

## Supporting Information

# A Formal Synthesis of (-)-Erinacine B Enabled by Asymmetric Organocatalysis

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## 1. General Information

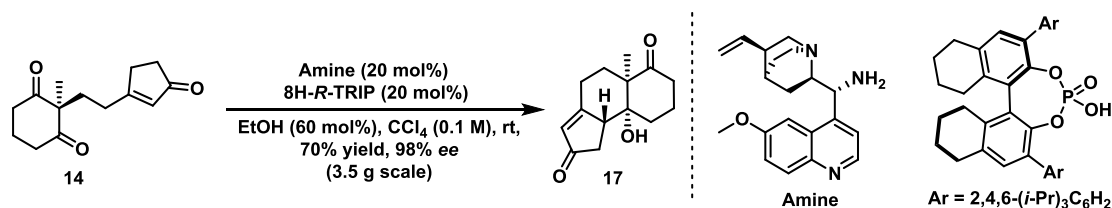
Unless otherwise noted, reagents were obtained from commercial sources and used without further purification. Non-aqueous reaction was conducted under an inert atmosphere of argon in flame-dried glassware. Anhydrous solvent was treated as follow: tetrahydrofuran and diethyl ether were distilled from sodium under argon atmosphere, dichloromethane and toluene was distilled from calcium hydride under argon atmosphere. Anhydrous chloroform, methanol, ethanol and ethyl acetate were commercially available (Adamas, SafeDry, with molecular sieves).

Thin layer chromatography was conducted on Merck 60 F254 pre-coated silica gel plates. Column chromatography was carried out by normal silica gel (40-60  $\mu\text{m}$ , 200-400 mesh, Silicycle P60). NMR data including  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker AVANCE III 500MHz. The chemical shifts ( $\delta$ ) for  $^1\text{H}$  and  $^{13}\text{C}$  are given in ppm relative to residual signals of the solvents ( $\text{CHCl}_3$  @ 7.26 ppm  $^1\text{H}$  NMR, 77.16 ppm  $^{13}\text{C}$  NMR). Coupling constants are given in Hz.

Low mass spectra were measured on a Shimadzu LCMS-2010EV mass spectrometer (ESI). High resolution mass spectra were obtained from IonSpec 4.7 Tesla FTMS mass spectrometer (MALDI), Bruker APEXIII 7.0 TESLA FTMS (ESI).

Optical rotations were measured on an Anton Paar MCP 300 polarimeter and are reported as follows:  $[\alpha]_D^{25}$  ( $c = \text{g}/100 \text{ mL}$  in solvent).

## 2. Experimental Procedures and Spectroscopic Data of Compounds

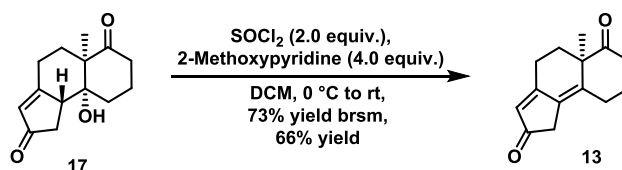


A 250 mL flask was charged with the **Amine** (20 mol%), **8H-R-TRIP** (20 mol%), ethanol (60 mol%), and triketone **14**<sup>[1]</sup> (15 mmol) dissolved in CCl<sub>4</sub> (150 mL). After that, the reaction mixture was stirred at room temperature until all triketone **14** was consumed as judged by TLC (about 20 days). The solvent was removed under vacuum. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3 to 2/1, v/v) to afford the product (2.46 g, 70% yield) as a brown oil.  $R_f = 0.32$  (ethyl acetate/petroleum ether = 2/1, v/v).  $[\alpha]_D^{20} = +76.74$  ( $c = 0.20$  in CHCl<sub>3</sub>).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  5.90 (s, 1H), 2.80 (d,  $J = 6.3$  Hz, 1H), 2.73–2.65 (m, 1H), 2.66–2.59 (m, 2H), 2.45–2.39 (m, 1H), 2.36–2.24 (m, 3H), 2.21–2.10 (m, 1H), 2.03–1.93 (m, 1H), 1.79–1.65 (m, 3H), 1.60–1.48 (m, 1H), 1.26 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)**  $\delta$  213.1, 208.7, 181.3, 129.1, 78.2, 54.8, 46.4, 36.1, 35.9, 31.2, 29.6, 27.4, 22.6, 19.5.

**HRMS (ESI) m/z:**  $[M + H]^+$  Calcd for C<sub>14</sub>H<sub>19</sub>O<sub>3</sub> 235.1329; Found 235.1325.

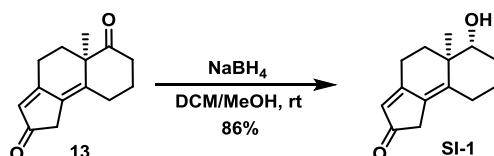


To a solution of tertiary alcohol **17** (843 mg, 3.6 mmol, 1.0 equiv.) in dichloromethane 72 mL at 0 °C 2-Methoxypyridine (1.5 mL, 4.0 equiv.) and thionyl chloride (0.52 mL, 2.0 equiv) was added and the reaction mixture was stirred at 0 °C for 10 min, then warm up to room temperature and additional stirred for 30 min. The reaction was quenched with water, and extracted with dichloromethane (3 × 20 mL) and the combined organic fractions were washed with brine (50 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated in *vacuo*. The residue was subjected to flash column chromatography (ethyl acetate/dichloromethane = 1/10, v/v) to afford the corresponding unsaturated ketone **13** (512 mg, 66% yield) as a yellow oil.  $R_f = 0.67$  (ethyl acetate/dichloromethane = 1/4, v/v).  $[\alpha]_D^{20} = -161.18$  ( $c = 0.15$  in CHCl<sub>3</sub>).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  5.88 (s, 1H), 2.86 (s, 2H), 2.80 (dt,  $J = 17.5, 4.0$  Hz, 1H), 2.72–2.63 (m, 1H), 2.63–2.54 (m, 1H), 2.50 (dd,  $J = 8.5, 4.5$  Hz, 2H), 2.41 (dt,  $J = 15.0, 4.5$  Hz, 1H), 2.15–2.04 (m, 1H), 2.02–1.94 (m, 1H), 1.84 (td,  $J = 14.0, 5.0$  Hz, 1H), 1.73–1.60 (m, 1H), 1.34 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)**  $\delta$  212.7, 204.7, 169.9, 141.1, 131.5, 127.8, 50.2, 38.1, 37.9, 29.4, 27.4, 23.7, 23.1, 22.2.

**HRMS (ESI) m/z:**  $[M + H]^+$  C<sub>14</sub>H<sub>21</sub>O<sub>3</sub> 217.1223; Found 217.1220.

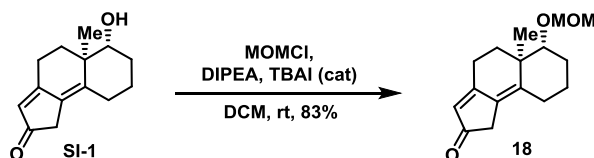


To a solution of ketone **13** (6.2 g, 29 mmol, 1.0 equiv.) in dichloromethane/methanol (1:1 v/v, 200 mL) at 0 °C was added NaBH<sub>4</sub> (1.3 g, 34.4 mmol, 1.2 equiv) slowly. The reaction mixture was stirred at 0 °C for 10 min, then warm up to room temperature and additional stirred for 30 min. The solvent was removed under vacuum and water (50 mL) was added, extracted with dichloromethane (3×20 mL) and the combined organic fractions were washed with brine (50 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated in *vacuo*. The residue was subjected to flash column chromatography (ethyl acetate/dichloromethane = 1/10, v/v) to afford the corresponding secondary alcohol **SI-1** (5.39 g, 86% yield) as a yellow oil *R<sub>f</sub>* = 0.51 (ethyl acetate/petroleum ether = 2/1, v/v). [ $\alpha$ ]<sub>D</sub><sup>20</sup> = -158.19 (*c* = 0.10 in CHCl<sub>3</sub>).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  5.86 (s, 1H), 3.34 (dt, *J* = 11.5, 4.5 Hz, 1H), 2.83 (d, *J* = 5.5 Hz, 2H), 2.76 (dt, *J* = 17.5, 3.5 Hz, 1H), 2.61–2.48 (m, 1H), 2.29–2.20 (m, 2H), 2.14–2.04 (m, 2H), 1.87–1.76 (m, 2H), 1.72–1.60 (m, 1H), 1.55 (td, *J* = 13.5, 4.5 Hz, 1H), 1.40–1.27 (m, 1H), 1.09 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)**  $\delta$  205.7, 171.5, 143.9, 130.8, 127.1, 78.8, 41.2, 38.2, 34.0, 30.3, 27.4, 23.3, 22.6, 15.5.

**HRMS (ESI)** *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>19</sub>O<sub>2</sub>; 219.1380; Found 219.1381.

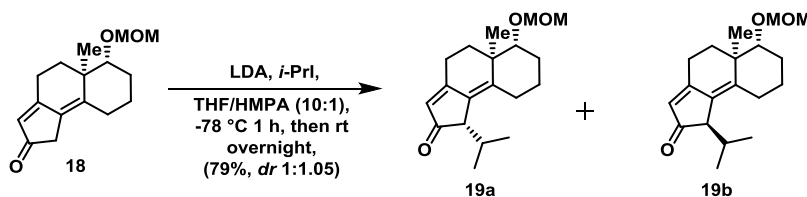


To a solution of Alcohol **SI-1** (1.22 g, 5.6 mmol, 1.0 equiv.) in dichloromethane 60 mL at 0 °C were added DIPEA (9.3 mL, 56 mmol, 10 equiv), TBAI (103 mg, 5 mol%) and MOMCl (2.1 mL, 28 mmol, 5 equiv). The reaction mixture was stirred at 0 °C for 10 min, then stirred at room temperature until all start material was consumed as judged by TLC. The reaction was quenched with 1 N HCl (aq), and extracted with dichloromethane (3×20 mL) and the combined organic fractions were washed with brine (50 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated in *vacuo*. The residue was subjected to flash column chromatography (ethyl acetate/petroleum ether = 1/10, v/v) to afford the corresponding unsaturated ketone **18** (1.22 g, 83% yield) as a yellow oil. *R<sub>f</sub>* = 0.67 (ethyl acetate/petroleum ether = 1/1, v/v). [ $\alpha$ ]<sub>D</sub><sup>20</sup> = -120.16 (*c* = 0.19 in CHCl<sub>3</sub>).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  5.85 (s, 1H), 4.71 (d, *J* = 6.9 Hz, 1H), 4.57 (d, *J* = 6.9 Hz, 1H), 3.35 (s, 3H), 3.20 (dd, *J* = 11.7, 4.2 Hz, 1H), 2.82 (d, *J* = 5.8 Hz, 2H), 2.77–2.69 (m, 1H), 2.60–2.49 (m, 1H), 2.28–2.20 (m, 1H), 2.14–2.03 (m, 2H), 1.95–1.88 (m, 1H), 1.88–1.79 (m, 1H), 1.66–1.47 (m, 2H), 1.35–1.19 (m, 1H), 1.10 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)**  $\delta$  205.3, 171.1, 143.6, 130.6, 127.1, 95.7, 84.4, 55.7, 40.8, 38.2, 34.1, 27.4, 27.1, 23.1, 22.5, 16.5.

**HRMS (ESI)** *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>23</sub>O<sub>3</sub> 263.1642; Found 263.1639.



A solution of *n*-BuLi (2.5 M in hexane, 1.85 mL, 5.0 mmol, 2.0 equiv) was added dropwise to a solution of *i*-Pr<sub>2</sub>NH (0.72 mL, 5.125 mmol, 2.05 equiv) in dry THF (10 mL) at 0 °C under argon atmosphere. The LDA solution was stirred for 0.5 h at this temperature, then cooled to -78 °C. After that a solution of ketone **18** (656 mg, 2.5 mmol, 1.0 equiv) in THF (10 mL) was added dropwise within 10 min. The reaction mixture was stirred for 1 h at -78 °C before 2-Iodopropane (1.25 mL, 12.5 mmol, 5.0 equiv) and HMPA (2 mL) in dry THF (3 mL) were introduced at this temperature. The mixture was stirred for 1 hour at -78 °C, then the mixture was allowed to stirred at room temperature overnight. The mixture was treated with saturated NH<sub>4</sub>Cl solution (20 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were washed with saturated brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated, and the residue purified by flash chromatography (ethyl acetate/petroleum ether = 1/50 to 1/10, v/v) to afford the corresponding **19a** (310 mg, 41% yield) and **19b** (295 mg, 39% yield).

**19a**, *R<sub>f</sub>* = 0.68 (ethyl acetate/petroleum ether = 1/3, v/v), [α]<sub>D</sub><sup>20</sup> = -56.32 (*c* = 0.20 in CHCl<sub>3</sub>).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 5.76 (s, 1H), 4.73 (d, *J* = 6.8 Hz, 1H), 4.59 (d, *J* = 6.8 Hz, 1H), 3.37 (s, 3H), 3.26 (dd, *J* = 11.7, 4.2 Hz, 1H), 2.78 (d, *J* = 3.3 Hz, 1H), 2.69 (dt, *J* = 16.8, 4.2 Hz, 1H), 2.64 – 2.53 (m, 1H), 2.39 – 2.31 (m, 1H), 2.19 – 2.02 (m, 3H), 1.98 – 1.89 (m, 1H), 1.89 – 1.82 (m, 1H), 1.67 – 1.55 (m, 2H), 1.34 – 1.20 (m, 1H), 1.15 (s, 3H), 1.14 (d, *J* = 6.9 Hz, 3H), 0.66 (d, *J* = 6.9 Hz, 3H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 208.2, 170.9, 142.7, 135.2, 126.8, 95.8, 84.0, 55.8, 53.2, 40.9, 34.5, 30.5, 27.3, 27.2, 23.5, 22.6, 20.3, 17.8, 17.2.

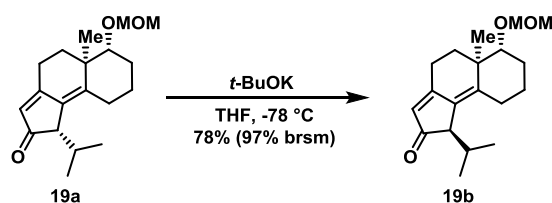
HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>29</sub>O<sub>3</sub> 305.2111; Found 305.2107.

**19b**, *R<sub>f</sub>* = 0.71 (ethyl acetate/petroleum ether = 1/3, v/v), [α]<sub>D</sub><sup>20</sup> = -171.34 (*c* = 0.14 in CHCl<sub>3</sub>).

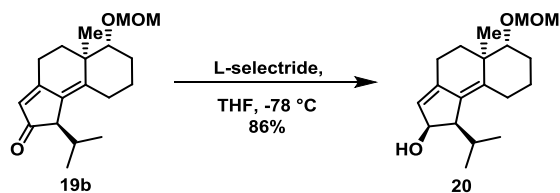
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 5.76 (s, 1H), 4.73 (d, *J* = 6.8 Hz, 1H), 4.59 (d, *J* = 6.8 Hz, 1H), 3.37 (s, 3H), 3.26 (dd, *J* = 11.7, 4.2 Hz, 1H), 2.78 (d, *J* = 3.3 Hz, 1H), 2.69 (dt, *J* = 16.8, 4.2 Hz, 1H), 2.59 (td, *J* = 15.4, 4.6 Hz, 1H), 2.39 – 2.31 (m, 1H), 2.19 – 2.02 (m, 3H), 1.98 – 1.89 (m, 1H), 1.89 – 1.82 (m, 1H), 1.67 – 1.55 (m, 2H), 1.34 – 1.20 (m, 1H), 1.15 (s, 3H), 1.14 (d, *J* = 6.9 Hz, 3H), 0.66 (d, *J* = 6.9 Hz, 3H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 208.2, 170.9, 142.7, 135.2, 126.8, 95.8, 84.0, 55.8, 53.2, 40.9, 34.5, 30.5, 27.3, 27.2, 23.5, 22.6, 20.3, 17.8, 17.2.

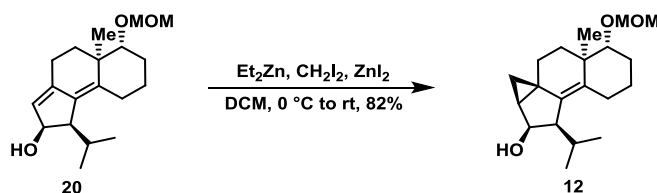
HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>29</sub>O<sub>3</sub> 305.2111; Found 305.2110.



To a suspension of *t*-BuOK (112 mg, 0.5 mmol, 5 equiv) in dry THF (1 mL) at -78 °C was added ketone **19a** (61 mg, 0.2 mmol, 1.0 equiv) in THF (0.5 mL), the reaction mixture stirred at same temperature for 5 h before quenched with 1 N HCl (aq) at -78 °C. Then the mixture was allowed to warm up to room temperature and extracted with ethyl acetate (3 × 5 mL). The combined organic extracts were washed with saturated brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated, and the residue purified by flash chromatography (ethyl acetate/petroleum ether = 1/20, v/v) to afford the corresponding **19b** (47 mg, 78% yield) and **19a** (12 mg).



To a solution of ketone **19b** (3.27 g, 10.7 mmol, 1.0 equiv) in dry THF (100 mL) at  $-78\text{ }^\circ\text{C}$  was added L-selectride (1.0 M in THF, 16 mL, 1.5 equiv) slowly under argon atmosphere. The reaction mixture was stirred at same temperature until all start material was consumed as judged by TLC, then quenched with 10 mL  $\text{H}_2\text{O}$  and 20 mL MeOH before warm up to  $0\text{ }^\circ\text{C}$ , and 10 mL 30%  $\text{H}_2\text{O}_2$  was added slowly, the mixture stirred for 10 min and 10 mL 2 M NaOH aqueous solution was added and stirred additional 10 min. Finally, the solvent was removed under vacuum and water (30 mL) was added. The mixture extracted with ethyl acetate ( $3 \times 40\text{ mL}$ ). The combined organic extracts were washed with saturated brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated, and the residue purified by flash chromatography (ethyl acetate/petroleum ether = 1/30 to 1/10, v/v) to afford the corresponding allyl alcohol **20** (2.82 g, 86% yield) as a yellow oil.  $R_f = 0.54$  (ethyl acetate/petroleum ether = 1/5, v/v) This compound was not fully characterized due to its instability while recording NMR spectrum.

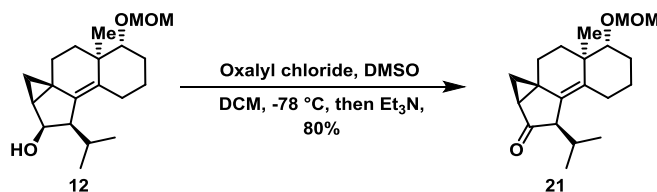


To a solution of allyl alcohol **20** (2.82 g, 9.2 mmol, 1.0 equiv) and  $\text{ZnI}_2$  (734 mg, 2.3 mmol, 0.25 equiv) in dry DCM (300 mL) at  $0\text{ }^\circ\text{C}$  was added  $\text{Et}_2\text{Zn}$  (1.0 M in hexane, 23 mL, 2.5 equiv) dropwise, and stirred at same temperature for 15 min. Then a solution of  $\text{CH}_2\text{I}_2$  (1.85 mL, 23 mmol, 2.5 equiv) in dry DCM (20 mL) was added slowly, and stirred for additional 10 min. The mixture stirred at room temperature until all start material was consumed as judged by TLC. The mixture was treated with saturated  $\text{NH}_4\text{Cl}$  solution (30 mL) and extracted with DCM ( $3 \times 40\text{ mL}$ ). The combined organic extracts were washed with saturated brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated, and the residue purified by flash chromatography (ethyl acetate/petroleum ether = 1/20, v/v) to afford the corresponding **12** (2.42 g, 82% yield) as a yellow oil.  $R_f = 0.55$  (ethyl acetate/petroleum ether = 1/5, v/v).  $[\alpha]_D^{20} = -131.87$  ( $c = 0.12$  in  $\text{CHCl}_3$ ).

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  4.72 (d,  $J = 6.7$  Hz, 1H), 4.62 (d,  $J = 6.8$  Hz, 1H), 4.59 (s, 1H), 3.39 (s, 3H), 3.17 (dd,  $J = 11.6, 3.2$  Hz, 1H), 2.39 (t,  $J = 8.5$  Hz, 1H), 2.13 (d,  $J = 13.8$  Hz, 1H), 2.01 – 1.80 (m, 4H), 1.75 (d,  $J = 12.9$  Hz, 1H), 1.71 – 1.65 (m, 1H), 1.62 – 1.46 (m, 4H), 1.32 – 1.11 (m, 2H), 1.04 (s, 3H), 0.99 (d,  $J = 6.2$  Hz, 3H), 0.91 (s, 1H), 0.77 (d,  $J = 7.0$  Hz, 3H), 0.46 – 0.40 (m, 1H).

