

# SUPPORTING INFORMATION

## Total Synthesis of (–)-Deglycocadambine

*Fang-Xin Wang,<sup>\*a</sup> Ying-Tao Chen,<sup>a,†</sup> Hui Liu,<sup>a,†</sup> Heng-Shan Wang,<sup>a</sup> Hong Liang,<sup>a</sup> Zhen-Feng Chen,<sup>a</sup>*

*Yonggui Robin Chi<sup>\*b,c</sup>*

<sup>a</sup>State Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources/Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources (Ministry of Education of China) & Collaborative Innovation Center for Guangxi Ethnic Medicine, School of Chemistry and Pharmaceutical Sciences, Guangxi Normal University, Guilin 541004, China

<sup>b</sup>School of Chemistry, Chemical Engineering, and Biotechnology, Nanyang Technological University, Singapore 637371, Singapore

<sup>c</sup>National Key Laboratory of Green Pesticide, Key Laboratory of Green Pesticide and Agricultural Bioengineering, Ministry of Education, Guizhou University, Huaxi District, Guiyang 550025, China

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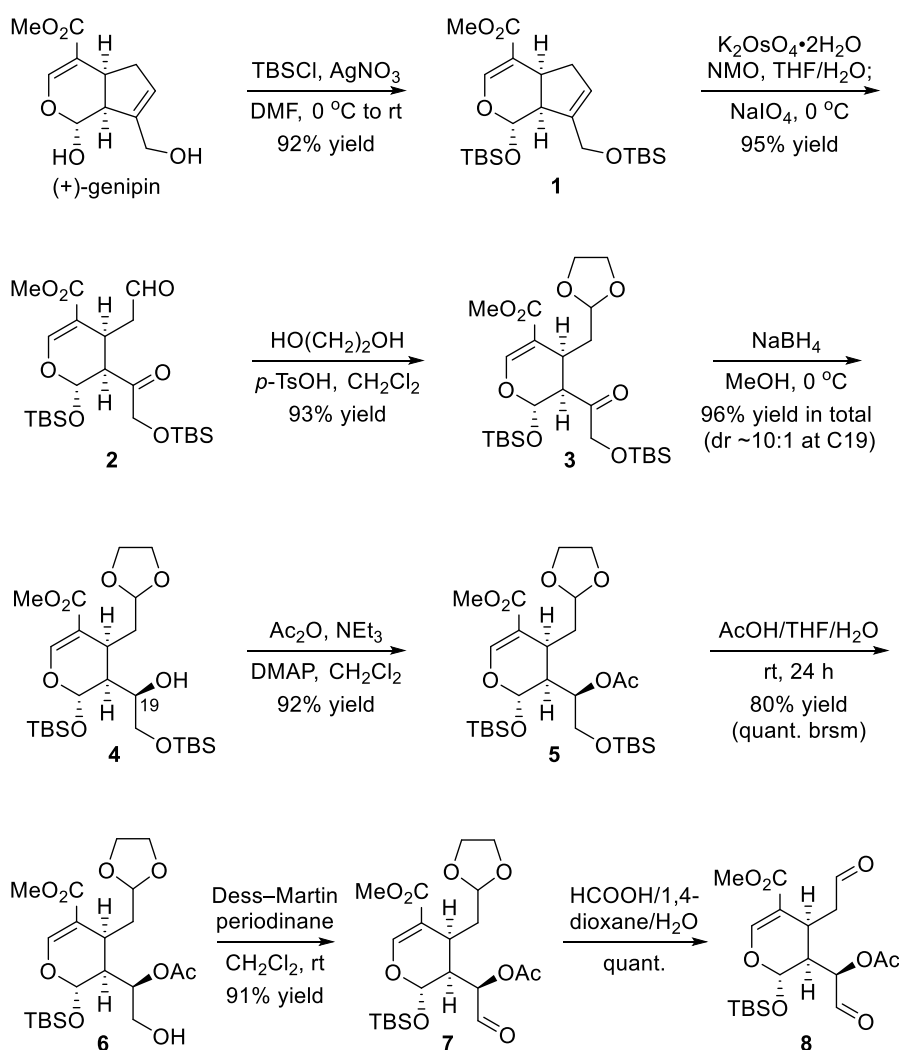
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## General

All moisture or oxygen-sensitive reactions were carried out under an argon atmosphere in heat-dried flasks. The solvents used were purified by distillation over the drying agents indicated and were transferred under argon: THF (Na), CH<sub>2</sub>Cl<sub>2</sub> (CaH<sub>2</sub>). Other solvents were all bought from Sigma-Aldrich as anhydrous reagent. All reactions were monitored by thin-layer chromatography (TLC) on silica gel F<sub>254</sub> plates using UV light as visualizing agent (if applicable), and a solution of ammonium molybdate tetrahydrate (50 g/L) in EtOH followed by heating as developing agents. The products were purified by flash column chromatography on silica gel (200-300 meshes).

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub>, CD<sub>3</sub>OD-*d*<sub>4</sub> solution on a Bruker AVIII 400 MHz or AV 500 MHz or Avance NEO 600 MHz instrument. Chemical shifts were denoted in ppm (δ), and calibrated by using residual undeuterated solvent (CDCl<sub>3</sub> (7.27 ppm), CD<sub>3</sub>OD-*d*<sub>4</sub> (3.31 ppm) or tetramethylsilane (0.00 ppm)) as internal reference for <sup>1</sup>H NMR and the deuterated solvent (CDCl<sub>3</sub> (77.00 ppm), CD<sub>3</sub>OD-*d*<sub>4</sub> (49.00 ppm) or tetramethylsilane (0.00 ppm)) as internal standard for <sup>13</sup>C NMR. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet, dd = double doublet, dt = double triplet, td = triple doublet. High-resolution mass spectral analysis (HRMS) data were measured on an Agilent 6545 Q-TOF LC/MS by means of the ESI technique. The IR spectra were recorded on Perkin-Elmer Spectrum Two FT-IR spectrometer. Optical rotations were measured on a JASCO P-2000 digital polarimeter with a sodium lamp. The X-ray single-crystal determination was performed on a Bruker APEX II X-ray single crystal diffractometer.

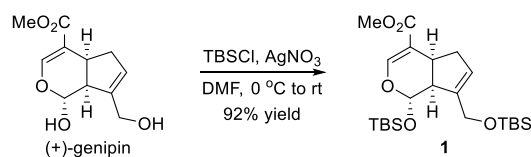
## 1. Outline for Synthesis of Compound 8



## 1.1. Compound 1

((+)-methyl

(1*S*,4*aS*,7*aS*)-1-((*tert*-butyldimethylsilyl)oxy)-7-(((*tert*-butyldimethylsilyl)oxy)methyl)-1,4*a*,5,7*a*-tetrahydrocyclo-penta[*c*]pyran-4-carboxylate)



To a stirred solution of (+)-genipin (52.5 g, 232.3 mmol) in DMF (250 mL) was added AgNO<sub>3</sub> (98.6 g, 580.5 mmol, 2.5 equiv) followed by portionwise addition of *tert*-butyldimethylsilyl chloride (TBSCl, 87.5 g, 580.5 mmol, 2.5 equiv) at 0 °C. The resulting reaction mixture was warmed to room temperature and vigorously stirred overnight. After filtration through a pad of celite, the filtrate was poured into cooled saturated NaHCO<sub>3</sub> solution (250 mL). AcOEt (250 mL) was added to the mixture. The organic phase was separated, and the aqueous layer was extracted with AcOEt (2 × 250 mL). The combined extracts were washed with brine (5 × 200 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with *n*-hexane/AcOEt (20:1) to afford the ether **1** (97.0 g, 213.7 mmol, 92% yield) as a light yellow liquid.

Note: when the reaction was conducted in the presence of TBSCl and imidazole at room temperature or higher temperatures, a mixture of **1** and **21-*epi*-1** was obtained with **1** as the major isomer, possibly due to the partial racemization of the hemiacetal in genipin under these specific reaction conditions.

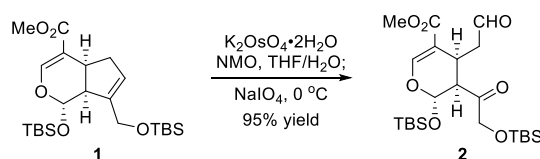
(+)-genipin (*dr* ~10:1, inseparable diastereomers): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.53 (d, *J* = 0.8 Hz, 1H), 5.89 (s, 1H), 5.51 (br, 1H), 4.82 (d, *J* = 8.4 Hz, 1H), 4.35, 4.28 (ABq, *J* = 13.2 Hz, 2H), 3.74 (s, 3H), 3.22 (ddd, *J* = 9.5, 8.5, 8.5 Hz, 1H), 3.06 (br, 1H), 2.89 (ddt, *J* = 16.8, 8.5, 1.4 Hz, 1H), 2.54 (ddd, *J* = 8.5, 8.5, 1.5 Hz, 1H), 2.07 ppm (ddt, *J* = 16.8, 9.5, 1.8 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 167.9, 152.5, 142.0, 130.9, 110.8, 96.3, 61.3, 51.3, 48.2, 39.0, 36.7 ppm.

**1**: R<sub>f</sub> = 0.7 (silica, petroleum ether/AcOEt = 8/1), [α]<sub>D</sub><sup>25</sup> = +32.2 (*c* 1.30, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.46 (s, 1H), 5.79 (s, 1H), 4.83 (d, *J* = 7.7 Hz, 1H), 4.40–4.13 (m, 2H), 3.69 (s, 3H), 3.16 (q, *J* = 8.1 Hz, 1H), 2.82 (dd, *J* = 15.4, 8.5 Hz, 1H), 2.45 (t, *J* = 7.7 Hz, 1H), 2.11–1.96 (m, 1H), 0.904 (s, 9H), 0.895 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H), 0.054 (s, 3H), 0.046 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 168.0, 152.3, 143.7, 126.6, 110.9, 96.8, 62.0, 51.1, 48.5, 38.7, 36.1, 25.9, 25.7, 18.3, 17.9, -4.2, -5.0, -5.3, -5.4 ppm. IR:  $\bar{\nu}$  = 2930, 2857, 1713, 1633, 1166, 1093, 838, 780 cm<sup>-1</sup>. HRMS (ESI): *m/z* calcd for C<sub>23</sub>H<sub>42</sub>O<sub>5</sub>Si<sub>2</sub>Na [*M* + Na]<sup>+</sup>: 477.2463; found: 477.2467.

## 1.2. Compound 2

((-)-methyl

(2*S*,3*R*,4*S*)-2-((*tert*-butyldimethylsilyl)oxy)-3-(2-((*tert*-butyldimethylsilyl)oxy)acetyl)-4-(2-oxoethyl)-3,4-dihydro-2-*H*-pyran-5-carboxylate)



To a stirred solution of alkene **1** (95.0 g, 209.1 mmol) in mixture solvents of THF (250 mL) and water (60 mL) was added K<sub>2</sub>OsO<sub>4</sub>·2H<sub>2</sub>O (770.1 mg, 2.09 mmol, 0.01 equiv) followed by *N*-methylmorpholine *N*-oxide (NMO, 73.5 g, 627.3 mmol, 3.0 equiv) at room temperature. The resulting reaction mixture was warmed to 50 °C and

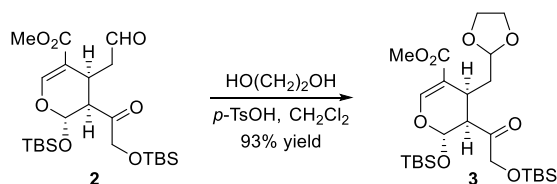
stirred for 3 h. After cooling to 0 °C, H<sub>2</sub>O (250 mL) and NaIO<sub>4</sub> (134.2 g, 627.3 mmol, 3.0 equiv) was added to the mixture and the resulting mixture was stirred vigorously at 0 °C for 1 h. The organic phase was separated, and the aqueous layer was extracted with AcOEt (2 × 250 mL). The combined extracts were washed with brine (5 × 200 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with *n*-hexane/AcOEt (8:1) to afford the aldehyde **2** (96.8 g, 199.0 mmol, 95% yield) as a colorless liquid.

**2:** *R<sub>f</sub>* = 0.75 (silica, petroleum ether/AcOEt = 4/1),  $[\alpha]_D^{25} = -90.9$  (*c* 2.60, CH<sub>2</sub>Cl<sub>2</sub>) **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ = 9.57 (s, 1H), 7.51 (s, 1H), 5.38 (d, *J* = 8.9 Hz, 1H), 4.20 (s, 2H), 3.69 (s, 3H), 3.66–3.60 (m, 1H), 3.28 (dd, *J* = 8.9, 5.3 Hz, 1H), 2.86 (dd, *J* = 18.4, 8.8 Hz, 1H), 2.53 (dd, *J* = 18.4, 3.0 Hz, 1H), 0.91 (s, 9H), 0.85 (s, 9H), 0.14 (s, 3H), 0.12 (s, 3H), 0.10 ppm (s, 6H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ = 209.8, 199.4, 166.7, 153.5, 108.2, 93.8, 70.2, 51.4, 48.2, 45.8, 27.1, 25.8, 25.4, 18.3, 17.8, -4.6, -5.5, -5.6, -5.6 ppm. **IR:**  $\bar{\nu}$  = 3500, 2954, 2858, 1714, 1634, 1254, 839, 782 cm<sup>-1</sup>. **HRMS** (ESI): *m/z* calcd for C<sub>23</sub>H<sub>42</sub>O<sub>7</sub>Si<sub>2</sub>Na [*M* + Na]<sup>+</sup>: 509.2361; found: 509.2361.

### 1.3. Compound 3

(–)-methyl

(2*S*,3*R*,4*S*)-4-((1,3-dioxolan-2-yl)methyl)-2-((*tert*-butyldimethylsilyl)oxy)-3-(2-((*tert*-butyldimethylsilyl)oxy)acetyl)-3,4-dihydro-2*H*-pyran-5-carboxylate)



To a stirred solution of aldehyde **2** (95.0 g, 195.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (500 mL) was added ethylene glycol (32.7 mL, 586.2 mmol, 3.0 equiv) followed by *p*-TsOH·H<sub>2</sub>O (3.72 g, 19.54 mmol, 0.1 equiv) at room temperature. The resulting reaction mixture was stirred overnight. H<sub>2</sub>O (500 mL) was added to the mixture and the organic phase was separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 250 mL). The combined extracts were washed sequentially with saturated aqueous solution of NaHCO<sub>3</sub> (100 mL) and brine (500 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with *n*-hexane/AcOEt (8:1) to afford ketone **3** (96.4 g, 181.7 mmol, 93% yield) as a colorless liquid.

