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Supporting Information

Total Synthesis, Stereochemical Revision, and Biological Reassessment of Mandelalide A: Chemical Mimicry of Intrafamily Relationships

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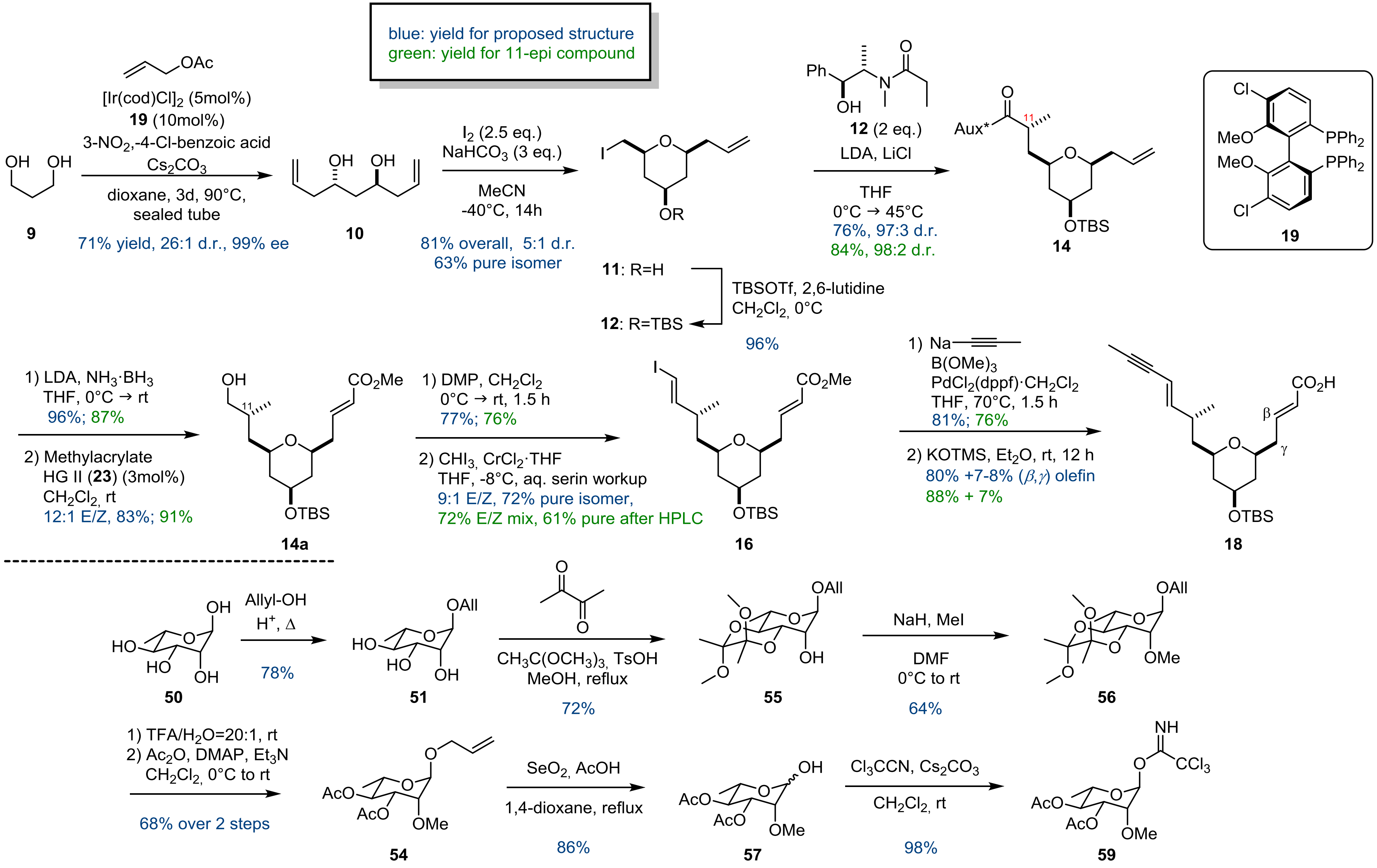
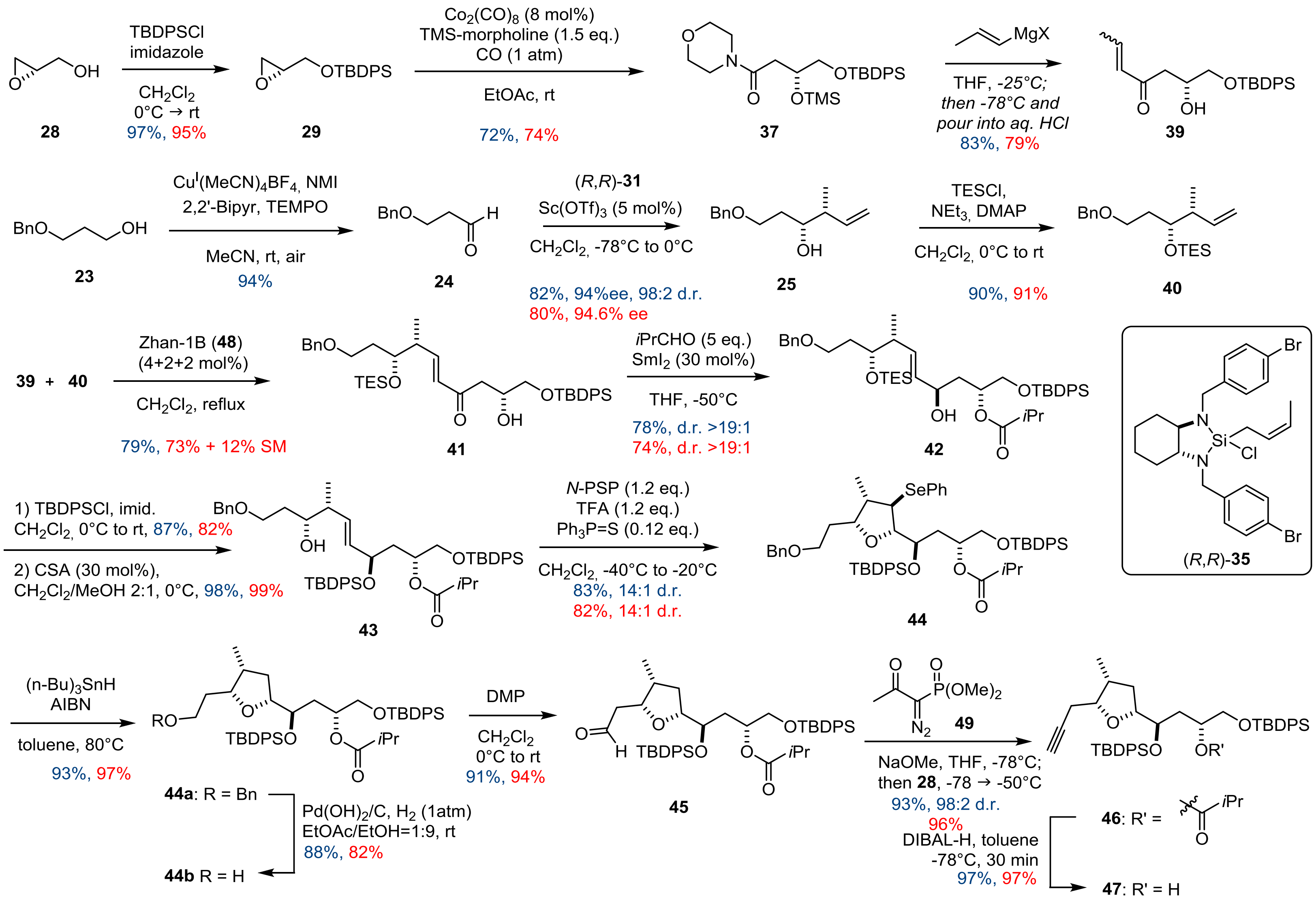
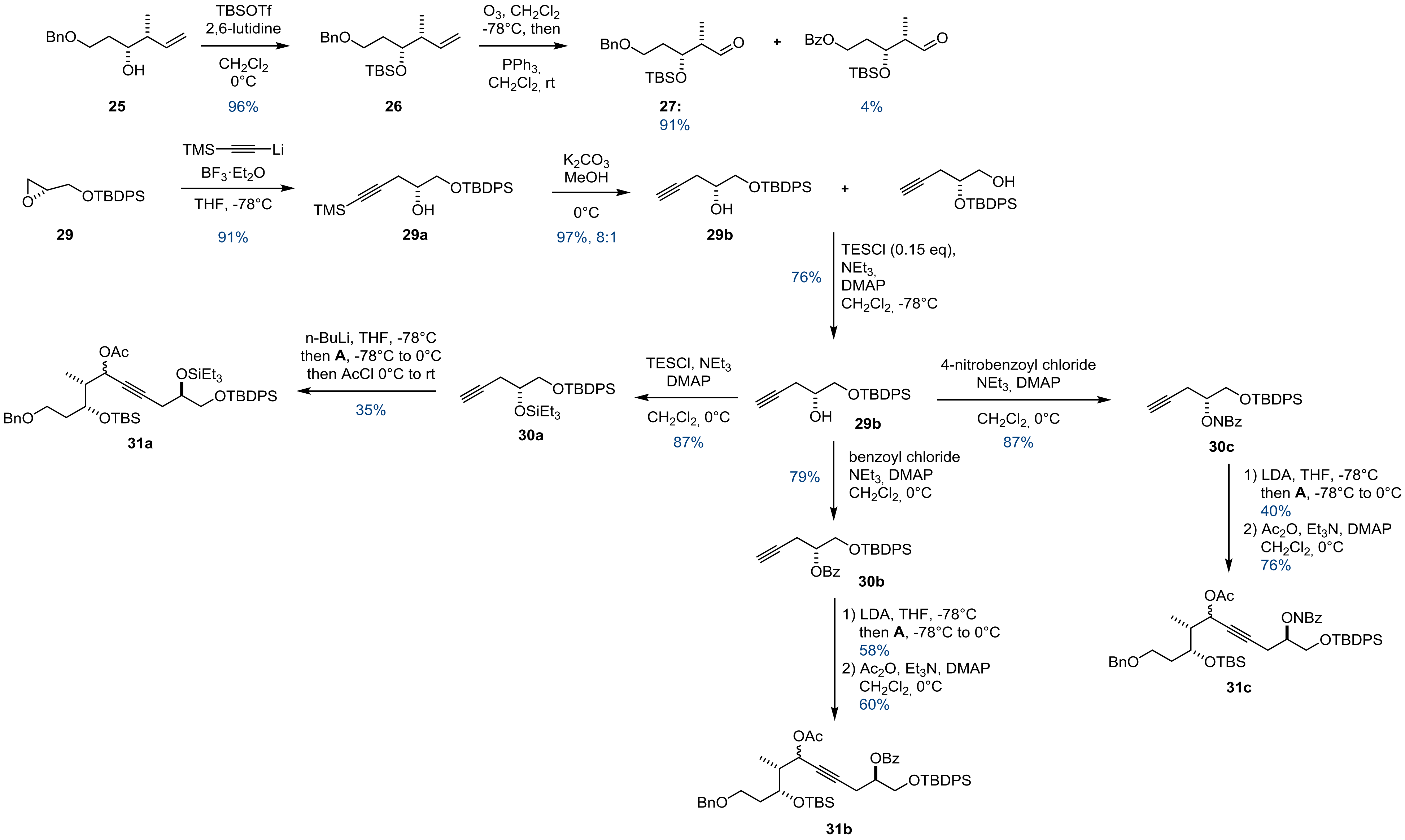


Scheme 1: Synthesis overview of the southern fragment **11** and rhamnosyl donor **40**.

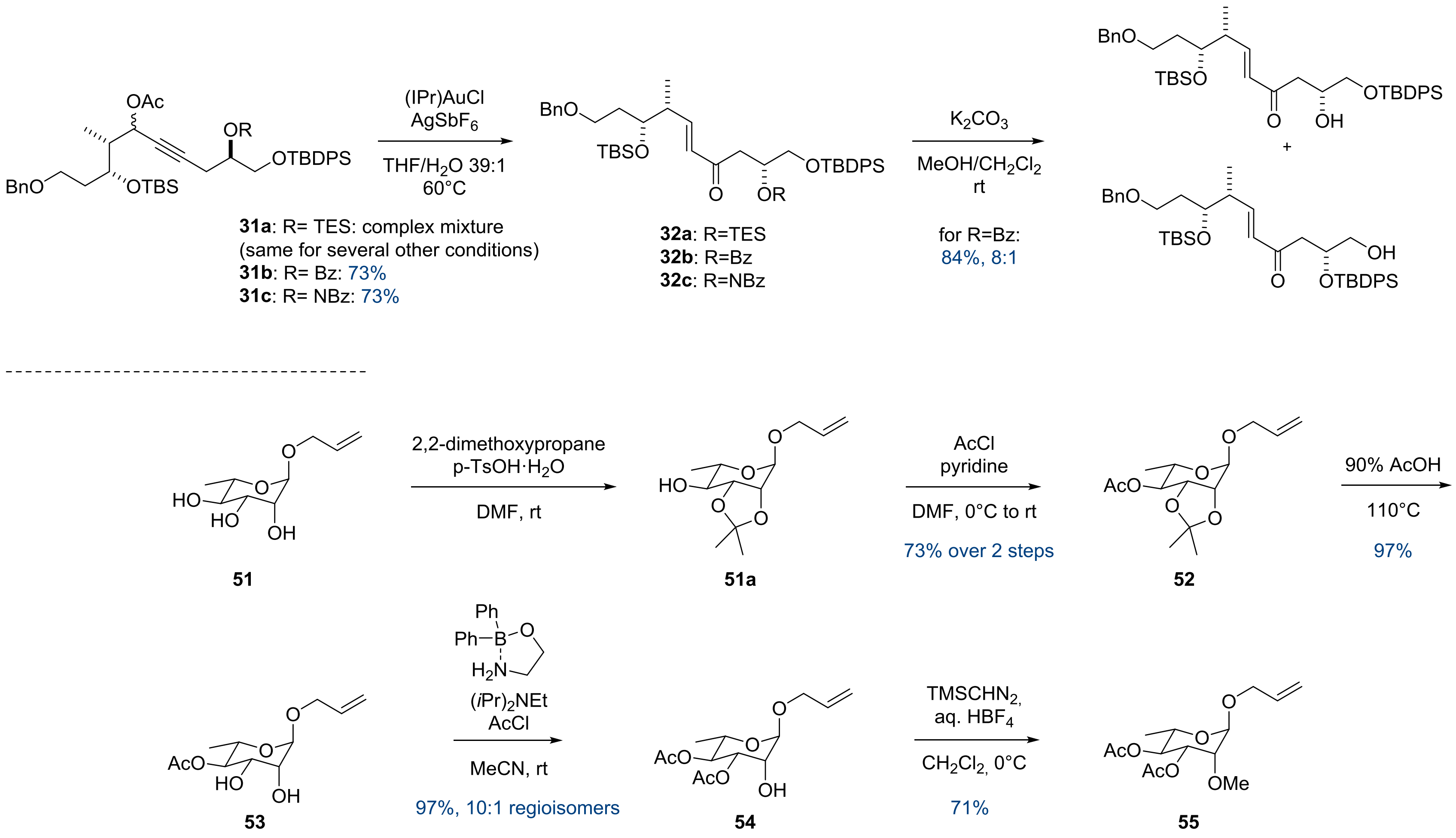
in red: yield for the enantiomer



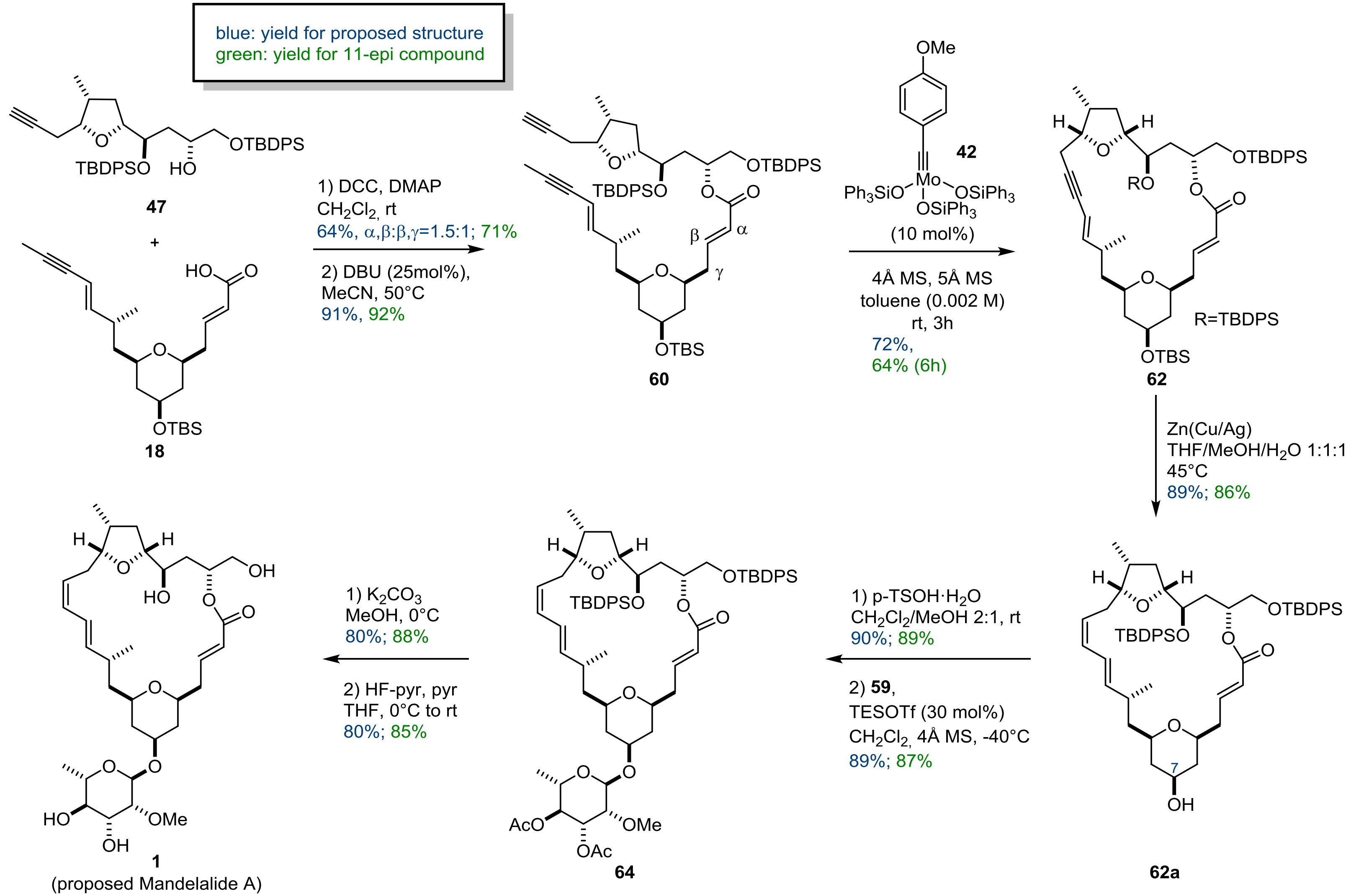
Scheme 2: Synthesis Overview of the northern Fragment **47**



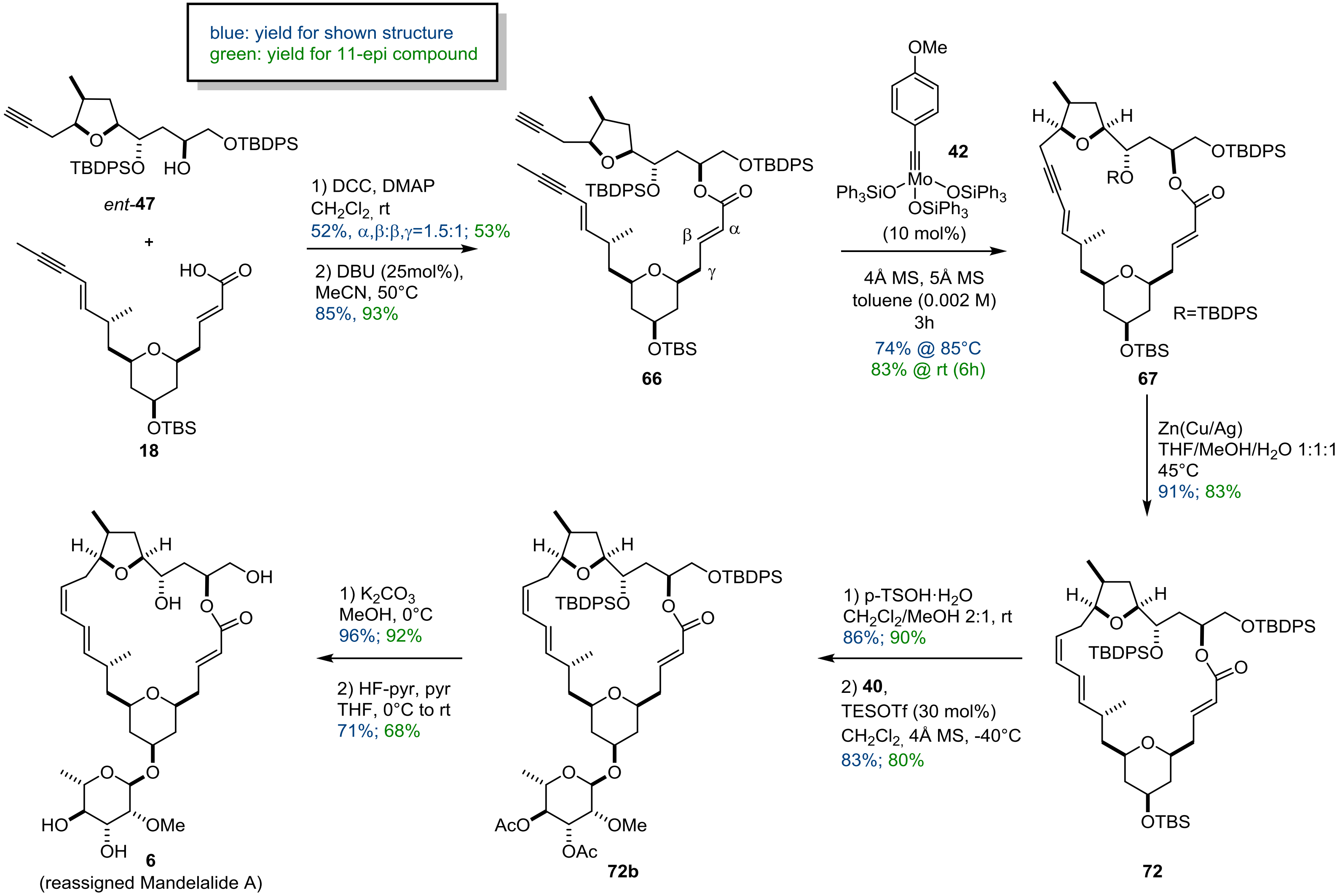
Scheme 3: Alternative Route to Enone **41**: Synthesis of the Meyer-Schuster Precursors.



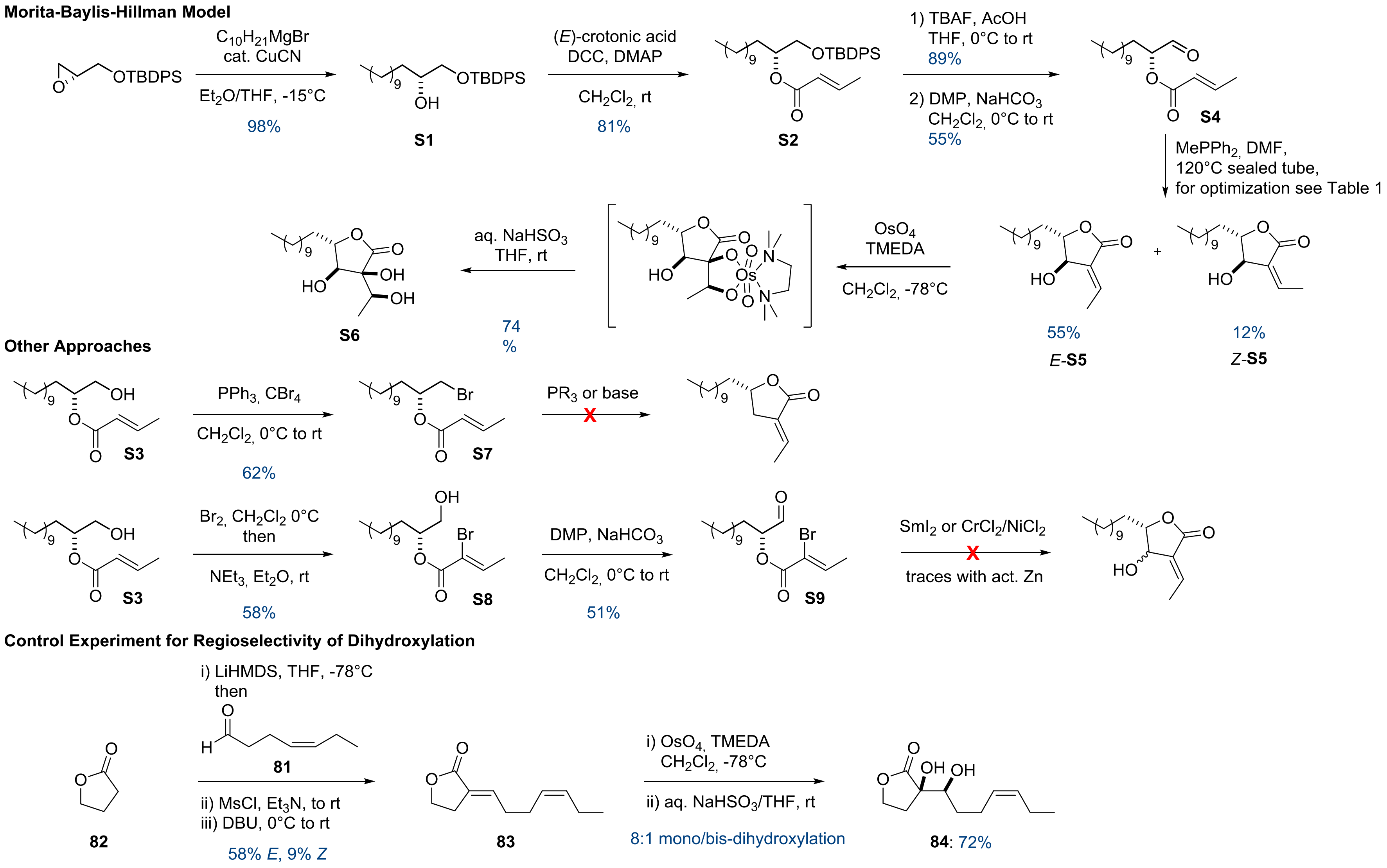
Scheme 4: Alternative Route to Enone **41**: Meyer-Schuster Rearrangement. Alternative Route to Rhamnosyl Compound **X**.



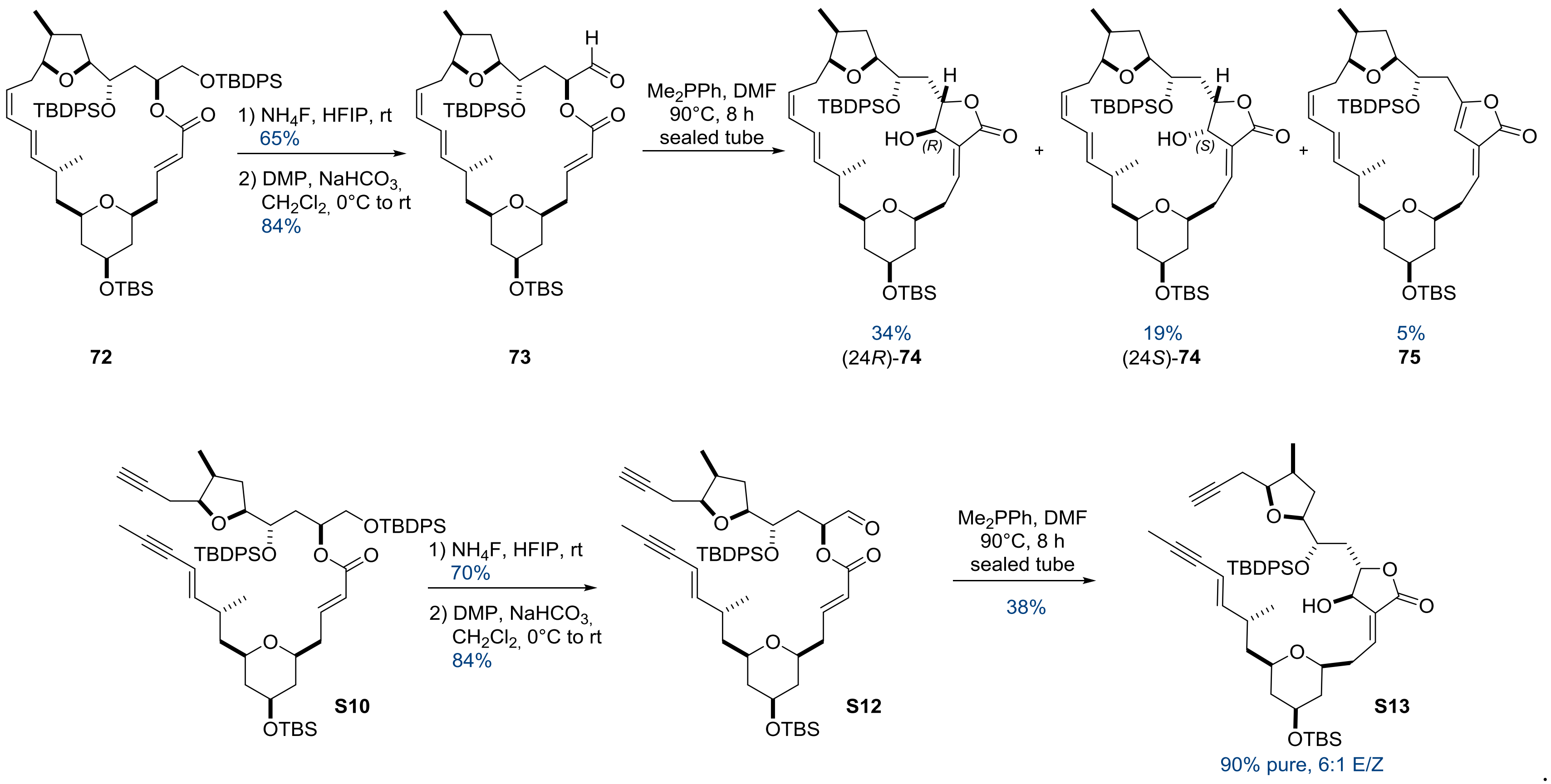
Scheme 5: Synthesis overview of the assembly stage and endgame for the proposed Structure



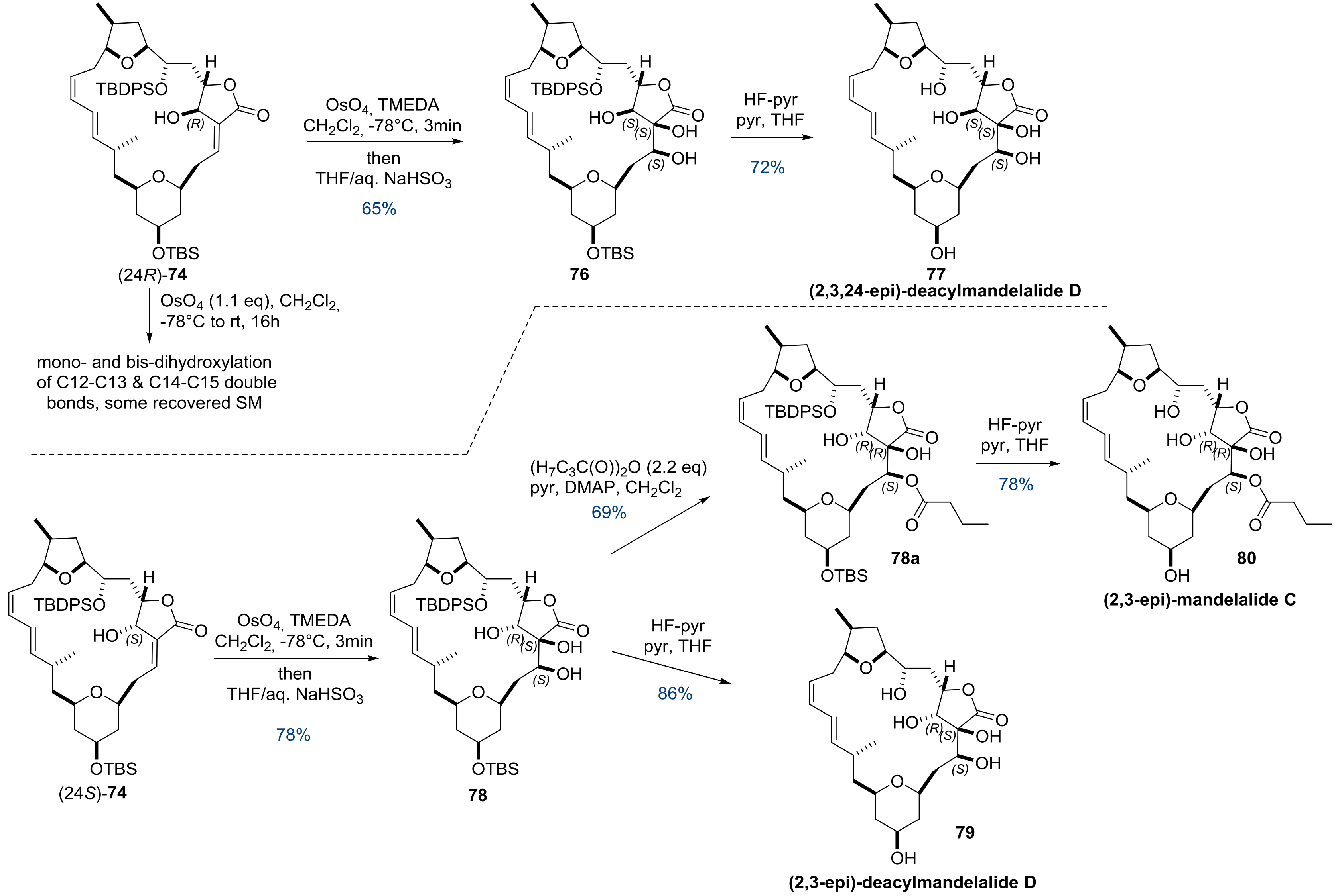
Scheme 6: Synthesis overview of the assembly stage and endgame for the reassigned structure.



Scheme 7: Model system for Morita-Baylis-Hilman reaction and Dihydroxylation Studies.



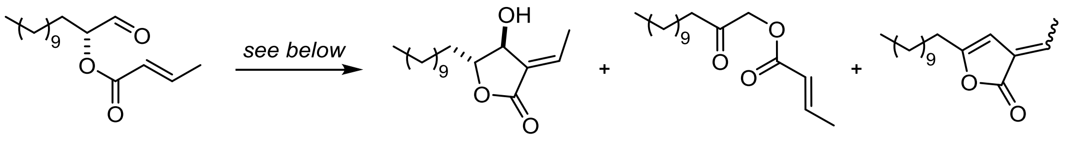
Scheme 8: Selective deprotection and Baylis-Hillman reactions.



Scheme 9: Completion of the synthesis of (2,3-epi)-deacylmandelalide D, (2,3,24-epi)-deacylmandelalide D and (2,3-epi)-mandelalide C.

Optimization of the MBH Reaction

Table 1: Selected attempts towards a MBH cyclization with model system **S4**.



S4 (*E*)-**S5** **S14** **S15**

entry	conditions1)	result2)
1	DABCO (50 mol%), CH_2Cl_2, rt to 50 °C	no reaction; then 95% **S14**
2	Quinuclidine (1 eq.), MeOH (1.5 eq), rt	97% **S14**
3	DBU (50 mol%), MeCN, 0 °C to rt	80% **S14**
4	DMAP, DMAP·HCl, EtOH, reflux	complex mixture
5	NMI-oxide (5 eq.), neat, rt	s.m., trace **S14**
6	$Ph_3P{=}S$, DMF, 90 °C	s.m.
7	$Et_3P{=}O$, DMF, 90 °C	s.m.
8	Et_2AlI, CH_2Cl_2/toluene, −78 to −20 °C	complex mixture
9	$PhSCH_2CH_2OH$ or Me_2S, $TiCl_4$, CH_2Cl_2, 0 °C	complex mixture
10	$N(CH_2CH_2NMe)_3P{=}S$, $TiCl_4$, CH_2Cl_2, 0 °C to rt	s.m.; complex mixture
11	$MgBr_2$, TMEDA, DMAP, MeOH	20% **S14**, complex mixture
12	*n*-BuSeLi, THF, −78 °C; H_2O_2 workup	trace **S14**, complex mixture
13	PhSeMgBr, THF, −78 °C to rt	two unidentified products
14	*n*-BuTeLi, THF, 0 °C	complex mixture

1) Unless stated otherwise, 1 eq. of MBH mediator was employed. 2) determined by ^{1}H NMR. s.m. = starting material

Table 2: Phosphine-catalyzed MBH reaction with model system **S4**.

entry	conditions1)	result (**S5**:**S14**:**S15**)2)	yield of **S5** (*E*/*Z*)3)
1	PMe_3, CH_2Cl_2, rt	(0 : 11 : 78)	-
2	Me_2PPh, CH_2Cl_2, rt	mainly s.m.	-
3	Me_2PPh, DMF, 90 °C	(4 : 9 : 73)	-
4	$MePPh_2$, DMF, 90 °C, 60 h	(70 : 6 : 8)	65% (7:1)
5	**$MePPh_2$, DMF, 120 °C, 24 h**	**(72 : 3 : 12)**	**67% (5:1)**
6	PPh_3, DMF, 90 °C	no reaction	-
7	P(2-furyl)$_3$, DMF, 90 °C	no reaction	-
8	P(4-MeO-Ph)$_3$, DMF, 90 °C	no reaction	-

1) Unless stated otherwise, 30 mol% of phosphine was employed. 2) determined by GC-MS analysis. Since several minor by-products were also formed, the products do not add up to 100. 3) determined by ^{1}H NMR.

Although this screening revealed $MePPh_2$ to be the ideal mediator of an intramolecular MBH reaction for β-substituted enoates, the application on substrates **73** and **S10** failed. It was eventually found, that the slimmer Me_2PPh furnished the products **74** with only trace amounts of elimination product **75** detectable.

Computational Section

Computational Methods

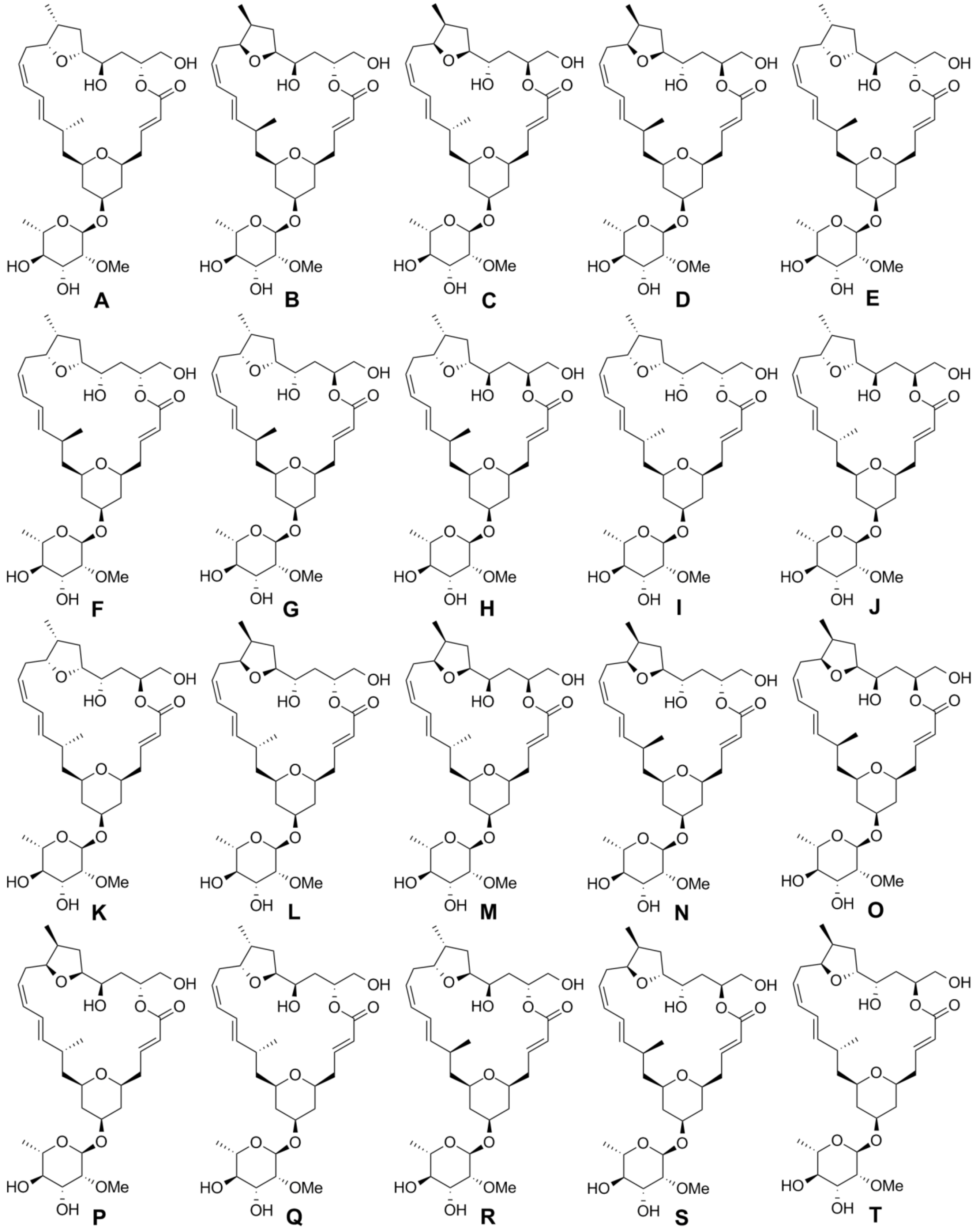
For conformer sampling, molecular dynamics (MD) simulations were performed employing the Nanoscale Molecular Dynamics (NAMD) code.[1] Nonbonded interactions were truncated at a cutoff radius of 12 Å and the CHARMM general force field was used.[2] The applied setup procedure started with an energy minimization followed by heating up the system to 500 K with Langevin temperature control and equilibration for 25 ps. This was followed by an MD run for 2 ns with time steps of 1 fs, with snapshots being taken every 250 ps. For each diastereoisomer an individual MD run was carried out, from which the ten lowest-energy conformers were selected for further quantum-chemical study.

These conformers were subjected to single-point calculations in the gas phase applying Density Functional Theory (DFT) at the B3LYP[3] level in combination with the 6-31G** basis set.[4] The nuclear shielding constants of the hydrogen and carbon atoms were computed with the GIAO ansatz[5] at the B3LYP/6-31G** level. All DFT calculations were performed using the Gaussian 09 package.[6]

Computational Results

DP4 probability

In total 20 diastereoisomers of Mandelalide A were studied as shown in Figure 1. Diastereoisomers A and C correspond to the originally suggested and the true structure of Mandelalide A, respectively. Experimental NMR data were available for the isolated natural product (iso) and for two synthetic compounds (syn-**1** and syn-11-*epi*-**1**) that are known to have structures A and E, respectively. The notation for the synthetic compounds is adopted from the main paper.



A B C D E F G H I J K L M N O P Q R S T

FIGURE 1: REPRESENTATION OF ALL 20 DIASTEREOISOMERS CONSIDERED

The computed nuclear shielding constants σ were Boltzmann-averaged over all conformers of a given diastereoisomer (*i.e.*, taking into account the thermal population of each conformer according to its Boltzmann weight derived from the B3LYP/6-31G** relative energies). Thereafter, the average chemical shifts δ of each diastereomer were computed by:

$$\delta = \frac{\sigma - \sigma_{ref}}{1 - \sigma / 10^6}$$

where σ_{ref} is the computed shielding constant of the reference compound, in this case TMS.

Following the procedure described by Smith and Goodman,[7] the computed average chemical shifts for all nuclei were scaled via linear regression with regard to the experimentally measured chemical shifts; this was done for each nucleus separately (^{13}C and ^{1}H). The difference of the scaled computed shift and the experimentally measured shift was taken as error. From these errors the DP4 probability was calculated by using Student's t distribution. The DP4 probability is a statistical measure of whether the computed and measured species (diastereomers) are the same despite the presence of errors, *i.e.* assuming that the errors are only due to inaccuracies of the NMR measurement and/or the computation but not due to considering different species (diastereomers). These probabilities were computed for each hydrogen and carbon atom independently. To obtain an overall probability for any given structure, the individual probabilities were multiplied either for all carbon atoms, all hydrogen atoms, or for both.

In Table 3, the calculated DP4 probabilities are listed for all 20 considered diastereomers with respect to the NMR data from the isolated Mandelalide A (iso, diastereomer C) and from two synthetic compounds (syn-**1**, diastereomer A; and syn-11-*epi*-**1**, diastereomer E). As shown in the main paper, isolated Mandelalide A corresponds to the synthetic compound syn-**6** with structure C, while syn-**1** and syn-11-*epi*-**1** have structures A and E, respectively.

Table 3: Computed DP4 probabilities.

	iso			syn-**1**			syn-11-*epi*-**1**		
	^{13}C	^{1}H	^{13}C/^{1}H	^{13}C	^{1}H	^{13}C/^{1}H	^{13}C	^{1}H	^{13}C/^{1}H
A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
B	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C	1.00	0.98	1.00	1.00	0.46	1.00	1.00	0.05	1.00
D	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
E	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
G	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
I	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
J	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
L	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
M	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Q	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
R	0.00	0.02	0.00	0.00	0.54	0.00	0.00	0.95	0.00
S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
T	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

The DP4 results are inconsistent. On the basis of the ^{13}C shifts they always assign diastereomer C (correct for iso, false for syn-**1** and syn-11-*epi*-**1**). The DP4 analysis of the ^{1}H shifts favors diastereomer C for iso (correct), diastereomer R for syn-11-*epi*-**1** (false), and almost equal probabilities for diastereomers C and R for syn-**1** (false). Considering both the ^{13}C and ^{1}H shifts again yields diastereomer C for all three compounds which is only correct for iso. While the DP4 results for iso might be encouraging at first sight, the failures for syn-**1** and syn-11-*epi*-**1** show that the DP4 analysis is unreliable for the systems studied presently.

Conformational analysis

Structures (24*R*)-**74** and (24*S*)-**74** were optimized at the B3LYP/6-31G* level. All structures were confirmed to be minima by performing a frequency analysis. To obtain Gibbs free energies, thermal and entropic corrections were computed at 298 K. In both cases several conformers were considered to find an optimum match with the measured NOE contacts. In the optimized structures NOE contacts were assumed to be present when the relevant through-space distances were less than 4 Å. To save CPU time the bulky TBS and TBDPS silyl groups were replaced by *tert*-butyl groups.

For (24*S*)-**74** this procedure yielded one conformer that perfectly matched all NOESY data (see Figure 2 in the main paper). In the case of (24*R*)-**74**, there are three low-lying conformers (within a range of 2 kcal/mol) that fit the NOESY data. Their structures and relative free energies are presented in Figure 2 and Table 4, respectively. None of these three conformers provides a perfect match; however, being close in energy they will most likely co-exist in solution, and together they account for all observed NOESY signals.

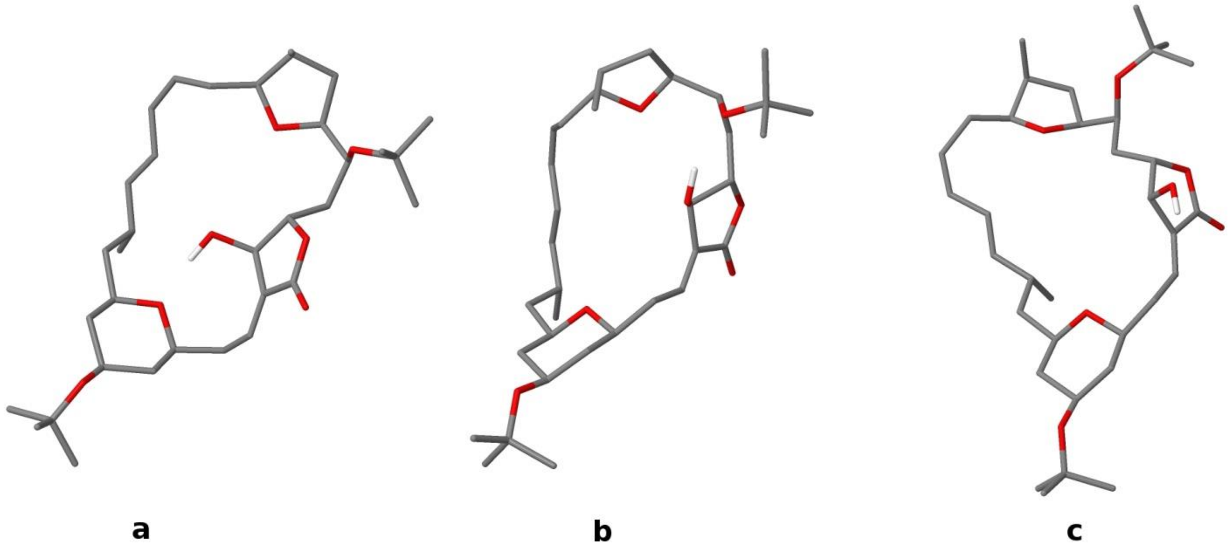


FIGURE 2: COMPUTED STRUCTURES OF THE LOWEST-LYING CONFORMERS OF (24R)-**74**.

TABLE 4: RELATIVE FREE ENERGIES OF THREE CONFORMERS OF (24R)-**74** OPTIMIZED AT THE B3LYP/6-31G* LEVEL.

conformer	**relative free energy / kcal/mol**
(24*R*)-**74**-a	0.0
(24*R*)-**74**-b	1.1
(24*R*)-**74**-c	2.0

References (Computational Section)

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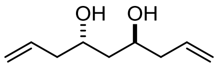
Total Synthesis of Mandelalide A

General. All reactions were carried out under Ar in flame-dried glassware unless H_2O was used as a solvent. The solvents were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Mg/anthracene), hexane, toluene (Na/K), MeOH (Mg, stored over MS 3Å), EtOH (MS 3Å), CH_2Cl_2 (CaH_2) EtOAc (P_2O_5, filter through dry Al_2O_3, store over 4Å MS); dioxane, DMF, MeCN , NEt_3 and pyridine were dried by an adsorbtion solvent purification system based on molecular sieves. Huenig base, DBU, DABCO (CaH_2), allyl acetate, TMS-morpholine were distilled prior to use. LiCl, K_2CO_3 were dried at 120 °C und high-vacuum overnight. Thin layer chromatography (TLC): Macherey-Nagel precoated plates (POLYGRAM® SIL/UV254); Flash chromatography: Merck silica gel 60 (40–63 µm) with predistilled or HPLC grade solvents. NMR: Spectra were recorded on Bruker DPX 300, AV 400, AV 500 or AVIII 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_C \equiv 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.24$ ppm; C_6D_6: $\delta_C \equiv 128.0$ ppm; residual C_6D_5H: $\delta_H \equiv 7.16$ ppm, pyr-d^5: $\delta_C \equiv 150.35$ ppm; residual C_5HD_4N in pyr-d^5: $\delta_H \equiv 8.74$ ppm, CD3OD: $\delta_C \equiv 49.15$ ppm; residual residual CD_2HOD in CD_3OD: $\delta_H \equiv 3.31$). IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ3000 (Bruker), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or Mat 95 (Finnigan). Optical rotations ($[\propto]_{20}^{D}$) were measured with a Perkin-Elmer Model 343 polarimeter. Unless stated otherwise, all commercially available compounds (Alfa Aesar, Aldrich, Fluka, Lancaster) were used as received.

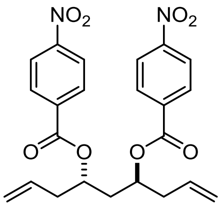
The spectra of all compounds and intermediates leading to **1** and 11-epi-**1** can be found in the Supporting Information of our original Communication.[2]

1 Synthesis of the Acid Fragment

(4*S*,6*S*)-Nona-1,8-diene-4,6-diol (10). According to the procedure from Krische et. al.,[3] a flame-dried Young tube was charged with $[Ir(cod)Cl]_2$ (974 mg, 1.45 mmol), (*S*)-Cl,MeO-BIPHEP (1.89 g, 2.90 mmol), Cs_2CO_3 (3.78 g, 11.6 mmol) and 4-chloro-3-nitrobenzoic acid (1.17 g, 5.80 mmol). 1,4-Dioxane (65 mL) and distilled allyl acetate (31.3 mL, 290 mmol) were added, the flask was sealed, and the suspension heated to 90 °C for 30 min and cooled back to room temperature. A solution of 1,3-propanediol (**9**) (2.10 mL, 29.0 mmol) in 1,4-dioxane (65 mL) was introduced, the flask sealed and stirring continued at 90 °C for 72 h. After cooling to ambient temperature, the mixture was filtered through a pad of Celite® (eluent: EtOAc) and the filtrate was concentrated. The brown residue was purified by flash chromatography (hexanes/EtOAc 3:1) to give the desired diol as a pale yellow oil (3.22 g, 71% yield, >99% ee, >29:1

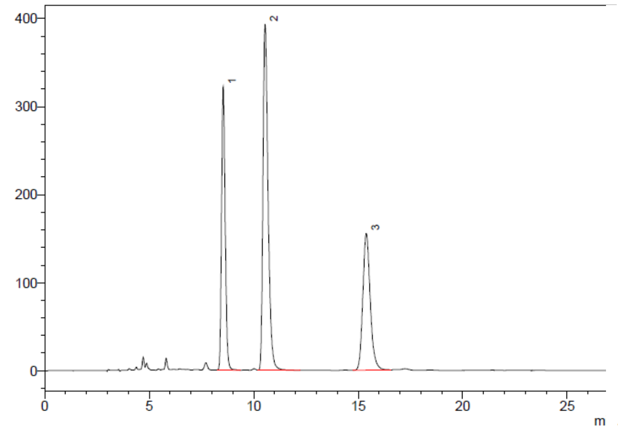


d.r.). $[\propto]_D^{20}$ = +24.5 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.85 – 5.72 (m, 2H), 5.13 – 5.09 (m, 2H), 5.09 – 5.07 (m, 2H), 4.01 – 3.91 (br s, 2H), 2.72 – 2.57 (br s, 2H), 2.27 – 2.21 (m, 4H), 1.60 (tr, J = 5.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.6, 118.0, 68.1, 42.0, 41.5 ppm. IR (film): $\tilde{\nu}$ = 3340, 3077, 2979, 2936, 1723, 1641, 1434, 1327, 1232, 1133, 1047, 994, 912, 871, 830 cm^{-1}. MS (EI) *m/z* (%) = 115 (10), 97 (74), 79 (38), 73 (19), 71 (89), 69 (52), 67 (49), 55 (19), 45 (39), 41 (100), 39 (29), 29 (13), 27 (28). HRMS (ESIpos): *m/z*: calcd for $C_9H_{16}O_2H$: 157.1228; found: 157.1229.



Bis-nitrobenzoate 10a. A Schlenck tube was charged with 4-nitrobenzoyl chloride (59 mg, 0.32 mmol), DMAP (1.6 mg, 0.013 mmol) and pyridine (52 µL, 0.64 mmol) before a solution of diol **10** (10. Mg, 0.064 mmol) in CH_2Cl_2 (0.32 mL) was added. The reaction mixture was stirred for 3 hours before the reaction was quenched by addition of sat. NH_4Cl solution (5 mL). It was extracted with EtOAc (3 x 5 ml) and the combined organic layers were dried over Na_2SO_4 and concentrated. The yellow residue was purified by flash chromatography (hexanes/EtOAc 5:1) to give an off-white solid (27.3 mg, 94%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 – 8.18 (m, 4H), 8.11 – 8.05 (m, 4H), 5.77 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 2H), 5.31 (dq, *J* = 7.3, 6.0 Hz, 2H), 5.17 – 5.05 (m, 4H), 2.49 (ddt, *J* = 7.2, 6.0, 1.2 Hz, 4H), 2.13 (dd, *J* = 7.1, 5.8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.1, 150.3, 135.6, 132.4, 130.6, 123.5, 118.9, 71.1, 39.0, 37.4 ppm; IR (film): $\tilde{\nu}$ = 1719, 1607, 1254, 1410, 1347, 1319, 1268, 1117, 1102, 1014, 993, 922, 872, 836, 783, 718 cm^{-1}; MS (EI) *m/z* (%): 413 (13), 246 (5), 151 (8), 150 (100), 120 (9), 104 (14), 92 (4), 76 (5). HRMS (ESIpos): *m/z*: calcd for $C_{23}H_{22}N_2O_8Na$: 477.1268, found 477.1266.

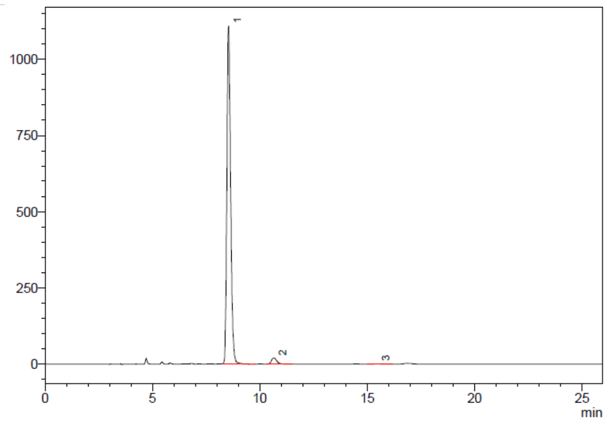
HPLC: 250 mm Chiralpak IB (Ø 4.6 mm), *n*-heptane/2-propanol 85:15, 1.0 mL/min, 298 K, 4.4 MPa: R_t = 8.54 min (major), 10.64 min (meso), 15.44 min (minor).



256nm,4nm

PDA Ch1 256nm

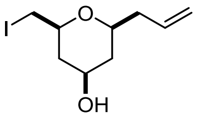
Peak #	Ret. Time	Area %	Name
1	8,54	27,09	1. Enantiomer
2	10,54	46,28	meso
3	15,38	26,63	2, Enantiomer
Total		100,00	



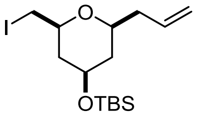
256nm,4nm

PDA Ch1 256nm

Peak #	Ret. Time	Area %	Name
1	8,54	97,18	1. Enantiomer
2	10,64	2,63	meso
3	15,44	0,19	2. Enantiomer
Total		100,00	

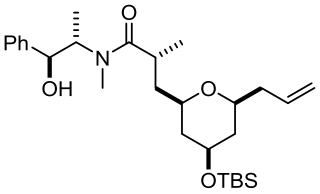


(2*S*,4*R*,6*S*)-2-Allyl-6-(iodomethyl)tetrahydro-2*H*-pyran-4-ol (11). $NaHCO_3$ (4.18 g, 49.8 mmol) was added at –40 °C to a solution of diol **10** (3.11 g, 19.9 mmol) in MeCN (360 mL) and the resulting suspension was vigorously stirred for 10 min. I_2 (15.2 g, 59.7 mmol) was carefully added in three portions and the resulting brown mixture stirred for 15 h at –40 °C. The mixture was poured into sat. $Na_2S_2O_3$-solution (200 mL) and the flask was rinsed with EtOAc (2 x 50 mL). After extraction of the aqueous phase with EtOAc (2 x 150 mL), the combined organic layers were dried over Na_2SO_4 and concentrated. The brown residue was purified by flash chromatography (hexanes/EtOAc 3:1) to yield a 5:1 mixture of diastereoisomers (based on ^{1}H-NMR integration, solvent: C_6D_6) as a colorless oil (4.55 g, 81%). This mixture was purified by flash chromatography (SiO_2 60 (15 x 40 µm), CH_2Cl_2/Et_2O 5:1) to give the desired all-*cis* diastereomer as a colorless oil (3.54 g, 63%), which solidified upon prolonged storage at –20 °C. $[\propto]_D^{20}$ = +25.7 (c = 0.37, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.84 (dddd, *J* = 16.8, 10.2, 7.5, 6.5 Hz, 1H), 5.11 – 5.02 (m, 2H), 3.80 (m, 1H), 3.36 (m, 2H), 3.19 (dd, *J* = 5.8, 3.8 Hz, 2H), 2.42 – 2.30 (m, 1H), 2.26 – 2.12 (m, 2H), 1.90 (ddt, *J* = 12.5, 4.3, 2.0 Hz, 1H), 1.63 (s, 1H), 1.14 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.3, 117.1, 75.4, 75.0, 67.8, 40.7, 40.2, 40.1, 8.7 ppm. IR (film): $\tilde{\nu}$ = 3346, 2942, 2917, 2850, 1641, 1446, 1430, 1414, 1368, 1325, 1270, 1185, 1136, 1080, 1038, 998, 916, 854 cm^{-1}. MS (EI) *m/z* (%) = 282 (0.3), 241 (100), 223 (23), 197 (38), 73 (14), 67 (17), 45 (15), 43 (10). HRMS (ESIpos): *m/z*: calcd for $C_9H_{15}O_2INa$: 305.0009; found: 305.0009.

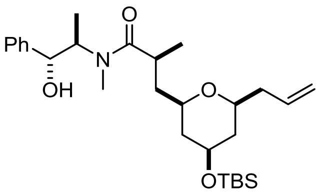


(((2*S*,4*R*,6*S*)-2-Allyl-6-(iodomethyl)tetrahydro-2*H*-pyran-4-yl)oxy)(*tert*-butyl)-dimethylsilane (12). A solution of alcohol **11** (3.10 g, 11.0 mmol) in CH_2Cl_2 (38 mL) was cooled to 0 °C before 2,6-lutidine (1.79 mL, 15.4 mmol) and TBSOTf (3.03 mL, 13.2 mmol) were added dropwise via syringe. The mixture was stirred for 1 h at 0 °C before the reaction was quenched with sat. NH_4Cl solution (40 mL). After phase separation, the aqueous layer was extracted with EtOAc (2 x 25 mL) and the combined organic layers were washed with brine (50 mL), dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 29:1) to yield the desired silyl ether as a colorless oil (4.18 g, 96%). $[\propto]_D^{20}$ = +15.8 (c = 1.21, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.90 – 5.77 (m, 1H), 5.12 – 4.97 (m, 2H), 3.74 (dddd, *J* = 10.8, 10.7, 4.8, 4.7 Hz, 1H), 3.35 – 3.24 (m, 2H), 3.16 (dd, *J* = 5.9, 1.5 Hz, 2H), 2.33 (dtt, *J* = 13.3, 6.6, 1.5 Hz, 1H), 2.18 (dddd, *J* = 14.4, 7.1, 5.7, 1.3 Hz, 1H), 2.00 (dddd, *J* = 12.4, 4.1, 1.9, 1.8 Hz, 1H), 1.79 – 1.68 (m, 1H), 1.23 – 1.11 (m, 2H), 0.85 (s, 9H), 0.03 (s, 6H) ppm. ^{1}H NMR (400 MHz, C_6D_6): δ = 5.92 (dddd, *J* = 16.7, 10.9, 8.3, 6.3 Hz, 1H), 5.09 – 4.98 (m, 2H), 3.54 (dddd, *J* = 10.8, 10.7, 4.9, 4.7 Hz, 1H), 3.07 (dddd, *J* = 11.5, 6.7, 5.1, 1.8 Hz, 1H), 2.93 (dddd, *J* = 11.2, 6.6, 4.6, 2.0 Hz, 1H), 2.85 (dd, *J* = 10.1, 6.7 Hz, 1H), 2.76 (dd, *J* = 10.1, 4.6 Hz, 1H), 2.29 (dtt, *J* = 13.2, 8.1, 6.6, 5.1 Hz, 1H), 2.08 (dddt, *J* = 14.0, 7.5, 5.2, 1.1 Hz, 1H), 1.74 (ddt, *J* = 12.3, 47, 2.0, 1H), 1.63 (dddd, *J* = 12.6, 4.6, 2.0, 2.0 Hz, 1H), 1.21 (ddd, *J* = 12.6, 11.1, 11.1 Hz, 1H), 1.11 (ddd, *J* = 12.2, 11.1, 11.0 Hz, 1H), 0.97 (s, 9H), 0.05 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.5, 116.8, 75.4, 75.1, 68.3, 41.1, 40.7, 40.2, 25.8, 18.0, 8.9, –4.6 ppm. IR (film): $\tilde{\nu}$ = 2950, 2928, 2856, 1642, 1471, 1462, 1383, 1251, 1126, 1087, 1068, 1005, 916, 833, 773, 669 cm^{-1}. MS (EI) *m/z* (%) = 340 (14), 339 (81), 271 (27), 269 (10), 172 (14), 171 (100), 141 (14), 129 (42), 101 (38), 79 (21), 75 (37), 73 (23), 67 (11), 59 (14), 43 (25), 41 (18). HRMS (ESIpos): *m/z*: calcd for $C_{15}H_{29}O_2SiINa$: 419.0872; found: 419.0874.

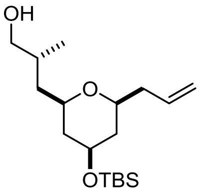
(*R*)-3-((2*R*,4*R*,6*S*)-6-Allyl-4-((*tert*-butyldimethylsilyl)oxy)tetrahydro-2*H*-pyran-2-yl)-*N*-((1*S*,2*S*)-1-Hydroxy-1-phenylpropan-2-yl)-*N*,2-dimethylpropanamide (14). A flame-dried 3-necked round-bottom flask equipped with a stirbar, a reflux condenser and a dropping funnel was charged with dry LiCl (5.13 g, 121 mmol), diisopropylamine (6.24 mL, 44.4 mmol) and THF (75 mL). After cooling to –78 °C, a solution of *n*-BuLi (1.50 M in hexanes, 29.0 mL, 43.5 mmol) was added dropwise over 20 min and the mixture was stirred for 10 min before it was warmed to 0 °C. After 10 min, the mixture was cooled to –78 °C and a solution of (1*S*,2*S*)-*N*-(2-hydroxy-1-methyl-2-phenylethyl)-*N*-methylpropionic amide (**13**) (4.69 g, 21.2 mmol) in THF (115 mL) was added over 45 min via dropping funnel. The resulting yellow suspension was stirred for 1 h at –78 °C, for 30 min at 0 °C and for 20 min at RT before it was re-cooled to 0 °C. A solution of alkyl iodide **12** (4.01 g, 10.1 mmol) in THF (6 mL + 2 x 2 mL rinse) was then added dropwise over 5 min via syringe. The mixture was warmed to 45 °C and stirred at this temperature for 48 h. After cooling to RT, the reaction was quenched with sat. NH_4Cl solution (300 mL) and the aqueous layer was extracted with EtOAc (4 x 200 mL). The combined extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 2:1) to give the alkylated compound as a white foam that collapsed to a colorless syrup upon storage (3.83 g, 76%).[∝]$_{D}^{20}$ = +50.7 (c = 0.96, CH_2Cl_2). ^{1}H and ^{13}C NMR spectra were complex and broadened due to the presence of amide bond rotamers. IR (film): $\tilde{\nu}$ = 3387, 2933, 2930, 2856, 1619, 1462, 1409, 1374, 1252, 1115, 1072, 913, 835, 774, 700, 673 cm^{-1}. MS (EI) *m/z* (%) = 433 (31), 432 (97), 383 (16), 382 (31), 325 (19), 258 (20), 257 (100), 216 (31), 193 (16), 171 (10), 148 (21), 129 (10), 119 (11), 101 (12), 99 (19), 79 (11), 75 (22), 73 (25), 58 (39). HRMS (ESIpos): *m/z*: calcd for $C_{28}H_{47}NO_4SiNa$: 512.3167; found: 512.3166.



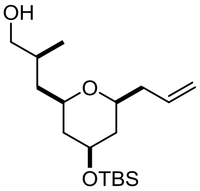
(*S*)-3-((2*R*,4*R*,6*S*)-6-Allyl-4-((*tert*-butyldimethylsilyl)oxy)tetrahydro-2*H*-pyran-2-yl)-*N*-((1*R*,2*R*)-1-hydroxy-1-phenylpropan-2-yl)-*N*,2-dimethylpropanamide (S14). Prepared analogously from (1*R*,2*R*)-*N*-(2-hydroxy-1-methyl-2-phenylethyl)-*N*-methylpropionic amide (*ent*-**13**) and alkyl iodide **12** (3.08 g, 7.77 mmol) as a sticky syrup (3.20 g, 84%). [∝]$_{20}^{D}$ = –24.3 (c = 0.77, CH_2Cl_2). ^{1}H and ^{13}C NMR spectra were complex and partially broadened due to the presence of amide bond rotamers. IR (film): $\tilde{\nu}$ = 3376, 2934, 2930, 2856, 1619, 1472, 1463, 1374, 1328, 1306,



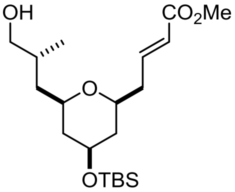
1254, 1120, 1073, 1006, 915, 857, 836, 775, 702, 671 cm^{-1}. MS (EI) *m/z* (%) = 474 (5), 433 (28), 432 (89), 383 (15), 382 (26), 325 (22), 258 (20), 257 (100), 222 (17), 193 (13), 148 (18), 119 (10), 99 (19), 75 (15), 73 (17), 58 (23). HRMS (ESIpos): *m/z*: calcd for $C_{28}H_{47}NO_4SiNa$: 512.3167; found: 512.3169.



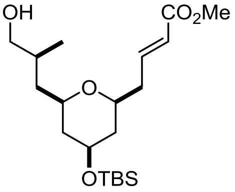
(*R*)-3-((2*R*,4*R*,6*S*)-6-Allyl-4-((*tert*-butyldimethylsilyl)oxy)tetrahydro-2*H*-pyran-2-yl)-2-methylpropan-1-ol (14a). A solution of *n*-BuLi (1.60 M in hexanes, 23.1 mL, 37.0 mmol) was added over 15 min at −78 °C to a solution of diisopropylamine (5.57 mL, 39.6 mmol) in THF (34 mL) and the resulting mixture was stirred at this temperature for 15 min and for 45 min at 0 °C. Solid $NH_3 \cdot BH_3$ (90%, 1.31 g, 38.1 mmol) was then added in one portion and the resulting mixture stirred for 40 min at 0 °C and for 45 min at ambient temperature. After cooling to 0 °C, a solution of amide **14** (3.80 g, 7.62 mmol) in THF (34 mL) was slowly added over 10 min. After stirring for 3 h at 0 °C, the mixture was warmed to ambient temperature and stirring continued for 1 h before the reaction was quenched with sat. NH_4Cl solution (200 mL). The mixture was vigorously stirred for 45 min before the phases were separated, the aqueous phase was extracted with EtOAc (3 x 120 mL) and the combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 5:1) to give the desired alcohol as a colorless oil (2.42 g, 96%). $[\alpha]_D^{20}$ = +17.8 (c = 0.83, CH_2Cl_2). ^{1}H NMR (400 MHz, C_6D_6): δ = 5.85 (dddd, *J* = 16.0, 9.2, 6.6, 6.6 Hz, 1H), 5.07 – 5.00 (m, 2H), 3.63 (dddd, *J* = 10.7, 10.4, 5.1, 5.1 Hz, 1H), 3.46 (ddd, *J* = 10.5, 5.2, 5.1 Hz, 1H), 3.36 (ddd, *J* = 10.4, 5.1, 5.1 Hz, 1H), 3.19 – 3.04 (m, 2H), 2.26 (dddt, J = 14.1, 7.0, 7.0, 1.2 Hz, 1H), 2.22 – 2.15 (br t, 1H), 2.12 – 2.04 (m, 1H), 1.78 (dq, *J* = 12.4, 6.2 Hz, 1H), 1.75 – 1.61 (m, 2H), 1.55 (ddd, *J* = 14.4, 9.6, 7.3 Hz, 1H), 1.34 – 1.21 (m, 2H), 1.09 (ddd, *J* = 14.4, 6.4, 2.3 Hz, 1H), 1.00 (s, 9H), 0.87 (d, *J* = 6.8 Hz, 3H), 0.09 (s, 3H), 0.08 (s, 3H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 134.9, 117.2, 75.3, 74.8, 69.1, 68.2, 43.0, 41.4, 41.2, 40.8, 34.5, 26.0, 18.2, 18.0, –4.3 ppm. IR (film): $\tilde{\nu}$ = 3395, 2926, 2929, 2856, 1643, 1472, 1462, 1375, 1253, 1152, 1123, 1070, 975, 914, 835, 774, 671 cm^{-1}. MS (EI) *m/z* (%) = 271 (33), 201 (20), 179 (37); 171 (47), 161 (16), 159 (47), 145 (46), 131 (12), 129 (69), 127 (12), 125 (15), 119 (15), 111 (12), 109 (65), 107 (12), 105 (22), 101 (44), 93 (18), 85 (93), 81 (28), 79 (26), 75 (100), 73 (49), 67 (43), 59 (22), 57 (14), 55 (24), 43 (17), 41 (32). HRMS (ESIpos): *m/z*: calcd for $C_{18}H_{36}O_3SiNa$: 351.2326; found: 351.2326.



(*S*)-3-((2*R*,4*R*,6*S*)-6-Allyl-4-((*tert*-butyldimethylsilyl)oxy)tetrahydro-2*H*-pyran-2-yl)-2-methylpropan-1-ol (11-*epi*-**14a).** Prepared analogously from amide **S14** (3.20 g, 6.53 mmol) as a colorless oil (1.86 g, 87%). $[\alpha]_D^{20}$ = +1.8 (c = 1.03, CH_2Cl_2). ^{1}H NMR (400 MHz, C_6D_6): δ = 5.85 (dddd, *J* = 17.7, 9.6, 7.0, 7.0 Hz, 1H), 5.08 – 4.99 (m, 2H), 3.65 (dddd, *J* = 10.7, 10.7, 5.0, 4.8 Hz, 1H), 3.50 – 3.40 (m, 1H), 3.36 (dd, *J* = 10.7, 6.6 Hz, 1H), 3.28 (dddd, *J* = 11.5, 8.3, 3.5, 1.9 Hz, 1H), 3.11 (dddd, *J* = 11.4, 7.1, 5.3, 1.9 Hz, 1H), 2.25 (dtt, *J* = 14.0, 7.0, 1.4 Hz, 1H), 2.08 (dddd, *J* = 14.1, 8.6, 4.0, 2.6 Hz, 1H), 2.01 (br s, 1H), 1.86 (qt, *J* = 6.8, 5.3 Hz, 1H), 1.77 – 1.64 (m, 2H), 1.52 (ddd, *J* = 13.9, 8.3, 5.4 Hz, 1H), 1.43 – 1.20 (m, 3H), 0.99 (s, 9H), 0.86 (d, *J* = 6.9 Hz, 3H), 0.08 (s, 6H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 135.0, 117.0, 75.3, 73.5, 69.2, 67.5, 42.3, 41.6, 40.8, 40.0, 32.9, 26.0, 18.2, 17.6, –4.3 ppm. IR (film): $\tilde{\nu}$ = 3394, 2950, 2929, 2857, 1375, 1254, 1151, 1123, 1072, 1005, 914, 836, 775, 672 cm^{-1}. MS (EI) *m/z* (%) = 271 (33), 201 (20), 179 (37); 171 (47), 161 (16), 159 (47), 145 (46), 131 (12), 129 (69), 127 (12), 125 (15), 119 (15), 111 (12), 109 (65), 107 (12), 105 (22), 101 (44), 95 (41), 93 (18), 85 (93), 81 (28), 79 (26), 75 (100), 73 (49), 67 (43), 59 (22), 57 (14), 55 (24), 43 (17), 41 (32). HRMS (ESIpos): *m/z*: calcd for $C_{18}H_{36}O_3SiNa$: 351.2326; found: 351.2327.

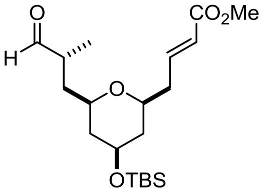


Methyl (*E*)-4-((2*S*,4*R*,6*R*)-4-((*tert*-butyldimethylsilyl)oxy)-6-((*R*)-3-hydroxy-2-methylpropyl)-tetrahydro-2*H*-pyran-2-yl)but-2-enoate (14b). Hoveyda-Grubbs 2nd gen. catalyst **20** (137 mg, 0.219 mmol) was added to a solution of the terminal alkene **14a** (2.40 g, 7.30 mmol) and methylacrylate (3.27 mmol, 36.5 mmol) in CH_2Cl_2 (70 mL). The mixture was stirred for 7.5 h at ambient temperature allowing the generated ethene to evaporate. After concentration, the residue (*E/Z* = 12:1 based on ^{1}H NMR integration of a crude sample) was purified by flash chromatography (hexanes/EtOAc 5:1 to 4:1) to give the title compound as a pale brown oil (2.33 g, single isomer, 83%). $[\alpha]_D^{20}$ = +9.0 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, C_6D_6): δ = 7.09 (dt, *J* = 15.6, 7.2 Hz, 1H), 5.90 (dt, *J* = 15.6, 1.5 Hz, 1H), 3.57 (dddd, *J* = 10.8, 10.6, 4.9, 4.8 Hz, 1H), 3.40 (s, 3H) 3.39 – 3.29 (m, 2H), 3.09 (dddd, *J* = 11.7, 9.7, 2.3, 2.3 Hz, 1H), 2.96 (dddd, *J* = 11.7, 7.0, 4.7, 1.9 Hz, 1H), 2.09 (dddd, *J* = 14.8, 7.4, 7.3, 1.5 Hz, 1H), 1.94 (dddd, *J* = 8.6, 8.6, 5.1, 2.0 Hz, 1H), 1.81 – 1.70 (m, 2H), 1.67 – 1.56 (m, 2H), 1.51 (ddd, *J* = 14.4, 9.6, 6.9 Hz, 1H), 1.29 – 1.12 (m, 2H), 1.07 – 1.01 (m, 1H), 0.99 (s, 9H), 0.87 (d, *J* = 6.8 Hz, 3H), 0.08 (s, 3H), 0.07 (s, 3H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 166.4, 145.1, 123.5, 74.6, 74.2, 68.9, 68.1, 51.0, 42.7, 41.5, 40.7, 38.7, 34.0, 26.0, 18.2, 17.7, –4.3, –4.3 ppm. IR (film): $\tilde{\nu}$ = 3436, 2933, 2929, 2856, 1725, 1659, 1462, 1436, 1376, 1324, 1255, 1175, 1122, 1069, 985, 855, 836, 775, 669 cm^{-1}. MS (EI) *m/z* (%) = 329 (14), 237 (54), 229 (17), 203 (11), 159 (26), 137 (11), 131 (12), 129 (20), 109 (30), 101 (23), 97 (20), 93 (21), 89 (11), 85 (100), 81 (15), 75 (46), 73 (32), 67 (18), 59 (13), 55 (12), 41 (15). HRMS (ESIpos): *m/z*: calcd for $C_{20}H_{38}O_5SiNa$: 409.2381; found: 409.2381.

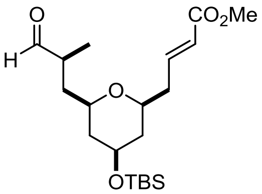


Methyl (*E*)-4-((2*S*,4*R*,6*R*)-4-((*tert*-butyldimethylsilyl)oxy)-6-((*S*)-3-hydroxy-2-methylpropyl)-tetrahydro-2*H*-pyran-2-yl)but-2-enoate (11-*epi*-**14b).** Prepared analogously from terminal alkene 11-*epi*-**14a** (1.82 g, 5.63 mmol) as a colorless oil (1.99 g, 91%). $[\propto]_D^{20}$ = –0.4 (c = 1.09, CH_2Cl_2). ^{1}H NMR (400 MHz, C_6D_6): δ = 7.09 (dt, *J* = 15.7, 7.1 Hz, 1H), 5.90 (dt, *J* = 15.7, 1.5 Hz, 1H), 3.59 (tt, *J* = 10.5, 4.7 Hz, 1H), 3.40 (m, 5H), 3.21 (dddd, *J* = 11.6, 8.6, 3.4, 1.8 Hz, 1H), 2.99 (dddd, *J* = 11.7, 7.4, 4.4, 2.1 Hz, 1H), 2.16 – 2.04 (m, 1H), 2.04 – 1.97 (br s, 1H), 1.93 (dddd, *J* = 14.9, 7.1, 4.5, 1.5 Hz, 1H), 1.84 (tdd, *J* = 12.8, 7.3, 1.3 Hz, 1H), 1.67 (ddt, *J* = 12.6, 4.8, 1.9 Hz, 1H), 1.59 (ddt, *J* = 12.4, 4.8, 1.9 Hz, 1H), 1.43 (ddd, J = 14.1, 8.3, 5.7 Hz, 1H), 1.35 (ddd, J = 14.2, 7.2, 3.9 Hz, 1H), 1.26 (ddd, J = 11.8, 11.6, 11.1 Hz, 1H), 1.19 (ddd, J = 11.7, 11.6, 11.2 Hz, 1H), 0.98 (s, 9H), 0.87 (d, J = 6.9 Hz, 3H), 0.06 (s, 6H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 166.6, 145.5, 123.3, 74.2, 73.8, 69.0, 67.5, 51.0, 42.2, 41.7, 40.0, 38.7, 32.9, 26.0, 18.2, 17.7, –4.3, –4.3 ppm. IR (film): $\tilde{\nu}$ = 3436, 2951, 2930, 2857, 1726, 1660, 1463, 1436, 1376, 1330, 1256, 1175, 1154, 1122, 1072, 987, 854, 837, 776 cm^{-1}. MS (EI) *m/z* (%) = 329 (14), 237 (54), 229 (17), 203 (11), 159 (26), 137 (11), 131 (12), 129 (20), 109 (30), 101 (23), 97 (20), 93 (21), 89 (11), 85 (100), 81 (15), 75 (46), 73 (32), 67 (18), 59 (13), 55 (12), 41 (15). HRMS (ESIpos): *m/z*: calcd for $C_{20}H_{38}O_5SiNa$: 409.2381; found: 409.2382.

Methyl (*E*)-4-((2*S*,4*R*,6*R*)-4-((*tert*-butyldimethylsilyl)oxy)-6-((*R*)-2-methyl-3-oxopropyl)tetrahydro-2*H*-pyran-2-yl)but-2-enoate (15). A solution of Dess-Martin periodinane (524 mg, 1.24 mmol) in CH_2Cl_2 (2 mL) was cooled to 0 °C before a solution of alcohol **14b** (398 mg, 1.03 mmol) in CH_2Cl_2 (2 mL + 1 mL rinse) was added dropwise via syringe. After 5 min, the mixture was allowed to warm to ambient temperature and stirring was continued for 3 h. The reaction was quenched by addition of aq. sat. $Na_2S_2O_3$ and $NaHCO_3$ solution (1:1, 15 mL) and the aqueous phase was extracted with CH_2Cl_2 (3x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated, and the residue was purified by flash chromatography (hexanes/EtOAc 12:1 to 9:1) to yield the desired aldehyde as a colorless oil (305 mg, 77%). $[\propto]_D^{20}$ = +3.4 (c = 0.81, hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.55 (d, J = 2.3 Hz, 1H), 6.91 (dd, J = 15.7, 7.3, 7.2 Hz, 1H), 5.83 (ddd, J = 15.7, 1.5, 1.5 Hz, 1H), 3.77 – 3.68 (m, 1H), 3.71 (s, 3H), 3.39 – 3.25 (m, 2H), 2.52 (dqd, J = 7.1, 7.0, 2.4 Hz, 1H), 2.43 – 2.24 (m, 2H), 1.93 (ddd, J = 14.3, 9.9, 7.0 Hz, 1H), 1.80 – 1.71 (m, 2H), 1.38 (ddd, J = 14.3, 7.1, 3.0 Hz, 1H), 1.26 – 1.14 (m, 2H), 1.06 (d, J = 7.0 Hz, 3H), 0.85 (s, 9H), 0.03 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.8, 166.8, 145.2, 123.0, 74.2, 73.4, 68.4, 51.5, 43.8, 41.8, 41.1, 38.6, 37.3, 25.8, 18.1, 13.8, –4.5 ppm. MS (EI) *m/z* (%) = 328 (15), 327 (60), 309 (27), 235 (20), 229 (49), 227 (16), 203 (51), 201 (22), 199 (22), 185 (15), 183 (36), 175 (16), 157 (33), 145 (30), 129 (33), 109 (15), 107 (23), 101 (48), 97 (29), 93 (29), 89 (22), 85 (31), 83 (25), 81 (36), 79 (15), 75 (100), 73 (54), 59 (27), 41 (25). HRMS (ESIpos): *m/z*: calcd for $C_{20}H_{36}O_5SiNa$: 407.2228; found: 407.2224.

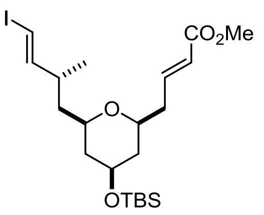


Methyl (*E*)-4-((2*S*,4*R*,6*R*)-4-((*tert*-butyldimethylsilyl)oxy)-6-((*S*)-2-methyl-3-oxopropyl)tetrahydro-2*H*-pyran-2-yl)but-2-enoate (11-*epi*-15). *A slightly modified procedure had to be used:* A solution of Dess-Martin periodinane (783 mg, 1.85 mmol) in CH_2Cl_2 (2 mL) was cooled to 0 °C and $NaHCO_3$ (358 mg, 4.27 mmol) was added as a solid, followed by addition of a solution of alcohol 11-*epi*-**14b** (550 mg, 1.42 mmol) in CH_2Cl_2 (2 mL + 1 mL rinse). After 5 min, the mixture was allowed to reach ambient temperature and stirring was continued for 3 h. The mixture was filtered and the filtrate loaded onto SiO_2. Purification by flash chromatography (hexanes/EtOAc 12:1 to 9:1) gave the desired



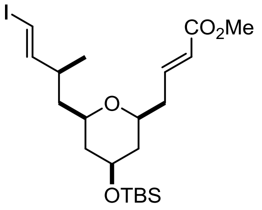
aldehyde as a colorless oil (414 mg, 76%). $[\propto]_D^{20}$ = +17.7 (c = 1.105, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.59 (d, *J* = 1.4 Hz, 1H), 6.90 (dt, *J* = 15.7, 7.2 Hz, 1H), 5.82 (dt, *J* = 15.7, 1.5 Hz, 1H), 3.71 (m, 4H), 3.39 – 3.26 (m, 2H), 2.61 – 2.48 (m, 1H), 2.41 – 2.23 (m, 2H), 1.79 (ddd, *J* = 14.4, 8.1, 3.4 Hz, 1H), 1.77 – 1.70 (m, 2H), 1.65 (ddd, *J* = 14.0, 9.2, 4.4 Hz, 1H), 1.24 – 1.12 (m, 2H), 1.08 (d, *J* = 7.2 Hz, 3H), 0.84 (s, 9H), 0.02 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.5, 166.8, 145.2, 122.9, 74.1, 72.8, 68.4, 51.4, 42.8, 41.6, 41.1, 38.6, 36.9, 25.8, 18.0, 13.8, –4.5, –4.5 ppm. IR (film): $\tilde{\nu}$ = 2951, 2939, 2856, 1725, 1660, 1462, 1436, 1376, 1330, 1255, 1175, 1122, 1072, 853, 776 cm^{-1}. MS (EI) *m/z* (%) = 328 (14), 327 (60), 309 (29), 235 (20), 229 (49), 227 (16), 203 (51), 201 (22), 199 (22), 185 (15), 183 (36), 175 (16), 157 (33), 155 (13), 153 (15), 151 (17), 145 (30), 143 (10), 129 (33), 109 (15), 107 (23), 101 (48), 97 (29), 93 (29), 89 (22), 85 (31), 83 (25), 81 (36), 79 (15), 75 (100), 73 (54), 67 (17), 59 (27), 43 (17), 41 (25). HRMS (ESIpos): *m/z*: calcd for $C_{20}H_{36}O_5SiNa$: 407.2224; found: 407.2224.

Methyl (*E*)-4-((2*S*,4*R*,6*R*)-4-((*tert*-butyldimethylsilyl)oxy)-6-((*R*,*E*)-4-iodo-2-methylbut-3-en-1-yl)-tetrahydro-2*H*-pyran-2-yl)but-2-enoate (16). A flame-dried Schlenk tube was charged with

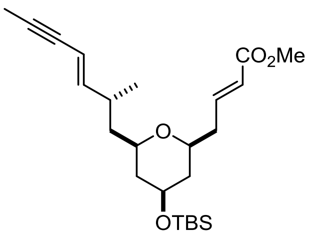


$CrCl_2 \cdot 1.7$ THF (1.21 g, 4.94 mmol) which was suspended in degassed THF (11.5 mL). The suspension was cooled to –8 °C, before solid CHI_3 (642 mg, 1.63 mmol) was added under vigorous stirring, causing a color change from green-grey to brown. After 5 min, a solution of aldehyde **15** (190 mg, 0.494 mmol) in degassed THF (1 mL + 2 x 0.5 mL rinse) was added dropwise. After 3 h at –8 °C, the reaction was quenched by addition of aq. serine/$KHCO_3$ solution (1 M, pH = 8, 25 mL) and hexanes/EtOAc (1:1, 40 mL). The mixture was allowed to warm to room temperature and was vigorously stirred for 30 min. After phase separation, the deep violet aqueous phase was extracted with hexanes/EtOAc (1:1, 3 x 40 mL) and the combined extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc, 100:0 (until all CHI_3 was removed) to 99:1 to 49:1 to 39:1 to 29:1) to yield the desired (*E*)-vinyl iodide as a colorless oil (181 mg, 72%) along with the isomeric (*Z*)-vinyl-iodide (18.8 mg, 8%). $[\propto]_D^{20}$ = –29.6 (c = 1.20, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.94 (dt, *J* = 15.7, 7.2 Hz, 1H), 6.43 (dd, *J* = 14.4, 8.0 Hz, 1H), 5.95 (dd, *J* = 14.4, 1.0 Hz, 1H), 5.86 (dt, *J* = 15.7, 1.5 Hz, 1H), 3.76 – 3.66 (m, 1H), 3.71 (s, 3H), 3.41 – 3.30 (m, 1H), 3.25 (dddd, *J* = 10.0, 8.4, 4.8, 1.8 Hz, 1H), 2.47 – 2.25 (m, 3H), 1.75 (m, 2H), 1.62 (ddd, *J* = 13.8, 8.4, 6.5 Hz, 1H), 1.28 (ddd, *J* = 13.9, 7.0, 4.9 Hz, 1H), 1.25 – 1.09 (m, 2H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.86 (s, 9H), 0.03 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 152.0, 145.4, 122.8, 74.1, 73.3, 73.2, 68.6, 51.4, 41.9, 41.6, 41.3, 38.7, 37.1, 25.8, 19.1, 18.1, –4.5 ppm. IR (film): $\tilde{\nu}$ = 2949, 2929, 2856, 1725, 1660, 1435, 1376, 1329, 1269, 1255, 1174, 1069, 950, 836, 775, 670 cm^{-1}. MS (EI) *m/z* (%) = 452 (23), 451 (100), 229 (47), 197 (11), 181 (37), 169 (10), 157 (11), 131 (34), 129 (31), 101 (19), 93 (12), 89 (13), 75 (28), 73 (21), 59 (11). HRMS (ESIpos): *m/z*: calcd for $C_{21}H_{37}O_4SiINa$: 531.1398; found: 531.1402.

Methyl (*E*)-4-((2*S*,4*R*,6*R*)-4-((*tert*-butyldimethylsilyl)oxy)-6-((*S*,*E*)-4-iodo-2-methylbut-3-en-1-yl)-tetrahydro-2*H*-pyran-2-yl)but-2-enoate (11-*epi*-**16).** Prepared analogously from aldehyde 11-*epi*-**15** (404 mg, 1.05 mmol) as a mixture of olefin isomers (384 mg, 72%, *E*/*Z* = 10:1). An aliquot (340 mg, 0.669 mmol) was purified by preparative HPLC (2 runs with 170 mg each, Nucleodur C18 HTec 10 µm, length: 250 mm, Ø: 40 mm, MeOH/H_2O =93:7, 75 mL/min) to give the desired (*E*)-isomer as a colorless syrup (286 mg, 84%). $[\propto]_D^{20}$ = +92.8 (c = 1. 01, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 6.95 (dt, *J* = 15.7, 7.1 Hz, 1H), 6.27 (dd, *J* = 14.3, 9.2 Hz, 1H), 6.00 (dd, *J* = 14.3, 0.7 Hz, 1H), 5.86 (dt, *J* = 15.7, 1.5 Hz, 1H), 3.73 (m, 4H), 3.30 (dddd, *J* = 11.5, 8.2, 4.3, 1.9 Hz, 1H), 3.18 (dddd, *J* = 12.0, 10.4, 3.1, 1.5 Hz, 1H), 2.49 (tdd, *J* = 9.2, 6.8, 3.9 Hz, 1H), 2.38 (dddd, *J* = 15.3, 8.4, 7.1, 1.5 Hz, 1H), 2.29 (dddd, *J* = 9.1, 7.1, 3.6, 1.4 Hz, 1H), 1.80 – 1.64 (m, 2H), 1.50 (ddd, *J* = 14.2, 10.2, 4.2 Hz, 1H), 1.29 – 1.11 (m, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.85 (s, 9H), 0.03 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 151.2, 145.9, 122.6, 74.4, 74.3, 73.2, 68.5, 51.5, 42.4, 41.9, 41.5, 38.6, 37.4, 25.8, 20.6, 18.1, –4.5, –4.5 ppm. IR (film): $\tilde{\nu}$ = 2950, 2928, 2855, 1724, 1660, 1435, 1375, 1253, 1219, 1175, 1156, 1126, 1067, 987, 955, 869, 834, 774, 669 cm^{-1}. MS (EI) *m/z* (%) = 452 (24), 451 (100), 229 (41), 181 (22), 131 (26), 129 (20), 101 (11), 75 (14), 73 (10). HRMS (ESIpos): *m/z*: calcd for $C_{21}H_{37}O_4SiINa$: 531.1398; found: 531.1393.

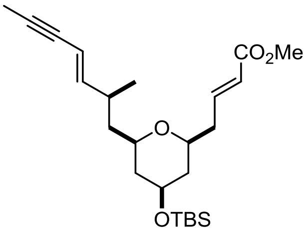


Methyl (*E*)-4-((2*S*,4*R*,6*R*)-4-((*tert*-butyldimethylsilyl)oxy)-6-((*R*,*E*)-2-methylhept-3-en-5-yn-1-yl)-tetrahydro-2*H*-pyran-2-yl)but-2-enoate ((*E*)-17). A flame-dried two-necked round-bottom flask equipped with a reflux condenser was charged with 1-propynylsodium (42.1 mg, 0.677 mmol), which was suspended in degassed THF (4 mL). Trimethyl borate (76.9 µL, 0.677 mmol) was added dropwise via syringe at rt. After stirring for 20 min, [Pd(dppf)Cl_2]·CH_2Cl_2 (42.5 mg, 0.0521 mmol) was added, causing the reaction mixture to turn dark red. Next, a solution of (*E*)-vinyl iodide **16** (265 mg, 0.521 mmol) in degassed THF (3 mL + 1 mL rinse) was added and the mixture stirred at 65 °C. After 2 h, the pale orange mixture was allowed to cool to ambient temperature, the reaction was quenched with sat. NH_4Cl/H_2O (1:1 v/v, 15 mL) and the aqueous phase was extracted with EtOAc (3x 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography (hexanes/EtOAc 49:1 to 39:1 to 29:1) to give the title compound as a pale yellow oil (177 mg, 81%). $[\propto]_D^{20}$= –30.0 (c = 0.92, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 6.94 (dt, *J* = 15.7, 7.2 Hz, 1H), 5.93 (ddd, *J* = 15.9, 7.9, 0.8 Hz, 1H), 5.85 (dt, *J* = 15.7, 1.5 Hz, 1H), 5.37 (dqd, *J* = 15.9, 2.2, 1.1 Hz, 1H), 3.76 – 3.66 (m, 1H), 3.71 (s, 3H), 3.39 – 3.30 (m, 1H), 3.25 (dddd, *J* = 11.2, 7.4, 5.5, 1.7 Hz, 1H), 2.47 – 2.25 (m, 3H), 1.90 (d, *J* = 2.2 Hz, 3H), 1.75 (dt, *J* = 4.8, 1.5 Hz, 1H), 1.75 (dt, *J* = 4.8, 1.5 Hz, 1H), 1.61 (dddd, *J* = 7.1, 7.1, 7.0, 6.9 Hz, 1H), 1.28 (ddd, *J* = 13.6, 7.7, 5.7 Hz, 1H), 1.24 – 1.09 (m, 2H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.86 (s, 9H), 0.03 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 148.5, 145.5,

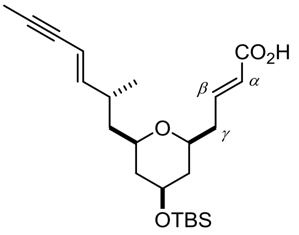


122.8, 108.2, 84.4, 78.3, 74.1, 73.2, 68.6, 51.4, 42.3, 41.5, 41.3, 38.7, 33.4, 25.8, 19.6, 18.1, 4.2, –4.5, –4.5 ppm. IR (film): $\tilde{\nu}$ = 2951, 2928, 2856, 1725, 1660, 1435, 1376, 1328, 1255, 1174, 1068, 985, 962, 836, 775, 670 cm^{-1}. MS (EI) *m/z* (%) = 420 (19), 364 (11), 363 (40), 313 (13), 288 (11), 229 (53), 189 (17), 181 (37), 171 (12), 169 (13), 159 (16), 157 (14), 145 (32), 131 (24), 129 (37), 123 (10), 121 (10), 120 (13), 119 (37), 108 (13), 105 (23), 101 (33), 97 (18), 93 (100), 91 (45), 89 (21), 81 (19), 79 (13), 77 (41), 75(48), 73 (46), 59 (17), 41 (14). HRMS (ESIpos): *m/z*: calcd for $C_{24}H_{40}O_4SiNa$: 443.2588; found: 443.2592.

Methyl (*E*)-4-((2*S*,4*R*,6*R*)-4-((*tert*-butyldimethylsilyl)oxy)-6-((*S*,*E*)-2-methylhept-3-en-5-yn-1-yl)-tetrahydro-2*H*-pyran-2-yl)but-2-enoate (11-*epi*-(*E*)-**17**)**. Prepared analogously from vinyl iodide 11-*epi*-**16** (185 mg, 1.05 mmol) as a pale yellow oil (117 mg, 76%). $[\propto]_D^{20}$ = +93.8 (c = 0.99, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.96 (dt, *J* = 15.7, 7.1 Hz, 1H), 5.86 (dt, *J* = 15.8, 1.5 Hz, 1H), 5.79 (ddd, *J* = 15.8, 9.0, 0.8 Hz, 1H), 5.41 (dqd, *J* = 15.9, 2.3, 0.8 Hz, 1H), 3.72 (m, 4H), 3.38 – 3.25 (m, 1H), 3.20 (dddd, *J* = 11.8, 10.2, 3.0, 1.9 Hz, 1H), 2.53 – 2.34 (m, 2H), 2.30 (tdd, *J* = 7.7, 4.6, 1.6 Hz, 1H), 1.91 (d, *J* = 2.3 Hz, 3H), 1.79 – 1.70 (m, 1H), 1.71 – 1.63 (m, 1H), 1.53 (ddd, *J* = 14.0, 10.1, 4.0 Hz, 1H), 1.28 – 1.10 (m, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.85 (s, 9H), 0.02 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 148.0, 145.8, 122.7, 109.2, 84.2, 78.4, 74.1, 73.3, 68.6, 51.4, 42.9, 42.0, 41.4, 38.6, 33.9, 25.8, 21.1, 18.1, 4.2, –4.5, –4.6 ppm. IR (film): $\tilde{\nu}$ = 2951, 2929, 2856, 1727, 1660, 1435, 1375, 1329, 1257, 1218, 1155, 1118, 1072, 962, 852, 837, 776 cm^{-1}. MS (EI) *m/z* (%) = 420 (19), 364 (11), 363 (40), 313 (13), 288 (11), 229 (53), 189 (17), 181 (37), 171 (12), 169 (13), 159 (16), 157 (14), 145 (32), 131 (24), 129 (37), 123 (10), 121 (10), 120 (13), 119 (37), 107 (13), 105 (23), 101 (33), 97 (18), 93 (100), 91 (45), 89 (21), 81 (19), 79 (14), 77 (41), 75(48), 73 (46), 59 (17), 41 (14). HRMS (ESIpos): *m/z*: calcd for $C_{24}H_{40}O_4SiNa$: 443.2588; found: 443.2586.

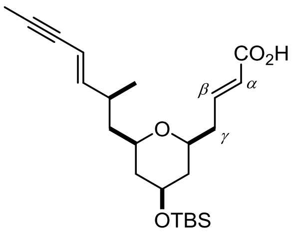


(*E*)-4-((2*S*,4*R*,6*R*)-4-((*tert*-Butyldimethylsilyl)oxy)-6-((*R*,*E*)-2-methylhept-3-en-5-yn-1-yl)tetrahydro-2*H*-pyran-2-yl)but-2-enoic acid (18). KOTMS (90%, 246 mg, 1.73 mmol) was added to a solution of methyl ester (*E*)-**17** (145 mg, 0.345 mmol) in Et_2O (7.0 mL). After stirring for 1h, additional KOTMS (90%, 246 mg, 1.73 mmol) was introduced and stirring of the yellow suspension continued for 5 h. Excess base was quenched with aq. HCl (0.5 M, 10 mL) and the aqueous layer was extracted with EtOAc (5 x 15 mL). The combined organic phases were dried over Na_2SO_4 and concentrated, and the residue purified by flash chromatography (hexanes/EtOAc 6:1 with 0.1% AcOH) to give the desired acid as a colorless oil (112 mg, 80%). As a by-product, the β,γ-olefin was isolated as a colorless oil (9.8 mg, 7%). $[\propto]_D^{20}$ = –28.2 (c = 1.37, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.0 – 10.4 (br s, 1H), 7.06 (dt, *J* = 15.7, 7.1 Hz, 1H), 5.93



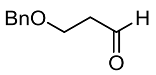
(dd, *J* = 15.9, 7.8 Hz, 1H), 5.84 (dt, *J* = 15.7, 1.2 Hz, 1H), 5.37 (ddd, *J* = 15.9, 2.1, 1.1 Hz, 1H), 3.72 (m, 1H), 3.43 – 3.31 (m, 1H), 3.31 – 3.19 (m, 1H), 2.51 – 2.28 (m, 3H), 1.90 (d, *J* = 2.3 Hz, 3H), 1.80 – 1.73 (m, 2H), 1.61 (dddd, *J* = 7.1, 7.0, 7.0, 6.9 Hz, 1H), 1.29 (ddd, *J* = 13.6, 7.7, 5.7 Hz, 1H), 1.25 – 1.08 (m, 2H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.86 (s, 9H), 0.04 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.4, 148.5, 148.2, 122.4, 108.2, 84.4, 78.3, 73.9, 73.3, 68.6, 42.3, 41.5, 41.4, 38.8, 33.4, 25.8, 19.6, 18.1, 4.2, –4.5, –4.5 ppm. IR (film): $\tilde{\nu}$ = 2928, 2926, 2855, 1698, 1654, 1462, 1443, 1376, 1282, 1255, 1152, 1068, 960, 852, 835, 815, 774, 699, 669 cm^{-1}. MS (EI) *m/z* (%) = 418 (5), 349 (8), 257 (13), 237 (24), 169 (23), 160 (12), 145 (27), 131 (33), 129 (11), 121 (10), 119 (28), 107 (12), 105 (12), 101 (24), 93 (100), 91 (37), 79 (13), 77 (37), 75 (47), 73 (32), 59 (11), 41 (11). HRMS (ESIpos): *m/z*: calcd for $C_{23}H_{38}O_4SiNa$: 429.2427; found: 429.2431.

(*E*)-4-((2*S*,4*R*,6*R*)-4-((*tert*-butyldimethylsilyl)oxy)-6-((*S*,*E*)-2-methylhept-3-en-5-yn-1-yl)tetrahydro-2*H*-pyran-2-yl)but-2-enoic acid (11-*epi*-18). Prepared analogously from methyl ester 11-*epi*-(*E*)-**17** (116 mg, 0.276 mmol) as a colorless oil (101 mg, 88%), along with the corresponding β,γ-olefin as a colorless oil (8.2 mg, 7%). $[\propto]_{D}^{20}$ = +84.0 (c = 1.02, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.6 – 9.40 (br s, 1H), 7.08 (dt, *J* = 15.8, 7.0 Hz, 1H), 5.87 (d, *J* = 15.7 Hz, 1H), 5.79 (ddd, *J* = 15.9, 8.9, 0.9 Hz, 1H), 5.41 (ddt, *J* = 16.0, 2.7, 1.9 Hz, 1H), 3.79 – 3.63 (m, 1H), 3.34 (dddd, *J* = 12.6, 6.1, 4.0, 1.7 Hz, 1H), 3.22 (dddd, *J* = 10.9, 10.4, 2.1, 1.8 Hz, 1H), 2.53 – 2.37 (m, 2H), 2.34 (m, 1H), 1.90 (dd, *J* = 2.3, 0.7 Hz, 3H), 1.81 – 1.63 (m, 2H), 1.53 (ddd, *J* = 14.1, 10.0, 4.1 Hz, 1H), 1.30 – 1.10 (m, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.85 (s, 9H), 0.02 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.5, 148.3, 148.0, 122.4, 109.2, 84.3, 78.4, 74.0, 73.4, 68.5, 42.9, 41.9, 41.5, 38.7, 33.9, 25.8, 21.1, 18.1, 4.2, –4.5, –4.6 ppm. IR (film): $\tilde{\nu}$ = 2952, 2928, 2856, 1696, 1653, 1421, 1375, 1304, 1283, 1254, 1154, 1117, 976, 960, 924, 852, 834, 774, 739, 669 cm^{-1}. MS (EI) *m/z* (%) = 418 (6), 349 (8), 257 (13), 237 (25), 169 (23), 160 (12), 145 (27), 131 (33), 129 (11), 121 (10), 119 (28), 107 (12), 105 (11), 101 (24), 93 (100), 91 (39), 79 (13), 77 (37), 75 (49), 73 (32), 59 (12). HRMS (ESIneg): *m/z*: calcd for $C_{23}H_{37}O_4Si$: 405.2467; found: 405.2468.

