Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Total Synthesis of Spirastrellolide F Methyl Ester—Part 2: Macrocyclization and Completion of the Synthesis**

*Stefan Benson, Marie-Pierre Collin, Gregory W. O'Neil, Julien Ceccon, Bernhard Fasching, Michaël D. B. Fenster, Cédrickx Godbout, Karin Radkowski, Richard Goddard, and Alois Fürstner**

anie_200906122_sm_miscellaneous_information.pdf

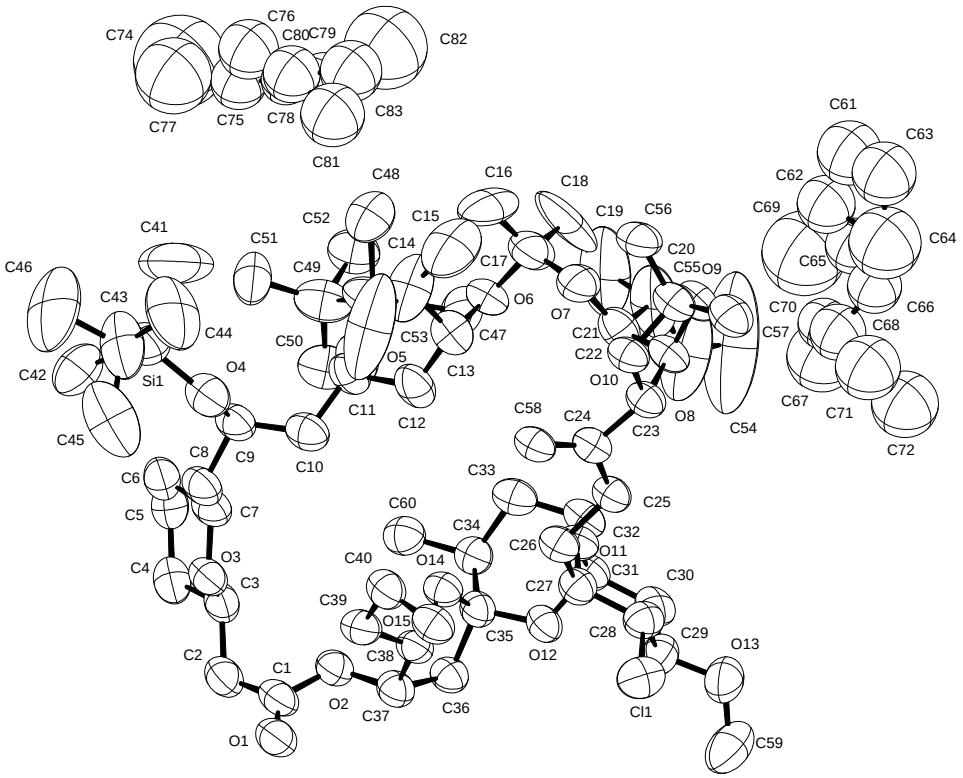


Figure S-1. Structure of compound **10**·2(C_6H_{14}) in the solid state. Anisotropic displacement parameters are drawn at the 50% probability level, hydrogen atoms are omitted for clarity.

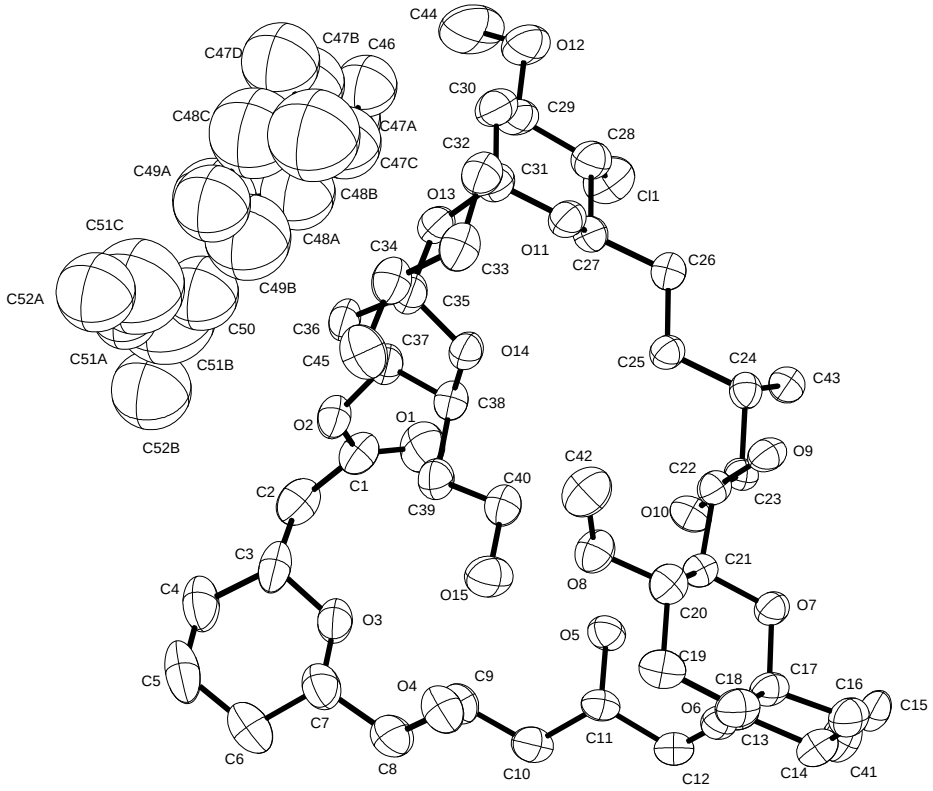


Figure S-2. Structure of compound **12**·1.2(C_7H_{16}) in the solid state. Anisotropic displacement parameters are drawn at the 50% probability level, hydrogen atoms are omitted for clarity.