**$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )**  $\delta$  137.4, 134.9, 95.9, 86.0, 74.1, 55.7, 47.4, 41.2, 36.2, 30.9, 30.7, 27.6, 26.8, 26.5, 26.4, 26.3, 23.8, 20.6, 17.7, 16.8.

**HRMS (ESI)**  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{20}\text{H}_{33}\text{O}_3$  321.2424; Found 321.2428.

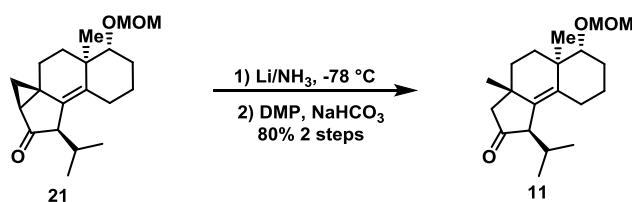


To a solution of (ClCO)<sub>2</sub> (0.53 mL, 6.6 mmol, 1.1 equiv) in DCM (40 mL) was added DMSO (0.92 mL, 13 mmol, 2.2 equiv) slowly at -78 °C under argon atmosphere. After stirring for 0.5 h, a solution of the alcohol **12** (1.92 g, 6.0 mmol, 1.0 equiv) in DCM (20 mL) was added dropwise into the mixture. After stirring for another 2 h at -78 °C, Et<sub>3</sub>N (2.5 mL, 18 mmol, 3.0 equiv) was added and the mixture was slowly warmed to rt. The mixture was quenched with satd. NH<sub>4</sub>Cl (20 mL) solution after stirring for another 1h stirring. The mixture was extracted with DCM (3 × 40 mL), and the combined organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo to give a residue, which was purified by flash chromatography (ethyl acetate/petroleum ether = 1/15, v/v) to afford the corresponding ketone **21** (1.51 g, 80% yield) as a yellow oil. R<sub>f</sub> = 0.63 (ethyl acetate/petroleum ether = 1/5, v/v). [α]<sub>D</sub><sup>20</sup> = -236.79 (c = 0.12 in CHCl<sub>3</sub>).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 4.72 (d, *J* = 6.7 Hz, 1H), 4.60 (d, *J* = 6.7 Hz, 1H), 3.37 (s, 3H), 3.21 (dd, *J* = 11.4, 3.9 Hz, 1H), 2.41 (d, *J* = 9.1 Hz, 1H), 2.11 – 1.98 (m, 3H), 1.96 – 1.81 (m, 3H), 1.76 (d, *J* = 12.1 Hz, 1H), 1.68 – 1.50 (m, 3H), 1.32 – 1.16 (m, 2H), 1.13 – 1.08 (m, 1H), 1.07 (s, 3H), 1.00 (d, *J* = 6.4 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 212.7, 136.5, 132.0, 95.7, 85.5, 55.7, 55.3, 41.5, 37.4, 36.3, 36.2, 32.4, 27.4, 26.2, 26.0, 23.8, 23.4, 22.2, 22.0, 17.8.

**HRMS (ESI) m/z:** [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>31</sub>O<sub>3</sub> 319.2268; Found 319.2268.



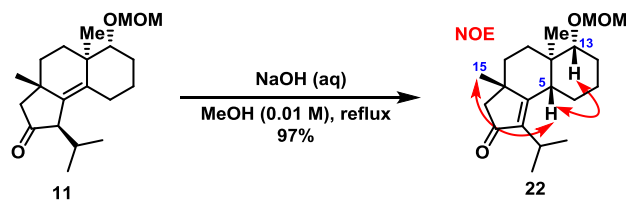
To a solution of ketone **21** (159 mg, 0.5 mmol, 1.0 equiv) in dry THF (5 mL) at -78 °C was added dry *t*-BuOH (0.25 mL) under argon atmosphere, Then, liquid ammonia (10 mL) was added, to this solution was added Lithium (35 mg, 5.0 mmol) in small pieces. After stirring for 30 min at -78 °C, the resulting mixture was quenched with saturated NH<sub>4</sub>Cl solution. The mixture extracted with ethyl acetate (3 × 15 mL). The combined organic extracts were washed with saturated brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated, and the residue was used directly without further purification.

To a solution of crude alcohol in DCM (5 mL) was added NaHCO<sub>3</sub> (252 mg, 3.0 mmol, 6.0 equiv) and Dess-Martin Periodinane (318 mg, 0.75 mmol, 1.5 equiv). The mixture stirred at room temperature until all start material was consumed as judged by TLC. Then the mixture was treated with water (10 mL) and extracted with DCM (3 × 10 mL). The combined organic extracts were washed with saturated brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated, and the residue purified by flash chromatography (ethyl acetate/petroleum ether = 1/20, v/v) to afford the corresponding **11** (133 mg, 80% yield) as a yellow oil. R<sub>f</sub> = 0.71 (ethyl acetate/petroleum ether = 1/5, v/v). [α]<sub>D</sub><sup>20</sup> = +5.30 (c = 0.10 in CHCl<sub>3</sub>).

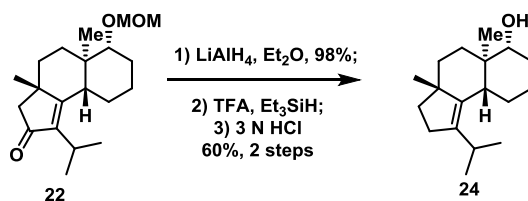
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 4.73 (d, *J* = 6.2 Hz, 1H), 4.62 (d, *J* = 6.2 Hz, 1H), 3.39 (s, 3H), 3.19 (d, *J* = 11.5 Hz, 1H), 2.57 (d, *J* = 9.6 Hz, 1H), 2.39 – 2.32 (m, 1H), 2.09 (d, *J* = 16.9 Hz, 2H), 1.98 – 1.75 (m, 5H), 1.73 – 1.65 (m, 1H), 1.65 – 1.53 (m, 2H), 1.53 – 1.44 (m, 1H), 1.29 – 1.18 (m, 1H), 1.18 – 1.14 (m, 6H), 1.05 (s, 3H), 0.91 (d, *J* = 6.5 Hz, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 219.0, 137.9, 137.6, 95.8, 85.9, 57.7, 56.2, 55.7, 41.4, 39.4, 34.3, 33.3, 31.8, 27.7, 27.5, 26.5, 23.7, 22.3, 21.2, 18.4.

**HRMS (ESI) m/z:** [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>33</sub>O<sub>3</sub> 321.2424; Found 321.2420.



To a solution of compound ketone **11** (32 mg, 0.1 mmol, 1.0 equiv) in MeOH (10 mL) was added aqueous NaOH (1.0 M, 2.0 mL, 20 equiv) solution, and the mixture was heated under reflux. After 2 h, the solvent was removed under vacuum and water (10 mL) was added. The mixture extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with saturated brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated, and the residue purified by flash chromatography (ethyl acetate/petroleum ether = 1/30 to 1/10, v/v) to afford the corresponding ketone **22** (31 mg, 97% yield) as a yellow oil. *R*<sub>f</sub> = 0.51 (ethyl acetate/petroleum ether = 1/8, v/v). [α]<sub>D</sub><sup>20</sup> = -66.13 (*c* = 0.16 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.72 (d, *J* = 6.9 Hz, 1H), 4.58 (d, *J* = 6.9 Hz, 1H), 3.37 (s, 3H), 3.30 (dd, *J* = 11.6, 4.1 Hz, 1H), 3.12 – 3.00 (m, 1H), 2.45 (dd, *J* = 12.3, 3.0 Hz, 1H), 2.21 – 2.05 (m, 2H), 1.91 – 1.82 (m, 4H), 1.80 – 1.70 (m, 2H), 1.55 – 1.40 (m, 3H), 1.30 – 1.23 (m, 1H), 1.21 (s, 3H), 1.18 (d, *J* = 7.0 Hz, 3H), 1.16 (d, *J* = 7.0 Hz, 3H), 0.82 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 208.7, 175.4, 143.9, 95.7, 85.0, 55.8, 52.4, 46.5, 43.5, 41.8, 37.0, 34.4, 27.3, 25.7, 25.0, 25.0, 24.6, 20.5, 20.4, 11.9. HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>33</sub>O<sub>3</sub> 321.2424; Found 321.2417.



To a suspension of LiAlH<sub>4</sub> (235 mg, 6.2 mmol, 3.0 equiv) in dry Et<sub>2</sub>O (15 mL) at 0 °C was added ketone **22** (661 mg, 2.06 mmol, 1.0 equiv) in Et<sub>2</sub>O (5 mL) dropwise under argon atmosphere, and stirred at this temperature for 30 min. then 0.3 mL H<sub>2</sub>O was added and followed by 0.6 mL (3 M) NaOH aqueous solution and stirred for 15 min. the mixture was filtered under vacuum through a pad of Celite and washed three times with DCM. The filtrate was concentrated and the residue was purified by flash chromatography (ethyl acetate/petroleum ether = 1/30 to 1/15, v/v) to afford the corresponding allyl alcohol (651 mg, 98% yield) as a yellow oil.

To a solution of all above allyl alcohol (651 mg, 2.02 mmol) in dry DCM (20 mL) was added Et<sub>3</sub>SiH (3.3 mL, 20.2 mmol, 10 equiv), and the mixture was cooled to -40 °C, after 5 min, TFA (0.9 mL, 10.3 mmol, 5 equiv) was added slowly to reaction mixture. Then stirred at same temperature for 15 min, the solvent was removed under vacuum and the residue was used directly without further purification.

To a solution of all above cyclopentadiene in THF (10 mL) was added 3 N HCl (14 mL) aqueous solution, and the mixture was heated under 50 °C. After 2 h, the solvent was removed under vacuum and water (10 mL) was added. The mixture extracted with ethyl acetate (3 × 15 mL). The combined organic extracts were washed with saturated brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated, and the residue purified by flash chromatography (ethyl acetate/petroleum ether = 1/20, v/v) to afford the corresponding alcohol **24** (318 mg, 60% yield for 2 steps) as colorless oil. *R*<sub>f</sub> = 0.51 (ethyl acetate/petroleum ether = 1/5, v/v). [α]<sub>D</sub><sup>20</sup> = -4.88 (*c* = 0.12 in CHCl<sub>3</sub>).

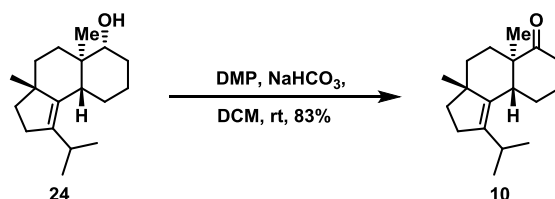
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.32 (dd, *J* = 11.5, 4.3 Hz, 1H), 3.08 – 2.99 (m, 1H), 2.29 – 2.21 (m,



2H), 2.07 – 1.99 (m, 1H), 1.82 – 1.73 (m, 3H), 1.73 – 1.67 (m, 1H), 1.65 – 1.59 (m, 1H), 1.55 – 1.34 (m, 6H), 1.33 – 1.20 (m, 1H), 1.01 (s, 3H), 0.98 (d,  $J = 6.8$  Hz, 3H), 0.91 (d,  $J = 6.8$  Hz, 3H), 0.78 (s, 3H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  140.0, 136.8, 80.0, 48.8, 45.0, 42.0, 39.4, 37.4, 35.2, 30.4, 28.7, 26.5, 26.1, 25.0, 23.9, 22.4, 21.6, 10.9.

HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{31}\text{O}_3$  263.2369; Found 263.2377.



To a solution of alcohol **24** (318 mg, 1.2 mmol) in DCM (10 mL) was added  $\text{NaHCO}_3$  (605 mg, 6.0 mmol, 6.0 equiv) and Dess-Martin Periodinane (763 mg, 1.8 mmol, 1.5 equiv). The mixture stirred at room temperature until all start material was consumed as judged by TLC. Then the mixture was treated with water (10 mL) and extracted with DCM ( $3 \times 10$  mL). The combined organic extracts were washed with saturated brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated, and the residue purified by flash chromatography (ethyl acetate/petroleum ether = 1/20, v/v) to afford the corresponding **10** (259 mg, 83% yield) as a yellow oil.  $R_f = 0.74$  (ethyl acetate/petroleum ether = 1/8, v/v).  $[\alpha]_D^{20} = -2.67$  ( $c = 0.10$  in  $\text{CHCl}_3$ ).

The analytic data ( $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra) of synthetic **10** were in good accordance with literature reports<sup>[2]</sup>.

Enantiomeric excess was found to be 97% by chiral HPLC (ChiralPak AD-H column, hexane/*i*-PrOH = 99:1, 214 nm, 0.7 mL/min,  $t_{\text{major}} = 6.86$  min,  $t_{\text{minor}} = 6.14$  min).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.14 – 3.03 (m, 1H), 2.64 (td,  $J = 14.3, 6.2$  Hz, 1H), 2.49 – 2.41 (m, 1H), 2.32 – 2.21 (m, 3H), 2.17 – 1.97 (m, 3H), 1.78 (td,  $J = 14.3, 4.3$  Hz, 1H), 1.67 – 1.39 (m, 6H), 1.06 (s, 3H), 1.03 (d,  $J = 6.8$  Hz, 3H), 0.99 (s, 3H), 0.95 (d,  $J = 6.8$  Hz, 3H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  216.3, 141.8, 135.5, 51.0, 48.7, 46.9, 39.2, 37.9, 36.8, 30.2, 29.0, 26.9, 26.6, 25.9, 23.9, 22.4, 21.7, 17.2.

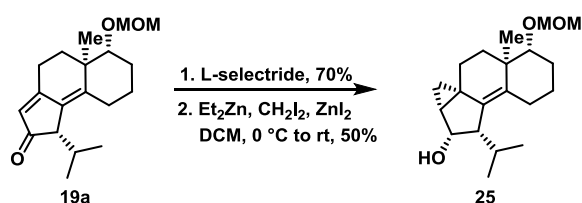
HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{29}\text{O}$  261.2213; Found 261.2210.

**Table S1.** Comparison of the <sup>1</sup>H NMR spectroscopic data (CDCl<sub>3</sub>) of compound **10**

<sup>1</sup> H NMR (lit. <sup>2</sup> ) δH [ppm, mult, <i>J</i> (Hz)] 400 MHz	<sup>1</sup> H NMR (Our synthetic) δH [ppm, mult, <i>J</i> (Hz)] 500 MHz	Err (lit. <sup>2</sup> –Our synthetic) ΔδH (ppm)
3.09 1H, sept, 6.8	3.09, 1H, m	0
2.64 1H, ddd, 7.2, 7.2, 6.1	2.64, 1H, td, 14.3, 6.2	0
2.45 1H, m	2.45, 1H, m	0
2.28 3H, m	2.27, 3H, m	0.01
2.08 3H, m	2.08, 3H, m	0
1.78 1H, ddd, 7.2, 7.2, 4.4	1.78, 1H, td, 14.3, 4.3	0
1.54 6H, m	1.55, 6H, m	-0.01
1.06 3H, s	1.06, 3H, s	0
1.03 3H, d, 6.8	1.03, 3H, d, 6.8	0
0.99 3H, s	0.99, 3H, s	0
0.96 3H, d, 6.8	0.95, 3H, d, 6.8	0.01

**Table S2.** Comparison of the <sup>13</sup>C NMR spectroscopic data (CDCl<sub>3</sub>) of compound **10**

<sup>13</sup> C NMR (lit. <sup>2</sup> ) δC [ppm] 100 MHz	<sup>13</sup> C NMR (Our synthetic) δC [ppm] 125 MHz	Err (lit. <sup>2</sup> –Our synthetic) ΔδC (ppm)
216.1	216.3	-0.2
141.5	141.8	-0.3
135.2	135.5	-0.3
50.9	51.0	-0.1
48.5	48.7	-0.2
46.7	46.9	-0.2
39.0	39.2	-0.2
37.8	37.9	-0.1
36.7	36.8	-0.1
30.1	30.2	-0.1
28.9	29.0	-0.1
26.8	26.9	-0.1
26.6	26.6	0
25.9	25.9	0
23.8	23.9	-0.1
22.4	22.4	0
21.6	21.7	-0.1
17.1	17.2	-0.1



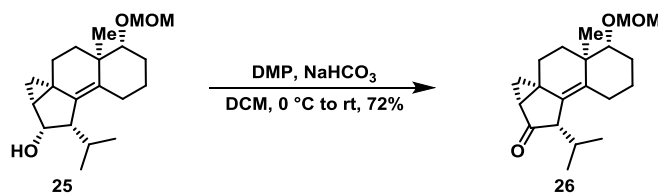
To a solution of ketone **19a** (375 mg, 1.23 mmol, 1.0 equiv) in dry THF (10 mL) at -78 °C was added L-selectride (1.0 M in THF, 1.85 mL, 1.85 mmol, 1.5 equiv) slowly under argon atmosphere. The reaction mixture was stirred at same temperature until all start material was consumed as judged by TLC, then quenched with 1 mL H<sub>2</sub>O and 2 mL MeOH before warm up to 0 °C, and 1 mL 30% H<sub>2</sub>O<sub>2</sub> was added slowly, the mixture stirred for 10 min and 1 mL 2 M NaOH aqueous solution was added and stirred additional 10 min. Finally, the solvent was removed under vacuum and water (10 mL) was added. The mixture extracted with ethyl acetate (3 × 15 mL). The combined organic extracts were washed with saturated brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated, and the residue purified by flash chromatography (ethyl acetate/petroleum ether = 1/30 to 1/10, v/v) to afford the corresponding allyl alcohol (264 mg, 70 % yield) as a yellow oil. R<sub>f</sub> = 0.53 (ethyl acetate/petroleum ether = 1/5, v/v).

To a solution of allyl alcohol (233 mg, 0.76 mmol, 1.0 equiv) and ZnI<sub>2</sub> (61 mg, 0.19 mmol, 0.25 equiv) in dry DCM (8 mL) at 0 °C was added Et<sub>2</sub>Zn (1.0 M in hexane, 1.9 mL, 2.5 equiv) dropwise, and stirred at same temperature for 15 min. Then a solution of CH<sub>2</sub>I<sub>2</sub> (0.15 mL, 1.9 mmol, 2.5 equiv) in dry DCM (2 mL) was added slowly, and stirred for additional 10 min. The mixture stirred at room temperature until all start material was consumed as judged by TLC. The mixture was treated with saturated NH<sub>4</sub>Cl solution (10 mL) and extracted with DCM (3 × 20 mL). The combined organic extracts were washed with saturated brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated, and the residue purified by flash chromatography (ethyl acetate/petroleum ether = 1/20, v/v) to afford the corresponding **25** (122 mg, 50% yield) as a yellow oil. R<sub>f</sub> = 0.52 (ethyl acetate/petroleum ether = 1/5, v/v). [α]<sub>D</sub><sup>20</sup> = +8.45 (c = 0.16 in CHCl<sub>3</sub>).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 4.70 (d, *J* = 6.7 Hz, 1H), 4.65 – 4.58 (m, 1H), 4.56 (d, *J* = 6.7 Hz, 1H), 3.49 (dd, *J* = 11.1, 4.1 Hz, 1H), 3.36 (s, 3H), 2.46 (t, *J* = 8.7 Hz, 1H), 2.18 – 2.09 (m, 2H), 1.99 – 1.82 (m, 3H), 1.76 – 1.54 (m, 5H), 1.39 (t, *J* = 13.8 Hz, 1H), 1.14 – 1.09 (m, 1H), 1.09 (d, *J* = 6.0 Hz, 5H), 0.99 (d, *J* = 6.2 Hz, 3H), 0.87 (s, 1H), 0.73 (d, *J* = 7.0 Hz, 3H), 0.48 (d, *J* = 5.1 Hz, 1H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 137.6, 136.4, 96.0, 78.9, 74.1, 55.6, 47.2, 41.2, 32.4, 31.3, 31.1, 27.9, 27.8, 27.4, 26.1, 26.1, 25.3, 21.7, 19.8, 16.1.

**HRMS (ESI)** m/z: [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>33</sub>O<sub>3</sub> 321.2424; Found 321.2421.