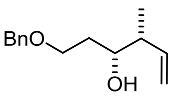


2 Synthesis of the Alcohol Fragment

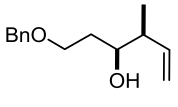
3-(Benzyloxy)propanal (24). According to the procedure of Stahl *et. al.*,[4] a 1 L-round-bottom flask was charged with 3-(benzyloxy)propanol (**23**) (7.20 g, 43.3 mmol) and MeCN (HPLC grade, 210 mL). $[Cu(MeCN)_4]BF_4$ (683 mg, 2.17 mmol) and 2,2'-bipyridine (339 mg, 2.17 mmol) were added as solids, followed by *N*-methyl imidazole (346 µL, 4.34 mmol) and TEMPO (339 mg, 2.17 mmol). The resulting red/brown mixture was vigorously stirred open to air for 3 h until the reaction mixture turned dark green. After concentration at reduced pressure, the residue was purified by flash chromatography (hexanes/EtOAc 6:1 to 5:1 to 4:1) to give the desired aldehyde as a colorless oil with an unpleasant smell (6.69 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.78 (t, *J* =



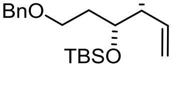
1.8 Hz, 1H), 7.41 – 7.22 (m, 5H), 4.52 (s, 2H), 3.80 (td, *J* = 6.1, 1.2 Hz, 2H), 2.68 (tt, *J* = 6.1, 1.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.1, 137.8, 128.4, 127.7, 127.7, 73.2, 63.8, 43.9 ppm. IR (film): $\tilde{\nu}$ = 3031, 2860, 2733, 1721, 1496, 1454, 1394, 1362, 1205, 1091, 1027, 899, 885, 736, 697 cm^{-1}. MS (EI) *m/z* (%) = 108 (79), 107 (85), 92 (17), 91 (66), 79 (100), 78 (14), 77 (56), 65 (14), 56 (29), 55 (22), 51 (18), 39 (10), 28 (11), 27 (22), 26 (11). HRMS (ESIpos): *m/z*: calcd for $C_{10}H_{12}O_2H$: 165.0916; found: 165.0914.



(3*R*,4*R*)-1-(Benzyloxy)-4-methylhex-5-en-3-ol (25). A solution of crotylsilane (*R*,*R*)-**35**[5] (1.0 M in CH_2Cl_2, 6.62 mmol, 6.62 mL) was added dropwise at –78 °C via syringe to a solution of aldehyde **24** (906 mg, 5.52 mmol) in CH_2Cl_2 (56 mL). Next, solid $Sc(OTf)_3$ (136 mg, 0.276 mmol) was added and the mixture stirred for 15 min at –78 °C before it was allowed to reach 0 °C. Stirring was continued for 2 h. At this point, NMR analysis of an aliquot (50 µL) confirmed full consumption of the aldehyde. The mixture was concentrated and treated with aq. HCl (1 M, 70 mL) and Et_2O (70 mL) under vigorous stirring for 1 h. The white precipitate formed was filtered off and washed with Et_2O (2 x 10 mL) (treatment of this solid with NaOH allowed the diamine ligand to be recovered after chromatographic purification in > 90%). The phases of the filtrate were separated and the aqueous layer extracted with Et_2O (3 x 50 mL). The combined extracts were washed with $NaHCO_3$ (70 mL), dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 5:1) to give the crotylated alcohol as a colorless oil (995 mg, 82% yield, 94% ee, 98:2 d.r.). The enantiomeric excess was determined by HPLC of the TBS ether (see conditions below). $[\alpha]_D^{20}$ = +16.5 (c = 1.18, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 – 7.25 (m, 5H), 5.77 (ddd, *J* = 17.7, 10.4, 7.6 Hz, 1H), 5.09 – 4.98 (m, 2H), 4.50 (s, 2H), 3.75 – 3.59 (m, 3H), 2.80 (br s, 1H), 2.25 (m, 1H), 1.82 – 1.62 (m, 2H), 1.03 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.0, 137.9, 128.4, 127.7, 127.7, 114.9, 74.5, 73.3, 69.4, 43.9, 33.5, 15.0 ppm. IR (film): $\tilde{\nu}$ = 3471, 3031, 2943, 2865, 1638, 1496, 1454, 1418, 1363, 1206, 1092, 1071, 1028, 997, 949, 913, 736, 697 cm^{-1}. MS (EI) *m/z* (%) = 220 (0.1), 165 (3), 107 (14), 92 (13), 91 (100), 79 (7), 65 (8), 55 (7). HRMS (ESIpos): *m/z*: calcd for $C_{14}H_{20}O_2Na$: 243.1355; found: 243.1356.

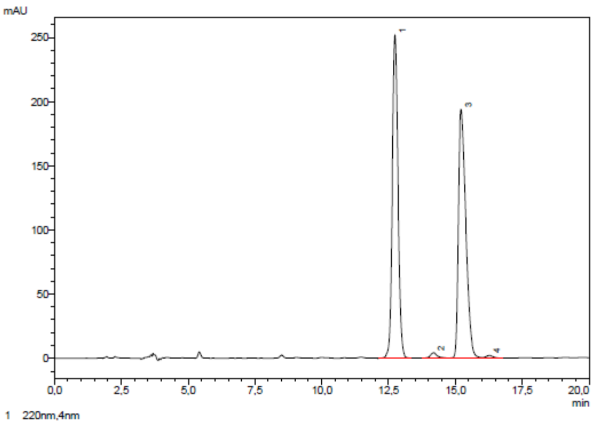


(3*S*,4*S*)-1-(Benzyloxy)-4-methylhex-5-en-3-ol (*ent*-25). Prepared analogously from aldehyde **24** (1.98 g, 12.0 mmol) and crotylsilane (*S*,*S*)-**35** (1.0 M in CH_2Cl_2, 8.21 mmol, 8.21 mL) as a colorless oil (2.13 g, 80% yield, 94.6% ee, 98:2 d.r.). The enantiomeric excess was determined by HPLC of the TBS ether (see conditions below).



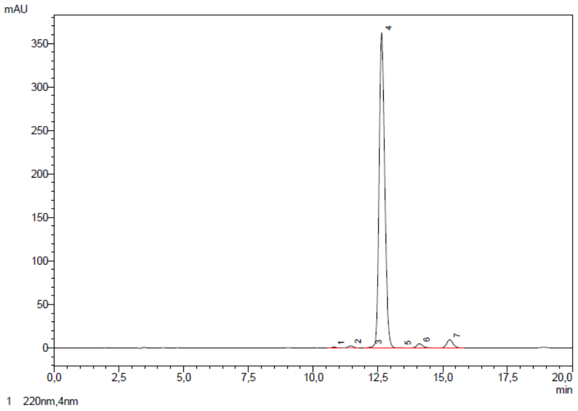
(((3*R*,4*R*)-1-(Benzyloxy)-4-methylhex-5-en-3-yl)oxy)(tert-butyl)dimethylsilane (26). TBSOTf (782 µL, 3.40 mmol) and 2,6-lutidine (463 µL, 3.98 mmol) were added to a solution of alcohol **25** (625 mg, 2.84 mmol) in CH_2Cl_2 (25 mL) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C before the reaction was quenched by addition of sat. NH_4Cl

solution (30 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were washed with brine (30 mL), dried over Na_2SO_4 and concentrated. Purification of the residue by flash chromatography (hexanes/EtOAc 35:1) yielded the target silyl ether as a colorless oil (908 mg, 96%). $[\propto]_D^{20}$= +37.4 (c = 1.39, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 – 7.30 (m, 4H), 7.30 – 7.24 (m, 1H), 5.87 (ddd, *J* = 17.3, 10.7, 6.8 Hz, 1H), 5.03 – 4.95 (m, 2H), 4.50 (d, *J* = 11.9 Hz, 1H), 4.45 (d, *J* = 11.9 Hz, 1H), 3.75 – 3.69 (m, 1H), 3.55 – 3.49 (m, 2H), 2.35 – 2.25 (m, 1H), 1.75 (dtd, *J* = 13.9, 7.4, 4.0 Hz, 1H), 1.65 (ddt, *J* = 13.9, 7.8, 6.2 Hz, 1H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.87 (s, 9H), 0.04 (s, 3H), 0.02 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.8, 138.5, 128.3, 127.6, 127.5, 114.2, 72.9, 72.9, 67.1, 43.0, 33.4, 25.9, 18.1, 14.9, −4.3, −4.6 ppm. IR (film): $\tilde{\nu}$ = 2955, 2928, 2885, 2856, 1472, 1461, 1455, 1361, 1253, 1092, 1050, 1028, 1005, 912, 835, 774, 733, 696 cm^{-1}. MS (EI) *m/z* (%) = 279 (11), 173 (21), 131 (8), 91 (100), 73 (13). HRMS (ESIpos): *m/z*: calcd for $C_{20}H_{34}O_2SiNa$: 357.2220; found: 357.2219. HPLC: 150 mm Chiralcel OJ-3R (Ø 4.6 mm), MeCN/water 70:30, 0.5 mL/min, 308 K, 9.2 MPa: R_t = 12.64 min (major *syn*), 14.10 min (*anti*), 15.27 min (minor *syn*).



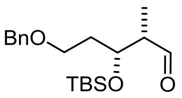
PDA Ch1 220nm

Peak #	Ret. Time	Area %	Name
1	12,74	49,16	1. Enantiomer
2	14,18	1,00	
3	15,21	49,32	2. Enantiomer
4	16,27	0,52	
Total		100,00	



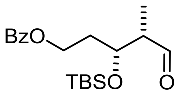
PDA Ch1 220nm

Peak #	Ret. Time	Area %	Name
1	10,80	0,18	
2	11,44	0,46	
3	12,25	0,14	
4	12,64	95,00	1. Enantiomer 94.3 % ee
5	13,38	0,06	
6	14,10	1,39	
7	15,27	2,78	2. Enantiomer
Total		100,00	

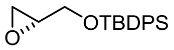


(2*S*,3*R*)-5-(Benzyloxy)-3-((*tert*-butyldimethylsilyl)oxy)-2-methylpentanal (27). The terminal alkene **27** (900 mg, 2.67 mmol) was dissolved in CH_2Cl_2 and the resulting solution cooled to −78 °C. Ozone was bubbled through the solution (~30 g/Nm^3) until TLC analysis showed complete conversion of the alkene (30 min) and the solution turned blue. Argon was then bubbled for 10 min through the solution, which turned colorless. Triphenylphosphine (842 mg, 3.21 mmol) was added as a solid and the reaction mixture was allowed to warm to ambient temperature and stirred for 3.5 h. The volatiles were then removed under reduced pressure and the residue purified by flash chromatography (hexanes/EtOAc 29:1 to 19:1) to yield the desired aldehyde as a colorless liquid (823 mg, 91%) along with the benzoate as a by-product. $[\propto]_D^{20}$ = +42.5 (c = 1.34, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.76 (d, *J* = 0.9 Hz, 1H), 7.37 – 7.24 (m, 5H), 4.50 (d, *J* = 11.9 Hz, 1H), 4.44 (d, *J* = 11.9 Hz, 1H), 4.30 (ddd, *J* = 7.3, 5.6, 3.6 Hz, 1H), 3.56 – 3.45 (m, 2H), 2.46

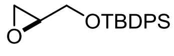
(qdd, *J* = 6.9, 3.7, 1.0 Hz, 1H), 1.89 – 1.69 (m, 2H), 1.04 (d, *J* = 7.0 Hz, 3H), 0.84 (s, 9H), 0.05 (s, 3H), 0.02 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.1, 138.3, 128.4, 127.6, 73.0, 69.3, 66.6, 51.6, 34.6, 25.8, 18.0, 7.9, −4.5, −4.6 ppm. IR (film): $\tilde{\nu}$ = 2953, 2929, 2856, 1725, 1496, 1472, 1455, 1361, 1252, 1148, 1099, 1028, 1005, 938, 834, 774, 734, 697 cm^{-1}. MS (EI) *m/z* (%) = 279 (1), 187 (4), 173 (9), 145 (10), 131 (16), 115 (5), 92 (9), 91 (100), 59 (5). HRMS (ESIpos): *m/z*: calcd for $C_{19}H_{32}O_3SiNa$: 359.2013; found: 357.2010.



(3*R*,4*S*)-3-((*tert*-Butyldimethylsilyl)oxy)-4-methyl-5-oxopentyl benzoate. Obtained as a by-product from the reaction described above as a colorless oil (37 mg, 4%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.76 (d, *J* = 1.0 Hz, 1H), 8.04 – 7.89 (m, 2H), 7.56 – 7.45 (m, 1H), 7.44 – 7.33 (m, 2H), 4.38 (dt, *J* = 11.7, 6.0 Hz, 1H), 4.33 – 4.22 (m, 2H), 2.50 (qdd, *J* = 7.0, 3.7, 1.0 Hz, 1H), 1.97 (dddd, *J* = 14.1, 7.8, 6.2, 5.1 Hz, 1H), 1.86 (ddt, *J* = 14.3, 7.7, 5.7 Hz, 1H), 1.06 (d, *J* = 7.1 Hz, 3H), 0.82 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.6, 166.4, 133.0, 130.1, 129.5, 128.4, 69.2, 61.6, 51.6, 33.5, 25.7, 18.0, 8.2, −4.5, −4.6 ppm. IR (film): $\tilde{\nu}$ = 2954, 2911, 2876, 1455, 1414, 1363, 1238, 1091, 1004, 911, 840, 725, 695 cm^{-1}. MS (EI) *m/z* (%) = 293 (1), 213 (3), 201 (1), 179 (25), 172 (14), 171 (100), 141 (10), 127 (8), 115 (32), 105 (74), 97 (41), 91 (10), 77 (25), 59 (14). HRMS (ESIpos): *m/z*: calcd for $C_{19}H_{30}O_4SiNa$: 373.1806; found: 373.1807.

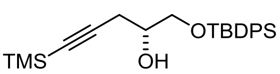


(*R*)-*tert*-Butyl(oxiran-2-ylmethoxy)diphenylsilane (29). A solution of TBDPSCl (18.1 mL, 69.4 mmol) in CH_2Cl_2 (50 mL) was added over 15 min via a dropping funnel to a solution of (*S*)-glycidol (**28**) (4.41 mL, 66.1 mmol) and imidazole (5.99 g, 87.9 mmol) in CH_2Cl_2 (200 mL) at 0 °C. A white solid started to precipitate after 5 min and the reaction mixture was allowed to warm to rt. After 2 h, H_2O (250 mL) was added and the aqueous phase extracted with CH_2Cl_2 (2 x 100 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 19:1 to 9:1) to give the desired silyl ether as a colorless oil (19.5 g, 94%). $[\propto]_D^{20}$ = +0.9 (c = 1.41, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 – 7.61 (m, 4H), 7.47 – 7.32 (m, 6H), 3.84 (dd, *J* = 11.8, 3.2 Hz, 1H), 3.70 (dd, *J* = 11.8, 4.7 Hz, 1H), 3.14 – 3.09 (m, 1H), 2.73 (dd, *J* = 5.2, 4.0 Hz, 1H), 2.60 (dd, *J* = 5.2, 2.7 Hz, 1H), 1.05 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.6, 135.5, 132.3, 129.7, 127.0, 64.3, 52.3, 44.4, 26.8, 19.2 ppm. IR (film): $\tilde{\nu}$ = 3071, 3049, 2998, 2930, 2894, 2857, 1472, 1427, 1390, 1361, 1254, 1159, 1136, 1111, 1091, 1030, 980, 917, 823, 739, 700, 690 cm^{-1}. MS (EI) *m/z* (%) = 256 (11), 255 (53), 226 (20), 225 (100), 211 (22), 184 (16), 183 (87), 181 (20), 177 (46), 117 (38), 105 (13), 77 (99). HRMS (ESIpos): *m/z*: calcd for $C_{19}H_{24}O_2SiNa$: 335.1438; found: 335.1435.

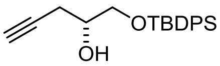


***(S)*-*tert*-Butyl(oxiran-2-ylmethoxy)diphenylsilane (*ent*-29).** Prepared analogously from (*R*)-glycidol (*ent*-**28**) (3.0 g, 40.5 mmol) as a colorless oil (12.0 g, 95%).

(*R*)-1-((tert-Butyldiphenylsilyl)oxy)-5-(trimethylsilyl)pent-4-yn-2-ol (29a). A solution of *n*-BuLi (1.65 M in hexane, 40.6 mL, 66.9 mmol) was added dropwise via dropping funnel over 12 min to a solution of trimethylsilylacetylene (7.17 g, 73.0 mmol) in THF (300 mL) at −78 °C. The resulting yellow solution was stirred for 15 min at −78 °C, when $BF_3 \cdot Et_2O$ (9.26 mL, 73.0 mmol) was added dropwise via syringe over 5 min. A solution of epoxide **29** (18.3 g, 58.6 mmol) in THF (15 mL) was then added dropwise via syringe over 6 min and the reaction mixture allowed to stir for further 90 min. The reaction was then quenched by careful addition of sat. NH_4Cl solution (300 mL) and EtOAc (200 mL) and the mixture subsequently warmed to ambient temperature. After phase separation, the aqeuos phase was extracted with EtOAc (2 x 200 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. Purification of the residue by flash chromatography (short column (~9cm), hexanes/EtOAc 14:1) yielded the desired alcohol as a colorless oil (21.9 g, 91%). $[\propto]_D^{20} = -5.3$ (c = 0.99, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.69 – 7.62 (m, 4H), 7.46 – 7.32 (m, 6H), 3.75 (ddd, *J* = 10.1, 4.3, 0.7 Hz, 1H), 3.91 – 3.82 (m, 1H), 3.69 (ddd, *J* = 10.1, 5.9, 0.8 Hz, 1H), 2.58 – 2.42 (m, 3H), 1.06 (s, 9H), 0.10 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.5, 133.1, 129.8, 127.8, 127.7, 102.6, 87.1, 70.2, 66.4, 26.9, 24.7, 19.3, 0.0 ppm. IR (film): $\tilde{\nu}$ = 3487, 2958, 2931, 2858, 2177, 1472, 1428, 1391, 1362, 1249, 1112, 1188, 1112, 1030, 1008, 970, 936, 840, 823, 759, 739, 700 cm^{-1}. MS (EI) *m/z* (%) = 353 (17), 272 (12), 271 (45), 242 (21), 241 (100), 223 (12), 221 (9), 211 (6), 200 (13), 199 (74), 193 (13), 163 (31), 105 (6), 73 (14). HRMS (ESIpos): *m/z*: calcd for $C_{24}H_{34}O_2Si_2Na$: 433.1990; found: 433.1987.

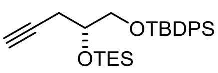


(*R*)-1-((tert-Butyldiphenylsilyl)oxy)-5-(trimethylsilyl)pent-4-yn-2-ol (29b). The secondary alcohol **29a** (21.8 g, 53.1 mmol) was dissolved in MeOH (200 mL) and the solution cooled to 15 °C. Potassium carbonate (14.6 g, 106 mmol) was added slowly and the reaction mixture stirred vigorously. After 1h, the reaction was quenched with sat. NH_4Cl solution (200 mL) and the mixture extracted with EtOAc (3 x 150 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue (17.5 g, 97%) thus obtained turned out to be a 8:1 mixture of two alkynes as the result of 1,2-silyl migration.

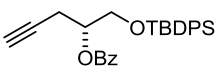


A part of the residue (16.7 g, 49.3 mmol) was dissolved in CH_2Cl_2 (250 mL), cooled to −78 °C, and treated with triethylamine (1.16 mL, 8.4 mmol), TESCl (1.24 mL, 7.4 mmol) and DMAP (30 mg, 0.25 mmol). The mixture was stirred for 4 h at −78 °C before the reaction was quenched with sat. NH_4Cl solution (200 mL). The aqueous phase was extracted with CH_2Cl_2 (2 x 200 mL) and the combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 13:1 to 4:1) to yield pure secondary alcohol **29b** as a colorless oil (12.7 g, 76%). $[\propto]_D^{20} = -2.5$ (c = 1.36, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.71 – 7.62 (m, 4H), 7.46 – 7.35 (m, 6H), 3.88 (qd, *J* = 6.2, 4.3 Hz, 1H), 3.75 (dd, *J* = 10.2, 4.3 Hz, 1H), 3.69 (dd, *J* = 10.2, 5.8 Hz, 1H), 2.46 m, 3H), 1.97 (t, *J* = 2.7 Hz, 1H), 1.07 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.5, 135.5, 133.0, 133.0, 129.8, 127.8, 80.3, 70.4, 70.1, 66.3, 26.8, 23.2, 19.2 ppm. IR (film): $\tilde{\nu}$ = 3433, 3301, 3072, 2931, 2858, 1472, 1427, 1391, 1361, 1259, 1188, 1111, 1072, 1043, 1007, 998, 971, 936, 909, 822, 798, 739, 699 cm^{-1}. MS (EI) *m/z* (%) = 281 (12), 242 (10), 241 (51), 200 (18), 199 (100), 181 (12), 163 (16), 139 (12), 135 (8), 105 (8), 77 (8). HRMS (ESIpos): *m/z*: calcd for $C_{21}H_{26}O_2Si_1Na$: 361.1594; found: 361.1591.

(*R*)-8,8-Diethyl-2,2-dimethyl-3,3-diphenyl-6-(prop-2-yn-1-yl)-4,7-dioxa-3,8-disiladecane (30a).

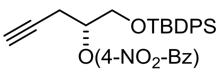


The secondary alcohol **29b** (1.96 g, 5.79 mmol) was dissolved in CH_2Cl_2 (29 mL) and cooled to 0 °C. Triethylamine (0.96 mL, 6.93 mmol) and TESCl (1.08 mL, 6.40 mmol) were added slowly via syringe, followed by DMAP (7.1 mg, 58 µmol) as a solid. The mixture was stirred for 3 h at 0 °C before the reaction quenched by addition of sat. NH_4Cl solution (12 mL). After separation of the layers, the aqueous phase was further extracted with EtOAc (3 x 7 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. Purification of the residue by flash chromatography (hexanes/EtOAc 29:1) yielded the desired silyl ether as a colorless oil (2.28 g, 87%). $[\propto]_D^{20}$ = +7.3 (c = 1.05, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.72 – 7.63 (m, 4H), 7.46 – 7.31 (m, 6H), 3.91 – 3.80 (m, 1H), 3.68 – 3.56 (m, 2H), 2.60 (dddd, *J* = 16.7, 5.5, 2.7, 0.8 Hz, 1H), 2.38 (dddd, *J* = 16.7, 5.9, 2.7, 0.8 Hz, 1H), 1.93 (t, *J* = 2.7 Hz, 1H), 1.04 (d, *J* = 0.8 Hz, 9H), 0.90 (dd, *J* = 8.3, 7.5 Hz, 9H), 0.54 (q, *J* = 8.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.6, 135.6, 133.6, 133.4, 129.6, 127.6, 81.6, 71.4, 69.6, 66.8, 26.8, 24.4, 19.2, 6.8, 4.8 ppm. IR (film): $\tilde{\nu}$ = 3312, 2954, 2933, 2876, 1472, 1462, 1427, 1390, 1361, 1239, 1111, 1072, 1003, 938, 855, 823, 807, 736, 699 cm^{-1}. MS (EI) *m/z* (%) = 423 (19), 396 (11), 395 (30), 315 (11), 314 (30), 313 (100), 285 (30), 243 (10), 197 (15), 183 (7), 163 (10), 143 (11), 135 (32), 87 (14). HRMS (ESIpos): *m/z*: calcd for $C_{27}H_{40}O_2Si_2Na$: 475.2459; found: 475.2461.

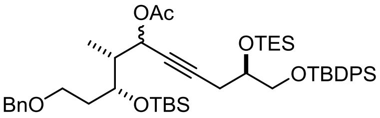


(*R*)-1-((*tert*-Butyldiphenylsilyl)oxy)pent-4-yn-2-yl benzoate (30b). The secondary Alcohol **29b** (1.20 g, 3.55 mmol) was dissolved in CH_2Cl_2 (10 mL) and the solution cooled to 0 °C. Triethylamine (0.589 mL, 4.25 mmol) and benzoyl chloride (0.452 mL, 3.89 mmol) were added slowly via syringe, followed by DMAP (21.7 mg, 178 µmol) as a solid. The mixture was stirred for 1 h at 0 °C and 3 h at ambient temperature before the reaction was quenched by addition of sat. NH_4Cl solution (15 mL). After separation of the layers, the aqueous phase was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4 and concentrated. Purification of the residue by flash chromatography (hexanes/EtOAc 9:1) yielded the desired silyl ether as a pale yellow oil (1.24 g, 79%). $[\propto]_D^{20}$ = −11.7 (c = 1.69, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.11 – 7.97 (m, 2H), 7.68 – 7.62 (m, 4H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.46 – 7.25 (m, 8H), 5.36 – 5.24 (m, 1H), 3.97 (dd, *J* = 11.0, 4.8 Hz, 1H), 3.92 (dd, *J* = 11.0, 4.7 Hz, 1H), 2.81 (ddd, *J* = 16.7, 6.5, 2.3 Hz, 1H), 2.72 (ddd, *J* = 16.7, 5.6, 2.2 Hz, 1H), 1.96 (t, *J* = 2.5 Hz, 1H), 1.04 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 135.5, 133.1, 133.0, 130.2, 129.7, 129.7, 128.3, 127.7, 127.7, 79.5, 72.6, 70.4, 63.6, 26.7, 20.6, 19.3 ppm. IR (film): $\tilde{\nu}$ =

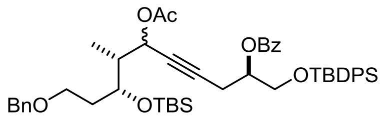
3305, 2958, 2931, 2858, 1718, 1602, 1588, 1472, 1451, 1427, 1391, 1361, 1315, 1266, 1176, 1108, 1069, 1047, 1026, 997, 823, 796, 738, 701, 615 cm^{-1}. MS (EI) *m/z* (%) = 386 (16), 385 (54), 304 (22), 303 (88), 259 (17), 105 (100), 77 (11). HRMS (ESIpos): *m/z*: calcd for $C_{28}H_{30}O_3Si_1Na$: 465.1856; found: 465.1857.



(*R*)-1-((*tert*-Butyldiphenylsilyl)oxy)pent-4-yn-2-yl 4-nitrobenzoate (30c). The secondary Alcohol **29b** (2.00 g, 5.91 mmol) was dissolved in CH_2Cl_2 (20 mL) and cooled to 0 °C. Triethylamine (0.98 mL, 7.1 mmol) and 4-nitrobenzoyl chloride (1.21 g, 6.50 mmol) were added slowly, followed by DMAP (36.1 mg, 296 µmol) as a solid. The mixture was stirred for 1.5 h at 0 °C before the reaction was quenched by addition of sat. NH_4Cl solution (15 mL). After separation of the layers, the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4 and concentrated. Purification of the residue by flash chromatography (hexanes/EtOAc 9:1) yielded the desired silyl ether as a yellow oil (2.52 g, 87%). $[\propto]_D^{20} = -13.3$ (c = 1.01, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.26 (d, *J* = 8.5 Hz, 2H), 8.16 (d, *J* = 8.6 Hz, 2H), 7.66 – 7.59 (m, 4H), 7.43 – 7.27 (m, 6H), 5.36 – 5.27 (m, 1H), 3.97 (dd, *J* = 11.0, 4.7 Hz, 1H), 3.93 (dd, *J* = 10.7, 4.2 Hz), 2.79 (ddd, *J* = 17.0, 6.4, 2.6 Hz, 1H), 2.73 (ddd, *J* = 17.1, 6.1, 2.7 Hz, 1H), 1.03 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.9, 150.6, 135.5, 135.5, 133.0, 132.9, 130.8, 129.8, 127.7, 127.7, 123.5, 79.0, 73.6, 70.7, 63.5, 26.7, 20.6, 19.2 ppm. IR (film): $\tilde{\nu}$ = 3297, 3072, 2931, 2858, 1725, 1608, 1527, 1472, 1427, 1348, 1320, 1269, 1112, 1102, 1044, 1014, 997, 873, 823, 783, 741, 718, 701 cm^{-1}. MS (EI) *m/z* (%) = 431 (11), 430 (35), 349 (26), 348 (100), 302 (8), 150 (30), 104 (11). HRMS (ESIpos): *m/z*: calcd for $C_{27}H_{40}O_2Si_2Na$: 475.2459; found: 475.2461.



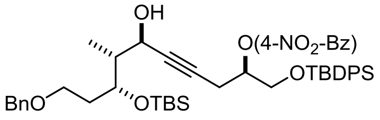
(5*R*,6*R*,11*R*)-5-(2-(Benzyloxy)ethyl)-2,2,3,3,6,15,15-heptamethyl-14,14-diphenyl-11-((triethylsilyl) oxy)-4,13-dioxa-3,14-disilahexadec-8-yn-7-yl acetate (31a). A solution of *n*-BuLi (1.60 M in hexane, 221 µL, 353 µmol) was added dropwise over 2 min to a −78 °C solution of terminal alkyne **30a** (160 mg, 353 µmol) in THF (2.0 mL). After 25 min stirring at −78 °C, a solution of aldehyde **27** (120 mg, 357 µmol) in THF (1.0 mL) was added dropwise. After 2 h, the reaction mixture was warmed to 0 °C and stirred for another 2 h. Acetyl chloride (25.5 µL, 0.357 mmol) was added, the reaction mixture allowed to warm to ambient temperature and stirred for another 2 h. The reaction was quenched by addition of water (5 mL) and brine (5 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography to give the desired propargylic acetate as a colorless oil as a mixture of diastereomers (2.9:1 d.r., 104 mg, 35%). ^1H NMR (400 MHz, C_6D_6, only the peaks of the major isomer are listed): δ = 7.86 – 7.77 (m, 4H), 7.33 – 7.23 (m, 8H), 7.23 – 7.17 (m, 2H), 7.10 (tt, *J* = 7.3, 1.4 Hz, 1H), 5.90 (dt, *J* = 7.6, 2.0 Hz, 1H), 4.38 (dd, *J* = 6.2, 3.4 Hz, 1H), 4.35 – 4.27 (m, 2H), 3.99 – 3.91 (m, 1H), 3.87 – 3.76 (m, 2H), 3.47 – 3.35 (m, 2H), 2.76 (ddd, *J* = 16.6, 5.6, 1.8 Hz, 1H), 2.53 (ddd, *J* = 16.5, 5.9, 2.2 Hz, 1H), 2.13 (qdd, *J* = 7.1, 7.0, 3.3 Hz, 1H), 1.89 (q, *J* = 6.4 Hz, 2H), 1.72 (s, 3H), 1.16 (s, 9H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.01 (s, 9H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.57 (q, J = 8.1 Hz, 6H), 0.23 (s, 3H), 0.13 (s, 3H) ppm. ^{13}C NMR (100 MHz, C_6D_6, only the peaks of the major isomer are listed): δ = 169.1, 139.2, 136.0, 136.0, 134.0, 133.8, 130.0, 128.5, 128.1, 128.1, 127.7, , 127.6, 83.7, 79.9, 73.1, 72.0, 70.5, 67.4, 67.0, 66.3, 43.5, 35.4, 27.1, 26.2, 25.0, 20.6, 19.5, 18.4, 10.1, 7.1, 5.2, −4.1, −4.2 ppm. IR (film): $\tilde{\nu}$ = 2953, 2931, 2877, 2857, 1744, 1472, 1462, 1428, 1362, 1230, 1111, 1016, 971, 940, 862, 835, 775, 737, 701 cm^{-1}. MS (EI) *m/z* (%) = 641 (6), 639 (6), 623 (6), 435 (9), 383 (6), 313 (21), 285 (16), 281 (12), 279 (43), 241 (10), 237 (21), 197 (11), 181 (10), 175 (15), 174 (12), 173 (85), 171 (17), 135 (28), 131 (43), 117 (31), 115 (10), 91 (100), 87 (11). HRMS (ESIpos): *m/z*: calcd for $C_{48}H_{74}O_6Si_3Na$: 853.4685; found: 853.4685.



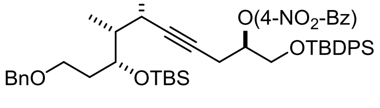
(6*R*,11*R*,12*R*)-10-Acetoxy-12-(2-(benzyloxy)ethyl)-2,2,11,14,14,15,15-heptamethyl-3,3-diphenyl-4,13-dioxa-3,14-disilahexadec-8-yn-6-yl benzoate (31b). A solution of *n*-BuLi (1.60 M in hexane, 0.111 mL, 0.178 mmol) was added dropwise to a solution of diisopropylamine (24.7 µL, 0.178 mmol) in THF (0.6 mL) at −78 °C. The resulting pale yellow solution was stirred for 5 min at −78 °C, 30 min at 0 °C and recooled to −78 °C, when a solution of alkyne **30a** (85.2 mg, 0.192 mmol) in THF (0.4 mL) was added dropwise. The reaction mixture was stirred for another 20 min at −78 °C before aldehyde **27** (51.5 µL, 0.148 mmol) was added carefully. The mixture was stirred for 2 h at −78 °C and 30 min at 0 °C before the reaction was quenched by the addition of sat. NH_4Cl solution (3 mL) and EtOAc (3 mL). The aqueous phase was extracted with EtOAc (3 x 3 mL). The combined organic extracts were washed with brine (5 mL), dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtoAc 9:1 to 7:1 to 5:1) and yielded a mixture of two inseparable diastereomers as a pale yellow liquid (67 mg, 58%, 90% purity). This mixture (2.4:1 d.r., 67.0 mg, 85.9 µmol) was dissolved in CH_2Cl_2 (0.6 mL) and the solution cooled to 0 °C. Triethylamine (13.7 µL, 98.8 µmol), acetic anhydride (8.9 µL, 95 µmol) and DMAP (1.05 mg, 8.6 µmol) were added successively and the mixture was stirred for 1 h at 0 °C. The reaction was then quenched by addition of sat. NH_4Cl solution (4 mL) and the aqueous phase extracted with CH_2Cl_2 (3 x 4 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. Purification of the residue by flash chromatography (hexanes/EtOAc 19:1 to 14:1) yielded the desired propargylic acetate as a colorless oil (2.4:1 d.r., 42.6 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$, the peaks of both diastereoisomers are listed): δ = 8.04 – 7.95 (m, 2H), 7.65 – 7.56 (m, 4H), 7.51 (dd, *J* = 9.2, 5.9 Hz, 1H), 7.42 – 7.20 (m, 13H), 5.33 (d, *J* = 7.1 Hz, 0.8H), 5.28 – 5.15 (m, *J* = 10.2, 8.6, 4.7 Hz, 1.2H), 4.45 – 4.33 (m, 2H), 3.96 (td, *J* = 6.2, 3.4 Hz, 0.8H), 3.92 – 3.78 (m, 2.2H), 3.43 – 3.32 (m, 2H), 2.86 – 2.64 (m, 2H), 1.93 (s, 2.1H), 1.90 (s, 0.85H), 1.82 – 1.60 (m, 3H), 0.99 (s, 9H), 0.89 (d, *J* = 6.6 Hz, 0.85H), 0.87 (d, *J* =

6.8 Hz, 2.1H), 0.82 – 0.78 (m, 9H), −0.02 – −0.09 (m, 6H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, only the peaks of the major isomer are listed): δ = 169.7, 165.7, 138.4, 135.5, 133.1, 133.0, 130.2, 129.7, 129.7, 129.7, 128.3, 127.7, 127.7, 127.5, 127.5, 127.4, 81.4, 79.8, 72.9, 72.7, 69.9, 66.9, 65.8, 63.7, 43.0, 34.5, 26.7, 25.8, 20.9, 19.2, 18.0, 9.8, −4.4, −4.6 ppm. IR (film): $\tilde{\nu}$ = 2954, 2930, 2856, 1743, 1721, 1472, 1462, 1453, 1362, 1314, 1268, 1228, 1176, 1106, 1045, 1026, 971, 938, 835, 794, 775, 739, 700 cm^{-1}. MS (ESIpos) *m/z* (%) = 843.5 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{49}H_{63}N_1O_9Si_2Na$: 843.4083; found: 843.4090.

(6*R*,10*R*,11*R*,12*R*)-12-(2-(Benzyloxy)ethyl)-10-hydroxy-2,2,11,14,14,15,15-heptamethyl-3,3-diphenyl-4,13-dioxa-3,14-disilahexadec-8-yn-6-yl 4-nitrobenzoate.[6] A solution of *n*-BuLi (1.60 M in hexane, 0.111 mL, 0.178 mmol) was added dropwise to a solution of diisopropylamine (24.7 µL, 0.178 mmol) in THF (0.6 mL) at −78 °C. The resulting pale yellow solution was stirred for 5 min at −78 °C, 25 min at 0 °C and recooled to −78 °C, when a solution of alkyne **30c** (93.7 mg, 0.192 mmol) in THF (0.4 mL + 2 x 0.1 mL rinse) was introduced dropwise via syringe. The reaction mixture was stirred for another 20 min at −78 °C before aldehyde **27** (51.5 µL, 0.148 mmol) was added carefully. The mixture was stirred for 2 h at −78 °C before the reaction was quenched by the addition of sat. NH_4Cl solution (3 mL) and EtOAc (3 mL). The aqueous phase was further extracted with EtOAc (3 x 3 mL). The combined organic extracts were washed with brine (5 mL), dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtoAc 8:1 to 7:1) to yield two separable diastereomers (major: 34.5 mg, 27%; minor: 17.3 mg, 13%) as pale yellow liquids. The two diastereomers were combined prior to the next step. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.21 (d, *J* = 8.6 Hz, 2H), 8.11 (d, *J* = 8.6 Hz, 2H), 7.64 – 7.54 (m, 4H), 7.40 – 7.24 (m, 10H), 7.21 (t, *J* = 4.8 Hz, 1H), 5.31 – 5.22 (m, 1H), 4.46 – 4.34 (m, 3H), 4.00 – 3.94 (m, 1H), 3.95 – 3.86 (m, 2H), 3.40 (t, *J* = 6.3 Hz, 2H), 2.78 (dd, *J* = 16.8, 6.2 Hz, 1H), 2.71 (dd, *J* = 16.9, 6.1 Hz, 1H), 2.57 (br s, 1H), 1.91 – 1.66 (m, 3H), 0.99 (s, 9H), 0.90 (d, *J* = 6.9 Hz, 3H), 0.81 (s, 9H), −0.01 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 163.9, 150.5, 138.3, 135.5, 135.5, 133.0, 133.0, 130.8, 129.8, 128.3, 127.7, 127.7, 127.5, 127.5, 123.4, 83.2, 80.3, 74.0, 72.9, 72.4, 66.7, 65.3, 63.7, 43.4, 34.4, 26.7, 25.8, 20.9, 19.2, 18.0, 9.3, −4.3, −4.6 ppm. IR (film): $\tilde{\nu}$ = 2953, 2931, 2877, 2857, 1744, 1472, 1462, 1428, 1362, 1230, 1111, 1016, 971, 940, 862, 835, 775, 737, 701 cm^{-1}. MS (ESIpos) *m/z* (%) = 846.5 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{47}H_{61}N_1O_8Si_2Na$: 846.3828; found: 846.3836.

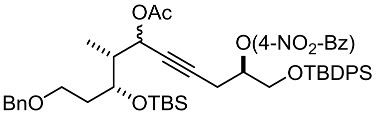


(6*R*,10*R*,11*R*,12*R*)-12-(2-(Benzyloxy)ethyl)-10-hydroxy-2,2,11,14,14,15,15-heptamethyl-3,3-diphenyl-4,13-dioxa-3,14-disilahexadec-8-yn-6-yl 4-nitrobenzoate. Obtained as the minor diastereomer from the reaction described above. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.25 (d, *J* = 8.5 Hz, 2H), 8.15 (d, *J* = 8.5 Hz, 2H), 7.65 – 7.57 (m, 4H), 7.40 – 7.26 (m, 11H), 5.31 (p, *J* =

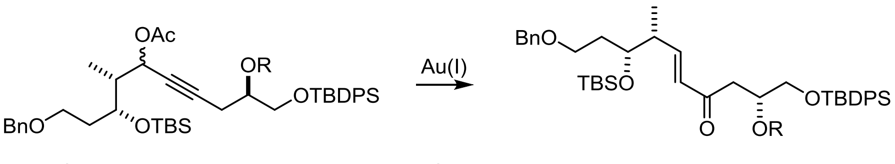


5.6 Hz, 1H), 4.48 (d, J = 11.8 Hz, 1H), 4.42 (d, J = 11.8 Hz, 1H), 4.27 (d, J = 9.2 Hz, 1H), 4.04 (dt, J = 7.9, 3.8 Hz, 1H), 3.98 – 3.88 (m, 2H), 3.56 – 3.38 (m, 3H), 2.82 (dd, J = 17.0, 6.9 Hz, 1H), 2.70 (dd, J = 16.8, 6.3 Hz, 1H), 1.84 – 1.70 (m, 3H), 1.01 (s, 9H), 0.84 (s, 9H), 0.81 (d, J = 7.0 Hz, 3H), 0.04 (s, 3H), 0.03 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.9, 150.5, 138.3, 135.6, 135.5, 133.0, 130.8, 129.8, 128.4, 127.7, 127.7, 127.6, 127.6, 123.5, 83.3, 80.1, 73.9, 73.0, 71.8, 66.7, 65.2, 63.8, 44.0, 32.4, 26.7, 25.8, 21.0, 19.2, 17.9, 12.5, −4.5, −4.8 ppm. IR (film): $\tilde{\nu}$ = 2954, 2931, 2878, 2857, 1745, 1471, 1462, 1429, 1362, 1231, 1110, 1016, 972, 940, 863, 835, 776, 737, 702 cm^{-1}. MS (ESIpos) *m/z* (%) = 846.5 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{47}H_{61}N_1O_8Si_2Na$: 846.3831; found: 846.3836.

(6*R*,11*R*,12*R*)-10-Acetoxy-12-(2-(benzyloxy)ethyl)-2,2,11,14,14,15,15-heptamethyl-3,3-diphenyl-4,13-dioxa-3,14-disilahexadec-8-yn-6-yl 4-nitrobenzoate (31c). A mixture of the propargylic alcohols described above (2.2:1 d.r., 39.0 mg, 47.4 µmol) was dissolved in CH_2Cl_2 (0.5 mL) and the solution cooled to 0 °C. Triethylamine (7.6 µL, 55 µmol), acetic anhydride (4.9 µL, 52 µmol) and DMAP (0.3 mg, 2.4 µmol) were added successively and the mixture stirred for 1h at 0 °C. The reaction was then quenched by addition of sat. NH_4Cl solution (3 mL) and extracted with CH_2Cl_2 (3 x 3 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. Purification of the residue by flash chromatography (hexanes/EtOAc 9:1) yielded the desired propargylic acetate as a yellow oil (2.2:1 d.r., 29.5 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$, only the peaks of the major isomer are listed): δ = 8.25 (dd, J = 8.7, 4.4 Hz, 2H), 8.14 (d, J = 8.5 Hz, 2H), 7.67 – 7.57 (m, 4H), 7.43 – 7.27 (m, 10H), 7.24 – 7.19 (m, 1H), 5.36 – 5.16 (m, 2H), 4.50 – 4.36 (m, 2H), 3.95 – 3.85 (m, 2H), 3.43 (q, J = 6.9 Hz, 2H), 2.89 – 2.66 (m, 2H), 1.96 (s, 3H), 1.90 – 1.63 (m, 3H), 1.02 (s, 9H), 0.91 (d, J = 6.8 Hz, 3H), 0.83 (s, 9H), −0.02 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, only the peaks of the major isomer are listed): δ = 169.7, 163.8, 150.5, 138.4, 135.5, 135.5, 133.0, 133.0, 130.8, 129.8, 128.3, 127.8, 127.7, 127.5, 127.5, 127.5, 123.4, 80.8, 80.1, 73.7, 72.9, 69.9, 66.9, 65.8, 63.7, 42.9, 34.5, 26.7, 25.8, 25.8, 20.9, 20.9, 19.2, 9.8, −4.4, −4.6 ppm. IR (film): $\tilde{\nu}$ = 2951, 2930, 2857, 1737, 1733, 1608, 1529, 1472, 1428, 1349, 1271, 1231, 1113, 1103, 1015, 835, 776, 741, 719, 702 cm^{-1}. MS (ESIpos) *m/z* (%) = 888.45 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{49}H_{63}N_1O_9Si_2Na$: 888.3934; found: 888.3936.

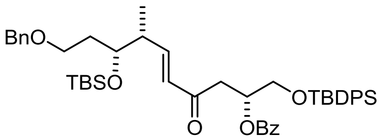


General Procedure for Au(I)-catalyzed Meyer-Schuster rearrangement of propargylic acetate

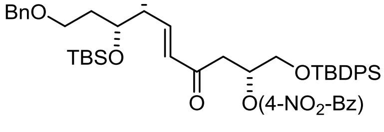


A stock solution of the catalyst was prepared as follows: A Schlenck tube is charged with Au(IPr)Cl **36** (8.5 mg, 13.7 µmol) and dry $AgSbF_6$ (3.7 mg, 13.7 µmol). THF (500 µL) was added and the resulting mixture stirred for 10 min. The white precipitate formed was allowed to settle and the supernatant used as catalyst solution (0.0274 M).

A flame-dried Young tube was charged with a solution of propargylic acetate **31** (1.00 equiv.) in THF/H_2O (39:1, 22.3 µL per µmol substrate). An aliquot of the catalyst solution (0.06 equiv., 2.47 µL per µmol substrate) was added via syringe. The Young tube was sealed and placed in a pre-heated oil bath and stirred at 60 °C for 15 h. The reaction mixture was cooled to room temperature and concentrated. The residue was purified by flash chromatography (hexanes/EtoAc 19:1 to 14:1 to 9:1) to give the desired enone.



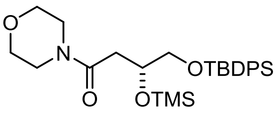
(6*R*,11*R*,12*R*,*E*)-12-(2-(benzyloxy)ethyl)-2,2,11,14,14,15,15-heptamethyl-8-oxo-3,3-diphenyl-4,13-dioxa-3,14-disilahexadec-9-en-6-yl benzoate (32b). Obtained from compound **31b** (42.0 mg, 51.2 µmol) following the general procedure as a colorless oil (29.2 mg, 73%). $[\propto]_D^{20}$ = +16.4 (c = 0.97, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.98 – 7.91 (m, 2H), 7.60 – 7.54 (m, 4H), 7.39 – 7.25 (m, 10H), 7.23 – 7.18 (m, 3H), 6.90 (dd, *J* = 16.2, 6.8 Hz, 1H), 6.06 (dd, *J* = 16.1, 1.4 Hz, 1H), 5.60 (tt, *J* = 6.7, 4.0 Hz, 1H), 4.43 (d, *J* = 11.9 Hz, 1H), 4.38 (d, *J* = 11.9 Hz, 1H), 3.87 (dd, *J* = 4.0, 2.2 Hz, 2H), 3.78 (dt, *J* = 8.3, 4.3 Hz, 1H), 3.43 (t, *J* = 6.0 Hz, 2H), 3.08 (dd, *J* = 16.3, 6.4 Hz, 1H), 3.03 (dd, *J* = 16.2, 6.7 Hz, 1H), 2.48 – 2.39 (m, 1H), 1.69 (dtd, *J* = 14.1, 7.1, 4.2 Hz, 1H), 1.54 (ddt, *J* = 13.9, 8.0, 5.8 Hz, 1H), 0.98 (s, 9H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.81 (s, 9H), −0.03 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.8, 165.6, 150.2, 138.4, 135.5, 135.4, 133.1, 132.8, 130.3, 130.1, 129.7, 129.7, 129.7, 128.3, 128.2, 127.7, 127.6, 127.5, 73.0, 72.3, 71.4, 66.7, 64.6, 42.2, 40.4, 33.7, 26.8, 25.8, 19.2, 18.1, 14.1, −4.4, −4.6 ppm. IR (film): $\tilde{\nu}$ = 2955, 2929, 2857, 1720, 1673, 1626, 1472, 1452, 1428, 1361, 1314, 1270, 1176, 1110, 1026, 983, 938, 836, 775, 739, 701 cm^{-1}. MS (EI) *m/z* (%) = 721 (3), 599 (8), 492 (12), 435 (4), 361 (4), 303 (11), 280 (10), 279 (45), 174 (15), 173 (100), 171 (10), 135 (15), 131 (71), 117 (8), 105 (27), 101 (13), 91 (98), 73 (24). HRMS (ESIpos): *m/z*: calcd for $C_{47}H_{62}O_6Si_2Na$: 801.3977; found: 801.3976.



(6*R*,11*R*,12*R*,*E*)-12-(2-(Benzyloxy)ethyl)-2,2,11,14,14,15,15-heptamethyl-8-oxo-3,3-diphenyl-4,13-dioxa-3,14-disilahexadec-9-en-6-yl 4-nitrobenzoate (32c). Obtained from compound **31c** (31.0 mg, 35.8 µmol) following the general procedure as a colorless oil (21.2 mg, 73%). $[\propto]_D^{20}$ = +8.8 (c = 0.94, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 8.4 Hz, 2H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.59 (ddt, *J* = 8.1, 2.7, 1.3 Hz, 4H), 7.42 – 7.25 (m, 11H), 6.95 (dd, *J* = 16.1, 6.8 Hz, 1H), 6.09 (dd, *J* = 16.1, 1.5 Hz, 1H), 5.68 (td, *J* = 6.4, 3.2 Hz, 1H), 4.48 (d, *J* = 11.9 Hz, 1H), 4.43 (d, *J* = 11.8 Hz, 1H), 3.92 (d, *J* = 4.0 Hz, 2H), 3.84 (dt, *J* = 8.3, 4.2 Hz, 1H), 3.49 (t, *J* = 6.5 Hz, 2H), 3.09 (d, *J* = 6.4 Hz, 2H), 2.55 – 2.44 (m, 1H), 1.75 (dtd, *J* = 14.3, 7.1, 4.2 Hz, 1H), 1.64 – 1.63 (m, 1H), 1.01 (d, *J* = 8.0 Hz, 12H), 0.85 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ =

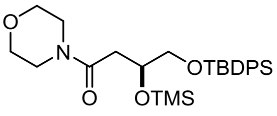
196.3, 163.7, 150.5, 150.5, 138.3, 135.7, 135.5, 135.4, 133.0, 133.0, 130.7, 129.9, 129.8, 129.8, 128.4, 127.8, 127.7, 127.7, 127.6, 127.6, 123.4, 73.0, 72.3, 72.3, 66.8, 64.5, 42.3, 40.2, 33.7, 26.8, 25.8, 19.2, 18.1, 14.1, −4.4, −4.6 ppm. IR (film): $\tilde{\nu}$ = 2954, 2929, 2857, 1726, 1672, 1528, 1471, 1462, 1348, 1318, 1270, 1188, 1101, 1029, 1014, 982, 939, 871, 836, 775, 737, 719, 700, 614 cm^{-1}. MS (ESIpos) *m/z* (%) = 846.5 (100 (M+Na^+)). HRMS (ESIpos): *m/z*: calcd for $C_{47}H_{61}N_1O_8Si_2Na$: 846.3828; found: 846.3824.

(*R*)-4-((*tert*-Butyldiphenylsilyl)oxy)-1-morpholino-3-((trimethylsilyl)oxy)butan-1-one (37).

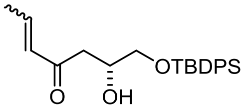


According to a modified protocol from Jacobsen et. al.,[7] a flame-dried two-necked round-bottom flask was charged with $Co_2(CO)_8$ (274 mg, 0.8 mmol). The flask was evacuated (1 x 10^{-1} mbar)[8] and backfilled with CO (1 atm, from a balloon, 3 cycles). Dry EtOAc (15 mL) was introduced and the suspension stirred for 10 min, after which freshly distilled *N*-trimethylsilyl morpholine (2.66 mL, 15.0 mmol) and silylated epoxide **29** (3.12 g, 10.0 mmol) were added via syringe. The brown mixture was vigorously stirred under a CO atmosphere (balloon) for 15 h, before it was concentrated. The residue was quickly purified by flash chromatography (hexanes/EtOAc 5:1 to 4:1) to yield the desired morpholine amide as a colorless oil (3.70 g, 74%). $[\propto]_D^{20}$ = +21.1 (c = 0.915, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (m, 4H), 7.43 – 7.34 (m, 6H), 4.25 (ddt, *J* = 8.5, 5.9, 4.3 Hz, 1H), 3.63 (m, 7H), 3.56 – 3.44 (m, 3H), 2.62 (dd, *J* = 14.4, 4.0 Hz, 1H), 2.53 (dd, *J* = 14.4, 8.3 Hz, 1H), 1.04 (s, 9H), 0.02 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 135.6, 135.6, 133.4, 129.7, 129.7, 127.7, 127.7, 70.7, 67.8, 66.9, 66.7, 46.5, 41.9, 37.5, 26.8, 26.8, 19.2, 0.1 ppm. IR (film): $\tilde{\nu}$ = 2958, 2930, 2857, 1644, 1460, 1428, 1249, 1186, 1111, 1070, 1033, 959, 840, 824, 741, 701, 612 cm^{-1}. MS (EI) *m/z* (%) = 484 (11), 444 (13), 443 (36), 442 (100), 364 (23), 271 (13), 230 (6), 193 (14), 135 (5), 114 (7), 73 (4). HRMS (ESIpos): *m/z*: calcd for $C_{27}H_{41}NO_4Si_2Na$: 522.2466; found: 522.2465.

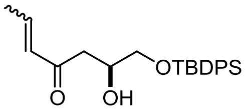
(*S*)-4-((*tert*-Butyldiphenylsilyl)oxy)-1-morpholino-3-((trimethylsilyl)oxy)butan-1-one (*ent*-37).



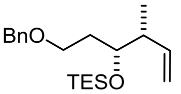
Prepared analogously from epoxide *ent*-**29** (3.12 g, 10.0 mmol) as a pale yellow oil (3.67 g, 74%).



(*R*)-7-((*tert*-Butyldiphenylsilyl)oxy)-6-hydroxyhept-2-en-4-one (39). A solution of propenylmagnesium bromide **38** (0.5 M in THF, 8.6 mL, 4.30 mmol) was added dropwise over 10 min at 0 °C to a solution of amide **37** (565 mg, 1.131 mmol) in THF (9 mL) and the resulting mixture was stirred at 0 °C for 2 h. The mixture was cooled to −78 °C and slowly transferred via canula into a vigorously stirred aq. solution of HCl (0.75 M, 130 mL). The reaction flask was rinsed with EtOAc (2 x 10 mL), which was also transferred to the aqueous acid layer. After stirring for 15 min at ambient temperature, EtOAc (20 mL) was added, the phases were separated and the aqueous phase extracted with EtOAc (3 x 40 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 9:1 to 7.5:1 to 6:1) to give the desired enone as an inconsequential mixture of olefin isomers (*E*/*Z* = 2:1, 360 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$, only the peaks assigned to the major isomer are given): δ = 7.70 – 7.57 (m, 4H), 7.47 – 7.31 (m, 6H), 6.84 (dq, *J* = 15.7, 6.8 Hz, 1H), 6.11 (dq, *J* = 15.8, 1.6 Hz, 1H), 4.25 – 4.14 (m, 1H), 3.65 (d, *J* = 5.5 Hz, 2H), 3.02 (d, *J* = 4.1 Hz, 1H), 2.72 (d, *J* = 5.9 Hz, 2H), 1.89 (dd, *J* = 6.9, 1.7 Hz, 3H), 1.05 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ only the peaks assigned to the major isomer are given): δ = 199.6, 143.7, 135.5, 135.5, 133.2, 133.1, 132.3, 129.8, 127.7, 68.5, 67.0, 42.8, 26.8, 19.2, 18.3 ppm. IR (film): $\tilde{\nu}$ = 3462, 3071, 2930, 2587, 1680, 1663, 1628, 1472, 1428, 1362, 1188, 1112, 969, 823, 741, 702 cm^{-1}. MS (ESIpos) *m/z* (%) = 405.2 (100 (M+Na$^+$)), 787.3 (85 ((2M+Na$^+$). HRMS (ESIpos): *m/z*: calcd for $C_{23}H_{30}O_3SiNa$: 405.1856; found: 405.1856.

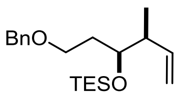


(*S*)-7-((*tert*-Butyldiphenylsilyl)oxy)-6-hydroxyhept-2-en-4-one (*ent*-39). Prepared analogously from morpholine amide *ent*-**37** (3.67 g, 10.0 mmol) as a pale yellow oil (*E*/*Z* = 2:1, 2.21 g, 79%).



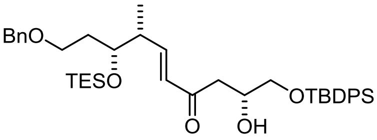
(((3*R*,4*R*)-1-(Benzyloxy)-4-methylhex-5-en-3-yl)oxy)triethylsilane (40). NEt_3 (0.951 mL, 6.86 mmol) and TESCl (1.05 mL, 6.29 mmol) were added via syringe at 0 °C to a solution of alcohol **25** (1.26 g, 5.72 mmol) in CH_2Cl_2 (28.6 mL). DMAP (34.9 mg, 0.286 mmol) was then introduced and the mixture stirred for 90 min at 0 °C and for another 30 min at RT before the reaction was quenched with sat. NH_4Cl-solution. The aqueous phase was extracted with CH_2Cl_2 (3 x 30 mL), the combined extracts were washed with brine, dried over Na_2SO_4 and concentrated. Purification of the residue by flash chromatography (hexanes/EtOAc 35:1) yielded the target silyl ether as a colorless oil (1.72 g, 90%). $[\propto]_D^{20}$ = +38.6 (c = 1.13, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 – 7.24 (m, 5H), 5.86 (ddd, *J* = 17.3, 10.5, 6.6 Hz, 1H), 5.03 – 4.95 (m, 2H), 4.50 (d, *J* = 11.6 Hz, 1H), 4.45 (d, *J* = 11.8 Hz, 1H), 3.74 (dt, *J* = 8.2, 4.3, 4.2 Hz, 1H), 3.53 (t, *J* = 6.7 Hz, 2H), 2.35 – 2.22 (m, 1H), 1.83 – 1.70 (m, 1H), 1.70 – 1.59 (m, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.94 (dd, *J* = 7.7 Hz, 9H), 0.58 (q, *J* = 8.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.8, 138.6, 128.3, 127.7, 127.5, 114.3, 73.2, 73.0, 67.2, 43.4, 33.7, 15.0, 7.0, 5.2 ppm. IR (film): $\tilde{\nu}$ = 2954, 2911, 2876, 1455, 1414, 1363, 1238, 1091, 1004, 911, 840, 725, 695 cm^{-1}. MS (EI) *m/z* (%) = 305 (8), 279 (17), 173 (33), 159 (6), 117 (9), 115 (10), 91 (100), 87 (9), 59 (5). HRMS (ESIpos): *m/z*: calcd for $C_{20}H_{34}O_2SiNa$: 357.2220; found: 357.2222.

(((3*S*,4*S*)-1-(Benzyloxy)-4-methylhex-5-en-3-yl)oxy)triethylsilane (*ent*-40).

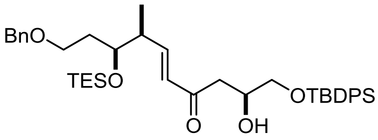


Prepared analogously from alcohol *ent*-**25** (1.70 g, 7.72 mmol) as a colorless oil (2.46 g, 91%).

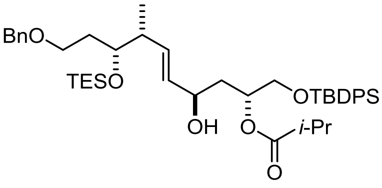
(6*R*,11*R*,12*R*,*E*)-12-(2-(Benzyloxy)ethyl)-14,14-diethyl-6-hydroxy-2,2,11-trimethyl-3,3-diphenyl-4,13-dioxa-3,14-disilahexadec-9-en-8-one (41). A flame-dried two necked round-bottom flask equipped with a reflux condenser and a septum was charged with a solution of olefin **40** (495 mg, 1.48 mmol) in CH_2Cl_2 (15 mL). Zhan-catalyst 1B **48** (39.4 mg, 53.7 µmol) was added and the resulting mixture was heated to 45 °C while a solution of enone **39** (514 mg, 1.34 mmol) in CH_2Cl_2 (2 mL) was added dropwise through the septum over the course of 1 h via syringe pump. After 16 h, the mixture was cooled to RT, another batch of Zhan-catalyst 1B **48** (19.7 mg, 26.9 µmol) was added and stirring continued at 45 °C. This procedure was repeated once again after additonal stirring for 12 h. After an overall reaction time of 48 h, the mixture was concentrated and the residue purified by flash chromatography (hexanes/EtOAc 14:1 to 12:1 to 9:1) to yield the title compound as a pale orange oil (716 mg, 79%). $[\alpha]_D^{20}$ = +41.2 (c = 0.96, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 – 7.60 (ddd, *J* = 7.9, 3.8, 1.7 Hz, 4H), 7.44 – 7.34 (m, 6H), 7.34 – 7.25 (m, 5H), 6.92 (dd, *J* = 16.2, 6.8 Hz, 1H), 6.06 (dd, *J* = 16.2, 1.5 Hz, 1H), 4.48 (d, *J* = 11.9 Hz, 1H), 4.43 (d, *J* = 11.9 Hz, 1H), 4.25 – 4.16 (m, 1H), 3.85 (dt, *J* = 8.3, 4.2 Hz, 1H), 3.64 (dd, *J* = 5.5, 1.5 Hz, 2H), 3.55 – 3.43 (m, 2H), 3.04 (d, *J* = 3.9 Hz, 1H), 2.82 – 2.66 (m, 2H), 2.53 – 2.41 (m, 1H), 1.79 – 1.69 (m, 1H), 1.62 – 1.52 (m, 1H), 1.05 (s, 9H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.57 (q, *J* = 8.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.8, 150.5, 138.4, 135.5, 135.5, 133.2, 133.2, 130.4, 129.8, 128.3, 127.7, 127.7, 127.6, 73.0, 72.4, 68.5, 67.1, 66.8, 42.6, 42.6, 33.9, 26.9, 19.3, 14.2, 7.0, 5.1 ppm. IR (film): $\tilde{\nu}$ = 3512, 3071, 2955, 2932, 2875, 1664, 1624, 1456, 1427, 1362, 1238, 1186, 1112, 1007, 823, 739, 701 cm^{-1}. MS (ESIpos) *m/z* (%) = 697.5 (100 (M+Na$^+$)). HRMS (ESIpos): *m/z*: calcd for $C_{40}H_{58}O_5Si_2Na$: 697.3715; found: 697.3720.



(6*S*,11*S*,12*S*,*E*)-12-(2-(Benzyloxy)ethyl)-14,14-diethyl-6-hydroxy-2,2,11-trimethyl-3,3-diphenyl-4,13-dioxa-3,14-disilahexadec-9-en-8-one (*ent*-41). Prepared analogously from *ent*-**40** (2.25 g, 6.43 mmol) and enone *ent*-**39** (2.05 g, 5.36 mmol) as a pale yellow oil (2.65 g, 73%) along with recovered enone (255 mg, 12%).

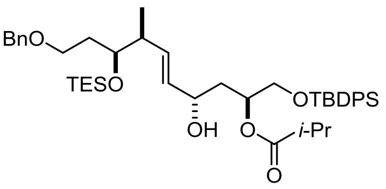


(6*R*,8*R*,11*R*,12*R*,*E*)-12-(2-(Benzyloxy)ethyl)-14,14-diethyl-8-hydroxy-2,2,11-trimethyl-3,3-diphenyl-4,13-dioxa-3,14-disilahexadec-9-en-6-yl isobutyrate (42). A freshly prepared solution of SmI_2 (0.096 M in THF, 3.80 mL, 0.363 mmol) was slowly added at –50 °C alongside the cold wall of the flask to a solution of enone **41** (700 mg, 1.04 mmol) and freshly distilled isobutyraldehyde (473 µL, 5.19 mmol) in degassed THF (9.4 mL). The mixture was stirred for 1 h at –50 °C before it was poured into sat. aq. $NaHCO_3$ solution (65 mL). The mixture was diluted with EtOAc (40 mL overall) and vigorously stirred until it reached ambient temperature. The

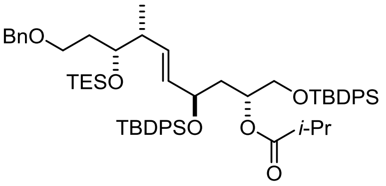


phases were separated and the aqueous layer was extracted with EtOAc (3 x 40 mL). The combined extracts were washed with brine (60 mL), dried over Na_2SO_4 and concentrated. During concentration, a small amount of SiO_2 was added and the crude product loaded on a silica gel column, from which the title compound was eluted with hexanes/EtOAc (12:1 to 9:1); colorless oil (598 mg, 78%). $[\propto]_D^{20}$ = +27.2 (c = 1.32, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 – 7.61 (m, 4H), 7.44 – 7.27 (m, 11H), 5.69 (ddd, *J* = 15.8, 6.9, 1.2 Hz, 1H), 5.43 (ddd, *J* = 15.6, 6.2, 1.3 Hz, 1H), 5.16 (ddt, *J* = 9.4, 5.5, 4.1 Hz, 1H), 4.47 (d, *J* = 11.9 Hz, 1H), 4.43 (d, *J* = 11.9 Hz, 1H), 3.99 (ddd, *J* = 9.8, 6.3, 3.5 Hz, 1H), 3.71 (m, 3H), 3.50 (dd, *J* = 7.4, 5.9 Hz, 2H), 2.73 (br s, 1H), 2.56 (hep, *J* = 7.0 Hz, 1H), 2.33 – 2.21 (m, 1H), 1.77 – 1.53 (m, 4H), 1.18 (d, *J* = 7.2 Hz, 3H), 1.16 (d, *J* = 7.2 Hz, 3H), 1.02 (s, 9H), 0.95 – 0.89 (m, 12H), 0.56 (q, *J* = 8.1 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.0, 138.5, 135.6, 135.5, 133.3, 133.3, 133.2, 131.8, 129.8, 129.7, 128.3, 127.7, 127.7, 127.5, 73.2, 73.0, 71.9, 68.3, 67.2, 65.7, 42.0, 39.0, 34.2, 33.7, 26.7, 19.2, 19.2, 19.0, 15.3, 7.0, 5.2 ppm. IR (film): $\tilde{\nu}$ = 3502, 2956, 2932, 2875, 1732, 1457, 1428, 1388, 1362, 1239, 1196, 1160, 1111, 1007, 975, 823, 738, 701, 612 cm^{-1}. MS (ESIpos) *m/z* (%) = 769.5 (100 (M+Na$^+$)). HRMS (ESIpos): *m/z*: calcd for $C_{44}H_{66}O_6Si_2Na$: 769.4290; found: 769.4291.

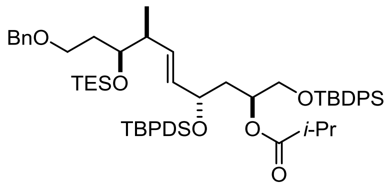
(6*S*,8*S*,11*S*,12*S*,*E*)-12-(2-(Benzyloxy)ethyl)-14,14-diethyl-8-hydroxy-2,2,11-trimethyl-3,3-diphenyl-4,13-dioxa-3,14-disilahexadec-9-en-6-yl isobutyrate (*ent*-42). Prepared analogously from *β*-hydroxy ketone *ent*-**41** (2.30 g, 3.41 mmol) as a colorless oil (1.88 g, 74%).



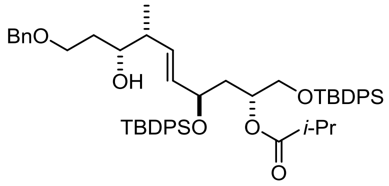
(6*R*,8*R*,11*R*,12*R*,*E*)-12-(2-(Benzyloxy)ethyl)-8-((*tert*-butyldiphenylsilyl)oxy)-14,14-diethyl-2,2,11-trimethyl-3,3-diphenyl-4,13-dioxa-3,14-disilahexadec-9-en-6-yl isobutyrate (42a). TBDPSCl (284 µL, 1.09 mmol) was added at 0 °C to a solution of the homoallylic alcohol **42** (584 mg, 0.782 mmol) and imidazole (90.5 mg, 1.33 mmol) in CH_2Cl_2 (5.2 mL). After 5 min, the mixture was allowed to reach ambient temperature and stirring was continued for 17 h before the reaction was quenched with sat. NH_4Cl solution (25 mL). The aqueous phase was extracted with CH_2Cl_2 (4 x 20 mL) and the combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 39:1) to afford the title compound as a colorless syrup (671 mg, 87%). $[\propto]_D^{20}$ = +36.7 (c = 1.00, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 – 7.60 (m, 8H), 7.44 – 7.25 (m, 17H), 5.34 (dd, *J* = 15.9, 6.8 Hz, 1H), 5.27 (dd, *J* = 15.8, 5.5 Hz, 1H), 5.20 – 5.10 (m, 1H), 4.51 – 4.46 (d, *J* = 11.9 Hz, 1H), 4.42 (d, *J* = 11.9 Hz, 1H), 4.14 (td, *J* = 7.5, 5.3 Hz, 1H), 3.67 – 3.53 (m, 3H), 3.49 – 3.36 (m, 2H), 2.43 (hep, *J* = 7.0 Hz, 1H), 2.05 – 1.96 (m, 1H), 1.89 (ddd, *J* = 14.0, 7.7, 4.9 Hz, 1H), 1.77 (ddd, *J* = 14.1, 7.9, 5.3 Hz, 1H), 1.62 – 1.52 (m, 1H), 1.45 – 1.34 (m, 1H), 1.10 (d, *J* = 6.9 Hz, 6H), 1.02 (s, 18H), 0.89 (t, *J* = 7.9 Hz, 9H), 0.73 (d, *J* = 6.9 Hz, 3H), 0.52 (q, *J* = 7.9 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$):



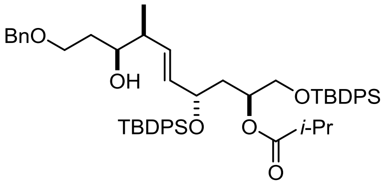
δ = 176.1, 138.7, 136.0, 135.9, 135.6, 135.5, 134.7, 134.0, 133.5, 133.5, 133.3, 129.6, 129.6, 129.4, 129.2, 128.3, 127.6, 127.6, 127.4, 127.2, 73.0, 72.9, 72.0, 71.4, 67.2, 65.2, 41.7, 39.8, 34.1, 33.5, 27.0, 26.8, 19.2, 19.0, 18.9, 15.0, 7.0, 5.1 ppm. IR (film): $\tilde{\nu}$ = 2956, 2932, 2875, 2858, 1734, 1471, 1427, 1387, 1361, 1259, 1191, 1157, 1105, 1007, 977, 822, 736, 698 cm^{-1}. MS (EI) *m/z* (%) = 927 (2), 820 (2), 561 (2), 509 (6), 493 (7), 469 (4), 467 (4), 377 (5), 322 (3), 319 (3), 280 (22), 279 (97), 269 (26), 199 (16), 174 (15), 173 (100), 171 (14), 135 (22), 131 (44), 91 (57), 73 (16). HRMS (ESIpos): *m/z*: calcd for $C_{60}H_{84}O_6Si_3Na$: 1007.5468; found: 1007.5473.



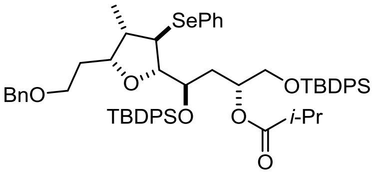
(6*R*,8*R*,11*R*,12*R*,*E*)-12-(2-(Benzyloxy)ethyl)-8-((*tert*-butyldiphenylsilyl)oxy)-14,14-diethyl-2,2,11-trimethyl-3,3-diphenyl-4,13-dioxa-3,14-disilahexadec-9-en-6-yl isobutyrate (*ent*-42a). Prepared analogously from alcohol *ent*-**42** (1.82 g, 2.44 mmol) as a colorless oil (1.96 g, 82%).



(6*R*,8*R*)-8-((3*R*,4*R*,*E*)-6-(Benzyloxy)-4-hydroxy-3-methylhex-1-en-1-yl)-2,2,11,11-tetramethyl-3,3,10,10-tetraphenyl-4,9-dioxa-3,10-disiladodecan-6-yl isobutyrate (43). Camphorsulfonic acid (47.7 mg, 0.205 mmol) was added at 0 °C to a solution of the tris-silylether **42a** (675 mg, 0.685 mmol) in CH_2Cl_2/MeOH (2:1, 12.6 mL). The resulting mixture was stirred for 90 min before the reaction was carefully quenched with sat. $NaHCO_3$ (40 mL) solution. After extraction with CH_2Cl_2 (3 x 40 mL), the combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated to give a colorless oil, which was purified by flash chromatography (hexanes/EtOAc 8:1) to give the title compound as a colorless oil (576 mg, 97%). $[\propto]_D^{20}$ = +22.9 (c = 1.32, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 – 7.57 (m, 8H), 7.43 – 7.25 (m, 18H), 5.35 (dd, *J* = 15.5, 7.9 Hz, 1H), 5.14 – 5.06 (m, 1H), 4.98 (dd, *J* = 15.5, 7.9 Hz, 1H), 4.45 (s, 2H), 4.08 (q, *J* = 7.0 Hz, 1H), 3.57 (d, *J* = 4.8 Hz, 2H), 3.51 – 3.37 (m, 2H), 3.30 (br t, 1H), 2.51 – 2.37 (m, 2H), 1.91 (ddd, *J* = 11.5, 7.4, 4.6 Hz, 2H), 1.73 (dt, *J* = 13.6, 6.5 Hz, 1H), 1.44 – 1.29 (m, 3H), 1.09 (d, *J* = 6.9 Hz, 6H), 0.99 (d, *J* = 7.7 Hz, 18H), 0.79 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 176.2, 138.0, 135.9, 135.9, 135.6, 135.5, 134.6, 134.2, 133.6, 133.4, 133.4, 132.8, 129.6, 129.6, 129.6, 129.3, 128.4, 127.7, 127.6, 127.5, 127.3, 74.0, 73.3, 72.0, 69.3, 65.2, 42.3, 39.7, 34.1, 33.5, 26.9, 26.7, 19.2, 19.0, 19.0, 15.0 ppm. IR (film): $\tilde{\nu}$ = 3511, 2960, 2931, 2858, 1734, 1472, 1427, 1389, 1361, 1260, 1193, 1158, 1111, 1082, 976, 822, 739, 701 cm^{-1}. MS (EI) *m/z* (%) = 527 (5), 467 (8), 393 (28), 363 (27), 319 (11), 271 (12), 270 (18), 269 (81), 209 (11), 200 (13), 199 (71), 197 (19), 135 (48), 108 (21), 91 (100), 81 (11), 43 (15). HRMS (ESIpos): *m/z*: calcd for $C_{54}H_{70}O_6Si_2Na$: 870.4711; found: 870.4715.

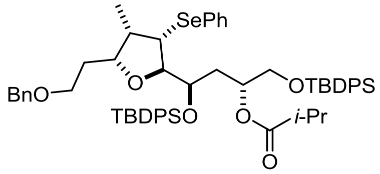


(6*R*,8*R*)-8-((3*R*,4*R*,*E*)-6-(Benzyloxy)-4-hydroxy-3-methylhex-1-en-1-yl)-2,2,11,11-tetramethyl-3,3,10,10-tetraphenyl-4,9-dioxa-3,10-disiladodecan-6-yl isobutyrate (*ent*-43). Prepared analogously from the tris-silylether *ent*-**42a** (1.93 g, 1.96 mmol) as a colorless oil (1.69 g, 99%).

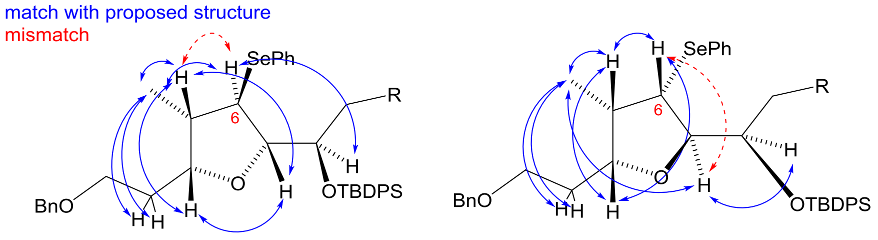


(6*R*,8*R*)-8-((2*S*,3*R*,4*S*,5*R*)-5-(2-(Benzyloxy)ethyl)-4-methyl-3-(phenylselanyl) tetrahydrofuran-2-yl)-2,2,11,11-tetramethyl-3,3,10,10-tetraphenyl-4,9-dioxa-3,10-disiladodecan-6-yl isobutyrate (44). According to a modified protocol from Denmark,[9] a solution of alcohol **43** (574 mg, 0.659 mmol) in CH_2Cl_2 (10 mL) was prepared and cooled to –40 °C. *N*-(Phenylseleno)phthalimide (239 mg, 0.791 mmol) followed by a solution of triphenylphosphine sulfide (23.3 mg, 79.1 µmol) and trifluoroacetic acid (56.7 µL, 0.791 mmol) in CH_2Cl_2 (1 mL) were added via syringe over 5 min. After complete addition, the mixture was allowed to warm to –20 °C and stirring was continued for 3 h before the mixture was poured into a stirred emulsion of sat. aq. $NaHCO_3$ solution and CH_2Cl_2 (1:1, 40 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 15 mL), the combined organic extracts were dried over Na_2SO_4 and concentrated. ^1H NMR and HPLC analysis of the crude mixture revealed a d.r. of 14:1. The residue was purified by flash chromatography (hexanes/EtOAc 100:0 to 49:1 to 29:1 to 24:1) to give the cyclized product as a colorless oil (560 mg, 83% yield, 14:1 d.r.). An analytically pure sample was obtained by preparative HPLC (Triart C18 5 µm, 12 nm, 150x30 mm, 100% MeCN, 35 °C, 35bar, 35mL/min). $[\propto]_D^{20}$ = +1.1 (c = 0.93, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.69 – 7.66 (m, 2H), 7.64 – 7.60 (m, 6H), 7.44 – 7.24 (m, 19H), 7.23 – 7.16 (m, 3H), 5.15 – 5.09 (m, 1H), 4.32 (s, 2H), 3.85 (ddd, *J* = 8.2, 5.5, 5.0 Hz, 1H), 3.68 (ddd, *J* = 6.9, 6.9, 3.8 Hz, 1H), 3.63 (dd, *J* = 6.5, 6.5 Hz, 1H), 3.52 (dd, *J* = 10.9, 4.1 Hz, 1H), 3.45 (dd, *J* = 10.9, 5.4 Hz, 1H), 3.14 – 3.09 (m, 2H), 2.93 (dd, *J* = 6.3, 3.5 Hz, 1H), 2.40 (hept, *J* = 7.0 Hz, 1H), 2.16 (ddd, *J* = 14.6, 9.8, 3.9 Hz, 1H), 2.07 (ddq, *J* = 12.4, 7.1, 3.6 Hz, 1H), 1.73 (ddd, *J* = 14.7, 7.1, 2.8 Hz, 1H), 1.49 – 1.44 (m, 2H), 1.07 (d, *J* = 7.0 Hz, 3H), 1.05 (d, *J* = 7.0 Hz, 3H), 1.01 (s, 9H), 0.98 (s, 9H) 0.49 (d, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 176.0, 138.7, 136.1, 135.8, 135.6, 135.6, 134.4, 134.4, 133.6, 133.4, 133.3, 129.6, 129.6, 129.3, 129.2, 129.1, 128.3, 127.7, 127.7, 127.6, 127.4, 127.3, 127.1, 85.8, 72.9, 72.7, 71.6, 67.9, 65.3, 49.6, 44.6, 36.1, 34.1, 30.6, 29.7, 27.1, 26.7, 19.7, 19.2, 19.0, 18.8, 14.9 ppm. IR (film): $\tilde{\nu}$ = 2961, 2929, 2855, 1733, 1472, 1427, 1361, 1260, 1192, 1111, 1021, 821, 802, 738, 701 cm^{-1}. MS (EI) *m/z* (%) = 970 (6), 969 (9), 883 (9), 882 (13), 881 (22), 880 (8), 879 (11), 805 (11), 724 (11), 723 (11), 563 (11), 467 (10), 361 (25), 349 (11), 319 (13), 296 (11), 295 (45), 270 (23), 269 (100), 241 (14), 239 (34), 200 (13), 199 (73), 197 (30), 136 (12), 135 (93), 91 (84), 43 (13). HRMS (ESIpos): *m/z*: calcd for $C_{60}H_{74}O_6Si_2SeNa$: 1049.4081; found: 1049.4072.

(6*R*,8*R*)-8-((2*R*,3*S*,4*S*,5*R*)-5-(2-(Benzyloxy)ethyl)-4-methyl-3-(phenylselanyl) tetrahydrofuran-2-yl)-2,2,11,11-tetramethyl-3,3,10,10-tetraphenyl-4,9-dioxa-3,10-disiladodecan-6-yl isobutyrate.



Obtained as the minor isomer by preparative HPLC (conditions see above) as a colorless oil. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.70 – 7.67 (m, 3H), 7.63 – 7.60 (m, 2H), 7.60 – 7.56 (m, 4H), 7.53 – 7.49 (m, 1H), 7.40 – 7.24 (m, 17H), 7.23 – 7.14 (m, 3H), 5.06 – 4.99 (m, 1H), 4.48 (d, *J* = 13.8 Hz, 2H), 4.04 (ddd, *J* = 7.9, 4.1, 1.4, 1H), 3.98 (ddd, *J* = 8.8, 4.5, 4.5 Hz, 1H), 3.92 (dd, *J* = 9.9, 1.3 Hz, 1H), 3.67 (dd, *J* = 9.9, 6.2 Hz, 1H), 3.59 (ddd, *J* = 9.1, 7.7, 5.4 Hz, 1H), 3.53 (dd, *J* = 11.0, 3.9 Hz, 1H), 3.50 (dd, *J* = 9.2, 7.2 Hz, 1H), 3.41 (dd, *J* = 10.9, 5.2 Hz, 1H), 2.27 (hept, *J* = 7.0 Hz, 1H), 2.23 – 2.16 (m, 1H), 1.99 (ddd, *J* = 14.5, 9.9, 4.3 Hz, 1H), 1.84 – 1.76 (m, 2H), 1.73 (ddd, *J* = 13.7, 7.3, 5.0 Hz, 1H), 1.01 (s, 9H) 1.00 (d, *J* = 7.0 Hz, 3H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.97 (s, 9H), 0.86 (d, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ = 176.1, 138.5, 136.1, 136.0, 135.6, 135.5, 134.2, 133.5, 133.4, 133.4, 133.1, 132.5, 130.9, 130.6, 129.6, 129.6, 129.4, 129.0, 128.8, 128.4, 127.7, 127.6, 127.6, 127.5, 127.3, 127.0, 83.3, 78.7, 73.0, 71.9, 71.6, 68.0, 65.3, 48.1, 40.2, 34.0, 33.6, 31.9, 27.1, 26.7, 19.4, 19.2, 19.0, 18.9, 11.6 ppm. IR (film): $\tilde{\nu}$ = 2962, 2930, 2854, 1732, 1472, 1427, 1360, 1260, 1192, 1110, 1021, 823, 799, 738, 701 cm^{-1}. MS (EI) *m/z* (%) = 970 (6), 969 (9), 883 (10), 882 (14), 881 (22), 880 (8), 879 (11), 805 (11), 724 (11), 723 (11), 563 (11), 467 (11), 361 (25), 349 (11), 319 (13), 296 (12), 295 (47), 270 (23), 269 (100), 241 (14), 239 (34), 200 (13), 199 (73), 197 (30), 135 (93), 91 (84). HRMS (ESIpos): *m/z*: calcd for C$_{60}$H$_{74}$O$_6$Si$_2$SeNa: 1049.4081; found: 1049.4075.



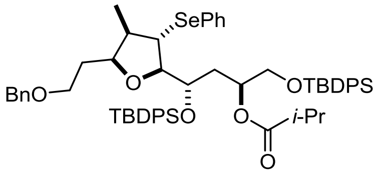
major isomer

minor isomer

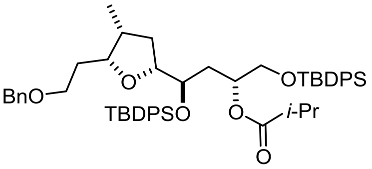
Additional support for this assignment was obtained by comparison of the chemical shift of H**6** of the two isomers. As reported in the literature,[10] the chemical shift is strongly dependent on the number of *syn*-alkyl groups, which cause an up-field shift.

Compound	# of *syn*-alkyl groups	δ (H6) /ppm	δ (Lit.) [10] /ppm
27 (major isomer)	2	2.93	2.80
minor isomer	1	3.67	3.50
-	0	-	3.90

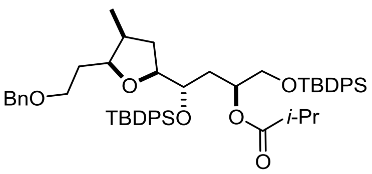
(6*S*,8*S*)-8-((2*R*,3*S*,4*R*,5*S*)-5-(2-(Benzyloxy)ethyl)-4-methyl-3-(phenylselanyl) tetrahydrofuran-2-yl)-2,2,11,11-tetramethyl-3,3,10,10-tetraphenyl-4,9-dioxa-3,10-disiladodecan-6-yl isobutyrate (*ent*-44). Prepared analogously from alcohol *ent*-**43** (1.59 g, 1.82 mmol) as a colorless oil (1.53 g, 82%).

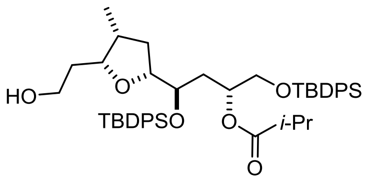


(6*R*,8*R*)-8-((2*R*,4*R*,5*R*)-5-(2-(Benzyloxy)ethyl)-4-methyltetrahydrofuran-2-yl)-2,2,11,11-tetramethyl-3,3,10,10-tetraphenyl-4,9-dioxa-3,10-disiladodecan-6-yl isobutyrate (44a). A flame-dried two-necked round-bottom flask equipped with a reflux condenser was charged with a solution of selenoether **44** (560 mg, 0.546 mmol) in degassed toluene (22 mL). (n-Bu)$_3$SnH (177 µL, 0.655 mmol) was added via syringe, followed by solid AIBN (0.9 mg, 5.5 µmol). The resulting mixture was stirred at 80 °C for 90 min under Argon, allowing the generated N_2 to evaporate. After cooling to room temperature, the mixture was concentrated and the residue purified by flash chromatography (hexanes/EtOAc 100:0 to 49:1 to 39:1 to 29:1) to yield the title compound as a sticky colorless syrup (440 mg, 93% yield, single diastereomer). $[\propto]_D^{20}$ = +34.1 (c = 0.95, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 – 7.61 (m, 8H), 7.42 – 7.25 (m, 17H), 5.24 – 5.17 (m, 1H), 4.30 (s, 2H), 3.72 – 3.63 (m, 2H), 3.61 – 3.54 (m, 3H), 3.15 – 3.03 (m, 2H), 2.36 (hep, *J* = 7.0 Hz, 1H), 2.05 (dddd, *J* = 13.3, 11.7, 6.7, 5.4 Hz, 1H), 1.94 (ddd, *J* = 12.3, 7.3, 7.2 Hz, 1H), 1.83 (ddd, *J* = 14.1, 9.1, 0.2 Hz, 1H), 1.72 (ddd, *J* = 14.4, 7.6, 2.9 Hz, 1H), 1.51 – 1.37 (m, 2H), 1.06 – 0.99 (m, 25H), 0.61 (d, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.1, 138.8, 136.2, 135.9, 135.6, 135.5, 135.0, 133.8, 133.5, 133.4, 129.6, 129.3, 129.0, 128.3, 127.7, 127.6, 127.6, 127.6, 127.4, 127.3, 127.0, 80.8, 78.3, 73.2, 72.8, 71.3, 68.2, 63.4, 36.1, 35.6, 35.2, 34.0, 31.0, 27.2, 26.7, 19.6, 19.3, 19.0, 18.8, 15.6 ppm. IR (film): $\tilde{\nu}$ = 2959, 2930, 2856, 1734, 1471, 1427, 1388, 1361, 1258, 1192, 1157, 1110, 998, 937, 822, 738, 700 cm^{-1}. MS (EI) *m/z* (%) = 814 (16), 813 (25), 726 (18), 725 (29), 563 (14), 558 (17), 557 (37), 469 (12), 319 (12), 301 (13), 296 (13), 295 (47), 271 (11), 270 (23), 269 (100), 241 (24), 239 (29), 200 (14), 199 (77), 197 (25), 163 (13), 136 (10), 135 (80), 91 (96). HRMS (ESIpos): *m/z*: calcd for $C_{54}H_{70}O_6Si_2Na$: 893.4603; found: 893.4594.

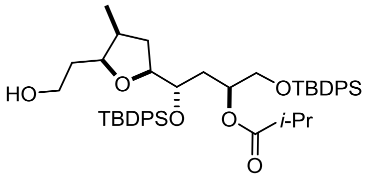


(6*S*,8*S*)-8-((2*S*,4*S*,5*S*)-5-(2-(Benzyloxy)ethyl)-4-methyltetrahydrofuran-2-yl)-2,2,11,11-tetramethyl-3,3,10,10-tetraphenyl-4,9-dioxa-3,10-disiladodecan-6-yl isobutyrate (*ent*-44a). Prepared analogously from selenoether *ent*-**44** (1.53 g, 1.49 mmol) as a colorless oil (1.26 g, 97%, single d.r.).

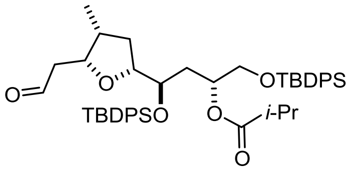




(6*R*,8*R*)-8-((2*R*,4*R*,5*R*)-5-(2-Hydroxyethyl)-4-methyltetrahydrofuran-2-yl)-2,2,11,11-tetramethyl-3,3,10,10-tetraphenyl-4,9-dioxa-3,10-disiladodecan-6-yl isobutyrate (44b). A flame-dried Schlenk tube was charged with $Pd(OH)_2/C$ (20 wt. %, 35.5 mg, 50.5 µmol). The flask was evacuated (5 x 10^{-1} mbar) and backfilled with H_2 from a balloon (two cycles). EtOH (27 mL) was added and the suspension vigorously stirred for 10 min before a solution of benzyl ether **44a** (440 mg, 0.505 mmol) in EtOAc (3 mL) was introduced. After stirring for 7.5 h under a H_2 atmosphere (balloon), the mixture was filtered through a short pad of Celite® that was carefully rinsed with EtOAc (3 x 20 mL). The combined filtrates were concentrated and the residue was purified by flash chromatography (hexanes/EtOAc 4:1) to yield the desired product as a white foam (345 mg, 88%). $[\propto]_D^{20}$ = +24.2 (c = 0.88, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.71 – 7.60 (m, 8H), 7.44 – 7.28 (m, 12H), 5.12 (ddd, *J* = 9.6, 4.8, 4.9, 3.1 Hz, 1H), 3.75 – 3.66 (m, 3H), 3.58 – 3.51 (m, 2H), 3.49 – 3.35 (m, 2H), 2.36 (hep, *J* = 7.0 Hz, 1H), 2.14 (dddd, *J* = 14.1, 14.1, 7.1, 6.9 Hz, 1H), 2.00 – 1.89 (m, 3H), 1.88 (dd, *J* = 9.6, 3.0 Hz, 1H), 1.73 (ddd, *J* = 14.3, 7.4, 3.1 Hz, 1H), 1.50 – 1.37 (m, 1H), 1.24 – 1.16 (m, 1H), 1.06 – 1.00 (m, 24H), 0.74 (d, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.1, 136.1, 135.8, 135.6, 135.5, 134.7, 133.5, 133.4, 133.3, 129.6, 129.6, 129.5, 129.2, 127.6, 127.6, 127.4, 127.2, 80.9, 80.3, 72.2, 71.2, 65.3, 61.4, 35.5, 35.3, 35.2, 34.0, 32.9, 27.1, 26.7, 19.5, 19.2, 19.0, 18.8, 15.5 ppm. IR (film): $\tilde{\nu}$ = 3487, 2960, 2930, 2857, 1735, 1472, 1428, 1388, 1259, 1193, 1158, 1112, 998, 823, 740, 702, 610 cm^{-1}. MS (EI) *m/z* (%) = 723 (12), 646 (10), 645 (18), 636 (13), 635 (23), 563 (12), 558 (20), 557 (41), 437 (16), 379 (31), 319 (13), 301 (18), 295 (34), 270 (18), 269 (82), 241 (32), 239 (32), 200 (18), 199 (97), 197 (38), 183 (12), 181 (14), 163 (14), 145 (11), 139 (12), 137 (12), 136 (14), 135 (100), 85 (29), 71 (14), 43 (26). HRMS (ESIpos): *m/z*: calcd for $C_{47}H_{64}O_6Si_2Na$: 803.4134; found: 803.4135.

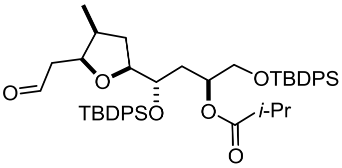


(6*S*,8*S*)-8-((2*S*,4*S*,5*S*)-5-(2-Hydroxyethyl)-4-methyltetrahydrofuran-2-yl)-2,2,11,11-tetramethyl-3,3,10,10-tetraphenyl-4,9-dioxa-3,10-disiladodecan-6-yl isobutyrate (*ent*-44b). Prepared analogously from benzyl ether *ent*-**44a** (1.25 g, 1.43 mmol) as a colorless oil (907 mg, 81%).

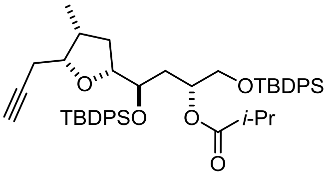


(6*R*,8*R*)-2,2,11,11-Tetramethyl-8-((2*R*,4*R*,5*R*)-4-methyl-5-(2-oxoethyl)tetrahydrofuran-2-yl)-3,3,10,10-tetraphenyl-4,9-dioxa-3,10-disiladodecan-6-yl isobutyrate (45). A solution of alcohol **44b** (341 mg, 0.437 mmol) in CH_2Cl_2 (1 mL + 2 x 0.5 mL rinse) was added dropwise at 0 °C to a solution of Dess-Martin periodinane (463 mg, 1.09 mmol) in CH_2Cl_2 (2.6 mL). After complete addition, the ice bath was removed and stirring continued at rt for 4.5 h before the reaction was quenched with sat. $Na_2S_2O_3$ and sat. $NaHCO_3$ solution (1:1, 20 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 15 mL), and the combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified flash chromatography (short column, hexanes/EtOAc 19:1) to give the desired aldehyde as a colorless sticky syrup (310 mg, 91%). $[\alpha]_D^{20}$ = +35.2 (c = 0.57, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.13 (t, *J* = 2.2 Hz, 1H), 7.70 – 7.59 (m, 8H), 7.46 – 7.25 (m, 12H), 5.18 (dddd, *J* = 9.5, 4.8, 4.7, 3.0 Hz, 1H), 3.93 (ddd, *J* = 8.8, 6.5, 4.7 Hz, 1H), 3.75 – 3.63 (m, 2H), 3.58 (d, *J* = 4.7 Hz, 2H), 2.37 (hep, *J* = 7.0 Hz, 1H), 2.25 – 2.19 (m, 1H), 2.16 (dd, *J* = 8.6, 1.8 Hz, 1H), 2.10 (ddd, *J* = 16.2, 4.9, 2.5 Hz, 1H), 2.02 – 1.92 (m, 1H), 1.83 (ddd, *J* = 14.2, 9.5, 2.5 Hz, 1H), 1.73 (ddd, *J* = 14.4, 7.6, 3.1 Hz, 1H), 1.14 – 1.09 (m, 1H), 1.05 (d, *J* = 7.0 Hz, 3H), 1.04 (d, *J* = 7.1 Hz, 3H), 1.02 (s, 9H), 0.99 (s, 9H), 0.63 (d, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.1, 176.1, 136.1, 135.7, 135.6, 135.5, 134.8, 133.7, 133.4, 133.4, 129.7, 129.4, 129.1, 127.7, 127.7, 127.3, 127.0, 81.3, 76.3, 72.9, 71.2, 65.3, 44.8, 35.8, 35.5, 35.2, 34.0, 27.1, 26.7, 19.6, 19.3, 19.0, 18.8, 15.6 ppm. IR (film): $\tilde{\nu}$ = 2959, 2929, 2856, 1729, 1472, 1427, 1388, 1240, 1192, 1158, 1111, 998, 822, 740, 701 cm^{-1}. MS (EI) *m/z* (%) = 721 (7), 635 (16), 634 (42), 633 (80), 563 (7), 377 (15), 319 (11), 295 (31), 270 (22), 269 (100), 241 (14), 239 (21), 225 (10), 200 (12), 199 (66), 197 (29), 183 (13), 179 (15), 163 (12), 136 (10), 136 (78), 43 (19). HRMS (ESIpos): *m/z*: calcd for $C_{47}H_{62}O_6Si_2Na$: 801.3977; found: 801.3977.

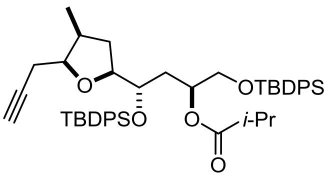
(6*S*,8*S*)-2,2,11,11-Tetramethyl-8-((2*S*,4*S*,5*S*)-4-methyl-5-(2-oxoethyl)tetrahydrofuran-2-yl)-3,3,10,10-tetraphenyl-4,9-dioxa-3,10-disiladodecan-6-yl isobutyrate (*ent*-45). Prepared analogously from alcohol *ent*-**44b** (907 mg, 1.16 mmol) as a colorless oil (847 mg, 94%).



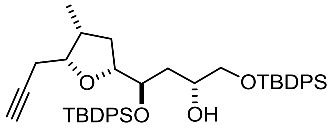
(6*R*,8*R*)-2,2,11,11-Tetramethyl-8-((2*R*,4*R*,5*R*)-4-methyl-5-(prop-2-yn-1-yl)tetrahydrofuran-2-yl)-3,3,10,10-tetraphenyl-4,9-dioxa-3,10-disiladodecan-6-yl isobutyrate (46). A flame-dried Schlenk tube was charged with dimethyl-1-diazo-2-oxopropylphosphonate (**49**) (306 mg, 1.592 mmol) and THF (8 mL). The resulting solution was cooled to –78 °C before a freshly prepared solution of NaOMe[11] (0.5 M, 3.18 mL, 1.592 mmol) was added over the course of 10 min via syringe, causing the mixture to turn intensively yellow. After stirring for 15 min at –78 °C, a precooled (–78 °C) solution of aldehyde **45** (310 mg, 0.398 mmol) in THF (5 mL + 2 x 1 mL rinse) was added slowly via canula. The reaction flask was then equipped with an Argon bubbler to allow the generated N_2 to evaporate. The mixture was slowly warmed to –50 °C, causing a heavy gas evolution. After stirring for 90 min at –50 °C, the reaction was quenched by addition of sat. NH_4Cl solution (20 mL) and H_2O (4 mL) and the aqueous layer was extracted with EtOAc (4 x 30 mL). The combined



extracts were washed with brine (35 mL), dried over Na_2SO_4 and concentrated. The orange residue was purified by flash chromatography (hexanes/EtOAc 39:1) to yield the desired alkyne as a white foam that collapsed upon storage (287 mg, 93%). $[\propto]_D^{20}$ = +19.4 (c = 1.10, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.72 – 7.57 (m, 8H), 7.48 – 7.25 (m, 12H), 5.13 (dddd, *J* = 9.5, 4.7, 4.6, 2.9 Hz, 1H), 3.78 – 3.64 (m, 3H), 3.57 (d, *J* = 4.7 Hz, 2H), 2.35 (hep, *J* = 7.0 Hz, 1H), 2.24 (ddd, *J* = 14.0, 7.0, 7.0 Hz, 1H), 2.05 – 2.00 (m, 2H), 1.97 – 1.84 (m, 2H), 1.83 (t, *J* = 2.7 Hz, 1H), 1.71 (ddd, *J* = 14.5, 7.8, 3.0 Hz, 1H), 1.27 – 1.15 (m, 1H), 1.06 – 0.98 (m, 24H), 0.81 (d, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.1, 136.1, 135.9, 135.6, 135.5, 134.7, 134.0, 133.5, 133.4, 129.6, 129.6, 129.3, 129.1, 127.7, 127.6, 127.3, 127.0, 81.6, 81.0, 79.3, 72.7, 71.2, 69.1, 65.3, 35.2, 35.1, 34.0, 27.2, 26.7, 20.6, 19.6, 19.2, 19.0, 18.8, 14.8 ppm. IR (film): $\tilde{\nu}$ = 2960, 2930, 2857, 1735, 1472, 1428, 1388, 1260, 1192, 1158, 1112, 1006, 822, 740, 702 cm^{-1}. MS (ESIpos) *m/z* (%) = 797.5 (100 ($M+Na^+$)). HRMS (ESIpos): *m/z*: calcd for $C_{48}H_{62}O_5Si_2Na$: 797.4028; found: 797.4028.

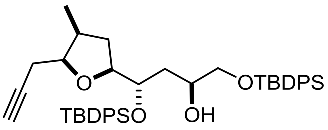


(6*S*,8*S*)-2,2,11,11-Tetramethyl-8-((2*S*,4*S*,5*S*)-4-methyl-5-(prop-2-yn-1-yl)tetrahydrofuran-2-yl)-3,3,10,10-tetraphenyl-4,9-dioxa-3,10-disiladodecan-6-yl isobutyrate (*ent*-46). Prepared analogously from aldehyde *ent*-**45** (847 mg, 1.087 mmol) as a colorless syrup (809 mg, 96%).



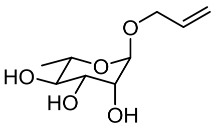
(6*R*,8*R*)-2,2,11,11-Tetramethyl-8-((2*R*,4*R*,5*R*)-4-methyl-5-(prop-2-yn-1-yl)tetrahydrofuran-2-yl)-3,3,10,10-tetraphenyl-4,9-dioxa-3,10-disiladodecan-6-ol (47). A solution of DIBAl-H in toluene (1.0 M, 1.10 mL, 1.10 mmol) was added dropwise at –78 °C to a solution of ester **46** (285 mg, 0.368 mmol) in toluene (24 mL) and the resulting mixture was stirred for 30 min at this temperature. The mixture was then poured via canula into a stirred sat. solution of Rochelle salt (150 mL), the flask was rinsed with EtOAc (2 x 20 mL) and the emulsion was vigorously stirred at ambient temperature for 4 h. The layers were separated, the aqueous phase was extracted with EtOAc (3 x 40 mL), and the combined organic extracts were dried over Na_2SO_4 and concentrated. The crude residue was purified by flash chromatography (hexanes/EtOAc 24:1 to 19:1) to give the title compound as a sticky colorless syrup (252 mg, 97%). $[\propto]_D^{20}$ = +18.2 (c = 1.07, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.75 – 7.68 (m, 4H), 7.64 – 7.59 (m, 4H), 7.45 – 7.28 (m, 12H), 4.06 (ddd, *J* = 6.7, 6.6, 4.1 Hz, 1H), 3.90 – 3.74 (m, 3H), 3.43 (d, *J* = 5.6 Hz, 2H), 2.60 (d, *J* = 3.4 Hz, 1H), 2.30 (hep, *J* = 7.1 Hz, 1H), 2.13 (ddd, *J* = 16.7, 6.0, 2.5 Hz, 1H), 2.07 (ddd, *J* = 16.6, 7.6, 2.6 Hz, 1H), 1.95 (ddd, *J* = 12.5, 7.8, 6.9 Hz, 1H), 1.86 (t, *J* = 2.7 Hz, 1H), 1.62 (ddd, *J* = 14.3, 9.3, 4.2 Hz, 1H), 1.56 (ddd, *J* = 14.4, 6.9, 3.1 Hz, 1H), 1.30 (ddd, *J* = 12.5, 9.0, 7.4 Hz, 1H), 1.06 (s, 9H), 1.03 (s, 9H), 0.87 (d, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.1, 136.0, 135.5, 135.5, 134.2, 134.1, 133.4, 133.4, 129.7, 129.4, 129.4, 127.7, 127.4, 127.2, 81.6, 81.0, 79.5, 73.2, 69.3, 68.8, 68.3, 36.6, 35.2, 35.1, 27.1, 26.8, 20.8, 19.6, 19.2, 14.8 ppm. IR (film): $\tilde{\nu}$ = 3311, 2957, 2928, 2856, 1472, 1469, 1427, 1390, 1362, 1269, 1189, 1111, 999, 822, 739, 701 cm^{-1}. MS (EI) *m/z* (%) = 570 (22), 569 (48), 491 (8), 417 (7), 319 (18), 299 (10), 259 (12), 257 (14), 241 (35), 239 (19), 223 (11), 221 (35), 200 (19), 199 (100), 197 (40), 183 (17), 181 (14), 175 (16), 163 (22), 149 (34), 139 (13), 136 (12), 135 (88), 117 (17), 93 (12), 91 (22), 79 (12). HRMS (ESIpos): *m/z*: calcd for $C_{44}H_{56}O_4Si_2Na$: 727.3609; found: 727.3610.

(6*S*,8*S*)-2,2,11,11-Tetramethyl-8-((2*S*,4*S*,5*S*)-4-methyl-5-(prop-2-yn-1-yl)tetrahydrofuran-2-yl)-3,3,10,10-tetraphenyl-4,9-dioxa-3,10-disiladodecan-6-ol (*ent*-47). Prepared analogously from ester *ent*-**46** (803 mg, 1.04 mmol) as a colorless syrup (709 mg, 97%).

