Supporting Information

Asymmetric Total Synthesis of Nodulisporiviridin E

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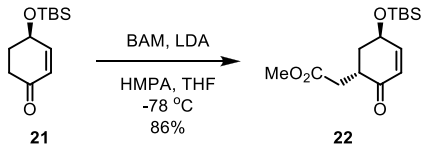
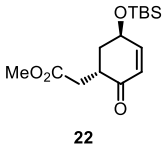
General Experimental Procedures:

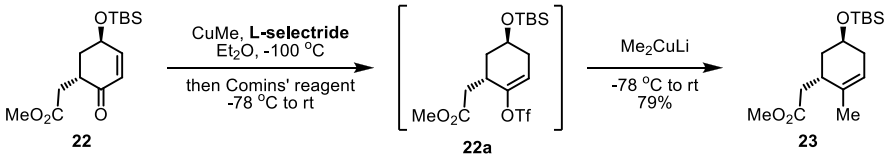
All reactions were carried out under nitrogen except noted. Anhydrous dichloromethane (DCM), N,N-dimethylformamide (DMF) and toluene were distilled from calcium hydride. Anhydrous acetone is obtained by molecular sieve treatment. Tetrahydrofuran (THF) distilled from sodium-benzophenone ketyl, anhydrous diethyl ether was distilled from sodium. Flash column chromatography was performed as described by Still [1], employing Qingdao Haiyang silica gel 60 (200–300 mesh). Thin Layer Chromatography (TLC) analyses were performed on EMD 250 μm Silica Gel $HSGF_{254}$ plates and visualized by quenching of UV fluorescence (λ_{max}=254 nm), or by staining ceric ammonium molybdate, ammonium molybdate, or potassium permanganate. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-500, 400 spectrometer. Chemical shifts for ^{1}H and ^{13}C NMR spectra are reported in ppm (δ) relative to residue protium in the solvent ($CDCl_3$: δ 7.26, 77.0 ppm; CD_3OD: δ 3.31, 49.00 ppm; and the multiplicities are presented as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectra (HRMS) were acquired on Waters Micromass GCT Premier or Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS. Mass spectra were acquired on Agilent 5975C.



In a 100 mL round bottle flask, diisopropylamine (1.88 g, 18.6 mmol, 1.2 equiv.) was dissolved in anhydrous tetrahydrofuran (12 mL). The reaction mixture was cooled to 0 °C and *n*-BuLi (2.5 M, 6.8 mL, 1.1 equiv.) was slowly added. The resulted solution was stirred for 0.5 h before the addition of hexamethylphosphoramide (4.19 g, 23.3 mmol, 1.5 equiv.) at -78 °C under an N_2 atmosphere. The resulted solution was stirred for 0.5 h. Then, it was slowly added **21**[2] (3.50 g, 15.5 mmol, 1.0 equiv.) at the same temperature. The resulted solution was stirred for 0.5 h before the addition of methyl bromoacetate (2.50 g, 16.3 mmol, 1.05 equiv.) at same temperature under an N_2 atmosphere. The resulted solution was stirred for 12 h at same temperature. Then, the reaction was quenched with sat. ammonium chloride (60 mL) and extracted with ethyl acetate (3×20 mL). The combined organic layer was washed with brine (100 mL), dried over sodium sulfate, filtered, and purified by silica gel column chromatography (2→5% ethyl acetate - petroleum ether) afforded **22** as yellow liquid (3.96 g, 86%).

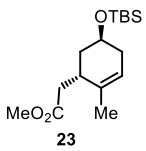


Compound **22:** R_f = 0.40 (10% ethyl acetate - petroleum ether). $[\alpha]_D^{20}$ = +32.1 (c = 1.0 in dichloromethane). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.75 (ddd, *J* = 10.0, 4.9, 1.2 Hz, 1H), 5.94 (d, *J* = 10.0 Hz, 1H), 4.41 (dt, *J* = 5.0, 3.6 Hz, 1H), 3.68 (s, 3H), 3.29 (ddt, *J* = 10.4, 7.5, 6.0 Hz, 1H), 2.76 (dd, *J* = 16.3, 5.6 Hz, 1H), 2.39 (dd, *J* = 16.3, 7.4 Hz, 1H), 2.12 – 1.94 (m, 2H), 0.90 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 199.7, 172.5, 147.5, 128.5, 63.3, 51.7, 38.7, 36.7, 34.0, 25.7 (3C), 18.1, -4.6, -4.9. HRMS (ESI–TOF): calculated [M + H^+] = 299.1673 for [$C_{15}H_{27}O_4Si+H^+$], found [M + H^+] = 299.2003.



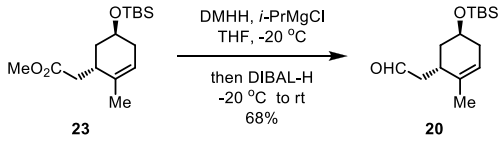
Preparation of lithium dimethyl-cuprate: Under N_2 atmosphere, to a two-necked flask was added cuprous iodide (9.53 g, 50 mmol, 5.0 equiv.) and diethyl ether (60 mL) at 0 °C. Then, the suspension was added methyllithium (100 mL, 1.6 M solution in diethyl ether, 62.5 mmoL, 10.0 equiv.) dropwise at the same temperature. After stirring for 1 h, the solution was cooled to -78 °C and give the freshly prepared lithium dimethyl-cuprate.

Under N_2 atmosphere, to a two-necked flask was added cuprous iodide (190.5 mg, 1.0 mmol, 0.1 equiv.) and diethyl ether (60 mL) at -20 °C. Then, the suspension was added methyllithium (0.6 mL, 1.6 M solution in diethyl ether, 1.0 mmoL, 0.1 equiv.) dropwise at the same temperature. After stirring for 0.5 h, the lithium dimethyl-cuprate solution was cooled to -78 °C and added the L-selectride (1.0 M in tetrahydrofuran, 11 mL, 11.0 mmol, 1.1 equiv.) dropwise. After stirring for 0.5 h, the solution was cooled to -100 °C and added the **22** (3.01 g, 10.0 mmol, 1.0 equiv.) in diethyl ether (5 mL) dropwise. After stirring for 10 min, it was added the solution of Comins' reagent (7.07 g, 15.0 mmol, 1.5 equiv.) in anhydrous diethyl ether (70 mL) at the same temperature. Then, the reaction was warmed to 0 °C over 2 h and following transferred to the freshly prepared lithium dimethyl-cuprate solution. The mixture was stirred for 4 h at room temperature. Then, the reaction was quenched with sat. ammonium chloride (200 mL) and extracted with diethyl ether (3×100 mL). The combined organic layer was washed with brine (100 mL), dried over sodium sulfate, filtered, and purified by silica gel column chromatography (2→5% ethyl acetate - petroleum ether) afforded **23** as yellow liquid (2.41 g, 79%).



23

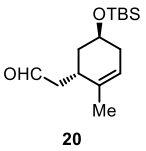
Compound **23:** R_f = 0.51 (10% ethyl acetate - petroleum ether). $[\alpha]_D^{20}$ = +85.4 (c = 0.8 in dichloromethane). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.33 (ddd, *J* = 6.1, 2.9, 1.5 Hz, 1H), 3.94 (ddt, *J* = 9.6, 7.4, 4.9 Hz, 1H), 3.72 (s, 3H), 2.71 – 2.64 (m, 1H), 2.64 – 2.54 (m, 1H), 2.32 – 2.17 (m, 2H), 2.06 – 1.92 (m, 1H), 1.75 – 1.56 (m, 5H), 0.91 (s, 12H), 0.09 (s, 6H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 173.5, 134.8, 121.2, 64.7, 51.5, 38.2, 36.6, 36.3, 35.4, 25.9 (3C), 21.4, 18.2, -4.6, -4.7. HRMS (ESI–TOF): calculated $[M + H^+]$ = 299.2037 for $[C_{16}H_{31}O_3Si+H^+]$, found $[M + H^+]$ = 299.2047.



23 **20**

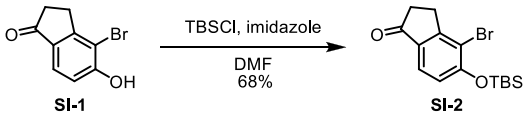
To a solution of **23** (2.30 g, 7.7 mmol, 1.0 equiv.) and N,O-dimethylhydroxylamine hydrochloride (1.13 g, 11.6 mmol, 1.5 equiv.) in anhydrous tetrahydrofuran (50 mL) was slowly added a solution of isopropylmagnesium chloride (2.0 M in tetrahydrofuran, 23.2 mmol, 11.6 mL, 3.0 equiv.) at -20 °C under an N_2 atmosphere. The mixture was stirred for 0.5 h, TLC analysis showed all of **23** was consumed. Then was added diisobutylaluminium hydride (1.5 M in toluene, 6.1 mL, 9.2 mmol, 1.2 equiv.), after stirring for 2 h at room temperature, the mixture was added ethyl acetate (50 mL) and sat.

seignette salt (50 mL). The mixture was stirred for 8 h then extracted with ethyl acetate (3×50 mL). The combined organic layer was washed with brine (50 mL), dried over sodium sulfate, filtered, concentrated, and purified by silica gel column chromatography (2→10% ethyl acetate - petroleum ether) to give **20** as colorless liquid (1.40 g, 68%).



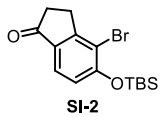
20

Compound **20:** R_f = 0.3 (10% ethyl acetate - petroleum ether). $[\alpha]_D^{20}$ = +17.2 (c = 1.0 in dichloromethane). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.77 (dd, *J* = 2.9, 1.6 Hz, 1H), 5.32 (ddt, *J* = 4.5, 2.9, 1.4 Hz, 1H), 3.89 (dddd, *J* = 10.5, 8.1, 5.3, 3.2 Hz, 1H), 2.74 (dq, *J* = 9.1, 4.4 Hz, 1H), 2.59 (ddd, *J* = 16.4, 4.1, 1.5 Hz, 1H), 2.37 (ddd, *J* = 16.5, 9.6, 2.9 Hz, 1H), 2.22 (dddt, *J* = 17.1, 5.0, 3.3, 1.6 Hz, 1H), 1.94 (ddq, *J* = 17.2, 7.5, 2.4 Hz, 1H), 1.74 (ddd, *J* = 12.8, 10.1, 5.7 Hz, 1H), 1.65 (s, 3H), 1.63 – 1.54 (m, 1H), 0.86 (s, 9H), 0.03 (s, 6H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 202.2, 134.3, 121.5, 64.7, 47.7, 37.2, 35.2, 33.4, 25.9 (3C), 21.5, 18.2, -4.67, -4.70. HRMS (ESI–TOF): calculated [M + H$^+$] = 269.1931 for [$C_{15}H_{28}O_2$+H$^+$], found [M + H$^+$] = 269.1924.



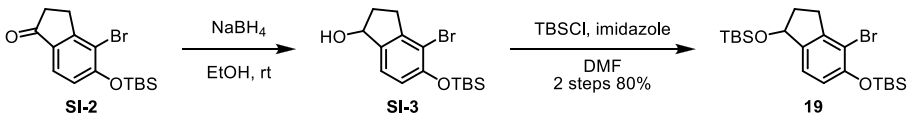
SI-1 **SI-2**

To a solution of **SI-1**[3] (5.56 g, 24.5mmol, 1.0 equiv.) in anhydrous N,N-dimethylformamide (98 mL) was added imidazole (3.33 g, 49.0 mmol, 2 equiv.), tert-butyldimethylsilyl chloride (6.31 g, 41.6 mmol, 1.7 equiv.) in sequence. After stirring for 12 h, the mixture was quenched with sat. sodium bicarbonate (150 mL) and extracted with ethyl acetate (3×200 mL). The combined organic layer was washed with water (5×100 mL), brine (3×50 mL), dried over sodium sulfate, filtered, concentrated, and purified by silica gel column chromatography (15% ethyl acetate - petroleum ether) to give **SI-2** as slight yellow solid (5.06 g, 68%).



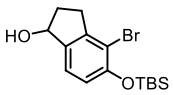
SI-2

Compound **SI-2:** R_f = 0.73 (20% ethyl acetate - petroleum ether). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.2 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 3.16 – 2.83 (m, 2H), 2.79 – 2.57 (m, 2H), 1.06 (s, 9H), 0.30 (s, 6H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 205.0, 158.4, 157.6, 132.2, 123.6, 119.6, 113.9, 36.4, 27.4, 25.6 (3C), 18.4, -4.2 (2C). HRMS (m/z): EI [M] calcd for $C_{15}H_{21}O_2BrSi$ [M]$^+$: 340.0494, Found 340.0498.



SI-2 **SI-3** **19**

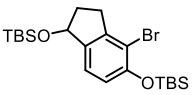
To a solution of **SI-2** (5.06 g, 14.8 mmol, 1.0 equiv.) in ethyl alcohol (75 mL) was added sodium borohydride (0.87 g, 22.2mmol, 1.5 equiv.) at room temperature. Then, the mixture was stirred for 4 h, TLC showed all of **SI-2** was consumed. The reaction was quenched with sat. ammonium chloride (25 mL). After removal the solvent, it was added ethyl acetate (25 mL). Then separation organic phase, the aqueous phase was extracted with ethyl acetate (2×25 mL). The combined organic layer was washed with brine (20 mL), dried over sodium sulfate, filtered, and purified by silica gel column chromatography (5→15% ethyl acetate - petroleum ether) afforded **SI-3** as colorless liquid (4.55 g, 89%).



SI-3

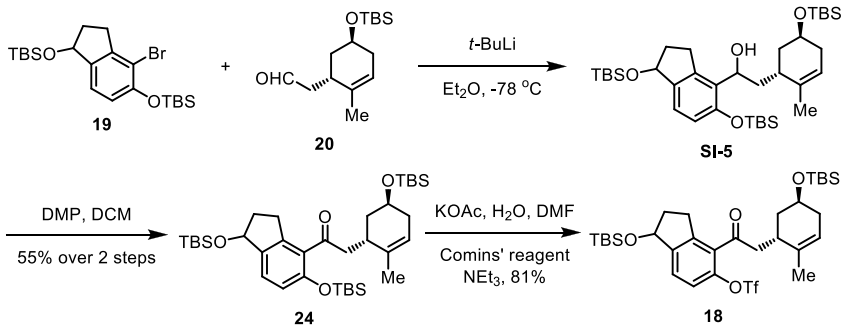
Compound **SI-3:** R_f = 0.58 (20% ethyl acetate - petroleum ether). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 8.0 Hz, 1H), 6.91 – 6.69 (m, 1H), 5.26 (dd, *J* = 6.9, 4.8 Hz, 1H), 3.06 (ddd, *J* = 16.8, 8.7, 5.1 Hz, 1H), 2.81 (ddd, *J* = 16.7, 8.6, 5.9 Hz, 1H), 2.50 (dddd, *J* = 13.7, 8.7, 6.9, 5.0 Hz, 1H), 2.07 – 1.87 (m, 1H), 1.78 (s, 1H), 1.05 (s, 9H), 0.24 (s, 6H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 152.8, 145.8, 138.8, 123.3, 118.8, 112.8, 35.5, 31.9, 25.7 (3C), 18.4, -4.21, -4.23. HRMS (m/z): EI [M] calcd for $C_{15}H_{23}O_2BrSi$ $[M]^+$: 342.0651, Found 342.0647.

To a solution of **SI-3** (4.01 g, 11.7 mmol, 1 equiv.) in anhydrous N,N-dimethylformamide (45 mL) was added imidazole (1.20 g, 17.5 mmol, 1.5 equiv.), *tert*-butyldimethylsilyl chloride (1.94 g, 12.8 mmol, 1.1 equiv.) in sequence. After stirring for 4 h, the mixture was added ethyl acetate (60 mL) and sat. sodium bicarbonate (45 mL), then the aqueous was extracted with ethyl acetate (2×60 mL). The combined organic layer was washed with water (5×50 mL), brine (3×50 mL), dried over sodium sulfate, filtered, concentrated, and purified by silica gel column chromatography (1% ethyl acetate - petroleum ether) to give **19** as whiter liquid (5.10 g, 93%).



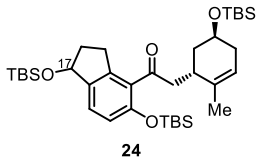
19

Compound **19:** R_f = 0.8 (1% ethyl acetate - petroleum ether). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.08 (d, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 5.28 (t, *J* = 6.8 Hz, 1H), 3.01 (ddd, *J* = 16.5, 9.1, 3.2 Hz, 1H), 2.73 (dt, *J* = 16.5, 8.2 Hz, 1H), 2.44 (dddd, *J* = 12.9, 8.2, 7.0, 3.2 Hz, 1H), 2.15 – 1.85 (m, 1H), 1.05 (s, 9H), 0.95 (s, 9H), 0.24 (s, 3H), 0.23 (s, 3H), 0.16 (s, 3H), 0.14 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 152.2, 144.8, 139.5, 123.0, 118.6, 112.7, 77.1, 36.0, 31.6, 25.9 (3C), 25.8 (3C), 18.4, 18.3, -4.2, -4.3, -4.4, -4.6. HRMS (m/z): EI [M] calcd for $C_{21}H_{37}O_2BrSi_2$ $[M]^+$: 456.1515, Found 456.1515.



Under N_2 atmosphere, to a solution of **19** (3.10 g, 6.9 mmol, 1.0 equiv.) in anhydrous diethyl ether (140 mL) was added *tert*-butyllithium solution (1.3 M solution in pentane, 10.3 mL,13.5 mmol, 2.0 equiv.) dropwise at -78 °C. After stirring for 0.5 h, it was added the solution of **20** (1.82 g, 6.9 mmol, 1.0 equiv.) in anhydrous diethyl ether (10 mL) dropwise and stirred for another 6 h. Then, the reaction was quenched with sat. ammonium chloride (50 mL) and extracted with ethyl acetate (3×50 mL). The combined organic layer was washed with brine (50 mL), dried over sodium sulfate, filtered, and purified by silica gel column chromatography (2% ethyl acetate - petroleum ether) afforded **SI-5** as yellow liquid (2.70 g, 60%). R_f = 0.25 (10% ethyl acetate - petroleum ether).

To a solution of **SI-5** (2.70 g, 4.1 mmol, 1.0 equiv.) in hydrous dichloromethane (20 mL, 1μL water in 1 mL dichloromethane) was added Dess-Martin oxidant (2.59 g, 6.1 mmol, 1.5 equiv.). After stirring for 0.5 h, TLC showed all of **SI-5** was consumed. The reaction solvent was removed under vacuum, an aqueous solution of 1:1 (v/v) sat. sodium thiosulfate/sat. sodium bicarbonate (20 mL) and ethyl acetate (20 mL) were added. After stirring for another 5 min, the above mixture was separated with a separatory funnel to obtain organic phase, and the aqueous phase was extracted with ethyl acetate (2×40 mL). The combined organic phase was washed with brine (20 mL) and dried over anhydrous sodium sulfate, filtered, and purified by silica gel column chromatography (0→5% ethyl acetate - petroleum ether) afforded **24** as slight yellow liquid (2.50 g, 92%).

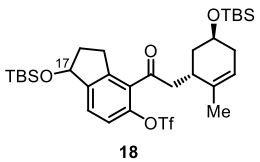


24

Compound **24** exists as a mixture of two inseparable diastereomers at C-17 (d.r.=1:1). R_f = 0.6 (5% ethyl acetate - petroleum ether). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.22 – 7.14 (m, 2H), 6.72 (d, *J* = 8.2 Hz, 2H), 5.33 – 5.24 (m, 2H), 5.17 (q, *J* = 7.1 Hz, 2H), 3.93 – 3.77 (m, 2H), 3.21 – 3.10 (m, 2H), 3.03 (ddd, *J* = 16.8, 8.9, 3.2 Hz, 1H), 2.90 (ddd, *J* = 16.7, 8.9, 2.8 Hz, 1H), 2.84 – 2.78 (m, 1H), 2.77 – 2.66 (m, 3H), 2.39 (ttd, *J* = 12.5, 7.5, 3.0 Hz, 2H), 2.20 (dt, *J* = 17.1, 5.4 Hz, 2H), 1.97 – 1.81 (m, 2H), 1.66 (s, 3H), 1.65 – 1.63 (m, 3H), 1.63 – 1.55 (m, 4H), 0.96 (s, 18H), 0.94 (s, 18H), 0.83 (s, 6H), 0.82 (s, 6H), 0.21 (s, 3H), 0.20 (s, 3H), 0.19 (s, 3H), 0.16 (s, 3H), 0.15 (s, 3H), 0.14 (s, 6H), -0.03 (s, 12H). ^{13}C NMR (125 MHz, Chloroform-*d*)

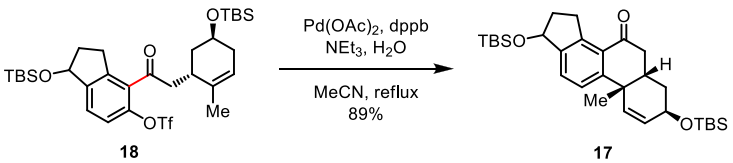
δ 205.7, 205.6, 152.9, 152.8, 142.5, 142.3, 139.5, 139.3, 135.6, 135.5, 129.5, 129.4, 126.4, 126.3, 120.8, 120.7, 118.5, 118.4, 75.91, 75.85, 65.0 (2C), 48.2, 48.1, 37.12, 37.07, 36.6, 36.5, 35.7, 35.6, 35.49, 35.47, 29.1, 29.04, 25.93 (3C), 25.90 (3C), 25.85 (9C), 25.82 (3C), 21.64, 21.62, 18.32 (2C), 18.27, 18.21, 18.11 (2C), -4.07, -4.09, -4.13, -4.17, -4.4 (2C), -4.60, -4.63, -4.67, -4.72 (3C). HRMS (ESI–TOF): calculated [M + Na^+] = 667.4005 for [$C_{36}H_{64}O_4Si_3$+Na^+], found [M + Na^+] = 667.3985.

