

# Supporting Information

## Asymmetric Total Syntheses of Five Pyrrole-Type *Stemona* Alkaloids

Xiaodong Wang,<sup>a,‡</sup> Tao Shi,<sup>a,‡</sup> Gaofeng Yin,<sup>a</sup> Yuqing Wang,<sup>a</sup> Zhao Li<sup>a</sup> and Zhen Wang<sup>a,b\*</sup>

<sup>[a]</sup>*School of Pharmacy, Lanzhou University, No. 199 West Donggang Road, Lanzhou 730000, Gansu, China.*

<sup>[b]</sup>*School of Pharmaceutical Science, University of South China, Hengyang 421001, Hunan, China.*

<sup>‡</sup>*These authors contributed equally to this work.*

*Corresponding authors: zhenw@lzu.edu.cn*

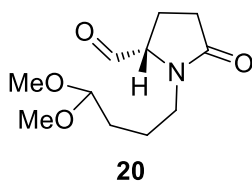
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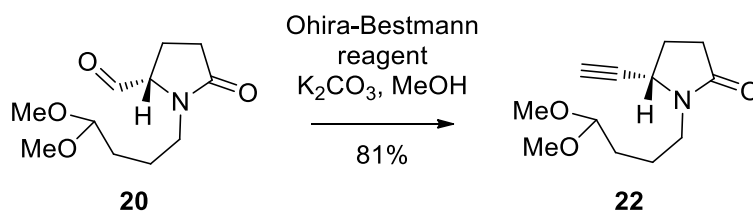
## I. General Information

All reactions were carried out in a dry solvent under argon atmosphere, and all reagents were obtained from commercial suppliers and used without further purification, unless otherwise noted. All solvents were processed through the reference Purification of Laboratory Chemicals (Seventh Edition). External bath temperatures were used to record all reaction temperatures. Silica gel (300~400 mesh) and petroleum ether, EtOAc, CH<sub>2</sub>Cl<sub>2</sub> and MeOH were used for product purification by flash column chromatography. NMR spectra were recorded on Bruker 300 MHz, 400 MHz or 600 MHz spectrometers. Proton chemical shifts are reported relative to internal standard TMS at  $\delta$  0.0 ppm or residual solvent peak (CDCl<sub>3</sub> at 7.26 ppm, methanol-*d*<sub>4</sub> at 3.31 ppm). Carbon chemical shifts are reported relative to a residual solvent peak (CDCl<sub>3</sub> at 77.06 ppm, methanol-*d*<sub>4</sub> at 49.03 ppm). The following abbreviations were used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad. Fourier transform infrared spectra (FT-) were recorded on an Agilent Cary 630 FT-IR instrument. LC-MS spectra were recorded on an Agilent Technologies 1260II-MSD 6125 Quotation with an Agilent HC-C18(2) column (4.6 mm x 250 mm, film: 5  $\mu$ m). High-resolution mass spectra (HRMS) were measured on a Bruker Daltonics Apex II 47e Specification (for HRMS).

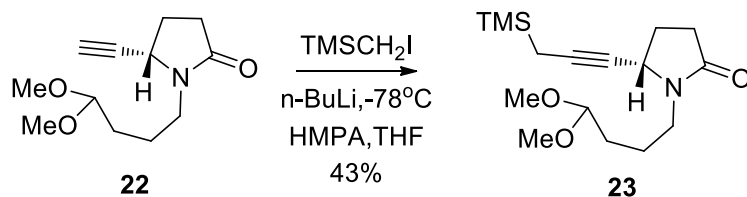
## II. Experimental Section and Characterization Data for Synthesized Compounds



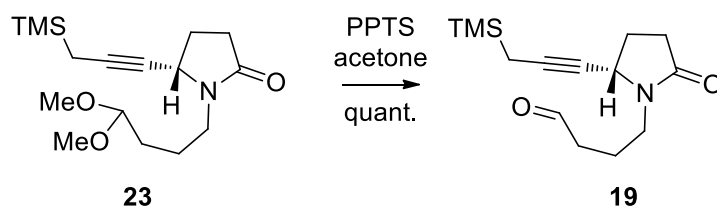
Compound **20** was prepared using our previous reported procedure <sup>[1]</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.56 (d, *J* = 2.6 Hz, 1H), 4.31 (t, *J* = 4.9 Hz, 1H), 4.11 (ddd, *J* = 9.3, 4.0, 2.7 Hz, 1H), 3.62 (dt, *J* = 14.2, 7.0 Hz, 1H), 3.27 (s, 6H), 3.08 – 2.98 (m, 1H), 2.46 – 2.32 (m, 2H), 2.30 – 2.18 (m, 1H), 2.17 – 1.94 (m, 2H), 1.54 (dd, *J* = 10.6, 4.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 198.99, 175.45, 104.37, 65.49, 53.35, 53.32, 42.05, 30.02, 29.53, 22.69, 19.57.



Compound **22**: To a stirred solution of compound **20** (4.5 g, 19.7 mmol) dissolved in 130ml anhydrous MeOH, Ohira-Bestmann reagent (4.5 g, 23.4 mmol) and K<sub>2</sub>CO<sub>3</sub> (6.8 g, 49.3 mmol) was added. After stirred at room temperature for 2 h, the solvent was removed under reduced pressure, and the residue was diluted with 50 ml of water, and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×50 ml). The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EA) to give compound **22** (3.6 g, 81% yield) as a pale yellow oil. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = -27.5 (*c* 0.4 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.38 – 4.30 (m, 2H), 3.69 – 3.58 (m, 1H), 3.30 (d, *J* = 1.1 Hz, 6H), 3.16 – 3.07 (m, 1H), 2.54 – 2.44 (m, 1H), 2.39 (d, *J* = 2.2 Hz, 1H), 2.38 – 2.27 (m, 2H), 2.16 – 2.02 (m, 1H), 1.69 – 1.51 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.1, 104.2, 81.4, 73.3, 53.0, 53.0, 48.8, 40.1, 29.9, 29.9, 26.2, 22.2. IR (KBr,  $\nu$  / cm<sup>-1</sup>) 3479, 3226, 2953, 2836, 2111, 1683, 1457, 1418, 1254, 1129, 1051, 833. LC-MS (ESI, *m/z*) [M + Na]<sup>+</sup> calcd C<sub>12</sub>H<sub>19</sub>NNaO<sub>3</sub><sup>+</sup> 248.1257, found 248.1.

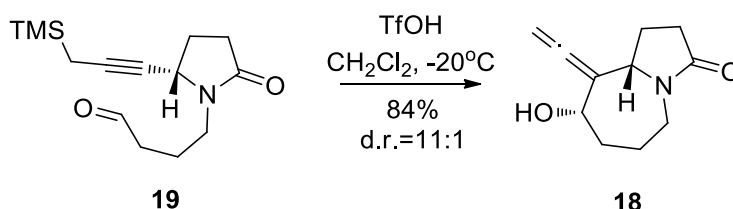


Compound **23**: To a stirred solution of compound **22** (1.2 g, 5.3 mmol) and HMPA (1.8 g, 10 mmol) dissolved in 40 mL anhydrous THF at  $-60^\circ\text{C}$ , *n*-BuLi (2.4 M in hexane, 2.5 mL, 6 mmol) was slowly added and the mixture was stirred for 45 min. Then TMSCH<sub>2</sub>I (1.4 g, 6.5 mmol) was added and the mixture was stirred at the same temperature for 2 h and quenched with saturated aqueous solution of NH<sub>4</sub>Cl (15 mL). Warmed to room temperature and diluted with 20 ml of water, the organic phase of the mixture was separated and the water phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×30 ml). The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EA) to give compound **23** (710 mg, 43% yield) as a yellow oil.  $[\alpha]_D^{20} = -5.0$  (*c* 0.2 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 4.37 (t, *J* = 5.3 Hz, 1H), 4.34 – 4.30 (m, 1H), 3.68 – 3.62 (m, 1H), 3.31 (s, 3H), 3.31 (s, 3H), 3.11 – 3.06 (m, 1H), 2.50 – 2.41 (m, 1H), 2.36 – 2.26 (m, 2H), 2.03 – 1.96 (m, 1H), 1.58 (dd, *J* = 12.2, 6.5 Hz, 4H), 1.47 (d, *J* = 2.2 Hz, 2H), 0.09 (s, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 174.2, 104.2, 83.8, 76.4, 53.0, 52.9, 49.5, 40.3, 30.2, 29.9, 27.1, 22.3, 7.0, -2.1. IR (KBr,  $\nu / \text{cm}^{-1}$ ) 2954, 2830, 2227, 1698, 1440, 1416, 1250, 1129, 1071, 853. LC-MS (ESI, *m/z*) [M + Na]<sup>+</sup> cacl C<sub>16</sub>H<sub>29</sub>NNaO<sub>3</sub> Si<sup>+</sup> 334.1809, found 334.1.

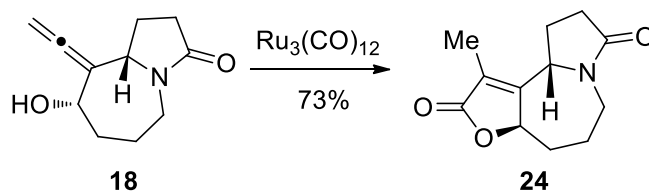


Compound **19**: Compound **23** (1.5 g, 4.8 mmol) and PPTS (2.4 g, 9.6 mmol) was dissolved in 50 ml wet acetone (with 0.5 mL of H<sub>2</sub>O added) and the mixture was heated to 50 °C for 5 h. Then the mixture was allowed to be cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EA) to give compound **19** (1.28 g, quant.) as a yellow oil.  $[\alpha]_D^{20} = -40.0$  (*c* 0.1 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.76 (s, 1H), 4.32 (dd, *J* = 7.1, 5.1 Hz, 1H), 3.64 – 3.54 (m, 1H),

3.22 – 3.13 (m, 1H), 2.52 – 2.38 (m, 3H), 2.36 – 2.25 (m, 2H), 2.03 – 1.95 (m, 1H), 1.86 (tt,  $J = 13.9, 7.1$  Hz, 2H), 1.46 (d,  $J = 2.2$  Hz, 2H), 0.08 (s, 9H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  201.72, 174.82, 84.30, 76.45, 49.93, 41.60, 40.40, 30.33, 27.41, 20.05, 7.20, -1.83. IR (KBr,  $\nu / \text{cm}^{-1}$ ) 2935, 2956, 2363, 1720, 1687, 1416, 1250, 1202, 852. LC-MS (ESI,  $m/z$ )  $[\text{M} + \text{H}]^+$  cacl  $\text{C}_{14}\text{H}_{24}\text{NO}_2\text{Si}^+$  266.1571, found 266.1.

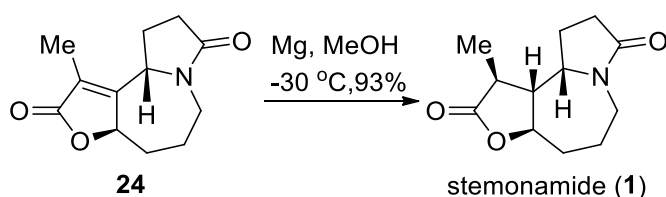


**Compound 18:** To a solution of compound **19** (500 mg, 1.9 mmol) in 40 mL  $\text{CH}_2\text{Cl}_2$  stirred at  $-20^\circ\text{C}$ ,  $\text{CF}_3\text{SO}_3\text{H}$  (570 mg in 6 mL  $\text{CH}_2\text{Cl}_2$ , 3.8 mmol) was added dropwise. The mixture was stirred at this temperature for 2 h and then quenched with aqueous solution of  $\text{Na}_2\text{CO}_3$  (5 mL). The organic phase was separated and the water phase was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL). The combined organic phases were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent:  $\text{CH}_2\text{Cl}_2$ : MeOH = 20: 1) to give compound **18** <sup>[2]</sup> (305 mg, 84% yield).  $[\alpha]_D^{20} = -130.0$  ( $c$  0.1 in  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.08 – 4.98 (m, 2H), 4.44 (td,  $J = 5.0, 2.5$  Hz, 1H), 4.20 (dd,  $J = 7.7, 6.5$  Hz, 1H), 3.78 – 3.68 (m, 1H), 3.13 (dd,  $J = 13.8, 8.7$  Hz, 1H), 2.54 – 2.43 (m, 1H), 2.42 – 2.31 (m, 1H), 2.18 (dtdd,  $J = 12.8, 9.8, 7.7, 5.9$  Hz, 2H), 2.02 – 1.81 (m, 3H), 1.78 (d,  $J = 5.2$  Hz, 1H), 1.66 (ddd,  $J = 7.1, 5.8, 2.3$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  203.95, 174.66, 108.68, 80.42, 71.94, 58.41, 42.73, 36.95, 30.60, 25.50, 22.22. IR (KBr,  $\nu / \text{cm}^{-1}$ ) 3371, 3366, 2926, 1664, 1459, 1418, 1105, 954. HRMS (ESI,  $m/z$ )  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{11}\text{H}_{16}\text{NO}_2$  194.1176, found 194.1181.

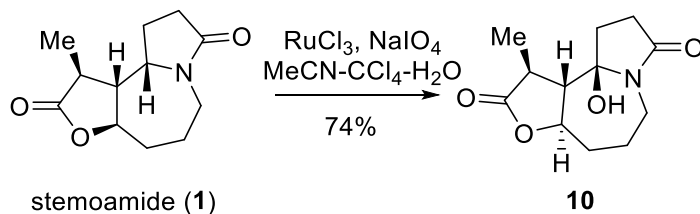


**Compound 24:** The mixture of compound **18** (300 mg, 1.6 mmol),  $\text{Ru}_3(\text{CO})_{12}$  (320 mg, 0.5 mmol) and 2,4,6-collidine (20 mL) was stirred and heated to  $100^\circ\text{C}$  for 2 h under CO atmosphere (1 atm). Then the mixture was cooled to room temperature and poured onto a silica

gel and chromatographed (eluent: PE: EA = 5: 1 to CH<sub>2</sub>Cl<sub>2</sub>: MeOH = 20: 1) to afford compound **24** (250 mg, 73% yield) as a white solid.  $[\alpha]_D^{21} = -256.0$  (*c* 1 in CHCl<sub>3</sub>) [Lit.  $[\alpha]_D^{24} = -246.3$  (*c* 0.33, MeOH)<sup>3a</sup>,  $[\alpha]_D^{27} = -261.14$  (*c* 0.33, MeOH)<sup>3b</sup>] <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.84 (ddt, *J* = 11.7, 3.8, 1.9 Hz, 1H), 4.71 (t, *J* = 7.9 Hz, 1H), 4.27 – 4.16 (m, 1H), 2.55 – 2.33 (m, 5H), 1.88 – 1.78 (m, 4H), 1.78 – 1.56 (m, 2H), 1.28 (tdd, *J* = 13.3, 11.5, 3.6 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.2, 173.3, 164.9, 123.6, 81.3, 57.5, 43.4, 34.7, 30.1, 25.6, 25.5, 8.9.

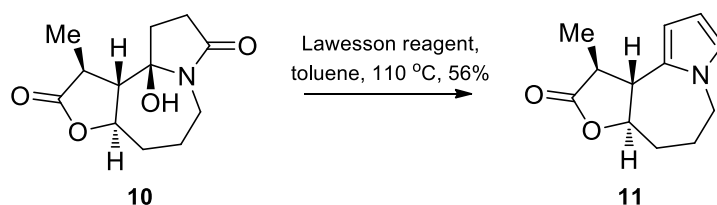


Stemoamide (**1**): To a stirred solution of compound **24** (500 mg, 2.3 mmol) dissolved in anhydrous MeOH (25 mL), Mg ribbon chips (550 mg, 23 mmol) was added and the mixture was stirred at -30 °C for 3 h. Then the mixture was filtered and the filtrate was adjusted to pH = 7 with 1M HCl. Then the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (5×20 mL). The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>: MeOH = 20: 1) to give stemoamide (**1**) (470 mg, 93% yield).  $[\alpha]_D^{21} = -162.0$  (*c* 0.5 in CHCl<sub>3</sub>) [lit.  $[\alpha]_D^{26} = -181$  (*c* 0.89, MeOH)<sup>4a</sup>,  $[\alpha]_D^{20} = -141$  (*c* 0.3, MeOH)<sup>4b</sup>] <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.26 – 4.07 (m, 2H), 3.98 (dt, *J* = 10.7, 6.4 Hz, 1H), 2.71 – 2.52 (m, 2H), 2.44-2.36 (m, 4H), 2.13 – 1.95 (m, 1H), 1.87 – 1.81 (m, 1H), 1.77 – 1.64 (m, 1H), 1.58 – 1.44 (m, 2H), 1.28 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 177.5, 174.0, 77.7, 55.8, 52.7, 40.2, 37.3, 34.8, 30.6, 25.6, 22.6, 14.1.

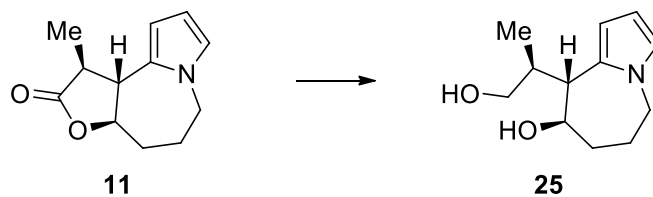


Compound **10**: Stemoamide (**1**) (292 mg, 1.3 mmol), NaHCO<sub>3</sub> (1.65 g, 19.6 mmol) NaIO<sub>4</sub> (1.4 g, 6.5 mmol) RuCl<sub>3</sub> (83 mg, 0.4 mmol) was dissolved in CCl<sub>4</sub>/MeCN/H<sub>2</sub>O (20 mL: 20 mL: 30 mL) and stirred vigorously at room temperature. Another two portions of NaIO<sub>4</sub> (1.4 g, 6.5 mmol)

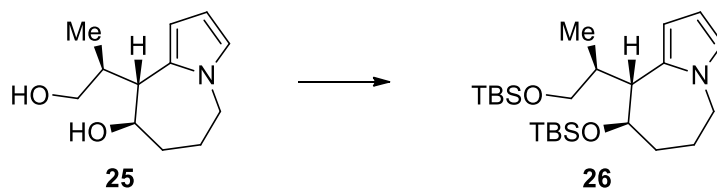
was added to the reaction every 0.5 h. Then the mixture was stirred for 2 h until quenched with aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (20 mL). The organic phase was separated and the water phase was extracted with CH<sub>2</sub>Cl<sub>2</sub>/MeOH (15: 1, 10×20 mL). The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub> : MeOH = 10 : 1) to give compound **10** (230 mg, 74%). <sup>1</sup>H NMR (400 MHz, Methanol-*d*<sub>4</sub>) δ 4.07 (td, *J* = 10.8, 2.8 Hz, 1H), 3.89 – 3.81 (m, 1H), 3.00 (t, *J* = 13.2 Hz, 1H), 2.88 (dq, *J* = 12.2, 7.0 Hz, 1H), 2.72 – 2.59 (m, 1H), 2.49 (dd, *J* = 11.9, 10.1 Hz, 1H), 2.38 – 2.19 (m, 3H), 2.02 – 1.93 (m, 1H), 1.87 – 1.76 (m, 1H), 1.70 – 1.55 (m, 1H), 1.55 – 1.42 (m, 1H), 1.33 (d, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Methanol-*d*<sub>4</sub>) δ 179.0, 175.5, 90.3, 78.2, 58.7, 37.3, 37.2, 34.3, 29.0, 28.1, 24.7, 14.1. LC-MS (ESI, *m/z*) [*M* + Na]<sup>+</sup> cacl C<sub>12</sub>H<sub>17</sub>NNaO<sub>4</sub><sup>+</sup> 262.1050, found 262.1.



Compound **11**: A Schlenk tube was charged with a mixture of compound **10** (316.0 mg, 1.32 mmol) and Lawesson's reagent (534 mg, 1.32 mmol, 1.0 equiv) in toluene (6.6 mL) under an argon atmosphere. The vial was sealed and stirred vigorously at 110 °C. After stirring for 2h, the reaction was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was directly subjected to column chromatography (eluent: PE: EA = 3: 1) on silica gel to give pure **11** as a colorless oil (151.5 mg, 56%). [ $\alpha$ ]<sub>D</sub><sup>24</sup> = -210.0 (*c* 0.1 in CHCl<sub>3</sub>) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.66 – 6.60 (m, 1H), 6.05 (t, *J* = 3.1 Hz, 1H), 5.99 – 5.94 (m, 1H), 4.12 (dd, *J* = 14.4, 5.2 Hz, 1H), 3.94 – 3.82 (m, 2H), 3.07 – 2.92 (m, 2H), 2.58 – 2.48 (m, 1H), 2.17 – 2.06 (m, 1H), 1.82 – 1.61 (m, 2H), 1.43 (d, *J* = 6.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 178.3, 128.6, 122.6, 106.5, 105.0, 81.6, 49.3, 49.1, 39.6, 34.1, 26.2, 13.8. IR (KBr,  $\nu$  / cm<sup>-1</sup>) 2937, 1774, 1489, 1454, 1323, 1221, 1202, 1169, 1146, 1013, 937, 723. LC-MS (ESI, *m/z*) [*M* + Na]<sup>+</sup> cacl C<sub>12</sub>H<sub>15</sub>NNaO<sub>2</sub><sup>+</sup> 228.0995, found 228.1.



Compound **25**: To a stirred solution of **11** (1 g, 4.9 mmol) in 50 mL THF at 0 °C, solid LiAlH<sub>4</sub> (280 mg, 7.4 mmol) was slowly added. Then the reaction was moved to room temperature. After stirring for 1 h, the reaction was quenched with 5 mL saturated aqueous Rochelle salt, stirred for another 20 min, diluted with 20 mL water, extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 × 30 mL). The resulting residue was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated under vacuum. The residue was purified by flash chromatography on silica gel (eluent: EA to CH<sub>2</sub>Cl<sub>2</sub>: MeOH= 15: 1) to give compound **25** (930 mg, 91% yield) as a colorless oil,  $[\alpha]_D^{21} = -68.0$  (*c* 0.5 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.51 (t, *J* = 2.2 Hz, 1H), 6.06 – 5.87 (m, 2H), 4.13 (t, *J* = 4.6 Hz, 1H), 4.01 – 3.83 (m, 2H), 3.74 – 3.57 (m, 2H), 2.92 (dd, *J* = 10.6, 5.6 Hz, 1H), 2.39 (s, 2H), 2.15 – 2.02 (m, 1H), 2.00 – 1.88 (m, 1H), 1.88 – 1.77 (m, 2H), 1.76 – 1.69 (m, 1H), 0.83 (d, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 129.6, 122.7, 112.5, 105.9, 68.3, 65.7, 48.9, 48.2, 35.8, 31.8, 22.9, 16.8. IR (KBr, ν / cm<sup>-1</sup>) 3357, 2928, 2876, 1659, 1489, 1456, 1357, 1303, 1210, 1079, 1019, 1000, 958, 759, 712. LC-MS (ESI, *m/z*) [M + Na]<sup>+</sup> calcd for C<sub>12</sub>H<sub>19</sub>NNaO<sub>2</sub><sup>+</sup> 232.1308, found 232.1.

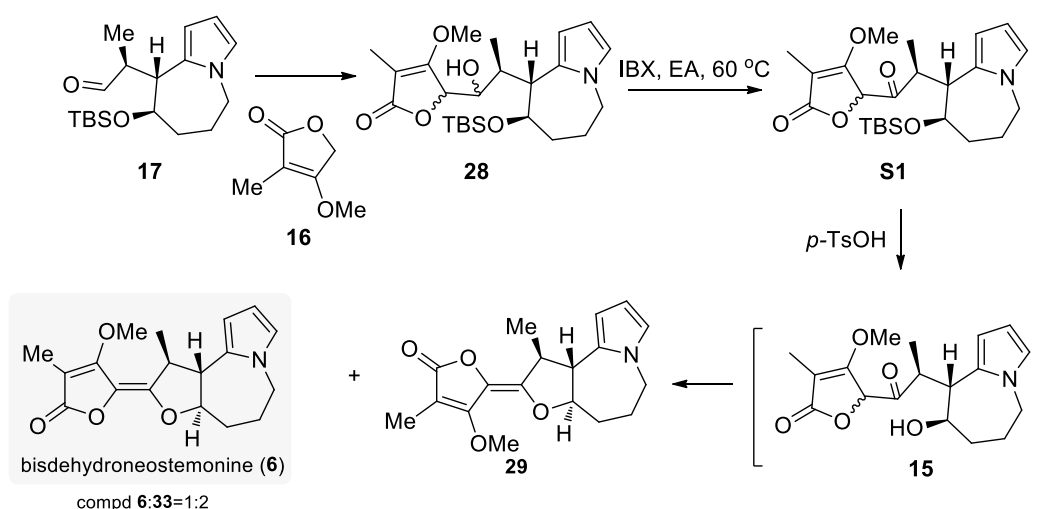


Compound **26**: To a stirred solution of **25** (530 mg, 2.5 mmol) and 2,4,6-lutidine (1.2 g, 10 mmol) in 25 mL CH<sub>2</sub>Cl<sub>2</sub> at 0 °C, TBSOTf (2.3 g, 8.7 mmol) was added, and then the reaction was moved to room temperature and stirred for 4 h. After being quenched with 10 mL saturated aqueous NaHCO<sub>3</sub>, the organic layer was separated and the water layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL). The combined organic phases were washed with brine (2 × 10 mL), concentrated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: PE: EA = 30 : 1) to give compound **26** (1.05 g, 95% yield) as a colorless oil,  $[\alpha]_D^{22} = 0.0$  (*c* 1.0 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.43 (t, *J* = 2.2 Hz, 1H), 5.91 (t, *J* = 3.0 Hz, 1H), 5.82 (dd, *J* = 3.1, 2.0 Hz, 1H), 4.30





Compound **17**: To a stirred solution of compound **27** (100 mg, 0.31 mmol) and pyridine (490 mg, 0.49 mL, 6.2 mmol) in 4.5 mL CH<sub>2</sub>Cl<sub>2</sub> at room temperature, Dess-Martin Periodinane (200 mg, 0.47 mmol) was added. After stirred for 30 min, the mixture was directly poured into a silica gel column chromatographed rapidly (eluent: PE: EA = 5: 1) to afford compound **17** (70 mg, 71% yield) as a yellow oil.  $[\alpha]_D^{24} = -32.0$  (*c* 1.0 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.61 (d, *J* = 3.3 Hz, 1H), 6.51 – 6.45 (m, 1H), 5.97 – 5.91 (m, 1H), 5.89 (dd, *J* = 3.4, 1.8 Hz, 1H), 4.00 – 3.91 (m, 1H), 3.91 – 3.82 (m, 2H), 3.23 (dd, *J* = 9.7, 6.6 Hz, 1H), 2.87 – 2.75 (m, 1H), 2.03 – 1.92 (m, 2H), 1.87 – 1.75 (m, 1H), 1.71 – 1.59 (m, 1H), 1.05 (d, *J* = 6.4 Hz, 3H), 0.82 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 204.0, 129.1, 121.8, 111.1, 105.8, 70.4, 49.4, 47.1, 46.9, 34.8, 25.8, 24.2, 18.2, 12.8, -4.5, -4.7. IR (KBr, ν / cm<sup>-1</sup>) 2953, 2930, 2857, 1724, 1463, 1254, 1079, 1049, 836, 705. LC-MS (ESI, *m/z*) [M + Na]<sup>+</sup> cacl C<sub>18</sub>H<sub>33</sub>NNaO<sub>2</sub>Si<sup>+</sup> 344.2016, found 344.2.



Compound **28**: To a stirred solution of compound **16** (400 mg, 3.1 mmol) in 10 mL THF at -78 °C, *n*-BuLi (1.6 mol/L in hexane, 1.55 mL, 2.5 mmol) was slowly added. The mixture was stirred at -78 °C for 30 min and then a solution of **17** (200 mg, 0.62 mmol) dissolved in 5 mL THF was added dropwise. After stirring for another 45 min, the reaction was quenched with saturated aqueous solution of NH<sub>4</sub>Cl (5.0 mL) and warmed to ambient temperature. After being diluted with 10 mL water, the organic layer was separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL). The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by flash

**S10 / S62**

chromatography on silica gel (eluent: PE: EA = 3: 1) to give compound **28** (258 mg, 92% yield) as a yellow oil. **LC-MS (ESI, m/z)**  $[M + Na]^+$  cacl  $C_{24}H_{39}NNaO_5Si^+$  472.2490, found 472.2.

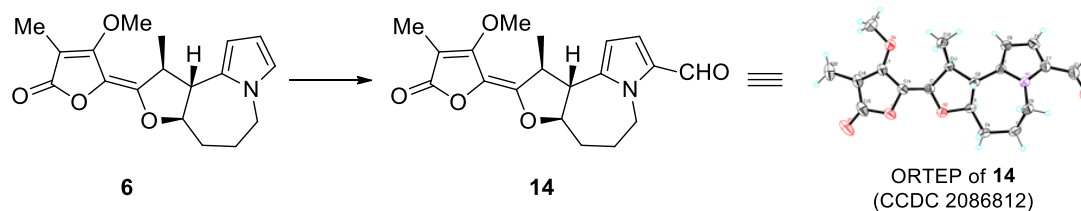
Compound **S1**: The mixture of compound **28** (90 mg, 0.1 mmol) and IBX (140 mg, 0.5 mmol) in ethyl acetate (4 mL) was stirred at 60 °C for 6 h. Then the mixture was cooled to room temperature and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent: PE: EA = 4: 1) to give compound **S1** (57 mg, 64%). **LC-MS (ESI, m/z)**  $[M + Na]^+$  cacl  $C_{24}H_{37}NNaO_5Si^+$  470.2333, found 470.2.

Compounds **6** and **29**: The mixture of compound **S1** (100.0 mg, 0.22 mmol), 5.0 mL  $CH_2Cl_2$  and *p*-TsOH (85.0 mg, 0.45 mmol) was stirred at room temperature for 24 h. Then the mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the mixture of bisdehydroneostemonine (**6**) and its isomer **29** (20.0 mg, 28%). The mixture of **6** and **29** was carefully separated by preparation TLC (PE: ether:  $CH_2Cl_2$  = 1: 2: 0.1,  $R_f$  = 0.3) to give pure **6** (6 mg) and **29** (13 mg).

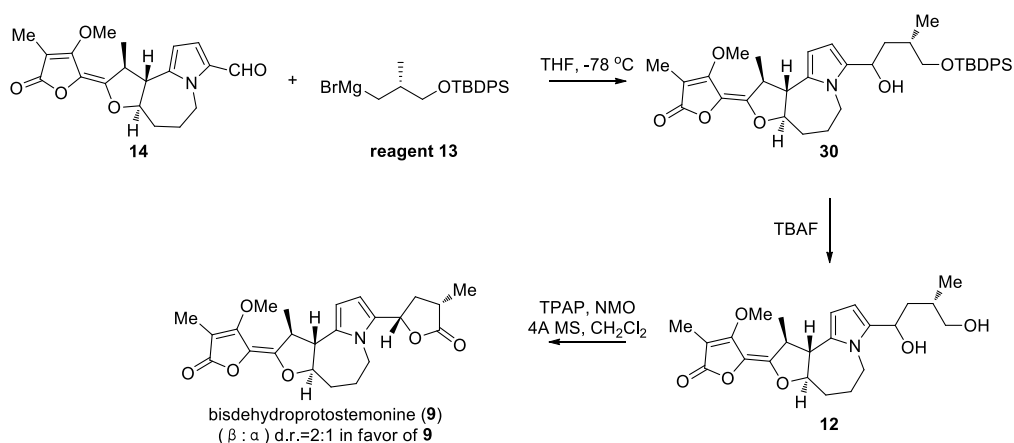
**Bisdehydroneostemonine (6)** <sup>[5-6]</sup>: Yellow oil,  $[\alpha]_D^{22} = +121.4$  (*c* 0.14 in EtOH). [lit.  $[\alpha]_D^{25} = +187$  (*c* 0.033, EtOH)<sup>5,6</sup>] **<sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )**  $\delta$  6.61 (t, *J* = 2.3 Hz, 1H), 6.04 (t, *J* = 3.1 Hz, 1H), 6.02 – 5.99 (m, 1H), 4.19 (s, 3H), 4.15 – 4.06 (m, 1H), 3.86 (dd, *J* = 14.8, 11.3 Hz, 1H), 3.77 (td, *J* = 10.7, 3.6 Hz, 1H), 3.56 – 3.47 (m, 1H), 2.93 (t, *J* = 10.2 Hz, 1H), 2.62 – 2.53 (m, 1H), 2.13 – 2.03 (m, 4H), 1.86 – 1.74 (m, 1H), 1.72 – 1.62 (m, 1H), 1.52 (d, *J* = 6.6 Hz, 3H). **<sup>13</sup>C NMR (101 MHz,  $CDCl_3$ )**  $\delta$  170.1, 163.2, 148.8, 128.6, 125.5, 122.7, 106.2, 104.8, 97.6, 86.0, 58.9, 52.0, 49.3, 39.8, 34.0, 26.2, 19.3, 9.3. **IR (KBr  $\nu/cm^{-1}$ ):** 2920, 1735, 1655, 1618, 1459, 1400, 1155, 1018, 755. **HRMS (ESI, m/z)**  $[M + Na]^+$  calcd for  $C_{18}H_{21}NNaO_4$  338.1363, found 338.1367.

