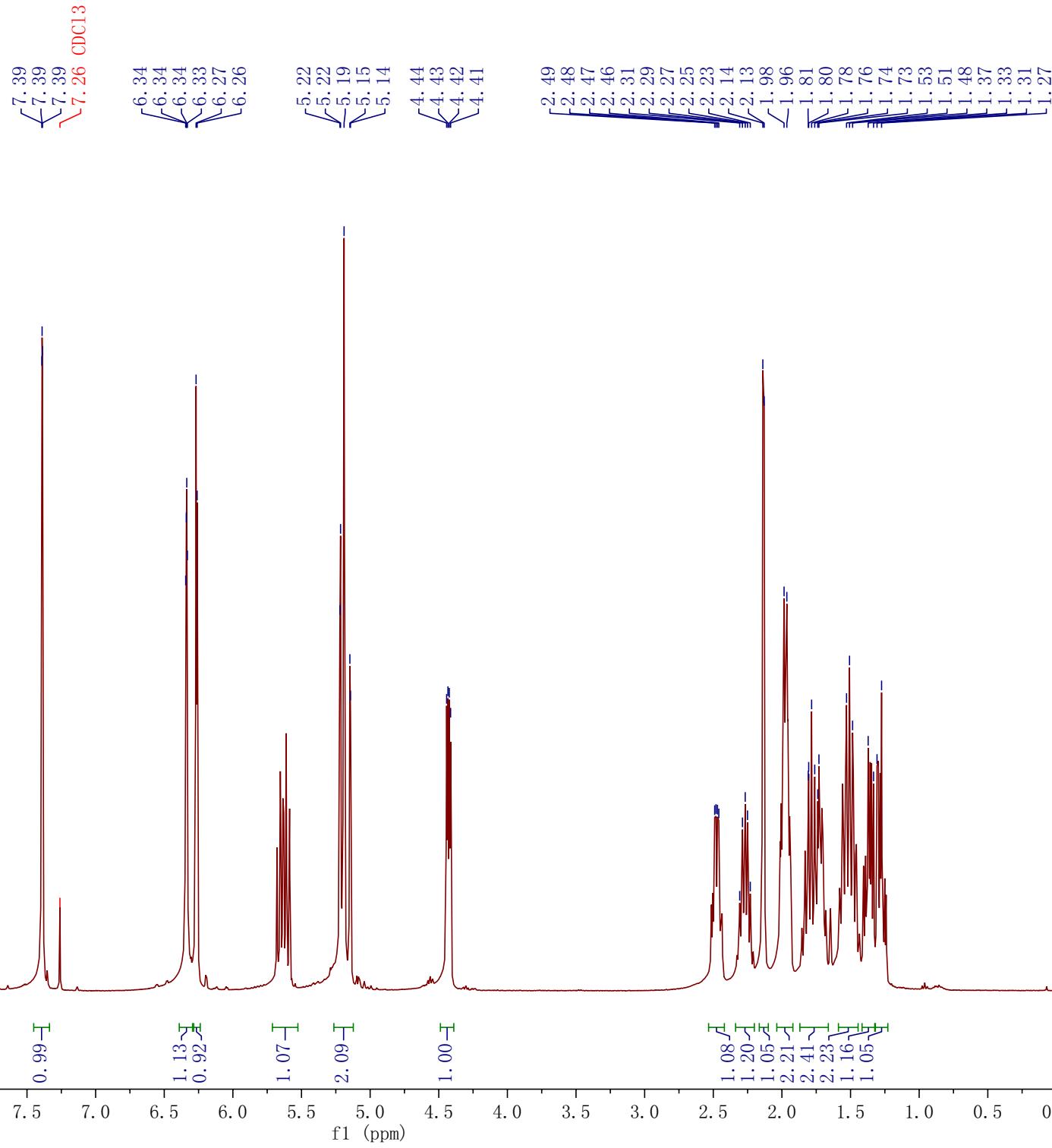
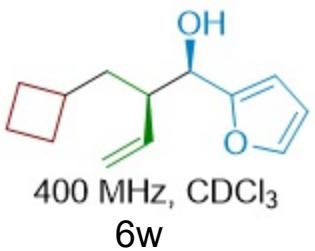


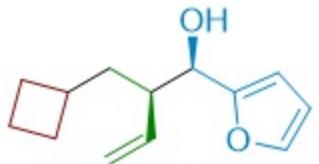
400 MHz, CDCl<sub>3</sub>

6v









101 MHz, CDCl<sub>3</sub>

**6w**

— 154.93

— 141.91

— 138.80

— 118.52

— 110.05

— 107.39

↙ 77.32 CDCl<sub>3</sub>  
↙ 77.00 CDCl<sub>3</sub>  
↙ 76.68 CDCl<sub>3</sub>  
— 70.03

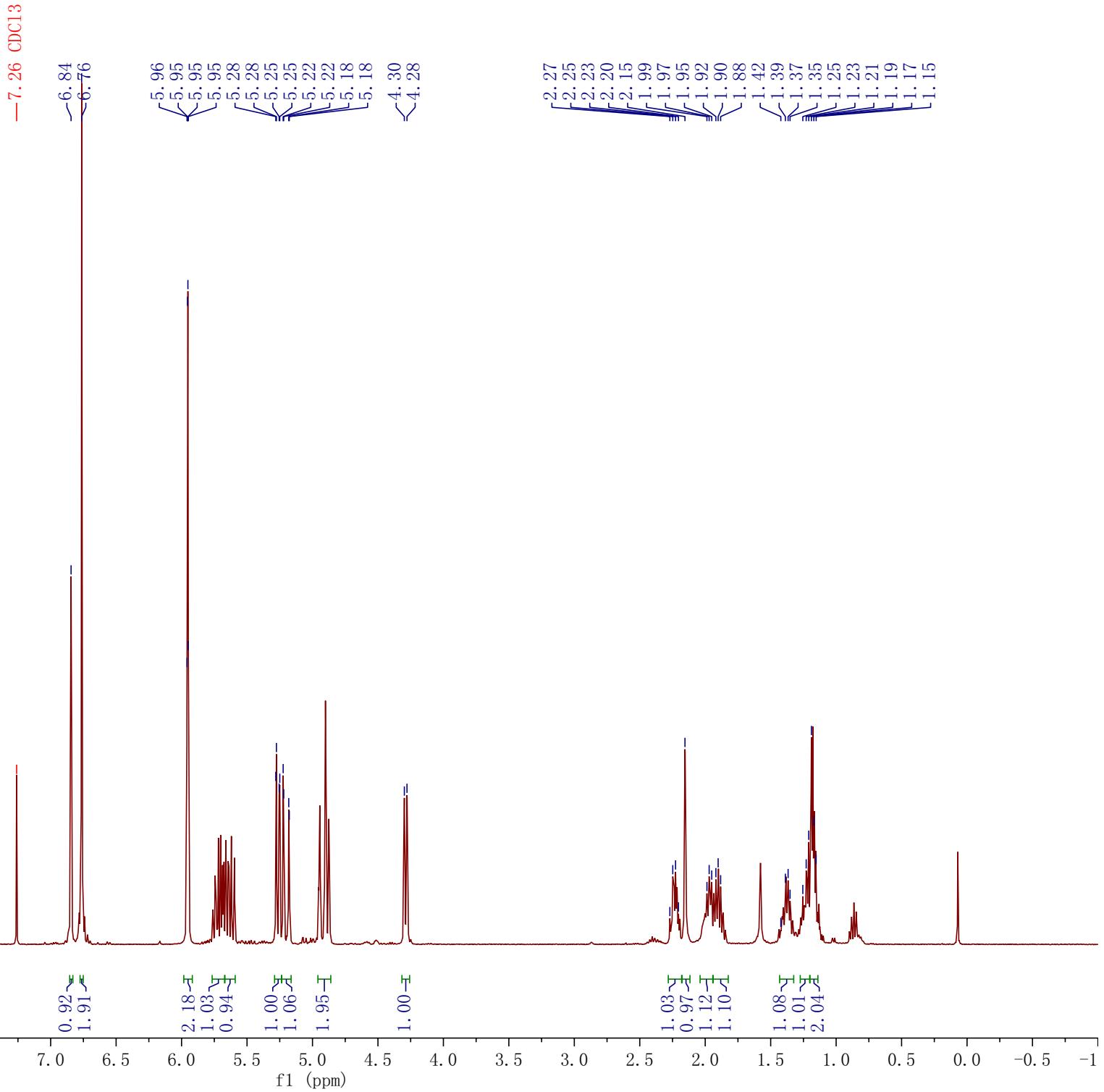
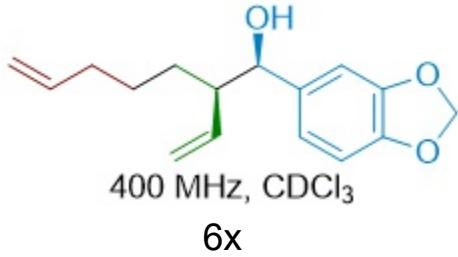
— 48.19

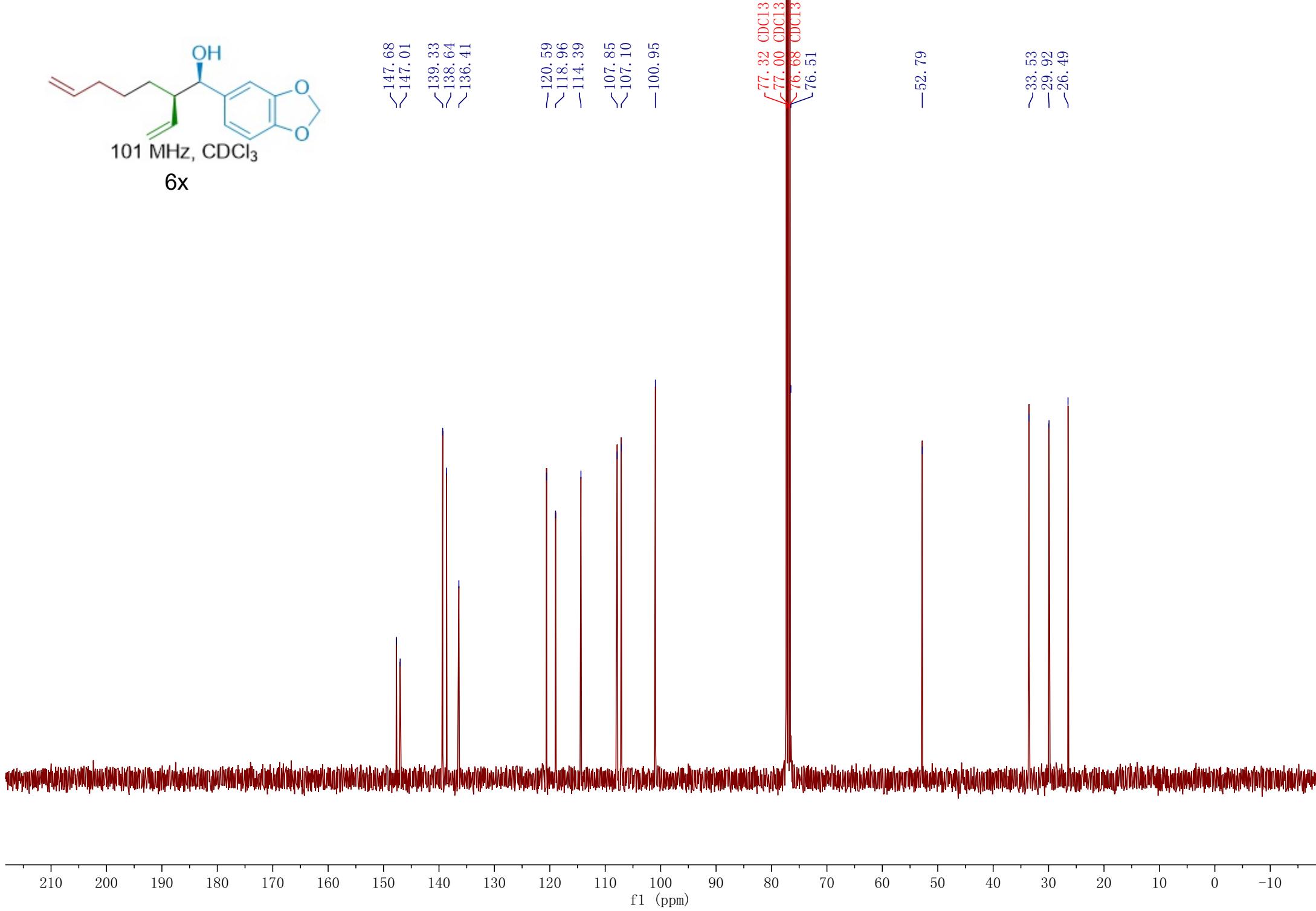
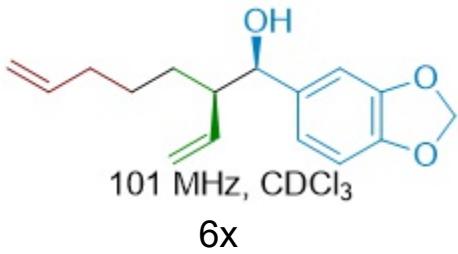
~ 37.80  
~ 33.72  
↙ 28.76  
↙ 28.08

