Natural Product Characterization General Experimental Procedures. The melting point measured using a Gallenkamp melting point apparatus is uncorrected. The optical rotations were recorded on a Perkin Elmer model 343 polarimeter. UV spectrophotometric data was acquired on a Hitachi U-3010 spectrophotometer. IR spectroscopic data were obtained on a Perkin Elmer Spectrum 100 FT-IR spectrometer. NMR data (of cocosolide collected from Cocos Lagoon) were collected on a JEOL ECA-600 spectrometer operating at 600 MHz for ^{1}H and 150 MHz for ^{13}C. The edited-HSQC experiment was optimized for $^1J_{CH}$ = 140 Hz and the HMBC spectrum was optimized for $^{2,3}J_{CH}$ = 8 Hz. ^{1}H NMR chemical shifts (referenced to residual CH_3CN observed at δ 1.93) were assigned using a combination of data from 2D DQF COSY and multiplicity-edited HSQC experiments. Similarly, ^{13}C NMR chemical shifts (referenced to CD_3CN observed at δ 118.2) were assigned on the basis of multiplicity-edited HSQC experiments. NMR data (of cocosolide collected from Tanguisson reef flat) were collected on a Varian Mercury-Plus-400 spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C. The HRMS data was obtained using an Agilent 6210 LC-TOF mass spectrometer equipped with an APCI/ESI multimode ion source detector at the Mass Spectrometer Facility at the University of California, Riverside, California. Silica gel 60 (EMD Chemicals, Inc. 230–400 mesh) and Varian BondElut octadecyl (C_{18}) were used for column chromatography. All solvents used were of HPLC grade (Fisher Scientific).

Biological Material Collection and Identification. The initial sample of cyanobacterial soft golden puffballs of cyanobacterium *Symploca* sp. was collected in December 1999 from the reef near Cocos Island, Guam. The sample was identified by one of us (VJP) based on morphological characteristics of the genus and the voucher specimen (VP-ECO 22) is maintained at the Smithsonian Marine Station, Fort Pierce, FL. A recollection at the same location was carried out in October 2000.

The sample of *Symploca* sp. NIH 393 was collected in September 6, 2001 from 18 m depth from a Reef wall north of Pago, Guam. The sample was identified on morphological characteristics of the genus and the voucher specimen is maintained at the Smithsonian Marine Station, Fort Pierce, FL.

Another sample of golden mat-forming *Symploca* sp. VPG 14-1 was collected from Tanguisson reef flat, Guam, on May 27, 2014. Two samples of golden puffballs VPG14-35 and VPG14-47 were collected from Piti Bomb Holes, Guam on May 31, 2014 and from Finger Reef, Guam on June 3, 2014. The samples were identified on morphological characteristics of the genus and the voucher specimens are maintained at the Smithsonian Marine Station, Fort Pierce, FL.

Extraction and Isolation. The freeze dried material from the 1999 collection from Cocos Lagoon was extracted with a mixture of CH_2Cl_2–MeOH (1:1) and then with aqueous MeOH (1:1). The combined extract (9.34 g) was subsequently partitioned between *n*-BuOH and H_2O. Concentration of these extracts furnished 0.440 g of *n*-BuOH-soluble fraction and 8.8 g H_2O-soluble material. The *n*-BuOH-soluble fraction (0.440 g) was chromatographed on a column of SiO_2 (20 g) using a hexanes–EtOAc step gradient system followed by an EtOAc–MeOH step gradient to give six sub-fractions. The sub-fraction 3 (30 mg), eluting with EtOAc was further chromatographed on a column of SiO_2 (5 g) using a hexanes–EtOAc system to give two sub-fractions. The sub-fraction 2 (14 mg) was further purified by reversed-phase HPLC (semi-prep

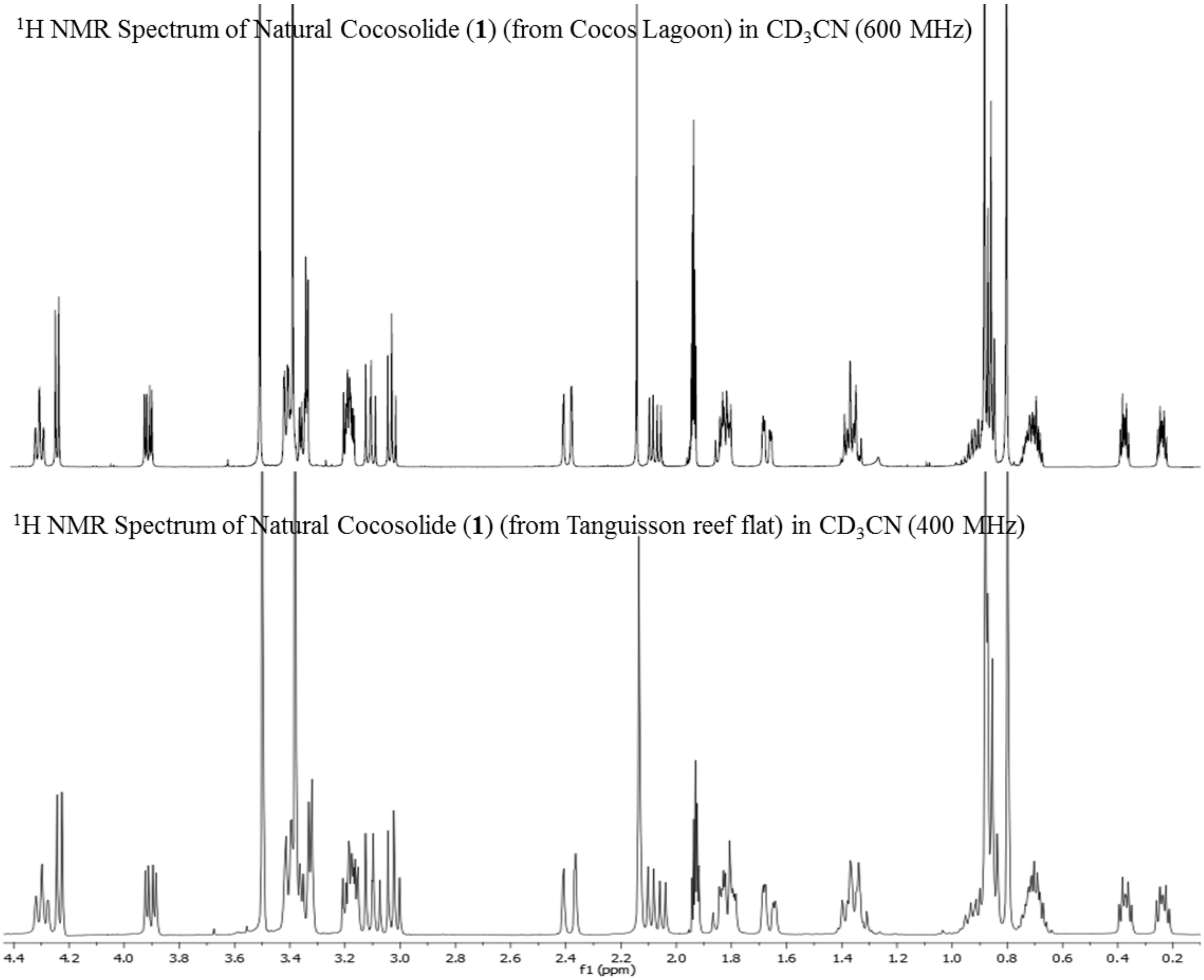
10 × 250 mm, 5 μm, RP-18, flow 3.0 mL/min) using 10% H_2O–MeOH to give 8.0 mg of cocosolide (**1**).

The recollection from Cocos Lagoon provided a lipophilic extract (6.5 g) that was subjected to same purification procedure to give 5.0 mg of cocosolide (**1**). Subsequent recollections of the same cyanobacterium furnished additional 10 mg of cocosolide (**1**).

The freeze dried material derived from *Symploca* sp. NIH 393 from Pago was extracted with a mixture of EtOAc–MeOH (1:1) and then with aqueous MeOH (1:1) to give 2.3 g and 4.6 g of extracts, respectively. The EtOAc–MeOH extract was partitioned between EtOAc and H_2O to give 0.110 g of EtOAc-soluble fraction. This fraction was chromatographed on a column of SiO_2 (20 g) using a hexanes–EtOAc step gradient system followed by an EtOAc–MeOH- step gradient to give four sub-fractions. The sub-fraction 2 (0.011 g), eluting with EtOAc, was pushed through a C-18 SepPak using H_2O–MeOH gradient followed by MeOH to give 4 sub-fractions. The first sub-fraction eluting with 15% H_2O–MeOH was separated again using a C-18 SepPak with 20% H_2O–MeOH and 15% H_2O–MeOH, and the latter fraction furnished pure cocosolide (**1**) 2.2 mg.

For the Tanguisson reef flat collection VPG 14-1, the freeze-dried material (207.25 g) was extracted twice with EtOAc-MeOH (1:1) to yield the nonpolar extract (8.28 g). This was partitioned between hexanes and 20% aqueous MeOH. The latter was concentrated under reduced pressure and further partitioned between *n*-BuOH and H_2O. The *n*-BuOH soluble fraction was concentrated to dryness (212.9 mg) and chromatographed on a column of Si gel eluting first with CH_2Cl_2, followed by increasing concentrations of *i*-PrOH; after 100% *i*-PrOH, increasing gradients of MeOH were used. The 6% *i*-PrOH fraction (29.1 mg) was subjected to a C_{18} SPE eluting with 100% MeOH for sample pre-cleaning and the eluted sample was dried under N_2. This was further purified by semipreparative reversed-phase HPLC (column, Phenomenex Synergi 4 μ Hydro-RP 80 Å, 250 × 10 mm, 4 μm; flow rate, 2.0 mL/min; UV detection at 200 nm and 220 nm) using a linear gradient of MeCN-H_2O (50-100% MeCN in 30 min, 100% MeCN for 10 min, and then 100%-50% MeCN in 10 min) to yield semipure cocosolide (t_R 28.1 min, 14.40 mg). The final purification of the semipure cocosolide was achieved by using the same chromatographic condition with a different linear gradient of MeCN-H_2O (50-83% MeCN in 60 min, 100% MeCN for 10 min) to yield cocosolide (t_R 51.3 min, 13.1 mg) as a colorless, amorphous solid.

The freeze dried samples 8.0 g of VPG14-35 and 1.2 g of VPG14-47 were extracted separately with a mixture of EtOAc–MeOH (1:1) and then with MeOH. The polar and the non-polar extracts from each sample were combined to give 135 mg and 64 mg of extracts, respectively. The ^1H NMR spectra of these extracts indicated the presence of the characteristic proton signals and the notable cyclopropyl signals present in cocosolide (**1**) and thus identified the presence of cocosolide in both collections.


^{1}H NMR Spectrum of Natural Cocosolide (**1**) (from Cocos Lagoon) in CD_3CN (600 MHz)

^{1}H NMR Spectrum of Natural Cocosolide (**1**) (from Tanguisson reef flat) in CD_3CN (400 MHz)

Figure S1. Comparison of ^{1}H spectrum of natural cocosolide (**1**) from Cocos Lagoon and Tanguisson reef flat.

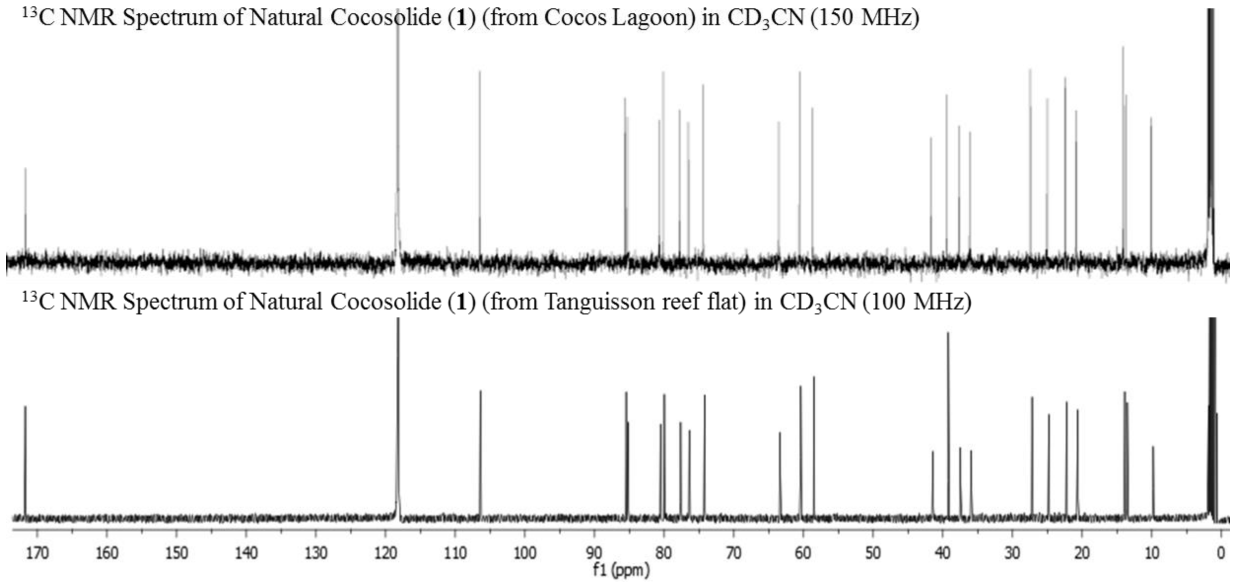
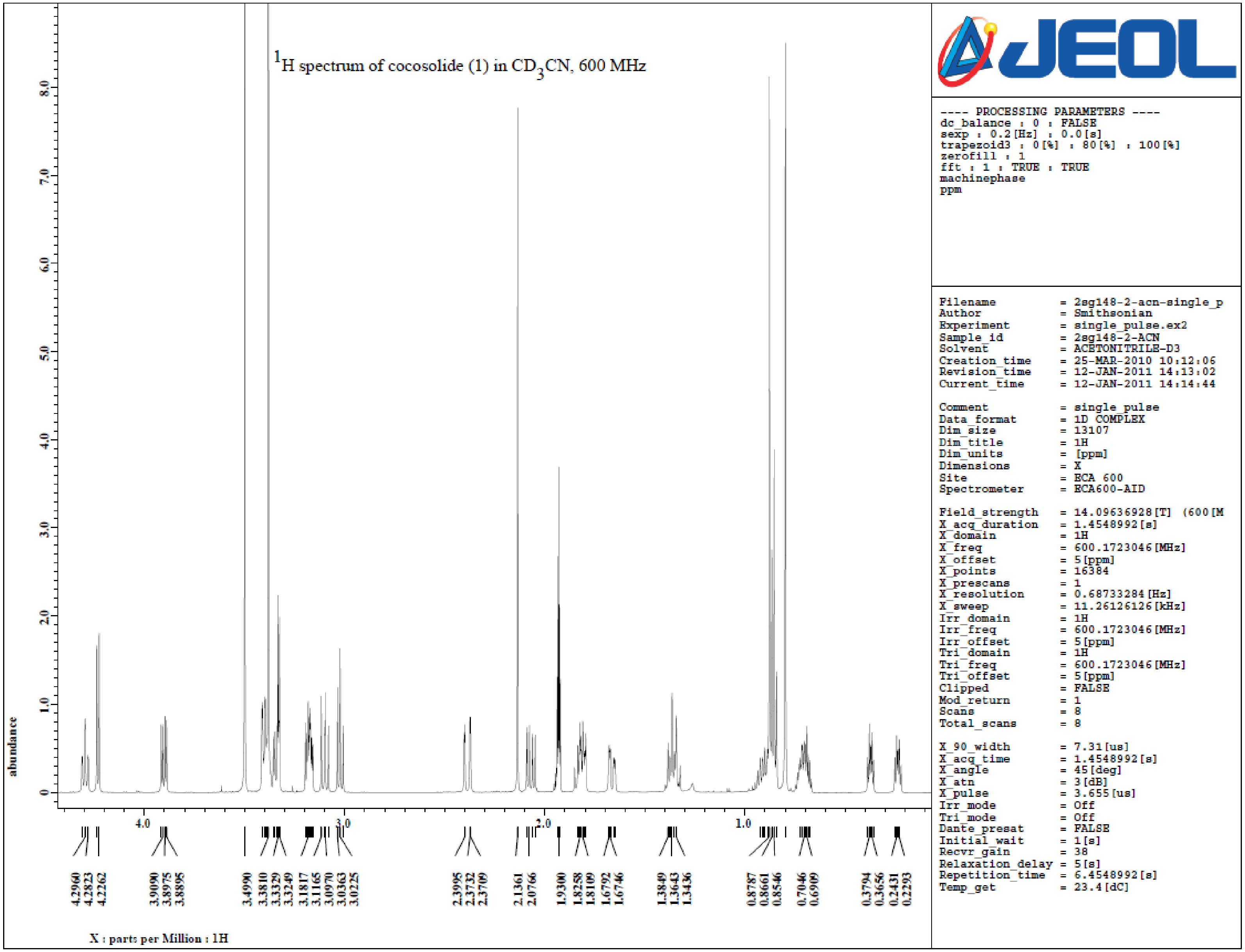


Figure S2. Comparison of ^{13}C spectrum of natural cocosolide (**1**) from Cocos Lagoon and Tanguisson reef flat.



^{1}H spectrum of cocosolide (1) in CD_3CN, 600 MHz

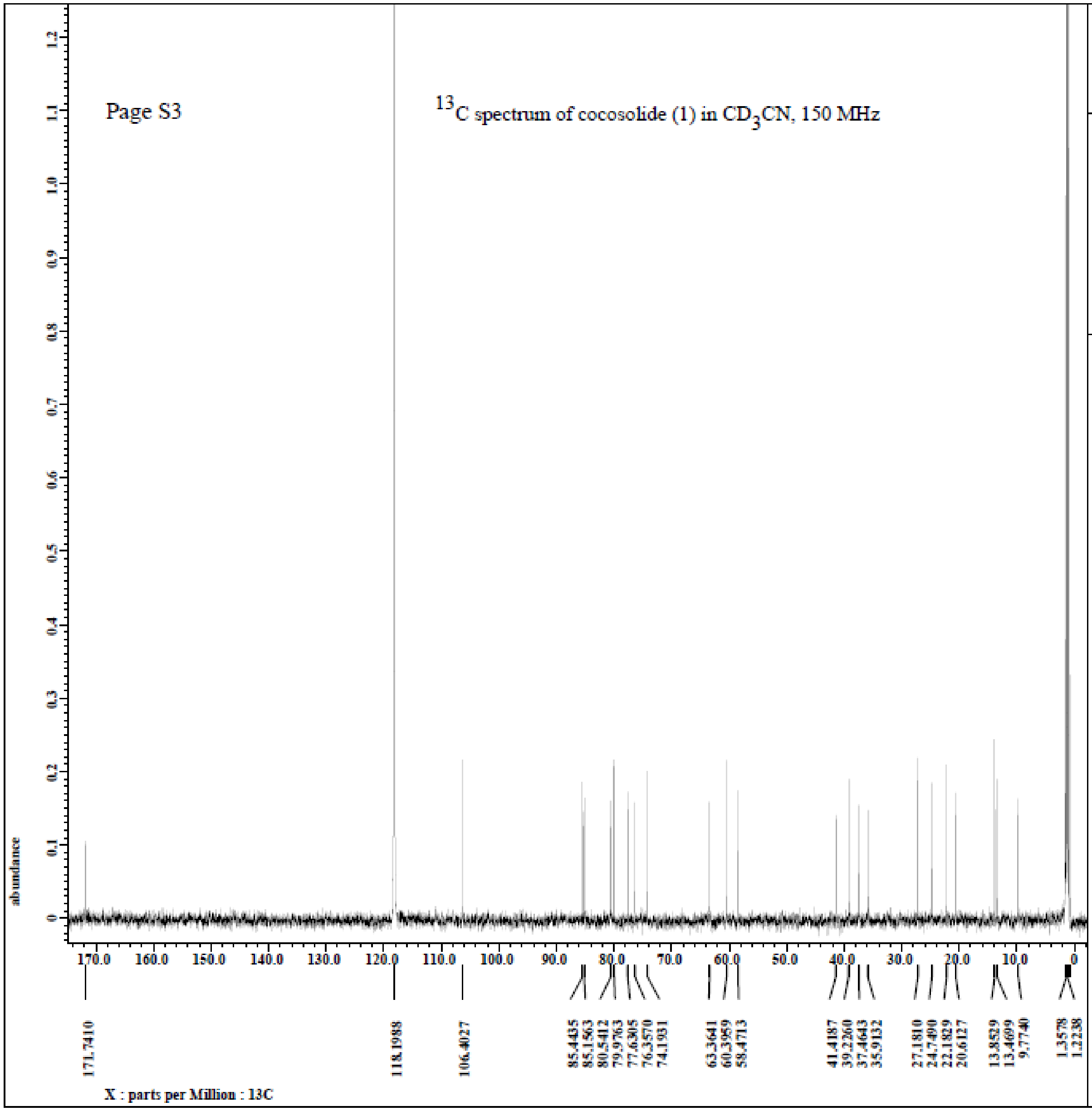
```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
```

```
Filename          = 2sg148-2-acn-single_p
Author            = Smithsonian
Experiment        = single_pulse.ex2
Sample_id         = 2sg148-2-ACN
Solvent           = ACETONITRILE-D3
Creation_time     = 25-MAR-2010 10:12:06
Revision_time     = 12-JAN-2011 14:13:02
Current_time      = 12-JAN-2011 14:14:44

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 600
Spectrometer      = ECA600-AID

Field_strength    = 14.09636928[T] (600[M
X_acq_duration    = 1.4548992[s]
X_domain          = 1H
X_freq            = 600.1723046[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.68733284[Hz]
X_sweep           = 11.26126126[kHz]
Irr_domain        = 1H
Irr_freq          = 600.1723046[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 600.1723046[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 7.31[us]
X_acq_time        = 1.4548992[s]
X_angle           = 45[deg]
X_atn             = 3[dB]
X_pulse           = 3.655[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 38
Relaxation_delay  = 5[s]
Repetition_time   = 6.4548992[s]
Temp_get          = 23.4[dC]
```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^{13}C spectrum of cocosolide (1) in CD_3CN, 150 MHz

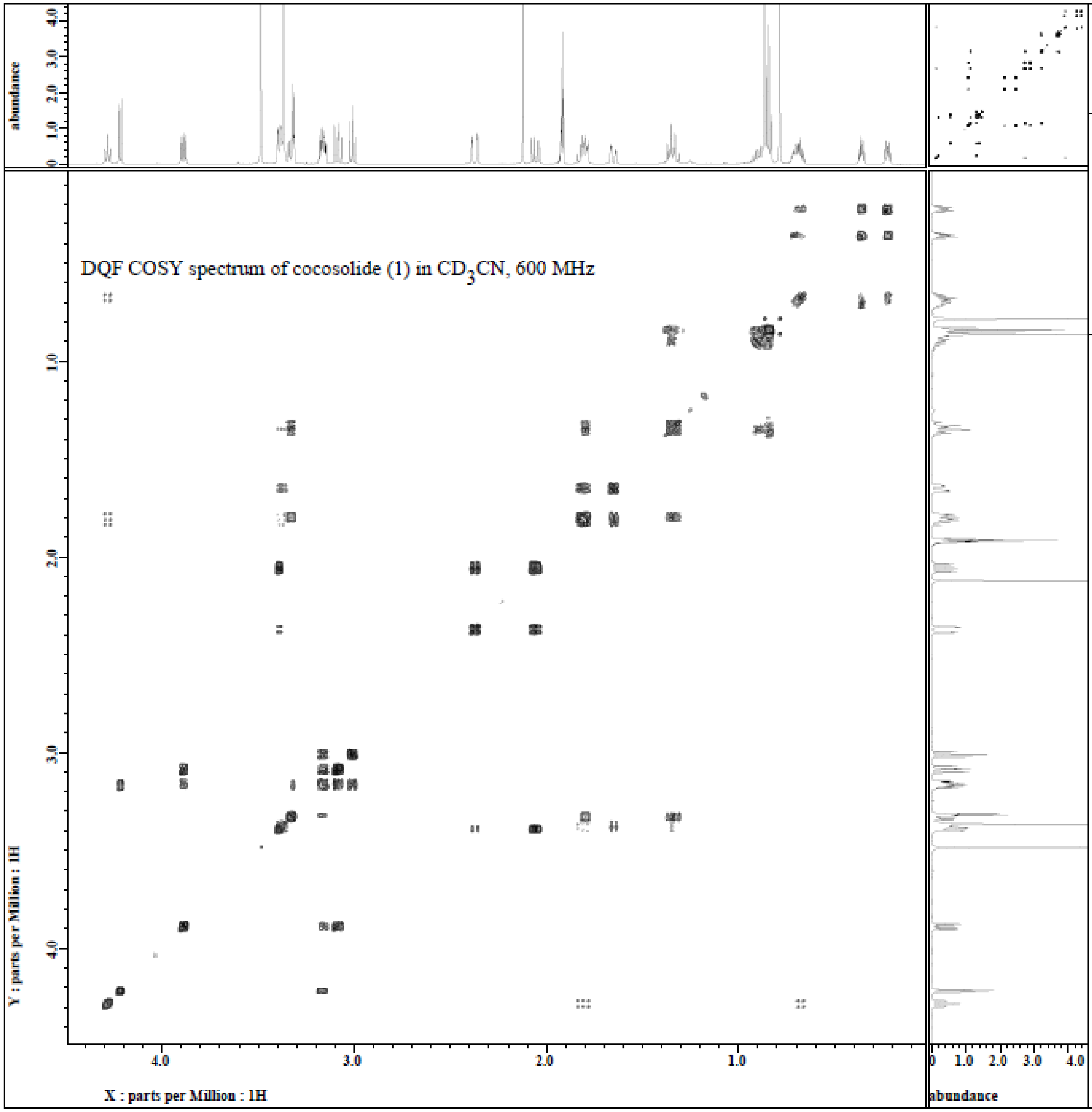
```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
```

```
Filename          = 2sg148-2-ACN-3-4-6-si
Author            = Smithsonian
Experiment        = single_pulse_dec
Sample_id         = 2sg148-2-ACN-3-4-6
Solvent           = ACETONITRILE-D3
Creation_time     = 25-MAR-2010 10:33:46
Revision_time     = 12-JAN-2011 14:23:11
Current_time      = 12-JAN-2011 14:24:00

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 600
Spectrometer      = ECA600-AID

Field_strength    = 14.09636928[T]  (600[M
X_acq_duration    = 0.69206016[s]
X_domain          = 13C
X_freq            = 150.91343039[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.44496109[Hz]
X_sweep           = 47.34848485[kHz]
Irr_domain        = 1H
Irr_freq          = 600.1723046[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 251.0
Total_scans       = 251.0

X_90_width        = 16[us]
X_acq_time        = 0.69206016[s]
X_angle           = 30[deg]
X_atn             = 2[dB]
X_pulse           = 5.33333333[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 60
Relaxation_delay  = 2[s]
Repetition_time   = 2.69206016[s]
Temp_get          = 23.6[dC]
```



DQF COSY spectrum of cocosolide (1) in CD_3CN, 600 MHz

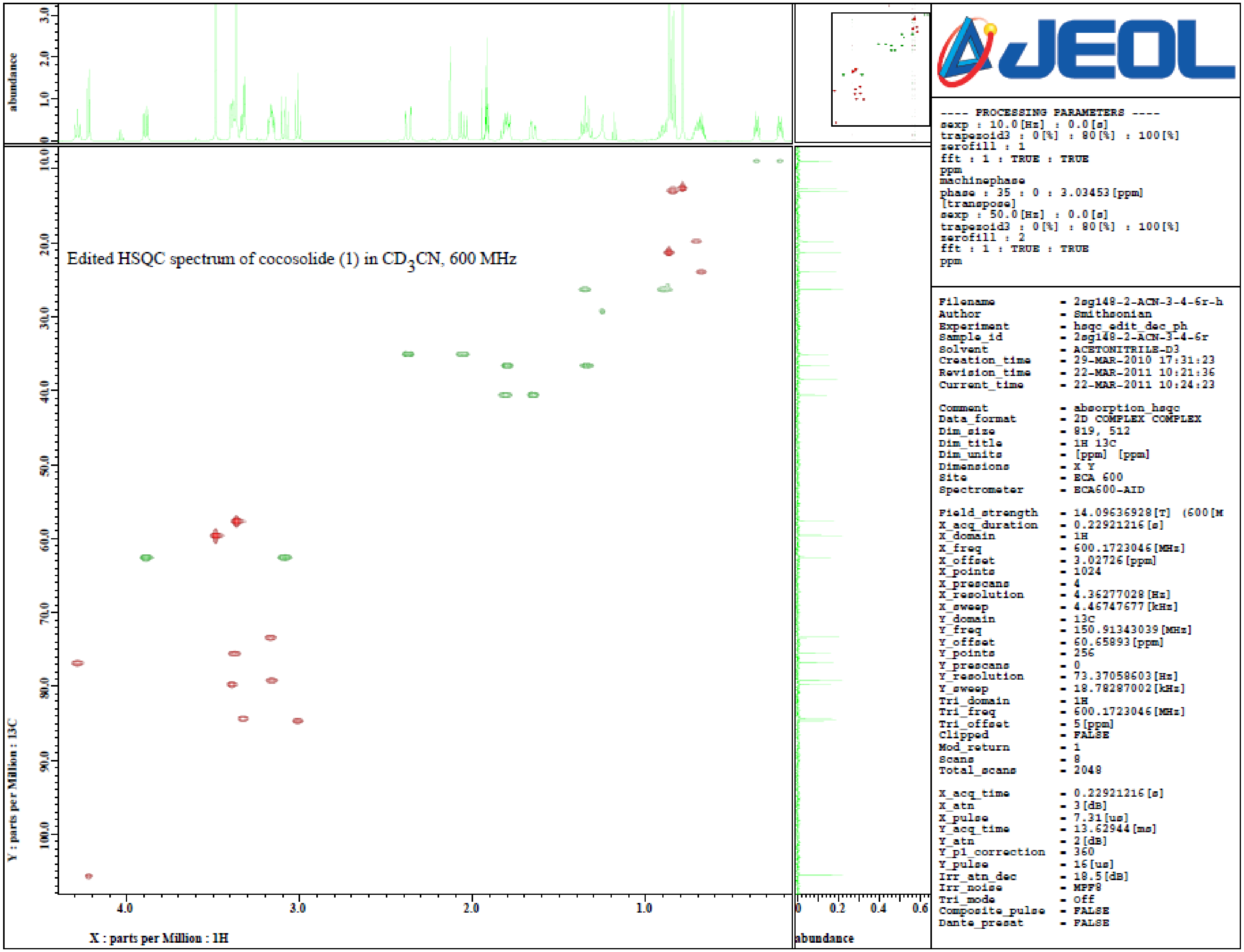
```
---- PROCESSING PARAMETERS ----
sinbell_auto
fft : 1 : TRUE : TRUE
ppm
[transpose]
zerofill : 4
sinbell_auto
fft : 1 : TRUE : TRUE
ppm
abs
thresh : 2[%] : 1
symmetrize : Cosy : 24
[transpose]
```

```
Filename          - 2sg148-2-ACN-3-4-6-dq
Author            - Smithsonian
Experiment        - dqf_cosy_pfg.ex2
Sample_id         - 2sg148-2-ACN-3-4-6
Solvent           - ACETONITRILE-D3
Creation_time     - 25-MAR-2010 10:54:49
Revision_time     - 24-JAN-2011 15:21:25
Current_time      - 24-JAN-2011 15:22:27

Comment           - gradient absolute val
Data_format       - 2D REAL REAL
Dim_size          - 1024, 1024
Dim_title         - 1H 1H
Dim_units         - [ppm] [ppm]
Dimensions        - X Y
Site              - ECA 600
Spectrometer      - ECA600-AID

Field_strength    - 14.09636928[T] (600[M
X_acq_duration    - 0.3818496[s]
X_domain          - 1H
X_freq            - 600.1723046[MHz]
X_offset          - 2.25683[ppm]
X_points          - 1280
X_prescans        - 4
X_resolution      - 2.61883213[Hz]
X_sweep           - 3.35210512[kHz]
Y_domain          - 1H
Y_freq            - 600.1723046[MHz]
Y_offset          - 2.25683[ppm]
Y_points          - 256
Y_prescans        - 0
Y_resolution      - 10.47364329[Hz]
Y_sweep           - 2.68125268[kHz]
Irr_domain        - 1H
Irr_freq          - 600.1723046[MHz]
Irr_offset        - 5[ppm]
Tri_domain        - 1H
Tri_freq          - 600.1723046[MHz]
Tri_offset        - 5[ppm]
Clipped           - FALSE
Mod_return        - 1
Scans             - 2
Total_scans       - 512

X_acq_time        - 0.3818496[s]
X_atn             - 3[dB]
X_pulse           - 7.31[us]
Y_acq_time        - 95.47776[ms]
Irr_mode          - Off
Tri_mode          - Off
Dante_presat      - FALSE
Grad_1            - 1[ms]
Grad_1_amp        - 60[mT/m]
```



Edited HSQC spectrum of cocosolide (1) in CD$_3$CN, 600 MHz

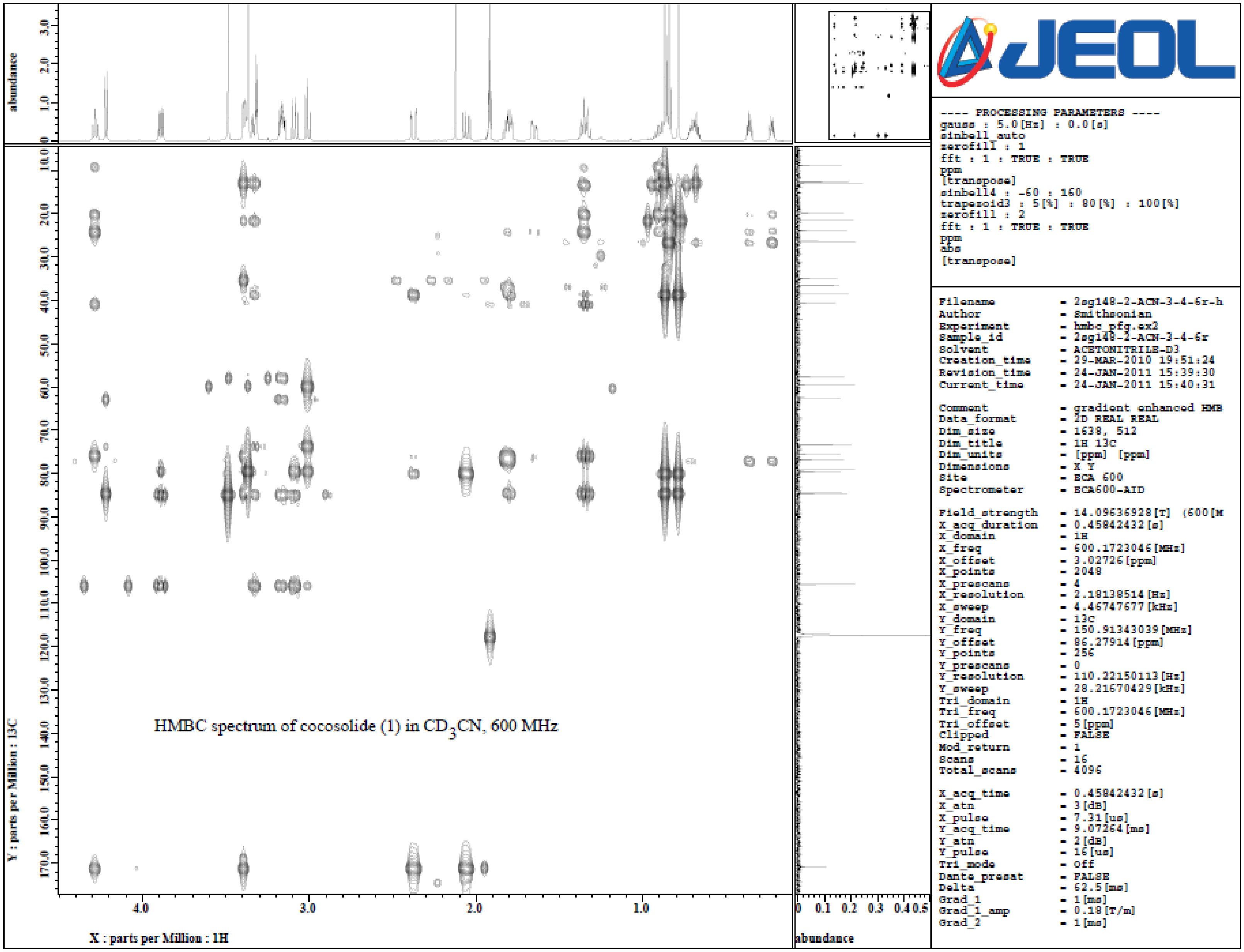
```
---- PROCESSING PARAMETERS ----
sexp : 10.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
ppm
machinephase
phase : 35 : 0 : 3.03453[ppm]
[transpose]
sexp : 50.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 2
fft : 1 : TRUE : TRUE
ppm
```

```
Filename            = 2sg148-2-ACN-3-4-6r-h
Author              = Smithsonian
Experiment          = hsqc_edit_dec_ph
Sample_id           = 2sg148-2-ACN-3-4-6r
Solvent             = ACETONITRILE-D3
Creation_time       = 29-MAR-2010 17:31:23
Revision_time       = 22-MAR-2011 10:21:36
Current_time        = 22-MAR-2011 10:24:23

Comment             = absorption_hsqc
Data_format         = 2D COMPLEX COMPLEX
Dim_size            = 819, 512
Dim_title           = 1H 13C
Dim_units           = [ppm] [ppm]
Dimensions          = X Y
Site                = ECA 600
Spectrometer        = ECA600-AID

Field_strength      = 14.09636928[T] (600[M
X_acq_duration      = 0.22921216[s]
X_domain            = 1H
X_freq              = 600.1723046[MHz]
X_offset            = 3.02726[ppm]
X_points            = 1024
X_prescans          = 4
X_resolution        = 4.36277028[Hz]
X_sweep             = 4.46747677[kHz]
Y_domain            = 13C
Y_freq              = 150.91343039[MHz]
Y_offset            = 60.65893[ppm]
Y_points            = 256
Y_prescans          = 0
Y_resolution        = 73.37058603[Hz]
Y_sweep             = 18.78287002[kHz]
Tri_domain          = 1H
Tri_freq            = 600.1723046[MHz]
Tri_offset          = 5[ppm]
Clipped             = FALSE
Mod_return          = 1
Scans               = 8
Total_scans         = 2048

X_acq_time          = 0.22921216[s]
X_atn               = 3[dB]
X_pulse             = 7.31[us]
Y_acq_time          = 13.62944[ms]
Y_atn               = 2[dB]
Y_p1_correction     = 360
Y_pulse             = 16[us]
Irr_atn_dec         = 18.5[dB]
Irr_noise           = MPF8
Tri_mode            = Off
Composite_pulse     = FALSE
Dante_presat        = FALSE
```



HMBC spectrum of cocosolide (1) in CD_3CN, 600 MHz

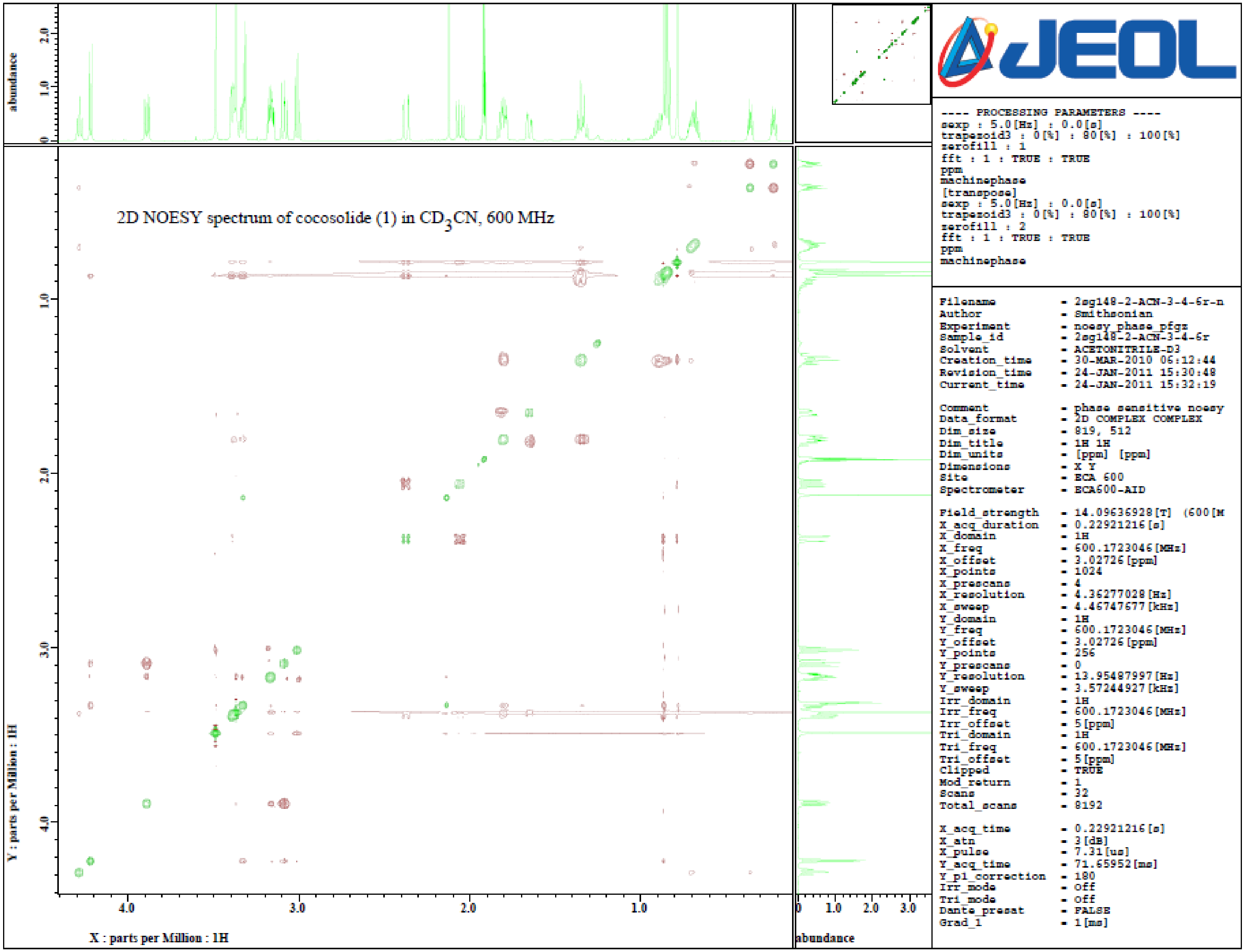
```
---- PROCESSING PARAMETERS ----
gauss : 5.0[Hz] : 0.0[s]
sinbell_auto
zerofill : 1
fft : 1 : TRUE : TRUE
ppm
[transpose]
sinbell4 : -60 : 160
trapezoid3 : 5[%] : 80[%] : 100[%]
zerofill : 2
fft : 1 : TRUE : TRUE
ppm
abs
[transpose]
```

```
Filename            = 2sg148-2-ACN-3-4-6r-h
Author              = Smithsonian
Experiment          = hmbc_pfg.ex2
Sample_id           = 2sg148-2-ACN-3-4-6r
Solvent             = ACETONITRILE-D3
Creation_time       = 29-MAR-2010 19:51:24
Revision_time       = 24-JAN-2011 15:39:30
Current_time        = 24-JAN-2011 15:40:31

Comment             = gradient enhanced HMB
Data_format         = 2D REAL REAL
Dim_size            = 1638, 512
Dim_title           = 1H 13C
Dim_units           = [ppm] [ppm]
Dimensions          = X Y
Site                = ECA 600
Spectrometer        = ECA600-AID

Field_strength      = 14.09636928[T] (600[M
X_acq_duration      = 0.45842432[s]
X_domain            = 1H
X_freq              = 600.1723046[MHz]
X_offset            = 3.02726[ppm]
X_points            = 2048
X_prescans          = 4
X_resolution        = 2.18138514[Hz]
X_sweep             = 4.46747677[kHz]
Y_domain            = 13C
Y_freq              = 150.91343039[MHz]
Y_offset            = 86.27914[ppm]
Y_points            = 256
Y_prescans          = 0
Y_resolution        = 110.22150113[Hz]
Y_sweep             = 28.21670429[kHz]
Tri_domain          = 1H
Tri_freq            = 600.1723046[MHz]
Tri_offset          = 5[ppm]
Clipped             = FALSE
Mod_return          = 1
Scans               = 16
Total_scans         = 4096

X_acq_time          = 0.45842432[s]
X_atn               = 3[dB]
X_pulse             = 7.31[us]
Y_acq_time          = 9.07264[ms]
Y_atn               = 2[dB]
Y_pulse             = 16[us]
Tri_mode            = Off
Dante_presat        = FALSE
Delta               = 62.5[ms]
Grad_1              = 1[ms]
Grad_1_amp          = 0.18[T/m]
Grad_2              = 1[ms]
```



2D NOESY spectrum of cocosolide (1) in CD_3CN, 600 MHz

```
---- PROCESSING PARAMETERS ----
sexp : 5.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
ppm
machinephase
[transpose]
sexp : 5.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 2
fft : 1 : TRUE : TRUE
ppm
machinephase
```

```
Filename           = 2sg148-2-ACN-3-4-6r-n
Author             = Smithsonian
Experiment         = noesy_phase_pfgz
Sample_id          = 2sg148-2-ACN-3-4-6r
Solvent            = ACETONITRILE-D3
Creation_time      = 30-MAR-2010 06:12:44
Revision_time      = 24-JAN-2011 15:30:48
Current_time       = 24-JAN-2011 15:32:19

Comment            = phase sensitive noesy
Data_format        = 2D COMPLEX COMPLEX
Dim_size           = 819, 512
Dim_title          = 1H 1H
Dim_units          = [ppm] [ppm]
Dimensions         = X Y
Site               = ECA 600
Spectrometer       = ECA600-AID

Field_strength     = 14.09636928[T] (600[M
X_acq_duration     = 0.22921216[s]
X_domain           = 1H
X_freq             = 600.1723046[MHz]
X_offset           = 3.02726[ppm]
X_points           = 1024
X_prescans         = 4
X_resolution       = 4.36277028[Hz]
X_sweep            = 4.46747677[kHz]
Y_domain           = 1H
Y_freq             = 600.1723046[MHz]
Y_offset           = 3.02726[ppm]
Y_points           = 256
Y_prescans         = 0
Y_resolution       = 13.95487997[Hz]
Y_sweep            = 3.57244927[kHz]
Irr_domain         = 1H
Irr_freq           = 600.1723046[MHz]
Irr_offset         = 5[ppm]
Tri_domain         = 1H
Tri_freq           = 600.1723046[MHz]
Tri_offset         = 5[ppm]
Clipped            = TRUE
Mod_return         = 1
Scans              = 32
Total_scans        = 8192

X_acq_time         = 0.22921216[s]
X_atn              = 3[dB]
X_pulse            = 7.31[us]
Y_acq_time         = 71.65952[ms]
Y_pl_correction    = 180
Irr_mode           = Off
Tri_mode           = Off
Dante_presat       = FALSE
Grad_1             = 1[ms]
```

Base Hydrolysis of Cocosolide (1): Compound **1** (2.0 mg) was dissolved in 1.0 mL of EtOH and treated 0.1 mL of 10% aqueous NaOH solution. The mixture was stirred for 1 hour at 65 °C. The EtOH was evaporated and neutralized with dilute HCl at 5 °C. Extraction with CH_2Cl_2 gave 2.0 mg of cocosolide seco-acid (**2**), isolated as white solid: $[\alpha]^{25}_{D}$ –40.5 (*c* 0.13, MeOH); IR (film) ν_{max} 3464, 2959, 2932, 1718, 1389, 1259, 1164, 1096, 1076, 999, 955 cm^{-1}; ^{1}H NMR (CD_3CN) δ 4.69 (1H, br s OH-9), 4.23 (1H, d, *J* = 7.6 Hz, H-17), 3.90 (1H, dd, *J* = 11.0, 4.8 Hz, Ha-21), 3.56 (1H, m, H-7), 3.50 (3H, s, H-22), 3.45 (1H, dd, *J* = 8.2, 2.0 Hz, 3-H), 3.37 (3H, s, H-23), 3.35 (1H, dd, *J* = 11.4, 4.8 Hz, H-5), 3.18 (1H, m, H-20), 3.17 (1H, m, H-18), 3.10 (1H, dd, *J* = 11.0, 9.6 Hz, Hb-21), 3.02 (1H, t, *J* = 8.3 Hz, H-19), 2.99 (1H, m, H-9), 2.46 (1H, dd, *J* = 17.2, 2.0 Hz, H-2a), 2.27 (1H, dd, *J* = 17.2, 8.2 Hz, H-2b), 1.80 (1H, ddd, *J* = 13.0, 4.8, 2.0 Hz, H-6a), 1.65 (1H, m, H-8a), 1.57 (1H, m, H-8b), 1.43 (1H, ddd, *J* = 13.0, 11.4, 11.0 Hz, H-6b), 1.20 (2H, m, H-12), 0.93 (3H, s, H-15), 0.93 (3H, t, *J* = 6.9 Hz, H-13), 0.82 (3H, s, H-16), 0.60 (1H, m, H-11), 0.50 (1H, m, H-10), 0.32 (1H, m, H-14a), 0.16 (1H, m, H-14b); ^{13}C NMR (CD_3CN, * indicates these signals may be interchanged) δ 173.4 (C, C-1), 106.4 (CH, C-17), 85.5 (CH, C-19), 85.0 (CH, C-5), 81.2 (CH, C-3), 79.9 (CH, C-18), 76.1 (CH, C-7), 74.3* (CH, C-20), 74.2* (CH, C-9), 63.3 (CH_2, C-21), 60.3 (CH_3, C-22), 58.4 (CH_3, C-23), 43.7 (CH_2, C-8), 39.3 (C, C-4), 37.3 (CH_2, C-6), 35.3 (CH_2, C-2), 27.4 (CH_2, C-12), 25.7 (CH, C-10), 22.2 (CH_3, C-15), 19.0 (CH, C-11), 13.9 (CH_3, C-13), 13.4 (CH_3, C-16), 9.3 (CH_2, C-14); HRESI/APCIMS *m/z* 483.2588 $[M + Na]^+$ (calcd for $C_{23}H_{40}O_9Na$, 483.2565).