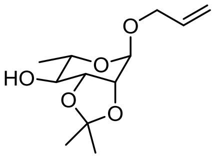


3 Synthesis of the Sugar Fragment

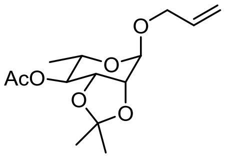
Allyl α-L-rhamnopyranoside (51). L-Rhamnose (**50**) (4.0 g, 22 mmol) was dissolved in allyl alcohol (30 mL) and conc. H_2SO_4 (0.4 mL) was added. The mixture was stirred at 100 °C for 1 h while its color changed to brown. After cooling to ambient temperature, solid K_2CO_3 (60 mg) was added and excess allyl alcohol was removed under reduced pressure. The residue was purified by flash chromatography (EtOAc) to yield the targeted compound as a highly viscous colorless oil (3.5 g, 78%). $[\propto]_D^{20}$ = –83.0 (c = 1.29, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.85 (dddd, *J* = 17.2, 10.3, 6.1, 5.2 Hz, 1H), 5.25 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.16 (dq, *J* = 10.4, 1.3 Hz, 1H), 4.77 (d, *J* = 1.5 Hz, 1H), 4.74 – 4.56 (br s, 1H), 4.39 – 4.23 (br s, 1H), 4.30 – 4.17 (br s, 1H), 4.12 (ddt, *J* = 13.0, 5.3, 1.5 Hz, 1H), 4.03 – 3.86 (m, 2H), 3.75 (dd, *J* = 9.5, 3.3 Hz, 1H), 3.61 (dq, *J* = 9.4, 6.2 Hz, 1H), 3.44 (t, *J* = 9.5 Hz, 1H), 1.27 (d, *J* = 6.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.7, 117.5, 98.9, 72.8, 71.7, 71.0, 68.2, 68.0, 17.5 ppm. IR (film): $\tilde{\nu}$ = 3371, 2977, 2915, 1450, 1422, 1383, 1265, 1128, 1046, 980, 880, 835, 808, 734, 685 cm^{-1}. MS (EI) *m/z* (%) = 131 (5), 100 (46), 87 (21), 85 (11), 83 (5), 74 (7), 73 (18), 72 (5), 71 (63), 61 (13), 60 (96), 59 (11), 58 (46), 57 (26), 56 (6), 55 (10), 45 (18), 43 (41), 42 (15), 41 (100), 39 (21), 31 (18), 29 (25), 27 (11). HRMS (ESIpos): *m/z*: calcd for $C_9H_{16}O_5Na$: 227.0889; found: 227.0891.



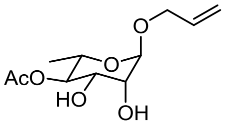
Acetal 51a. 2,2-Dimethoxypropane (4.4 mL, 35.3 mmol) was added dropwise to a stirred solution of rhamnoside **51** (3.60 g, 17.6 mmol) and *p*TsOH·H_2O (60.6 mg, 0.352 mmol) in DMF (17.6 mL) at ambient temperature. The reaction mixture was stirred for 16 h and used as a solution for the next step. An aliquot (0.5 mL) was removed from the reaction mixture and used to obtain an analytically pure sample. This aliquot was diluted with NH_4Cl solution (3 mL) and the aqueous phase was extracted with Et_2O (2 x 3 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by



flash chromatography (hexanes/EtOAc 3:1) to yield the desired compound as a colorless oil. $[\propto]_D^{20}$ = −27.1 (c = 0.67, CH_2Cl_2). ^{1}H NMR (400 MHz, C_6D_6): δ = 5.74 (dddd, *J* = 17.2, 10.4, 6.0, 5.1 Hz, 1H), 5.15 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.09 (s, 1H), 5.00 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.21 – 4.12 (m, 2H), 4.02 (ddt, *J* = 13.0, 5.2, 1.5 Hz, 1H), 3.81 – 3.71 (m, 2H), 3.50 (ddd, *J* = 9.5, 6.9, 4.2 Hz, 1H), 3.17 (d, *J* = 4.2 Hz, 1H), 1.48 (s, 3H), 1.36 (d, *J* = 6.2 Hz, 3H), 1.23 (s, 3H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 134.4, 116.9, 109.4, 96.8, 79.3, 76.5, 74.9, 67.9, 66.2, 28.2, 26.3, 17.8 ppm. IR (film): $\tilde{\nu}$ = 3461, 2986, 2936, 2922, 1454, 1382, 1372, 1243, 1219, 1171, 1139, 1106, 1072, 1050, 1021, 993, 919, 858, 818, 787, 734, 668 cm^{-1}. MS (EI) *m/z* (%) = 229 (9), 187 (8), 129 (6), 111 (5), 101 (18), 100 (100), 85 (40), 71 (31), 59 (31), 57 (10), 55 (13), 43 (29), 41 (34). HRMS (ESIpos): *m/z*: calcd for $C_{12}H_{20}O_5Na$: 267.1203; found: 267.1202.

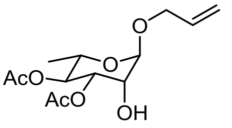


Acetylated Acetal 52. Pyridine (20 mL) and acetyl chloride (4.25 mL, 70.4 mmol) were added to the crude reaction mixture (see above) at 0 °C. The icebath was removed after 5 min and the reaction mixture was stirred at ambient temperature for further 24 h. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with aq. HCl (1 N, 30 mL), water (30 mL) and sat. $NaHCO_3$ solution (30 mL). The organic extract was dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 21:1 to 15:1 to 9:1) to give a colorless oil (3.87 g, 73% over 2 steps). $[\propto]_D^{20}$ = −23.0 (c = 0.82, CH_2Cl_2). ^{1}H NMR (400 MHz, C_6D_6): δ = 5.73 (dddd, *J* = 17.2, 10.4, 5.9, 5.1 Hz, 1H), 5.29 (dd, *J* = 10.1, 7.8 Hz, 1H), 5.15 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.10 (s, 1H), 5.00 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.26 – 4.16 (m, 2H), 3.98 (ddt, *J* = 13.1, 5.2, 1.5 Hz, 1H), 3.79 – 3.67 (m, 2H), 1.66 (s, 3H), 1.61 (s, 3H), 1.21 (d, *J* = 0.8 Hz, 3H), 1.17 (d, *J* = 6.3 Hz, 3H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 169.5, 134.3, 116.9, 109.8, 96.8, 76.6, 76.3, 74.8, 68.0, 64.5, 28.0, 26.6, 20.5, 17.2 ppm. IR (film): $\tilde{\nu}$ = 2985, 2938, 2925, 1742, 1455, 1373, 1219, 1176, 1139, 1122, 1082, 1045, 1027, 999, 923, 888, 857, 840, 814, 785, 740 cm^{-1}. MS (EI) *m/z* (%) = 271 (28), 229 (15), 169 (9), 151 (7), 142 (6), 129 (7), 113 (17), 112 (50), 111 (17), 101 (15), 100 (89), 85 (40), 83 (26), 82 (15), 71 (10), 59 (11), 43 (100), 41 (34). HRMS (ESIpos): *m/z*: calcd for $C_{14}H_{22}O_6Na$: 309.1309; found: 309.1309.

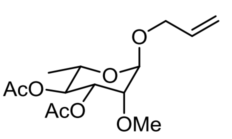


Monoacetylated Diol 53. Compound **52** (2.30 g, 7.63 mmol) was dissolved in 90% AcOH (15 mL) and the resulting solution stirred at 110 °C for 1 h. After cooling back to ambient temperature, the reaction mixture was concentrated and the residue was purified by flash chromatography (hexanes/EtOAc 1:1) to yield the desired diol as a white solid (1.83 g, 97% yield). $[\propto]_D^{20}$ = −94.1 (c = 1.46, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.88 (dddd, *J* = 17.2, 10.4, 6.0, 5.1 Hz, 1H), 5.28 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.19 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.85 (d, *J* = 1.7 Hz, 1H), 4.78 (t, *J* = 9.6 Hz, 1H), 4.16 (ddt, *J* = 13.0, 5.1, 1.5 Hz, 1H), 3.98 (ddt, *J* = 13.0, 6.1, 1.4 Hz, 1H), 3.94 (dd, *J* = 3.5, 1.7 Hz, 1H), 3.88 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.80 (ddt, *J* = 9.8, 6.6, 5.9 Hz, 1H), 2.11 (s, 3H), 1.20 (d, *J* = 6.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.1, 133.6, 117.5, 98.4, 75.6, 71.0, 70.3, 68.1, 65.6, 21.0, 17.4 ppm. IR (film): $\tilde{\nu}$ = 3327, 2982, 2940, 2895, 1735, 1459, 1426, 1378, 1295, 1241, 1133, 1104, 1070, 1044, 1002, 982, 923, 834, 793, 700 cm^{-1}. MS (EI) *m/z* (%) = 189 (5), 142 (5), 131 (4), 129 (5), 116 (13), 101 (25), 100 (39), 83 (4), 71 (42), 60 (26), 43 (100), 41 (38). HRMS (ESIpos): *m/z*: calcd for $C_{11}H_{18}O_6Na$: 269.0996; found: 269.0997.

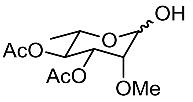
Bisacetylated alcohol 54. Diol **53** (1.00 g, 4.06 mmol) and 2-aminoethyl diphenylborinate (91.4 mg, 0.406 mmol) were dissolved in MeCN (20 mL). Diisopropylethylamine (0.880 mL, 5.28 mmol) and acetylchloride (0.319 mL, 5.28 mmol) were added dropwise at ambient temperature. The mixture was stirred for 3 hours and the reaction quenched by addition of H_2O (20 mL). The aqueous phase was then extracted with EtOAc (3 x 15 mL), the combined organic extracts were dried over Na_2SO_4 and concentrated. ^{1}H NMR analysis of the crude mixture revealed a ratio of regioisomers of 10:1. The residue was purified by flash chromatography (CH_2Cl_2/Et_2O =3:1) to give several pure fractions of the desired isomer (440 mg, 38%) along with mixed fractions (700 mg, 59% 5:1 ratio of regioisomers). $[\propto]_D^{20}$ = −83.0 (c = 1.51, CH_2Cl_2). ^{1}H NMR (400 MHz, C_6D_6): δ = 5.66 (dddd, *J* = 17.2, 10.4, 6.0, 5.1 Hz, 1H), 5.53 (dd, *J* = 10.0, 3.2 Hz, 1H), 5.49 – 5.42 (m, 1H), 5.13 (dq, *J* = 17.2, 1.7 Hz, 1H), 4.96 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.76 (d, *J* = 1.7 Hz, 1H), 4.06 (s, 1H), 3.97 – 3.86 (m, 2H), 3.70 (ddt, *J* = 13.1, 6.0, 1.4 Hz, 1H), 2.22 (d, *J* = 4.5 Hz, 1H), 1.74 (s, 3H), 1.69 (s, 3H), 1.19 (d, *J* = 6.3 Hz, 3H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 169.7, 169.6, 134.0, 117.1, 99.0, 72.3, 71.8, 69.9, 68.1, 66.8, 20.5, 20.4, 17.6 ppm. IR (film): $\tilde{\nu}$ = 3466, 2983, 2937, 1738, 1427, 1369, 1316, 1220, 1176, 1126, 1100, 1068, 1036, 984, 937, 922, 832, 801, 699, 601 cm^{-1}. MS (EI) *m/z* (%) = 231 (3), 171 (2), 142 (14), 115 (11), 113 (11), 102 (15), 100 (31), 83 (12), 82 (14), 71 (17), 60 (4), 43 (100), 41 (21). HRMS (ESIpos): *m/z*: calcd for $C_{13}H_{20}O_7Na$: 311.1101; found: 311.1099.



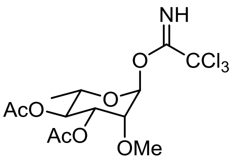
Allyl 3,4-bis-O-acetyl-2-O-methyl-α-L-rhamnopyranoside (57). Alcohol **54** (50.0 mg, 0.173 mmol) was dissolved in CH_2Cl_2 (0.7 mL) and the solution cooled to 0 °C. Aqueous HBF_4 (48%, 45.0 µL, 0.347 mmol) was added via syringe, followed by trimethylsilyldiazomethane (1.51 M in hexane, 0.70 mL, 1.0 mmol). The resulting solution was stirred for 2 hours at 0 °C, when the addition of HBF_4 (48%, 45.0 µL, 0.347 mmol) and trimethylsilyldiazomethane (1.51 M in hexane, 0.70 mL, 1.0 mmol) was repeated. After 1h, a third portion of both reagents was added and the reaction mixture stirred for one more hour. It was then carefully quenched by addition of sat. $NaHCO_3$ solution (10 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 5:1) to give the methylated compound as a colorless oil (37.0 mg, 71%). $[\propto]_D^{20}$ = –72.3 (c = 0.98, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.86 (dddd, *J* = 17.3, 10.4, 6.1, 5.1 Hz, 1H), 5.27 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.22 – 5.15 (m, 2H), 5.07 (t, *J* = 9.9 Hz, 1H), 4.82 (d, *J* = 1.8 Hz, 1H), 4.15 (ddt, *J* = 12.9, 5.1, 1.5 Hz, 1H), 3.96 (ddt, *J* = 12.9, 6.1,



1.3 Hz, 1H), 3.78 (dq, J = 9.6, 5.2 Hz, 1H), 3.59 (dd, J = 3.3, 1.9 Hz, 1H), 3.43 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H), 1.16 (d, J = 6.3 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 169.8, 133.5, 117.5, 96.4, 78.4, 71.6, 71.5, 68.1, 66.4, 59.5, 20.9, 20.7, 17.4 ppm. IR (film): $\tilde{\nu}$ = 2924, 1740, 1455, 1370, 1239, 1219, 1107, 1074, 1036, 1000, 976, 915, 835, 798 cm^{-1}. MS (EI) *m/z* (%) = 157 (8), 156 (16), 129 (18), 125 (7), 116 (28), 115 (8), 114 (17), 113 (15), 103 (5), 96 (13), 87 (22), 85 (13), 83 (12), 74 (50), 45 (9), 43 (100), 41 (20). HRMS (ESIpos): *m/z*: calcd for $C_{14}H_{22}O_7Na$: 325.1258; found: 325.1255.

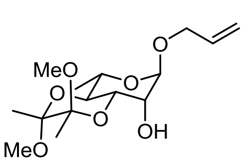


3,4-Bis-O-acetyl-2-O-methyl-α-L-rhamnopyranose (58). SeO_2 (488 mg, 4.40 mmol) was added to a solution of compound **57** (1.20 g, 3.97 mmol) and acetic acid (183 µL, 3.20 mmol) in 1,4-dioxane (10 mL) and the resulting suspension was stirred at reflux temperature for 2 h. After cooling to room temperature, the mixture was neutralized with triethylamine (0.44 mL) and concentrated under reduced pressure. The residue was purified by flash chromatography (hexanes/EtOAc 3:2) to give the desired hemiacetal as a white solid (0.891 g, 86%). $[\propto]_D^{20}$ = –42.3 (c = 0.94, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, data of the major anomer only): δ = 5.26 – 5.17 (m, 2H), 5.05 (t, J = 9.9 Hz, 1H), 4.04 (dq, J = 9.8, 6.2 Hz, 1H), 3.66 (d, J = 3.8 Hz, 1H), 3.61 (dd, J = 3.3, 1.8 Hz, 1H), 3.43 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.13 (d, J = 6.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, data of the major anomer only): δ = 170.4, 170.0, 92.0, 78.6, 71.5, 71.3, 66.3, 59.5, 20.9, 20.7, 17.4 ppm. IR (film): $\tilde{\nu}$ = 3453, 2923, 2854, 1741, 1456, 1373, 1243, 1225, 1108, 1074, 1050, 916, 797 cm^{-1}. MS (EI) *m/z* (%) = 156 (14), 129 (34), 116 (12), 115 (5), 114 (14), 113 (7), 87 (54), 85 (6), 83 (7), 74 (56), 45 (7), 43 (100), 29 (6). HRMS (ESIpos): *m/z*: calcd for $C_{11}H_{18}O_7Na$: 285.0945; found: 285.0947.

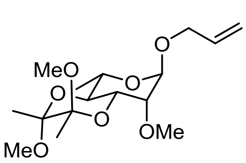


Trichloroacetimidate 59. Cl_3CCN (0.934 mL, 9.31 mmol) was added dropwise to a suspension of hemiacetal **58** (348 mg, 0.19 mmol) and Cs_2CO_3 (86.7 mg, 0.039 mmol) in CH_2Cl_2 (7.0 mL). After stirring for 3 h at room temperature, the mixture was filtered and the filtrate was evaporated. The residue was purified by flash chromatography (hexanes/EtOAc 4:1) to give the desired trichloroacetimidate as a white solid (532 mg, 98%). $[\propto]_D^{20}$ = –59.9 (c = 1.06, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62 (s, 1H), 6.25 (d, J = 2.0 Hz, 1H), 5.28 – 5.10 (m, 2H), 3.98 (dq, J = 9.0, 6.3 Hz, 1H), 3.80 (dd, J = 3.0, 2.0 Hz, 1H), 3.48 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.20 (d, J = 6.3 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.9, 169.3, 160.0, 94.6, 90.5, 76.1, 70.7, 70.2, 69.0, 59.2, 20.5, 20.4, 17.2 ppm. IR (film): $\tilde{\nu}$ = 3332, 2988, 2922, 2851, 1741, 1673, 1448, 1368, 1279, 1236, 1219, 1156, 1107, 1056, 1039, 968, 943, 926, 842, 831, 793, 734 cm^{-1}. MS (EI) *m/z* (%) = 245 (28), 184 (19), 143 (14), 142 (24), 129 (16), 125 (28), 116 (18), 113 (13), 87 (22), 74 (34), 43 (100). HMRS (ESIpos): *m/z*: calcd for $C_{13}H_{18}O_7NCl_3Na$: 428.0041; found: 428.0042.

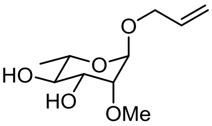
Bisacetal 55. Trimethylorthoacetate (44.8 mL, 350 mmol) and 2,3-butadione (7.7 mL, 88 mmol) were dissolved in MeOH (200 mL) and the solution treated with *p*TsOH·H_2O (1.25 g, 6.57 mmol) before the mixture was stirred at 75 °C for 24 h. After cooling to ambient temperature, a solution of rhamnoside **51** (3.02 g, 14.8 mmol) in MeOH (7 mL+7 mL rinse) was added and the mixture stirred at 75 °C overnight. After cooling to ambient temperature, NEt_3 (1.2 mL) was added to neutralize the medium prior to evaporation of the solvents under reduced pressure. The residue was purified by flash chromatography (hexanes/EtOAc 4:1) to give the desired bisacetal as a highly viscous colorless syrup (3.21 g, 72%). $[\alpha]_D^{20}$ = –182.6 (c = 0.99, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.86 (dddd, *J* = 16.8, 10.3, 6.3, 5.2 Hz, 1H), 5.24 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.15 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.79 (d, *J* = 1.5 Hz, 1H), 4.13 (ddt, *J* = 12.9, 5.2, 1.5 Hz, 1H), 4.00 – 3.87 (m, 3H), 3.78 (dq, *J* = 9.7, 6.0 Hz, 1H), 3.68 (t, *J* = 9.9 Hz, 1H), 3.22 (s, 3H), 3.19 (s, 3H), 2.46 (d, *J* = 2.3 Hz, 1H), 1.27 (s, 3H), 1.24 (s, 3H), 1.22 (d, *J* = 6.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.8, 117.4, 100.2, 99.8, 98.9, 69.9, 68.4, 68.2, 67.9, 66.5, 48.0, 47.6, 17.8, 17.6, 16.5 ppm. IR (film): $\tilde{\nu}$ = 3464, 2932, 2834, 1454, 1376, 1138, 1111, 1076, 1034, 984, 929, 915, 882, 848, 734, 701, 672 cm^{-1}. MS (EI) *m/z* (%) = 116 (7), 113 (7), 101 (33), 85 (7), 84 (100), 83 (23), 75 (16), 73 (11), 57 (5), 55 (11), 43 (34), 41 (21), 29 (7). HRMS (ESIpos): *m/z*: calcd for $C_{15}H_{27}O_7Na$: 341.1571; found: 341.1571.



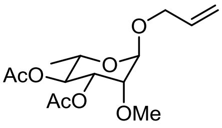
Methylated bisacetal 56. A solution of bisacetal **55** (3.17 g, 10.4 mmol) in DMF (10 mL) was slowly added at 0 °C to a suspension of NaH (748 mg, 31.2 mmol) in DMF (60 mL). The resulting mixture was stirred for about 30 min at 0 °C until gas evolution had ceased. MeI (1.95 mL, 31.2 mmol) was then added dropwise, causing a color change to yellow. The mixture was warmed to room temperature overnight before the reaction was quenched with sat. NH_4Cl solution (300 mL). The aqueous phase was extracted with EtOAc (3 x 150 mL), the combined organic extracts were washed with brine (200 mL), dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 3:2) to give the methylated product as pale yellow oil (2.21 g, 64%). $[\alpha]_D^{20}$ = –214.0 (c = 0.88, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.91 (m, 1H), 5.24 (dd, *J* = 17.3, 1.3 Hz, 1H), 5.15 (dd, *J* = 10.4, 1.3 Hz, 1H), 4.82 (d, *J* = 1.5 Hz, 1H), 4.13 (m, 1H), 3.99 (dd, *J* = 9.9, 3.0 Hz, 1H), 3.93 (m, 1H), 3.75 (dq, *J* = 9.8, 6.0 Hz, 1H), 3.68 (dd, *J* = 9.9, 9.8 Hz, 1H), 3.44 (dd, *J* = 3.0, 1.5 Hz, 1H), 3.47 (s, 3H), 3.24 (s, 3H), 3.22 (s, 3H), 1.29 (s, 3H), 1.26 (s, 3H), 1.23 (d, *J* = 6.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.9, 117.3, 99.8, 99.5, 97.1, 78.8, 68.7, 68.4, 67.9, 66.9, 59.2, 47.9, 47.6, 17.8, 17.8, 16.6 ppm. IR (film): $\tilde{\nu}$ = 2932, 2832, 1453, 1375, 1197, 1138, 1114, 1083, 1037, 994, 932, 882, 848, 815 cm^{-1}. MS (EI) *m/z* (%) = 116 (9), 115 (11), 101 (25), 99 (11), 98 (100), 97 (17), 83 (16), 75 (5), 73 (16), 71 (5), 67 (9), 55 (7), 45 (10), 43 (30), 41 (29), 39 (6), 29 (7). HRMS (ESIpos): *m/z*: calcd for $C_{16}H_{28}$O7Na: 355.1727; found: 355.1725.



Allyl 2-O-methyl-α-L-rhamnopyranoside. Trifluoroacetic acid (19 mL) was added to an emulsion of compound **56a** (2.05 g, 6.17 mmol) in H_2O (1 mL) at 0 °C. The mixture turned slightly yellow and was allowed to stir for 7 min at this temperature. The mixture was diluted with CH_2Cl_2 (300 mL), the organic phase was dried over Na_2SO_4 and concentrated to give the diol as a pale orange oil that was used in the next step without further purification (1.32 g, 98%, 95% purity). An analytically pure sample was obtained by flash chromatography (hexanes/EtOAc = 1:1 to 1:2). $[\propto]_D^{20}$ = –46.3 (c = 1.00, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.84 (dddd, *J* = 17.2, 10.4, 6.1, 5.0 Hz, 1H), 5.23 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.14 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.84 (d, *J* = 1.6 Hz, 1H), 4.13 (ddt, *J* = 13.0, 5.1, 1.6 Hz, 1H), 3.92 (ddt, *J* = 13.0, 6.1, 1.4 Hz, 1H), 3.75 – 3.66 (br s, 1H), 3.56 (dq, *J* = 9.2, 6.2 Hz, 1H), 3.50 – 3.42 (br s, 1H), 3.43 (dd, *J* = 3.8, 1.5 Hz, 1H), 3.41 (s, 3H), 3.33 (t, *J* = 9.5 Hz, 1H), 3.24 – 3.11 (m, 1H), 1.24 (d, *J* = 6.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.7, 117.2, 95.4, 80.4, 73.5, 71.4, 67.9, 67.8, 58.8, 17.5 ppm. IR (film): $\tilde{\nu}$ = 3416, 2976, 2932, 2907, 2832, 1453, 1382, 1192, 1133, 1103, 1075, 1038, 990, 975, 926, 912, 874, 836, 807 cm^{-1}. MS (EI) *m/z* (%) = 157 (8), 156 (16), 129 (18), 125 (7), 116 (28), 115 (8), 114 (17), 113 (15), 103 (5), 96 (13), 87 (22), 85 (13), 83 (12), 74 (50), 45 (9), 43 (100), 41 (20).

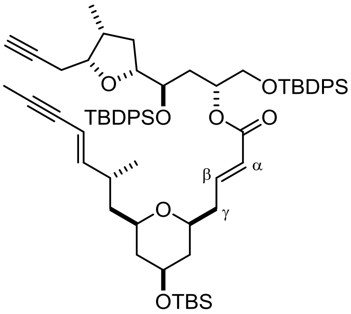


Allyl 3,4-bis-O-acetyl-2-O-methyl-α-L-rhamnopyranoside (57). Triethylamine (2.8 mL, 21 mmol) and acetic anhydride (1.4 mL, 21 mmol) were successively added via syringe at 0 °C to a solution of DMAP (152 mg, 1.2 mmol) and the crude diol **56a** described above (1.4 g, 6.2 mmol) in CH_2Cl_2 (40 mL). The ice bath was removed and stirring continued for 2 h at ambient temperature, before sat. NH_4Cl (20 mL) was added and the aqueous phase extracted with EtOAc (3 x 7 mL). The combined extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 3:2) to give the desired bisacetate as a white crystalline solid (1.28 g, 68%). The physical and spectroscopic data were identical with those of the sample obtained by the alternative route outlined above.



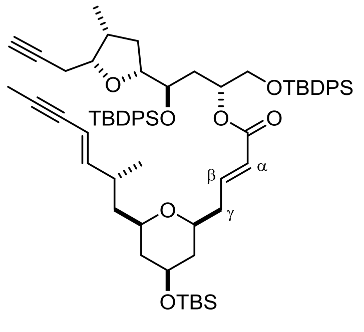
4 Fragment Assembly, Completion of the Synthesis and Structure Reassignment

Diyne 60. A flame-dried Schlenk tube was charged with a solution of alcohol **47** (224 mg, 0.318 mmol) in CH_2Cl_2 (1.8 mL) and a solution of acid **18** (142 mg, 0.350 mmol) in CH_2Cl_2 (0.3 mL). DMAP (194 mg, 1.59 mmol) and DCC (138 mg, 0.668 mmol) were introduced as solids and the resulting mixture was stirred at ambient temperature for 18 h. The white precipitate was filtered off through a short pad of Celite$^{®}$ that was rinsed with CH_2Cl_2. The combined filtrates were concentrated and the residue purified by flash chromatography (hexanes/EtOAc 24:1) to



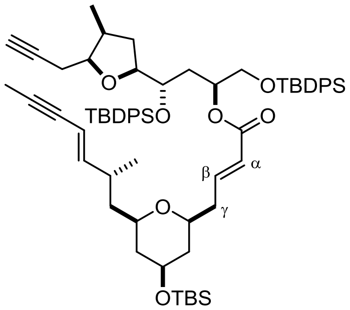
give the diyne **60** as a mixture of *α,β*- and *β,γ*-olefins (1.5:1, 222 mg, 64%) as a white foam, along with recovered alcohol **47** (63.1 mg, 28%) as a colorless oil.

A solution of DBU (0.5 M in MeCN, 102 µL, 0.051 mmol) was added to a solution of the just mentioned mixture of isomeric diynes (222 mg, 0.203 mmol) in MeCN (25 mL) and the resulting solution was stirred at 50 °C for 70 h. After cooling to ambient temperature, sat. NH_4Cl solution (30 mL) containing 10 drops of 1 M HCl was added, the aqueous phase was extracted with EtOAc (4 x 30 mL), and the combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 24:1) to yield the desired *α,β*-olefin as a white foam (202 mg, 91%). $[\propto]_D^{20}$ = –10.5 (c = 1.03, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 – 7.57 (m, 8H), 7.47 – 7.25 (m, 12H), 6.85 (dt, *J* = 15.5, 7.2 Hz, 1H), 5.90 (dd, *J* = 15.9, 7.9 Hz, 1H), 5.72 (dt, *J* = 15.6, 1.5 Hz, 1H), 5.36 (ddd, *J* = 15.9, 2.0, 0.2 Hz, 1H), 5.22 – 5.11 (m, 1H), 3.79 (ddd, *J* = 7.9, 6.4, 3.3 Hz, 1H), 3.76 – 3.67 (m, 3H), 3.61 (dd, *J* = 10.6, 4.5 Hz, 1H), 3.57 (dd, *J* = 10.5, 4.2 Hz, 1H), 3.33 (ddd, *J* = 11.4, 5.8, 5.8 Hz, 1H), 3.26 (dd, *J* = 11.6, 6.2, 6.1 Hz, 1H), 2.45 – 2.19 (m, 4H), 2.11 – 2.01 (m, 2H), 1.96 – 1.87 (m, 2H), 1.90 (d, *J* = 2.1 Hz, 3H), 1.83 (t, *J* = 2.6 Hz, 1H), 1.80 – 1.73 (dd, *J* = 11.7, 3.7 Hz, 3H), 1.61 (ddd, *J* = 13.8, 7.4, 7.2 Hz, 1H), 1.37 – 1.27 (m, 1H), 1.23 – 1.07 (m, 3H), 1.01 (s, 9H), 1.00 (s, 9H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.86 (s, 9H), 0.83 (d, *J* = 7.0 Hz, 3H), 0.04 (s, 3H), 0.03 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 148.4, 144.7, 136.0, 136.0, 135.9, 135.6, 135.6, 134.6, 134.0, 133.5, 133.4, 129.6, 129.3, 129.1, 127.6, 127.6, 127.3, 127.1, 123.4, 108.3, 84.4, 81.7, 80.9, 79.3, 78.3, 74.1, 73.2, 72.3, 69.2, 68.6, 65.2, 42.3, 41.4, 41.3, 38.8, 35.1, 35.0, 34.6, 33.3, 27.2, 26.8, 25.8, 20.7, 19.8, 19.6, 19.2, 18.1, 3.2, –4.5, –4.5 ppm. IR (film): $\tilde{\nu}$ = 2956, 2930, 2856, 1720, 1656, 1472, 1462, 1427, 1376, 1361, 1257, 1175, 1111, 1071, 1006, 836, 823, 776, 740, 701 cm^{-1}. MS (ESIpos) *m/z* (%) = 1115.7 (100 (M+Na). HRMS (ESIpos): *m/z*: calcd for $C_{67}H_{92}O_7Si_3Na$: 1115.6043; found: 1115.6049.

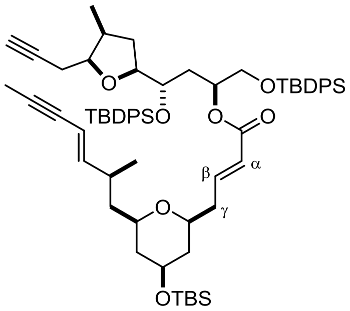


Diyne 11-*epi*-**60.** Prepared analogously from acid 11-*epi*-**18** (34.9 mg, 85.8 µmol) and alcohol **47** (55 mg, 78.0 µmol) as a white foam (1st step: 216 mg, 71% yield, 2nd step: 56 mg, 92%). $[\propto]_D^{20}$ = +32.5 (c = 0.72, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 – 7.58 (m, 8H), 7.44 – 7.25 (m, 12H), 6.86 (dt, *J* = 15.6, 7.0 Hz, 1H), 5.81 (dd, *J* = 15.8, 8.7 Hz, 1H), 5.73 (dt, *J* = 15.6, 1.5 Hz, 1H), 5.42 (dd, *J* = 15.7, 2.2 Hz, 1H), 5.22 – 5.14 (m, 1H), 3.81 (ddd, *J* = 7.8, 6.6, 3.1 Hz, 1H), 3.77 – 3.67 (m, 3H), 3.64 (dd, *J* = 10.7, 4.8 Hz, 1H), 3.58 (dd, *J* = 10.7, 4.8 Hz, 1H), 3.37 – 3.28 (m, 1H), 3.27 – 3.18 (m, 1H), 2.51 – 2.34 (m, 2H), 2.34 – 2.19 (m, 2H), 2.07 – 2.02 (m, 2H), 1.96 – 1.88 (m, 2H), 1.86 (d, *J* = 2.2 Hz, 3H), 1.83 (t, *J* = 2.6 Hz, 1H), 1.81 – 1.67 (m, 3H), 1.54 (ddd, *J* = 14.0, 9.7, 4.2 Hz, 1H), 1.26 – 1.12 (m, 4H), 1.02 (s, 9H), 1.01 (s, 9H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.86 (s, 9H), 0.83 (d, *J* = 7.1 Hz, 3H), 0.04 (s, 3H), 0.03 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 148.0, 144.7, 136.0, 135.9, 135.9, 135.6, 135.5, 134.6, 133.9, 133.5, 133.4, 129.6, 129.3, 129.1, 127.6, 127.6, 127.3, 127.1, 123.3, 109.2, 84.3, 81.6, 81.0, 79.3, 78.4, 74.0, 73.3, 72.3, 71.4, 69.2, 68.6, 65.2, 42.9, 41.9, 41.3, 38.8, 35.1, 35.0, 34.7, 33.9, 27.2, 26.8, 25.8, 21.0, 20.7, 19.5, 19.2, 18.1, 14.8, 4.2, –4.5, –4.5 ppm. IR (film): $\tilde{\nu}$ = 2956, 2930, 2856, 1721, 1472, 1462, 1428, 1361, 1258, 1112, 1075, 1006, 836, 776, 740, 702, 612 cm^{-1}. MS (ESIpos) *m/z* (%) = 1115.7 (100 (M+Na). HRMS (ESIpos): *m/z*: calcd for $C_{67}H_{92}O_7Si_3Na$: 1115.6043; found:1115.6053.

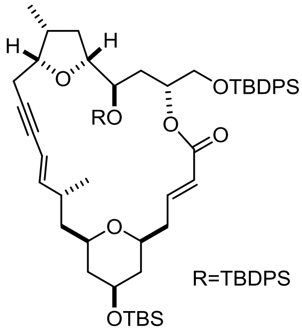
Diyne 66. Prepared analogously from acid **18** (170 mg, 0,418 mmol) and alcohol *ent*-**47** (268 mg, 0.380 mmol) as a white foam (1st step: 216 mg, 52% yield, 2nd step: 183 mg, 85%). $[\propto]_D^{20}$ = –9.0 (c = 1.53, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 – 7.58 (m, 8H), 7.42 – 7.24 (m, 12H), 6.86 (dt, *J* = 15.6, 7.2 Hz, 1H), 5.91 (dd, *J* = 15.8, 8.0 Hz, 1H), 5.72 (dt, *J* = 15.7, 1.4 Hz, 1H), 5.37 (ddd, *J* = 15.9, 2.2, 1.1 Hz, 1H), 5.16 (dtd, *J* = 7.9, 4.6, 3.0 Hz, 1H), 3.82 – 3.69 (m, 4H), 3.61 (dd, *J* = 10.8, 4.6 Hz, 1H), 3.58 (dd, *J* = 10.9, 4.5 Hz, 1H), 3.35 (ddd, *J* = 11.0, 5.5, 5.4 Hz, 1H), 3.27 (ddd, *J* = 11.4, 5.8, 5.7 Hz, 1H), 2.46 – 2.20 (m, 4H), 2.10 – 2.01 (m, 2H), 1.97 – 1.87 (m, 5H), 1.84 (t, *J* = 2.6 Hz, 1H), 1.81 – 1.67 (m, 3H), 1.69 (dd, *J* = 13.8, 7.2 Hz, 1H), 1.34 – 1.20 (m, 3H), 1.17 – 1.11 (m, 1H), 1.01 (s, 9H), 1.01 (s, 9H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.87 (s, 9H), 0.84 (d, *J* = 7.1 Hz, 3H), 0.05 (s, 3H), 0.04 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 148.4, 144.7, 136.0, 135.9, 135.6, 135.5, 135.5, 134.5, 133.8, 133.4, 133.4, 129.6, 129.3, 129.1, 127.7, 127.6, 127.6, 127.6, 127.3, 127.1, 123.4, 108.2, 84.4, 81.6, 80.9, 79.3, 78.3, 74.1, 73.2, 72.2, 71.3, 69.2, 68.6, 65.2, 42.3, 41.3, 41.3, 38.8, 35.1, 34.9, 34.5, 33.3, 27.2, 26.7, 25.8, 20.7, 19.8, 19.5, 19.2, 18.1, 14.8, 4.2, –4.5, –4.5 ppm. IR (film): $\tilde{\nu}$ = 2955, 2930, 2856, 1720, 1472, 1462, 1428, 1377, 1257, 1176, 1110, 1070, 1006, 836, 776, 739, 702, 611 cm^{-1}. MS (ESIpos) *m/z* (%) = 1115.8 (100 (M+Na). HRMS (ESIpos): *m/z*: calcd for $C_{67}H_{92}O_7Si_3Na$: 1115.6043; found:1115.6052.



Diyne (11-*epi*-**66**)**.** Prepared analogously from acid 11-*epi*-**18** (89 mg, 0.219 mmol) and alcohol *ent*-**47** (140 mg, 0.199 mmol) as a white foam (1st step: 116 mg, 53% yield, 2nd step: 108 mg, 93%). $[\propto]_D^{20}$ = +40.9 (c = 0.90, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 – 7.57 (m, 8H), 7.41 – 7.25 (m, 12H), 6.85 (dt, *J* = 15.6, 7.1 Hz, 1H), 5.80 (dd, *J* = 15.8, 8.7 Hz, 1H), 5.72 (dt, *J* = 15.6, 1.2 Hz, 1H), 5.41 (dd, *J* = 15.8, 2.2 Hz, 1H), 5.16 (dtd, *J* = 9.0, 4.6, 4.1 Hz, 1H), 3.82 – 3.75 (m, 1H), 3.76 – 3.67 (m, 3H), 3.62 (dd, *J* = 10.6, 4.8 Hz, 1H), 3.57 (dd, *J* = 10.7, 4.7 Hz, 1H), 3.33 (dtd, *J* = 11.8, 5.8, 0.7 Hz, 1H), 3.26 – 3.17 (m, 1H), 2.49 – 2.35 (m, 2H), 2.31 (ddd, *J* = 6.3, 6.2, 1.3 Hz, 1H), 2.23 (dt, *J* = 14.2, 7.1 Hz, 1H), 2.05 (t, *J* = 3.0 Hz, 1H), 2.03 (dd, *J* = 5.0, 2.7 Hz, 1H), 1.95 – 1.86 (m, 2H), 1.89 (d, *J* = 2.2 Hz, 3H), 1.84 (t, *J* = 2.7 Hz, 1H), 1.80 – 1.65 (m, 3H), 1.53 (ddd, *J* = 13.9, 9.7, 4.2 Hz, 1H), 1.27 – 1.21 (m, 2H), 1.21 – 1.14 (m, 2H), 1.00 (s, 9H), 0.99 (s, 9H), 0.92 (d, *J* = 6.8 Hz,

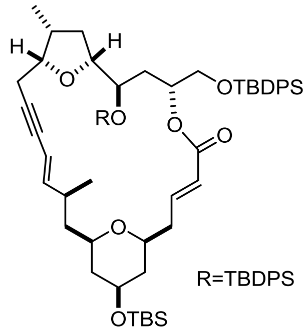


3H), 0.85 (s, 9H), 0.84 (d, J = 7.0 Hz, 3H), 0.03 (s, 3H), 0.02 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 148.1, 144.8, 136.0, 135.9, 135.6, 135.5, 134.5, 133.8, 133.4, 133.4, 129.7, 129.6, 129.3, 129.1, 127.6, 127.6, 127.4, 127.1, 123.3, 109.1, 84.3, 81.6, 80.9, 79.3, 78.4, 73.9, 73.3, 72.2, 71.3, 69.2, 68.5, 65.2, 42.9, 41.9, 41.3, 38.8, 35.1, 34.9, 34.6, 33.9, 27.2, 27.1, 26.7, 26.7, 25.8, 21.0, 20.6, 19.5, 19.2, 18.1, 14.8, 4.2, −4.5, −4.5 ppm. IR (film): $\tilde{\nu}$ = 2955, 2930, 2857, 1721, 1472, 1462, 1428, 1361, 1257, 1155, 1112, 1071, 1006, 836, 776, 702, 610 cm^{-1}. MS (ESIpos) *m/z* (%) = 1115.6 (100 (M+Na). HRMS (ESIpos): *m/z*: calcd for $C_{67}H_{92}O_7Si_3Na$: 1115.6043; found:1115.6047.

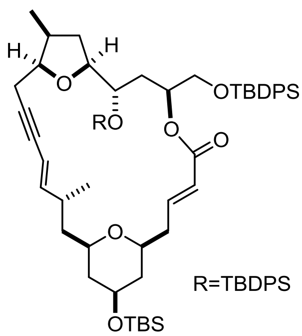


Macrocyclic Enyne 62. A flame-dried Schlenk tube was charged with powdered 4 Å molecular sieves (~1.2 g) and 5 Å molecular sieves (~1.5 g). The flask was then evacuated and the molecular sieves were flame-dried. After reaching ambient temperature, a solution of diyne **60** (191 mg, 0.175 mmol) in toluene (85 mL) was added and the resulting suspension was stirred for 45 min. In a separate flame-dried Schlenk tube, a solution of the molybdenum alkylidyne complex **61** (18.2 mg, 17.5 µmol) in toluene (2 mL) was prepared. This solution was added dropwise to the flask containing the diyne via syringe and the resulting mixture was stirred at ambient temperature for 3 h. The mixture was filtered through a short pad of Celite® that was carefully rinsed with Et_2O (100 mL). The combined filtrates were evaporated and the brown residue was purified by flash chromatography (hexanes/EtOAc 29:1 to 24:1 to 19:1) to yield the target macrocycle as a white foam (133 mg, 72%). $[\propto]_D^{20}$ = –7.4 (c = 0.87, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 – 7.60 (m, 8H), 7.45 – 7.24 (m, 12H), 6.87 (ddd, J = 15.7, 8.2, 5.7 Hz, 1H), 5.97 (dd, J = 16.0, 7.3 Hz, 1H), 5.73 (dt, J = 15.6, 1.3 Hz, 1H), 5.32 (dq, J = 15.9, 1.7 Hz, 1H), 5.22 – 5.15 (m, 1H), 4.09 (ddd, J = 9.6, 5.7, 2.6 Hz, 1H), 3.82 – 3.74 (m, 2H), 3.74 – 3.69 (m, 1H), 3.67 (dd, J = 10.3, 4.9 Hz, 1H), 3.62 (dd, J = 10.4, 5.0 Hz, 1H), 3.27 (dddd, J = 11.2, 9.2, 2.1, 1.8 Hz, 1H), 3.22 – 3.14 (m, 1H), 2.31 (tdd, J = 9.1, 4.6, 1.5 Hz, 1H), 2.26 – 2.12 (m, 5H), 2.10 (ddd, J = 14.2, 9.3, 2.5 Hz, 1H), 1.86 – 1.67 (m, 4H), 1.61 – 1.50 (m, 1H), 1.35 – 1.30 (m, 2H), 1.22 – 1.11 (m, 2H), 1.03 (s, 9H), 1.01 (s, 9H), 1.00 (d, J = 6.6 Hz, 3H), 0.92 (d, J = 6.9 Hz, 3H), 0.87 (s, 9H), 0.04 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 148.5, 144.9, 135.9, 135.8, 135.6, 135.2, 135.0, 134.9, 133.9, 133.6, 133.0, 129.5, 129.3, 129.2, 127.9, 127.6, 127.6, 127.4, 127.2, 123.6, 107.8, 86.8, 81.3, 81.2, 78.5, 75.6, 74.5, 71.9, 71.7, 68.6, 65.5, 43.2, 42.2, 41.8, 38.4, 36.5, 35.1, 34.0, 33.8, 29.7, 27.2, 26.8, 25.8, 21.6, 19.6, 19.3, 18.1, 13.8, –4.5 ppm. IR (film): $\tilde{\nu}$ = 2955, 2929, 2856, 1718, 1472, 1462, 1428, 1361, 1328, 1256, 1174, 1112, 1071, 986, 836, 823, 775, 737, 700 cm^{-1}. MS (ESIpos) *m/z* (%) = 1075.7 (100 (M+Na). HRMS (ESIpos): *m/z*: calcd for $C_{64}H_{88}O_7Si_3Na$: 1075.5730; found: 1075.5725.

Macrocyclic Enyne 11-*epi*-**62.** Prepared analogously (at room temperature) from diyne 11-*epi*-**60** (52 mg, 47.5 µmol) as a white foam (32 mg, 64%). $[\propto]_D^{20}$ = +54.6 (c = 1.04, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (ddd, *J* = 7.7, 3.3, 1.7 Hz, 4H), 7.63 – 7.56 (m, 4H), 7.44 – 7.25 (m, 12H), 6.97 (ddd, *J* = 15.4, 8.2, 7.0 Hz, 1H), 5.73 (dt, *J* = 15.5, 1.1 Hz, 1H), 5.60 (dd, *J* = 15.7, 9.6 Hz, 1H), 5.30 (dt, *J* = 15.7, 1.8 Hz, 1H), 5.09 – 5.02 (m, 1H), 4.16 (ddd, *J* = 8.8, 6.8, 1.8 Hz, 1H), 3.85 (ddd, *J* = 8.2, 5.8, 3.9 Hz, 1H), 3.80 – 3.68 (m, 2H), 3.65 (dd, *J* = 11.0, 3.4 Hz, 1H), 3.47 (dd, *J* = 11.0, 5.4 Hz, 1H), 3.20 – 3.08 (m, 2H), 2.63 – 2.50 (m, 1H), 2.39 – 2.17 (m, 3H), 2.13 (dd, *J* = 12.9, 7.9, 1H), 2.07 (ddd, *J* = 16.9, 5.7, 0.2 Hz, 1H), 1.90 (ddd, *J* = 14.5, 7.1, 2.1 Hz, 1H), 1.80 – 1.64 (m, 4H), 1.59 – 1.51 (m, 1H), 1.51 – 1.41 (m, 1H), 1.30 – 1.14 (m, 3H), 1.02 (s, 9H), 1.01 (m, 3H), 1.00 (s, 9H), 0.97 (d, *J* = 6.3 Hz, 3H), 0.86 (s, 9H), 0.03 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 146.2, 146.0, 135.9, 135.9, 135.6, 134.8, 134.6, 133.6, 133.6, 129.5, 129.2, 129.1, 127.6, 127.5, 127.3, 127.2, 123.3, 110.4, 86.6, 81.6, 81.0, 78.8, 75.5, 74.1, 72.9, 72.9, 68.7, 65.8, 42.6, 42.2, 41.9, 38.6, 36.6, 35.8, 35.3, 33.8, 27.3, 26.8, 25.8, 23.1, 21.3, 19.7, 19.3, 18.1, 13.7, −4.5, −4.6 ppm. IR (film): $\tilde{\nu}$ = 2955, 2930, 2857, 1722, 1472, 1462, 1428, 1361, 1327, 1257, 1176, 1112, 1067, 854, 836, 823, 776, 739, 701, 608 cm^{-1}. MS (ESIpos) *m/z* (%) = 1075.6 (100 (M+Na). HRMS (ESIpos): *m/z*: calcd for $C_{64}H_{88}O_7Si_3Na$: 1075.5730; found:1075.5722.

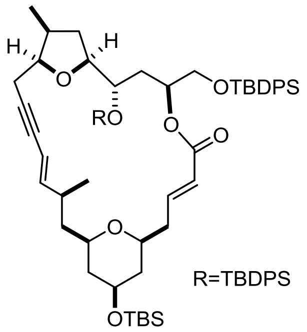


Macrocyclic Enyne 67. *A slightly modified procedure had to be used:* A flame-dried Schlenk tube was charged with powdered 4 Å molecular sieves (~0.7 g) and 5 Å molecular sieves (~0.9 g). The flask was then evacuated and the molecular sieves were flame-dried. After reaching ambient temperature, a solution of diyne **66** (90 mg, 82.3 µmol) in toluene (40 mL) was added and the resulting suspension was stirred for 45 min. The solution was then placed in a pre-heated oilbath (85 °C). In a separate flame-dried Schlenk tube, a solution of the molybdenum alkylidyne complex **61** (8.6 mg, 8.2 µmol) in toluene (2 mL) was prepared. This solution was added dropwise to the flask containing the diyne via syringe at 85 °C and the resulting mixture was stirred for 2 h. After cooling to room temperature, the mixture was filtered through a short pad of Celite® that was carefully rinsed with Et_2O (100 mL). The combined filtrates were evaporated and the brown residue was purified by flash chromatography (hexanes/EtOAc 29:1 to 24:1 to 19:1) to yield the targeted macrocycle as a white foam (64 mg, 74%). $[\propto]_D^{20}$ = +8.5 (c = 1.31, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 – 7.58 (m, 8H), 7.42 – 7.25 (m, 12H), 6.82 (ddd, *J* = 15.9, 5.3, 5.3 Hz, 1H), 5.87 (dd, *J* = 15.9, 7.8 Hz, 1H), 5.74 (dt, *J* = 15.9, 1.4 Hz, 1H), 5.36 (dt, *J* = 15.9, 1.9 Hz, 1H), 5.13 – 5.05 (m, 1H), 4.08 (ddd, *J* = 9.9, 5.4, 1.1 Hz, 1H), 3.86 (ddd, *J* = 8.0, 8.0, 4.2 Hz, 1H), 3.82 – 3.70 (m, 2H), 3.70 (dd, *J* = 10.7,4.4 Hz, 1H), 3.67 (dd, *J* = 10.6, 4.0 Hz, 1H), 3.42 (dd, *J* = 11.0, 9.5 Hz, 1H), 3.22 (dt, *J* = 10.4, 5.4 Hz, 1H), 2.38 – 2.07 (m,

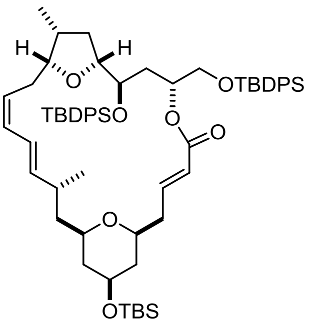


7H), 1.86 – 1.67 (m, 4H), 1.52 (ddd, *J* = 13.8, 8.2, 5.5 Hz, 1H), 1.47 (d, *J* = 10.9 Hz, 1H), 1.39 (ddd, *J* = 13.9, 6.3, 4.0 Hz, 1H), 1.28 (q, *J* = 11.5 Hz, 1H), 1.14 (dq, *J* = 11.1, 10.2 Hz, 1H), 1.05 (s, 9H), 1.00 (s, 9H), 0.99 (d, *J* = 7.6 Hz, 3H), 0.91 (d, *J* = 6.9 Hz, 3H), 0.88 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =165.9, 147.8, 145.0, 135.9, 135.8, 135.6, 134.9, 134.7, 133.7, 133.6, 133.4, 129.6, 129.5, 129.2, 129.2, 127.9, 127.7, 127.6, 127.4, 127.2, 122.3, 108.8, 86.2, 81.2, 80.5, 78.6, 74.2, 73.2, 71.4, 71.2, 68.7, 65.3, 42.7, 41.9, 41.4, 37.3, 36.4, 34.5, 33.4, 33.3, 27.2, 27.1, 26.8, 25.8, 23.2, 21.5, 19.5, 19.3, 18.1, 13.5, −4.5 ppm. IR (film): $\tilde{\nu}$ = 2956, 2930, 2856, 1720, 1472, 1462, 1428, 1361, 1331, 1257, 1178, 1111, 1070, 937, 837, 823, 776, 739, 702, 610 cm^{-1}. MS (ESIpos) *m/z* (%) = 1075.7 (100 (M+Na). HRMS (ESIpos): *m/z*: calcd for $C_{64}H_{88}O_7Si_3Na$: 1075.5730; found: 1075.5736.

Macrocyclic Enyne 11-*epi*-**67.** Prepared analogously (at room temperature) from diyne 11-*epi*-**66** (107 mg, 97.8 µmol) as a white foam (85.1 mg, 83%). $[\propto]_D^{20}$ = +57.4 (c = 0.56, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72 – 7.60 (m, 8H), 7.42 – 7.25 (m, 12H), 6.85 (dt, *J* = 15.9, 5.2 Hz, 1H), 5.73 (dt, *J* = 15.8, 1.6 Hz, 1H), 5.69 (dd, *J* = 15.8, 8.8 Hz, 1H), 5.56 (dt, *J* = 15.8, 1.7 Hz, 1H), 5.22 – 5.13 (m, 1H), 4.24 (dd, *J* = 10.3, 6.0 Hz, 1H), 3.91 – 3.73 (m, 5H), 3.44 (t, *J* = 10.6 Hz, 1H), 3.27 (t, *J* = 11.1 Hz, 1H), 2.56 – 2.33 (m, 2H), 2.29 – 2.19 (m, 2H), 2.18 – 2.08 (m, 2H), 1.86 – 1.63 (m, 5H), 1.54 (ddd, *J* = 14.0, 11.3, 2.9 Hz, 1H), 1.34 – 1.14 (m, 4H), 1.05 (s, 9H), 1.04 (m, 3H), 1.01 (s, 9H), 0.90 (s, 9H), 0.82 (d, *J* = 6.7 Hz, 3H), 0.09 (s, 3H), 0.08 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 146.2, 145.7, 136.0, 135.8, 135.5, 135.5, 135.1, 134.0, 133.5, 133.4, 129.6, 129.5, 129.0, 128.9, 127.6, 127.3, 127.0, 121.6, 110.1, 87.1, 82.4, 81.7, 78.2, 73.5, 72.8, 72.2, 72.0, 68.6, 65.1, 43.0, 42.1, 37.8, 36.9, 33.9, 33.6, 33.2, 27.2, 26.8, 26.8, 25.9, 25.8, 23.0, 21.4, 19.5, 19.3, 18.1, 13.2, −4.5, −4.6 ppm. IR (film): $\tilde{\nu}$ = 2955, 2929, 2856, 1720, 1472, 1462, 1378, 1361, 1291, 1256, 1176, 1111, 1075, 1006, 837, 776, 739, 702, 611 cm^{-1}. MS (ESIpos) *m/z* (%) = 1075.8 (100 (M+Na). HRMS (ESIpos): *m/z*: calcd for $C_{64}H_{88}O_7Si_3Na$: *m/z*: 1075.5730; found:1075.5724.

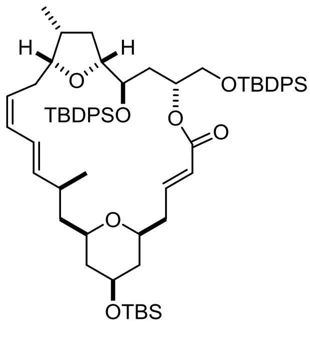


Macrocyclic Diene 62a. *In order to obtain reproducible results, all solvents used for the preparation of the activated Zn(Cu/Ag) and the reaction were degassed by bubbling Ar through the solvent for at least 20 min.*

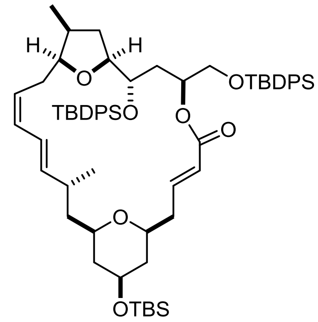


A Young tube was evacuated, backfilled with Argon and charged with a mixture of MeOH/H_2O (1:1, 1.8 mL). Freshly prepared Zn(Cu/Ag)[12] (1.6 g) was added, followed by a solution of enyne **62** (130 mg, 0.123 mmol) in THF (0.5 mL + 2 x 0.2 mL rinse). The Young tube was sealed and placed in a preheated (45 °C) oil bath. The suspension was vigorously stirred at this temperature for 70 h before it was allowed to reach ambient temperature. The mixture was filtered through a short pad of Celite® that was rinsed with EtOAc/EtOH (9:1, 75 mL). The combined filtrates were concentrated to ≈1/10 of the original volume before brine (10 mL) was added. The aqueous phase was extracted with EtOAc (3 x 10 mL) and the combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 29:1 to 24:1 to 19:1) to give the desired diene as a white foam (115 mg, 89%). $[\propto]_D^{20}$ = –47.9 (c = 0.70, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 – 7.54 (m, 8H), 7.40 – 7.22 (m, 12H), 6.84 (ddd, *J* = 15.7, 8.0, 5.5 Hz, 1H), 6.19 (dd, *J* = 15.4, 10.8 Hz, 1H), 5.88 (t, *J* = 10.8 Hz, 1H), 5.76 (dt, *J* = 15.7, 1.4 Hz, 1H), 5.55 (dd, *J* = 15.4, 6.8 Hz, 1H), 5.18 – 5.08 (m, 2H), 3.99 (ddd, *J* = 8.8, 6.0, 2.3 Hz, 1H), 3.73 (td, *J* = 7.9, 6.3 Hz, 1H), 3.66 (dt, *J* = 10.0, 4.8 Hz, 1H), 3.64 – 3.59 (m, 2H), 3.56 (dt, *J* = 7.0, 5.7 Hz, 1H), 3.28 – 3.14 (m, 2H), 2.43 – 2.33 (m, 1H), 2.32 – 2.24 (m, 1H), 2.20 (ddd, *J* = 16.0, 8.2, 2.7 Hz, 1H), 2.14 – 1.95 (m, 3H), 1.90 (dt, *J* = 15.7, 7.5 Hz, 1H), 1.85 – 1.77 (m, 2H), 1.75 – 1.64 (m, 3H), 1.34 (ddd, *J* = 12.7, 7.3, 5.2 Hz, 1H), 1.29 – 1.25 (m, 1H), 1.23 – 1.17 (m, 2H), 1.17 – 1.07 (m, 1H), 0.99 (s, 9H), 0.97 (s, 9H), 0.94 (d, *J* = 6. 7 Hz, 3H), 0.83 (s, 9H), 0.76 (d, *J* = 7.1 Hz, 3H), 0.00 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 145.0, 140.2, 136.0, 136.0, 135.6, 135.6, 134.7, 133.9, 133.5, 133.5, 129.6, 129.5, 129.4, 127.6, 127.6, 127.4, 127.2, 126.4, 124.3, 123.3, 81.4, 80.1, 74.2, 73.4, 72.0, 71.6, 68.7, 65.4, 43.1, 41.9, 41.9, 38.5, 35.4, 34.4, 34.3, 32.1, 30.0, 27.2, 26.8, 25.8, 20.7, 19.5, 19.3, 18.1, 15.4, –4.5 ppm. IR (film): $\tilde{\nu}$ = 2956, 2930, 2857, 1721, 1654, 1472, 1462, 1428, 1375, 1257, 1175, 1112, 1073, 1006, 836, 823, 775, 739, 702 cm^{-1}. MS (ESIpos) *m/z* (%) = 1077.6 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{64}H_{90}O_7Si_3Na$: 1077.5887; found: 1075.5884.

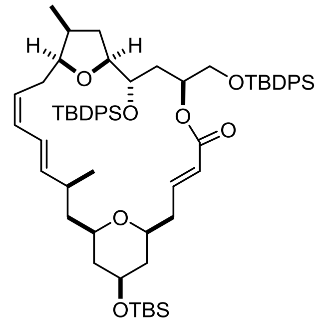
Macrocyclic Diene 11-*epi*-**62a.** Prepared analogously from enyne 11-*epi*-**62** (31.0 mg, 29.4 µmol) as a white foam (26.8 mg, 86%). $[\propto]_D^{20}$ = +15.2 (c = 1.22, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 – 7.53 (m, 8H), 7.42 – 7.20 (m, 12H), 7.09 (ddd, *J* = 15.1, 10.3, 4.3 Hz, 1H), 6.21 (dd, *J* = 14.9, 11.1 Hz, 1H), 5.89 (tt, *J* = 10.9, 1.9 Hz, 1H), 5.74 (dd, *J* = 15.6, 1.6 Hz, 1H), 5.25 (dd, *J* = 14.9, 9.7 Hz, 1H), 5.12 – 5.02 (m, 2H), 3.92 – 3.82 (m, 2H), 3.77 – 3.65 (m, 2H), 3.41 (dd, *J* = 11.2, 3.3 Hz, 1H), 3.34 (dd, *J* = 11.2, 5.3 Hz, 1H), 3.18 – 3.04 (m, 2H), 2.71 – 2.59 (m, 1H), 2.40 (tdd, *J* = 9.6, 4.6, 1.9 Hz, 1H), 2.26 – 2.11 (m, 4H), 2.03 (dt, *J* = 15.1, 7.4 Hz, 1H), 1.93 (dt, *J* = 14.6, 5.9 Hz, 1H), 1.85 – 1.72 (m, 2H), 1.66 (dd, *J* = 12.5, 4.7 Hz, 1H), 1.56 (ddd, *J* = 14.0, 10.6, 2.9 Hz, 2H), 1.49 – 1.38 (m, 1H), 1.25 – 1.12 (m, 4H), 1.01 (s, 9H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.97 (s, 9H), 0.85 (s, 9H), 0.79 (d, *J* = 7.0 Hz, 3H), 0.02 (s, 3H), 0.02 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.2, 145.7, 139.8, 135.9, 135.8, 135.7, 135.6, 134.1, 133.9, 133.7, 133.4, 129.6, 129.5, 127.6, 127.5, 127.5, 127.4, 125.9, 125.6, 122.8, 81.3, 80.7, 75.1, 73.0, 72.3, 72.0, 68.5, 65.1, 43.5, 42.3, 42.1, 39.3, 35.6, 34.6, 34.6, 33.9, 29.4, 27.1, 26.7, 25.8, 22.1, 19.4, 19.2, 18.1, 15.1, −4.5, −4.5 ppm. IR (film): $\tilde{\nu}$ = 2957, 2928,



2856, 1724, 1427, 1257, 1157, 1113, 1076, 833, 822, 778, 741, 703, 557 cm^{-1}. MS (ESIpos) *m/z* (%) = 1077.6 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{64}H_{90}O_7Si_3Na$: 1077.5887; found: 1077.5884.

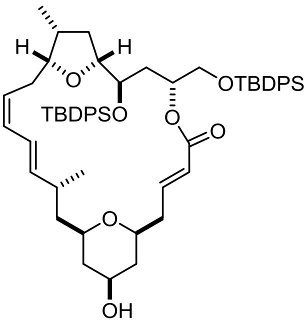


Macrocyclic Diene 72. Prepared analogously from enyne **67** (26.3 mg, 25.0 µmol) as a white foam (24.1 mg, 91%). $[\propto]_D^{20}$ = +13.2 (c = 1.21, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 – 7.58 (m, 8H), 7.42 – 7.25 (m, 12H), 6.88 (ddd, *J* = 15.7, 7.6, 6.2 Hz, 1H), 6.21 (dd, *J* = 15.0, 11.0 Hz, 1H), 5.93 (t, *J* = 10.7 Hz, 1H), 5.83 (dt, *J* = 15.7, 1.2 Hz, 1H), 5.20 (dd, *J* = 15.2, 8.1 Hz, 1H), 5.24 – 5.13 (m, 2H), 4.01 (ddd, *J* = 8.6, 5.6, 3.0 Hz, 1H), 3.80 – 3.66 (m, 2H), 3.64 – 3.57 (m, 2H), 3.54 (dd, *J* = 10.8, 4.9 Hz, 1H), 3.40 – 3.32 (m, 1H), 3.31 – 3.23 (m, 1H), 2.40 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.36 – 2.29 (m, 1H), 2.20 – 2.08 (m, 2H), 1.99 (dt, *J* = 13.9, 7.2 Hz, 1H), 1.93 (dt, *J* = 14.6, 5.9 Hz, 1H), 1.91 (ddd, *J* = 14.5, 8.4, 3.0 Hz, 1H), 1.85 – 1.69 (m, 4H), 1.36 (dt, *J* = 12.8, 7.6 Hz, 1H), 1.34 – 1.25 (m, 2H), 1.23 – 1.13 (m, 2H), 1.00 (s, 18H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 7.3 Hz, 3H) 0.87 (s, 9H), 0.05 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 145.2, 140.1, 136.0, 135.9, 135.6, 135.6, 134.7, 134.0, 133.5, 133.4, 129.9, 129.5, 129.3, 127.6, 127.3, 127.3, 126.8, 124.3, 123.3, 81.2, 80.1, 73.8, 73.2, 72.7, 71.6, 68.8, 65.5, 43.0, 41.9, 41.8, 38.5, 35.7, 34.4, 34.1, 33.3, 30.2, 27.2, 26.7, 25.8, 20.2, 19.5, 19.2, 18.1, 15.2, −4.5 ppm. IR (film): $\tilde{\nu}$ = 2956, 2929, 2857, 1722, 1428, 1293, 1258, 1177, 1107, 741, 702 cm^{-1}. MS (ESIpos) *m/z* (%) = 1077.7 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{64}H_{90}O_7Si_3Na$: 1077.5887; found: 1077.5896.

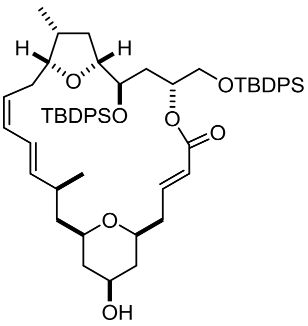


Macrocyclic Diene 11-*epi*-**72.** Prepared analogously from enyne 11-*epi*-**67** (71.0 mg, 67.4 µmol) as a white foam (59.2 mg, 83%). $[\propto]_D^{20}$ = +79.1 (c = 1.05, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 – 7.57 (m, 8H), 7.42 – 7.25 (m, 12H), 6.84 (ddd, *J* = 15.8, 7.2, 5.6 Hz, 1H), 6.26 (dd, *J* = 15.2, 10.9 Hz, 1H), 5.98 (t, *J* = 10.9 Hz, 1H), 5.72 (dt, *J* = 15.7, 1.4 Hz, 1H), 5.36 (dd, *J* = 15.1, 8.6 Hz, 1H), 5.22 (td, *J* = 10.0, 6.3 Hz, 1H), 5.02 – 4.94 (m, 1H), 4.10 (ddd, *J* = 8.8, 4.9, 2.3 Hz, 1H), 3.82 (td, *J* = 7.8, 4.8 Hz, 1H), 3.76 – 3.61 (m, 4H), 3.28 (ddt, *J* = 10.9, 9.6, 1.6 Hz, 1H), 3.21 (t, *J* = 10.9 Hz, 1H), 2.59 – 2.47 (m, 1H), 2.45 – 2.16 (m, 5H), 2.09 (dtd, *J* = 14.7, 5.4, 1.1 Hz, 1H), 1.90 (dt, *J* = 13.0, 7.8 Hz, 1H), 1.82 – 1.72 (m, 2H), 1.69 – 1.62 (m, 1H), 1.59 – 1.48 (m, 2H), 1.28 – 1.13 (m, 3H), 1.03 (s, 9H), 1.01 (s, 9H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.88 (s, 9H) 0.82 (d, *J* = 7.0 Hz, 3H), 0.06 (s, 3H), 0.05 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 145.0, 141.2, 135.9, 135.9, 135.6, 135.5, 134.3, 133.6, 133.4, 133.3, 130.0, 129.6, 129.5, 129.4, 129.4, 127.6, 127.6, 127.5, 127.4, 126.8, 125.5, 122.9, 81.3, 79.7, 73.8, 73.2, 72.4, 70.8, 68.5, 65.4, 44.2, 42.4, 42.3, 39.0, 35.7, 33.3, 33.3, 33.1, 30.8, 27.1, 26.7, 25.8, 22.9, 19.4, 19.2, 18.1, 15.3, −4.5 ppm. IR (film): $\tilde{\nu}$ = 2955, 2931, 2857, 1718, 1472, 1462, 1428, 1257, 1177, 1155, 1112, 1076, 1005, 836, 776, 737, 702 cm^{-1}. MS (ESIpos) *m/z* (%) = 1077.7 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{64}H_{90}O_7Si_3Na$: 1077.5887; found: 1077.5878.

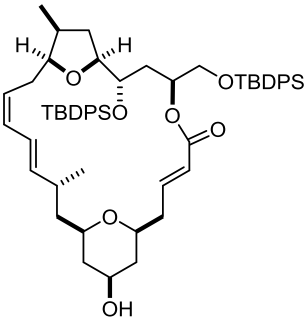
Alcohol 63. *p*TsOH·H_2O (6.2 mg, 32.6 µmol) was added to a solution of silyl ether **62a** (114 mg, 0.109 mmol) in CH_2Cl_2/MeOH (2:1, 12 mL) and the mixture was stirred for 5 h. The reaction was quenched by addition of sat. $NaHCO_3$ solution (12 mL) and the aqueous layer was extracted with CH_2Cl_2 (3 x 8 mL). The combined extracts were dried over Na_2SO_4 and concentrated, and the residue was purified by flash chromatography (hexanes/EtOAc 2:1) to yield the desired alcohol as a white foam (92 mg, 90%). $[\propto]_D^{20}$ = –42.5 (c = 0.89, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 – 7.58 (m, 8H), 7.43 – 7.25 (m, 12H), 6.87 (ddd, *J* = 15.8, 7.9, 5.7 Hz, 1H), 6.23 (ddt, *J* = 15.6, 10.8, 1.2 Hz, 1H), 5.92 (t, *J* = 10.8 Hz, 1H), 5.80 (dt, *J* = 15.8, 1.4 Hz, 1H), 5.59 (dd, *J* = 15.4, 6.9 Hz, 1H), 5.23 – 5.12 (m, 2H), 4.03 (ddd, *J* = 8.8, 6.0, 2.3 Hz, 1H), 3.83 – 3.71 (m, 2H), 3.71 – 3.56 (m, 3H), 3.35 – 3.21 (m, 2H), 2.46 – 2.30 (m, 2H), 2.27 (tdd, *J* = 7.5, 3.0, 1.3 Hz, 1H), 2.18 – 2.05 (m, 2H), 2.03 (ddd, *J* = 14.5, 10.1, 0.1 Hz, 1H), 1.99 – 1.81 (m, 5H), 1.76 (ddd, *J* = 14.0, 8.2, 6.0 Hz, 1H), 1.52 – 1.44 (br s, 1H), 1.38 (ddd, *J* = 12.8, 7.3, 5.4 Hz, 1H), 1.33 (ddd, *J* = 13.5, 8.1, 4.8 Hz, 1H), 1.22 (ddd, *J* = 11.5, 10.9, 10.6 Hz, 1H), 1.13 (ddd, *J* = 11.6, 11.3, 1.09 Hz, 1H), 1.03 (s, 9H), 1.01 (s, 9H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.80 (d, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 143.7, 140.0, 136.0, 136.0, 135.6, 135.6, 134.6, 133.9, 133.5, 130.0, 129.6, 129.6, 129.4, 129.2, 127.6, 127.6, 127.4, 127.2, 126.4, 124.4, 123.3, 81.4, 80.1, 74.2, 73.4, 72.1, 71.6, 68.1, 65.4, 42.9, 41.4, 41.3, 38.4, 35.4, 34.5, 34.3, 32.1, 30.0, 27.2, 26.8, 20.9, 19.5, 15.4 ppm. IR (film): $\tilde{\nu}$ = 3454, 2957, 2930, 2857, 1720, 1654, 1472, 1427, 1361, 1265, 1176, 1112, 1006, 822, 739, 702 cm^{-1}. MS (ESIpos) *m/z* (%) = 963.6 (100 (M+Na). HRMS (ESIpos): *m/z*: calcd for $C_{58}H_{76}O_7Si_2Na$: 963.5022; found: 963.5028.



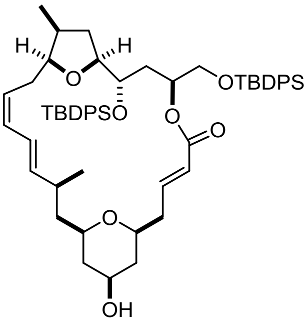
Alcohol 11-*epi*-**63.** Prepared analogously from silyl ether 11-*epi*-**62a** (24.2 mg, 22.9 µmol) as a white foam (19.3 mg, 89%). $[\propto]_D^{20}$ = +28.4 (c = 0.96, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 – 7.53 (m, 8H), 7.42 – 7.20 (m, 12H), 7.07 (ddd, *J* = 15.1, 10.2, 4.4 Hz, 1H), 6.20 (dd, *J* = 14.9, 11.0 Hz, 1H), 5.87 (tt, *J* = 10.9, 1.9 Hz, 1H), 5.75 (dd, *J* = 15.6, 1.7 Hz, 1H), 5.24 (dd, *J* = 14.9, 9.7 Hz, 1H), 5.11 – 5.01 (m, 2H), 3.93 – 3.83 (m, 2H), 3.79 – 3.68 (m, 2H), 3.41 (dd, *J* = 11.1, 3.5 Hz, 1H), 3.35 (dd, *J* = 11.2, 5.3 Hz, 1H), 3.21 – 3.07 (m, 2H), 2.64 (tt, *J* = 9.5, 3.4 Hz, 1H), 2.42 (tdd, *J* = 9.6, 4.7, 1.9 Hz, 1H), 2.27 – 2.10 (m, 4H), 2.02 (dd, *J* = 8.0, 7.7, 7.4 Hz, 1H), 1.96 – 1.86 (m, 2H), 1.84 – 1.75 (m, 2H), 1.63 – 1.52 (m, 2H), 1.42 (ddd, *J* = 13.6, 7.2, 3.5 Hz, 1H), 1.23 – 1.11 (m, 3H), 1.01 (s, 9H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.97 (s, 9H), 0.78 (d, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.2, 145.4, 139.6, 135.9, 135.8, 135.7, 135.6, 134.1, 133.9, 133.6, 133.5, 129.6, 129.5, 127.6, 127.5,



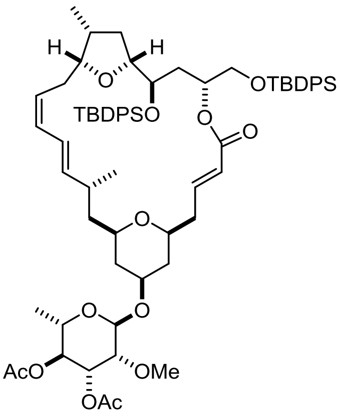
127.5, 127.4, 126.0, 125.7, 122.9, 81.3, 80.8, 75.0, 73.1, 72.4, 72.1, 68.0, 65.2, 43.4, 41.7, 41.6, 39.2, 35.6, 34.6, 34.6, 34.0, 29.5, 27.1, 26.7, 20.1, 19.4, 19.2, 15.1 ppm. IR (film): $\tilde{\nu}$ = 3414, 2957, 2930, 2857, 1722, 1655, 1472, 1428, 1361, 1326, 1262, 1177, 1111, 990, 822, 739, 702, 610 cm^{-1}. MS (ESIpos) *m/z* (%) = 963.6 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{58}H_{76}O_7Si_2Na$: 963.5022; found: 963.5017.



Secondary alcohol 72a. Prepared analogously from silyl ether **72** (24.1 mg, 22.8 µmol) as a white foam (18.4 mg, 86%). $[\alpha]_D^{20}$ = +13.8 (c = 0.92, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 – 7.57 (m, 8H), 7.43 – 7.23 (m, 12H), 6.87 (ddd, *J* = 15.7, 7.3, 6.3 Hz, 1H), 6.25 (dd, *J* = 15.1, 10.9 Hz, 1H), 5.93 (t, *J* = 10.9 Hz, 1H), 5.83 (dt, *J* = 15.7, 1.0 Hz, 1H), 5.53 (dd, *J* = 15.1, 8.0 Hz, 1H), 5.25 – 5.13 (m, 2H), 4.02 (ddd, *J* = 8.8, 5.6, 3.1 Hz, 1H), 3.79 (ddt, *J* = 10.7, 10.2, 5.1 Hz, 1H), 3.70 (ddd, *J* = 7.7, 7.6, 5.7 Hz, 1H), 3.64 – 3.58 (m, 2H), 3.54 (dd, *J* = 10.9, 4.9 Hz, 1H), 3.43 – 3.35 (m, 1H), 3.30 (dddd, *J* = 10.6, 8.9, 3.7, 1.7 Hz, 1H), 2.45 – 2.29 (m, 3H), 2.21 – 2.09 (m, 2H), 2.01 (dt, *J* = 13.9, 6.8 Hz, 1H), 1.97 – 1.81 (m, 4H), 1.75 (ddd, *J* = 14.5, 9.0, 3.4 Hz, 1H), 1.64 (ddd, *J* = 13.9, 8.6, 5.4 Hz, 1H), 1.60 – 1.47 (br d, 1H), 1.43 – 1.30 (m, 2H), 1.23 – 1.08 (m, 2H), 1.00 (s, 9H), 1.00 (s, 9H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 144.9, 140.0, 136.0, 135.9, 135.6, 135.6, 134.6, 134.0, 133.4, 129.9, 129.5, 129.4, 127.6, 127.3, 127.3, 126.8, 124.3, 123.4, 81.2, 80.0, 73.7, 73.2, 72.5, 71.6, 68.1, 65.4, 43.0, 41.3, 41.3, 38.4, 35.6, 34.3, 34.0, 33.1, 30.2, 27.2, 26.7, 20.2, 19.5, 19.2, 15.2 ppm. IR (film): $\tilde{\nu}$ = 3422, 2957, 2931, 2857, 1719, 1656, 1472, 1428, 1362, 1265, 1177, 1111, 982, 823, 740, 702, 611 cm^{-1}. MS (ESIpos) *m/z* (%) = 963.6 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{58}H_{76}O_7Si_2Na$: 963.5022; found: 963.5021.

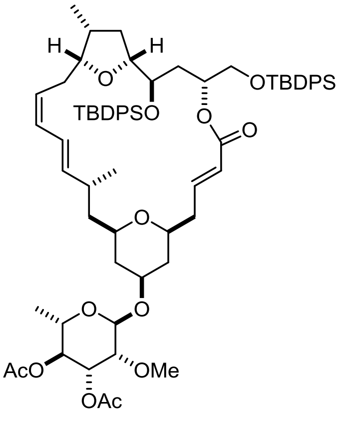


Alcohol 11-*epi*-**72a.** Prepared analogously from silyl ether 11-*epi*-**72** (23.1 mg, 21.9 µmol) as a white foam (18.5 mg, 90%). $[\alpha]_D^{20}$ = +100.5 (c = 0.92, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 – 7.55 (m, 8H), 7.42 – 7.23 (m, 12H), 6.82 (ddd, *J* = 15.8, 7.2, 5.4 Hz, 1H), 6.25 (dd, *J* = 15.2, 10.9 Hz, 1H), 5.96 (t, *J* = 10.9 Hz, 1H), 5.71 (dt, *J* = 15.7, 1.4 Hz, 1H), 5.34 (dd, *J* = 15.1, 8.5 Hz, 1H), 5.22 (td, *J* = 10.2, 6.1 Hz, 1H), 5.02 – 4.95 (m, 1H), 4.10 (ddd, *J* = 8.9, 4.8, 2.3 Hz, 1H), 3.80 (td, *J* = 7.8, 4.8 Hz, 1H), 3.77 – 3.70 (m, 2H), 3.70 – 3.62 (m, 2H), 3.31 (ddt, *J* = 11.3, 9.5, 2.0 Hz, 1H), 3.24 (t, *J* = 10.7 Hz, 1H), 2.57 – 2.47 (m, 1H), 2.42 (dddd, *J* = 16.4, 9.5, 5.4, 1.7 Hz, 1H), 2.38 – 2.16 (m, 4H), 2.08 (dt, *J* = 14.9, 5.2 Hz, 1H), 1.95 – 1.85 (m, 2H), 1.82 – 1.73 (m, 2H), 1.60 – 1.50 (m, 2H), 1.25 – 1.12 (m, 4H), 1.03 (s, 9H), 1.00 (s, 9H), 0.98 (d, *J* = 7.2 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 144.7, 141.0, 135.9, 135.9, 135.5, 135.5, 134.2, 133.5, 133.4, 133.3, 130.0, 129.6, 129.5, 129.4, 129.4, 127.6, 127.5, 127.4, 126.9, 125.6, 123.0, 81.3, 79.6, 73.6, 73.2, 72.3, 70.6, 67.9, 65.4, 44.2, 41.8, 41.7, 38.9, 35.6, 33.3, 33.2, 33.0, 30.8, 27.1, 26.7, 22.9, 19.4, 19.2, 15.4 ppm. IR (film): $\tilde{\nu}$ = 3456, 2957, 2931, 2857, 1714, 1472, 1462, 1428, 1362, 1268, 1180, 1110, 1089, 1048, 999, 908, 822, 731, 701, 610 cm^{-1}. MS (ESIpos) *m/z* (%) = 963.6 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{58}H_{76}O_7Si_2Na$: 963.5022; found: 963.5024.

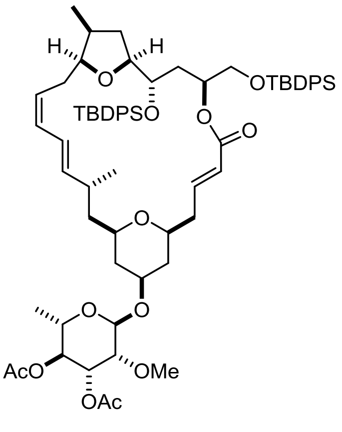


Glycoside 64. A Schlenk tube was charged with powdered 4 Å MS (400 mg) and flame-dried in vacuo. After reaching RT, the molecular sieves were suspended in CH_2Cl_2 (10 mL) and a solution of alcohol **63** (87.0 mg, 92.4 µmol) in CH_2Cl_2 (1.6 mL) was introduced. Rhamnosyl donor **59** (56.3 mg, 139 µmol) was added as a solid and the resulting suspension was stirred for 45 min at ambient temperature before it was cooled to –50 °C. A solution of TESOTf (0.1 M, 277 µL, 27.7 µmol) was added dropwise via syringe over 1 min. After stirring for 30 min at –50 °C, the reaction was quenched with NEt_3 (0.1 mL), the mixture was filtered through a pad of Celite® and the filtrate was evaporated. The crude residue was purified by flash chromatography (hexanes/EtOAc 3:1) to yield the desired glycoside as a white foam (97.0 mg, 88% yield, 16:1 d.r.). $[\propto]_D^{20}$ = –61.5 (c = 0.82, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.70 – 7.55 (m, 8H), 7.43 – 7.24 (m, 12H), 6.85 (ddd, *J* = 15.8, 8.1, 5.5 Hz, 1H), 6.23 (dd, *J* = 15.4, 10.8 Hz, 1H), 5.91 (t, *J* = 10.8 Hz, 1H), 5.80 (dt, *J* = 15.7, 1.1 Hz, 1H), 5.58 (dd, *J* = 15.4, 6.8 Hz, 1H), 5.23 – 5.14 (m, 3H), 5.08 (t, *J* = 9.9 Hz, 1H), 4.95 (d, *J* = 1.9 Hz, 1H), 4.02 (ddd, *J* = 8.8, 6.1, 2.4 Hz, 1H), 3.82 (dq, *J* = 9.7, 6.3 Hz, 1H), 3.79 – 3.70 (m, 2H), 3.65 (dd, *J* = 10.7, 4.5 Hz, 2H), 3.60 (q, *J* = 6.4 Hz, 1H), 3.54 (dd, *J* = 3.3, 1.8 Hz, 1H), 3.45 (s, 3H), 3.32 – 3.23 (m, 2H), 2.44 – 2.37 (m, 1H), 2.37 – 2.31 (m, 1H), 2.25 (ddd, *J* = 15.3, 8.1, 2.6 Hz, 1H), 2.14 – 2.06 (m, 2H), 2.05 (s, 3H), 2.03 – 1.99 (m, 1H), 2.00 (s, 3H), 1.98 – 1.90 (m, 2H), 1.90 – 1.81 (m, 3H), 1.75 (ddd, *J* = 14.1, 8.5, 6.0 Hz, 1H), 1.37 (ddd, *J* = 12.7, 7.3, 5.1 Hz, 1H), 1.34 – 1.28 (m, 2H), 1.27 – 1.26 (m, 1H), 1.17 (d, *J* = 6.3 Hz, 3H), 1.02 (s, 9H), 1.00 (s, 9H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.79 (d, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.3, 169.9, 165.7, 144.5, 140.0, 136.0, 136.0, 135.6, 135.6, 135.6, 134.6, 133.9, 133.5, 130.0, 129.6, 129.6, 129.4, 129.2, 127.6, 127.6, 127.4, 127.2, 126.5, 124.4, 123.5, 95.4, 81.4, 80.1, 78.8, 74.1, 73.4, 73.2, 72.1, 71.7, 71.6, 71.6, 66.7, 65.4, 59.6, 43.0, 39.1, 38.5, 37.6, 35.4, 34.5, 34.3, 32.1, 29.9, 29.7, 27.2, 26.8, 21.0, 20.8, 19.5, 19.3, 17.5, 15.3 ppm. IR (film): $\tilde{\nu}$ = 2958, 2929, 2857, 1745, 1720, 1654, 1472, 1361, 1427, 1365, 1241, 1223, 1177, 1107, 1074, 1040, 998, 822, 803, 755, 702 cm^{-1}. MS (ESIpos) *m/z* (%) = 1207.6 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{69}H_{92}O_{13}Si_2Na$: 1207.5969; found: 107.5976.

Glycoside 11-*epi*-64. Prepared analogously from 11-*epi*-**63** (24.2 mg, 22.9 µmol) as a white foam (20.6 mg, 87% yield, single diastereomer). $[\propto]_D^{20}$ = –17.4 (c = 0.87, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.67 – 7.52 (m, 8H), 7.43 – 7.24 (m, 11H), 7.23 – 7.20 (m, 1H), 7.05 (ddd, *J* = 15.2, 10.3, 4.4 Hz, 1H), 6.19 (dd, *J* = 14.9, 11.0 Hz, 1H), 5.87 (t, *J* = 11.0 Hz, 1H), 5.74 (dd, *J* = 15.6, 1.1 Hz, 1H), 5.24 (dd, *J* = 15.0 Hz, 9.7 Hz, 1H), 5.18 (dd, *J* = 10.1, 3.2 Hz, 1H), 5.12 – 5.00 (m, 3H), 4.91 (d, *J* = 1.9 Hz, 1H), 3.92 – 3.83 (m, 2H), 3.80 (dq, *J* = 9.5, 6.2 Hz, 1H), 3.77 – 3.66 (m, 2H), 3.52 (dd, *J* = 3.18, 1.98 Hz, 1H), 3.43 (s, 3H), 3.40 (dd, *J* = 11.1, 3.5 Hz, 1H), 3.35 (dd, *J* = 11.2, 5.1 Hz, 1H), 3.21 – 3.06 (m, 2H), 2.69 – 2.56 (m, 1H), 2.43 (dddd, *J* = 14.1, 9.3, 4.3, 1.5 Hz, 1H), 2.25 – 2.17 (m, 2H), 2.17 – 2.10 (m, 2H), 2.04 (s, 3H), 2.01 (s, 3H), 1.96 – 1.87 (m, 2H), 1.83 – 1.74 (m, 2H), 1.56 (dd, *J* = 14.0, 2.8 Hz, 1H), 1.45 – 1.37 (m, 1H), 1.31 (q, *J* = 11.7 Hz, 2H), 1.23 – 1.16 (m, 2H), 1.15 (d, *J* = 6.2 Hz, 3H), 1.00 (s, 9H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.96 (s, 9H), 0.78 (d, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 169.9, 165.2, 145.3, 139.5, 135.9, 135.8, 135.6, 135.6, 134.1, 133.9, 133.6, 133.4, 129.6, 129.5, 129.5, 127.6, 127.5, 127.5, 127.4, 126.0, 125.7, 123.0, 95.4, 81.3, 80.8, 78.8, 75.0, 73.1, 73.1, 72.4, 72.1, 71.6, 71.6, 66.6, 65.1, 59.6, 43.4, 39.3, 39.3, 37.9, 35.6, 34.6, 33.9, 29.4, 27.0, 26.7, 22.0, 21.0, 20.8, 19.4, 19.2, 17.4, 15.1 ppm. IR (film): $\tilde{\nu}$ = 2956, 2930, 2857, 1725, 1428, 1365, 1327, 1243, 1223, 1178, 1110, 1042, 912, 824, 736, 703, 611 cm^{-1}. MS (ESIpos) *m/z* (%) = 1207.6 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{69}H_{92}O_{13}Si_2Na$: 1207.5969; found: 1207.5966.

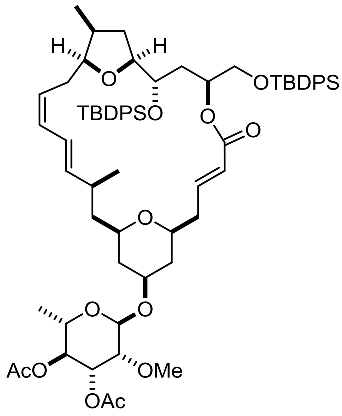


Glycoside 72b. Prepared analogously from **72a** (18.4 mg, 19.5 µmol) as a white foam (20.5 mg, 94% purity, 83% yield, single diastereomer). $[\propto]_D^{20}$ = –10.2 (c = 0.97, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.68 – 7.54 (m, 8H), 7.43 – 7.21 (m, 12H), 6.86 (dt, *J* = 15.6, 6.9 Hz, 1H), 6.24 (dd, *J* = 15.1, 11.0 Hz, 1H), 5.93 (t, *J* = 10.9 Hz, 1H), 5.82 (dt, *J* = 15.8, 1.2 Hz, 1H), 5.52 (dd, *J* = 15.1 Hz, 8.0 Hz, 1H), 5.26 – 5.13 (m, 3H), 5.08 (t, *J* = 9.8 Hz, 1H), 4.96 (d, *J* = 1.5 Hz, 1H), 4.00 (ddd, *J* = 8.4, 5.3, 3.2 Hz, 1H), 3.88 – 3.66 (m, 3H), 3.65 – 3.50 (m, 4H), 3.46 (s, 3H), 3.43 – 3.25 (m, 2H), 2.46 – 2.29 (m, 3H), 2.21 – 2.09 (m, 2H), 2.09 – 2.03 (m, 1H), 2.05 (s, 3H), 2.01 (s, 3H), 1.99 – 1.90 (m, 2H), 1.84 (dd, *J* = 7.2, 5.4 Hz, 1H), 1.74 (ddd, *J* = 14.5, 9.0, 3.6 Hz, 1H), 1.64 (ddd, *J* = 13.9, 8.4, 5.4 Hz, 1H), 1.47 – 1.15 (m, 5H), 1.17 (d, *J* = 6.2 Hz, 3H), 1.00 (s, 18H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 169.9, 165.6, 144.8, 140.0, 136.0, 135.9, 135.6, 135.5, 134.6, 134.0, 133.5, 133.4, 129.8, 129.5, 129.4, 127.6, 127.3, 126.9, 124.3, 123.5, 95.3, 81.2, 80.0, 78.8, 73.6, 73.3, 73.2, 72.6, 71.7, 71.6, 71.5, 66.6, 65.4, 59.6, 42.9, 39.1, 38.5, 37.4, 35.6, 34.4, 34.1, 33.2, 30.2, 27.1, 26.7, 21.0, 20.8, 20.2, 19.5, 19.2, 17.4, 15.2 ppm. IR (film): $\tilde{\nu}$ = 2957, 2930, 2857,

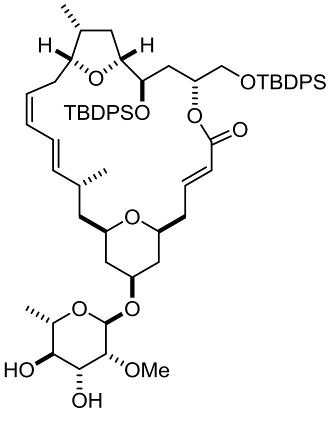


1725, 1472, 1461, 1428, 1365, 1242, 1224, 1110, 1043, 999, 913, 823, 736, 703, 611 cm^{-1}. MS (ESIpos) *m/z* (%) = 1207.6 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{69}H_{92}O_{13}Si_2Na$: 1207.5969; found: 1207.5963.

Glycoside 11-*epi*-**72b.** Prepared analogously from 11-*epi*-**72a** (18.6 mg, 19.8 µmol) as a white foam (19.9 mg, 94% purity, 80% yield, single diastereomer). $[\propto]_D^{20}$ = +41.2 (c = 0.95, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 – 7.56 (m, 8H), 7.42 – 7.22 (m, 12H), 6.86 (ddd, *J* = 15.7, 7.1, 5.6 Hz, 1H), 6.24 (dd, *J* = 15.2, 10.9 Hz, 1H), 5.96 (t, *J* = 10.9 Hz, 1H), 5.70 (dt, *J* = 15.7, 1.4 Hz, 1H), 5.34 (dd, *J* = 15.2 Hz, 8.6 Hz, 1H), 5.26 – 5.19 (m, 1H), 5.20 (dd, *J* = 10.0, 3.2 Hz, 1H), 5.08 (t, *J* = 9.9 Hz, 1H), 5.00 – 4.93 (m, 1H), 4.97 (d, *J* = 1.7 Hz, 1H), 4.08 (ddd, *J* = 8.8, 4.7, 2.5 Hz, 1H), 3.86 – 3.77 (m, 2H), 3.76 – 3.61 (m, 4H), 3.55 (dd, *J* = 3.2, 1.9 Hz, 1H), 3.46 (s, 3H), 3.33 – 3.18 (m, 2H), 2.56 – 2.46 (m, 1H), 2.41 (dddd, *J* = 16.5, 9.5, 5.6, 1.7 Hz, 1H), 2.37 – 2.17 (m, 4H), 2.06 (s, 3H), 2.02 (s, 3H), 1.99 – 1.94 (m, 1H), 1.90 (dt, *J* = 13.0, 7.9 Hz, 1H), 1.84 – 1.78 (m, 1H), 1.75 (ddd, *J* = 14.5, 8.9, 2.2 Hz, 1H), 1.58 – 1.49 (m, 2H), 1.34 – 1.26 (m, 1H), 1.27 – 1.20 (m, 2H), 1.20 – 1.15 (m, 1H), 1.17 (d, *J* = 6.3 Hz, 3H), 1.02 (s, 9H), 1.00 (s, 9H), 0.98 (d, *J* = 7.3 Hz, 3H), 0.81 (d, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 169.9, 165.7, 144.5, 141.0, 135.9, 135.9, 135.5, 135.5, 134.2, 133.5, 133.4, 133.3, 130.0, 129.6, 129.5, 129.4, 127.6, 127.5, 127.4, 126.9, 125.6, 123.0, 95.4, 81.3, 79.6, 78.8, 73.6, 73.3, 73.2, 72.4, 71.6, 70.7, 66.6, 65.4, 59.6, 44.2, 39.7, 39.0, 37.9, 35.6, 33.3, 33.2, 33.0, 30.8, 27.1, 26.7, 22.9, 21.0, 20.8, 19.4, 19.2, 17.4, 15.4 ppm. IR (film): $\tilde{\nu}$ = 2955, 2929, 2857, 1722, 1461, 1428, 1356, 1330, 1242, 1223, 1179, 1110, 1076, 1041, 999, 823, 739, 703, 611 cm^{-1}. MS (ESIpos) *m/z* (%) = 1207.7 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{69}H_{92}O_{13}Si_2Na$: 1207.5969; found: 1207.5967.

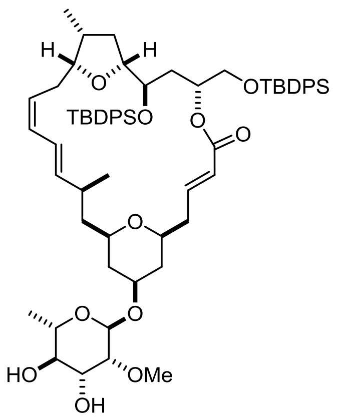


Diol 64a. Dry K_2CO_3 (28.3 mg, 205 µmol) was added to a solution of compound **64** (96.9 mg, 81.8 µmol) in MeOH (11 mL) at 0 °C. The mixture was stirred at this temperature for 2 h before a second portion of K_2CO_3 (22.6 mg, 164 µmol) was introduced. After an additonal 2 h at 0 °C, the reaction was quenched with NH_4Cl solution (15 mL) and the mixture allowed to reach ambient temperature. The aqueous phase was extracted with EtOAc (4 x 15 mL) and the combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 2:3) to give the desired product as a white foam (72.3 mg, 80%). $[\propto]_D^{20}$ = –53.1 (c = 0.57, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.66 – 7.59 (m, 8H), 7.41 – 7.25 (m, 12H), 6.86 (ddd, *J* = 15.8, 8.2, 5.6 Hz,

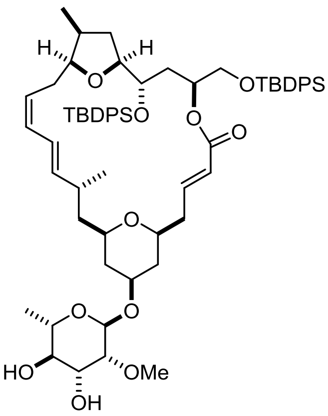


1H), 6.22 (ddt, *J* = 15.5, 10.8, 1.2 Hz, 1H), 5.91 (t, *J* = 10.8 Hz, 1H), 5.80 (dt, *J* = 15.7, 1.4 Hz, 1H), 5.59 (dd, *J* = 15.4, 6.8 Hz, 1H), 5.21 – 5.09 (m, 2H), 5.02 (d, *J* = 1.5 Hz, 1H), 4.02 (ddd, *J* = 8.9, 6.2, 2.3 Hz, 1H), 3.80 – 3.72 (m, 2H), 3.69 (td, *J* = 9.6, 3.7 Hz, 1H), 3.69 – 3.65 (m, 2H), 3.64 – 3.58 (m, 2H), 3.45 (s, 3H), 3.40 (dd, *J* = 3.8, 1.5 Hz, 1H), 3.36 (dd, *J* = 9.6, 9.4 Hz, 1H), 3.35 – 3.25 (m, 2H), 2.45 – 2.39 (m, 1H), 2.38 – 2.31 (m, 2H), 2.31 – 2.23 (m, 2H), 2.13 – 2.06 (m, 2H), 2.02 (ddd, *J* = 14.9, 10.1, 2.5 Hz, 1H), 1.97 – 1.90 (m, 2H), 1.90 – 1.82 (m, 3H), 1.75 (ddd, *J* = 14.0, 8.4, 5.9 Hz, 1H), 1.37 (ddd, *J* = 12.8, 7.4, 5.3 Hz, 1H), 1.32 (ddd, *J* = 13.7, 8.0, 4.2 Hz, 1H), 1.28 (d, *J* = 6.2 Hz, 3H), 1.24 – 1.17 (m, 2H), 1.03 (s, 9H), 1.00 (s, 9H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.79 (d, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ = 165.7, 144.5, 140.0, 136.0, 136.0, 135.6, 135.5, 134.6, 134.0, 133.5, 130.0, 129.6, 129.6, 129.3, 129.2, 127.6, 127.6, 127.4, 127.2, 126.5, 124.4, 123.5, 93.9, 81.4, 80.6, 80.1, 74.0, 74.0, 73.5, 72.7, 72.1, 71.7, 71.4, 67.9, 65.4, 58.9, 43.0, 39.1, 38.5, 37.5, 35.4, 34.5, 34.3, 32.1, 29.9, 27.2, 26.8, 20.8, 19.5, 19.3, 17.5, 15.4 ppm. IR (film): $\tilde{\nu}$ = 3411, 2958, 2930, 2857, 1719, 1656, 1462, 1428, 1360, 1327, 1263, 1176, 1111, 1076, 1045, 823, 740, 702 cm^{-1}. MS (ESIpos) *m/z* (%) = 1123.7 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for C$_{65}$H$_{88}$O$_{11}$Si$_2$Na: 1123.5757; found: 1123.5748.

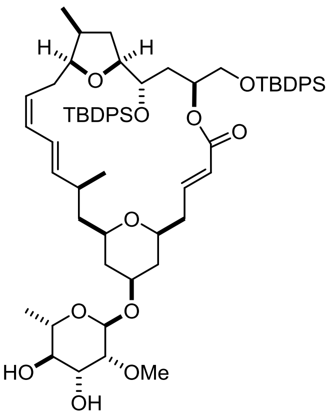
Diol 11-*epi*-**64a.** Prepared analogously from compound 11-*epi*-**64** (20.0 mg, 16.9 µmol) as a white foam (16.4 mg, 88%). $[\propto]_{D}^{20}$ = –5.9 (c = 0.67, CH$_2$Cl$_2$). ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.65 – 7.53 (m, 8H), 7.42 – 7.24 (m, 10H), 7.24 – 7.19 (m, 2H), 7.05 (ddd, *J* = 15.5, 10.3, 4.3 Hz, 1H), 6.20 (dd, *J* = 15.0, 11.0 Hz, 1H), 5.88 (tt, *J* = 11.0, 1.9 Hz, 1H), 5.77 – 5.71 (m, 1H), 5.25 (dd, *J* = 14.9, 9.7 Hz, 1H), 5.11 – 5.00 (m, 2H), 4.97 (d, *J* = 1.4 Hz, 1H), 3.91 – 3.83 (m, 2H), 3.76 – 3.69 (m, 2H), 3.67 (dd, *J* = 9.4, 3.8 Hz, 1H), 3.61 (dq, *J* = 9.4, 6.2 Hz, 1H), 3.42 (s, 3H), 3.40 – 3.33 (m, 3H), 3.32 (t, *J* = 9.3 Hz, 1H), 3.17 (tt, *J* = 11.3, 1.9 Hz, 1H), 3.11 (m, 1H), 2.70 – 2.57 (m, 1H), 2.43 (dddd, *J* = 14.4, 9.2, 4.3, 1.9 Hz, 1H), 2.36 – 2.28 (br s, 1H), 2.23 – 2.17 (m, 2H), 2.18 – 2.11 (m, 2H), 2.03 (dt, *J* = 13.1, 7.6 Hz, 1H), 1.97 – 1.88 (m, 2H), 1.83 – 1.75 (m, 2H), 1.56 (ddd, *J* = 14.1, 11.1, 3.1 Hz, 1H), 1.41 (ddd, *J* = 13.6, 7.7, 5.9 Hz, 1H), 1.31 – 1.22 (m, 2H), 1.26 (d, *J* = 6.1 Hz, 3H), 1.22 – 1.10 (m, 2H), 1.00 (s, 9H), 0.99 (d, *J* = 6.5 Hz, 3H), 0.97 (s, 9H), 0.78 (d, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ = 165.2, 145.3, 139.6, 135.9, 135.8, 135.7, 135.6, 134.1, 133.9, 133.6, 133.4, 129.6, 129.5, 129.5, 129.5, 127.6, 127.5, 127.5, 127.4, 126.0, 125.7, 123.0, 93.9, 81.3, 80.7, 80.6, 74.9, 74.0, 73.1, 72.6, 72.4, 72.1, 71.4, 67.8, 65.1, 58.8, 43.4, 39.3, 37.9, 35.6, 34.6, 34.6, 33.9, 29.4, 27.0, 26.7, 22.0, 19.4, 19.2, 17.5, 15.2 ppm. IR (film): $\tilde{\nu}$ = 3426, 2956, 2929, 2857, 1722, 1461, 1428, 1390, 1361, 1326, 1261, 1178, 1108, 1077, 1043, 909, 822, 734, 702, 611 cm^{-1}. MS (ESIpos) *m/z* (%) = 1123.6 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for C$_{65}$H$_{88}$O$_{11}$Si$_2$Na: 1123.5757; found: 1123.5754.



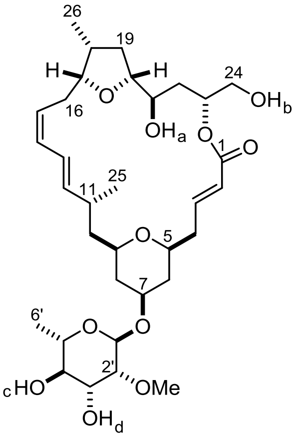
Diol 72c. Prepared analogously from compound **72b** (20.5 mg, 16.3 µmol) as a white foam (17.3 mg, 96%). $[\propto]_D^{20}$ = –2.2 (c = 0.80, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.65 – 7.57 (m, 8H), 7.42 – 7.24 (m, 12H), 6.86 (ddd, *J* = 15.7, 7.2, 6.6 Hz, 1H), 6.24 (dd, *J* = 15.2, 10.9 Hz, 1H), 5.93 (tt, *J* = 10.9, 1.4 Hz, 1H), 5.82 (dt, *J* = 15.7, 1.3 Hz, 1H), 5.53 (dd, *J* = 15.2, 8.0 Hz, 1H), 5.21 (dt, *J* = 10.0, 8.1 Hz, 1H), 5.16 (m, 1H), 5.02 (d, *J* = 1.1 Hz, 1H), 4.00 (ddd, *J* = 8.8, 5.5, 3.3 Hz, 1H), 3.77 (tt, *J* = 10.8, 4.9 Hz, 1H), 3.70 (td, *J* = 7.8, 5.6 Hz, 1H), 3.70 – 3.65 (m, 1H), 3.63 (dq, *J* = 9.5, 6.3 Hz, 1H), 3.61 (t, *J* = 6.2 Hz, 1H), 3.62 – 3.58 (m, 1H), 3.53 (dd, *J* = 10.8, 4.9 Hz, 1H), 3.46 (s, 3H), 3.41 – 3.36 (m, 1H), 3.39 (dd, *J* = 3.9, 1.4 Hz, 1H), 3.34 (t, *J* = 9.4 Hz, 1H), 3.34 – 3.28 (m, 1H), 2.43 – 2.36 (m, 1H), 2.36 – 2.25 (m, 4H), 2.18 – 2.10 (m, 2H), 2.02 (ddt, *J* = 14.0, 6.9, 1.2 Hz, 1H), 1.99 – 1.95 (m, 1H), 1.93 (ddd, *J* = 14.5, 8.5, 3.3 Hz, 1H), 1.88 – 1.81 (m, 2H), 1.74 (ddd, *J* = 14.5, 8.9, 3.4 Hz, 1H), 1.63 (ddd, *J* = 14.0, 8.5, 5.5 Hz, 1H), 1.38 (ddd, *J* = 12.7, 8.2, 7.5 Hz, 1H), 1.33 (ddd, *J* = 13.7, 7.9, 3.9 Hz, 1H), 1.28 (d, *J* = 6.2 Hz, 3H), 1.26 – 1.22 (m, 2H), 1.00 (s, 9H), 0.99 (s, 9H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 165.6, 144.7, 140.0, 136.0, 135.9, 135.6, 135.6, 134.6, 134.0, 133.6, 133.4, 129.9, 129.5, 129.4, 129.3, 127.6, 127.6, 127.3, 127.3, 126.8, 124.4, 123.6, 93.9, 81.3, 80.6, 80.1, 74.0, 73.7, 73.3, 72.9, 72.6, 71.7, 71.4, 67.9, 65.5, 58.9, 43.0, 39.2, 38.5, 37.4, 35.7, 34.4, 34.1, 33.2, 30.3, 27.2, 26.7, 20.3, 19.5, 19.2, 17.5, 15.2 ppm. IR (film): $\tilde{\nu}$ = 3436, 2957, 2929, 2856, 1719, 1461, 1428, 1373, 1265, 1242, 1178, 1106, 1078, 1044, 985, 822, 739, 702, 609 cm^{-1}. MS (ESIpos) *m/z* (%) = 1123.6 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{65}H_{88}O_{11}Si_2Na$: 1123.5757; found: 1123.5760.