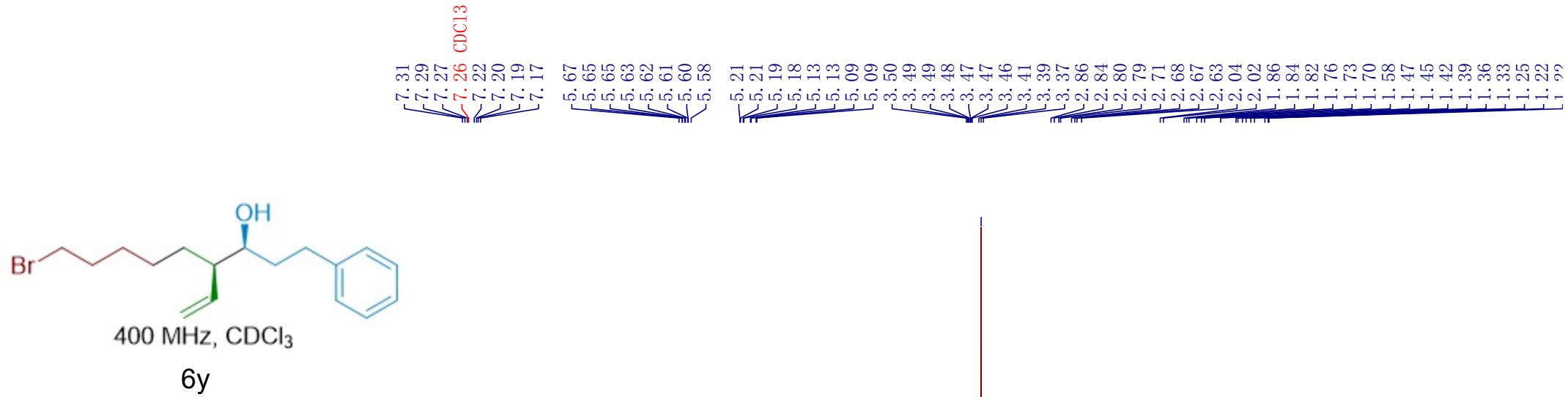
— 18.38

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

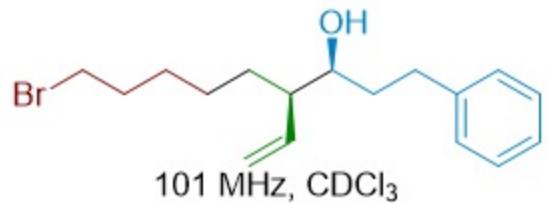




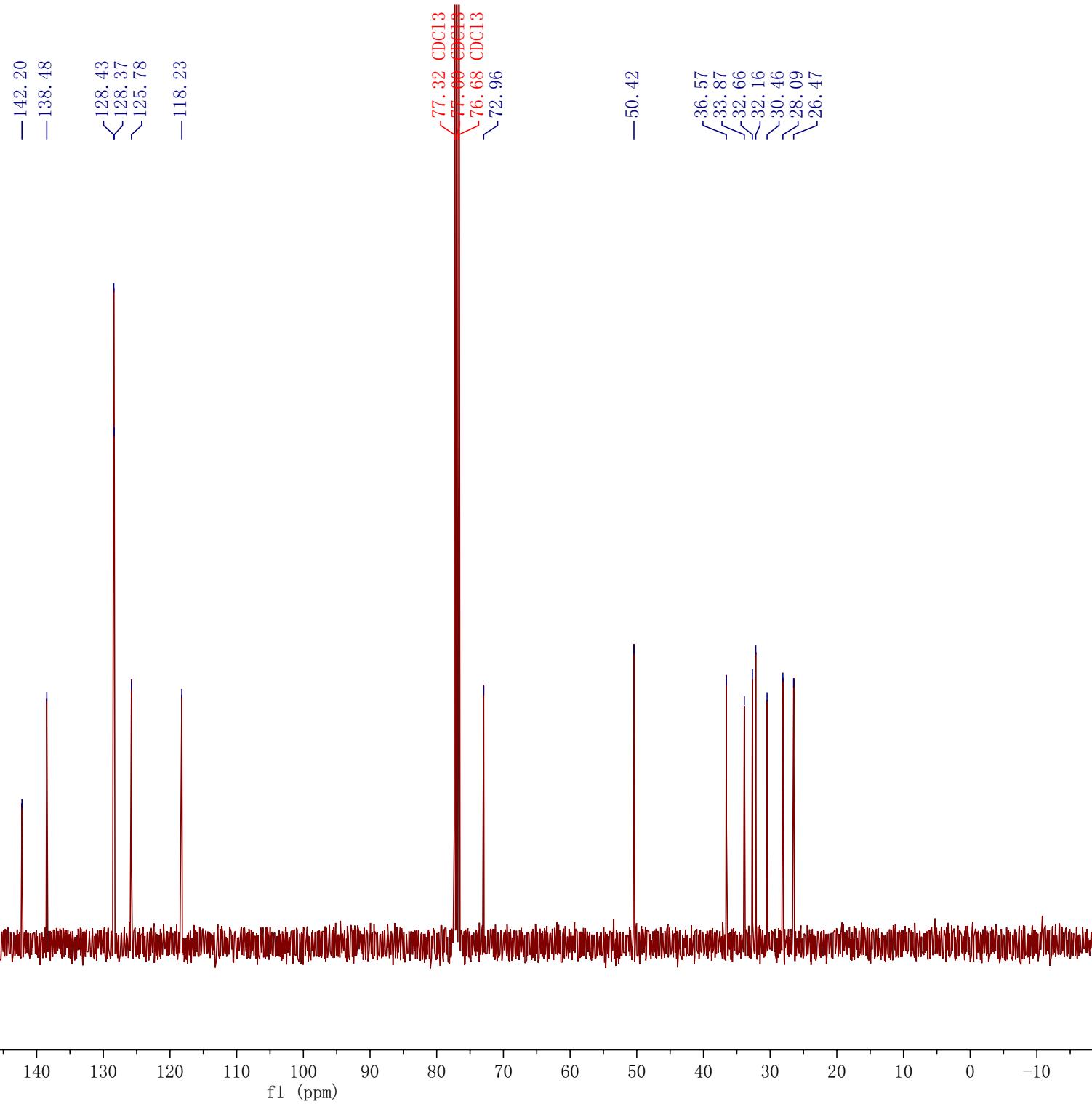


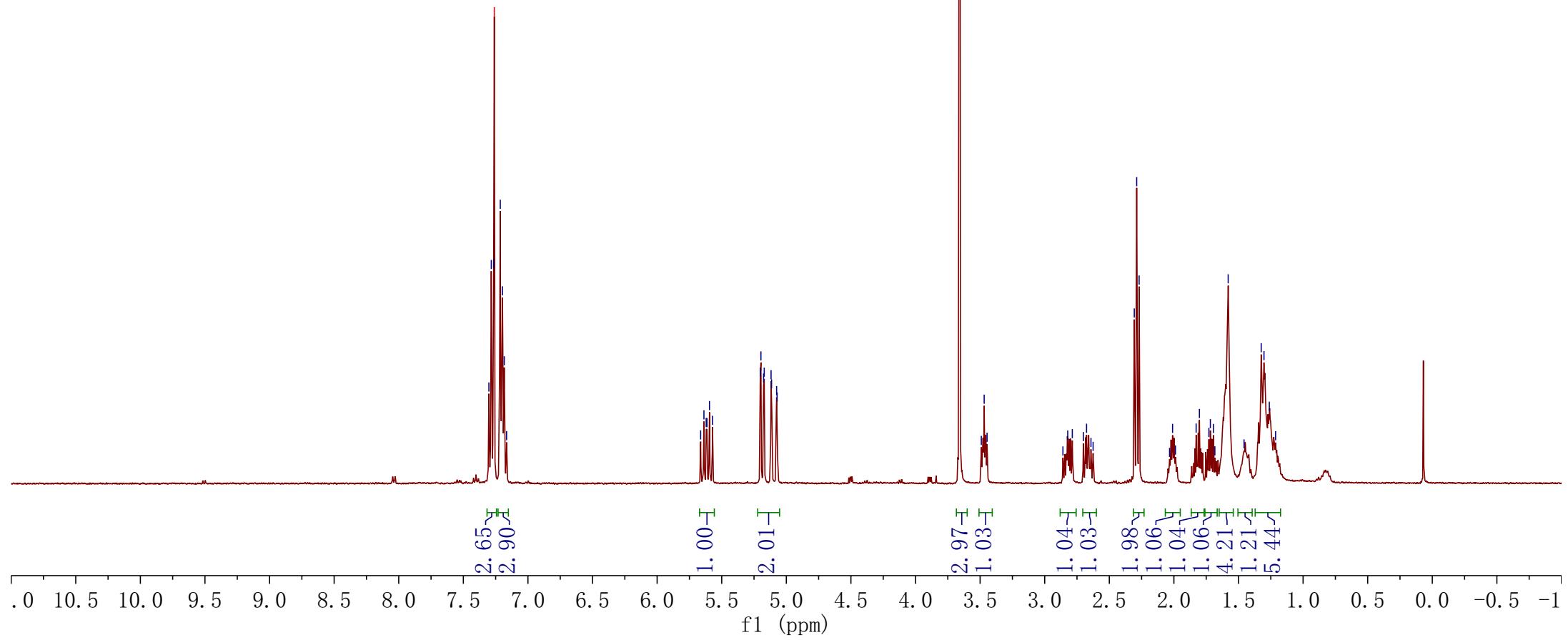
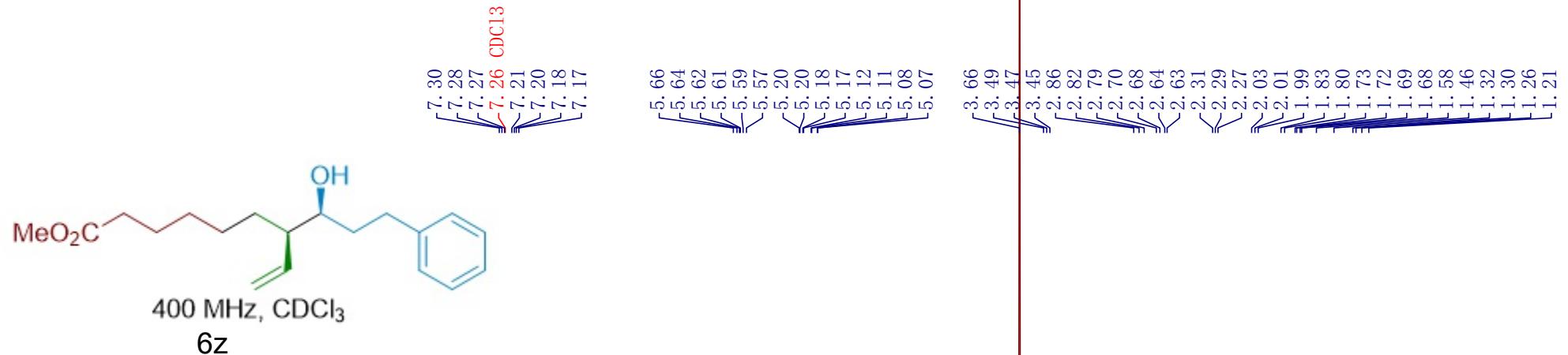
0.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 -0.5 -1

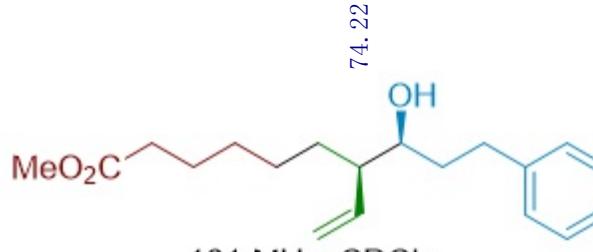
f1 (ppm)



**6y**







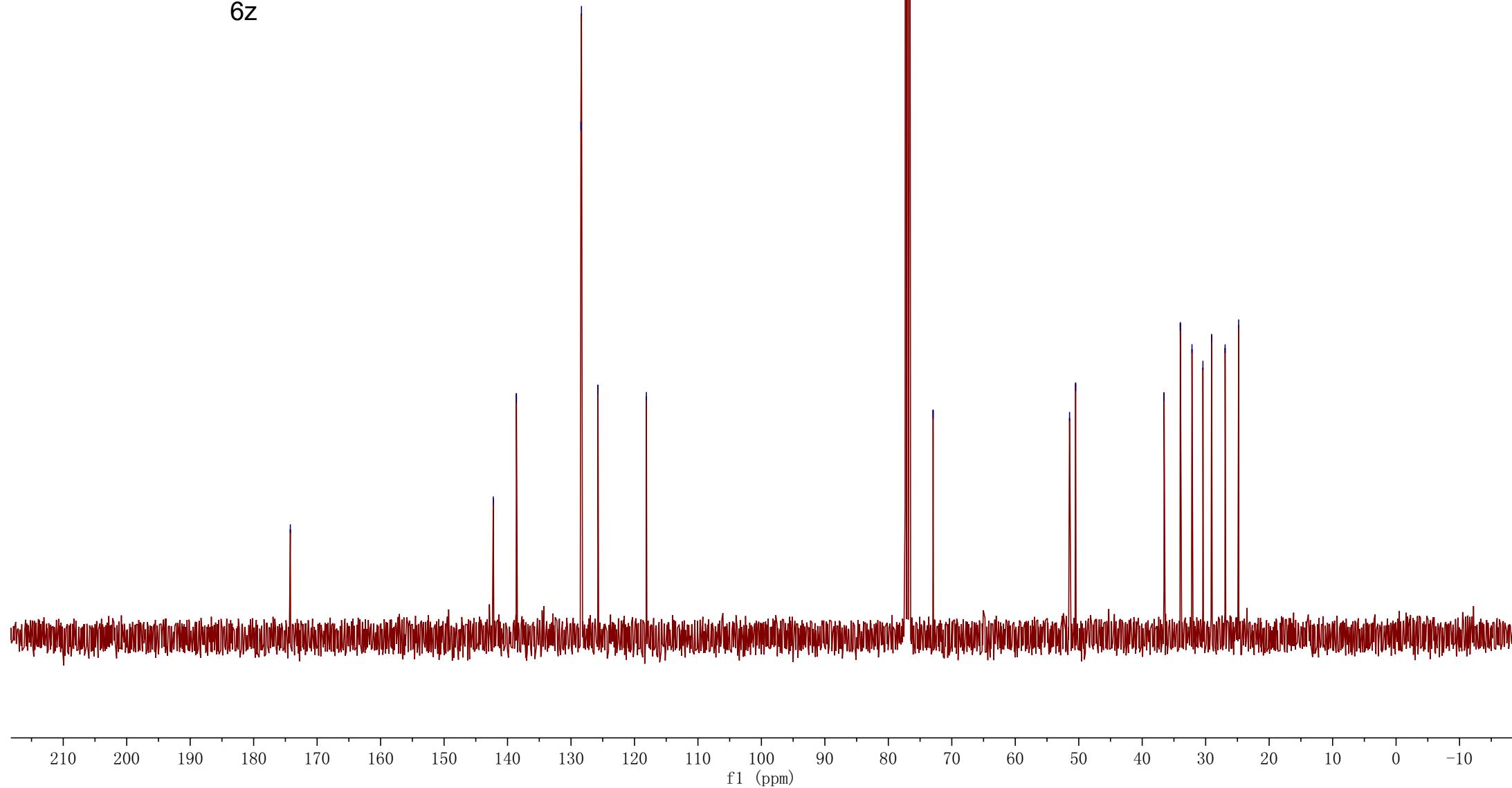
101 MHz,  $\text{CDCl}_3$

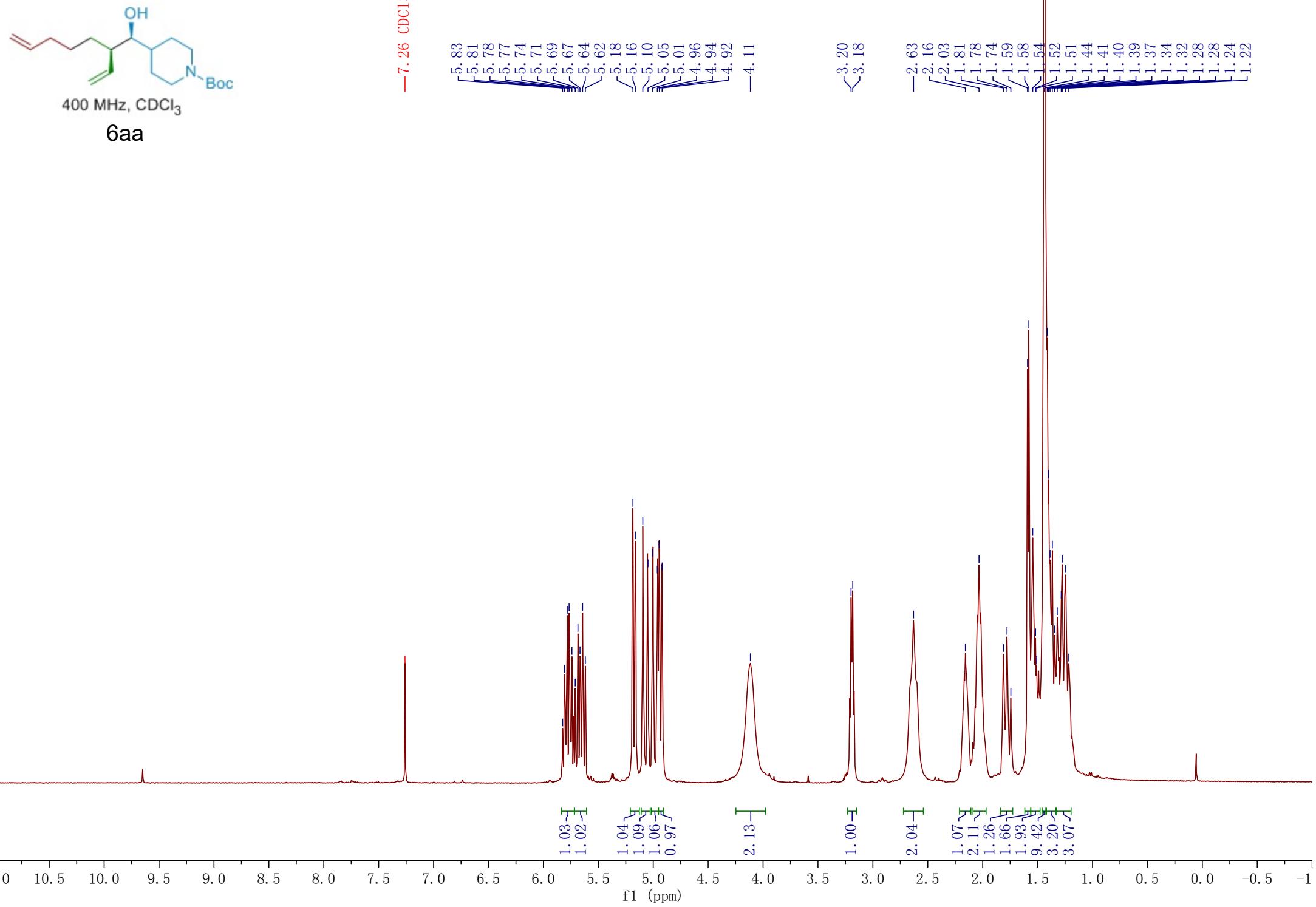
**6z**

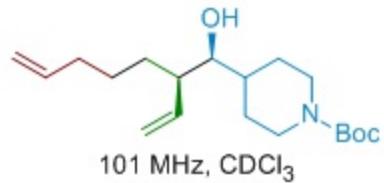
— 142.25  
— 138.60  
— 128.43  
< 128.35  
~ 125.75  
— 118.13

77.32  $\text{CDCl}_3$   
77.03  $\text{CDCl}_3$   
76.68  $\text{CDCl}_3$   
~ 72.95

~ 51.45  
— 36.55  
✓ 34.00  
✓ 32.16  
— 30.43  
~ 29.07  
~ 26.94  
~ 24.80







6aa

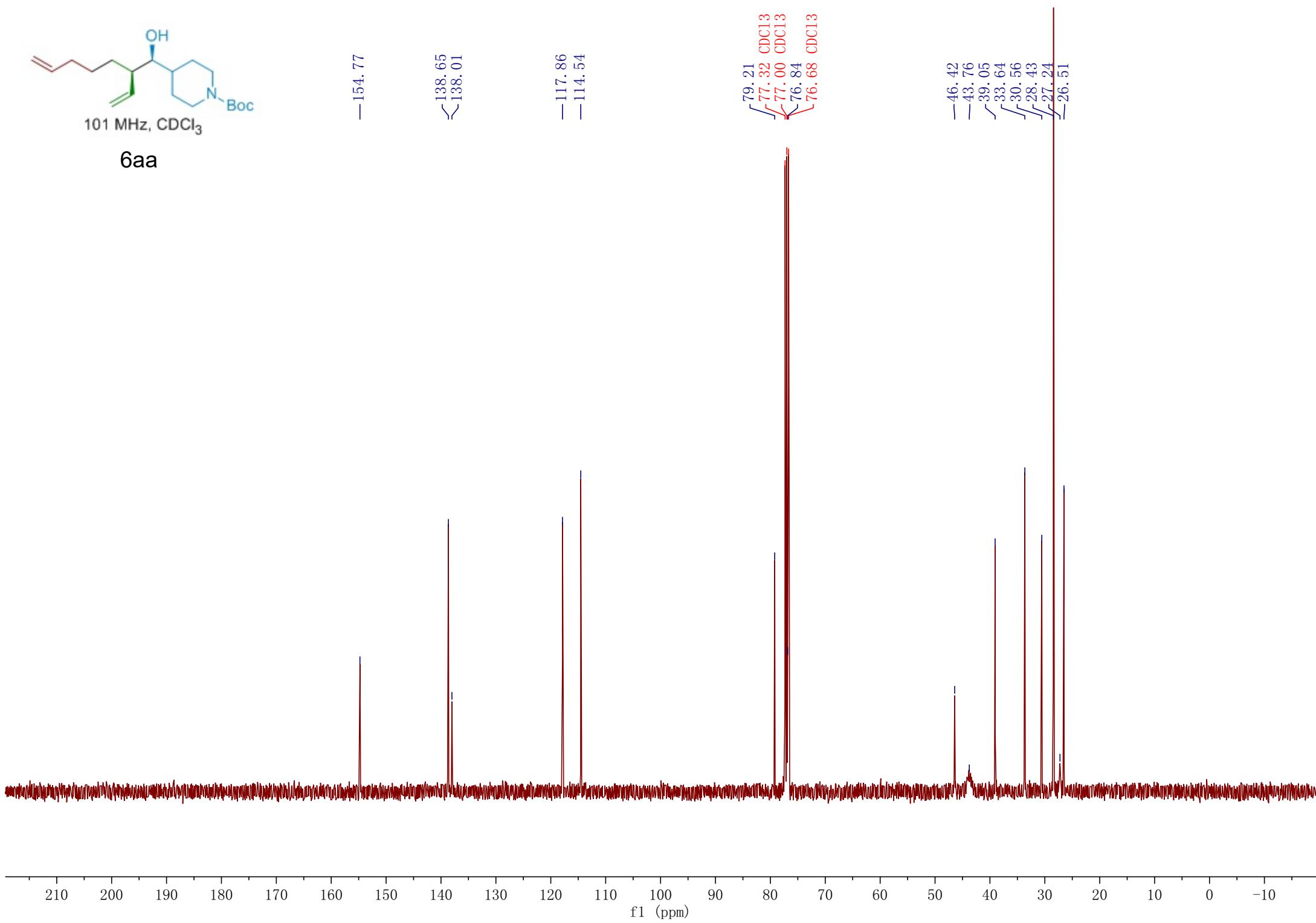
—154.77

≤138.65  
≤138.01

—117.86  
—114.54

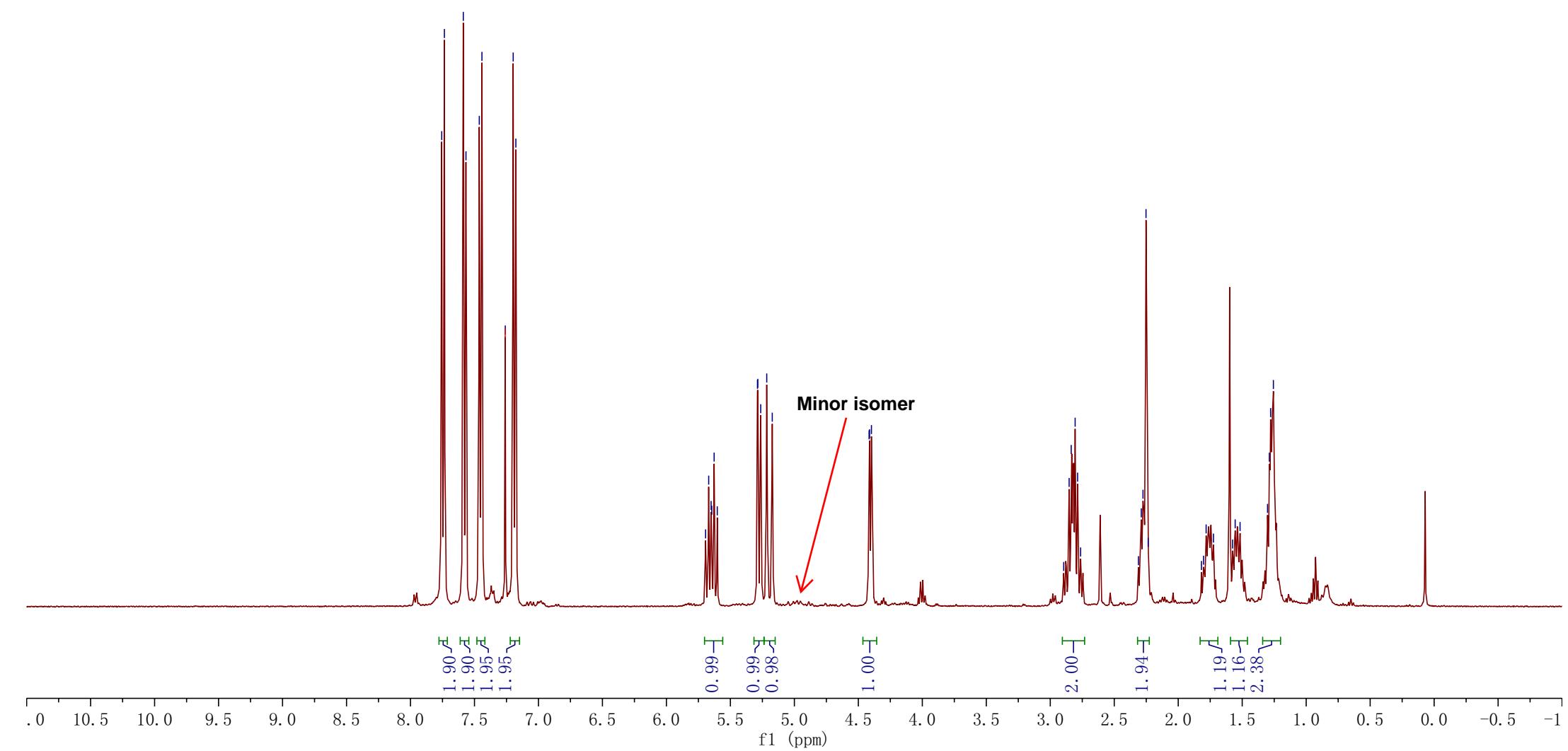
79.21  
77.32 CDCl<sub>3</sub>  
77.00 CDCl<sub>3</sub>  
76.84  
76.68 CDCl<sub>3</sub>

