Supporting Information

Pyrrole Strategy for the γ-Lactam-Containing *Stemona* Alkaloids: (±)Stemoamide, (±)Tuberostemoamide, and (±)Sessilifoliamide A

Xianglin Yin, Kaiqing Ma, Ying Dong, and Mingji Dai*

Department of Chemistry and Center for Cancer Research
Purdue University, 560 Oval Drive, West Lafayette, IN 47907 (USA)

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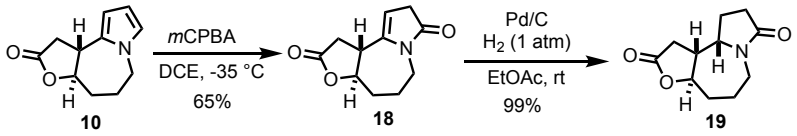
Part 1. Experimental procedures and spectra data.

General Methods. NMR spectra were recorded on Bruker spectrometers (^{1}H at 500 MHz and ^{13}C at 125 MHz). Chemical shifts (δ) were given in ppm with reference to solvent signals [^{1}H NMR: $CHCl_3$ (7.26); ^{13}C NMR: $CDCl_3$ (77.2)]. High-resolution mass measurements for compound characterization were carried out using a Waters SYNAPT G2-Si system with QuanTof analyzer or an Agilent 6550 QTOF system. Column chromatography was performed on silica gel. All reactions sensitive to air or moisture were conducted under argon atmosphere in dry and freshly distilled solvents under anhydrous conditions, unless otherwise noted. Anhydrous 1,2-dichloroethane was distilled over calcium hydride under Argon. All other solvents and reagents were used as obtained from commercial sources without further purification. All the reaction heating used oil bath and the reported temperature was the oil bath temperature measured by a thermometer. Room temperature (rt) was around 22-23 °C.

Experiment procedure



In a flame-dried 8 mL vial, compound **10** (10.0 mg, 0.05 mmol) was dissolved in 1 mL anhydrous DCE under argon atmosphere and the solution was cooled to -35 °C. *m*CPBA (18.0 mg, 0.1 mmol, freshly purified, >90% purity, **handle with caution**) was dissolved in 1 mL anhydrous DCE and the solution was added dropwise to the reaction slowly. After the *m*CPBA was added completely, the reaction was stirred at

-35 °C for 30 min before 2 mL saturated $NaHCO_3$ solution and 2 mL saturated $Na_2S_2O_3$ solution were added. The aqueous phase was extracted by DCM for 3 times and dried over Na_2SO_4. After solid was filtered off, the solution was concentrated and purified by column chromatography (40% ethyl acetate in hexanes) to obtain the product **18** as a colorless oil (7.1 mg, 65% yield) and starting material (3.1 mg, 28%) was recovered. The product was used directly for the next step.

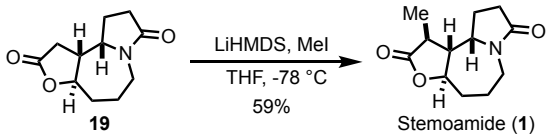
In a flame-dried 8 mL vial, γ-lactam **18** (5.0 mg, 0.024 mmol) was dissolved in 2 mL EtOAc under argon atmosphere, and Pd/C (1 mg) was added in one portion. H_2 was flushed into the reaction for 5 times and the reaction was stirred under H_2 atmosphere for 30 min before the solution was passed through a plug of celite. The organic layer was dried over Na_2SO_4. After solid was filtered off, the solution was concentrated and purified by prep-TLC (40% EtOAc in hexanes) to obtain compound **19** as a white solid (4.9 mg, 99% yield).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{16}NO_3$ 210.1125; found 210.1123.

FTIR (neat, cm^{-1}) 2924, 2514, 2159, 2028, 1977, 1777, 1261, 1017, 712.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.28 (td, 1H, *J* = 10.2, 3.0 Hz), 4.14 (dt, 1H, *J* = 13.1, 3.1 Hz), 3.99 (dt, 1H, *J* = 10.6, 6.4 Hz), 2.84 (ddt, 1H, *J* = 12.7, 9.5, 4.6 Hz), 2.71 – 2.59 (m, 2H), 2.51 (dd, 1H, *J* = 17.4, 12.7 Hz), 2.46 – 2.34 (m, 4H), 2.07 (dtd, 1H, *J* = 11.8, 5.9, 3.9 Hz), 1.90 – 1.79 (m, 2H), 1.78 – 1.67 (m, 2H), 1.60 – 1.48 (m, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 174.8, 174.3, 79.9, 56.2, 45.0, 40.4, 34.8, 31.2, 30.7, 25.6, 22.8.



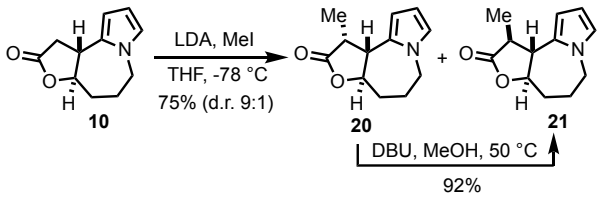
In an 8 mL flame-dried vial, compound **19** (20.9 mg, 0.1 mmol) was dissolved in anhydrous 1 mL THF and was cooled to -78 °C. Freshly prepared LiHMDS (0.5 M, 0.3 mL, 0.15 mmol) was added dropwise to the solution. The suspension was allowed to warm to -40 °C, and stirred for 1 h at this temperature. After the reaction was cooled to -78 °C, methyl iodide (28.2 mg, 0.2 mmol) was added dropwise at –78 °C. The reaction was slowly warmed up to room temperature and was stirring for 2 h at room temperature. The reaction was quenched with aqueous 1 M HCl (2 mL) and extracted with $CHCl_3$ for 3 times. The combined organic layer was dried over Na_2SO_4. After solid was filtered off, the solution was concentrated and purified by column chromatography (EtOAc/MeOH 1:0 to 19:1) to obtain racemic stemoamide (15.2 mg, 59%) as a white solid.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{18}NO_3$ 224.1281; found 224.1283.

FTIR (neat, cm^{-1}) 2925, 2854, 1766, 1671, 1420, 1275, 1189, 1009, 720, 607.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.19 (td, 1H, *J* = 10.2, 3.1 Hz), 4.16 – 4.11 (m, 1H), 3.98 (dt, 1H, *J* = 10.7, 6.4 Hz), 2.76 – 2.62 (m, 1H),2.59 (dd, 1H, *J* = 12.4, 7.0 Hz), 2.45 – 2.33 (m, 4H), 2.08 – 1.94 (m, 1H), 1.90 – 1.73 (m, 1H), 1.79 – 1.60 (m, 1H), 1.52 (m, 2H), 1.29 (d, 3H, *J* = 6.9 Hz).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 177.5, 174.2, 77.8, 55.9, 52.8, 40.3, 37.4, 34.9, 30.7, 25.7, 22.7, 14.2.



To a stirred solution of lactone **10** (191 mg, 1.0 mmol) was added dropwise LDA (freshly prepared, 0.3 M solution in THF, 10.0 ml, 3.0 mmol) at -78 °C. After stirring for 30 min, HMPA (18 μl) was added, followed by the dropwise addition of methyl iodide (0.31 ml, 5.0 mmol). The resulting reaction mixture was raised to -20 °C and stirred for 4 h at this temperature. The reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The combined organic layer was concentrated to afford a crude product and was purified by column chromatography (Hexane: EtOAc = 4:1) to obtain a 9:1 mixture of **20** and **21** as a colorless oil (160 mg, 78% yield).