**Compound 29**: Colorless solid, mp 217-219 °C.  $[\alpha]_D^{25} = -30.0$  (*c* 0.1 in  $CHCl_3$ ). **<sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )**  $\delta$  6.61 (t, *J* = 2.2 Hz, 1H), 6.07 – 6.02 (m, 1H), 6.01 – 5.98 (m, 1H), 4.13 (s, 3H), 4.12 – 4.06 (m, 1H), 3.91 – 3.81 (m, 2H), 3.63 – 3.53 (m, 1H), 2.86 (t, *J* = 10.7 Hz, 1H), 2.59 – 2.52 (m, 1H), 2.13 – 2.07 (m, 1H), 2.06 (s, 3H), 1.87 – 1.75 (m, 1H), 1.72 – 1.66 (m, 1H), 1.62 (d, *J* = 6.7 Hz, 3H). **<sup>13</sup>C NMR (101 MHz,  $CDCl_3$ )**  $\delta$  170.7, 163.6, 150.6, 128.3, 126.4, 122.5, 106.4, 105.1, 98.0, 86.9, 59.5, 50.3, 49.2, 41.9, 34.3, 26.2, 16.9, 8.9. **IR (KBr  $\nu/cm^{-1}$ ):**

2945, 2918, 2885, 1731, 1685, 1608, 1453, 1400, 1165, 1006, 727. **HRMS (ESI, m/z)** [M + Na]<sup>+</sup> calcd for C<sub>18</sub>H<sub>21</sub>NNaO<sub>4</sub> 338.1363, found 338.1367.



Compound **14**: (COCl)<sub>2</sub> (0.1 M in CH<sub>2</sub>Cl<sub>2</sub>, 1 mL, 0.1 mmol) was added dropwise to anhydrous DMF (15 mg, 0.2 mmol) at room temperature, and the mixture was stirred for 15 min. Then the mixture was diluted with 30.0 mL CH<sub>2</sub>Cl<sub>2</sub>, and a solution of compound **6** (30 mg, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added dropwise. After stirring for 30 min, a solution of NaOAc (33 mg, 0.4 mmol) in 1 mL water was added and the mixture was stirred for another 1 h. Then the organic layer was separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (7 × 5 mL). The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: PE: EA = 2 : 1) to give compound **14** (20 mg, 62% yield) as a pale yellow solid, mp 209.5 °C. [ $\alpha$ ]<sub>D</sub><sup>23</sup> = -5.0 (c 0.2 in CHCl<sub>3</sub>). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  9.47 (s, 1H), 6.86 (d, *J* = 4.0 Hz, 1H), 6.15 (d, *J* = 4.0 Hz, 1H), 5.80 (dd, *J* = 14.5, 5.6 Hz, 1H), 4.20 (s, 3H), 3.79 (td, *J* = 10.8, 3.7 Hz, 1H), 3.66 (dd, *J* = 14.7, 11.5 Hz, 1H), 3.61 – 3.52 (m, 1H), 3.00 (t, *J* = 10.2 Hz, 1H), 2.66 – 2.56 (m, 1H), 2.18 – 2.11 (m, 1H), 2.10 (s, 3H), 1.91 – 1.80 (m, 1H), 1.69 – 1.61 (m, 1H), 1.52 (d, *J* = 6.6 Hz, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  179.7, 169.9, 163.0, 147.6, 140.2, 132.5, 125.7, 124.8, 106.8, 97.9, 84.6, 59.0, 51.8, 45.6, 39.3, 34.3, 25.3, 19.4, 9.3. **LC-MS (ESI, m/z)** [M + H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>22</sub>NO<sub>5</sub> 344.1491, found 344.1.

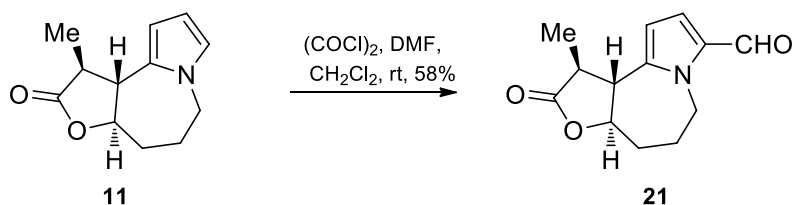


**Bisdehydroprotostemonine (9)**<sup>6</sup>: To a solution of compound **14** (15 mg, 0.04 mmol) in anhydrous THF (2.0 mL) stirred at  $-78\text{ }^{\circ}\text{C}$ , freshly prepared Grignard reagent **13** (0.2 mmol/mL, 1.0 mL, 0.2 mmol) was added. The mixture was then stirred at  $-78\text{ }^{\circ}\text{C}$  for 30 min and quenched with saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (2.0 mL). Then the mixture was extract with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 5\text{ mL}$ ), the organic layers were combined and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: PE: EA = 3 : 1) to give compound **30** as a yellow oil.

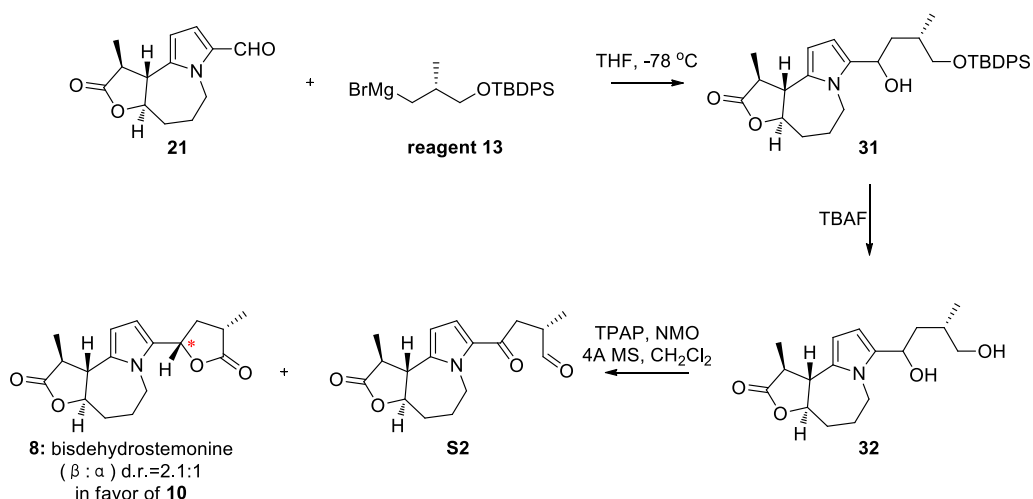
To a stirred solution of compound **30** in 2.0 mL THF, 0.1 mL of 1 M TBAF in THF was added. After stirred for 30 min, the reaction completed and was concentrated under reduced pressure. The resulting residue was purified by flash chromatography on aluminium oxide (pH 9.0-10.0, eluent:  $\text{CH}_2\text{Cl}_2$ : MeOH = 50: 1 to 30:1) to give crude product **12** as a yellow oil.

To a stirred mixture of compound **12** and 4Å MS (30.0 mg) in 2.0 mL  $\text{CH}_2\text{Cl}_2$ , TPAP (1.0 mg) was added and the mixture was stirred for 2 min. Then NMO (30.0 mg, 0.26 mmol) was added. After stirred for 15 min, the mixture was poured to a silica gel and chromatographed (eluent:  $\text{CH}_2\text{Cl}_2$ : EA = 5: 1) to give bisdehydroprotostemonine (**9**) along with its C18 emiper as an inseparable mixture (d.r. = 2:1, 1.2 mg, 9.6% yield over 3 steps,). **mp** 192-194  $^{\circ}\text{C}$ . **<sup>1</sup>H NMR (600 MHz,  $\text{CDCl}_3$ )**  $\delta$  6.14 (d,  $J = 3.6\text{ Hz}$ , 1H), 6.00 (d,  $J = 3.5\text{ Hz}$ , 1H), 5.38 (dd,  $J = 10.9, 5.3\text{ Hz}$ , 1H), 4.34 (dd,  $J = 14.3, 5.4\text{ Hz}$ , 1H), 4.19 (s, 3H), 3.76 – 3.72 (m, 2H), 3.53 – 3.50 (m, 1H), 3.00 – 2.97 (m, 1H), 2.81 – 2.78 (m, 1H), 2.73 – 2.70 (m, 1H), 2.62 – 2.60 (m, 1H), 2.25 – 2.22 (m, 1H), 2.15 – 2.13 (m, 1H), 2.10 (s, 3H), 1.84 – 1.82 (m, 1H), 1.72 – 1.69 (m, 1H), 1.51 (d,  $J = 6.6\text{ Hz}$ , 3H), 1.36 (d,  $J = 7.1\text{ Hz}$ , 3H). **<sup>13</sup>C NMR (125 MHz,  $\text{CDCl}_3$ )**  $\delta$  178.9, 170.1, 163.2, 148.5, 132.4, 129.5, 125.6, 107.1, 103.7, 97.8,

85.7, 71.6, 59.0, 52.1, 45.6, 39.6, 36.1, 35.0, 34.3, 25.8, 19.4, 15.2, 9.4. **IR (KBr,  $\nu / \text{cm}^{-1}$ )** 2941, 2875, 1777, 1737, 1681, 1617. **HRMS (ESI,  $m/z$ )**  $[M + H]^+$  calcd for  $\text{C}_{23}\text{H}_{28}\text{NO}_6^+$  414.1911, found 414.1922.



**Compound 21:**  $(\text{COCl})_2$  (2 M in  $\text{CH}_2\text{Cl}_2$ , 0.8 mL, 1.6 mmol) was added dropwise to anhydrous DMF (220 mg, 0.24 mL, 3 mmol) at room temperature, and the mixture was stirred for 15 min. Then the mixture was diluted with 30.0 mL  $\text{CH}_2\text{Cl}_2$ , and a solution of compound **11** (300.0 mg, 1.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL) was added dropwise. After stirring for 30 min, a solution of NaOAc (660.0 mg, 8 mmol) in 7.0 mL water was added and the mixture was stirred for another 1 h. Then the organic layer was separated, and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $7 \times 5$  mL). The combined organic phases were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: PE : EA = 2 : 1) to give compound **21** (200 mg, 58% yield) as a white solid, **mp** 187-188 °C.  $[\alpha]_D^{23} = -228.0$  ( $c$  0.5 in  $\text{CHCl}_3$ ).  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.49 (s, 1H), 6.87 (d,  $J = 4.0$  Hz, 1H), 6.09 (d,  $J = 4.0$  Hz, 1H), 5.81 (ddt,  $J = 14.7, 5.9, 1.5$  Hz, 1H), 3.93 (ddd,  $J = 11.4, 9.7, 3.7$  Hz, 1H), 3.67 (dd,  $J = 14.7, 11.4$  Hz, 1H), 3.12 – 2.95 (m, 2H), 2.62 – 2.52 (m, 1H), 2.22 – 2.11 (m, 1H), 1.88 – 1.75 (m, 1H), 1.72 – 1.60 (m, 1H), 1.43 (d,  $J = 6.7$  Hz, 3H).  **$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  179.8, 177.2, 139.9, 132.4, 124.8, 106.8, 80.1, 48.9, 45.4, 39.2, 34.5, 25.4, 13.8. **IR (KBr,  $\nu / \text{cm}^{-1}$ )** 3116, 2960, 2932, 2794, 1778, 1661, 1489, 1448, 1377, 1325, 1202, 1167, 1139, 1023, 768. **LC-MS (ESI,  $m/z$ )**  $[M + \text{Na}]^+$  calcd for  $\text{C}_{13}\text{H}_{15}\text{NNaO}_3$  256.0944, found 256.0.



To a solution of compound **21** (30.0 mg, 0.13 mmol) in anhydrous THF (3.0 mL) stirred at -78 °C, freshly prepared Grignard reagent **13** (0.2 mmol/mL, 3.0 mL, 0.6 mmol) was added. The mixture was then stirred at -78 °C for 30 min and quenched with saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (5.0 mL). Then the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL), the organic layers were combined and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: PE: EA = 3: 1) to give compound **31** as a yellow oil.

To a stirred solution of compound **31** in 2.0 mL THF, 0.15 mL of 1 M TBAF in THF was added. After stirred for 30 min, the reaction completed and was concentrated under reduced pressure. The resulting residue was purified by flash chromatography on aluminium oxide (pH 9.0-10.0, eluent:  $\text{CH}_2\text{Cl}_2$ : MeOH = 50: 1 to 30:1) to give crude product **32** as a yellow oil.

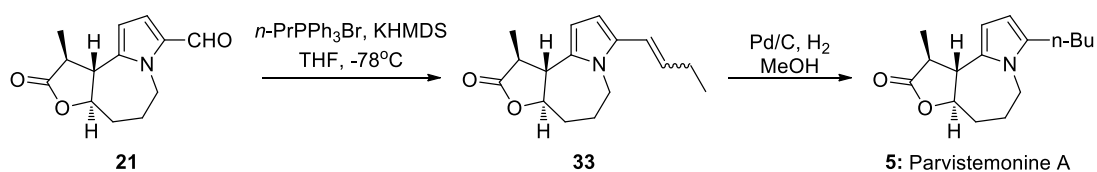
To a stirred mixture of compound **32** and 4Å MS (50.0 mg) in 2.0 mL  $\text{CH}_2\text{Cl}_2$ , TPAP (1.0 mg) was added and the mixture was stirred for 2 min. Then NMO (60.0 mg, 0.51 mmol) was added. After stirred for 15 min, the mixture was poured to a silica gel and chromatographed (eluent:  $\text{CH}_2\text{Cl}_2$ : EA = 5 : 1) to give bisdehydrostemonine (**8**) with its C13 epimer (dr=2:1, 7.0 mg, 18% yield over 3 steps, dr=4:1 after recrystallization) and compound **S2** (6.0 mg, 15% yield over 3 steps).

**Bisdehydrostemonine (8)**<sup>7</sup>: colorless solid, mp 185.9 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.15 (d,  $J$  = 3.7 Hz, 1H), 5.95 (d,  $J$  = 3.7 Hz, 1H), 5.38 (dd,  $J$  = 11.0, 5.2 Hz, 1H), 4.36 (dd,  $J$  = 14.4, 5.6 Hz, 1H), 3.92 – 3.85 (m, 1H), 3.73 (dd,  $J$  = 14.5, 10.6 Hz, 1H), 3.11 – 3.00 (m, 1H), 3.00 – 2.92 (m, 1H), 2.86 – 2.68 (m, 2H), 2.59 – 2.52 (m, 1H), 2.28 – 2.13 (m, 2H), 1.82 – 1.69 (m, 2H), 1.42 (d,  $J$  = 6.8 Hz, 3H), 1.36 (d,  $J$  = 6.8 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.9,

178.0, 132.2, 129.5, 107.2, 103.8, 81.2, 71.4, 49.2, 45.4, 39.4, 36.0, 34.8, 34.4, 25.8, 15.1, 13.8.

**IR (KBr,  $\nu / \text{cm}^{-1}$ )** 2926, 2878, 2853, 1769, 1456, 1439, 1200, 1165, 1014, 759, 719. **HRMS (ESI,  $m/z$ )**  $[M + H]^+$  calcd for  $C_{17}H_{22}NO_4^+$  304.1543, found 304.1546.

**Compound S2:** colorless oil.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.77 (s, 1H), 6.98 (d,  $J = 4.1$  Hz, 1H), 6.01 (d,  $J = 4.1$  Hz, 1H), 5.87 (dd,  $J = 14.6, 5.9$  Hz, 1H), 3.97 – 3.84 (m, 1H), 3.59 (dd,  $J = 14.6, 11.3$  Hz, 1H), 3.28 (dd,  $J = 16.6, 6.6$  Hz, 1H), 3.10 – 2.93 (m, 3H), 2.92 – 2.84 (m, 1H), 2.59 – 2.50 (m, 1H), 2.18 – 2.08 (m, 1H), 1.85 – 1.74 (m, 1H), 1.70 – 1.61 (m, 1H), 1.42 (d,  $J = 6.6$  Hz, 3H), 1.19 (d,  $J = 7.2$  Hz, 3H).  **$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  203.6, 188.8, 177.4, 138.7, 131.0, 119.5, 105.5, 80.3, 49.0, 45.5, 42.1, 40.2, 39.2, 34.5, 25.4, 13.8, 13.7. **IR (KBr,  $\nu / \text{cm}^{-1}$ )** 2932, 2857, 2876, 1780, 1726, 1646, 1485, 1461, 1403, 1202, 1169, 1131, 1029. **LC-MS (ESI,  $m/z$ )**  $[M + H]^+$  calcd for  $C_{17}H_{22}NO_4^+$  304.1543, found 304.1.

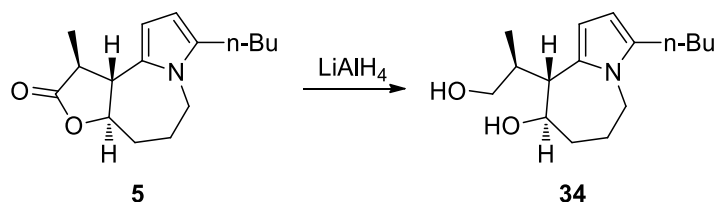


**Parvistemonine A (5).**<sup>8</sup> To a solution of *n*-propyltriphenylphosphonium bromide (600 mg, 2.0 mmol) in THF (6 mL) stirring at  $-78^\circ\text{C}$ , KHMDS (1.3 mL, 1.3 mol/L in THF, 1.7 mmol) was added dropwise. Then the mixture was moved to room temperature. 1 h later, the mixture was moved to  $-78^\circ\text{C}$  again and compound **21** (200 mg, 0.86 mmol) dissolved in 2 mL THF was slowly added. The reaction was stirred for another 1 h before being quenched with saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (5 mL). After dilution with 10 mL water, the organic layer was separated and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL). The combined organic phases were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: PE: EA = 5: 1) to give compound **33** (190 mg, 85% yield) as a yellow oil.

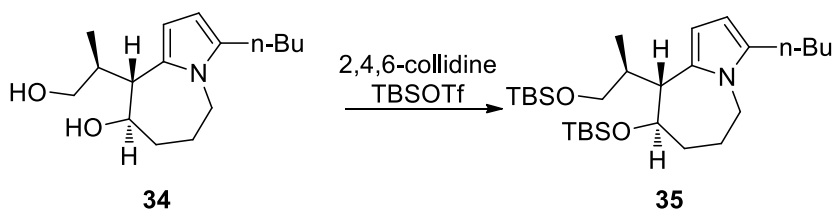
Compound **33** (190 mg, 0.73 mmol) and 10% Pd/C (150 mg, 0.14 mmol) was dissolved in 10 mL MeOH and the mixture was stirred under a hydrogen atmosphere at room temperature overnight. Then the mixture was filtered, and the filtrate was evaporated under reduced pressure. The residue was directly purified by silica column chromatography (eluent: PE: EA = 3: 1) to



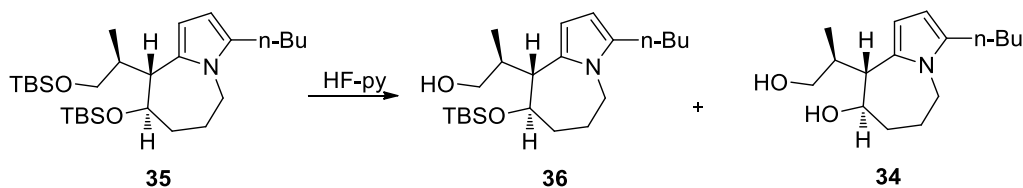
give compound **parvistemonine A (5)** as a colorless oil (170 mg, 89%).  $[\alpha]_D^{25} = -43.0$  (*c* 0.1 in  $\text{CHCl}_3$ ). [lit.  $[\alpha]_D^{28} = -75.1$  (*c* 0.04, MeOH)<sup>8</sup>]  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  5.86 (d, *J* = 3.4 Hz, 1H), 5.82 (d, *J* = 3.4 Hz, 1H), 4.19 (dd, *J* = 14.8, 5.7 Hz, 1H), 3.89 (ddd, *J* = 11.4, 9.4, 3.6 Hz, 1H), 3.63 (dd, *J* = 14.8, 11.4 Hz, 1H), 3.07 – 2.91 (m, 2H), 2.57 – 2.47 (m, 3H), 2.18 – 2.07 (m, 1H), 1.84 – 1.71 (m, 1H), 1.62 – 1.49 (m, 3H), 1.45 – 1.35 (m, 5H), 0.94 (t, *J* = 7.3 Hz, 3H).  **$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  178.5, 134.3, 128.1, 104.3, 103.0, 81.8, 49.4, 44.1, 39.4, 34.3, 31.5, 26.3, 26.0, 22.6, 14.0, 13.9. **IR (KBr,  $\nu / \text{cm}^{-1}$ ):** 2933, 2876, 1780, 1460, 1431, 1200, 1167, 1018, 747. **LC-MS (ESI, *m/z*)**  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{16}\text{H}_{23}\text{NNaO}_2$  284.1621, found 284.1.



**Compound 34.** To a stirred solution of **5** (500 mg, 1.9 mmol) in 20 mL THF at 0 °C, solid  $\text{LiAlH}_4$  (110 mg, 2.9 mmol) was slowly added. Then the reaction was moved to room temperature. After stirring for 1 h, the reaction was quenched with 5 mL saturated aqueous Rochelle salt, stirred for another 20 min, diluted with 20 mL water, extracted with  $\text{CH}_2\text{Cl}_2$  (5  $\times$  30 mL). The resulting residue was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and evaporated under vacuum. The residue was purified by flash chromatography on silica gel (eluent: EA) to give compound **34** (470 mg, 93% yield) as a pale yellow oil.  $[\alpha]_D^{24} = -30.0$  (*c* 1.0 in  $\text{CHCl}_3$ ).  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  5.86 (d, *J* = 3.3 Hz, 1H), 5.73 (d, *J* = 3.3 Hz, 1H), 4.12 – 4.05 (m, 1H), 4.04 – 3.94 (m, 1H), 3.80 – 3.65 (m, 3H), 2.85 (dd, *J* = 10.6, 5.8 Hz, 1H), 2.54 – 2.46 (m, 2H), 2.46 – 2.20 (m, 2H), 2.19 – 2.07 (m, 1H), 1.95 – 1.82 (m, 1H), 1.81 – 1.63 (m, 3H), 1.55 (p, *J* = 7.4 Hz, 2H), 1.38 (h, *J* = 7.3 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 3H).  **$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  133.7, 129.1, 109.9, 103.9, 69.0, 65.9, 48.5, 43.3, 35.8, 32.0, 31.6, 26.6, 22.5, 17.1, 14.0. **IR (KBr,  $\nu / \text{cm}^{-1}$ )** 3388, 2960, 2932, 2876, 1724, 1459, 1429, 1288, 1135, 1072, 1044, 1023, 992, 749. **LC-MS (ESI, *m/z*)**  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{16}\text{H}_{27}\text{NNaO}_2$  288.1934, found 288.2.

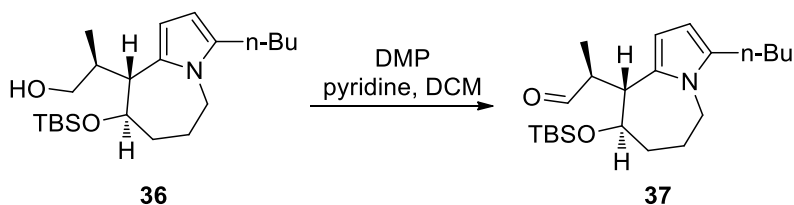


**Compound 35.** To a stirred solution of **34** (470 mg, 1.8 mmol) and 2,4,6-lutidine (1 g, 8.3 mmol) in 20 mL  $\text{CH}_2\text{Cl}_2$  at 0 °C, TBSOTf (1.8 g, 6.8 mmol) was added, and then the reaction was moved to room temperature and stirred for 4 h. After being quenched with 10 mL saturated aqueous  $\text{NaHCO}_3$ , the organic layer was separated and the water layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 20$  mL). The combined organic phases were washed with brine ( $2 \times 10$  mL), concentrated, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: PE: EA = 30 : 1) to give compound **35** (720 mg, 82% yield) as a pale yellow oil.  $[\alpha]_D^{20} = -5.0$  (*c* 0.2 in  $\text{CHCl}_3$ ).  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  5.69 (d,  $J = 3.1$  Hz, 1H), 5.66 (d,  $J = 2.8$  Hz, 1H), 4.23 (t,  $J = 5.1$  Hz, 1H), 3.98 (dd,  $J = 14.4, 5.5$  Hz, 1H), 3.69 – 3.56 (m, 3H), 2.85 (dd,  $J = 9.5, 5.6$  Hz, 1H), 2.59 – 2.43 (m, 2H), 2.11 – 1.99 (m, 1H), 1.92 – 1.78 (m, 3H), 1.70 – 1.58 (m, 1H), 1.56 – 1.47 (m, 2H), 1.35 (h,  $J = 7.6$  Hz, 2H), 0.94 – 0.90 (m, 12H), 0.82 – 0.77 (m, 12H), 0.07 (s, 3H), 0.06 (s, 3H), 0.04 (s, 3H), 0.01 (s, 3H).  **$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  131.6, 131.5, 109.2, 103.5, 68.9, 66.9, 49.0, 44.2, 35.8, 33.3, 31.9, 26.8, 26.0, 25.8, 23.1, 22.3, 18.4, 18.1, 16.7, 14.0, -4.61, -4.62, -5.4. **IR (KBr,  $\nu / \text{cm}^{-1}$ ):** 2958, 2930, 2861, 1472, 1429, 1361, 1254, 1087, 1051, 837, 773.

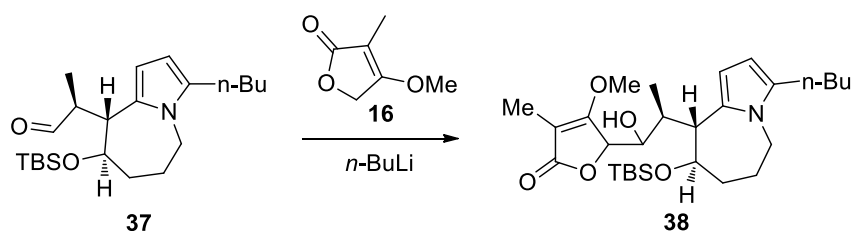


**Compound 36.** To a stirred solution of **35** (200 mg, 0.41 mmol) in 4 mL acetonitrile at room temperature in a 10 mL plastic tube, 70% pyridine hydrofluoride (60  $\mu\text{L}$ , 66 mg, 0.47 mmol) was added and the reaction was stirred for 12 h. Then the reaction was quenched with 5 mL saturated aqueous  $\text{NaHCO}_3$ , and extracted with  $\text{CH}_2\text{Cl}_2$  ( $5 \times 10$  mL). The combined organic phases were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: PE: EA = 5: 1 to pure

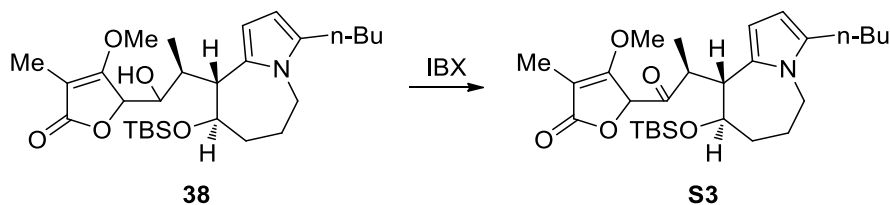
EA) to give compound **36** (95.0 mg, 62% yield) as a yellow oil as well as compound **34** (17.0 mg, 16% yield).  $[\alpha]_D^{22} = -20.0$  (*c* 0.1 in  $\text{CHCl}_3$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.73 (d,  $J = 3.3$  Hz, 1H), 5.69 (d,  $J = 3.3$  Hz, 1H), 4.15 – 4.08 (m, 1H), 4.01 – 3.91 (m, 1H), 3.75 – 3.60 (m, 3H), 2.82 (dd,  $J = 9.3, 6.0$  Hz, 1H), 2.57 – 2.43 (m, 2H), 2.16 – 2.04 (m, 1H), 1.93 – 1.82 (m, 1H), 1.81 – 1.73 (m, 1H), 1.71 – 1.59 (m, 2H), 1.58 – 1.48 (m, 3H), 1.35 (h,  $J = 7.3$  Hz, 2H), 0.91 (t,  $J = 7.3$  Hz, 6H), 0.82 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  131.9, 131.0, 108.4, 103.7, 69.9, 66.5, 48.5, 43.4, 35.9, 32.9, 31.8, 26.6, 25.8, 22.8, 22.4, 18.1, 16.2, 14.0, -4.4, -4.7. IR (KBr,  $\nu / \text{cm}^{-1}$ ): 3440, 2954, 2930, 2859, 1472, 1430, 1359, 1254, 1137, 1094, 1051, 1023, 837, 773, 749.



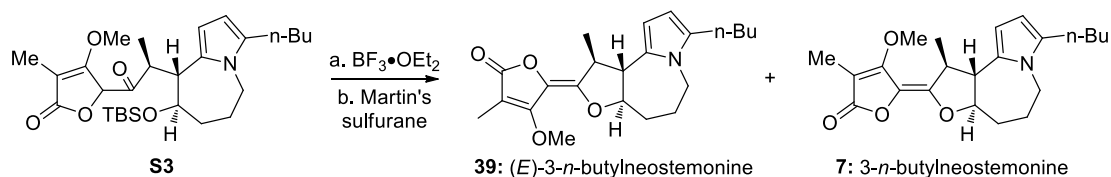
**Compound 37.** To a stirred solution of compound **36** (50 mg, 0.13 mmol) and pyridine (210 mg, 0.21 mL, 2.7 mmol) in 2 mL  $\text{CH}_2\text{Cl}_2$  at room temperature, Dess-Martin Periodinane (85 mg, 0.2 mmol) was added. After stirred for 30 min, the mixture was directly poured into a silica gel column chromatographed rapidly (eluent: PE: EA = 6 : 1) to afford compound **37** (26 mg, 52% yield) as a yellow oil.  $[\alpha]_D^{23} = -35.0$  (*c* 0.2 in  $\text{CHCl}_3$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.62 (d,  $J = 2.9$  Hz, 1H), 5.77 (d,  $J = 3.4$  Hz, 1H), 5.72 (d,  $J = 3.4$  Hz, 1H), 3.94 – 3.75 (m, 3H), 3.22 (t,  $J = 8.0$  Hz, 1H), 2.92 – 2.79 (m, 1H), 2.53 – 2.47 (m, 2H), 1.98 – 1.87 (m, 2H), 1.82 – 1.72 (m, 1H), 1.63 – 1.49 (m, 3H), 1.37 (h,  $J = 7.3$  Hz, 2H), 1.12 (d,  $J = 6.3$  Hz, 3H), 0.92 (t,  $J = 7.3$  Hz, 3H), 0.84 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  204.2, 132.7, 128.8, 108.2, 104.1, 71.4, 47.3, 46.9, 43.8, 35.8, 31.6, 26.6, 25.9, 24.4, 22.5, 18.1, 14.0, 12.6, -4.3, -4.7. IR (KBr,  $\nu / \text{cm}^{-1}$ ): 2952, 2928, 2859, 2723, 2702, 1722, 1651, 1459, 1429, 1254, 1079, 1051, 837, 775, 749.