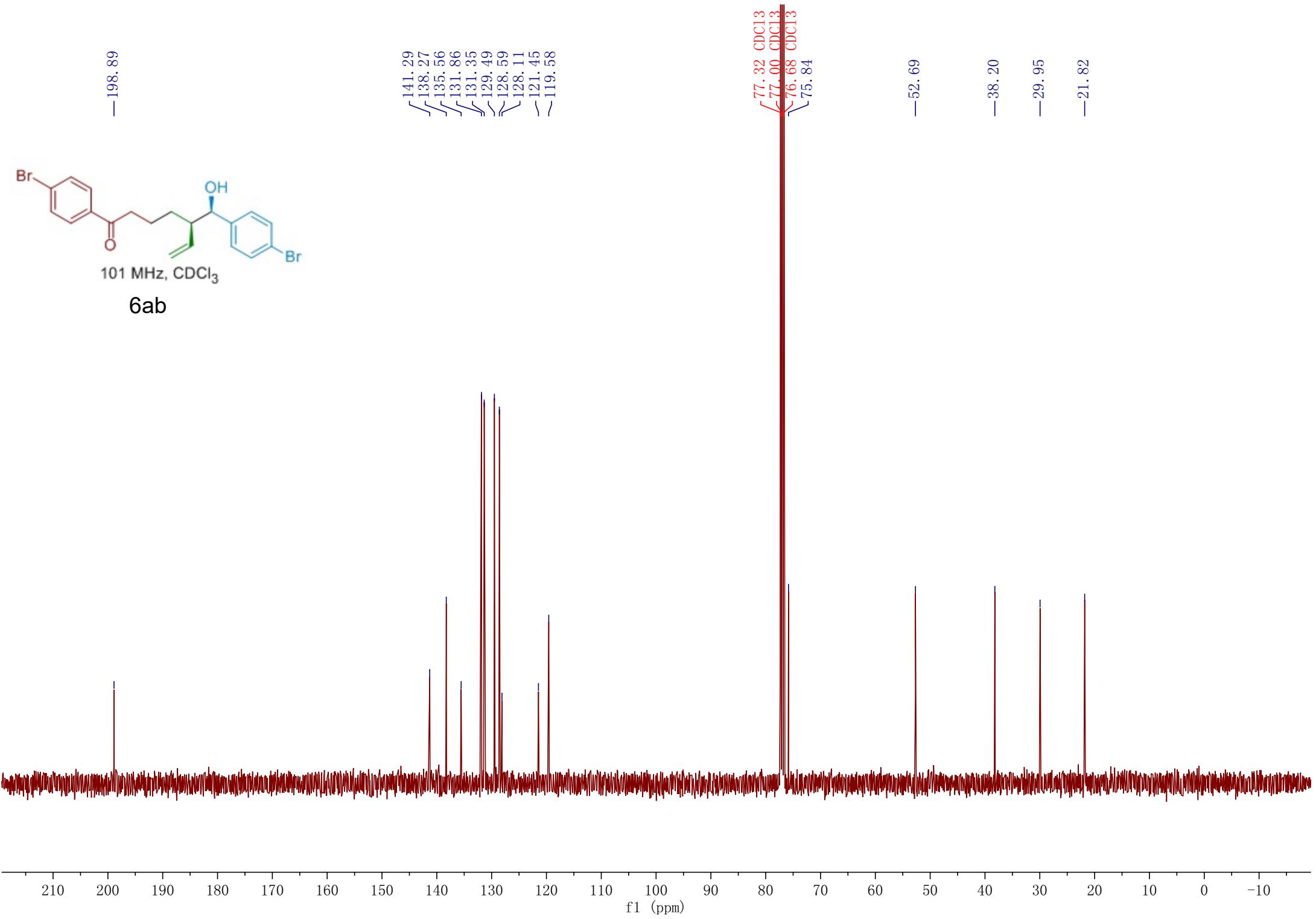
—46.42  
—43.76  
—39.05  
—33.64  
—30.56  
—28.43  
—27.24  
—26.51

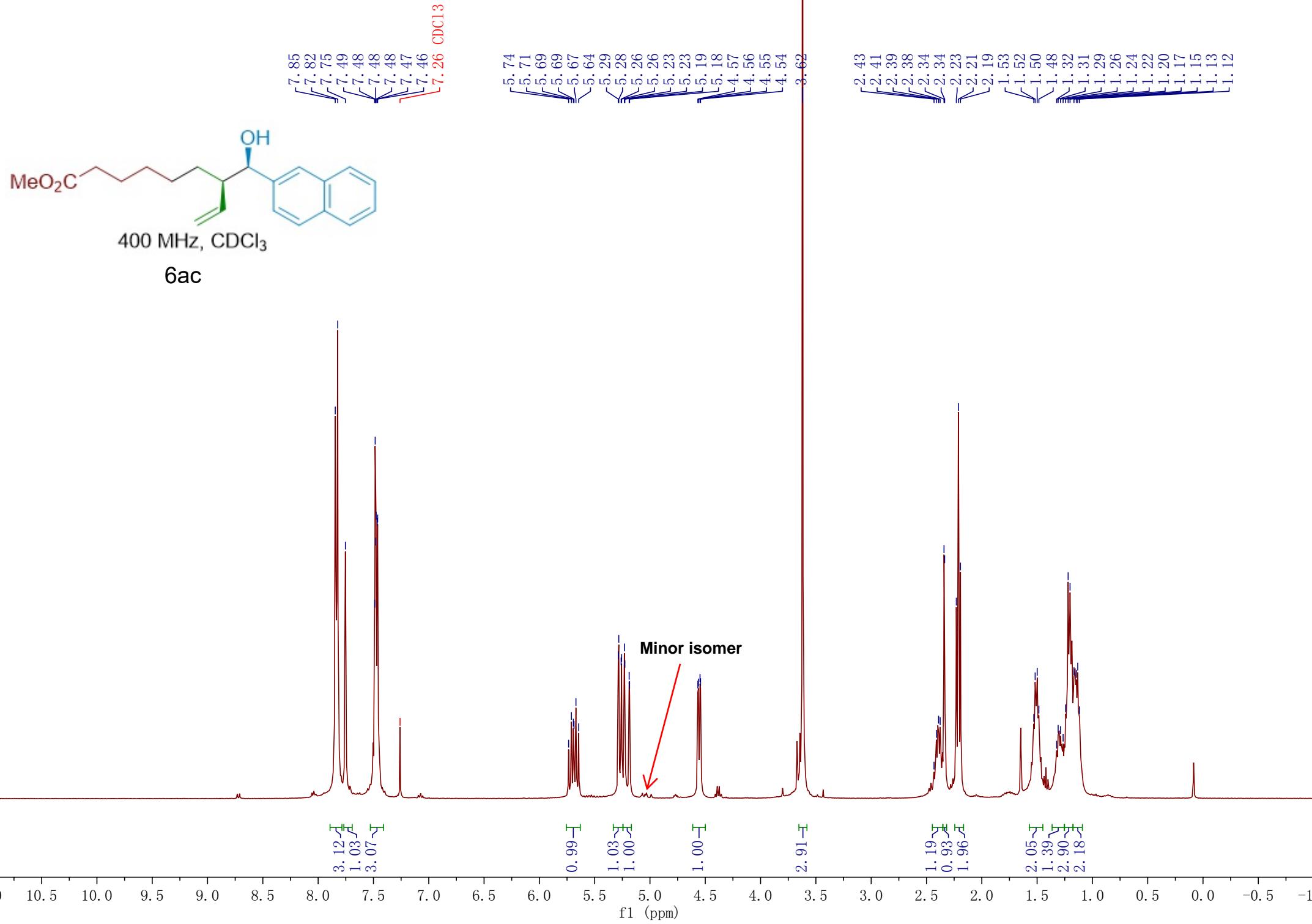


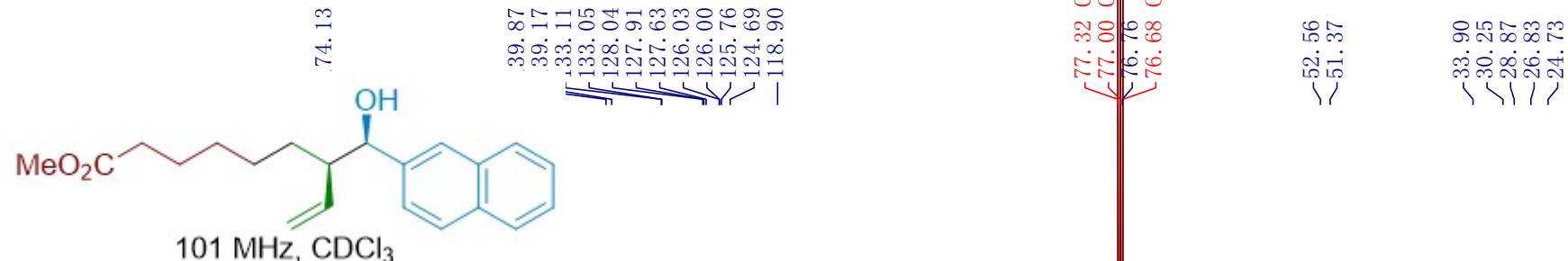


6ab

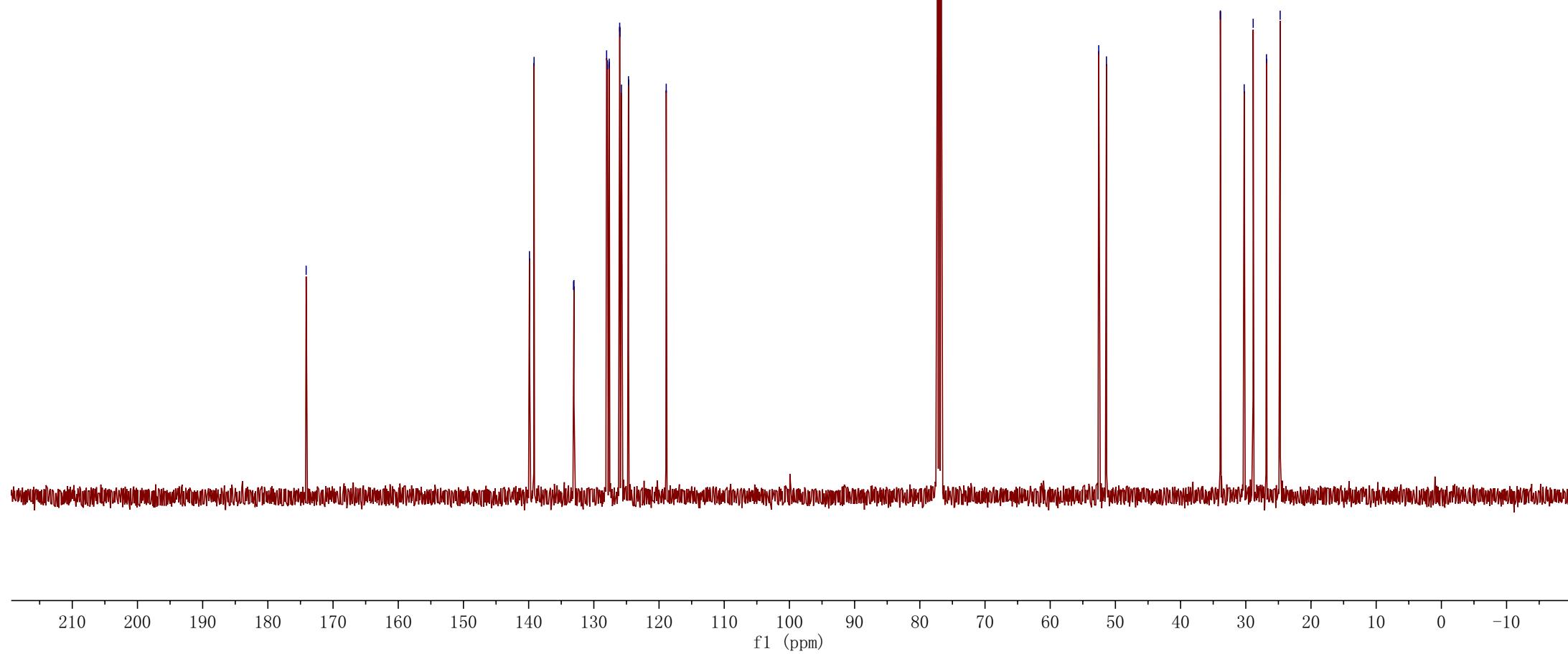


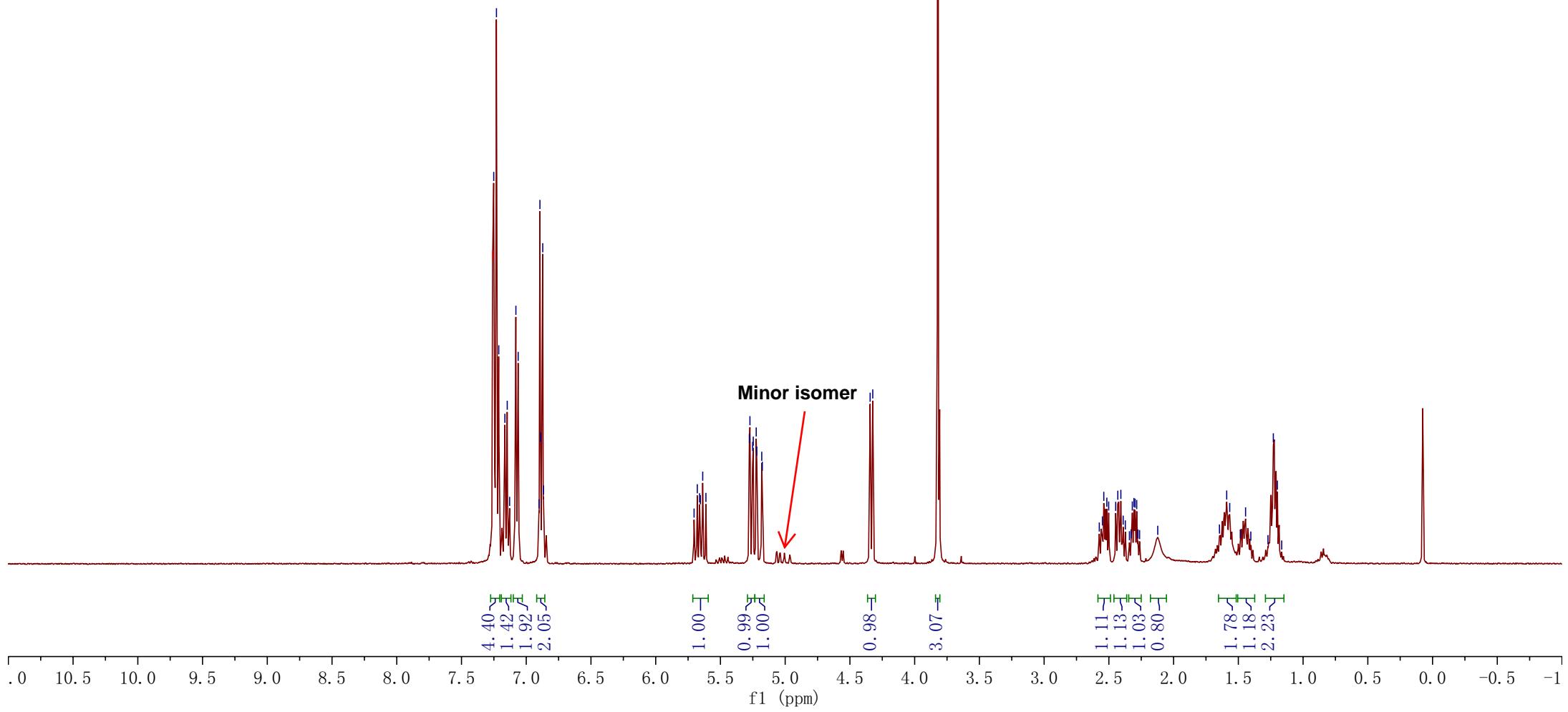
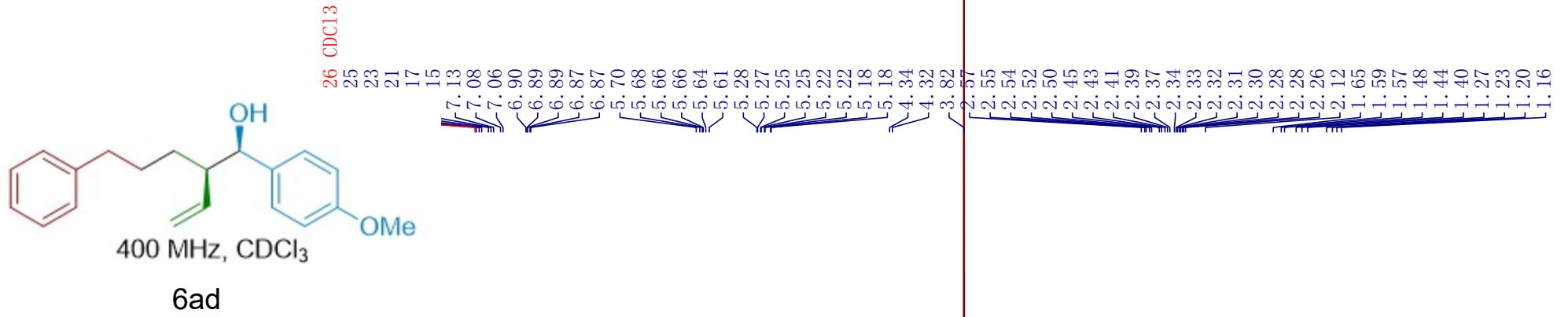