Methylation of Cocosolide Seco-acid (2). Compound **2** (1.0 mg) was dissolved in 1.0 mL of MeOH and cooled to 4 °C. The cooled solution was treated with 50 μL of 2.0 M trimethylsilyl diazomethane in diethylether. Evaporation of MeOH and excess trimethylsilyl diazomethane gave 1.0 mg of cocosolide seco-ester (**3**), isolated as white, glassy solid: $[\alpha]^{25}_{D}$ –42.8 (*c* 0.17, MeOH); IR (film) ν_{max} 3520, 2959, 1741, 1435, 1370, 1259, 1162, 1096, 1073, 991 cm^{-1}; ^{1}H NMR (CD_3CN) δ 4.23 (1H, d, *J* = 7.6 Hz, H-17), 3.90 (1H, dd, *J* = 11.0, 4.8 Hz, Ha-21), 3.59 (3H, s, H-24), 3.55 (1H, m, H-7), 3.50 (3H, s, H-22), 3.45 (1H, dd, *J* = 8.2, 2.0 Hz, 3-H), 3.37 (3H, s, H-23), 3.35 (1H, dd, *J* = 11.4, 4.8 Hz, H-5), 3.18 (1H, m, H-20), 3.17 (1H, m, H-18), 3.10 (1H, dd, *J* = 11.0, 9.6 Hz, Hb-21), 3.02 (1H, t, *J* = 8.3 Hz, H-19), 2.98 (1H, m, H-9), 2.87 (1H, d, *J* = 2.8 Hz, OH-9), 2.46 (1H, dd, *J* = 17.2, 2.0 Hz, H-2a), 2.27 (1H, dd, *J* = 17.2, 8.2 Hz, H-2b), 1.80 (1H, ddd, *J* = 13.0, 4.8, 2.0 Hz, H-6a), 1.63 (1H, m, H-8a), 1.55 (1H, m, H-8b), 1.43 (1H, ddd, *J* = 13.0, 11.4, 11.0 Hz, H-6b), 1.20 (2H, m, H-12), 0.93 (3H, s, H-15), 0.93 (3H, t, *J* = 6.9 Hz, H-13), 0.82 (3H, s, H-16), 0.58 (1H, m, H-11), 0.48 (1H, m, H-10), 0.30 (1H, m, H-14a), 0.16 (1H, m, H-14b); ^{13}C NMR (CD_3CN, * indicates these signals may be interchanged) δ 173.3 (C, C-1), 106.4 (CH, C-17), 85.4 (CH, C-19), 84.9 (CH, C-5), 81.4 (CH, C-3), 79.9 (CH, C-18), 75.9 (CH, C-7), 74.1* (CH, C-20), 73.9* (CH, C-9), 63.3 (CH_2, C-21), 60.3 (CH_3, C-22), 58.4 (CH_3, C-23), 52.0 (CH_3, C-24), 43.8 (CH_2, C-8), 39.3 (C, C-4), 37.3 (CH_2, C-6), 35.6 (CH_2, C-2), 27.4 (CH_2, C-12), 25.6 (CH, C-10), 22.2 (CH_3, C-15), 18.9 (CH, C-11), 13.9 (CH_3, C-13), 13.4 (CH_3, C-16), 9.2 (CH_2, C-14); HRESI/APCIMS *m/z* 497.2738 $[M + Na]^+$ (calcd for $C_{24}H_{42}O_9Na$, 497.2721).

Preparation of (*R*)-MTPA and (*S*)-MTPA Diesters of Seco-ester (3): Compound **3** (0.3 mg) was dissolved in $CHCl_3$ (20 μL) and added pyridine (60 μL) and a catalytic amount of 4-DMAP. The solution was treated with *S*-(–)-MTPA chloride (2.0 μL) and stirred at room temperature for 24 hours. The reaction was terminated with the addition of MeOH (50 μL) and the solvent was evaporated to give the (*R*)-MTPA diester of **3**. Similarly, the (*S*)-MTPA diester of **3** was prepared with *R*-(–)-MTPA chloride using the same procedure. Both esters were subjected to HPLC (semi-prep 250 × 10 mm, 5 μm, SiO_2, flow 3.0 mL/min) using hexanes − 25% EtOAc to yield the pure (*R*)-MTPA diester of **3** (0.3 mg) and (*S*)-MTPA diesters of **3** (0.3 mg).

***R*-MTPA ester of 3**: ^{1}H NMR (CD_3CN) δ (only key resonances are listed) 1.912, 1.464 (2H, m, H-6), 3.567 (1H, m, H-7), 1.912. 1.807 (2H, m, H-8), 4.488 (H, m, H-9), 0.659 (H, m, H-10), 0.618 (H, m, H-11), 1.114, 1.023 (2H, m, H-12), 0.757 (3H, t, J = 6.9 Hz, H-13), 0.534, 0.348 (2H, m, H-14); HRESI/TOFMS *m/z* 929.3543 $[M + Na]^+$ (calcd for $C_{44}H_{56}F_6O_{13}Na$, 929.3517).

***S*-MTPA ester of 3**: ^{1}H NMR (CD_3CN) δ (only key resonances are listed) 1.717, 1.358 (2H, m, H-6), 3.289 (1H, m, H-7), 1.816. 1.740 (2H, m, H-8), 4.426 (H, m, H-9), 0.779 (H, m, H-10), 0.742 (H, m, H-11), 1.292, 1.116 (2H, m, H-12), 0.885 (3H, t, J = 6.9 Hz, H-13), 0.540, 0.370 (2H, m, H-14); HRESI/TOFMS *m/z* 929.3528 $[M + Na]^+$ (calcd for $C_{44}H_{56}F_6O_{13}Na$, 929.3517).

Single-crystal X-ray Structure Determination: A Leica MZ 75 microscope was used to identify a suitable colorless multi-faceted crystal with very well defined faces with dimensions (max, intermediate, and min) 0.3 mm × 0.2 mm × 0.1 mm from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K. An APEXII BRUKER X-ray (three-circle) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX2 software suite.[1] The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The detector was set at 6.0 cm from the crystal sample. The X-ray radiation employed was generated from a Mo sealed X-ray tube (K_α = 0.70173Å with a potential of 40 kV and a current of 40 mA) fitted with a graphite monochromator in the parallel mode (175 mm collimator with 0.5 mm pinholes). Sixty data frames were taken at widths of 0.5° with an exposure time of 60 s. These reflections were used in the auto-indexing procedure to determine the unit cell. A suitable cell was found and refined by nonlinear least squares and Bravais lattice procedures. The unit cell was verified by examination of the *h k l* overlays on several frames of data. No super-cell or erroneous reflections were observed. After careful examination of the unit cell, a standard data collection procedure was initiated using omega scans. Each frame was exposed for 60 s and contrasted against a 60 s dark current exposure. The measurements are reported in Table S1 of Supporting Information. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2.[1] The integration method employed a three dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally the data was merged and scaled to produce a suitable data set. The absorption correction program SADABS[2] was employed to correct the data for absorption effects. Systematic reflection conditions and statistical tests for the data suggested the space group $P2_1$. A solution was obtained readily using SHELXTL (SHELXS).[3] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bound to carbon were placed in idealized positions [C–H = 0.96 Å, $U_{iso}(H) = 1.2 \times U_{iso}(C)$]. The structure was refined (weighted least squares refinement on F^2) to convergence.[3] X-seed was employed for the final data presentation and structure plots.[4]

Table S1. Crystal data and structure refinement for cocosolide (1)

Identification code	Cocosolide	
Empirical formula	C46 H76.25 O16.12	
Formula weight	887.32	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 14.201(5) Å	α= 90°.
	b = 18.976(7) Å	β= 102.985(5)°.
	c = 18.547(7) Å	γ = 90°.
Volume	4870(3) Å^3	
Z	4	
Density (calculated)	1.210 Mg/m^3	
Absorption coefficient	0.090 mm^{-1}	
F(000)	1925	
Crystal size	0.30 x 0.18 x 0.10 mm^3	
Theta range for data collection	1.82 to 28.69°.	
Index ranges	-19<=h<=18, -24<=k<=25, -24<=l<=24	
Reflections collected	57028	
Independent reflections	22990 [R(int) = 0.0523]	
Completeness to theta = 28.69°	94.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9910 and 0.9734	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22990 / 1 / 1148	
Goodness-of-fit on F^2	1.006	
Final R indices [I>2sigma(I)]	R1 = 0.0494, wR2 = 0.0861	
R indices (all data)	R1 = 0.0884, wR2 = 0.1002	
Absolute structure parameter	-0.2(4)	
Largest diff. peak and hole	0.260 and -0.200 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for cocosolide (1). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
O(1A)	2059(1)	3450(1)	698(1)	28(1)
O(2A)	4461(1)	4084(1)	1266(1)	38(1)
O(3A)	5072(1)	2987(1)	1506(1)	27(1)
O(4A)	4599(1)	2851(1)	3015(1)	28(1)
O(5A)	3102(1)	4156(1)	2526(1)	37(1)
O(6A)	1741(1)	3506(1)	2194(1)	26(1)
O(7A)	1005(1)	3633(1)	-1572(1)	27(1)
O(8A)	1396(1)	3859(1)	-3005(1)	35(1)
O(9A)	-292(1)	4090(1)	-4104(1)	40(1)
O(10A)	-1543(1)	5122(1)	-3671(1)	45(1)
O(11A)	-386(1)	4269(1)	-1909(1)	30(1)
O(12A)	5646(1)	2388(1)	5250(1)	31(1)
O(13A)	7209(1)	2017(1)	5573(1)	34(1)
O(14A)	5874(2)	3133(1)	6580(1)	57(1)
O(15A)	7432(1)	2635(1)	7747(1)	48(1)
O(16A)	9188(1)	2367(1)	7151(1)	52(1)
C(1A)	2769(2)	3538(1)	265(1)	25(1)
C(2A)	2346(2)	3369(1)	-559(1)	26(1)
C(3A)	1448(2)	3836(1)	-819(1)	26(1)
C(4A)	738(2)	3780(1)	-320(1)	28(1)
C(5A)	1268(2)	3925(1)	476(1)	27(1)
C(6A)	3622(2)	3077(1)	630(1)	27(1)
C(7A)	4406(2)	3458(1)	1166(1)	26(1)
C(8A)	5936(2)	3260(1)	2021(1)	27(1)
C(9A)	6135(2)	2777(1)	2695(1)	29(1)
C(10A)	5612(2)	2974(1)	3294(1)	27(1)
C(11A)	5956(2)	2569(1)	4010(1)	30(1)
C(12A)	5374(2)	2782(1)	4567(1)	28(1)
C(13A)	4280(2)	2697(1)	4264(1)	29(1)
C(14A)	4039(2)	3096(1)	3519(1)	27(1)
C(15A)	2997(2)	3026(1)	3098(1)	28(1)
C(16A)	2656(2)	3629(1)	2577(1)	26(1)
C(17A)	1207(2)	4108(1)	1810(1)	30(1)
C(18A)	658(2)	3864(1)	1049(1)	31(1)
C(19A)	3094(2)	3563(2)	-1003(1)	36(1)
C(20A)	2080(2)	2590(1)	-672(1)	35(1)
C(21A)	557(2)	4170(1)	-2044(1)	26(1)
C(22A)	463(2)	3908(1)	-2836(1)	28(1)
C(23A)	-133(2)	4408(1)	-3393(1)	29(1)
C(24A)	-1086(2)	4575(1)	-3193(1)	32(1)

C(25A)	-916(2)	4800(1)	-2385(1)	34(1)
C(26A)	-96(2)	4534(2)	-4665(1)	50(1)
C(27A)	-2551(2)	5202(2)	-3678(2)	66(1)
C(28A)	6750(2)	3261(1)	1629(1)	29(1)
C(29A)	7542(2)	3805(1)	1869(1)	32(1)
C(30A)	6859(2)	3854(1)	1121(1)	32(1)
C(31A)	7264(2)	3716(2)	444(1)	41(1)
C(32A)	7815(2)	4359(2)	250(2)	52(1)
C(33A)	6553(2)	2553(1)	5686(1)	30(1)
C(34A)	6498(2)	2570(1)	6491(1)	32(1)
C(35A)	7492(2)	2688(1)	6985(1)	36(1)
C(36A)	8222(2)	2172(2)	6816(1)	36(1)
C(37A)	8175(2)	2167(2)	5989(1)	39(1)
C(38A)	7657(2)	3251(1)	8168(1)	41(1)
C(39A)	9543(2)	2134(2)	7883(1)	42(1)
C(40A)	3979(2)	1920(1)	4155(2)	39(1)
C(41A)	3754(2)	3045(2)	4816(1)	41(1)
C(42A)	610(2)	4372(2)	2322(1)	37(1)
C(43A)	199(3)	5105(2)	2248(2)	63(1)
C(44A)	1041(2)	4922(2)	2880(2)	50(1)
C(45A)	948(2)	4875(2)	3677(2)	54(1)
C(46A)	1747(2)	4419(2)	4138(2)	49(1)
O(1B)	7128(1)	1377(1)	10102(1)	28(1)
O(2B)	9131(1)	1854(1)	10873(1)	29(1)
O(3B)	9294(1)	938(1)	11660(1)	36(1)
O(4B)	8309(1)	1590(1)	12894(1)	23(1)
O(5B)	6472(1)	892(1)	12136(1)	24(1)
O(6B)	7194(1)	231(1)	11406(1)	36(1)
O(7B)	5177(1)	1010(1)	8085(1)	27(1)
O(8B)	5917(1)	960(1)	7111(1)	30(1)
O(9B)	5272(1)	61(1)	5314(1)	43(1)
O(10B)	3444(1)	245(1)	5718(1)	37(1)
O(11B)	3693(1)	92(1)	7297(1)	33(1)
O(12B)	10042(1)	2178(1)	14914(1)	27(1)
O(13B)	10449(1)	1250(1)	15690(1)	32(1)
O(14B)	11593(1)	2972(1)	15719(1)	33(1)
O(15B)	12211(1)	969(1)	17411(1)	40(1)
O(16B)	12347(1)	2503(1)	17205(1)	35(1)
C(1B)	6296(2)	958(1)	10118(1)	25(1)
C(2B)	5476(2)	1081(1)	9425(1)	27(1)
C(3B)	5908(2)	892(1)	8759(1)	25(1)
C(4B)	6832(2)	1297(1)	8761(1)	32(1)
C(5B)	7544(2)	1177(1)	9494(1)	30(1)
C(6B)	6049(2)	1122(1)	10859(1)	26(1)
C(7B)	6654(2)	698(1)	11483(1)	24(1)
C(8B)	6833(2)	430(1)	12774(1)	24(1)

C(9B)	7252(2)	886(1)	13438(1)	25(1)
C(10B)	8274(2)	1130(1)	13500(1)	24(1)
C(11B)	8693(2)	1500(1)	14231(1)	27(1)
C(12B)	9696(2)	1779(1)	14240(1)	25(1)
C(13B)	9736(2)	2240(1)	13565(1)	25(1)
C(14B)	9284(2)	1785(1)	12890(1)	24(1)
C(15B)	9239(2)	2109(1)	12135(1)	27(1)
C(16B)	9216(2)	1561(1)	11547(1)	26(1)
C(17B)	9231(2)	1382(1)	10274(1)	30(1)
C(18B)	8486(2)	1583(2)	9579(1)	34(1)
C(19B)	4653(2)	566(2)	9445(1)	37(1)
C(20B)	5116(2)	1844(1)	9387(1)	39(1)
C(21B)	5280(2)	595(1)	7480(1)	25(1)
C(22B)	4293(2)	522(1)	6958(1)	25(1)
C(23B)	4362(2)	181(1)	6228(1)	28(1)
C(24B)	5142(2)	511(1)	5903(1)	32(1)
C(25B)	6071(2)	565(1)	6489(1)	31(1)
C(26B)	2961(2)	-400(2)	5523(2)	53(1)
C(27B)	5781(2)	387(2)	4818(2)	51(1)
C(28B)	5993(2)	-6(1)	12873(1)	26(1)
C(29B)	6178(2)	-732(1)	13214(1)	33(1)
C(30B)	5714(2)	-645(1)	12400(1)	31(1)
C(31B)	4671(2)	-814(2)	12096(1)	42(1)
C(32B)	4251(2)	-363(2)	11415(2)	71(1)
C(33B)	10806(2)	1870(1)	15406(1)	26(1)
C(34B)	11192(2)	2388(1)	16027(1)	25(1)
C(35B)	11968(2)	2022(1)	16615(1)	27(1)
C(36B)	11533(2)	1370(1)	16880(1)	31(1)
C(37B)	11187(2)	894(1)	16213(1)	34(1)
C(38B)	13384(2)	2523(2)	17374(1)	39(1)
C(39B)	12213(2)	1096(2)	18159(1)	49(1)
C(40B)	9190(2)	2933(1)	13580(1)	32(1)
C(41B)	10798(2)	2391(1)	13576(1)	35(1)
C(42B)	10257(2)	1415(1)	10194(1)	32(1)
C(43B)	10629(2)	811(2)	9804(1)	45(1)
C(44B)	10998(2)	919(1)	10629(1)	36(1)
C(45B)	12026(2)	1155(2)	10932(2)	44(1)
C(46B)	12132(2)	1587(2)	11638(2)	52(1)
O(1W)	5457(6)	2483(4)	7763(4)	61(2)

Table S3. Bond lengths [Å] and angles [°] for cocosolide (1)

O(1A)-C(5A)	1.427(3)
O(1A)-C(1A)	1.434(3)
O(2A)-C(7A)	1.202(3)
O(3A)-C(7A)	1.350(3)
O(3A)-C(8A)	1.470(3)
O(4A)-C(10A)	1.434(3)
O(4A)-C(14A)	1.435(3)
O(5A)-C(16A)	1.199(3)
O(6A)-C(16A)	1.353(3)
O(6A)-C(17A)	1.464(3)
O(7A)-C(21A)	1.400(3)
O(7A)-C(3A)	1.449(3)
O(8A)-C(22A)	1.431(3)
O(9A)-C(26A)	1.415(3)
O(9A)-C(23A)	1.422(3)
O(10A)-C(24A)	1.423(3)
O(10A)-C(27A)	1.436(3)
O(11A)-C(21A)	1.429(3)
O(11A)-C(25A)	1.436(3)
O(12A)-C(33A)	1.395(3)
O(12A)-C(12A)	1.447(3)
O(13A)-C(33A)	1.426(3)
O(13A)-C(37A)	1.443(3)
O(14A)-C(34A)	1.423(3)
O(15A)-C(38A)	1.402(3)
O(15A)-C(35A)	1.438(3)
O(16A)-C(39A)	1.408(3)
O(16A)-C(36A)	1.422(3)
C(1A)-C(6A)	1.523(3)
C(1A)-C(2A)	1.545(3)
C(2A)-C(19A)	1.527(3)
C(2A)-C(20A)	1.528(3)
C(2A)-C(3A)	1.540(3)
C(3A)-C(4A)	1.518(3)
C(4A)-C(5A)	1.524(3)
C(5A)-C(18A)	1.519(3)
C(6A)-C(7A)	1.501(3)
C(8A)-C(28A)	1.497(3)
C(8A)-C(9A)	1.523(3)
C(9A)-C(10A)	1.514(3)
C(10A)-C(11A)	1.519(3)
C(11A)-C(12A)	1.514(3)
C(12A)-C(13A)	1.538(3)
C(13A)-C(40A)	1.536(3)

C(13A)-C(41A)	1.543(3)
C(13A)-C(14A)	1.545(3)
C(14A)-C(15A)	1.515(3)
C(15A)-C(16A)	1.506(3)
C(17A)-C(42A)	1.494(3)
C(17A)-C(18A)	1.523(3)
C(21A)-C(22A)	1.528(3)
C(22A)-C(23A)	1.513(3)
C(23A)-C(24A)	1.514(3)
C(24A)-C(25A)	1.524(3)
C(28A)-C(30A)	1.498(3)
C(28A)-C(29A)	1.519(3)
C(29A)-C(30A)	1.507(3)
C(30A)-C(31A)	1.516(3)
C(31A)-C(32A)	1.535(4)
C(33A)-C(34A)	1.513(3)
C(34A)-C(35A)	1.517(3)
C(35A)-C(36A)	1.510(4)
C(36A)-C(37A)	1.521(3)
C(42A)-C(44A)	1.500(4)
C(42A)-C(43A)	1.503(4)
C(43A)-C(44A)	1.514(4)
C(44A)-C(45A)	1.516(4)
C(45A)-C(46A)	1.528(4)
O(1B)-C(1B)	1.430(3)
O(1B)-C(5B)	1.436(3)
O(2B)-C(16B)	1.349(3)
O(2B)-C(17B)	1.461(3)
O(3B)-C(16B)	1.202(3)
O(4B)-C(10B)	1.434(3)
O(4B)-C(14B)	1.434(3)
O(5B)-C(7B)	1.346(3)
O(5B)-C(8B)	1.469(3)
O(6B)-C(7B)	1.201(3)
O(7B)-C(21B)	1.405(3)
O(7B)-C(3B)	1.452(3)
O(8B)-C(21B)	1.430(3)
O(8B)-C(25B)	1.433(3)
O(9B)-C(27B)	1.431(3)
O(9B)-C(24B)	1.432(3)
O(10B)-C(26B)	1.411(3)
O(10B)-C(23B)	1.433(3)
O(11B)-C(22B)	1.424(3)
O(12B)-C(33B)	1.382(3)
O(12B)-C(12B)	1.450(3)
O(13B)-C(37B)	1.427(3)

O(13B)-C(33B)	1.429(3)
O(14B)-C(34B)	1.423(3)
O(15B)-C(39B)	1.408(3)
O(15B)-C(36B)	1.431(3)
O(16B)-C(35B)	1.434(3)
O(16B)-C(38B)	1.435(3)
C(1B)-C(6B)	1.524(3)
C(1B)-C(2B)	1.547(3)
C(2B)-C(19B)	1.531(3)
C(2B)-C(20B)	1.531(3)
C(2B)-C(3B)	1.539(3)
C(3B)-C(4B)	1.520(3)
C(4B)-C(5B)	1.518(3)
C(5B)-C(18B)	1.519(3)
C(6B)-C(7B)	1.509(3)
C(8B)-C(28B)	1.497(3)
C(8B)-C(9B)	1.514(3)
C(9B)-C(10B)	1.503(3)
C(10B)-C(11B)	1.523(3)
C(11B)-C(12B)	1.515(3)
C(12B)-C(13B)	1.539(3)
C(13B)-C(40B)	1.529(3)
C(13B)-C(41B)	1.531(3)
C(13B)-C(14B)	1.538(3)
C(14B)-C(15B)	1.517(3)
C(15B)-C(16B)	1.502(3)
C(17B)-C(42B)	1.498(3)
C(17B)-C(18B)	1.521(3)
C(21B)-C(22B)	1.521(3)
C(22B)-C(23B)	1.522(3)
C(23B)-C(24B)	1.511(3)
C(24B)-C(25B)	1.513(3)
C(28B)-C(30B)	1.496(3)
C(28B)-C(29B)	1.514(3)
C(29B)-C(30B)	1.514(3)
C(30B)-C(31B)	1.496(3)
C(31B)-C(32B)	1.530(4)
C(33B)-C(34B)	1.519(3)
C(34B)-C(35B)	1.533(3)
C(35B)-C(36B)	1.513(3)
C(36B)-C(37B)	1.522(3)
C(42B)-C(44B)	1.506(3)
C(42B)-C(43B)	1.513(4)
C(43B)-C(44B)	1.517(3)
C(44B)-C(45B)	1.510(4)
C(45B)-C(46B)	1.522(4)

C(5A)-O(1A)-C(1A)	111.87(16)
C(7A)-O(3A)-C(8A)	117.69(18)
C(10A)-O(4A)-C(14A)	111.75(17)
C(16A)-O(6A)-C(17A)	116.90(18)
C(21A)-O(7A)-C(3A)	116.55(17)
C(26A)-O(9A)-C(23A)	114.4(2)
C(24A)-O(10A)-C(27A)	113.4(2)
C(21A)-O(11A)-C(25A)	111.55(17)
C(33A)-O(12A)-C(12A)	114.90(18)
C(33A)-O(13A)-C(37A)	110.73(19)
C(38A)-O(15A)-C(35A)	115.6(2)
C(39A)-O(16A)-C(36A)	116.1(2)
O(1A)-C(1A)-C(6A)	105.91(18)
O(1A)-C(1A)-C(2A)	111.39(18)
C(6A)-C(1A)-C(2A)	114.48(19)
C(19A)-C(2A)-C(20A)	109.9(2)
C(19A)-C(2A)-C(3A)	108.67(19)
C(20A)-C(2A)-C(3A)	110.64(19)
C(19A)-C(2A)-C(1A)	108.66(19)
C(20A)-C(2A)-C(1A)	111.4(2)
C(3A)-C(2A)-C(1A)	107.49(18)
O(7A)-C(3A)-C(4A)	111.40(18)
O(7A)-C(3A)-C(2A)	107.33(18)
C(4A)-C(3A)-C(2A)	112.70(19)
C(3A)-C(4A)-C(5A)	109.07(19)
O(1A)-C(5A)-C(18A)	106.56(18)
O(1A)-C(5A)-C(4A)	110.57(18)
C(18A)-C(5A)-C(4A)	115.4(2)
C(7A)-C(6A)-C(1A)	114.6(2)
O(2A)-C(7A)-O(3A)	124.7(2)
O(2A)-C(7A)-C(6A)	126.1(2)
O(3A)-C(7A)-C(6A)	109.1(2)
O(3A)-C(8A)-C(28A)	107.87(18)
O(3A)-C(8A)-C(9A)	107.19(19)
C(28A)-C(8A)-C(9A)	112.27(19)
C(10A)-C(9A)-C(8A)	115.0(2)
O(4A)-C(10A)-C(9A)	108.23(18)
O(4A)-C(10A)-C(11A)	109.37(18)
C(9A)-C(10A)-C(11A)	113.78(19)
C(12A)-C(11A)-C(10A)	110.14(19)
O(12A)-C(12A)-C(11A)	112.30(19)
O(12A)-C(12A)-C(13A)	108.30(18)
C(11A)-C(12A)-C(13A)	112.6(2)
C(40A)-C(13A)-C(12A)	112.1(2)
C(40A)-C(13A)-C(41A)	109.7(2)

C(12A)-C(13A)-C(41A)	108.2(2)
C(40A)-C(13A)-C(14A)	110.7(2)
C(12A)-C(13A)-C(14A)	106.12(18)
C(41A)-C(13A)-C(14A)	109.9(2)
O(4A)-C(14A)-C(15A)	104.83(18)
O(4A)-C(14A)-C(13A)	112.34(18)
C(15A)-C(14A)-C(13A)	114.35(19)
C(16A)-C(15A)-C(14A)	113.6(2)
O(5A)-C(16A)-O(6A)	124.4(2)
O(5A)-C(16A)-C(15A)	125.8(2)
O(6A)-C(16A)-C(15A)	109.8(2)
O(6A)-C(17A)-C(42A)	104.97(18)
O(6A)-C(17A)-C(18A)	108.44(19)
C(42A)-C(17A)-C(18A)	116.5(2)
C(5A)-C(18A)-C(17A)	111.8(2)
O(7A)-C(21A)-O(11A)	107.33(18)
O(7A)-C(21A)-C(22A)	107.10(18)
O(11A)-C(21A)-C(22A)	109.13(18)
O(8A)-C(22A)-C(23A)	107.17(19)
O(8A)-C(22A)-C(21A)	110.28(18)
C(23A)-C(22A)-C(21A)	111.53(19)
O(9A)-C(23A)-C(22A)	108.37(19)
O(9A)-C(23A)-C(24A)	110.6(2)
C(22A)-C(23A)-C(24A)	111.00(19)
O(10A)-C(24A)-C(23A)	108.0(2)
O(10A)-C(24A)-C(25A)	111.0(2)
C(23A)-C(24A)-C(25A)	110.3(2)
O(11A)-C(25A)-C(24A)	110.7(2)
C(8A)-C(28A)-C(30A)	120.5(2)
C(8A)-C(28A)-C(29A)	117.4(2)
C(30A)-C(28A)-C(29A)	59.94(16)
C(30A)-C(29A)-C(28A)	59.35(15)
C(28A)-C(30A)-C(29A)	60.71(15)
C(28A)-C(30A)-C(31A)	120.3(2)
C(29A)-C(30A)-C(31A)	117.8(2)
C(30A)-C(31A)-C(32A)	111.4(2)
O(12A)-C(33A)-O(13A)	107.69(18)
O(12A)-C(33A)-C(34A)	109.3(2)
O(13A)-C(33A)-C(34A)	109.9(2)
O(14A)-C(34A)-C(33A)	107.6(2)
O(14A)-C(34A)-C(35A)	109.7(2)
C(33A)-C(34A)-C(35A)	110.6(2)
O(15A)-C(35A)-C(36A)	110.7(2)
O(15A)-C(35A)-C(34A)	109.3(2)
C(36A)-C(35A)-C(34A)	111.5(2)
O(16A)-C(36A)-C(35A)	112.4(2)

O(16A)-C(36A)-C(37A)	105.17(19)
C(35A)-C(36A)-C(37A)	109.6(2)
O(13A)-C(37A)-C(36A)	111.25(19)
C(17A)-C(42A)-C(44A)	118.1(2)
C(17A)-C(42A)-C(43A)	121.2(2)
C(44A)-C(42A)-C(43A)	60.56(19)
C(42A)-C(43A)-C(44A)	59.60(18)
C(42A)-C(44A)-C(43A)	59.84(19)
C(42A)-C(44A)-C(45A)	121.3(3)
C(43A)-C(44A)-C(45A)	122.7(3)
C(44A)-C(45A)-C(46A)	111.3(2)
C(1B)-O(1B)-C(5B)	110.99(17)
C(16B)-O(2B)-C(17B)	116.62(19)
C(10B)-O(4B)-C(14B)	111.39(16)
C(7B)-O(5B)-C(8B)	117.27(17)
C(21B)-O(7B)-C(3B)	114.78(17)
C(21B)-O(8B)-C(25B)	111.06(17)
C(27B)-O(9B)-C(24B)	113.8(2)
C(26B)-O(10B)-C(23B)	114.46(19)
C(33B)-O(12B)-C(12B)	114.41(17)
C(37B)-O(13B)-C(33B)	111.87(18)
C(39B)-O(15B)-C(36B)	116.06(19)
C(35B)-O(16B)-C(38B)	112.03(18)
O(1B)-C(1B)-C(6B)	105.36(18)
O(1B)-C(1B)-C(2B)	111.71(18)
C(6B)-C(1B)-C(2B)	115.88(19)
C(19B)-C(2B)-C(20B)	110.8(2)
C(19B)-C(2B)-C(3B)	108.38(19)
C(20B)-C(2B)-C(3B)	111.9(2)
C(19B)-C(2B)-C(1B)	108.62(19)
C(20B)-C(2B)-C(1B)	111.2(2)
C(3B)-C(2B)-C(1B)	105.70(19)
O(7B)-C(3B)-C(4B)	111.95(18)
O(7B)-C(3B)-C(2B)	108.57(18)
C(4B)-C(3B)-C(2B)	112.32(19)
C(5B)-C(4B)-C(3B)	109.14(19)
O(1B)-C(5B)-C(4B)	110.7(2)
O(1B)-C(5B)-C(18B)	107.00(19)
C(4B)-C(5B)-C(18B)	114.3(2)
C(7B)-C(6B)-C(1B)	112.12(19)
O(6B)-C(7B)-O(5B)	124.4(2)
O(6B)-C(7B)-C(6B)	124.8(2)
O(5B)-C(7B)-C(6B)	110.66(19)
O(5B)-C(8B)-C(28B)	106.55(17)
O(5B)-C(8B)-C(9B)	108.49(18)
C(28B)-C(8B)-C(9B)	113.27(18)

C(10B)-C(9B)-C(8B)	115.80(19)
O(4B)-C(10B)-C(9B)	109.32(17)
O(4B)-C(10B)-C(11B)	110.00(18)
C(9B)-C(10B)-C(11B)	112.83(18)
C(12B)-C(11B)-C(10B)	110.43(19)
O(12B)-C(12B)-C(11B)	109.11(18)
O(12B)-C(12B)-C(13B)	109.69(19)
C(11B)-C(12B)-C(13B)	113.36(18)
C(40B)-C(13B)-C(41B)	110.0(2)
C(40B)-C(13B)-C(14B)	112.14(19)
C(41B)-C(13B)-C(14B)	110.20(19)
C(40B)-C(13B)-C(12B)	111.27(19)
C(41B)-C(13B)-C(12B)	108.18(19)
C(14B)-C(13B)-C(12B)	104.93(18)
O(4B)-C(14B)-C(15B)	105.57(17)
O(4B)-C(14B)-C(13B)	111.54(17)
C(15B)-C(14B)-C(13B)	116.58(19)
C(16B)-C(15B)-C(14B)	112.2(2)
O(3B)-C(16B)-O(2B)	123.6(2)
O(3B)-C(16B)-C(15B)	124.7(2)
O(2B)-C(16B)-C(15B)	111.7(2)
O(2B)-C(17B)-C(42B)	108.22(19)
O(2B)-C(17B)-C(18B)	108.8(2)
C(42B)-C(17B)-C(18B)	114.4(2)
C(5B)-C(18B)-C(17B)	112.9(2)
O(7B)-C(21B)-O(8B)	107.53(18)
O(7B)-C(21B)-C(22B)	108.27(18)
O(8B)-C(21B)-C(22B)	109.32(18)
O(11B)-C(22B)-C(21B)	109.19(18)
O(11B)-C(22B)-C(23B)	108.30(19)
C(21B)-C(22B)-C(23B)	111.79(19)
O(10B)-C(23B)-C(24B)	109.95(19)
O(10B)-C(23B)-C(22B)	108.72(19)
C(24B)-C(23B)-C(22B)	112.2(2)
O(9B)-C(24B)-C(23B)	106.8(2)
O(9B)-C(24B)-C(25B)	110.4(2)
C(23B)-C(24B)-C(25B)	109.97(19)
O(8B)-C(25B)-C(24B)	110.30(19)
C(30B)-C(28B)-C(8B)	119.4(2)
C(30B)-C(28B)-C(29B)	60.39(16)
C(8B)-C(28B)-C(29B)	119.2(2)
C(30B)-C(29B)-C(28B)	59.22(15)
C(31B)-C(30B)-C(28B)	120.2(2)
C(31B)-C(30B)-C(29B)	121.6(2)
C(28B)-C(30B)-C(29B)	60.39(15)
C(30B)-C(31B)-C(32B)	111.2(2)

O(12B)-C(33B)-O(13B)	107.47(18)
O(12B)-C(33B)-C(34B)	108.84(19)
O(13B)-C(33B)-C(34B)	110.55(18)
O(14B)-C(34B)-C(33B)	108.02(18)
O(14B)-C(34B)-C(35B)	110.45(18)
C(33B)-C(34B)-C(35B)	108.96(19)
O(16B)-C(35B)-C(36B)	112.53(19)
O(16B)-C(35B)-C(34B)	109.92(19)
C(36B)-C(35B)-C(34B)	108.68(19)
O(15B)-C(36B)-C(35B)	113.4(2)
O(15B)-C(36B)-C(37B)	106.7(2)
C(35B)-C(36B)-C(37B)	107.5(2)
O(13B)-C(37B)-C(36B)	109.0(2)
C(17B)-C(42B)-C(44B)	119.9(2)
C(17B)-C(42B)-C(43B)	117.8(2)
C(44B)-C(42B)-C(43B)	60.33(17)
C(42B)-C(43B)-C(44B)	59.61(16)
C(42B)-C(44B)-C(45B)	121.0(2)
C(42B)-C(44B)-C(43B)	60.06(17)
C(45B)-C(44B)-C(43B)	120.2(2)
C(44B)-C(45B)-C(46B)	112.4(2)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (Å^{2}x 10^{3}) for cocosolide (1). The anisotropic displacement factor exponent takes the form: $-2\pi^{2}$[h^{2} a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1A)	24(1)	33(1)	27(1)	7(1)	7(1)	6(1)
O(2A)	36(1)	25(1)	47(1)	-3(1)	-4(1)	4(1)
O(3A)	20(1)	28(1)	31(1)	0(1)	-1(1)	0(1)
O(4A)	22(1)	31(1)	31(1)	-3(1)	5(1)	0(1)
O(5A)	34(1)	34(1)	42(1)	4(1)	6(1)	-8(1
O(6A)	22(1)	27(1)	29(1)	3(1)	5(1)	4(1)
O(7A)	29(1)	27(1)	24(1)	2(1)	1(1)	1(1)
O(8A)	38(1)	37(1)	33(1)	3(1)	13(1)	8(1)
O(9A)	63(1)	32(1)	22(1)	0(1)	4(1)	-5(1)
O(10A)	50(1)	38(1)	39(1)	9(1)	-4(1)	11(1)
O(11A)	27(1)	36(1)	28(1)	7(1)	6(1)	7(1)
O(12A)	26(1)	33(1)	32(1)	4(1)	3(1)	0(1)
O(13A)	26(1)	48(1)	28(1)	-9(1)	3(1)	0(1)
O(14A)	84(2)	44(1)	50(1)	0(1)	31(1)	25(1)
O(15A)	74(1)	50(1)	25(1)	-12(1)	19(1)	-29(1)
O(16A)	37(1)	83(2)	29(1)	14(1)	-6(1)	-28(1)
C(1A)	26(1)	27(1)	21(1)	2(1)	4(1)	1(1)
C(2A)	26(1)	27(1)	26(1)	0(1)	6(1)	-1(1)
C(3A)	27(1)	26(1)	22(1)	1(1)	1(1)	-4(1)
C(4A)	26(1)	32(1)	27(1)	3(1)	4(1)	5(1)
C(5A)	24(1)	29(1)	26(1)	3(1)	5(1)	4(1)
C(6A)	24(1)	28(1)	28(1)	0(1)	3(1)	2(1)
C(7A)	21(1)	31(1)	26(1)	4(1)	8(1)	4(1)
C(8A)	20(1)	30(1)	28(1)	-1(1)	1(1)	1(1)
C(9A)	20(1)	34(2)	30(1)	0(1)	2(1)	4(1)
C(10A)	22(1)	28(1)	30(1)	-2(1)	3(1)	2(1)
C(11A)	23(1)	35(1)	31(1)	-2(1)	2(1)	2(1)
C(12A)	29(1)	27(1)	27(1)	3(1)	4(1)	1(1)
C(13A)	22(1)	29(1)	36(1)	3(1)	6(1)	2(1)
C(14A)	24(1)	26(1)	32(1)	-1(1)	8(1)	2(1)
C(15A)	22(1)	29(1)	32(1)	1(1)	5(1)	2(1)
C(16A)	25(1)	27(1)	28(1)	-4(1)	11(1)	3(1)
C(17A)	34(1)	29(1)	28(1)	7(1)	11(1)	10(1)
C(18A)	28(1)	36(2)	28(1)	3(1)	7(1)	8(1)
C(19A)	30(1)	49(2)	28(1)	-1(1)	7(1)	2(1)
C(20A)	29(1)	29(1)	41(2)	-5(1)	-2(1)	4(1)
C(21A)	24(1)	24(1)	28(1)	3(1)	5(1)	1(1)
C(22A)	32(1)	24(1)	26(1)	-1(1)	6(1)	-1(1)
C(23A)	40(2)	22(1)	24(1)	1(1)	4(1)	-4(1)
C(24A)	35(2)	26(1)	29(1)	4(1)	-2(1)	1(1)

C(25A)	30(1)	35(2)	32(1)	5(1)	0(1)	8(1)
C(26A)	66(2)	55(2)	26(2)	4(1)	10(2)	-3(2)
C(27A)	53(2)	82(3)	55(2)	4(2)	-5(2)	36(2)
C(28A)	22(1)	31(1)	32(1)	0(1)	3(1)	1(1)
C(29A)	26(1)	29(1)	40(2)	-1(1)	5(1)	0(1)
C(30A)	25(1)	36(2)	35(2)	6(1)	6(1)	6(1)
C(31A)	31(2)	54(2)	37(2)	6(1)	6(1)	-1(1)
C(32A)	40(2)	72(2)	46(2)	16(2)	12(1)	-5(2)
C(33A)	32(1)	29(1)	29(1)	-2(1)	4(1)	-5(1)
C(34A)	40(2)	27(1)	32(1)	-3(1)	12(1)	-1(1)
C(35A)	54(2)	31(2)	24(1)	-1(1)	13(1)	-16(1)
C(36A)	30(1)	48(2)	29(1)	2(1)	3(1)	-14(1)
C(37A)	25(1)	63(2)	27(1)	-2(1)	1(1)	-5(1)
C(38A)	48(2)	43(2)	30(2)	-10(1)	3(1)	8(1)
C(39A)	40(2)	53(2)	29(2)	7(1)	0(1)	6(1)
C(40A)	30(1)	38(2)	46(2)	10(1)	0(1)	-7(1)
C(41A)	34(2)	52(2)	41(2)	5(1)	15(1)	9(1)
C(42A)	42(2)	42(2)	30(1)	3(1)	12(1)	19(1)
C(43A)	88(3)	62(2)	43(2)	9(2)	21(2)	47(2)
C(44A)	71(2)	42(2)	41(2)	4(1)	21(2)	22(2)
C(45A)	70(2)	60(2)	37(2)	-1(2)	20(2)	29(2)
C(46A)	54(2)	61(2)	34(2)	4(2)	15(1)	15(2)
O(1B)	31(1)	31(1)	23(1)	-3(1)	10(1)	-8(1)
O(2B)	34(1)	31(1)	22(1)	3(1)	9(1)	-3(1)
O(3B)	51(1)	30(1)	29(1)	3(1)	12(1)	1(1)
O(4B)	22(1)	27(1)	21(1)	2(1)	5(1)	-3(1)
O(5B)	28(1)	25(1)	19(1)	-1(1)	6(1)	-2(1)
O(6B)	44(1)	39(1)	27(1)	2(1)	14(1)	11(1)
O(7B)	34(1)	26(1)	21(1)	-3(1)	5(1)	3(1)
O(8B)	38(1)	30(1)	23(1)	-2(1)	11(1)	-6(1)
O(9B)	62(1)	44(1)	30(1)	-12(1)	21(1)	-5(1)
O(10B)	36(1)	36(1)	32(1)	-2(1)	-6(1)	2(1)
O(11B)	31(1)	35(1)	36(1)	2(1)	12(1)	1(1)
O(12B)	26(1)	30(1)	22(1)	-5(1)	-2(1)	2(1)
O(13B)	24(1)	31(1)	36(1)	5(1)	1(1)	-7(1)
O(14B)	40(1)	30(1)	28(1)	-2(1)	5(1)	-9(1)
O(15B)	37(1)	54(1)	30(1)	13(1)	8(1)	16(1)
O(16B)	32(1)	40(1)	26(1)	-10(1)	-5(1)	6(1)
C(1B)	29(1)	23(1)	23(1)	-2(1)	9(1)	-4(1)
C(2B)	30(1)	29(1)	23(1)	-1(1)	7(1)	2(1)
C(3B)	28(1)	27(1)	21(1)	-1(1)	7(1)	-1(1)
C(4B)	39(2)	36(2)	23(1)	-1(1)	9(1)	-6(1)
C(5B)	33(1)	37(2)	22(1)	-2(1)	13(1)	-4(1)
C(6B)	27(1)	29(1)	23(1)	-1(1)	7(1)	2(1)
C(7B)	25(1)	27(1)	24(1)	-3(1)	11(1)	-4(1)
C(8B)	24(1)	27(1)	19(1)	1(1)	5(1)	0(1)