**Compound 38.** To a stirred solution of compound **16** (170 mg, 1.3 mmol) in 5 mL THF at -78 °C, *n*-BuLi (1.6 mol/L in hexane, 0.65 mL, 1.0 mmol) was slowly added. The mixture was stirred at -78 °C for 30 min and then a solution of **37** (100 mg, 0.27 mmol) dissolved in 1.0 mL THF was added dropwise. After stirring for another 45 min, the reaction was quenched with saturated aqueous solution of NH<sub>4</sub>Cl (5.0 mL) and warmed to ambient temperature. After being diluted with 10 mL water, the organic layer was separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL). The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: PE: EA = 3: 1) to give compound **38** (123 mg, 92% yield) as a yellow oil.



**Compound S3.** The mixture of compound **38** (50 mg, 0.1 mmol) and IBX (70 mg, 0.25 mmol) in ethyl acetate (2 mL) was stirred at 60 °C for 3 h. Then the mixture was cooled to room temperature and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent: PE: EA = 4: 1) to give compound **38** (20 mg recovered) and compound **S3** (18 mg, 60% b.r.s.m.).



**3-*n*-butylneostemonine (7) and its isomer 39.** To a solution of **S3** (20 mg, 0.04 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL), BF<sub>3</sub>·Et<sub>2</sub>O (98%, 26 μL, 0.20 mmol) was added at 0 °C. Then the mixture was moved to room temperature before being quenched with saturated aqueous solution of NaHCO<sub>3</sub> (1 mL). The organic layer was separated, and the water layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 5 mL). The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was dissolved in 2 mL CH<sub>2</sub>Cl<sub>2</sub> and Martin's sulfurane (40 mg, 0.06 mmol) was then added, the mixture was stirred for 30 min at room temperature. Then the mixture was purified by flash chromatography on silica gel to give the mixture of **7** and **39** (6 mg, 41% yield). The mixture of **7** and **39** was carefully separated by preparative TLC (eluent: PE: ether: CH<sub>2</sub>Cl<sub>2</sub> = 1: 1: 0.2, R<sub>f</sub> = 0.4) to give pure isomer **39** (2.0 mg) and 3-*n*-butylneostemonine (**7**) (4.0 mg) as a colorless oil.

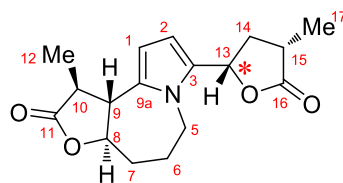
**Compound 39:**  $[\alpha]_D^{23} = -20.0$  (*c* 0.1 in CHCl<sub>3</sub>). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 5.89 (d, *J* = 3.3 Hz, 1H), 5.81 (d, *J* = 3.3 Hz, 1H), 4.18 (dd, *J* = 14.5, 5.8 Hz, 1H), 4.13 (s, 3H), 3.85 (td, *J* = 10.9, 3.7 Hz, 1H), 3.66 – 3.53 (m, 2H), 2.86 (t, *J* = 10.7 Hz, 1H), 2.58 – 2.48 (m, 3H), 2.14 – 2.07 (m, 1H), 2.06 (s, 3H), 1.87 – 1.76 (m, 1H), 1.61 (d, *J* = 6.7 Hz, 3H), 1.58 – 1.56 (m, 1H), 1.55 – 1.48 (m, 2H), 1.44 – 1.35 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 170.7, 163.8, 150.8, 134.1, 127.8, 126.4, 104.4, 103.2, 98.3, 87.0, 59.6, 50.6, 44.3, 41.8, 34.6, 31.6, 26.4, 26.1, 22.6, 17.0, 14.0, 8.8. **IR (KBr, ν / cm<sup>-1</sup>):** 2926, 2855, 1739, 1683, 1616, 1456, 1400, 1161, 1003, 753. **HRMS (ESI, *m/z*)** [M + Na]<sup>+</sup> calcd for C<sub>22</sub>H<sub>29</sub>NNaO<sub>4</sub> 394.1989; found 394.2002.

**3-*n*-butylneostemonine (7):**  $[\alpha]_D^{24} = -20.0$  (*c* 0.1 in CHCl<sub>3</sub>). [lit.  $[\alpha]_D^{28} = -5.4$  (*c* 0.05, MeOH)<sup>8</sup>]. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 5.90 (d, *J* = 3.3 Hz, 1H), 5.80 (d, *J* = 3.3 Hz, 1H), 4.22 – 4.13 (m, 4H), 3.77 (td, *J* = 10.8, 3.7 Hz, 1H), 3.61 (dd, *J* = 14.7, 11.5 Hz, 1H), 3.55 – 3.45 (m, 1H), 2.93 (t, *J* = 10.3 Hz, 1H), 2.61 – 2.55 (m, 1H), 2.55 – 2.49 (m, 2H), 2.14 – 2.04 (m, 4H), 1.87 – 1.75 (m, 1H), 1.61 – 1.57 (m, 2H), 1.55 – 1.53 (m, 1H), 1.51 (d, *J* = 6.6 Hz, 3H), 1.45 – 1.36 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 170.1, 163.3, 149.1, 134.3, 128.1, 125.4, 104.1, 102.7, 97.5, 86.2, 58.9, 52.2, 44.3, 39.6, 34.3, 31.5, 26.4, 26.0, 22.6, 19.3, 14.0, 9.3. **IR (KBr, ν / cm<sup>-1</sup>):** 2960, 2935, 2874, 1743, 1679, 1621, 1461, 1398, 1366, 1210,

1154, 1064, 1019, 755, 734. **HRMS (ESI, m/z)**  $[M + Na]^+$  calcd for  $C_{22}H_{29}NNaO_4$  394.1989;  
found 394.1990.

## Comparison of the NMR data

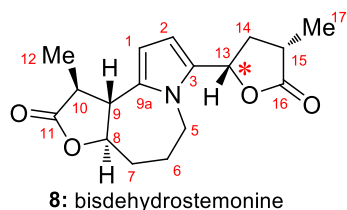
### Comparison of the <sup>1</sup>H NMR data of synthetic bisdehydrostemonine (8) with the natural sample



Proton position	natural sample Ye/Xu group	synthetic sample Chida/Sato group <sup>9</sup>	our synthetic sample <sup>[a]</sup>
	<sup>1</sup> H NMR (? MHz, CDCl <sub>3</sub> ) *MHz was not reported	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> )	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> )
<b>2</b>	6.16 (d)	6.15 (d, J=3.7 Hz, 1H)	6.15 (d, J = 3.7 Hz, 1H)
<b>1</b>	5.95 (d)	5.94 (d, J=3.7 Hz, 1H)	5.95 (d, J = 3.7 Hz, 1H)
<b>13</b>	5.40 (dd)	5.38 (dd, J=11.0, 5.0 Hz, 1H)	5.38 (dd, J = 11.0, 5.2 Hz, 1H)
<b>5</b>	4.39 (ddd)	4.36 (dd, J=14.6, 6.0 Hz, 1H)	4.36 (dd, J = 14.4, 5.6 Hz, 1H)
<b>8</b>	3.88 (m)	3.89 (ddd, J=10.1, 9.6, 3.7 Hz, 1H)	3.92 – 3.85 (m, 1H)
<b>5</b>	3.74 (m)	3.73 (dd, J=14.6, 10.5 Hz, 1H)	3.73 (dd, J = 14.5, 10.6 Hz, 1H)
<b>9</b>	3.07 (dd)	3.06 (dd, J=12.4, 9.6 Hz, 1H)	3.11 – 3.00 (m, 1H)
<b>10</b>	<sup>1</sup> H is missing	2.97 (dq, J=12.4, 6.9 Hz, 1H)	3.00 – 2.92 (m, 1H)
<b>15</b>	2.85 (m)	2.81 (m, 1H)	2.86 – 2.68 (m, 2H)
<b>14</b>	2.82 (m)	2.72 (ddd, J=11.9, 8.2, 5.0 Hz, 1H)	2.86 – 2.68 (m, 2H)
<b>7</b>	2.57 (m)	2.55 (m, 1H)	2.59 – 2.52 (m, 1H)
<b>14</b>	<sup>1</sup> H is missing	2.21 (ddd, J=11.9, 11.4, 11.0 Hz, 1H)	2.28 – 2.13 (m, 2H)
<b>6</b>	2.15 (m)	2.16 (m, 1H)	2.28 – 2.13 (m, 2H)
<b>7,6</b>	1.77 (m) <sup>1</sup> H is missing	1.85-1.66 (m, 2H)	1.82 – 1.69 (m, 2H)
<b>12</b>	1.43 (d)	1.42 (d, J=6.9, 3H)	1.42 (d, J = 6.8 Hz, 3H)
<b>17</b>	1.37 (d)	1.36 (d, J=6.9, 3H)	1.36 (d, J = 6.8 Hz, 3H)

[a] Proton chemical shifts are reported relative to internal standard TMS at δ 0.0 ppm or residual solvent peak of CDCl<sub>3</sub> at 7.26 ppm.

Comparison of the  $^{13}\text{C}$  NMR data of synthetic bisdehydrostemonine (**8**) with the natural sample

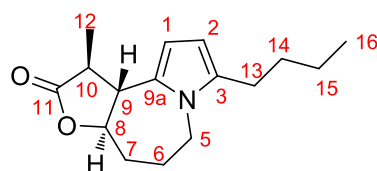


carbon position	natural sample Ye/Xu group	synthetic sample Chida/Sato group <sup>9</sup>	our synthetic sample <sup>[a]</sup>
	$^{13}\text{C}$ NMR (? MHz $\text{CDCl}_3$ ) *MHz was not reported	$^{13}\text{C}$ NMR (125 MHz, $\text{CDCl}_3$ )	$^{13}\text{C}$ NMR (101 MHz, $\text{CDCl}_3$ )
<b>16</b>	177.9	179.0	178.9
<b>11</b>	178.8	178.1	178.0
<b>9a</b>	129.4	132.3	132.2
<b>3</b>	132.1	129.5	129.5
<b>2</b>	107.1	107.3	107.2
<b>1</b>	103.7	103.9	103.8
<b>8</b>	81.1	81.3	81.2
<b>13</b>	71.4	71.5	71.4
<b>9</b>	49.2	49.3	49.2
<b>5</b>	45.3	45.5	45.4
<b>10</b>	39.3	39.5	39.4
<b>15</b>	36.0	36.1	36.0
<b>14</b>	34.7	34.9	34.8
<b>7</b>	34.7	34.5	34.4
<b>6</b>	25.7	25.9	25.8
<b>17</b>	15.0	15.2	15.1
<b>12</b>	13.7	13.9	13.8

[a] Carbon chemical shifts are reported relative to a residual solvent peak of  $\text{CDCl}_3$  at 77.06 ppm.



Comparison of the NMR data of synthetic parvistemonine A (5) with the natural one.



5: parvistemonine A

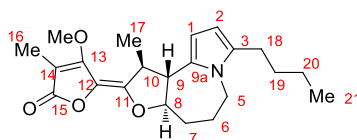
position	$\delta_{\text{H}}$ mult. ( $J$ in Hz)			$\delta_{\text{C}}$		
	natural sample	our synthetic sample <sup>[b]</sup>	deviation <sup>[a]</sup>	natural sample	our synthetic sample <sup>[c]</sup>	deviation <sup>[a]</sup>
	<sup>1</sup> H NMR (500 MHz, CDCl <sub>3</sub> )	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> )		<sup>13</sup> C NMR (125 MHz, CDCl <sub>3</sub> )	<sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> )	
<b>1<math>\beta</math></b>	5.88 d (3.4)	5.86 d (3.4)	-0.02	103.0	103.0	0
<b>1<math>\alpha</math></b>						
<b>2<math>\alpha</math></b>	5.84 d (3.4)	5.82 d (3.4)	-0.02	104.3	104.3	0
<b>2<math>\beta</math></b>						
<b>3</b>	—	—	—	134.3	134.3	0
<b>5<math>\beta</math></b>	4.21 dd (14.7, 5.6)	4.19 dd (14.8, 5.7)	-0.02	44.2	44.1	-0.1
<b>5<math>\alpha</math></b>	3.65 dd (14.7, 11.6)	3.63 dd (14.8, 11.4)	-0.02			
<b>6<math>\alpha</math></b>	2.13 m	2.18 – 2.07 m	-0.06~0.05	26.0	26.0	0
<b>6<math>\beta</math></b>	1.57 m	1.62 – 1.49 m	-0.08~0.05			
<b>7<math>\beta</math></b>	2.54 m	2.57 – 2.47 m	-0.07~0.03	34.4	34.3	-0.1
<b>7<math>\alpha</math></b>	1.79 m	1.84 – 1.71 m	-0.08~0.05			
<b>8</b>	3.91 dd (9.5, 3.6)	3.89 ddd, (11.4, 9.4, 3.6)	-0.02	81.8	81.8	0
<b>9</b>	3.02 m	3.07 – 2.91 m	-0.11~0.05	49.4	49.4	0
<b>9<math>\alpha</math></b>	—	—	—	128.1	128.1	0
<b>10</b>	2.98 m	3.07 – 2.91 m	-0.07~0.09	39.4	39.4	0
<b>11</b>	—	—	—	178.5	178.5	0
<b>12</b>	1.43 d (6.6)	1.45 – 1.35 m	-0.08~0.02	13.9	14.0	0.1
<b>13</b>	2.55 t (7.1)	2.57 – 2.47 m	-0.08~0.02	26.3	26.3	0
<b>14</b>	1.58 m	1.62 – 1.49 m	-0.09~0.04	31.6	31.5	-0.1
<b>15</b>	1.41 m	1.45 – 1.35 m	-0.06~0.04	22.6	22.6	0
<b>16</b>	0.96 t (7.3)	0.94 t (7.3)	-0.02	13.9	13.9	0

[a] deviation=synthesized-natural

[b] Proton chemical shifts are reported relative to internal standard TMS at  $\delta$  0.0 ppm or residual solvent peak of CDCl<sub>3</sub> at 7.26 ppm.

[c] Carbon chemical shifts are reported relative to a residual solvent peak of CDCl<sub>3</sub> at 77.06 ppm.

Comparison of the NMR data of synthetic 3-*n*-butylneostemonine (7) with the natural one.

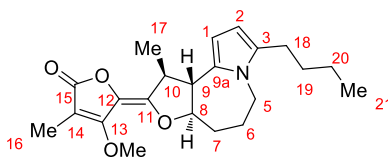


7: 3-*n*-butylneostemonine

position	$\delta_H$ mult. ( <i>J</i> in Hz)			$\delta_C$		
	natural sample	our synthetic sample <sup>[b]</sup>	deviation <sup>[a]</sup>	natural sample	our synthetic sample <sup>[b]</sup>	deviation <sup>[a]</sup>
	<sup>1</sup> H NMR (500 MHz, CDCl <sub>3</sub> )	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> )		<sup>13</sup> C NMR (125 MHz, CDCl <sub>3</sub> )	<sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> )	
<b>1<math>\beta</math></b>	5.91 d (3.1)	5.90 d (3.3)	-0.01	102.7	102.7	0
<b>1<math>\alpha</math></b>						
<b>2<math>\alpha</math></b>	5.82 d (3.1)	5.80 d (3.3)	-0.02	104.1	104.1	0
<b>2<math>\beta</math></b>						
<b>3</b>	—	—	—	134.3	134.3	0
<b>5<math>\beta</math></b>	4.18 m	4.22 – 4.13 m	-0.05~0.04	44.3	44.3	0
<b>5<math>\alpha</math></b>	3.63 m	3.55 – 3.45 m	-0.18~0.08			
<b>6<math>\alpha</math></b>	2.13 m	2.14 – 2.04 m	-0.09~0.01	26.0	26.0	0
<b>6<math>\beta</math></b>	1.56 m	1.55 – 1.53 m	-0.03~-0.01			
<b>7<math>\beta</math></b>	2.58 m	2.61 – 2.55 m	-0.03~0.03	34.2	34.3	0.1
<b>7<math>\alpha</math></b>	1.82 m	1.87 – 1.75 m	-0.07~0.05			
<b>8<math>\alpha</math></b>	3.78 ddd (3.5, 10.2, 11.0)	3.77 td (10.8, 3.7)	-0.01	86.2	86.2	0
<b>8<math>\beta</math></b>	—	—	—			
<b>9</b>	2.95 dd (9.8, 10.2)	2.93 t (10.3)	-0.02	52.1	52.2	0.1
<b>9<math>\alpha</math></b>	—	—	—	128.0	128.1	0.1
<b>10</b>	3.52 dq (6.5, 9.8)	3.61 dd (14.7, 11.5)	0.09	39.6	39.6	0
<b>11</b>	—	—	—	149.1	149.1	0
<b>12</b>	—	—	—	125.3	125.4	0.1
<b>13</b>	—	—	—	163.3	163.3	0
<b>14</b>	—	—	—	97.4	97.5	0.1
<b>15</b>	—	—	—	170.2	170.1	-0.1
<b>16</b>	2.11 s	2.14 – 2.04 m	-0.07~0.03	9.2	9.3	0.1
<b>17</b>	1.53 d (6.5)	1.51 d (6.6)	-0.02	19.2	19.3	0.1
<b>18</b>	2.54 m	2.55 – 2.49 m	-0.05~0.01	26.4	26.4	0
<b>19</b>	1.58 m	1.61 – 1.57 m	-0.01~0.03	31.5	31.5	0
<b>20</b>	1.42 m	1.45 – 1.36 m	-0.06~0.03	22.6	22.6	0
<b>21</b>	0.96 t (7.3)	0.94 t (7.3)	-0.02	13.9	14.0	0.1
<b>OMe</b>	4.20 s	4.22 – 4.13 m	-0.07~0.02	58.9	58.9	0

[a]. deviation=synthesized-natural. [b] Proton or carbon chemical shifts are reported relative to residual solvent peak of CDCl<sub>3</sub> at 7.26 ppm or at 77.06 ppm.

Comparison of the NMR data of synthetic (*E*)-3-*n*-butylneostemonine (39) with the natural 3-*n*-butylneostemonine (7)



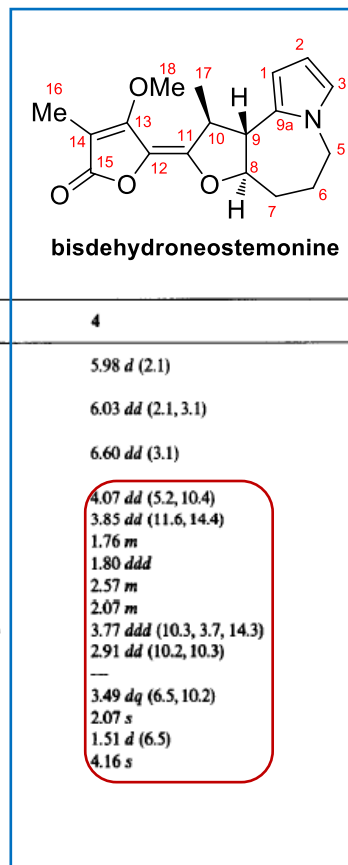
39: (*E*)-3-*n*-butylneostemonine

position	$\delta_H$ mult. ( <i>J</i> in Hz)			$\delta_C$		
	natural sample	our synthetic sample <sup>[b]</sup>	deviation <sup>[a]</sup>	natural sample	our synthetic sample <sup>[b]</sup>	deviation <sup>[a]</sup>
	<sup>1</sup> H NMR (500 MHz, CDCl <sub>3</sub> )	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> )		<sup>13</sup> C NMR (125 MHz, CDCl <sub>3</sub> )	<sup>13</sup> C NMR (151 MHz, CDCl <sub>3</sub> )	
<b>1<math>\beta</math></b>	5.91 d (3.1)	5.89 d (3.3)	-0.02	102.7	103.2	0.5
<b>1<math>\alpha</math></b>						
<b>2<math>\alpha</math></b>	5.82 d (3.1)	5.81 d (3.3)	-0.01	104.1	104.4	0.3
<b>2<math>\beta</math></b>						
<b>3</b>	—	—	—	134.3	134.1	-0.2
<b>5<math>\beta</math></b>	4.18 m	4.18 dd (14.5, 5.8)	0	44.3	44.3	0
<b>5<math>\alpha</math></b>	3.63 m	3.66 – 3.53 m	-0.10~0.03			
<b>6<math>\alpha</math></b>	2.13 m	2.14 – 2.07 m	-0.06~0.01	26.0	26.1	0.1
<b>6<math>\beta</math></b>	1.56 m	1.58 – 1.56 m	0~0.02			
<b>7<math>\beta</math></b>	2.58 m	2.58 – 2.48 m	-0.10~0	34.2	34.6	0.4
<b>7<math>\alpha</math></b>	1.82 m	1.87 – 1.76 m	-0.06~0.05			
<b>8<math>\alpha</math></b>	3.78 ddd (3.5, 10.2, 11.0)	3.85 td (10.9, 3.7)	0.07	86.2	87.0	0.8
<b>8<math>\beta</math></b>	—	—	—			
<b>9</b>	2.95 dd (9.8, 10.2)	2.86 t (10.7)	-0.09	52.1	50.6	-1.5
<b>9a</b>	—	—	—	128.0	127.8	-0.2
<b>10</b>	3.52 dq (6.5, 9.8)	3.66 – 3.53 m	0.01~0.14	39.6	41.8	2.2
<b>11</b>	—	—	—	149.1	150.8	1.7
<b>12</b>	—	—	—	125.3	126.4	1.1
<b>13</b>	—	—	—	163.3	163.8	0.5
<b>14</b>	—	—	—	97.4	98.3	0.9
<b>15</b>	—	—	—	170.2	170.7	0.5
<b>16</b>	2.11 s	2.06 s	-0.05	9.2	8.8	-0.4
<b>17</b>	1.53 d (6.5)	1.61 d (6.7)	0.08	19.2	17.0	-2.2
<b>18</b>	2.54 m	2.58 – 2.48 m	-0.06~0.04	26.4	26.4	0
<b>19</b>	1.58 m	1.55 – 1.48 m	-0.10~-0.03	31.5	31.6	0.1
<b>20</b>	1.42 m	1.44 – 1.35 m	-0.07~0.02	22.6	22.6	0
<b>21</b>	0.96 t (7.3)	0.94 t (7.3)	-0.02	13.9	14.0	0.1
<b>OMe</b>	4.20 s	4.13 s	-0.07	58.9	59.6	0.7

[a] deviation=synthesized-natural. [b] Proton or carbon chemical shifts are reported relative to residual solvent peak of CDCl<sub>3</sub> at 7.26 ppm or at 77.06 ppm.

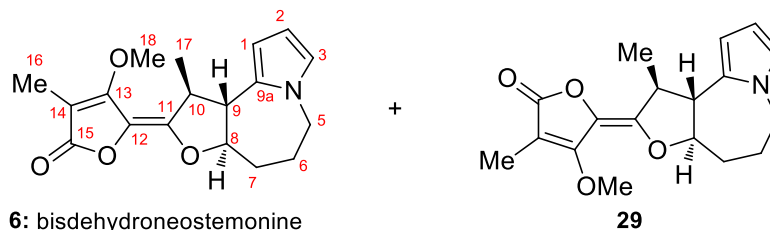
Comparison of the  $^1\text{H}$  NMR data of synthetic bisdehydroneostemonine (**6**) with the natural **6** and its E-isomer **29**.

The H-NMR data of bisdehydroneostemonine in the original paper<sup>6</sup>:



H	1	2	5	3	4
1	5.95 <i>d</i> (3.8)	1.89 <i>ddd</i>	1.92 <i>m</i>	2.24 <i>m</i>	5.98 <i>d</i> (2.1)
2	6.13 <i>d</i> (3.8)	1.55 <i>m</i>	1.55 <i>m</i>	1.85 <i>m</i>	6.03 <i>dd</i> (2.1, 3.1)
3	—	1.87 <i>m</i>	1.89 <i>m</i>	2.25 <i>m</i>	6.60 <i>dd</i> (3.1)
5	—	1.48 <i>m</i>	1.48 <i>m</i>	2.05 <i>m</i>	4.07 <i>dd</i> (5.2, 10.4)
6	—	3.24 <i>ddd</i> (7.3, 7.5, 11.5)	3.27 <i>ddd</i>	3.67 <i>ddd</i>	3.85 <i>dd</i> (11.6, 14.4)
7	—	$\alpha$ 3.50 <i>dd</i> (14.8, 4.8)	$\alpha$ 3.48 <i>dd</i> (4.0, 15.5)	3.10 <i>ddd</i> (6.4, 3.0, 15.8)	1.76 <i>m</i>
8	—	$\beta$ 2.89 <i>dd</i> (11.2, 14.8)	$\beta$ 2.92 <i>dd</i> (7.1, 15.2)	3.35 <i>m</i>	1.80 <i>ddd</i>
9	—	1.50 <i>m</i>	1.50 <i>m</i>	3.35 <i>m</i>	2.57 <i>m</i>
10	—	1.65 <i>m</i>	1.65 <i>m</i>	2.14 <i>m</i>	2.07 <i>m</i>
11	—	2.32 <i>m</i>	2.32 <i>m</i>	1.85 <i>m</i>	3.77 <i>ddd</i> (10.3, 3.7, 14.3)
12	—	1.50 <i>m</i>	1.50 <i>m</i>	1.62 <i>m</i>	2.91 <i>dd</i> (10.2, 10.3)
13	—	4.18 <i>ddd</i>	4.08 <i>ddd</i> (10.4, 3.4, 14.3)	2.57 <i>m</i>	—
14	—	2.12 <i>ddd</i> (10.4, 10.3, 5.3)	2.19 <i>ddd</i> (10.4, 4.1, 9.5)	4.18 <i>ddd</i> (10.8, 10.7, 3.7)	3.49 <i>dq</i> (6.5, 10.2)
15	—	3.69 <i>ddd</i> (5.6, 10.7, 10.6)	3.73 <i>m</i>	2.22 <i>ddd</i>	2.07 <i>s</i>
16	—	3.01 <i>dq</i> (6.7, 10.5)	2.89 <i>m</i>	4.27 <i>m</i>	1.51 <i>d</i> (6.5)
17	—	2.01 <i>s</i>	2.04 <i>s</i>	2.91 <i>dq</i> (6.8, 10.1)	2.07 <i>s</i>
18	—	1.32 <i>d</i> (6.7)	1.41 <i>d</i> (6.6)	2.05 <i>s</i>	4.16 <i>s</i>
19	—	4.14 <i>ddd</i>	4.15 <i>ddd</i> (11.1, 5.5, 5.4)	1.40 <i>d</i> (6.8)	—
20	—	$\alpha$ 2.36 <i>ddd</i>	2.35 <i>m</i>	4.10 <i>s</i>	—
21	—	$\beta$ 1.52 <i>m</i>	1.52 <i>m</i>	—	—
22	—	2.58 <i>ddq</i>	2.60 <i>ddq</i> (12.0, 8.5, 7.0)	—	—
23	—	1.24 <i>d</i> (6.9)	1.23 <i>d</i> (7.0)	—	—
24	—	4.10 <i>s</i>	4.10 <i>s</i>	—	—

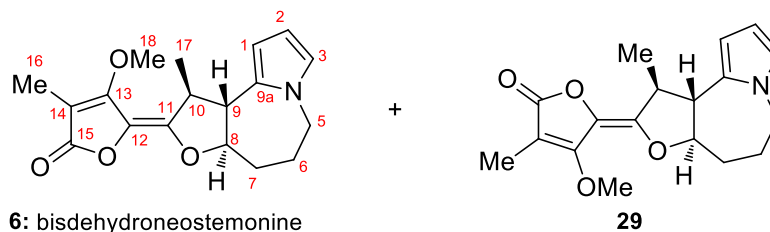
When we compared the H-NMR of our synthesised bisdehydroneostemonine (**6**) with the natural sample, we found that the authors of the original paper incorrectly attributed the chemical shifts of H-5, H-6, H-7, H-8, H-9, H-10, H-11, H-12, H-13, H-14, H-15, H-16, H-17 and H-18. The revised H-NMR data are shown in the table below.



position	$\delta_{\text{H}}$ mult. ( $J$ in Hz)		
	natural sample (after revision)	our synthetic sample 6 <sup>[a]</sup>	our synthetic sample 29 <sup>[a]</sup>
	<sup>1</sup> H NMR (500 MHz, CDCl <sub>3</sub> )	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> )	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> )
1	5.98 (d, $J=2.1$ )	6.02 – 5.99 (m, 1H)	6.01 – 5.98 (m, 1H)
2	6.03 (dd, $J=2.1, 3.1$ )	6.04 (t, $J = 3.1$ Hz, 1H)	6.07 – 6.02 (m, 1H)
3	6.60 (dd, $J=3.1$ )	6.61 (t, $J = 2.3$ Hz, 1H)	6.61 (t, $J = 2.2$ Hz, 1H)
5	4.07 (dd, $J=5.2, 10.4$ )	4.15 – 4.06 (m, 1H)	4.12 – 4.06 (m, 1H)
	3.85 (dd, $J=11.6, 14.4$ )	3.86 (dd, $J = 14.8, 11.3$ Hz, 1H)	3.91 – 3.81 (m, 1H)
6	1.76 (m)	1.72 – 1.62 (m, 1H)	1.72 – 1.66 (m, 1H)
	1.80 (ddd)	1.86 – 1.74 (m, 1H)	1.87 – 1.75 (m, 1H)
7	2.57 (m)	2.62 – 2.53 (m, 1H)	2.59 – 2.52 (m, 1H)
	2.07 (m)	2.13 – 2.03 (m, 1H)	2.13 – 2.07 (m, 1H)
8	3.77 (ddd, $J=10.3, 3.7, 14.3$ )	3.77 (td, $J = 10.7, 3.6$ Hz, 1H)	3.91 – 3.81 (m, 1H)
9	2.91 (dd, $J=10.2, 10.3$ )	2.93 (t, $J = 10.2$ Hz, 1H)	2.86 (t, $J = 10.7$ Hz, 1H)
10	3.49 (dq, $J=6.5, 10.2$ )	3.56 – 3.47 (m, 1H)	3.63 – 3.53 (m, 1H)
16	2.07 (s)	2.13 – 2.03 (m, 3H)	2.06 (s, 3H)
17	1.51 (d, $J=6.5$ )	1.52 (d, $J = 6.6$ Hz, 3H)	1.62 (d, $J = 6.7$ Hz, 3H)
18	4.16 (s)	4.19 (s, 3H)	4.13 (s, 3H)

[a] Proton chemical shifts are reported relative to residual solvent peak of CDCl<sub>3</sub> at 7.26 ppm.

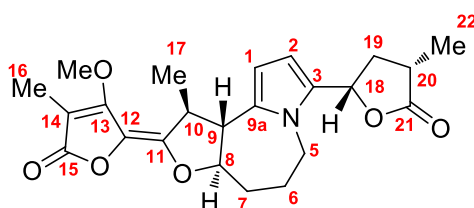
Comparison of the  $^{13}\text{C}$  NMR data of synthetic bisdehydroneostemonine (**6**) with the natural **6** and its E-isomer **29**.