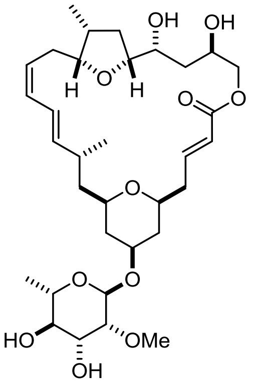
Diol 11-*epi*-**72c.** Prepared analogously from compound 11-*epi*-**72b** (19.1 mg, 15.1 µmol) as a white foam (15.4 mg, 92%). $[\propto]_D^{20}$ = +50.6 (c = 0.77, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.64 – 7.57 (m, 8H), 7.41 – 7.24 (m, 12H), 6.81 (ddd, *J* = 15.8, 7.2, 5.6 Hz, 1H), 6.25 (dd, *J* = 15.1, 10.7 Hz, 1H), 5.97 (tt, *J* = 10.9, 1.3 Hz, 1H), 5.71 (dt, *J* = 15.8, 1.6 Hz, 1H), 5.34 (dd, *J* = 15.1, 8.6 Hz, 1H), 5.21 (td, *J* = 10.1, 6.2 Hz, 1H), 5.03 (d, *J* = 1.1 Hz, 1H), 4.99 – 4.94 (m, 1H), 4.09 (ddd, *J* = 8.8, 4.8, 2.4 Hz, 1H), 3.81 (td, *J* = 7.9, 4.8 Hz, 1H), 3.76 – 3.60 (m, 6H), 3.47 (s, 3H), 3.40 (dd, *J* = 3.8, 1.4 Hz, 1H), 3.34 (t, *J* = 9.4 Hz, 1H), 3.29 (ddt, *J* = 11.2, 9.5, 1.9 Hz, 1H), 3.24 (tt, *J* = 10.9, 1.5 Hz, 1H), 2.56 – 2.46 (m, 1H), 2.41 (dddd, *J* = 16.4, 9.4, 5.6, 1.7 Hz, 1H), 2.36 – 2.17 (m, 6H), 2.09 (dddd, *J* = 14.8, 5.5, 5.4, 1.7 Hz, 1H), 1.96 (ddt, *J* = 12.3, 3.9, 2.0 Hz, 1H), 1.90 (dt, *J* = 13.0, 7.9 Hz, 1H), 1.80 (ddt, *J* = 12.6, 4.6, 1.9 Hz, 1H), 1.75 (ddd, *J* = 14.5, 8.9, 2.4 Hz, 1H), 1.57 – 1.50 (m, 2H), 1.28 – 1.23 (m, 1H), 1.28 (d, *J* = 6.2 Hz, 3H), 1.21 – 1.12 (m, 2H), 1.02 (s, 9H), 1.00 (s, 9H), 0.98 (d, *J* = 7.1 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H) ppm.



^{13}C NMR (150 MHz, CDCl$_3$): δ = 165.7, 144.5, 140.9, 135.9, 135.9, 135.6, 135.5, 134.3, 133.6, 133.5, 133.3, 130.0, 129.6, 129.5, 129.4, 129.4, 127.6, 127.5, 127.4, 126.9, 125.7, 123.1, 94.1, 81.3, 80.6, 79.7, 74.1, 73.7, 73.2, 72.9, 72.4, 71.5, 70.8, 67.9, 65.5, 58.8, 44.1, 39.7, 39.1, 38.0, 35.6, 33.4, 33.3, 33.1, 30.8, 27.1, 26.8, 22.9, 19.4, 19.2, 17.5, 15.4 ppm. IR (film): $\tilde{\nu}$ = 3428, 2957, 2931, 2857, 1717, 1462, 1428, 1361, 1267, 1179, 1111, 1079, 1045, 998, 910, 823, 736, 703, 611 cm^{-1}. MS (ESIpos) *m/z* (%) = 1123.7 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{65}H_{88}O_{11}Si_2Na$: 1123.5757; found: 1123.5760.

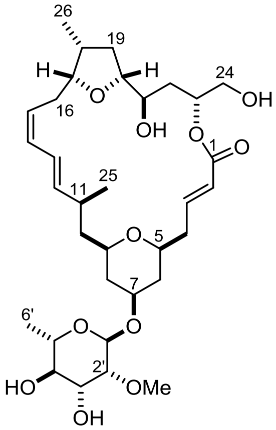


Putative mandelalide A (1). A Teflon vial was charged with diol **64a** (42.0 mg, 38.1 µmol) and THF (2.5 mL). The solution was cooled to 0 °C before pyridine (2.5 mL) and HF·pyridine (2.5 mL) were slowly added via an Eppendorf pipette. After stirring for 5 min at 0 °C, the ice bath was removed and stirring continued at ambient temperature for 46 h. The mixture was diluted with EtOAc (10 mL) and carefully poured into $NaHCO_3$ solution (30 mL). The aqueous phase was extracted with EtOAc/EtOH (9:1, 4 x 15 mL). The combined organic extracts were washed with NH_4Cl solution (20 mL), dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (CH_2Cl_2/MeOH 97:3 to 96:4 to 95:5 to 96:4) to give the desired compound as a white amorphous solid (19.1 mg, 80%). $[\propto]_D^{23}$ = –29 (c = 0.25, MeOH). ^{1}H NMR (600 MHz, CDCl$_3$): see table 5; ^{13}C NMR (150 MHz, CDCl$_3$): see table 5; IR (film): $\tilde{\nu}$ = 3414, 2955, 2924, 2854, 1714, 1653, 1457, 1374, 1323, 1277, 1228, 1179, 1106, 1071, 1043, 988, 955, 911, 814, 732 cm^{-1}. MS (ESIpos) *m/z* (%) = 647.4 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{33}H_{52}O_{11}Na$: 647.3402; found: 647.3406.

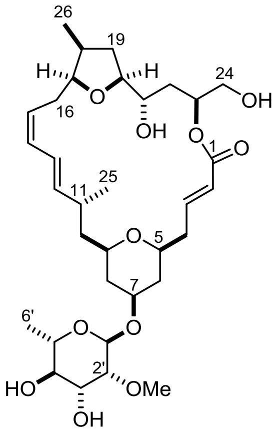


Ring-expanded mandelalide A isomer (65). Obtained as a by-product from the reaction described above. $[\propto]_D^{23}$ = +10 (c = 0.21, MeOH). ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.04 (ddd, *J* = 15.8, 7.3, 6.6 Hz, 1H), 6.35 (ddt, *J* = 15.3, 10.9, 1.3 Hz, 1H), 6.08 (t, *J* = 10.9 Hz, 1H), 5.91 (dt, *J* = 15.8, 1.4 Hz, 1H), 5.73 (dd, *J* = 15.3, 6.5 Hz, 1H), 5.36 (dt, *J* = 10.5, 8.1 Hz, 1H), 5.01 (d, *J* = 1.4 Hz, 1H), 4.16 (dd, *J* = 11.1, 5.6 Hz, 1H), 4.14 (dd, *J* = 11.2, 5.0 Hz, 1H), 4.10 – 4.04 (m, 2H), 3.81 – 3.74 (m, 2H), 3.68 (dd, *J* = 9.5, 3.8 Hz, 1H), 3.66 (br s, 1H), 3.62 (dq, *J* = 9.3, 6.2 Hz, 1H), 3.45 (s, 3H), 3.39 (dd, *J* = 3.8, 1.5 Hz, 1H), 3.37 – 3.29 (m, 3H), 2.97 (br s, 1H), 2.64 – 2.48 (m, 2H), 2.47 – 2.23 (m, 7H), 1.99 (ddt, *J* = 12.2, 4.4, 1.7 Hz, 1H), 1.94 (ddd, *J* = 12.1, 7.2, 6.1 Hz, 1H), 1.86 (ddt, *J* = 12.5, 4.5, 1.7 Hz, 1H), 1.71 (ddd, *J* = 14.4, 8.9, 3.2 Hz, 1H), 1.64 (ddd, *J* = 14.1, 10.2, 4.7 Hz, 1H), 1.59 (ddd, *J* = 14.4, 8.6, 3.5 Hz, 1H), 1.52 – 1.44 (m, 1H), 1.27 – 1.26 (m, 5H), 1.19 (td, *J* = 11.6, 11.5 Hz, 1H), 1.04 (d, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 6.6 Hz, 3H) ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ = 166.4, 146.0, 142.0, 130.9, 126.4, 123.1, 122.8, 94.0, 81.4, 80.8, 80.6, 74.2, 74.0, 73.3, 72.7, 71.4, 71.1, 68.1, 68.0, 67.9, 58.9, 42.8, 39.3, 38.1, 37.5, 37.2, 36.9, 35.6, 32.7, 30.4, 18.0, 17.5, 14.5 ppm. IR (film): $\tilde{\nu}$ = 3427, 2924, 1714, 1653, 1454, 1373, 1323, 1275, 1179, 1106, 1043, 988, 734 cm^{-1}. MS (ESIpos) *m/z* (%) = 647.3 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{33}H_{52}O_{11}Na$: 647.3402; found: 647.3404.

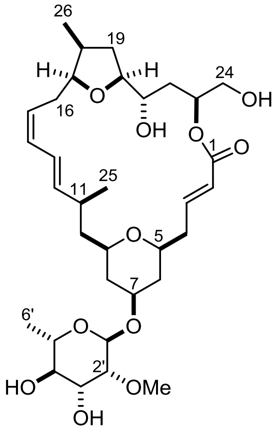
11-*epi*-Isomer of putative mandelalide A 11-*epi*-**1.** Prepared analogously from diol 11-*epi*-**64a** (10.0 mg, 9.08 µmol) as a white amorphous solid (4.8 mg, 85%). $[\propto]_D^{23}$ = –25.8 (c = 0.41, MeOH). ^{1}H NMR (600 MHz, $CDCl_3$): see table 6. ^{13}C NMR (150 MHz, $CDCl_3$): see table 6. IR (film): $\tilde{\nu}$ = 3411, 2924, 2854, 1716, 1654, 1457, 1373, 1246, 1178, 1107, 1045, 992, 812, 733 cm^{-1}. MS (ESIpos) *m/z* (%) = 647.4 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{33}H_{52}O_{11}Na$: 647.3402; found: 647.3402.



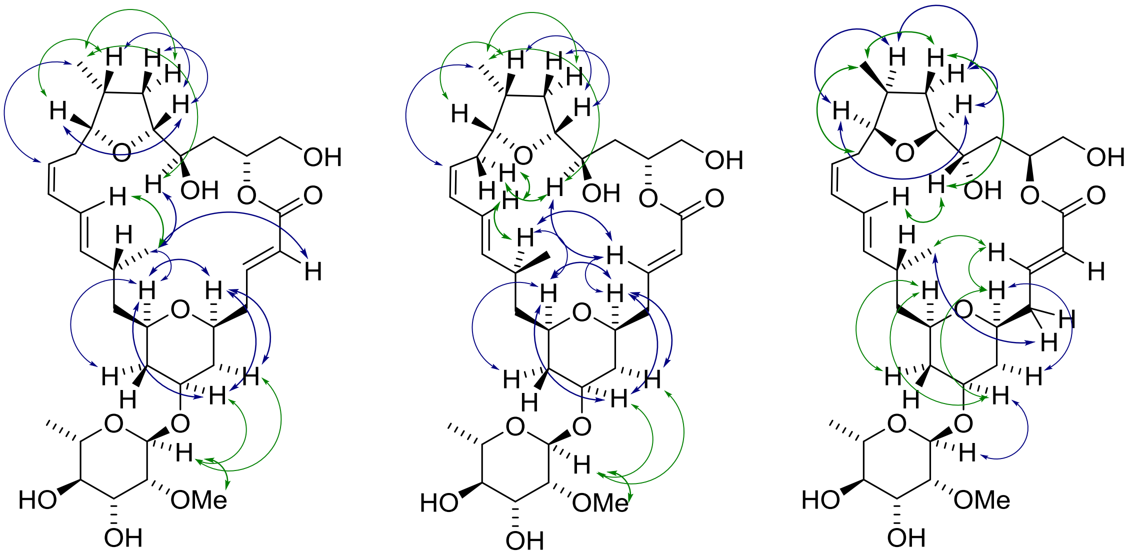
Reassigned mandelalide A (**6**)**.** Prepared analogously from diol **72c** (14.0 mg, 12.7 µmol) as a white amorphous solid (5.6 mg, 71%). $[\propto]_D^{23}$ = –40.1 (c = 0.27, MeOH). ^{1}H NMR (600 MHz, $CDCl_3$): see table 7. ^{13}C NMR (150 MHz, $CDCl_3$): see table 7. IR (film): $\tilde{\nu}$ = 3404, 2958, 2922, 1716, 1657, 1454, 1372, 1318, 1262, 1221, 1181, 1105, 1042, 985, 813, 734 cm^{-1}. MS (ESIpos) *m/z* (%) = 647.5 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{35}H_{52}O_{11}Na$: 647.3402; found: 647.3401.



11-*epi*-Isomer of actual mandelalide A 11-*epi*-**6.** Prepared analogously from diol 11-*epi*-**72c** (15.0 mg, 13.6 µmol) as a white amorphous solid (5.8 mg, 68%). $[\propto]_D^{23}$ = –18.8 (c = 0.47, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): see table 8. ^{13}C NMR (150 MHz, $CDCl_3$): see table 8. IR (film): $\tilde{\nu}$ = 3424, 2921, 1713, 1655, 1454, 1369, 1329, 1262, 1181, 1132, 1105, 1044, 990, 813 cm^{-1}. MS (ESIpos) *m/z* (%) = 647.37 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{35}H_{52}O_{11}Na$: 647.3402; found: 647.3402.



The following Scheme shows key NOESY contacts observed for proposed Mandelalide A (**1**), 11-*epi*-**1** and actual Mandelalide A (**6**). The structural assignments made above for the different building blocks were confirmed by the observed NOE contacts between H5, H7 and H9 for the southern THP unit. Furthermore, the NOE contacts between H17, H18, H19 and H20 indicate once again an all-*cis* configured THF ring. Interesting to note are the different NOE contacts across the macrocycle for the three isomers. Due to extensive signal overlap in the ^{1}H NMR spectrum of 11-*epi*-**6**, no NOE contacts were assigned.



key NOESY correlations for proposed Mandelalide A (**1**)

key NOESY correlations for (11-*epi*)-**1**

key NOESY correlations for actual Mandelalide A (north-epi-**1**)

different colors were used only for better overview

For comparison with the natural product, the ^{13}C NMR spectra of all synthetic isomers of Mandelalide A were referenced to $CDCl_3$ = 77.23 ppm as in the isolation paper[13] (in other spectra reported above, the solvent signal was set to 77.00 ppm).

Table 5:^{1}H & ^{13}C NMR data of putative Mandelalide A (**1**) (4.2 mg in 0.45 mL $CDCl_3$).

atom n°	**^{1}H NMR ($CDCl_3$, 600 MHz)**					**^{13}C NMR ($CDCl_3$, 150**	
	δ /ppm	**m**	***J* /Hz**	**COSY**	**NOESY**	**δ /ppm**	**HMBC**
1	-	-	-	-	-	167.3	-
2	5.92	dt	15.6, 1.5	3, (4ab)	4(a)b, (25)	123.1	1, (3), 4
3	7.02	ddd	15.5, 8.6, 5.5	2, 4a(b)	4a(b), 5, (6a)	146.3	1, 2, 4, 5
4a	2.34	ddd	15.2, 6.5, 5.6, 1.8	(3), 4b, 5	(2), 3, 4b, 5	38.5	2, 3, 5, 6
4b	2.46	dddd	15.2, 8.6, 3.7, 1.2	3, 4a, (5)	2, 3, 4a, 5, 25		2, 3, 5, (6)
5	3.42	m	-	4a(b), 6a	(3), 4ab, 6b, 7, 9	73.4	3, (4), 7, 9
6a	1.26	m	-	5, 6b, 7	-	36.7	4, 5, 7, 8
6b	1.94	ddt	12.0, 4.6, 1.9	6a, 7	(5), 6a, 7, 1'		7, 8
7	3.77	m	-	6ab, 8ab	5, 6b, 8b, 9, 1'	72.8	6, 8, (1')
8a	1.22	m	-	7, 8b, 9	-	39.3	-
8b	1.84	dddd	12.5, 4.2, 1.9, 1.9	7, 8a, (9)	7, 8a, 9, 1‘, 5‘		6, 7
9	3.33	m	-	8a(b), 10ab	5, 7, 8b, 10b, 11, 25	73.1	(5), (7), 10, 11
10a	1.27	m	-	9, 10b, 11	-	42.9	-
10b	1.69	ddd	14.1, 9.1, 5.1	9, 10a, (11)	8a, 9, 10a, 11, 12, 13, 25		8, 9, 11, 12, 25
11	2.44	m	-	10a(b), 12, 25	8b, 9, 10b, 12, 13, 25	32.8	9, 10, 12, 13, 25
12	5.61	dd	15.2, 7.6	11, 13	(10ab), 11, 14, 25	140.9	10, 11, 14, (15), 25
13	6.22	ddt	15.2, 10.8, 1.0	12, 14	10b, 11, 16ab, 25	123.8	11, 14, 15
14	6.01	tt	10.8, 1.8	13, 15	12, 15	130.5	12, 13, 16
15	5.27	ddd	10.8, 8.3, 7.5	14, 16ab	14, 16ab, 17, (26)	126.5	13, 16, 17
16a	2.14	dddd	14.8, 6.8, 5.1, 1.9	15, 16b, 17	13, (15), 16a, 21, (26)	31.2	14, 15, 17, 18
16b	2.29	dtd	14.8, 8.5, 1.6	15, 16a, 17	13, 15, 16b, 21, 26		(13), 14, 15, 17, 18
17	4.03	ddd	8.6, 7.2, 4.9	16ab, 18	15, 18, (20), (26)	81.3	15, 19, 20, 26
18	2.43	m	-	17, 19a(b), 26	17, 19ab, 20, 26	37.1	16, 17, 19, (20), 26
19a	1.28	m	-	18, 19b, 20	(18), 19b, 21, 26	36.0	-
19b	2.04	dt	12.3, 6.7	(18), 19a, 20	18, 19a, 20, (26)		17, 18, (20), 21, 26
20	3.71	ddd	8.4, 8.2, 6.7	19ab, 21	17, 18, 19b, 21, 22a(b)	82.7	(17), (18), 19, 21,
21	3.45	m	-	20, 22(a)b	13, 19a, 22b, 23, 25, 26	72.5	(19), 20, 22, 23
22a	1.54	ddd	14.4, 10.5, 2.5	21, 22b, (23)	20, 21, 22b, 23, 24ab	34.1	20, 23, 24
22b	1.77	ddd	14.4, 10.8, 2.0	(21), 22a, 23	(19b), 21, 22a, 23, (24a)		(20), 23, 24
23	5.24	m	-	22(a)b, 24ab	21, 22a(b)	72.5	(22), (1)
24a	3.65	m	-	23, 24b	(22ab), 24b	65.7	22, 23
24b	3.78	dd	12.1, 3.3	23, 24a	24a		22
25	1.00	d	6.7	11	2, 9, (10b), 11, 12, 13, 21	20.1	10, 11, 12
26	0.98	d	7.0	18	15ab, 16a(b), (17), 18, (21)	14.7	17, 18, 19
1'	5.02	d	1.5	2'	6b, 7, 2', 7'	94.0	7, 2', 3', 5'
2'	3.40	dd	3.8, 1.5	1', 3'	1', 7', 3'	80.9	3', 4', 7'
3'	3.69	m	-	2', 4'	(1‘), (2'), 5'	71.7	(2'), 4'
4'	3.34	t	9.4	3', 5'	6', 7'	74.2	3', 5', 6‘
5'	3.63	dd	9.4, 6.1	4', 6'	(2'), 3', 6', 8b	68.2	(1'), 3', 4', (6')
6'	1.28	d	6.3	5'	1‘, 4', 5'	17.7	4', 5'
7'	3.46	s	-	-	1', 6'	59.2	2'
OHa	2.56-2.33	-	-	21		-	21,22
OHb	2.56-2.33	-	-			-	
OHc	2.44-2.34	-	-	3'		-	3'
OHd	2.78-2.64	br s	-	4'		-	4'

Table 6: ^{1}H & ^{13}C NMR data of 11-*epi*-Isomer of putative mandelalide A (11-*epi*-**1**) (3.1 mg in 0.25 mL $CDCl_3$).

atom n°	^{1}H NMR ($CDCl_3$, 600 MHz)					^{13}C NMR ($CDCl_3$, 150 MHz)	
	δ /ppm	m	*J* /Hz	COSY	NOESY	δ /ppm	HMBC
1	-	-	-	-	-	166.8	-
2	5.92	dt	15.6, 1.1	3, (4a)	3, 4b	123.6	1, 3, 4, (5)
3	7.09	ddd	15.6, 8.2, 6.7	2, 4ab	2, 4ab, 5, 11, 13, (21)	146.1	1, 2, 4, 5
4a	2.31	dddd	14.3, 8.2, 2.7, 0.8	3, 4b, (5)	2, 3, 4b, 5, (6b)	39.5	2, 3, 5, (6)
4b	2.39	m	-	3, 4a, 5	2, 3, 4a, 6a		2, 3, 5, 6
5	3.26	dddd	11.2, 10.5, 3.0, 2.1	4a, 4b, 6a(b)	2, 3, 4a, 6b, 7, 9	74.0	(3), (4), (7), (9)
6a	1.15	ddd	11.8, 11.7, 11.6	5, 6b, 7	4ab, 6b, 8a, 1‘	38.2	4, 5, 7, 8
6b	1.98	ddt	12.2, 4.7, 1.9	5, 6a, 7	4a, 5, 6a, 7, 1'		(5), 7, 8
7	3.76	m	-	6a(b), 8a(b)	5, 6b, 8b, 9, 1'	72.7	8, (9), 1'
8a	1.27	m	-	7, 8b, 9	6a, 8b	39.2	6, 7, 9, 10
8b	1.75	ddt	12.4, 4.7, 1.9, 1.7	7, 8a, (9)	7, 8a, 9, 10a		6, 7, 9
9	3.16	tt	11.1, 1.5	8a, 10(a)b	5, 7, 8b, 10a	73.2	5, 7, 10, 11
10a	1.14	m	-	(9), 10b, 11	8b, 9, 10b, (12), (25)	43.5	11, 12, 25
10b	1.52	ddd	13.9, 11.0, 2.8	9, (11), 10a	(8a), 10a, 11, 25		9, 11, 12, 25
11	2.48	m	-	10a, 12, 25	9, 10b, (12), 13, 25	34.1	9, 10, 12, 13, (25)
12	5.32	dd	14.9, 9.7	11, 13	(9), 10a, (11), 14, 25	141.3	10, 11, 14, 25
13	6.10	dd	14.9, 11.0	12, 14	(3), 11, 16(a)b, (21)	124.9	11, 14, 15
14	6.00	ddt	11.0, 10.9, 1.5	(10ab), 13, 15	12, 15, 16b	130.6	12, 13, 16
15	5.20	m	-	14, 16ab	13, 14, 16ab, 17, 26	126.2	13, 16, 17
16a	2.08	ddd	14.6, 5.9, 1.9	15, 16b, 17	13, 21, 26	31.0	(13), 14, 15, 17, 18
16b	2.25	dddd	14.7, 9.0, 7.5, 1.4	(14), 15, 16a, 17	13, 19a, 21, 26		14, 15, 17, 18
17	3.99	dt	7.3, 6.2	18, 16ab	15, 18, 20, (26)	81.8	15, 19, 20, 26
18	2.46	m	-	17, 19ab, 26	17, 19(a)b, 20, 23, 26	36.9	16, 17, 19, 26
19a	1.26	m	-	18, 19b, 20	(18), 19b, 21, 26	36.4	18, (20), 21, 26
19b	2.09	ddd	12.3, 7.1, 7.1	(18), 19a, 20	19a, 21		18, 20, 21, 26
20	3.74	m	-	19ab, 21	17, 18, 19b, 21-OH, (22b)	82.1	17, 19, 21, 22
21	3.46	dddd	9.1, 7.6, 2.8, 1.6	20, 22ab, OHa	(3), 13, 19a, 22ab, 23, OHa	73.3	20, 22, 23
22a	1.55	ddd	14.7, 9.2, 2.1	21, 22b, (23)	21, 22b, 23, 24ab	34.7	20, 21, 24
22b	1.88	dddt	14.4, 11.5, 1.4	21, 22a, 23	19a(b), 21, 22a, 23, 24ab		20, 23, 24
23	5.23	dddd	11.2, 5.3, 2.8, 2.7	22(a)b, 24ab	21, 22ab, 24ab	73.9	(1), 22
24a	3.65	m	-	23, 24b	22ab, 24b, 24-OH	65.7	22, 23
24b	3.79	m	-	23, 24a	22a(b), 23, 24a, 24-OH		22
25	0.98	d	6.8	11	10ab, 11, 12	22.0	10, 11, 12
26	0.98	d	7.0	18	16a(b), (15), (17), 18	14.9	17, 18, 19
1'	4.99	d	1.2	2'	2', 7', 6b, 7	94.1	2', 3', 5', 7
2'	3.38	dd	3.8, 1.5	1', 3'	1', 3', 3‘-OH, 7'	80.9	3', 4', 7'
3'	3.68	td	9.7, 3.8	2', 4', OHc	2', 5', OHc, OHd	71.6	4'
4'	3.33	td	9.5, 1.9	3', 5', OHd	1‘, 6', OHc, OHd	74.2	3', 5', 6', 7'
5'	3.61	dq	9.4, 6.2	4', 6'	3', 6', 8b	68.2	1', 3', 4', 6'
6'	1.26	d	6.2	5'	1‘, 4', 5', 7'	17.7	4', 5'
7'	3.44	s	-		1‘, 2', OH3	59.1	2'
OHa	2.74-2.72	br s	-	21		-	21,22
OHb	2.37	m	-	3‘		-	2‘, 3‘
OHc	2.38	m	-	24ab		-	24
OHd	2.45	m	-	4'		-	3‘, 4', 5‘

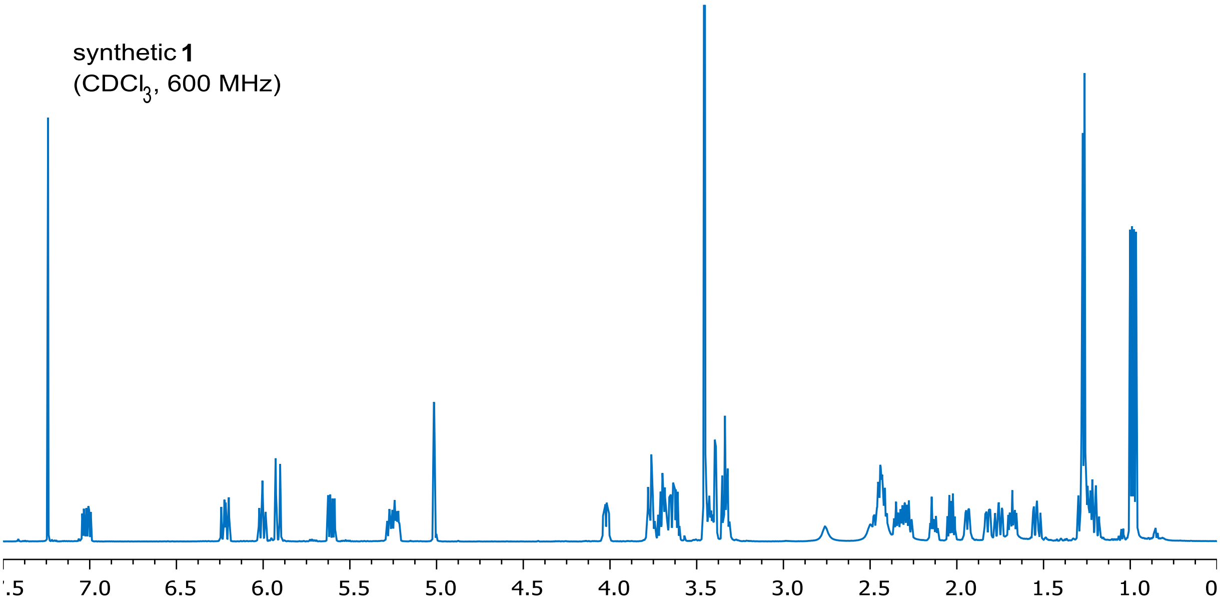
Table 7: ^{1}H & ^{13}C NMR data of synthetic mandelalide A (**6**) (5.2 mg in 0.25 mL $CDCl_3$).

atom n°	**^{1}H NMR ($CDCl_3$, 600 MHz)**					**^{13}C NMR ($CDCl_3$, 150**	
	δ /ppm	**m**	***J* /Hz**	**COSY**	**NOESY**	**δ**	**HMBC**
1	-	-	-	-	-	167.4	-
2	6.01	dt	15.5, 0.8	3, 4a	4ab, (5)	123.1	1, 3, 4, (5)
3	6.96	ddd	15.3, 10.4, 4.9	2, 4ab	4ab, 5, 25	147.1	1, 2, 4, 5
4a	2.36	m	-	3, 4b, (5)	2, 3, 5, 6a, 12, 13, 25	38.8	2, 3, 5, (6)
4b	2.39	ddd	13.9, 10.8, 10.7	3, 4a, 5			2, 3, 5, (6)
5	3.37	m	-	4a, 4b, 6ab	2, 3, 4ab, 6b, 7	73.9	3, 4, 9
6a	1.20	m	-	5, 6b, 7	6b, 8a, 10b	37.6	4, 5, 7, 8
6b	2.02	dddd	12.1, 5.6, 2.3, 1.6	5, 6a, 7, (8b)	4b, (5), 6a, 7, 1‘		(5), 7, 8, 2‘
7	3.82	dddd	11.3, 10.6, 4.8, 4.5	6ab, 8ab	5, 6b, 8b, 9, 1‘	73.1	8, (9), 1'
8a	1.22	m	-	7, 8b, 9	8b, 10b, (12), 25	39.7	6, 7, 9, 10
8b	1.87	dddt	13.2, 7.8, 5.3, 1.9	6b, 7, 8a, 9	7, 8a, 9, 1‘, 5‘		6, 7, 9
9	3.31	tt	10.7, 2.1	8ab, 10ab	7, 8b, 10a, 25	72.5	(10)
10a	1.21	m	-	9, 10b, 11	10b, (11), 12, 25	43.1	8, 11, 12, 25
10b	1.52	ddd	14.1, 11.1, 3.3	9, 10a, (11)	10a, 11, (12)		8, 9, 11, 12, 25
11	2.37	m	-	10a, 12, 25	10ab, 12, 13, 25	34.2	9, 10, 12, 13, 25
12	5.44	dd	14.9, 9.9	11, 13	(10a), 11, 14, 25	141.5	10, 11, 13, 14, 25
13	6.27	dd	14.8, 11.1	12, 14	11, 16b, 21, (25)	123.9	10, 11, 14, 15
14	6.05	dd	10.9, 10.9	13, 15	12, 15	131.3	12, 13, 16, 17
15	5.28	dt	10.8, 5.6	14, 16ab	14, 16ab, 17	126.9	13, 16, 17
16a	1.88	m	-	15, 16b, 17	15, 16b, 17, 26	31.1	14, 15, 17, 18
16b	2.25	m	m	15, 16a, 17	13, (15), 16a, 19a, 21, 26		14, 15, 17, 18
17	3.98	ddd	10.9, 8.5, 1.7	16ab, 18	15, 16a, 18, 20, 26	81.0	15, (18), 19, 20
18	2.52	dddq	12.3, 7.0, 7.0, 6.9	17, 19ab, 26	17, 19b, 20, 26	37.4	16, 17, (20), 26
19a	1.17	ddd	12.2, 12.1, 10.2	18, 19b, 20	16b, 19b, 20, 21, 22b, 26	36.8	18, (20), 21, 26
19b	2.01	ddd	11.8, 7.1, 6.0	18, 19a, 20	18, 19a, 22b, 20		17, 18, 21
20	3.63	m	-	19ab, 21	17, 18, 19b, 22a	83.2	(19), 21, 22
21	3.42	ddd	11.2, 8.9, 1.8	20, 22ab, (OHa)	13, 18, 19a, 22b, 23, OHa	73.1	19, 20, 22, (23)
22a	1.46	ddd	14.2, 11.3, 1.9	21, 22b, 23	20, 22b, 23, 24b	34.1	20, 21
22b	1.76	ddt	12.8, 12.6, 1.5	21, 22a, 23	(19ab), 20, 21, 22a, (23)		21, 24
23	5.23	dddd	11.6, 5.1, 3.1, 2.0	22ab, 24ab	(OHb, 18), 22ab, 21, 24ab	72.3	1, 22
24a	3.61	m	-	23, 24b	22a(b), 23, 24b	66.1	22, 23
24b	3.79	m	-	23, 24a	22a, 23, 24		22, 23
25	0.85	d	6.6	11	2, 3, 9, 10a, 11, 12, (13)	18.3	10, 11, 12
26	1.02	d	7.0	18	16ab, (17), 18, 19a(b)	14.5	17, 18, 19
1'	5.02	d	1.1	2'	6b, 7, 8b, 2‘, 6‘, 7‘	94.2	2', 3', 5', 7
2'	3.40	dd	3.9, 1.5	1', 3'	1‘, 3‘, 7‘	80.8	3', 4', 7'
3'	3.68	td	9.8, 3.7	2', 4', OHc	(1‘), 2‘, 5‘, OHd	71.7	4'
4'	3.34	dd	10.5, 9.3	3', 5', OHd	7, 6‘, OHd	74.3	3', 5', 6'
5'	3.62	dd	9.9, 5.9	4', 6'	3‘, 6‘	68.1	1', 3', 4', 6'
6'	1.26	d	6.3	5'	4‘, 5‘	17.7	4', 5'
7'	3.45	s	-	-	1‘	59.1	2'
OHa	2.69	br s	-	21		-	21,22
OHb	2.31	br s	-	24ab		-	(24)
OHc	2.35	m	-	3'		-	3', 4‘
OHd	2.53	br s	-	4'		-	2‘, 5‘

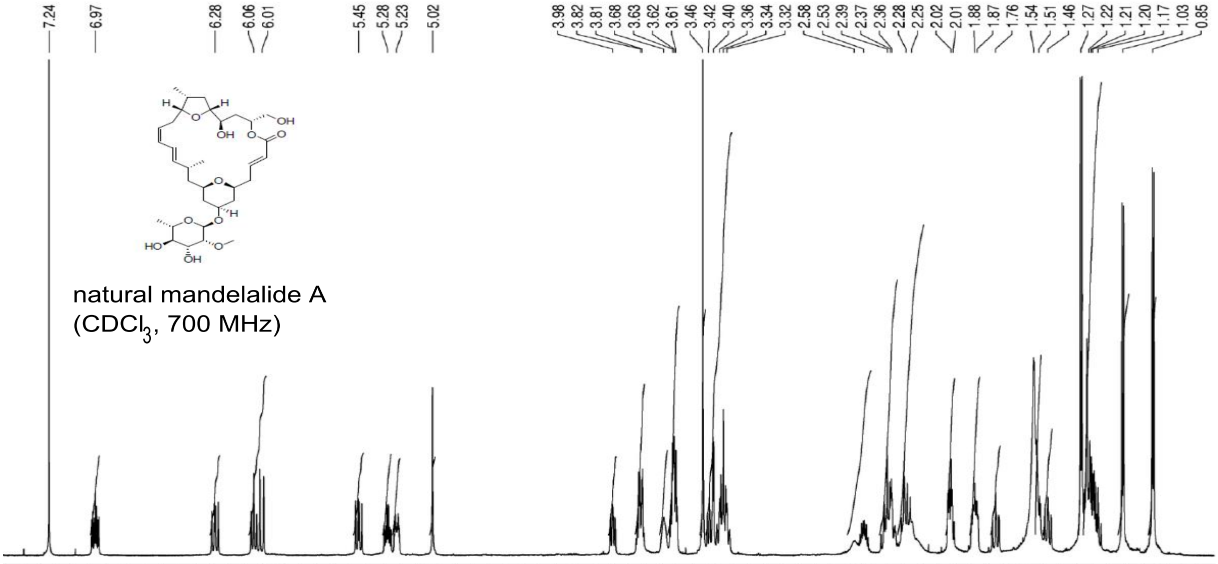
Table 8: ^{1}H & ^{13}C NMR data of 11-*epi*-isomer of actual mandelalide A 11-*epi*-**6** (3.5 mg in 0.25 mL $CDCl_3$).

atom n°	^{1}H NMR ($CDCl_3$, 600 MHz)				^{13}C NMR ($CDCl_3$, 150 MHz)	
	δ /ppm	m	*J*/Hz	COSY	δ /ppm	HMBC
1	-	-	-	-	167.4	-
2	5.93	dd	15.5, 0.7	3, (4a)	123.4	1, 3, 4, 5
3	6.98	ddd	15.3, 8.1, 7.0	2, 4a	146.8	1, 2, 4, 5
4a	2.31	m	-	3, 4b, 5	39.5	2, 3, 5, 6
4b	2.42	ddd	14.1, 6.3, 3.2	3, 4a, 5		2, 3, 5, 6
5	3.30	m	-	4ab, 6a(b)	74.2	(3), 4, 6, 7, (9)
6a	1.17	dt	11.5, 11.4	5, 6b, 7	37.5	5, 7, 8
6b	2.00	m	-	(5), 6a, 7		7, 8, 2’
7	3.75	m	-	6ab, 8ab	73.1	8, 1’
8a	1.23	m	-	7, 8b, 9	39.5	6, 7, 9, 10
8b	1.82	m	-	7, 8a, 9		6, 7, 9, 10
9	3.27	tt	9.9, 2.1	8a, 10ab	72.9	8, 10, 11
10a	1.37	ddd	14.1, 8.7, 2.7	9, 10b, 11	43.0	8, 11, 12, (25)
10b	1.49	ddd	14.3, 9.4, 5.1	9, 10a, 11		8, 11, 12, 25
11	2.45	m	-	10ab, 12, 25	33.5	10, 12, 13, 25
12	5.60	dd	15.2, 7.7	11, 13	141.0	10, 11, 14, 25
13	6.20	dd	15.2, 10.7	12, 14	124.7	11, 14, (15)
14	6.00	dd	10.8, 10.8	13, 15	130.5	12, 13, 16
15	5.28	td	10.5, 7.7	14, 16ab	126.8	13, 16, 17
16a	2.21	m	-	(14), 15, 16b, 17	31.5	14, 15, 17, 18
16b	2.20	m	-	15, 16a, 17		14, 15, 17, 18
17	4.01	q	6.7	16ab, 18	80.9	15, (18), 19, 20, 26
18	2.44	m	-	17, 19a(b), 26	37.5	17, 19, 26
19a	1.28	m	-	18, 19b, 20	35.8	17, 18, 21, 26
19b	2.00	m	-	19a		18, 20, 21, 26
20	3.73	ddd	9.3, 6.9, 6.9	19ab, 21	82.5	19, 21, 22
21	3.76	m	-	20, 22ab	73.1	19, 22
22a	1.53	m	-	21, 22b, 23	33.8	21, 24
22b	1.83	ddd	14.1, 11.0, 2.8	21, 22a, 23		19, 20, 23
23	5.17	ddd	10.2, 8.1, 1.9	22ab, 24ab	72.2	19, 21, 22
24a	3.67	m	-	23, 24b	65.6	22, 23
24b	3.78	m	-	23, 24a		22, 23
25	1.00	d	6.9	11	21.4	10, 11, 12
26	0.98	d	6.9	18	14.7	17, 18, 19
1'	5.00	d	1.3	2‘	94.3	7, 2‘, 3‘, 5‘
2'	3.38	dd	3.6, 1.3	1‘, 3‘	80.8	3‘, 4‘, 7‘
3'	3.69	m	-	2‘, 4‘	71.7	4‘
4'	3.33	dd	9.4, 9.4	3‘, 5‘	74.4	3‘, 5‘, 6‘, 7‘
5'	3.61	m	-	4‘, 6‘	68.1	3‘, 4‘, 6‘
6'	1.26	d	6.2	4‘, 5‘	17.8	5‘
7'	3.45	d	0.6	-	59.1	2‘
OHa	not assigned					
OHb	not assigned					
OHc	not assigned					
OHd	not assigned					

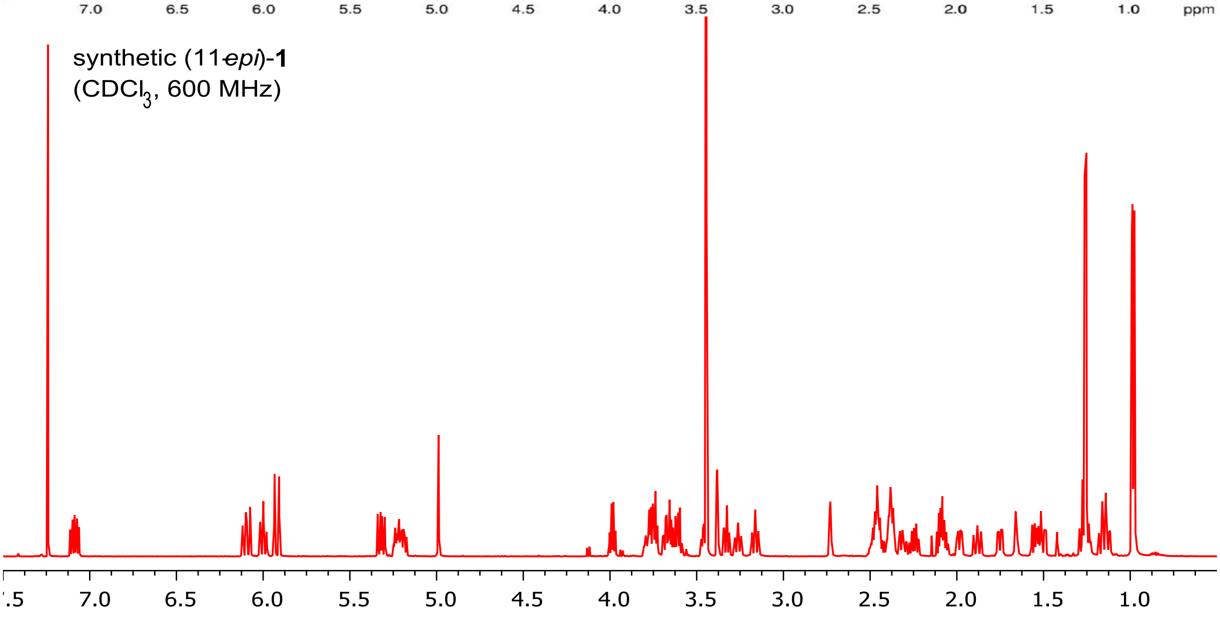
Comparison of synthetic isomers and natural mandelalide A



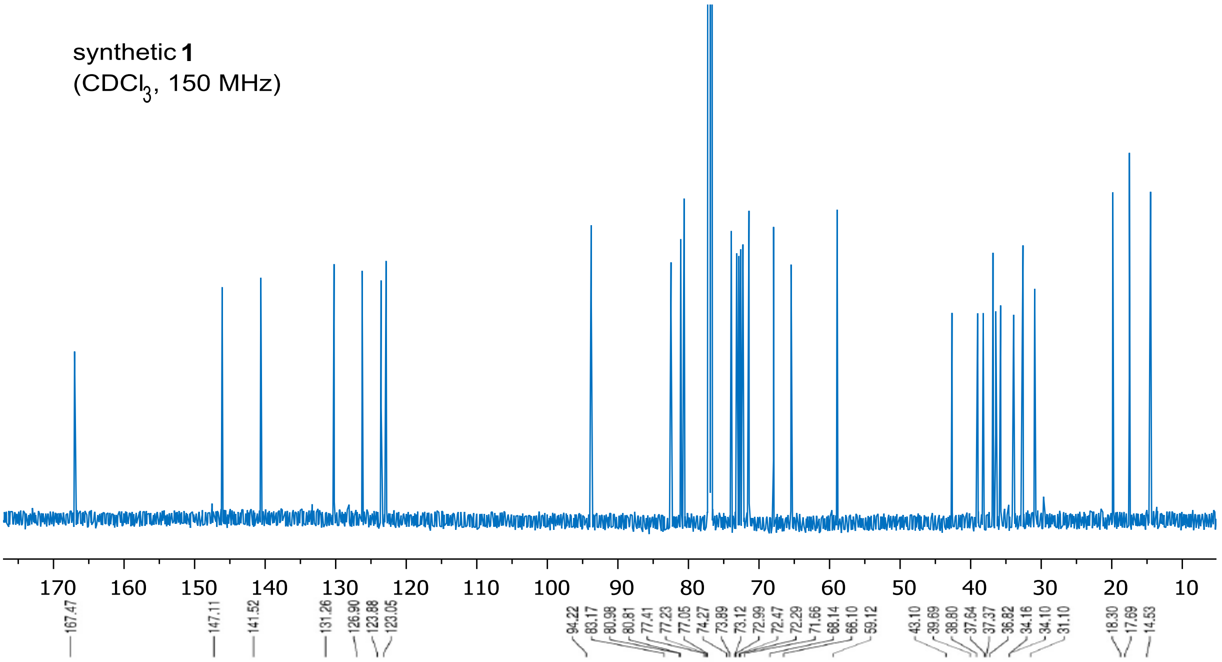
synthetic **1**
(CDCl$_3$, 600 MHz)



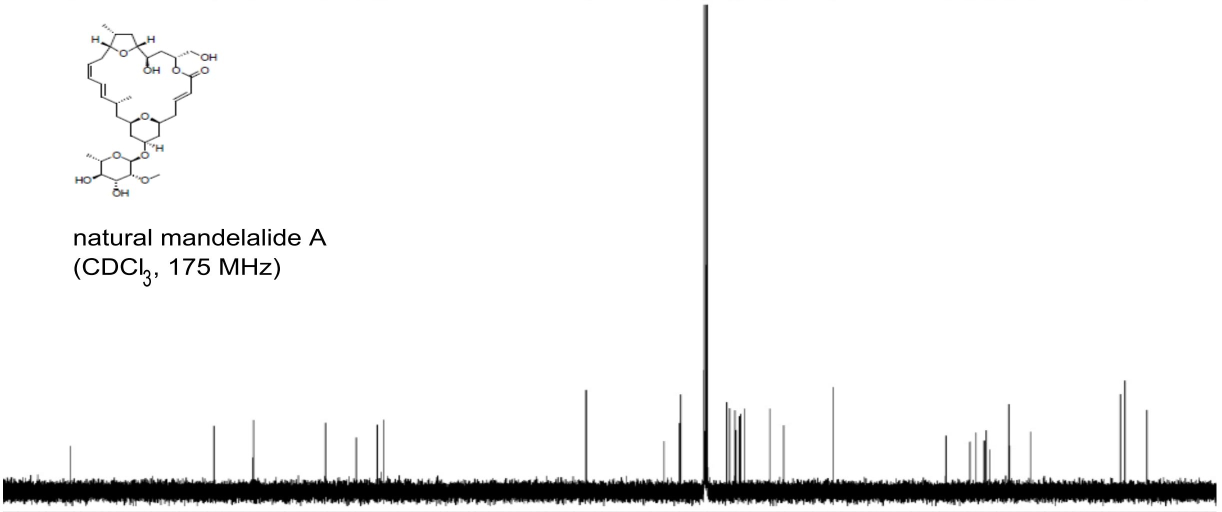
natural mandelalide A
(CDCl$_3$, 700 MHz)



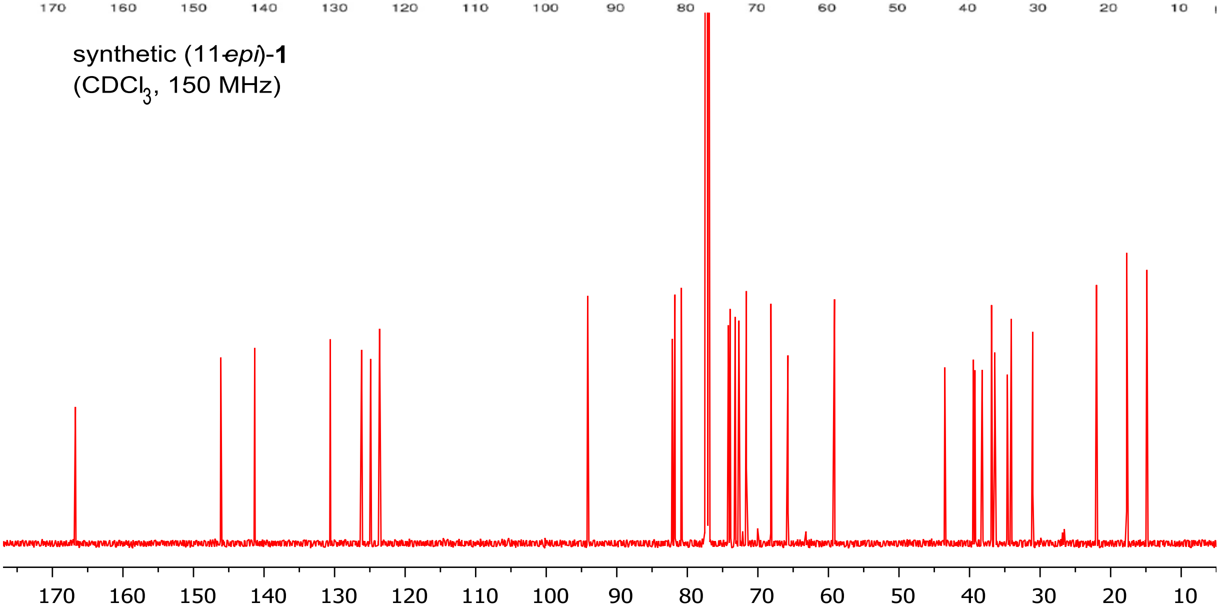
synthetic (11-*epi*)-**1**
(CDCl$_3$, 600 MHz)



synthetic **1**
(CDCl$_3$, 150 MHz)



natural mandelalide A
(CDCl$_3$, 175 MHz)



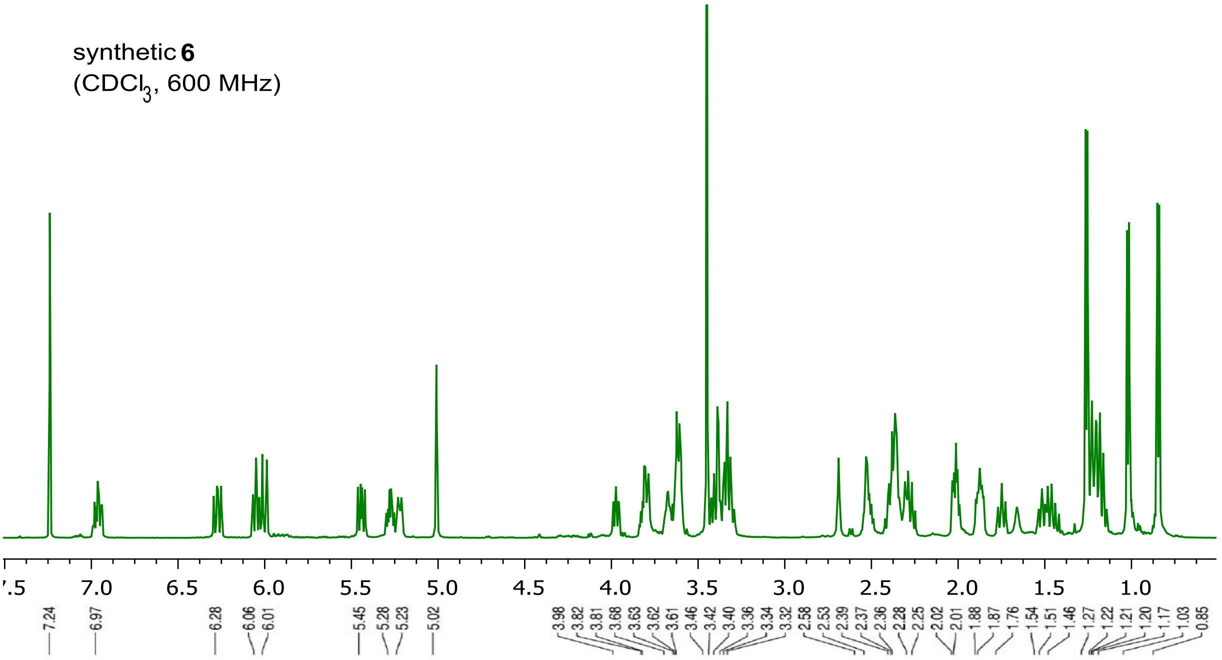
synthetic (11-*epi*)-**1**
(CDCl$_3$, 150 MHz)

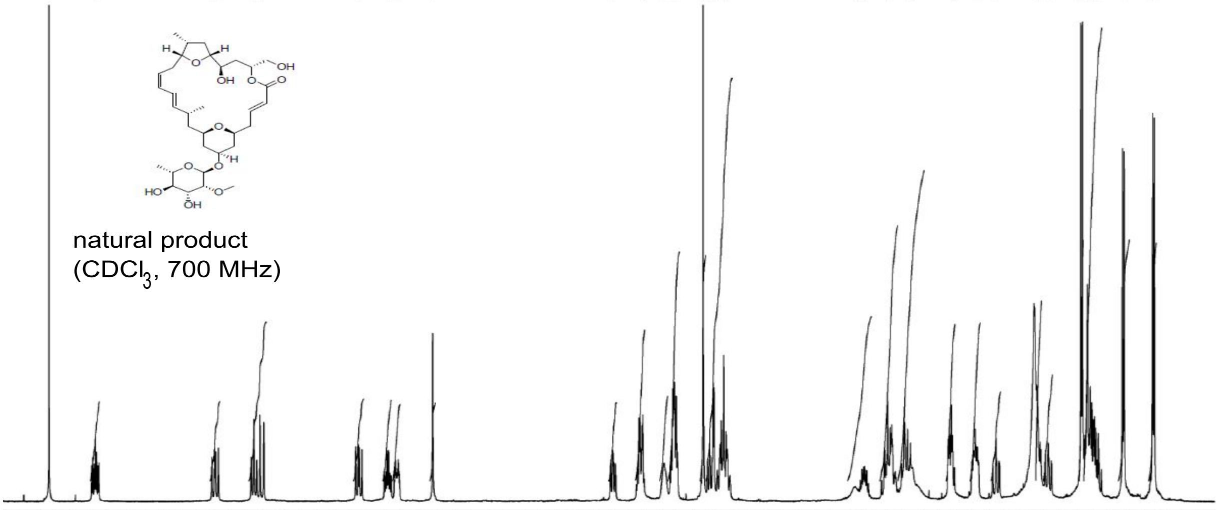
Table 9: Comparison of the ^{1}H NMR chemical shifts of **1** (600 MHz, $CDCl_3$) and 11-*epi*-**1** with the data of the natural product (Lit.[13]; 700 MHz, $CDCl_3$).

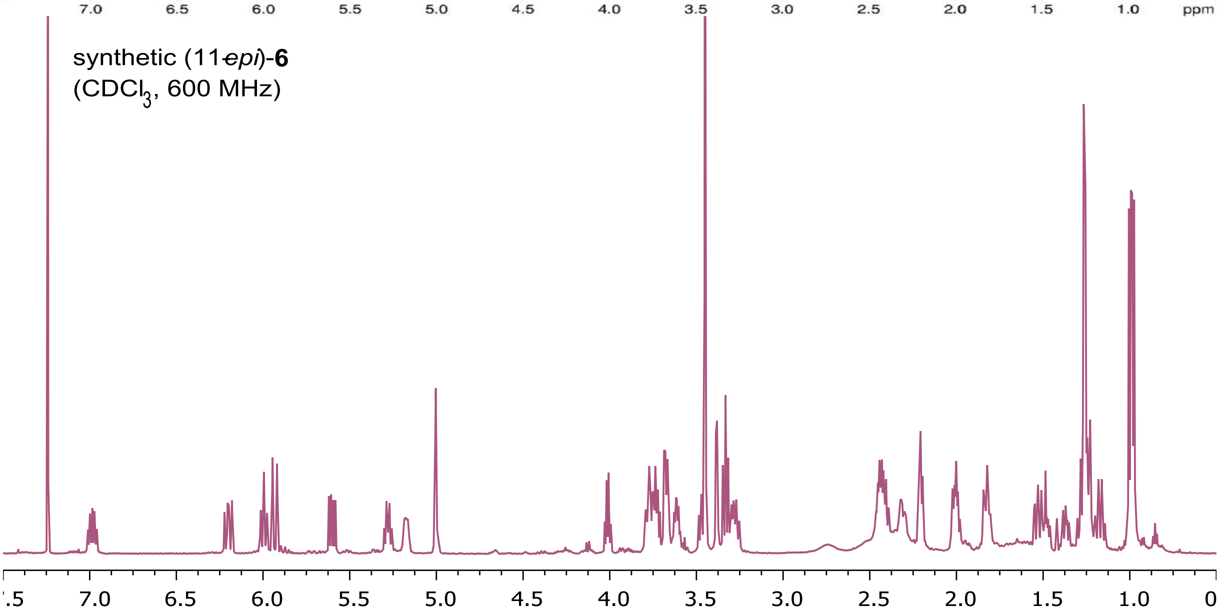
atom n°	**δ (Lit.) /ppm**	**δ(1) /ppm**	**Δδ (1–Lit.)**	δ(11-*epi*-**1**) **/ppm**	**Δδ (11-*epi*-1–Lit)**
1	-	-	-	-	-
2	6.01	5.92	-0.09	5.92	-0.09
3	6.97	7.02	0.05	7.09	0.12
4a	2.36	2.34	-0.02	2.31	-0.05
4b	2.39	2.46	0.07	2.39	0.00
5	3.36	3.42	0.06	3.26	-0.10
6a	1.20	1.26	0.06	1.15	-0.05
6b	2.02	1.94	-0.08	1.98	-0.04
7	3.82	3.77	-0.05	3.76	-0.06
8a	1.22	1.22	0.00	1.27	0.05
8b	1.87	1.84	-0.03	1.75	-0.12
9	3.32	3.33	0.01	3.16	-0.16
10a	1.21	1.27	0.06	1.14	-0.07
10b	1.51	1.69	0.18	1.52	0.01
11	2.37	2.44	0.07	2.48	0.11
12	5.45	5.61	0.16	5.32	-0.13
13	6.28	6.22	-0.06	6.10	-0.18
14	6.05	6.01	-0.04	6.00	-0.05
15	5.28	5.27	-0.01	5.20	-0.08
16a	1.88	2.14	0.26	2.08	0.20
16b	2.28	2.29	0.01	2.25	-0.03
17	3.98	4.03	0.05	3.99	0.01
18	2.52	2.43	-0.09	2.46	-0.06
19a	1.17	1.28	0.11	1.26	0.09
19b	2.01	2.04	0.03	2.09	0.08
20	3.63	3.71	0.08	3.74	0.11
21	3.42	3.45	0.03	3.46	0.04
22a	1.46	1.54	0.08	1.55	0.09
22b	1.76	1.77	0.01	1.88	0.12
23	5.23	5.24	0.01	5.23	0.00
24a	3.61	3.65	0.04	3.65	0.04
24b	3.81	3.78	-0.03	3.79	-0.02
25	0.85	1.00	0.15	0.98	0.13
26	1.03	0.98	-0.05	0.98	-0.05
1'	5.02	5.02	0.00	4.99	-0.03
2'	3.40	3.40	0.00	3.38	-0.02
3'	3.68	3.69	0.01	3.68	0.00
4'	3.34	3.34	0.00	3.33	-0.01
5'	3.62	3.63	0.01	3.61	-0.01
6'	1.27	1.28	0.01	1.26	-0.01
7'	3.45	3.46	0.01	3.44	-0.01

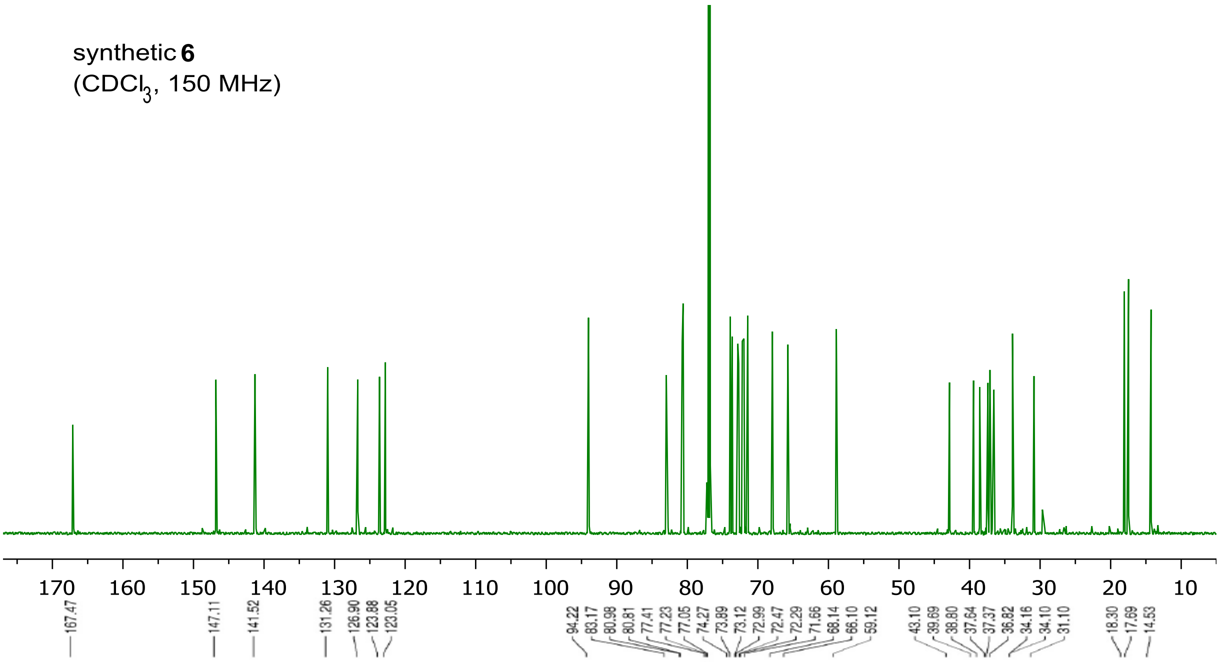
Table 10: Comparison of the ^{13}C NMR chemical shifts of **1** and 11-*epi*-**1** (150 MHz, $CDCl_3$)with the data of the natural product (Lit.[13]; 175 MHz, $CDCl_3$).

atom n°	**δ (Lit.) /ppm**	**δ(1) /ppm**	**Δδ (1–Lit.)**	**δ(11-*epi*-1) /ppm**	**Δδ (11-*epi*-1–Lit)**
1	167.5	167.3	-0.2	166.8	-0.7
2	123.1	123.1	0.0	123.6	0.5
3	147.1	146.3	-0.8	146.1	-1.0
4	38.8	38.5	-0.3	39.5	0.7
5	73.9	73.4	-0.5	74.0	0.0
6	37.6	36.7	-0.9	38.2	0.6
7	73.1	72.8	-0.3	72.7	-0.4
8	39.7	39.3	-0.4	39.2	-0.5
9	72.5	73.1	0.6	73.2	0.7
10	43.1	42.9	-0.2	43.5	0.4
11	34.2	32.8	**-1.4**	34.1	-0.1
12	141.5	140.9	-0.6	141.3	-0.2
13	123.9	123.8	-0.1	124.9	1.0
14	131.3	130.5	-0.8	130.6	-0.7
15	126.9	126.5	-0.4	126.2	-0.7
16	31.1	31.2	0.1	31.0	-0.1
17	81.0	81.3	0.3	81.8	0.8
18	37.4	37.1	-0.3	36.9	-0.5
19	36.8	36.0	-0.8	36.4	-0.4
20	83.2	82.7	-0.5	82.1	-1.1
21	73.0	72.5	0.4	73.3	0.3
22	34.1	34.1	0.0	34.7	0.6
23	72.3	72.5	0.2	73.9	1.7
24	66.1	65.7	-0.4	65.7	-0.4
25	18.3	20.1	**1.8**	22.0	3.7
26	14.5	14.7	0.2	14.9	0.4
1'	94.2	94.0	-0.2	94.1	-0.1
2'	80.8	80.9	0.1	80.9	0.1
3'	71.7	71.7	0.0	71.6	-0.1
4'	74.3	74.2	-0.1	74.2	-0.1
5'	68.1	68.2	0.1	68.2	0.1
6'	17.7	17.7	0.0	17.7	0.0
7'	59.1	59.2	0.1	59.1	0.0

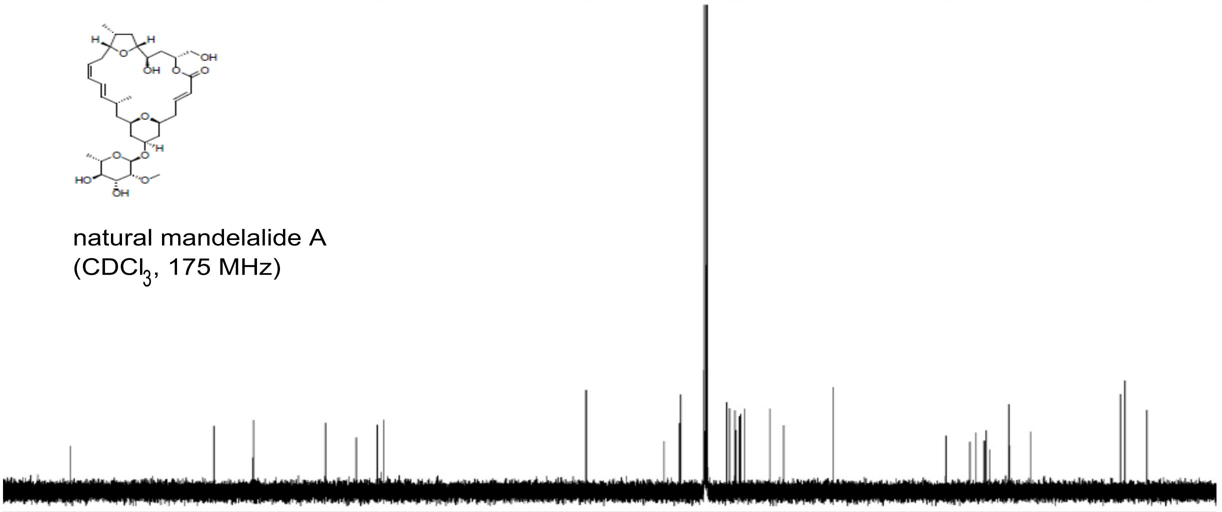

synthetic **6**
($CDCl_3$, 600 MHz)


natural product
($CDCl_3$, 700 MHz)

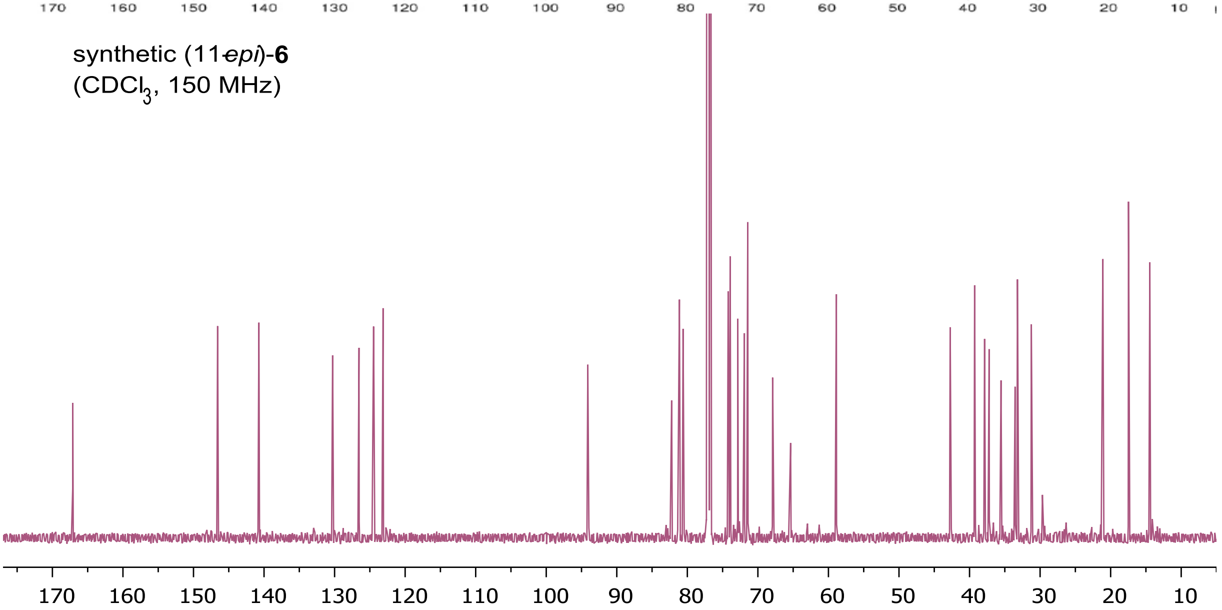

synthetic (11-*epi*)-**6**
($CDCl_3$, 600 MHz)



synthetic **6**
(CDCl$_3$, 150 MHz)



natural mandelalide A
(CDCl$_3$, 175 MHz)



synthetic (11-*epi*)-**6**
(CDCl$_3$, 150 MHz)

Table 11: Comparison of the ^{1}H NMR chemical shifts of **6** and 11-*epi*-**6** (600 MHz, $CDCl_3$) with the data of the natural product (Lit.[13]; 700 MHz, $CDCl_3$).

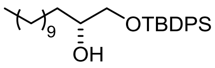
atom n°	**δ (Lit.) /ppm**	**δ(6) /ppm**	**Δδ (6–Lit.)**	**δ(11-*epi*-6) /ppm**	**Δδ (11-*epi*-6–Lit.)**
1	-	-	-	-	-
2	6.01	6.01	0.00	5.93	-0.08
3	6.97	6.96	-0.01	6.98	0.01
4a	2.36	2.36	0.00	2.31	-0.05
4b	2.39	2.39	0.00	2.42	0.03
5	3.36	3.37	0.01	3.3	-0.06
6a	1.20	1.20	0.00	1.17	-0.03
6b	2.02	2.02	0.00	2.00	-0.02
7	3.82	3.82	0.00	3.75	-0.07
8a	1.22	1.22	0.00	1.23	0.01
8b	1.87	1.87	0.00	1.82	-0.05
9	3.32	3.31	-0.01	3.27	-0.05
10a	1.21	1.21	0.00	1.37	0.16
10b	1.51	1.52	0.01	1.49	-0.02
11	2.37	2.37	0.00	2.45	0.08
12	5.45	5.44	-0.01	5.6	0.15
13	6.28	6.27	-0.01	6.2	-0.08
14	6.05	6.05	0.00	6.00	-0.05
15	5.28	5.28	0.00	5.28	0.00
16a	1.88	1.88	0.00	2.21	0.33
16b	2.28	2.25	-0.03	2.2	-0.08
17	3.98	3.98	0.00	4.01	0.03
18	2.52	2.52	0.00	2.44	-0.08
19a	1.17	1.17	0.00	1.28	0.11
19b	2.01	2.01	0.00	2.00	-0.01
20	3.63	3.63	0.00	3.73	0.10
21	3.42	3.42	0.00	3.76	0.34
22a	1.46	1.46	0.00	1.53	0.07
22b	1.76	1.76	0.00	1.83	0.07
23	5.23	5.23	0.00	5.17	-0.06
24a	3.61	3.61	0.00	3.67	0.06
24b	3.81	3.79	-0.02	3.78	-0.03
25	0.85	0.85	0.00	1.00	0.15
26	1.03	1.02	-0.01	0.98	-0.05
1'	5.02	5.02	0.00	5.00	-0.02
2'	3.40	3.40	0.00	3.38	-0.02
3'	3.68	3.68	0.00	3.69	0.01
4'	3.34	3.34	0.00	3.33	-0.01
5'	3.62	3.62	0.00	3.61	-0.01
6'	1.27	1.26	-0.01	1.26	-0.01
7'	3.45	3.45	0.00	3.45	0.00

Table 12: Comparison of the ^{13}C NMR chemical shifts of **6** and 11-*epi*-**6** (150 MHz, $CDCl_3$) with the data of the natural product (Lit.[13]; 175 MHz, $CDCl_3$).

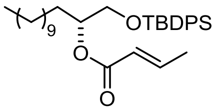
atom n°	**δ (Lit.) /ppm**	**δ(6) /ppm**	**Δδ (6–Lit.)**	**δ(11-*epi*-6) /ppm**	**Δδ (11-*epi*-6–Lit.)**
1	167.5	167.4	-0.1	167.4	-0.1
2	123.1	123.1	0.0	123.4	0.3
3	147.1	147.1	0.0	146.8	-0.3
4	38.8	38.8	0.0	39.5	0.7
5	73.9	73.9	0.0	74.2	0.3
6	37.6	37.6	0.0	37.5	-0.1
7	73.1	73.1	0.0	73.1	0.0
8	39.7	39.7	0.0	39.5	-0.2
9	72.5	72.5	0.0	72.9	0.4
10	43.1	43.1	0.0	43	-0.1
11	34.2	34.2	0.0	33.5	-0.7
12	141.5	141.5	0.0	141	-0.5
13	123.9	123.9	0.0	124.7	0.8
14	131.3	131.3	0.0	130.5	-0.8
15	126.9	126.9	0.0	126.8	-0.1
16	31.1	31.1	0.0	31.5	0.4
17	81.0	81	0.0	80.9	-0.1
18	37.4	37.4	-0.1	37.5	0.1
19	36.8	36.8	0.0	35.8	-1.0
20	83.2	83.2	0.0	82.5	-0.7
21	73.0	73.1	-0.1	73.1	0.1
22	34.1	34.1	0.0	33.8	-0.3
23	72.3	72.3	0.0	72.2	-0.1
24	66.1	66.1	0.0	65.6	-0.5
25	18.3	18.3	0.0	21.4	3.1
26	14.5	14.5	0.0	14.7	0.2
1'	94.2	94.2	0.0	94.3	0.1
2'	80.8	80.8	0.0	80.8	0.0
3'	71.7	71.7	0.0	71.7	0.0
4'	74.3	74.3	0.0	74.4	0.1
5'	68.1	68.1	0.0	68.1	0.0
6'	17.7	17.7	0.0	17.8	0.1
7'	59.1	59.1	0.0	59.1	0.0

Studies towards the Synthesis of Mandelalide C and D.

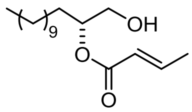
1-((*tert*-Butyldiphenylsilyl)oxy)tridecan-2-ol (S1). A flame-dried Schlenck flask was charged with a solution of *n*-decylmagnesium bromide (1 M in Et_2O, 22 mL, 22 mmol), which was cooled to −15 °C. Copper cyanide (36 mg, 0.40 mmol) was, followed by a solution of (*R*)-*tert*-butyl(oxiran-2-ylmethoxy)diphenylsilane (**29**) (6.25 g, 20.0 mmol) in THF (17 mL) via dropping funnel. After stirring for 30 min, the reaction mixture was quenched by pouring into sat. NH_4Cl solution (100 mL). The aqueous phase was extracted with EtOAc (3 x 50 mL) and the combined organic layers were dried over $NaSO_4$ and concentrated. The pale yellow residue (8.9 g, 98%) was used in the next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 – 7.56 (m, 4H), 7.37 – 7.26 (m, 6H), 3.68 – 3.52 (m, 2H), 3.41 (dd, *J* = 9.9, 7.3 Hz, 1H), 2.18 (br s, 1H), 1.37 – 1.27 (m, 2H), 1.22 – 1.13 (m, 18H), 0.99 (s, 9H), 0.83 – 0.78 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.6, 135.5, 133.3, 133.3, 129.8, 127.7, 72.0, 68.1, 32.8, 31.9, 29.7, 29.6, 29.6, 29.6, 29.5, 29.3, 26.9, 25.5, 22.7, 19.3, 14.1 ppm. IR (film): $\tilde{\nu}$ = 3470, 2924, 2854, 1754, 1463, 1428, 1361, 1263, 1189, 1110, 1031, 1007, 938, 882, 823, 739, 700, 638, 613 cm^{-1}. MS (EI) *m/z* (%) = 397 (15), 229 (12), 200 (18), 199 (100), 139 (49), 111 (6), 97 (8) 69 (5). HRMS (ESIpos): *m/z*: calcd for $C_{29}H_{46}O_2Si_1Na$: 477.3159; found: 477.3158.



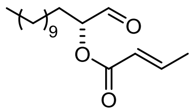
(*R*)-1-((*tert*-Butyldiphenylsilyl)oxy)tridecan-2-yl (*E*)-but-2-enoate (S2). (*E*)-Crotonic acid (3.06 g, 35.6 mmol), DMAP (7.25 g, 59.3 g) and *N,N'*-dicyclohexylcarbodiimide (8.98 g, 43.5 mmol) were added successively to a stirred solution of crude alcohol **S1** (8.02 g, 19.8 mmol) in CH_2Cl_2 (100 mL) at ambient temperature. After 17 h, the reaction mixture was filtered through a pad of Celite®, which was rinsed with CH_2Cl_2 (2 x 10 mL). The filtrate was concentrated and the residue purified by flash chromatography (hexanes/EtOAc 15:1) to give the desired ester as a colorless oil (8.32 g, 81% yield). $[\propto]_D^{20}$ = +12.4 (c = 0.89, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 – 7.58 (m, 4H), 7.45 – 7.31 (m, 6H), 6.94 (dq, *J* = 15.5, 6.9 Hz, 1H), 5.83 (dq, *J* = 15.5, 1.7 Hz, 1H), 5.03 (ddd, *J* = 10.1, 7.4, 5.1 Hz, 1H), 3.70 (dd, *J* = 10.9, 5.4 Hz, 1H), 1.87 (dd, *J* = 6.9, 1.7 Hz, 3H), 1.64 – 1.54 (m, 2H), 1.26 (s, 18H), 1.02 (s, 9H), 0.89 – 0.84 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 144.3, 135.6, 135.6, 133.5, 129.6, 127.6, 127.6, 127.6, 123.0, 74.1, 65.0, 34.9, 31.9, 30.5, 29.6, 29.6, 29.5, 29.5, 29.5, 29.3, 26.7, 25.4, 25.2, 24.7, 22.7, 19.2, 18.0, 14.1 ppm. IR (film): $\tilde{\nu}$ = 2925, 2854, 2118, 1720, 1660, 1446, 1428, 1360, 1293, 1262, 1181, 1112, 1046, 1005, 969, 823, 802, 739, 700, 614 cm^{-1}. MS (EI) *m/z* (%) = 465 (14), 268 (22), 267 (100), 207 (25), 199 (16), 135 (5), 69 (19). HRMS (ESIpos): *m/z*: calcd for $C_{33}H_{50}O_3Si_1Na$: 545.3421; found: 545.3419.



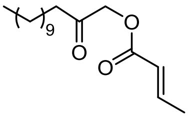
(*R*)-1-Hydroxytridecan-2-yl (*E*)-but-2-enoate (S3). Silyl ether **S2** (5.01 g, 9.56 mmol) was dissolved in THF (50 mL) and the solution cooled to 0 °C. Acetic acid (1.92 mL, 33.5 mmol) and a solution of TBAF (1 M in THF, 28.7 mL, 28.7 mmol) were added slowly. After 5 min stirring at 0 °C, the ice bath was removed and the mixture was allowed to warm to ambient temperature. After 3.5 h, it was diluted with EtOAc (20 mL), poured into sat. $NaHCO_3$ solution (40 mL) and the aqueous phase was extracted with EtOAc (3 x 40 mL). The combined organic phases were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 8:1 to 6:1 to 4:1 to give the desired primary alcohol as a colorless oil (2.42 g, 89% yield). $[\propto]_D^{20}$ = +9.8 (c = 0.64, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.00 (dq, *J* = 15.5, 6.9 Hz, 1H), 5.87 (dq, *J* = 15.5, 1.7 Hz, 1H), 4.95 (dtd, *J* = 7.4, 6.2, 3.2 Hz, 1H), 3.73 (dd, *J* = 12.0, 3.2 Hz, 1H), 3.64 (dd, *J* = 12.1, 6.3 Hz, 1H), 2.07 (br s, 1H), 1.89 (dd, *J* = 6.9, 1.7 Hz, 3H), 1.65 – 1.54 (m, 2H), 1.31 – 1.22 (m, 18H), 0.87 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 145.3, 122.6, 75.5, 65.0, 31.9, 30.6, 29.6, 29.5, 29.4, 29.3, 25.3, 22.7, 18.0, 14.1 ppm. IR (film): $\tilde{\nu}$ = 3428, 2955, 2923, 2854, 1719, 1658, 1465, 1444, 1377, 1308, 1292, 1265, 1182, 1101, 1057, 1002, 968, 919, 838, 722, 688 cm^{-1}. MS (EI) *m/z* (%) = 285 (1), 142 (9), 100 (8), 87 (12), 69 (100), 55 (6), 41 (12). HRMS (ESIpos): *m/z*: calcd for $C_{17}H_{32}O_3Na$: 307.2244; found: 307.2244.



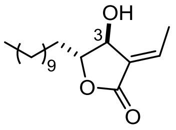
(*R*)-1-Oxotridecan-2-yl (*E*)-but-2-enoate (S4). Dess-Martin periodinane (4.65 g, 11.0 mmol) and $NaHCO_3$ (2.13 g, 25.3 mmol) were added successively to a solution of primary alcohol **S3** (1.20 g, 4.22 mmol) in CH_2Cl_2 (60 mL) at 0 °C. The icebath was removed after 5 min and the white suspension was stirred vigorously at ambient temperature for 4 h. The reaction was then poured into a sat. solution of $NaHCO_3/Na_2S_2O_3$ (1:1, 100 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 x 75 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (10 cm SiO_2, hexanes/EtOAc 19:1 to 15:1 to 12:1 to 9:1) to give the product as a colorless liquid (661 mg, 55% yield). $[\propto]_D^{20}$ = +31.0 (c = 0.64, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.51 (d, *J* = 0.9 Hz, 1H), 7.06 (dq, *J* = 15.5, 6.9 Hz, 1H), 5.92 (dq, *J* = 15.5, 1.7 Hz, 1H), 4.99 (ddd, *J* = 8.3, 4.8, 0.9 Hz, 1H), 1.90 (dd, *J* = 6.9, 1.7 Hz, 3H), 1.86 – 1.78 (m, 1H), 1.76 – 1.67 (m, 1H), 1.43 – 1.35 (m, 2H), 1.28 – 1.20 (m, 16H), 0.87 – 0.82 (t, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.8, 165.9, 146.5, 121.6, 78.1, 31.9, 29.6, 29.5, 29.3, 29.3, 29.2, 28.8, 24.9, 22.7, 18.1, 14.1 ppm. IR (film): $\tilde{\nu}$ = 2923, 2854, 1721, 1657, 1465, 1444, 1377, 1292, 1258, 1175, 1102, 968, 837, 722, 688 cm^{-1}. MS (ESIpos) *m/z* (%) = 337.3 (100 (M+MeOH+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{17}H_{30}O_3Na$: 305.2087; found: 305.2085.



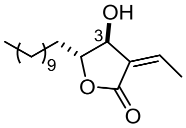
2-Oxotridecyl (*E*)-but-2-enoate (S14). DBU (5.3 µL, 35 µmol) was added to a solution of aldehyde **S4** (20.0 mg, 70.8 µmol) in CH_3CN (0.7 mL) at 0 °C. After stirring at 0 °C for 1 h, the reaction mixture was stirred for 12 h at rt. The reaction was then quenched by



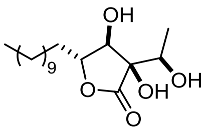
addition of sat. NH_4Cl solution (3 mL) and the aqueous phase was extracted with EtOAc (3 x 3 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. The crude residue was purified by flash chromatography to yield the rearranged ketone as a colorless oil (16.1 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05 (dq, *J* = 15.6, 6.9 Hz, 1H), 5.91 (dq, *J* = 15.5, 1.7 Hz, 1H), 4.67 (s, 2H), 2.39 (t, *J* = 7.3 Hz, 2H), 1.89 (dd, *J* = 6.9, 1.8 Hz, 3H), 1.85 – 1.70 (m, 2H), 1.64 – 1.53 (m, 2H), 1.28 – 1.20 (m, 14H), 0.85 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.4, 165.6, 146.4, 121.6, 67.8, 38.8, 31.9, 29.6, 29.4, 29.3, 29.2, 28.8, 24.9, 22.7, 18.1, 14.1 ppm. IR (film): $\tilde{\nu}$ = 2953, 2922, 2853, 1722, 1656, 1468, 1444, 1377, 1294, 1258, 1175, 1101, 969, 720 cm^{-1}. MS (ESIpos) *m/z* (%) = 305.2 (100 (M+Na$^+$)). HRMS (ESIpos): *m/z*: calcd for $C_{17}H_{30}O_3Na$: 305.2087; found: 305.2084.



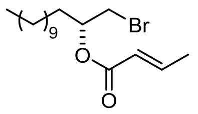
Morita-Baylis-Hillman product (*E*)-(S5).A flame-dried Young tube was charged with a solution of aldehyde **S4** (150 mg, 0.531 mmol) in DMF (5 mL). Methyldiphenylphosphine (29.6 µL, 0.159 mmol) was added via syringe and the Young tube was sealed. It was placed in a preheated oil-bath at 120 °C and the reaction mixture was stirred at this temperature for 22 h. After cooling to rt, it was poured into NH_4Cl (15 mL) and the aqueous phase was extracted with Et_2O (3 x 5 mL). The combined organic extracts were washed with brine (25 mL), dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 4:1 to 3:1 to 2:1) to give the Baylis-Hillman alcohol (*E*)-**S5** as a white solid (82 mg, 55% yield, 16:1 d.r. at C.3) along with the minor isomer (*Z*)-**S5** (see below). $[\propto]_D^{20}$ = +4.9 (c = 1.21, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, data is given only for the major diastereomer): δ = 6.95 (qd, *J* = 7.2, 1.9 Hz, 1H), 4.53 (br s, 1H), 4.28 (ddd, *J* = 8.1, 6.0, 2.3 Hz, 1H), 2.78 (br s, 1H), 1.98 (dd, *J* = 7.3, 1.0 Hz, 3H), 1.59 – 1.44 (m, 2H), 1.43 – 1.30 (m, 2H), 1.25 – 1.15 (m, 16H), 0.84 – 0.78 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, data is given only for the major diastereomer): δ = 169.8, 143.4, 130.5, 86.5, 70.8, 34.0, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 24.7, 22.7, 15.4, 14.1 ppm. IR (film): $\tilde{\nu}$ = 3420, 2922, 2853, 1734, 1680, 1465, 1440, 1377, 1332, 1215, 1143, 1207, 980, 814, 722, 610 cm^{-1}. MS (EI) *m/z* (%) = 282 (1), 99 (6), 98 (100), 70 (22), 69 (6). HRMS (ESIpos): *m/z*: calcd for $C_{17}H_{30}O_3Na$: 305.2087; found: 305.2086.



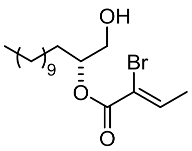
Morita-Baylis-Hillman product (*Z*)-(S5). Obtained as the minor isomer as a mixture of diastereomers at C.3 (18.2 mg, 12% yield, 18:1 d.r.). $[\propto]_D^{20}$ = +8.0 (c = 0.98, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, data is given only for the major diastereomer): δ = 6.61 (qd, *J* = 7.3, 1.7 Hz, 1H), 4.37 (br s, 1H), 4.19 (ddd, *J* = 7.8, 5.7, 3.7 Hz, 1H), 2.55 (br s, 1H), 2.26 – 2.16 (dd, *J* = 7.4, 1.6 Hz, 3H), 1.66 – 1.55 (m, 2H), 1.50 – 1.36 (m, 2H), 1.23 (m, 16H), 0.88 – 0.82 (t, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, data is given only for the major diastereomer): δ = 168.6, 144.0, 129.8, 85.1, 74.1, 33.7, 31.9, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 29.3, 24.9, 22.7, 14.3, 14.1 ppm. IR (film): $\tilde{\nu}$ = 3429, 2922, 2853, 1735, 1677, 1465, 1439, 1378, 1353, 1207, 1123, 1075, 1038, 970, 865, 816, 722, 663 cm^{-1}. MS (EI) *m/z* (%) = 282 (1), 99 (6), 98 (100), 70 (22), 69 (6). HRMS (ESIpos): *m/z*: calcd for $C_{17}H_{30}O_3Na$: 305.2087; found: 305.2085.



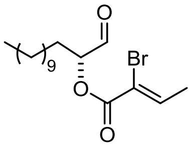
(3*R*,4*R*,5*R*)-3,4-Dihydroxy-3-((*S*)-1-hydroxyethyl)-5-undecyldihydrofuran-2(3*H*)-one (S6). A flame-dried Schlenck tube was charged with a solution of alcohol (*E*)-**S5** (16.0 mg, 56.7 µmol) in CH_2Cl_2 (3.0 mL) and the solution cooled to −78 °C. TMEDA (9.8 µL, 65 µmol) was added via syringe and the resulting solution was stirred for 5 min. A solution of OsO_4 (0.6 m in CH_2Cl_2, 104 µL, 62.3 µmol) was then added dropwise via syringe over the course of 4 min. After 20 min stirring at −78 °C, the cooling bath was removed and the reaction mixture concentrated by applying an Ar flow and finally dried under high vacuum. The residue was redissolved in THF (0.7 mL) and the solution treated with sat. $NaHSO_3$[14] (0.7 mL) for 36 h under vigorous stirring. The biphasic mixture was then diluted with sat. NH_4Cl solution and extracted with EtOAc (3 x 4 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 3:2) to give the desired triol as a white solid (13.2 mg, 74%). $[\propto]_D^{20}$ = +36.8 (c = 0.58, DMSO). ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 5.46 (d, *J* = 6.8 Hz, 1H), 5.39 (s, 1H), 4.94 (d, *J* = 4.7 Hz, 1H), 4.03 (td, *J* = 7.8, 4.4 Hz, 1H), 3.96 (t, *J* = 7.1 Hz, 1H), 3.67 (qd, *J* = 6.4, 4.7 Hz, 1H), 1.70 (dtd, *J* = 9.5, 7.4, 6.4, 4.5 Hz, 1H), 1.60 – 1.51 (m, 1H), 1.46 – 1.33 (m, 2H), 1.27 (d, *J* = 6.6 Hz, 3H), 1.31 – 1.21 (m, 16H), 0.85 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, [D$_6$]-DMSO): δ = 174.1, 81.4, 75.9, 72.4, 67.1, 32.3, 31.3, 29.1, 29.1, 29.0, 29.0, 28.9, 28.8, 25.0, 22.1, 16.7, 14.0 ppm. IR (film): $\tilde{\nu}$ = 3400, 2955, 2922, 2853, 1762, 1465, 1377, 1345, 1270, 1212, 1108, 1078, 1001, 967, 895, 798, 746, 721, 700 cm^{-1}. MS (ESIpos) *m/z* (%) = 339.3 (100 (M+Na)), 655.2 (45 (2M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{17}H_{32}O_5Na$: 339.2142; found: 339.2142.



(*R*)-1-Bromotridecan-2-yl (*E*)-but-2-enoate (S7). Alcohol **S3** (362 mg, 1.27 mmol) was dissolved in CH_2Cl_2 (6.4 mL) and the resulting solution cooled to 0 °C. Triphenylphosphine (401 mg, 1.53 mmol) and CBr_4 (464 mg, 1.40 mmol) were added as solids at 0 °C. The ice bath was removed and the orange solution allowed to warm to ambient temperature and stirred for further 30 min. Hexane (14 mL) was added and the suspension filtered through Celite® (10 mL rinse with hexanes). The filtrate was washed with aq. H_2O_2 solution (5%, 10 mL) and the aqueous washings were extracted with hexanes/EtOAc (9:1, 2 x 10 mL). The combined organic fractions were dried over Na_2SO_4 and concentrated. The brown residue was purified by flash chromatography (hexanes/EtOAc 29:1 to 24:1) to give the desired alkyl bromide as a colorless oil (273 mg, 62% yield). $[\propto]_D^{20}$ = +11.7 (c = 0.76, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.99 (dq, *J* = 15.5, 6.9 Hz, 1H), 5.84 (dq, *J* = 15.5, 1.7 Hz, 1H), 5.02 (tt, *J* = 6.5, 4.9 Hz, 1H), 3.50 (dd, *J* = 10.8, 4.6 Hz, 1H), 3.43 (dd, *J* = 10.8, 5.2 Hz, 1H), 1.87 (dd, *J* = 6.9, 1.7 Hz, 3H), 1.71 – 1.63 (m, 2H), 1.29 – 1.20 (m, 18H), 0.85 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 145.4, 122.4, 72.0, 34.4, 32.5, 31.9, 29.6, 29.5, 29.4, 29.4, 29.3, 29.3, 25.0, 22.7, 18.0, 14.1 ppm. IR (film): $\tilde{\nu}$ = 2922, 2853, 1721, 1658, 1465, 1443, 1293, 1259, 1172, 1101, 1017, 968, 837 cm^{-1}. MS (EI) *m/z* (%) = 349 (0.3), 347 (0.3), 267 (1), 180 (4), 111 (5), 97 (9), 87 (39), 69 (100), 41 (25). HRMS (ESIpos): *m/z*: calcd for $C_{17}H_{31}O_2BrNa$: 369.1400; found: 369.1396.

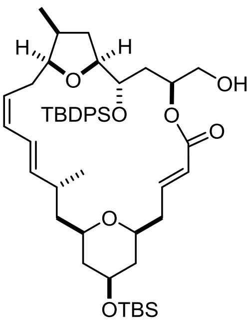


(*R*)-1-Hydroxytridecan-2-yl (*Z*)-2-bromobut-2-enoate (S8). Alcohol **S3** (117 mg, 0.411 mmol) was dissolved in CH_2Cl_2 (1.5 mL) and the resulting solution cooled to 0 °C. Bromine (31.6 µL, 0.617 mmol) was added dropwise via syringe. After 45 min at 0 °C, TLC analysis indicated full consumption of the s.m. and all volatiles were removed under vacuum. The residue was redissolved in Et_2O (2 mL), before triethylamine (68.8 µL, 0.494 mmol) was added at ambient temperature. After stirring for 38 h, the white precipitate formed was filtered off. The filtrate was concentrated and purified by flash chromatography (hexanes/EtOAc 12:1 to 9:1 to 7:1) to give the title compound as a pale-yellow oil (86 mg, 58% yield). Due to the unstable nature (1,2-Acyl shift), it was immediately engaged in the next step. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (q, *J* = 6.8 Hz, 1H), 4.97 (dtd, *J* = 7.5, 6.0, 3.3 Hz, 1H), 3.79 – 3.71 (m, 1H), 3.66 (dd, *J* = 12.2, 6.1 Hz, 1H), 2.05 – 1.89 (br s, 1H), 1.93 (d, *J* = 6.8 Hz, 3H), 1.70 – 1.55 (m, 2H), 1.36 – 1.18 (m, 18H), 0.88 – 0.82 (t, *J* = 6.7 Hz, 3H) ppm. IR (film): $\tilde{\nu}$ = 3428, 2923, 2853, 1715, 1630, 1465, 1376, 1335, 1249, 1227, 1108, 1036, 953, 845, 739 cm^{-1}. MS (ESIpos) *m/z* (%) = 467.1 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{17}H_{31}O_3BrNa$: 465.9611; found: 465.0611.

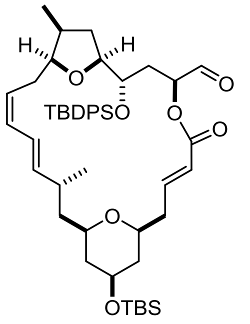


(*R*)-1-Oxotridecan-2-yl (*Z*)-2-bromobut-2-enoate (S9). Dess-Martin periodinane (298 mg, 0.702 mmol) and $NaHCO_3$ (157 mg, 1.88 mmol) were added to a solution of primary alcohol **S8** (85.1 mg, 0.234 mmol) in CH_2Cl_2 (2.4 mL) at 0 °C. After 5 min, the ice bath was removed and the white suspension allowed to warm to ambient temperature under vigorous stirring. After 100 min, the reaction mixture was poured into sat. $Na_2S_2O_3$/$NaHCO_3$ solution (1:1, 8 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 x 6 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 9:1) to give a colorless oil (43 mg, 51% yield, 90% purity). $[\propto]_D^{20}$ = +20.0 (c = 0.89, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.51 (d, *J* = 0.8 Hz, 1H), 7.47 (q, *J* = 6.9 Hz, 1H), 5.05 (dd, *J* = 8.2, 4.7 Hz, 1H), 1.96 (d, *J* = 6.8 Hz, 3H), 1.90 – 1.74 (m, 2H), 1.47 – 1.39 (m, *J* = 7.6 Hz, 2H), 1.26 (m, 16H), 0.86 – 0.82 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.8, 162.0, 143.0, 116.4, 79.9, 31.9, 29.6, 29.4, 29.3, 29.3, 29.2, 28.6, 24.8, 22.7, 18.0, 14.1 ppm. IR (film): $\tilde{\nu}$ = 2923, 2853, 1726, 1629, 1465, 1376, 1245, 1107, 1074, 1035, 944, 839, 775, 737 cm^{-1}. MS (EI) *m/z* (%) = 361 (1), 363 (1), 331 (0.5), 183 (8), 167 (16), 165 (11), 149 (100), 137 (99), 119 (9), 98 (36), 83 (7), 69 (10), 68 (9), 57 (12, 55 (14), 43 (19), 41 (14), 39 (12). HRMS (ESIpos): *m/z*: calcd for $C_{17}H_{29}O_3BrNa$: 383.1192; found: 383.1192.

Alcohol 72d. Ammonium fluoride (328 mg, 8.86 mmol) was added as a solid to a stirred solution of diene **72** (85.0 mg, 80.5 µmol) in hexafluoroisopropanol (8.5 mL) at 5 °C. The reaction mixture was allowed to warm to 15 °C after 12 h and stirred at this temperature for further 36 h. The reaction was then quenched by pouring it into sat. NH_4Cl solution (25 mL). The aqueous phase was extracted with CH_2Cl_2 (1 x 15 mL) and EtOAc (3 x 15 mL) and the combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 6:1) to give the desired primary alcohol as a white foam (43.0 mg, 65% yield). $[\propto]_D^{20}$ = +11.8 (c = 0.96, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 – 7.61 (m, 4H), 7.42 – 7.29 (m, 6H), 6.91 (dt, *J* = 15.7, 6.9 Hz, 1H), 6.23 (dd, *J* = 15.1, 10.9 Hz, 1H), 5.94 (t, *J* = 10.9 Hz, 1H), 5.85 (dt, *J* = 15.6, 1.2 Hz, 1H), 5.50 (dd, *J* = 15.0, 8.5 Hz, 1H), 5.20 (dt, *J* = 10.4, 7.8 Hz, 1H), 4.96 (ddd, *J* = 12.4, 6.3, 3.1 Hz, 1H), 4.04 (ddd, *J* = 7.9, 5.6, 4.3 Hz, 1H), 3.81 (dd, *J* = 7.7, 5.8 Hz, 1H), 3.74 (ddd, *J* = 10.7, 5.8, 4.9 Hz, 1H), 3.69 (dd, *J* = 6.7, 6.6 Hz, 1H), 3.51 (dd, *J* = 12.2, 2.7 Hz, 1H), 3.41 – 3.30 (m, 2H), 3.29 – 3.21 (m, 1H), 2.45 – 2.36 (m, 1H), 2.36 – 2.30 (m, 2H), 2.28 – 2.14 (m, 2H), 2.06 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.93 (dt, *J* = 13.0, 7.7 Hz, 1H), 1.90 – 1.81 (m, 2H), 1.78 (ddt, *J* = 12.4, 4.3, 1.9 Hz, 1H), 1.69 (ddt, *J* = 12.6, 4.2, 1.7 Hz, 1H), 1.64 – 1.54 (m, 2H), 1.41 (ddd, *J* = 12.7, 8.3, 6.6 Hz, 1H), 1.32 – 1.27 (m, 1H), 1.21 – 1.16 (m, 2H), 1.01 (s, 9H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.88 (d, *J* = 7.1 Hz, 3H), 0.86 (s, 9H), 0.04 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 146.5, 140.4, 136.0, 134.3, 134.0, 130.0, 129.6, 129.6, 127.6, 127.5, 127.5, 126.4, 124.1, 122.7, 81.2, 80.1, 73.7, 73.6, 73.2, 72.1, 68.8, 65.5, 42.8, 41.9, 41.7, 38.5, 35.3, 34.4, 33.9, 33.6, 30.1, 27.1, 25.8, 20.1, 19.5, 18.1, 15.2, −4.5 ppm. IR (film): $\tilde{\nu}$ = 3466, 2955, 2929, 2856, 1718, 1656, 1472, 1462, 1428, 1374, 1319, 1256, 1177, 1155, 1107, 1069, 961, 836, 775, 740, 703, 609 cm^{-1}. MS (ESIpos) *m/z* (%) = 839.6 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{48}H_{72}O_7Si_2Na$: 839.4709; found: 839.4703.

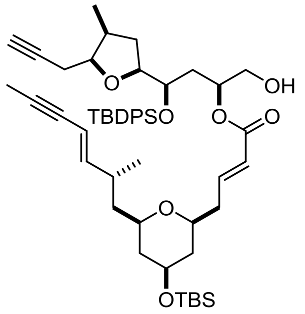


Aldehyde 73. Dess-Martin periodinane (46.8 mg, 0.110 mmol) and $NaHCO_3$ (25.3 mg, 0.301 mmol) were added as solids to a solution of alcohol **72d** (41.0 mg, 50.2 µmol) in CH_2Cl_2 (9.6 mL) at 0 °C. The ice bath was removed 5 min after the addition and the reaction mixture allowed to warm to ambient temperature while stirring vigorously. After 2.5 h, the reaction mixture was quenched by pouring it into sat. $NaHCO_3/Na_2S_2O_5$ solution (1:1, 15 mL) and the aqueous phase was extracted with CH_2Cl_2 (4 x 12 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (8 cm SiO_2, hexanes/EtOAc 9:1) keeping the contact time with silica gel as short as possible to yield the desired aldehyde as a white foam (34.3 mg, 84% yield). $[\propto]_D^{20}$ = +15.6 (c = 0.98, CH_2Cl_2). ^{1}H NMR (400 MHz, C_6D_6): δ = 9.22 (s, 1H), 7.88 – 7.81 (m, 4H), 7.29 – 7.22 (m, 6H), 7.09

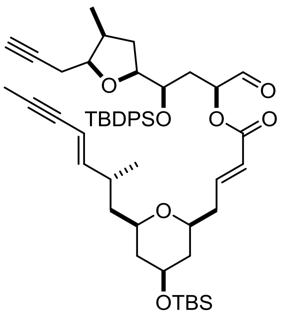


(ddd, *J* = 15.3, 8.7, 6.2 Hz, 1H), 6.50 (dd, *J* = 15.0, 11.0 Hz, 1H), 6.11 (t, *J* = 10.8 Hz, 1H), 5.99 (dd, *J* = 15.7, 1.0 Hz, 1H), 5.54 (dd, *J* = 15.1, 8.3 Hz, 1H), 5.46 (dd, *J* = 9.9, 3.6 Hz, 1H), 5.19 (dt, *J* = 10.7, 7.7 Hz, 1H), 4.22 (ddd, *J* = 9.4, 6.3, 3.1 Hz, 1H), 3.82 (dt, *J* = 8.9, 6.7 Hz, 1H), 3.65 – 3.55 (m, 2H), 3.14 (td, *J* = 9.8, 1.6 Hz, 1H), 2.88 (td, *J* = 10.0, 0.8 Hz, 1H), 2.67 – 2.55 (m, 1H), 2.11 (dt, *J* = 15.3, 7.6 Hz, 1H), 1.99 (dt, *J* = 15.0, 8.8 Hz, 1H), 1.92 – 1.75 (m, 5H), 1.73 – 1.62 (m, 2H), 1.56 – 1.46 (m, 2H), 1.21 (s, 9H), 1.19 – 1.12 (m, 4H), 1.04 – 0.99 (m, 12H), 0.70 – 0.65 (d, *J* = 6.9 Hz, 3H), 0.09 (s, 6H). ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 197.3, 165.6, 147.1, 140.3, 136.5, 136.4, 135.0, 134.5, 130.4, 129.9, 129.9, 127.9, 127.9, 126.9, 125.2, 122.7, 81.2, 81.0, 76.1, 73.7, 73.5, 72.8, 69.0, 43.5, 42.4, 42.0, 38.6, 36.3, 35.2, 33.7, 32.6, 30.7, 27.5, 26.0, 20.1, 19.9, 18.2, 14.7, −4.3 ppm. IR (film): $\tilde{\nu}$ = 2955, 2928, 2956, 1722, 1655, 1471, 1462, 1428, 1257, 1171, 1106, 1052, 1005, 982, 941, 836, 775, 738, 702, 609 cm^{-1}. MS (ESIpos) *m/z* (%) = 837.5 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{48}H_{70}O_7Si_2Na$: 837.4552; found: 837.4550.