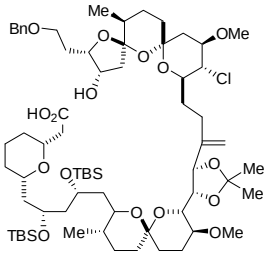
X-ray crystal structure analysis of 10·2(C_6H_{14}): [$C_{60}H_{105}ClO_{15}Si_2$]·2 [$C_6H_{14}$], M_r = 1330.41 g·mol^{-1}, colorless needle, crystal size 0.55 x 0.08 x 0.08 mm, orthorhombic, space group $P2_12_12_1$, a = 13.4977(3) Å, 20.8183(4) Å, c = 28.2234(6) Å, V = 7930.8(3) Å^3, T = 200 K, Z = 4, D_{calc} = 1.114 g·cm^3, λ = 1.54178 Å, $\mu(Cu\text{-}K_\alpha)$ = 1.175 mm^{-1}, Gaussian absorption correction (T_{min} = 0.73, T_{max} = 0.93), scaling SADABS, Bruker AXS Proteum X8 diffractometer, 2.64 < θ < 67.83, 177382 measured reflections, 14001 independent reflections, 8054 reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.087 [$I > 2\sigma(I)$], wR_2 = 0.267, 815 parameters. The crystal contains two molecules of disordered hexane, which was modelled by 24 C atoms each with half occupancy. H atoms on the disordered hexane molecules were not included in the refinement, otherwise H atoms riding. Solute C atoms were refined using isotropic atomic displacement parameters. The highest residual electron density is close to Si2 indicating that

the siloxy group may be slightly disordered. The somewhat high R_{int} of 0.137 is in part due to the high redundancy of the dataset and relatively low $I/\sigma(I)$ at higher angles. Absolute structure parameter = 0.03(3), S = 1.016, residual electron density +0.98 / -0.93 e Å^{-3}. CCDC 749791.

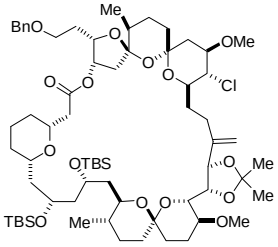
X-ray crystal structure analysis of 12·1.2(C_7H_{16}): $[C_{45}H_{75}ClO_{15}]\cdot 1.2\ [C_7H_{16}]$, M_r = 1012.99 g·mol^{-1}, colorless needle, crystal size 0.016 x 0.005 x 0.005 mm, tetragonal, space group $P4_1$, a = 16.262(2) Å, b = 16.262(2) Å, c = 20.833(2) Å, V = 5510(1) Å^3, T = 150 K, Z = 4, D_{calc} = 1.221 g·cm^3, synchrotron radiation, λ = 0.8 Å, μ = 0.134 mm^{-1}, Gaussian absorption correction (T_{min} = 0.99, T_{max} = 1.00), scaling SADABS, Bruker AXS Smart Apex2 diffractometer at the ANKA synchrotron facility Karlsruhe, 2.97 < θ < 28.81, 84935 measured reflections, 10040 independent reflections, 6629 reflections with $I > 2\sigma(I)$. Structure solved by isomorphic replacement and refined by full-matrix least-squares against F^2 to R_1 = 0.078 [$I > 2\sigma(I)$], wR_2 = 0.209, 628 parameters. The crystal contains disordered heptane solute. The solute was modelled by 17 carbon atoms each with an occupancy of 0.5 giving a crystal formula of $C_{45}H_{75}ClO_{15}\cdot 1.2\ (C_7H_{16})$. Hydrogen atoms were not included in the solute. Otherwise H atoms were calculated and allowed to refine using a riding model. Solute C atoms were refined using isotropic atomic displacement parameters. It cannot be ruled out that the solute region of the crystal contains dichloromethane since another crystal (0.081 x 0.010 x 0.010 mm) from the same batch recrystallized from dichloromethane/heptane appeared to contain dichloromethane based on distances between peaks obtained from a Fourier synthesis map calculated with the macrocycle (CCDC 749792). The relatively high R_{int} of 0.141 can be attributed to the relatively weak data, the average redundancy of over 8 with which the data were measured and the difficulty of scaling data measured using synchrotron radiation due to the beam decay over the 12 h measurement time. Absolute structure parameter = 0.46(12), S = 1.019, residual electron density +0.23 / -0.34 e Å^{-3}. CCDC 752194.

Spectrosocopic Data of Selected Compounds

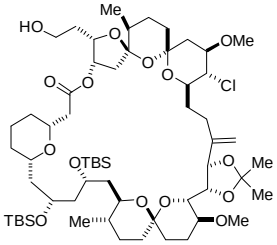
***seco*-Acid 8.** $[\alpha]_D^{20}$ = +19.2° (c = 0.81, CH_2Cl_2); IR (neat): 3463, 2970, 2930, 2855, 1738, 1439, 1365, 1229, 1217, 1092, 980, 921, 835, 774 cm^{-1}; ^1H NMR (600 MHz, C_6D_6): see Table S-1; ^{13}C NMR (150 MHz, C_6D_6): see Table S-1; HRMS (ESI^+): calcd for $C_{67}H_{113}ClO_{16}Si_2Na$ $[M+Na]^+$: 1287.7159; found: 1287.7148.