Carbon position	natural sample	our synthetic sample <b>6</b> <sup>[a]</sup>	our synthetic sample <b>29</b> <sup>[a]</sup>
	$^{13}\text{C}$ NMR (? MHz, $\text{CDCl}_3$ )	$^{13}\text{C}$ NMR (101 MHz, $\text{CDCl}_3$ )	$^{13}\text{C}$ NMR (101 MHz, $\text{CDCl}_3$ )
<b>1</b>	104.8	104.8	105.1
<b>2</b>	106.6	106.2	106.4
<b>3</b>	122.6	122.7	122.5
<b>5</b>	49.3	49.3	49.2
<b>6</b>	26.3	26.2	26.2
<b>7</b>	34.1	34.0	34.3
<b>8</b>	86.1	86.0	<b>86.9</b>
<b>9</b>	52.2	52.0	<b>50.3</b>
<b>9a</b>	128.7	128.6	128.3
<b>10</b>	39.8	39.8	<b>41.9</b>
<b>11</b>	148.7	148.8	<b>150.6</b>
<b>12</b>	122.6	<b>125.5</b>	<b>126.4</b>
<b>13</b>	165.4	<b>163.2</b>	<b>163.6</b>
<b>14</b>	98.0	97.6	98.0
<b>15</b>	167.9	<b>170.1</b>	<b>170.7</b>
<b>16</b>	19.3	19.3	<b>16.9</b>
<b>17</b>	9.2	9.3	8.9
<b>18</b>	58.9	58.9	<b>59.5</b>

[a] Carbon chemical shifts are reported relative to residual solvent peak of  $\text{CDCl}_3$  at 77.06 ppm.

Comparison of the <sup>1</sup>H NMR data of synthetic bisdehydroprotostemonine (9) with the natural sample

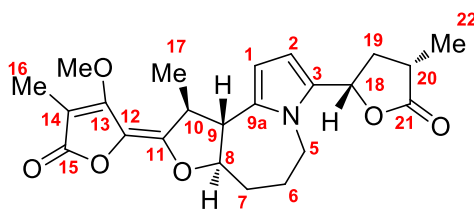


9: bisdehydroprotostemonine

Carbon position	natural sample Ye/Xu group	synthetic sample Chida/Sato group <sup>9</sup>	our synthetic sample <sup>[a]</sup>
	<sup>1</sup> H NMR (? MHz CDCl <sub>3</sub> ) *MHz was not reported	<sup>1</sup> H NMR (500 MHz, CDCl <sub>3</sub> )	<sup>1</sup> H NMR (600 MHz, CDCl <sub>3</sub> )
2	6.13 (d, J = 3.8 Hz, 1H)	6.14 (d, J = 3.7 Hz, 1H)	6.14 (d, J = 3.6 Hz, 1H)
1	5.95 (d, J = 3.8 Hz, 1H)	6.00 (d, J = 3.7 Hz, 1H)	6.00 (d, J = 3.5 Hz, 1H)
18	5.50 (dd, J = 11.0, 5.2 Hz, 1H)	5.39 (dd, J = 10.9, 5.2 Hz, 1H)	5.38 (dd, J = 10.9, 5.3 Hz, 1H)
5	4.37 (dd, J = 14.7, 5.6 Hz, 1H)	4.34 (dd, J = 14.6, 5.7 Hz, 1H)	4.34 (dd, J = 14.3, 5.4 Hz, 1H)
OMe	4.25 (s, 3H)	4.19 (s, 3H)	4.19 (s, 3H)
8	3.70 (ddd, J = 10.9, 10.2, 3.7 Hz, 1H)	3.77 (ddd, J = 10.3, 10.3, 3.7 Hz, 1H)	3.76 – 3.72 (m, 2H)
5	3.82 (dd, J = 14.7, 11.3 Hz, 1H)	3.72 (dd, J = 14.6, 11.2 Hz, 1H)	3.76 – 3.72 (m, 2H)
10	3.53 (dq, J = 10.2, 6.5 Hz, 1H)	3.52 (dq, J = 10.3, 6.6 Hz, 1H)	3.53 – 3.50 (m, 1H)
9	3.10 (t, J = 10.2, 1H)	2.98 (dd, J = 10.3, 10.3 Hz, 1H)	3.00 – 2.97 (m, 1H)
20	2.85 (m, 1H)	2.81 (m, 1H)	2.81 – 2.78 (m, 1H)
19	2.70 (ddd, 1H)	2.72 (ddd, J = 12.3, 8.3, 5.2 Hz, 1H)	2.73 – 2.70 (m, 1H)
7	2.47 (m, 1H)	2.60 (m, 1H)	2.62 – 2.60 (m, 1H)
19	2.15 (m, 1H)	2.21 (ddd, J = 12.3, 11.7, 10.9 Hz, 1H)	2.25 – 2.22 (m, 1H)
6	2.10 (m, 1H)	2.13 (m, 1H)	2.15 – 2.13 (m, 1H)
16	2.05 (s, 3H)	2.10 (s, 3H)	2.10 (s, 3H)
7	1.85 (m, 1H)	1.83 (m, 1H)	1.84 – 1.82 (m, 1H)
6	1.55 (m, 1H)	1.70 (m, 1H)	1.72 – 1.69 (m, 1H)
17	1.51 (d, J = 6.5 Hz, 3H)	1.51 (d, J = 6.6 Hz, 3H)	1.51 (d, J = 6.6 Hz, 3H)
22	1.25 (d, J = 7.1 Hz, 3H)	1.35 (d, J = 6.9 Hz, 3H)	1.36 (d, J = 7.1 Hz, 3H)

[a] Proton chemical shifts are reported relative to residual solvent peak of CDCl<sub>3</sub> at 7.26 ppm.

Comparison of the  $^{13}\text{C}$  NMR data of synthetic bisdehydroprotostemonine (**9**) with the natural sample



**9**: bisdehydroprotostemonine

Carbon position	natural sample Ye/Xu group	synthetic sample Chida/Sato group <sup>9</sup>	our synthetic sample <sup>[a]</sup>
	$^{13}\text{C}$ NMR (? MHz $\text{CDCl}_3$ ) *MHz was not reported	$^{13}\text{C}$ NMR (125 MHz, $\text{CDCl}_3$ )	$^{13}\text{C}$ NMR (151 MHz, $\text{CDCl}_3$ )
<b>21</b>	178.7	179.0	178.9
<b>15</b>	169.9	170.1	170.1
<b>13</b>	163.1	163.2	163.2
<b>11</b>	148.4	148.5	148.5
<b>3</b>	132.1	132.4	132.4
<b>9a</b>	129.8	129.5	129.5
<b>12</b>	125.4	125.6	125.6
<b>2</b>	106.9	107.1	107.1
<b>1</b>	103.4	103.7	103.7
<b>14</b>	97.6	97.8	97.8
<b>8</b>	85.5	85.7	85.7
<b>18</b>	71.4	71.6	71.6
<b>OMe</b>	58.8	59.0	59.0
<b>9</b>	51.9	52.0	52.1
<b>5</b>	45.3	45.6	45.6
<b>10</b>	39.4	39.6	39.6
<b>20</b>	35.9	36.1	36.1
<b>19</b>	34.8	34.9	35.0
<b>7</b>	34.1	34.3	34.3
<b>6</b>	25.6	25.8	25.8
<b>17</b>	19.2	19.4	19.4
<b>22</b>	14.9	15.2	15.2
<b>16</b>	9.1	9.4	9.4

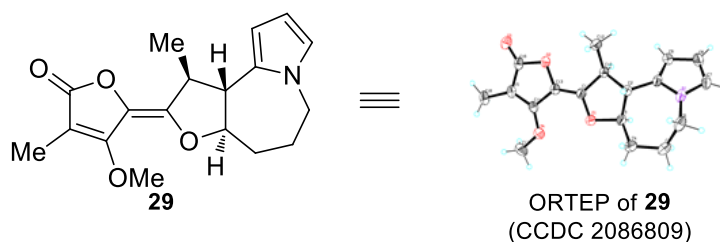
[a] Carbon chemical shifts are reported relative to residual solvent peak of  $\text{CDCl}_3$  at 77.06 ppm.



### III. CIF Check Reports for Compounds 29 and 14

#### CIF check report for compound 29

(CCDC: 2086809)



Bond precision: C-C = 0.0035 Å      Wavelength=1.54184

Cell:                    a=7.8432 (4)            b=8.2643 (4)            c=24.8497 (13)  
                          alpha=90                beta=90                 gamma=90

Temperature:            293 K

	Calculated	Reported
Volume	1610.72 (14)	1610.72 (15)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C18 H21 N O4	C18 H21 N O4
Sum formula	C18 H21 N O4	C18 H21 N O4
Mr	315.36	315.36
Dx, g cm <sup>-3</sup>	1.301	1.300
Z	4	4
Mu (mm <sup>-1</sup> )	0.750	0.750
F000	672.0	672.0
F000'	674.12	
h, k, lmax	9, 10, 30	9, 9, 30
Nref	3051 [ 1784]	2983
Tmin, Tmax	0.922, 0.993	0.659, 1.000
Tmin'	0.894	

Correction method= # Reported T Limits: Tmin=0.659 Tmax=1.000  
AbsCorr = MULTI-SCAN

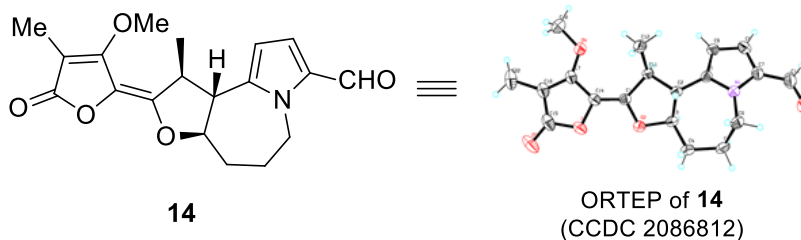
Data completeness= 1.67/0.98            Theta(max)= 69.987

R(reflections)= 0.0379 ( 2684)            wR2(reflections)= 0.0982 ( 2983)

S = 1.041                                    Npar= 211

CIF check report for compound 14

(CCDC: 2086812)



Bond precision: C-C = 0.0042 Å

Wavelength=0.71073

Cell: a=7.3435 (17) b=8.676 (2) c=13.843 (3)  
 alpha=90 beta=102.933 (3) gamma=90  
 Temperature: 296 K

	Calculated	Reported
Volume	859.6 (3)	859.6 (3)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C19 H21 N O5	?
Sum formula	C19 H21 N O5	C19 H21 N O5
Mr	343.37	343.37
Dx, g cm <sup>-3</sup>	1.327	1.327
Z	2	2
Mu (mm <sup>-1</sup> )	0.096	0.096
F000	364.0	364.0
F000'	364.19	
h, k, lmax	9, 10, 17	9, 10, 17
Nref	3626 [ 1938]	3526
Tmin, Tmax	0.977, 0.981	0.545, 0.745
Tmin'	0.972	

Correction method= # Reported T Limits: Tmin=0.545 Tmax=0.745  
 AbsCorr = MULTI-SCAN

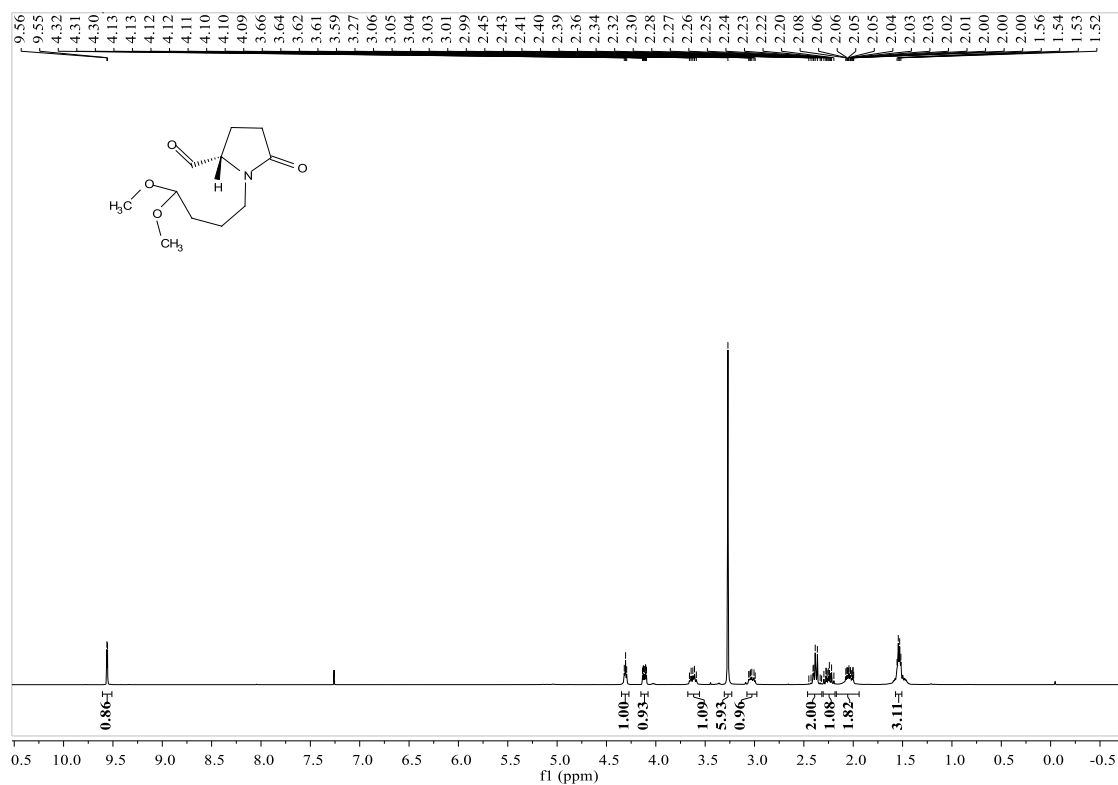
Data completeness= 1.82/0.97      Theta(max)= 26.652

R(reflections)= 0.0398 ( 2833)      wR2(reflections)= 0.0794 ( 3526)

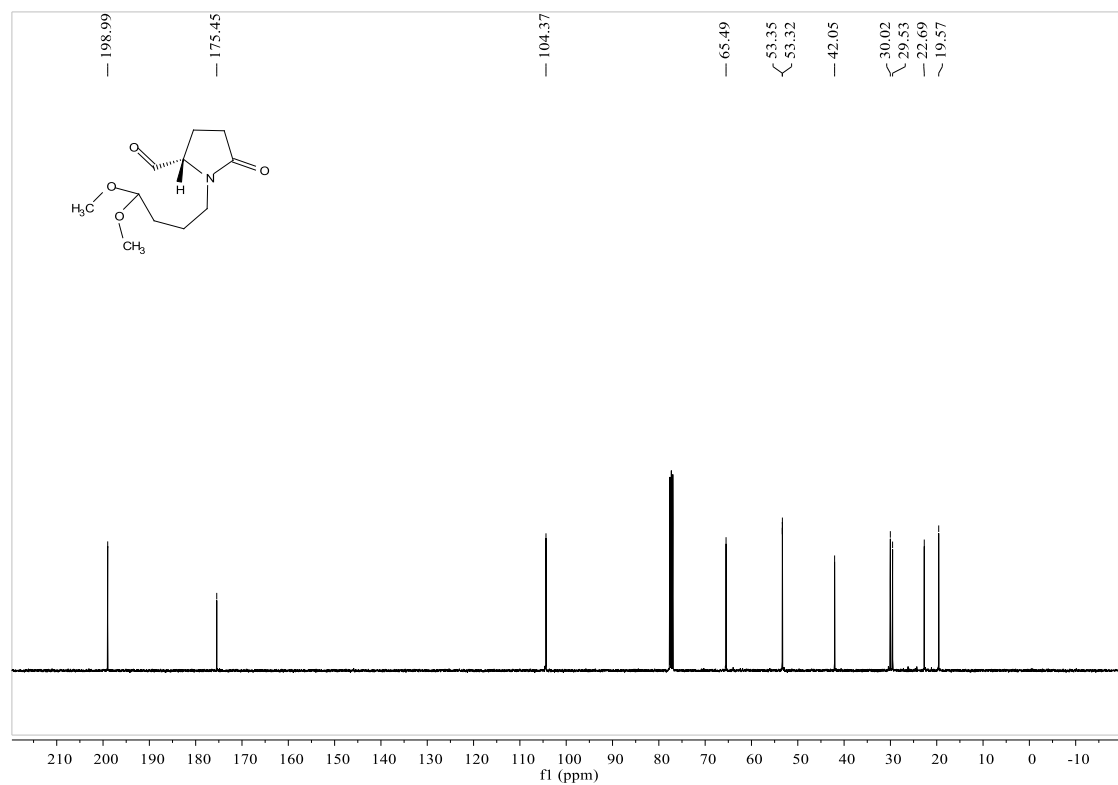
S = 0.999      Npar= 229

## IV. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

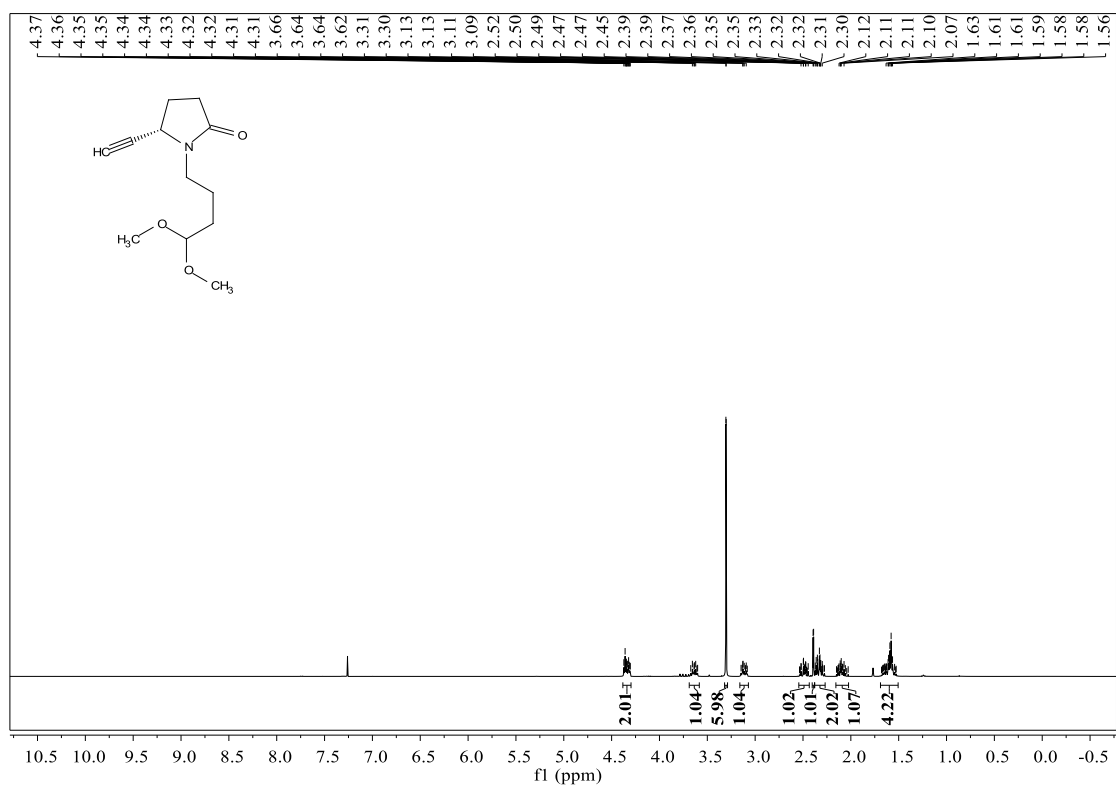
### $^1\text{H}$ NMR spectrum of compound 20 (400 MHz, $\text{CDCl}_3$ )



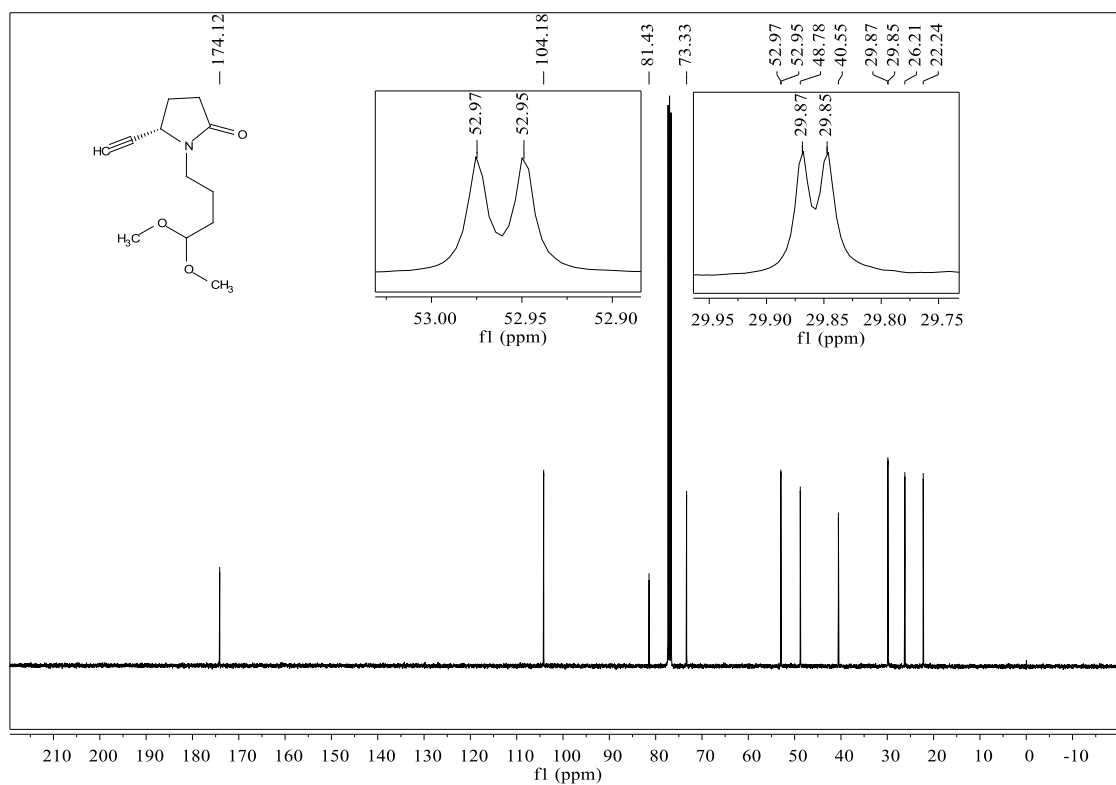
### $^{13}\text{C}$ NMR spectrum of compound 20 (101 MHz, $\text{CDCl}_3$ )



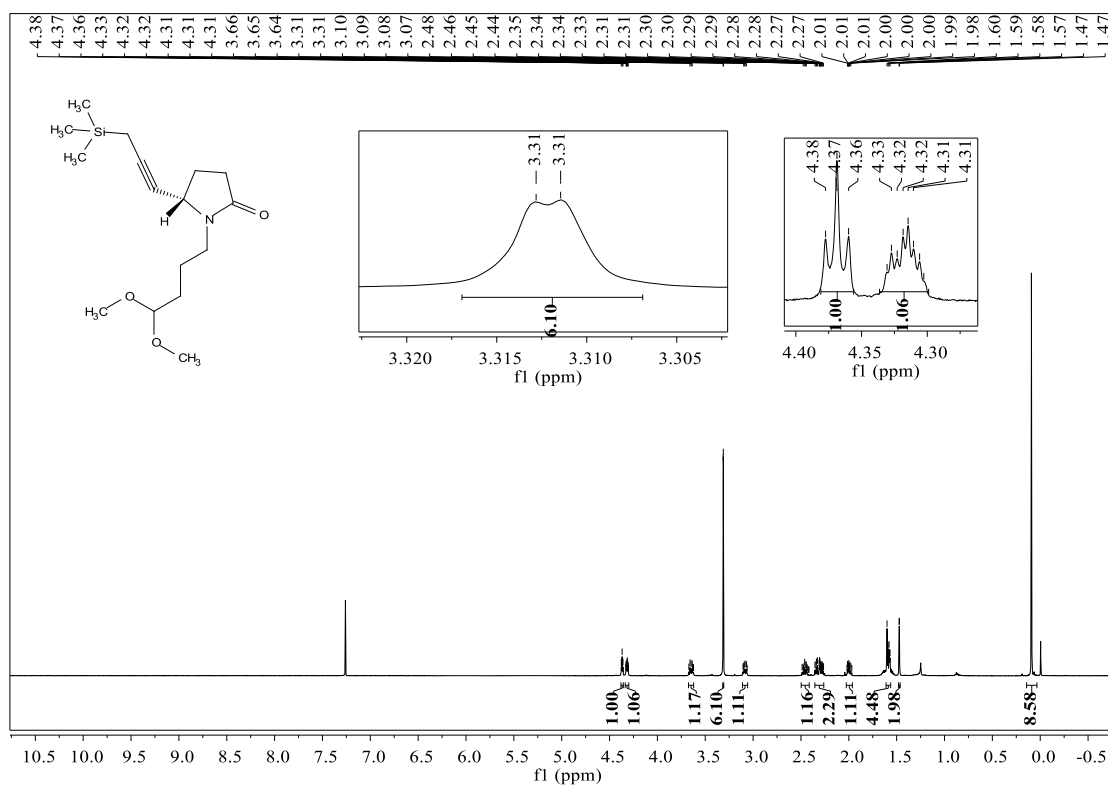
**<sup>1</sup>H NMR spectrum of compound 22 (400 MHz, CDCl<sub>3</sub>)**



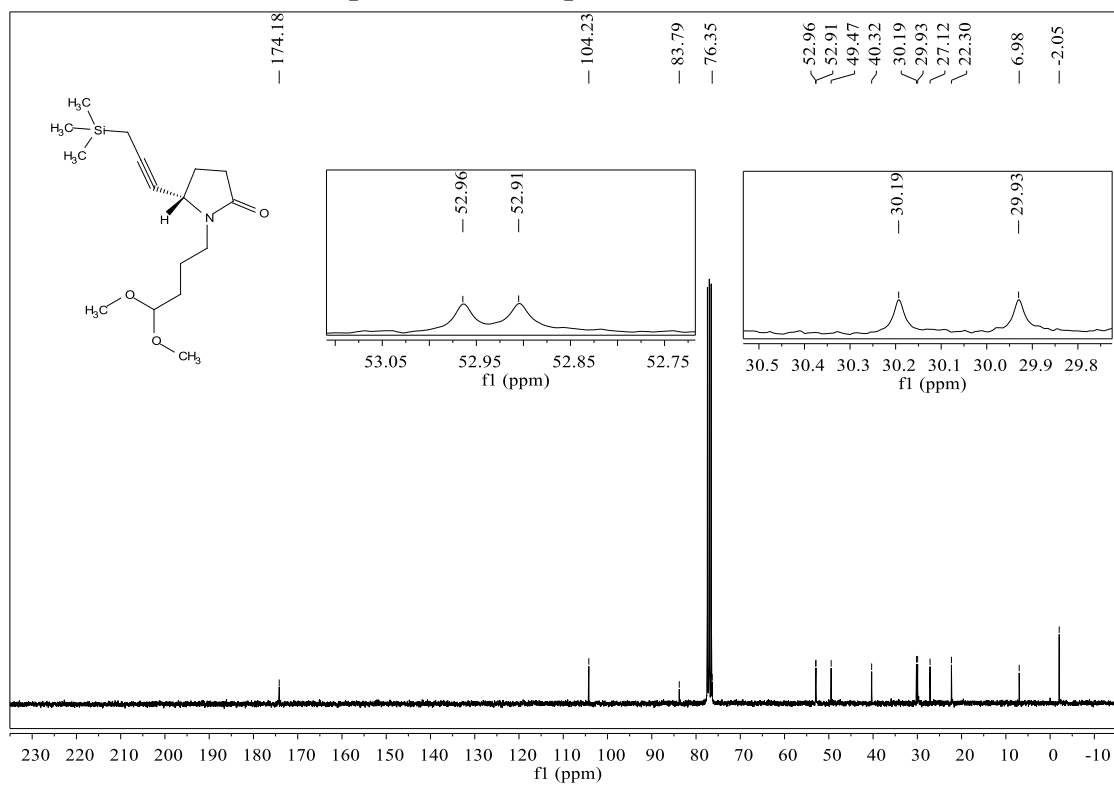
**<sup>13</sup>C NMR spectrum of compound 22 (101 MHz, CDCl<sub>3</sub>)**



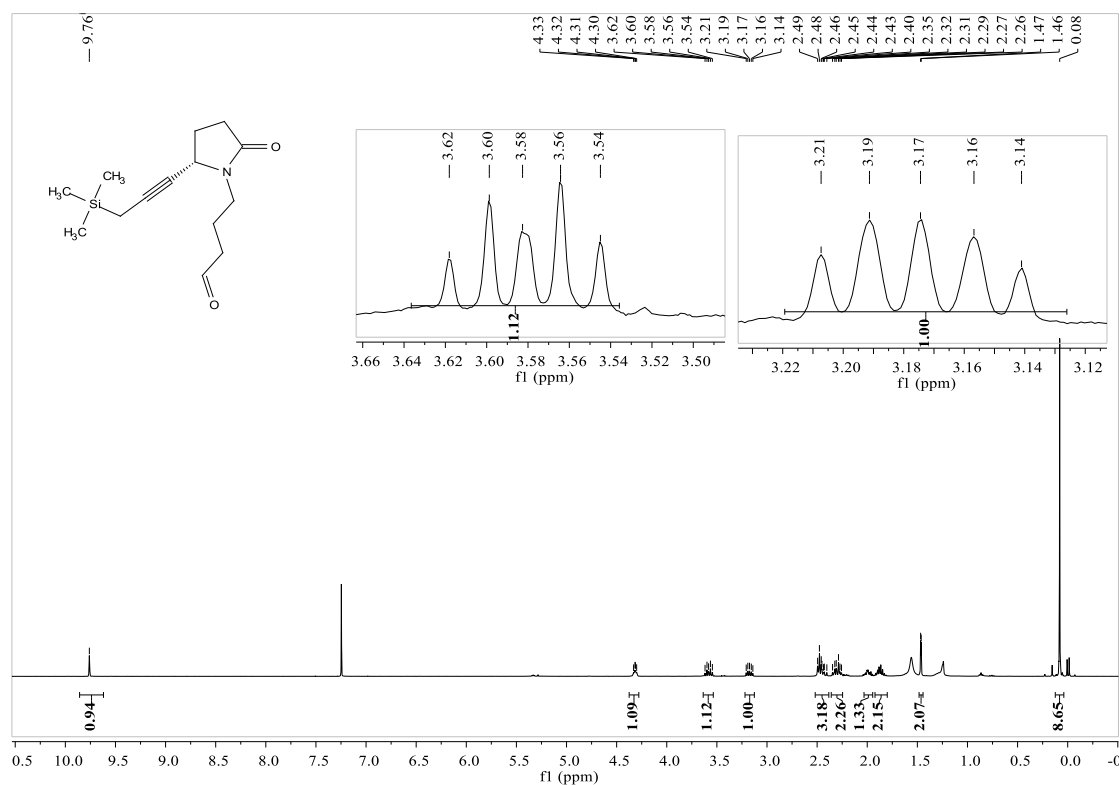
### <sup>1</sup>H NMR spectrum of compound 23 (600 MHz, CDCl<sub>3</sub>)