C(9B)	26(1)	28(1)	22(1)	-3(1)	6(1)	-4(1)
C(10B)	26(1)	24(1)	20(1)	1(1)	5(1)	-1(1)
C(11B)	25(1)	32(1)	22(1)	-1(1)	3(1)	-2(1)
C(12B)	24(1)	27(1)	22(1)	-4(1)	1(1)	1(1)
C(13B)	21(1)	29(1)	25(1)	0(1)	2(1)	-1(1)
C(14B)	22(1)	27(1)	25(1)	-1(1)	9(1)	-3(1)
C(15B)	28(1)	29(1)	24(1)	1(1)	6(1)	-2(1)
C(16B)	24(1)	30(1)	28(1)	5(1)	10(1)	-4(1)
C(17B)	35(1)	33(2)	24(1)	-5(1)	8(1)	-6(1)
C(18B)	36(2)	45(2)	24(1)	2(1)	11(1)	-9(1)
C(19B)	35(2)	51(2)	26(1)	-2(1)	9(1)	-8(1)
C(20B)	49(2)	39(2)	28(1)	-1(1)	5(1)	17(1)
C(21B)	30(1)	24(1)	21(1)	-1(1)	8(1)	0(1)
C(22B)	31(1)	22(1)	23(1)	1(1)	8(1)	3(1)
C(23B)	32(1)	28(1)	22(1)	0(1)	1(1)	4(1)
C(24B)	48(2)	30(1)	21(1)	-3(1)	12(1)	6(1)
C(25B)	40(2)	32(1)	24(1)	-1(1)	14(1)	0(1)
C(26B)	49(2)	46(2)	52(2)	-12(2)	-13(2)	0(2)
C(27B)	75(2)	57(2)	30(2)	5(1)	28(2)	14(2)
C(28B)	28(1)	26(1)	24(1)	-2(1)	8(1)	-4(1)
C(29B)	38(2)	30(1)	31(1)	5(1)	7(1)	-3(1)
C(30B)	36(2)	33(1)	25(1)	-6(1)	9(1)	-10(1)
C(31B)	44(2)	47(2)	34(2)	0(1)	4(1)	-22(1)
C(32B)	57(2)	91(3)	49(2)	26(2)	-20(2)	-35(2)
C(33B)	25(1)	27(1)	24(1)	0(1)	4(1)	-2(1)
C(34B)	25(1)	28(1)	23(1)	-1(1)	5(1)	-2(1)
C(35B)	25(1)	32(1)	23(1)	-7(1)	3(1)	-1(1)
C(36B)	26(1)	39(2)	27(1)	10(1)	3(1)	7(1)
C(37B)	33(2)	29(1)	37(2)	5(1)	3(1)	-2(1)
C(38B)	34(2)	41(2)	36(2)	-10(1)	-6(1)	3(1)
C(39B)	51(2)	66(2)	27(2)	0(1)	-1(1)	18(2)
C(40B)	34(1)	29(1)	32(1)	-1(1)	5(1)	-2(1)
C(41B)	26(1)	43(2)	33(2)	4(1)	1(1)	-7(1)
C(42B)	34(2)	34(2)	31(1)	-3(1)	13(1)	-5(1)
C(43B)	48(2)	55(2)	35(2)	-12(1)	17(1)	-3(2)
C(44B)	40(2)	38(2)	32(1)	-2(1)	11(1)	-2(1)
C(45B)	40(2)	46(2)	46(2)	0(1)	9(1)	5(1)
C(46B)	51(2)	52(2)	50(2)	-8(2)	4(2)	-5(2)
O(1W)	75(6)	38(5)	70(6)	5(4)	17(5)	14(4)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for cocosolide (1).

	x	y	z	U(eq)
H(8A)	1688	3505	-2793	42
H(14A)	5496	2998	6842	69
H(1A)	2986	4040	304	30
H(3A)	1664	4338	-822	31
H(4A1)	452	3302	-358	34
H(4A2)	209	4126	-476	34
H(5A)	1533	4415	499	32
H(6A1)	3381	2688	894	32
H(6A2)	3905	2865	239	32
H(8A1)	5814	3750	2174	32
H(9A1)	5949	2291	2529	35
H(9A2)	6839	2778	2912	35
H(10A)	5712	3489	3401	33
H(11A)	5881	2057	3912	36
H(11B)	6649	2668	4215	36
H(12A)	5506	3292	4687	34
H(14B)	4182	3607	3619	32
H(15A)	2925	2582	2811	34
H(15B)	2579	2994	3458	34
H(17A)	1677	4482	1747	36
H(18A)	457	3367	1079	37
H(18B)	66	4153	891	37
H(19A)	3630	3226	-894	54
H(19B)	3340	4038	-866	54
H(19C)	2793	3549	-1533	54
H(20A)	1783	2505	-1195	52
H(20B)	1622	2464	-369	52
H(20C)	2665	2302	-524	52
H(21A)	941	4616	-1956	31
H(22A)	152	3433	-2890	33
H(23A)	237	4856	-3398	35
H(24A)	-1505	4146	-3272	38
H(25A)	-550	5248	-2313	40
H(25B)	-1545	4880	-2253	40
H(26A)	-527	4943	-4725	74
H(26B)	-202	4273	-5133	74
H(26C)	577	4693	-4527	74
H(27A)	-2865	4740	-3738	99
H(27B)	-2855	5509	-4090	99
H(27C)	-2620	5414	-3211	99

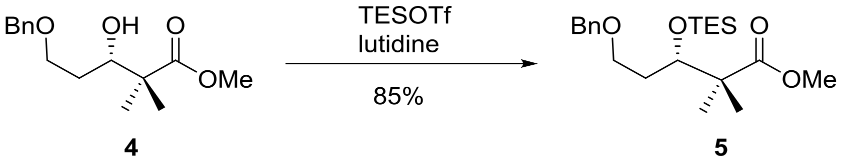
H(28A)	6966	2787	1493	35
H(29A)	7466	4151	2251	38
H(29B)	8217	3658	1888	38
H(30A)	6359	4233	1066	39
H(31A)	6729	3600	18	49
H(31B)	7705	3306	539	49
H(32A)	7373	4761	136	78
H(32B)	8082	4250	-180	78
H(32C)	8343	4477	672	78
H(33A)	6770	3021	5537	36
H(34A)	6227	2114	6625	39
H(35A)	7708	3176	6896	43
H(36A)	8085	1689	6983	43
H(37A)	8382	2632	5838	47
H(37B)	8625	1807	5877	47
H(38A)	8345	3359	8228	62
H(38B)	7512	3182	8656	62
H(38C)	7270	3644	7915	62
H(39A)	9160	2346	8205	63
H(39B)	10220	2276	8051	63
H(39C)	9494	1620	7901	63
H(40A)	4279	1709	3779	59
H(40B)	3275	1888	3992	59
H(40C)	4193	1666	4623	59
H(41A)	3959	2819	5301	62
H(41B)	3054	2989	4636	62
H(41C)	3915	3548	4860	62
H(42A)	206	4009	2500	45
H(43A)	-441	5178	2366	76
H(43B)	329	5406	1846	76
H(44A)	1677	5109	2820	60
H(45A)	311	4671	3692	65
H(45B)	982	5354	3892	65
H(46A)	1676	3933	3955	73
H(46B)	1700	4429	4657	73
H(46C)	2379	4602	4098	73
H(11E)	3211	327	7350	50
H(14D)	11617	3323	16000	49
H(1B)	6490	451	10123	30
H(3B)	6068	378	8790	30
H(4B1)	7115	1134	8349	39
H(4B2)	6688	1806	8692	39
H(5B)	7700	663	9540	36
H(6B1)	6154	1630	10968	32
H(6B2)	5358	1018	10825	32
H(8B)	7349	115	12665	28

H(9B1)	6836	1306	13424	30
H(9B2)	7225	618	13891	30
H(10B)	8683	708	13464	28
H(11C)	8266	1895	14299	32
H(11D)	8727	1165	14645	32
H(12B)	10136	1367	14243	30
H(14C)	9672	1342	12921	29
H(15C)	8653	2407	11997	32
H(15D)	9809	2417	12161	32
H(17B)	9094	890	10415	36
H(18C)	8349	2093	9594	41
H(18D)	8759	1493	9141	41
H(19D)	4922	98	9589	55
H(19E)	4219	540	8954	55
H(19F)	4292	730	9806	55
H(20D)	4632	1916	8925	59
H(20E)	5660	2165	9403	59
H(20F)	4824	1938	9808	59
H(21B)	5549	121	7651	30
H(22B)	3994	999	6857	30
H(23B)	4512	-330	6317	34
H(24B)	4934	990	5706	39
H(25C)	6305	87	6652	37
H(25D)	6572	800	6279	37
H(26D)	3371	-714	5306	79
H(26E)	2354	-314	5161	79
H(26F)	2822	-621	5965	79
H(27D)	5396	779	4562	77
H(27E)	5891	40	4454	77
H(27F)	6403	565	5099	77
H(28B)	5446	261	13001	31
H(29C)	6854	-901	13349	40
H(29D)	5763	-892	13546	40
H(30B)	6149	-753	12059	37
H(31C)	4302	-728	12481	51
H(31D)	4605	-1319	11959	51
H(32D)	4306	136	11552	106
H(32E)	3569	-484	11228	106
H(32F)	4609	-454	11030	106
H(33B)	11328	1743	15147	31
H(34B)	10653	2551	16252	30
H(35B)	12507	1873	16382	32
H(36B)	10973	1507	17095	38
H(37C)	11733	779	15984	41
H(37D)	10929	449	16370	41
H(38D)	13639	2056	17539	59

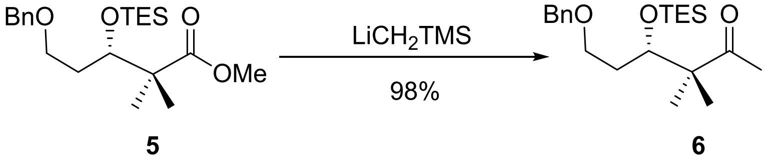
H(38E)	13613	2868	17769	59
H(38F)	13608	2660	16932	59
H(39D)	12570	1531	18322	74
H(39E)	12524	700	18461	74
H(39F)	11546	1145	18216	74
H(40D)	8501	2834	13533	48
H(40E)	9272	3232	13168	48
H(40F)	9446	3177	14049	48
H(41D)	11110	2602	14052	52
H(41E)	10838	2718	13175	52
H(41F)	11125	1950	13508	52
H(42B)	10499	1894	10101	38
H(43C)	11071	925	9476	54
H(43D)	10188	410	9639	54
H(44B)	10743	576	10948	43
H(45C)	12242	1442	10554	53
H(45D)	12449	736	11036	53
H(46D)	11768	2027	11527	78
H(46E)	12816	1694	11837	78
H(46F)	11879	1317	12004	78
H(1WA)	4935	2678	7807	73
H(1WB)	5382	2052	7858	73

Synthesis General Experimental Procedures. All reactions were conducted in flame-dried or oven-dried glassware under an atmosphere of dry nitrogen or argon. Oxygen and/or moisture sensitive solids and liquids were transferred appropriately. Concentration of solutions *in vacuo* was accomplished using a rotary evaporator fitted with a water aspirator. Residual solvents were removed under high vacuum (0.1-0.2 mm Hg). All reaction solvents were purified before use: Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl. Toluene was distilled over molten sodium metal. Dichloromethane, dimethylformamide, diethylamine, triethylamine and diisoproylethylamine were distilled from CaH_2. Methanol was distilled from Mg/I_2, Flash column chromatography was performed using the indicated solvents on E. Qingdao silica gel 60 (230 – 400 mesh ASTM). TLC was carried out using pre-coated sheets (Qingdao silica gel 60-F250, 0.2 mm). Compounds were visualized with UV light, iodine, *p*-anisaldehyde stain, ceric ammonium molybdate stain, or phosphomolybdic acid in EtOH. NMR spectra were recorded on Bruker DPX 300 MHz, Avance 400 MHz or AV 500 MHz spectrometers. Chemical shifts were reported in parts per million (ppm), relative to either a tetramethylsilane (TMS) internal standard or the signals due to the solvent. The following abbreviations are used to describe spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet, br = broad, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddd = doublet of doublet of doublets; other combinations are derived from those listed above. AB quartet relationships are noted, but listed as a pair of doublets. Coupling constants (*J*) are reported in Hertz. ^{13}C NMR spectra were completely heterodecoupled and measured at 125, 100, or 75 MHz. Residual chloroform (δ_C 77.0 ppm) was used as internal reference for spectra measured in this solvent. Low-and high- resolution EI and ESI mass spectra were obtained using an AB QSTAR Elite mass spectrometer. Optical rotations were recorded on a Rudolph AutoPol I Polarimeter.

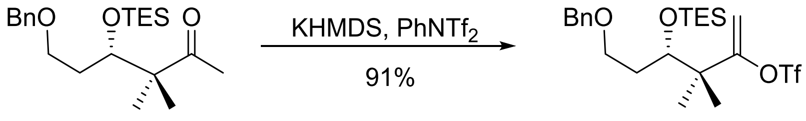
Synthesis Details.



To a solution of compound **4** (354 mg, 1.3 mmol) and 2,6-lutidine (0.35 mL, 4.1 mmol) in CH_2Cl_2 (10 mL), TES-triflate (0.31 mL, 1.9 mmol) was added at 0 °C. The reaction mixture was stirred for an additional hour and then quenched by the addition of a saturated aqueous solution of $NaHCO_3$ (10 mL). The reaction mixture was extracted with EtOAc (2 × 30 mL); and the combined organic layers were washed successively with a saturated aqueous solution of NH_4Cl (10 mL), brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel (hexanes/ethyl ether = 95/5) to afford compound **5** (428 mg, 85%) as a colorless oil. $[\alpha]_D^{20}$= –10.2 (*c* 5.0, DCM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 5H), 4.48 (t, *J* = 11.9 Hz, 2H), 4.08 (dd, *J* = 8.6, 1.9 Hz, 1H), 3.63 (s, 3H), 3.53 – 3.46 (m, 2H), 1.81 – 1.67 (m, 1H), 1.67 – 1.55 (m, 1H), 1.16 (s, 3H), 1.08 (s, 3H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.55 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.53, 138.41, 128.34, 127.71, 127.53, 74.09, 72.88, 67.65, 51.64, 48.31, 33.55, 21.14, 20.48, 6.99, 5.41; HRMS (ESI) *m/z* calcd for $C_{21}H_{36}O_4NaSi$ $[M + Na]^+$: 403.2275, found: 403.2273.

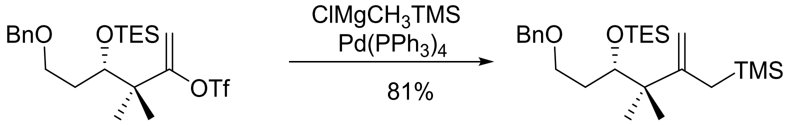


To a solution of compound **5** (5.3 g, 13.90 mmol) in pentane (100 mL), (trimethylsilyl)-methyllithium (27.5 mL, 27.50 mmol, 1.0 M in pentane) was cooled at 0 °C and stirred for 5 hours. MeOH (15 mL) was added dropwise to the reaction mixture and then stirred for 2 hours. The reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$ (30 mL) and then extracted with EtOAc (2 × 60 mL). The combined organic layers were washed successively with a saturated aqueous solution of NH_4Cl (30 mL), brine (30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/ethyl ether = 95/5) to give rise to compound **6** (5.0 g, 98%) as a colorless oil. $[\alpha]_D^{20}$= –10.4 (*c* 10.0, DCM); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 5H), 4.54 – 4.44 (dd, *J* = 14.7, 11.8 Hz, 2H), 4.08 (dd, *J* = 8.5, 2.6 Hz, 1H), 3.51 (dd, *J* = 7.8, 5.4 Hz, 2H), 2.14 (s, 3H), 1.79 – 1.67 (m, 1H), 1.61 – 1.51 (m, 1H), 1.12 (s, 3H), 1.07 (s, 3H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.60 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.46, 138.52, 128.42, 127.77, 127.62, 74.25, 73.00, 67.55, 53.30, 34.21, 26.95, 21.78, 20.15, 7.11, 5.54; HRMS (ESI) *m/z* calcd for $C_{21}H_{36}NaO_3Si$ $[M + Na]^+$: 387.2326, found: 387.2323.



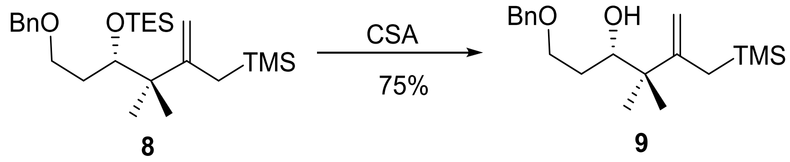
6 **7**

To a solution of ketone **6** (2.6 g, 7.1 mmol) in THF (35 mL) at –78 °C, KHMDS (11.5 mL, 9.2 mmol, 0.8 M in THF) was added dropwise. After being stirred at –78 °C for 1 hour, a solution of *N*-phenyltrifluoromethanesulfonimide (2.9 g, 8.1 mmol) in THF (10 mL) was added dropwise to the reaction mixture and stirred for additional 2 hours. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl (20 mL) and then extracted with hexanes (2 × 100 mL). The combined organic layers were washed successively with a saturated aqueous solution of $NaHCO_3$ (50 mL), brine (50 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/ethyl ether =96/4) to afford compound **7** (3.2 g, 91%) as a colorless oil. $[\alpha]_D^{20}$= –10.6 (*c* 2.0, DCM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 5H), 5.13 (d, *J* = 4.3 Hz, 1H), 5.01 (d, *J* = 4.3 Hz, 1H), 4.49 (dd, *J* = 15.3, 11.9 Hz, 2H), 3.83 (dd, *J* = 8.8, 2.2 Hz, 1H), 3.56 – 3.44 (m, 2H), 1.88 (dtd, *J* = 14.1, 8.0, 2.2 Hz, 1H), 1.63 – 1.51 (m, 2H), 1.57 (s, 1H), 1.15 (s, 3H), 1.09 (s, 3H), 0.92 (t, *J* = 8.0 Hz, 9H), 0.56 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.09, 138.34, 128.33, 127.67, 127.54, 102.59, 72.92, 72.87, 67.55, 45.33, 33.31, 22.74, 20.40, 6.98, 5.35; HRMS (ESI) *m/z* calcd for $C_{22}H_{35}F_3NaO_5SSi$[M + Na]$^+$: 519.1819, found: 519.1820.

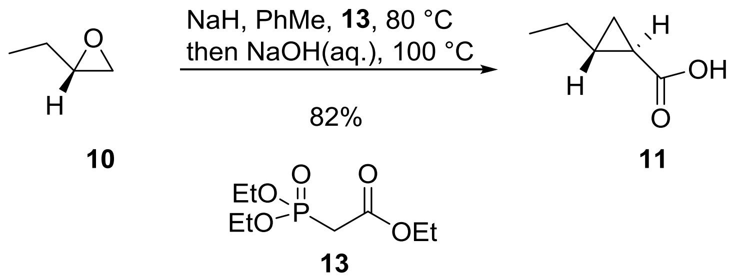


7 **8**

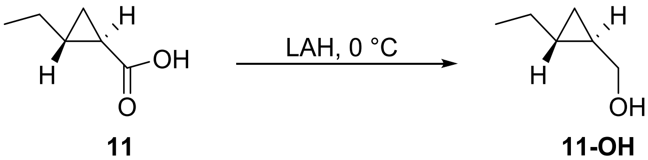
A dry flask was charged with LiCl (900 mg, 21.2 mmol) and the solid was flame-dried under reduced pressure and purged with argon. Et_2O (25 mL) was added, followed by a solution of triflate **7** (2.5 g, 5.1 mmol) in 15 mL of Et_2O. The suspension was cooled to 0 °C and tetrakis(triphenylphosphine)-palladium(0) (471 mg, 0.4 mmol) was added, followed by (trimethylsilyl)methylmagnesium chloride (13.0 mL, 13.0 mmol, 1.0 M in Et_2O). After being stirred for 5 hours, the yellow suspension was filtered over a pad of a Celite, eluting with Et_2O (100 mL). The organic solution was poured over 50 mL of a saturated aqueous solution of $NaHCO_3$ and then extracted with Et_2O (2 × 50 mL). The combined organic layers were washed successively with a saturated aqueous solution of $NaHCO_3$ (50 mL), brine (50 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/ethyl ether =99/1) to afford compound **8** (1.8 g, 81%) as a colorless oil. $[\alpha]_D^{20}$= –0.96 (*c* 2.4, DCM); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.20 (m, 5H), 4.84 (s, 1H), 4.70 (s, 1H), 4.51 (dd, *J* = 13.6, 12.1 Hz, 2H), 3.85 (dd, *J* = 8.8, 1.9 Hz, 1H), 3.58 – 3.46 (m, 2H), 1.86 (dtd, *J* = 14.3, 8.1, 2.0 Hz, 1H), 1.65 – 1.44 (m, 3H), 1.02 (s, 3H), 1.02 (s, 3H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.63 (q, *J* = 7.6 Hz, 6H), 0.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.70, 138.83, 128.39, 127.69, 127.51, 109.21, 75.07, 72.88, 68.37, 45.16, 33.69, 25.85, 21.41, 20.50, 7.27, 5.71, -0.32; HRMS (ESI) *m/z* calcd for $C_{25}H_{46}NaO_2Si_2$ [M + Na]$^+$: 457.2929, found: 457.2927.



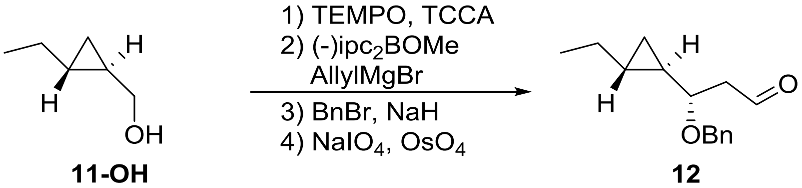
To a solution of compound **8** (450 mg, 1.04 mmol) in MeOH (5 ml) was added a solution of camphorsulfonic acid (21 mg, 0.09 mmol) in 1.5 mL of MeOH. The reaction mixture was stirred for 2 hours at room temperature before being quenched by Et_3N (1 mL). The reaction mixture was poured over a saturated aqueous solution of $NaHCO_3$ (20 mL), and extracted with EtOAc (2 × 50 mL). The combined organic layers were washed successively with a saturated aqueous solution of NH_4Cl (20 mL), brine (20 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc =6/1) to give rise to compound **9** (250 mg, 75%) as a colorless oil. $[\alpha]_D^{20}= -7.3$ (*c* 2.0, DCM); ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 4.86 (d, *J* = 1.0 Hz, 1H), 4.79 (d, *J* = 0.7 Hz, 1H), 4.53 (dd, *J* =14.5, 11.9 Hz, 2H), 3.75 – 3.64 (m, 3H), 2.46 (d, *J* = 2.1 Hz, 1H), 1.76 (ddd, *J* = 11.6, 6.6, 1.4 Hz, 1H), 1.62 (s, 2H), 1.66 – 1.57 (m, 3H), 1.53 (s, 2H), 1.05 (s, 3H), 1.00 (s, 3H), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.61, 138.38, 128.48, 127.76, 127.70, 109.85, 74.47, 73.37, 69.85, 44.33, 31.33, 22.19, 22.16, 21.22, -0.42; HRMS (ESI) *m/z* calcd for $C_{19}H_{32}NaO_2Si$ $[M + Na]^+$: 343.2064, found: 343.2064.



To a suspension of sodium hydride (2.5 g, 60 mmol, 60% suspension in mineral oil) in toluene (100 mL) at 0 °C, triethylphosphonoacetate (**13**) (13 mL, 65 mmol) was added dropwise over 15 min. After being stirred for 10 min, epoxide **10** (4.2 mL, 50 mmol) was added dropwise over 35 min to the solution, and stirred for 6 hours. The reaction mixture was cooled to room temperature, water (50 mL) and 30% NaOH (50 mL) were added. The mixture was stirred under reflux for 2 hours. The layers were separated, and the organic phase is discarded. The pH value of the reaction mixture was adjusted to 2-3 by the addition of an aqueous solution of HCl. The mixture was then extracted with EtOAc (2 × 200 mL). The combined organic layers were washed with 10% NaCl (3 × 50 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 1/1) to yield compound **11** (4.7 g, 82%) as a light yellow oil. $[\alpha]_D^{20}= -88.4$ (*c* 1.0, DCM); ^1H NMR (500 MHz, $CDCl_3$) δ 11.30 (br, 1H), 1.44–1.35 (m, 1H), 1.35–1.24 (m, 3H), 1.18 (dt, *J* = 8.7, 4.3 Hz, 1H), 0.95 (t, *J* = 7.3 Hz, 3H), 0.75 (ddd, *J* = 8.0, 6.4, 4.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.43, 26.19, 25.72, 19.98, 16.21, 13.17; HRMS (ESI) *m/z* calcd for $C_6H_9O_2$ [M - H]$^-$: 113.0608, found: 113.0608.



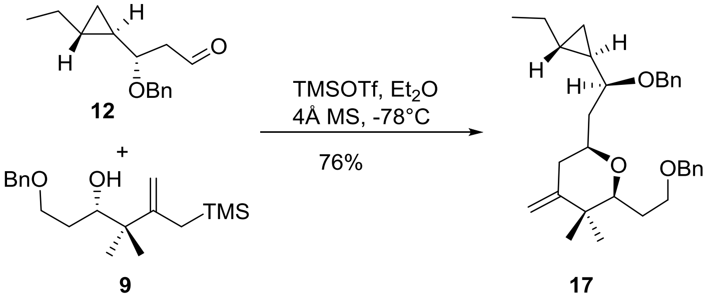
A solution of acid **11** (1.5 g, 40 mmol) in 20 mL was added dropwise to a solution of $LiAlH_4$ (3.5 g, 30 mmol) in diethyl ether (100 mL) at 0 °C. After being slowly warmed to room temperature and stirred for 2 hours, the reaction mixture was re-cooled to 0 °C and quenched by the addition of MeOH (10 mL), and followed by the addition of a saturated aqueous solution of Rochelle's salt (sodium potassium tartrate) (100 mL) and stirred for another 4 hours. The mixture was extracted with ethyl ether (2 × 100 mL), and the combined organic layers were washed successively with saturated aqueous $NaHCO_3$ (50 mL), brine (50 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure at low temperature to give a solution of alcohol **11-OH** in ethyl ether, which was directly used in the next step. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.40 (dd, *J* = 7.1, 2.5 Hz, 2H), 1.64 (s, 1H), 1.27–1.19 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.84–0.75 (m, 1H), 0.59–0.50 (m, 1H), 0.35–0.29 (m, 1H), 0.29–0.24 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 67.25, 26.70, 21.08, 19.09, 13.74, 9.80.



To a solution of alcohol **11-OH** (30 mmol) in ethyl ether (100 mL) was added $NaHCO_3$ (7.6 g, 90 mmol), TEMPO (468 mg, 3.0 mmol). The reaction mixture was cooled to 0 °C and TCCA (7.7 g, 33 mmol) was added. After being stirred for an additional hour at 0 °C, the reaction mixture was filtered through a pad of silica gel. The filtrate was washed successively with saturated aqueous $NaHCO_3$ (30 mL), NH_4Cl (30 mL), brine (30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure at low temperature to afford the crude aldehyde, which was used in the next step without further purification.

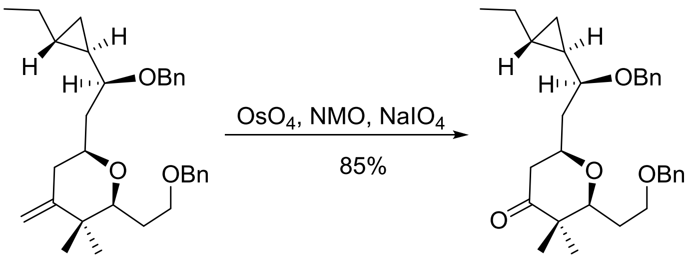
A solution of salt-free (-)-*B*-allyl bis(isopinocampheyl)borane (35 mmol) in Et_2O (50 mL) was cooled to −82 °C. A solution of above fresh prepared aldehyde in Et_2O (30 mL) was cooled to −78 °C and added via cannula over 30 min to the allylboron reagent while maintaining the reaction temperature below −80 °C. After being stirred at −82 °C for 3 hours, the reaction was slowly warmed to room temperature over 2 hours. A solution of 3 N NaOH (40 mL) and H_2O_2 (30%, 80 mL) was added dropwise over 30 min. The mixture was stirred for 18 hours at room temperature. The product was extracted with diethyl ether (2 × 200 ml). The combined organic layers were washed successively with saturated aqueous $NaHCO_3$ (50 mL), NH_4Cl (50 mL), brine (50 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure at low temperature to give rise to a crude oil consisting of the desired allylation product and isopinocampheol. The product mixture was dissolved in THF (300 mL) and cooled to 0 °C. Sodium hydride (6.0 g, 150 mmol, 60% suspension in mineral oil) was added in portions to control the exothermic release of hydrogen. BnBr (16 mL, 135 mmol) and tetrabutylammonium iodide (3.5 g, 9.5 mmol) was then added and the mixture was gradually warmed to room temperature (the release of hydrogen was controlled by placing of the reaction vessel in an ice bath). The mixture was stirred at ambient temperature for 24 hours, then re-cooled to 0 °C and quenched by slow addition of MeOH (20 mL), followed by H_2O (50 mL). The mixture was extracted with Et_2O (2 × 300 mL). The combined organic layers were washed successively with saturated aqueous NH_4Cl (50 mL), brine (50 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/ethyl ether =95/5) to afford an inseparable mixture of desired benzyl ether and isopinocampheol-benzyl ether as a light yellow oil.

To a solution of above mixture in 60 mL of H_2O and 200 mL of acetone was added with 2,6-lutidine (7.0 mL, 60 mmol), osmium tetroxide (50 mL, 1 mmol, 0.02 M in *t*-BuOH) and sodium periodate (8.5 g, 40 mmol) at room temperature. After being stirred for 3 hours, the mixture was filtered, eluting with 50 mL of EtOAc and then concentrated. The slurry was then extracted with EtOAc (2 × 200 mL) and the combined organic layers were washed successively with saturated aqueous $NaHCO_3$ (50 mL), brine (50 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/ethyl ether = 90/15) to yield compound **12** (1.84 g, 26 % for 5 steps) as a colorless oil. $[\alpha]_D^{20}$= –34.0 (*c* 2.0, DCM); ^1H NMR (500 MHz, $CDCl_3$) δ 9.81 (t, *J* = 2.4 Hz, 1H), 7.38 – 7.24 (m, 5H), 4.79 (d, *J* = 11.6 Hz, 1H), 4.54 (d, *J* = 11.6 Hz, 1H), 3.29 (td, *J* = 8.5, 4.2 Hz, 1H), 2.77 (ddd, *J* = 15.9, 8.2, 2.8 Hz, 1H), 2.63 (ddd, *J* = 15.9, 4.1, 2.0 Hz, 1H), 1.45 – 1.33 (m, 1H), 1.33 – 1.22 (m, 1H), 1.03 (t, *J* = 7.4 Hz, 3H), 0.89 – 0.77 (m, 1H), 0.73 (ddd, *J* = 13.4, 8.9, 4.8 Hz, 1H), 0.34 – 0.21 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.61, 138.56, 128.47, 127.69, 127.67, 78.42, 70.90, 49.47, 26.71, 22.30, 21.43, 13.51, 8.03; HRMS (ESI) *m/z* calcd for $C_{15}H_{20}O_2Na$ $[M + Na]^+$: 255.1356, found: 255.1355.



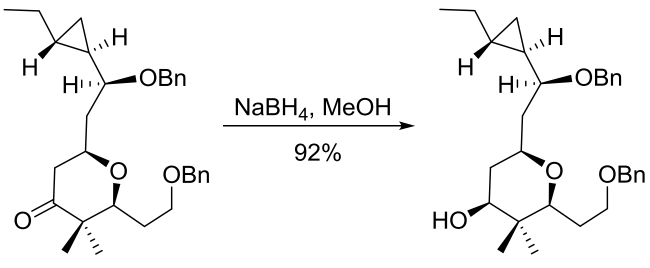
To a –78 °C ether solution of aldehyde **12** (19 mg, 82 µmol) and flame-dried powdered 4Å molecular sieves (30 mg), was added allylsilane **9** (20 mg, 62 µmol) in diethyl ether (2 mL). After being stirred for 30 min, TMSOTf (17 µL, 94 µmol) was added slowly and allowed to stir rapidly for an additional hour, then quenched with cooled saturated aqueous solution of $NaHCO_3$ (0.5 mL). The biphasic mixture was extracted with EtOAc (2 × 25 mL), and the combined organic layers were washed successively with saturated aqueous NH_4Cl (10 mL), brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/ethyl ether =95/5) to yield compound **17** (22 mg, 76%) as a colorless oil. $[\alpha]_D^{20}$= –58.4 (*c* 1.0, DCM); ^1H NMR (500 MHz, $CDCl_3$); δ 7.37 – 7.24 (m, 10H), 4.73 (d, *J* = 11.7 Hz, 1H), 4.71 (s, 1H), 4.65 (s, 1H), 4.51 (d, *J* =

11.7 Hz, 1H), 4.47 (s, 2H), 3.59 – 3.53 (m, 1H), 3.53 – 3.46 (m, 2H), 3.12 (dd, *J* = 10.7, 1.7 Hz, 1H), 2.90 (dt, *J* = 8.5, 6.7 Hz, 1H), 2.24 – 2.16 (m, 1H), 2.08 – 2.00 (m, 2H), 1.85 (ddd, *J* = 9.5, 7.9, 3.9 Hz, 1H), 1.68 (ddd, *J* = 9.1, 6.5, 2.1 Hz, 2H), 1.44 – 1.34 (m, 1H), 1.27 – 1.18 (m, 2H), 1.06 – 0.97 (m, 9H), 0.74 – 0.66 (m, 1H), 0.63 – 0.56 (m, 1H), 0.28 – 0.20 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.97, 139.32, 138.76, 128.41, 128.38, 127.73, 127.71, 127.53, 127.43, 106.09, 81.59, 79.50, 76.10, 73.10, 70.54, 68.33, 42.37, 39.68, 39.48, 30.23, 26.90, 22.58, 22.47, 20.59, 20.14, 13.65, 8.36; HRMS (ESI) *m/z* calcd for $C_{31}H_{42}O_3Na$ $[M + Na]^+$: 485.3026, found: 485.3027.



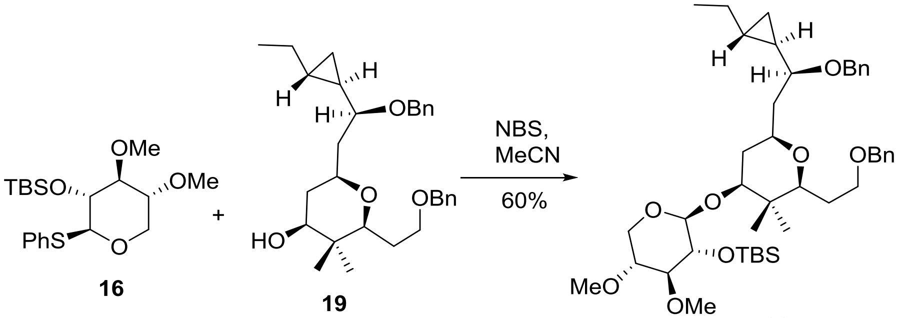
17 **18**

To a solution of compound **17** (193 mg, 0.42 mmol) in 6.0 mL of H_2O and 20.0 mL of acetone was added osmium tetroxide (0.5 mL, 0.05 mmol, 0.1M in *t*-BuOH) and *N*-methylmorpholine *N*-oxide (467 mg, 1.67 mmol). After being stirred for 24 hours, a solution of sodium periodate (450 mg, 2.10 mmol) in 10 mL of H_2O was added, and the yellow solution was stirred for additional 3 hours. The mixture was filtered, eluted with 50 mL of EtOAc and then concentrated. The slurry was extracted with EtOAc (2 × 50 mL) and the combined organic layers were washed successively with saturated aqueous $NaHCO_3$ (30 mL), brine (30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/ethyl ether = 85/15) to afford ketone **18** (164 mg, 85%) as a colorless oil. $[\alpha]_D^{20}$= –87.4 (*c* 1.0, DCM); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 10H), 4.74 (d, *J* = 11.6 Hz, 1H), 4.45 (s, 2H), 4.45 (d, *J* = 11.4 Hz, 1H), 3.86 – 3.75 (m, 1H), 3.61 – 3.47 (m, 2H), 3.39 (dd, *J* = 8.6, 3.8 Hz, 1H), 2.87 (dt, *J* = 8.6, 6.5 Hz, 1H), 2.47 (dd, *J* = 14.2, 11.9 Hz, 1H), 2.24 (dd, *J* = 14.2, 2.6 Hz, 1H), 2.10 (dt, *J* = 13.9, 7.0 Hz, 1H), 1.82 – 1.75 (m, 2H), 1.75 – 1.65 (m, 1H), 1.42 – 1.31 (m, 1H), 1.26 – 1.15 (m, 1H), 1.08 (s, 3H), 1.02 – 0.96 (m, 6H), 0.73 – 0.65 (m, 1H), 0.65 – 0.51 (m, 1H), 0.28 – 0.15 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.80, 139.04, 138.56, 128.46, 127.69, 127.66, 127.64, 127.56, 80.63, 79.28, 74.59, 73.12, 70.67, 67.58, 49.15, 44.70, 42.50, 29.87, 26.83, 22.35, 20.40, 19.40, 18.91, 13.62, 8.27; HRMS (ESI) *m/z* calcd for $C_{30}H_{40}NaO_4$ $[M + Na]^+$: 487.2819, found: 487.2815.



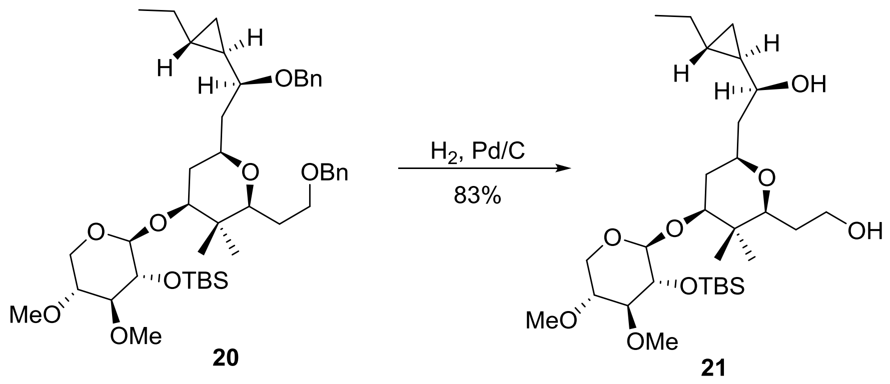
18 **19**

To a –40 °C solution of ketone **18** (41 mg, 88 µmol) in MeOH (1.5 mL) was added $NaBH_4$ (10 mg, 0.26 mmol). The reaction was stirred at this temperature for 30 min. then quenched with saturated aqueous NH_4Cl (10 mL). The biphasic mixture was extracted with EtOAc (2 × 50 mL), and the combined organic layers were washed successively with saturated aqueous $NaHCO_3$ (15 mL), brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 3/1) to yield compound **19** (39 mg, 92%) as a colorless oil. $[\alpha]_D^{20}$= –49.1 (*c* 1.0, DCM); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 10H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.46 (d, *J* = 11.5 Hz, 3H), 3.60 (dd, *J* = 11.2, 5.6 Hz, 1H), 3.58 – 3.53 (m, 1H), 3.53 – 3.46 (m, 1H), 3.39 (dd, *J* = 11.4, 4.3 Hz, 1H), 3.08 (d, *J* = 9.5 Hz, 1H), 2.88 (dd, *J* = 15.2, 6.7 Hz, 1H), 2.02 (dt, *J* = 14.1, 7.2 Hz, 1H), 1.87 – 1.78 (m, 1H), 1.68 – 1.63 (m, 2H), 1.44 – 1.34 (m, 2H), 1.32 (d, *J* = 12.0 Hz, 1H), 1.25 (dt, *J* = 14.0, 7.6 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.93 (s, 3H), 0.83 (s, 3H), 0.71 (dd, *J* = 12.3, 5.7 Hz, 1H), 0.64 – 0.56 (m, 1H), 0.28 – 0.21 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.29, 138.74, 128.43, 128.39, 127.75, 127.70, 127.56, 127.46, 80.28, 79.54, 76.04, 73.08, 73.04, 70.62, 68.13, 42.04, 38.85, 37.13, 29.53, 26.90, 22.42, 20.24, 13.65, 12.55, 8.29; HRMS (ESI) *m/z* calcd for $C_{30}H_{42}O_4Na$ $[M + Na]^+$: 489.2975, found: 489.2974.

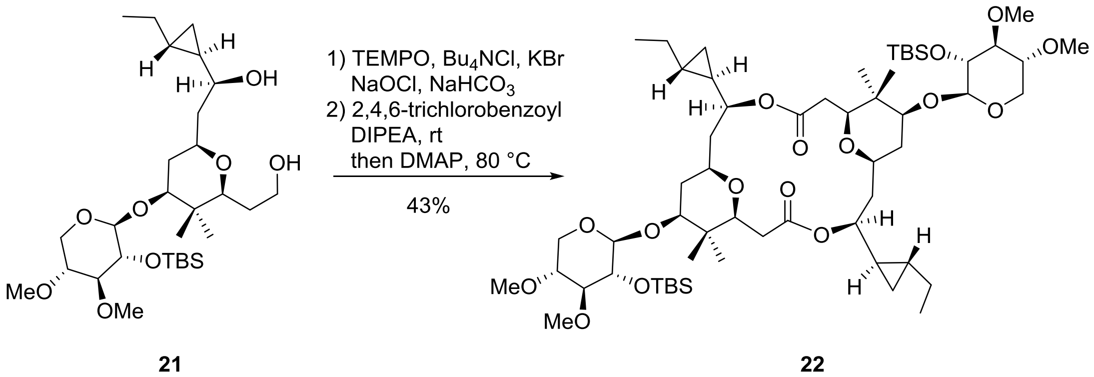


16 **19** **20**

The suspended solution of compound **16** (16 mg, 42 µmol) and flame-dried, powdered 4Å molecular sieves (90 mg) in dry acetonitrile (1 mL) was stirred under nitrogen at room temperature for 1.5 hours. To this solution at –25 °C, was added a solution of *N*-bromosuccinimide (7.5 mg, 42 µmol) in dry acetonitrile (0.5 mL). 10 min later a solution of alcohol **19** (10 mg, 21 µmol) in dry acetonitrile (0.5 mL) was added. The reaction mixture was stirred for 30 min at –25 °C before it was allowed to warm to room temperature over 3 hours. The reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL). The biphasic mixture was extracted with EtOAc (2 × 50 mL), and the combined organic layers were washed successively with saturated aqueous NH_4Cl (15 mL), brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to yield a crude product consisting a mixture of alpha:beta (3:5) isomers. The mixture was further purified by flash column chromatography on silica gel (hexanes/EtOAc = 3/1) to yield 9.4 mg of beta isomer (**20**) (60% yield) as a colorless oil. $[\alpha]_D^{20}$= –51.8 (*c* 1.0, DCM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 10H), 4.74 (d, *J* = 11.5 Hz, 1H), 4.46 (s, 2H), 4.45 (d, *J* = 11.6 Hz, 1H), 4.23 (d, *J* = 7.3 Hz, 1H), 3.93 (dd, *J* = 11.5, 5.2 Hz, 1H), 3.63 – 3.57 (m, 2H), 3.55 (s, 3H), 3.54 – 3.51 (m, 1H), 3.51 – 3.45 (m, 2H), 3.44 (s, 3H), 3.41 – 3.34 (m, 1H), 3.30 – 3.22 (m, 2H), 3.09 (dd, *J* = 21.0, 10.9 Hz, 2H), 3.00 (t, *J* = 8.7 Hz, 1H), 2.92 – 2.86 (m, 1H), 2.05 – 1.98 (m, 1H), 1.88 – 1.82 (m, 1H), 1.82 – 1.75 (m, 1H), 1.68 – 1.60 (m, 1H), 1.42 – 1.33 (m, 1H), 1.25 – 1.17 (m, 1H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.95 (s, 3H), 0.92 (s, 9H), 0.91 – 0.87 (m, 5H), 0.72 – 0.65 (m, 1H), 0.62 – 0.55 (m, 1H), 0.28 – 0.22 (m, 2H), 0.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.23, 138.61, 128.32, 128.29, 127.61, 127.44, 127.34, 106.17, 86.26, 84.56, 80.68, 80.44, 79.96, 77.33, 77.01, 76.69, 74.31, 72.95, 70.71, 67.92, 63.13, 61.01, 58.34, 41.97, 38.97, 36.66, 29.69, 29.20, 26.82, 26.08, 22.32, 20.06, 18.11, 13.61, 13.49, 8.23, -3.70, -4.11; HRMS (ESI) *m/z* calcd for $C_{43}H_{68}O_8NaSi$ $[(M + Na]^+$: 763.4576, found: 763.4579.