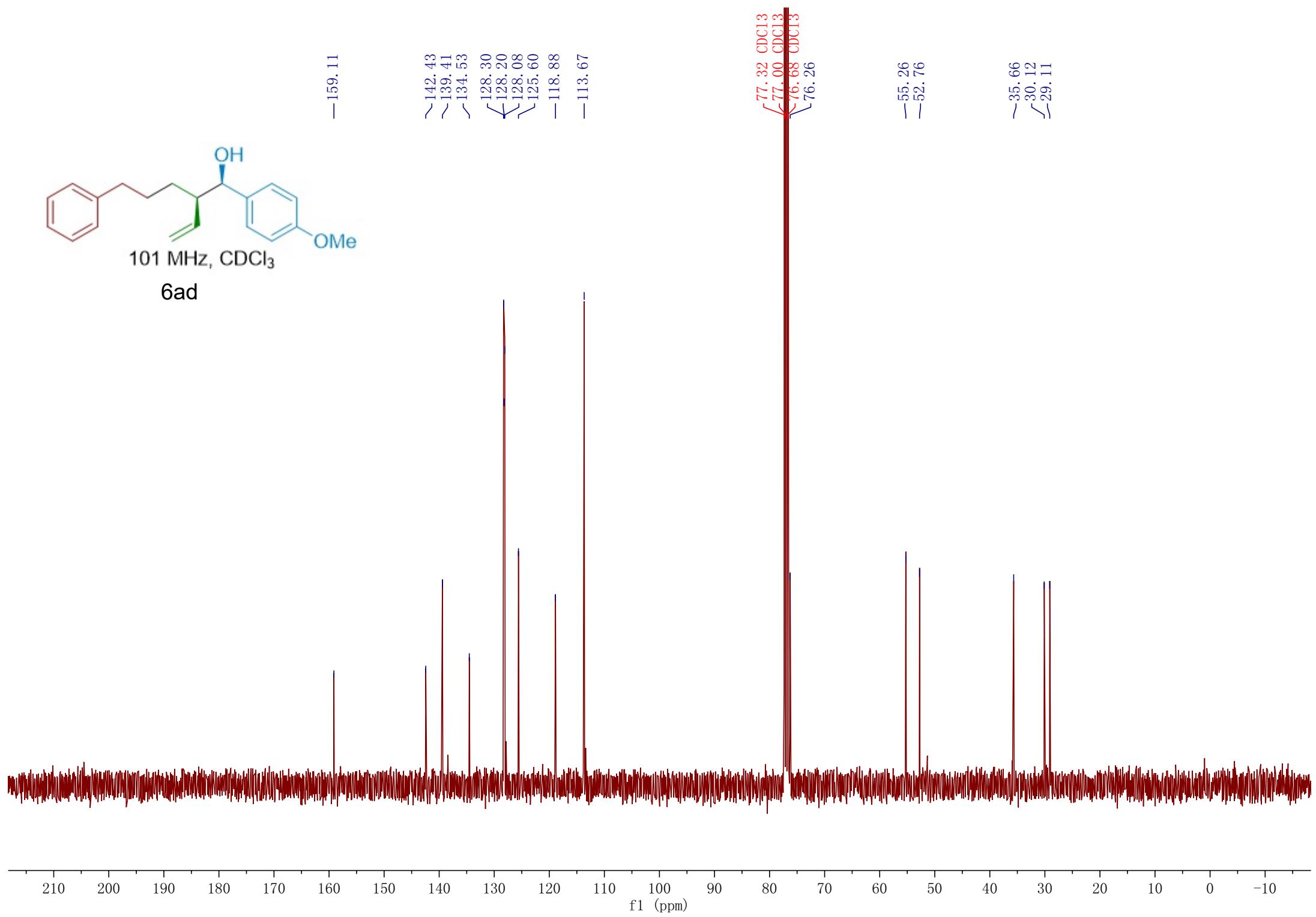


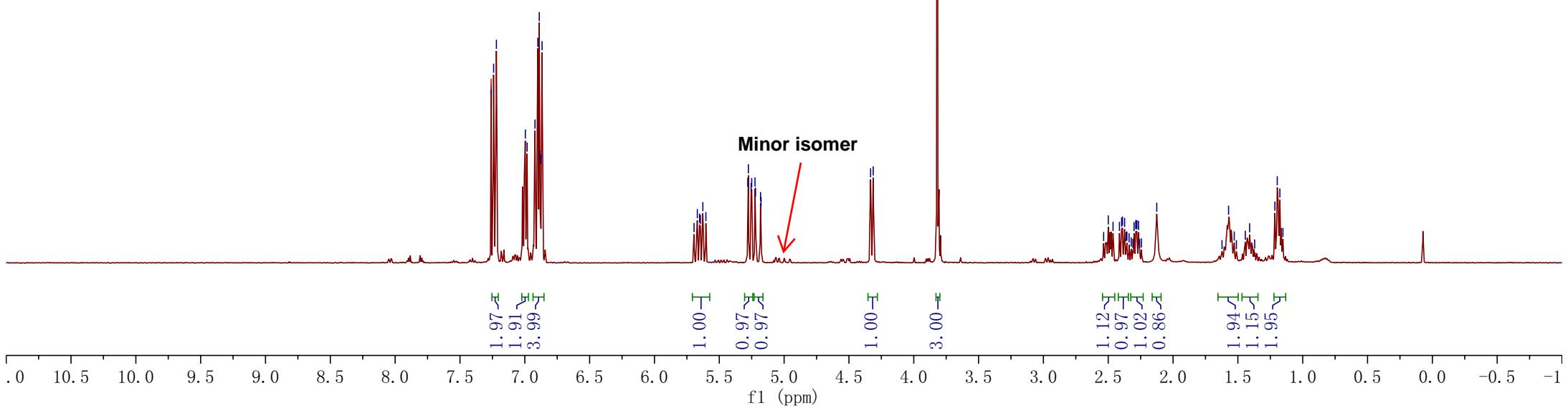


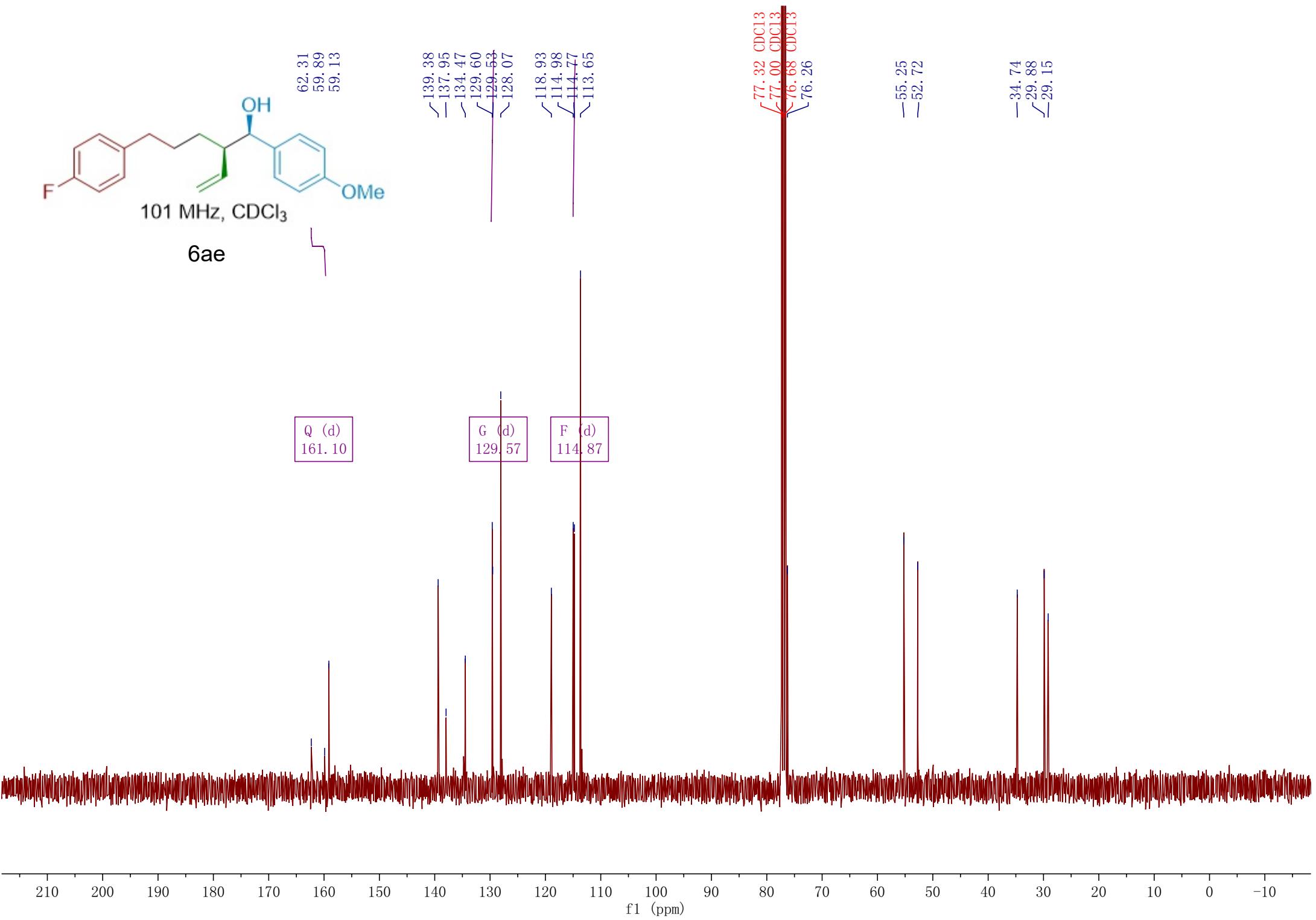
**6ac**

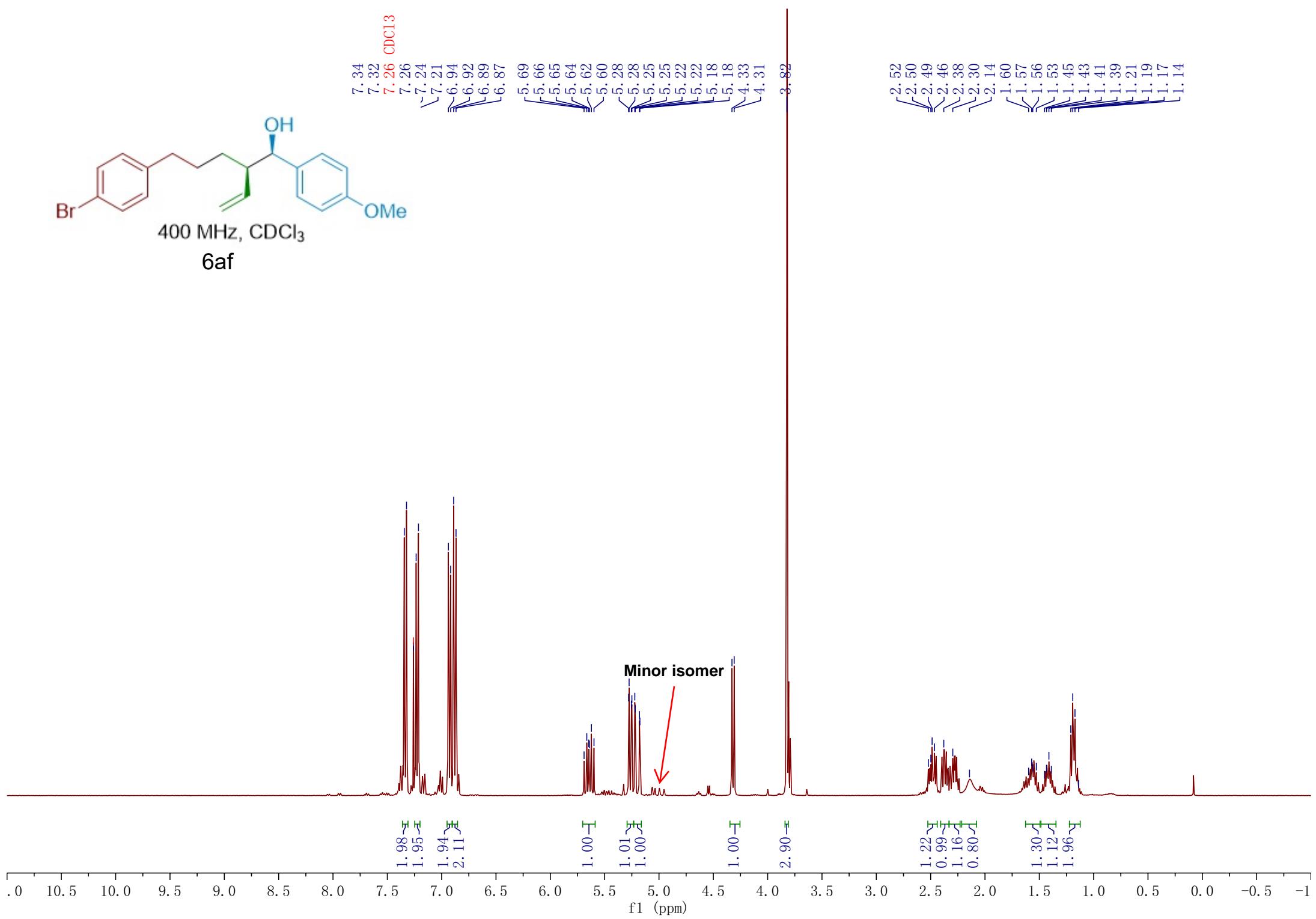


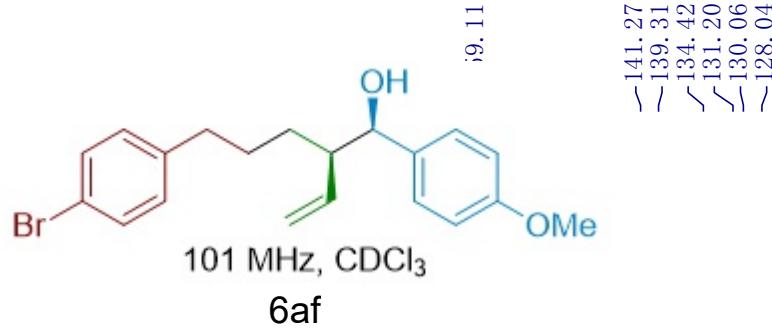












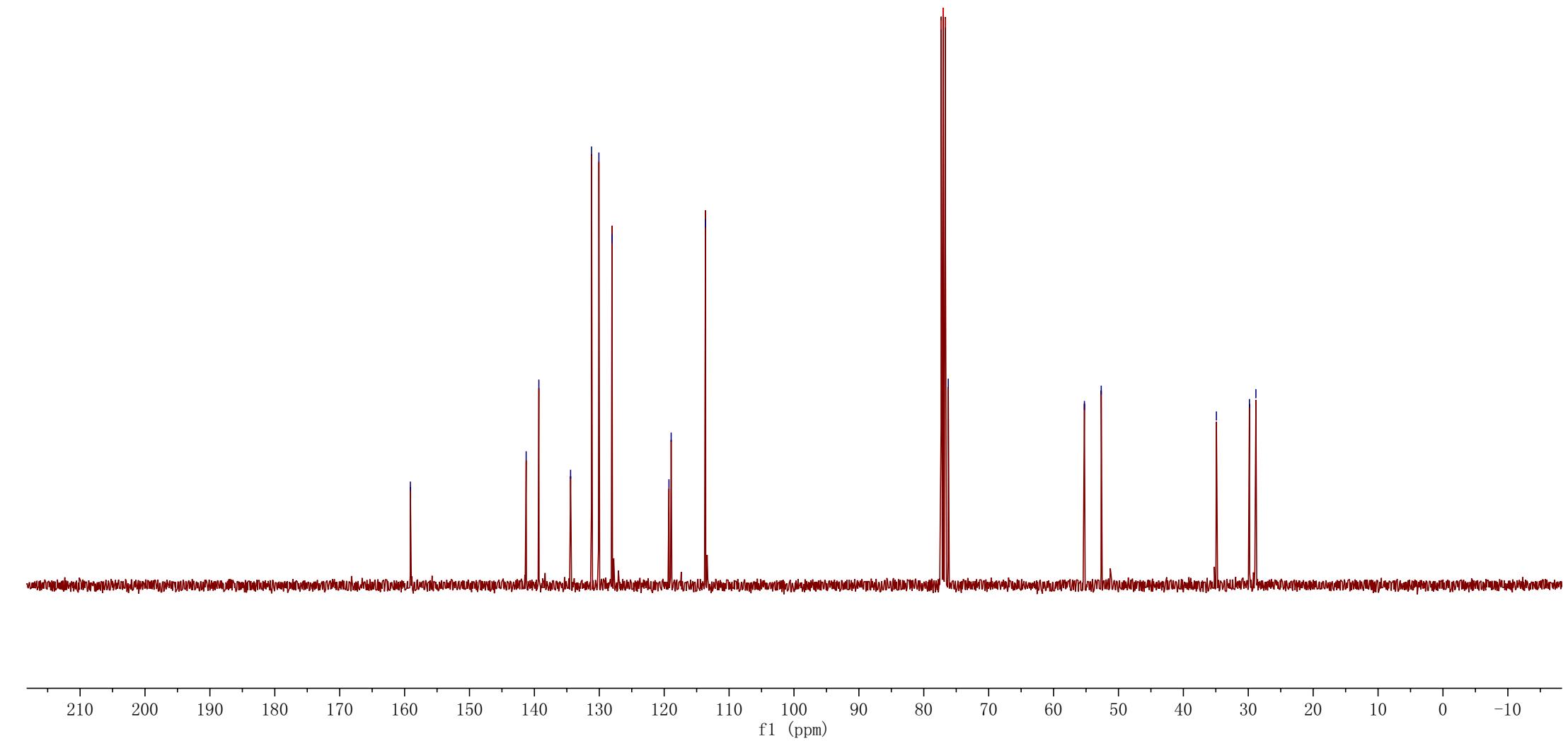
141.27  
139.31  
134.42  
131.20  
130.06  
128.04