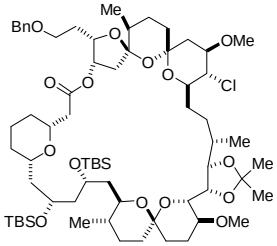
Macrolactone 9. $[\alpha]_D^{20}$ = +8,1° (c = 0.49, CH_2Cl_2). IR (neat): 2930, 2855, 1737, 1461, 1377, 1363, 1247, 1215, 1159, 1145, 1088, 1069, 1005, 972, 934, 879, 865, 834, 806, 772, 734, 697 cm^{-1}; ^1H NMR (600 MHz, C_6D_6): see Table S-2; ^{13}C NMR (150 MHz, C_6D_6): see Table S-2; HRMS (ESI^+): calcd for $C_{67}H_{111}ClO_{15}Si_2Na$ $[M+Na]^+$: 1269.7042; found: 1269.7042.



Macrolactone 10. $[\alpha]_D^{20}$ = +10.4° (c = 0.26, CH_2Cl_2). IR (neat): 3477, 2931, 2856, 1737,1461, 1377, 1247, 1215, 1158, 1087, 1068, 1004, 975, 933, 878, 834, 807, 772,704 cm^{-1}; ^1H NMR (600 MHz, C_6D_6): see Table S-3; ^{13}C NMR (150 MHz, C_6D_6): see Table S-3; HRMS (ESI^+): calcd for $C_{60}H_{105}ClO_{15}Si_2Na$ $[M+Na]^+$: 1179.6572; found: 1179.6573.



Macrolactone 11. $[\alpha]_D^{20}$ = +13.0° (c = 0.41, CH_2Cl_2). IR (neat): 2931, 2857, 1738, 1461, 1436, 1377, 1362, 1249, 1216, 1193, 1082, 1049, 1030, 1005, 982, 932, 878, 834, 806, 773,735, 697 cm^{-1}; ^1H NMR (600 MHz, C_6D_6): see Table S-4; ^{13}C NMR (150 MHz, C_6D_6): see Table S-4; HRMS (ESI^+): calcd for $C_{67}H_{113}ClO_{15}Si_2Na$ $[M+Na]^+$: 1271.7189; found: 1271.7199.



Spirastrellolide F Methyl Ester (2). ^1H NMR (600 MHz, C_6D_6): see Table S-5; ^{13}C NMR (150 MHz, C_6D_6): see Table S-6; HRMS (ESI^+): calcd for $C_{53}H_{85}ClO_{17}Na$ $[M+Na]^+$: 1051.5362; found: 1051.5368.

Table S-1. ^{1}H NMR and ^{13}C NMR Data of *seco*-Acid 8 in C_6D_6.

H-Atom	^{1}H NMR (600 MHz)[a]	C-Atom	^{13}C NMR (150 MHz)[b]
-	-	**1**	173.3
2a	2.54 dd (14.7, 9.1)	**2**	41.9
2b	2.28 dd (14.7, 3.9)		
3	3.73	**3**	74.4
4a	1.24	**4**	31.3
4b	1.04		
5a	1.54	**5**	23.8
5b	1.30		
6a	1.38	**6**	32.1
6b	1.17		
7	3.56 br dd (11.0, 8.7)	**7**	74.6
8a	2.11	**8**	45.5
8b	1.59		
9	4.28	**9**	68.8
10a	2.20	**10**	48.2
10b	1.95		
11	4.19	**11**	68.9
12a	2.03	**12**	42.8
12b	1.93		
13	3.75	**13**	73.8
14	1.45	**14**	35.0
15a	1.86	**15**	28.1
15b	1.43		
16a	1.78	**16**	35.9
16b	1.47		
-	-	**17**	95.6
18a	1.82	**18**	35.3
18b	1.39		
19a	2.04	**19**	23.8
19b	1.85		
20	3.47 ddd (11.2, 9.5, 4.8)	**20**	76.6
21	3.76 br d (9.5)	**21**	71.2
22	4.93 dd (6.7, 0.7)	**22**	76.9
23	5.04 br d (6.5)	**23**	79.5
-	-	**24**	145.7
25a	2.67 ddd (14.4, 11.9, 3.9)	**25**	29.3
25b	2.58 ddd(14.4, 11.9, 4.9)		
26a	2.51	**26**	32.5
26b	2.17		
27	4.14	**27**	73.1
28	3.95 t (9.8)	**28**	64.2
29	3.90 ddd (10.8, 9.5, 4.9)	**29**	79.6
30a	2.16 dd (12.5, 4.8)	**30**	43.5
30b	1.46 dd (12.3, 10.8)		
-	-	**31**	97.8
32a	1.81	**32**	36.3
32b	1.38		
33a	2.16	**33**	24.3

33b	1.29		
34	1.57	**34**	38.4
-	-	**35**	109.3
36a	2.39 dd (14.7, 6.5)	**36**	48.4
36b	2.71 d (14.6)		
37	4.17	**37**	71.6
38	4.17	**38**	84.5
39a	2.19	**39**	29.3
39b	2.10		
40a	3.39 ddd (9.3, 4.4, 3.3)	**40**	67.4
40b	3.19 ddd (10.9, 9.3, 2.0)		
48	0.91 d (6.3)	**48**	18.3
49	3.24 s	**49**	56.4
50a	5.64 s	**50**	112.1
50b	5.24 s		
51	3.29 s	**51**	57.4
52	1.21 d (7.0)	**52**	16.8
Me (acetonide)	1.70 s	**Me (acetonide)**	27.0
Me (acetonide)	1.42 s	**Me (acetonide)**	26.2
-	-	**$(CH_3)_2C$**	108.1
***t*Bu**	1.08 s	***t*Bu**	26.4
***t*Bu**	1.07 s	***t*Bu**	26.3
MeSi	0.29 s	**MeSi**	-2.6
MeSi	0.25 s	**MeSi**	-3.4
MeSi	0.26 s	**MeSi**	-3.7
MeSi	0.32 s	**MeSi**	-3.7
-	-	**$(CH_3)_3CSi$**	18.5
-	-	**$(CH_3)_3CSi$**	18.3
-	-	***i*-Ph**	137.9
***o*-Ph**	7.15	***o*-Ph**	127.9
***m*-Ph**	7.12 t	***m*-Ph**	128.7
***p*-Ph**	7.05 t	***p*-Ph**	128.1
$PhCH_a$	4.15 d (11.6)	**$PhCH_2$**	73.6
$PhCH_b$	4.10 d (11.7)		

[a] δ_H (ppm), multiplicity, coupling constant *J* (Hz); [b] δ_C (ppm).