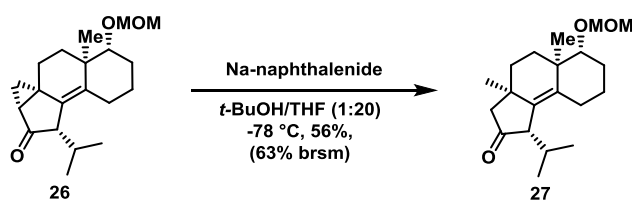


To a solution of cyclopropane **25** (156 mg, 0.49 mmol, 1.0 equiv) in dry DCM (5 mL) at 0 °C was added NaHCO<sub>3</sub> (202 mg, 2.4 mmol, 5.0 equiv) and Dess-Martin Periodinane (309 mg, 0.73 mmol, 1.5 equiv). The mixture stirred at same temperature until all start material was consumed as judged by TLC. Then the mixture was treated with water (10 mL) and extracted with DCM (3 × 10 mL). The combined organic extracts were washed with saturated brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated, and the residue purified by flash chromatography (ethyl acetate/petroleum ether = 1/15, v/v) to afford the corresponding **26** (113 mg, 72% yield) as a yellow oil. R<sub>f</sub> = 0.61 (ethyl acetate/petroleum ether = 1/5, v/v). [α]<sub>D</sub><sup>20</sup> = +90.95 (c = 0.13 in CHCl<sub>3</sub>).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 4.71 (d, *J* = 6.5 Hz, 1H), 4.57 (d, *J* = 6.4 Hz, 1H), 3.53 – 3.46 (m, 1H), 3.37 (s, 3H), 2.48 (d, *J* = 9.4 Hz, 1H), 2.28 (d, *J* = 13.7 Hz, 1H), 2.14 – 1.98 (m, 3H), 1.94 (d, *J* = 9.5 Hz, 2H), 1.74 (d, *J* = 12.8 Hz, 1H), 1.71 – 1.57 (m, 3H), 1.47 (t, *J* = 14.0 Hz, 1H), 1.23 – 1.13 (m, 3H), 1.13 (s, 3H), 1.01 (d, *J* = 6.1 Hz, 3H), 0.90 (d, *J* = 6.5 Hz, 3H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  213.2, 137.9, 132.4, 96.1, 78.8, 55.7, 55.1, 41.6, 37.8, 36.3, 33.1, 32.4, 27.7, 27.2, 26.0, 24.8, 23.0, 21.9, 21.9, 21.7.

HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{20}\text{H}_{31}\text{O}_3$  319.2268; Found 319.2270.

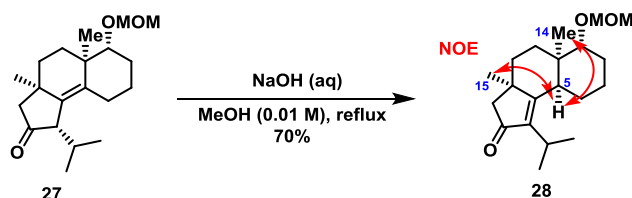


To a solution of ketone **26** (113 mg, 0.35 mmol, 1.0 equiv) in dry THF (8 mL) at  $-78\text{ }^\circ\text{C}$  was added dry *t*-BuOH (0.4 mL) under argon atmosphere, Then, a solution of sodium naphthalenide (0.65 M in THF, 1.1 mL, 0.7 mmol, 2.0 equiv) was added dropwise, and the resulting mixture was stirred for 2 h before quenched with saturated  $\text{NH}_4\text{Cl}$  solution. The mixture extracted with ethyl acetate ( $3 \times 15$  mL). The combined organic extracts were washed with saturated brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated, and the residue purified by flash chromatography (ethyl acetate/petroleum ether = 1/30 to 1/15, v/v) to afford the corresponding ketone **27** (63 mg, 56% yield) as a yellow oil.  $R_f = 0.67$  (ethyl acetate/petroleum ether = 1/5, v/v).  $[\alpha]_D^{20} = -94.25$  ( $c = 0.16$  in  $\text{CHCl}_3$ ).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.71 (d,  $J = 6.8$  Hz, 1H), 4.57 (d,  $J = 6.8$  Hz, 1H), 3.37 (s, 3H), 3.34 (d,  $J = 4.7$  Hz, 1H), 2.62 (d,  $J = 9.6$  Hz, 1H), 2.40 – 2.27 (m, 1H), 2.15 – 2.05 (m, 3H), 2.03 – 1.93 (m, 1H), 1.96 – 1.89 (m, 1H), 1.84 (dt,  $J = 9.4, 6.7$  Hz, 1H), 1.71 (d,  $J = 15.7$  Hz, 1H), 1.61 (dd,  $J = 12.6, 8.5$  Hz, 2H), 1.51 – 1.38 (m, 2H), 1.17 (s, 3H), 1.15 (d,  $J = 6.5$  Hz, 3H), 1.11 (s, 3H), 1.09 – 1.03 (m, 1H), 0.88 (d,  $J = 6.9$  Hz, 3H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  219.3, 139.2, 138.1, 96.2, 79.3, 56.9, 56.2, 55.7, 41.1, 39.3, 34.5, 32.5, 29.1, 27.9, 27.5, 27.0, 24.7, 22.3, 22.1, 20.8.

HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{20}\text{H}_{33}\text{O}_3$  321.2424; Found 321.2427.



To a solution of compound ketone **27** (63 mg, 0.2 mmol, 1.0 equiv) in MeOH (20 mL) was added aqueous NaOH (1.0 M, 4.0 mL, 20 equiv) solution, and the mixture was heated under reflux. After 2 h, the solvent was removed under vacuum and water (10 mL) was added. The mixture extracted with ethyl acetate ( $3 \times 15$  mL). The combined organic extracts were washed with saturated brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated, and the residue purified by flash chromatography (ethyl acetate/petroleum ether = 1/30 to 1/10, v/v) to afford the corresponding allyl alcohol **28** (44 mg, 70% yield) as a yellow oil.  $R_f = 0.55$  (ethyl acetate/petroleum ether = 1/8, v/v).  $[\alpha]_D^{20} = -39.05$  ( $c = 0.14$  in  $\text{CHCl}_3$ ).

The configuration of ketone **28** was established by *NOE* experiments (from the observed C5–C14 and C5–C15 proton correlations).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.68 (d,  $J = 7.0$  Hz, 1H), 4.50 (d,  $J = 7.0$  Hz, 1H), 3.50 (dd,  $J = 11.1, 4.6$  Hz, 1H), 3.33 (s, 3H), 2.98 – 2.86 (m, 1H), 2.67 (s, 1H), 2.19 – 2.08 (m, 2H), 2.07 – 1.97 (m, 2H), 1.94 – 1.83 (m, 2H), 1.71 – 1.63 (m, 1H), 1.63 – 1.54 (m, 2H), 1.52 – 1.39 (m, 2H), 1.24 (d,  $J = 6.9$  Hz, 3H), 1.16 (s, 3H), 1.13 (d,  $J = 7.0$  Hz, 3H), 1.11 (s, 3H).

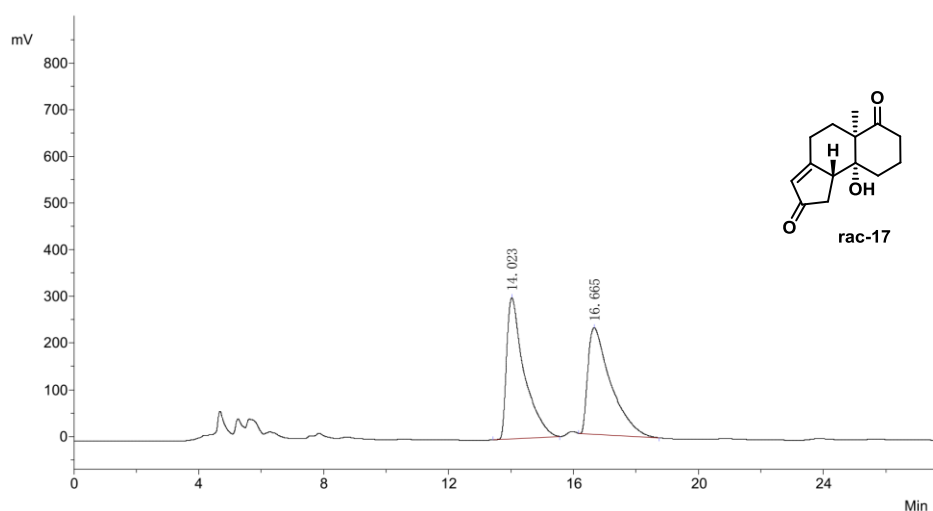
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 209.1, 173.8, 142.4, 95.2, 74.3, 55.7, 52.8, 45.3, 42.4, 42.4, 33.6, 30.4, 27.6, 27.1, 25.9, 22.5, 22.4, 21.8, 20.9, 19.4.

**HRMS (ESI) m/z:** [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>33</sub>O<sub>3</sub> 321.2424; Found 321.2427.

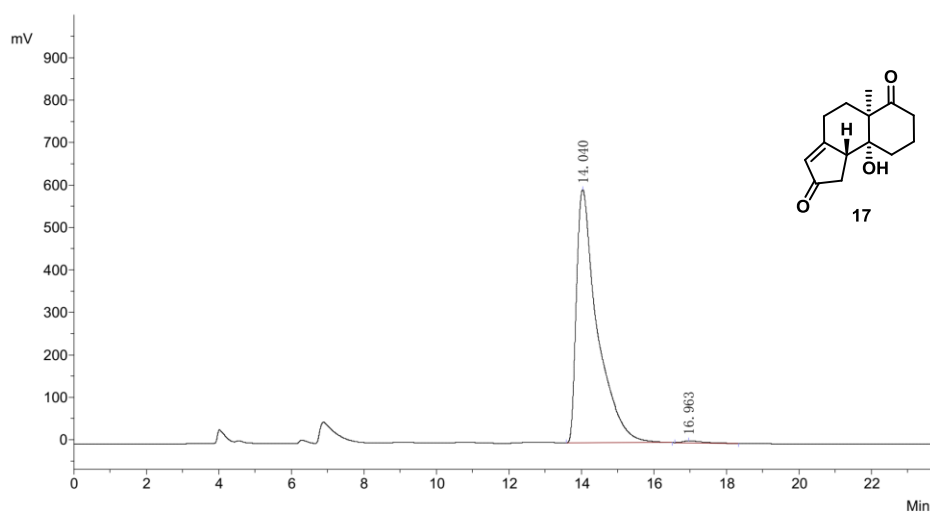
### 3 Reference

- [1] Zhou Z., Xu D., Jiang W., Chen J., Zhen Y., Huo J., Yan J., Gao J., & Xie W. *Org. Lett.* **2022**, 24(49), 9017-9022.
- [2] Watanabe H., Takano M., Umino A., Ito T., Ishikawa H., & Nakada M. *Org. Lett.* **2007**, 9(2), 359-362.

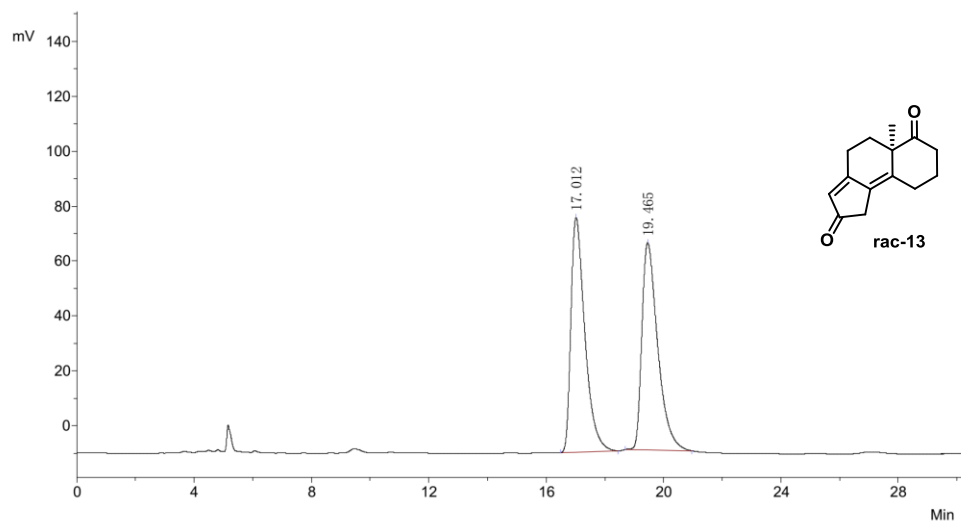
#### 4. HPLC Charts



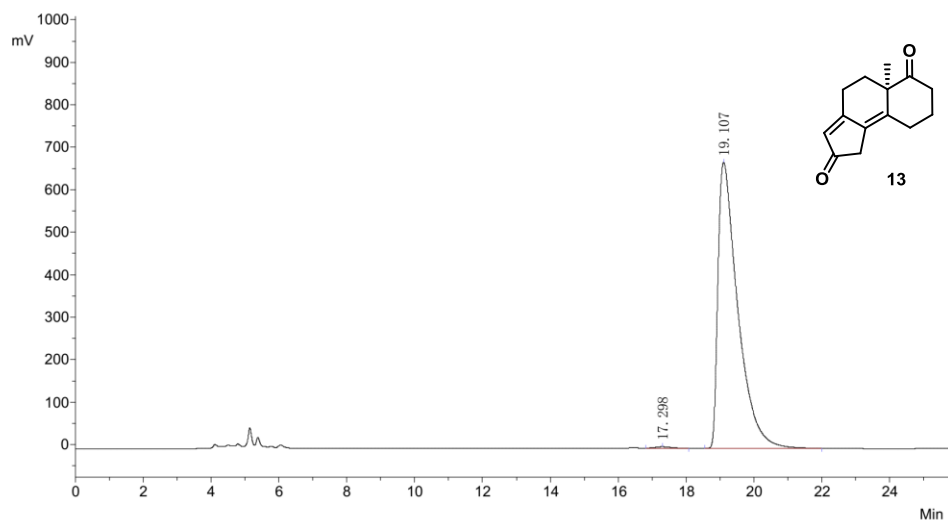
No.	R. Time	PeakHeight	PeakArea	PerCent	Conc
1	14.023	302597.6	11754217.8	50.3517	50.3517
2	16.665	227805.4	11590007.1	49.6483	49.6483
<b>Total</b>		530403.0	23344224.9	100.0000	100.0000



No.	R. Time	PeakHeight	PeakArea	PerCent	Conc
1	14.040	596814.2	23719501.2	99.2904	99.2904
2	16.963	4289.5	169515.0	0.7096	0.7096
<b>Total</b>		601103.7	23889016.2	100.0000	100.0000

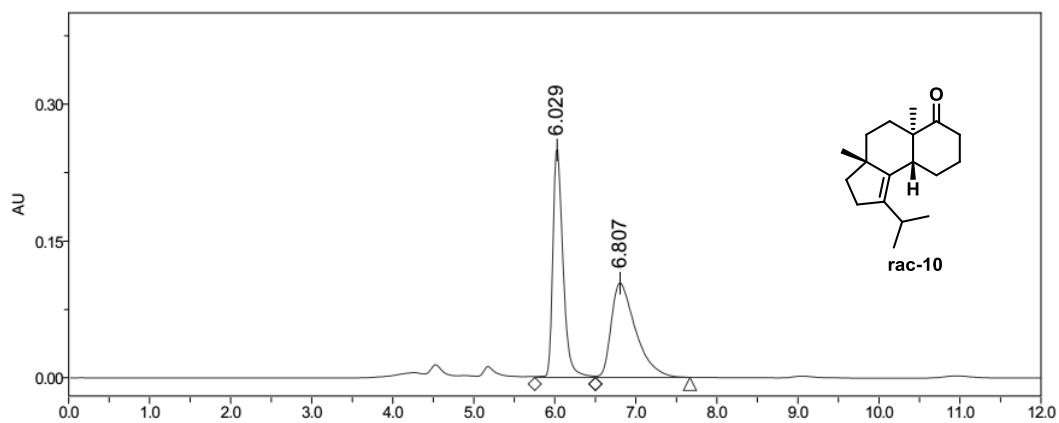


No.	R. Time	PeakHeight	PeakArea	PerCent	Conc
1	17.012	85424.8	2826704.8	49.9728	49.9728
2	19.465	75452.1	2829786.7	50.0272	50.0272
<b>Total</b>		<b>160876.9</b>	<b>5656491.5</b>	<b>100.0000</b>	<b>100.0000</b>

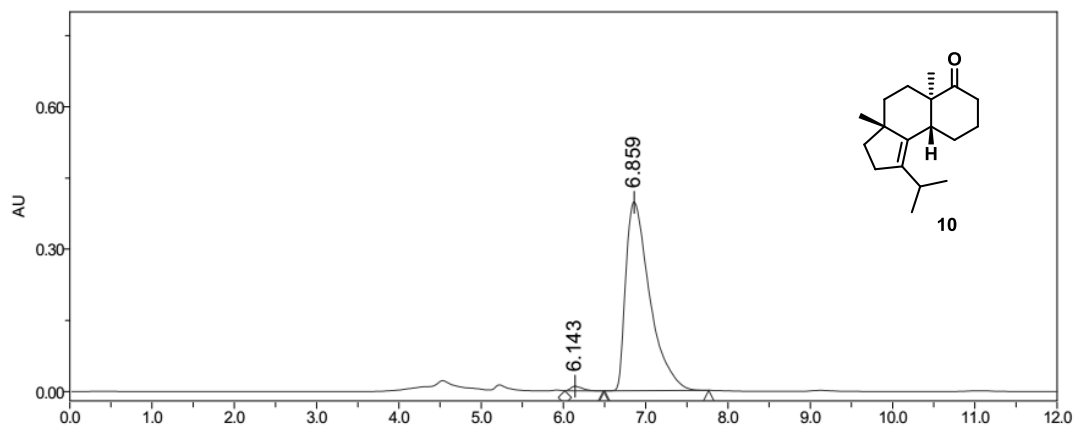


No.	R. Time	PeakHeight	PeakArea	PerCent	Conc
1	17.298	3555.9	107425.6	0.3927	0.3927
2	19.107	673900.8	27248529.7	99.6073	99.6073
<b>Total</b>		<b>677456.7</b>	<b>27355955.3</b>	<b>100.0000</b>	<b>100.0000</b>