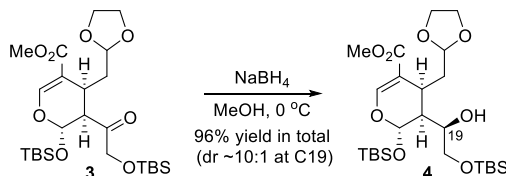
**Note: Compounds 2 and 3 have almost the same *R<sub>f</sub>* value.**

**3:** *R<sub>f</sub>* = 0.75 (silica, petroleum ether/AcOEt = 4/1),  $[\alpha]_D^{25} = -72.4$  (*c* 2.16, CH<sub>2</sub>Cl<sub>2</sub>). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ = 7.40 (s, 1H), 5.52 (d, *J* = 8.8 Hz, 1H), 4.91 (dd, *J* = 5.8, 4.5 Hz, 1H), 4.20, 4.15 (ABq, *J* = 17.5 Hz, 2H), 3.90–3.84 (m, 1H), 3.84–3.77 (m, 1H), 3.75–3.69 (m, 2H), 3.69–3.64 (m, 3H), 3.17 (dd, *J* = 11.6, 5.0 Hz, 1H), 3.12 (dd, *J* = 8.8, 4.8 Hz, 1H), 1.85 (dt, *J* = 14.3, 5.4 Hz, 1H), 1.62–1.53 (m, 1H), 0.88 (s, 9H), 0.83 (s, 9H), 0.12 (d, *J* = 5.1 Hz, 3H), 0.09 (s, 3H), 0.07 (s, 3H), 0.05 ppm (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ = 207.8, 167.1, 152.4, 110.1, 103.1, 93.6, 69.8, 64.8, 64.2, 51.1, 49.7, 36.2, 28.5, 25.7, 25.4, 18.2, 17.7, -4.7, -5.6, -5.6, -5.7 ppm. **IR:**  $\bar{\nu}$  = 2954, 1713, 1638, 1464, 1255, 1093, 840, 782 cm<sup>-1</sup>. **HRMS** (ESI): *m/z* calcd for C<sub>25</sub>H<sub>46</sub>O<sub>8</sub>Si<sub>2</sub>Na [*M* + Na]<sup>+</sup>: 553.2623; found: 553.2630.

#### 1.4. Compound 4

((-)-methyl

(2*S*,3*S*,4*S*)-4-((1,3-dioxolan-2-yl)methyl)-2-((*tert*-butyldimethylsilyl)oxy)-3-((*R*)-2-((*tert*-butyldimethylsilyl)oxy)-1-hydroxyethyl)-3,4-dihydro-2*H*-pyran-5-carboxylate)



To a stirred solution of ketone **3** (95.0 g, 179.2 mmol) in MeOH (500 mL) was portionwise added NaBH<sub>4</sub> (8.1 g, 215.0 mmol, 1.2 equiv) at 0 °C. The resulting reaction mixture was stirred for 45 min. The mixture was quenched carefully by slow addition of water (500 mL). AcOEt (500 mL) was added and the organic phase was separated, and the aqueous layer was extracted with AcOEt (2 × 250 mL). The combined extracts were washed sequentially with saturated aqueous solution of NaHCO<sub>3</sub> (500 mL) and brine (500 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with *n*-hexane/AcOEt (8:1) to afford the corresponding alcohol **4** (91.6 g, 172.1 mmol, 96% yield in total, *dr* ~10:1 at C19, inseparable diastereomers) as a light yellow liquid.

**4**: *R<sub>f</sub>* = 0.65 (silica, petroleum ether/AcOEt = 4/1),  $[\alpha]_D^{25} = -85.6$  (*c* 2.45, CH<sub>2</sub>Cl<sub>2</sub>) **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.40$  (s, 1H), 5.56 (d, *J* = 9.0 Hz, 1H), 4.91 (t, *J* = 4.9 Hz, 1H), 3.96–3.74 (m, 6H), 3.67 (s, 3H), 3.62 (dd, *J* = 9.6, 3.1 Hz, 1H), 3.10 (s, 1H), 2.99–2.90 (m, 1H), 2.20–2.11 (m, 1H), 1.77 (dt, *J* = 8.8, 4.3 Hz, 1H), 1.70–1.62 (m, 1H), 0.90 (s, 9H), 0.87 (s, 9H), 0.15 (s, 3H), 0.14 (s, 3H), 0.05 ppm (s, 6H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta = 167.4, 152.5, 110.5, 103.4, 95.7, 72.1, 65.7, 64.8, 64.4, 51.1, 42.9, 36.5, 30.4, 25.8, 25.6, 18.2, 17.8, -4.4, -5.1, -5.4, -5.5$  ppm. **IR**:  $\bar{\nu} = 3527, 2954, 2858, 1710, 1635, 1254, 839, 781$  cm<sup>-1</sup>. **HRMS** (ESI): *m/z* calcd for C<sub>25</sub>H<sub>48</sub>O<sub>2</sub>Si<sub>2</sub>Na [*M* + Na]<sup>+</sup>: 555.2780; found: 555.2785

#### 1.5. Compound 5

((-)-methyl

(2*S*,3*S*,4*S*)-4-((1,3-dioxolan-2-yl)methyl)-3-((*R*)-1-acetoxy-2-((*tert*-butyldimethylsilyl)oxy)ethyl)-2-((*tert*-butyldimethylsilyl)oxy)-3,4-dihydro-2*H*-pyran-5-carboxylate)



To a stirred solution of alcohol **4** (30.0 g, 56.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (150 mL) were sequentially added NEt<sub>3</sub> (23.6 mL, 169.2 mmol, 3.0 equiv), DMAP (1.38 g, 11.3 mmol, 0.2 equiv) and Ac<sub>2</sub>O (15.9 mL, 169.2 mmol, 3.0 equiv) at room temperature and the resulting solution was stirred overnight. Saturated aqueous solution of NH<sub>4</sub>Cl (100 mL) was added to the mixture and the organic phase was separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 100 mL). The combined extracts were washed with brine (250 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with *n*-hexane/AcOEt (4:1) to afford the ester **5** (29.8 g, 51.9 mmol, 92% yield, *dr* ~10:1 at C19, inseparable diastereomers) as a colorless liquid.

**5**: *R<sub>f</sub>* = 0.64 (silica, petroleum ether/AcOEt = 4/1),  $[\alpha]_D^{25} = -93.6$  (*c* 2.80, CH<sub>2</sub>Cl<sub>2</sub>) **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.39$  (s, 1H), 5.49 (d, *J* = 8.4 Hz, 1H), 5.12 (td, *J* = 6.5, 1.7 Hz, 1H), 4.86 (t, *J* = 4.9 Hz, 1H), 3.92–3.83

(m, 2H), 3.78–3.70 (m, 4H), 3.65 (s, 3H), 2.95–2.86 (m, 1H), 2.15–2.08 (m, 1H), 1.99 (s, 3H), 1.88–1.80 (m, 1H), 1.67–1.57 (m, 1H), 0.89 (s, 9H), 0.82 (s, 9H), 0.13 (s, 3H), 0.11 (s, 3H), 0.00 ppm (s, 6H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 169.7, 167.4, 152.5, 109.8, 103.1, 94.8, 74.0, 64.8, 64.2, 63.3, 51.0, 40.5, 35.6, 30.9, 25.7, 25.6, 21.2, 18.0, 17.8, -4.5, -5.1, -5.4, -5.6 ppm. **IR**:  $\bar{\nu}$  = 2954, 2862, 1747, 1641, 1253, 1132, 839, 778  $\text{cm}^{-1}$ . **HRMS** (ESI):  $m/z$  calcd for  $\text{C}_{27}\text{H}_{50}\text{O}_9\text{Si}_2\text{Na}$  [ $M + \text{Na}$ ] $^+$ : 597.2886; found: 597.2891.

## 1.6. Compound 6

((-)-methyl

(2*S*,3*S*,4*S*)-4-((1,3-dioxolan-2-yl)methyl)-3-((*R*)-1-acetoxy-2-hydroxyethyl)-2-((*tert*-butyldimethylsilyl)oxy)-3,4-dihydro-2*H*-pyran-5-carboxylate)



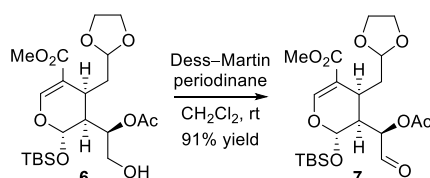
The solution of ester **5** (28.0 g, 48.8 mmol) in mixed solvents of AcOH/THF/ $\text{H}_2\text{O}$  (60 mL/40 mL/40 mL) was stirred at room temperature for 24 h. Water (100 mL) and AcOEt (50 mL) were added and the organic phase was separated. The aqueous layer was extracted with AcOEt (2  $\times$  50 mL). The combined extracts were washed sequentially with saturated aqueous solution of  $\text{NaHCO}_3$  (3  $\times$  150 mL, **take care, a lot of gases were generated**) and brine (150 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with *n*-hexane/AcOEt (1:1) to afford the alcohol **6** (18.0 g, 39.0 mmol, 80% yield, quant. brsm, *dr* ~10:1 at C19, inseparable diastereomers) as a colorless liquid.

**6**:  $R_f$  = 0.54 (silica, petroleum ether/AcOEt = 1/1),  $[\alpha]_D^{25}$  = -112.0 (*c* 2.72,  $\text{CH}_2\text{Cl}_2$ )  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.36 (s, 1H), 5.45 (d,  $J$  = 8.5 Hz, 1H), 5.12 (t,  $J$  = 5.0 Hz, 1H), 4.82 (t,  $J$  = 4.9 Hz, 1H), 3.87–3.80 (m, 2H), 3.78–3.68 (m, 4H), 3.62 (s, 3H), 2.95–2.85 (m, 1H), 2.11–2.06 (m, 1H), 2.00 (s, 3H), 1.81 (dt,  $J$  = 14.0, 4.7 Hz, 1H), 1.64–1.55 (m, 1H), 0.86 (s, 9H), 0.11 (s, 3H), 0.10 ppm (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 170.6, 167.2, 152.4, 109.8, 103.0, 94.4, 75.3, 64.7, 64.4, 64.2, 51.0, 41.5, 35.5, 31.0, 25.4, 21.1, 17.7, -4.6, -5.2 ppm. **IR**:  $\bar{\nu}$  = 3671, 2953, 1740, 1636, 1259, 1087, 840, 749  $\text{cm}^{-1}$ . **HRMS** (ESI):  $m/z$  calcd for  $\text{C}_{21}\text{H}_{36}\text{O}_9\text{SiNa}$  [ $M + \text{Na}$ ] $^+$ : 483.2021; found: 483.2030.

## 1.7. Compound 7

((-)-methyl

(2*S*,3*S*,4*S*)-4-((1,3-dioxolan-2-yl)methyl)-3-((*R*)-1-acetoxy-2-oxoethyl)-2-((*tert*-butyldimethylsilyl)oxy)-3,4-dihydro-2*H*-pyran-5-carboxylate)



To a stirred solution of alcohol **6** (17.0 g, 36.9 mmol) in  $\text{CH}_2\text{Cl}_2$  (150 mL) was added Dess–Martin periodinane (18.8 g, 44.3 mmol, 1.2 equiv) at 0  $^\circ\text{C}$ . The resulting mixture was stirred at room temperature for 1 h. An additional portion of Dess–Martin periodinane (9.4 g, 22.1 mmol, 0.6 equiv) was added to the solution and the mixture was stirred further for 2 h before quenching by addition of saturated aqueous solution of  $\text{Na}_2\text{S}_2\text{O}_3$  (50 mL) to the solution and vigorous stirring for 30 min. Water (100 mL) was added and the organic phase was separated.

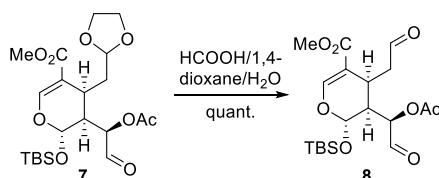
The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 50 mL). The combined extracts were washed with brine (150 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with *n*-hexane/AcOEt (4:1) to afford the aldehyde **7** (15.4 g, 33.6 mmol, 91% yield) as a colorless liquid.

**7**:  $R_f$  = 0.32 (silica, petroleum ether/AcOEt = 4/1),  $[\alpha]_D^{25} = -97.2$  (*c* 2.20, CH<sub>2</sub>Cl<sub>2</sub>) **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.36 (s, 1H), 7.37 (s, 1H), 5.37 (d, *J* = 8.8 Hz, 1H), 5.24 (s, 1H), 4.84 (t, *J* = 5.0 Hz, 1H), 3.89–3.80 (m, 2H), 3.78–3.70 (m, 2H), 3.66 (s, 3H), 2.99 (q, *J* = 5.4 Hz, 1H), 2.57 (dd, *J* = 8.7, 4.9 Hz, 1H), 2.13 (s, 3H), 1.98 (dt, *J* = 15.5, 5.3 Hz, 1H), 1.71–1.62 (m, 1H), 0.84 (s, 9H), 0.11 (s, 3H), 0.08 ppm (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 197.6, 169.9, 167.0, 151.9, 110.4, 103.2, 93.0, 78.0, 64.7, 64.3, 51.2, 43.6, 36.4, 31.2, 25.4, 20.6, 17.7, -4.8, -5.0 ppm. **IR**:  $\bar{\nu}$  = 2954, 2859, 1744, 1710, 1635, 1228, 1082, 841 cm<sup>-1</sup>. **HRMS** (ESI): *m/z* calcd for C<sub>21</sub>H<sub>34</sub>O<sub>9</sub>SiNa [*M* + Na]<sup>+</sup>: 481.1864; found: 481.1866.

## 1.8. Compound 8

(-)-methyl

(2*S*,3*S*,4*S*)-3-((*R*)-1-acetoxy-2-oxoethyl)-2-((*tert*-butyldimethylsilyl)oxy)-4-(2-oxoethyl)-3,4-dihydro-2*H*-pyran-5-carboxylate)



The solution of aldehyde **7** (14.0 g, 30.6 mmol) in mixed solvents of HCOOH/1,4-dioxane/H<sub>2</sub>O (60 mL/20 mL/20 mL) was stirred at room temperature for 24 h. Water (100 mL) and AcOEt (50 mL) were added and the organic phase was separated. The aqueous layer was extracted with AcOEt (2 × 50 mL). The combined extracts were washed sequentially with saturated aqueous solution of NaHCO<sub>3</sub> (3 × 100 mL, **take care, a lot of gases were generated**) and brine (150 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with *n*-hexane/AcOEt (2:1) to afford the dialdehyde **8** (12.7 g, 30.6 mmol, quant.) as a colorless liquid.

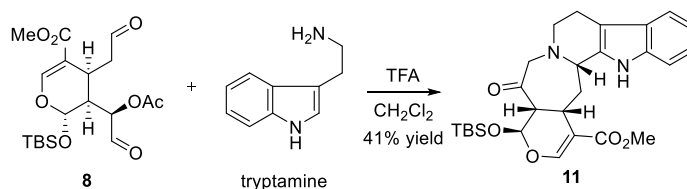
**8**:  $R_f$  = 0.42 (silica, petroleum ether/AcOEt = 2/1),  $[\alpha]_D^{25} = -66.5$  (*c* 2.46, CH<sub>2</sub>Cl<sub>2</sub>) **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.66 (s, 1H), 9.33 (s, 1H), 7.48 (s, 1H), 5.31 (d, *J* = 8.7 Hz, 1H), 5.08 (s, 1H), 3.67 (s, 3H), 3.49–3.42 (m, 1H), 2.74–2.64 (m, 2H), 2.57–2.48 (m, 1H), 2.13 (s, 3H), 0.85 (s, 9H), 0.12 (s, 3H), 0.09 ppm (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 199.8, 196.6, 169.7, 166.5, 153.5, 108.1, 92.8, 77.4, 51.4, 46.3, 43.2, 29.5, 25.4, 20.4, 17.7, -4.8, -4.9 ppm. **IR**:  $\bar{\nu}$  = 2954, 2858, 1741, 1635, 1438, 1253, 1136, 841 cm<sup>-1</sup>. **HRMS** (ESI): *m/z* calcd for C<sub>19</sub>H<sub>30</sub>O<sub>8</sub>SiNa [*M* + Na]<sup>+</sup>: 437.1602; found: 437.1604.

