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Supporting Information

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Toward the Total Synthesis of Spirastrellolide A, Part 2: Conquest of the Northern Hemisphere

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General: All reactions were carried out under Ar in flame-dried glassware. IR: Nicolet FT-7199 spectrometer, wavenumbers ($\tilde{n}$) in cm^{-1}. MS (ESI): Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker DMX 600 spectrometer in the C_6D_6; chemical shifts (d) are given in ppm, coupling constants (J) in Hz. The solvent signal was used as references (C_6D_6: $\delta_C \equiv 128.0$ ppm; residual C_6H_6 in C_6D_6: $\delta_H \equiv 7.15$ ppm). ***Where indicated, the signal assignments are unambiguous***; the numbering scheme is arbitrary and is shown in the inserts. The assignments are based upon 1D and 2D spectra recorded using the following pulse sequences from the Bruker standard pulse program library: DEPT; COSY (*cosygs* and *cosydqtp*); HSQC (*invietgssi*) optimized for ^1J(C,H) = 145 Hz; HMBC (*inv4gslplrnd*) for correlations via ^nJ(C,H); HSQC-TOCSY (*invietgsml*) using an MLEV17 mixing time of 120 ms.

Compound 37. $[a]_D^{20}$ = -13.5° (*c* 0.90, CH_2Cl_2). IR (neat): 3493, 2930, 2870, 1673, 1454, 1380, 1260, 1088, 1012, 973, 925, 796 cm^{-1}. ^1H NMR (600 MHz, C_6D_6): δ 7.15-7.11 (m, 4H), 7.08-7.04 (m, 1H), 6.19 (ddd, *J* = 5.3, 10.6, 17.1 Hz, 1H), 5.61 (ddd, *J* = 1.6, 2.0, 17.1 Hz, 1H), 5.23 (ddd, *J* = 1.5, 2.0, 10.6 Hz, 1H), 4.51 (tdd, *J* = 1.5, 5.3, 10.4 Hz, 1H), 4.11-4.07 (m, 2H), 4.08 (d, *J* = 11.7 Hz, 1H), 4.03 (d, *J* = 11.7 Hz, 1H), 3.88 (ddd, *J* = 5.1, 9.6, 11.3 Hz, 1H), 3.65 (dd, *J* = 9.6, 10.4 Hz, 1H), 3.28 (s, 3H), 3.17 (ddd, *J* = 3.6, 4.8, 9.2 Hz, 1H), 3.06 (ddd, *J* = 2.5, 9.5, 10.6 Hz, 1H), 2.79 (d, *J* = 1.5 Hz, 1H –OH), 2.33 (ddd, *J* = 0.9, 6.4, 14.6 Hz, 1H), 2.20 (d, *J* = 14.6 Hz, 1H), 2.16 (dd, *J* = 3.3, 13.0 Hz, 1H), 2.11 (dd, *J* = 5.0, 12.7 Hz, 1H), 2.09-2.04 (m, 1H), 1.85 (dtd, *J* = 2.5, 4.7, 14.8 Hz, 1H), 1.69 (td, *J* = 3.3, 13.1 Hz, 1H), 1.53 (dqd, *J* = 3.7, 6.7, 13.3 Hz, 1H), 1.34 (dd, *J* = 11.3, 12.7 Hz, 1H), 1.33 (dt, *J* = 4.2, 13.4 Hz, 1H), 1.22 (ddd, *J* = 3.8, 7.0, 13.0 Hz, 1H), 1.16 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (150 MHz, C_6D_6): δ 138.1, 135.7, 128.7, 128.3, 127.8, 117.9, 109.4, 98.0, 84.2, 79.6, 74.0, 73.5, 71.7, 67.3, 64.7, 57.4, 48.3, 43.5, 38.3, 36.3, 29.3, 24.3, 16.8. HRMS (ESI+): Calcd for $C_{25}H_{35}ClO_6Na$ $(M+Na)^+$: 489.2014. Found: 489.2016.