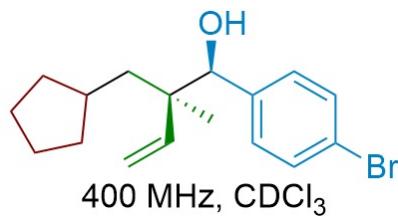
119.27  
118.93  
113.64

77.32 CDCl<sub>3</sub>  
77.00 CDCl<sub>3</sub>  
76.68 CDCl<sub>3</sub>  
76.23

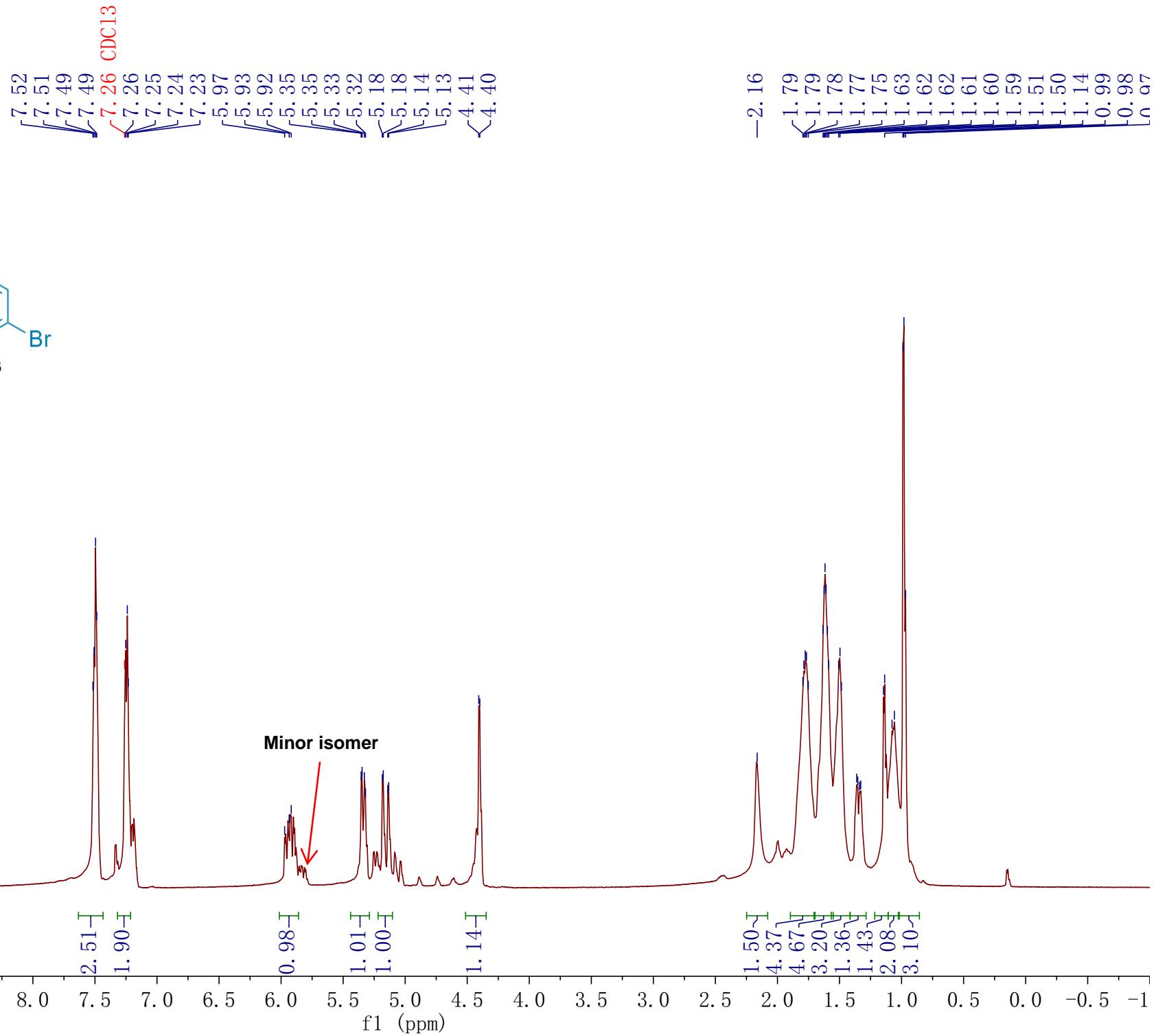
55.25  
52.66

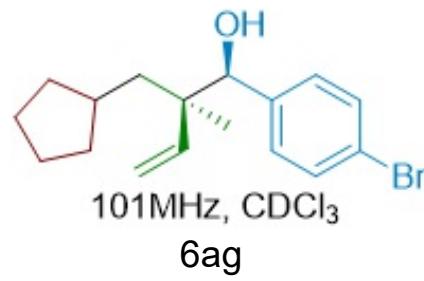
34.91  
29.82  
28.82





6ag

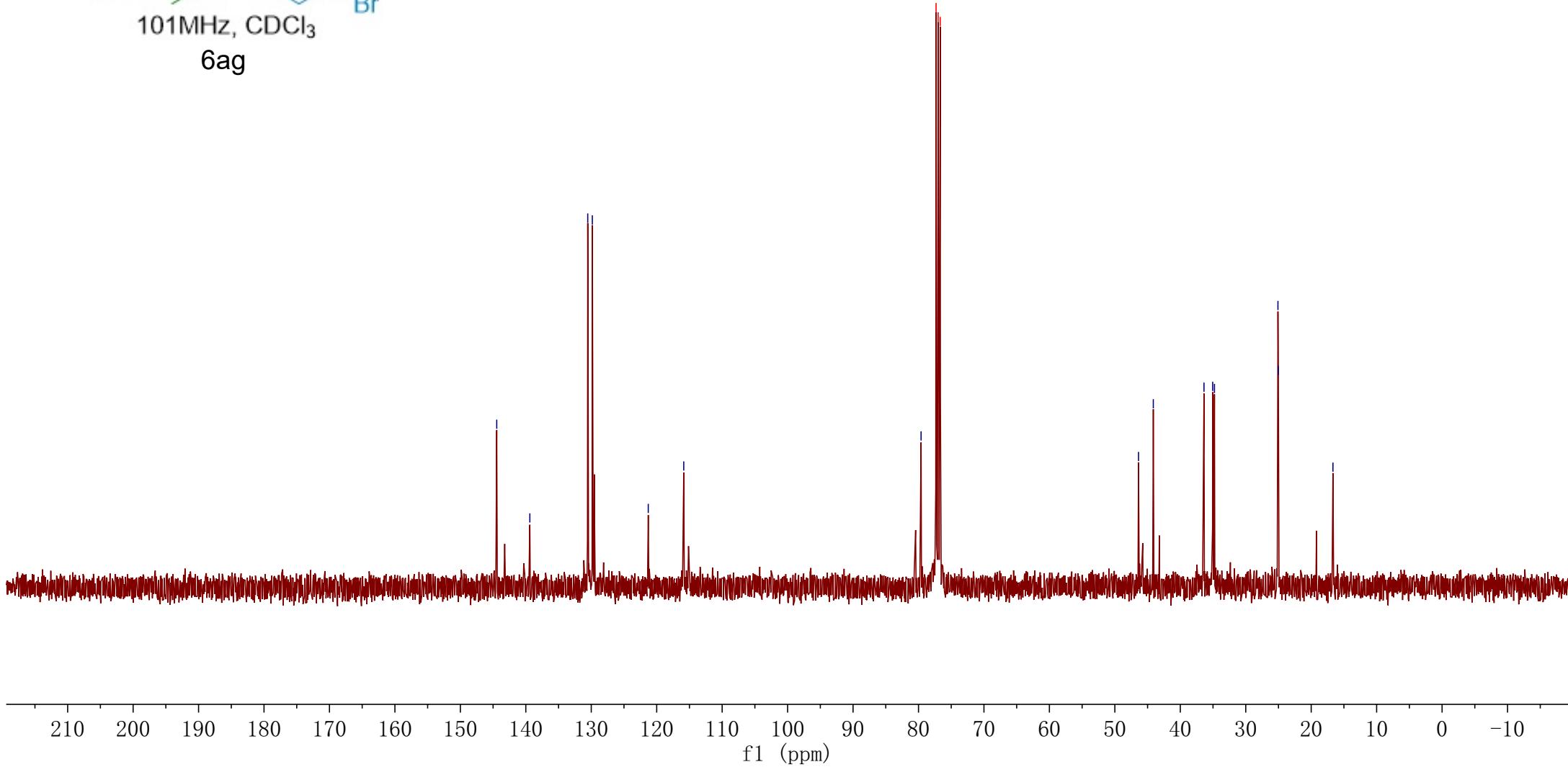


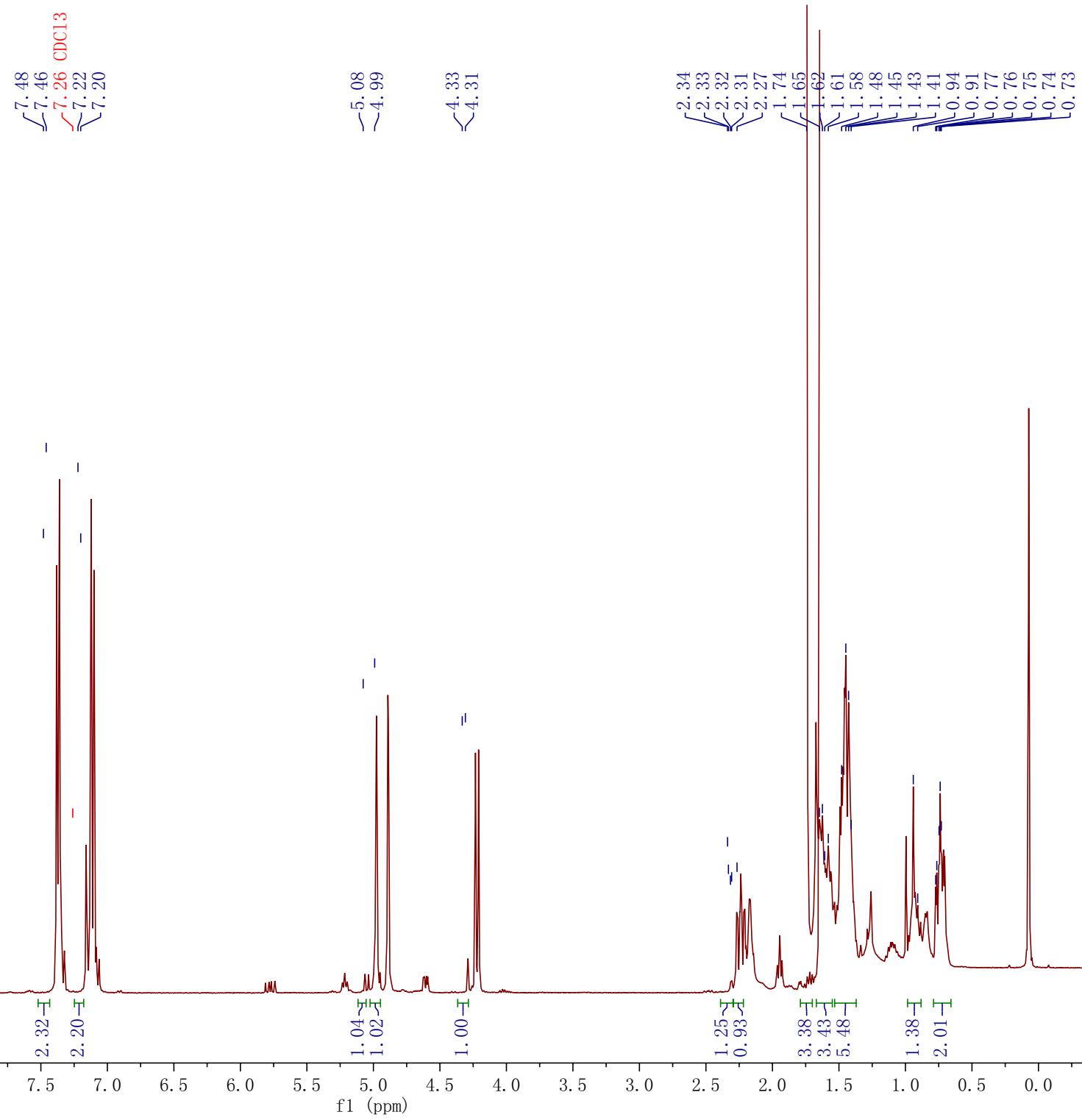


-144.44  
-139.38  
<130.54  
<129.84  
-121.29  
-115.87

79.61  
77.32 CDCl<sub>3</sub>  
77.00 CDCl<sub>3</sub>  
76.68 CDCl<sub>3</sub>

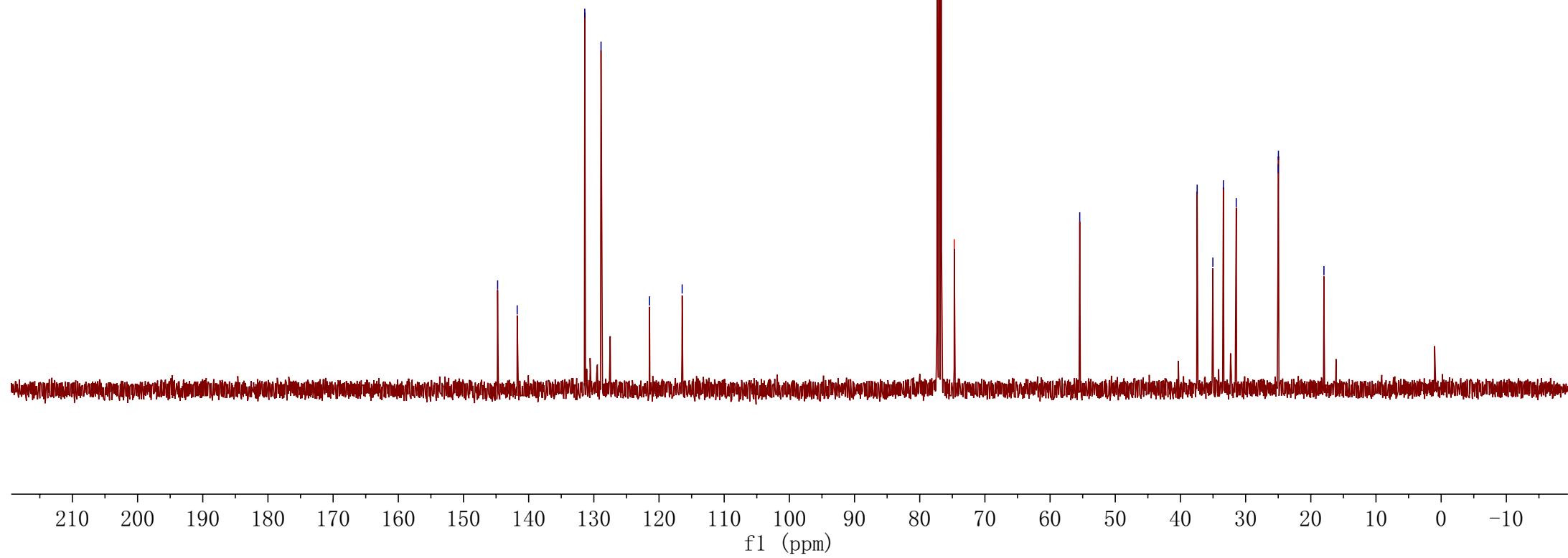
-46.38  
~44.12  
36.38  
<35.05  
<34.78  
<25.08  
<25.02  
-16.68

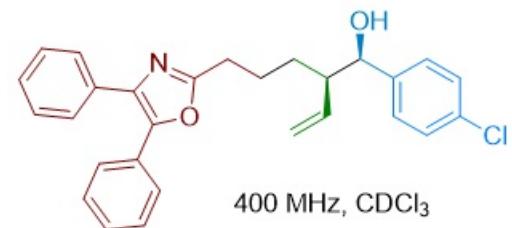






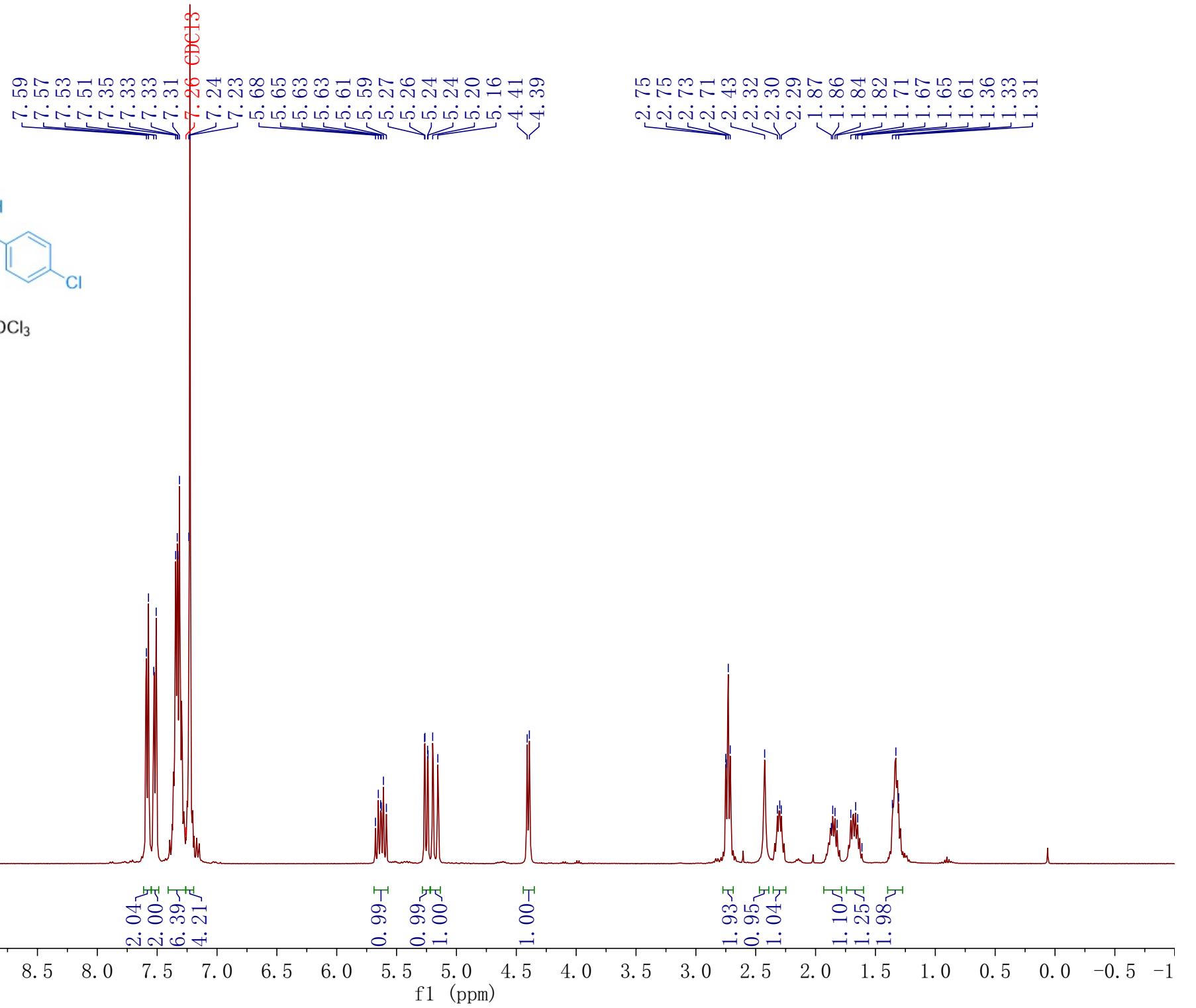
-144.76  
-141.76  
-131.39  
-128.90  
-121.46  
-116.45  
-55.45  
77.32 CDCl<sub>3</sub>  
77.00 CDCl<sub>3</sub>  
74.70 CDCl<sub>3</sub>  
37.44  
35.03  
33.42  
31.44  
25.00  
24.97  
17.99