## 2. Compound 11 and Screening of reaction conditions

### 2.1. Compound 11

(-)-methyl

(4*S*,4*aR*,14*bS*,15*aS*)-4-((*tert*-butyldimethylsilyl)oxy)-5-oxo-4,4*a*,5,6,8,9,14,14*b*,15,15*a*-decahydropyrano[4'',3''':4',5']azepino[1',2':1,2]pyrido[3,4-*b*]indole-1-carboxylate)



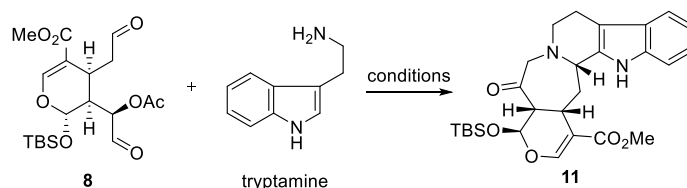


To a stirred solution of dialdehyde **8** (3.0 g, 7.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added tryptamine (1.3 g, 8.0 mmol, 1.1 equiv) at 0 °C. 10 min later, TFA (1.6 mL, 21.7 mmol, 3.0 equiv) was added dropwise and the mixed solution was stirred at 0 °C for 3 h and warmed to room temperature in 30 min and stirred for 48 h. Water (50 mL) was added and the organic phase was separated. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 25 mL). The combined extracts were washed sequentially with saturated aqueous solution of NaHCO<sub>3</sub> (3 × 40 mL, take care, a lot of gases were generated) and brine (40 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with *n*-hexane/AcOEt/NEt<sub>3</sub> (*V/V/V* = 160:20:1) to afford the ketone **11** (1.5 g, 2.9 mmol, 41% yield) as a light yellow foam.

**11**: *R*<sub>f</sub> = 0.50 (silica, petroleum ether/AcOEt = 4/1), [α]<sub>D</sub><sup>25</sup> = -85.0 (*c* 0.10, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.92 (s, 1H), 7.53 (s, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 1H), 5.57 (s, 1H), 3.98 (s, 1H), 3.80 (s, 3H), 3.58 (d, *J* = 8.6 Hz, 1H), 3.52, 3.39 (ABq, *J* = 16.7 Hz, 2H), 3.27–3.17 (m, 1H), 3.11–2.96 (m, 3H), 2.78 (d, *J* = 11.5 Hz, 1H), 2.61 (d, *J* = 14.7 Hz, 1H), 2.01 (dd, *J* = 24.1, 13.9 Hz, 1H), 0.85 (s, 9H), 0.13 (s, 3H), 0.12 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 210.4, 167.8, 153.7, 136.4, 133.9, 127.6, 121.5, 119.4, 117.9, 111.5, 109.0, 108.6, 91.9, 64.2, 58.7, 53.5, 52.1, 51.5, 33.4, 25.6, 25.1, 21.3, 17.8, -4.7, -5.2 ppm. IR:  $\bar{\nu}$  = 2926, 2355, 1696, 1383, 1262, 1091, 747, 667 cm<sup>-1</sup>. HRMS (ESI): *m/z* calcd for C<sub>27</sub>H<sub>37</sub>N<sub>2</sub>O<sub>5</sub>Si [*M* + H]<sup>+</sup>: 497.2466; found: 497.2469.

## 2.2. Screening of reaction conditions for compound **11**

This cascade annulation reaction is sensitive to the reaction conditions, as in many cases, we can't get the desired product, culminating in unidentified mixtures. The highly functionality of compound **8** might partially account for these negative results. Below is the details of conditions screening for this cascade annulation.



Entry	Conditions	<i>T</i> [°C]	<i>t</i> [h]	Yield [%] <sup>a</sup>
1	TFA, CH <sub>2</sub> Cl <sub>2</sub>	0 to rt	51	41
2	TFA, THF	0 to rt	16	no product
3	TFA, CH <sub>3</sub> CN	0 to rt	16	10
4	TFA, Et <sub>2</sub> O	0 to rt	16	no product
5	TFA, 1,4-dioxane	0 to rt	16	no product
6	TFA, DCE	0 to rt	21	13
7	TFA, CHCl <sub>3</sub>	0 to rt	40	no product
8	TFA, DMF	0 to rt	40	no product

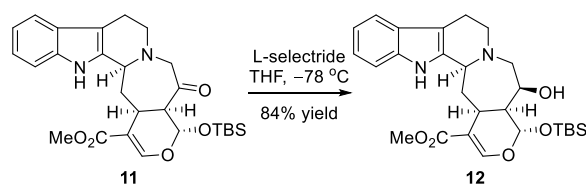
9	TFA, DMSO	rt	21	no product
10	TFA, toluene	0 to rt	21	7
11	<i>p</i> -TsOH, CH <sub>2</sub> Cl <sub>2</sub>	0 to rt	16	1
12	TiCl <sub>4</sub> , CH <sub>2</sub> Cl <sub>2</sub>	-40 to 0	21	8
13	TMSOTf, CH <sub>2</sub> Cl <sub>2</sub>	0 to rt	16	no product
14	AlCl <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub>	0 to rt	16	11
15	BF <sub>3</sub> ·OEt <sub>2</sub> , CH <sub>2</sub> Cl <sub>2</sub>	-40 to 0 to rt	21	2
16	CH <sub>2</sub> Cl <sub>2</sub> /AcOH (2/1)	0 to rt	21	no product
17	HCl (4 M in 1,4-dioxane), H <sub>2</sub> O	0 to rt	136	no product
18	toluene/AcOH (2/1)	rt to 50 to 80 to 110	51	no product
19	TFA, CH <sub>2</sub> Cl <sub>2</sub> (5 mL)	0 to rt	21	10

<sup>a</sup>Unless otherwise noted, all reactions were performed with **8** (50.0 mg, 0.12 mmol), trptamine (21.0 mg, 1.1 eq., 0.13 mmol) and indicated solvent (1.2 mL) at indicated temperature within indicated time.

### 3. Compound 12

((-)-methyl

(4*S*,4*aS*,5*S*,14*bS*,15*aS*)-4-((*tert*-butyldimethylsilyl)oxy)-5-hydroxy-4,4*a*,5,6,8,9,14,14*b*,15,15*a*-decahydropyrano[4'',3'':4',5']azepino[1',2':1,2]pyrido[3,4-*b*]indole-1-carboxylate)



To a stirred solution of ketone **11** (0.8 g, 1.6 mmol) in THF (10 mL) was dropwise added L-selectride (1 M in THF, 1.8 mL, 1.8 mmol, 1.1 equiv) at -78 °C. The resulting mixture was stirred at -78 °C for 3 h and then quenched by slow addition of saturated aqueous Rochelle's salt (3 mL). Water (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL) were added and the organic phase was separated. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 6 mL). The combined extracts were washed with brine (10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with *n*-hexane/AcOEt/NEt<sub>3</sub> (*V/V/V* = 160:20:1) to afford the alcohol **12** (669.6 mg, 1.1 mmol, 84% yield) as a light yellow liquid.

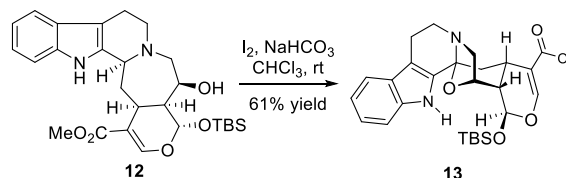
**12**: *R*<sub>f</sub> = 0.75 (silica, petroleum ether/AcOEt = 4/1), [α]<sub>D</sub><sup>25</sup> = -73.9 (*c* 0.30, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 10.82 (s, 1H), 7.61 (s, 1H), 7.53–7.47 (m, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 5.37 (d, *J* = 8.8 Hz, 1H), 4.57 (br, 1H), 4.22 (t, *J* = 6.4 Hz, 1H), 3.82 (s, 3H), 3.47–3.36 (m, 1H), 3.30–3.20 (m, 1H), 3.09–2.94 (m, 3H), 2.80–2.69 (m, 2H), 2.43 (dd, *J* = 15.4, 4.1 Hz, 1H), 2.31–2.21 (m, 1H), 1.67–1.59 (m, 1H), 0.96 (s, 9H), 0.23 (s, 3H), 0.21 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 169.3, 155.0, 136.3, 132.7, 127.6, 121.2,

119.0, 117.8, 111.7, 108.3, 108.1, 95.3, 64.8, 57.9, 54.1, 51.6, 49.8, 46.5, 31.5, 29.2, 25.6, 18.5, 18.0, -4.5, -5.4 ppm. **IR**:  $\bar{\nu}$  = 3431, 2927, 2855, 1682, 1633, 1178, 945, 740  $\text{cm}^{-1}$ . **HRMS** (ESI):  $m/z$  calcd for  $\text{C}_{27}\text{H}_{39}\text{N}_2\text{O}_5\text{Si}$  [ $M + \text{H}$ ]<sup>+</sup>: 499.2623; found: 499.2621.

#### 4. Compound 13

((-)-methyl

(4*S*,4*aS*,5*S*,14*bS*,15*aS*)-4-((*tert*-butyldimethylsilyl)oxy)-4,4*a*,5,6,9,14,15,15*a*-octahydro-8*H*-5,14*b*-epoxy-pyrano[4'',3'':4',5']azepino[1',2':1,2]pyrido[3,4-*b*]indole-1-carboxylate)



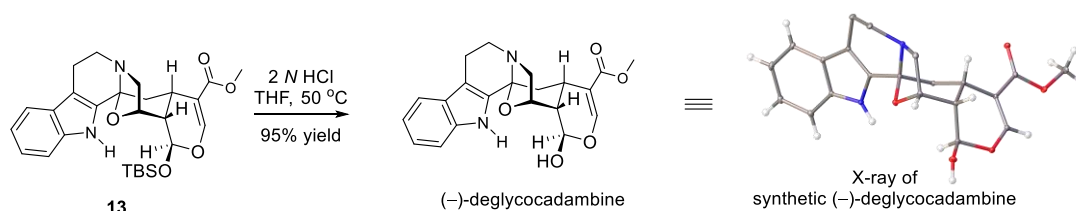
To a stirred solution of alcohol **12** (500.0 mg, 1.0 mmol) in a mixed solvent of saturated aqueous solution of  $\text{NaHCO}_3$  (2.5 mL) and  $\text{CHCl}_3$  (5 mL) was added  $\text{I}_2$  (275.0 mg, 1.1 mmol, 1.1 equiv). The resulting mixture was stirred at room temperature for 3h and then quenched by slow addition of saturated aqueous solution of  $\text{Na}_2\text{S}_2\text{O}_3$  (5 mL). Water (5 mL) and  $\text{CH}_2\text{Cl}_2$  (5 mL) were added and the organic phase was separated. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 5$  mL). The combined extracts were washed with brine (15 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with n-hexane/AcOEt/ $\text{NEt}_3$  ( $V/V/V = 80:20:1$ ) to afford the hexacyclic compound **13** (300.0 mg, 0.6 mmol, 61% yield) as a white foam.

**13**:  $R_f = 0.30$  (silica, petroleum ether/AcOEt = 4/1),  $[\alpha]_D^{25} = -86.7$  ( $c$  0.24,  $\text{CH}_2\text{Cl}_2$ ).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.97$  (s, 1H), 7.57–7.50 (m, 2H), 7.35 (d,  $J = 8.1$  Hz, 1H), 7.20 (t,  $J = 7.6$  Hz, 1H), 7.12 (t,  $J = 7.4$  Hz, 1H), 5.55 (d,  $J = 8.8$  Hz, 1H), 4.85 (d,  $J = 7.1$  Hz, 1H), 3.65 (s, 3H), 3.47 (d,  $J = 10.2$  Hz, 1H), 3.35–3.18 (m, 2H), 3.02 (dd,  $J = 10.2, 7.1$  Hz, 1H), 2.89–2.72 (m, 3H), 2.15 (dd,  $J = 13.2, 5.9$  Hz, 1H), 1.84–1.72 (m, 1H), 1.69–1.61 (m, 1H), 0.98 (s, 9H), 0.25 ppm (s, 6H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 167.4, 153.3, 136.6, 132.6, 126.0, 122.6, 119.7, 119.1, 112.0, 111.2, 109.8, 94.4, 90.9, 73.4, 59.0, 52.1, 51.2, 43.6, 42.4, 25.8, 25.7, 21.9, 18.0, -4.2, -5.1$  ppm. **IR**:  $\bar{\nu} = 3680, 2925, 2859, 1678, 1624, 1166, 1151, 833$   $\text{cm}^{-1}$ . **HRMS** (ESI):  $m/z$  calcd for  $\text{C}_{27}\text{H}_{37}\text{N}_2\text{O}_5\text{Si}$  [ $M + \text{H}$ ]<sup>+</sup>: 497.2466; found: 497.2470.

#### 5. (-)-Deglycocadambine

((-)-methyl

(4*R*,4*aS*,5*S*,14*bS*,15*aS*)-4-hydroxy-4,4*a*,5,6,9,14,15,15*a*-octahydro-8*H*-5,14*b*-epoxy-pyrano[4'',3'':4',5']azepino[1',2':1,2]pyrido[3,4-*b*]indole-1-carboxylate)



To a stirred solution of the hexacyclic compound **13** (250 mg, 0.5 mmol) in THF (3 mL) was added 2 *N* HCl (1.5 mL). The resulting mixture was stirred at 50 °C overnight and then quenched by slow addition of saturated aqueous solution of  $\text{NaHCO}_3$  (3 mL). Water (5 mL) and AcOEt (5 mL) were added and the organic phase was separated. The aqueous layer was extracted with AcOEt ( $2 \times 5$  mL). The combined extracts were washed with brine

(10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with AcOEt/NEt<sub>3</sub> (*V/V* = 100:1) to afford deglycocadambine (181.5 mg, 0.48 mmol, 95% yield) as a white solid.

(-)-**Deglycocadambine**: *R*<sub>f</sub> = 0.60 (silica, AcOEt), [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -63.0 (*c* 0.10, CH<sub>3</sub>OH). mp 132–133 °C. <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>OD):  $\delta$  = 7.55 (s, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.9 Hz, 1H), 5.65 (d, *J* = 9.1 Hz, 1H), 4.91–4.88 (m, 1H), 3.63 (s, 3H), 3.49 (d, *J* = 11.3 Hz, 1H), 3.24 (t, *J* = 6.0 Hz, 1H), 3.17–3.12 (m, 1H), 3.00 (dd, *J* = 10.7, 7.2 Hz, 1H), 2.84–2.75 (m, 3H), 2.07–2.00 (m, 1H), 1.66–1.61 ppm (m, 1H). It should be noted that 3 protons including N–H and O–H are missing. <sup>13</sup>C NMR (150 MHz, CD<sub>3</sub>OD):  $\delta$  = 169.1, 155.1, 138.4, 133.5, 126.9, 123.1, 120.0, 119.6, 112.4, 111.2, 110.7, 95.3, 92.7, 74.8, 59.5, 53.6, 51.6, 43.2, 42.6, 27.0, 22.7 ppm. IR:  $\bar{\nu}$  = 3674, 2924, 2859, 1696, 1456, 1260, 1166, 753 cm<sup>-1</sup>. HRMS (ESI): *m/z* calcd for C<sub>21</sub>H<sub>23</sub>N<sub>2</sub>O<sub>5</sub> [*M* + H]<sup>+</sup>: 383.1601; found: 383.1605.