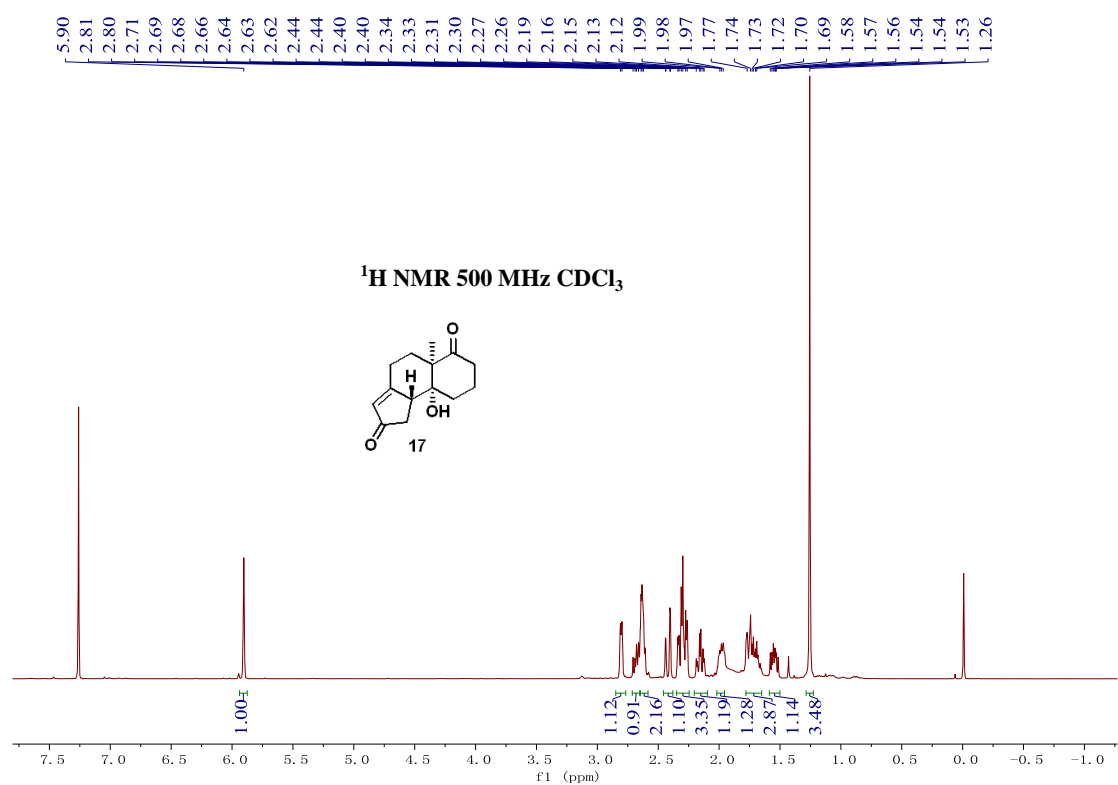


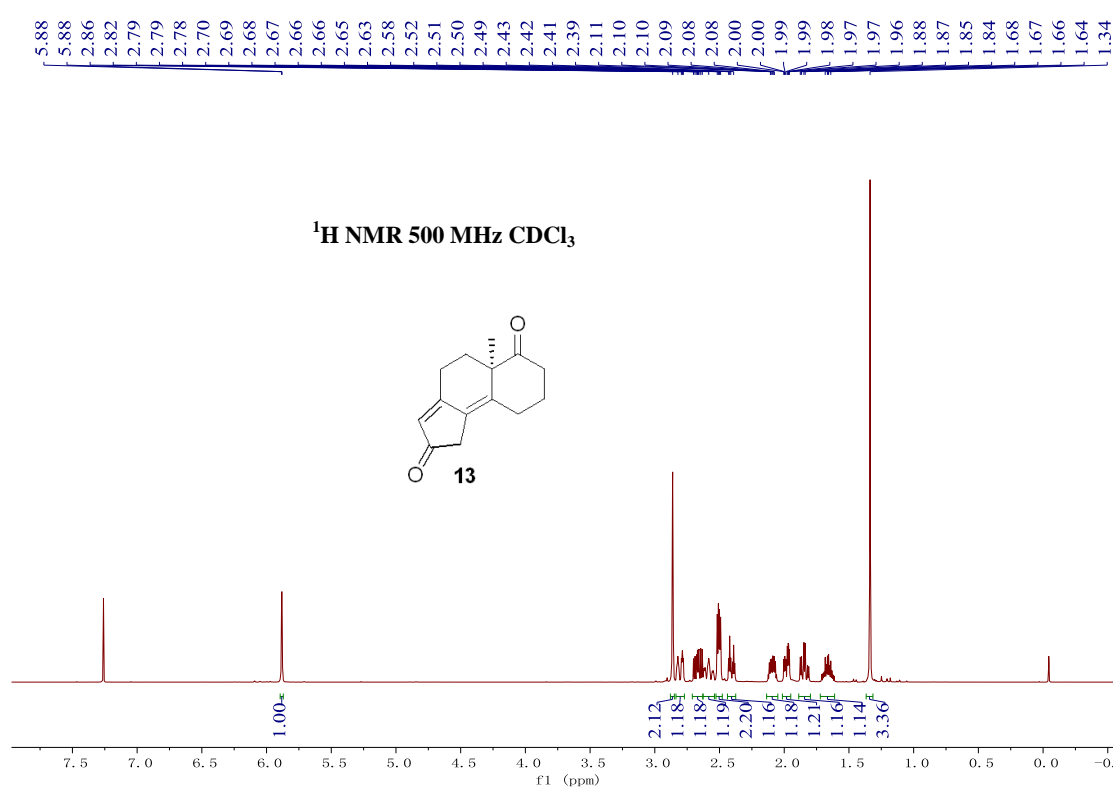
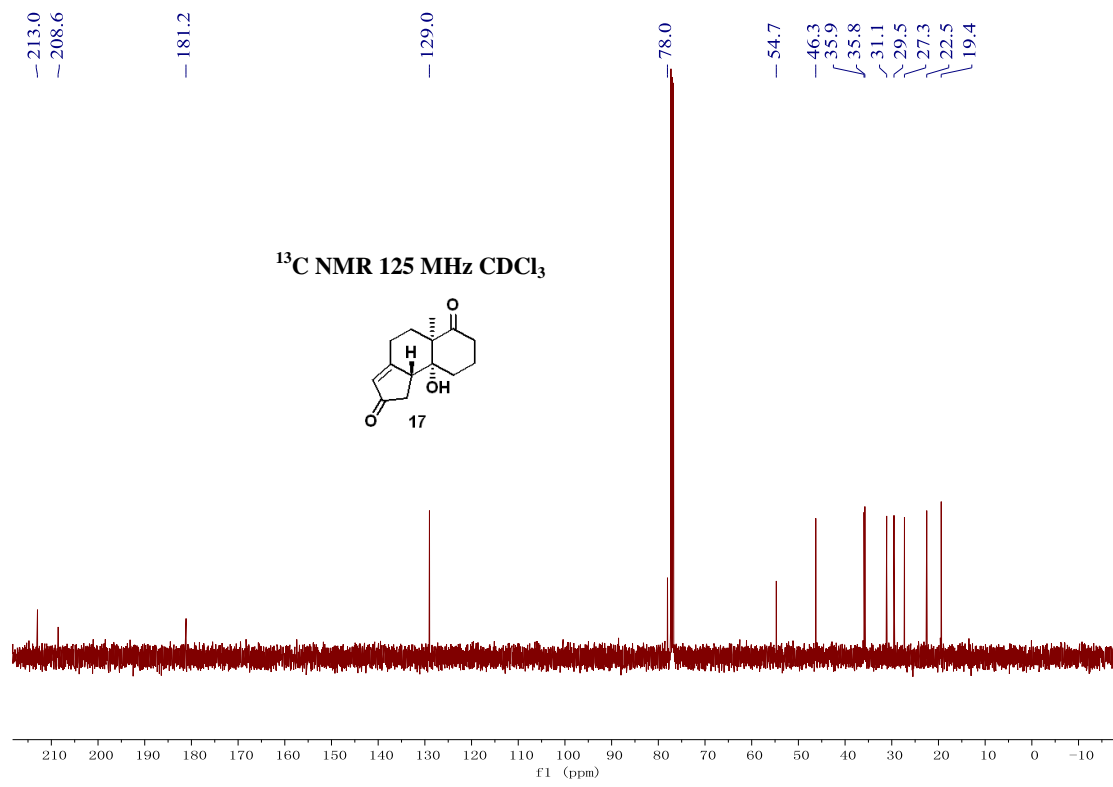
	R.Time	PeakArea	PeakHeight	PerCent%
1	6.029	2188867	250475	50.29
2	6.807	2163673	103557	49.71

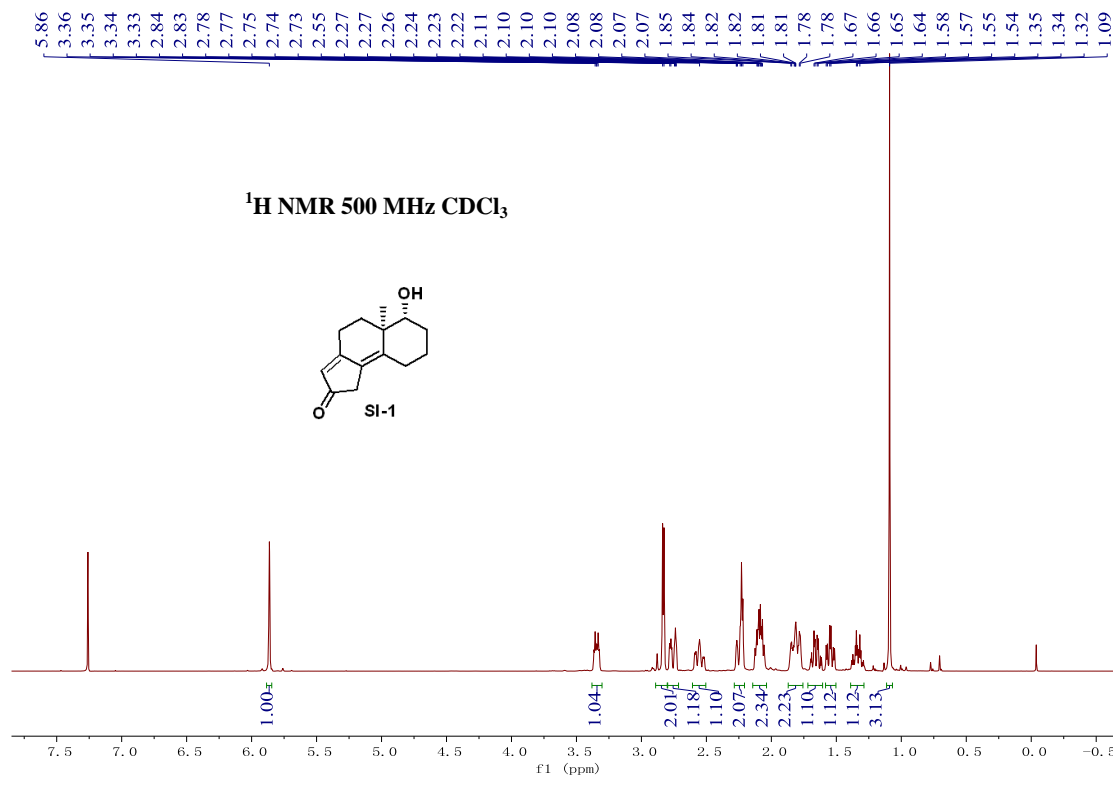
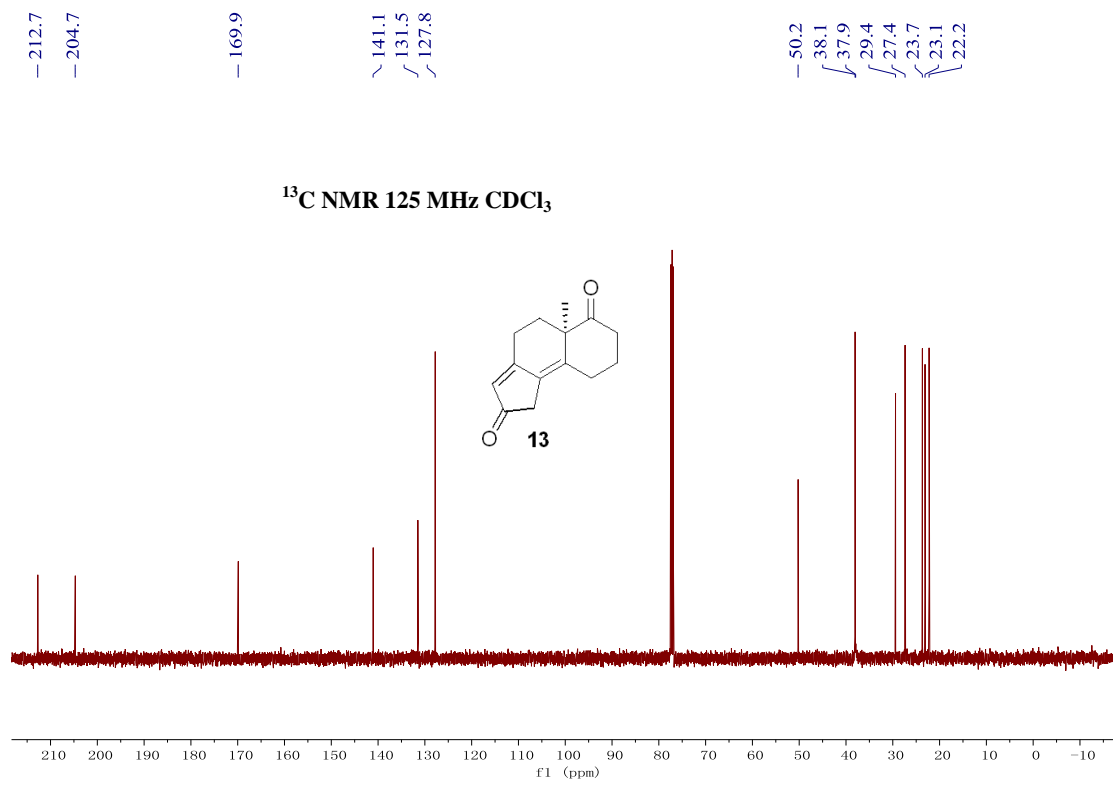


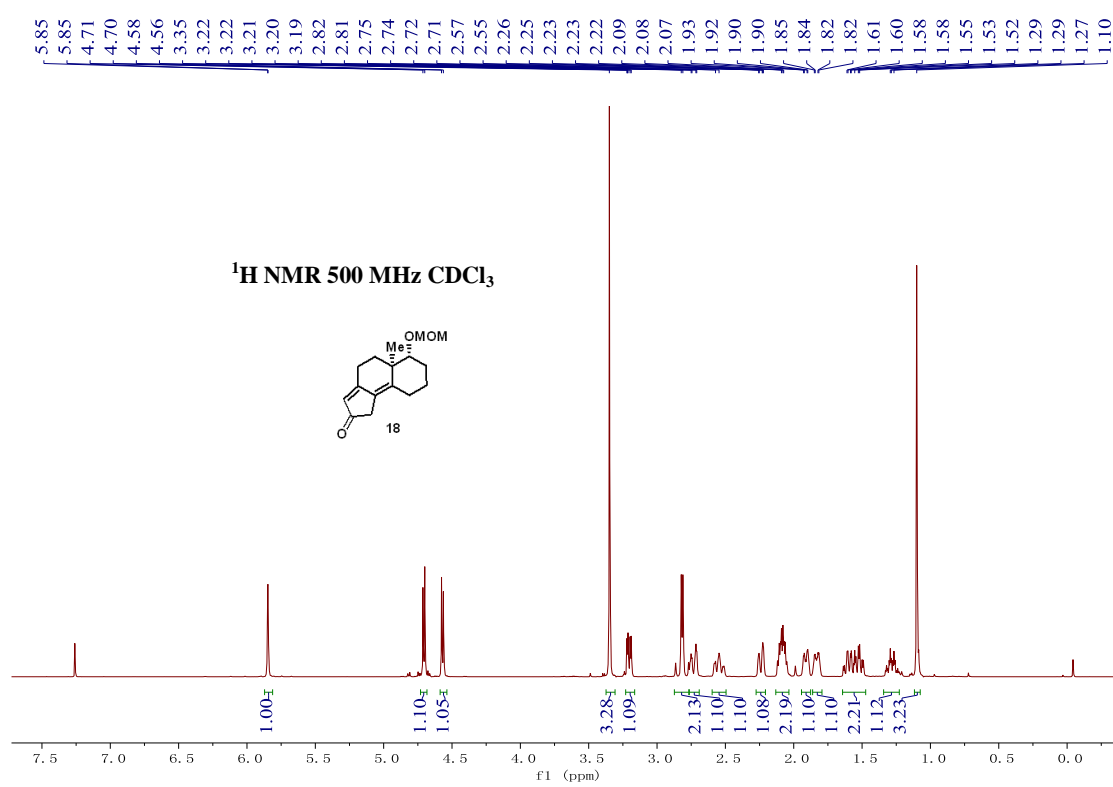
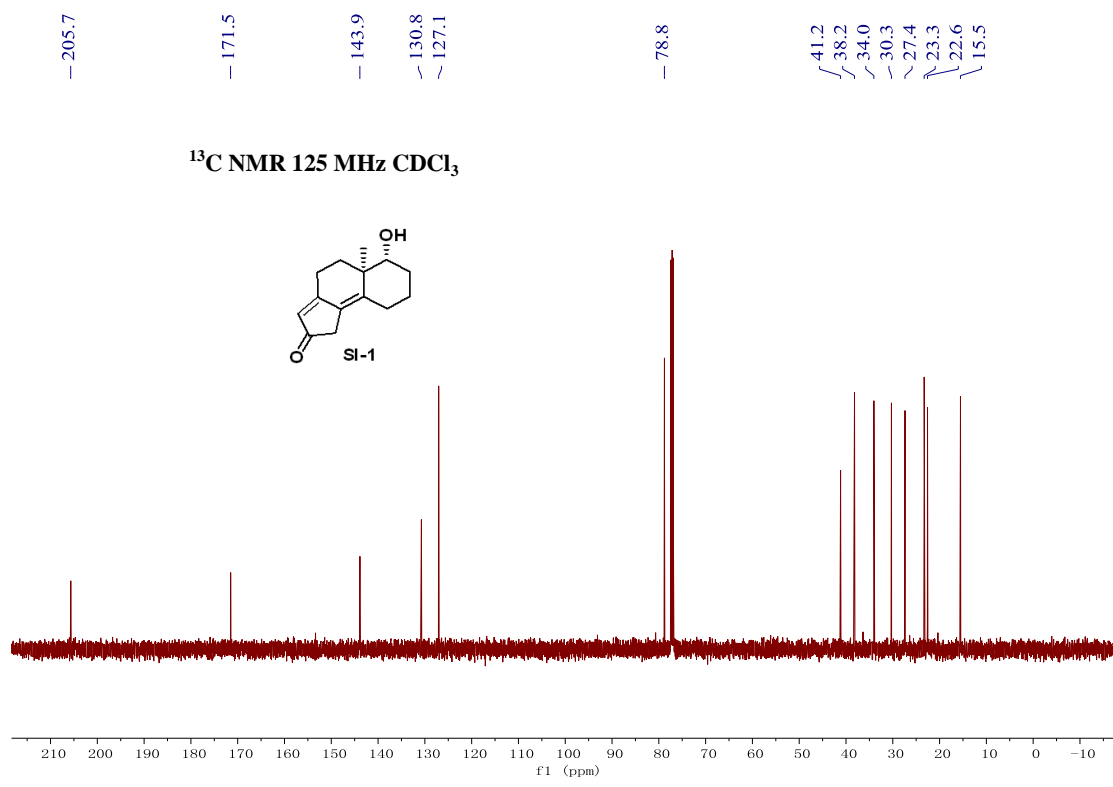
	R.Time	PeakArea	PeakHeight	PerCent%
1	6.143	100610	9928	1.23
2	6.859	8088382	398455	98.77

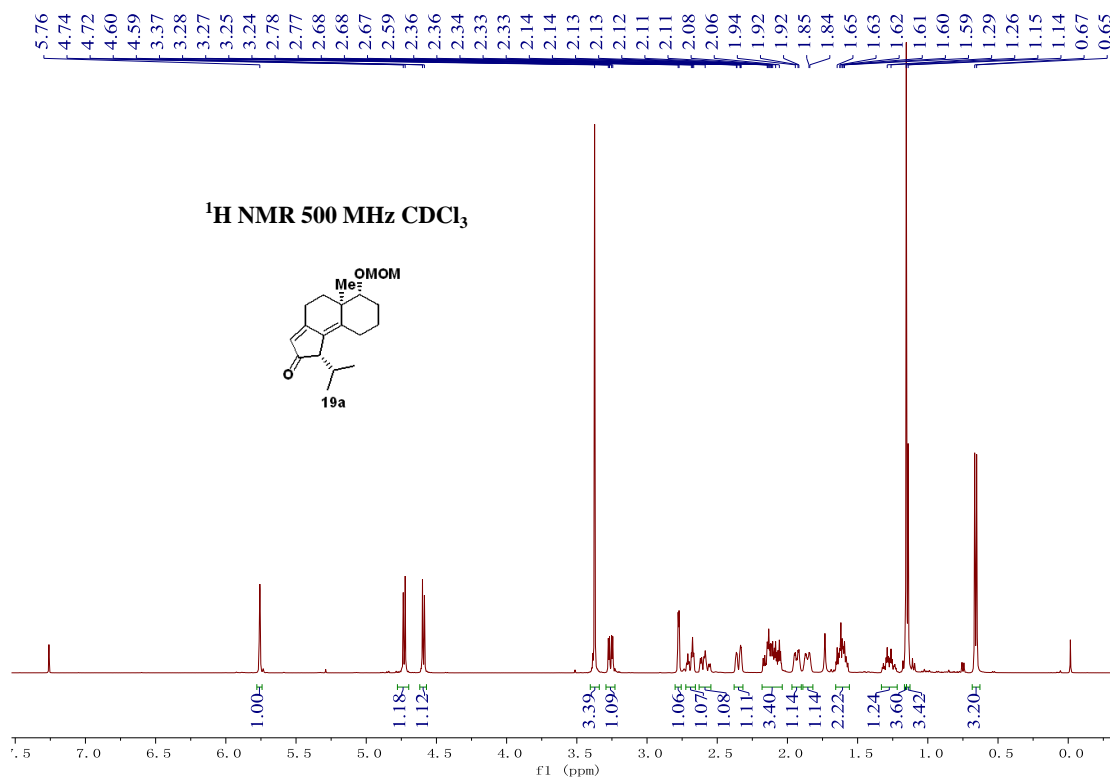
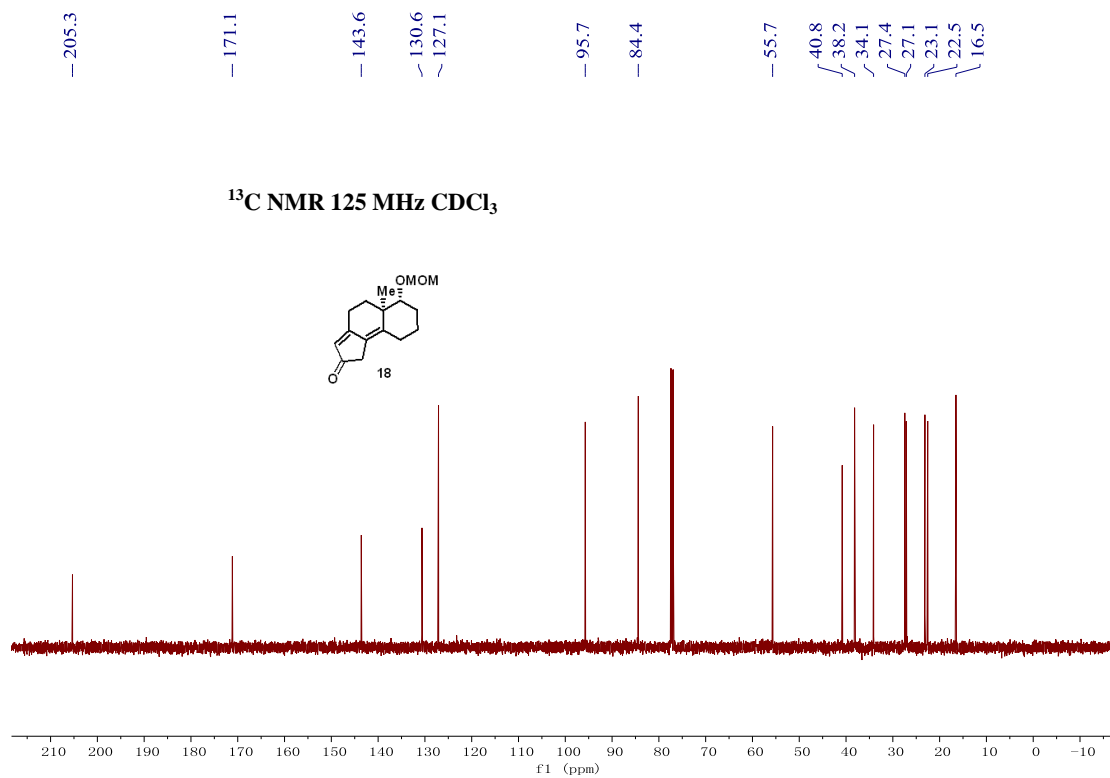
## 5. $^1\text{H}$ & $^{13}\text{C}$ NMR Spectra of Compounds