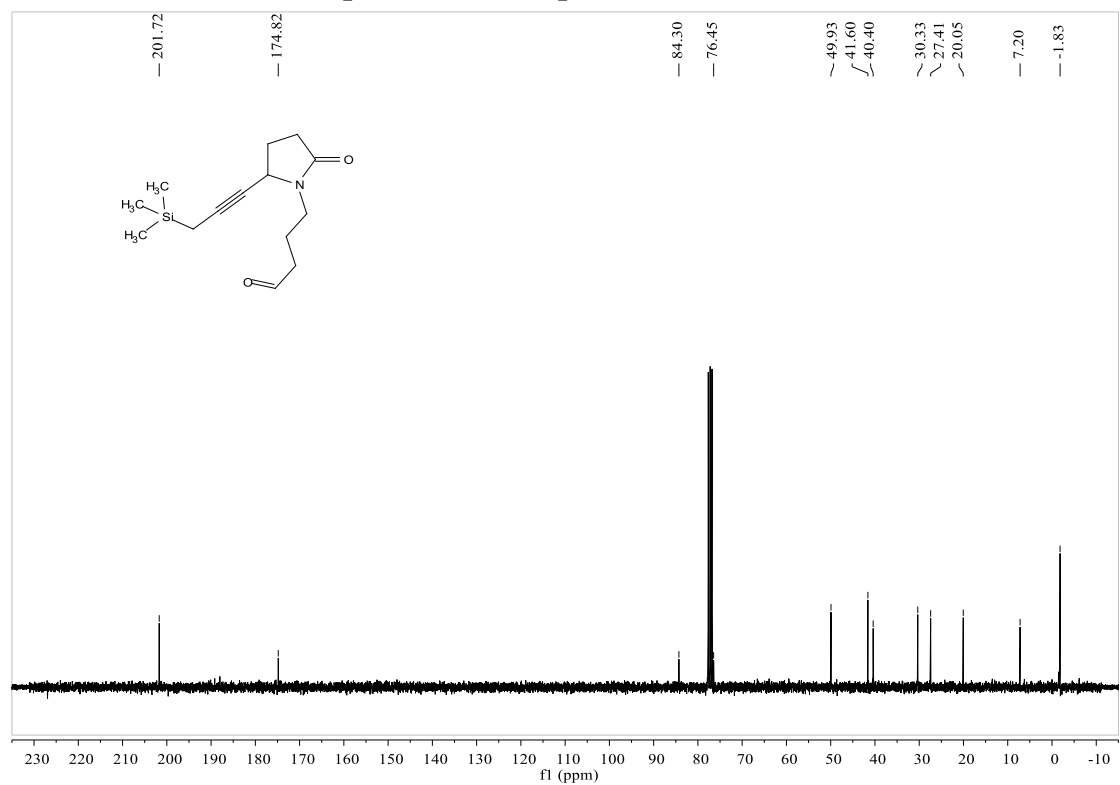
### <sup>13</sup>C NMR spectrum of compound 23 (75 MHz, CDCl<sub>3</sub>)



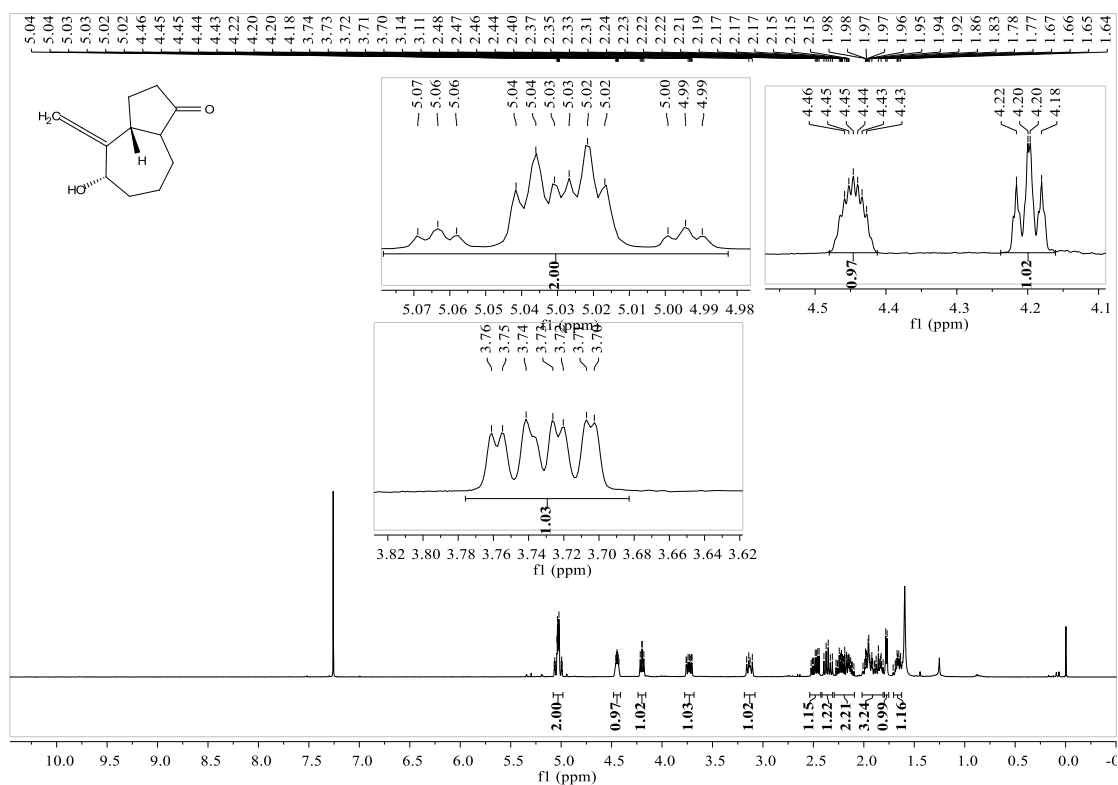
### <sup>1</sup>H NMR spectrum of compound 19 (400 MHz, CDCl<sub>3</sub>)



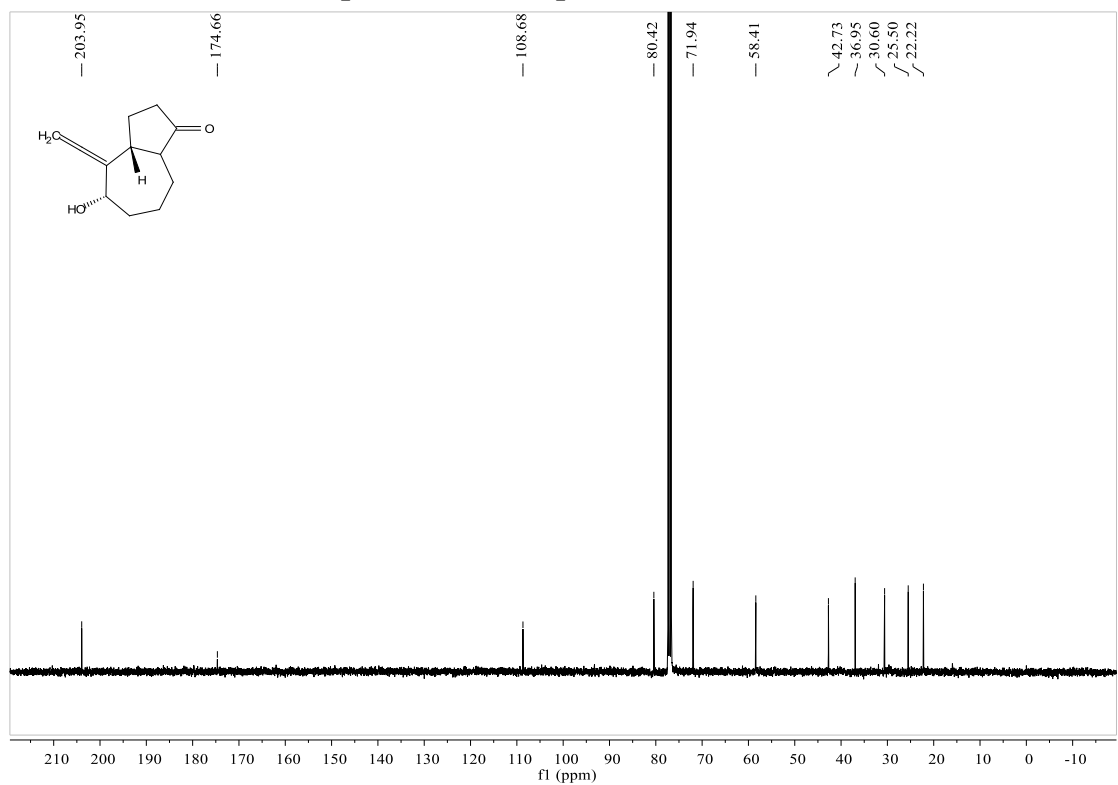
### <sup>13</sup>C NMR spectrum of compound 19 (101 MHz, CDCl<sub>3</sub>)



**<sup>1</sup>H NMR spectrum of compound 18 (400 MHz, CDCl<sub>3</sub>)**



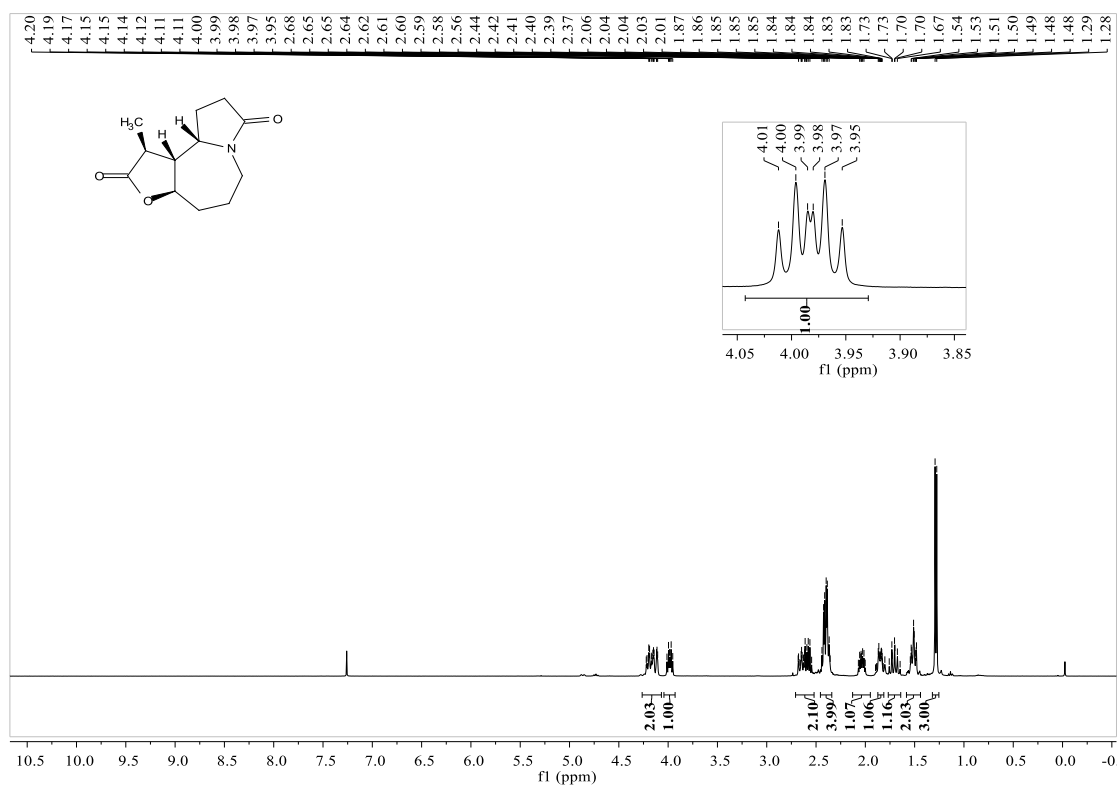
**<sup>13</sup>C NMR spectrum of compound 18 (101 MHz, CDCl<sub>3</sub>)**



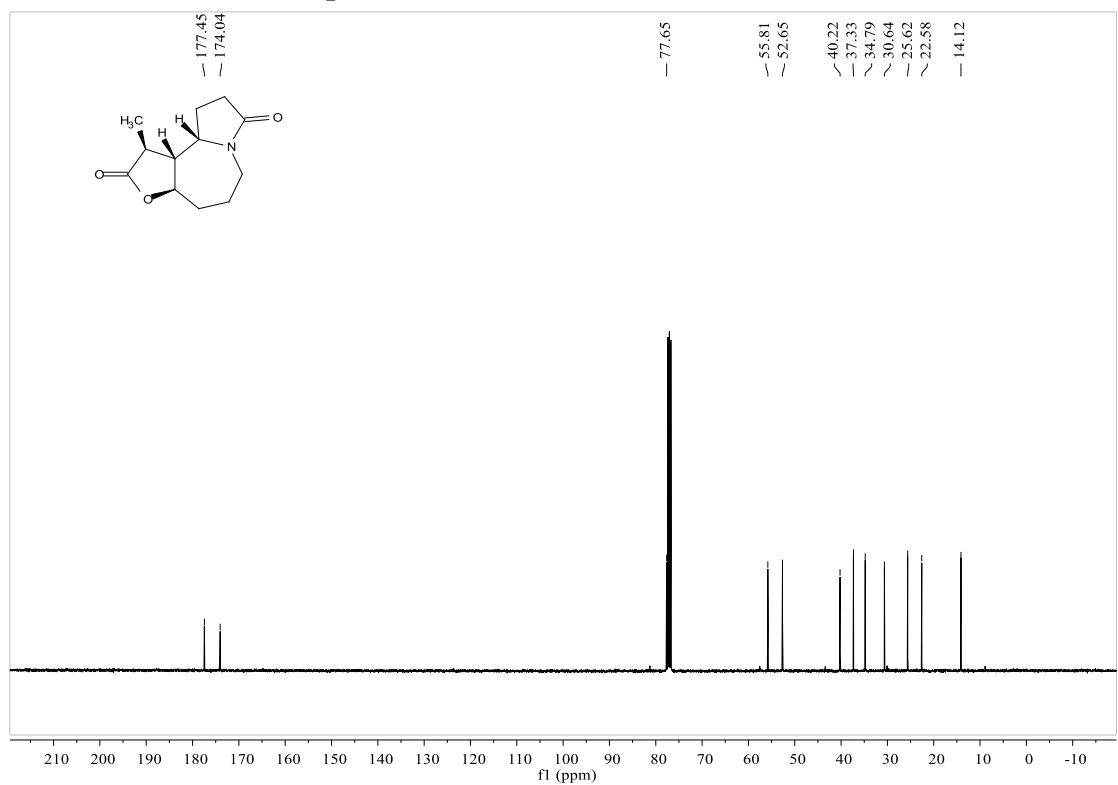




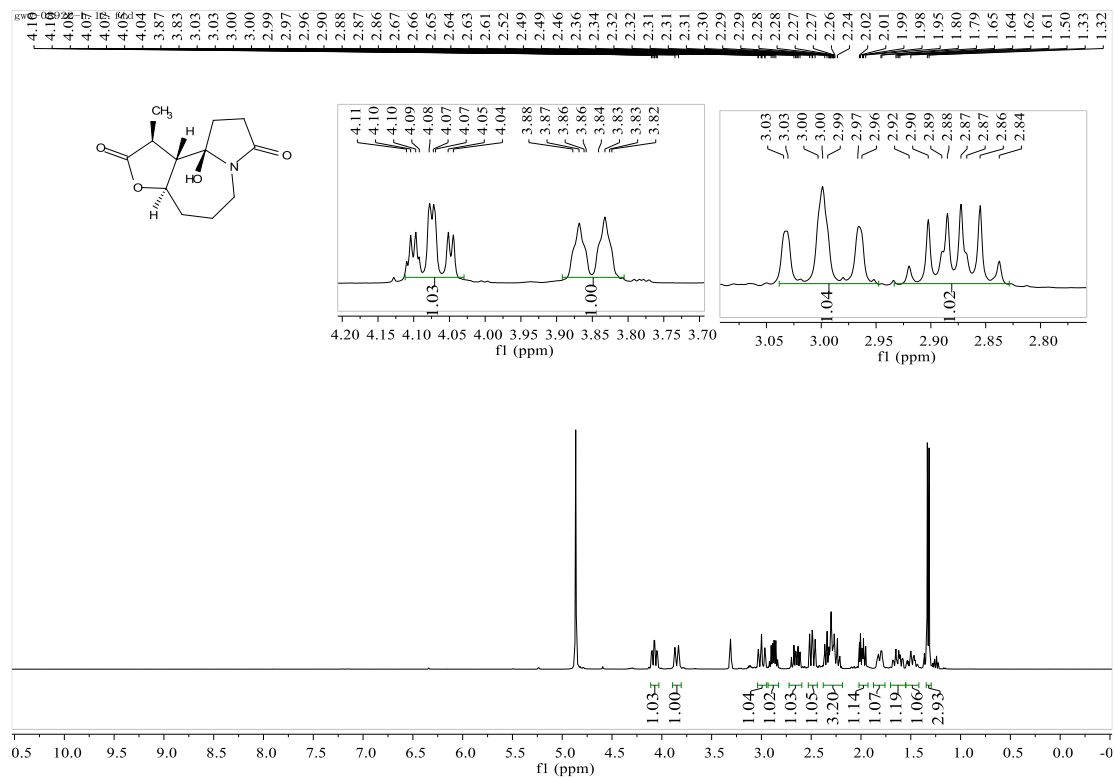
### <sup>1</sup>H NMR spectrum of Stemoamide (1) (400 MHz, CDCl<sub>3</sub>)



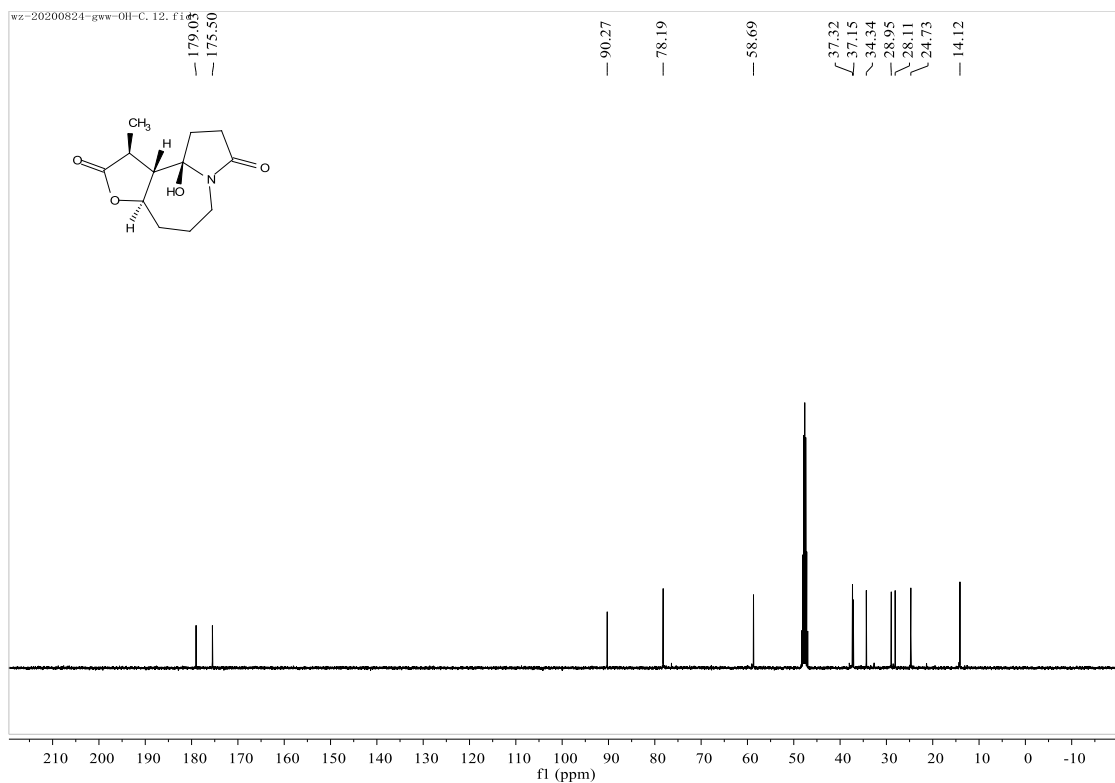
### <sup>13</sup>C NMR spectrum of Stemoamide (1) (101 MHz, CDCl<sub>3</sub>)



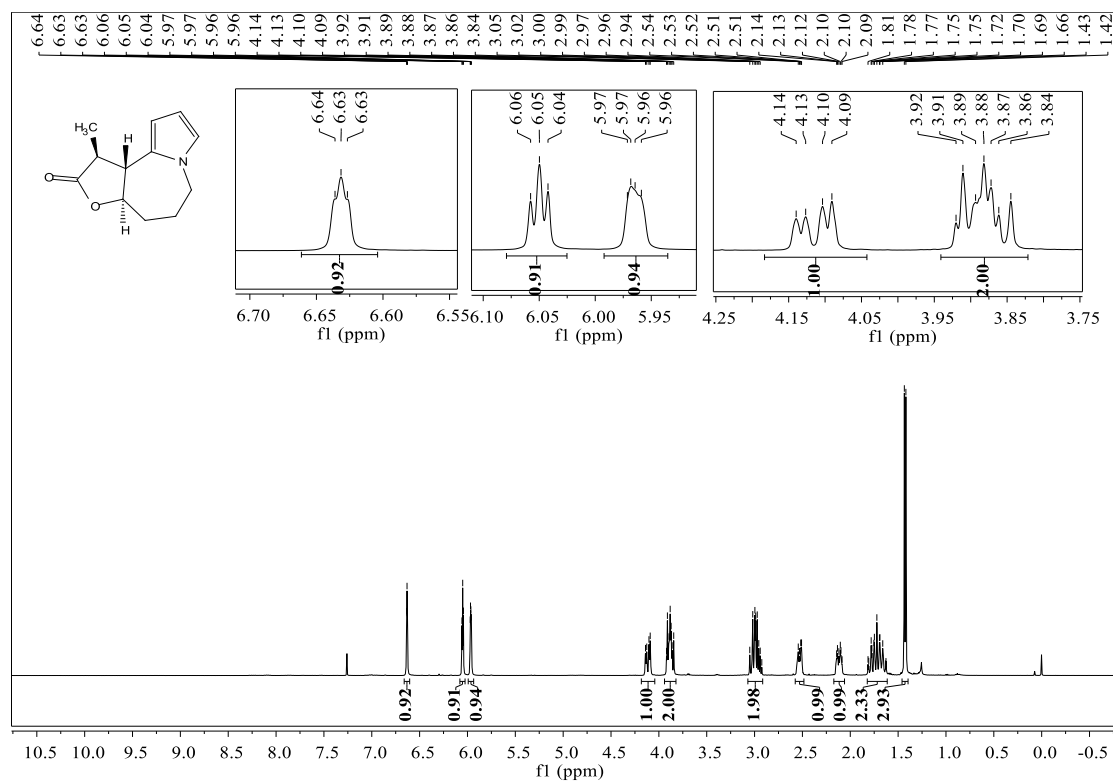
### <sup>1</sup>H NMR spectrum of compound 10 (400 MHz, methanol-d<sub>4</sub>)



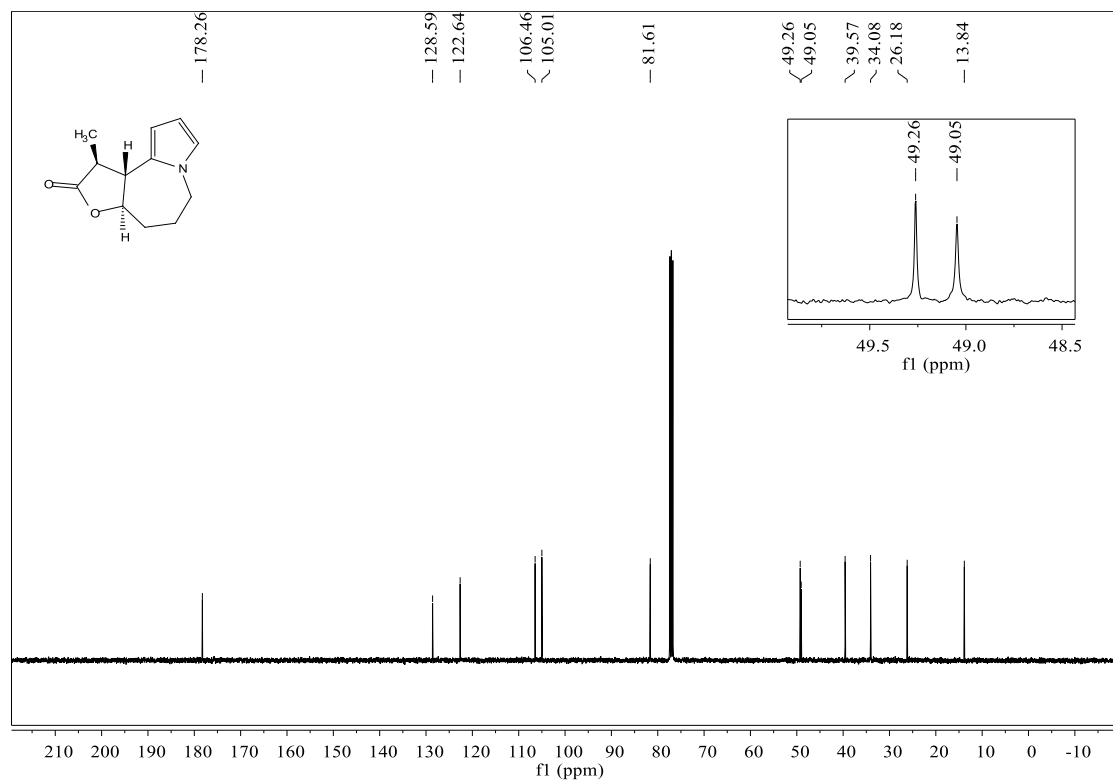
### <sup>13</sup>C NMR spectrum of compound 10 (101 MHz, methanol-d<sub>4</sub>)



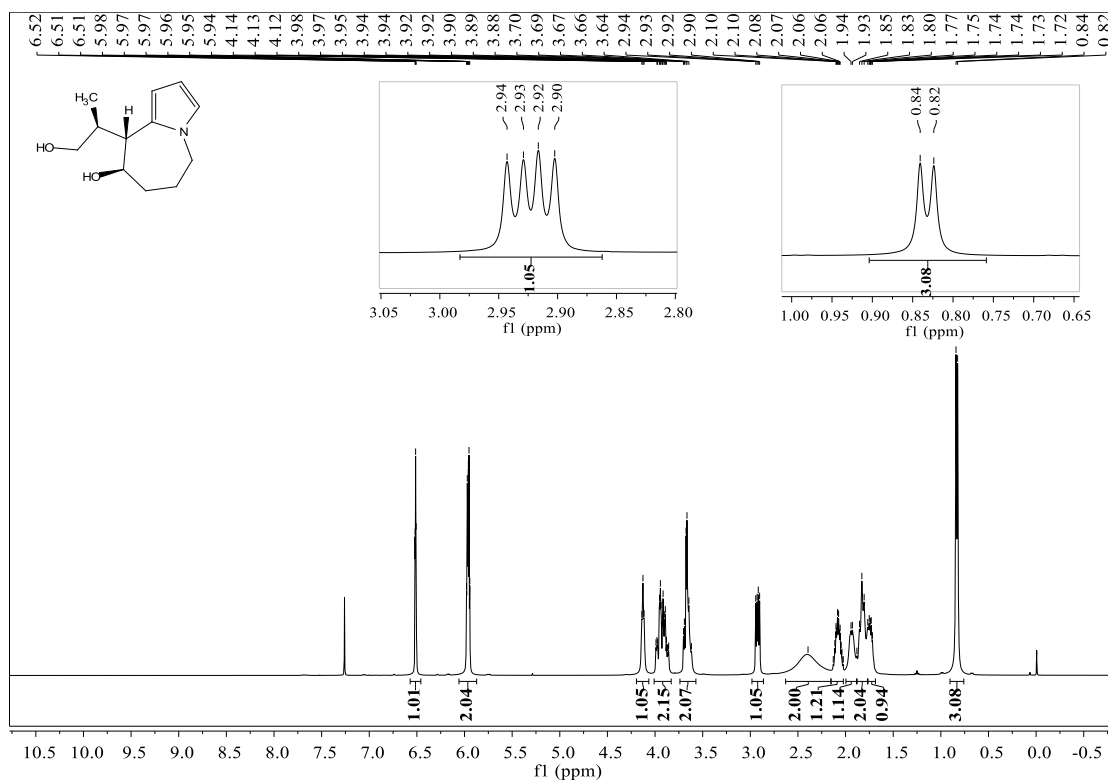
### <sup>1</sup>H NMR spectrum of compound 11 (400 MHz, CDCl<sub>3</sub>)



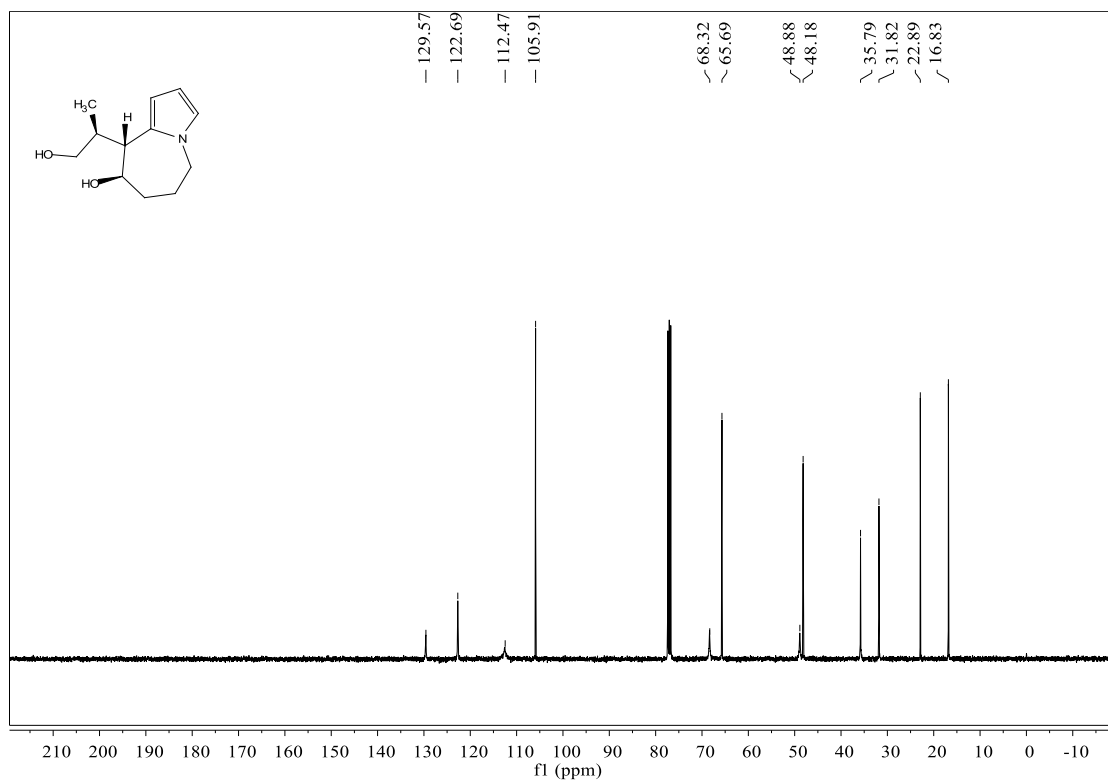
### <sup>13</sup>C NMR spectrum of compound 11 (101 MHz, CDCl<sub>3</sub>)