## 6. Comparison of NMR Spectral Data of (-)-Deglycocadambine

Qin-Shi Zhao *et al.* first reported the isolation of deglycocadambine from the twigs and leaves of *Emmenopterys henryi* in 2013 (Wu, X.-D.; Wang, L.; He, J.; Li, X.-Y.; Dong, L.-B.; Gong, X.; Gao, X.; Song, L.-D.; Li, Y.; Peng, L.-Y. and Zhao, Q.-S. *Helvetica Chimica Acta*, 2013, 96, 2207–2213) and its absolute configuration was determined on the basis of extensive spectroscopic analyses, including 1D- and 2D-NMR experiments, and single-crystal X-ray diffraction studies.

<sup>1</sup>H and <sup>13</sup>C NMR spectral data of our synthetic deglycocadambine are in accord with those from Zhao's lab. Below is the comparison of <sup>1</sup>H and <sup>13</sup>C NMR spectral data from these two labs.

Comparison of <sup>1</sup>H NMR Spectral Data of Deglycocadambine

NMR Region $\delta$ (ppm)	Zhao's lab <sup>1</sup> H NMR (400 MHz, CD <sub>3</sub> OD) $\delta$ (ppm) <sup>a</sup>	Our lab <sup>1</sup> H NMR (600 MHz, CD <sub>3</sub> OD) $\delta$ (ppm)
8.0–6.0		7.55 (s, 1H)
	7.49 (d, <i>J</i> = 7.6 Hz, 1H)	7.46 (d, <i>J</i> = 7.9 Hz, 1H)
	7.34 (d, <i>J</i> = 7.6 Hz, 1H)	7.32 (d, <i>J</i> = 8.2 Hz, 1H)
	7.13 (t, <i>J</i> = 7.6 Hz, 1H)	7.10 (t, <i>J</i> = 7.6 Hz, 1H)
	7.02 (t, <i>J</i> = 7.6 Hz, 1H)	7.00 (t, <i>J</i> = 7.9 Hz, 1H)
6.0–4.0	5.67 (d, <i>J</i> = 9.1 Hz, 1H)	5.65 (d, <i>J</i> = 9.1 Hz, 1H)
	4.90–4.95 (m, 1H)	4.88–4.91 (m, 1H)
4.0–2.5	3.66 (s, 3H)	3.63 (s, 3H)
	3.52 (d, <i>J</i> = 10.7 Hz, 1H)	3.49 (d, <i>J</i> = 11.3 Hz, 1H)
	3.26 (t, <i>J</i> = 5.8 Hz, 1H)	3.24 (t, <i>J</i> = 6.0 Hz, 1H)
	3.14–3.19 (m, 1H)	3.12–3.17 (m, 1H)
	3.03 (dd, <i>J</i> = 10.7, 7.3 Hz, 1H)	3.00 (dd, <i>J</i> = 10.7, 7.2 Hz, 1H)
	2.80–2.84 (m, 1H) 2.79–2.85 (m, 2H)	2.75–2.84 (m, 3H)
2.5–1.0	2.02–2.07 (m)	2.00–2.07 (m, 1H)
	1.63–1.69 (m, 1H)	1.61–1.66 (m, 1H)

<sup>a</sup> For the reference, see: Wu, X.-D.; Wang, L.; He, J.; Li, X.-Y.; Dong, L.-B.; Gong, X.; Gao, X.; Song, L.-D.; Li, Y.; Peng, L.-Y. and Zhao, Q.-S. *Helvetica Chimica Acta*, **2013**, 96, 2207–2213

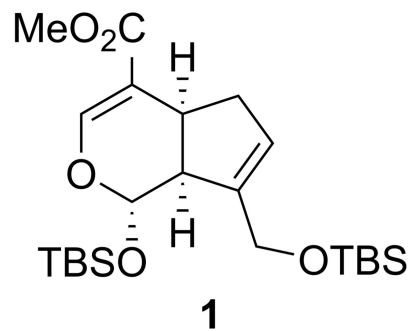
### Comparison of <sup>13</sup>C NMR Spectral Data of Deglycocadambine

Zhao's lab <sup>13</sup> C NMR (100 MHz, CD <sub>3</sub> OD) $\delta$ (ppm) <sup>a</sup>	Our lab <sup>13</sup> C NMR (150 MHz, CD <sub>3</sub> OD) $\delta$ (ppm)	$\Delta\delta$ (ppm)
169.5	169.1	0.4
155.6	155.1	0.5
138.9	138.4	0.5
133.9	133.5	0.4
127.3	126.9	0.4
123.6	123.1	0.5
120.4	120.0	0.4
120.1	119.6	0.5
112.8	112.4	0.4
111.6	111.2	0.4
111.2	110.7	0.5
95.7	95.3	0.4
93.1	92.7	0.4
75.2	74.8	0.4
59.9	59.5	0.4
54.0	53.6	0.4
52.0	51.6	0.4
43.0	42.8	0.2
43.0	42.6	0.4
27.4	27.0	0.4
23.1	22.7	0.4

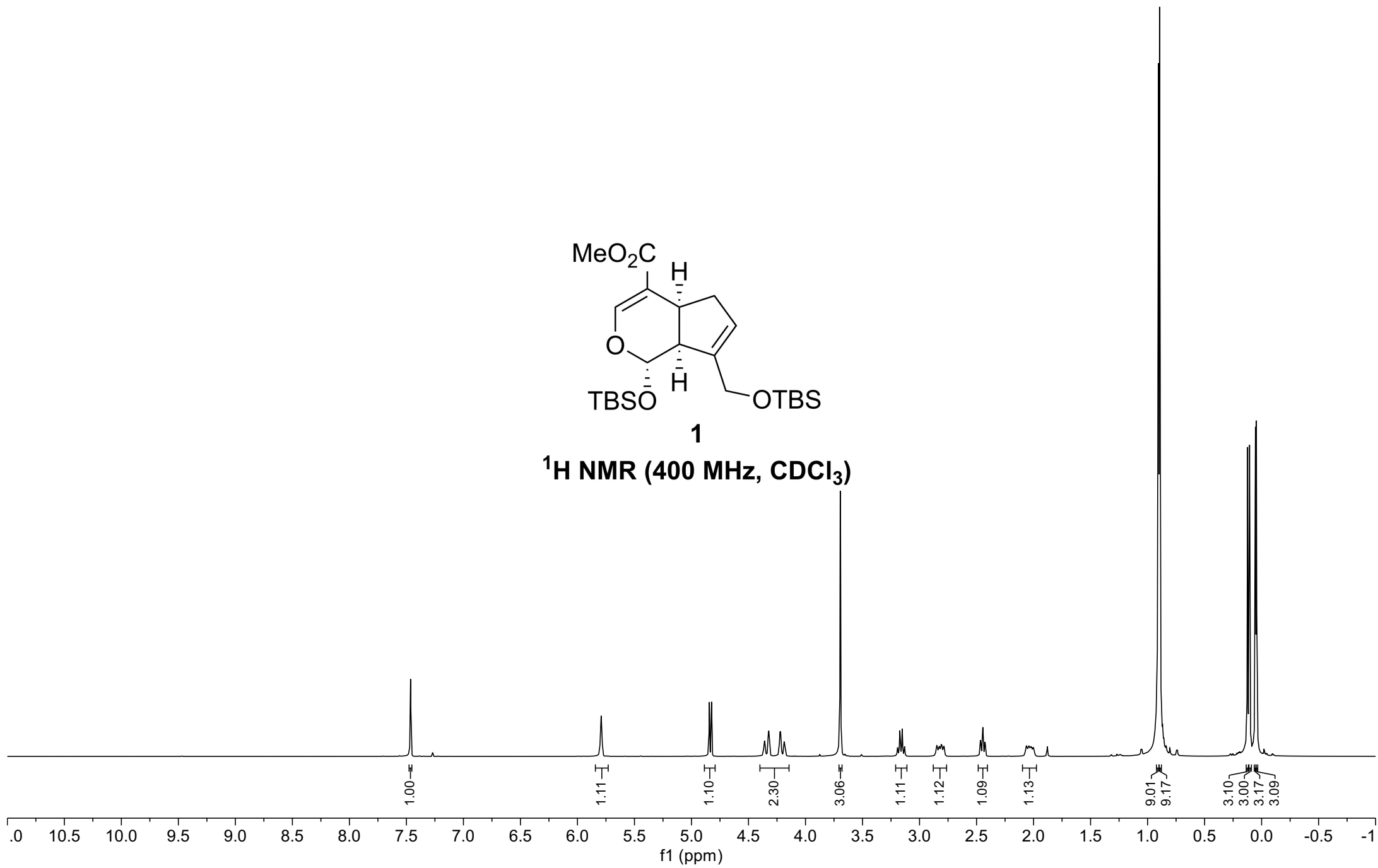
<sup>a</sup> For the reference, see: Wu, X.-D.; Wang, L.; He, J.; Li, X.-Y.; Dong, L.-B.; Gong, X.; Gao, X.; Song, L.-D.; Li, Y.; Peng, L.-Y. and Zhao, Q.-S. *Helvetica Chimica Acta*, **2013**, 96, 2207–2213.

## 7. Copies of NMR Spectra

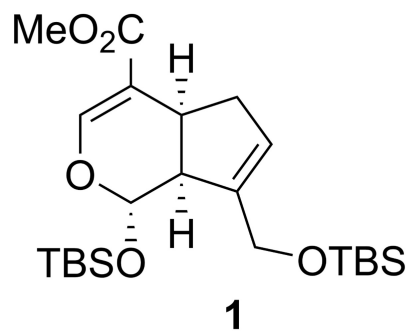
See the next page.



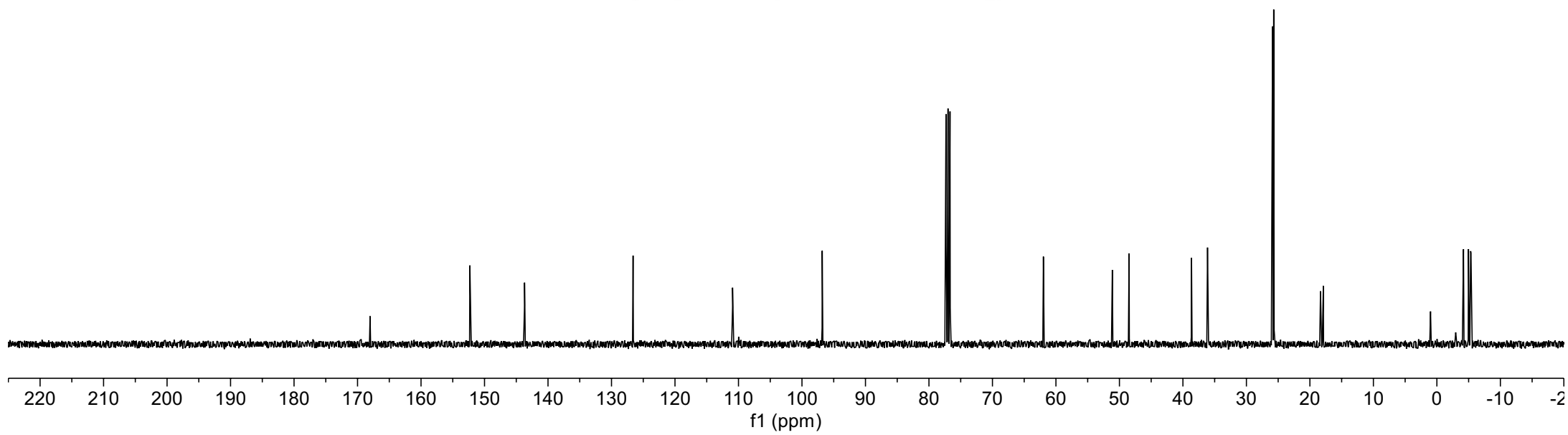
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



— 168.02 — 152.31 — 143.69 — 126.60 — 110.93 — 96.81 — 77.32 — 77.00 — 76.68 — 61.98 — 51.12 — 48.48 — 38.65 — 36.12 — 25.88 — 25.70 — 18.33 — 17.89 — 1.00 — 4.19 — 4.98 — 5.32 — 5.37



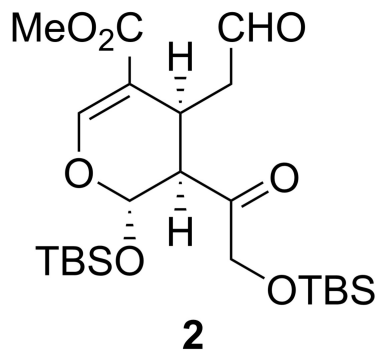
**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )**



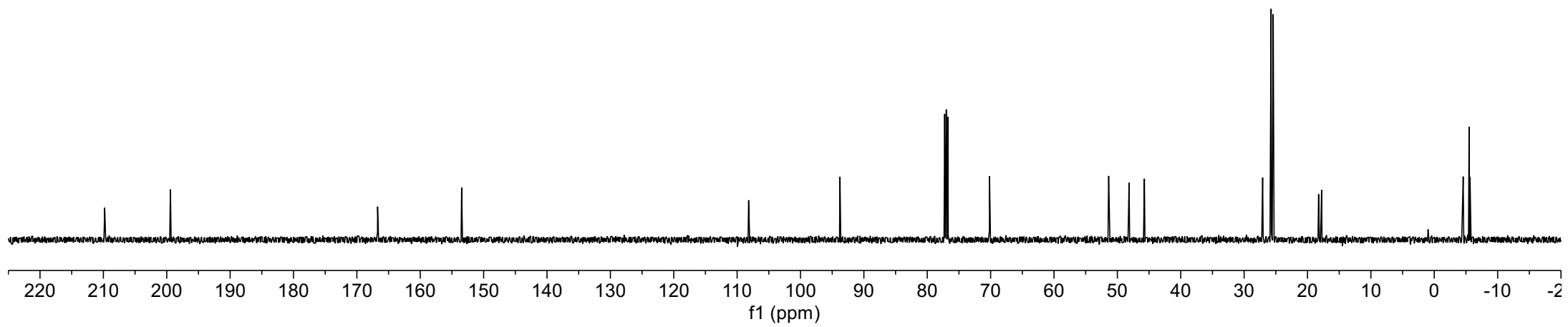


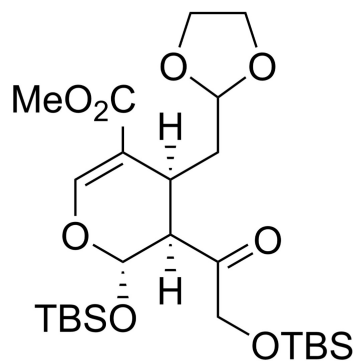


—209.79    —199.42    —166.73    —153.47    —108.18    —93.77    77.25  
77.00    76.75    —70.17    —51.38    —48.15    —45.74    27.08  
25.74    25.41    18.25    17.78    —4.57    —5.50    —5.64