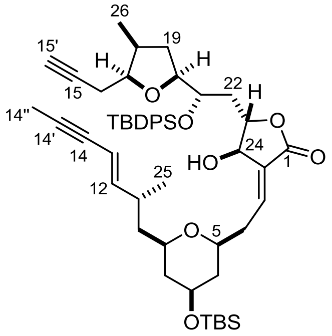
Alcohol S10. Ammonium fluoride (54.2 mg, 1.46 mmol) was added to a solution of diyne **66** (16.0 mg, 0.146 mmol) in 1,1,1,3,3,3-hexafluro-2-propanol (1.5 mL) and the resulting solution stirred for 40 h at ambient temperature. The reaction mixture was then poured into sat. aq. $NaHCO_3$ solution and the aqueous phase was extracted with CH_2Cl_2 (4 x 5 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 15:1 to 9:1 to 7:1 5:1) to yield the title compound as a white foam (8.8 mg, 70%). $[\propto]_D^{20}$ = −16.4 (c = 0.86, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 – 7.61 (m, 4H), 7.40 – 7.35 (m, 2H), 7.35 – 7.28 (m, 4H), 6.87 (dt, *J* = 15.6, 7.2 Hz, 1H), 5.92 (dd, *J* = 15.9, 7.9 Hz, 1H), 5.71 (dt, *J* = 15.7, 1.2 Hz, 1H), 5.36 (ddq, *J* = 15.9, 2.6, 1.3 Hz, 1H), 4.98 (ddt, *J* = 8.4, 4.7, 4.3 Hz, 1H), 3.84 (ddd, *J* = 7.1, 6.1, 3.9 Hz, 1H), 3.82 – 3.74 (m, 2H), 3.70 (tt, *J* = 10.6, 4.9 Hz, 1H), 3.58 (dd, *J* = 12.1, 3.3 Hz, 1H), 3.47 (dd, *J* = 12.3, 5.7 Hz, 1H), 3.33 (dddd, *J* = 11.4, 6.6, 5.2, 1.2 Hz, 1H), 3.25 (dd, *J* = 11.2, 7.2, 5.8, 1.4 Hz, 1H), 2.44 – 2.24 (m, 4H), 2.18 – 2.04 (m, 3H), 2.01 – 1.89 (m, 2H), 1.90 (d, *J* = 2.2 Hz, 3H), 1.87 (t, *J* = 2.6 Hz, 1H), 1.80 – 1.71 (m, 2H), 1.69 – 1.57 (m, 2H), 1.32 (ddd, *J* = 12.4, 8.4, 7.9 Hz, 1H), 1.35 – 1.26 (ddd, *J* = 13.4, 7.0, 6.4 Hz, 1H), 1.23 – 1.07 (m, 2H), 1.00 (s, 9H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.86 (d, *J* = 7.0 Hz, 3H), 0.86 (s, 9H), 0.04 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 148.5, 145.9, 136.0, 135.9, 134.1, 133.9, 129.5, 129.4, 127.5, 127.3, 122.9, 108.2, 84.5, 81.7, 81.0, 79.3, 78.3, 74.0, 73.3, 73.1, 71.8, 69.3, 68.6, 65.3, 42.3, 41.4, 41.3, 38.8, 35.2, 34.8, 34.4, 33.4, 27.1, 25.8, 20.9, 19.8, 19.5, 18.1, 14.7, 4.2, −4.5, −4.5 ppm. IR (film): $\tilde{\nu}$ = 3466, 2954, 2929, 2856, 1718, 1656, 1472, 1462, 1428, 1377, 1256, 1219, 1177, 1109, 1069, 1005, 837, 776, 739, 703, 611 cm^{-1}. MS (ESIpos) *m/z* (%) = 877.6 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{51}H_{74}O_7Si_2Na$: 877.4865; found: 877.4860.



Aldehyde S11. Dess-Martin periodinane (9.8 mg, 23 µmol) and $NaHCO_3$ (5.2 mg, 62 µmol) were added as solids to a stirred solution of alcohol **S10** (6.6 mg, 7.7 µmol) in CH_2Cl_2 (2.4 mL) at room temperature. The resulting white suspension was stirred vigorously for 2.5 h. The reaction mixture was then poured into sat. $NaHCO_3/Na_2S_2O_5$ solution (1:1, 6 mL) and the aqueous phase was extracted with CH_2Cl_2 (4 x 5 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (8 cm SiO_2, hexanes/EtOAc 12:1), keeping the contact time with silica gel as short as possible, to give the rather unstable aldehyde as a colorless oil (5.5 mg, 84% yield). $[\propto]_D^{20}$ = −11.7 (c = 0.48, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$): δ = 9.39 (d, *J* = 0.8 Hz, 1H), 7.65 – 7.60 (m, 4H), 7.39 – 7.35 (m, 2H), 7.33 – 7.29 (m, 4H), 6.91 (dt, *J* = 15.7, 7.1 Hz, 1H), 5.91 (ddd, *J* = 15.9, 8.0, 0.8 Hz, 1H), 5.74 (dt, *J* = 15.7, 1.5 Hz, 1H), 5.36 (dqd, *J* = 15.9, 2.3, 1.1 Hz, 1H), 5.03 (dd, *J* = 9.9, 3.6 Hz, 1H), 3.93 (ddd, *J* = 8.3, 6.0, 3.4 Hz, 1H), 3.82 – 3.77 (m, 2H), 3.73 (tt, *J* = 10.8, 4.7 Hz, 1H), 3.36 (dddd, *J* = 11.8, 7.0, 5.0, 1.8 Hz, 1H), 3.26 (dddd, *J* = 11.2, 7.3, 5.7, 1.6 Hz, 1H), 2.41 (dtd, *J* = 15.0, 7.1, 1.6 Hz, 1H), 2.38 – 2.26 (m, 3H), 2.12 – 2.08 (m, 2H), 1.96 (dt, *J* = 12.8, 7.4 Hz, 1H), 1.92 – 1.89 (m, 1H), 1.90 (d, *J* = 2.2 Hz, 3H), 1.87 (t, *J* = 2.7 Hz, 1H), 1.80 – 1.73 (m, 2H), 1.62 (dt, *J* = 13.7, 7.1 Hz, 1H), 1.34 – 1.27 (m, 2H), 1.22 – 1.17 (m, 2H), 1.16 – 1.10 (m, 1H), 1.01 (s, 9H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.87 (d, *J* = 7.1 Hz, 1H), 0.86 (s, 9H), 0.04 (s, 6H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.3, 165.5, 148.4, 147.0, 135.9, 133.8, 133.5, 129.6, 129.5, 127.6, 127.3, 121.9, 108.2, 84.4, 81.5, 80.6, 79.4, 78.3, 75.5, 73.9, 73.3, 71.0, 69.5, 68.6, 42.3, 41.4, 41.4, 38.9, 35.2, 34.7, 33.4, 31.8, 27.1, 25.8, 20.9, 19.7, 19.5, 18.1, 14.7, 4.2, −4.5, −4.5.ppm. IR (film): $\tilde{\nu}$ = 2955, 2929, 2856, 1725, 1655, 1472, 1462, 1428, 1376, 1258, 1171, 1110, 1060, 1006, 962, 837, 776, 740, 703, 611 cm^{-1}. MS (ESIpos) *m/z* (%) = 875.5 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{51}H_{72}O_7Si_2Na$: 875.4711; found: 875.4709.

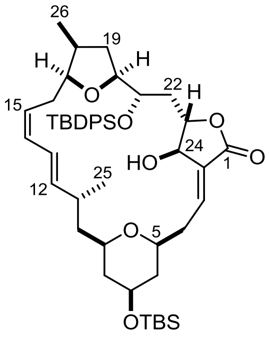


Baylis-Hillman alcohol S12. A flame-dried Young tube was charged with a solution of aldehyde **S11** (1.2 mg, 1.41 µmol) in DMF (30 µL) followed by a solution of dimethylphenylphosphine (0.05 M in DMF, 8.4 µL, 0.42 µmol). The Young tube was sealed and place in a preheated oil bath (90 °C). The reaction mixture was stirred at this temperature for 8 h before being cooled to room temperature. It was then poured into sat. NH_4Cl solution (3 mL) and the aqueous phase was extracted with Et_2O (3 x 2 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 9.1 to 8:1 to 7:1 to 6:1 to 5:1) to give alcohol **250** as a white amorphous solid (0.45 mg, 38% yield, 6:1 E/Z, ~90% pure). ^1H NMR (600 MHz, C_6D_6): see table 14. ^{13}C NMR (150 MHz, C_6D_6): see table 14. IR (film): $\tilde{\nu}$ = 3461, 2956, 2931, 2855, 1724, 1658, 1472, 1463, 1428, 1376, 1256, 1172, 1111, 1060, 1005, 960, 835, 778, 742,

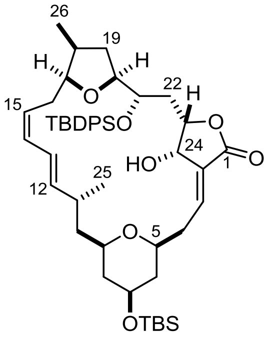


706 cm^{-1}. MS (ESIpos) *m/z* (%) = 875.5 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{51}H_{72}O_7Si_2Na$: 875.4711; found: 875.4707.

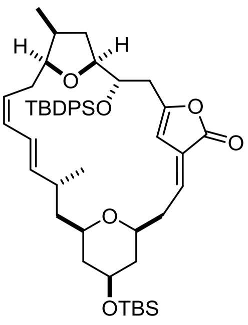
Baylis-Hillman alcohol ((24*R*)-74, major isomer). A flame-dried Young-tube was charged with a solution of aldehyde **73** (34.3 mg, 42.1 µmol) in DMF (1.1 mL). A solution of dimethylphenylphosphine (0.2 M in DMF, 63.1 µL, 12.6 µmol) was added via syringe, the Young tube was sealed, placed in a preheated oil bath (90 °C) and the reaction mixture was stirred for 60 h at this temperature. After cooling to ambient temperature, the reaction mixture was poured into sat. NH_4Cl solution (10 mL) and the aqueous phase was extracted with Et_2O (3 x 4 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The pale yellow residue was purified by flash chromatography (hexanes/EtoAc 12:1 to 9:1 to 8:1 to 7:1) to yield alcohol (24*R*)-**74** (11.7 mg, 34% yield) along with its isomer (24*S*)-**74** (see below) and elimination product **75** (see below). $[\propto]_D^{20}$ = +47 (c = 0.28, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): see table 14. ^{13}C NMR (150 MHz, $CDCl_3$): see table 14. IR (film): $\tilde{\nu}$ = 3426, 2955, 2930, 2894, 2857, 1760, 1744, 1683, 1462, 1428, 1376, 1362, 1331, 1252, 1195, 1111, 1077, 1029, 1006, 945, 856, 836, 775, 739, 704 cm^{-1}. MS (ESIpos) *m/z* (%) = 837.5 (100 (M+Na)). HRMS (ESIpos): calcd for $C_{48}H_{70}O_7Si_2Na$: *m/z*: 837.4552; found: 837.4549.



Baylis-Hillman alcohol ((24*S*)-74, minor isomer). Obtained from the reaction described above as the minor isomer (6.4 mg, 19% yield). $[\propto]_D^{20}$ = +46.1 (c = 0.67, CH_2Cl_2). ^{1}H NMR (600 MHz, C_6D_6): δ = see table 15. ^{13}C NMR (150 MHz, $CDCl_3$): δ = see table 15. IR (film): $\tilde{\nu}$ = 3417, 2955, 2928, 2856, 2856, 1760, 1742, 1682, 1462, 1428, 1376, 1252, 1194, 1110, 1075, 1006, 945, 856, 836, 775, 739, 703 cm^{-1}. MS (ESIpos) *m/z* (%) = 837.5 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{48}H_{70}O_7Si_2Na$: 837.4552; found: 837.4551.



Elimination product 75. Obtained from the reaction described above as an unpolar by-product (1.6 mg, 5% yield). $[\propto]_D^{20}$ = +27.8 (c = 0.34, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 – 7.61 (m, 4H), 7.40 – 7.30 (m, 6H), 6.40 (dd, *J* = 10.6, 6.5 Hz, 1H), 6.16 (dd, *J* = 15.0, 11.1 Hz, 1H), 5.99 (t, *J* = 11.0 Hz, 1H), 5.91 (s, 1H), 5.48 (dd, *J* = 15.0, 8.4 Hz, 1H), 5.31 (td, *J* = 10.1, 6.4 Hz, 1H), 4.30 (ddd, *J* = 8.3, 5.6, 4.4 Hz, 1H), 3.74 – 3.66 (m, 3H), 3.17 – 3.06 (m, 2H), 2.89 (dd, *J* = 14.8, 5.6 Hz, 1H), 2.54 (dd, *J* = 14.8, 8.2 Hz, 1H), 2.44 (ddd, *J* = 13.0, 10.7, 7.8 Hz, 1H), 2.33 – 2.23 (m, 4H), 2.12 – 2.06 (m, 1H), 1.93 (ddd, *J* = 12.4, 7.6, 6.2 Hz, 1H), 1.83 (ddt, *J* = 12.4, 4.7, 1.6 Hz, 1H), 1.68 (ddt, *J* = 12.5, 4.6, 1.6 Hz, 1H), 1.58 (dt, *J* =



12.4, 9.5 Hz, 1H), 1.47 (ddd, *J* = 13.8, 9.9, 6.2 Hz, 1H), 1.26 (dd, *J* = 6.6, 2.7 Hz, 1H), 1.21 – 1.13 (m, 2H), 1.01 (s, 9H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.86 (s, 9H), 0.80 (d, *J* = 6.7 Hz, 3H), 0.03 (s, 3H), 0.03 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 168.1, 156.9, 141.5, 135.9, 135.9, 133.8, 133.7, 133.6, 130.9, 130.4, 129.7, 129.6, 127.6, 127.5, 126.5, 123.3, 103.6, 81.6, 79.7, 74.4, 73.5, 69.6, 68.7, 42.3, 42.1, 41.5, 36.5, 35.6, 34.4, 33.7, 32.3, 29.9, 27.0, 25.8, 19.6, 19.4, 18.1, 15.5, −4.5, −4.5 ppm. IR (film): $\tilde{\nu}$ = 2955, 2928, 2856, 1782, 1655, 1471, 1462, 1428, 1376, 1324, 1254, 1151, 1105, 1081, 1006, 927, 867, 837, 823, 776, 740, 703 cm^{-1}. MS (EI) *m/z* (%) = 796 (14), 741 (16), 740 (34), 739 (58), 711 (29), 607 (22), 540 (38), 483 (17), 408 (51), 295 (38), 239 (25), 217 (26), 199 (63), 197 (44), 135 (100), 131 (18), 93 (20), 73 (32). HRMS (ESIpos): *m/z*: calcd for $C_{48}H_{68}O_6Si_2Na$: 819.4447; found: 819.4443.

Table 13: Assignment of the ^{1}H & ^{13}C NMR data for the *anti*-Baylis-Hillman alcohol **S12**.*

atom n°	**^{1}H NMR (C_6D_6, 600 MHz)**					**^{13}C NMR (C_6D_6, 150 MHz) δ /ppm**
	δ /ppm	**m**	***J*/Hz**	**COSY**	**NOESY**	
1	-	-	-	-	-	168.2
2	-	-	-	-	-	134.3
3	6.95	ddd	9.8, 7.1, 2.0	4ab, 5, 6b, 24	4a(b)	139.8
4a	2.33	ddd	14.0, 9.8, 4.0	3, 4b, 5, 24	4b, 5, 24	34.9
4b	1.95	m	-	3, 4a, 5	4a, 5	
5	2.95	dm	11.5	4ab, 6ab	4ab, 6a, 7, 9	73.7
6a	1.53	m	-	5, 6b, 7	6b	40.3
6b	1.28	m	-	5, 6a, 7	5, 6a, 7	
7	3.50	dddd	10.5, 10.3, 5.0, 4.9	6ab, 8ab	5, 6a, 8a, 9	68.9
8a	1.60	ddt	12.9, 4.4, 2.1	7, 8b, 9	7, 8b, 9, 11	41.1
8b	0.97	m	-	7, 8a, 9	8a	
9	3.09	dtd	11.2, 6.7, 1.2	8ab, 10ab	5, 7, 8a, 10a, (11), 25	74.2
10a	1.51	t	11.3	9, 10b, 11	9, 10b, 11	42.0
10b	1.08	m	-	9, 10a, 11	9, 10a, 11, (25)	
11	2.16	m	-	10ab, 12, 25	8a, (9), 10a(b), (12), 13, 25	33.8
12	5.96	dd	15.8, 8.3	11, 13	10a, (11), 25	147.9
13	5.52	dqd	15.9, 2.2, 0.9	(11), 12, 14“	11, (25)	109.6
14	-	-	-	-	-	78.9
14‘	-	-	-	-	-	84.9
14“	1.63	d	2.3	13	-	3.9
15‘	1.70	t	2.7	16ab	-	70.0
15	-	-	-	-	-	81.7
16a	2.03	ddd	16.7, 5.6, 2.7	16b, 17	16b, 17, 18	21.1
16b	1.93	m	-	16a, 17	16a, 17, 26	
17	3.64	ddd	7.8, 7.1, 5.6	16ab, 18	16ab, 18	79.7
18	1.93	m	-	17, 19a, 26	17, 19a, 26	35.6
19a	1.53	m	-	18, 19b, 20	18, 19b, 20, 21	35.5
19b	1.06	m	-	18, 19a, 20	19a, (22b), 26	
20	3.68	dt	8.9, 6.7	19a, 21	18, 19ab, 21, 22b	81.7
21	4.18	ddd	7.2, 7.0, 4.2	20, 22ab	19a, 20, 22b, 23, 24	72.8
22a	1.71	m	-	21, 22b, 23	20, 21, 22b, 23, 24	39.1
22b	1.71	m	-	21, 22a, 23	20, 21, 22a, 23, 24	
23	4.82	ddd	9.0, 5.0, 2.4	22ab, 24	(20), 21, 22b, 24	82.3
24	4.34	dd	2.4, 2.1	23, OH	4ab, (21), 22b, 23	70.9
25	0.78	d	6.6	11	9, 10a(b), 11, 12, (13)	20.0
26	0.66	d	7.0	18	16a, 18, 19, (20)	14.6
OH	3.35	br s	-	23	24	-

* The signals of the TBS & TBDPS group are not listed and appear as follows: ^{1}H NMR (600 MHz, C_6D_6): δ = 7.93 – 7.88 (m, 4H), 7.30 – 7.22 (m, 6H), 1.23 (s, 9H), 0.99 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H) ppm. ^{13}C NMR (150 MHz, C_6D_6): δ = 136.5, 134.8, 134.5, 129.9, 129.7, 127.9, 27.5, 26.0, −4.4 ppm.

Table 14: Assignment of the ^{1}H & ^{13}C NMR data for the *anti*-Baylis-Hillman alcohol (24*R*)-**74**.*

atom n°	**^{1}H ($CDCl_3$, 600 MHz)**					**^{13}C ($CDCl_3$, 150 MHz)**	
	δ /ppm	**m**	***J* /Hz**	**COSY**	**NOESY**	**δ /ppm**	**HMBC**
1	-	-	-	-	-	168.7	-
2	-	-	-	-	-	132.8	-
3	6.85	ddd	9.7, 7.0, 2.1	4ab	4ab, 5, 6a, (24), (25)	142.3	1, (5), 24
4a	2.63	ddd	14.0, 9.7, 8.3	3, 4b, (5)	3, 4b, 5, (6a), 24	35.0	2, 3, 5
4b	2.39	ddd	14.0, 7.1, 2.4	3, 4a, 5	3, 4a, 5, 24		2, 3, 5
5	3.45	dddd	11.1, 8.5, 2.0, 1.7	4(a)b, 6a	3, 4ab, 6b, 7, 9	74.3	
6a	1.29	m	-	5, 6b, 7	3, (4a), 6b, 8a	40.7	5, 7
6b	1.83	ddt	12.5, 4.7, 1.7	6a, 7	5, 6a, 7		7, 8
7	3.75	m	-	6ab, 8ab	5, 6b, 8b, 9, 25	68.6	
8a	1.16	m	-	7, 8b, 9	6a, 8b	41.8	7, 9
8b	1.68	ddt	12.7, 4.7, 1.7	7, 8a, (9)	7, 8a, 9		6, 7
9	3.29	tt	10.9, 2.0	8a(b), 10b	5, 7, 8b, 10b, 11, 25	73.1	
10a	1.19	m	-	10b, 11	9, 10b, 11, 12	43.7	8, 12
10b	1.47	m	-	9, 10a	10a, 11, 12, 13		9
11	2.31	m	-	10ab, 12, 25	9, 10a, 12, 13, 24, 25, OH	32.8	
12	5.45	dd	15.1, 8.3	11, 13	10ab, (11), 14, 25	141.0	11, 14, 25
13	6.34	dd	15.2, 10.9	12, 14	10a, 11, 16a, (17), 22a, 25	125.0	11
14	5.93	dd	10.8, 10.8	13, 15	12, 15	130.5	12, 16
15	5.28	dt	10.2, 6.6	14, 16ab	14, 16ab, 17, (26)	127.0	13
16a	2.00	dddd	14.5, 6.6, 3.1, 0.5	15, 16b, 17	15, 16b, 17, 26	30.4	14, 15
16b	2.36	m	-	15, 16a, 17	13, 15, 17, 16a, 23, 26		14, 15, 17
17	3.72	ddd	8.7, 7.3, 3.0	16ab, 18	(13), 15, 16ab, 18, 20, 26	81.5	15
18	2.20	ddq	7.4, 7.3, 7.3	17, 19ab, 26	17, 19ab, 20, 26	35.4	19, (20), 26
19a	1.48	m	-	18, 19b, 20	18, 19b, 21, 23	33.7	17, 18, (20), 26
19b	1.92	ddd	12.9, 7.7, 7.0	18, 19a, 20	18, 19a, 20, 22a		18, 20, (21), 26
20	3.83	ddd	9.3, 6.6, 4.9	19ab, 21	17, 18, 19b, 21	80.0	(18), 22
21	4.34	m	-	20, 22ab	19b, 20, 22a	69.0	19, 20
22a	1.74	ddd	14.2, 7.5, 5.9	21, 22b, 23	19b, 21, 22b, 23, 24	36.0	20, 21 23, 24
22b	1.93	ddd	14.4, 8.2, 6.0	21, 22a, 23	(11), 21, 22a, 23, 24		(20), (21), 23, 24
23	4.54	ddd	8.7, 5.9, 3.5	22ab, 24	16b, 19, 22, 24, 26, OH	82.0	
24	4.33	ddd	-	23, OH	(3), 4ab, 11, (13), 22, 23	71.0	
25	0.86	d	6.4	11	(3), 7, 9, 11, 12, (13)	18.6	10, 11, 12
26	0.95	d	7.1	18	15, 16, 17, 18, 19b, 22, 23	15.7	17, 18, 19
OH	2.84	br d	4.4	23	11, 23, 24	-	-

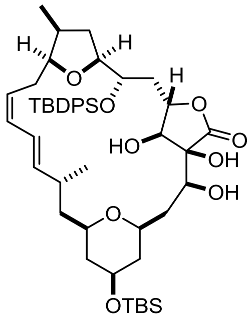
*The signals of the TBS & TBDPS group are not listed and appear as follows: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.68 – 7.63 (m, 4H), 7.42 – 7.31 (m, 6H), 1.04 (s, 9H), 0.85 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 136.0, 133.8, 133.7, 129.7, 129.7, 127.6, 127.5, 27.1, 25.8, 19.5, 18.1, −4.5, −4.6 ppm

Table 15: Assignment of the ^{1}H & ^{13}C NMR data for the *syn*-Baylis-Hillman alcohol (24*S*)-**74**.*

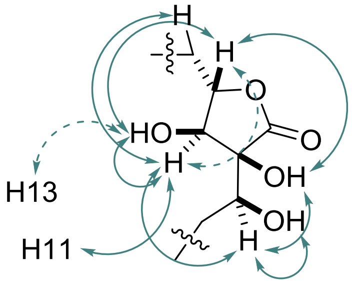
atom n°	**^{1}H (CDCl$_3$, 600 MHz)**					**^{13}C (CDCl$_3$, 150 MHz)**	
	δ /ppm	**m**	***J* /Hz**	**COSY**	**NOESY**	**δ /ppm**	**HMBC**
1	-	-	-	-	-	168.7	-
2	-	-	-	-	-	134.8	-
3	6.79	ddd	11.3, 6.0, 1.6	4ab	4ab, 5	140.0	1, 24
4a	2.46	m	-	3, 4b, (5)	3, 5, 24, OH	36.7	2, 3, 5
4b	2.46	m	-	3, 4a, 5	3, 5, 24, OH		2, 3, 5
5	3.38	dddd	11.3, 11.3, 3.5, 1.8	4(a)b, 6a	3, 4ab, 6b, 7, 9	72.8	
6a	1.31	ddd	11.9, 11.7, 11.2	5, 6b, 7	6b	41.9	5
6b	1.91	m	-	6a, 7	5, 6a, 7		
7	3.79	dddd	10.6, 10.6, 4.8, 4.8	6ab, 8ab	5, 6b, 8b, 9	68.3	
8a	1.24	ddd	12.5, 11.4, 11.3	7, 8b, 9	8b	41.9	9
8b	1.69	ddt	12.8, 4.8, 1.7	7, 8a, (9)	7, 8a, 9, 10b		7
9	3.29	tt	11.2, 2.0	8a(b), 10b	5, 7, 8b, 10b, 25	73.7	
10a	1.53	m	-	10b, 11	10b, (11)	43.5	
10b	1.15	ddd	14.2, 12.4, 1.1	9, 10a	8b, 9, 10a, 25		
11	2.39	m	-	10b, 12, 25	13, 25, OH	31.3	
12	5.39	dd	15.2, 7.6	11, 13	(13), 14, 25	141.2	11, 14, 25
13	6.35	dd	15.2, 10.9	12, 14	11, 16a, (OH)	125.1	
14	5.92	dd	10.9, 10.9	13, 15	12, 15	130.3	
15	5.17	td	10.9, 5.1	14, 16ab	14, 16b, 17	127.6	
16a	2.33	m	-	15, 16b, 17	13, 16b	31.2	
16b	1.92	dddd	14.6, 11.1, 2.3, 2.2	15, 16a, 17	16a, 17, 26		14, 15
17	3.85	m	-	16ab, 18	15, 16b, 18	81.5	15
18	2.24	ddq	10.8, 7.4, 7.1	17, 19b, 26	17, 19a, 20, 26	35.7	
19a	1.86	ddd	12.6, 6.4, 6.3	19b, 20	18, 19b, 20	33.2	17, 18, 21
19b	1.51	m	-	18, 19a, 20	19a, 26		
20	3.88	m	-	19ab, 21	19a, 21	80.0	
21	4.49	ddd	11.6, 4.8, 1.9	20, 22b	20, 22a	69.6	
22a	2.35	m	-	22b, 23	21, 22b	29.7	23
22b	1.83	dd	13.2, 0.5	21, 22a	22a, 23, (24)		21
23	4.51	ddd	12.4, 5.3, 1.6	22a, 24	22b, 24	78.5	
24	4.72	dd	5.3, 1.3	(23), OH	4ab, 23, OH	65.8	1, 23
25	0.80	d	6.6	11	9, 10b, 11, 12	18.1	10, 11, 12
26	0.98	d	7.0	18	16b, 18	15.2	17, 18, 19
OH	4.23	s	-	(24)	4ab, 11, (13), 24	-	2, 23, 24

*The signals of the TBS & TBDPS group are not listed and appear as follows: ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.67 – 7.61 (m, 4H), 7.41 – 7.30 (m, 6H), 1.03 (s, 9H), 0.86 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 135.9, 135.9 133.9, 133.9, 129.7, 129.7, 127.5, 27.2, 27.1, 25.8, 19.7, 18.0, −4.5, −4.6 ppm.

Triol 76. A flame-dried Schlenck tube was charged with a solution of alcohol (24*R*)-**74** (10.0 mg,

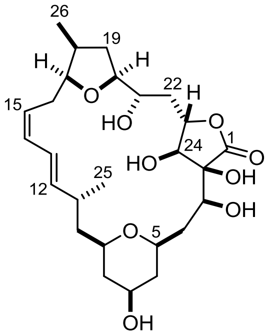


12.3 µmol) in CH_2Cl_2 (1.3 mL) and the solution was cooled to −78 °C. A solution of TMEDA (0.2 m in CH_2Cl_2, 70.5 µL, 14.1 µmol) was introduced and the reaction mixture stirred at −78 °C for 5 min. A solution of osmium tetroxide (0.12 M in CH_2Cl_2, 103 µL, 12.4 µmol) was added dropwise via syringe through a septum over 3 min. After stirring at −78 °C for 20 min, the mixture was allowed to warm to rt, the volatiles were removed by first applying an Ar flow and the residue was dried under high vacuum. The residue was redissolved in THF (0.6 mL) and the solution treated with aq. sat. $NaHSO_3$ solution (0.6 mL) for 23 h under vigorous stirring. The resulting emulsion was diluted with EtOAc/NaCl solution (1:1, 6 mL) and the layers were separated. The aqueous phase was extracted with EtoAc (3 x 4 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The pale red residue was purified by flash chromatography (hexanes/EtOAc 5:1) to afford the triol as a white foam (6.8 mg, 65%). $[\propto]_D^{20}$ = +13.6 (c = 0.59, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.67 – 7.61 (m, 4H), 7.42 – 7.38 (m, 2H), 7.36 – 7.32 (m, 4H), 6.16 (ddt, *J* = 15.2, 10.8, 1.1 Hz, 1H), 5.92 (tt, *J* = 10.9, 1.7 Hz, 1H), 5.55 (dd, *J* = 15.2, 8.0 Hz, 1H), 5.25 (ddd, *J* = 10.8, 9.2, 5.4 Hz, 1H), 4.35 (ddd, *J* = 8.5, 4.8, 3.4 Hz, 1H), 4.25 (ddd, *J* = 10.5, 7.7, 2.9 Hz, 1H), 3.94 – 3.87 (m, 2H), 3.84 (ddd, *J* = 8.2, 7.6, 4.7 Hz, 1H), 3.75 (dddd, *J* = 10.7, 10.7, 4.7, 4.7 Hz, 1H), 3.72 (br s, 1H), 3.59 (dd, *J* = 9.3, 7.6 Hz, 1H), 3.50 (d, *J* = 2.9 Hz, 1H), 3.46 (ddt, *J* = 11.3, 10.5, 1.9 Hz, 1H), 3.32 (ddt, *J* = 11.9, 9.9, 2.3 Hz, 1H), 2.78 (d, *J* = 9.3 Hz, 1H), 2.37 – 2.26 (m, 3H), 2.06 (dtd, *J* = 15.4, 5.1, 1.9 Hz, 1H), 2.01 (ddd, *J* = 14.5, 8.9, 2.9 Hz, 1H), 2.01 – 1.92 (m, 2H), 1.85 (ddd, *J* = 14.2, 10.4, 3.4 Hz, 1H), 1.77 (ddt, *J* = 12.5, 4.7, 1.7 Hz, 1H), 1.70 (ddd, *J* = 12.5, 4.7, 2.0 Hz, 1H), 1.57 – 1.48 (m, 3H), 1.29 (ddd, *J* = 13.9, 10.0, 2.5 Hz, 1H), 1.25 – 1.18 (m, 2H), 1.05 (s, 9H), 0.98 (d, *J* = 7.0 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.85 (s, 9H), 0.03 (s, 6H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 175.8, 140.7, 135.9, 133.7, 133.6, 129.8, 129.8, 127.6, 126.7, 123.9, 80.9, 80.2, 79.9, 74.4, 74.1, 73.2, 72.9, 71.3, 69.1, 68.6, 44.0, 42.2, 41.7, 36.4, 35.8, 34.7, 33.6, 33.1, 31.0, 27.1, 25.8, 19.5, 19.3, 18.1, 14.9, −4.5, −4.5 ppm. IR (film): $\tilde{\nu}$ = 3477, 2956, 2930, 2857, 1763, 1472, 1462, 1428, 1376, 1362, 1255, 11943, 1111, 1078, 1031, 1006, 981, 922, 857, 837, 776, 739, 703, 611 cm^{-1}. MS (ESIpos) *m/z* (%) = 871.59 (100 (M+Na)). HRMS (ESIpos) *m/z*: calcd for $C_{48}H_{72}O_9Si_2Na$: 871.4607; found: 871.4607.

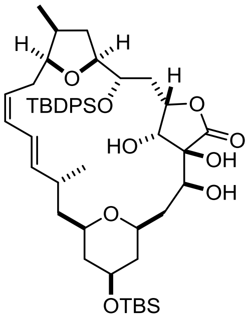


Key NOE contacts of the γ-lactone observed for triol **76**.

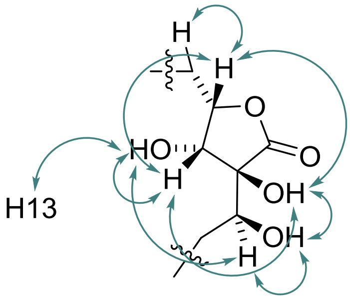
2,3,24-*epi*-**Deacylmandelalide D (77).** A teflon vial was charged with a solution of triol **76** (5.0 mg, 5.9 µmol) in THF (0.5 mL) and pyridine (0.5 mL) and the mixture cooled to 0 °C. HF·pyr (500 µL) was then added slowly via an Eppendorf pipette. After stirring 5 min at 0 °C, the reaction mixture was allowed to warm to ambient temperature and stirred for further 24 h. The reaction was then quenched by pouring it into pH 7.2 buffer (NaH_2PO_4/Na_2HPO_4, 5 mL) and the buffered aqueous phase was extracted with EtOAc/EtOH (9:1, 4 x 6 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (CH_2Cl_2/MeOH 93:7 to 92:8 to 91:9 to 90:10) to yield the desired pentaol as a white solid (2.1 mg, 72% yield). $[\propto]_D^{27}$ = −2.0 (c = 0.34, MeOH). ^{1}H NMR (600 MHz, CD_3OD): see table 16. ^{13}C NMR (150 MHz, CD_3OD): see table 16. IR (film): $\tilde{\nu}$ = 3379, 2957, 2924, 2873, 2856, 1763, 1650, 1455, 1375, 1261, 1375, 1214, 1109, 1063, 1036, 998, 948, 883, 732 cm^{-1}. MS (ESIpos) *m/z* (%) = 519.20 (100 (M+Na)), 1016.37 (32 (2M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{26}H_{40}O_9Na$: 519.2565; found: 519.2564.



Triol 78. A flame-dried Schlenck tube was charged with a solution of alcohol (24*S*)-**74** (6.0 mg, 7.4 µmol) in CH_2Cl_2 (1.0 mL) and the resulting mixture cooled to −78 °C. A solution of TMEDA (0.2 m in CH_2Cl_2, 42.3 µL, 8.5 µmol) was introduced and the reaction mixture stirred 5 min at −78 °C. A solution of osmium tetroxide (0.12 M in CH_2Cl_2, 61.3 µL, 7.4 µmol) was added dropwise via syringe through a septum over 3 min. After stirring at −78 °C for 20 min, the cooling bath was removed and the volatiles were removed by first applying an Ar flow. The residue was finally dried under high vacuum before it was redissolved in THF (0.4 mL) and the solution treated with aq. sat. $NaHSO_3$ (0.4 mL) for 23 h under vigorous stirring. The resulting emulsion was diluted with EtOAc/NaCl solution (1:1, 6 mL) and the layers were separated. The aqueous phase was further extracted with EtoAc (3 x 4 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The pale red residue was purified by flash chromatography (hexanes/EtOAc 7:1 to 6:1) to afford the triol as a white foam (4.9 mg, 78%). $[\propto]_D^{20}$ = +30.2 (c = 0.42, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67 – 7.61 (m, 4H), 7.41 – 7.37 (m, 2H), 7.36 – 7.32 (m, 4H), 6.30 (ddt, *J* = 15.3, 10.9, 1.2 Hz, 1H), 5.87 (ddt, *J* = 10.8, 10.7, 1.9 Hz, 1H), 5.43 (dd, *J* = 15.2, 7.7 Hz, 1H), 5.16 (ddd, *J* = 10.8, 8.8, 4.5 Hz, 1H), 4.87 (ddt, *J* = 11.2, 3.3, 1.6 Hz, 1H), 4.34 (ddd, *J* = 10.8, 4.8, 2.2 Hz, 1H), 4.26 (dt, *J* = 5.1, 2.1 Hz, 1H), 4.08 (t, *J* = 1.6 Hz, 1H), 4.01 (dd, *J* = 3.3, 1.8 Hz, 1H), 4.00 – 3.92 (m, 2H), 3.78 (tt, *J* = 10.7, 4.7 Hz, 1H), 3.55 (tt, *J* = 11.3, 2.2 Hz, 1H), 3.48 (br s, 1H), 3.43 – 3.38 (m, 1H), 3.21 (br s, 1H), 2.43 – 2.30 (m, 4H), 2.18 (dddd, *J* = 16.3, 6.8, 4.7, 2.3 Hz, 1H), 1.90 – 1.83 (m, 2H), 1.79 (ddt, *J* = 15.8, 11.5, 1.6 Hz, 1H), 1.73 – 1.67 (m, 2H), 1.67 – 1.62 (m, 1H), 1.59 (dd, *J* = 10.1, 2.5 Hz, 1H), 1.57 – 1.54 (m, 1H), 1.27 – 1.24 (m, 1H), 1.20 (dd, *J* = 4.0, 1.8 Hz, 1H), 1.17 (dd, *J* = 13.4, 2.0 Hz, 1H), 1.05 (s, 9H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.94



(d, *J* = 6.6 Hz, 3H), 0.86 (s, 9H), 0.04 (s, 6H) ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ = 177.5, 140.2, 135.9, 135.9, 133.9, 133.4, 129.7, 129.7, 129.0, 127.6, 127.5, 127.1, 125.1, 81.5, 80.1, 79.1, 78.7, 74.9, 74.4, 74.1, 69.7, 68.2, 68.2, 44.1, 42.1, 41.9, 38.9, 36.5, 32.5, 32.5, 32.4, 29.5, 27.1, 25.8, 19.6, 19.4, 18.1, 14.4, −4.6, −4.6 ppm. IR (film): $\tilde{\nu}$ = 3374, 2956, 2929, 2856, 1759, 1471, 1461, 1427, 1375, 1362, 1332, 1259, 1203, 1107, 1069, 979, 856, 836, 801, 775, 737, 702 cm^{-1}. MS (ESIpos) *m/z* (%) = 871.6 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{48}H_{72}O_9Si_2Na$: 871.4607; found: 871.4606.



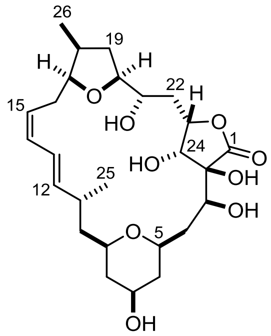
Key NOE contacts of the γ-lactone observed for Triol **78**.

Table 16: ^{1}H and ^{13}C NMR data of 2,3,24-*epi*-deacylmandelalide D (**77**).

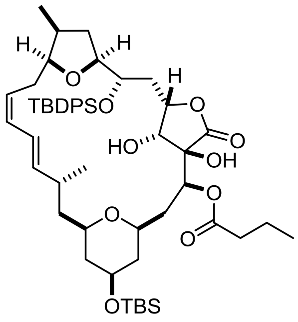
atom n°	^{1}H NMR (CD$_3$OD, 600 MHz)					^{13}C NMR (CD$_3$OD, 600 MHz) δ /ppm
	δ /ppm	**m**	***J* /Hz**	**COSY**	**NOESY**	
1	-	-			-	177.9
2	-	-			-	76.9
3	3.92	m	-	4ab, 5	-	73.3
4a	1.74	ddd	14.9, 8.5, 2.3	3, 4b, 5	4b, 5, 6a	38.0
4b	1.96	m	14.9, 9.8, 2.2	3, 4a, 5	3, 4a	
5	3.58	dddd	11.4, 10.0, 1.9, 1.8	4ab, 6ab	3, 4a, 6b, 7, 9	74.2
6a	1.19	dt	12.0, 11.3	5, 6b, 7	(4b), 6b	42.3
6b	1.89	ddt	12.1, 4.2, 1.8	5, 6a, 7	(4a), 6a, 5, 7	
7	3.78	dddd	11.0, 10.9, 4.8, 4.6	6ab, 8ab	5, 6b, 8b, 9	68.8
8a	1.11	dt	12.1, 11.3	7, 8b, 9	8b, (10a)	42.9
8b	1.88	dddd	12.3, 4.7, 1.7, 1.7	7, 8a, 9	7, 8a, 9, (10b)	
9	3.41	ddt	11.1, 10.1, 2.1	8ab, 10ab	5, 7, 8b, 10a, (11), 25	74.2
10a	1.35	ddd	13.7, 10.7, 2.9	10b, 11	(8b), 9, 10b, (11), 25	45.3
10b	1.54	ddd	13.8, 10.1, 3.8	10a, 11	8a, 10a, 11	
11	2.52	m	-	10ab, 12, 25	(9), (10b), 12, 13, 25	34.9
12	5.55	dd	15.2, 8.3	11, 13	(10ab), (11), 14, 25	141.9
13	6.44	ddt	15.1, 10.8, 0.9	12, 14	(10a), 11, 16b, (17), 25	126.2
14	5.98	tq	10.8, 0.7	13, 15	12, 15	131.6
15	5.33	m	-	14, 16ab	14, 16a, 17, (26)	127.9
16a	2.16	dddd	15.1, 6.2, 4.3, 1.6	15, 16b, 17	15, 16b, 17, 26	31.8
16b	2.38	m	-	15, 16a, 17	13, 16a, 17	
17	3.91	m	-	-	-	82.9*
18	2.40	m	-	17, 19ab, 26	17, 19b, 26	37.9
19a	1.51	td	12.4, 9.0	18, 19b, 20	19b, 20, (22ab), (26)	35.1
19b	2.05	ddd	12.4, 7.2, 6.3	18, 19a, 20	17, 18, 19a, 20	
20	3.90	m	-	-	-	82.6*
21	3.91	m	-	-	-	69.7**
22a	1.95	m	-	21, 22b, 23	21, 22b, 23	36.3
22b	1.96	m	-	21, 22a, 23	19a, 21, 22a	
23	4.48	ddd	8.3, 6.0, 4.4	22ab, 24	22ab, 24	82.8
24	3.90	m	-	-	-	75.2**
25	0.99	d	6.8	11	9, 10b, 11, 12	19.8
26	1.03	d	7.1	18	16ab, 19a	15.3
OH	not observed due to H/D exchange with CD$_3$OD					

*,**: Due to overlap in the spectra, these signals could not be assigned and are listed arbitrarily.

2,3-*epi*-Deacylmandelalide D (79). A teflon vial was charged with a solution of triol **78** (1.0 mg, 1.2 µmol) in THF (0.1 mL) and the mixture cooled to 0 °C. Pyridine (100 µL) and HF·pyr (100 µL) were added slowly via an Eppendorf pipette. After stirring for 5 min at 0 °C, the reaction mixture was allowed to warm to ambient temperature and stirred for further 41 h. The reaction was then quenched by pouring the mixture into pH 7.2 buffer (NaH_2PO_4/Na_2HPO_4, 5 mL) and the buffered aqueous phase was extracted with EtOAc/EtOH (9:1, 4 x 6 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (CH_2Cl_2/MeOH 93:7 to 92:8 to 91:9) to yield the desired pentaol as a white solid (0.5 mg, 86% yield). $[\propto]_D^{27}$ = +14 (c = 0.16, MeOH). ^{1}H NMR (600 MHz, CD_3OD): see table 17. ^{13}C NMR (150 MHz, CD_3OD): see table 17. IR (film): $\tilde{\nu}$ = 3357, 2956, 2922, 2853, 1758, 1665, 1632, 1609, 1510, 1458, 1408, 1376, 1249, 1205, 1102, 1086, 1046, 979, 707 cm^{-1}. MS (ESIpos) *m/z* (%) = 519.3 (100 (M+Na)), 1016.37 (32 (2M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{26}H_{40}O_9Na$: 519.2565; found: 519.2563.



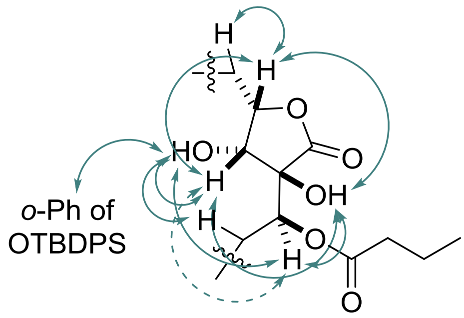
Monobutyrate (2*R*,3*S*)-78a. Triol **78** (2.0 mg, 2.4 µmol) was dissolved in CH_2Cl_2 (0.2 mL) and the resulting solution cooled to 0 °C. Pyridine (4.8 µL, 59 µmol) was added via syringe followed by a solution of *n*-butyric anhydride (0.6 M in CH_2Cl_2, 8.6 µL, 5.2 µmol) and DMAP (1 crystal, ~0.1 mg). The ice bath was removed after 10 min and the reaction mixture was stirred for another 2 h at ambient temperature. The reaction was quenched by addition of sat. NH_4Cl solution (5 mL) and the aqueous phase was extracted with EtOAc (4 x 4 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 12:1 to 9:1) to give the monobutyrate as a white amorphous solid (1.5 mg, 69% yield). $[\propto]_D^{20}$ = +26.2 (c = 0.31, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.66 – 7.61 (m, 4H), 7.40 – 7.36 (m, 2H), 7.35 – 7.31 (m, 4H), 6.30 (ddt, *J* = 15.2, 10.8, 1.1 Hz, 1H), 5.89 (t, *J* = 10.8 Hz, 1H), 5.48 (dd, *J* = 15.2, 7.3 Hz, 1H), 5.42 (dd, *J* = 4.7, 2.8 Hz, 1H), 5.15 (ddd, *J* = 10.8, 9.8, 4.7 Hz, 1H), 4.87 (br d, *J* = 10.7 Hz, 1H), 4.38 (br s, 1H), 4.35 (ddd, *J* =10.5, 4.7, 2.6 Hz, 1H), 4.00 (dd, *J* = 3.2, 2.2 Hz, 1H), 3.93 – 3.87 (m, 2H), 3.78 (tt, *J* = 10.4, 4.7 Hz, 1H), 3.70 (tt, *J* = 11.3, 1.7 Hz, 1H), 3.49 (dd, *J* = 11.6, 9.7 Hz, 1H), 2.89 (s, 1H), 2.53 – 2.45 (m, 1H), 2.41 (ddd, *J* = 16.0, 8.4, 6.8 Hz, 1H), 2.36 – 2.26 (m, 4H), 2.12 (dtd, *J* = 15.8, 5.1, 2.1 Hz, 1H), 2.02 (ddd, *J* = 16.3, 11.2, 2.8 Hz, 1H), 1.84 (dt, *J* = 12.6, 6.4 Hz, 1H), 1.78 (dddd, *J* = 12.7, 4.8, 1.9, 1.9 Hz, 1H), 1.72 – 1.65 (m, 5H), 1.61 (ddd, *J* = 13.4, 10.0, 2.9 Hz, 1H), 1.55 (m, 1H), 1.28 – 1.24 (m, 1H), 1.22 – 1.18 (m, 1H), 1.15 (m, 1H), 1.04 (s, 9H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.96 (d, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.85 (s, 9H), 0.03 (s, 6H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 173.1, 172.8, 140.6, 135.9, 135.9, 134.0, 133.6, 129.7, 129.6, 129.4, 127.6, 127.5, 127.1, 124.9, 81.5, 80.2, 78.8, 77.4, 75.2, 74.2, 73.7, 69.7, 69.3, 68.1, 43.9, 42.1, 41.8, 39.2, 36.3, 36.1, 32.6, 32.1,



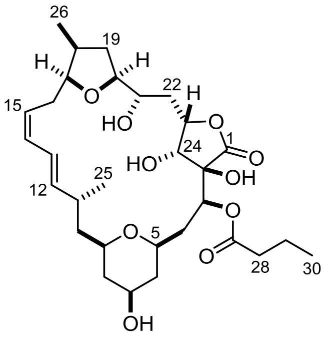
32.1, 29.7, 29.5, 27.1, 25.8, 19.6, 19.2, 18.2, 18.1, 14.7, 13.7, −4.5, −4.6 ppm. IR (film): $\tilde{\nu}$ = 3380, 2956, 2928, 2856, 1782, 1743, 1462, 1428, 1376, 1362, 1257, 1177, 1110, 1070, 979, 858, 836, 776, 704 cm^{-1}. MS (ESIpos) *m/z* (%) = 941.6 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{52}H_{78}O_{10}Si_2Na$: 941.5026; found: 941.5022.

Table 17: ^{1}H and ^{13}C NMR data of 2,3-*epi*-deacylmandelalide D (**79**).

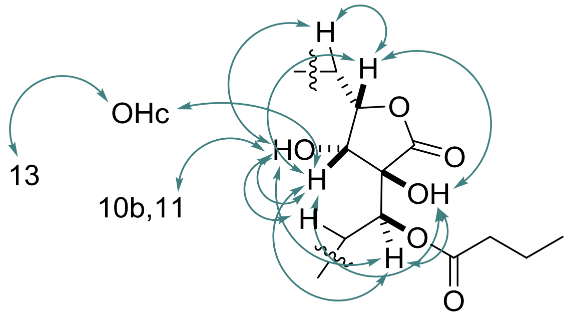
atom n°	**^{1}H NMR (CD_3OD, 600 MHz)**					**^{13}C NMR (CD_3OD, 600 MHz)**	
	δ /ppm	**m**	***J* /Hz**	**COSY**	**NOESY**	**δ /ppm**	**HMBC**
1	-	-		-	-	178.9	-
2	-	-		-	-	80.1	-
3	4.34	dd	6.6, 2.0	4ab	4b, 5, 11, (24)	69.5	1, 4, 5
4a	1.70	ddd	15.3, 6.6, 2.0	3, 4b, 5	(3), 4b, (5)	40.4	3
4b	1.90	ddd	15.4, 10.8, 2.0	3, 4a, 5	3, 4a, 24		2, 5
5	3.64	tt	11.0, 1.8	4ab, 6ab	3, 4a, 6b, 7, 9	75.2	(4)
6a	1.17	ddd	12.0, 11.3, 11.3	5, 6b, 7	6b	42.5	4, 7, 8
6b	1.94	ddt	12.3, 4.4, 1.9	5, 6a, 7	(4a9; 5, 6a, 7		7, 8
7	3.81	tt	11.0, 4.7	6ab, 8ab	5, 6b, 8b, 9	68.6	-
8a	1.15	td	11.6, 11.2	7, 8b, 9	8b, (10b)	42.7	6, 7, 9, 10
8b	1.85	m	-	7, 8a, 9	7, 8a, 9		6, 7
9	3.50	ddt	11.2, 10.2, 1.8	8ab, 10ab	5, 7, 8b (10a), (11), 25	74.8	7
10a	1.28	m	-	9, 10b, 11	(8b), (9), 10b, 25	45.2	11, 25
10b	1.58	ddd	13.8, 10.3, 2.8	9, 10a, 11	(8a), (11), 10a		9, 25
11	2.58	m	-	10ab, 12, 25	3, 9, 10b, (12), 13, 25	34.0	(13)
12	5.53	dd	15.1, 7.8	11, 13	(11), 14, 25	141.9	10, 11, 14, 25
13	6.40	ddt	15.2, 11.1, 0.6	12, 14	(10b), 11, 16b, (25)	126.2	11, 14, 15
14	5.93	tt	10.9, 1.6	13, 15, (16ab)	12, 15	130.8	12, 13, 16
15	5.23	ddd	10.9, 8.8, 5.3	14, 16ab	14, 16a, 17, 26	128.0	13, (16)
16a	2.27	dtd	15.8, 5.8, 2.1	15, 16b, 17	(13), (15), 16a, (17), 26	33.1	14, 15, 17, 18
16b	2.42	dddd	15.7, 9.1, 6.4, 1.6	15, 16a, 17	13, 16b, (17)		14, 15, 17 , (18)
17	4.01	td	7.1, 4.7	16ab, 18	15, (16b), 18	83.4	
18	2.47	dqd	7.1, 7.0, 3.9	17, 19ab, 26	17 ,19a, 26	38.4	16, 17, 19, 26
19a	1.62	m	-	18, 19b, 20	17, 19b, 20, 22b, 26	34.1	18, 20, 21, 26
19b	2.00	dt	12.6, 6.6	18, 19a, 20	18, 19a, 20, (26)		17, 18, 26
20	4.04	ddd	9.6, 6.3, 4.1	19ab, 21	17, 18, 19b, 21	83.0	22
21	3.95	ddd	11.0, 4.1, 2.2	20, 22ab	20, 22a, 23	69.3	19
22a	2.22	ddd	14.7, 8.7, 2.2	21, 22b, 23	21, 22b, (23), 24	31.5	23, 24
22b	1.85	m	-	21, 22a, 23	22a, 23		
23	4.95	ddd	8.7, 4.9, 3.6	22ab, 24	21, 22ab, 24	80.8	
24	4.14	d	3.6	23	(3), 4b, 23	77.1	1, 2, 23
25	1.00	d	6.7	11	9, 10a, 11, 12	20.0	10, 11, 12
26	1.04	d	7.0	18	(15), 16(a)b, 18, 19a	14.9	17, 18, 19
OH	not observed due to H/D exchange with CD_3OD						



Key NOE contacts for the γ-lactone region of monobutyrate **78a**.



2,3-*epi*-Mandelalide C (80). A teflon vial was charged with a solution of mono-butyrate **78a** (1.5 mg, 1.6 µmol) in THF (0.15 mL). Pyridine (0.15 mL) was added and the reaction mixture was cooled to 0 °C. HF·pyr (0.15 mL) was added carefully and the ice bath was removed 5 min after the addition. The reaction mixture was stirred for 25 h before the reaction was quenched with EtOAc (3 mL) and pH 7.2 buffer (NaH_2PO_4/Na_2HPO_4, 5 mL). The aqueous phase was extracted with EtOAc/EtOH (9:1, 3 x 4 mL), the combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (CH_2Cl_2/MeOH 97:3 to 96:4 to 95:5) to give a white amorphous solid (0.72 mg, 78% yield). $[\propto]_D^{20} = -19$ (c = 0.14, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): see table 18. ^{13}C NMR (150 MHz, $CDCl_3$): see table 18. IR (film): $\tilde{\nu}$ = 3377, 2961, 2930, 2875, 1775, 1737, 1455, 1413, 1367, 1329, 1262, 1179, 1102, 1057, 979, 947, 733 cm^{-1}. MS (ESIpos) *m/z* (%) = 589.4 (100 (M+Na)). HRMS (ESIpos): *m/z*: calcd for $C_{30}H_{46}O_{10}Na$: 589.2983; found: 589.2978.

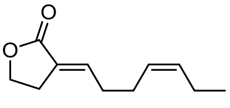


Key NOE contacts for the γ-lactone region of **80**.

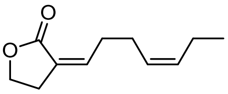
Table 18: ^{1}H and ^{13}C NMR data for 2,3-*epi*-mandelalide C (**80**).

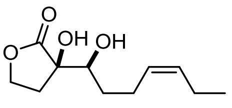
atom n°	^{1}H NMR (CDCl$_3$, 600 MHz)					^{13}C NMR (CDCl$_3$, 150 MHz) δ /ppm
	δ /ppm	m	*J* /Hz	COSY	NOESY	
1	-	-	-	-	-	172.5
2	-	-	-	-	-	78.3
3	5.51	dd	4.8, 4.8	4ab	4a, 5, 11, (24), 28a OHd	69.3
4a	1.73	ddd	16.2, 4.6, 1.6	3, 4b, 5	3, 4b, 5, 6b	38.6
4b	2.11	m	-	3, 4a, 5	4a, (6b)	
5	3.74	dddd	11.0, 11.0, 1.9, 1.7	4ab, 6ab	3, 4a, 6b, 7, 9	73.5
6a	1.23	ddd	12.3, 11.7, 11.6	5, 6b, 7	-	41.2
6b	1.93	m	-	6a	4a(b), 5, 7	
7	3.85	dddd	11.0, 11.0, 4.8, 4.8	6ab, 8ab	5, 6b, 8b, 9	67.5
8a	1.28	ddd	12.6, 11.3, 11.3	7, 8b, 9	-	40.8
8b	1.94	m	-	8a	7, 9	
9	3.50	m	-	8ab, 10ab	5, 7, 8b, 10ab, 12, (25)	74.5
10a	1.33	ddd	14.0, 9.9, 4.0	9, 10b, 11	(8a), 9, 10b, (11), 25	42.6
10b	1.71	m	-	9, 10a, 11	8a, 9, 10a, 11, 13, 24, 25, OHd	
11	2.46	m	-	10, 12, 13, 25	3, 9, 10a, 12, (13, 24), 25	30.6
12	5.72	dd	15.5, 5.2	11, 13	9, (10ab), 11, 14, 25	140.6
13	6.26	dddd	15.6, 10.7, 1.2, 1.1	11, 12, 14	10a, 11, 16a, 21, 25, OHc	123.3
14	6.06	dd	10.7, 10.7	13, 15, 16ab	12, 15	130.9
15	5.31	ddd	11.0, 5.0, 5.0	14, 16ab	14, 16b, 17	127.3
16a	1.98	ddt	14.0, 4.7, 2.1	14, 15, 16b, 17	15, 16b, 17, 18, 26	30.4
16b	2.39	m	-	14, 15, 16a, 17	13, 16a, 21	
17	3.95	ddd	10.6, 7.2, 1.9	16ab, 18	16a, 18, 26	81.7
18	2.41	m	-	17, 19ab, 26	17, 19a, 20, 26	36.5
19a	1.54	m	-	18, 19b, 20	18, 19b, 22b, 26	35.7
19b	2.10	m	-	18, 19a, 20	18, 19a, 20, (21), 26	
20	3.80	ddd	8.5, 7.3, 3.6	19ab, 21	9, 17, 18, 19a, 22b	81.1
21	3.46	m	-	20, 22ab, OHc	13, 16b, (19b), 20, 23, 24	70.6
22a	1.93	m	-	21, 22b, 23	-	31.7
22b	2.24	ddd	14.1, 11.3, 11.3	21, 22a, 23	20, 22a, 23, 24, OHc, OHd	
23	4.74	ddd	11.3, 4.3, 3.2	22ab, 24	21, 24	80.0
24	4.21	dd	3.1, 2.1	23, OHd	4a, 5, 9, 23, OHa, OHc, OHd	74.3
25	1.05	d	6.8	11	9, 10a, 11, 12, 13	20.2
26	1.02	d	7.0	18	16a, 17, 18, 19a	14.8
27	-	-	-	-	-	172.9
28a	2.42	ddd	15.9, 8.2, 6.8	28b, 29ab	28b, 30	36.0
28b	2.33	ddd	16.0, 8.1, 6.9	28a, 29ab	28a, 30	
29	1.68	m	-	28ab, 30	-	18.2
30	0.94	t	7.4	29	28ab	13.7
OHa	3.42	br s	-	-	OH d	-
OHb	1.56	m	-	-	-	-
OHc	2.87	d	6.6	21	13, 24	-
OHd	4.81	d	2.1	(23), 24	3, 4b, 5, 10b, 11, 22b, 24	-

(*E*)-3-((*Z*)-Hept-4-en-1-ylidene)dihydrofuran-2(3H)-one ((*E*)-83). LiHMDS (475 mg, 2.83 mmol) was dissolved in THF (6 mL) and the solution cooled to −78 °C before a solution of γ-butyrolactone (**82**) (200 µL, 2.60 mmol) in THF (2.4 mL) was introduced via canula. The resulting yellow mixture was stirred for 30 min at −78 °C before a solution of *cis*-4-heptenal (**81**) (313 µL, 2.37 mmol) in THF (3.8 mL) was added via canula. The reaction mixture was allowed to stir for 1 h at −78 °C, when triethylamine (494 µL, 3.54 mmol) and methanesulfonyl chloride (0.238 mL, 3.07 mmol) were added via syringe. The reaction mixture was allowed to warm to ambient temperature and stirred for further 2 h. It was then cooled to 0 °C and DBU (530 µL, 3.54 mmol) was added via syringe. The cooling bath was removed after 5 min and the reaction mixture stirred for another 1 h at ambient temperature. The reaction was quenched by pouring the mixture into sat. $NaHCO_3$ solution (20 mL). After dilution with Et_2O (15 mL), the organic phase was washed with sat. $NaHCO_3$ solution (15 mL) and the combined aqueous washings were re-extracted with Et_2O (2 x 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (pentane/Et_2O 4:1 to 3.5:1 to 3:1) to yield the major (*E*)-isomer (246 mg, 58%) as a pale yellow oil along with the minor (*Z*)-isomer (40 mg, 9%).^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.71 (ttd, *J* = 7.4, 2.9, 0.9 Hz, 1H), 5.44 – 5.36 (m, 1H), 5.27 (dtt, *J* = 10.6, 7.1, 1.6 Hz, 1H), 4.37 – 4.32 (m, 2H), 2.84 (tdd, *J* = 7.4, 3.0, 1.5 Hz, 2H), 2.26 – 2.15 (m, 4H), 2.06 – 1.95 (m, 2H), 0.93 (td, *J* = 7.5, 0.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 140.2, 133.3, 126.9, 125.5, 65.3, 30.4, 25.6, 25.1, 20.5, 14.2 ppm. IR (film): $\tilde{\nu}$ = 3005, 2963, 2932, 2873, 1746, 1679, 1440, 1378, 1352, 1306, 1282, 1217, 1197, 1177, 1139, 1028, 961, 868, 719, 614 cm^{-1}. MS (EI) *m/z* (%) = 112 (100), 91 (4), 83 (11), 79 (6), 77 (5), 69 (21), 67 (22), 41 (32). HRMS (ESIpos): *m/z*: calcd for $C_{11}H_{16}O_2Na$: 203.1042; found: 203.1042.



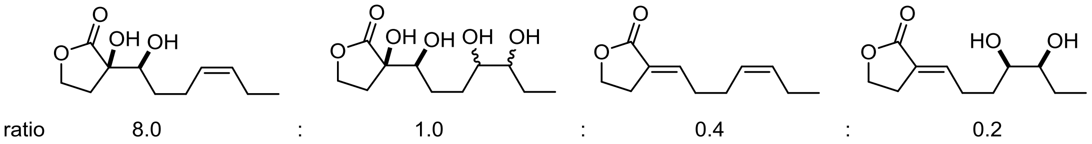
(*Z*)-3-((*Z*)-Hept-4-en-1-ylidene)dihydrofuran-2(3H)-one ((*Z*)-83). Obtained as the minor isomer from the reaction described above. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.20 (tt, *J* = 7.7, 2.4 Hz, 1H), 5.43 – 5.35 (m, 1H), 5.34 – 5.26 (m, 1H), 4.28 (t, *J* = 7.4 Hz, 2H), 2.88 (tq, *J* = 7.4, 2.1 Hz, 2H), 2.75 (qt, *J* = 7.5, 2.0 Hz, 2H), 2.15 (qd, *J* = 7.3, 1.4 Hz, 2H), 2.05 – 1.96 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 143.4, 132.7, 127.5, 123.7, 65.3, 29.1, 27.4, 26.5, 20.5, 14.2 ppm. IR (film): $\tilde{\nu}$ = 3005, 2963, 2931, 2872, 1747, 1671, 1443, 1374, 1221, 1168, 1126, 1077, 1025, 958, 867, 866, 798, 756, 717 cm^{-1}. MS (EI) *m/z* (%) = 180 (6), 151 (8), 125 (5), 123 (9), 113 (7), 112 (100), 95 (10), 91 (15), 83 (15), 79 (20), 77 (11), 69 (16), 67 (37), 53 (14), 41 (34), 39 (13). HRMS (ESIpos): *m/z*: calcd for $C_{11}H_{16}O_2Na$: 203.1042; found: 203.1043.



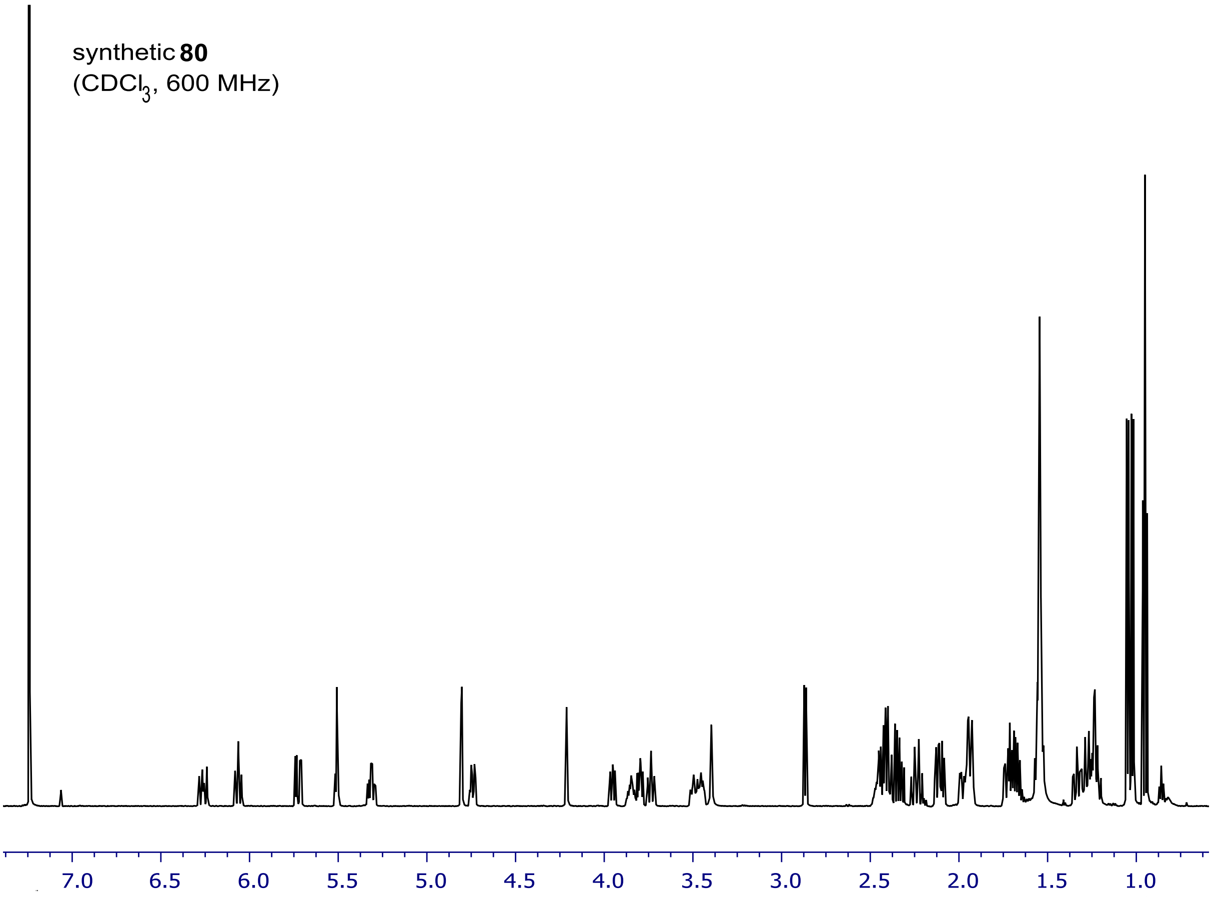


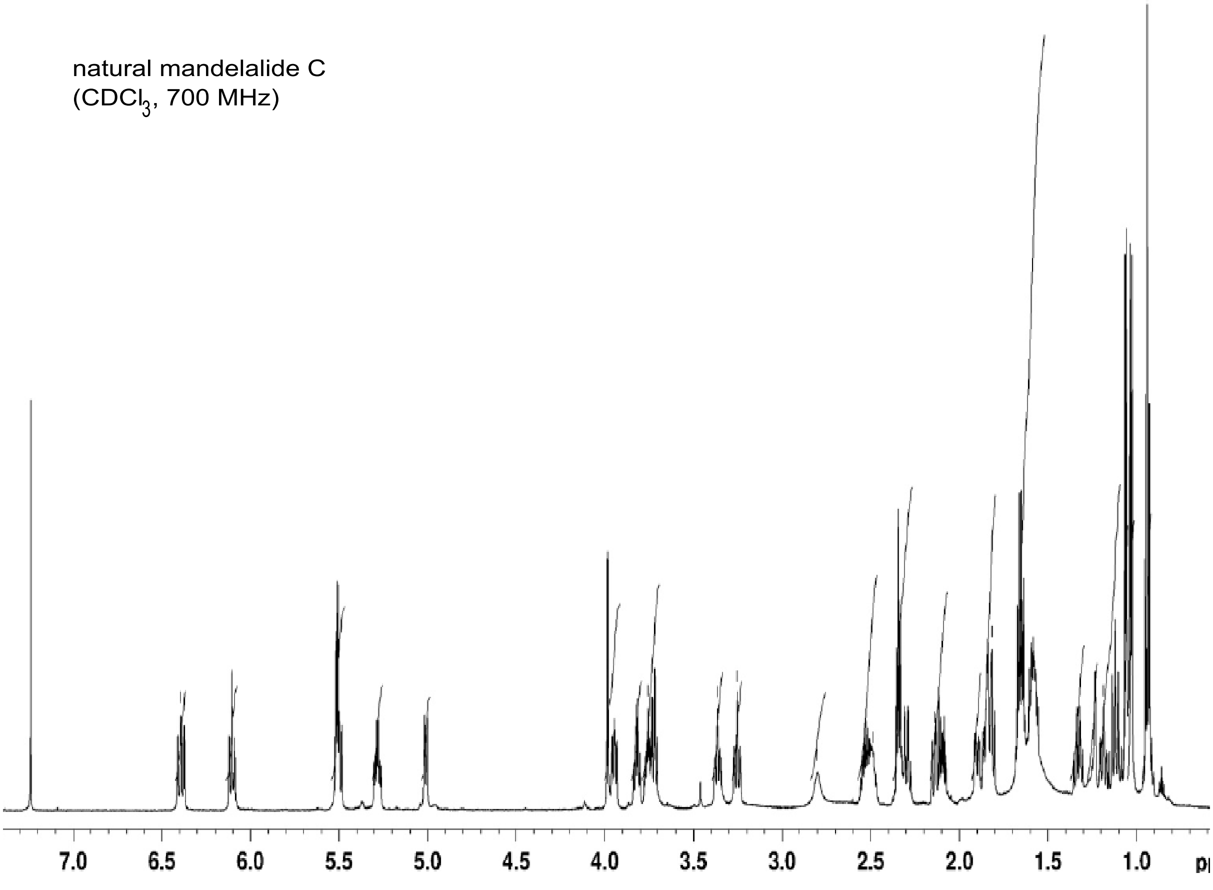
Diol 84. A solution of diene (*E*)-**83** (10.0 mg, 55.5 µmol) was dissolved in CH_2Cl_2 (1.1 mL) and cooled to −78 °C. TMEDA (9.6 µL, 63.8 µmol) was added via syringe and the reaction mixture was equilibrated at −78 °C for 5 min. A solution of OsO_4 (0.6 M in CH_2Cl_2, 105 µL, 62.7 µmol) was then added dropwise until no more SM was detected by TLC analysis (after every three drops (~8-10 µL), the reaction mixture was controlled by TLC). Upon complete consumption of the s.m., all volatiles were removed under reduced pressure and the composition of the residue controlled by ^{1}H NMR analysis (see below). The residue was redissolved in THF (0.7 mL) and treated with sat. $NaHSO_3$ (0.7 mL) under vigorous stirring for 16 h. For work up, brine (5 mL) was added and the aqueous phase was extracted with EtOAc (3 x 5 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 3:2 to 1:1) to yield the desired diol as a colorless oil (8.5 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.46 – 5.37 (m, 1H), 5.28 (dddt, *J* = 10.9, 8.2, 6.8, 1.5 Hz, 1H), 4.44 (td, *J* = 8.8, 6.8 Hz, 1H), 4.32 (ddd, *J* = 9.0, 8.1, 3.4 Hz, 1H), 3.74 (dd, *J* = 10.6, 2.3 Hz, 1H), 3.45 (br s, 1H), 3.38 (br s, 1H), 2.29 – 2.13 (m, 4H), 2.09 – 1.98 (m, 2H), 1.68 (dddd, *J* = 13.9, 10.6, 7.8, 5.4 Hz, 1H), 1.34 (dtd, *J* = 13.9, 8.2, 2.3 Hz, 1H), 0.94 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.7, 133.1, 127.6, 75.1, 72.9, 66.3, 32.0, 29.6, 23.0, 20.5, 14.3 ppm. IR (film): $\tilde{\nu}$ = 3446, 3004, 2962, 2932, 2873, 1758, 1455, 1381, 1307, 1202, 1155, 1119, 1082, 1023, 984, 953, 690 cm^{-1}. MS (EI) *m/z* (%) = 196 (2), 178 (7), 123 (10), 115 (36), 109 (13), 102 (100), 95 (45), 83 (23), 67 (62), 56 (64), 55 (51), 41 (52). HRMS (ESIpos): *m/z*: calcd for $C_{13}H_{20}O_7Na$: 237.1097; found: 237.1097.

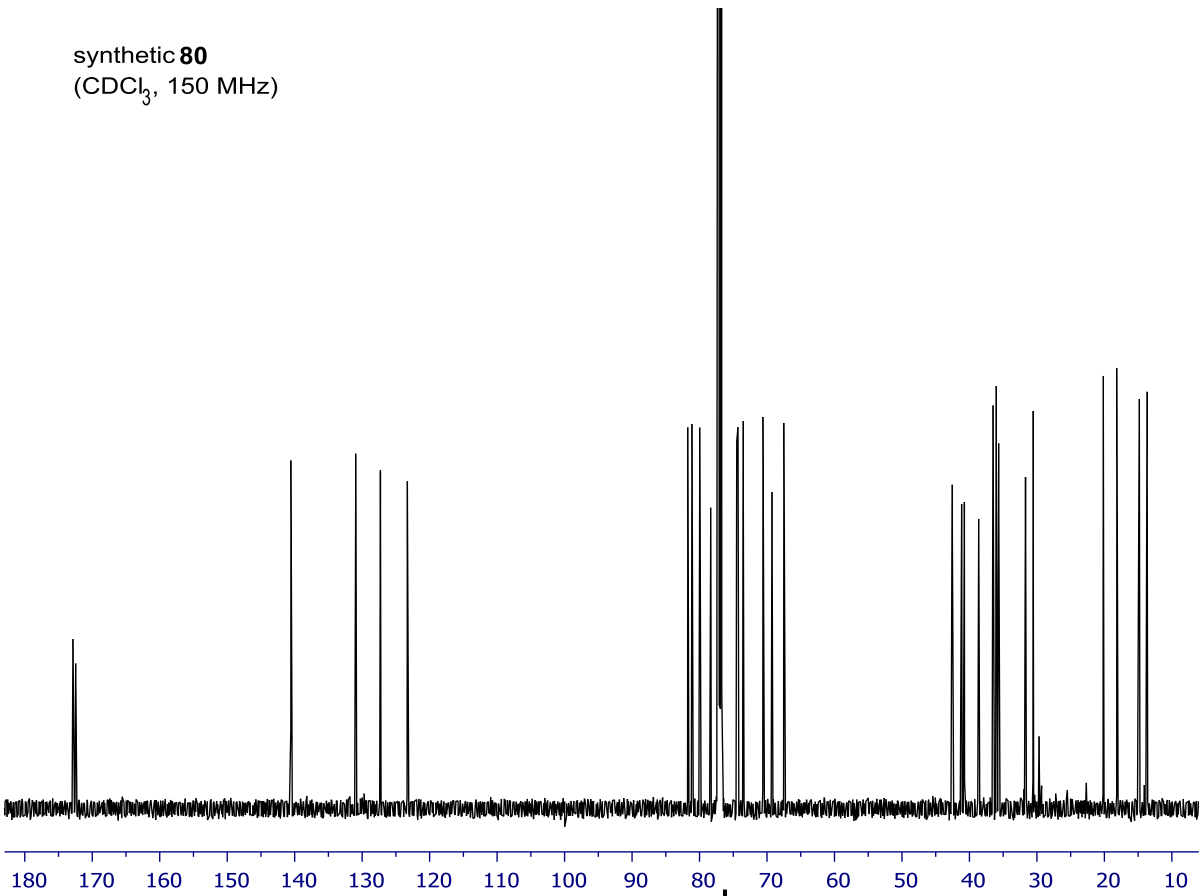
Four compounds were contained in the crude product, they were assigned to the following compounds on the basis of ^{1}H NMR and ESI-MS.



Comparison of synthetic 2,3-*epi*-mandelalide C (80) with the natural product.



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($CDCl_3$, 150 MHz)
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170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

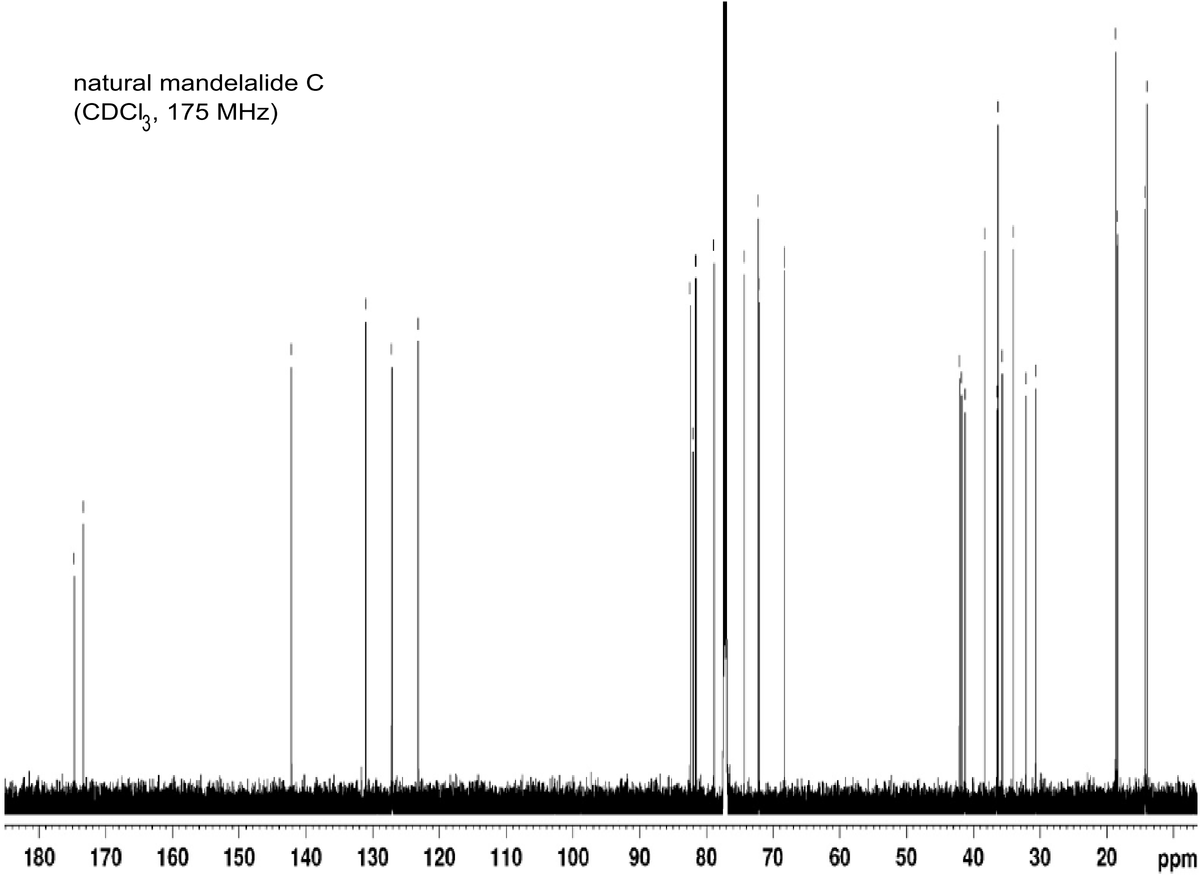
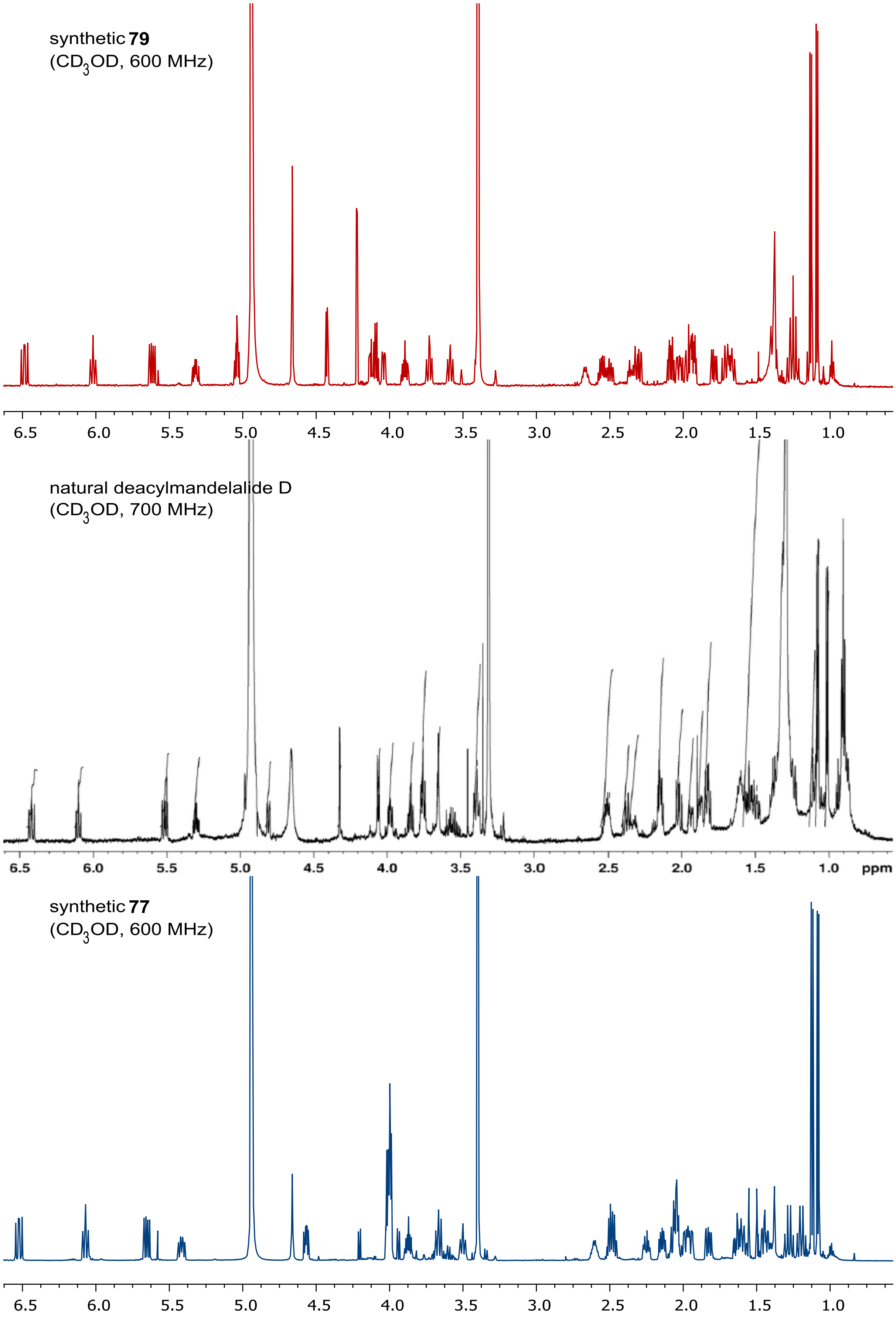

natural mandelalide C
($CDCl_3$, 175 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

Table 19: Comparison of ^{1}H and ^{13}C NMR chemical shifts of **80** (^{1}H: 600 MHz, ^{13}C: 150 MHz $CDCl_3$) with the data of the natural product (Lit.[13]; ^{1}H: 600 MHz, ^{13}C: 175 MHz, $CDCl_3$).

	^{1}H NMR			^{13}C NMR		
atom n°	**δ(Lit.) /ppm**	**δ(80) /ppm**	**Δδ (80-Lit.)**	**δ(Lit.) /ppm**	**δ(80) /ppm**	**Δδ (80-Lit.)**
1	-	-	-	174.7	172.5	2.2
2	-	-	-	82.0	78.3	3.7
3	5.51	5.51	0.00	68.3	69.3	-1.0
4a	1.65	1.73	-0.08	36.4	38.6	-2.2
4b	2.14	2.11	0.03			
5	3.25	3.74	-0.49	72.3	73.5	-1.2
6a	1.11	1.23	-0.12	41.2	41.2	0.0
6b	1.86	1.93	-0.07			
7	3.76	3.85	-0.09	68.3	67.5	0.8
8a	1.13	1.28	-0.15	41.8	40.8	1.0
8b	1.83	1.94	-0.11			
9	3.37	3.50	-0.13	72.3	74.5	-2.2
10a	1.19	1.33	-0.14	42.1	42.6	-0.5
10b	1.57	1.71	-0.14			
11	2.49	2.46	0.03	34.0	30.6	3.4
12	5.5	5.72	-0.22	142.2	140.6	1.6
13	6.39	6.26	0.13	123.2	123.3	-0.1
14	6.1	6.06	0.04	131.1	130.9	0.2
15	5.28	5.31	-0.03	127.1	127.3	-0.2
16a	1.9	1.98	-0.08	30.7	30.4	0.3
16b	2.3	2.39	-0.09			
17	3.95	3.95	0	81.6	81.7	-0.1
18	2.53	2.41	0.12	38.3	36.5	1.8
19a	1.33	1.54	-0.21	35.7	35.7	0.0
19b	2.1	2.10	0			
20	3.82	3.80	0.02	82.4	81.1	1.3
21	3.73	3.46	0.27	74.4	70.6	3.8
22a	1.59	1.93	-0.34	32.1	31.7	0.4
22b	1.82	2.24	-0.42			
23	5.01	4.74	0.27	78.9	80.0	-1.1
24	3.98	4.21	-0.23	72.2	74.3	-2.1
25	1.06	1.05	0.01	18.4	20.2	-1.8
26	1.03	1.02	0.01	14.2	14.8	-0.6
27	-	-	-	173.4	172.9	0.5
28a	2.34	2.42	-0.08	36.3	36.0	0.3
28b	2.34	2.33	0.01			
29	1.65	1.68	-0.03	18.7	18.2	0.5
30	0.94	0.94	0.00	13.9	13.7	0.2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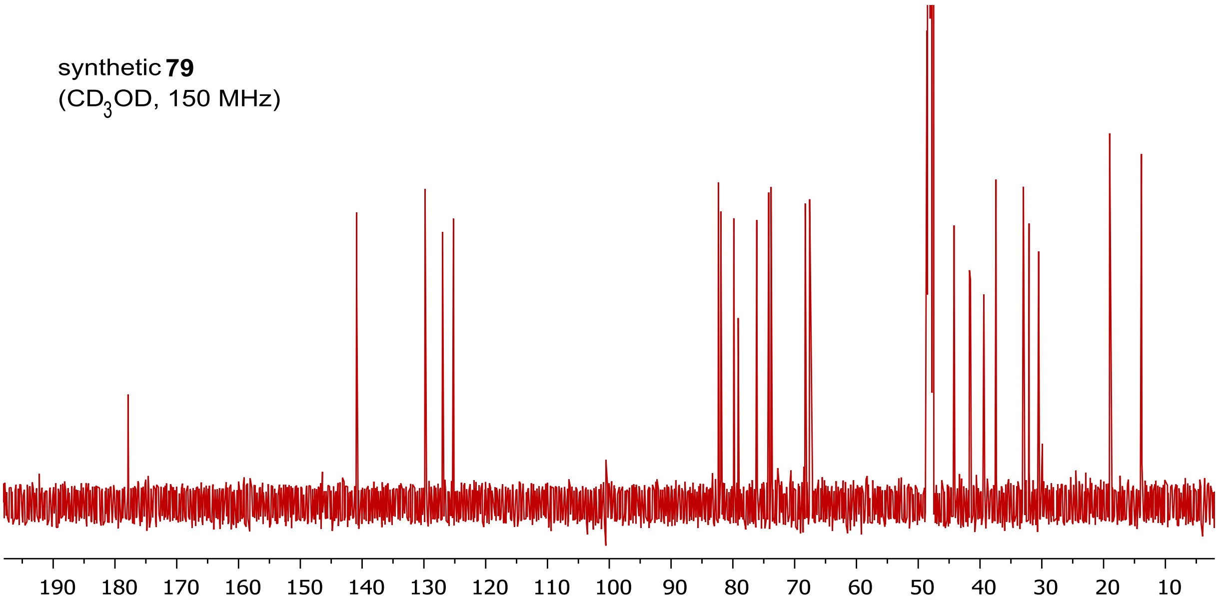
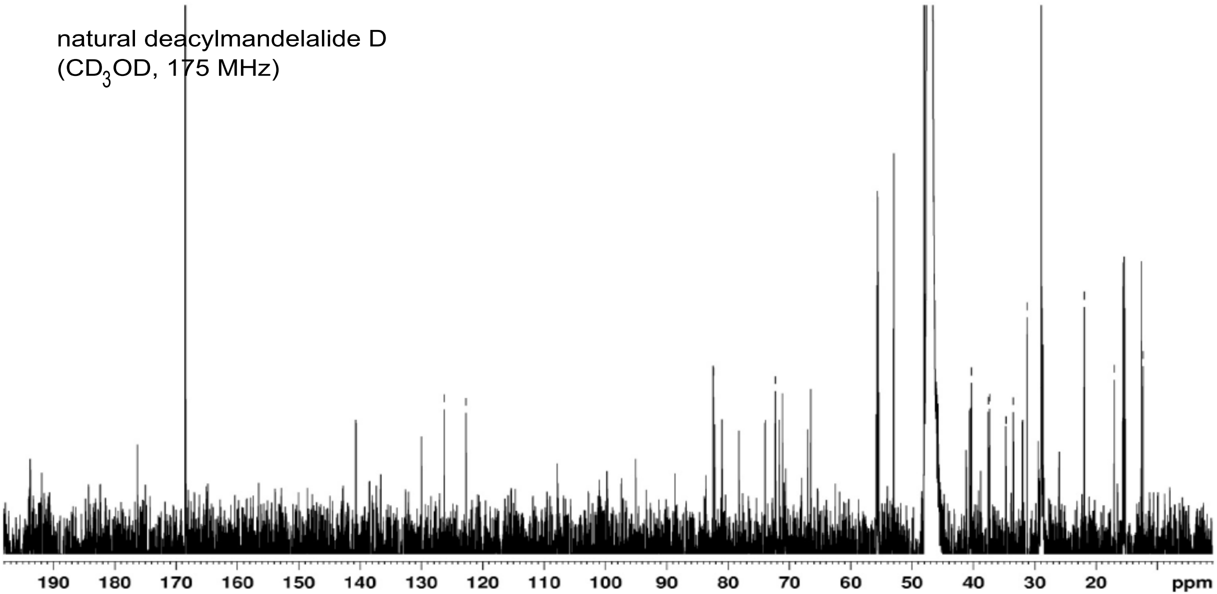
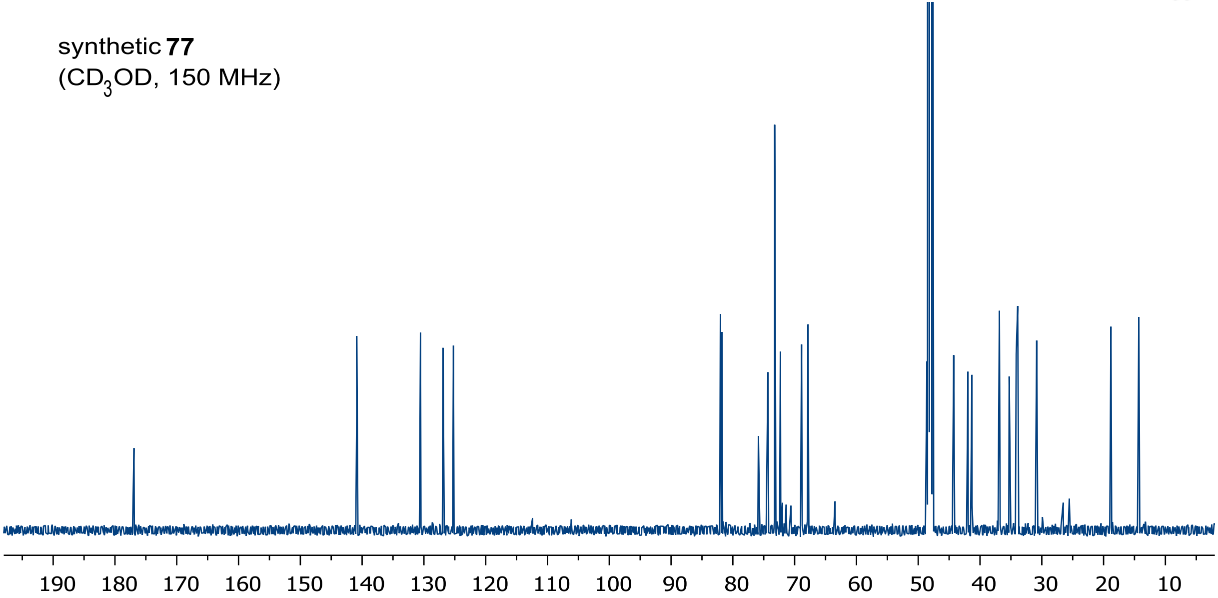
(CD_3OD, 600 MHz)
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
natural deacylmandelalide D
(CD_3OD, 700 MHz)
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
synthetic **77**
(CD_3OD, 600 MHz)
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0



synthetic **79**
(CD_3OD, 150 MHz)



natural deacylmandelalide D
(CD_3OD, 175 MHz)



synthetic **77**
(CD_3OD, 150 MHz)

Table 20: Comparison of ^{1}H NMR chemical shifts of **77** and **79** (600 MHz, CD_3OD) with the data of the natural product (Lit.[13]; 700 MHz, CD_3OD).

atom n°	**δ (Lit.) /ppm**	**δ(79) /ppm**	**Δδ (79–Lit.)**	**δ(77) /ppm**	**Δδ (77–Lit.)**
1	-	-	-	-	-
2	-	-	-	-	-
3	4.06	4.34	−0.28	3.92	0.14
4a	1.56	1.70	−0.14	1.74	−0.18
4b	2.02	1.90	0.12	1.96	0.06
5	3.39	3.64	−0.25	3.58	−0.19
6a	1.11	1.17	−0.06	1.19	−0.08
6b	1.88	1.94	−0.06	1.89	−0.01
7	3.76	3.81	−0.05	3.78	−0.02
8a	1.08	1.15	−0.07	1.11	−0.03
8b	1.83	1.85	−0.02	1.88	−0.05
9	3.39	3.50	−0.11	3.41	−0.02
10a	1.23	1.28	−0.05	1.35	−0.12
10b	1.49	1.58	−0.09	1.54	−0.05
11	2.49	2.58	−0.09	2.52	−0.03
12	5.51	5.53	−0.02	5.55	−0.04
13	6.42	6.4	0.02	6.44	−0.02
14	6.1	5.93	0.17	5.98	0.12
15	5.3	5.23	0.07	5.33	−0.03
16a	1.94	2.27	−0.33	2.16	−0.22
16b	2.38	2.42	−0.04	2.38	0.00
17	3.98	4.01	−0.03	3.91	0.07
18	2.52	2.47	0.05	2.40	0.12
19a	1.37	1.62	−0.25	1.51	−0.14
19b	2.14	2.00	0.14	2.05	0.09
20	3.84	4.04	−0.20	3.90	−0.06
21	3.75	3.95	−0.20	3.91	−0.16
22a	1.52	1.85	−0.33	1.95	−0.43
22b	1.81	2.22	−0.41	1.96	−0.15
23	4.81	4.95	−0.14	4.48	0.33
24	4.32	4.14	0.18	3.90	0.42
25	1.01	1.00	0.01	0.99	0.02
26	1.08	1.04	0.04	1.03	0.05

Table 21: Comparison of ^{13}C NMR chemical shifts of **253** and **255** (150 MHz, CD_3OD) with the data of the natural product (Lit.[13]; 175 MHz, CD_3OD).

atom n°	δ (Lit.) /ppm	δ(79) /ppm	Δδ (79–Lit.)	δ(77) /ppm	Δδ (77–Lit.)
1	176.3	178.9	−2.6	177.9	0.2
2	82.4	80.1	2.3	76.9	5.5
3	66.6	69.5	−2.9	73.3	−6.7
4	37.4	40.4	−3.0	38.0	−0.6
5	72.3	75.2	−2.9	74.2	−1.9
6	40.3	42.5	−2.2	42.3	−2.0
7	67.1	68.6	−1.5	68.8	−1.7
8	40.7	42.7	−2.0	42.9	−2.2
9	71.1	74.8	−3.7	74.2	−3.1
10	41.2	45.2	−4.0	45.3	−4.1
11	33.5	34.0	−0.5	34.9	−1.4
12	140.7	141.9	−1.2	141.9	−1.2
13	122.8	126.2	−3.4	126.2	−3.4
14	130.0	130.8	−0.8	131.6	−1.6
15	126.3	128.0	−1.7	127.9	−1.6
16	31.2	33.1	−1.9	31.8	−0.6
17	81.0	83.4	−2.4	82.9	−1.9
18	37.6	38.4	−0.8	37.9	−0.3
19	34.7	34.1	0.6	35.1	−0.4
20	82.2	83.0	−0.8	82.6	−0.4
21	73.9	69.3	4.6	69.7	−4.2
22	32.0	31.5	0.5	36.3	−4.3
23	78.3	80.8	−2.5	82.8	−4.5
24	71.7	77.1	−5.4	75.2	−3.5
25	17.0	20.0	−3.0	19.8	−2.8
26	12.3	14.9	−2.6	15.3	−3.0

References

[1] The calculations were performed by Ms. Berit Heggen, group of Prof. Dr. Walter Thiel, Department of Theoretical Chemistry, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr.

[2] J. Willwacher, A. Fürstner, *Angew. Chem. Int. Ed.* **2014**, *53*, 4217.

[3] Y. Lu, I. S. Kim, A. Hassan, D. J. Del Valle, M. J. Krische, *Angew. Chem. Int. Ed.* **2009**, *48*, 5018.

[4] J. M. Hoover, S. S. Stahl, *J. Am. Chem. Soc.* **2011**, *133*, 16901.

[5] B. M. Hackman, P. J. Lombardi, J. L. Leighton, *Org. Lett.* **2004**, *6*, 4375.

[6] The configuration of the stereogenic center of the propgargylic alcohol was assigned by comparison with the result of a Carreira alkynylation (D. E. Frantz, R. Fässler, E. M. Carreira, *J. Am. Chem. Soc.* **2000**, *122*, 1806) using (+)-N-methyl ephedrine, $Zn(OTf)_2$ and triethylamine. This alkynylation gave almost exclusively the alcohol, that was also the major diastereomer of the addition of lithiated alkyne. Although the overall yield was higher (72%), partial epimerization at the α-position of the aldehyde was observed.

[7] S. N. Goodman, E. N. Jacobsen, *Angew. Chem.* **2002**, *114*, 4897.

[8] Due to the volatility of the catalyst, a higher vacuum should be avoided.

[9] S. E. Denmark, W. R. Collins, *Org. Lett.* **2007**, *9*, 3801.

[10] (a) E. D. Mihelich, G. A. Hite, *J. Am. Chem. Soc.* **1992**, *114*, 7318; (b) D. R. Williams, Y. Harigaya, J. L. Moore, A. D'Sa, *J. Am. Chem. Soc.* **1984**, *106*, 2641.

[11] A solution of NaOMe was prepared by adding an equimolar amount of MeOH to a suspension of NaH in THF at 0 °C, which was allowed to stir at room-temperature until gas evolution had ceased (~1 h).

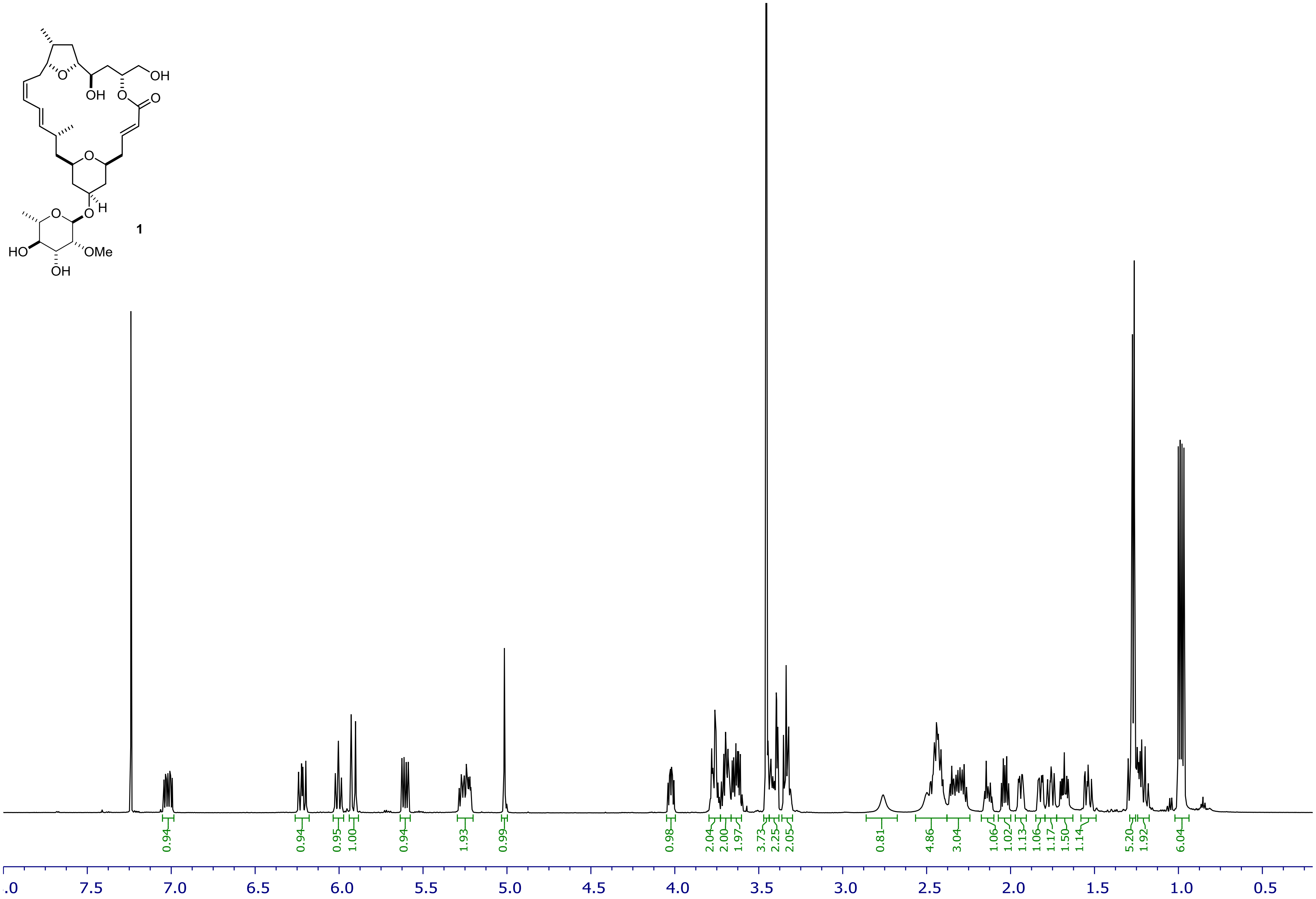
[12] W. Boland, N. Schroer, C. Sieler, M. Feigel, *Helv. Chim. Acta* **1987**, *70*, 1025.

[13] J. Sikorska, A. M. Hau, C. Anklin, S. Parker-Nance, M. T. Davies-Coleman, J. E. Ishmael, K. L. McPhail, *J. Org. Chem.* **2012**, *77*, 6066.

[14] Obtained from Sigma Aldrich as an unspecified mixture of $NaHSO_3$ and $Na_2S_2O_5$. On this model system, use of sat. aq. $Na_2S_2O_5$ gave comparable results. It is presumed, that $NaHSO_3$ is formed from $Na_2S_2O_5$ upon contact with water.