Table S-2. ^{1}H NMR and ^{13}C NMR data of Macrolactone 9 in C_6D_6

H-Atom	^{1}H NMR (600 MHz)[a]	C-Atom	^{13}C NMR (150 MHz)[b]
-	-	**1**	169.6
2a	2.49 dd (15.8, 10.6)	**2**	42.8
2b	2.10		
3	3.78 tt (10.7, 2.0)	**3**	74.5
4a	1.04	**4**	30.8
4b	1.01		
5a	1.62	**5**	24.0
5b	1.37		
6a	1.78	**6**	33.1
6b	1.18		
7	3.22 br t (9.5)	**7**	75.9
8a	2.01 br t (11.8)	**8**	47.6
8b	1.86		
9	3.86 br t (10.3)	**9**	68.2
10a	2.17	**10**	51.9
10b	1.74		
11	4.39	**11**	66.0
12	2.07	**12**	42.1
13	3.88	**13**	72.9
14	1.83	**14**	31.9
15a	1.93	**15**	28.4
15b	1.52		
16a	1.71	**16**	36.0
16b	1.55		
-	-	**17**	95.9
18a	1.79	**18**	34.4
18b	1.40		
19a	1.95	**19**	23.3
19b	1.83		
20	3.44 ddd (10.8, 9.4, 4.5)	**20**	75.0
21	3.37 d (9.4)	**21**	71.3
22	4.65 d (6.7)	**22**	76.5
23	4.53 br d (6.5)	**23**	79.8
-	-	**24**	143.1
25a	2.06	**25**	25.0
25b	1.89		
26a	2.40	**26**	27.6
26b	2.05		
27	4.21 dt (10.4, 3.2)	**27**	72.0
28	3.80 t (10.1)	**28**	62.1
29	3.88	**29**	79.2
30a	2.13	**30**	43.6
30b	1.30		
-	-	**31**	97.8
32a	1.71	**32**	36.0
32b	1.31		
33a	2.13	**33**	24.3
33b	1.36		

34	1.53	**34**	38.9
-	-	**35**	108.5
36a	2.24 dd (15.4, 6.7)	**36**	47.4
36b	1.95 d (15.3)		
37	5.34 dd (6.6, 3.1)	**37**	74.1
38	4.41 td (6.3, 3.1)	**38**	80.6
39	2.18 q (6.3)	**39**	29.6
40a	3.71 dt (9.3, 6.3)	**40**	67.8
40b	3.65 dt (9.3, 6.3)		
48	1.00 d (6.2)	**48**	18.2
49	3.16 s	**49**	55.9
50a	5.75 s	**50**	109.1
50b	5.07 s		
51	3.36 s	**51**	57.7
52	1.15 d (6.7)	**52**	17.7
Me (acetonide)	1.49 s	**Me (acetonide)**	26.9
Me (acetonide)	1.75 s	**Me (acetonide)**	26.8
-	-	**$(CH_3)_2C$**	108.3
***t*Bu**	1.07 s	***t*Bu**	26.6
***t*Bu**	1.00 s	***t*Bu**	26.0
MeSi	0.35 s	**MeSi**	-2.3
MeSi	0.15 s	**MeSi**	-3.4
MeSi	0.33 s	**MeSi**	-3.8
MeSi	0.21 s	**MeSi**	-3.8
-	-	**$(CH_3)_3CSi$**	18.7
-	-	**$(CH_3)_3CSi$**	18.2
-	-	***i*-Ph**	139.1
***o*-Ph**	7.37 d	***o*-Ph**	127.7
***m*-Ph**	7.23 t	***m*-Ph**	128.5
***p*-Ph**	7.08 t	***p*-Ph**	127.5
$PhCH_a$	4.38 d (11.9)	**$PhCH_2$**	72.9
$PhCH_b$	4.34 d (11.4)		

[a] δ_H (ppm), multiplicity, coupling constant *J* (Hz); [b] δ_C (ppm).

Table S-3. ^{1}H NMR and ^{13}C NMR data of Macrolactone 10 in C_6D_6

H-Atom	^{1}H NMR (600 MHz)[a]	C-Atom	^{13}C NMR (150 MHz)[b]
-		**1**	169.6
2a	2.43 dd (15.2, 10.3)	**2**	42.7
2b	2.14 dd (15.2, 2.4)		
3	3.72	**3**	74.5
4a	1.07	**4**	30.9
4b	1.04		
5a	1.61	**5**	23.9
5b	1.36		
6a	1.87	**6**	33.0
6b	1.22		
7	3.31	**7**	76.6
8a	2.08	**8**	47.1
8b	1.88		
9	4.04	**9**	69.0
10a	2.05	**10**	51.2
10b	1.91		
11	4.33	**11**	67.1
12	1.96	**12**	43.4
13	3.84 ddd (10.5, 5.7, 2.5)	**13**	73.5
14	1.64	**14**	33.3
15a	1.93	**15**	28.1
15b	1.46		
16a	1.70	**16**	36.1
16b	1.50		
-	-	**17**	95.7
18a	1.79	**18**	34.6
18b	1.38		
19a	1.93	**19**	23.5
19b	1.80		
20	3.42	**20**	75.5
21	3.39	**21**	71.6
22	4.68 d (6.5)	**22**	76.5
23	4.64 br d (6.5)	**23**	79.7
-	-	**24**	143.1
25a	2.18	**25**	26.6
25b	2.08		
26a	2.25	**26**	29.9
26b	2.17		
27	4.13 br dd (10.2, 7.1)	**27**	72.5
28	3.73 t (10.0)	**28**	63.4
29	3.90 ddd (11.2, 9.6, 4.8)	**29**	79.1
30a	2.13 dd (12.6, 4.9)	**30**	43.5
30b	1.30 dd (12.6, 11.4)		
-	-	**31**	97.8
32a	1.73	**32**	36.0
32b	1.31		
33a	2.09	**33**	24.1
33b	1.30		