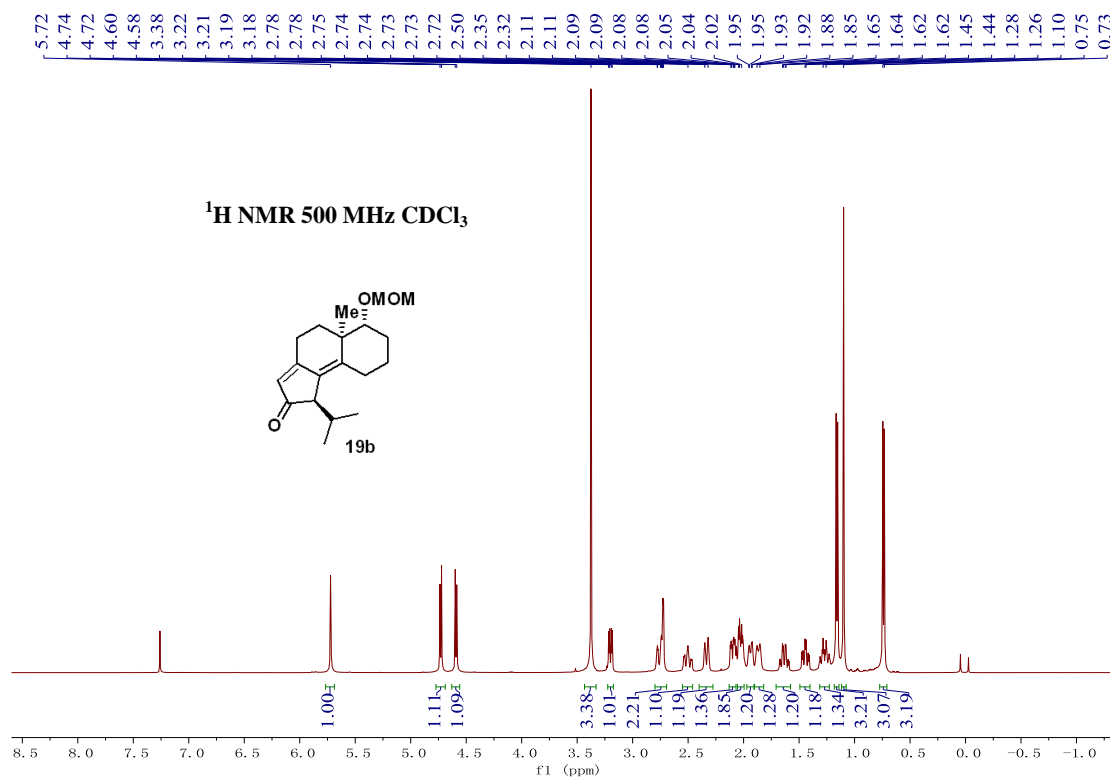
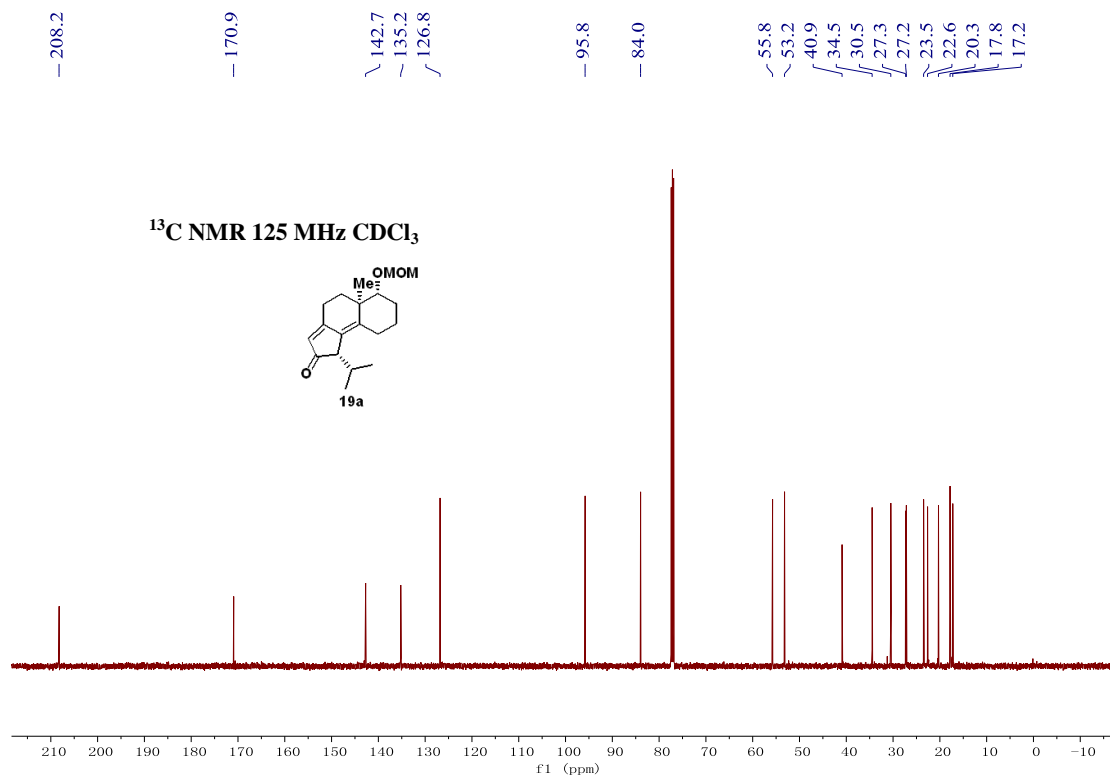


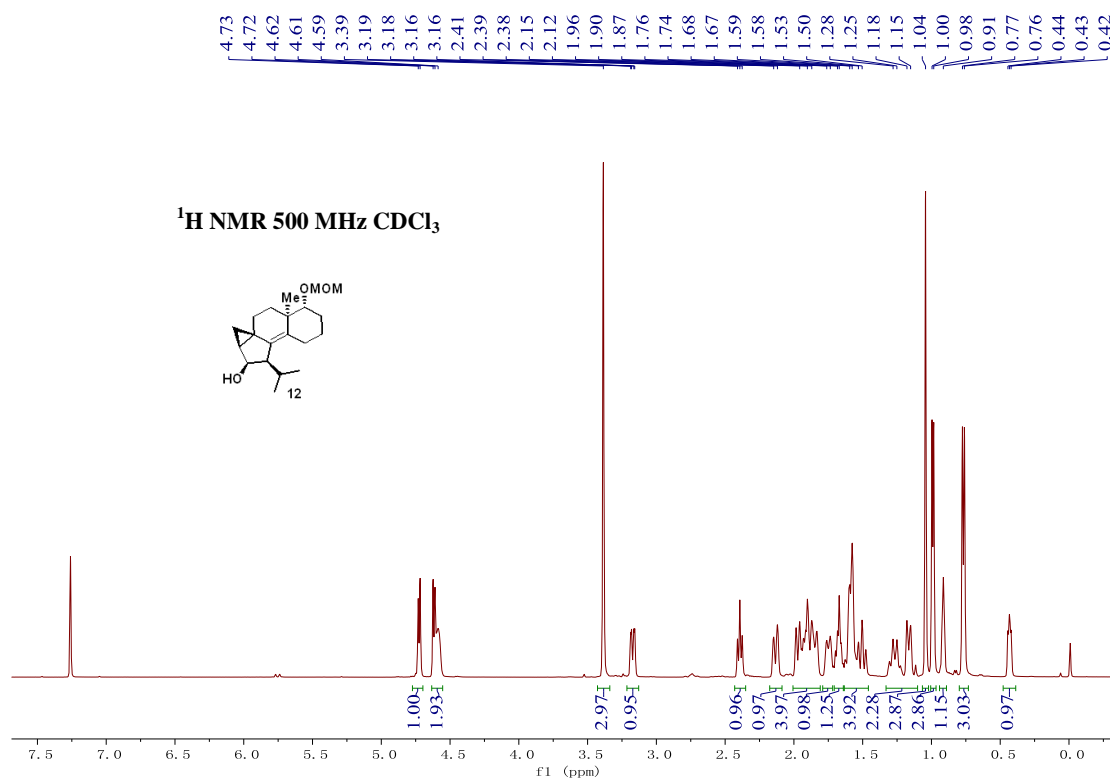
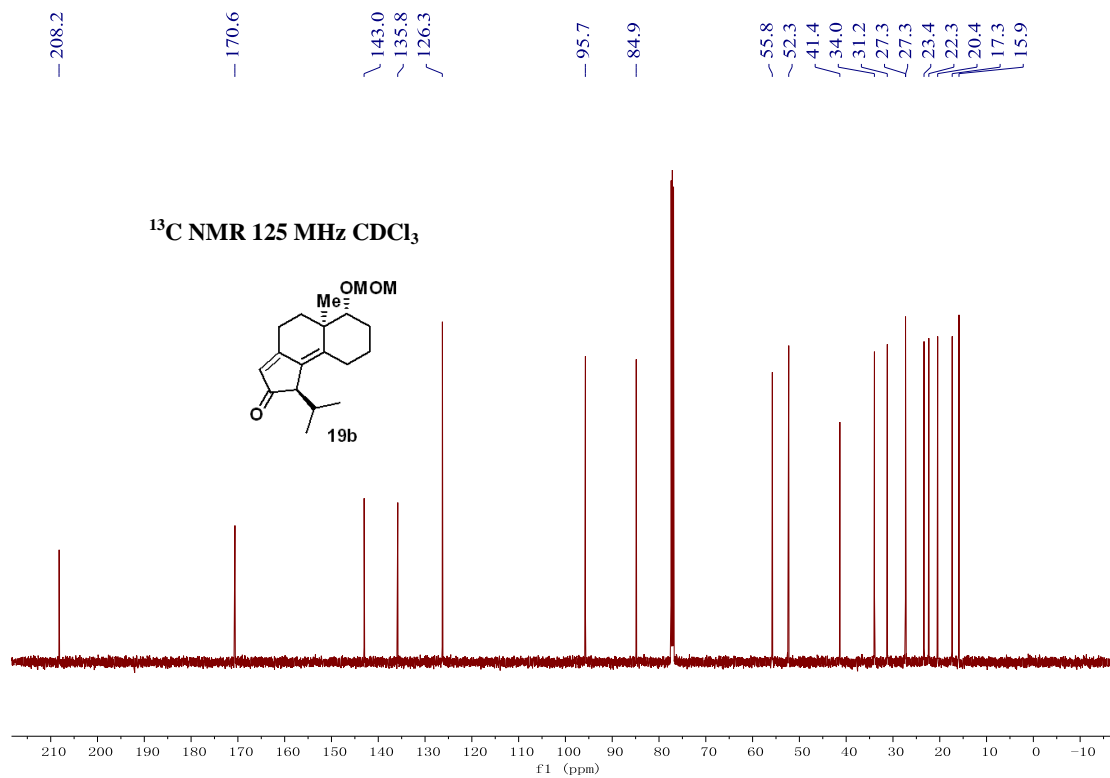




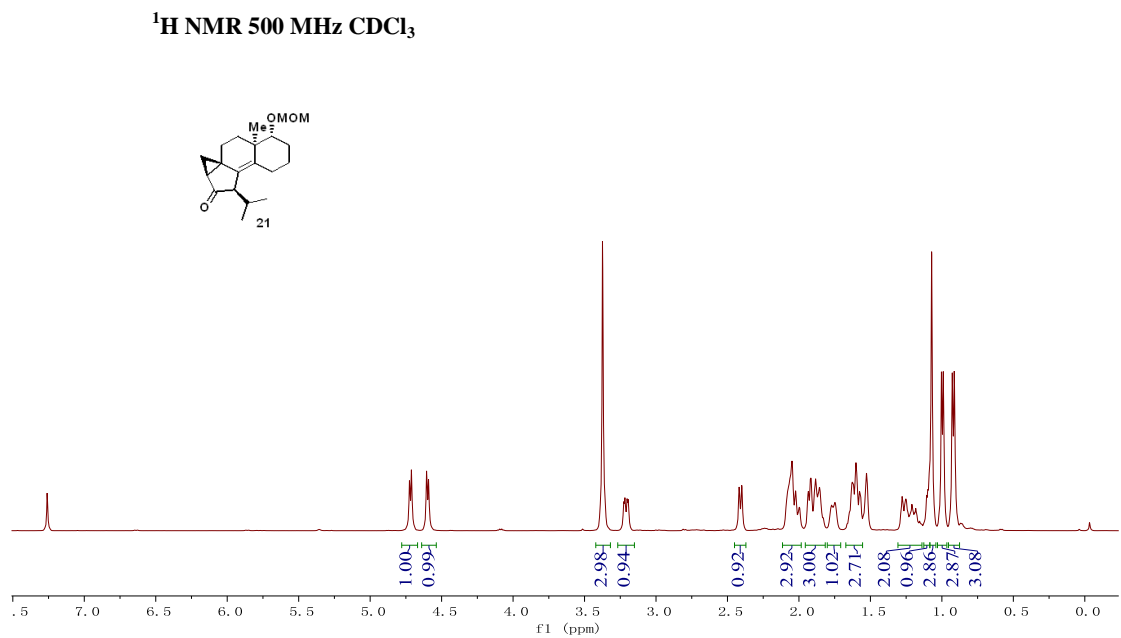
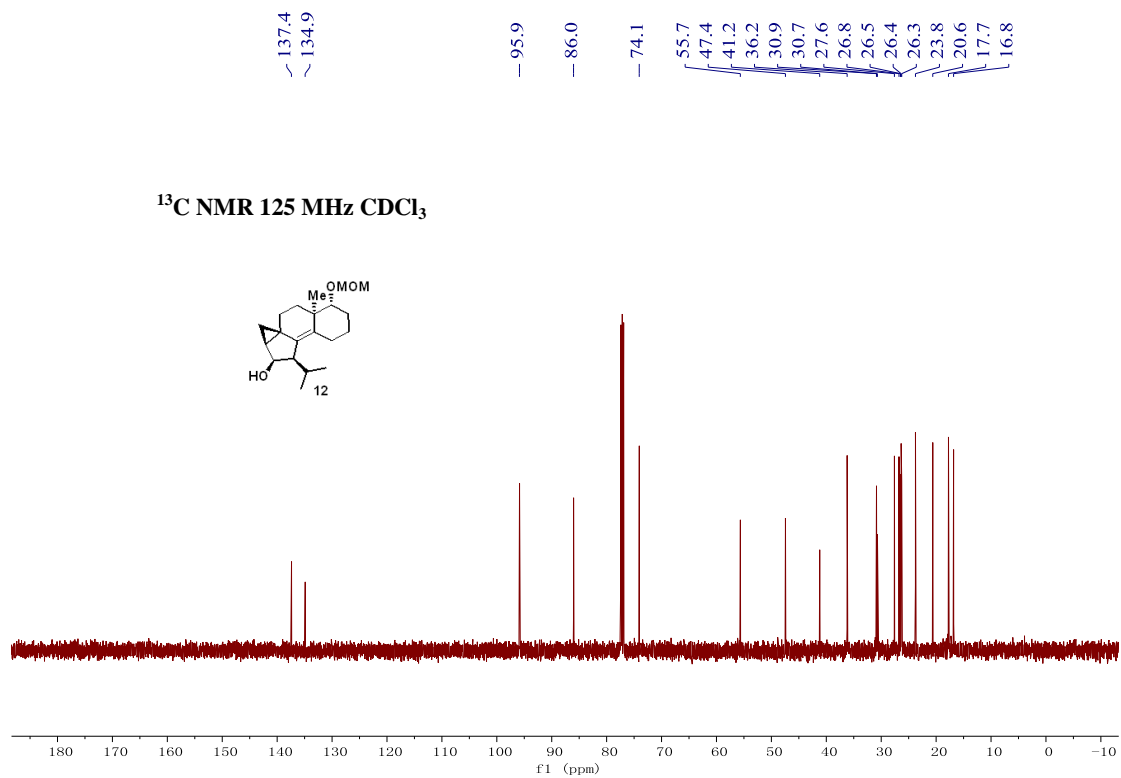


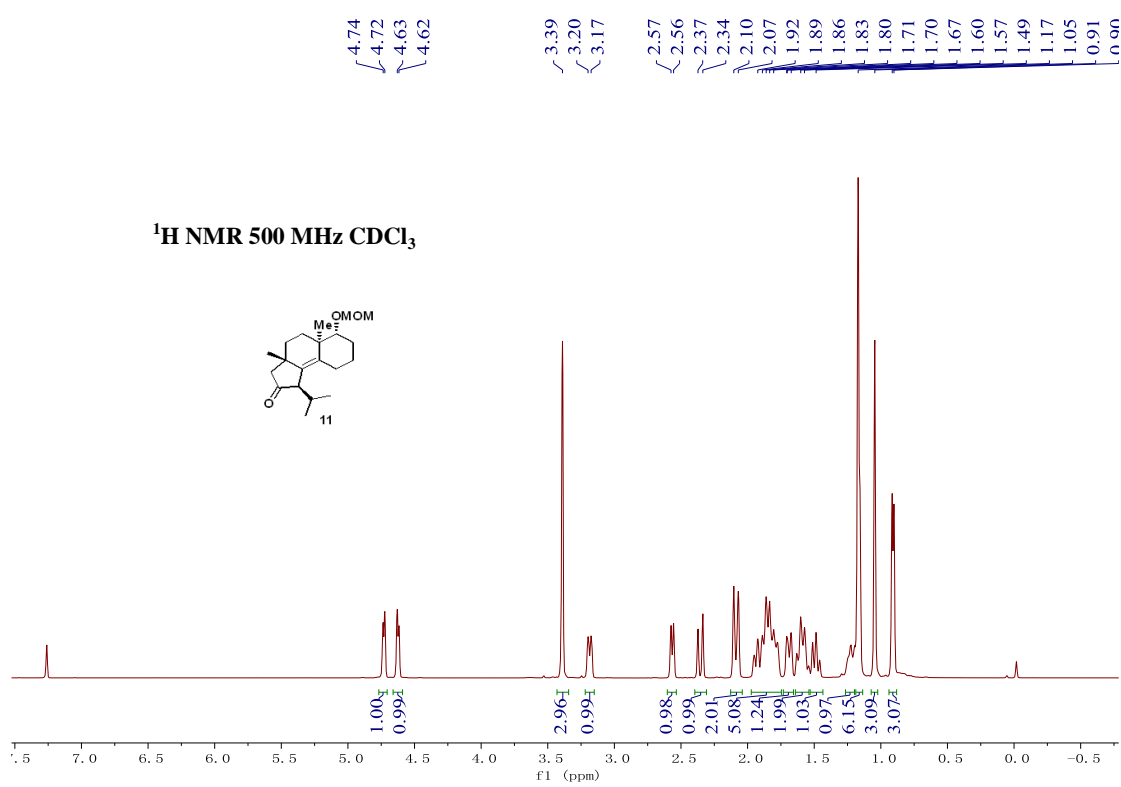
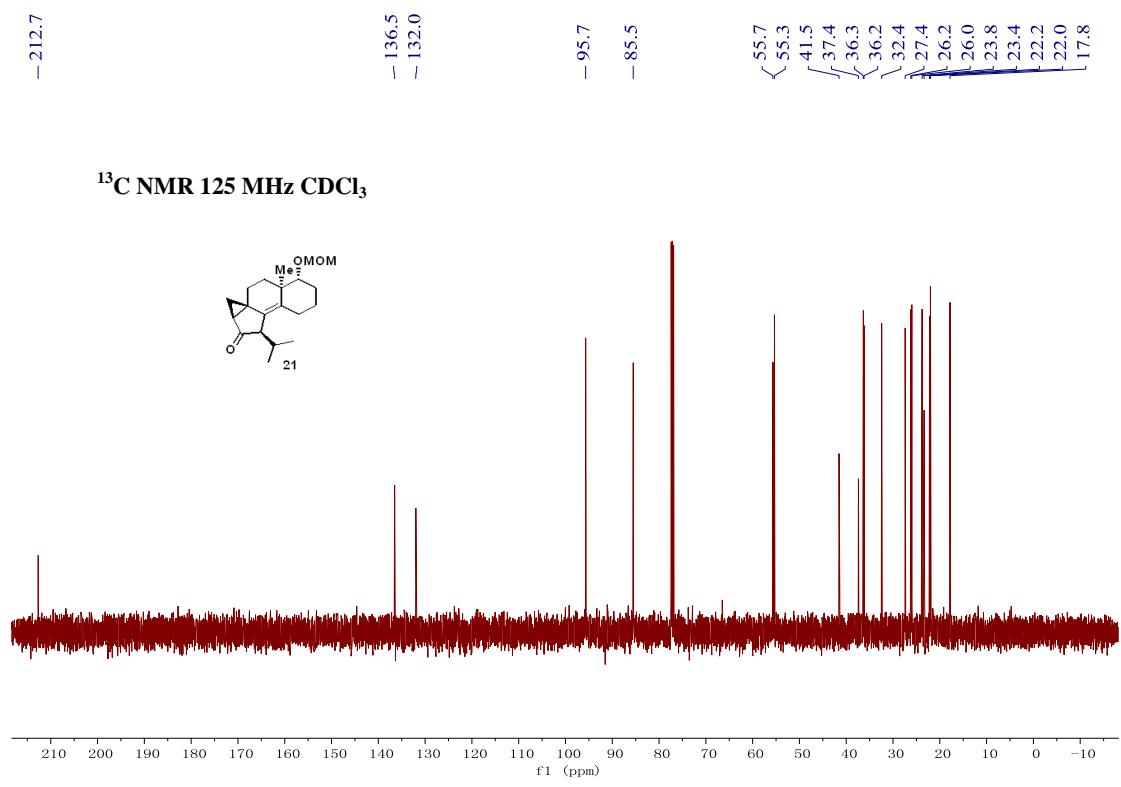