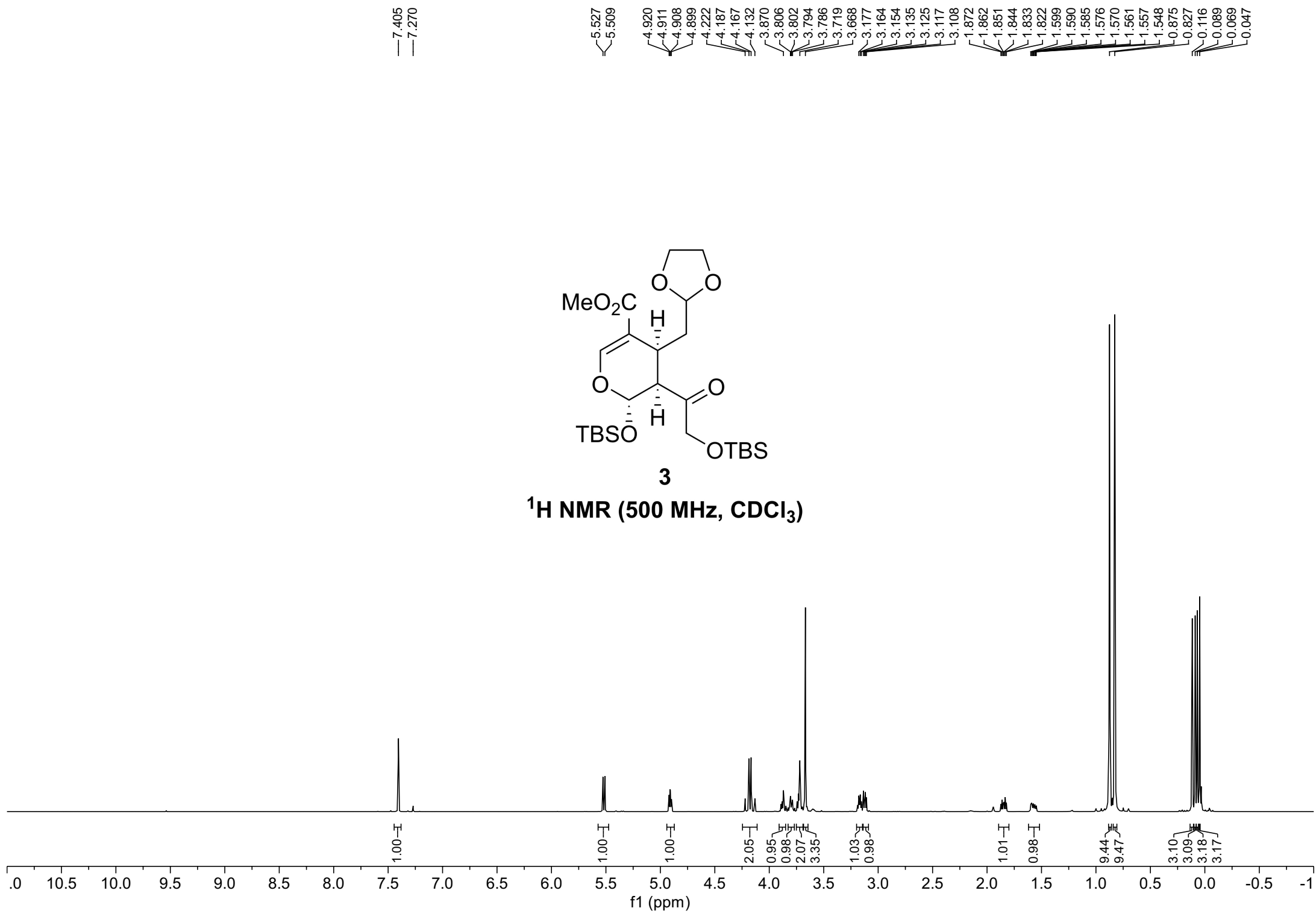
$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )





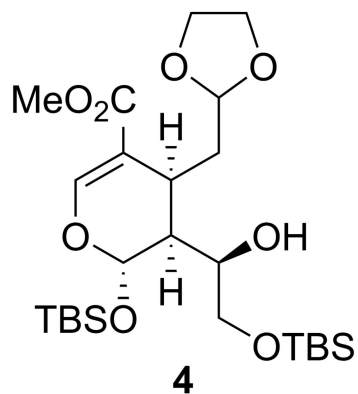
3

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

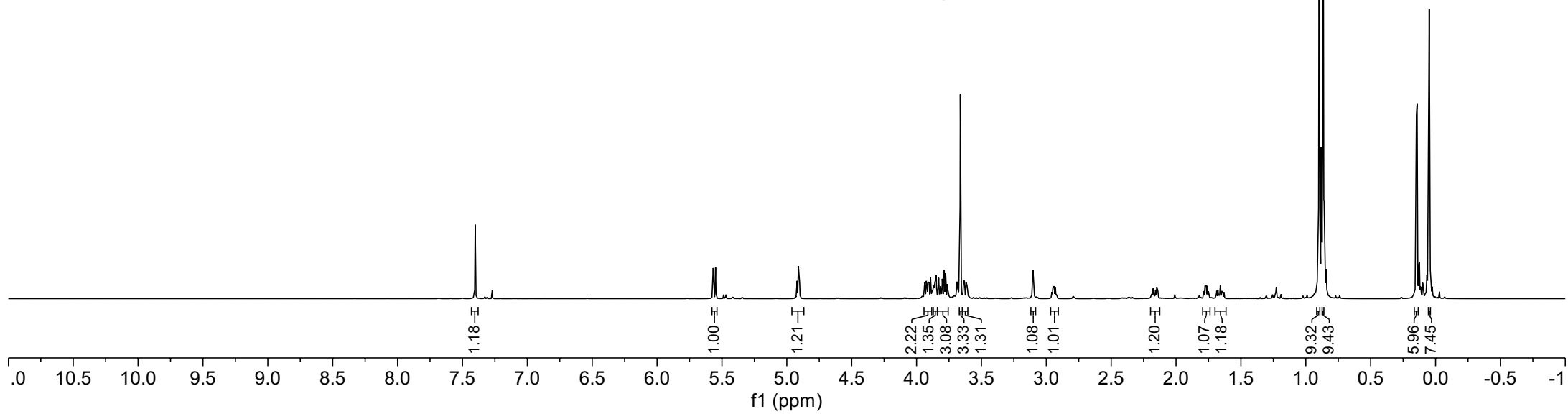




7.402  
7.270  
5.567  
5.549  
4.921  
4.911  
4.901  
3.937  
3.925  
3.918  
3.913  
3.906  
3.903  
3.892  
3.879  
3.868  
3.861  
3.848  
3.829  
3.821  
3.815  
3.812  
3.802  
3.791  
3.787  
3.776  
3.763  
3.753  
3.691  
3.688  
3.682  
3.663  
3.637  
3.631  
3.618  
3.612  
3.103  
2.957  
2.949  
2.940  
2.931  
2.922  
2.186  
2.177  
2.169  
2.158  
2.148  
2.140  
1.785  
1.777  
1.768  
1.759  
1.750  
1.687  
1.677  
1.668  
1.658  
1.649  
1.640  
1.630  
0.898  
0.866  
0.148  
0.142  
0.055  
0.049



**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**



—167.44

—152.50

—110.49

—103.37

—95.71

77.26

77.00

76.75

72.06

65.74

64.81

64.38

—51.05

—42.91

—36.46

—30.41

25.81

25.61

18.18

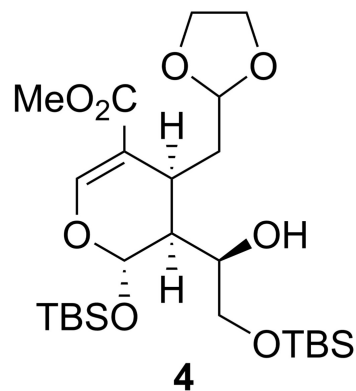
17.81

—4.43

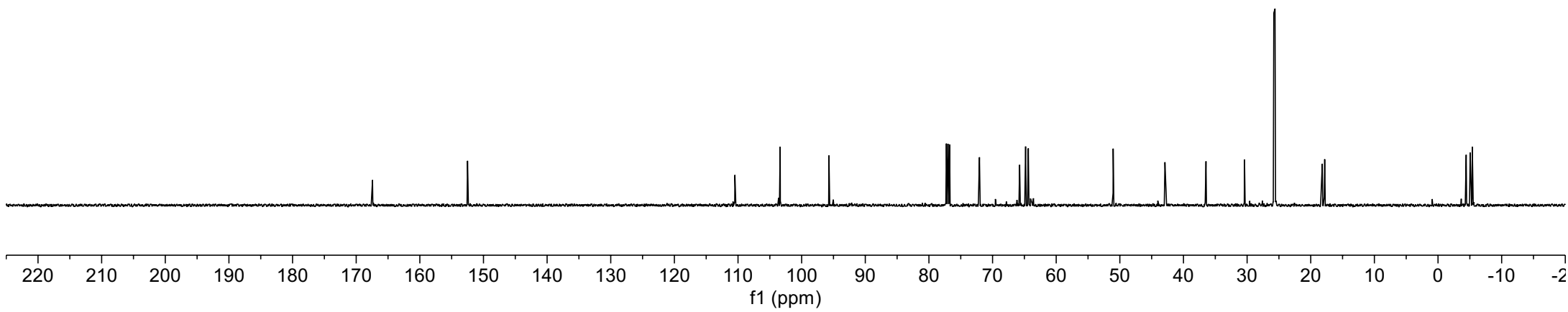
—5.06

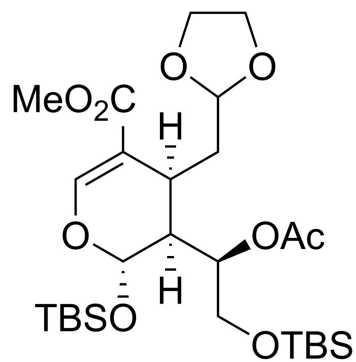
—5.39

—5.47



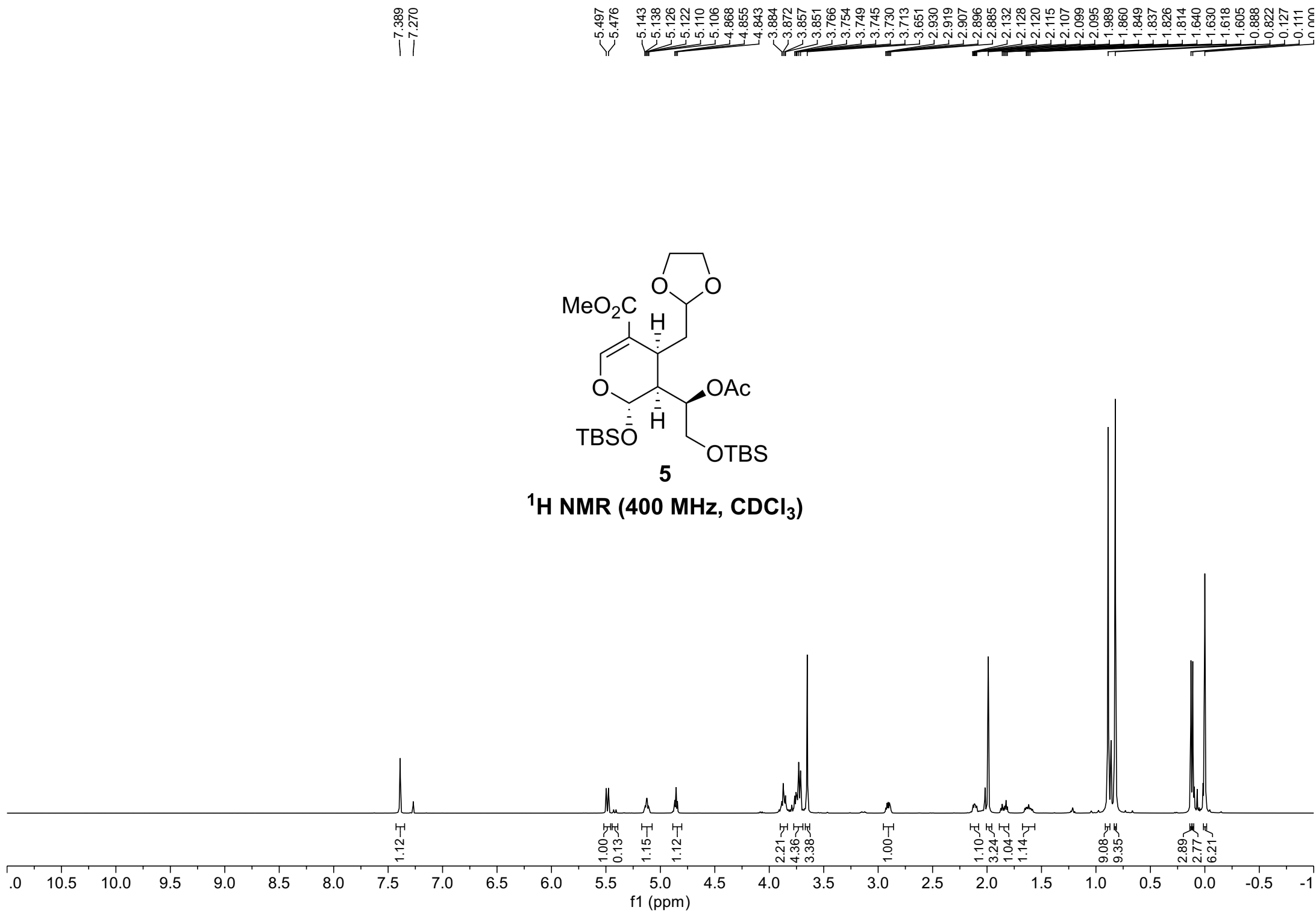
$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )



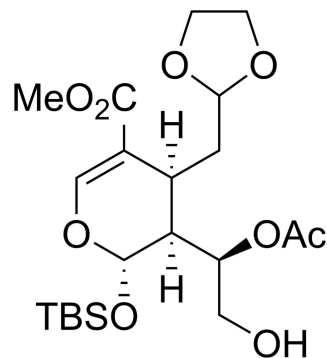


**5**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

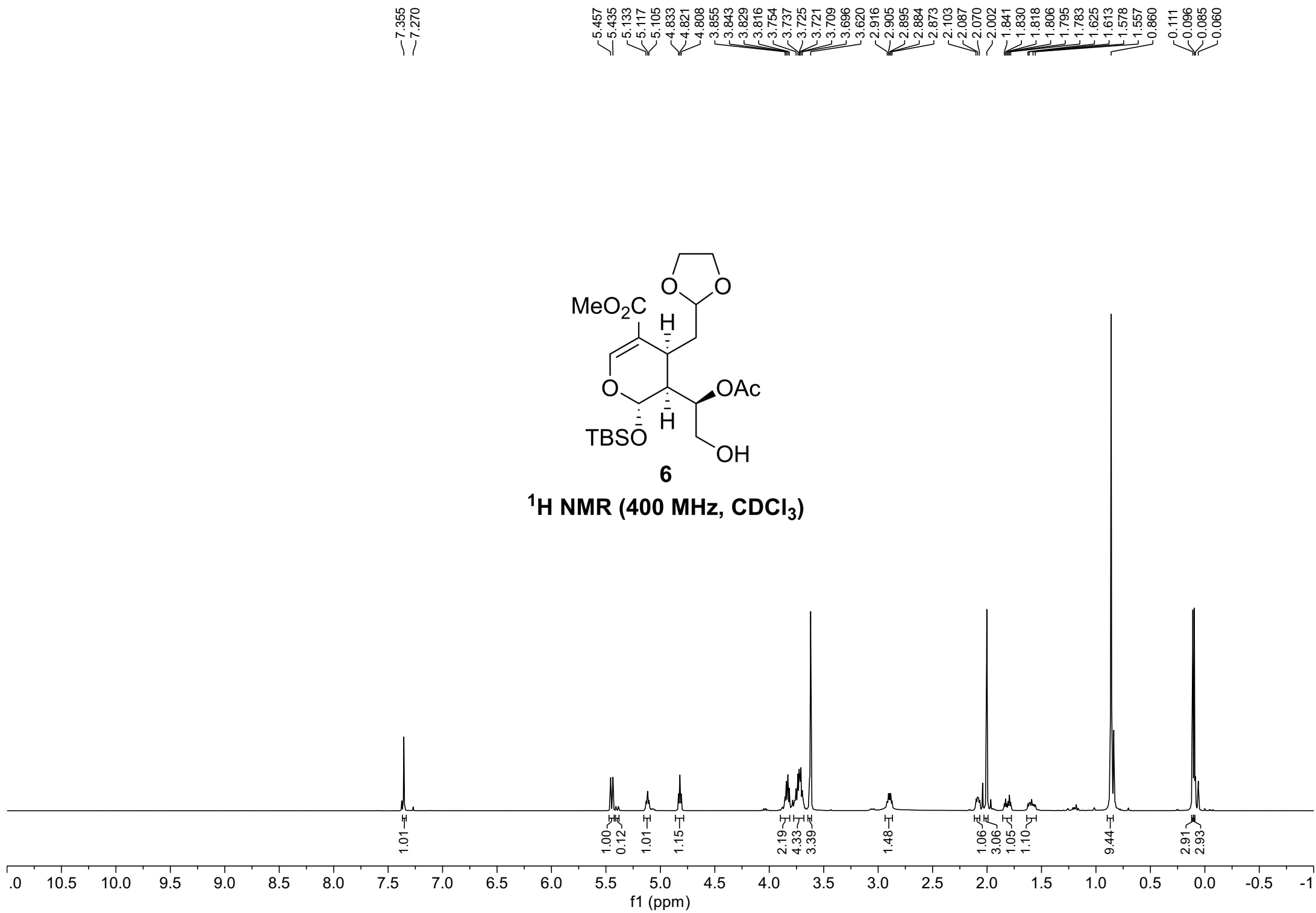






**6**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**





—170.65  
—167.25

—152.35

—109.78

—102.97

—94.36

77.32  
77.00  
76.68  
75.25

64.72  
64.37  
64.16

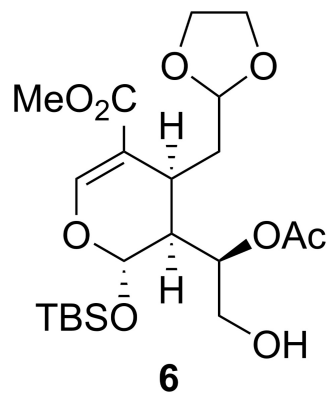
—51.05

—41.50

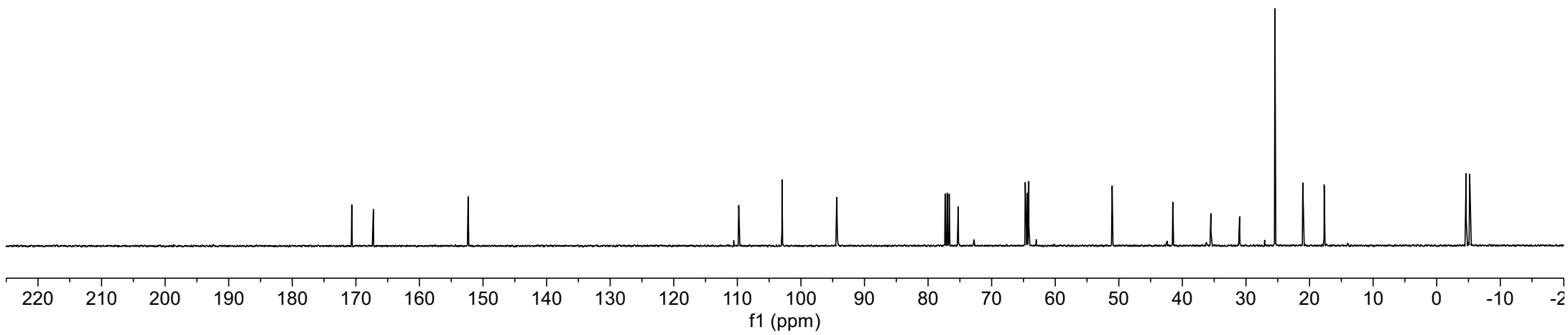
—35.52

25.44  
21.06  
17.70

-4.63  
-5.19



<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)







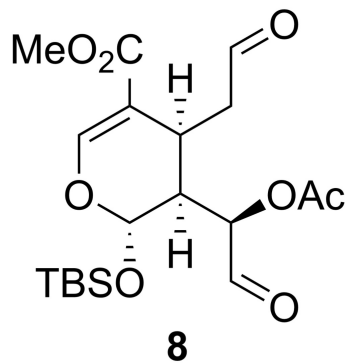
9.661  
9.657  
9.653  
9.326

7.475  
7.270

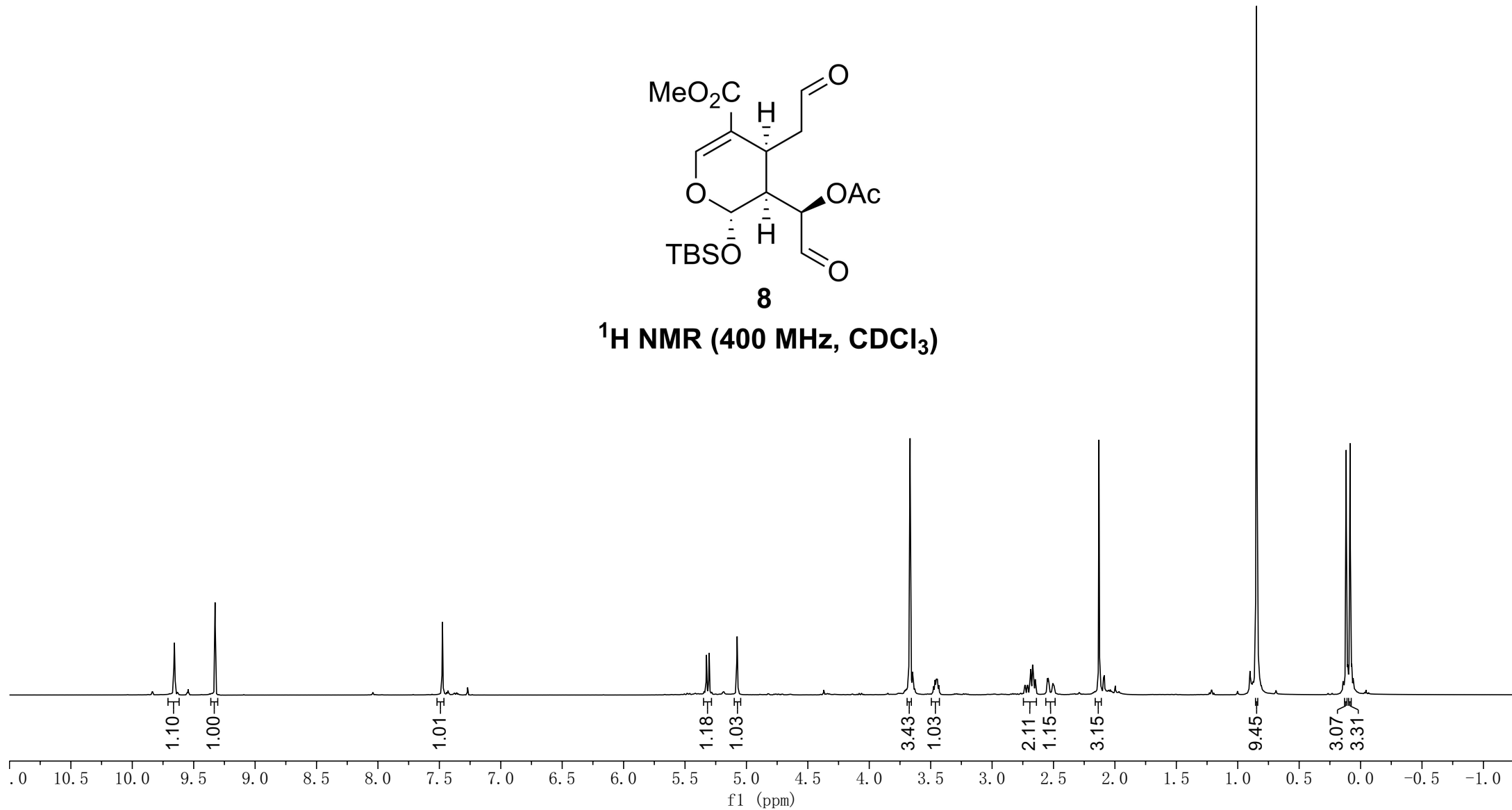
5.325  
5.303  
5.076  
3.668  
3.476  
3.464  
3.454  
2.734  
2.730  
2.714  
2.710  
2.685  
2.670  
2.663  
2.649  
2.553  
2.510  
2.505  
2.500  
2.130

0.847

0.117  
0.085



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



—199.82  
—196.60

—169.65  
—166.53

—153.52

—108.10

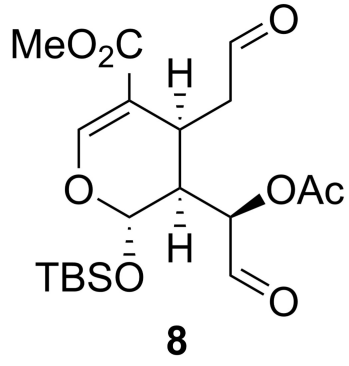
—92.78

77.36  
77.32  
77.00  
76.68

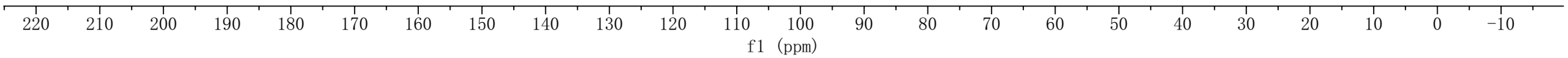
~51.37  
~46.28  
~43.21

~29.52  
—25.37  
~20.44  
~17.71

—4.85

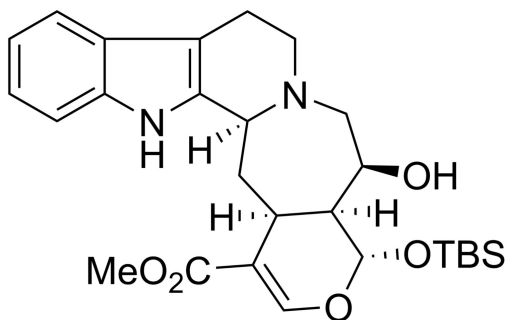


<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)