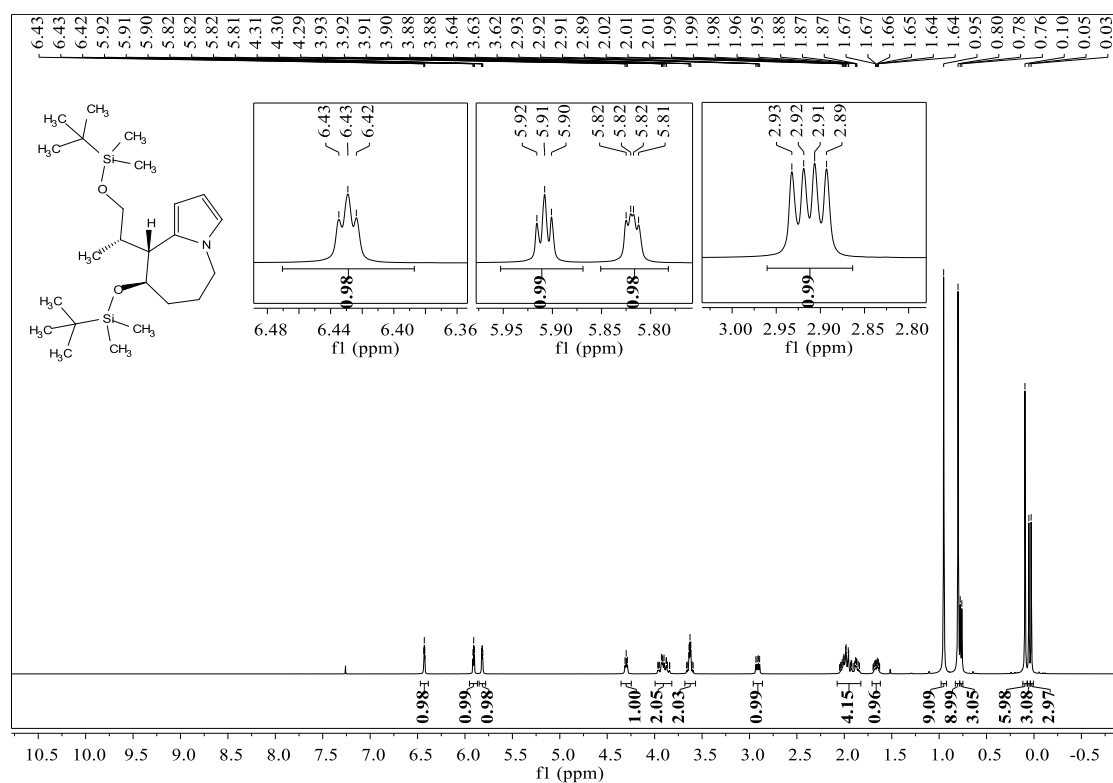
### <sup>1</sup>H NMR spectrum of compound 25 (400 MHz, CDCl<sub>3</sub>)



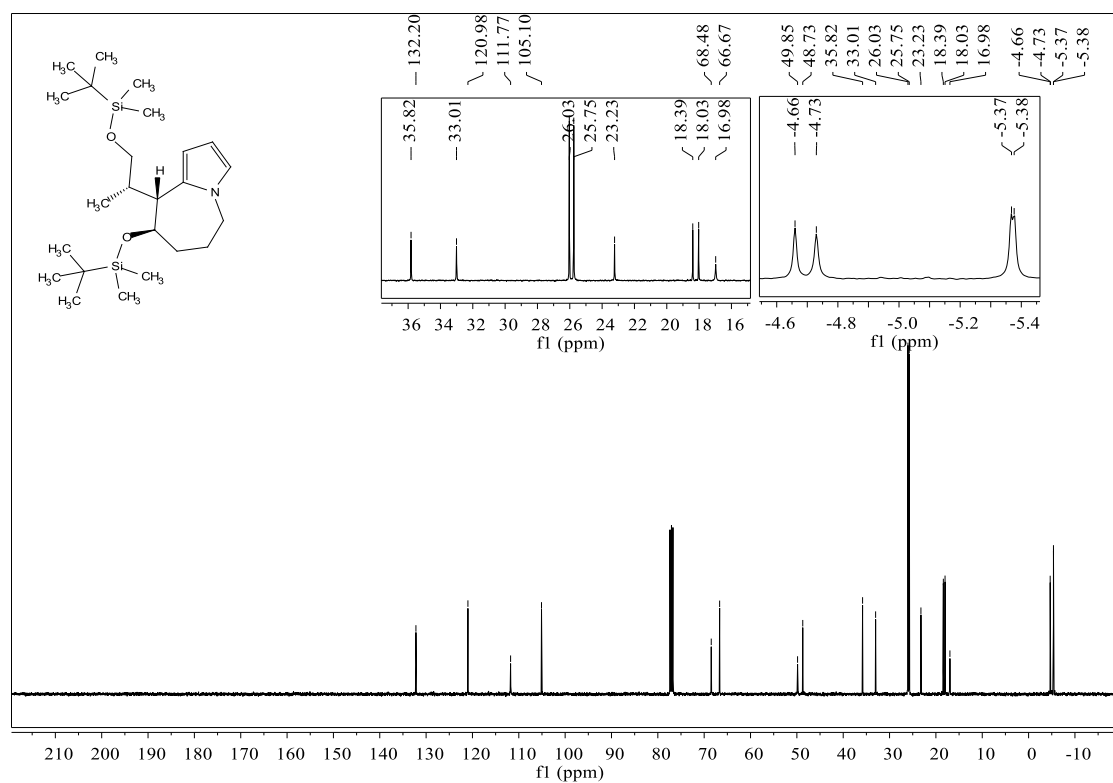
### <sup>13</sup>C NMR spectrum of compound 25 (101 MHz, CDCl<sub>3</sub>)



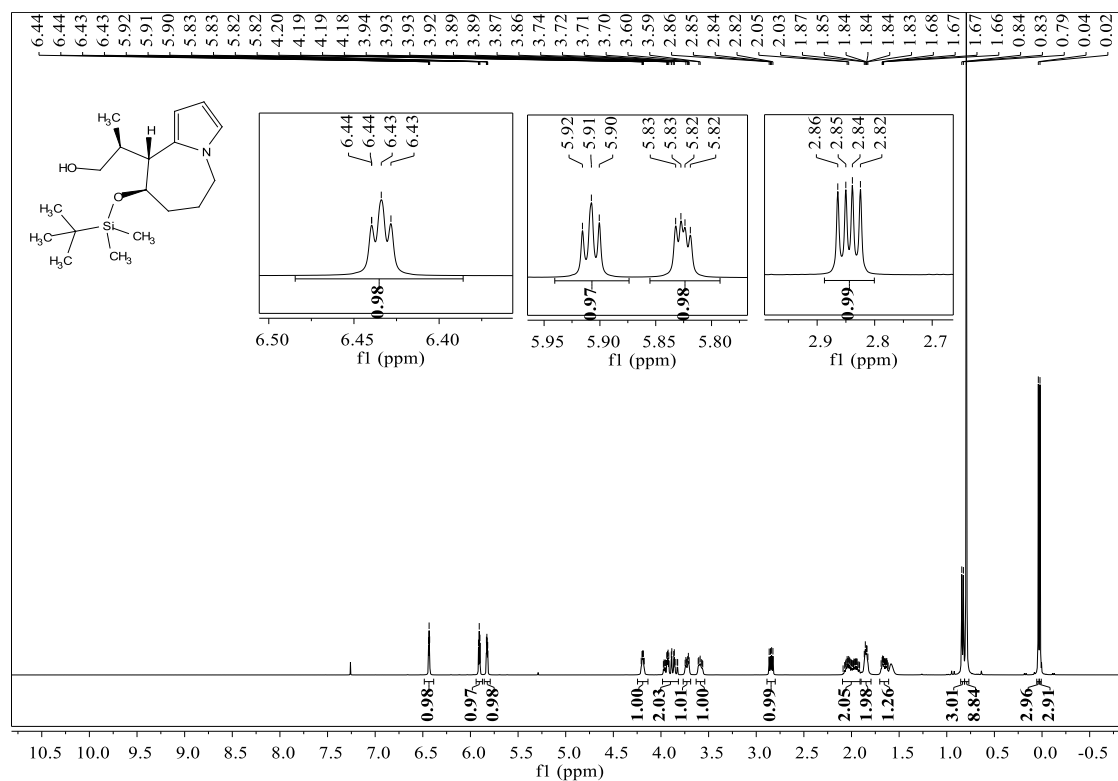
**<sup>1</sup>H NMR spectrum of compound 26 (400 MHz, CDCl<sub>3</sub>)**



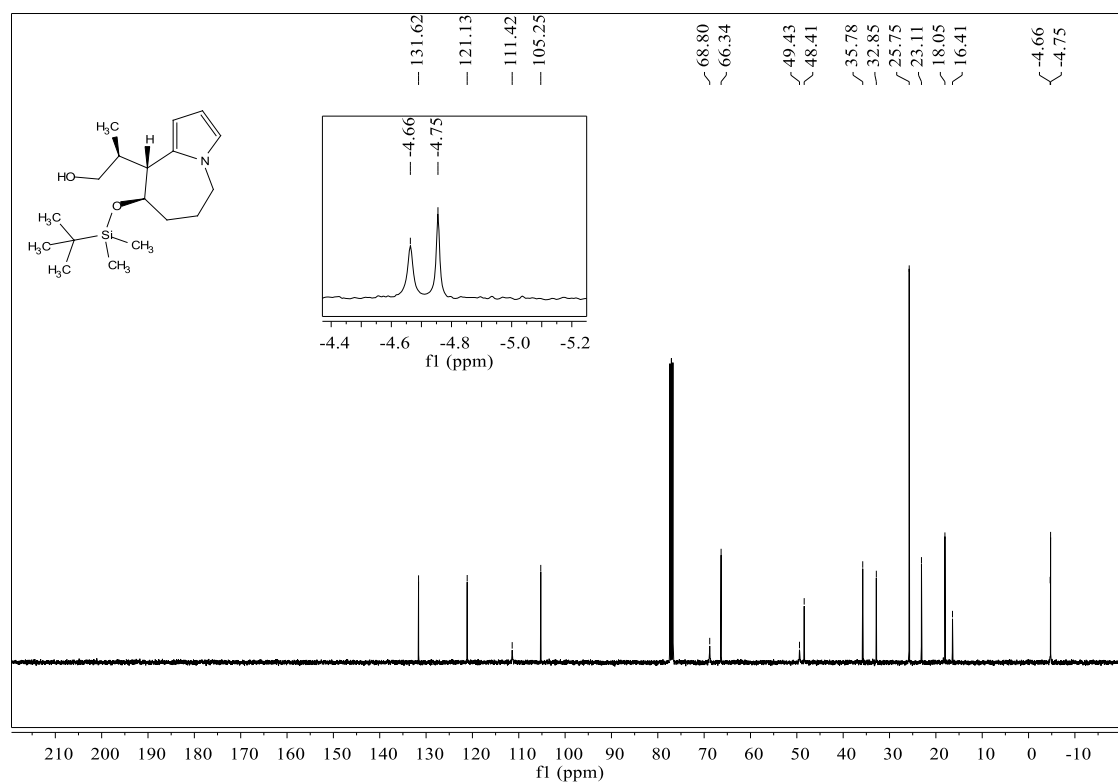
**<sup>13</sup>C NMR spectrum of compound 26 (101 MHz, CDCl<sub>3</sub>)**



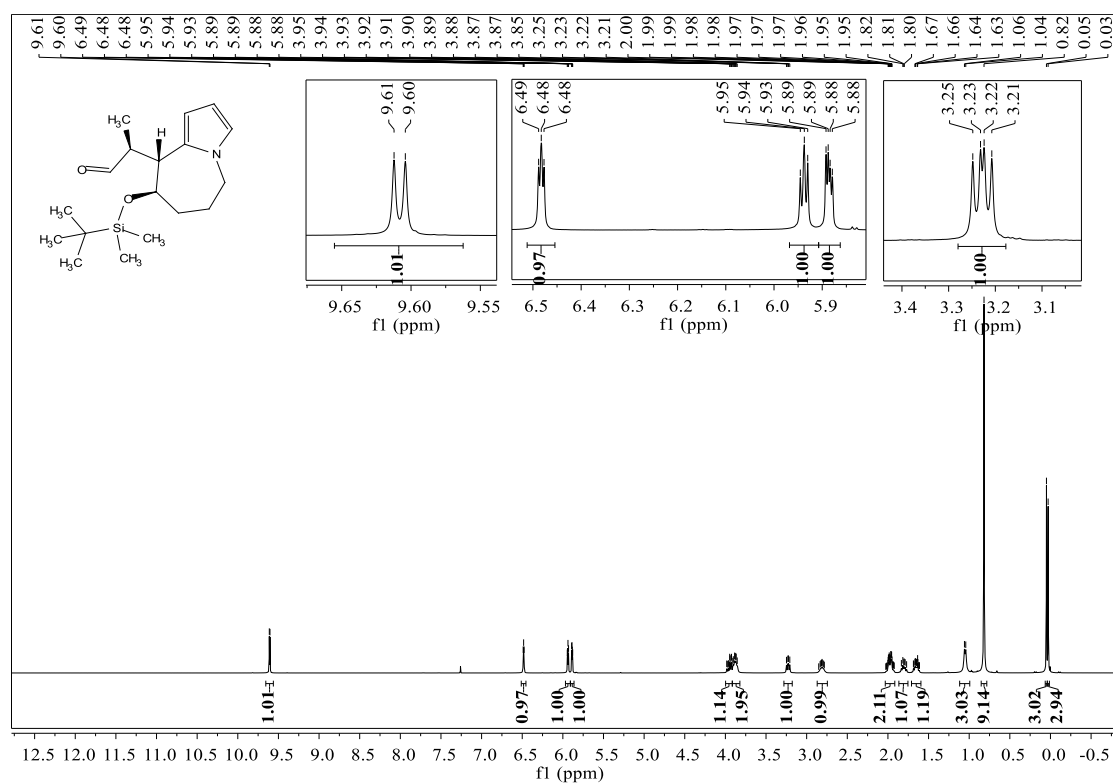
### <sup>1</sup>H NMR spectrum of compound 27 (400 MHz, CDCl<sub>3</sub>)



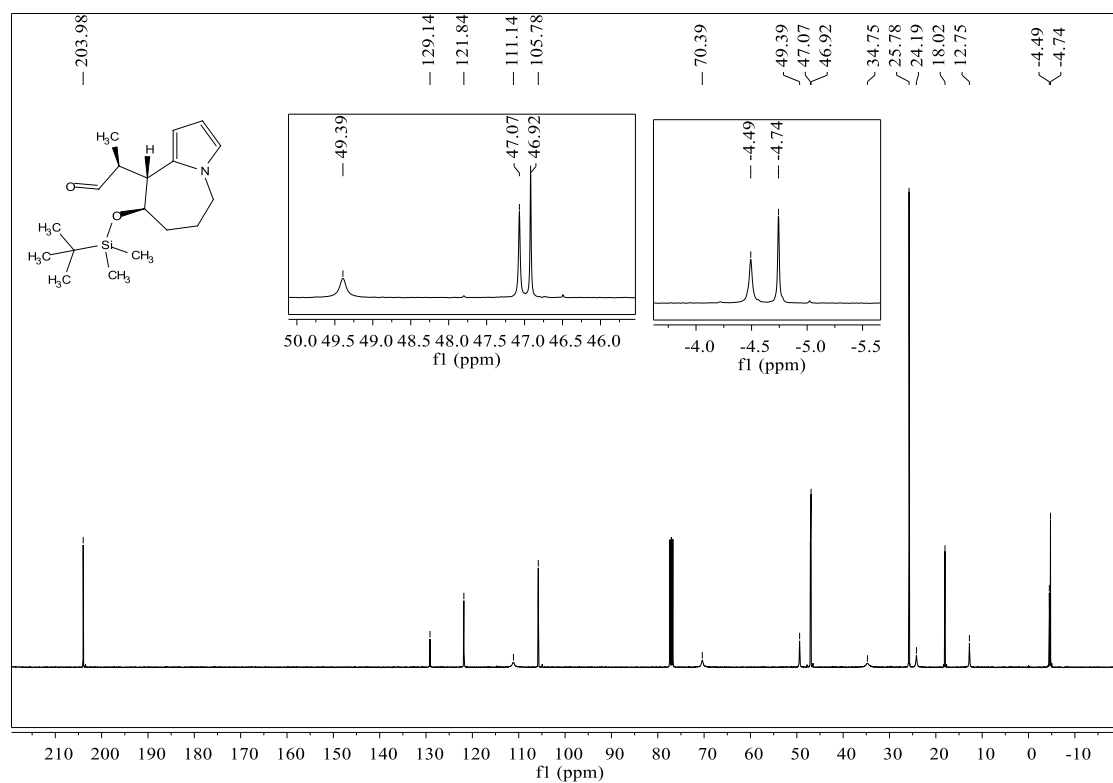
### <sup>13</sup>C NMR spectrum of compound 27 (101 MHz, CDCl<sub>3</sub>)



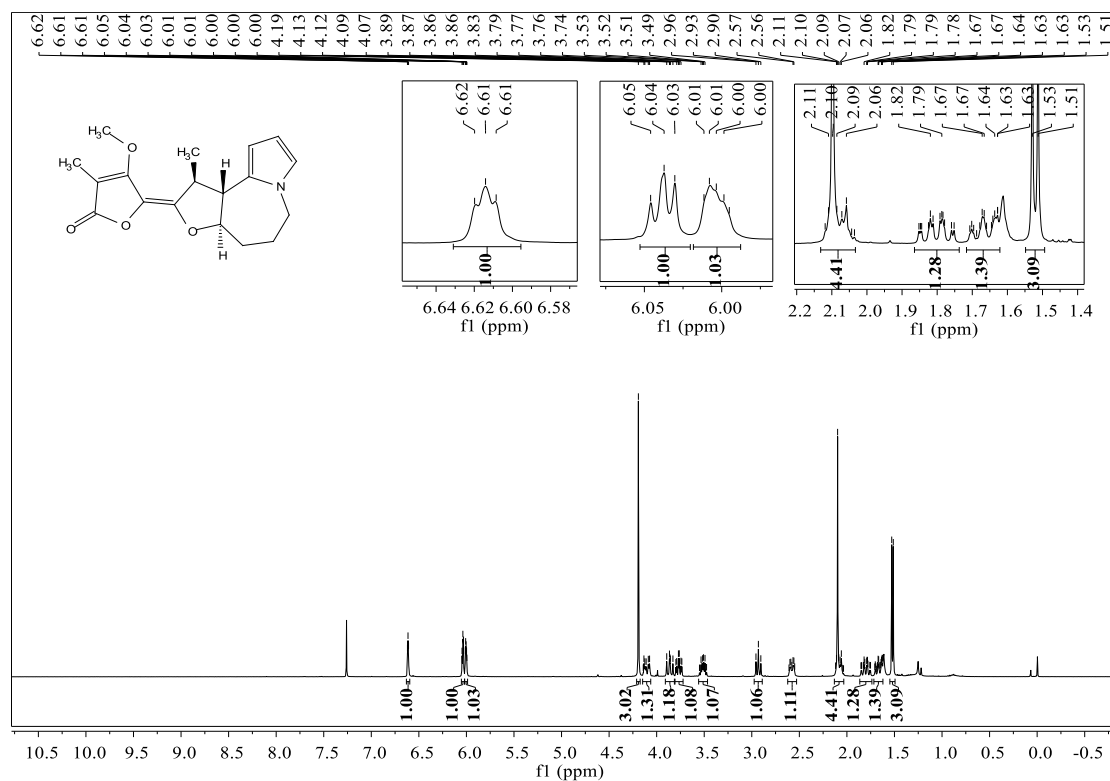
**<sup>1</sup>H NMR spectrum of compound 17 (400 MHz, CDCl<sub>3</sub>)**



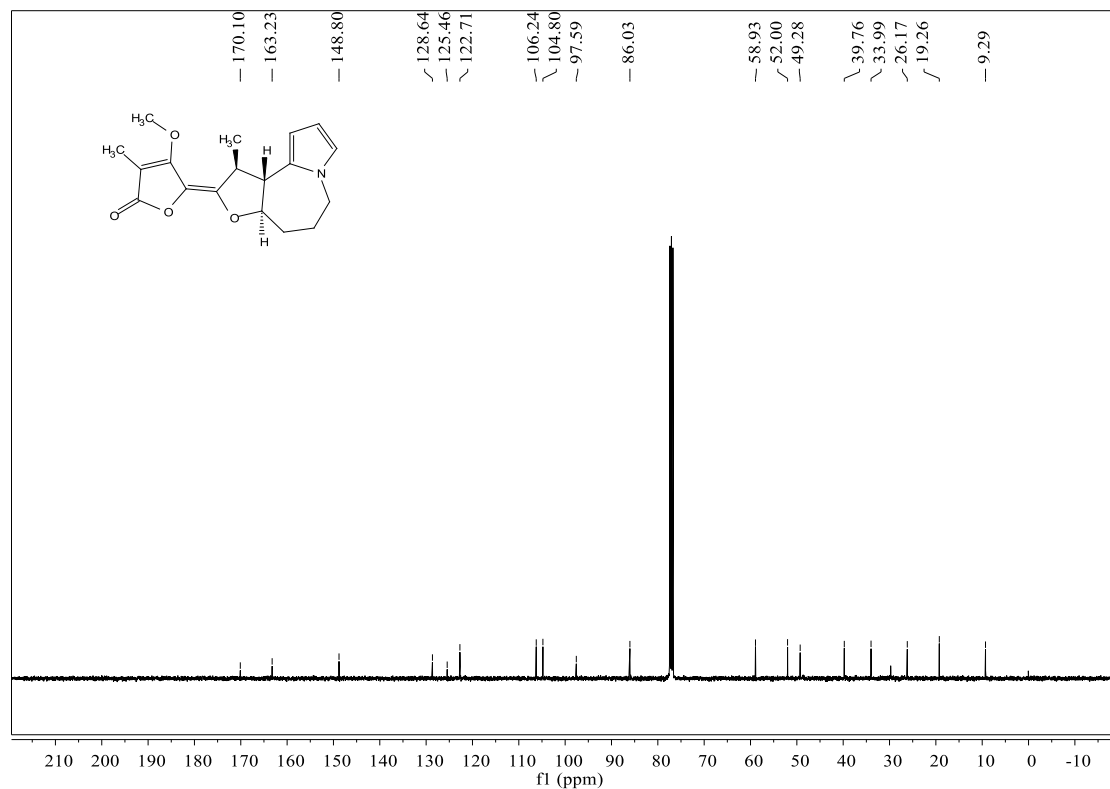
**<sup>13</sup>C NMR spectrum of compound 17 (101 MHz, CDCl<sub>3</sub>)**



**<sup>1</sup>H NMR spectrum of bisdehydroneostemonine (6) (400 MHz, CDCl<sub>3</sub>)**

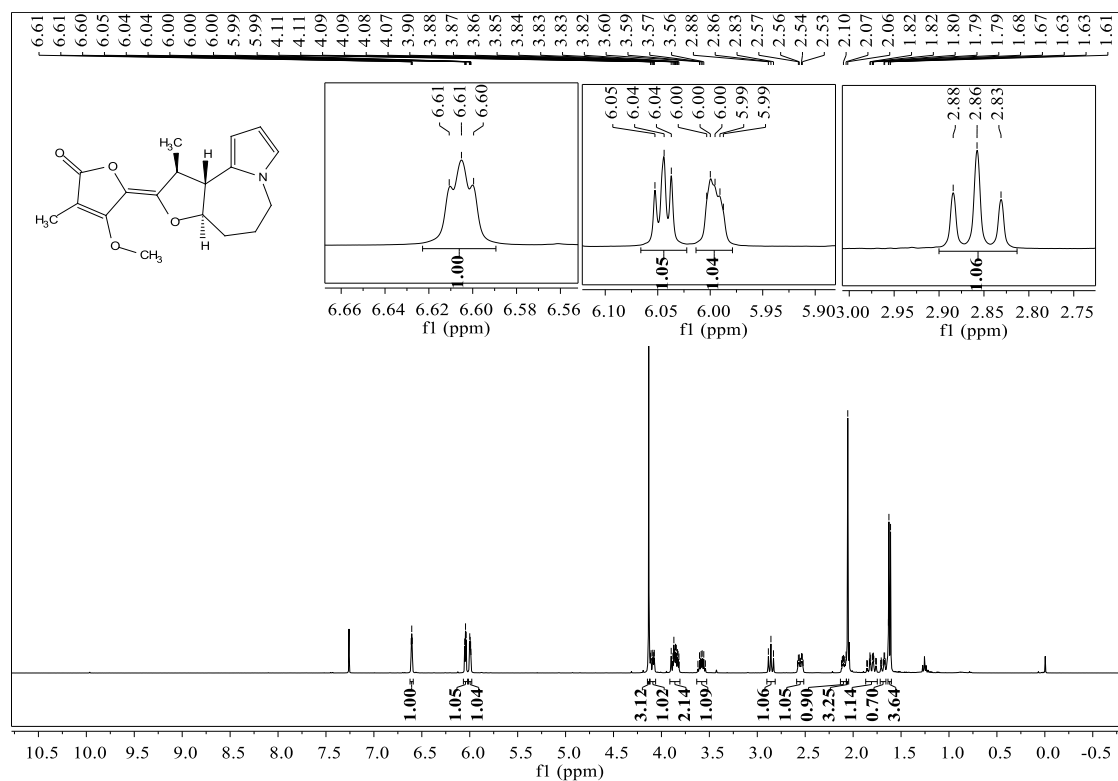


**<sup>13</sup>C NMR spectrum of bisdehydroneostemonine (6) (101 MHz, CDCl<sub>3</sub>)**

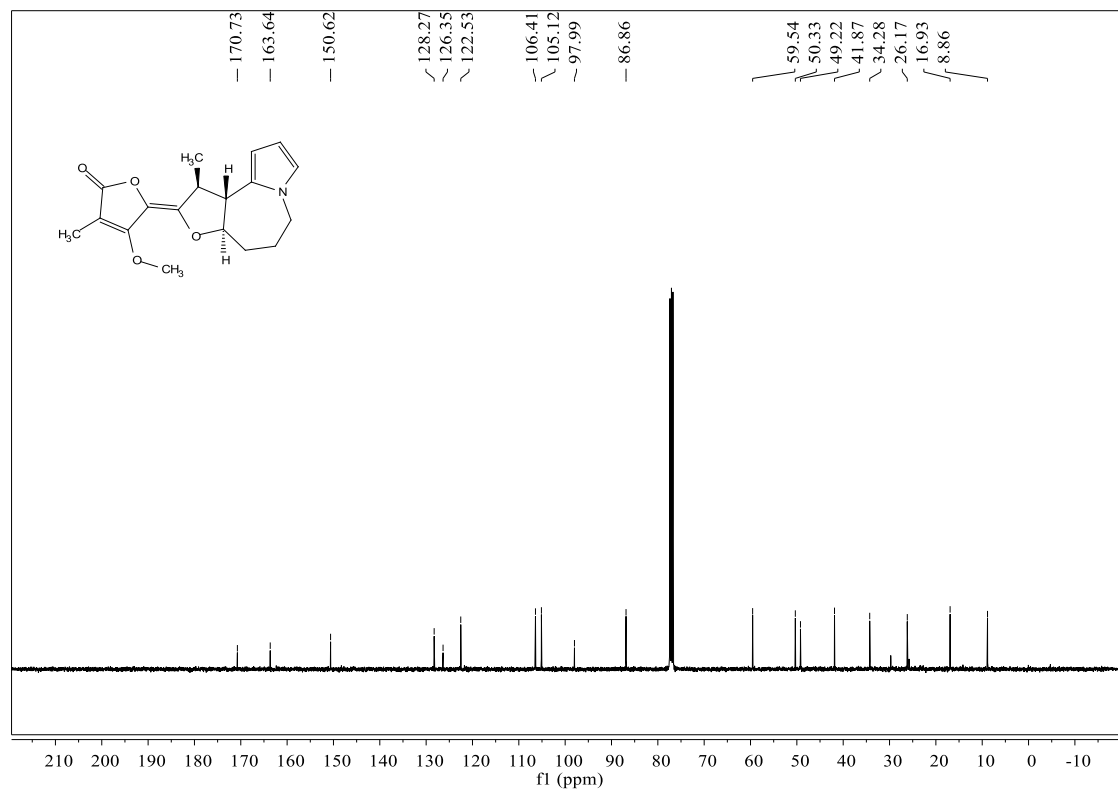




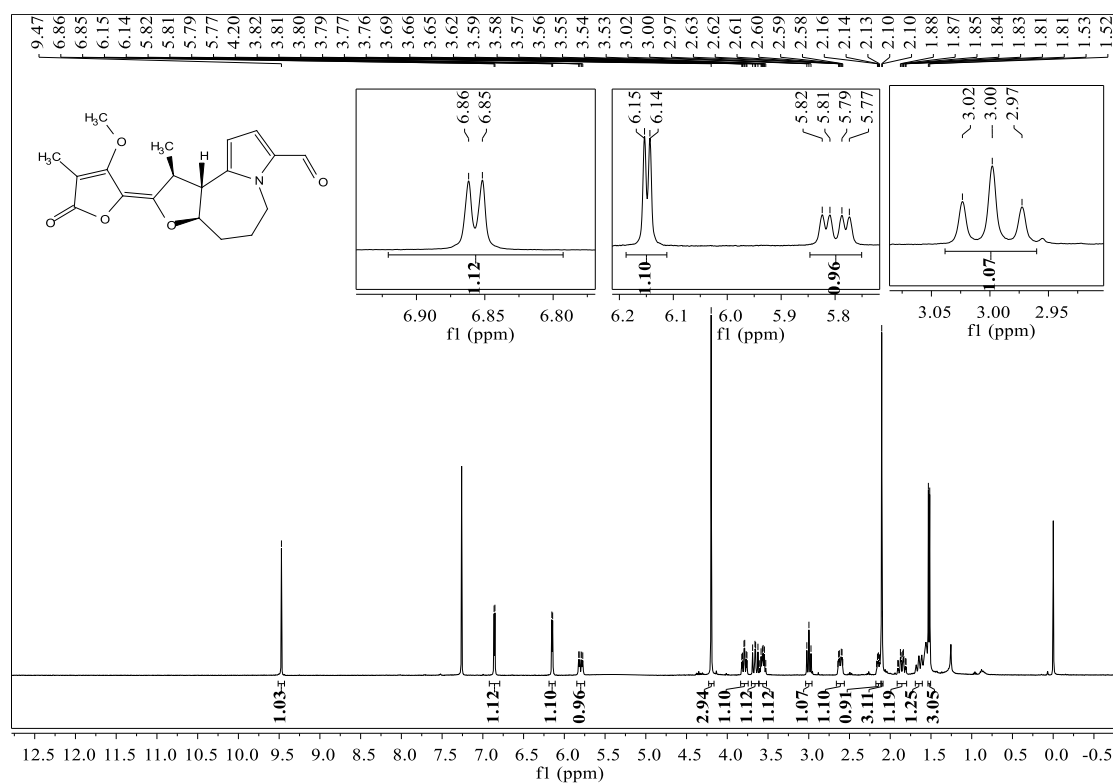
### <sup>1</sup>H NMR spectrum of compound 29 (400 MHz, CDCl<sub>3</sub>)



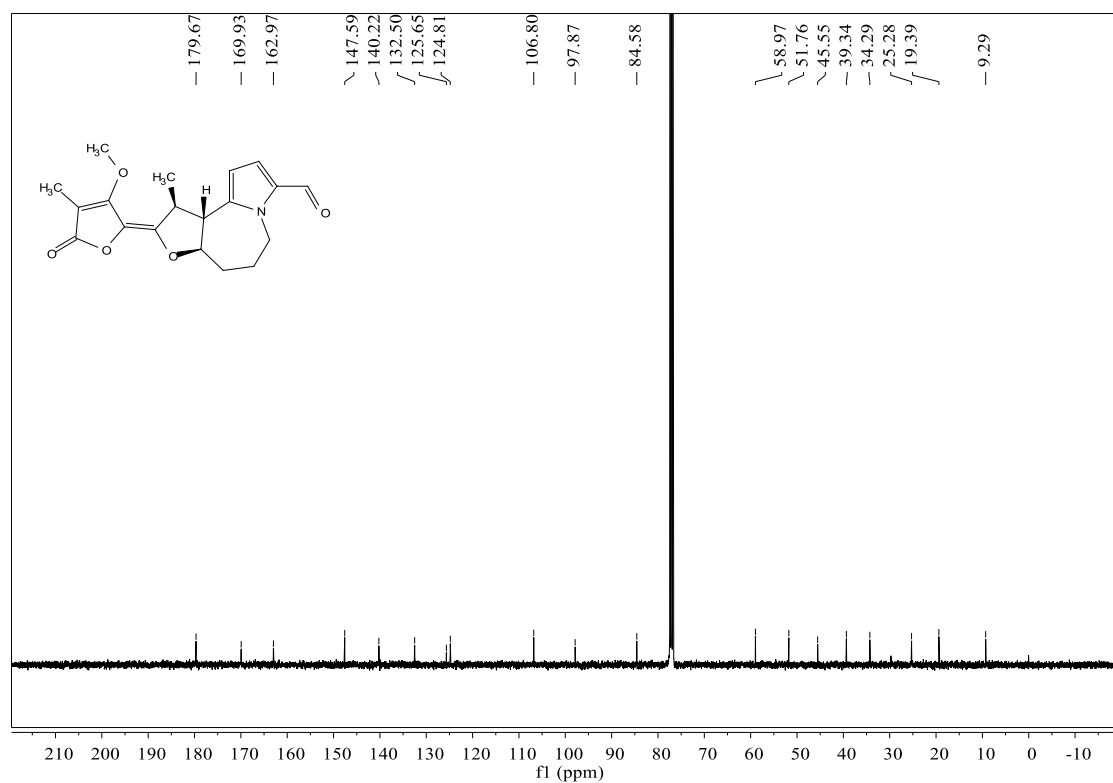
### <sup>13</sup>C NMR spectrum of compound 29 (101 MHz, CDCl<sub>3</sub>)