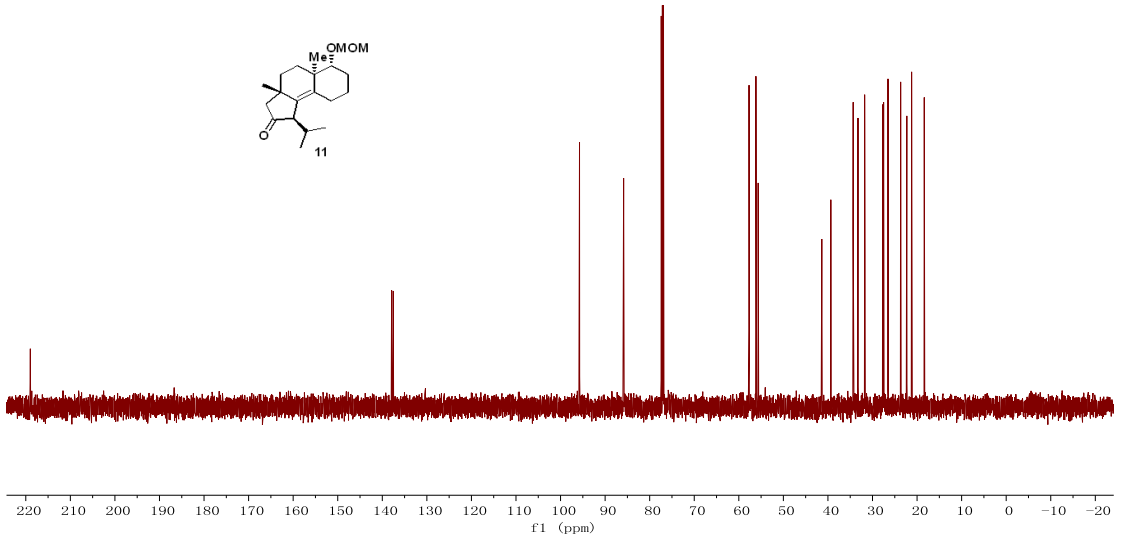
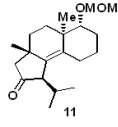
-219.0

137.9  
137.6

-95.8  
-85.9

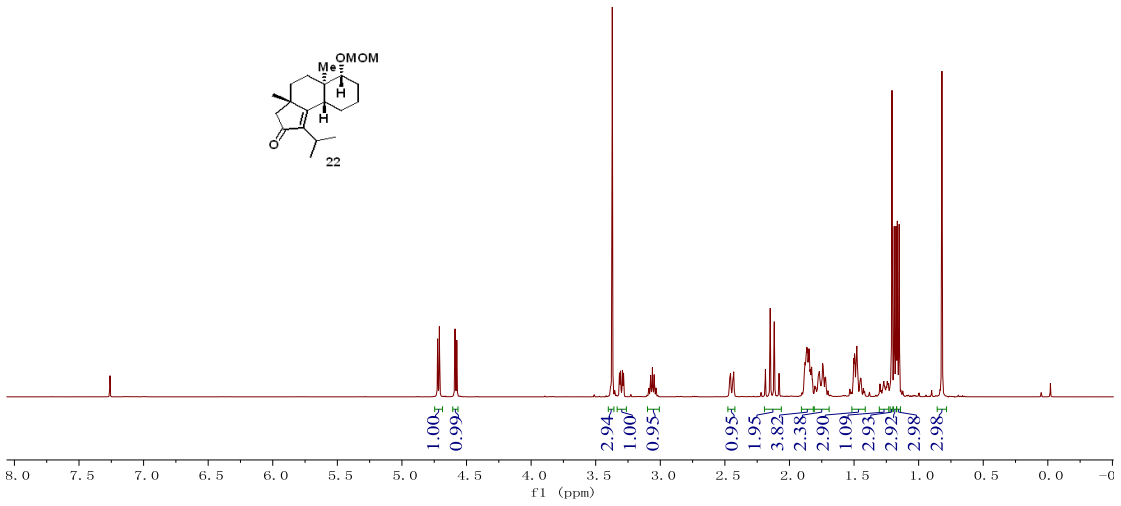
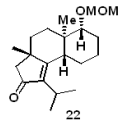
57.7  
56.2  
55.7  
41.4  
39.4  
34.3  
33.3  
31.8  
27.7  
27.5  
26.5  
23.7  
22.3  
21.2  
18.4

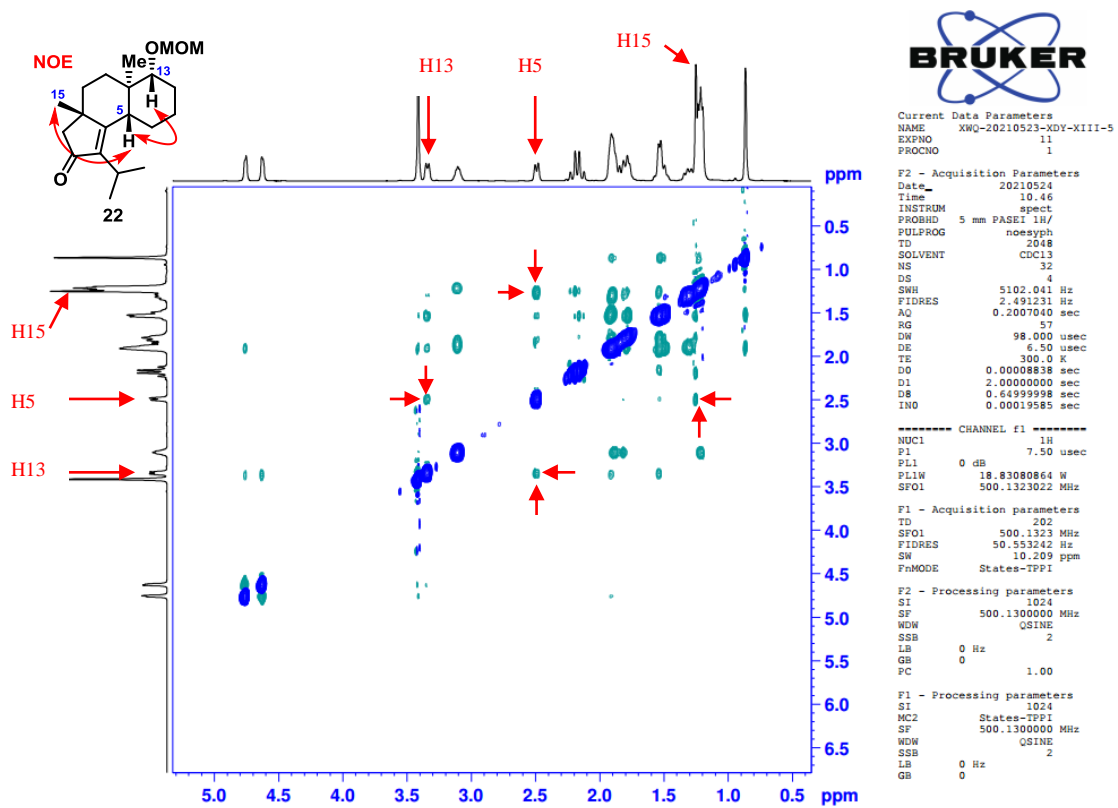
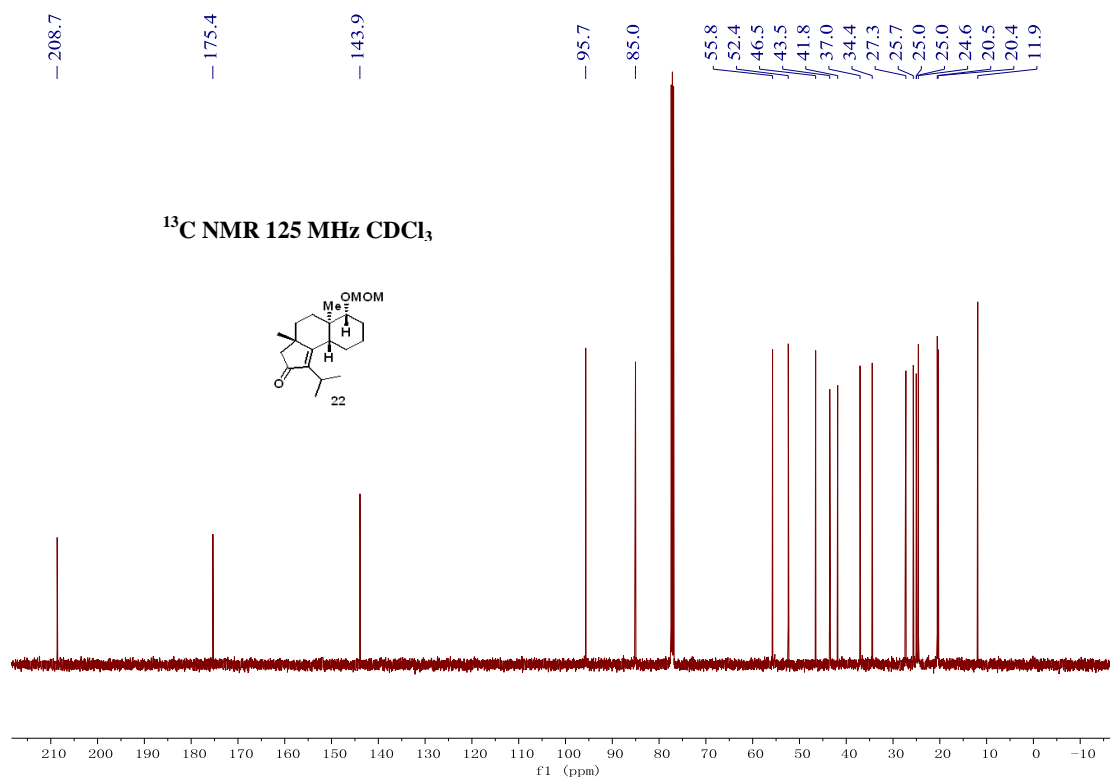
<sup>13</sup>C NMR 125 MHz CDCl<sub>3</sub>

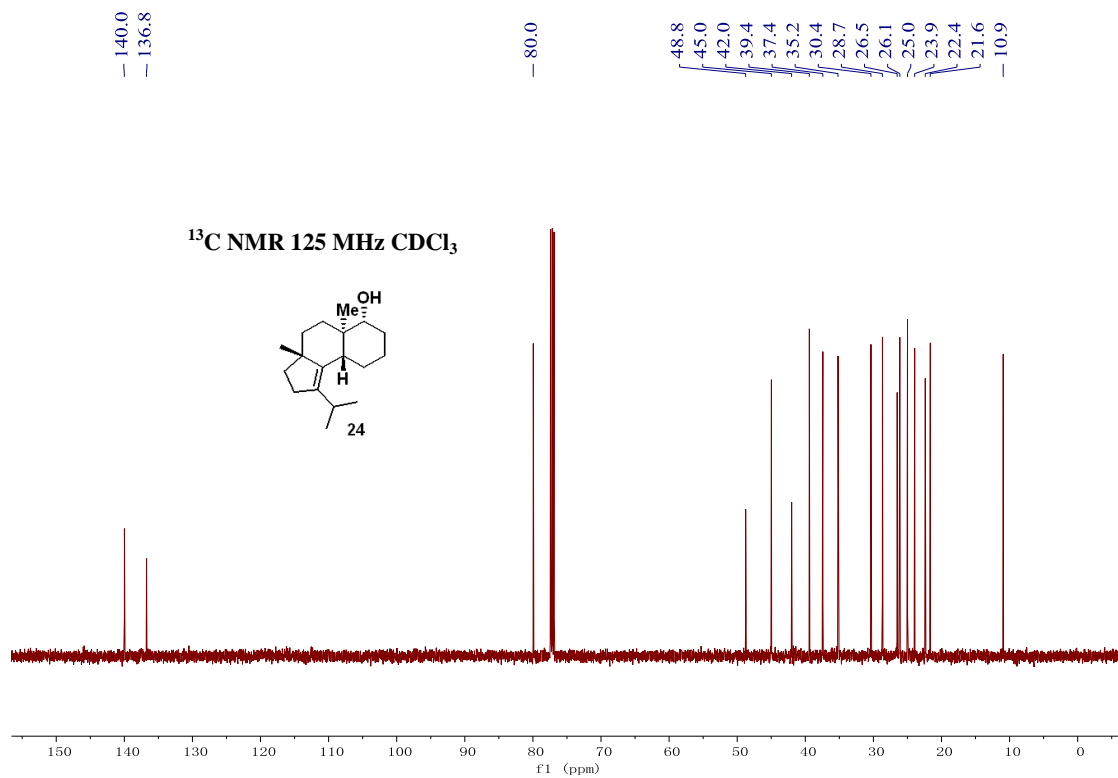
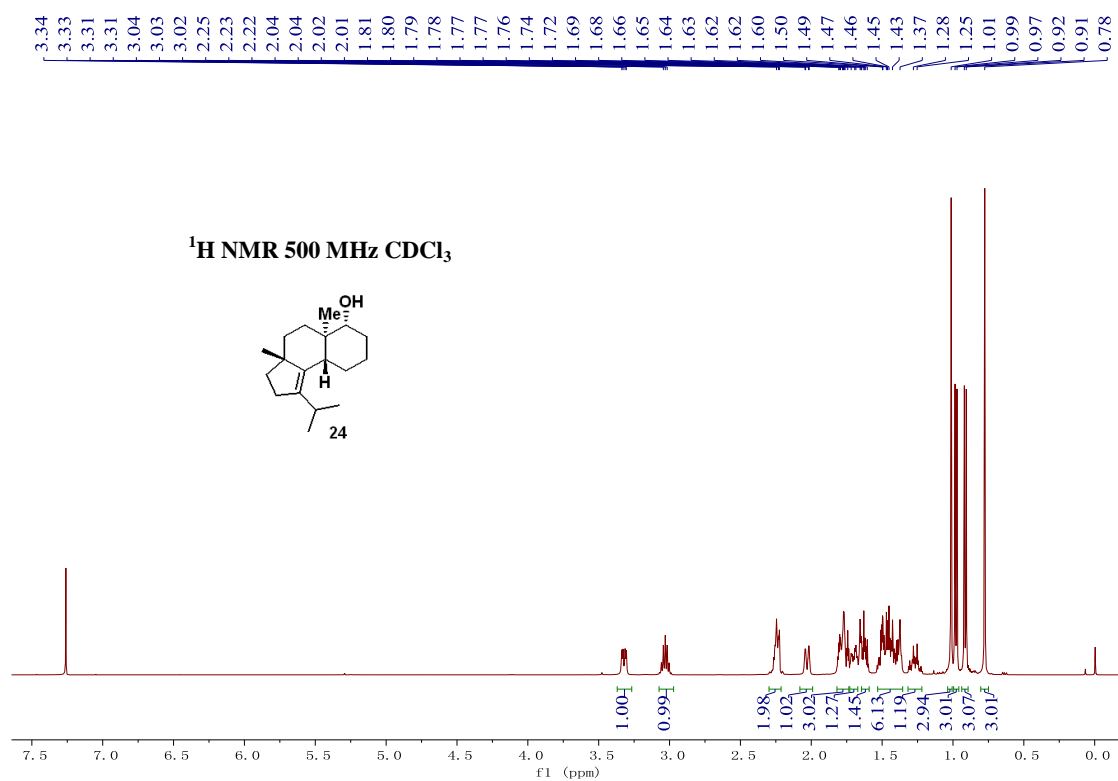


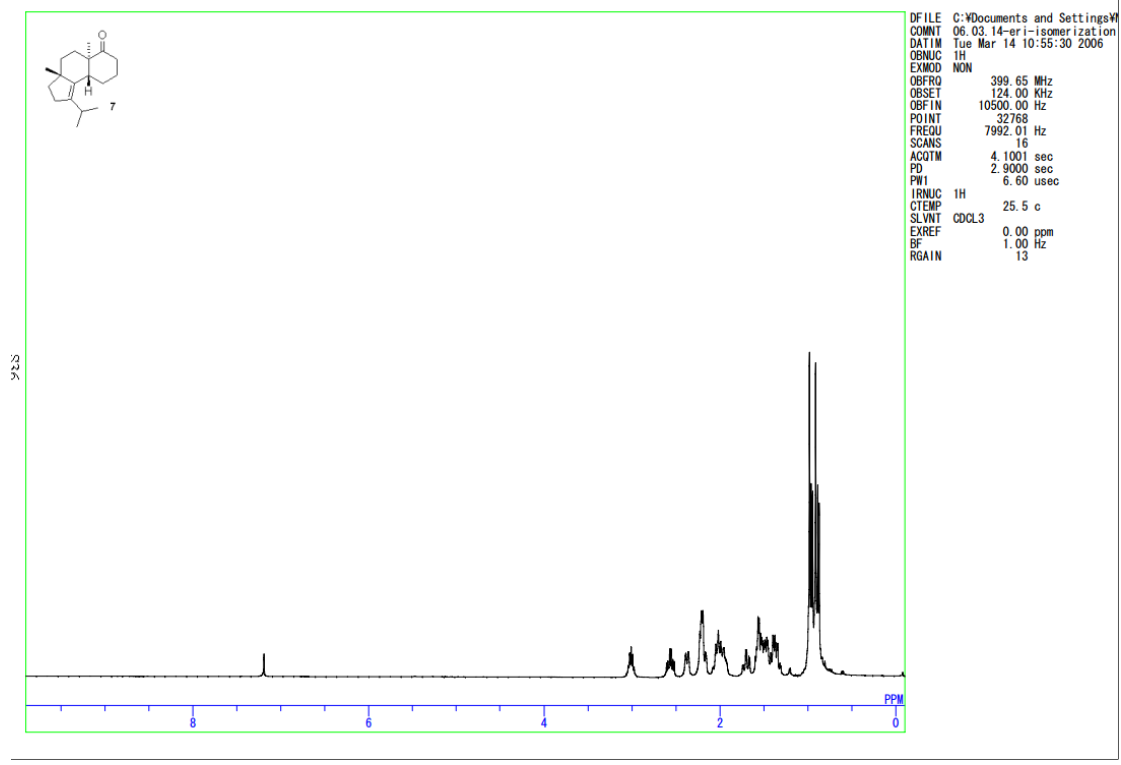
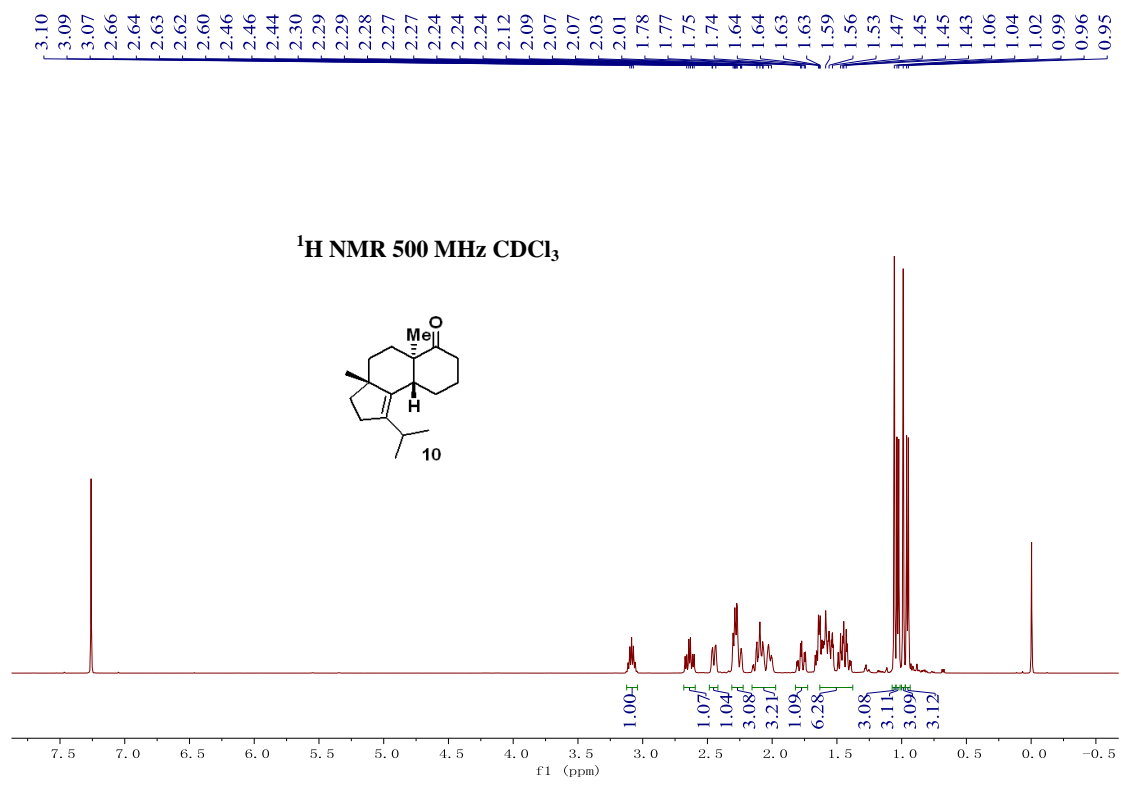
4.72  
4.71  
4.59  
4.58  
3.37  
3.32  
3.31  
3.29  
3.28  
3.09  
3.07  
3.06  
3.05  
3.03  
2.46  
2.46  
2.44  
2.43  
2.19  
2.15  
2.12  
2.08  
1.87  
1.86  
1.85  
1.78  
1.77  
1.74  
1.73  
1.72  
1.50  
1.50  
1.48  
1.45  
1.45  
1.45  
1.30  
1.27  
1.24  
1.24  
1.21  
1.19  
1.18  
1.16  
1.15  
0.82