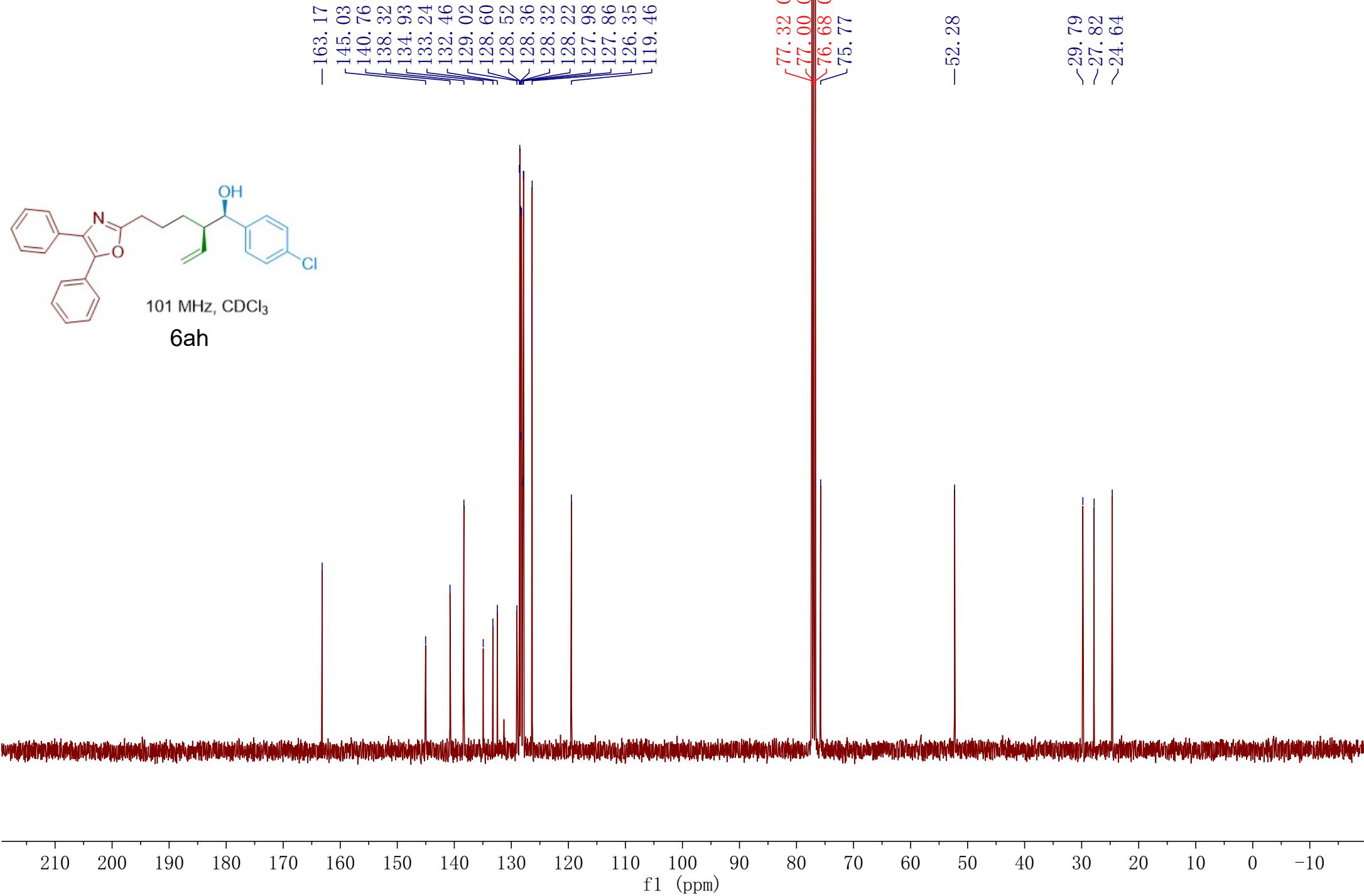


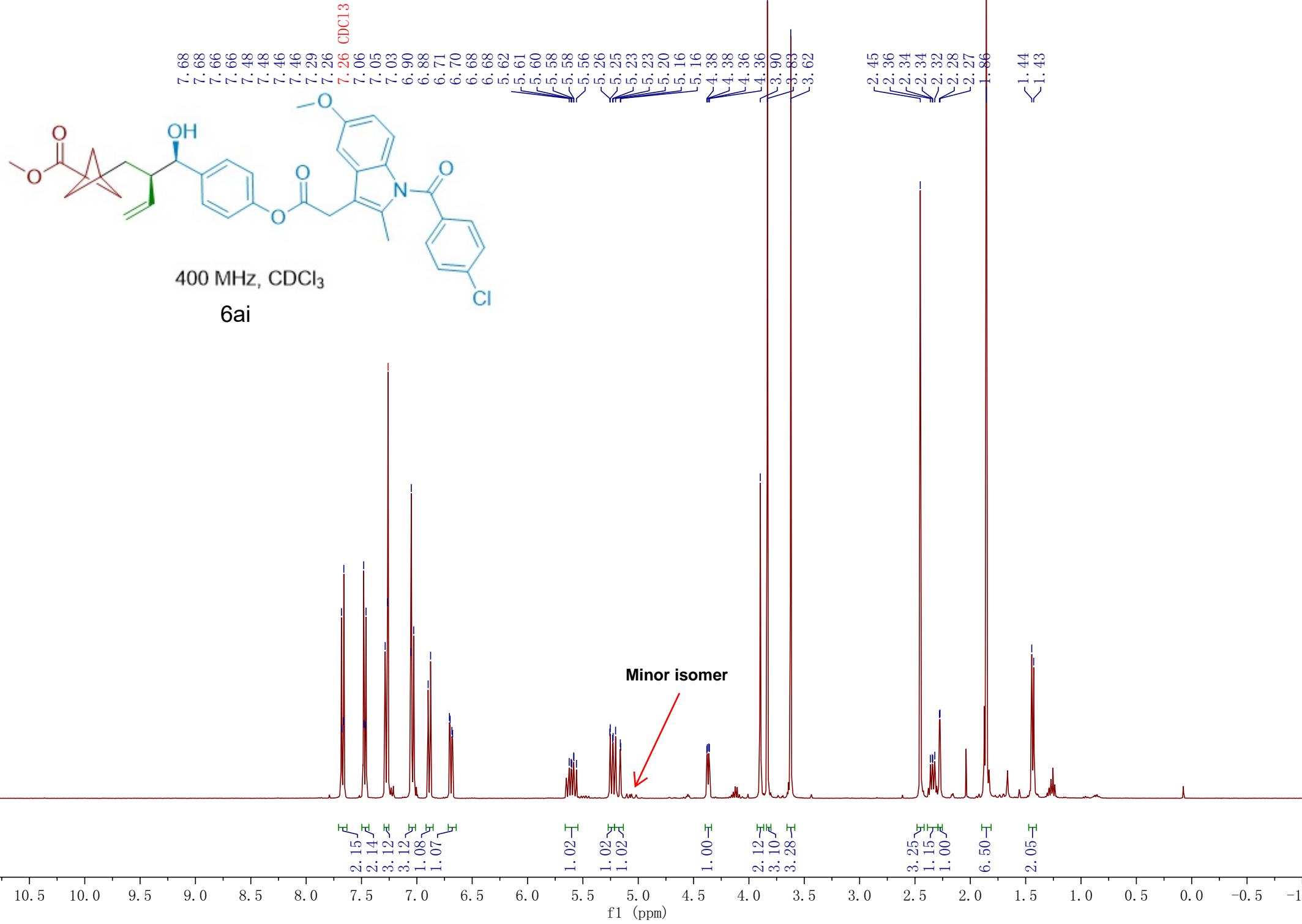


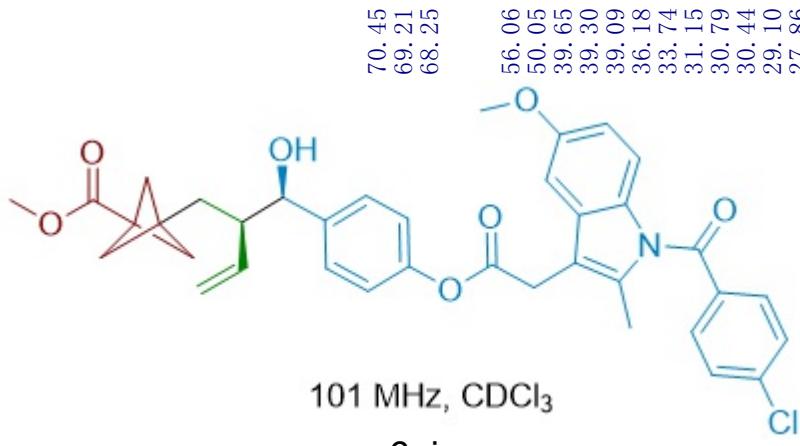
400 MHz, CDCl<sub>3</sub>

6ah









101 MHz, CDCl<sub>3</sub>

**6ai**

70.45  
69.21  
68.25  
56.06  
50.05  
39.65  
39.30  
39.09  
36.18  
33.74  
31.15  
30.79  
30.44  
29.10  
27.86  
-121.10  
-119.26  
-114.97  
-111.92  
-111.71

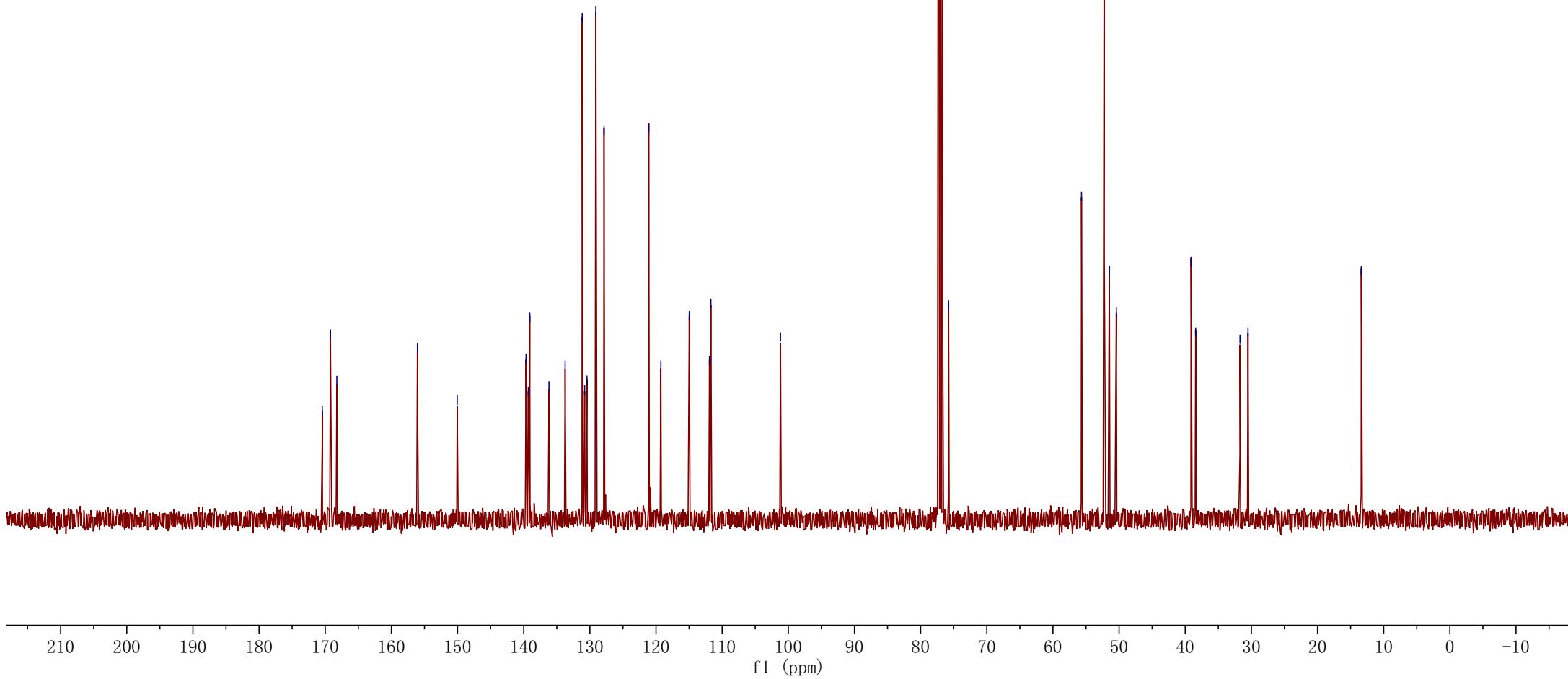
-101.18

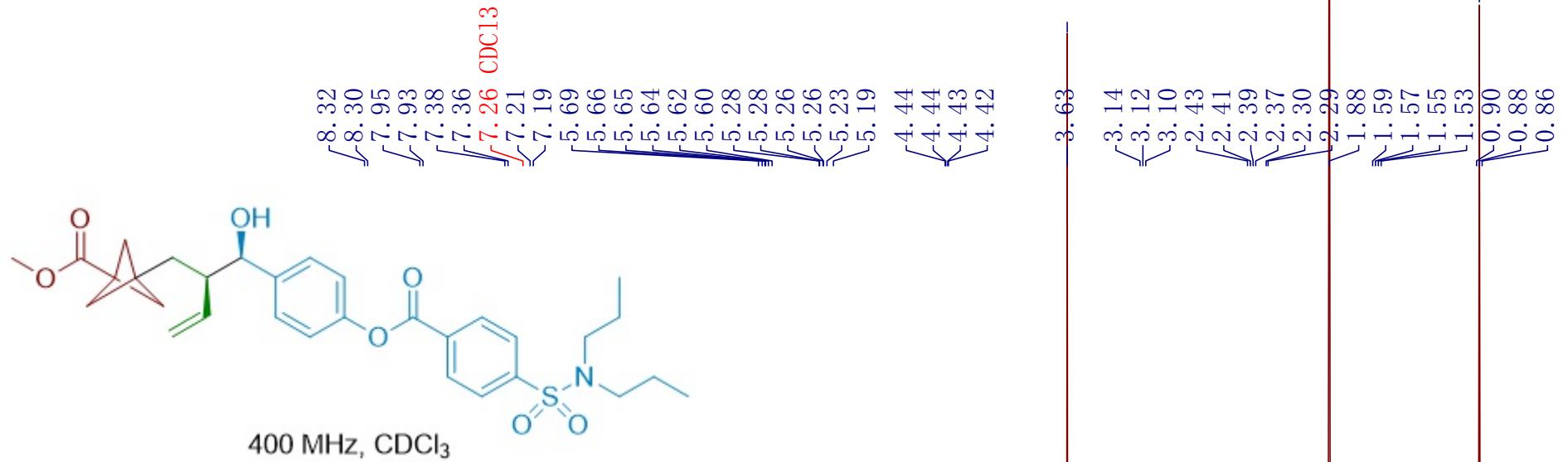
77.32 CDCl<sub>3</sub>  
77.00 CDCl<sub>3</sub>  
76.68 CDCl<sub>3</sub>  
75.77

55.68  
52.24  
51.47  
50.42

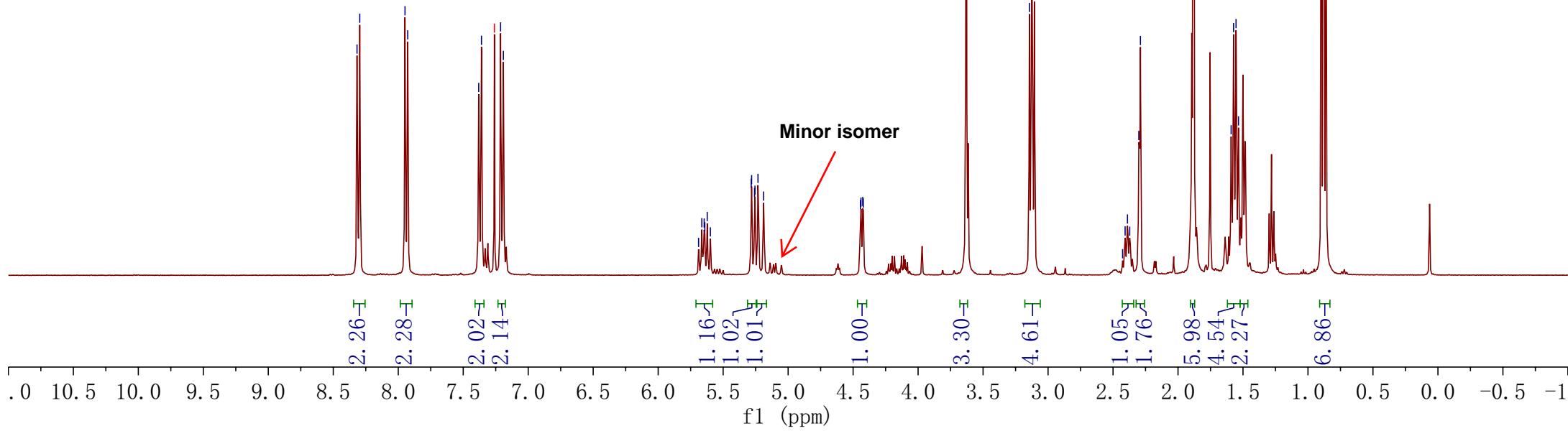
39.12  
38.42  
31.72  
30.51

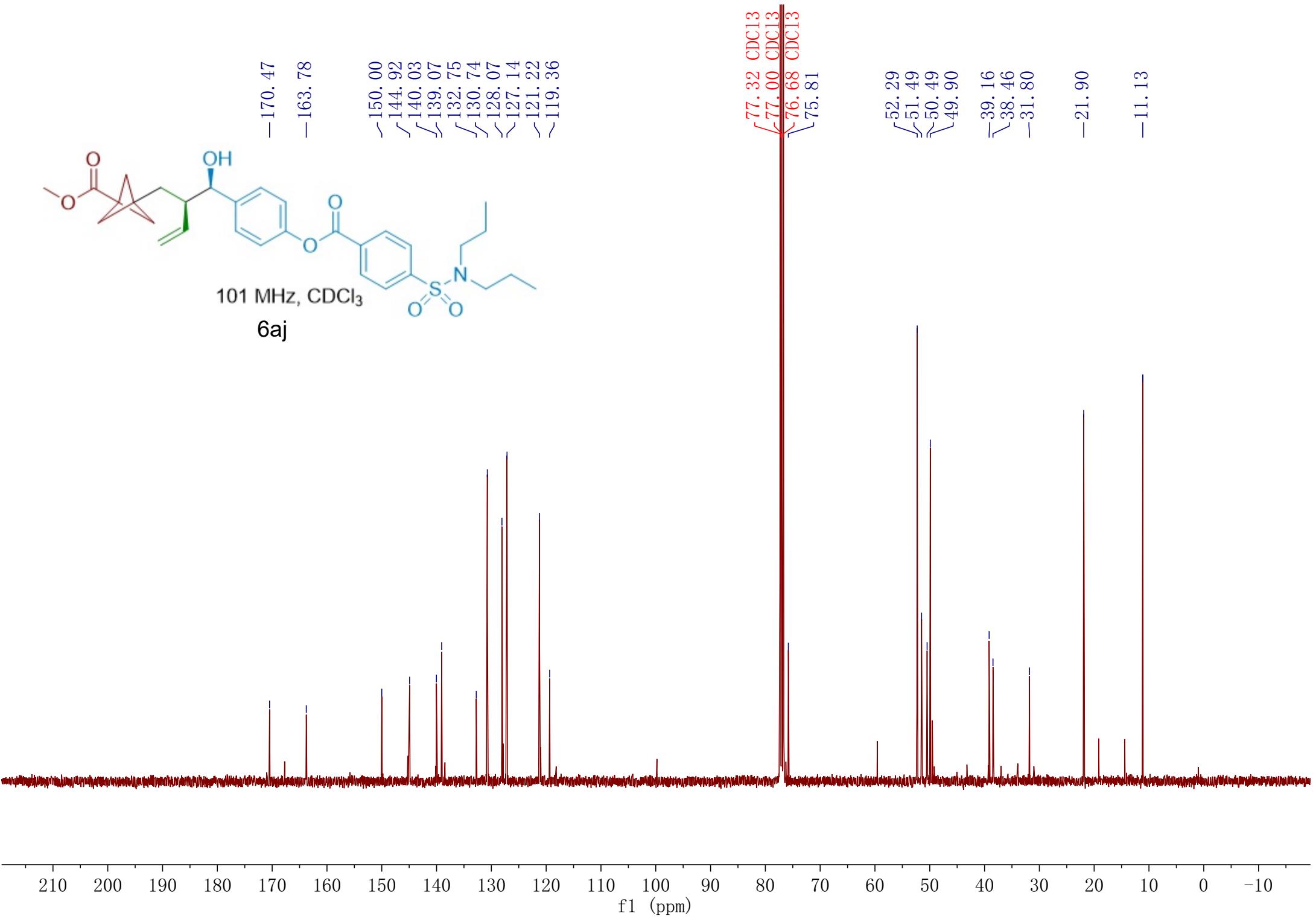
-13.38

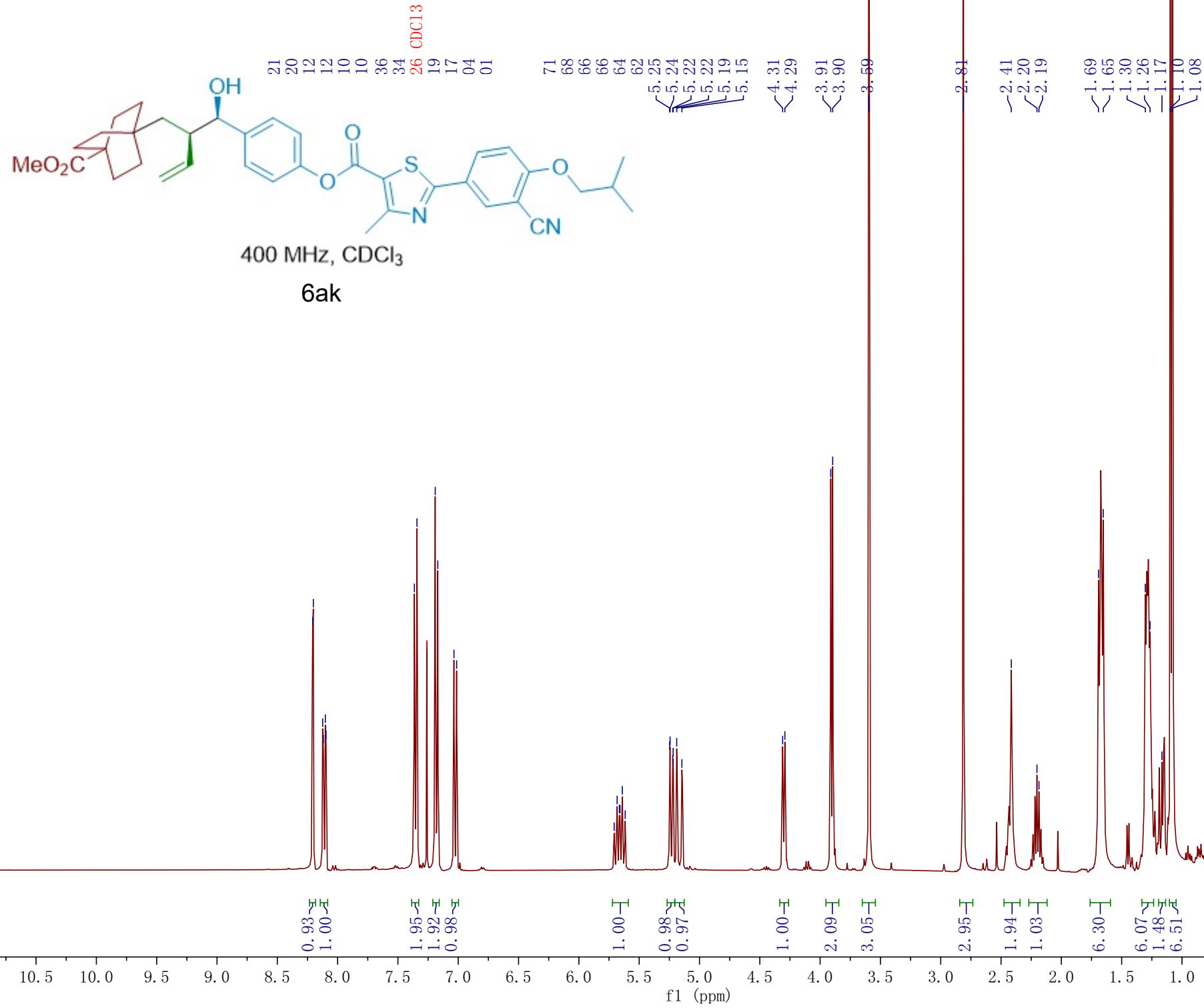


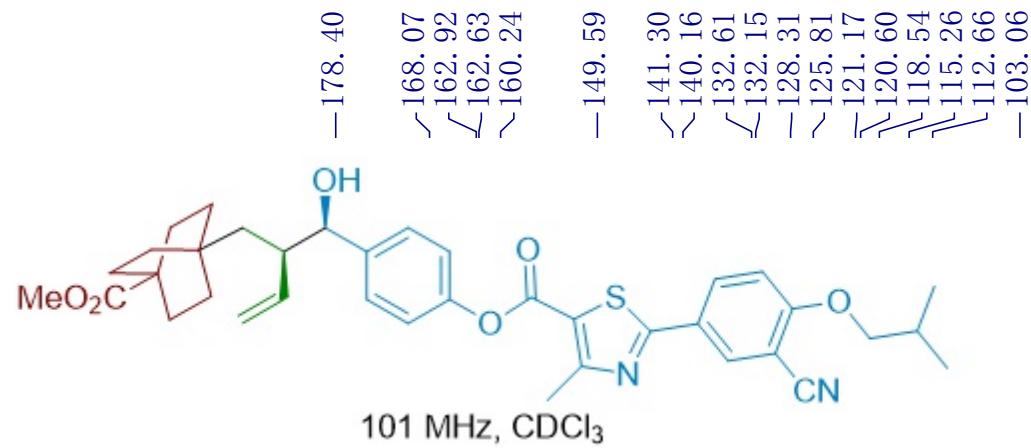


6aj







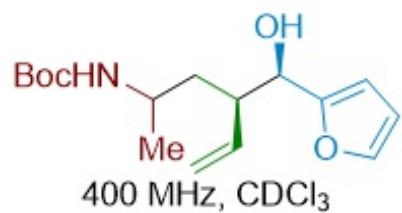


-178.40  
 >168.07  
 <162.92  
 <162.63  
 >160.24  
 -149.59  
 <141.30  
 <140.16  
 <132.61  
 <132.15  
 -128.31  
 <125.81  
 <121.17  
 <120.60  
 <118.54  
 <115.26  
 <112.66  
 -103.06