34	1.51	**34**	38.0
-	-	**35**	108.2
36a	2.24 dd (14.5, 6.8)	**36**	45.4
36b	1.98 dd (14.5, 3.1)		
37	5.59	**37**	73.8
38	4.45	**38**	79.8
39	1.93	**39**	32.7
40	3.67	**40**	59.9
48	0.96	**48**	18.3
49	3.15 s	**49**	56.1
50a	5.78 s	**50**	110.2
50b	5.18 s		
51	3.33 s	**51**	57.6
52	1.08	**52**	17.4
Me (acetonide)	1.45 s	**Me (acetonide)**	26.8
Me (acetonide)	1.73 s	**Me (acetonide)**	26.7
-	-	**$(CH_3)_2C$**	108.5
***t*Bu**	1.09 s	***t*Bu**	26.6
***t*Bu**	1.04 s	***t*Bu**	26.2
MeSi	0.33 s	**MeSi**	-2.2
MeSi	0.37 s	**MeSi**	-3.4
MeSi	0.22 s	**MeSi**	-3.6
MeSi	0.20 s	**MeSi**	-3.6
-	-	**$(CH3)_3CSi$**	18.6
-	-	**$(CH3)_3CSi$**	18.3
OH-40	1.78	**-**	-

[a] δ_H (ppm), multiplicity, coupling constant *J* (Hz); [b] δ_C (ppm).

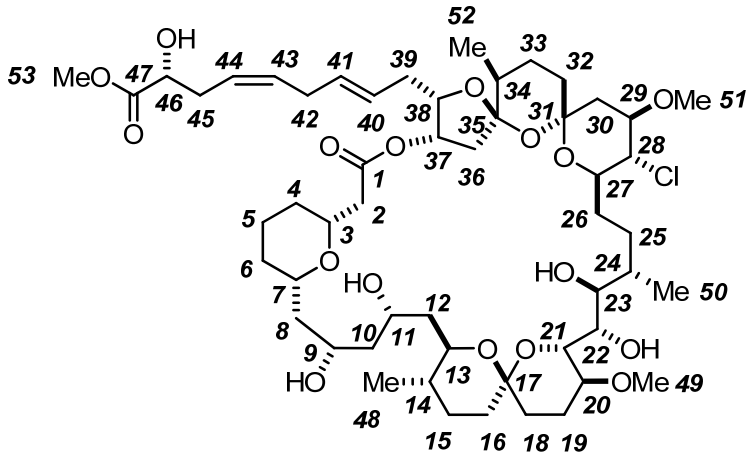
Table S-4. ^{1}H NMR and ^{13}C NMR Data of Macrolactone 11 in C_6D_6

H-Atom	^{1}H NMR (600 MHz)[a]	C-Atom	^{13}C NMR (150 MHz)[b]
-	-	**1**	169.4
2a	2.46 dd (15.0, 9.5)	**2**	43.1
2b	2.18 dd (15.0, 2.4)		
3	3.77	**3**	74.9
4a	1.13	**4**	31.2
4b	1.10		
5a	1.61	**5**	23.9
5b	1.39		
6a	1.74	**6**	32.7
6b	1.19		
7	3.35 br t (9.5)	**7**	75.9
8a	1.99	**8**	47.0
8b	1.86		
9	3.97	**9**	68.4
10	2.00	**10**	50.4
11	4.37	**11**	66.3
12a	2.21	**12**	42.0
12b	2.15		
13	4.01 dt (10.3, 3.5)	**13**	74.1
14	1.70	**14**	32.1
15a	1.77	**15**	29.0
15b	1.50		
16a	1.75	**16**	35.7
16b	1.51		
-	-	**17**	96.8
18a	1.84	**18**	34.6
18b	1.45		
19a	1.95	**19**	24.0
19b	1.84		
20	3.48 td (9.7, 4.3)	**20**	75.5
21	3.82 d (9.3)	**21**	70.9
22	4.74 d (6.0)	**22**	75.8
23	3.96 dd (10.5, 5.9)	**23**	82.1
24	2.25	**24**	34.5
25a	2.34	**25**	27.3
25b	1.42		
26a	2.48	**26**	29.5
26b	1.96		
27	4.09 ddd (10.1, 4.8, 2.8)	**27**	72.9
28	3.77 t (9.85)	**28**	62.9
29	3.82 ddd (10.9, 9.5, 4.7)	**29**	79.3
30a	2.12 dd (12.7, 4.7)	**30**	43.2
30b	1.31 dd (12.5, 11.0)		
-	-	**31**	97.8
32a	1.63	**32**	36.3
32b	1.34		
33a	2.11	**33**	24.3
33b	1.27		