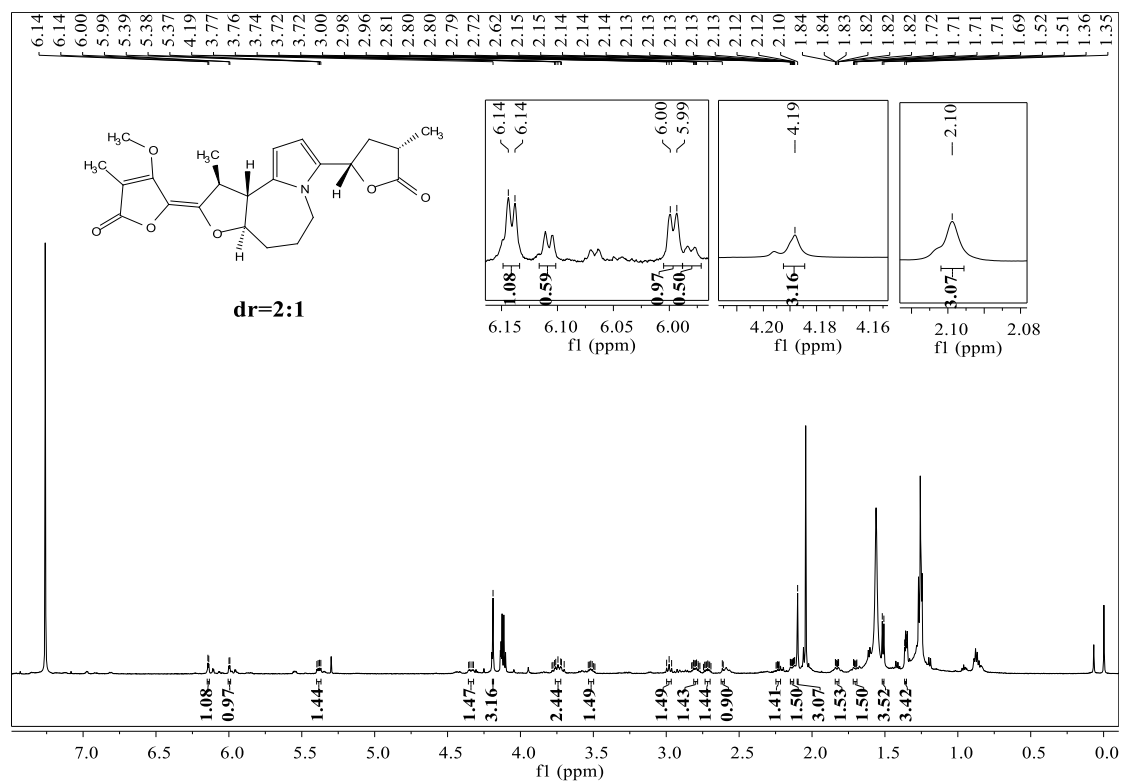
**<sup>1</sup>H NMR spectrum of compound 14 (400 MHz, CDCl<sub>3</sub>)**



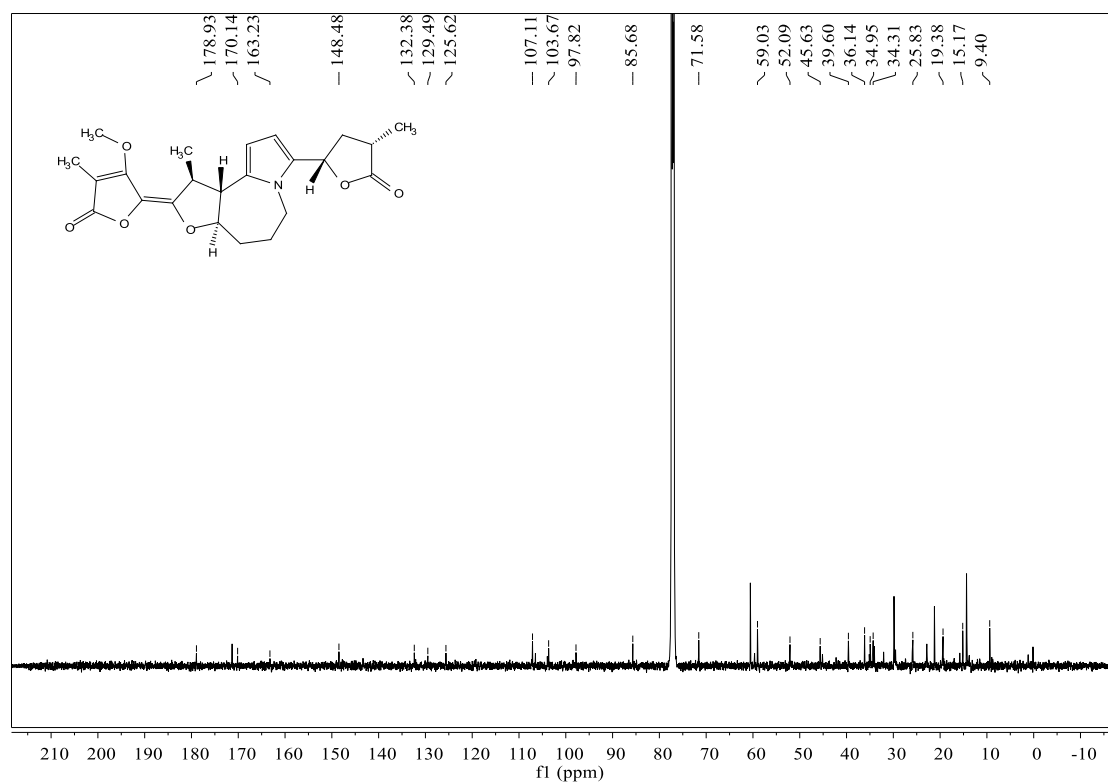
**<sup>13</sup>C NMR spectrum of compound 14 (101 MHz, CDCl<sub>3</sub>)**



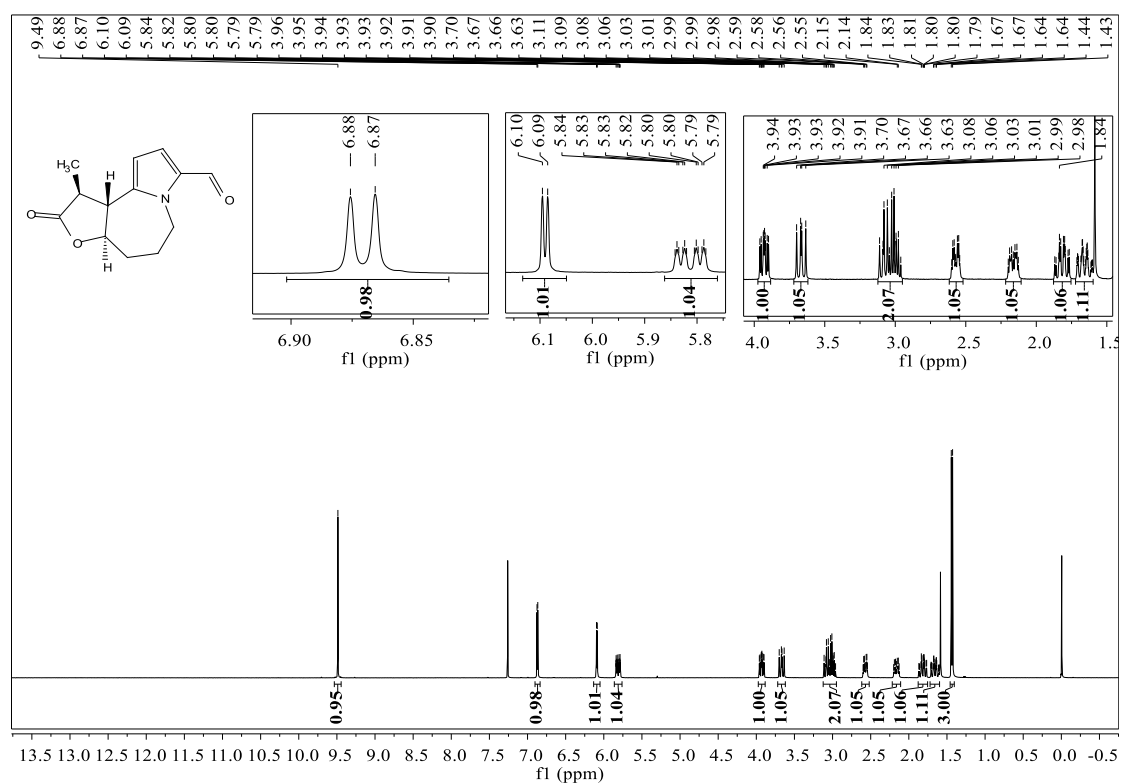
### <sup>1</sup>H NMR spectrum of bisdehydroprotostemonine (9) (600 MHz, CDCl<sub>3</sub>)



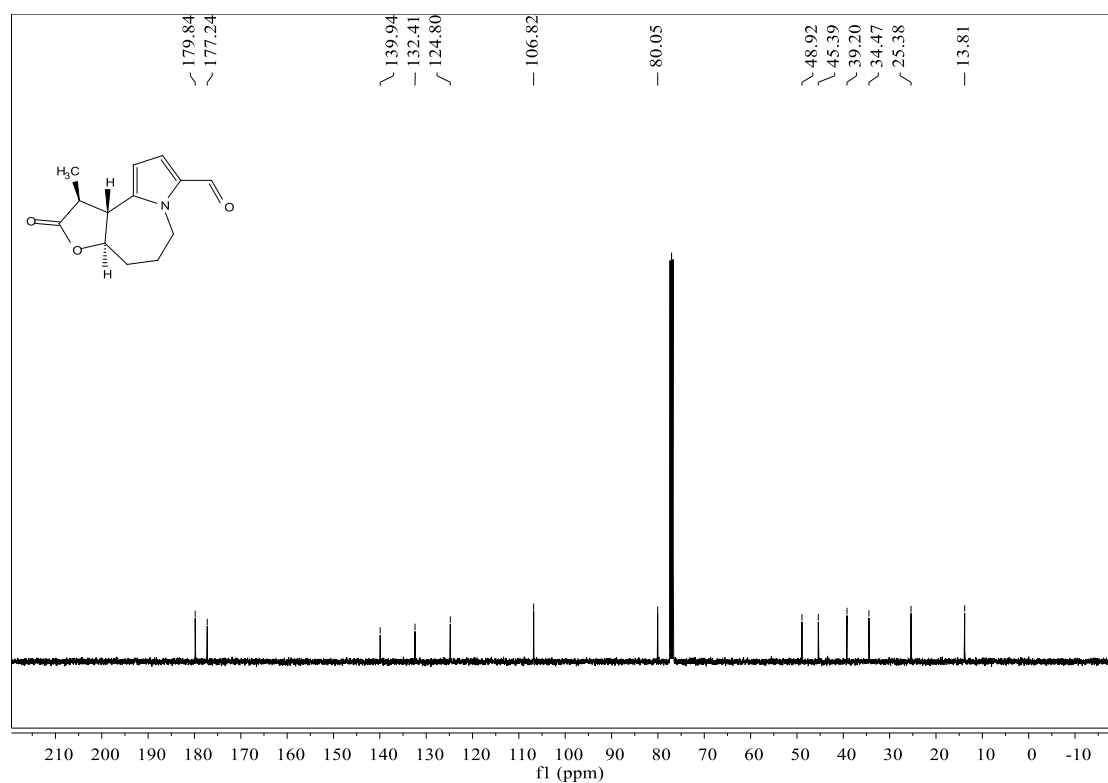
### <sup>13</sup>C NMR spectrum of bisdehydroprotostemonine (9) (151 MHz, CDCl<sub>3</sub>)



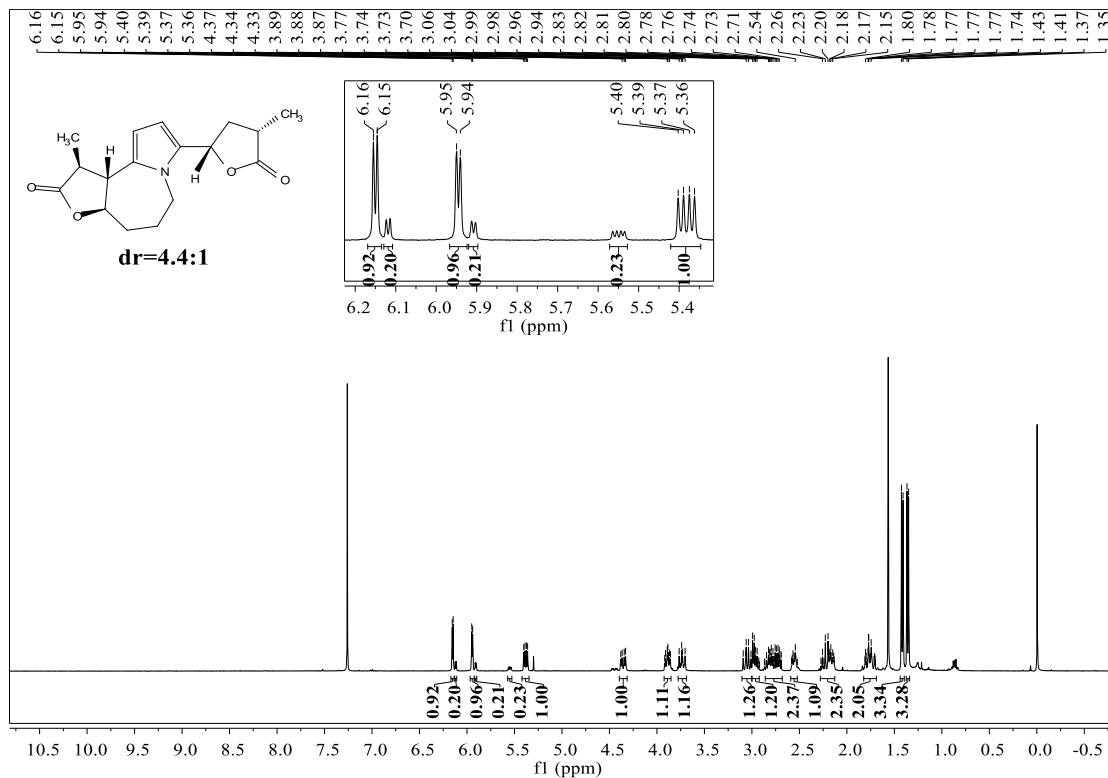
### <sup>1</sup>H NMR spectrum of compound 21 (400 MHz, CDCl<sub>3</sub>)



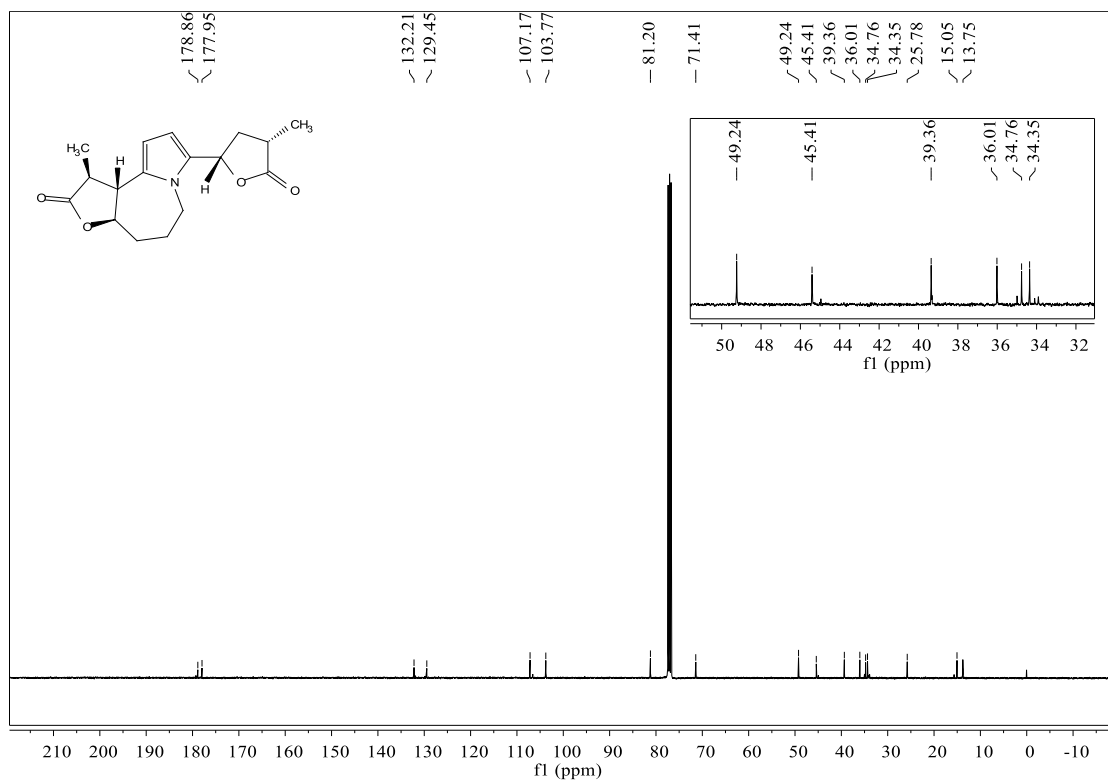
### <sup>13</sup>C NMR spectrum of compound 21 (101 MHz, CDCl<sub>3</sub>)



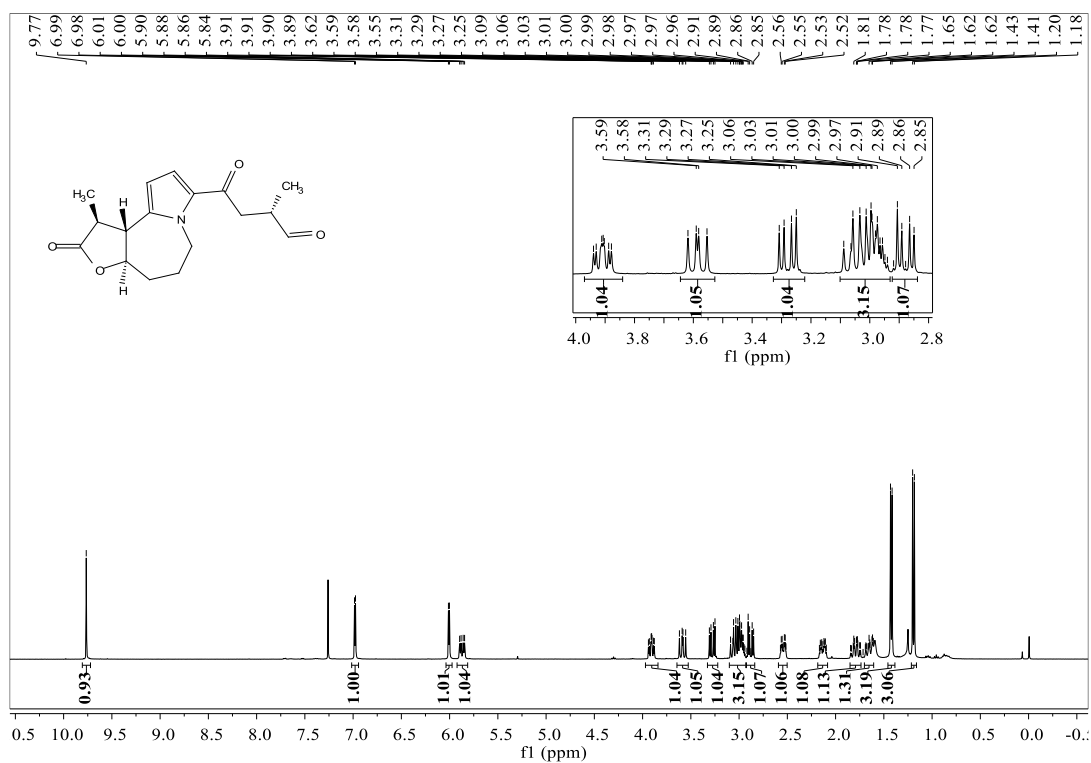
**<sup>1</sup>H NMR spectrum of bisdehydrostemonine (8) (400 MHz, CDCl<sub>3</sub>)**



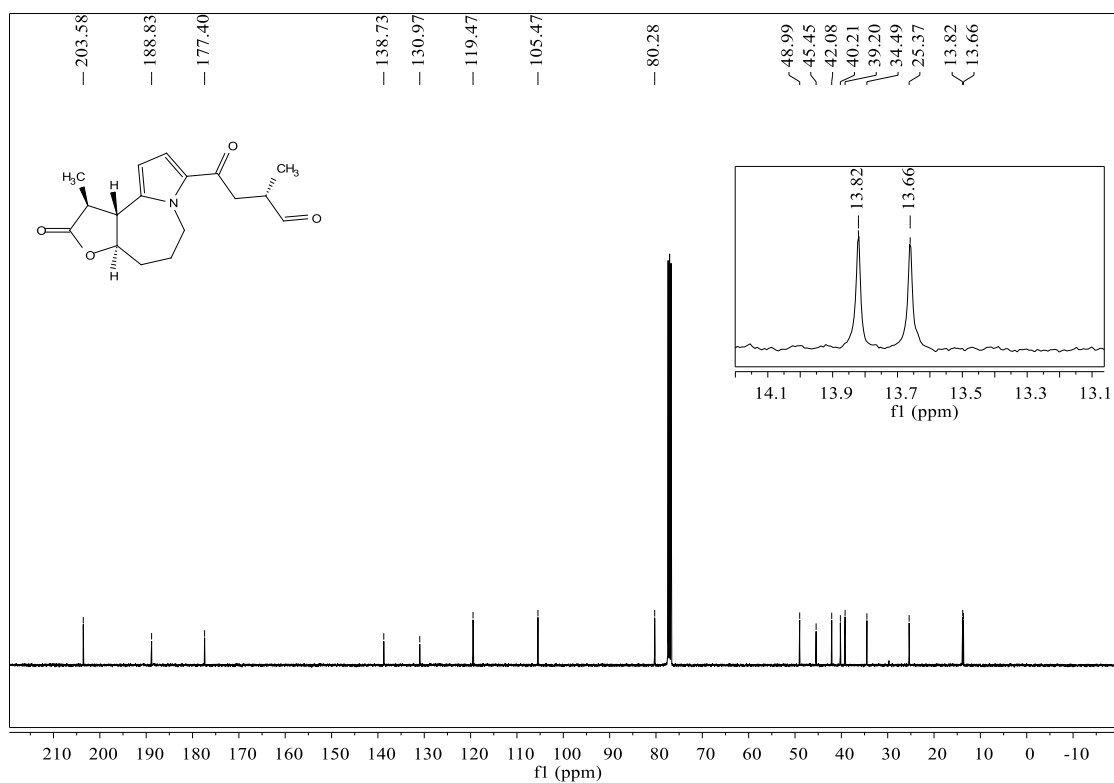
**<sup>13</sup>C NMR spectrum of bisdehydrostemonine (8) (101 MHz, CDCl<sub>3</sub>)**



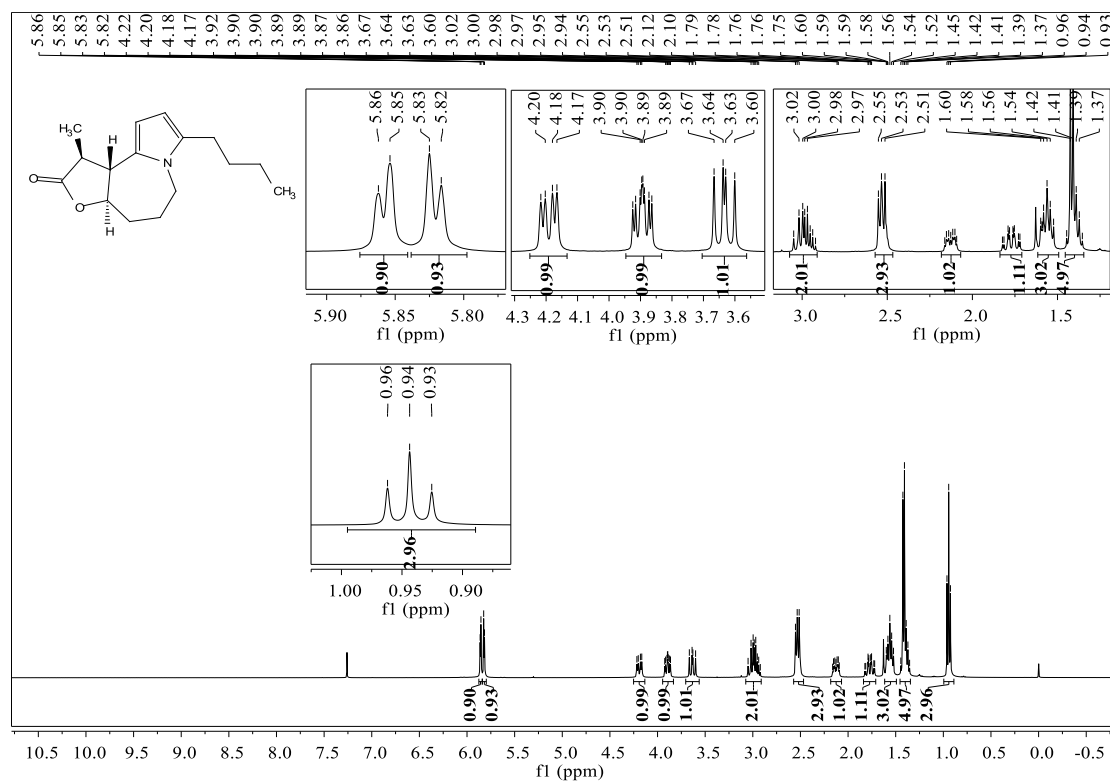
### <sup>1</sup>H NMR spectrum of compound S2 (400 MHz, CDCl<sub>3</sub>)



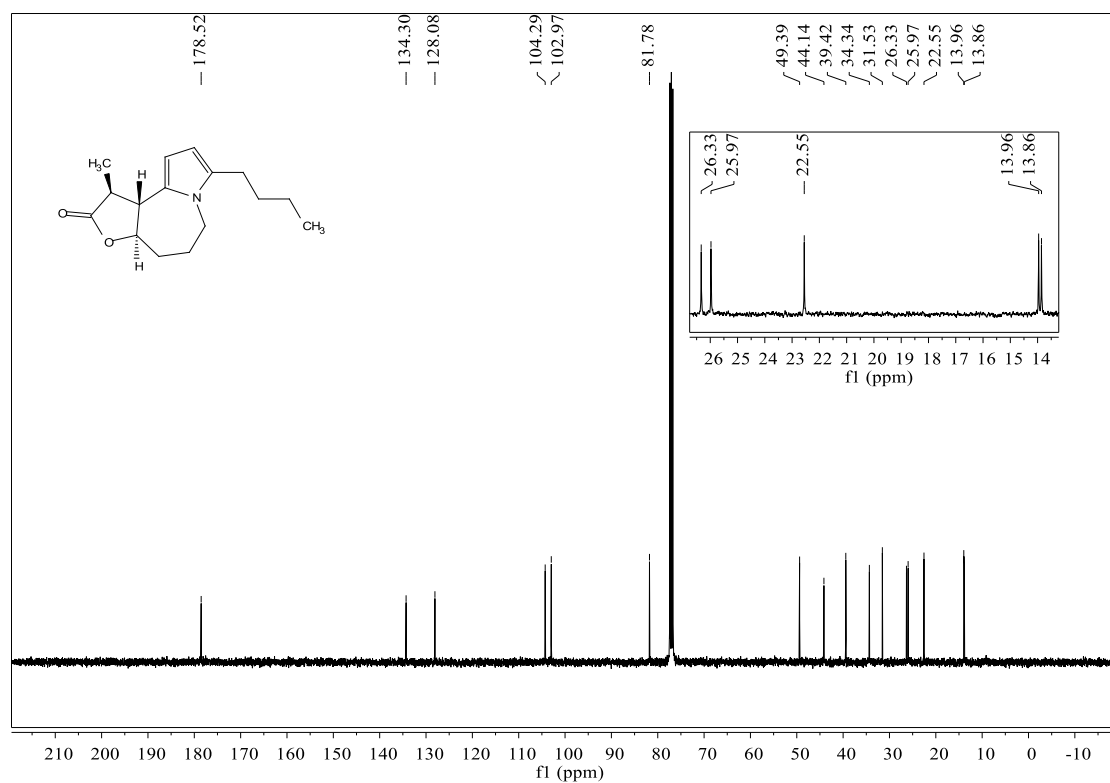
### <sup>13</sup>C NMR spectrum of compound S2 (101 MHz, CDCl<sub>3</sub>)



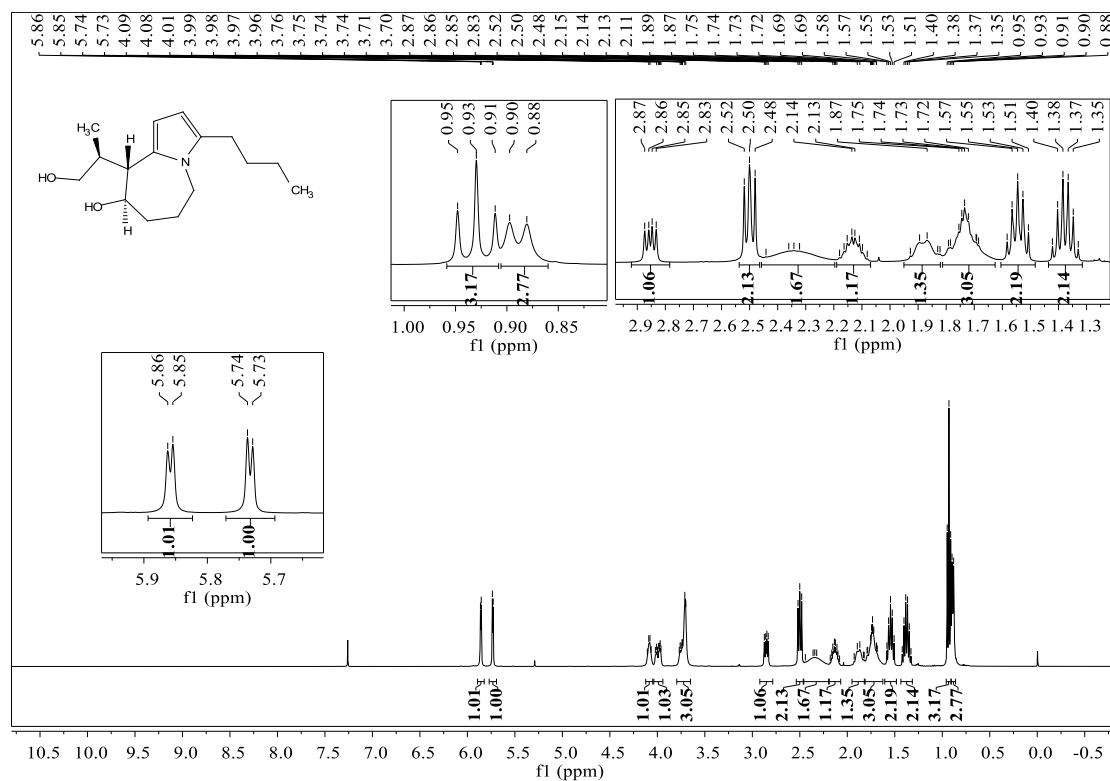
### <sup>1</sup>H NMR spectrum of parvistemonine A (5) (400 MHz, CDCl<sub>3</sub>)