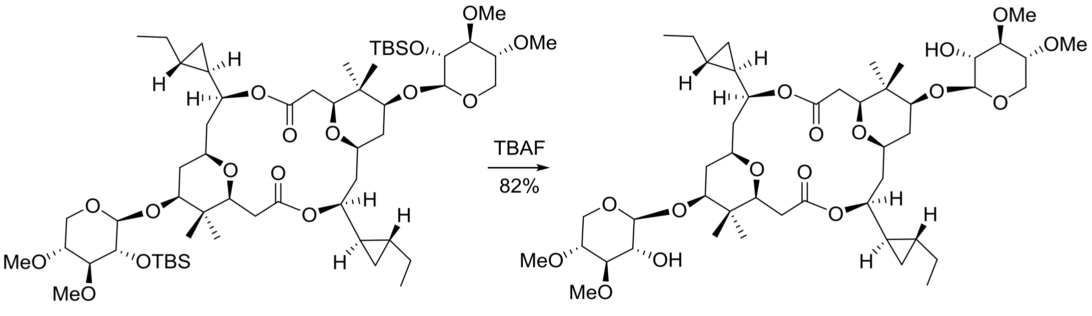


To a solution of Bn ether **20** (21 mg, 28 µmol) in MeOH (3 mL) was added 10% Pd/C (5 mg). The reaction flask was evacuated and purged with hydrogen three times. The reaction mixture was stirred under a H_2 atmosphere at ambient temperature for 2 hours. The flask was then evacuated and purged with nitrogen three times and the catalyst was removed by filtration through Celite. The filtrate was concentrated and the crude product purified by flash column chromatography on silica gel (hexanes/EtOAc = 2/1) to yield compound **21** (13 mg, 83%) as a colorless oil. $[\alpha]_D^{20}$= –25.8 (*c* 1.0, DCM); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.21 (d, *J* = 7.2 Hz, 1H), 3.95 (dd, *J* = 11.4, 5.2 Hz, 1H), 3.71 (dd, *J* = 10.4, 4.4 Hz, 2H), 3.60 (dd, *J* = 11.6, 8.8 Hz, 1H), 3.53 (s, 3H), 3.43 (s, 3H), 3.35 (dd, *J* = 8.7, 7.3 Hz, 1H), 3.24 (ddd, *J* = 11.8, 8.2, 4.9 Hz, 2H), 3.18 – 3.13 (m, 1H), 3.10 (dd, *J* = 11.4, 10.1 Hz, 2H), 2.98 (t, *J* = 8.7 Hz, 1H), 2.58 (s, 2H), 1.85 – 1.75 (m, 2H), 1.65 (dd, *J* = 11.3, 6.4 Hz, 3H), 1.29 – 1.16 (m, 3H), 0.93 (dd, *J* = 9.4, 5.1 Hz, 6H), 0.90 (d, *J* = 1.7 Hz, 12H), 0.65 (dd, *J* = 13.3, 8.1 Hz, 1H), 0.60 (dt, *J* = 12.9, 4.2 Hz, 1H), 0.33 – 0.27 (m, 1H), 0.27 – 0.21 (m, 1H), 0.10 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 106.24, 86.27, 83.95, 80.81, 76.35, 75.42, 74.42, 63.22, 61.70, 60.96, 58.36, 42.78, 39.06, 37.06, 31.08, 26.80, 26.17, 25.60, 22.44, 18.88, 18.19, 13.74, 13.62, 9.32, 0.06, -3.65, -4.01; HRMS (ESI) *m/z* calcd for $C_{29}H_{56}NaO_8Si$ $[M + Na]^+$: 583.3637, found: 583.3534.



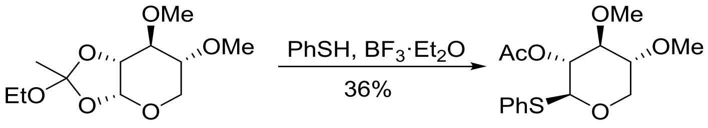
To a solution of the diol **21** (13 mg, 23 µmol) in CH_2Cl_2 (300 µL) was added TEMPO (0.2 mg, 1.2 µmol) and saturated $NaHCO_3$ (130 µL). KBr (50 µL, 2.5 µmol, 0.05 M aqueous solution) and Bu_4NCl (30 µL, 1.5 µmol, 0.05 M aqueous solution) were added subsequently and the mixture was cooled to 0 °C. To the vigorously stirring biphasic solution was added a stock solution of saturated $NaHCO_3$ (33 µL), brine (61 µL) and bleach (40 µL, 0.06 mmol, 1.5 M) dropwise over 45 min. The mixture was allowed to stir for an additional 30 min at 0 °C upon completion of the addition. The solution was then diluted with H_2O (2 mL) and CH_2Cl_2 (2 mL). The diluted mixture was acidified with 10% citric acid (4-10 drops) to pH 3-4. The biphasic mixture was extracted with EtOAc (2 × 50 mL), and the combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give rise to the corresponding carboxylic acid, which was employed in the next step of reaction without further purification.

To the above acid in dry toluene (2 ml) was added DIPEA (*N*,*N*-diisopropylethylamine) (30 µL, 0.18 mmol) and 2,4,6-trichlorobenzoyl chloride (20 µL, 0.13 mmol) dropwise. The reaction mixture was stirred at room temperature for 2 hours, then the mixture was added dropwise over 3 hours to a stirred solution of DMAP (4-dimethylaminopyridine) (35 mg, 0.29 mmol) in toluene (10 mL) at 80 °C, the reaction was allowed to stir for another 3 hours before it was quenched with saturated aqueous NH_4Cl (15 mL). The biphasic mixture was extracted with EtOAc (2 × 70 mL), and the combined organic layers were washed successively with saturated aqueous $NaHCO_3$ (15 mL), brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 3/1) to yield compound **22** (5.5 mg, 43%) as a colorless oil. $[\alpha]_D^{20}$= –67.6 (*c* 0.2, DCM); ^1H NMR (500 MHz, CD_3CN) δ 4.30 (t, *J* = 8.4 Hz, 2H), 4.24 (d, *J* = 7.2 Hz, 2H), 3.90 (dd, *J* = 11.3, 5.0 Hz, 2H), 3.47 (s, 6H), 3.40 – 3.38 (m, 2H), 3.37 (s, 6H), 3.34 (dd, *J* = 11.6, 4.8 Hz, 2H), 3.28 (dd, *J* = 8.6, 7.2 Hz, 2H), 3.22 – 3.16 (m, 2H), 3.11 (dd, *J* = 11.2, 9.7 Hz, 2H), 2.95 (t, *J* = 8.5 Hz, 2H), 2.66 (s, 2H), 2.37 (dd, *J* = 17.3, 1.7 Hz, 2H), 2.08 – 2.05 (m, 2H), 1.80 (dd, *J* = 4.9, 2.5 Hz, 2H), 1.79 – 1.75 (m, 2H), 1.66 (dd, *J* = 14.5, 2.9 Hz, 2H), 1.39 – 1.32 (m, 4H), 0.93 (d, *J* = 7.6 Hz, 2H), 0.90 (s, 18H), 0.87 (s, 6H), 0.85 (t, *J* = 7.0 Hz, 6H), 0.81 (s, 6H), 0.72 (dd, *J* = 11.5, 6.9 Hz, 2H), 0.69 – 0.64 (m, 2H), 0.40 – 0.32 (m, 2H), 0.26 – 0.18 (m, 2H), 0.10 (s, 6H), 0.09 (s, 6H); ^{13}C NMR (125 MHz, CD_3CN) δ 170.94, 108.71, 105.74, 89.27, 85.95, 84.05, 83.39, 81.51, 80.62, 80.27, 79.95, 77.24, 76.86, 76.60, 75.78, 74.56, 74.34, 66.23, 62.71, 61.46, 60.11, 57.62, 57.44, 56.42, 40.72, 39.14, 38.51, 38.15, 36.89, 36.08, 35.11, 27.12, 26.37, 26.27, 25.61, 24.40, 23.98, 21.95, 21.57, 20.41, 19.77, 18.81, 17.84, 14.61, 12.97, 9.29, 8.97, 8.27, -4.32, -4.63; HRMS (ESI) *m/z* calcd for $C_{58}H_{104}NaO_{16}Si_2$ $[M + Na]^+$: 1135.6755, found: 1135.6753.



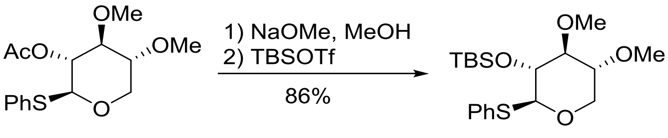
22 *Cocosolide* (**1**)

To a stirred solution of silyl ether **22** (2.0 mg, 1.8 µmol) in THF (1.5 mL) at 0 °C was added TBAF (300 µL, 1 M in THF, 300 µmol), immediately producing a yellow solution. The mixture was stirred for 3 hours, then the reaction mixture was poured into a mixture of EtOAc (20 mL), H_2O (10 mL). The layers were separated and the aqueous layer was further extracted with EtOAc (2 × 20 mL). The combined organic extracts were washed successively with saturated aqueous $NaHCO_3$ (15 mL), NH_4Cl (15 mL), brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel (hexanes/EtOAc = 1/1) to yield cocosolide (**1**) (1.3 mg, 82%) as a colorless oil. $[\alpha]_D^{20}$= -55.5 (*c* 0.4, DCM); ^1H NMR (500 MHz, CD_3CN) δ 4.30 (t, *J* = 8.3 Hz, 2H), 4.23 (d, *J* = 7.3 Hz, 2H), 3.90 (dd, *J* = 11.3, 4.8 Hz, 2H), 3.50 (s, 6H), 3.40 (dd, *J* = 8.2, 1.5 Hz, 2H), 3.39 – 3.38 (m, 2H), 3.38 (s, 6H), 3.34 (dd, *J* = 11.6, 4.9 Hz, 6H), 3.32 (d, *J* = 4.7 Hz, 6H), 3.21 – 3.18 (m, 2H), 3.18 – 3.15 (m, 2H), 3.10 (dd, *J* = 11.2, 9.7 Hz, 2H), 3.02 (t, *J* = 8.5 Hz, 2H), 2.39 (dd, *J* = 17.2, 1.7 Hz, 2H), 2.07 (dd, *J* = 17.2, 8.3 Hz, 2H), 1.84 – 1.81 (m, 2H), 1.81 – 1.78 (m, 2H), 1.69 – 1.64 (m, 2H), 1.40 – 1.36 (m, 2H), 1.35 – 1.31 (m, 2H), 0.93 – 0.90 (m, 2H), 0.88 (s, 6H), 0.87 – 0.84 (m, 6H), 0.80 (s, 6H), 0.75 – 0.70 (m, 2H), 0.70 – 0.66 (m, 2H), 0.37 (dt, *J* = 8.7, 4.8 Hz, 2H), 0.24 (dt, *J* = 8.5, 5.0 Hz, 2H); ^{13}C NMR (125 MHz, CD_3CN) δ171.79, 106.37, 85.42, 85.21, 80.64, 80.00, 77.60, 76.36, 74.19, 63.36, 60.29, 58.44, 41.52, 39.26, 37.49, 35.98, 27.18, 24.73, 22.23, 20.60, 13.78, 13.48, 9.78; HRMS (ESI) *m/z* calcd for $C_{46}H_{76}NaO_{16}$ $[M + Na]^+$: 907.5026, found: 907.5023.



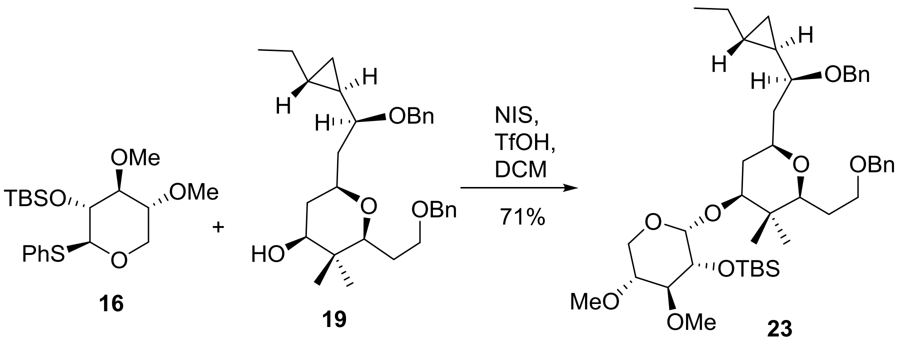
14 **15**

To a –45 °C solution of compound **14** (1.3g, 5.2 mmol) in CH_2Cl_2 (50 mL) was added dropwise $BF_3{\cdot}Et_2O$ (980 µL, 8 mmol), followed by the addition of PhSH (650 µL, 6.3 mmol). The reaction mixture was allowed to stir for an additional 2 hours before it was quenched by the addition of Et_3N (5 mL). The mixture was poured carefully into an Erlenmeyer flask and then partitioned between and then partitioned between H_2O (50 mL) and EtOAc (150 mL). The layers were separated and the aqueous layer was extracted with EtOAc (100 mL). The combined organic layers were washed successively with saturated aqueous $NaHCO_3$ (30 mL), NH_4Cl (30 mL), brine (30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 1/1) to yield compound **15** (650 mg, 36%) as a colorless oil. $[\alpha]_D^{20}$= –29.9 (*c* 1.0, DCM); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.38 (m, 2H), 7.36 – 7.15 (m, 3H), 4.93 (t, *J* = 7.9 Hz, 1H), 4.76 (d, *J* = 8.1 Hz, 1H), 4.32 – 4.08 (m, 1H), 3.53 (s, 3H), 3.47 (s, 3H), 3.34 (ddd, *J* = 24.0, 14.0, 5.7 Hz, 3H), 2.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.72, 133.78, 131.96, 129.01, 127.71, 86.75, 82.61, 78.30, 71.03, 65.69, 59.92, 58.61, 21.15; HRMS (ESI) *m/z* calcd for $C_{15}H_{20}NaO_5S$ $[M + Na]^+$: 335.0924, found: 335.0922.



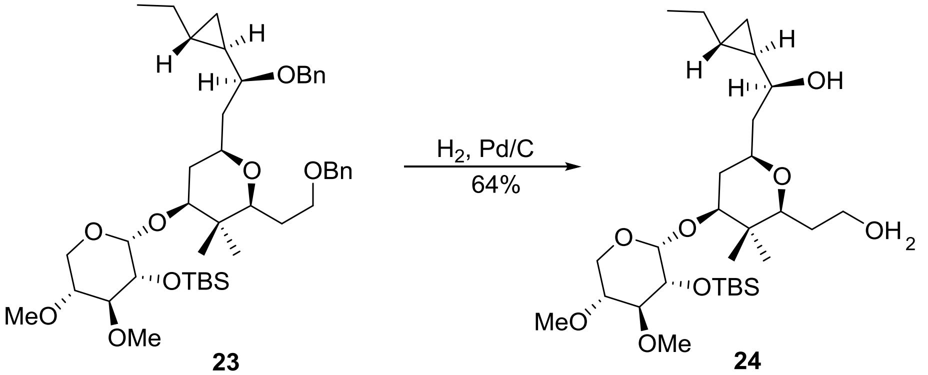
15 **16**

To a solution of compound **15** (142 mg, 0.45 mmol) in MeOH (5 mL) was added a catalytic amount of sodium methoxide at room temperature. The reaction mixture was stirred for an hour, before it was concentrated under reduced pressure. The residue was dissolved in dry CH_2Cl_2 (15 mL). To this solution at 0 °C was added 2,6-lutidine (0.18 mL, 1.5 mmol), followed by the addition of TBS-triflate (0.22 mL, 1.0 mmol). After being stirred for an additional hour, the reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL), and the biphasic mixture was extracted with EtOAc (2 × 30 mL). The combined organic layers were washed successively with saturated aqueous NH_4Cl (10 mL), brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/ethyl ether = 95/5) to yield compound **16** (150 mg, 86%) as a colorless oil. $[\alpha]_D^{20}$= –42.7 (*c* 1.0, DCM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.38 (m, 2H), 7.36 – 7.15 (m, 3H), 4.57 (d, *J* = 9.1 Hz, 1H), 4.13 – 4.04 (m, 1H), 3.58 (s, 2H), 3.51 – 3.47 (m, 1H), 3.45 (d, *J* = 6.3 Hz, 3H), 3.35 – 3.28 (m, 1H), 3.17 (dd, *J* = 11.4, 9.9 Hz, 1H), 3.08 (t, *J* = 8.4 Hz, 1H), 0.95 (s, 9H), 0.19 (s, 3H), 0.14 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.77, 131.24, 128.87, 127.16, 90.38, 87.12, 80.30, 73.20, 66.55, 60.93, 58.27, 26.10, 18.31, -3.89, -4.34; HRMS (ESI) *m/z* calcd for $C_{19}H_{32}NaO_2Si$ $[M + Na]^+$: 407.1683, found: 407.1684.



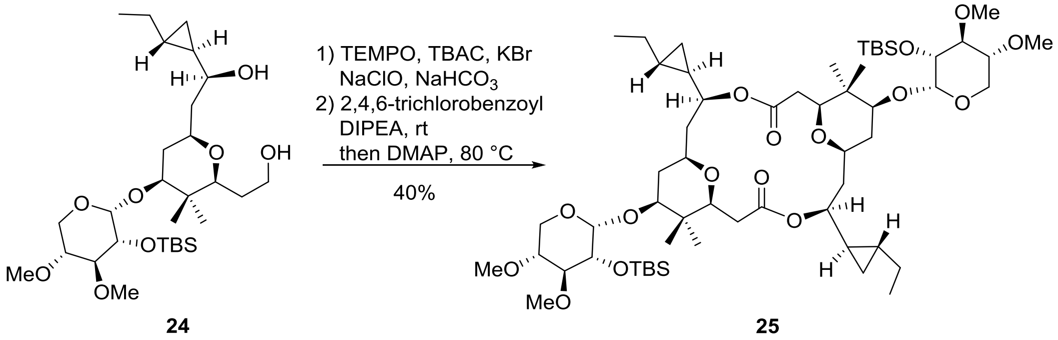
16 **19** **23**

The suspended solution of compound **16** (12 mg, 31 μmol) and flame-dried powdered 4Å molecular sieves (60 mg) in dry dichloromethane (1 mL) was stirred under nitrogen at room temperature for an hour and then cooled to– 78 °C. To this solution at –78 °C, was added a solution of *N*-iodosuccinimide (7 mg, 31 μmol) in dry dichloromethane (0.5 mL), followed by the addition of TfOH (0.30 µL, 3.4 µmol). 10 min later a solution of alcohol **19** (10 mg, 21 µmol) in dry dichloromethane (0.5 mL) was added. The reaction mixture was stirred for 0.5 hour at –78 °C before it was allowed to warm to room temperature over 2 hours. The reaction mixture was quenched by the addition of triethylamine (2 mL) and then partitioned between H_2O (15 mL) and EtOAc (50 mL). The layers were separated and the aqueous layer was extracted with EtOAc (50 mL). The combined organic layers were washed successively with saturated aqueous $NaHCO_3$ (10 mL), NH_4Cl (10 mL), brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 10/1) to yield compound **23** (11 mg, 71%) as a colorless oil. $[\alpha]_D^{20}$= 3.3 (*c* 1.0, DCM); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.22 (m, 10H), 4.73 (d, *J* = 11.7 Hz, 1H), 4.69 (d, *J* = 3.7 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.47 (s, 2H), 3.68 (dd, *J* = 11.0, 5.7 Hz, 1H), 3.58 (s, 3H), 3.54 (ddd, *J* = 12.3, 8.5, 3.0 Hz, 3H), 3.49 (s, 3H), 3.48 – 3.42 (m, 1H), 3.36 (dd, *J* = 11.4, 4.4 Hz, 1H), 3.30 (t, *J* = 9.1 Hz, 1H), 3.22 (ddd, *J* = 10.6, 8.9, 5.8 Hz, 1H), 3.10 (d, *J* = 9.3 Hz, 1H), 2.85 (dd, *J* = 15.3, 6.7 Hz, 1H), 2.08 – 1.99 (m, 1H), 1.89 – 1.80 (m, 1H), 1.77 – 1.71 (m, 1H), 1.68 – 1.62 (m, 1H), 1.38 (dt, *J* = 21.2, 7.0 Hz, 1H), 1.21 (dd, *J* = 14.5, 9.2 Hz, 2H), 1.00 (dd, *J* = 14.2, 6.8 Hz, 6H), 0.90 (d, *J* = 4.8 Hz, 3H), 0.89 – 0.85 (m, 9H), 0.72 – 0.64 (m, 1H), 0.61 – 0.54 (m, 1H), 0.24 (ddd, *J* = 8.4, 6.6, 4.2 Hz, 2H), 0.08 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.28, 138.78, 128.41, 128.39, 127.73, 127.67, 127.52, 127.47, 94.90, 83.35, 80.55, 80.51, 79.46, 79.02, 73.16, 73.05, 72.73, 70.49, 68.15, 61.27, 60.28, 58.91, 42.41, 38.50, 32.61, 29.78, 29.50, 26.88, 25.92, 23.31, 22.35, 20.12, 18.08, 13.63, 13.43, 8.28, -4.57, -4.62; HRMS (ESI) *m/z* calcd for $C_{43}H_{68}O_8NaSi$ $[M + Na]^+$: 763.4576, found: 763.4579.



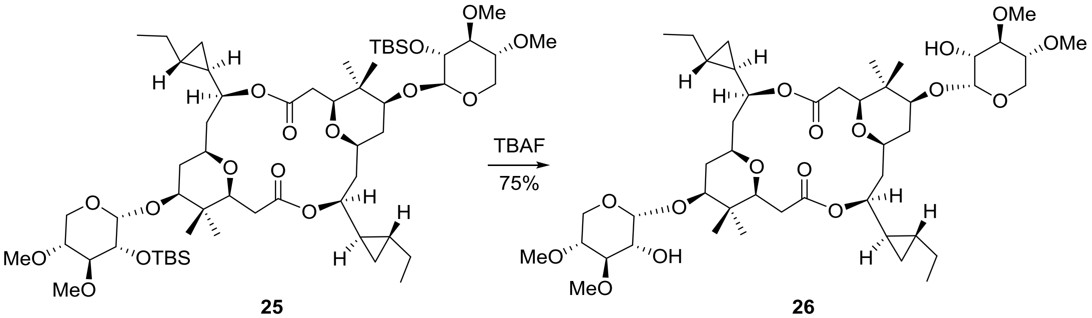
23 **24**

To a solution of Bn ether **23** (72 mg, 97 µmol) in MeOH (6 mL) was added 10% Pd/C (10 mg). The reaction flask was evacuated and purged with hydrogen three times. The reaction mixture was stirred under a H_2 atmosphere at ambient temperature for 2 hours. The flask was then evacuated and purged with nitrogen three times and the catalyst was removed by filtration through Celite. The filtrate was concentrated and the crude product purified by flash column chromatography on silica gel (hexanes/EtOAc = 2/1) to yield compound **24** (35 mg, 64%) as a colorless oil. $[\alpha]_D^{20}$= 33.6 (*c* 1.0, DCM); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.73 (d, *J* = 3.5 Hz, 1H), 3.79 – 3.70 (m, 2H), 3.68 (dd, *J* = 11.0, 5.7 Hz, 1H), 3.58 (s, 3H), 3.54 – 3.47 (m, 2H), 3.49 (s, 3H), 3.37 (dd, *J* = 11.3, 4.3 Hz, 1H), 3.30 (t, *J* = 9.1 Hz, 1H), 3.25 – 3.16 (m, 2H), 3.15 – 3.05 (m, 1H), 1.88 – 1.80 (m, 2H), 1.74 – 1.64 (m, 4H), 1.60 (br, 3H), 1.39 – 1.31 (m, 2H), 1.24 – 1.19 (m, 1H), 0.98 (s, 3H), 0.97 – 0.93 (m, 6H), 0.91 (s, 9H), 0.73 – 0.65 (m, 1H), 0.65 – 0.58 (m, 1H), 0.35 – 0.31 (m, 1H), 0.31 – 0.23 (m, 1H), 0.10 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 95.04, 83.87, 83.33, 80.48, 75.91, 73.16, 61.72, 61.28, 60.35, 58.95, 42.93, 38.54, 32.81, 29.77, 26.79, 25.89, 25.58, 23.22, 18.89, 18.09, 13.72, 13.46, 9.34, -4.56, -4.62; HRMS (ESI) *m/z* calcd for $C_{29}H_{56}NaO_8Si$ [M + Na]$^+$: 583.3637, found: 583.3534.



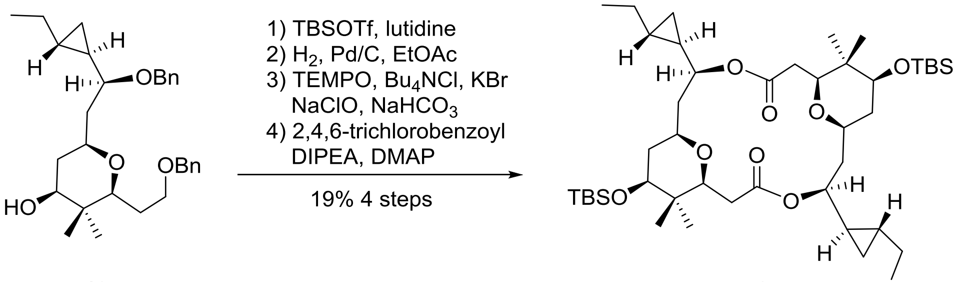
To a solution of the diol **24** (35 mg, 62 µmol) in CH_2Cl_2 (0.7 mL) was added TEMPO (0.5 mg, 3.2 µmol) and saturated $NaHCO_3$ (380 µL). KBr (125 µL, 6.2 µmol, 0.05 M aqueous solution) and Bu_4NCl (100 µL, 5.0 µmol, 0.05 M aqueous solution) were added subsequently and the mixture was cooled to 0 °C. To the vigorously stirring biphasic solution was added a stock solution of saturated $NaHCO_3$ (90 µL), brine (165 µL) and bleach (108 µL, 0.16 mmol, 1.5 M) dropwise over 70 min. The mixture was allowed to stir for an additional 30 min at 0 °C upon completion of the addition. The solution was then diluted with H_2O (2 mL) and CH_2Cl_2 (2 mL). The diluted mixture was acidified with 10% citric acid (4-10 drops) to pH 3-4. The biphasic mixture was extracted with EtOAc (2 × 50 mL), and the combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give rise to the corresponding carboxylic acid (22 mg, 38 µmol), which was employed in the next step of reaction without further purification.

To the above acid (4 mg, 7 µmol) in dry toluene (2 mL) was added DIPEA (*N*,*N*-diisopropylethylamine) (15 µL, 90 µmol) and 2,4,6-trichlorobenzoyl chloride (10 µL, 64 µmol) dropwise. The reaction mixture was stirred at room temperature for 2 hours, then the mixture was added dropwise over 3 hours to a stirred solution of DMAP (4-dimethylaminopyridine) (17 mg, 0.14 mmol) in toluene (10 mL) at 80 °C, the reaction was allowed to stir for another 3 hours before it was quenched with saturated aqueous NH_4Cl (15 mL). The biphasic mixture was extracted with EtOAc (2 × 70 mL), and the combined organic layers were washed successively with saturated aqueous $NaHCO_3$ (15 mL), brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 3/1) to yield compound **25** (2.5 mg, 40%) as a colorless oil. $[\alpha]_D^{20}$= 29.4 (*c* 1.0, DCM); ^1H NMR (500 MHz, CD_3CN) δ 4.74 (d, *J* = 3.7 Hz, 2H), 4.26 (t, *J* = 8.5 Hz, 2H), 3.66 (dd, *J* = 11.0, 5.3 Hz, 2H), 3.49 (d, *J* = 4.6 Hz, 6H), 3.51 – 3.46 (m, 2H), 3.46 – 3.41 (m, 2H), 3.39 (s, 6H), 3.38 (d, *J* = 7.5 Hz, 4H), 3.33 – 3.27 (m, 2H), 3.21 – 3.10 (m, 4H), 2.40 (dd, *J* = 16.2, 1.4 Hz, 2H), 2.09 (s, 2H), 1.95 – 1.85 (m, 4H), 1.68 (dd, *J* = 13.6, 5.3 Hz, 2H), 1.34 (dt, *J* = 20.0, 6.5 Hz, 2H), 1.20 – 1.12 (m, 2H), 1.00 – 0.93 (m, 2H), 0.91 (s, 6H), 0.90 (s, 18H), 0.87 (t, *J* = 7.2 Hz, 6H), 0.84 (s, 6H), 0.78 – 0.73 (m, 2H), 0.71 (dd, *J* = 11.2, 6.1 Hz, 2H), 0.40 – 0.30 (m, 2H), 0.30 – 0.22 (m, 2H), 0.08 (s, 6H), 0.05 (s, 6H); ^{13}C NMR (125 MHz, CD_3CN) δ 171.36, 95.16, 83.25, 80.42, 80.29, 78.55, 76.44, 74.84, 73.04, 60.46, 60.04, 57.98, 41.18, 38.03, 35.41, 32.83, 26.36, 25.42, 23.68, 22.26, 19.85, 17.81, 12.98, 12.76, 9.06, -5.26, -5.34; HRMS (ESI) *m/z* calcd for $C_{58}H_{104}NaO_{16}Si_2$ [M + Na]$^+$: 1135.6755, found: 1135.6753.



25 **26**

To a stirred solution of silyl ether **25** (2.0 mg, 1.8 µmol) in THF (1 mL) at 0 °C was added TBAF (200 µL, 1 M in THF, 200 µmol), immediately producing a yellow solution. The mixture was stirred for 3 hours, then the reaction mixture was poured into a mixture of EtOAc (20 mL), H_2O (10 mL). The layers were separated and the aqueous layer was further extracted with EtOAc (2 × 20 mL). The combined organic extracts were washed successively with saturated aqueous $NaHCO_3$ (15 mL), NH_4Cl (15 mL), brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel (hexanes/EtOAc = 1/1) to yield compound **26** (1.2 mg, 75%) as a colorless oil. $[\alpha]_D^{20}$= 18.0 (*c* 1.0, DCM); ^{1}H NMR (500 MHz, CD_3CN) δ 4.81 (d, *J* = 3.8 Hz, 2H), 4.32 (t, *J* = 8.1 Hz, 2H), 3.69 (dd, *J* = 11.0, 4.9 Hz, 2H), 3.54 (s, 6H), 3.50 – 3.42 (m, 6H), 3.41 (s, 6H), 3.39 – 3.32 (m, 4H), 3.24 – 3.12 (m, 4H), 2.70 (d, *J* = 9.0 Hz, 2H), 2.70 (br, 2H), 2.44 (dd, *J* = 16.8, 1.5 Hz, 2H), 1.92 – 1.84 (m, 4H), 1.73 (dd, *J* = 14.8, 3.1 Hz, 2H), 1.38 (dd, *J* = 14.9, 7.6 Hz, 4H), 1.00 – 0.94 (m, 2H), 0.93 (s, 6H), 0.91 – 0.85 (m, 12H), 0.75 (dd, *J* = 10.7, 7.9 Hz, 4H), 0.44 – 0.34 (m, 2H), 0.27 (dd, *J* = 13.5, 4.9 Hz, 2H); ^{13}C NMR (125 MHz, CD_3CN) δ 171.12, 95.36, 83.23, 80.15, 79.38, 79.34, 76.64, 75.25, 72.00, 60.21, 59.71, 57.87, 40.88, 37.89, 35.33, 32.80, 29.43, 26.38, 23.84, 22.23, 19.80, 12.98, 12.84, 9.01; HRMS (ESI) *m/z* calcd for $C_{46}H_{76}NaO_{16}$ [M + Na]$^+$: 907.5026, found: 907.5023.



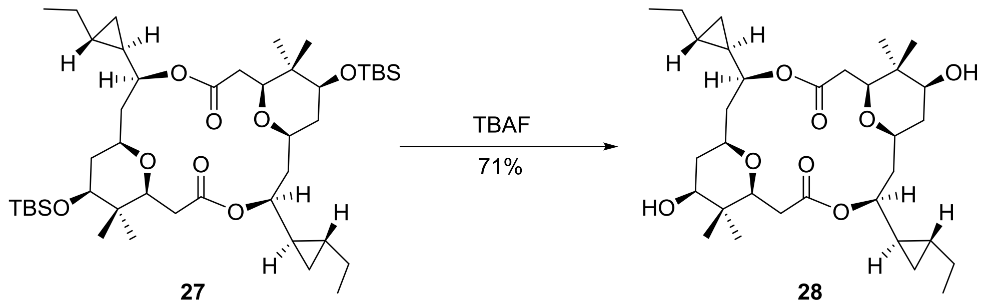
19 **27**

To a solution of compound **19** (37 mg, 0.08 mmol) and 2,6-lutidine (0.30 mL, 0.24 mmol) in CH_2Cl_2 (1.5 mL), TBS-triflate (0.26 mL, 0.12 mmol) was added at 0 °C. The reaction mixture was stirred for one hour and then quenched by the addition of a saturated aqueous solution of $NaHCO_3$ (10 mL). The reaction mixture was extracted with EtOAc (2 × 30 mL); and the combined organic layers were washed successively with saturated aqueous solution of NH_4Cl (10 mL), brine (10 mL),

dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes/ethyl ether = 85/15) to afford the corresponding TBS silyl ether (25 mg, 54%) as a light yellow oil.
To a solution of TBS silyl ether (25 mg, 0.043 mmol) in EtOAc (1 mL) was added 10% Pd/C (5 mg). The reaction flask was evacuated and purged with hydrogen three times. The reaction mixture was stirred under H_2 atmosphere at ambient temperature for 2 hours. The flask was then evacuated and purged with nitrogen three times and the catalyst was removed by filtration through a pad of Celite. The filtrate was concentrated and the crude product was purified by flash column chromatography on silica gel (hexanes/EtOAc = 3/1) to yield the corresponding diol (17 mg, 99%) as a colorless oil.

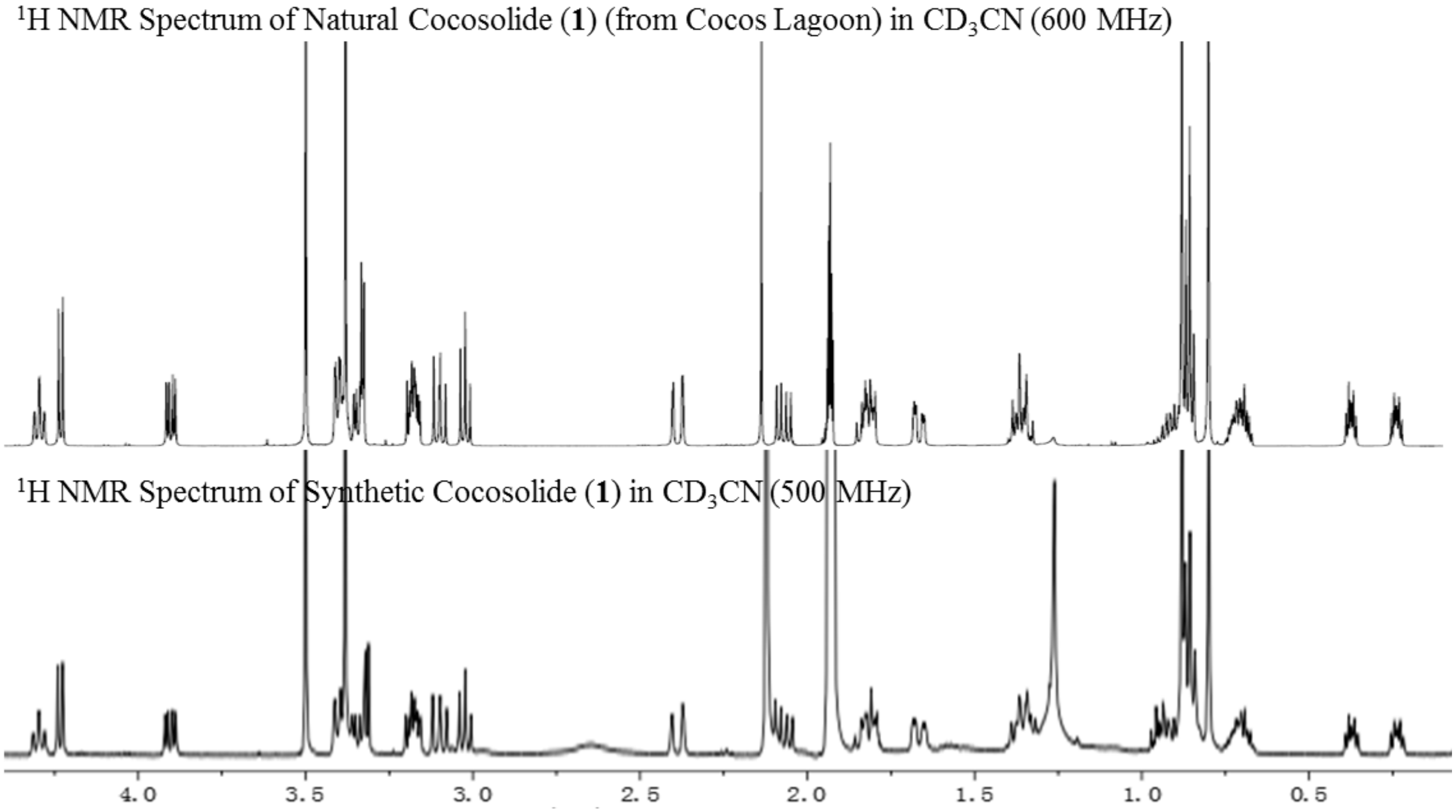
To a solution of the diol (17 mg, 0.043 μmol) in CH_2Cl_2 (300 μL) was added TEMPO (0.3 mg, 2 μmol) and saturated $NaHCO_3$ (115 μL). KBr (10 μL, 5 μmol, 0.05 M aqueous solution) and Bu_4NCl (40 μL, 3.2 μmol, 0.08 M aqueous solution) were added subsequently and the mixture was cooled to 0 °C. To the vigorously stirring biphasic solution was added a stock solution of saturated $NaHCO_3$ (31 μL), brine (60 μL) and bleach (85 μL, 0.136 mmol, 1.6 M) dropwise over 60 min. The mixture was allowed to stir for an additional 30 min at 0 °C upon completion of the addition. The solution was then diluted with H_2O (2 mL) and CH_2Cl_2 (2 mL). The diluted mixture was acidified with 10% citric acid (4-10 drops) to pH 3-4. The biphasic mixture was extracted with EtOAc (2 × 30 mL), and the combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give rise to the corresponding carboxylic acid, which was employed in the next step of reaction without further purification.

To the above acid (8 mg, 0.02 mmol) in dry dichloromethane (0.6 ml) was added DIPEA (*N*,*N*-diisopropylethylamine) (40 μL, 0.24 mmol) and 2,4,6-trichlorobenzoyl chloride (20 μL, 0.13 mmol) dropwise. The reaction mixture was stirred at room temperature for 2 hours, then the mixture was added dropwise over 3 hours to a stirred solution of DMAP (4-dimethylaminopyridine) (35 mg, 0.29 mmol) in dry dichloromethane (8 mL) at room temperature, the reaction was allowed to stir for another 10 hours before it was quenched with saturated aqueous NH_4Cl (15 mL). The biphasic mixture was extracted with EtOAc (2 × 40 mL), and the combined organic layers were washed successively with saturated aqueous $NaHCO_3$ (15 mL), brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 3/1) to yield compound **27** (2.8 mg, 36%) as a colorless oil. $[\alpha]_D^{20}$= -14.7 (*c* 0.4, DCM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.43 (t, *J* = 9.2 Hz, 2H), 3.44 (d, *J* = 6.5 Hz, 4H), 3.39 (dd, *J* = 11.3, 4.9 Hz, 2H), 2.40 (dd, *J* = 17.4, 1.6 Hz, 1H), 2.24 (dd, *J* = 17.4, 8.2 Hz, 2H), 1.95 – 1.84 (m, 2H), 1.69 (dd, *J* = 14.9, 3.5 Hz, 2H), 1.55 (d, *J* = 5.0 Hz, 2H), 1.43 – 1.33 (m, 4H), 1.33 – 1.27 (m, 2H), 0.91 – 0.88 (m, 18H), 0.86 (s, 6H), 0.80 (s, 6H), 0.79 (s, 6H), 0.67 (ddd, *J* = 13.4, 9.0, 4.7 Hz, 2H), 0.41 – 0.31 (m, 2H), 0.26 (dt, *J* = 9.7, 4.8 Hz, 2H), 0.04 (s, 6H), 0.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 79.6, 77.2, 75.7, 75.6, 41.0, 38.8, 38.1, 35.3, 29.7, 26.6, 25.8, 24.3, 22.7, 19.8, 18.0, 13.5, 12.9, 9.6, -3.9, -5.0; HRMS (ESI) *m/z* calcd for $C_{44}H_{81}O_8Si_2$ $[M + H]^+$: 793.5464, found: 793.5502.



27 **28**

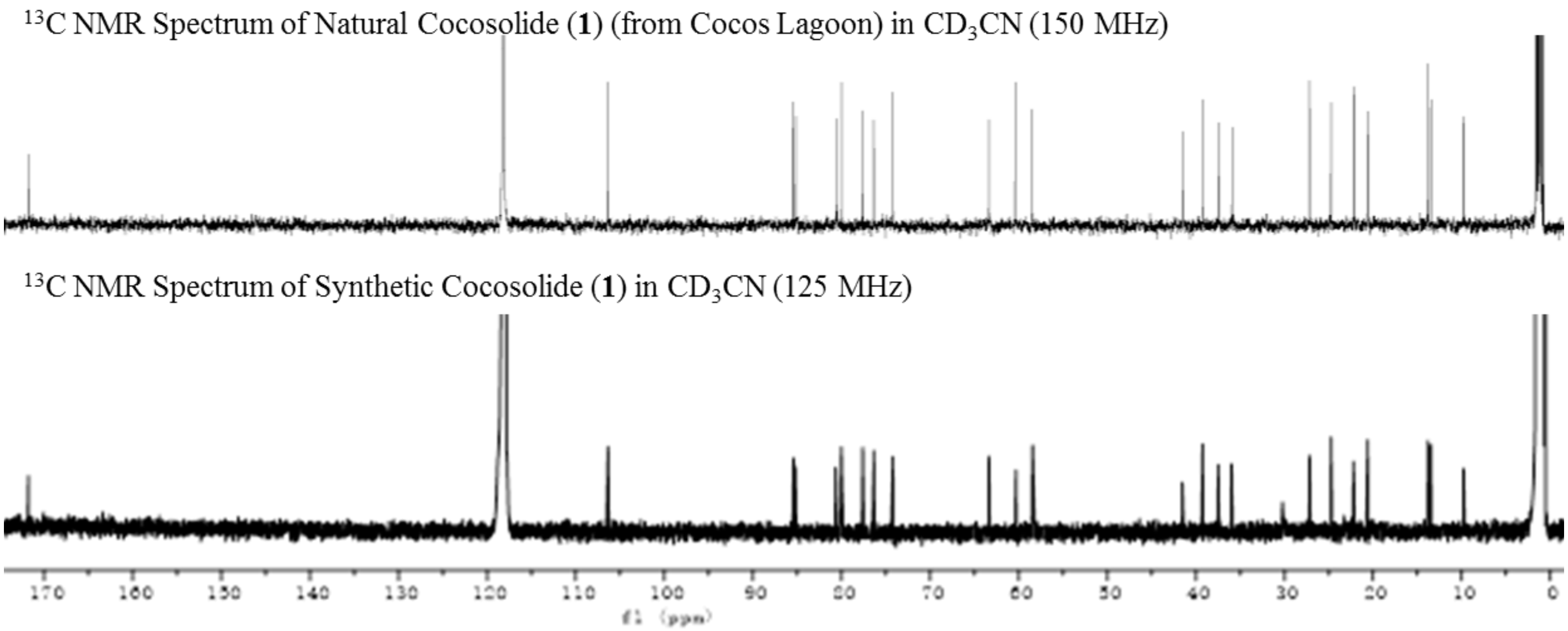
To a stirred solution of silyl ether **27** (2.0 mg, 2.5 μmol) in THF (1 mL) at 0 °C was added TBAF (1 mL, 0.5 mmol, 0.5 M in THF). The reaction mixture was stirred at room temperature for 28 hours, then it was poured into a biphasic mixture solution of EtOAc (20 mL) and H_2O (10 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic extracts were washed successively with saturated aqueous $NaHCO_3$ (15 mL), NH_4Cl (15 mL), brine (15 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 2/1) to yield compound **28** (1.0 mg, 71%) as a colorless oil. $[\alpha]_D^{20}$= 5.0 (*c* 0.4, DCM); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.41 (t, *J* = 9.1 Hz, 2H), 3.52 – 3.37 (m, 6H), 2.45 – 2.24 (m, 4H), 2.02 – 1.88 (m, 2H), 1.83 – 1.69 (m, 4H), 1.41 – 1.30 (m, 4H), 1.00 – 0.93 (m, 2H), 0.90 (s, 6H), 0.87 (d, *J* = 6.4 Hz, 6H), 0.82 (s, 6H), 0.74 – 0.63 (m, 2H), 0.40 – 0.31 (m, 2H), 0.31 – 0.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 79.9, 77.2, 75.5, 75.3, 41.1, 38.4, 35.1, 26.6, 24.2, 22.2, 19.9, 13.5, 12.5, 9.6; HRMS (ESI) *m/z* calcd for $C_{32}H_{53}O_8$ $[M + H]^+$: 565.3735, found: 565.3732.



^{1}H NMR Spectrum of Natural Cocosolide (**1**) (from Cocos Lagoon) in CD_3CN (600 MHz)

^{1}H NMR Spectrum of Synthetic Cocosolide (**1**) in CD_3CN (500 MHz)

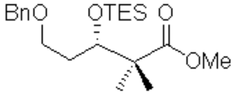
Figure S3. Comparison of ^{1}H spectrum of natural cocosolide (**1**) (from Cocos Lagoon) and the synthetic cocosolide (**1**).


^{13}C NMR Spectrum of Natural Cocosolide (**1**) (from Cocos Lagoon) in CD_3CN (150 MHz)

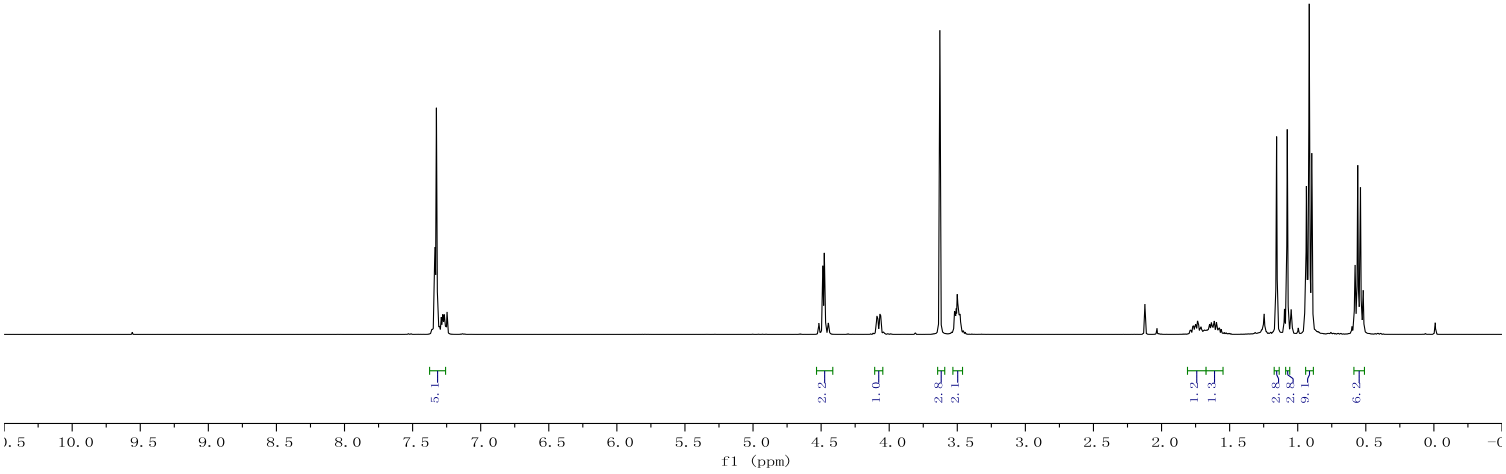
^{13}C NMR Spectrum of Synthetic Cocosolide (**1**) in CD_3CN (125 MHz)

Figure S4. Comparison of ^{13}C spectrum of natural cocosolide (**1**) (from Cocos Lagoon) and the synthetic cocosolide (**1**).

400M, CDCl3


BnO
OTES
O
OMe

5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1.0
2.8
2.1
1.2
1.3
2.8
2.8
9.1
6.2
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
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1.5
1.0
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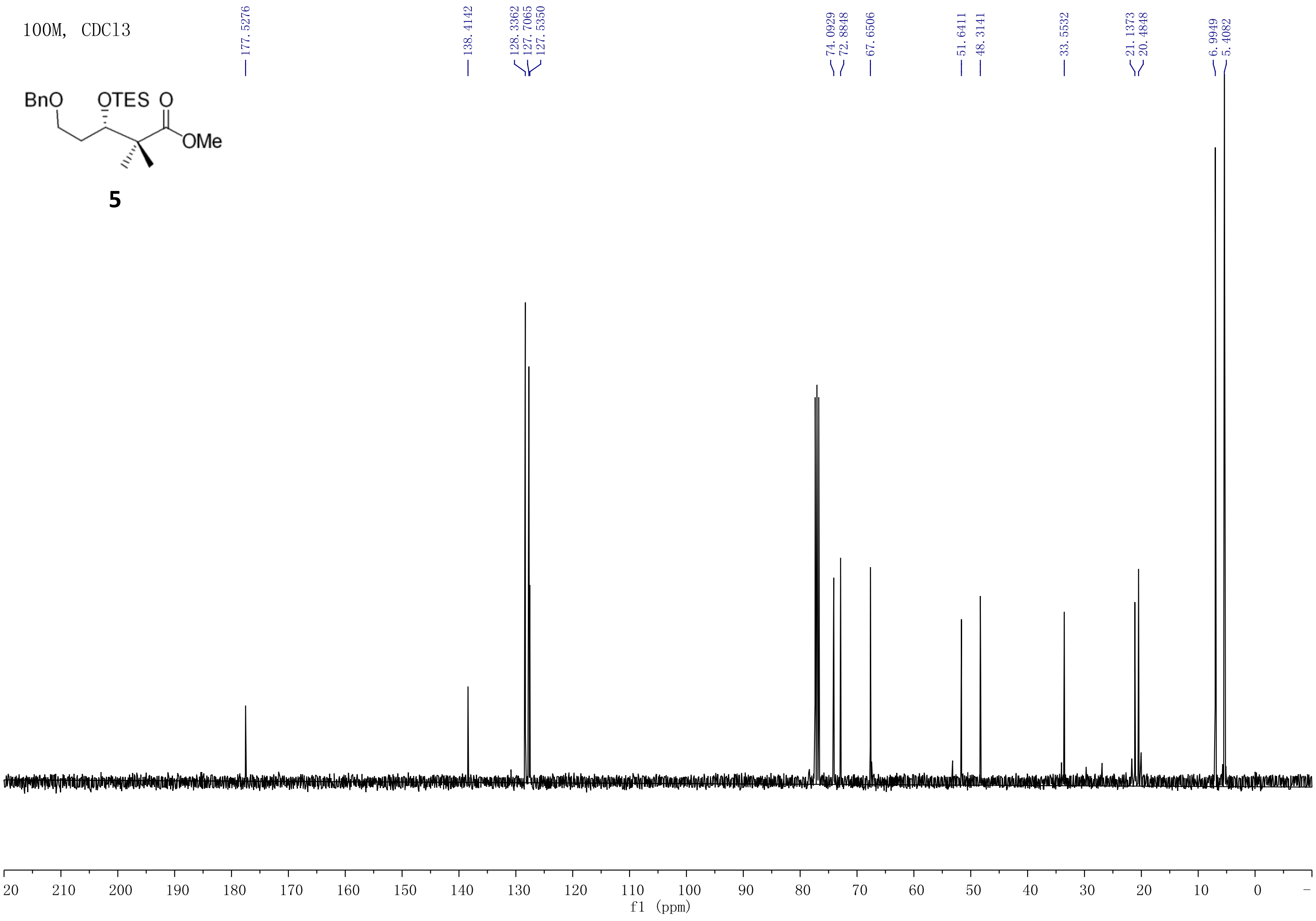
0.0
f1 (ppm)


100M, CDCl3
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OTES
O
OMe
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127.7065
127.5350
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67.6506
51.6411
48.3141
33.5532
21.1373
20.4848
6.9949
5.4082
20
210
200
190
180
170
160
150
140
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50
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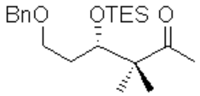
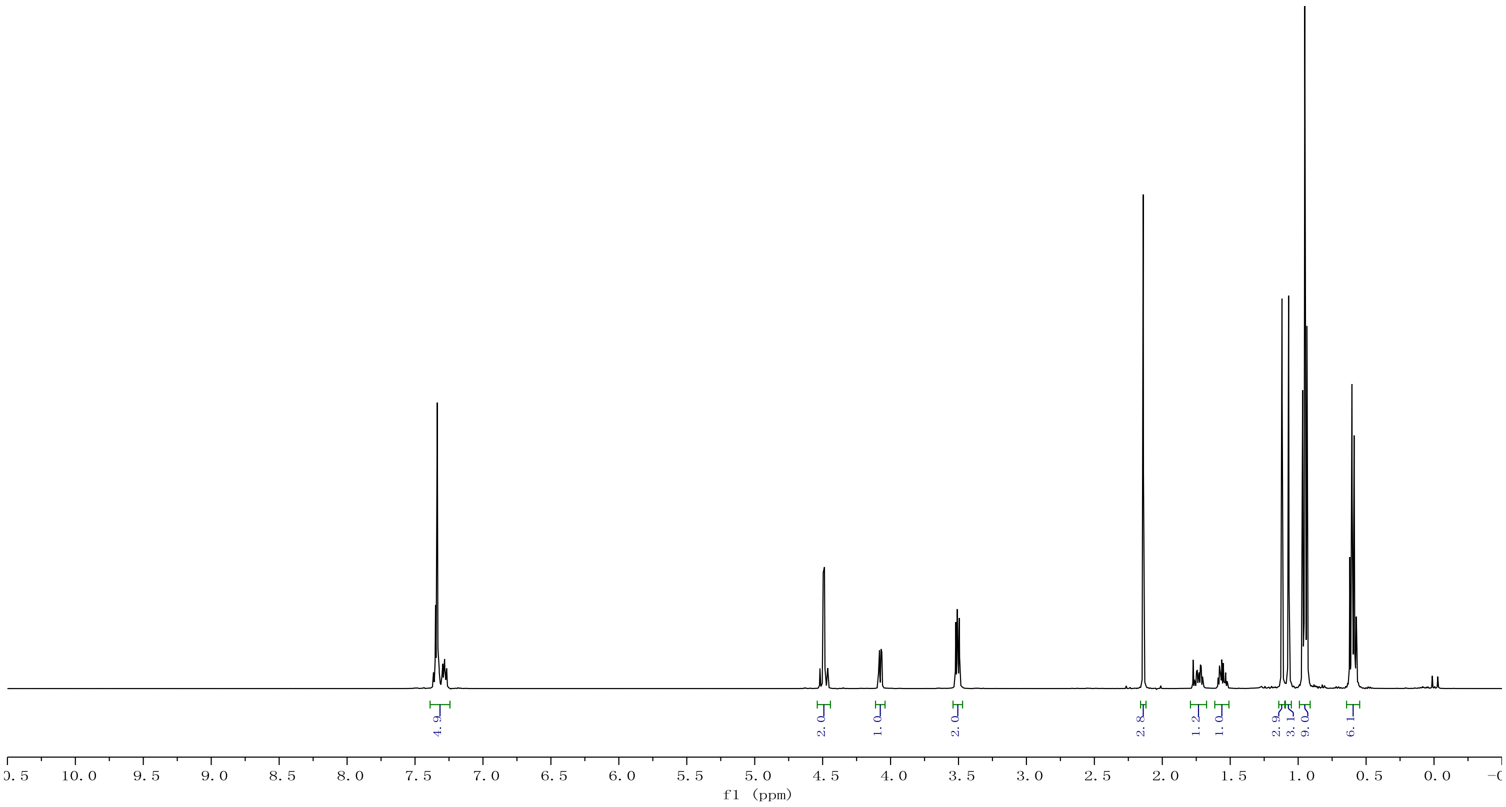
30
20
10
0
f1 (ppm)

5

500M, CDCl3


BnO
OTES
O

6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6.5
6.0
5.5
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3.0
2.5
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1.0
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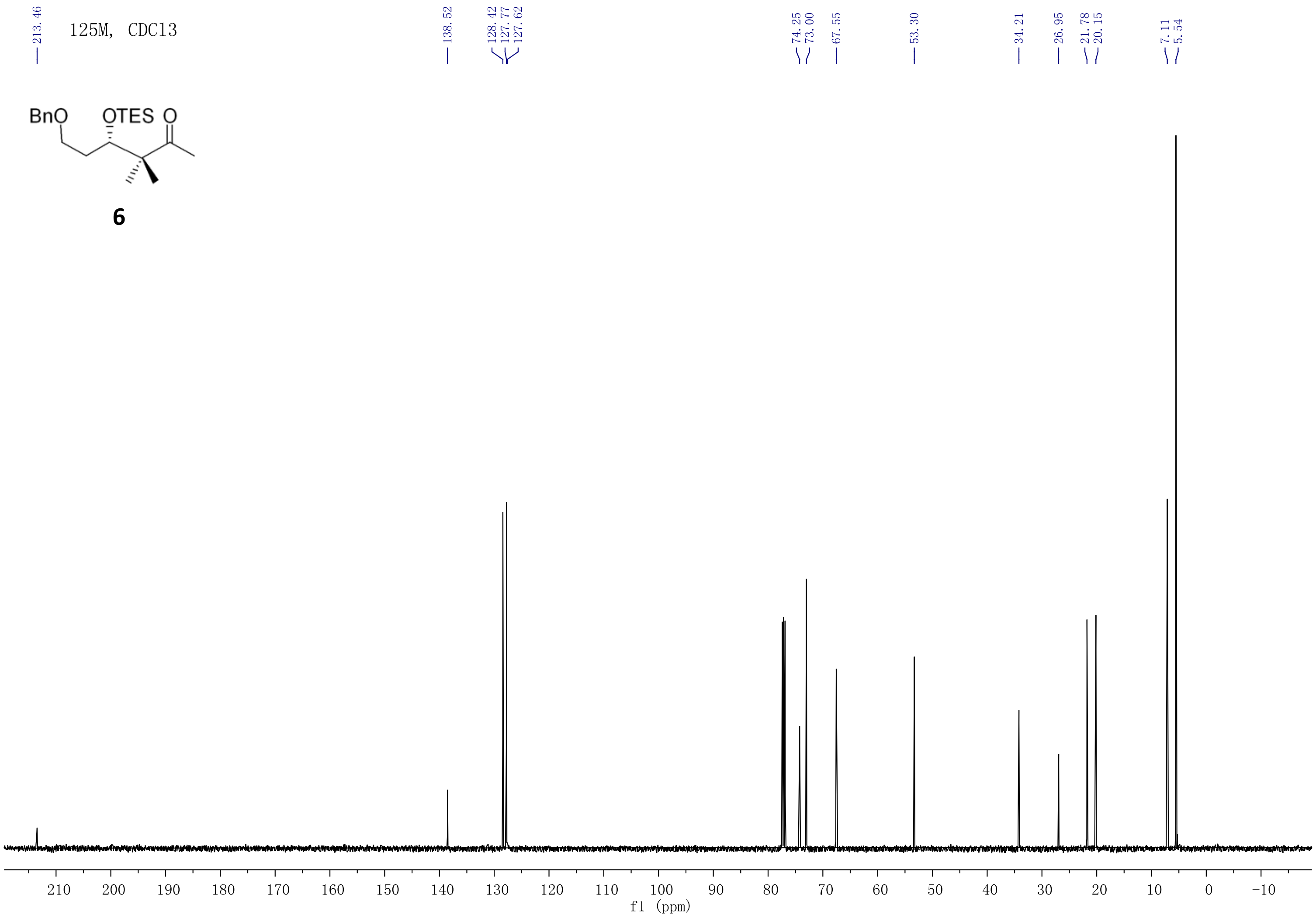
f1 (ppm)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125M, CDCl3
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21.78
20.15
7.11
5.54
BnO
OTES
O
6
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200
190
180
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30
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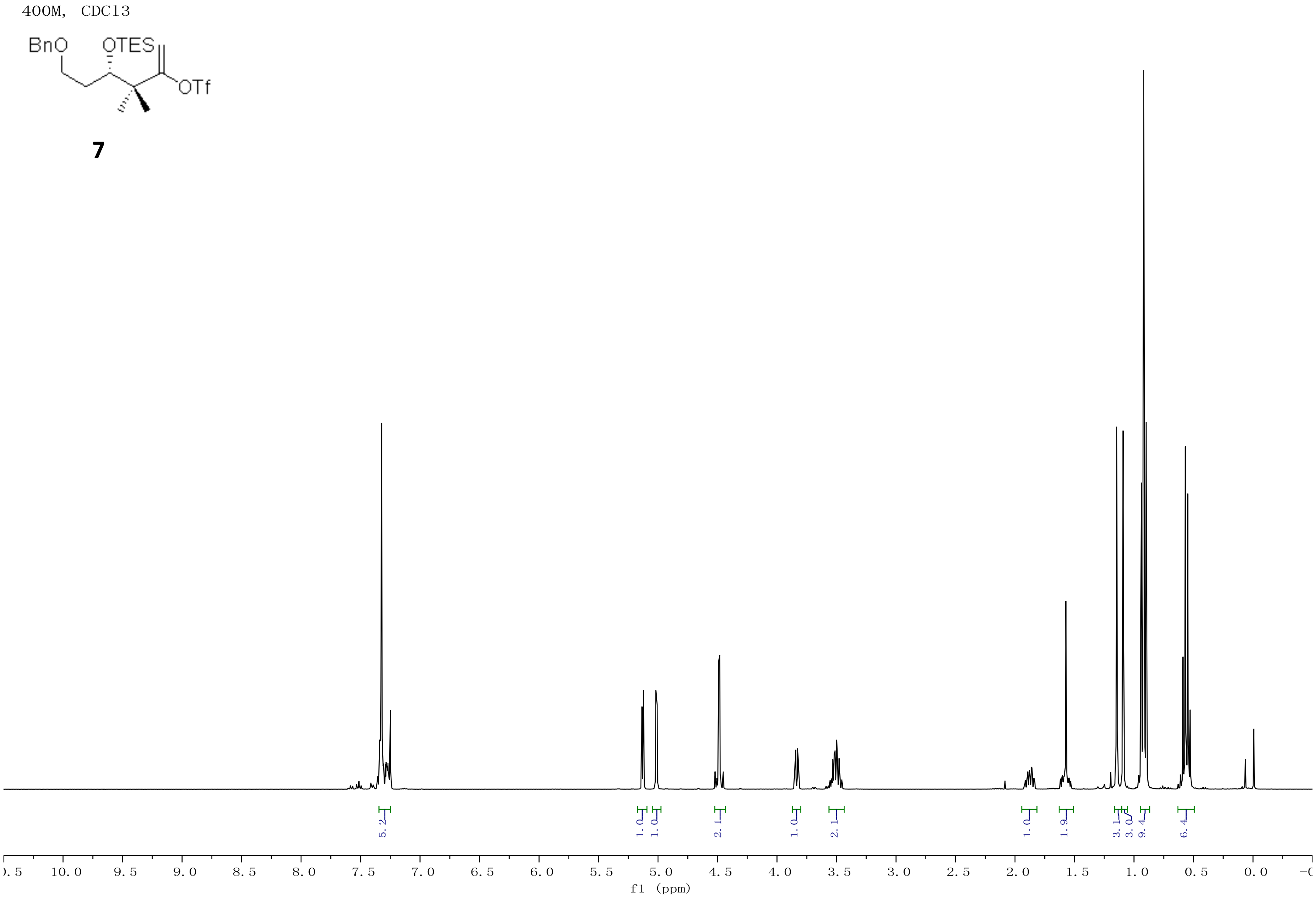
f1 (ppm)


400M, CDCl3
BnO
OTES
OTf
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2.1
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3.1
3.0
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6.4
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10.0
9.5
9.0
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7.0
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6.0
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5.0
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0.5
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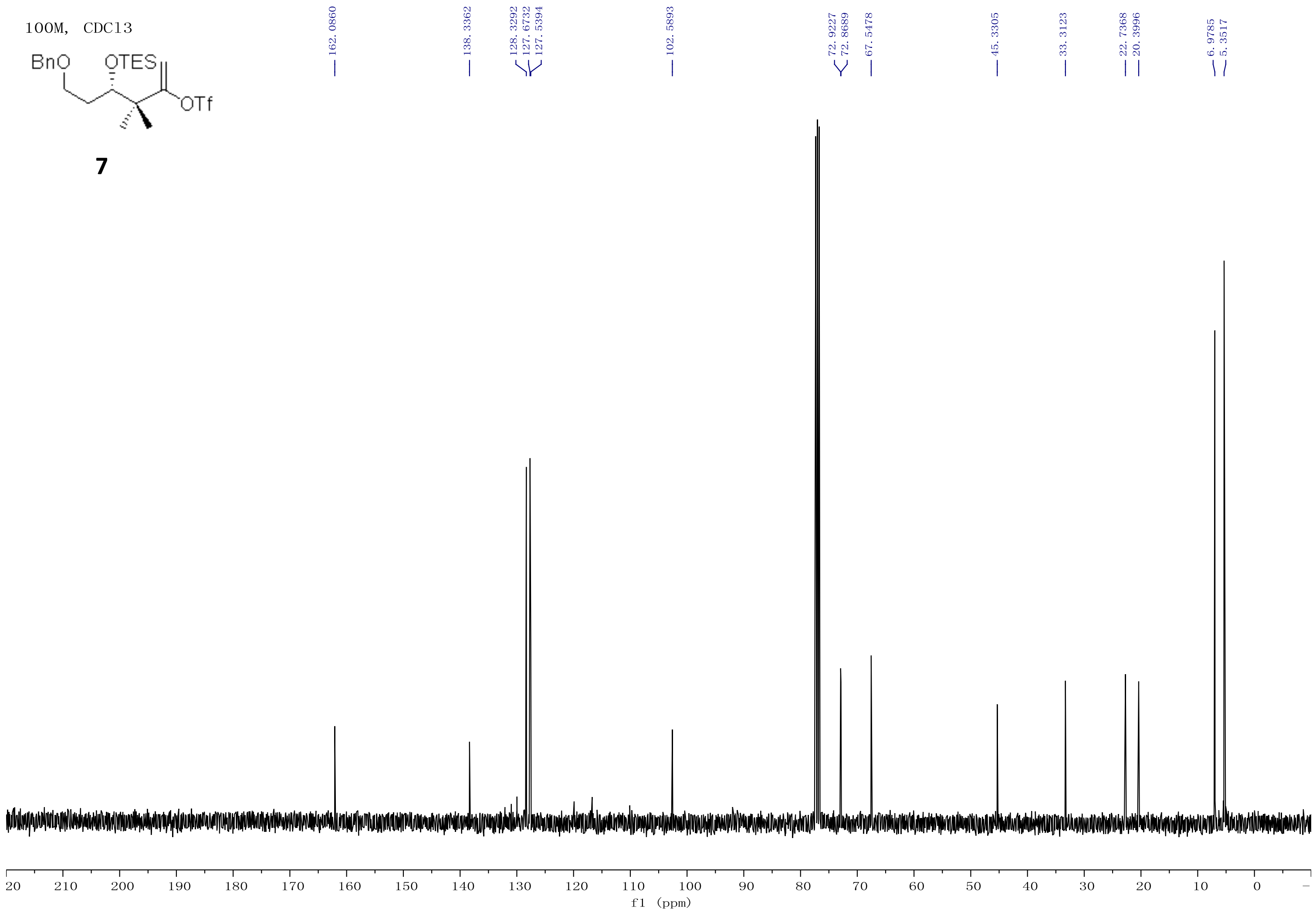
f1 (ppm)

7


100M, CDCl3
BnO
OTES
OTf
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72.9227
72.8689
67.5478
45.3305
33.3123
22.7368
20.3996
6.9785
5.3517
20
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200
190
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160
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20
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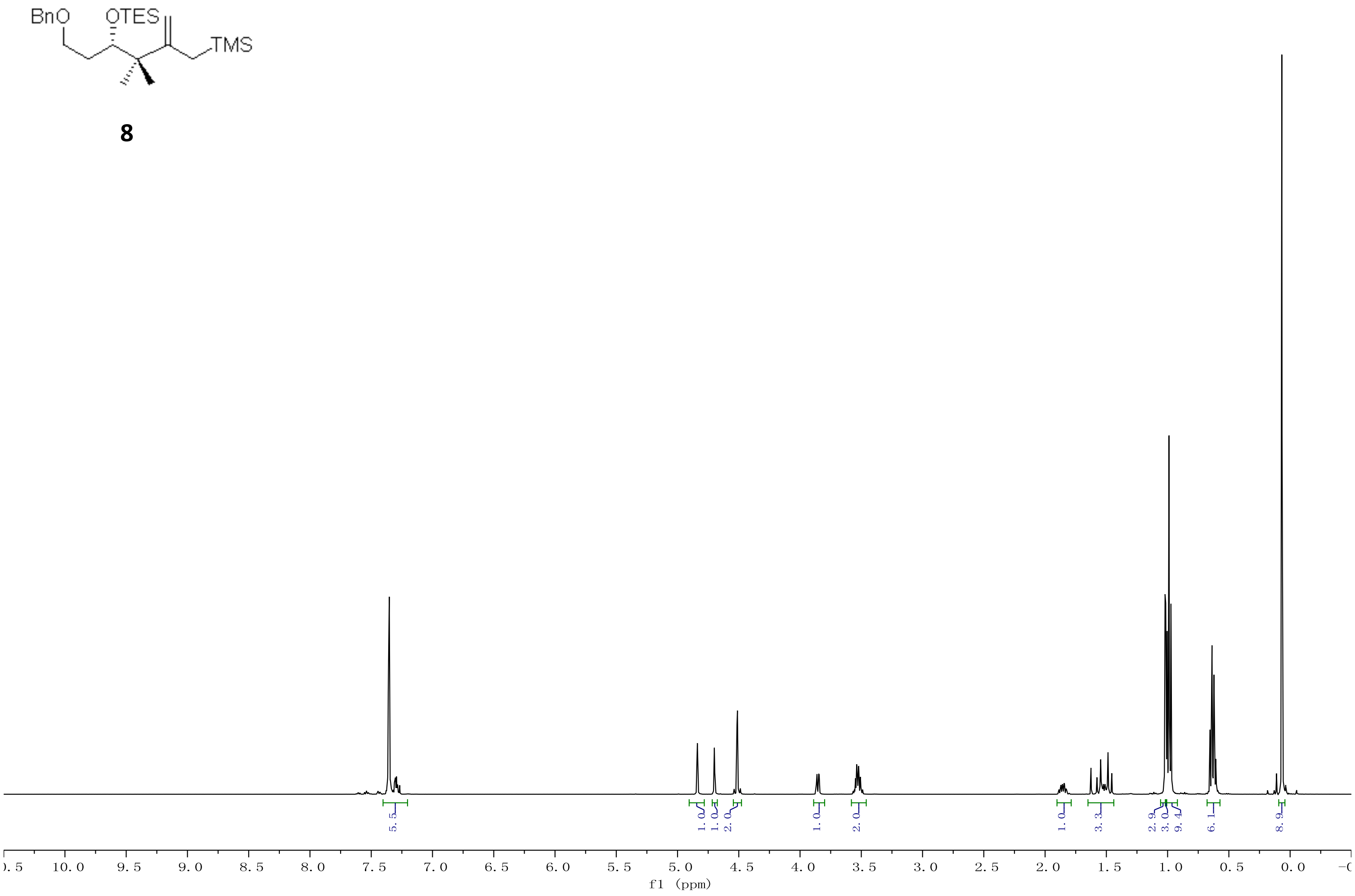
f1 (ppm)

500M, CDCl3



BnO
OTES
TMS
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1.0
2.0
1.0
2.0
1.0
3.3
2.9
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6.1
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6.5
6.0
5.5
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3.0
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2.0
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1.0
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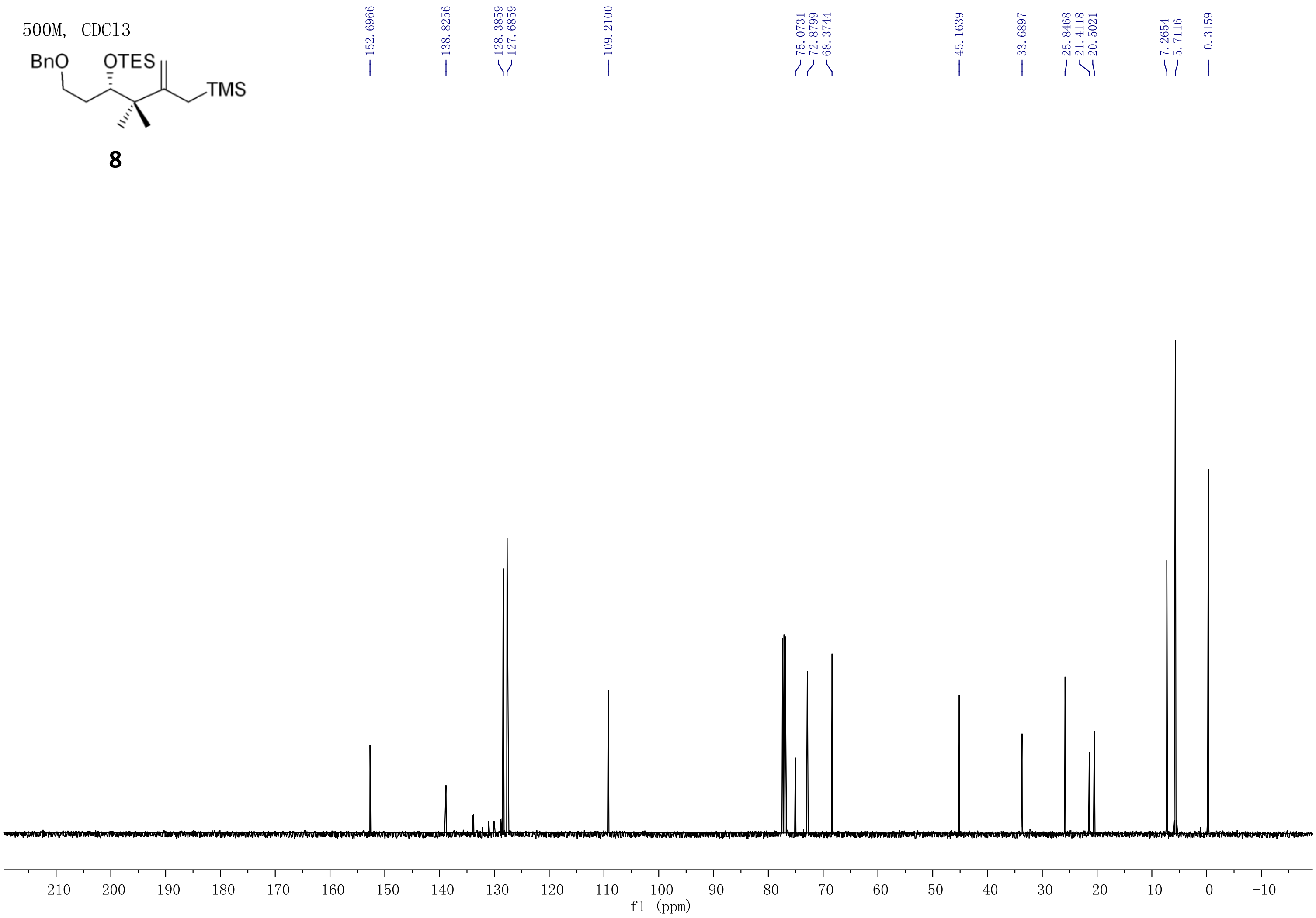
f1 (ppm)

8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33.6897
25.8468
21.4118
20.5021
7.2654
5.7116
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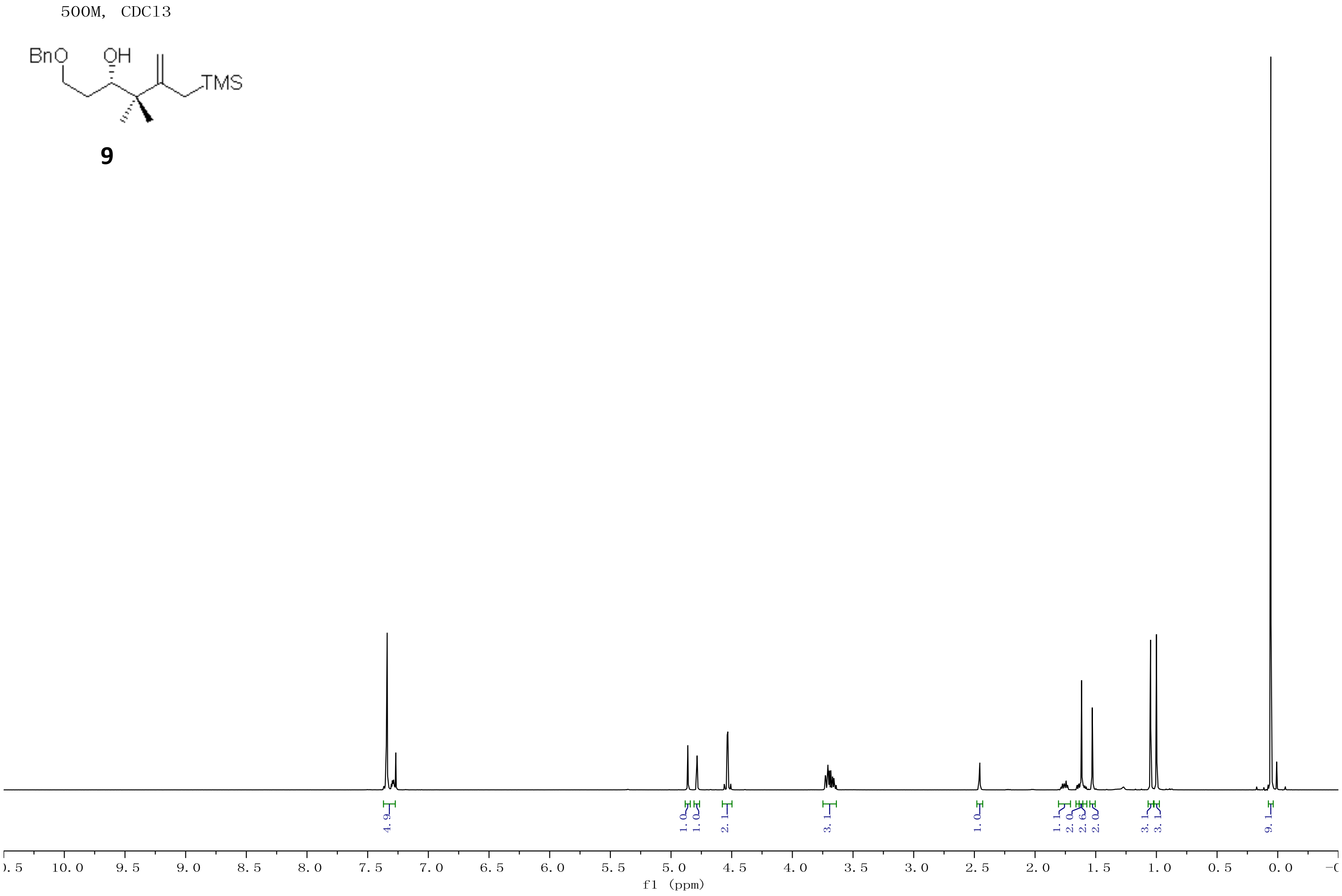
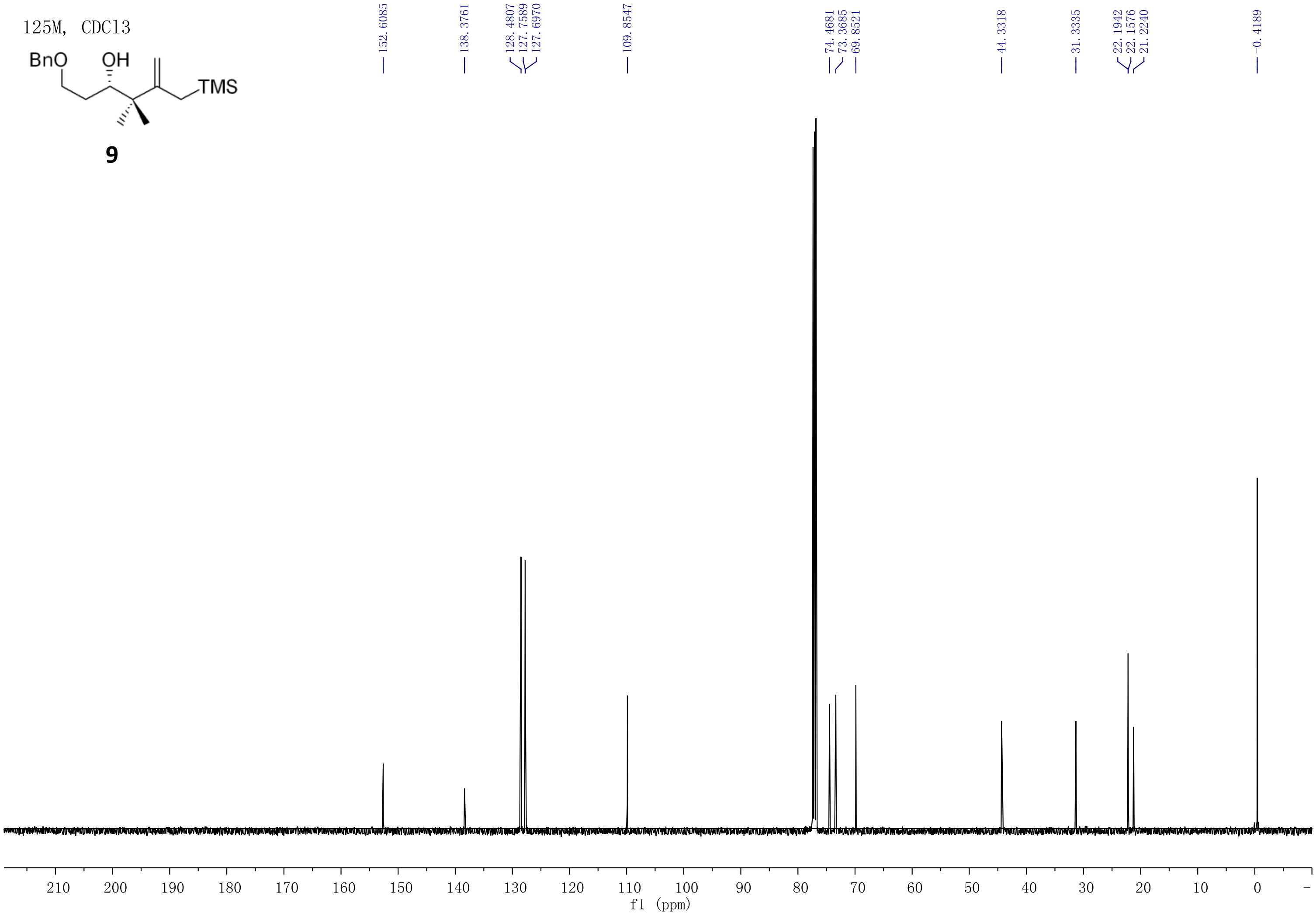
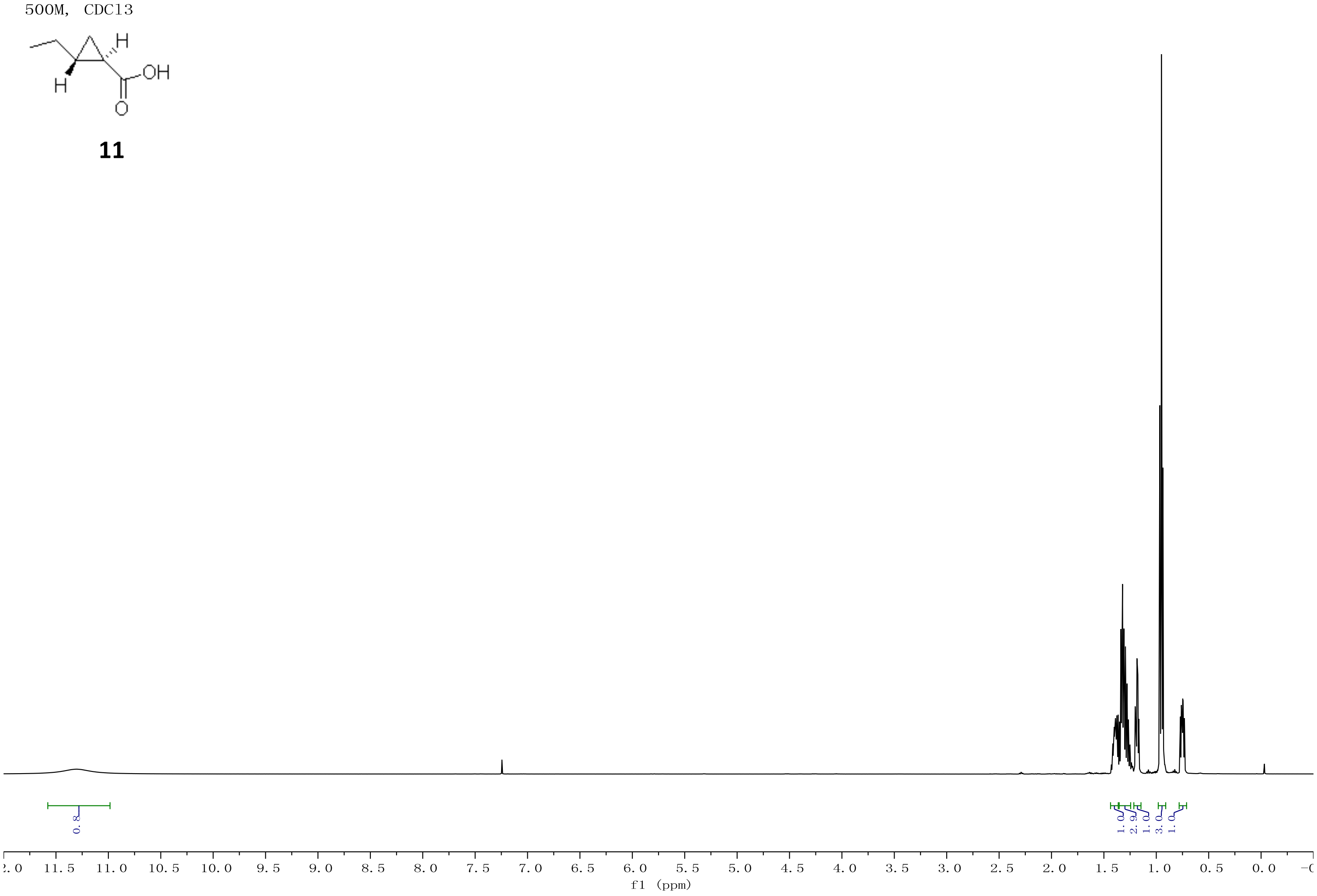
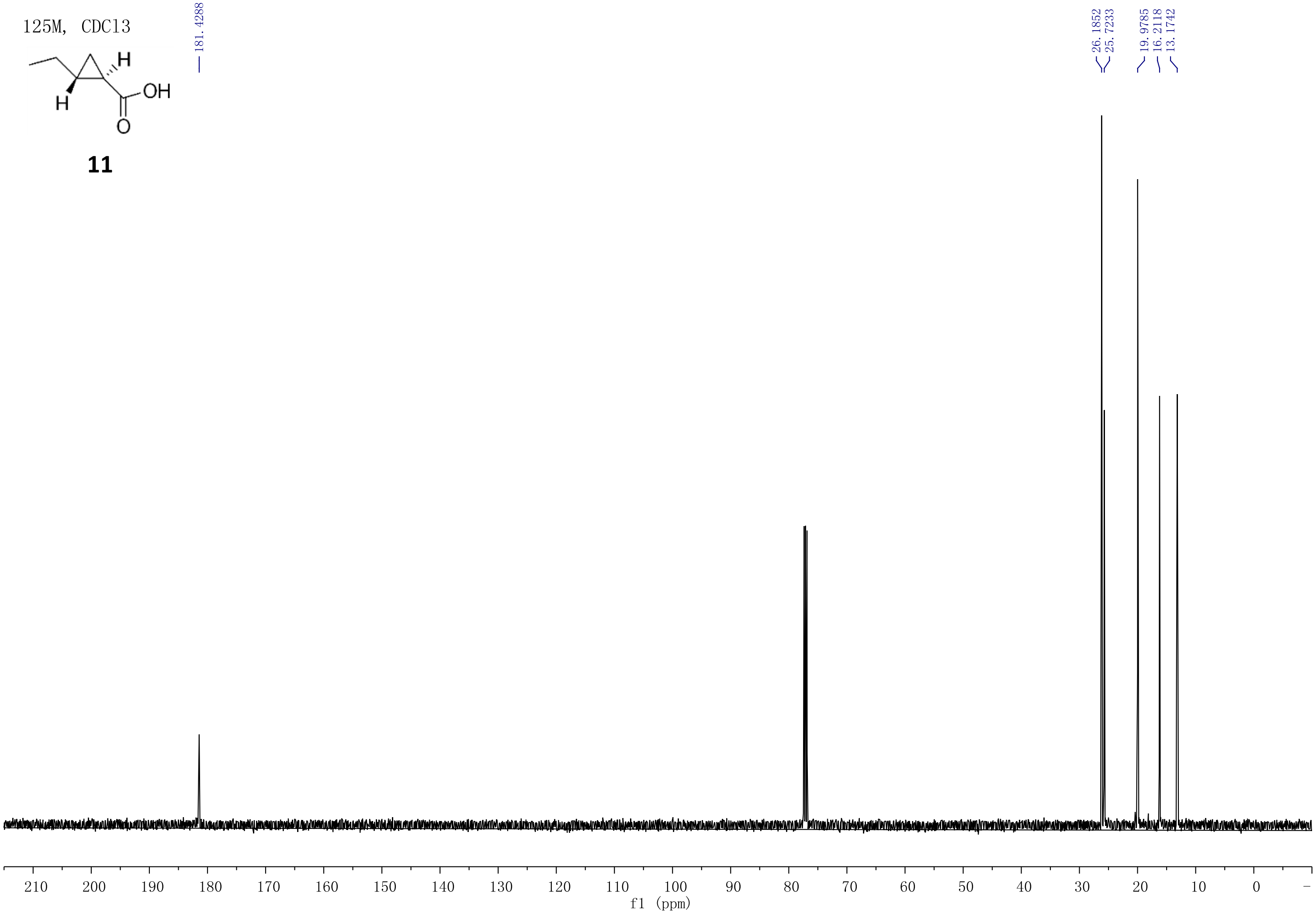
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

