# Supporting Information

## Total Synthesis of (–)-14-Hydroxygelsenicine and Six Biogenetically Related *Gelsemium* Alkaloids

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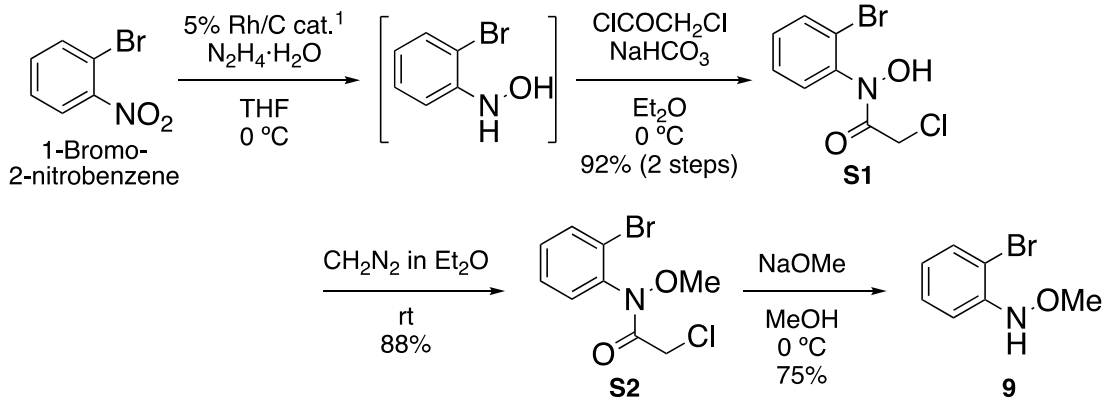
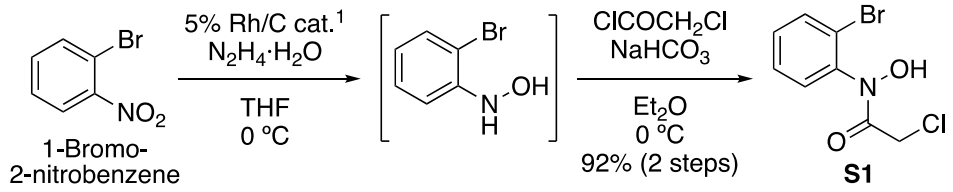
## General Information

UV spectra were recorded in MeOH on a JASCO V-560 instrument. IR spectra were recorded on a JASCO FT/IR-230 spectrophotometer. $^{1}H$ and $^{13}C$ NMR spectra were recorded using TMS as the internal standard with JEOL JNM ECZ-400 and JNM ECP-400 at 400 MHz ($^{1}H$) or 100 MHz ($^{13}C$), and JNM ECZ-600 and JNM ECA-600 at 600 MHz ($^{1}H$) or 150 MHz ($^{13}C$), respectively. J values are given in Hz. ESIMS and HR-ESIMS spectra were recorded on a JEOL AccuTOF LC-plus JMS-T100LP. TLC was carried out on Merck precoated silica gel 60 F254 plates (0.25 mm thick) and Fuji Silysia Chemical precoated amino-silica gel plates. Column chromatography was performed using Kanto Chemical silica gel 60N [40–50 μm (for flash column chromatography)] and Fuji Silysia Chemical Chromatorex NH [100–200 mesh (for amino-silica gel column chromatography)]. Medium pressure liquid chromatography (MPLC) was performed using Kusano Kagakukikai C.I.G. prepacked column CPS-HS-221-05 ($SiO_2$), JASCO UV-2075 Plus (pump), and UV-2080 Plus (UV detector). All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

## Synthesis of Aniline Derivative 9



## Experimental Procedure and Characterization Data




To a stirred solution of 1-bromo-2-nitrobenzene (100 mg, 495 μmol, 1.0 equiv) and rhodium 5% on carbon (3.1 mg, 1.49 μmol, 0.3 mol%) in dry THF (4.95 mL) was added dropwise $N_2H_4 \cdot H_2O$ (43.3 μL, 891 μmol, 1.8 equiv) at 0 ºC under Ar atmosphere. The reaction mixture was stirred at 0 ºC for 3.5 hours. The resulting mixture was filtered through Celite®. The filtrate was evaporated under reduced pressure.

The residue was dissolved in dry $Et_2O$ (4.95 mL). To this solution, $NaHCO_3$ (49.9 μL, 594 μmol, 1.2 equiv) was added and chloroacetyl chloride (47.2 μL, 594 μmol, 1.2 equiv) was added drop by drop at 0 ºC under Ar atmosphere. The reaction mixture was stirred at the same temperature for 30 minutes. The resulting mixture was filtered through Celite®. The filtrate was evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/*n*-hexane = 3/7) to afford **S1** (120 mg, 454 μmol) in 92% yield in two steps as a pale yellow solid.

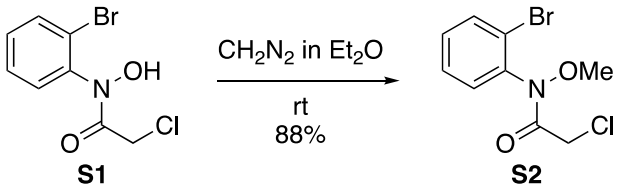
**S1**

$^1$H-NMR (Acetone-$d_6$, 600 MHz, VT 50 °C) $\delta$ ppm: 9.72 (1H, br-s), 7.73 (1H, d, $J$ = 7.2 Hz), 7.54 (1H, br-d, $J$ = 7.2 Hz), 7.48 (1H, dd, $J$ = 7.2, 7.2 Hz), 7.36 (1H, br-d, $J$ = 7.2, 7.2 Hz), 4.52 (2H, br-s).

$^{13}$C NMR: Due to the mixture of rotational isomers of amide moiety, the peaks in complicated spectrum could not be identified.

IR (ATR) $\nu_{max}$ [cm$^{-1}$]: 3202, 1656, 1476, 1410, 1266.

HR-ESIMS: calcd. for $C_8H_7BrClNNaO_2$ $[M+Na]^+$ 285.9246; found 285.9217.




**S1** **S2**

A solution containing **S1** (150 mg, 567 μmol, 1.0 equiv) and an $Et_2O$ solution of freshly prepared $CH_2N_2$ (excess) was stirred for 3 hours at room temperature. The reaction was quenched by adding AcOH and the resulting mixture was evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/*n*-hexane = 3/7) to afford **S2** (138 mg, 495 μmol) in 88% yield as a pale yellow solid.

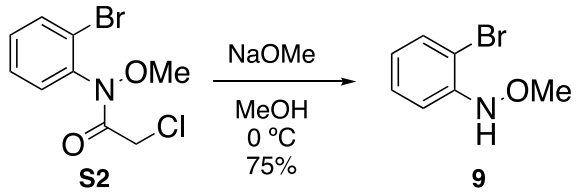
**S2**

$^1$H-NMR (Acetone-$d_6$, 600 MHz, VT 50 °C) $\delta$ ppm: 7.76 (1H, d, $J$ = 8.4 Hz), 7.52-7.50 (2H, overlapped), 7.40 (1H, m), 4.49 (2H, br-s), 3.79 (3H, s).

$^{13}$C NMR (Acetone-$d_6$, 150 MHz, VT 50 °C) $\delta$ ppm: 138.8, 134.6, 132.1, 131.6, 129.6, 124.2, 62.7, 42.6; The signal of carbonyl carbon could not be detected.

IR (ATR) $\nu_{max}$ [cm$^{-1}$]: 1698, 1469, 1375, 1259.

HR-ESIMS: calcd. for $C_9H_9BrClNNaO_2$ $[M+Na]^+$ 299.9403; found 299.9393.




**S2** **9**

To a solution of **S2** (1.17 g, 4.20 mmol, 1.0 equiv) in dry MeOH (41.0 mL) was added NaOMe (227 mg, 4.20 μmol, 1.0 equiv) at 0 ºC under Ar atmosphere. The reaction mixture was stirred for 1 hour at the same temperature. The reaction was quenched by adding water at room temperature. The resulting mixture was evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (toluene/*n*-hexane = 1/3) to afford **9** (634 mg, 3.14 mmol) in 75% yield as a yellow oil.

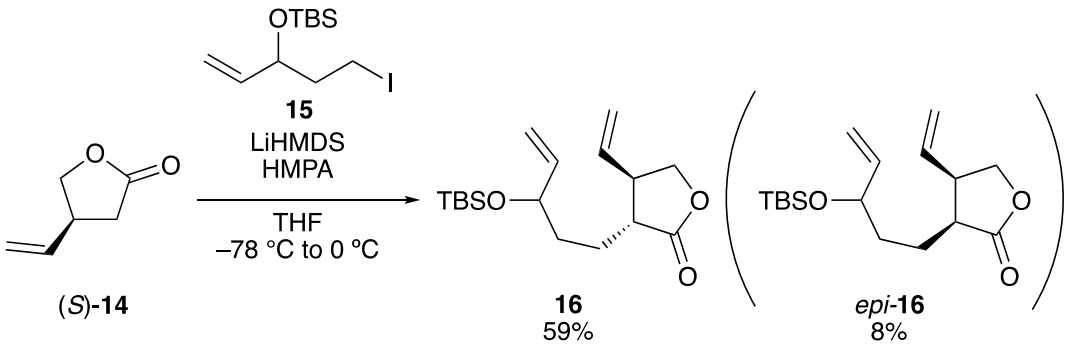
**9**

$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 7.43 (1H, d, $J$ = 7.8 Hz), 7.35 (1H, br-s), 7.28 (1H, dd, $J$ = 7.8, 7.8 Hz), 7.18 (1H, d, $J$ = 7.8 Hz), 6.82 (1H, dd, $J$ = 7.8, 7.8 Hz), 3.81 (3H, s).

$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 145.6, 132.2, 128.4, 122.5, 115.2, 107.9, 63.5.

IR (ATR) $\nu_{max}$ [cm$^{-1}$]: 3283, 1589, 1471, 1294.

HR-ESIMS: calcd. for $C_7H_8NNaO_1$ $[M–Br+Na]^+$ 145.0504; found 145.0492.




To a stirred solution of (*S*)-**14**[2] (>99% *ee*, 702 mg, 6.26 mmol, 1.0 equiv) in dry THF (21.9 mL) was added dropwise lithium bis(trimethylsilyl)amide (1.0 M in THF, 31.3 mL, 1.0 equiv) at –78 ºC under Ar atmosphere. The reaction mixture was stirred at –78 ºC for 30 minutes before a solution of **15**[3] (4.09 g, 12.5 mmol, 2.0 equiv) and hexamethylphosphoric triamide (2.18 mL, 6.26 mmol, 1.0 equiv) in dry THF (9.4 mL) was added drop by drop. The reaction mixture was warmed slowly to 0 °C and then stirred for 18 hours at the same temperature. The reaction was quenched by adding saturated aqueous $NH_4Cl$ and then diluted with EtOAc. After separation of the two layers, the aqueous layer was extracted two times with EtOAc. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/*n*-hexane = 1/9) to afford **16** (1.15 g, 3.70 mmol, diastereomixture) in 59% yield as a colorless oil and *epi*-**16** (146 mg, 0.47 mmol, diastereomixture) in 8% yield as a colorless oil.

**16** (diastereomixture)

$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 5.80-5.74 (2H, overlapped), 5.73-5.67 (2H, overlapped), 5.22-5.13 (6H, overlapped), 5.04-5.03 (2H, overlapped), 4.35-4.32 (2H, overlapped), 4.14-4.09 (2H, overlapped), 3.88-3.85 (2H, overlapped), 2.91-2.84 (2H, overlapped), 2.37-2.29 (2H, overlapped), 1.84-1.55 (8H, overlapped), 0.88 (18H, s), 0.04 (6H, s), 0.02 (6H, s).

$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 178.1, 144.1, 141.0, 135.5, 118.62, 118.58, 114.11, 114.08, 73.4, 73.3, 69.8, 46.7, 46.4, 44.7, 34.8, 34.4, 25.8, 24.3, 23.9, 18.2, –4.41, –4.43, –4.9.

IR (ATR) $\nu_{max}$ [cm$^{-1}$]: 2938, 2857, 1777, 1468, 1367, 1252, 1157, 1077, 1021, 922, 835.

HR-ESIMS: calcd. for $C_{17}H_{30}NaO_3Si$ $[M+Na]^+$ 333.1862; found 333.1878.

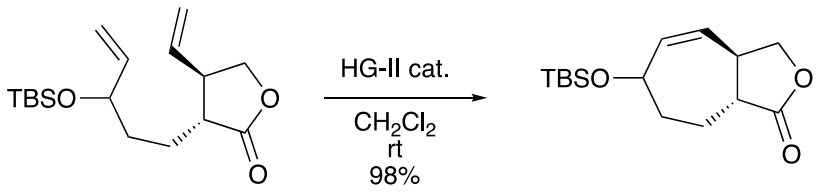
***epi*-16** (diastereomixture)

$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 5.78-5.68 (4H, overlapped), 5.19-5.11 (6H, overlapped), 5.02-5.03 (2H, overlapped), 4.30-4.27 (2H, overlapped), 4.14-4.05 (4H, overlapped), 3.15-3.11 (2H, overlapped), 2.59-2.55 (2H, overlapped), 1.77-1.67 (2H, overlapped), 1.61-1.40 (6H, overlapped), 0.87-0.86 (18H, overlapped), 0.02-0.00 (12H, overlapped).

$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 178.14, 178.06, 141.0, 140.9, 133.54, 133.50, 118.42, 118.37, 114.2, 114.0, 73.42, 73.33, 70.96, 70.92, 43.42, 43.39, 43.3, 43.2, 35.4, 35.2, 25.8, 21.6, 21.2, 18.1, –4.49, –4.52, –4.96, –4.99.

IR (ATR) $\nu_{max}$ [cm$^{-1}$]: 2954, 2929, 2857, 1776, 1253, 1026, 836, 776.

HR-ESIMS: calcd. for $C_{17}H_{30}NaO_3Si$ [M+Na]$^+$ 333.1862; found 333.1865.




**16** **13**

To a solution of **16** (1.02 g, 3.28 mmol, 1.0 equiv) in dry $CH_2Cl_2$ (219 mL) was added Hoveyda-Grubbs catalyst® 2$^{nd}$ generation (103 mg, 0.164 mmol, 5 mol%) at room temperature under Ar atmosphere, and the reaction mixture was stirred for 66 hours at the same temperature. The resultant mixture was evaporated under reduced pressure. The residue was purified by amino-silica gel flash column chromatography (EtOAc/*n*-hexane = 1/9) to afford **13** (905 mg, 3.20 mmol, diastereomixture) in 98% yield as a white solid.

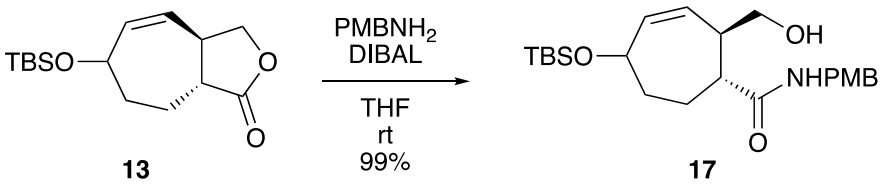
**13** (diastereomixture)

$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 5.95-5.90 (1.4H, overlapped), 5.60 (1H, dd, $J$ = 15.6, 4.8 Hz), 5.56 (0.4H, m), 4.45-4.41 (1.4H, overlapped), 4.40-4.37 (1.4H, overlapped), 3.92 (0.4H, dd, $J$ = 17.4, 12.6 Hz), 3.82 (1H, dd, $J$ = 17.4, 13.2 Hz), 3.35 (1H, m), 2.98 (0.4H, m), 2.44 (0.4H, m), 2.29 (1H, ddd, $J$ = 18.6, 18.6, 6.6 Hz), 2.21-2.10 (1.4H, overlapped), 2.04-1.86 (2.4H, overlapped), 1.72-0.89 (1.8H, overlapped), 0.90-0.89 (12.6H, overlapped), 0.07-0.05 (8.4H, overlapped).

$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 178.0, 177.6, 142.9, 137.9, 128.1, 124.5, 72.3, 70.0, 69.7, 68.4, 44.5, 43.6, 42.6, 41.1, 34.6, 32.9, 26.8, 25.8, 23.3, 18.1, –4.7, –4.79, –4.84.

IR (ATR) $\nu_{max}$ [cm$^{-1}$]: 2937, 2857, 1781, 1465, 1376, 1300, 1254, 1152, 1085, 1017, 836, 777.

HR-ESIMS: calcd. for $C_{15}H_{26}NaO_3Si$ [M+Na]$^+$ 305.1549; found 305.1538.




To a stirred solution of 4-methoxybenzylamine (1.16 mL, 8.91 mmol, 3.0 equiv) in dry THF (3.3 mL) was added dropwise diisobutylaluminum hydride (1.02 M in *n*-hexane, 8.59 mL, 2.95 equiv) at 0 ºC under Ar atmosphere. The reaction mixture was stirred at room temperature for 2 hours before a solution of **13** (840 mg, 2.97 mmol, 1.0 equiv) in dry THF (6.6 mL) was added dropwise at 0 ºC. The reaction mixture was stirred at room temperature for 5 hours. The reaction was quenched by adding water and 1*N* aqueous HCl, and then diluted with EtOAc. After separation of the two layers, the aqueous layer was extracted two times with EtOAc. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/*n*-hexane = 1/1) to afford **17** (1.24 g, 2.95 mmol, diastereomixture) in 99% yield as a colorless amorphous solid.

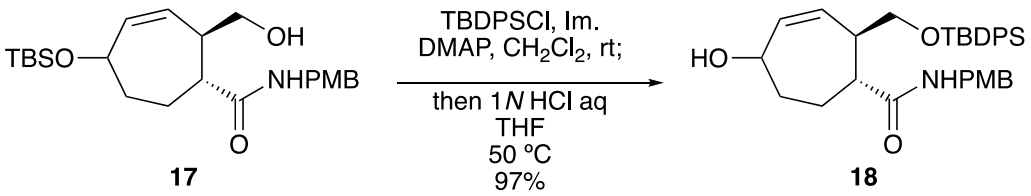
**17** (diastereomixture)

$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 7.20-7.19 (3.3H, overlapped), 6.87-6.85 (3.3H, overlapped) 5.94-5.93 (1.65H, overlapped), 5.83 (0.65H, m), 5.76 (1H, m), 5.54-5.49 (1.65H, overlapped), 4.38-4.34 (4.95H, overlapped), 3.79 (4.95H, s), 3.64-3.55 (3.3, overlapped), 2.85 (1H, m), 2.62 (0.65H, m), 2.49 (1H, ddd, $J$ = 9.6, 9.6, 3.6 Hz), 2.15 (1H, ddd, $J$ = 10.2, 10.2, 3.0 Hz), 2.11-1.75 (7.6H, overlapped), 1.56 (0.65H, m), 0.88-0.87 (14.85, overlapped), 0.06-0.04 (9.9H, overlapped).

$^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ ppm: 175.6, 175.4, 159.0, 140.5, 137.1, 130.3, 129.5, 129.1, 128.7, 114.1, 72.1, 69.1, 65.4, 65.0, 60.4, 55.3, 46.9, 46.1, 43.6, 43.2, 43.0, 42.9, 35.2, 33.8, 30.7, 26.3, 25.8, 18.2, 14.2, –4.7, –4.8, –4.9.

IR (ATR) $\nu_{max}$ [$cm^{-1}$]: 3300, 2941, 2861, 1516, 1461, 1250, 1072, 1034, 836.

HR-ESIMS: calcd. for $C_{23}H_{37}NNaO_4Si$ $[M+Na]^+$ 442.2390; found 442.2392.




To a solution of **17** (1.16 g, 2.76 mmol, 1.0 equiv) in dry $CH_2Cl_2$ (27.6 mL) were added *tert*-butyldiphenylchlorosilane (1.08 mL, 4.14 mmol, 1.5 equiv), imidazole (376 mg, 5.52 mmol, 2.0 equiv), and *N*,*N*-dimethyl-4-aminopyridine (33.7 mg, 0.276 mmol, 0.1 equiv) at room temperature under Ar atmosphere, and the reaction mixture was stirred for 1 hour at the same temperature. The resultant mixture was evaporated under reduced pressure. The residue was dissolved in THF (13.8 mL) and 1*N* aqueous HCl (13.8 mL) was added at room temperature. The reaction mixture was stirred for 9 hours at 50 ºC. The reaction was quenched by adding saturated aqueous $NaHCO_3$ at 0 ºC and then diluted with $CHCl_3$. After separation of the two layers, the aqueous layer was extracted two times with $CHCl_3$. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/*n*-hexane = 1/1) to afford **18** (1.45 g, 2.67 mmol, diastereomixture) in 97% yield as a colorless amorphous solid.

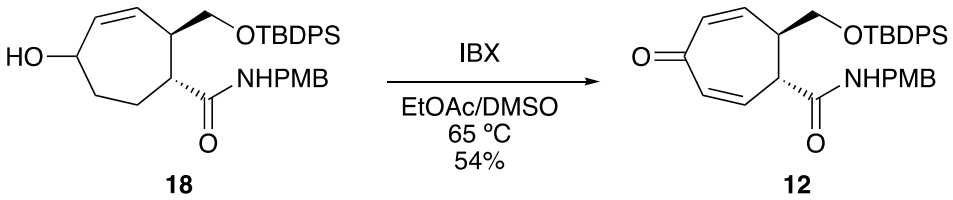
**18** (diastereomixture)

$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 7.63-7.60 (6H, overlapped), 7.44-7.40 (3H, overlapped), 7.38-7.35 (6H, overlapped), 7.09 (2H, d, $J$ = 9.0 Hz), 6.80 (1H, d, $J$ = 9.0 Hz), 6.80 (2H, d, $J$ = 9.0 Hz), 6.76 (1H, d, $J$ = 9.0 Hz), 5.79-5.74 (1.5H, overlapped), 5.63-5.56 (3H, overlapped), 4.41-4.35 (2H, overlapped), 4.32 (1H, m), 4.13 (1H, dd, $J$ = 14.4, 5.4 Hz) , 3.97 (0.5H, dd, $J$ = 14.4, 4.2 Hz), 3.78 (3H, s), 3.77 (1.5H, s), 3.71-3.64 (3H, overlapped), 2.89 (1H, m), 2.69 (0.5H, m), 2.59 (1H, m), 2.24 (1H, m), 2.11-1.88 (6H, overlapped), 1.75 (1H, m), 1.57 (0.5H, m), 1.04 (13.5H, s).

$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 175.1, 174.8, 159.0, 137.4, 135.72, 135.68, 135.6, 135.0, 133.7, 133.6, 133.3, 133.2, 130.43, 130.36, 130.32, 130.27, 129.81, 129.75, 129.1, 127.7, 114.1, 71.3, 69.5, 66.1, 65.3, 55.3, 46.8, 45.2, 43.3, 43.0, 42.9, 42.8, 34.8, 33.0, 29.9, 27.0, 26.9, 25.3, 19.4, 19.3.

IR (ATR) $\nu_{max}$ [cm$^{-1}$]: 3300, 2933, 2866, 1651, 1520, 1461, 1241, 1111, 1026, 823, 701.

HR-ESIMS: calcd. for $C_{33}H_{41}NNaO_4Si$ $[M+Na]^+$ 566.2703; found 566.2681.




**18** **12**

To a solution of **18** (42.0 mg, 77.2 μmol, 1.0 equiv) in EtOAc/DMSO (9/1, 386 μL) was added 2-iodoxybenzoic acid (108 mg, 361 μmol, 5.0 equiv) at room temperature under Ar atmosphere, and the reaction mixture was stirred for 44 hours at 65 ºC. The reaction was quenched by adding water at room temperature. The resulting emulsion was filtered through Celite® to give two separable layers. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/*n*-hexane = 3/7) to afford **12** (22.6 mg, 41.9 mmol) in 54% yield as a white solid.

**12**

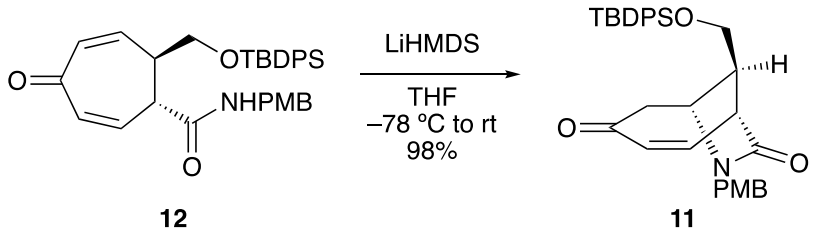
$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 7.61 (4H, d, $J$ = 6.6 Hz), 7.44 (2H, m), 7.38 (4H, m), 7.09 (2H, d, $J$ = 9.0 Hz), 6.82 (2H, d, $J$ = 9.0 Hz), 6.45 (1H, dd, $J$ = 12.0, 6.0 Hz), 6.38 (1H, dd, $J$ = 12.0, 7.2 Hz), 6.20 (1H, dd, $J$ = 11.4, 1.2 Hz), 6.06 (1H, dd, $J$ = 11.4, 2.4 Hz), 5.94 (1H, br-dd, $J$ = 5.4, 5.4 Hz), 4.35 (1H, dd, $J$ = 14.4, 5.4 Hz), 4.27 (1H, dd, $J$ = 14.4, 5.4 Hz), 3.80-3.77 (5H, overlapped), 3.61 (1H, dd, $J$ = 10.2, 8.4 Hz), 3.51 (1H, m), 1.05 (9H, s).

$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 191.2, 169.8, 159.1, 143.5, 137.8, 135.7, 135.6, 135.5, 133.5, 132.9, 129.97, 129.95, 129.6, 129.1, 127.8, 114.1, 63.6, 55.3, 47.1, 43.7, 43.5, 26.9, 19.2.

$[\alpha]_D^{23}$ = –197 (*c* 1.08, $CHCl_3$)

IR (ATR) $\nu_{max}$ [$cm^{-1}$]: 2935, 2866, 1650, 1617, 1514, 1247, 1105, 820, 701.

HR-ESIMS: calcd. for $C_{33}H_{37}NNaO_4Si$ $[M+Na]^+$ 562.2390; found 562.2355.




**12** **11**

To a stirred solution of **12** (455 mg, 843 μmol, 1.0 equiv) in dry THF (843 μL) was added dropwise lithium bis(trimethylsilyl)amide (1.0 M in THF, 1.01 mL, 1.2 equiv) at –78 ºC under Ar atmosphere. The reaction mixture was stirred at –78 ºC for 2 hours before it was warmed to room temperature and then stirred for 1 hour at the same temperature. The reaction was quenched by adding saturated aqueous $NH_4Cl$ and then diluted with EtOAc. After separation of the two layers, the aqueous layer was extracted two times with EtOAc. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/*n*-hexane = 4/6) to afford **11** (446 mg, 826 μmol) in 98% yield as a white solid.

**11**

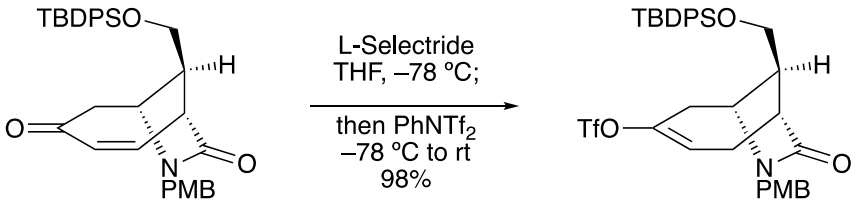
$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 7.56 (4H, m), 7.43 (2H, m), 7.36 (4H, m), 7.13 (2H, d, $J$ = 9.0 Hz), 6.86 (2H, d, $J$ = 9.0 Hz), 6.52 (1H, dd, $J$ = 12.6, 3.0 Hz), 6.01 (1H, d, $J$ = 12.6 Hz), 4.76 (1H, d, $J$ = 15.0 Hz), 4.00 (1H, d, $J$ = 15.0 Hz), 3.82-3.79 (4H, overlapped), 3.76 (1H, dd, $J$ = 10.2, 7.8 Hz), 3.61 (1H, m), 3.37 (1H, dd, $J$ = 9.0, 6.0 Hz), 2.87 (1H, dd, $J$ = 18.6, 4.2 Hz), 2.83 (1H, m) 2.54 (1H, dd, $J$ = 18.6, 3.0 Hz), 1.01 (9H, s).

$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 198.9, 174.1, 159.3, 140.1, 135.44, 135.41, 134.9, 132.80, 132.78, 130.01, 129.97, 129.2, 128.0, 127.8, 114.3, 60.2, 55.3, 53.6, 46.7, 44.2, 43.6, 43.0, 26.8, 19.1.

$[\alpha]_D^{24}$ = –98.2 (*c* 1.33, $CHCl_3$)

IR (ATR) $\nu_{max}$ [$cm^{-1}$]: 2937, 2861, 1697, 1655, 1507, 1422, 1245, 1111, 1026.

HR-ESIMS: calcd. for $C_{33}H_{37}NNaO_4Si$ $[M+Na]^+$ 562.2390; found 562.2355.




**11** **10**

To a stirred solution of **11** (388 mg, 719 μmol, 1.0 equiv) in dry THF (5.39 mL) was added dropwise L-Selectride® (1.0 M in THF, 2.16 mL, 3.0 equiv) at –78 ºC under Ar atmosphere. The reaction mixture was stirred at –78 ºC for 4 hours before a solution of *N*-phenyl-bis(trifluoromethanesulfonimide) (722 mg, 2.16 mmol, 3.0 equiv) in dry THF (1.80 mL) was added dropwise at the same temperature. The reaction mixture was warmed at room temperature and stirred for 17 hours at the same temperature. The reaction was quenched by adding water and then diluted with EtOAc. After separation of the two layers, the aqueous layer was extracted two times with EtOAc. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/*n*-hexane = 3/7) to afford **10** (476 mg, 706 μmol) in 98% yield as a colorless oil.

**10**

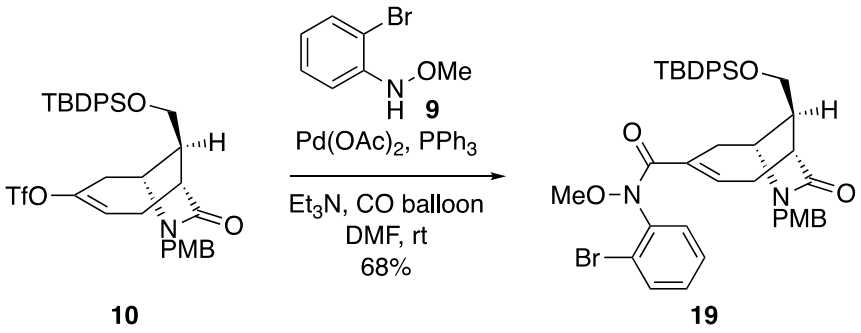
$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 7.59 (4H, m), 7.43 (2H, m), 7.37 (4H, m), 7.17 (2H, d, $J$ = 9.0 Hz), 6.88 (2H, d, $J$ = 9.0 Hz), 5.66 (1H, m), 4.83 (1H, d, $J$ = 15.0 Hz), 4.02 (1H, d, $J$ = 15.0 Hz), 3.81 (3H, s), 3.79-3.75 (2H, overlapped), 3.66 (1H, m), 2.74 (1H, m), 2.70 (1H, m), 2.62-2.58 (3H, overlapped), 2.27 (1H, m), 1.01 (9H, s).

$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 175.1, 159.3, 146.0, 135.42, 135.37, 132.9, 132.8, 129.97, 129.95, 129.3, 128.1, 127.9, 121.3, 118.4 (q, $J$ = 318 Hz), 114.2, 60.7, 55.3, 53.9, 43.8, 42.0, 41.3, 33.5, 26.7, 24.3, 19.1.

$[\alpha]_D^{24}$ = +2.27 (*c* 1.46, $CHCl_3$)

IR (ATR) $\nu_{max}$ [$cm^{-1}$]: 2933, 2866, 1697, 1507, 1416, 1211, 1140, 958.

HR-ESIMS: calcd. for $C_{34}H_{38}F_3NNaO_6SSi$ $[M+Na]^+$ 696.2039; found 696.2080.