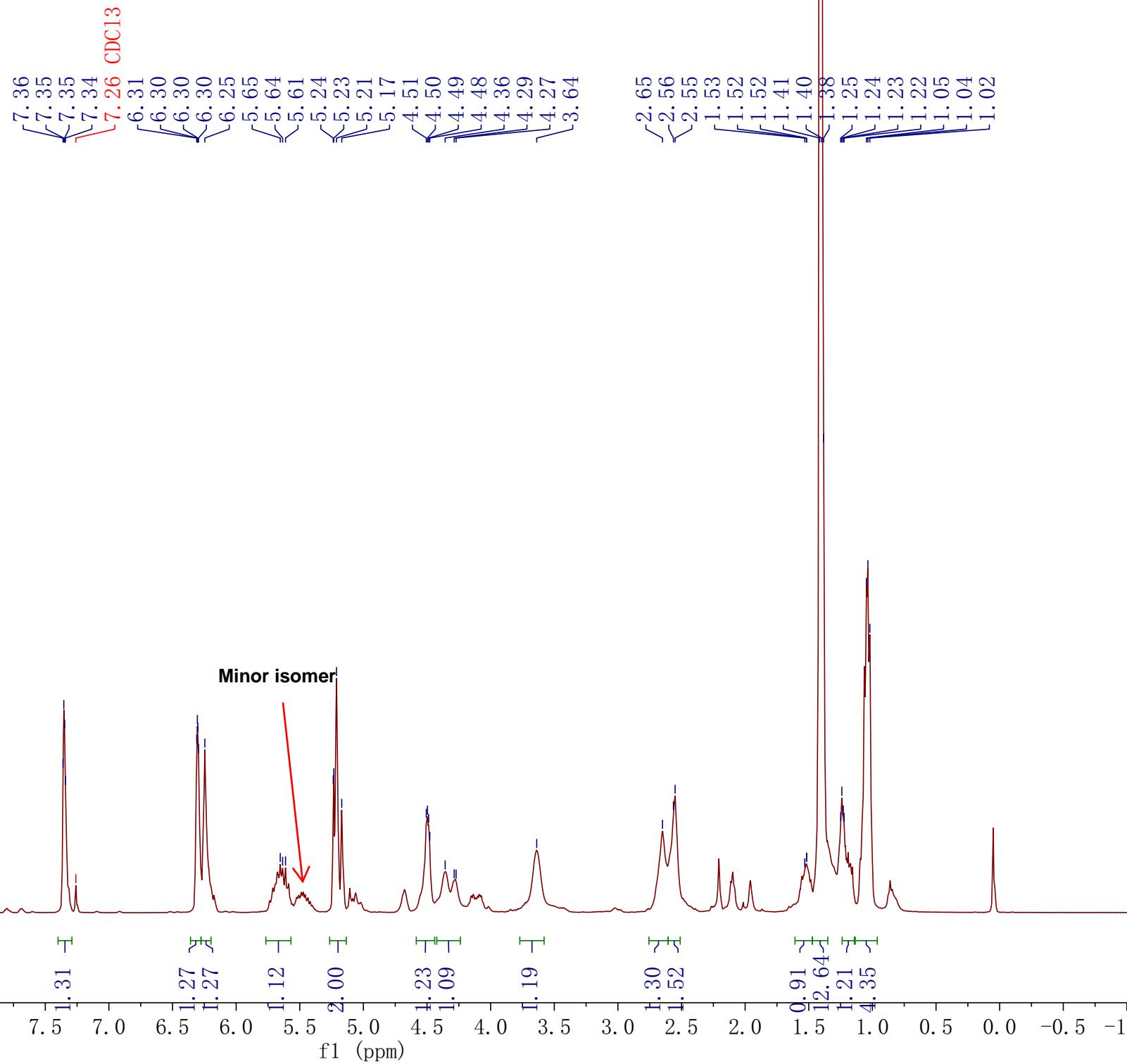
77.32  $\text{CDCl}_3$   
 77.20  $\text{CDCl}_3$   
 77.00  $\text{CDCl}_3$   
 76.68  $\text{CDCl}_3$   
 76.40  
 75.71

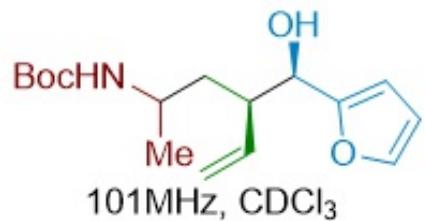
>51.49  
 >48.30  
 <41.58  
 <38.82  
 <31.02  
 <30.83  
 <28.40  
 <28.11  
 <18.99  
 <17.64

f1 (ppm)



6al





101MHz, CDCl<sub>3</sub>

6al

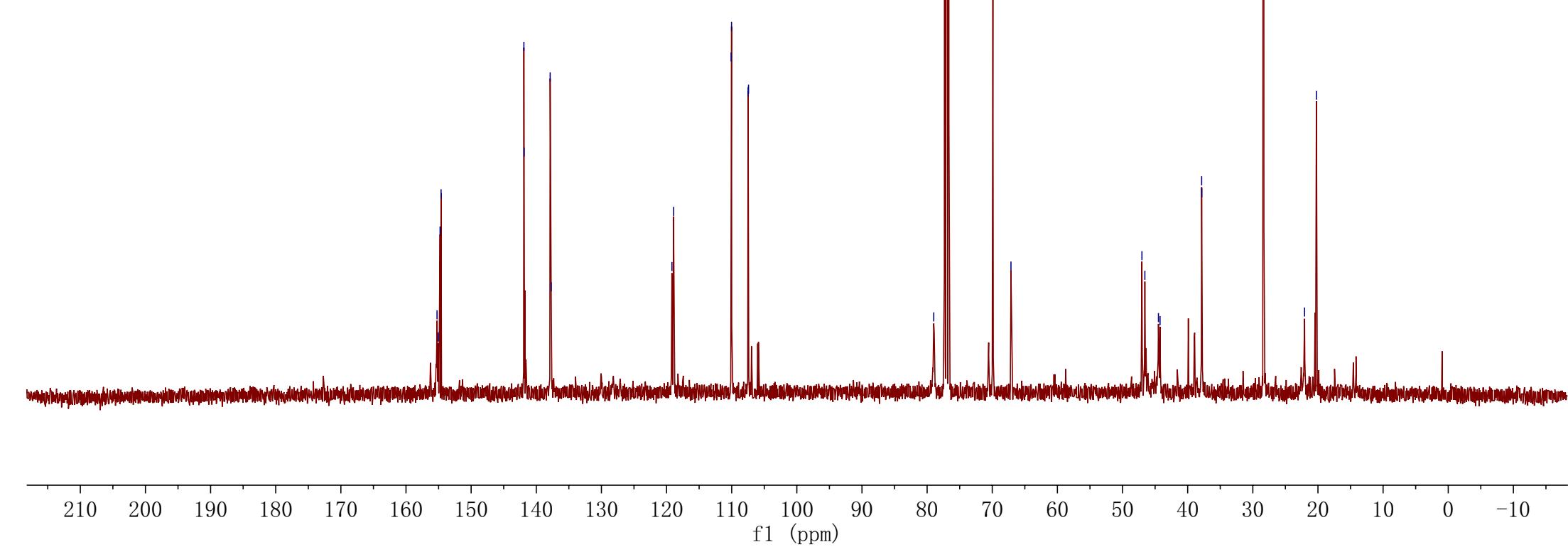
155.24  
155.04  
154.77  
154.62  
141.90  
141.87  
137.87  
137.71

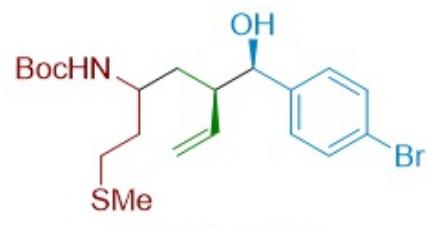
119.18  
118.91  
110.08  
110.03  
107.48  
107.42

78.98  
77.32 CDCl<sub>3</sub>  
77.00 CDCl<sub>3</sub>  
76.68 CDCl<sub>3</sub>  
69.90  
67.13

47.02  
46.57  
44.49  
44.24  
37.85  
37.83

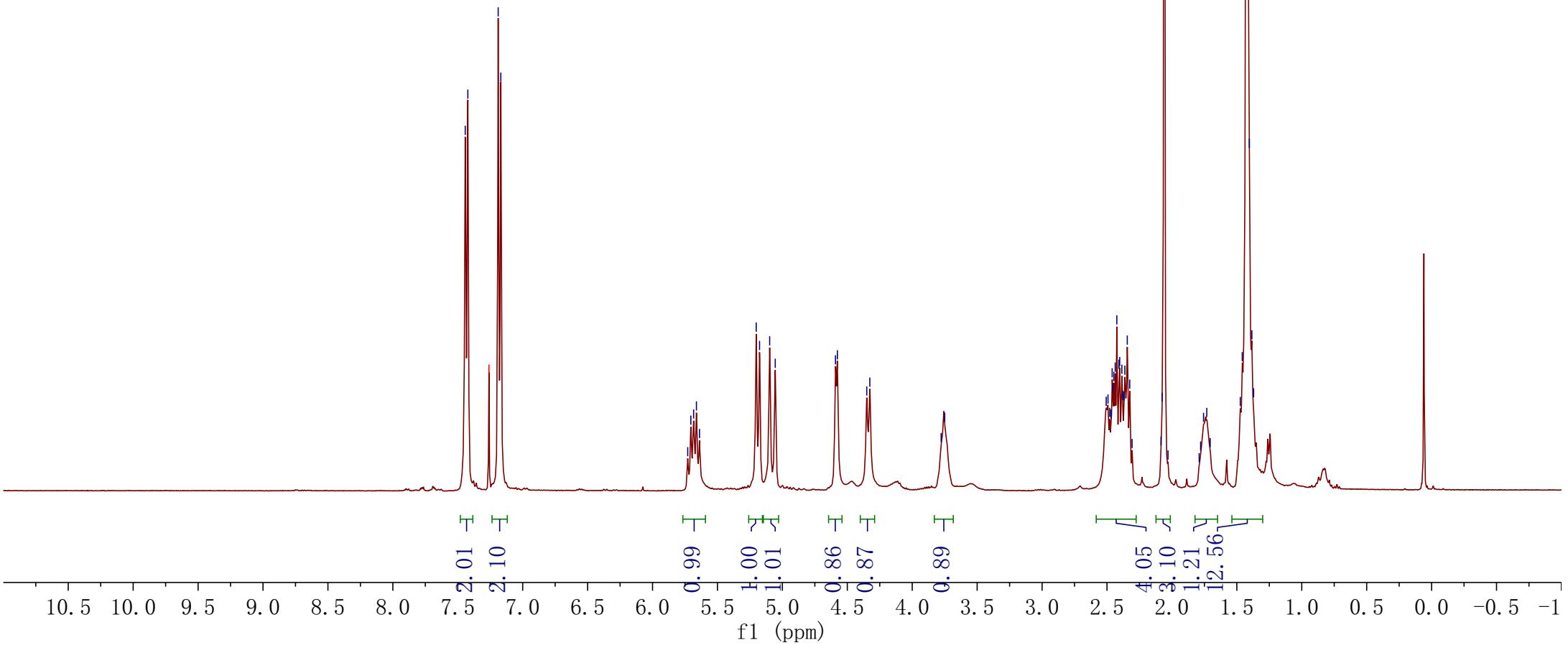
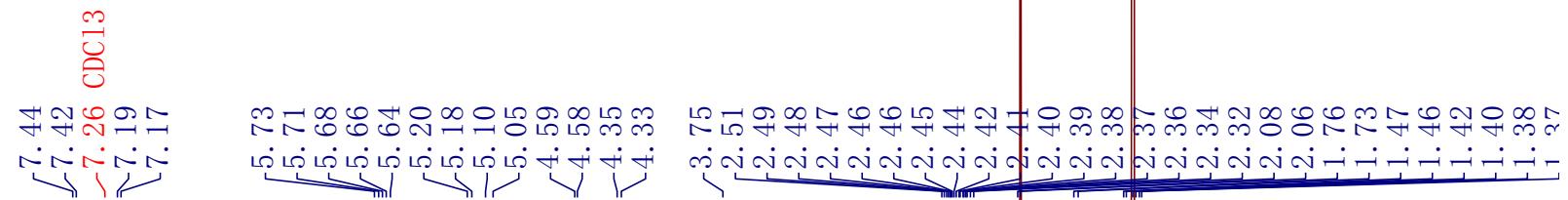
28.34  
22.06  
20.24