Spectra

The spectra of all compounds and intermediates leading to **1** and 11-*epi*-**1** can be found in the Supporting Information of our original Communication.[2]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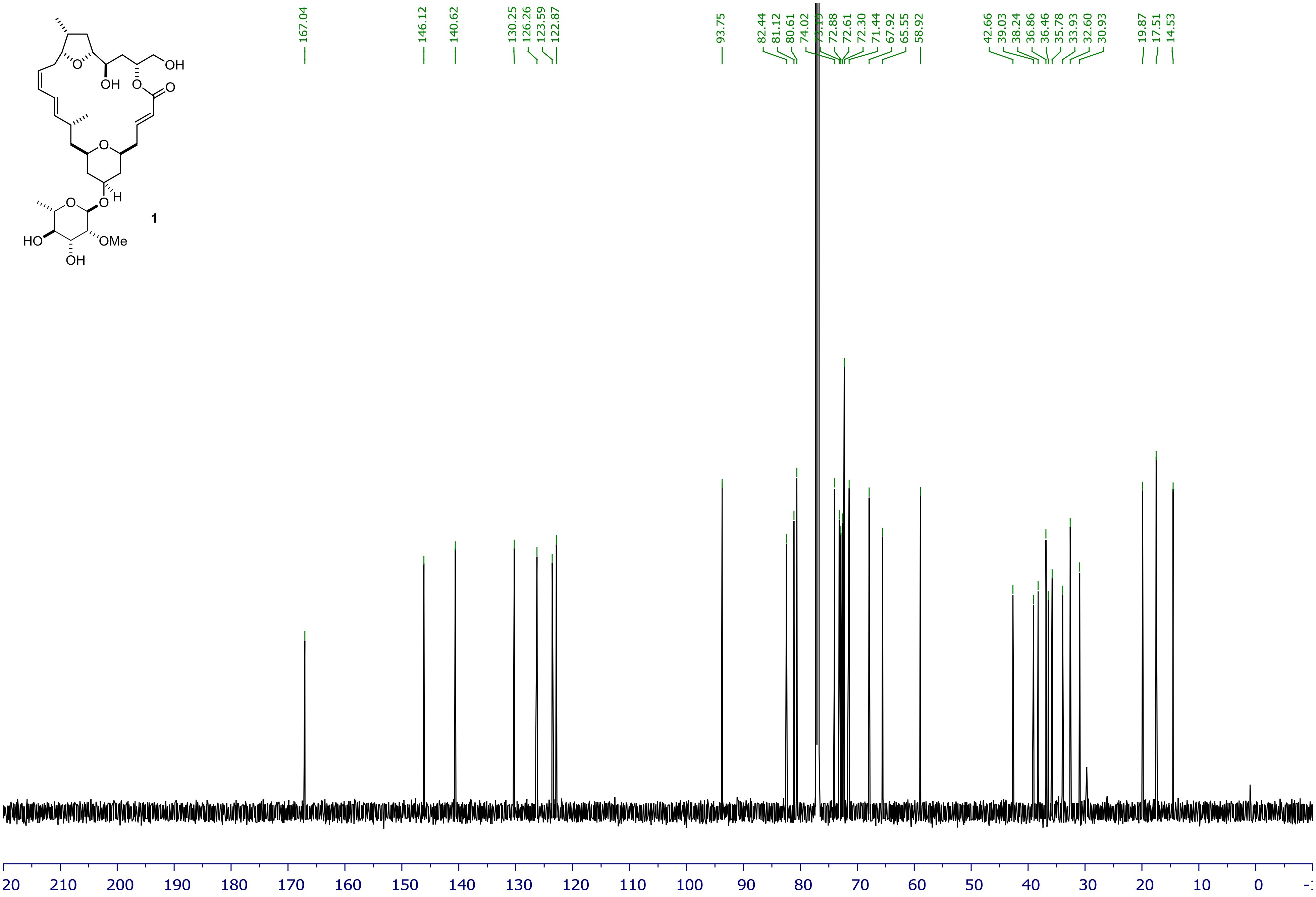
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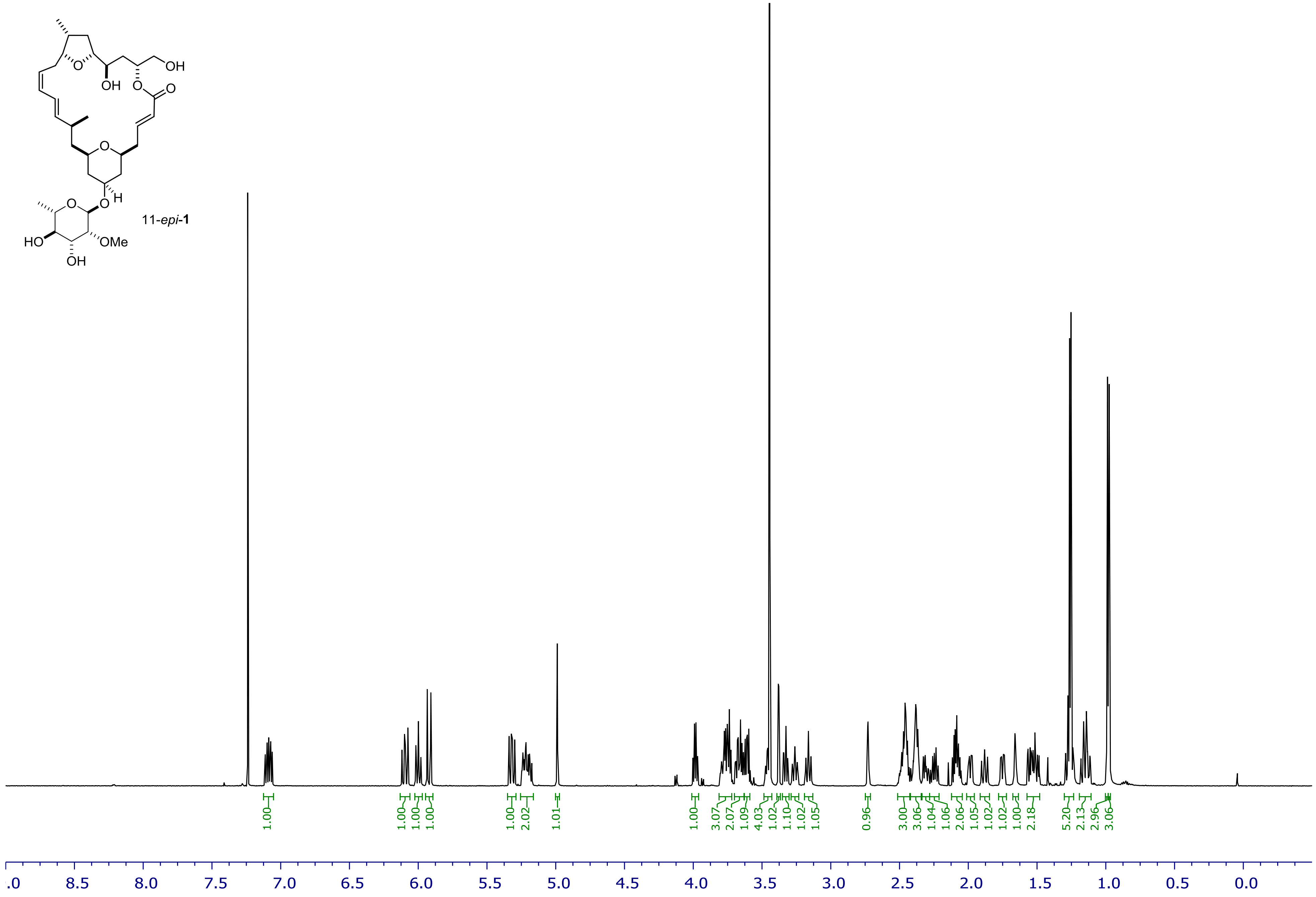
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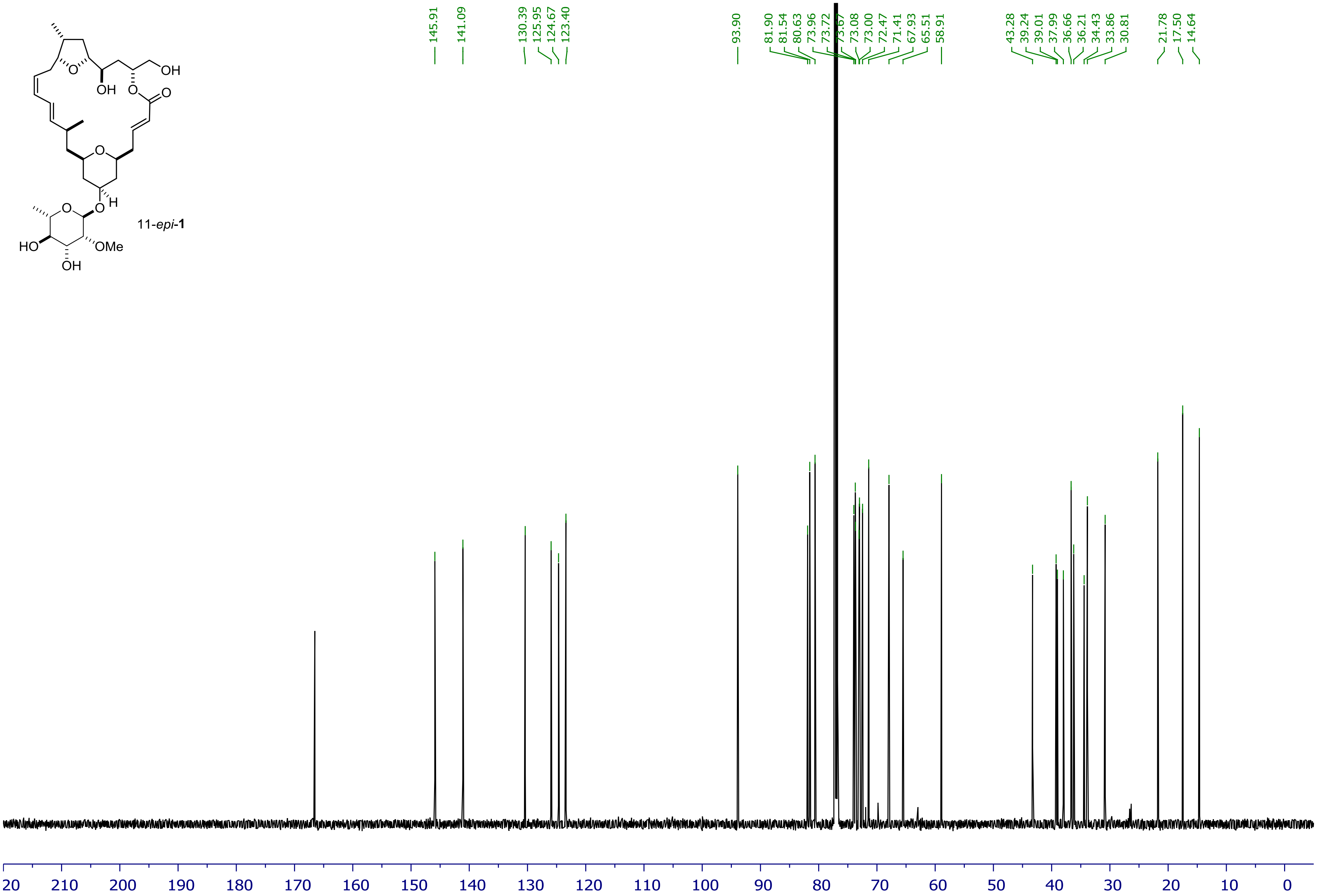
11-*epi*-**1**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36.66
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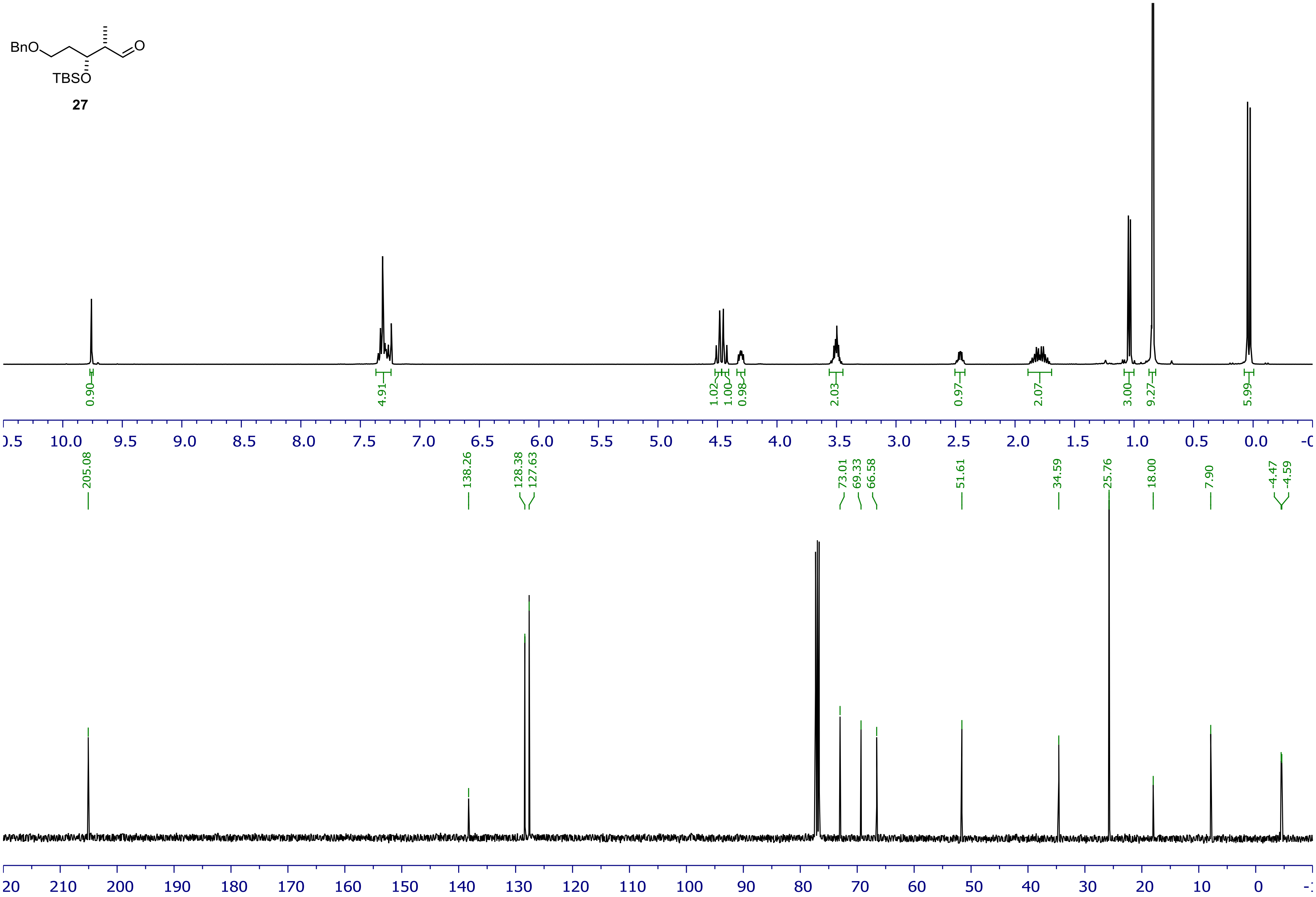
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27

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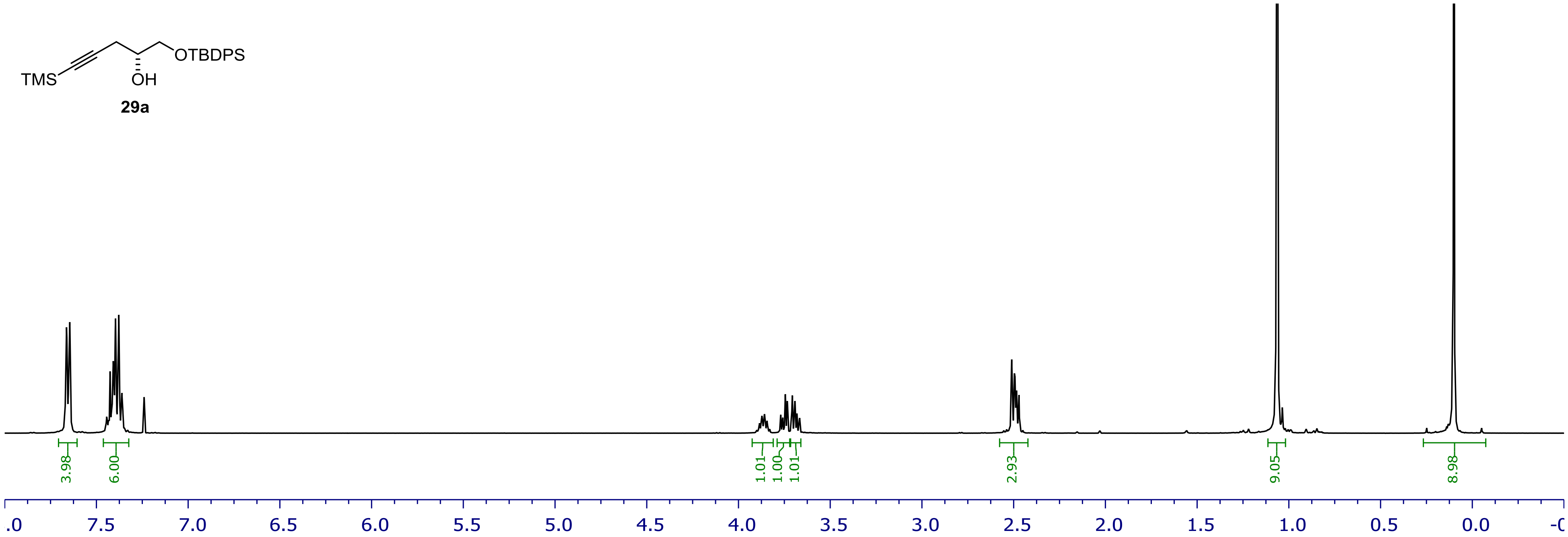
29a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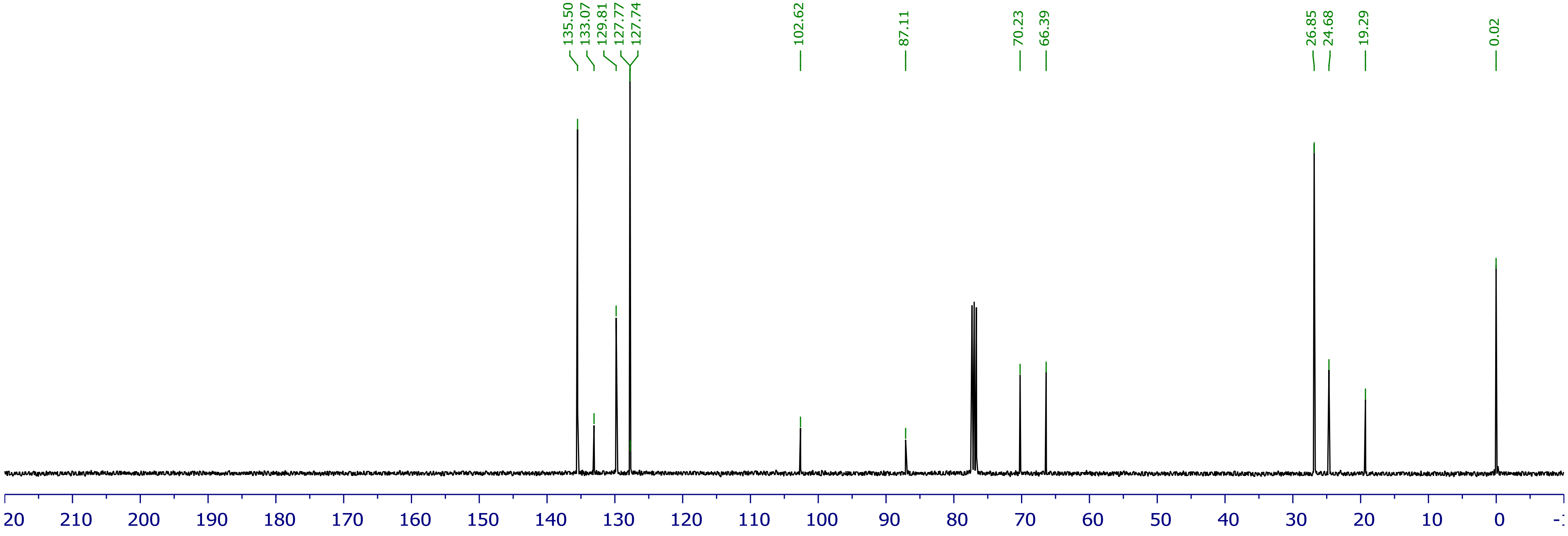
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127.77
127.74
102.62
87.11
70.23
66.39
26.85
24.68
19.29
0.02
20
210
200
190
180
170
160
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140
130
120
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100
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50
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20
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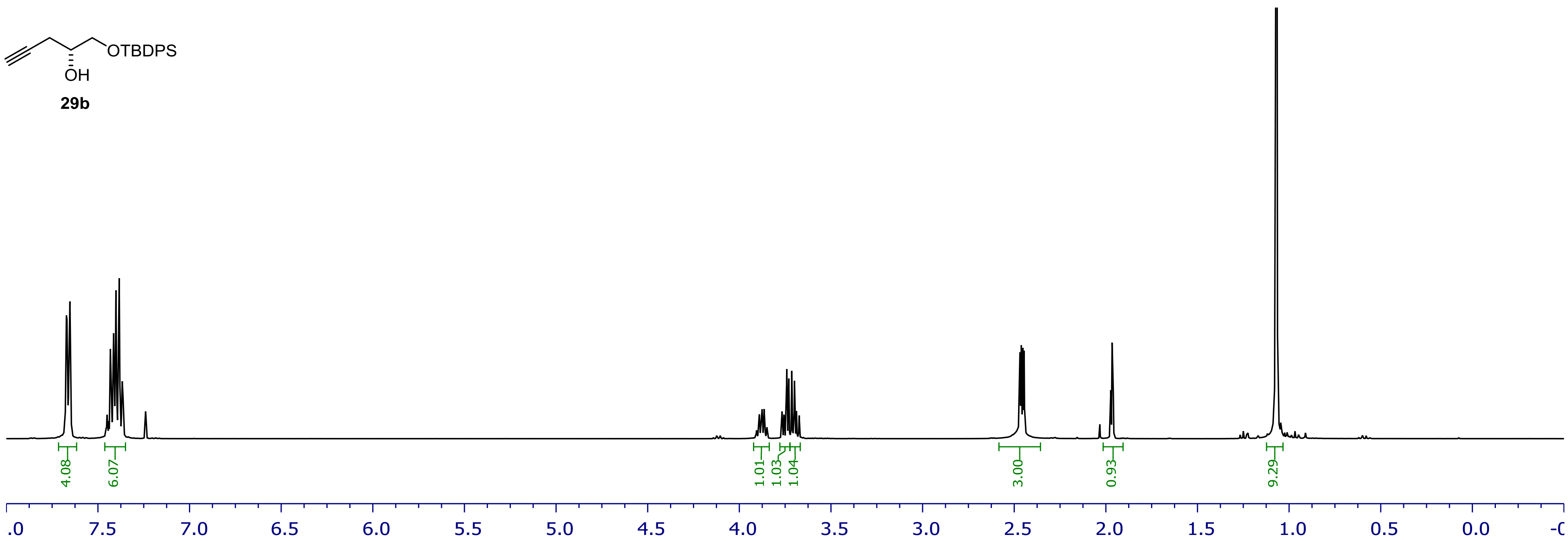
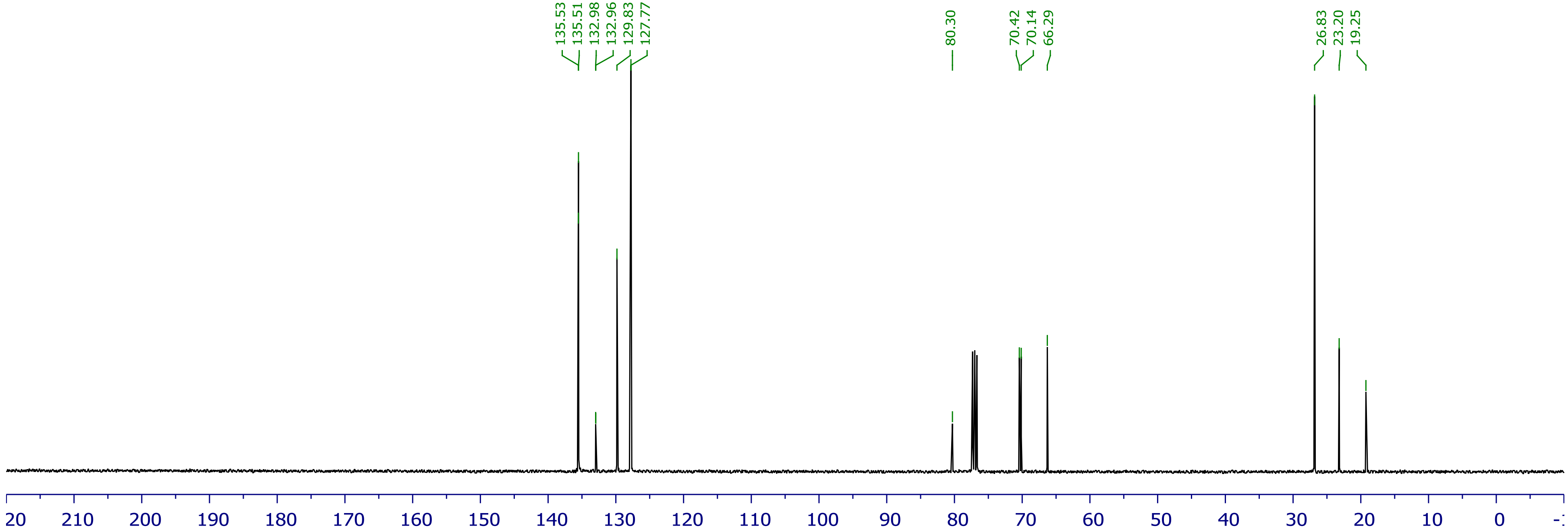
0
-:


OTBDPS
OH

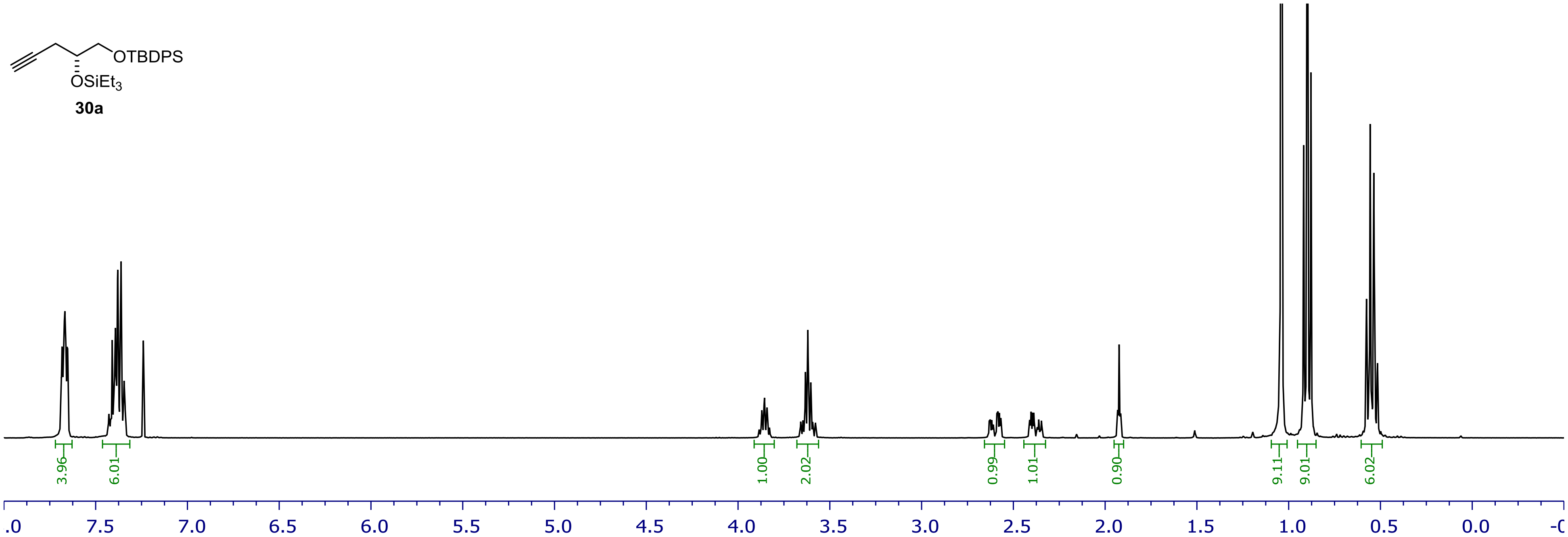
29b

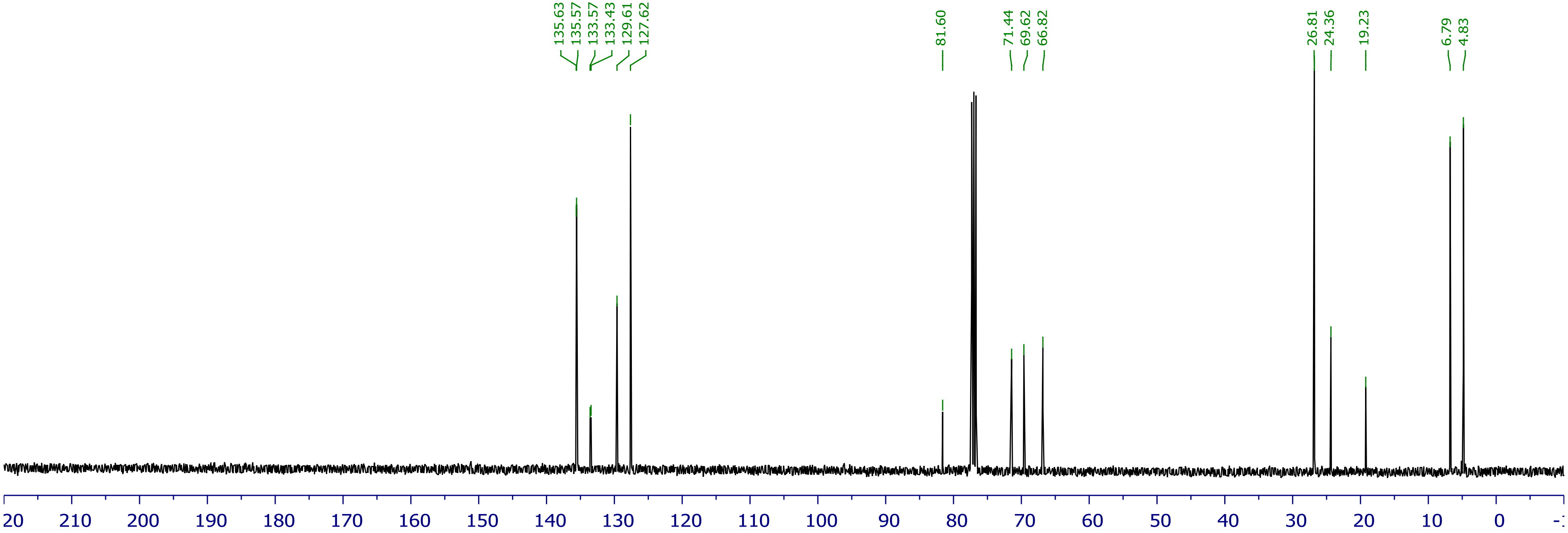
4.08
6.07
1.01
1.03
1.04
3.00
0.93
9.29
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(


135.53
135.51
132.98
132.96
129.83
127.77
80.30
70.42
70.14
66.29
26.83
23.20
19.25
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-:

OTBDPS
OSiEt3

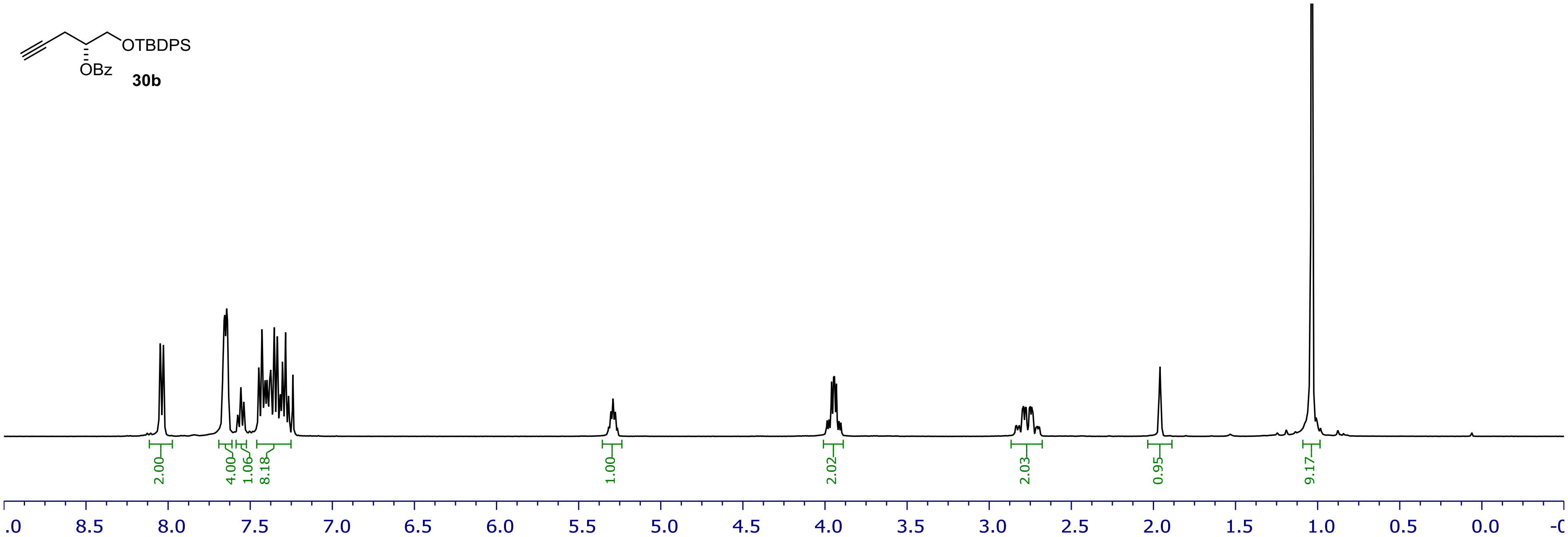
30a

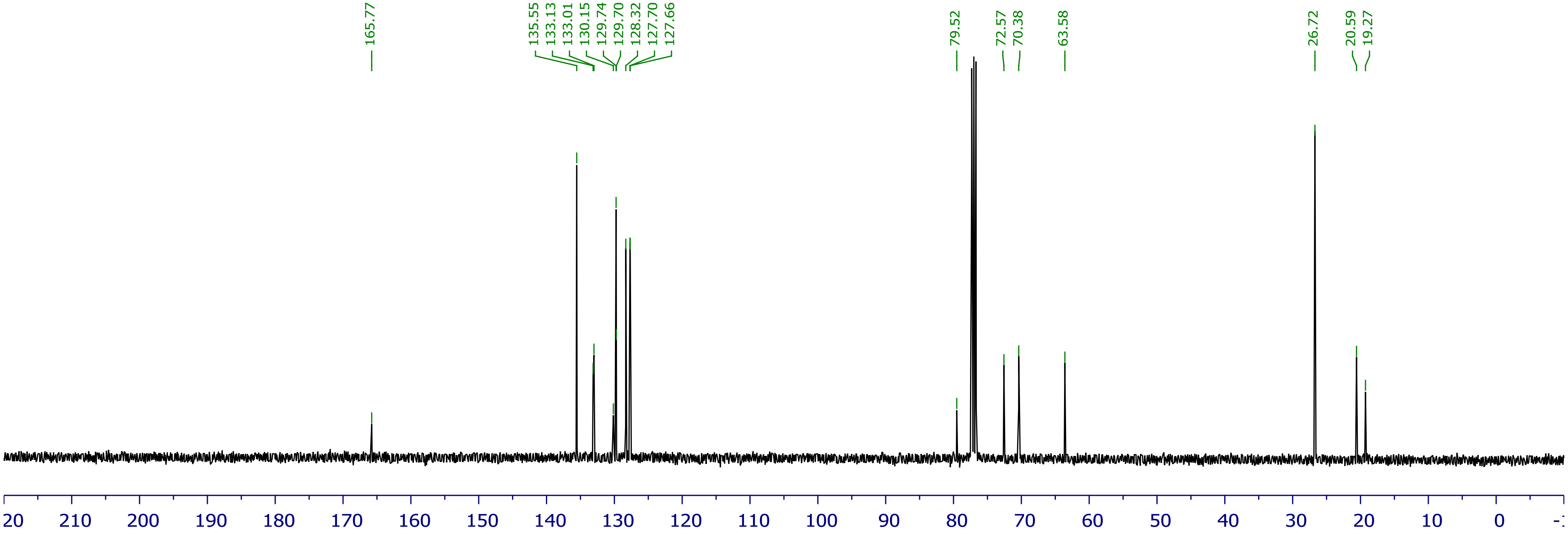

3.96
6.01
1.00
2.02
0.99
1.01
0.90
9.11
9.01
6.02
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(

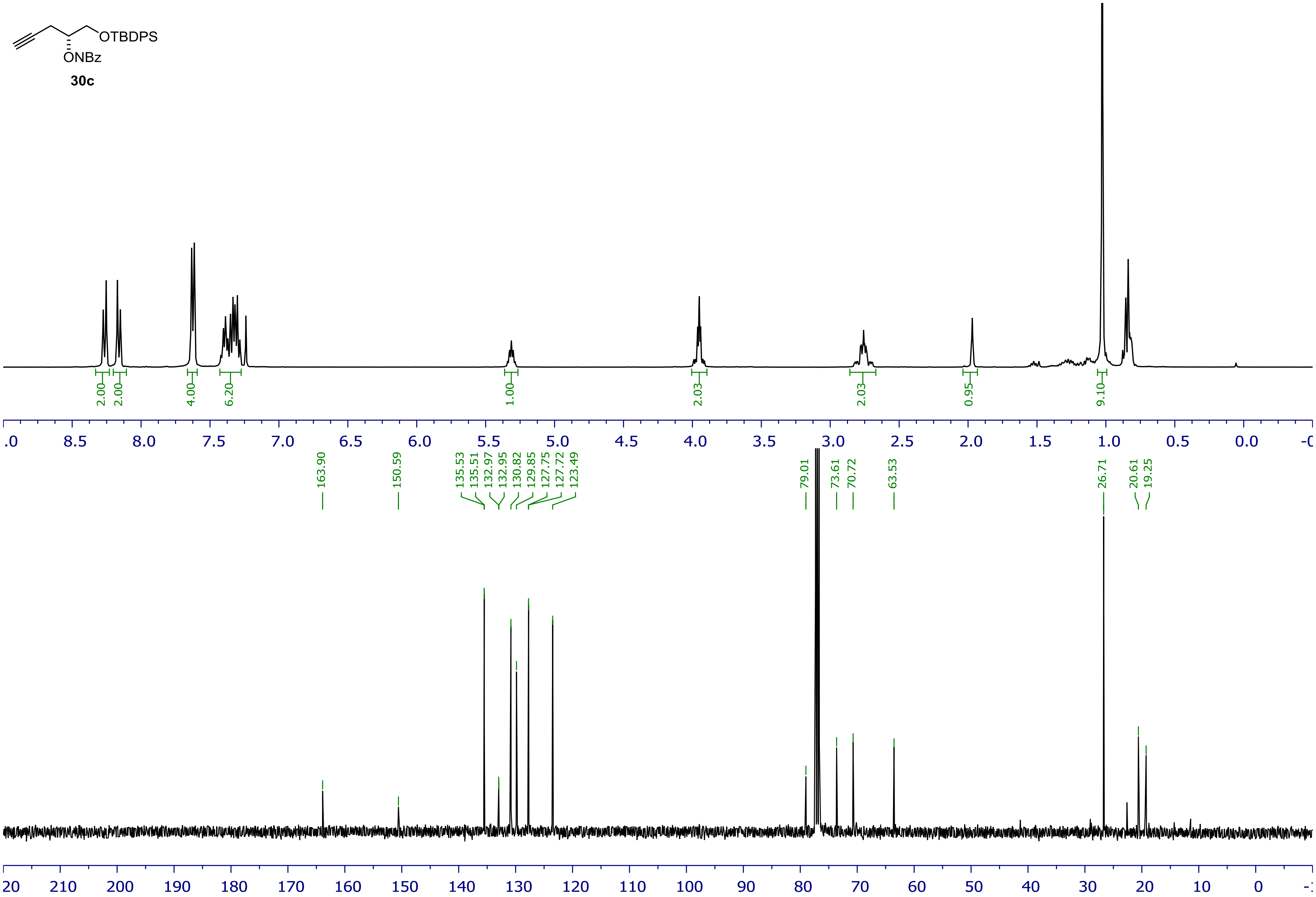

135.63
135.57
133.57
133.43
129.61
127.62
81.60
71.44
69.62
66.82
26.81
24.36
19.23
6.79
4.83
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-:

OTBDPS
OBz

30b

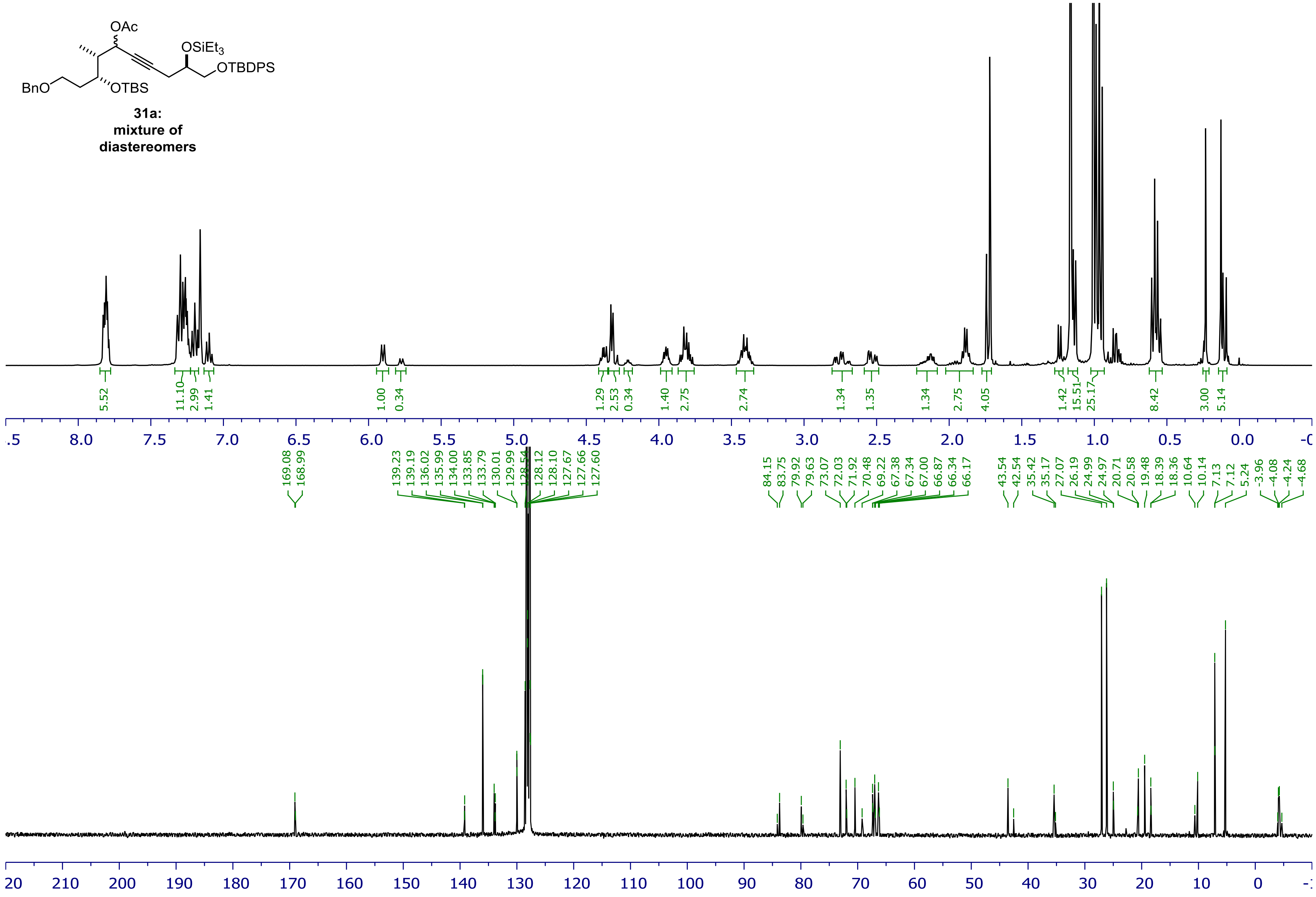

2.00
4.00
1.06
8.18
1.00
2.02
2.03
0.95
9.17
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


165.77
135.55
133.13
133.01
130.15
129.74
129.70
128.32
127.70
127.66
79.52
72.57
70.38
63.58
26.72
20.59
19.27
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

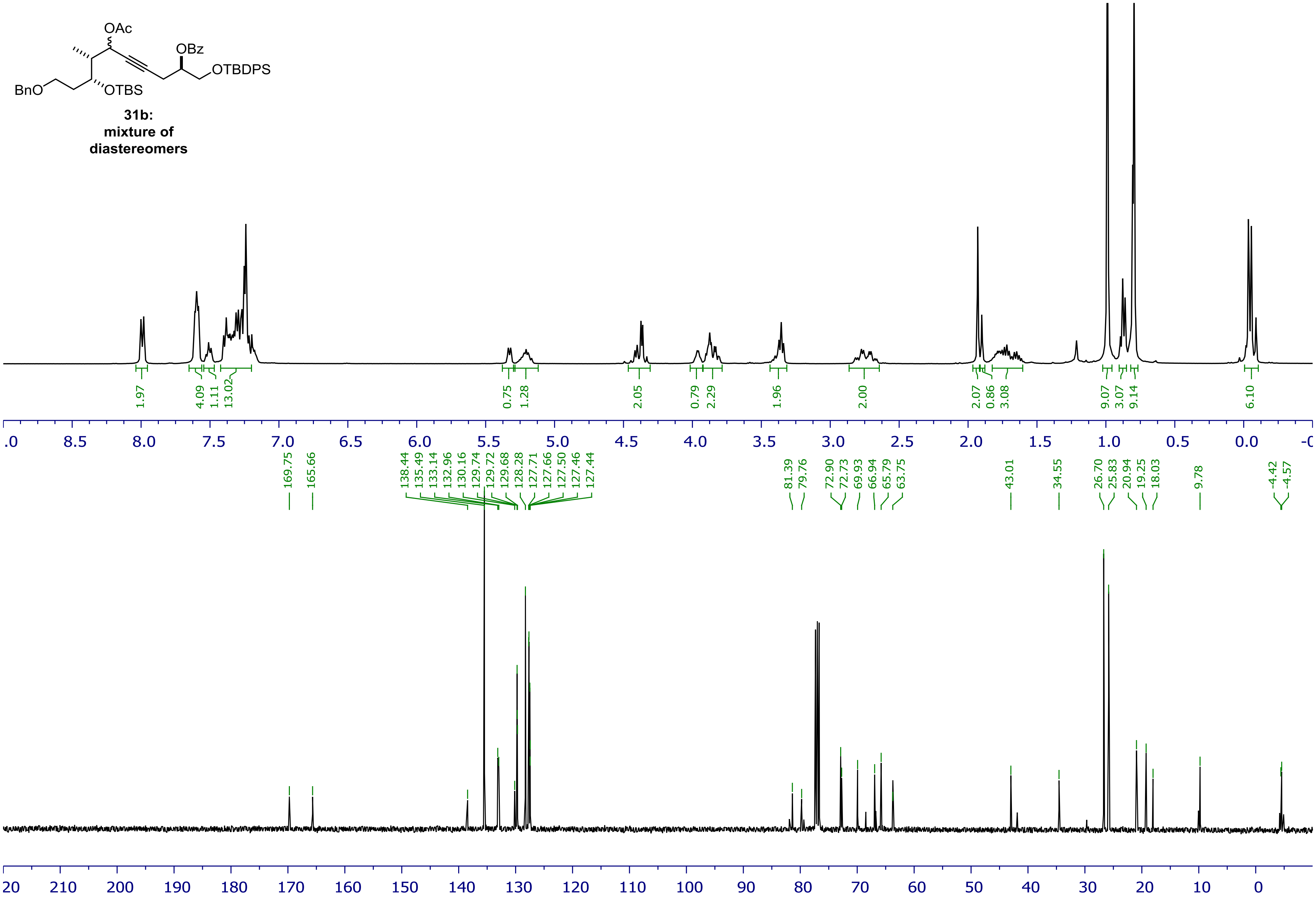


30c

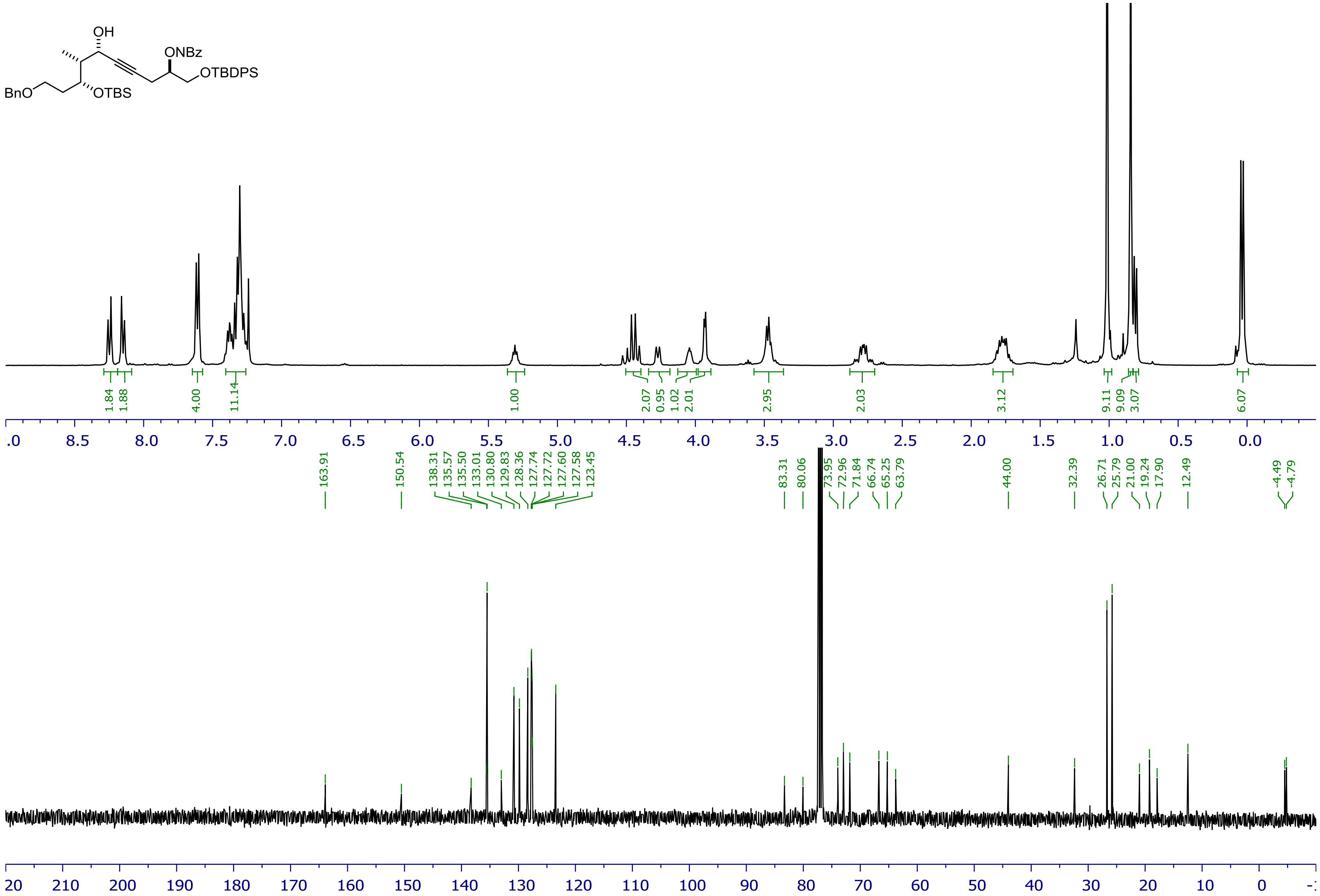
OTBDPS
ONBz
2.00
2.00
4.00
6.20
1.00
2.03
2.03
0.95
9.10
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
163.90
150.59
135.53
135.51
132.97
132.95
130.82
129.85
127.75
127.72
123.49
79.01
73.61
70.72
63.53
26.71
20.61
19.25
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-:

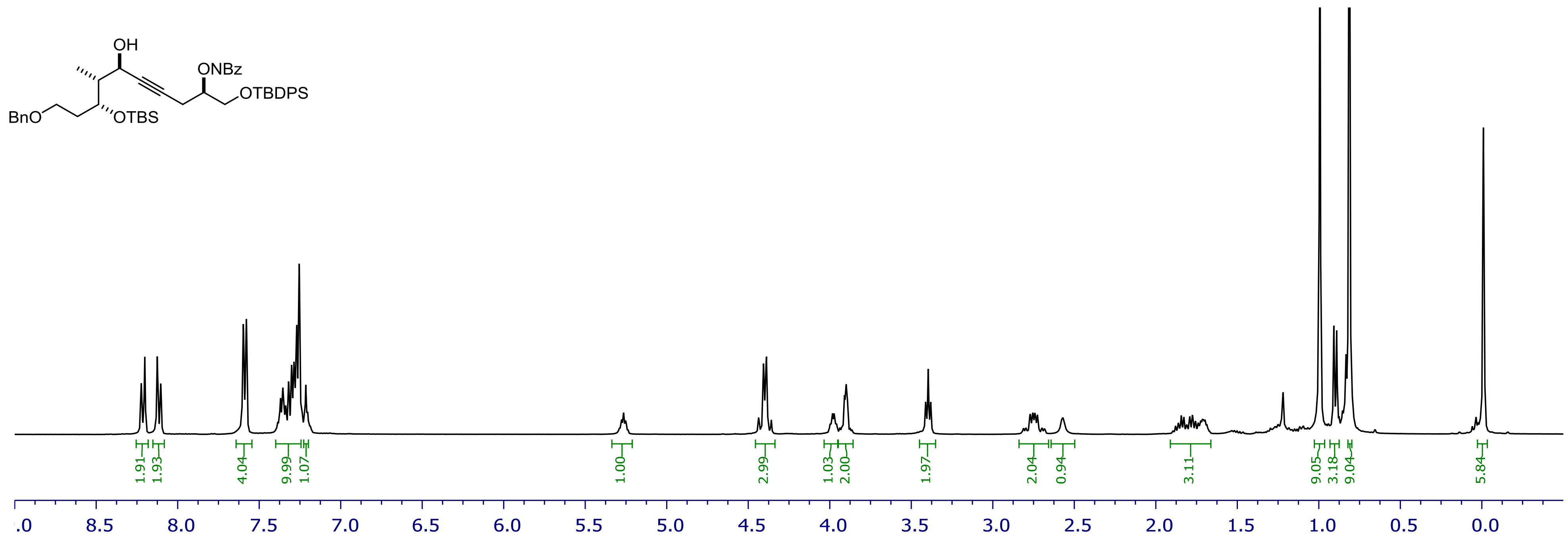


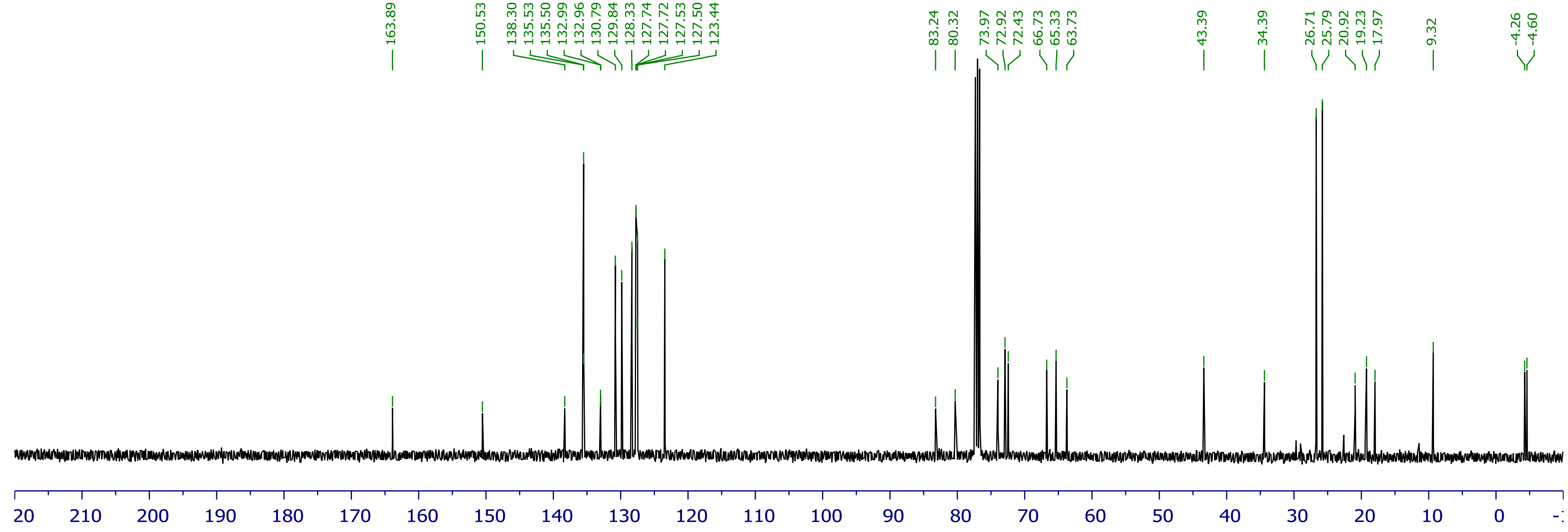
31a: mixture of diastereomers

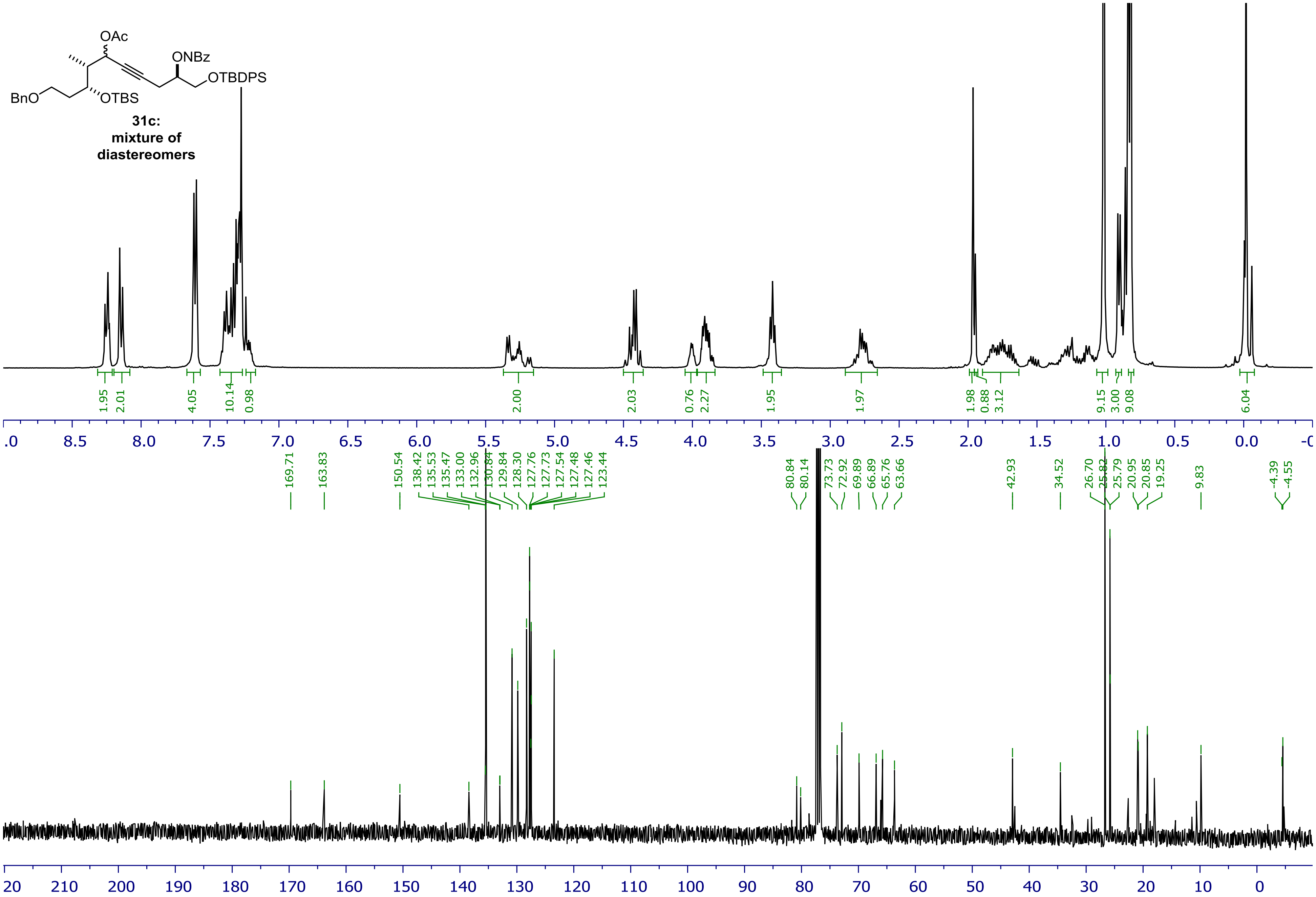


31b: mixture of diastereomers

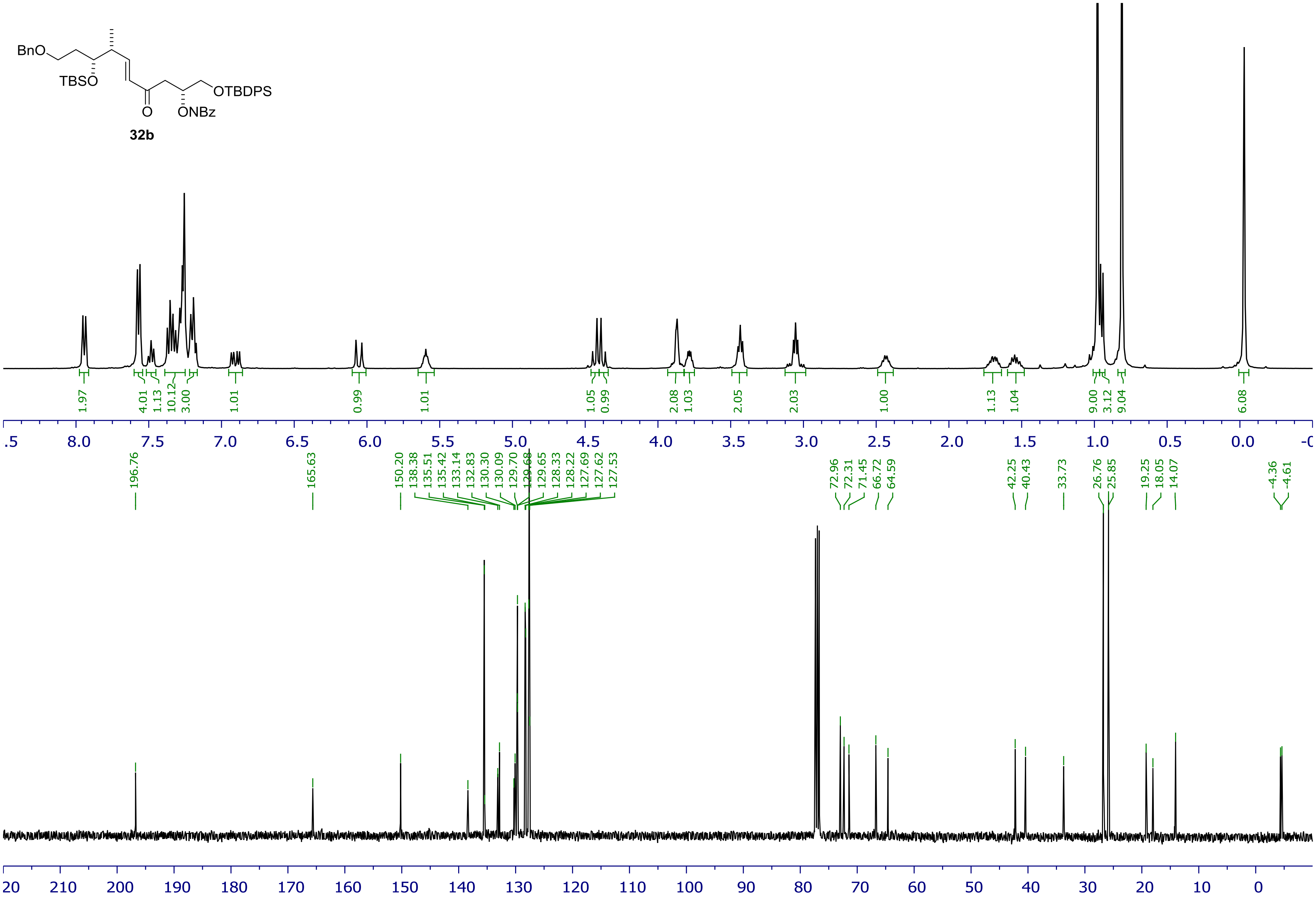

OH
ONBz
OTBDPS
BnO
OTBS
1.84
1.88
4.00
11.14
1.00
2.07
0.95
1.02
2.01
2.95
2.03
3.12
9.11
9.09
3.07
6.07
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
163.91
150.54
138.31
135.57
135.50
133.01
130.80
129.83
128.36
127.74
127.72
127.60
127.58
123.45
83.31
80.06
73.95
72.96
71.84
66.74
65.25
63.79
44.00
32.39
26.71
25.79
21.00
19.24
17.90
12.49
-4.49
-4.79
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


OH
ONBz
OTBDPS
BnO
OTBS
1.91
1.93
4.04
9.99
1.07
1.00
2.99
1.03
2.00
1.97
2.04
0.94
3.11
9.05
3.18
9.04
5.84
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

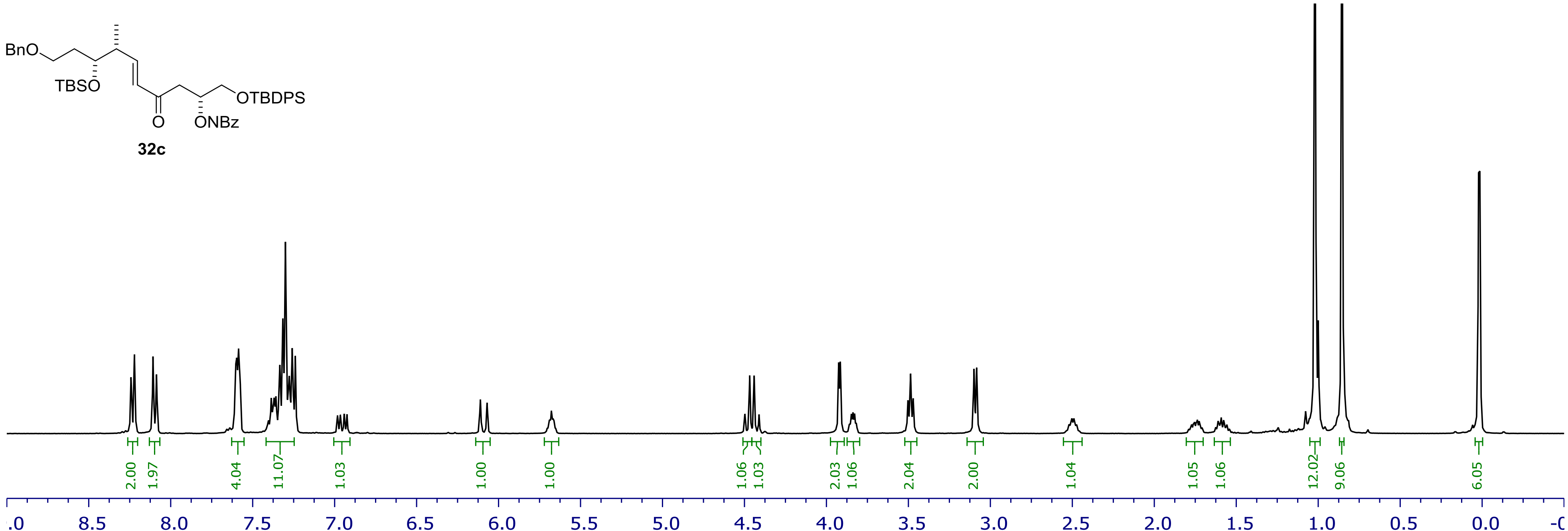

163.89
150.53
138.30
135.53
135.50
132.99
132.96
130.79
129.84
128.33
127.74
127.72
127.53
127.50
123.44
83.24
80.32
73.97
72.92
72.43
66.73
65.33
63.73
43.39
34.39
26.71
25.79
20.92
19.23
17.97
9.32
-4.26
-4.60
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-:



31c:
mixture of diastereomers

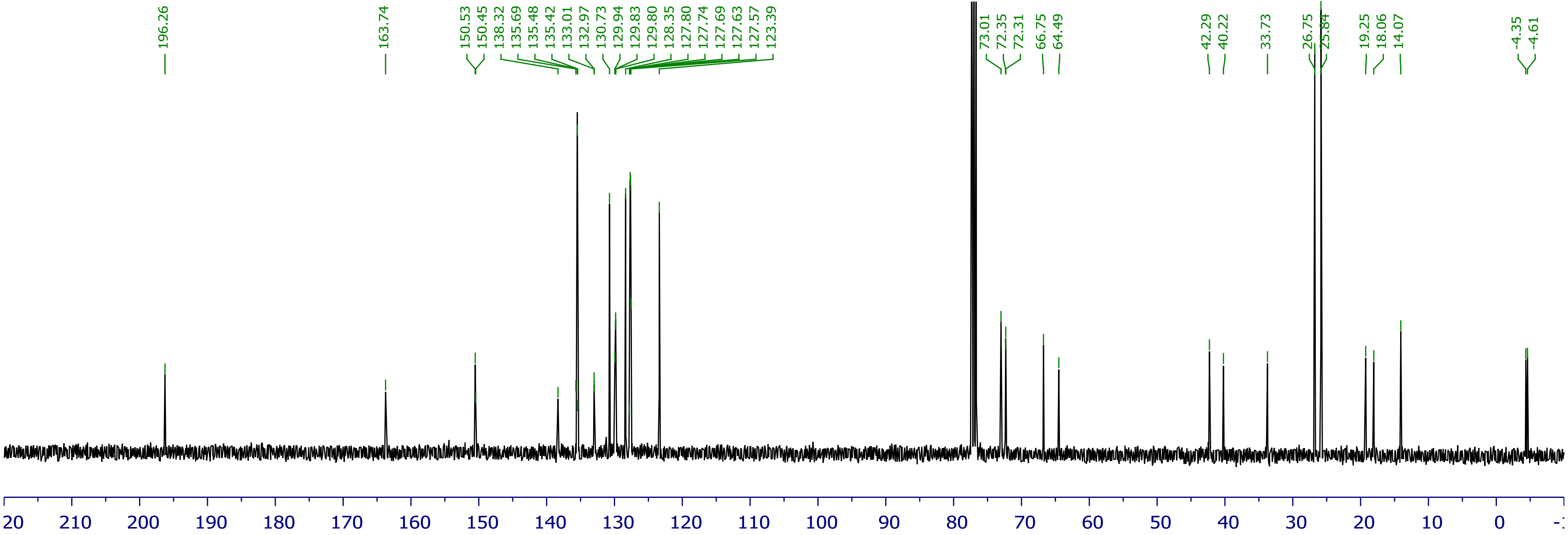

32b

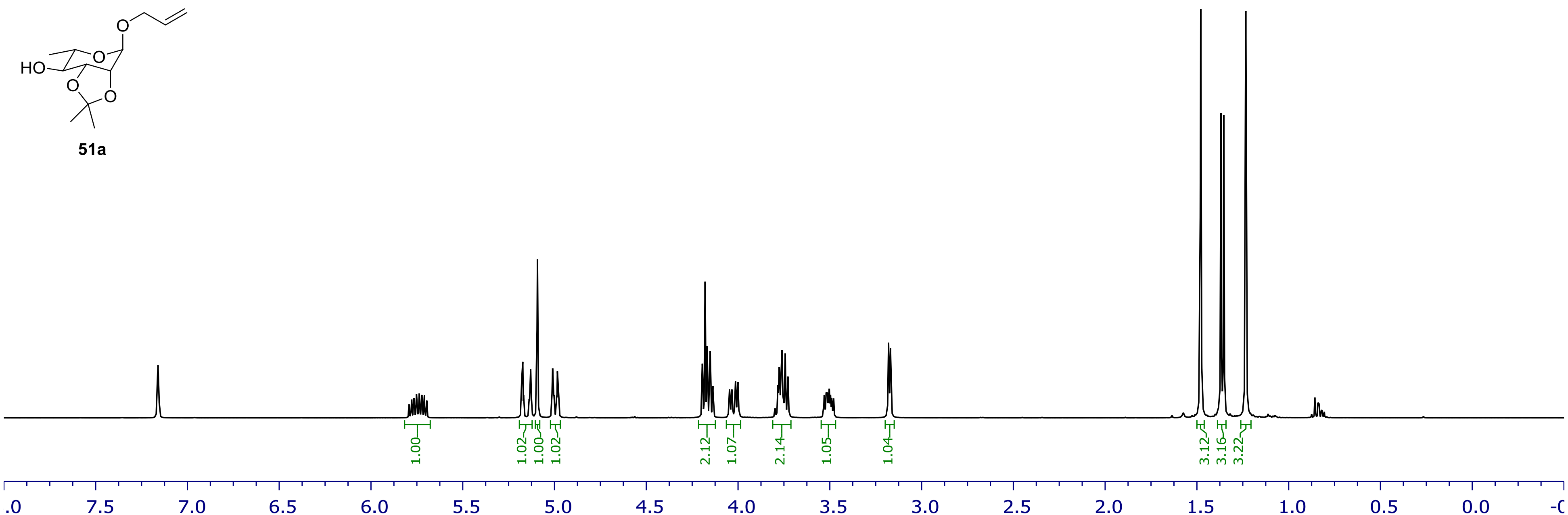
BnO
TBSO
O
ONBz
OTBDPS
1.97
4.01
1.13
10.12
3.00
1.01
0.99
1.01
1.05
0.99
2.08
1.03
2.05
2.03
1.00
1.13
1.04
9.00
3.12
9.04
6.08
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
196.76
165.63
150.20
138.38
135.51
135.42
133.14
132.83
130.30
130.09
129.70
129.68
129.65
128.33
128.22
127.69
127.62
127.53
72.96
72.31
71.45
66.72
64.59
42.25
40.43
33.73
26.76
25.85
19.25
18.05
14.07
-4.36
-4.61
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

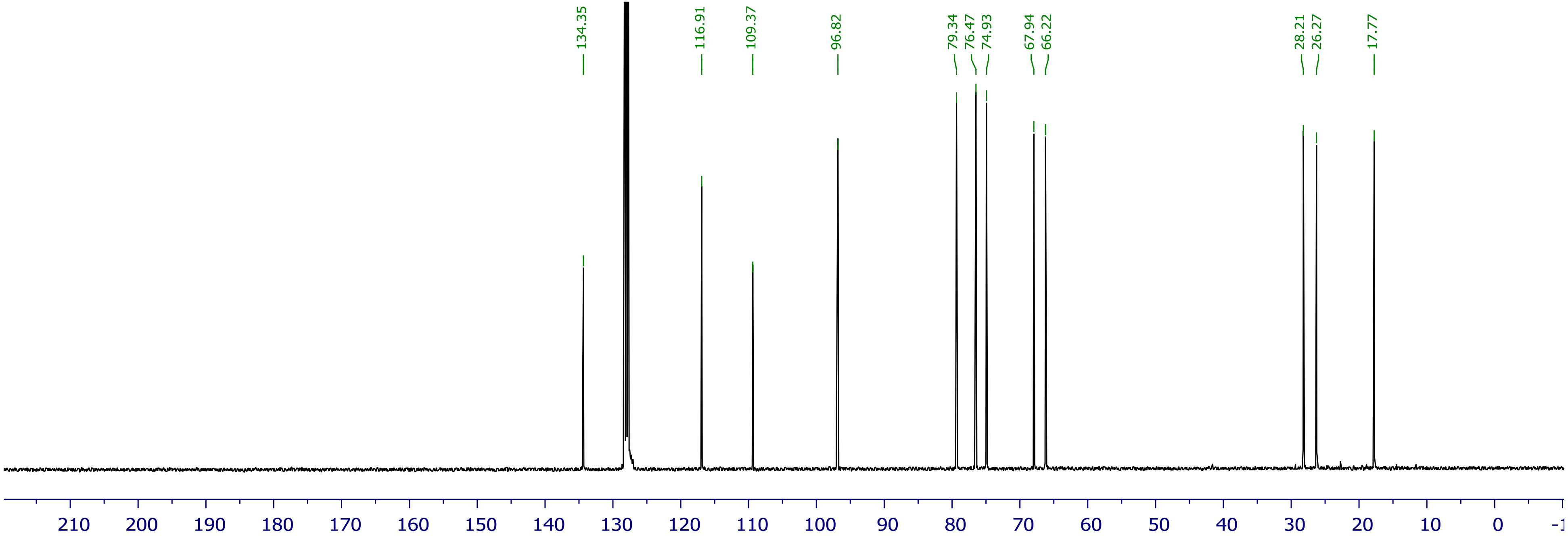

BnO
TBSO
O
ONBz
OTBDPS

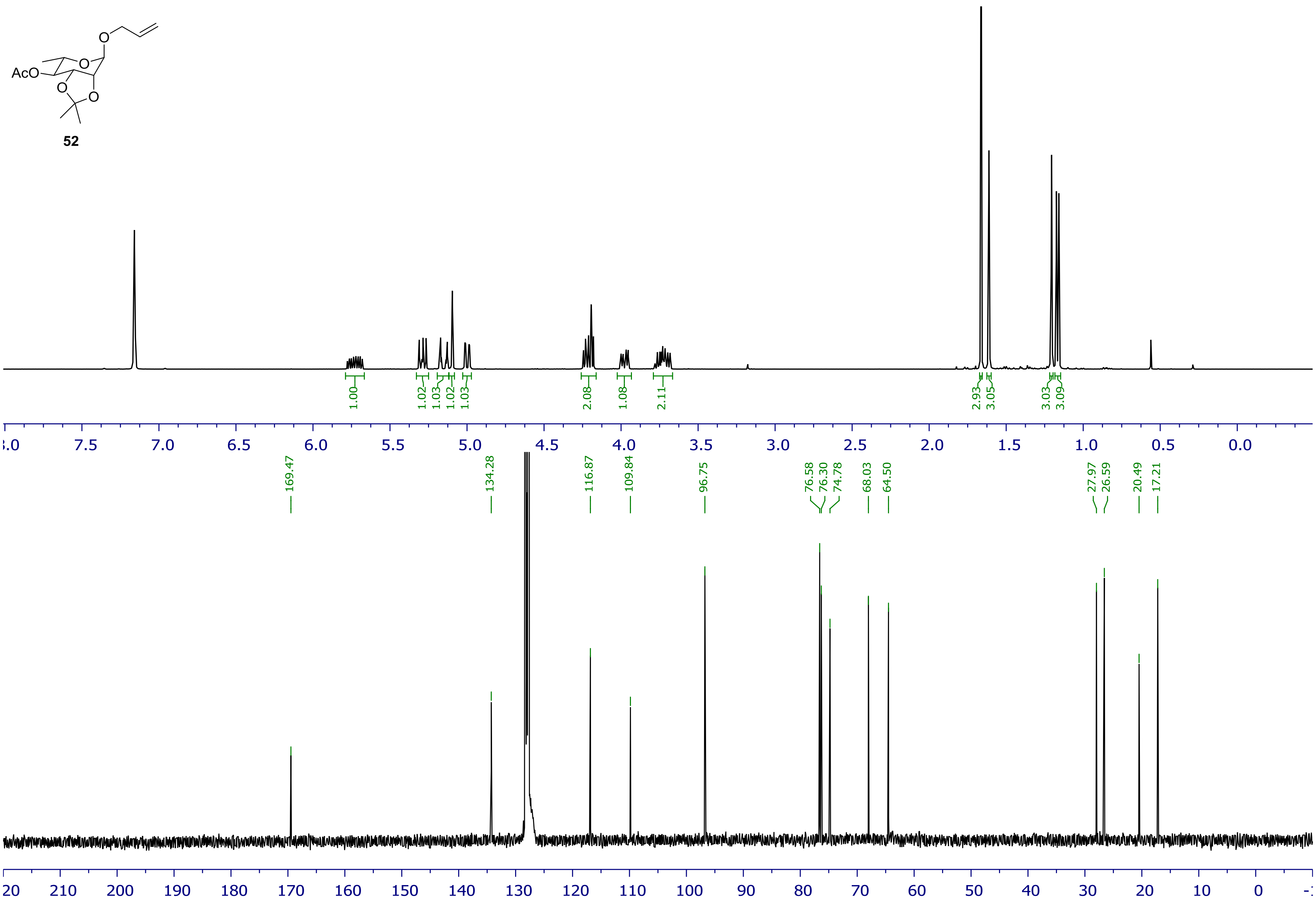
32c

2.00
1.97
4.04
11.07
1.03
1.00
1.00
1.06
1.03
2.03
1.06
2.04
2.00
1.04
1.05
1.06
12.02
9.06
6.05
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(


196.26
163.74
150.53
150.45
138.32
135.69
135.48
135.42
133.01
132.97
130.73
129.94
129.83
129.80
128.35
127.80
127.74
127.69
127.63
127.57
123.39
73.01
72.35
72.31
66.75
64.49
42.29
40.22
33.73
26.75
25.84
19.25
18.06
14.07
-4.35
-4.61
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-:


HO
O
O
O
O
51a
1.00
1.02
1.00
1.02
2.12
1.07
2.14
1.05
1.04
3.12
3.16
3.22
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(

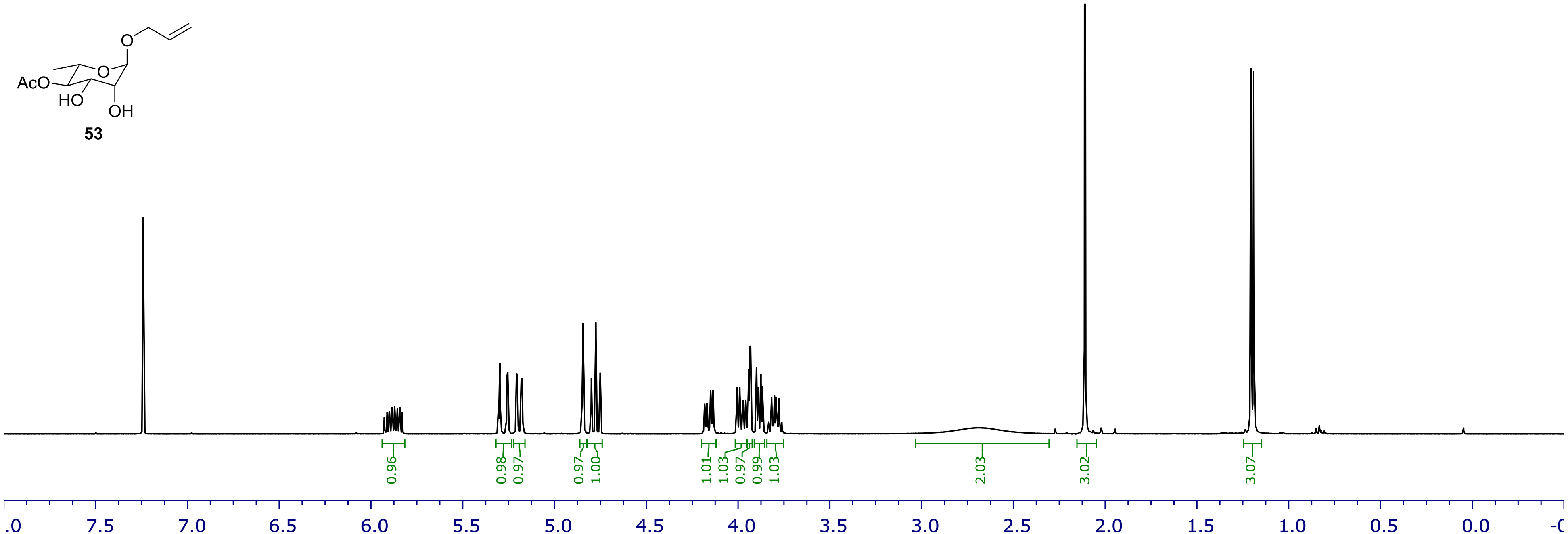

134.35
116.91
109.37
96.82
79.34
76.47
74.93
67.94
66.22
28.21
26.27
17.77
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

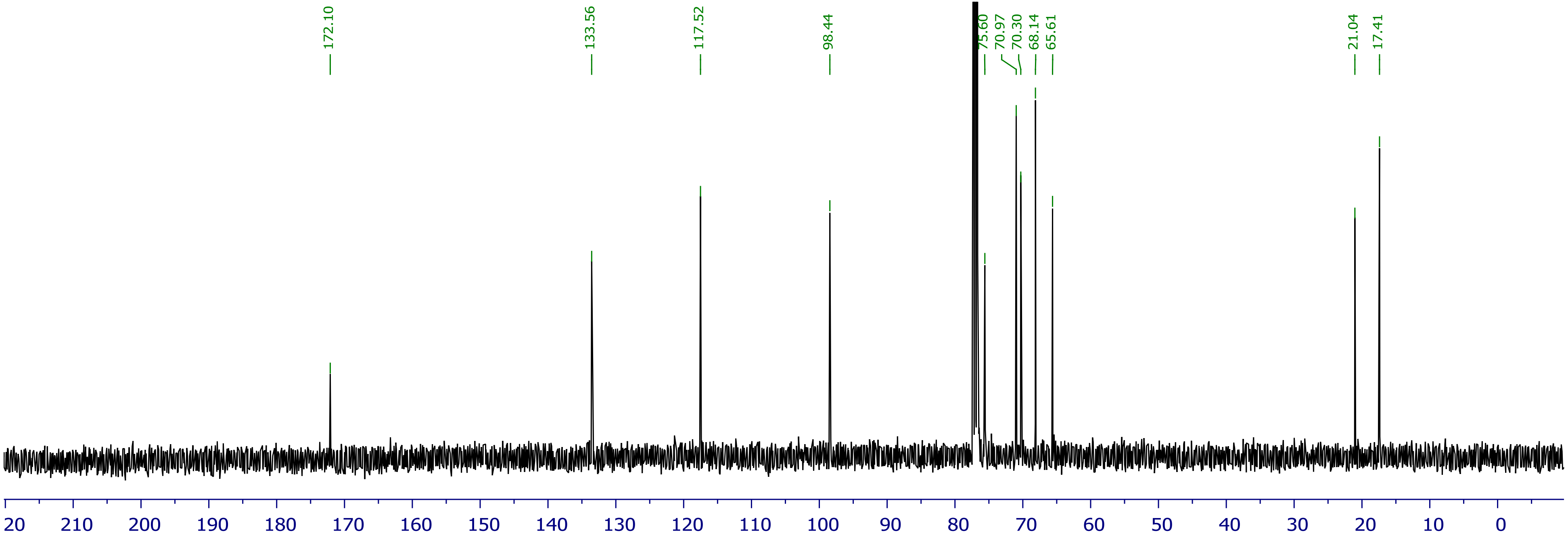

AcO
O
O
O
O
1.00
1.02
1.03
1.02
1.03
2.08
1.08
2.11
2.93
3.05
3.03
3.09
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
169.47
134.28
116.87
109.84
96.75
76.58
76.30
74.78
68.03
64.50
27.97
26.59
20.49
17.21
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-

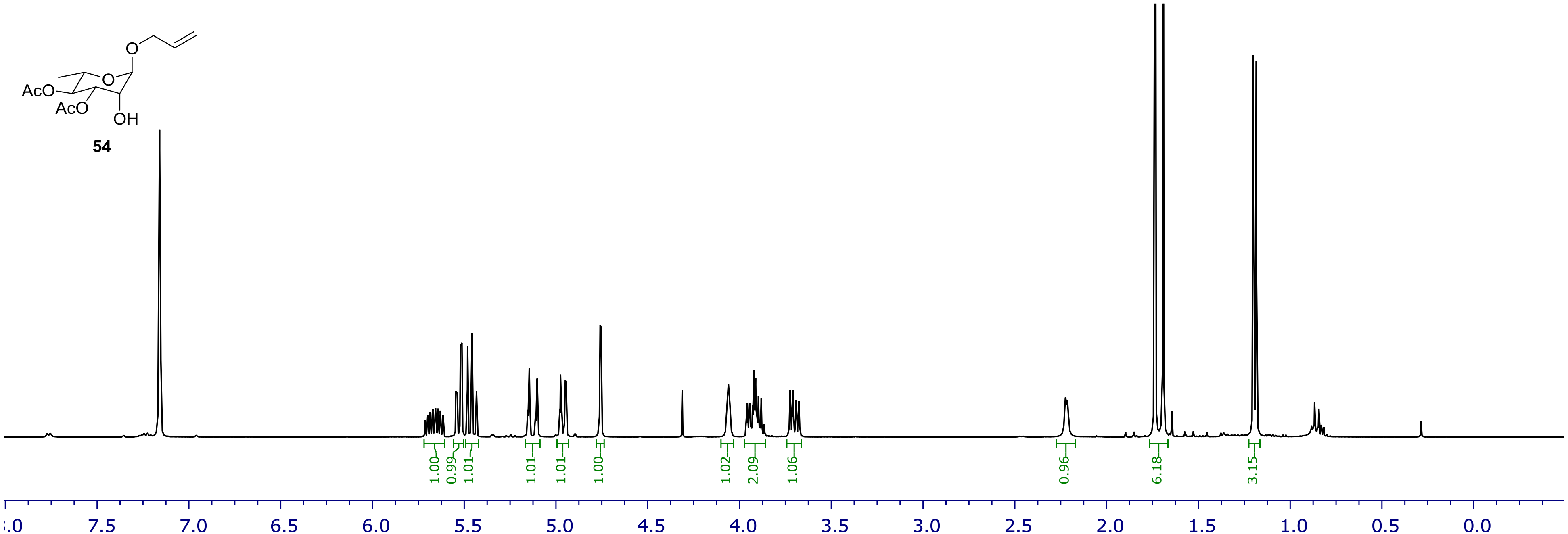
52

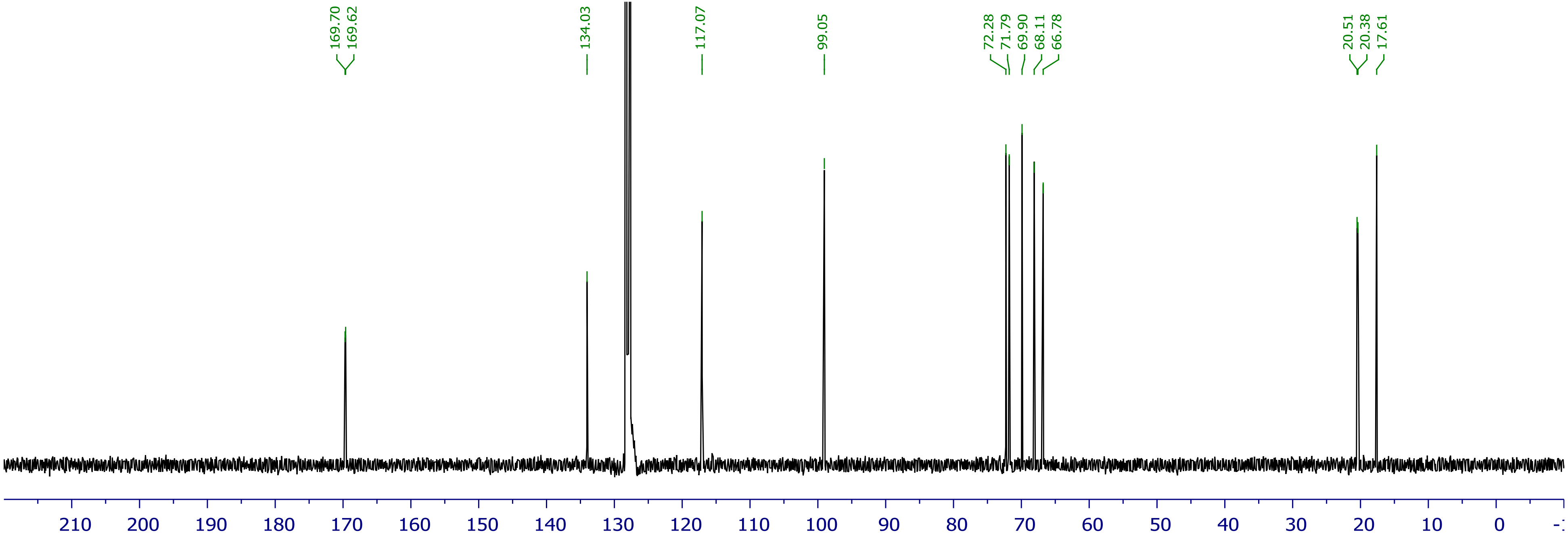
O
AcO
O
HO
OH

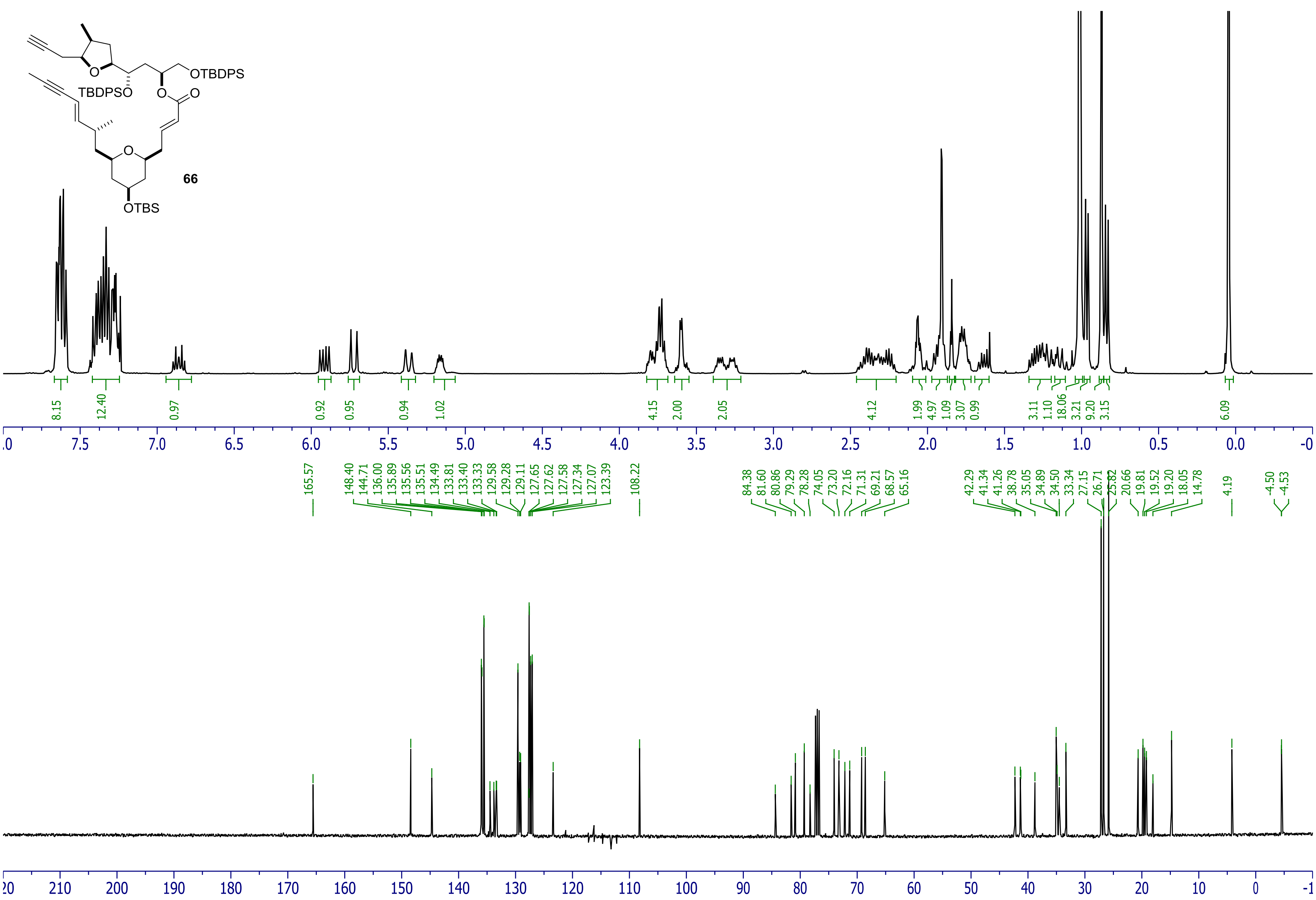
53

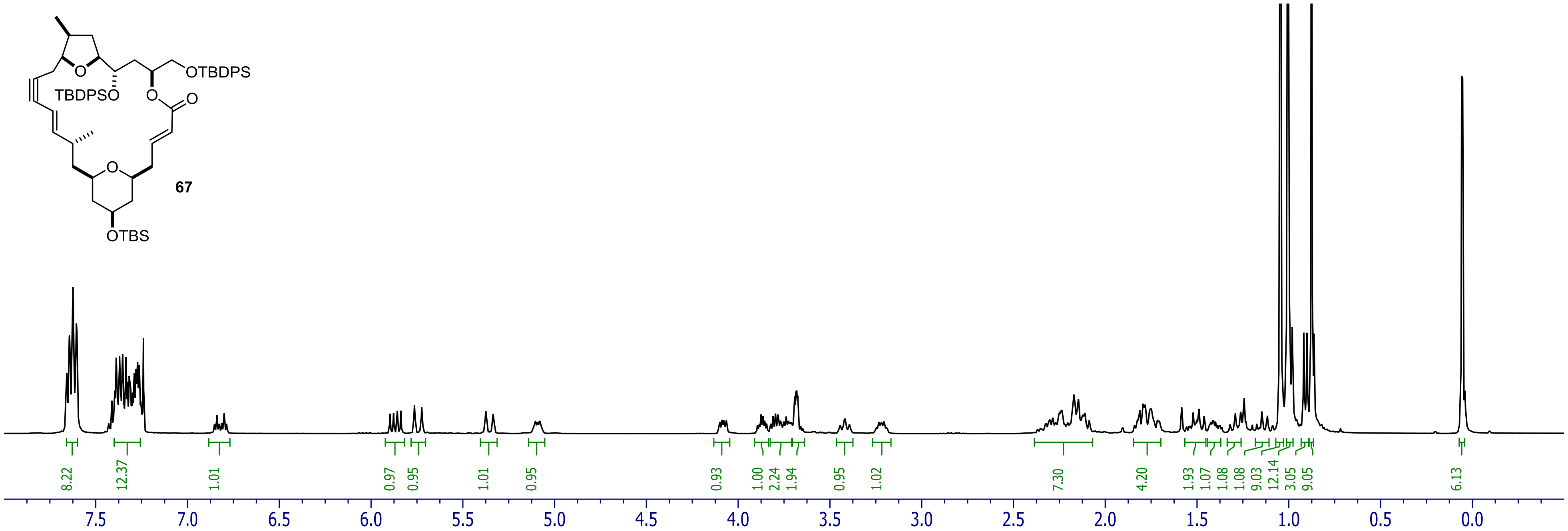

0.96
0.98
0.97
0.97
1.00
1.01
1.03
0.97
0.99
1.03
2.03
3.02
3.07
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(


172.10
133.56
117.52
98.44
75.60
70.97
70.30
68.14
65.61
21.04
17.41
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


AcO
AcO
O
O
OH
54
1.00
0.99
1.01
1.01
1.01
1.00
1.02
2.09
1.06
0.96
6.18
3.15
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

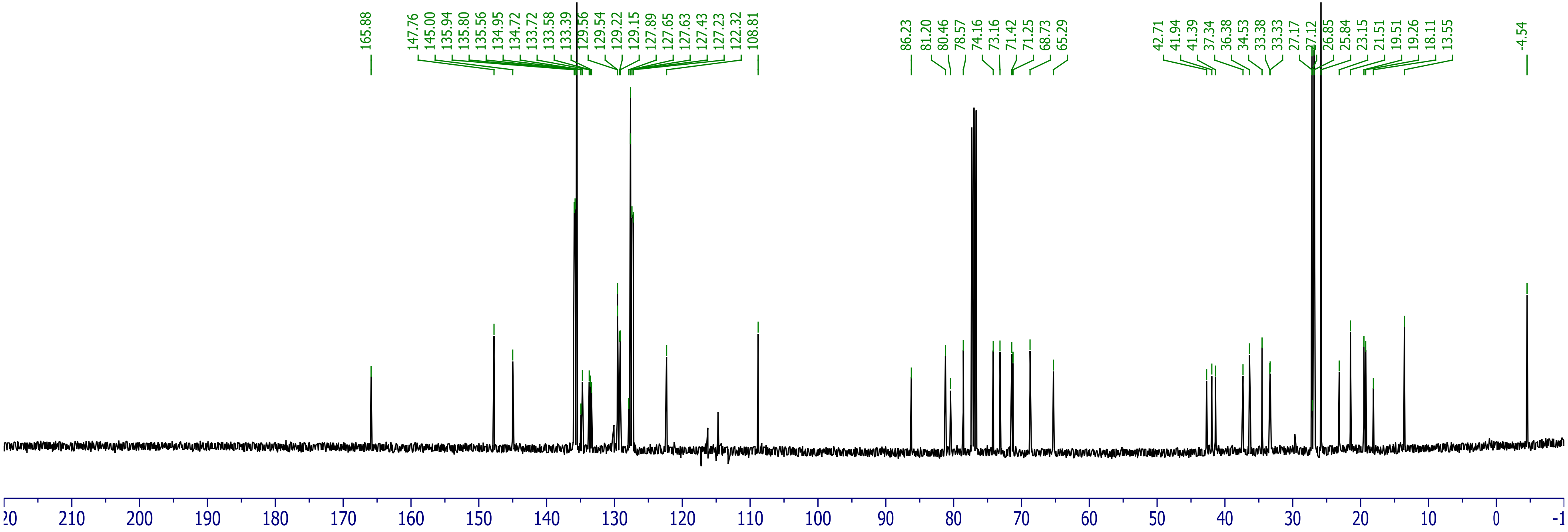

169.70
169.62
134.03
117.07
99.05
72.28
71.79
69.90
68.11
66.78
20.51
20.38
17.61
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-


OTBDPS
TBDPSO
O
O
O
OTBS
66
8.15
12.40
0.97
0.92
0.95
0.94
1.02
4.15
2.00
2.05
4.12
1.99
4.97
1.09
3.07
0.99
3.11
1.10
18.06
3.21
9.20
3.15
6.09
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
165.57
148.40
144.71
136.00
135.89
135.56
135.51
134.49
133.81
133.40
133.33
129.58
129.28
129.11
127.65
127.62
127.58
127.34
127.07
123.39
108.22
84.38
81.60
80.86
79.29
78.28
74.05
73.20
72.16
71.31
69.21
68.57
65.16
42.29
41.34
41.26
38.78
35.05
34.89
34.50
33.34
27.15
26.71
25.82
20.66
19.81
19.52
19.20
18.05
14.78
4.19
-4.50
-4.53
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1


OTBDPS
TBDPSO
O
O
O
O
OTBS

67

8.22
12.37
1.01
0.97
0.95
1.01
0.95
0.93
1.00
2.24
1.94
0.95
1.02
7.30
4.20
1.93
1.07
1.08
1.08
9.03
12.14
3.05
9.05
6.13
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


165.88
147.76
145.00
135.94
135.80
135.56
134.95
134.72
133.72
133.58
133.39
129.56
129.54
129.22
129.15
127.89
127.65
127.63
127.43
127.23
122.32
108.81
86.23
81.20
80.46
78.57
74.16
73.16
71.42
71.25
68.73
65.29
42.71
41.94
41.39
37.34
36.38
34.53
33.38
33.33
27.17
27.12
26.85
25.84
23.15
21.51
19.51
19.26
18.11
13.55
-4.54
20
210
200
190
180
170
160
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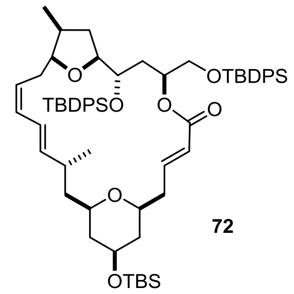
OTBDPS
TBDPSO
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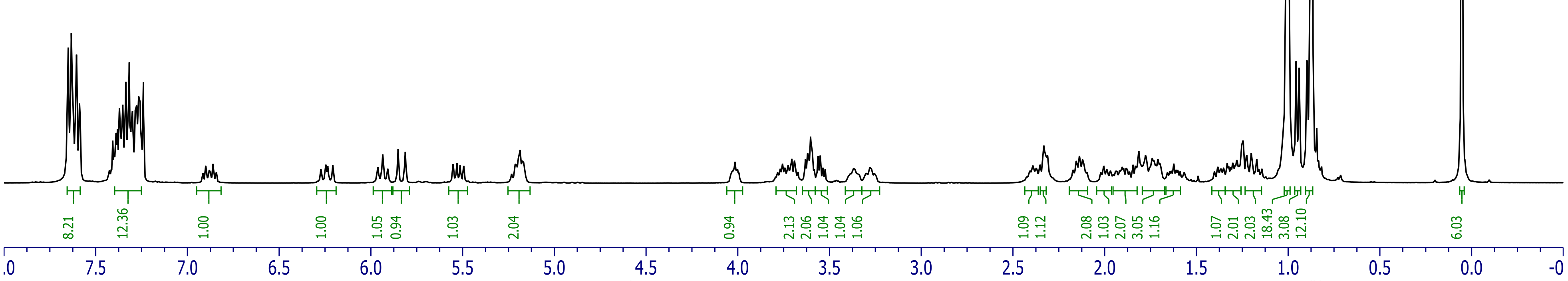
O
O
OTBS