A solution of **10** (23.2 mg, 34.4 μmol, 1.0 equiv), **9** (30.3 mg, 103 μmol, 3.0 equiv), palladium(II) acetate (0.4 mg, 1.7 μmol, 5 mol%), triphenylphosphine (0.9 mg, 3.4 μmol, 10 mol%), and $Et_3N$ (24.0 μL, 172 μmol, 5.0 equiv) in degassed dry DMF (115 μL) was stirred at room temperature under CO atmosphere. After 20 hours, the resulting mixture was filtered through Celite®. The filtrate was evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/*n*-hexane = 3/7) to afford **19** (17.6 mg, 23.3 mmol) in 68% yield as a colorless oil.

**19**

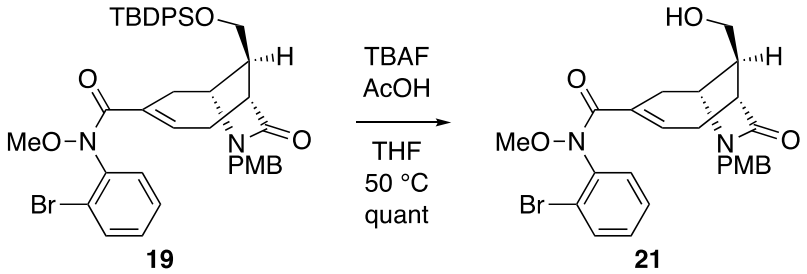
$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 7.63 (1H, d, $J$ = 7.8 Hz), 7.57 (4H, m), 7.43 (2H, m), 7.36 (4H, m), 7.33-7.30 (2H, overlapped), 7.22 (1H, dd, $J$ = 7.8, 7.8 Hz), 7.16 (2H, d, $J$ = 9.0 Hz), 6.87 (2H, d, $J$ = 9.0 Hz), 5.92 (1H, m), 4.94 (1H, d, $J$ = 15.0 Hz), 3.81 (3H, s), 3.69-3.63 (7H, overlapped), 2.95 (1H, br-d, $J$ = 18.6 Hz), 2.71-2.59 (3H, overlapped), 2.44 (1H, br-d, $J$ = 18.6 Hz), 2.34 (1H, br-d, $J$ = 18.6 Hz), 0.99 (9H, s).

$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 175.9, 170.9, 159.1, 135.5, 135.4, 133.9, 133.3, 133.2, 132.0, 130.6, 130.2, 129.9, 129.8, 129.3, 128.4, 128.3, 127.8, 123.4, 114.1, 61.9, 61.0, 55.3, 54.9, 42.8, 42.5, 41.8, 30.4, 29.4, 26.8, 19.2.

$[\alpha]_D^{25}$ = –18.1 (*c* 0.70, $CHCl_3$)

IR (ATR) $\nu_{max}$ [$cm^{-1}$]: 2962, 2932, 2857, 1687, 1513, 1471, 1431, 1248, 1110.

HR-ESIMS: calcd. for $C_{41}H_{45}BrN_2NaO_5Si$ $[M+Na]^+$ 775.2179; found 775.2222.




To a solution of **19** (29.1 mg, 38.6 μmol, 1.0 equiv) in THF (386 μL) were added tetrabutylammonium fluoride (1 M in THF, 77.2 μL, 2.0 equiv) and AcOH (4.4 μL, 77.2 μmol, 2.0 equiv) at room temperature under Ar atmosphere, and the reaction mixture was stirred for 2 hours at 50 ºC. The reaction mixture was diluted with water and EtOAc at room temperature. After separation of the two layers, the aqueous layer was extracted two times with EtOAc. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/*n*-hexane = 1/1) to afford **21** (1.24 g, 2.95 mmol) in quantitative yield as a colorless amorphous powder.

**21**

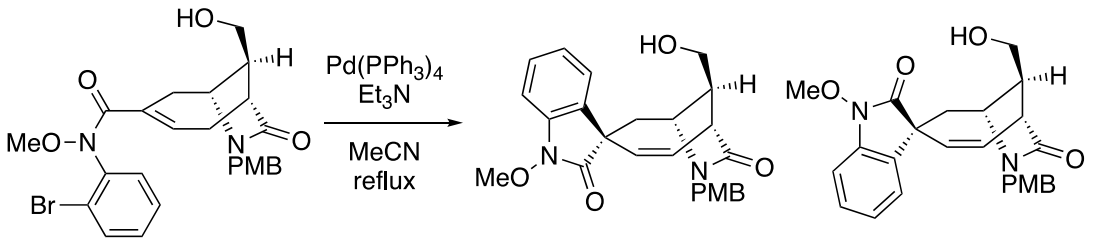
$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 7.69 (1H, dd, $J$ = 7.8, 1.2 Hz), 7.41 (1H, ddd, $J$ = 7.8, 7.8, 1.2 Hz), 7.35 (1H, dd, $J$ = 7.8, 1.2 Hz), 7.28 (1H, ddd, $J$ = 7.8, 7.8, 1.2 Hz), 7.17 (2H, d, $J$ = 9.0 Hz), 6.86 (2H, d, $J$ = 9.0 Hz), 5.97 (1H, m), 4.97 (1H, d, $J$ = 14.4 Hz), 3.80 (3H, s), 3.75-3.71 (5H, overlapped), 3.64-3.62 (2H, overlapped), 3.00 (1H, br-d, $J$ = 18.6 Hz), 2.77 (1H, br-d, $J$ = 19.8 Hz), 2.67-2.64 (2H, overlapped), 2.52 (1H, br-d, $J$ = 18.6 Hz), 2.40 (1H, br-d, $J$ = 18.6 Hz).

$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 175.6, 171.0, 159.2, 138.3, 134.0, 132.3, 130.8, 130.4, 129.4, 128.4, 128.2, 123.5, 114.2, 62.0, 59.9, 55.3, 54.9, 42.9, 42.2, 41.7, 30.3, 29.6.

$[\alpha]_D^{25}$ = –31.2 ($c$ 0.373, $CHCl_3$)

IR (ATR) $\nu_{max}$ [$cm^{-1}$]: 1729, 1673, 1614, 1513, 1464, 1245, 1035.

HR-ESIMS: calcd. for $C_{25}H_{27}BrN_2NaO_5$ $[M+Na]^+$ 537.1001; found 537.0953.




**21** **8** 84% *epi*-**8** 12%

A solution of **21** (19.1 mg, 37.1 μmol, 1.0 equiv), tetrakis(triphenylphosphine)palladium(0) (17.1 mg, 14.8 μmol, 0.4 equiv), and $Et_3N$ (51.7 μL, 371 μmol, 10 equiv) in degassed dry MeCN (1.24 mL) was stirred under reflux for 90 hours under Ar atmosphere. The resulting mixture was filtered through Celite®. The filtrate was evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (MeOH/$CHCl_3$ = 3/97) to afford **8** (13.5 mg, 31.1 μmol) in 84% yield as a white solid and *epi*-**8** (2.0 mg, 4.6 μmol) in 12% yield as a white solid.

**8**

$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 7.30 (1H, dd, $J$ = 7.8, 7.8 Hz), 7.25 (1H, d, $J$ = 7.8 Hz), 7.13 (2H, d, $J$ = 9.0 Hz), 7.08 (1H, dd, $J$ = 7.8, 7.8 Hz), 6.96 (1H, d, $J$ = 7.8 Hz), 6.80 (2H, d, $J$ = 9.0 Hz), 6.02 (1H, dd, $J$ = 10.2, 10.2 Hz), 5.23 (1H, d, $J$ = 15.0 Hz), 5.21 (1H, d, $J$ = 10.2 Hz), 4.05-3.98 (5H, overlapped), 3.81 (1H, d, $J$ = 15.0 Hz), 3.77 (1H, m),3.76 (3H, s), 3.21 (1H, dd, $J$ = 9.0, 7.2 Hz), 2.72 (1H, m), 2.35 (1H, br-s), 2.30 (1H, dd, $J$ = 16.8, 3.6 Hz), 2.23 (1H, dd, $J$ = 16.8, 1.8 Hz).

$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 174.3, 171.9, 158.9, 138.7, 131.5, 129.5, 129.3, 128.8, 123.8, 123.4, 114.0, 107.5, 63.5, 59.7, 56.4, 55.3, 54.0, 45.4, 45.1, 44.7, 33.1.

$[\alpha]_D^{25}$ = +15.9 ($c$ 0.71, $CHCl_3$)

IR (ATR) $\nu_{max}$ [$cm^{-1}$]: 3389, 3006, 2936, 1725, 1670, 1613, 1512, 1463, 1243, 1174, 1033, 744.

HR-ESIMS: calcd. for $C_{25}H_{26}N_2NaO_5$ $[M+Na]^+$ 457.1739; found 457.1694.

UV (MeOH) $\lambda_{max}$ nm (log $\varepsilon$): 205 (2.63), 227 (1.25), 258 (0.46).

***epi*-8**

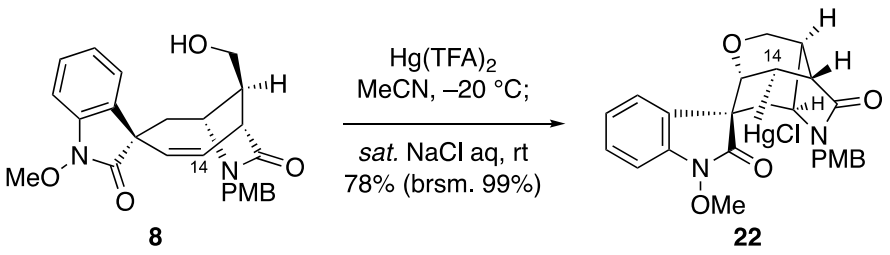
$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 7.32 (1H, m), 7.13-7.12 (2H, overlapped), 7.08 (2H, d, $J$ = 9.0 Hz), 7.01 (1H, d, $J$ = 7.8 Hz), 6.82 (2H, d, $J$ = 9.0 Hz), 6.01 (1H, dd, $J$ = 12.0, 9.0 Hz), 5.32 (1H, d, $J$ = 12.0 Hz), 5.20 (1H, d, $J$ = 14.4 Hz), 4.09 (1H, dd, $J$ = 10.8, 8.4 Hz), 4.05-4.02 (4H, overlapped), 3.81 (1H, m), 3.78 (3H, s), 3.38 (1H, d, $J$ = 14.4 Hz), 3.28 (1H, dd, $J$ = 9.0, 7.2 Hz), 2.71 (1H, m), 2.54 (1H, dd, $J$ = 15.0, 1.2 Hz), 2.13 (1H, dd, $J$ = 15.0, 4.8 Hz).

$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 175.2, 174.9, 159.3, 138.7, 130.5, 130.3, 129.3, 128.8, 128.1, 127.5, 125.7, 124.0, 114.2, 107.7, 63.5, 59.3, 56.3, 55.3, 54.2, 45.1, 44.7, 44.5, 34.5.

IR (ATR) $\nu_{max}$ [$cm^{-1}$]: 3402, 2934, 1730, 1672, 1613, 1513, 1464, 1245, 1034, 752.

HR-ESIMS: calcd. for $C_{25}H_{26}N_2NaO_5$ $[M+Na]^+$ 457.1739; found 457.1734.

UV (MeOH) $\lambda_{max}$ nm (log $\varepsilon$): 204 (2.39), 226 (1.08), 258 (0.36).




**8** **22**

To a stirred solution of **8** (3.4 mg, 7.8 μmol, 1.0 equiv) in dry MeCN (157 μL) was added mercury(II) trifluoroacetate (3.7 mg, 8.6 μmol, 1.1 equiv) at –20 ºC under Ar atmosphere. The reaction mixture was stirred at –20 ºC for 5 hours before saturated aqueous NaCl (157 μL) was added at the same temperature. The reaction mixture was warmed to room temperature and stirred at the same temperature for 14 hours. The reaction mixture was diluted with 5% MeOH-$CHCl_3$. After separation of the two layers, the aqueous layer was extracted two times with 5% MeOH-$CHCl_3$. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel preparative thin-layer chromatography (MeOH/$CHCl_3$ = 3/97) to afford **22** (4.1 mg, 6.1 μmol) in 78% yield as a white solid together with recovered starting material **8** (0.7 mg, 1.6 μmol) in 20% yield.

**22**

$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 7.50 (1H, d, $J$ = 7.8 Hz), 7.32 (1H, dd, $J$ = 7.8, 7.8 Hz), 7.15 (2H, d, $J$ = 9.0 Hz), 7.12 (1H, dd, $J$ = 7.8, 7.8 Hz), 6.99 (1H, d, $J$ = 7.8 Hz), 6.83 (2H, d, $J$ = 9.0 Hz), 5.25 (1H, d, $J$ = 15.0 Hz), 4.28 (1H, dd, $J$ = 11.4, 3.0 Hz), 4.19 (1H, d, $J$ = 11.4 Hz), 4.10 (3H, s), 3.95 (1H, d, $J$ = 4.2 Hz), 3.91 (1H, m), 3.78 (3H, s), 3.73 (1H, d, $J$ = 15.0 Hz), 3.31 (1H, dd, $J$ = 9.0, 7.2 Hz), 2.97 (1H, m), 2.74 (1H, m), 2.27 (1H, dd, $J$ = 16.2, 3.0 Hz), 2.23 (1H, dd, $J$ = 16.2, 2.4 Hz).

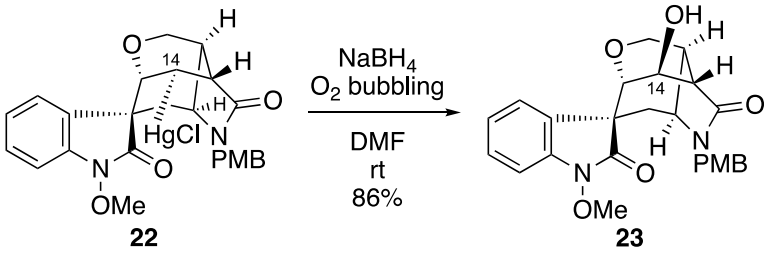
$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 179.2, 173.1, 159.1, 138.0, 131.3, 129.5, 128.7, 128.3, 124.7, 124.0, 114.1, 107.4, 79.8, 64.4, 61.5, 59.0, 56.7, 55.3, 46.1, 44.1, 43.4, 36.8, 32.7.

$[\alpha]_D^{25}$ = –14.5 ($c$ 0.27, $CHCl_3$)

IR (ATR) $\nu_{max}$ [$cm^{-1}$]: 3008, 2930, 1698, 1666, 1614, 1512, 1464, 1241, 1104, 1036, 745.

HR-ESIMS: calcd. for $C_{25}H_{25}ClHgN_2NaO_5$ $[M+Na]^+$ 693.1056; found 693.1079.

UV (MeOH) $\lambda_{max}$ nm (log $\varepsilon$): 204 (2.03), 263 (0.28).




**22** **23**

A stirred solution of **22** (61.3 mg, 91.6 μmol, 1.0 equiv) in dry DMF (2.44 mL) was vigorously bubbled with $O_2$ and to this, a solution of $NaBH_4$ (5.2 mg, 137 μmol, 1.5 equiv) in dry DMF (0.61 mL) was added at room temperature. $O_2$ was vigorously bubbled through the reaction mixture for 10 minutes at the same temperature. The reaction was quenched by adding water and then diluted with 5% MeOH-$CHCl_3$. After separation of the two layers, the aqueous layer was extracted two times with 5% MeOH-$CHCl_3$. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (MeOH/$CHCl_3$ = 3/97) to afford **23** (35.6 mg, 79.0 μmol) in 86% yield as a colorless oil.

**23**

$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 7.48 (1H, d, $J$ = 7.8 Hz), 7.30 (1H, dd, $J$ = 7.8, 7.8 Hz), 7.13 (2H, d, $J$ = 9.0 Hz), 7.09 (1H, dd, $J$ = 7.8, 7.8 Hz), 6.95 (1H, d, $J$ = 7.8 Hz), 6.83 (2H, d, $J$ = 9.0 Hz), 5.21 (1H, d, $J$ = 15.0 Hz), 4.64 (1H, br-s), 4.39 (1H, dd, $J$ = 11.4, 2.4 Hz), 4.21 (1H, d, $J$ = 11.4 Hz), 4.02 (3H, s), 3.80 (1H, br-s), 3.77 (3H, s), 3.76 (1H, m), 3.62 (1H, d, $J$ = 15.0 Hz), 3.16 (1H, br-s), 2.85 (1H, d, $J$ = 8.4 Hz), 2.66 (1H, m), 2.22 (1H, dd, $J$ = 15.6, 3.6 Hz), 2.19 (1H, dd, $J$ = 15.6, 1.8 Hz).

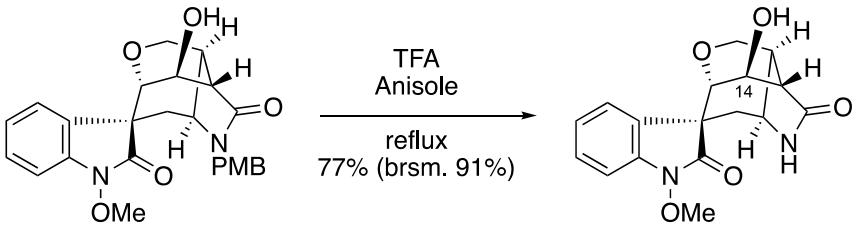
$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 173.3, 170.9, 159.1, 138.4, 130.8, 129.5, 128.7, 128.4, 124.5, 123.7, 114.1, 107.2, 79.4, 66.8, 63.9, 61.4, 57.8, 55.3, 53.6, 47.2, 43.9, 33.9, 31.9.

$[\alpha]_D^{25}$ = –94 ($c$ 0.07, $CHCl_3$)

IR (ATR) $\nu_{max}$ [$cm^{-1}$] : 3390, 2923, 1722, 1673, 1614, 1513, 1464, 1320, 1245, 1034, 751.

HR-ESIMS: calcd. for $C_{25}H_{26}N_2NaO_6$ $[M+Na]^+$ 473.1689; found 473.1671.

UV (MeOH) $\lambda_{max}$ nm (log $\varepsilon$): 203 (1.55), 259 (0.20).




**23** (–)-14-Hydroxygelsedilam (**2**)

A solution of **23** (28.0 mg, 62.2 μmol, 1.0 equiv), anisole (311 μL), and trifluoroacetic acid (3.11 mL) was stirred under reflux for 49 hours under Ar atmosphere. The reaction was quenched by adding saturated aqueous $NaHCO_3$ at 0 ºC and then diluted with 10% MeOH-$CHCl_3$. After separation of the two layers, the aqueous layer was extracted two times with 10% MeOH-$CHCl_3$. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (MeOH/$CHCl_3$ = 1/9) to afford 14-hydroxygelsedilam (**2**) (15.7 mg, 47.5 μmol) in 77% yield as a white solid together with recovered starting material **23** (4.3 mg, 9.5 μmol) in 15% yield. The spectral and physical properties of synthetic **2** were in good agreement with those of the authentic natural product.

**14-Hydroxygelsedilam (2)**

$^1$H-NMR ($CD_3OD$, 600 MHz) $\delta$ ppm: 7.55 (1H, d, $J$ = 7.8 Hz), 7.32 (1H, dd, $J$ = 7.8, 7.8 Hz), 7.12 (1H, dd, $J$ = 7.8, 7.8 Hz), 6.98 (1H, d, $J$ = 7.8 Hz), 4.59 (1H, br-s), 4.49 (1H, d, $J$ = 1.8 Hz), 4.35 (1H, dd, $J$ = 10.8, 3.6 Hz), 4.29 (1H, d, $J$ = 10.8 Hz), 4.08 (1H, m), 3.95 (3H, s), 3.64 (1H, br-s), 2.87 (1H, m), 2.53 (1H, d, $J$ = 7.8 Hz), 2.47 (1H, dd, $J$ = 15.6, 4.2 Hz), 2.00 (1H, dd, $J$ = 15.6, 2.4 Hz).

$^{13}$C NMR ($CD_3OD$, 150 MHz) $\delta$ ppm: 179.6, 173.0, 139.3, 132.9, 129.6, 125.8, 124.8, 108.1, 80.5, 67.5, 64.0, 62.1, 57.8, 55.2, 47.7, 37.4, 37.0.

$[\alpha]_D^{24}$ = –109 (*c* 0.08, MeOH)

IR (ATR) $\nu_{max}$ [cm$^{-1}$]: 3341, 2917, 1713, 1687, 1618, 1469, 1331, 1240, 1048, 754.

HR-ESIMS: calcd. for $C_{17}H_{18}N_2NaO_5$ $[M+Na]^+$ 353.1113; found 353.1118.

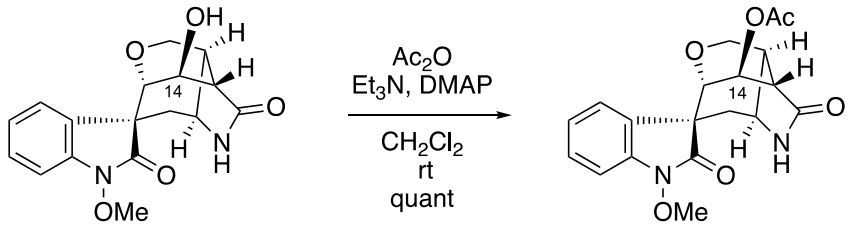
UV (MeOH) $\lambda_{max}$ nm (log $\varepsilon$): 204 (2.31), 256 (0.50).

CD (MeOH, 24 °C, *c* 0.279 mM)

$\Delta\varepsilon$ ($\lambda$ nm): 0 (304), –1.49 (261), 0 (248), +1.57 (236), 0 (227), –7.71 (212).

Natural product: CD (MeOH, 24 °C, *c* 0.280 mM)

$\Delta\varepsilon$ ($\lambda$ nm): 0 (304), –3.11 (260), 0 (248), +4.33 (235), 0 (224), –12.65 (213).




(–)-14-Hydroxygelsedilam (**2**) (–)-14-Acetoxygelsedilam (**3**)

To a solution of **2** (3.9 mg, 12 μmol, 1.0 equiv) in dry $CH_2Cl_2$ (240 μL) were added acetic anhydride (1.3 μL, 14 μmol, 1.2 equiv), $Et_3N$ (3.3 μL, 24 μmol, 2.0 equiv), and *N*,*N*-dimethyl-4-aminopyridine (0.3 mg, 2.4 μmol, 0.2 equiv) at room temperature under Ar atmosphere, and the reaction mixture was stirred for 75 minutes at the same temperature. The reaction was quenched by adding water and then diluted with $CHCl_3$. After separation of the two layers, the aqueous layer was extracted two times with $CHCl_3$. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (MeOH/$CHCl_3$ = 1/9) to afford 14-acetoxygelsedilam (**3**) (4.6 mg, 12 μmol) in quantitative yield as a colorless oil. The spectral and physical properties of synthetic **3** were in good agreement with those of the authentic natural product.

**14-Acetoxygelsedilam (3)**

$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 7.44 (1H, d, $J$ = 7.8 Hz), 7.28 (1H, dd, $J$ = 7.8, 7.8 Hz), 7.08 (1H, dd, $J$ = 7.8, 7.8 Hz), 6.90 (1H, d, $J$ = 7.8 Hz), 6.32 (1H, br-s), 5.63 (1H, d, $J$ = 2.4 Hz), 4.36 (1H, dd, $J$ = 10.8, 3.6 Hz), 4.28 (1H, dd, $J$ = 10.8, 1.2 Hz), 4.14 (1H, m), 3.92 (3H, s), 2.90 (1H, m), 2.71 (1H, dd, $J$ = 8.4, 1.2 Hz), 2.38 (1H, dd, $J$ = 16.2, 3.6 Hz), 2.16 (1H, dd, $J$ = 16.2, 2.4 Hz), 2.02 (3H, s).

$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 175.9, 170.7, 169.8, 138.5, 130.4, 128.6, 124.1, 123.5, 107.2, 75.6, 69.2, 63.7, 61.6, 55.9, 53.7, 42.8, 36.0, 35.5, 21.1.

$[\alpha]_D^{24}$ = –81.4 (*c* 0.18, $CHCl_3$)

IR (ATR) $\nu_{max}$ [cm$^{-1}$]: 2925, 1724, 1615, 1464, 1235, 1055, 753.

HR-ESIMS: calcd. for $C_{19}H_{20}N_2NaO_6$ $[M+Na]^+$ 395.1219; found 395.1241.

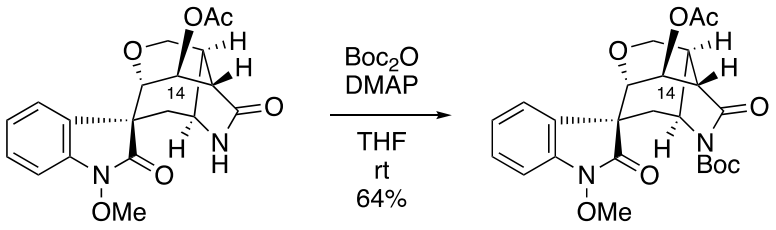
UV (MeOH) $\lambda_{max}$ nm (log $\varepsilon$): 210 (2.67), 257 (0.61).

CD (MeOH, 24 °C, *c* 0.166 mM)

$\Delta\varepsilon$ ($\lambda$ nm): 0 (306), –10.78 (261), 0 (248), +12.39 (236), 0 (226), –29.92 (212).

Natural product: CD (MeOH, 24 °C, *c* 0.280 mM)

$\Delta\varepsilon$ ($\lambda$ nm): 0 (300), –5.07 (262), 0 (248), +7.72 (235), 0 (223), –15.10 (211).




(–)-14-Acetoxygelsedilam (**3**) **24**

To a solution of **3** (2.0 mg, 5.4 μmol, 1.0 equiv) in dry THF (270 μL) were added di-*tert*-butyl dicarbonate (9.3 μL, 43 μmol, 8.0 equiv) and *N*,*N*-dimethyl-4-aminopyridine (3.9 mg, 32 μmol, 6.0 equiv) at room temperature under Ar atmosphere, and the reaction mixture was stirred for 19 hours at the same temperature. The resultant mixture was evaporated under reduced pressure. The residue was purified by silica gel preparative thin-layer chromatography (MeOH/$CHCl_3$ = 5/95) to afford **24** (1.6 mg, 3.4 μmol) in 64% yield as a colorless oil.

**24**

$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 7.44 (1H, d, $J$ = 7.8 Hz), 7.29 (1H, dd, $J$ = 7.8, 7.8 Hz), 7.08 (1H, dd, $J$ = 7.8, 7.8 Hz), 6.92 (1H, d, $J$ = 7.8 Hz), 5.67 (1H, br-s), 4.57 (1H, m), 4.33 (1H, dd, $J$ = 10.8, 3.6 Hz), 4.30 (1H, br-d, $J$ = 10.8 Hz), 3.97 (3H, s), 3.92 (1H, br-s), 2.90 (1H, d, $J$ = 9.0 Hz), 2.78 (1H, m), 2.60 (1H, dd, $J$ = 15.6, 1.8 Hz), 2.35 (1H, dd, $J$ = 15.6, 3.0 Hz), 2.03 (3H, s), 1.54 (9H, s).

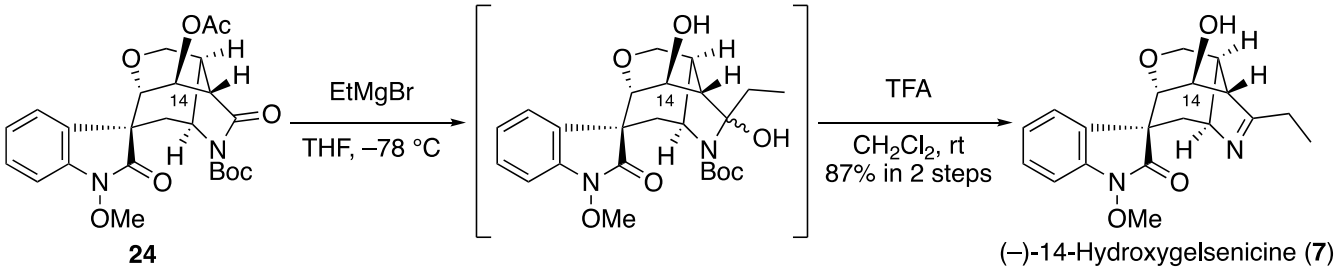
$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 171.6, 170.4, 169.6, 150.1, 138.6, 130.3, 128.8, 114.0, 123.6, 107.2, 83.3, 75.6, 68.8, 63.7, 61.1, 59.6, 53.6, 45.6, 32.9, 32.3, 28.1, 21.1.

$[\alpha]_D^{24}$ = –28.5 ($c$ 0.04, $CHCl_3$)

IR (ATR) $\nu_{max}$ [$cm^{-1}$]: 2975, 2930, 2887, 1789, 1721, 1312, 1230, 1146, 753.

HR-ESIMS: calcd. for $C_{24}H_{28}N_2NaO_8$ $[M+Na]^+$ 495.1743; found 495.1750.

UV (MeOH) $\lambda_{max}$ nm (log $\varepsilon$): 209 (1.99), 256 (0.36).




To a stirred solution of **24** (1.6 mg, 3.4 μmol, 1.0 equiv) in dry THF (843 μL) was added dropwise ethylmagnesium bromide (3.0 M in $Et_2O$, 6.8 μL, 6.0 equiv) at –78 ºC under Ar atmosphere. The reaction mixture was stirred for 30 minutes at –78 ºC before warming to room temperature and stirred for another 15 minutes at the same temperature. The reaction was quenched by adding saturated aqueous $NH_4Cl$ and then diluted with 10% MeOH-$CHCl_3$. After separation of the two layers, the aqueous layer was extracted two times with 10% MeOH-$CHCl_3$. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure.

The residue was dissolved in $CH_2Cl_2$ (169 μL) and trifluoroacetic acid (3.4 μL) was added to the solution at room temperature under Ar atmosphere. The reaction mixture was stirred for 2 hours at the same temperature. The reaction was quenched by adding saturated aqueous $NaHCO_3$ at 0 ºC and then diluted with 5% MeOH-$CHCl_3$. After separation of the two layers, the aqueous layer was extracted two times with 5% MeOH-$CHCl_3$. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel preparative thin-layer chromatography (MeOH/$CHCl_3$ = 7/93) to afford 14-hydroxygelsenicine (**7**) (1.0 mg, 2.9 μmol) in 87% yield in two steps as a colorless oil. The spectral and physical properties of synthetic **7** were in good agreement with those of the authentic natural product.

**14-Hydroxygelsenicine (7)**

$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 7.50 (1H, d, $J$ = 7.8 Hz), 7.26 (1H, dd, $J$ = 7.8, 7.8 Hz), 7.07 (1H, dd, $J$ = 7.8, 7.8 Hz), 6.87 (1H, d, $J$ = 7.8 Hz), 4.45 (1H, br-s), 4.44 (1H, dd, $J$ = 10.8, 3.6 Hz), 4.41 (1H, m), 4.31 (1H, d, $J$ = 10.8 Hz), 3.93 (3H, s), 3.67 (1H, br-s), 2.89 (1H, d, $J$ = 8.4 Hz), 2.77 (1H, dq, $J$ = 17.4, 7.2 Hz), 2.59 (1H, m), 2.50 (1H, dq, $J$ = 17.4, 7.2 Hz), 2.41 (1H, dd, $J$ = 15.6, 4.8 Hz), 2.30 (1H, dd, $J$ = 15.6, 1.8 Hz), 1.29 (1H, dd, $J$ = 7.2, 7.2 Hz).

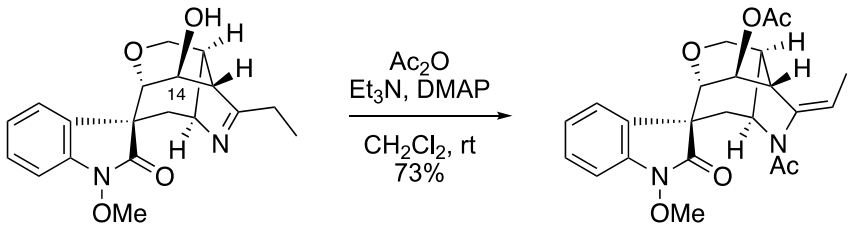
$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 181.4, 170.8, 138.0, 131.6, 128.3, 124.5, 123.5, 106.8, 79.2, 71.7, 66.4, 63.4, 61.7, 53.7, 52.2, 38.3, 37.5, 26.0, 9.9.