A mixture of **20** and **21** (1.2 g, 5.9 mmol) was dissolved in 260 mL MeOH and DBU (897 mg, 5.9 mmol) was added dropwise. The reaction was stirred at 50 °C (oil bath) for 24 h before the solution was concentrated. The crude product was purified by column chromatography (Hexane: EtOAc = 4:1) to obtain a single stereoisomer of **21** as a colorless oil (1.1 g, 92% yield).

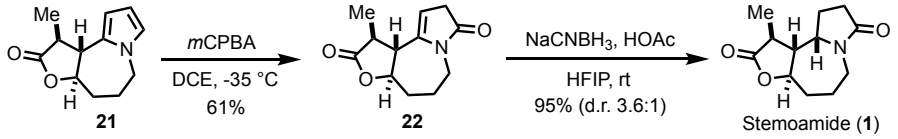
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{16}NO_2$ 206.1175; found 206.1175.

FTIR (neat, cm^{-1}) 2932, 1773, 1454, 1323, 1220, 1201, 1168, 1145, 1012, 721.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.63 (m, 1H), 6.05 (dd, 1H, *J* = 3.5, 2.7 Hz), 5.97 (m, 1H), 4.11 (m, 1H), 3.93 – 3.83 (m, 2H), 3.06 – 2.91 (m, 2H), 2.57 – 2.48 (m, 1H), 2.16 – 2.06 (m, 1H), 1.82 – 1.61 (m, 2H), 1.43 (d, 3H, *J* = 6.5 Hz).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 178.4, 128.7, 122.8, 106.6, 105.2, 81.7, 49.4, 49.2,

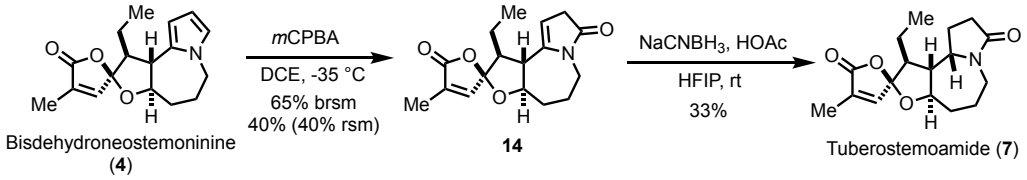
39.7, 34.2, 26.3, 14.0.



In a flame-dried 8 mL vial, compound **21** (41.0 mg, 0.2 mmol) was dissolved in 4 mL anhydrous DCE under argon atmosphere and the solution was cooled to -35 ^{o}C. *m*CPBA (69.0 mg, 0.4 mmol, freshly purified, >90% purity, **handle with caution**) was dissolved in anhydrous DCE and the solution was added dropwise to the reaction slowly. After the *m*CPBA was added completely, the reaction was stirred at -35 ^{o}C for 30 min before 10 mL saturated $NaHCO_3$ solution and 10 mL saturated $Na_2S_2O_3$ solution were added. The aqueous phase was extracted by DCM for 3 times and dried over Na_2SO_4. After solid was filtered off, the solution was concentrated and purified by column chromatography (40% ethyl acetate in hexanes) to obtain product **22** (25.2 mg, 61% yield). The product was used directly for the next step.

In a flame-dried 8 mL vial, γ-lactam **22** (5.4 mg, 0.024 mmol) was dissolved in 2 mL HFIP under argon atmosphere. $NaCNBH_3$ (15.1 mg, 0.24 mmol) was added in one portion followed by 0.1 mL HOAc. The solution was stirred at rt overnight before the solution was passed through a silica gel plug. Solvent was removed under vacuum before a flush column (EtOAc then 5% MeOH in EtOAc). The second fraction was concentrated to afford racemic stemoamide (**1**) as a 3.6:1 mixture of stereoisomer (5.2 mg, 95% yield). The analytic data of major product stemoamide (**1**) is the same as the

one synthesized above.



In a flame-dried 8 mL vial, bisdehydroneostemoninine (**4**, 5.0 mg, 0.017 mmol) was dissolved in 1 mL anhydrous DCE under argon atmosphere and the solution was cooled to -35 °C. *m*CPBA (5.8 mg, 0.034 mmol, freshly purified, >90% purity, **handle with caution**) was dissolved in anhydrous DCE and the solution was added dropwise to the reaction slowly. After the *m*CPBA was added completely, the reaction was stirred at -35 °C for 30 min before 2 mL saturated $NaHCO_3$ solution and 2 mL saturated $Na_2S_2O_3$ solution were added. The aqueous phase was extracted by DCM for 3 time and dried over Na_2SO_4. After solid was filtered off, the solution was concentrated and purified by prep-TLC (40% ethyl acetate in hexanes) to obtain product **14** as a colorless oil (2.1 mg, 40% yield) and starting material (2.1 mg, 40%) was recovered. The product was used directly for the next step.

In a flame-dried 8 mL vial, γ-lactam **14** (10.0 mg, 0.03 mmol) was dissolved in 3 mL HFIP under argon atmosphere, and $NaCNBH_3$ (103 mg, 0.6 mmol) was added in one portion. HOAc (18 mg, 0.3 mmol) was added dropwise and the reaction was stirred for 30 min before the reaction was quenched by saturated $NaHCO_3$, and extracted by DCM for 3 times. The organic layer was dried over Na_2SO_4. After solid was filtered off, the solution was concentrated and purified by prep-TLC (40% EtOAc in hexanes)

to obtain racemic tuberostemoamide (**7**) as a white solid (3.0 mg, 33% yield).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{24}NO_4$ 306.1700; found 306.1701.

FTIR (neat, cm^{-1}) 2923, 2853, 1766, 1686, 1454, 1274, 974, 874, 714.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.65 (q, 1H, *J* = 1.6 Hz), 4.09 (dt, 1H, *J* = 14.3, 3.3 Hz), 4.05 – 3.97 (m, 2H), 2.74 – 2.58 (m, 2H), 2.47 – 2.33 (m, 2H), 2.21 – 2.10 (m, 2H), 2.00 (m, 1H), 1.94 (d, 3H, *J* = 1.7 Hz), 1.85 – 1.63 (m, 3H), 1.55 – 1.37 (m, 3H), 0.90 (t, 3H, *J* = 7.6 Hz).

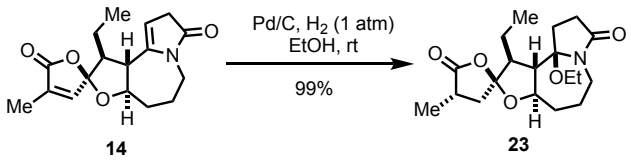
^{13}C NMR ($CDCl_3$, 125 MHz) δ 174.0, 171.4, 144.0, 134.4, 113.8, 80.9, 56.3, 52.0, 49.8, 40.4, 35.9, 30.9, 25.7, 22.2, 20.4, 13.1, 10.8.