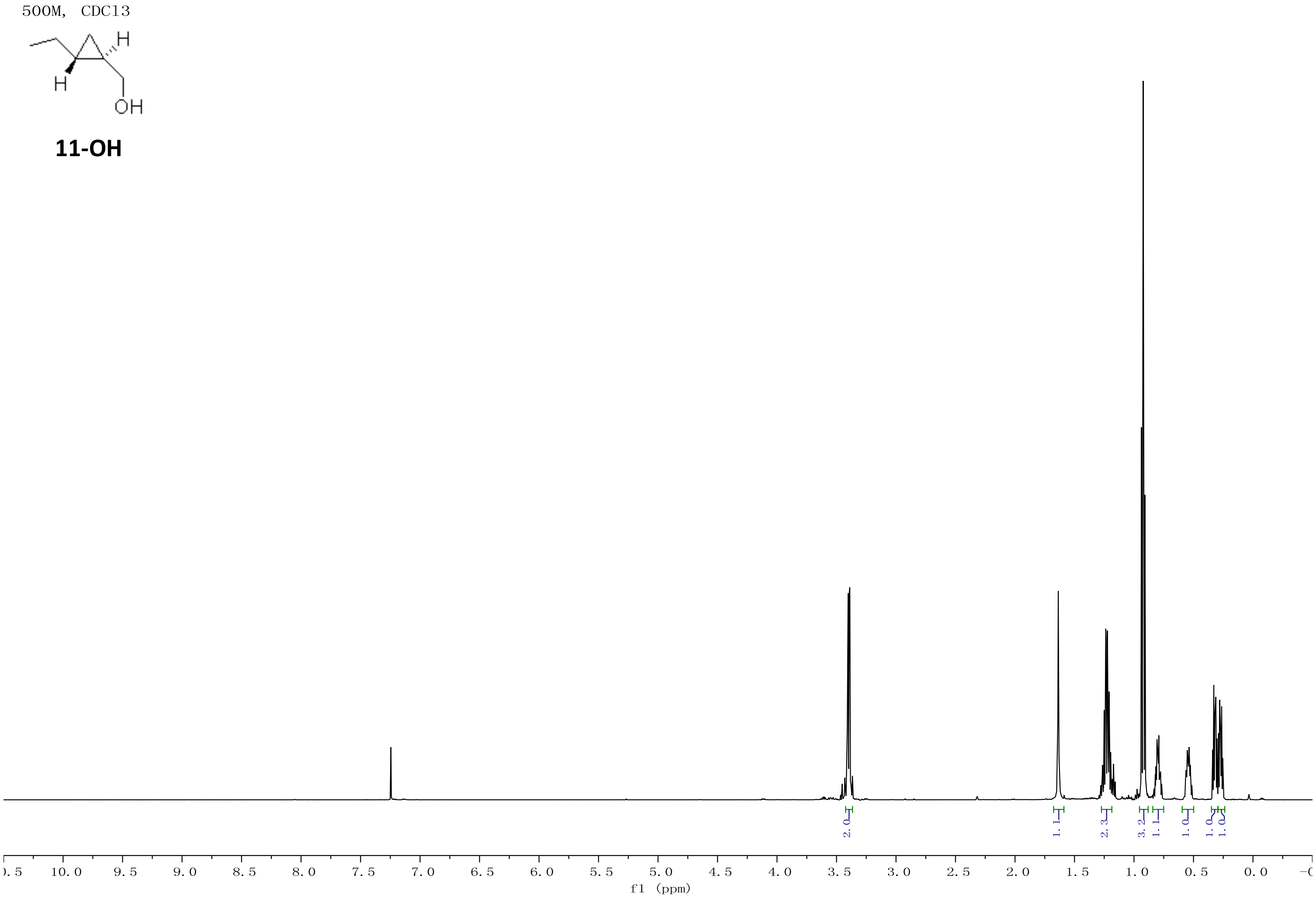
8


500M, CDCl3
BnO
OH
TMS
9
4.9
1.0
1.0
2.1
3.1
1.0
1.1
2.0
2.0
2.0
3.1
3.1
9.1
).5
10.0
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
-(
f1 (ppm)


125M, CDCl3
BnO
OH
TMS
9
152.6085
138.3761
128.4807
127.7589
127.6970
109.8547
74.4681
73.3685
69.8521
44.3318
31.3335
22.1942
22.1576
21.2240
-0.4189
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


500M, CDCl3
H
H
OH
O
11
0.8
1.0
2.9
1.0
3.0
1.0
2.0
11.5
11.0
10.5
10.0
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
f1 (ppm)

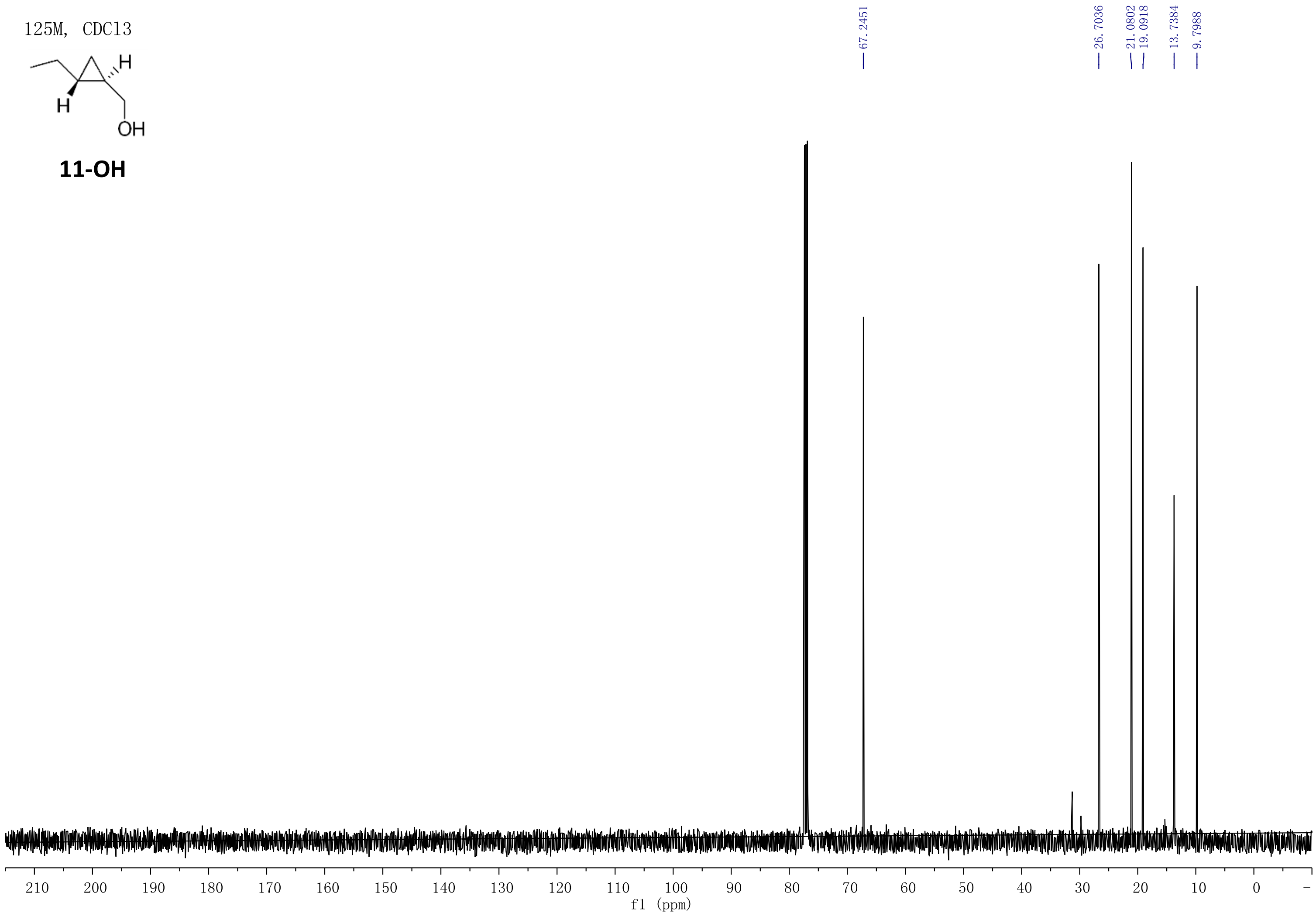

125M, CDCl3
H
OH
H
O
11
181.4288
26.1852
25.7233
19.9785
16.2118
13.1742
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


500M, CDCl3

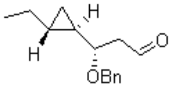
11-OH

125M, CDCl3

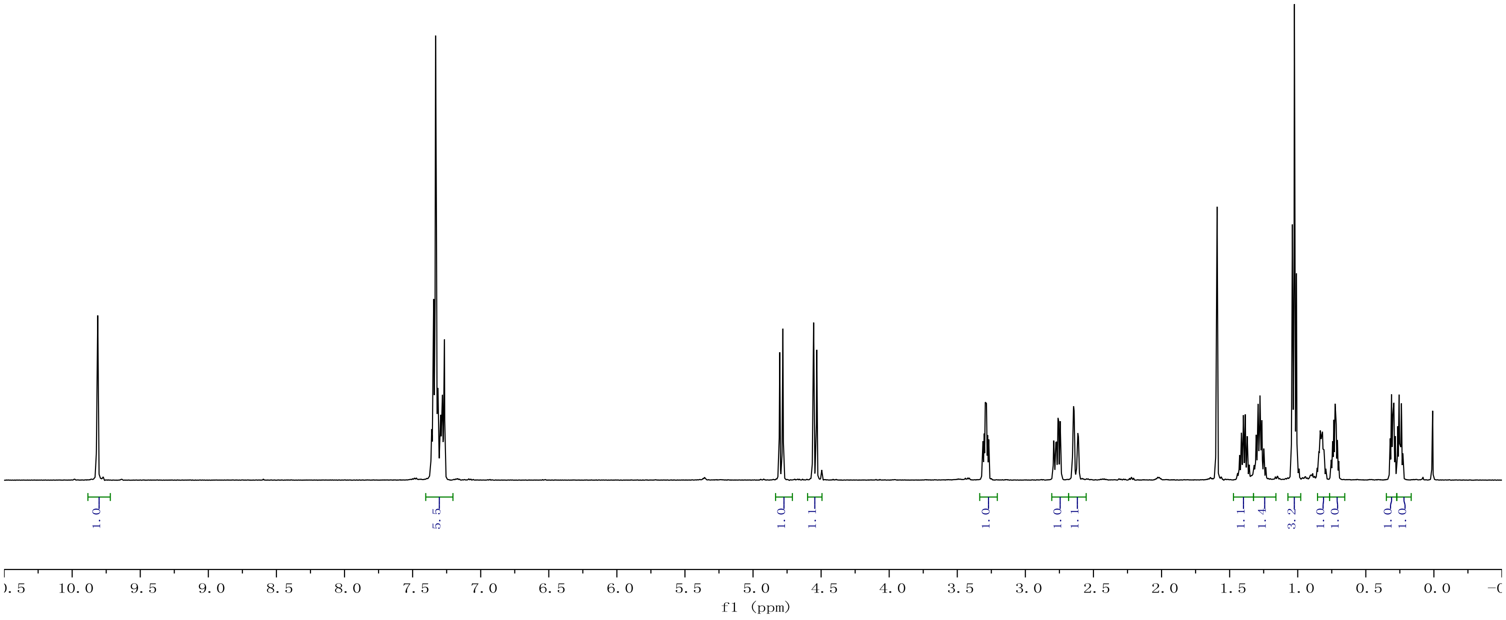
11-OH

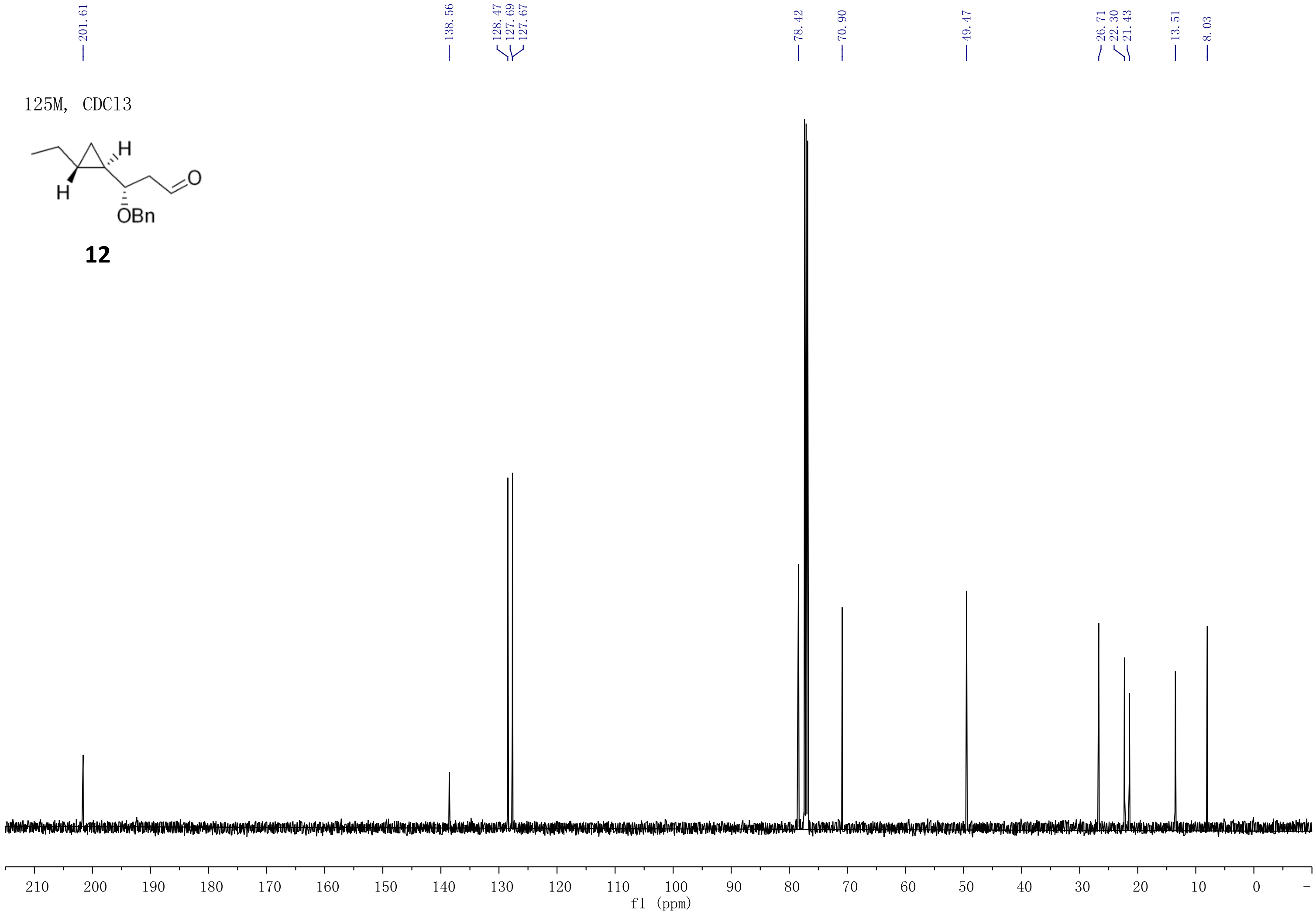


500M, CDCl3



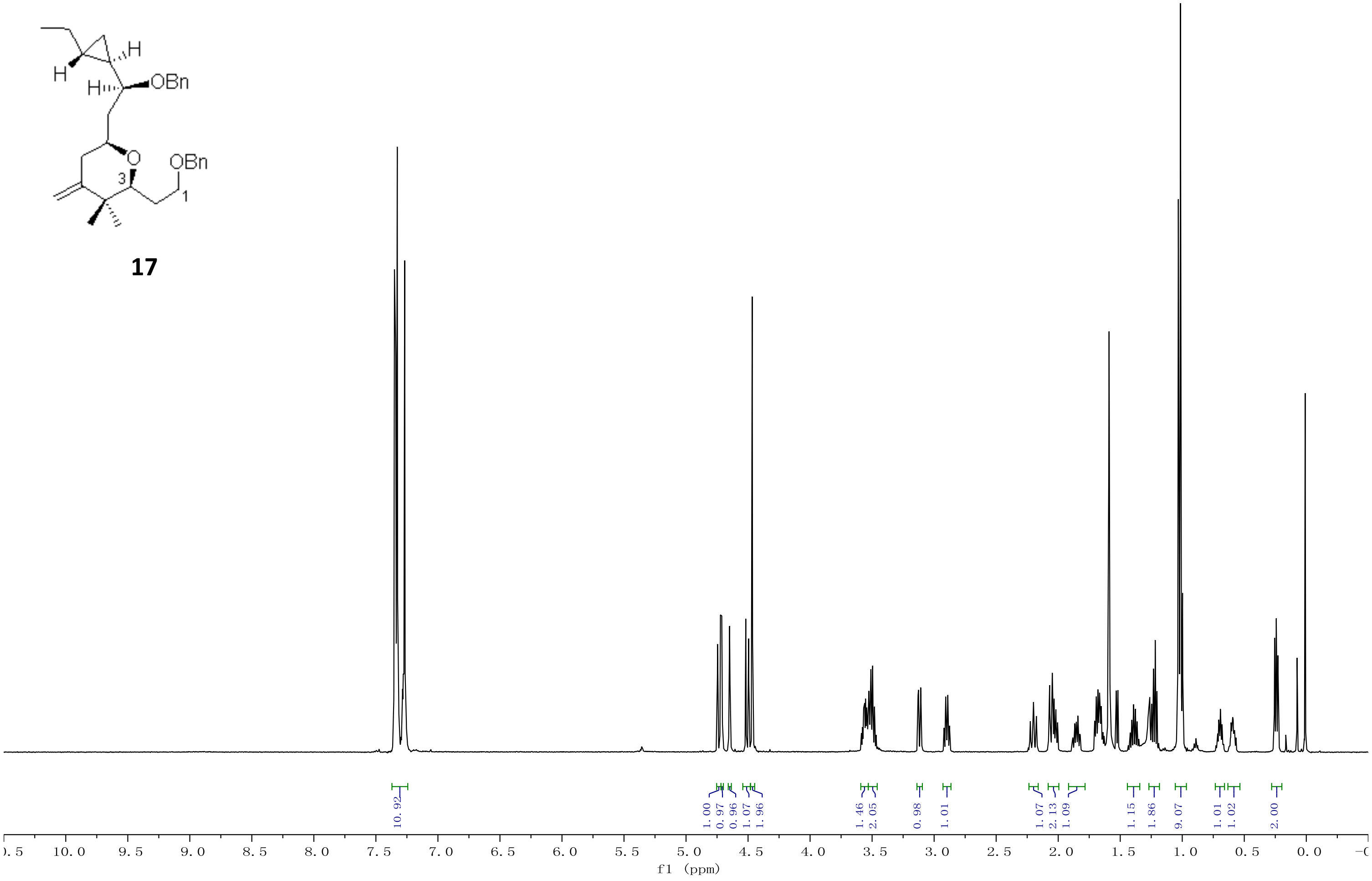
12



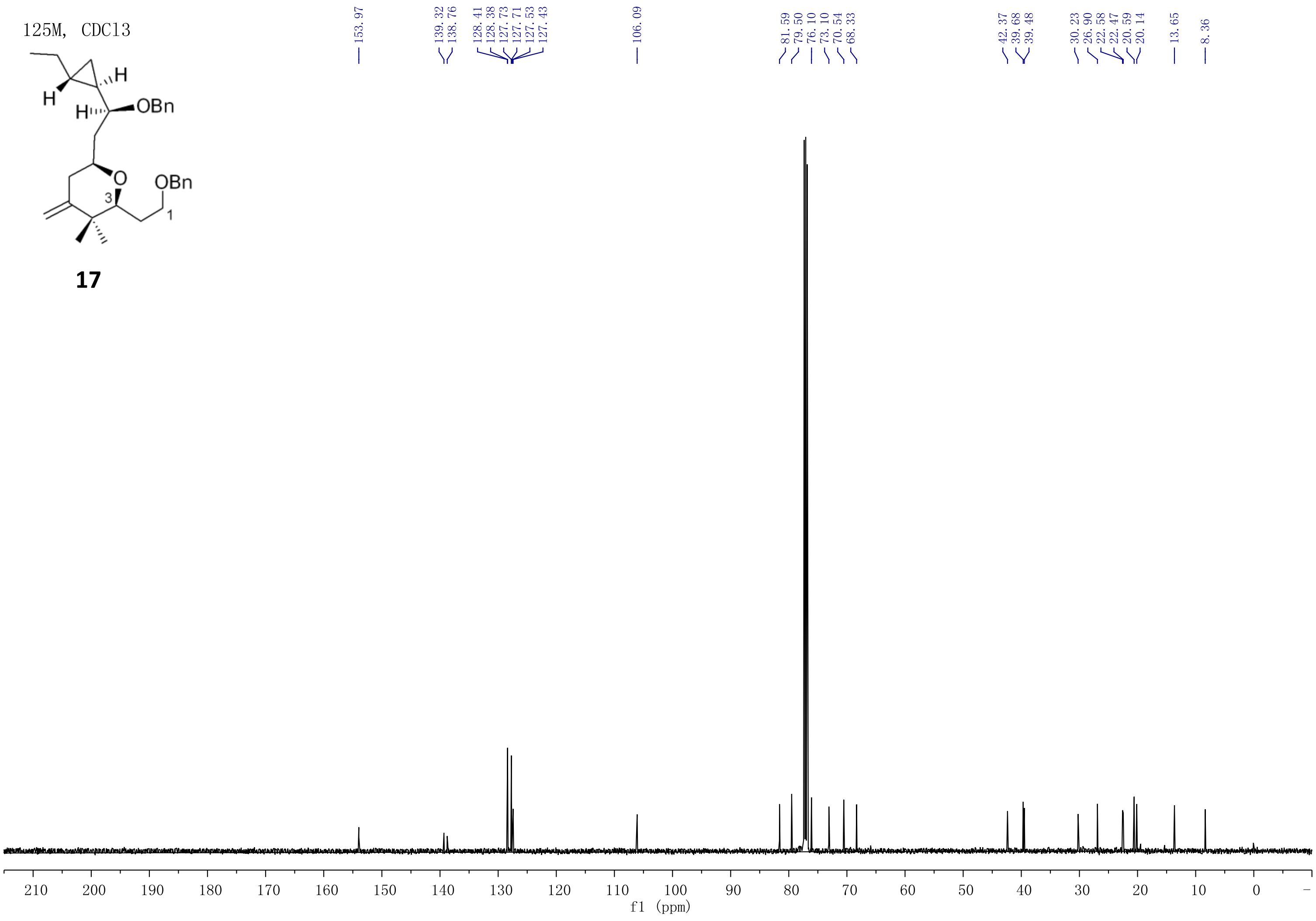

201.61
138.56
128.47
127.69
127.67
78.42
70.90
49.47
26.71
22.30
21.43
13.51
8.03
125M, CDCl3
H
H
O
OBn
12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

500M, CDCl3

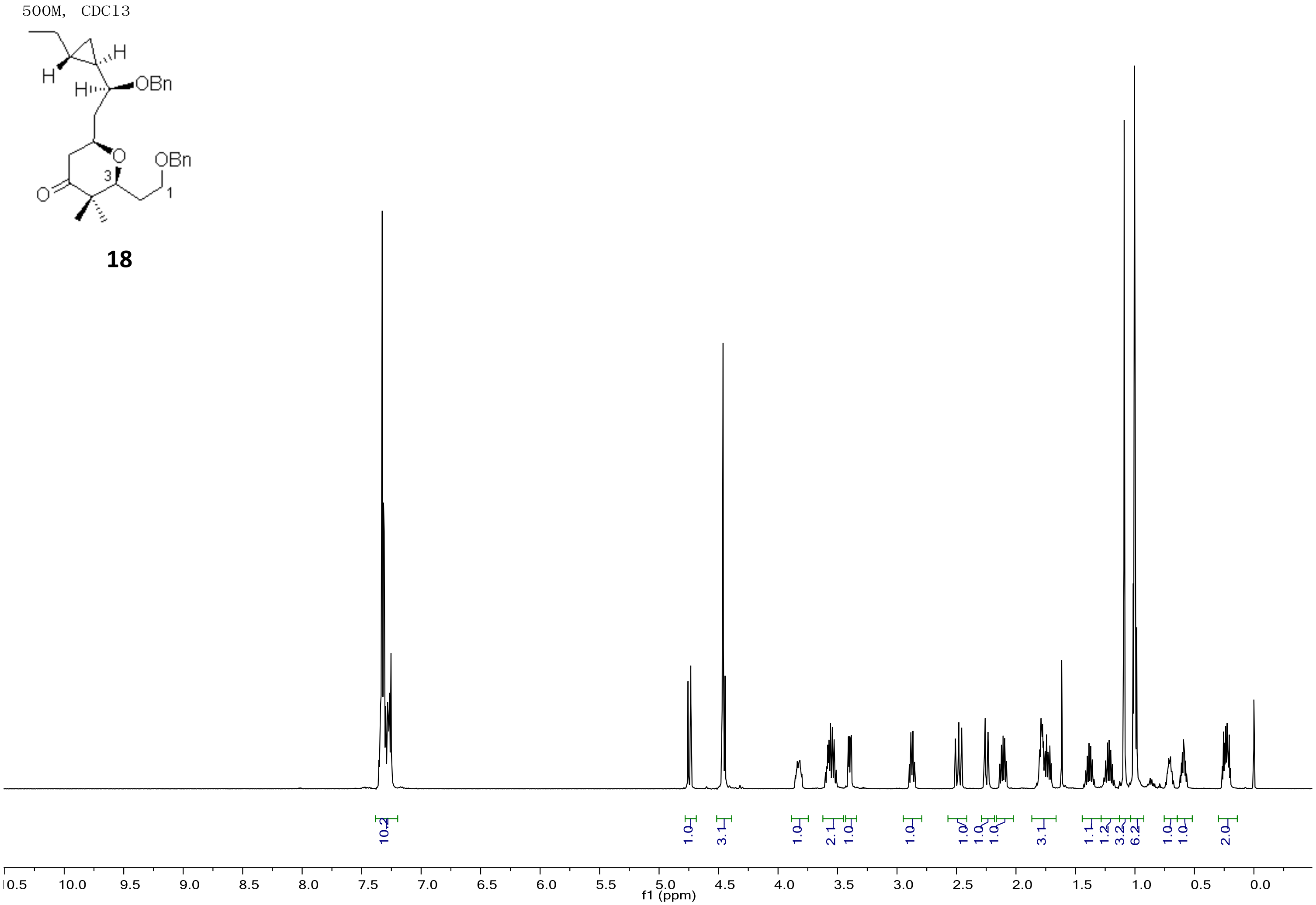
17

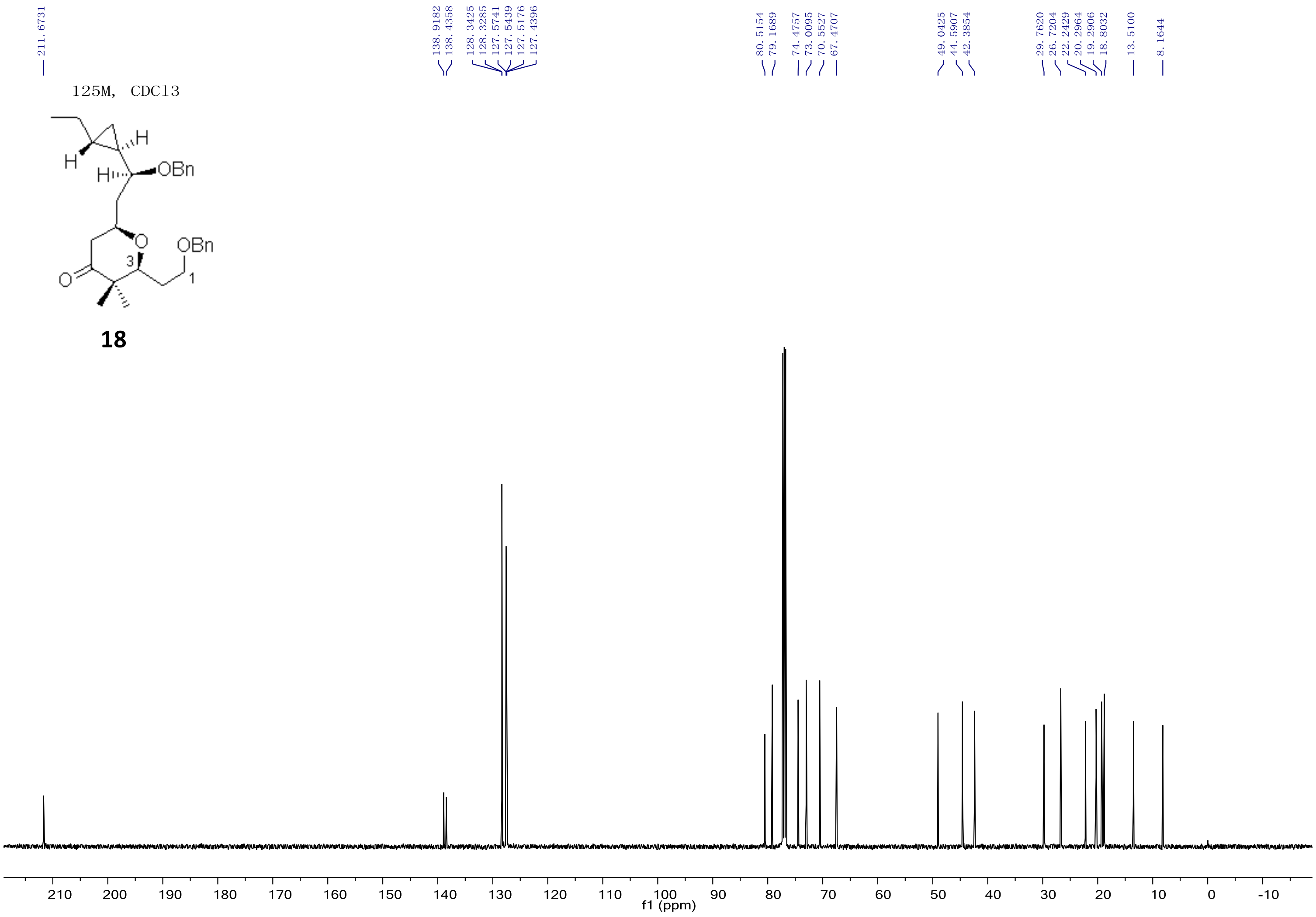


125M, CDCl3

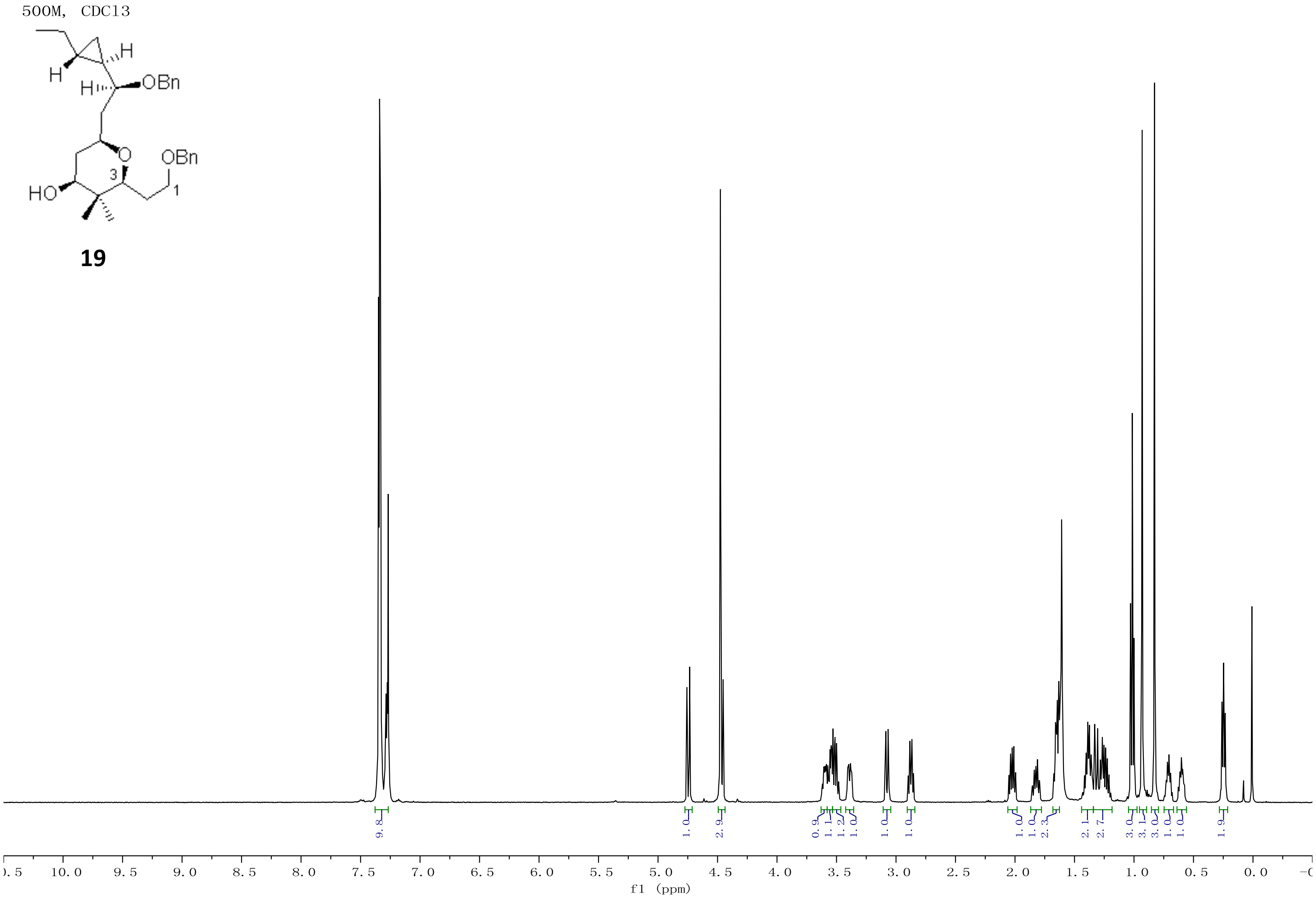


17

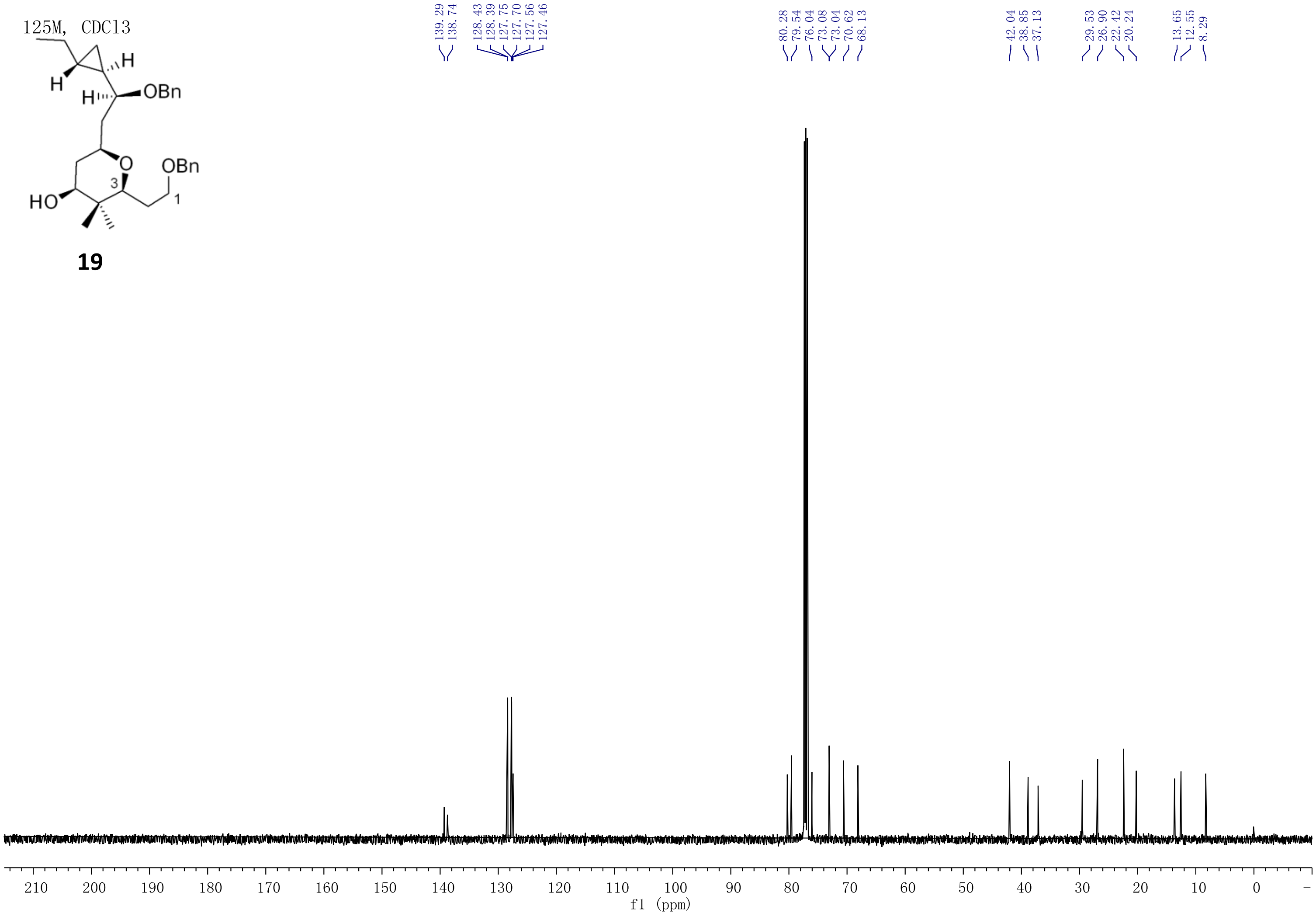

500M, CDCl3
H
H
H
OBn
O
OBn
3
1
O
18
10.2
1.0
3.1
1.0
2.1
1.0
1.0
1.0
1.0
1.0
3.1
1.1
1.2
3.2
6.2
1.0
1.0
2.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


211.6731
138.9182
138.4358
128.3425
128.3285
127.5741
127.5439
127.5176
127.4396
80.5154
79.1689
74.4757
73.0095
70.5527
67.4707
49.0425
44.5907
42.3854
29.7620
26.7204
22.2429
20.2964
19.2906
18.8032
13.5100
8.1644
125M, CDCl3
H
OBn
H
H
O
OBn
3
1
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

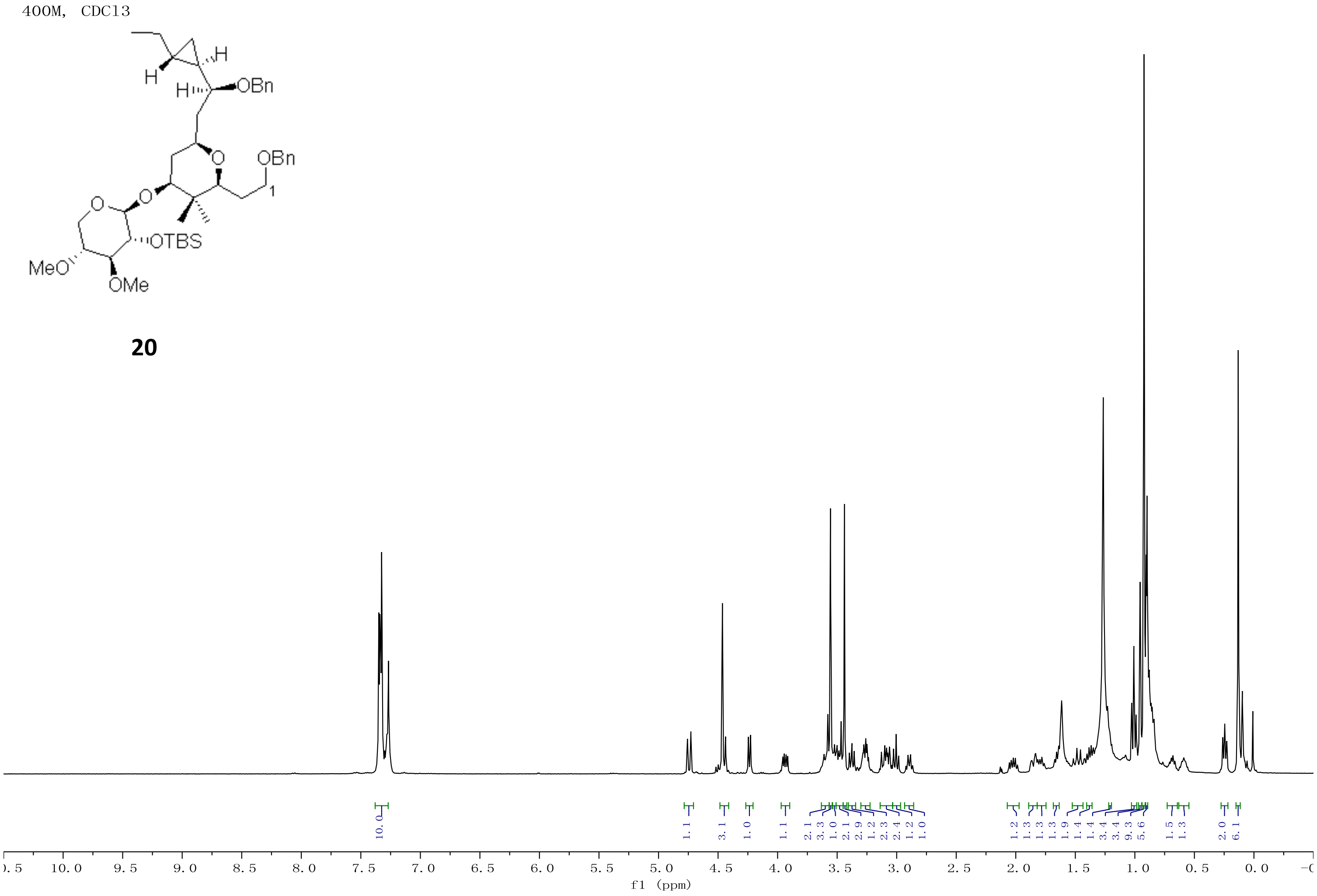
18

500M, CDCl3
H
H
H
OBn
OBn
O
3
1
HO
9.8
1.0
2.9
0.9
1.1
1.2
1.0
1.0
1.0
1.0
1.0
2.3
2.1
2.7
3.0
3.1
3.0
1.0
1.0
1.9
0.5
10.0
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
f1 (ppm)

19


125M, CDCl3
OBn
OBn
HO
O
H
H
H
3
1
139.29
138.74
128.43
128.39
127.75
127.70
127.56
127.46
80.28
79.54
76.04
73.08
73.04
70.62
68.13
42.04
38.85
37.13
29.53
26.90
22.42
20.24
13.65
12.55
8.29
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