72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1.04
1.06
1.09
1.12
2.08
1.03
2.07
3.05
1.16
1.07
2.01
2.03
18.43
3.08
12.10
6.03
.0
7.5
7.0
6.5
6.0
5.5
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3.5
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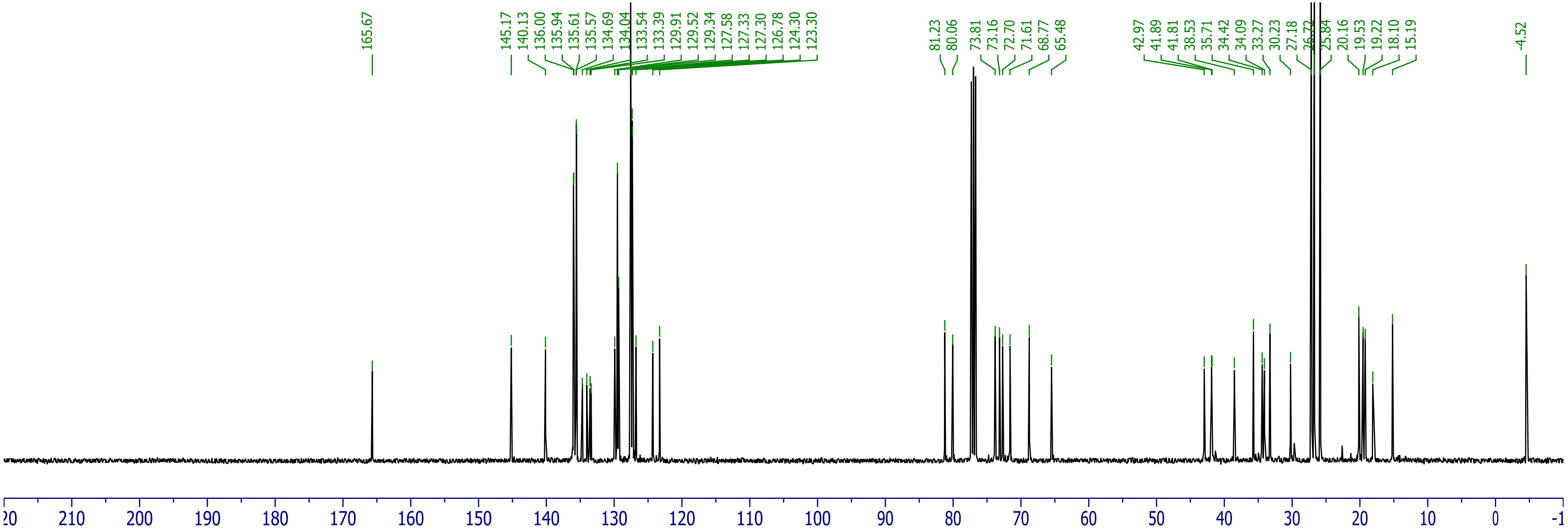
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134.69
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133.39
129.91
129.52
129.34
127.58
127.33
127.30
126.78
124.30
123.30
81.23
80.06
73.81
73.16
72.70
71.61
68.77
65.48
42.97
41.89
41.81
38.53
35.71
34.42
34.09
33.27
30.23
27.18
26.72
25.84
20.16
19.53
19.22
18.10
15.19
-4.52
0
210
200
190
180
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140
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100
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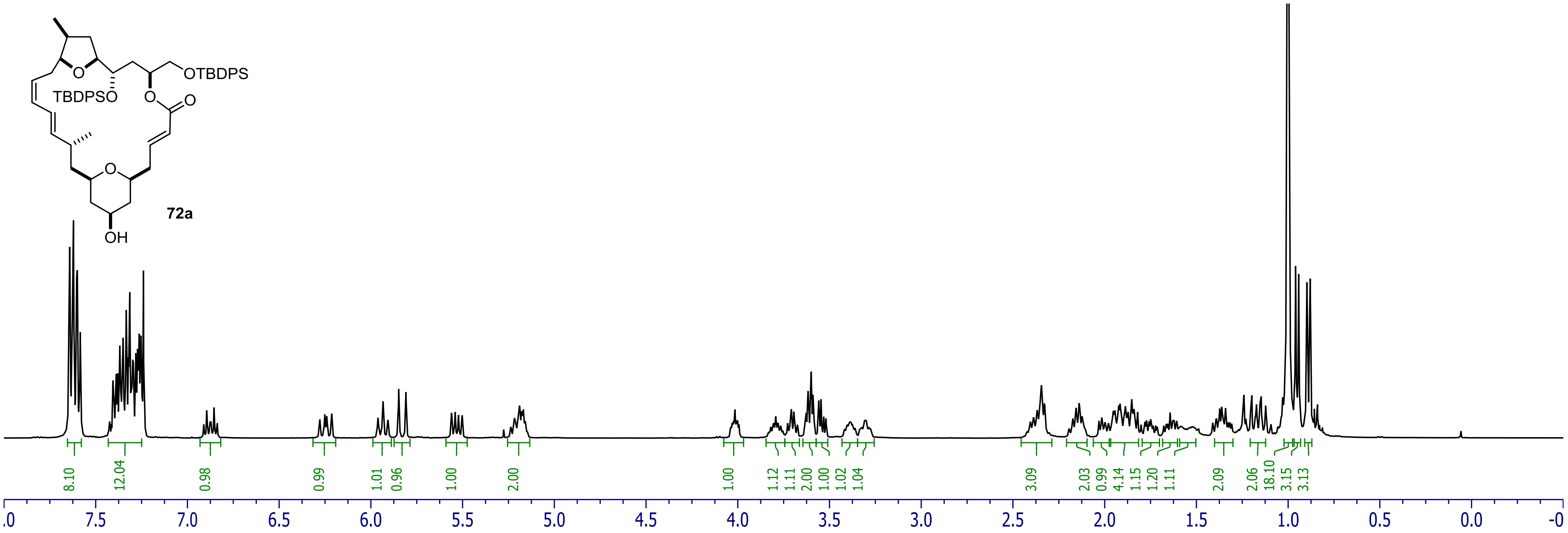

OTBDPS
TBDPSO
O
O
O
O
OH
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0.98
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0.96
1.00
2.00
1.00
1.12
1.11
2.00
1.00
1.02
1.04
3.09
2.03
0.99
4.14
1.15
1.20
1.11
2.09
2.06
18.10
3.15
3.13
.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
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0.0
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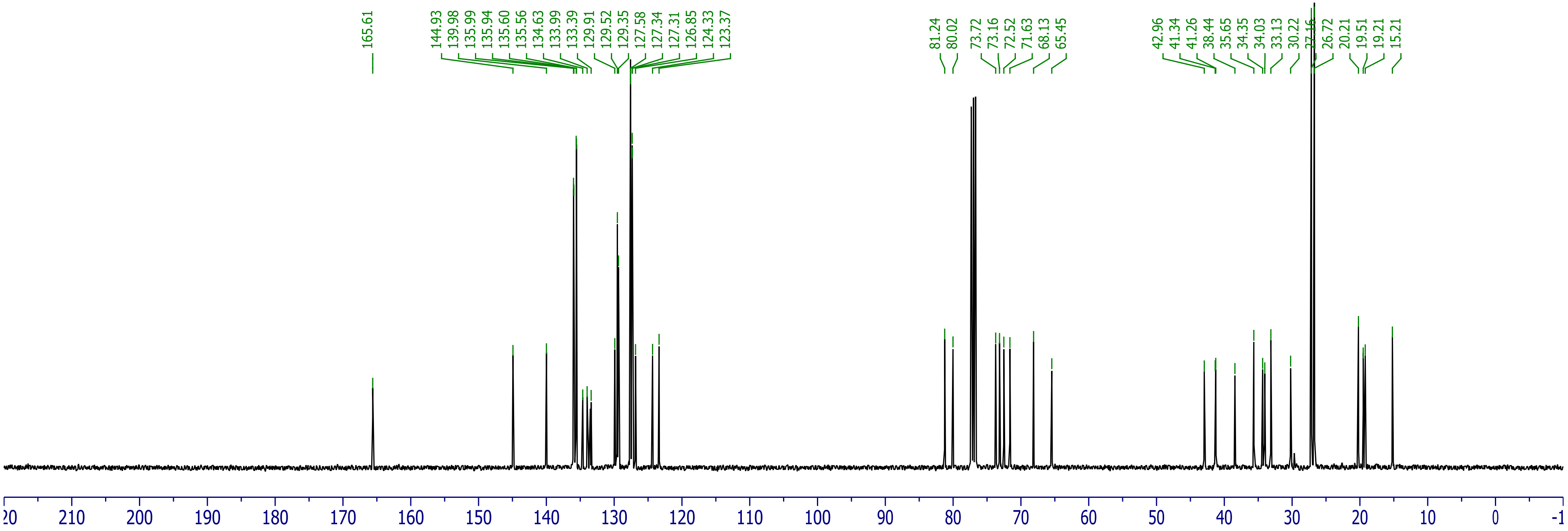
72a



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139.98
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134.63
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129.91
129.52
129.35
127.58
127.34
127.31
126.85
124.33
123.37
81.24
80.02
73.72
73.16
72.52
71.63
68.13
65.45
42.96
41.34
41.26
38.44
35.65
34.35
34.03
33.13
30.22
27.16
26.72
20.21
19.51
19.21
15.21
20
210
200
190
180
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110
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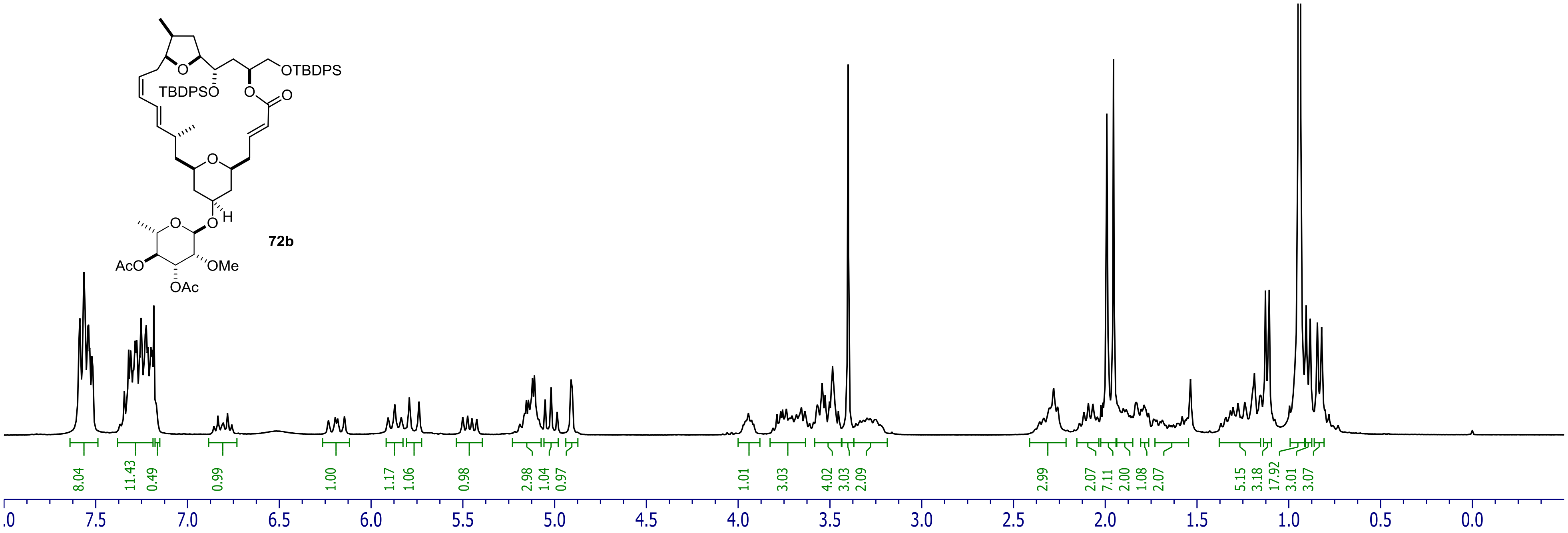
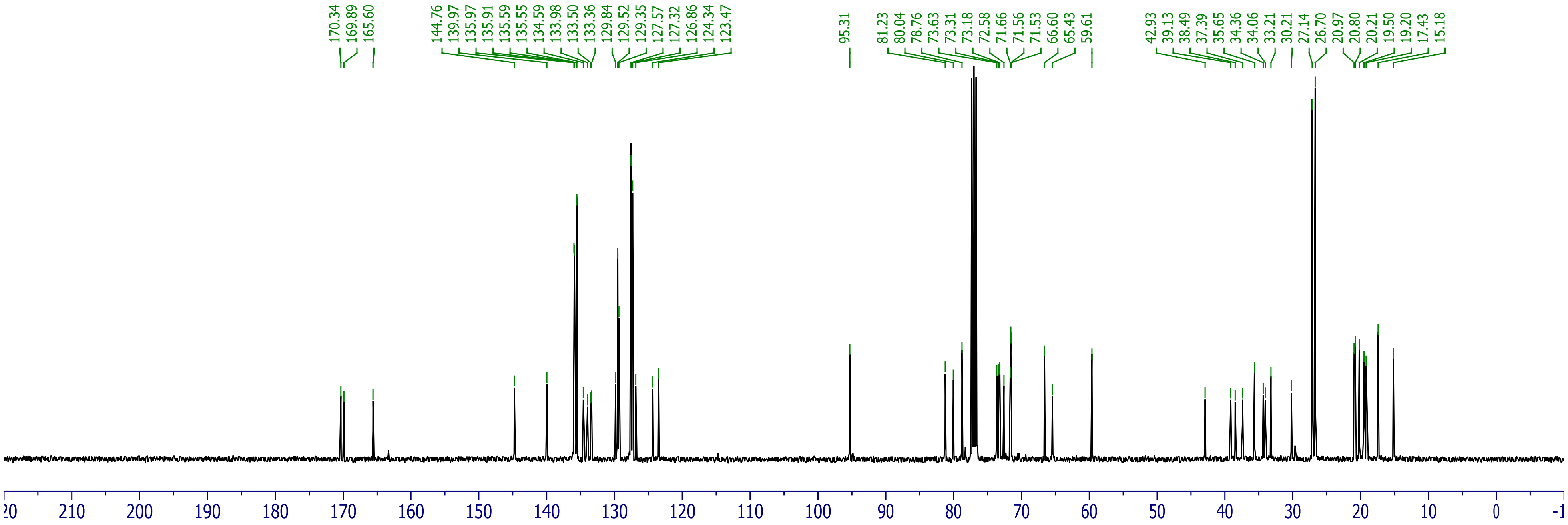


72b

OTBDPS
TBDPSO
O
O
O
O
H
O
AcO
OMe
OAc
8.04
11.43
0.49
0.99
1.00
1.17
1.06
0.98
2.98
1.04
0.97
1.01
3.03
4.02
3.03
2.09
2.99
2.07
7.11
2.00
1.08
2.07
5.15
3.18
17.92
3.01
3.07
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



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169.89
165.60
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135.91
135.59
135.55
134.59
133.98
133.50
133.36
129.84
129.52
129.35
127.57
127.32
126.86
124.34
123.47
95.31
81.23
80.04
78.76
73.63
73.31
73.18
72.58
71.66
71.56
71.53
66.60
65.43
59.61
42.93
39.13
38.49
37.39
35.65
34.36
34.06
33.21
30.21
27.14
26.70
20.97
20.80
20.21
19.50
19.20
17.43
15.18
20
210
200
190
180
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150
140
130
120
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100
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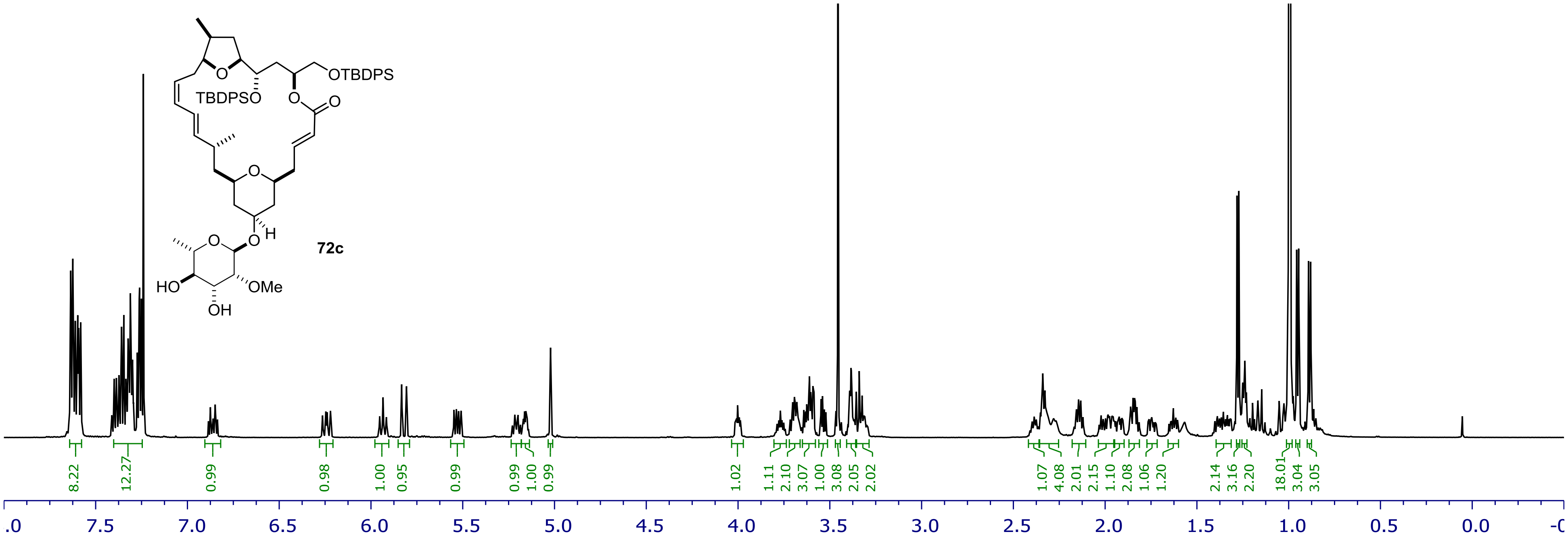
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TBDPSO
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O
O
O
H
O
O
HO
OH
OMe
72c
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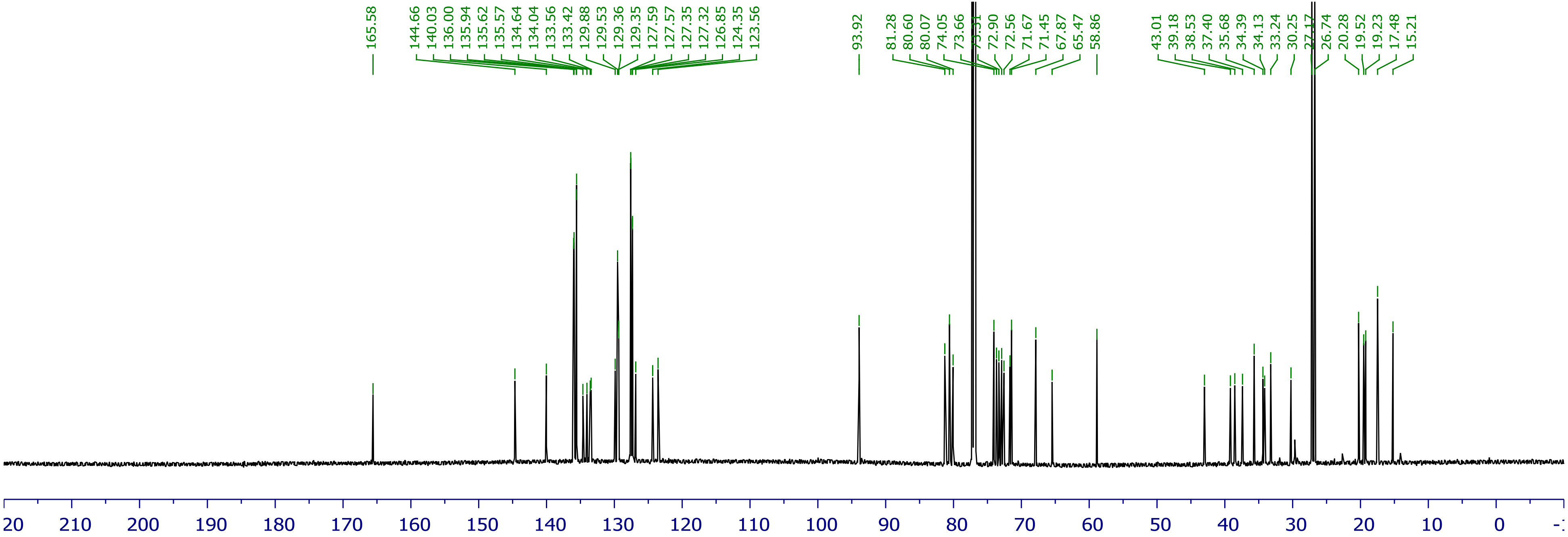
0.98
1.00
0.95
0.99
0.99
1.00
0.99
1.02
1.11
2.10
3.07
1.00
3.08
2.05
2.02
1.07
4.08
2.01
2.15
1.10
2.08
1.06
1.20
2.14
3.16
2.20
18.01
3.04
3.05
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-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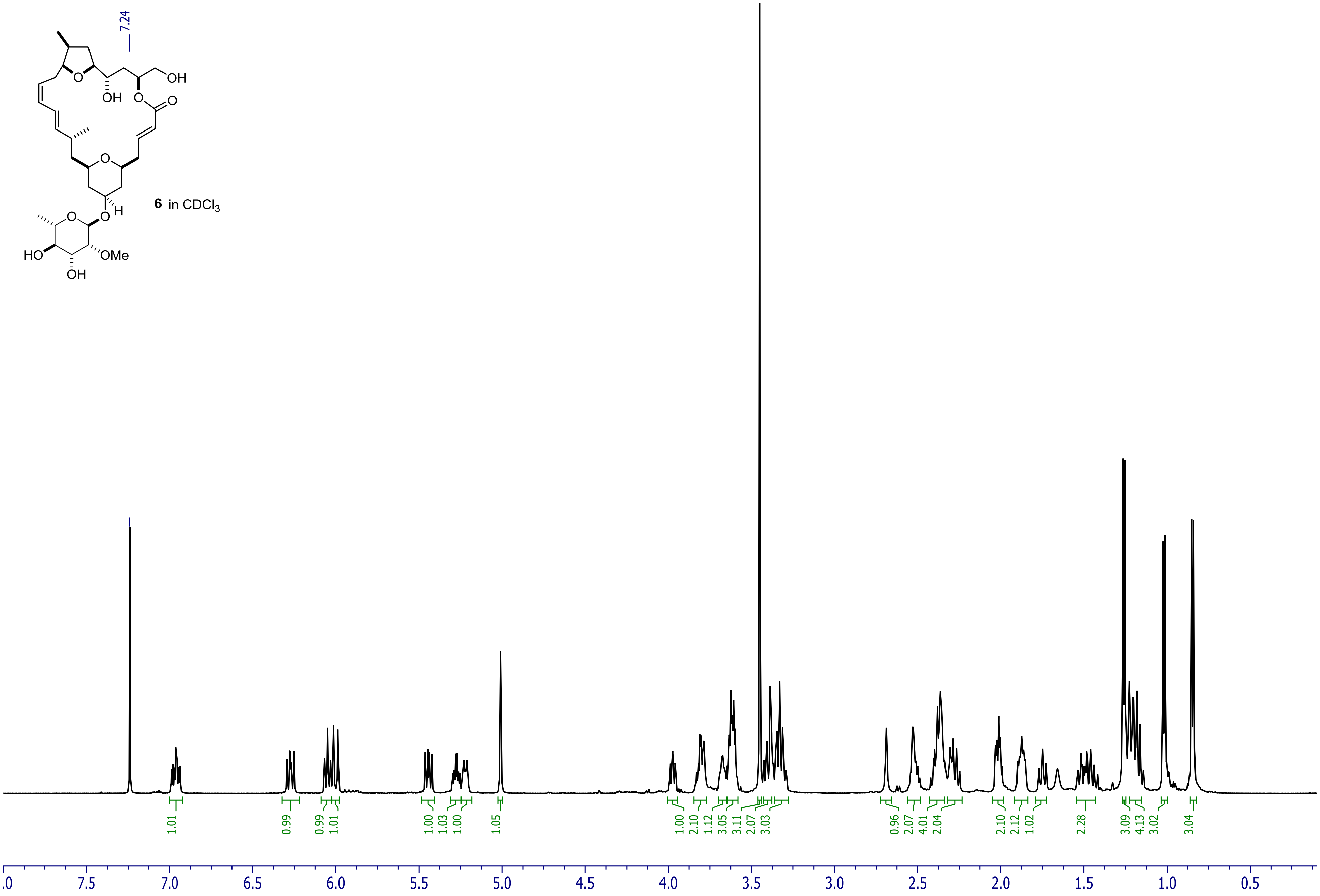
135.57
134.64
134.04
133.56
133.42
129.88
129.53
129.36
129.35
127.59
127.57
127.35
127.32
126.85
124.35
123.56
93.92
81.28
80.60
80.07
74.05
73.66
73.31
72.90
72.56
71.67
71.45
67.87
65.47
58.86
43.01
39.18
38.53
37.40
35.68
34.39
34.13
33.24
30.25
27.17
26.74
20.28
19.52
19.23
17.48
15.21
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-


7.24
OH
OH
O
O
O
OH
HO
OMe
H
6 in CDCl3
1.01
0.99
0.99
1.01
1.00
1.03
1.00
1.05
1.00
2.10
1.12
3.05
3.11
2.07
3.03
0.96
2.07
4.01
2.04
2.10
2.12
1.02
2.28
3.09
4.13
3.02
3.04
.0
7.5
7.0
6.5
6.0
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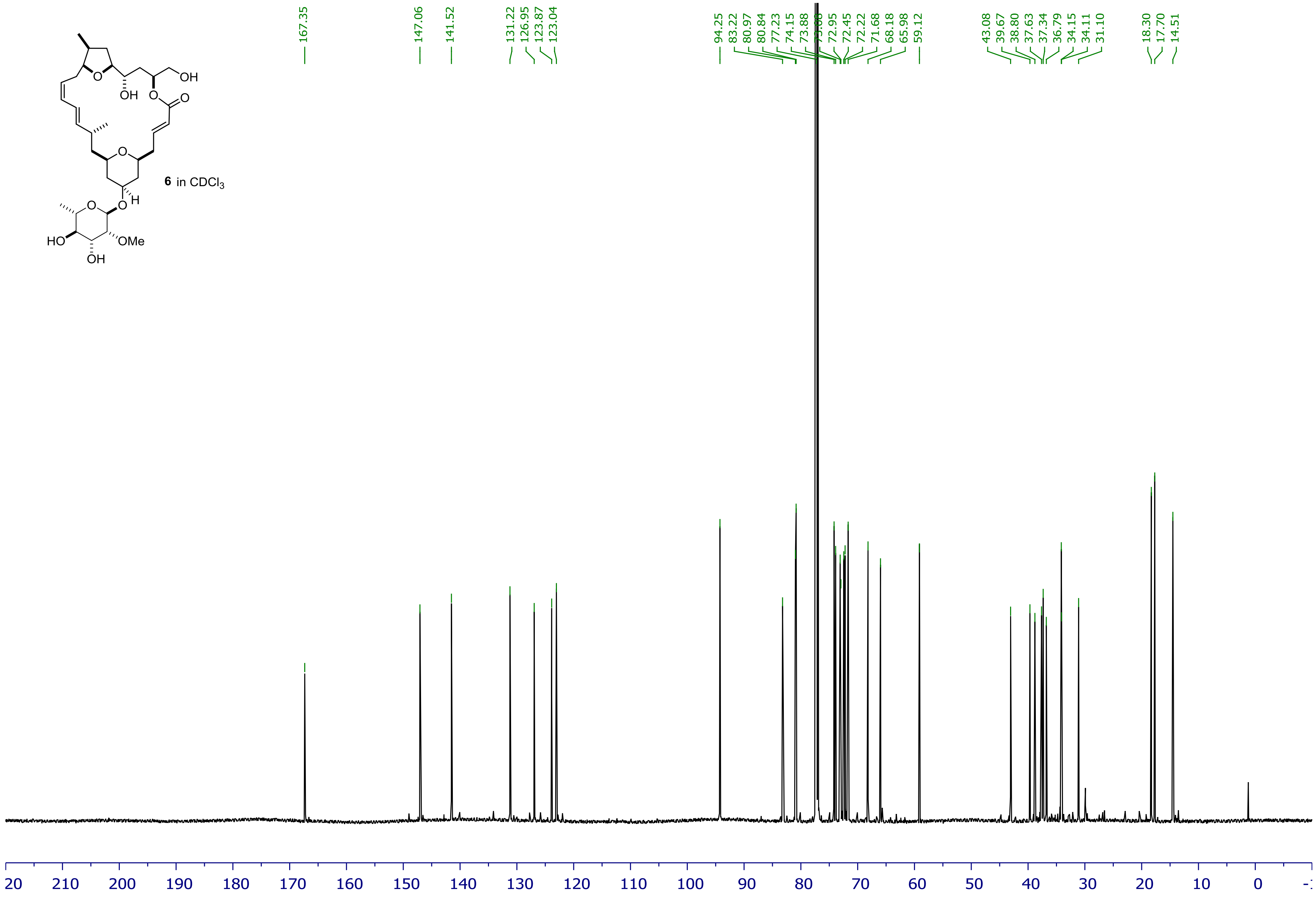
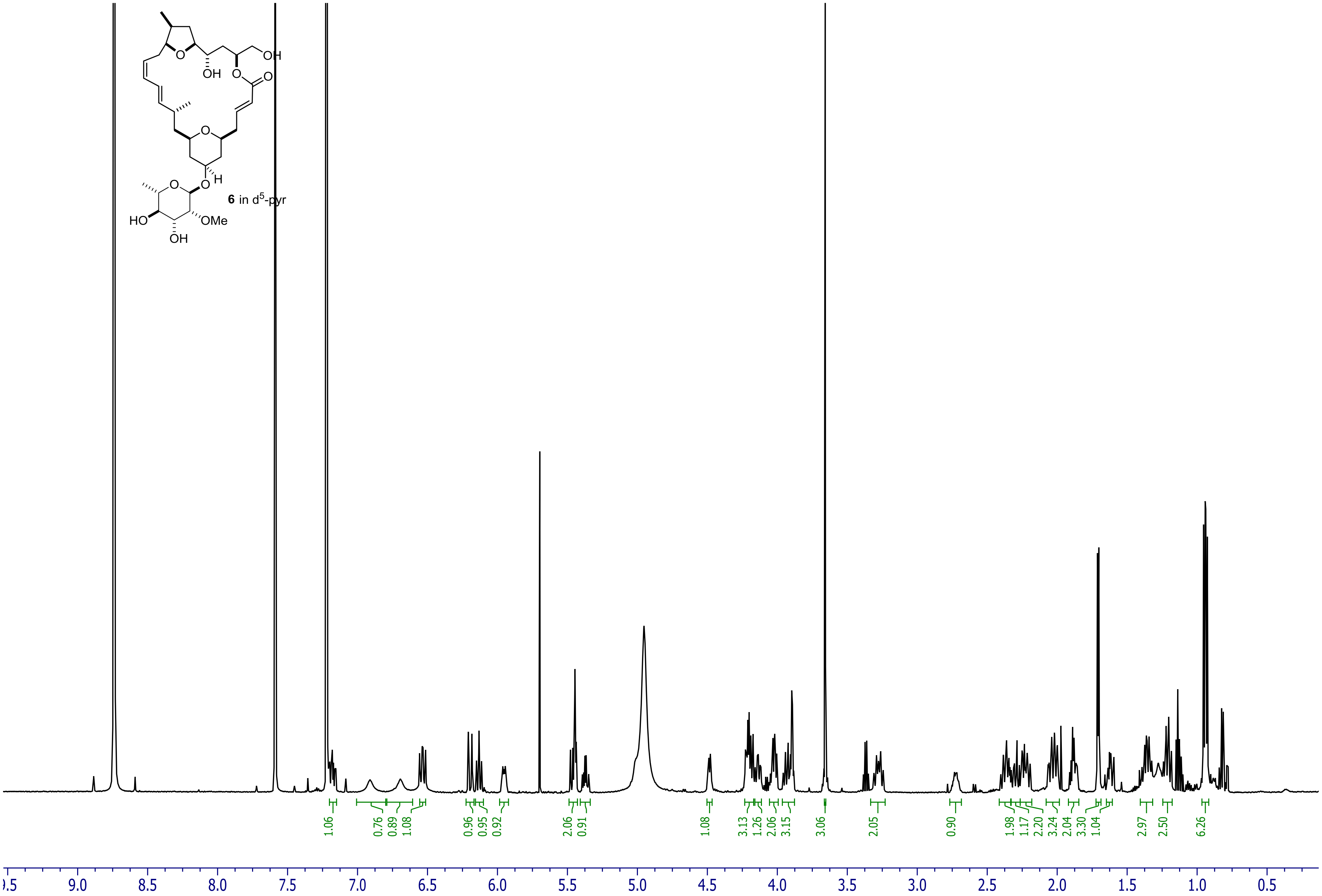
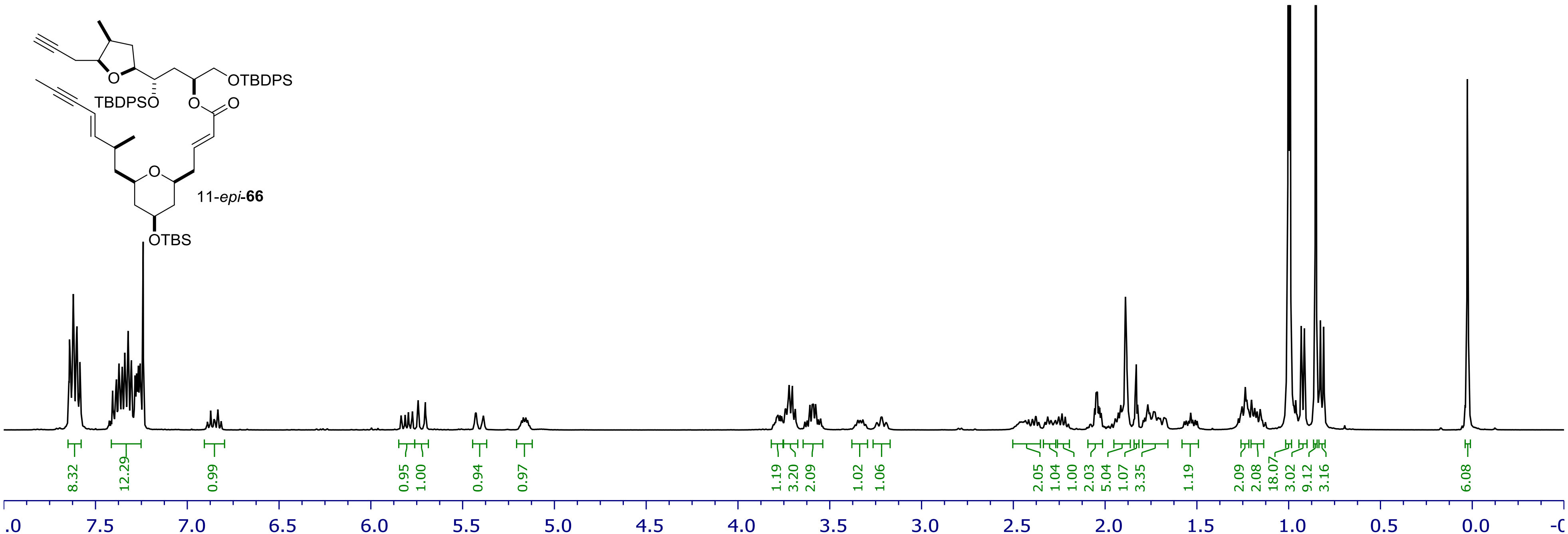
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5



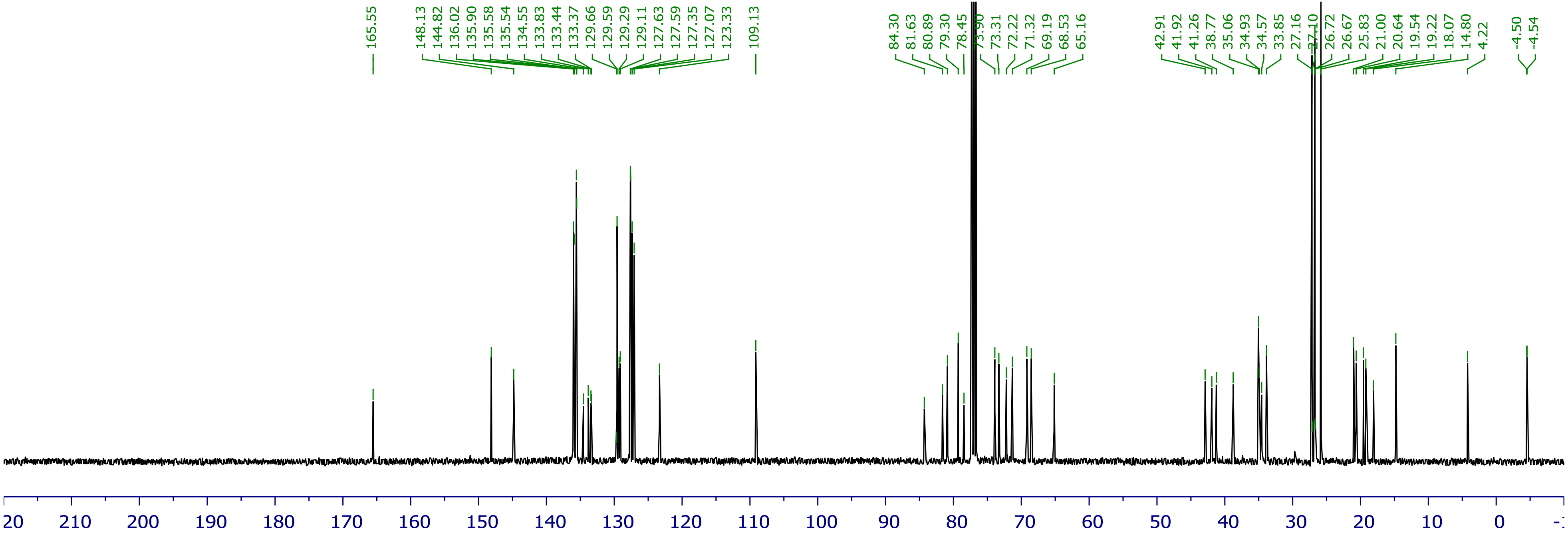
6 in CDCl$_3$
OH
OH
O
O
O
O
H
O
O
HO
OMe
OH
167.35
147.06
141.52
131.22
126.95
123.87
123.04
94.25
83.22
80.97
80.84
77.23
74.15
73.88
73.08
72.95
72.45
72.22
71.68
68.18
65.98
59.12
43.08
39.67
38.80
37.63
37.34
36.79
34.15
34.11
31.10
18.30
17.70
14.51
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-



6 in d^5-pyr
OH
OH
O
O
O
O
H
OMe
HO
OH
1.06
0.76
0.89
1.08
0.96
0.95
0.92
2.06
0.91
1.08
3.13
1.26
2.06
3.15
3.06
2.05
0.90
1.98
1.17
2.20
3.24
2.04
3.30
1.04
2.97
2.50
6.26
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


O
OTBDPS
TBDPSO
O
O
O
OTBS
8.32
12.29
0.99
0.95
1.00
0.94
0.97
1.19
3.20
2.09
1.02
1.06
2.05
1.04
1.00
2.03
5.04
1.07
3.35
1.19
2.09
2.08
18.07
3.02
9.12
3.16
6.08
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(

11-*epi*-**66**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133.37
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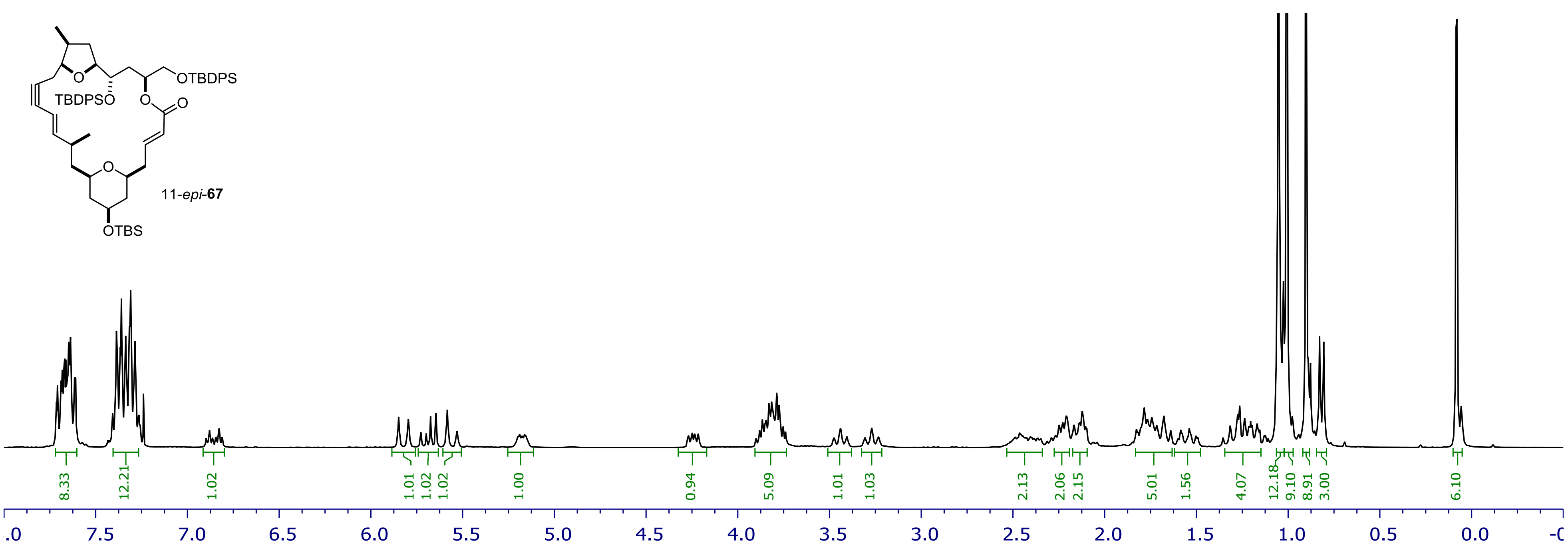
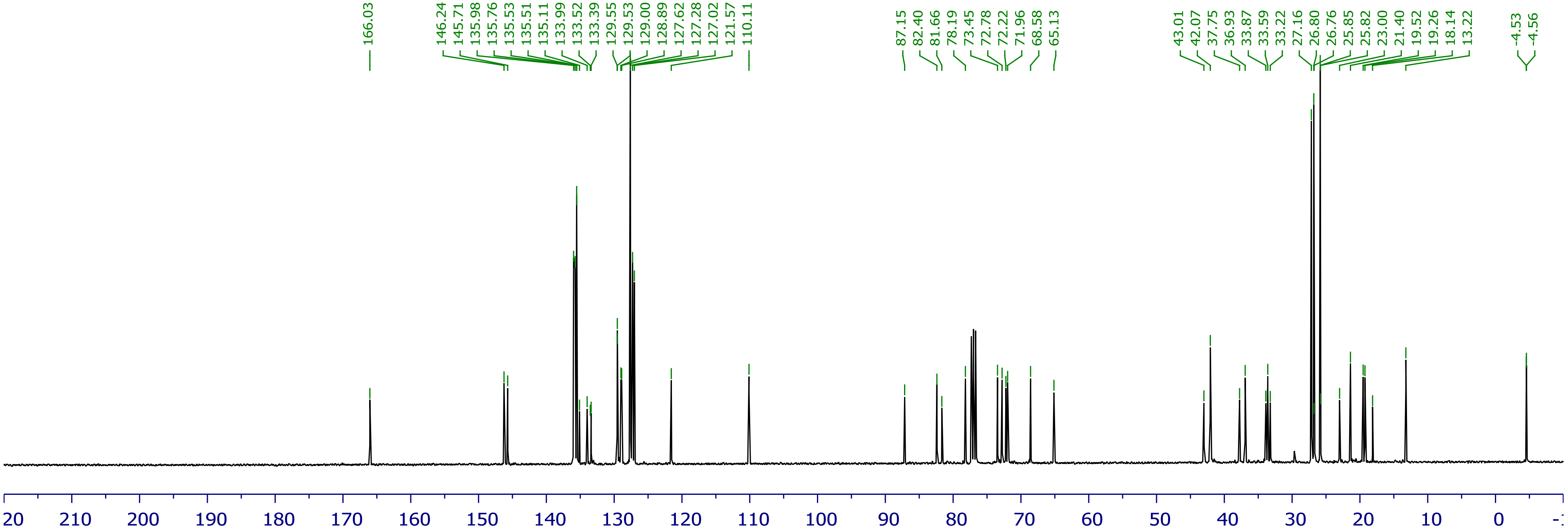
129.59
129.29
129.11
127.63
127.59
127.35
127.07
123.33
109.13
84.30
81.63
80.89
79.30
78.45
73.90
73.31
72.22
71.32
69.19
68.53
65.16
42.91
41.92
41.26
38.77
35.06
34.93
34.57
33.85
27.16
27.10
26.72
26.67
25.83
21.00
20.64
19.54
19.22
18.07
14.80
4.22
-4.50
-4.54
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-:


OTBDPS
TBDPSO
O
O
O
O
OTBS
8.33
12.21
1.02
1.01
1.02
1.02
1.00
0.94
5.09
1.01
1.03
2.13
2.06
2.15
5.01
1.56
4.07
12.18
9.10
8.91
3.00
6.10
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(

11-*epi*-**67**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129.55
129.53
129.00
128.89
127.62
127.28
127.02
121.57
110.11
87.15
82.40
81.66
78.19
73.45
72.78
72.22
71.96
68.58
65.13
43.01
42.07
37.75
36.93
33.87
33.59
33.22
27.16
26.80
26.76
25.85
25.82
23.00
21.40
19.52
19.26
18.14
13.22
-4.53
-4.56
20
210
200
190
180
170
160
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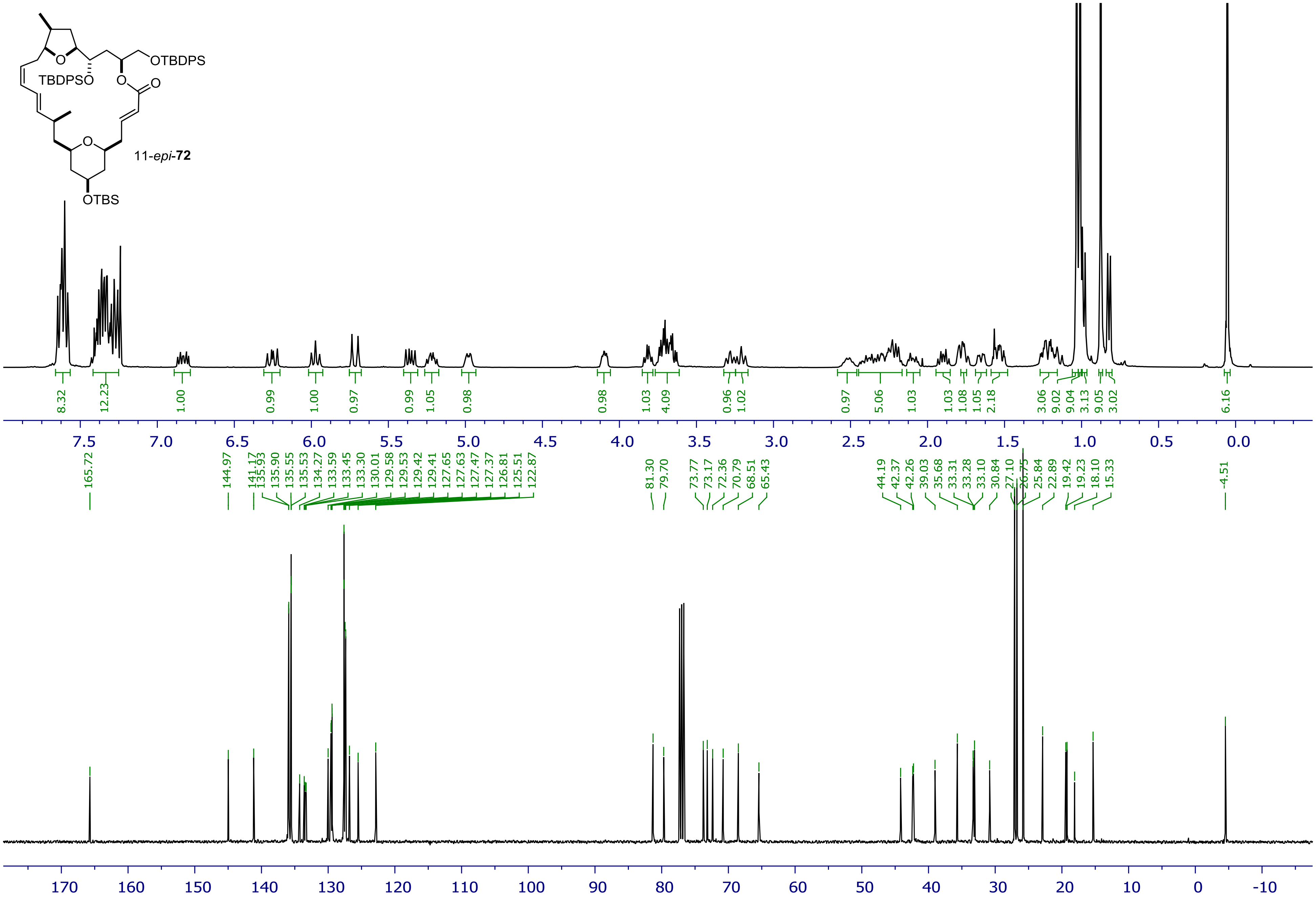
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-:


11-*epi*-**72**

OTBDPS
TBDPSO
O
O
O
O
OTBS
8.32
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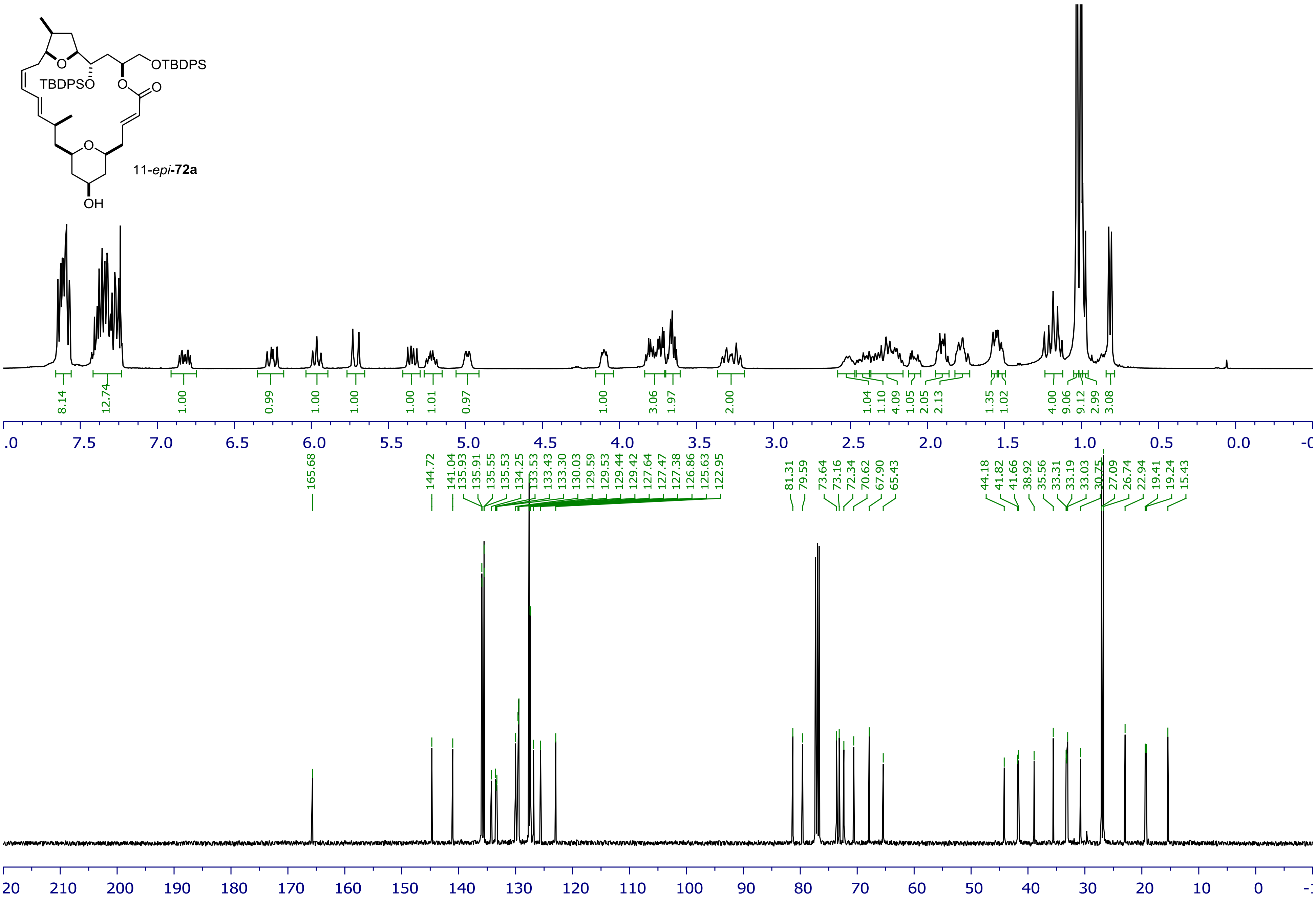
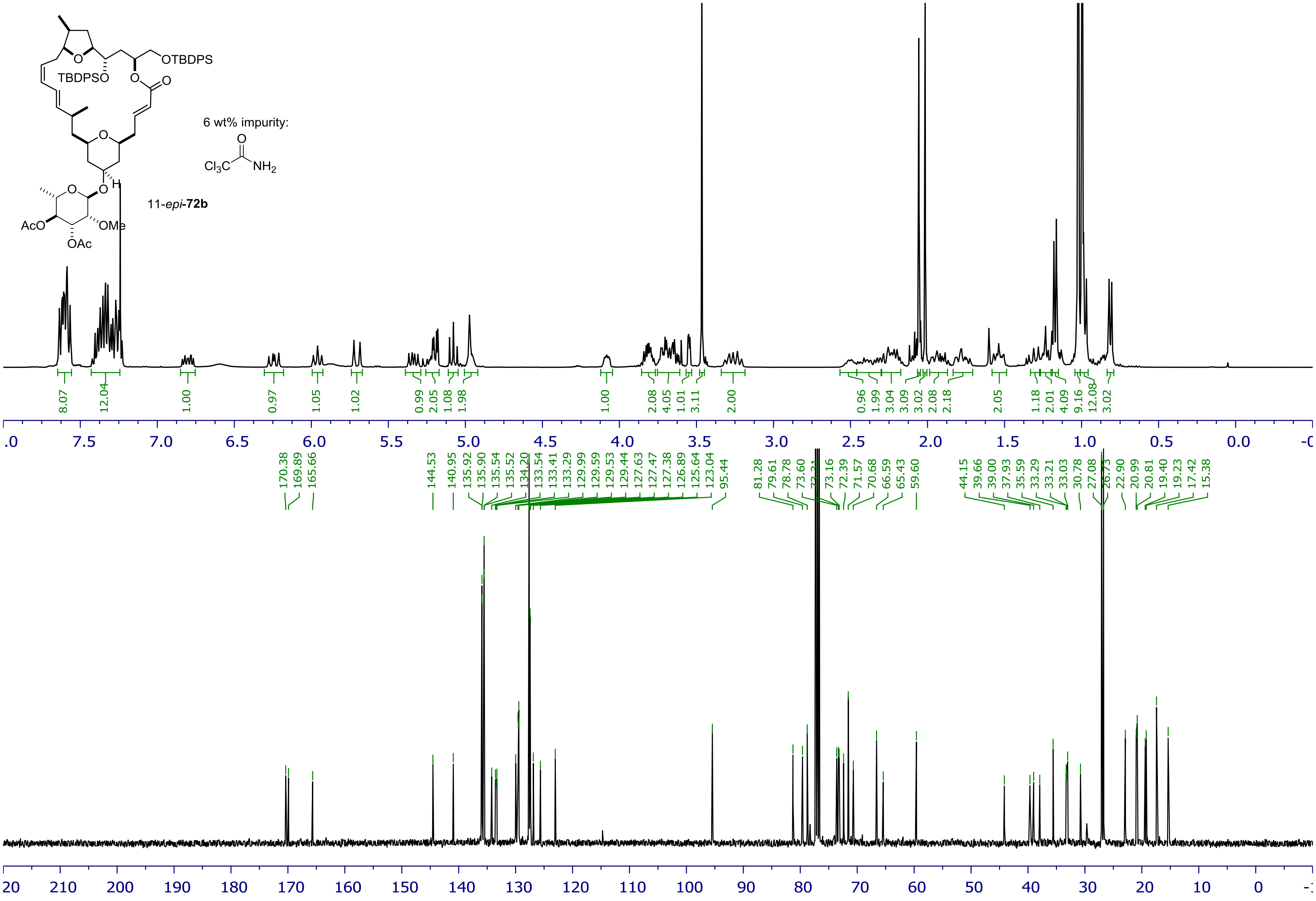
1.00
0.99
1.00
0.97
0.99
1.05
0.98
0.98
1.03
4.09
0.96
1.02
0.97
5.06
1.03
1.03
1.08
1.05
2.18
3.06
9.02
9.04
3.13
9.05
3.02
6.16
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
165.72
144.97
141.17
135.93
135.90
135.55
135.53
134.27
133.59
133.45
133.30
130.01
129.58
129.53
129.42
129.41
127.65
127.63
127.47
127.37
126.81
125.51
122.87
81.30
79.70
73.77
73.17
72.36
70.79
68.51
65.43
44.19
42.37
42.26
39.03
35.68
33.31
33.28
33.10
30.84
27.10
26.75
25.84
22.89
19.42
19.23
18.10
15.33
-4.51
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

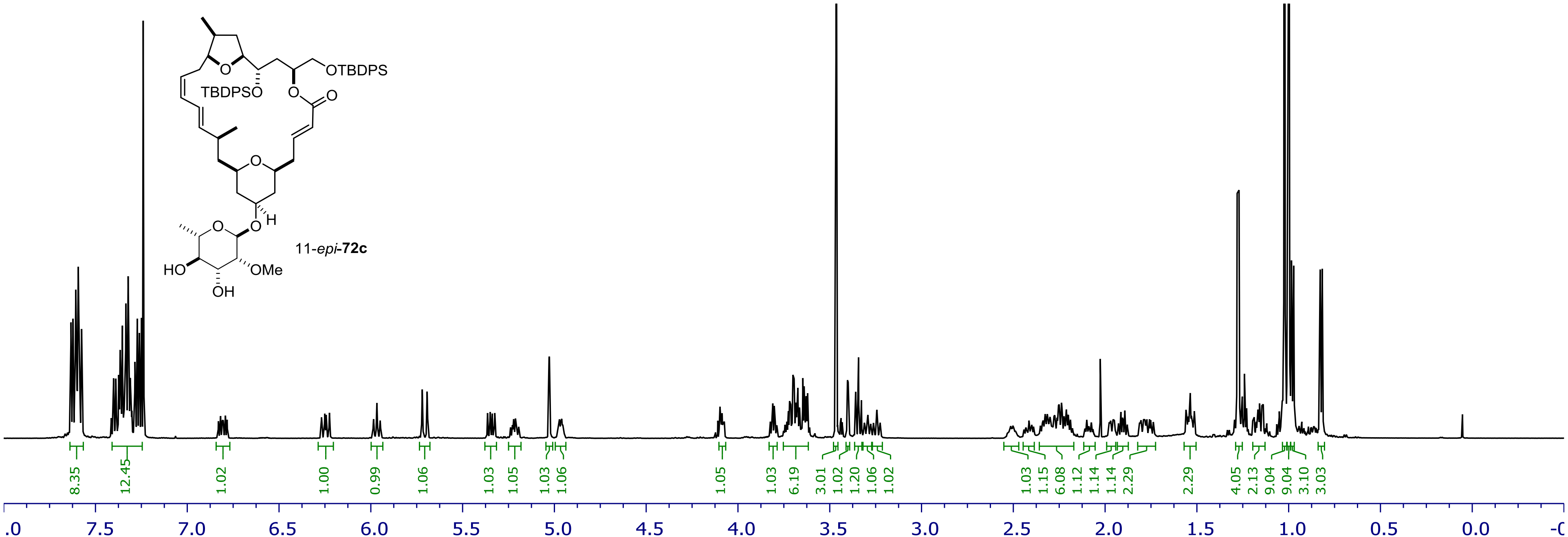

OTBDPS
TBDPSO
O
O
O
O
OH
8.14
12.74
1.00
0.99
1.00
1.00
1.00
1.01
0.97
1.00
3.06
1.97
2.00
1.04
1.10
4.09
1.05
2.05
2.13
1.35
1.02
4.00
9.06
9.12
2.99
3.08
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
165.68
144.72
141.04
135.93
135.91
135.55
135.53
134.25
133.53
133.43
133.30
130.03
129.59
129.53
129.44
129.42
127.64
127.47
127.38
126.86
125.63
122.95
81.31
79.59
73.64
73.16
72.34
70.62
67.90
65.43
44.18
41.82
41.66
38.92
35.56
33.31
33.19
33.03
30.75
27.09
26.74
22.94
19.41
19.24
15.43
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-:

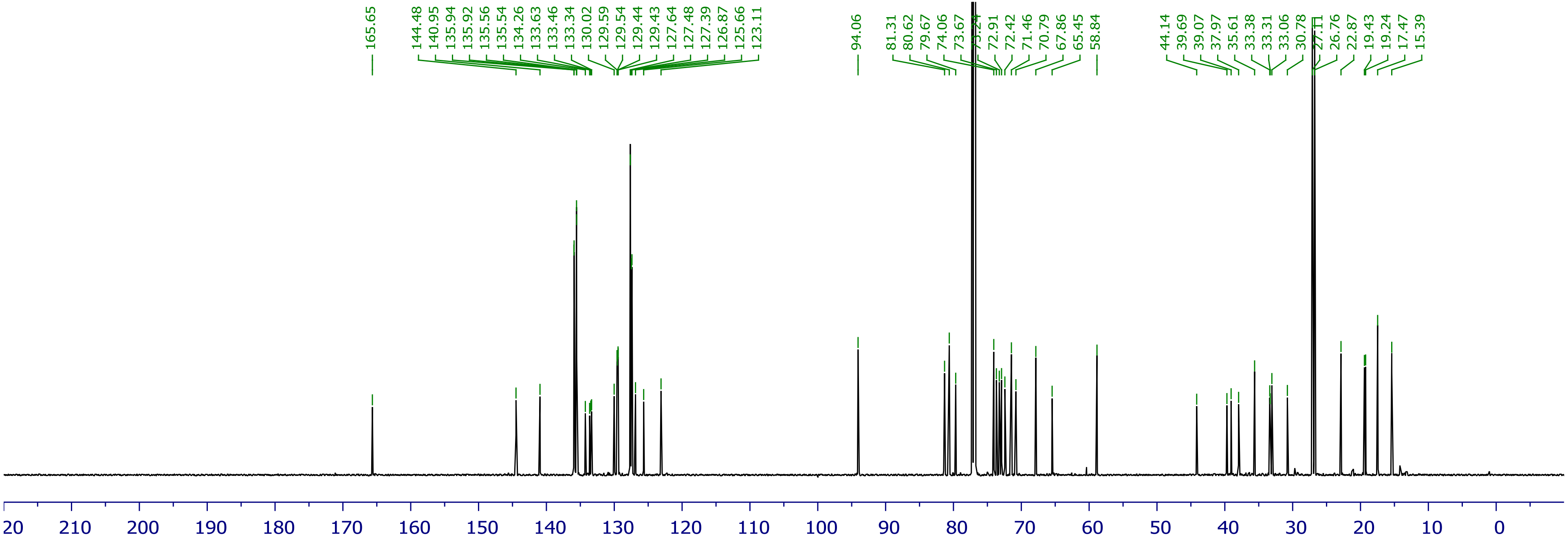
11-*epi*-**72a**



6 wt% impurity:

11-*epi*-**72b**


11-*epi*-**72c**
OTBDPS
TBDPSO
O
O
O
H
O
O
HO
OMe
OH
8.35
12.45
1.02
1.00
0.99
1.06
1.03
1.05
1.03
1.06
1.05
1.03
6.19
3.01
1.02
1.20
1.06
1.02
1.03
1.15
6.08
1.12
1.14
1.14
2.29
2.29
4.05
2.13
9.04
9.04
3.10
3.03
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


165.65
144.48
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135.94
135.92
135.56
135.54
134.26
133.63
133.46
133.34
130.02
129.59
129.54
129.44
129.43
127.64
127.48
127.39
126.87
125.66
123.11
94.06
81.31
80.62
79.67
74.06
73.67
73.24
72.91
72.42
71.46
70.79
67.86
65.45
58.84
44.14
39.69
39.07
37.97
35.61
33.38
33.31
33.06
30.78
27.11
26.76
22.87
19.43
19.24
17.47
15.39
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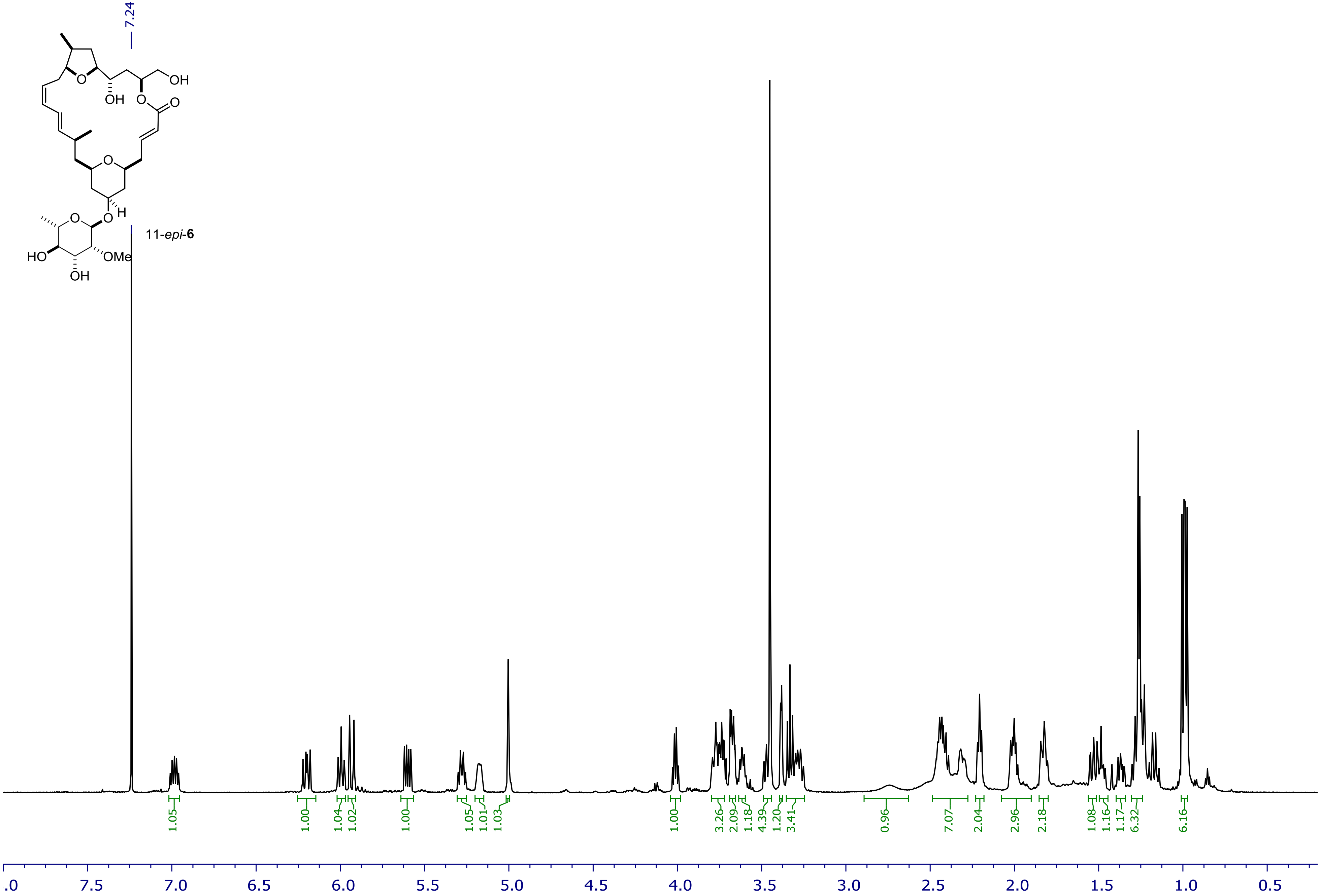
7.24
OH
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OH
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H
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HO
OMe
OH
11-epi-6
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1.02
1.00
1.05
1.01
1.03
1.00
3.26
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1.18
4.39
1.20
3.41
0.96
7.07
2.04
2.96
2.18
1.08
1.16
1.17
6.32
6.16
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6.5
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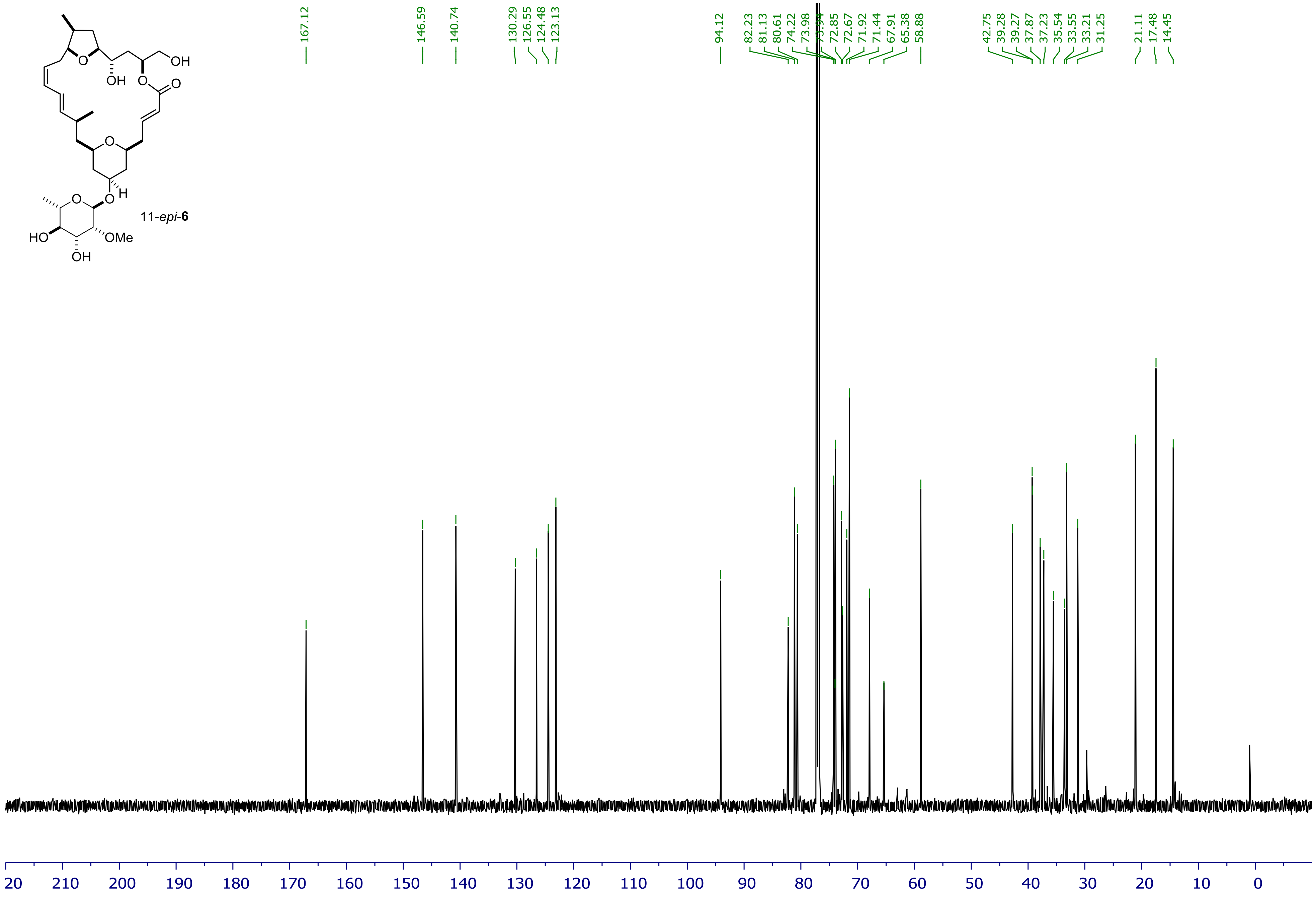

11-*epi*-**6**

167.12
146.59
140.74
130.29
126.55
124.48
123.13
94.12
82.23
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80.61
74.22
73.98
73.94
72.85
72.67
71.92
71.44
67.91
65.38
58.88
42.75
39.28
39.27
37.87
37.23
35.54
33.55
33.21
31.25
21.11
17.48
14.45
20
210
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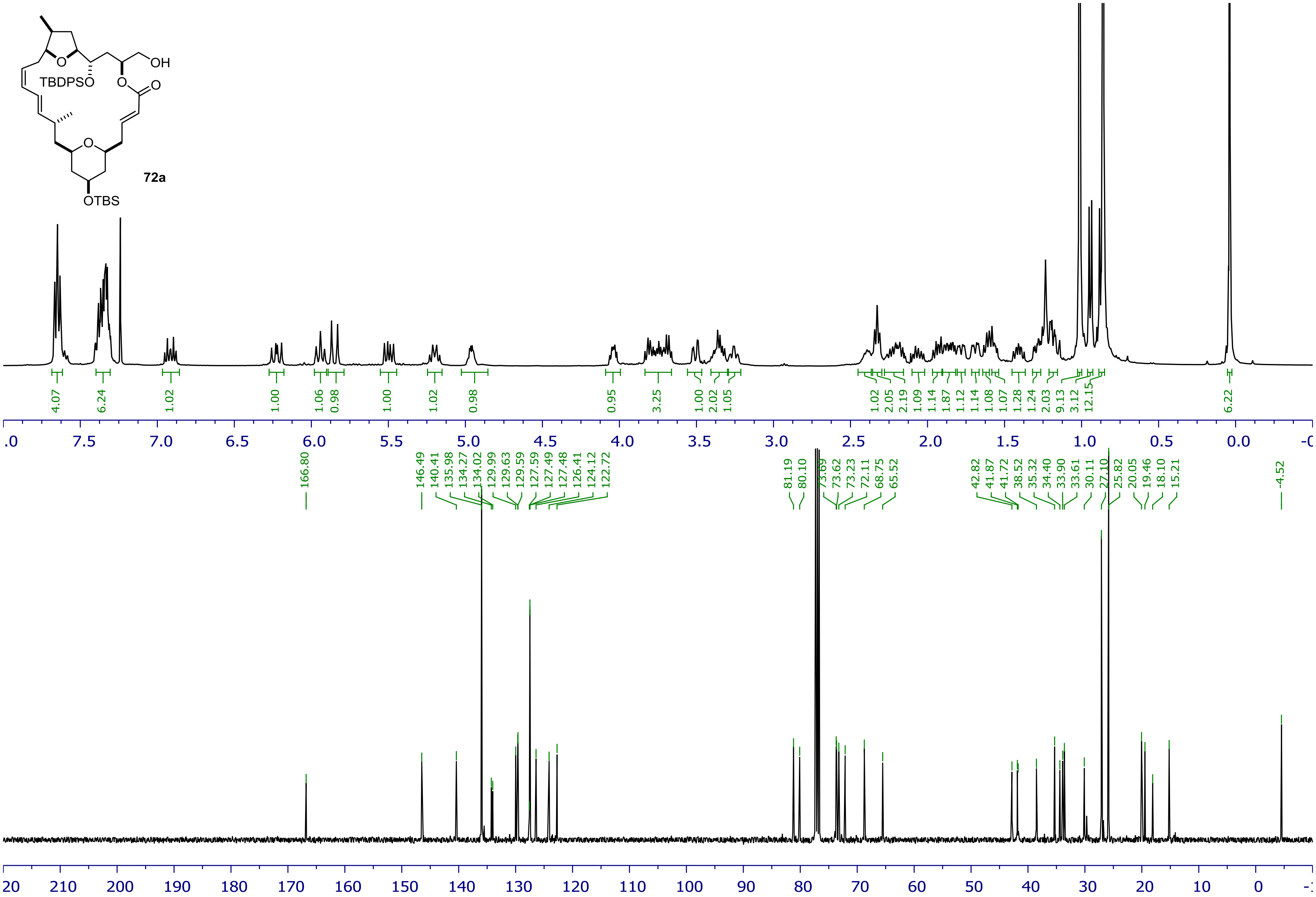
OH
TBDPSO
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O
O
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OTBS
72a
4.07
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1.02
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0.95
3.25
1.00
2.02
1.05
1.02
2.05
2.19
1.09
1.14
1.87
1.12
1.14
1.08
1.07
1.28
1.24
2.03
9.13
3.12
12.15
6.22
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.5
1.0
0.5
0.0
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166.80
146.49
140.41
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134.27
134.02
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126.41
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73.23
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42.82
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41.72
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35.32
34.40
33.90
33.61
30.11
27.10
25.82
20.05
19.46
18.10
15.21
-4.52
20
210
200
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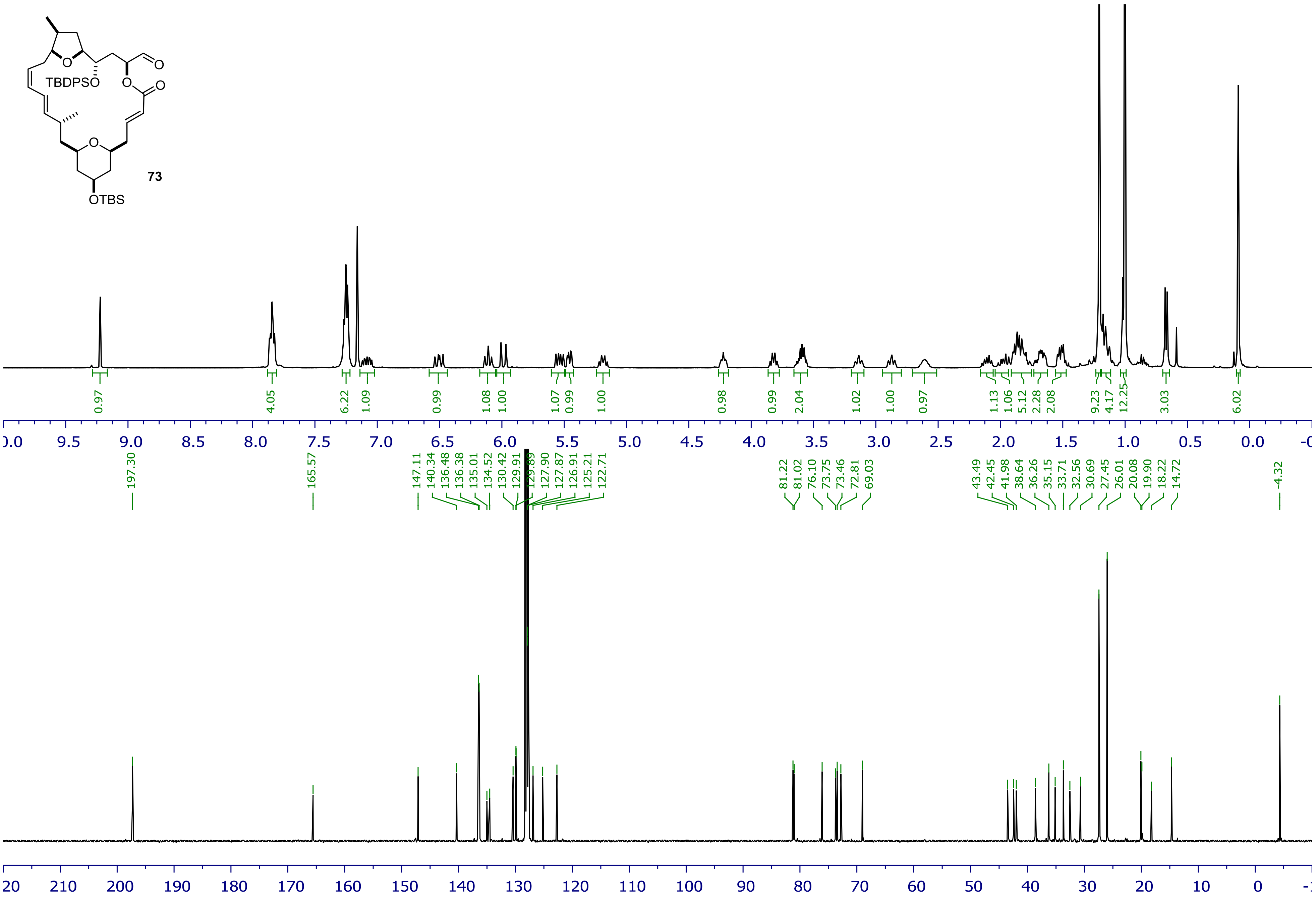

73

TBDPSO
O
OTBS
0.97
4.05
6.22
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1.00
0.98
0.99
2.04
1.02
1.00
0.97
1.13
1.06
5.12
2.28
2.08
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4.17
12.25
3.03
6.02
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
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165.57
147.11
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127.87
126.91
125.21
122.71
81.22
81.02
76.10
73.75
73.46
72.81
69.03
43.49
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20.08
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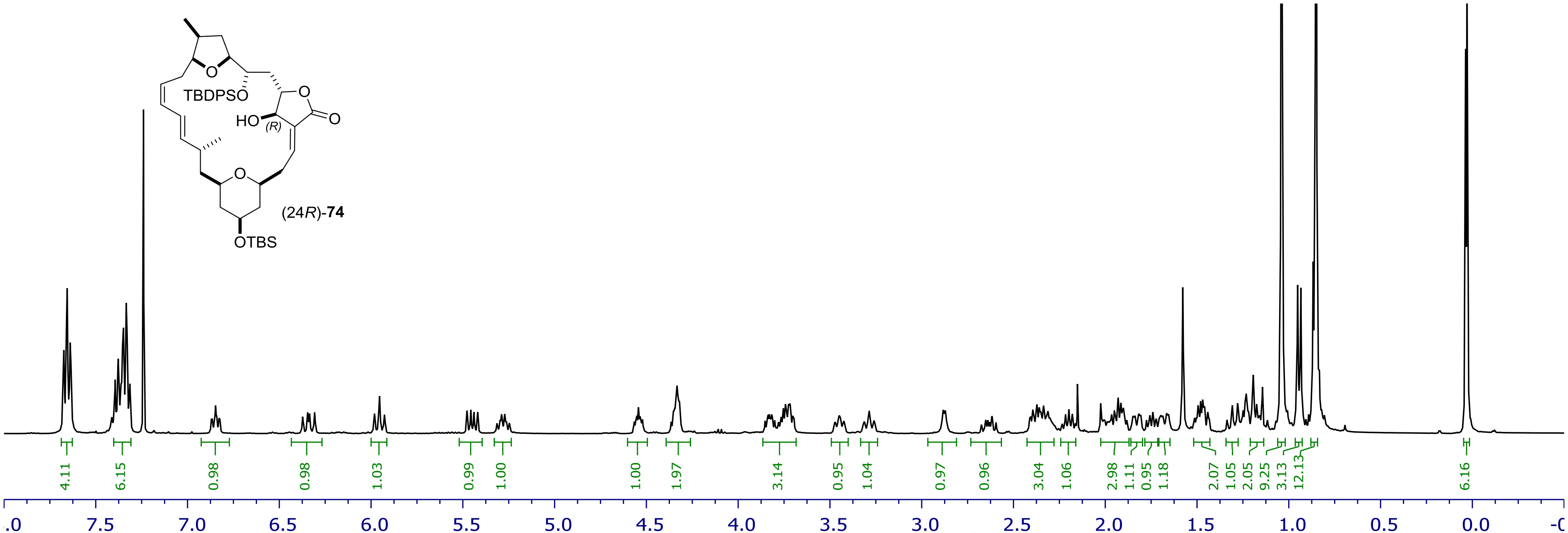
TBDPSO
HO
(R)
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O
O
O
OTBS
(24R)-74
4.11
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0.99
1.00
1.00
1.97
3.14
0.95
1.04
0.97
0.96
3.04
1.06
2.98
1.11
0.95
1.18
2.07
1.05
2.05
9.25
3.13
12.13
6.16
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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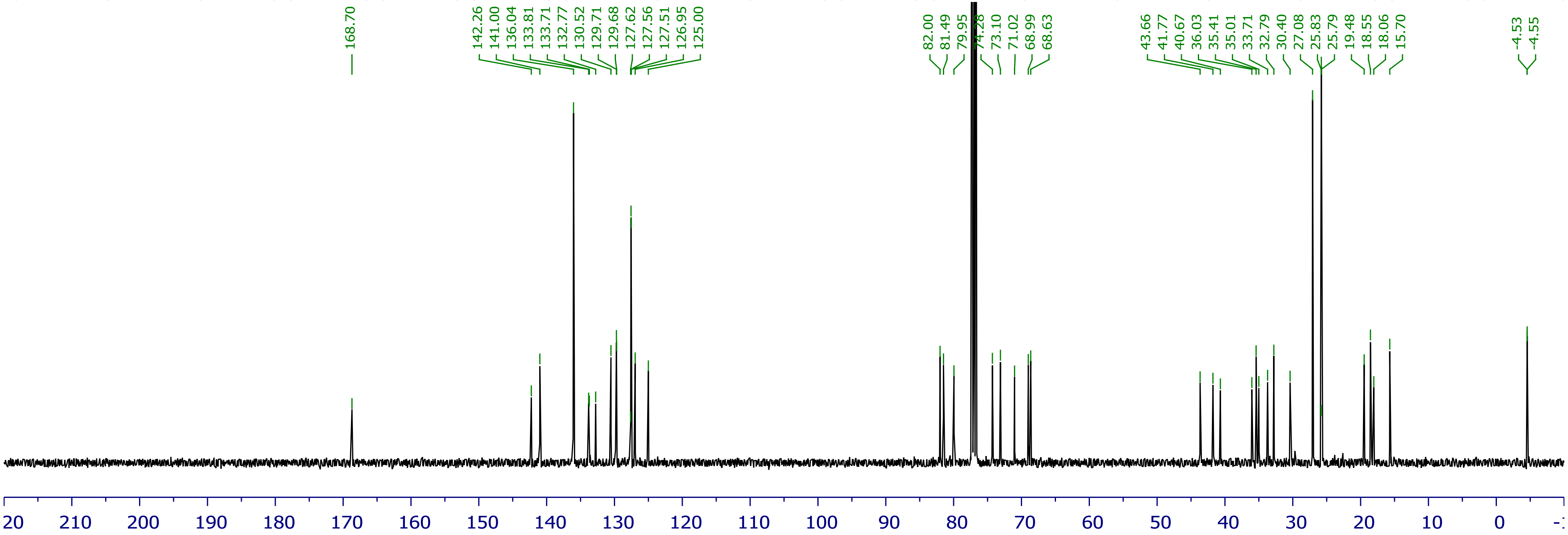
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133.71
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130.52
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129.68
127.62
127.56
127.51
126.95
125.00
82.00
81.49
79.95
74.28
73.10
71.02
68.99
68.63
43.66
41.77
40.67
36.03
35.41
35.01
33.71
32.79
30.40
27.08
25.83
25.79
19.48
18.55
18.06
15.70
-4.53
-4.55
20
210
200
190
180
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140
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100
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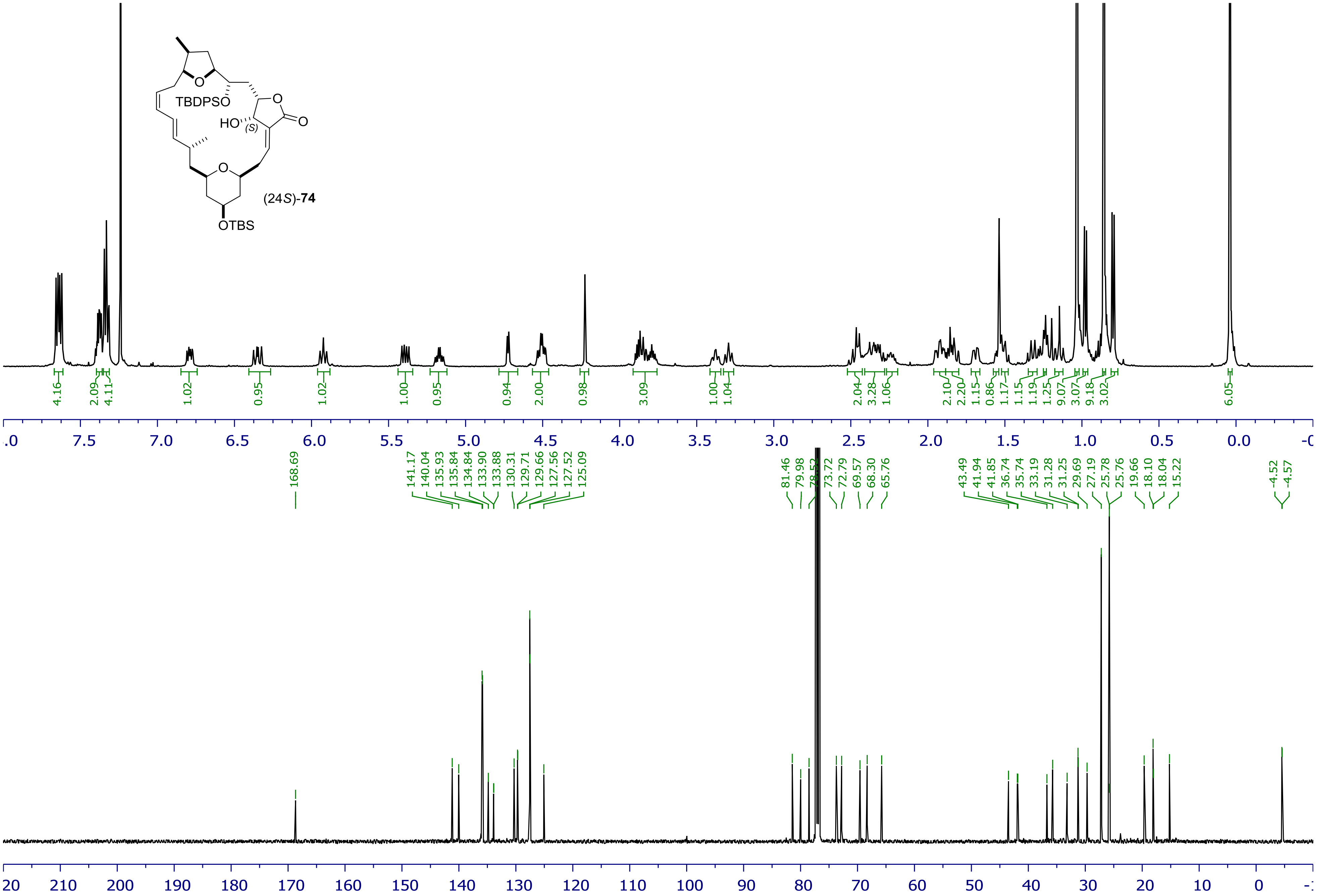
-:



TBDPSO
HO
(S)
O
O
O
O
OTBS
4.16
2.09
4.11
1.02
0.95
1.02
1.00
0.95
0.94
2.00
0.98
3.09
1.00
1.04
2.04
3.28
1.06
2.10
2.20
1.15
0.86
1.17
1.15
1.19
1.25
9.07
3.07
9.18
3.02
6.05
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
168.69
141.17
140.04
135.93
135.84
134.84
133.90
133.88
130.31
129.71
129.66
127.56
127.52
125.09
81.46
79.98
78.52
73.72
72.79
69.57
68.30
65.76
43.49
41.94
41.85
36.74
35.74
33.19
31.28
31.25
29.69
27.19
25.78
25.76
19.66
18.10
18.04
15.22
-4.52
-4.57
20
210
200
190
180
170
160
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140
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120
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100
90
80
70
60
50
40
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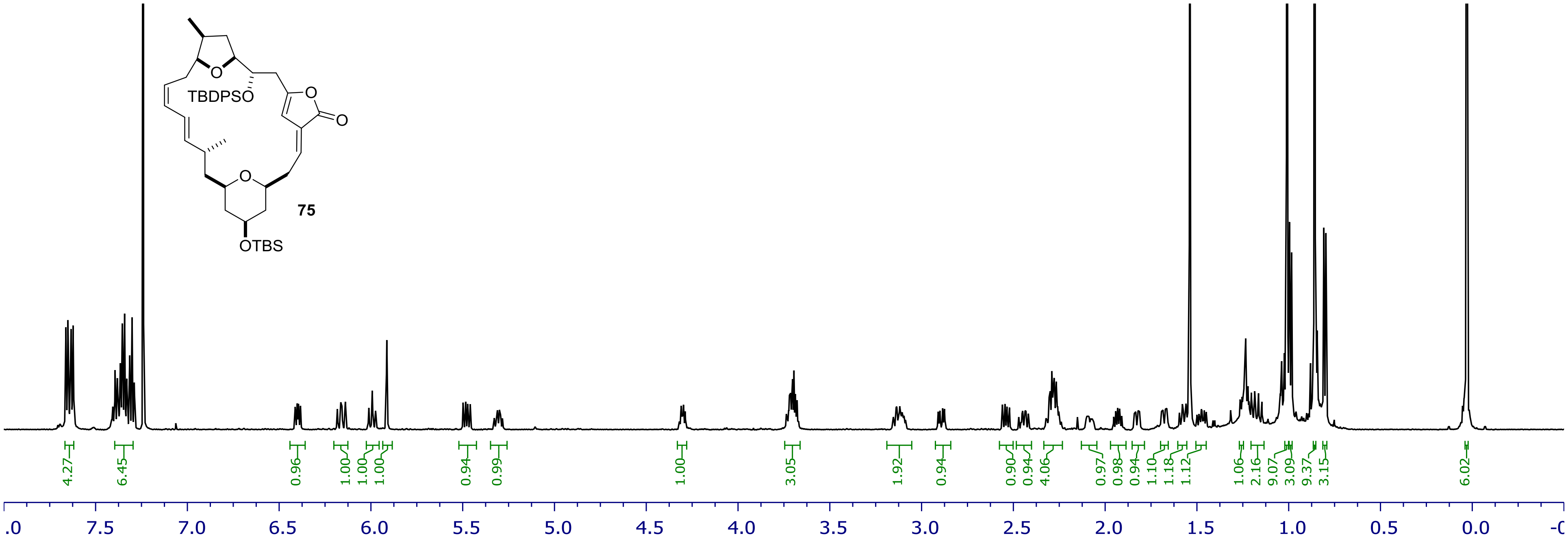
20
10
0
-:

(24*S*)-**74**


75

TBDPSO
O
O
O
OTBS
4.27
6.45
0.96
1.00
1.00
1.00
0.94
0.99
1.00
3.05
1.92
0.94
0.90
0.94
4.06
0.97
0.98
0.94
1.10
1.18
1.12
1.06
2.16
9.07
3.09
9.37
3.15
6.02
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
1.0
0.5
0.0
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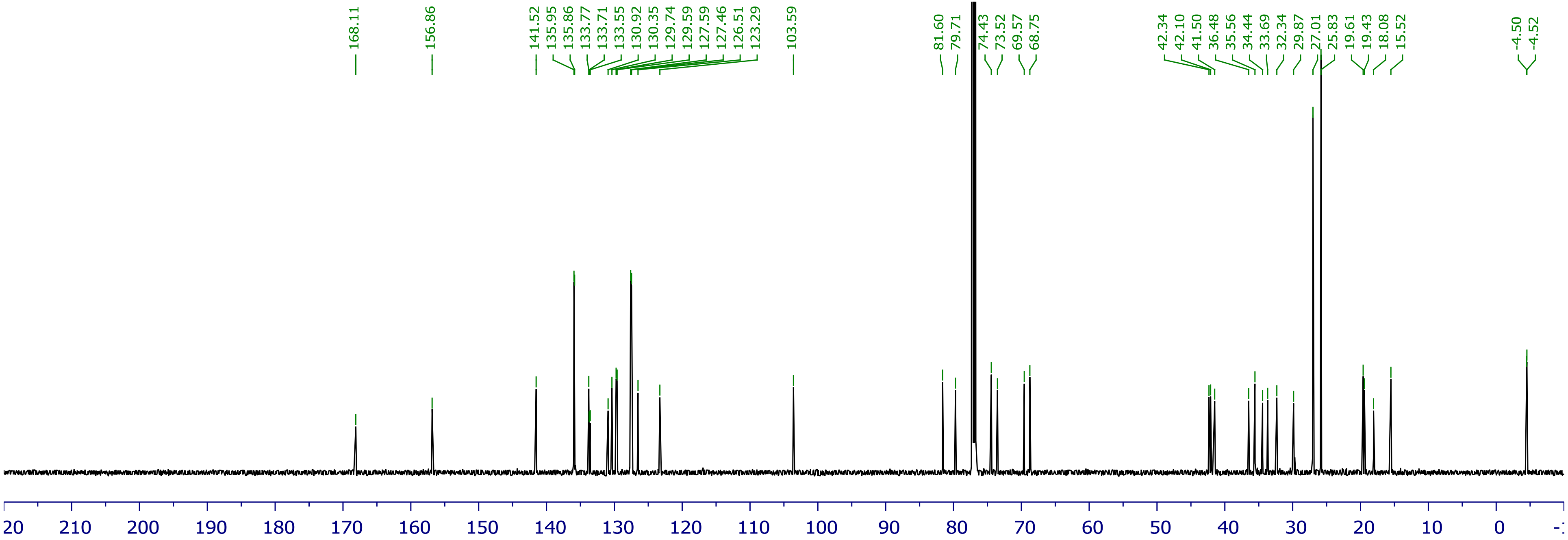

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135.95
135.86
133.77
133.71
133.55
130.92
130.35
129.74
129.59
127.59
127.46
126.51
123.29
103.59
81.60
79.71
74.43
73.52
69.57
68.75
42.34
42.10
41.50
36.48
35.56
34.44
33.69
32.34
29.87
27.01
25.83
19.61
19.43
18.08
15.52
-4.50
-4.52
20
210
200
190
180
170
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150
140
130
120
110
100
90
80
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60
50
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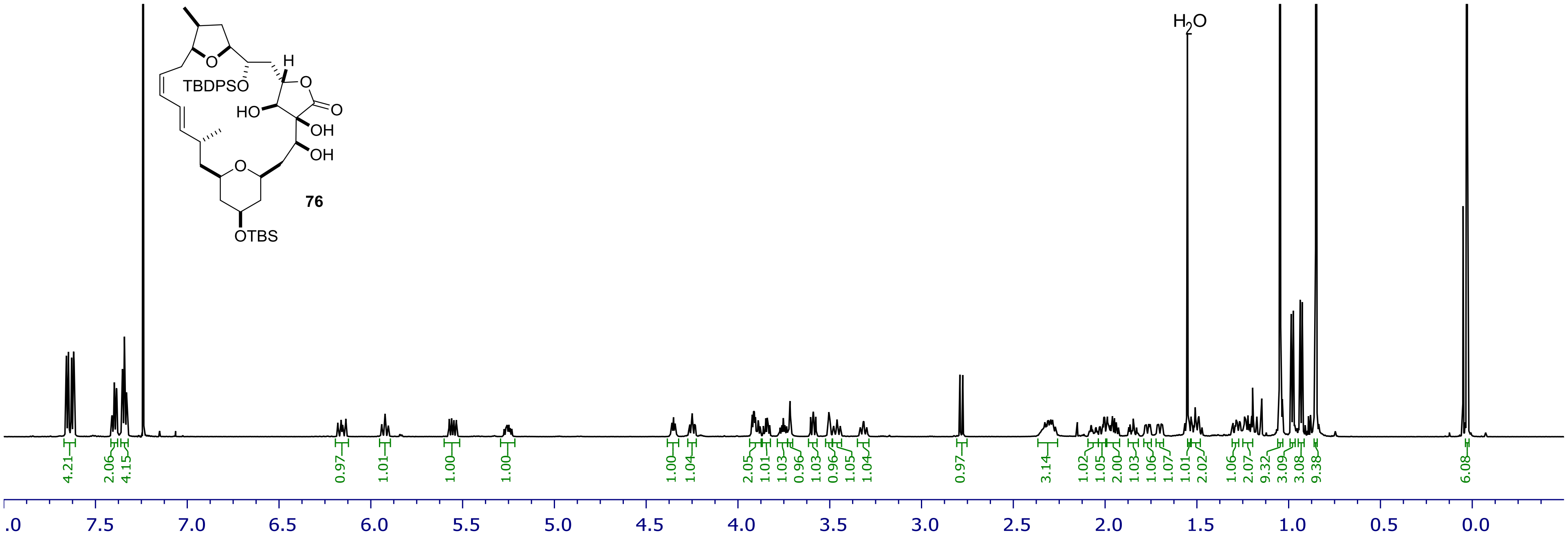
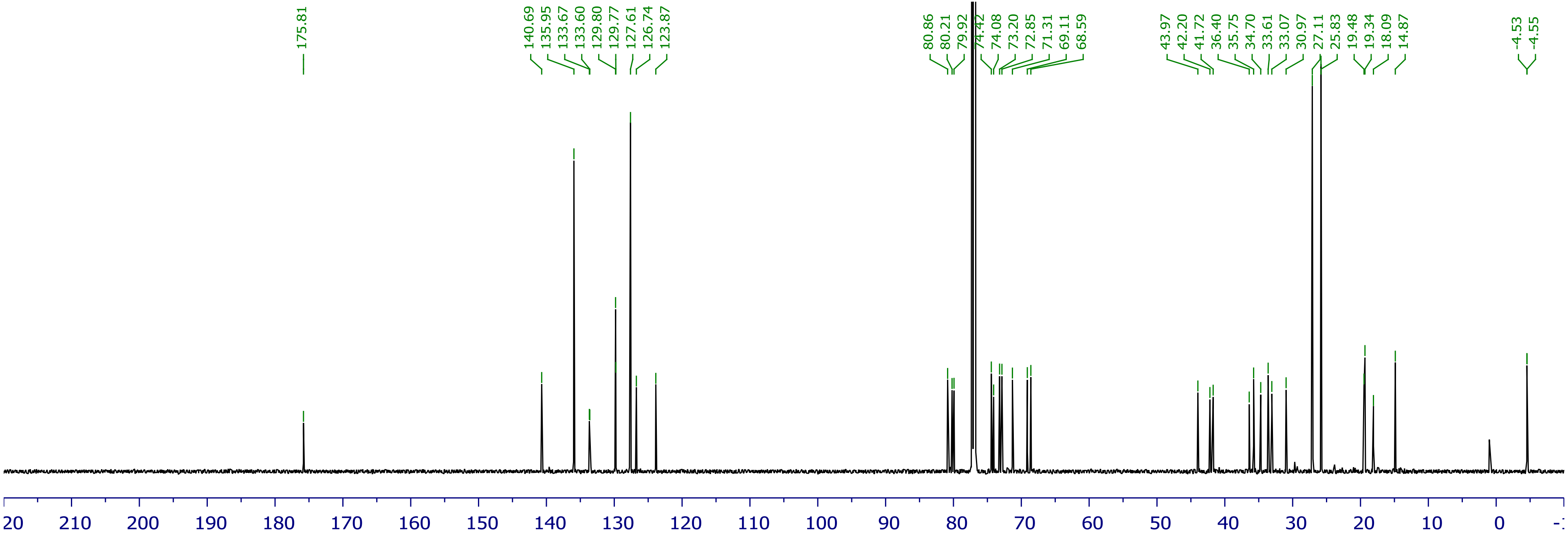
20
10
0
-:


H
O
TBDPSO
HO
OH
OH
O
O
OTBS
H2O
4.21
2.06
4.15
0.97
1.01
1.00
1.00
1.00
1.04
2.05
1.01
1.03
0.96
1.03
0.96
1.05
1.04
0.97
3.14
1.02
1.05
2.00
1.03
1.06
1.07
1.01
2.02
1.06
2.07
9.32
3.09
3.08
9.38
6.08
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