^{1}H position	Natural tuberostemoamide (**7**)[1, a, d]	Synthetic (Wang's) tuberostemoamide (**7**)[2, b, d, e]	Synthetic (ours) tuberostemoamide (**7**)[c, d, e]
1	1.61 (m)	1.81-1.59 (m)	1.85-1.63 (m)
	1.68 (m)	1.81-1.59 (m)	1.85-1.63 (m)
2	2.12 (m)	2.19-2.11 (m)	2.21-2.10 (m)
5	4.05 (ddd, 14.2, 2.9, 2.9)	4.11-3.97 (m)	4.09 (dt, 14.2, 3.3)
	2.65 (ddd, 14.2 12.5, 1.0)	2.77-2.57 (m)	2.74-2.58 (m)
6	1.42 (m)	1.54-1.34 (m)	1.55-1.37 (m)
	1.70 (m)	1.81-1.59 (m)	1.85-1.63 (m)
7	1.71 (m)	2.44-2.36 (m)	2.47-2.33 (m)
	1.97 (m)	2.04-1.96 (m)	2.05-1.97 (m)
8	4.00 (ddd)	4.11-3.97 (m)	4.05-3.97 (m)
9	2.59 (ddd, 5.7, 9.6, 11.83)	2.77-2.57 (m)	2.74-2.58 (m)
9a	3.97 (m)	4.11-3.97 (m)	4.05-3.97 (m)
10	2.37 (m)	2.44-2.36 (m)	2.47-2.33 (m)
12	6.62 (d, 1.5)	6.65 (q, 1.4)	6.65 (q, 1.6)
15	1.91 (s)	1.94 (d, 1.6)	1.94 (d, 1.7)
16	1.42 (m)	1.54-1.34 (m)	1.55-1.37 (m)
17	0.86 (t, 7.6)	0.89 (t, 7.6)	0.90 (t, 7.6)

[a] Recorded in $CDCl_3$, 300 MHz. [b] Recorded in $CDCl_3$, 400 MHz. [c] Recorded in $CDCl_3$, 500 MHz. [d] Multiplicity and J values in Hz are given in parentheses. [e] Distinct ^{1}H NMR deviations was marked in red.

^{13}C position	Natural tuberostemoamide (**7**)[1, a]	Synthetic (Wang's) tuberostemoamide (**7**)[2, b, d, e] (deviation)	Synthetic (ours) tuberostemoamide (**7**)[c, d, e] (deviation)
1	34.6[f]	30.7 (+3.9)	30.9 (+3.7)
2	35.7	35.7 (0)	35.9 (-0.2)
3	173.8	173.7 (+0.1)	174.0 (-0.2)
5	40.2	40.2 (0)	40.4 (-0.2)
6	22.0	22.0 (0)	22.2 (-0.2)
7	25.5	25.5 (0)	25.7 (-0.2)
8	80.6	80.6 (0)	80.9 (-0.3)
9	49.6	49.6 (0)	49.8 (-0.3)
9a	56.1	56.0 (+0.1)	56.3 (-0.2)
10	51.7	51.7 (0)	52.0 (-0.3)
11	113.5	113.5 (0)	113.8 (-0.3)
12	143.9	143.9 (0)	144.0 (-0.1)
13	134.0	134.1 (-0.1)	134.4 (-0.4)
14	171.1	171.2 (-0.1)	171.4 (-0.3)
15	10.4	10.5 (-0.1)	10.8 (-0.4)
16	20.2	20.2 (0)	20.4 (-0.2)
17	12.7	12.8 (-0.1)	13.1 (-0.4)

[a] Recorded in $CDCl_3$, 75 MHz. [b] Recorded in $CDCl_3$, 100 MHz. [c] Recorded in $CDCl_3$, 125 MHz. [d] Deviations (given in parentheses)=Natural-Synthetic. [e] Distinct ^{13}C NMR deviations was marked in red. [f]This number was recorded incorrectly in the isolation paper[1] and corrected by Wang et al.[2]



14 **23**

In a flame-dried 8 mL vial, γ-lactam **14** (8.0 mg, 0.026 mmol) was dissolved in 3 mL EtOH under argon atmosphere, and Pd/C (0.8 mg) was added in one portion to the solution. H_2 was bubbled into the solution for 30 min. The solution was passed through a plug of celite to remove Pd/C catalyst and the solution was concentrated to give compound **23** as a white solid (9.0 mg, 99% yield).

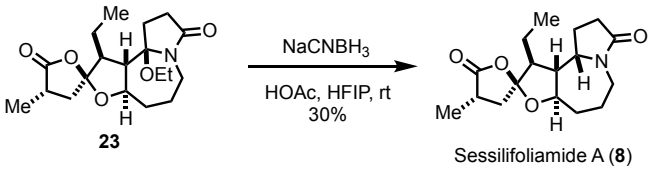
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{30}NO_5$ 352.2118; found 352.2120.

FTIR (neat, cm^{-1}) 2920, 2850, 1667, 1559, 1418, 1260, 1087, 1020, 800, 714.

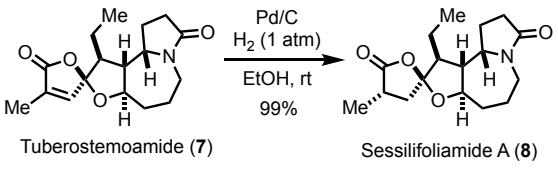
^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.84 (d, 1H, *J* = 14.1 Hz), 3.65 – 3.53 (m, 1H), 3.33 – 3.17 (m, 2H), 3.00 – 2.87 (m, 1H), 2.87 – 2.79 (m, 1H), 2.63 (dd, 1H, *J* = 11.9, 9.6

Hz,), 2.59 – 2.44 (m, 1H), 2.44 – 2.29 (m, 2H), 2.16 – 2.03 (m, 4H), 2.03 – 1.91 (m, 2H), 1.82 – 1.68 (m, 2H), 1.68 – 1.45 (m, 2H), 1.27 (d, 3H, J = 7.2 Hz), 1.15 (t, 3H, J = 7.0 Hz), 1.01 (t, 3H, J = 7.6 Hz).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 179.0, 174.1, 114.9, 93.7, 80.2, 58.3, 56.9, 50.0, 39.1, 38.1, 36.5, 34.6, 30.0, 25.4, 24.6, 21.3, 15.4, 15.4, 13.2.



In a flame-dried 8 mL vial, γ-lactam **23** (2.0 mg, 0.006 mmol) was dissolved in 1 mL HFIP under argon atmosphere, and $NaCNBH_3$ (10.3 mg, 0.06 mmol) was added in one portion. HOAc (3.6 mg, 0.06 mmol) was added dropwise and the reaction was stirred for 30 min before the reaction was quenched by saturated $NaHCO_3$, and extracted by DCM for 3 times. The organic layer was dried over Na_2SO_4. After solid was filtered off, the solution was concentrated and purified by prep-TLC (40% EtOAc in hexanes) to obtain racemic sessilifoliamide A (**8**) as a white solid (0.51 mg, 30% yield). The analytic data of this synthetic sessilifoliamide A (**8**) is the same as the one shown below.