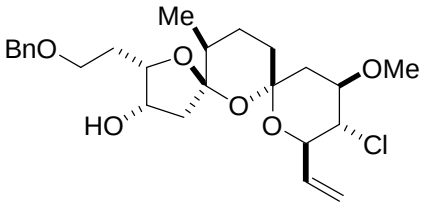
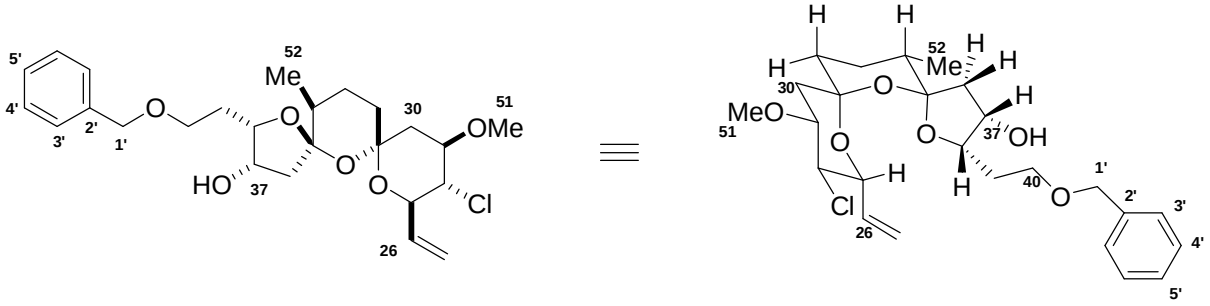


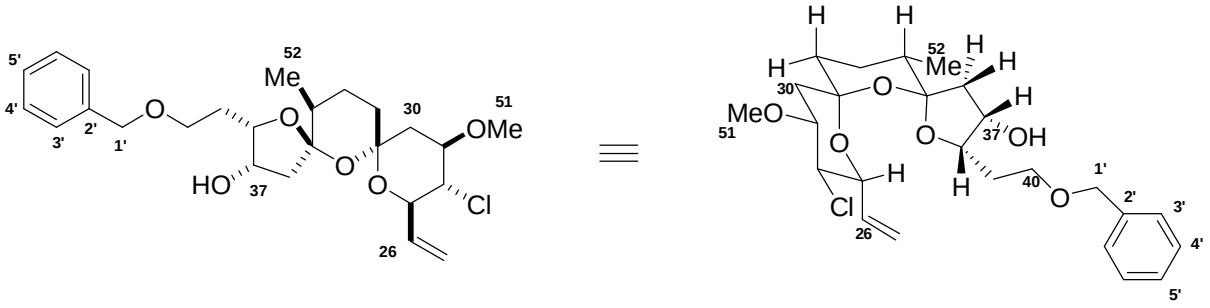
Table 1. Selected NMR-Data for Compound **37**.