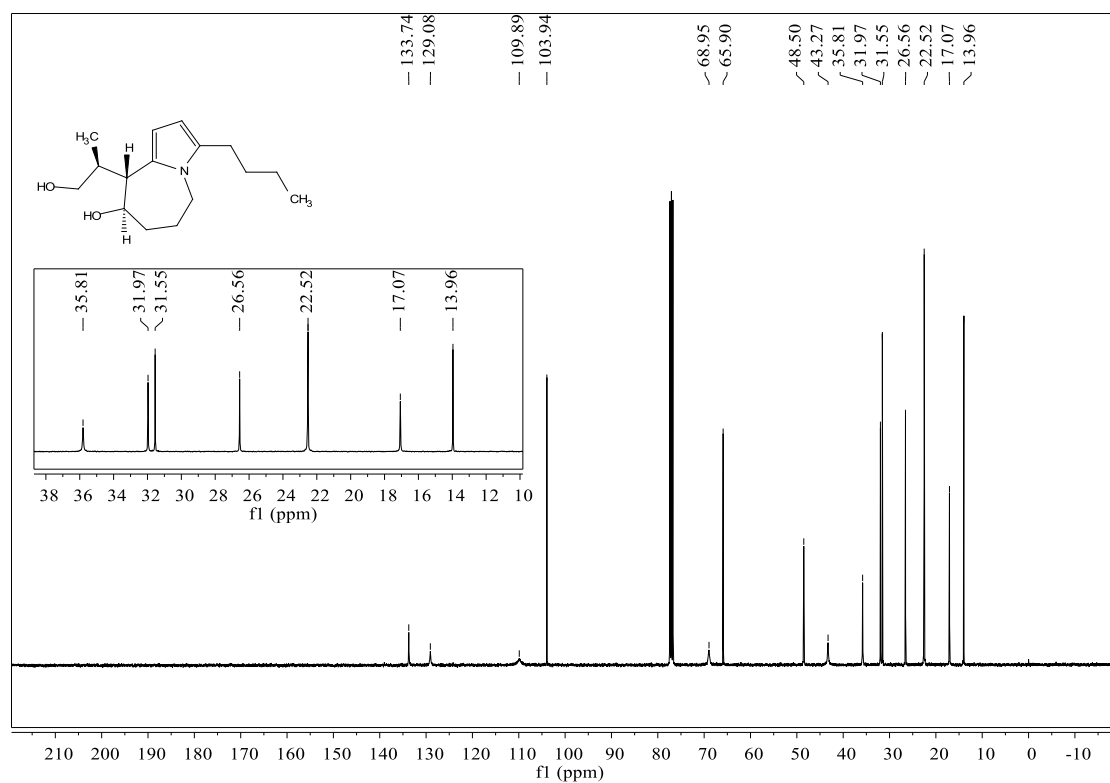
### <sup>13</sup>C NMR spectrum of parvistemonine A (5) (101 MHz, CDCl<sub>3</sub>)



**<sup>1</sup>H NMR spectrum of compound 34 (400 MHz, CDCl<sub>3</sub>)**

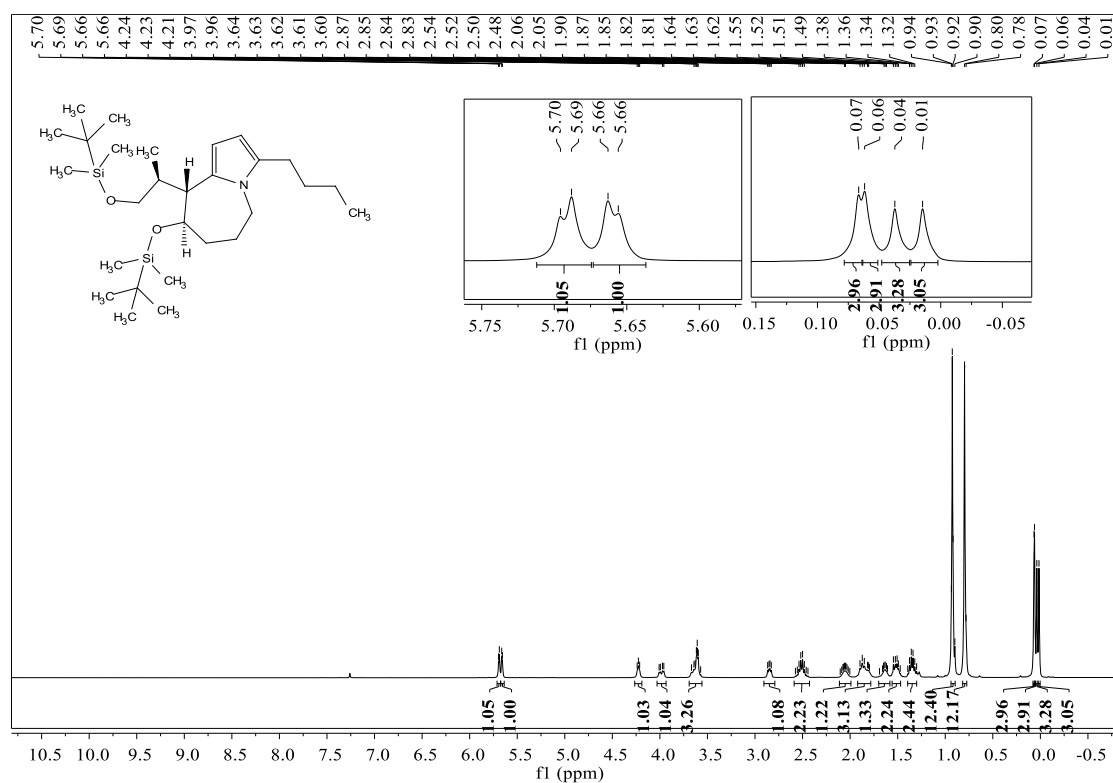


**<sup>13</sup>C NMR spectrum of compound 34 (101 MHz, CDCl<sub>3</sub>)**

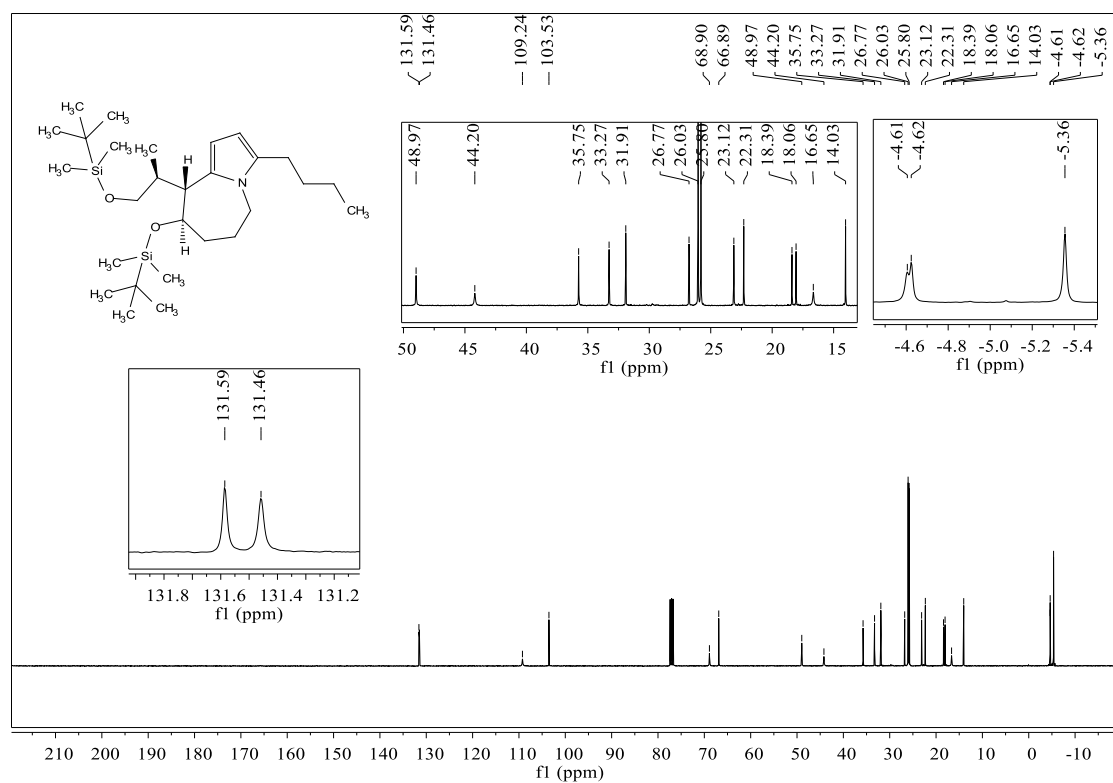




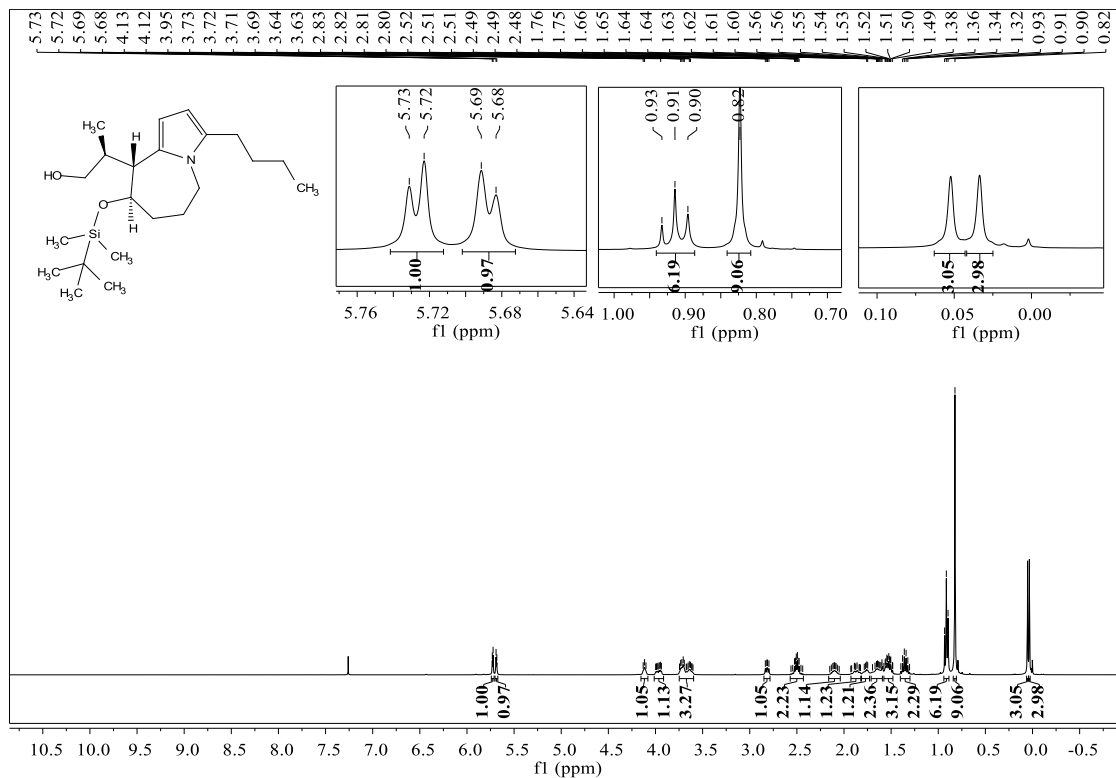
**<sup>1</sup>H NMR spectrum of compound 35 (400 MHz, CDCl<sub>3</sub>)**



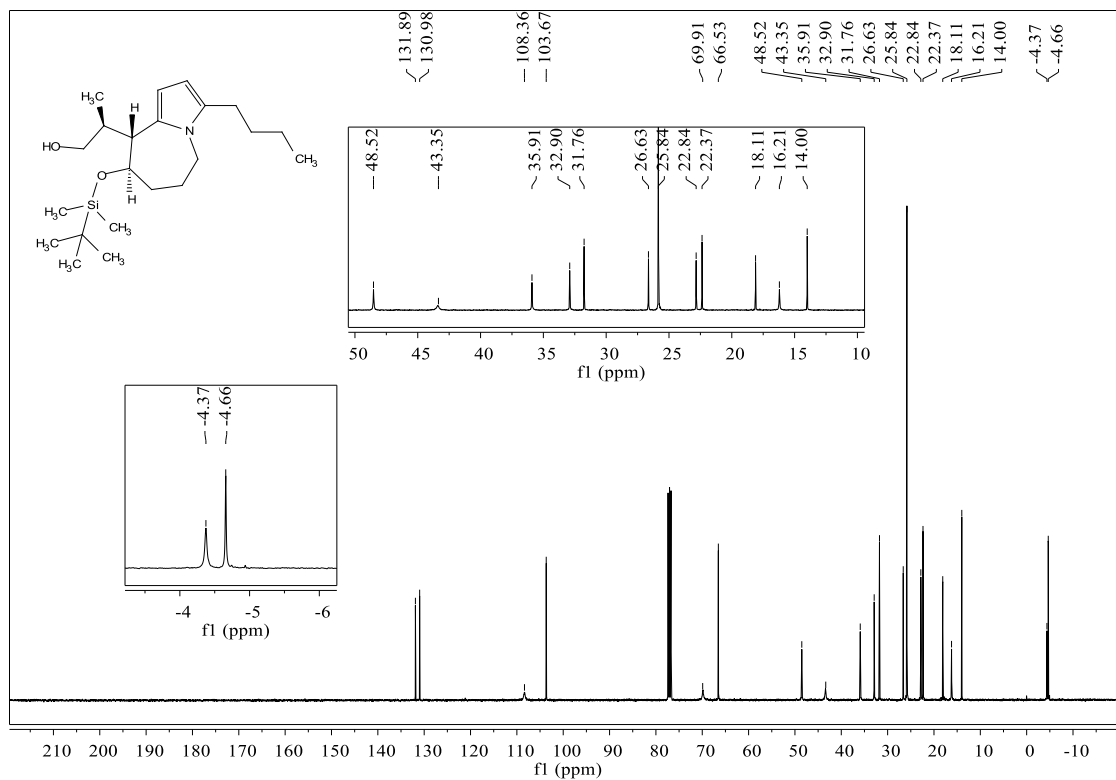
**<sup>13</sup>C NMR spectrum of compound 35 (101 MHz, CDCl<sub>3</sub>)**



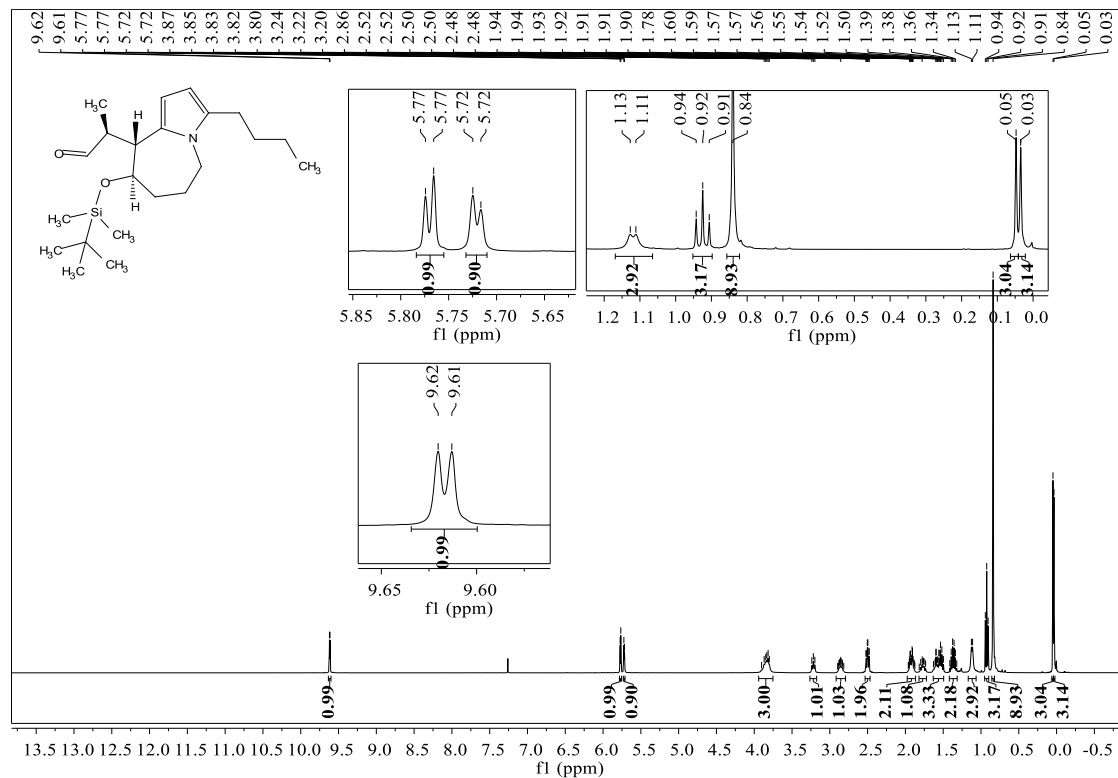
**<sup>1</sup>H NMR spectrum of compound 36 (400 MHz, CDCl<sub>3</sub>)**



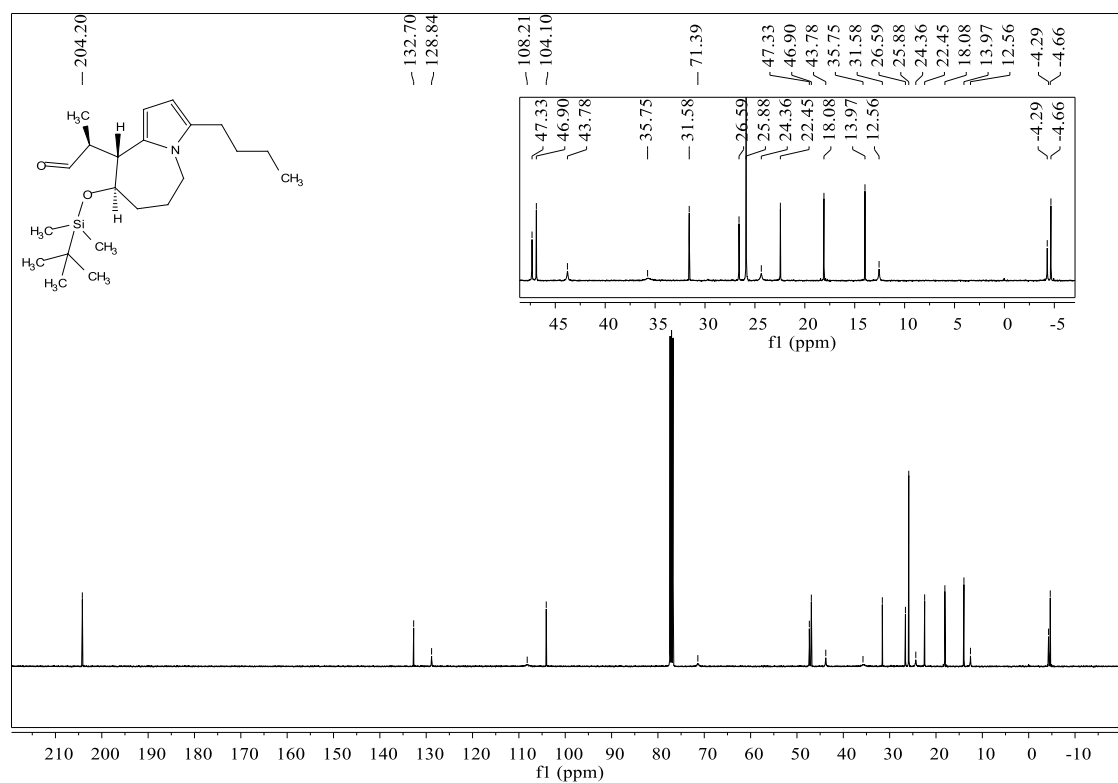
**<sup>13</sup>C NMR spectrum of compound 36 (101 MHz, CDCl<sub>3</sub>)**



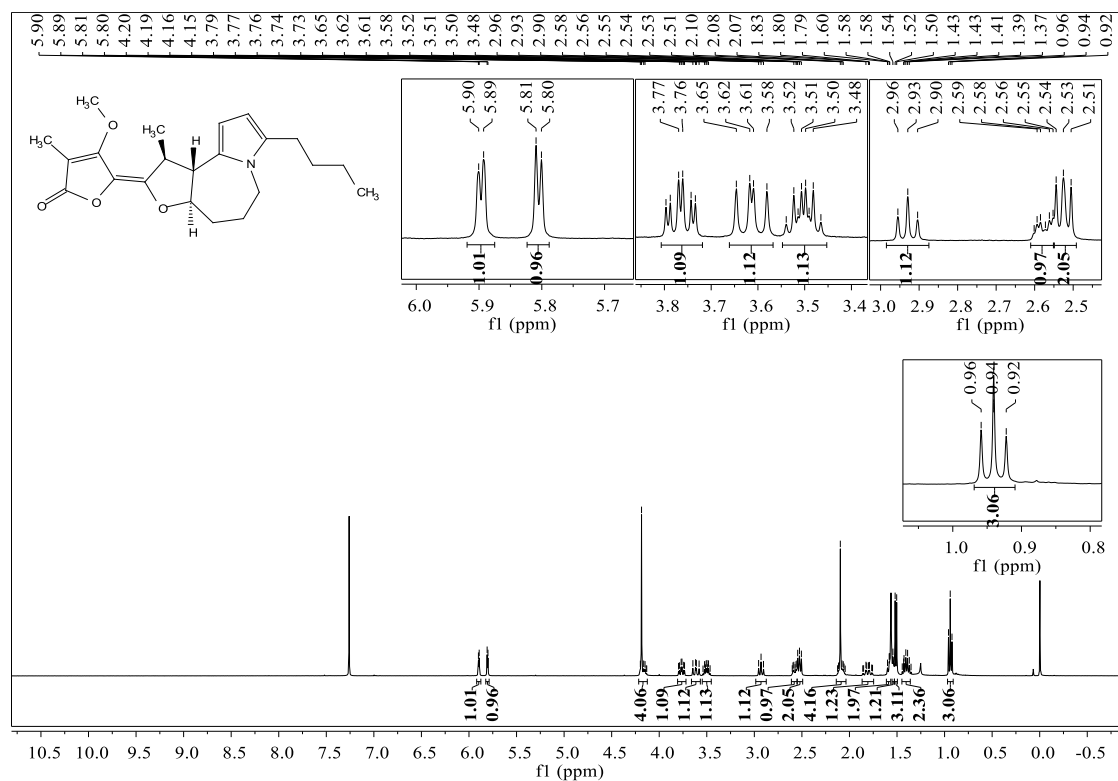
### <sup>1</sup>H NMR spectrum of compound 37 (400 MHz, CDCl<sub>3</sub>)



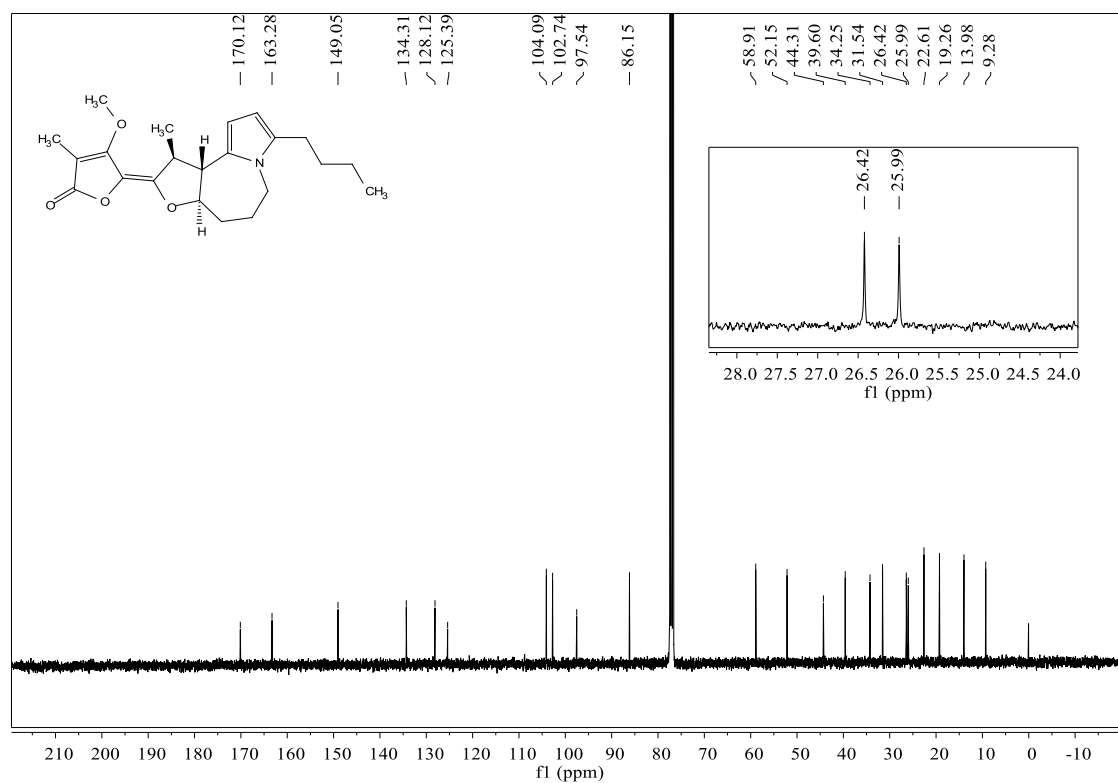
### <sup>13</sup>C NMR spectrum of compound 37 (101 MHz, CDCl<sub>3</sub>)



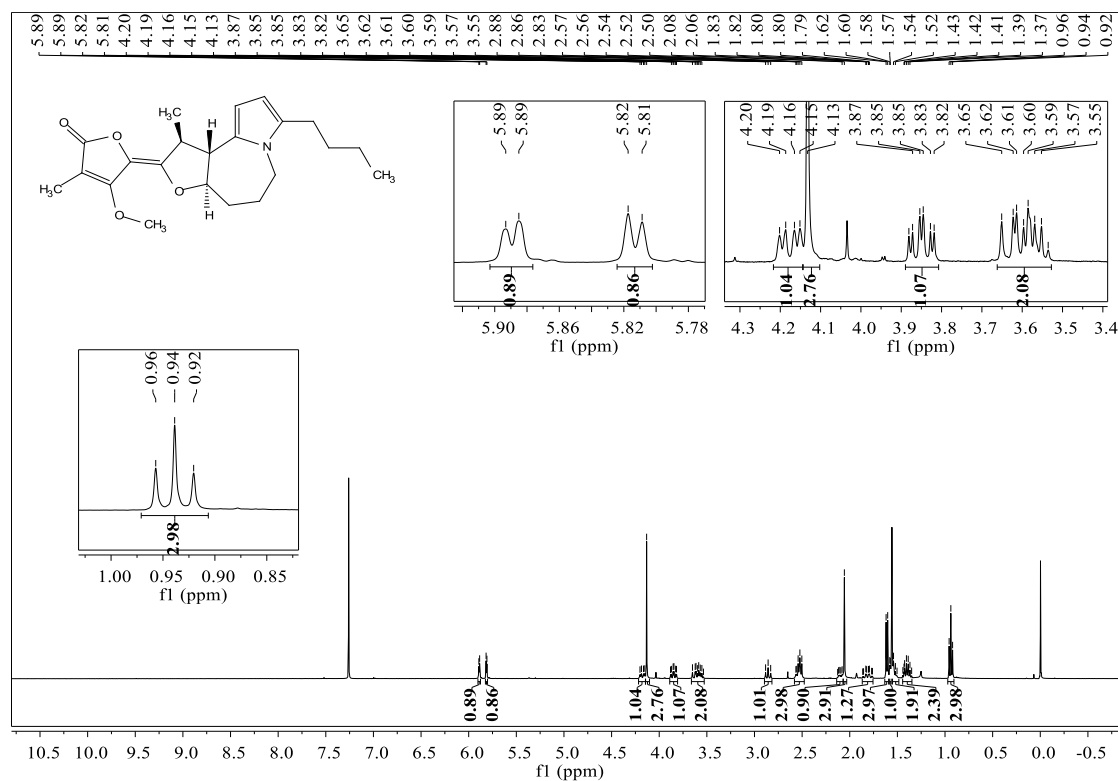
**<sup>1</sup>H NMR spectrum of 3-*n*-butylneostemonine (7) (400 MHz, CDCl<sub>3</sub>)**



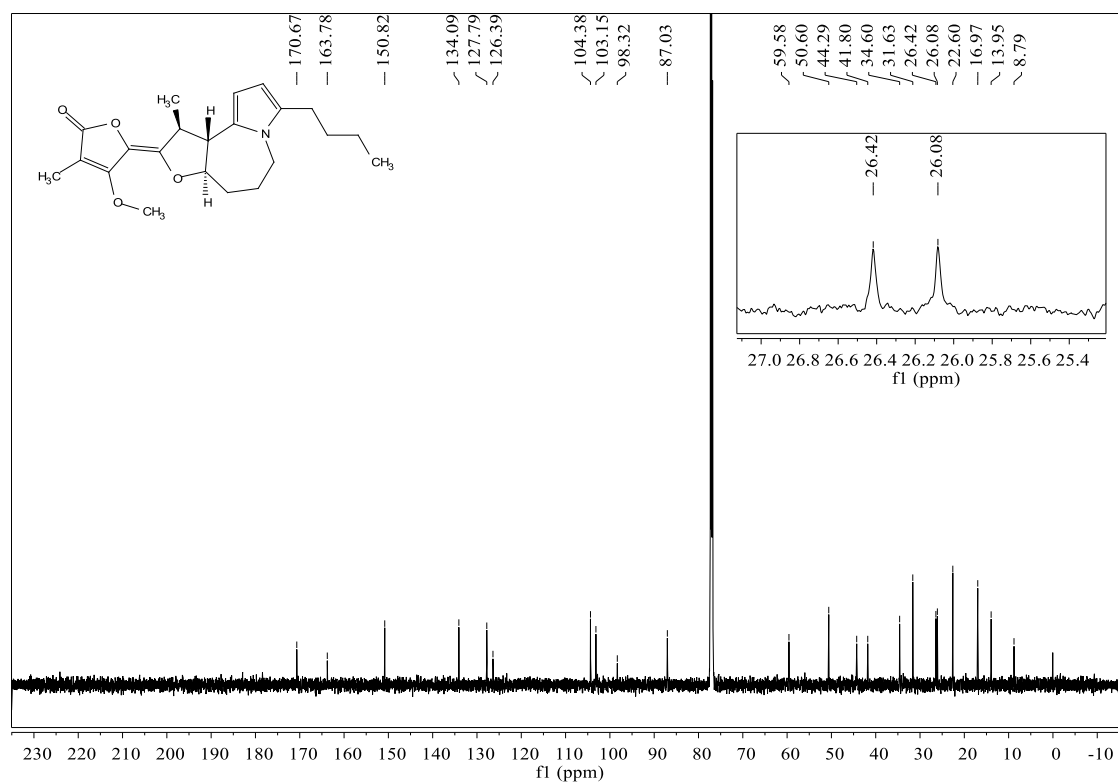
**<sup>13</sup>C NMR spectrum of 3-*n*-butylneostemonine (7) (101 MHz, CDCl<sub>3</sub>)**



**<sup>1</sup>H NMR spectrum of compound 39 (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR spectrum of compound 39 (101 MHz, CDCl<sub>3</sub>)**



## V. References

1. Y. Hou, T. Shi, Y. Yang, X. Fan, J. Chen, F. Cao and Z. Wang, Asymmetric total syntheses and biological studies of tuberostemoamide and sessilifoliamide A. *Org. Lett.* **2019**, *21*, 2952–2956.
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