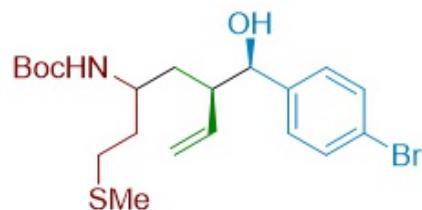




400MHz, CDCl<sub>3</sub>

6am





101MHz, CDCl<sub>3</sub>

6am

-155.51

~141.47  
~137.58  
~131.19  
~128.37

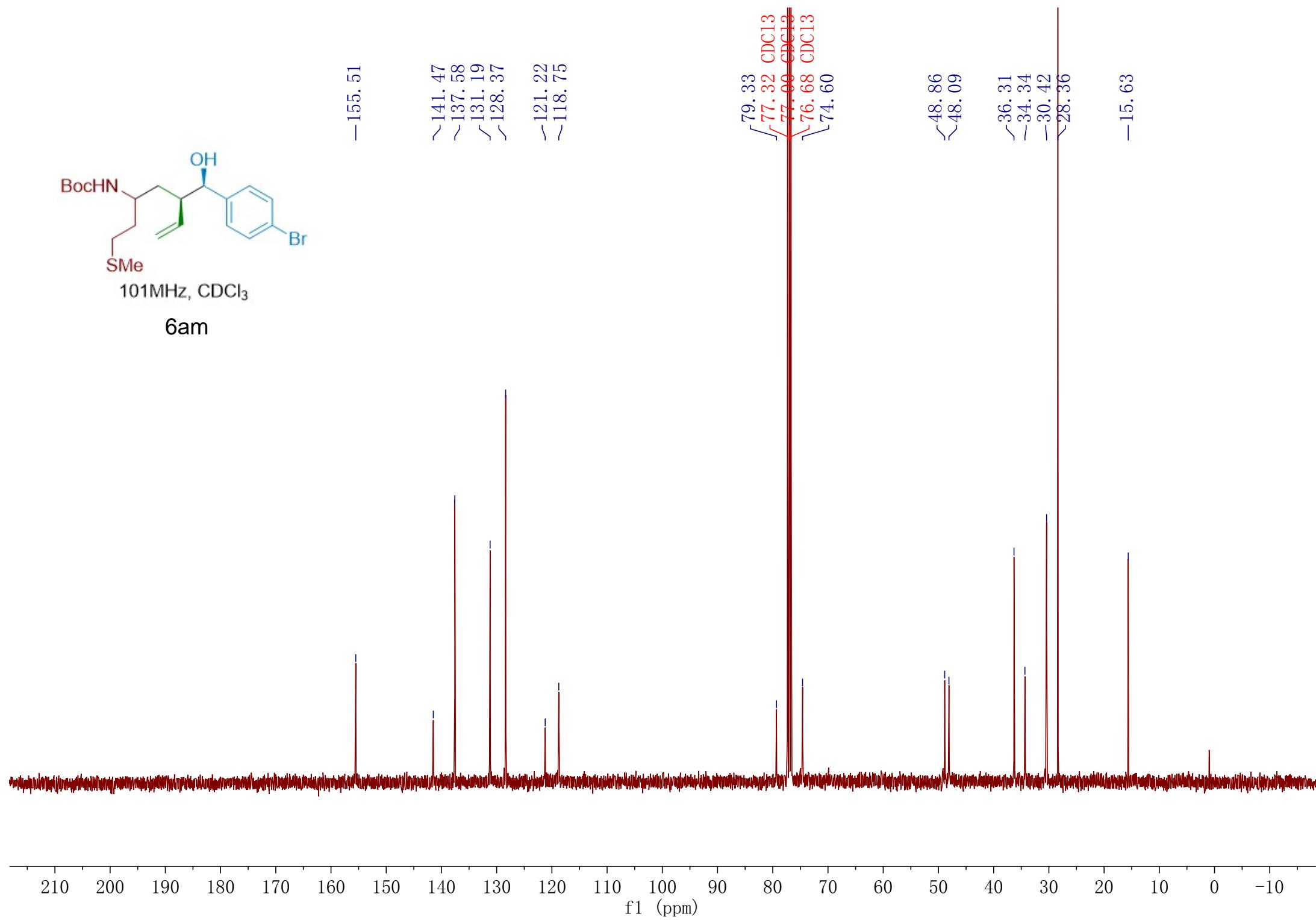
~121.22  
~118.75

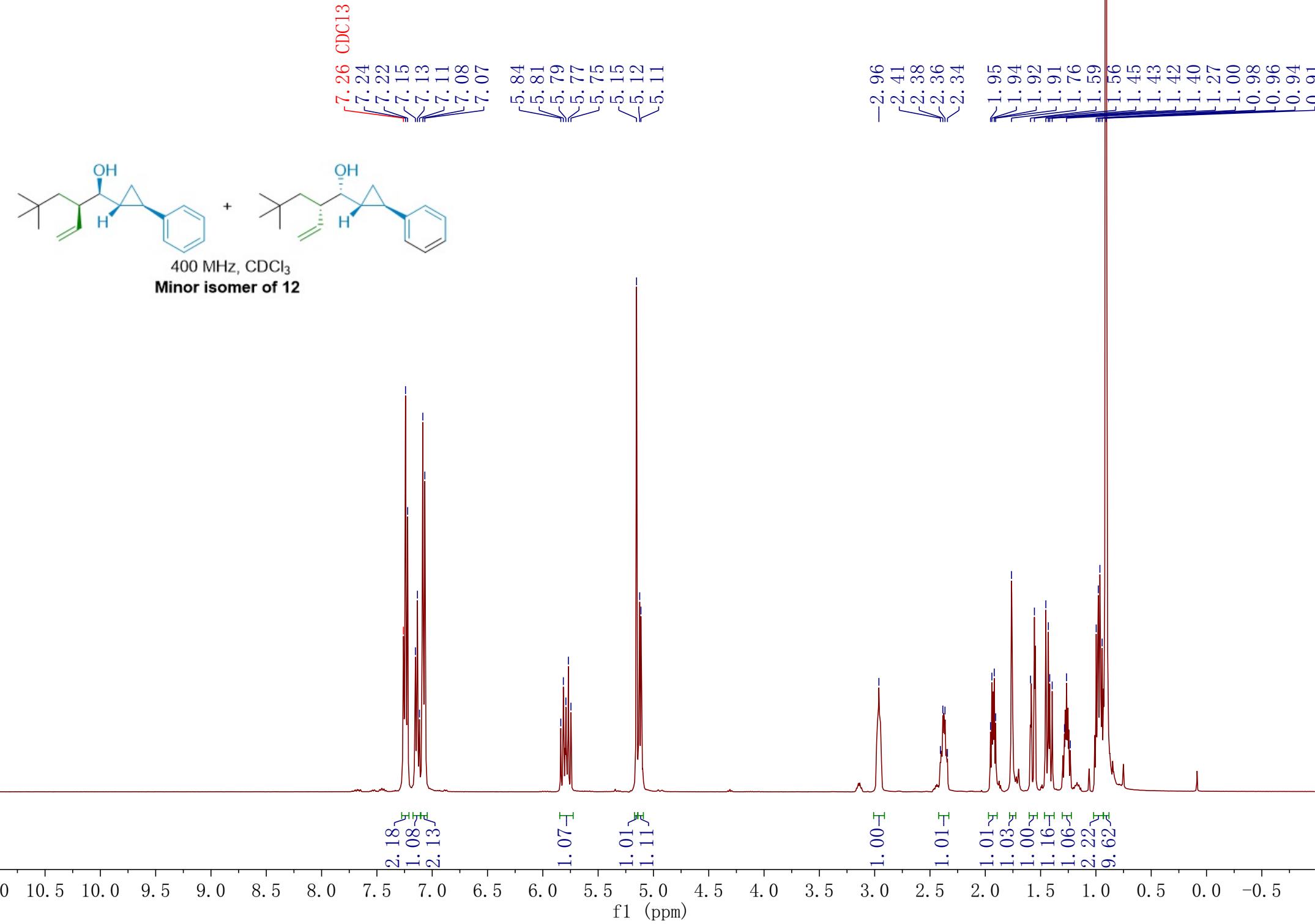
79.33  
77.32 CDCl<sub>3</sub>  
77.00 CDCl<sub>3</sub>  
76.68 CDCl<sub>3</sub>  
74.60

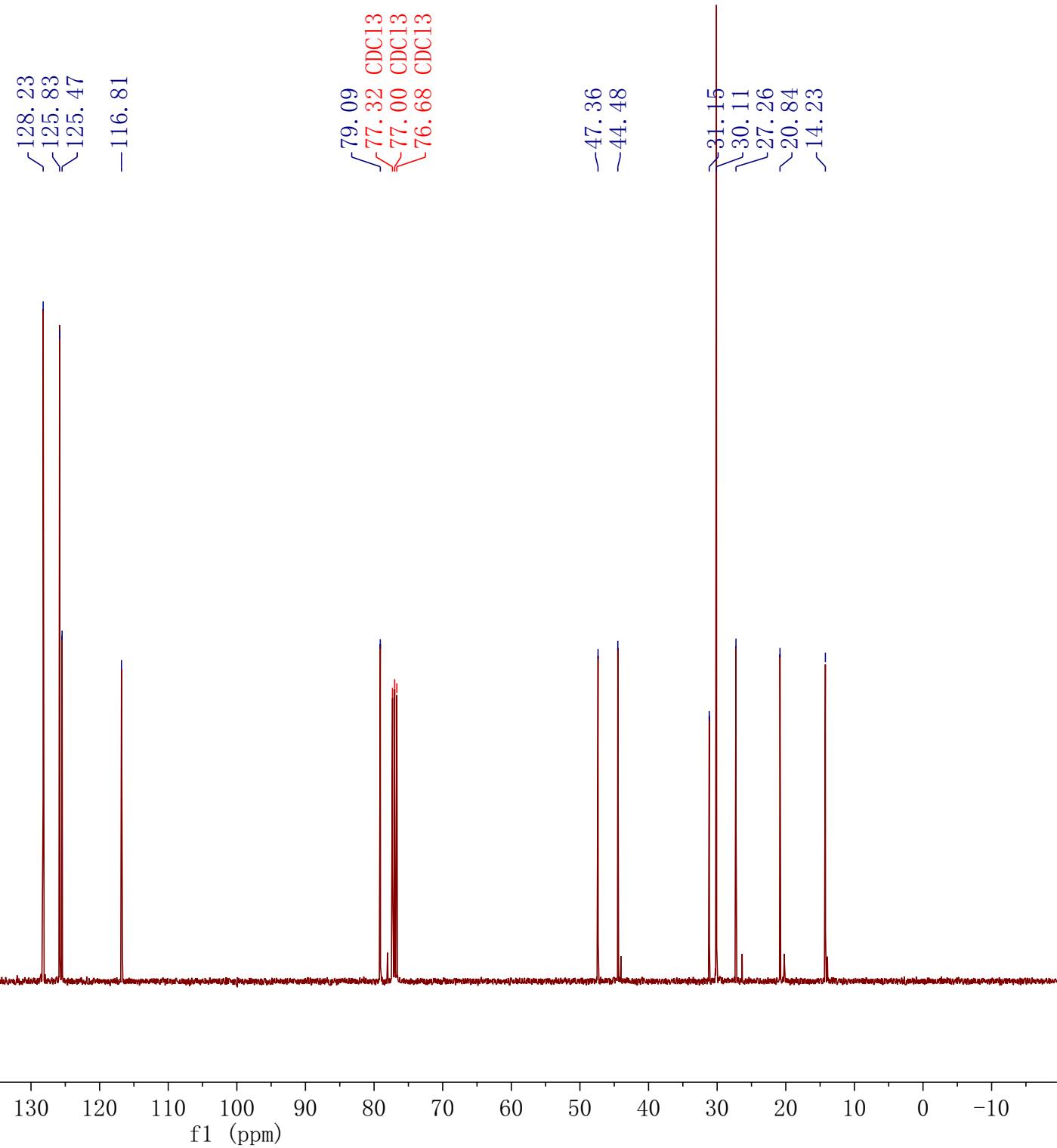
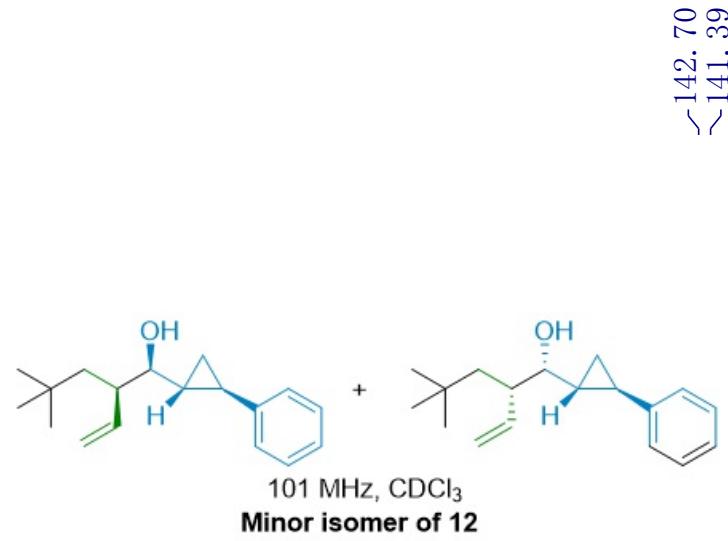
~48.86  
~48.09

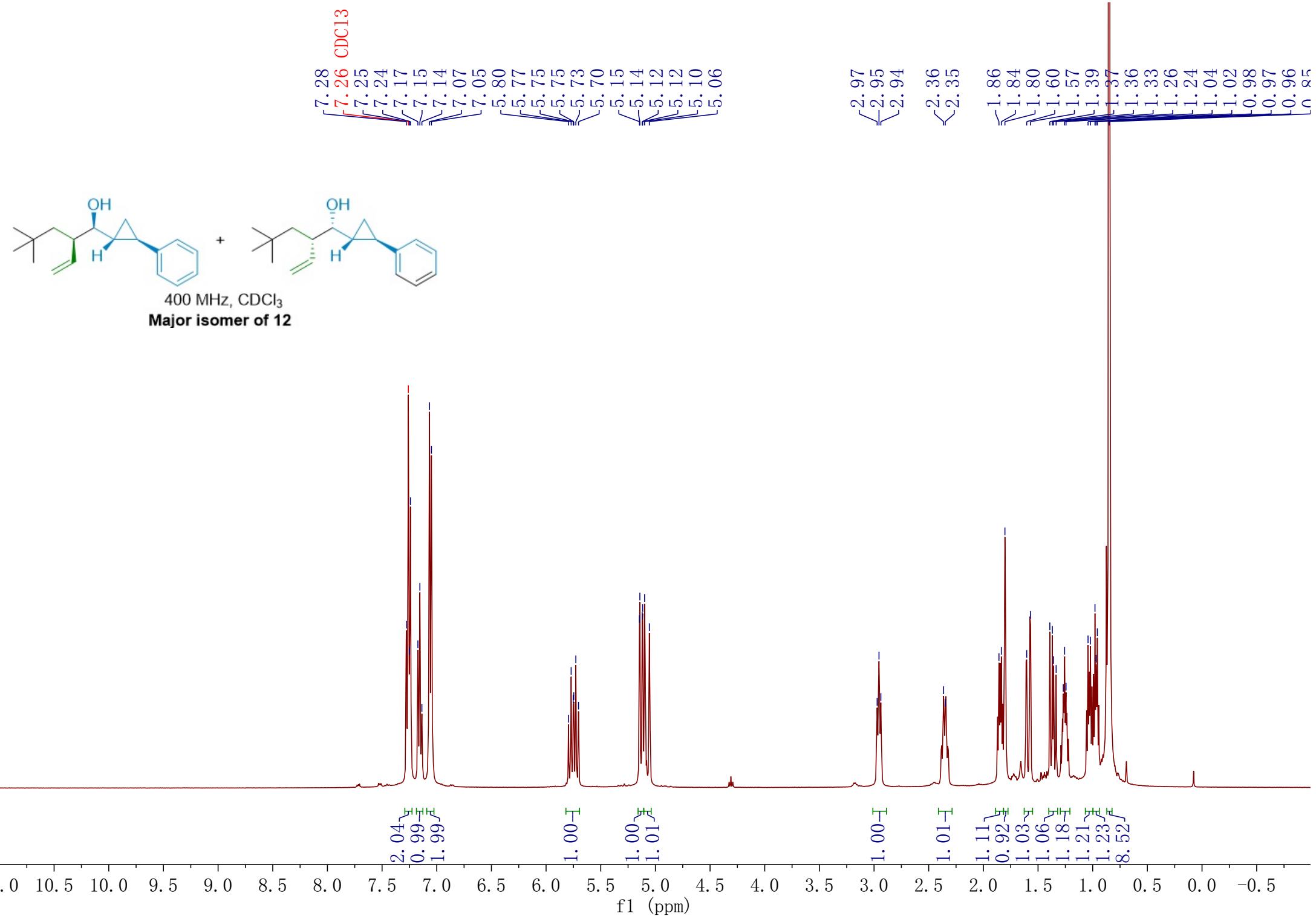
~36.31  
~34.34  
~30.42  
~28.36

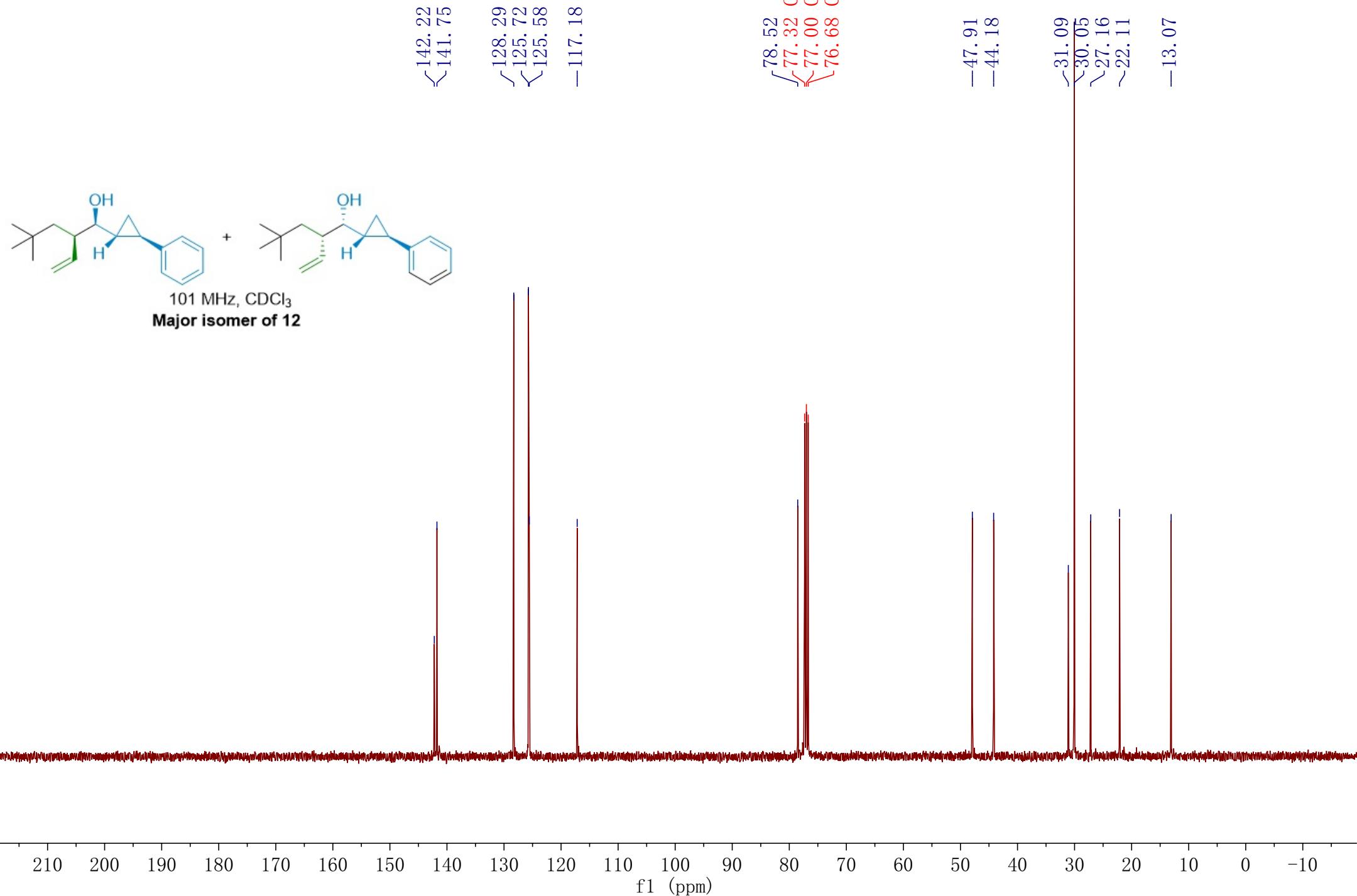
-15.63





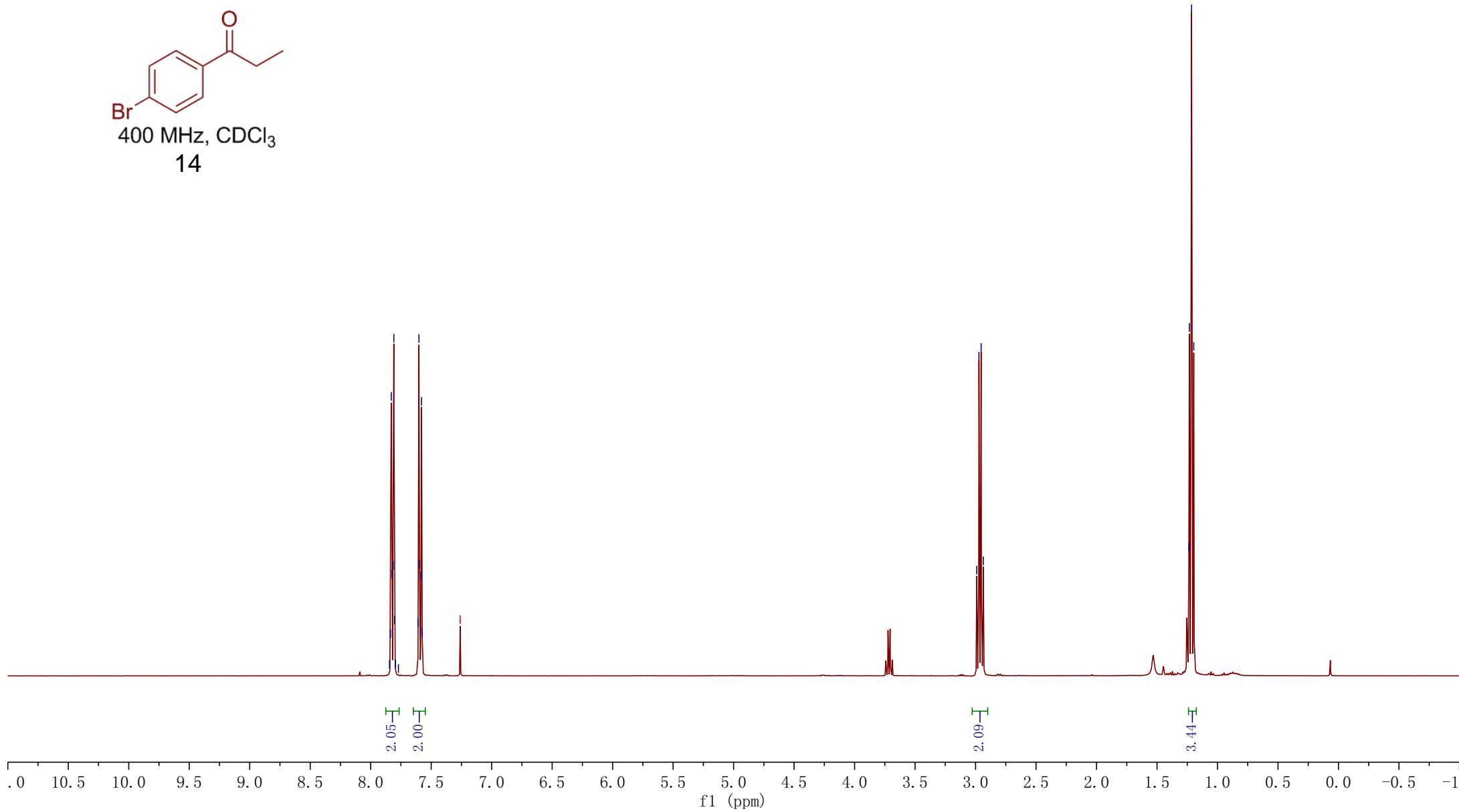








400 MHz,  $\text{CDCl}_3$



— 199.68

— 135.59  
— 131.83  
— 129.49  
— 127.95

— 77.32 CDCl<sub>3</sub>  
— 77.00 CDCl<sub>3</sub>  
— 76.68 CDCl<sub>3</sub>

— 31.75

— 8.10



101 MHz, CDCl<sub>3</sub>

14