Carbon No.	^{13}C d (ppm)[a]	APT[a]	^{1}H d (ppm) (mult., J (Hz))[b,c,d]	HMBC Correlations[e]
25	117.9	CH_2	H-25*E*: 5.61 (ddd, 1.6, 2.0, 17.1) H-25*Z*: 5.23 (ddd, 1.5, 2.0, 10.6)	
26	135.7	CH	H-26: 6.19 (ddd, 5.3, 10.6, 17,1)	H-25*E*, H-27, H-28
27	74.0	CH	H-27: 4.51 (tdd, 1.5, 5.3, 10.4)	H-26, H-25*E*, H-25*Z*, H-28, H-29
28	64.7	CH	H-28: 3.65 (dd, 9.6, 10.4)	H-26, H-27, H-29, H-30_{eq}, H-30_{ax}
29	79.6	CH	H-29: 3.88 (ddd, 5.1, 9.6, 11.3)	H-28, H-51, H-30_{eq}, H-30_{ax}
30	43.5	CH_2	H-30_{eq}: 2.11 (dd, 5.0, 12.7) H-30_{ax}: 1.34 (dd, 11.3, 12.7)	H-29
31	98.0	Q		H-27, H-30_{eq}, H-30_{ax}, H-32_{eq}, H-32_{ax}
32	36.3	CH_2	H-32_{eq}: 1.69 (td, 3.3, 13.1) H-32_{ax}: 1.34 (dt, 4.2, 13.4)	H-33_{eq}
33	24.3	CH_2	H-33_{eq}: 2.16 (dd, 3.3, 13.0) H-33_{ax}: 1.22 (ddd, 3.8, 7.0, 13.0)	H-34, H-32_{ax}, H-52
34	38.3	CH	H-34: 1.53 (dqd, 3.7, 6.7, 13.3)	H-32_{eq}, H-32_{ax}, H-33_{ax}, H-33_{eq}, H-36_b, H-52
35	109.4	Q		H-32_{ax}, H-33_{ax}, H-34, H-36_b, H-52
36	48.3	CH_2	H-36_a: 2.33 (ddd, 0.9, 6.4, 14.6) H-36_b: 2.20 (d, 14.6)	
37	71.7	CH	H-37: 4.11-4.07 (m)	H-36a, H-36b, H-38, H-39a, H-39b
38	84.2	CH	H-38: 4.11-4.07 (m)	H-37, H-40_a, H-40_b, H-36_a, H-36_b, H-39_a, H-39_b
39	29.3	CH_2	H-39_a: 2.09-2.04 (m) H-39_b: 1.85 (dtd, 2.5, 4.7, 14.8)	H-40_a, H-40_b
40	67.3	CH_2	H-40_a: 3.17 (ddd, 3.6, 4.8, 9.2) H-40_b: 3.06 (ddd, 2.5, 9.5, 10.6)	H-1'$_a$, H1'b, H-39_a
51	57.4	CH_3	H-51: 3.28 (s)	H-29, H-28
52	16.8	CH_3	H-52: 1.16 (d, 6.7)	H-34
1'	73.5	CH_2	H-1'$_a$: 4.08 (d, 11.7) H-1'$_b$: 4.03 (d, 11.7)	H-3', H-4', H-40_a
2'	138.1	Q		H-1'a, H-1'b, H-3', H-4'
3'	127.8	CH	H-3': 7.14-7.11 (m)	H-5', H-1'$_a$, H-1'$_b$
4'	128.7	CH	H-4': 7.14-7.11 (m)	H-5'
5'	128.3	CH	H-5': 7.08-7.04 (m)	H-3', H-4'

[a] Recorded at 150 MHz. [b] Recorded at 600 MHz. [c] Assignments based on HMQC data. [d] Methylene protons are designated H-X_{ax} and H-X_{eq} if the are known to occupy axial and equatorial position or arbitrarily designated H-X_a and H-X_b. [e] Only those correldations which could be unambiguously assigned are reported.

Table 2. Selected nOe Data for Compound **37**.



Proton No	^{1}H d (ppm) (mult J (Hz))[a,b]	nOe correlations[a,c]
H-27	4.51 (tdd, 1.5, 5.3, 10.4)	H-29, H-37, H-38
H-28	3.65 (dd, 9.6, 10.4)	H-30ax
H-29	3.88 (ddd, 5.1, 9.6, 11.3)	H-27
H-30eq	2.11 (dd, 5.0, 12.7)	H-32ax
H-30ax	1.34 (dd, 11.3, 12.7)	H-28, H-32eq
H-32eq	1.69 (td, 3.3, 13.1)	H-30ax
H-32ax	1.34 (dt, 4.2, 13.4)	H-30eq, H-34
H-34	1.53 (dqd, 3.7, 6.7, 13.3)	H-32ax, H-36b
H-36a	2.33 (ddd, 0.9, 6.4, 14.6)	H-37, H-38
H-36b	2.20 (d, 14.6)	H-34, H-52
H-37	4.11-4.07 (m)	H-36a, H-27
H-38	4.11-4.07 (m)	H-36a, H-27
H-52	1.16 (d, 6.7)	H-36b

[a] Recorded at 600 MHz. [b] Assignements based on APT, HMQC, and HMBC. [c] Only those correlations which were unambiguously assigned are reported.