$[\alpha]_D^{24}$ = –113 ($c$ 0.05, $CHCl_3$), Natural product: $[\alpha]_D^{24}$ = –116 ($c$ 0.78, $CHCl_3$)

IR (ATR) $\nu_{max}$ [cm$^{-1}$]: 2936, 2909, 1719, 1643, 1616, 1464, 1319, 1232, 1040, 1013, 878, 747.

HR-ESIMS: calcd. for $C_{19}H_{23}N_2O_4$ $[M+H]^+$ 343.1658; found 343,1703.

UV (MeOH) $\lambda_{max}$ nm (log $\varepsilon$): 210 (2.07), 258 (0.46).




(–)-14-Hydroxygelsenicine (**7**) **25**

To a solution of **7** (6.9 mg, 20 μmol, 1.0 equiv) in dry $CH_2Cl_2$ (240 μL) were added acetic anhydride (5.7 μL, 61 μmol, 3.0 equiv), $Et_3N$ (14.1 μL, 101 μmol, 5.0 equiv), and *N*,*N*-dimethyl-4-aminopyridine (2.5 mg, 20 μmol, 1.0 equiv) at room temperature under Ar atmosphere, and the reaction mixture was stirred for 18 hours at the same temperature. The reaction was quenched by adding water and then diluted with 5% MeOH-$CHCl_3$. After separation of the two layers, the aqueous layer was extracted two times with 5% MeOH-$CHCl_3$. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel MPLC (MeOH/$CHCl_3$ = 3/97) to afford **25** (6.3 mg, 15 μmol) in 73% yield as a colorless oil.

**25**

$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 7.41 (1H, d, $J$ = 7.8 Hz), 7.26 (1H, dd, $J$ = 7.8, 7.8 Hz), 7.06 (1H, dd, $J$ = 7.8, 7.8 Hz), 6.89 (1H, d, $J$ = 7.8 Hz), 5.61 (1H, br-s), 5.21 (1H, q, $J$ = 6.6 Hz), 4.74 (1H, m), 4.36 (1H, dd, $J$ = 10.8, 3.6 Hz), 4.33 (1H, d, $J$ = 10.8 Hz), 3.95 (3H, s), 3.70 (1H, br-s), 3.18 (1H, d, $J$ = 8.4 Hz), 2.80 (1H, dd, $J$ = 16.2, 1.8 Hz), 2.56 (1H, m), 2.37 (3H, s), 2.11 (1H, dd, $J$ = 16.2, 3.6 Hz), 2.06 (3H, s), 1.76 (1H, d, $J$ = 6.6 Hz).

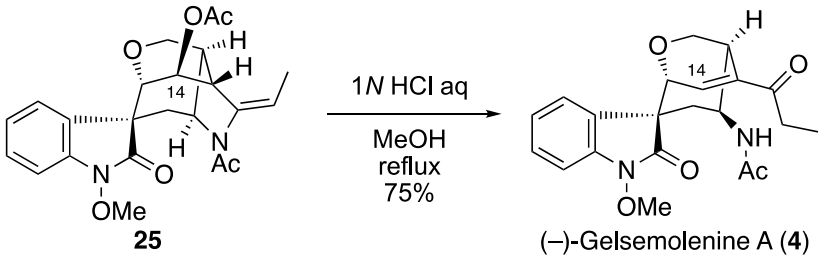
$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 170.7, 170.6, 169.8, 141.1, 138.2, 130.9, 128.5, 124.3, 123.4, 106.9, 103.8, 75.9, 71.3, 63.5, 61.9, 60.6, 53.6, 41.8, 34.2, 30.8, 26.0, 21.1, 14.2.

$[\alpha]_D^{24}$ = –91.4 (*c* 0.12, $CHCl_3$)

IR (ATR) $\nu_{max}$ [$cm^{-1}$]: 2923, 2879, 2853, 1723, 1670, 1642, 1388, 1234, 1024, 750.

HR-ESIMS: calcd. for $C_{23}H_{26}N_2NaO_6$ $[M+Na]^+$ 449.1689; found 449.1686.

UV (MeOH) $\lambda_{max}$ nm (log $\varepsilon$): 207 (1.19), 254 (0.44).




A solution of **25** (3.4 mg, 8.0 μmol, 1.0 equiv), MeOH (200 μL), and 1*N* aqueous HCl (80 μL) was stirred under reflux for 22 hours under Ar atmosphere. The reaction was quenched by adding saturated aqueous $NaHCO_3$ at 0 ºC and then diluted with 5% MeOH-$CHCl_3$. After separation of the two layers, the aqueous layer was extracted two times with 5% MeOH-$CHCl_3$. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel preparative thin-layer chromatography (MeOH/$CHCl_3$ = 5/95) to afford gelsemolenine A (**4**) (2.3 mg, 6.0 μmol) in 75% yield as a white solid. The spectral and physical properties of synthetic **4** were in good agreement with the reported data[5] of the natural product.

**Gelsemolenine A (4)**

$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 7.47 (1H, d, $J$ = 7.8 Hz), 7.35 (1H, dd, $J$ = 7.8, 7.8 Hz), 7.30 (1H, dd, $J$ = 6.0, 1.2 Hz), 7.15 (1H, dd, $J$ = 7.8, 7.8 Hz), 7.01 (1H, d, $J$ = 7.8 Hz), 6.44 (1H, br-d, $J$ = 7.8 Hz), 4.40 (1H, m), 4.29 (1H, d, $J$ = 5.4 Hz), 4.26 (1H, d, $J$ = 9.6 Hz), 3.99 (3H, s), 3.71 (1H, dd, $J$ = 9.6, 3.0 Hz), 3.31 (1H, br-d, $J$ = 1.2 Hz), 3.04 (1H, dq, $J$ = 18.0, 7.2 Hz), 2.78 (1H, dq, $J$ = 18.0, 7.2 Hz), 2.05 (1H, dd, $J$ = 13.8, 4.8 Hz), 1.94 (3H, s), 1.61 (1H, dd, $J$ = 13.8, 10.2 Hz), 1.21 (3H, dd, $J$ = 7.2, 7.2 Hz).

$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 201.2, 171.7, 169.0, 139.7, 139.0, 137.5, 128.8, 126.8, 126.5, 123.7, 107.5, 72.0, 67.5, 63.6, 53.0, 47.1, 38.1, 35.4, 30.6, 23.4, 8.3.

$[\alpha]_D^{25}$ = –142 (*c* 0.05, MeOH), Natural product[5]: $[\alpha]_D^{25}$ = –19.4 (*c* 0.310, MeOH)

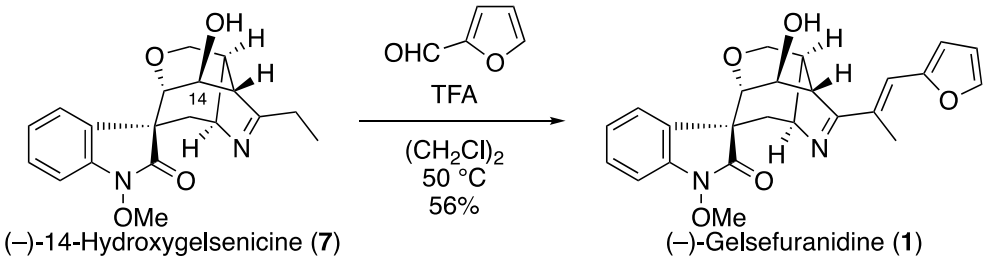
IR (ATR) $\nu_{max}$ [$cm^{-1}$]: 3304, 2923, 2852, 1718, 1660, 1617, 1525, 1463, 1190, 748.

HR-ESIMS: calcd. for $C_{21}H_{24}N_2Na_1O_5$ $[M+Na]^+$ 407.1583; found 407.1582.

UV (MeOH) $\lambda_{max}$ nm (log $\varepsilon$): 204 (2.14), 245 (1.01).

CD (MeOH, 24 °C, *c* 0.466 mM)

$\Delta\varepsilon$ ($\lambda$ nm): 0 (377), –0.83 (325), 0 (301), +0.48 (287), 0 (268), –8.82 (231), 0 (218), +6.87 (207).




To a solution of **7** (5.1 mg, 15 μmol, 1.0 equiv) in dry $(CH_2Cl)_2$ (300 μL) were added 2-furaldehyde (6.2 μL, 74.5 μmol, 5.0 equiv) and trifluoroacetic acid (1.1 μL, 15 μmol, 1.0 equiv) at room temperature under Ar atmosphere, and the reaction mixture was stirred for 41 hours at 50 ºC. The reaction was quenched by adding saturated aqueous $NaHCO_3$ at 0 ºC and then diluted with $CHCl_3$. After separation of the two layers, the aqueous layer was extracted two times with $CHCl_3$. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel MPLC (MeOH/$CHCl_3$ = 2/98) to afford gelsefuranidine (**1**) (3.5 mg, 8.3 μmol) in 56% yield as a white solid. The spectral and physical properties of synthetic **1** were in good agreement with those of the authentic natural product.

**Gelsefuranidine (1)**

$^1$H-NMR ($CDCl_3$, 600 MHz) $\delta$ ppm: 7.53 (1H, d, $J$ = 7.8 Hz), 7.49 (1H, s), 7.27 (1H, dd, $J$ = 7.8, 7.8 Hz), 7.09 (1H, dd, $J$ = 7.8, 7.8 Hz), 6.97 (1H, s), 6.88 (1H, d, $J$ = 7.8 Hz), 6.61 (1H, d, $J$ = 3.6 Hz), 6.49 (1H, br-s), 4.63 (1H, m), 4.52 (1H, br-s), 4.51 (1H, dd, $J$ = 10.8, 3.6 Hz), 4.38 (1H, d, $J$ = 10.8 Hz), 3.91 (3H, s), 3.66 (1H, br-s), 3.43 (1H, d, $J$ = 9.0 Hz), 2.67 (1H, m), 2.50 (1H, dd, $J$ = 15.6, 4.8 Hz), 2.46 (3H, s), 2.39 (1H, dd, $J$ = 15.6, 1.8 Hz).

$^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ ppm: 177.0, 170.6, 152.8, 142.9, 138.1, 131.5, 130.8, 128.4, 124.6, 123.5, 122.9, 112.9, 111.9, 106.8, 79.5, 72.6, 67.5, 63.4, 61.9, 53.7, 49.0, 38.3, 37.4, 15.0.

$[\alpha]_D^{20}$ = –152 ($c$ 0.18, $CHCl_3$)

IR (ATR) $\nu_{max}$ [cm$^{-1}$]: 2923, 2853, 1722, 1617, 1588, 1465, 1315, 1041, 1016, 748.

HR-ESIMS: calcd. for $C_{24}H_{25}N_2O_5$ $[M+H]^+$ 421.1764; found 421.1771.

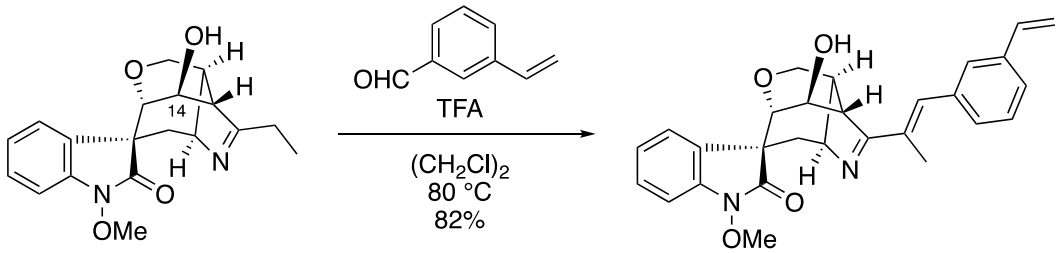
UV (MeOH) $\lambda_{max}$ nm (log $\varepsilon$): 204 (1.15), 308 (0.97).

CD (MeOH, 24 °C, $c$ 0.252 mM)

$\Delta\varepsilon$ ($\lambda$ nm): 0 (347), +2.65 (306), 0 (281), –9.04 (260), 0 (244), +2.23 (236), 0 (231), –20.51 (214).

Natural product: CD (MeOH, 24 °C, $c$ 0.305 mM)

$\Delta\varepsilon$ ($\lambda$ nm): 0 (338), +0.85 (308), 0 (296), –4.90 (260), 0 (224), +2.15 (236), 0 (277), –11.91 (212), 0 (202).




(–)-14-Hydroxygelsenicine (**7**) (–)-Gelselegandine B (**5**)

To a solution of **7** (4.2 mg, 12 μmol, 1.0 equiv) in dry $(CH_2Cl)_2$ (246 μL) were added 3-vinylbenzaldehyde (7.8 μL, 61.3 μmol, 5.0 equiv) and trifluoroacetic acid (0.9 μL, 12 μmol, 1.0 equiv) at room temperature under Ar atmosphere, and the reaction mixture was stirred for 18 hours at 80 ºC. The reaction was quenched by adding saturated aqueous $NaHCO_3$ at 0 ºC and then diluted with $CHCl_3$. After separation of the two layers, the aqueous layer was extracted two times with $CHCl_3$. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel MPLC (MeOH/$CHCl_3$ = 2/98) to afford gelselegandine B (**5**) (4.6 mg, 10 μmol) in 82% yield as a white solid. The spectral and physical properties of synthetic **5** were in good agreement with reported data[4] of the natural product.

**Gelselegandine B (5)**

$^1$H-NMR ($CD_3OD$, 600 MHz) $\delta$ ppm: 7.61 (1H, d, $J$ = 7.8 Hz), 7.57 (1H, s), 7.40 (3H, overlapped), 7.36 (1H, s), 7.32 (1H, dd, $J$ = 7.8, 7.8 Hz), 7.14 (1H, dd, $J$ = 7.8, 7.8 Hz), 6.96 (1H, d, $J$ = 7.8 Hz), 6.80 (1H, dd, $J$ = 17.4, 10.8 Hz), 5.85 (1H, d, $J$ = 17.4 Hz), 5.28 (1H, d, $J$ = 10.8 Hz), 4.57 (1H, m), 4.51 (1H, dd, $J$ = 10.8, 3.0 Hz), 4.47 (1H, br-d, $J$ = 1.8 Hz), 4.40 (1H, d, $J$ = 10.8 Hz), 3.91 (3H, s), 3.61 (1H, br-s), 3.50 (1H, d, $J$ = 8.4 Hz), 2.71 (1H, m), 2.64 (1H, dd, $J$ = 15.6, 4.8 Hz), 2.29 (3H, s), 2.22 (1H, br-d, $J$ = 15.6 Hz).

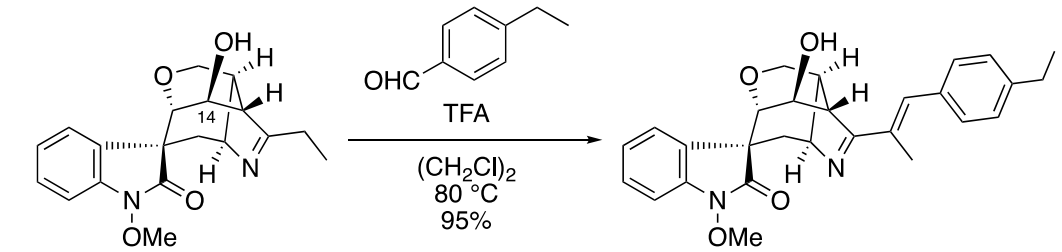
$^{13}$C NMR ($CD_3OD$, 150 MHz) $\delta$ ppm: 180.0, 173.0, 139.14, 139.09, 138.5, 138.0, 137.7, 134.3, 133.2, 130.1, 129.57, 129.55, 128.6, 126.6, 126.0, 124.8, 114.6, 108.0, 80.7, 73.5, 68.2, 64.0, 62.1, 55.5, 50.4, 39.6, 38.2. 15.1.

$[\alpha]_D^{25}$ = –64.1 (*c* 0.23, MeOH), Natural product[4]: $[\alpha]_D^{24}$ = –65.0 (*c* 0.1, MeOH)

IR (ATR) $\nu_{max}$ [cm$^{-1}$]: 2920, 2868, 1721, 1617, 1594, 1475, 1464, 1317, 1233, 1040, 747.

HR-ESIMS: calcd. for $C_{28}H_{29}N_2O_4$ $[M+H]^+$ 457.2127; found 457.2104.

UV (MeOH) $\lambda_{max}$ nm (log $\varepsilon$): 207 (2.35), 254 (2.48).




(–)-14-Hydroxygelsenicine (**7**) **26**

To a solution of **7** (4.0 mg, 12 μmol, 1.0 equiv) in dry $(CH_2Cl)_2$ (234 μL) were added 4-ethylbenzaldehyde (7.8 μL, 58.4 μmol, 5.0 equiv) and trifluoroacetic acid (0.9 μL, 12 μmol, 1.0 equiv) at room temperature under Ar atmosphere, and the reaction mixture was stirred for 18 hours at 80 ºC. The reaction was quenched by adding saturated aqueous $NaHCO_3$ at 0 ºC and then diluted with $CHCl_3$. After separation of the two layers, the aqueous layer was extracted two times with $CHCl_3$. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel preparative thin-layer chromatography (MeOH/$CHCl_3$ = 5/95) to afford **26** (5.1 mg, 11 μmol) in 95% yield as a white solid.

**26**

$^1$H-NMR ($CD_3OD$, 600 MHz) $\delta$ ppm: 7.49 (1H, d, $J$ = 7.8 Hz), 7.33 (2H, d, $J$ = 7.8 Hz), 7.24 (1H, s), 7.21 (1H, dd, $J$ = 7.8, 7.8 Hz), 7.17 (2H, d, $J$ = 7.8 Hz), 7.03 (1H, dd, $J$ = 7.8, 7.8 Hz), 6.86 (1H, d, $J$ = 7.8 Hz), 4.46 (1H, m), 4.40 (1H, dd, $J$ = 10.8, 3.6 Hz), 4.36 (1H, br-d, $J$ = 1.8 Hz), 4.29 (1H, d, $J$ = 10.8 Hz), 3.80 (3H, s), 3.50 (1H, br-s), 3.39 (1H, d, $J$ = 8.4 Hz), 2.60-2.56 (3H, overlapped), 2.52 (1H, dd, $J$ = 15.0, 4.8 Hz), 2.19 (3H, s), 2.11 (1H, br-d, $J$ = 15.0 Hz), 1.16 (1H, t, $J$ = 7.2 Hz).

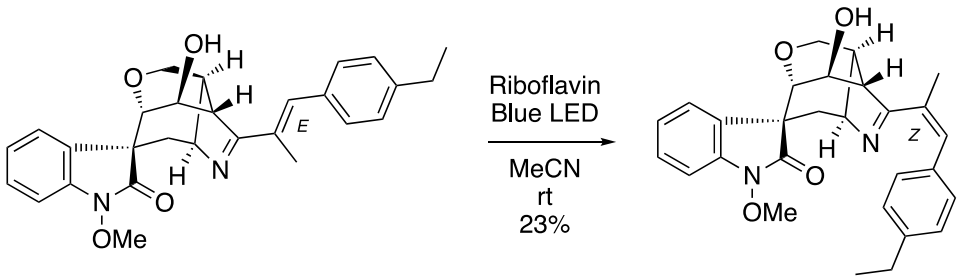
$^{13}$C NMR ($CD_3OD$, 150 MHz) $\delta$ ppm: 180.2, 173.0, 145.5, 139.1, 138.1, 135.6, 133.3, 133.2, 130.9, 129.5, 128.8, 126.0, 124.8, 108.0, 80.8, 73.4, 68.3, 64.0, 62.2, 55.5, 50.3, 39.6, 38.2, 29.7, 16.0, 15.1.

$[\alpha]_D^{26}$ = –85.7 ($c$ 0.26, MeOH)

IR (ATR) $\nu_{max}$ [cm$^{-1}$]: 2966, 2925, 2868, 1725, 1617, 1586, 1465, 1317, 1041, 748.

HR-ESIMS: calcd. for $C_{28}H_{31}N_2O_4$ $[M+H]^+$ 459.2284; found 459.2253.

UV (MeOH) $\lambda_{max}$ nm (log $\varepsilon$): 210 (2.11), 285 (1.82).




**26** (–)-Gelselegandine C (**6**)

To a solution of **26** (4.7 mg, 10 μmol, 1.0 equiv) in dry MeCN (152 μL) was added riboflavin (0.2 mg, 0.5 μmol, 5 mol%) at room temperature under Ar atmosphere, and the reaction mixture was stirred for 24 hours at the same temperature under blue LED irradiation (450 nm, radiant flux 10 W). The resulting mixture was passed through a silica gel short column and the eluate was evaporated under reduced pressure. The residue was purified by silica gel preparative thin-layer chromatography (MeOH/$CHCl_3$ = 2/98) to afford gelselegandine C (**6**) (1.1 mg, 2.4 μmol) in 23% yield as a white solid together with 23% of the recovered starting material. The spectral and physical properties of synthetic **6** were in good agreement with the reported data[4] of the natural product.

**Gelselegandine (6)**

$^1$H-NMR ($CD_3OD$, 600 MHz) $\delta$ ppm: 7.51 (1H, d, $J$ = 7.8 Hz), 7.31 (1H, dd, $J$ = 7.8, 7.8 Hz), 7.18 (2H, d, $J$ = 7.8 Hz), 7.14 (2H, d, $J$ = 7.8 Hz), 7.11 (1H, dd, $J$ = 7.8, 7.8 Hz), 6.97-6.96 (2H, overlapped), 4.50 (1H, m), 4.32 (1H, d, $J$ = 10.8 Hz), 4.22 (1H, dd, $J$ = 10.8, 4.2 Hz), 4.20 (1H, d, $J$ = 1.2 Hz), 3.94 (3H, s), 3.38 (1H, br-s), 2.79 (1H, d, $J$ = 8.4 Hz), 2.64 (1H, q, $J$ = 7.8 Hz), 2.58-2.53 (2H, overlapped), 2.48 (3H, s), 2.26 (1H, br-d, $J$ = 15.6 Hz), 1.23 (1H, t, $J$ = 7.8 Hz).

$^{13}$C NMR ($CD_3OD$, 150 MHz) $\delta$ ppm: 180.4, 173.1, 145.2, 139.3, 136.4, 135.1, 134.4, 132.9, 129.7, 129.5, 128.9, 126.3, 124.7, 108.0, 81.4, 73.1, 66.9, 63.9, 62.0, 55.0, 53.1, 38.9, 38.0, 29.6, 24.2, 16.0.

$[\alpha]_D^{27}$ = –49.3 ($c$ 0.07, MeOH), Natural product[4]: $[\alpha]_D^{25}$ = –35.6 ($c$ 0.09, MeOH)

IR (ATR) $\nu_{max}$ [$cm^{-1}$]: 2962, 2917, 2868, 1726, 1615, 1581, 1464, 1232, 1041, 751.

HR-ESIMS: calcd. for $C_{28}H_{31}N_2O_4$ $[M+H]^+$ 459.2284; found 459.2280.

UV (MeOH) $\lambda_{max}$ nm (log $\varepsilon$): 203 (1.34), 282 (0.79).

## References


(1) Hojczyk, K. N.; Feng, P.; Zhan, C.; Ngai, M.-Y. *Angew. Chem. Int. Ed.* **2014**, *53*, 14559–14563.

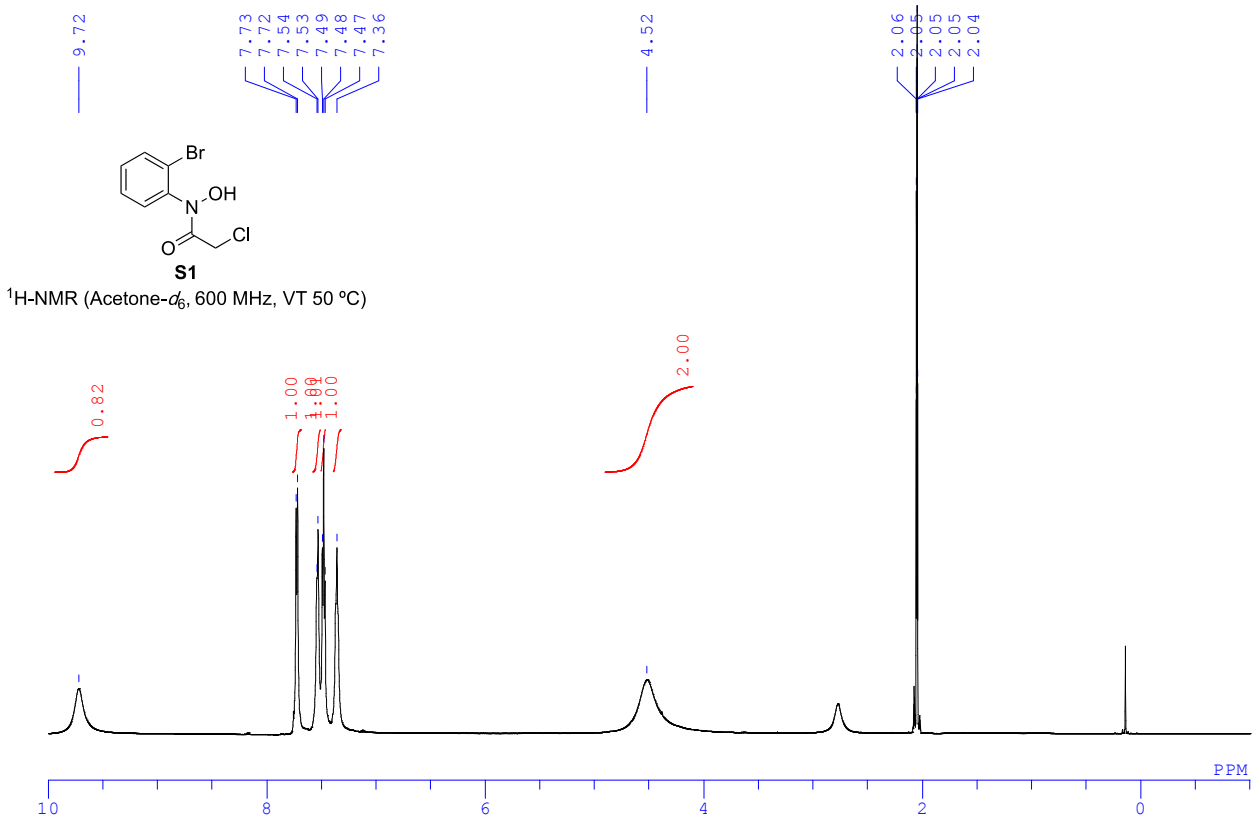
(2) von Kieseritzky, F.; Wang, Y.; Axelson, M. *Org. Process Res. Dev.* **2014**, *18*, 643–645.

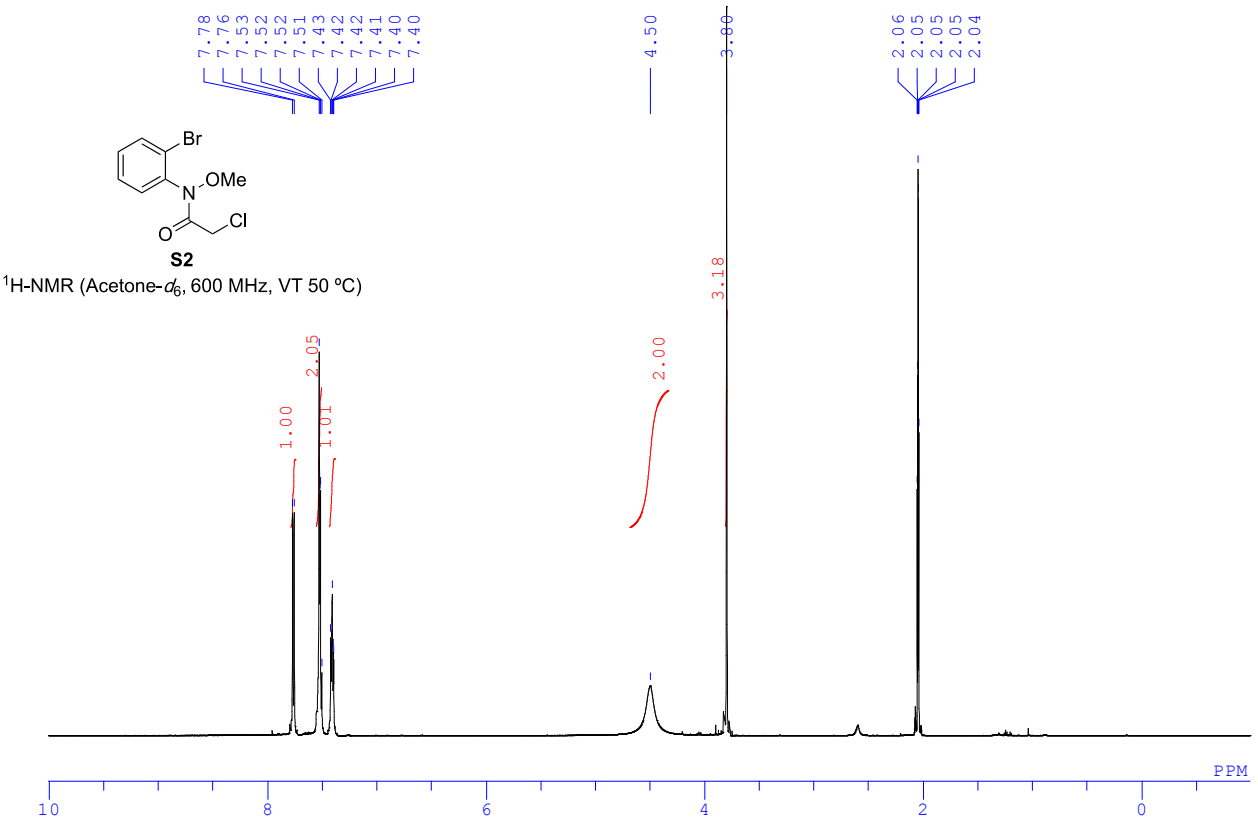
(3) Hekking, K. F. W.; Waalboer, D. C. J.; Moelands, M. A. H.; van Delft, F. L.; Rutjes, F. P. J. T. *Adv. Synth. Catal.* **2008**, *350*, 95–106.

(4) Wei, X.; Yang, J.; Ma, H. X.; Ding, C. F.; Yu, H. F.; Zhao, Y. L.; Liu, Y. P.; Khan, A.; Wang, Y. F.; Yang, Z. F.; Huang, W. Y.; Wang, X. H.; Luo, X. D. *Tetrahedron Lett.* **2018**, *59*, 2066–2070.

(5) Ouyang, S.; Wang, L.; Zhang, Q. W.; Wang, G. C.; Wang, Y.; Huang, X. J.; Zhang, X. Q.; Jiang, R. W.; Yao, X. S.; Che, C. T.; Ye, W. C. *Tetrahedron* **2011**, *67*, 4807–4813.

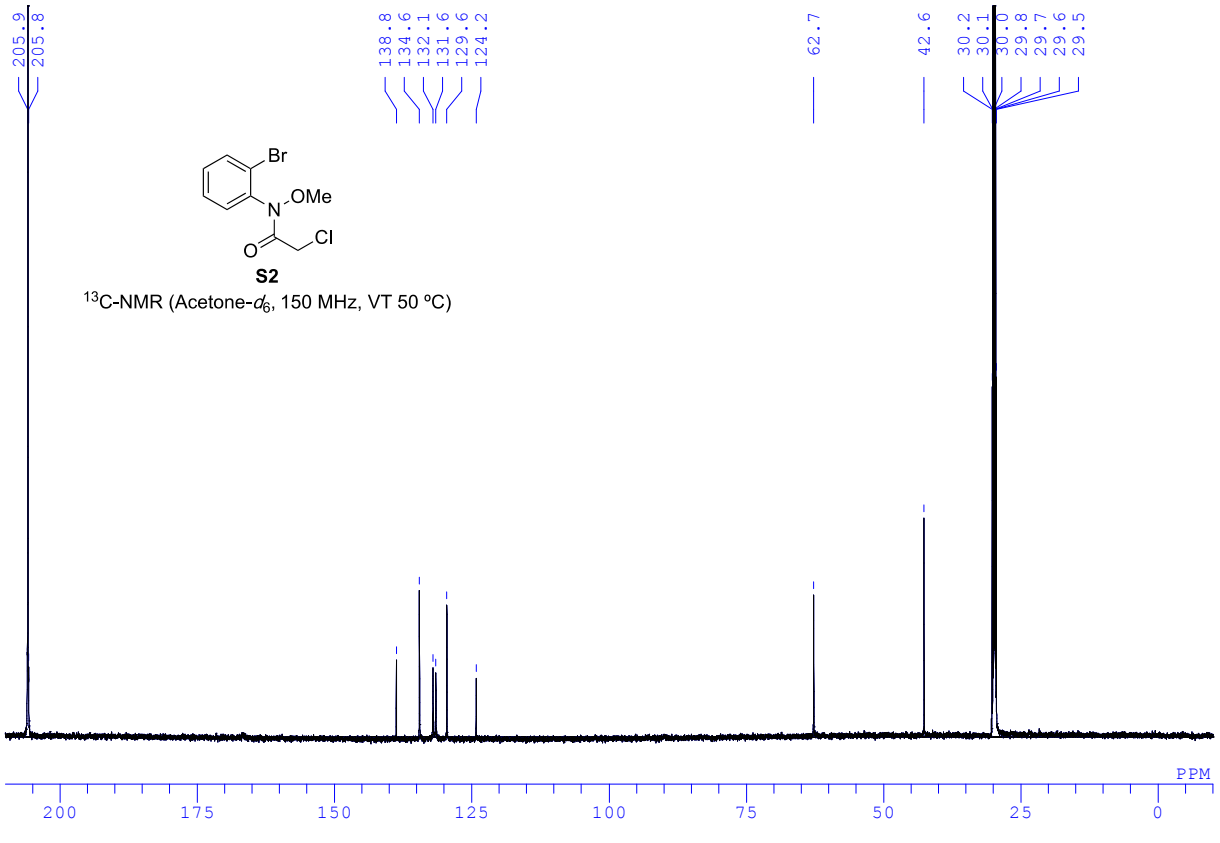

## $^{1}$H and $^{13}$C NMR Data for All New Compounds





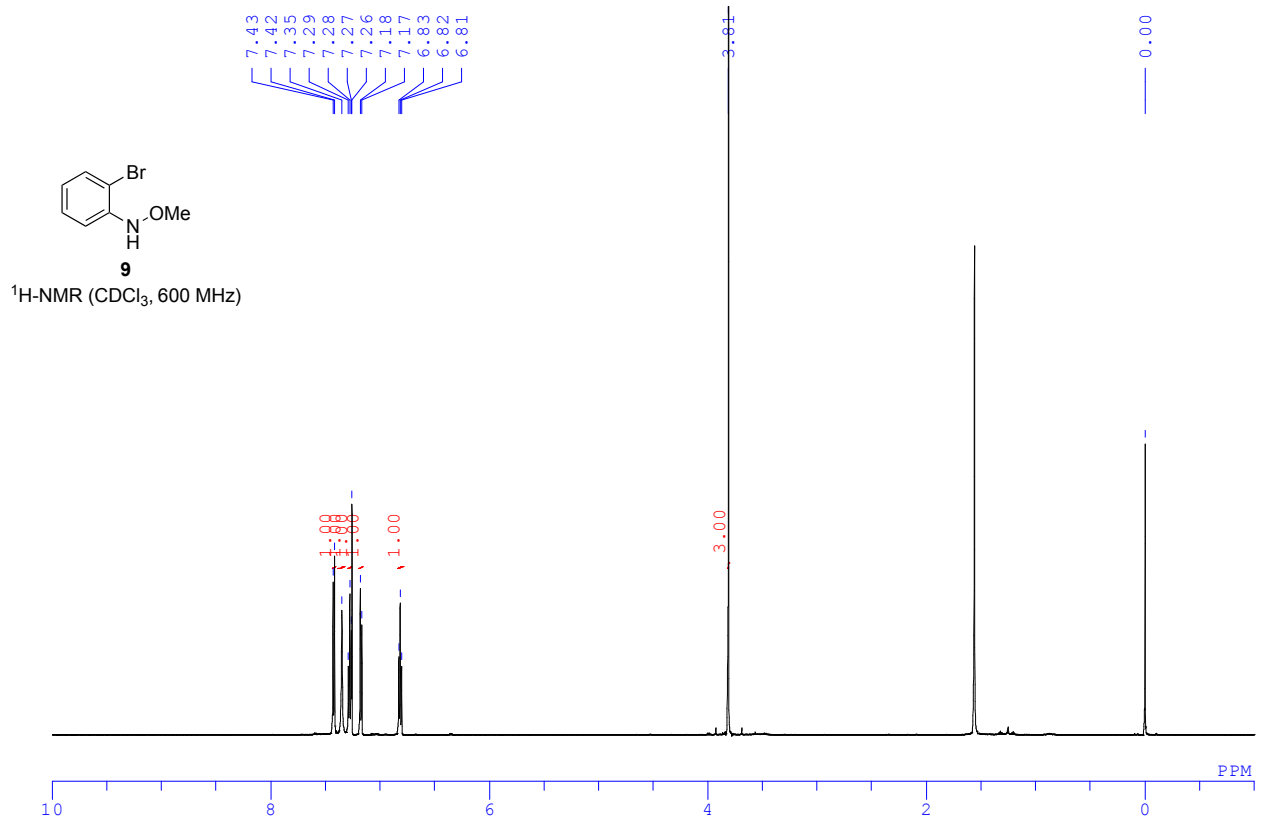

**S2**

$^{1}$H-NMR (Acetone-$d_6$, 600 MHz, VT 50 ºC)



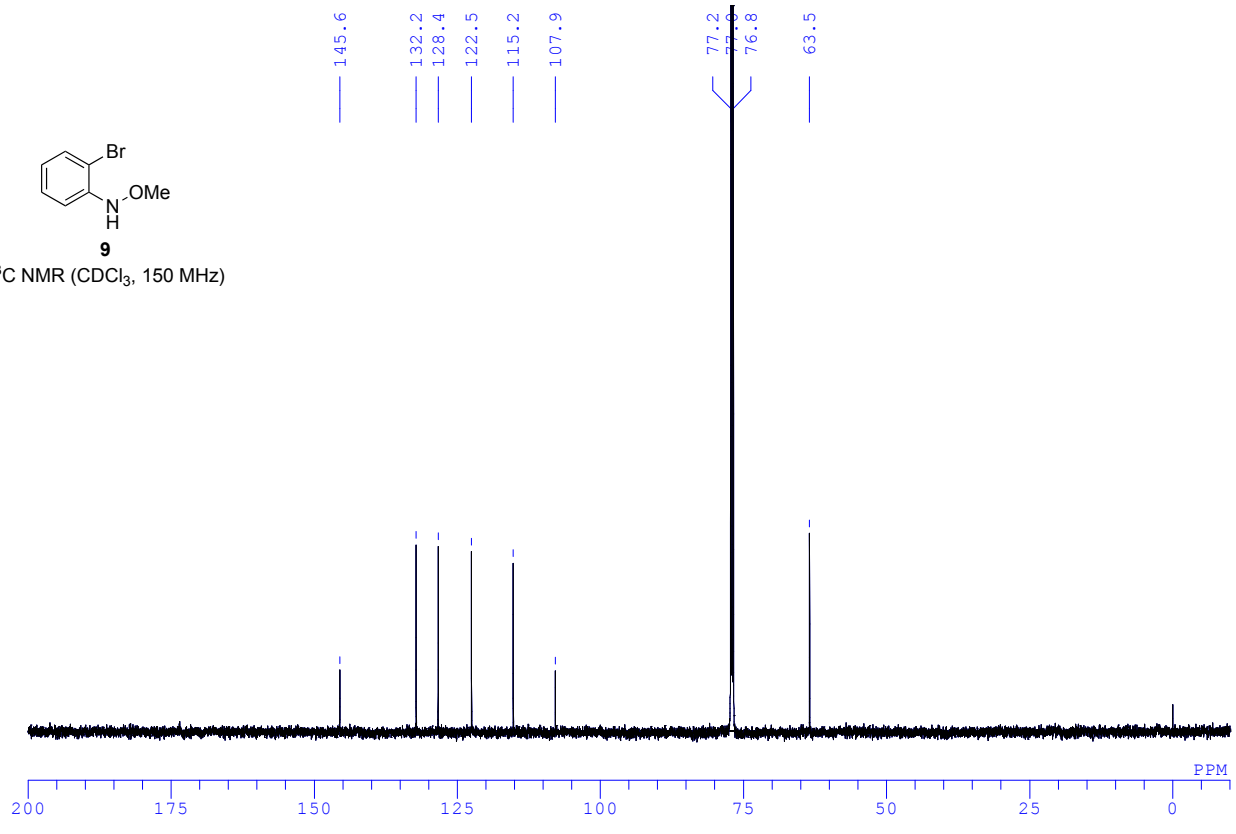

**S2**

$^{13}$C-NMR (Acetone-$d_6$, 150 MHz, VT 50 ºC)



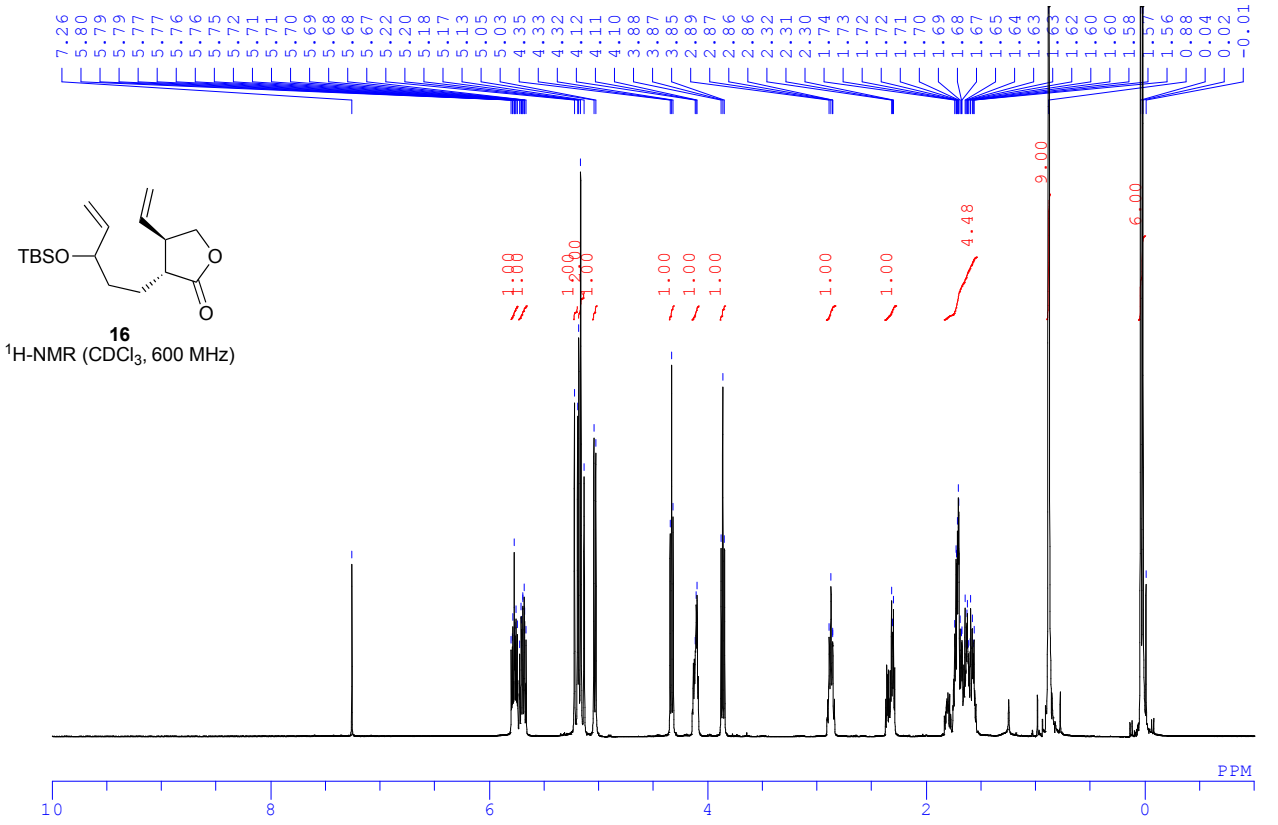

**9**

$^{1}$H-NMR ($CDCl_3$, 600 MHz)




**9**

$^{13}$C NMR ($CDCl_3$, 150 MHz)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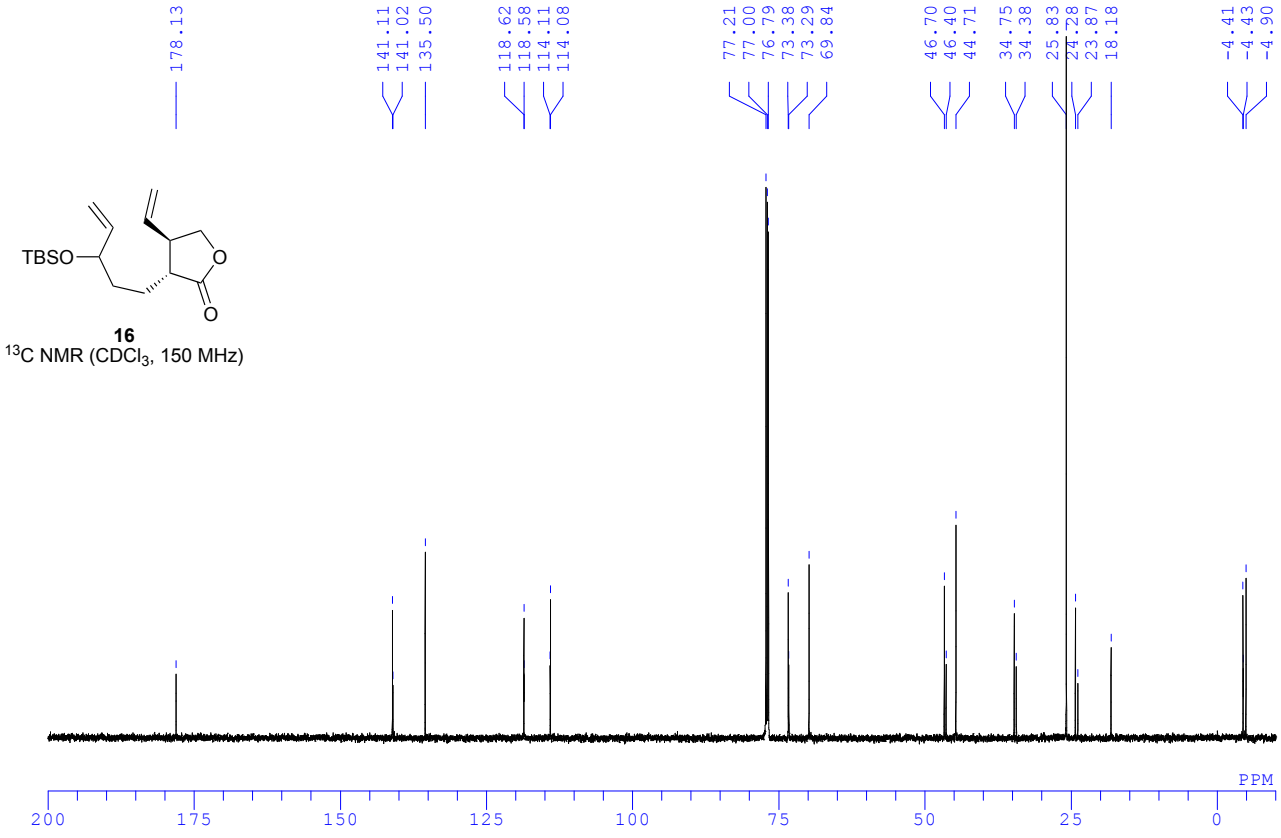
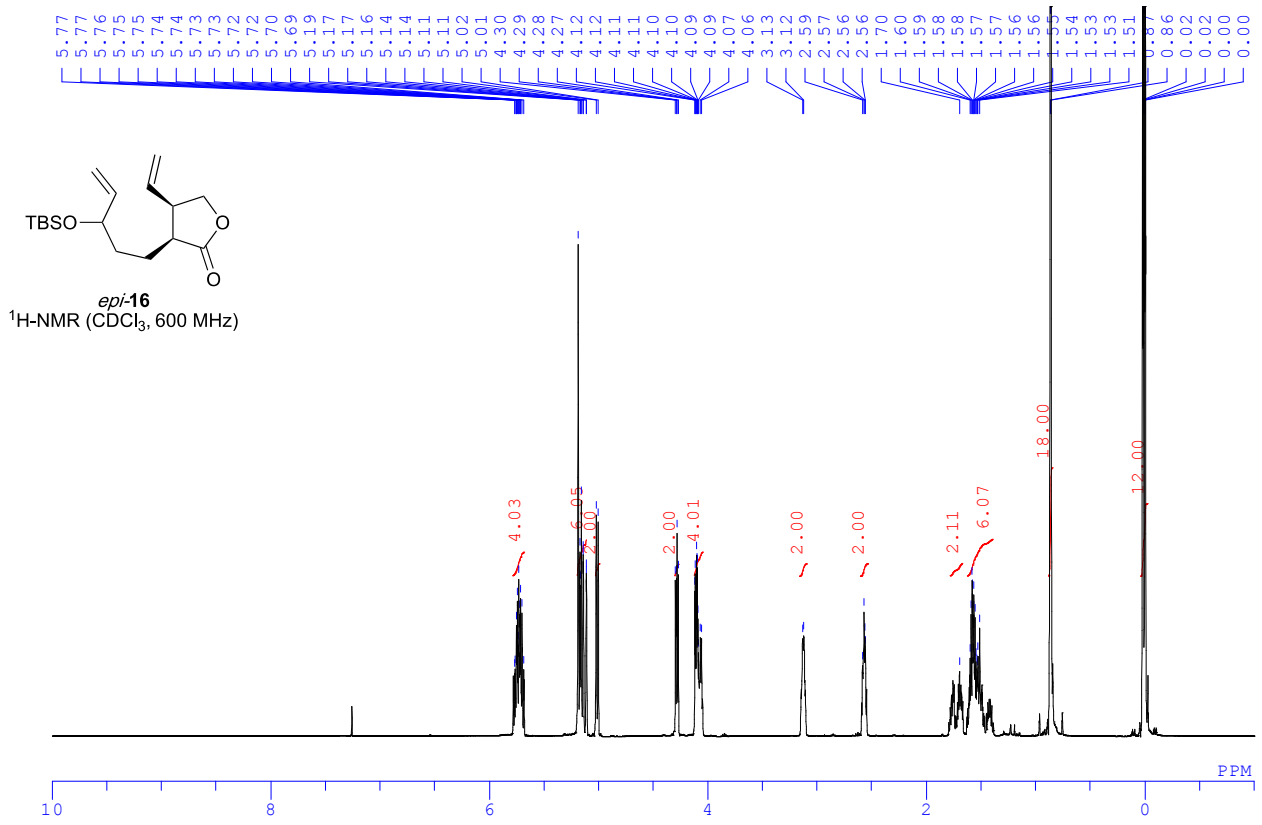
O
O
16
1H-NMR (CDCl3, 600 MHz)
PPM


TBSO
O
O
16
13C NMR (CDCl3, 150 MHz)
PPM

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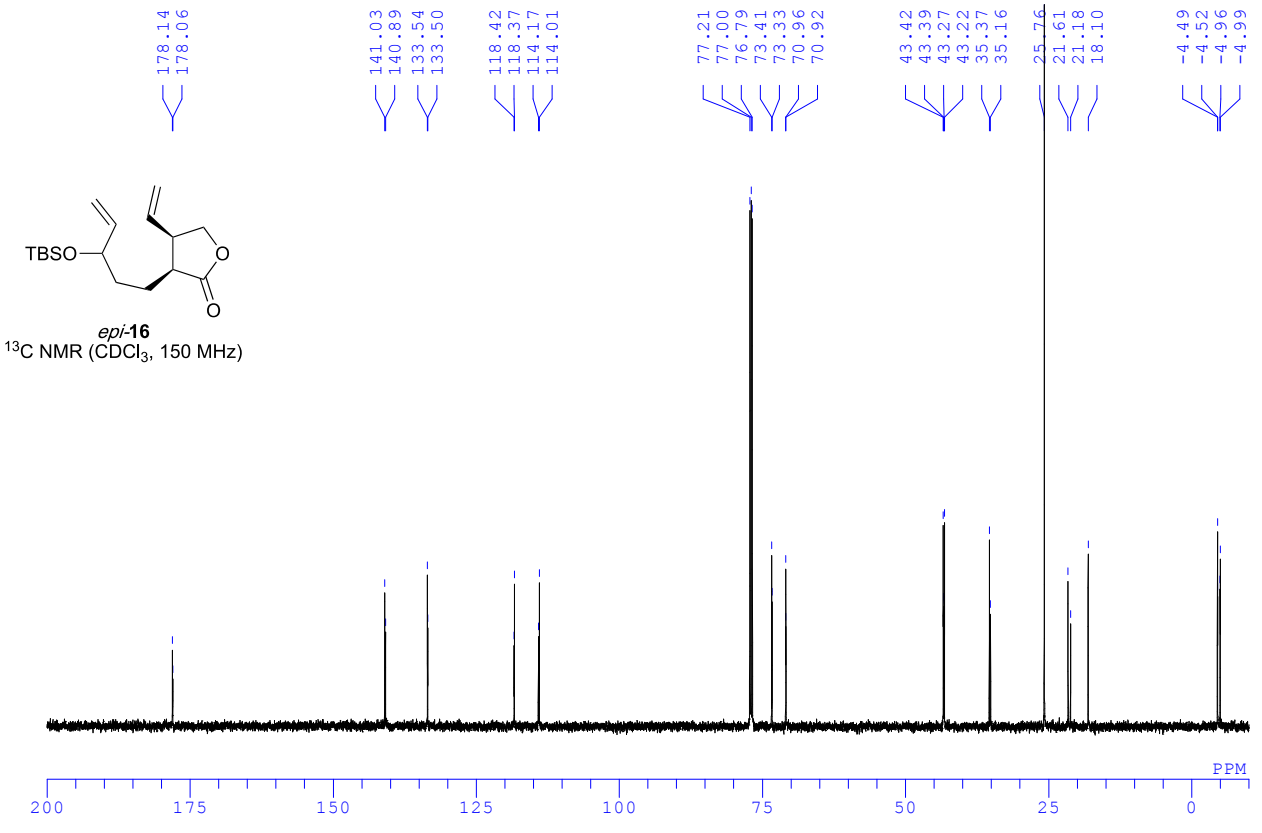


*epi*-**16**
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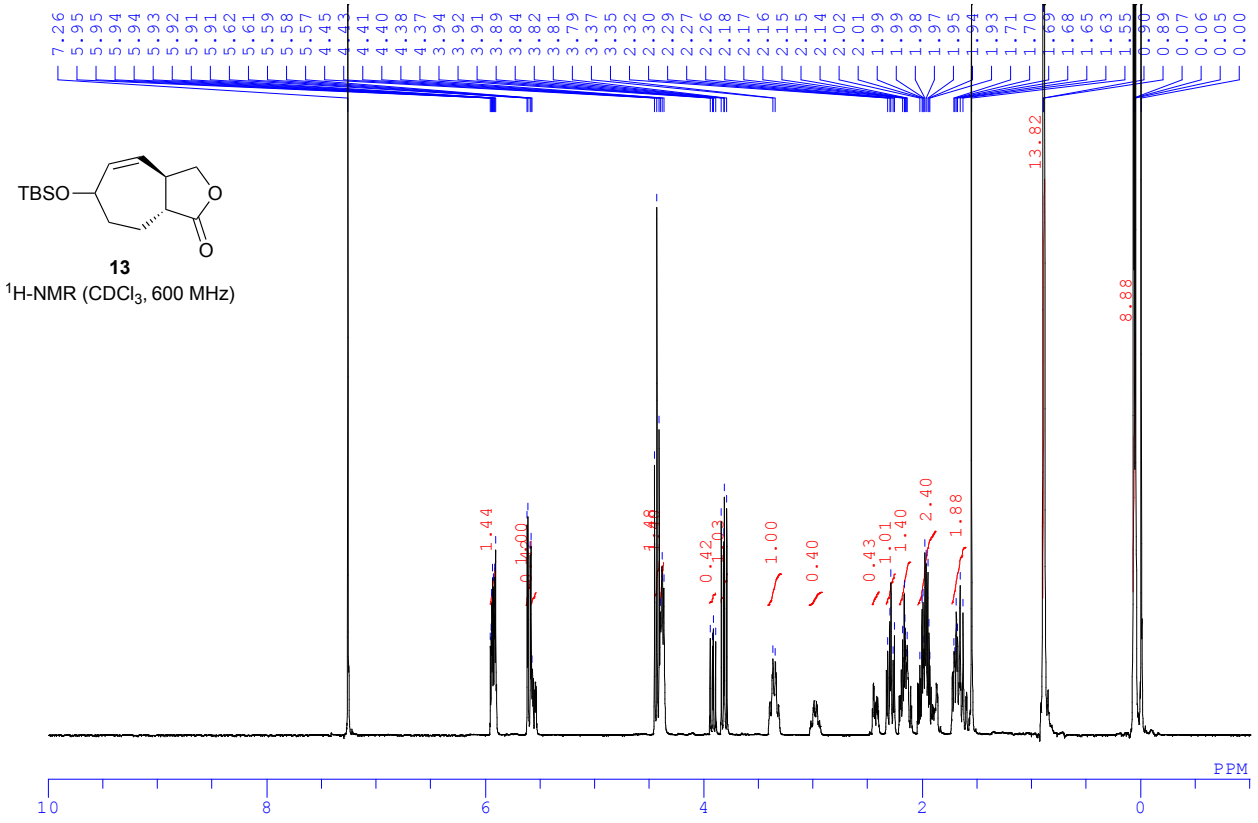
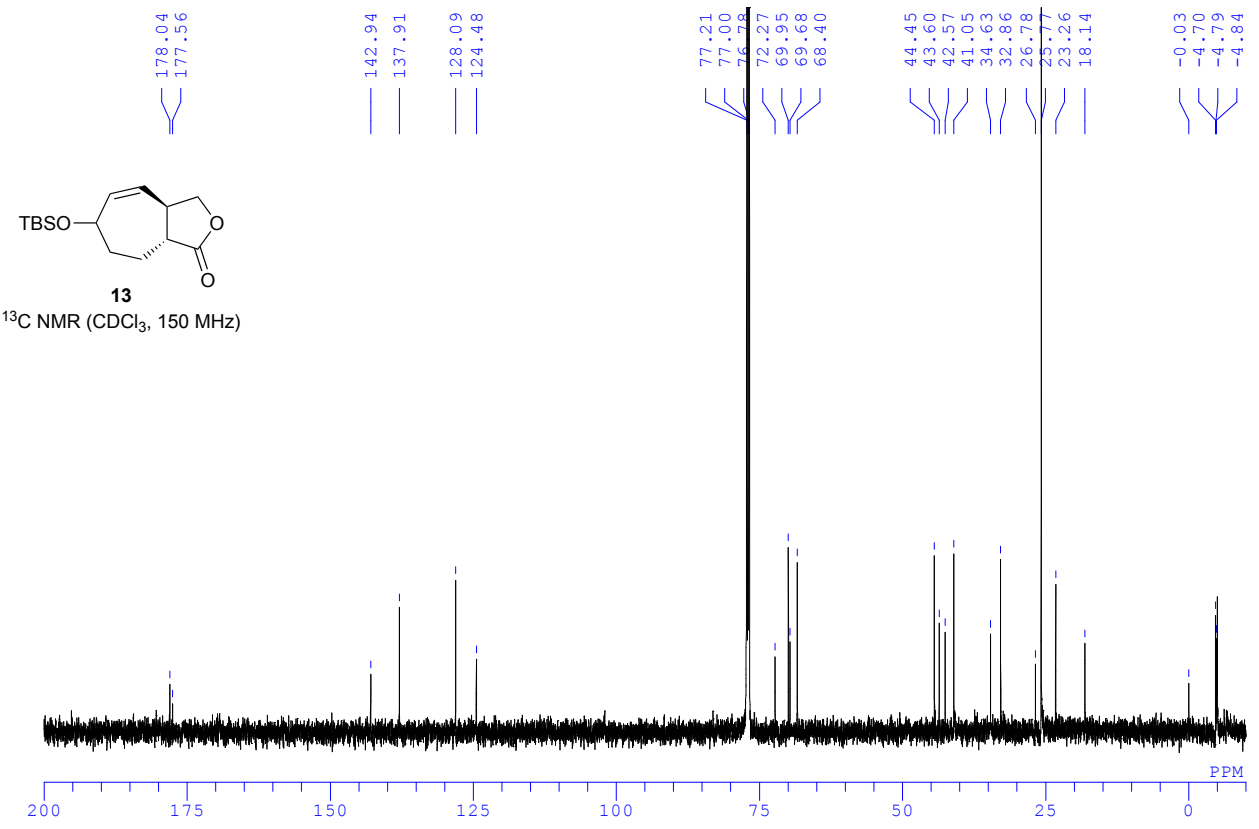
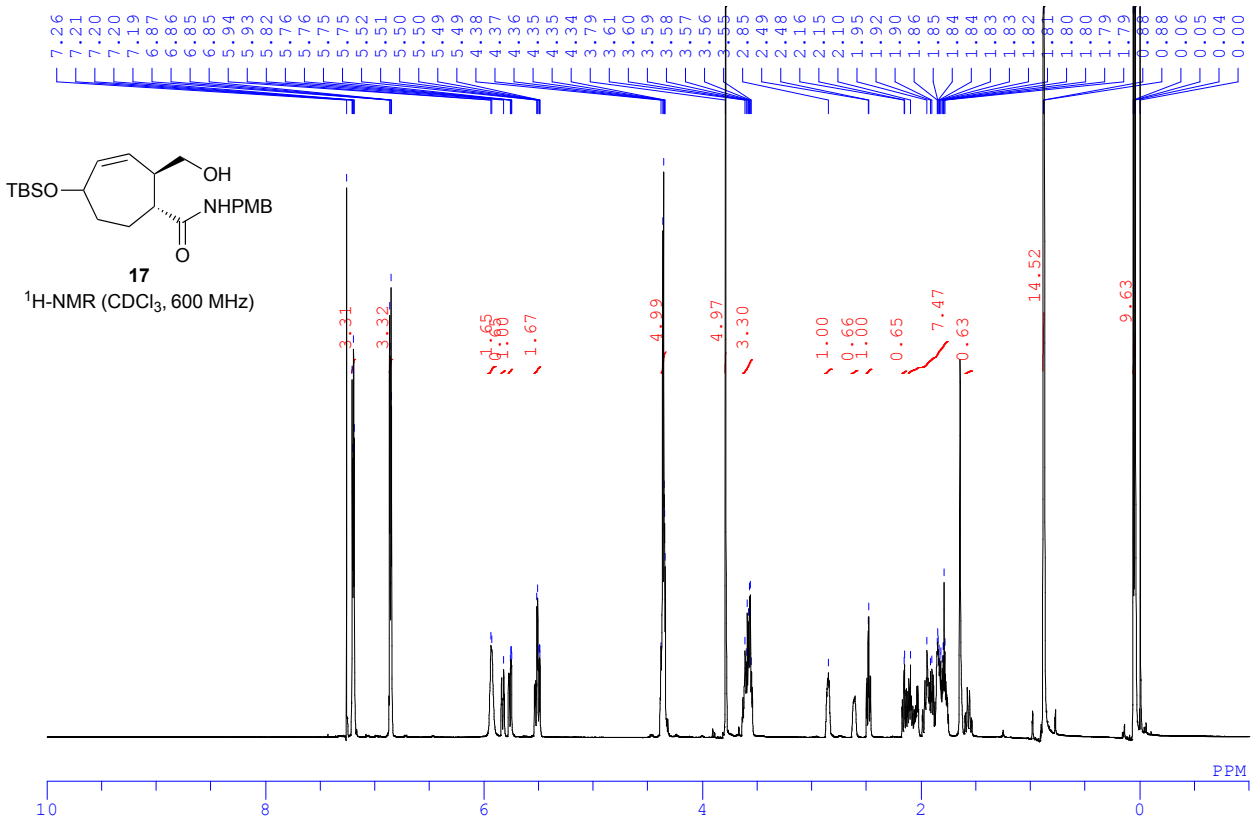

TBSO
O
O
13
1H-NMR (CDCl3, 600 MHz)
PPM


TBSO
O
O
13
13C NMR (CDCl3, 150 MHz)
PPM


TBSO
OH
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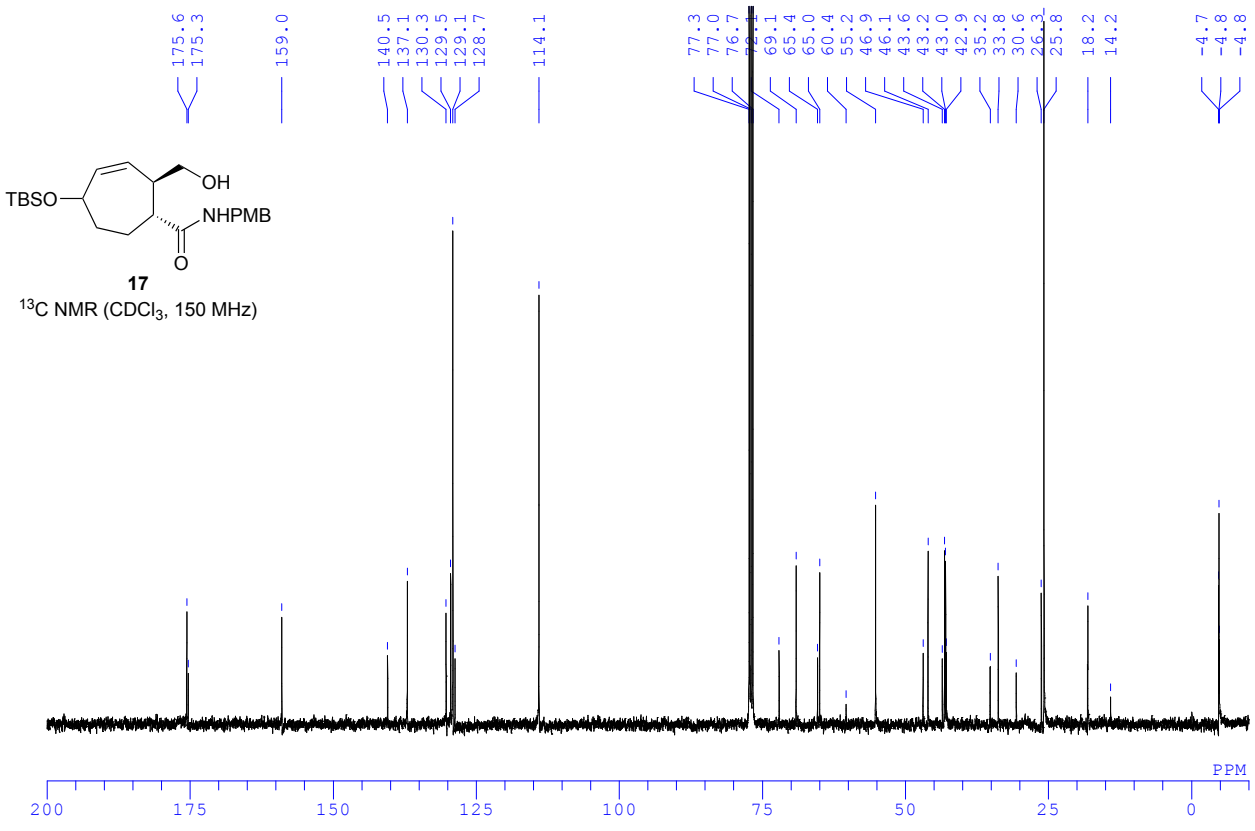
O
17
1H-NMR (CDCl3, 600 MHz)
PPM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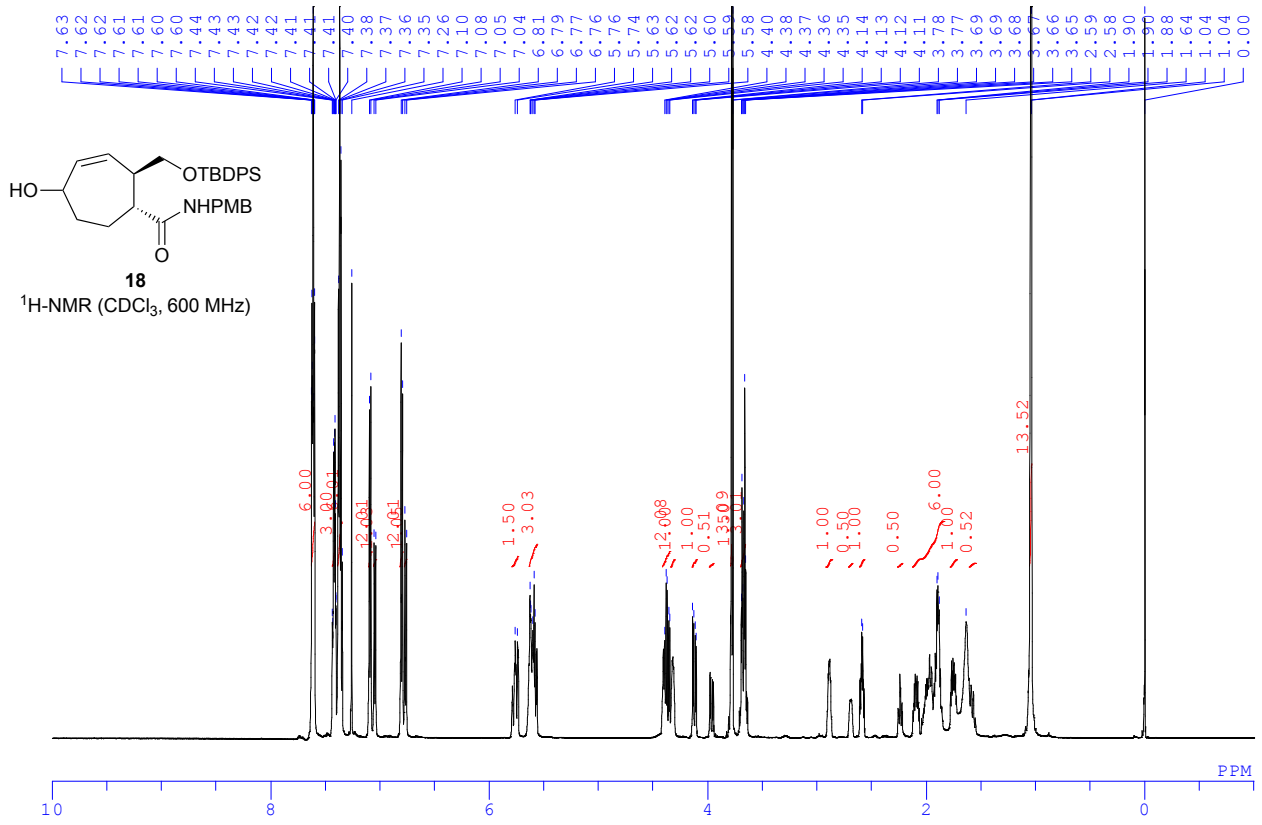
O
17
13C NMR (CDCl3, 150 MHz)
PPM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OTBDPS
NHPMB
O
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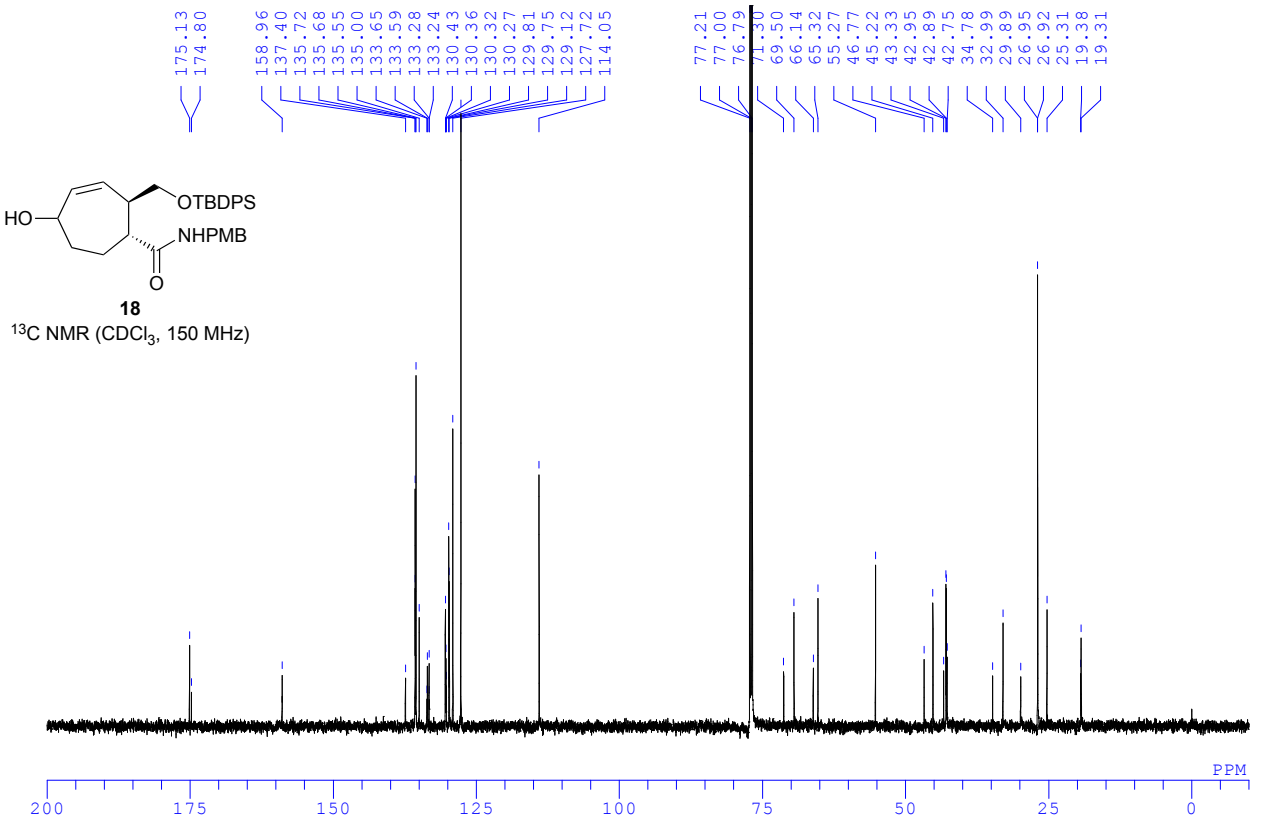
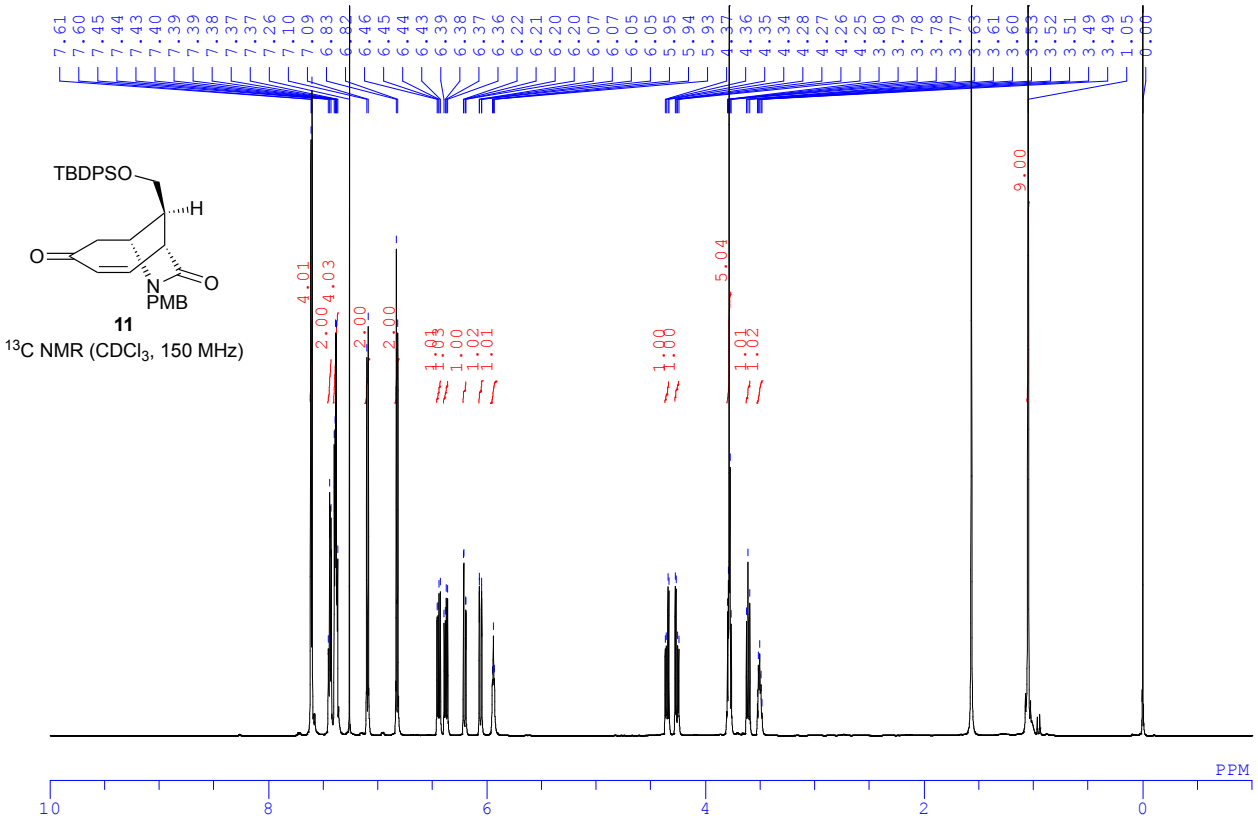
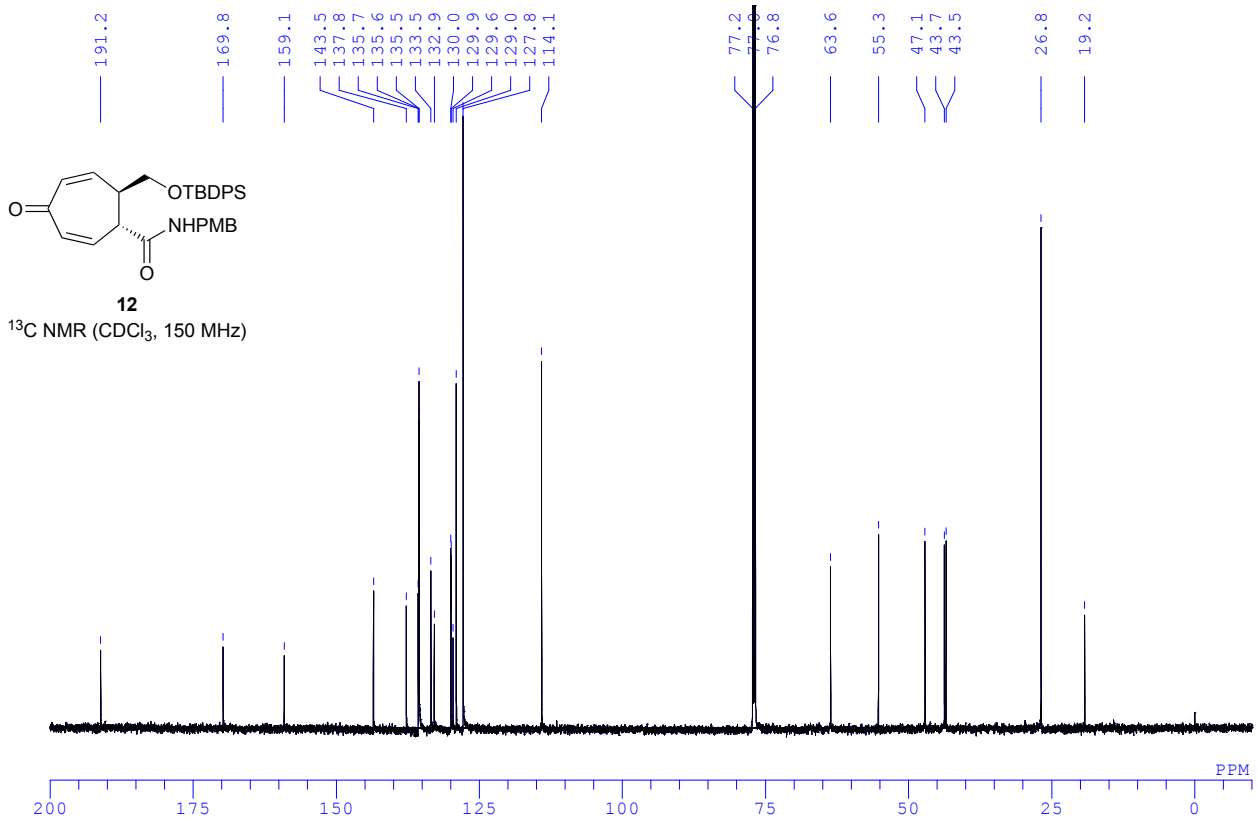
PPM


HO
OTBDPS
NHPMB
O
18
13C NMR (CDCl3, 150 MHz)
PPM



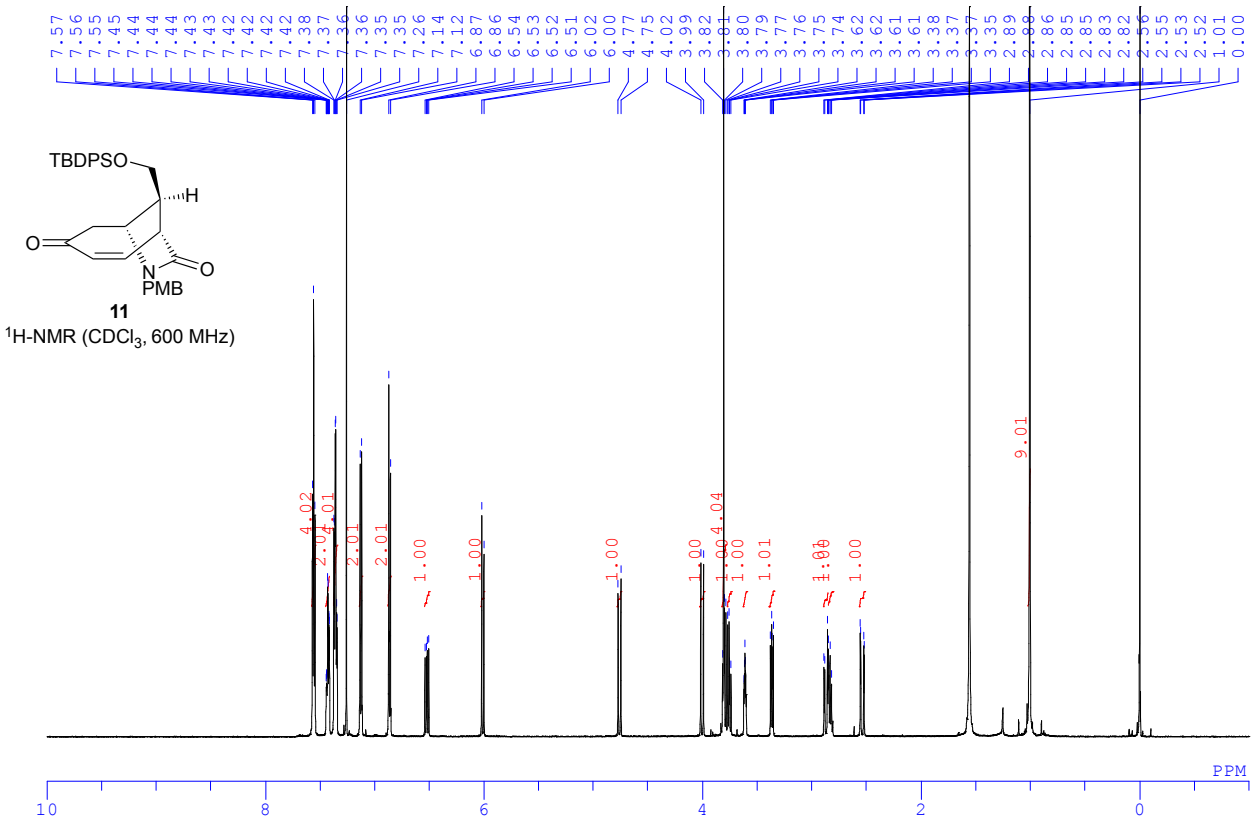

**11**

$^{13}$C NMR ($CDCl_3$, 150 MHz)




**12**

$^{13}$C NMR ($CDCl_3$, 150 MHz)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O
N
O
PMB
11
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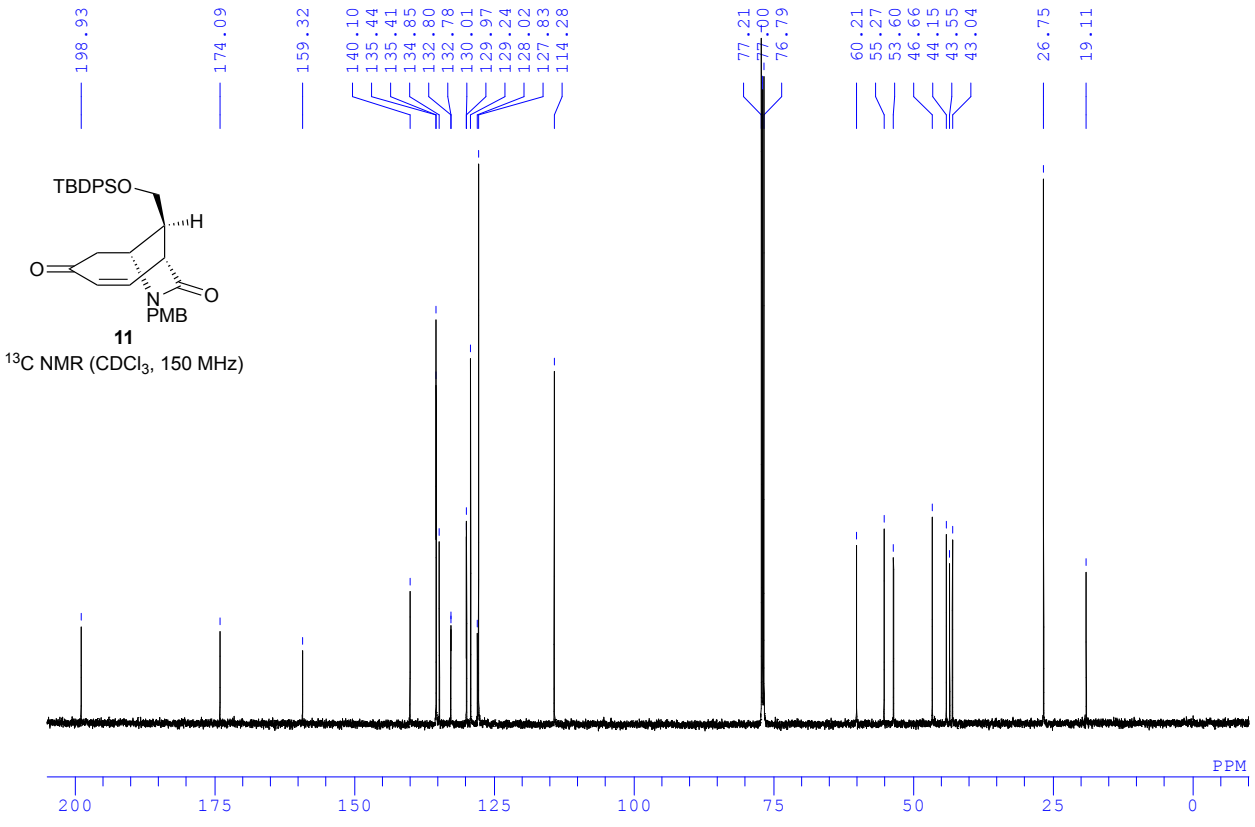
PPM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O
N
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11
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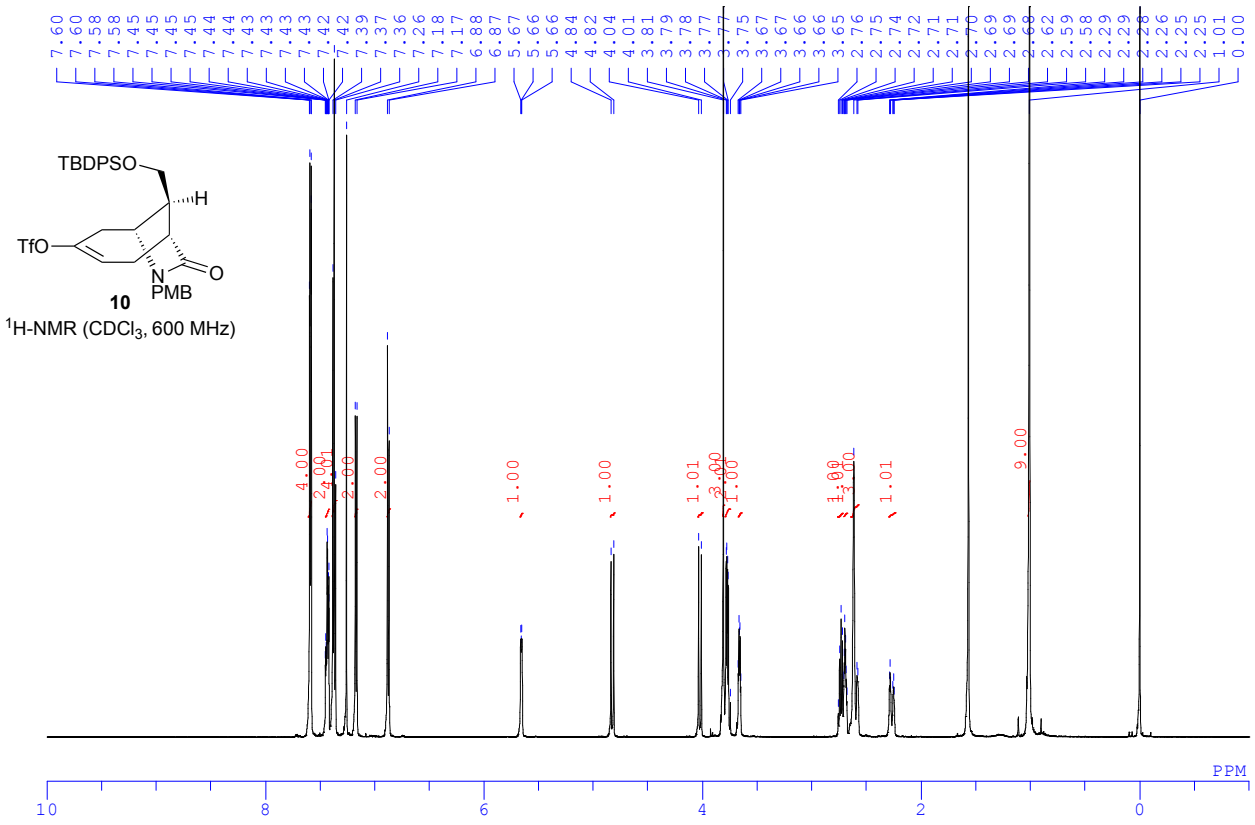
PPM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H
TfO
N
O
PMB
10
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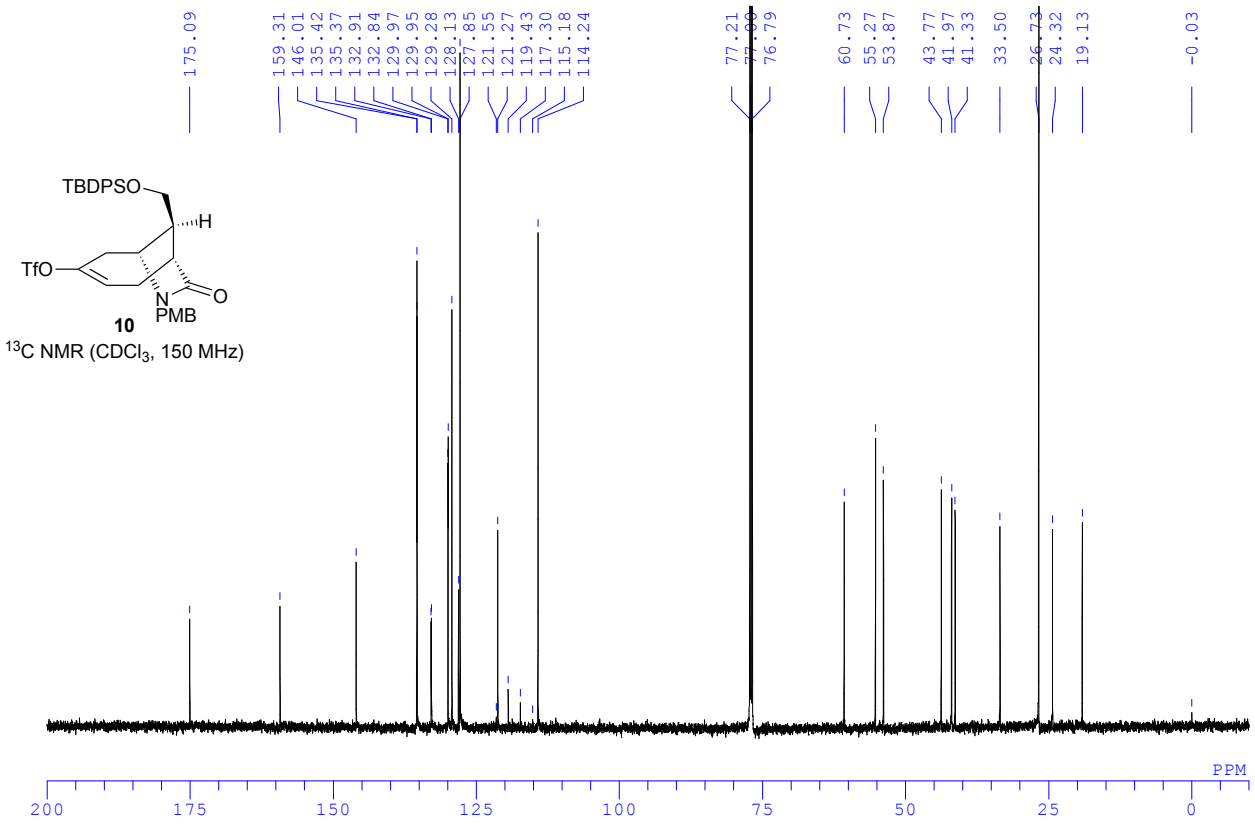
PPM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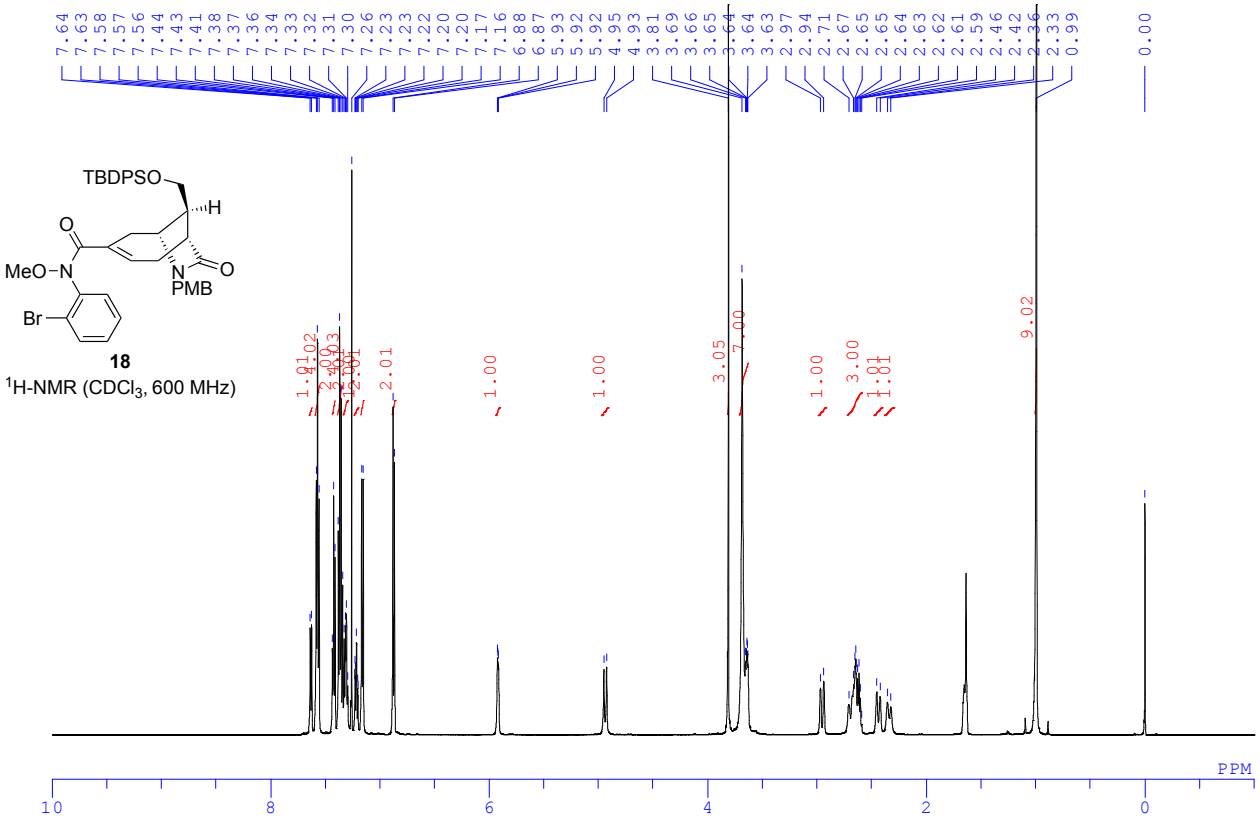
TfO
N
O
PMB
10
$^{13}$C NMR (CDCl$_3$, 150 MHz)
PPM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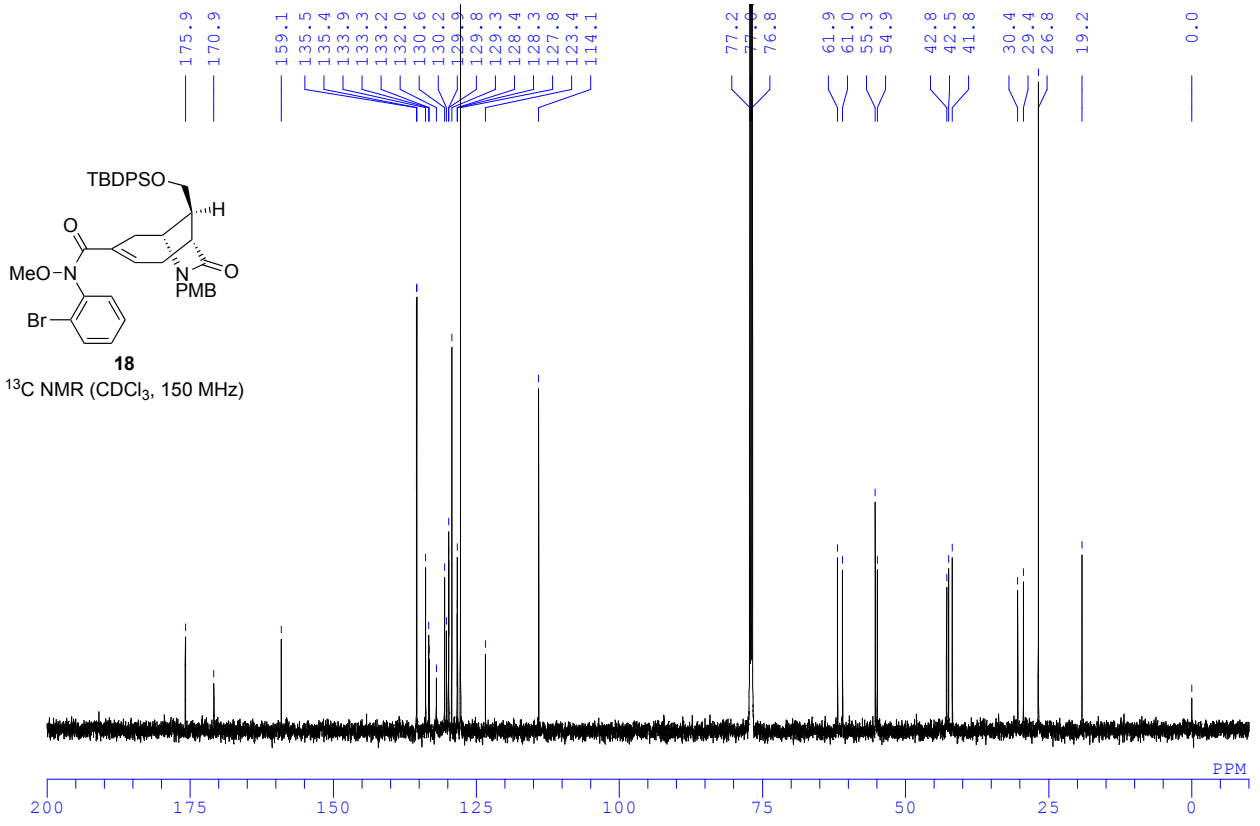
Br
18
1H-NMR (CDCl3, 600 MHz)
PPM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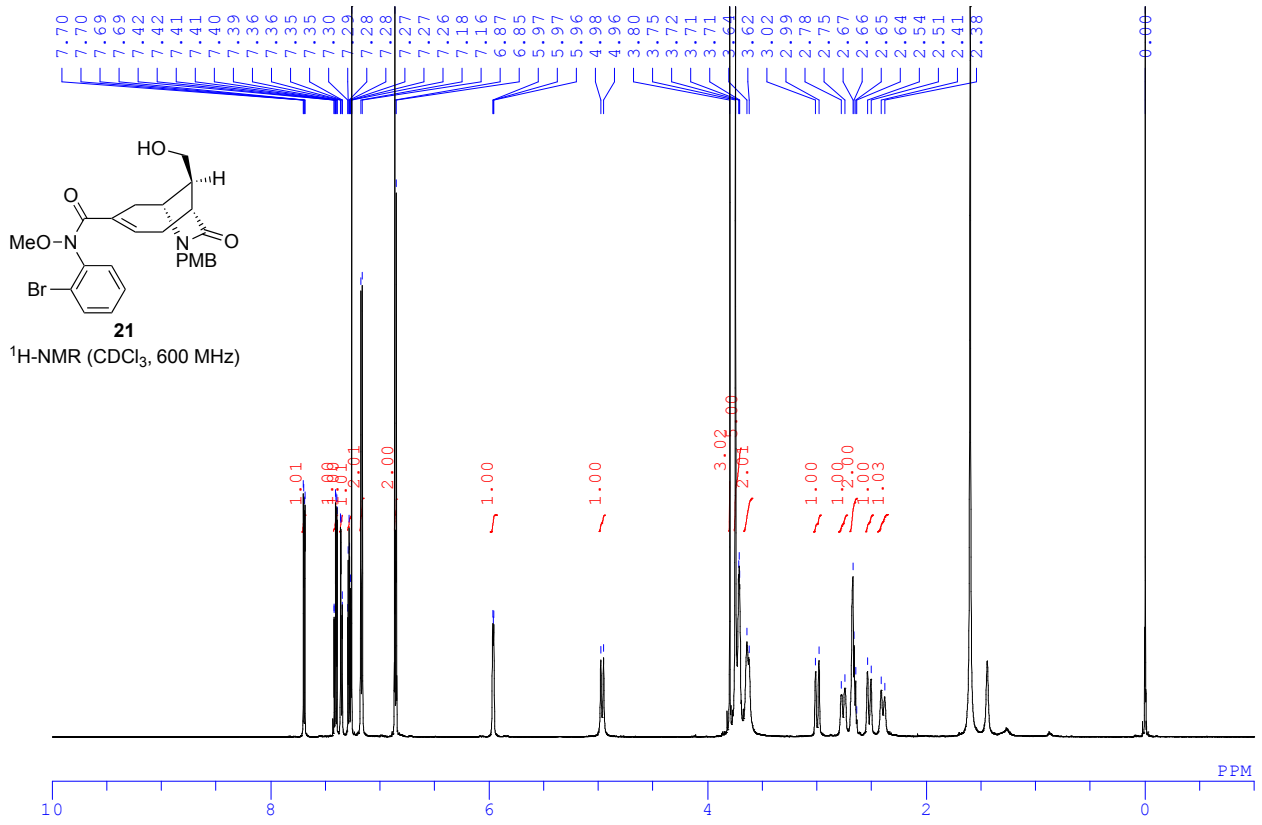
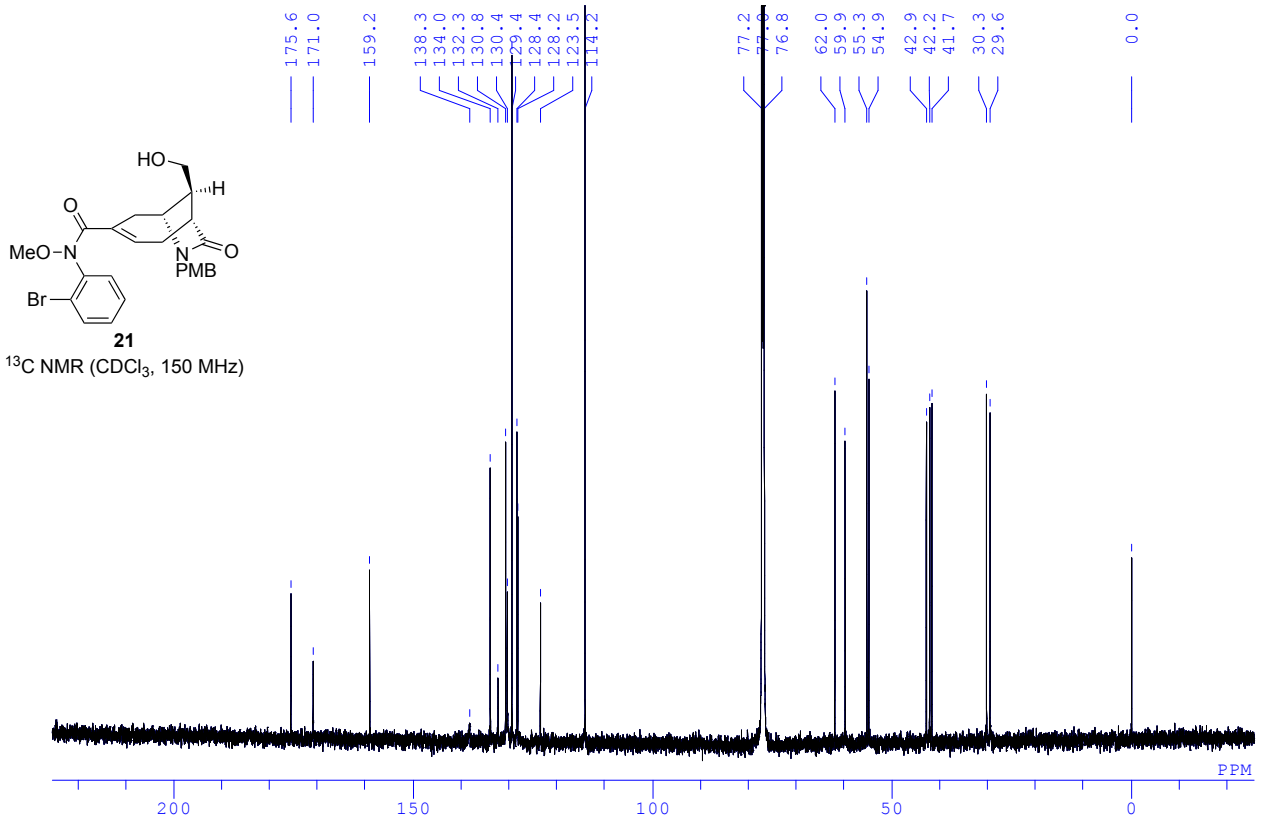
O
PMB
Br
18
13C NMR (CDCl3, 150 MHz)
PPM



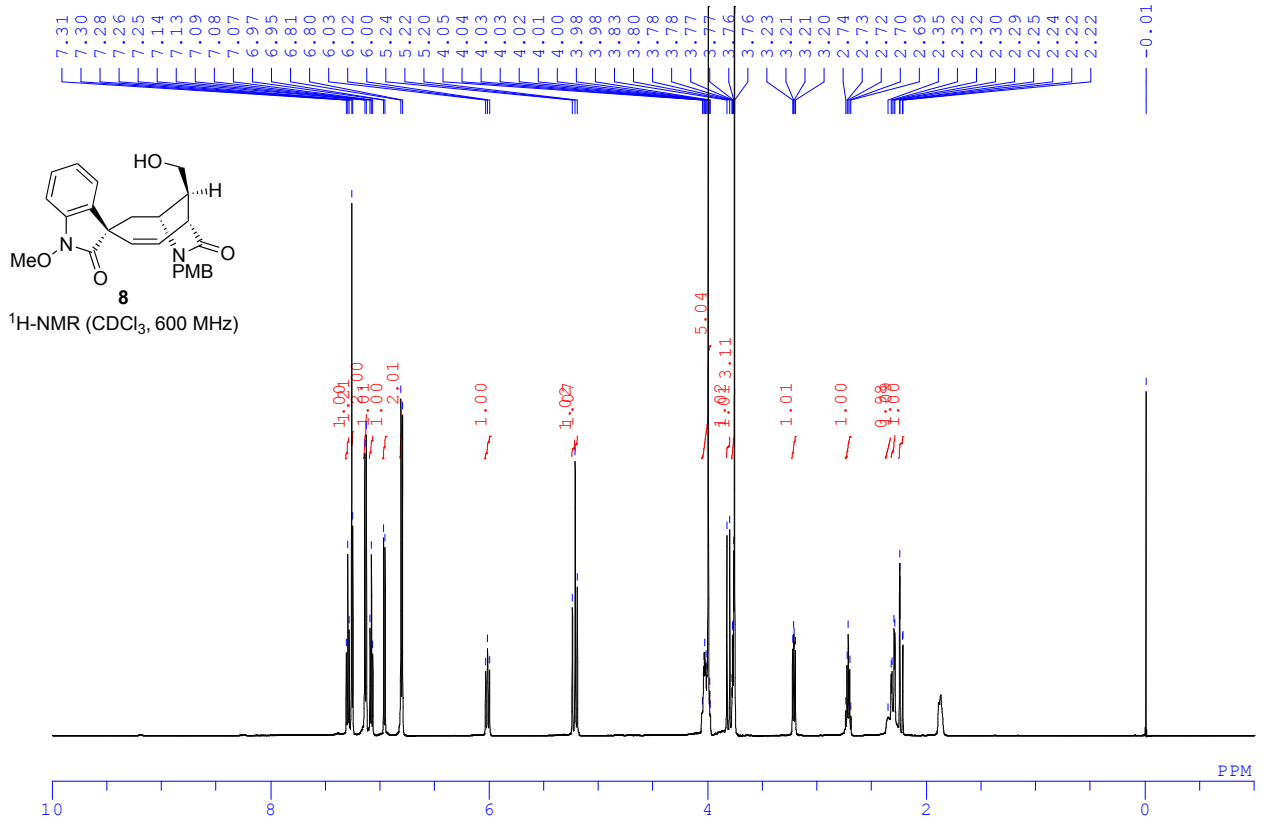

**21**

$^{1}$H-NMR ($CDCl_3$, 600 MHz)

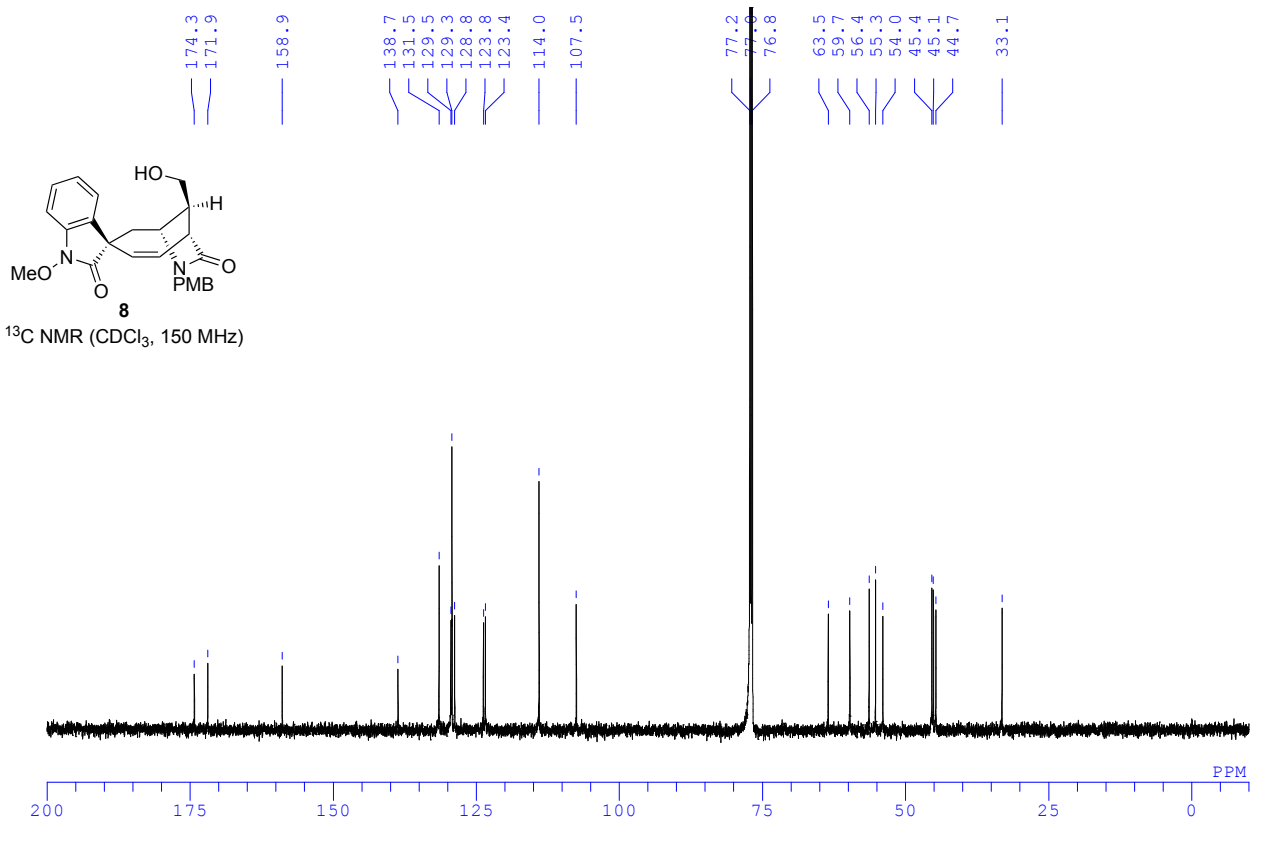



**21**

$^{13}$C NMR ($CDCl_3$, 150 MHz)




$^{1}$H-NMR ($CDCl_3$, 600 MHz)

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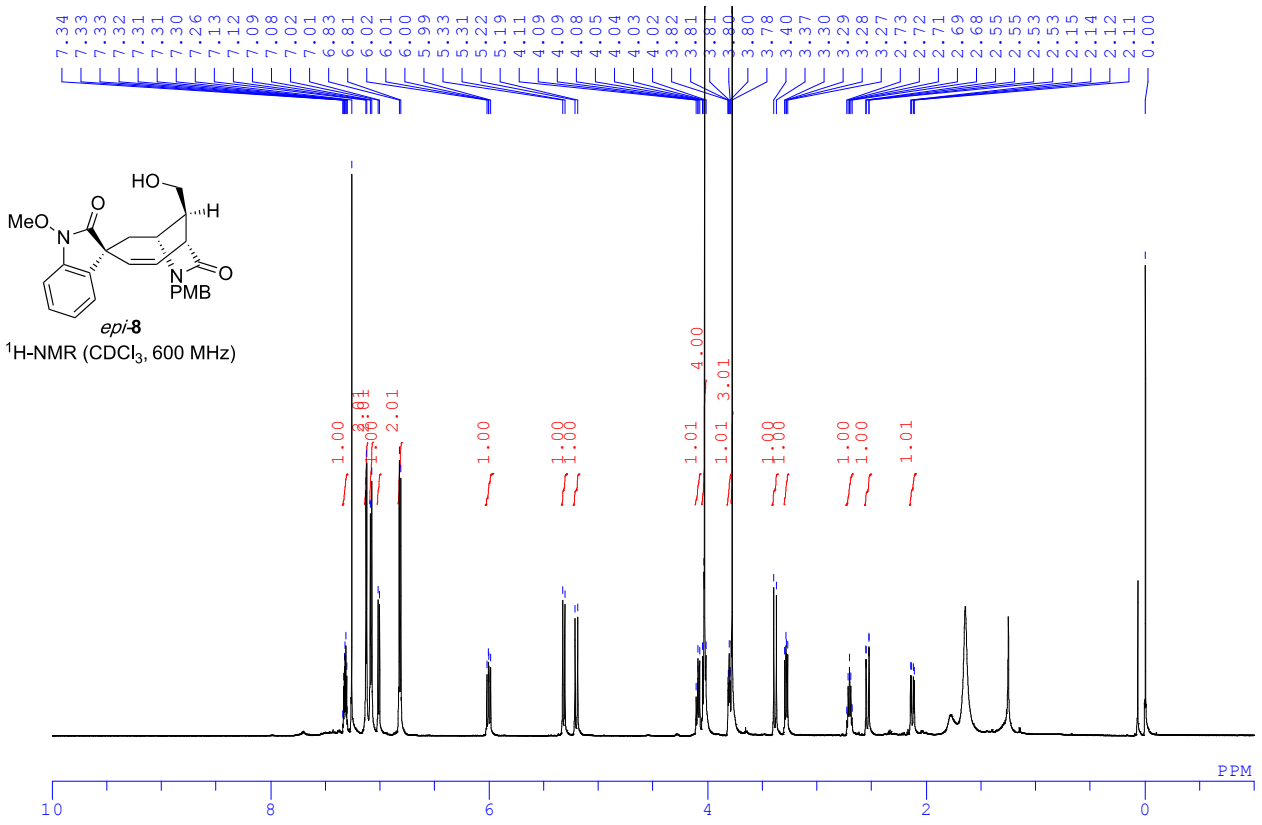
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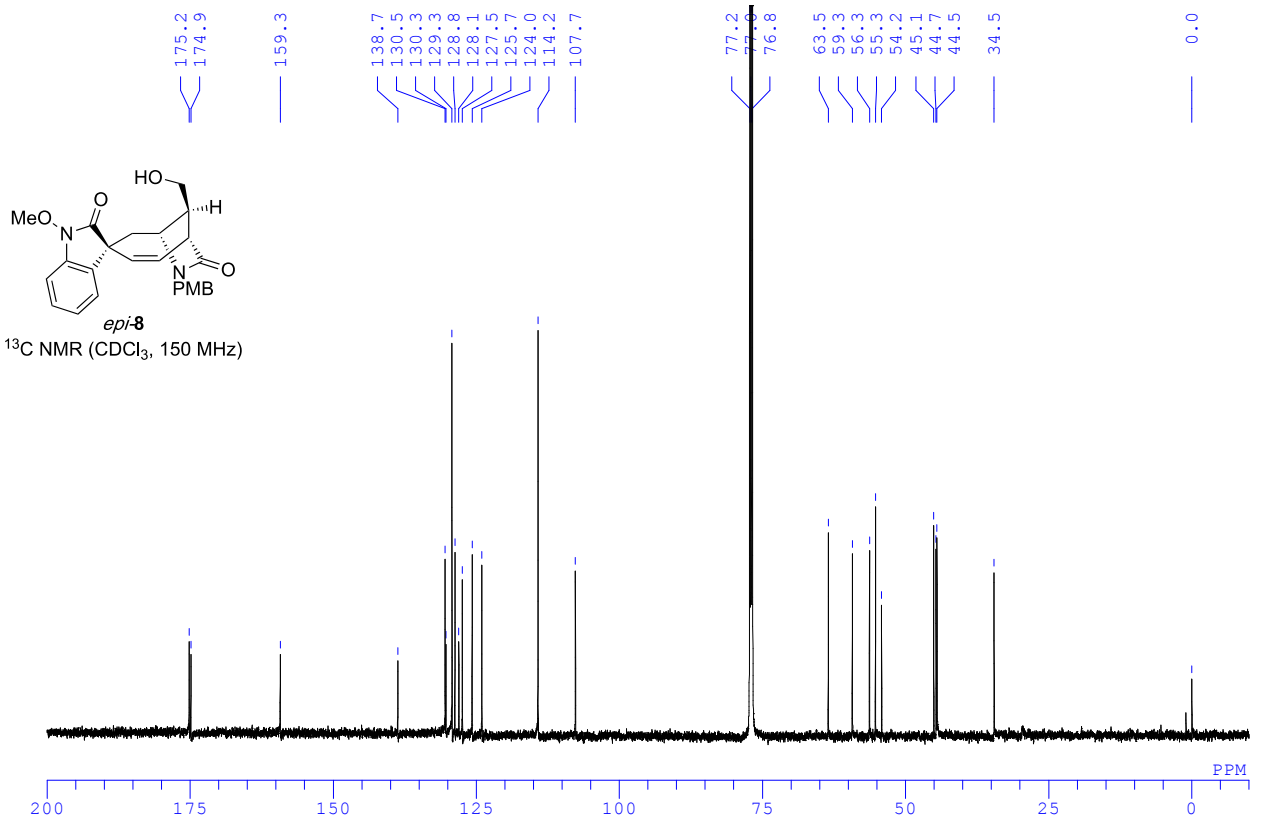
PPM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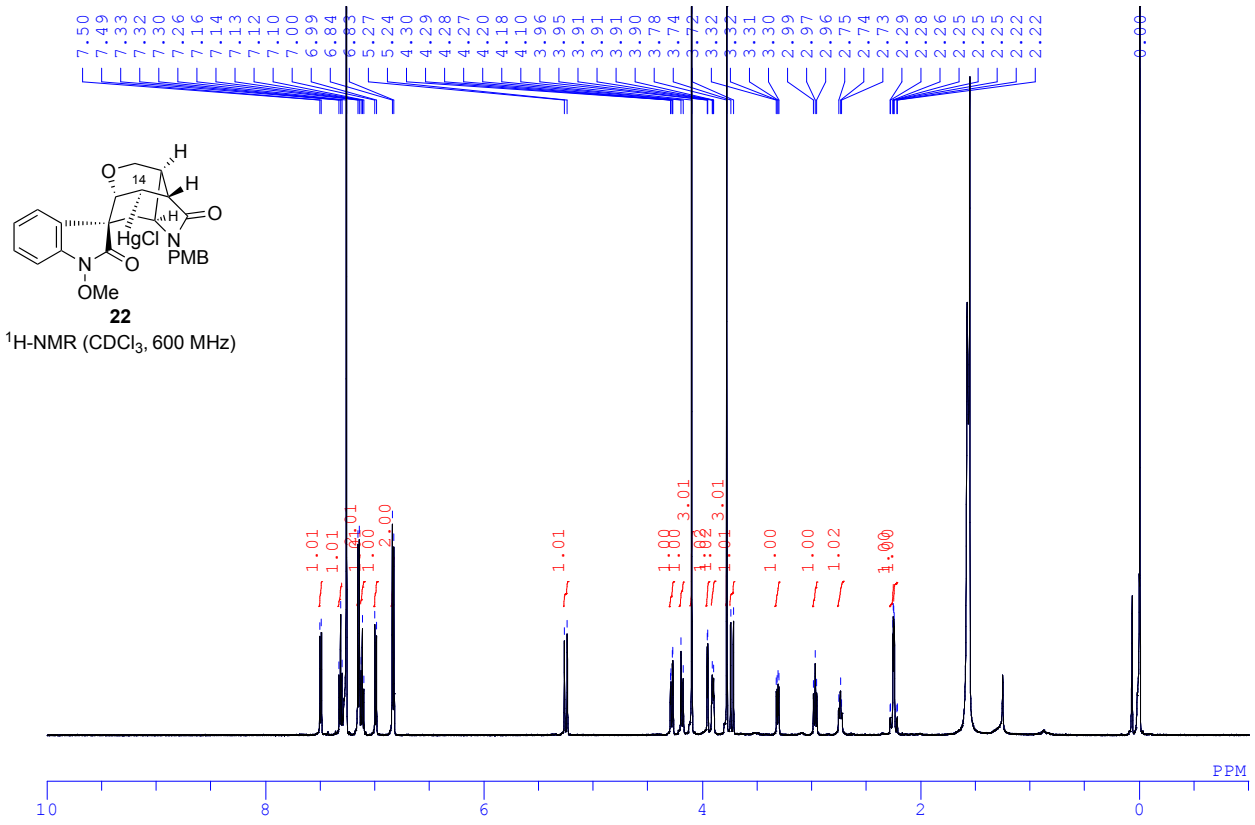
epi-8
13C NMR (CDCl3, 150 MHz)
PPM

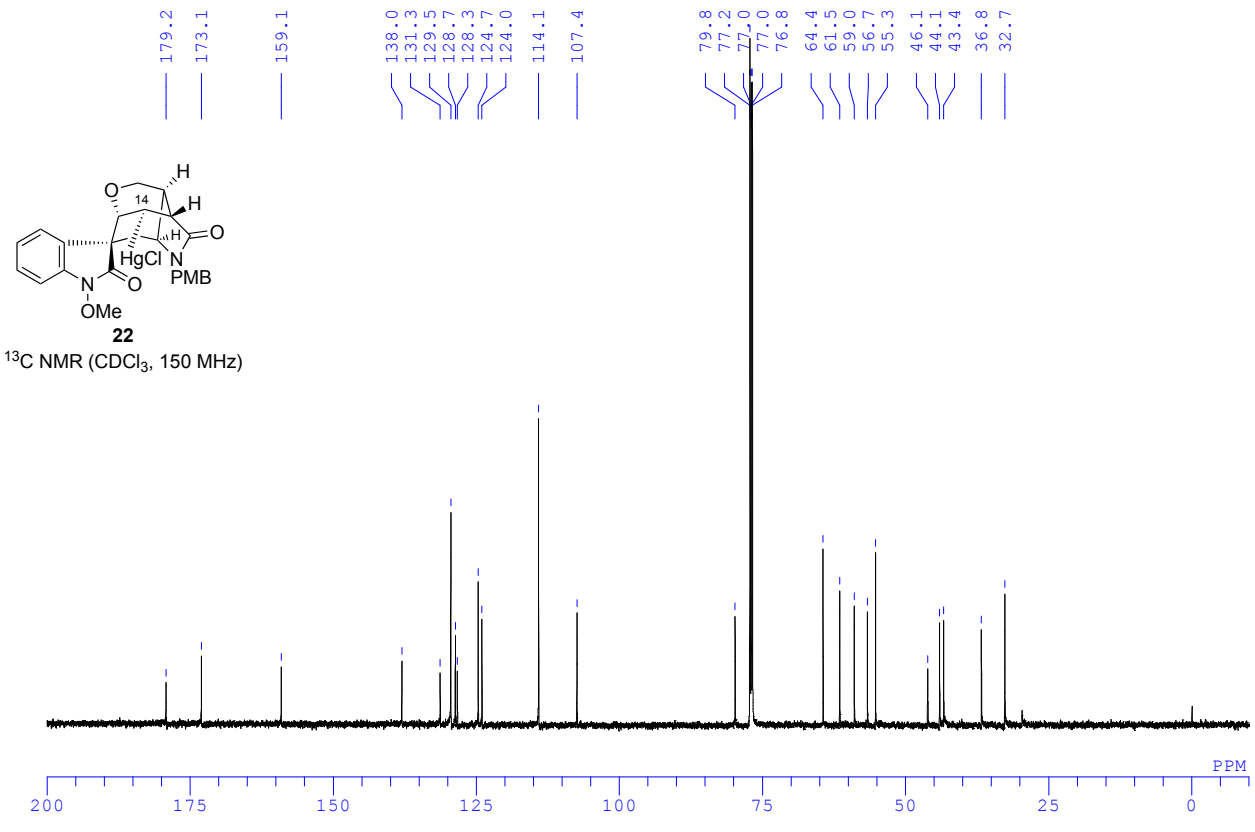






**22**

$^{1}$H-NMR ($CDCl_3$, 600 MHz)

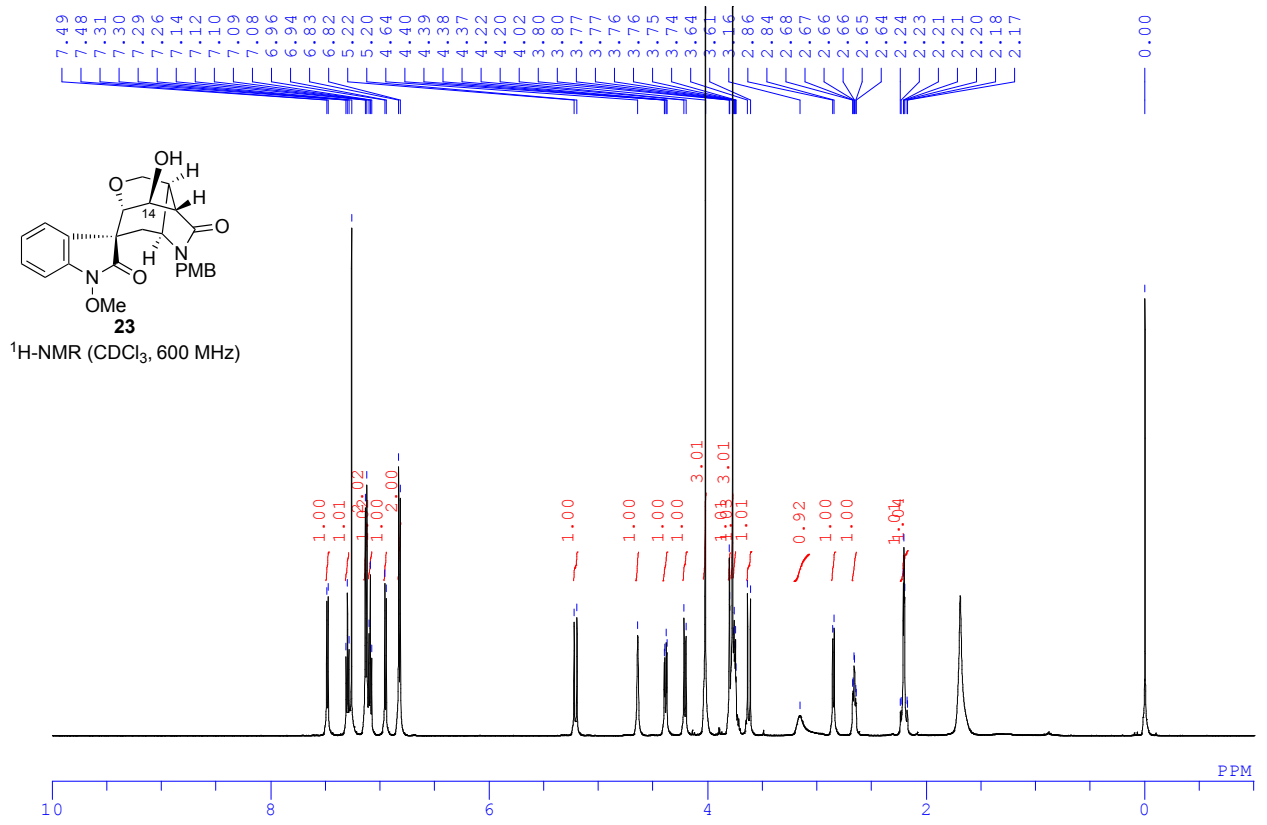




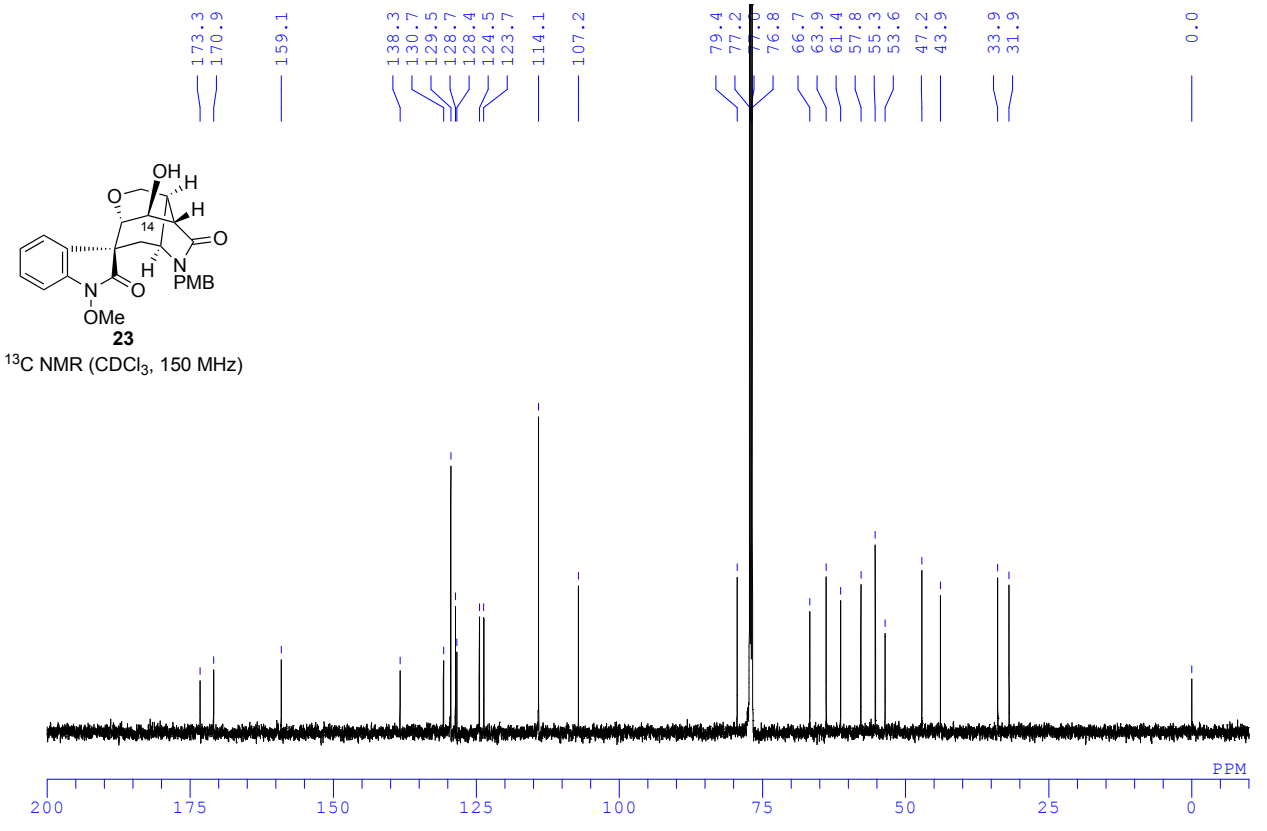


**22**

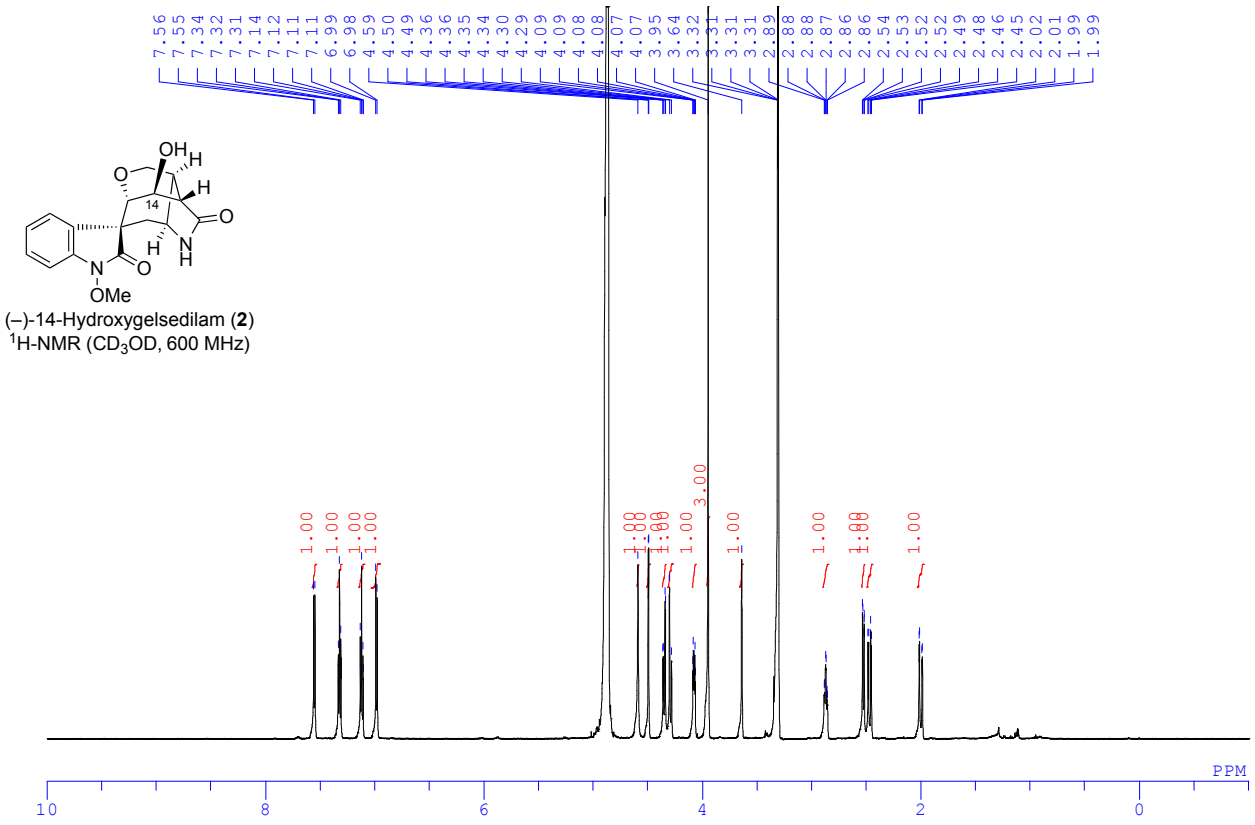
$^{13}$C NMR ($CDCl_3$, 150 MHz)




$^{1}$H-NMR ($CDCl_3$, 600 MHz)



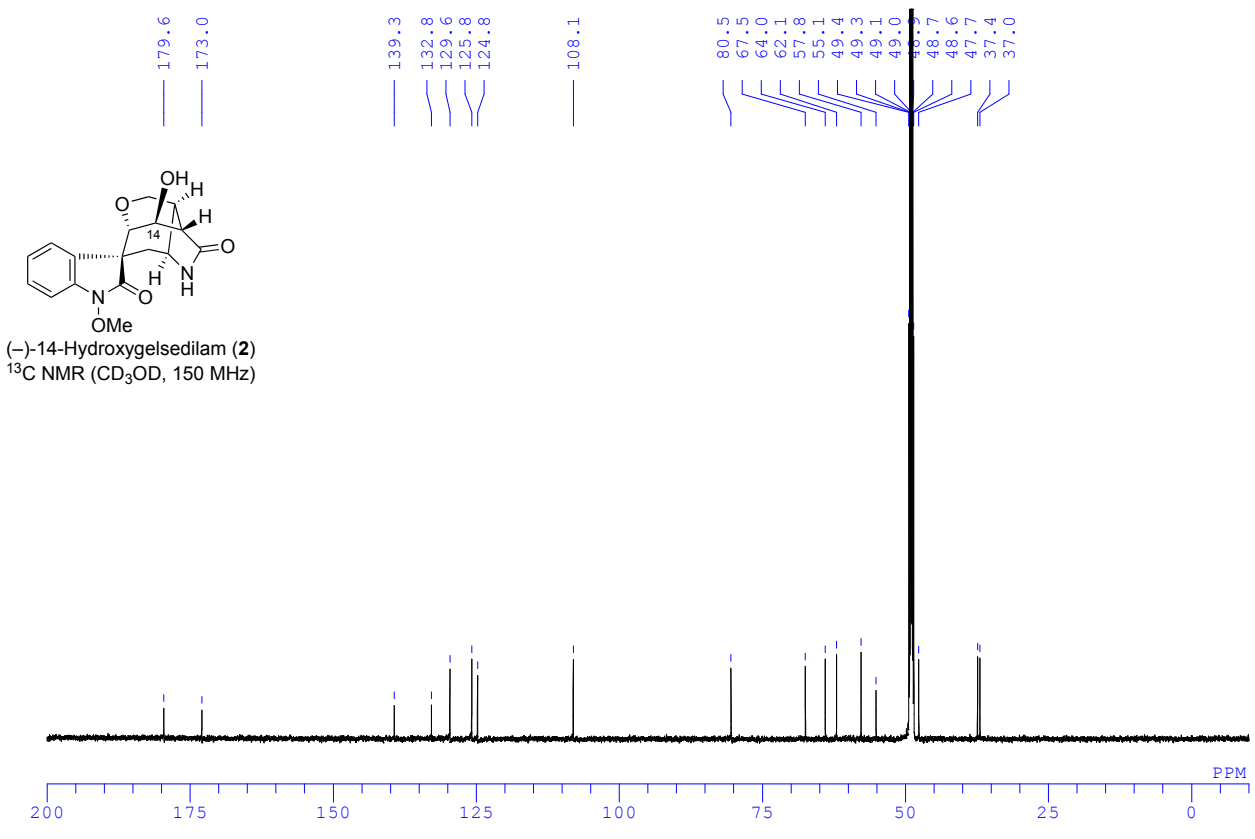

$^{13}$C NMR ($CDCl_3$, 150 MHz)







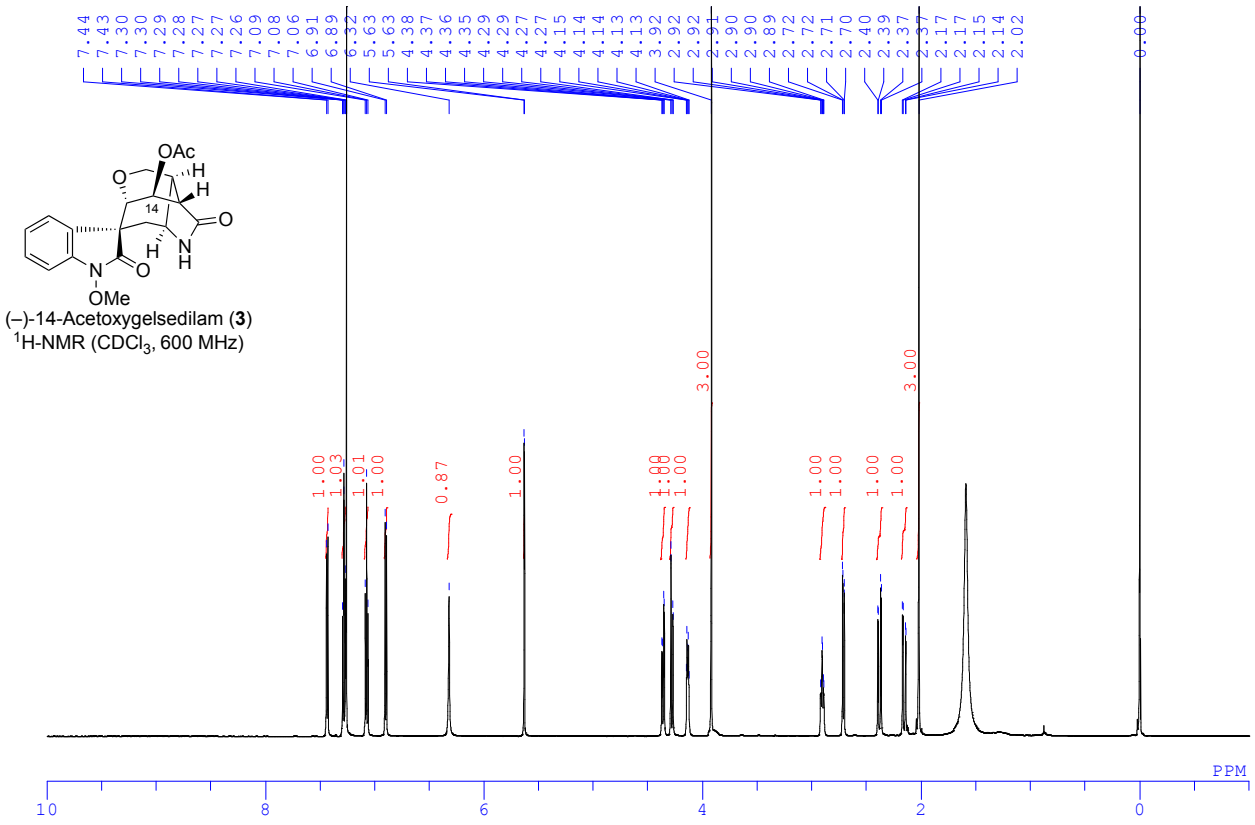
(–)-14-Hydroxygelsedilam (**2**)
$^{1}$H-NMR ($CD_3OD$, 600 MHz)







(–)-14-Hydroxygelsedilam (**2**)
$^{13}$C NMR ($CD_3OD$, 150 MHz)




(–)-14-Acetoxygelsedilam (**3**)
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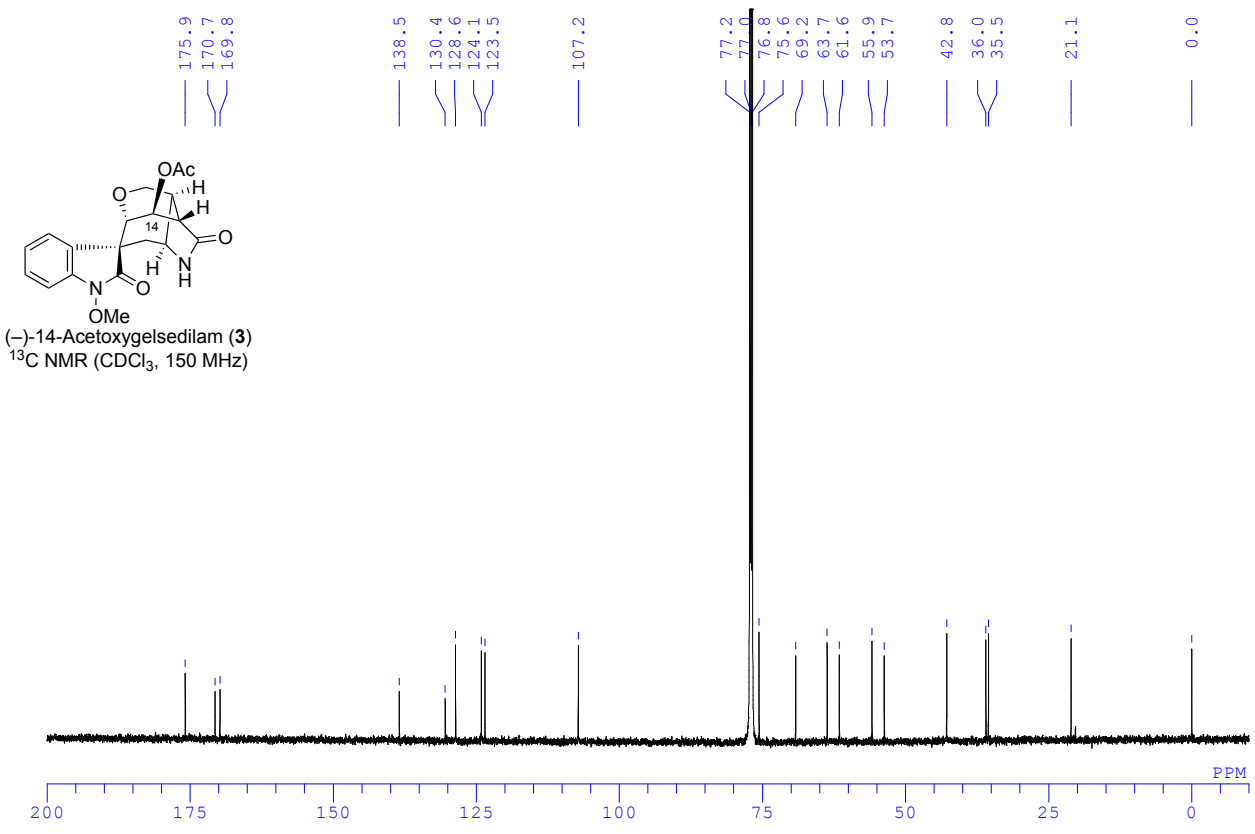


(–)-14-Acetoxygelsedilam (**3**)
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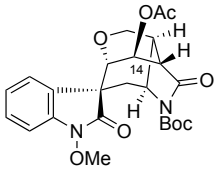
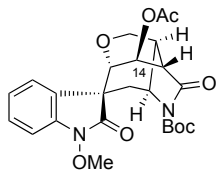



**24**

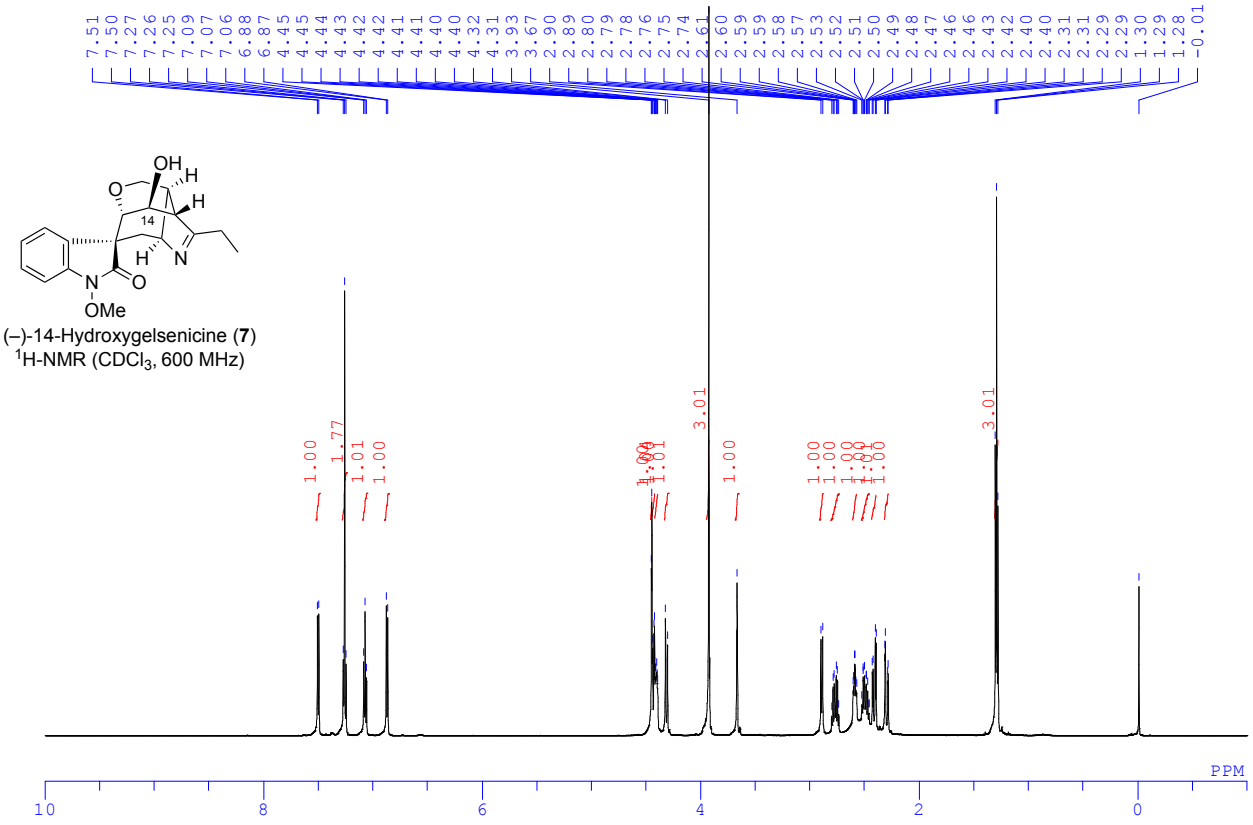
$^{1}$H-NMR ($CDCl_3$, 600 MHz)



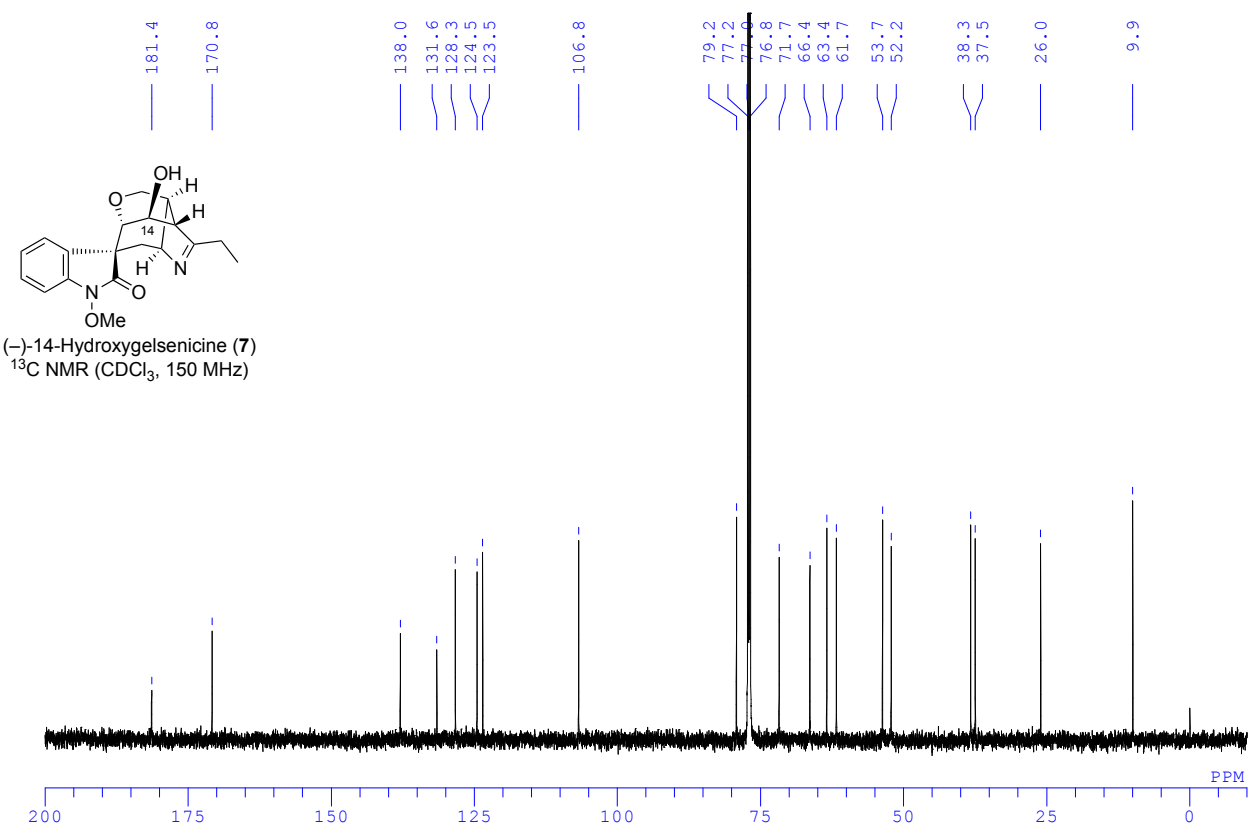




**24**

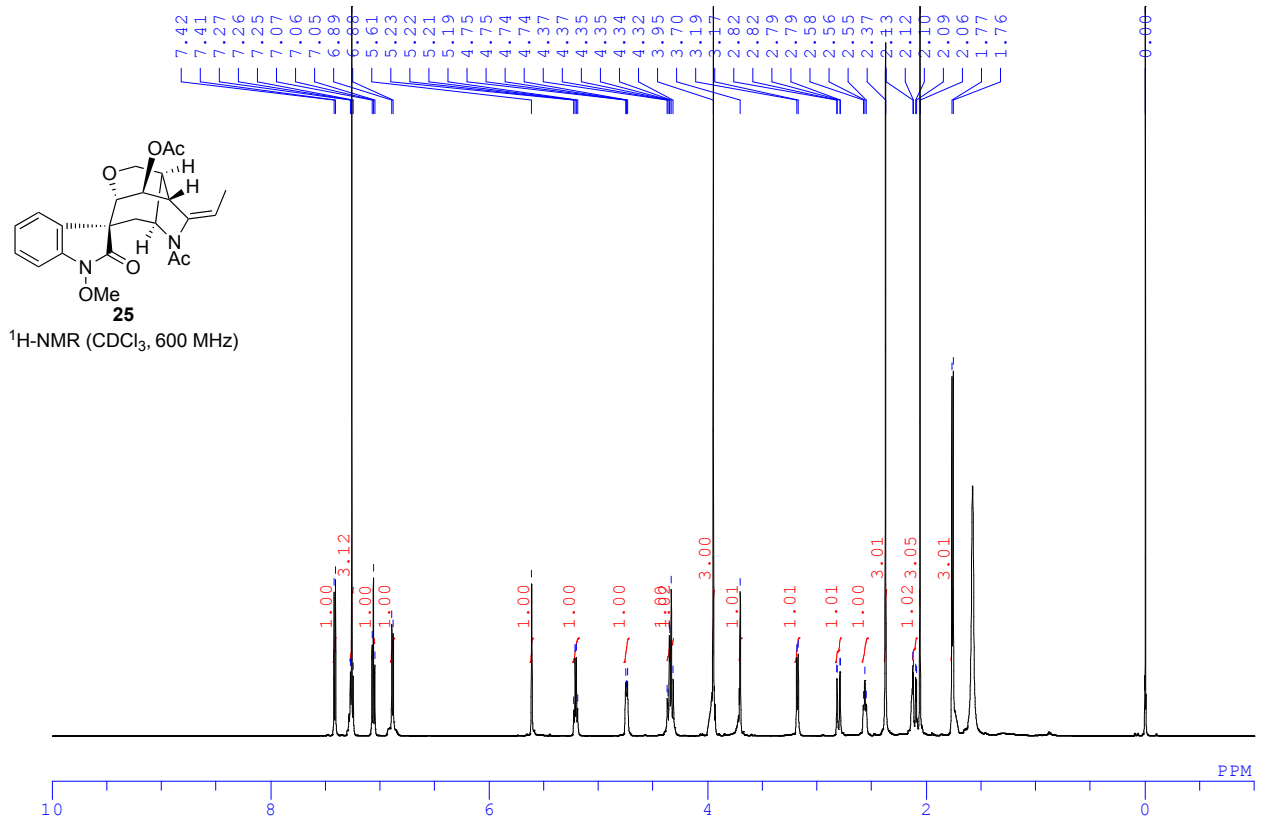
$^{13}$C NMR ($CDCl_3$, 150 MHz)




(–)-14-Hydroxygelsenicine (**7**)
$^{1}$H-NMR ($CDCl_3$, 600 MHz)

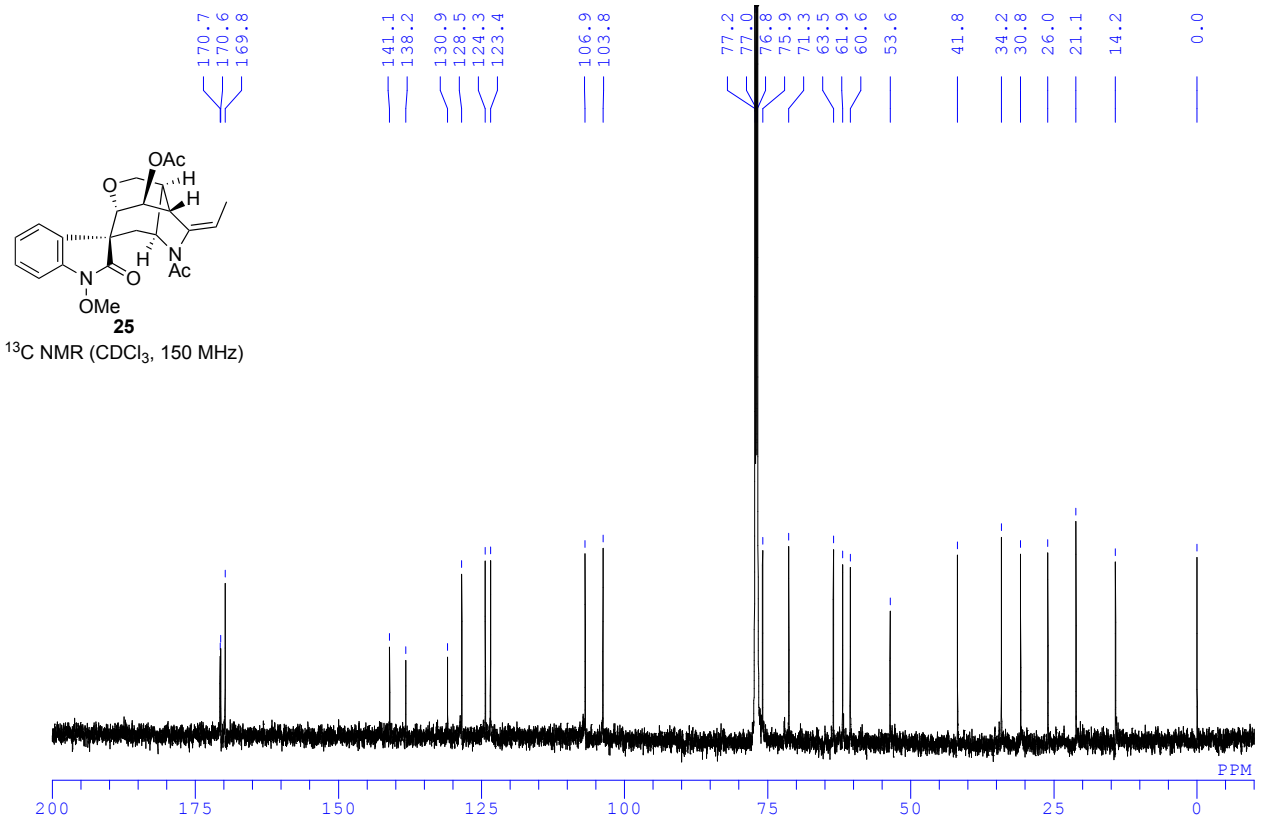



(–)-14-Hydroxygelsenicine (**7**)
$^{13}$C NMR ($CDCl_3$, 150 MHz)



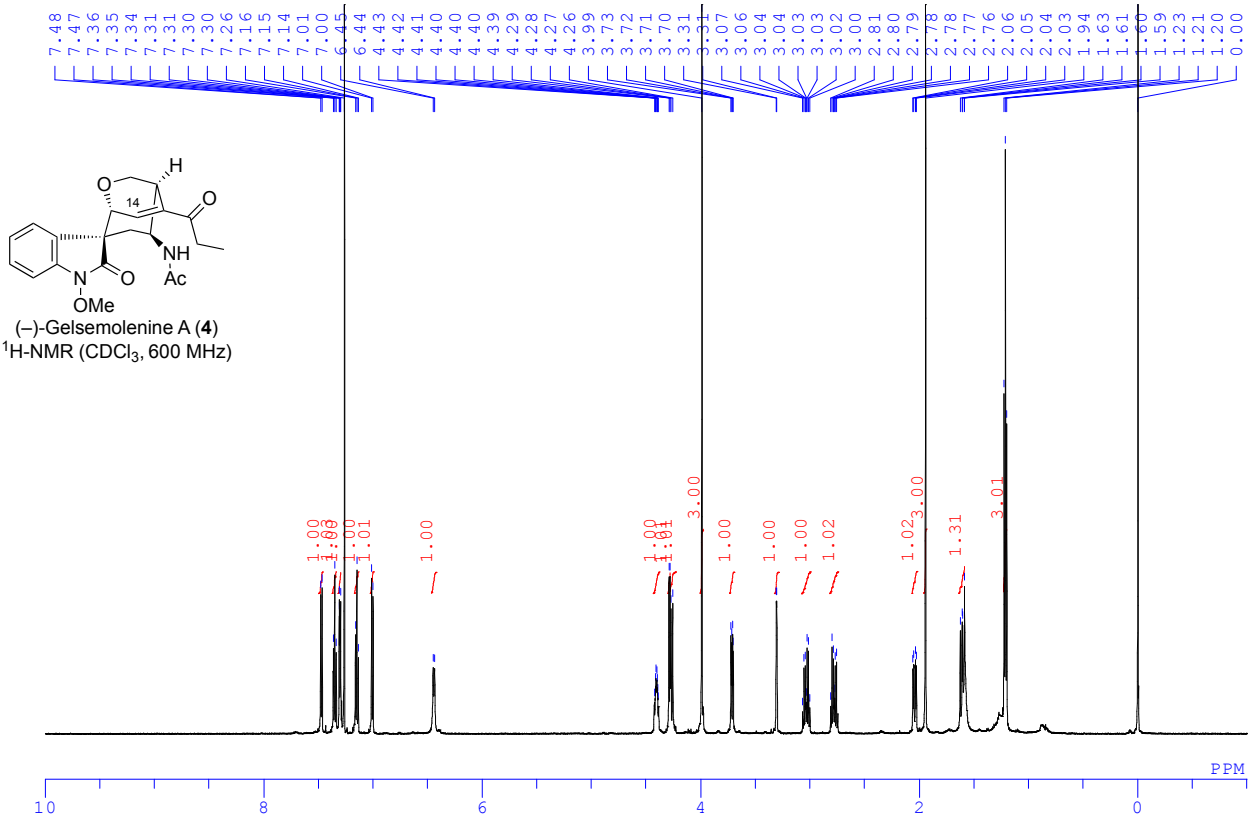

**25**

$^{1}$H-NMR ($CDCl_3$, 600 MHz)

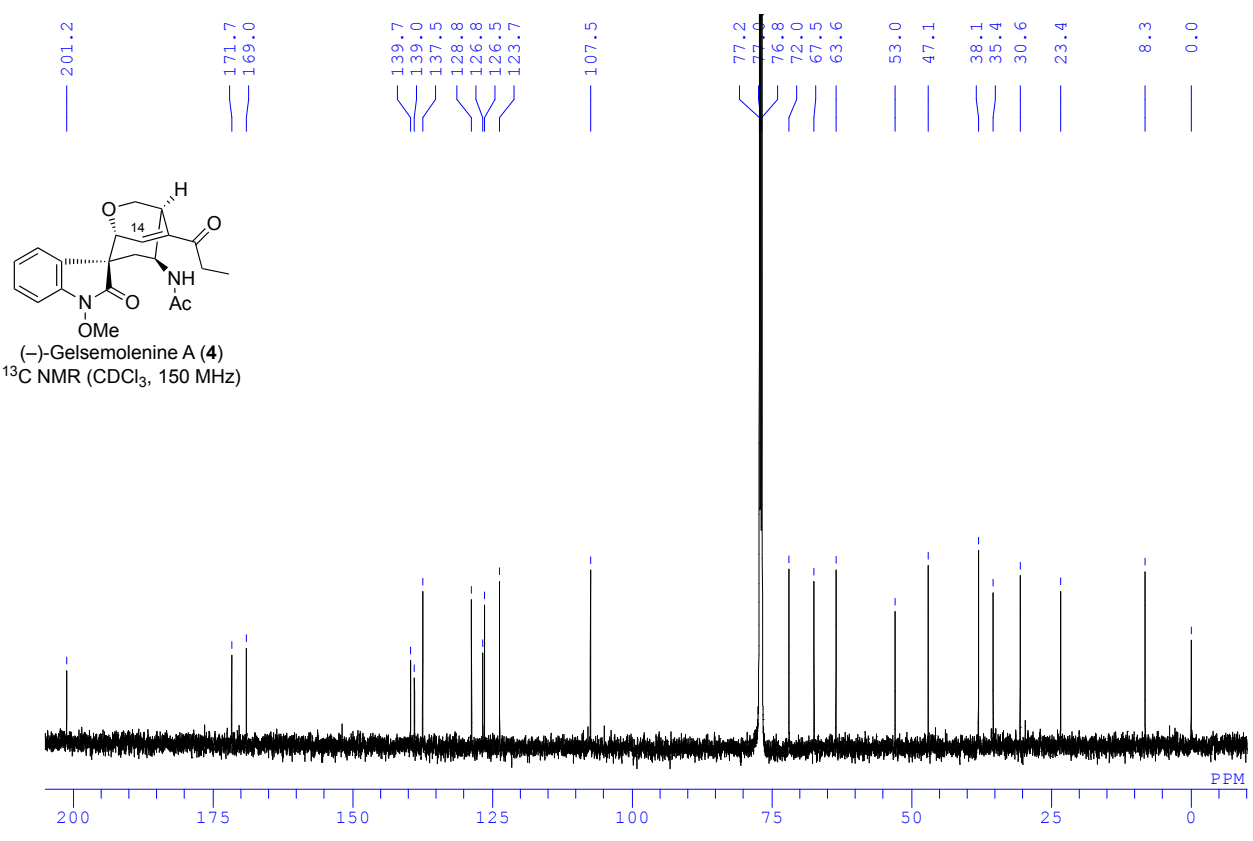



**25**

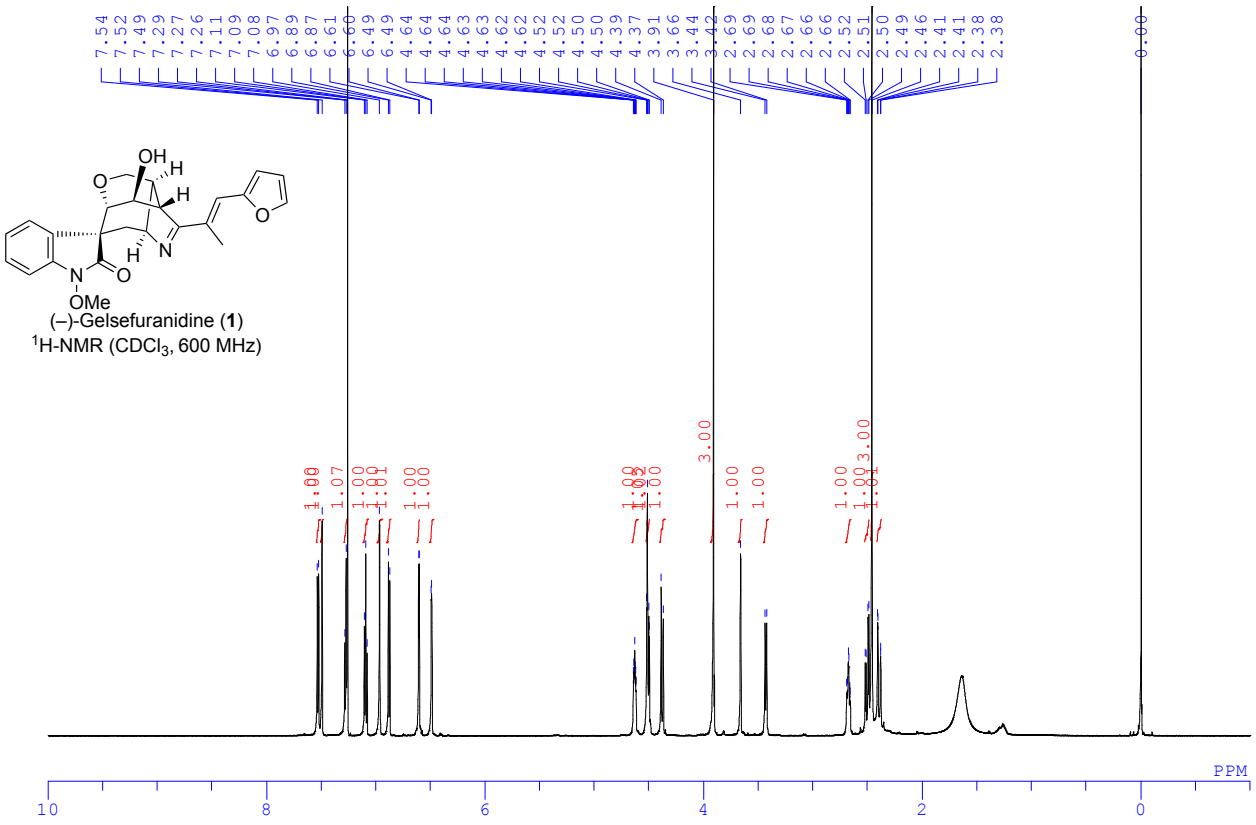
$^{13}$C NMR ($CDCl_3$, 150 MHz)



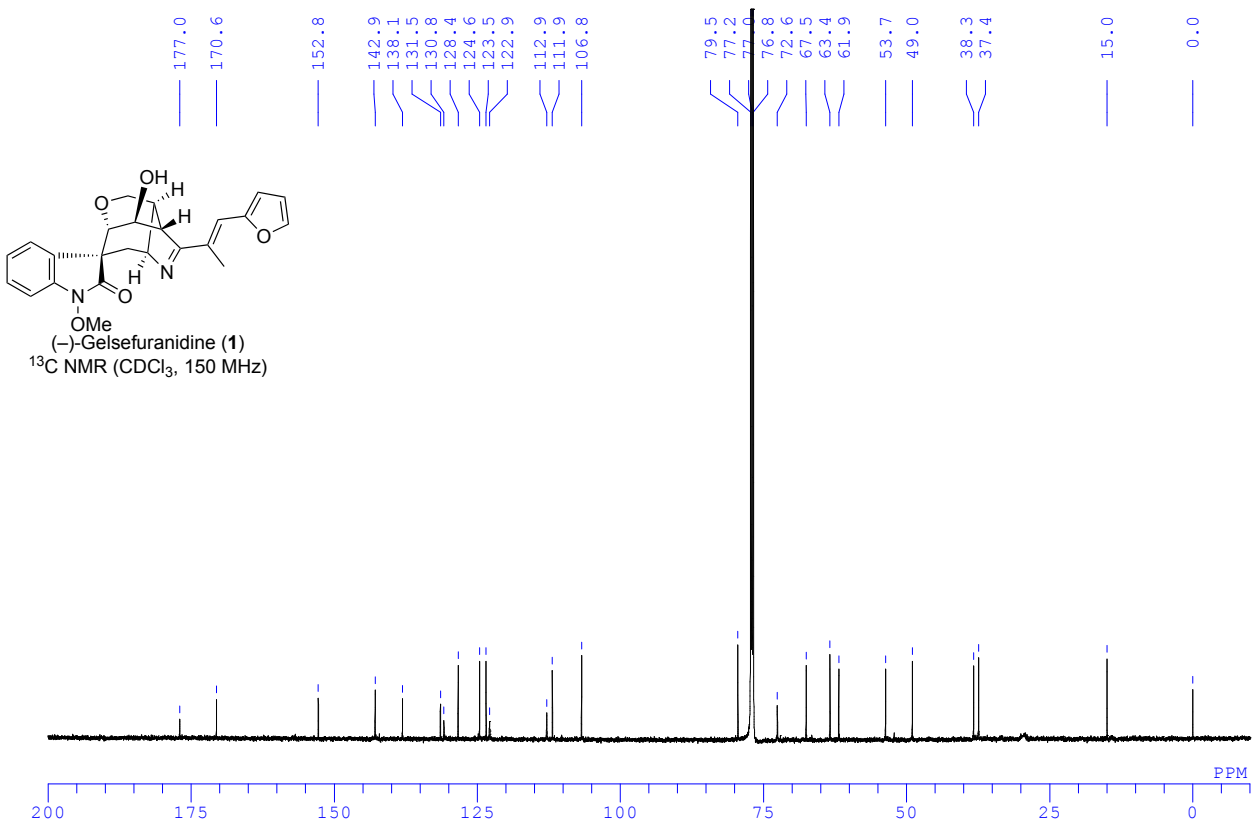

(–)-Gelsemolenine A (**4**)
$^{1}$H-NMR ($CDCl_3$, 600 MHz)



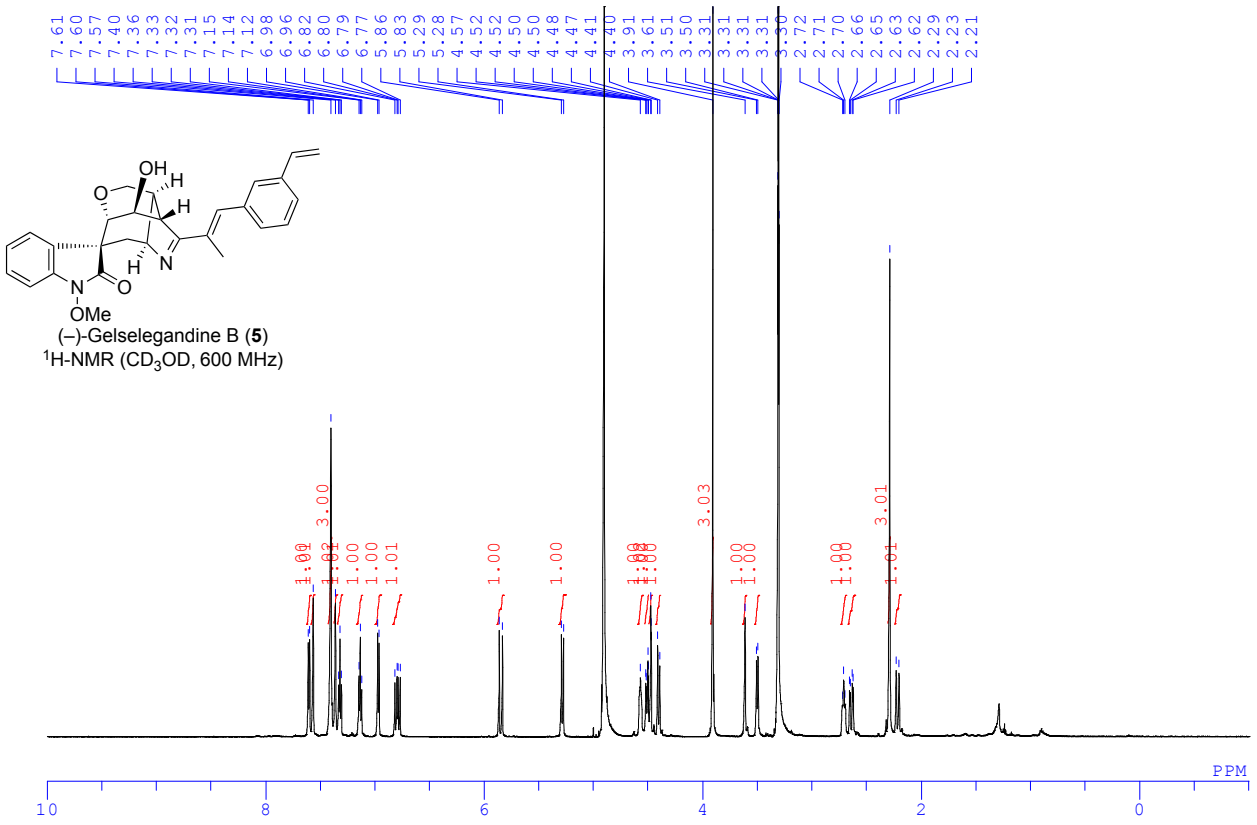

(–)-Gelsemolenine A (**4**)
$^{13}$C NMR ($CDCl_3$, 150 MHz)



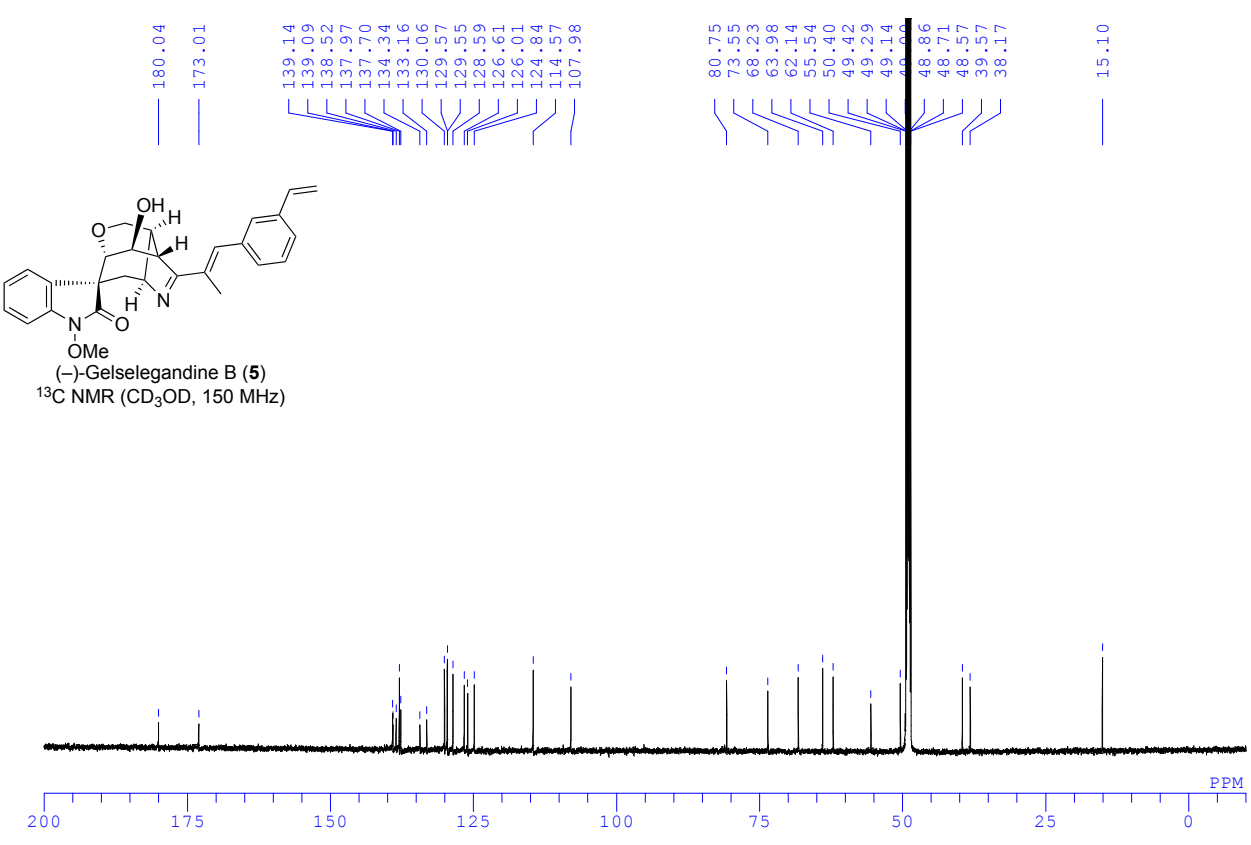

(–)-Gelsefuranidine (**1**)
$^{1}$H-NMR ($CDCl_3$, 600 MHz)



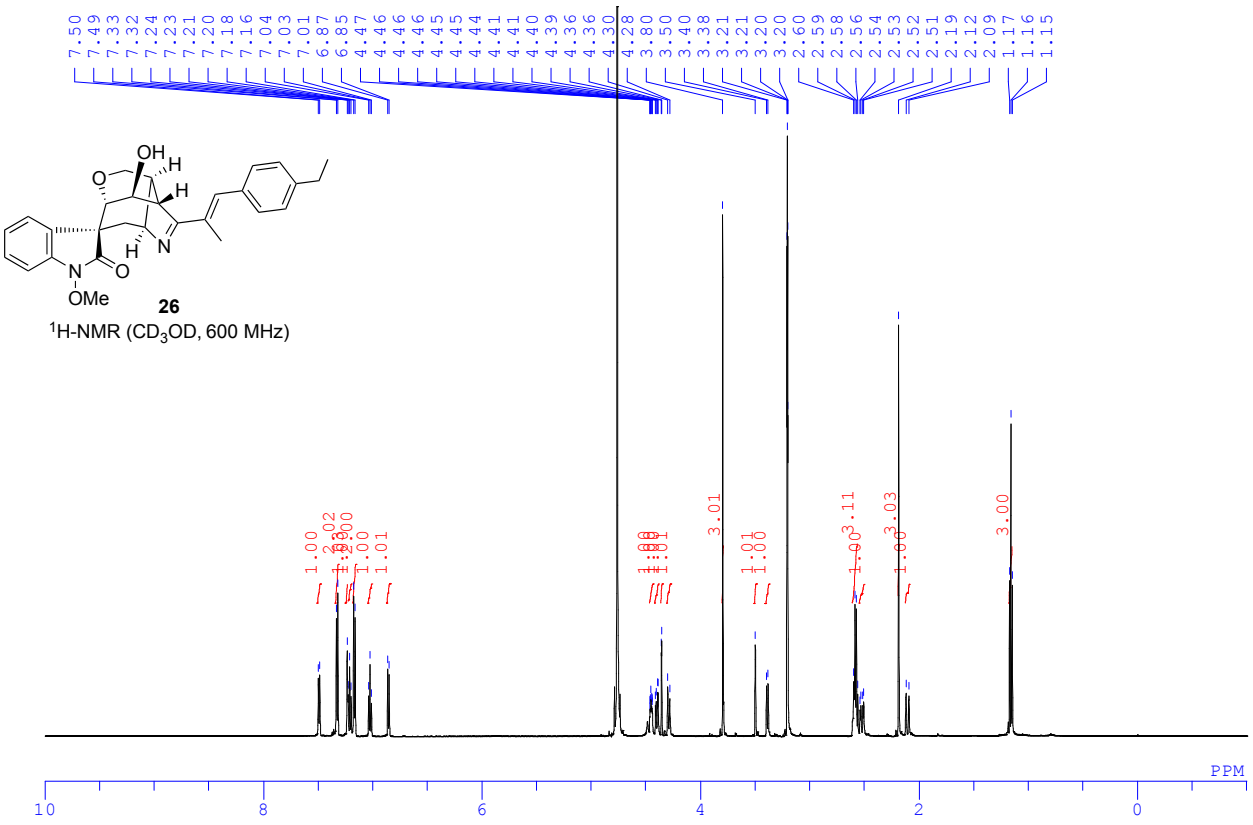

(–)-Gelsefuranidine (**1**)
$^{13}$C NMR ($CDCl_3$, 150 MHz)

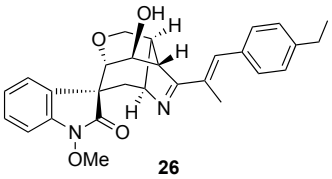



(–)-Gelselegandine B (**5**)
$^{1}$H-NMR ($CD_3OD$, 600 MHz)




(–)-Gelselegandine B (**5**)
$^{13}$C NMR ($CD_3OD$, 150 MHz)



**26**

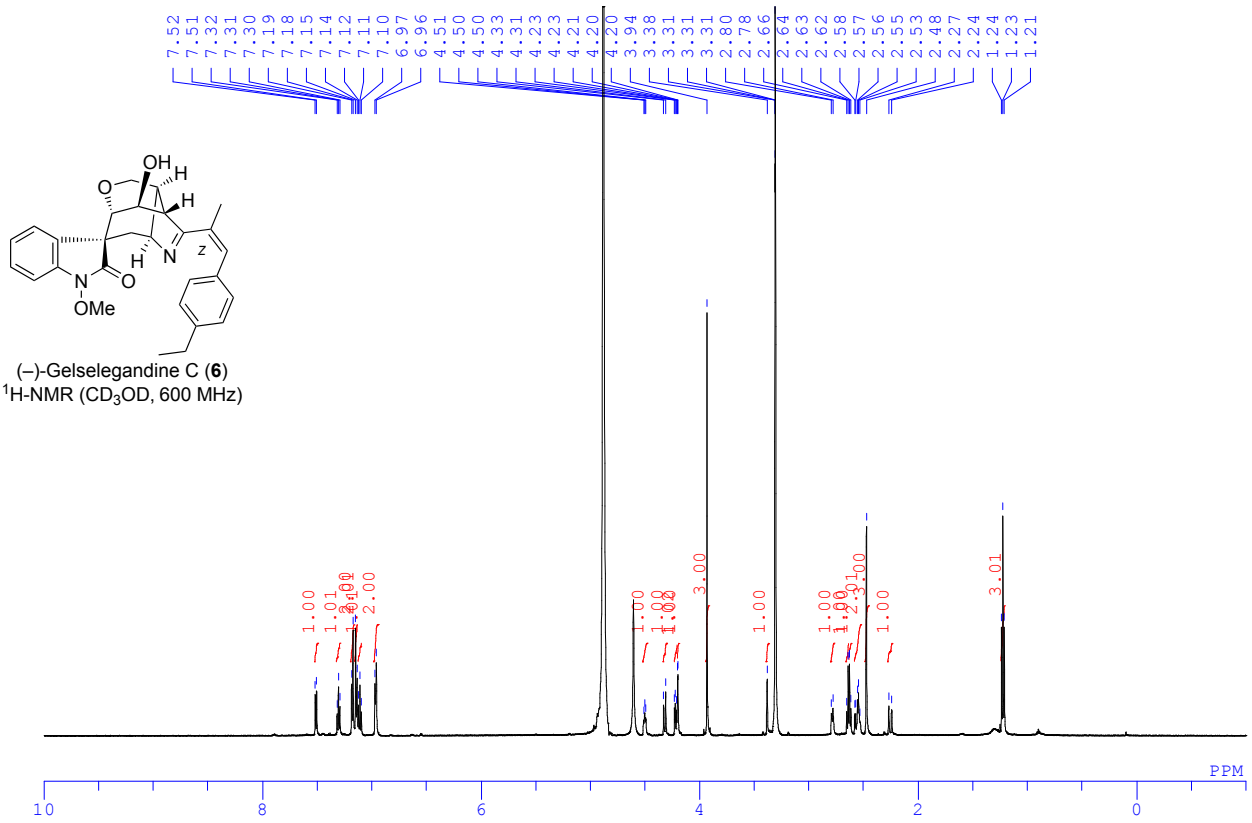
$^{1}$H-NMR ($CD_3OD$, 600 MHz)



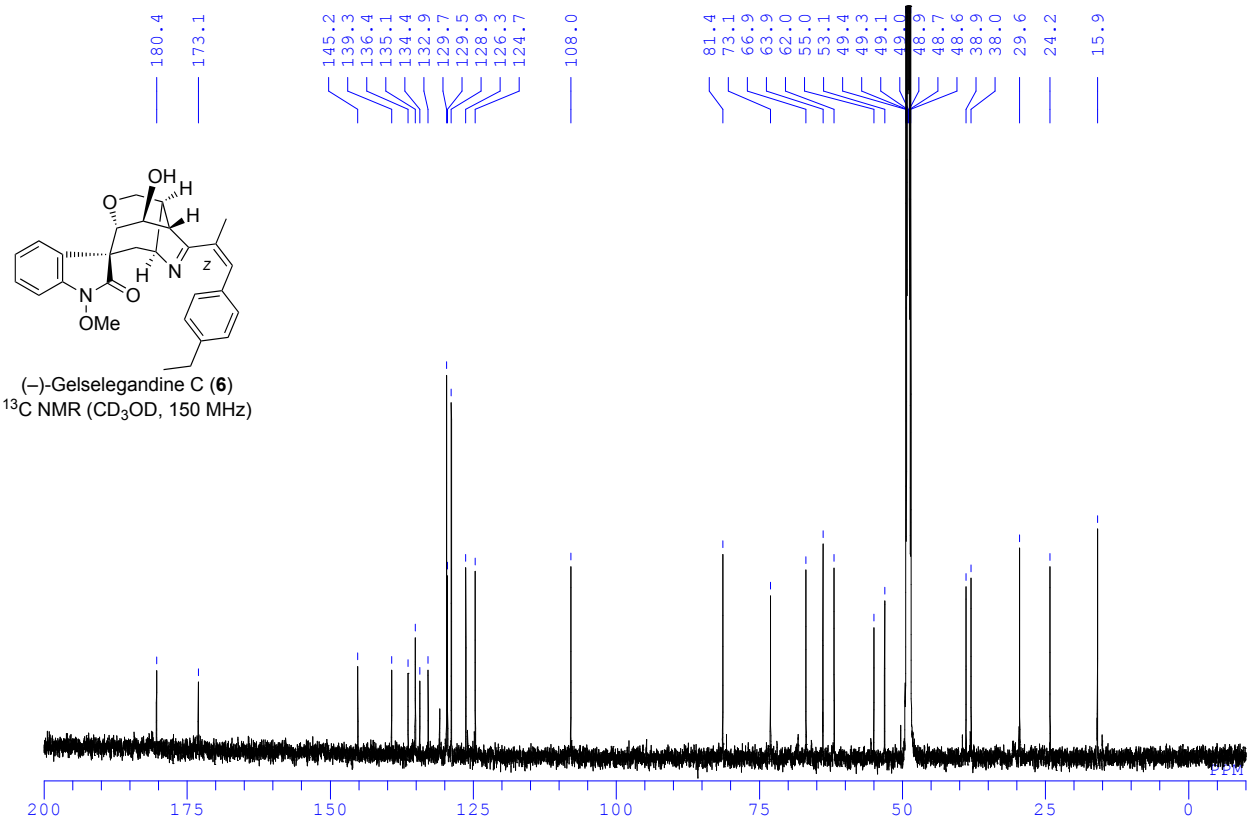



**26**

$^{13}$C NMR ($CD_3OD$, 150 MHz)




(–)-Gelselegandine C (**6**)
$^{1}$H-NMR ($CD_3OD$, 600 MHz)




(–)-Gelselegandine C (**6**)
$^{13}$C NMR ($CD_3OD$, 150 MHz)