To a solution of **24** (2.55 g, 3.95 mmol, 1.0 equiv.) in anhydrous N,N-dimethylformamide (20 mL) was added potassium acetate (38.7 mg, 0.4 mmol, 0.1 equiv.) and water (78 mg, 4.35 mmol, 1.1 equiv.) . After stirring for 4 h, TLC showed all of **24** was consumed. It was added the triethylamine (1 mL, 7.9 mmol, 2.0 equiv.) and Comins' reagent (2.35 g, 5.93 mmol, 1.5 equiv.) and stirred for another 6 h. The mixture was added water (20 mL) and aqueous was extracted with ethyl acetate (3×40 mL). The combined organic layer was washed with water (5×20 mL), brine (3×20 mL), dried over sodium sulfate, filtered, concentrated, and purified by silica gel column chromatography (5% ethyl acetate - petroleum ether) to give **18** as colorless liquid (2.12 g, 81%).



18

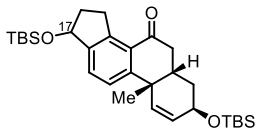
Compound **18** exists as a mixture of two inseparable diastereomers at C-17 (d.r.=1:1). R_f = 0.55 (5% ethyl acetate - petroleum ether). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.47 – 7.36 (m, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 5.40 – 5.25 (m, 2H), 5.27 – 5.18 (m, 2H), 4.02 – 3.77 (m, 2H), 3.17 – 3.09 (m, 2H), 3.08 – 2.95 (m, 2H), 2.94 – 2.82 (m, 2H), 2.82 – 2.70 (m, 4H), 2.53 – 2.41 (m, 2H), 2.27 – 2.17 (m, 2H), 2.01 – 1.87 (m, 2H), 1.75 – 1.68 (m, 1H), 1.67 (s, 3H), 1.65 (s, 3H), 1.63 – 1.58 (m, 1H), 0.95 (s, 9H), 0.95 (s, 9H), 0.83 (s, 9H), 0.82 (s, 9H), 0.18 (s, 6H), 0.16 (s, 3H), 0.15 (s, 3H), 0.01 (s, 3H), -0.01 (s, 3H), -0.03 (s, 3H), -0.04 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 201.2, 201.1, 147.6, 147.5, 145.39, 145.35, 143.5, 143.4, 134.8, 134.7, 130.8, 130.5, 127.1 (2C), 121.4, 121.3, 120.4 (2C), 118.5 (dd, *J* = 320.8 Hz , 2C), 75.50, 75.47, 64.84, 64.78, 47.9, 47.7, 37.0, 36.9 36.7, 36.6, 35.4, 35.3 (2C), 35.1, 29.33, 29.31, 25.82 (9C), 25.78 (3C), 21.38, 21.36, 18.2, 18.13, 18.11 (2C), -4.4 (2C), -4.68, -4.71(2), -4.72, -4.80, -4.84. HRMS (ESI–TOF): calculated [M + H^+] = 663.2813 for [$C_{31}H_{49}O_6F_3Si_2S$+H^+], found [M + H^+] = 663.2794.



18 **17**

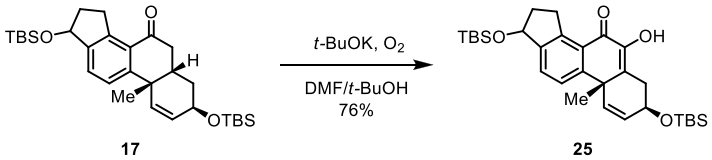
Under N_2 atmosphere, palladium (II) acetate (202.1 mg, 0.9 mmol, 0.3 equiv.) and 1,4-Bis(diphenylphosphino)butane (dppb, 383.9 mg, 0.9 mmol, 0.9 equiv.) were dissolved in degassed

acetonitrile (100 mL). After stirring for 0.5 h, the solution was introduced into the solution of **18** (2.01 g, 3.0 mmol, 1.0 equiv.) in degassed acetonitrile (10 mL). Then, the mixture was added water (0.27 mL, 15 mmol, 5.0 equiv.) and triethylamine (2.1 mL, 15 mmol, 5.0 equiv.) under stirring. The reaction system was heated at 80 °C for 5 h, TLC showed all of **18** was consumed. After cooling to room temperature and removal the solvent, the residue was purified by silica gel column chromatography (2→5% ethyl acetate - petroleum ether) to afford **17** as yellow foam solid (1.37 g, 89%).



17

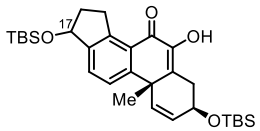
Compound **17** exists as a mixture of two inseparable diastereomers at C-17 (d.r.=1:1). R_f = 0.5 (5% ethyl acetate - petroleum ether). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 6.17 (d, *J* = 10.0 Hz, 1H), 6.14 (d, *J* = 9.9 Hz, 1H), 5.79 – 5.69 (m, 2H), 5.24 – 5.14 (m, 2H), 4.06 (q, *J* = 3.9 Hz, 2H), 3.56 – 3.38 (m, 2H), 3.18 – 2.95 (m, 4H), 2.54 – 2.35 (m, 6H), 1.87 (dtd, *J* = 12.7, 8.9, 7.0 Hz, 2H), 1.77 – 1.63 (m, 4H), 1.49 (s, 3H), 1.49 (s, 3H), 0.94 (s, 9H), 0.94 (s, 9H), 0.89 (s, 9H), 0.89 (s, 9H), 0.16 (s, 6H), 0.14 (s, 6H), 0.11 – 0.03 (m, 12H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 198.8 198.7, 149.2 (2C), 149.0, 144.9, 143.99, 143.95, 137.3, 137.1, 129.0, 128.90, 128.4, 128.2, 126.9, 126.8, 126.41, 126.38, 75.6, 75.5, 63.8, 63.7, 42.3, 42.0, 38.5, 38.4, 36.07, 36.05, 35.3, 35.2, 35.2, 35.0, 31.4, 31.3, 30.5, 30.4, 25.67 (6C), 25.65 (6C), 18.00, 17.98, -4.58, -4.60, -4.8 (2C), -4.91 (2C), -4.94 (2C). HRMS (ESI–TOF): calculated [M + Na^+] = 535.3034 for [$C_{30}H_{48}O_3Si_2$+Na^+], found [M + Na^+] = 535.3048.



17 **25**

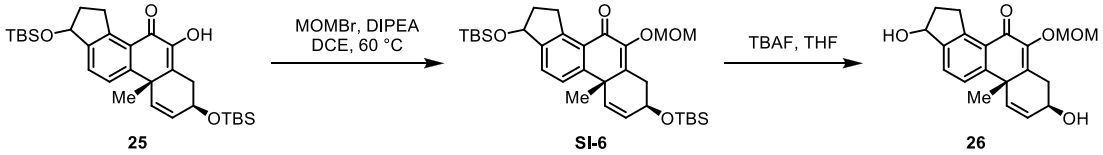
To a solution of **17** (1.45 g, 2.8 mmol, 1.0 equiv.) in *tert*-Butanol (28 mL) was added potassium *tert*-butoxide (1.58 g, 14.1 mmol, 5.0 equiv.). The flask was then evacuated with vacuum and carefully backfilled with oxygen by attaching a balloon of oxygen to the flask. After stirring for 10 min, it was added anhydrous N,N-dimethylformamide (9 mL) and stirred for another 0.5 h. The reaction was quenched with sat. ammonium chloride (30 mL) and ethyl acetate (50 mL). After separation organic phase the aqueous phase was extracted with ethyl acetate (2×50 mL). The combined organic layer was washed with brine (50 mL), dried over sodium sulfate, filtered, and purified by silica gel column

chromatography (1→5% ethyl acetate - petroleum ether) afforded **25** as yellow foam solid (1.21 g, 76%).



25

Compound **25** exists as a mixture of two inseparable diastereomers at C-17 (d.r.=1:1). R_f = 0.55 (5% ethyl acetate - petroleum ether). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 – 7.52 (m, 4H), 6.78 – 6.73 (m, 2H), 6.21 – 6.10 (m, 2H), 5.72 – 5.64 (m, 2H), 5.31 – 5.21 (m, 2H), 4.39 – 4.33 (m, 2H), 3.71 (ddd, *J* = 18.0, 9.2, 2.9 Hz, 1H), 3.63 (ddd, *J* = 18.0, 9.1, 3.0 Hz, 1H), 3.53 – 3.47 (m, 2H), 3.30 – 3.10 (m, 2H), 2.56 – 2.46 (m, 2H), 2.44 – 2.38 (m, 2H), 2.01 – 1.88 (m, 2H), 1.58 (s, 3H), 1.57 (s, 3H), 0.97 (s, 9H), 0.95 (s, 9H), 0.94 – 0.92 (m, 18H), 0.20 (s, 3H), 0.18 (s, 3H), 0.17 (s, 3H), 0.16 (s, 3H), 0.15 – 0.12 (m, 12H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 180.6 (2C), 150.2, 150.1, 145.7, 145.5, 144.9, 144.9, 142.6 (2C), 133.3, 133.2, 132.83, 132.75 130.0, 129.9, 128.4 (2C), 125.32, 125.25, 124.99, 124.96, 75.8, 75.7, 69.51, 69.50, 41.31, 41.25, 36.40, 36.36, 33.92, 33.86, 32.3 (2C), 31.5, 31.4, 25.92 (3C), 25.89 (9C), 18.3 (3C), 18.2, -4.3 (2C), -4.56 (2C), -4.61, -4.63, -4.8 (2C). HRMS (ESI–TOF): calculated [M + H^+] = 526.2935 for [$C_{30}H_{46}O_4Si_2$+H^+], found [M + H^+] = 526.2897.

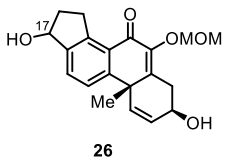


25 **SI-6** **26**

To a stirred solution of **25** (876.3 mg, 1.66 mmol, 1.0 equiv.) in anhydrous 1,2-dichloroethane (10 mL) was added N,N-diisopropylethylamine (1.4 mL, 8.3 mmol, 5.0 equiv.) at room temperature under N_2, followed by addition of methoxymethyl bromide (0.4 mL, 5.0 mmol, 3.0 equiv.), the reaction mixture was stirred at 60 ^{o}C for 4 h. After cooling to room temperature, the reaction mixture was quenched with sat. sodium bicarbonate (10 mL). The resulting mixture was extracted with ethyl acetate (3×20 mL), the combined organic layer was washed with brine (20 mL) and dried over anhydrous sodium sulfate. The dried solution was filtered which was then filtered and concentrated under vacuum to give crude **SI-6** as a colorless foam solid. R_f = 0.5 (30% ethyl acetate - petroleum ether).

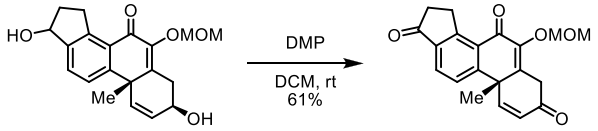
To a solution of **SI-6** in tetrahydrofuran (20 mL) was added tetrabutylammonium fluoride (1.0 M in tetrahydrofuran, 4.2 mL, 4.2 mmol, 2.5 equiv.). After stirring for 1 h, it was added methanol (20 mL), calcium carbonate (2.1 g) and Dowex® 50WX8 (2.1 g),then stirred for another 0.5 h. The suspension was filtered through a celite column and concentrated under vacuum on a rotary evaporator and purified

by silica gel column chromatography (1→5% methanol – dichloromethane) afforded **26** as yellow liquid (443.1 mg, 78% from **25**).



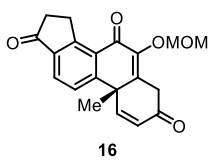
26

Compound **26** exists as a mixture of two inseparable diastereomers at C-17 (d.r.=1:1). R_f = 0.33 (5% methanol – dichloromethane). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 6.25 – 6.12 (m, 2H), 5.81 – 5.70 (m, 2H), 5.28 – 5.18 (m, 2H), 5.10 (s, 4H), 4.43 – 4.33 (m, 2H), 3.77 – 3.69 (m, 2H), 3.67 (dt, *J* = 8.7, 4.8 Hz, 1H), 3.57 (s, 6H), 3.52 (ddd, *J* = 18.0, 8.7, 4.3 Hz, 1H), 3.35 (dt, *J* = 18.3, 7.7 Hz, 1H), 3.22 (ddd, *J* = 18.3, 8.5, 6.0 Hz, 1H), 2.60 – 2.45 (m, 2H), 2.40 – 2.31 (m, 2H), 2.03 – 1.90 (m, 2H), 1.60 (s, 6H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 181.1 (2C), 149.0, 148.9, 145.8, 145.6, 145.11 (2C), 145.09 (2C), 145.06, 144.9, 133.87, 133.85, 131.5 (2C), 128.4, 128.3, 127.61, 127.59, 125.1 (2C), 97.8 (2C), 75.5, 75.3, 69.3, 69.2, 57.5 (2C), 42.21, 42.18, 36.0, 35.8, 34.37, 34.35, 32.41, 32.37, 31.8, 31.7. HRMS (ESI–TOF): calculated [M + H^+] =343.1540 for [$C_{20}H_{22}O_5$+H^+], found [M + H^+] = 343.1536



26 **16**

To a solution of **26** (443.1 mg, 1.3 mmol, 1.0 equiv.) in anhydrous dichloromethane (20 mL). The reaction mixture was cooled to 0 ^{o}C and Dess–Martin periodinane (2.19 g, 5.2 mmol, 4.0 equiv.) was added at the same temperature. The mixture was stirred for 1 h, TLC analysis showed consumption of **26**. The reaction solvent was removed under vacuum, an aqueous solution of 1:1 (v/v) sat. sodium thiosulfate/sat. sodium bicarbonate (20 mL) and ethyl acetate (20 mL) were added. After stirring for another 5 min, the above mixture was separated with a separatory funnel to obtain organic phase, and the aqueous phase was extracted with ethyl acetate (2×40 mL). The combined organic phase was washed with brine (20 mL) and dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated under vacuum, and purified by silica gel column chromatography (5 % ethyl acetate - petroleum ether) to give **16** as a yellow solid (267.9 mg, 61%).

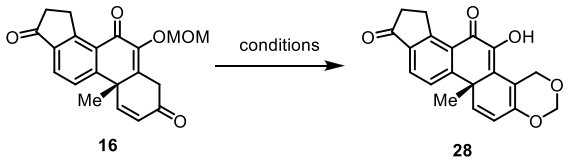


16

Compound **16:** R_f = 0.61 (ethyl acetate - petroleum ether), $[\alpha]_D^{20}$ = -136.3 (c = 0.4 in dichloromethane), ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 10.0 Hz, 1H), 6.16 (dd, *J* = 9.9, 1.0 Hz, 1H), 5.22 (d, *J* = 6.4 Hz, 1H), 5.14 (d, *J* = 6.5 Hz, 1H), 4.25 (dd, *J* = 18.6, 1.1 Hz, 1H), 3.74 (ddd, *J* = 19.6,

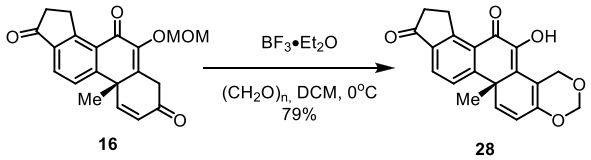
6.7, 4.7 Hz, 1H), 3.62 (ddd, *J* = 19.5, 6.8, 4.6 Hz, 1H), 3.55 (s, 3H), 3.42 (d, *J* = 18.6 Hz, 1H), 2.76 (ddd, *J* = 7.0, 4.6, 2.3 Hz, 2H), 1.83 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 206.4, 194.0, 180.0, 158.1, 152.9, 152.6, 145.0, 141.6, 137.5, 128.8, 128.5, 127.5, 125.8, 97.7, 57.7, 43.5, 37.9, 36.5, 32.4, 28.3. HRMS (ESI–TOF): calculated [M + H$^+$] = 337.1059 for [$C_{20}H_{18}O_5$+H$^+$], found [M + H$^+$] = 337.1066

Table S1. Acid promotes aldol reaction to construct the furan ring

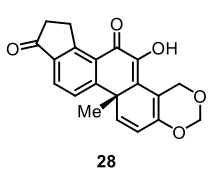


entry	reaction condition	temperature	result
1	TFA	-78 to rt	ND
2	TMSCl, NEt_3 then $TiCl_4$	-78 to rt	decompose
3	TMSCl, NEt_3 then $SnCl_4$	-78 to rt	ND
4	TMSCl, NEt_3 then BF_3•Et_2O	-78 to rt	NR
5	TMSOTf	-78 to 0 ^oC	decompose
6	$TiCl_4$	-78	ND
7	$SnCl_4$	-78	unknown product
8	BF_3•Et_2O	0	**28** (45%)
9	BF_3•Et_2O ,(CH_2O)n	0	**28** (79%)

[a] isolation yield.

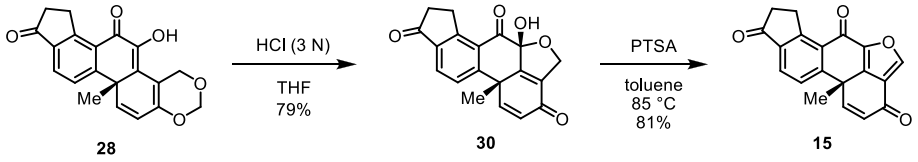


To a solution of **16** (267.9 mg, 0.8 mmol, 1.0 equiv.) and paraformaldehyde (240 mg) in anhydrous dichloromethane (75 mL) was added boron trifluoride diethyl etherate (0.2 mL, 1.6 mmol, 2.0 equiv.) at 0 ^oC under an N_2 atmosphere. After stirring at 0 ^oC for 12 h, the reaction was quenched by sat. sodium bicarbonate (20 mL) and extracted with dichloromethane (3×40 mL). The combined organic phase was washed with brine (40 mL), dried over sodium sulfate, filtered, concentrated and purified by silica gel column chromatography(10%→40% ethyl acetate - petroleum ether) to give **28** as a yellow solid (211.6 mg, 79%).



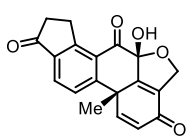
Compound **28:** R_f = 0.40 (40% ethyl acetate - petroleum ether), $[\alpha]_D^{20}$ = -157.8 (c = 0.7 in dichloromethane), ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.2 Hz,

1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.13 (s, 1H), 6.77 (d, *J* = 10.0 Hz, 1H), 6.02 (d, *J* = 10.0 Hz, 1H), 5.31 – 5.24 (m, 2H), 5.23 (d, *J* = 5.4 Hz, 1H), 4.77 (d, *J* = 15.9 Hz, 1H), 3.80 – 3.70 (m, 1H), 3.61 (dt, *J* = 19.4, 5.3 Hz, 1H), 2.80 – 2.69 (m, 2H), 1.71 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 206.1, 178.6, 157.9, 154.2, 149.2, 142.9, 138.3, 137.0, 131.3, 127.5, 125.7, 124.9, 121.5, 107.1, 91.0, 66.5, 44.3, 38.7, 36.5, 28.2. HRMS (ESI–TOF): calculated [M + H$^+$] = 337.1059 for [$C_{20}H_{16}O_5$+H$^+$], found [M + H$^+$] = 337.1059.



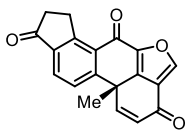
28 30 15

To a solution of **28** (100.0 mg, 0.3 mmol, 1.0equiv.) in tetrahydrofuran (8 mL) was added hydrochloric acid (3 M in water, 8 mL) at room temperature under an O_2 atmosphere. After stirring for 8 h, the reaction was quenched by sat. sodium bicarbonate (30 mL) and extracted with ethyl acetate (3×40 mL). The combined organic phase was washed with brine (40 mL), dried over sodium sulfate, filtered, concentrated and purified by silica gel column chromatography (10%→40% ethyl acetate - petroleum ether) to give **30** as a white solid (76.3 mg, 79%).