76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129.80
129.77
127.61
126.74
123.87
80.86
80.21
79.92
74.42
74.08
73.20
72.85
71.31
69.11
68.59
43.97
42.20
41.72
36.40
35.75
34.70
33.61
33.07
30.97
27.11
25.83
19.48
19.34
18.09
14.87
-4.53
-4.55
20
210
200
190
180
170
160
150
140
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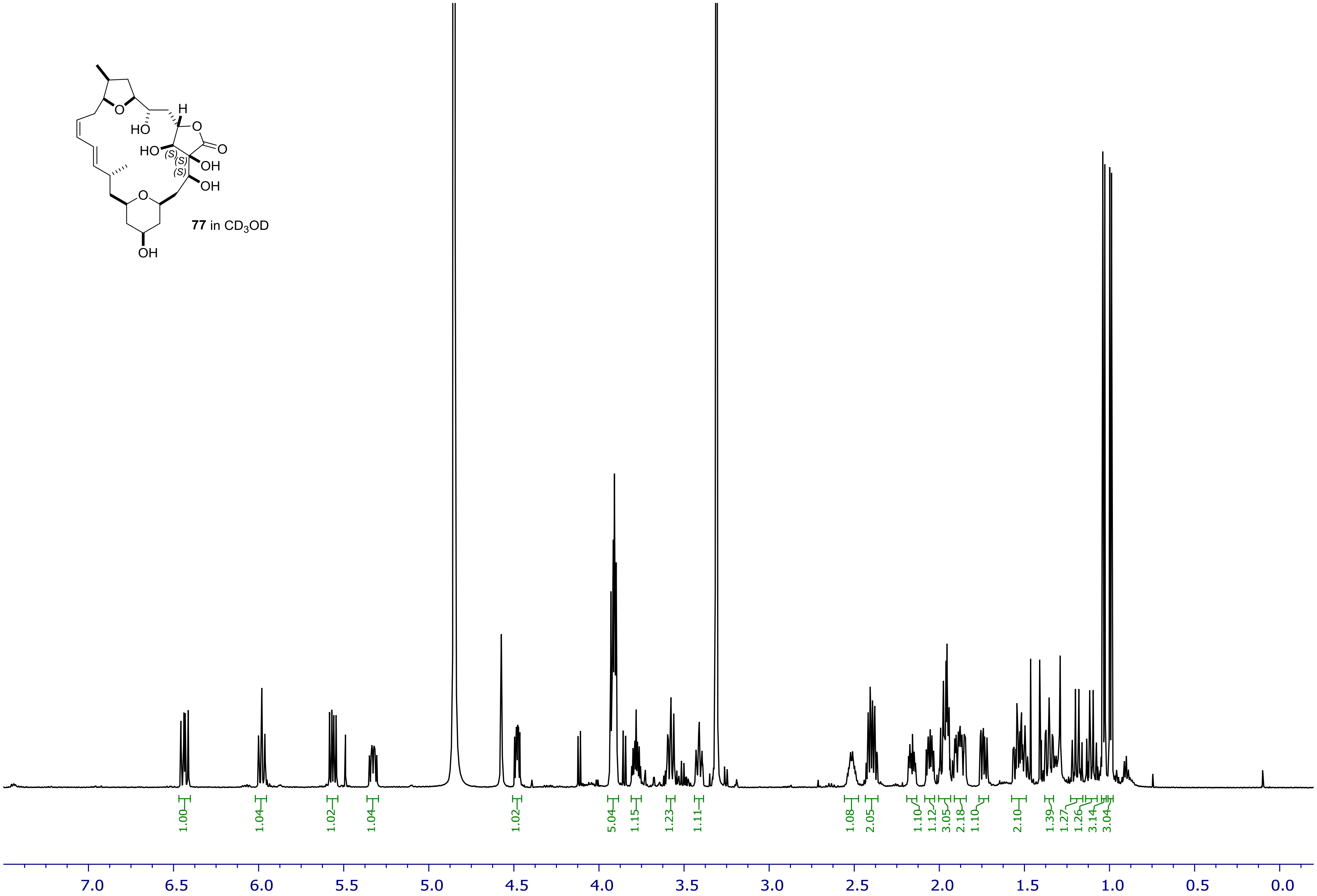
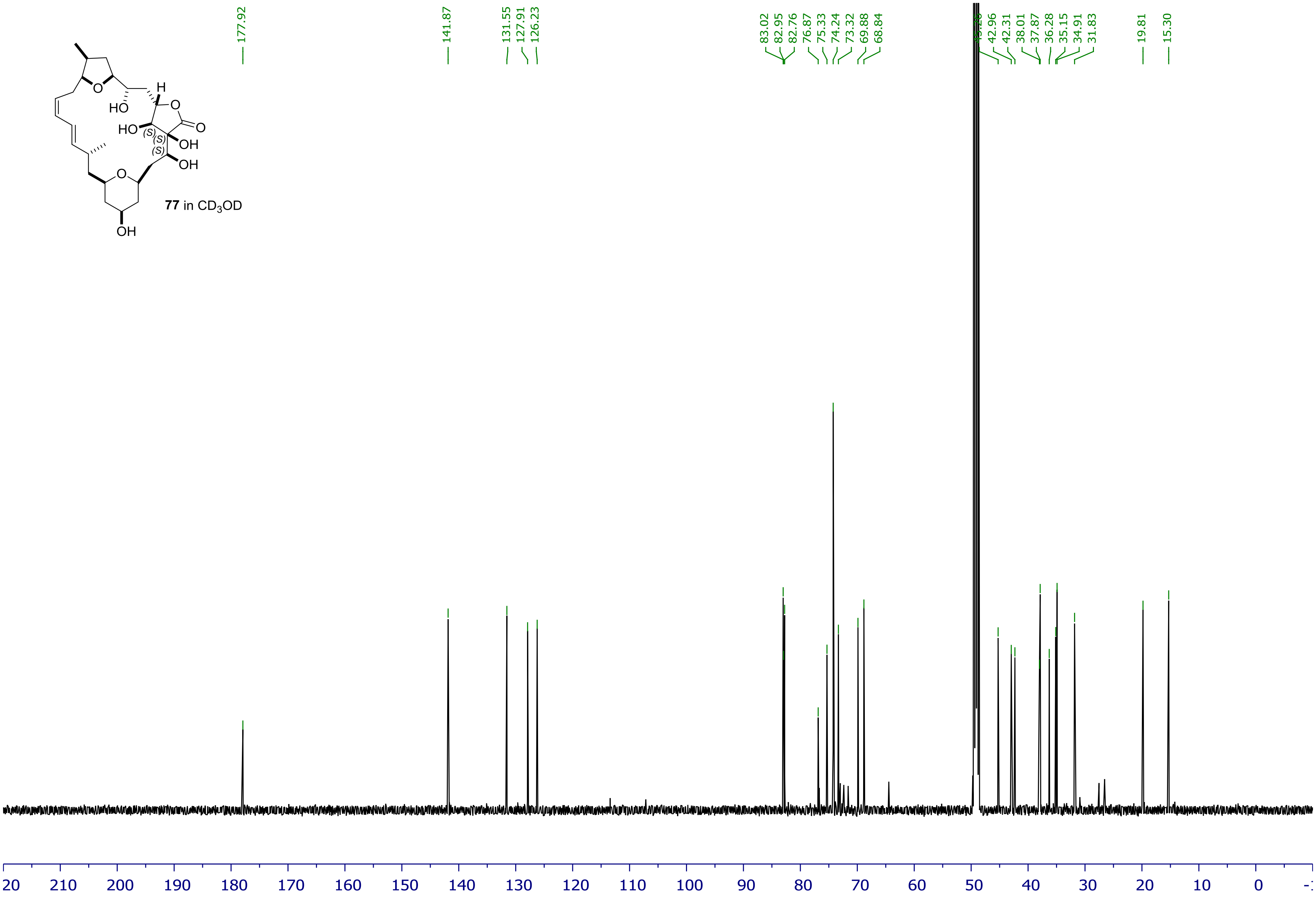
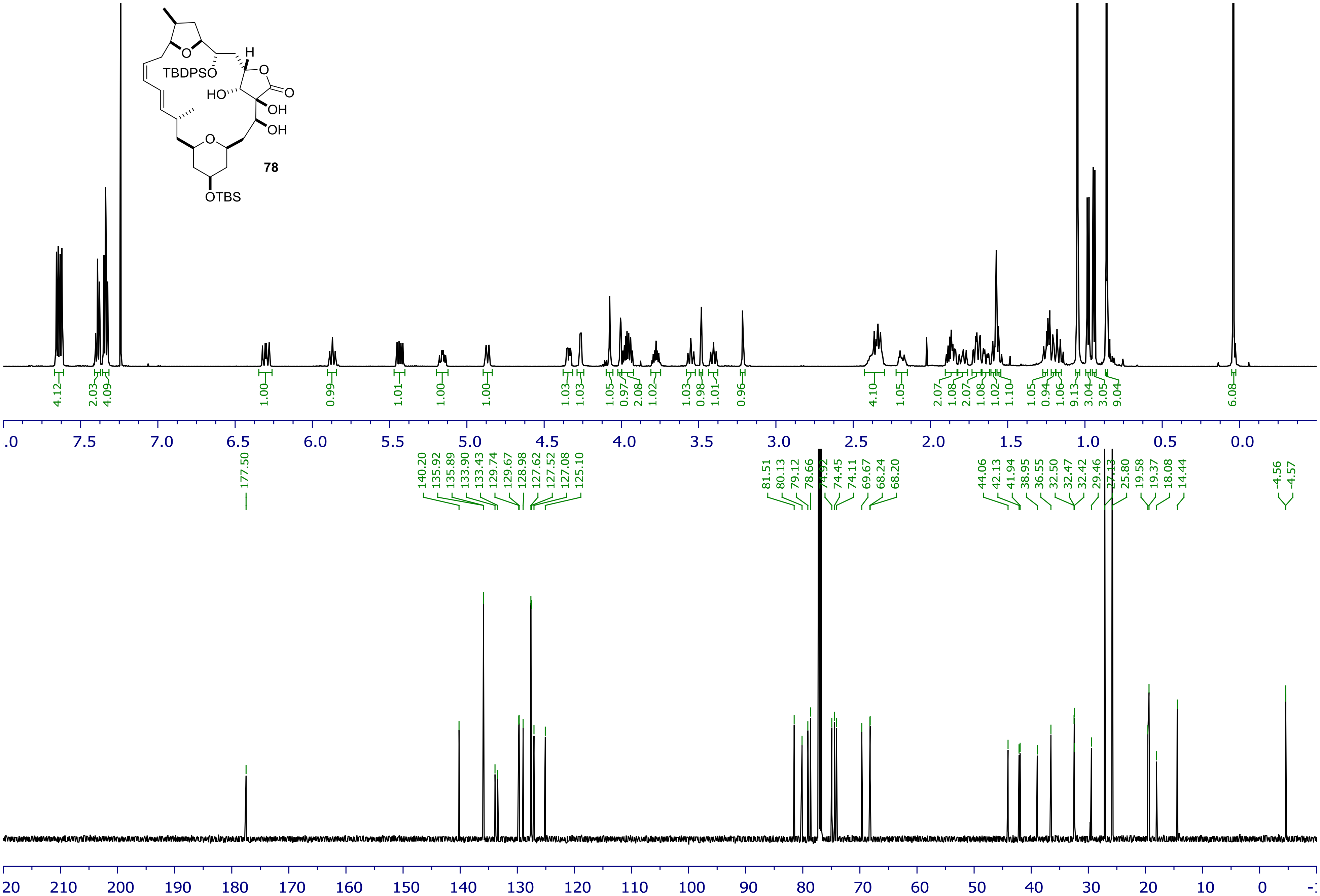
120
110
100
90
80
70
60
50
40
30
20
10
0
-:


HO
H
O
O
HO
(S)
(S)
(S)
OH
OH
O
O
OH
77 in CD_3OD
1.00
1.04
1.02
1.04
1.02
5.04
1.15
1.23
1.11
1.08
2.05
1.10
1.12
3.05
2.18
1.10
2.10
1.39
1.27
1.26
3.14
3.04
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



77 in CD$_3$OD

177.92
141.87
131.55
127.91
126.23
83.02
82.95
82.76
76.87
75.33
74.24
73.32
69.88
68.84
45.26
42.96
42.31
38.01
37.87
36.28
35.15
34.91
31.83
19.81
15.30
HO
O
H
O
O
HO
(S)
(S)
(S)
OH
OH
O
OH
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


TBDPSO
O
H
O
O
HO
OH
OH
O
OTBS
78
4.12
2.03
4.09
1.00
0.99
1.01
1.00
1.00
1.03
1.03
1.05
0.97
2.08
1.02
1.03
0.98
1.01
0.96
4.10
1.05
2.07
1.08
2.07
1.08
1.02
1.10
1.05
0.94
1.06
9.13
3.04
3.05
9.04
6.08
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
177.50
140.20
135.92
135.89
133.90
133.43
129.74
129.67
128.98
127.62
127.52
127.08
125.10
81.51
80.13
79.12
78.66
74.92
74.45
74.11
69.67
68.24
68.20
44.06
42.13
41.94
38.95
36.55
32.50
32.47
32.42
29.46
27.13
25.80
19.58
19.37
18.08
14.44
-4.56
-4.57
20
210
200
190
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170
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150
140
130
120
110
100
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80
70
60
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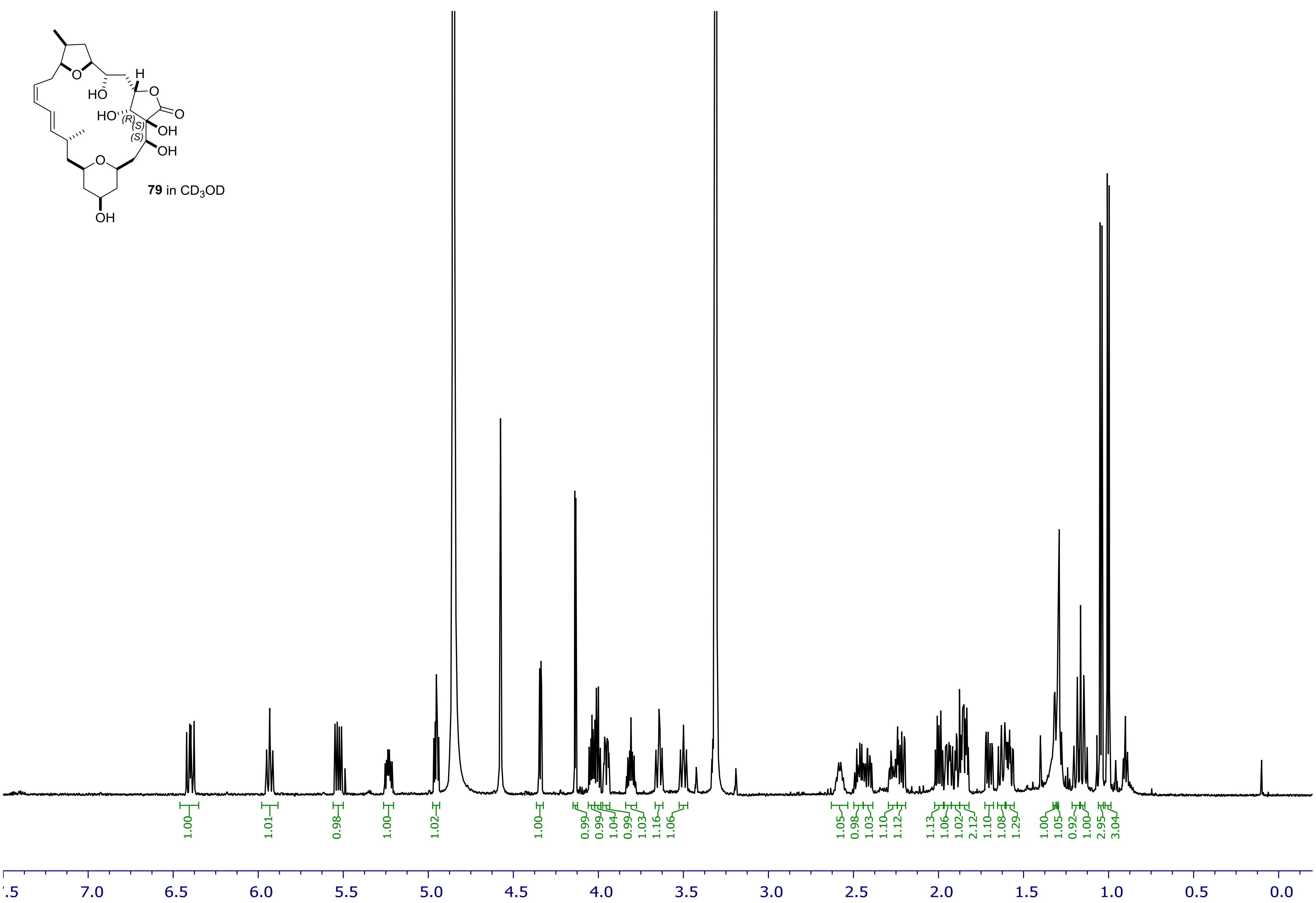
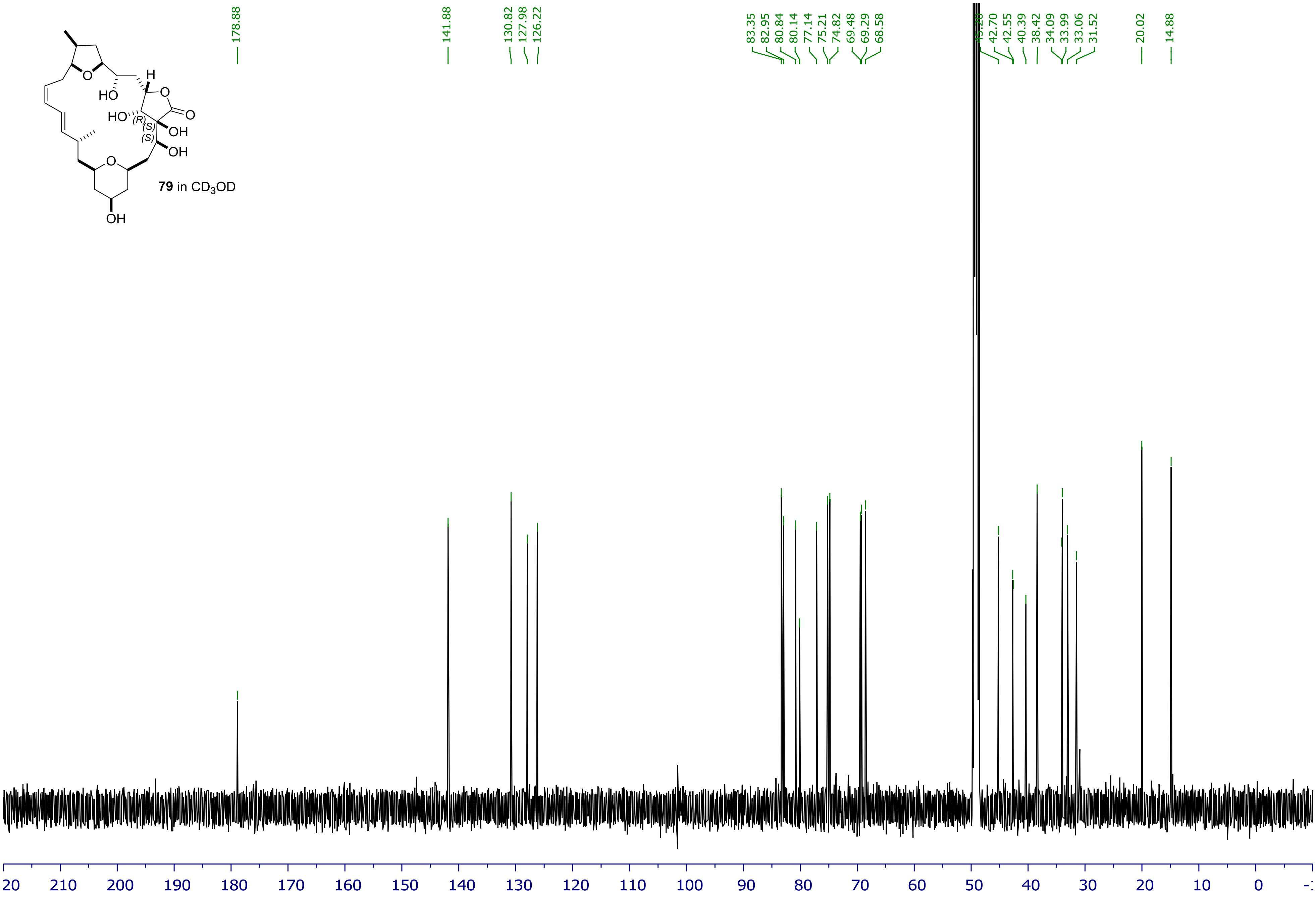
40
30
20
10
0


O
H
HO
O
O
HO
(R)
(S)
(S)
OH
OH
O
OH
79 in CD$_3$OD
1.00
1.01
0.98
1.00
1.02
1.00
0.99
0.99
1.04
0.99
1.03
1.16
1.06
1.05
0.98
1.03
1.10
1.12
1.13
1.06
1.02
2.12
1.10
1.08
1.29
1.00
1.05
0.92
1.00
2.95
3.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



79 in CD_3OD

HO
HO
(R)
(S)
(S)
OH
OH
O
O
O
H
OH
O
178.88
141.88
130.82
127.98
126.22
83.35
82.95
80.84
80.14
77.14
75.21
74.82
69.48
69.29
68.58
45.20
42.70
42.55
40.39
38.42
34.09
33.99
33.06
31.52
20.02
14.88
20
210
200
190
180
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140
130
120
110
100
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60
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20
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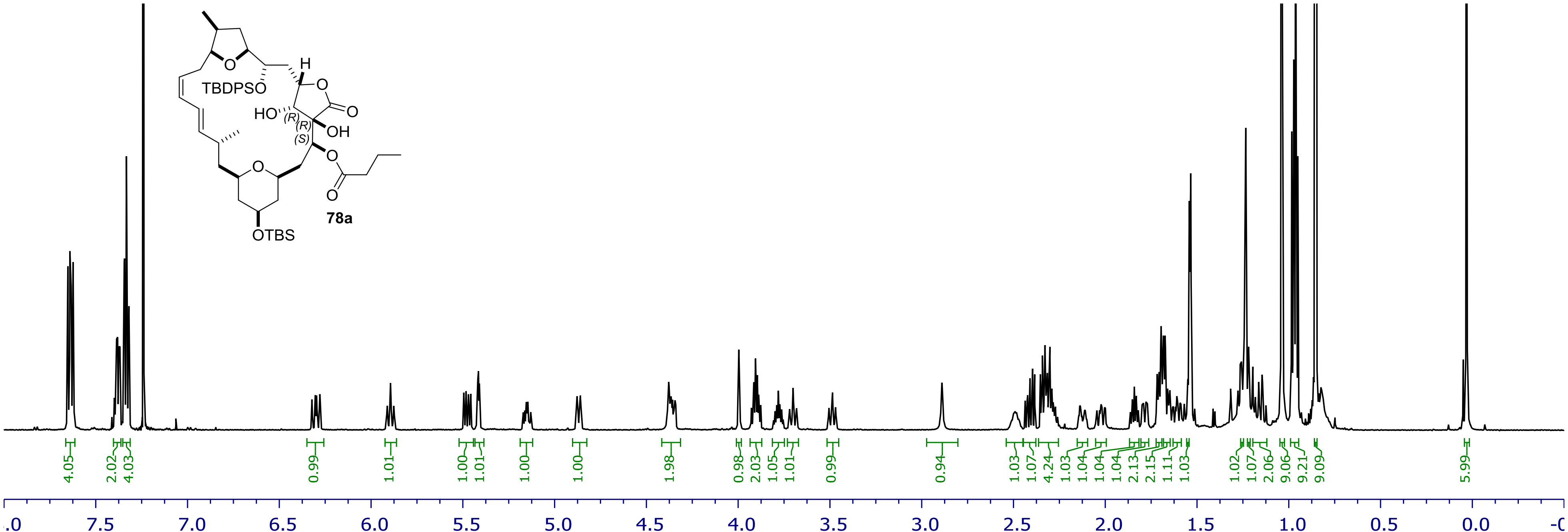
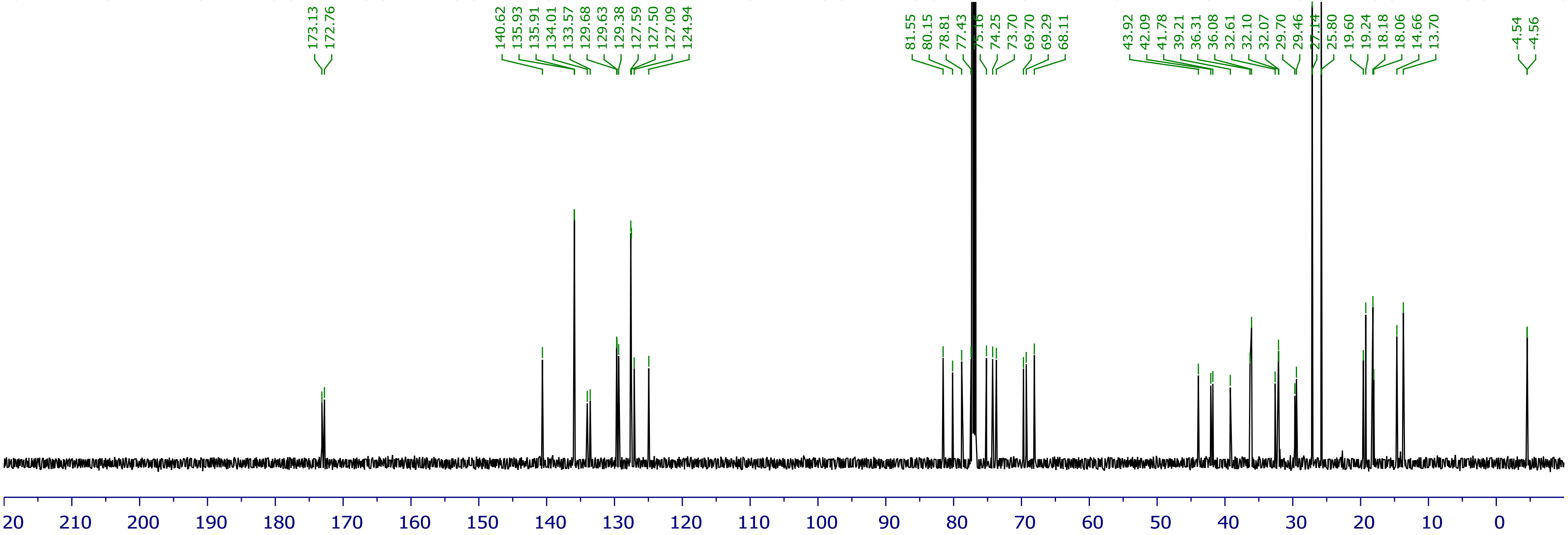
0
-


TBDPSO
H
O
O
HO
(R)
(R)
(S)
OH
O
O
OTBS
4.05
2.02
4.03
0.99
1.01
1.00
1.01
1.00
1.00
1.98
0.98
2.03
1.05
1.01
0.99
0.94
1.03
1.07
4.24
1.03
1.04
1.04
1.04
2.13
2.15
1.11
1.03
1.02
1.07
2.06
9.06
9.21
9.09
5.99
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(

78a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129.68
129.63
129.38
127.59
127.50
127.09
124.94
81.55
80.15
78.81
77.43
75.16
74.25
73.70
69.70
69.29
68.11
43.92
42.09
41.78
39.21
36.31
36.08
32.61
32.10
32.07
29.70
29.46
27.14
25.80
19.60
19.24
18.18
18.06
14.66
13.70
-4.54
-4.56
20
210
200
190
180
170
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140
130
120
110
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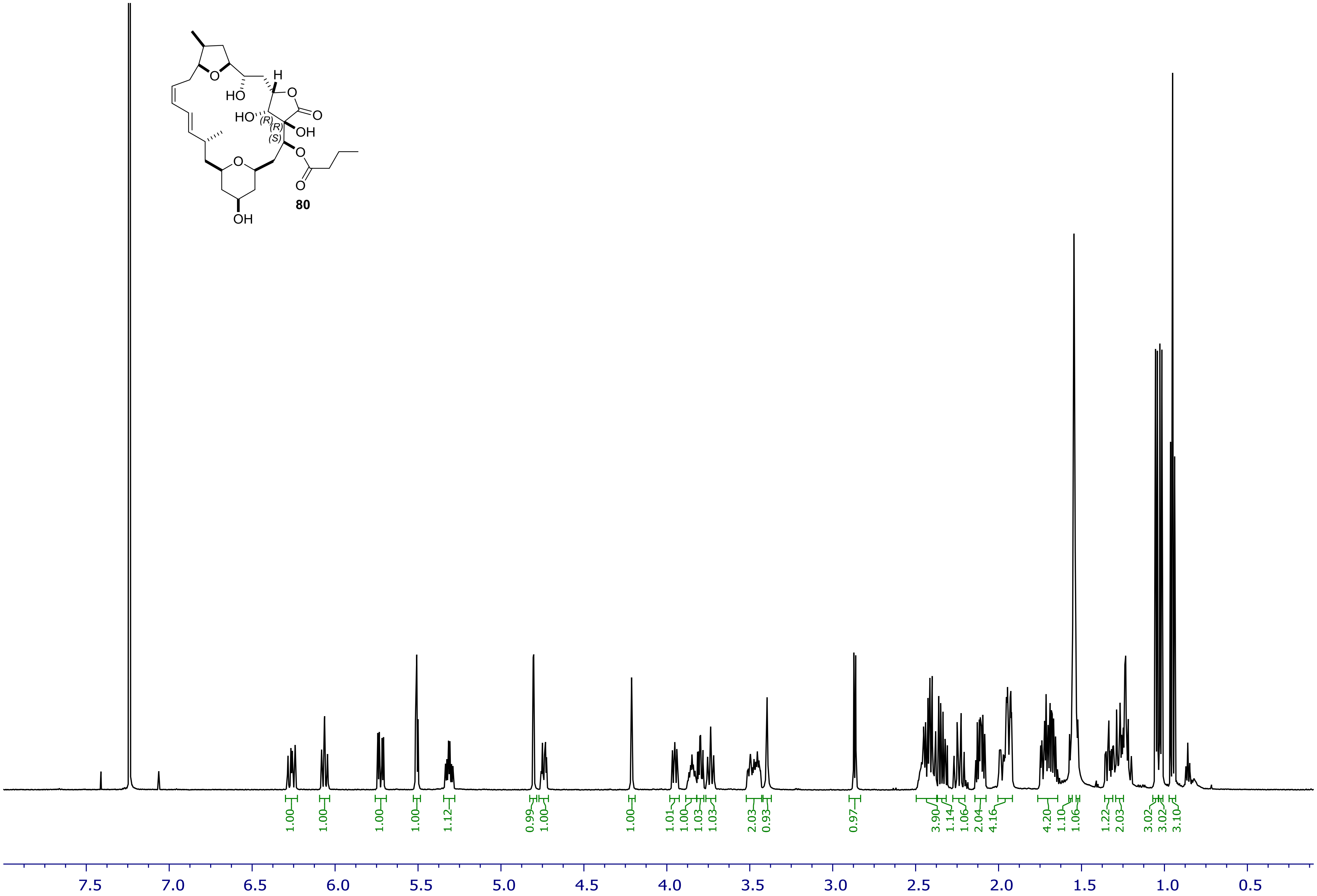
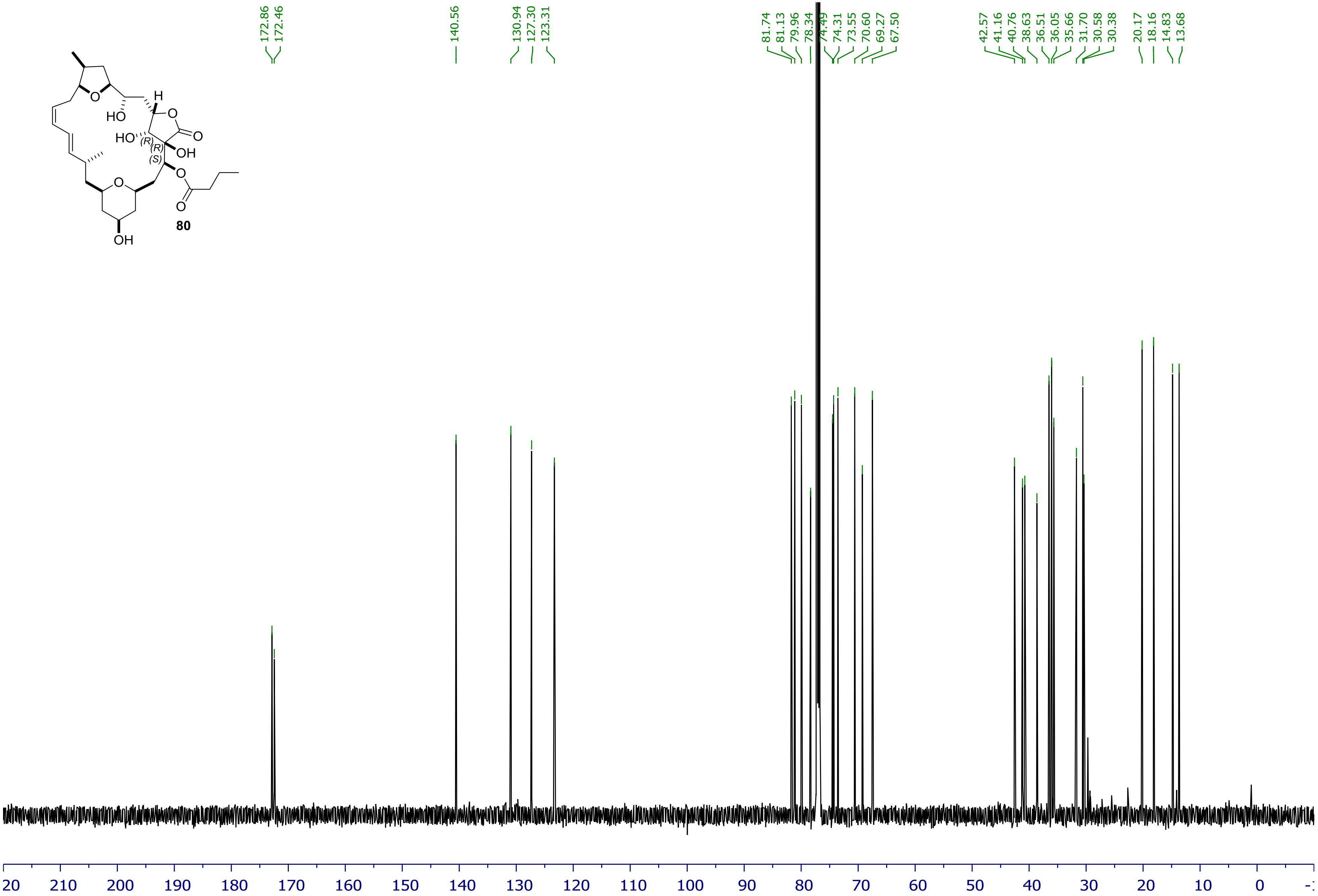
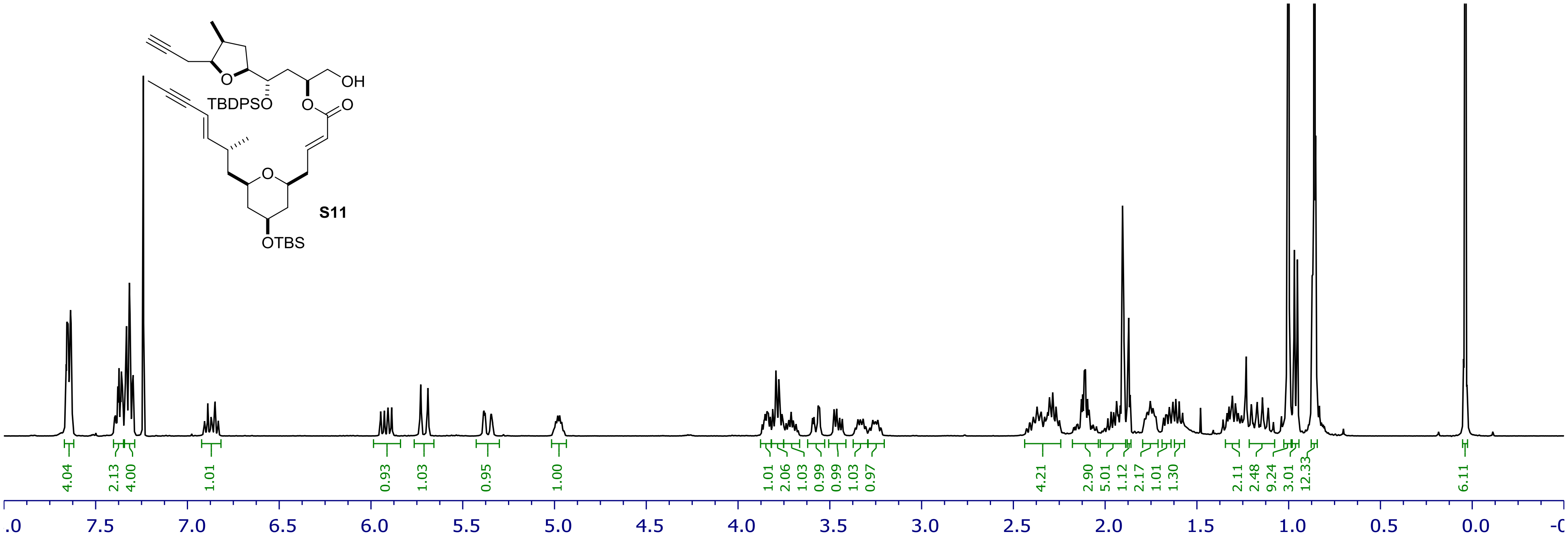
20
10
0

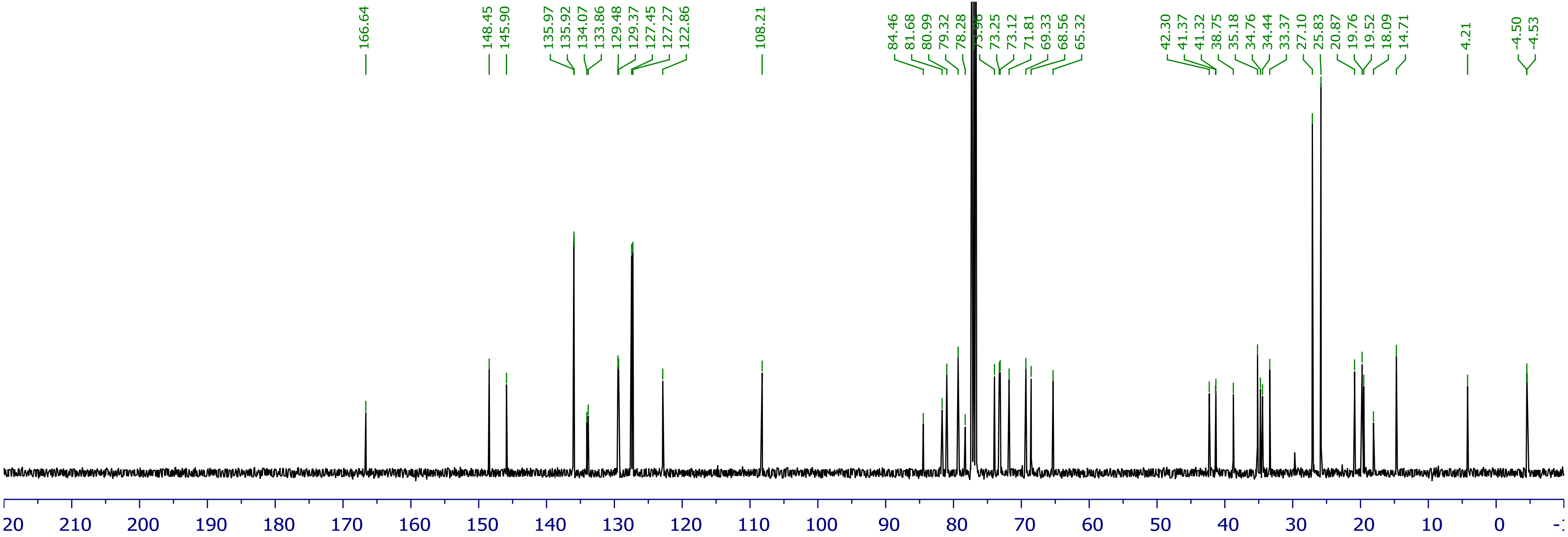

H
O
HO
O
HO
(R)
(R)
O
OH
(S)
O
O
O
OH
80
1.00
1.00
1.00
1.00
1.12
0.99
1.00
1.00
1.01
1.00
1.03
1.03
2.03
0.93
0.97
3.90
1.14
1.06
2.04
4.16
4.20
1.10
1.06
1.22
2.03
3.02
3.02
3.10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

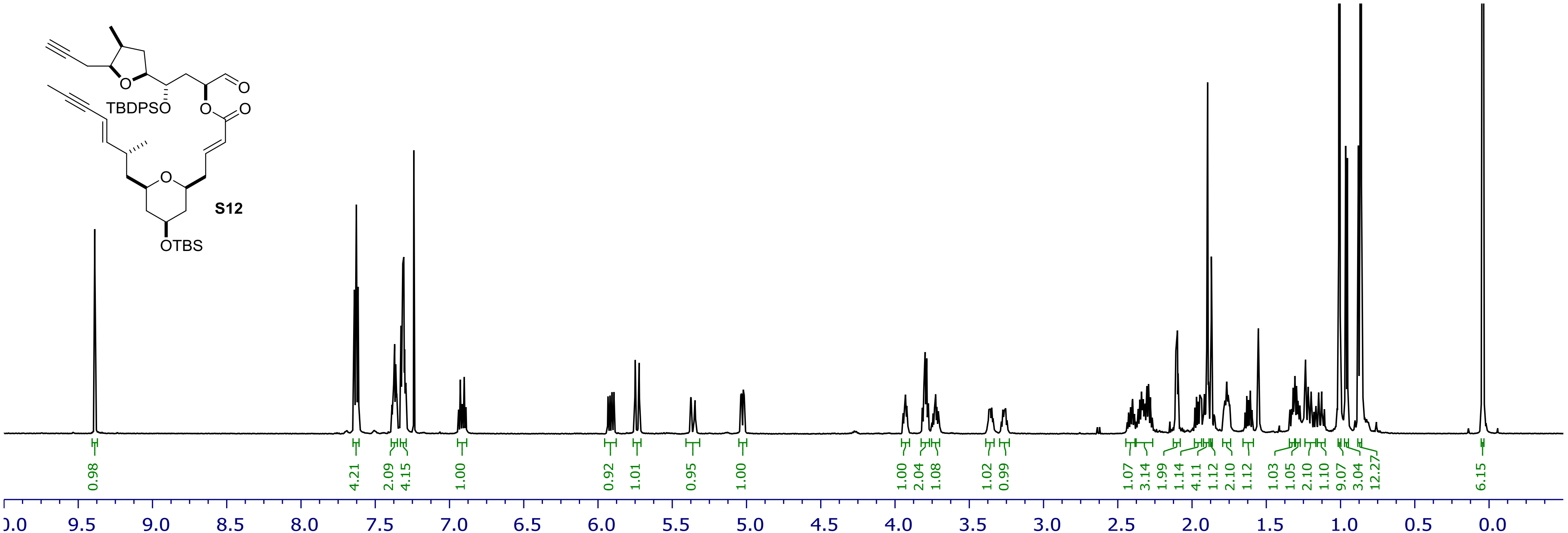

172.86
172.46
140.56
130.94
127.30
123.31
81.74
81.13
79.96
78.34
74.49
74.31
73.55
70.60
69.27
67.50
42.57
41.16
40.76
38.63
36.51
36.05
35.66
31.70
30.58
30.38
20.17
18.16
14.83
13.68
H
O
HO
HO
(R)
(R)
(S)
O
OH
O
O
O
OH
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-

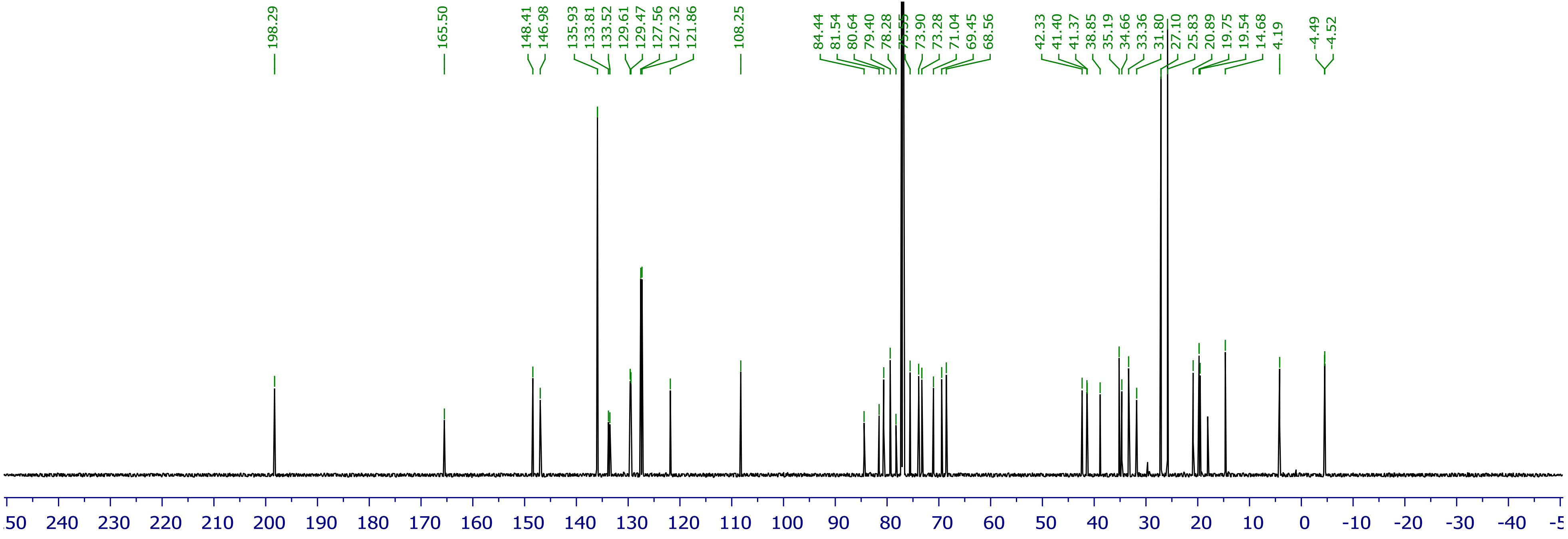
80

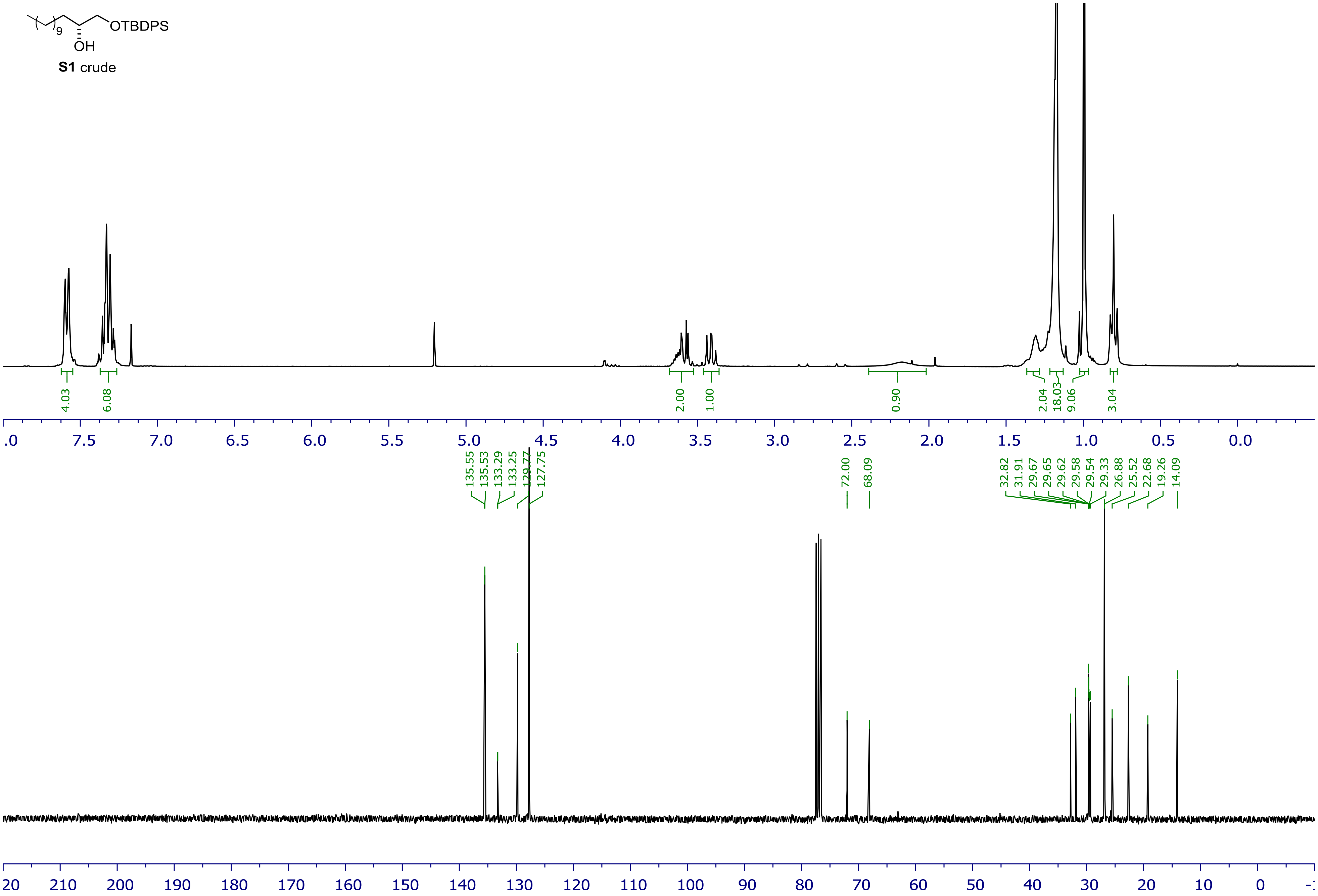

OH
TBDPSO
O
O
O
OTBS
4.04
2.13
4.00
1.01
0.93
1.03
0.95
1.00
1.01
2.06
1.03
0.99
0.99
1.03
0.97
4.21
2.90
5.01
1.12
2.17
1.01
1.30
2.11
2.48
9.24
3.01
12.33
6.11
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

S11


166.64
148.45
145.90
135.97
135.92
134.07
133.86
129.48
129.37
127.45
127.27
122.86
108.21
84.46
81.68
80.99
79.32
78.28
73.25
73.12
71.81
69.33
68.56
65.32
42.30
41.37
41.32
38.75
35.18
34.76
34.44
33.37
27.10
25.83
20.87
19.76
19.52
18.09
14.71
4.21
-4.50
-4.53
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

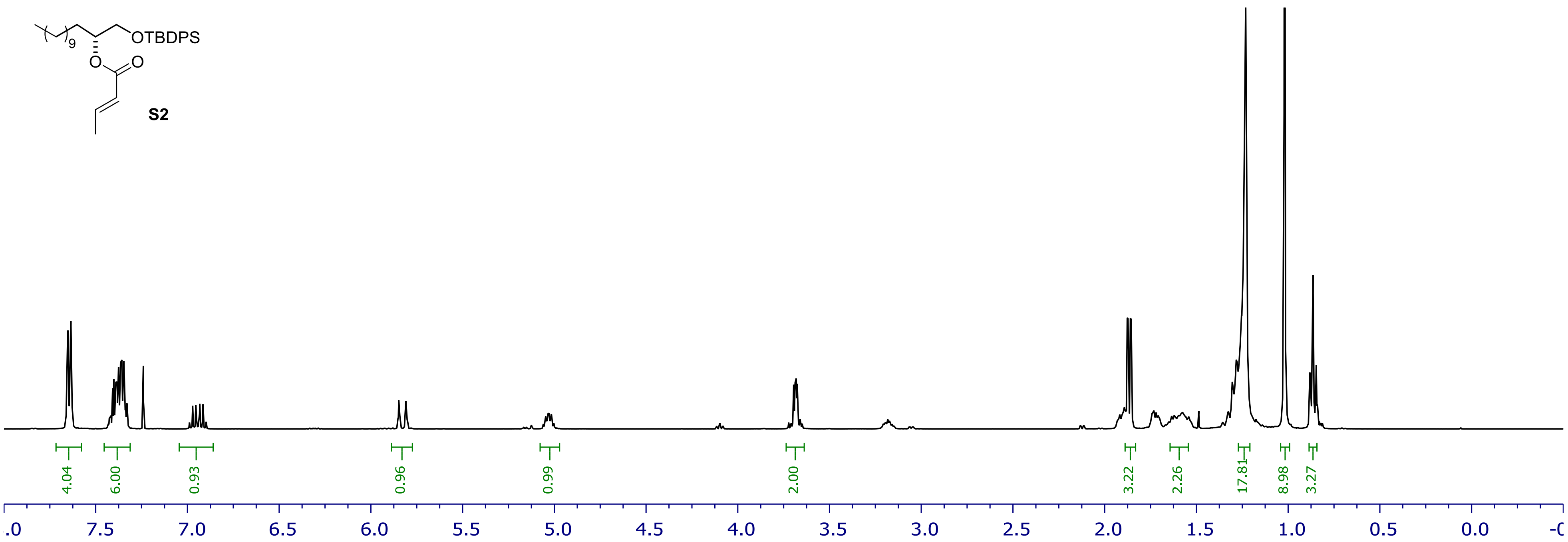

TBDPSO
O
O
O
O
O
OTBS
S12
0.98
4.21
2.09
4.15
1.00
0.92
1.01
0.95
1.00
1.00
2.04
1.08
1.02
0.99
1.07
3.14
1.99
1.14
4.11
1.12
2.10
1.12
1.03
1.05
2.10
1.10
9.07
3.04
12.27
6.15
).0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


198.29
165.50
148.41
146.98
135.93
133.81
133.52
129.61
129.47
127.56
127.32
121.86
108.25
84.44
81.54
80.64
79.40
78.28
75.55
73.90
73.28
71.04
69.45
68.56
42.33
41.40
41.37
38.85
35.19
34.66
33.36
31.80
27.10
25.83
20.89
19.75
19.54
14.68
4.19
-4.49
-4.52
50
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-5



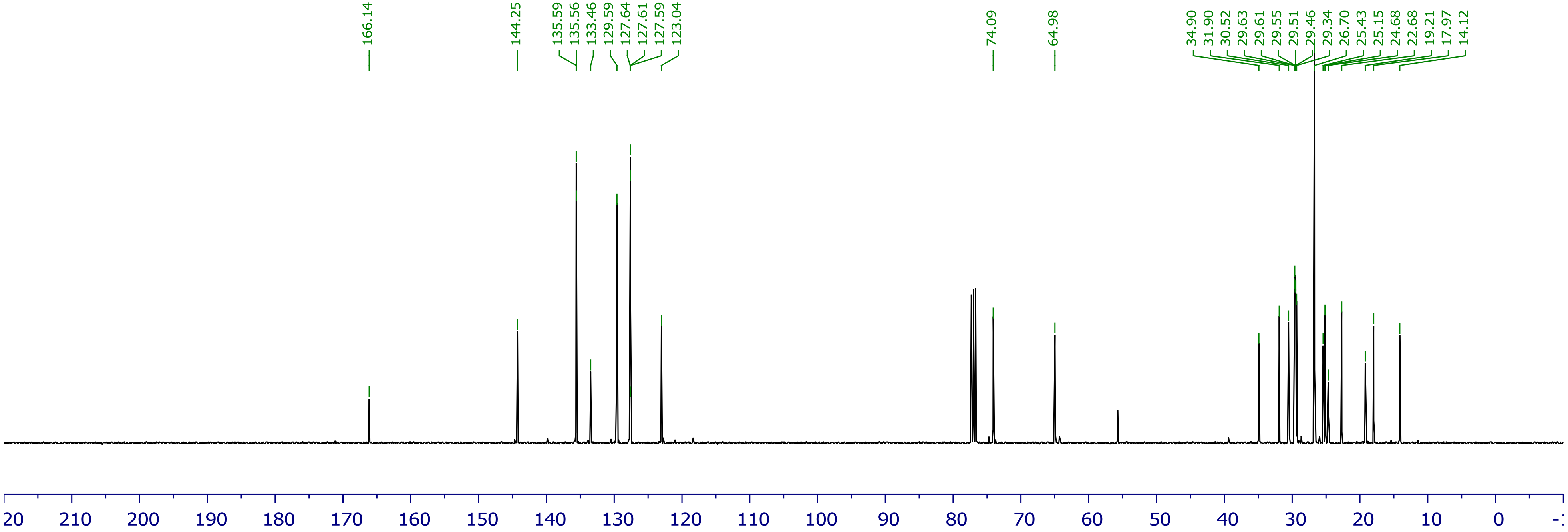
9
OTBDPS
OH
4.03
6.08
2.00
1.00
0.90
2.04
18.03
9.06
3.04
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
135.55
135.53
133.29
133.25
129.77
127.75
72.00
68.09
32.82
31.91
29.67
29.65
29.62
29.58
29.54
29.33
26.88
25.52
22.68
19.26
14.09
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

S1 crude



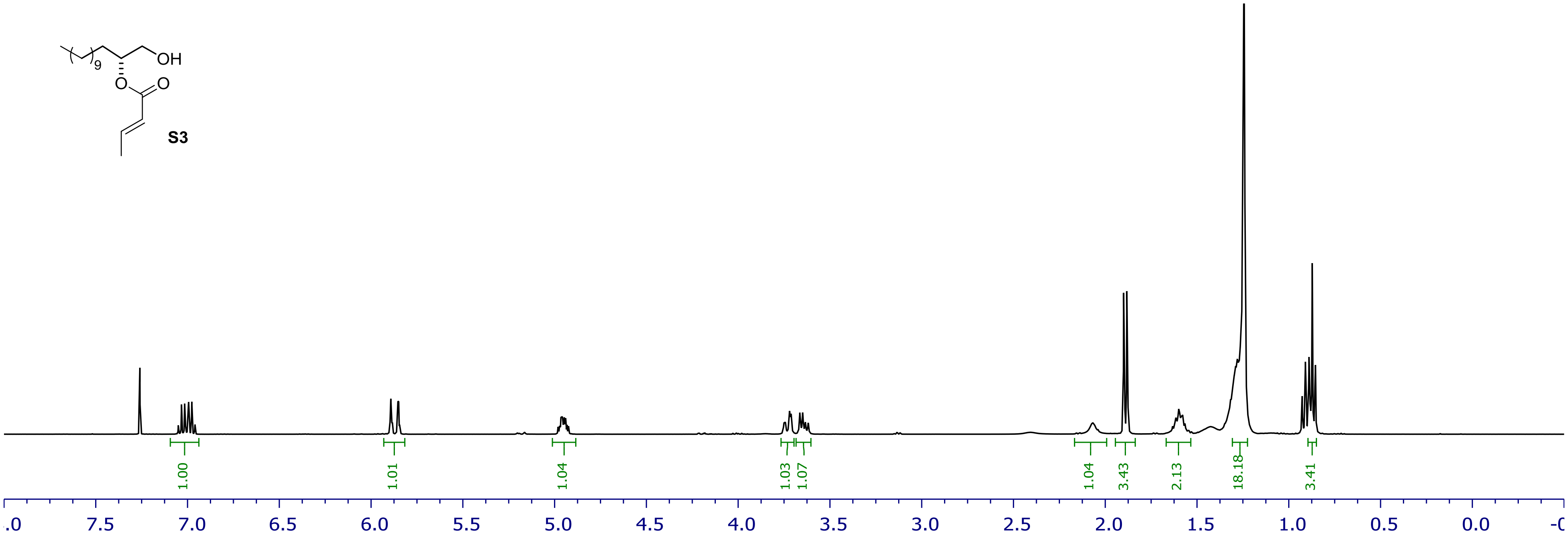
S2

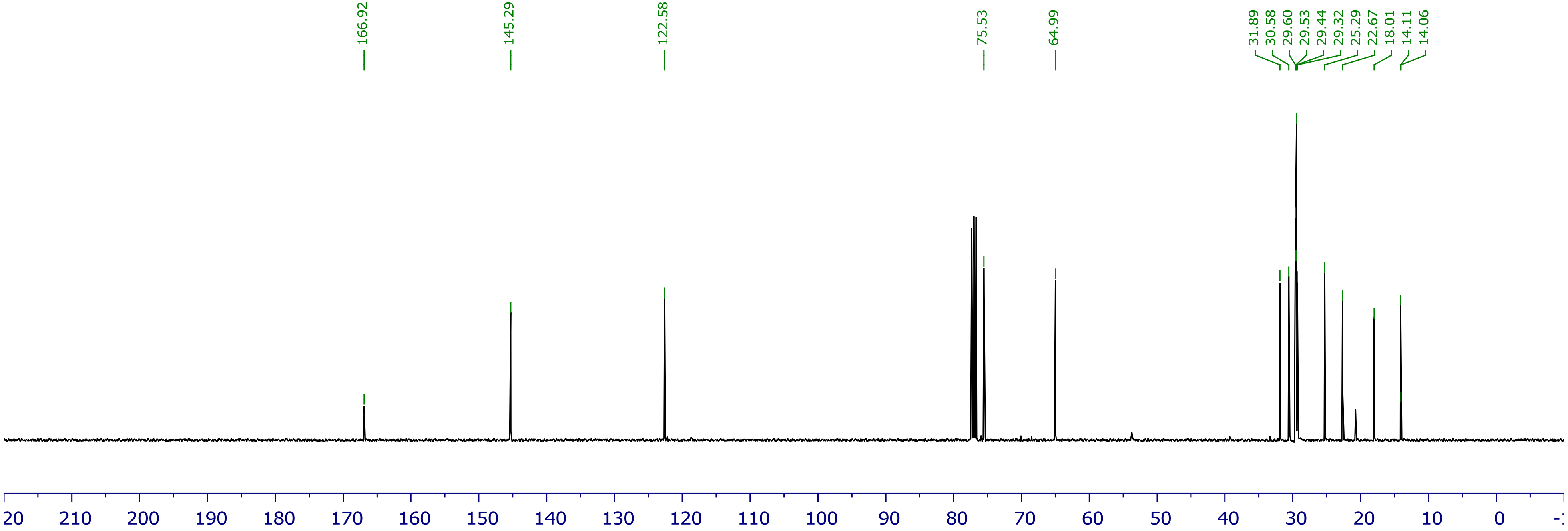
OTBDPS
O
O
9
4.04
6.00
0.93
0.96
0.99
2.00
3.22
2.26
17.81
8.98
3.27
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

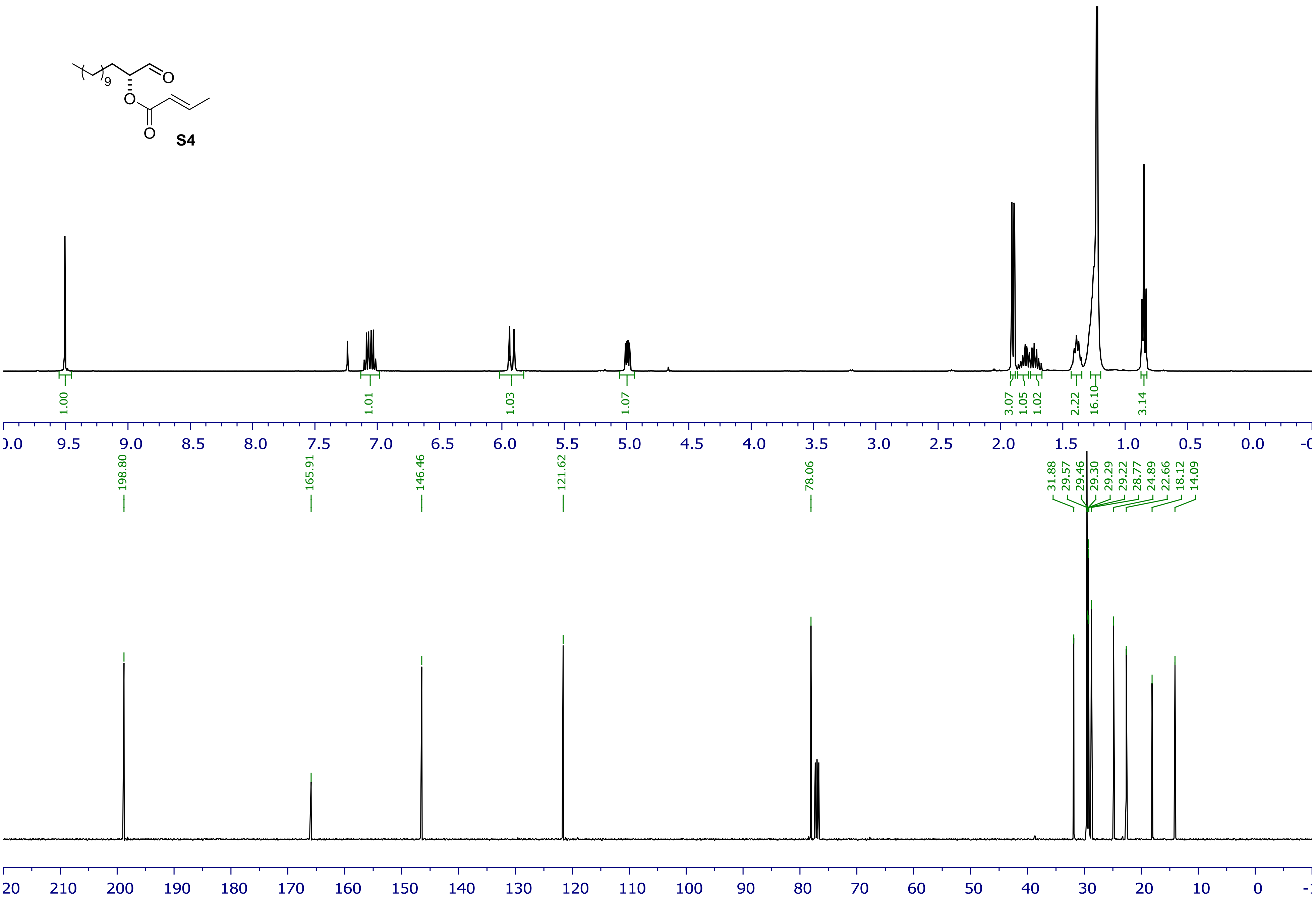


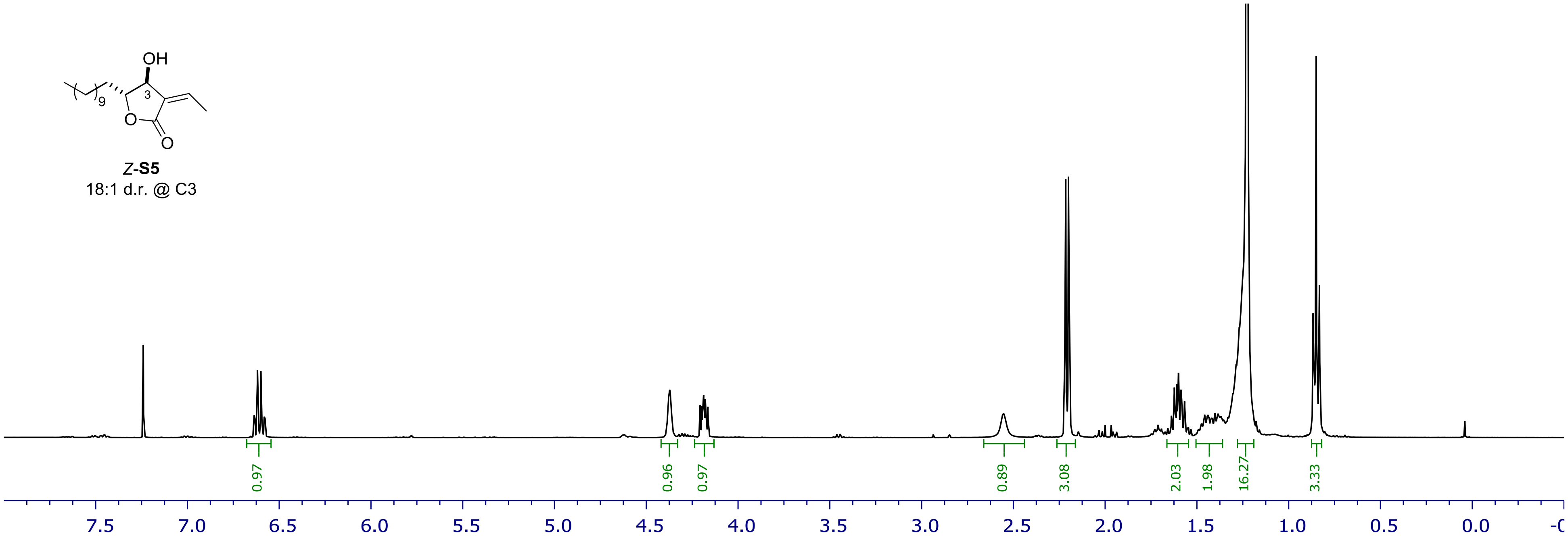
166.14
144.25
135.59
135.56
133.46
129.59
127.64
127.61
127.59
123.04
74.09
64.98
34.90
31.90
30.52
29.63
29.61
29.55
29.51
29.46
29.34
26.70
25.43
25.15
24.68
22.68
19.21
17.97
14.12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

S3


1.00
1.01
1.04
1.03
1.07
1.04
3.43
2.13
18.18
3.41
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

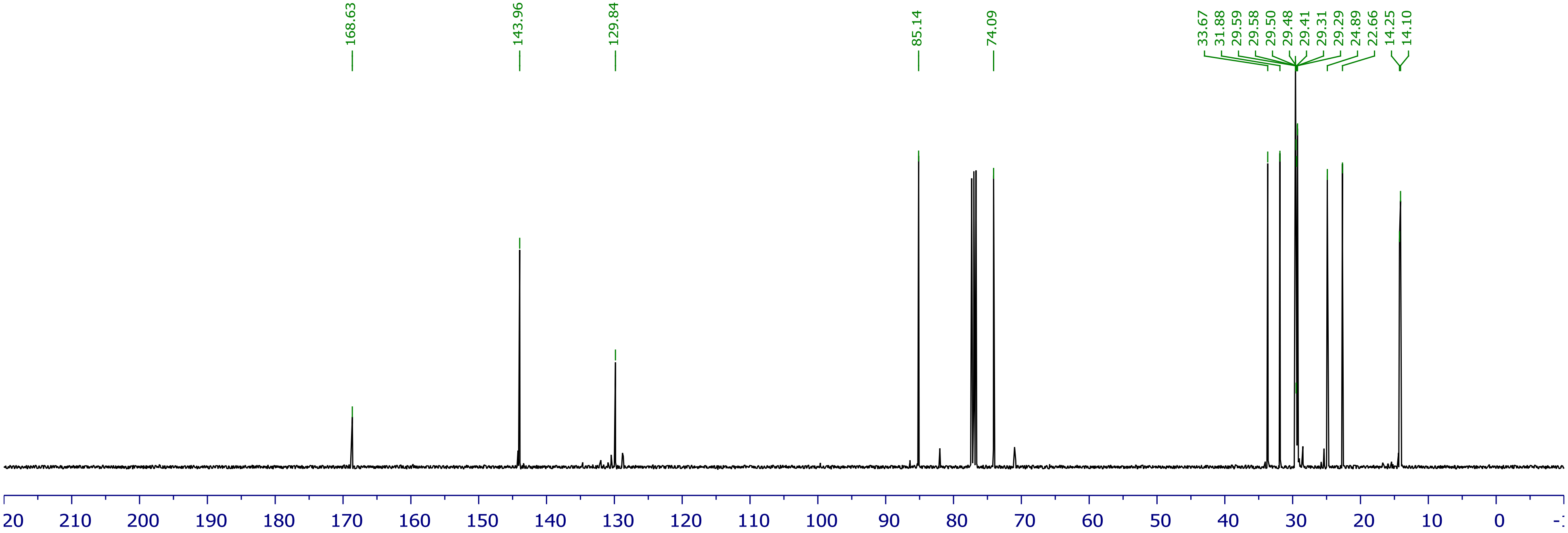

166.92
145.29
122.58
75.53
64.99
31.89
30.58
29.60
29.53
29.44
29.32
25.29
22.67
18.01
14.11
14.06
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

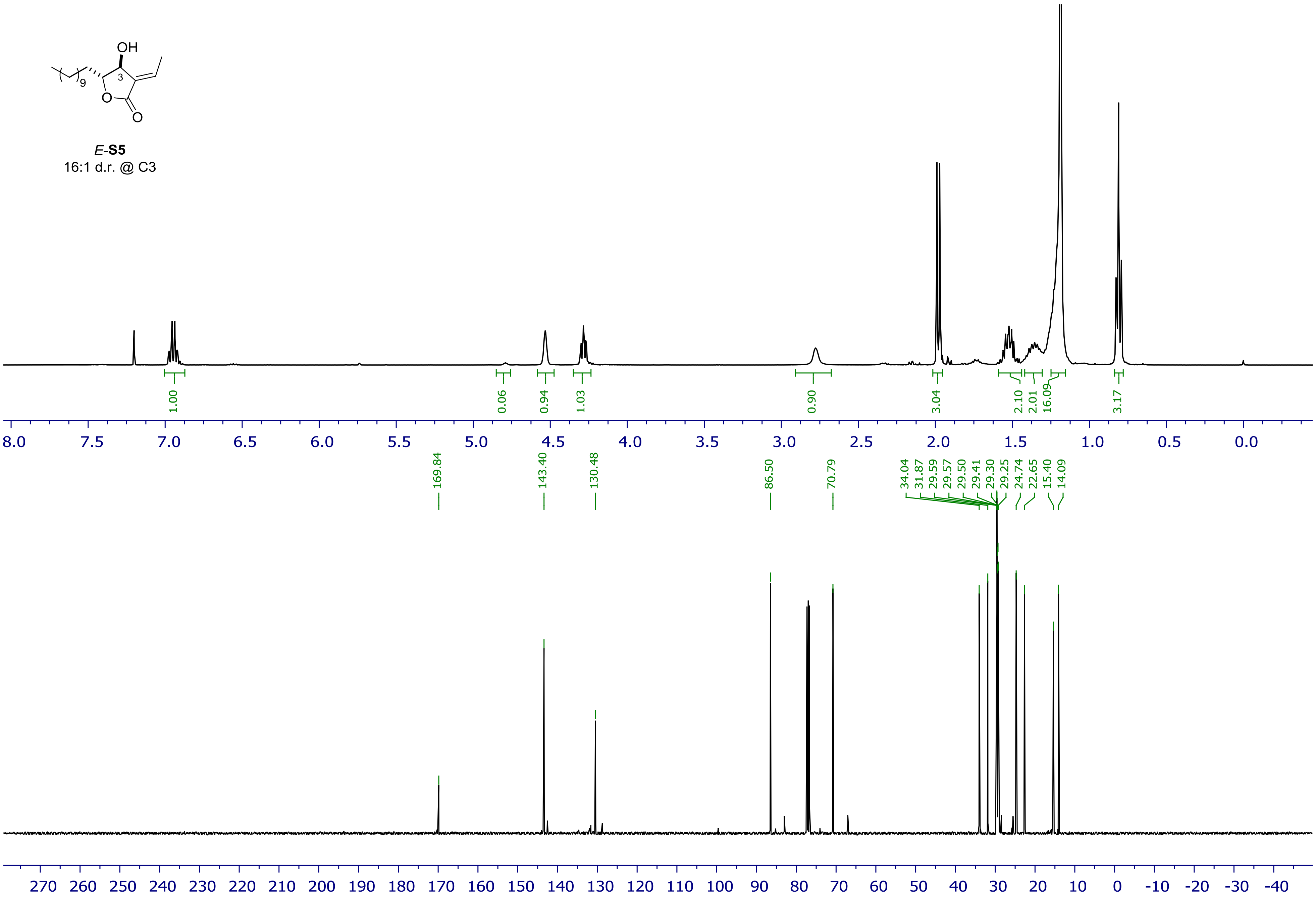

9
O
O
O
S4
1.00
1.01
1.03
1.07
3.07
1.05
1.02
2.22
16.10
3.14
).0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
198.80
165.91
146.46
121.62
78.06
31.88
29.57
29.46
29.30
29.29
29.22
28.77
24.89
22.66
18.12
14.09
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-:


OH
3
9
O
O

Z-**S5**
18:1 d.r. @ C3

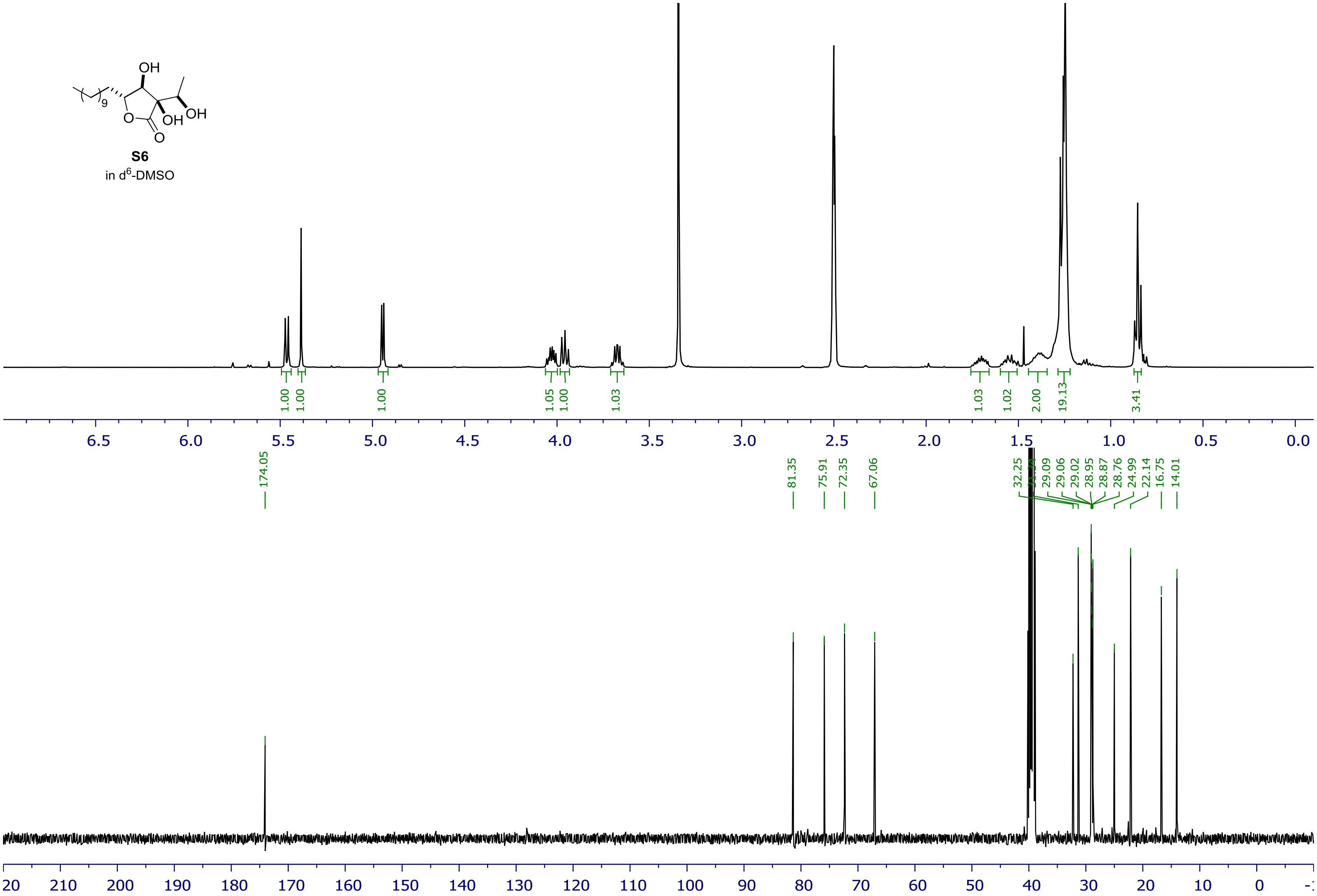
0.97
0.96
0.97
0.89
3.08
2.03
1.98
16.27
3.33
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


168.63
143.96
129.84
85.14
74.09
33.67
31.88
29.59
29.58
29.50
29.48
29.41
29.31
29.29
24.89
22.66
14.25
14.10
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



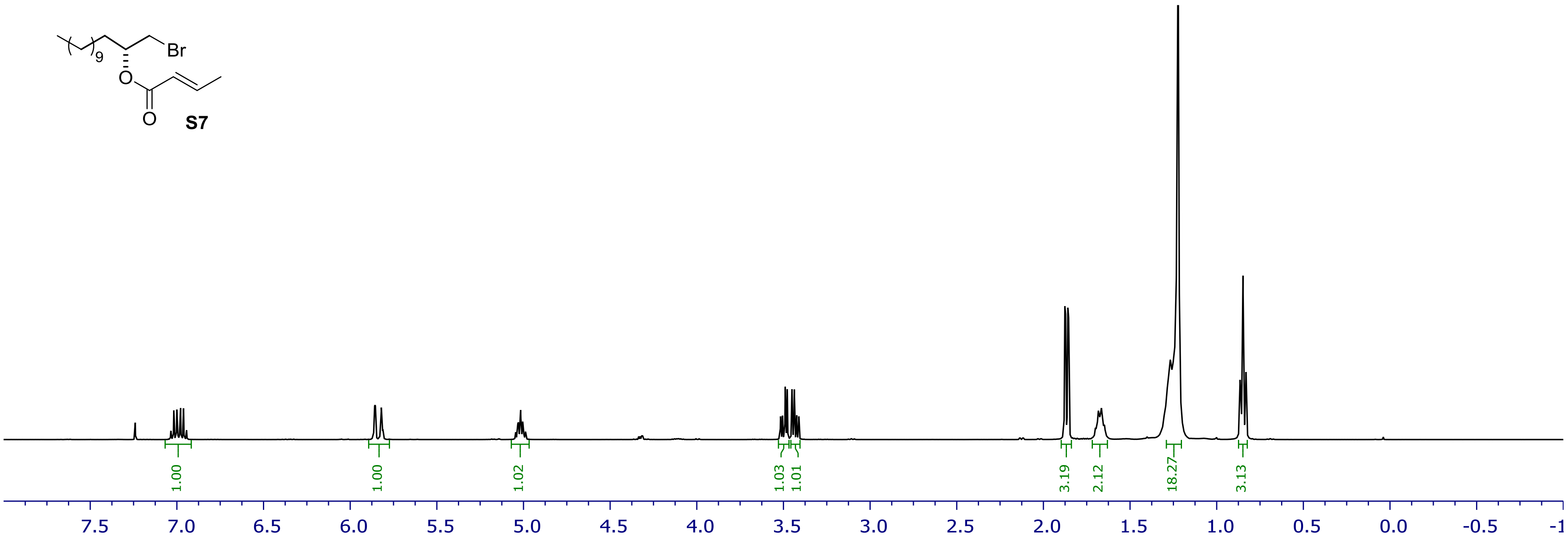
E-**S5**
16:1 d.r. @ C3

OH
3
9
O
O
1.00
0.06
0.94
1.03
0.90
3.04
2.10
2.01
16.09
3.17
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
169.84
143.40
130.48
86.50
70.79
34.04
31.87
29.59
29.57
29.50
29.41
29.30
29.25
24.74
22.65
15.40
14.09
270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40

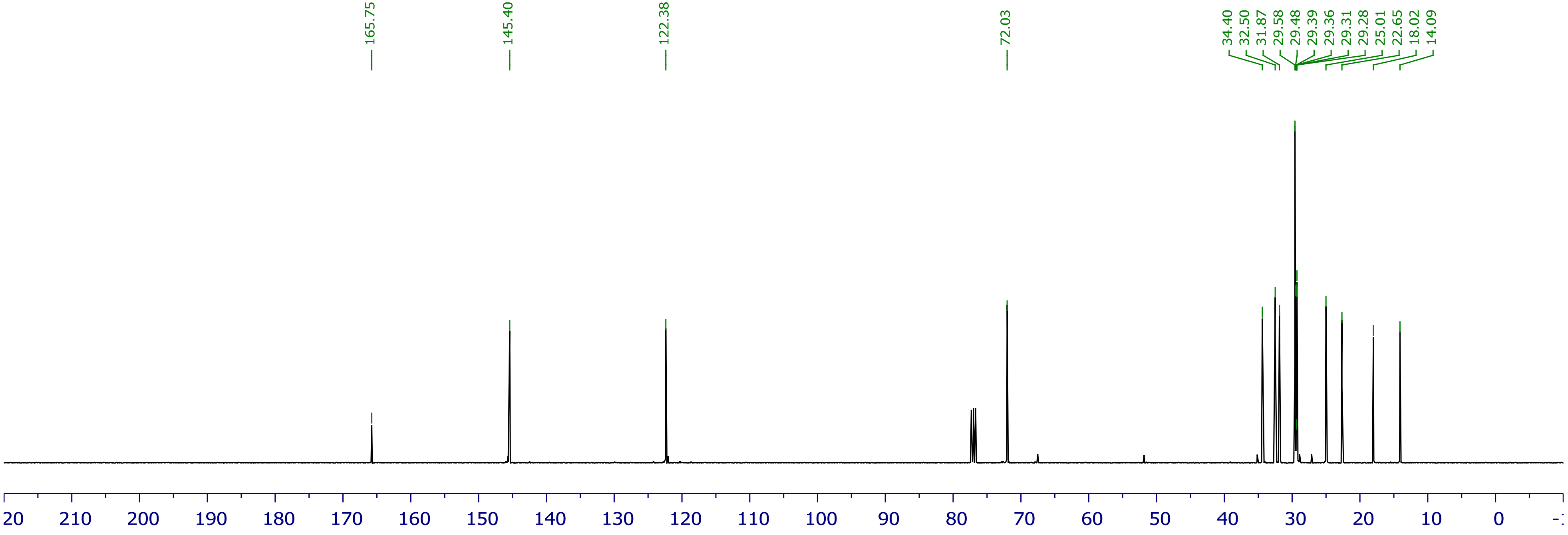

S6

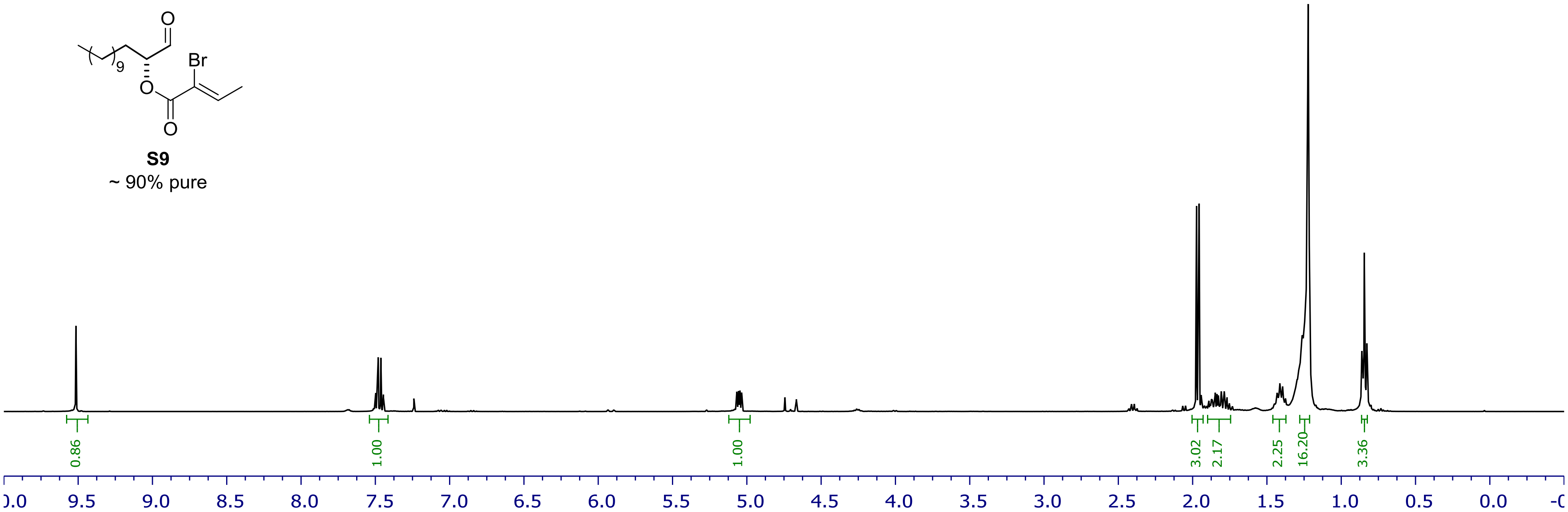
in d^6-DMSO

OH
OH
OH
O
O
9
1.00
1.00
1.00
1.05
1.00
1.03
1.03
1.02
2.00
19.13
3.41
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
174.05
81.35
75.91
72.35
67.06
32.25
31.34
29.09
29.06
29.02
28.95
28.87
28.76
24.99
22.14
16.75
14.01
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


S7

Br
O
O
9
1.00
1.00
1.02
1.03
1.01
3.19
2.12
18.27
3.13
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1

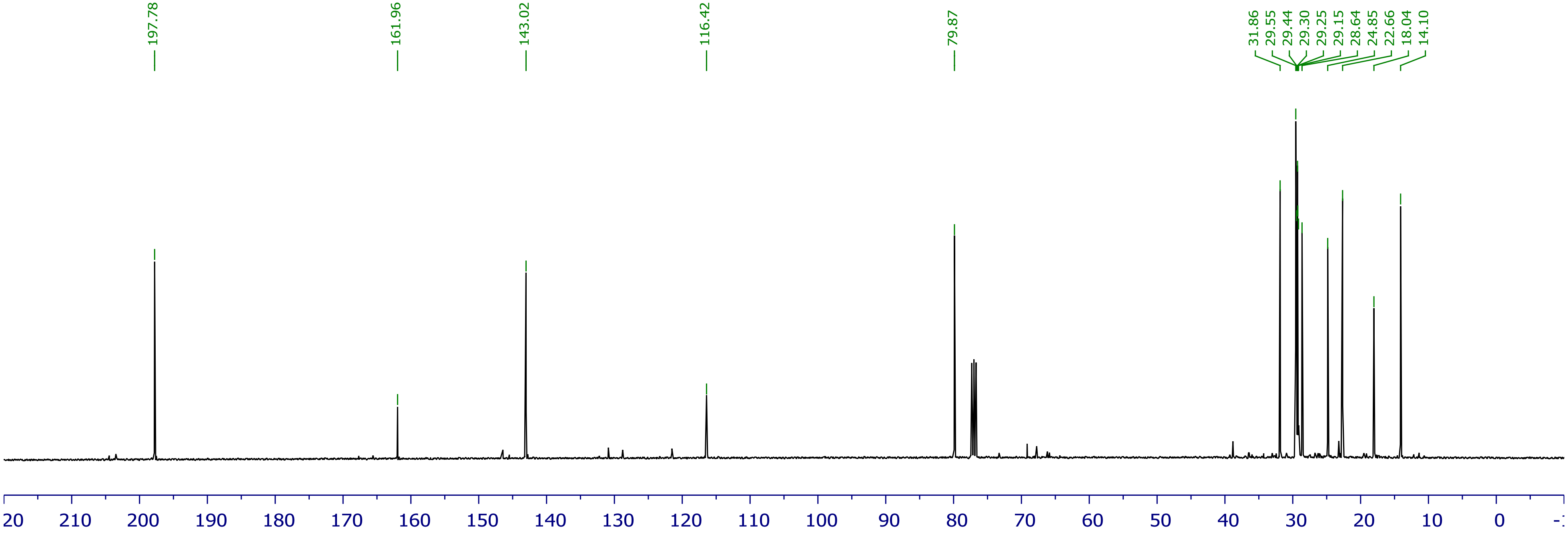

165.75
145.40
122.38
72.03
34.40
32.50
31.87
29.58
29.48
29.39
29.36
29.31
29.28
25.01
22.65
18.02
14.09
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-


O
Br
9
O
O

S9

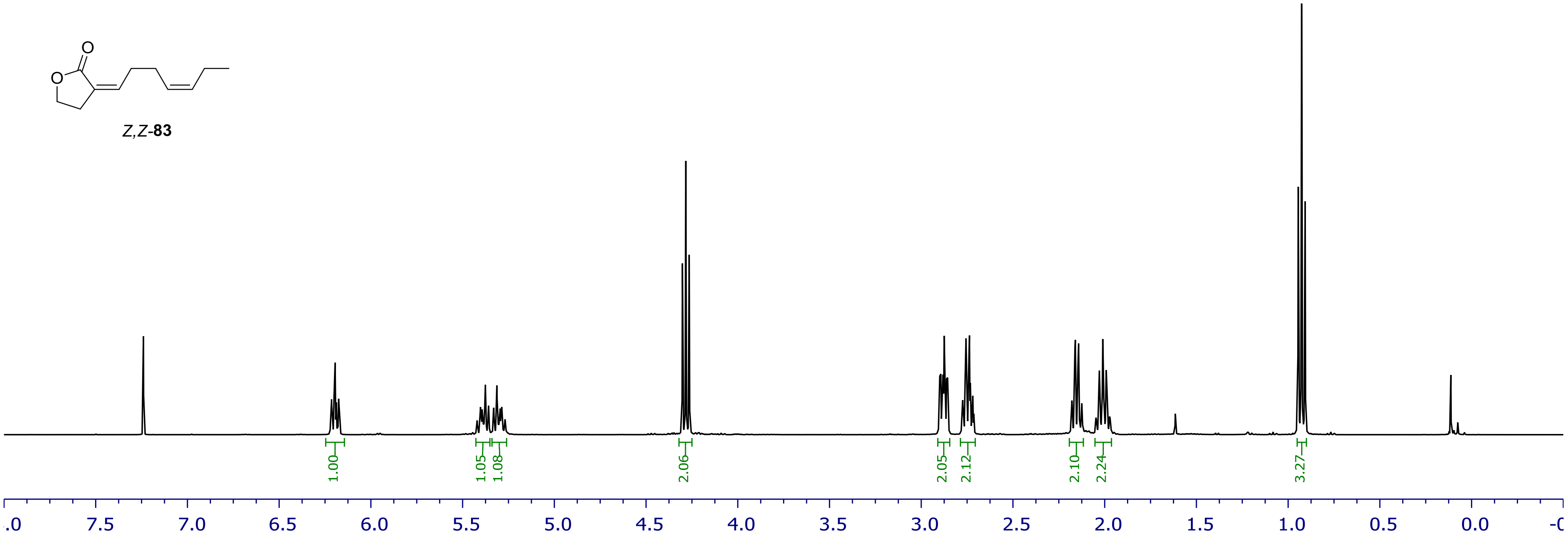
~ 90% pure

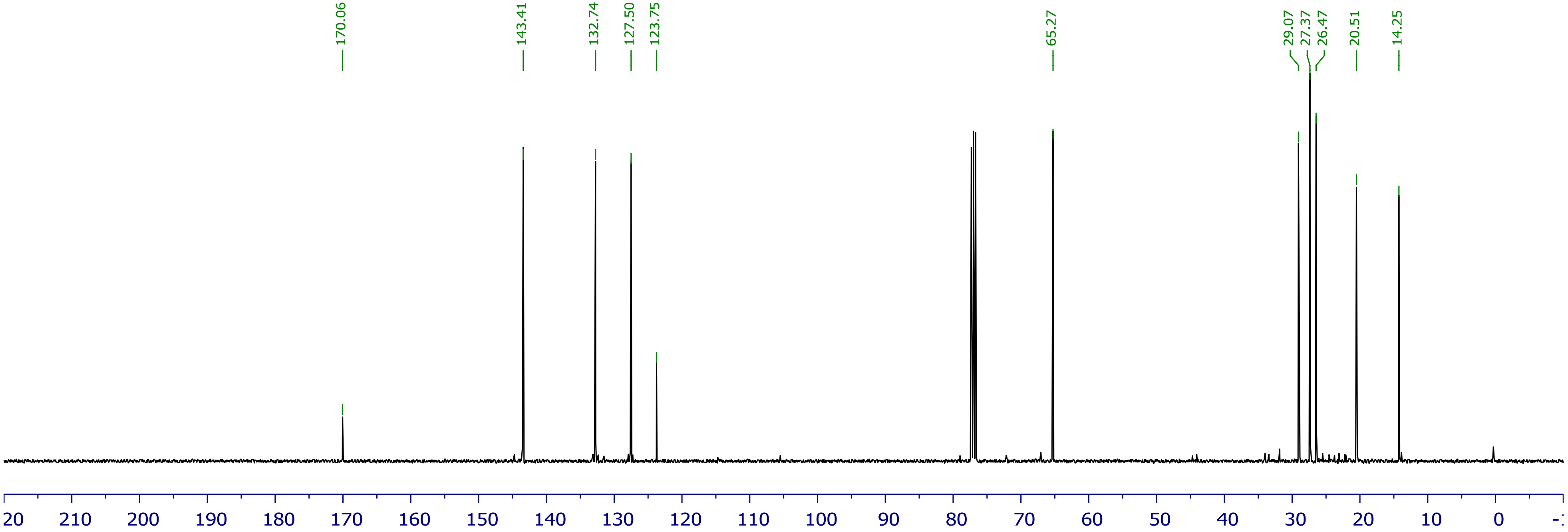
0.86
1.00
1.00
3.02
2.17
2.25
16.20
3.36
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

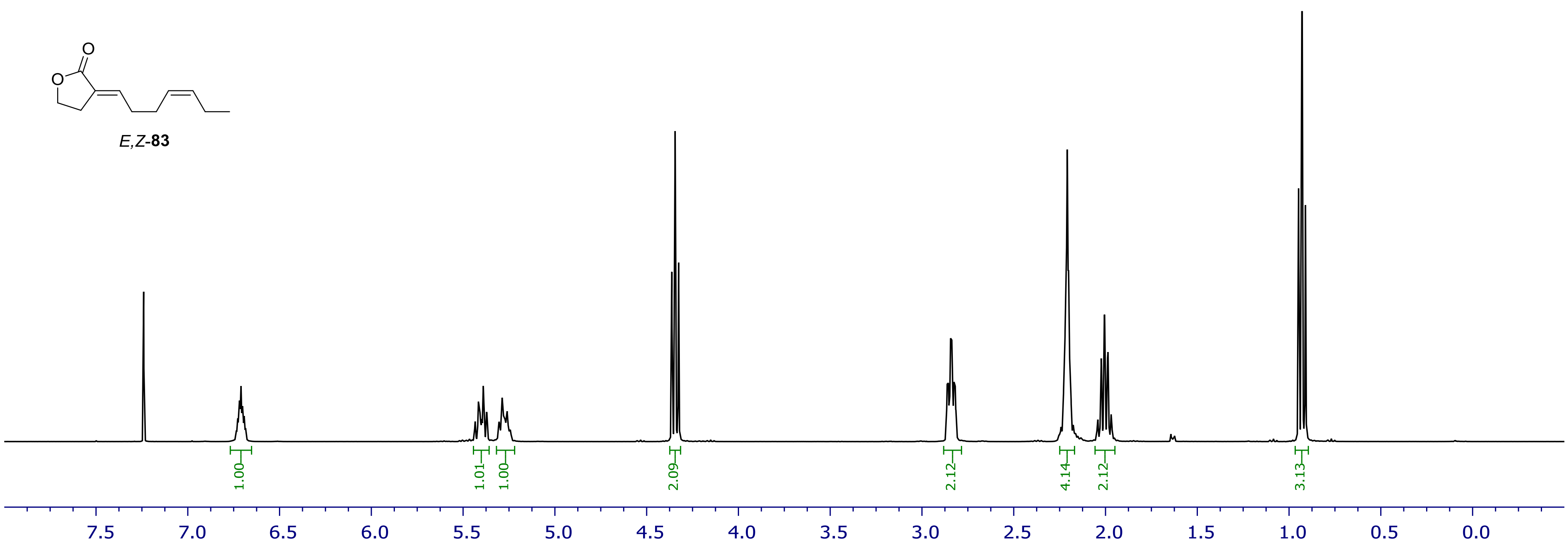

197.78
161.96
143.02
116.42
79.87
31.86
29.55
29.44
29.30
29.25
29.15
28.64
24.85
22.66
18.04
14.10
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

O
O

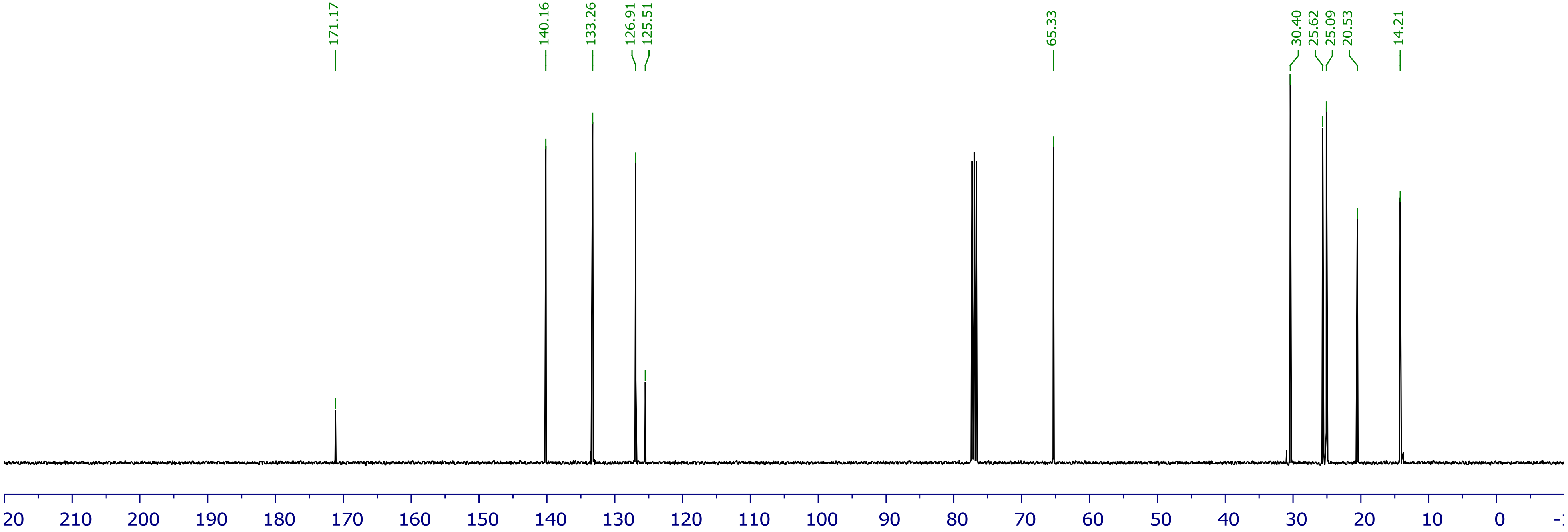
Z,*Z*-**83**

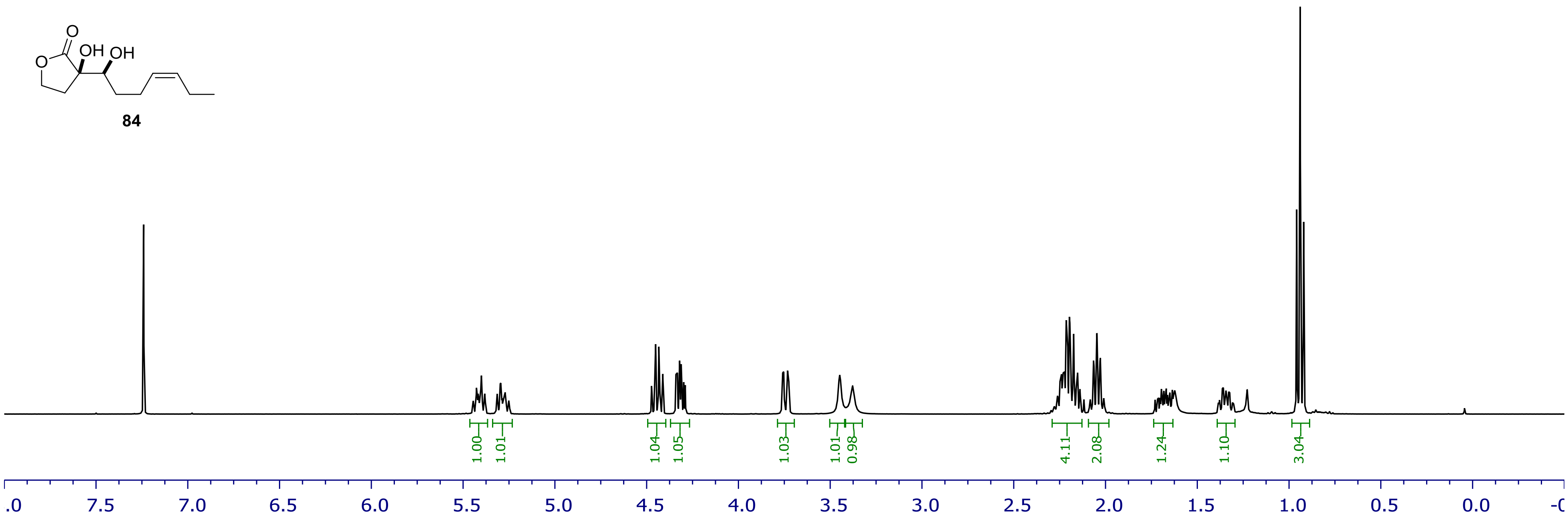

1.00
1.05
1.08
2.06
2.05
2.12
2.10
2.24
3.27
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(


170.06
143.41
132.74
127.50
123.75
65.27
29.07
27.37
26.47
20.51
14.25
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-:

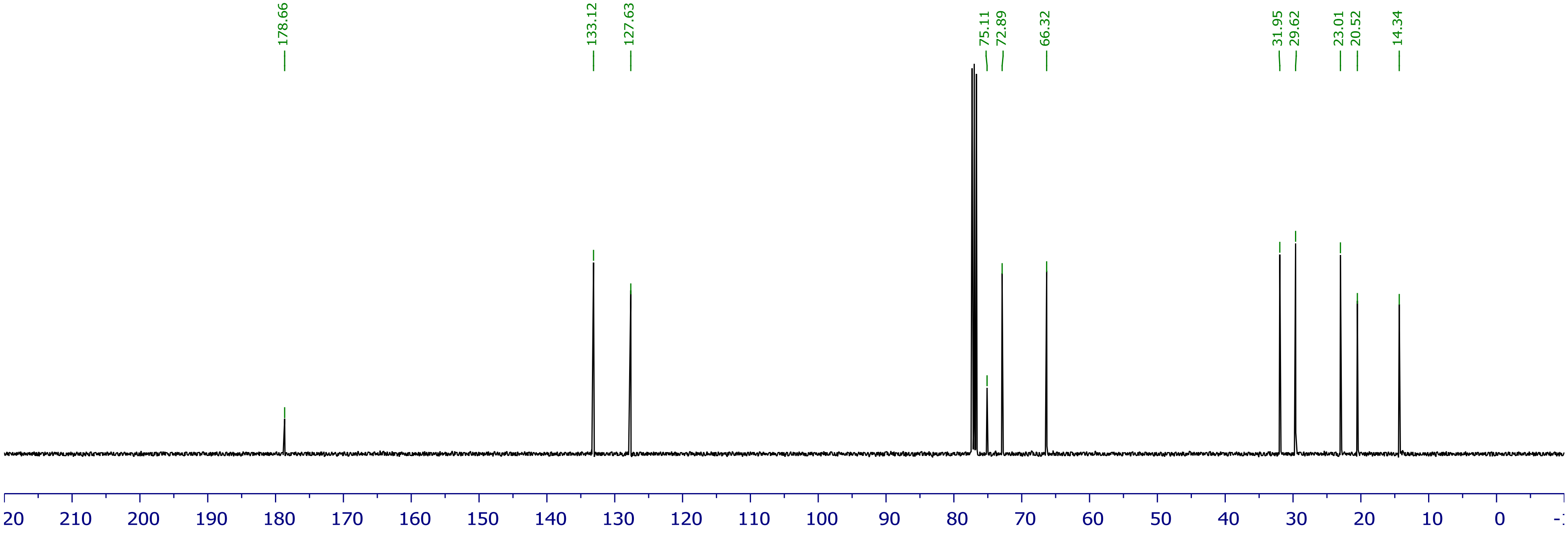

E,Z-**83**

O
O
1.00
1.01
1.00
2.09
2.12
4.14
2.12
3.13
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


171.17
140.16
133.26
126.91
125.51
65.33
30.40
25.62
25.09
20.53
14.21
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



84
1.00
1.01
1.04
1.05
1.03
1.01
0.98
4.11
2.08
1.24
1.10
3.04
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(


178.66
133.12
127.63
75.11
72.89
66.32
31.95
29.62
23.01
20.52
14.34
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-: