Supporting Information

Formal total synthesis of (±)-7-deoxycylindrospermopsin and its 8-epi isomer

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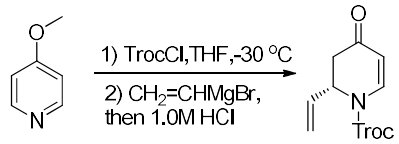
1. General Information.

All reactions were carried out under nitrogen atmosphere in anhydrous conditions, unless otherwise noted. Dry solvents tetrahydrofuran (THF) were obtained by sodium and freshly distilled, dry methylene chloride (CH_2Cl_2) were obtained by calcium hydride and freshly distilled. Anhydrous methanol (MeOH), triethylamine (Et_3N), acetic acid (CH_3COOH) and N, N-Dimethylformamide (DMF) were purchased from Adamas-beta or other commercial suppliers and used without further purification. HPLC water, methanol and trifluoroacetic acid (TFA) were purchased from sigma-aldrich. Other reagents were purchased commercially and used without further purification. NMR spectra were recorded on a Bruker AV-400 instrument, operating for ^1H NMR at 400 MHz, ^{13}C NMR at 100 MHz, chemical shifts were given relative to $CDCl_3$ (7.26 ppm for ^1H NMR, 77.16 ppm for ^{13}C NMR) The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument using EI ionization or ESI ionization in several cases. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer.

2. Experiment Details and Characterization Data



8 (90%)

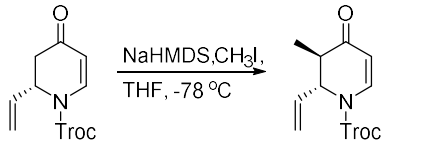
To a solution of 4-methoxy-pyridine (7.64 g, 70 mmol) in 500 mL THF at -30℃ was added TrocCl (10.6 mL, 77 mmol) dropwise, the reaction was stirred for 1 hour at -30℃ before 1.0 M vinyl Grignard (90 mL) was transferred. The reaction was stirred for 3 hours at -30℃ and 1.0 M Hydrochloric acid (100 mL) was added, the mixture was stirred at room temperature for 1 hour and then diluted with water (100 mL). The organic layers was concentrated *in vacuo*, then the water layer was extracted with EtOAc (3×100 mL), the organic layers was washed with brine (100 mL)，dried with Na_2SO_4 and concentrated. Flash column chromatography (silica gel, hexane: EtOAc = 4:1) afforded **8** (18.87 g, 90%) as a colorless oil. R_f = 0.50 (hexane:EtOAc = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 1H), 5.90 – 5.71 (ddd, *J*=5.2,10.4,17.2, 1H), 5.37 (d, *J* = 8.0 Hz, 1H), 5.21 (d, *J* = 10.5 Hz, 1H), 5.17 (m, 2H), 4.83 (s, 2H), 2.91 (dd, *J* = 16.6, 6.9 Hz, 1H), 2.55 (d, *J* = 16.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 151.0, 140.5, 132.3, 118.0, 108.9, 94.4, 75.9, 55.2, 39.9.

HRMS (TOF, EI) calcd for $C_{10}H_{10}Cl_3NO_3$ 296.9726, found 296.9726.

IR (film) ν_{max} 3090, 2960, 1736, 1672, 1607, 1420, 1380, 1328, 1300, 1260, 1221, 1188, 1127, 1059, 995, 933, 825, 787, 756, 717, 679 cm^{-1}.



8 **9** (56%, dr > 20:1)

To a solution of **8** (9.00 g, 30.1 mmol) in 150 mL THF at -78℃ was added 2.0 M sodium bis(trimethylsilyl)amide (16.6 mL, 33.2 mmol) dropwise, the reaction was stirred for 1 hour at -78℃ before methyl iodide (5.6 mL, 90.3 mmol) was added dropwise. The reaction was stirred for 12 hour at -78℃, the reaction mixture was allowed to warm to room temperature and then diluted with water (100

mL). The organic layer was concentrated *in vacuo*, then the water layer was extracted with EtOAc (3×80 mL), the organic layers was washed with brine (80 mL), dried with Na_2SO_4 and concentrated. Flash column chromatography (silica gel, hexane: EtOAc = 5:1) afforded **9** (5.27 g, 56%, dr > 20:1) as a colorless oil.

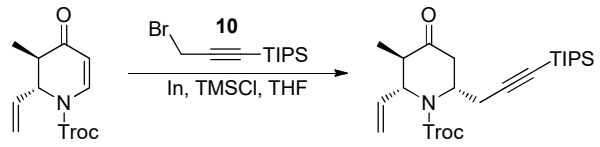
R_f = 0.45 (hexane:EtOAc = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 1H), 5.85 – 5.68 (ddd, *J* = 5.6,10.8,16.2Hz,1H), 5.28 (d, *J* = 8.1 Hz, 1H), 5.18(d, *J* = 11.2 Hz,1H), 5.15(d, *J* = 16.2 Hz,1H), 4.97 – 4.75 (m, 3H), 2.51 (dd, *J* = 14.2, 7.0 Hz, 1H), 1.22 (d, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 151.7, 139.6, 132.3, 117.8, 107.0, 94.5, 75.8, 61.5, 44.1, 16.9.

HRMS (TOF, EI) calcd for $C_{11}H_{12}Cl_3NO_3$ 310.9883, found 310.9879.

IR (film) ν_{max} 3089, 2969, 1736, 1672, 1605, 1419, 1378, 1322, 1264, 1206, 1125, 1091, 1057, 996, 894, 814, 792, 757, 715, 647 cm^{-1}.



9 **11** (74%)

To a solution of indium (7.00 g, 61 mmol) in 60 mL THF was added (3-bromoprop-1-yn-1-yl) triisopropylsilane **10** (25.22 g, 91.6 mmol) at room temperature. After stirred for 30 min, the reaction was removed to water bath at room temperature, then chlorotrimethylsilane (19.3 mL, 152.5 mmol) was added. After stirred for 1 hour, then **9** (9.53 g, 30.5 mmol) was added to reaction mixture. After 12 hours, the reaction mixture was poured into pH 7.0 buffer solution (100mL, K_2HPO_4/KH_2PO_4) which was pre-cooled. The organic layer was concentrated *in vacuo*, then the water layer was extracted with EtOAc (3×80 mL), the organic layers was washed with brine (80 mL), dried with Na_2SO_4 and concentrated. Flash column chromatography (silica gel, hexane: EtOAc = 10:1) afforded **11** (11.52 g, 74%) as a colorless oil.

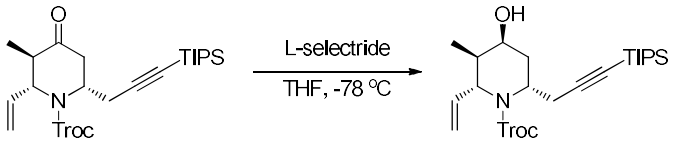
R_f = 0.35 (hexane:EtOAc = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 (ddd, *J* = 5.2, 10.4, 17.2 Hz, 1H), 5.25 (dd, *J* = 11.6, 1.6 Hz, 1H),5.22 (dd, *J* = 4.8, 1.6 Hz, 1H), 4.83 (s, 2H), 4.74 (s, 1H), 4.68 – 4.56 (m, 1H), 2.88 – 2.58 (m, 5H), 1.21 (d, *J* = 7.2 Hz, 3H), 1.02 (s, 21H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 208.8, 154.2, 137.9, 117.6, 103.5, 95.3, 84.1, 75.3, 60.1, 52.0, 45.6, 40.7, 27.7, 18.6, 15.3, 11.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{37}Cl_3NO_3Si$ 508.1603; Found 508.1618.

IR (film) ν_{max} 2943, 2865, 1714, 1461, 1402, 1378, 1325, 1274, 1122, 1062, 995, 929, 883, 823, 762, 717, 677 cm^{-1}.



11 **12** (85%,dr=7:5)

To a solution of **11** (13.6 g, 26.7 mmol) in 150 mL THF at -78℃ was added 1.0 M L-selectride (107 mL, 107 mmol) dropwise, the reaction was stirred for 24 hours at -78℃ and 2.0M aqueous NaOH (55 mL, 110 mmol) and 30% aqueous H_2O_2 (36.4 mL, 321 mmol) were added slowly. The reaction mixture was allowed to warm to room temperature and then diluted with water (60 mL). The organic layers was concentrated *in vacuo*, then the water layer was extracted with EtOAc (3×100 mL), the organic layers was washed with brine (100 mL)，dried with Na_2SO_4 and concentrated. Flash column chromatography (silica gel, hexane: EtOAc = 10:1 to 5:1) afforded **12** (6.65 g, 49%) and C12 diasteomer **12'** (4.86 g, 36%) as a colorless oil.

12: R_f = 0.45 (hexane:EtOAc = 5:1)

12: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 – 5.80 (m, 1H), 5.21 (dd, *J* = 36.8, 14.1 Hz, 2H), 4.86 (d, *J* = 11.9 Hz, 1H), 4.65 (ddd, *J* = 22.8, 14.7, 4.4 Hz, 3H), 4.22 (d, *J* = 10.4 Hz, 1H), 2.56 (d, *J* = 7.7 Hz, 2H), 2.28 (s, 1H), 2.05 (dd, *J* = 13.2, 3.6 Hz, 1H), 1.94 – 1.83 (m, 1H), 1.63 (s, 1H), 1.01 (dd, *J* = 18.3, 6.2 Hz, 24H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 138.2, 116.5, 105.0, 95.6, 83.0, 75.2, 63.1, 59.3, 51.8, 36.2, 29.0, 26.6, 18.6, 11.2, 11.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{39}Cl_3NO_3Si$ 510.1759; Found 510.1762.

IR (film) ν_{max} 3478, 2943, 2865, 2174, 1714, 1461, 1410, 1381, 1324, 1267, 1121, 1064, 996, 920, 883, 819, 765, 716, 678 cm^{-1}.

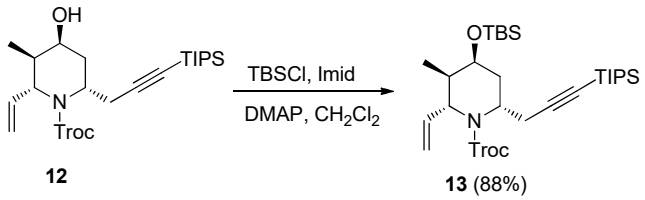
C12 diasteomer **12'**: R_f = 0.50 (hexane:EtOAc = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (ddd, *J* = 17.2, 10.3, 7.1 Hz, 1H), 5.22 (d, *J* = 17.1 Hz, 1H), 5.11 (d, *J* = 10.3 Hz, 1H), 4.84 (d, *J* = 11.9 Hz, 1H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.51 – 4.34 (m, 2H), 3.69 (s, 1H), 2.86 – 2.67 (m, 2H), 2.34 – 2.19 (m, 1H), 1.95 (ddd, *J* = 14.3, 10.4, 4.3 Hz, 2H), 1.65 (d, *J* = 3.1 Hz, 1H), 1.10 (d, *J* = 6.9 Hz,3H), 1.05 (d, *J* = 4.0 Hz, 21H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 139.4, 116.5, 105.3, 95.6, 82.8, 75.2, 70.6, 59.7, 50.6, 39.9, 31.7, 28.2, 18.6, 17.9, 11.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{39}Cl_3NO_3Si$ 510.1759; Found 510.1763.

IR (film) ν_{max} 3487, 2942, 2865, 2174, 1713, 1461, 1410, 1382, 1317, 1277, 1122, 1062, 995, 925, 883, 823, 764, 716, 678 cm^{-1}.



12 **13** (88%)

To a solution of **12** (1.76 g, 3.44 mmol) in 20 mL CH_2Cl_2 was added imidazole (1.43 g, 21 mmol), t-butyldimethylchlorosilane (1.05g, 7.0 mmol) and DMAP (130 mg, 1.05 mmol). The mixture was stirred at room temperature for 24 hours and was added 20 mL saturated NH_4Cl solution. The water layer was extracted with CH_2Cl_2 (3×20 mL), the organic layers was washed with brine (20 mL), dried with Na_2SO_4 and concentrated. Flash column chromatography (silica gel, hexane: EtOAc = 20:1) afforded **13** (1.90 g, 88%) as a colorless oil.

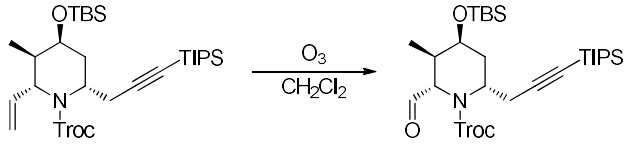
R_f = 0.7 (hexane:EtOAc = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (ddd, *J* = 16.0, 10.7, 4.9 Hz, 1H), 5.30 – 5.08 (m, 2H), 4.83 (d, *J* = 11.9 Hz, 1H), 4.74 – 4.62 (m, 2H), 4.56 (dd, *J* = 13.5, 6.6 Hz, 1H), 4.20 – 4.07 (m, 1H), 2.63 – 2.49 (m, 2H), 2.13 (s, 1H), 2.03 – 1.93 (m, 1H), 1.93 – 1.80 (m, 1H), 1.01 (m, 24H), 0.87 (s, 9H), 0.06 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 138.7, 115.9, 105.1, 95.7, 82.6, 75.1, 63.5, 59.3, 51.9, 36.9, 29.4, 26.5, 25.8, 18.6, 18.0, 11.6, 11.2, -4.7, -4.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{53}Cl_3NO_3Si_2$ 624.2624; Found 624.2629.

IR (film) ν_{max} 2953, 2864, 2174, 1715, 1462, 1408, 1323, 1260, 1115, 1091, 996, 920, 883, 853, 836, 775, 742, 713, 674 cm^{-1}.



13 **14** (71%)

The ozone was dried by calcium chloride before it was introduced into a solution of **13** (0.85 g, 1.37 mmol) in 20 mL CH_2Cl_2 at -78 ℃ until the material completely disappeared. Nitrogen was bubbled through the solution for 5 min to purge the excess ozone before 1.0 mL Me_2S was added, and the mixture was then slowly warmed to room temperature. The solution was concentrated, flash column chromatography (silica gel, hexane: EtOAc = 10:1) afforded **14** (0.62 g, 71%) as a colorless oil.

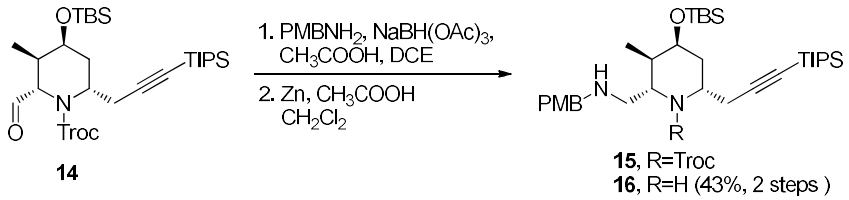
R_f = 0.5 (hexane:EtOAc = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 4.85 (d, *J* = 11.9 Hz, 1H), 4.72 (d, *J* = 9.7 Hz, 1H), 4.58 (m, 2H), 3.86 – 3.74 (m, 1H), 2.58 (m, 2H), 2.35 (dd, *J* = 16.6, 10.3 Hz, 1H), 1.96 – 1.81 (m, 2H), 1.07 (d, *J* = 7.0 Hz, 3H), 1.04 (m, 21H), 0.87 (s, 9H), 0.06 (d, *J* = 5.3 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 154.6, 104.1, 95.3, 83.3, 75.4, 66.9, 64.0, 51.7, 32.6, 29.6, 25.7, 18.6, 18.0, 11.4, 11.2, -4.8, -4.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{51}Cl_3NO_4Si_2$ 626.2417; Found 626.2410.

IR (film) ν_{max} 2954, 2864, 2174, 1719, 1462, 1410, 1331, 1254, 1115, 1092, 922, 883, 856, 837, 776, 741, 715, 676, 614 cm^{-1}.



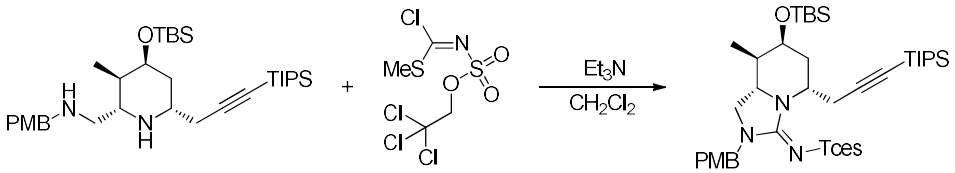
To a solution of **14** (7.10 g, 11.32 mmol) in 30 mL dichloroethane at -78℃ was added CH_3COOH (323uL, 5.66 mmol), 4-methoxybenzylamine (1.8 mL, 13.6 mmol) and sodium triacetoxyborohydride (3.6 g, 17 mmol). The mixture was then slowly warmed to room temperature and stirred for 12 hours at room temperature before neutralized with saturated aqueous Na_2CO_3 and extracted with CH_2Cl_2 (3×30 mL). The organic layers were washed with brine (30 mL), dried with Na_2SO_4 and concentrated. Flash column chromatography (silica gel, hexane: EtOAc = 4:1) afforded the crude product as a colorless oil. To a solution of the crude product in 7 mL CH_2Cl_2 and 21 mL CH_3COOH was added zinc dust (3.10 g, 47.15 mmol) and stirred vigorously at room temperature for 6 h. The mixture was filtered and the filtrate was neutralized with saturated Na_2CO_3 solution and extracted with CH_2Cl_2 (3×40 mL), the organic layers was washed with brine (40 mL), dried with Na_2SO_4 and concentrated. Flash column chromatography (silica gel, hexane: EtOAc = 1:1) afforded **16** (2.79 g, 43%, 2 steps) as a colorless oil. R_f = 0.4 (hexane:EtOAc = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 1H), 3.79 (s, 3H), 3.70 (q, *J* = 13.1 Hz, 2H), 3.18 – 3.05 (m, 1H), 2.79 (m, 2H), 2.40 (dd, *J* = 11.6, 9.2 Hz, 1H), 2.31 (d, *J* = 6.0 Hz, 2H), 1.97 (s, 2H), 1.80 (d, *J* = 13.2 Hz, 1H), 1.34 (m, 2H), 1.04 (m, 21H), 0.89 (s, 9H), 0.82 (d, *J* = 6.7 Hz, 3H), 0.03 (d, *J* = 5.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 132.8, 129.3, 113.7, 105.9, 82.2, 55.2, 55.1, 71.2, 53.7, 52.1, 49.2, 40.5, 39.7, 27.9, 25.9, 18.7, 18.1, 15.0, 11.3, -4.3, -4.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{33}H_{61}N_2O_2Si_2$ 573.4266; Found 573.4256.

IR (film) ν_{max} 2939, 2863, 2349, 2171, 1716, 1613, 1586, 1512, 1462, 1350, 1249, 1174, 1110, 1037, 940, 883, 837, 775, 743, 677, 636 cm^{-1}.



16 **17** **18** (76%)

To a solution of **16**(1.28 g, 2.24 mmol) in 20 mL CH_2Cl_2 was added **17**(1.39 g, 4.48 mmol) and triethylamine (0.78 mL, 5.6 mmol). The mixture was stirred at room temperature for 12 hours. The solution was concentrated, flash column chromatography (silica gel, hexane: EtOAc = 10:1) afforded **18** (1.38 g, 88%) as a flocculent solid.

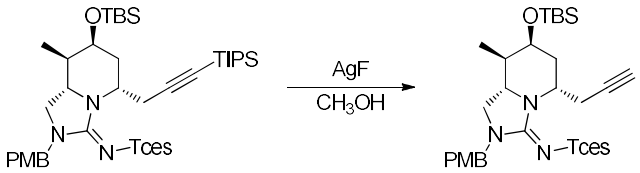
R_f = 0.5 (hexane: EtOAc = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.80 (d, *J* = 14.9 Hz, 1H), 4.69 – 4.58 (m, 2H), 4.55 (d, *J* = 14.9 Hz, 1H), 3.86 (s, 1H), 3.84 – 3.68 (m, 4H), 3.57 (dd, *J* = 19.5, 9.8 Hz, 1H), 3.41 – 3.20 (m, 3H), 2.86 (t, *J* = 9.9 Hz, 1H), 2.13 – 2.01 (m, 1H), 1.80 (d, *J* = 12.0 Hz, 1H), 1.60 – 1.49 (m, 1H), 0.99 (dd, *J* = 18.9, 5.8 Hz, 21H), 0.84 (s, 9H), 0.75 (d, *J* = 6.6 Hz, 3H), 0.02 (d, *J* = 12.5 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 157.4, 130.1, 126.8, 114.2, 104.9, 94.5, 83.0, 78.0, 68.6, 57.5, 55.3, 50.7, 50.6, 49.4, 39.9, 39.3, 25.9, 24.4, 18.7, 18.0, 13.6, 11.3, -4.3, -4.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{36}H_{61}Cl_3N_3O_5SSi_2$ 808.2931; Found 808.2906.

IR (film) ν_{max} 2942, 2864, 2173, 1572, 1462, 1345, 1249, 1179, 1141, 1092, 1034, 938, 883, 838, 775, 728, 678, 616 cm^{-1}.



18 **19** (87%)

To a stirred solution of **18** (144 mg, 0.18 mmol) in 10 mL CH_3OH was added AgF (45.2 mg, 0.36 mmol) in the dark. The reaction mixture was stirred at room temperature for 24 hours in dark and then 1 M HCl (5.0 mL) was added. The mixture was stirred for 15 min, diluted with water (5 mL) then was concentrated *in vacuo*, then the water layer was extracted with CH_2Cl_2 (3×10 mL), the organic layers was washed with

brine (10 mL), dried with Na_2SO_4 and concentrated. Flash column chromatography (silica gel, hexane: EtOAc = 2:1) afforded **19** (101 mg, 87%) as a colorless oil.

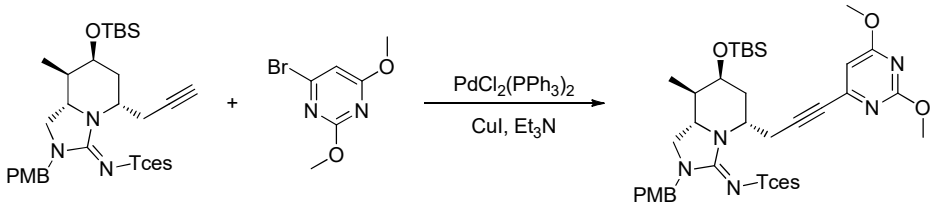
R_f = 0.4 (hexane: EtOAc = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.75 (d, *J* = 14.9 Hz, 1H), 4.62 (m, 3H), 3.87 (s, 1H), 3.75 (s, 4H), 3.57 (dd, *J* = 19.0, 8.8 Hz, 1H), 3.30 (t, *J* = 9.4 Hz, 1H), 3.20 (t, *J* = 6.6 Hz, 2H), 2.92 (t, *J* = 9.1 Hz, 1H), 2.03 (t, *J* = 14.9 Hz, 1H), 1.96 (s, 1H), 1.74 (t, *J* = 12.6 Hz, 1H), 1.62 – 1.48 (m, 1H), 0.85 (s, 9H), 0.74 (d, *J* = 6.6 Hz, 3H), 0.02 (d, *J* = 13.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 157.1, 130.0, 126.8, 114.2, 94.6, 81.2, 77.9, 70.7, 68.8, 57.8, 55.3, 51.0, 50.5, 49.0, 39.8, 39.0, 25.9, 22.6, 18.1, 13.5, -4.4, -5.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{41}Cl_3N_3O_5SSi$ 652.1596; Found 652.1579.

IR (film) ν_{max} 3309, 2930, 1562, 1513, 1462, 1348, 1306, 1247, 1178, 1139, 1111, 1090, 1030, 938, 836, 774, 726, 616 cm^{-1}.



To a solution of 6-bromo-2,4-dimethoxypyrimidine **20**(0.38 g,1.72 mmol) and **19** (0.75 g, 1.15 mmol) in 10 mL of triethylamine was added a mixture of bis(triphenylphosphine)palladium(II) chloride (16.1 mg, 0.023 mmol) and copper(I) iodide (9 mg, 0.046 mmol). The resulting mixture was stirred vigorously at room temperature for 24 hours. The reaction mixture filtered through a plug of Celite and the filtrate was concentrated. Flash column chromatography (silica gel, hexane: EtOAc = 2:1) afforded **21** (101 mg, 87%) as a flocculent solid.

R_f = 0.35 (hexane: EtOAc = 2:1).

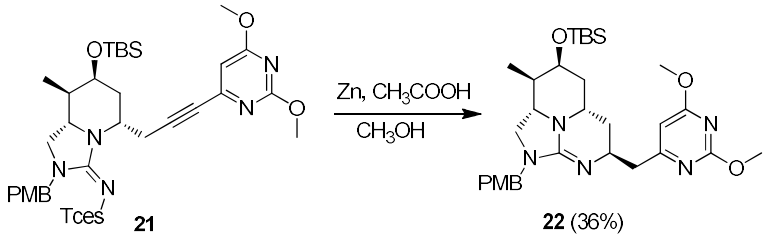
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 6.40 (s, 1H), 4.79 – 4.62 (m, 4H), 3.93 (s, 1H), 3.91 (s, 1H), 3.87 (m, 2H), 3.74 (s, 3H), 3.60 (dd, *J* = 19.3, 8.8 Hz, 1H), 3.49

(d, *J* = 6.0 Hz, 2H), 3.32 (t, *J* = 9.4 Hz, 1H), 2.94 (t, *J* = 9.3 Hz, 1H), 2.07 (d, *J* = 13.9 Hz, 1H), 1.82 (t, *J* = 12.2 Hz, 1H), 1.58 (dd, *J* = 8.5, 7.0 Hz, 1H), 0.84 (s, 9H), 0.76 (d, *J* = 6.7 Hz, 3H), 0.02 (d, *J* = 13.5 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 165.3, 159.5, 157.1, 151.6, 129.9, 126.7, 114.2, 104.7, 94.5, 90.7, 81.0, 77.9, 68.7, 57.8, 55.2, 54.9, 53.9, 50.7, 50.4, 49.0, 39.7, 39.4, 25.8, 23.7, 18.0, 13.5, -4.3, -5.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{33}H_{47}Cl_3N_5O_7SSi$ 790.2026; Found 790.1997.

IR (film) ν_{max} 2953, 2236, 1576, 1556, 1513, 1480, 1459, 1389, 1347, 1248, 1202, 1139, 1104, 1029, 965, 939, 835, 775, 730, 615 cm^{-1}.



To a solution of **21** (638 mg，0.807 mmol) in 10 mL CH_3OH and 10 mL CH_3COOH was added zinc dust (264 mg，4.04 mmol) and stirred vigorously at room temperature for 1 h. The mixture was filtered and the filtrate was neutralized with saturated Na_2CO_3 solution and concentrated *in vacuo* then extracted with CH_2Cl_2 (3×20 mL), the organic layers was washed with brine (20 mL)，dried with Na_2SO_4 and concentrated. Flash column chromatography (CH_2Cl_2/CH_3OH = 10/1) afforded **22** (223 mg，36%) as a colorless oil.

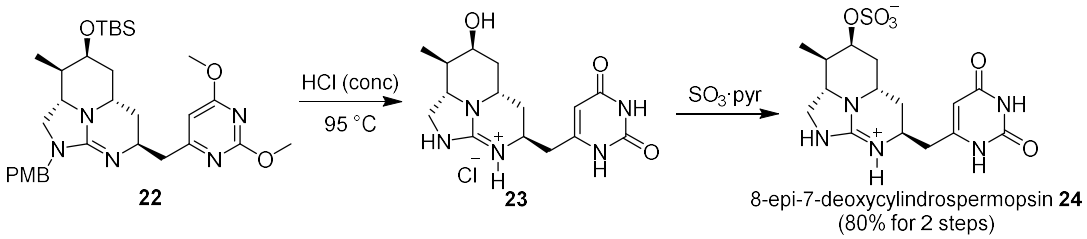
R_f = 0.4 (CH_2Cl_2/CH_3OH = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.3 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.43 (s, 1H), 5.26 (d, *J* = 15.1 Hz, 1H), 4.99 (s, 1H), 4.39 (d, *J* = 15.1 Hz, 1H), 3.95 (m, 7H), 3.81 (s, 4H), 3.68 (dd, *J* = 20.6, 10.3 Hz, 1H), 3.54 (t, *J* = 10.2 Hz, 1H), 3.20 (t, *J* = 10.4 Hz, 1H), 3.02 (dd, *J* = 13.8, 7.5 Hz, 1H), 2.67 (dd, *J* = 13.9, 8.8 Hz, 1H), 2.17 – 2.07 (m, 1H), 1.96 (dd, *J* = 18.7, 9.8 Hz, 2H), 1.65 – 1.55 (m, 1H), 1.54 – 1.45 (m, 1H), 0.94 – 0.82 (m, 12H), 0.06 (d, *J* = 1.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 166.4, 164.4, 158.7, 152.8, 129.2, 125.8, 113.4, 99.6, 67.3, 54.3, 54.1, 53.7, 52.9, 52.4, 50.6, 49.0, 42.5, 41.3, 39.2, 38.4, 28.0, 24.8, 17.1, 12.8, -5.5, -5.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{48}N_5O_4Si$ 582.3470; Found 582.3460.

IR (film) ν_{max} 2929, 2348, 1712, 1570, 1514, 1461, 1357, 1251, 1206, 1177, 1112, 1050, 938, 839, 776, 683, 614 cm^{-1}.



22 **23**

A solution of **22** (49.3 mg, 0.085 mmol) in 10 mL concentrated HCl was heated at 95 ℃ for 18 hours. The mixture was evaporated under reduced pressure to give **23** without further purification.

^{1}H NMR (400 MHz, D_2O) δ 5.67 (s, 1H), 4.02 (s, 1H), 3.93 (m, 1H), 3.88 – 3.77 (m, 2H), 3.72 (dddd, *J* = 11, 11, 3.6, 3.6 Hz, 1H), 3.30 – 3.18 (m, 1H), 2.75 – 2.63 (m, 2H), 2.16 (dt, *J* = 13.6, 3.4 Hz, 1H), 2.06 (*J* = 13.6, 3.4 Hz, 1H), 1.82 (ddd, *J* = 14.8, 10.4, 4.8 Hz, 1H), 1.77 – 1.65 (m, 1H), 1.54 (t, *J* = 12.0 Hz, 1H), 0.95 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, D_2O) δ 166.9, 154.3, 153.7, 152.9, 100.8, 67.9, 56.8, 46.7, 40.9, 39.2, 37.8, 37.3, 30.6, 12.9.

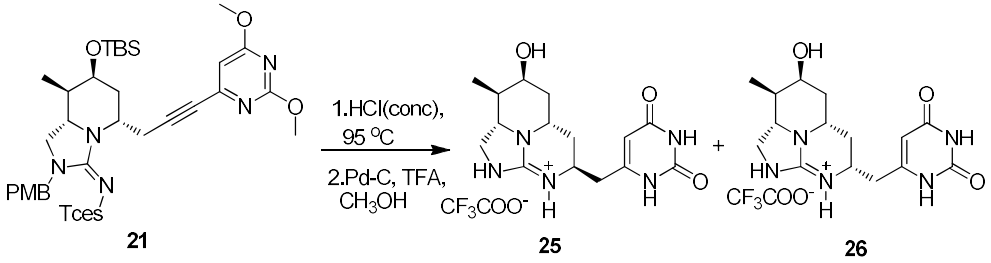
To a solution of **23** in dry DMF was added SO_3.pyr (160 mg, 1.07 mmol), the resulting mixture was stirred vigorously at room temperature for 12 hours. The filtrate was concentrated and the residue was purified by HPLC as same as Willimas, using the Waters Symmetry C-18 colum (4.6×250 mm) eluting with 8% MeOH/H_2O with 1% TFA at 1.0 mL/min, monitoring at 263 nm to give 8-epi-7-deoxycylindrospermopsin **24** (26.2 mg, 80% for 2 steps, t_R = 10.2 min).

(±)-8-epi-7-deoxycylindrospermopsin 24: **^{1}H NMR** (400 MHz, D_2O) δ 5.71 (s, 1H), 4.67 (s, 1H), 4.00-3.93 (m, 1H), 3.93-3.79 (m, 3H), 3.35 -3.25 (m, 1H), 2.78-2.67 (m, 2H), 2.48 (dt, *J* = 14.1, 3.5 Hz, 1H), 2.26-2.17 (dt, *J* = 14.0, 3.6 Hz, 1H), 1.89 (m, 2H), 1.60 (t, *J* = 12.8 Hz, 1H), 1.03 (d, *J* = 6.7 Hz, 3H).

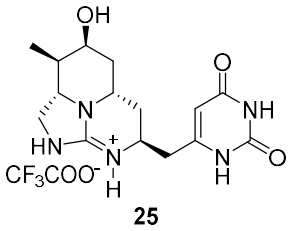
^{13}C NMR (100 MHz, D_2O) δ 166.9, 154.3, 153.7, 153.0, 100.8, 77.1, 56.9, 46.8, 46.6, 41.2, 38.6, 37.8, 34.9, 30.4, 12.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{22}N_5O_6S$ 400.1291; Found 400.1301.

IR (film) ν_{max} 3208, 2366, 1628, 4136, 1203, 1141, 839, 801, 723 cm^{-1}.



A solution of **21** (42 mg, 0.053 mmol) in 10 mL concentrated HCl was heated at 95 ℃ for 12 hours. The mixture was evaporated under reduced pressure to give the crude product which was used for hydrogenation step without any purification. To a solution of crude product in 1 mL methanol and 1 mL trifluoroacetic acid was added 100 mg 5% Pd/C, under a hydrogen atmosphere for 24 h, and then filtered through Celite, the filtrate was concentrated. The residue was purified by HPLC, using the Waters Symmetry C-18 colum (4.6×250 mm) eluting with 8% MeOH/H_2O with 1% TFA at 1.0 mL/min, monitoring at 263 nm to give **25** (1.6 mg, 7%, t_R = 26.1 min) and **26** (7.0 mg, 30%, t_R = 50.2 min).

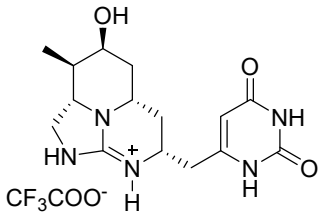


25: **^{1}H NMR** (400 MHz, D_2O) δ 5.71 (s, 1H), 4.06 (s, 1H), 4.02 – 3.94 (m, 1H), 3.94 – 3.82 (m, 2H), 3.75 (dddd, *J* = 11, 11, 3.6, 3.6 Hz, 1H), 3.28 (m, 1H), 2.79 – 2.69 (m, 2H), 2.20 (dt, *J* = 13.6, 3.4 Hz, 1H), 2.10 (dt, *J* = 13.9, 3.4 Hz, 1H), 1.86 (ddd, *J* = 14.8, 10.4, 4.8 Hz, 1H), 1.81 – 1.69 (m, 1H), 1.58 (t, *J* = 12.0 Hz, 1H), 0.99 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, D_2O) δ 166.9, 163.0 (q, *J* = 35.3 Hz), 154.3, 153.7, 153.0, 116.3 (q, *J* = 289.8 Hz), 100.8, 67.9, 56.7, 46.7,46.7, 40.9, 39.2, 37.8, 37.3, 30.7, 12.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{22}N_5O_3$ 320.1717; Found 320.1712.

IR (film) ν_{max} 3329, 3194, 1663, 1429, 1345, 1201, 1136, 837, 801, 721 cm^{-1}.



26

26: **^{1}H NMR** (400 MHz, D_2O) δ 5.75 (s, 1H), 4.03 (s, 1H), 3.85 (m, 2H), 3.76 (ddd, *J* = 10.8, 10.8, 8.8 Hz,1H), 3.64 (ddt, *J* = 10.8, 10.8, 3.6 Hz, 1H), 3.26 (dd, *J* = 10.6, 9.0 Hz, 1H), 2.76 (d, *J* = 6.8 Hz, 2H), 2.29 (dt, *J* = 13.2, 3.5 Hz, 1H), 2.10 (dt, *J* = 14.0, 3.5 Hz, 1H), 1.71 (m, 1H), 1.52 (dd, *J* = 24.2, 11.5 Hz, 2H), 0.97 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, D_2O) δ 166.8, 162.9 (q, *J* = 35.5 Hz), 154.9, 153.3, 152.9, 116.3 (q, *J* = 289.8 Hz), 100.9, 67.9, 56.4, 47.6, 47.3, 44.0, 39.4, 37.3, 36.9, 33.1, 12.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{22}N_5O_3$ 320.1717; Found 320.1713.

IR (film) ν_{max} 3188, 2921, 1662, 1425, 1344, 1200, 1134, 836, 802 cm^{-1}.

3. ^{1}H NMR Signal Assignment of Compound 22

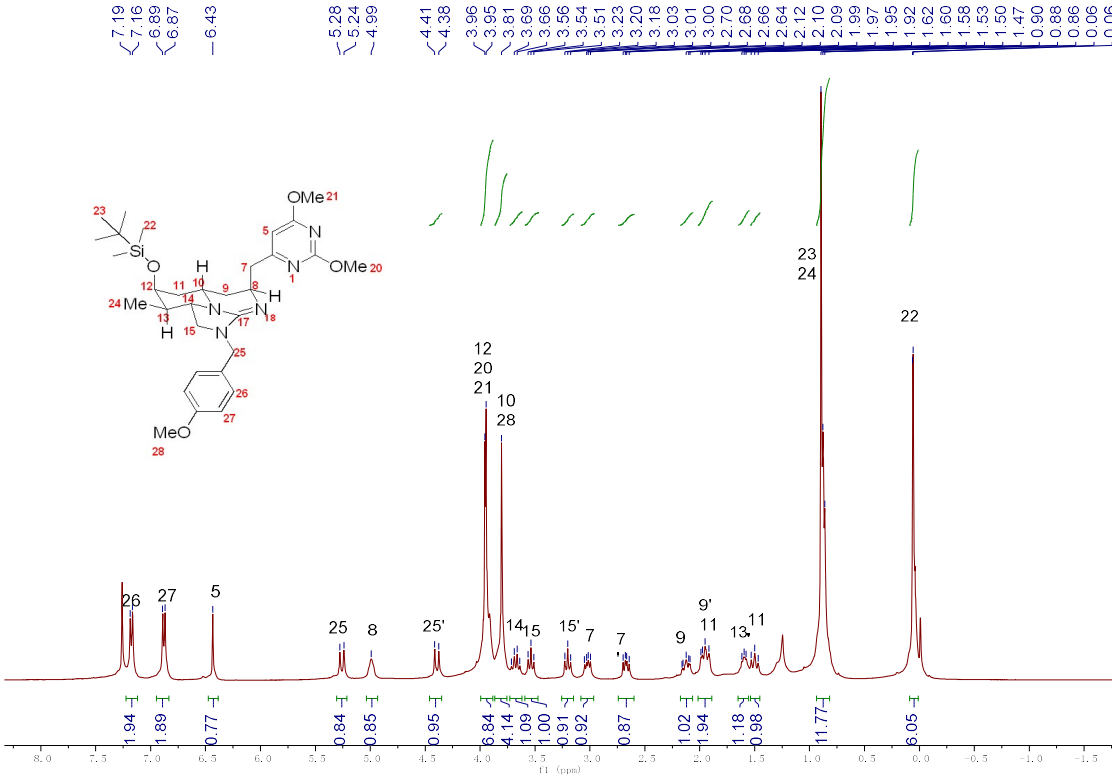
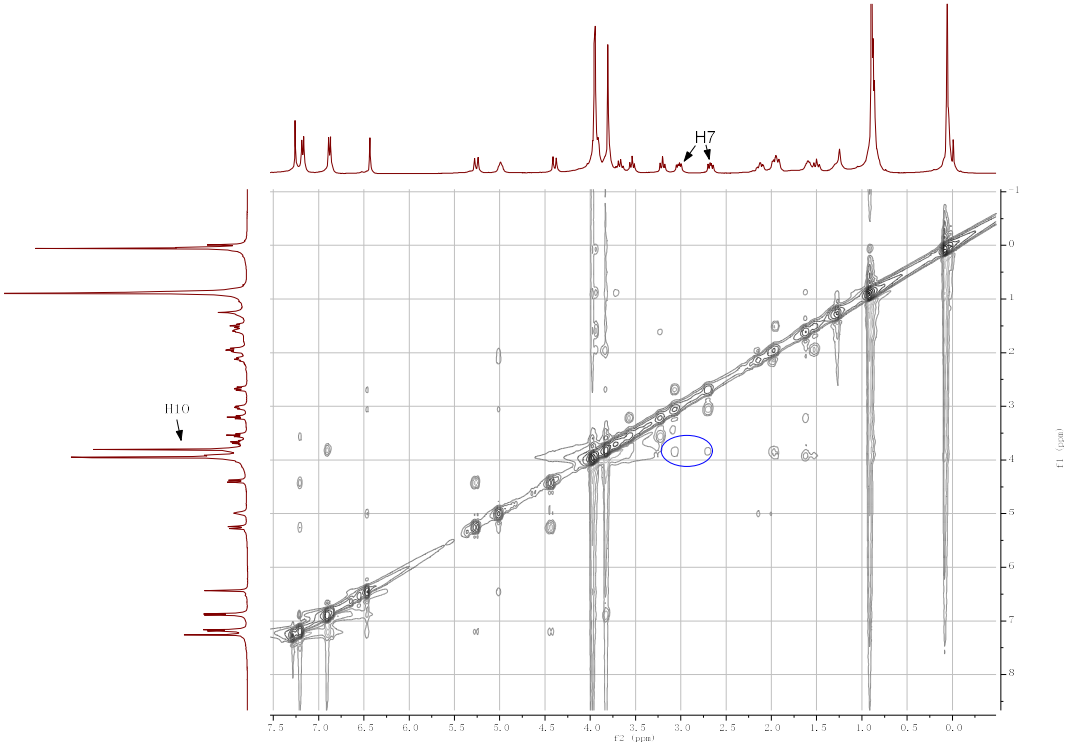
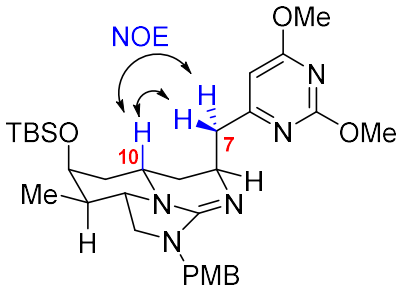