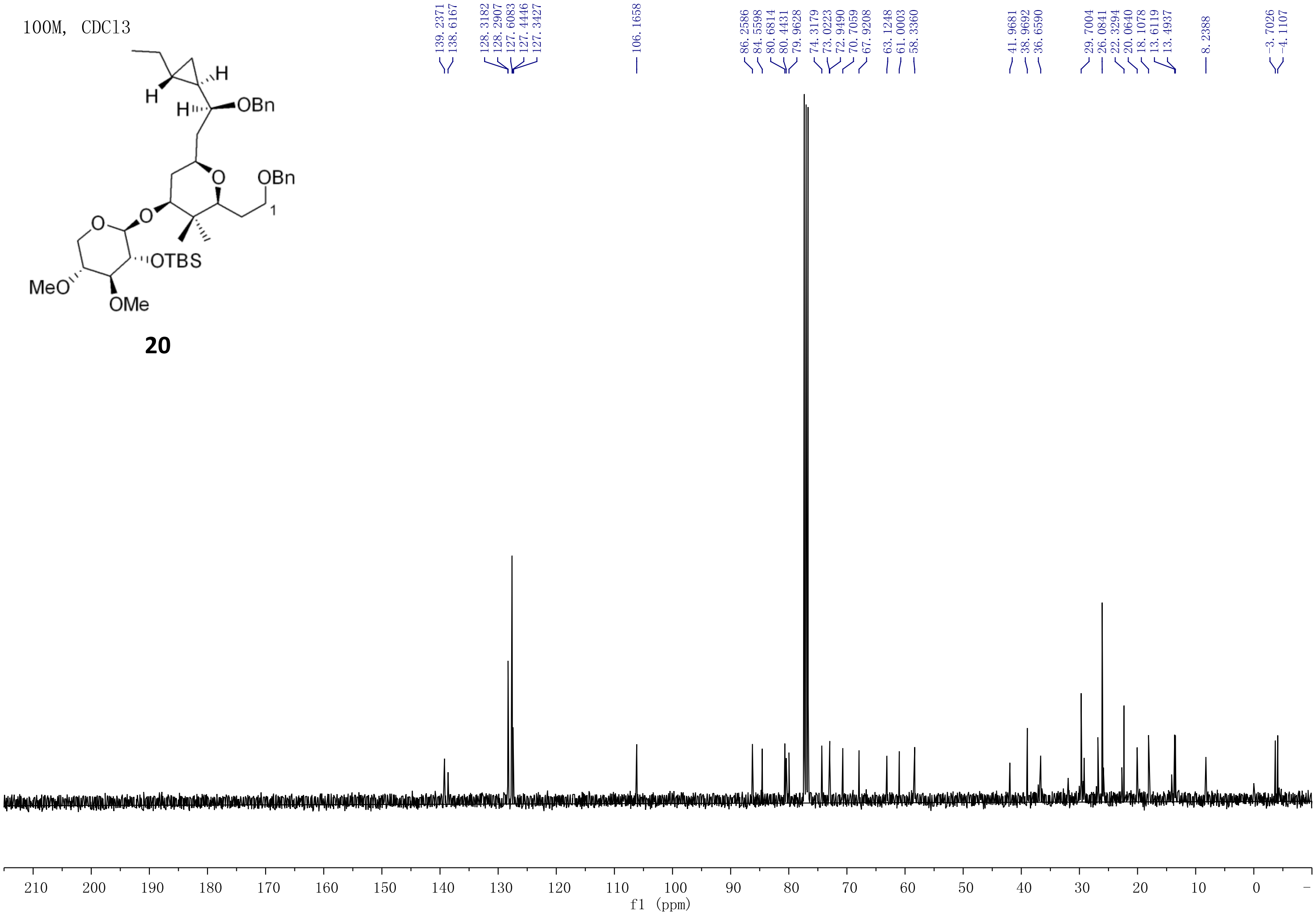
19

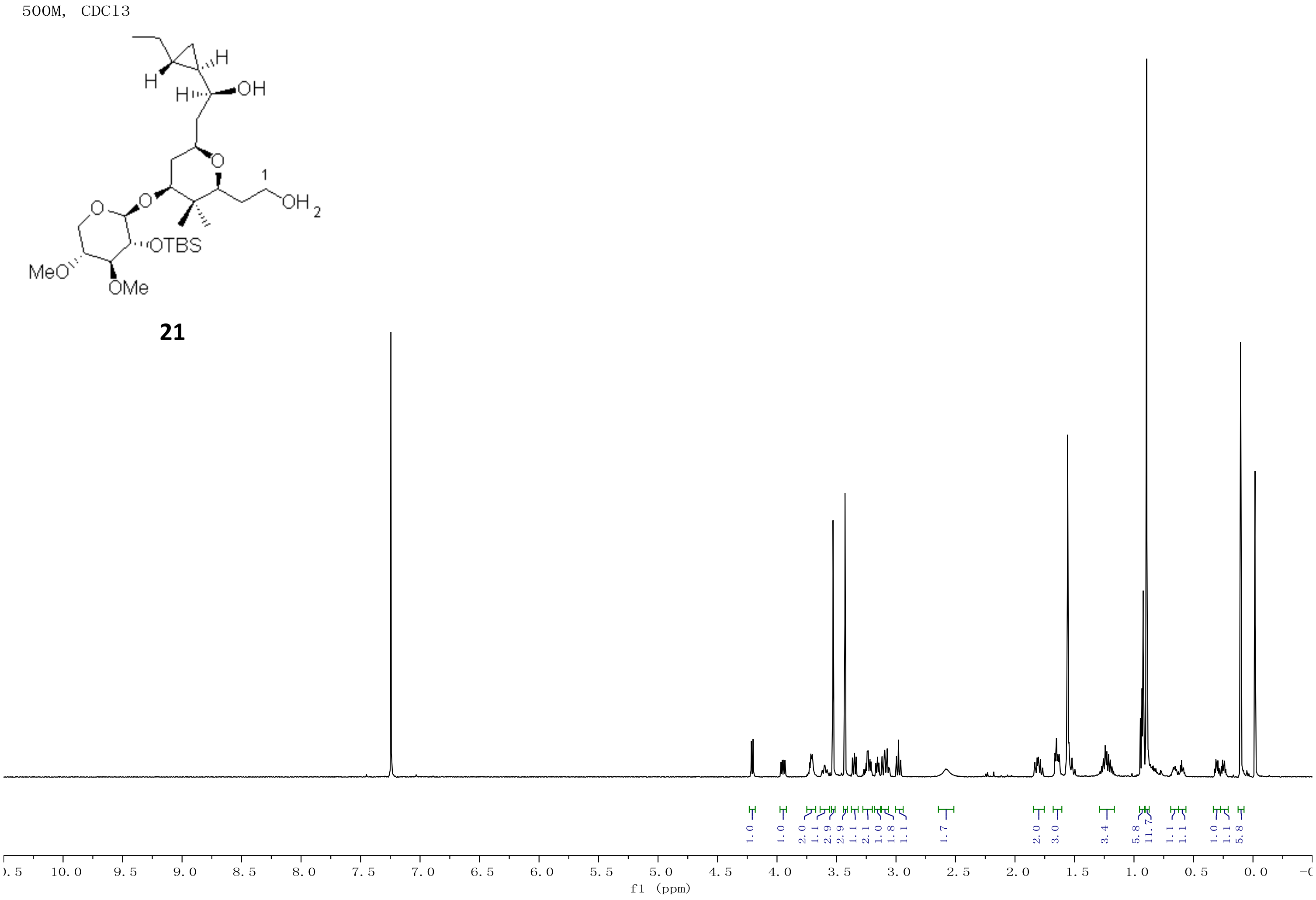

400M, CDCl3
OBn
OBn
OTBS
MeO
OMe
H
H
H
O
O
O
1
10.0
1.1
3.1
1.0
1.1
2.1
3.3
1.0
2.1
2.9
1.2
2.3
2.4
1.2
1.0
1.2
1.3
1.3
1.3
1.9
1.4
1.4
3.4
3.4
9.3
5.6
1.5
1.3
2.0
6.1
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

20

100M, CDCl3

20

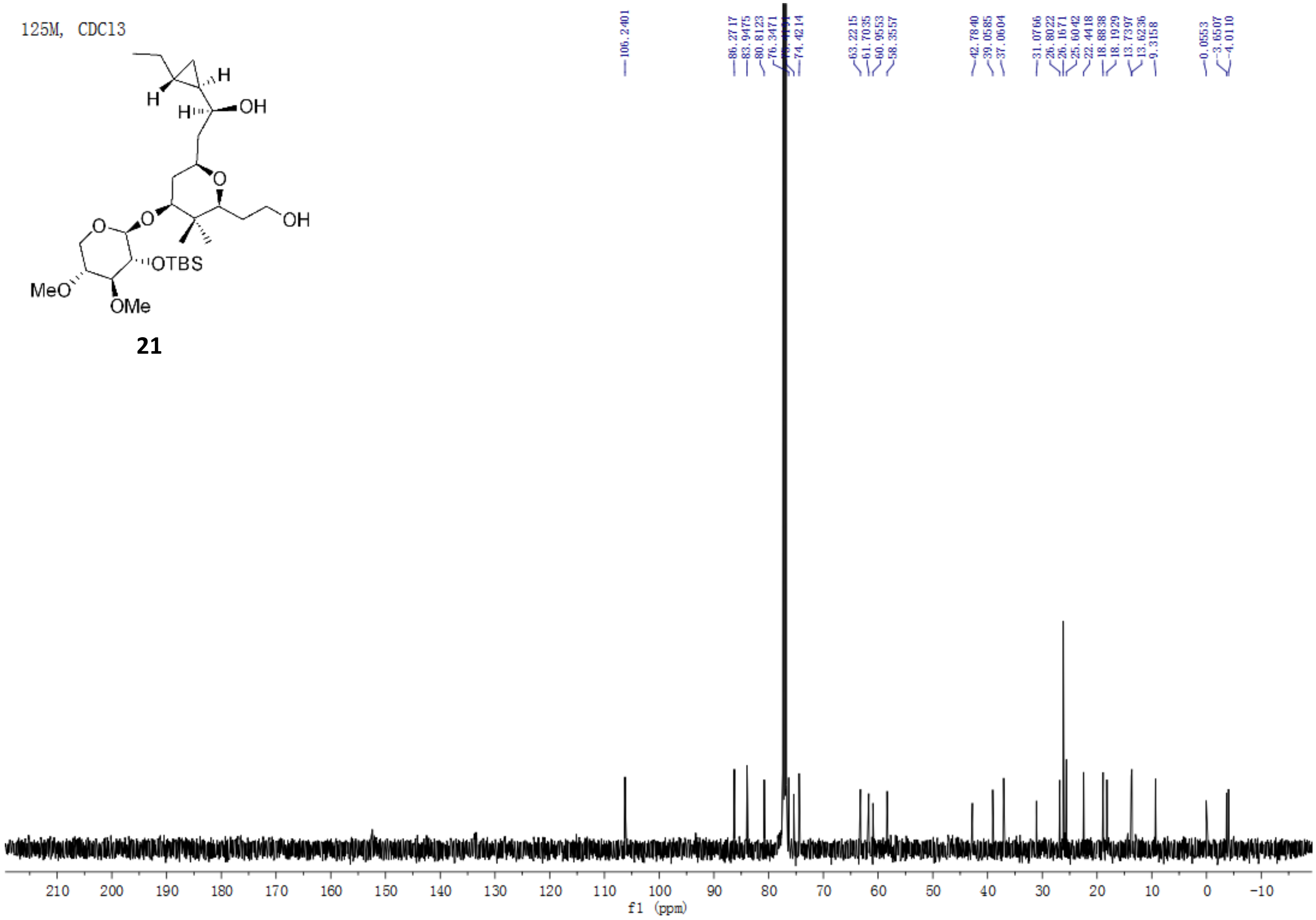


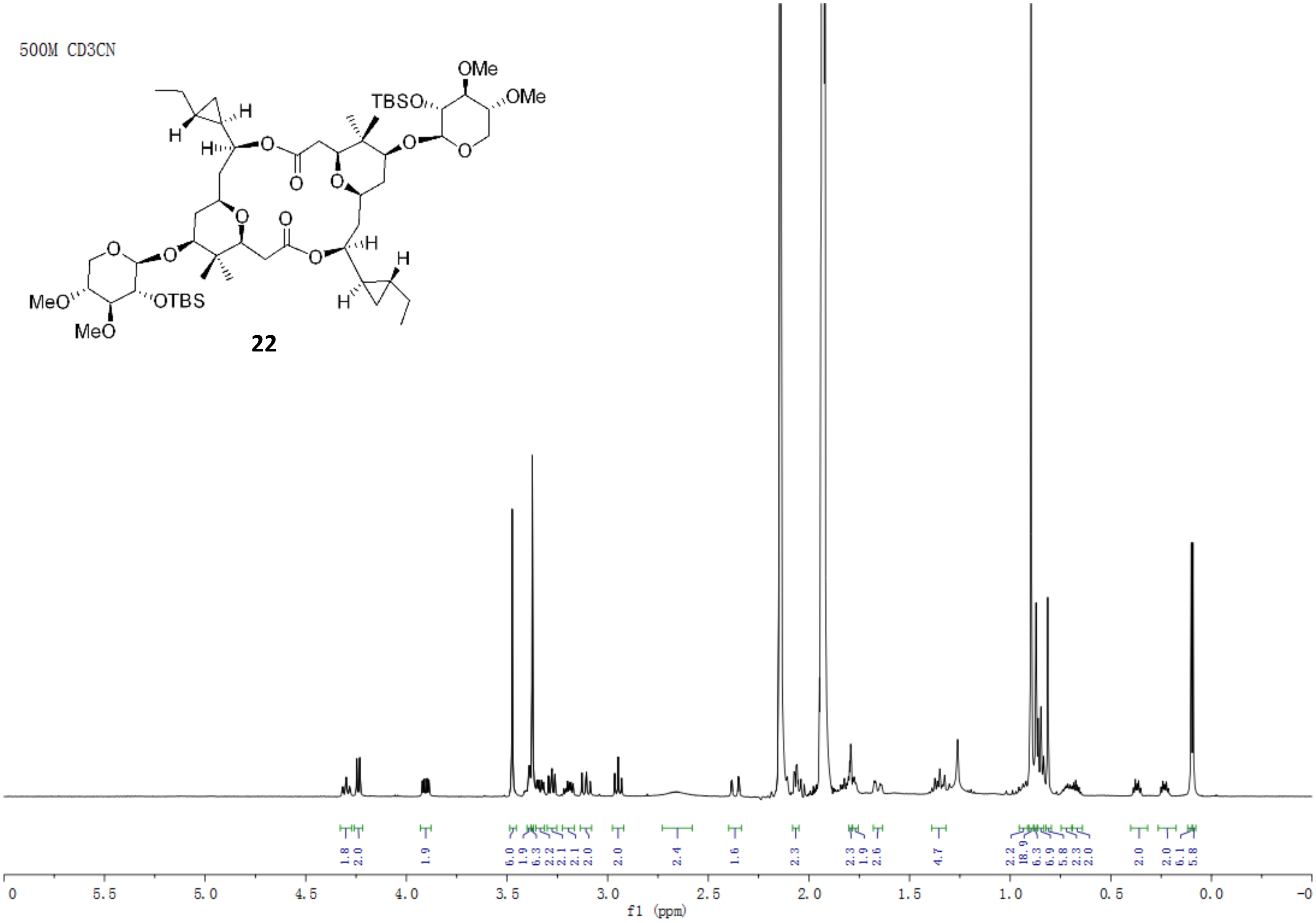

500M, CDCl3
H
H
H
OH
O
1
OH
2
O
O
OTBS
MeO
OMe
1.0
1.0
2.0
1.1
2.9
2.9
1.1
2.1
1.0
1.8
1.1
1.7
2.0
3.0
3.4
5.8
11.7
1.1
1.1
1.0
1.1
5.8
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

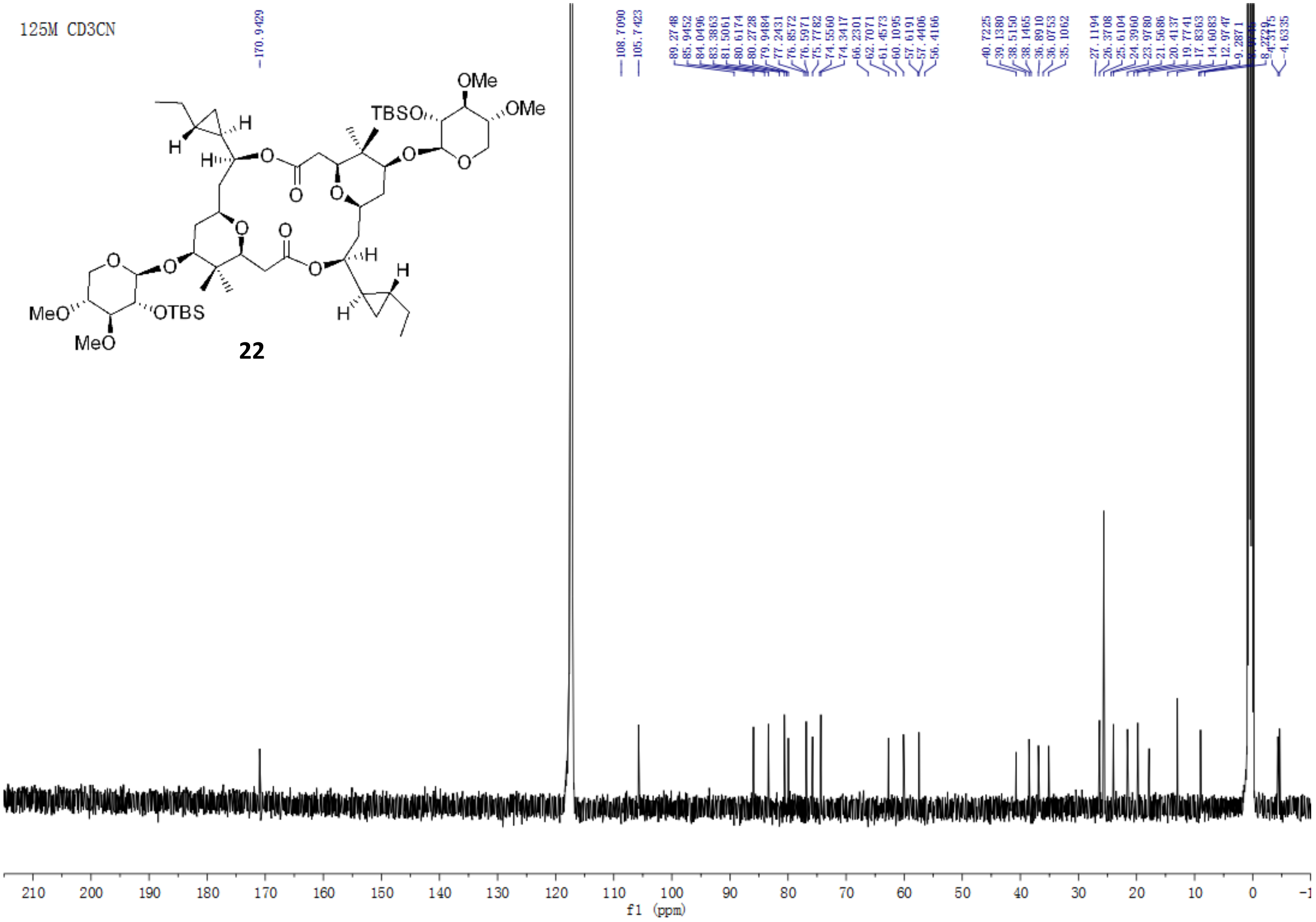
21

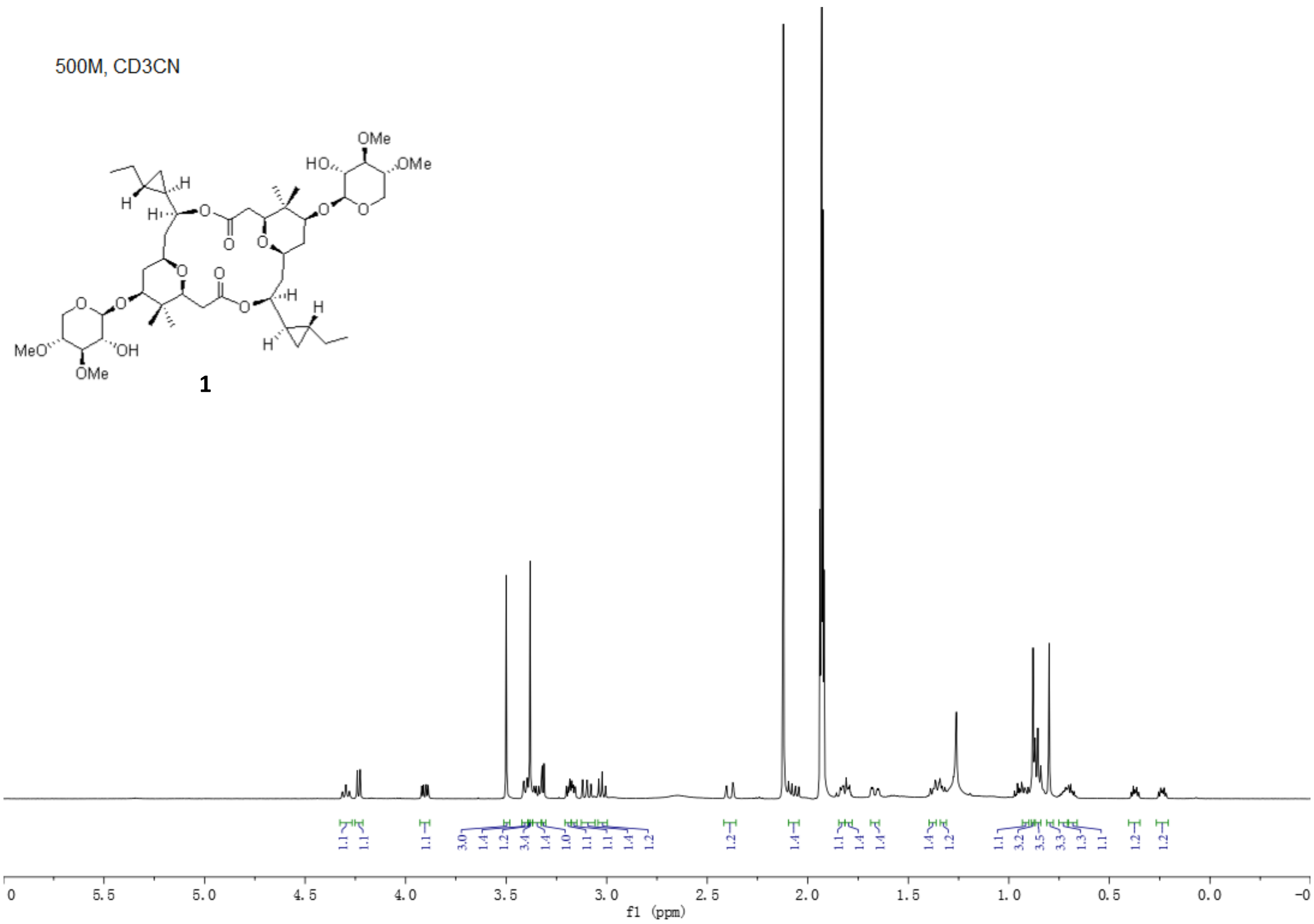
125M, CDCl3

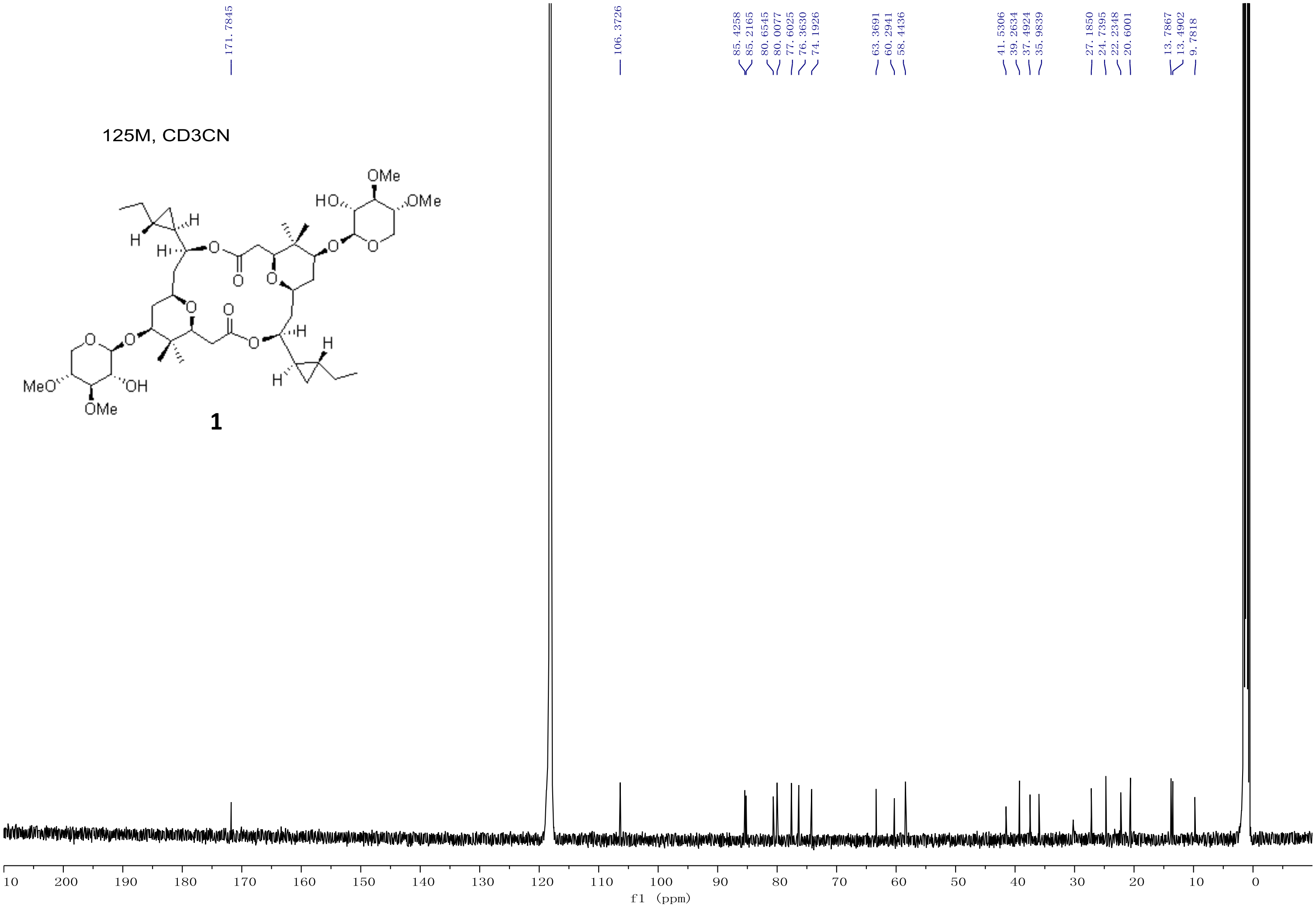
21




500M CD3CN
OMe
TBSO
OMe
H
H
H
O
O
O
O
O
O
O
O
O
H
H
H
MeO
OTBS
MeO
22
1.8
2.0
1.9
6.0
1.9
6.3
2.2
2.1
2.1
2.0
2.0
2.4
1.6
2.3
2.3
1.9
2.6
4.7
2.2
18.9
6.3
6.9
5.8
2.3
2.0
2.0
2.0
6.1
5.8
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
f1 (ppm)

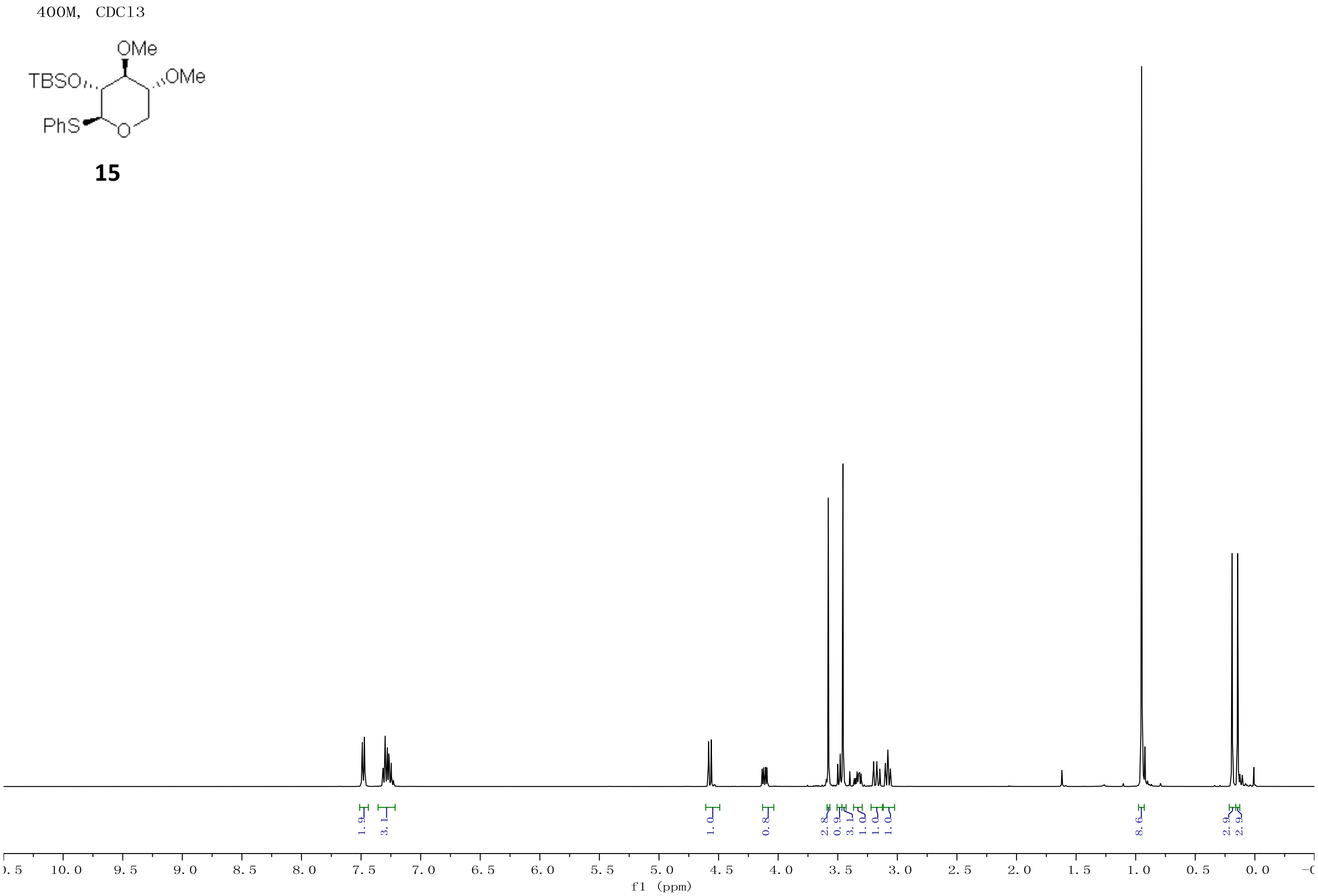

125M CD3CN
170.9429
108.7090
105.7423
89.2748
85.9452
84.0496
83.3863
81.5061
80.6174
80.2728
79.9484
77.2431
76.8572
76.5971
75.7782
74.5560
74.3417
66.2301
62.7071
61.4573
60.1095
57.6191
57.4406
56.4166
40.7225
39.1380
38.5150
38.1465
36.8910
36.0753
35.1062
27.1194
26.3708
25.6104
24.3960
23.9780
21.5686
20.4137
19.7741
17.8363
14.6083
12.9747
9.2871
8.9745
8.2229
-4.4175
-4.6335
OMe
TBSO
OMe
O
O
H
H
H
O
O
O
O
O
O
H
O
O
H
H
MeO
OTBS
MeO
22
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


500M, CD3CN
OMe
HO
OMe
H
H
H
O
O
O
O
O
O
O
O
H
H
H
MeO
OH
OMe
1
1.1
1.1
1.1
3.0
1.4
1.2
3.4
1.4
1.0
1.1
1.1
1.4
1.2
1.2
1.4
1.1
1.4
1.4
1.4
1.2
1.1
3.2
3.5
3.3
1.3
1.1
1.2
1.2
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
f1 (ppm)

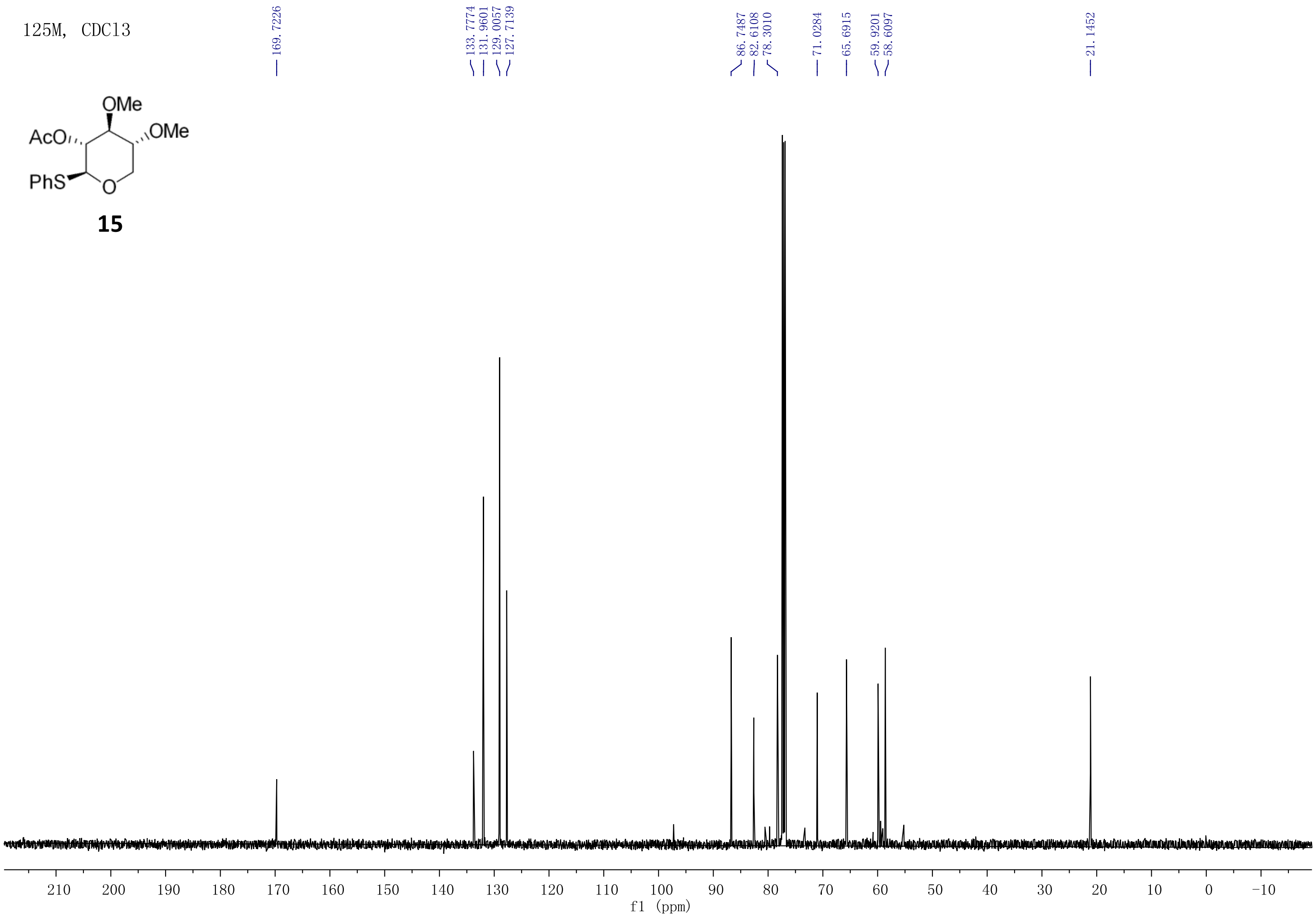

171. 7845
106. 3726
85. 4258
85. 2165
80. 6545
80. 0077
77. 6025
76. 3630
74. 1926
63. 3691
60. 2941
58. 4436
41. 5306
39. 2634
37. 4924
35. 9839
27. 1850
24. 7395
22. 2348
20. 6001
13. 7867
13. 4902
9. 7818
125M, CD3CN
OMe
HO
OMe
H
H
H
O
O
O
O
O
O
O
O
O
O
H
H
H
MeO
OH
OMe
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1

1

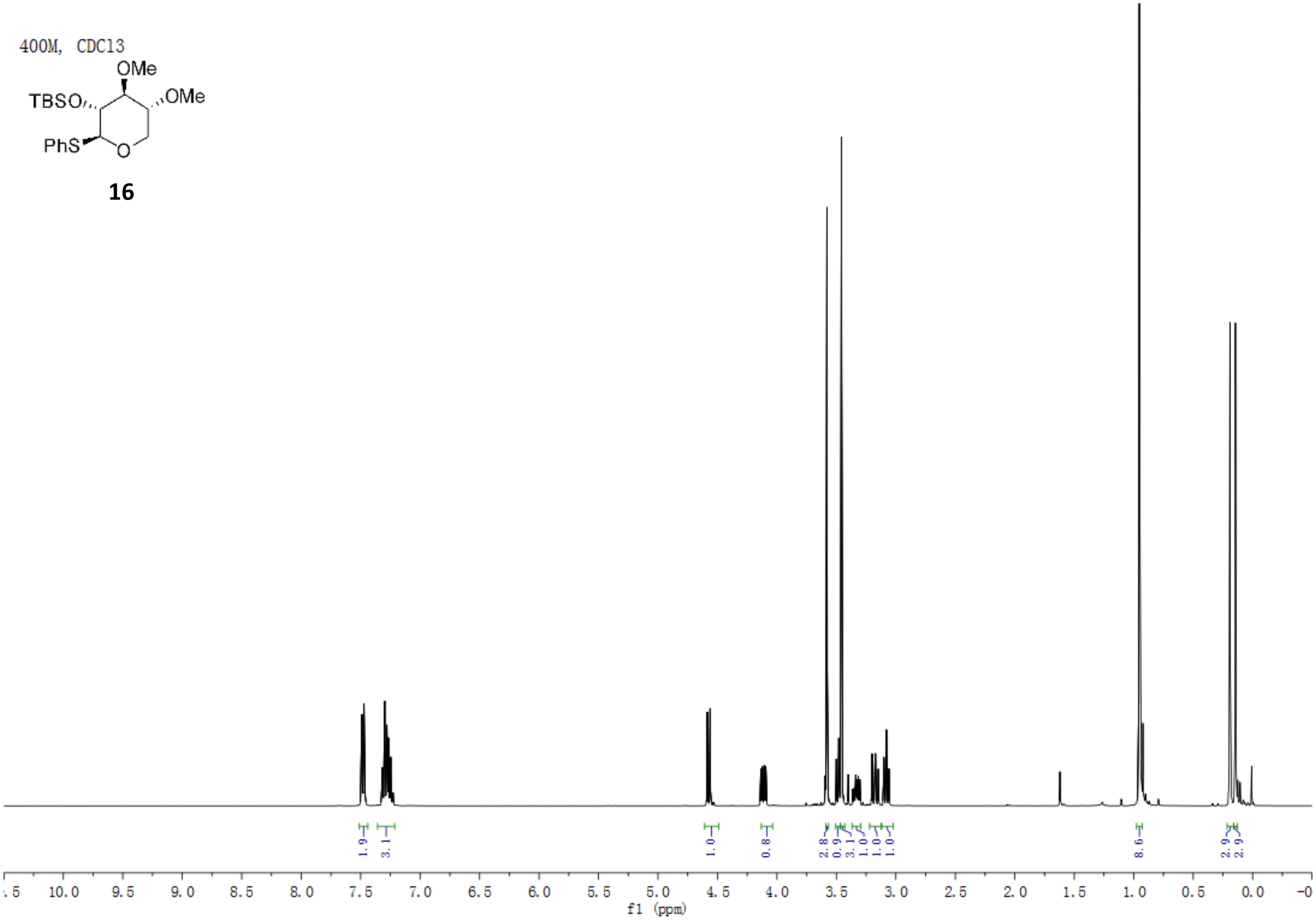

400M, CDC13
OMe
TBSO
OMe
PhS
O
1.9
3.1
1.0
0.8
2.8
0.9
3.1
1.0
1.0
1.0
8.6
2.9
2.9
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

15

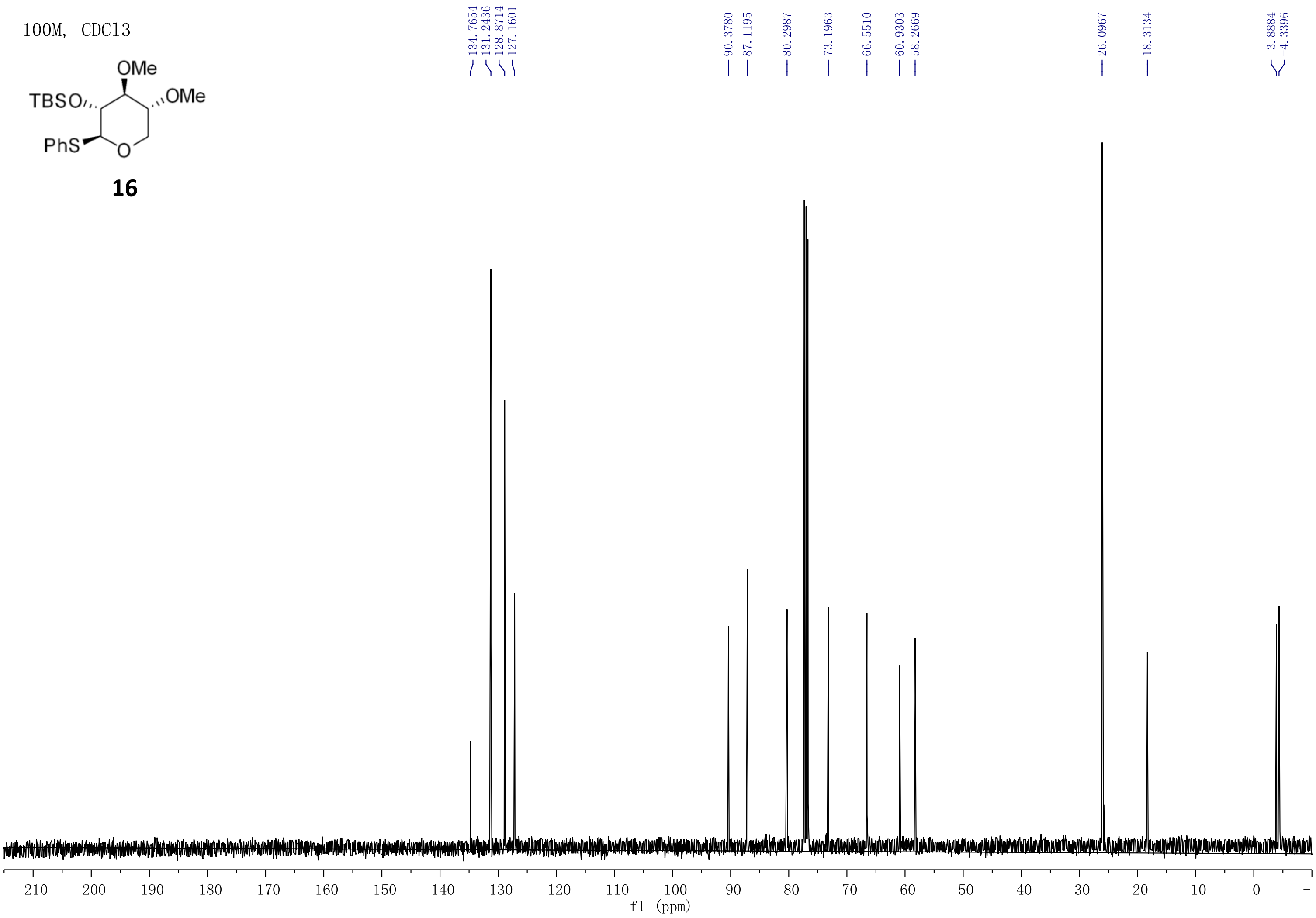


125M, CDCl3

15

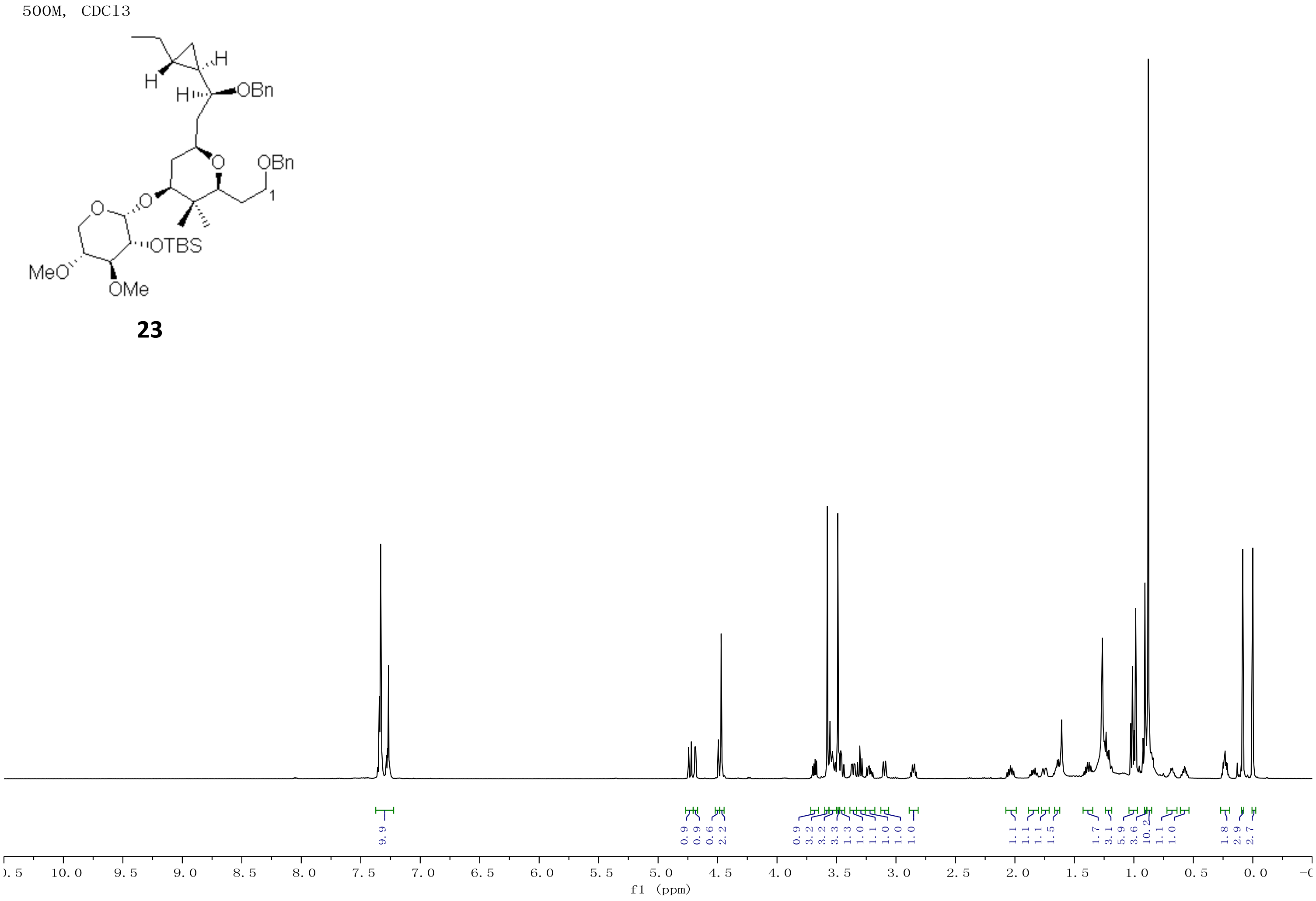

400M, CDCl3
OMe
TBSO
OMe
PhS
O
1.9
3.1
1.0
0.8
2.8
0.9
3.1
1.0
1.0
1.0
8.6
2.9
2.9
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