30

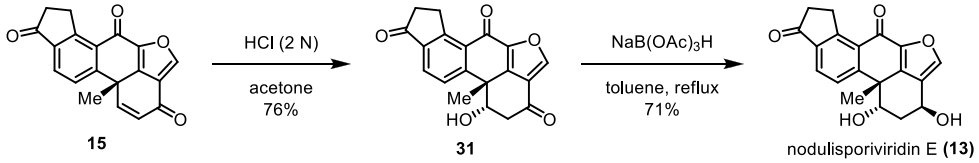
Compound **30:** R_f = 0.32 (ethyl acetate - petroleum ether). $[\alpha]_D^{20}$ = -143.2 (c = 0.1 in dichloromethane), ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.79 – 7.64 (m, 1H), 7.52 (dd, *J* = 9.9, 1.6 Hz, 1H), 6.44 (dd, *J* = 10.0, 1.6 Hz, 1H), 5.28 (dd, *J* = 13.8, 1.6 Hz, 1H), 4.88 (dd, *J* = 13.7, 1.6 Hz, 1H), 4.16 (s, 1H), 3.61 (t, *J* = 5.8 Hz, 2H), 2.75 (td, *J* = 5.1, 4.2, 2.1 Hz, 2H), 1.88 (d, *J* = 1.6 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 205.6, 192.2, 181.1, 159.9, 152.7, 151.9, 150.9, 138.1, 137.7, 129.8, 129.6, 127.1, 126.1, 104.4, 72.23, 42.4, 36.3, 29.5, 28.3. HRMS (ESI–TOF): calculated [M + H$^+$] = 323.0914 for [$C_{19}H_{14}O_5$+H$^+$], found [M + H$^+$] = 323.0908.

To a solution of **30** (81.0 mg, 0.27 mmol, 1.0 equiv.) in toluene (10 mL) was added *p*-toluenesulfonic acid (20.3 mg, 1.1 mmol, 4.0 equiv.) at room temperature under an N_2 atmosphere. The reaction mixture was stirred for 4 h, then concentrated under vacuum, and purified by silica gel column chromatography (20% ethyl acetate - petroleum ether) to give **15** as a white solid (66.3 mg, 81%).


15

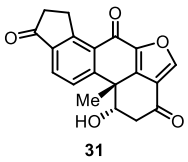
Rroduct **15** is a known compound. The synthetic sample showed the same spectra of ^{1}H and ^{13}C NMR as the data reported by Hanson[4] and Rodrigo[5] groups. R_f = 0.4

(20% ethyl acetate - petroleum ether). $[\alpha]_D^{20}$ = -87.4 (c = 0.61 in dichloromethane), ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.29 (s, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 10.1 Hz, 1H), 6.42 (d, *J* = 10.1 Hz, 1H), 3.87 (ddd, *J* = 19.5, 7.0, 4.7 Hz, 1H), 3.72 (ddd, *J* = 19.5, 7.1, 4.6 Hz, 1H), 2.86 – 2.61 (m, 2H), 1.78 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 206.0, 179.3, 172.9, 159.1, 151.9, 148.2, 147.9, 145.8, 145.4, 137.8, 131.3, 130.7, 127.6, 124.2, 121.6, 41.1, 40.7, 36.4, 28.5. HRMS (ESI–TOF): calculated [M + H$^+$] = 305.0736 for [$C_{19}H_{12}O_4$+H$^+$], found [M + H$^+$] = 305.0805.



15 **31** nodulisporiviridin E **(13)**

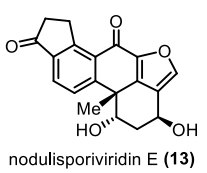
To a solution of **15** (16.0 mg, 0.05 mmol, 1.0 equiv.) in acetone (1 mL) was added hydrochloric acid (2 M in water, 1 mL) at room temperature under an N_2 atmosphere. The reaction mixture was stirred for 12 h, then concentrated under vacuum, and purified by silica gel column chromatography (5 % methanol-dichloromethane) to give **31** as a white solid (12.1 mg, 76%).



31

Product **31** is a known compound reported by Hanson[4] group. R_f = 0.4 (10% methanol-dichloromethane). $[\alpha]_D^{20}$ = -32.2 (c = 0.3 in methanol), ^{1}H NMR (500 MHz, Methanol-d_4) δ 8.55 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 5.51 (s, 1H), 5.10 (t, *J* = 2.9 Hz, 1H), 3.86 – 3.67 (m, 2H), 3.41 – 3.34 (m, 1H), 3.35 (d, *J* = 2.8 Hz, 1H), 2.86 (d, *J* = 2.8 Hz, 1H), 2.85 – 2.70 (m, 2H), 1.67 (s, 3H). ^{13}C NMR (125 MHz, Methanol-d_4) δ 207.3, 190.8, 173.6, 158.7, 155.4, 149.1, 147.1, 145.2, 136.8, 131.0, 126.8, 125.8, 122.0, 73.7, 44.9, 43.2, 35.8, 29.6, 28.1. HRMS (ESI–TOF): calculated [M + H$^+$] = 323.0914 for [$C_{19}H_{14}O_5$+H$^+$], found [M + H$^+$] = 323.0914.

To a solution of **31** (12.1 mg, 0.038 mmol, 1.0 equiv.) in anhydrous toluene (8 mL) was added sodium triacetoxyborohydride (79.6 mg, 0.38 mmol, 10.0 equiv.) at room temperature under an N_2 atmosphere. The reaction mixture was wormed to 110 ^{o}C. The mixture was stirred for 4 h, then concentrated under vacuum, and purified by silica gel column chromatography (5 % methanol – dichloromethane) to give **13** as a white solid (8.7 mg, 71%).

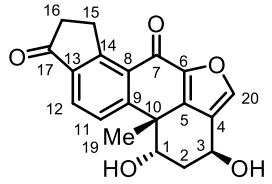


nodulisporiviridin E **(13)**

Compound nodulisporiviridin E (**13**)**:** R_f = 0.30 (10% methanol-dichloromethane), $[\alpha]_D^{20}$ = +25.4 (c = 0.11 in methanol), ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.07 (d, *J* = 1.1 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 5.41 (d, *J* = 6.3 Hz, 1H),

4.92 (d, *J* = 3.9 Hz, 1H), 4.85 (q, *J* = 7.0 Hz, 1H), 4.76 (td, *J* = 3.7, 2.0 Hz, 1H), 3.65 (dt, *J* = 19.1, 5.3 Hz, 1H), 3.55 (dt, *J* = 19.1, 5.3 Hz, 1H), 2.67 (ddd, *J* = 6.4, 4.8, 1.2 Hz, 2H), 2.43 (ddd, *J* = 14.5, 7.6, 3.6 Hz, 1H), 2.17 (ddd, *J* = 14.5, 8.4, 2.2 Hz, 1H), 1.47 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 205.7, 172.9, 157.5, 156.7, 146.8, 145.0, 144.9, 136.2, 130.9, 125.9, 125.9, 125.3, 72.5, 58.5, 43.1, 40.1, 40.0, 40.0, 39.9, 39.8, 39.7, 39.6, 39.5, 39.5, 39.4, 39.2, 39.0, 37.8, 36.0, 32.4, 28.1. HRMS (ESI–TOF): calculated [M + H^+] = 325.1076 for [$C_{19}H_{16}O_5$+H^+], found [M + H^+] = 325.1067.

Comparison of NMR spectroscopic data of synthetic nodulisporiviridin E:



nodulisporiviridin E **(13)**

Natural product: $[\alpha]_D^{19}$ = +35.3 (c = 0.10, methanol)

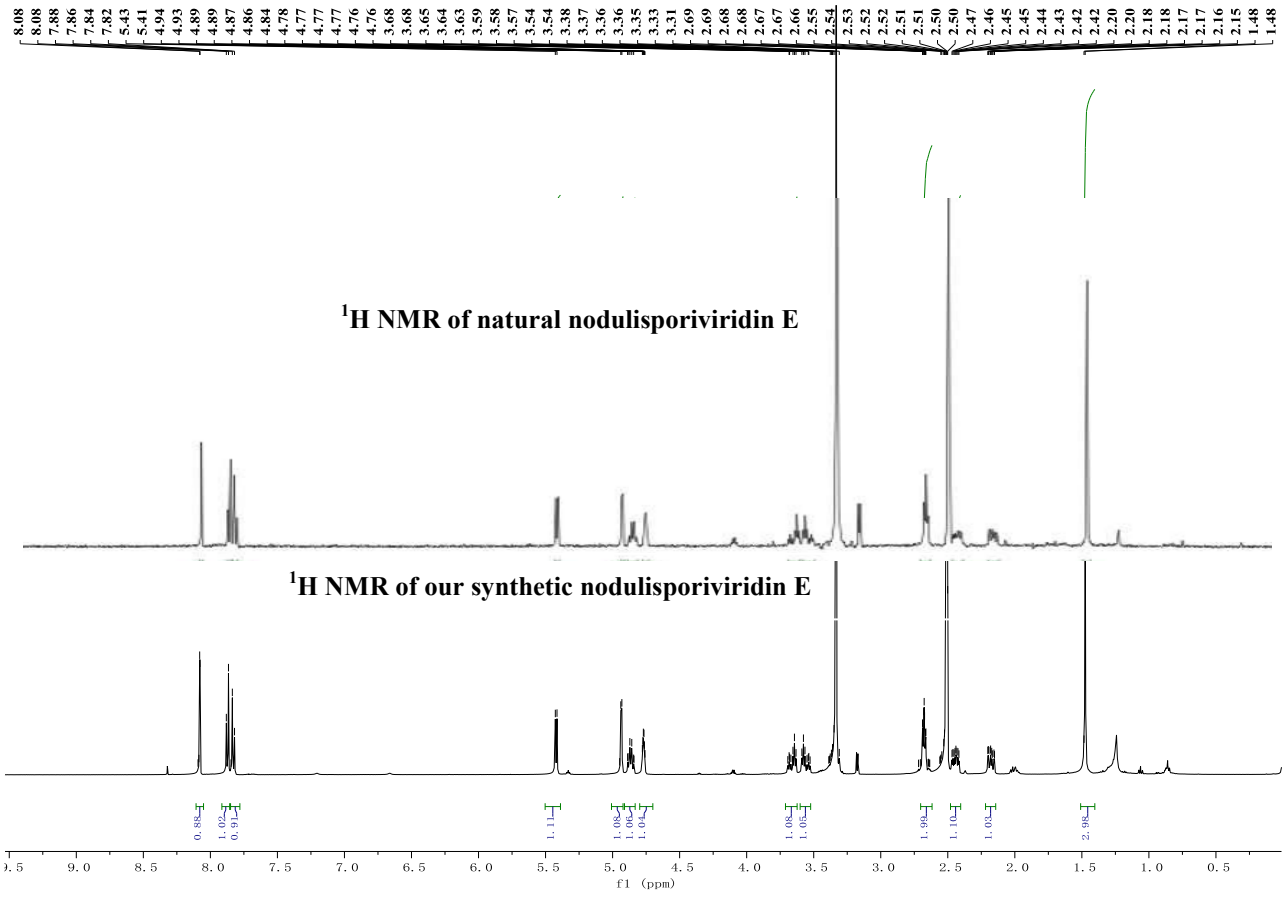
Our Synthetic nodulisporiviridin E: $[\alpha]_D^{20}$ = +25.4 (c = 0.11 methanol)

Table S2 Comparison of ^{1}H MR spectroscopic data of natural [6] and synthetic synthetic nodulisporiviridin E

position	natural δ ^{1}H [ppm; mult; *J* (Hz)] 400 MHz	synthetic δ ^{1}H [ppm; mult; *J* (Hz)] 500 MHz	deviation (natural–our) Δδ (ppm)
1	4.76 (m)	4.76 (td, 3.7, 2.0 H)	0
2-a	2.43 (ddd, 14.7, 7.6, 3.6 Hz)	2.43 (ddd, 14.5, 7.6, 3.6 Hz),	0
2-b	2.16 (ddd, 14.7, 8.4, 1.8 Hz)	2.17 (ddd, 14.5, 8.4, 2.2 Hz)	-0.01
3	4.85 (q 7.3 Hz)	4.85 (q, 7.0 Hz)	0
11	7.82(d, 8 Hz)	7.82 (d, 8.1 Hz),	0
12	7.86 (d, 8 Hz)	7.86 (d, 8.0 Hz)	0
15-a	3.66 (dt 19.0, 5.7 Hz)	3.65 (dt, 19.1, 5.3 Hz),	0.01
15-b	3.54 (dt 19.0, 5.7 Hz)	3.55 (dt, 19.1, 5.3 Hz)	-0.01
16	2.67 (t 5.7 Hz)	2.67 (ddd, 6.4, 4.8, 1.2 Hz),	0
19	1.47 (s)	1.47 (s).	0
20	8.07 (s)	8.07 (d, 1.1 Hz)	0
OH-1	4.93 (d 3.8 Hz)	4.92 (d, 3.9 Hz)	0.01
OH-2	5.42 (d 6.2 Hz)	5.41 (d, 6.3 Hz),	0.01

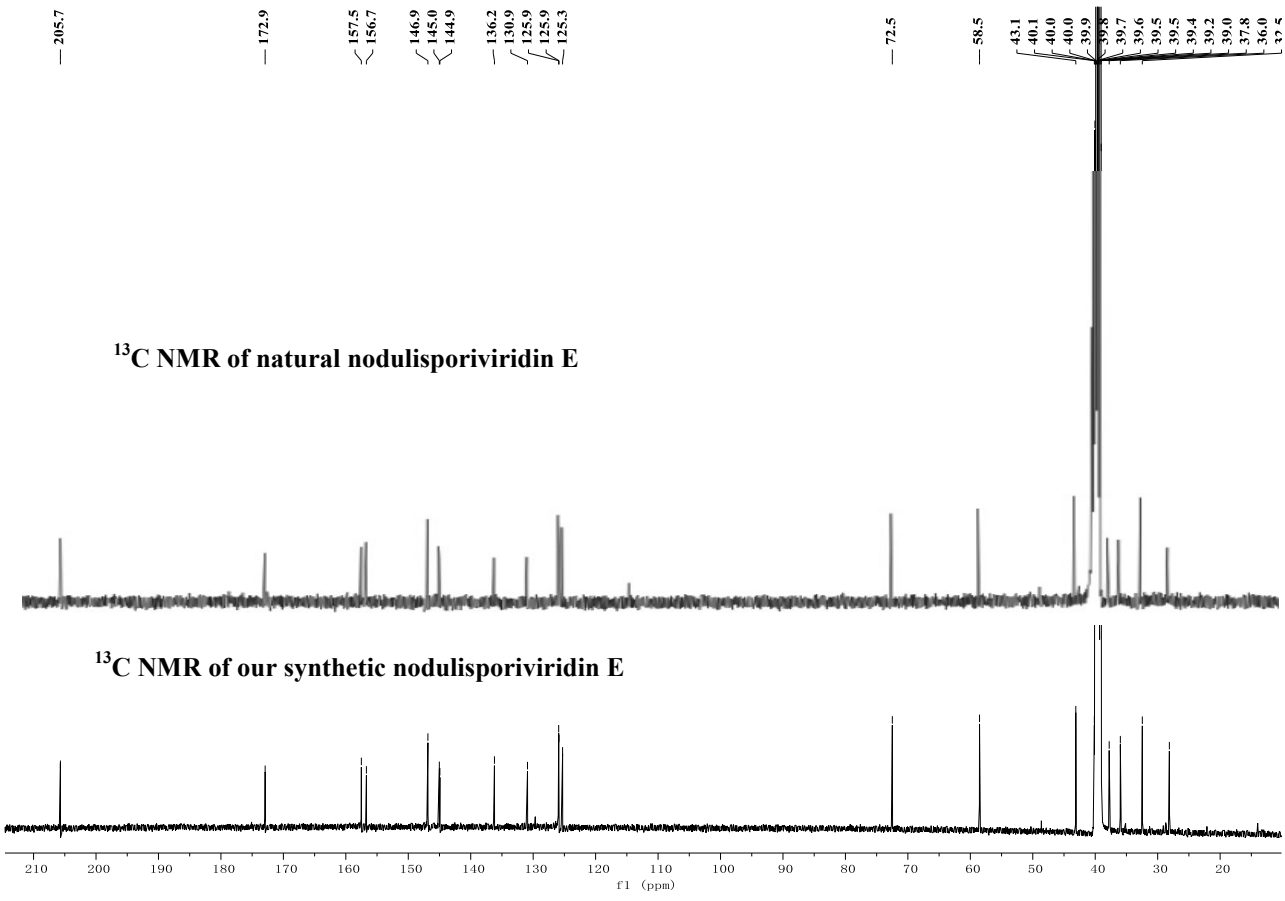
Table S3 Comparison of ^{13}C NMR spectroscopic data of natural [6] and synthetic synthetic nodulisporiviridin E

position	natural δ ^{13}C [ppm], 100Hz	synthetic δ ^{13}C [ppm], 125 MHz	deviation (natural–our) Δδ (ppm)
1	72.4	72.5	-0.1
2	37.7	37.8	-0.1
3	58.5	58.5	0
4	125.3	125.3	0
5	145.0	145.0	0
6	144.9	144.9	0
7	172.9	172.9	0
8	130.9	130.9	0
9	156.7	156.7	0
10	43.1	43.1	0
11	125.9	125.9	0
12	125.8	125.8	0
13	136.2	136.2	0
14	157.5	157.5	0
15	28.1	28.1	0
16	35.9	36.0	-0.1
17	205.7	205.7	0
19	32.4	32.5	-0.1
20	146.8	146.9	-0.1



^{1}H NMR of natural nodulisporiviridin E

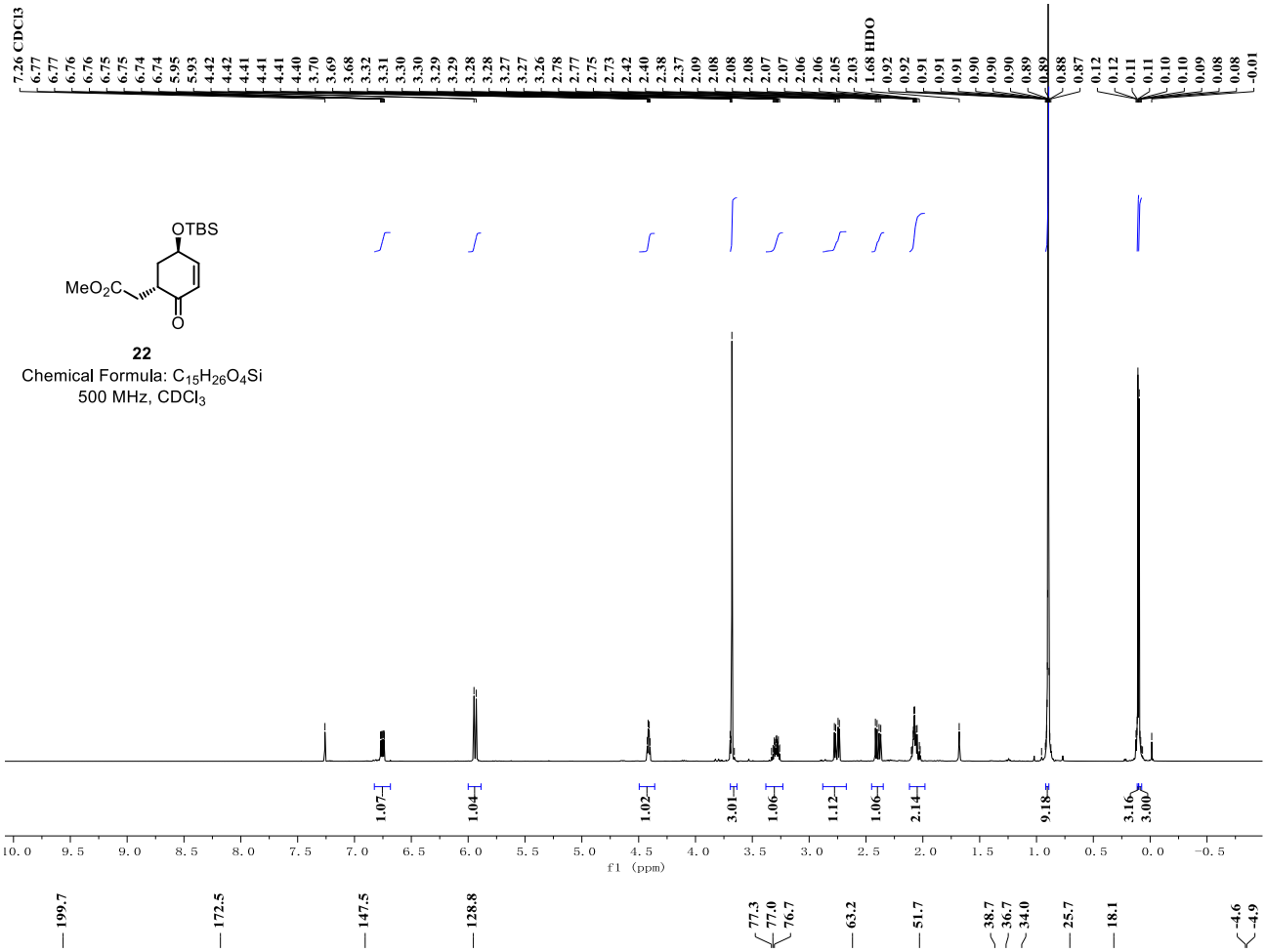
^{1}H NMR of our synthetic nodulisporiviridin E