34	1.53	**34**	38.5
-	-	**35**	108.0
36a	2.23 dd (15.3, 6.3)	**36**	47.8
36b	1.91 d (15.3)		
37	5.46 dd (6.3, 2.7)	**37**	72.7
38	4.56 br dd (10.1, 6.2)	**38**	80.6
39a	2.25	**39**	29.3
39b	2.14		
40a	3.71 td (9.9, 3.3)	**40**	67.0
40b	3.60 dt (9.7, 4.7)		
48	1.00 d (6.3)	**48**	18.9
49	3.17 s	**49**	56.1
50	1.14 d (6.5)	**50**	16.9
51	3.30 s	**51**	57.6
52	1.08 d (6.7)	**52**	16.9
Me (acetonide)	1.68 s	**Me (acetonide)**	26.9
Me (acetonide)	1.49 s	**Me (acetonide)**	26.6
-	-	**$(CH_3)_2C$**	108.5
***t*Bu**	1.05 s	***t*Bu**	26.5
***t*Bu**	1.03 s	***t*Bu**	26.1
MeSi	0.35 s	**MeSi**	-2.8
MeSi	0.15 s	**MeSi**	-3.5
MeSi	0.31 s	**MeSi**	-4.1
MeSi	0.20 s	**MeSi**	-4.1
-	-	**$(CH_3)_3C$Si**	18.5
-	-	**$(CH_3)_3C$Si**	18.3
-	-	***i*-Ph**	139.1
***o*-Ph**	7.36 d	***o*-Ph**	127.5
***m*-Ph**	7.23 t	***m*-Ph**	128.5
***p*-Ph**	7.08 t	***p*-Ph**	127.4
$PhCH_a$	4.37 d (12.1)	**$PhCH_2$**	72.8
$PhCH_b$	4.27 d (12.1)		

[a] δ_H (ppm), multiplicity, coupling constant *J* (Hz); [b] δ_C (ppm).

Table S-5. ^{1}H NMR data of natural and synthetic Spirastrellolide F Methyl Ester (2) in C_6D_6; arbitrary numbering scheme as shown in the Insert.



Spirastrellolide F Methyl Ester (**2**)

H-Atom	^{1}H NMR (500 MHz)[a] literature data	^{1}H NMR (600 MHz)[b] synthetic sample	Δδ
2a	2.47 dd (16.9, 9.5)	2.55 dd (17.1, 9.5)	-0.08
2b	2.14	2.16 d (16.9)	-0.02
3	3.63	3.67	-0.04
4	0.99	1.02	-0.03
5a	1.51	1.52	-0.01
5b	1.20	1.26	-0.06
6a	1.27	1.18	0.09
6b	1.01	1.09	-0.08
7	3.69	3.75	0.06
8a	2.11	1.90	0.21
8b	1.36	1.56	-0.20
9	4.34	4.37	-0.03
10a	1.93	1.86	0.07
10b	1.36	1.34	0.02
11	4.60 br t (8.7)	4.60 t (9.0)	0.00
12a	2.08	2.03	0.05
12b	1.40-1.38	1.42	
13	3.71	3.71 t (10.9)	0.00
14	1.23	1.25	-0.02
15a	1.56	1.54	0.02
15b	1.39	1.39	0.00
16a	1.54	1.53	0.01
16b	1.40	1.40	0.00
18a	1.64	1.65 ddd (13.5, 3.8, 3.2)	-0.01
18b	1.29	1.27	0.02
19a	1.89	1.92	-0.03
19b	1.79	1.76	0.03
20	3.35	3.33	0.02
21	4.20	4.24 d (9.2)	-0.04
22	4.19	4.18 t (10.3)	0.01

23	3.79	3.76	0.03
24	2.25	2.25	0.00
25a	2.37	2.28	0.09
25b	1.46	1.46	0.00
26a	2.57	2.56	0.01
26b	1.46	1.49	-0.03
27	3.97 br t (9.6)	3.98 ddd (10.0, 9.0, 1.5)	-0.01
28	3.61 t (9.6)	3.62 t (9.9)	-0.01
29	3.84 td (9.6, 4.8)	3.84 ddd (11.3, 9.6, 5.0)	0.00
30a	2.13	2.11 dd (12.7, 5.0)	0.02
30b	1.38	1.37 dd (12.8, 11.4)	0.01
32a	1.71	1.69 dt (13.3, 3.1)	0.02
32b	1.36	1.34	0.02
33a	2.13	2.07	0.06
33b	1.21	1.21	0.00
34	1.50	1.48	0.02
36a	2.29 dd (15.5, 7.0)	2.28 dd (15.7, 7.1)	0.01
36b	1.98 d (15.5)	1.97 d (15.5)	0.01
37	5.53	5.51 dd (6.9, 3.5)	0.02
38	4.24	4.24	0.00
39a	3.17	3.09	0.08
39b	2.52	2.58	-0.06
40	5.56	5.55 br dt (15.2, 7.2)	0.01
41	5.87 dt (15.4, 6.8)	5.87 dt (15.3, 6.4)	0.00
42a	2.75 dt (15.1, 6.8)	2.74 dt (15.4, 6.9)	0.01
42b	2.65 dt (15.1, 6.8)	2.64 dt (15.4, 7.3)	0.01
43	5.68	5.67 br dt (10.8, 7.7)	0.01
44	5.46	5.46 br dt (10.7, 7.6)	0.00
45a	2.52	2.51 dddd (14.4, 8.0, 4.7, 1.3)	0.01
45b	2.37	2.36 dddd (14.5, 7.2, 5.8, 1.2)	0.01
46	4.22	4.20	0.02
48	0.84 d (6.5)	0.83 d (6.6)	0.01
49	3.27 s	3.21 $\rightarrow$ 3.25 (s $\rightarrow$ br)[c]	0.06/0.02
50	1.32 d (6.9)	1.32 d (7.0)	0.00
51	3.36 s	3.35 s	0.01
52	1.07 d (6.6)	1.08 d (6.7)	-0.01
53	3.32 s	3.32 s	0.00
OH-11		4.60 $\rightarrow$ 4.59	
OH-23		4.39 $\rightarrow$ 4.31 [c]	
OH-46		4.06 d (8.0) $\leftarrow$ 4.20 [c]	
OH-9		3.74 $\rightarrow$ 3.65 [c]	
OH-22	1.69	1.71 $\rightarrow$ 1.70 [c]	

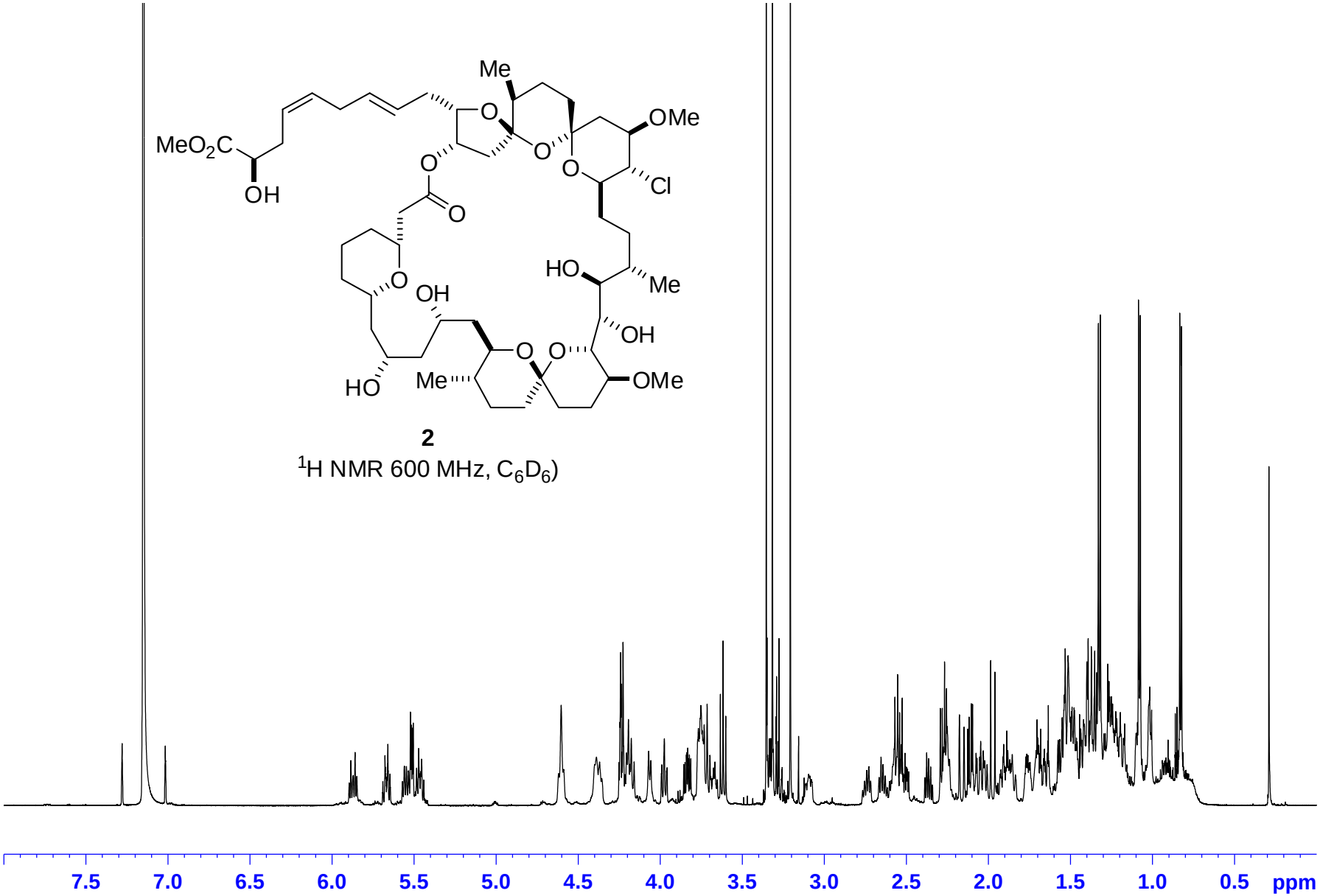
[a] *J. Org. Chem.* **2007**, *72*, 9842-9845; [b] δ_H (ppm), multiplicity, coupling constant *J* (Hz); [c] the signal shows a time-dependent behavior, cf. Text.

Table S-6. ^{13}C NMR data of Synthetic and Natural Spirastrellolide F Methyl Ester (2) in C_6D_6;[c] arbitrary numbering scheme as shown in the insert to the previous Table.

C-Atom	^{13}C NMR (100 MHz)[a] literature data	^{13}C NMR (150 MHz)[b] synthetic sample	Δδ
1	169.1	169.5	-0.4
2	42.5	br 42.8	-0.3
3	74.3	br 74.0	0.3
4	31.1	br 31.5	-0.4
5	23.9	24.1	-0.2
6	29.9	br 30.6	-0.7
7	76.8	br 76.1	0.7
8	41.4	42.6	-1.2
9	66.7	br 65.6	1.1
10	44.0	br 44.8	-0.8
11	66.0	br 65.4	0.6
12	41.4	41.4	0.0
13	73.7	73.6	0.1
14	35.0	34.9	0.1
15	29.3	29.3	0.0
16	35.5	35.4	0.1
17	95.6	95.6	0.0
18	35.3	35.2	0.1
19	24.9	24.7	0.2
20	74.6	74.7	-0.1
21	70.2	br 69.8	0.4
22	69.1	69.0	0.1
23	75.5	75.7	-0.2
24	34.1	33.9	0.2
25	26.1	25.9	0.2
26	31.3	br 31.0	0.3
27	74.8	74.8	0.0
28	65.8	br 65.4	0.4
29	79.4	79.3	0.1
30	44.1	44.1	0.0
31	97.6	97.7	-0.1
32	36.5	36.4	0.1
33	24.2	24.1	0.1
34	38.6	38.4	0.2
35	108.7	108.8	-0.1
36	47.0	47.0	0.0
37	73.3	73.2	0.1
38	84.0	83.9	0.1
39	30.3	30.6	-0.3
40	126.3	125.9	0.4
41	131.6	131.9	-0.3
42	31.0	31.0	0.0
43	131.8	131.7	0.1
44	124.4	124.4	0.0
45	32.8	32.7	0.1
46	70.7	70.6	0.1

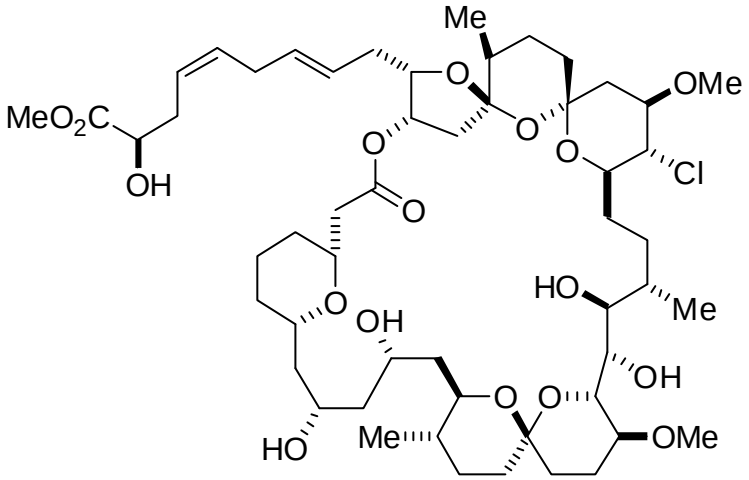
47	174.7	174.8	-0.1
48	18.0	18.0	0.0
49	56.8	56.6	0.2
50	18.5	18.5	0.0
51	57.6	57.6	0.0
52	16.9	16.7	0.2
53	51.5	51.6	-0.1

[a] *J. Org. Chem.* **2007**, *72*, 9842-9845; [b] δ_C (ppm); [c] signals featuring a significant line-broadening are marked “br”



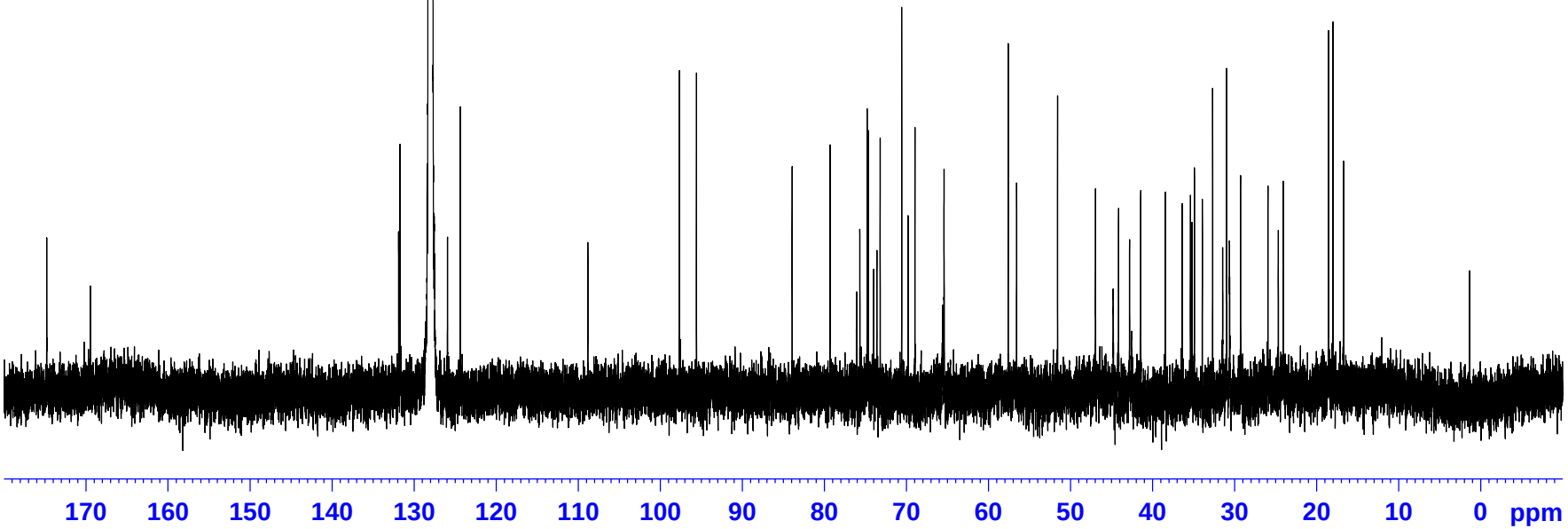
2

^{1}H NMR 600 MHz, C_6D_6)

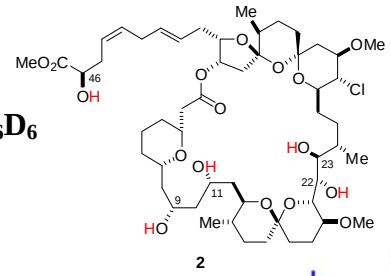


2

^{13}C NMR (150 MHz, C_6D_6)



NOESY spectrum of spirastrellolide F methyl ester (2) after 93h in C_6D_6



2