In a flame-dried 8 mL vial, tuberostemoamide (**7**) (5.0 mg, 0.016 mmol) was dissolved in 2 mL EtOH under argon atmosphere. Pd/C (0.5 mg) was added in one

portion to the solution. H_2 was bubbled into the solution for 30 min and the reaction was stirred under H_2 atmosphere at rt overnight. The solution was passed through a plug of celite to remove Pd/C catalyst and the solution was concentrated to give pure racemic sessilifoliamide A (**8**) as a white solid (4.9 mg, 99% yield).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{26}NO_4$ 308.1856; found 308.1857.

FTIR (neat, cm^{-1}) 2922, 2852, 1721, 1668, 1456, 1261, 1096, 1026, 803, 713, 610.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.07 (d, 1H, *J* = 14.3 Hz), 4.01 (dt, 1H, *J* = 10.4, 6.3 Hz), 3.90 (ddd, 1H, *J* = 11.3, 9.5, 2.8 Hz), 2.95 (ddd, 1H, *J* = 11.3, 8.6, 7.2 Hz), 2.66 (ddd, 1H, *J* = 14.1, 12.3, 1.6 Hz), 2.59 – 2.49 (m, 1H), 2.47 – 2.32 (m, 3H), 2.15 – 2.08 (m, 1H), 2.05 – 1.91 (m, 3H), 1.79 – 1.66 (m, 2H), 1.66 – 1.46 (m, 4H), 1.27 (t, 3H, *J* = 7.3 Hz), 1.03 (t, 3H, *J* = 7.6 Hz).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 178.9, 174.0, 114.7, 79.9, 56.5, 52.2, 49.6, 40.4, 39.0, 36.3, 34.7, 30.9, 25.8, 22.3, 21.4, 15.4, 13.1.

^{1}H position	Natural sessilifoliamide A (**8**)[3, a, c]	Synthetic (Wang's) sessilifoliamide A (**8**)[2, b, c, d]	Synthetic (ours) sessilifoliamide A (**8**)[a, c, d]
1	1.67 (m), 1.98 (m)	1.66-1.42 (m), 2.03-1.91 (m)	1.66-1.46 (m), 2.05-1.91 (m)
2	2.37 (m)	2.44-2.31 (m)	2.47-2.32 (m)
5	2.64 (brt, 12.4) 3.61 (brd, 14.0)	2.65 (t, 13.2) 3.94-3.85 (m)	2.66 (ddd, 14.1, 12.3, 1.6) 3.90 (ddd, 11.3, 9.5, 2.8)
6	1.44 (m), 1.69 (m)	1.66-1.42 (m), 1.77-1.66 (m)	1.66-1.46 (m), 1.79-1.66 (m)
7	1.53 (m), 2.09 (m)	1.77-1.66 (m), 2.14-2.06 (m)	1.79-1.66 (m), 2.15-2.08 (m)
8	3.90 (ddd, 2.6, 9.9, 10.6)	4.09-3.97 (m)	4.01 (dt, 10.4, 6.3)
9	2.52 (m)	2.57-2.48 (m)	2.59-2.49 (m)
9a	4.00 (m)	4.09-3.97 (m)	4.07 (d, 14.3)
10	1.93 (m)	2.03-1.91 (m)	2.05-1.91 (m)
12	1.97 (m), 2.36 (m)	2.03-1.91 (m), 2.44-2.31 (m)	2.05-1.91 (m), 2.47-2.32 (m)
13	2.93 (m)	3.01-2.88 (m)	2.95 (ddd, 11.3, 8.6, 7.2)
15	1.25 (d, 7.2)	1.26 (d, 7.2)	1.27 (t, 7.3)
16	1.56 (m)	1.66-1.42 (m)	1.66-1.46 (m)
17	1.01 (t, 7.7)	1.02 (t, 7.6)	1.03 (t, 7.6)

[a] Recorded in $CDCl_3$, 500 MHz. [b] Recorded in $CDCl_3$, 400 MHz. [c] Multiplicity and J values in Hz are given in parentheses. [d] Distinct ^{1}H NMR deviations was marked in red.

^{13}C position	Natural sessilifoliamide A (**8**)[3, a]	Synthetic (Wang's) sessilifoliamide A (**8**)[2, b, c] (deviation)	Synthetic (ours) sessilifoliamide A (**8**)[a, c] (deviation)
1	22.1	22.1 (0)	22.3 (-0.2)
2	30.8	30.8 (0)	30.9 (-0.1)
3	174.0	173.9 (+0.1)	174.2 (-0.2)
5	40.3	40.3 (0)	40.4 (-0.1)
6	25.6	25.6 (0)	25.8 (-0.2)
7	36.1	36.1 (0)	36.3 (-0.2)
8	79.7	79.8 (-0.1)	79.9 (-0.2)
9	52.0	52.0 (0)	52.2 (-0.2)
9a	56.4	56.3 (+0.1)	56.5 (-0.1)
10	49.4	49.4 (0)	49.6 (-0.2)
11	114.6	114.6 (0)	114.7 (-0.1)
12	38.9	38.8 (+0.1)	39.0 (-0.1)
13	34.5	34.5 (0)	34.7 (-0.2)
14	178.8	178.8 (0)	178.9 (-0.1)
15	15.2	15.2 (0)	15.4 (-0.2)
16	21.2	21.1 (0)	21.4 (-0.2)
17	12.9	12.9 (0)	13.1 (-0.2)

[a] Recorded in $CDCl_3$, 125 MHz. [b] Recorded in $CDCl_3$, 100 MHz. [c] Deviations (given in parentheses)=Natural-Synthetic.

References:

(1) Lin, W. H.; Ma, L.; Cai, M. S.; Barnes, R. A. *Phytochemistry* **1994**, *36*, 1333-1335.

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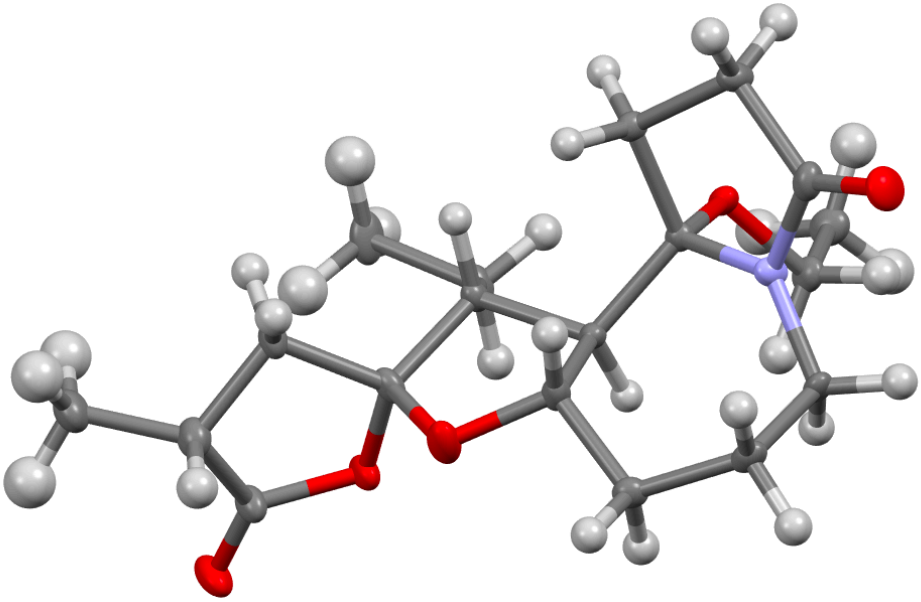
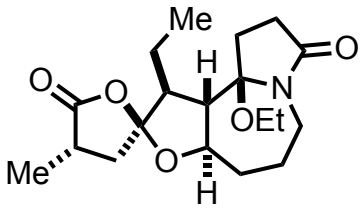
(3) Kakuta, D.; Hitotsuyanagi, Y.; Matsuura, N.; Fukaya, H.; Takeya, K. *Tetrahedron* **2003**, *59*, 7779-7786.

Part 2. X-Ray structure and analysis data.

Single crystals of the investigated compounds were coated with a trace of Fomblin oil and were transferred to the goniometer head of a Bruker Quest diffractometer with a fixed chi angle, a Mo Kα wavelength (λ = 0.71073 Å) sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator, a Photon100 CMOS area detector (**23**), or onto a Bruker Quest diffractometer with kappa geometry, a Cu Kα wavelength (λ = 1.54178 Å) I-μ-S microsource X-ray tube, laterally graded multilayer (Goebel) mirror for monochromatization, a Photon2 CMOS area detector (**7**, **8**). Both instruments were equipped with an Oxford Cryosystems low temperature device and examination and data collection were performed at 150 K. Data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3[1] and SADABS[2]. The space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs[3] and refined by full matrix least squares against F^2 with all reflections using Shelxl2018[4] using the graphical interface Shelxle[5]. H atoms attached to carbon were positioned geometrically and constrained to ride on their parent atoms. C-H bond distances were constrained to 0.95 Å for alkene C-H moieties, and to 1.00, 0.99 and 0.98 Å for aliphatic C-H, CH_2 and CH_3 moieties, respectively. Methyl CH_3 were allowed to rotate but not to tip to best fit the experimental electron density. U_{iso}(H) values were set to a multiple of U_{eq}(C) with 1.5 for CH_3, and 1.2 for C-H and CH_2 units, respectively.

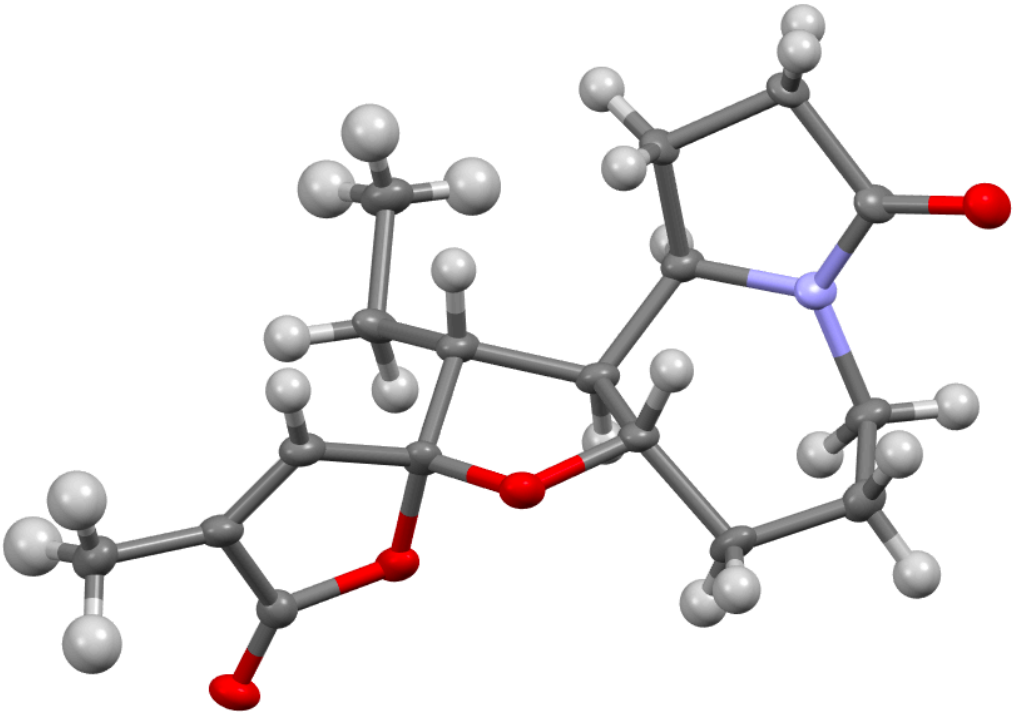


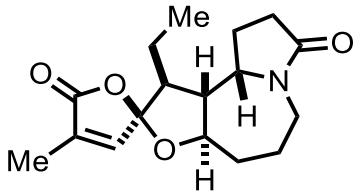


23

Figure S1. X-ray Structure of **23** (probability level (20%))

The colorless platelet crystal was grown by vapor diffusion from ethyl acetates and hexanes. The structure crystallizes in monoclinic in space group Cc but is metrically orthorhombic. It is twinned by the orthorhombic symmetry, by a 180° rotation around real or reciprocal a or c. Application of the twin matrix 1 0 0, 0 -1 0, 0 0 -1 resulted in a BASF value of 0.472(3), indicating close to perfect 1:1 twinning. CCDC. 1996683.

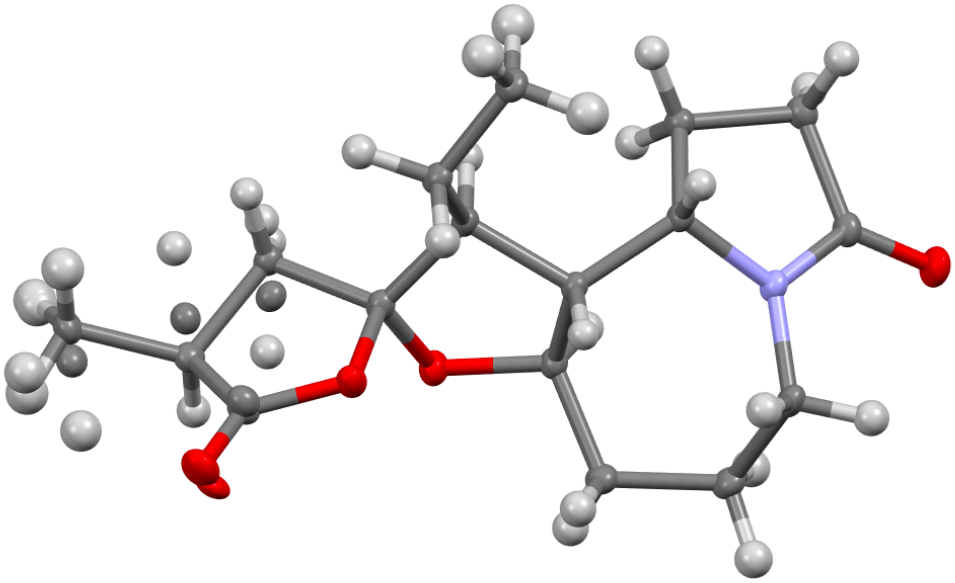


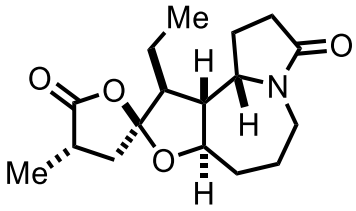


Tuberstemoamide (**7**)

Figure S2. X-ray Structure of racemic tuberostemoamide (**7**, probability level (20%))

The colorless fragment crystal was grown by vapor diffusion from ethyl acetates and hexanes. The structure is metrically close to orthorhombic and was refined as a pseudo-merohedral twin. The twin matrix applied has been 1 0 0, 0 -1 0, 0 0 -1. The twin ratio refined to 0.634(6) to 0.366(6). U^{ij} components of ADPs of atoms C8B, C9B, N1B and O2B were restrained to be similar. CCDC. 1996684.