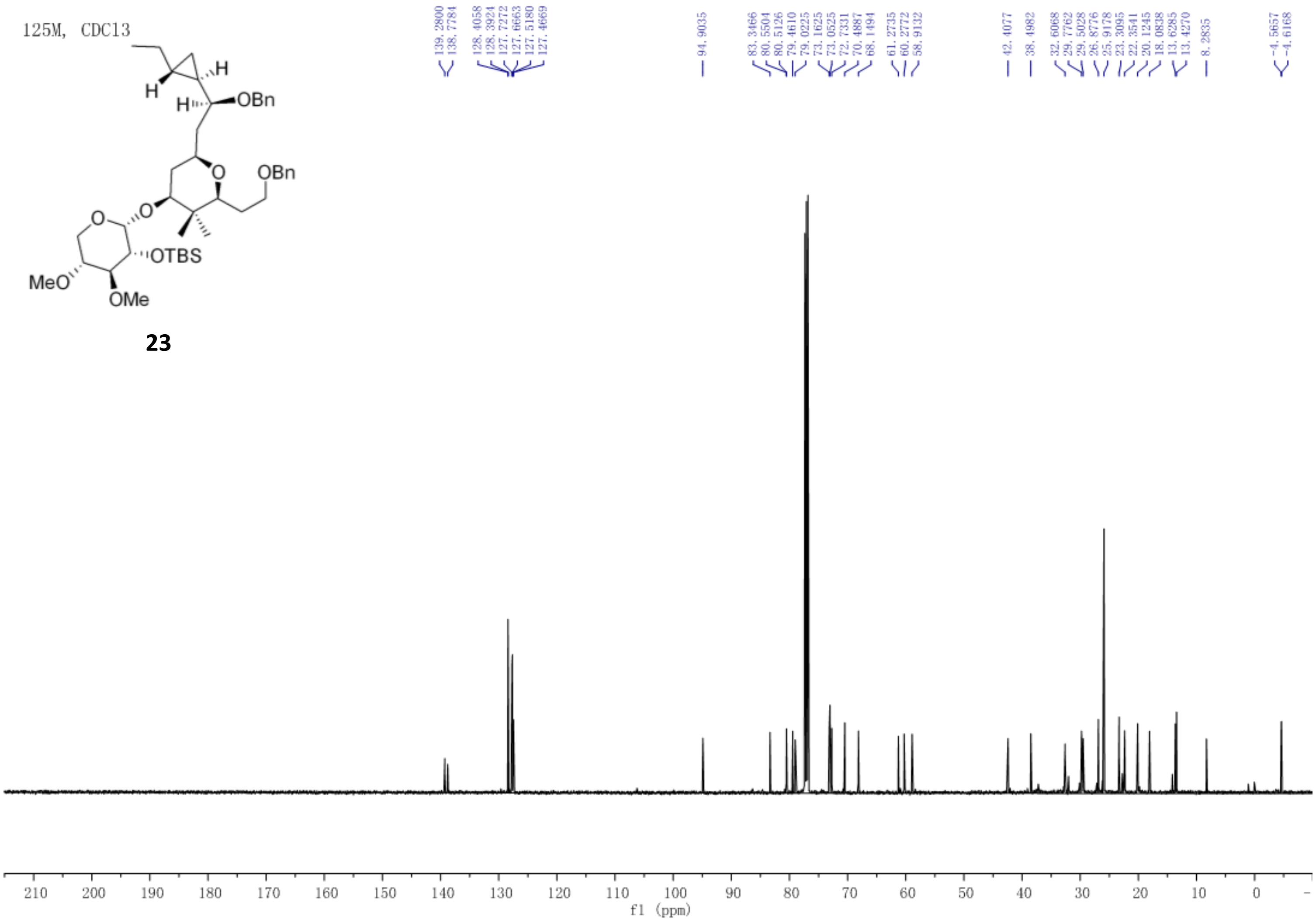
16



16

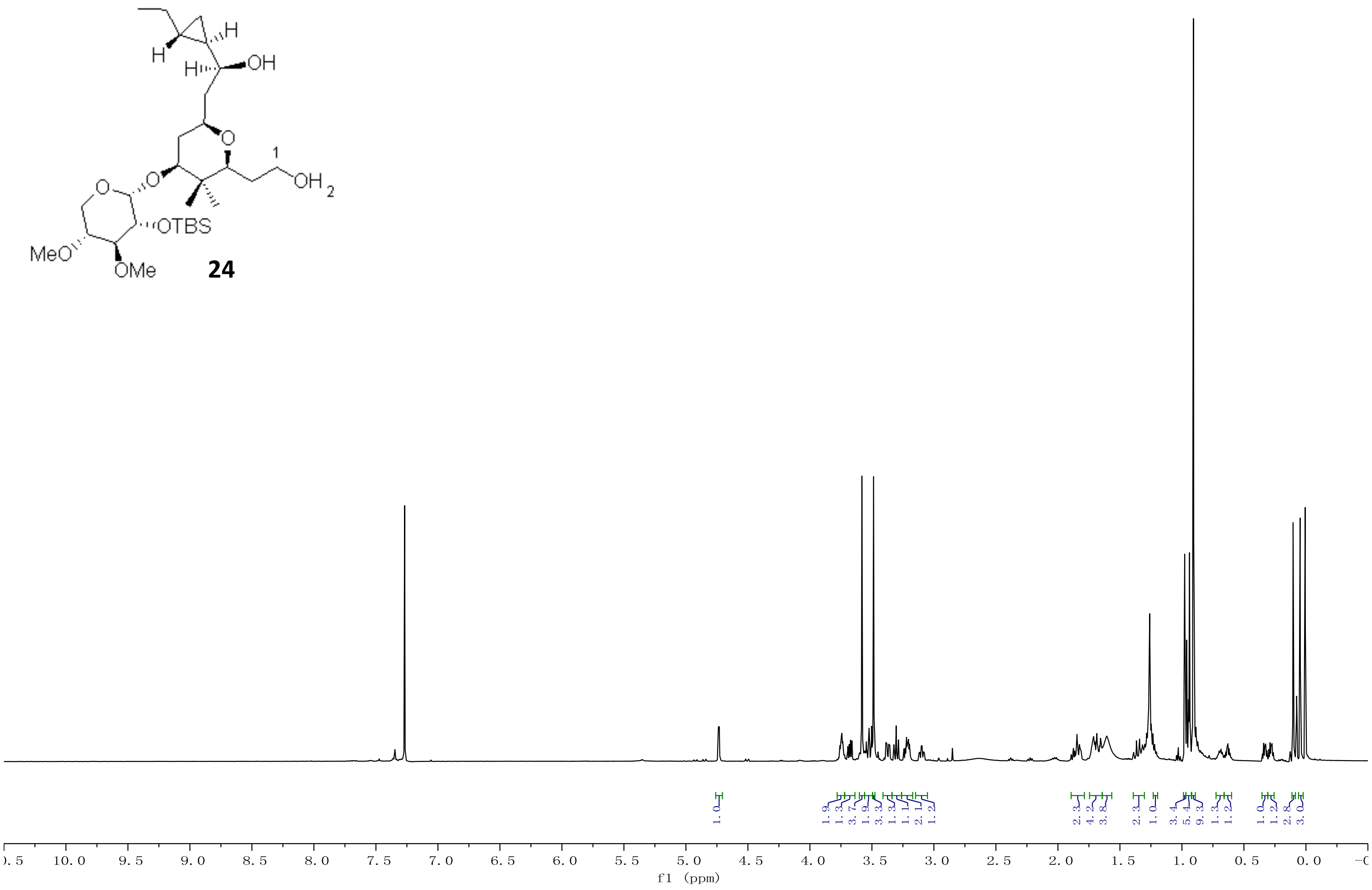
100M, CDCl3
OMe
TBSO
OMe
PhS
O
134.7654
131.2436
128.8714
127.1601
90.3780
87.1195
80.2987
73.1963
66.5510
60.9303
58.2669
26.0967
18.3134
-3.8884
-4.3396
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


500M, CDC13
H
H
H
OBn
OBn
1
O
O
O
OTBS
MeO
OMe
23
9.9
0.9
0.9
0.6
2.2
0.9
3.2
3.2
3.3
1.3
1.0
1.1
1.0
1.0
1.0
1.1
1.1
1.1
1.5
1.7
3.1
5.9
3.6
10.2
1.1
1.0
1.8
2.9
2.7
).5
10.0
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
-(
f1 (ppm)

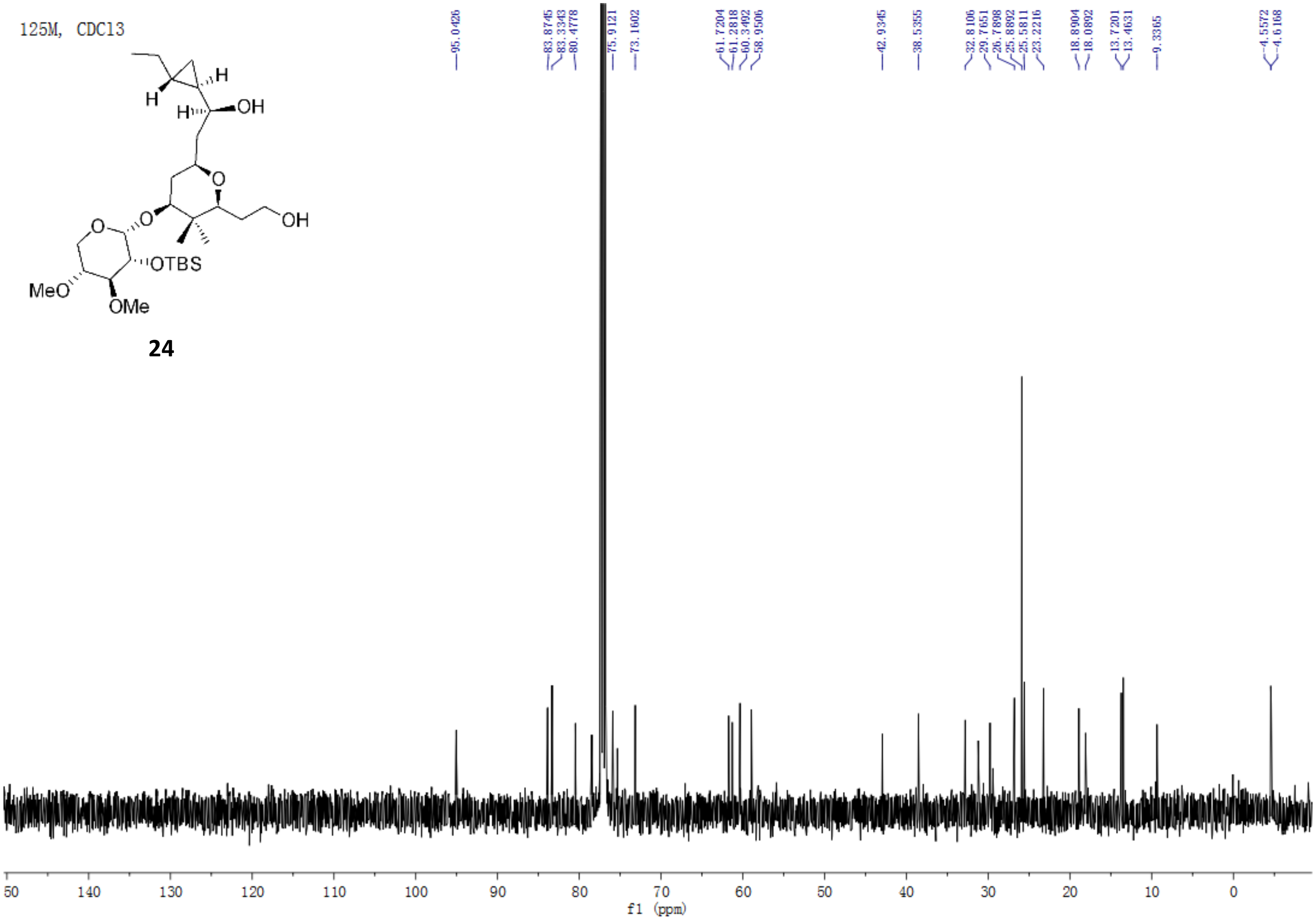

125M, CDCl3
OBn
OBn
OTBS
MeO
OMe
H
H
H
O
O
O
139.2800
138.7784
128.4058
128.3924
127.7272
127.6663
127.5180
127.4669
94.9035
83.3466
80.5504
80.5126
79.4610
79.0225
73.1625
73.0525
72.7331
70.4887
68.1494
61.2735
60.2772
58.9132
42.4077
38.4982
32.6068
29.7762
29.5028
26.8776
25.9178
23.3095
22.3541
20.1245
18.0838
13.6285
13.4270
8.2835
-4.5657
-4.6168
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

23

500M, CDCl3

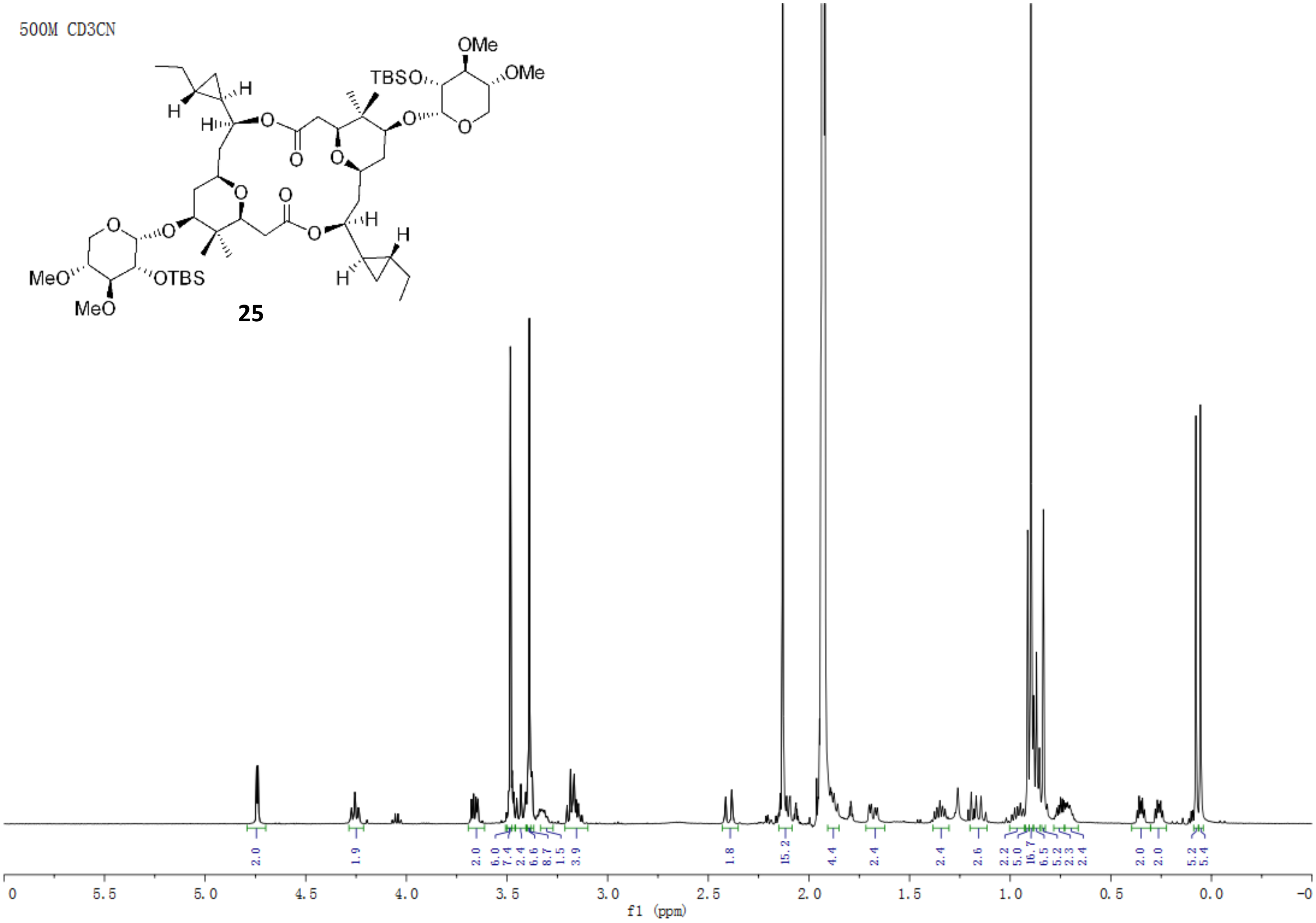


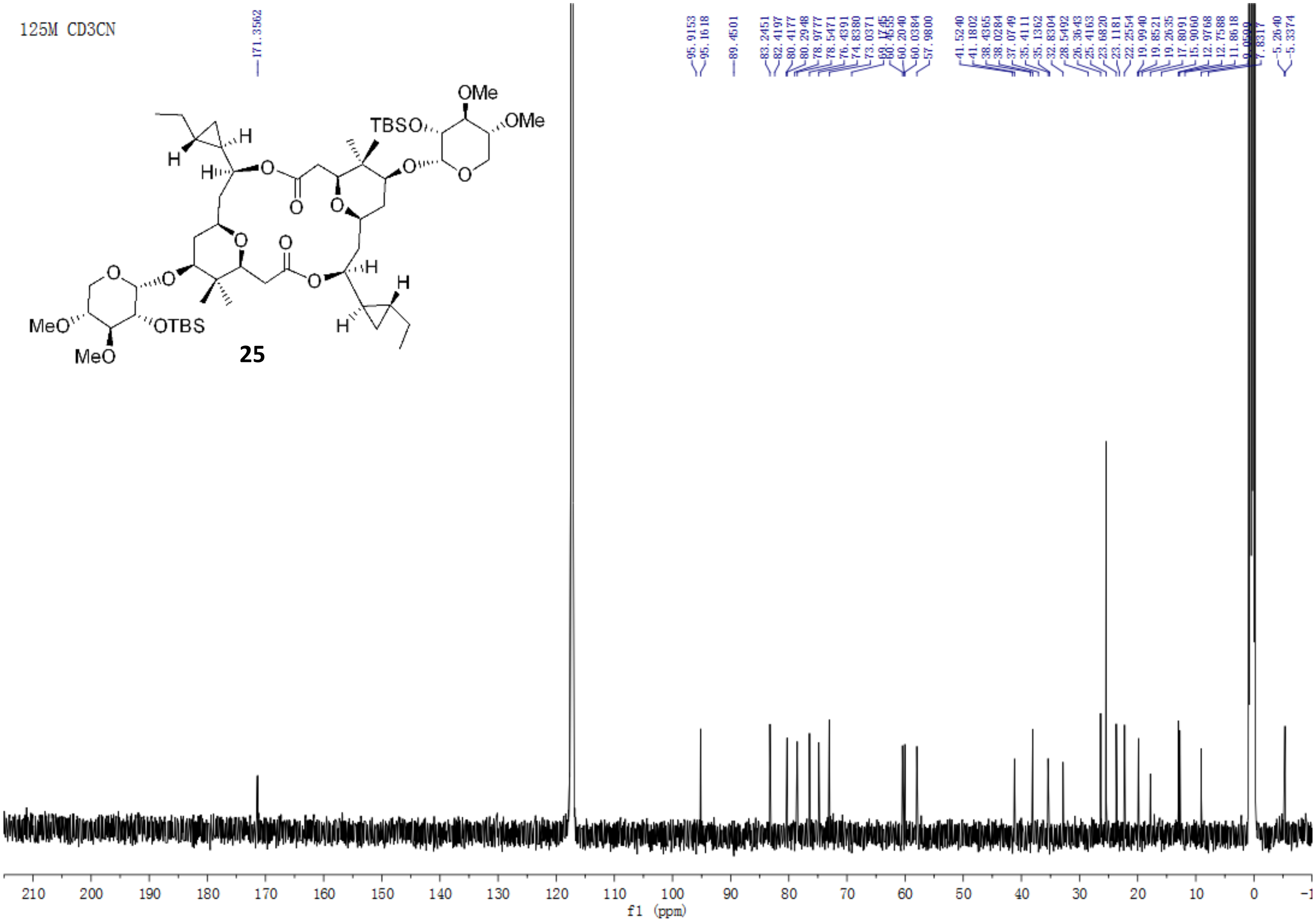
24



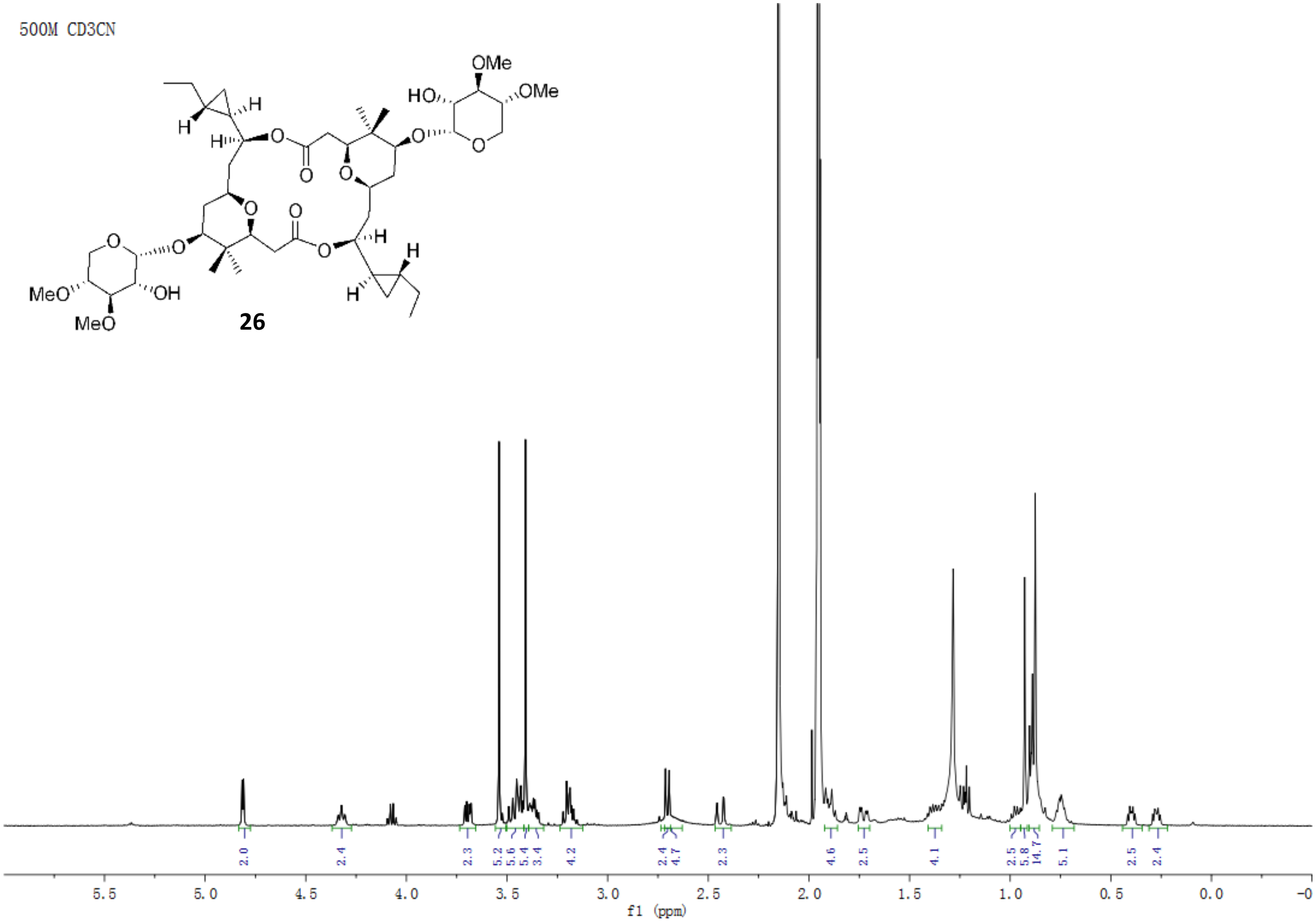
24

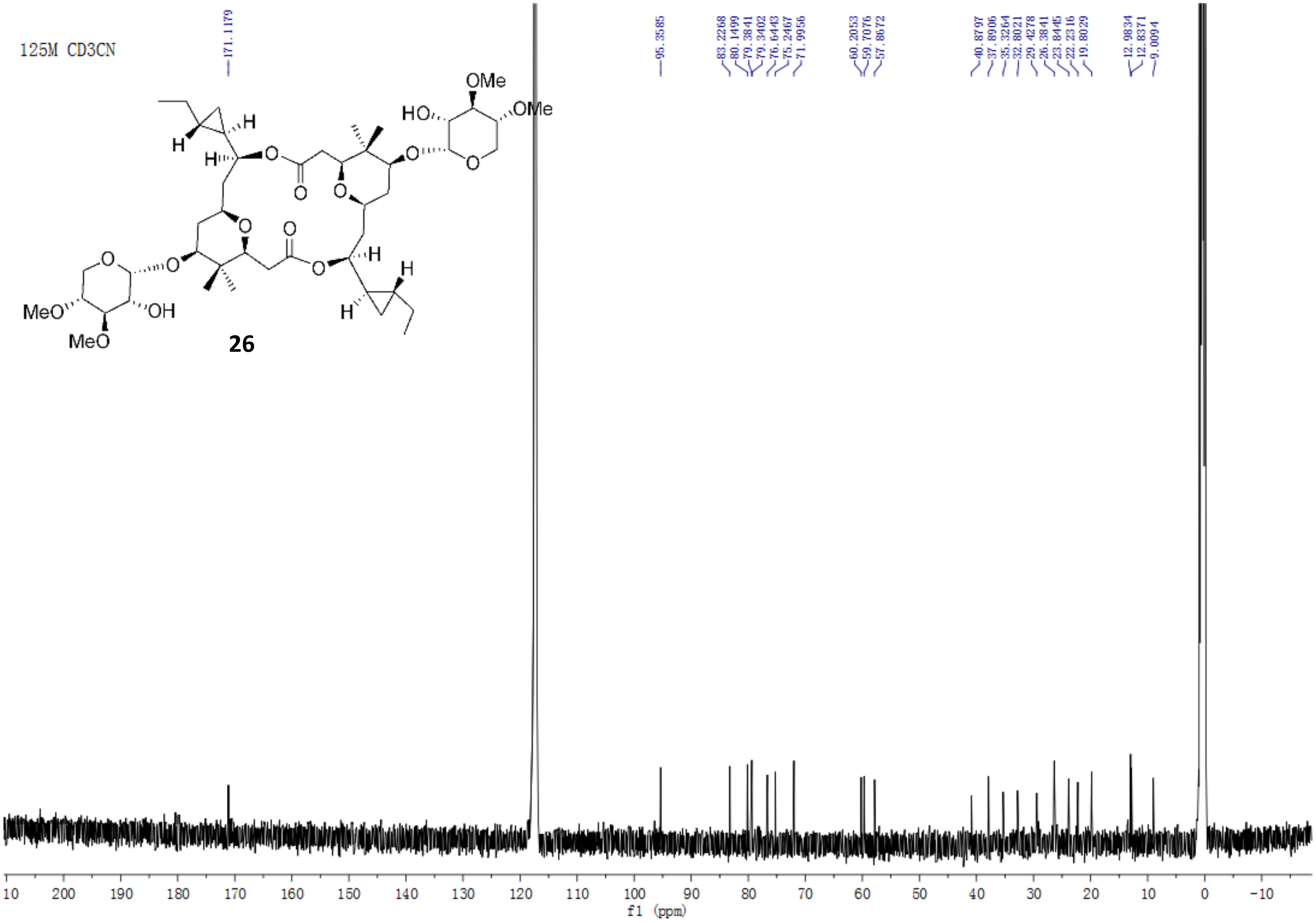
125M, CDCl3
H
H
H
OH
O
OH
O
O
OTBS
MeO
OMe
95.0426
83.8745
83.3343
80.4778
75.9121
73.1602
61.7204
61.2818
60.3492
58.9506
42.9345
38.5355
32.8106
29.7651
26.7898
25.8892
25.5811
23.2216
18.8904
18.0892
13.7201
13.4631
9.3365
-4.5572
-4.6168
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

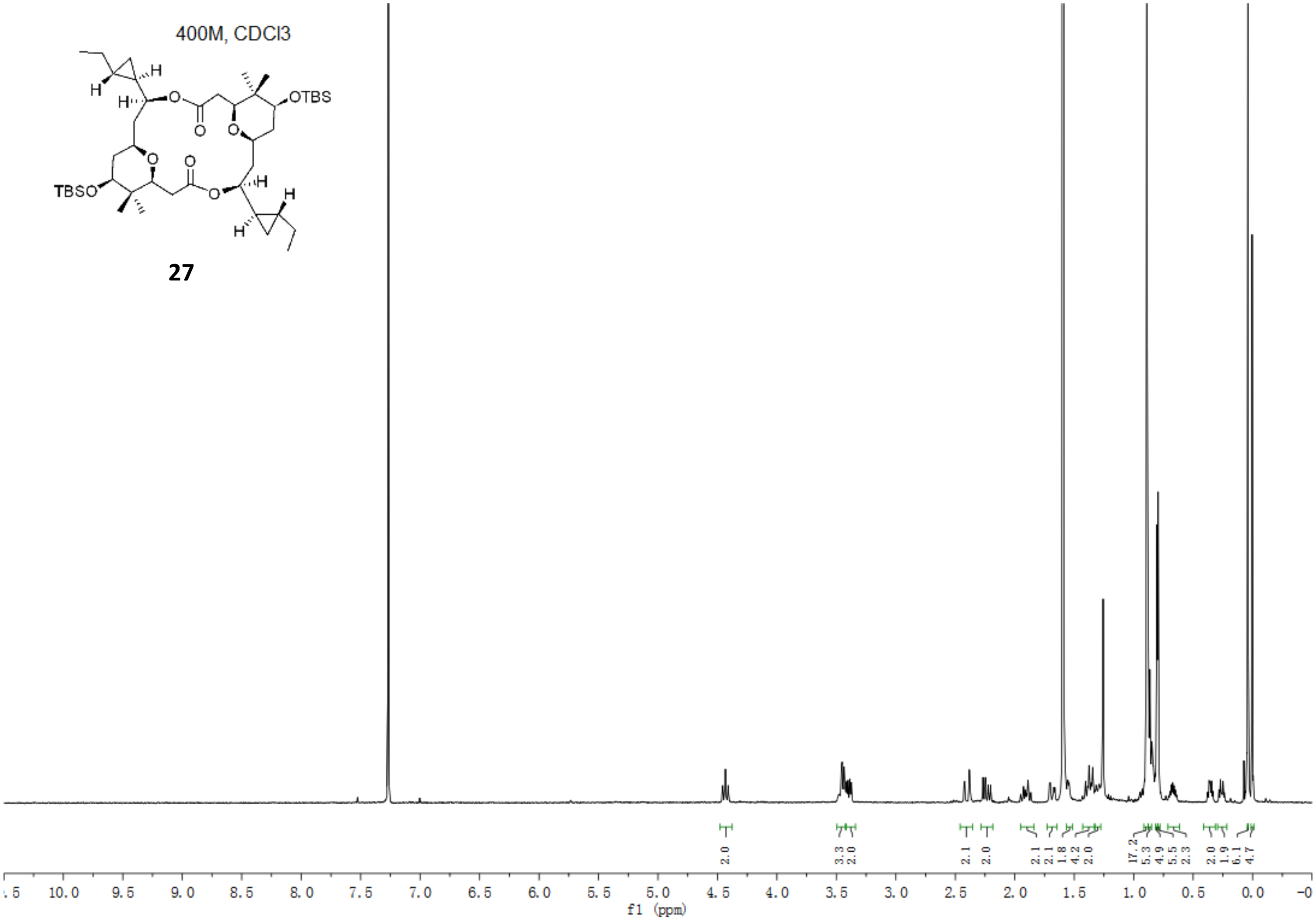

500M CD3CN
OMe
OMe
TBSO
H
H
H
O
O
O
O
O
O
O
O
O
O
H
H
H
MeO
MeO
OTBS
25
2.0
1.9
2.0
6.0
7.4
2.4
6.6
8.7
1.5
3.9
1.8
15.2
4.4
2.4
2.4
2.6
2.2
5.0
16.7
6.5
5.2
2.3
2.4
2.0
2.0
5.2
5.4
0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

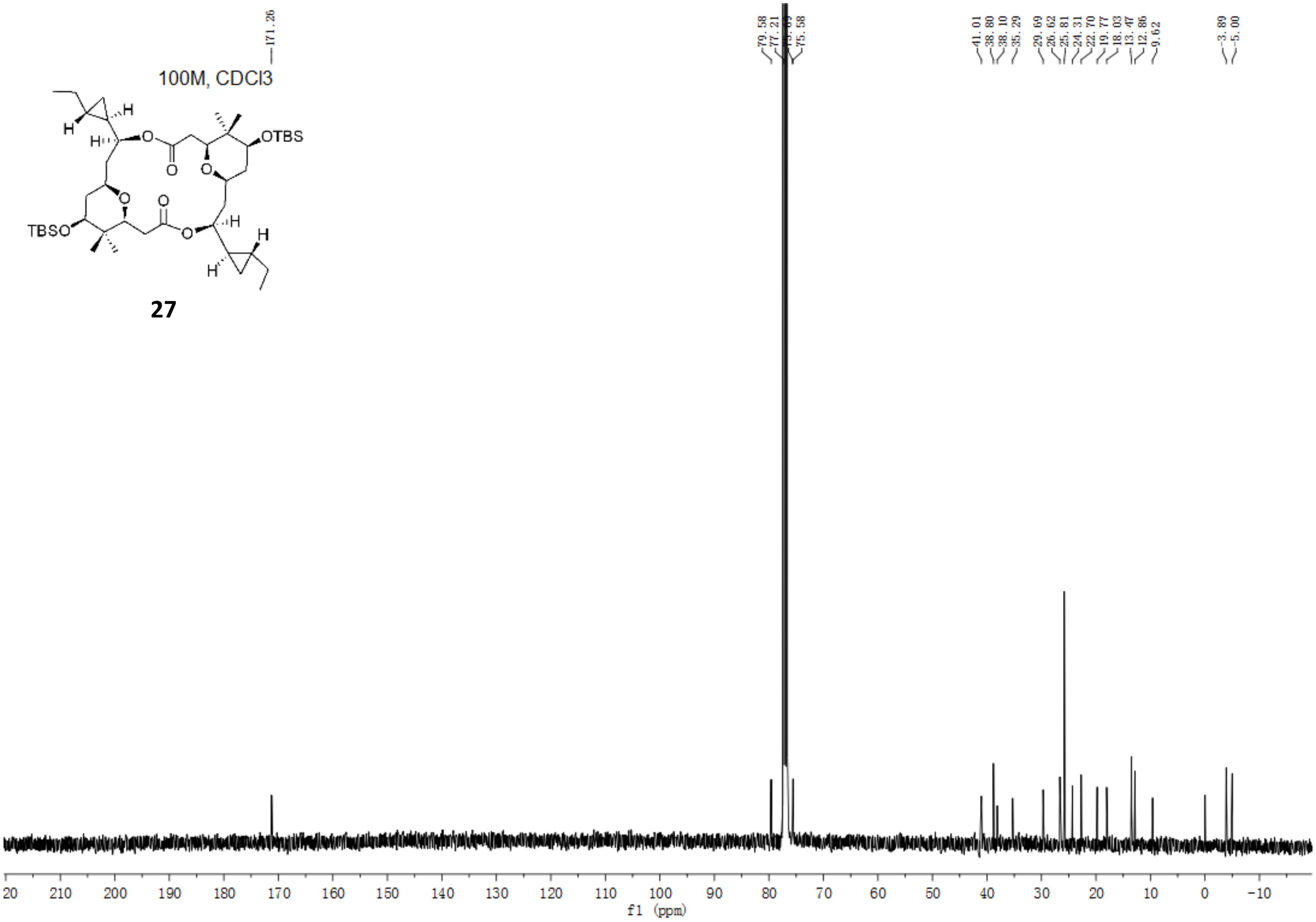

125M CD3CN
171.3562
95.9153
95.1618
89.4501
83.2451
82.4197
80.4177
80.2948
78.9777
78.5471
76.4391
74.8380
73.0371
69.1745
60.4555
60.2040
60.0384
57.9800
41.5240
41.1802
38.4365
38.0284
37.0749
35.4111
35.1362
32.8304
28.5492
26.3643
25.4163
23.6820
23.1181
22.2554
19.9940
19.8521
19.2635
17.8091
15.9060
12.9768
12.7588
11.8618
9.0599
7.8317
-5.2640
-5.3374
OMe
TBSO
OMe
O
O
O
O
H
H
H
O
O
O
O
O
O
O
H
H
H
MeO
MeO
OTBS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

25


500M CD3CN
OMe
HO
OMe
O
H
H
H
O
O
O
O
O
O
O
O
O
H
H
H
MeO
OH
MeO
26
2.0
2.4
2.3
5.2
5.6
5.4
3.4
4.2
2.4
4.7
2.3
4.6
2.5
4.1
2.5
5.8
14.7
5.1
2.5
2.4
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
f1 (ppm)


125M CD3CN
171.1179
95.3585
83.2268
80.1499
79.3841
79.3402
76.6443
75.2467
71.9956
60.2053
59.7076
57.8672
40.8797
37.8906
35.3264
32.8021
29.4278
26.3841
23.8445
22.2316
19.8029
12.9834
12.8371
9.0094
OMe
HO
OMe
O
H
H
H
O
O
O
O
O
O
O
O
H
H
H
MeO
MeO
OH
26
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

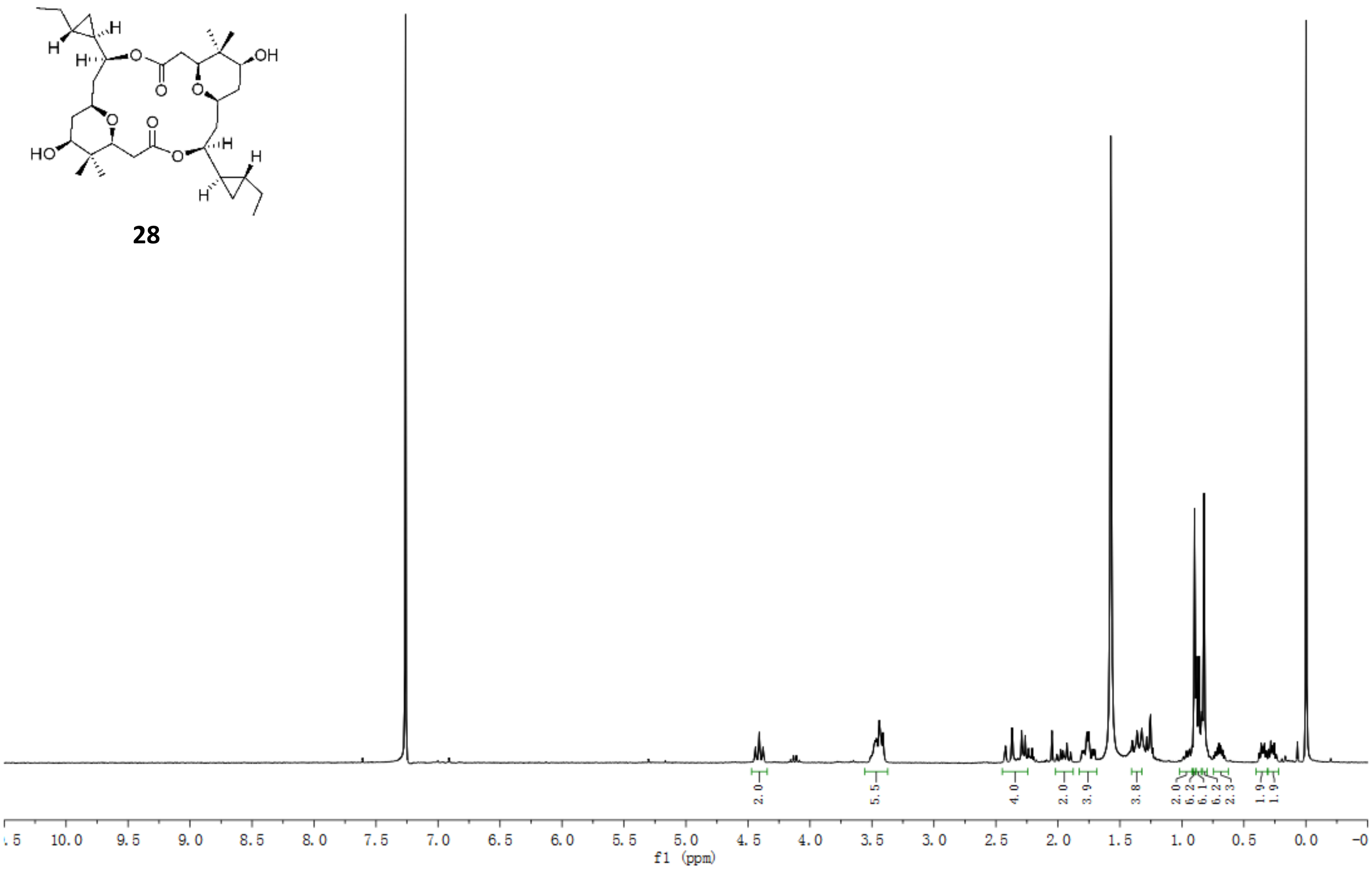

400M, CDCl3
27
OTBS
TBSO
H
O
2.0
3.3
2.0
2.1
2.0
2.1
2.1
1.8
4.2
2.0
17.2
5.3
4.9
5.5
2.3
2.0
1.9
6.1
4.7
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)



171.26
100M, CDCl3
OTBS
TBSO
H
O
79.58
77.21
75.58
41.01
38.80
38.10
35.29
29.69
26.62
25.81
24.31
22.70
19.77
18.03
13.47
12.86
9.62
-3.89
-5.00
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

27

300M, CDCl3



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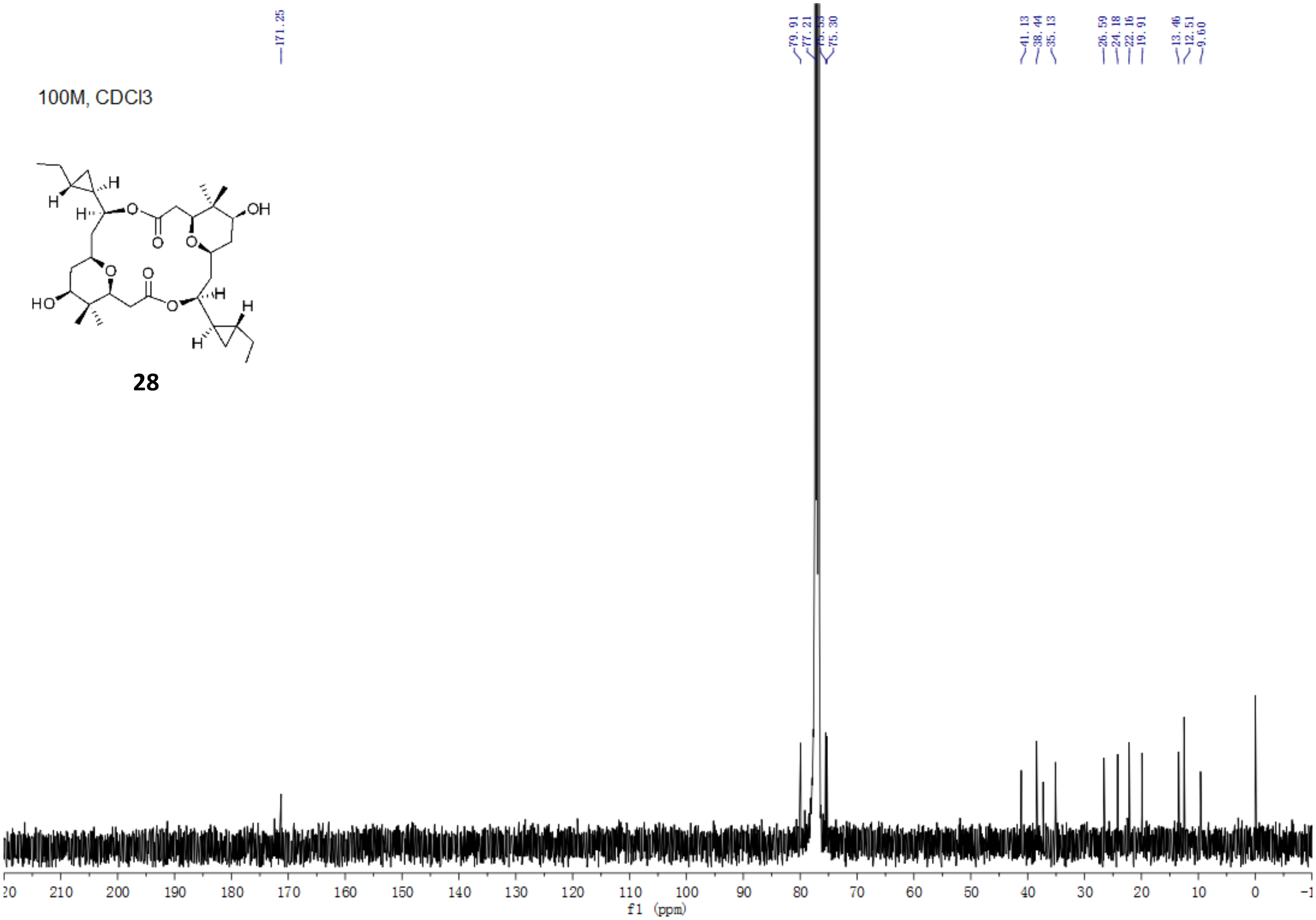
100M, CDCl3
171.25
79.91
77.21
75.53
75.30
41.13
38.44
35.13
26.59
24.18
22.16
19.91
13.46
12.51
9.60
H
H
H
O
O
O
O
OH
HO
O
O
O
O
H
H
H
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

28

SUPPLEMENTARY REFERENCES

(1) APEX2 “Program for Data Collection on Area Detectors” BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.

(2) SADABS, Sheldrick, G.M. “Program for Absorption Correction of Area Detector Frames”, BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.

(3) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

(4) Barbour, L. J. *J. Supramol. Chem.* **2001**, *1*, 189.