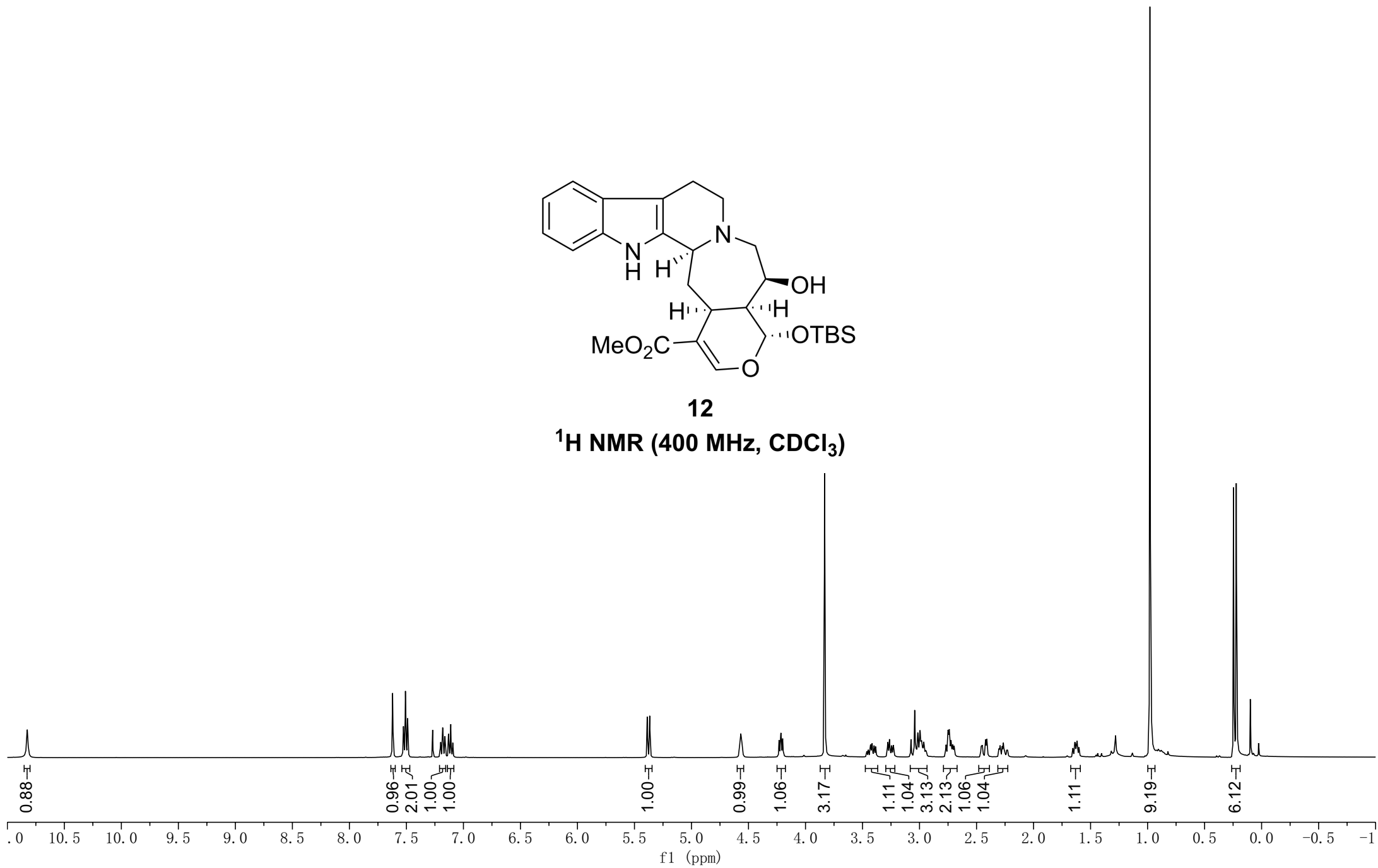






**12**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**





— 169.28

— 154.99

~ 136.28

~ 132.69

~ 127.52

~ 121.14

~ 119.00

~ 117.73

~ 111.66

~ 108.25

~ 108.08

— 95.26

~ 77.32

~ 77.00

~ 76.68

— 64.79

~ 57.83

~ 54.07

~ 51.64

~ 49.73

~ 46.45

~ 31.47

~ 29.13

~ 25.63

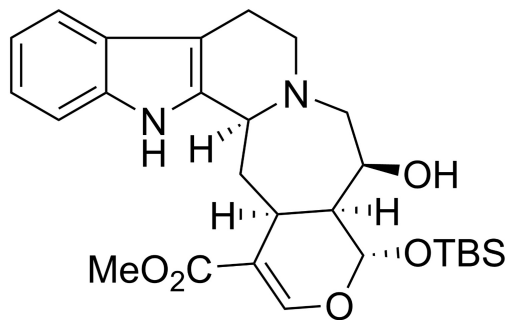
~ 18.47

~ 17.95

— 1.00

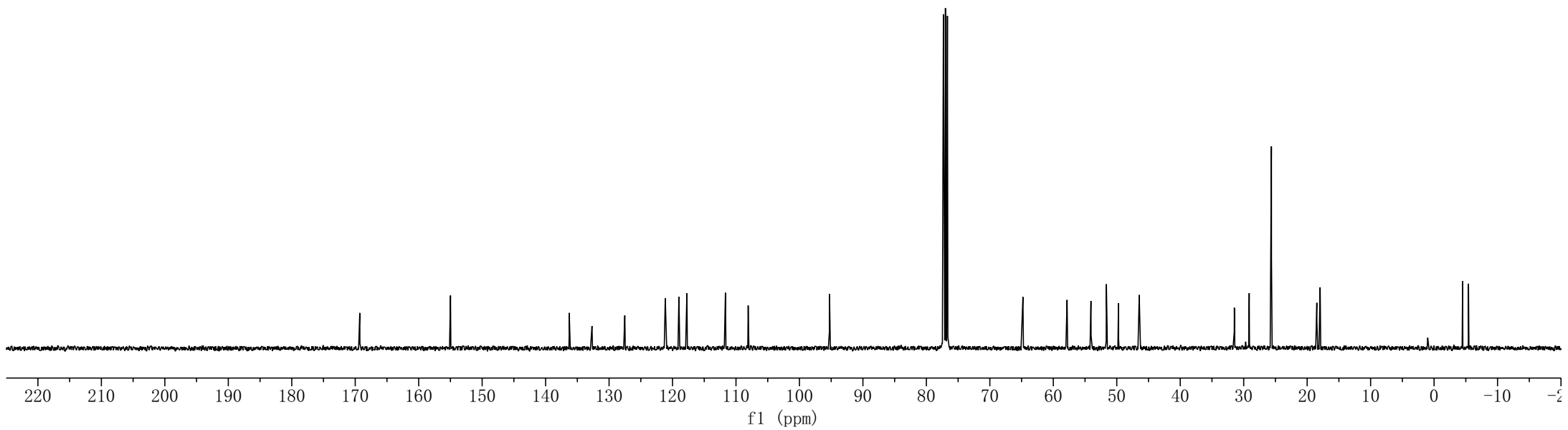
~ 4.49

~ 5.42

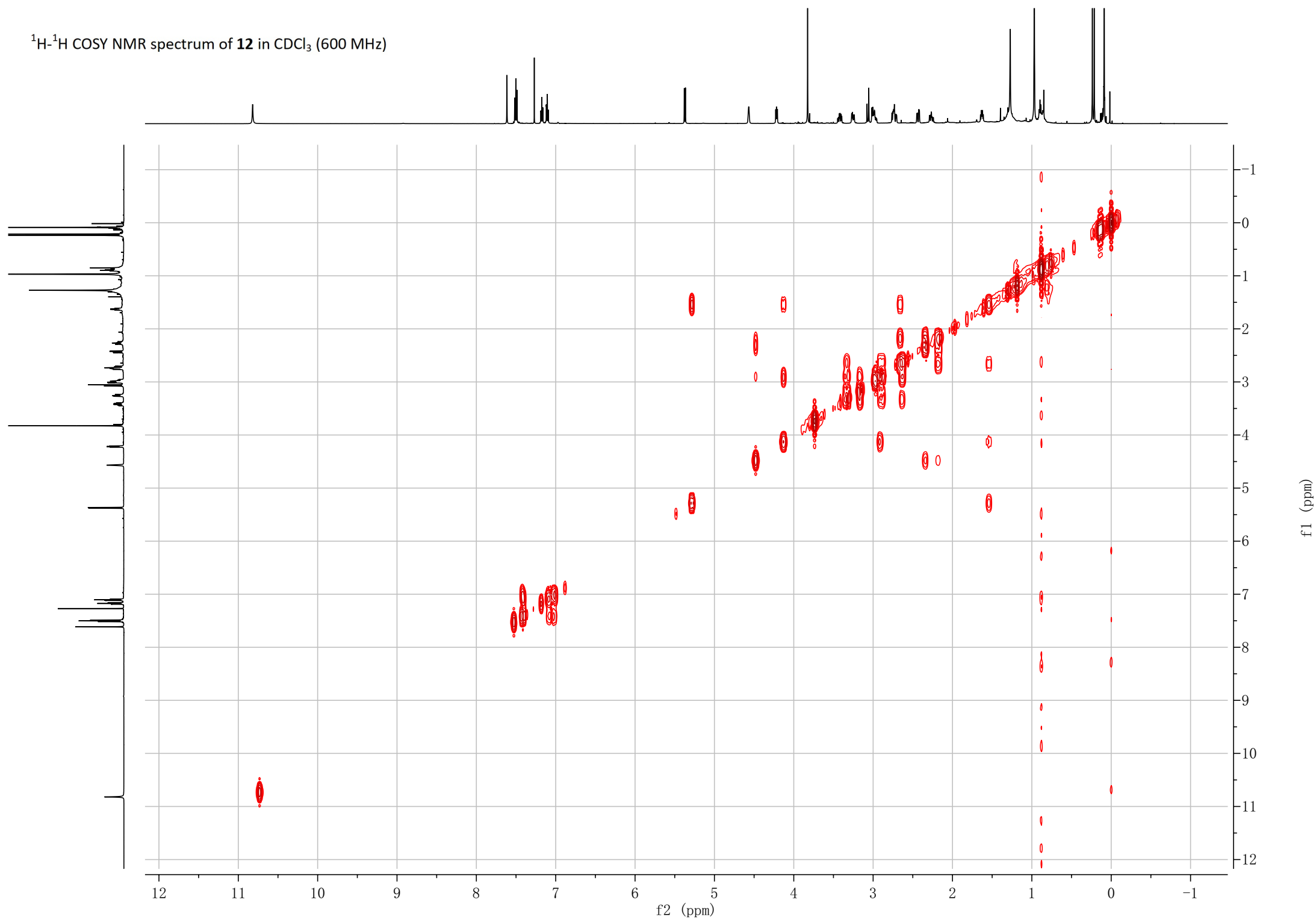


**12**

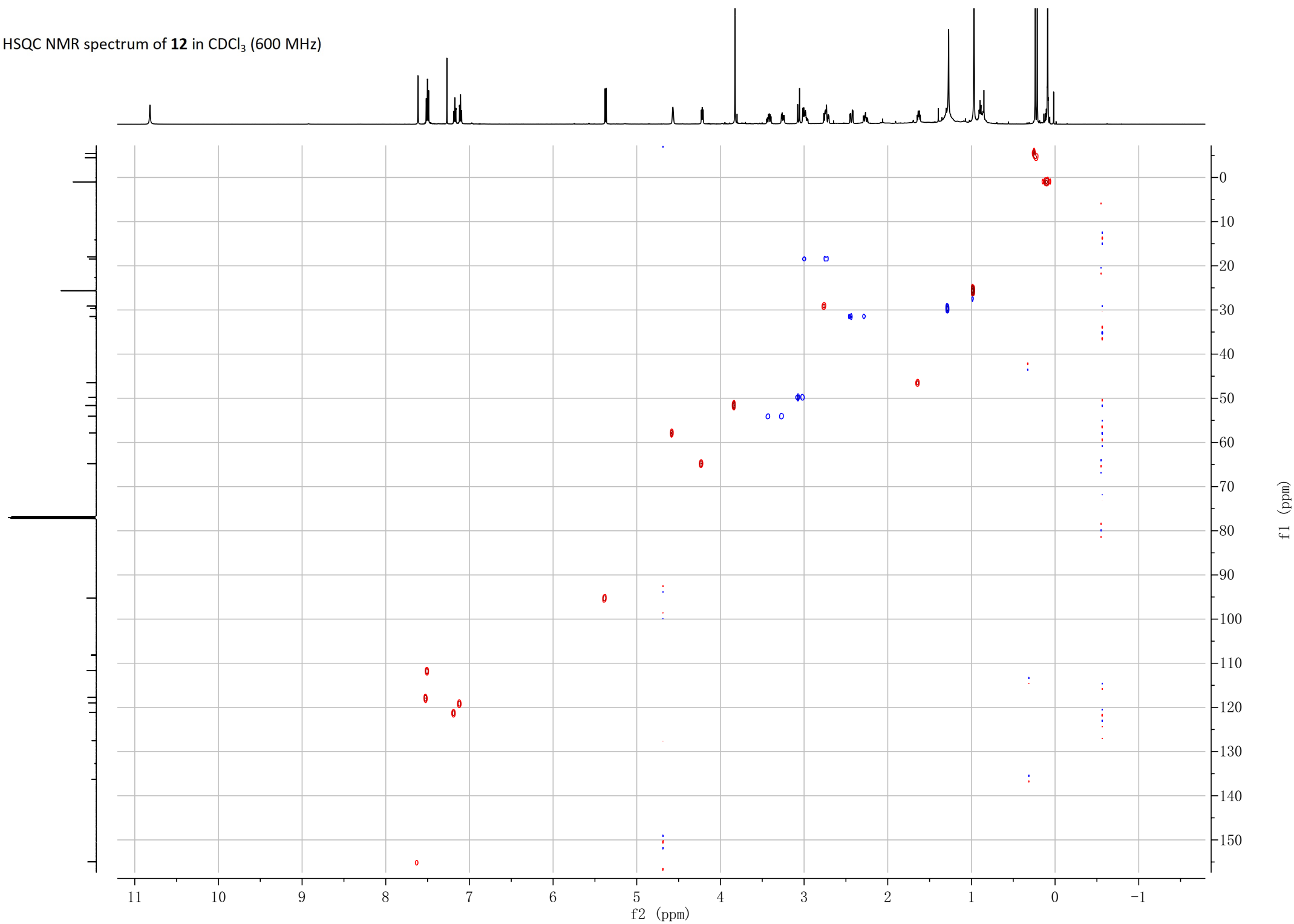
**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)**



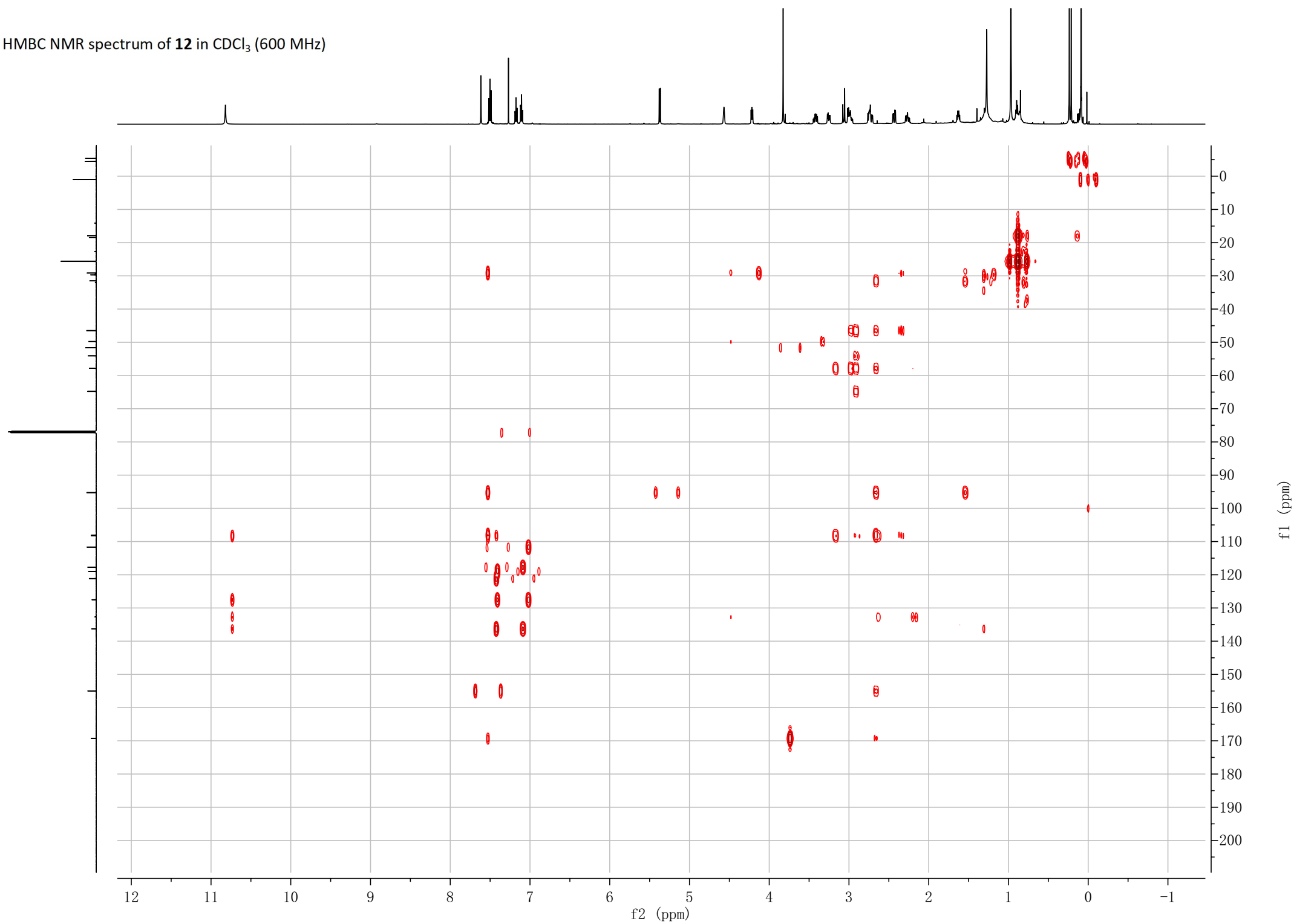
$^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of **12** in  $\text{CDCl}_3$  (600 MHz)



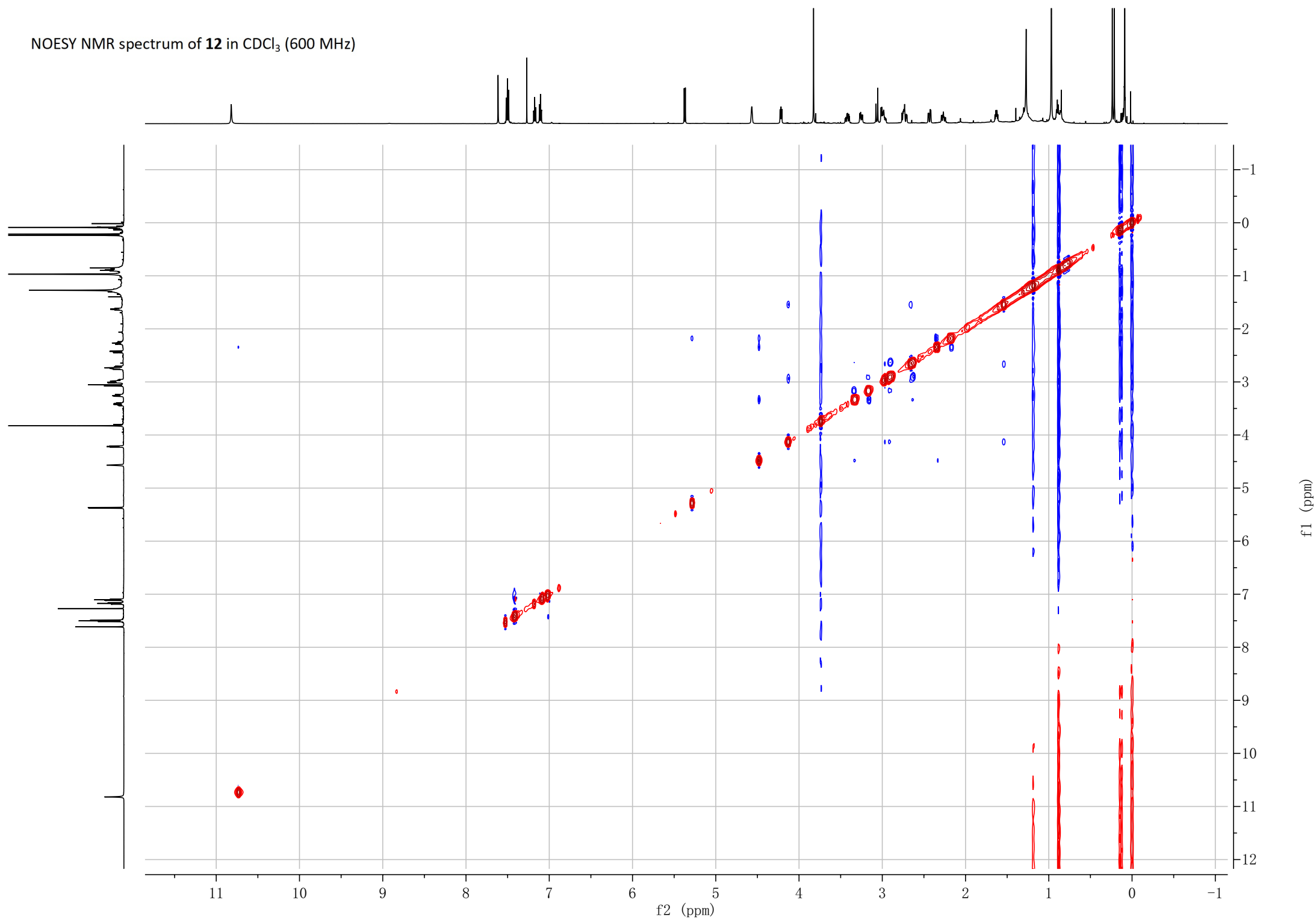
HSQC NMR spectrum of **12** in CDCl<sub>3</sub> (600 MHz)



HMBC NMR spectrum of **12** in CDCl<sub>3</sub> (600 MHz)



NOESY NMR spectrum of **12** in CDCl<sub>3</sub> (600 MHz)



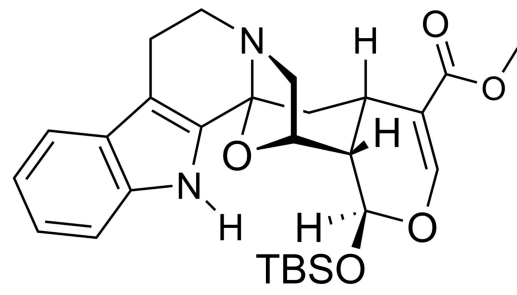
7.972  
7.554  
7.534  
7.527  
7.362  
7.341  
7.270  
7.218  
7.200  
7.182  
7.141  
7.121  
7.104

5.565  
5.543

4.857  
4.840

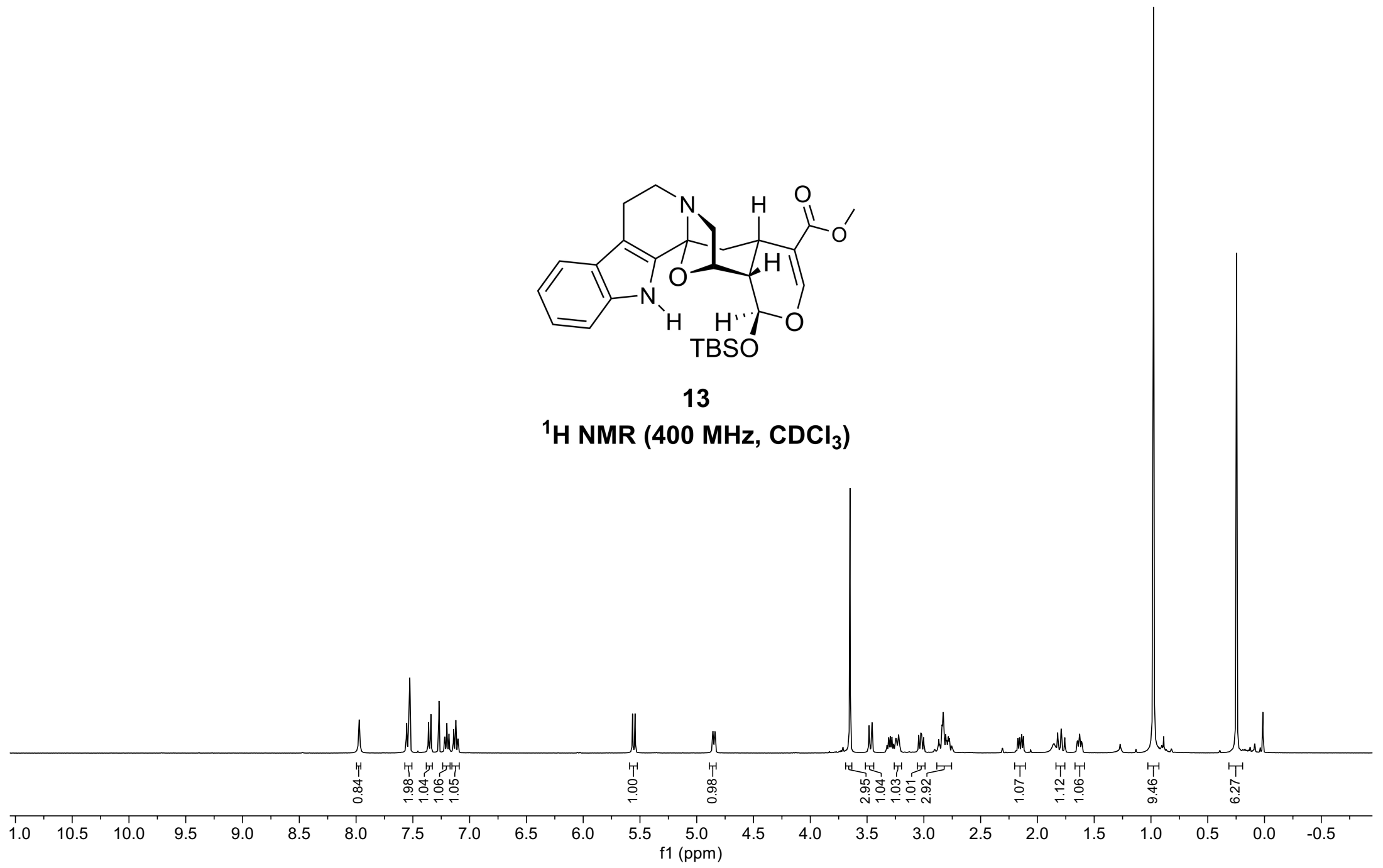
3.651  
3.482  
3.457  
3.267  
3.244  
3.222  
3.045  
3.027  
3.019  
3.002  
2.869  
2.830  
2.807  
2.775  
2.747  
2.747  
2.172  
2.157  
2.138  
2.124  
1.821  
1.791  
1.759  
1.648  
1.628  
1.608

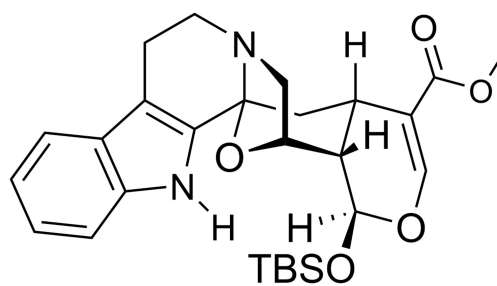
0.978  
0.246  
0.014



13

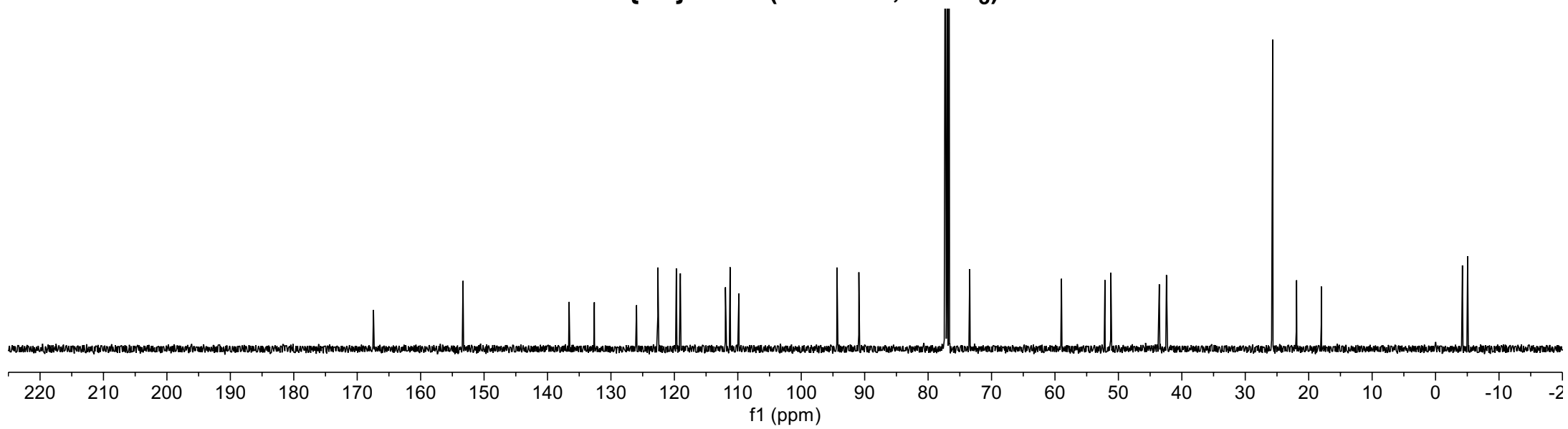
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)





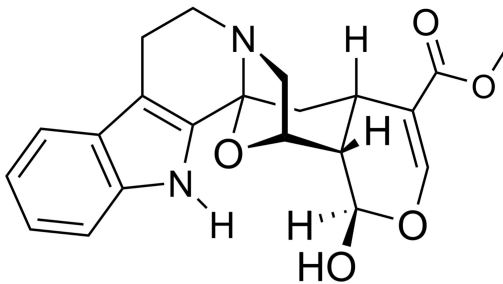
13

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

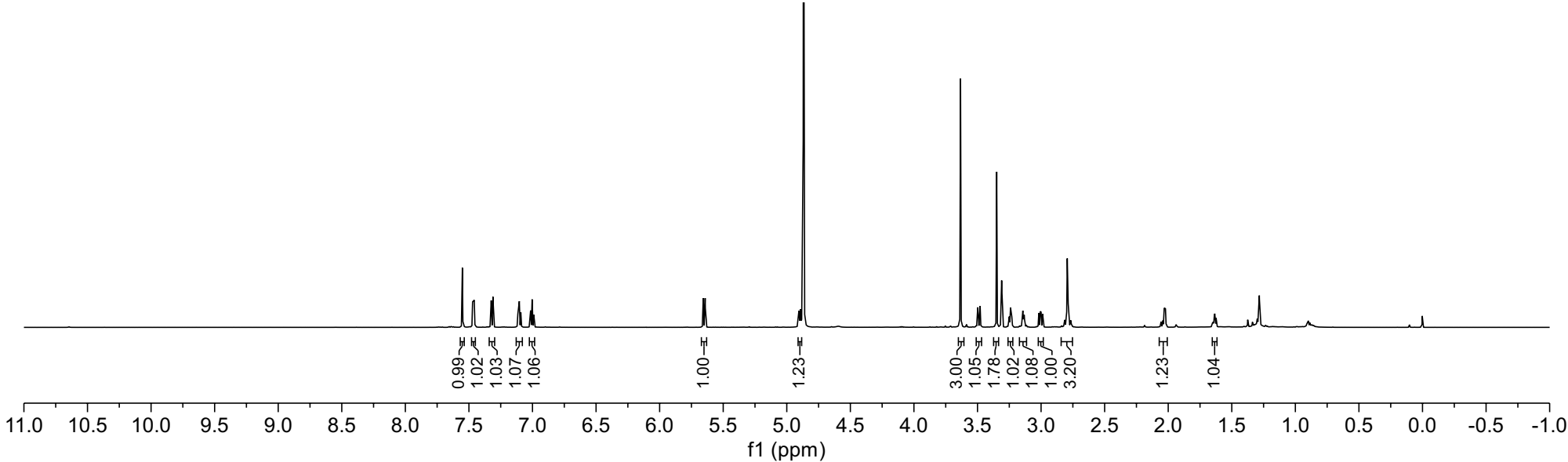


7.552  
7.471  
7.458  
7.325  
7.311  
7.117  
7.103  
7.092  
7.016  
7.003  
6.990

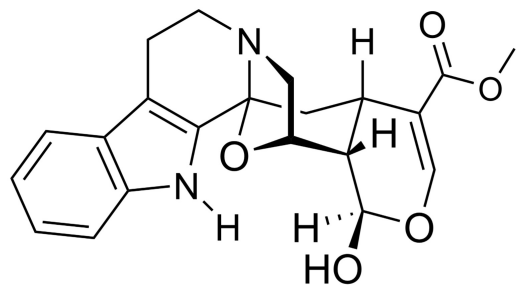
5.657  
5.642  
4.905  
4.892  
3.633  
3.498  
3.479  
3.315  
3.313  
3.310  
3.307  
3.305  
3.250  
3.240  
3.230  
3.167  
3.160  
3.149  
3.143  
3.137  
3.132  
3.116  
3.018  
3.006  
3.000  
2.988  
2.814  
2.794  
2.791  
2.766  
2.070  
2.056  
2.041  
2.031  
2.022  
2.009  
1.648  
1.645  
1.638  
1.634  
1.630  
1.623  
1.620  
1.283  
0.002



(-)-deglycocadambine  
**<sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>OD)**







(-)-deglycocadambine  
<sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CD<sub>3</sub>OD)