Sessilifoliamide A (**8**)

Figure S3. X-ray Structure of racemic sessilifoliamide (**8**, probability level (20%))

The colorless fragment crystal was grown by vapor diffusion from ethyl acetates and hexanes. The structure is disordered by inversion at C15. The two disordered moieties were restrained to have similar bond distances and angles. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.906(5) to 0.094(5). CCDC. 1996685.

Table 1. X-ray Experimental details

	23	8	7
Crystal data			
Chemical formula	$C_{19}H_{29}NO_5$	$C_{17}H_{25}NO_4$	$C_{17}H_{23}NO_4$
M_r	351.43	307.38	305.36
Crystal system, space group	Monoclinic, *Cc*	Monoclinic, $P2_1/n$	Monoclinic, *Pc*
Temperature (K)	150	150	150
a, *b*, *c* (Å)	34.277 (5), 7.6326 (11), 13.722 (2)	11.2192 (3), 8.9862 (3), 15.9877 (5)	15.7907 (13), 8.2695 (7), 12.2765 (11)
β (°)	90.095 (6)	96.3466 (8)	90.831 (6)
V (Å^3)	3589.8 (9)	1601.97 (8)	1602.9 (2)
Z	8	4	4
F(000)	1520	664	656
D_x (Mg m^{-3})	1.300	1.274	1.265
Radiation type	Mo *K*α	Cu *K*α	Cu *K*α
No. of reflections for cell measurement	5536	9975	4993
θ range (°) for cell measurement	2.4–27.9	4.6–80.6	2.8–79.5
μ (mm^{-1})	0.09	0.73	0.73
Crystal shape	Platelet	Fragment	Needle
Colour	Colourless	Colourless	Colourless
Crystal size (mm)	0.45 × 0.19 × 0.01	0.21 × 0.14 × 0.12	0.40 × 0.02 × 0.02
Data collection			
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer	Bruker AXS D8 Quest CMOS diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Radiation source	sealed tube X-ray source	I-mu-S microsource X-ray tube	I-mu-S microsource X-ray tube
Monochromator	Triumph curved graphite crystal	Laterally graded multilayer (Goebel) mirror	Laterally graded multilayer (Goebel) mirror
Scan method	ω and phi scans	ω and phi scans	ω and phi scans

Absorption correction	Multi-scan (*SADABS* 2016/2, Krause *et al.*, 2015)	Multi-scan (*SADABS* 2016/2, Krause *et al.*, 2015)	Multi-scan (*SADABS* 2016/2, Krause *et al.*, 2015)
T_{min}, T_{max}	0.554, 0.746	0.627, 0.754	0.165, 0.330
No. of meas., indep. and obs. [$I > 2\sigma(I)$] reflections	18811, 7798, 4740	16315, 3402, 3046	11510, 5908, 3749
R_{int}	0.097	0.037	0.107
θ values (°)	θ_{max} = 28.3, θ_{min} = 2.7	θ_{max} = 81.1, θ_{min} = 4.6	θ_{max} = 81.7, θ_{min} = 3.6
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.667	0.641	0.642
Range of *h*, *k*, *l*	*h* = -39→45, *k* = -9→10, *l* = -18→17	*h* = -14→14, *k* = -9→11, *l* = -20→18	*h* = -19→20, *k* = -10→8, *l* = -15→14
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.067, 0.169, 1.02	0.047, 0.134, 1.16	0.096, 0.278, 1.02
No. of reflections	7798	3402	5908
No. of parameters	458	248	402
No. of restraints	2	136	20
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0667P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2 + 0.4015P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1062P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	< 0.001	< 0.001	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.31, -0.29	0.23, -0.24	0.33, -0.34
Absolute structure	Flack x determined using 1652 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013).	n/a	Flack x determined using 920 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013).
Absolute structure parameter	-1.2 (10)	n/a	0.1 (4)

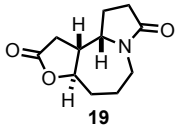
Computer programs: Apex3 v2017.3-0 (Bruker, 2016), *SADABS* 2016/2 (Krause *et al.*, 2015), *SAINT* V8.38A (Bruker, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL2018*/3

(Sheldrick, 2015, 2018), SHELXLE Rev924 (Hübschle *et al.*, 2011).

References

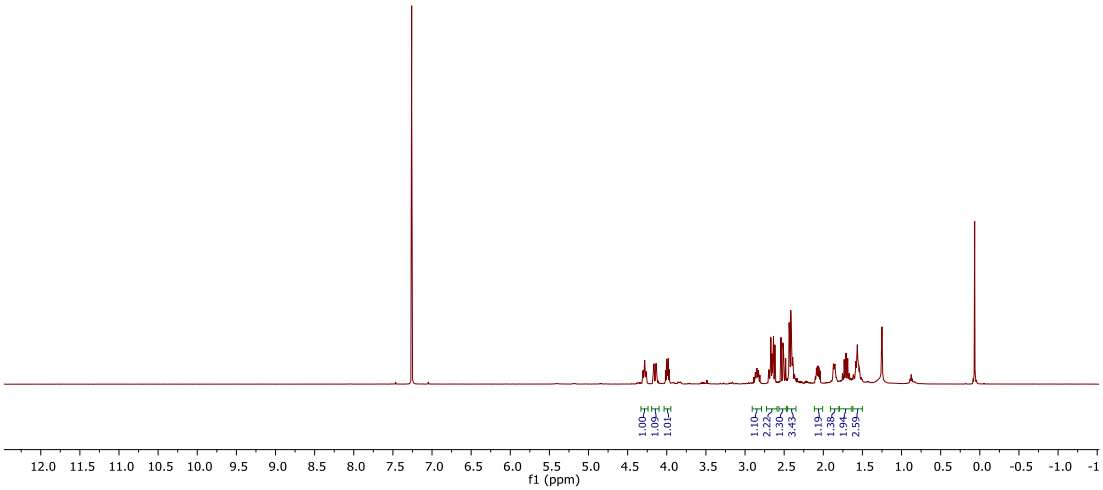
(1) Bruker (2018). Apex3, Saint, Bruker AXS Inc.: Madison (WI), USA.
(2) Krause, L., Herbst-Irmer, R., Sheldrick G. M. & Stalke D. (2015). *J. Appl. Cryst.* **48**, 3–10.
(3) (a) SHELXTL suite of programs, Version 6.14, 2000-2003, Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin: USA (b) Sheldrick G. M. (2008). A short history of SHELX. *Acta Cryst.* **A**64 (1), 112–122.
(4) (a) Sheldrick, G. M. University of Göttingen, Germany, **2018**. (b) Sheldrick G. M. (2015). Crystal structure refinement with SHELXL. *Acta Cryst.* C**71** (1), 3–8.
(5) Hübschle, C. B., Sheldrick G. M., Dittrich B. (2011). ShelXle: a Qt graphical user interface for SHELXL. *J. Appl. Crystallogr.* **44** (6), 1281–1284.