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

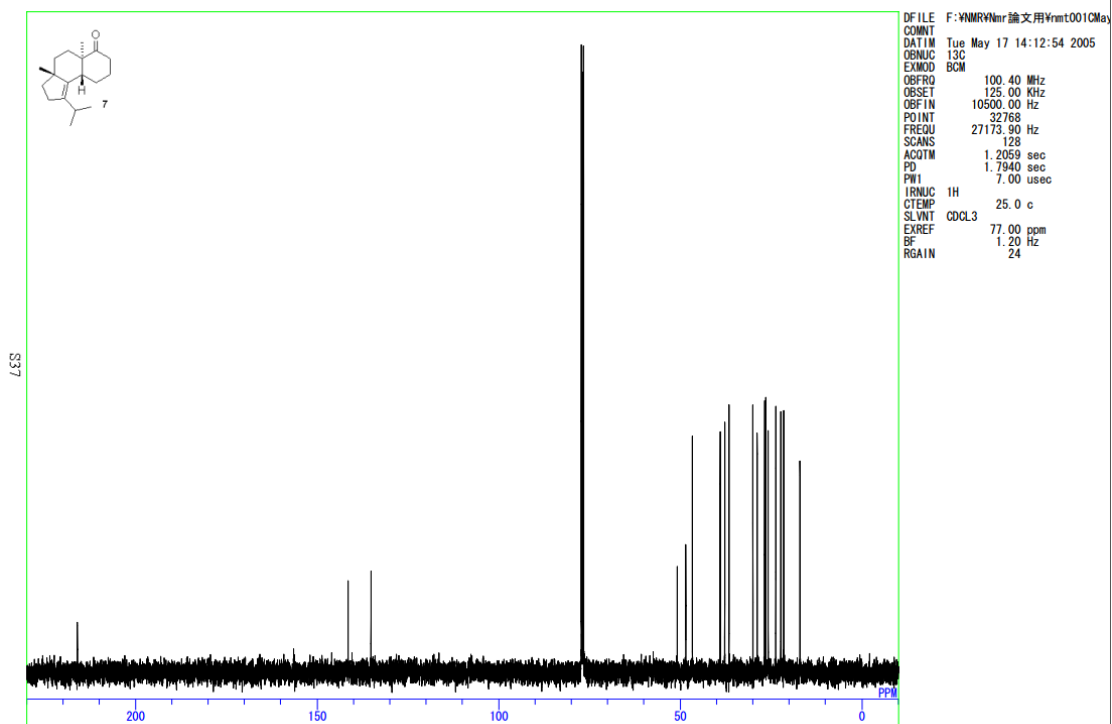
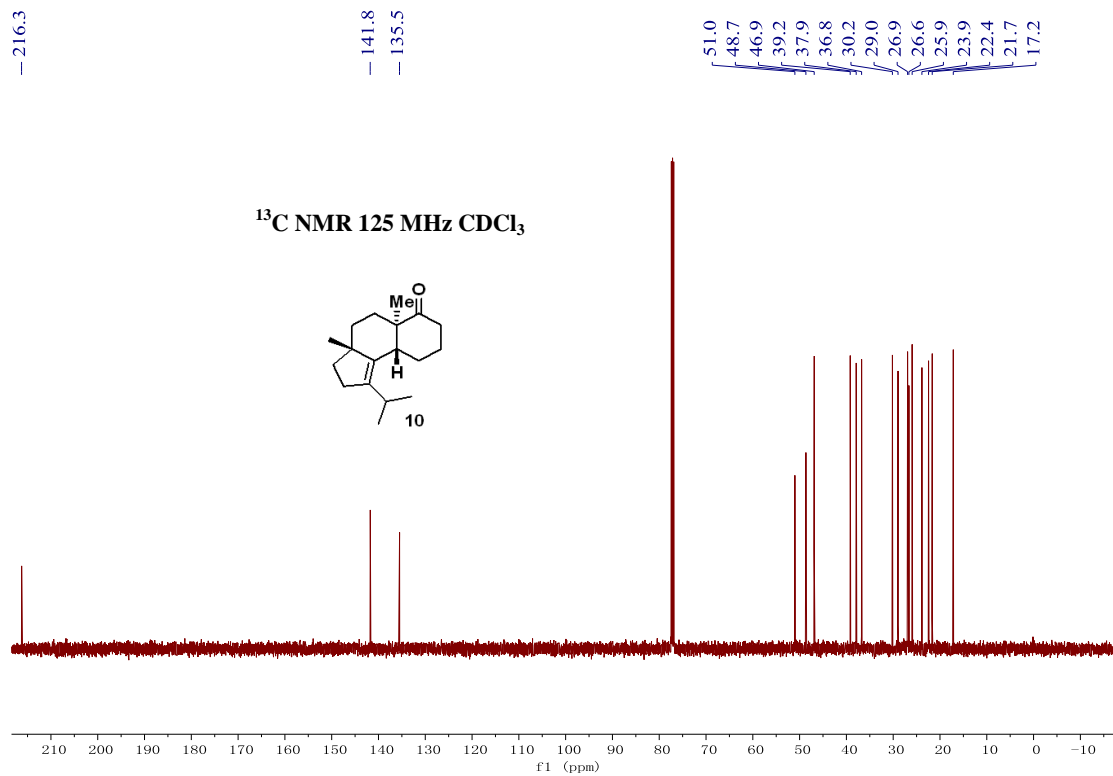




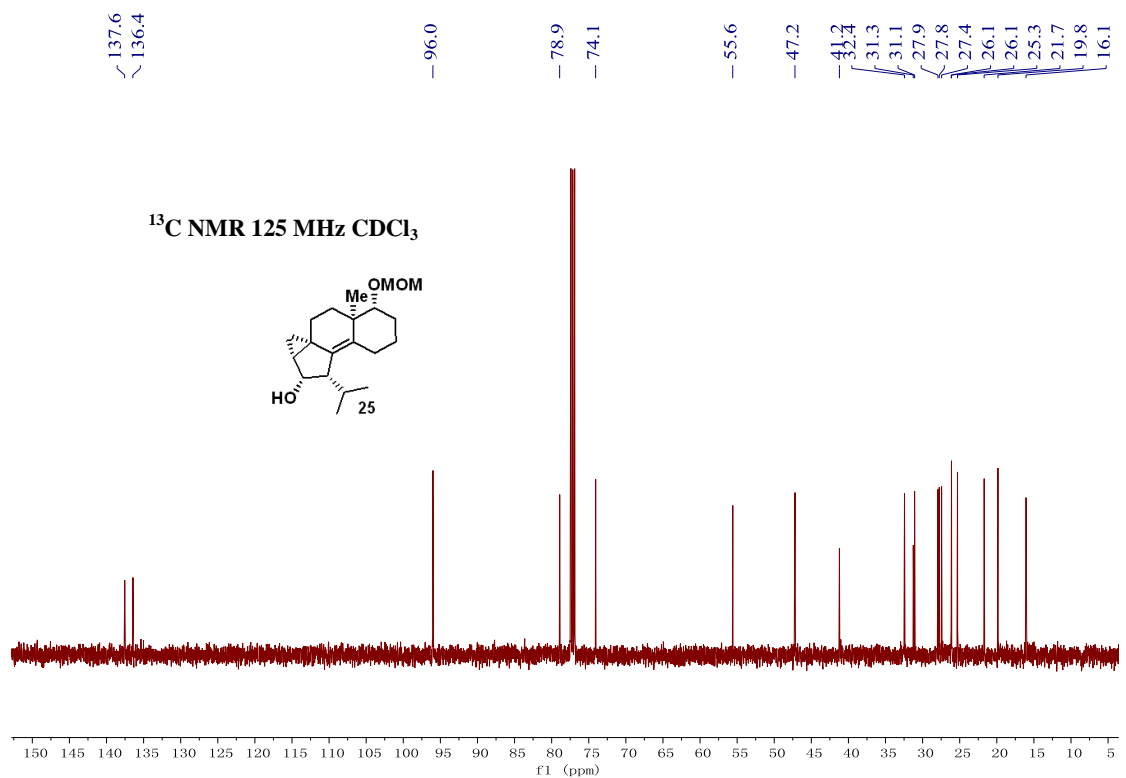
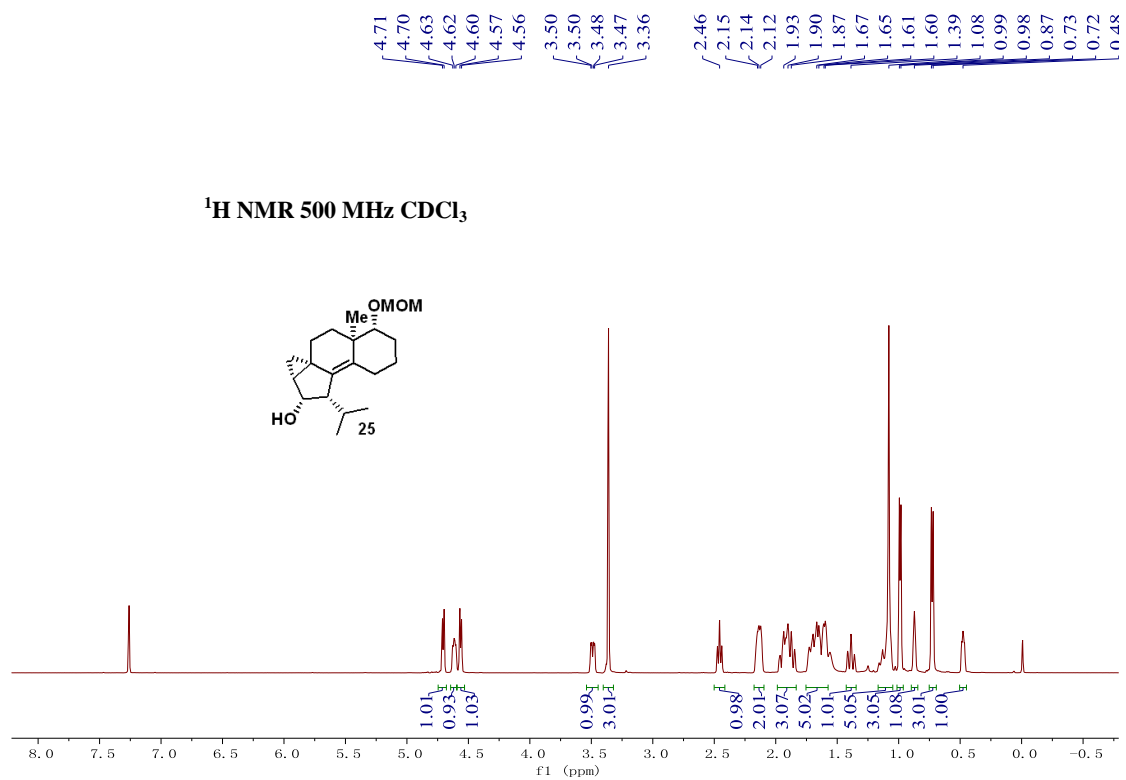




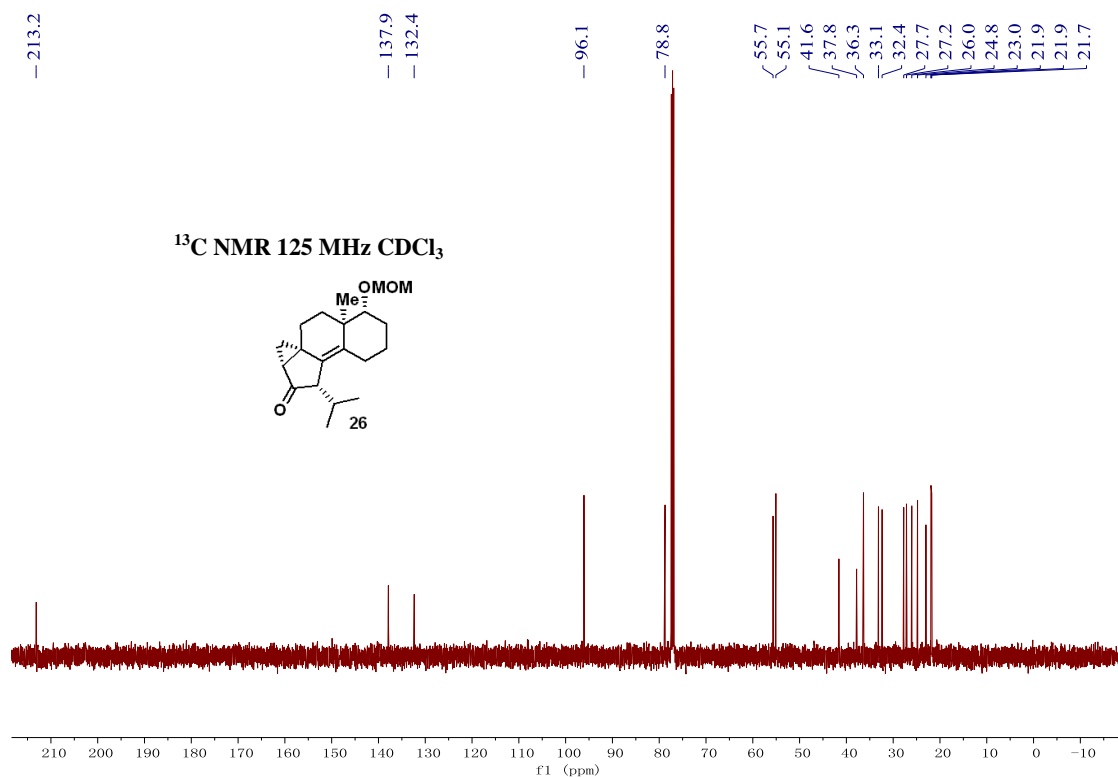
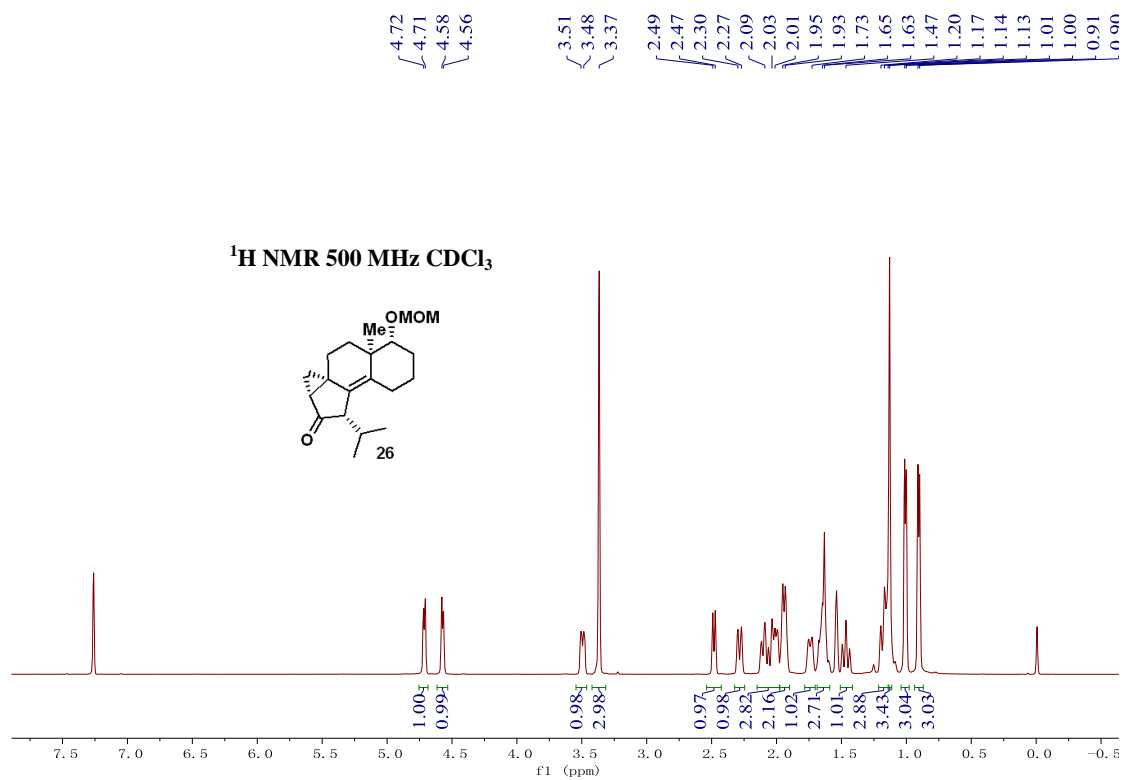
**<sup>1</sup>H NMR spectra of compound 10 reported by Nakada**