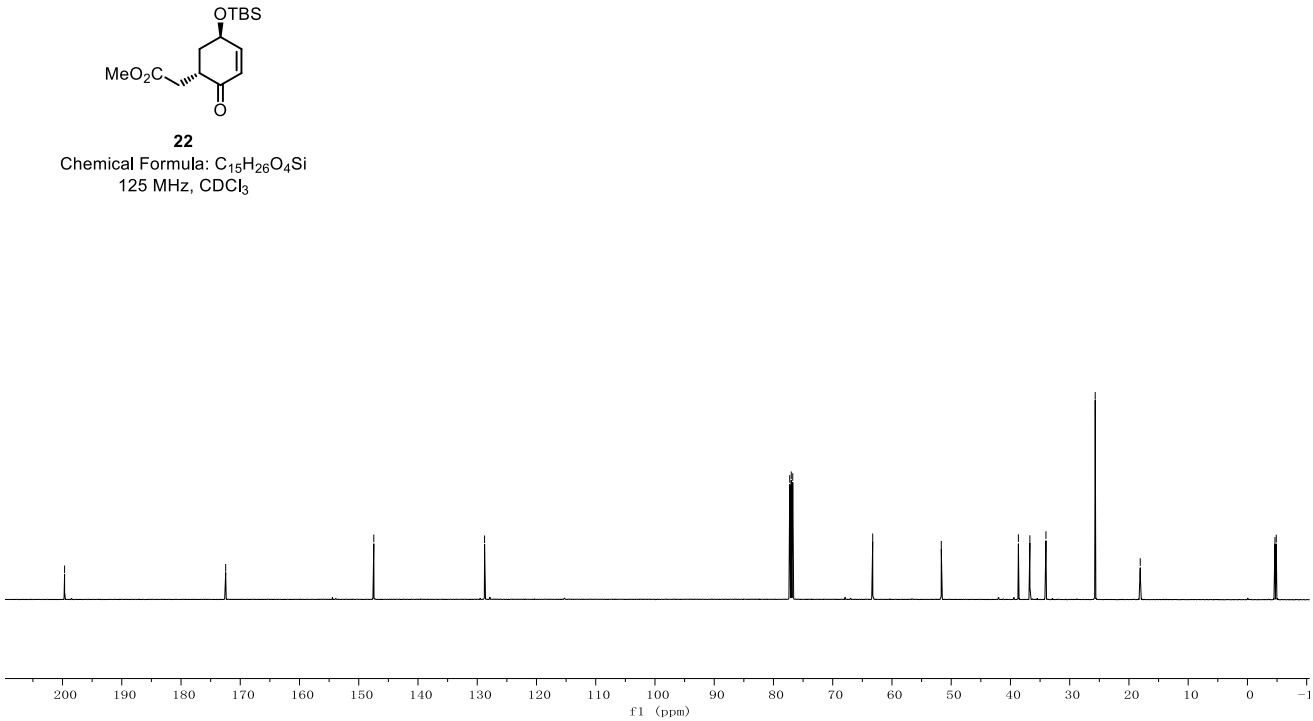


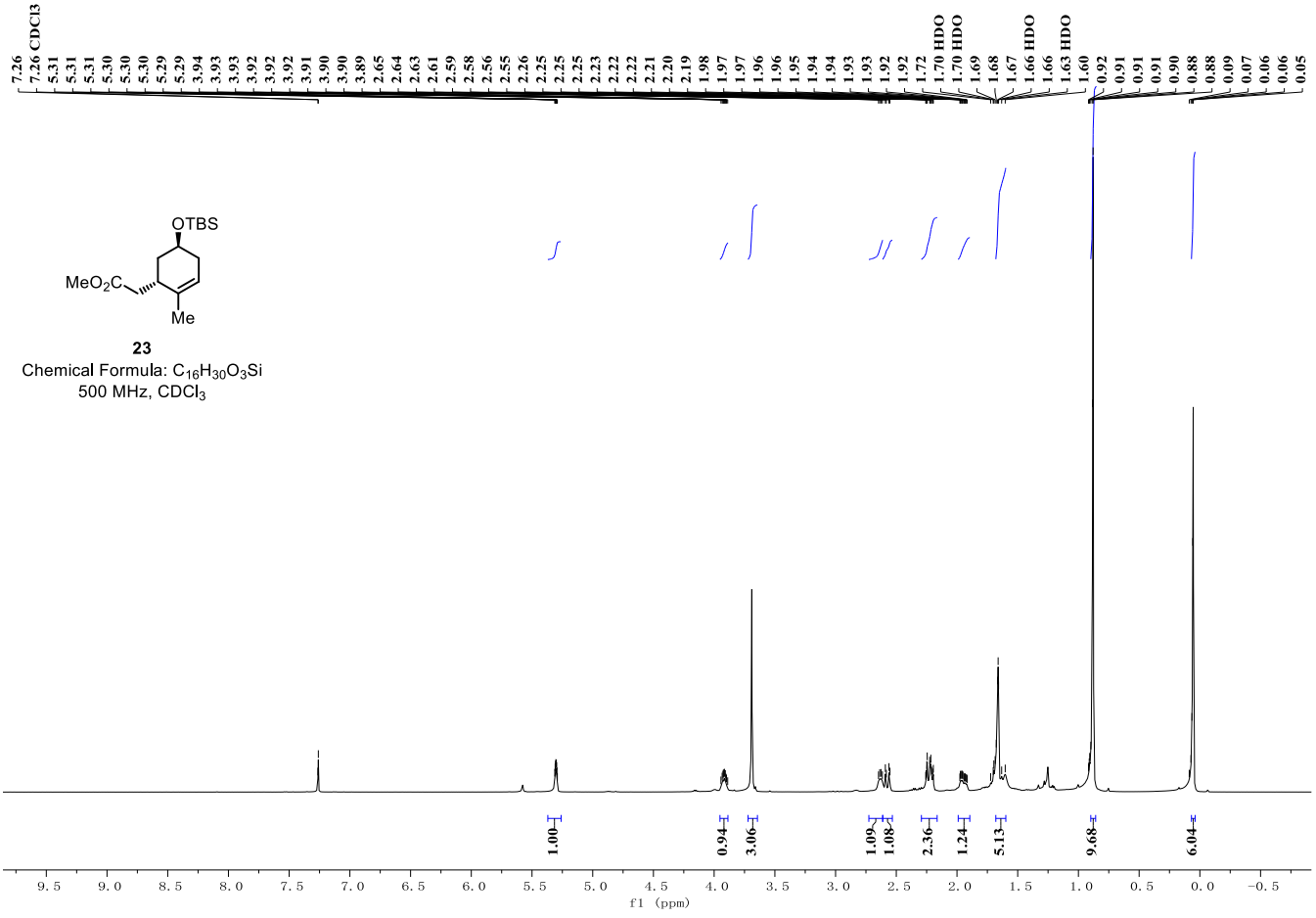
^{13}C NMR of natural nodulisporiviridin E