Figure S1 ^{1}H NMR signal assignment of compound **22**

4. NOESY of Compound 22





22

Figure S2 NOESY spectral contour plot of **22**

5. Comparison of ^{1}H NMR Spectra of Reported and Synthetic 8-epi-7-deoxycylindrospermopsin

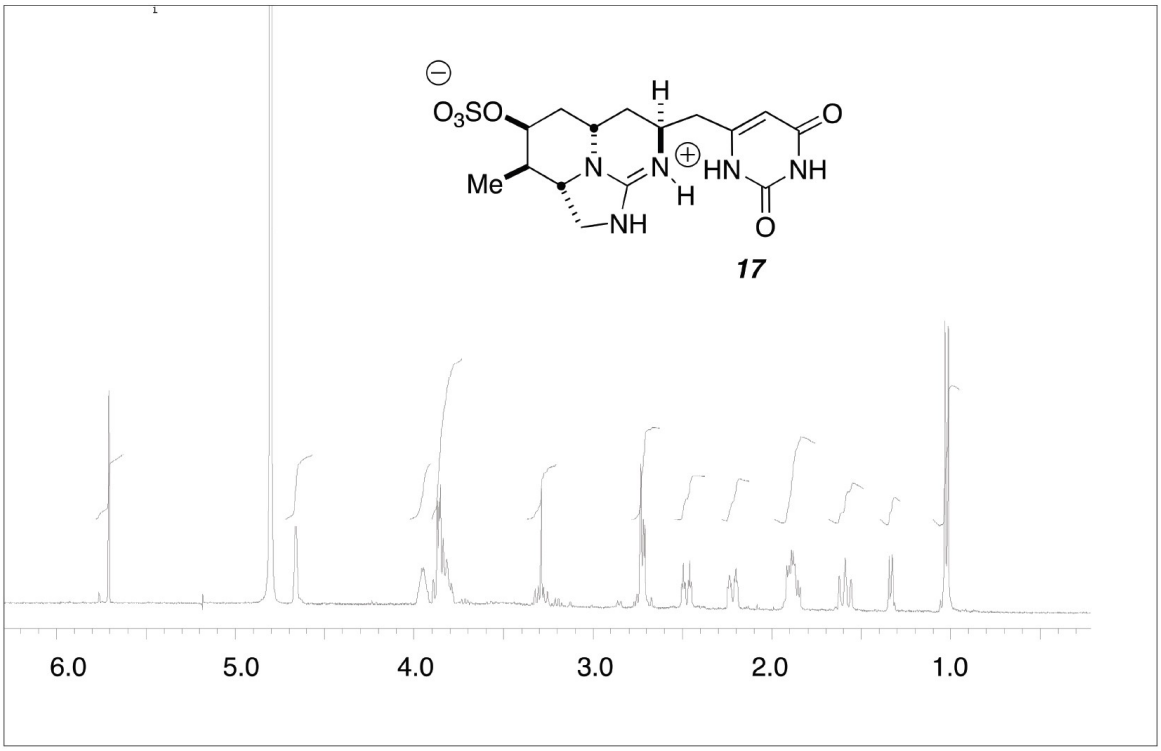


Figure S3 ^{1}H NMR spectrum of Reported 8-epi-7-Deoxycylindrospermopsin (**17)** by Williams (Copyright: Williams *et al. Angew. Chem., Int. Ed.*, 2005, **44**, 3879).

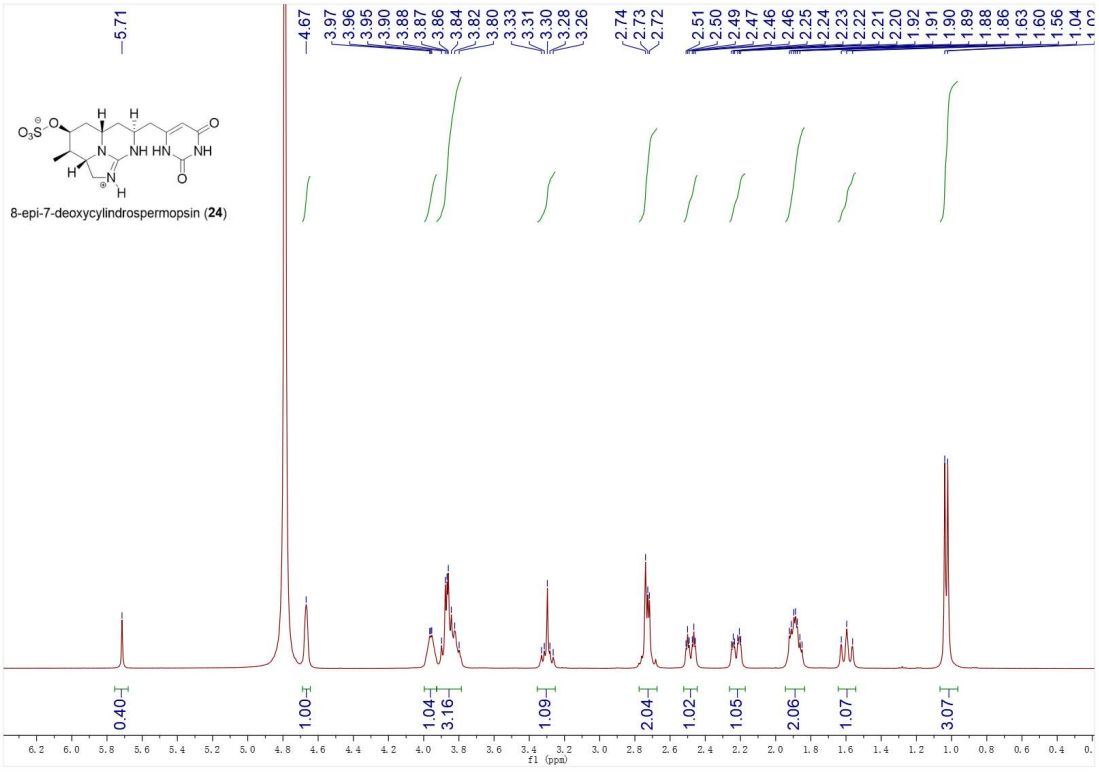
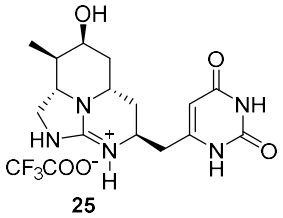


Figure S4 ^{1}H NMR spectrum of Synthetic 8-epi-7-deoxycylindrospermopsin (**24**)

6. Comparison of NMR Data of Reported and Synthetic 25



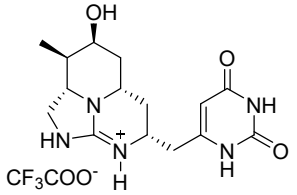
25

Table S1 Comparison of ^{1}H NMR Data of 25

Reported Data by Williams (500 MHz, D_2O)[a]	Synthetic Data (400 MHz, D_2O)
5.68 (s, 1H)	5.71 (s, 1H)
4.03 (br s, 1H)	4.06 (s, 1H)
3.92 (m, 1H)	4.02 – 3.94 (m, 1H)
3.82 (dd, *J* = 9, 9 Hz, 1H)	3.94 – 3.82 (m, 2H)
3.78 (dd, *J* = 9,9 Hz, 1H)	
3.72 (dddd, *J* = 11, 11, 4, 4 Hz, 1H)	3.75 (dddd, *J* = 11, 11, 3.6, 3.6 Hz, 1H)
3.25 (m, 1H)	3.28 (m, 1H)
2.71 (dd, *J* = 14, 5.5 Hz, 1H)	2.79 – 2.69 (m, 2H)
2.67 (dd, *J* = 14, 9 Hz, 1H)	
2.16 (dt, *J* = 14, 4, 4 Hz, 1H)	2.20 (dt, *J* = 13.6, 3.4 Hz, 1H)
2.06 (dt, *J* = 15, 3 Hz, 1H)	2.10 (dt, *J* = 13.9, 3.4 Hz, 1H)
1.83(ddd, *J* = 15, 11, 5 Hz, 1H)	1.86 (ddd, *J* = 14.8, 10.4, 4.8 Hz, 1H)
1.72 (ddq, *J* = 14, 7, 3 Hz, 1H)	1.81 – 1.69 (m, 1H)
1.55 (ddd, *J* = 14, 14, 1.5 Hz, 1H)	1.58 (t, *J* = 12.0 Hz, 1H)
0.95 (d, *J* = 7 Hz, 3H)	0.99 (d, *J* = 6.9 Hz, 3H)

[a] Compound **15**: Williams *et al. Angew. Chem., Int. Ed.* 2005, **44**, 3879-3881.

7. Comparison of NMR Data of Reported and Synthetic 26



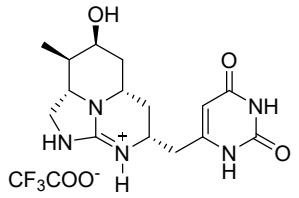
26

Table S2 Comparison of ^{1}H NMR Data of 26

Reported Data by Williams (500 MHz, D_2O)[a]	Reported Data by Zakarian (600 MHz, D_2O)[b]	Synthetic Data (400 MHz, D_2O)
5.72 (s, 1H)	5.72 (s, 1H)	5.75 (s, 1H)
4.00 (br s, 1H)	4.00 (s, 1H)	4.03 (s, 1H)
3.86 (buried m, 1H)	3.91 – 3.80 (m, 2H)	3.85 (m, 2H)
3.82 (dd, *J* = 9.0, 9.0 Hz, 1H)		
3.74 (dd, *J* =10,10 Hz, 1H)	3.78 – 3.68 (m, 1H)	3.76 (ddd, *J* = 10.8, 10.8, 8.8 Hz, 1H)
3.61 (ddt, *J* = 11, 11, 3.5 Hz, 1H)	3.66 – 3.55 (m, 1H)	3.64 (ddt, *J* = 10.8, 10.8, 3.6 Hz, 1H)
3.23 (dd, *J* = 10, 10 Hz, 1H)	3.23 (dd, *J* = 10.8, 9.4 Hz, 1H)	3.26 (dd, *J* = 10.6, 9.0 Hz, 1H)
2.73 (app d, *J* = 5 Hz, 1H)	2.74 (d, *J* = 6.9 Hz, 2H)	2.76 (d, *J* = 6.8 Hz, 2H)
2.26 (dt, *J* = 15, 5, 5 Hz, 1H)	2.31 – 2.23 (m, 1H)	2.29 (dt, *J* = 13.2, 3.5 Hz, 1H)
2.07 (dt, *J* = 15, 3, 3, Hz, 1H)	2.16 – 2.03 (m, 1H)	2.10 (dt, *J* = 14.0, 3.5 Hz, 1H)
1.70 (ddq, *J* = 9, 6.5, 2.5, 1H)	1.75 – 1.65 (m, 1H)	1.71 (m, 1H)
1.50 (app q, *J* = 11 Hz, 2H)	1.56 – 1.43 (m, 2H)	1.52 (dd, *J* = 24.2, 11.5 Hz, 2H)
0.95 (d, *J* = 6.5 Hz, 3H)	0.95 (d, *J* = 6.9 Hz, 3H)	0.97 (d, *J* = 6.9 Hz, 3H).

[a] Compound **14**: Williams *et al*. *Angew. Chem., Int. Ed.* 2005, **44**, 3879-3881.

[b] Compound **18**: Zakarian *et al*. *J. Am. Chem. Soc*. 2018, **140**, 6027-6032.



26

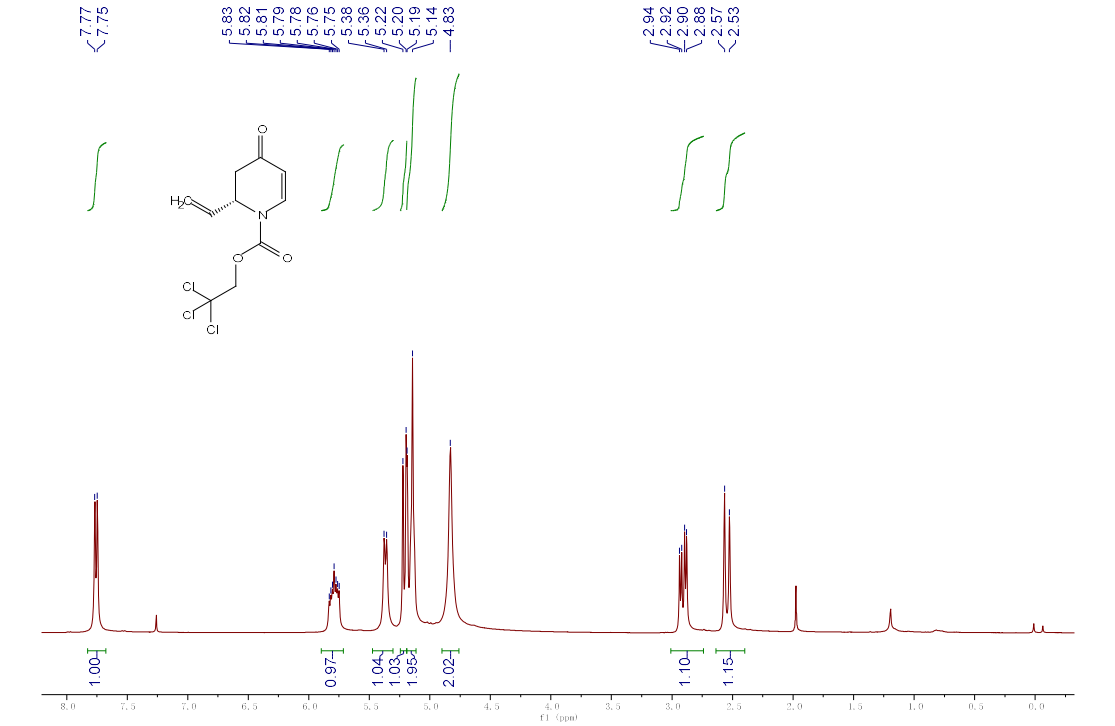
Table S3 Comparison of ^{13}C NMR Data of 26

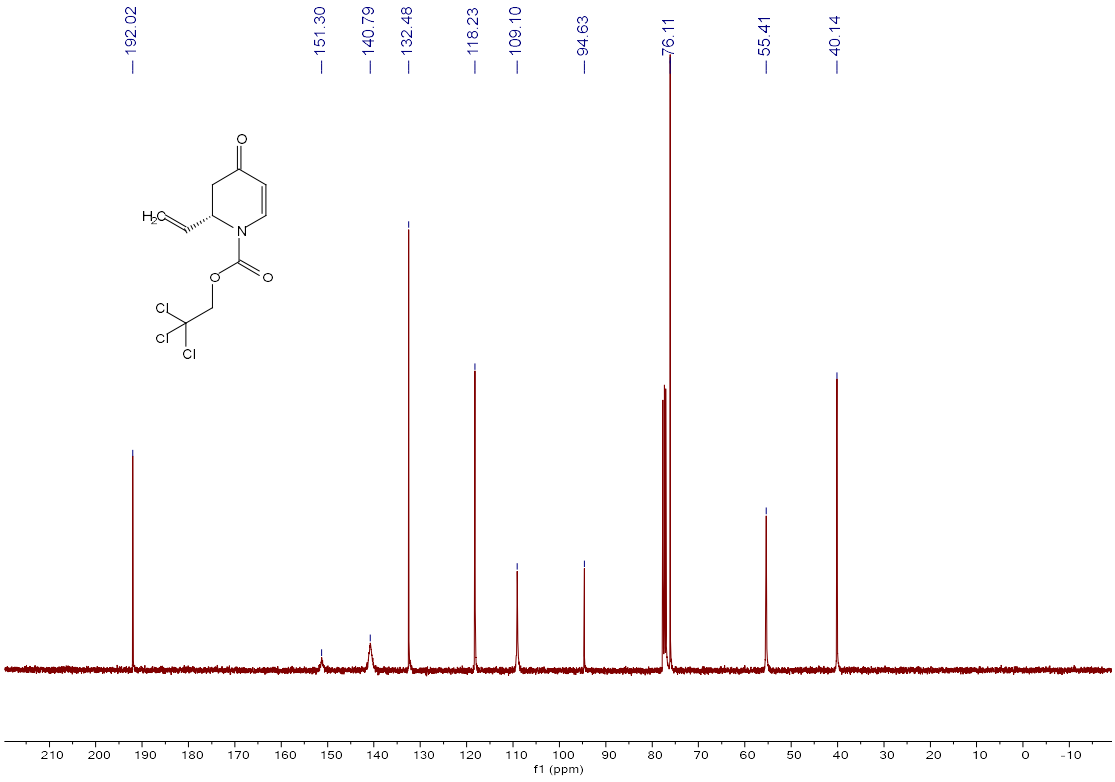
Reported Data by Zakarian (150 MHz, D_2O)[a]	Synthetic Data (100 MHz, D_2O)
166.6	166.8
162.6 (q, *J* = 35.6 Hz)	162.9 (q, *J* = 35.5 Hz)
154.7	154.9
153.1	153.3
152.7	152.9
116.1 (q, *J* = 291.4 Hz)	116.3 (q, *J* = 289.8 Hz)
100.7	100.9
67.7	67.9
56.2	56.4
47.4	47.6
47.1	47.3
43.8	44.0
39.2	39.4
37.1	37.3
36.7	36.9
32.9	33.1,
12.6	12.7

[a] Compound **18**: Zakarian *et al*. *J. Am. Chem. Soc*. 2018, **140**, 6027-6032.

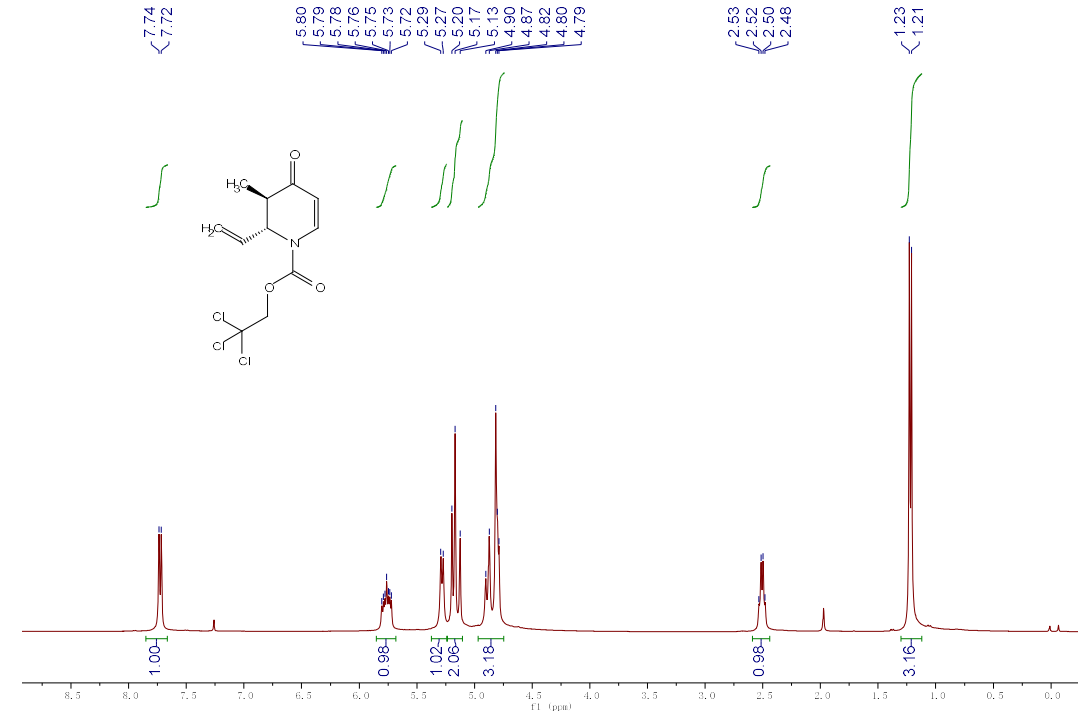
8. NMR Spectra

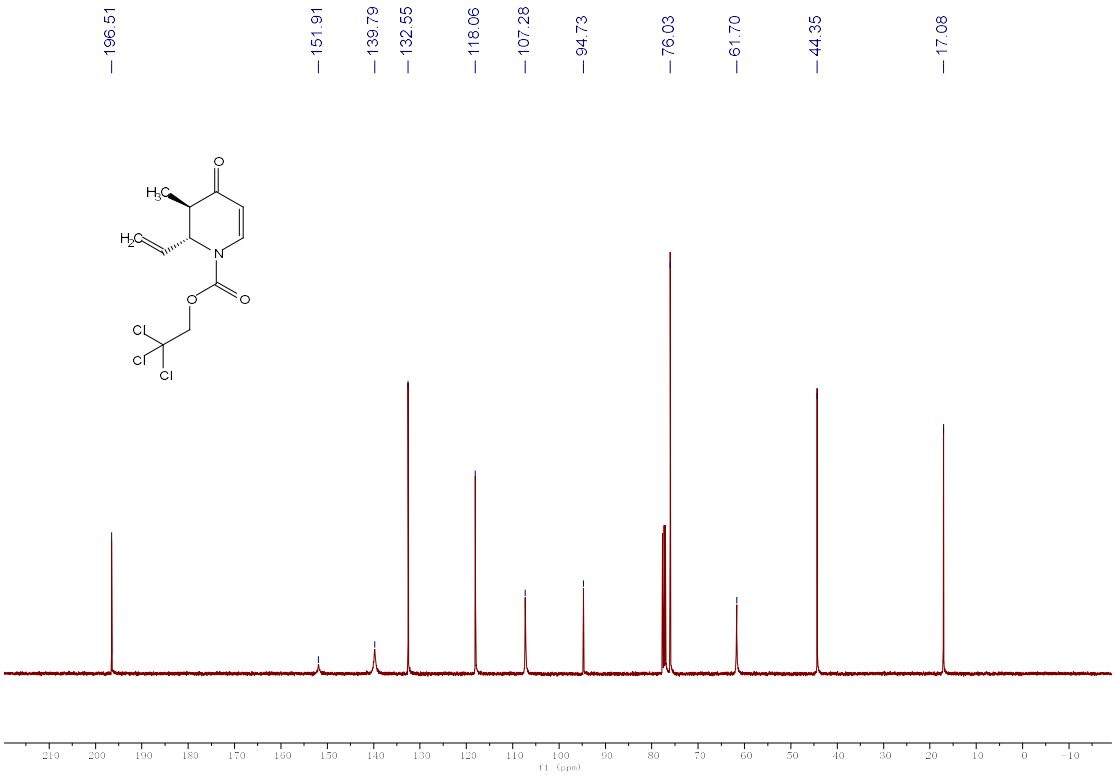
Compound **8**



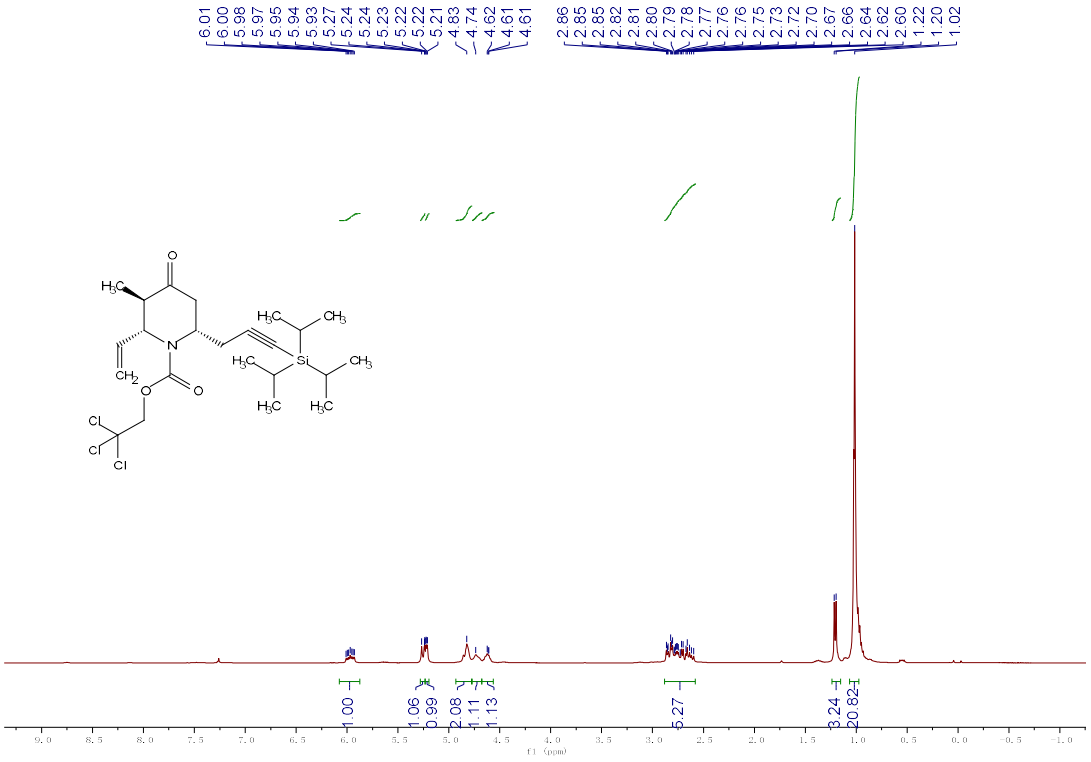


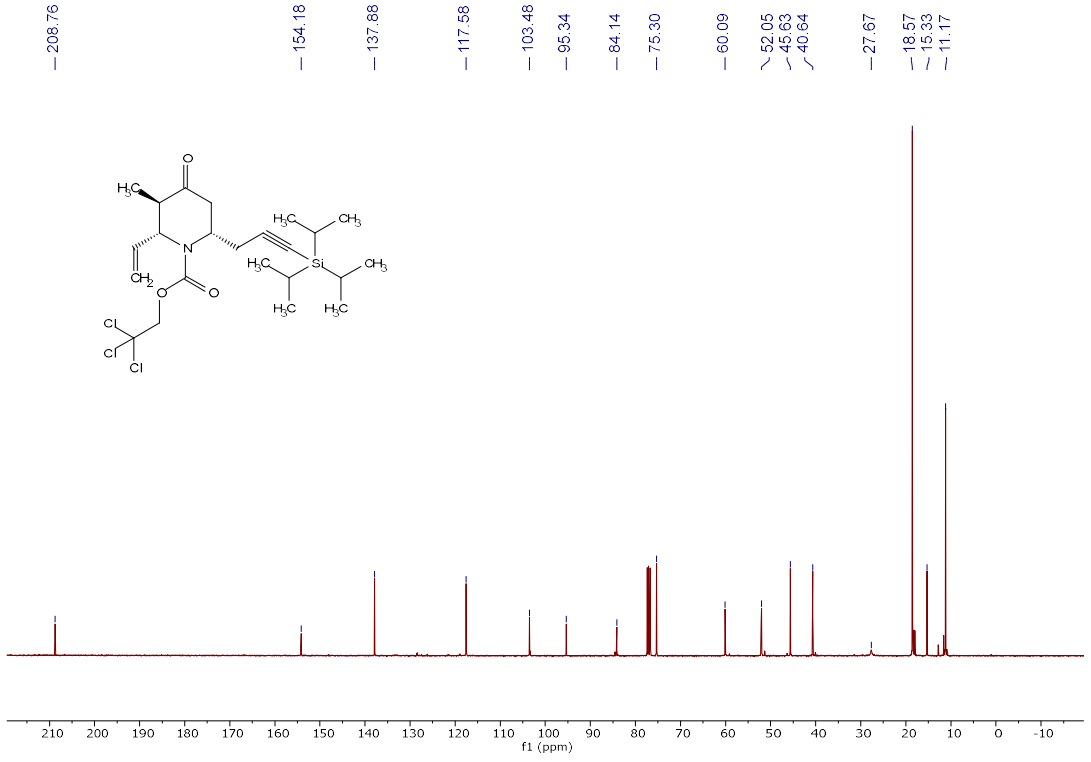
Compound **9**


7.74
7.72
5.80
5.79
5.78
5.76
5.75
5.73
5.72
5.29
5.27
5.20
5.17
5.13
4.90
4.87
4.82
4.80
4.79
2.53
2.52
2.50
2.48
1.23
1.21
1.00
0.98
1.02
2.06
3.18
0.98
3.16

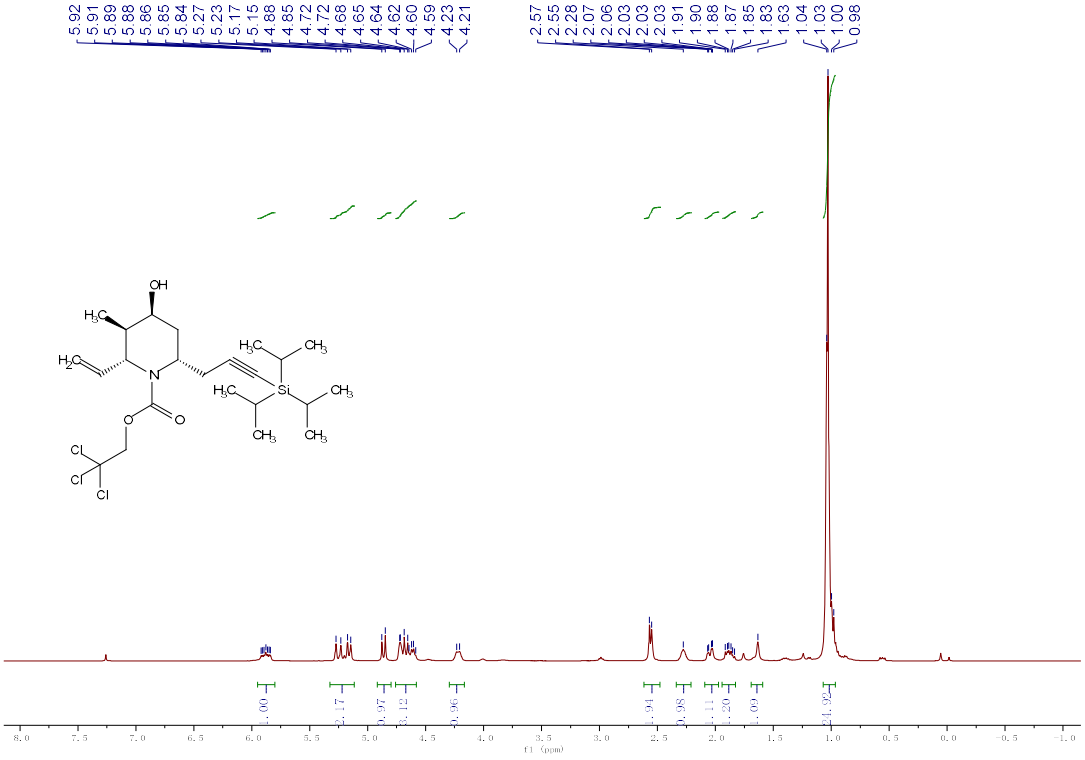

196.51
151.91
139.79
132.55
118.06
107.28
94.73
76.03
61.70
44.35
17.08

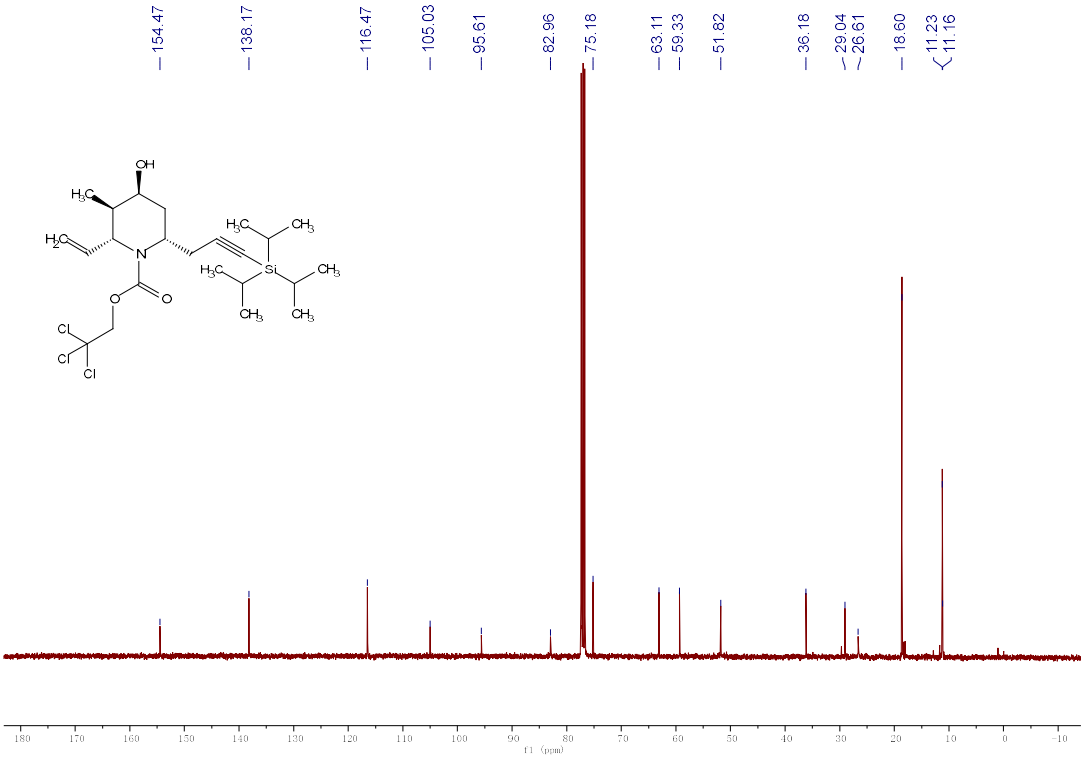
Compound **11**

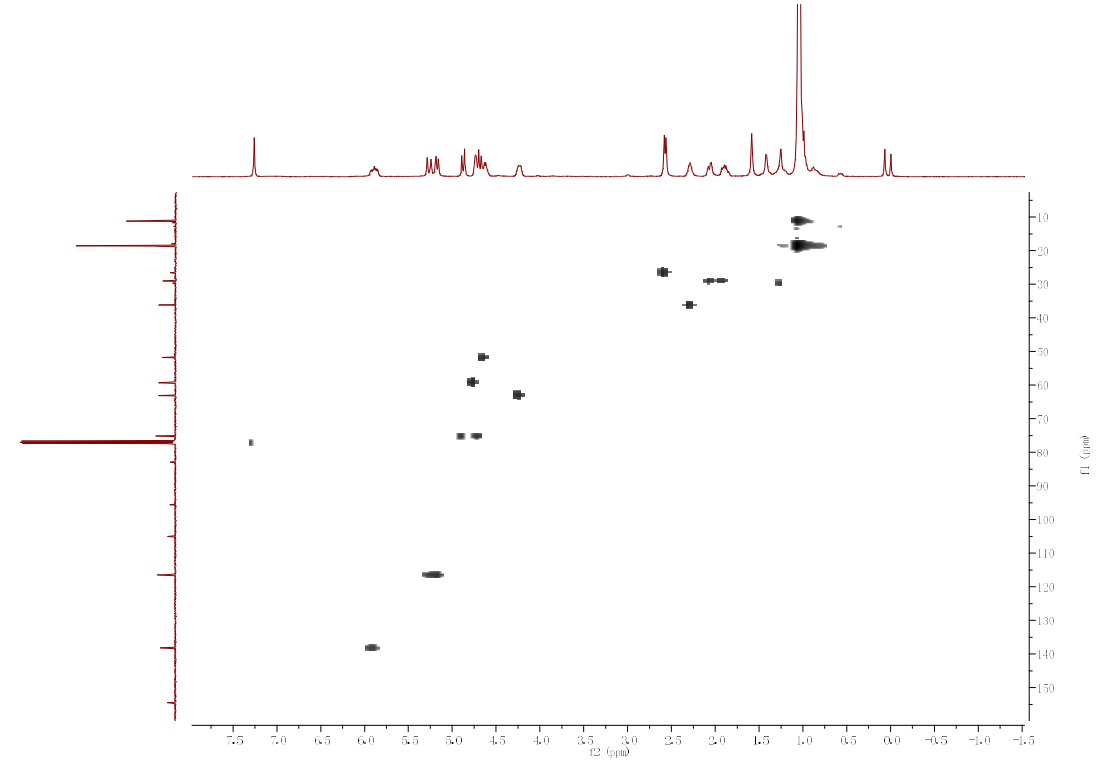

6.01
6.00
5.98
5.97
5.95
5.94
5.93
5.27
5.24
5.24
5.23
5.22
5.22
5.21
4.83
4.74
4.62
4.61
4.61
2.86
2.85
2.85
2.82
2.81
2.80
2.79
2.78
2.77
2.76
2.76
2.75
2.73
2.72
2.70
2.67
2.66
2.64
2.62
2.60
1.22
1.20
1.02
1.00
1.06
0.99
2.08
1.11
1.13
6.27
3.24
20.82
f1 (ppm)

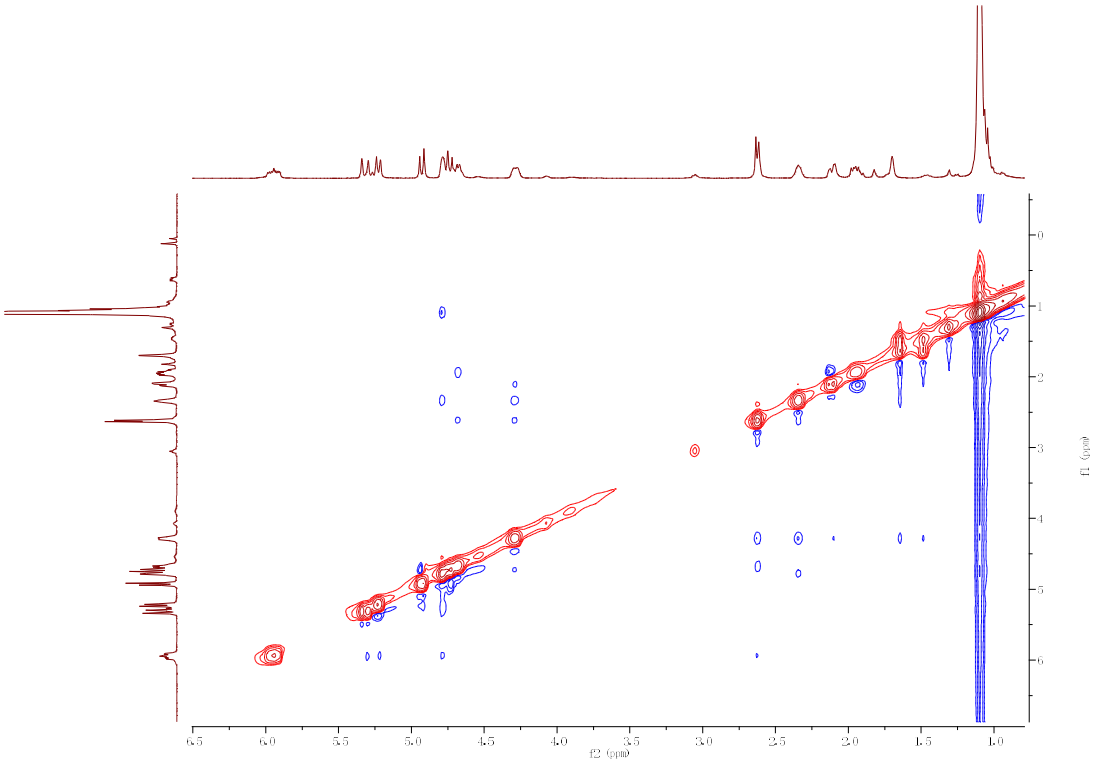

208.76
154.18
137.88
117.58
103.48
95.34
84.14
75.30
60.09
52.05
45.63
40.64
27.67
18.57
15.33
11.17
f1 (ppm)

Compound **12**

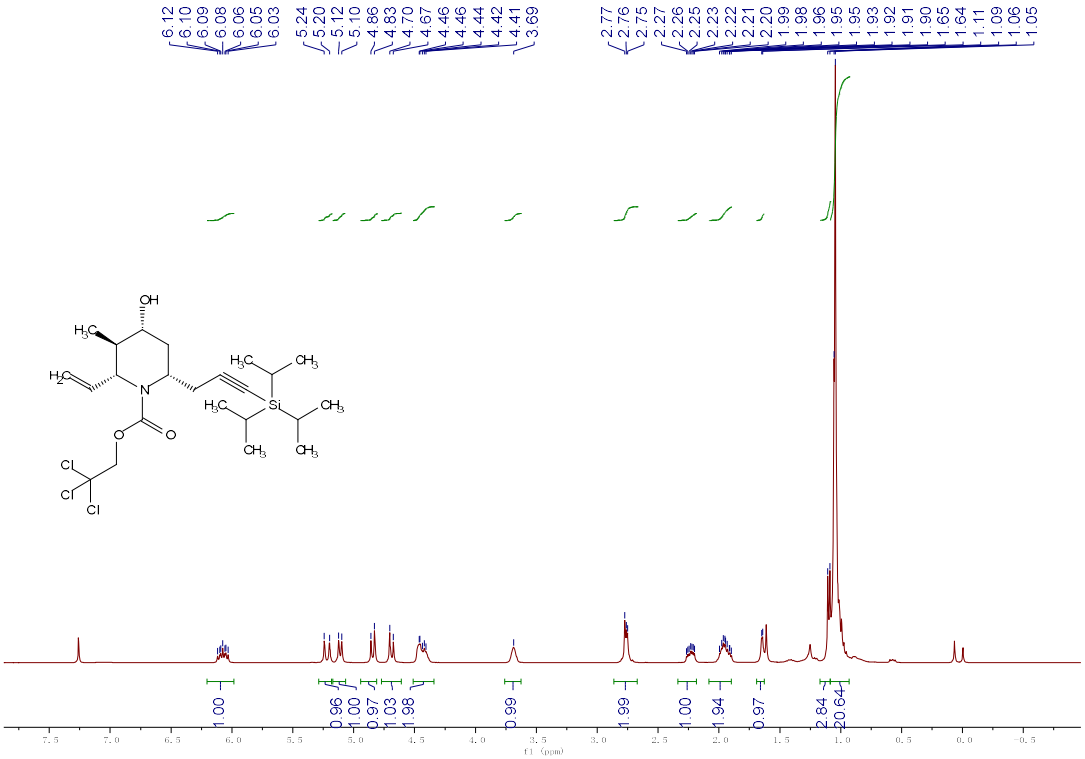

5.92
5.91
5.89
5.88
5.86
5.85
5.84
5.27
5.23
5.17
5.15
4.88
4.85
4.72
4.72
4.68
4.65
4.64
4.62
4.60
4.59
4.23
4.21
2.57
2.55
2.28
2.07
2.06
2.03
2.03
2.03
1.91
1.90
1.88
1.87
1.85
1.83
1.63
1.04
1.03
1.00
0.98
OH
H3C
H2C
N
O
O
H3C
CH3
H3C
Si
CH3
H3C
CH3
CH3
Cl
Cl
Cl
1.00
2.17
0.97
3.12
0.96
3.94
0.98
1.11
1.20
1.09
24.92
f1 (ppm)

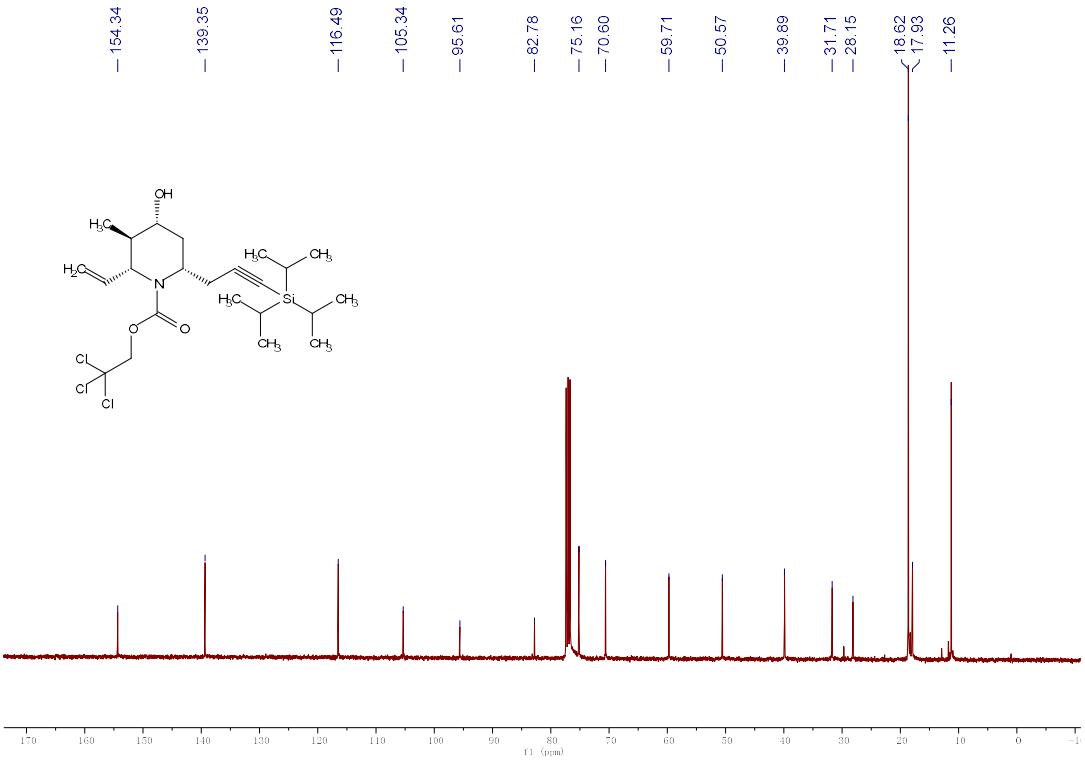

154.47
138.17
116.47
105.03
95.61
82.96
75.18
63.11
59.33
51.82
36.18
29.04
26.61
18.60
11.23
11.16
OH
H3C
H2C
N
O
O
H3C
CH3
H3C
Si
CH3
H3C
CH3
CH3
Cl
Cl
Cl
f1 (ppm)

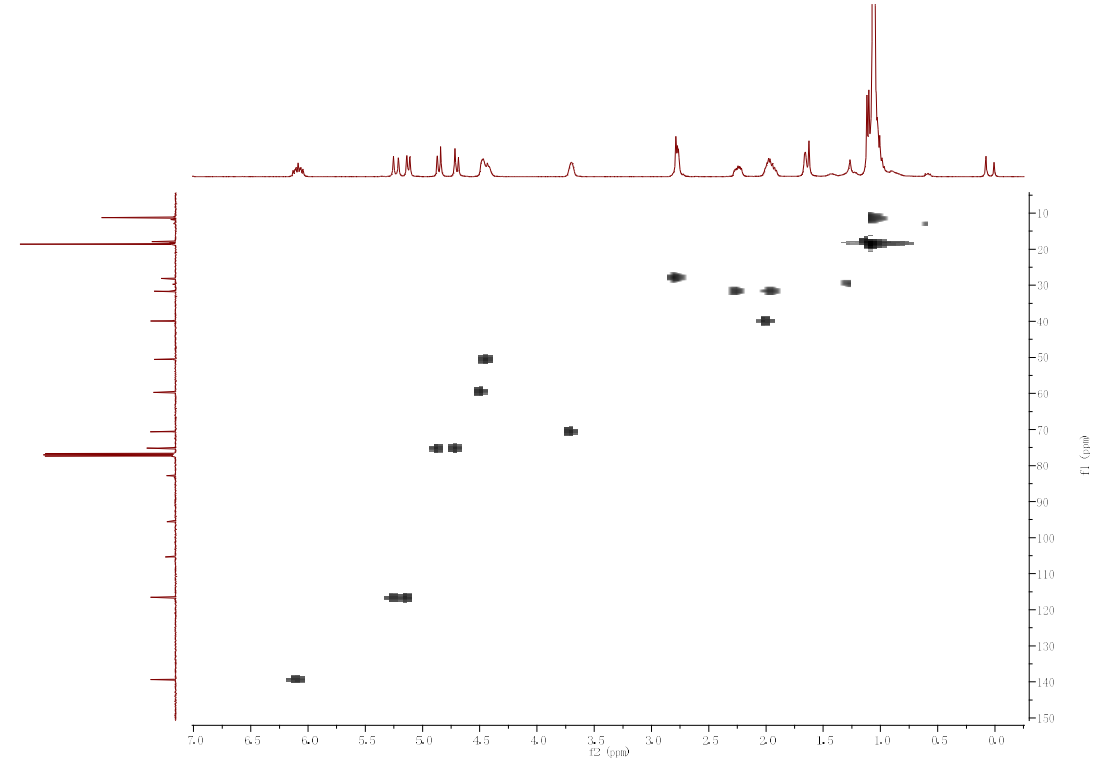

f2 (ppm)
f1 (ppm)

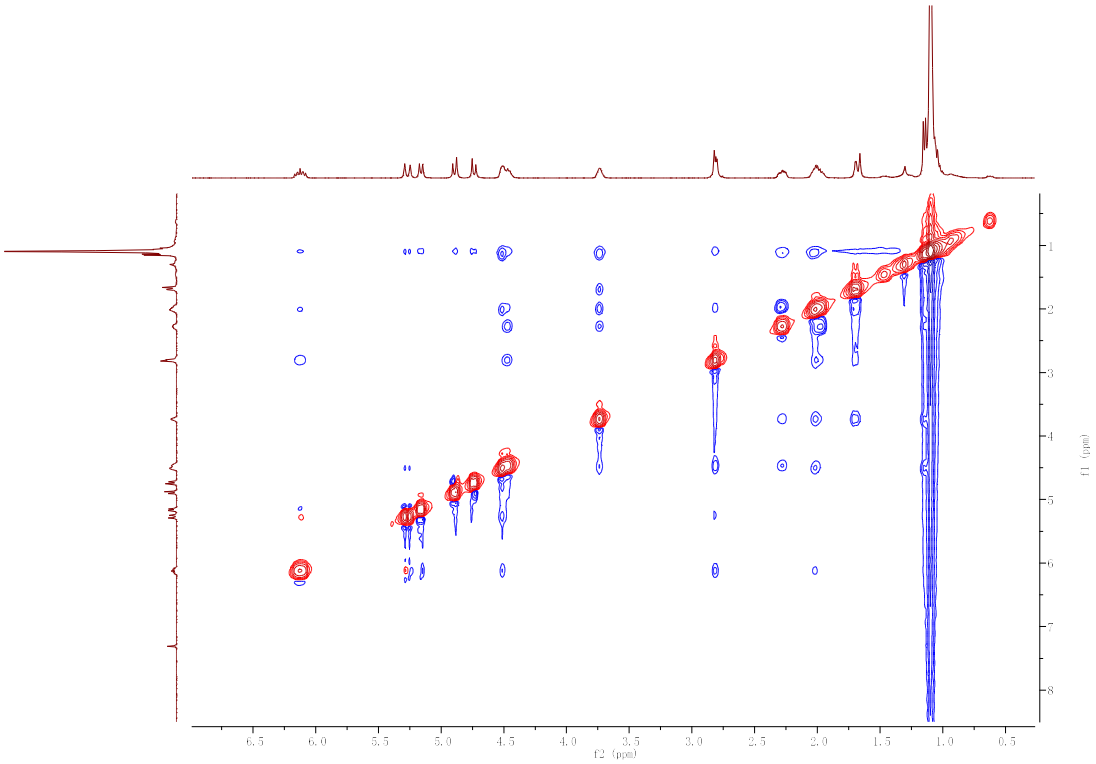

f2 (ppm)
f1 (ppm)

Compound **12'**

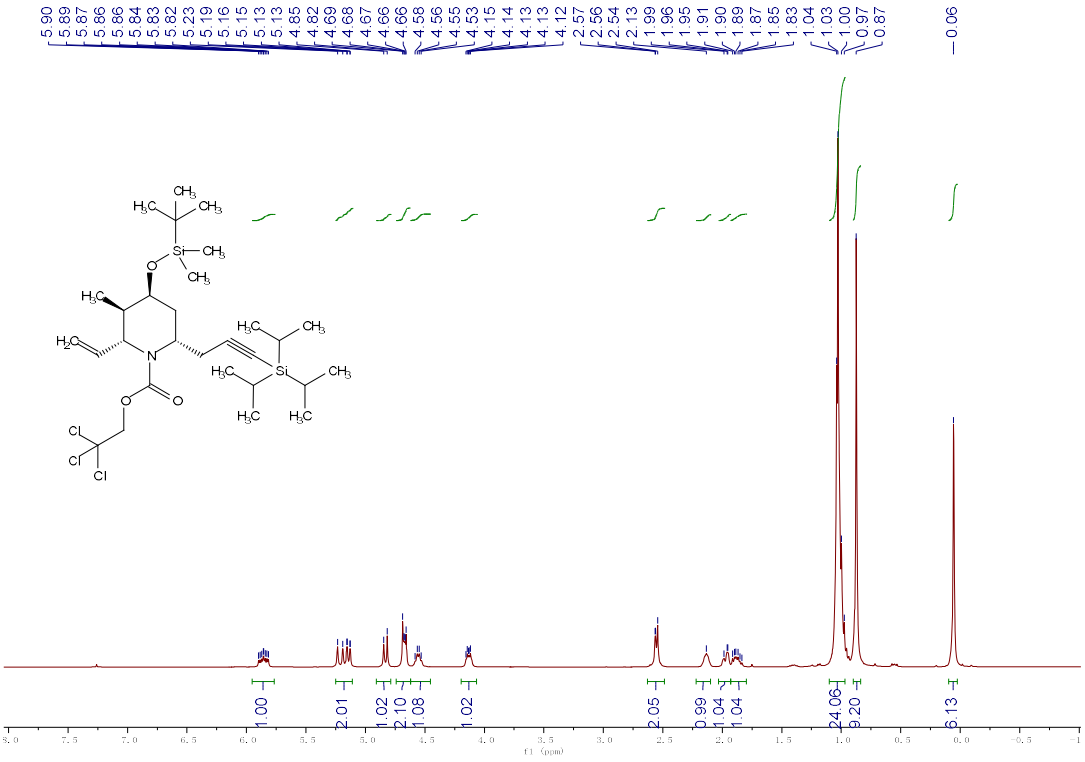

6.12
6.10
6.09
6.08
6.06
6.05
6.03
5.24
5.20
5.12
5.10
4.86
4.83
4.70
4.67
4.46
4.46
4.44
4.42
4.41
3.69
2.77
2.76
2.75
2.27
2.26
2.25
2.23
2.22
2.21
2.20
1.99
1.98
1.96
1.95
1.95
1.93
1.92
1.91
1.90
1.65
1.64
1.11
1.09
1.06
1.05
OH
H3C
H2C
N
O
O
H3C
CH3
H3C
Si
CH3
CH3
CH3
Cl
Cl
Cl
1.00
0.96
1.00
0.97
1.03
1.98
0.99
1.99
1.00
1.94
0.97
2.84
20.64
f1 (ppm)

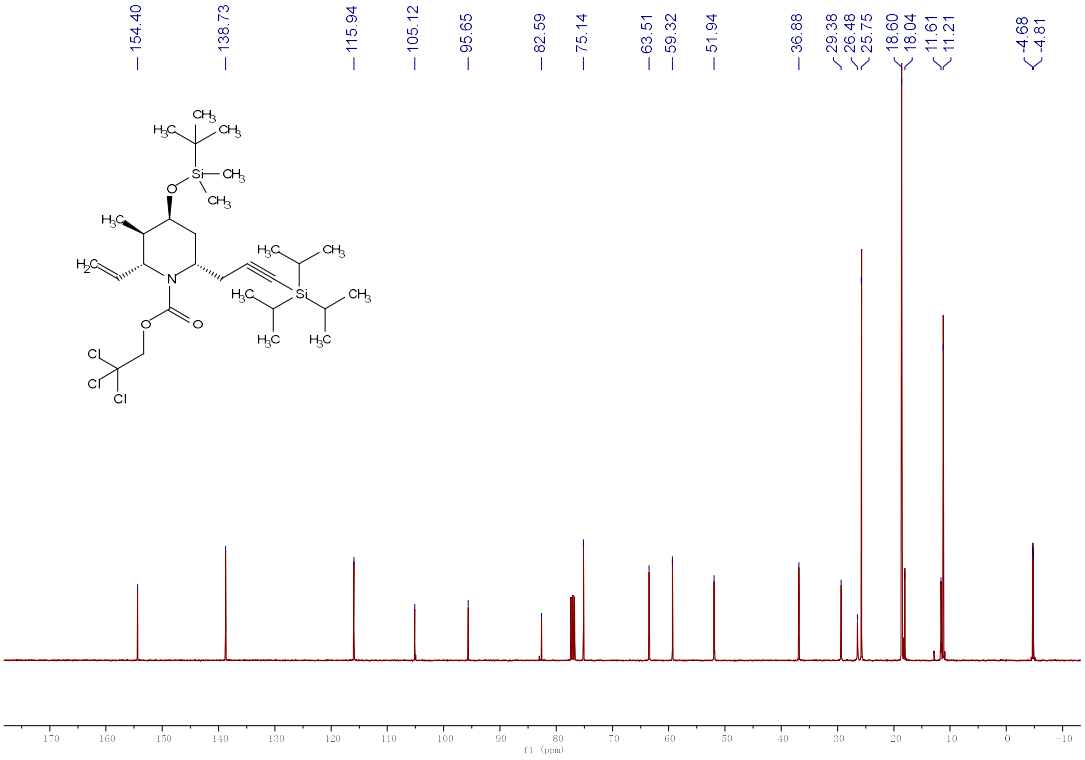

154.34
139.35
116.49
105.34
95.61
82.78
75.16
70.60
59.71
50.57
39.89
31.71
28.15
18.62
17.93
11.26
OH
H3C
H2C
N
O
O
H3C
CH3
H3C
Si
CH3
CH3
CH3
Cl
Cl
Cl
f1 (ppm)


f2 (ppm)
f1 (ppm)

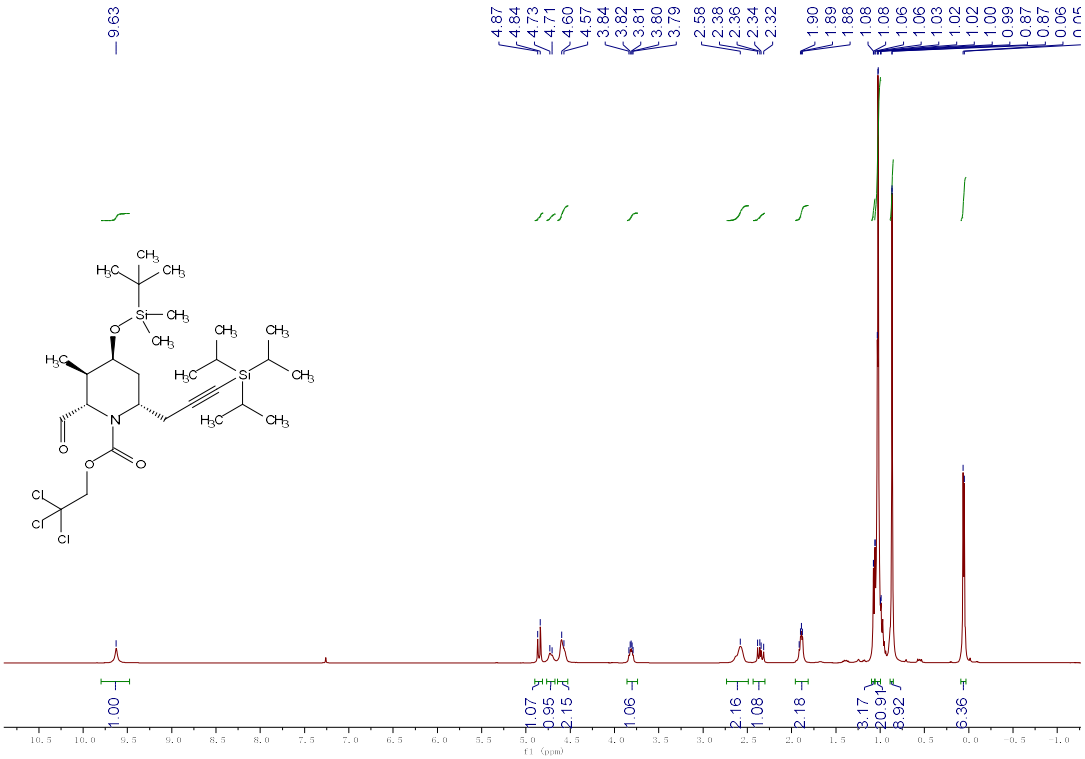

f2 (ppm)
f1 (ppm)

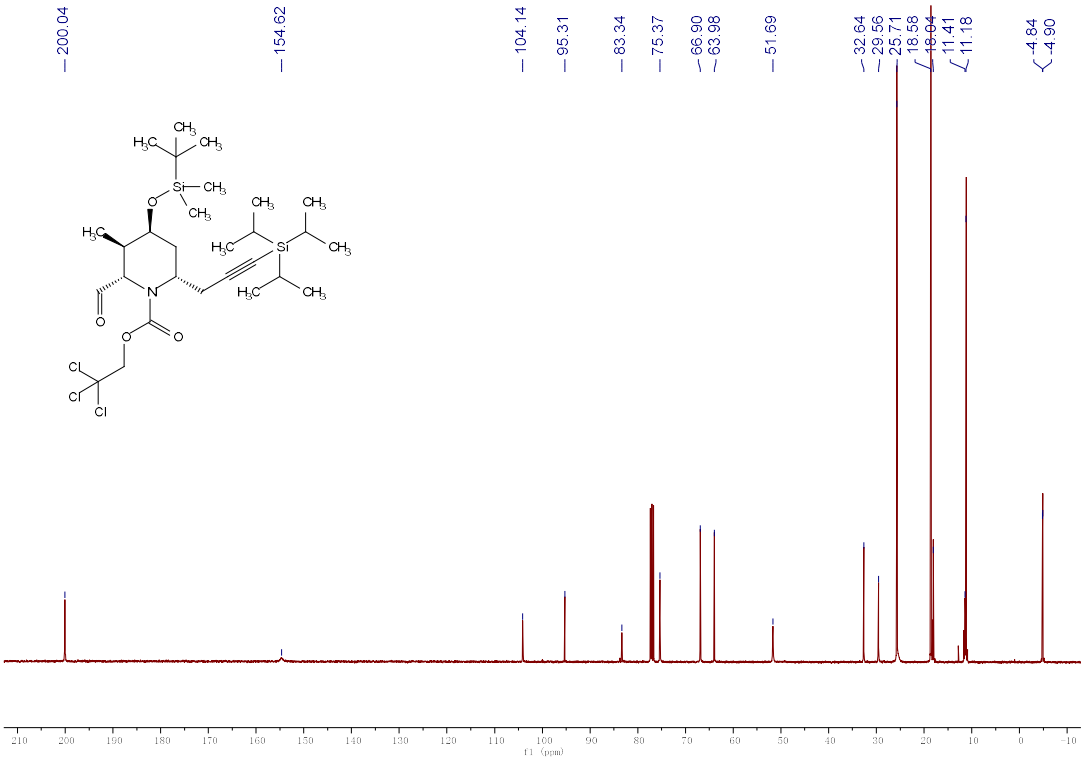
Compound **13**


5.90
5.89
5.87
5.86
5.86
5.84
5.83
5.82
5.23
5.19
5.16
5.15
5.13
5.13
4.85
4.82
4.69
4.68
4.67
4.66
4.66
4.58
4.56
4.55
4.53
4.15
4.14
4.13
4.12
2.57
2.56
2.54
2.13
1.99
1.96
1.95
1.91
1.90
1.89
1.87
1.85
1.83
1.04
1.03
1.00
0.97
0.87
0.06
1.00
2.01
1.02
2.10
1.08
1.02
2.05
0.99
1.04
1.04
24.06
9.20
6.13
f1 (ppm)

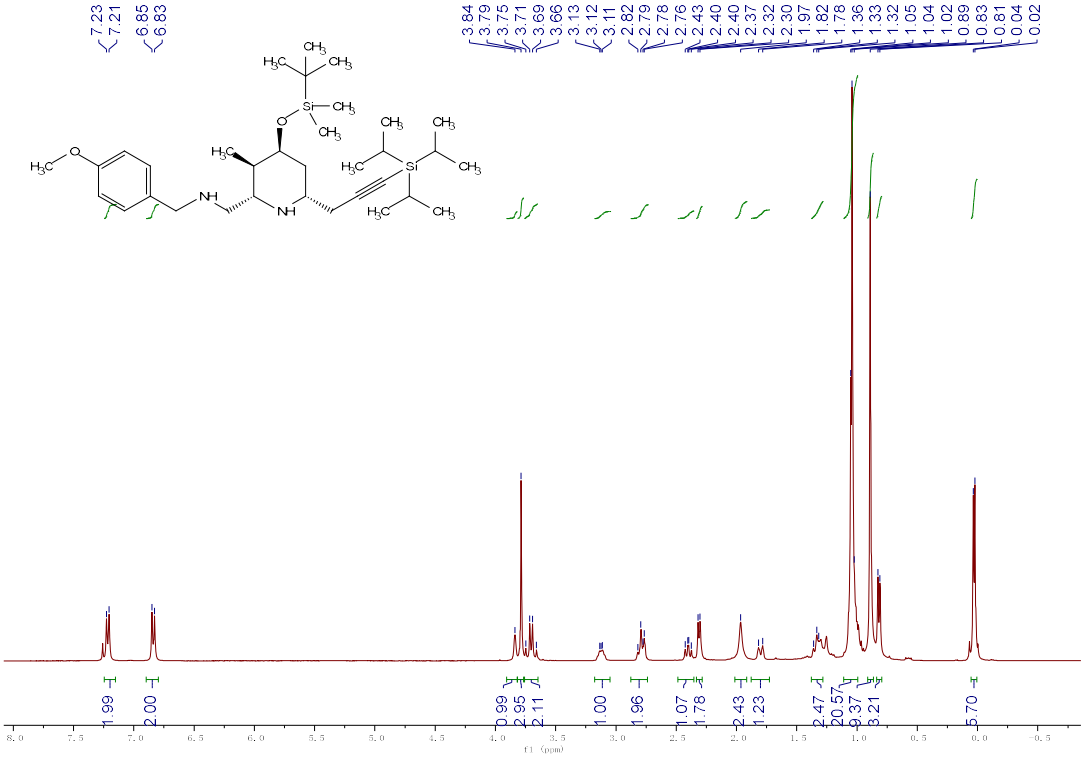

154.40
138.73
115.94
105.12
95.65
82.59
75.14
63.51
59.32
51.94
36.88
29.38
26.48
25.75
18.60
18.04
11.61
11.21
-4.68
-4.81
f1 (ppm)

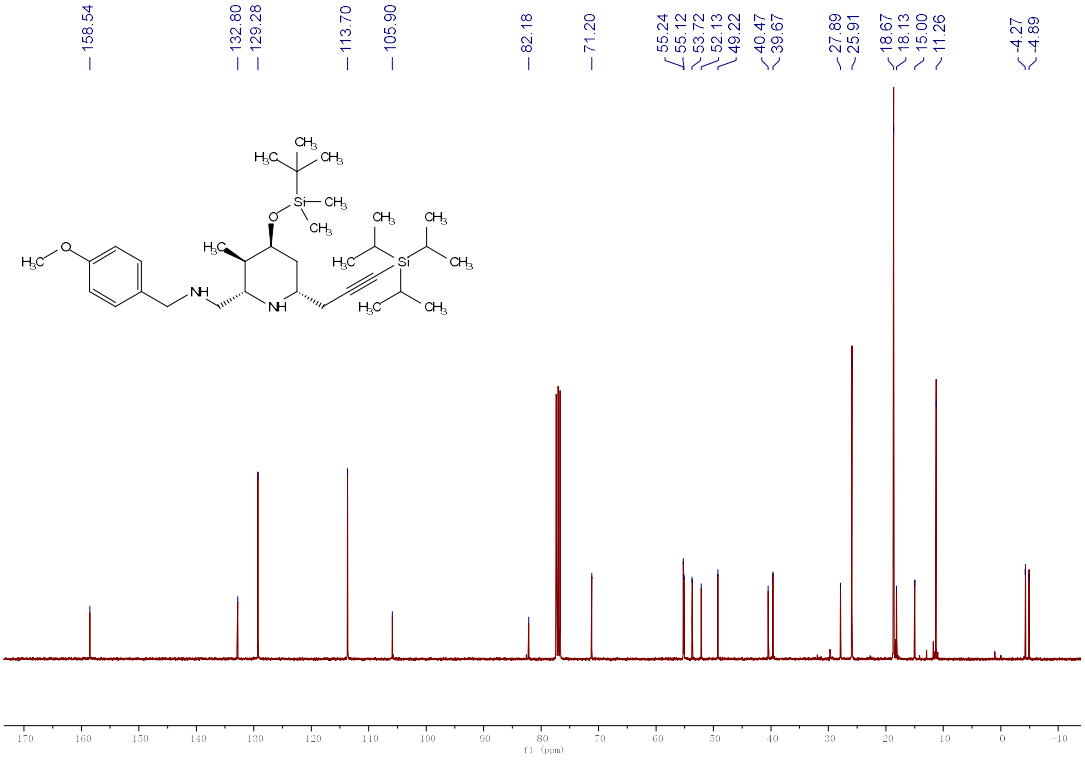
Compound **14**


9.63
4.87
4.84
4.73
4.71
4.60
4.57
3.84
3.82
3.81
3.80
3.79
2.58
2.38
2.36
2.34
2.32
1.90
1.89
1.88
1.08
1.08
1.06
1.06
1.03
1.02
1.02
1.00
0.99
0.87
0.87
0.06
1.00
1.07
0.95
2.15
1.06
2.16
1.08
2.18
3.17
20.91
8.92
6.36
f1 (ppm)

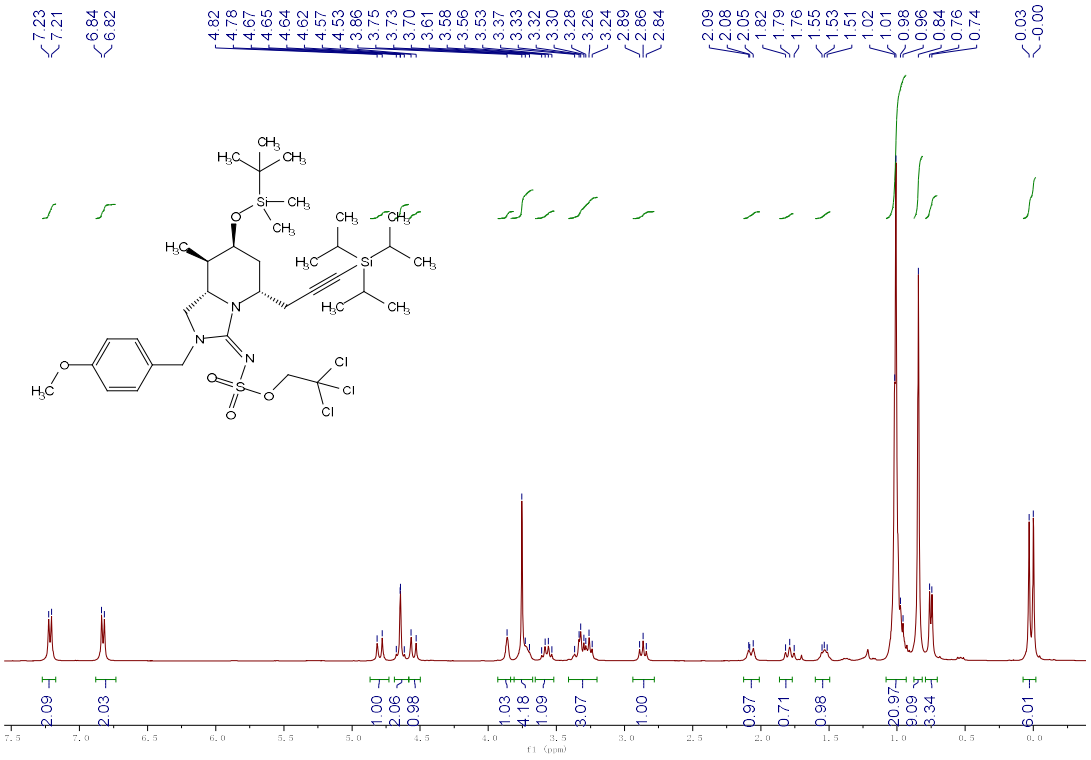

200.04
154.62
104.14
95.31
83.34
75.37
66.90
63.98
51.69
32.64
29.56
25.71
18.58
18.04
11.41
11.18
-4.84
-4.90
f1 (ppm)

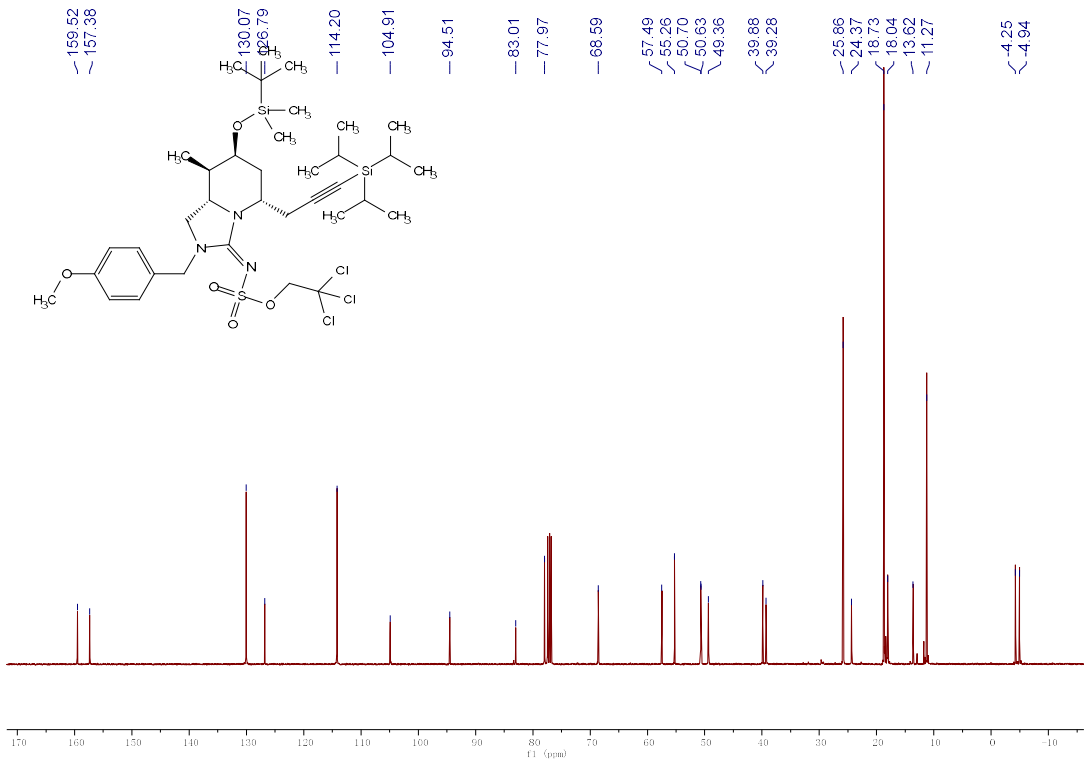
Compound **16**


7.23
7.21
6.85
6.83
3.84
3.79
3.75
3.71
3.69
3.66
3.13
3.12
3.11
2.82
2.79
2.78
2.76
2.43
2.40
2.37
2.32
2.30
1.97
1.82
1.78
1.36
1.33
1.32
1.05
1.04
1.02
0.89
0.83
0.81
0.04
0.02
1.99
2.00
0.99
2.95
2.11
1.00
1.96
1.07
1.78
2.43
1.23
2.47
20.57
9.37
8.21
5.70

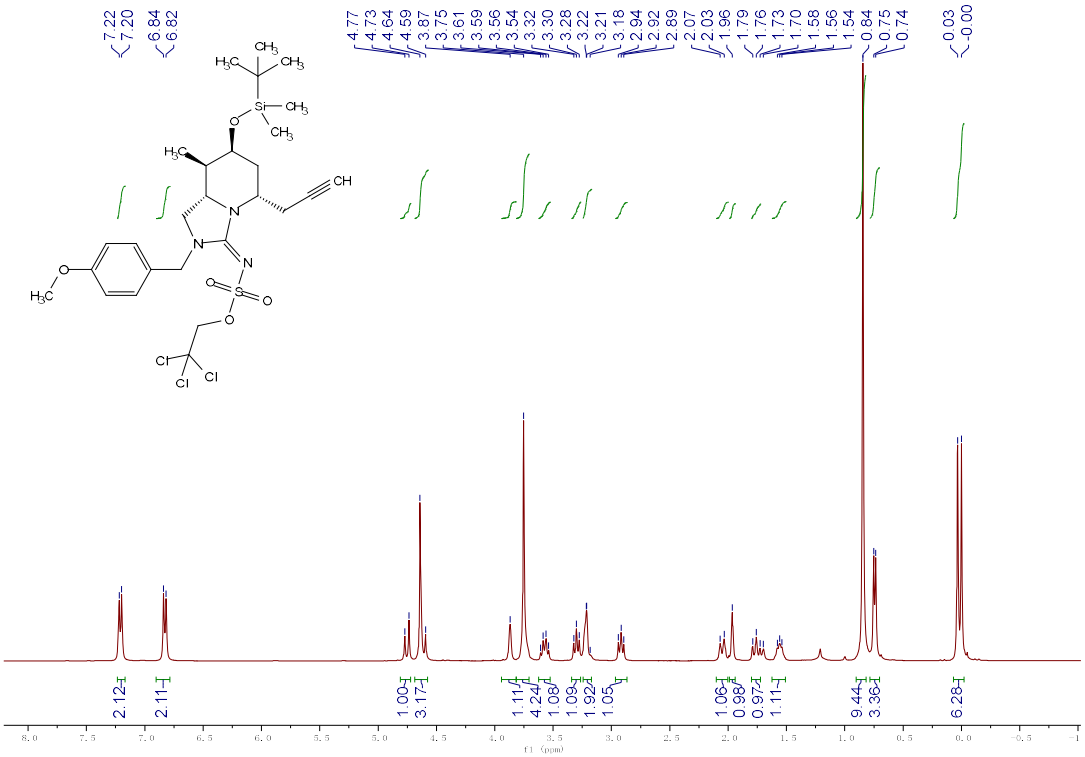

158.54
132.80
129.28
113.70
105.90
82.18
71.20
55.24
55.12
53.72
52.13
49.22
40.47
39.67
27.89
25.91
18.67
18.13
15.00
11.26
-4.27
-4.89

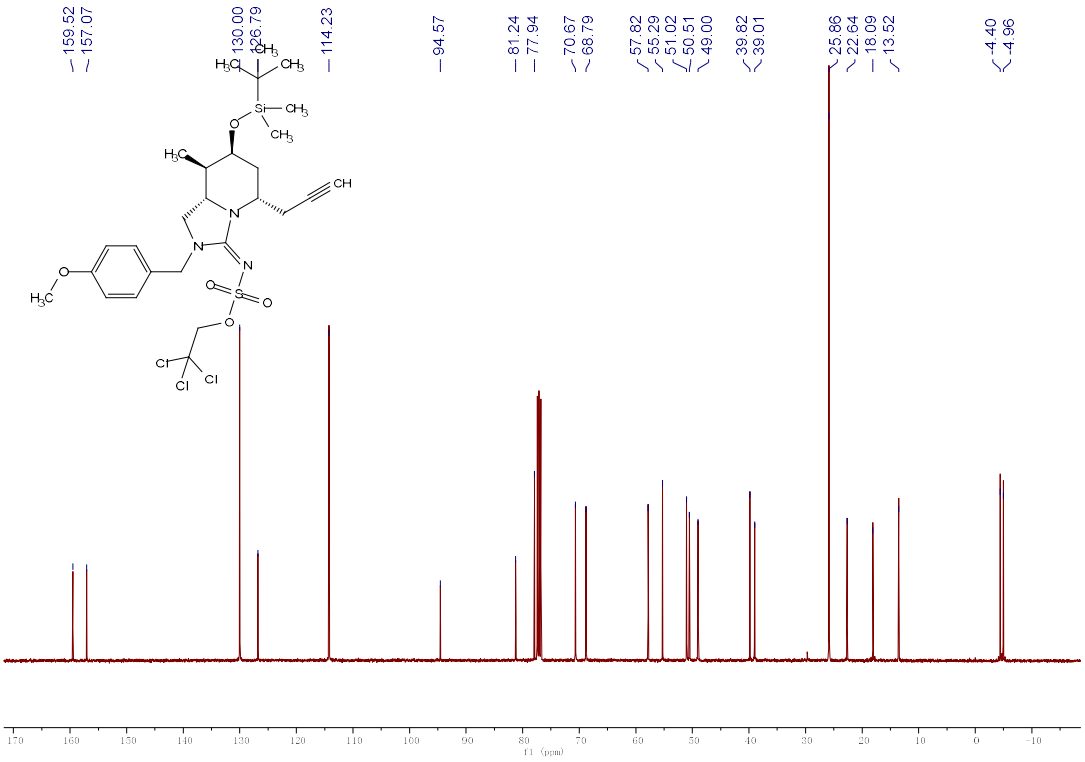
Compound **18**


7.23
7.21
6.84
6.82
4.82
4.78
4.67
4.65
4.64
4.62
4.57
4.53
3.86
3.75
3.73
3.70
3.61
3.58
3.56
3.53
3.37
3.33
3.32
3.30
3.28
3.26
3.24
2.89
2.86
2.84
2.09
2.08
2.05
1.82
1.79
1.76
1.55
1.53
1.51
1.02
1.01
0.98
0.96
0.84
0.76
0.74
0.03
-0.00
2.09
2.03
1.00
2.06
0.98
1.03
4.18
1.09
3.07
1.00
0.97
0.71
0.98
20.97
9.09
3.34
6.01
f1 (ppm)

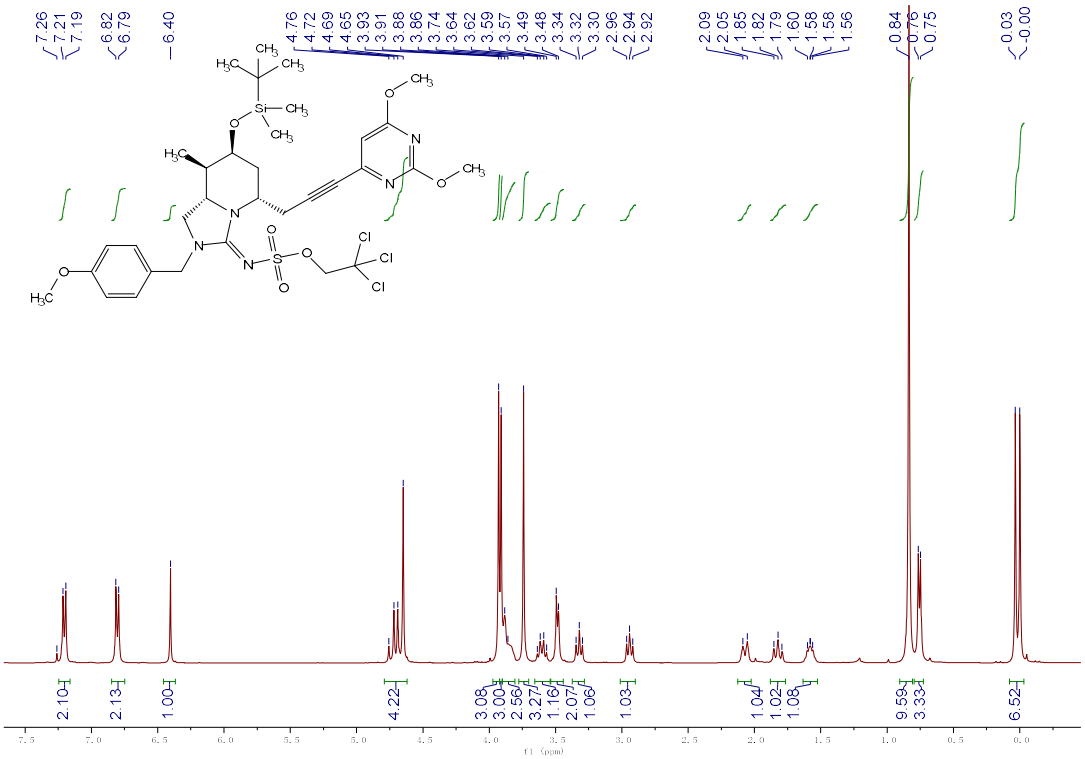

159.52
157.38
130.07
126.79
114.20
104.91
94.51
83.01
77.97
68.59
57.49
55.26
50.70
50.63
49.36
39.88
39.28
25.86
24.37
18.73
18.04
13.62
11.27
-4.25
-4.94
f1 (ppm)

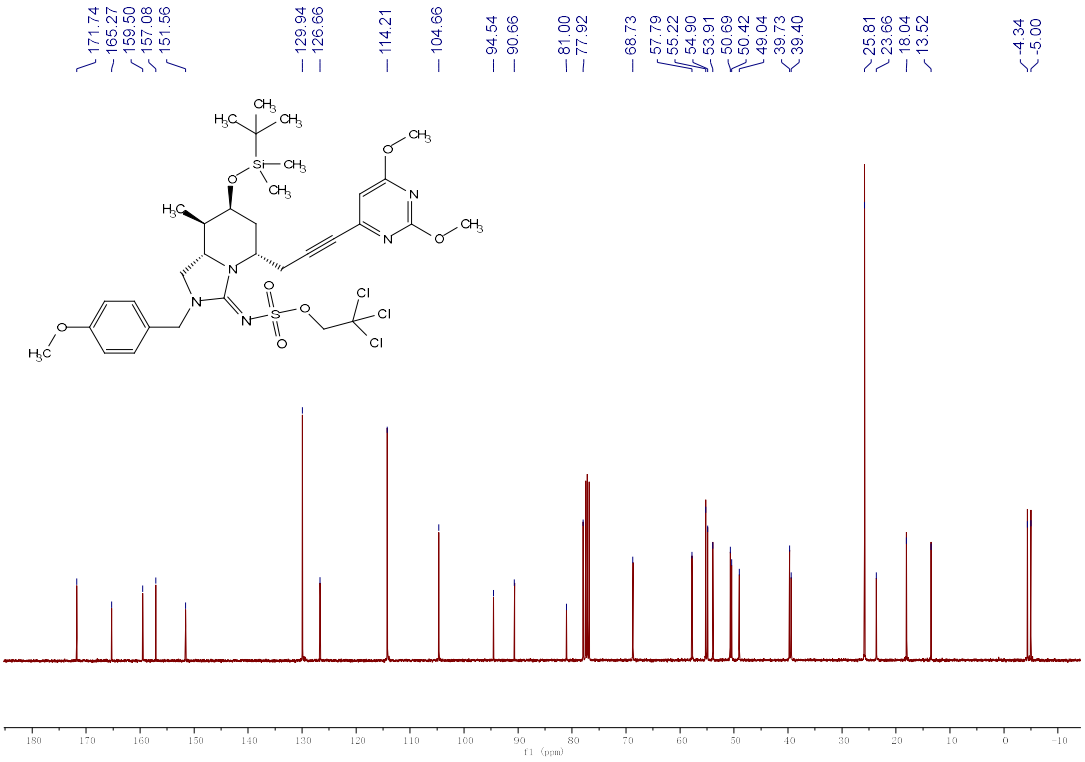
Compound **19**


7.22
7.20
6.84
6.82
4.77
4.73
4.64
4.59
3.87
3.75
3.61
3.59
3.56
3.54
3.32
3.30
3.28
3.22
3.21
3.18
2.94
2.92
2.89
2.07
2.03
1.96
1.79
1.76
1.73
1.70
1.58
1.56
1.54
0.84
0.75
0.74
0.03
-0.00
2.12
2.11
1.00
3.17
1.11
4.24
1.08
1.09
1.92
1.05
1.06
0.98
0.97
1.11
9.44
3.36
6.28

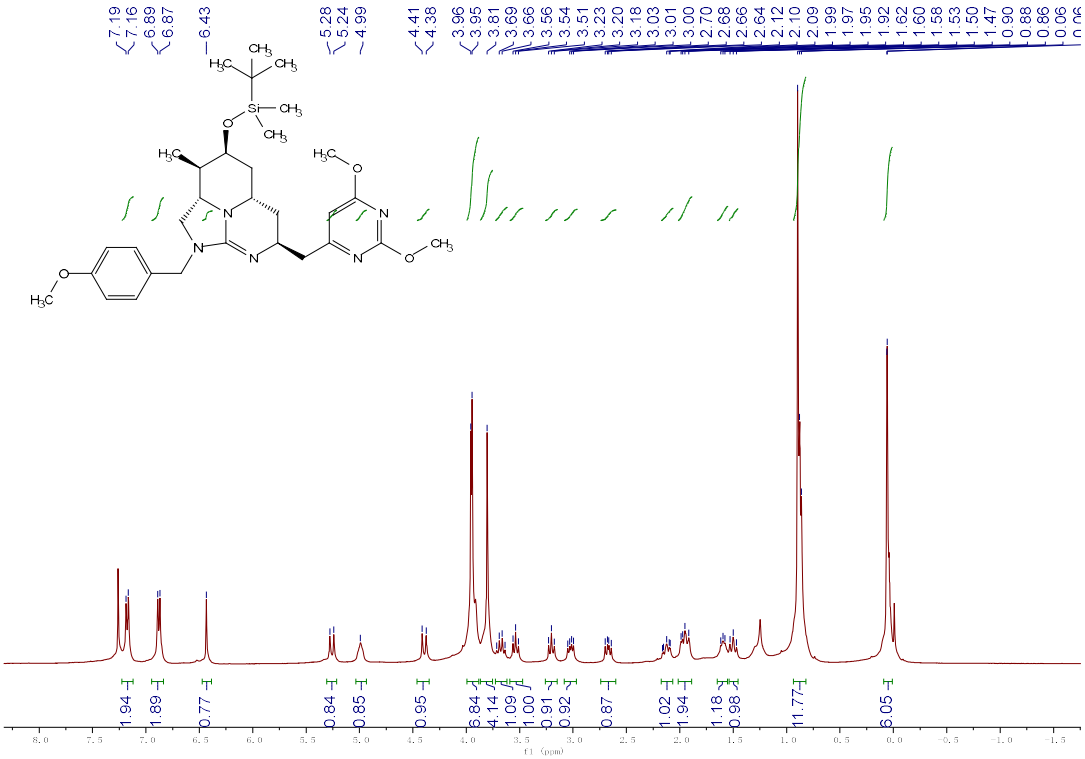

159.52
157.07
130.00
126.79
114.23
94.57
81.24
77.94
70.67
68.79
57.82
55.29
51.02
50.51
49.00
39.82
39.01
25.86
22.64
18.09
13.52
-4.40
-4.96

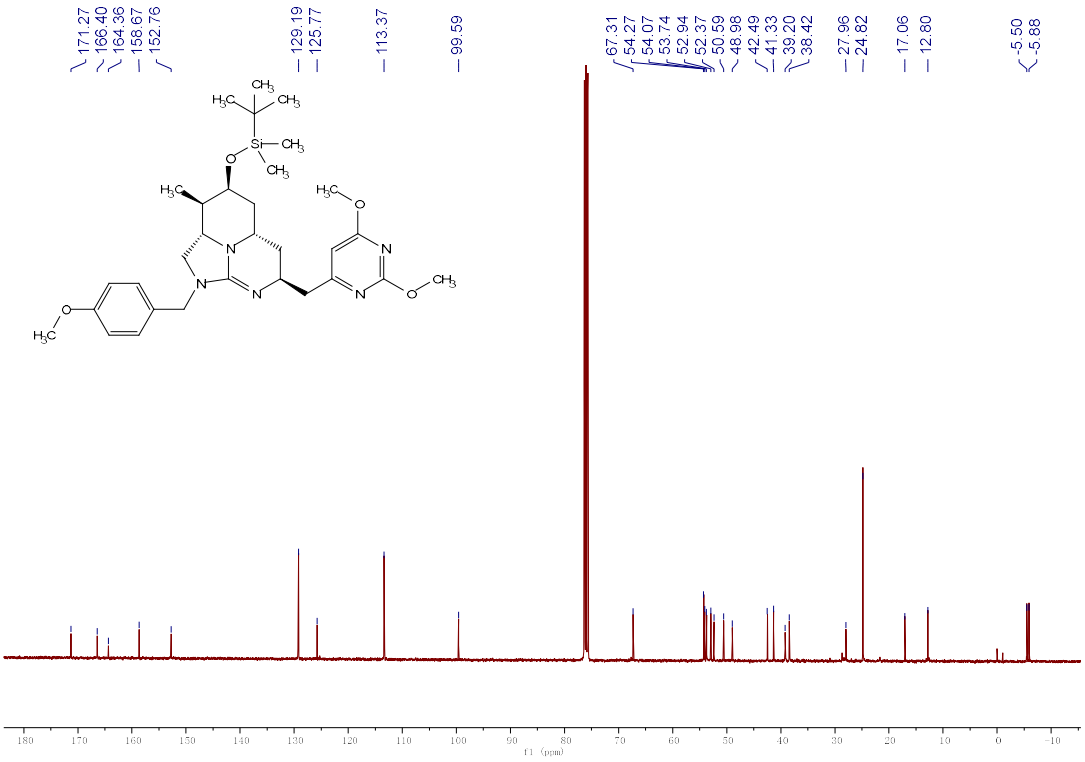
Compound **21**



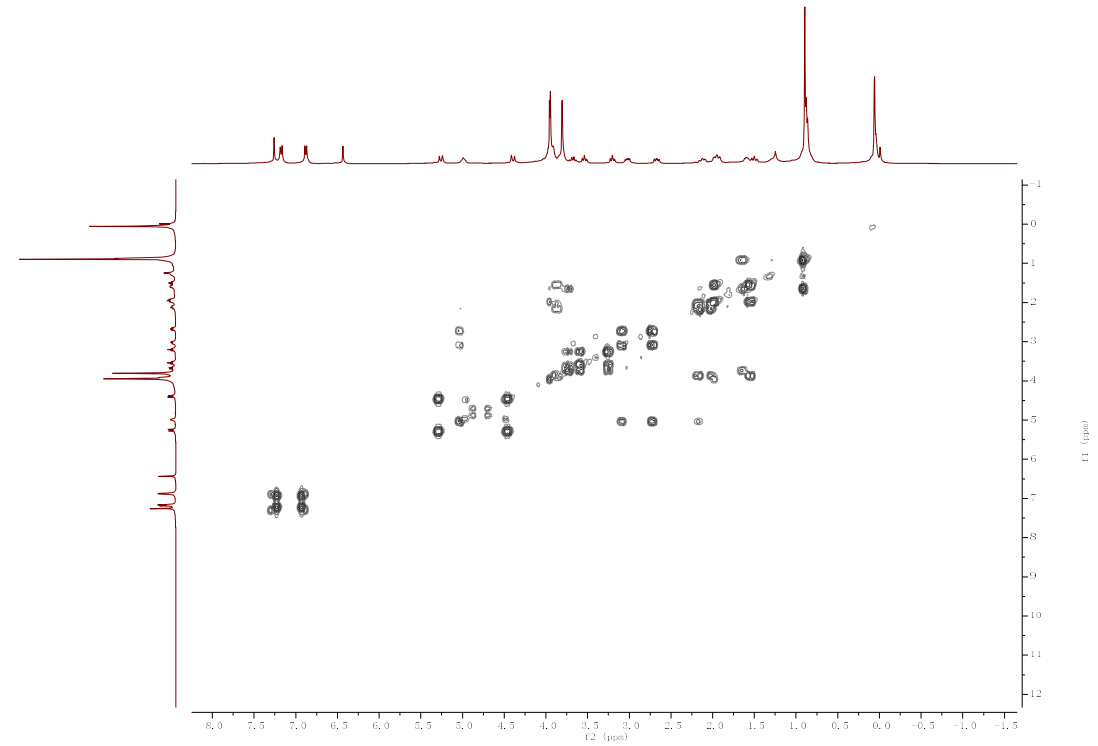


Compound **22**

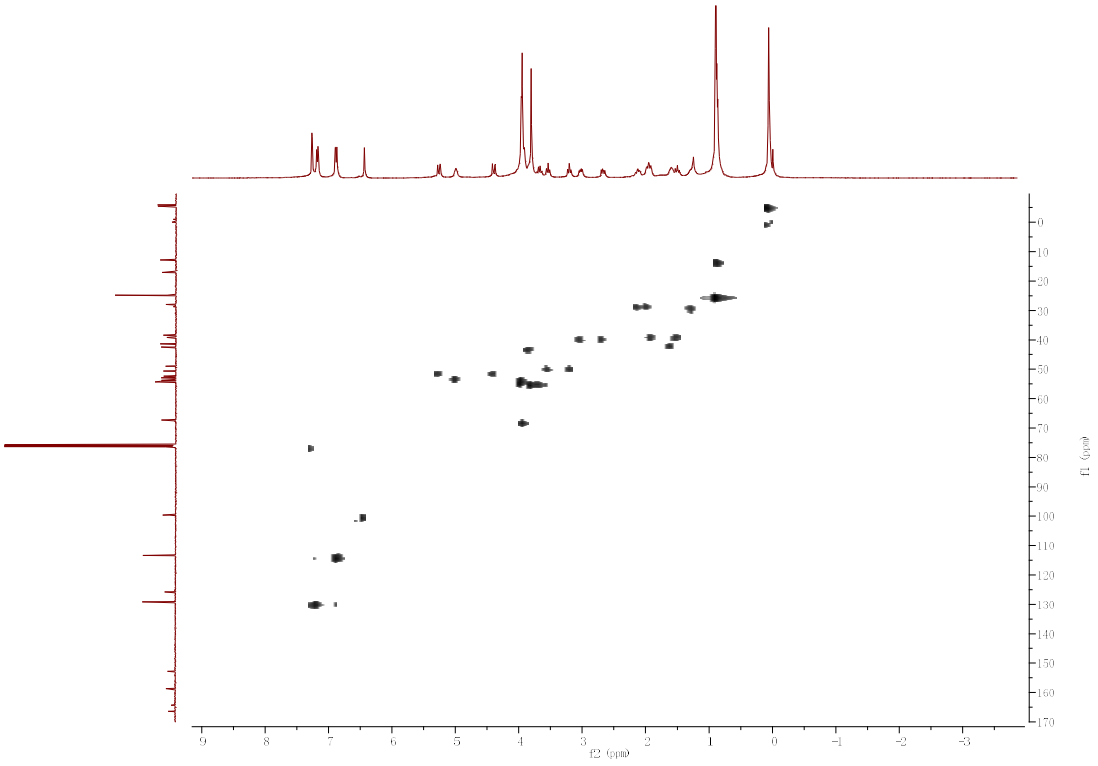




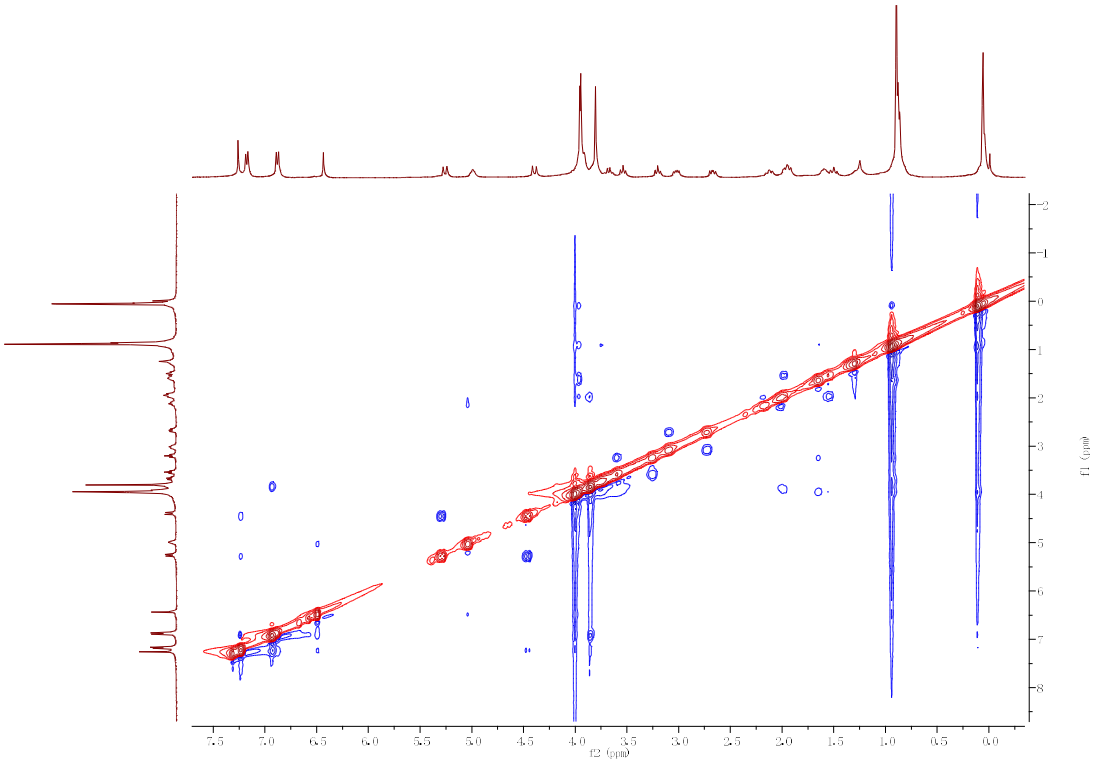
^{1}H-^{1}H COSY



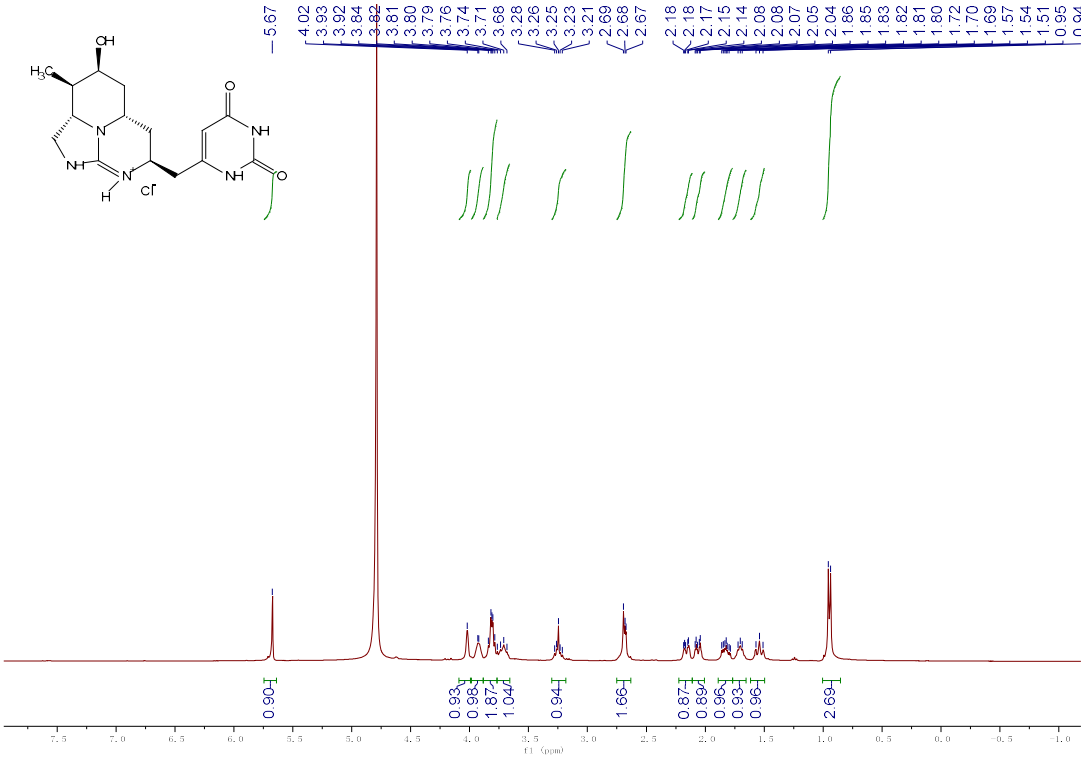
HSQC

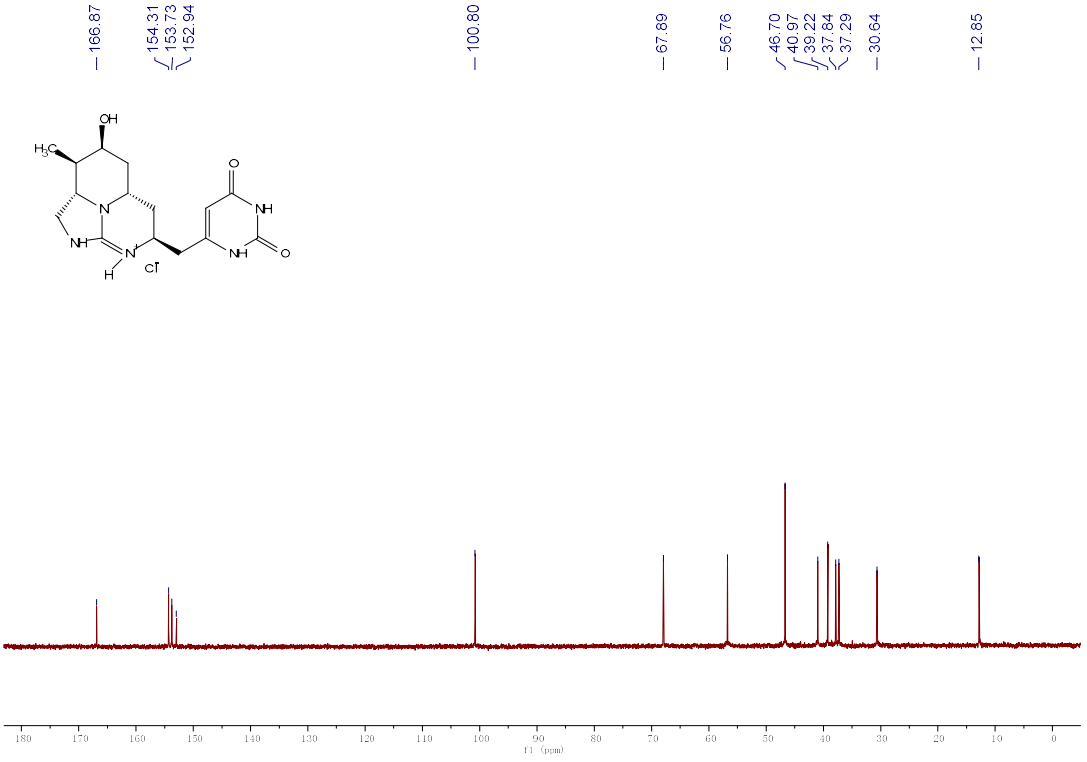


NOESY

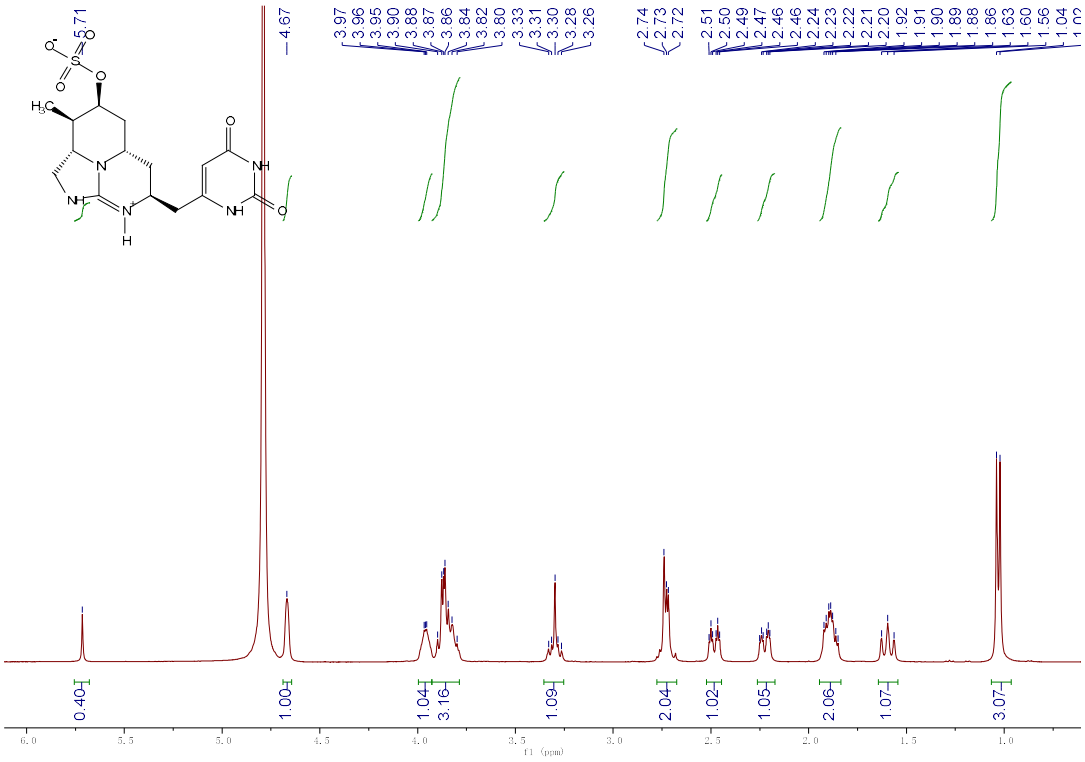


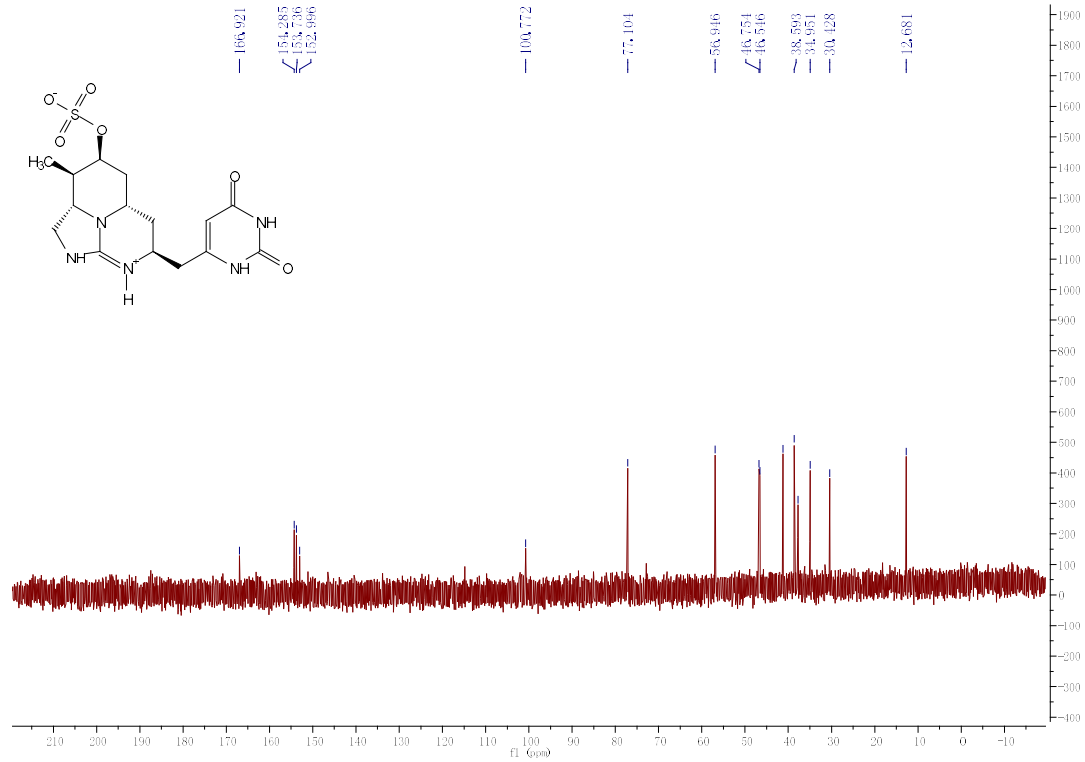
Compound **23**



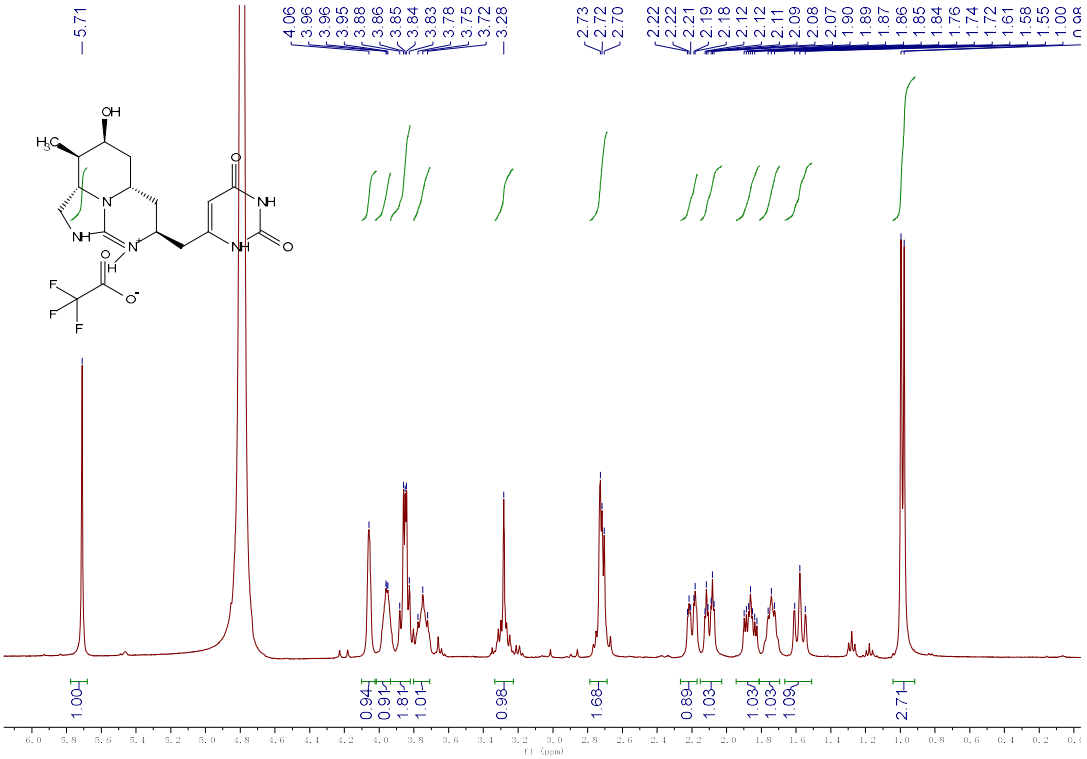


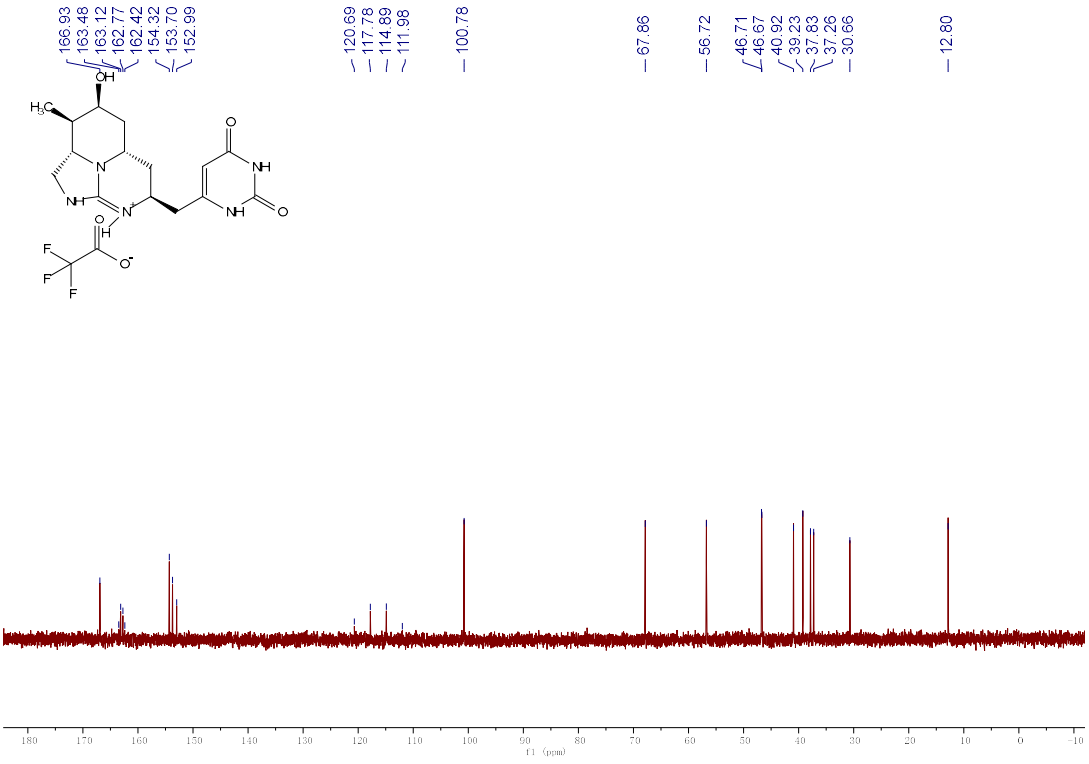
(±)-8-epi-7-deoxycylindrospermopsin **24**



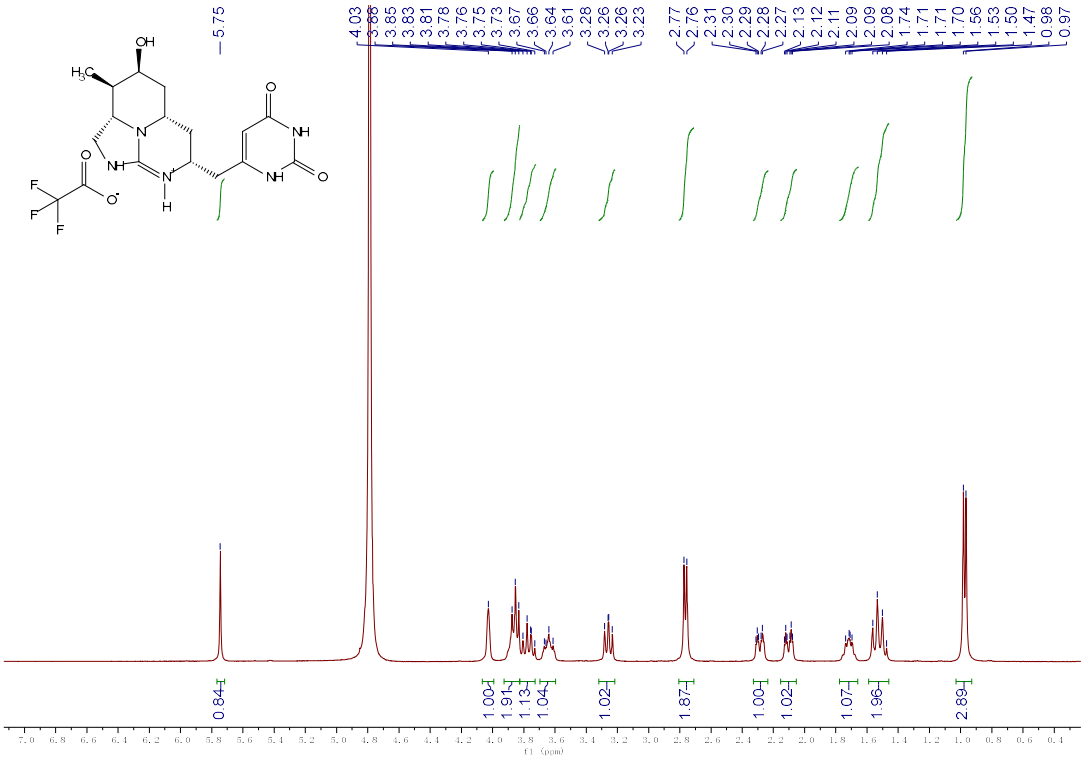


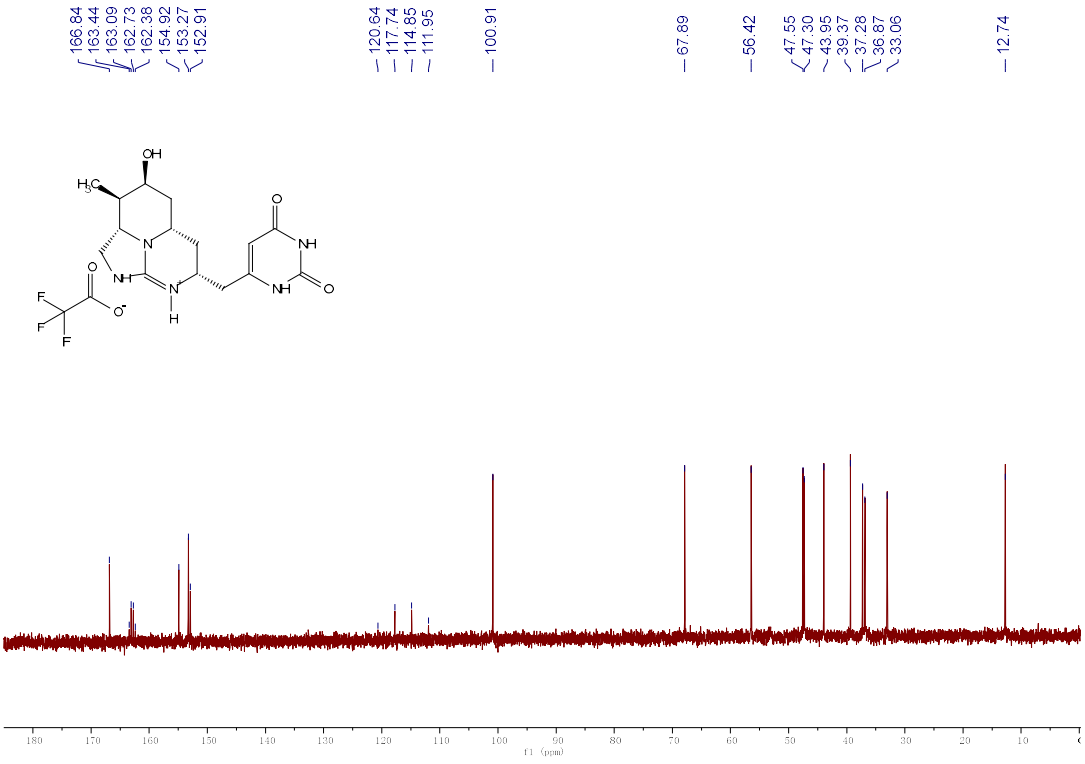
Compound **25**


5.71
4.06
3.96
3.96
3.95
3.88
3.86
3.85
3.84
3.83
3.78
3.75
3.72
3.28
2.73
2.72
2.70
2.22
2.22
2.21
2.19
2.18
2.12
2.12
2.11
2.09
2.08
2.07
1.90
1.89
1.87
1.86
1.85
1.84
1.76
1.74
1.72
1.61
1.58
1.55
1.00
0.94
0.91
1.81
1.01
0.98
1.68
0.89
1.03
1.03
1.03
1.09
2.71
f1 (ppm)


166.93
163.48
163.12
162.77
162.42
154.32
153.70
152.99
120.69
117.78
114.89
111.98
100.78
67.86
56.72
46.71
46.67
40.92
39.23
37.83
37.26
30.66
12.80
f1 (ppm)

Compound **26**


5.75
4.03
3.86
3.85
3.83
3.81
3.78
3.76
3.75
3.73
3.67
3.66
3.64
3.61
3.28
3.26
3.26
3.23
2.77
2.76
2.31
2.30
2.29
2.28
2.27
2.13
2.12
2.11
2.09
2.09
2.08
1.74
1.71
1.71
1.70
1.56
1.53
1.50
1.47
0.98
0.97
0.84
1.00
1.91
1.13
1.04
1.02
1.87
1.00
1.02
1.07
1.96
2.89
f1 (ppm)


166.84
163.44
163.09
162.73
162.38
154.92
153.27
152.91
120.64
117.74
114.85
111.95
100.91
67.89
56.42
47.55
47.30
43.95
39.37
37.28
36.87
33.06
12.74
f1 (ppm)