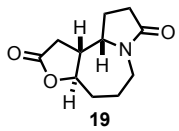
Part 3. ^{1}H and ^{13}C NMR spectra



19

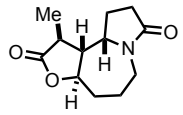
^{1}H NMR (500 MHz, Chloroform-d)





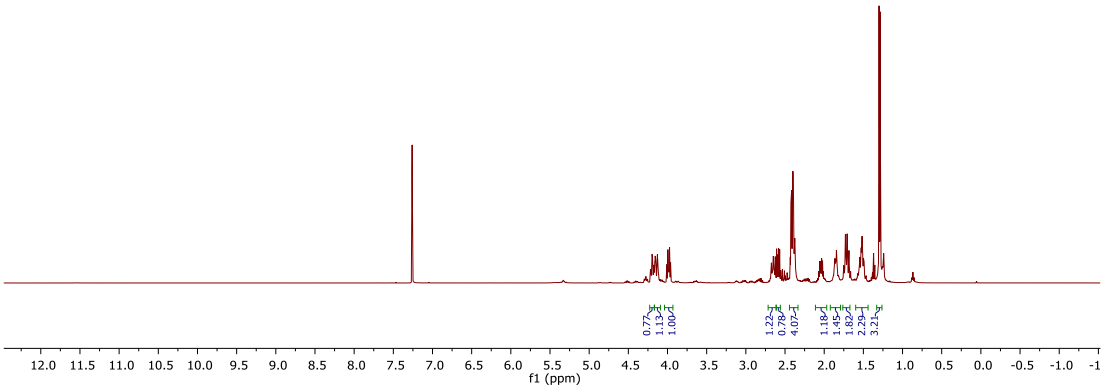
19

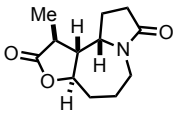
^{13}C NMR (125 MHz, Chloroform-d)



Stemoamide (**1**)

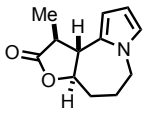
^{1}H NMR (500 MHz, Chloroform-d)





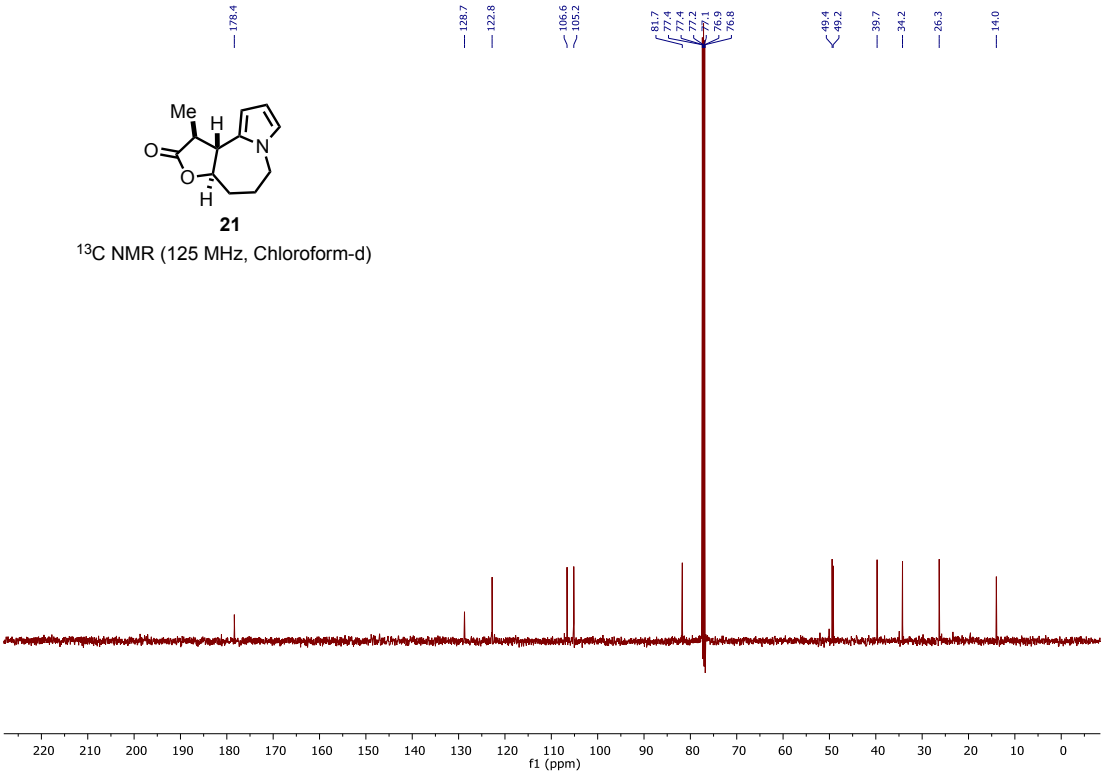
Stemoamide (**1**)

^{13}C NMR (125 MHz, Chloroform-d)



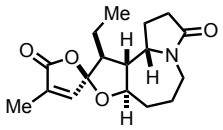
21

^{1}H NMR (500 MHz, Chloroform-d)



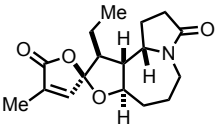
21

^{13}C NMR (125 MHz, Chloroform-d)



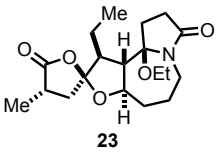
Tuberostemoamide (**7**)

^{1}H NMR (500 MHz, Chloroform-d)



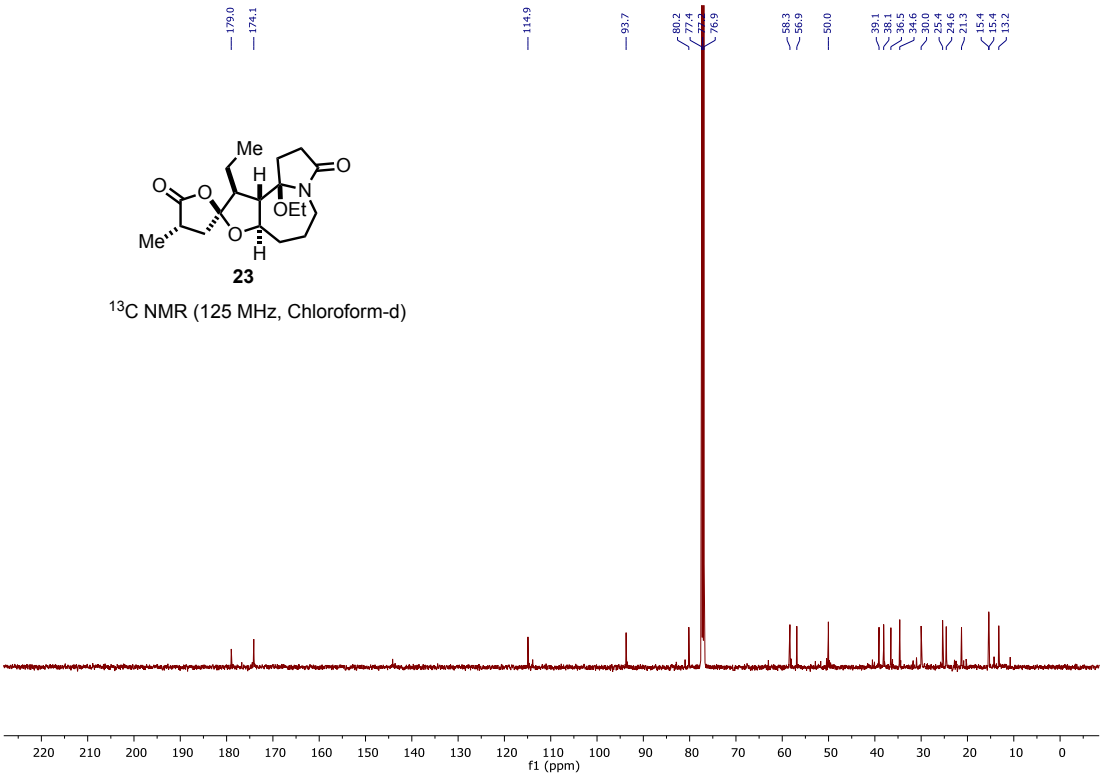
Tuberostemoamide (**7**)

^{13}C NMR (125 MHz, Chloroform-d)



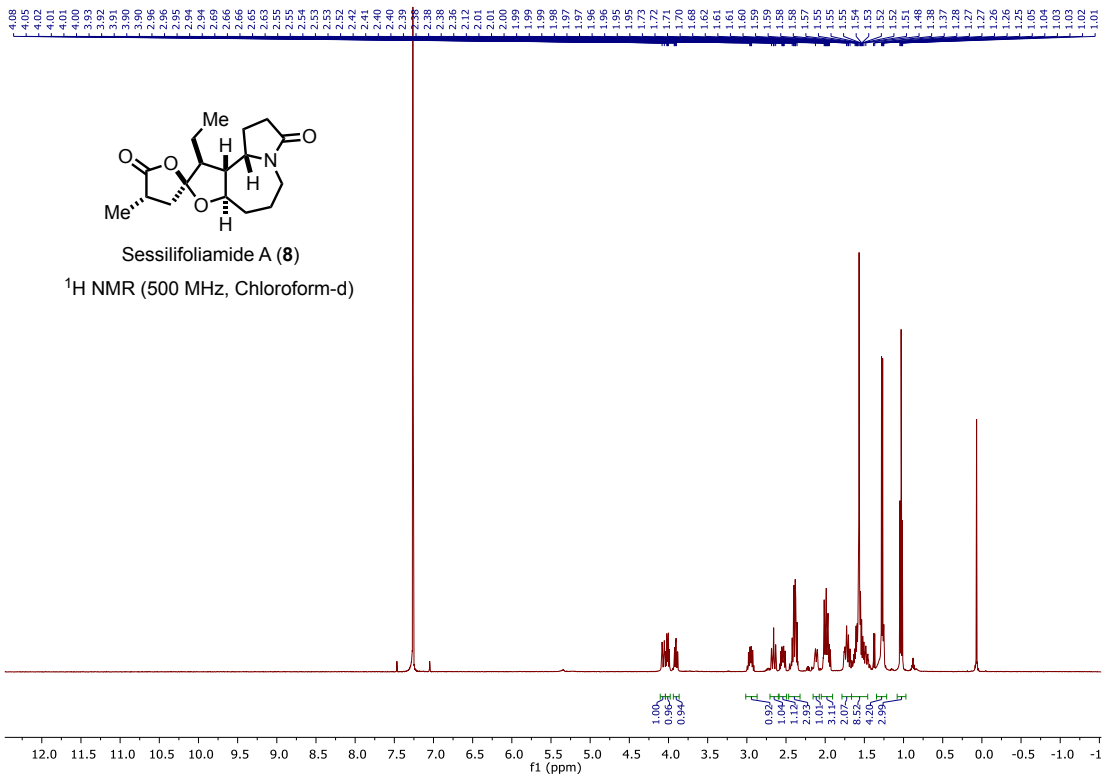
23

^{1}H NMR (500 MHz, Chloroform-d)



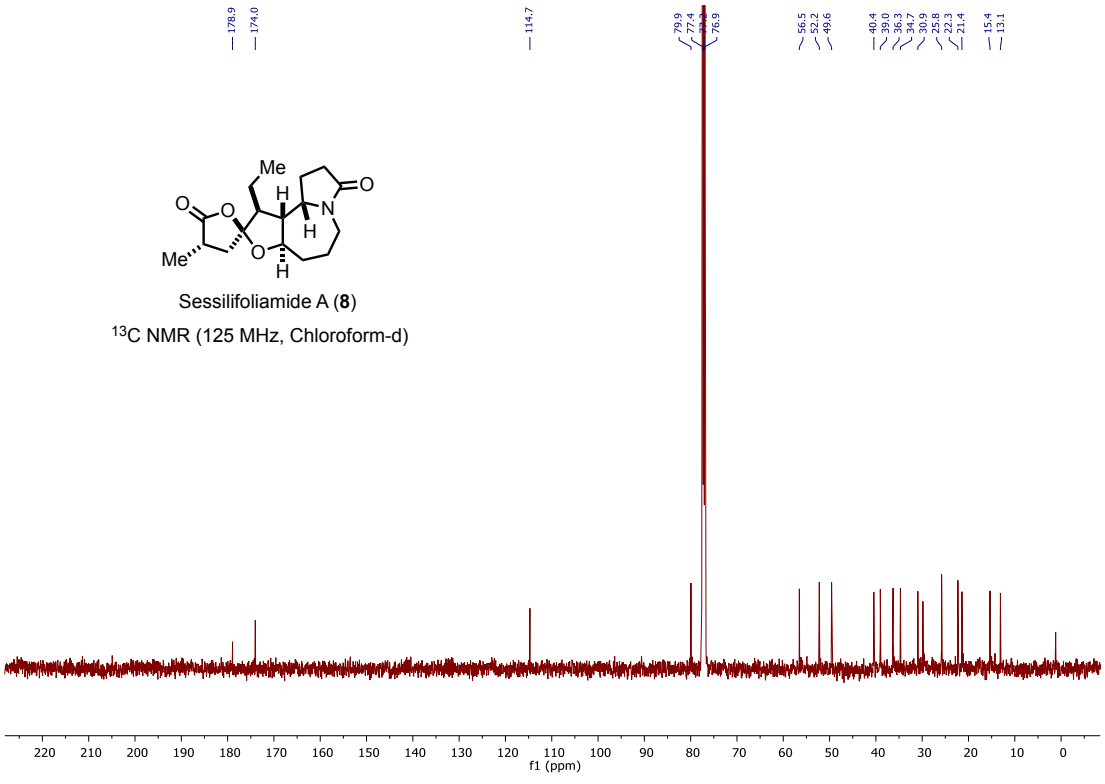
23

^{13}C NMR (125 MHz, Chloroform-d)



Sessilifoliamide A (**8**)

^{1}H NMR (500 MHz, Chloroform-d)



Sessilifoliamide A (**8**)

^{13}C NMR (125 MHz, Chloroform-d)