^{13}C NMR of our synthetic nodulisporiviridin E

1H and 13C NMR Spectra of the Synthetic Intermediates and products



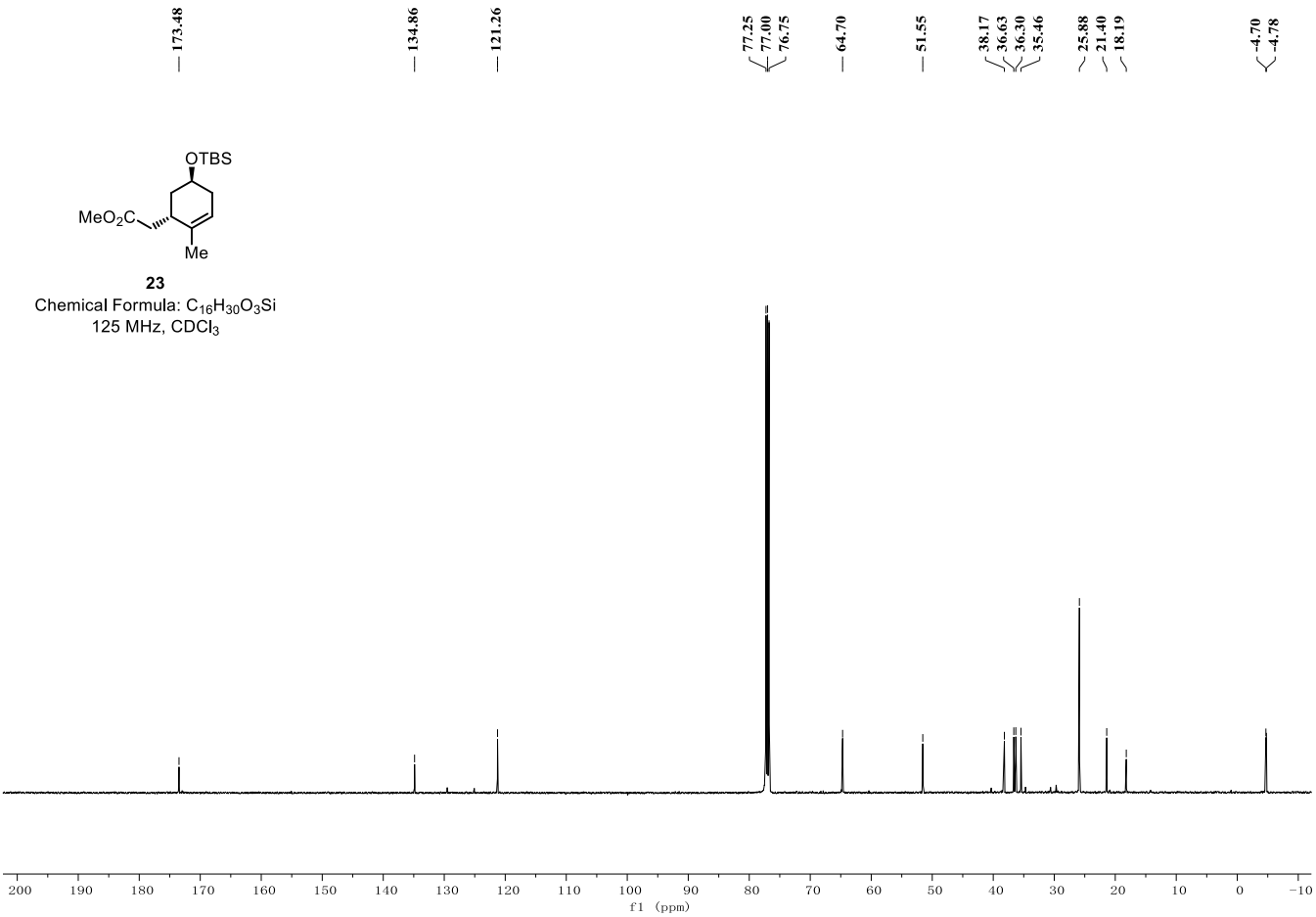




23

Chemical Formula: $C_{16}H_{30}O_3Si$

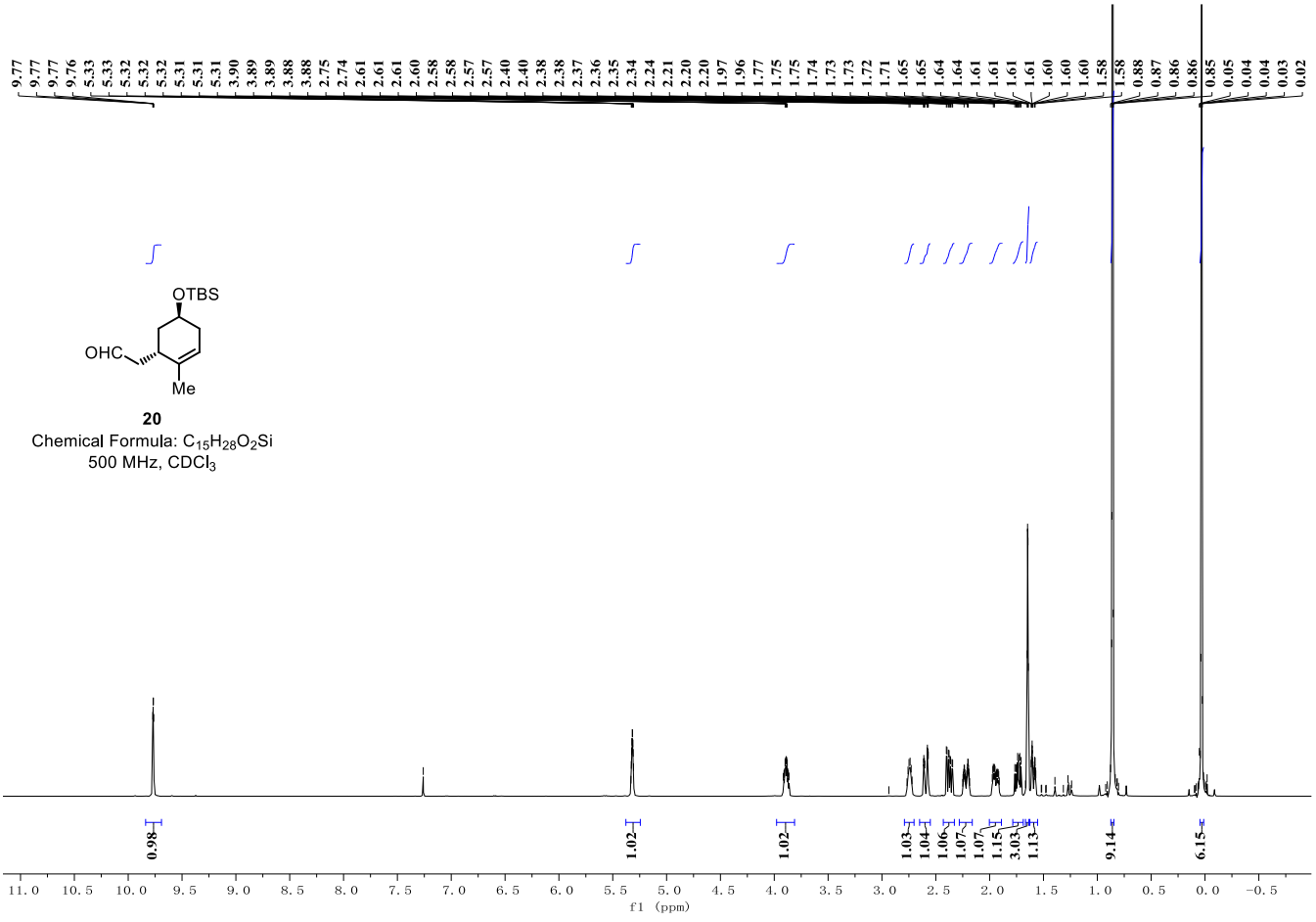
500 MHz, $CDCl_3$



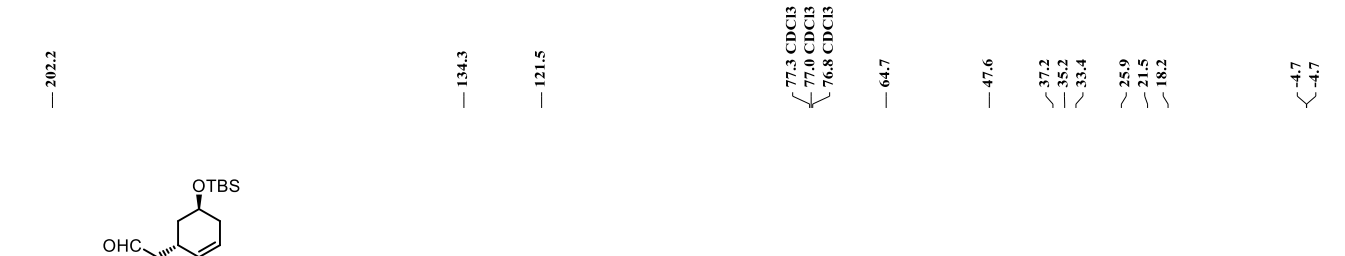
23

Chemical Formula: $C_{16}H_{30}O_3Si$

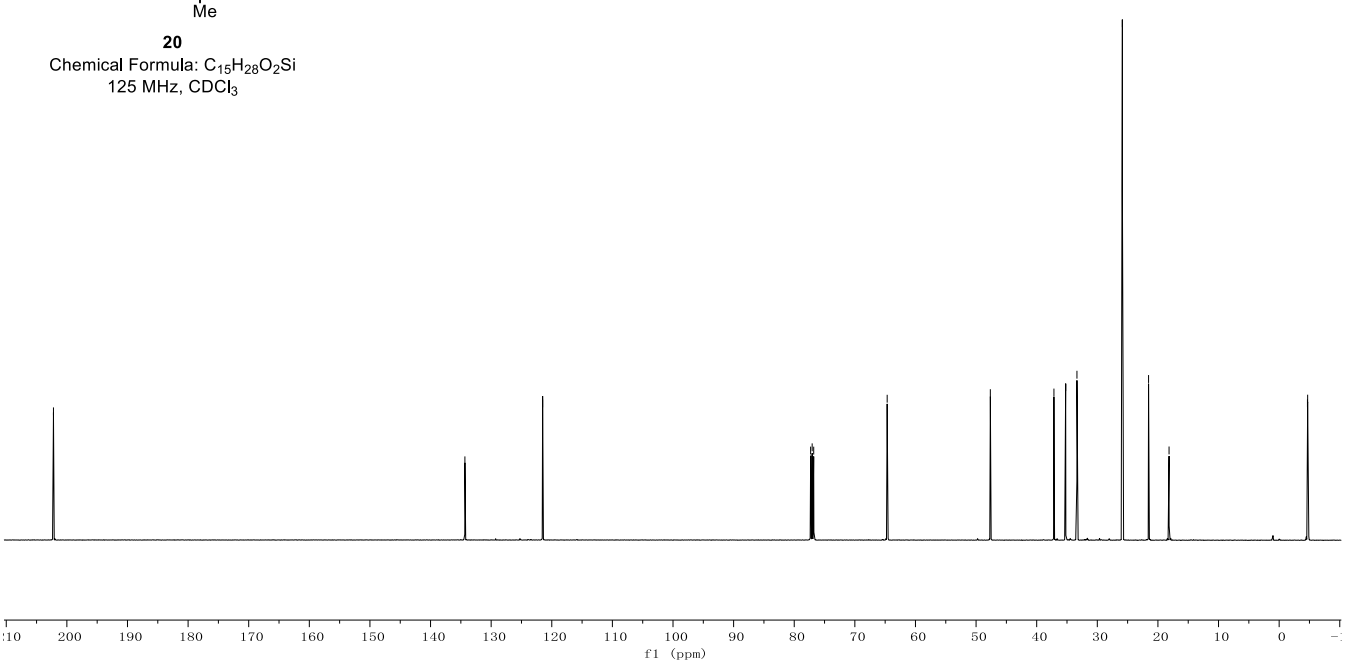
125 MHz, $CDCl_3$

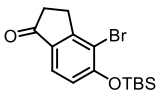


20
Chemical Formula: $C_{15}H_{28}O_2Si$
500 MHz, $CDCl_3$

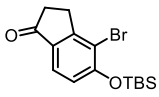


20
Chemical Formula: $C_{15}H_{28}O_2Si$
125 MHz, $CDCl_3$

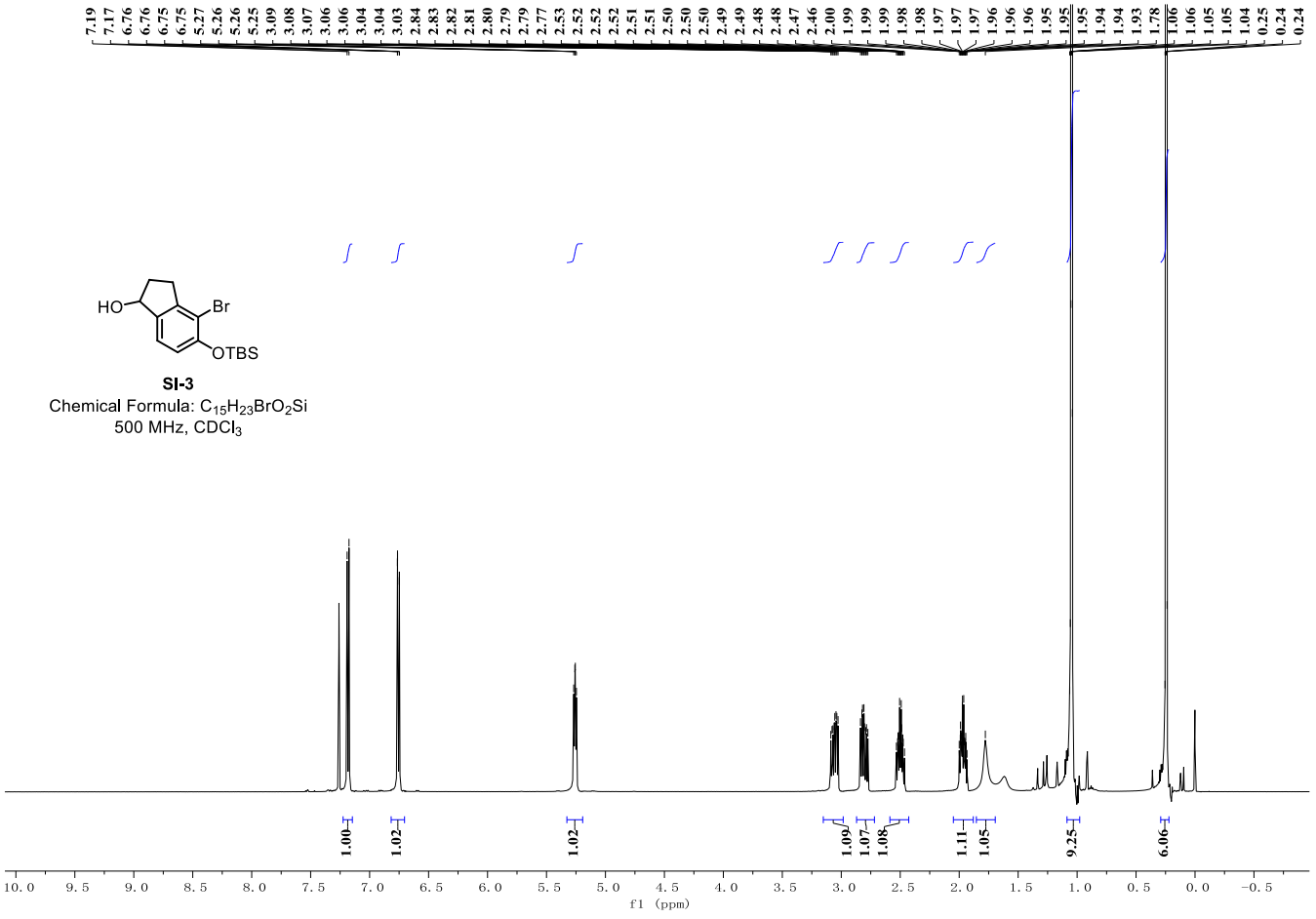




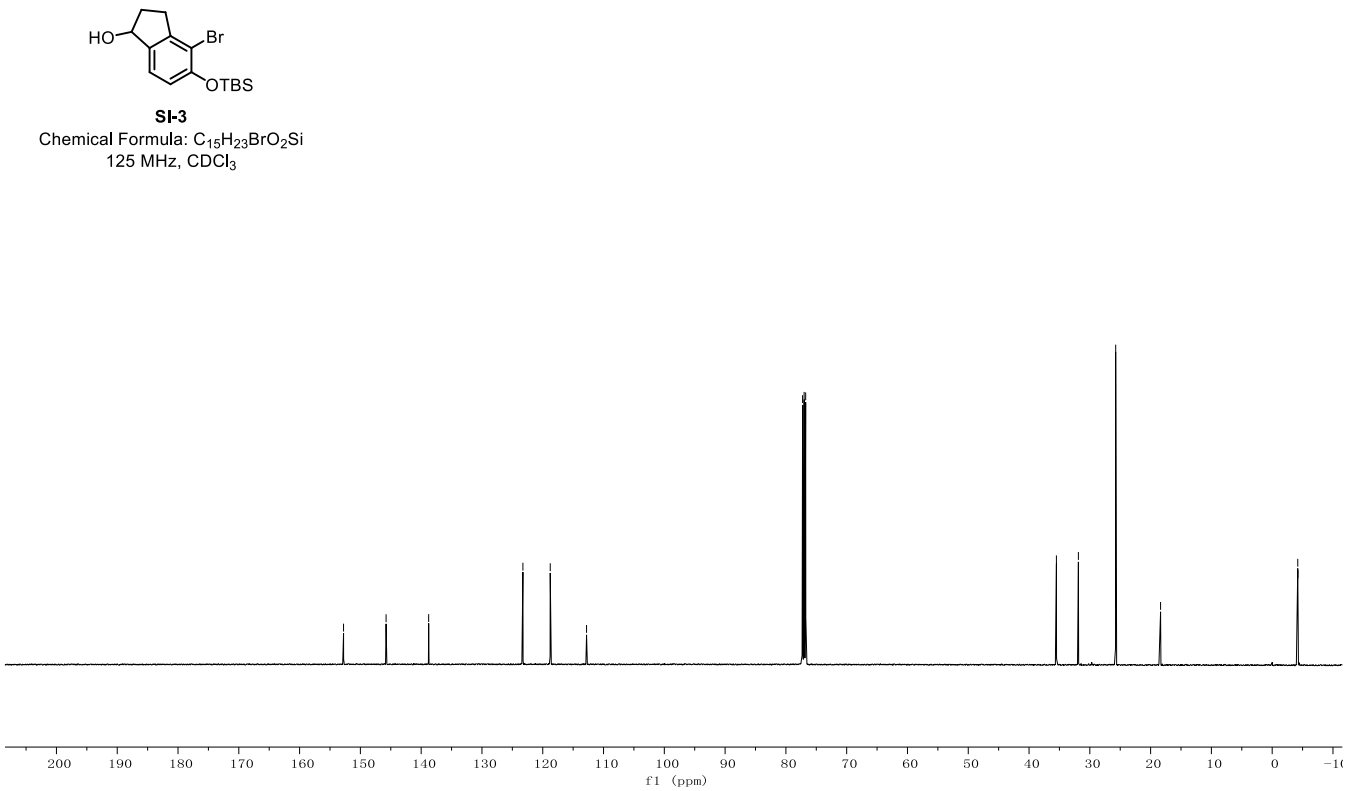
SI-2
Chemical Formula: $C_{15}H_{21}BrO_2Si$
500 MHz, $CDCl_3$



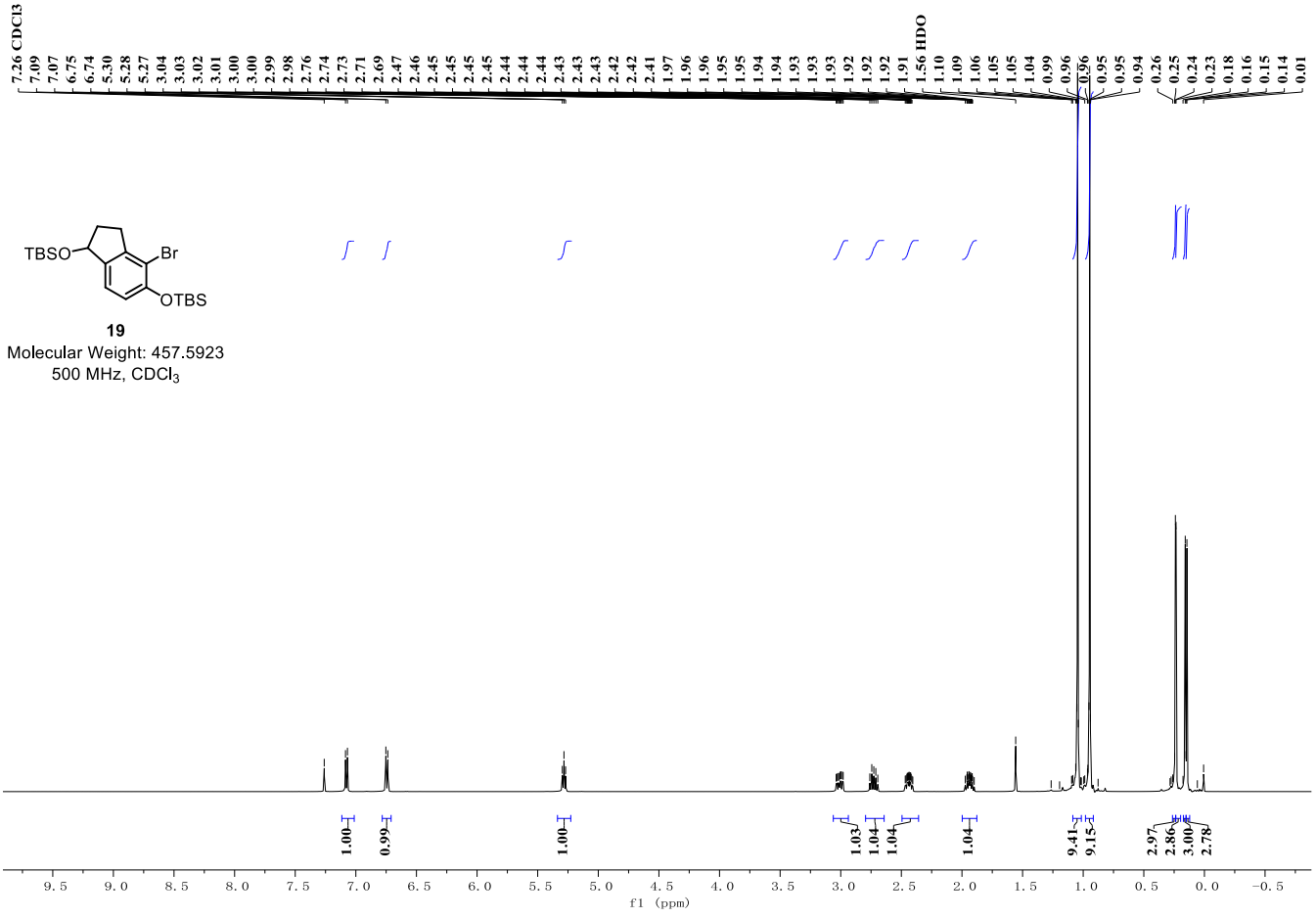
SI-2
Chemical Formula: $C_{15}H_{21}BrO_2Si$
125 MHz, $CDCl_3$



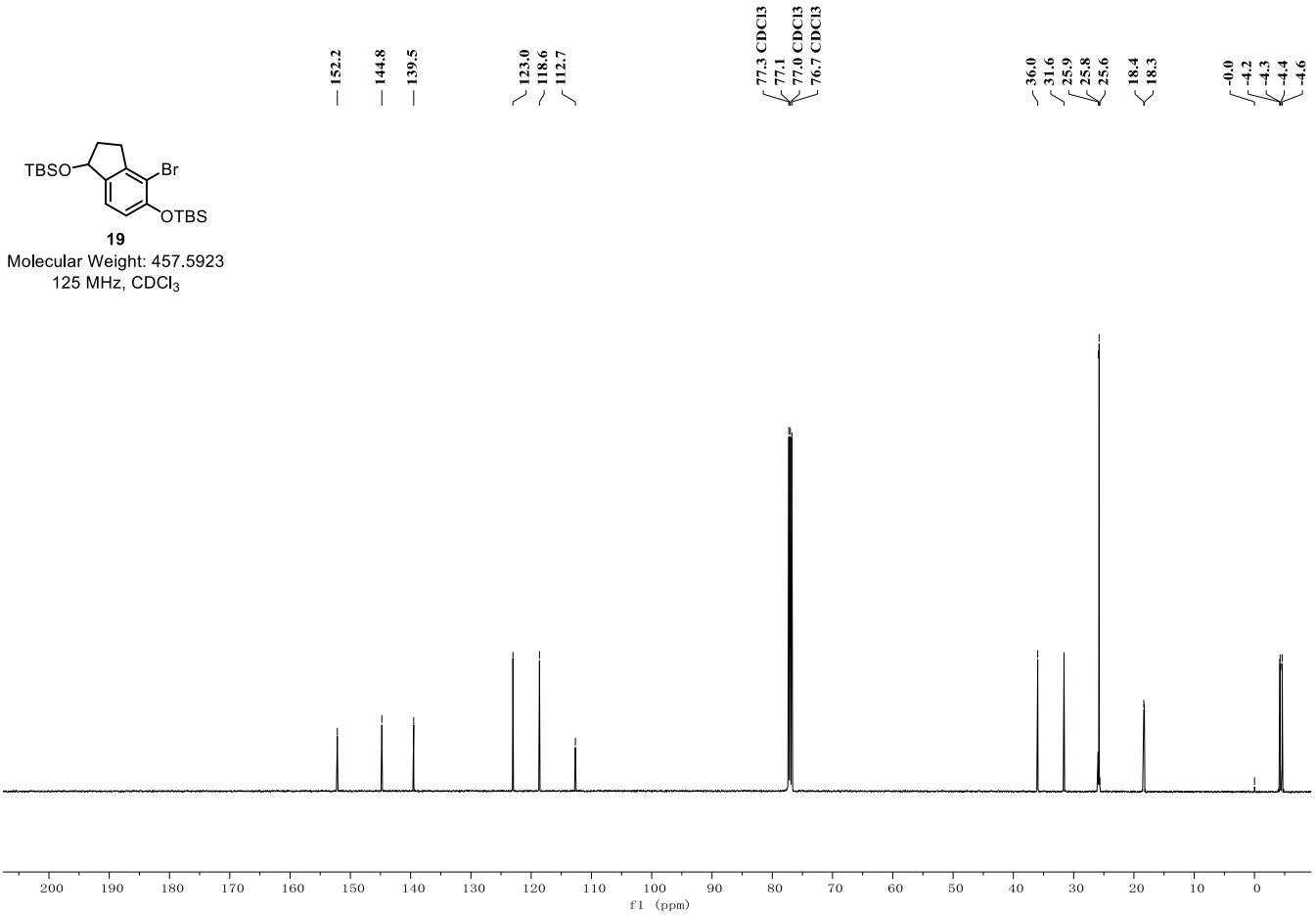
SI-3
Chemical Formula: $C_{15}H_{23}BrO_2Si$
500 MHz, $CDCl_3$



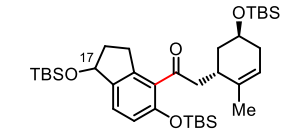
SI-3
Chemical Formula: $C_{15}H_{23}BrO_2Si$
125 MHz, $CDCl_3$



19
Molecular Weight: 457.5923
500 MHz, $CDCl_3$

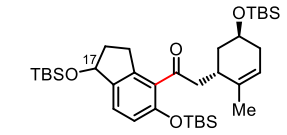


19
Molecular Weight: 457.5923
125 MHz, $CDCl_3$



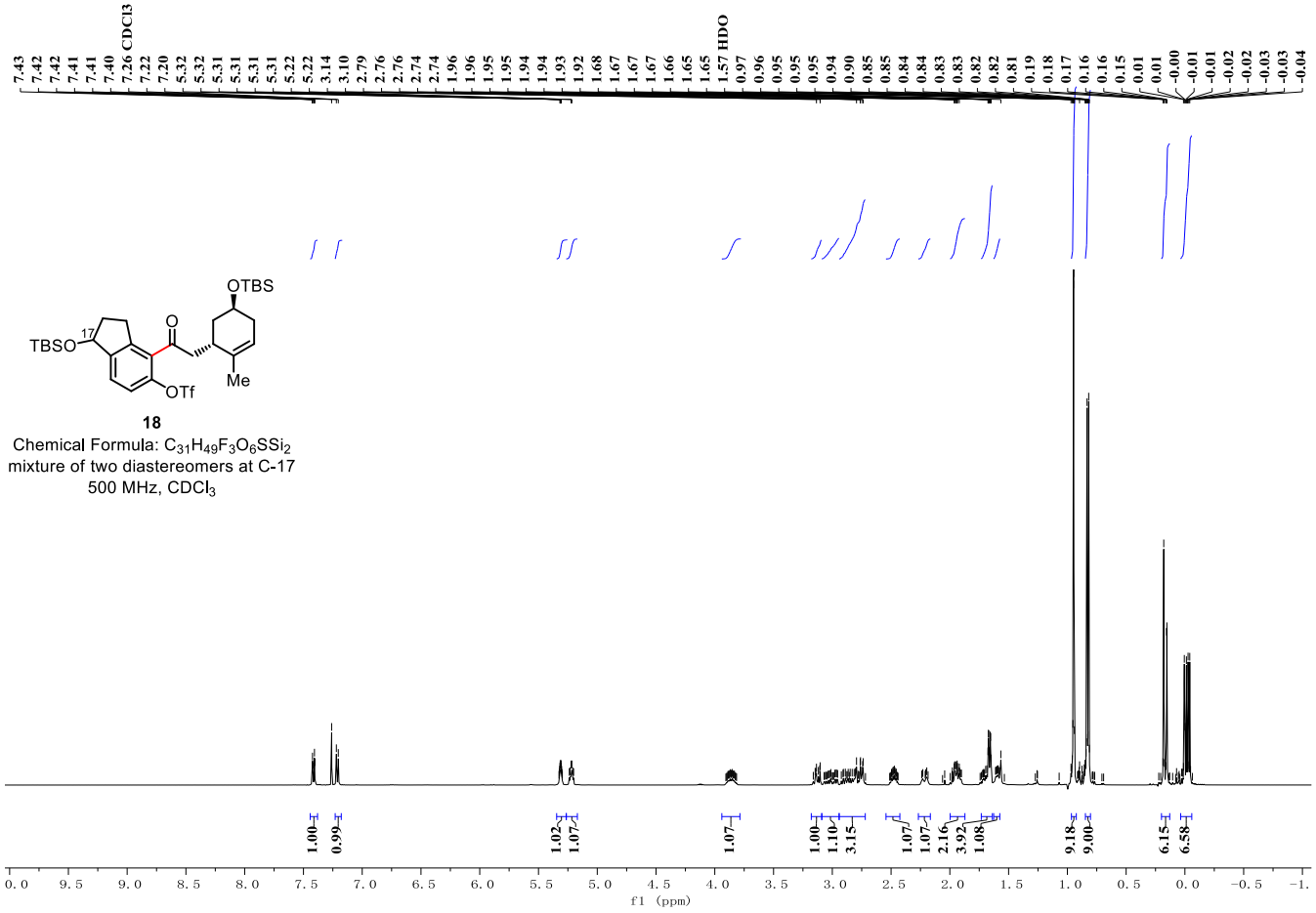
24

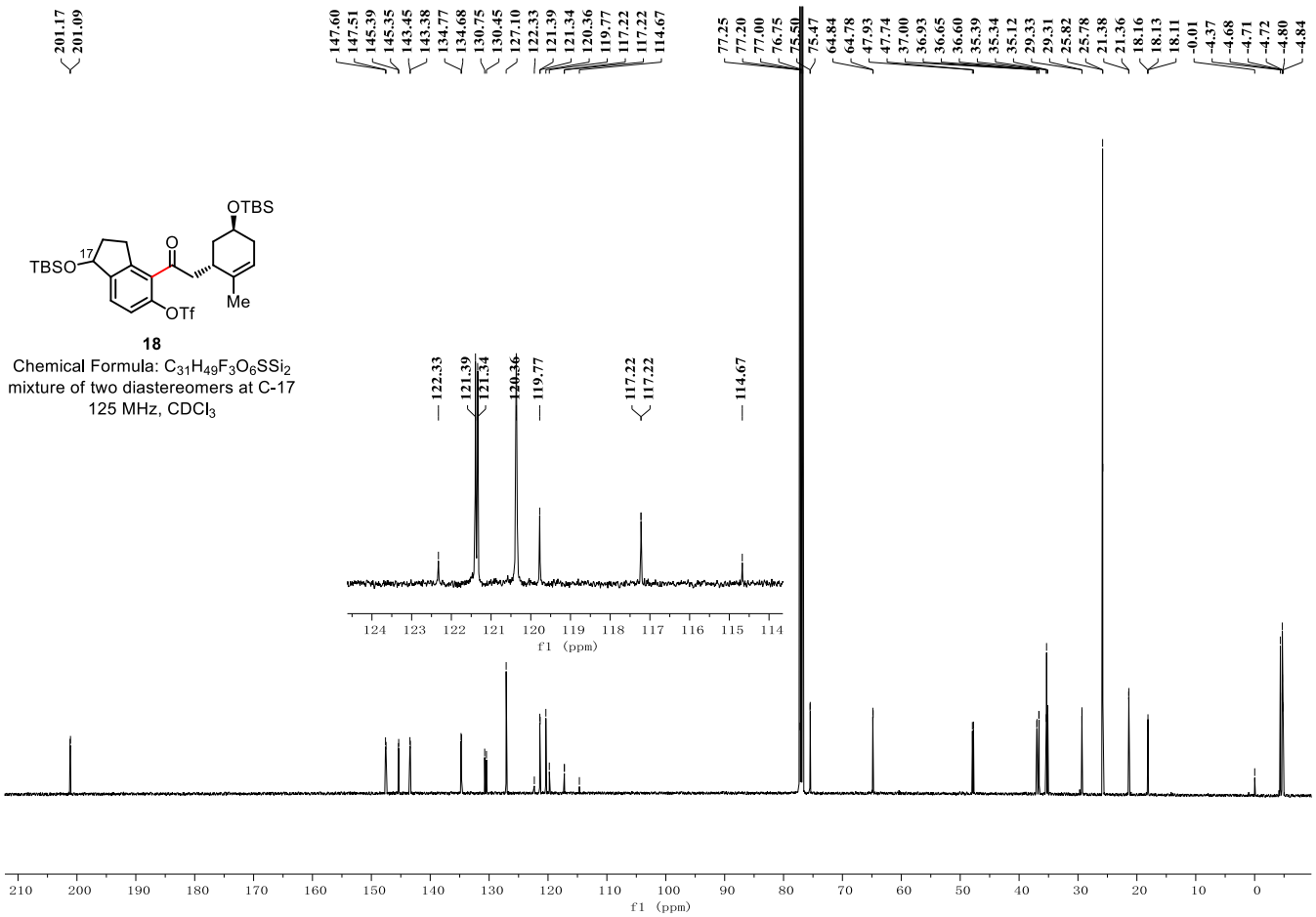
Chemical Formula: $C_{36}H_{64}O_4Si_3$
mixture of two diastereomers at C-17
500 MHz, $CDCl_3$

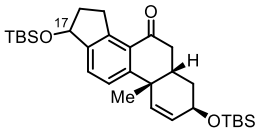


24

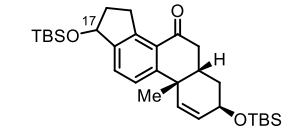
Chemical Formula: $C_{36}H_{64}O_4Si_3$
mixture of two diastereomers at C-17
125 MHz, $CDCl_3$


7.43 7.42 7.42 7.41 7.41 7.40 7.26 CDCl3 7.22 7.20 5.32 5.32 5.31 5.31 5.31 5.31 5.22 5.22 3.14 3.10 2.79 2.76 2.76 2.74 2.74 1.96 1.96 1.95 1.95 1.94 1.94 1.93 1.92 1.68 1.67 1.67 1.67 1.66 1.65 1.65 1.57 HDO 0.97 0.96 0.95 0.95 0.95 0.94 0.90 0.85 0.85 0.84 0.84 0.83 0.83 0.82 0.82 0.81 0.19 0.18 0.17 0.16 0.16 0.15 0.01 0.01 -0.00 -0.01 -0.01 -0.02 -0.02 -0.03 -0.04
OTBS
TBSO
17
O
Me
OTf
18
Chemical Formula: C31H49F3O6SSi2
mixture of two diastereomers at C-17
500 MHz, CDCl3
1.00 0.99 1.02 1.07 1.07 1.00 1.10 3.15 1.07 1.07 2.16 3.92 1.08 9.18 9.00 6.15 6.58
f1 (ppm)

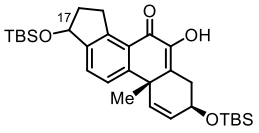

201.17 201.09
147.60 147.51 145.39 145.35 143.45 143.38 134.77 134.68 130.75 130.45 127.10 122.33 121.39 121.34 120.36 119.77 117.22 117.22 114.67
77.25 77.20 77.00 76.75 75.50 75.47 64.84 64.78 47.93 47.74 37.00 36.93 36.65 36.60 35.39 35.34 35.12 29.33 29.31 25.82 25.78 21.38 21.36 18.16 18.13 18.11 -0.01 -4.37 -4.68 -4.71 -4.72 -4.80 -4.84
OTBS
TBSO
17
O
Me
OTf
18
Chemical Formula: C31H49F3O6SSi2
mixture of two diastereomers at C-17
125 MHz, CDCl3
122.33 121.39 121.34 120.36 119.77 117.22 117.22 114.67
f1 (ppm)
f1 (ppm)



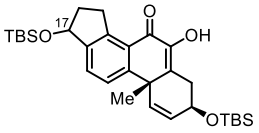
17
Chemical Formula: $C_{30}H_{48}O_3Si_2$
mixture of two diastereomers at C-17
500 MHz, $CDCl_3$



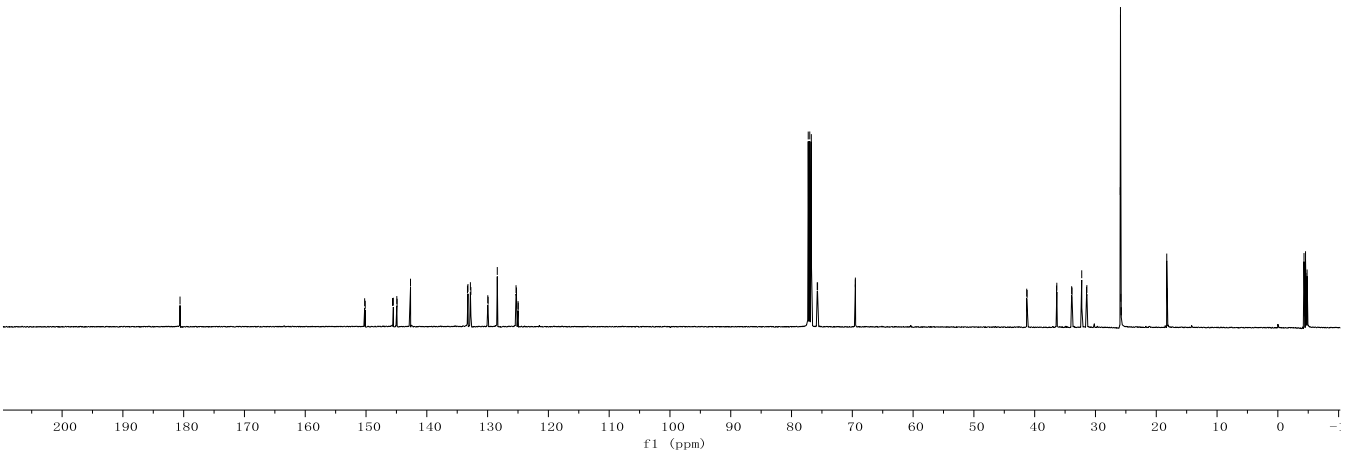
17
Chemical Formula: $C_{30}H_{48}O_3Si_2$
mixture of two diastereomers at C-17
125 MHz, $CDCl_3$

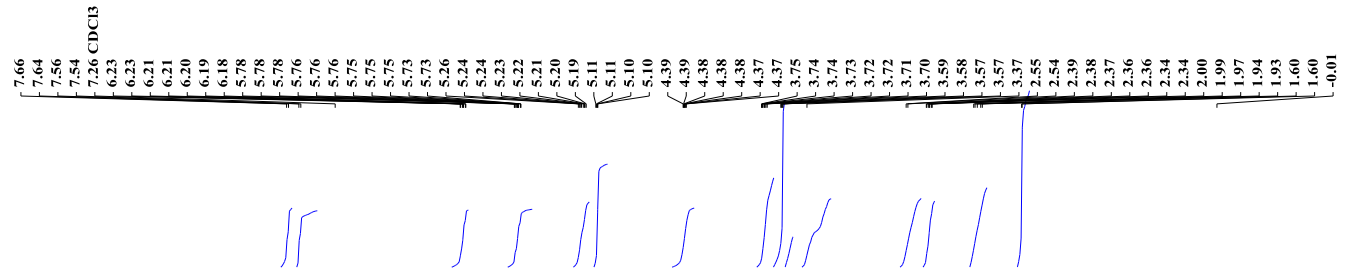


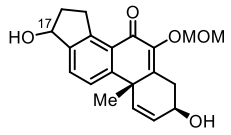
25
Chemical Formula: $C_{30}H_{46}O_4Si_2$
mixture of two diastereomers at C-17
500 MHz, $CDCl_3$



25
Chemical Formula: $C_{30}H_{46}O_4Si_2$
mixture of two diastereomers at C-17
125 MHz, $CDCl_3$





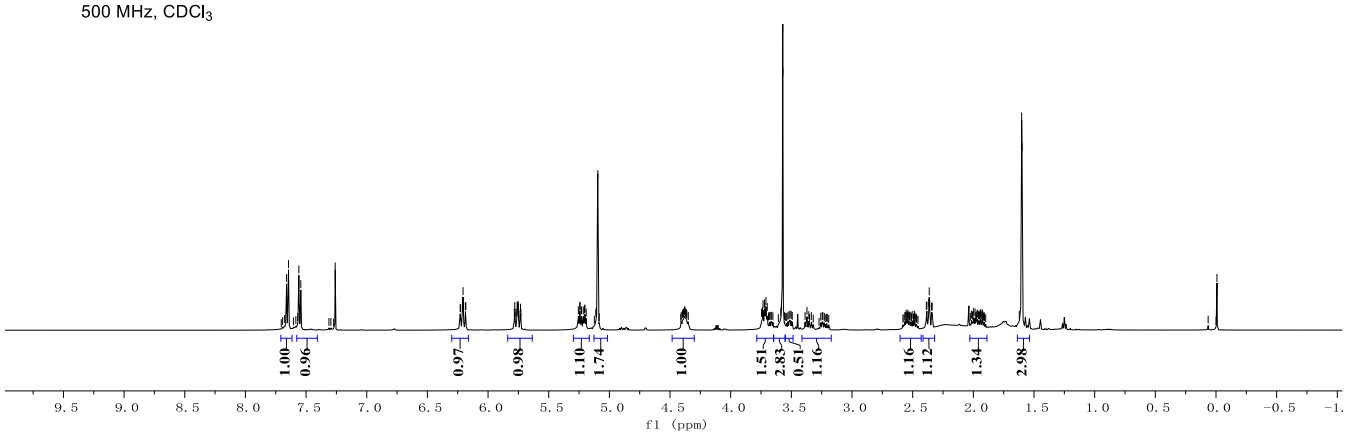


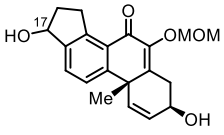
26

Chemical Formula: $C_{32}H_{50}O_5Si_2$

mixture of two diastereomers at C-17

500 MHz, $CDCl_3$



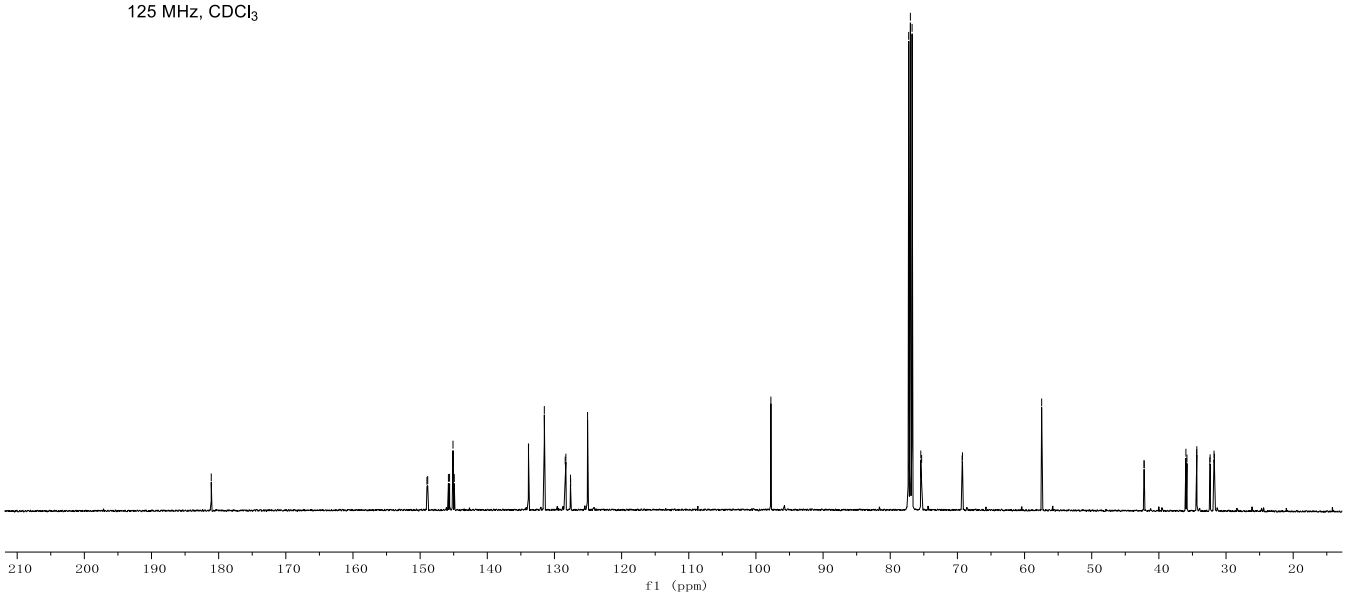


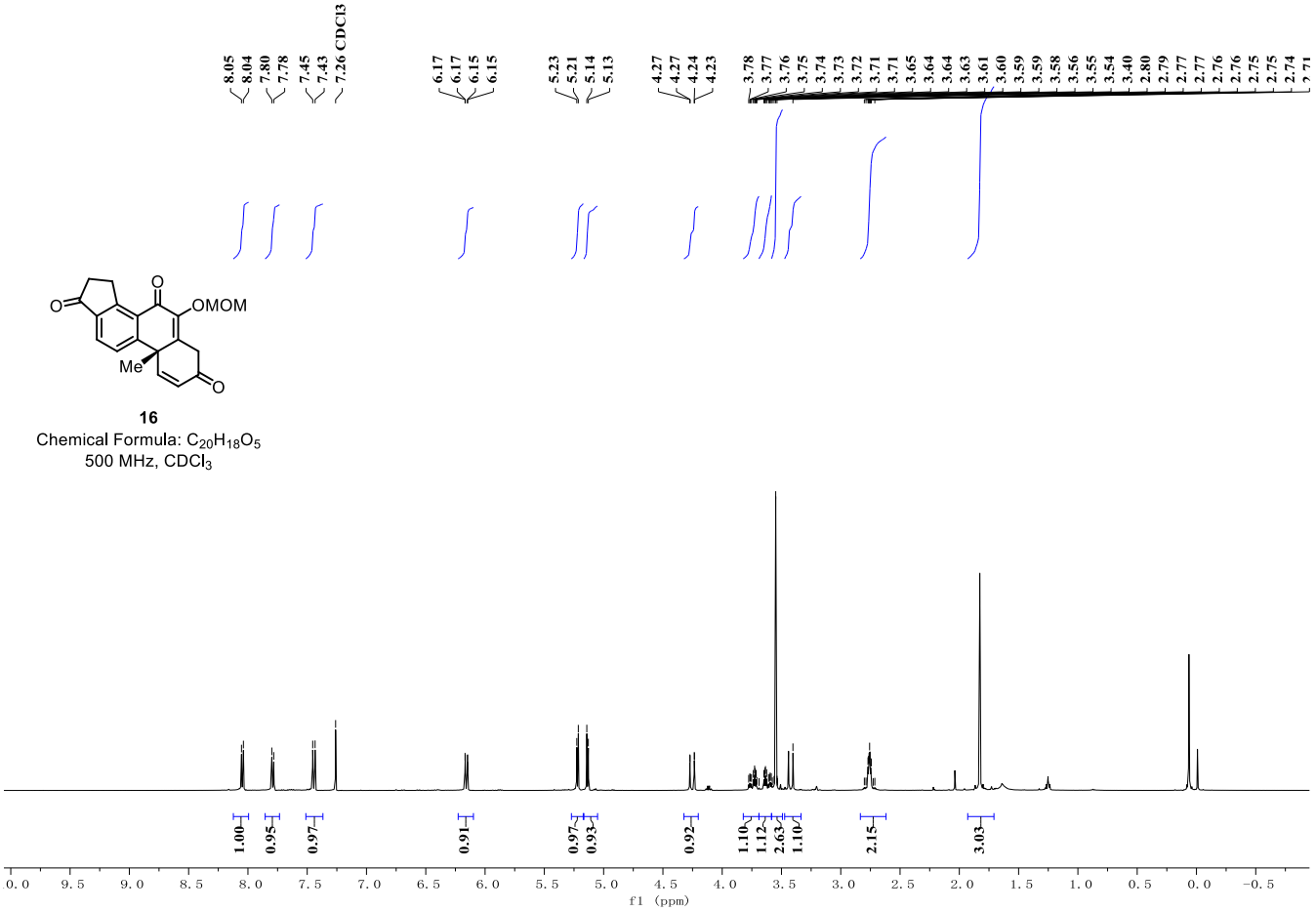
26

Chemical Formula: $C_{32}H_{50}O_5Si_2$

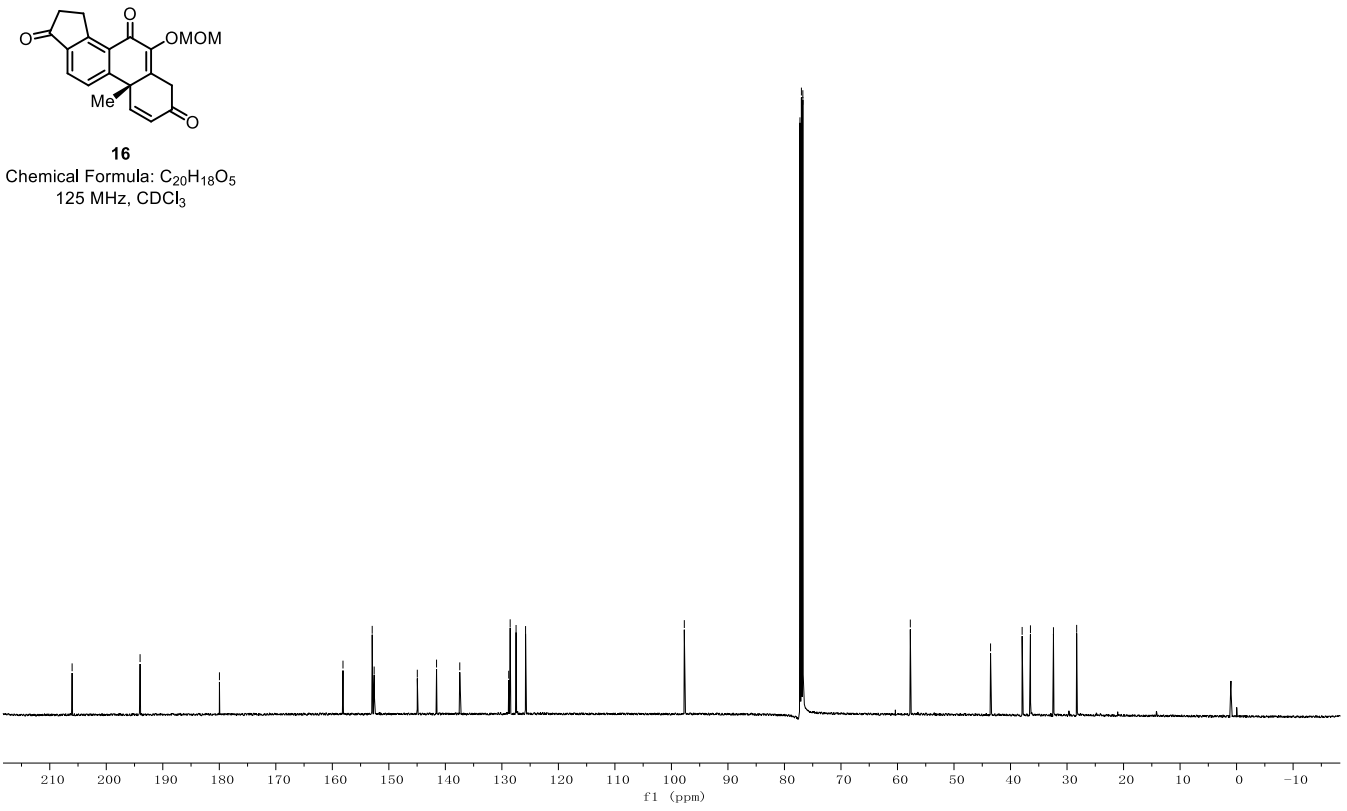
mixture of two diastereomers at C-17

125 MHz, $CDCl_3$

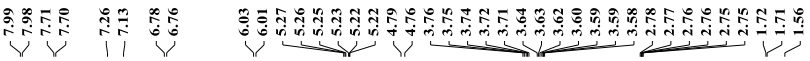


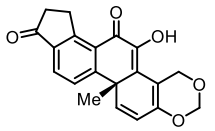


16
Chemical Formula: $C_{20}H_{18}O_5$
500 MHz, $CDCl_3$



16
Chemical Formula: $C_{20}H_{18}O_5$
125 MHz, $CDCl_3$

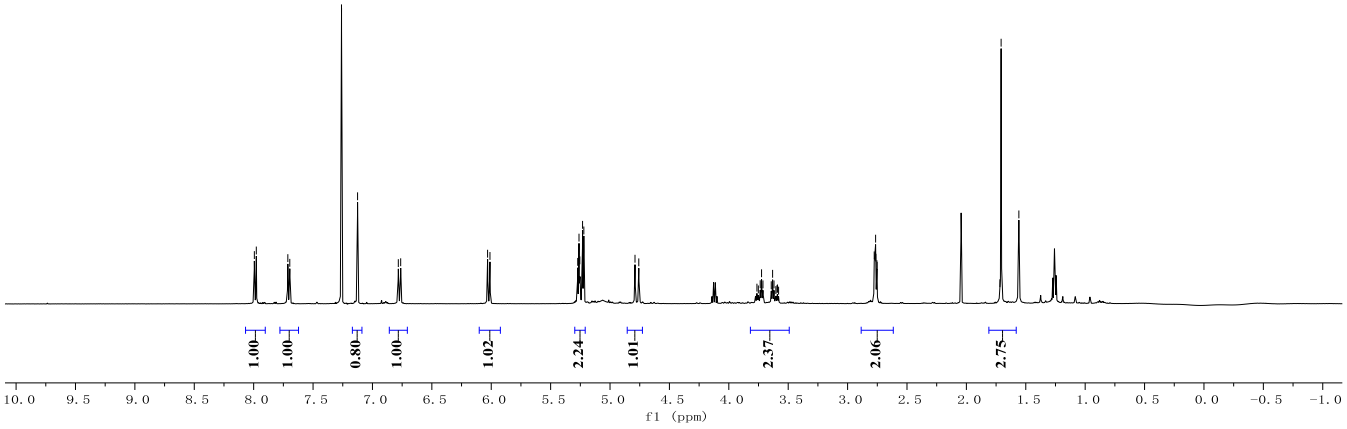


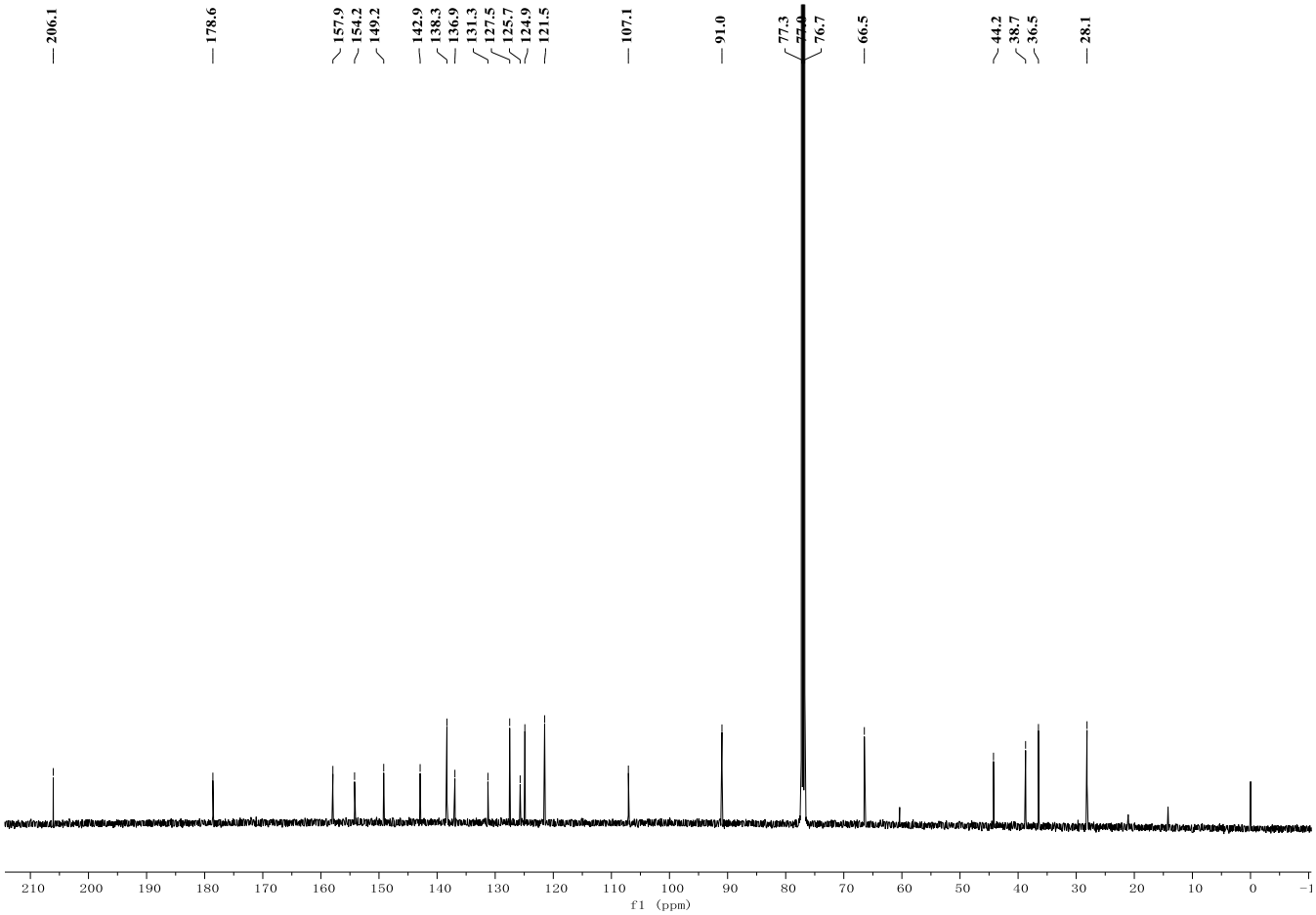


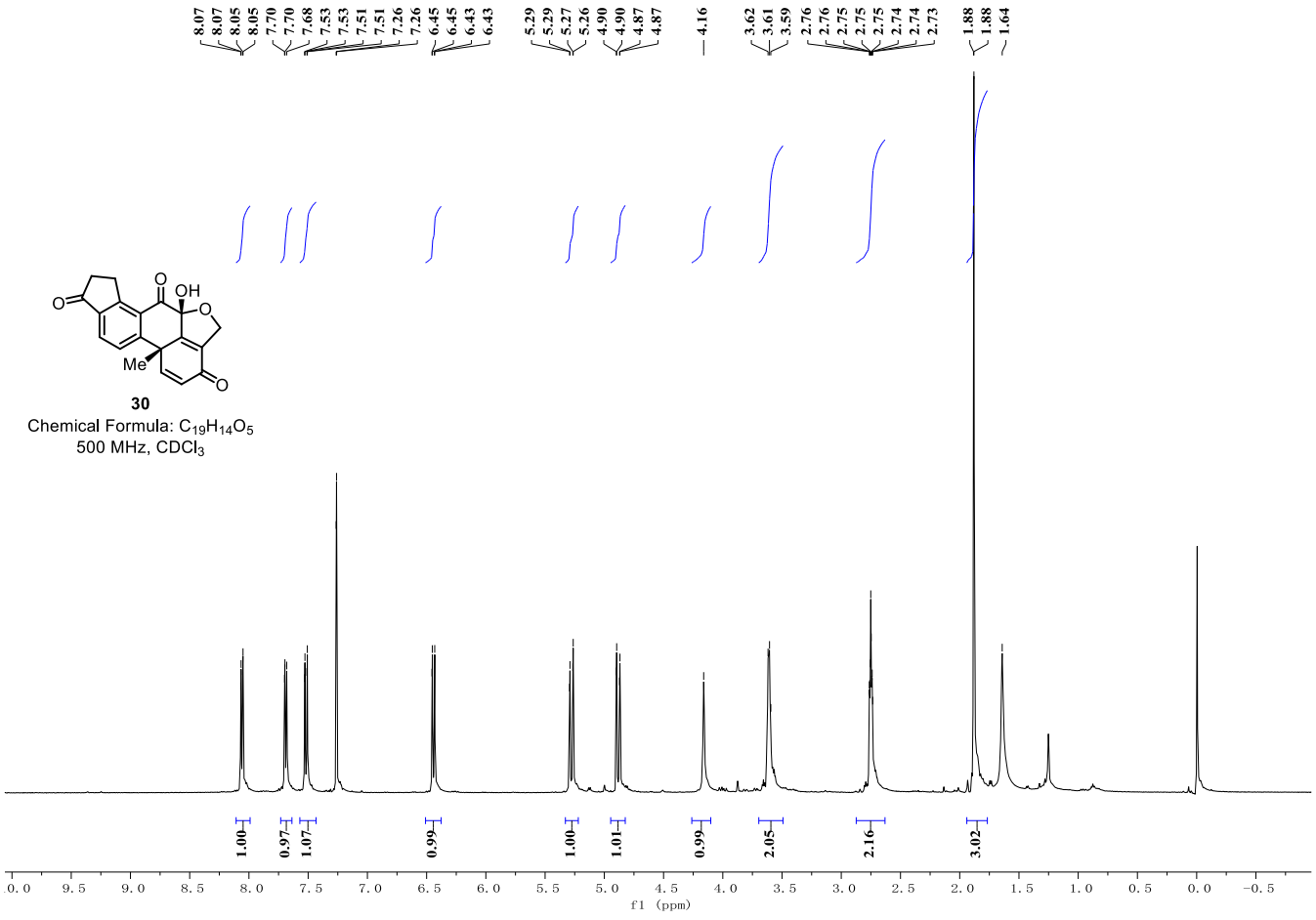
28

Chemical Formula: $C_{20}H_{16}O_5$

500 MHz, $CDCl_3$



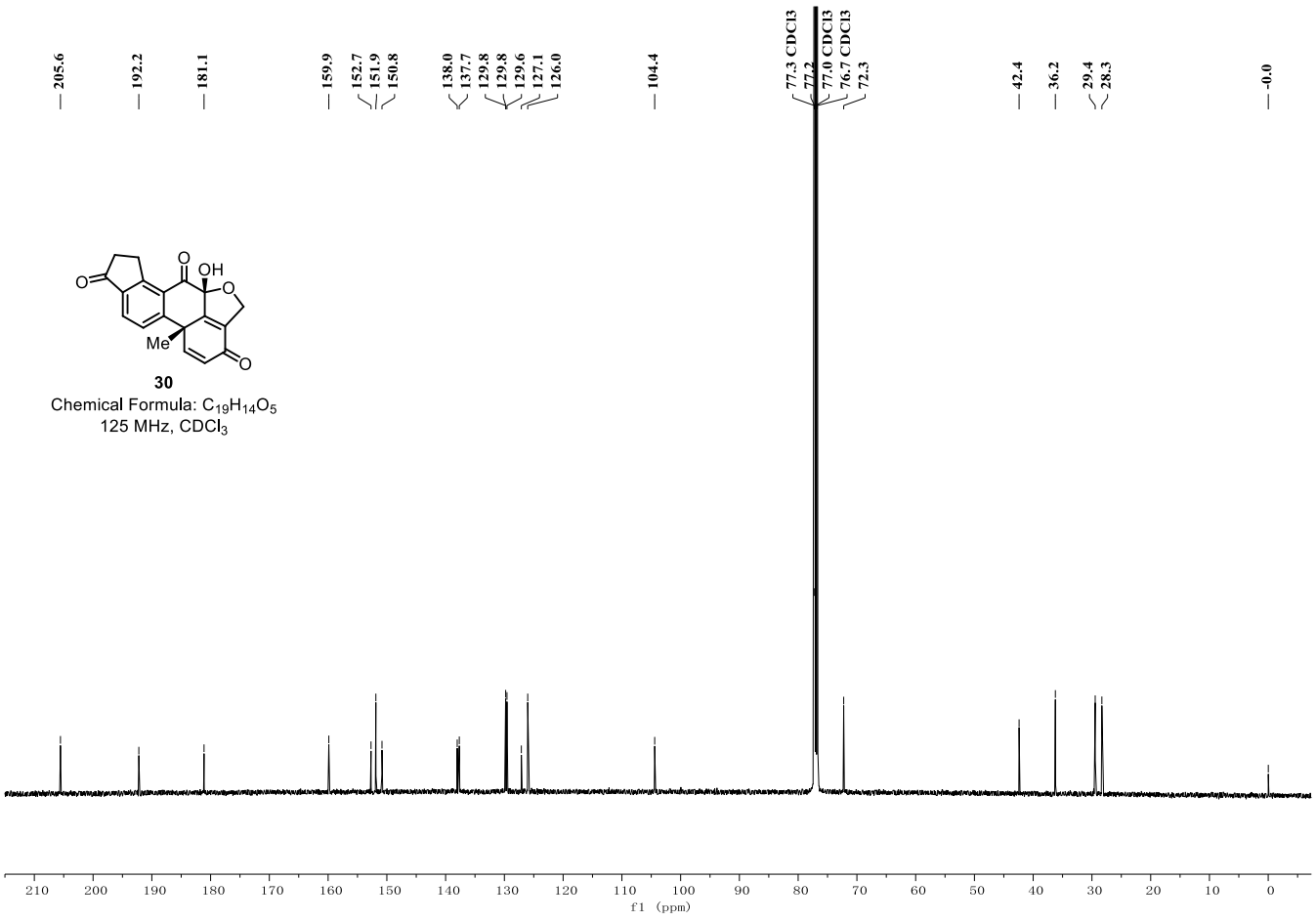




30

Chemical Formula: $C_{19}H_{14}O_5$

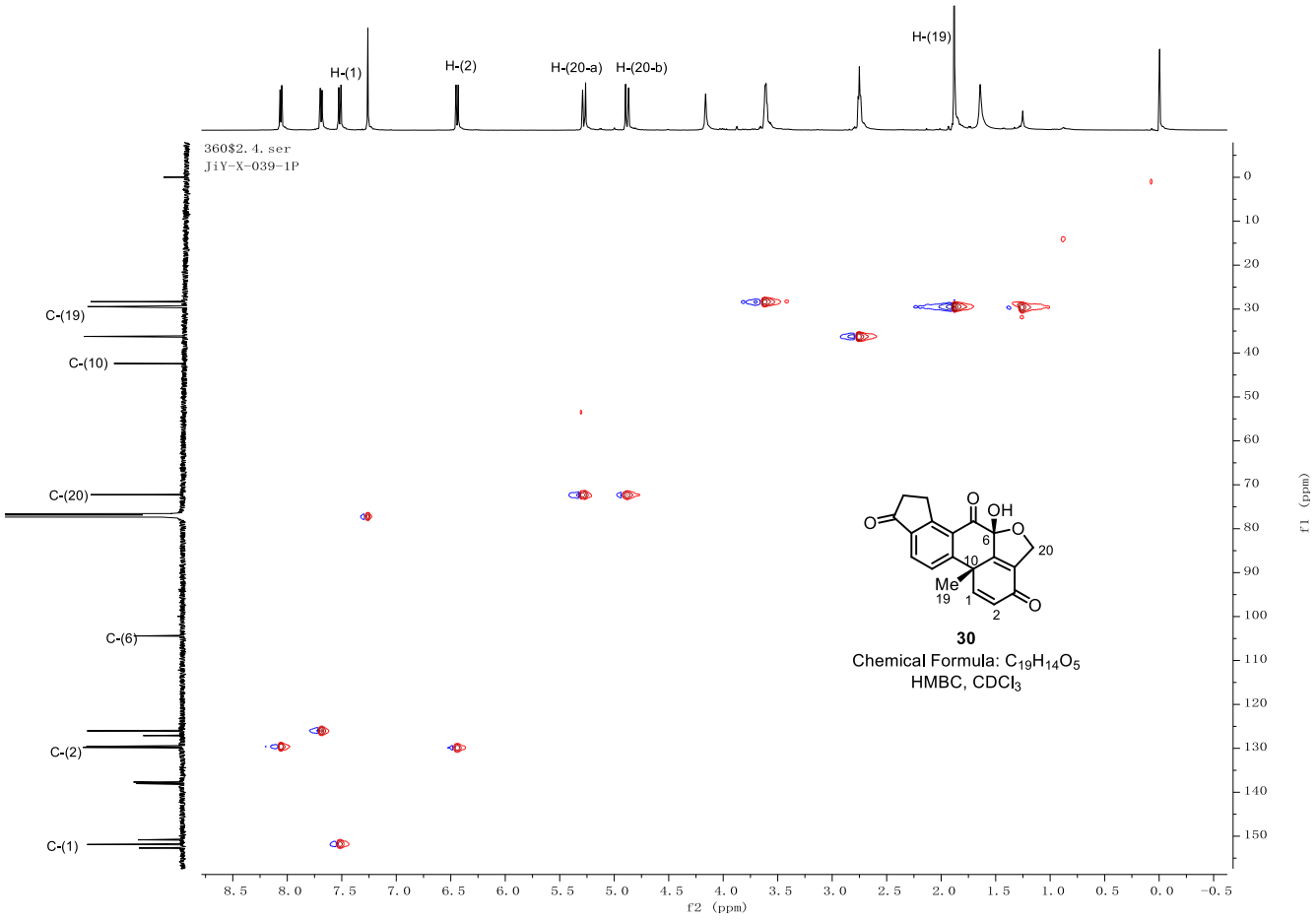
500 MHz, $CDCl_3$

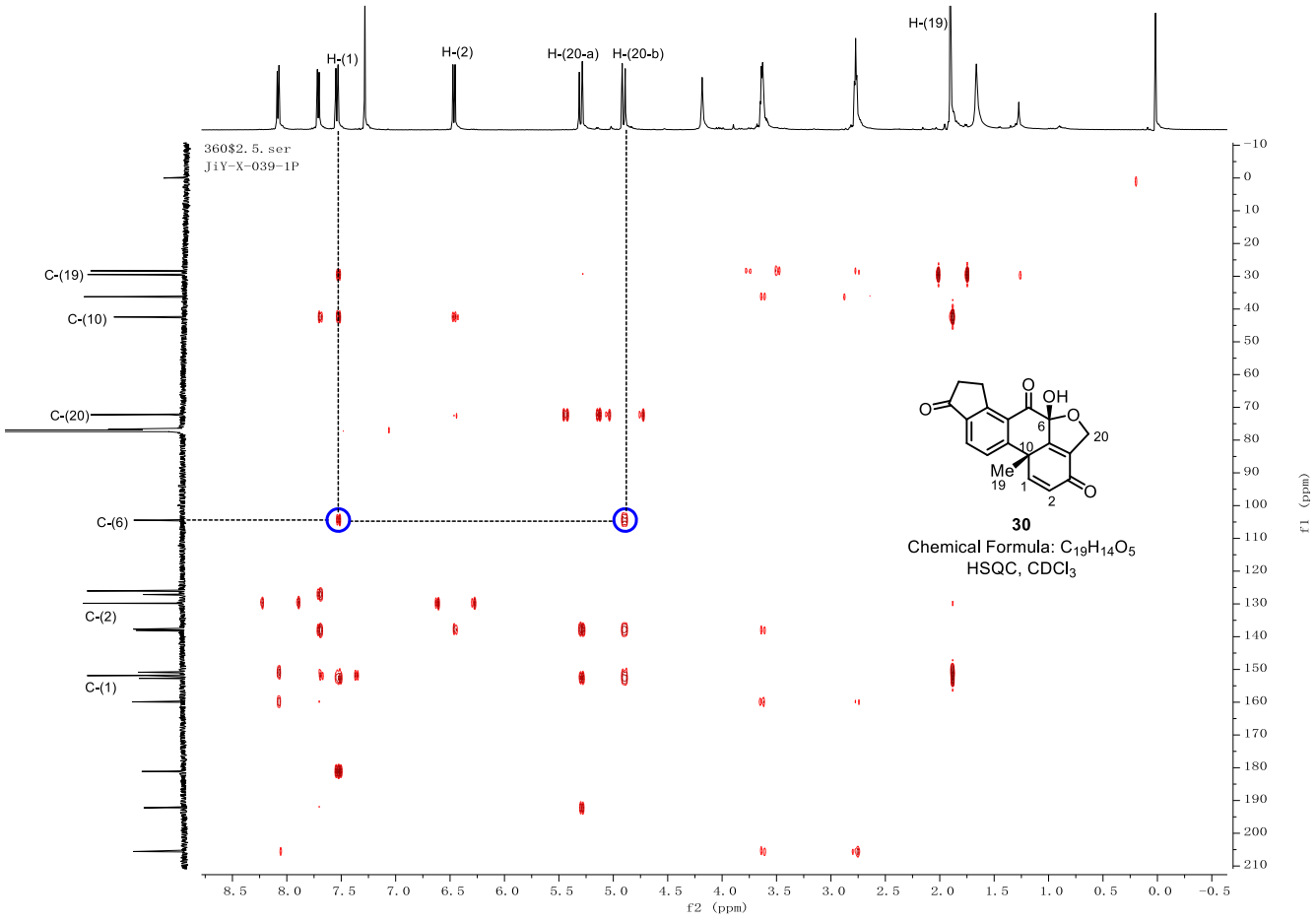


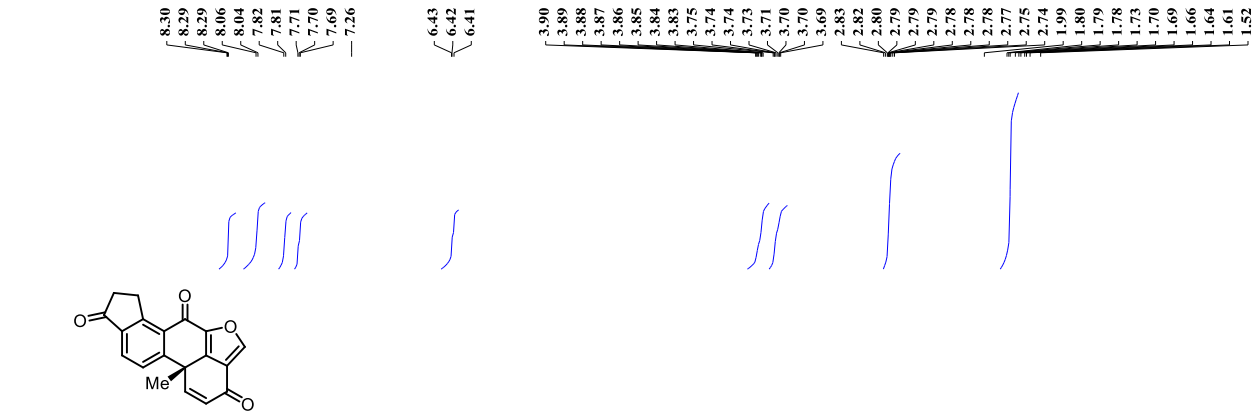
30

Chemical Formula: $C_{19}H_{14}O_5$

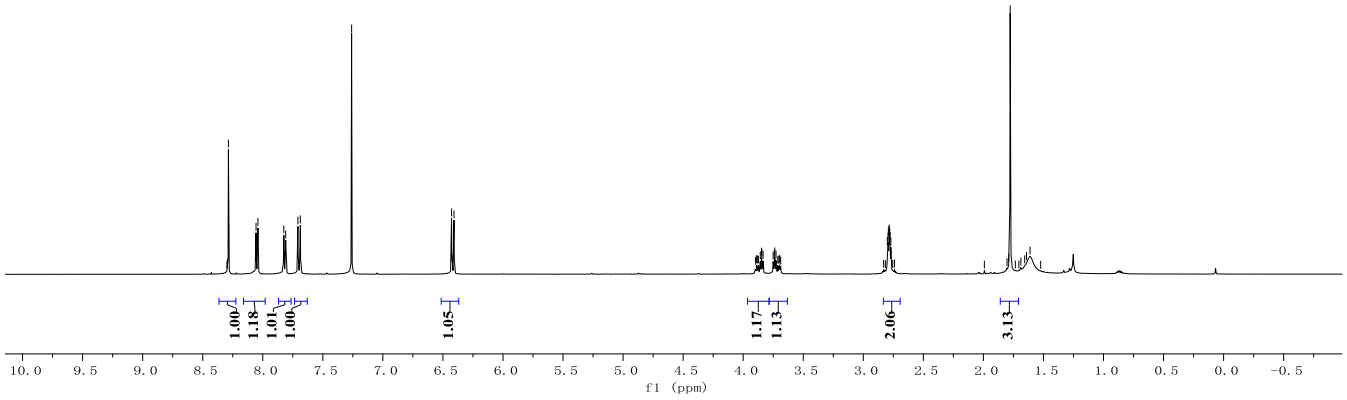
125 MHz, $CDCl_3$

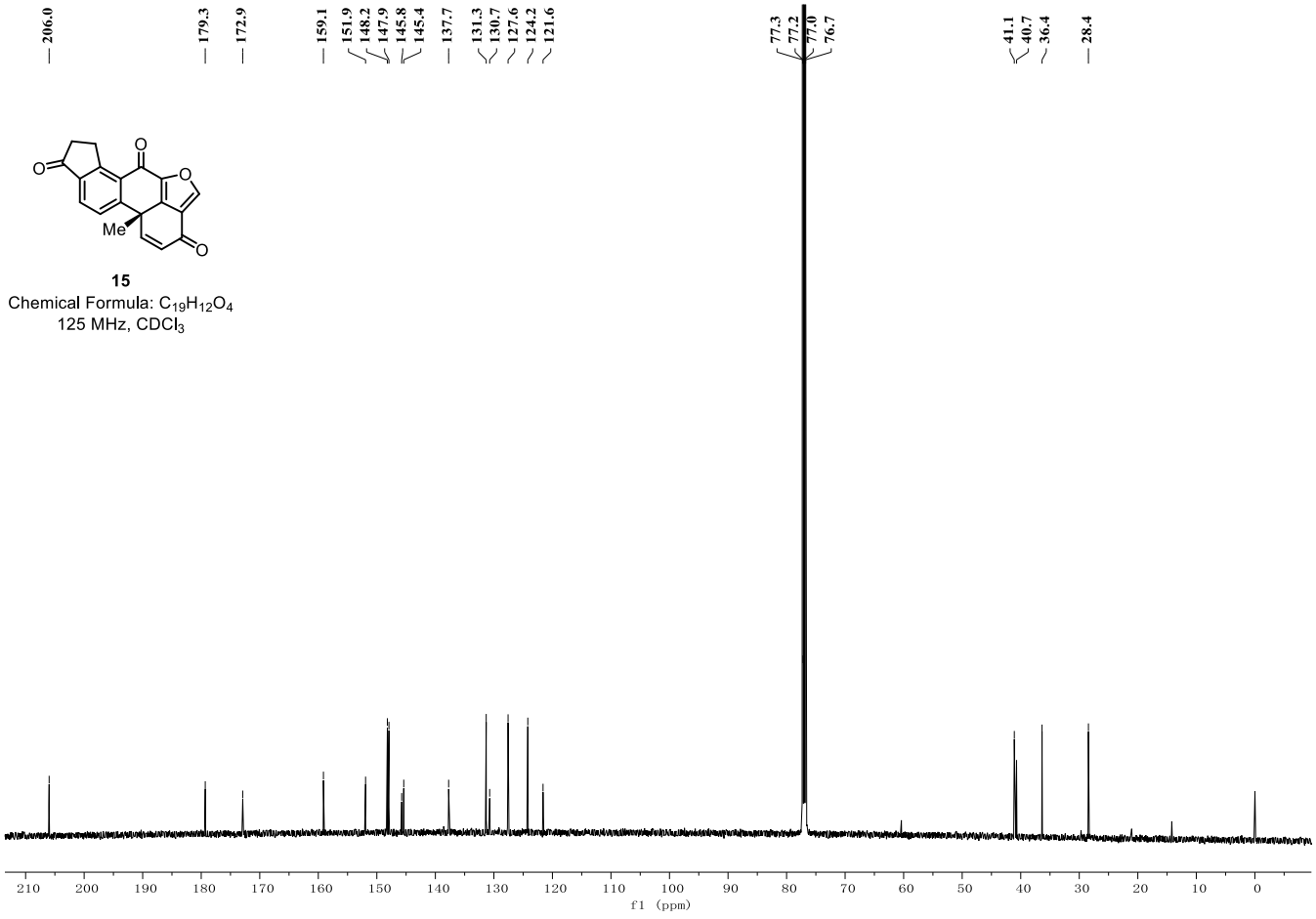

H-(19)
H-(1)
H-(2)
H-(20-a)
H-(20-b)
360$2.4.ser
JiY-X-039-1P
C-(19)
C-(10)
C-(20)
C-(6)
C-(2)
C-(1)
f2 (ppm)
f1 (ppm)
30
Chemical Formula: C19H14O5
HMBC, CDCl3


H-(19)
H-(1)
H-(2)
H-(20-a)
H-(20-b)
360$2.5.ser
JiY-X-039-1P
C-(19)
C-(10)
C-(20)
C-(6)
C-(2)
C-(1)
f2 (ppm)
f1 (ppm)
30
Chemical Formula: C19H14O5
HSQC, CDCl3

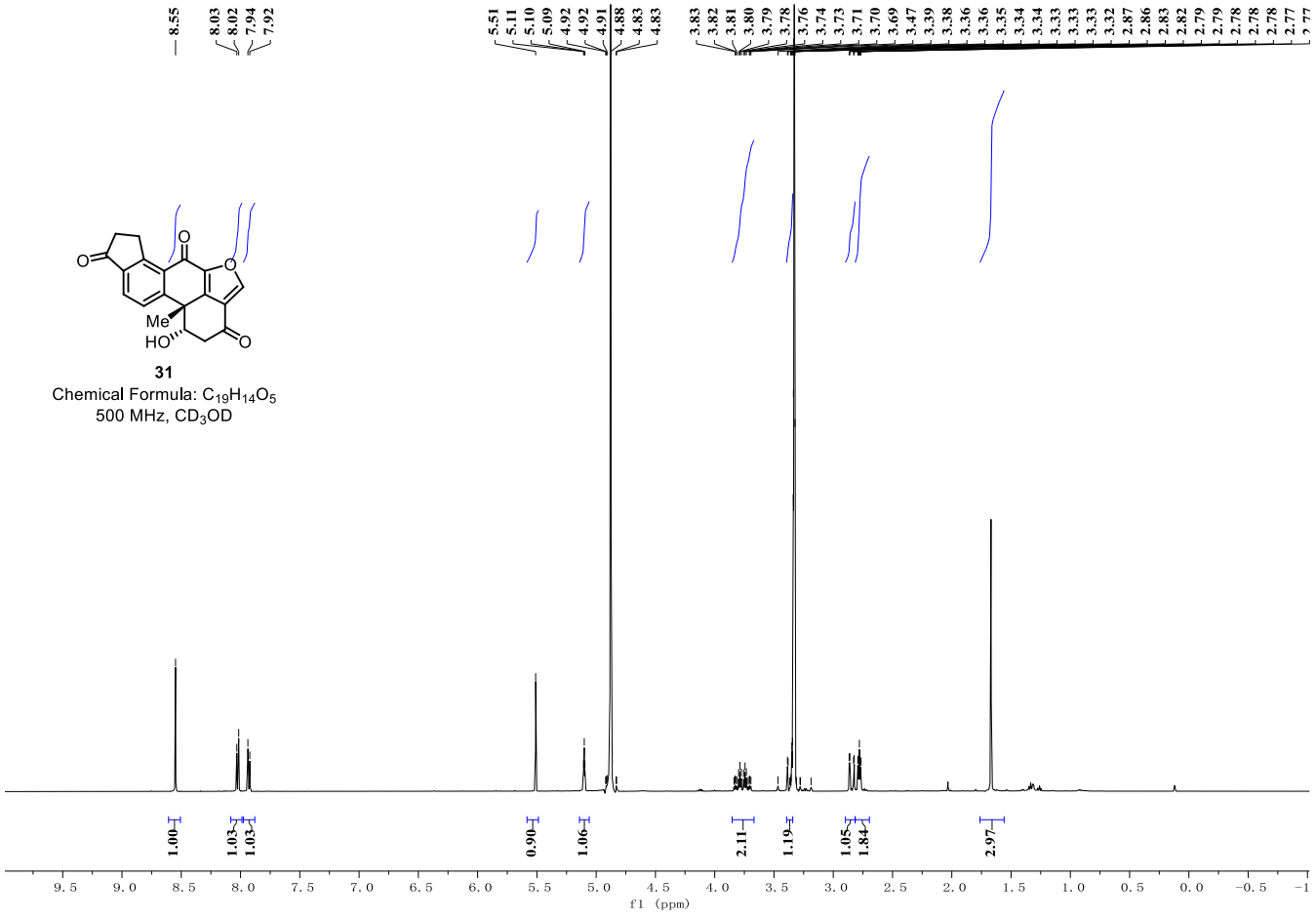


15
Chemical Formula: $C_{19}H_{12}O_4$
500 MHz, $CDCl_3$

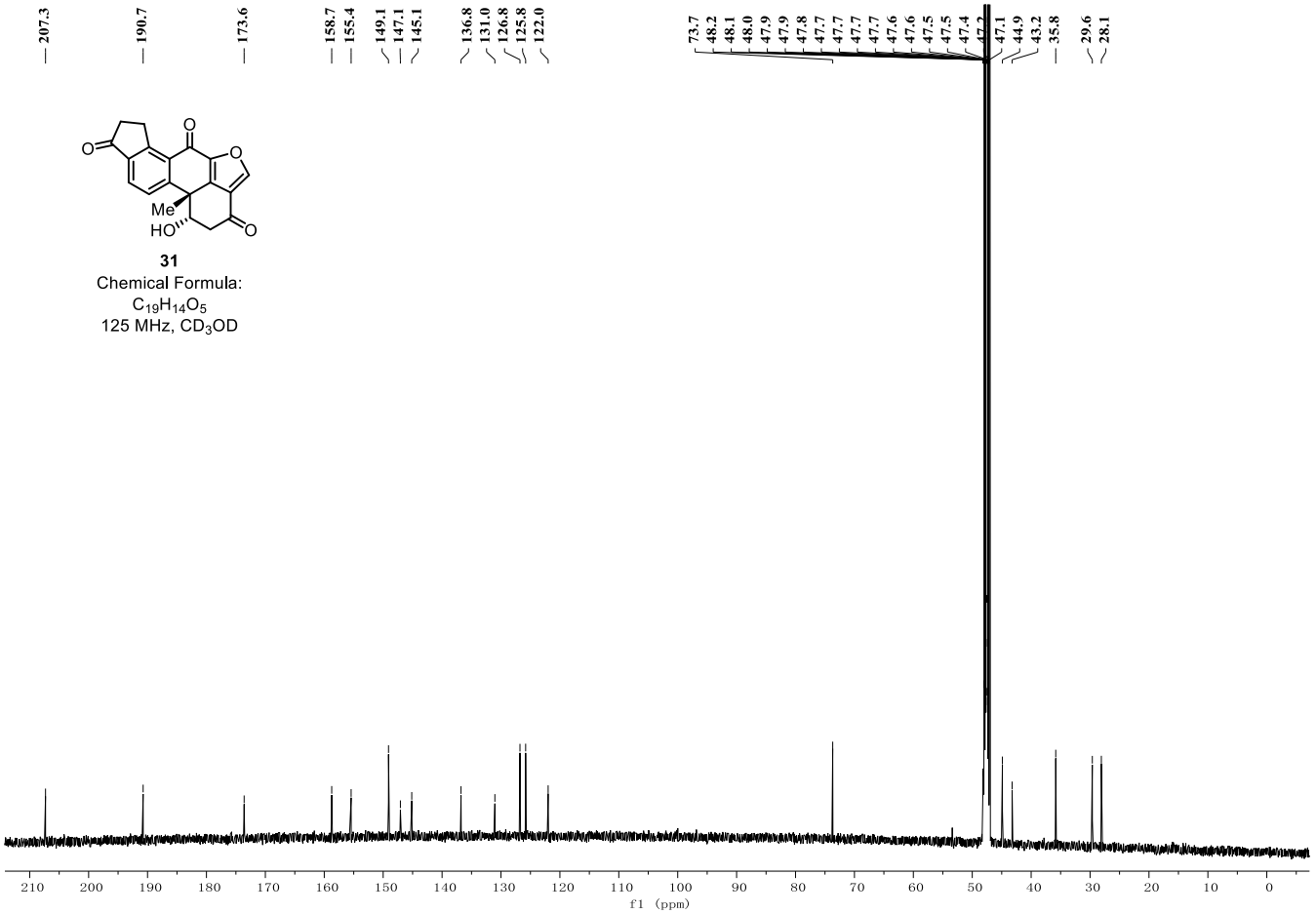




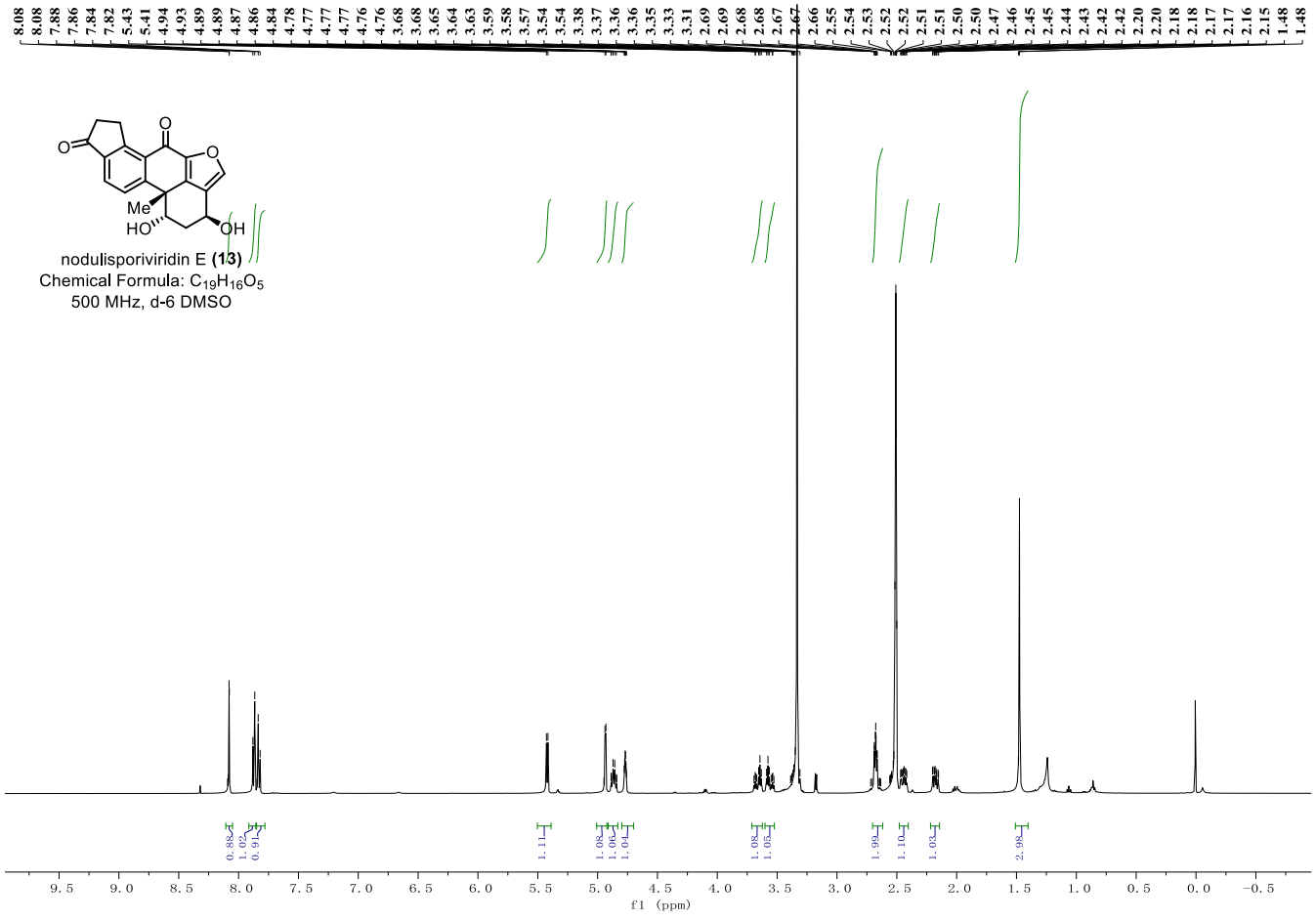
15
Chemical Formula: $C_{19}H_{12}O_4$
125 MHz, $CDCl_3$

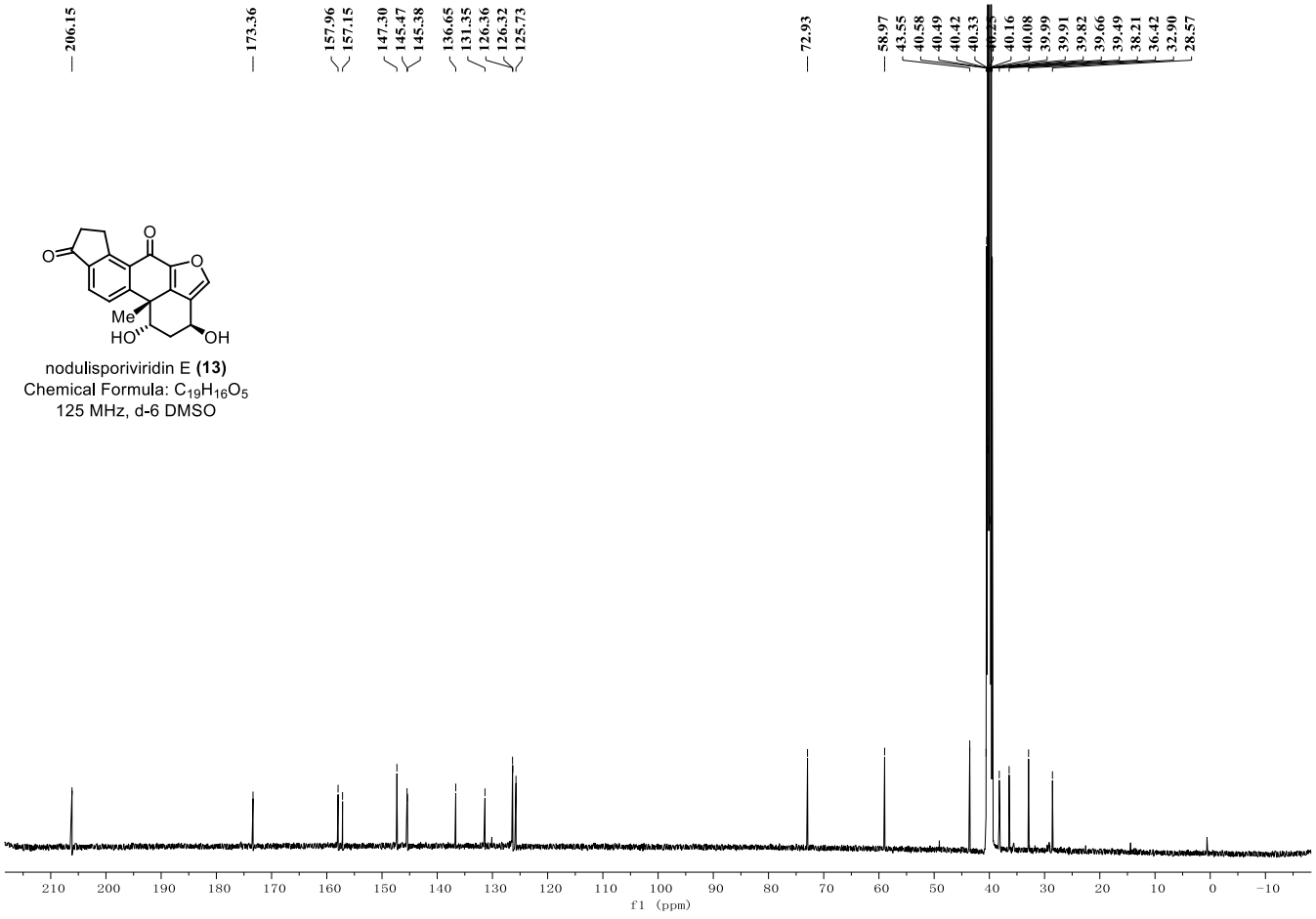


31
Chemical Formula: $C_{19}H_{14}O_5$
500 MHz, CD_3OD



31
Chemical Formula:
$C_{19}H_{14}O_5$
125 MHz, CD_3OD


nodulisporiviridin E (13)
Chemical Formula: C19H16O5
500 MHz, d-6 DMSO
f1 (ppm)


nodulisporiviridin E (13)
Chemical Formula: C19H16O5
125 MHz, d-6 DMSO
f1 (ppm)

Reference:

[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.,* 1978, **43**, 2923.

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[5] Y. Lang, F. E. S. Souza, X. Xu, N.J. Taylor, A. Assoud, R. Rodrigo, *J. Org. Chem*., 2009, **74**, 5429.

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