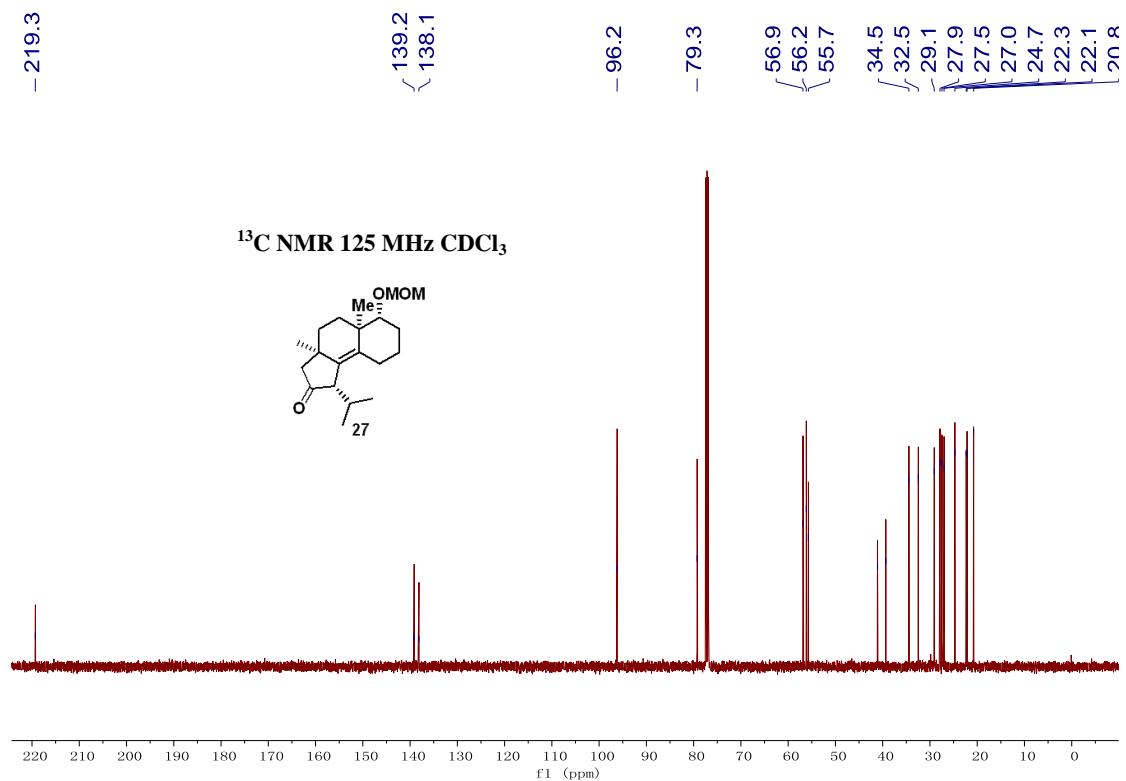
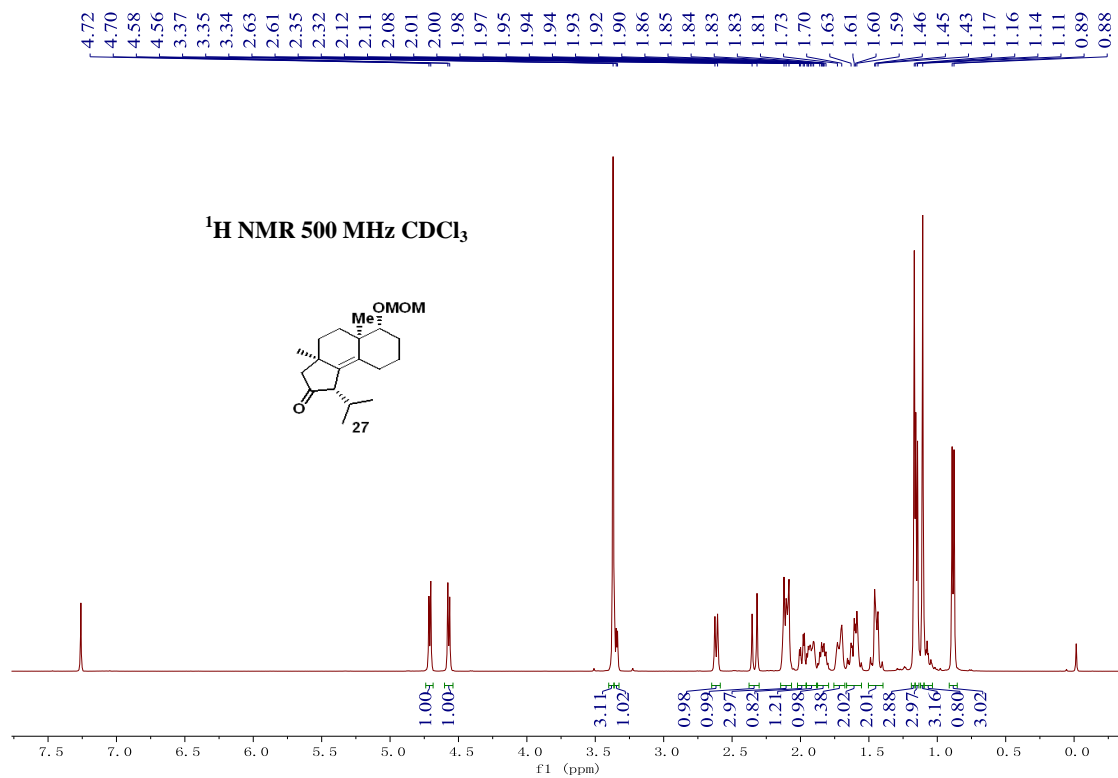


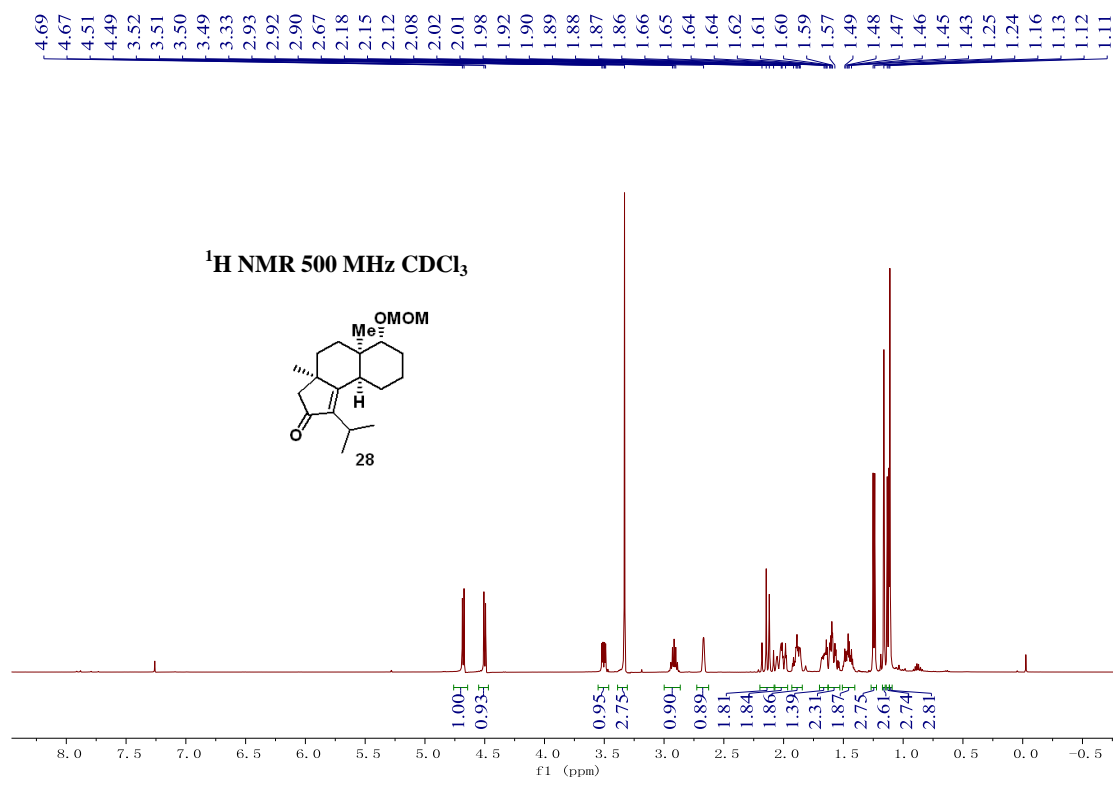
<sup>13</sup>C NMR spectra of compound 10 reported by Nakada



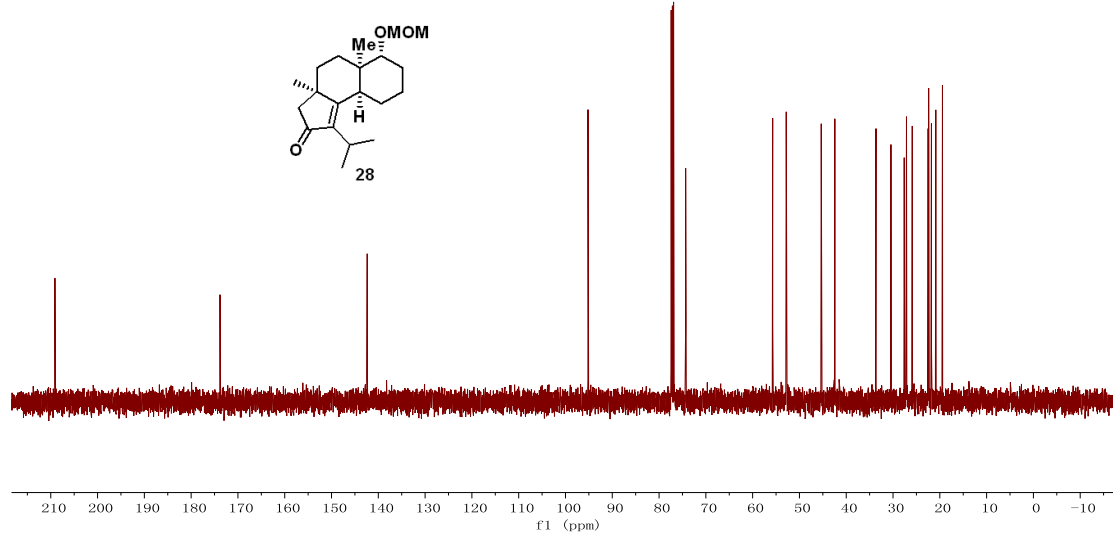


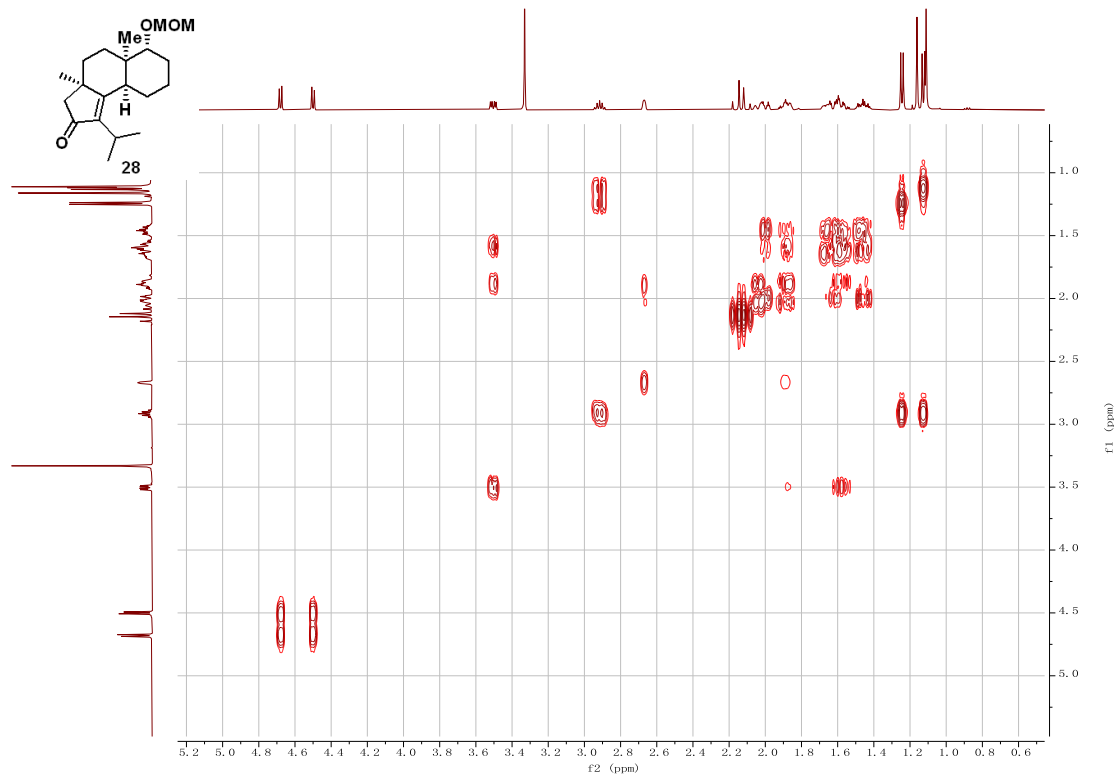




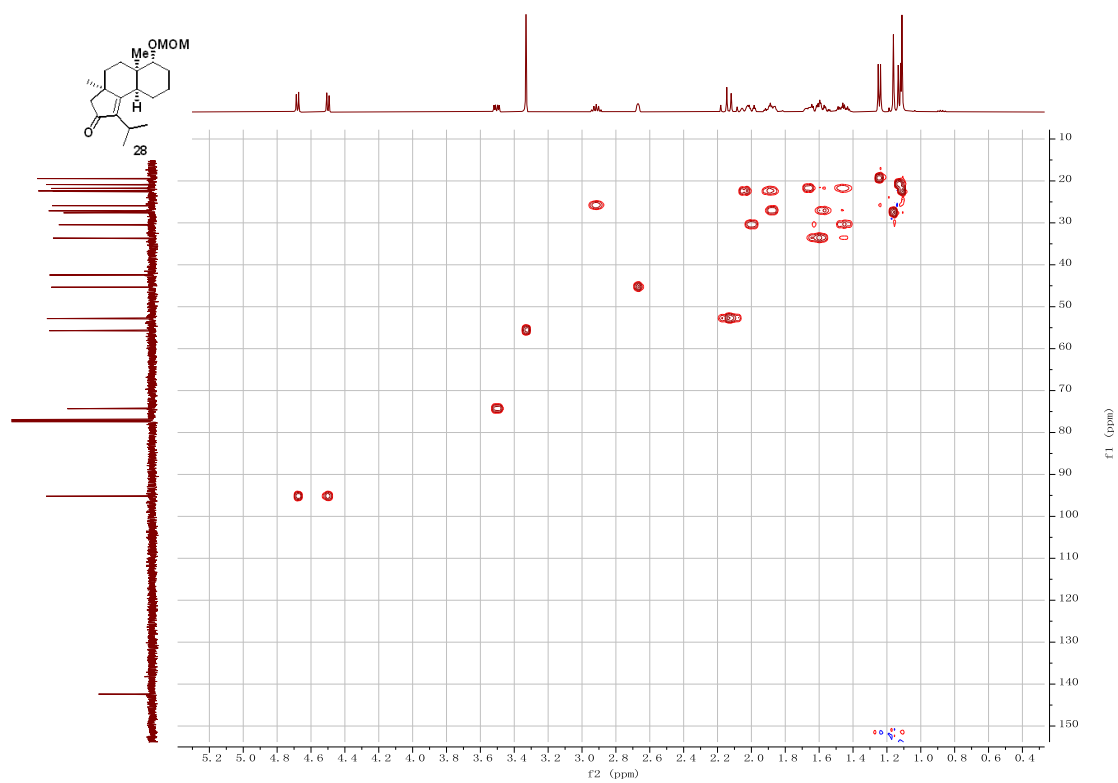


**<sup>13</sup>C NMR 125 MHz CDCl<sub>3</sub>**

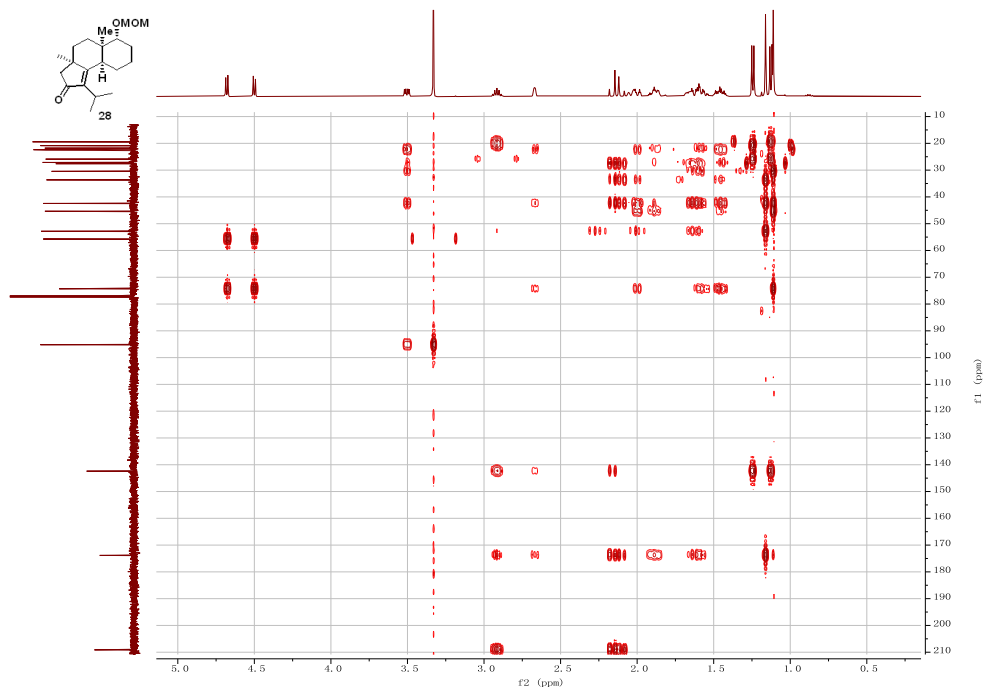




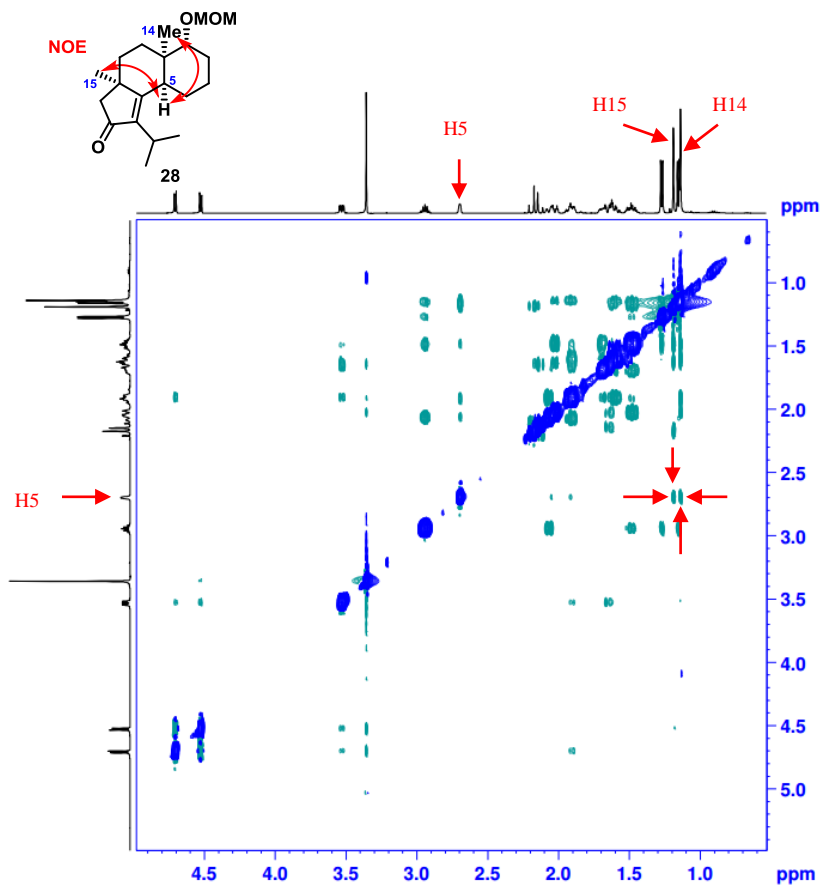
**$^1\text{H}$ - $^1\text{H}$  COSY Spectrum of Compound 28 in  $\text{CDCl}_3$**



**$^1\text{H}$ - $^{13}\text{C}$  HSQC (500 MHz & 125 MHz) Spectrum of Compound 28 in  $\text{CDCl}_3$**



**$^1\text{H}$ - $^{13}\text{C}$  HMBC (500 MHz & 125 MHz) Spectrum of Compound 28 in  $\text{CDCl}_3$**



```

Current Data Parameters
NAME      HWG-20201228-MDY-XIII-1-2
EXPNO    15
PROCNO   1

F2 - Acquisition Parameters
Date_    20201230
Time     20.26
INSTRUM  spect
PROBHD   5 mm PASEI 1H/
PULPROG  noesyph
TD        2048
SOLVENT  CDCl3
NS        32
DS        4
SWH       4201.681 Hz
FIDRES    2.051602 Hz
AQ        0.2437120 sec
RG        16
DW        119.000 usec
DE        6.50 usec
TE        300.6 K
DO        0.00010945 sec
D1        1.95699203 sec
D8        0.64999998 sec
TNO       0.00023800 sec

===== CHANNEL f1 =====
NUC1     1H
P1        7.50 usec
PL1       0 dB
PL1W     18.83080864 W
SF01     500.1313889 MHz

F1 - Acquisition parameters
TD        256
SF01     500.1314 MHz
FIDRES    32.825630 Hz
SW        8.401 ppm
FrMODE    States-TFPI

F2 - Processing parameters
SI        1024
SF        500.1300101 MHz
WDW       QSINE
SSB       2
LB        0 Hz
GB        0
PC        1.00

F1 - Processing parameters
SI        1024
MC2       States-TFPI
SF        500.1300101 MHz
WDW       QSINE
SSB       2
LB        0 Hz
GB        0
  
```

$^1\text{H}$ - $^1\text{H}$  NOESY Spectrum (500 MHz) of Compound 28 in  $\text{CDCl}_3$